Supporting Information

for

General Stereoretentive Preparation of Chiral Secondary Mixed Alkylmagnesium Reagents and Their Use for Enantioselective Electrophilic Aminations

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1 General

All reactions were carried out with magnetic stirring and under argon atmosphere in glassware dried with a heat gun. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon three times prior to use. Unless otherwise indicated, yields as stated are isolated yields of compounds and are estimated to be >95% pure as determined by ^{1}H-NMR analysis (25 °C) and capillary gas chromatography analysis. The ratio of diastereoisomers was determined by ^{1}H-NMR or ^{13}C-NMR spectroscopy and GC-analysis.

1.1 Solvents

All solvents were dried according to standard methods by distillation over drying agents as stated below and were stored under argon atmosphere. Solvents for column chromatography were distilled on a vacuum evaporator prior to use.

CH_2Cl_2 was predried over $CaCl_2$ and distilled from CaH_2.

Diethyl ether was predried over calcium hydride and dried with the solvent purification system SPS-400-2 from INNOVATIVE TECHNOLOGIES INC.

1.2 Chromatography

Gas chromatography analyses were performed with machines of *Agilent* Technologies 7890, using a column of type HP 5 (*Agilent* 5% phenylmethylpolysiloxane; length: 15 m; diameter: 0.25 mm; film thickness: 0.25 μm) or *Hewlett-Packard* 6890 or 5890 series II, using a column of type HP 5 (*Hewlett-Packard*, 5% phenylmethylpolysiloxane; length: 15 m; diameter: 0.25 mm; film thickness: 0.25 μm).

Flash column chromatography was performed using SiO_2 (0.040–0.063 mm, 230–400 mesh ASTM) from Merck if not specially indicated.

Thin layer chromatography (TLC) was performed using SiO_2 pre-coated aluminium plates (Merck 60, F-254). The chromatograms were examined by 254 nm UV irradiation or visualized by molybdatophosphoric acid stain and heating.

Reagents

All reagents were obtained from commercial sources and used without further purification unless otherwise stated.

Analytic Data

^{1}H-NMR and **^{13}C-NMR** spectra were recorded on BRUKER ARX 300, VARIAN VXR 300 S, Bruker Avance III HD spectrometer equipped with a CryoProbeTM (at 400 MHz and 100 MHz, respectively) and Bruker AMX 600 instruments. Chemical shifts are reported as δ-values in ppm relative to the solvent peak in $CDCl_3$ (residual chloroform: δ 7.26 ppm for ^{1}H-NMR, δ 77.0 ppm for ^{13}C-NMR). Abbreviations for signal coupling are as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet).

Mass spectroscopy (MS): High resolution (HRMS) and low resolution (LRMS) spectra were recorded on a FINNIGAN MAT 95Q instrument. Electron impact ionization (EI) was conducted with an ionization energy of 70 eV.

Infrared spectra (IR) were recorded from 4500 cm^{-1} to 650 cm^{-1} on a PERKIN ELMER Spectrum BX-59343 instrument. For detection a SMITHS DETECTION DuraSampl*IR* II Diamond ATR sensor was used and the absorption bands are reported in wavenumbers. The abbreviations for intensity are as follows: vs (very strong; maximum intensity), s (strong; above 75% of max. intensity), m (medium; from 50% to 75% of max. intensity), w (weak; below 50% of max. intensity) as well as br (broad).

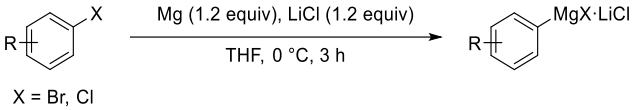
Optical rotation values were recorded in a Perkin Elmer 241 or anton Paar MCP 200 polarimeter. The specific rotation is calculated as follows:

$$[\alpha]_{\lambda}^{\varphi} = \frac{[\alpha] \cdot 100}{c \cdot d}$$

Thereby, the wavelength λ is reported in nm and the measuring temperature ϕ in °C. α represents the recorded optical rotation, c the concentration of the analyte in 10 mg/mL and d the length of the cuvette in dm. Thus, the specific rotation is given in $10^{-1}\cdot deg\cdot cm^{2}\cdot g^{-1}$.Usage of the sodium D line (λ = 589 nm) is indicated by D instead of the wavelength in nm. The respective concentration as well as the solvent is reported at the relevant section of the experimental section.

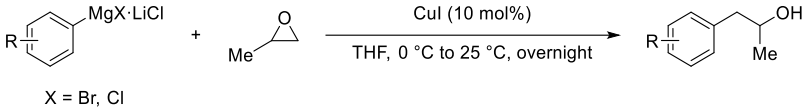
2 Typical procedures

2.1 Typical procedure for the preparation of arylmagnesium reagents (TP1)



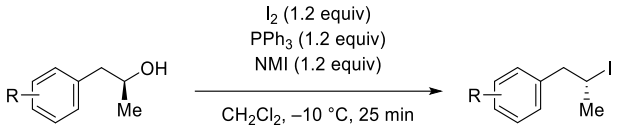
A dry and argon-flushed *Schlenk*-flask was charged with magnesium turnings (1.2 equiv) and anhydrous lithium chloride (1.2 equiv) in THF (ca. 1.0 M solution) and cooled to 0 °C. The aryl halide (1.0 equiv) was added and the reaction mixture was stirred for 3 h at 0 °C. The concentration of the resulting arylmagnesium species was determined via titration with iodine in THF.[1]

2.2 Typical procedure for the preparation of secondary alkyl alcohols (TP2)



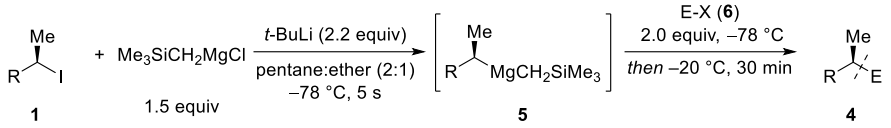
A dry and argon-flushed *Schlenk*-flask was charged with a solution of an arylmagnesium reagent (1.2 equiv) and diluted with THF to afford a ca. 0.5 M solution. The mixture was cooled to 0 °C and copper(I) iodide (10 mol%) was added to the reaction mixture. Then, propylene oxide (1.0 equiv, dissolved in 5 mL THF) was added dropwise to the reaction mixture at 0 °C and allowed to warm to room temperature overnight. Thereafter, the mixture was quenched with sat. aq. NH_4Cl solution. The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The remaining crude product was purified by flash column chromatography on silica gel to afford the corresponding alkyl alcohol.

2.3 Typical procedure for the preparation of secondary alkyl iodides (*Appel*-reaction, TP3)



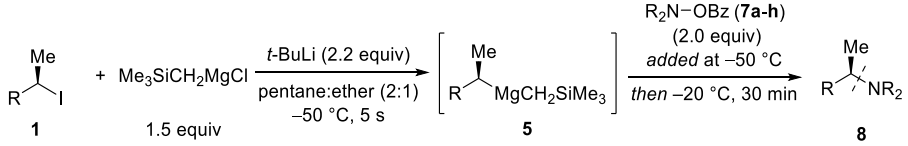
A dry and argon-flushed *Schlenk*-flask was charged with a solution of iodine (1.2 equiv) in CH_2Cl_2 (ca. 0.1 M solution) and cooled to −10 °C. Triphenylphosphine (1.2 equiv) was added in one portion and the resulting yellow suspension was stirred for 1 h at −10 °C. Then *N*-methylimidazole (NMI, 1.2 equiv) was added dropwise. The reaction mixture was further stirred for 10 min after which the corresponding alcohol (1.0 equiv, dissolved in 10 mL CH_2Cl_2) was added over a period of 15 min. The reaction was stirred for further 10 min at −10 °C and then quenched with freshly prepared sat. aq. $NaHSO_3{\cdot}Na_2S_2O_5$. The layers were separated and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure at 30 °C. The resulting oil was triturated three times with a mixture of *n*-pentane/diethyl ether. The precipitate was filtered off and the filtrate was concentrated under reduced pressure at 30 °C. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding alkyl iodide.

2.4 Typical procedure for the Barbier-type preparation of chiral secondary alkylmagnesium reagents and subsequent trapping with electrophiles (TP4)



A dry and argon-flushed *Schlenk*-flask was charged with the secondary alkyl iodide (**1**, 1.0 equiv) in *n*-pentane/diethyl ether (0.125 M/0.40 M) and cooled to −78 °C. A solution of Me_3SiCH_2MgCl (ca. 1.0 M in diethyl ether, 1.5 equiv) was added to the reaction mixture. Subsequently, *t*-BuLi (2.2 equiv, ca. 2.0 M in pentane) was quickly added dropwise at −78 °C. After 30 s, the electrophile (2.0 equiv, neat or in 0.5 mL of diethyl ether) was added directly to the reaction mixture at −78 °C. After addition of the electrophile, the reaction mixture was stirred for 30 min at −20 °C. After quenching with sat. aq. NH_4Cl solution, the reaction mixture was extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford products of type **4**.

2.5 Typical procedure for the Barbier-type preparation of chiral secondary alkylmagnesium reagents and subsequent trapping with *O*-benzoyl hydroxylamines (TP5)

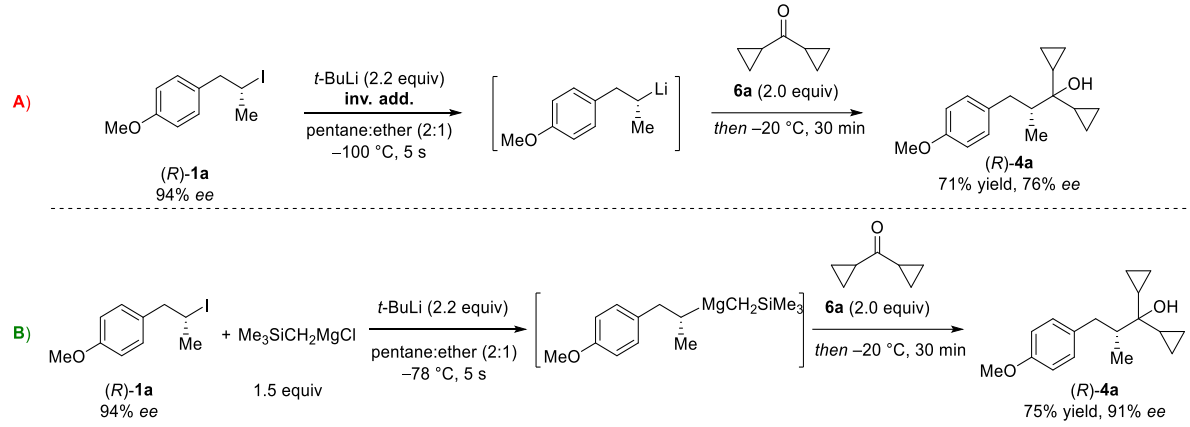


A dry and argon-flushed *Schlenk*-flask was charged with the secondary alkyl iodide (**1**, 1.0 equiv) in *n*-pentane/diethyl ether (0.125 M/0.40 M) and cooled to −50 °C. A solution of Me_3SiCH_2MgCl (ca. 1.0 M in diethyl ether, 1.5 equiv) was added to the reaction mixture. Subsequently, *t*-BuLi (2.2 equiv, ca. 2.0 M in pentane) was quickly added dropwise at −50 °C. After 30 s, the *O*-hydroxylamine benzoate (**7**, 2.0 equiv, in 0.5 mL of dichloro methane) was added directly to the reaction mixture at −50 °C. After addition of the electrophile, the reaction mixture was stirred for 30 min at −20 °C. After quenching with sat. aq. $NaHCO_3$ solution, the reaction mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford products of type **8**.

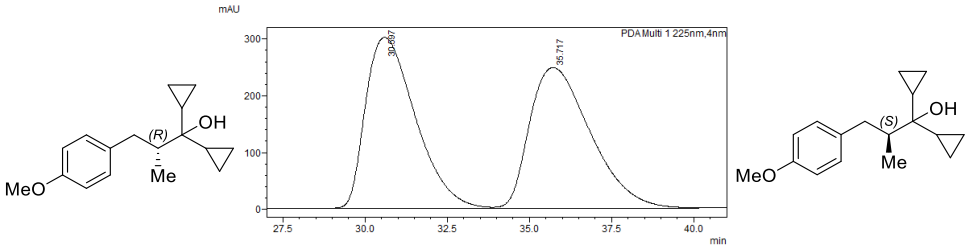
3 Optimization of reaction conditions

3.1 Proof of stereoretention for the transmetalation of secondary alkyllithiums to the corresponding secondary alkylmagnesiums

The reaction of the secondary alkyllithium species obtained after a stereoretentive[2] I/Li-exchange from the enantiomerically enriched (*R*)-enantiomer of the secondary alkyl iodide (*R*)-**1a** with *t*-BuLi at −100 °C reacted with the electrophile **6a** affording (*R*)-**4a** in 76% *ee* (**A**). Experiment **B** shows that the transmetalation from lithium to magnesium proceeds with retention of configuration as in the presence of 1.5 equiv. of Me_3SiCH_2MgCl the same enantiomer of the tertiary alcohol (*R*)-**4a** was obtained in 91% *ee*.

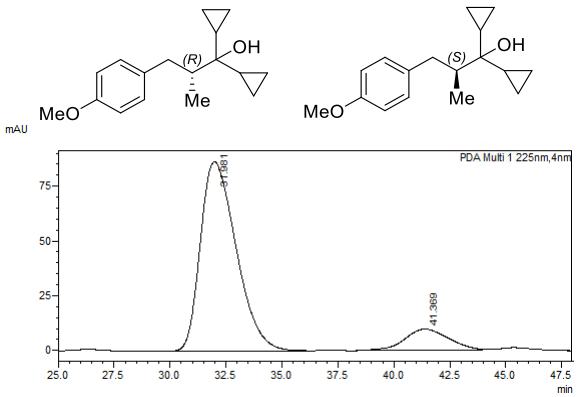


Racemate:



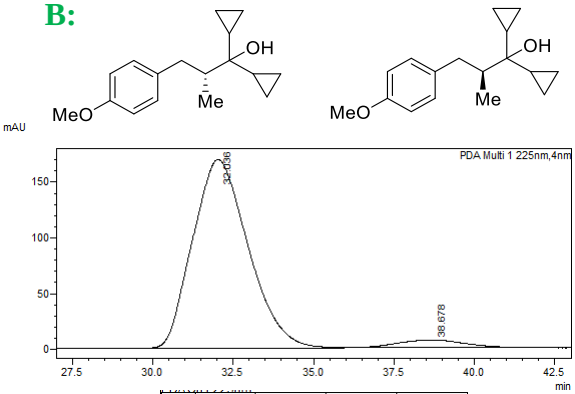
Peak#	Ret. Time	Area	Height	Area%
1	30.597	31717245	300745	49.856
2	35.717	31900167	247589	50.144
Total		63617412	548334	100.000

A:



Peak#	Ret. Time	Area	Height	Area%
1	31.981	9640135	86459	88.085
2	41.369	1304015	9624	11.915
Total		10944150	96084	100.000

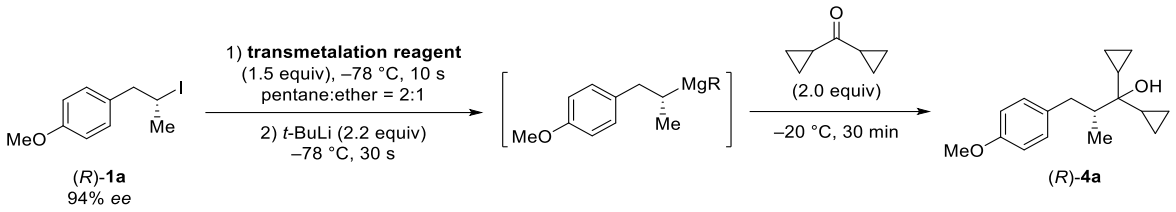
B:



Peak#	Ret. Time	Area	Height	Area%
1	32.036	20354365	169281	95.558
2	38.678	946215	6756	4.442
Total		21300581	176037	100.000

3.2 Test of different transmetalation reagents

Table 1: Optimization of the transmetalation reaction

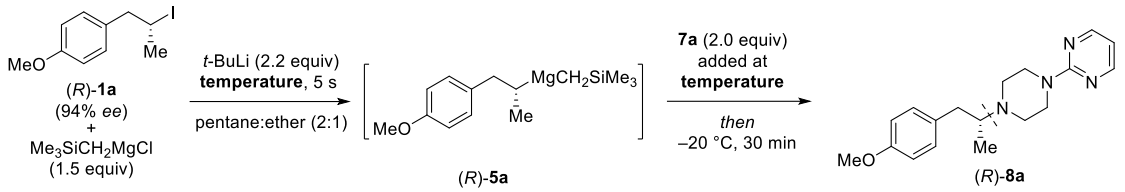


Entry	Transmetalation reagent	Yield of (*R*)-**4a**[a]	*ee* of (*R*)-**4a**[b]
1	–	*traces*	n.d
2	EtMgBr	35%	30%
3	PhMgBr	34%	34%
4	MeMgBr·LiBr	56%	12%
5	*t*-BuMgBr·LiBr	77%	76%
6	Me_3SiCH_2MgCl	80% (75%)	91%
7	$Me_3SiCH_2MgBr{\cdot}LiBr$	78%	86%
8	$Me_3SiCH_2MgBr{\cdot}LiBr$[c]	12%	2%
9	$MgBr_2$	29%	52%
10	$MgBr_2$[d]	28%	32%

[a] The yield was determined by GC-analysis. [b] The enantiomeric excess (% *ee*) was determined by chiral HPLC-analysis. [c] The transmetalation reagent was dissolved in THF instead of diethyl ether. [d] 0.6 Equiv. of transmetalation reagent were used.

3.3 Optimization of the electrophilic amination

Table 2: Temperature dependence of the electrophilic amination



Entry	Temperature	Yield of (*R*)-**8a**[a]	*ee* of (*R*)-**8a**[b]
1	–78 °C	30%	nd
3	–50 °C	78% (73%)	91%
4	–30 °C	52%	nd

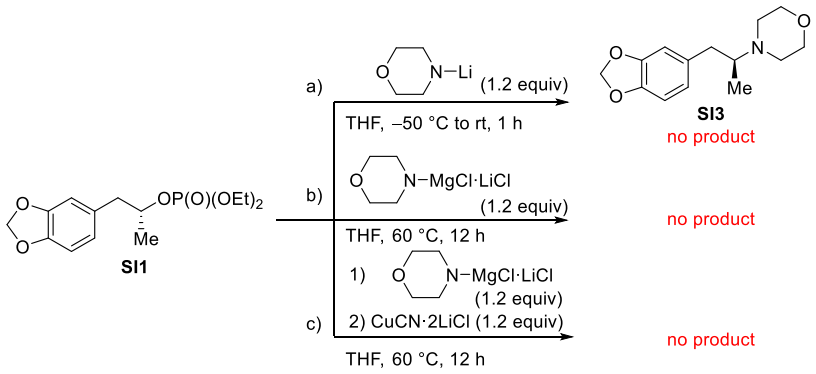
[a] The yield was determined by GC-analysis. [b] The enantiomeric excess (% *ee*) was determined by chiral HPLC-analysis.

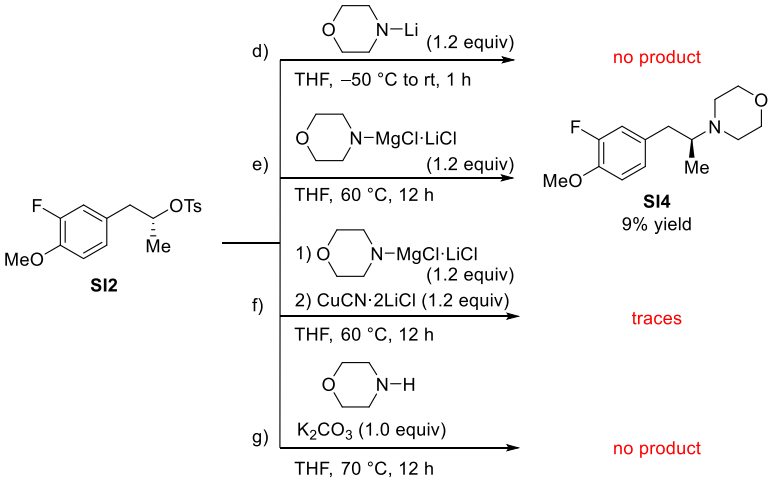
3.4 Comparison of electrophilic and nucleophilic amination

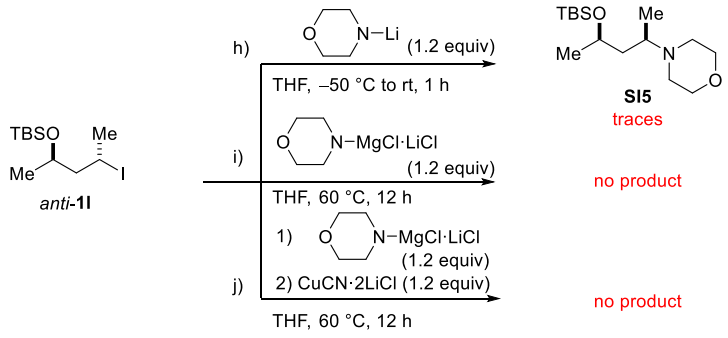
To compare our method with a nucleophilic amination, we prepared three organometallic morpholino amides and reacted them with the optically enriched secondary alkyl phosphate **SI1**[3], the tosylate **SI2**[4] and the secondary alkyl iodide *anti*-**1k**. When **SI1** was treated with lithium morpholino amide, the tertiary amine was not detected (reaction a). However, the corresponding alcohol was obtained in almost quantitative yield (96%). Treating **SI1** with the analogous magnesium or copper morpholino derivatives did not afford the expected tertiary amine **SI3** either (reactions b and c).

Analogously, **SI2** was treated with the organometallic morpholino amides (reactions d-f). Only magnesium morphplino amide provided the tertiary amine **SI4** in detectable yield, however harsh reaction conditions were required. Treating **SI2** with a mixture of morpholine and potassium carbonate[5] afforded the corresponding alcohol exclusively (reaction g).

Treating the diastereomerically enriched secondary alkyl iodide *anti*-**1l** with the organometallic amides led in all cases to complete epimerization of the starting material and only traces of **SI5** were detected (reactions h-j).

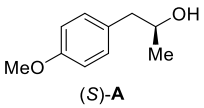

OP(O)(OEt)2
Me
SI1
a)
(1.2 equiv)
THF, –50 °C to rt, 1 h
SI3
no product
b)
N–MgCl·LiCl
(1.2 equiv)
THF, 60 °C, 12 h
no product
1)
(1.2 equiv)
c)
2) CuCN·2LiCl (1.2 equiv)
THF, 60 °C, 12 h
no product


F
OTs
MeO
Me
SI2
d)
(1.2 equiv)
THF, –50 °C to rt, 1 h
no product
e)
N–MgCl·LiCl
(1.2 equiv)
THF, 60 °C, 12 h
SI4
9% yield
1)
(1.2 equiv)
f)
2) CuCN·2LiCl (1.2 equiv)
THF, 60 °C, 12 h
traces
N–H
g)
K2CO3 (1.0 equiv)
THF, 70 °C, 12 h
no product


TBSO
Me
Me
I
anti-1l
h)
(1.2 equiv)
THF, –50 °C to rt, 1 h
TBSO
Me
Me
SI5
traces
i)
N–MgCl·LiCl
(1.2 equiv)
THF, 60 °C, 12 h
no product
1)
(1.2 equiv)
j)
2) CuCN·2LiCl (1.2 equiv)
THF, 60 °C, 12 h
no product

4 Preparation of starting materials

4.1 Preparation of secondary alkyl alocohols 0a-m



(*S*)-**A**

The alcohol (*S*)-**A** was prepared according to **TP2** from (*S*)-propylene oxide (4.18 mL, 3.48 g, 59.7 mmol, 1.0 equiv) dissolved in THF (60 mL) and the corresponding arylmagnesium reagent in THF (75.0 mL, 71.6 mmol, 0.95 M, 1.2 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (2:1) to afford (*S*)-**A** (7.09 g, 42.4 mmol, 71%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.17–7.09 (m, 2H), 6.90–6.82 (m, 2H), 4.04–3.91 (m, 1H), 3.80 (s, 3H), 2.74 (dd, *J* = 13.6, 4.7 Hz, 1H), 2.62 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.49 (d, *J* = 3.7 Hz, 1H), 1.24 (d, *J* = 6.2 Hz, 3H).

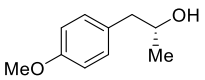
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 158.4, 130.6, 130.5, 114.1, 69.1, 55.4, 45.0, 22.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3371 (w), 2965 (w), 2930 (w), 2907 (w), 2836 (w), 1612 (m), 1510 (vs), 1463 (m), 1456 (m), 1446 (w), 1441 (w), 1372 (w), 1300 (m), 1243 (vs), 1203 (w), 1176 (s), 1109 (m), 1076 (m), 1033 (s), 941 (m), 930 (m), 846 (m), 831 (m), 806 (s), 754 (m).

MS (70 eV, EI): m/z (%): 166 (10), 122 (64), 121 (100), 107 (13), 91 (12).

HRMS (EI) for $C_{10}H_{14}O_2$: calc. $[M]^{+\bullet}$: 166.0994, found: 166.0987.

$[\alpha]_D^{20}$: +28.4 (c = 1.23, $CHCl_3$).



(*R*)-**A**

The alcohol (*R*)-**A** was prepared according to **TP2** from (*R*)-propylene oxide (1.04 mL, 863 mg, 14.9 mmol, 1.0 equiv) dissolved in in THF (15 mL) and the corresponding arylmagnesium reagent in THF (18.8 mL, 17.9 mmol, 0.95 M, 1.2 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (2:1) to afford (*R*)-**A** (1.73 g, 10.4 mmol, 70%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.17–7.09 (m, 2H), 6.90–6.82 (m, 2H), 4.03–3.92 (m, 1H), 3.80 (s, 3H), 2.74 (dd, *J* = 13.6, 4.7 Hz, 1H), 2.62 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.51 (d, *J* = 3.2 Hz, 1H), 1.24 (d, *J* = 6.2 Hz, 3H).

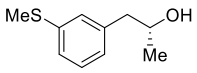
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = δ 158.4, 130.6, 130.5, 114.1, 69.1, 55.4, 45.0, 22.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3363 (w), 2964 (w), 2928 (w), 2924 (w), 2906 (w), 2834 (w), 1612 (m), 1510 (vs), 1462 (m), 1456 (m), 1442 (w), 1373 (w), 1300 (m), 1243 (vs), 1176 (s), 1109 (m), 1076 (m), 1033 (s), 941 (m), 930 (m), 846 (m), 832 (w), 805 (s), 754 (m).

MS (70 eV, EI): m/z (%): 166 (5), 122 (68), 121 (100), 107 (17), 91 (20).

HRMS (EI) for $C_{10}H_{14}O_2$: calc. $[M]^{+\bullet}$: 166.0994, found: 166.0987.

$[\alpha]_D^{20}$: −29.0 (c = 1.35, $CHCl_3$).



(*R*)-**B**

The alcohol (*R*)-**B** was prepared according to **TP2** from (*R*)-propylene oxide (0.34 mL, 283 mg, 4.87 mmol, 1.0 equiv) dissolved in THF (5 mL) and the corresponding arylmagnesium reagent in THF (7.04 mL, 5.84 mmol, 0.83 M, 1.2 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (2:1) to afford (*R*)-**B** (577 mg, 3.16 mmol, 65%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.24 (t, *J* = 7.6 Hz, 1H), 7.17–7.08 (m, 2H), 6.98 (dt, *J* = 7.5, 1.4 Hz, 1H), 4.07–3.97 (m, 1H), 2.76 (dd, *J* = 13.5, 4.8 Hz, 1H), 2.66 (dd, *J* = 13.4, 8.0 Hz, 1H), 2.48 (s, 3H), 1.54 (d, *J* = 3.6 Hz, 1H), 1.25 (d, *J* = 6.2 Hz, 3H).

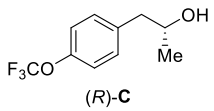
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 139.4, 138.8, 129.1, 127.5, 126.2, 124.7, 68.9, 45.8, 23.0, 15.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3397 (m), 3334 (m), 2970 (m), 2930 (m), 2919 (m), 1592 (m), 1570 (m), 1487 (m), 1475 (m), 1441 (s), 1425 (m), 1372 (m), 1356 (m), 1331 (m), 1278 (w), 1210 (m), 1111 (s), 1084 (s), 1071 (s), 1049 (m), 1028 (m), 936 (s), 879 (w), 775 (s), 769 (s), 755 (s), 699 (s), 693 (vs), 684 (s).

MS (70 eV, EI): m/z (%): 182 (55), 138 (95), 123 (24), 121 (10), 91 (100).

HRMS (EI) for $C_{10}H_{14}OS$: calc. $[M]^{+\bullet}$: 182.0765, found: 182.0759.

$[\alpha]_D^{20}$: −28.6 (c = 0.85, $CHCl_3$).



(*R*)-**C**

The alcohol (*R*)-**C** was prepared according to **TP2** from (*R*)-propylene oxide (0.686 mL, 569 mg, 9.80 mmol, 1.0 equiv) dissolved in THF (10 mL) and the corresponding arylmagnesium reagent in THF (11.5 mL, 11.8 mmol, 1.02 M, 1.2 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (*R*)-**C** (1.51 g, 6.86 mmol, 70%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.26–7.21 (m, 2H), 7.19–7.13 (m, 2H), 4.09–3.96 (m, 1H), 2.79 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.71 (dd, *J* = 13.6, 7.8 Hz, 1H), 1.42 (s, 1H), 1.25 (d, *J* = 6.1 Hz, 3H).

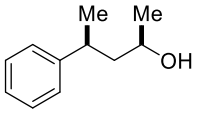
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 148.0, 137.5, 130.8, 121.2, 68.9, 45.1, 23.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3352 (w), 2972 (vw), 2929 (vw), 1509 (m), 1458 (vw), 1376 (vw), 1253 (vs), 1219 (s), 1195 (s), 1154 (vs), 1106 (s), 1080 (m), 1048 (w), 1020 (m), 946 (w), 935 (m), 921 (w), 858 (w), 841 (w), 827 (w), 806 (m), 773 (w), 672 (w).

MS (70 eV, EI): m/z (%): 176 (100), 109 (11), 91 (14).

HRMS (EI) for $C_{17}H_{16}FO_2$: calc. $[M-H]^{+\bullet}$: 219.0633, found: 219.0626.

$[\alpha]_D^{20}$: −20.3 (c = 0.95, $CHCl_3$).



syn-**D**

2,4-*syn*-*tert*-Butyldimethyl((4-phenylpentan-2-yl)oxy)silane[2b] (3.98 g, 14 mmol, 1.0 equiv) was dissolved in THF (45 mL) and cooled to 0 °C. Tetrabutylammonium fluoride trihydrate (8.83 g, 28 mmol, 2.0 equiv) was added in one portion and the reaction mixture was warmed to ambient temperature overnight. The reaction mixture was quenched with sat. aq. NH_4Cl and extracted with diethyl ether (3 × 100 mL). The combined organic phases were dried over $MgSO_4$ and evaporated. The obtained crude product was purified by flash column chromatography with *i*-hexane/diethyl ether (2:1) to afford *syn*-**D** (1.82 g, 11.21 mmol, 80%, dr = 99:1) as light yellow oil.

syn-**D:**

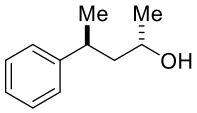
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.33–7.27 (m, 2H), 7.23–7.16 (m, 3H), 3.83–3.71 (m, 1H), 2.93–2.80 (m, 1H), 1.91–1.77 (m, 1H), 1.71–1.60 (m, 1H), 1.31–1.25 (m, 4H), 1.19 (d, J = 6.1 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.4, 128.7, 127.0, 126.3, 66.6, 48.0, 37.1, 23.9, 22.5.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3344 (w), 3083 (w), 3059 (w), 3025 (w), 2960 (m), 2924 (m), 2870 (m), 1493 (m), 1452 (m), 1375 (m), 1302 (w), 1255 (w), 1130 (m), 1082 (w), 1060 (m), 1033 (w), 1002 (w), 948 (w), 907 (w), 837 (w), 761 (m), 699 (vs).

MS (70 eV, EI): m/z (%): 146 (16), 131 (100), 129 (20), 115 (17), 105 (38), 91 (39).

HRMS (EI) for $C_{11}H_{16}O$: calc. $[M-H]^{+\bullet}$: 163.1123, found: 163.1071.



anti-**D**

Analogous to *syn*-**D**, *anti*-**D** (2.24 g, 13.64 mmol, 97%, dr = 1:99) was obtained as light yellow oil.

anti-**D:**

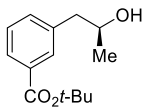
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.35–7.28 (m, 2H), 7.25–7.15 (m, 3H), 3.60–3.51 (m, 1H), 3.04–2.90 (m, 1H), 1.73–1.67 (m, 2H), 1.33 (s, 1H), 1.27 (d, J = 7.0 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 146.9, 128.6, 127.3, 126.2, 66.1, 47.8, 36.7, 24.3, 23.2.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3343 (w), 3083 (w), 3063 (w), 3026 (w), 2960 (s), 2925 (m), 2872 (m), 2358 (m), 1602 (w), 1494 (m), 1452 (m), 1374 (m), 1139 (m), 1113 (w), 1083 (w), 1054 (m), 1025 (m), 951 (w), 899 (w), 830 (w), 762 (s), 699 (vs).

MS (70 eV, EI): m/z (%): 146 (23), 131 (58), 105 (100), 91 (47), 77 (20), 74 (22), 59 (39), 45 (44), 43 (21).

HRMS (EI) for $C_{11}H_{16}O$: calc. $[M]^{+\bullet}$: 164.1201, found: 164.1176.



(*S*)-**E**

A solution of *tert*-butyl 3-iodobenzoate (1.52 g, 5 mmol, 1.0 equiv) in THF (10 mL) was cooled to −50 °C before dropwise addition of *i*PrMgCl·LiCl (1.2 M, 5 mL, 6 mmol, 1.2 equiv). The reaction mixture was stirred at −50 °C for 1 and subsequently charged with CuI (95 mg, 0.5 mmol, 0.1 equiv). Then, (*S*)-propylene oxide (0.35 mL, 290 mg, 5.0 mmol, 1.0 equiv) in THF (5 mL) was added. The reaction was let warm to ambient temperature overnight and quenched with sat. aq. NH_4Cl solution. The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via flash column chromatography on silica gel with *i*-hexane/ethyl acetate (2:1) to afford (*S*)-**E** (922 mg, 3.9 mmol, 78%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.91–7.80 (m, 2H), 7.42–7.33 (m, 2H), 4.11–4.01 (m, 1H), 2.83 (dd, *J* = 13.5, 4.9 Hz, 1H), 2.75 (dd, *J* = 13.5, 7.9 Hz, 1H), 1.59 (s, 9H), 1.47 (d, *J* = 4.0 Hz, 1H), 1.26 (dd, *J* = 6.1, 0.9 Hz, 3H).

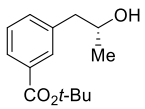
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 165.9, 138.8, 133.7, 132.4, 130.4, 128.5, 127.8, 81.2, 69.0, 45.6, 28.3, 23.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3410 (w), 2974 (w), 2931 (w), 1710 (s), 1695 (m), 1586 (w), 1477 (w), 1456 (w), 1442 (w), 1392 (w), 1367 (m), 1293 (s), 1256 (m), 1206 (m), 1158 (vs), 1110 (s), 1085 (s), 1048 (m), 1001 (w), 943 (m), 929 (w), 849 (m), 823 (w), 811 (w), 755 (m), 745 (s), 707 (w), 696 (m), 674 (w).

MS (70 eV, EI): m/z (%): 163 (27), 136 (100), 91 (18).

HRMS (EI) for $C_{14}H_{20}O_3$: calc. $[M-C_2H_8O]^{+\bullet}$: 192.1150, found: 192.1148.

$[\alpha]_D^{20}$: +19.9 (c = 1.00, $CHCl_3$).



(*R*)-**E**

A solution of *tert*-butyl 3-iodobenzoate (3.04 g, 10 mmol, 1.0 equiv) in THF (10 mL) was cooled to −50 °C before dropwise addition of *i*PrMgCl·LiCl (1.2 M, 10 mL, 12 mmol, 1.2 equiv). The reaction mixture was stirred at −50 °C for 1 and subsequently charged with CuI (190 mg, 1.0 mmol, 0.1 equiv). Then, (*R*)-propylene oxide (0.70 mL, 580 mg, 10.0 mmol, 1.0 equiv) in THF (10 mL) was added. The reaction was let warm to ambient temperature overnight and quenched with sat. aq. NH_4Cl solution. The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via flash column chromatography on silica gel with *i*-hexane/ethyl acetate (2:1) to afford (*R*)-**E** (1.75 g, 7.4 mmol, 74%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.90–7.81 (m, 2H), 7.41–7.32 (m, 2H), 4.10–4.01 (m, 1H), 2.83 (dd, *J* = 13.5, 4.9 Hz, 1H), 2.75 (dd, *J* = 13.5, 7.8 Hz, 1H), 1.59 (s, 9H), 1.48 (d, *J* = 4.0 Hz, 1H), 1.26 (d, *J* = 6.2 Hz, 3H).

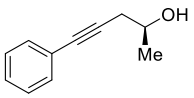
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 165.9, 138.8, 133.7, 132.4, 130.4, 128.5, 127.8, 81.2, 69.0, 45.6, 28.3, 23.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3417 (w), 2974 (w), 2930 (w), 1710 (s), 1695 (m), 1586 (w), 1477 (w), 1456 (w), 1441 (w), 1393 (w), 1367 (m), 1293 (s), 1256 (m), 1206 (m), 1158 (vs), 1110 (s), 1085 (s), 1049 (m), 1001 (w), 943 (m), 849 (m), 823 (w), 810 (w), 755 (m), 745 (s), 708 (w), 696 (m), 673 (w).

MS (70 eV, EI): m/z (%): 163 (29), 136 (100), 91 (21), 57 (70).

HRMS (EI) for $C_{14}H_{20}O_3$: calc. $[M-C_2H_8O]^{+\bullet}$: 192.1150, found: 192.1147.

$[\alpha]_D^{20}$: −17.0 (c = 1.04, $CHCl_3$).



(*S*)-**F**

A solution of ethynylbenzene (1.02 g, 10 mmol, 1.0 equiv) in THF (10 mL) was cooled to −78 °C before dropwise addition of *i*PrMgCl·LiCl (1.2 M, 12.5 mL, 15 mmol, 1.5 equiv). The reaction mixture was let warm to room temperature overnight and subsequently charged with CuI (190 mg, 1 mmol, 0.1 equiv). Then, (*S*)-propylene oxide (0.84 mL, 697 mg, 12.0 mmol, 1.2 equiv) in THF (12 mL) was added. The reaction was let warm to ambient temperature overnight and quenched with sat. aq. NH_4Cl solution. The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (3:1) to afford (*S*)-**F** (1.01 g, 6.3 mmol, 63%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.46–7.37 (m, 2H), 7.36–7.26 (m, 4H), 4.11–4.00 (m, 1H), 2.64 (dd, *J* = 16.6, 5.1 Hz, 1H), 2.56 (dd, *J* = 16.6, 6.6 Hz, 1H), 1.96 (d, *J* = 4.8 Hz, 1H), 1.33 (d, *J* = 6.1 Hz, 3H).

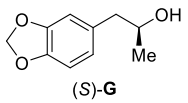
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 131.8, 128.4, 128.1, 123.5, 86.2, 83.2, 66.7, 30.2, 22.6.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3399 (m), 3338 (w), 2976 (w), 2931 (w), 1596 (w), 1487 (m), 1446 (m), 1441 (m), 1427 (w), 1371 (w), 1356 (m), 1332 (m), 1283 (w), 1210 (m), 1176 (w), 1110 (m), 1092 (m), 1071 (s), 1027 (m), 1000 (w), 934 (s), 919 (m), 880 (w), 768 (m), 760 (s), 755 (vs), 693 (vs).

MS (70 eV, EI): m/z (%): 160(31), 115 (100), 105 (62), 77 (17).

HRMS (EI) for $C_{11}H_{12}O$: calc. $[M]^{+\bullet}$: 160.0888, found: 160.0881.

$[\alpha]_D^{20}$: +18.4 (c = 0.48, $CHCl_3$).



(*S*)-**G**

The alcohol (*S*)-**G** was prepared according to **TP2** from (*S*)-propylene oxide (0.66 mL, 549 mg, 9.5 mmol, 1.0 equiv) dissolved in THF (10 mL) and the corresponding arylmagnesium reagent in THF (12.7 mL, 11.3 mmol, 0.89 M, 1.2 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (2:1) to afford (*S*)-**G** (1.26 g, 6.99 mmol, 74%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.76 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 1.7 Hz, 1H), 6.66 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.94 (s, 2H), 3.99–3.93 (m, 1H), 2.71 (dd, *J* = 13.6, 4.6 Hz, 1H), 2.59 (dd, *J* = 13.6, 8.1 Hz, 1H), 1.53 (d, *J* = 3.6 Hz, 1H), 1.23 (d, *J* = 6.2 Hz, 3H).

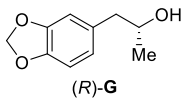
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.9, 146.3, 132.3, 122.4, 109.8, 108.5, 101.0, 69.1, 45.6, 22.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3373 (w), 2967 (w), 2890 (w), 2228 (w), 1607 (w), 1501 (s), 1488 (s), 1440 (s), 1372 (w), 1347 (w), 1243 (vs), 1187 (m), 1118 (m), 1098 (m), 1077 (m), 1035 (vs), 936 (s), 927 (s), 920 (s), 865 (w), 838 (w), 802 (s), 777 (m), 771 (m), 757 (w), 714 (w).

MS (70 eV, EI): m/z (%): 180 (25), 136 (49), 135 (100), 77 (13).

HRMS (EI) for $C_{10}H_{12}O_3$: calc. $[M]^{+\bullet}$: 180.0786, found: 180.0779.

$[\alpha]_D^{20}$: +27.3 (c = 1.14, $CHCl_3$).



(*R*)-**G**

The alcohol (*R*)-**G** was prepared according to **TP2** from (*R*)-propylene oxide (0.66 mL, 549 mg, 9.5 mmol, 1.0 equiv) dissolved in THF (10 mL) and the corresponding arylmagnesium reagent in THF (12.7 mL, 11.3 mmol, 0.89 M, 1.2 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (2:1) to afford (*R*)-**G** (1.32 g, 7.33 mmol, 76%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.75 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 1.7 Hz, 1H), 6.67–6.63 (m, 1H), 5.92 (s, 2H), 3.99–3.91 (m, 1H), 2.70 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.59 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.22 (d, *J* = 6.2 Hz, 3H).

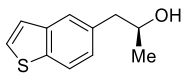
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.9, 146.3, 132.3, 122.4, 109.8, 108.4, 101.0, 69.0, 45.5, 22.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3378 (w), 2967 (w), 2887 (w), 2228 (w), 1607 (w), 1501 (s), 1488 (s), 1440 (s), 1372 (w), 1347 (w), 1243 (vs), 1187 (m), 1118 (m), 1098 (m), 1077 (m), 1035 (vs), 992 (vw), 936 (s), 927 (s), 865 (w), 838 (w), 802 (s), 777 (m), 771 (m), 757 (w), 724 (vw), 714 (w).

MS (70 eV, EI): m/z (%): 180 (25), 135 (100), 106 (7), 77 (13).

HRMS (EI) for $C_{10}H_{12}O_3$: calc. $[M]^{+\bullet}$: 180.0786, found: 180.0780.

$[\alpha]_D^{20}$: −26.4 (c = 0.93, $CHCl_3$).



(*S*)-**H**

The alcohol (*S*)-**H** was prepared according to **TP2** from (*S*)-propylene oxide (0.70 mL, 581 mg, 10.0 mmol, 1.0 equiv) dissolved in THF (10 mL) and the corresponding arylmagnesium reagent in THF (18.8 mL, 12.0 mmol, 0.64 M, 1.2 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (3:1) to afford (*S*)-**H** (1.25 g, 6.49 mmol, 65%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.83 (d, *J* = 8.2 Hz, 1H), 7.71–7.64 (m, 1H), 7.44 (d, *J* = 5.5 Hz, 1H), 7.30 (dd, *J* = 5.4, 0.8 Hz, 1H), 7.21 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.08 (m, 1H), 2.93 (dd, *J* = 13.5, 4.7 Hz, 1H), 2.80 (dd, *J* = 13.5, 8.1 Hz, 1H), 1.52 (d, *J* = 3.8 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 3H).

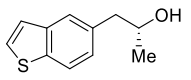
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.2, 138.2, 134.7, 127.0, 126.1, 124.3, 123.8, 122.7, 69.2, 45.8, 23.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3335 (w), 2965 (w), 2924 (w), 1454 (m), 1435 (s), 1420 (s), 1372 (s), 1345 (w), 1326 (w), 1306 (w), 1274 (w), 1259 (w), 1223 (w), 1202 (w), 1159 (w), 1145 (w), 1120 (vs), 1078 (vs), 1048 (vs), 946 (s), 935 (s), 925 (s), 897 (m), 893 (m), 831 (s), 800 (vs), 768 (m) 754 (vs) 702 (vs), 689 (vs), 668 (s).

MS (70 eV, EI): m/z (%): 192 (15), 147 (100), 121 (6), 45 (2).

HRMS (EI) for $C_{11}H_{12}OS$: calc. $[M]^{+\bullet}$: 192.0609, found: 192.0601.

$[\alpha]_D^{20}$: +18.1 (c = 1.09, $CHCl_3$).



(*R*)-**H**

The alcohol (*R*)-**H** was prepared according to **TP2** from (*R*)-propylene oxide (0.70 mL, 581 mg, 10.0 mmol, 1.0 equiv) dissolved in THF (10 mL) and the corresponding arylmagnesium reagent in THF (18.8 mL, 12.0 mmol, 0.64 M, 1.2 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (3:1) to afford (*R*)-**H** (1.42 g, 7.4 mmol, 74%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.82 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.30 (dd, *J* = 5.4, 0.8 Hz, 1H), 7.20 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.12–4.00 (m, 1H), 2.90 (dd, *J* = 13.5, 4.9 Hz, 1H), 2.80 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.45 (s, 1H), 1.27 (d, *J* = 6.1 Hz, 3H).

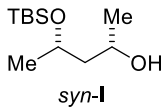
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.1, 138.0, 134.6, 126.9, 126.0, 124.3, 123.7, 122.6, 69.1, 45.7, 22.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3337 (w), 2965 (m), 2931 (m), 2929 (m), 2917 (w), 2915 (w), 1709 (w), 1696 (w), 1454 (w), 1436 (m), 1420 (m), 1370 (m), 1308 (m), 1306 (m), 1260 (m), 1158 (m), 1146 (w), 1118 (s), 1075 (s), 1046 (s), 946 (m), 936 (m), 924 (m), 904 (w), 900 (m), 891 (w), 845 (m), 832 (m), 803 (s), 800 (s), 768 (m), 761 (m), 754 (s), 702 (vs), 690 (vs), 668 (m)

MS (70 eV, EI): m/z (%): 192 (29), 148 (100), 147 (95), 45 (13).

HRMS (EI) for $C_{11}H_{12}OS$: calc. $[M]^{+\bullet}$: 192.0609, found: 192.0608.

$[\alpha]_D^{20}$: −17.7 (c = 2.01, $CHCl_3$).



syn-**I**

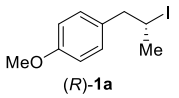
A dry and argon-flushed *Schlenk*-flask was charged with a suspension of NaH (0.88 g, 60 wt% in mineral oil, 22.0 mmol) in THF (220 mL) and cooled to 0 °C. A solution of *syn*-pentan-2,4-diol (2.08 g, 20.0 mmol, dr = 99:1) in THF (20 mL) was added and the resulting solution was stirred for 30 min at 0 °C before let warm to room temperature. Then a solution of TBSCl (3.01 g, 20.0 mmol) in THF (10 mL) was added dropwise and the mixture was stirred for 20 h at room temperature. The reaction mixture was quenched with saturated NH_4Cl aqueous solution at 0 °C and was extracted with EtOAc (3 × 100 mL). The combined organic phase was dried over $MgSO_4$ and the solvents were evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with *i*-hexane/ethyl acetate (5:1) to afford *syn*-**I** (4.20 g, 95%, dr = 99:1) as yellow oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 4.24–4.12 (m, 2H), 3.44 (d, J = 2.1 Hz, 1H), 1.71–1.61 (m, 1H), 1.54–1.44 (m, 1H), 1.23 (d, J = 6.3 Hz, 3H), 1.17 (d, J = 6.2 Hz, 3H), 0.89 (s, 9H), 0.09 (d, J = 0.9 Hz, 3H), 0.08 (s, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 67.9, 64.5, 45.8, 25.9, 23.9, 22.8, 18.1, –4.4, –4.9.

The analytical data was in accordance with literature values.[2b]

4.2 Preparation of secondary alkyl iodides 5a-m



(*R*)-**1a**

The secondary alkyl iodide (*R*)-**1a** was prepared according to **TP3** from the alcohol (*S*)-**A** (1.66 g, 10.0 mmol, 1.0 equiv). To a solution of PPh_3 (3.15 g, 12.0 mmol, 1.2 equiv) and iodine (3.05 g, 12.0 mmol, 1.2 equiv), in 40 mL CH_2Cl_2 was added NMI (0.96 mL, 985 mg, 12.0 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*S*)-**A** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (200:1) to afford (*R*)-**1a** (1.64 g, 5.94 mmol, 59%, 94% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.12–7.08 (m, 2H), 6.87–6.83 (m, 2H), 4.35–4.26 (m, 1H), 3.80 (s, 3H), 3.23 (dd, *J* = 14.2, 7.1 Hz, 1H), 3.00 (dd, *J* = 14.2, 7.6 Hz, 1H), 1.89 (d, *J* = 6.8 Hz, 3H).

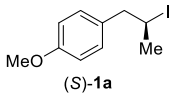
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] 158.6, 132.0, 130.1, 113.9, 55.4, 48.7, 29.6, 28.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2961 (w), 2933 (w), 2916 (w), 2909 (w), 2862 (w), 2833 (w), 2166 (w), 1610 (m), 1583 (w), 1509 (vs), 1463 (w), 1451 (w), 1440 (m), 1375 (w), 1301 (m), 1245 (vs), 1225 (s), 1198 (w), 1176 (s), 1145 (m), 1113 (m), 1090 (w), 1055 (w), 1033 (s), 987 (w), 886 (w), 832 (m), 808 (m), 753 (m), 711 (w).

MS (70 eV, EI): m/z (%): 149 (98), 121 (100), 115 (5), 91 (18), 77 (8).

HRMS (EI) for $C_{10}H_{13}IO$: calc. $[M]^{+\bullet}$: 276.0011, found: 276.0005.

$[\alpha]_D^{20}$: −33.0 (c = 0.95, $CHCl_3$).



(*S*)-**1a**

The secondary alkyl iodide (*S*)-**1a** was prepared according to **TP3** from the alcohol (*R*)-**A** (1.66 g, 10.0 mmol, 1.0 equiv). To a solution of PPh_3 (3.15 g, 12.0 mmol, 1.2 equiv) and iodine (3.05 g, 12.0 mmol, 1.2 equiv), in 40 mL CH_2Cl_2 was added NMI (0.96 mL, 985 mg, 12.0 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*R*)-**A** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (200:1) to afford (*S*)-**1a** (1.44 g, 5.21 mmol, 52%, 94% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.13–7.07 (m, 2H), 6.88–6.81 (m, 2H), 4.35-4.26 (m, 1H), 3.80 (s, 3H), 3.23 (dd, *J* = 14.2, 7.2 Hz, 1H), 3.00 (dd, *J* = 14.2, 7.6 Hz, 1H), 1.89 (d, *J* = 6.8 Hz, 3H).

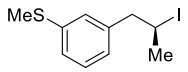
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 158.6, 132.0, 130.1, 113.9, 55.4, 48.8, 29.6, 28.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2954 (w), 2916 (w), 2833 (w), 2166 (w), 1610 (m), 1583 (w), 1509 (vs), 1463 (w), 1451 (w), 1440 (m), 1375 (w), 1301 (m), 1245 (vs), 1225 (s), 1198 (w), 1176 (s), 1145 (m), 1113 (m), 1055 (w), 1033 (s), 987 (w), 886 (w), 832 (m), 808 (m), 753 (m).

MS (70 eV, EI): m/z (%): 149 (100), 147 (8), 121 (99), 115 (8), 91 (20), 77 (11).

HRMS (EI) for $C_{10}H_{13}IO$: calc. $[M]^{+\bullet}$: 276.0011, found: 276.0005.

$[\alpha]_D^{20}$: +33.6 (c = 0.99, $CHCl_3$).



(*S*)-**1b**

The secondary alkyl iodide (*S*)-**1b** was prepared according to **TP3** from the alcohol (*R*)-**B** (260 mg, 1.43 mmol, 1.0 equiv). To a solution of PPh_3 (449 mg, 1.71 mmol, 1.2 equiv) and iodine (434 mg, 1.71 mmol, 1.2 equiv), in 6.8 mL CH_2Cl_2 was added NMI (0.14 mL, 140 mg, 1.71 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*R*)-**B** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (100:1) to afford (*S*)-**1b** (212 mg, 0.73 mmol, 51%, 99% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.23 (t, *J* = 7.7 Hz, 1H), 7.17–7.14 (m, 1H), 7.07 (t, *J* = 1.9 Hz, 1H), 6.95 (dt, *J* = 7.4, 1.4 Hz, 1H), 4.37–4.28 (m, 1H), 3.26 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.03 (dd, *J* = 14.1, 7.5 Hz, 1H), 2.49 (s, 3H), 1.90 (d, *J* = 6.8 Hz, 3H).

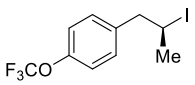
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.4, 138.7, 129.0, 127.2, 125.9, 125.0, 49.4, 28.2, 28.1, 15.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2979 (m), 2963 (m), 2917 (m), 2886 (m), 2861 (m), 2226 (s), 2166 (m), 2155 (m), 1607 (m), 1590 (m), 1571 (m), 1504 (m), 1474 (m), 1439 (s), 1429 (s), 1419 (m), 1412 (m), 1375 (s), 1225 (s), 1204 (m), 1146 (s), 1135 (s), 1116 (m), 1090 (m), 1057 (s), 989 (m), 967 (m), 895 (m), 884 (m), 872 (m), 843 (s), 814 (s), 779 (vs), 699 (vs), 682 (s).

MS (70 eV, EI): m/z (%): 291 (10), 165 (76), 137 (100), 117 (42), 115 (29), 91 (17).

HRMS (EI) for $C_{10}H_{13}IS$: calc. $[M]^{+\bullet}$: 291.9783, found: 291.9777.

$[\alpha]_D^{20}$: −17.3 (c = 0.42, $CHCl_3$).



(*S*)-**1c**

The secondary alkyl iodide (*S*)-**1c** was prepared according to **TP3** from the alcohol (*R*)-**C** (220 mg, 1.00 mmol, 1.0 equiv). To a solution of PPh_3 (314 mg, 1.20 mmol, 1.2 equiv) and iodine (303 mg, 1.20 mmol, 1.2 equiv), in 4.0 mL CH_2Cl_2 was added NMI (0.09 mL, 97 mg, 1.20 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*R*)-**C** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (500:1) to afford (*S*)-**1c** (247 mg, 0.75 mmol, 75%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.22–7.19 (m, 2H), 7.16 (d, J = 8.3 Hz, 2H), 4.34. – 4.26 (m, 1H), 3.25 (dd, J = 14.2, 7.5 Hz, 1H), 3.07 (dd, J = 14.2, 7.1 Hz, 1H), 1.91 (d, J = 6.8 Hz, 3H).

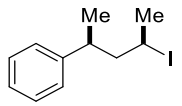
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 148.2, 138.4, 130.4, 128.8, 128.1, 126.8, 121.9, 121.1, 119.3, 77.2, 48.7, 28.3, 27.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2964 (vw), 2921 (vw), 2166 (w), 1595 (vw), 1508 (m), 1490 (w), 1451 (w), 1445 (w), 1436 (w), 1419 (vw), 1378 (w), 1252 (vs), 1217 (vs), 1195 (s), 1154 (vs), 1111 (m), 1057 (m), 1020 (m), 989 (w), 943 (w), 920 (w), 892 (w), 869 (w), 842 (m), 809 (m), 787 (w), 771 (w), 743 (w), 696 (w), 671 (m).

MS (70 eV, EI): m/z (%): 203 (88), 175 (100), 114 (8), 108 (9).

HRMS (EI) for $C_{10}H_{10}F_3IO$: calc. $[M]^{+\bullet}$: 329.9728, found: 329.9715.

$[\alpha]_D^{20}$: +28.8 (c = 0.94, $CHCl_3$).



syn-**1d**

The secondary alkyl iodide *syn*-**1d** was prepared according to **TP3** from the alcohol *anti*-**D** (820 mg, 5.00 mmol, 1.0 equiv). To a solution of PPh_3 (1.89 mg, 7.20 mmol, 1.2 equiv) and iodine (1.83 mg, 7.20 mmol, 1.2 equiv), in 12 mL CH_2Cl_2 was added NMI (0.57 mL, 591 mg, 7.2 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, *anti*-**D** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (1000:1) to afford *syn*-**1d** (890 g, 3.2 mmol, 65%, dr =2:98) as a pale yellow oil.

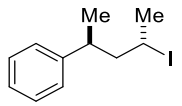
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.34–7.29 (m, 2H), 7.23–7.19 (m, 3H), 4.13–4.05 (m, 1H), 2.97–2.88 (m, 1H), 2.33–2.26 (m, 1H), 1.92 (d, J = 6.8 Hz, 3H), 1.88–1.79 (m, 1H), 1.23 (d, J = 6.9 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 146.2, 128.8, 127.1, 126.4, 51.6, 40.0, 28.8, 27.8, 21.3.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3060 (w), 3025 (w), 2960 (m), 2921 (m), 2867 (w), 1603 (w), 1492 (m), 1452 (m), 1377 (m), 1234 (w), 1204 (w), 1150 (w), 1121 (m), 1061 (w), 762 (m), 699 (vs).

MS (70 eV, EI): m/z (%): 131 (11), 127 (13), 105 (100), 91 (29), 79 (11).

HRMS (EI) for $C_{11}H_{15}I$: calc. $[M]^{+\bullet}$: 274.0218, found: 274.0214.



anti-**1d**

The secondary alkyl iodide *anti*-**1d** was prepared according to **TP3** from the alcohol *syn*-**D** (820 mg, 5.00 mmol, 1.0 equiv). To a solution of PPh_3 (1.57 g, 6 mmol, 1.2 equiv) and iodine (1.52 g, 6 mmol, 1.2 equiv), in 45 mL CH_2Cl_2 was added NMI (0.48 mL, 492 mg, 6 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, *syn*-**D** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (1000:1) to afford *anti*-**1d** (768 g, 2.9 mmol, 58%, dr = 99:1) as a pale yellow oil.

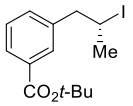
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.33–7.28 (m, 2H), 7.25–7.19 (m, 3H), 3.74–3.65 (m, 1H), 3.01–2.95 (m, 1H), 2.14–2.07 (m, 1H), 1.87 (d, J = 6.8 Hz, 3H), 1.73–1.65 (m, 1H), 1.30 (d, J = 7.0 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 145.6, 128.7, 127.3, 126.6, 51.3, 40.5, 29.9, 29.7, 22.6.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3081 (vw), 3060 (vw), 3025 (w), 2957 (w), 2912 (w), 2867 (w), 2358 (vw), 1739 (vw), 1602 (w), 1493 (m), 1451 (m), 1441 (w), 1423 (w), 1376 (w), 1359 (w), 1267 (vw), 1231 (m), 1201 (w), 1149 (m), 1122 (w), 1089 (w), 1064 (w), 1031 (w), 1011 (w), 934 (vw), 908 (w), 869 (w), 762 (s), 744 (w), 699 (vs).

MS (70 eV, EI): m/z (%): 131 (16), 127 (17), 105 (100), 91 (34), 79 (11).

HRMS (EI) for $C_{11}H_{15}I$: calc. $[M]^{+\bullet}$: 274.0218, found: 274.0215.



(*R*)-**1e**

The secondary alkyl iodide (*R*)-**1e** was prepared according to **TP3** from the alcohol (*S*)-**E** (1.18 g, 5.0 mmol, 1.0 equiv). To a solution of PPh_3 (1.57 g, 6 mmol, 1.2 equiv) and iodine (1.52 g, 6 mmol, 1.2 equiv), in 45 mL CH_2Cl_2 was added NMI (0.48 mL, 492 mg, 6 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*S*)-**E** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (200:1) to afford (*R*)-**1e** (1.07 g, 3.1 mmol, 62%, 96% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.90–7.87 (m, 1H), 7.80 (q, *J* = 1.4 Hz, 1H), 7.39–7.34 (m, 2H), 4.35 (h, *J* = 7.0 Hz, 1H), 3.31 (dd, *J* = 14.1, 7.5 Hz, 1H), 3.11 (dd, *J* = 14.1, 7.2 Hz, 1H), 1.91 (d, *J* = 6.8 Hz, 3H), 1.60 (s, 9H).

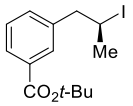
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 165.8, 139.9, 133.2, 132.4, 129.9, 128.5, 128.1, 81.3, 49.2, 28.3, 28.3, 28.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2975 (w), 2928 (w), 2865 (vw), 1709 (s), 1607 (vw), 1587 (w), 1477 (w), 1441 (w), 1392 (w), 1376 (w), 1366 (m), 1293 (s), 1256 (m), 1228 (w), 1204 (m), 1158 (vs), 1111 (s), 1102 (s), 1083 (m), 1057 (w), 1001 (w), 990 (w), 933 (w), 918 (w), 849 (m), 821 (w), 810 (w), 756 (s), 744 (s), 696 (m), 672 (w).

MS (70 eV, EI): m/z (%): 273 (23), 219 (100), 163 (24), 135 (77), 91 (11).

HRMS (EI) for $C_{14}H_{19}O_2I$: calc. $[M]^{+\bullet}$: 346.0430, found: 346.0421.

$[\alpha]_D^{20}$: −31.5 (c = 0.95, $CHCl_3$).



(*S*)-**1e**

The secondary alkyl iodide (*S*)-**1e** was prepared according to **TP3** from the alcohol (*R*)-**E** (1.18 g, 5.0 mmol, 1.0 equiv). To a solution of PPh_3 (1.57 g, 6 mmol, 1.2 equiv) and iodine (1.52 g, 6 mmol, 1.2 equiv), in 45 mL CH_2Cl_2 was added NMI (0.48 mL, 492 mg, 6 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*R*)-**E** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (200:1) to afford (*S*)-**1e** (1.02 g, 2.95 mmol, 59%, 97% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.91–7.86 (m, 1H), 7.80 (q, *J* = 1.4 Hz, 1H), 7.39–7.34 (m, 2H), 4.34 (h, *J* = 7.0 Hz, 1H), 3.31 (dd, *J* = 14.1, 7.5 Hz, 1H), 3.11 (dd, *J* = 14.1, 7.3 Hz, 1H), 1.91 (d, *J* = 6.8 Hz, 3H), 1.60 (s, 9H).

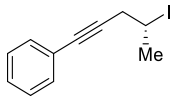
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 165.8, 139.9, 133.2, 132.4, 129.9, 128.1, 81.3, 49.2, 28.3, 28.3, 28.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2976 (w), 2929 (w), 2863 (vw), 1709 (s), 1607 (vw), 1587 (w), 1476 (w), 1442 (w), 1392 (w), 1376 (w), 1366 (m), 1293 (s), 1256 (m), 1228 (w), 1204 (m), 1158 (vs), 1111 (s), 1101 (s), 1083 (m), 1057 (w), 1001 (w), 990 (w), 933 (w), 917 (w), 883 (vw), 849 (m), 821 (w), 810 (w), 756 (s), 744 (s), 696 (m), 672 (w).

MS (70 eV, EI): m/z (%): 273 (22), 219 (87), 163 (27), 135 (100), 91 (21), 57 (23).

HRMS (EI) for $C_{14}H_{19}O_2I$: calc. $[M]^{+\bullet}$: 346.0430, found: 346.0432.

$[\alpha]_D^{20}$: +31.9 (c = 0.93, $CHCl_3$).



(*R*)-**1f**

The secondary alkyl iodide (*R*)-**1f** was prepared according to **TP3** from the alcohol (*S*)-**F** (160 mg, 1.00 mmol, 1.0 equiv). To a solution of PPh_3 (310 mg, 1.20 mmol, 1.2 equiv) and iodine (303 mg, 1.20 mmol, 1.2 equiv), in 4.0 mL CH_2Cl_2 was added NMI (0.10 mL, 99 mg, 1.20 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*S*)-**F** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (100:1) to afford (*R*)-**1f** (130 mg, 0.48 mmol, 48%, 94% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.46–7.41 (m, 2H), 7.32–7.28 (m, 3H), 4.35–4.26 (m, 1H), 3.07 (dd, *J* = 17.2, 5.9 Hz, 1H), 2.97 (dd, *J* = 17.2, 7.3 Hz, 1H), 2.02 (d, *J* = 6.9 Hz, 3H).

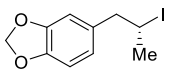
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 131.7, 128.4, 128.2, 123.4, 87.7, 83.1, 34.0, 28.1, 23.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 4334 (w), 2982 (w), 2963 (w), 2915 (w), 2912 (w), 2859 (w), 2226 (s), 2166 (m), 1607 (m), 1504 (m), 1445 (m), 1412 (m), 1376 (m), 1296 (w), 1283 (w), 1247 (w), 1226 (m), 1204 (w), 1199 (w), 1178 (w), 1150 (m), 1136 (m), 1117 (m), 1100 (w), 1089 (w), 1063 (m), 1058 (m), 1039 (w), 1020 (w), 990 (m), 895 (m), 871 (w), 843 (s), 813 (vs), 780 (w), 769 (w), 743 (w), 739 (w), 735 (w), 722 (w), 696 (w).

MS (70 eV, EI): m/z (%): 143 (49), 141 (19), 128 (100), 115 (28).

HRMS (EI) for $C_{11}H_{11}I$: calc. $[M]^{+\bullet}$: 269.9905, found: 269.9899.

$[\alpha]_D^{20}$: −20.1 (c = 0.67, $CHCl_3$).



(*R*)-**1g**

The secondary alkyl iodide (*R*)-**1g** was prepared according to **TP3** from the alcohol (*S*)-**G** (901 mg, 5.0 mmol, 1.0 equiv). To a solution of PPh_3 (1.57 mg, 6.00 mmol, 1.2 equiv) and iodine (1.51 mg, 6.00 mmol, 1.2 equiv), in 20 mL CH_2Cl_2 was added NMI (0.48 mL, 493 mg, 6.00 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*S*)-**G** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (75:1) to afford (*R*)-**1g** (839 mg, 2.89 mmol, 58%, 95% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.75 (d, J = 7.9 Hz, 1H), 6.67 (d, J = 1.5 Hz, 1H), 6.63 (dd, J = 7.9, 1.6 Hz, 1H), 5.95 (s, 2H), 4.32–4.23 (m, 1H), 3.20 (dd, J = 14.2, 7.2 Hz, 1H), 2.96 (dd, J = 14.2, 7.5 Hz, 1H), 1.90 (d, J = 6.8 Hz, 3H).

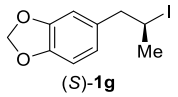
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.8, 146.5, 133.7, 122.2, 109.4, 108.4, 101.1, 49.3, 29.1, 28.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2979 (w), 2970 (w), 2962 (w), 2920 (w), 2891 (w), 2882 (w), 2860 (w), 2834 (vw), 2775 (vw), 2163 (w), 1607 (w), 1500 (s), 1486 (vs), 1440 (s), 1374 (w), 1359 (w), 1273 (w), 1244 (vs), 1222 (m), 1187 (m), 1145 (m), 1121 (m), 1096 (m), 1058 (m), 1035 (vs), 988 (w), 963 (vw), 939 (m), 927 (s), 893 (m), 872 (w), 852 (w), 806 (s), 780 (w), 769 (s), 753 (w), 743 (w), 724 (w), 714 (w), 696 (w), 653 (w).

MS (70 eV, EI): m/z (%): 163 (100), 135 (49), 133 (19), 105 (24).

HRMS (EI) for $C_{10}H_{11}IO_2$: calc. $[M]^{+\bullet}$: 289.9804, found: 289.9800.

$[\alpha]_D^{20}$: −34.4 (c = 0.94, $CHCl_3$).



(*S*)-**1g**

The secondary alkyl iodide (*S*)-**1g** was prepared according to **TP3** from the alcohol (*R*)-**G** (1.08 g, 6.00 mmol, 1.0 equiv). To a solution of PPh_3 (1.89 g, 7.20 mmol, 1.2 equiv) and iodine (1.83 g, 7.20 mmol, 1.2 equiv), in 12 mL CH_2Cl_2 was added NMI (0.57 mL, 591 mg, 7.2 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*R*)-**G** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (75:1) to afford (*S*)-**1g** (1.46 g, 5.05 mmol, 84%, 93% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.75 (d, *J* = 7.9 Hz, 1H), 6.67–6.62 (m, 2H), 5.95 (s, 2H), 4.32–4.23 (m, 1H), 3.20 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.96 (dd, *J* = 14.2, 7.5 Hz, 1H), 1.89 (d, *J* = 6.8 Hz, 3H).

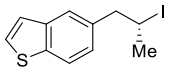
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.7, 146.5, 133.6, 122.2, 109.4, 108.3, 101.1, 49.2, 29.1, 28.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2963 (w), 2891 (w), 2882 (w), 2834 (vw), 2775 (vw), 2166 (w), 1607 (w), 1500 (s), 1486 (vs), 1440 (s), 1374 (w), 1359 (w), 1273 (w), 1244 (vs), 1222 (m), 1188 (m), 1145 (m), 1121 (m), 1096 (m), 1058 (m), 1035 (vs), 988 (w), 939 (m), 927 (s), 893 (m), 871 (w), 852 (w), 805 (s), 783 (w), 769 (m), 744 (w), 725 (w), 721 (w), 714 (w), 696 (w), 654 (w).

MS (70 eV, EI): m/z (%): 163 (100), 135 (60), 11 (24), 105 (37), 79 (14).

HRMS (EI) for $C_{10}H_{11}IO_2$: calc. $[M]^{+\bullet}$: 289.9804, found: 289.9797.

$[\alpha]_D^{20}$: +38.5 (c = 0.99, $CHCl_3$).



(*R*)-**1h**

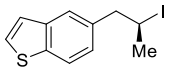
The secondary alkyl iodide (*R*)-**1h** was prepared according to **TP3** from the alcohol (*S*)-**H** (961 mg, 5.0 mmol, 1.0 equiv). To a solution of PPh_3 (1.57 g, 6.00 mmol, 1.2 equiv) and iodine (1.52 g, 6.00 mmol, 1.2 equiv), in 20 mL CH_2Cl_2 was added NMI (0.48 mL, 493 mg, 6.00 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*S*)-**H** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane to afford (*R*)-**1h** (1.12 g, 3.7 mmol, 74%, 93% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.82 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.45 (d, *J* = 5.4 Hz, 1H), 7.31 (d, *J* = 5.4 Hz, 1H), 7.18 (dd, *J* = 8.3, 1.7 Hz, 1H), 4.45–4.36 (m, 1H), 3.42 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.18 (dd, *J* = 14.1, 7.6 Hz, 1H), 1.92 (d, *J* = 6.8 Hz, 3H).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.0, 138.4, 136.0, 127.0, 125.6, 124.0, 123.8, 122.6, 49.6, 28.9, 28.2.
IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2962 (w), 2914 (w), 2871 (w), 1436 (s), 1420 (s), 1374 (m), 1325 (w), 1260 (w), 1230 (m), 1219 (m), 1159 (m), 1147 (s), 1139 (s), 1115 (m), 1088 (m), 1061 (s) 1049 (vs), 987 (m), 939 (w), 892 (m), 858 (w), 830 (s), 805 (s), 767 (m), 753 (vs), 703 (vs) 668 (vs).

MS (70 eV, EI): m/z (%): 301 (2), 175 (59), 147 (100), 134 (8).

HRMS (EI) for $C_{11}H_{11}IS$: calc. $[M]^{+\bullet}$: 301.9626, found: 301.9621.

$[\alpha]_D^{20}$: +35.3 (c = 0.98, $CHCl_3$).



(*S*)-**1h**

The secondary alkyl iodide (*S*)-**1h** was prepared according to **TP3** from the alcohol (*R*)-**H** (961 mg, 5.0 mmol, 1.0 equiv). To a solution of PPh_3 (1.57 g, 6.00 mmol, 1.2 equiv) and iodine (1.52 g, 6.00 mmol, 1.2 equiv), in 20 mL CH_2Cl_2 was added NMI (0.48 mL, 493 mg, 6.00 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, (*R*)-**H** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane to afford (*S*)-**1h** (1.16 g, 3.85 mmol, 77%, 97% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.84–7.82 (m, 1H), 7.68–7.61 (m, 1H), 7.45 (d, *J* = 5.5 Hz, 1H), 7.32 (dd, *J* = 5.4, 0.8 Hz, 1H), 7.18 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.41 (h, *J* = 7.0 Hz, 1H), 3.43 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.19 (dd, *J* = 14.1, 7.6 Hz, 1H), 1.93 (d, *J* = 6.8 Hz, 3H).

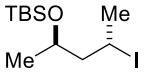
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 134.0, 138.4, 135.9, 127.0, 125.5, 123.9, 123.8, 122.6, 77.5, 77.2, 76.8, 49.5, 28.9, 28.2.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2963 (w), 2917 (w), 2857 (w), 1434 (m), 1420 (m), 1374 (m), 1325 (w), 1260 (w), 1230 (w), 1218 (w), 1159 (w), 1147 (m), 1140 (m), 1115 (m), 1101 (w), 1088 (m), 1061 (m), 1049 (s), 1026 (w), 987 (w), 892 (m), 830 (m), 806 (m), 767 (m), 753 (s), 743 (m), 701 (vs), 688 (vs), 668 (m).

MS (70 eV, EI): m/z (%): 175 (63), 147 (100).

HRMS (EI) for $C_{11}H_{11}IS$: calc. $[M]^{+\bullet}$: 301.9626, found:301.9617.

$[\alpha]_D^{20}$: −35.5 (c = 1.02, $CHCl_3$).



anti-**1i**

The secondary alkyl iodide *anti*-**1i** was prepared according to **TP3** from the alcohol *syn*-**I** (1.09 g, 5.0 mmol, 1.0 equiv). To a solution of PPh_3 (1.57 g, 6.0 mmol, 1.2 equiv) and iodine (1.52 g, 6.0 mmol, 1.2 equiv), in 20 mL CH_2Cl_2 was added NMI (0.48 mL, 492 mg, 6.0 mmol, 1.2 equiv) at −10 °C. After 10 min of stirring, *syn*-**I** was added dropwise over 15 min and the solution was stirred for further 10 min at −10 °C. The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (100:1) to afford *anti*-**1i** (1.24 g, 3.78 mmol, 76%, dr = 99:1) as a colorless oil.

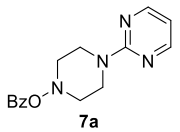
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 4.17 (m, 1H), 3.92 (m, 1H), 2.19 (m, 1H), 1.93 (d, J = 6.8 Hz, 3H), 1.70 (dt, J = 14.1 and 6.5 Hz, 1H), 1.12 (d, J = 6.0 Hz, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.07 (s, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] =68.9, 52.9, 28.9, 26.0, 25.2, 23.1, 18.2, –4.1, –4.6.

The analytical data was in accordance with literature values.[2b]

4.3 Preparation of electrophiles

All electrophiles were prepared according to literature.[6-7]

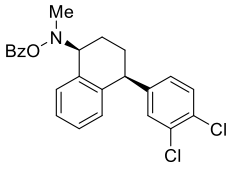


7a

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.34 (d, *J* = 4.8 Hz, 2H), 8.05–7.99 (m, 2H), 7.61–7.54 (m, 1H), 7.45 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.55 (t, *J* = 4.8 Hz, 1H), 4.65 (d, *J* = 13.3 Hz, 2H), 3.54 (q, *J* = 11.8, 11.3 Hz, 4H), 3.02 (t, *J* = 10.6 Hz, 2H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 164.8, 161.5, 158.0, 133.4, 129.6, 128.6, 110.5, 56.0, 42.3.

The analytical data was in accordance with literature values.[6]

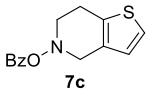


7b

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.93–7.83 (m, 2H), 7.76 (dd, *J* = 8.9, 7.5 Hz, 1H), 7.58–7.52 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.26–7.23 (m, 2H), 7.22–7.16 (m, 1H), 7.15–7.10 (m, 1H), 6.87 (m, 2H), 4.24 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.17–4.10 (m, 1H), 2.99 (s, 3H), 2.32–2.23 (m, 1H), 2.23–2.09 (m, 2H), 2.07–1.97 (m, 1H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 164.8, 147.6, 138.6, 136.0, 133.1, 132.3, 130.8, 130.3, 130.1, 130.0, 129.6, 129.5, 129.5, 128.6, 128.6, 127.9, 126.9, 65.6, 44.2, 42.8, 29.4, 20.0.

The analytical data was in accordance with literature values.[6]

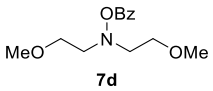


7c

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.99 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.48–7.36 (m, 2H), 7.15 (d, J = 5.2 Hz, 1H), 6.76 (d, J = 5.2 Hz, 1H), 4.62–4.15 (m, 2H), 3.58 (t, J = 6.0 Hz, 2H), 3.11 (t, J = 6.1 Hz, 2H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 165.1, 133.3, 132.5, 131.2, 129.7, 129.3, 128.6, 125.4, 123.7, 55.8, 53.2, 23.0.

The analytical data was in accordance with literature values.[6]



7d

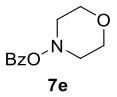
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.05–7.97 (m, 2H), 7.59–7.52 (m, 1H), 7.43 (t, J = 7.8 Hz, 2H), 3.60 (t, J = 5.8 Hz, 4H), 3.28 (s, 6H), 3.25 (t, J = 5.8 Hz, 4H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 165.6, 133.2, 129.6, 129.3, 128.5, 77.5, 77.2, 76.8, 69.8, 59.3, 59.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2887 (w), 1740 (s), 1450 (m), 1314 (w), 1242 (s), 1199 (m), 1176 (w), 1160 (w), 1116 (s), 1087 (m), 1079 (m), 1056 (s), 1023 (s), 1002 (w), 962 (w), 837 (w), 802 (w), 706 (vs), 687 (m), 668 (w).

MS (70 eV, EI): m/z (%): 208 (25), 121 (18), 105 (100), 77 (27), 59 (7).

HRMS (EI) for $C_{13}H_{19}NO_4$: calc. $[M]^{+\bullet}$: 253.1314, found: 253.1314.



7e

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.04–7.98 (m, 2H), 7.60–7.54 (m, 1H), 7.44 (dd, *J* = 8.4, 7.1 Hz, 2H), 4.02–3.93 (m, 2H), 3.91–3.82 (m, 2H), 3.45 (d, *J* = 10.3 Hz, 2H), 3.04 (td, *J* = 10.5, 3.5 Hz, 2H).

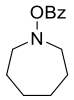
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 164.7, 133.3, 129.6, 129.2, 128.6, 77.5, 77.2, 76.8, 66.0, 57.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2846 (w), 1728 (s), 1454 (w), 1315 (w), 1268 (m), 1263 (m), 1246 (s), 1177 (w), 1165 (w), 1099 (m), 1082 (m), 1066 (m), 1049 (m), 1023 (m), 1007 (m), 998 (w), 921 (w), 872 (w), 857 (m), 852 (m), 794 (w), 709 (vs), 686 (w), 677 (m).

MS (70 eV, EI): m/z (%): 122 (5), 105 (100), 77 (22).

HRMS (EI) for $C_{11}H_{13}NO_3$: calc. $[M]^{+\bullet}$: 207.0895, found: 207.0896.

The analytical data was in accordance with literature values.[7]



7f

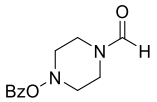
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.04–7.96 (m, 2H), 7.59–7.48 (m, 1H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 3.42–3.23 (m, 4H), 1.86–1.78 (m, 4H), 1.73–1.64 (m, 4H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 164.9, 133.0, 129.8, 129.5, 128.5, 77.5, 77.2, 76.8, 59.6, 26.5, 24.2.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2942 (w), 2936 (w), 2924 (w), 2907 (w), 2846 (w), 1728 (s), 1450 (m), 1311 (w), 1248 (s), 1212 (w), 1197 (w), 1176 (m), 1085 (m), 1065 (s), 1022 (m), 1001 (w), 943 (m), 935 (w), 810 (w), 801 (w), 715 (vs), 688 (m), 668 (w).

MS (70 eV, EI): m/z (%): 122 (23), 105 (100), 77 (27).

HRMS (EI) for $C_{13}H_{17}NO_2$: calc. $[M]^{+\bullet}$: 219.1259, found: 219.1255.



7g

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.06 (s, 1H), 8.01–7.95 (m, 2H), 7.60–7.54 (m, 1H), 7.43 (dd, *J* = 8.5, 7.1 Hz, 2H), 4.29 (d, *J* = 12.3 Hz, 1H), 3.74–3.20 (m, 5H), 3.04–2.76 (m, 2H).

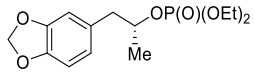
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 164.5, 160.7, 133.5, 129.5, 128.8, 128.6, 77.5, 77.2, 76.8, 56.3, 55.3, 43.6, 38.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2922 (w), 2859 (w), 2851 (w), 2358 (w), 1724 (s), 1706 (w), 1700 (w), 1695 (w), 1669 (vs), 1662 (vs), 1635 (s), 1616 (m), 1596 (m), 1580 (w), 1569 (w), 1558 (w), 1539 (w), 1506 (w), 1490 (w), 1464 (w), 1440 (s), 1437 (s), 1424 (m), 1398 (m), 1373 (w), 1357 (w), 1316 (w), 1295 (w), 1275 (m), 1246 (vs), 1238 (s), 1208 (m), 1179 (m), 1166 (w), 1128 (w), 1113 (m), 1089 (m), 1080 (m), 1063 (s), 1022 (s), 1000 (m), 965 (w), 869 (w), 809 (w), 789 (w), 781 (w), 713 (s), 689 (m), 677 (m), 667 (m).

MS (70 eV, EI): m/z (%):122 (14), 105 (100), 77 (25), 56 (6).

HRMS (EI) for $C_{12}H_{14}N_2O_3$: calc. $[M]^{+\bullet}$: 234.1004, found: 234.1000.

4.4 Preparation of SI1, SI2 and SI4[3-4]



SI1

A flask was charged with (*R*)-**G** (180.1 mg, 1.0 mmol, 1.0 equiv) and THF (6 mL) and cooled to −78 °C. Then, a solution of *t*-BuLi (2.0 M in pentane, 0.55 mL, 1.1 mmol, 1.1 equiv) was added dropwise and the reaction mixture wasstirred for 30 min at this temperature. Diethyl chlorophosphate (189.8 mg, 1.1 mmol, 1.1 equiv) was added and the reaction mixture stirred for another 45 min at −78 °C before let warm to room temperature and stirred for 15 min at ambient temperature. The reaction mixture was quenched with sat. aq. NH_4Cl and extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over MgSO4 and the solvent evaporated. The crude product was purified by flash column chromatography with diethyl ether to afford **SI1** (164.5 mg, 0.52 mmol, 52%) as a colorless oil.

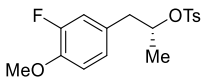
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.76–6.62 (m, 3H), 5.91 (s, 2H), 4.71–4.53 (m, 1H), 4.16–3.86 (m, 4H), 2.89 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.79–2.65 (m, 1H), 1.37–1.20 (m, 9H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.6, 146.3, 131.1, 122.7, 110.1, 108.2, 101.0, 76.4, 63.6, 43.6, 21.2, 16.3.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2982 (w), 2909 (w), 1609 (vw), 1504 (m), 1490 (m), 1460 (w), 1443 (m), 1392 (w), 1383 (w), 1369 (w), 1247 (s), 1212 (w), 1190 (w), 1166 (w), 1100 (w), 1028 (s), 991 (vs), 976 (vs), 940 (s), 928 (s), 859 (w), 808 (s), 774 (m), 742 (w), 726 (w), 714 (w).

MS (70 eV, EI): m/z (%): 122 (23), 105 (100), 77 (27).

HRMS (EI) for $C_{14}H_{21}PO_6$: calc. $[M-OEt]^{+\bullet}$: 271.0735, found: 271.0732.



SI3

A flask was charged with TsCl (1.43 g, 7.5 mmol, 1.5 equiv), DMAP (1.22 g, 10.0 mmol, 2.0 equiv) and DCM (50 mL). Then, 1-(3-fluoro-4-methoxyphenyl)propan-2-ol (921 mg, 5.0 mmol, 1.0 equiv) dissolved in DCM (10 mL) was added in one portion. The reaction mixture was stirred overnight at ambient temperature and quenched with H_2O. The reaction mixture was extracted with DCM (3 x 100 mL) and the combined organic phases were dried over MgSO**4** before concentration *in vacuo*. The crude product was purified by flash column chromatography with *i*-hex/EtOAc (9:1) and 1% triethylamine to afford **SI3** (778 mg, 2.3 mmol, 46%) as a colorless solid.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.60–7.56 (m, 2H), 7.23–7.17 (m, 2H), 6.81–6.72 (m, 2H), 6.67–6.61 (m, 1H), 4.65 (dp, *J* = 7.4, 6.2 Hz, 1H), 3.85 (s, 3H), 2.79 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.70 (dd, *J* = 14.2, 5.6 Hz, 1H), 2.42 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 3H).

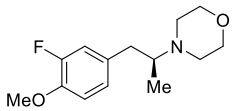
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.3, 150.9, 146.6, 146.5, 144.6, 133.9, 129.7, 129.4, 129.3, 127.7, 125.3, 117.1, 116.9, 113.2, 80.6, 56.3, 42.0, 21.7, 21.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2998 (w), 2939 (w), 1597 (w), 1585 (w), 1518 (m), 1516 (m), 1501 (m), 1492 (m), 1462 (m), 1454 (m), 1448 (m), 1432 (m), 1378 (m), 1369 (w), 1359 (s), 1343 (m), 1321 (m), 1303 (w), 1292 (w), 1279 (m), 1270 (m), 1228 (m), 1220 (m), 1208 (w), 1185 (s), 1172 (s), 1147 (m), 1132 (s), 1124 (m), 1118 (m), 1101 (m), 1094 (s), 1026 (s), 1017 (m), 961 (m), 936 (w), 914 (s), 906 (s), 888 (vs), 871 (vs), 844 (w), 832 (w), 819 (m), 807 (s), 799 (m), 762 (s), 746 (s), 714 (w), 703 (m), 663 (m).

MS (70 eV, EI): m/z (%): 166 (100), 155 (63), 139 (92), 91 (87).

HRMS (EI) for $C_{17}H_{19}SFO_4$: calc. $[M]^{+\bullet}$: 338.0988, found: 338.0983.

M.p. (°C): 93.



SI4

SI2 (169.2 mg, 0.5 mmol, 1.0 equiv) was dissolved in THF (1 mL) and magnesium morpholino amide (1.0 M, 0.6 mL, 0.6 mmol, 1.2 equiv) was added dropwise. The reaction mixture was heated at 60 °C for 12 h. The reaction was quenched with sat. aq. $NaHCO_3$ and extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography with EtOAc affording **SI4** (11.4 mg, 0.045 mmol, 9% yield) as a light brown oil.**^{1}H-NMR ($CDCl_3$, 400 MHz):** δ [ppm] = δ 6.95–6.84 (m, 3H), 3.87 (s, 3H), 3.72 (t, *J* = 4.6 Hz, 4H), 2.91 (dd, *J* = 13.3, 4.7 Hz, 1H), 2.60 (dd, *J* = 5.6, 3.7 Hz, 4H), 2.35 (dd, *J* = 13.3, 9.3 Hz, 1H), 0.95 (d, *J* = 6.6 Hz, 3H).

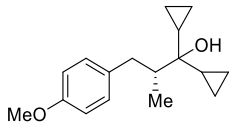
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.5, 151.1, 145.9, 145.8, 133.6, 133.6, 124.9, 124.8, 117.0, 116.8, 113.4, 113.3, 67.5, 61.6, 56.5, 49.2, 38.5, 14.3.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2958 (w), 2926 (m), 2852 (m), 2812 (w), 1516 (s), 1460 (m), 1458 (m), 1443 (m), 1431 (w), 1376 (w), 1352 (w), 1272 (s), 1224 (m), 1208 (w), 1175 (w), 1115 (vs), 1067 (w), 1028 (m), 969 (m), 955 (m), 917 (w), 872 (w), 862 (m), 808 (m), 760 (m), 742 (w).

MS (70 eV, EI): m/z (%): 139 (8), 114 (100), 84 (8), 70 (9).

HRMS (EI) for $C_{14}H_{20}FNO_2$: calc. $[M–C_6H_{12}ON]^{+\bullet}$: 139.0559, found: 139.0553.

5 Characterization of new compounds



(*R*)-**4a**

The tertiary alcohol (*R*)-**4a** was prepared according to **TP4** from the iodide (*R*)-**1a** (27.6 mg, 0.1 mmol, 1.0 equiv) and dicyclopropyl ketone (**6a**, 22.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (10:1) to afford (*R*)-**4a** (19.5 mg, 0.075 mmol, 75%, 91% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.13–7.09 (m, 2H), 6.85–6.81 (m, 2H), 3.79 (s, 3H), 3.19 (dd, *J* = 13.2, 3.0 Hz, 1H), 2.26 (dd, *J* = 13.2, 11.3 Hz, 1H), 1.93–1.87 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.92–0.85 (m, 2H), 0.51–0.40 (m, 6H), 0.35–0.26 (m, 2H).

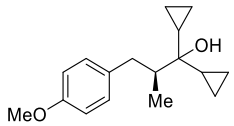
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 157.7, 134.4, 130.2, 113.7, 72.7, 55.4, 47.9, 37.3, 16.8, 15.9, 14.2, 1.6, 1.4, −0.9, –1.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3005 (w), 2961 (w), 2937 (w), 1748 (w), 1710 (vs), 1610 (w), 1511 (s), 1464 (w), 1441 (w), 1419 (w), 1360 (s), 1299 (w), 1246 (s), 1220 (s), 1177 (m), 1091 (w), 1033 (m), 999 (m), 977 (w), 928 (w), 913 (w), 901 (w), 833 (w), 809 (w), 758 (w).

MS (70 eV, EI): m/z (%): 213 (5), 150 (15), 134 (16), 121 (100), 111 (91), 91 (15), 69 (69).

HRMS (EI) for $C_{17}H_{24}O_2$: calc. $[M]^{+\bullet}$: 260.1776, found: 260.1770.

$[\alpha]_D^{20}$: +14.0 (c = 0.94, $CHCl_3$).



(*S*)-**4a**

The tertiary alcohol (*S*)-**4a** was prepared according to **TP4** from the iodide (*S*)-**1a** (27.6 mg, 0.1 mmol, 1.0 equiv) and dicyclopropyl ketone (**6a**, 22.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (10:1) to afford (*S*)-**4a** (21.1 mg, 0.081 mmol, 81%, 90% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.13–7.09 (m, 2H), 6.85–6.81 (m, 2H), 3.79 (s, 3H), 3.19 (dd, *J* = 13.3, 3.0 Hz, 1H), 2.26 (dd, *J* = 13.2, 11.3 Hz, 1H), 1.39–1.86 (m, 1H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.90–0.85 (m, 2H), 0.48–0.40 (m, 6H), 0.36–0.25 (m, 2H).

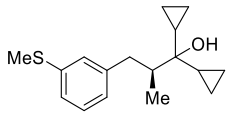
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 157.7, 134.4, 130.2, 113.7, 72.7, 55.4, 47.9, 37.3, 16.8, 15.9, 14.2, 1.6, 1.4, -0.9, -1.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3528 (vw), 3084 (vw), 3003 (w), 2956 (w), 2925 (w), 2876 (w), 2854 (w), 2833 (w), 1610 (w), 1583 (w), 1511 (vs), 1484 (vw), 1464 (w), 1441 (w), 1421 (w), 1373 (w), 1300 (w), 1246 (s), 1177 (m), 1102 (w), 1034 (m), 994 (m), 976 (w), 927 (w), 913 (w), 901 (w), 884 (vw), 831 (w), 807 (w), 757 (w).

MS (70 eV, EI): m/z (%): 150 (13), 134 (15), 121 (100), 111 (73), 91 (19), 77 (12), 69 (74).

HRMS (EI) for $C_{17}H_{24}O_2$: calc. $[M]^{+\bullet}$: 260.1776, found: 260.1771.

$[\alpha]_D^{20}$: −17.8 (c = 1.46, $CHCl_3$).



(*S*)-**4b**

The tertiary alcohol (*S*)-**4b** was prepared according to **TP4** from the iodide (*S*)-**1b** (29.2 mg, 0.1 mmol, 1.0 equiv) and dicyclopropyl ketone (**6a**, 22.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (*S*)-**4b** (20.2 mg, 0.073 mmol, 73%, 99% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.21 (t, *J* = 7.6 Hz, 1H), 7.11–7.07 (m, 2H), 6.98 (dt, *J* = 7.4, 1.4 Hz, 1H), 3.23 (dd, *J* = 13.1, 2.9 Hz, 1H), 2.49 (s, 3H), 2.29 (dd, *J* = 13.1, 11.4 Hz, 1H), 1.96–1.91 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.91–0.85 (m, 3H), 0.50–0.41 (m, 6H), 0.36–0.26 (m, 2H).

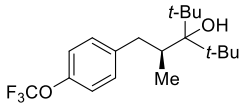
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 143.2, 138.1, 128.8, 127.6, 126.3, 123.9, 72.7, 47.7, 38.2, 16.9, 16.0, 15.8, 14.2, 1.7, 1.4, −0.9, –0.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3006 (s), 2962 (s), 2931 (s), 2924 (s), 2921 (s), 2361 (s), 2258 (s), 2234 (s), 2219 (s), 2169 (vs), 2156 (s), 2139 (s), 2094 (s), 2067 (s), 1591 (s), 1570 (s), 1476 (s), 1458 (s), 1440 (s), 1424 (s), 1374 (s), 1023 (s), 995 (s), 975 (s), 780 (s), 777 (s).

MS (70 eV, EI): m/z (%): 166 (10), 137 (18), 111 (100), 91 (15), 69 (69).

HRMS (EI) for $C_{17}H_{24}OS$: calc. $[M]^{+\bullet}$: 276.1548, found: 276.1544.

$[\alpha]_D^{20}$: −25.4 (c = 0.56, $CHCl_3$).



(*S*)-**4c**

The tertiary alcohol (*S*)-**4c** was prepared according to **TP4** from the iodide (*S*)-**1c** (33.0 mg, 0.1 mmol, 1.0 equiv) and 2,2,4,4-tetramethylpentan-3-one (**6b**, 28.4 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (30:1) to afford (*S*)-**4c** (22.5 mg, 0.065 mmol, 65%, 98% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.22–7.18 (m, 2H), 7.13–7.10 (m, 2H), 3.53–3.46 (m, 1H), 2.42–2.31 (m, 2H), 1.48 (s, 1H), 1.22 (s, 9H), 1.15 (s, 9H).

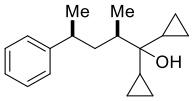
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.3, 143.0, 130.4, 120.9, 81.8, 43.9, 43.7, 43.5, 40.0, 30.2, 30.1, 18.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3006 (w), 2964 (m), 2912 (m), 2877 (m), 1502 (m), 1488 (vs), 1440 (m), 1394 (m), 1381 (w), 1369 (m), 1244 (vs), 1205 (m), 1187 (m), 1085 (w), 1038 (vs), 983 (m), 929 (s), 867 (w), 802 (m), 792 (m), 768 (w).

MS (70 eV, EI): m/z (%): 289 (8), 202 (27), 174 (100), 87 (33), 57 (79).

HRMS (EI) for $C_{15}H_{20}F_3O_2$: calc. $[M\text{-}(t\text{-Bu})]^{+\bullet}$: 289.1415, found: 289.1413.

$[\alpha]_D^{20}$: −13.6 (c = 0.62, $CHCl_3$).



syn-**4d**

The tertiary alcohol *syn*-**4d** was prepared according to **TP4** from the iodide *syn*-**1d** (27.4 mg, 0.1 mmol, 1.0 equiv) and dicyclopropyl ketone (**6a**, 22.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford *syn*-**4d** (19.1 mg, 0.074 mmol, 74%, dr = 4:96) as a colorless oil.

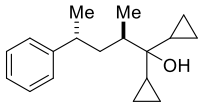
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.29 (dd, *J* = 7.6, 1.1 Hz, 2H), 7.20–7.17 (m, 3H), 2.81 (m, 1H), 2.13 (m, 1H), 1.45-1.41 (m, 1H), 1.35–1.34 (m, 1H), 1.26–1.24 (m, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.75–0.71 (m, 3H), 0.58 (s, 1H), 0.44–0.08 (m, 8H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.0, 128.5, 128.5, 127.4, 127.1, 126.0, 72.5, 42.7, 39.8, 38.0, 24.8, 16.4, 16.1, 14.5, 1.5, 1.2, 1.1, -1.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2975 (m), 2932 (m), 2858 (m), 2364 (m), 2336 (m), 2184 (w), 2172 (m), 2145 (w), 1731 (w), 1717 (w), 1556 (w), 1381 (m), 1350 (m), 1296 (w), 1236 (w), 1194 (w), 1179 (w), 1151 (m), 1118 (vs), 1076 (m), 1042 (w), 1024 (w), 929 (w), 853 (vw), 784 (vw), 748 (vw), 730 (vw), 702 (vw), 658 (vw).

MS (70 eV, EI): m/z (%): 111 (63), 91 (39), 69 (100).

HRMS (EI) for $C_{18}H_{26}O$: calc. $[M-C_3H_5]^{+\bullet}$: 217.1592, found: 217.1586.



anti-**4d**

The tertiary alcohol a*nti*-**4d** was prepared according to **TP4** from the iodide *anti*-**1d** (27.4 mg, 0.1 mmol, 1.0 equiv) and dicyclopropyl ketone (**6a**, 22.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford *anti*-**4d** (18.1 mg, 0.7 mmol, 70%, dr = 95:5) as a colorless oil.

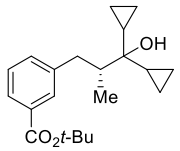
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.32–7.28 (m, 2H), 7.24–7.21 (m, 2H), 7.21–7.17 (m, 1H), 2.80–2.78 (m, 1H), 2.00–1.94 (m, 1H), 1.79 (m, 1H), 1.50–1.43 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.87–0.79 (m, 3H), 0.44–0.35 (m, 6H), 0.27–0.22 (m, 2H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 149.3, 128.5, 127.1, 125.9, 72.8, 43.1, 40.8, 37.7, 20.8, 16.4, 16.2, 14.9, 1.7, 1.3, -1.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3006 (w), 2954 (m), 2924 (s), 2870 (m), 2854 (m), 2166 (w), 1493 (w), 1455 (m), 1419 (w), 1375 (m), 1260 (w), 1179 (w), 1139 (w), 1101 (w), 1051 (w), 1020 (m), 990 (m), 974 (m), 930 (w), 906 (m), 845 (w), 824 (w), 815 (w), 778 (w), 773 (w), 760 (m), 745 (m), 736 (w), 732 (w), 727 (w), 722 (m), 718 (w), 713 (w), 699 (vs), 681 (w), 672 (m), 667 (m), 659 (w).

MS (70 eV, EI): m/z (%): 225 (28), 105 (34), 97 (100), 75 (68).

HRMS (EI) for $C_{18}H_{26}O$: calc. $[M]^{+\bullet}$: 258.1984, found: 258.1978.



(*R*)-**4e**

The tertiary alcohol (*R*)-**4e** was prepared according to **TP4** from the iodide (*R*)-**1e** (34.6 mg, 0.1 mmol, 1.0 equiv) and dicyclopropyl ketone (**6a**, 22.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (2:1) to afford (*R*)-**4e** (21.5 mg, 0.65 mmol, 65%, 93% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.83–7.79 (m, 2H), 7.37–7.30 (m, 2H), 3.29 (dd, *J* = 13.2, 2.9 Hz, 1H), 2.38 (dd, *J* = 13.1, 11.5 Hz, 1H), 1.99–1.94 (m, 1H), 1.60 (s, 9H), 0.95–0.86 (m, 6H), 0.55–0.43 (m, 6H), 0.37–0.27 (m, 2H).

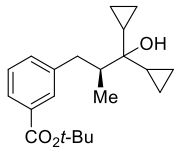
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 166.2, 142.6, 133.5, 132.0, 130.2, 128.1, 126.9, 81.0, 72.7, 47.7, 38.0, 28.4, 16.9, 15.9, 14.1, 1.7, 1.4, -0.8, -0.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3527 (vw), 3005 (w), 2975 (w), 2931 (w), 2878 (vw), 1711 (s), 1699 (s), 1605 (w), 1586 (w), 1477 (w), 1457 (w), 1440 (w), 1392 (w), 1368 (m), 1291 (s), 1256 (m), 1208 (w), 1159 (vs), 1110 (m), 1087 (m), 1062 (w), 1054 (w), 1023 (m), 998 (m), 977 (m), 935 (w), 929 (w), 914 (w), 865 (w), 849 (m), 824 (w), 812 (w), 758 (m), 746 (m), 704 (w), 668 (w).

MS (70 eV, EI): m/z (%): 257 (17), 207 (23), 164 (26), 135 (41), 111 (100), 91 (19), 69 (83).

HRMS (EI) for $C_{17}H_{21}O_2$: calc. $[M-O\textit{t}\text{-Bu}]^{+\bullet}$: 257.1542, found: 257.1536.

$[\alpha]_D^{20}$: +10.1 (c = 0.81, $CHCl_3$).



(*S*)-**4e**

The tertiary alcohol (*S*)-**4e** was prepared according to **TP4** from the iodide (*R*)-**1e** (34.6 mg, 0.1 mmol, 1.0 equiv) and dicyclopropyl ketone (**6a**, 22.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (2:1) to afford (*S*)-**4e** (23.8 mg, 0.72 mmol, 72%, 93% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.81 (dt, *J* = 9.0, 1.9 Hz, 2H), 7.37–7.30(m, 2H), 3.29 (dd, *J* = 13.1, 2.9 Hz, 1H), 2.38 (dd, *J* = 13.1, 11.5 Hz, 1H), 2.00–1.94 (m, 1H), 1.60 (s, 9H), 0.93–0.86 (m, 6H), 0.51–0.43 (m, 6H), 0.37–0.27 (m, 2H).

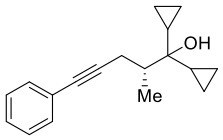
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 166.2, 142.6, 133.5, 132.0, 130.2, 128.1, 126.9, 81.0, 72.7, 47.7, 38.0, 28.4, 16.9, 15.9, 14.2, 1.7, 1.4, -0.8, -0.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3528 (vw), 3006 (w), 2976 (w), 2933 (w), 2879 (w), 1711 (s), 1699 (s), 1605 (w), 1587 (w), 1478 (w), 1458 (w), 1441 (w), 1392 (w), 1368 (m), 1292 (s), 1256 (m), 1208 (w), 1160 (vs), 1111 (m), 1087 (m), 1055 (w), 1023 (m), 997 (m), 978 (m), 930 (w), 914 (w), 850 (m), 825 (w), 758 (m), 746 (m), 704 (w).

MS (70 eV, EI): m/z (%): 257 (18), 207 (14), 164 (27), 135 (41), 111 (100), 91 (18), 69 (80).

HRMS (EI) for $C_{17}H_{21}O_2$: calc. $[M-O\textit{t}\text{-Bu}]^{+\bullet}$: 257.1542, found: 257.1535.

$[\alpha]_D^{20}$: −12.7 (c = 1.0, $CHCl_3$).



(*R*)-**4f**

The tertiary alcohol (*R*)-**4f** was prepared according to **TP4** from the iodide (*R*)-**1f** (27.0 mg, 0.1 mmol, 1.0 equiv) and dicyclopropyl ketone (**6a**, 22.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1) to afford (*R*)-**4f** (18.6 mg, 0.73 mmol, 73%, 93% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.38 (dq, *J* = 8.6, 3.2, 2.8 Hz, 2H), 7.27 (t, *J* = 2.9 Hz, 1H), 7.25 (s, 1H), 2.83 (dd, *J* = 16.7, 4.5 Hz, 1H), 2.46 (dd, *J* = 16.7, 9.2 Hz, 1H), 2.04–2.02 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.21 (s, 1H), 0.88–0.82 (m, 2H), 0.51–0.38 (m, 5H), 0.35–0.29 (m, 2H).

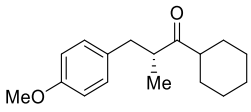
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 131.6, 128.3, 127.7, 124.0, 90.4, 81.8, 72.5, 45.0, 22.4, 17.6, 15.6, 15.3, 1.5, 0.7, -0.5, -0.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3006 (w), 2969 (w), 2965 (w), 2935 (w), 1597 (w), 1490 (m), 1460 (w), 1442 (w), 1424 (w), 1373 (w), 1303 (w), 1177 (w), 1114 (w), 1069 (w), 1023 (m), 995 (m), 973 (m), 928 (w), 912 (m), 880 (w), 864 (w), 843 (w), 823 (w), 754 (vs), 734 (w), 690 (vs), 669 (w).

MS (70 eV, EI): m/z (%): 213 (27), 211 (100), 178 (18), 141 (25), 128 (40), 115 (50), 111 (47).

HRMS (EI) for $C_{18}H_{22}O$: calc. $[M-H]^{+\bullet}$: 253.1592, found: 253.1586

$[\alpha]_D^{20}$: −12.2 (c = 0.41, $CHCl_3$).



(*R*)-**4g**

The ketone (*R*)-**4g** was prepared according to **TP4** from the iodide (*R*)-**1a** (27.6 mg, 0.1 mmol, 1.0 equiv) and cyclohexanecarbaldehyde (**6c**, 24 µL, 22.4 mg, 0.2 mmol, 2.0 equiv). The crude alcohol was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1). Both diastereoisomers of the alcohol were then dissolved in DCM (1 mL) and oxidized with DMP (212 mg, 0.15 mmol, 1.5 equiv). The reaction was stirred for 10 min at ambient temperature before quenching with sat. aq. NH_4Cl and extracted with Et_2O (3 × 50 mL). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). to afford (*R*)**-4g** (17.7 mg, 0.068 mmol, 68%, 90% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.07–7.02 (m, 2H), 6.82–6.77 (m, 2H), 3.78 (s, 3H), 2.98–2.84 (m, 2H), 2.51–2.42 (m, 1H), 2.35–2.18 (m, 1H), 1.78–1.66 (m, 3H), 1.35–1.08 (m, 7H), 1.06–1.02 (m, 3H).

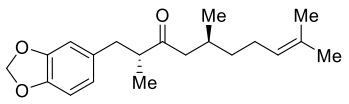
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 217.5, 158.1, 132.3, 130.1, 113.8, 55.4, 50.7, 46.9, 38.6, 28.4, 28.1, 26.0, 25.8, 25.8, 17.1.z

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3411 (vw), 2929 (m), 2855 (w), 1708 (vs), 1612 (w), 1584 (vw), 1512 (s), 1449 (m), 1420 (w), 1361 (s), 1300 (w), 1246 (s), 1220 (s), 1178 (m), 1144 (w), 1107 (w), 1091 (w), 1035 (m), 992 (m), 892 (vw), 833 (w), 824 (w), 809 (w), 754 (vw).

MS (70 eV, EI): m/z (%): 177 (15), 121 (100), 83 (14).

HRMS (EI) for $C_{17}H_{24}O_2$: calc. $[M]^{+\bullet}$: 260.1776, found: 260.1771.

$[\alpha]_D^{20}$: +59.2 (c = 0.76, $CHCl_3$).



(2*R*,5*S*)-4h

The ketone (2*R*,5*S*)-**4h** was prepared according to **TP4** from the iodide (*R*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and (*S*)-(−)-citronellal (**6d**, 30.9 mg, 0.2 mmol, 2.0 equiv). The crude alcohol was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). Both diastereoisomers of the alcohol were then dissolved in DCM (1 mL) and oxidized with DMP (212 mg, 0.15 mmol, 1.5 equiv). The reaction was stirred for 10 min at ambient temperature before quenching with sat. aq. NH_4Cl and extracted with Et_2O (3 × 50 mL). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). to afford (2*R*,5*S*)-**4h** (23.4 mg, 0.074 mmol, 74%, dr = 95:5) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.71 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 1.7 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.93–5.90 (m, 2H), 5.09–5.02 (m, 1H), 2.88 (dd, *J* = 13.5, 7.2 Hz, 1H), 2.75 (h, *J* = 7.0 Hz, 1H), 2.49–2.42 (m, 1H), 2.37 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.12 (dd, *J* = 16.4, 7.9 Hz, 1H), 2.03–1.84 (m, 3H), 1.69–1.64 (m, 3H), 1.60–1.57 (m, 3H), 1.24–1.07 (m, 2H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H).

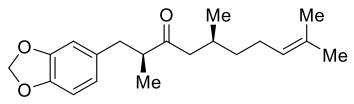
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 214.2, 147.7, 146.0, 133.7, 131.6, 124.5, 122.1, 109.5, 108.3, 101.0, 49.8, 48.7, 38.9, 37.1, 28.6, 25.9, 25.6, 19.9, 17.8, 16.5.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3402 (w), 2923 (m), 2873 (m), 2854 (m), 1709 (m), 1504 (m), 1489 (s), 1456 (m), 1442 (s), 1402 (w), 1375 (m), 1245 (vs), 1190 (m), 1121 (w), 1099 (w), 1039 (s), 930 (m), 858 (w), 810 (m), 770 (w), 724 (vw).

MS (70 eV, EI): m/z (%): 147 (7), 135 (100), 105 (9), 79 (16), 77 (13).

HRMS (EI) for $C_{20}H_{28}O_3$: calc. $[M]^{+\bullet}$: 316.2038, found: 316.2034.

$[\alpha]_D^{20}$: −27.7 (c = 0.6, $CHCl_3$).



(2*S*,5*S*)-**4h**

The ketone (2*S*,5*S*)-**4h** was prepared according to **TP4** from the iodide (*S*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and (*S*)-(−)-citronellal (**6d**, 30.9 mg, 0.2 mmol, 2.0 equiv). The crude alcohol was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). Both diastereoisomers of the alcohol were then dissolved in DCM (1 mL) and oxidized with DMP (212 mg, 0.15 mmol, 1.5 equiv). The reaction was stirred for 10 min at ambient temperature before quenching with sat. aq. NH_4Cl and extracted with Et_2O (3 × 50 mL). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). to afford (2*S*,5*S*)-**4h** (24.0 mg, 0.076 mmol, 76%, dr = 5:95) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.71 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (q, *J* = 1.4 Hz, 2H), 5.10–5.02 (m, 1H), 2.89 (dd, *J* = 13.5, 7.2 Hz, 1H), 2.75 (h, *J* = 7.0 Hz, 1H), 2.46 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.24 (qd, *J* = 16.4, 6.8 Hz, 2H), 1.93 (tq, *J* = 15.0, 7.1 Hz, 3H), 1.68 (d, *J* = 1.5 Hz, 3H), 1.58 (d, *J* = 1.3 Hz, 3H), 1.27–1.06 (m, 2H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H).

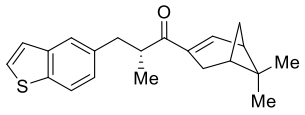
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 214.0, 147.7, 146.0, 133.8, 131.6, 124.5, 122.1, 109.5, 108.3, 101.0, 49.7, 48.7, 38.8, 37.1, 28.6, 25.8, 25.6, 19.9, 17.8, 16.5.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2923 (m), 2873 (w), 2854 (w), 1709 (m), 1504 (m), 1489 (s), 1455 (m), 1442 (s), 1402 (w), 1375 (m), 1245 (vs), 1189 (m), 1121 (w), 1099 (w), 1039 (vs), 985 (w), 930 (m), 858 (w), 810 (m), 771 (w).

MS (70 eV, EI): m/z (%): 147 (8), 135 (100), 105 (9), 79 (17), 77 (14).

HRMS (EI) for $C_{20}H_{28}O_3$: calc. $[M]^{+\bullet}$: 316.2038, found: 316.2032.

$[\alpha]_D^{20}$: +27.7 (c = 0.9, $CHCl_3$).



(2*R*,1'*R*,5'*S*)-**4i**

The ketone (2*R*,1'*R*,5'*S*)-**4i** was prepared according to **TP4** from the iodide (*R*)-**1h** (30.2 mg, 0.1 mmol, 1.0 equiv) and (1*R*)-(−)-myrtenal (**6e**, 31 µL, 30.9 mg, 0.2 mmol, 2.0 equiv). The crude alcohol was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). Both diastereoisomers of the alcohol were then dissolved in DCM (1 mL) and oxidized with DMP (212 mg, 0.15 mmol, 1.5 equiv). The reaction was stirred for 10 min at ambient temperature before quenching with sat. aq. NH_4Cl and extracted with Et_2O (3 × 50 mL). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). to afford (2*R*,1'*R*,5'*S*)-**4i** (14.9 mg, 0.046 mmol, 46%, dr = 5:95) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.75 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.56 (d, *J* = 1.7 Hz, 1H), 7.39 (d, *J* = 5.4 Hz, 1H), 7.24 (dd, *J* = 5.4, 0.8 Hz, 1H), 7.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.65 (tt, *J* = 3.3, 1.5 Hz, 1H), 3.54 (q, *J* = 7.0 Hz, 1H), 3.11 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.92 (td, *J* = 5.7, 1.6 Hz, 1H), 2.72 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.49–2.25 (m, 3H), 2.09–2.04 (m, 1H), 1.27 (s, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 9.1 Hz, 1H), 0.44 (s, 3H).

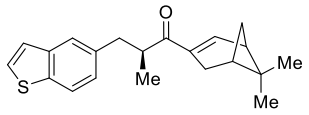
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 202.8, 148.8, 140.0, 137.7, 136.8, 136.4, 126.6, 125.8, 123.9, 123.8, 122.3, 41.3, 40.3, 40.2, 39.7, 37.4, 32.7, 31.1, 25.9, 20.6, 18.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2922 (vs), 2869 (m), 2854 (m), 1726 (w), 1657 (vs), 1612 (m), 1585 (w), 1456 (m), 1436 (m), 1421 (m), 1380 (m), 1367 (m), 1327 (w), 1309 (w), 1278 (w), 1264 (m), 1247 (m), 1230 (m), 1208 (w), 1196 (w), 1185 (w), 1175 (w), 1161 (w), 1136 (m), 1102 (w), 1090 (m), 1073 (w), 1049 (m), 1016 (w), 975 (w), 959 (w), 946 (w), 935 (w), 890 (m), 846 (w), 832 (m), 806 (m), 781 (w), 768 (w), 754 (m), 743 (m), 718 (w), 700 (s), 693 (s).

MS (70 eV, EI): m/z (%): 281 (15), 161 (24), 147 (100), 119 (20), 91 (25), 57 (31).

HRMS (EI) for $C_{21}H_{24}OS$: calc. $[M]^{+\bullet}$: 324.1548, found: 324.1553.

$[\alpha]_D^{20}$: −45.9 (c = 0.88, $CHCl_3$).



(2*S*,1'*R*,5'*S*)-**4i**

The ketone (2*S*,1'*R*,5'*S*)-**4i** was prepared according to **TP4** from the iodide (*S*)-**1h** (30.2 mg, 0.1 mmol, 1.0 equiv) and (1*R*)-(−)-myrtenal (**6e**, 31 µL, 30.9 mg, 0.2 mmol, 2.0 equiv). The crude alcohol was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). Both diastereoisomers of the alcohol were then dissolved in DCM (1 mL) and oxidized with DMP (212 mg, 0.15 mmol, 1.5 equiv). The reaction was stirred for 10 min at ambient temperature before quenching with sat. aq. NH_4Cl and extracted with Et_2O (3 × 50 mL). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1). to afford (2*S*,1'*R*,5'*S*)-**4i** (15.9 mg, 0.049 mmol, 49%, dr = 3:97) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.76 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.41 (d, *J* = 5.5 Hz, 1H), 7.28–7.25 (m, 1H), 7.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.67–6.62 (m, 1H), 3.50 (h, *J* = 7.0 Hz, 1H), 3.10 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.91 (td, *J* = 5.7, 1.6 Hz, 1H), 2.72 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.39–2.32 (m, 3H), 2.11–2.03 (m, 1H), 1.30 (s, 3H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 9.1 Hz, 1H), 0.71 (s, 3H).

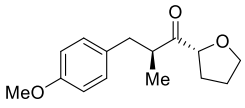
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 202.8, 148.7, 140.0, 137.7, 136.6, 136.5, 126.6, 125.9, 124.0, 123.8, 122.3, 41.6, 40.3, 40.1, 39.8, 37.5, 32.6, 31.1, 26.0, 20.9, 18.1.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2971 (w), 2924 (w), 1655 (m), 1612 (w), 1456 (w), 1436 (w), 1421 (w), 1381 (w), 1367 (w), 1327 (vw), 1310 (w), 1278 (w), 1264 (w), 1229 (w), 1220 (w), 1175 (w), 1160 (w), 1137 (w), 1102 (w), 1089 (w), 1048 (w), 975 (w), 959 (w), 945 (w), 936 (w), 890 (w), 832 (w), 807 (w), 751 (vs), 721 (w), 700 (m), 692 (m), 666 (w).

MS (70 eV, EI): m/z (%): 281 (30), 147 (100), 91 (16).

HRMS (EI) for $C_{21}H_{24}OS$: calc. $[M]^{+\bullet}$: 324.1548, found: 324.1539.

$[\alpha]_D^{20}$: +63.3 (c = 1.21, $CHCl_3$).



(2*S*,2'*R*)-**4j**

The ketone (2*S*,2*'R*)-**4j** was prepared according to **TP4** from the iodide (*S*)-**1a** (27.6 mg, 0.1 mmol, 1.0 equiv) and (*R*)-tetrahydrofuran-2-carbonyl chloride (**6f**, 26.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (2:1) to afford (2*S*,2*'R*)-**4j** (22.1 mg, 0.089 mmol, 89%, dr = 11:89) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.09–7.05 (m, 2H), 6.82–6.78 (m, 2H), 4.35–4.30 (m, 1H), 3.95–3.84 (m, 2H), 3.77 (s, 3H), 3.13–3.08 (m, 1H), 3.00 (dd, *J* = 13.3, 7.3 Hz, 1H), 2.47 (dd, *J* = 13.4, 7.1 Hz, 1H), 2.02–1.97 (m, 1H), 1.84–1.72 (m, 2H), 1.65–1.59 (m, 1H), 1.16–1.12 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H).

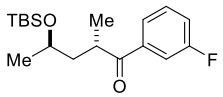
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 214.8, 158.2, 132.1, 130.2, 113.9, 82.9, 69.5, 55.4, 44.6, 38.1, 28.4, 25.5, 16.7.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2974 (m), 2934 (m), 2930 (m), 2916 (m), 2867 (m), 2858 (m), 2851 (m), 2178 (w), 1727 (m), 1723 (m), 1712 (m), 1612 (m), 1512 (s), 1461 (m), 1442 (m), 1380 (m), 1350 (w), 1300 (m), 1246 (vs), 1176 (m), 1152 (m), 1116 (vs), 1073 (m), 1035 (s), 933 (w), 843 (m), 833 (m), 830 (m), 816 (m), 809 (m), 803 (m).

MS (70 eV, EI): m/z (%): 147 (9), 127 89), 121 (100), 115 (7), 91 (28), 77 (19), 71 (90).

HRMS (EI) for $C_{15}H_{20}O_3$: calc. $[M]^{+\bullet}$:248.1412, found: 248.1406.

$[\alpha]_D^{20}$: +33.2 (c = 0.47, $CHCl_3$).



anti-**4k**

The ketone *anti*-**4k** was prepared according to **TP4** from the iodide *anti*-**1i** (32.8 mg, 0.1 mmol, 1.0 equiv) and 3-fluorobenzoyl chloride (**6g**, 31.7 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (10:1) to afford *anti*-**4k** (15.4 mg, 0.052 mmol, 52%, dr = 5:95) as a colorless oil.

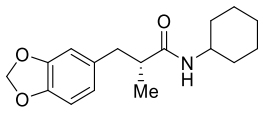
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.76–7.74 (m, 1H), 7.67–7.63 (m, 1H), 7.47–7.41 (m, 1H), 7.28–7.23 (m, 1H), 3.84–3.78 (m, 1H), 3.66–3.69 (m, 1H), 2.11–2.04 (m, 1H), 1.51–1.45 (m, 1H), 1.17 (d, J = 6.1 Hz, 3H), 0.81 (s, 9H), -0.0 (s, 3H), -0.2 (s, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 202.9, 130.4, 130.3, 124.3, 120.1, 119.9, 115.4, 115.2, 66.9, 43.1, 37.5, 26.0, 24.4, 19.2, 18.1, -4.1, -4.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2954 (m), 2927 (s), 2855 (m), 1716 (w), 1689 (m), 1588 (m), 1484 (w), 1471 (m), 1461 (m), 1441 (m), 1373 (w), 1361 (m), 1254 (vs), 1225 (m), 1166 (w), 1146 (m), 1124 (m), 1085 (m), 1044 (s), 1023 (m), 1006 (m), 989 (m), 971 (m), 938 (w), 888 (w), 835 (vs), 824 (s), 805 (s), 774 (vs), 747 (s), 700 (w), 674 (m).

MS (70 eV, EI): m/z (%): 267 (27), 175 (38), 123 (53), 75 (100).

HRMS (EI) for $C_{18}H_{29}FO_2Si$: calc. $[M\text{-}Me]^{+\bullet}$:309.1686, found: 309.1682.



(*R*)-**4l**

The amide (*R*)-**4l** was prepared according to **TP4** from the iodide (*R*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and cyclohexylisocyanate (**6h**, 26 µL, 25.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (*R*)-**4l** (23.2 mg, 0.080 mmol, 80%, 94% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.71 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.93–5.88 (m, 2H), 5.04 (d, *J* = 8.3 Hz, 1H), 3.76–3.64 (m, 1H), 2.84 (dd, *J* = 13.5, 8.7 Hz, 1H), 2.58 (dd, *J* = 13.5, 6.1 Hz, 1H), 2.35–2.23 (m, 1H), 1.87–1.78 (m, 1H), 1.77–1.66 (m, 2H), 1.67–1.50 (m, 2H), 1.39–1.23 (m, 2H), 1.15 (d, *J* = 6.7 Hz, 3H), 1.12–0.83 (m, 3H).

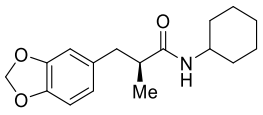
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 174.5, 147.6, 146.0, 133.9, 122.0, 109.5, 108.2, 100.9, 47.9, 44.4, 40.5, 33.2, 25.6, 24.9, 24.9, 17.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3285 (m), 2961 (w), 2960 (w), 2958 (w), 2934 (m), 2923 (m), 2873 (w), 2851 (w), 1636 (s), 1539 (m), 1537 (m), 1504 (s), 1483 (s), 1459 (w), 1457 (w), 1445 (m), 1436 (m), 1419 (w), 1401 (w), 1399 (w), 1395 (vw), 1380 (w), 1366 (w), 1349 (w), 1312 (w), 1273 (vw), 1260 (w), 1243 (vs), 1231 (m), 1200 (m), 1185 (m), 1152 (w), 1124 (w), 1100 (m), 1088 (w), 1073 (vw), 1062 (w), 1051 (m), 1041 (m), 974 (w), 939 (m), 928 (s), 912 (w), 903 (vw), 892 (m), 883 (m), 875 (m), 849 (vw), 816 (m), 806 (m), 792 (w), 781 (w), 770 (w), 728 (m), 718 (m), 696 (w), 694 (w), 684 (m), 668 (w).

MS (70 eV, EI): m/z (%): 289 (18), 175 (17), 162 (42), 135 (100).

HRMS (EI) for $C_{17}H_{23}NO_3$: calc. $[M]^{+\bullet}$: 289.1678, found: 289.1673.

$[\alpha]_D^{20}$: +52.2 (c = 0.96, $CHCl_3$).



(*S*)-**4l**

The amide (*S*)-**4l** was prepared according to **TP4** from the iodide (*S*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and cyclohexylisocyanate (**6h**, 26 µL, 25.0 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (*S*)-**4l** (23.4 mg, 0.081 mmol, 81%, 94% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.71 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 1H), 6.61 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.93–5.89 (m, 2H), 5.02 (d, *J* = 8.3 Hz, 1H), 3.70 (tdt, *J* = 10.6, 8.1, 3.9 Hz, 1H), 2.84 (dd, *J* = 13.5, 8.8 Hz, 1H), 2.58 (dd, *J* = 13.6, 6.1 Hz, 1H), 2.28 (dp, *J* = 8.7, 6.7 Hz, 1H), 1.87–1.79 (m, 1H), 1.75–1.60 (m, 2H), 1.58 (s, 2H), 1.41–1.23 (m, 2H), 1.13–0.80 (m, 3H).

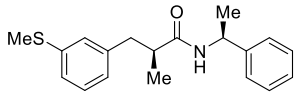
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 174.5, 147.6, 146.0, 133.9, 122.0, 109.5, 108.3, 100.9, 47.9, 44.5, 40.5, 33.2, 25.6, 24.9, 24.9, 17.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3285 (m), 2933 (m), 2923 (m), 2851 (w), 1636 (s), 1609 (w), 1542 (m), 1539 (m), 1536 (m), 1534 (m), 1518 (w), 1512 (w), 1504 (s), 1483 (s), 1469 (w), 1465 (w), 1459 (w), 1457 (w), 1445 (m), 1437 (m), 1380 (w), 1366 (w), 1312 (w), 1260 (w), 1244 (vs), 1231 (m), 1200 (m), 1185 (m), 1152 (w), 1124 (w), 1101 (m), 1062 (w), 1052 (m), 1041 (m), 974 (w), 939 (m), 928 (m), 912 (w), 892 (m), 883 (m), 875 (m), 816 (m), 805 (m), 792 (w), 781 (w), 771 (w), 728 (w), 718 (m), 684 (m).

MS (70 eV, EI): m/z (%): 289 (16), 175 (13), 162 (40), 135 (100).

HRMS (EI) for $C_{17}H_{23}NO_3$: calc. $[M]^{+\bullet}$: 289.1678, found: 289.1672.

$[\alpha]_D^{20}$: −50.5 (c = 0.84, $CHCl_3$).



(2*S*,1'*S*)-**4m**

The amide (2*S*,1'*S*)-**4m** was prepared according to **TP4** from the iodide (*S*)-**1b** (29.2 mg, 0.1 mmol, 1.0 equiv) and (*S*)-(−)-α-methylbenzyl isocyanate (**6i**, 28 µL, 29.4 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (2*S*,1'*S*)-**4m** (22.3 mg, 0.071 mmol, 71%, dr = 96:4) as a colorless oil.

A scale-up of this reaction on 0.5 mmol scale was performed while doubling the amount of solvent used for the reaction (from 0.083 M to 0.42 M). Thus, the iodide (*S*)-**1b** (146.1 mg, 0.5 mmol, 91% *ee*, 1.0 equiv) was dissolved in pentane (7.4 mL) and diethyl ether (3.3 mL) before addition of Me_3SiCH_2MgCl (1 M, 0.75 mL, 0.75 mmol, 1.5 equiv). The reaction mixture was cooled to −78 °C and *t*-BuLi (2.2 equiv) was slowly added dropwise over two minutes. The resulting optically enriched secondaryl alkylmagnesium reagent was quenched with (*S*)-(−)-α-methylbenzyl isocyanate (**6i**, 141 µL, 147 mg, 1.0 mmol, 2.0 equiv). After work-up according to the typical procedure, the crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (2*S*,1'*S*)-**4m** (100.3 mg, 0.032 mmol, 63%, dr = 92:8) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.29–7.26 (m, 1H), 7.25–7.18 (m, 2H), 7.15–7.06 (m, 2H), 7.03 (dtd, *J* = 8.0, 1.5, 0.6 Hz, 3H), 6.88 (dt, *J* = 7.1, 1.6 Hz, 1H), 5.47 (d, *J* = 8.0 Hz, 1H), 5.12–5.01 (m, 1H), 2.92 (dd, *J* = 13.4, 8.8 Hz, 1H), 2.64 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.50–2.38 (m, 4H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H).

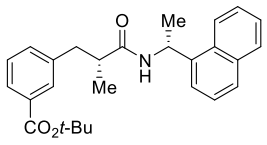
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 174.5, 143.0, 140.7, 138.6, 129.0, 128.7, 127.3, 127.1, 126.2, 125.9, 124.5, 48.4, 44.1, 40.5, 21.7, 18.1, 15.8.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3298 (m), 3061 (w), 3030 (w), 2966 (w), 2923 (m), 2870 (w), 2854 (w), 1639 (vs), 1591 (m), 1571 (w), 1536 (s), 1494 (m), 1474 (m), 1448 (m), 1420 (m), 1376 (m), 1281 (w), 1242 (m), 1210 (m), 1182 (w), 1169 (w), 1131 (w), 1098 (w), 1089 (m), 1076 (w), 1031 (w), 1016 (m), 966 (w), 949 (w), 905 (w), 880 (w), 854 (vw), 782 (m), 774 (m), 761 (m), 746 (w), 697 (vs).

MS (70 eV, EI): m/z (%): 313 (27), 176 (38), 165 (24), 137 (64), 120 (62) 117 (60), 105 (100), 91 (61), 79 (30).

HRMS (EI) for $C_{19}H_{23}ONS$: calc. $[M]^{+\bullet}$: 313.1500, found: 313.1495.

$[\alpha]_D^{20}$: −3.1 (c = 1.39, $CHCl_3$).



(2*R*,1'*R*)-**4n**

The amide (2*R*,1'*R*)-**4n** was prepared according to **TP4** from the iodide (*R*)-**1e** (34.6 mg, 0.1 mmol, 1.0 equiv) and (*R*)-(−)-1-(1-naphthyl)ethyl isocyanate (**6j**, 35 µL, 39.5 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (2*R*,1'*R*)-**4n** (22.1 mg, 0.053 mmol, 53%, dr = 97:3) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.98–7.92 (m, 1H), 7.86–7.81 (m, 1H), 7.77–7.71 (m, 3H), 7.50–7.41 (m, 2H), 7.35 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.23–7.18 (m, 2H), 7.10 (td, *J* = 7.6, 0.8 Hz, 1H), 5.85 (p, *J* = 6.9 Hz, 1H), 5.56 (d, *J* = 8.0 Hz, 1H), 2.98 (dd, *J* = 13.6, 8.2 Hz, 1H), 2.70 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.52–2.41 (m, 1H), 1.60 (d, *J* = 6.8 Hz, 3H), 1.57 (s, 9H), 1.19 (d, *J* = 6.8 Hz, 3H).

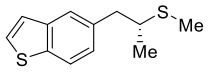
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 174.3, 166.0, 139.9, 138.3, 134.0, 133.5, 132.1, 131.1, 129.8, 128.8, 128.3, 128.3, 127.5, 126.6, 125.9, 125.3, 123.5, 122.5, 81.1, 44.6, 43.7, 40.0, 28.3, 20.9, 18.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3298 (vw), 3051 (vw), 2975 (w), 2930 (w), 2361 (vw), 1710 (m), 1641 (m), 1600 (w), 1588 (w), 1537 (m), 1511 (w), 1477 (w), 1450 (w), 1393 (w), 1368 (m), 1294 (m), 1256 (w), 1215 (w), 1160 (s), 1111 (m), 1085 (w), 1034 (vw), 1000 (vw), 932 (vw), 850 (w), 799 (w), 777 (m), 748 (vs), 696 (w), 666 (w).

MS (70 eV, EI): m/z (%): 361 (31), 170 (100), 155 (75), 135 (22).

HRMS (EI) for $C_{27}H_{31}NO_3$: calc. $[M]^{+\bullet}$: 417.2304, found: 417.2291

$[\alpha]_D^{20}$: −19.1 (c = 1.45, $CHCl_3$).



(*R*)-**4o**

The thioether (*R*)-**4m** was prepared according to **TP4** from the iodide (*R*)-**1h** (30.2 mg, 0.1 mmol, 1.0 equiv) and *S*-Methyl methanethiosulfonate (**6k**, 25.2 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1) to afford (*R*)-**4m** (17.6 mg, 0.79 mmol, 79%, 71% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.80 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.64 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.43 (dd, *J* = 5.5, 0.5 Hz, 1H), 7.29 (dd, *J* = 5.5, 0.8 Hz, 1H), 7.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.10 (dd, *J* = 13.4, 5.9 Hz, 1H), 3.01–2.92 (m, 1H), 2.79 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.12 (s, 3H), 1.26 (d, *J* = 6.7 Hz, 3H).

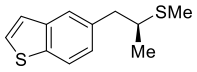
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.0, 138.0, 135.8, 126.8, 126.0, 124.1, 123.8, 122.4, 43.3, 43.2, 20.4, 13.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2958 (m), 2918 (m), 2853 (w), 1436 (m), 1421 (m), 1373 (w), 1318 (w), 1261 (w), 1222 (w), 1186 (w), 1160 (w), 1145 (w), 1089 (m), 1067 (w), 1050 (m), 1019 (w), 953 (w), 891 (m), 832 (m), 808 (s), 769 (m), 754 (s), 731 (m), 713 (m), 703 (s), 690 (vs).

MS (70 eV, EI): m/z (%): 222 (48), 174 (13), 147 (100), 121 (9), 115 (9), 75 (74)

HRMS (EI) for $C_{12}H_{14}S_2$: calc. $[M]^{+\bullet}$: 222.0537, found: 222.0529

$[\alpha]_D^{20}$: −3.4 (c = 0.68, $CHCl_3$).



(*S*)-**4o**

The thioether (*S*)-**4o** was prepared according to **TP4** from the iodide (*S*)-**1h** (30.2 mg, 0.1 mmol, 1.0 equiv) and *S*-Methyl methanethiosulfonate (**6k**, 25.2 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (9:1) to afford (*S*)-**4o** (18.9 mg, 0.085 mmol, 85%, 78% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.81 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.43 (d, *J* = 5.4 Hz, 1H), 7.30 (dd, *J* = 5.5, 0.8 Hz, 1H), 7.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.10 (dd, *J* = 13.4, 5.9 Hz, 1H), 3.01–2.92 (m, 1H), 2.79 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.12 (s, 3H), 1.26 (d, *J* = 6.7 Hz, 3H).

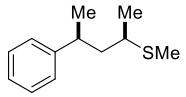
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.0, 138.0, 135.8, 126.8, 126.0, 124.1, 123.8, 122.4, 43.3, 43.2, 20.4, 13.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2968 (s), 2916 (s), 2362 (s), 2360 (s), 2358 (s), 2357 (s), 2354 (s), 2172 (s), 2169 (vs), 2164 (vs), 2160 (s), 2151 (s), 1445 (s), 1440 (s), 1436 (s), 1422 (s), 1379 (s), 1366 (s), 1198 (s), 1153 (s), 1089 (s), 1050 (s), 946 (m), 825 (m), 804 (s), 722 (vs).

MS (70 eV, EI): m/z (%): 222 (37), 174 (13), 147 (100), 121 (11), 115 (11), 75 (57)

HRMS (EI) for $C_{12}H_{14}S_2$: calc. $[M]^{+\bullet}$: 222.0537, found: 222.0529

$[\alpha]_D^{20}$: +4.4 (c = 0.67, $CHCl_3$).



syn-**4p**

The thioether *syn*-**4p** was prepared according to **TP4** from the iodide *syn*-**1d** (27.4 mg, 0.1 mmol, 1.0 equiv) and *S*-Methyl methanethiosulfonate (**6k**, 25.2 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (20:1) to afford *syn*-**4p** (12.1 mg, 0.062 mmol, 62%, dr = 93:7) as a colorless oil.

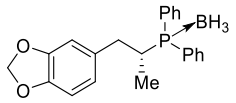
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.33–7.28 (m, 2H), 7.20 (dtd, *J* = 7.1, 3.8, 2.0 Hz, 3H), 2.92 (dp, *J* = 9.0, 6.8 Hz, 1H), 2.48 (dq, *J* = 8.5, 6.5 Hz, 1H), 2.01 (s, 3H), 1.97–1.90 (m, 1H), 1.68–1.61 (m, 1H), 1.26 (dd, *J* = 6.8, 1.8 Hz, 6H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 146.8, 128.6, 127.1, 126.2, 45.0, 38.7, 37.5, 22.8, 20.6, 12.9.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3086 (vw), 2975 (m), 2932 (w), 2861 (m), 2369 (vw), 1611 (w), 1511 (s), 1464 (w), 1444 (w), 1381 (m), 1350 (w), 1299 (w), 1246 (s), 1176 (m), 1151 (m), 1117 (vs), 1075 (m), 1038 (m), 1023 (m), 997 (m), 977 (m), 929 (w), 914 (w), 844 (m), 833 (m), 806 (m), 758 (w), 668 (w).

MS (70 eV, EI): m/z (%): 194 (13). 143 (19), 131 (100), 105 (21), 91 (11).

HRMS (EI) for $C_{12}H_{18}S$: calc. $[M]^{+\bullet}$: 194.1129, found: 194.1124.



(*R*)-**4q**

The BH_3-phosphine complex (*R*)-**4q** was prepared according to **TP4** from the iodide (*R*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and chlorodiphenylphosphine (**6l**, 36 µL, 44.2 mg, 0.2 mmol, 2.0 equiv). After stirring the reaction mixture at −20 °C for 30 minutes, $BH_3{\cdot}SMe_2$ (2.0 M in THF, 0.15 mL, 3.0 equiv) was added and the reaction was further stirred at 0 °C for 1 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (*R*)-**4q** (25.4 mg, 0.070 mmol, 70%, 90% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.90–7.74 (m, 4H), 7.56–7.40 (m, 6H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.60–6.53 (m, 2H), 5.92 (s, 2H), 2.88–2.78 (m, 1H), 2.78–2.66 (m, 1H), 2.52–2.41 (m, 1H), 1.04 (dd, *J* = 16.3, 6.9 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.8, 146.2, 133.5 (*J* = 14.3 Hz), 132.7 (*J* = 3.3 Hz), 131.4 (*J* = 3.8 Hz), 129.0 (*J* = 10.2 Hz), 128.4 (*J* = 3.5 Hz), 122.1, 109.3, 108.3, 101.04 36.6 (*J* = 4.2 Hz), 31.4 (*J* = 34.5 Hz), 13.3 (*J* = 2.1 Hz).

^{11}B-NMR ($CDCl_3$, 128 MHz): δ [ppm] = −42.4 (d, *J* = 56.3 Hz).

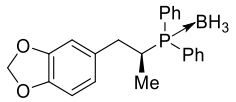
^{31}P-NMR ($CDCl_3$, 162 MHz): δ [ppm] = 23.7 (d, *J* = 79.0 Hz).

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3058 (vw), 2929 (w), 2892 (w), 2380 (m), 2345 (w), 1608 (vw), 1502 (m), 1488 (s), 1455 (w), 1437 (s), 1378 (w), 1364 (w), 1248 (s), 1218 (w), 1188 (m), 1136 (w), 1106 (m), 1063 (m), 1037 (s), 1008 (w), 1000 (m), 940 (w), 928 (m), 872 (w), 852 (w), 808 (m), 779 (m), 752 (s), 736 (vs), 719 (m), 692 (vs), 667 (m).

MS (70 eV, EI): m/z (%): 347 (100), 213 (89), 183 (81), 162 (72), 135 (51), 109 (70).

HRMS (EI) for $C_{22}H_{21}O_2P$: calc. $[M-H]^{+\bullet}$: 347.1195, found: 347.1196.

$[\alpha]_D^{20}$: −17.3 (c = 1.68, $CHCl_3$).



(*S*)-**4q**

The BH_3-phosphine complex (*S*)-**4q** was prepared according to **TP4** from the iodide (*S*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and chlorodiphenylphosphine (**6l**, 36 µL, 44.2 mg, 0.2 mmol, 2.0 equiv). After stirring the reaction mixture at −20 °C for 30 minutes, $BH_3{\cdot}SMe_2$ (2.0 M in THF, 0.15 mL, 3.0 equiv) was added and the reaction was further stirred at 0 °C for 1 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (*S*)-**4q** (27.2 mg, 0.075 mmol, 75%, 90% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.89–7.75 (m, 4H), 7.55–7.40 (m, 6H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.60–6.52 (m, 2H), 5.92 (s, 2H), 2.87–2.78 (m, 1H), 2.78–2.66 (m, 1H), 2.52–2.40 (m, 1H), 1.05 (dd, *J* = 16.3, 6.9 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.6, 146.1, 133.3 (*J* = 14.3 Hz), 132.6 (*J* = 4.4 Hz), 131.2 (*J* = 3.8 Hz), 128.8 (*J* = 10.1 Hz), 122.0, 109.14, 108.17, 100.87, 36.4 (*J* = 4.3 Hz), 31.2 (*J* = 34.8 Hz), 13.1 (*J* = 2.3 Hz).

^{11}B-NMR ($CDCl_3$, 128 MHz): δ [ppm] = −42.5 (d, *J* = 57.1 Hz).

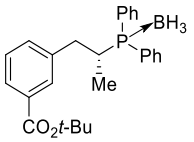
^{31}P-NMR ($CDCl_3$, 162 MHz): δ [ppm] = 23.8 (d, *J* = 80.2 Hz).

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3355 (vs), 2925 (w), 2384 (w), 2349 (vw), 1643 (m), 1634 (m), 1538 (vw), 1502 (w), 1489 (m), 1454 (w), 1437 (m), 1375 (w), 1365 (w), 1249 (m), 1189 (w), 1106 (w), 1064 (w), 1038 (w), 928 (w), 807 (vw), 778 (w), 736 (w), 718 (w), 692 (m).

MS (70 eV, EI): m/z (%): 347 (100), 213 (73), 183 (52), 162 (55), 135 (39), 109 (47).

HRMS (EI) for $C_{22}H_{21}O_2P$: calc. $[M-H]^{+\bullet}$: 347.1195, found: 347.1194.

$[\alpha]_D^{20}$: +20.7 (c = 1.08, $CHCl_3$).



(*R*)-**4r**

The BH_3-phosphine complex (*S*)-**4r** was prepared according to **TP4** from the iodide (*S*)-**1e** (34.6 mg, 0.1 mmol, 1.0 equiv) and chlorodiphenylphosphine (**6l**, 36 µL, 44.2 mg, 0.2 mmol, 2.0 equiv). After stirring the reaction mixture at −20 °C for 30 minutes, $BH_3{\cdot}SMe_2$ (2.0 M in THF, 0.15 mL, 3.0 equiv) was added and the reaction was further stirred at 0 °C for 1 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (*S*)-**4r** (26.4 mg, 0.063 mmol, 63%, 88% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.91–7.84 (m, 2H), 7.84–7.77 (m, 3H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.54–7.42 (m, 6H), 7.34–7.25 (m, 2H), 2.98–2.90 (m, 1H), 2.89–2.74 (m, 1H), 2.67–2.58 (m, 1H), 1.60 (s, 9H), 1.03 (dd, *J* = 16.3, 6.9 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 165.7, 139.7 (*J* = 14.2 Hz), 133.3, 132.6 (*J* = 4.2 Hz), 132.2, 131.3 (*J* = 4.3 Hz), 129.6, 128.9 (*J* = 7.5 Hz), 128.6 (*J* = 4.1 Hz), 128.3, 128.1 (*J* = 4.4 Hz), 127.6, 81.1, 36.4 (*J* = 4.4 Hz), 30.8 (*J* = 35.2 Hz), 28.2, 13.1 (*J* = 2.2 Hz).

^{11}B-NMR ($CDCl_3$, 128 MHz): δ [ppm] = −42.5 (d, *J* = 58.4 Hz).

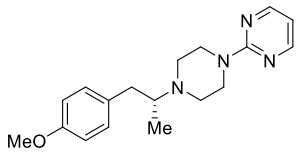
^{31}P-NMR ($CDCl_3$, 162 MHz): δ [ppm] = 24.0 (d, *J* = 71.4 Hz).

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3060 (vw), 3007 (vw), 2977 (w), 2931 (w), 2384 (w), 1708 (m), 1588 (vw), 1478 (w), 1457 (w), 1437 (m), 1393 (w), 1378 (vw), 1368 (w), 1296 (m), 1256 (w), 1215 (w), 1159 (s), 1107 (m), 1079 (w), 1063 (m), 1029 (vw), 1008 (vw), 1000 (w), 935 (vw), 890 (vw), 849 (w), 812 (vw), 747 (vs), 736 (vs), 692 (s), 667 (m).

MS (70 eV, EI): m/z (%): 404 (100), 347 (81), 213 (74), 186 (47), 109 (51).

HRMS (EI) for $C_{26}H_{29}O_2P$: calc. $[M]^{+\bullet}$: 404.1905, found: 404.1896.

$[\alpha]_D^{20}$: −17.2 (c = 1.37, $CHCl_3$).



(*R*)-**8a**

The tertiary amine (*R*)-**8a** was prepared according to **TP5** from the iodide (*R*)-**1a** (27.6 mg, 0.1 mmol, 1.0 equiv) and 4-(pyrimidin-2-yl)piperazin-1-yl benzoate (**7a**, 56.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/ethyl acetate (1:1) to afford (*R*)-**8a** (22.8 mg, 0.073 mmol, 73%, 91% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.31 (d, J = 4.7 Hz, 2H), 7.11–7.08 (m, 2H), 6.84–6.81 (m, 2H), 6.47 (t, J = 4.7 Hz, 1H), 3.84 (t, J = 5.1 Hz, 4H), 3.79 (s, 3H), 2.96 (dd, J = 13.3, 4.2 Hz, 1H), 2.83 (s, 1H), 2.67 (t, J = 5.2 Hz, 4H), 2.39 (dd, J = 13.2, 9.6 Hz, 1H), 0.96 (d, J = 6.6 Hz, 3H).

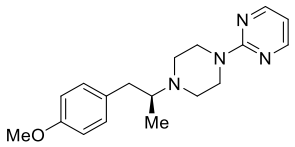
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 161.9, 158.0, 157.9 132.7, 130.3, 113.8, 110.2, 109.9, 61.9, 55.4, 48.6, 44.3, 38.7, 14.4.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2961 (w), 2950 (w), 2942 (w), 2930 (w), 2929 (w), 2925 (w), 2906 (w), 2855 (w), 2851 (w), 2358 (w), 1610 (w), 1585 (vs), 1570 (w), 1558 (w), 1546 (m), 1533 (w), 1511 (s), 1499 (m), 1496 (m), 1477 (m), 1474 (m), 1468 (m), 1465 (m), 1463 (m), 1457 (m), 1448 (m), 1437 (m), 1430 (w), 1419 (w), 1392 (w), 1358 (m), 1306 (w), 1260 (m), 1247 (m), 1230 (w), 1222 (w), 1220 (w), 1178 (w), 1092 (w), 1087 (w), 1083 (w), 1036 (m), 1018 (w), 1014 (w), 982 (m), 976 (w), 816 (w), 812 (w), 797 (m), 668 (w).

MS (70 eV, EI): m/z (%): 191 (100), 148 (45), 122 (81).

HRMS (EI) for $C_{18}H_{25}N_4O$: calc. $[M+H]^{+\bullet}$: 313.2028, found: 313.2025.

$[\alpha]_D^{20}$: −21.4 (c = 0.84, $CHCl_3$).



(*S*)-**8a**

The tertiary amine (*S*)-**8a** was prepared according to **TP5** from the iodide (*S*)-**1a** (27.6 mg, 0.1 mmol, 1.0 equiv) and 4-(pyrimidin-2-yl)piperazin-1-yl benzoate (**7a**, 56.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/ethyl acetate (1:1) to afford (*S*)-**8a** (22.9 mg, 0.073 mmol, 73%, 88% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.31 (d, J = 4.7 Hz, 2H), 7.12–7.08 (m, 2H), 6.85–6.81 (m, 2H), 6.48 (t, J = 4.7 Hz, 1H), 3.84 (t, J = 5.1 Hz, 4H), 3.79 (s, 3H), 3.00–2.92 (m, 1H), 2.83 (s, 1H), 2.67 (t, J = 5.1 Hz, 4H), 2.39 (dd, J = 13.1, 9.6 Hz, 1H), 0.96 (d, J = 6.6 Hz, 3H).

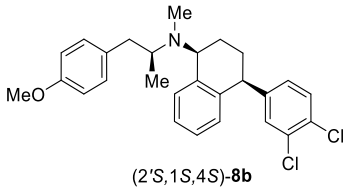
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 161.8, 158.0, 157.9, 132.6, 130.3, 113.8, 110.2, 109.9, 61.9, 55.4, 48.6, 44.3, 38.7, 14.3.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2992 (w), 2958 (w), 2955 (w), 2928 (m), 2926 (m), 2924 (m), 2882 (w), 2878 (w), 2854 (w), 2852 (w), 2838 (w), 2832 (w), 2813 (w), 2810 (w), 2362 (w), 2360 (w), 2358 (w), 2357 (w), 1611 (w), 1585 (vs), 1546 (m), 1533 (w), 1511 (vs), 1447 (m), 1392 (w), 1377 (w), 1375 (w), 1358 (m), 1306 (w), 1261 (m), 1247 (s), 1226 (w), 1220 (w), 1179 (w), 1159 (w), 1139 (w), 1117 (w), 1037 (w), 982 (m), 803 (w), 800 (w), 797 (w), 778 (w), 668 (w).

MS (70 eV, EI): m/z (%): 191 (82), 148 (49), 122 (100).

HRMS (EI) for $C_{18}H_{25}N_4O$: calc. $[M+H]^{+\bullet}$: 313.2028, found: 313.2022.

$[\alpha]_D^{20}$: +19.4 (c = 0.92, $CHCl_3$).



(2'*S*,1*S*,4*S*)-**8b**

The tertiary amine (*2'S,1S,4S*)-**8b** was prepared according to **TP5** from the iodide (*R*)-**1a** (27.6 mg, 0.1 mmol, 1.0 equiv) and *O*-benzoyl-*N*-((1*S*,4*S*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methylhydroxylamine (**7b**, 85.3 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (4:1) to afford (*R*)-**8b** (23.6 mg, 0.052 mmol, 52%, dr = 91:9) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.56–7.51 (m, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.19–7.15 (m, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 7.11 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.07–7.03 (m, 2H), 6.85–6.82 (m, 2H), 6.81–6.77 (m, 2H), 4.07 (t, *J* = 5.6 Hz, 1H), 3.94 (dd, *J* = 8.8, 4.9 Hz, 1H), 3.77 (s, 3H), 3.09–3.00 (m, 1H), 2.92 (dd, *J* = 13.3, 5.4 Hz, 1H), 2.54 (dd, *J* = 13.4, 8.6 Hz, 1H), 2.26 (s, 3H), 2.09–2.04 (m, 2H), 1.98–1.91 (m, 1H), 1.83–1.75 (m, 1H), 1.70–1.62 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H).

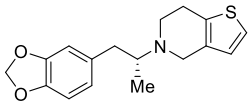
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 157.9, 148.1, 140.1, 138.6, 132.9, 132.2, 130.9, 130.3, 130.1, 129.8, 129.5, 128.3, 126.9, 126.8, 126.6, 113.7, 77.5, 77.2, 76.8, 59.9, 57.8, 55.4, 44.1, 41.1, 33.0, 29.8, 21.1, 16.6.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3344 (w), 3188 (vw), 3061 (w), 2925 (vs), 2854 (s), 1734 (w), 1716 (w), 1669 (m), 1612 (m), 1585 (w), 1560 (w), 1541 (vw), 1512 (s), 1466 (s), 1419 (w), 1394 (m), 1378 (m), 1301 (m), 1286 (w), 1247 (vs), 1201 (w), 1177 (m), 1131 (m), 1114 (w), 1069 (w), 1031 (m), 881 (vw), 847 (w), 820 (w), 764 (w), 741 (w), 721 (w), 711 (w), 677 (vw).

MS (70 eV, EI): m/z (%): 332 (17), 275 (25), 161 (21), 159 (34).

HRMS (EI) for $C_{27}H_{29}Cl_2NO$: calc. $[M-C_8H_9O]^{+\bullet}$: 332.0973, found: 332.0944.

$[\alpha]_D^{20}$: −45.8 (c = 0.48, $CHCl_3$).



(*R*)-**8c**

The tertiary amine (*R*)-**8c** was prepared according to **TP5** from the iodide (*R*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and 6,7-dihydrothieno[3,2-c]pyridin-5(4*H*)-yl benzoate (**7c**, 51.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/ethyl acetate (4:1) to afford (*R*)-**8c** (25.6 mg, 0.085 mmol, 85%, 87% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.07 (d, *J* = 5.1 Hz, 1H), 6.76–6.69 (m, 3H), 6.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.93 (s, 2H), 3.74 (s, 2H), 3.06–2.94 (m, 2H), 2.90 (t, *J* = 1.0 Hz, 4H), 2.50–2.40 (m, 1H), 1.04 (d, *J* = 6.5 Hz, 3H).

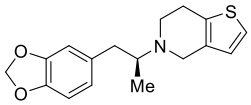
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.6, 145.8, 134.5, 134.4, 133.7, 125.5, 122.8, 122.2, 109.7, 108.3, 100.9, 61.4, 48.8, 46.4, 39.5, 26.5, 14.5.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2961 (m), 2956 (m), 2946 (m), 2942 (m), 2926 (s), 2924 (s), 2921 (s), 2908 (m), 2901 (m), 2898 (m), 2893 (m), 2882 (m), 2880 (m), 2874 (m), 2854 (m), 1502 (s), 1489 (vs), 1457 (m), 1440 (m), 1437 (m), 1249 (vs), 1122 (m), 1117 (m), 1114 (m), 1112 (m),), 1091 (m), 1087 (m), 1084 (m), 1080 (m), 1079 (m), 1075 (m), 1073 (m), 1070 (m), 1067 (m), 1065 (m), 1064 (m), 1062 (m), 1060 (m), 1038 (vs), 1023 (s), 1020 (m), 928 (m), 814 (m), 808 (s), 803 (s), 800 (s), 797 (s), 668 (m).

MS (70 eV, EI): m/z (%): 166 (100), 123 (6), 56 (12).

HRMS (EI) for $C_{17}H_{19}NO_2S$: calc. $[M+H]^{+\bullet}$: 302.1215, found: 302.1208.

$[\alpha]_D^{20}$: −15.5 (c = 0.51, $CHCl_3$).



(*S*)-**8c**

The tertiary amine (*S*)-**8c** was prepared according to **TP5** from the iodide (*S*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and 6,7-dihydrothieno[3,2-c]pyridin-5(4*H*)-yl benzoate (**7c**, 51.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/ethyl acetate (4:1) to afford (*S*)-**8c** (22.0 mg, 0.073 mmol, 73%, 88% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.08 (d, *J* = 5.1 Hz, 1H), 6.78–6.69 (m, 3H), 6.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.93 (s, 2H), 3.74 (d, *J* = 1.8 Hz, 2H), 3.06–2.93 (m, 2H), 2.90 (d, *J* = 1.3 Hz, 4H), 2.50–2.40 (m, 1H), 1.04 (d, *J* = 6.4 Hz, 3H).

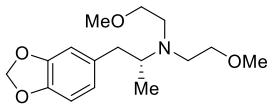
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.6, 145.8, 134.5, 134.4, 133.7, 125.5, 122.8, 122.2, 109.7, 108.3, 100.9, 61.4, 48.8, 46.4, 39.5, 26.5, 14.4.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2958 (w), 2955 (w), 2922 (m), 2901 (m), 2895 (m), 2885 (w), 2882 (w), 2874 (w), 2863 (w), 2853 (w), 1739 (w), 1734 (w), 1652 (w), 1646 (w), 1501 (s), 1488 (vs), 1456 (m), 1440 (s), 1380 (w), 1370 (w), 1358 (w), 1334 (w), 1317 (w), 1247 (vs), 1208 (m), 1188 (m), 1174 (m), 1167 (w), 1122 (w), 1120 (w), 1098 (m), 1079 (w), 1038 (s), 940 (m), 928 (m), 832 (w), 807 (m), 781 (w), 772 (w), 705 (m), 702 (m), 668 (w).

MS (70 eV, EI): m/z (%): 166 (100), 135 (10), 56 (25).

HRMS (EI) for $C_{17}H_{19}NO_2S$: calc. $[M+H]^{+\bullet}$: 302.1215, found: 302.1213.

$[\alpha]_D^{20}$: +18.8 (c = 0.70, $CHCl_3$).



(*R*)-**8d**

The tertiary amine (*R*)-**8d** was prepared according to **TP5** from the iodide (*R*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and *O*-benzoyl-*N*,*N*-bis(2-methoxyethyl)hydroxylamine (**7d**, 50.7 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with ethyl acetate to afford (*R*)-**8d** (23.0 mg, 0.078 mmol, 78%, 93% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.74–6.66 (m, 2H), 6.60 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 3.39 (t, *J* = 6.5 Hz, 4H), 3.34 (s, 6H), 2.99–2.86 (m, 1H), 2.82 (dd, *J* = 13.1, 5.0 Hz, 1H), 2.71 (td, *J* = 6.6, 2.8 Hz, 4H), 2.31 (dd, *J* = 13.1, 9.1 Hz, 1H), 0.93 (d, *J* = 6.5 Hz, 3H).

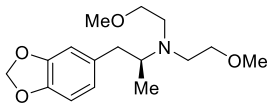
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.5, 145.7, 134.7, 122.1, 109.7, 108.1, 100.9, 72.7, 59.6, 59.0, 50.7, 39.6, 15.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2958 (m), 2923 (s), 2872 (s), 2854 (s), 1503 (m), 1489 (vs), 1455 (m), 1441 (m), 1370 (w), 1247 (vs), 1190 (m), 1152 (w), 1119 (vs), 1039 (s), 962 (w), 941 (m), 928 (m), 808 (m).

MS (70 eV, EI): m/z (%): 160 (100), 158 (50), 135 (18), 126 (14), 102 (11), 94 (18), 59 (10).

HRMS (EI) for $C_{16}H_{25}NO_4$: calc. $[M-H_2]^{+\bullet}$: 293.1627, found: 293.1623.

$[\alpha]_D^{20}$: −8.3 (c = 0.59, $CHCl_3$).



(*S*)-**8d**

The tertiary amine (*S*)-**8d** was prepared according to **TP5** from the iodide (*S*)-**1g** (29.0 mg, 0.1 mmol, 1.0 equiv) and *O*-benzoyl-*N*,*N*-bis(2-methoxyethyl)hydroxylamine (**7d**, 50.7 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with ethyl acetate to afford (*S*)-**8d** (20.7 mg, 0.070 mmol, 70%, 84% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.74–6.66 (m, 2H), 6.60 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.92 (s, 2H), 3.39 (t, *J* = 6.5 Hz, 4H), 3.34 (s, 6H), 2.97–2.88 (m, 1H), 2.82 (dd, *J* = 13.1, 4.9 Hz, 1H), 2.75–2.67 (m, 4H), 2.32 (dd, *J* = 13.2, 9.1 Hz, 1H), 0.93 (d, *J* = 6.6 Hz, 3H).

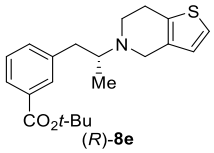
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 147.5, 145.7, 134.7, 122.2, 109.7, 108.1, 100.9, 72.7, 59.6, 59.0, 50.7, 39.6, 15.0.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2958 (m), 2924 (m), 2873 (m), 2853 (m), 2815 (w), 1743 (m), 1503 (m), 1489 (s), 1450 (m), 1442 (m), 1365 (w), 1246 (vs), 1197 (m), 1119 (vs), 1080 (m), 1059 (m), 1039 (s), 1024 (m), 962 (w), 940 (w), 928 (m), 808 (w), 710 (m).

MS (70 eV, EI): m/z (%): 160 (100), 135 (14), 102 (20), 96 (9), 70 (18), 59 (25).

HRMS (EI) for $C_{16}H_{25}NO_4$: calc. $[M-H]^{+\bullet}$: 294.1705, found: 294.1696.

$[\alpha]_D^{20}$: +9.2 (c = 0.61, $CHCl_3$).



(*R*)-**8e**

The tertiary amine (*R*)-**8e** was prepared according to **TP5** from the iodide (*R*)-**1e** (34.6 mg, 0.1 mmol, 1.0 equiv) and 6,7-dihydrothieno[3,2-c]pyridin-5(4*H*)-yl benzoate (**7c**, 51.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with ethyl acetate to afford (*R*)-**8e** (24.3 mg, 0.068 mmol, 68%, 83% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.82 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.40–7.28 (m, 2H), 7.08 (d, *J* = 5.1 Hz, 1H), 6.75 (d, *J* = 5.1 Hz, 1H), 3.76 (d, *J* = 1.9 Hz, 2H), 3.16–3.01 (m, 2H), 2.99–2.87 (m, 4H), 2.64–2.54 (m, 1H), 1.59 (s, 9H), 1.04 (d, *J* = 6.6 Hz, 3H).

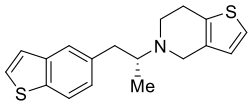
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 166.1, 140.7, 134.4, 133.7, 133.5, 132.2, 130.3, 128.3, 127.3, 125.5, 122.8, 81.1, 61.1, 48.7, 46.4, 39.5, 28.3, 26.5, 14.5.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2961 (w), 2927 (m), 2856 (w), 1741 (m), 1711 (s), 1606 (vw), 1587 (w), 1477 (w), 1456 (w), 1404 (w), 1392 (w), 1367 (m), 1336 (w), 1292 (s), 1256 (m), 1219 (m), 1209 (m), 1160 (vs), 1110 (s), 1088 (m), 1053 (w), 1043 (w), 1001 (w), 978 (w), 934 (w), 903 (w), 850 (w), 832 (w), 747 (s), 697 (s), 675 (w), 666 (w).

MS (70 eV, EI): m/z (%):284 (4), 166 (100), 110 (3), 56 (12).

HRMS (EI) for $C_{21}H_{27}SNO_2$: calc. $[M]^{+\bullet}$: 357.1762, found: 357.1762.

$[\alpha]_D^{20}$: −18.8 (c = 0.51, $CHCl_3$).



(*R*)-**8f**

The tertiary amine (*R*)-**8f** was prepared according to **TP5** from the iodide (*R*)-**1h** (30.2 mg, 0.1 mmol, 1.0 equiv) and 6,7-dihydrothieno[3,2-c]pyridin-5(4*H*)-yl benzoate (**7c**, 51.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with i-hexanes/dichloro methane/ethyl acetate (1:1:1) to afford (*R*)-**8f** (26.3 mg, 0.084 mmol, 84%, 88% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.80 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.65 (d, *J* = 1.7 Hz, 1H), 7.43 (d, *J* = 5.5 Hz, 1H), 7.29 (dd, *J* = 5.4, 0.8 Hz, 1H), 7.21 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.09 (d, *J* = 5.1 Hz, 1H), 6.76 (d, *J* = 5.1 Hz, 1H), 3.80 (s, 2H), 3.22 (dd, *J* = 12.9, 4.0 Hz, 1H), 3.12 (m, 1H), 2.98–2.91 (m, 4H), 2.65 (dd, *J* = 12.9, 9.8 Hz, 1H), 1.07 (d, *J* = 6.6 Hz, 3H).

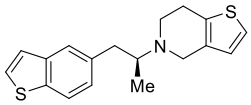
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.0, 137.6, 136.7, 134.5, 133.7, 126.7, 126.1, 125.5, 124.1, 123.7, 122.9, 122.4, 61.6, 48.8, 46.6, 39.7, 26.5, 14.6.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2965 (m), 2959 (m), 2954 (m), 2935 (m), 2930 (m), 2928 (m), 2924 (m), 2921 (m), 2919 (m), 2911 (m), 2908 (m), 2360 (w), 2336 (w), 1584 (w), 1517 (vs), 1453 (m), 1445 (m), 1443 (m), 1275 (s), 1224 (m), 1127 (m), 1029 (m), 760 (m), 702 (m), 668 (m).

MS (70 eV, EI): m/z (%): 207 (5), 166 (100), 147 (16), 110 (10), 56 (27).

HRMS (EI) for $C_{18}H_{19}NS_2$: calc. $[M-H]^{+\bullet}$: 312.0875, found: 312.0870.

$[\alpha]_D^{20}$: −5.0 (c = 0.60, $CHCl_3$).



(*S*)-**8f**

The tertiary amine (*S*)-**8f** was prepared according to **TP5** from the iodide (*S*)-**1h** (30.2 mg, 0.1 mmol, 1.0 equiv) and 6,7-dihydrothieno[3,2-c]pyridin-5(4*H*)-yl benzoate (**7c**, 51.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with i-hexanes/dichloro methane/ethyl acetate (1:1:1) to afford (*S*)-**8f** (26.3 mg, 0.085 mmol, 85%, 97% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.80 (d, *J* = 8.2 Hz, 1H), 7.66–7.63 (m, 1H), 7.43 (d, *J* = 5.4 Hz, 1H), 7.29 (dd, *J* = 5.4, 0.8 Hz, 1H), 7.21 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.09 (d, *J* = 5.1 Hz, 1H), 6.76 (d, *J* = 5.1 Hz, 1H), 3.79 (d, *J* = 1.6 Hz, 2H), 3.22 (dd, *J* = 12.9, 4.0 Hz, 1H), 3.18–3.05 (m, 1H), 2.98–2.90 (m, 4H), 2.65 (dd, *J* = 12.9, 9.9 Hz, 1H), 1.07 (d, *J* = 6.5 Hz, 3H).

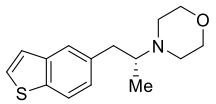
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.0, 137.6, 136.7, 134.5, 133.7, 126.7, 126.1, 125.5, 124.1, 123.7, 122.8, 122.4, 61.6, 48.8, 46.5, 39.7, 26.5, 14.6.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2965 (m), 2962 (m), 2932 (m), 2929 (m), 2922 (m), 2910 (w), 2908 (w), 2903 (w), 2838 (w), 2167 (m), 1624 (w), 1517 (vs), 1460 (m), 1456 (m), 1444 (m), 1442 (m), 1434 (m), 1313 (m), 1273 (vs), 1225 (m), 1135 (m), 1125 (s), 1029 (m), 955 (w), 809 (w), 807 (w), 805 (w), 761 (m).

MS (70 eV, EI): m/z (%): 166 (100), 147 (23), 110 (8), 56 (34).

HRMS (EI) for $C_{18}H_{19}NS_2$: calc. $[M-H_2]^{+\bullet}$: 311.0797, found: 311.0804.

$[\alpha]_D^{20}$: +6.7 (c = 0.58, $CHCl_3$).



(*R*)-**8g**

The tertiary amine (*R*)-**8g** was prepared according to **TP5** from the iodide (*R*)-**1h** (30.2 mg, 0.1 mmol, 1.0 equiv) and morpholino benzoate (**7e**, 41.5 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with ethyl acetate to afford (*R*)-**8g** (18.8 mg, 0.072 mmol, 78%, 89% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.79 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 5.5 Hz, 1H), 7.29–7.27 (m, 1H), 7.17 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.76 (t, *J* = 4.7 Hz, 4H), 3.14 (dd, *J* = 13.0, 4.3 Hz, 1H), 2.88–2.78 (m, 1H), 2.66 (t, *J* = 4.6 Hz, 4H), 2.53 (dd, *J* = 13.2, 9.7 Hz, 1H), 0.98 (d, *J* = 6.5 Hz, 3H).

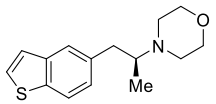
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.0, 137.6, 127.2, 126.7, 126.1, 124.1, 123.7, 122.3, 67.5, 62.1, 49.3, 39.3, 14.5.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2968 (m), 2964 (m) 2930 (s), 2928 (s), 2925 (s), 2922 (s), 2912 (m), 2906 (m), 2903 (m), 2900 (m), 2866 (m), 2853 (m), 2851 (m), 1739 (w), 1683 (w), 1674 (w), 1662 (w), 1456 (m), 1454 (m), 1448 (m), 1436 (m), 1255 (m), 1145 (m), 1116 (vs), 1104 (m), 1091 (m), 969 (m), 708 (m), 706 (m), 689 (m).

MS (70 eV, EI): m/z (%): 147 (15), 114 (100),

HRMS (EI) for $C_{15}H_{19}NOS$: calc. $[M]^{+\bullet}$: 260.1104, found: 260.1104.

$[\alpha]_D^{20}$: −5.3 (c = 0.95, $CHCl_3$).



(*S*)-**8g**

The tertiary amine (*S*)-**8g** was prepared according to **TP5** from the iodide (*S*)-**1h** (30.2 mg, 0.1 mmol, 1.0 equiv) and morpholino benzoate (**7e**, 41.5 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with ethyl acetate to afford (*S*)-**8g** (19.1 mg, 0.073 mmol, 73%, 94% *ee*) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.79 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 5.4 Hz, 1H), 7.28 (dd, *J* = 5.5, 0.8 Hz, 1H), 7.17 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.79–3.73 (m, 4H), 3.14 (dd, *J* = 13.1, 4.3 Hz, 1H), 2.88–2.80 (m, 1H), 2.69–2.63 (m, 4H), 2.53 (dd, *J* = 13.1, 9.7 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 3H).

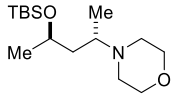
^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 140.0, 137.6, 136.6, 126.7, 126.1, 124.1, 123.7, 122.3, 67.5, 62.0, 49.3, 39.2, 14.4.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2964 (m), 2962 (m), 2958 (m), 2950 (m), 2924 (m), 2922 (m), 2856 (m), 2362 (w), 2336 (w), 1739 (vs), 1719 (w), 1702 (w), 1644 (w), 1456 (m), 1451 (m), 1257 (vs), 1255 (vs), 1250 (vs), 1116 (s), 1103 (vs), 1085 (s), 1065 (s), 1049 (s), 1025 (m), 1009 (m), 709 (vs).

MS (70 eV, EI): m/z (%): 147 (51), 114 (100), 105 (28), 57 (21).

HRMS (EI) for $C_{15}H_{19}NOS$: calc. $[M-H]^{+\bullet}$: 260.1109, found: 260.1104.

$[\alpha]_D^{20}$: +5.8 (c = 1.08, $CHCl_3$).



anti-**8h**

The amine *anti*-**8h** was prepared according to **TP5** from the iodide *anti*-**1i** (32.8 mg, 0.1 mmol, 1.0 equiv) and morpholino benzoate (41.4 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with diethyl ether and 2% triethylamine to afford *anti*-**8h** (17.9 mg, 0.063 mmol, 63%, dr = 14:86) as a colorless oil.

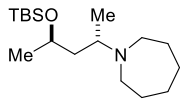
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 3.91–3.84 (m, 1H), 3.71–3.68 (m, 4H), 2.73–2.64 (m, 1H), 2.52–2.48 (m, 4H), 1.74 (m, 1H), 1.25–1.19 (m, 1H), 1.14 (d, J = 6.1 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 67.6, 66.3, 56.1, 48.9, 42.9, 26.0, 24.3, 18.2, 14.7, -4.0, -4.7.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2957 (s), 2928 (s), 2891 (m), 2889 (m), 2854 (m), 2814 (w), 1472 (m), 1462 (m), 1374 (m), 1361 (m), 1255 (m), 1157 (m), 1137 (m), 1118 (vs), 1079 (m), 1046 (m), 1031 (m), 1005 (m), 987 (m), 919 (m), 913 (m), 852 (w), 835 (s), 826 (m), 807 (m), 774 (s).

MS (70 eV, EI): m/z (%): 230 (4), 144 (6), 114 (100), 103 (7), 75 (10).

HRMS (EI) for $C_{15}H_{33}NO_2Si$: calc. $[M]^{+\bullet}$: 287.2281, found: 287.2275.



anti-**8i**

The amine *anti*-**8i** was prepared according to **TP5** from the iodide *anti*-**1i** (32.8 mg, 0.1 mmol, 1.0 equiv) and azepan-1-yl benzoate (43.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with diethyl ether to afford *anti*-**8i** (16.8 mg, 0.056 mmol, 56%, dr = 3:97) as a colorless oil.

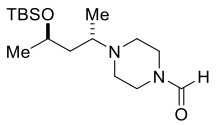
^{1}H-NMR ($CDCl_3$, 400 MHz): δ [ppm] = 3.95–3.83 (m, 1H), 2.77 (m, 1H), 2.63–2.45 (m, 4H), 1.70 (dt, *J* = 13.7, 7.0 Hz, 2H), 1.62–1.55 (m, 7H), 1.33–1.21 (m, 1H), 1.21–1.15 (m, 1H), 1.13 (d, *J* = 6.0 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ [ppm] = 66.7, 57.2, 51.3, 43.8, 29.8, 27.0, 26.1, 23.9, 18.3, 15.0, -4.1, -4.6.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2955 (s), 2926 (vs), 2890 (m), 2884 (m), 2854 (s), 1472 (m), 1462 (m), 1445 (m), 1373 (m), 1361 (m), 1255 (s), 1177 (m), 1151 (m), 1135 (m), 1099 (m), 1060 (s), 1039 (s), 1005 (m), 834 (vs), 826 (s), 807 (m), 773 (vs), 722 (m).

MS (70 eV, EI): m/z (%): 284 (3), 127 (9), 126 (100), 103 (5), 75 (5).

HRMS (EI) for $C_{17}H_{37}NOSi$: calc. $[M]^{+\bullet}$: 299.2644, found: 299.2637.



anti-**8j**

The amine *anti*-**8j** was prepared according to **TP5** from the iodide *anti*-**1i** (32.8 mg, 0.1 mmol, 1.0 equiv) and (46.9 mg, 0.2 mmol, 2.0 equiv). The crude product was purified via flash column chromatography on silica gel with *n*-pentane/diethyl ether (10:1) and 2% triethylamine to afford *anti*-**8j** (19.5 mg, 0.062 mmol, 62%, dr = 8:92) as a colorless oil.

^{1}H-NMR (CD_2Cl_2, 400 MHz): δ [ppm] = 7.95 (s, 1H), 3.89 (dp, *J* = 7.6, 6.0 Hz, 1H), 3.50–3.41 (m, 2H), 3.31 (h, *J* = 4.3 Hz, 2H), 2.77 (q, *J* = 6.7 Hz, 1H), 2.55–2.37 (m, 4H), 1.68 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.26–1.19 (m, 1H), 1.13 (d, *J* = 6.1 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 6H).

^{13}C-NMR (CD_2Cl_2, 100 MHz): δ [ppm] = 161.0, 66.7, 60.7, 56.5, 49.4, 48.1, 46.7, 43.8, 40.9, 26.2, 24.3, 18.5, 14.3, -4.0, -4.6.

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3388 (m), 3386 (m), 3220 (w), 3217 (w), 3214 (w), 3212 (w), 3199 (w), 3196 (m), 3194 (m), 3192 (m), 3188 (m), 3186 (w), 3182 (w), 3180 (w), 3177 (w), 2362 (w), 2358 (w), 2357 (w), 2354 (w), 1645 (vs), 1628 (m), 1624 (m), 1617 (m), 1577 (m), 1513 (vw), 1448 (w), 1405 (w), 1300 (w), 1269 (vw), 1115 (w), 930 (vw), 773 (vw), 699 (w), 694 (w), 668 (w).

MS (70 eV, EI): m/z (%): 141 (100), 113 (18), 75 (13).

HRMS (EI) for $C_{16}H_{34}N_2O_2Si$: calc. $[M]^{+\bullet}$: 312.2390, found: 314.2381.

6 Crystallographic Data

6.1 Single Crystal X-Ray Diffraction Studies

Single crystals of compound (*S*)-**8g** as hydrochloride derivative, suitable for X-ray diffraction, were obtained by slow evaporation of water. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K_α radiation (λ = 0.71071 Å).

Data collection and data reduction were performed with the CrysAlisPro software.[8] Absorption correction using the multiscan method[8] was applied. The structures were solved with SHELXS-97,[9] refined with SHELXL-97[10] and finally checked using PLATON.[11] Details for data collection and structure refinement are summarized in Table 1.

CCDC-**2110720** contains supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Details for X-ray data collection and structure refinement for compound (*S*)-**8g**.

	1
Empirical formula	$C_{15}H_{20}ClNOS$
Formula mass	297.83
T[K]	123(2)
Crystal size [mm]	0.35 × 0.20 × 0.02
Crystal description	colorless platelet
Crystal system	orthorhombic
Space group	*P*212121
a [Å]	7.2165(2)
b [Å]	12.5371(4)
c [Å]	16.4763(6)
α [°]	90.0
β [°]	90.0
γ [°]	90.0
V [Å^3]	1490.68(8)
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	1.327
μ [mm^{-1}]	0.388
F(000)	632
Θ range [°]	2.04 – 25.24
Index ranges	$-10 \leq h \leq 10$
	$-17 \leq k \leq 17$
	$-23 \leq l \leq 23$
Reflns. collected	30202
Reflns. obsd.	4002
Reflns. unique	4545 (R_{int} = 0.0539)
R_1, wR_2 (2σ data)	0.0382, 0.0823
R_1, wR_2 (all data)	0.0470, 0.0862
GOOF on F^2	1.058
Peak/hole [e Å^{-3}]	0.385 / -0.203

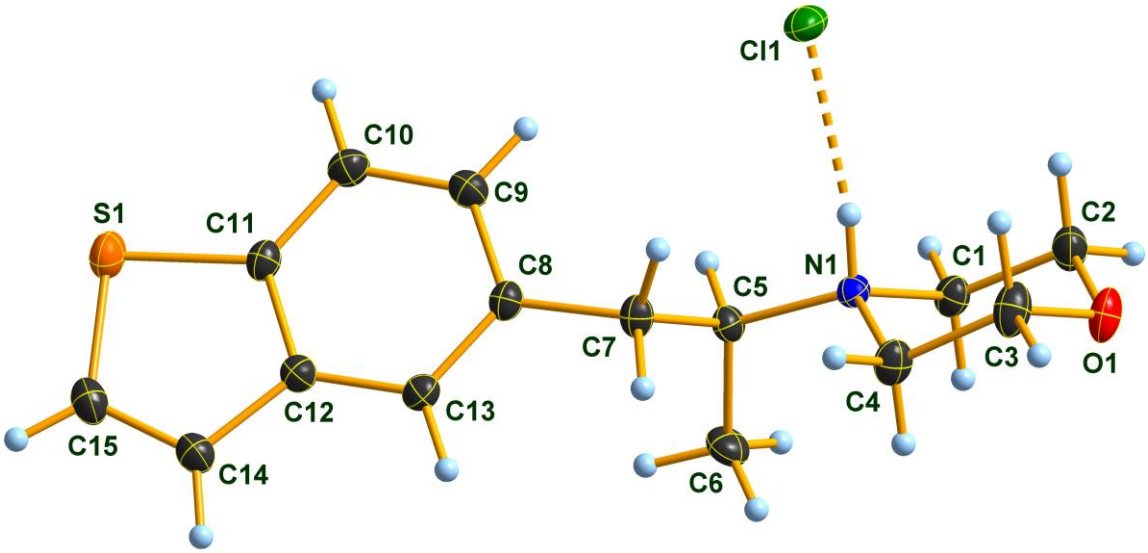


Figure 1. Molecular structure of compound **1** in the crystal. DIAMOND.[12] representation; thermal ellipsoids are drawn at 50 % probability level. Symmetry code for chloride anion: -0.5+x, 1.5-y, 1-z.

Table 2. Selected bond lengths (Å) of compound **1**.

S1 – C15	1.724(3)	C9 – C10	1.380(3)
S1 – C11	1.737(2)	C14 – C15	1.354(3)
C1 – N1	1.495(3)	C14 – C12	1.439(3)
C1 – C2	1.512(3)	C13 – C12	1.405(3)
C5 – C6	1.520(3)	C8 – C9	1.410(3)
C5 – N1	1.522(3)	C8 – C7	1.510(3)
C5 – C7	1.533(3)	O1 – C3	1.421(3)
C11 – C10	1.395(3)	O1 – C2	1.426(3)
C11 – C12	1.412(3)	C4 – N1	1.496(3)
C8 – C13	1.386(3)	C4 – C3	1.519(3)

Table 3. Selected bond angles (°) of compound **1**.

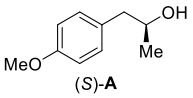
C15 – S1 – C11	91.5(1)	C9 – C10 – C11	118.2(2)
N1 – C1 – C2	109.7(2)	C15 – C14 – C12	112.6(2)
C6 – C5 – N1	112.6(2)	C1 – N1 – C4	108.8(2)
C6 – C5 – C7	113.4(2)	C1 – N1 – C5	113.3(2)

N1 – C5 – C7	108.0(2)	C4 – N1 – C5	115.4(2)
C10 – C11 – C12	121.4(2)	C8 – C13 – C12	120.1(2)
C10 – C11 – S1	127.5(2)	O1 – C2 – C1	111.9(2)
C12 – C11 – S1	111.1(2)	C14 – C15 – S1	113.4(2)
C13 – C8 – C9	119.5(2)	C13 – C12 – C11	118.9(2)
C13 – C8 – C7	120.7(2)	C13 – C12 – C14	129.5(2)
C9 – C8 – C7	119.7(2)	C11 – C12 – C14	111.6(2)
C3 – O1 – C2	110.3(2)	O1 – C3 – C4	111.8(2)
N1 – C4 – C3	108.5(2)	C8 – C7 – C5	114.1(2)
C10 – C9 – C8	121.9(2)		

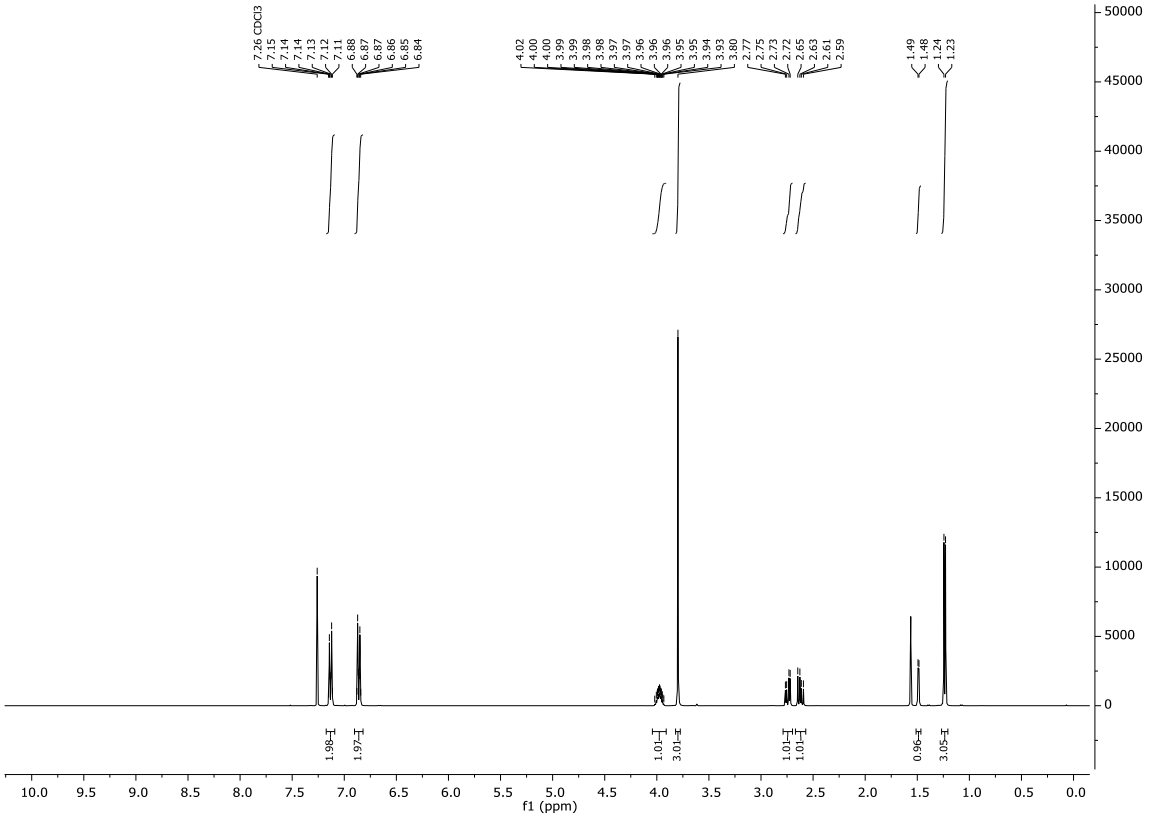
Table 4. Selected torsion angles (°) of compound **1**.

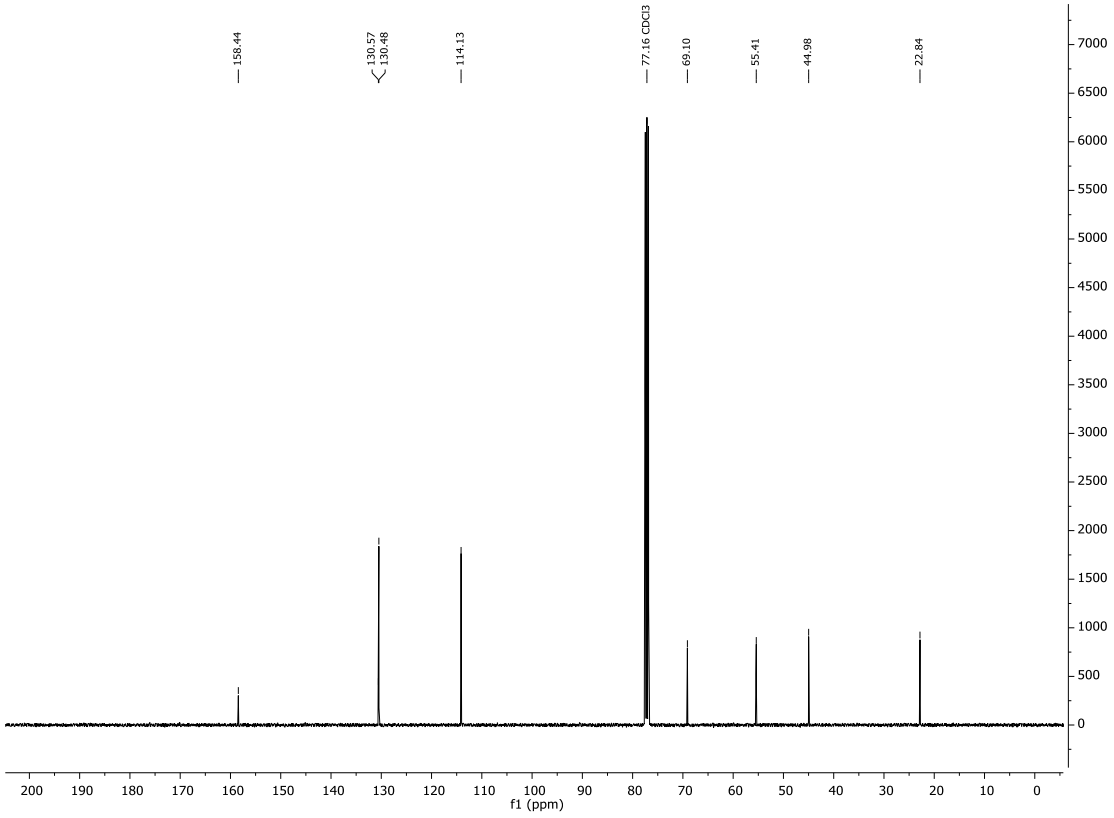
C15 – S1 – C11 – C10	-178.0(2)	C7 – C5 – N1 – C4	53.1(2)
C15 – S1 – C11 – C12	-0.3(2)	C9 – C8 – C13 – C12	-0.3(3)
C13 – C8 – C9 – C10	0.3(3)	C7 – C8 – C13 – C12	175.8(2)
C7 – C8 – C9 – C10	-175.9(2)	C3 – O1 – C2 – C1	-58.2(3)
C13 – C8 – C7 – C5	113.6(2)	N1 – C1 – C2 – O1	57.5(3)
C9 – C8 – C7 – C5	-70.3(3)	C12 – C14 – C15 – S1	0.4(3)
C6 – C5 – C7 – C8	-75.6(3)	C11 – S1 – C15 – C14	-0.1(2)
N1 – C5 – C7 – C8	158.9(2)	C8 – C13 – C12 – C11	0.0(3)
C8 – C9 – C10 – C11	0.0(3)	C8 – C13 – C12 – C14	-177.8(2)
C12 – C11 – C10 – C9	-0.3(3)	C10 – C11 – C12 – C13	0.3(3)
S1 – C11 – C10 – C9	177.3(2)	S1 – C11 – C12 – C13	-177.6(2)
C2 – C1 – N1 – C4	-56.9(2)	C10 – C11 – C12 – C14	178.4(2)
C2 – C1 – N1 – C5	173.4(2)	S1 – C11 – C12 – C14	0.5(2)
C3 – C4 – N1 – C1	57.5(2)	C15 – C14 – C12 – C13	177.3(2)
C3 – C4 – N1 – C5	-174.0(2)	C15 – C14 – C12 – C11	-0.6(3)
C6 – C5 – N1 – C1	53.4(2)	C2 – O1 – C3 – C4	59.6(3)
C7 – C5 – N1 – C1	179.4(2)	N1 – C4 – C3 – O1	-59.7(3)
C6 – C5 – N1 – C4	-72.9(2)		

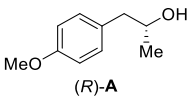
7 NMR Spectra



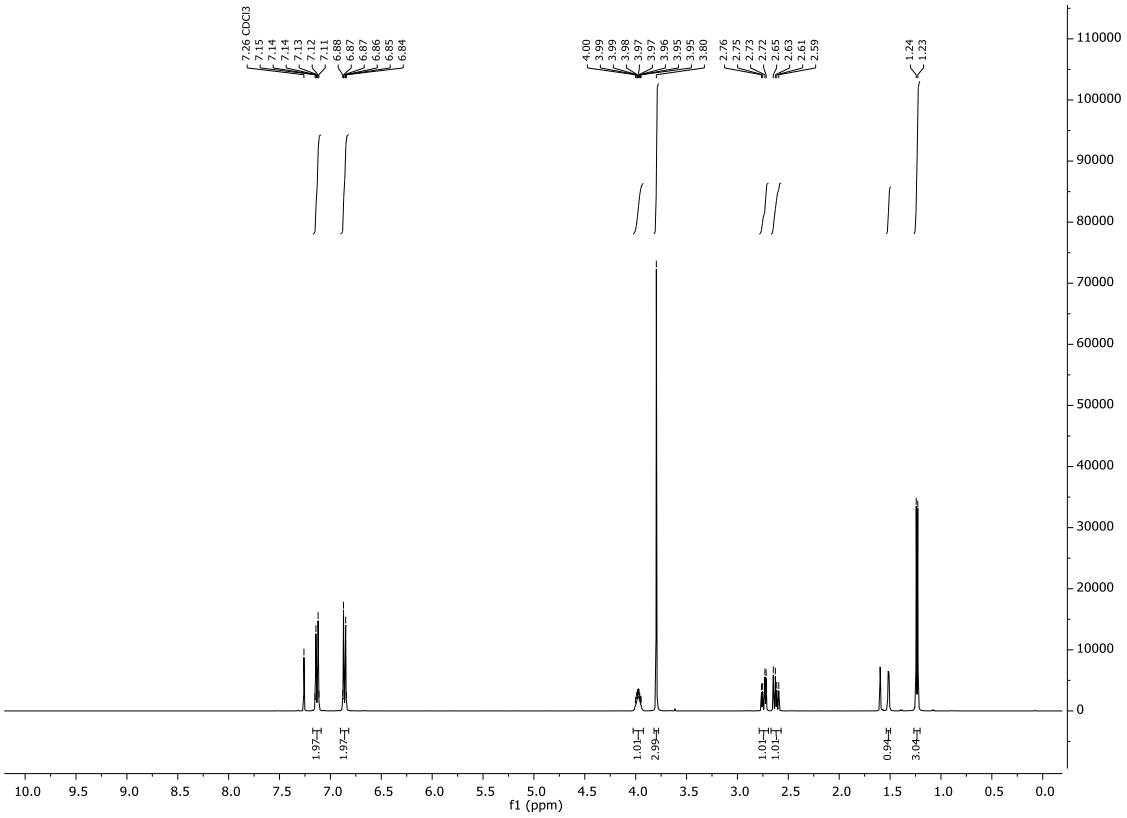
(*S*)-**A**

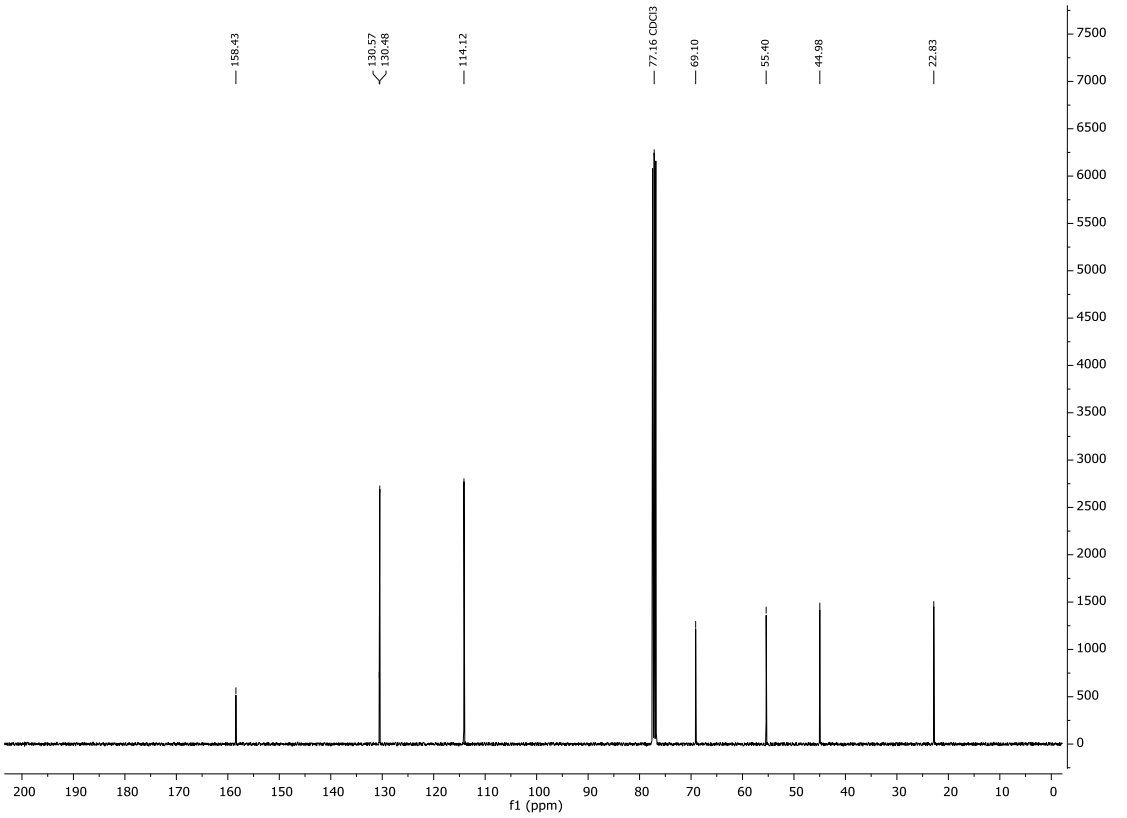


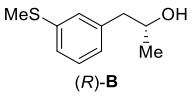



OH
Me
MeO

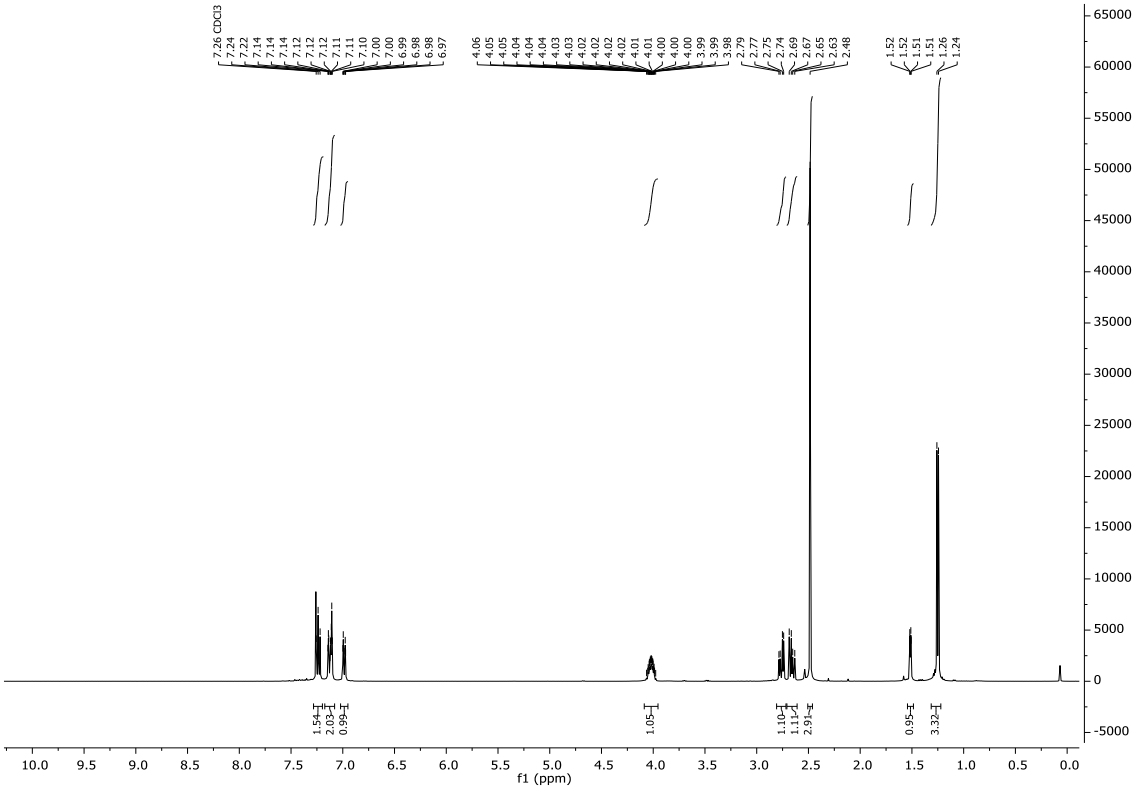
(*R*)-**A**

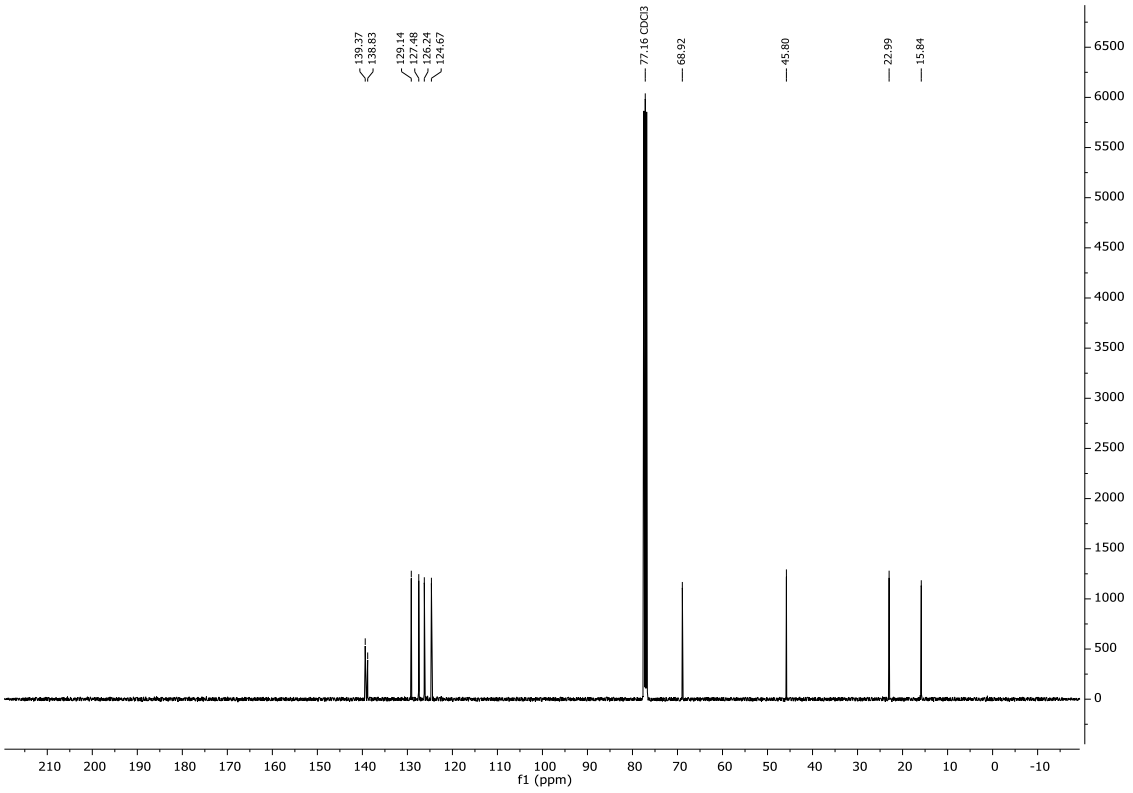

7.26 CDCl3
7.15
7.14
7.14
7.13
7.12
7.11
6.88
6.87
6.87
6.86
6.85
6.84
4.00
3.99
3.99
3.98
3.97
3.97
3.96
3.95
3.95
3.80
2.76
2.75
2.73
2.72
2.65
2.63
2.61
2.59
1.24
1.23
1.97
1.97
1.01
2.99
1.01
1.01
0.94
3.04
f1 (ppm)

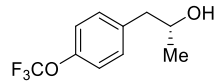

158.43
130.57
130.48
114.12
77.16 CDCl3
69.10
55.40
44.98
22.83
f1 (ppm)


MeS
OH
Me

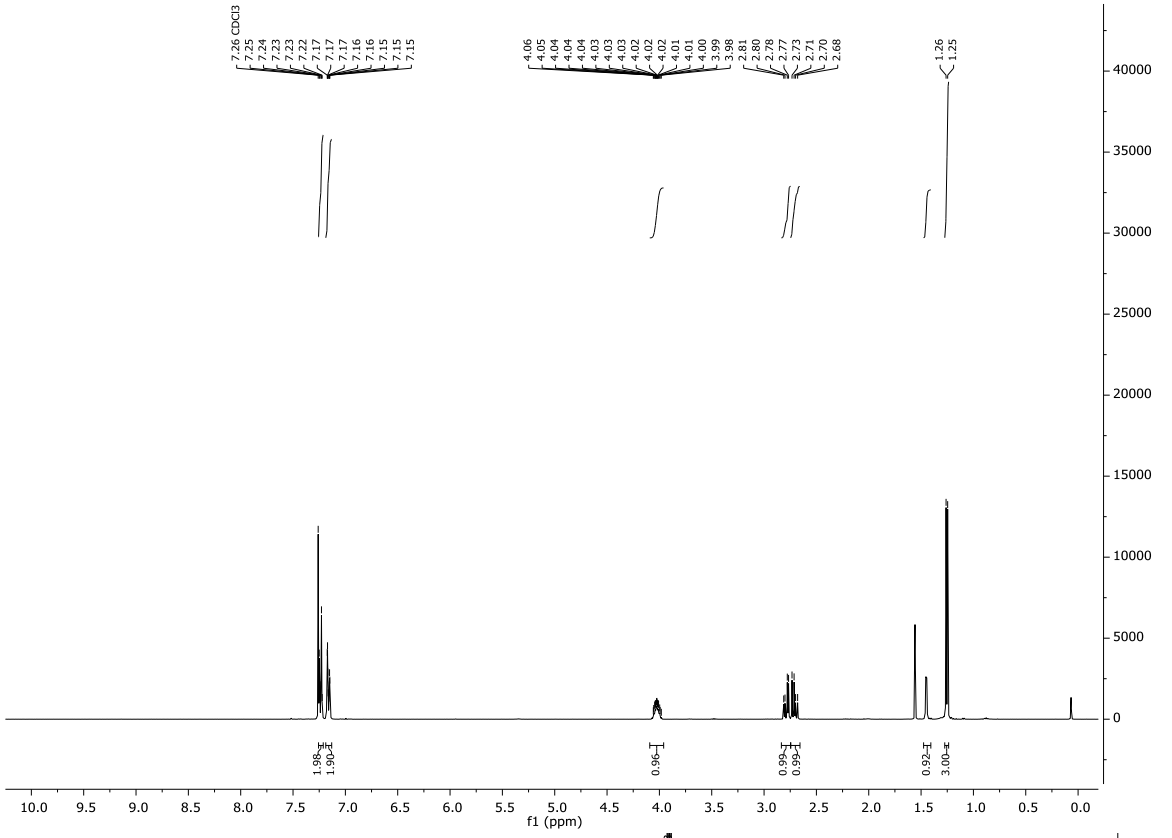
(*R*)-**B**

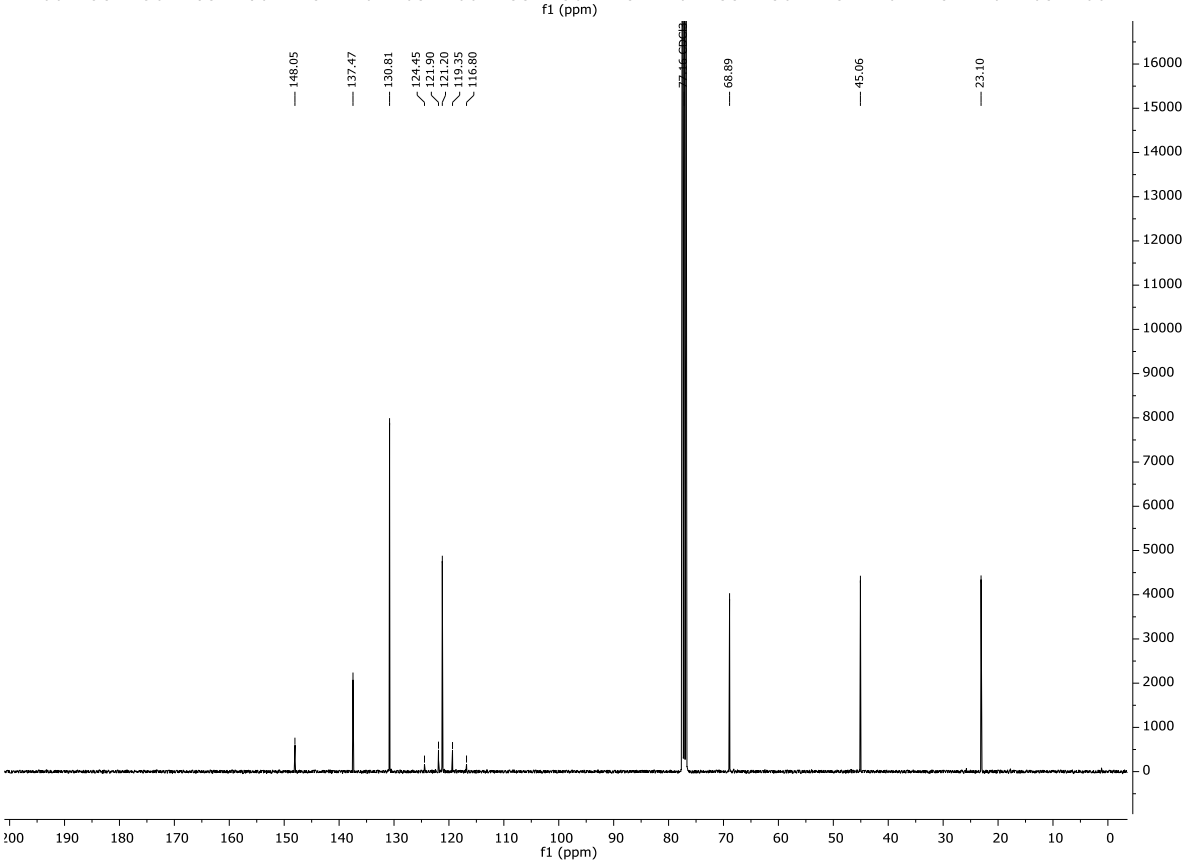

7.26 CDCl3
7.24
7.22
7.14
7.14
7.14
7.12
7.12
7.12
7.11
7.11
7.10
7.00
7.00
6.99
6.98
6.98
6.97
4.06
4.05
4.05
4.04
4.04
4.04
4.03
4.03
4.02
4.02
4.02
4.02
4.01
4.01
4.00
4.00
4.00
3.99
3.99
3.99
3.98
2.79
2.77
2.75
2.74
2.69
2.67
2.65
2.63
2.48
1.52
1.52
1.51
1.51
1.26
1.24
1.54
2.03
0.99
1.05
1.10
1.11
2.91
0.95
3.32
f1 (ppm)

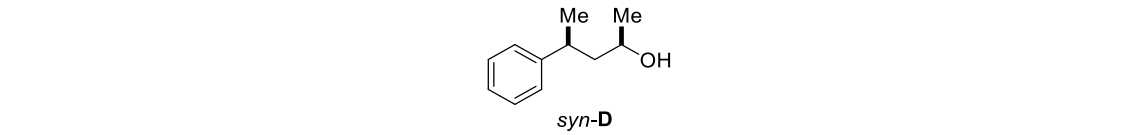

139.37
138.83
129.14
127.48
126.24
124.67
77.16 CDCl3
68.92
45.80
22.99
15.84
f1 (ppm)


OH
Me
F3CO

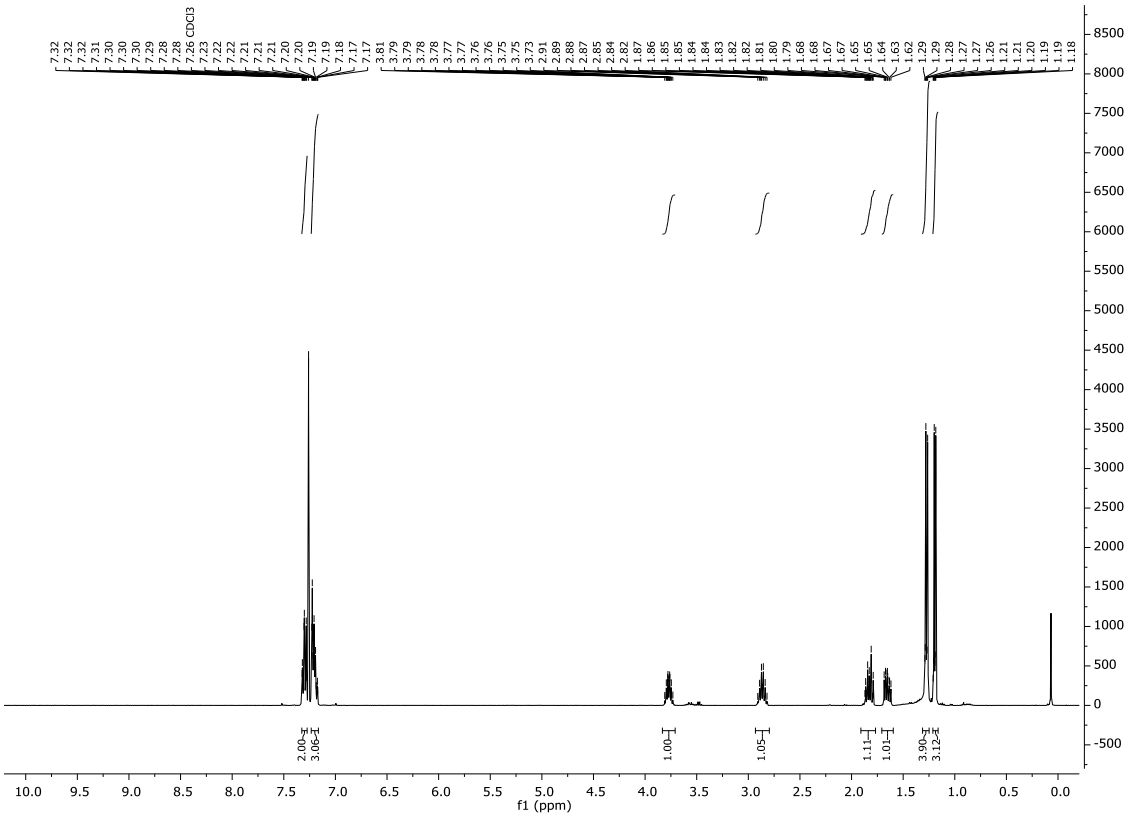
(*R*)-**C**

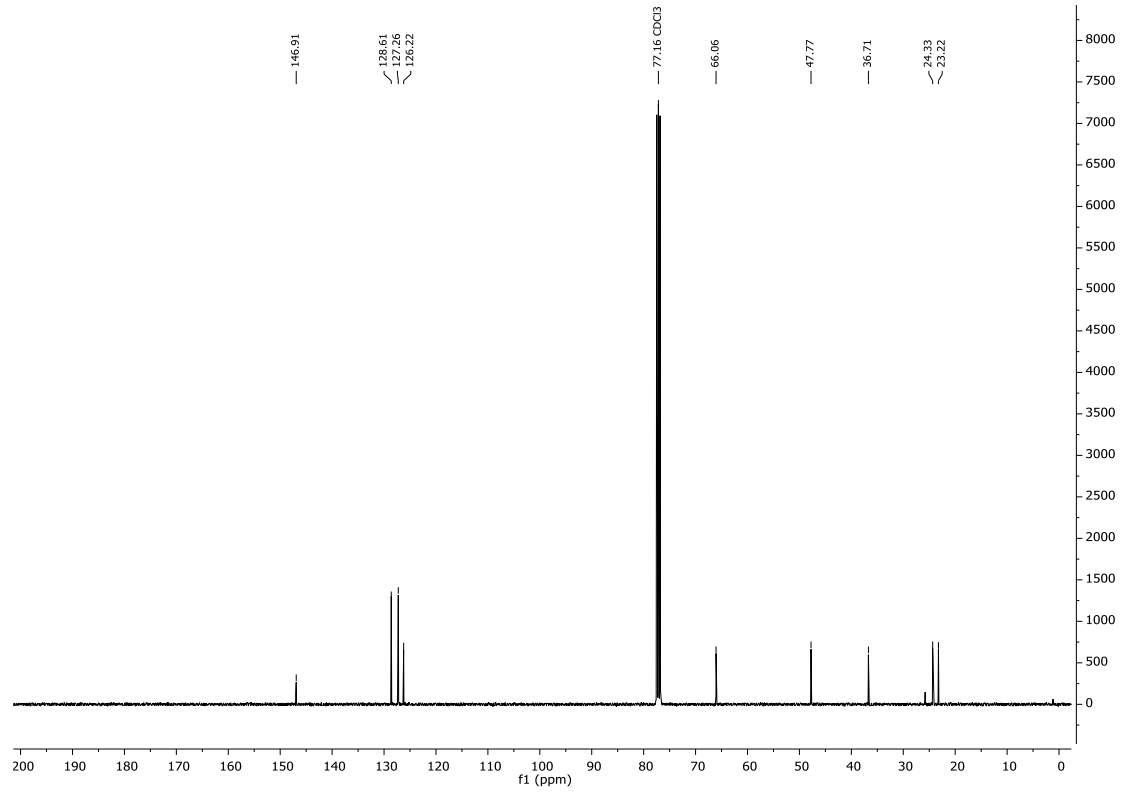

7.26 CDCl3
7.25
7.24
7.23
7.23
7.22
7.17
7.17
7.17
7.16
7.16
7.15
7.15
7.15
4.06
4.05
4.04
4.04
4.04
4.03
4.03
4.03
4.02
4.02
4.02
4.01
4.01
4.00
3.99
3.98
2.81
2.80
2.78
2.77
2.73
2.71
2.70
2.68
1.26
1.25
1.98
1.90
0.96
0.99
0.99
0.92
3.00
f1 (ppm)

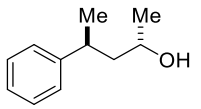

148.05
137.47
130.81
124.45
121.90
121.20
119.35
116.80
77.16
68.89
45.06
23.10
f1 (ppm)


Me
Me
OH

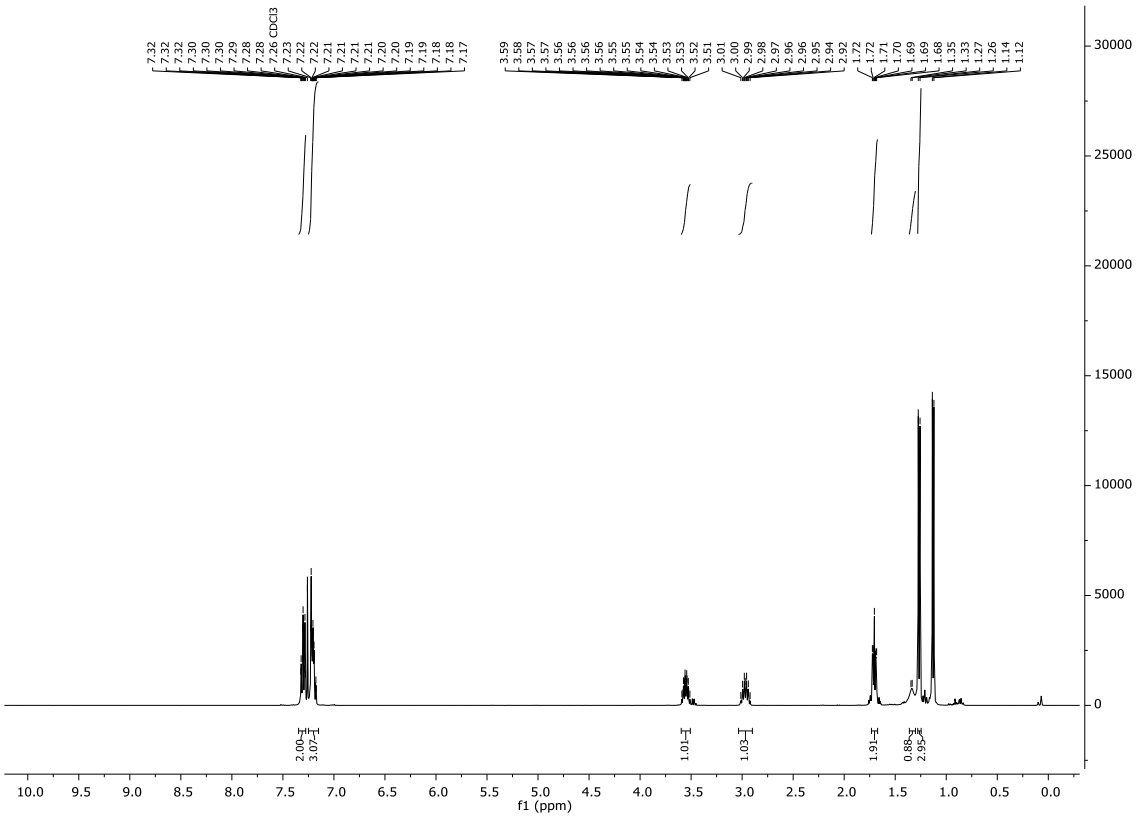
syn-**D**

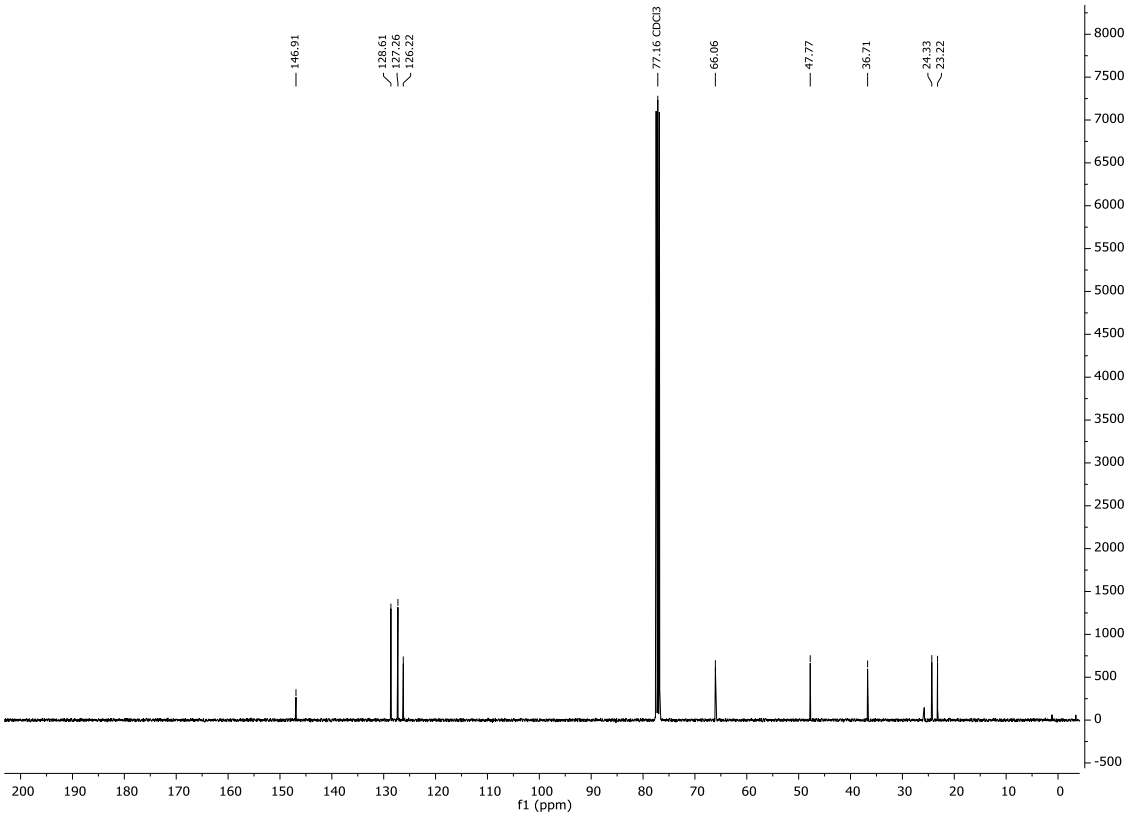

7.32
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.28
7.26 CDCl3
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
3.81
3.79
3.79
3.78
3.78
3.77
3.77
3.76
3.76
3.75
3.75
3.73
2.91
2.89
2.88
2.87
2.85
2.84
2.82
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.82
1.82
1.81
1.80
1.79
1.68
1.68
1.67
1.67
1.65
1.65
1.64
1.63
1.62
1.29
1.29
1.28
1.27
1.27
1.26
1.21
1.21
1.20
1.19
1.19
1.18
2.00
3.06
1.00
1.05
1.11
1.01
3.90
3.12
f1 (ppm)

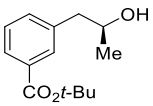

146.91
128.61
127.26
126.22
77.16 CDCl3
66.06
47.77
36.71
24.33
23.22
f1 (ppm)


Me
Me
OH

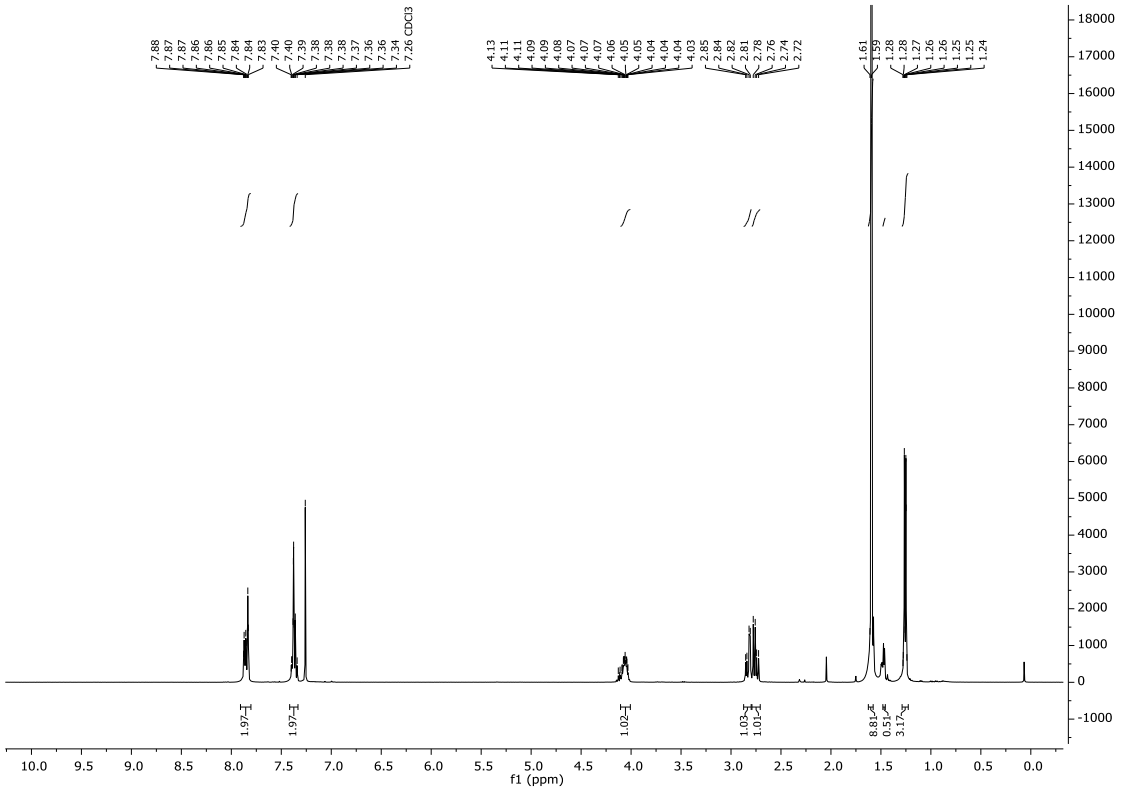
anti-**D**


7.32
7.32
7.32
7.30
7.30
7.30
7.29
7.28
7.26 CDCl3
7.23
7.22
7.22
7.21
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
3.59
3.58
3.57
3.57
3.56
3.56
3.56
3.56
3.55
3.55
3.54
3.54
3.53
3.53
3.52
3.51
3.01
3.00
2.99
2.98
2.97
2.96
2.96
2.95
2.94
2.92
1.72
1.72
1.71
1.70
1.69
1.69
1.68
1.35
1.33
1.27
1.26
1.14
1.12
2.00
3.07
1.01
1.03
1.91
0.88
2.95
f1 (ppm)


146.91
128.61
127.26
126.22
77.16 CDCl3
66.06
47.77
36.71
24.33
23.22
f1 (ppm)


OH
Me
CO2t-Bu

(*S*)-**E**


7.88
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7.86
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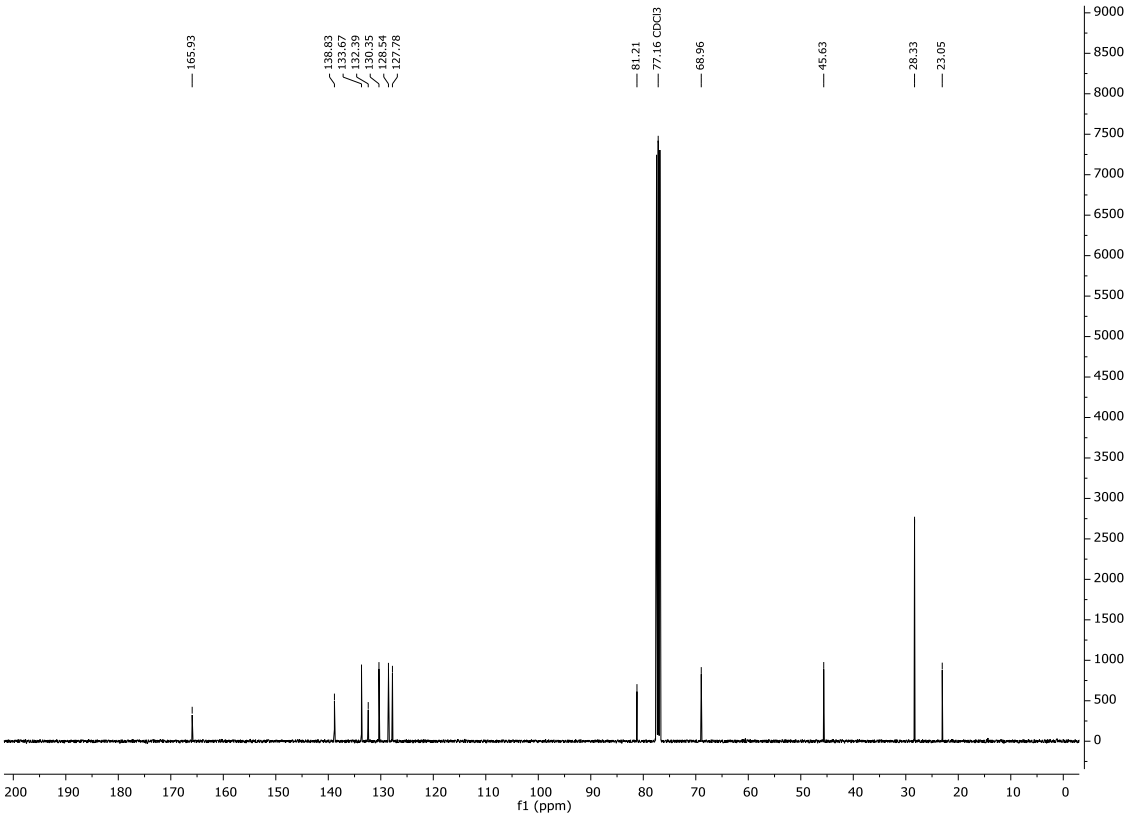
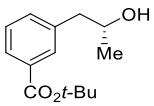
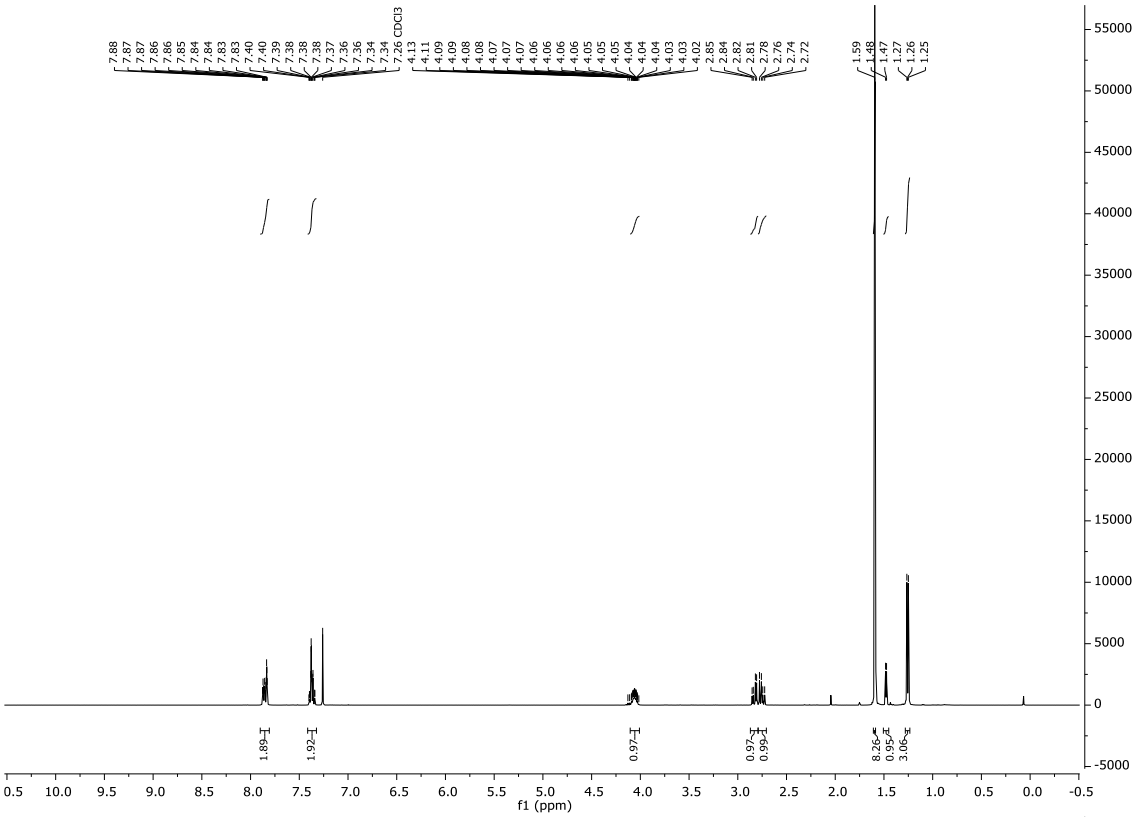
7.84
7.84
7.83
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.36
7.36
7.34
7.26 CDCl3
4.13
4.11
4.11
4.09
4.09
4.08
4.07
4.07
4.07
4.06
4.05
4.05
4.04
4.04
4.04
4.03
2.85
2.84
2.82
2.81
2.78
2.76
2.74
2.72
1.61
1.59
1.28
1.28
1.27
1.26
1.26
1.25
1.25
1.24
1.97
1.97
1.02
1.03
1.01
8.81
0.51
3.17
f1 (ppm)


165.93
138.83
133.67
132.39
130.35
128.54
127.78
81.21
77.16 CDCl3
68.96
45.63
28.33
23.05
f1 (ppm)


OH
Me
CO2t-Bu

(*R*)-**E**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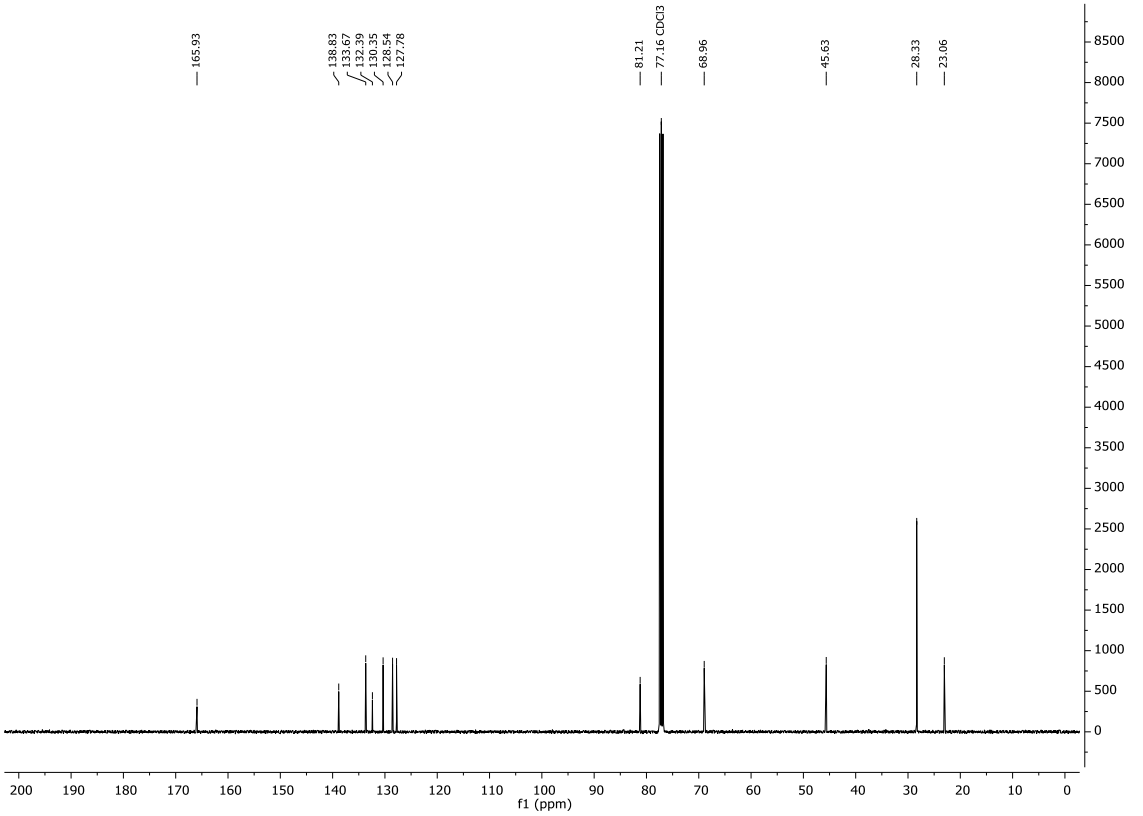
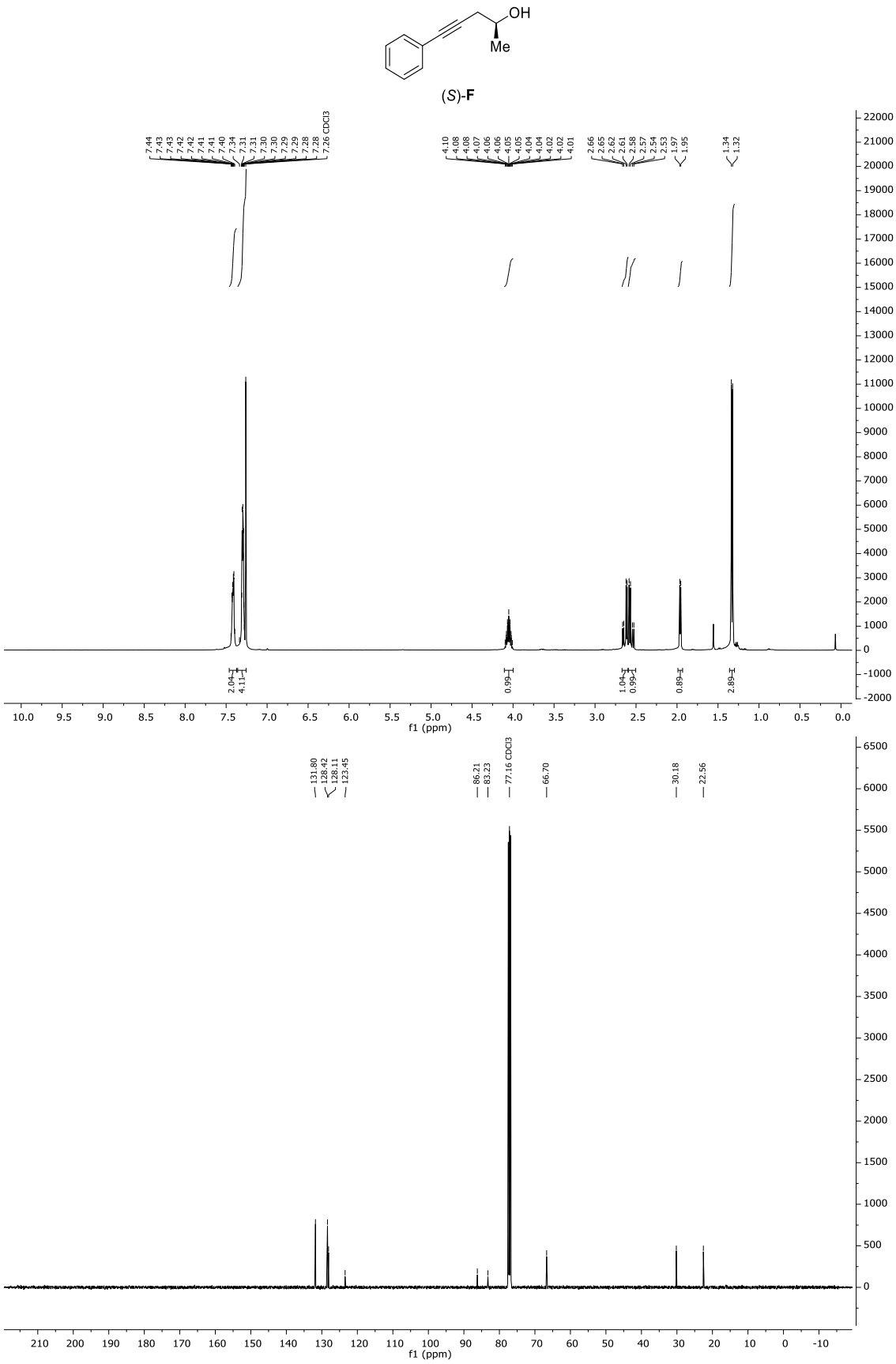
7.84
7.83
7.83
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.36
7.36
7.34
7.26 CDCl3
4.13
4.11
4.09
4.09
4.08
4.08
4.07
4.07
4.07
4.06
4.06
4.06
4.06
4.05
4.05
4.05
4.04
4.04
4.04
4.03
4.03
4.02
2.85
2.84
2.82
2.81
2.78
2.76
2.74
2.72
1.59
1.48
1.47
1.27
1.26
1.25
1.89
1.92
0.97
0.97
0.99
8.26
0.95
3.06
f1 (ppm)


165.93
138.83
133.67
132.39
130.35
128.54
127.78
81.21
77.16 CDCl3
68.96
45.63
28.33
23.06
f1 (ppm)


OH
Me
(S)-F
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.34
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.26 CDCl3
4.10
4.08
4.08
4.07
4.06
4.06
4.05
4.05
4.04
4.04
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4.02
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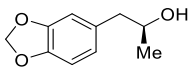
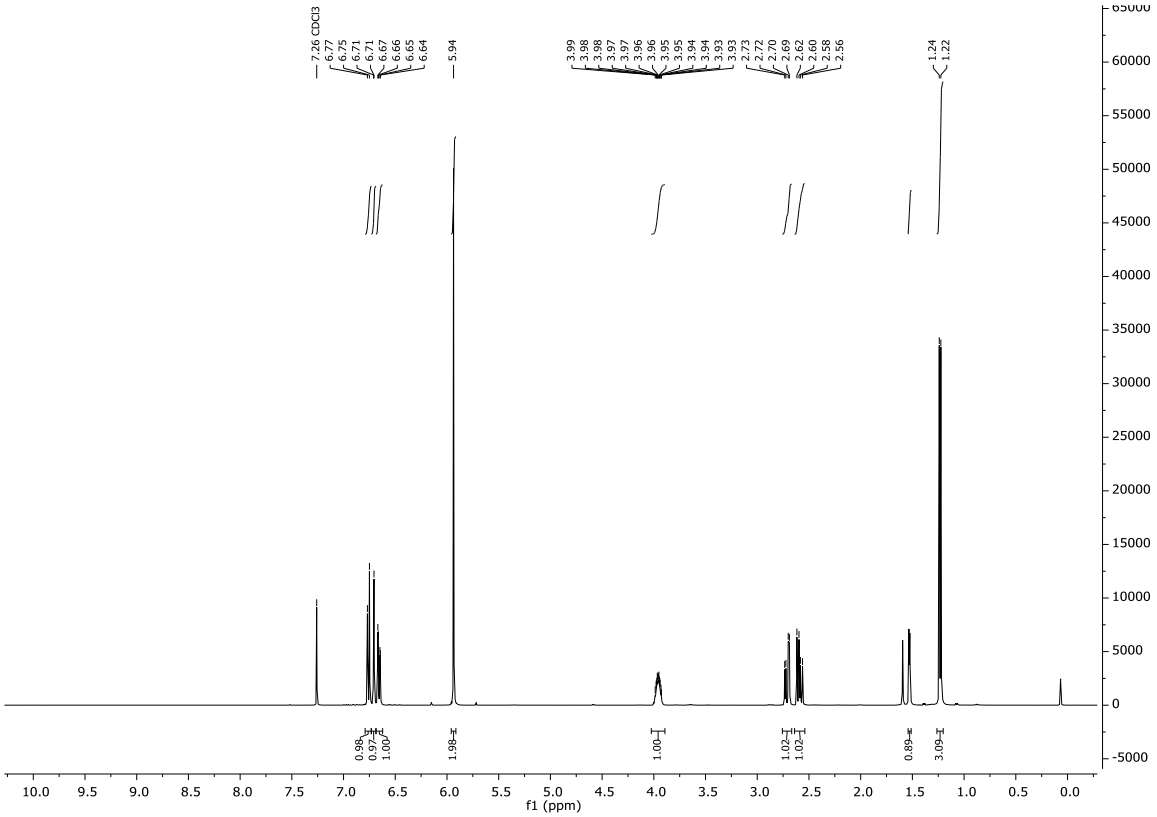
2.62
2.61
2.58
2.57
2.54
2.53
1.97
1.95
1.34
1.32
2.04
4.11
0.99
1.04
0.99
0.89
2.89
f1 (ppm)
131.80
128.42
128.11
123.45
86.21
83.23
77.16 CDCl3
66.70
30.18
22.56
f1 (ppm)


O
O
OH
Me

(*S*)-**G**


7.26 CDCl3
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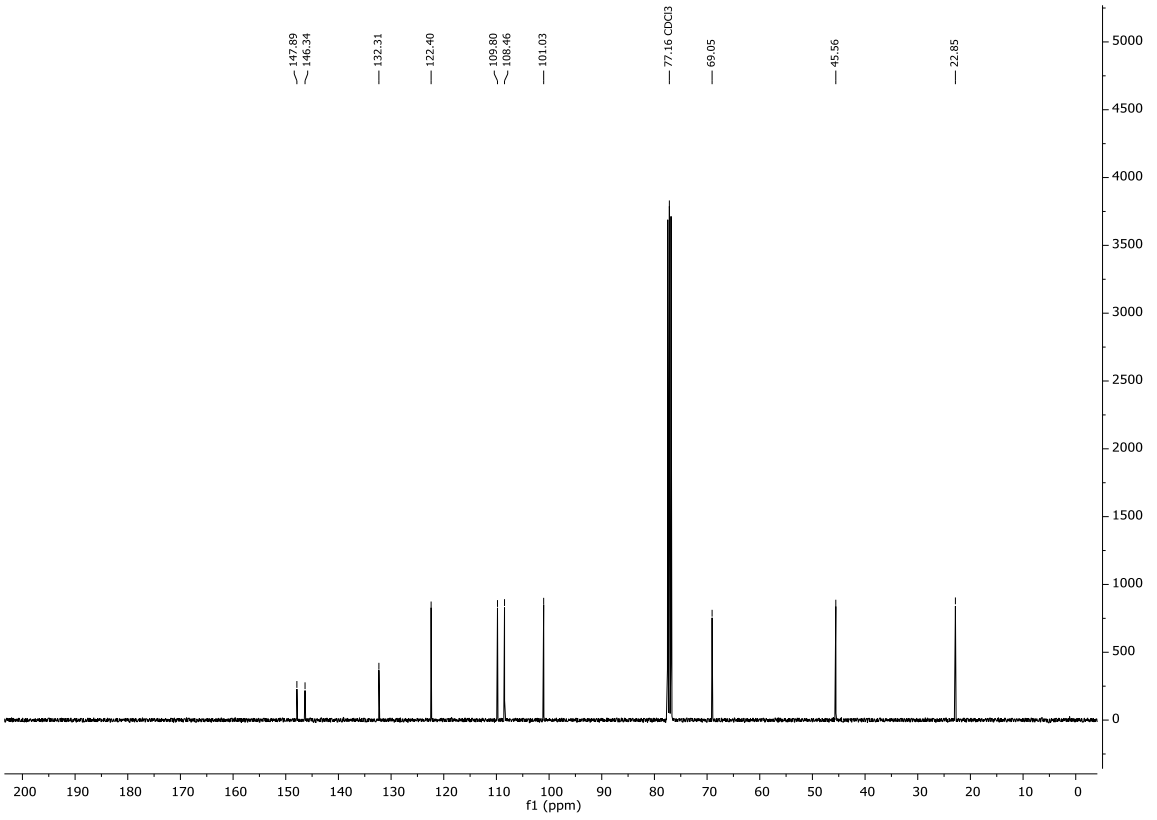
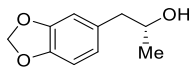
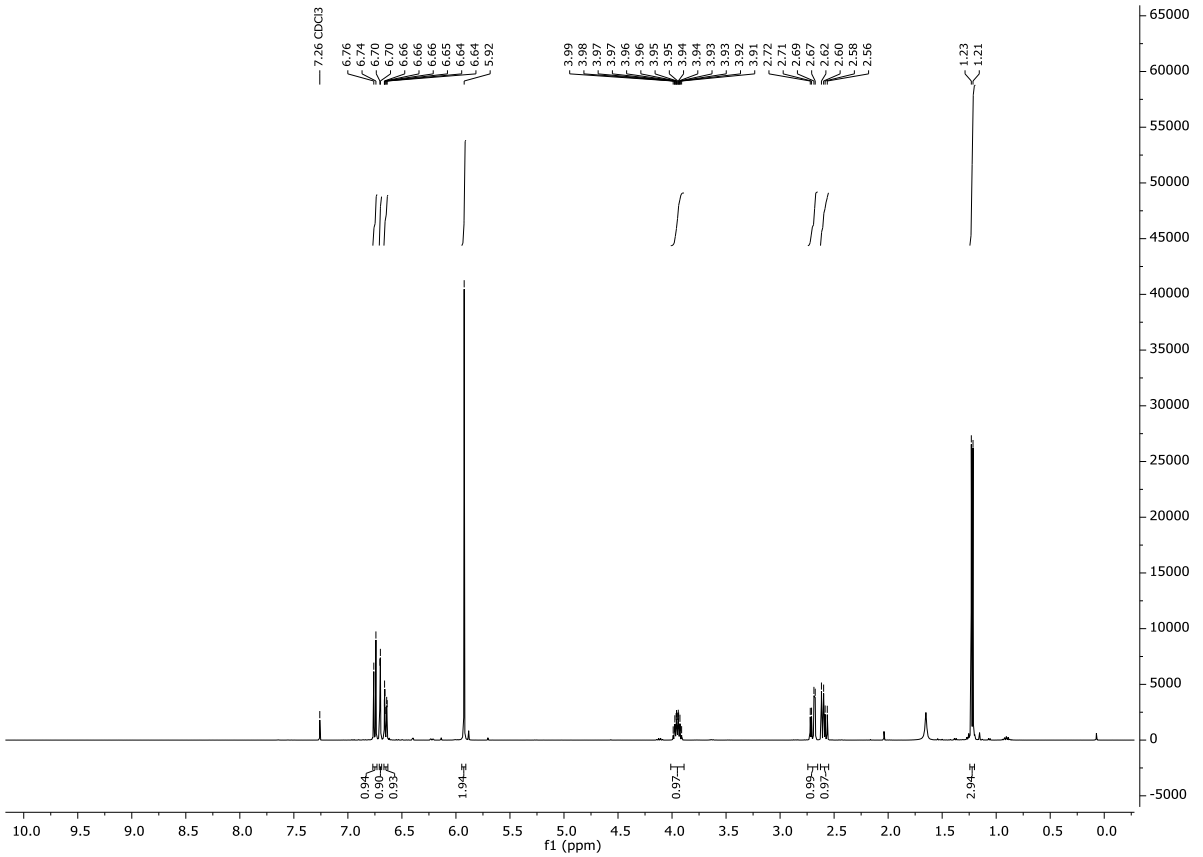
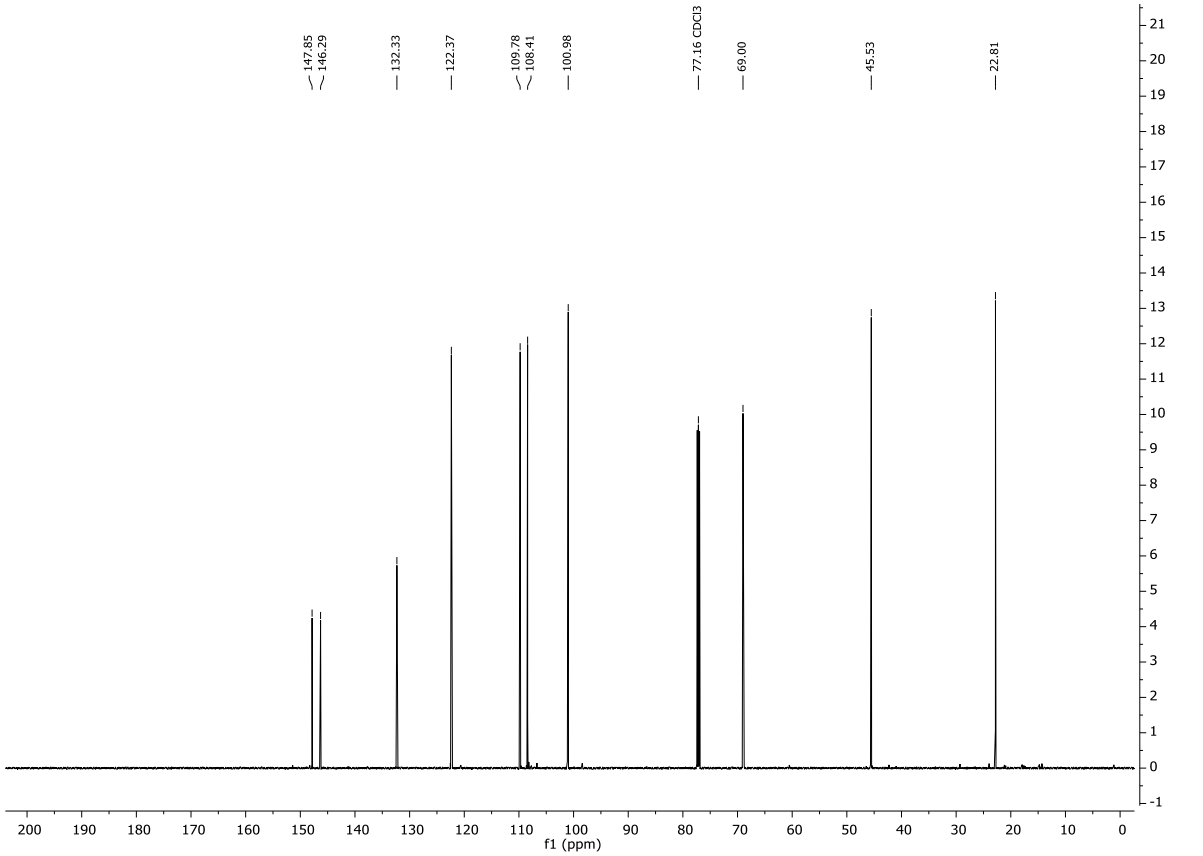
6.75
6.71
6.71
6.67
6.66
6.65
6.64
5.94
3.99
3.98
3.98
3.97
3.97
3.96
3.96
3.95
3.95
3.94
3.94
3.93
3.93
2.73
2.72
2.70
2.69
2.62
2.60
2.58
2.56
1.24
1.22
0.98
0.97
1.00
1.93
1.00
1.02
1.02
0.89
3.09
f1 (ppm)

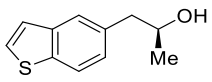

147.89
146.34
132.31
122.40
109.80
108.46
101.03
77.16 CDCl3
69.05
45.56
22.85
f1 (ppm)


O
O
OH
Me

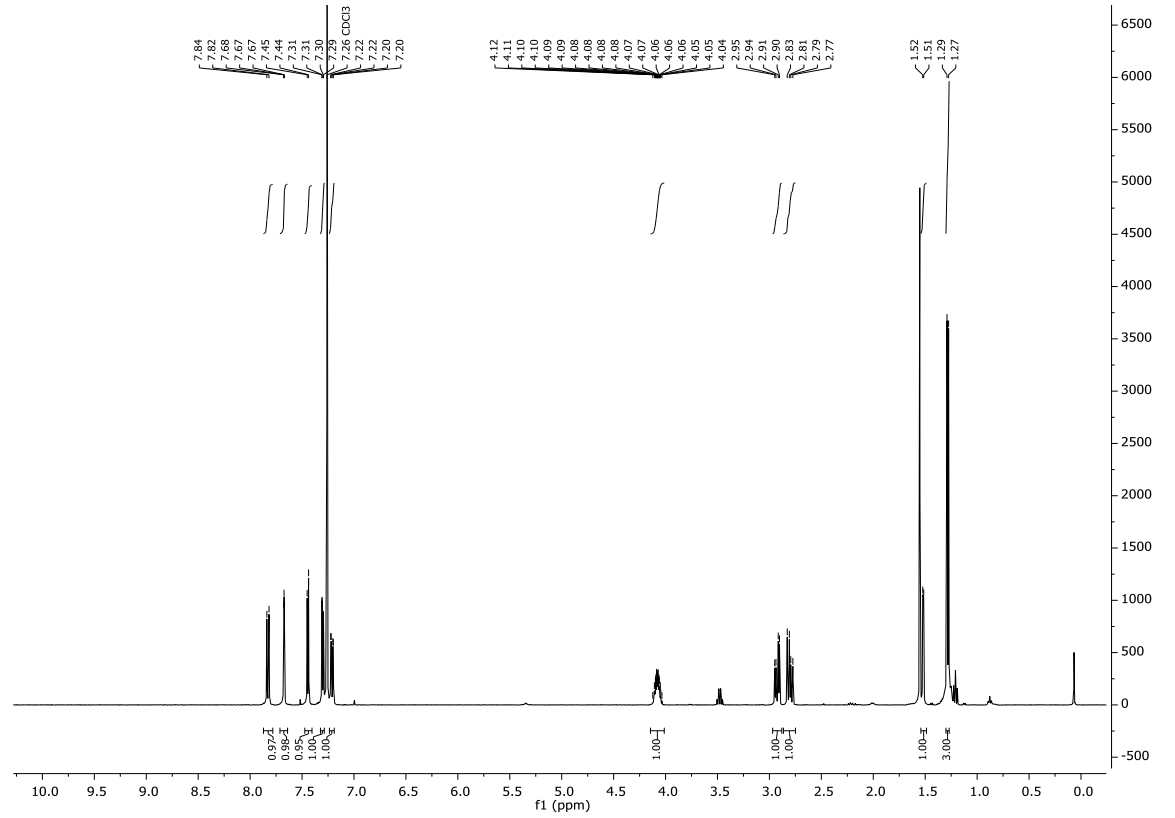
(*R*)-**G**

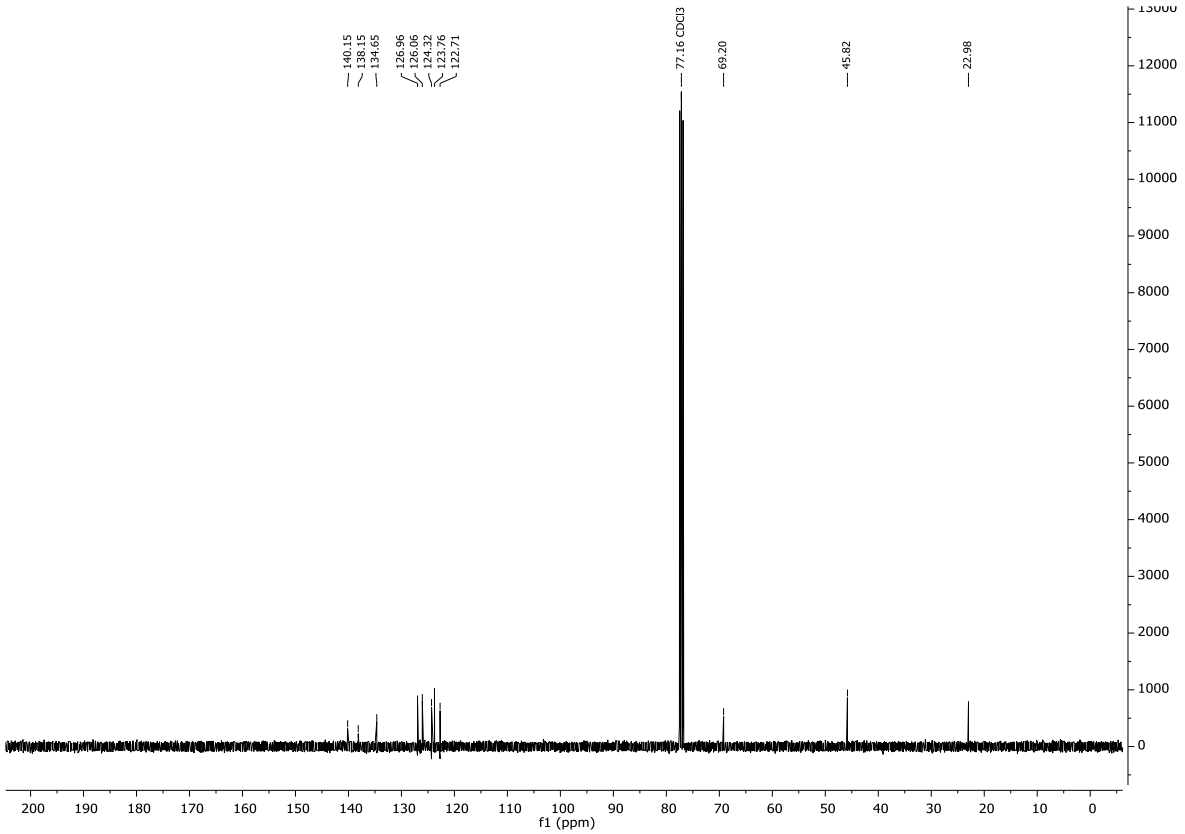

7.26 CDCl3
6.76
6.74
6.70
6.70
6.66
6.66
6.66
6.65
6.64
6.64
5.92
3.99
3.98
3.97
3.97
3.96
3.96
3.95
3.95
3.94
3.94
3.93
3.93
3.92
3.91
2.72
2.71
2.69
2.67
2.62
2.60
2.58
2.56
1.23
1.21
0.94
0.90
0.93
1.94
0.97
0.99
0.97
2.94
f1 (ppm)

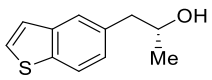

147.85
146.29
132.33
122.37
109.78
108.41
100.98
77.16 CDCl3
69.00
45.53
22.81
f1 (ppm)


OH
Me
S

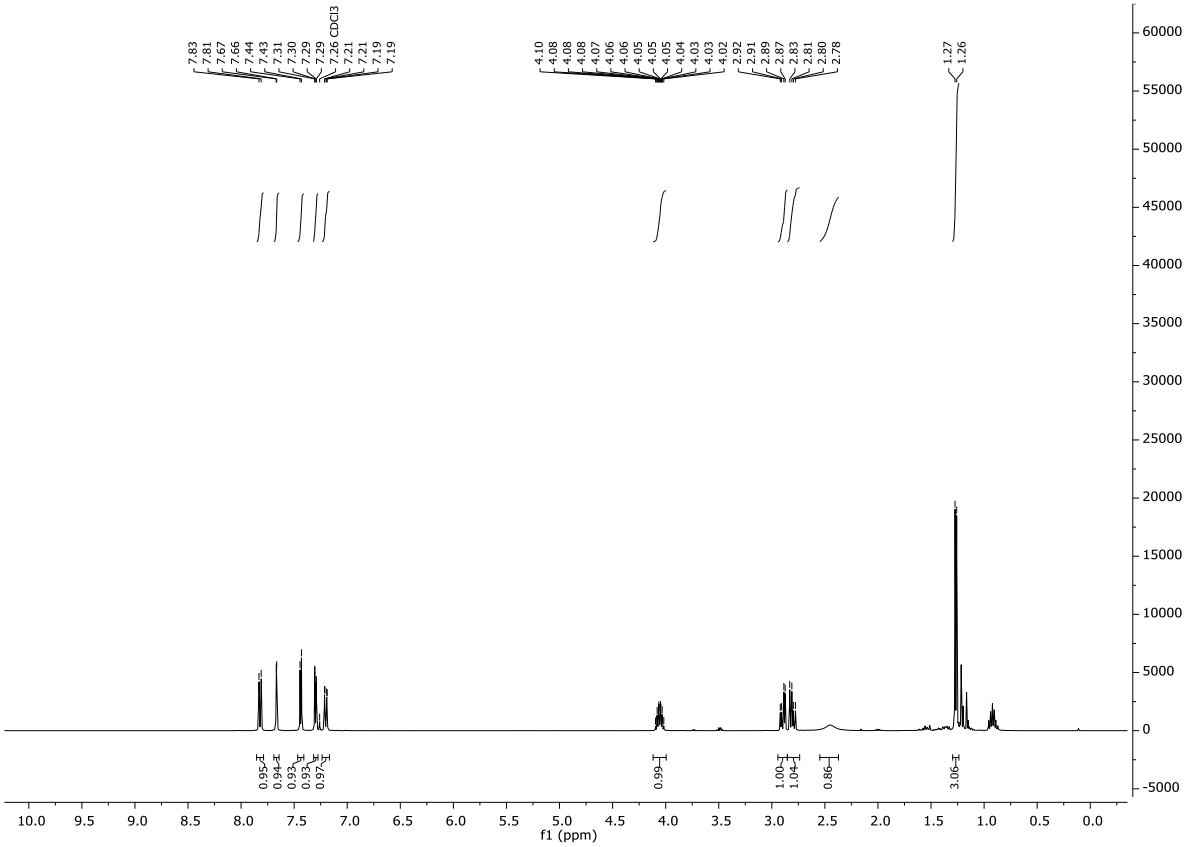
(*S*)-**H**

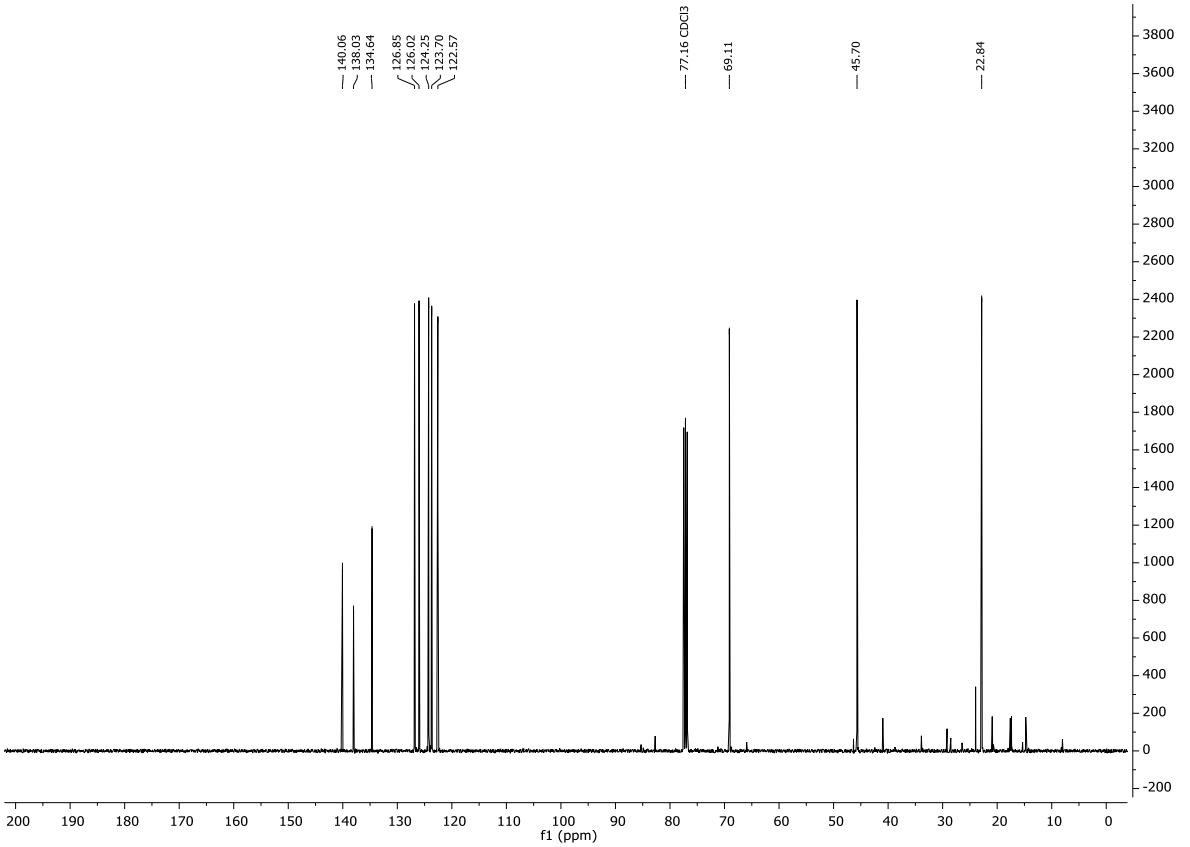

7.84
7.82
7.68
7.67
7.67
7.45
7.44
7.31
7.31
7.30
7.29
7.26 CDCl3
7.22
7.22
7.20
7.20
4.12
4.11
4.10
4.10
4.09
4.09
4.08
4.08
4.08
4.08
4.07
4.07
4.06
4.06
4.06
4.05
4.05
4.04
2.95
2.94
2.91
2.90
2.83
2.81
2.79
2.77
1.52
1.51
1.29
1.27
0.97
0.98
0.95
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

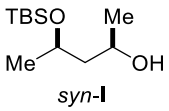

140.15
138.15
134.65
126.96
126.06
124.32
123.76
122.71
77.16 CDCl3
69.20
45.82
22.98
f1 (ppm)


OH
Me
S

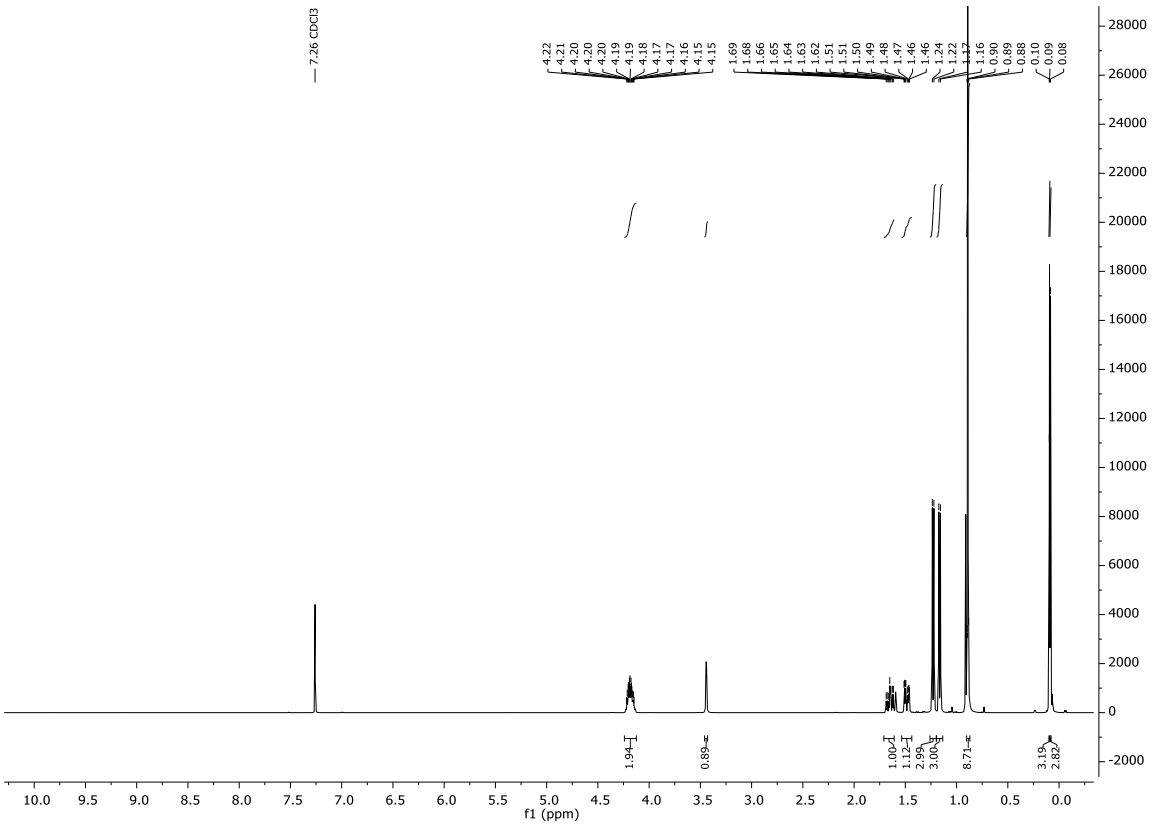
(*R*)-**H**

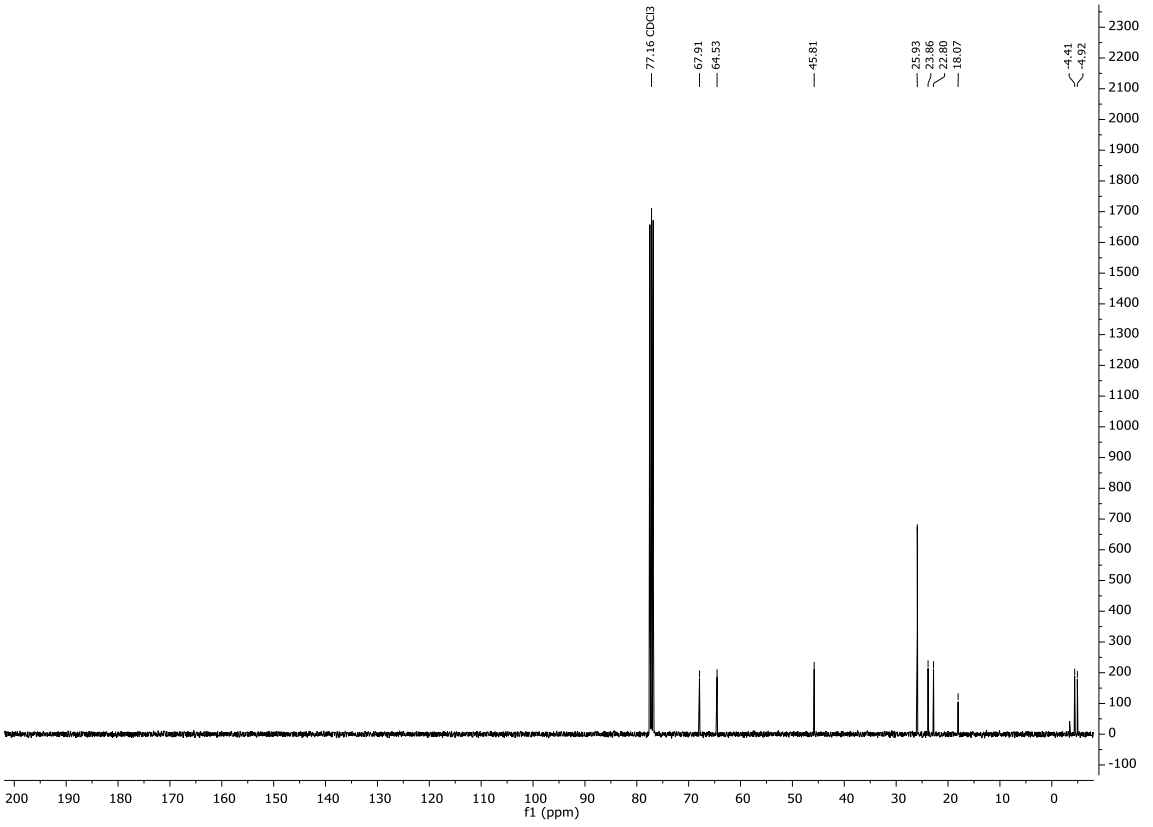

7.83
7.81
7.67
7.66
7.44
7.43
7.31
7.30
7.29
7.29
7.26 CDCl3
7.21
7.21
7.19
7.19
4.10
4.08
4.08
4.08
4.07
4.06
4.06
4.05
4.05
4.05
4.04
4.03
4.02
2.92
2.91
2.89
2.87
2.83
2.81
2.80
2.78
1.27
1.26
0.95
0.94
0.93
0.93
0.97
0.99
1.00
1.04
0.86
3.06
f1 (ppm)

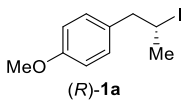

140.06
138.03
134.64
126.85
126.02
124.25
123.70
122.57
77.16 CDCl3
69.11
45.70
22.84
f1 (ppm)


TBSO
Me
Me
OH

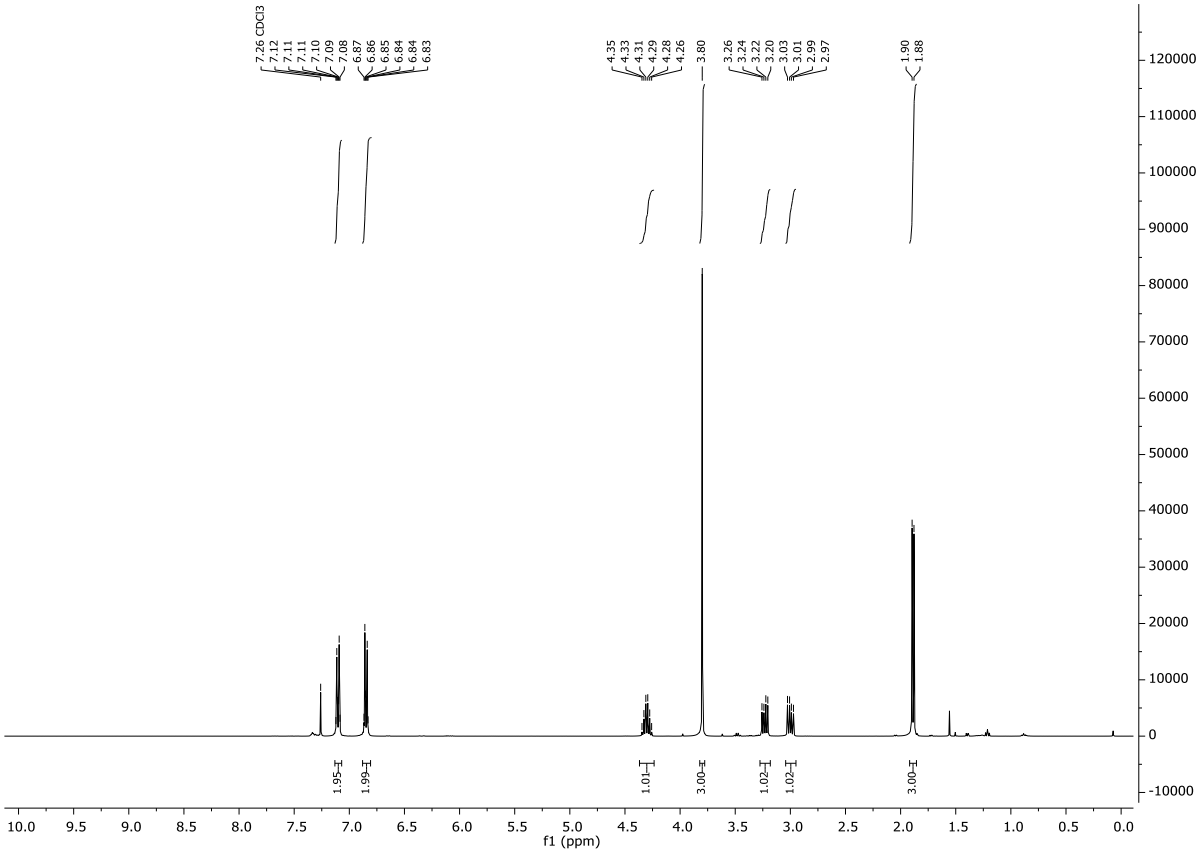
syn-**I**

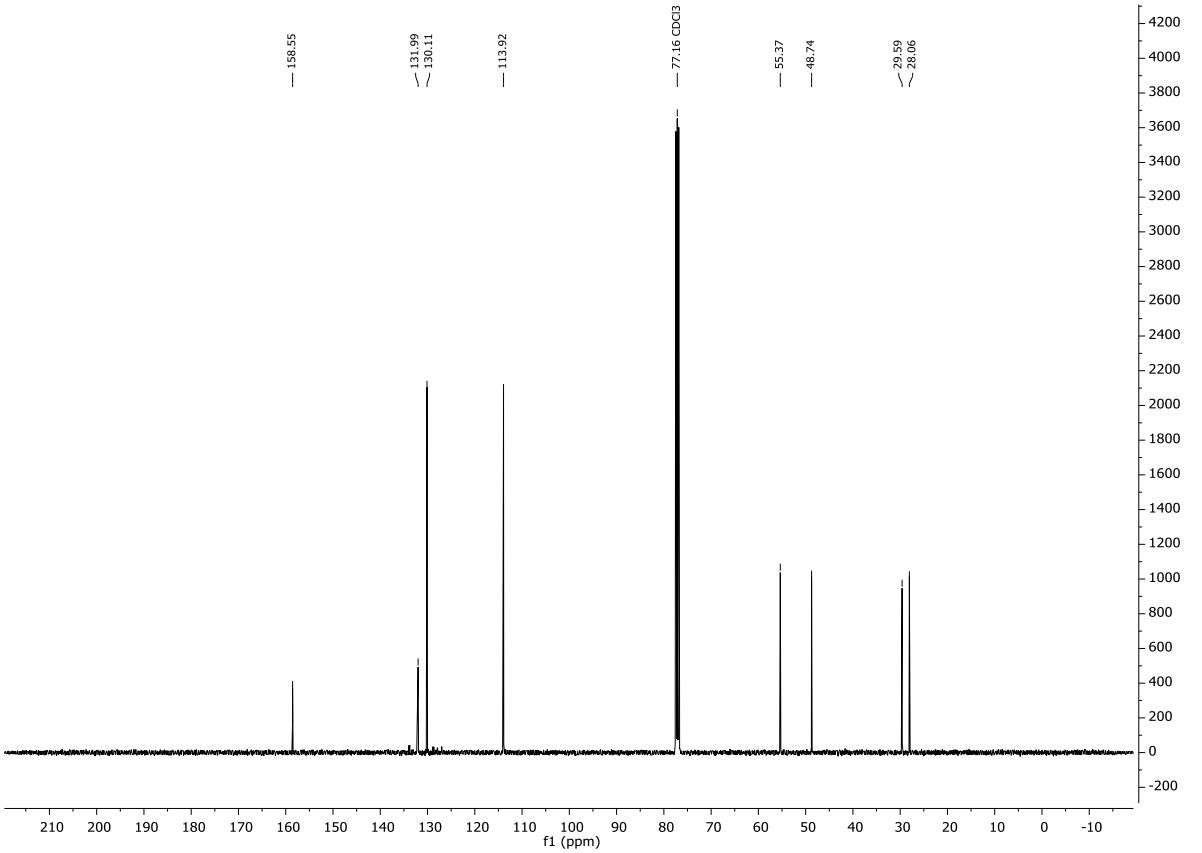

7.26 CDCl3
4.22
4.21
4.20
4.20
4.20
4.19
4.19
4.18
4.17
4.17
4.16
4.15
4.15
1.69
1.68
1.66
1.65
1.64
1.63
1.62
1.51
1.51
1.50
1.49
1.48
1.47
1.46
1.46
1.24
1.22
1.17
1.16
0.90
0.89
0.88
0.10
0.09
0.08
1.94
0.89
1.00
1.12
2.99
3.00
8.71
3.19
2.82
f1 (ppm)

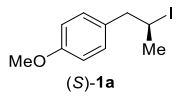

77.16 CDCl3
67.91
64.53
45.81
25.93
23.86
22.80
18.07
-4.41
-4.92
f1 (ppm)


I
Me
MeO

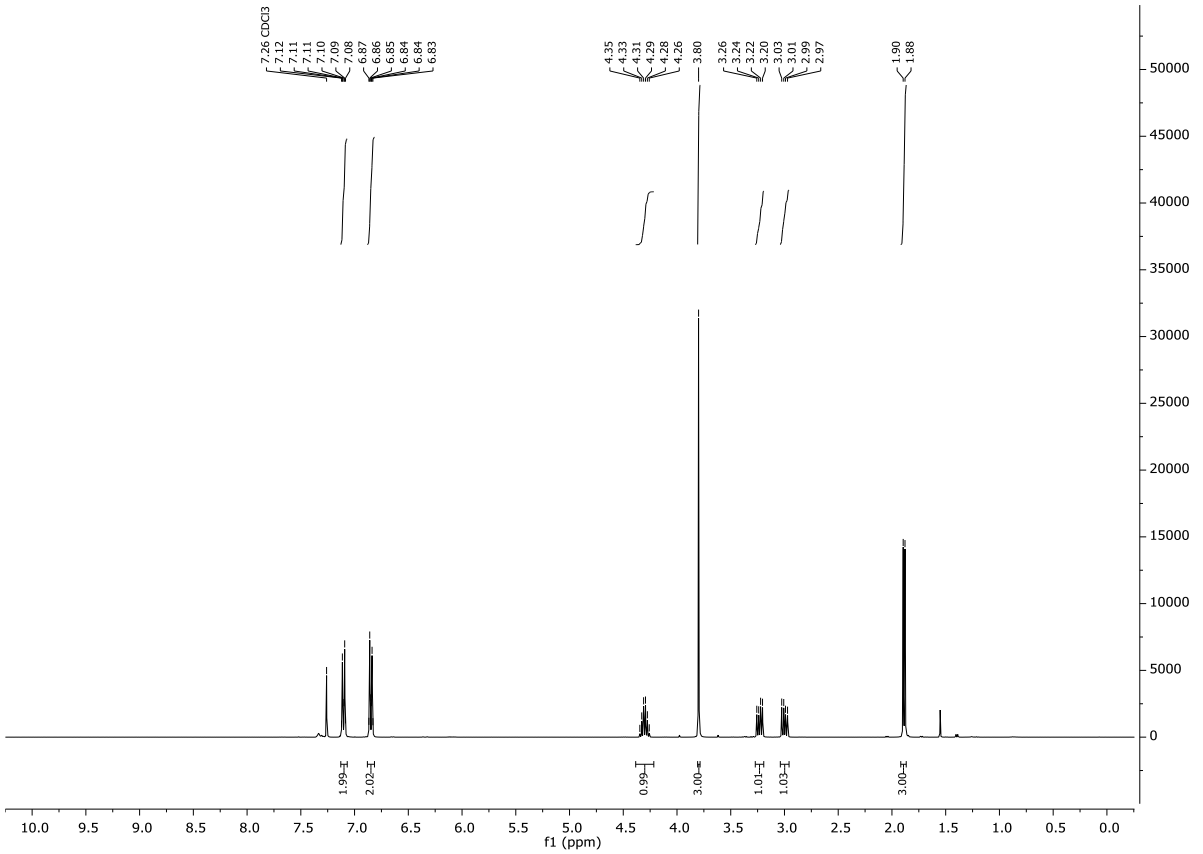
(*R*)-**1a**

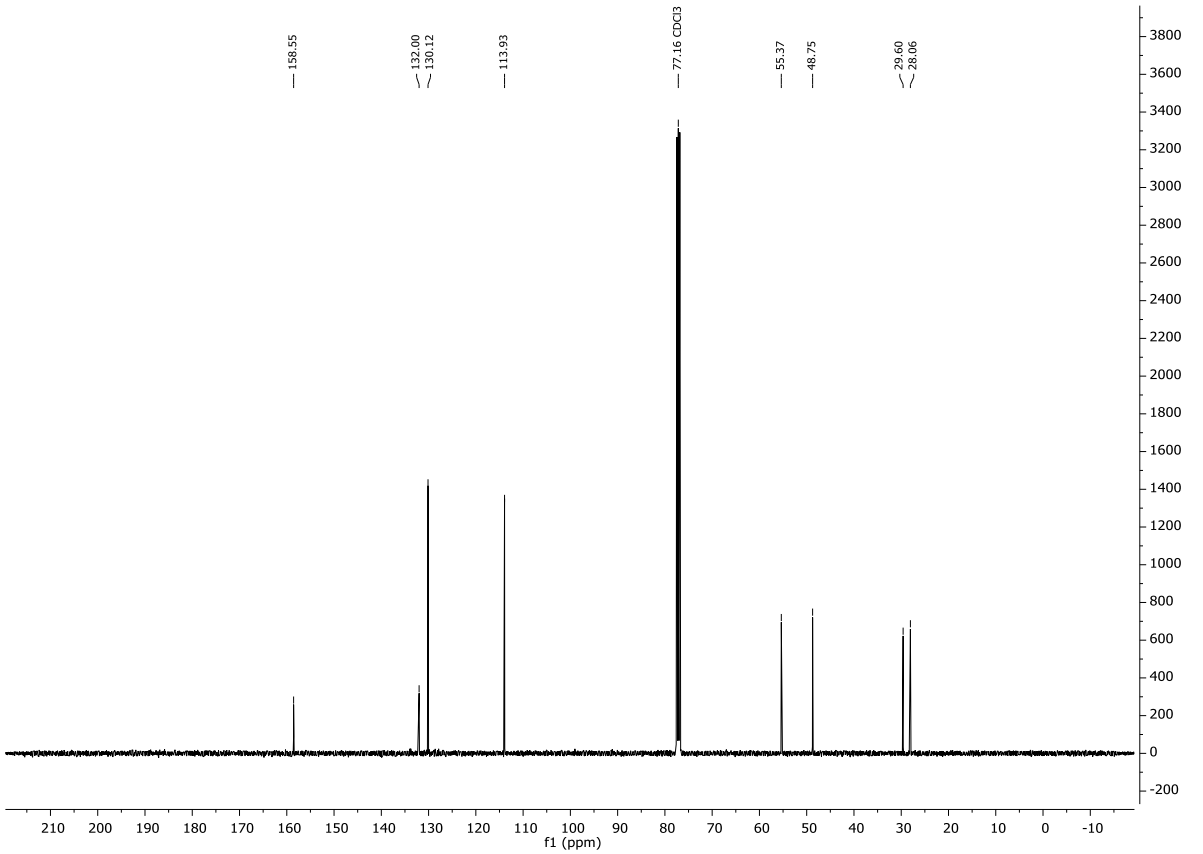

7.26 CDCl3
7.12
7.11
7.11
7.10
7.09
7.08
6.87
6.86
6.85
6.84
6.84
6.83
4.35
4.33
4.31
4.29
4.28
4.26
3.80
3.26
3.24
3.22
3.20
3.03
3.01
2.99
2.97
1.90
1.88
1.95
1.99
1.01
3.00
1.02
1.02
3.00
f1 (ppm)

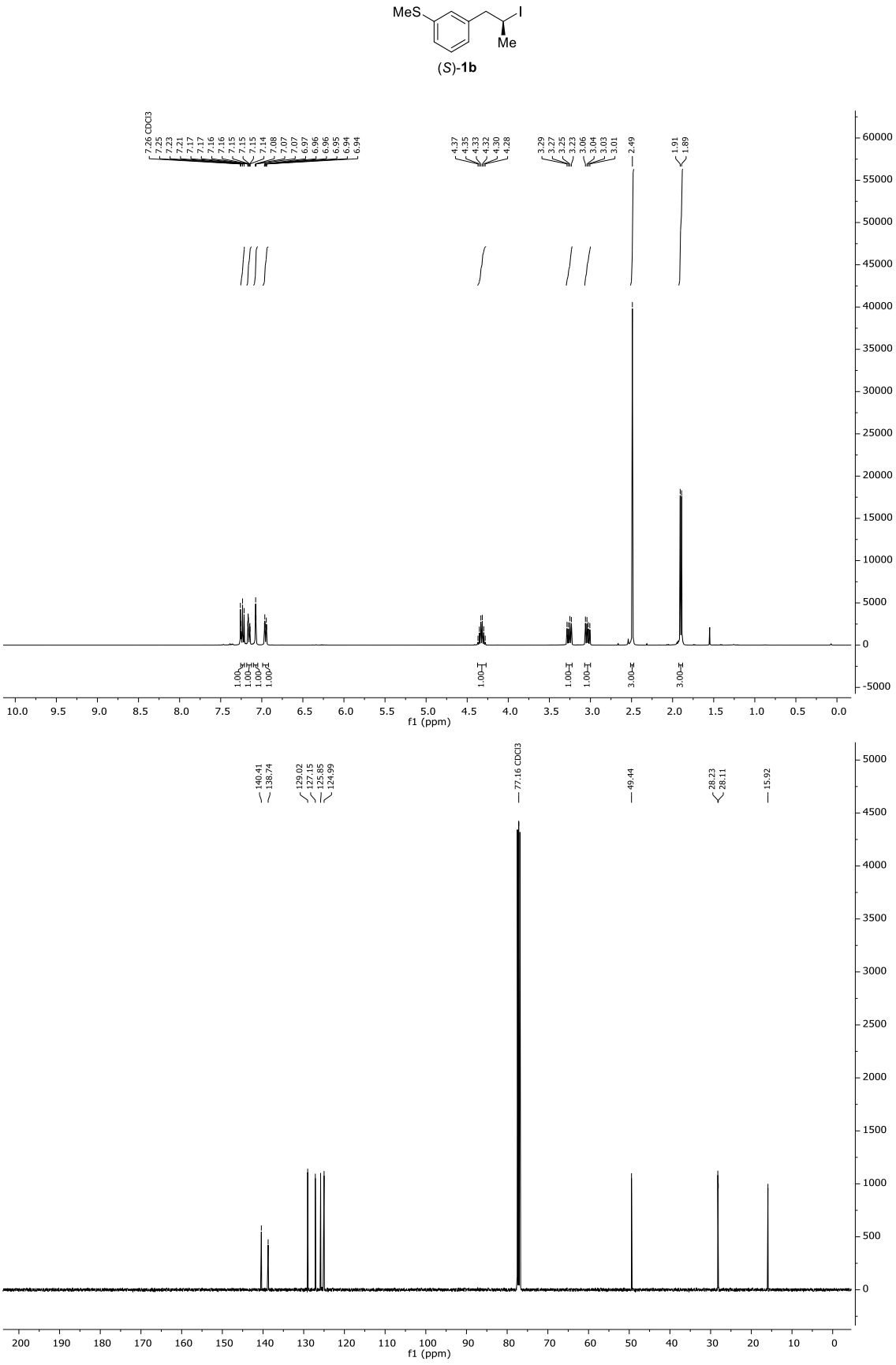

158.55
131.99
130.11
113.92
77.16 CDCl3
55.37
48.74
29.59
28.06
f1 (ppm)

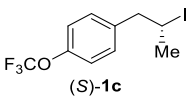

I
Me
MeO

(*S*)-**1a**

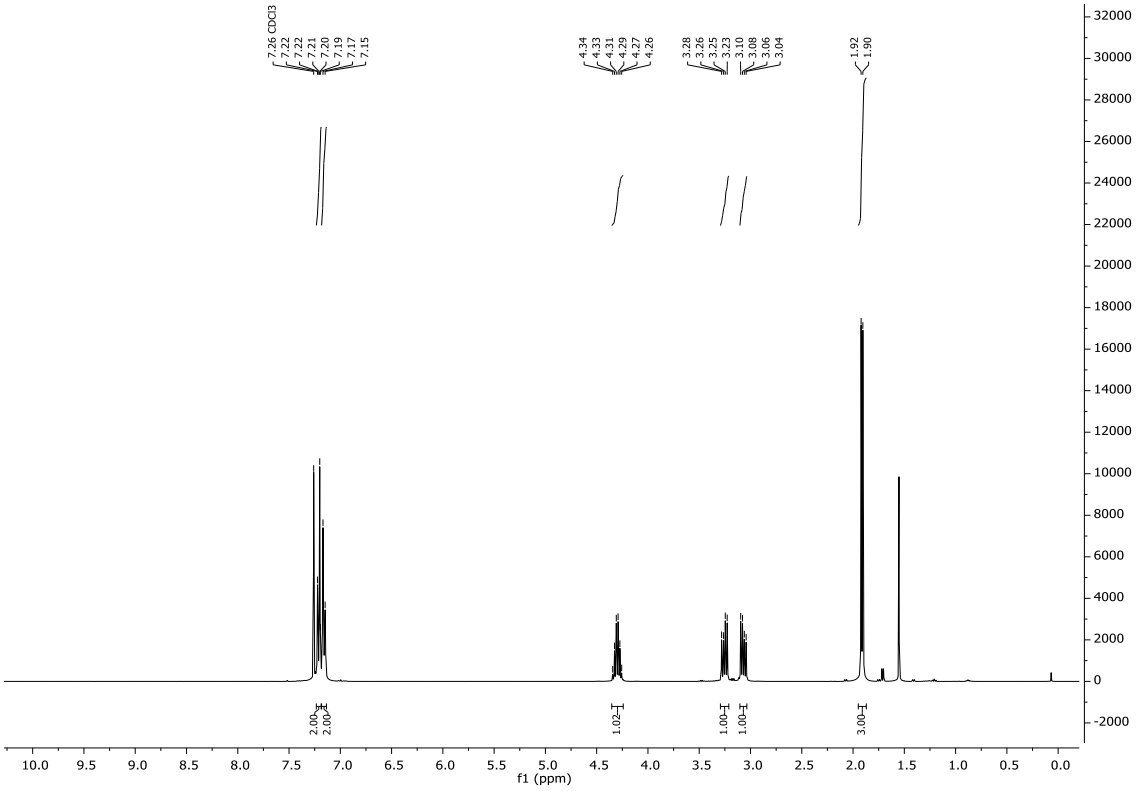

7.26 CDCl3
7.12
7.11
7.11
7.10
7.09
7.08
6.87
6.86
6.85
6.84
6.84
6.83
4.35
4.33
4.31
4.29
4.28
4.26
3.80
3.26
3.24
3.22
3.20
3.03
3.01
2.99
2.97
1.90
1.88
1.99
2.02
0.99
3.00
1.01
1.03
3.00
f1 (ppm)

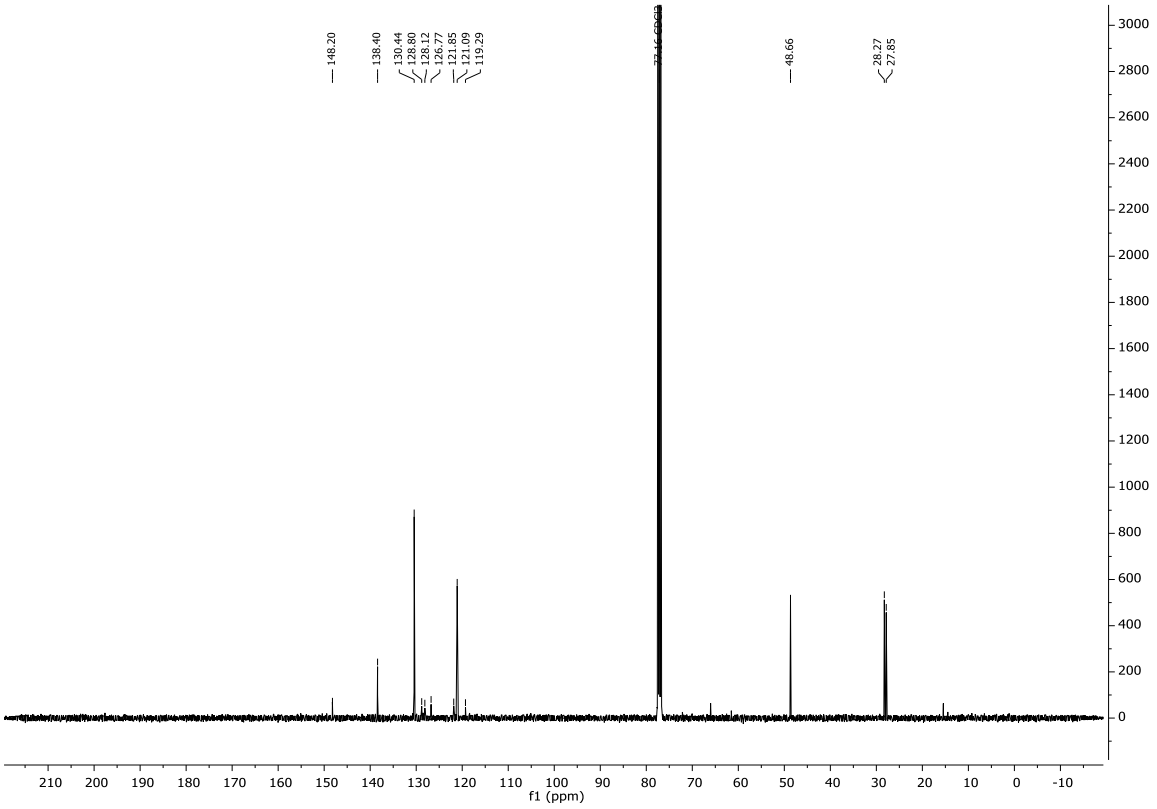

158.55
132.00
130.12
113.93
77.16 CDCl3
55.37
48.75
29.60
28.06
f1 (ppm)

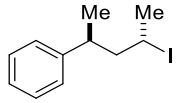

MeS
I
Me
(S)-1b
7.26 CDCl3
7.25
7.23
7.21
7.17
7.17
7.16
7.16
7.15
7.15
7.15
7.14
7.08
7.07
7.07
6.97
6.96
6.96
6.95
6.94
6.94
4.37
4.35
4.33
4.32
4.30
4.28
3.29
3.27
3.25
3.23
3.06
3.04
3.03
3.01
2.49
1.91
1.89
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)
140.41
138.74
129.02
127.15
125.85
124.99
77.16 CDCl3
49.44
28.23
28.11
15.92
f1 (ppm)


I
Me
F3CO

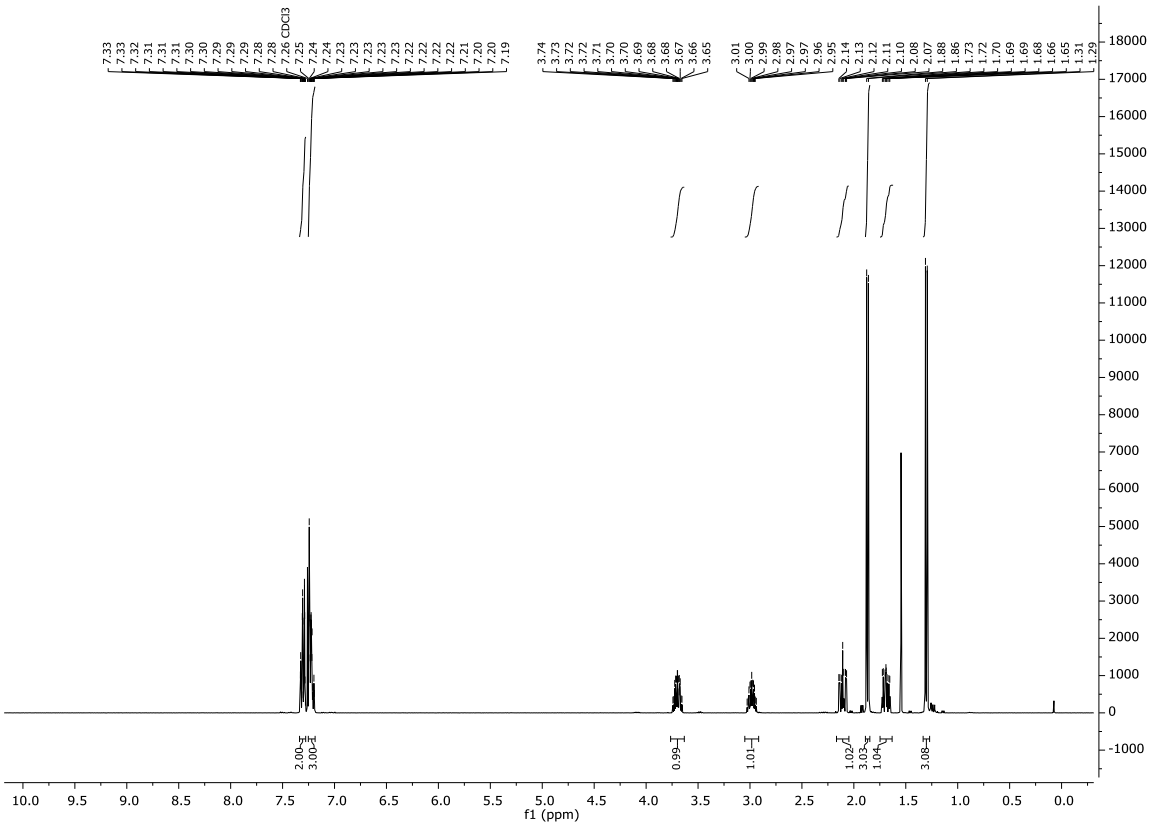
(*S*)-**1c**

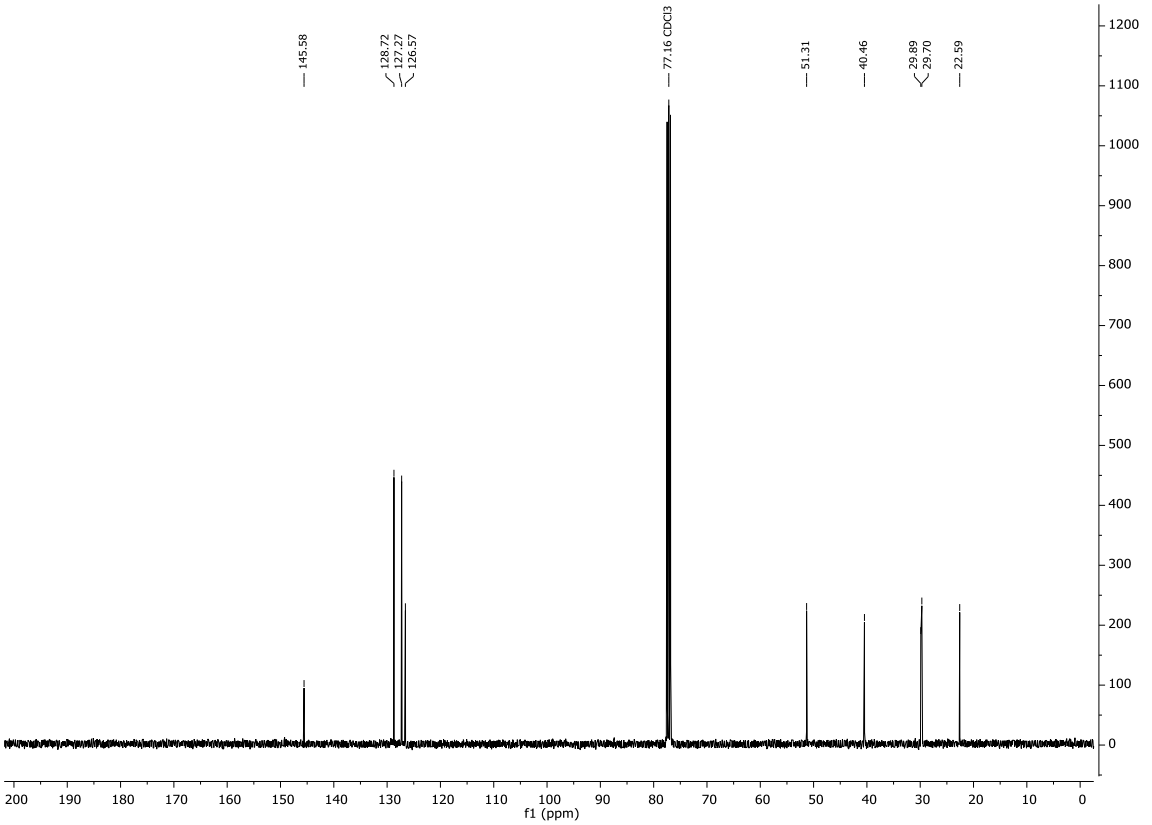

7.26 CDCl3
7.22
7.22
7.21
7.20
7.19
7.17
7.15
4.34
4.33
4.31
4.29
4.27
4.26
3.28
3.26
3.25
3.23
3.10
3.08
3.06
3.04
1.92
1.90
2.00
2.00
1.02
1.00
1.00
3.00
f1 (ppm)

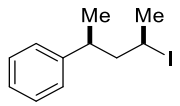

148.20
138.40
130.44
128.80
128.12
126.77
121.85
121.09
119.29
77.16 CDCl3
48.66
28.27
27.85
f1 (ppm)


Me
Me
I

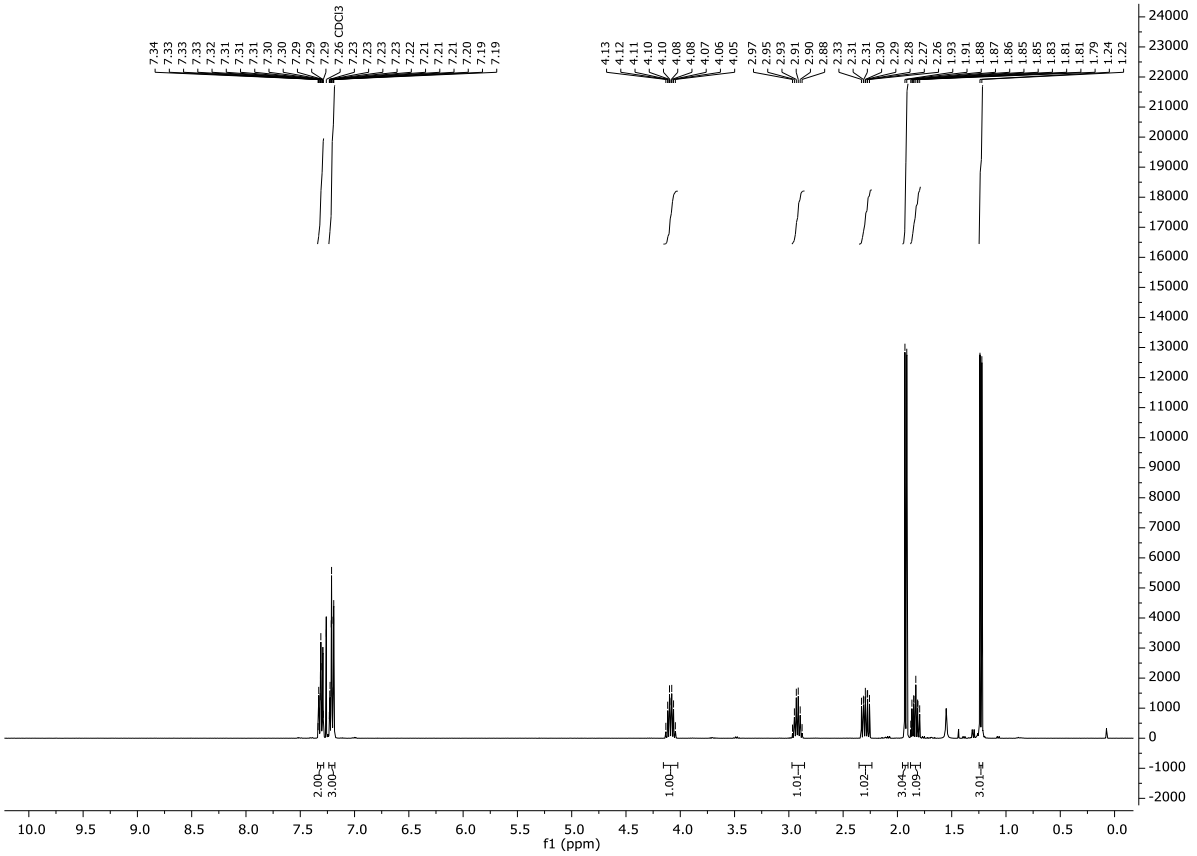
anti-**1d**

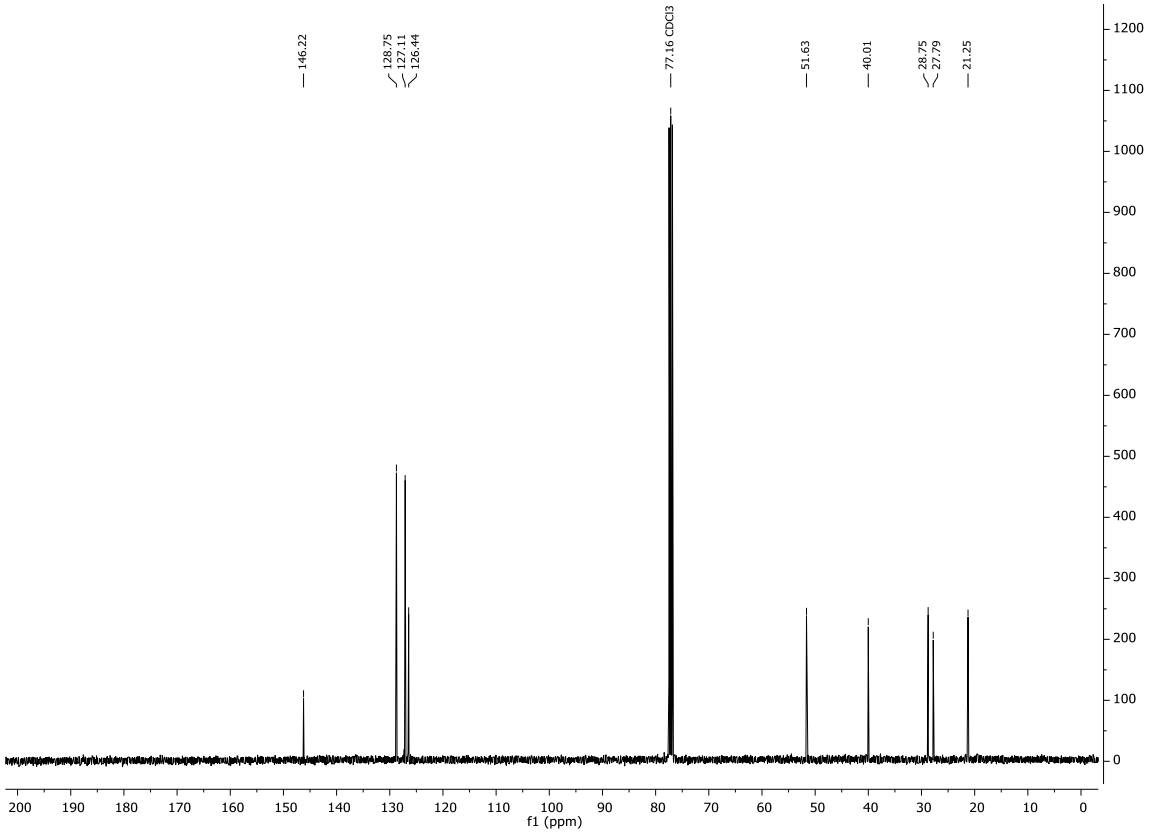

7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.26 CDCl3 7.25 7.24 7.24 7.23 7.23 7.23 7.23 7.22 7.22 7.22 7.21 7.20 7.20 7.19
3.74 3.73 3.72 3.72 3.71 3.70 3.70 3.69 3.68 3.68 3.67 3.66 3.65
3.01 3.00 2.99 2.98 2.97 2.97 2.96 2.95 2.14 2.13 2.12 2.11 2.10 2.08 2.07 1.88 1.86 1.73 1.72 1.70 1.69 1.69 1.68 1.66 1.65 1.31 1.29
2.00 3.00 0.99 1.01 1.02 3.03 1.04 3.08
f1 (ppm)

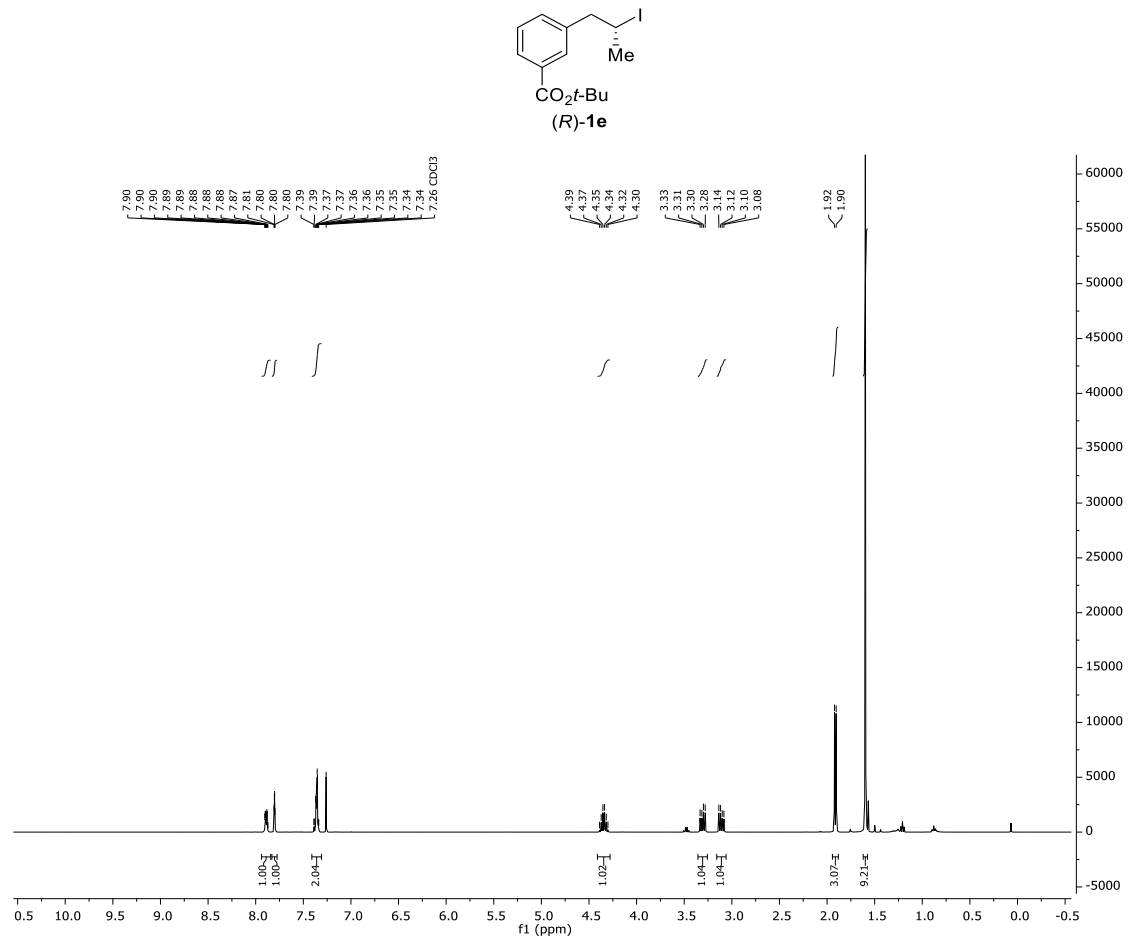

145.58
128.72 127.27 126.57
77.16 CDCl3
51.31
40.46
29.89 29.70
22.59
f1 (ppm)

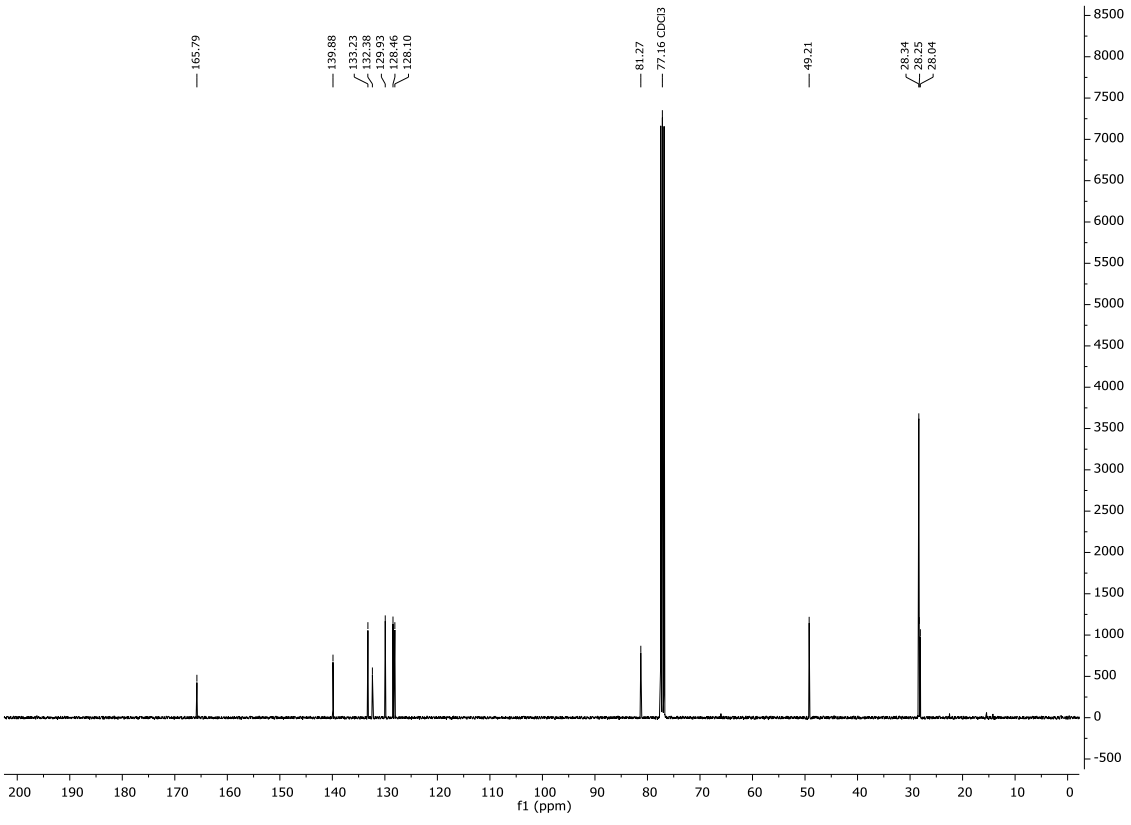

Me
Me
I

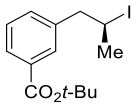
syn-**1d**


7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.26 CDCl3 7.23 7.23 7.23 7.22 7.21 7.21 7.21 7.20 7.19 7.19
4.13 4.12 4.11 4.10 4.10 4.08 4.08 4.07 4.06 4.05 2.97 2.95 2.93 2.91 2.90 2.88 2.33 2.31 2.31 2.30 2.29 2.28 2.27 2.26 1.93 1.91 1.88 1.87 1.86 1.85 1.85 1.83 1.81 1.81 1.79 1.24 1.22
2.00 3.00 1.00 1.01 1.02 3.04 1.09 3.01
f1 (ppm)

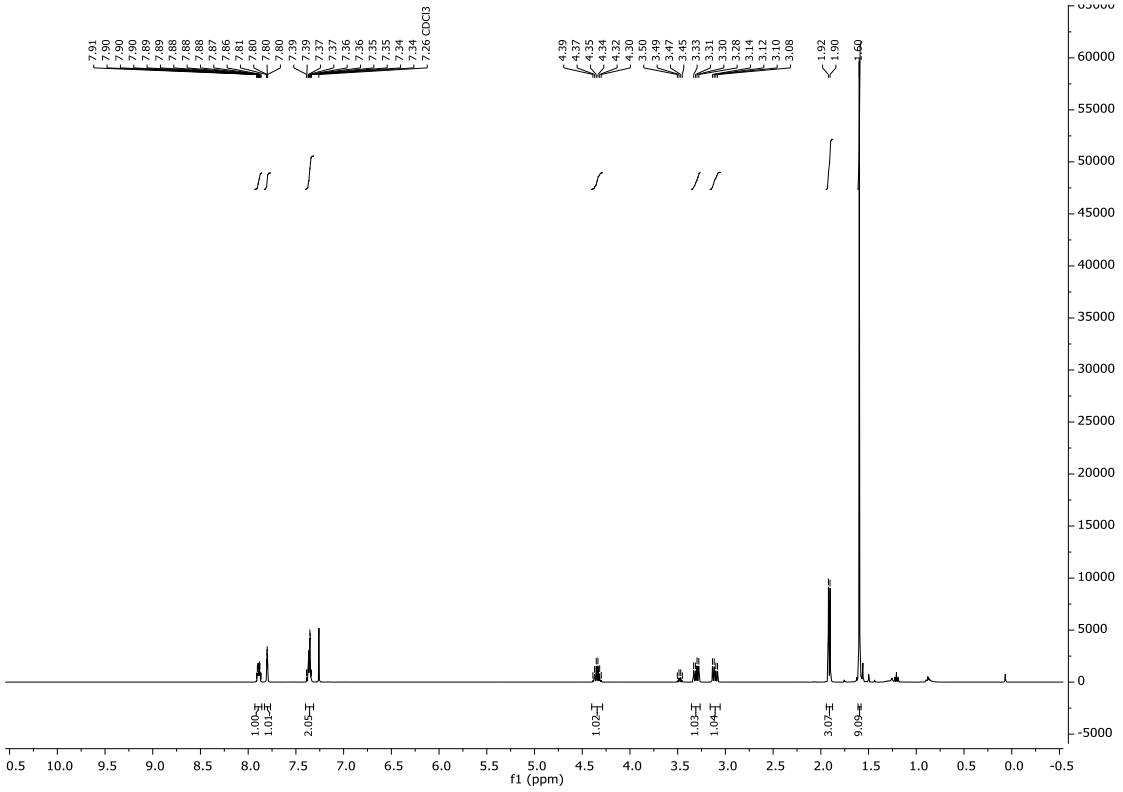

146.22 128.75 127.11 126.44 77.16 CDCl3 51.63 40.01 28.75 27.79 21.25
f1 (ppm)

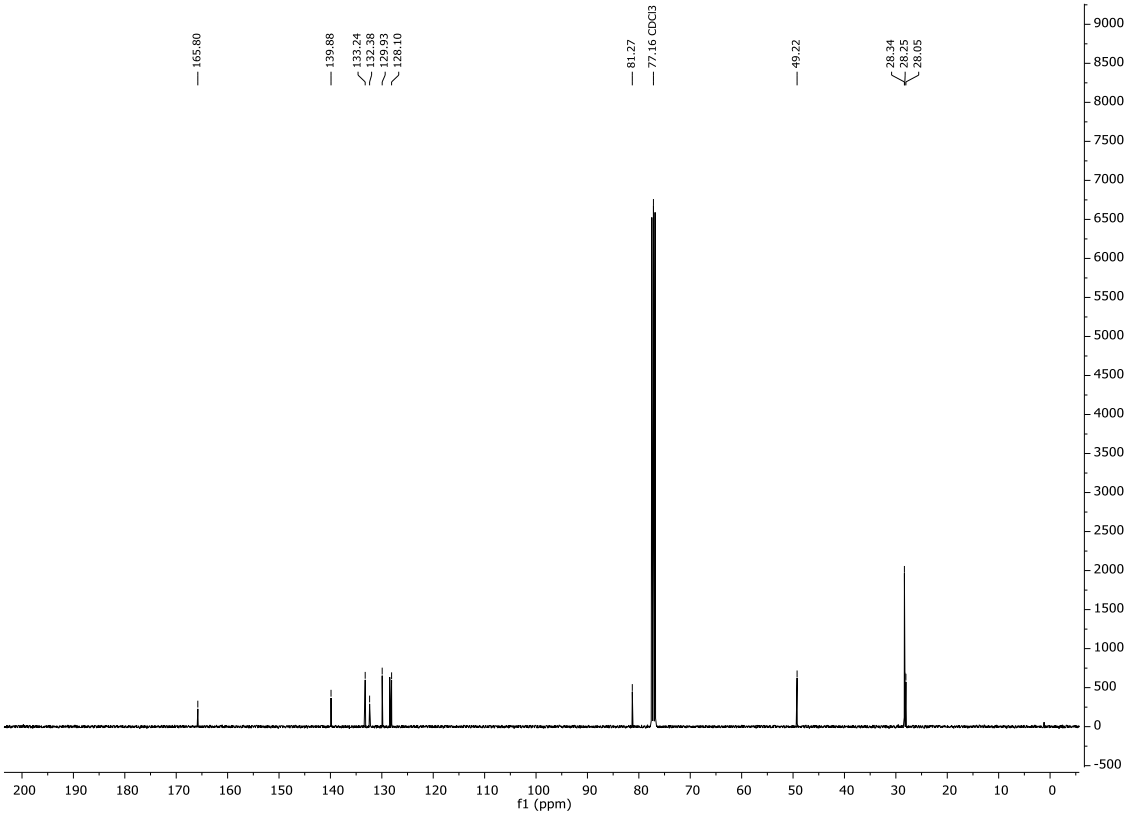

I
Me
CO2t-Bu
(R)-1e
7.90
7.90
7.90
7.89
7.89
7.88
7.88
7.87
7.81
7.80
7.80
7.80
7.39
7.39
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.26 CDCl3
4.39
4.37
4.35
4.34
4.32
4.30
3.33
3.31
3.30
3.28
3.14
3.12
3.10
3.08
1.92
1.90
1.00
1.00
2.04
1.02
1.04
1.04
3.07
9.21
f1 (ppm)

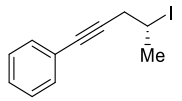

165.79
139.88
133.23
132.38
129.93
128.46
128.10
81.27
77.16 CDCl3
49.21
28.34
28.25
28.04
f1 (ppm)


I
Me
CO2t-Bu

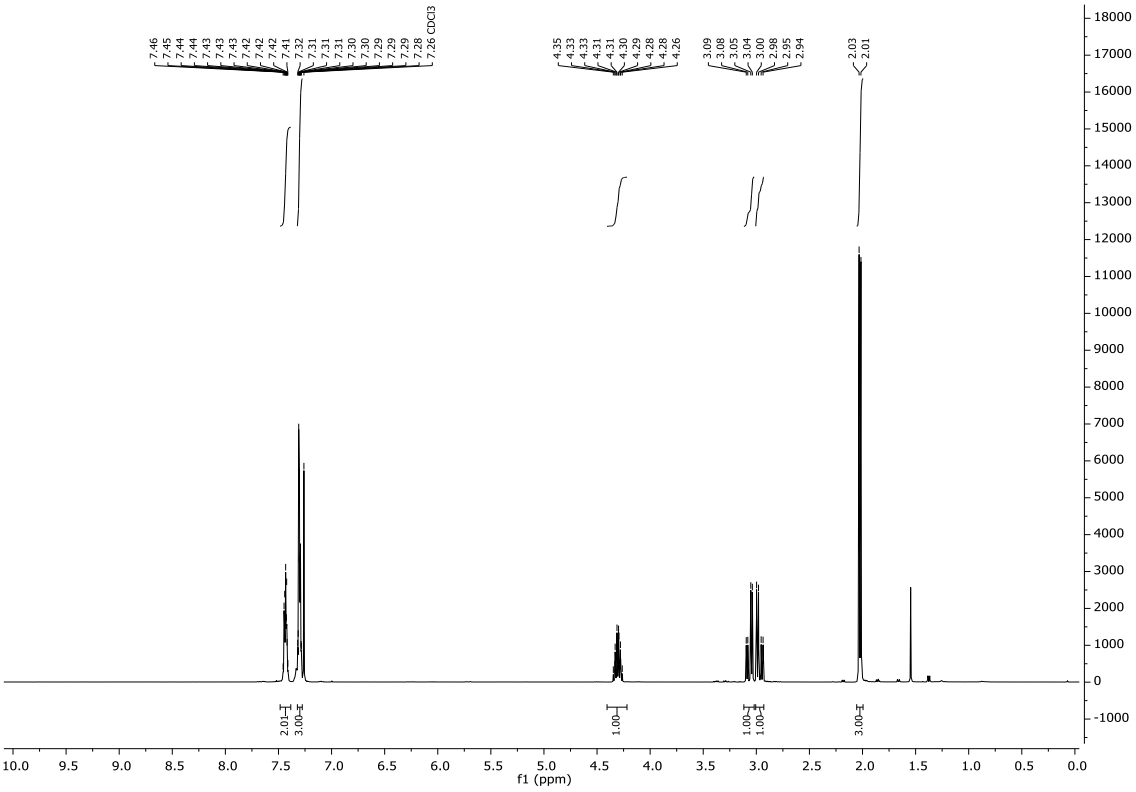
(*S*)-**1e**

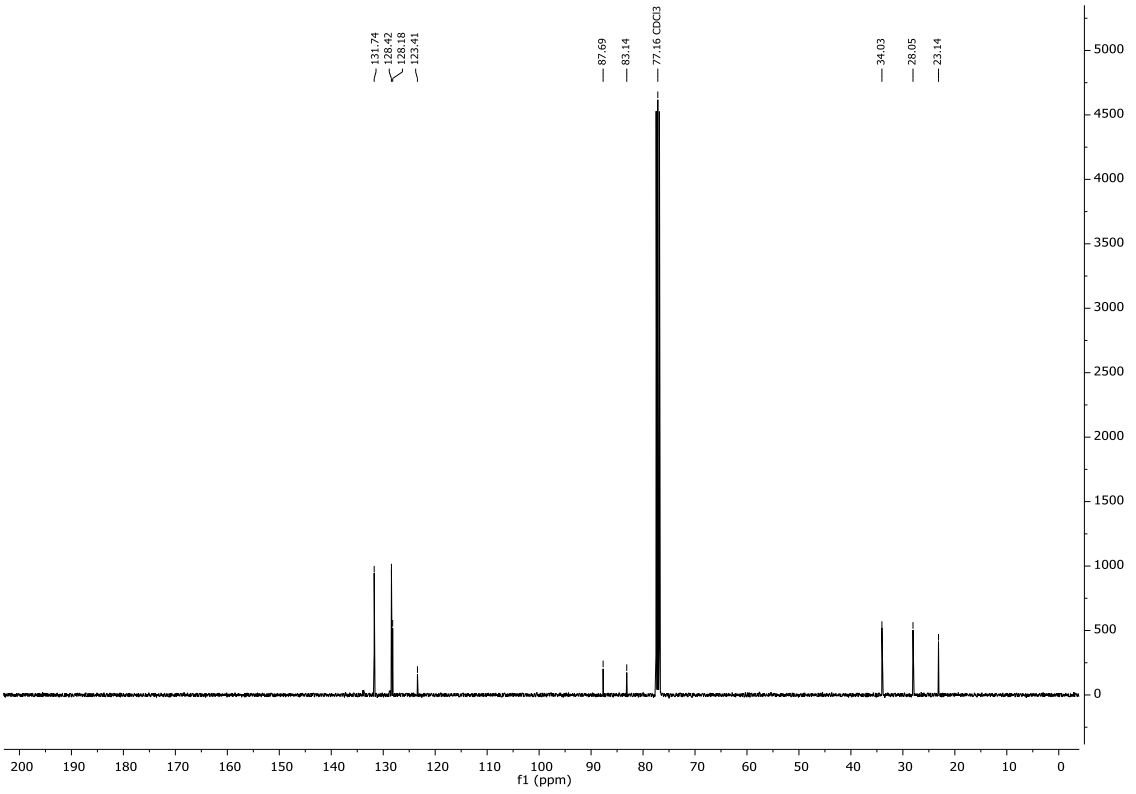

7.91
7.90
7.90
7.90
7.89
7.89
7.88
7.88
7.88
7.87
7.86
7.81
7.80
7.80
7.80
7.39
7.39
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.26 CDCl3
4.39
4.37
4.35
4.34
4.32
4.30
3.50
3.49
3.47
3.45
3.33
3.31
3.30
3.28
3.14
3.12
3.10
3.08
1.92
1.90
1.60
1.00
1.01
2.05
1.02
1.03
1.04
3.07
9.09
f1 (ppm)

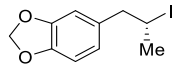

165.80
139.88
133.24
132.38
129.93
128.10
81.27
77.16 CDCl3
49.22
28.34
28.25
28.05
f1 (ppm)


I
Me

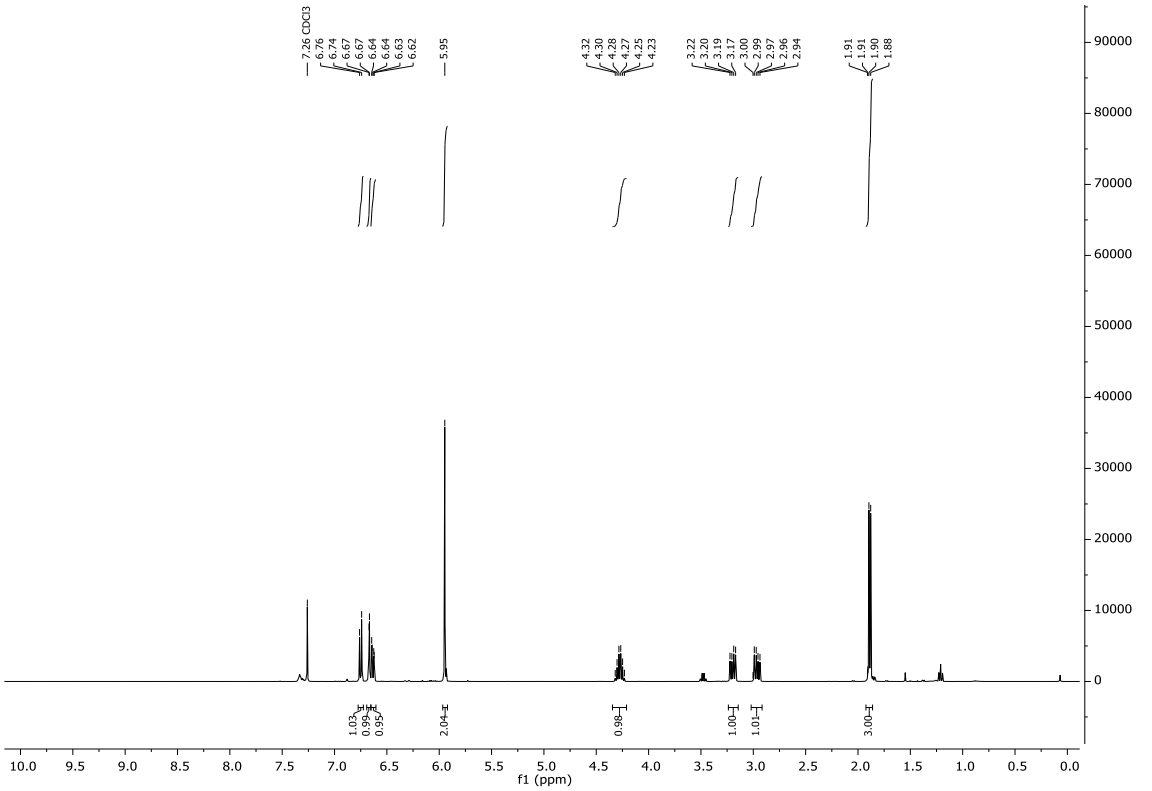
(*R*)-**1f**

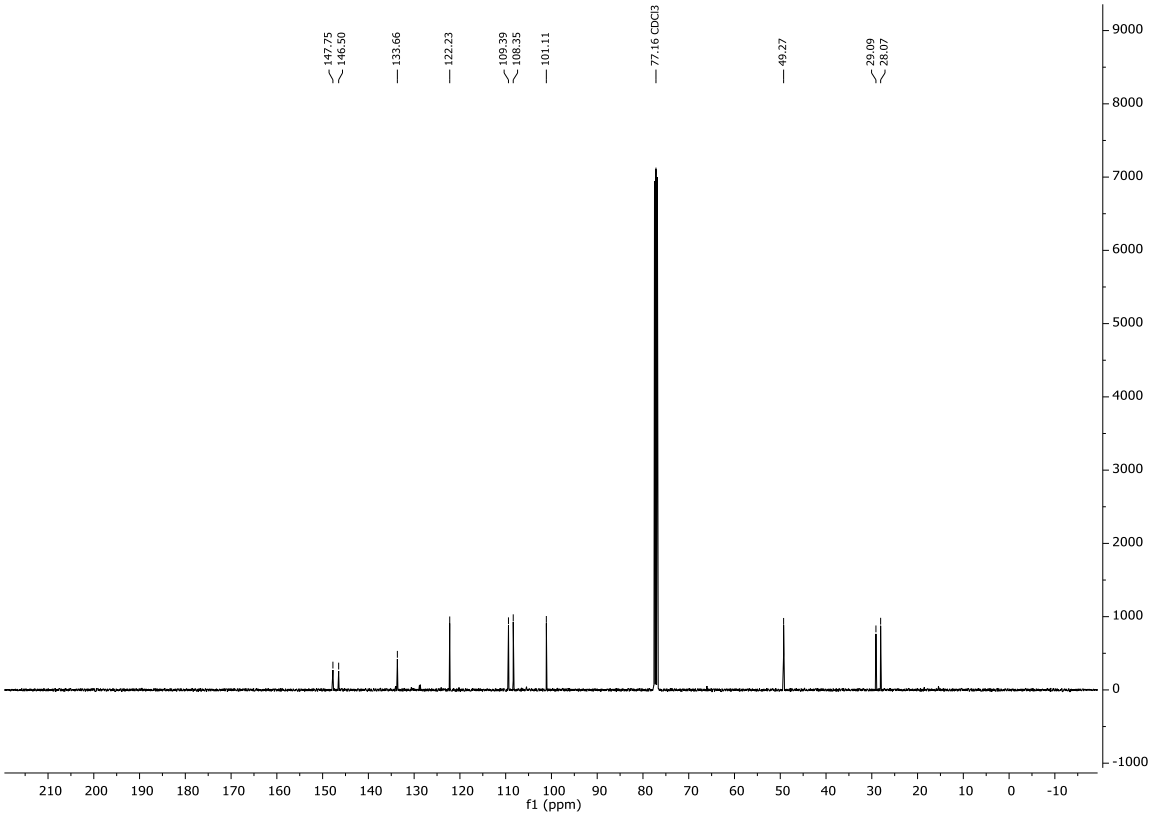

7.46
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.26 CDCl3
4.35
4.33
4.33
4.31
4.31
4.30
4.29
4.28
4.28
4.26
3.09
3.08
3.05
3.04
3.00
2.98
2.95
2.94
2.03
2.01
2.01
3.00
1.00
1.00
1.00
3.00
f1 (ppm)

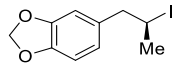

131.74
129.42
128.18
123.41
87.69
83.14
77.16 CDCl3
34.03
28.05
23.14
f1 (ppm)


O
O
I
Me

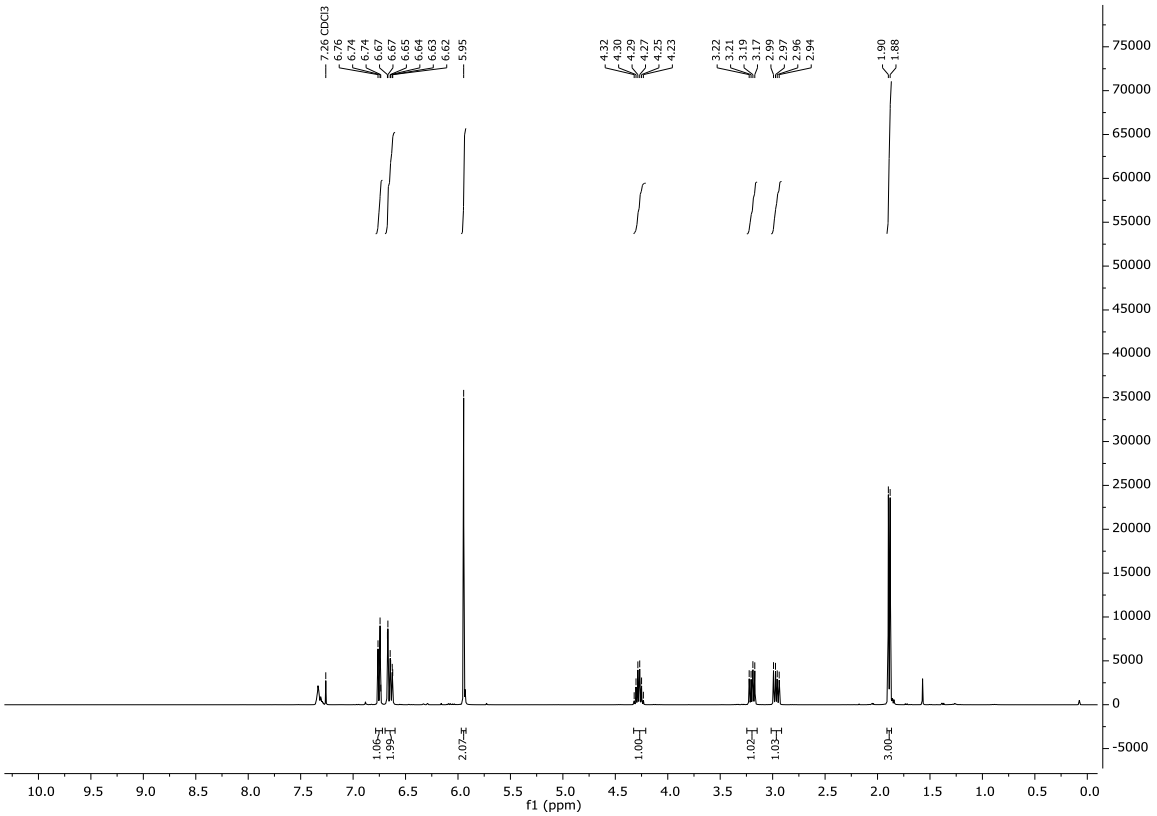
(*R*)-**1g**

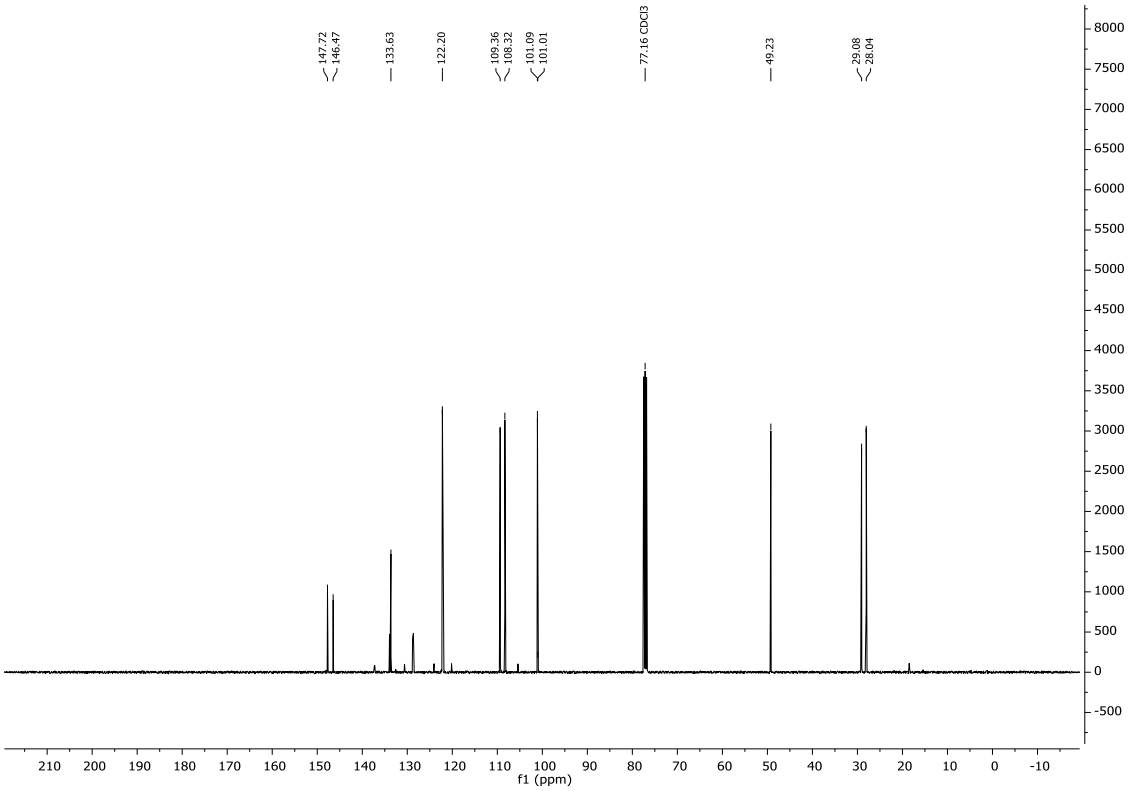

7.26 CDCl3
6.76
6.74
6.67
6.67
6.64
6.64
6.63
6.62
5.95
4.32
4.30
4.28
4.27
4.25
4.23
3.22
3.20
3.19
3.17
3.00
2.99
2.97
2.96
2.94
1.91
1.91
1.90
1.88
1.03
0.99
0.95
2.04
0.98
1.00
1.01
3.00
f1 (ppm)

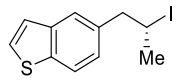

147.75
146.50
133.66
122.23
109.39
108.35
101.11
77.16 CDCl3
49.27
29.09
28.07
f1 (ppm)


O
O
I
Me

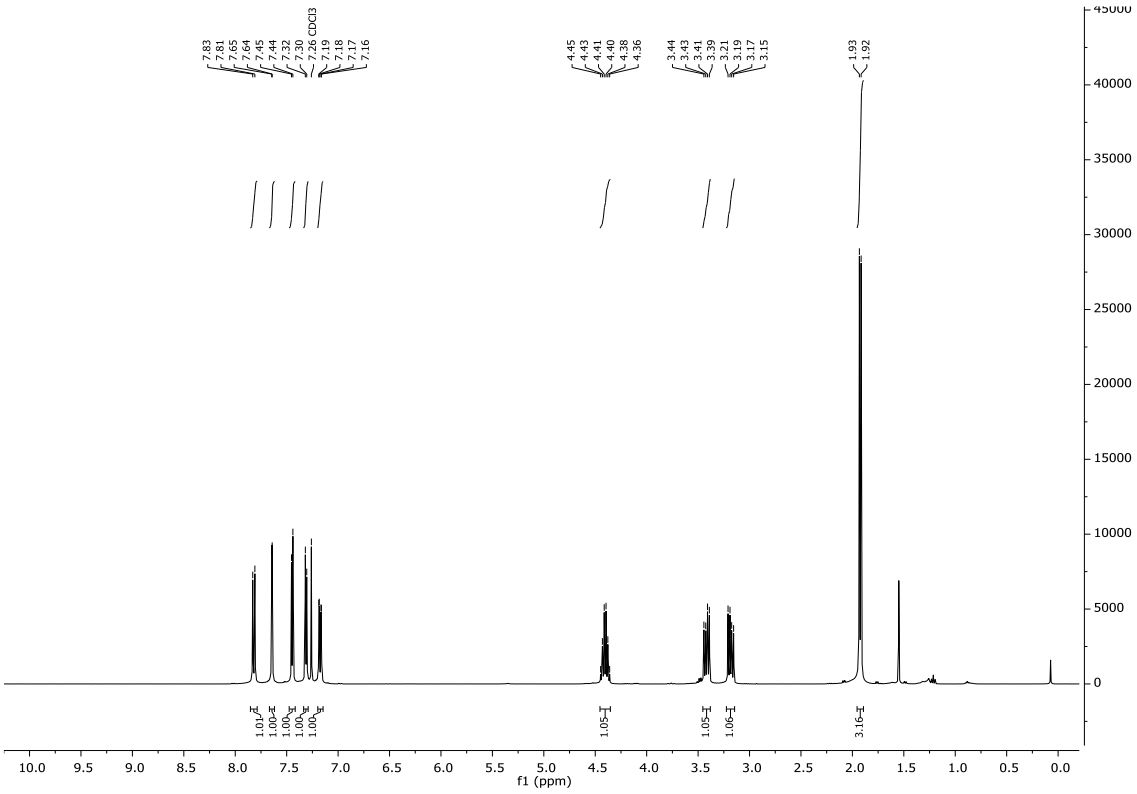
(*S*)-**1g**

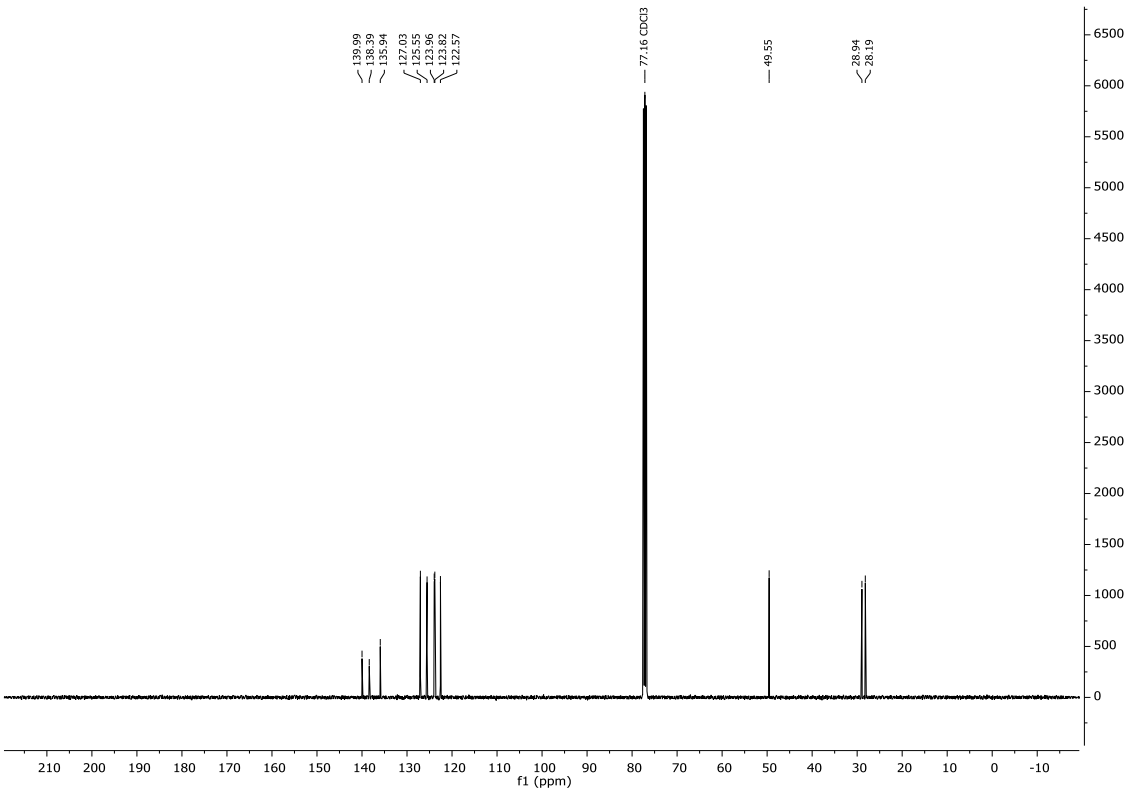

7.26 CDCl3
6.76
6.74
6.74
6.67
6.67
6.65
6.64
6.63
6.62
5.95
4.32
4.30
4.29
4.27
4.25
4.23
3.22
3.21
3.19
3.17
2.99
2.97
2.96
2.94
1.90
1.88
1.06
1.99
2.07
1.00
1.02
1.03
3.00
f1 (ppm)

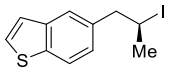

147.72
146.47
133.63
122.20
109.36
108.32
101.09
101.01
77.16 CDCl3
49.23
29.08
28.04
f1 (ppm)


I
Me
S

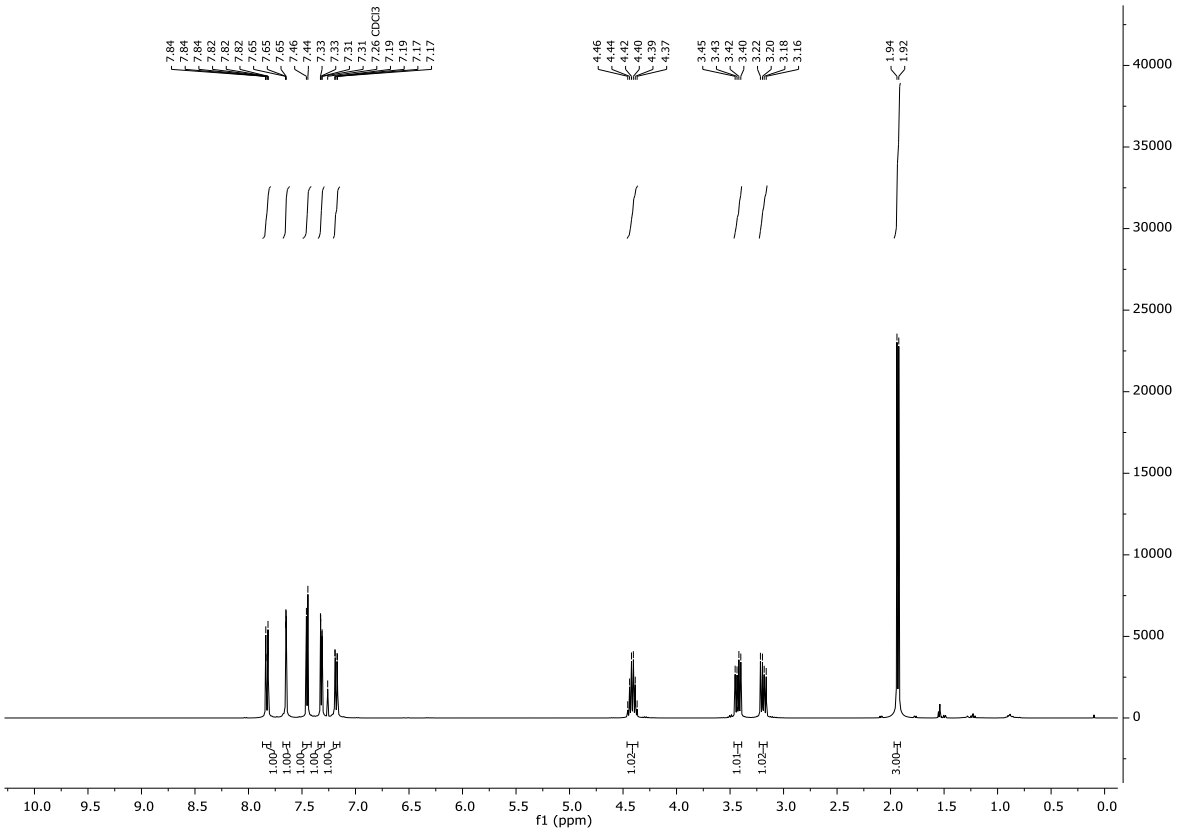
(*R*)-**1h**

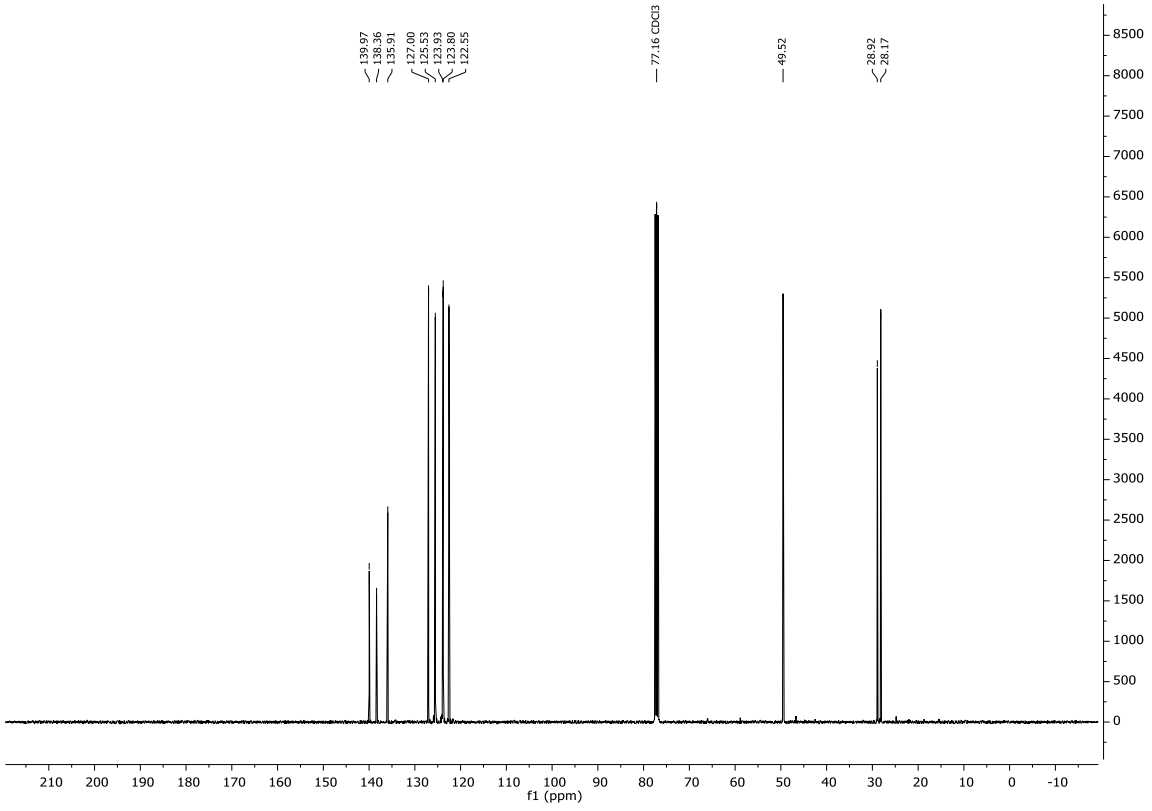

7.83
7.81
7.65
7.64
7.45
7.44
7.32
7.30
7.26 CDCl3
7.19
7.18
7.17
7.16
4.45
4.43
4.41
4.40
4.38
4.36
3.44
3.43
3.41
3.39
3.21
3.19
3.17
3.15
1.93
1.92
1.01
1.00
1.00
1.00
1.00
1.05
1.05
1.06
3.16
f1 (ppm)

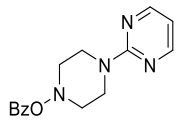

139.99
138.39
135.94
127.03
125.55
123.96
123.82
122.57
77.16 CDCl3
49.55
28.94
28.19
f1 (ppm)


I
Me
S

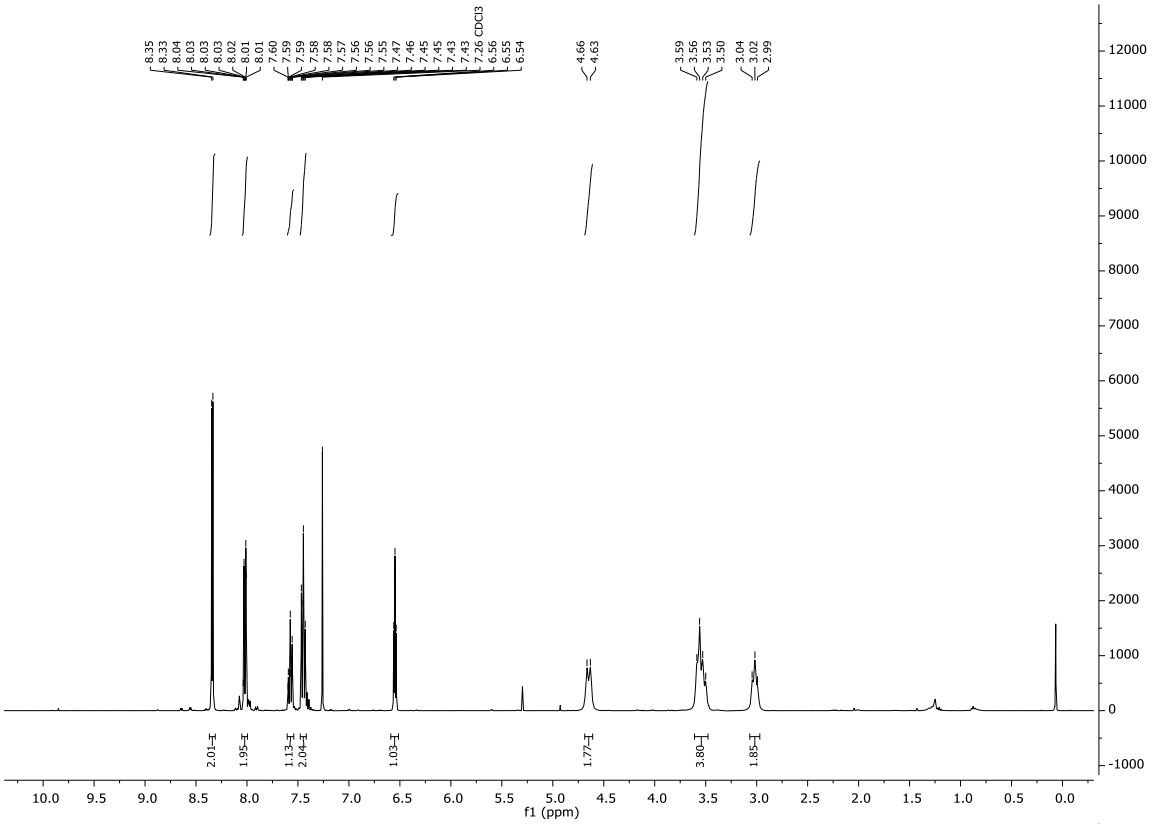
(*S*)-**1h**

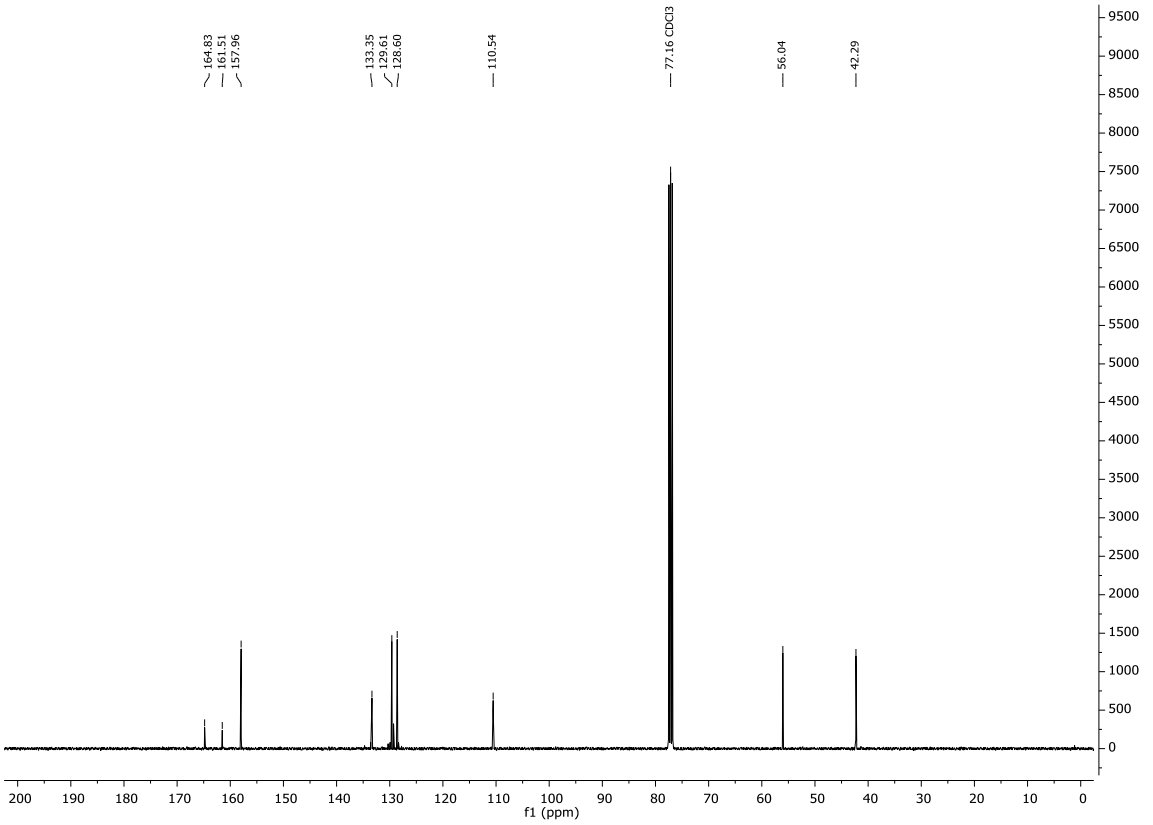

7.84
7.84
7.84
7.82
7.82
7.82
7.65
7.65
7.65
7.46
7.44
7.33
7.33
7.31
7.31
7.26 CDCl3
7.19
7.19
7.17
7.17
7.17
4.46
4.44
4.42
4.40
4.39
4.37
3.45
3.43
3.42
3.40
3.22
3.20
3.18
3.16
1.94
1.92
1.00
1.00
1.00
1.00
1.00
1.02
1.01
1.02
3.00
f1 (ppm)

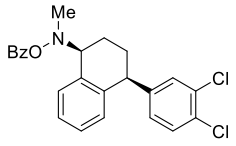

139.97
138.36
135.91
127.00
125.53
123.93
123.80
122.55
77.16 CDCl3
49.52
28.92
28.17
f1 (ppm)


N
N
N
BzO
N

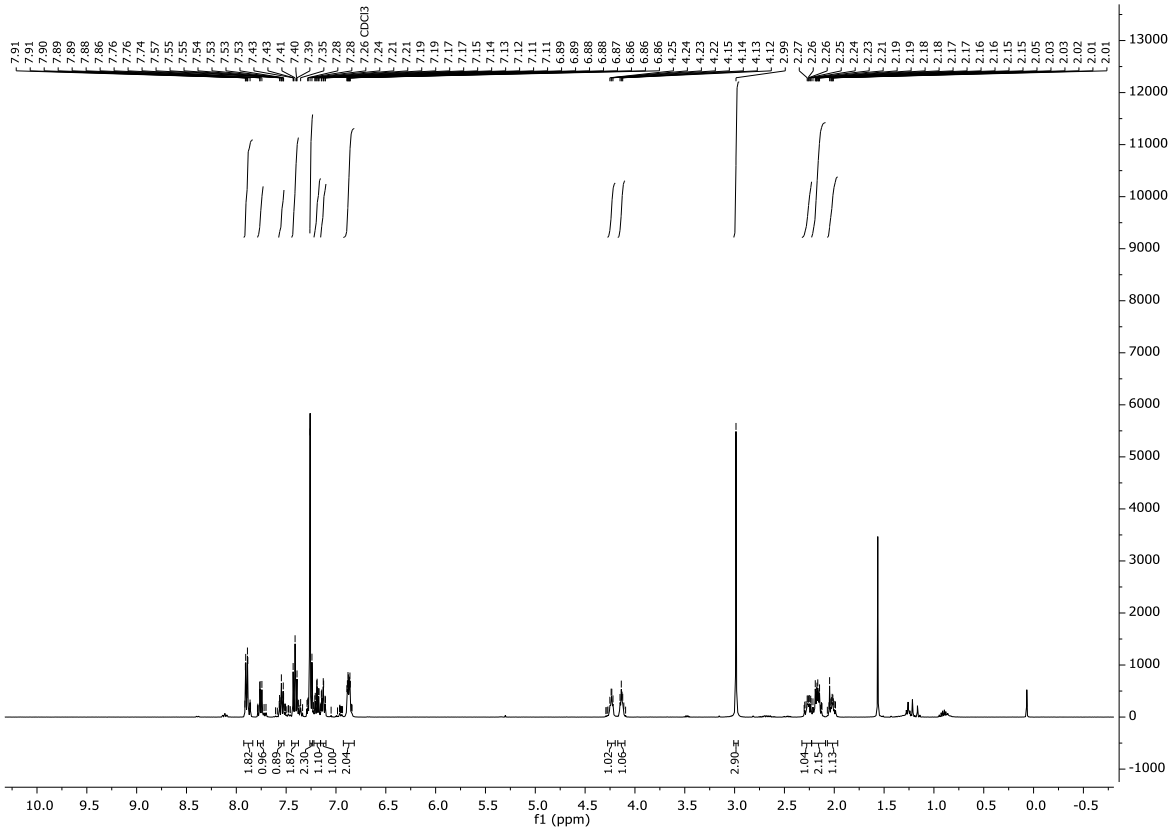
7a

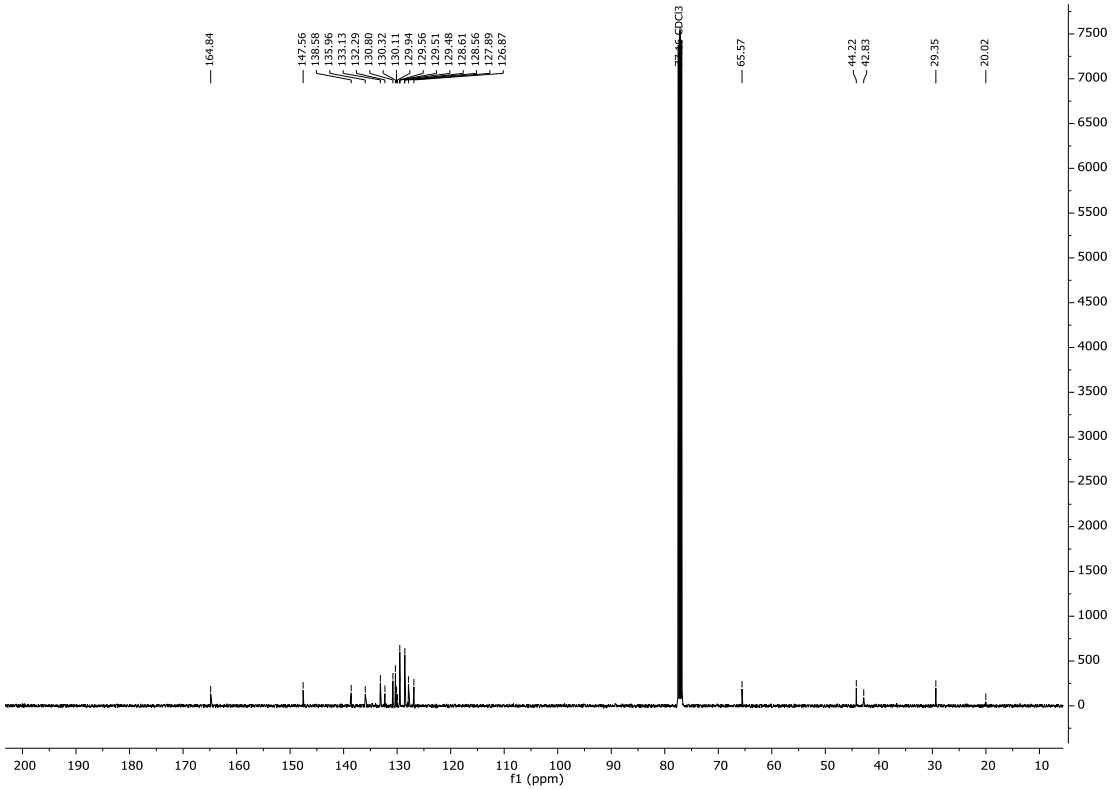

8.35
8.33
8.04
8.03
8.03
8.03
8.02
8.01
8.01
7.60
7.59
7.59
7.58
7.58
7.57
7.56
7.56
7.56
7.55
7.47
7.46
7.45
7.45
7.43
7.43
7.26 CDCl3
6.56
6.55
6.54
4.66
4.63
3.59
3.56
3.53
3.50
3.04
3.02
2.99
2.01
1.95
1.13
2.04
1.03
1.77
3.80
1.85
f1 (ppm)

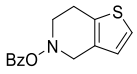

164.83
161.51
157.96
133.35
129.61
128.60
110.54
77.16 CDCl3
56.04
42.29
f1 (ppm)


Me
N
BzO
Cl
Cl

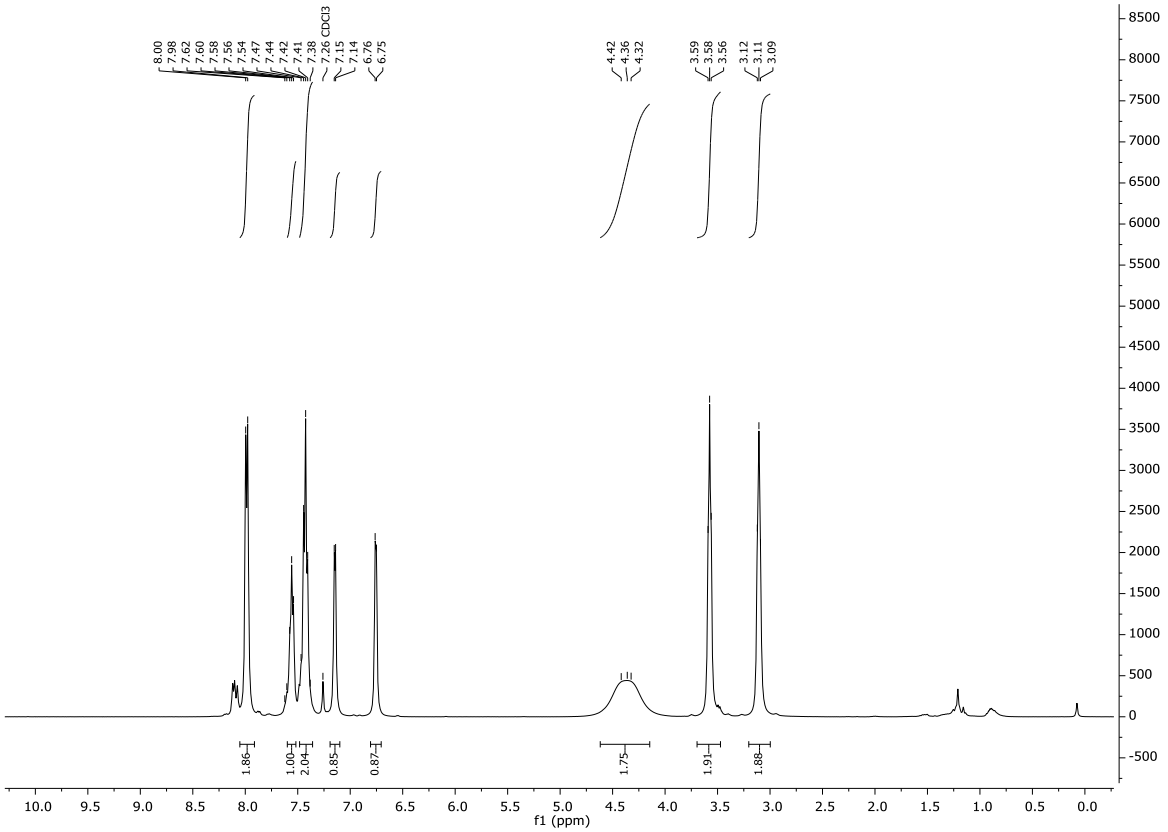
7b

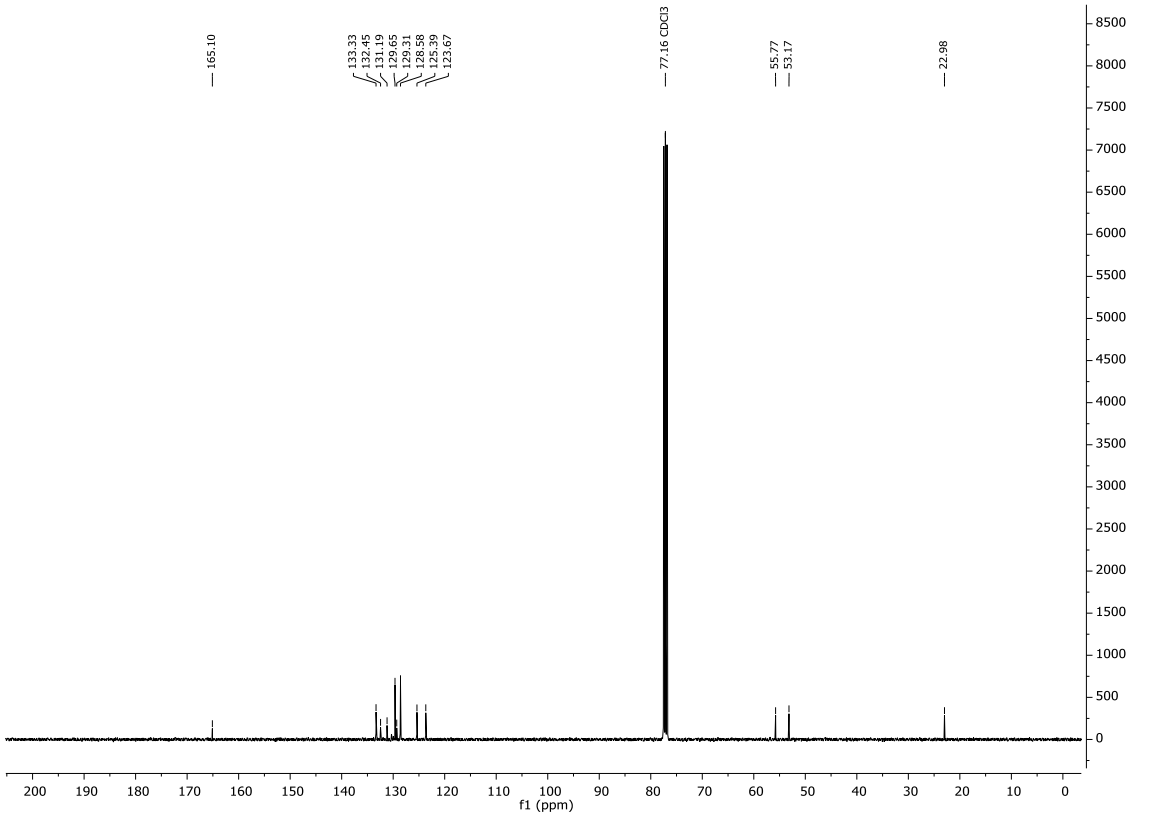

CDCl3
1.82
0.96
0.89
1.87
2.30
1.10
1.00
2.04
1.02
1.06
2.90
1.04
2.15
1.13
f1 (ppm)

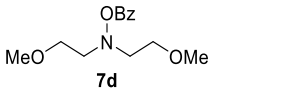

164.84
147.56
138.58
135.96
133.13
132.29
130.80
130.32
130.11
129.94
129.56
129.51
129.48
128.61
128.56
127.89
126.87
77.16 CDCl3
65.57
44.22
42.83
29.35
20.02
f1 (ppm)


S
N
BzO

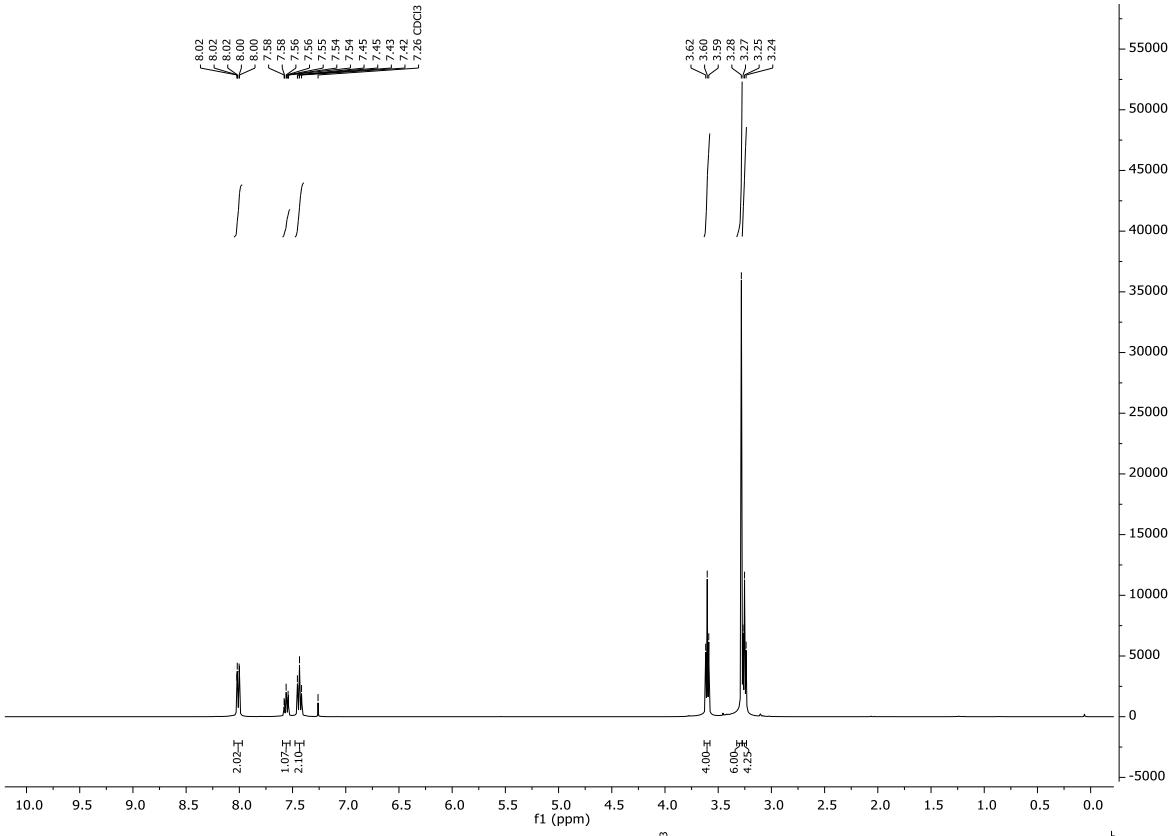
7c

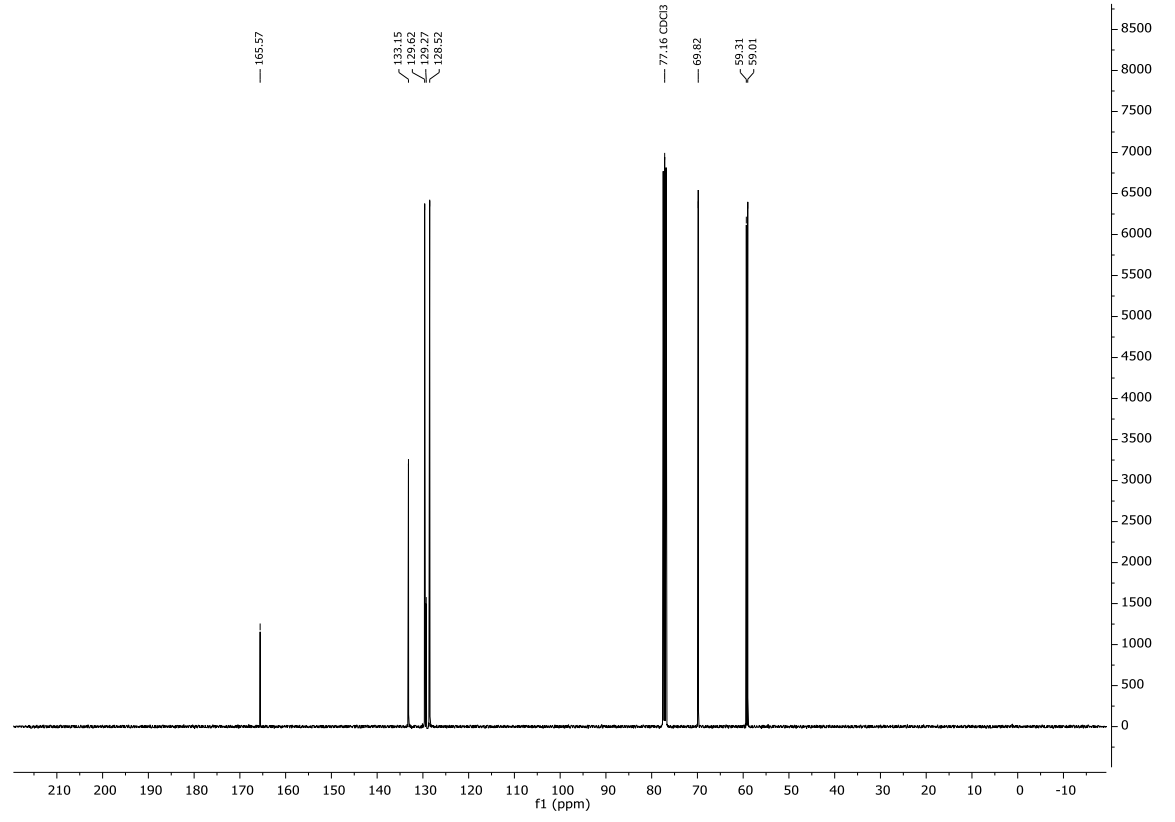

8.00
7.98
7.62
7.60
7.58
7.56
7.54
7.47
7.44
7.42
7.41
7.38
7.26 CDCl3
7.15
7.14
6.76
6.75
4.42
4.36
4.32
3.59
3.58
3.56
3.12
3.11
3.09
1.86
1.00
2.04
0.85
0.87
1.75
1.91
1.88
f1 (ppm)

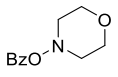

165.10
133.33
132.45
131.19
129.65
129.31
128.58
125.39
123.67
77.16 CDCl3
55.77
53.17
22.98
f1 (ppm)


OBz
N
MeO
OMe

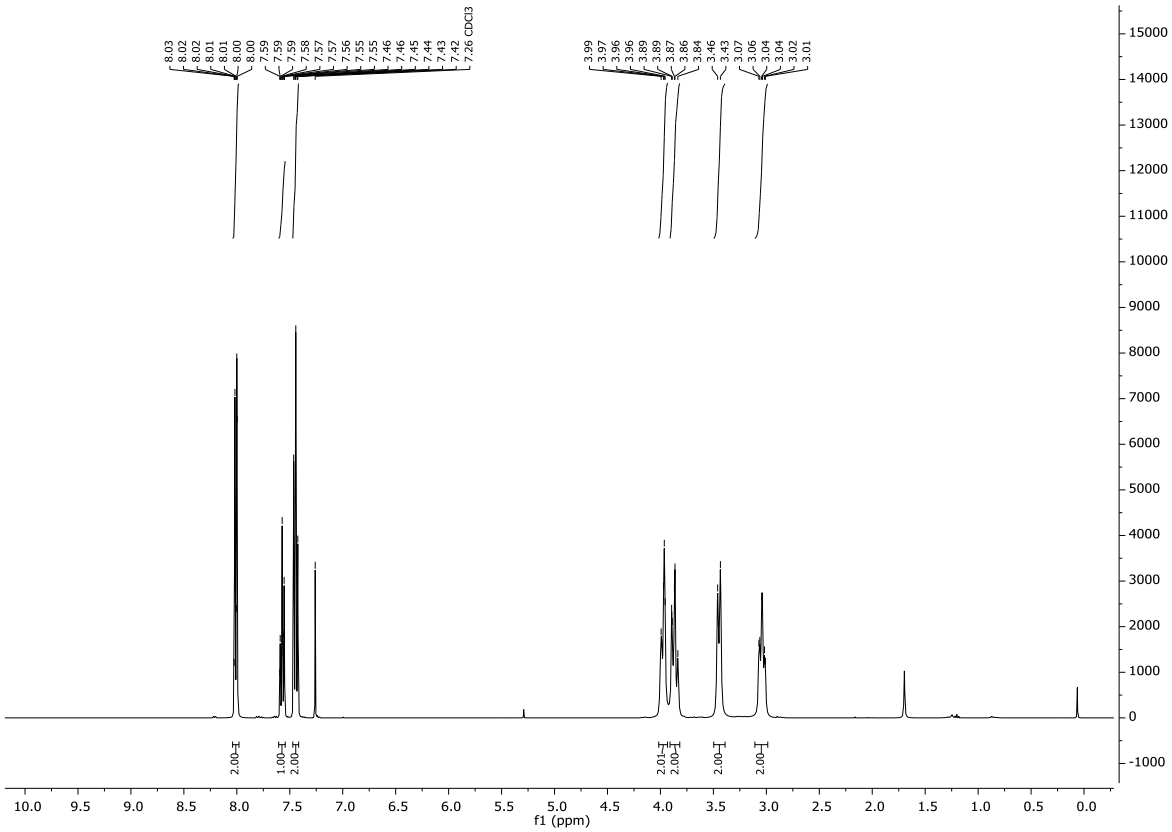
7d

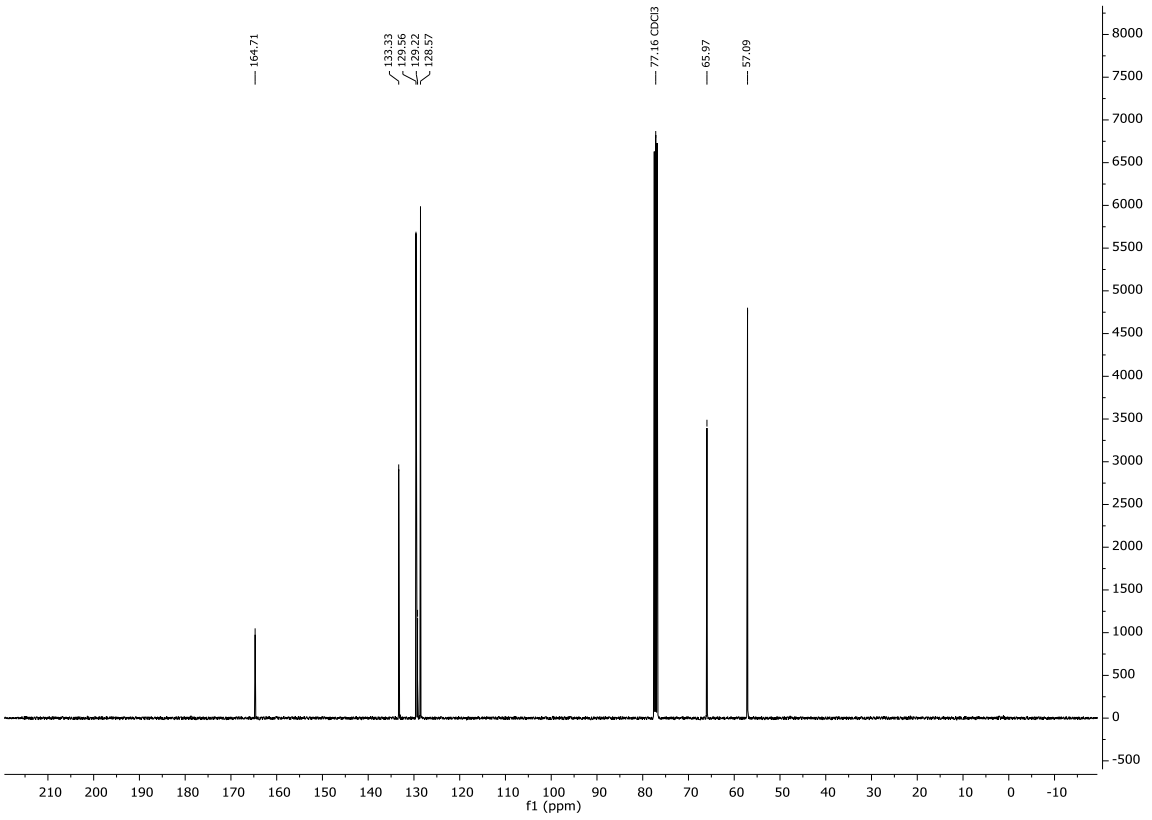

8.02
8.02
8.02
8.00
8.00
7.58
7.58
7.56
7.55
7.54
7.54
7.45
7.45
7.43
7.42
7.26 CDCl3
3.62
3.60
3.59
3.28
3.27
3.25
3.24
2.02
1.07
2.10
4.00
6.00
4.25
f1 (ppm)

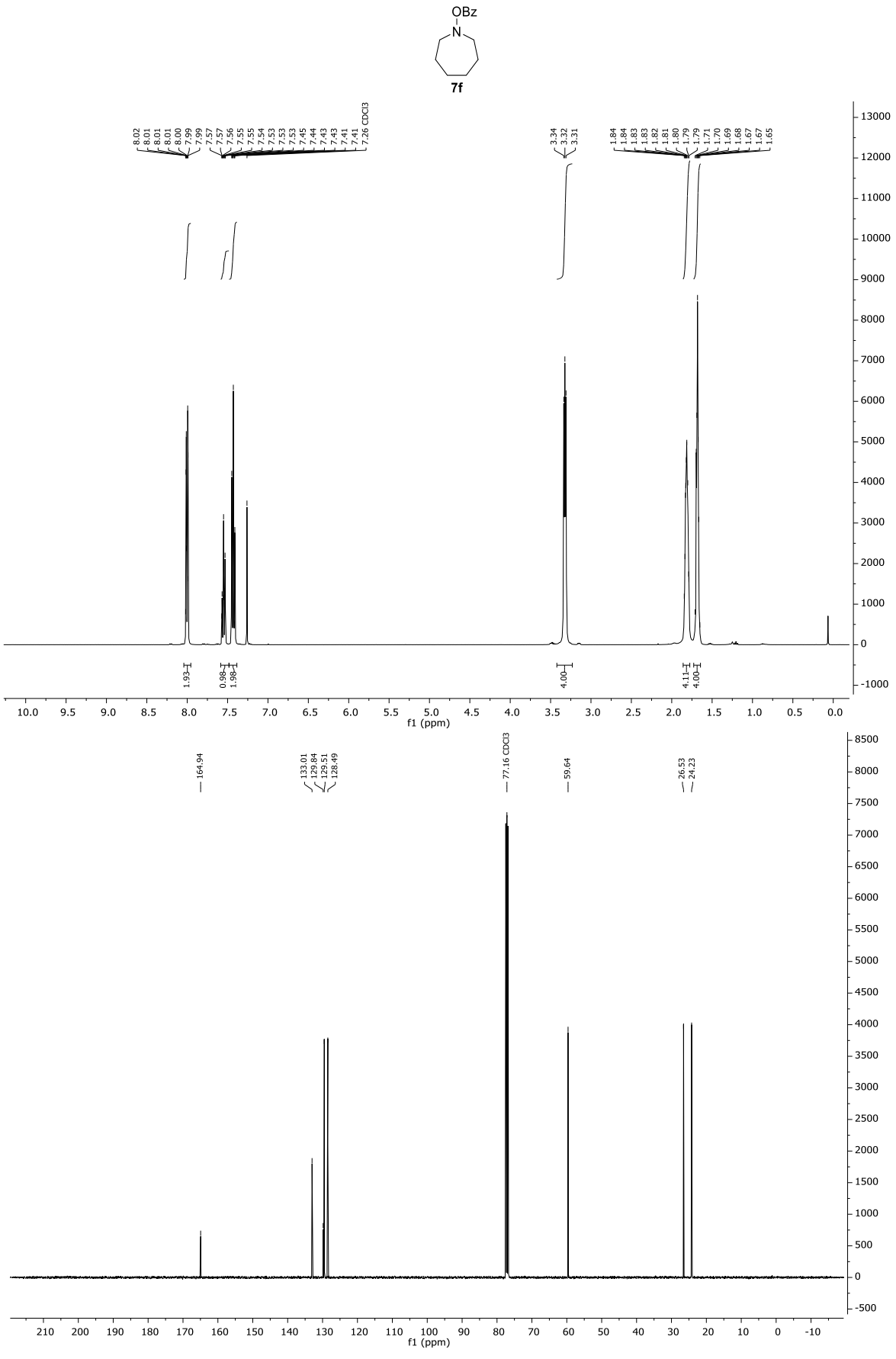

165.57
133.15
129.62
129.27
128.52
77.16 CDCl3
69.82
59.31
59.01
f1 (ppm)

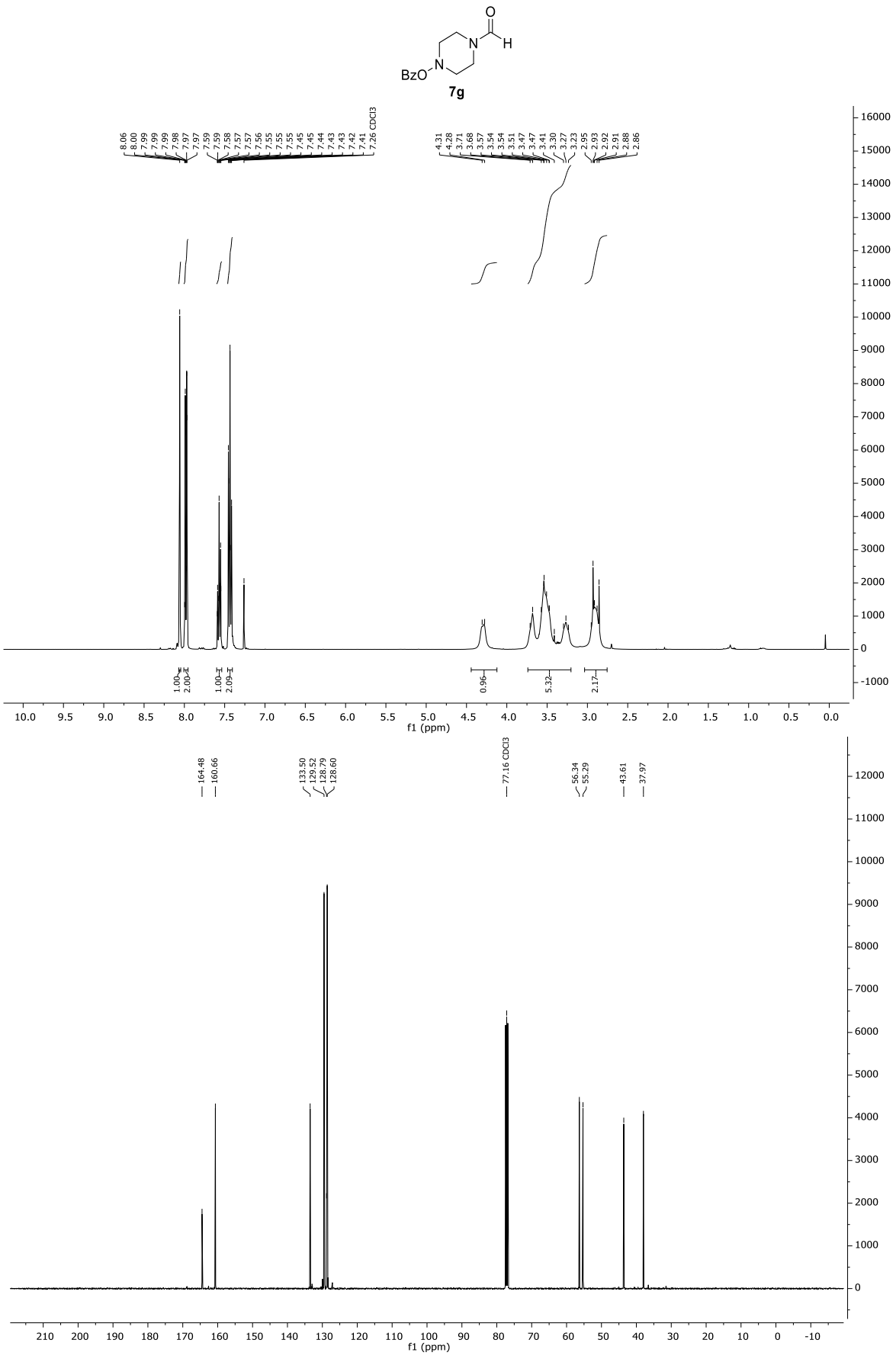

BzO
N
O

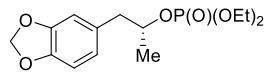
7e


8.03
8.02
8.02
8.01
8.01
8.00
8.00
7.59
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.46
7.46
7.45
7.44
7.43
7.42
7.26 CDCl3
3.99
3.97
3.96
3.96
3.89
3.89
3.87
3.86
3.84
3.46
3.43
3.07
3.06
3.04
3.04
3.02
3.01
2.00
1.00
2.00
2.01
2.00
2.00
2.00
f1 (ppm)

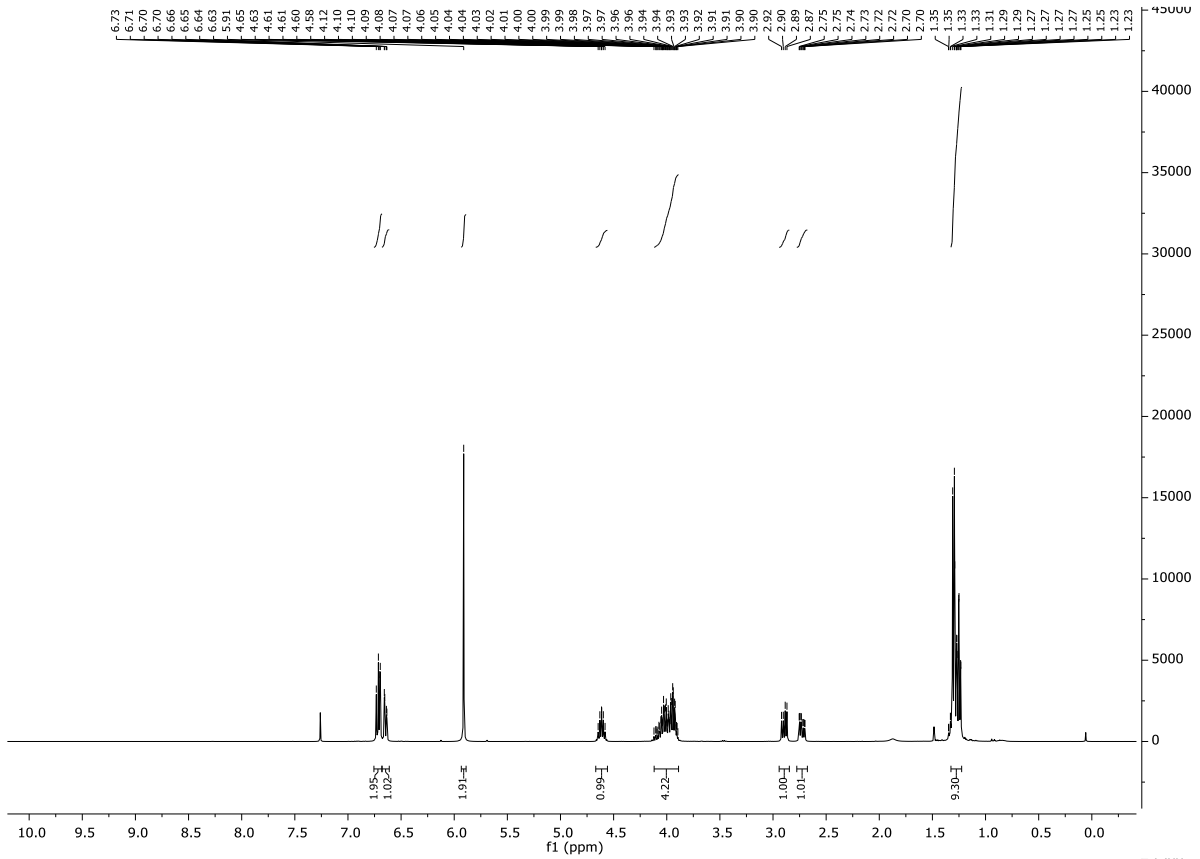

164.71
133.33
129.56
129.22
128.57
77.16 CDCl3
65.97
57.09
f1 (ppm)

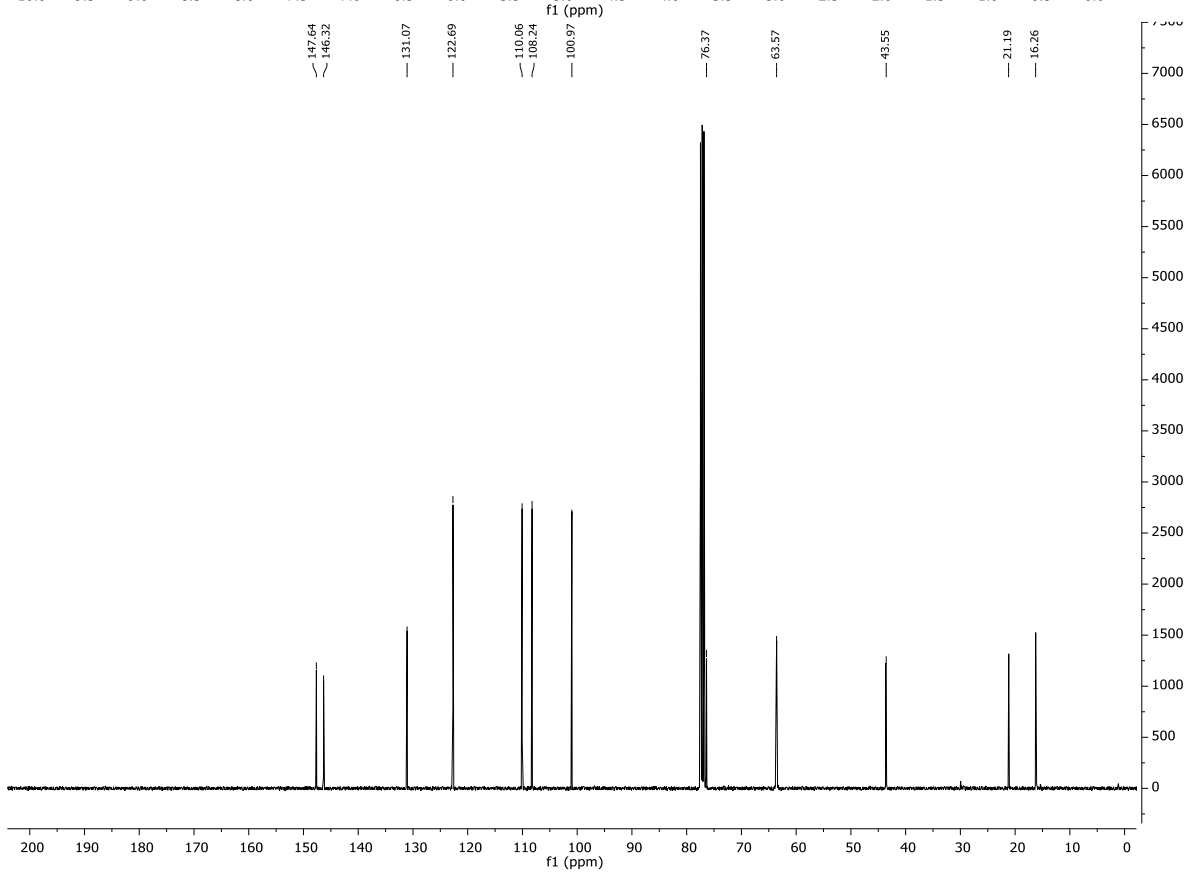

OBz
N
7f
8.02
8.01
8.01
8.01
8.00
7.99
7.99
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.53
7.45
7.44
7.43
7.43
7.41
7.41
7.26 CDCl3
3.34
3.32
3.31
1.84
1.84
1.83
1.83
1.82
1.81
1.80
1.79
1.79
1.71
1.70
1.69
1.68
1.67
1.67
1.65
1.93
0.98
1.98
4.00
4.11
4.00
f1 (ppm)
164.94
133.01
129.84
129.51
128.49
77.16 CDCl3
59.64
26.53
24.23
f1 (ppm)

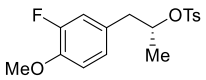

O
N
H
BzO
N
7g
8.06
8.00
7.99
7.99
7.99
7.98
7.97
7.97
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.55
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.26 CDCl3
4.31
4.28
4.21
3.68
3.57
3.54
3.54
3.51
3.47
3.47
3.41
3.30
3.27
3.23
2.95
2.93
2.92
2.91
2.88
2.86
1.00
2.00
1.00
2.09
0.96
5.32
2.17
f1 (ppm)
164.48
160.66
133.50
129.52
128.79
128.60
77.16 CDCl3
56.34
55.29
43.61
37.97
f1 (ppm)


OP(O)(OEt)2
Me

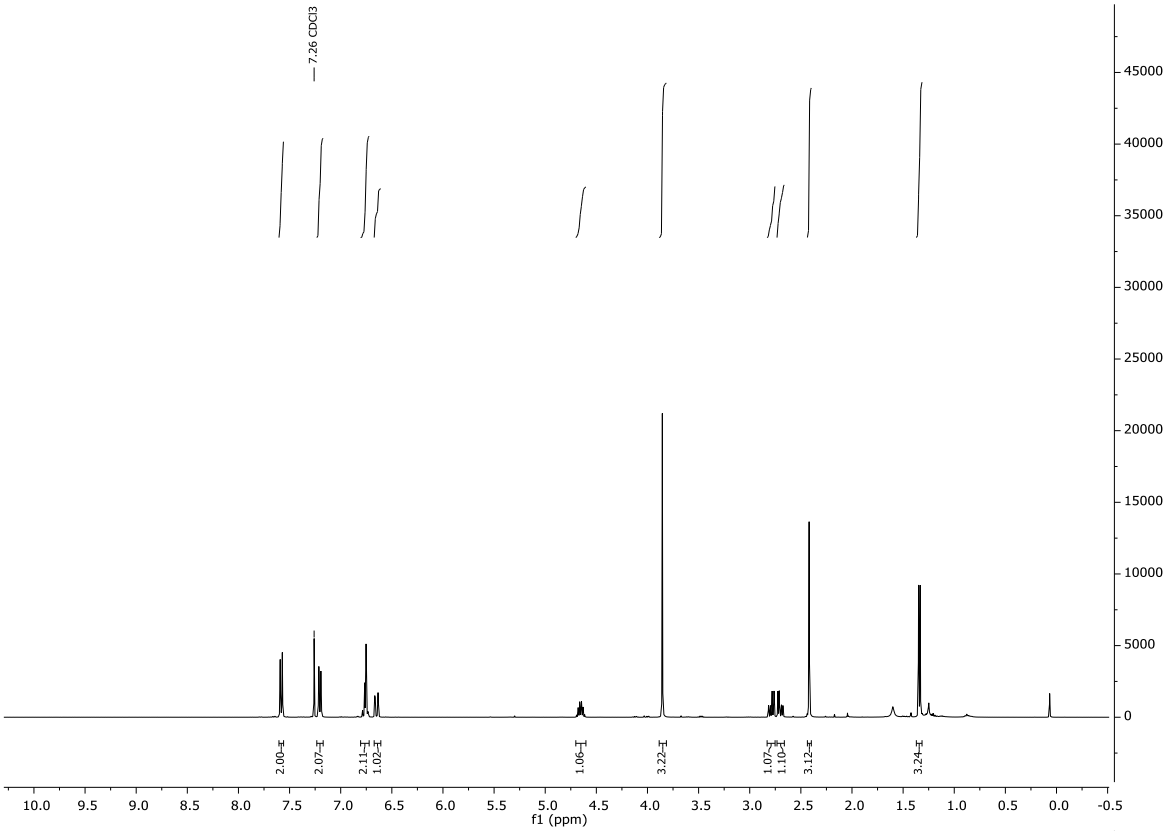
SI1

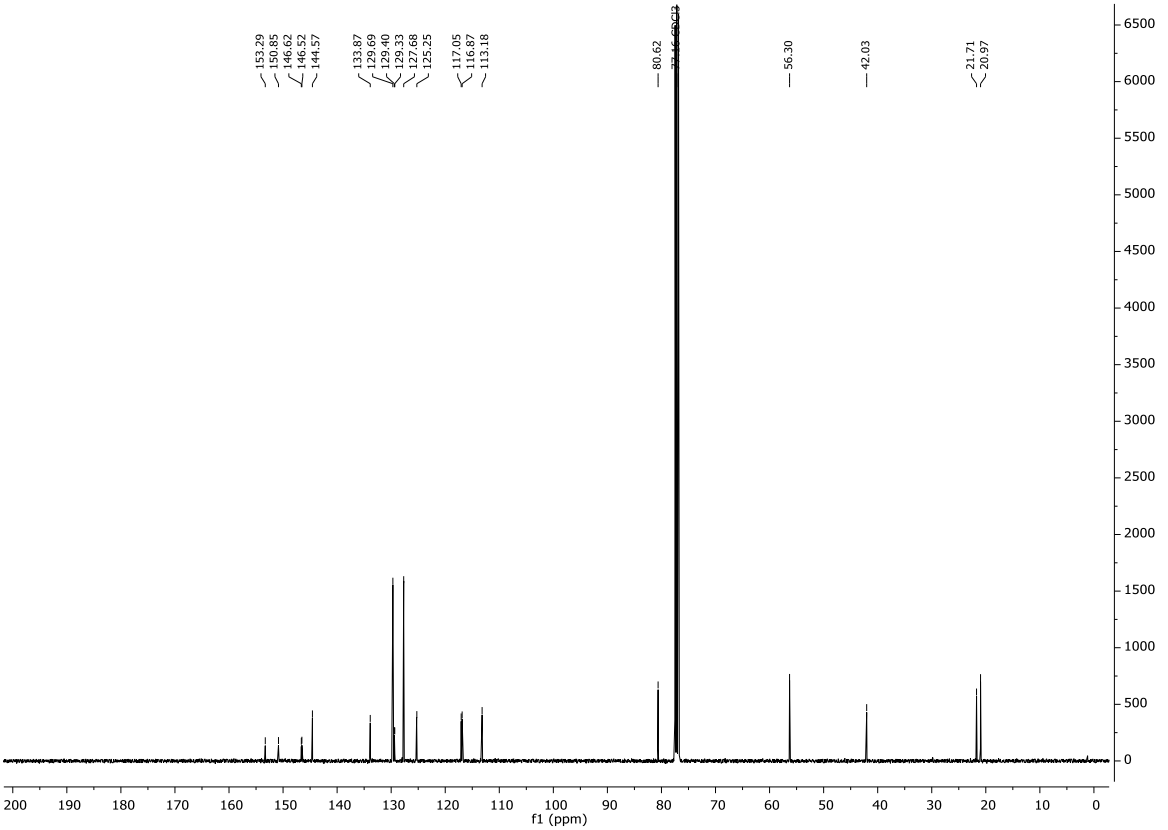

6.73 6.71 6.70 6.70 6.66 6.65 6.64 6.63 5.91 4.65 4.63 4.61 4.61 4.60 4.58 4.12 4.10 4.10 4.09 4.08 4.07 4.07 4.06 4.05 4.04 4.04 4.03 4.02 4.01 4.00 4.00 3.99 3.99 3.98 3.97 3.97 3.96 3.96 3.94 3.94 3.93 3.93 3.92 3.91 3.91 3.90 3.90 3.90 2.92 2.90 2.89 2.87 2.75 2.75 2.74 2.73 2.72 2.72 2.70 2.70 1.35 1.35 1.33 1.33 1.31 1.29 1.29 1.27 1.27 1.27 1.27 1.25 1.25 1.23 1.23 1.23
1.95
1.02
1.91
0.99
4.22
1.00
1.01
9.30
f1 (ppm)

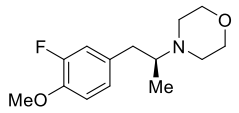

147.64
146.32
131.07
122.69
110.06
108.24
100.97
76.37
63.57
43.55
21.19
16.26
f1 (ppm)


F
OTs
MeO
Me

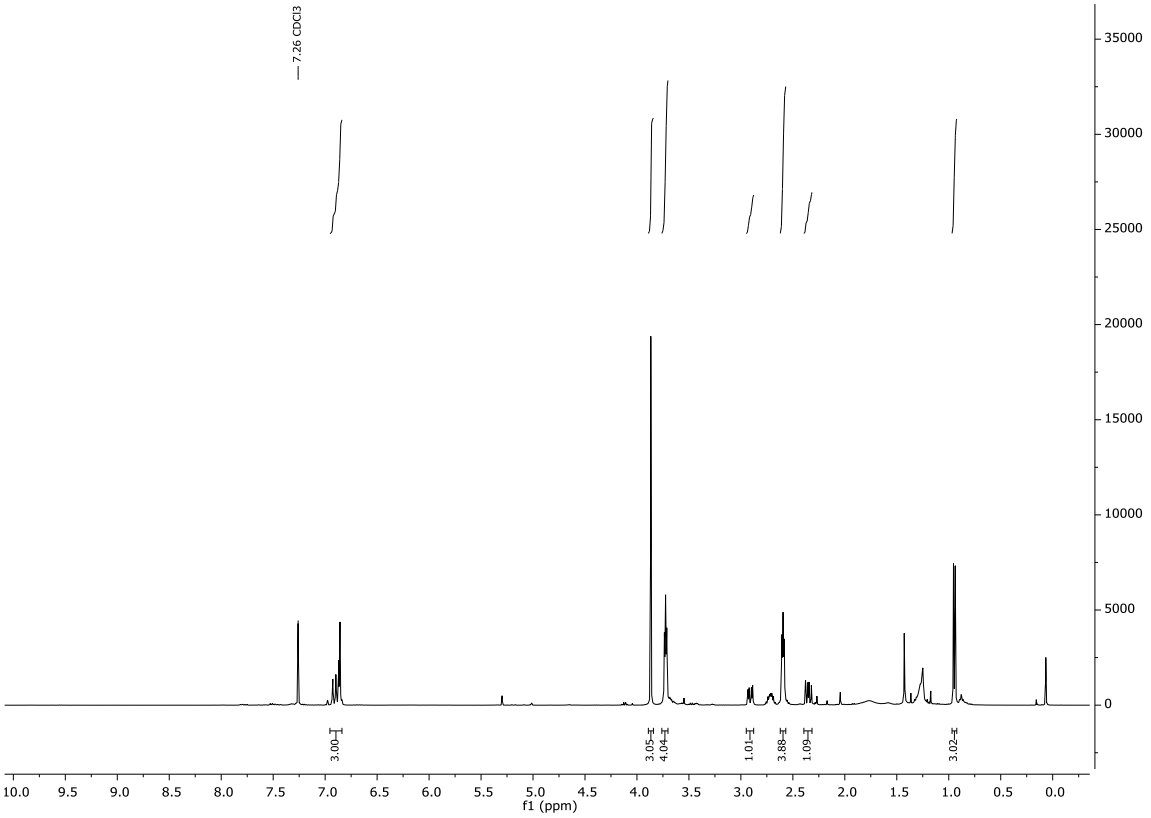
SI2

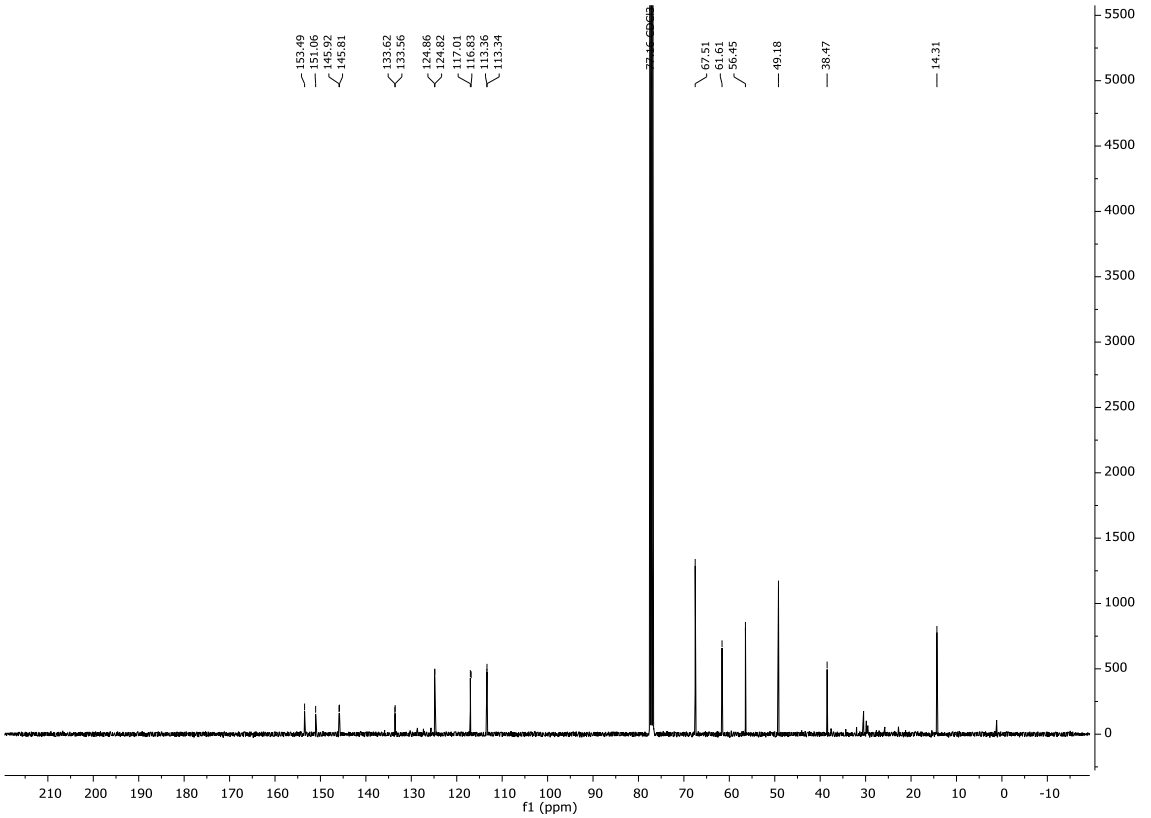

7.26 CDCl3
2.00
2.07
2.11
1.02
1.06
3.22
1.07
1.10
3.12
3.24
f1 (ppm)

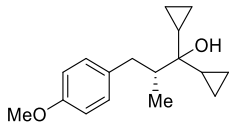

153.29
150.85
146.62
146.52
144.57
133.87
129.69
129.40
129.33
127.68
125.25
117.05
116.87
113.18
80.62
77.16 CDCl3
56.30
42.03
21.71
20.97
f1 (ppm)


F
O
N
MeO
Me

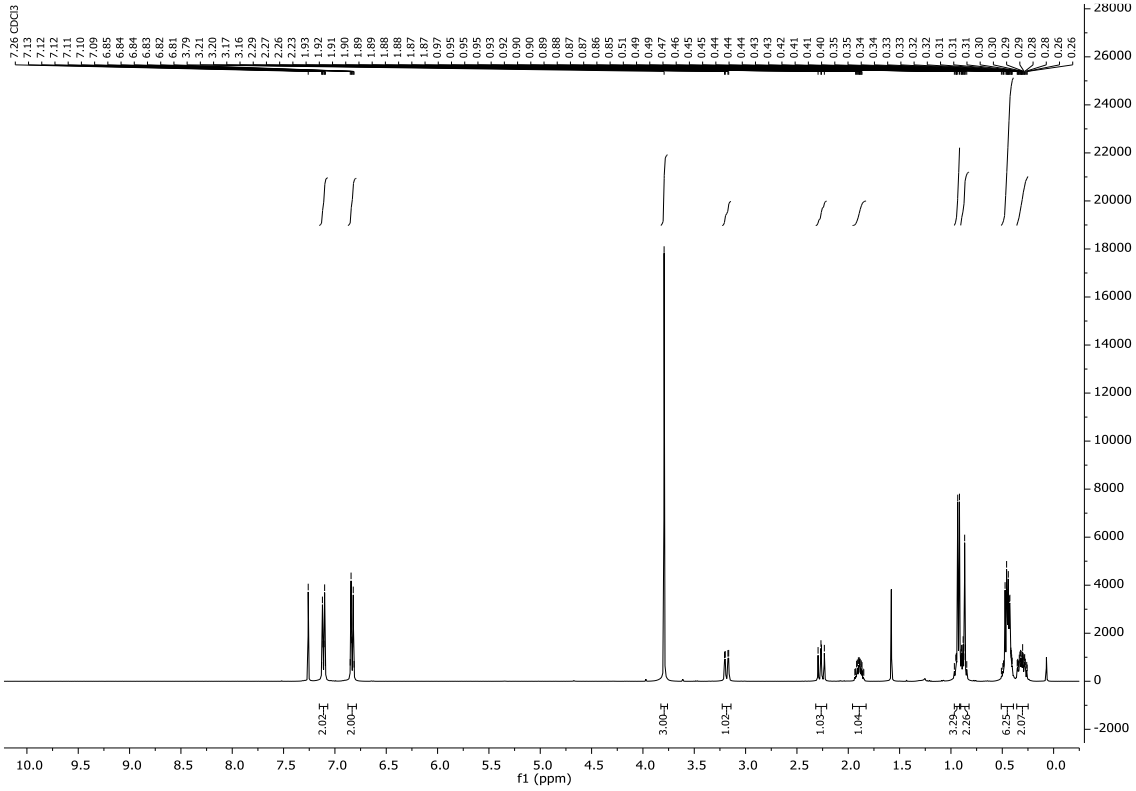
SI4

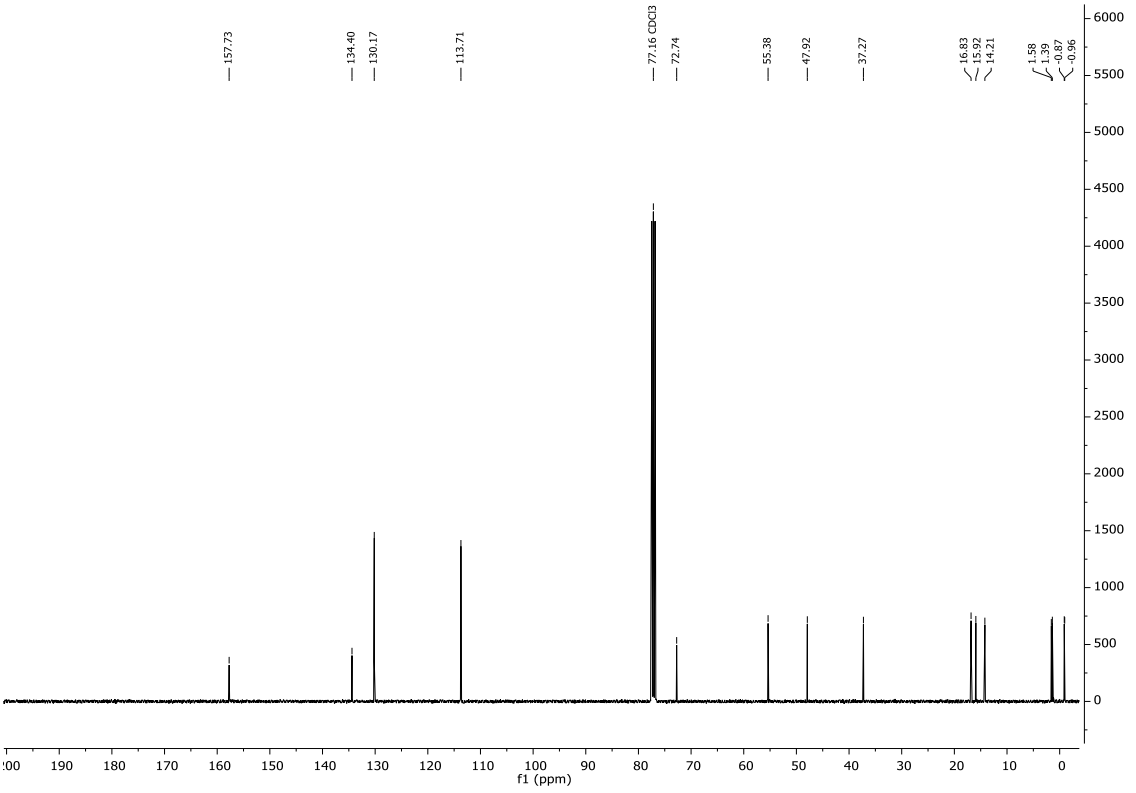

7.26 CDCl3
3.00
3.05
4.04
1.01
3.88
1.09
3.02
f1 (ppm)

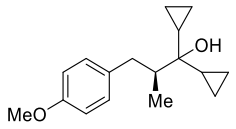

153.49
151.06
145.92
145.81
133.62
133.56
124.86
124.82
117.01
116.83
113.36
113.34
77.16 CDCl3
67.51
61.61
56.45
49.18
38.47
14.31
f1 (ppm)


OH
Me
MeO

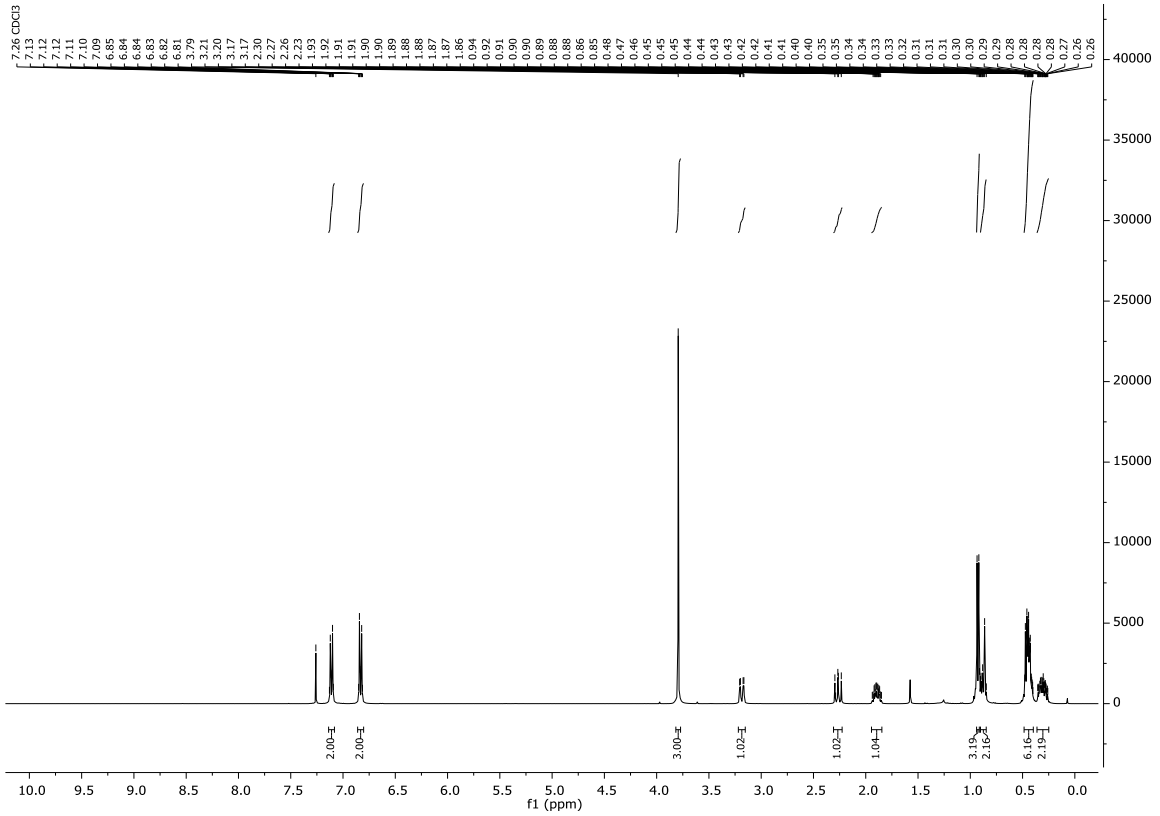
(*R*)-**4a**

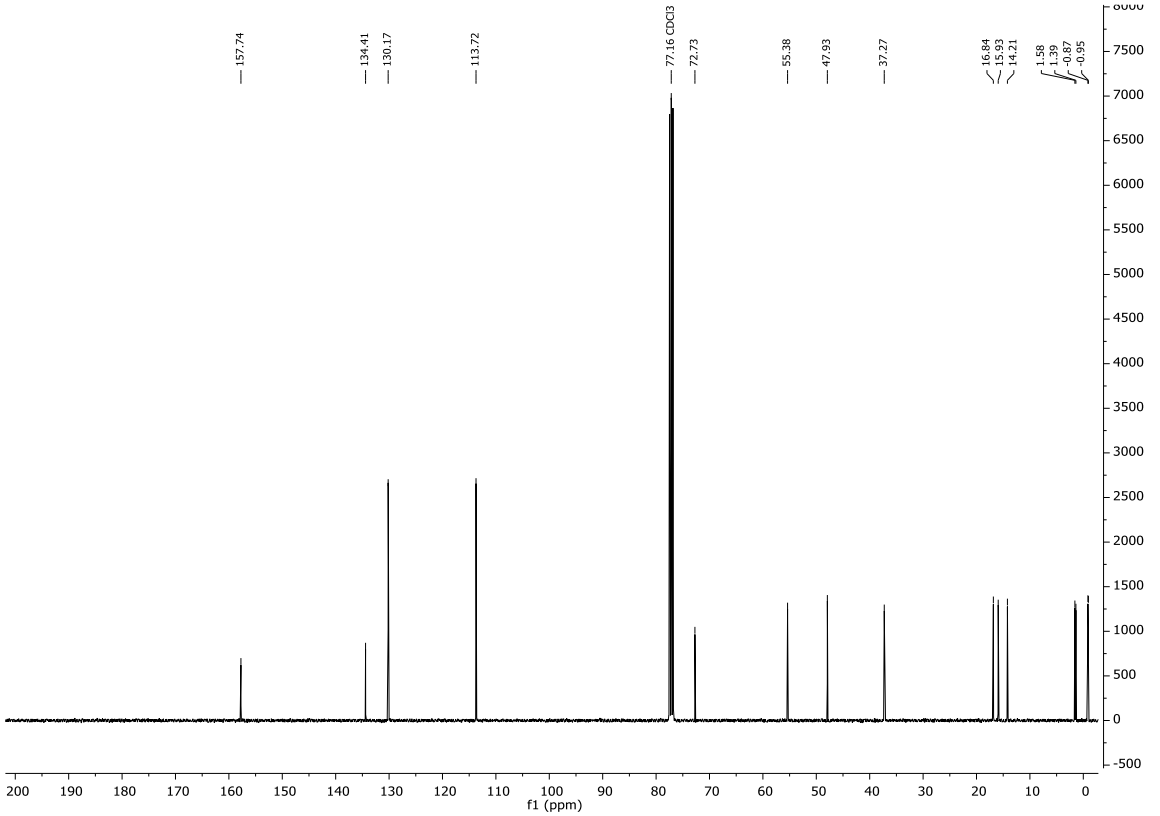

7.26 CDCl3
2.02
2.00
3.00
1.02
1.03
1.04
3.29
2.26
6.25
2.07
f1 (ppm)

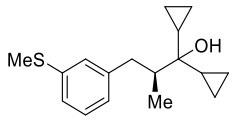

157.73
134.40
130.17
113.71
77.16 CDCl3
72.74
55.38
47.92
37.27
16.83
15.92
14.21
1.58
1.39
-0.87
-0.96
f1 (ppm)


OH
Me
MeO

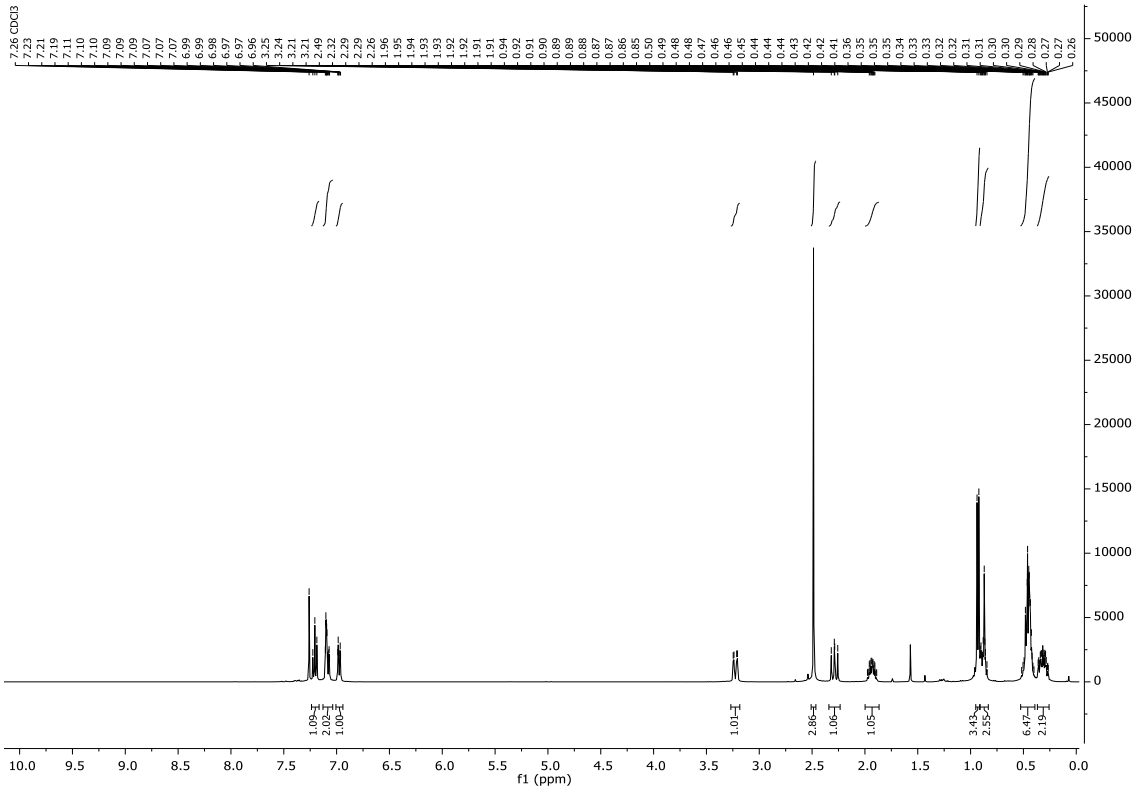
(*S*)-**4a**

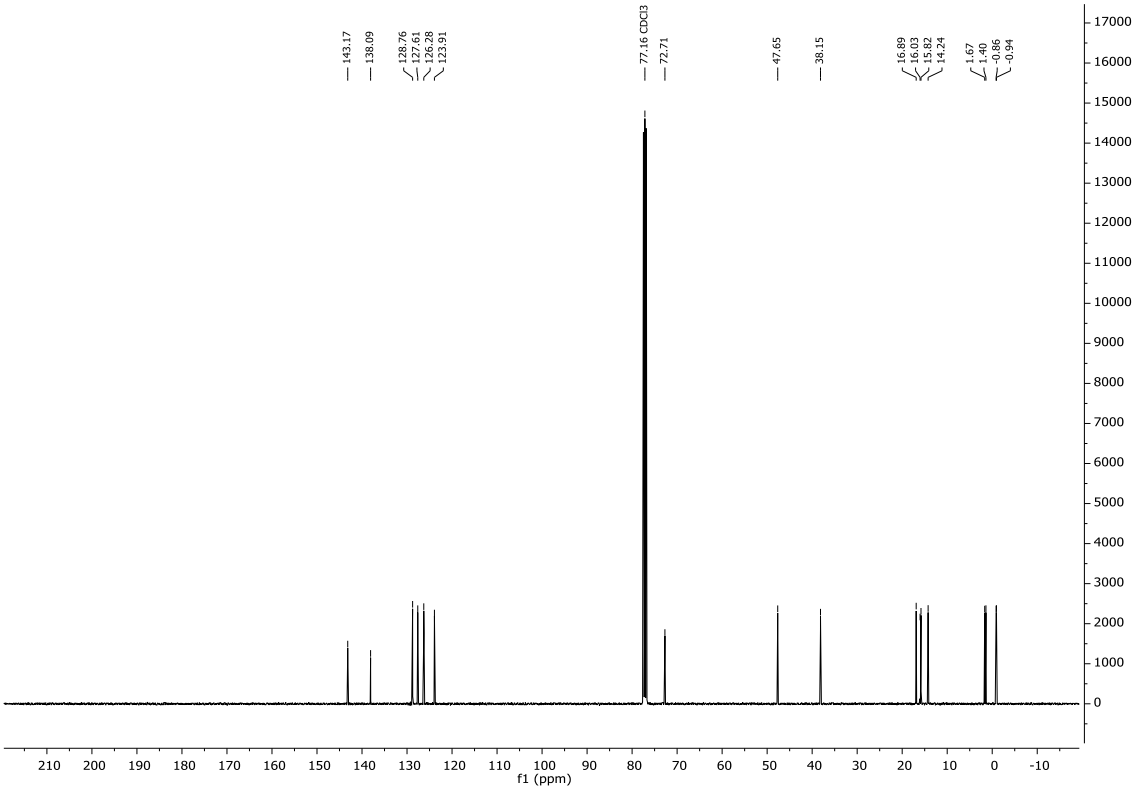

7.26 CDCl3
2.00
2.00
3.00
1.02
1.02
1.04
3.19
2.16
6.16
2.19
f1 (ppm)

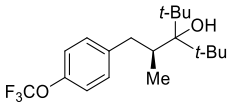

157.74
134.41
130.17
113.72
77.16 CDCl3
72.73
55.38
47.93
37.27
16.84
15.93
14.21
1.58
1.39
-0.87
-0.95
f1 (ppm)


MeS
OH
Me

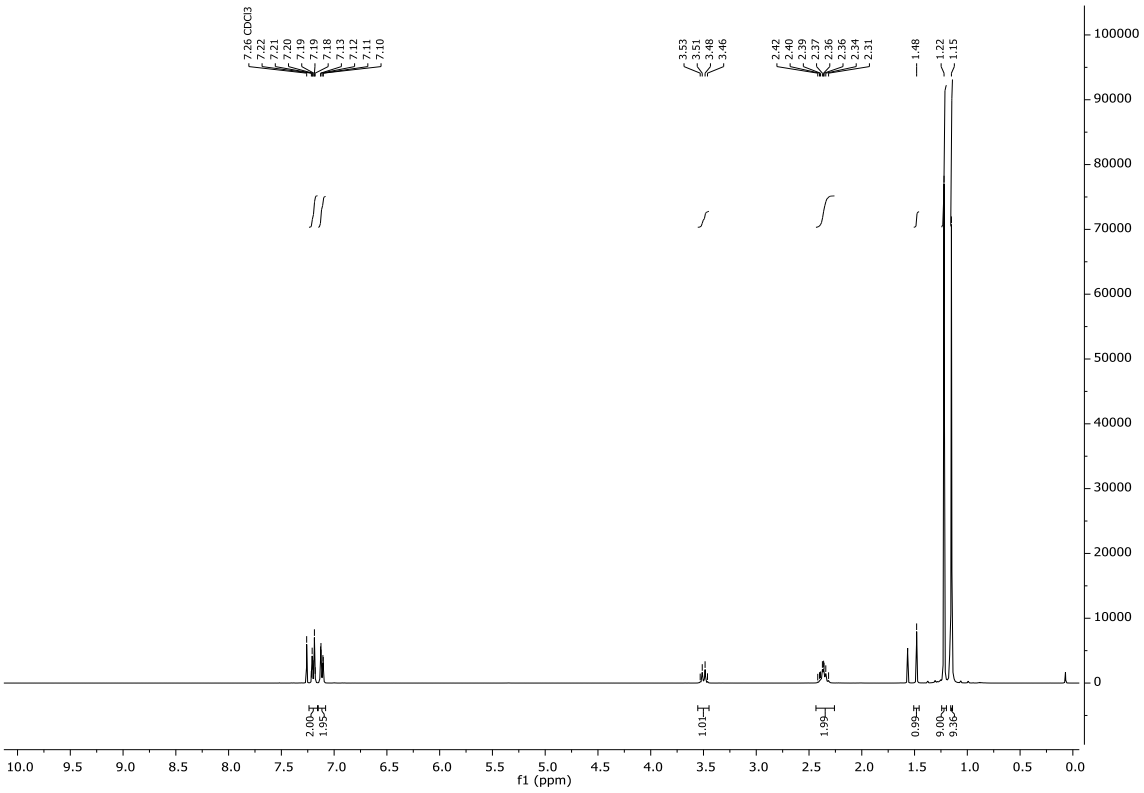
(*S*)-**4b**

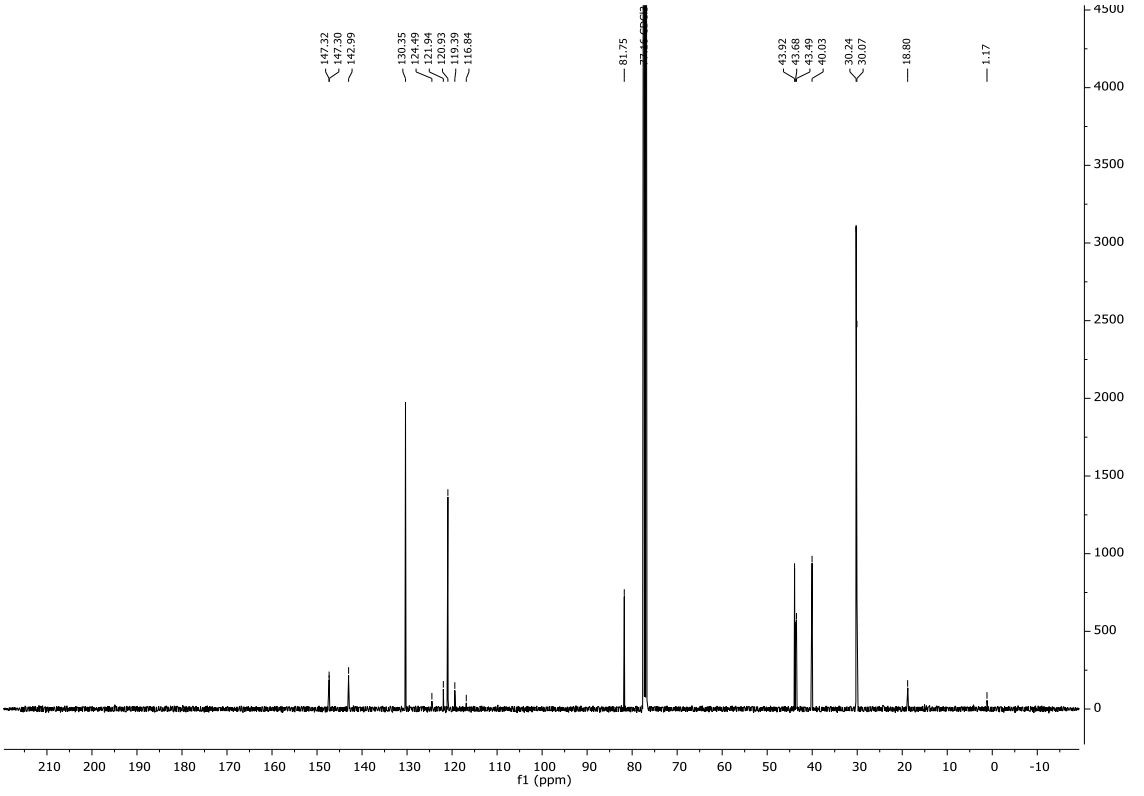

7.26 CDCl3
1.09
2.02
1.00
1.01
2.86
1.06
1.05
3.43
2.55
6.47
2.19
f1 (ppm)

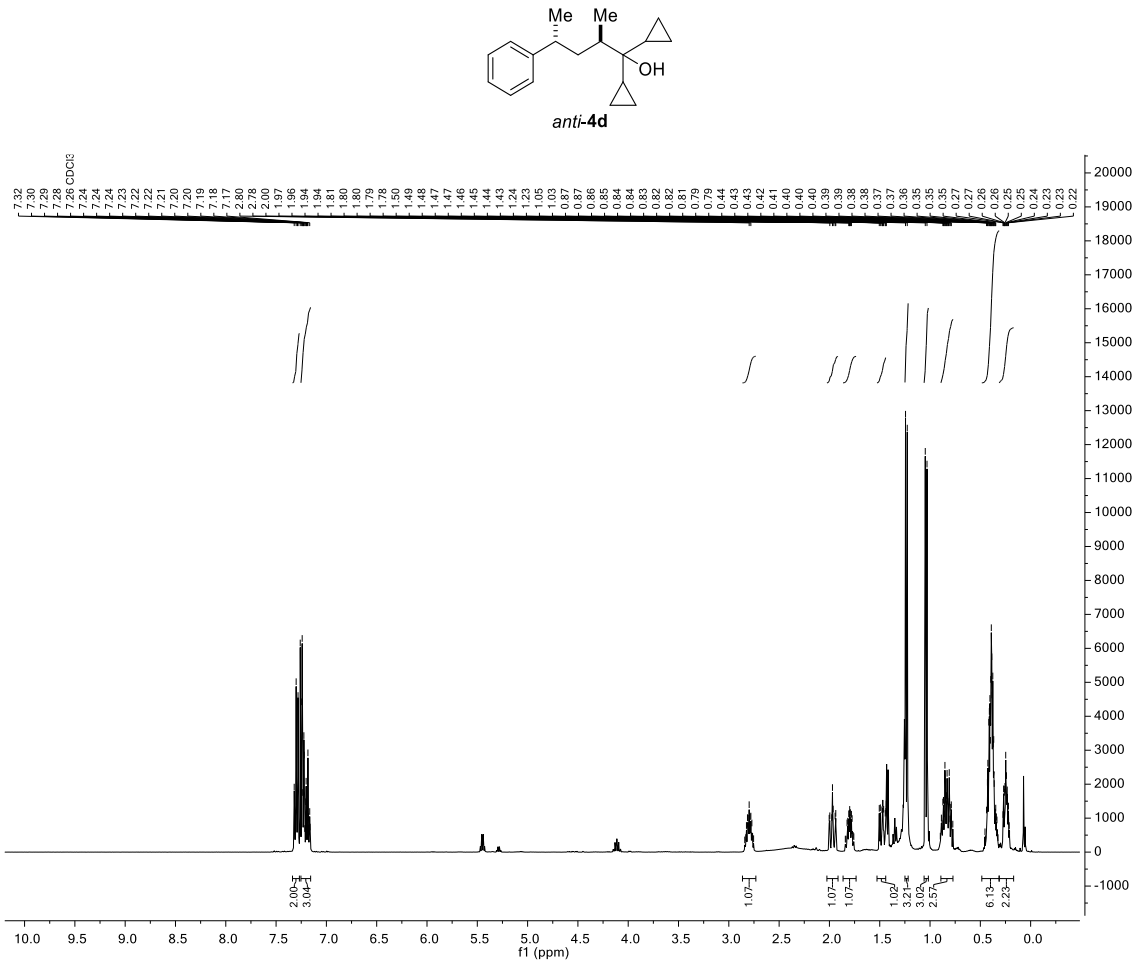

143.17
138.09
128.76
127.61
126.28
123.91
77.16 CDCl3
72.71
47.65
38.15
16.89
16.03
15.82
14.24
1.67
1.40
-0.86
-0.94
f1 (ppm)

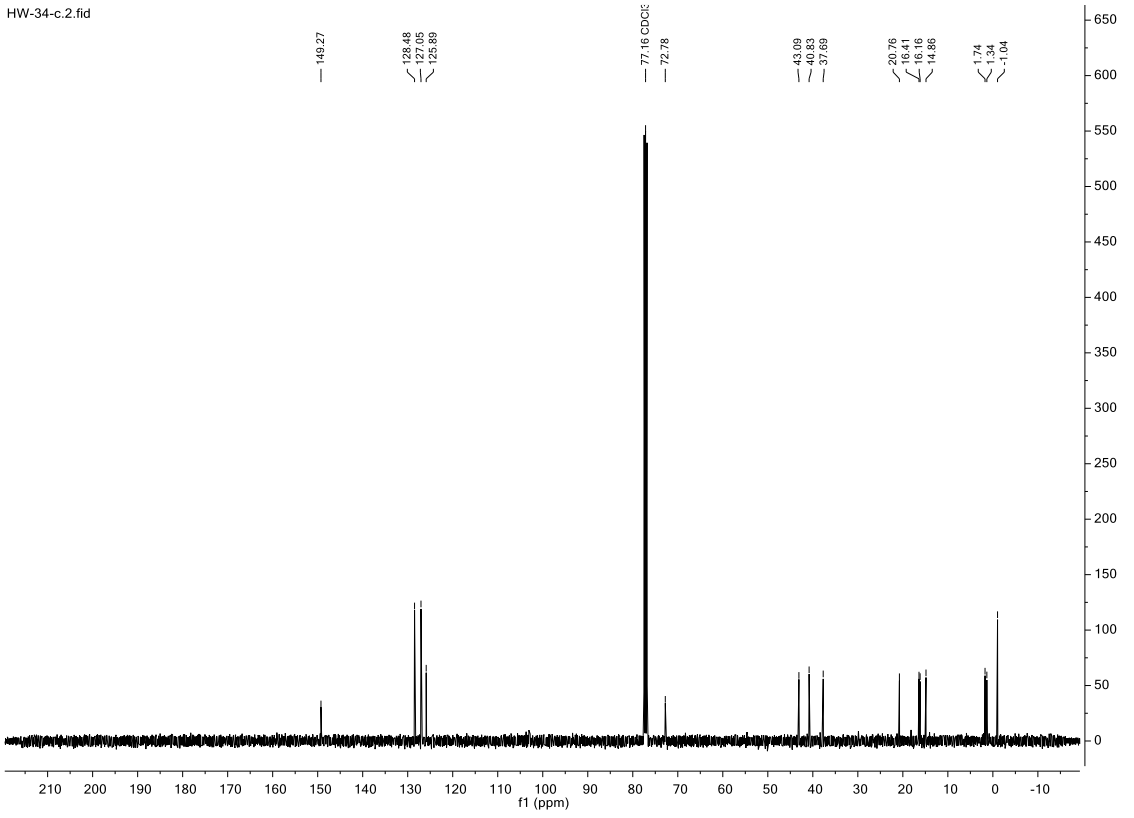

t-Bu
OH
t-Bu
Me
F3CO

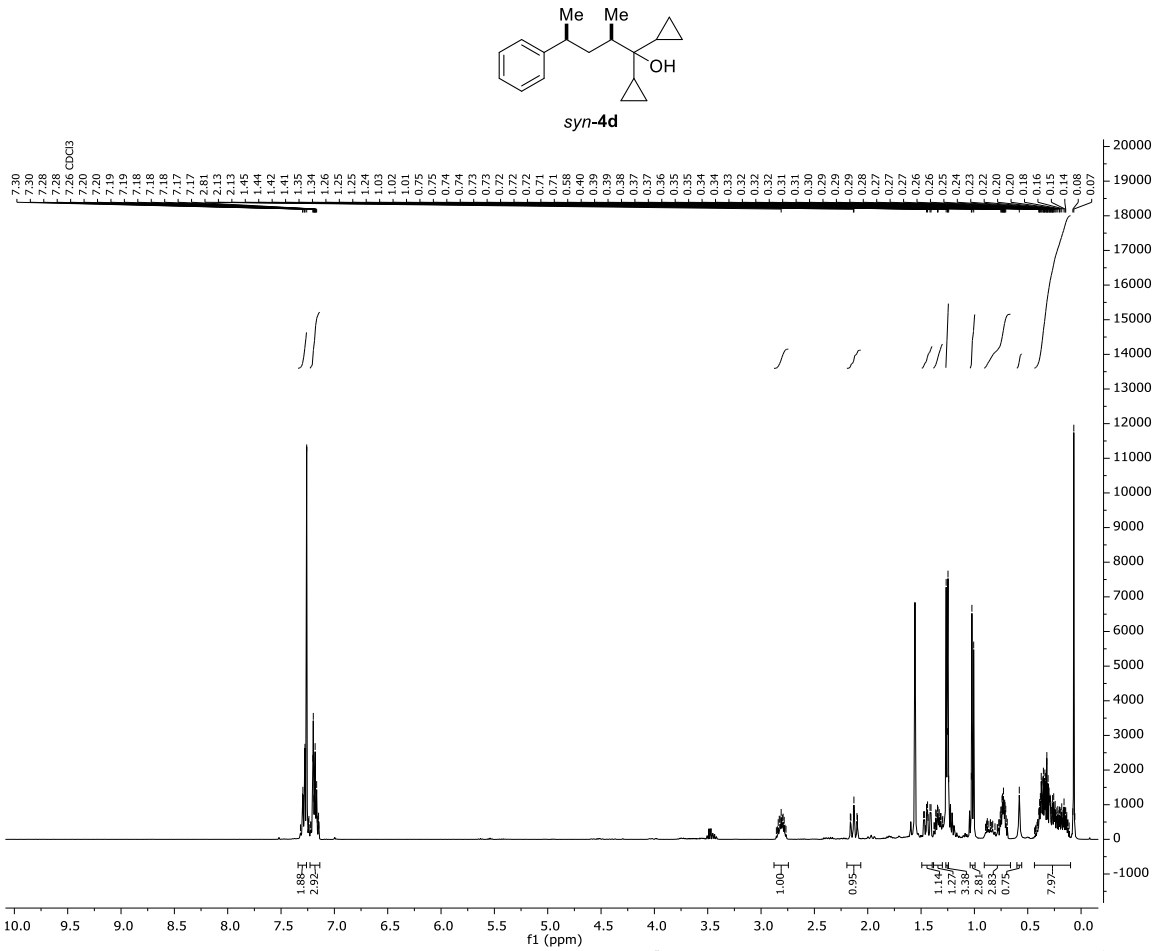
(*S*)-**4c**


7.26 CDCl3
7.22
7.21
7.20
7.19
7.19
7.18
7.13
7.12
7.11
7.10
3.53
3.51
3.48
3.46
2.42
2.40
2.39
2.37
2.36
2.36
2.34
2.31
1.48
1.22
1.15
2.00
1.95
1.01
1.99
0.99
9.00
9.36
f1 (ppm)

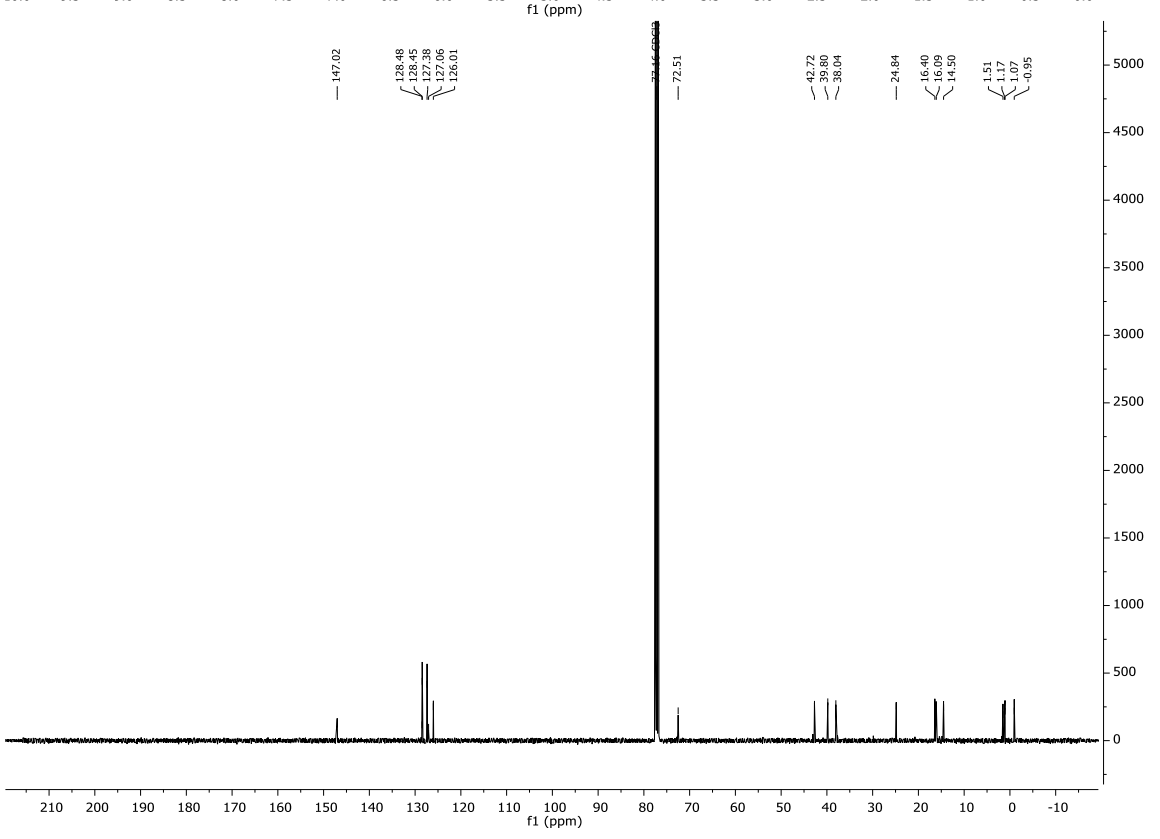

147.32
147.30
142.99
130.35
124.49
121.94
120.93
119.39
116.84
81.75
77.16 CDCl3
43.92
43.68
43.49
40.03
30.24
30.07
18.80
1.17
f1 (ppm)

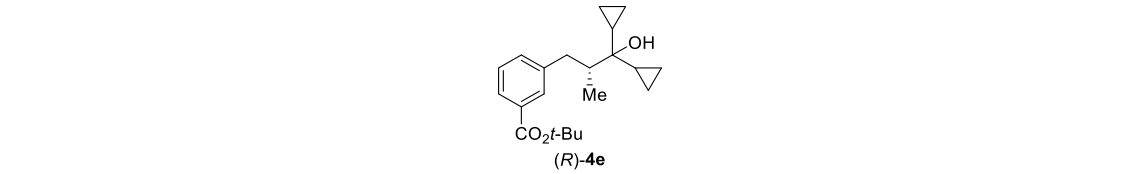

Me
Me
OH
anti-4d
7.32 7.30 7.29 7.28 7.26 CDCl3 7.24 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.17 2.80 2.78 2.00 1.97 1.96 1.94 1.94 1.81 1.80 1.80 1.79 1.78 1.50 1.49 1.48 1.47 1.47 1.46 1.45 1.44 1.43 1.24 1.23 1.05 1.03 0.87 0.87 0.86 0.85 0.84 0.84 0.83 0.82 0.82 0.81 0.79 0.79 0.44 0.43 0.43 0.42 0.41 0.40 0.40 0.40 0.39 0.39 0.38 0.38 0.37 0.37 0.36 0.35 0.35 0.35 0.27 0.27 0.26 0.26 0.25 0.25 0.24 0.23 0.23 0.23 0.22
2.00 3.04 1.07 1.07 1.07 1.02 3.21 3.02 2.57 6.13 2.23
f1 (ppm)


HW-34-c.2.fid
149.27
128.48 127.05 125.89
77.16 CDCl3
72.78
43.09 40.83 37.69
20.76 16.41 16.16 14.86
1.74 1.34 -1.04
f1 (ppm)

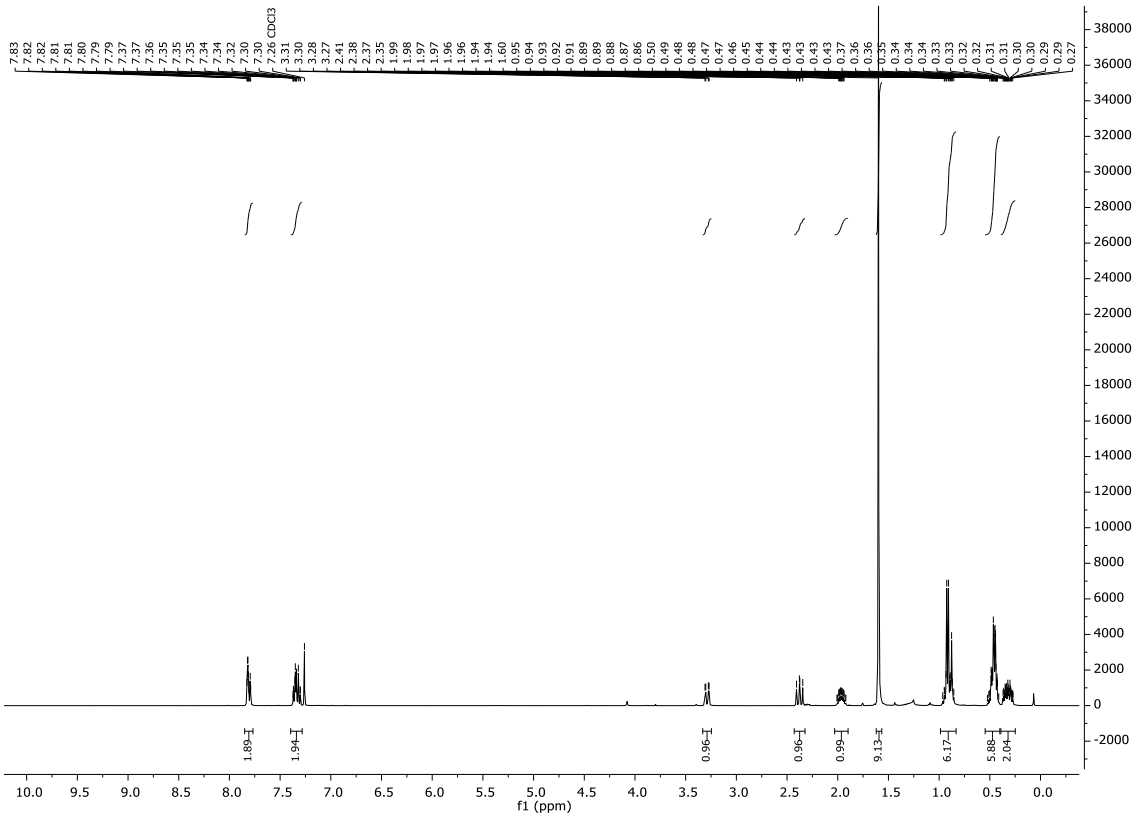


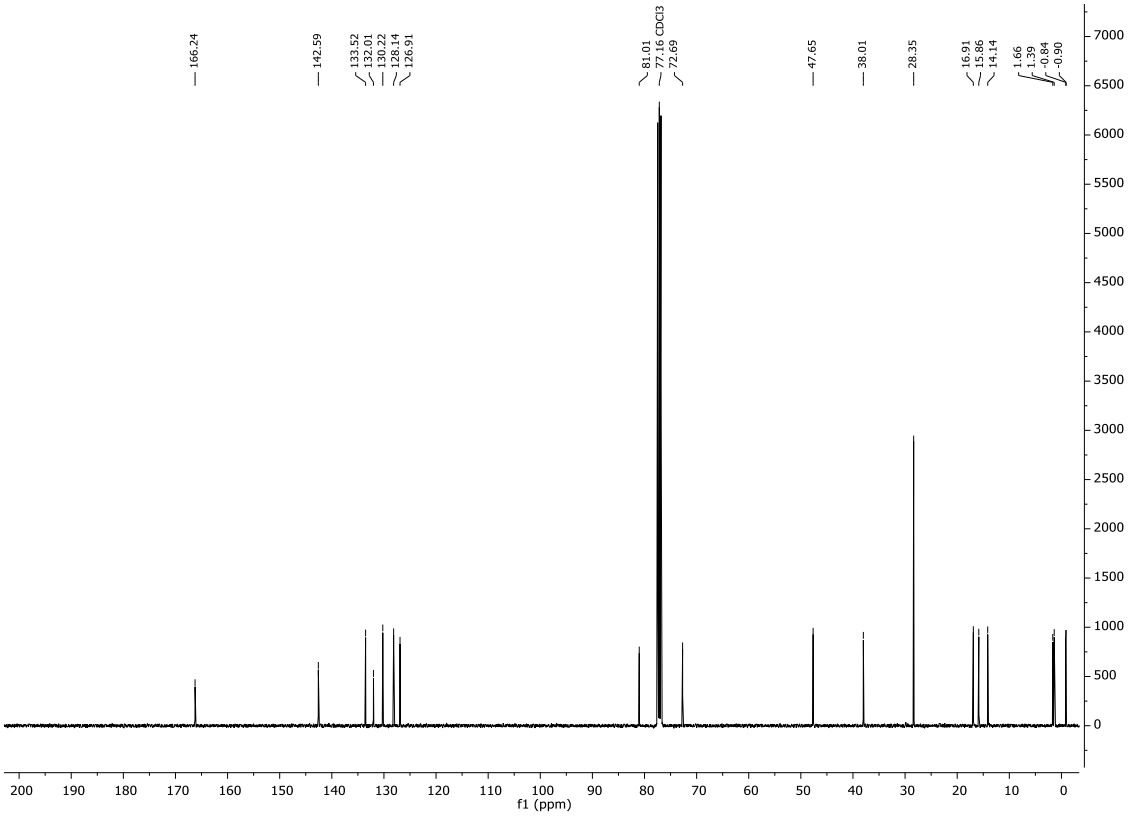
syn-**4d**

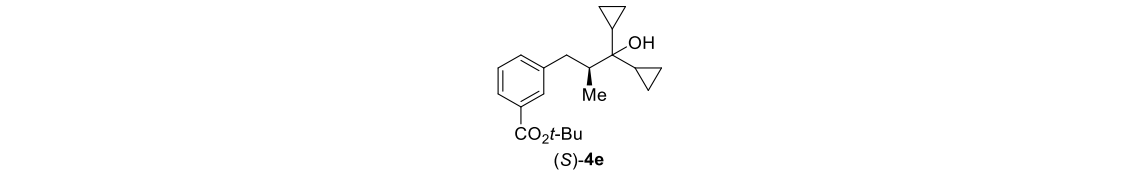



OH
Me
CO2t-Bu

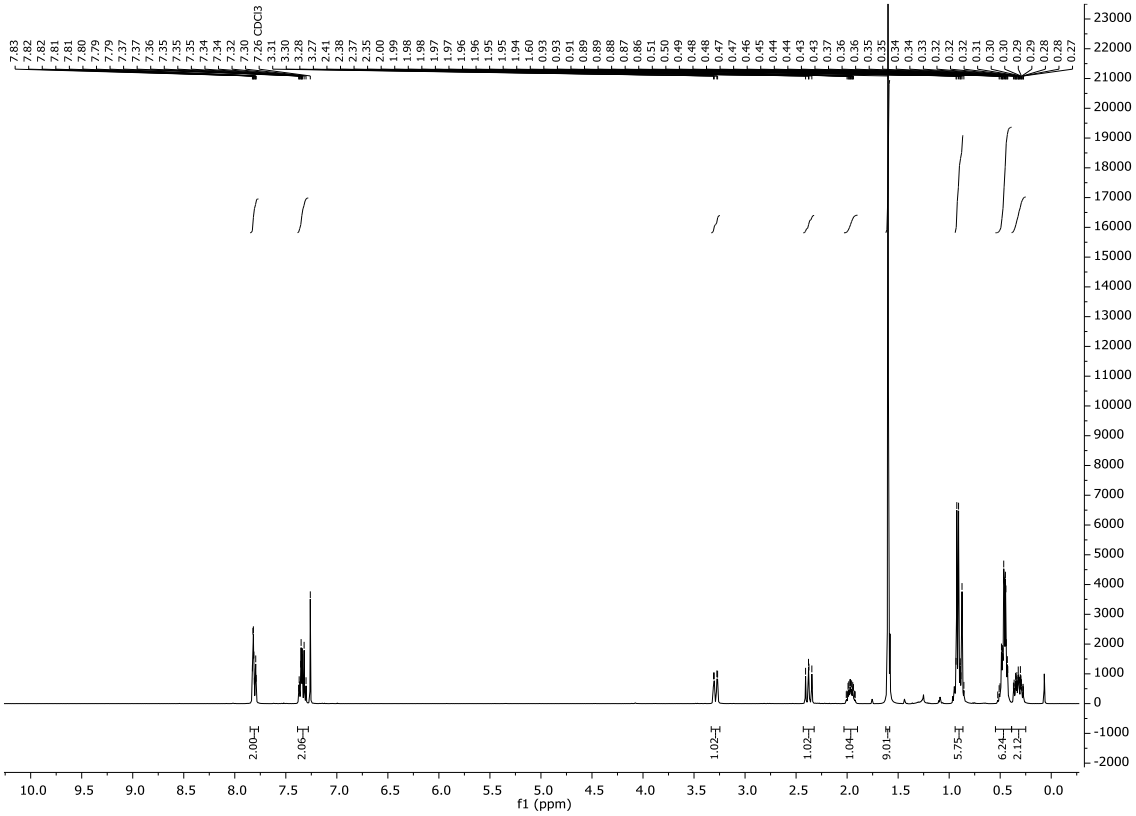
(*R*)-**4e**

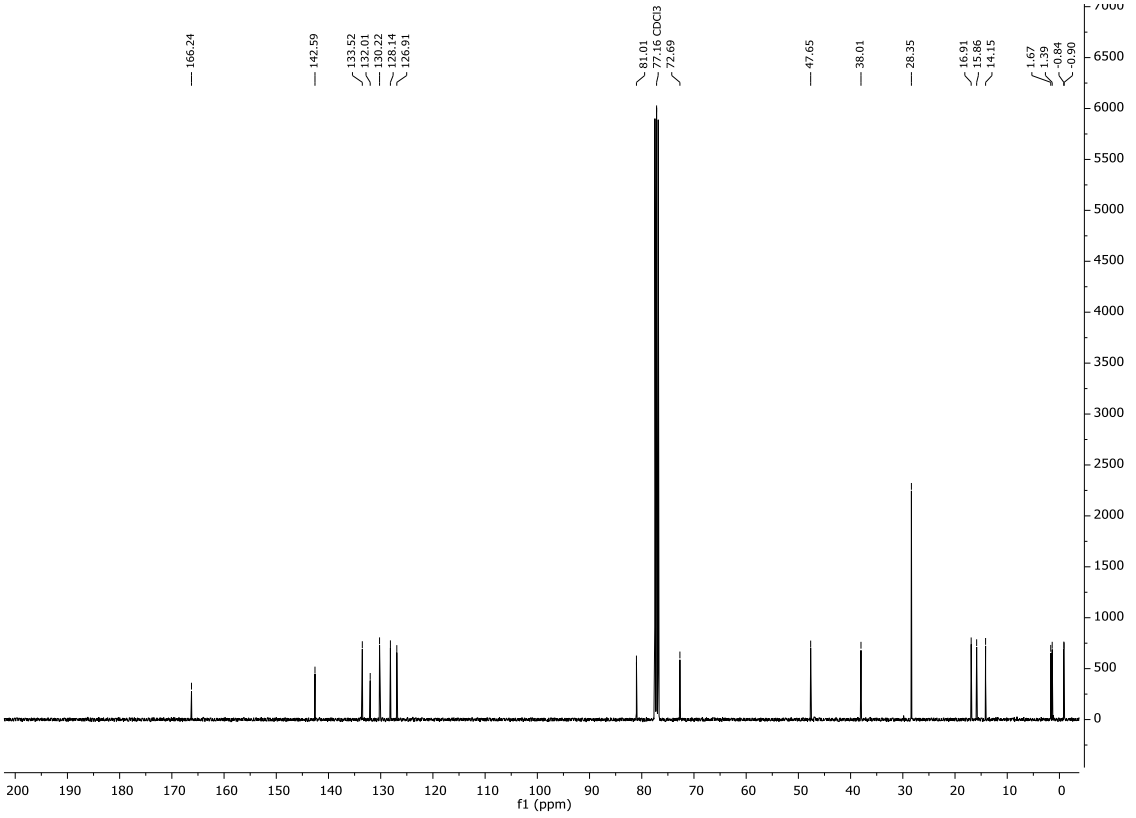

7.83 7.82 7.82 7.81 7.81 7.80 7.79 7.79 7.37 7.36 7.35 7.35 7.34 7.34 7.32 7.30 7.30 7.26 CDCl3 3.31 3.30 3.28 3.27 2.41 2.38 2.37 2.35 1.99 1.98 1.97 1.97 1.96 1.96 1.94 1.94 1.60 0.95 0.94 0.93 0.92 0.91 0.89 0.89 0.88 0.87 0.86 0.50 0.49 0.48 0.48 0.47 0.47 0.46 0.45 0.44 0.44 0.43 0.43 0.43 0.37 0.36 0.36 0.35 0.34 0.34 0.34 0.33 0.32 0.32 0.31 0.31 0.30 0.30 0.29 0.29 0.27
1.89 1.94 0.96 0.96 0.99 9.13 6.17 5.88 2.04
f1 (ppm)

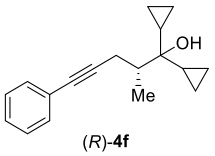

166.24 142.59 133.52 132.01 130.22 128.14 126.91 81.01 77.16 CDCl3 72.69 47.65 38.01 28.35 16.91 15.86 14.14 1.66 1.39 -0.84 -0.90
f1 (ppm)


OH
Me
CO2t-Bu

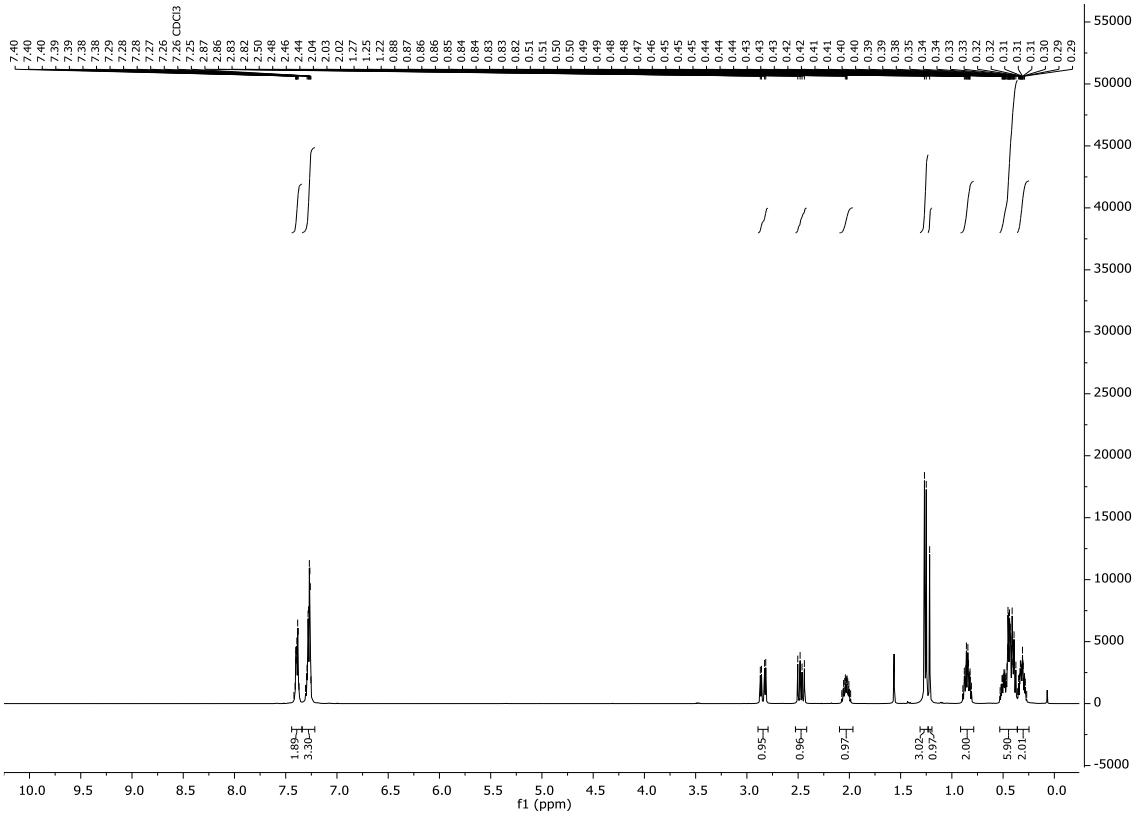
(*S*)-**4e**

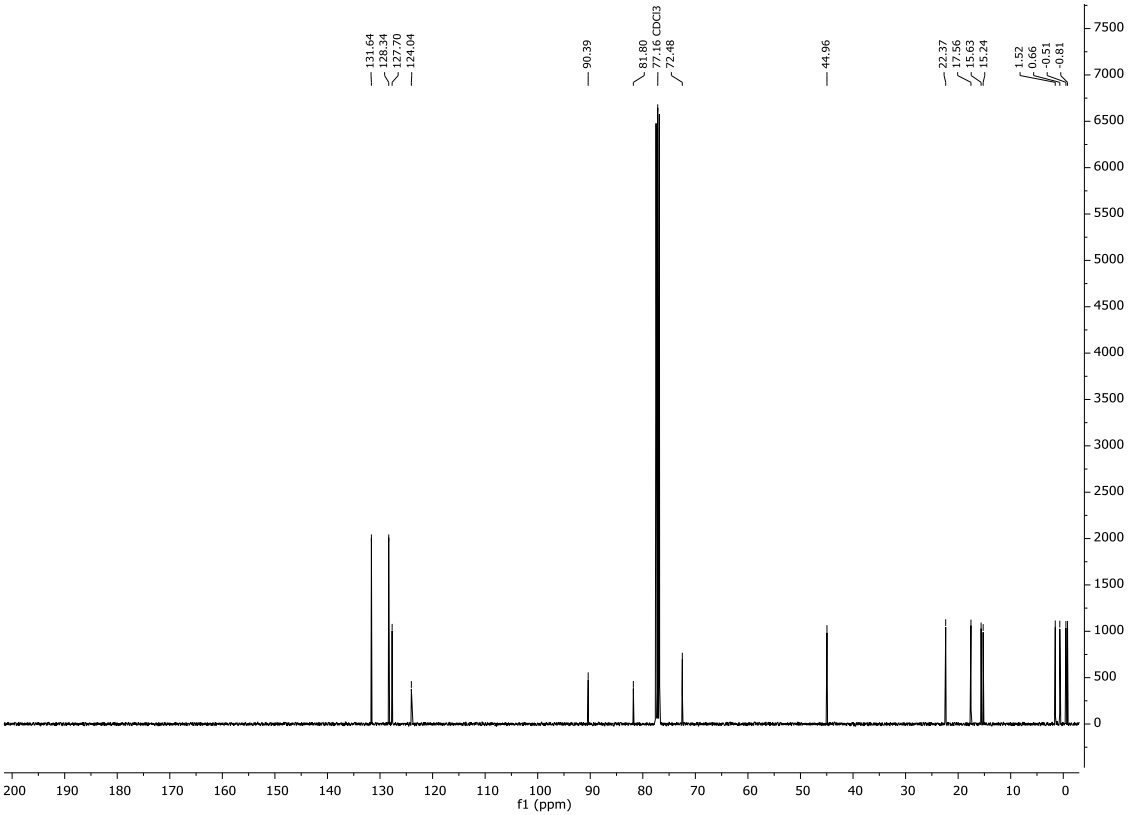

7.83 7.82 7.82 7.81 7.81 7.80 7.79 7.79 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.32 7.30 7.26 CDCl3 3.31 3.30 3.28 3.27 2.41 2.38 2.37 2.35 2.00 1.99 1.98 1.98 1.97 1.97 1.96 1.96 1.95 1.95 1.94 1.60 0.93 0.93 0.91 0.89 0.89 0.88 0.88 0.87 0.86 0.51 0.50 0.49 0.48 0.48 0.47 0.47 0.46 0.45 0.44 0.44 0.43 0.43 0.37 0.36 0.36 0.35 0.35 0.34 0.34 0.33 0.32 0.32 0.32 0.31 0.30 0.30 0.29 0.29 0.28 0.28 0.27
2.00 2.06 1.02 1.02 1.04 9.01 5.75 6.24 2.12
f1 (ppm)

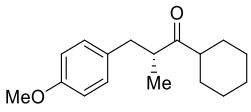

166.24 142.59 133.52 132.01 130.22 128.14 126.91 81.01 77.16 CDCl3 72.69 47.65 38.01 28.35 16.91 15.86 14.15 1.67 1.39 -0.84 -0.90
f1 (ppm)


OH
Me

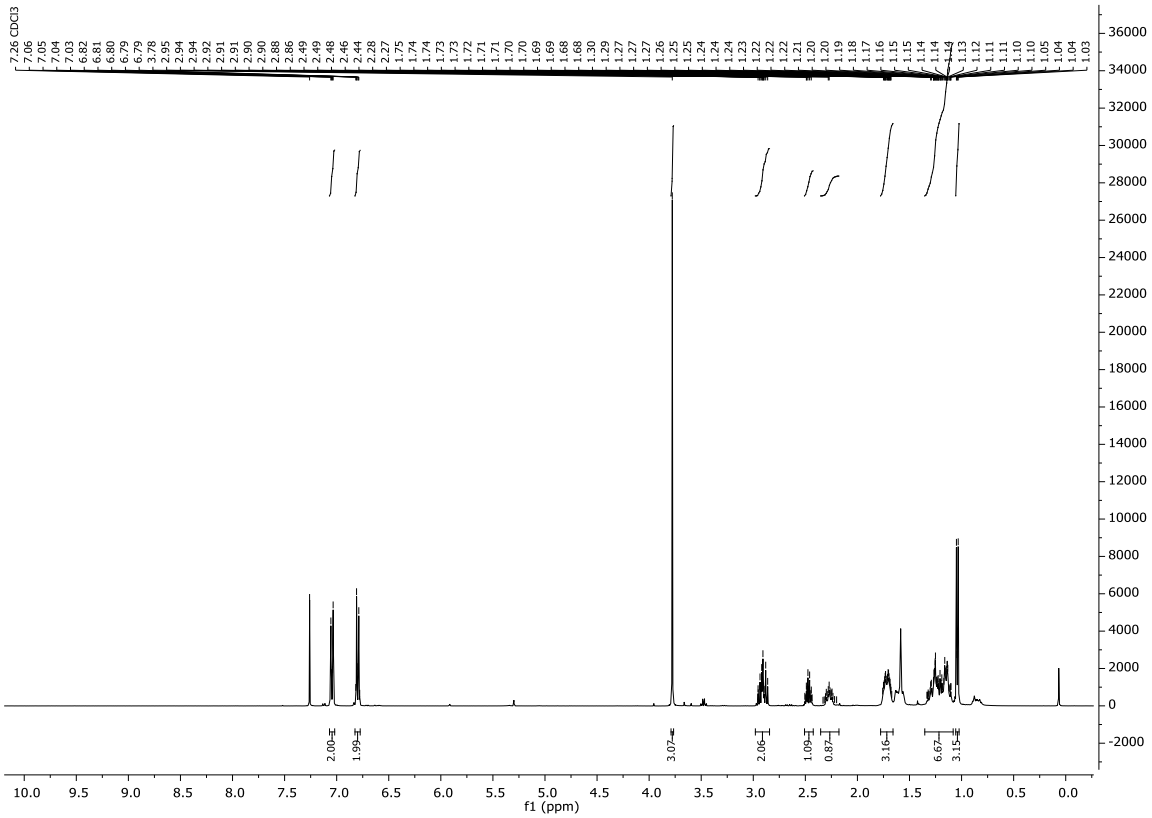
(*R*)-**4f**

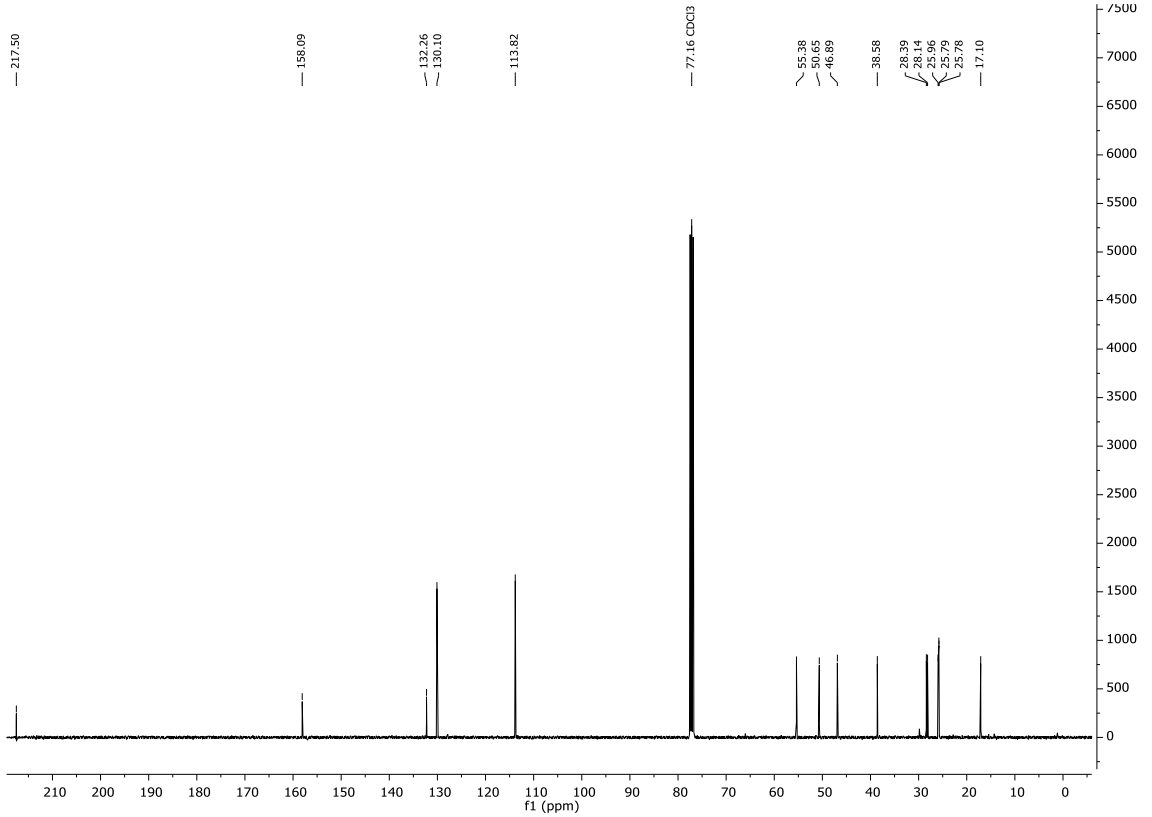

7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.29
7.28
7.28
7.27
7.26
7.26 CDCl3
7.25
2.87
2.86
2.83
2.82
2.50
2.48
2.46
2.44
2.04
2.03
2.02
1.27
1.25
1.22
0.88
0.87
0.86
0.86
0.85
0.84
0.84
0.84
0.83
0.83
0.82
0.51
0.51
0.50
0.50
0.49
0.49
0.48
0.48
0.47
0.46
0.45
0.45
0.45
0.44
0.44
0.44
0.43
0.43
0.43
0.42
0.42
0.41
0.41
0.40
0.40
0.39
0.39
0.38
0.35
0.34
0.34
0.33
0.33
0.32
0.32
0.31
0.31
0.31
0.30
0.29
0.29
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
1.89
3.30
0.95
0.96
0.97
3.02
0.97
2.00
5.90
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

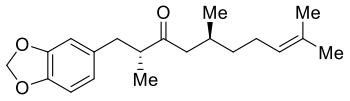

131.64
128.34
127.70
124.04
90.39
81.80
77.16 CDCl3
72.48
44.96
22.37
17.56
15.63
15.24
1.52
0.66
-0.51
-0.81
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Me
MeO

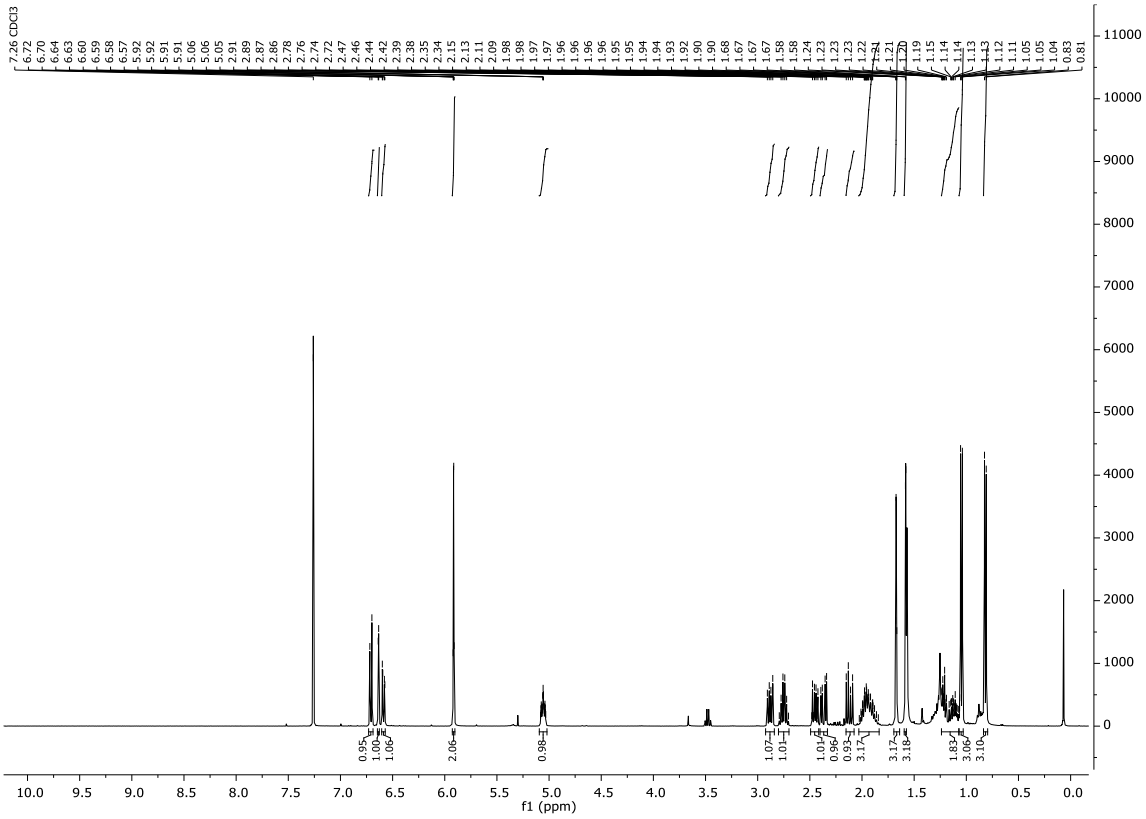
(*R*)-**4g**

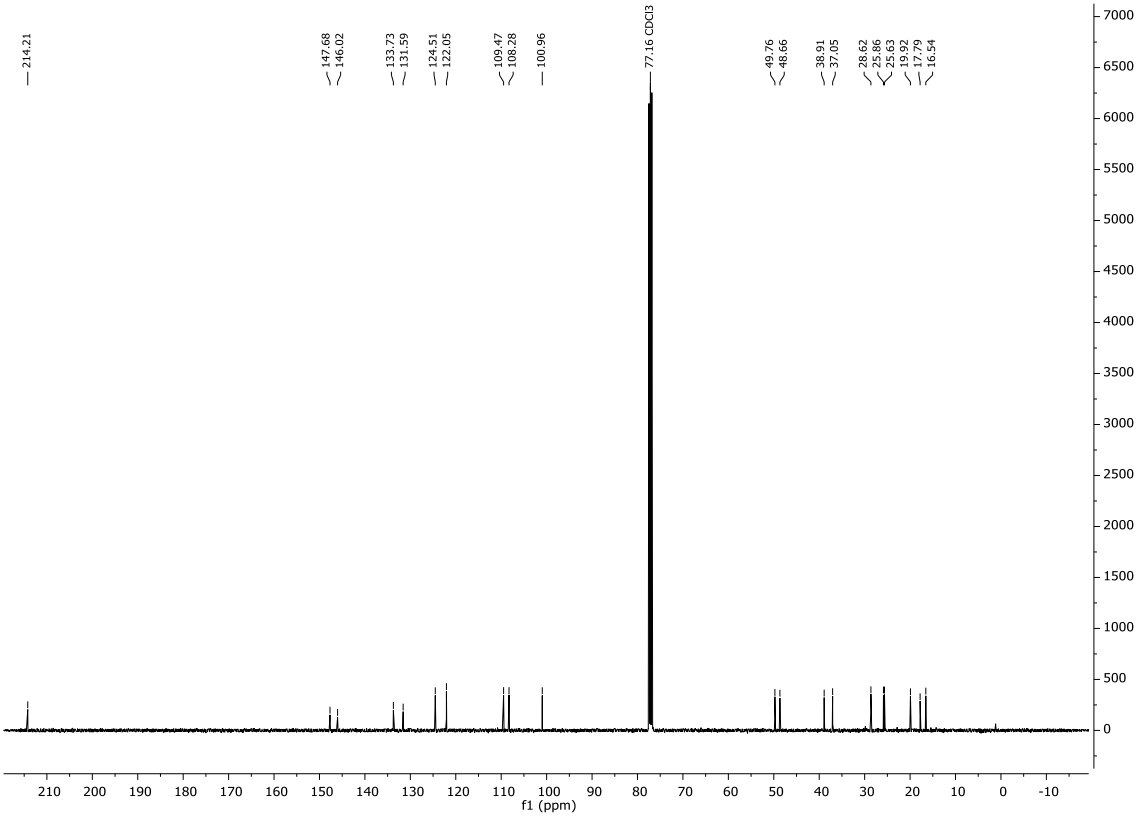

7.26 CDCl3
2.00
1.99
3.07
2.06
1.09
0.87
3.16
6.67
3.15
f1 (ppm)

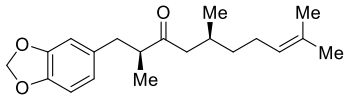

217.50
158.09
132.26
130.10
113.82
77.16 CDCl3
55.38
50.65
46.89
38.58
28.39
28.14
25.96
25.79
25.78
17.10
f1 (ppm)


O
Me
Me
Me
O
O
Me

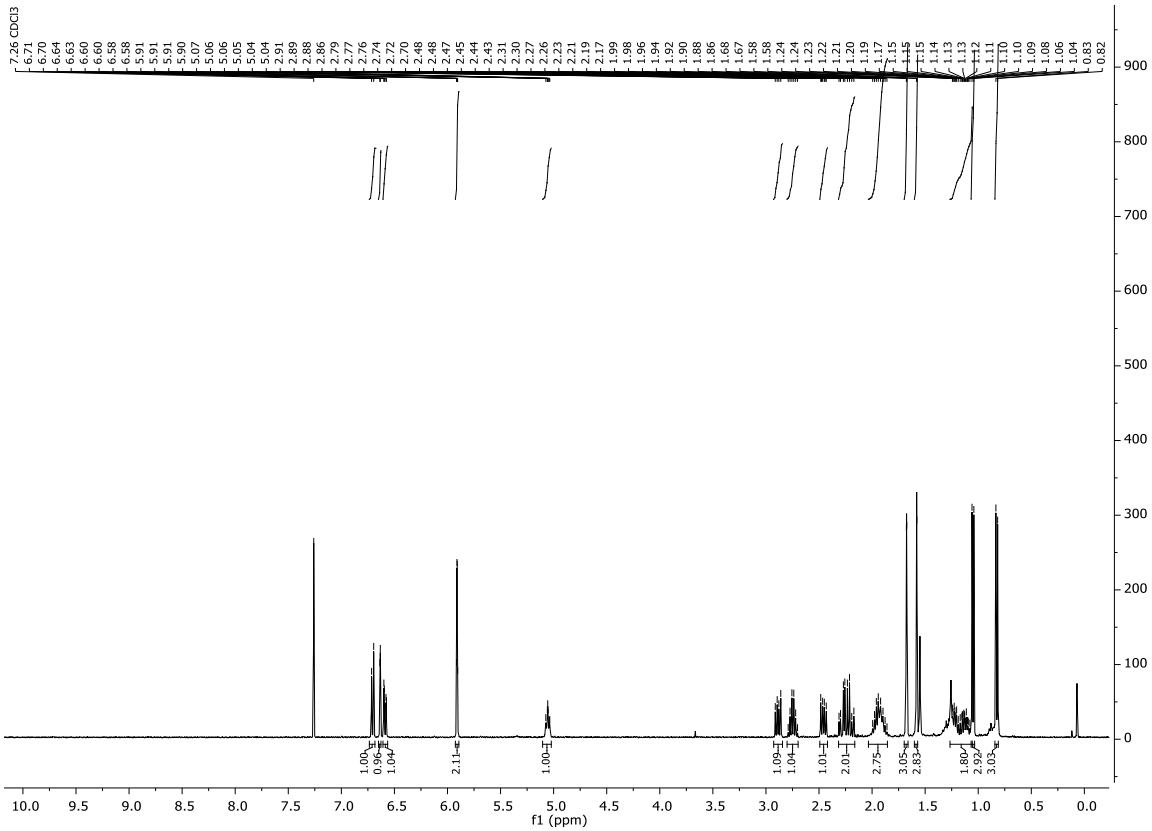
(2*R*,5*S*)-4h

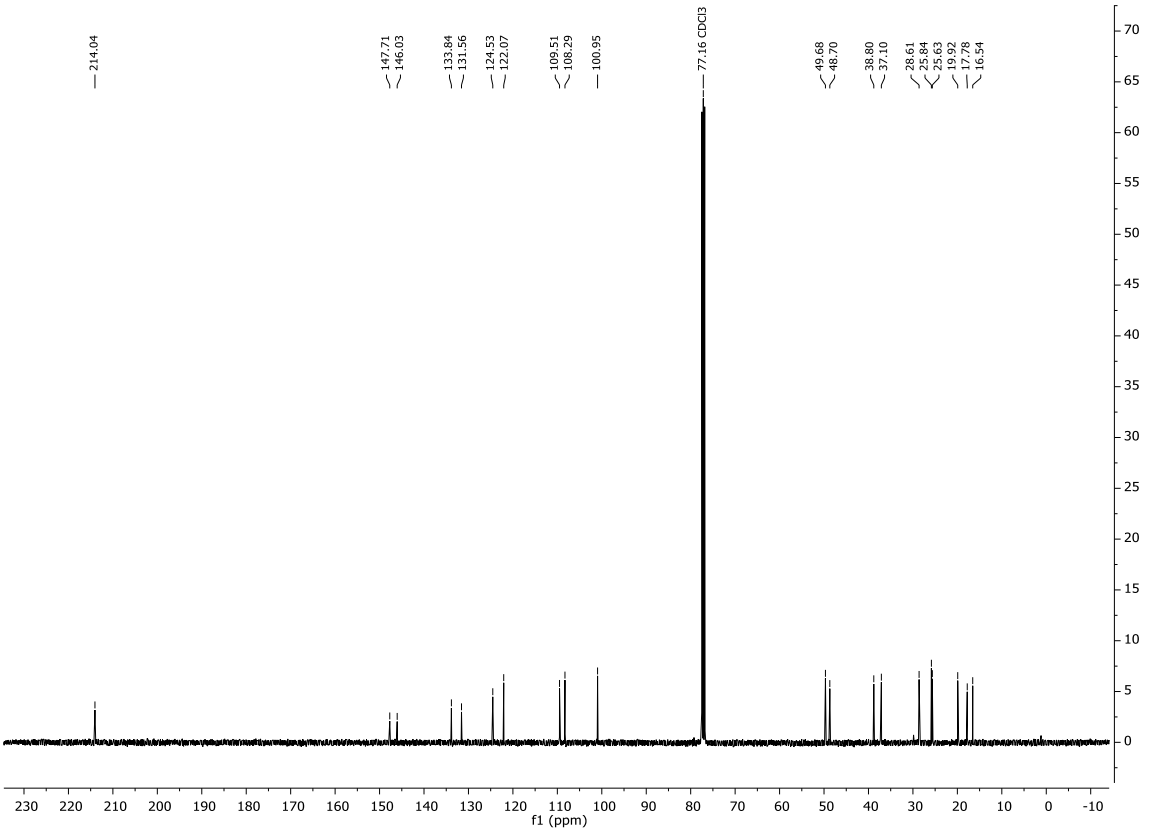

7.26 CDCl3
f1 (ppm)

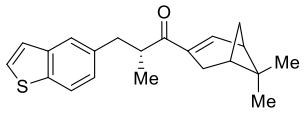

214.21
147.68
146.02
133.73
131.59
124.51
122.05
109.47
108.28
100.96
77.16 CDCl3
49.76
48.66
38.91
37.05
28.62
25.86
25.63
19.92
17.79
16.54
f1 (ppm)


O
Me
Me
Me
O
O
Me

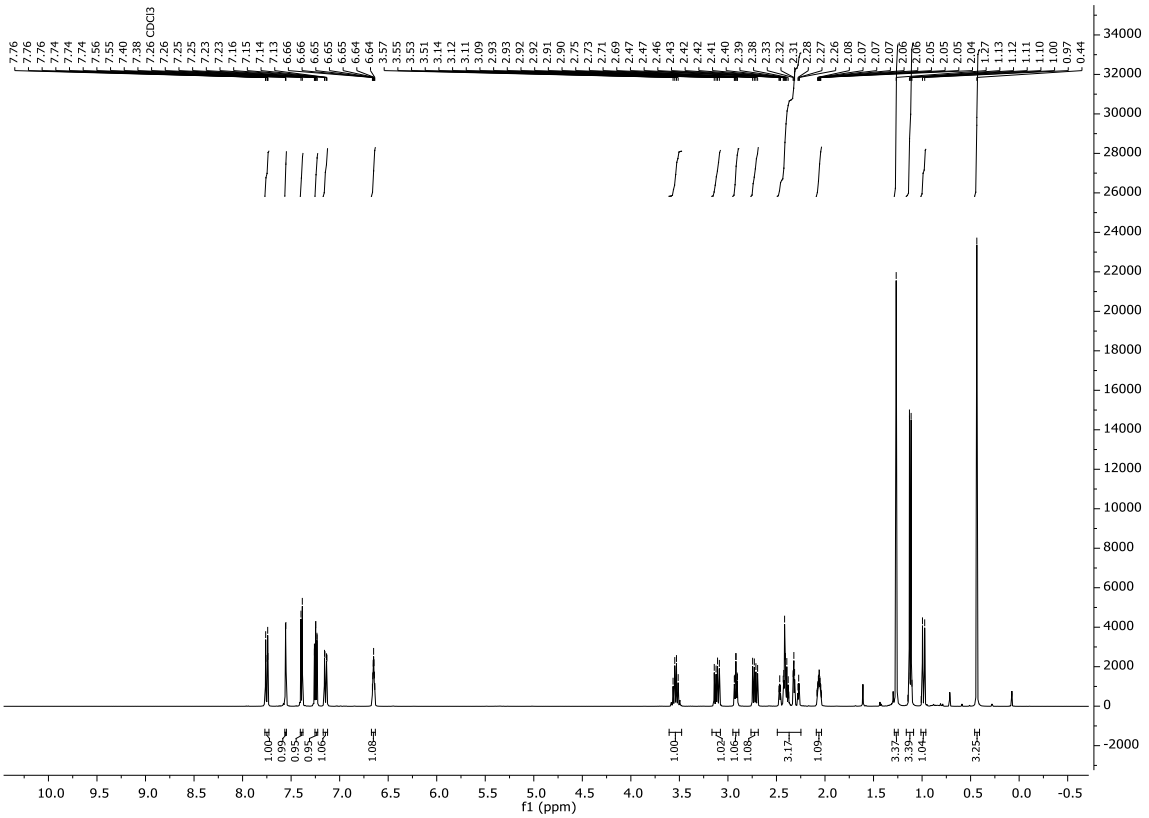
(2*S*,5*S*)-4h

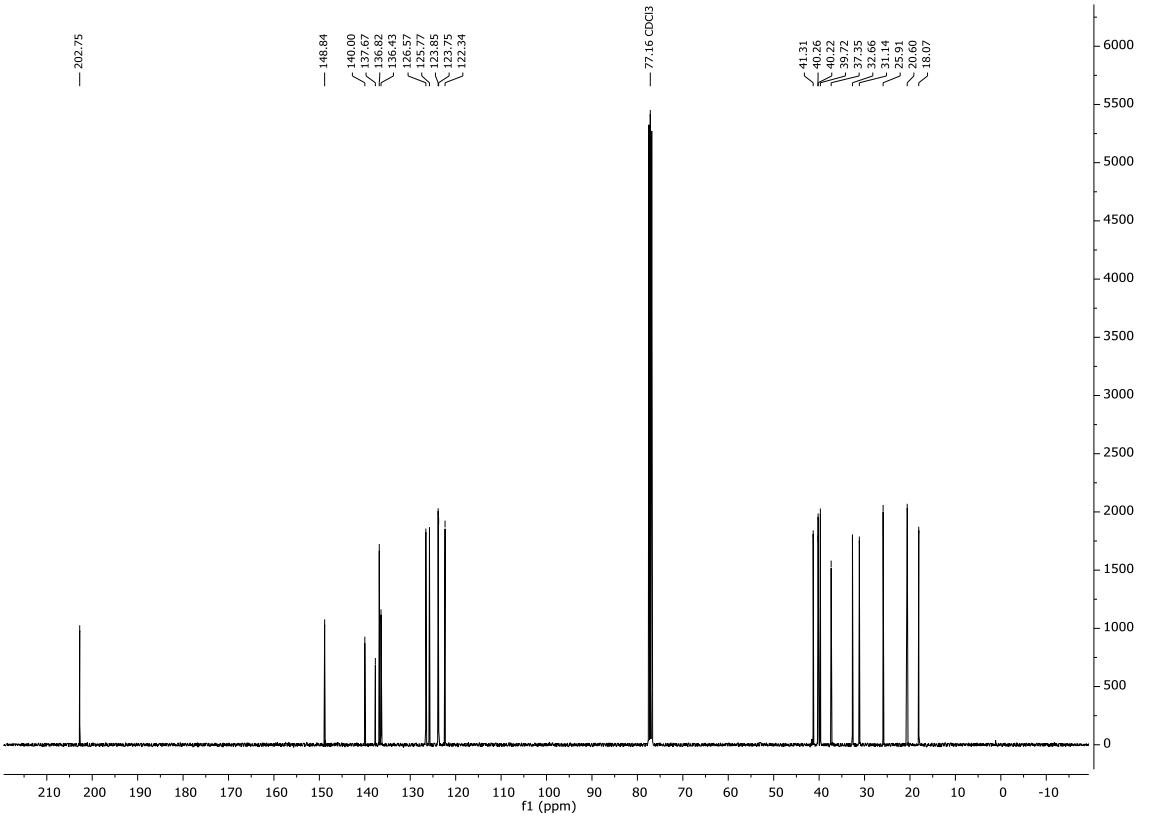

7.26 CDCl3
6.71
6.70
6.64
6.63
6.60
6.60
6.58
6.58
5.91
5.91
5.91
5.90
5.07
5.06
5.06
5.05
5.04
5.04
2.91
2.89
2.88
2.86
2.79
2.77
2.76
2.74
2.72
2.70
2.48
2.48
2.47
2.45
2.44
2.43
2.31
2.30
2.27
2.26
2.23
2.21
2.19
2.17
1.99
1.98
1.96
1.94
1.92
1.90
1.88
1.86
1.68
1.67
1.58
1.58
1.24
1.24
1.23
1.22
1.21
1.20
1.19
1.17
1.15
1.15
1.14
1.13
1.13
1.12
1.11
1.10
1.10
1.09
1.08
1.06
1.04
0.83
0.82
1.00
0.96
1.04
2.11
1.00
1.09
1.04
1.01
2.01
2.75
3.05
2.83
1.80
2.92
3.03
f1 (ppm)

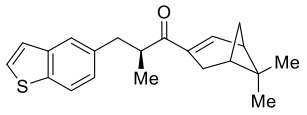

214.04
147.71
146.03
133.84
131.56
124.53
122.07
109.51
108.29
100.95
77.16 CDCl3
49.68
48.70
38.80
37.10
28.61
25.84
25.63
19.92
17.78
16.54
f1 (ppm)


O
S
Me
Me
Me

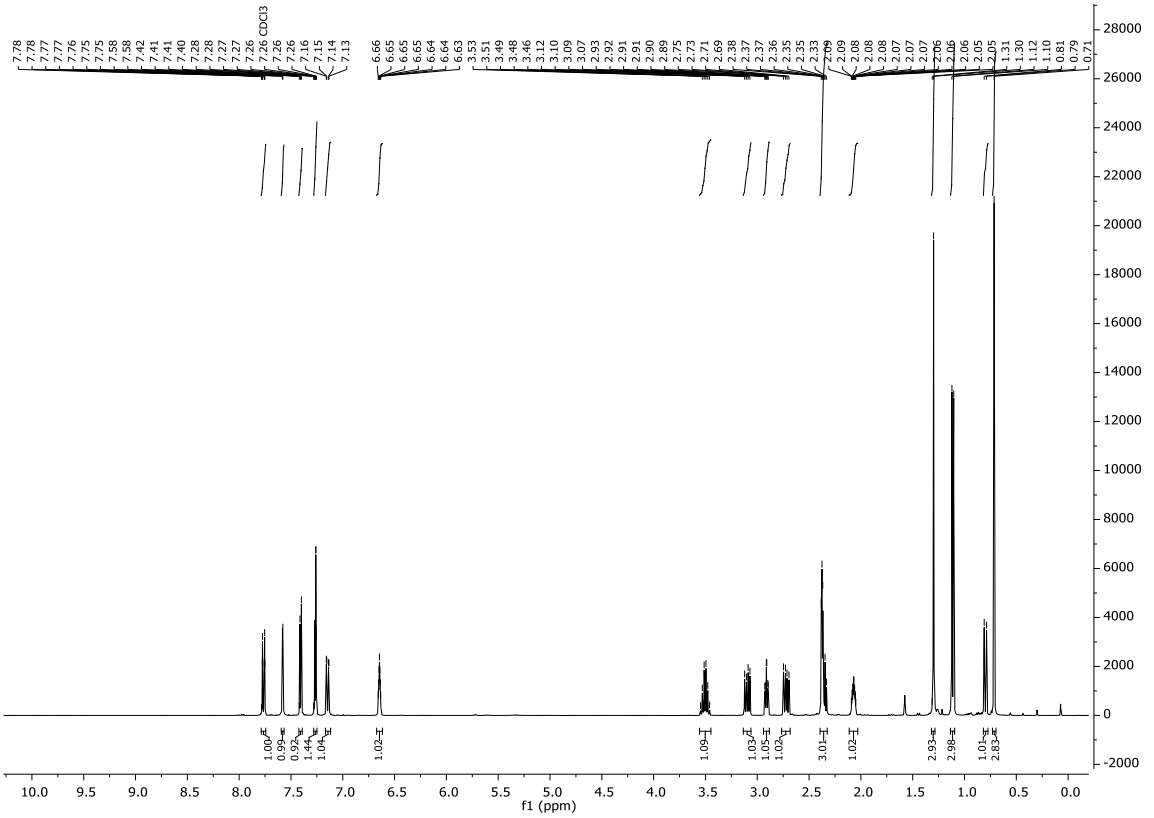
(2*R*,1'*R*,5'*S*)-**4i**

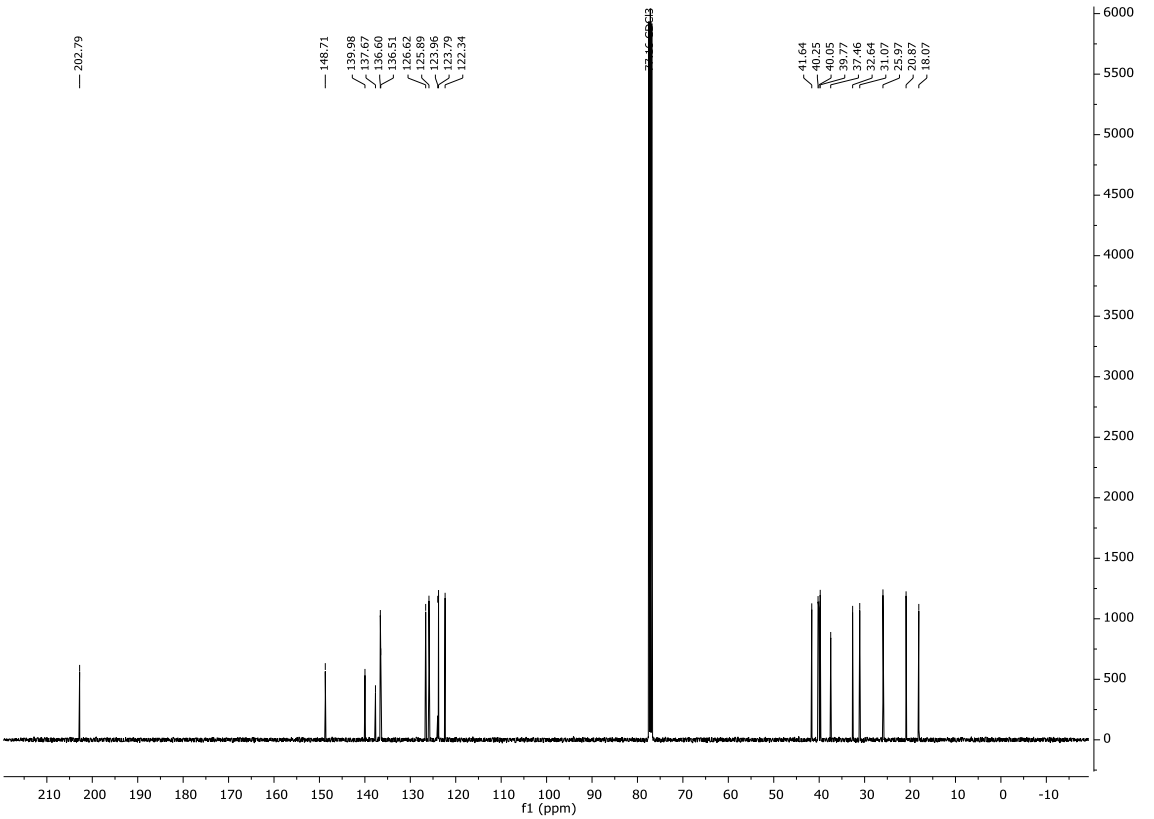

7.76
7.76
7.76
7.74
7.74
7.56
7.55
7.40
7.38
7.26 CDCl3
7.26
7.25
7.25
7.23
7.23
7.16
7.15
7.14
7.13
6.66
6.66
6.65
6.65
6.65
6.64
6.64
3.57
3.55
3.53
3.51
3.14
3.12
3.11
3.09
2.93
2.93
2.92
2.92
2.91
2.90
2.75
2.73
2.71
2.69
2.47
2.47
2.46
2.43
2.42
2.42
2.41
2.40
2.39
2.38
2.33
2.32
2.31
2.28
2.27
2.26
2.08
2.07
2.07
2.07
2.06
2.06
2.05
2.05
2.05
2.04
1.27
1.13
1.12
1.11
1.10
1.00
0.97
0.44
1.00
0.99
0.95
0.95
1.06
1.08
1.00
1.02
1.06
1.08
3.17
1.09
3.37
3.39
1.04
3.25
f1 (ppm)

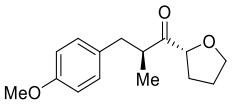

202.75
148.84
140.00
137.67
136.82
136.43
126.57
125.77
123.85
123.75
122.34
77.16 CDCl3
41.31
40.26
40.22
39.72
37.35
32.66
31.14
25.91
20.60
18.07
f1 (ppm)


O
Me
Me
Me
S

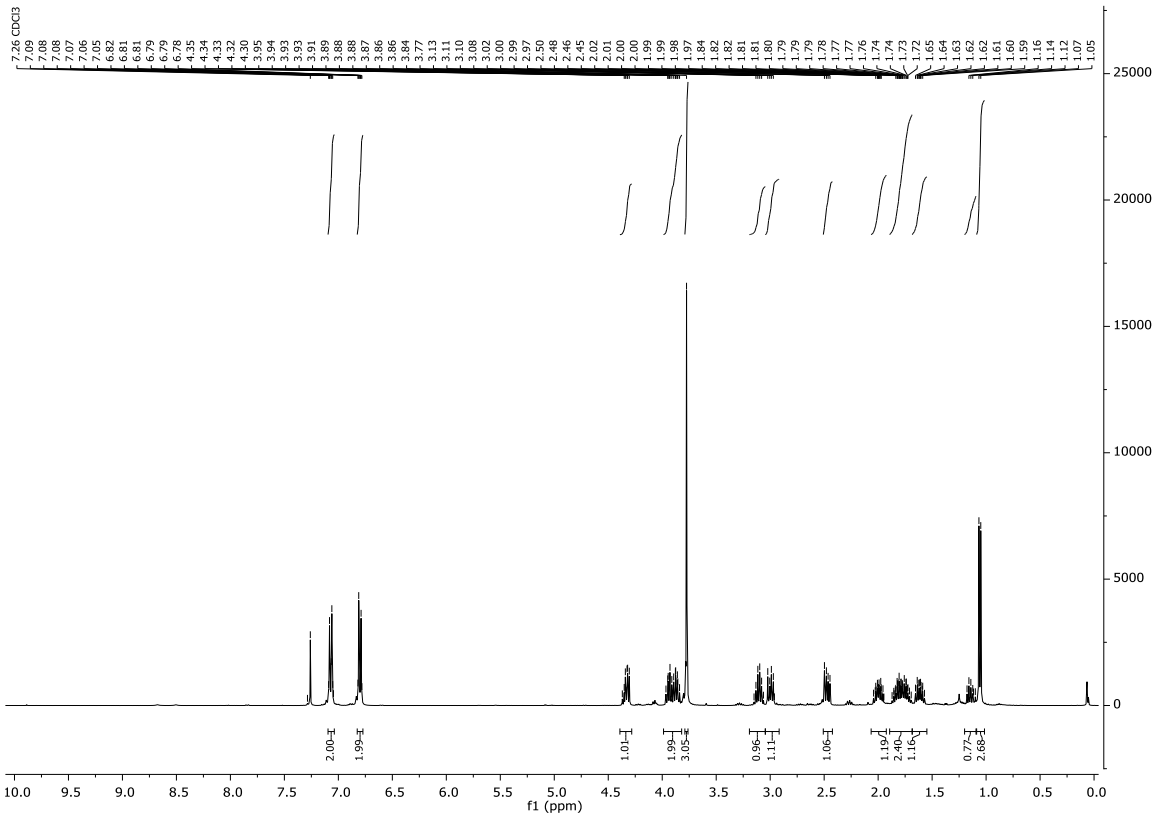
(2*S*,1'*R*,5'*S*)-**4i**

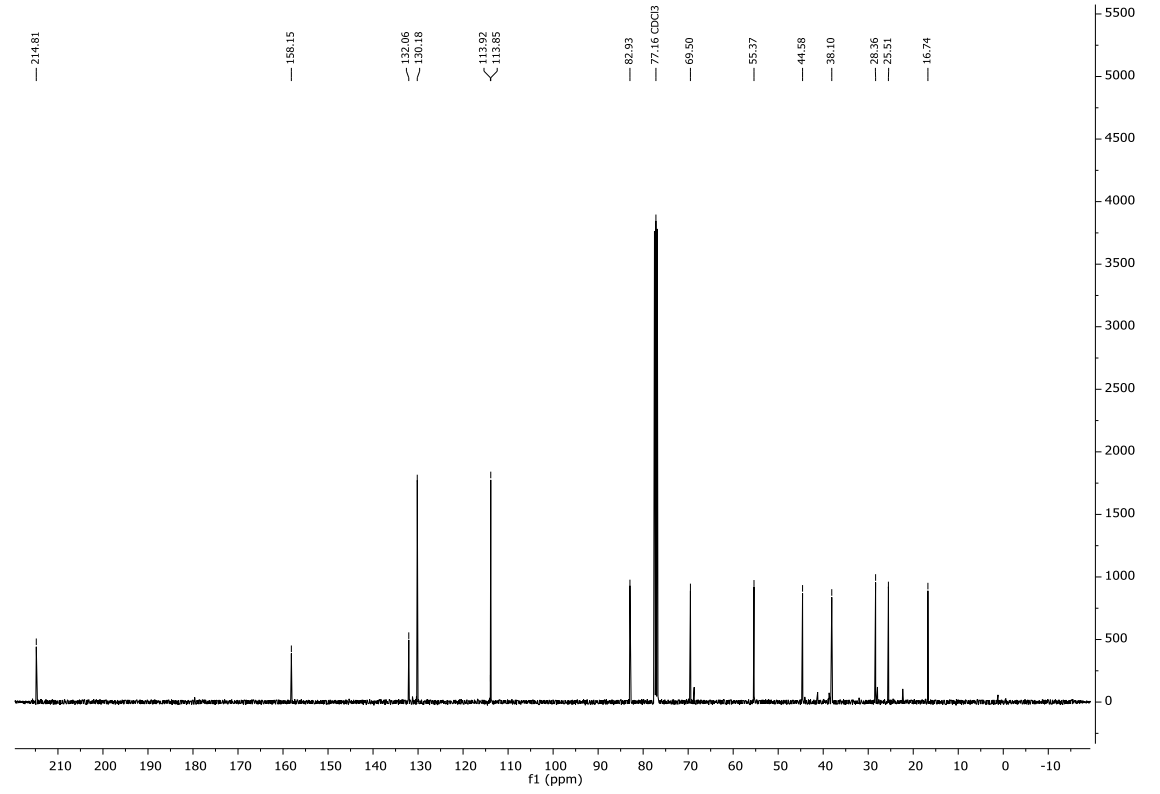

7.78 7.78 7.77 7.77 7.77 7.76 7.75 7.75 7.58 7.58 7.42 7.41 7.41 7.40 7.28 7.28 7.27 7.27 7.26 7.26 CDCl3 7.26 7.26 7.16 7.15 7.14 7.13
6.66 6.65 6.65 6.65 6.64 6.64 6.63 3.53 3.51 3.49 3.48 3.46 3.12 3.10 3.09 3.07 2.93 2.92 2.91 2.91 2.90 2.89 2.75 2.73 2.71 2.69 2.38 2.37 2.37 2.36 2.35 2.35 2.33 2.09 2.09 2.08 2.08 2.08 2.07 2.07 2.07 2.06 2.06 2.06 2.05 2.05 1.31 1.30 1.12 1.10 0.81 0.79 0.71
1.00 0.99 0.92 1.44 1.04 1.02 1.09 1.03 1.05 1.02 3.01 1.02 2.93 2.98 1.01 2.83
f1 (ppm)

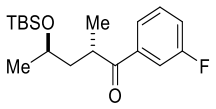

202.79 148.71 139.98 137.67 136.60 136.51 126.62 125.89 123.96 123.79 122.34 77.16 CDCl3 41.64 40.25 40.05 39.77 37.46 32.64 31.07 25.97 20.87 18.07
f1 (ppm)


O
O
Me
MeO

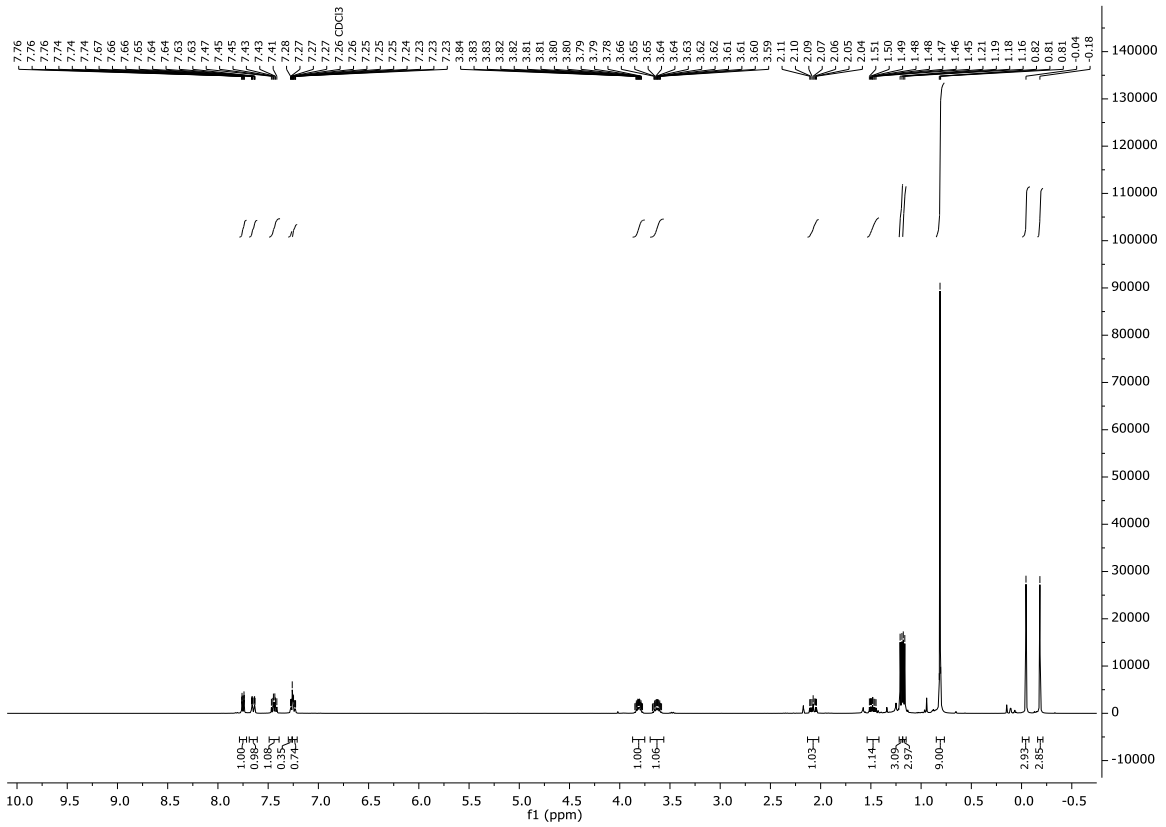
(2*R*,2'*S*)-**4j**

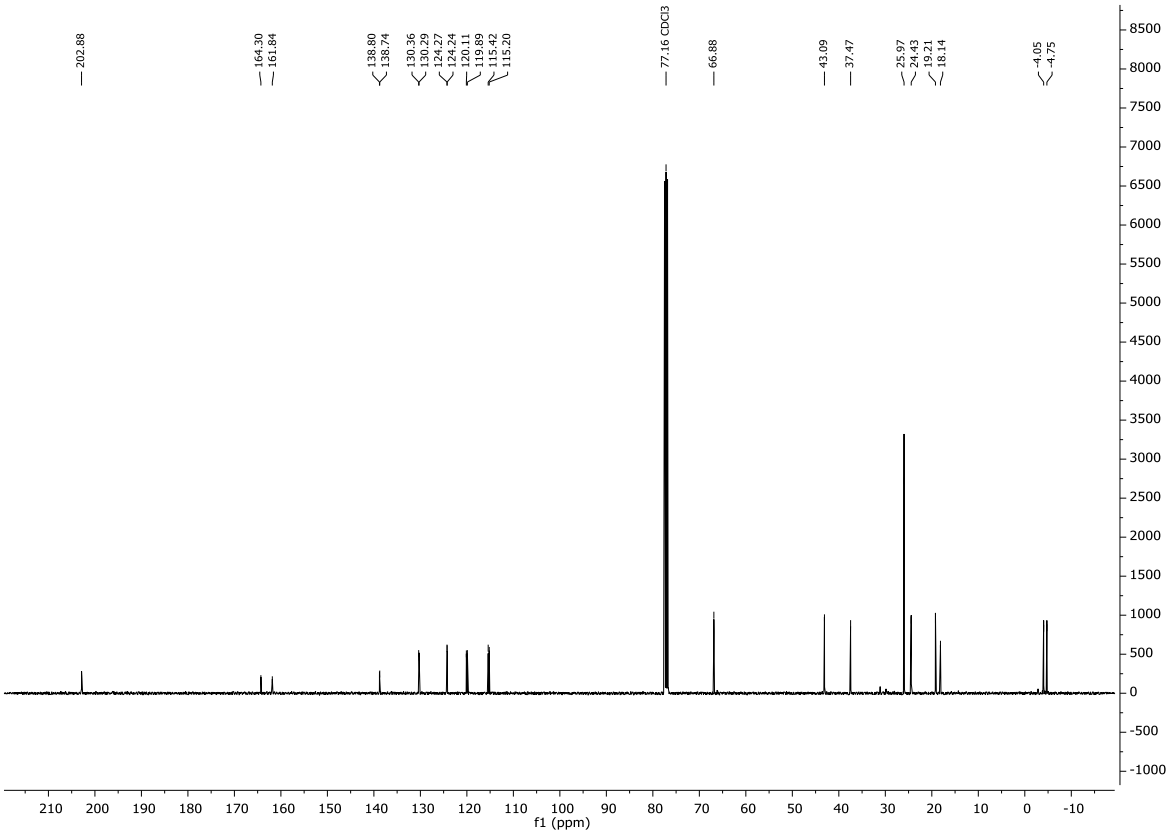

7.26 CDCl3
2.00
1.99
1.01
1.99
3.05
0.96
1.11
1.06
1.19
2.40
1.16
0.77
2.68
f1 (ppm)

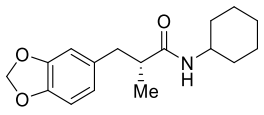

214.81
158.15
132.06
130.18
113.92
113.85
82.93
77.16 CDCl3
69.50
55.37
44.58
38.10
28.36
25.51
16.74
f1 (ppm)


TBSO
Me
Me
F
O

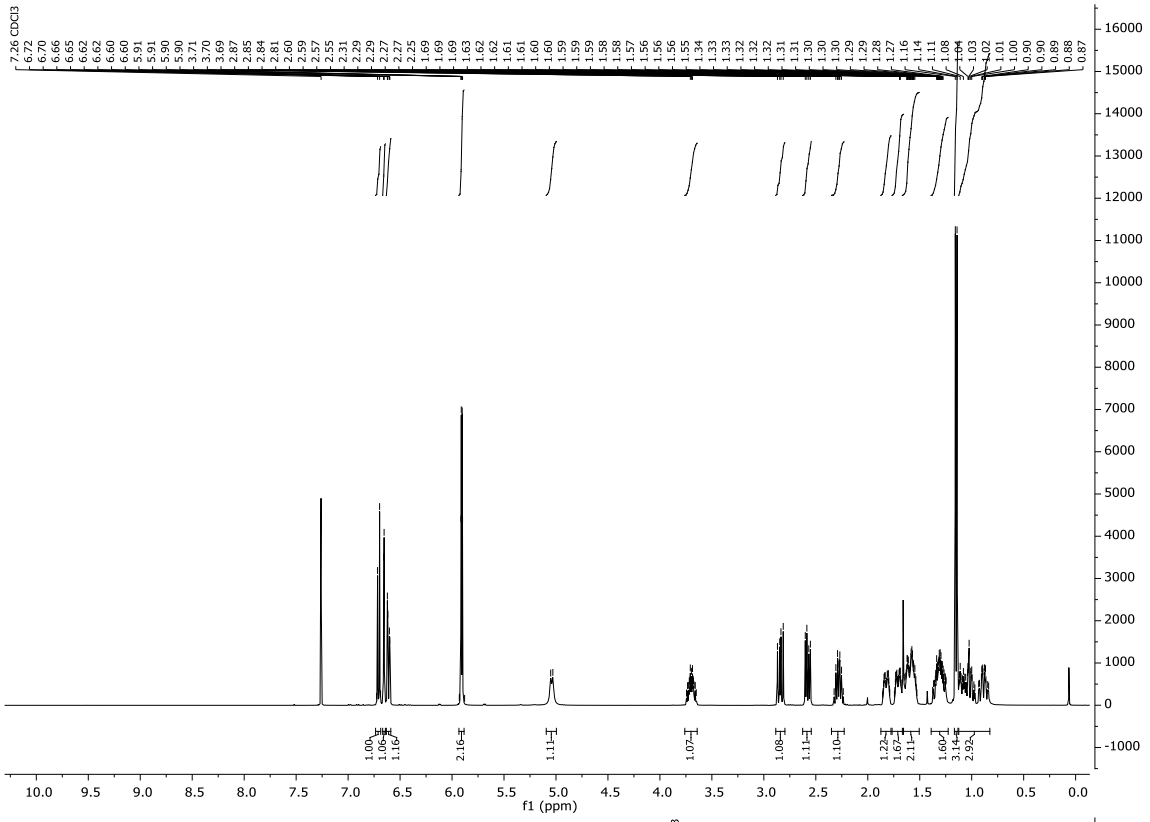
anti-**4k**

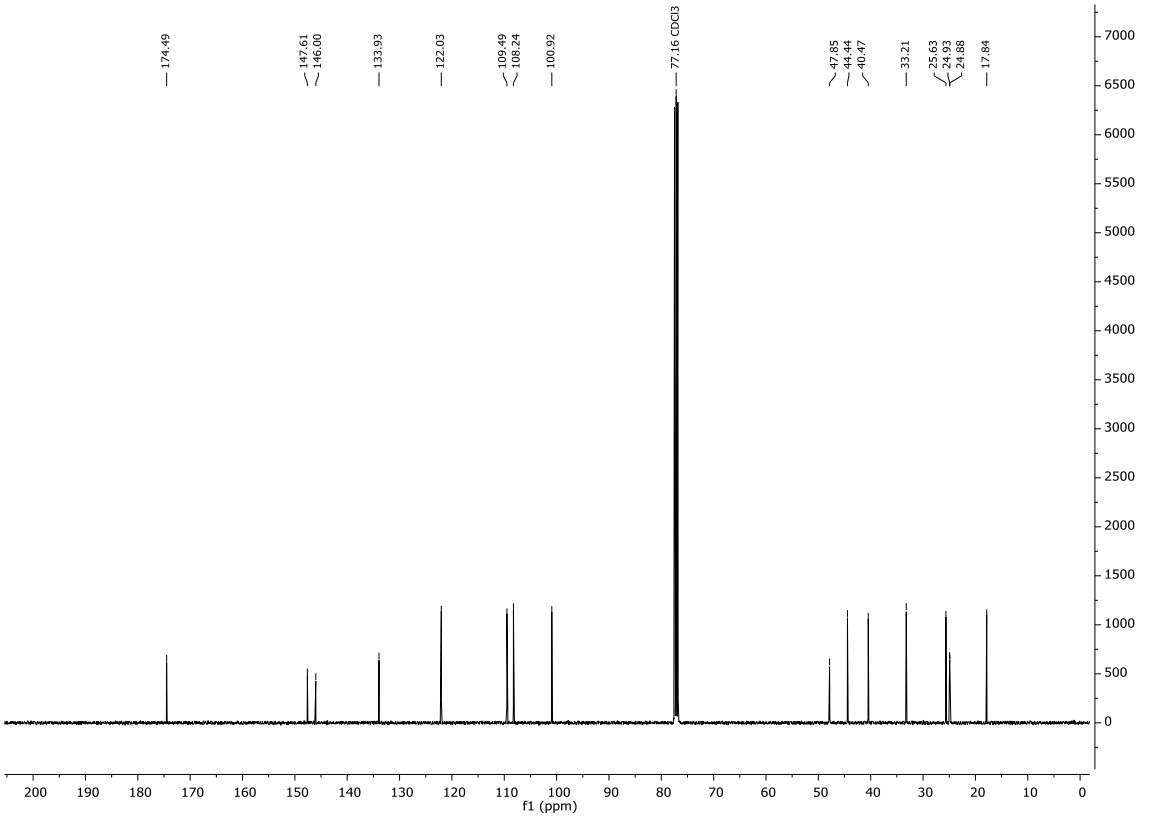

f1 (ppm)

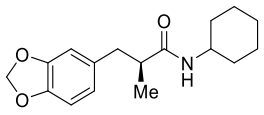

202.88
164.30
161.84
138.80
138.74
130.36
130.29
124.27
124.24
120.11
119.89
115.42
115.20
77.16 CDCl3
66.88
43.09
37.47
25.97
24.43
19.21
18.14
-4.05
-4.75
f1 (ppm)


O
O
O
N
H
Me

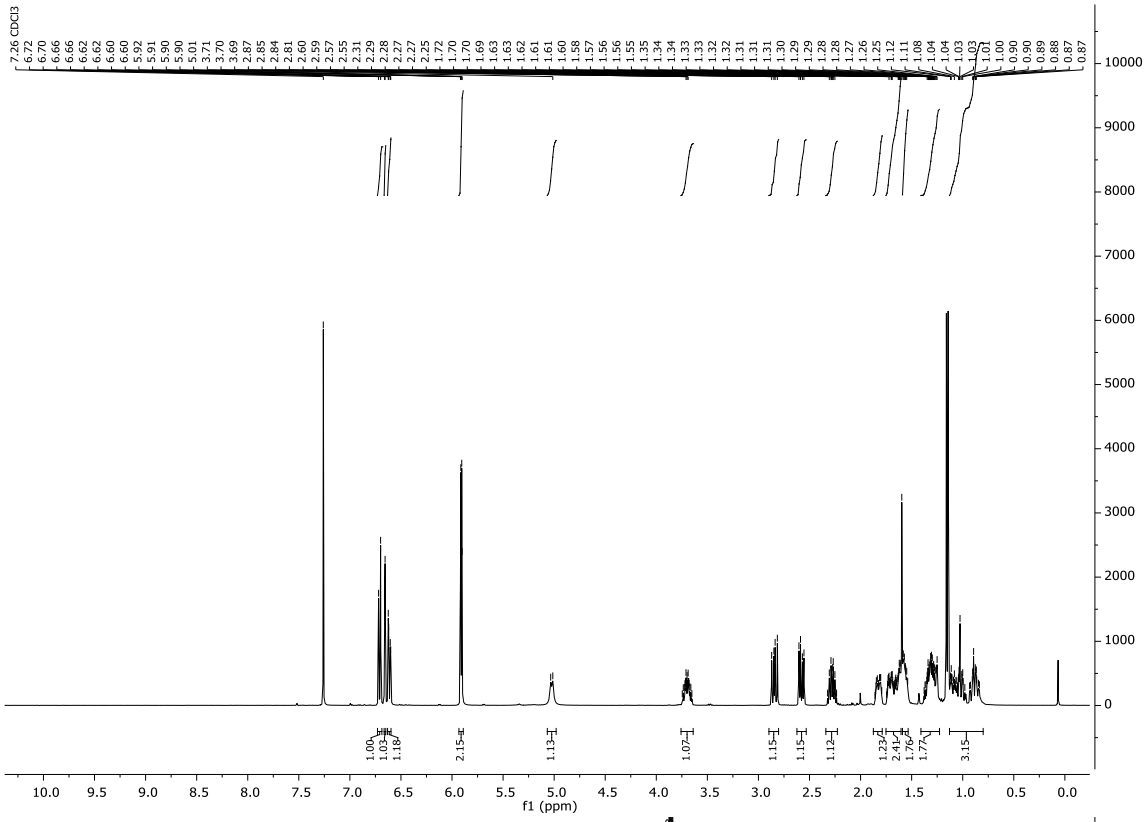
(*R*)-**4l**

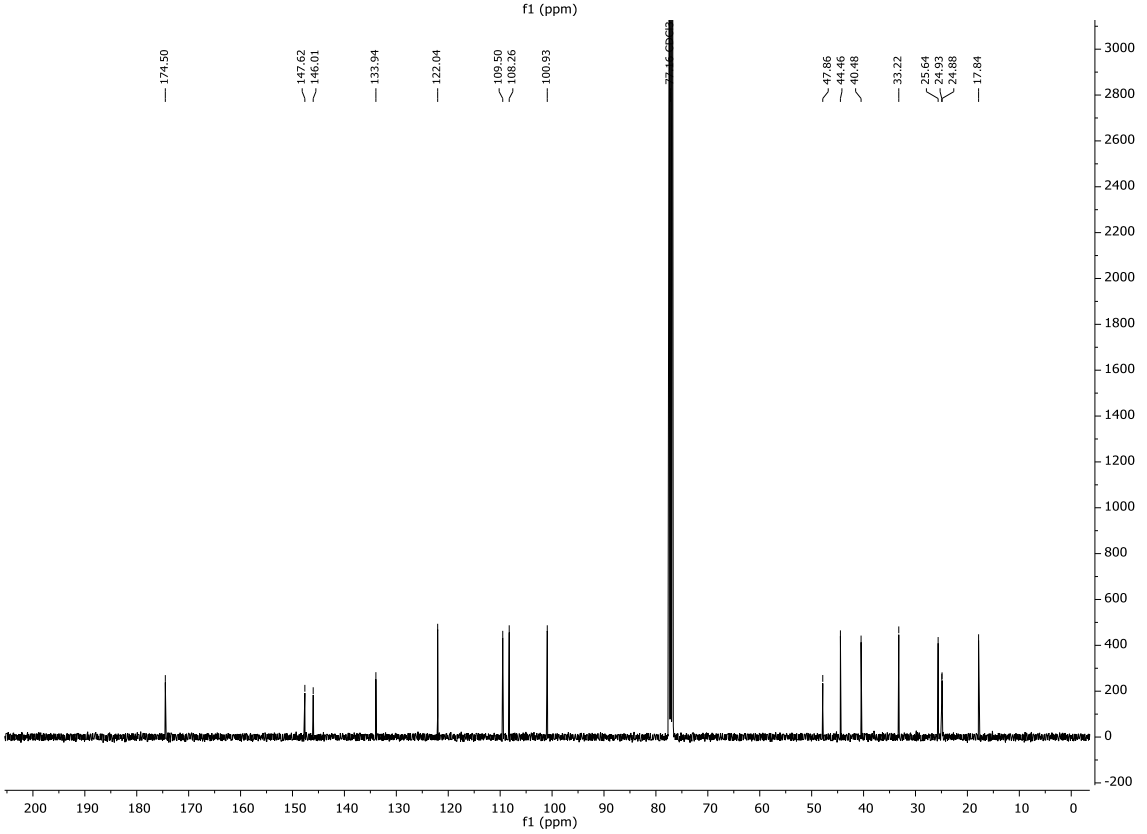

7.26 CDCl3
6.72
6.70
6.66
6.65
6.62
6.62
6.60
6.60
5.91
5.91
5.90
5.90
3.71
3.70
3.69
2.87
2.85
2.84
2.81
2.60
2.59
2.57
2.55
2.31
2.29
2.29
2.27
2.27
2.25
1.69
1.69
1.69
1.63
1.62
1.62
1.61
1.61
1.60
1.60
1.59
1.59
1.58
1.58
1.57
1.56
1.56
1.56
1.55
1.34
1.33
1.33
1.32
1.32
1.32
1.31
1.31
1.30
1.30
1.30
1.29
1.29
1.28
1.27
1.16
1.14
1.11
1.08
1.04
1.03
1.02
1.01
1.00
0.90
0.90
0.89
0.88
0.87
1.00
1.06
1.16
2.16
1.11
1.07
1.08
1.11
1.10
1.22
1.67
2.11
1.60
3.14
2.92
f1 (ppm)

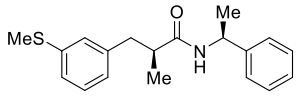

174.49
147.61
146.00
133.93
122.03
109.49
108.24
100.92
77.16 CDCl3
47.85
44.44
40.47
33.21
25.63
24.93
24.88
17.84
f1 (ppm)


O
O
O
N
H
Me

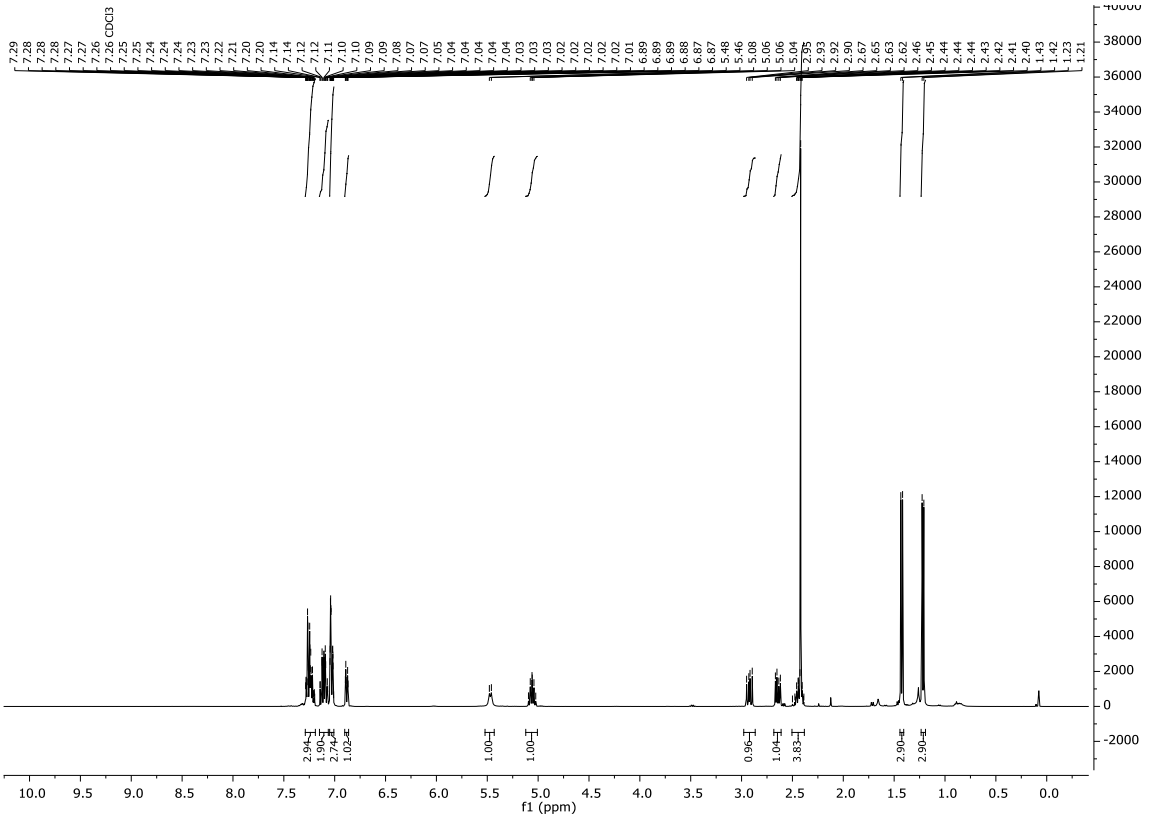
(*S*)-**4l**

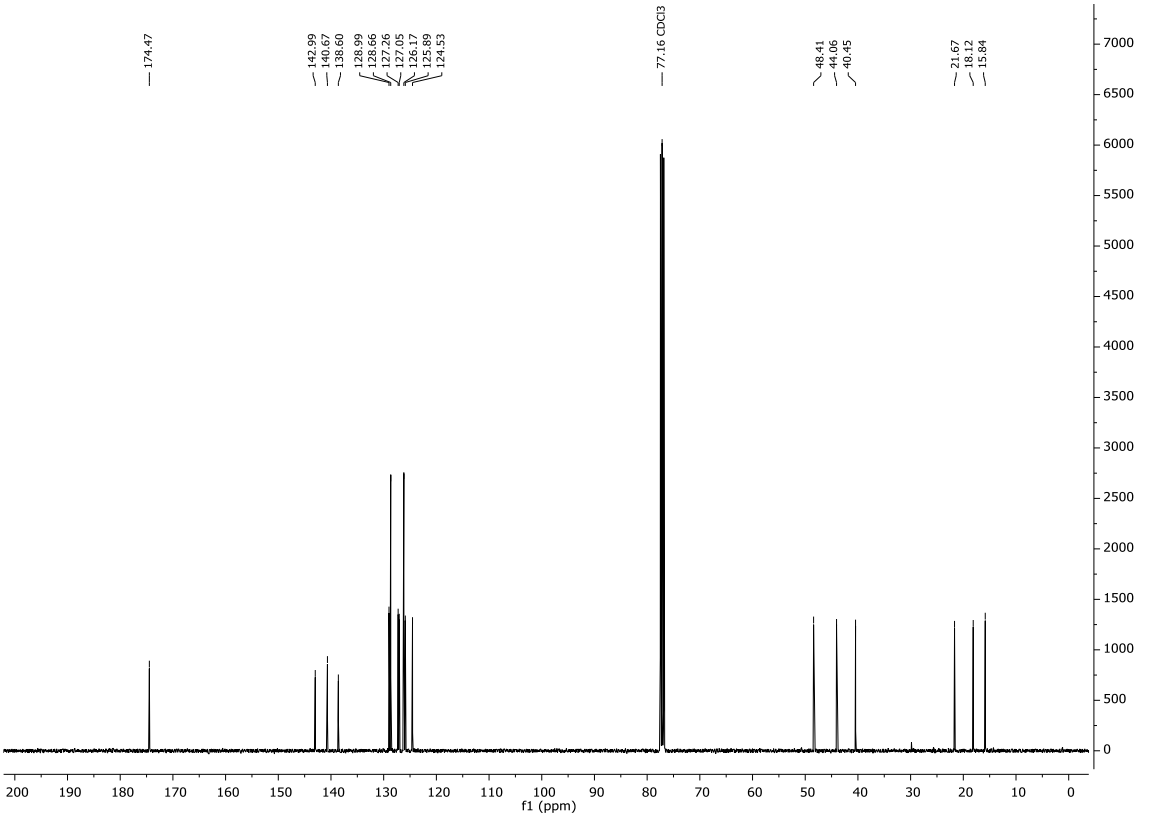

7.26 CDCl3
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.00
1.03
1.18
2.15
1.13
1.07
1.15
1.15
1.12
1.23
2.41
1.76
1.77
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

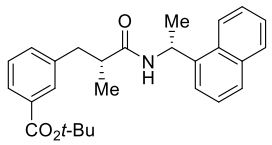

174.50
147.62
146.01
133.94
122.04
109.50
108.26
100.93
77.16 CDCl3
47.86
44.46
40.48
33.22
25.64
24.93
24.88
17.84
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeS
O
Me
N
H
Me

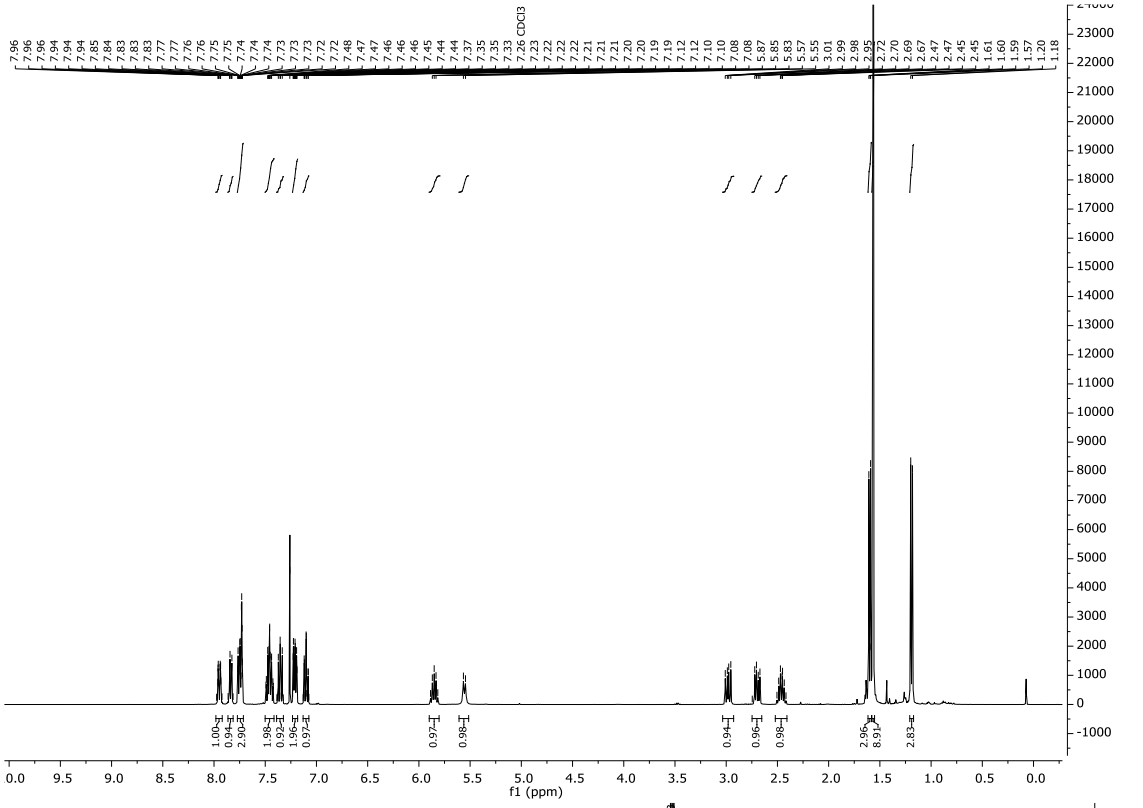
(2*S*,1'*S*)-**4m**

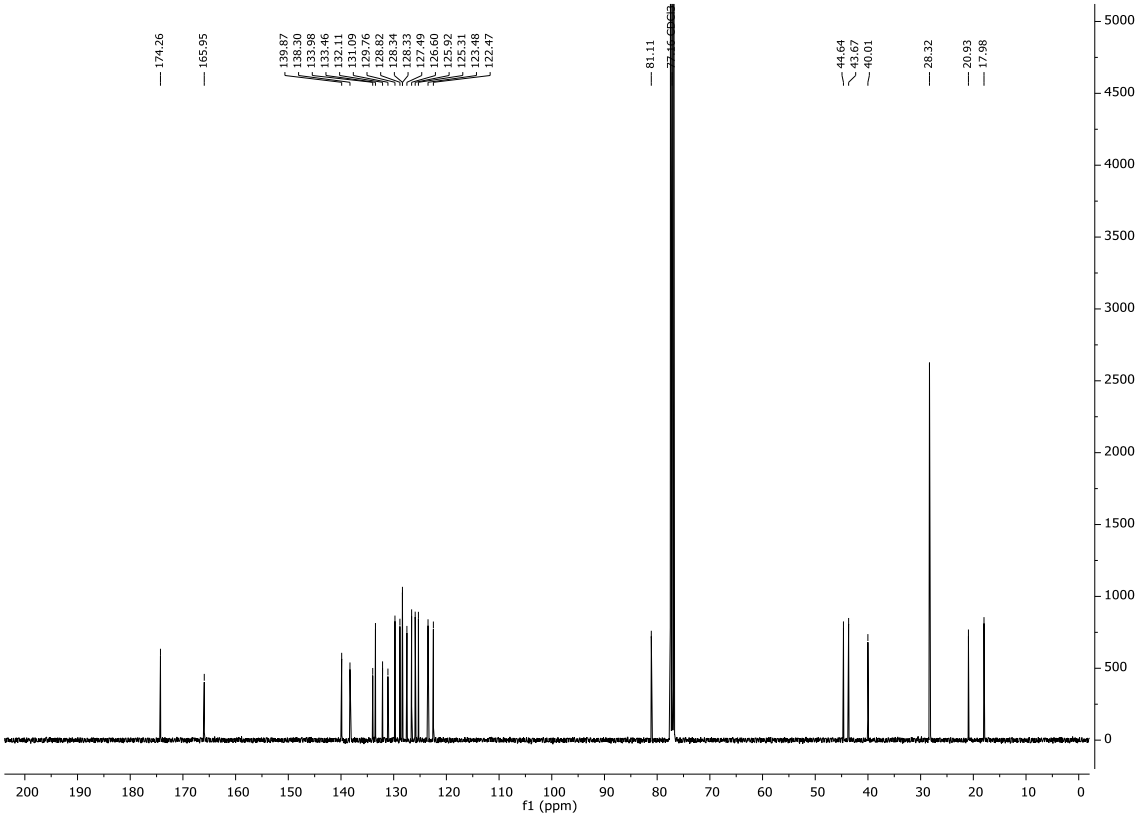

7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 CDCl3 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.21 7.20 7.20 7.14 7.12 7.12 7.11 7.10 7.10 7.09 7.09 7.08 7.07 7.07 7.05 7.04 7.04 7.04 7.04 7.04 7.03 7.03 7.03 7.02 7.02 7.02 7.02 7.02 7.01 6.89 6.89 6.89 6.88 6.87 6.87 5.48 5.46 5.08 5.06 5.06 5.04 2.95 2.93 2.92 2.90 2.67 2.65 2.63 2.62 2.46 2.45 2.44 2.44 2.43 2.42 2.42 2.41 2.40 1.43 1.42 1.23 1.21
2.94 1.90 2.74 1.02 1.00 1.00 0.96 1.04 3.83 2.90 2.90
f1 (ppm)

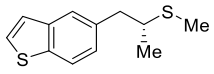

174.47
142.99 140.67 138.60 128.99 128.66 127.26 127.05 126.17 125.89 124.53
77.16 CDCl3
48.41 44.06 40.45
21.67 18.12 15.84
f1 (ppm)


O
Me
N
H
Me
CO2t-Bu

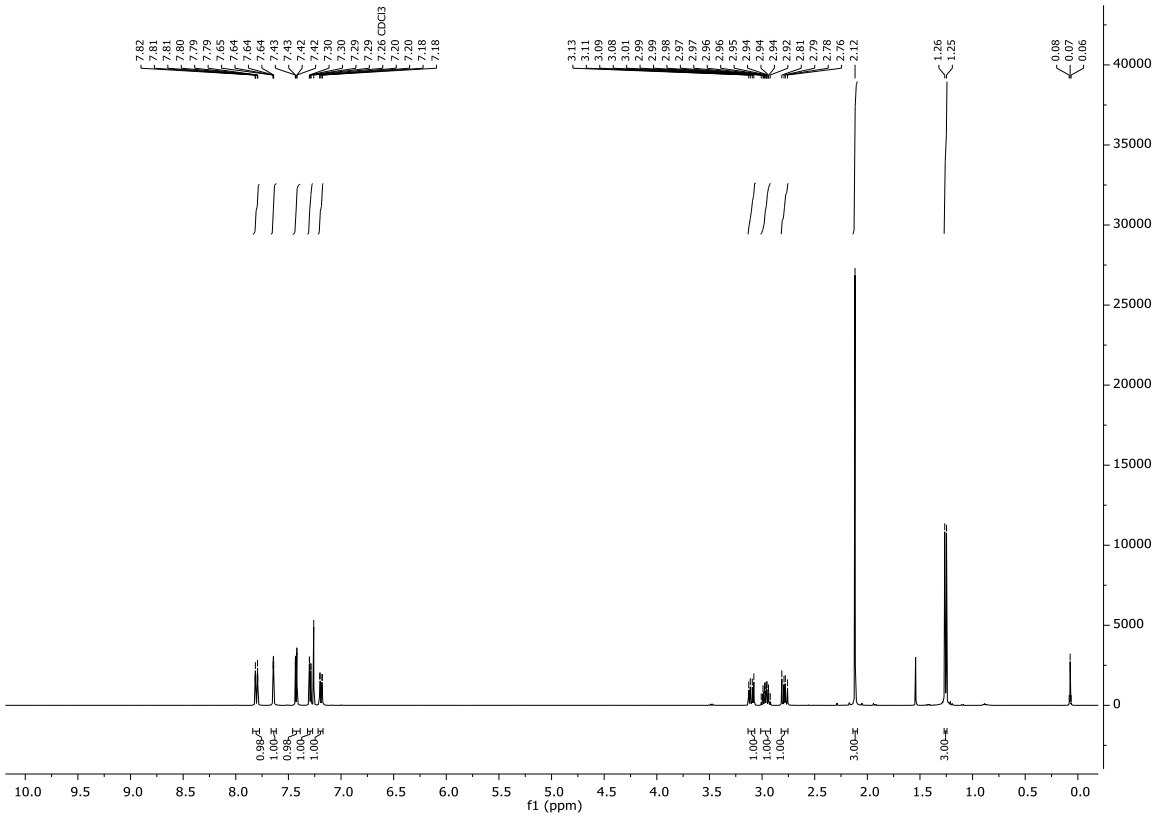
(2*R*,1'*R*)-**4n**

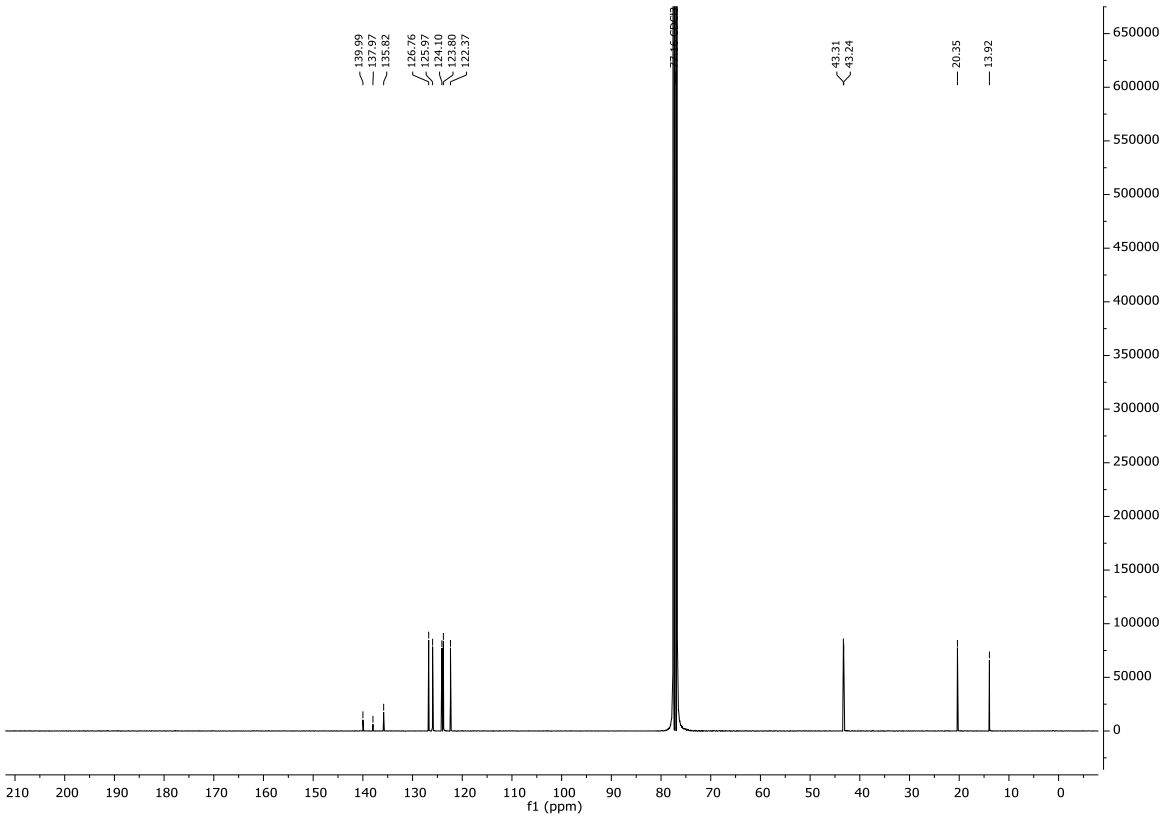

CDCl3
f1 (ppm)

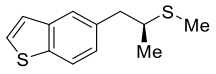

174.26
165.95
139.87
138.30
133.98
133.46
132.11
131.09
129.76
128.82
128.34
128.33
127.49
126.60
125.92
125.31
123.48
122.47
81.11
44.64
43.67
40.01
28.32
20.93
17.98
f1 (ppm)


S
Me
Me
S

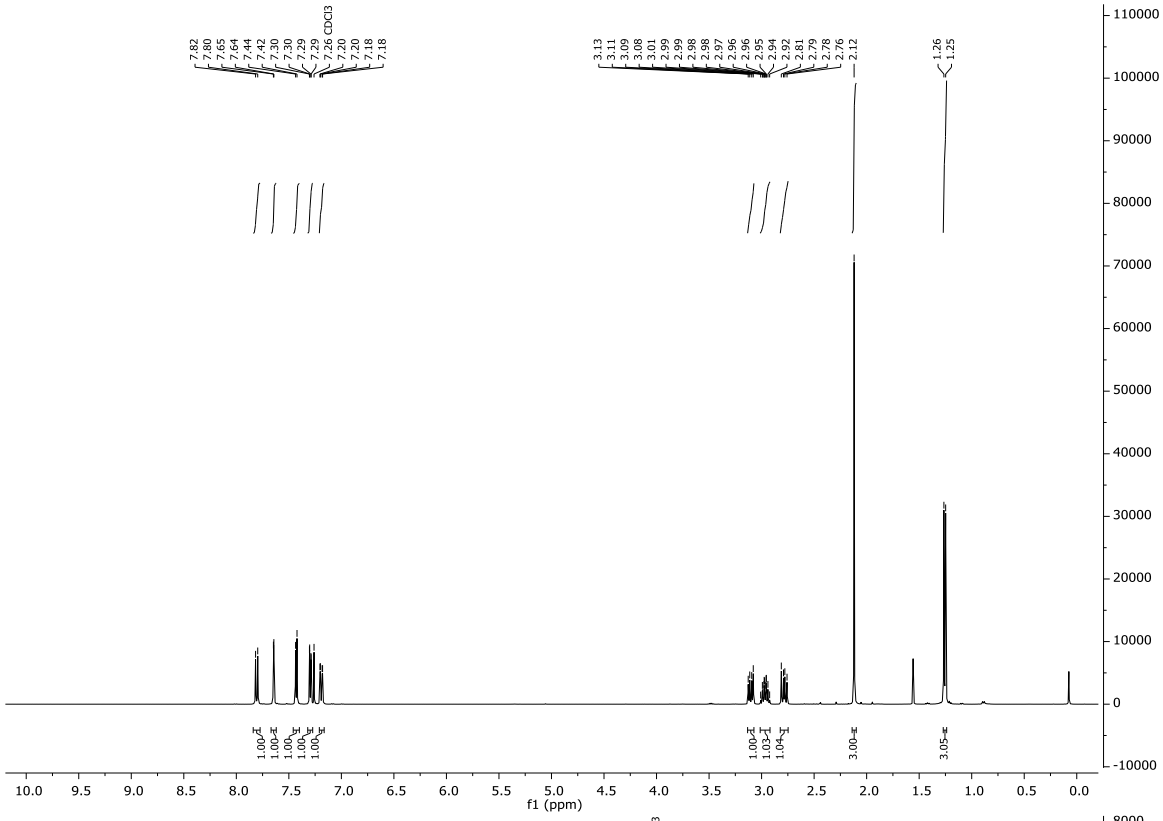
(*R*)-**4o**

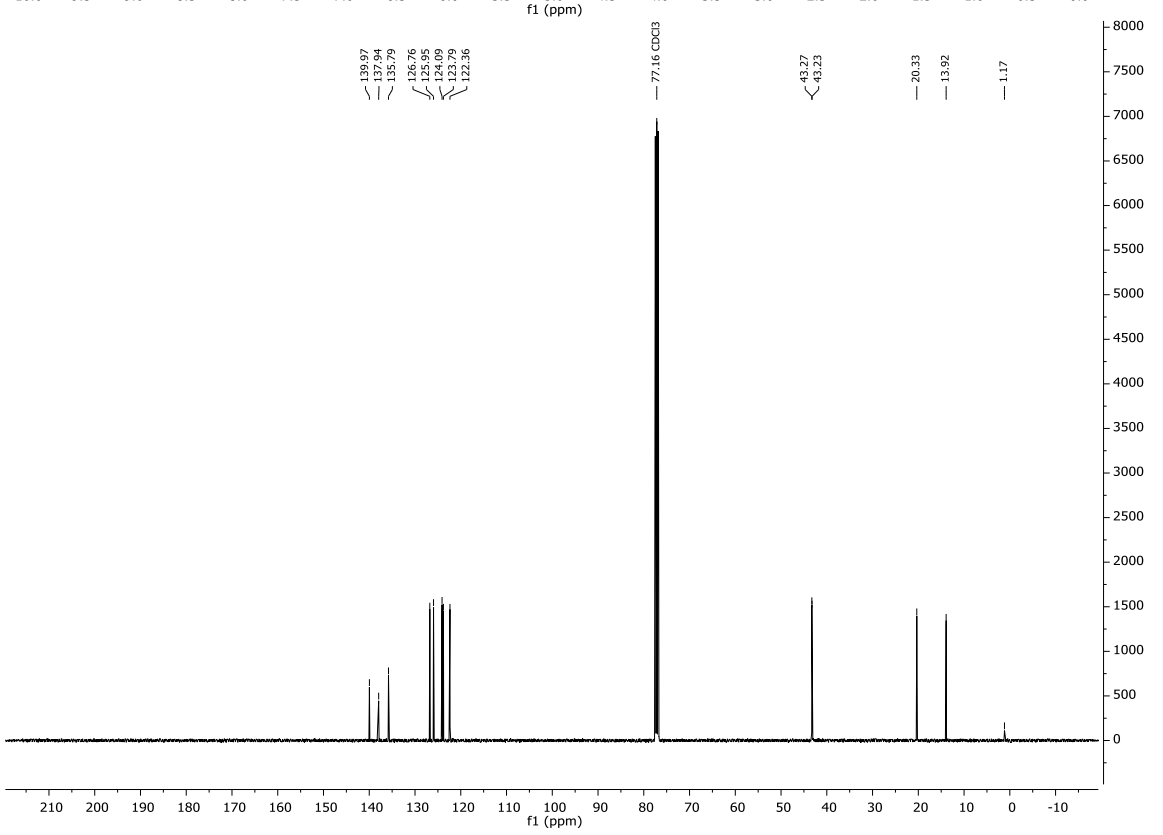

7.82
7.81
7.81
7.80
7.79
7.79
7.65
7.64
7.64
7.64
7.43
7.43
7.42
7.42
7.30
7.30
7.29
7.29
CDCl3
7.26
7.20
7.20
7.18
7.18
3.13
3.11
3.09
3.08
3.01
2.99
2.99
2.98
2.97
2.97
2.96
2.96
2.95
2.94
2.94
2.94
2.92
2.81
2.79
2.78
2.76
2.12
1.26
1.25
0.08
0.07
0.06
0.98
1.00
0.98
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

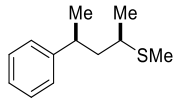

139.99
137.97
135.82
126.76
125.97
124.10
123.80
122.37
77.16
43.31
43.24
20.35
13.92
f1 (ppm)


S
Me
Me
S

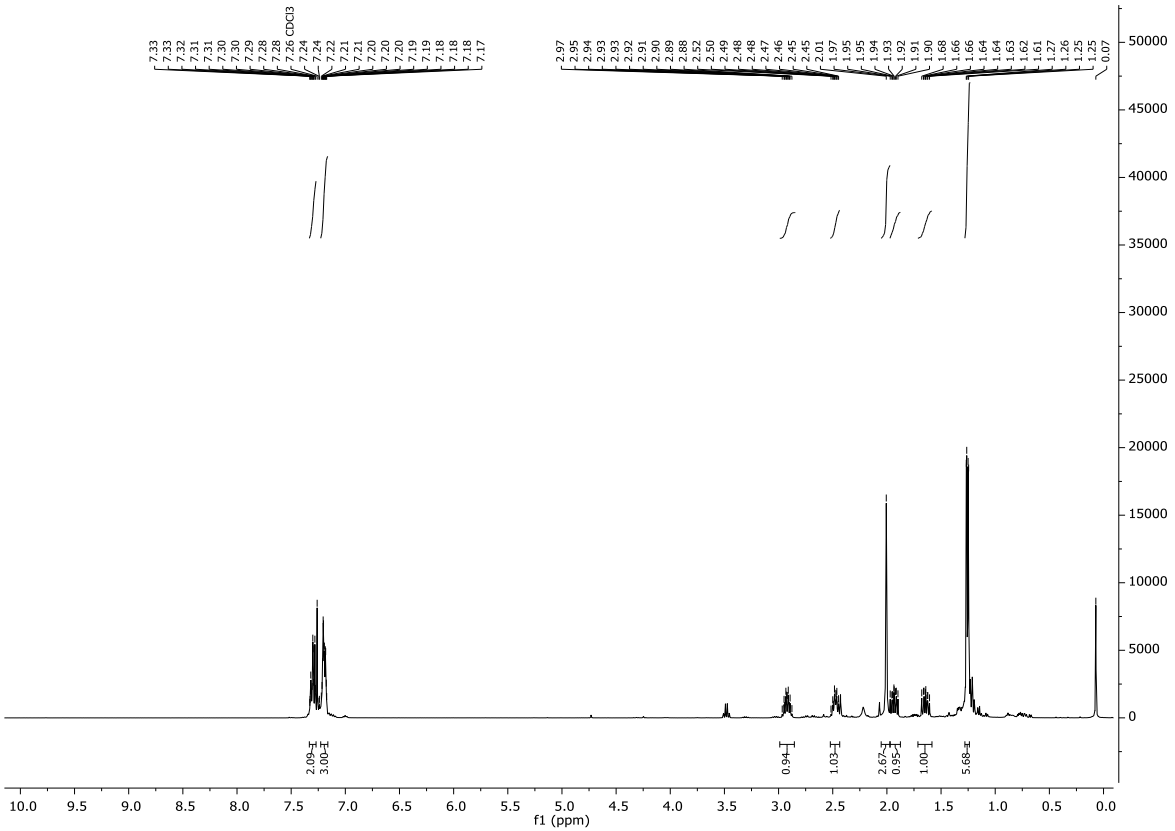
(*S*)-**4o**

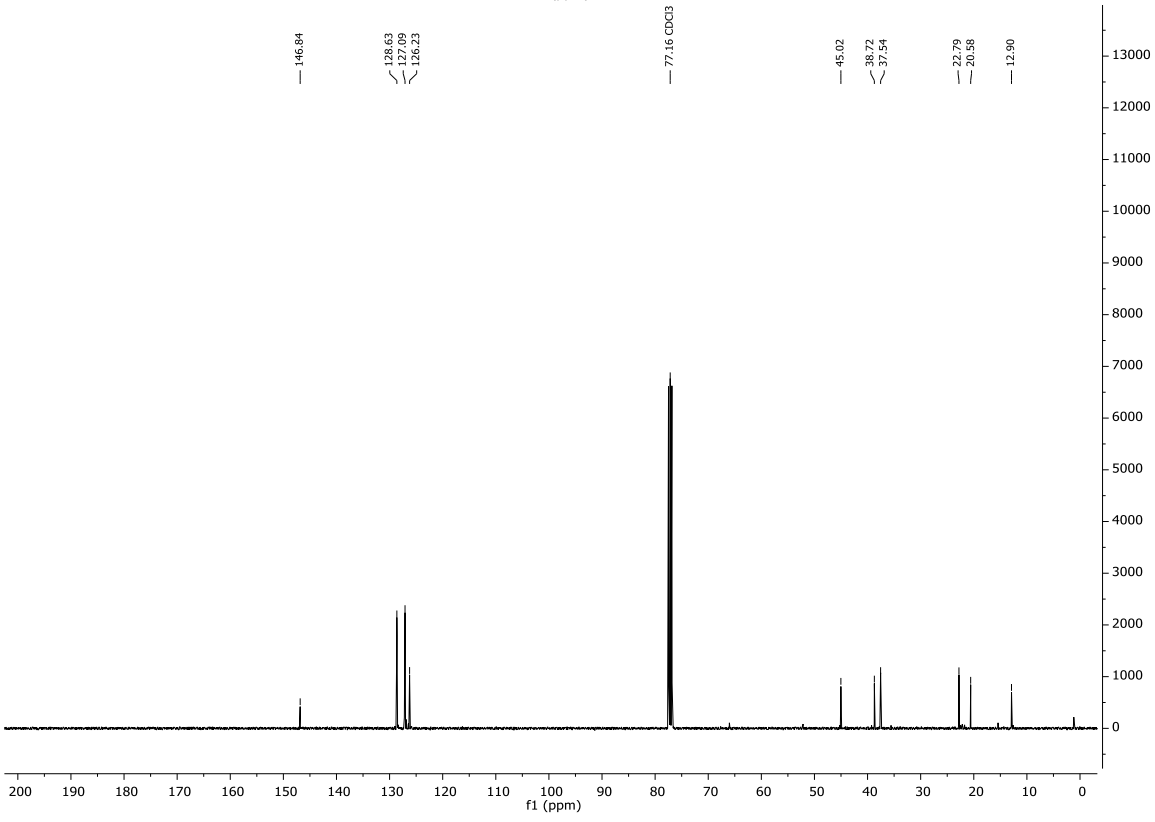

7.82
7.80
7.65
7.64
7.44
7.42
7.30
7.30
7.29
7.29
7.26 CDCl3
7.20
7.20
7.18
7.18
3.13
3.11
3.09
3.08
3.01
2.99
2.99
2.98
2.98
2.97
2.96
2.96
2.95
2.94
2.92
2.81
2.79
2.78
2.76
2.12
1.26
1.25
1.00
1.00
1.00
1.00
1.00
1.00
1.03
1.04
3.00
3.05
f1 (ppm)

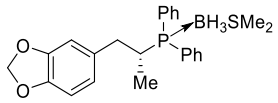

139.97
137.94
135.79
126.76
125.95
124.09
123.79
122.36
77.16 CDCl3
43.27
43.23
20.33
13.92
1.17
f1 (ppm)


Me
Me
SMe

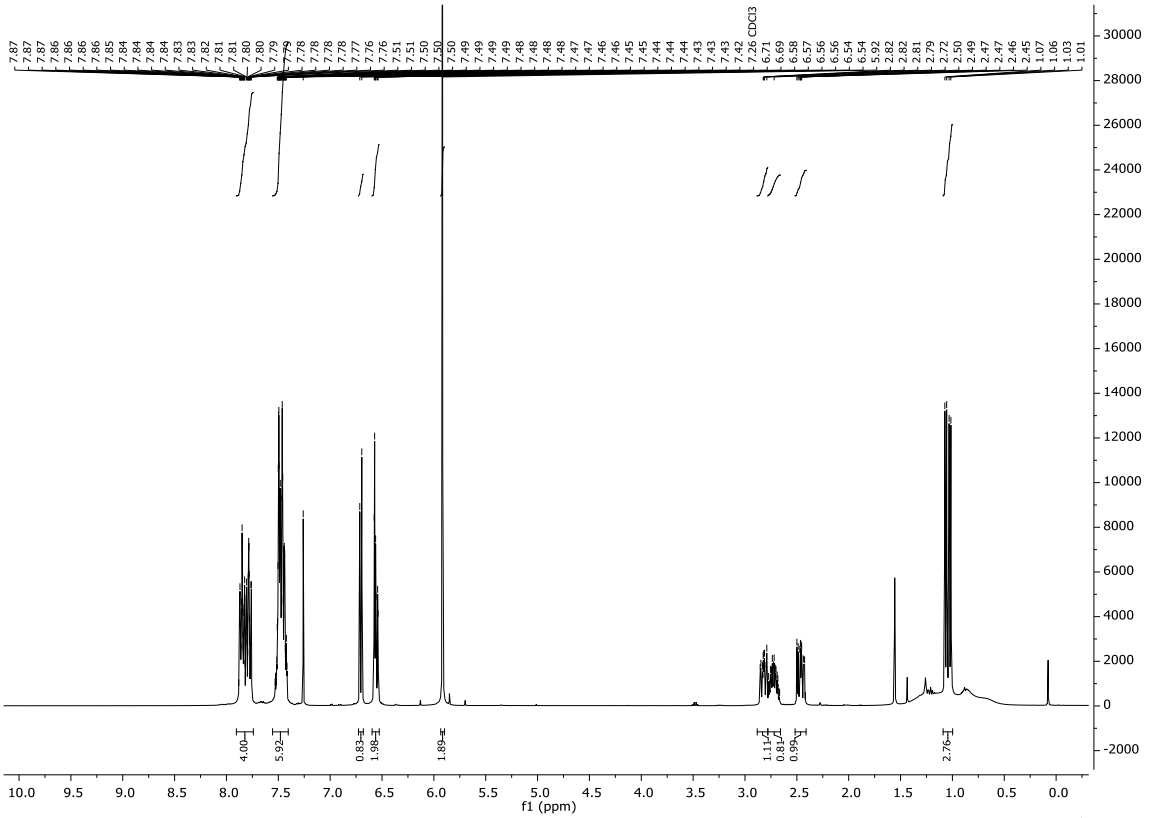
syn-**4p**

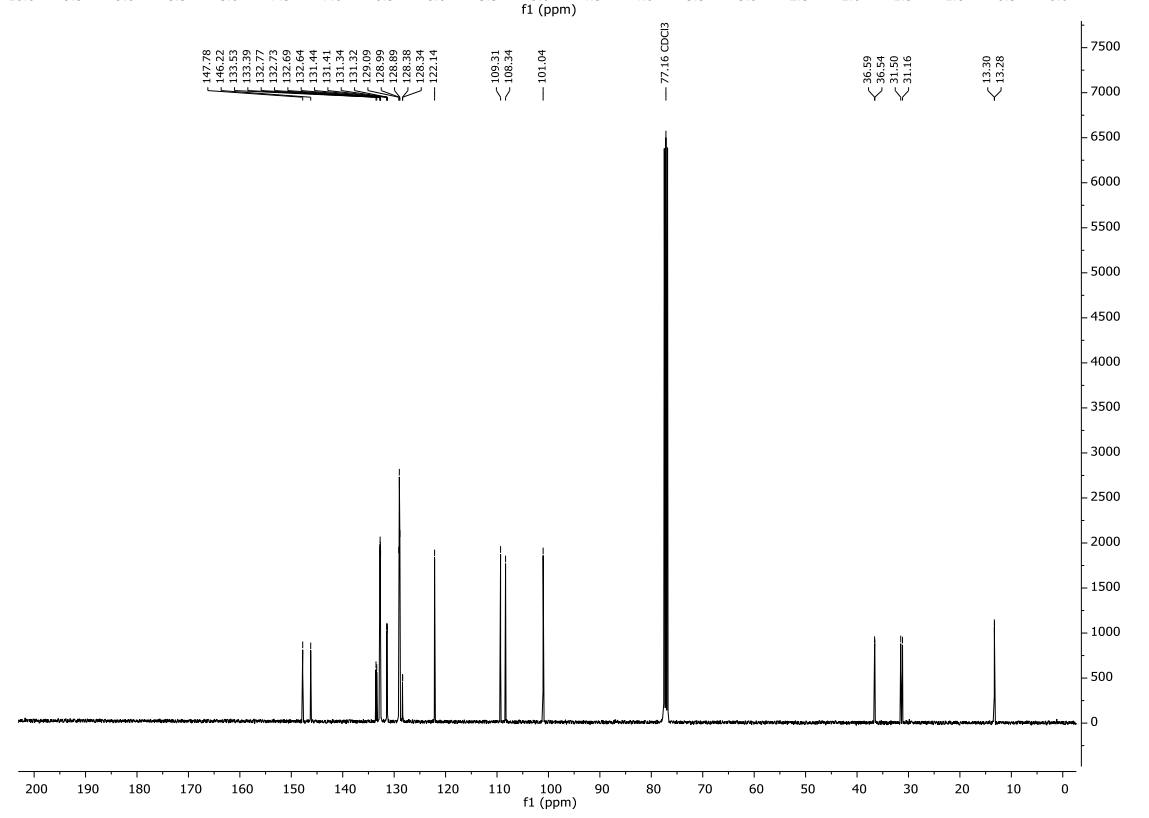

7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.26 CDCl3
7.24
7.24
7.22
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.18
7.18
7.17
2.97
2.95
2.94
2.93
2.93
2.92
2.91
2.90
2.89
2.88
2.52
2.50
2.49
2.48
2.48
2.47
2.46
2.45
2.45
2.01
1.97
1.95
1.95
1.94
1.93
1.92
1.91
1.90
1.68
1.66
1.66
1.64
1.64
1.63
1.62
1.61
1.27
1.26
1.25
1.25
0.07
2.09
3.00
0.94
1.03
2.67
0.95
1.00
5.68
f1 (ppm)

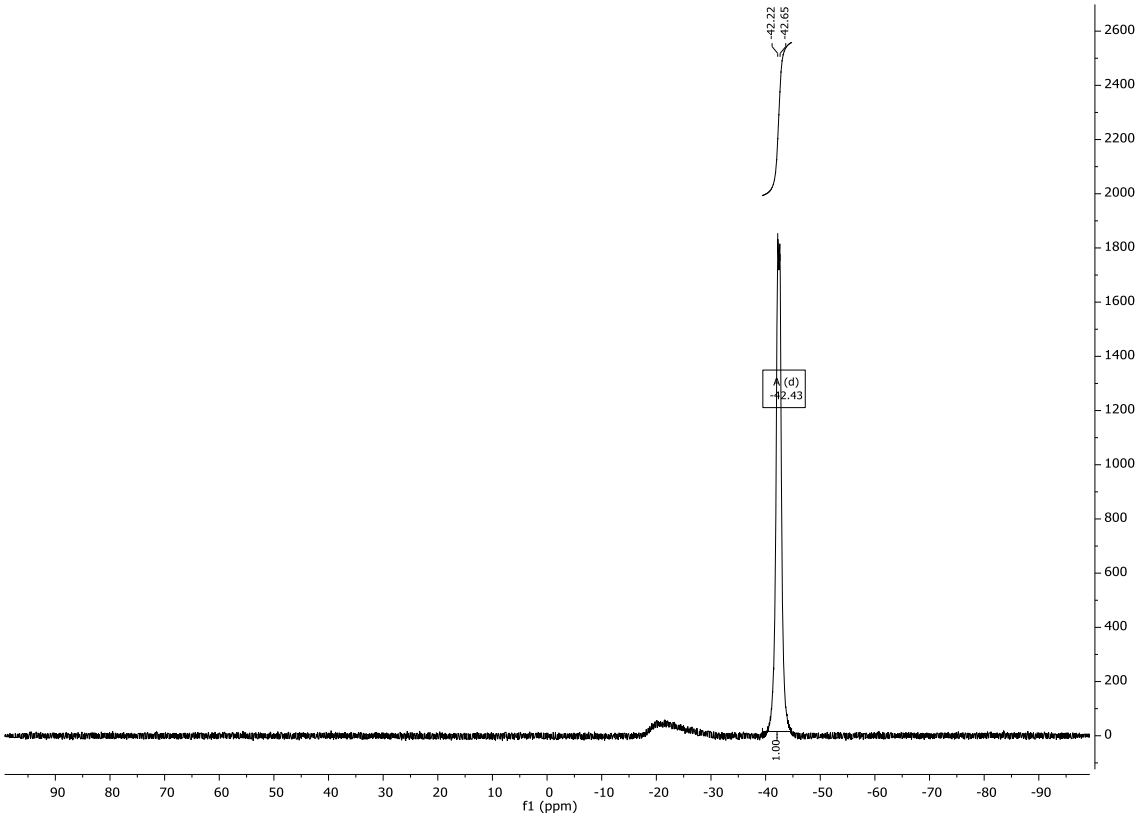

146.84
128.63
127.09
126.23
77.16 CDCl3
45.02
38.72
37.54
22.79
20.58
12.90
f1 (ppm)

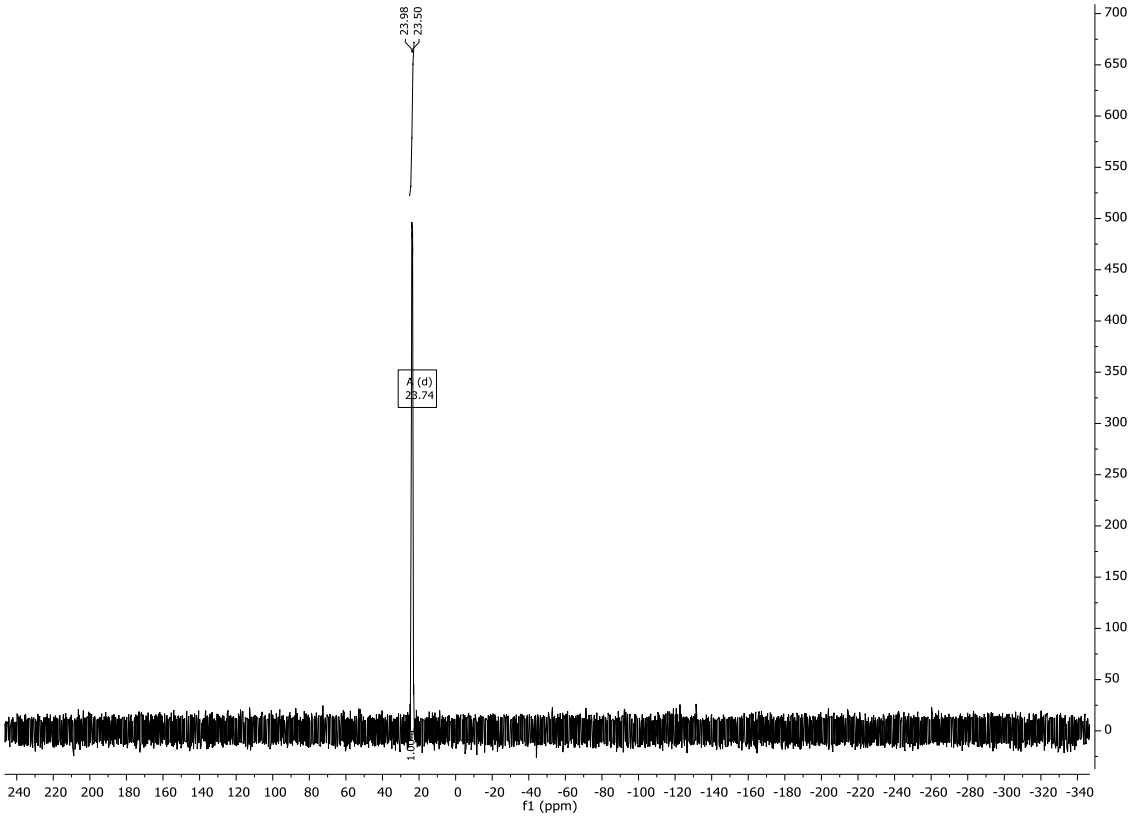

Ph
BH3SMe2
P
Ph
O
O
Me

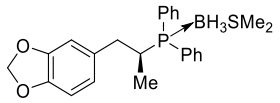
(*R*)-**4q**


7.87 7.87 7.87 7.86 7.86 7.86 7.85 7.84 7.84 7.84 7.83 7.82 7.81 7.81 7.80 7.80 7.79 7.79 7.78 7.78 7.78 7.78 7.77 7.76 7.76 7.51 7.50 7.50 7.50 7.49 7.49 7.49 7.49 7.48 7.48 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.26 CDCl3 6.71 6.69 6.58 6.57 6.56 6.56 6.54 6.54 5.92 2.82 2.82 2.81 2.79 2.72 2.50 2.49 2.47 2.47 2.46 2.45 1.07 1.06 1.03 1.01
4.00 5.92 0.83 1.98 1.89 1.11 0.81 0.99 2.76
f1 (ppm)

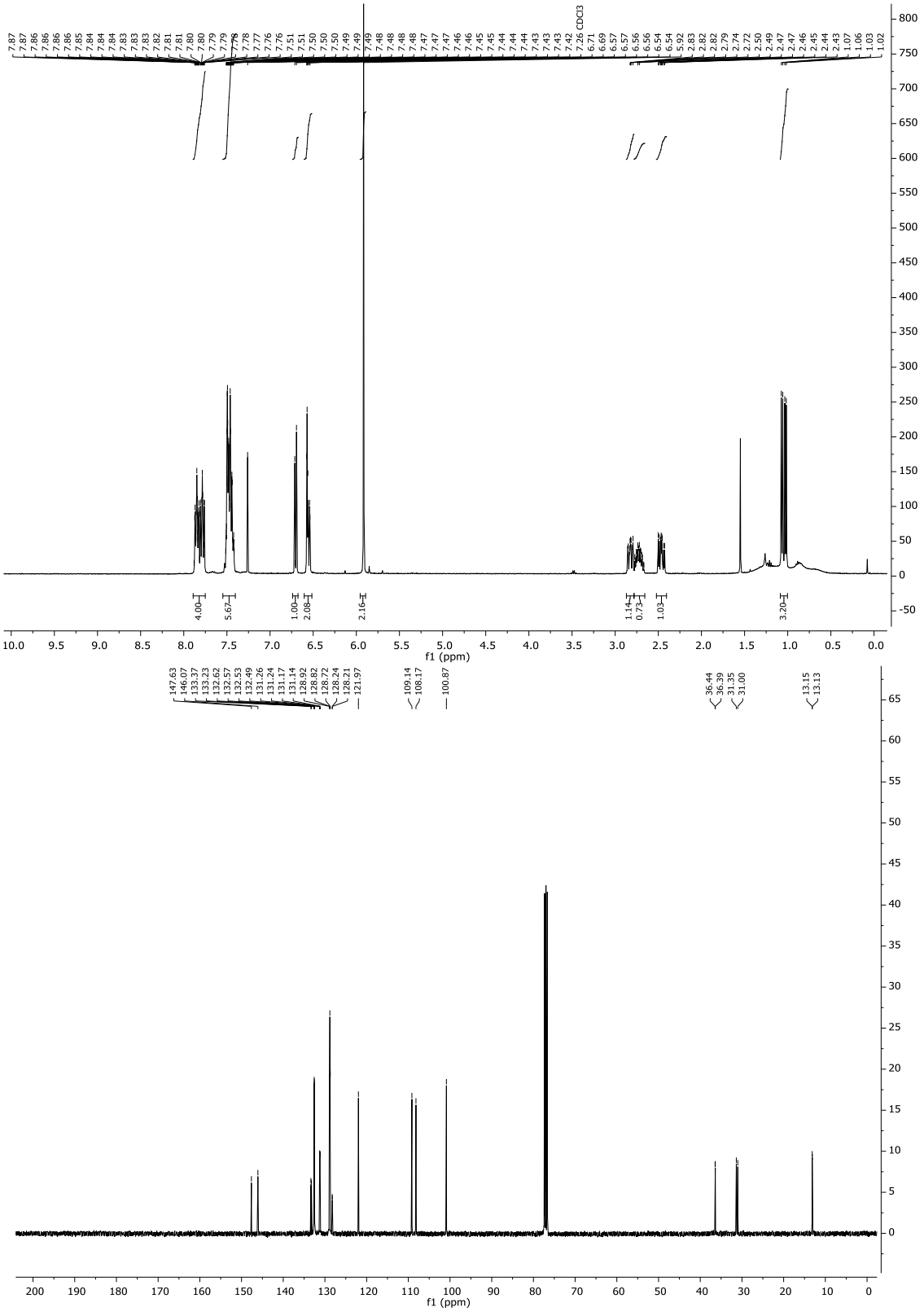

147.78 146.22 133.53 133.39 132.77 132.73 132.69 132.64 131.44 131.41 131.34 131.32 129.09 128.99 128.89 128.38 128.34 122.14 109.31 108.34 101.04 77.16 CDCl3 36.59 36.54 31.50 31.16 13.30 13.28
f1 (ppm)

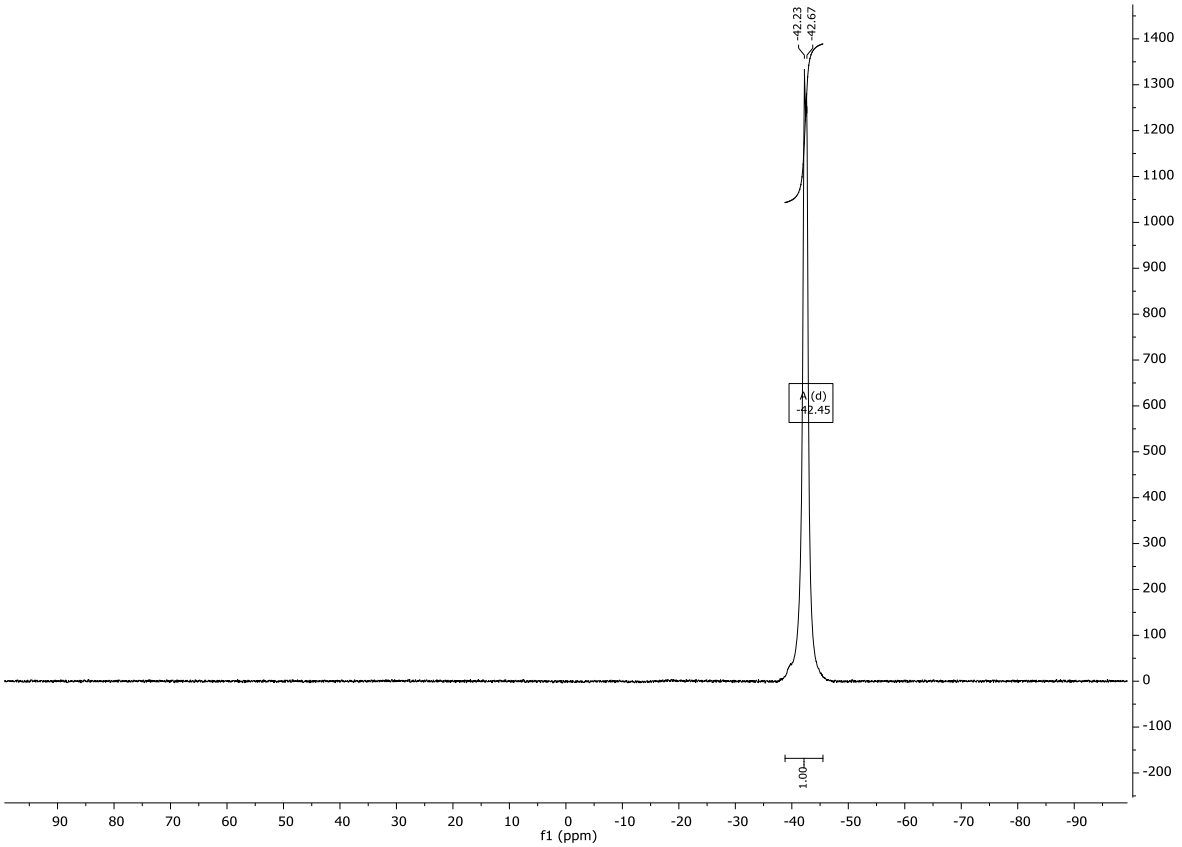

-42.22
-42.65
A (d)
-42.43
1.00
f1 (ppm)

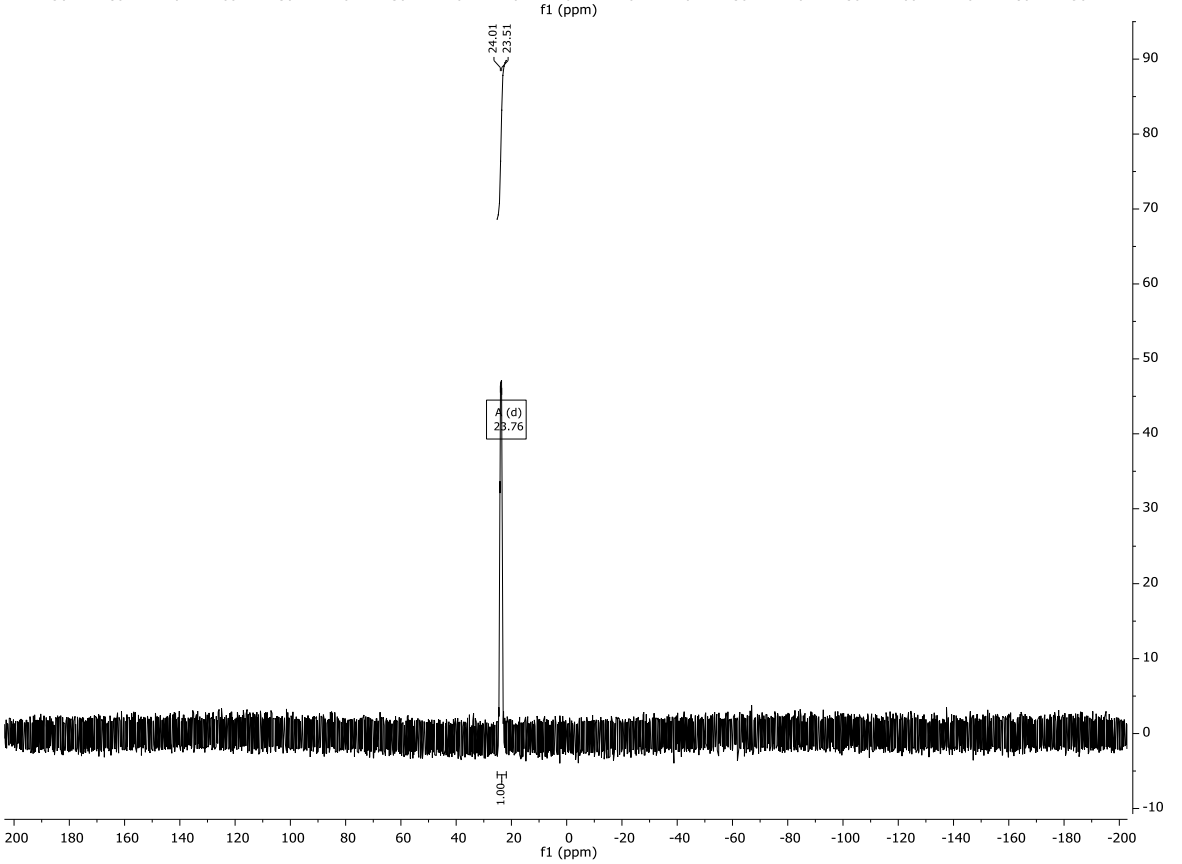

23.98
23.50
A (d)
23.74
1.00
f1 (ppm)

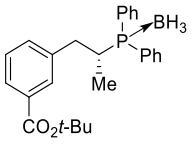


(*S*)-**4q**

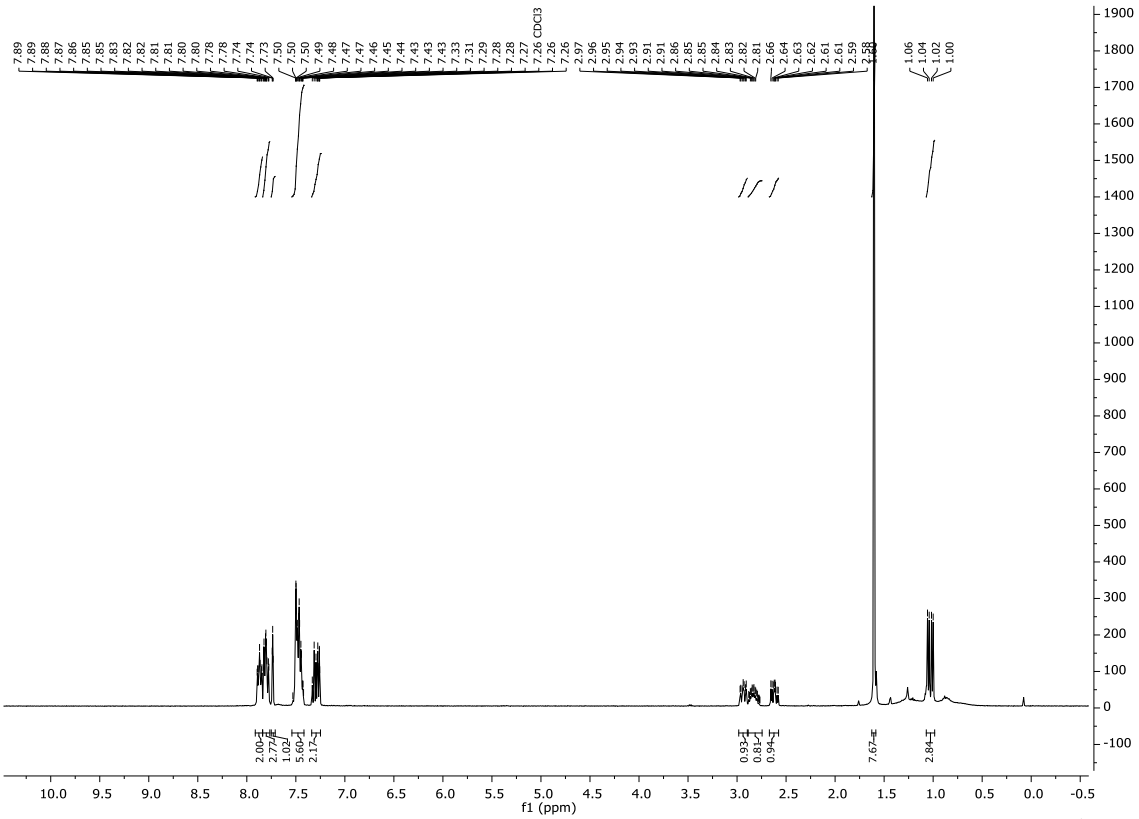


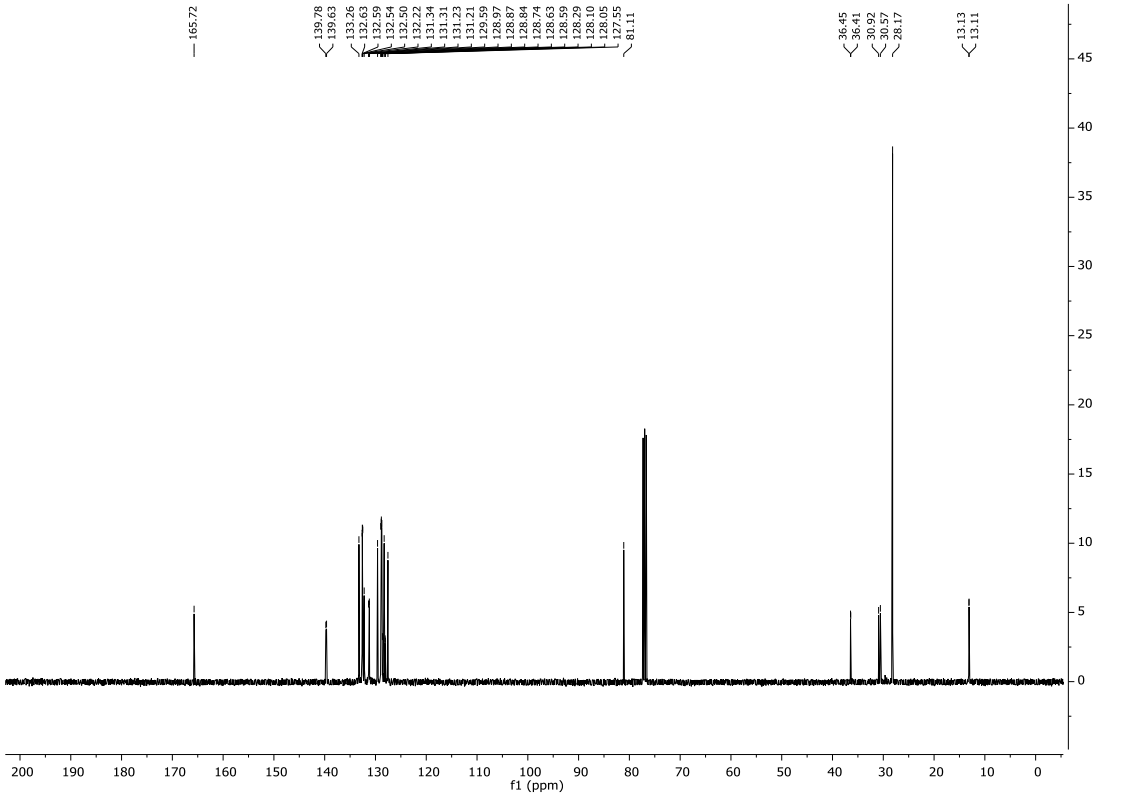

-42.23
-42.67
A (d)
-42.45
1.00
f1 (ppm)

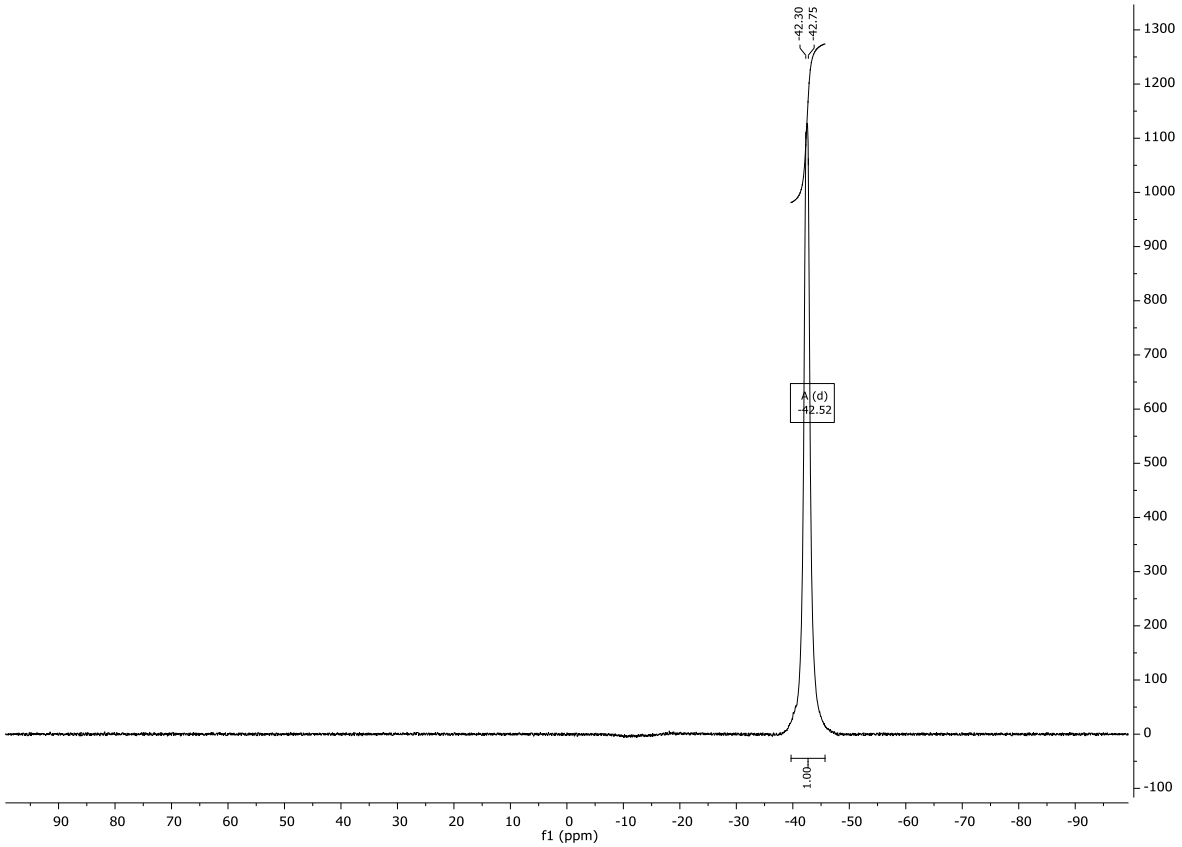

24.01
23.51
A (d)
23.76
1.00
f1 (ppm)

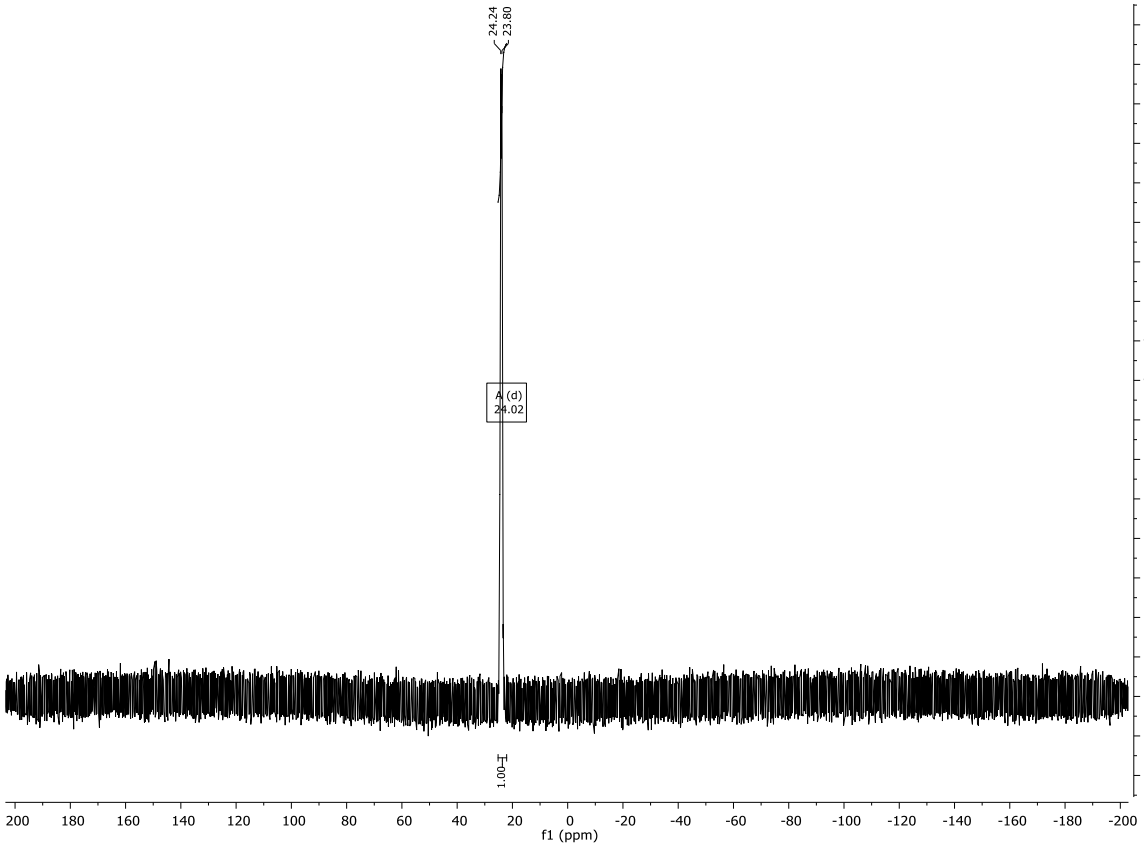

Ph
BH3
P
Ph
Me
CO2t-Bu

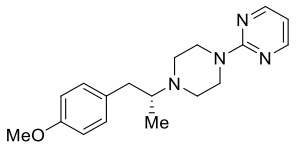
(*R*)-**4r**


7.89 7.89 7.88 7.87 7.86 7.85 7.85 7.83 7.82 7.82 7.81 7.81 7.80 7.80 7.78 7.78 7.74 7.74 7.73 7.73 7.50 7.50 7.50 7.49 7.48 7.47 7.47 7.46 7.45 7.44 7.43 7.43 7.43 7.33 7.31 7.29 7.28 7.28 7.27 7.26 CDCl3 7.26 7.26
2.97 2.96 2.95 2.94 2.93 2.91 2.91 2.86 2.85 2.85 2.84 2.83 2.82 2.81 2.66 2.64 2.63 2.62 2.61 2.61 2.59 2.58 1.60
1.06 1.04 1.02 1.00
2.00 2.77 1.02 5.60 2.17
0.93 0.84 0.94
7.67
2.84
f1 (ppm)

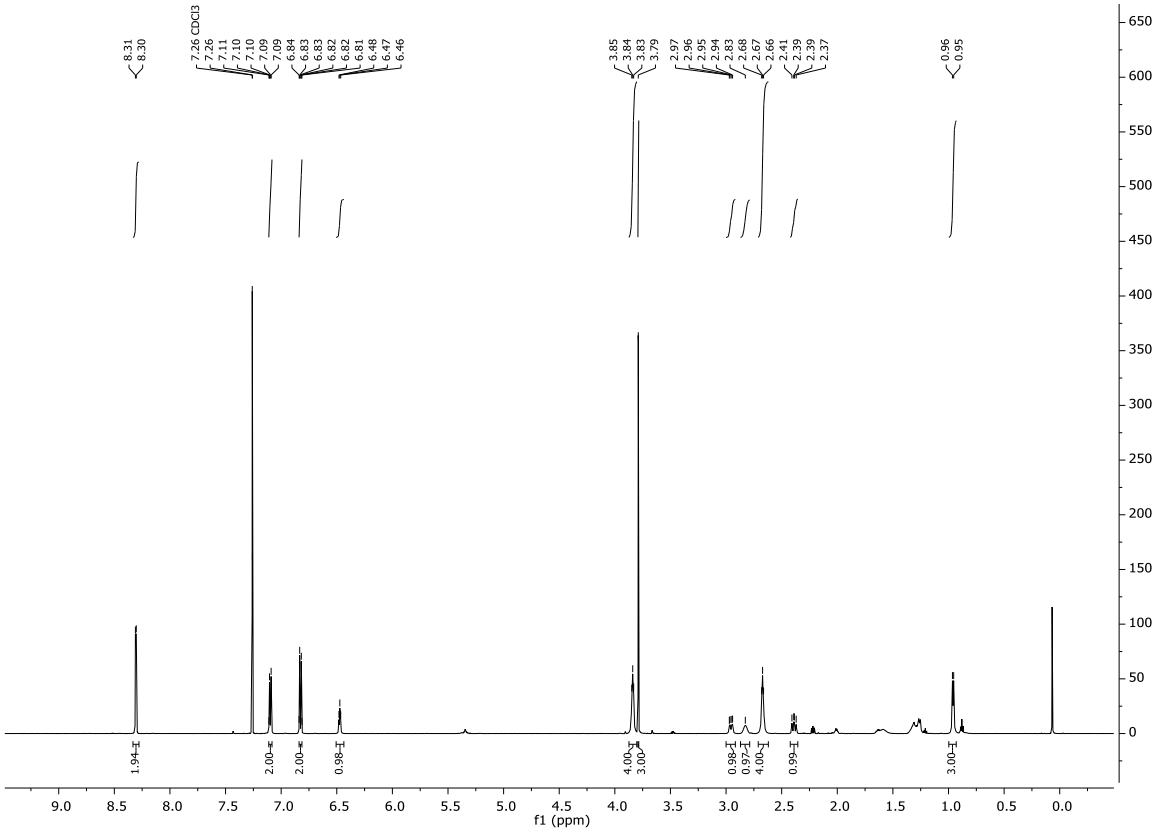

165.72
139.78 139.63 133.26 132.63 132.59 132.54 132.50 132.22 131.34 131.31 131.23 131.21 129.59 128.97 128.87 128.84 128.74 128.63 128.59 128.29 128.10 128.05 127.55 81.11
36.45 36.41 30.92 30.57 28.17
13.13 13.11
f1 (ppm)

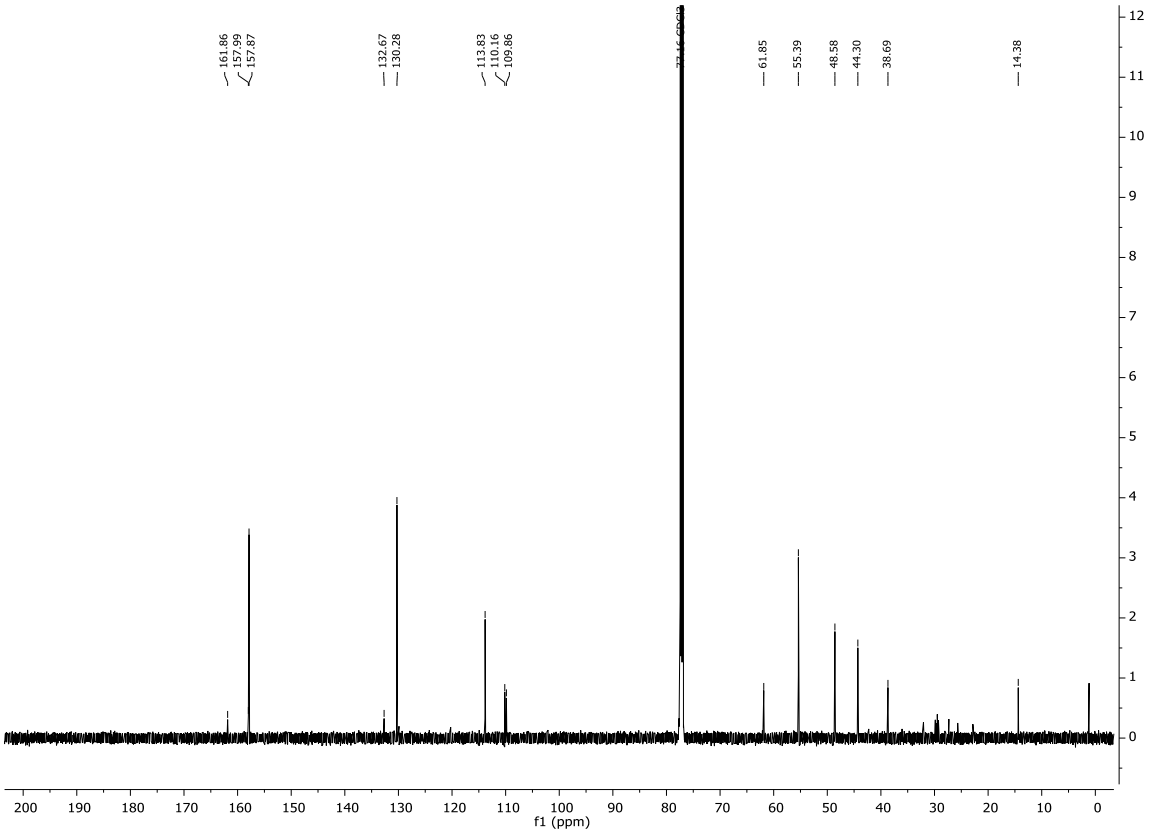

-42.30
-42.75
A (d)
-42.52
1.00
f1 (ppm)

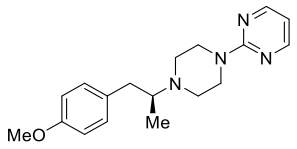

24.24
23.80
A (d)
24.02
1.00
f1 (ppm)


N
N
N
N
MeO
Me

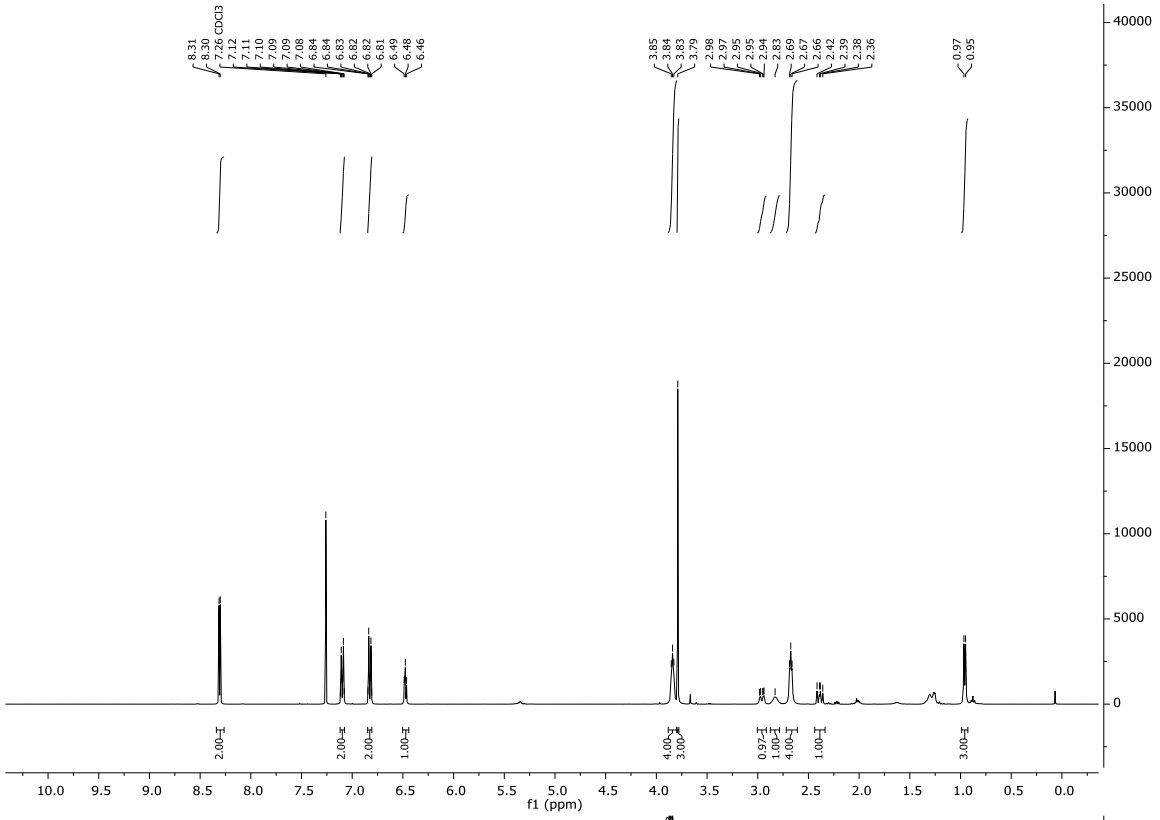
(*R*)-**8a**

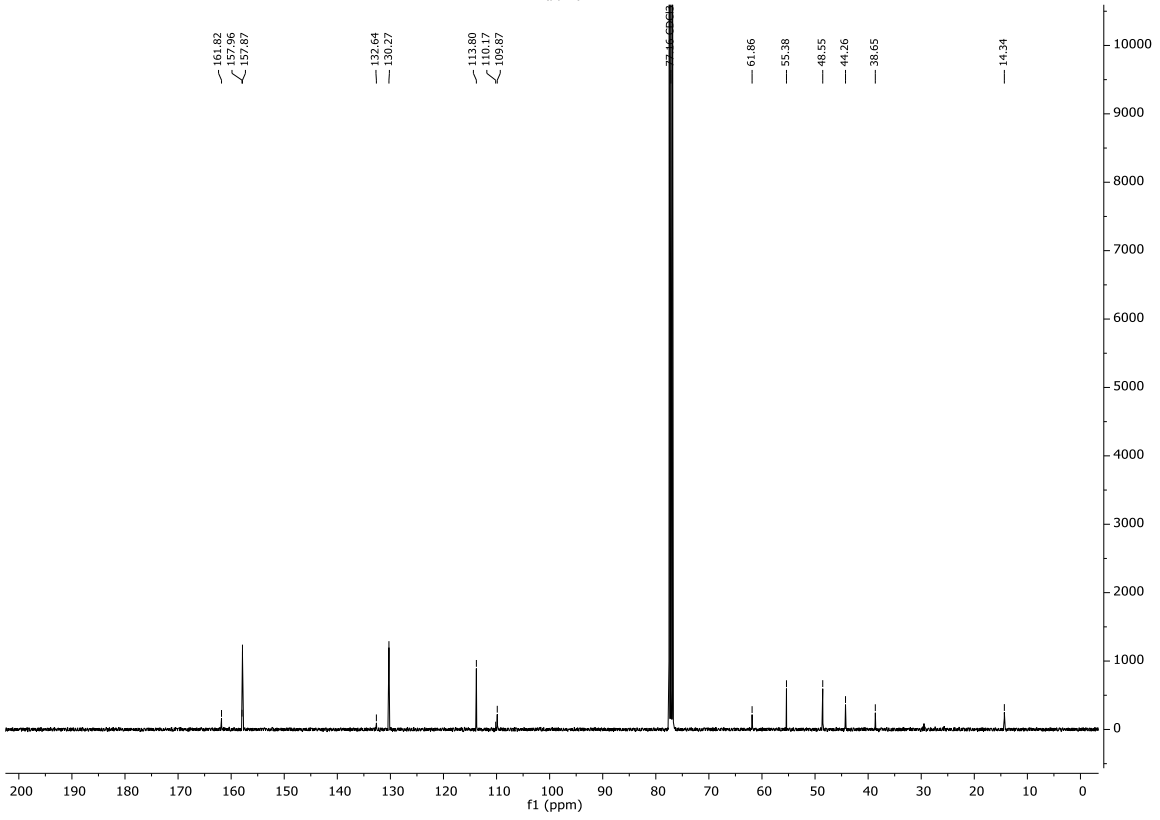

8.31
8.30
7.26 CDCl3
7.26
7.11
7.10
7.09
7.09
6.84
6.83
6.83
6.82
6.82
6.81
6.48
6.47
6.46
3.85
3.84
3.83
3.79
2.97
2.96
2.95
2.94
2.83
2.68
2.67
2.66
2.41
2.39
2.39
2.37
0.96
0.95
1.94
2.00
2.00
0.98
4.00
3.00
0.98
0.97
4.00
0.99
3.00
f1 (ppm)

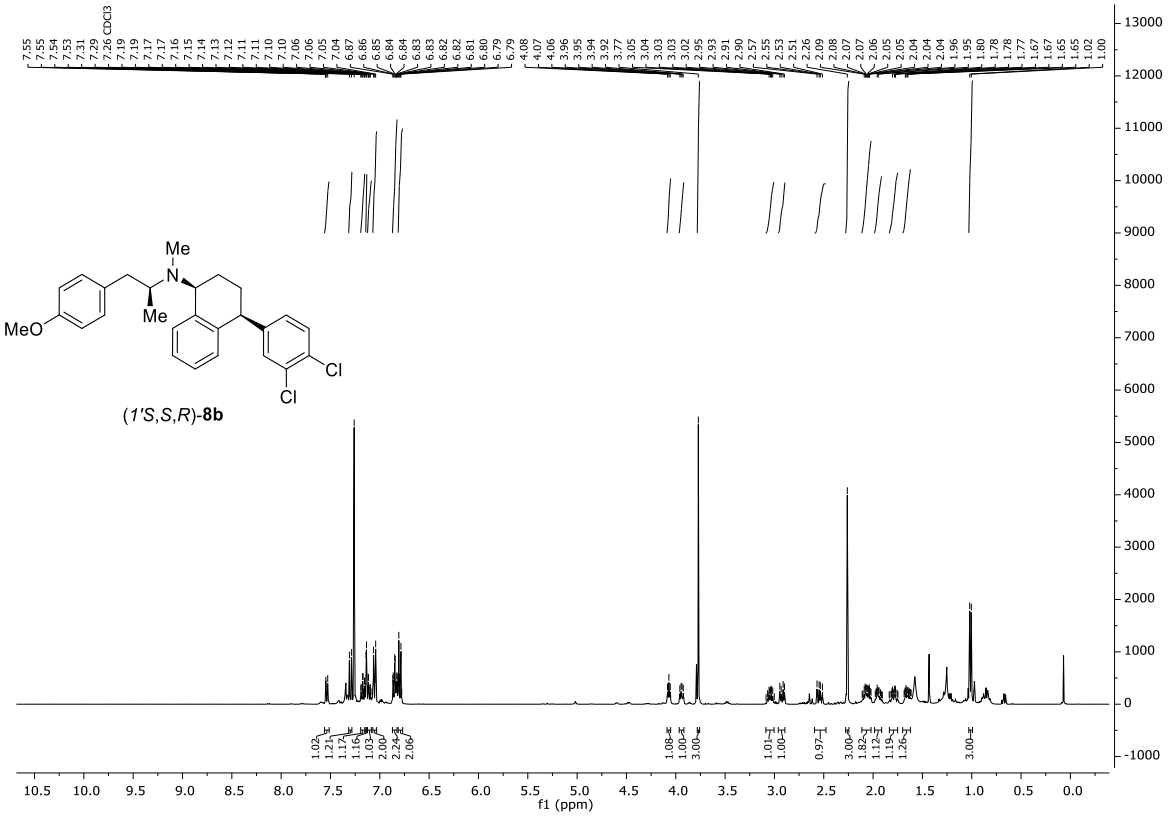

161.86
157.99
157.87
132.67
130.28
113.83
110.16
109.86
77.16 CDCl3
61.85
55.39
48.58
44.30
38.69
14.38
f1 (ppm)

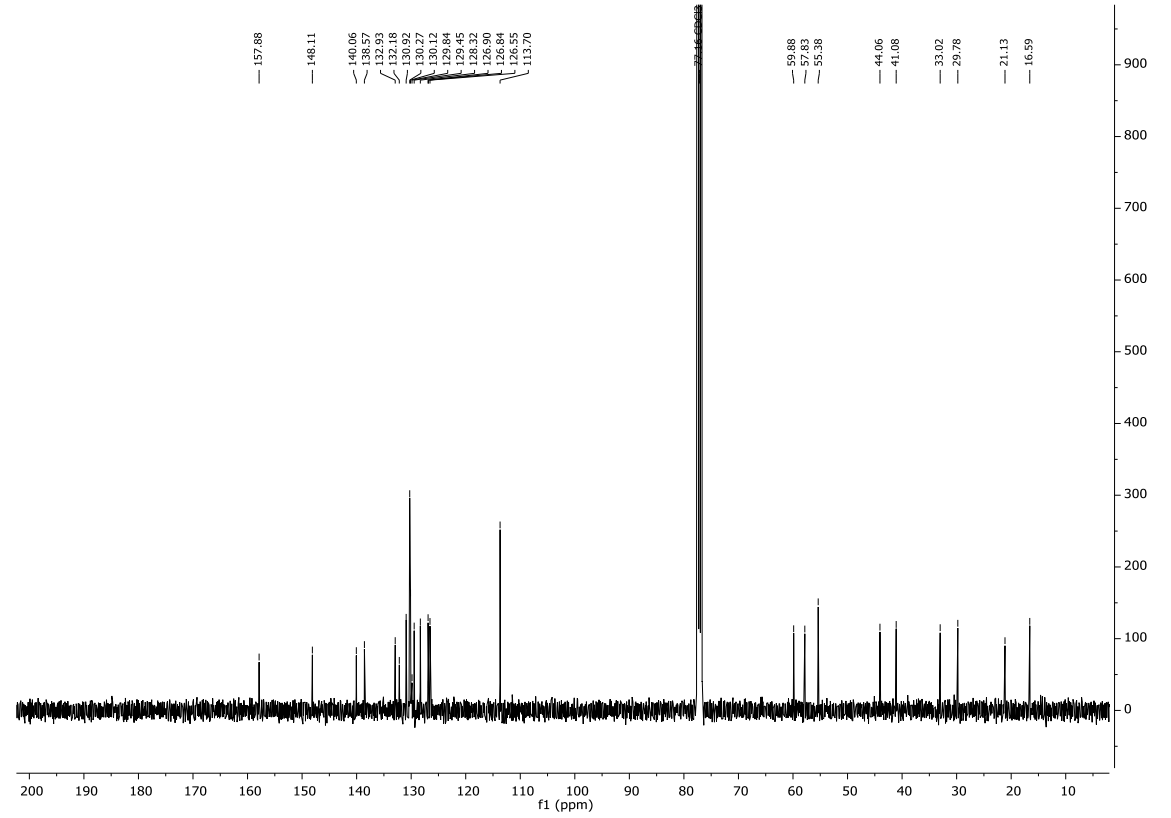

N
N
N
N
MeO
Me

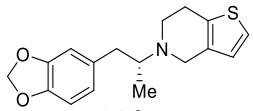
(*S*)-**8a**


8.31
8.30
7.26 CDCl3
7.12
7.11
7.10
7.09
7.09
7.08
6.84
6.84
6.83
6.82
6.82
6.81
6.49
6.48
6.46
3.85
3.84
3.83
3.79
2.98
2.97
2.95
2.95
2.94
2.83
2.69
2.67
2.66
2.42
2.39
2.38
2.36
0.97
0.95
2.00
2.00
2.00
1.00
4.00
3.00
0.97
1.00
4.00
1.00
3.00
f1 (ppm)

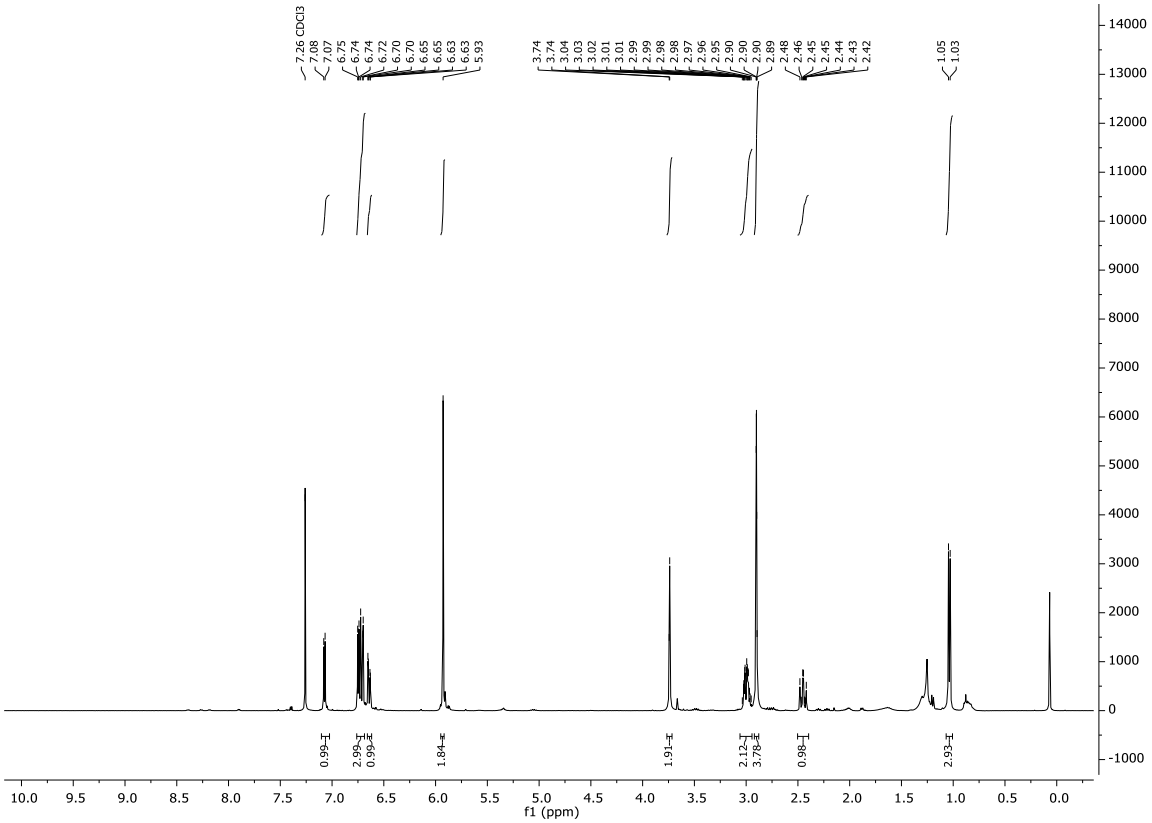

161.82
157.96
157.87
132.64
130.27
113.80
110.17
109.87
77.16 CDCl3
61.86
55.38
48.55
44.26
38.65
14.34
f1 (ppm)

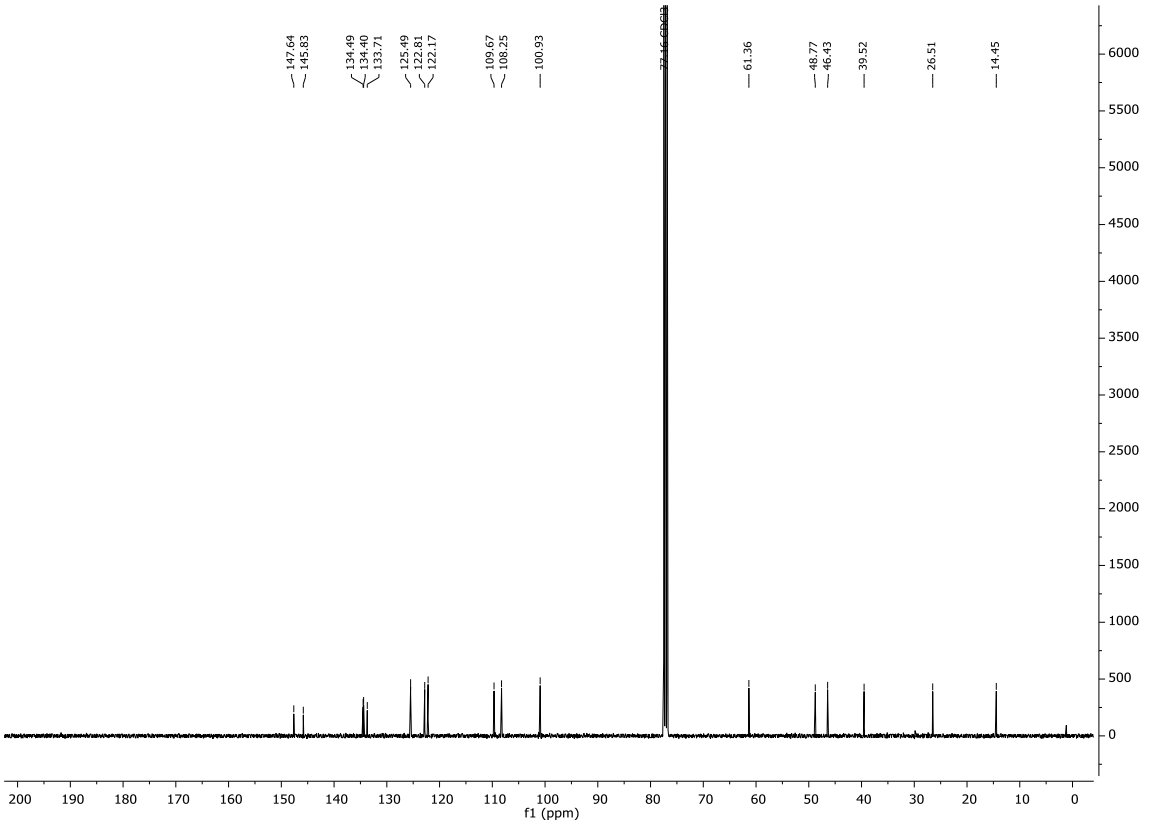

Me
N
Me
MeO
Cl
Cl
(1'S,S,R)-8b
f1 (ppm)

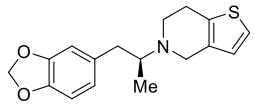

f1 (ppm)


O
O
N
S
Me

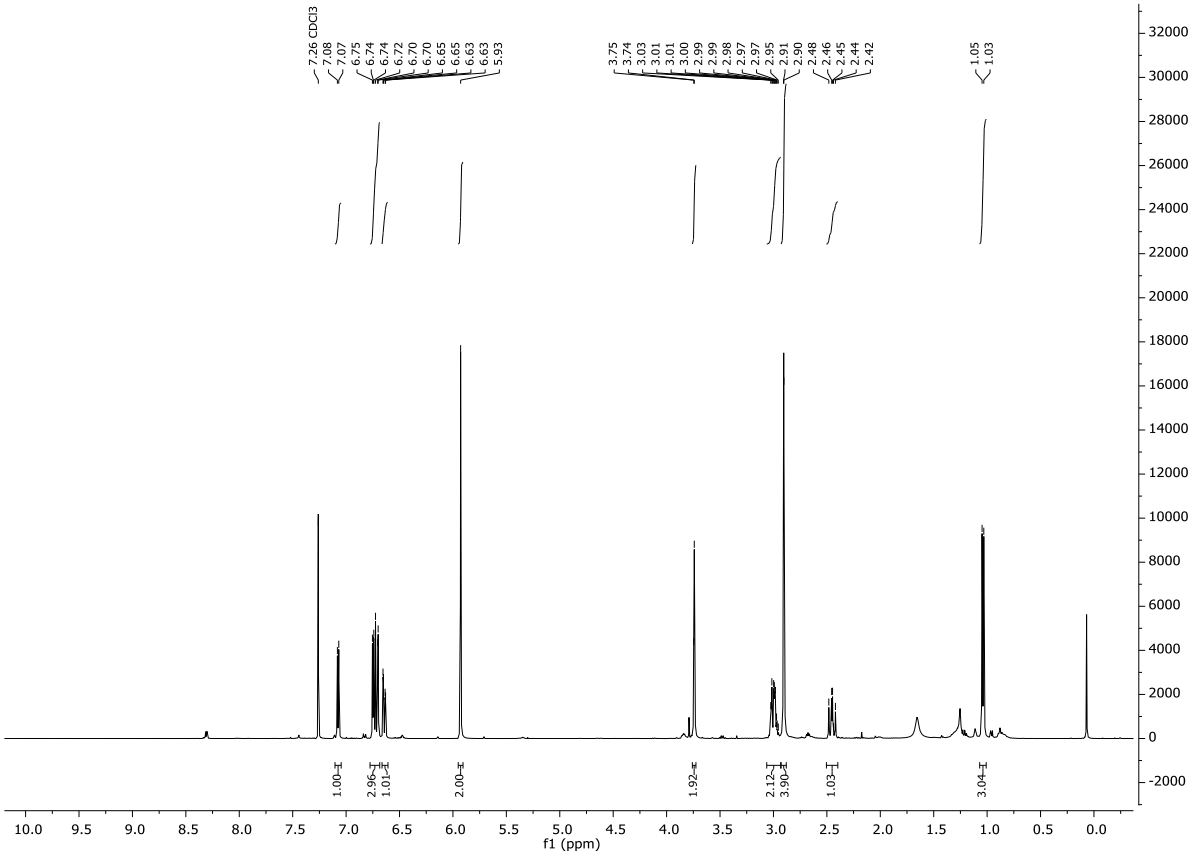
(*R*)-**8c**

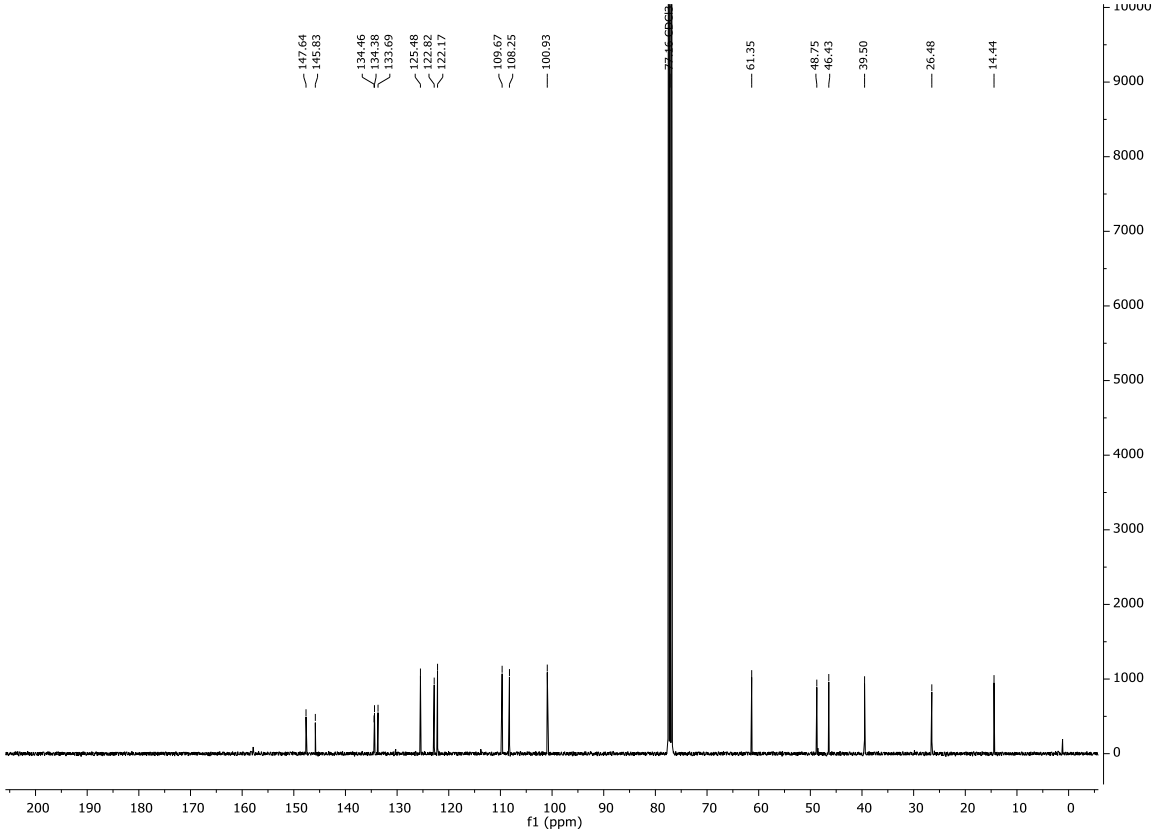

7.26 CDCl3
7.08
7.07
6.75
6.74
6.74
6.72
6.70
6.70
6.65
6.65
6.63
6.63
5.93
3.74
3.74
3.04
3.03
3.02
3.01
3.01
2.99
2.99
2.98
2.98
2.97
2.96
2.95
2.90
2.90
2.90
2.89
2.48
2.46
2.45
2.45
2.44
2.43
2.42
1.05
1.03
0.99
2.99
0.99
1.84
1.91
2.12
3.78
0.98
2.93
f1 (ppm)

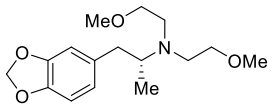

147.64
145.83
134.49
134.40
133.71
125.49
122.81
122.17
109.67
108.25
100.93
77.16
61.36
48.77
46.43
39.52
26.51
14.45
f1 (ppm)


O
O
N
S
Me

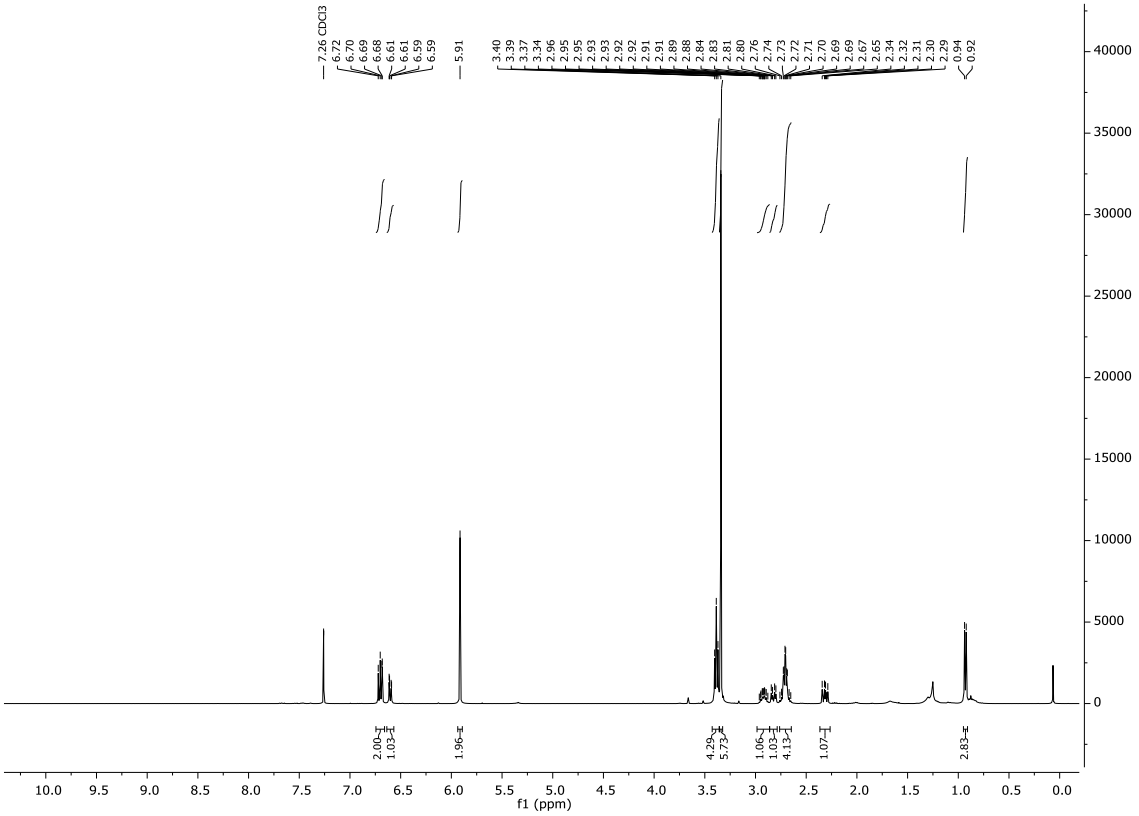
(*S*)-**8c**

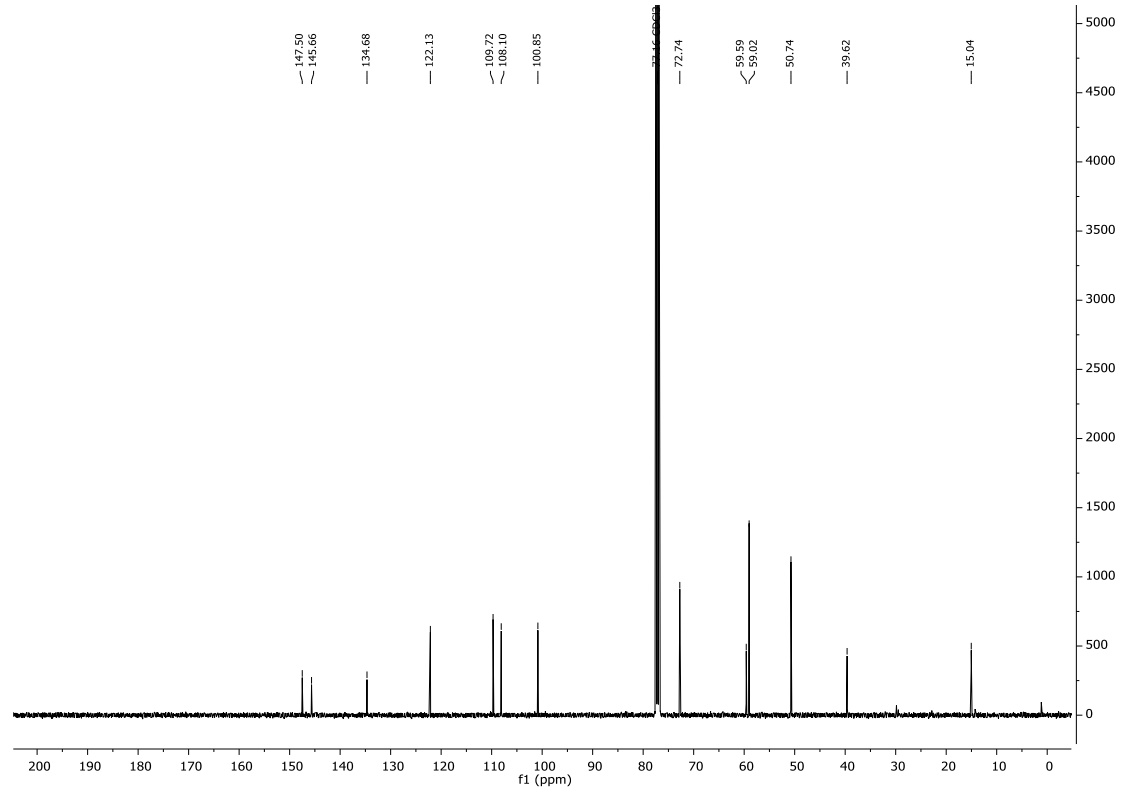

7.26 CDCl3
7.08
7.07
6.75
6.74
6.74
6.72
6.70
6.70
6.65
6.65
6.63
6.63
5.93
3.75
3.74
3.03
3.01
3.01
3.00
2.99
2.99
2.98
2.97
2.97
2.95
2.91
2.90
2.48
2.46
2.45
2.44
2.42
1.05
1.03
1.00
2.96
1.01
2.00
1.92
2.12
3.90
1.03
3.04
f1 (ppm)

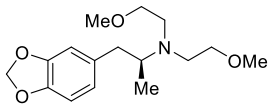

147.64
145.83
134.46
134.38
133.69
125.48
122.82
122.17
109.67
108.25
100.93
77.16 CDCl3
61.35
48.75
46.43
39.50
26.48
14.44
f1 (ppm)


MeO
N
OMe
O
O
Me

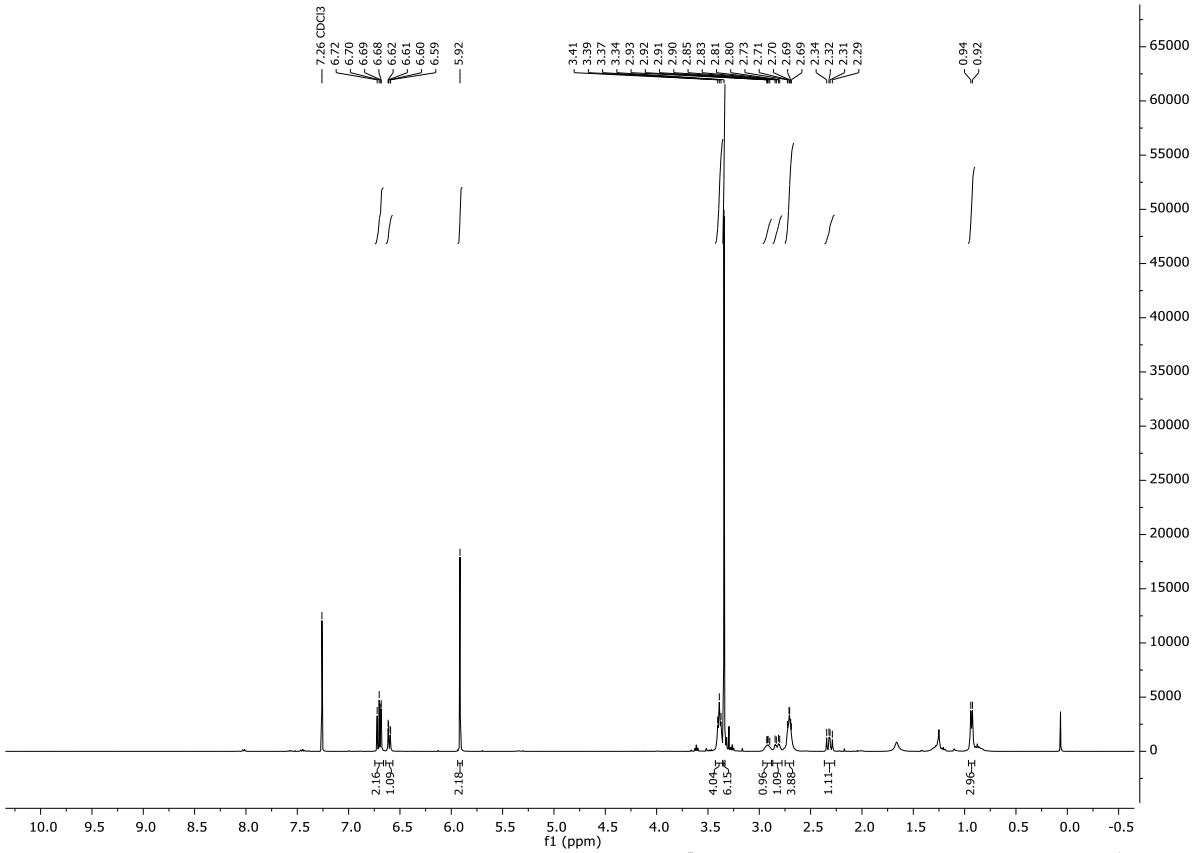
(*R*)-**8d**

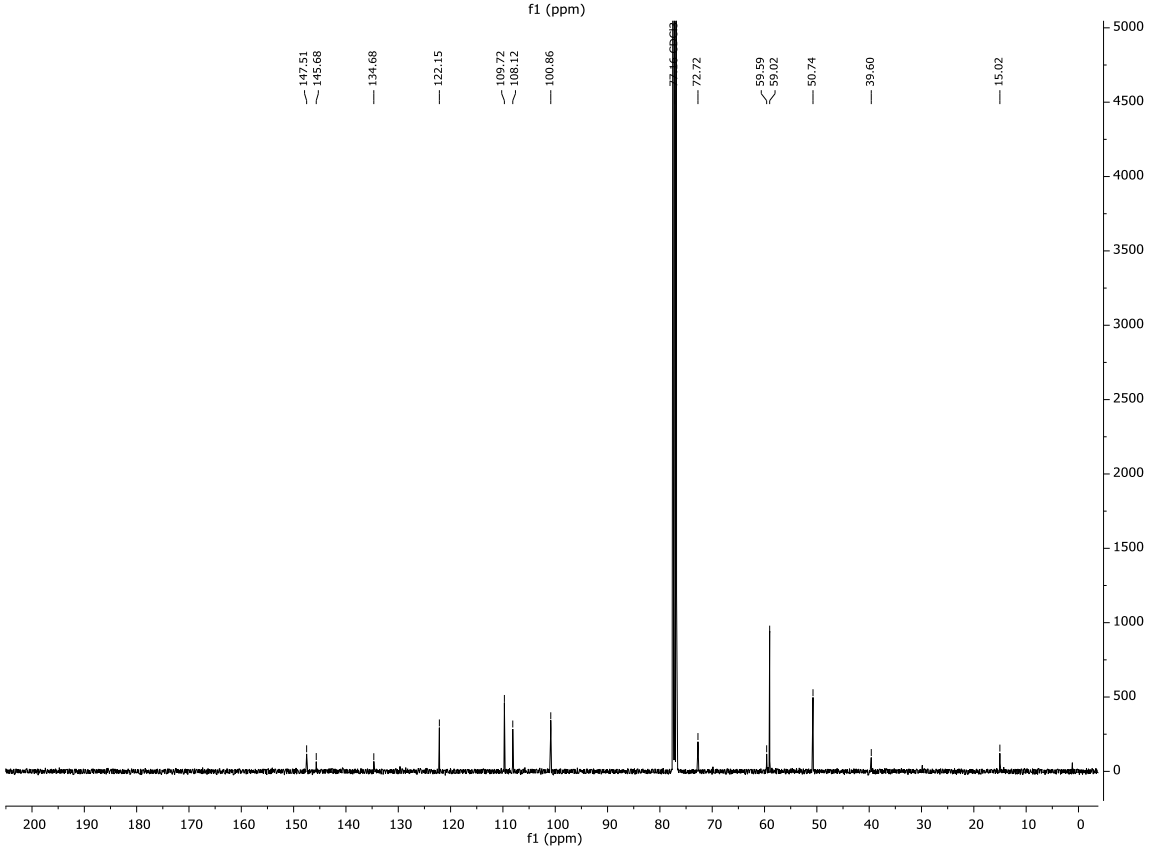

7.26 CDCl3
6.72
6.70
6.69
6.68
6.61
6.61
6.59
6.59
5.91
3.40
3.39
3.37
3.34
2.96
2.95
2.95
2.93
2.93
2.92
2.92
2.91
2.91
2.89
2.88
2.84
2.83
2.81
2.80
2.76
2.74
2.73
2.72
2.71
2.70
2.69
2.69
2.67
2.65
2.34
2.32
2.31
2.30
2.29
0.94
0.92
2.00
1.03
1.96
4.29
5.73
1.06
1.03
4.13
1.07
2.83
f1 (ppm)

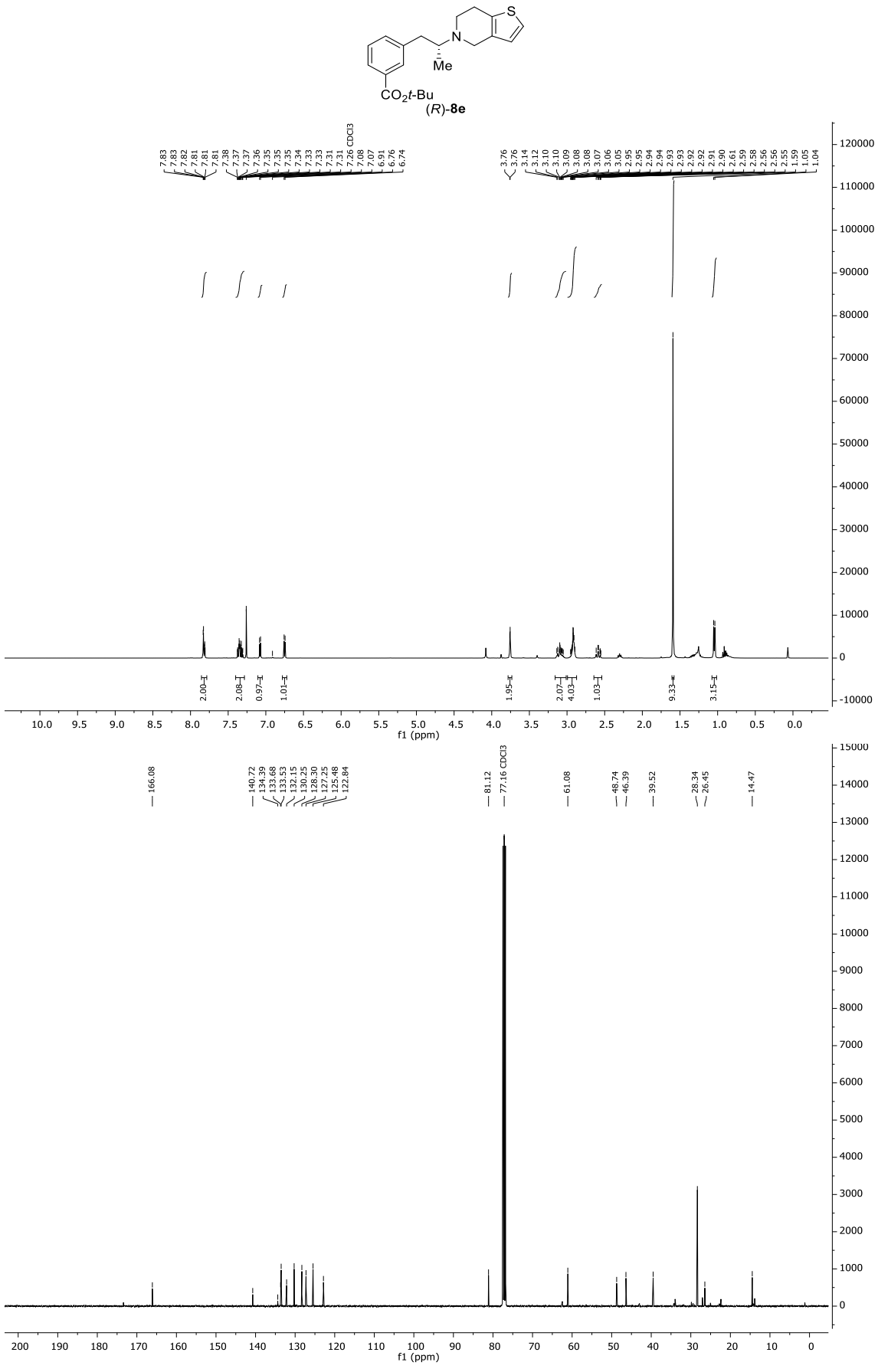

147.50
145.66
134.68
122.13
109.72
108.10
100.85
77.16
72.74
59.59
59.02
50.74
39.62
15.04
f1 (ppm)

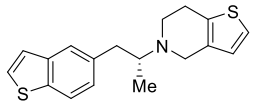

MeO
N
OMe
O
O
Me

(*S*)-**8d**

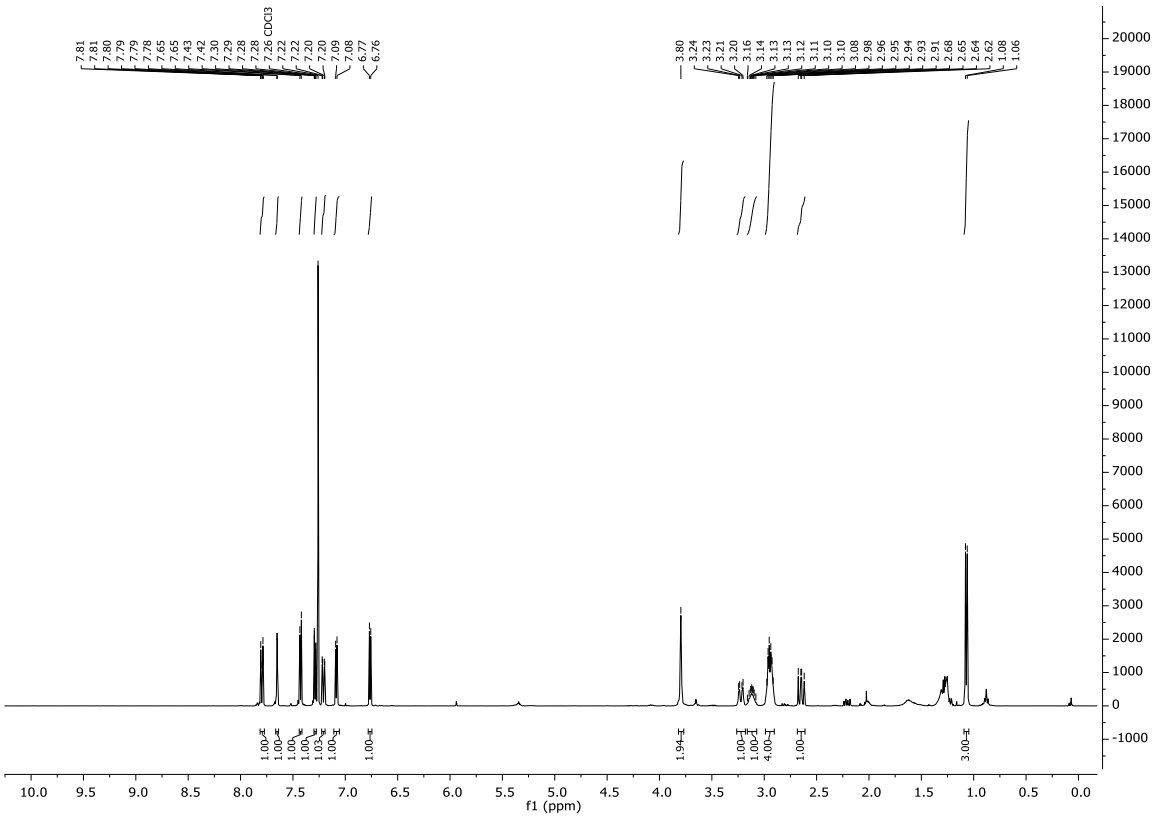

7.26 CDCl3
6.72
6.70
6.69
6.68
6.62
6.61
6.60
6.59
5.92
3.41
3.39
3.37
3.34
2.93
2.92
2.91
2.90
2.85
2.83
2.81
2.80
2.73
2.71
2.70
2.69
2.69
2.34
2.32
2.31
2.29
0.94
0.92
2.16
1.09
2.18
4.04
6.15
0.96
1.09
3.88
1.11
2.96
f1 (ppm)

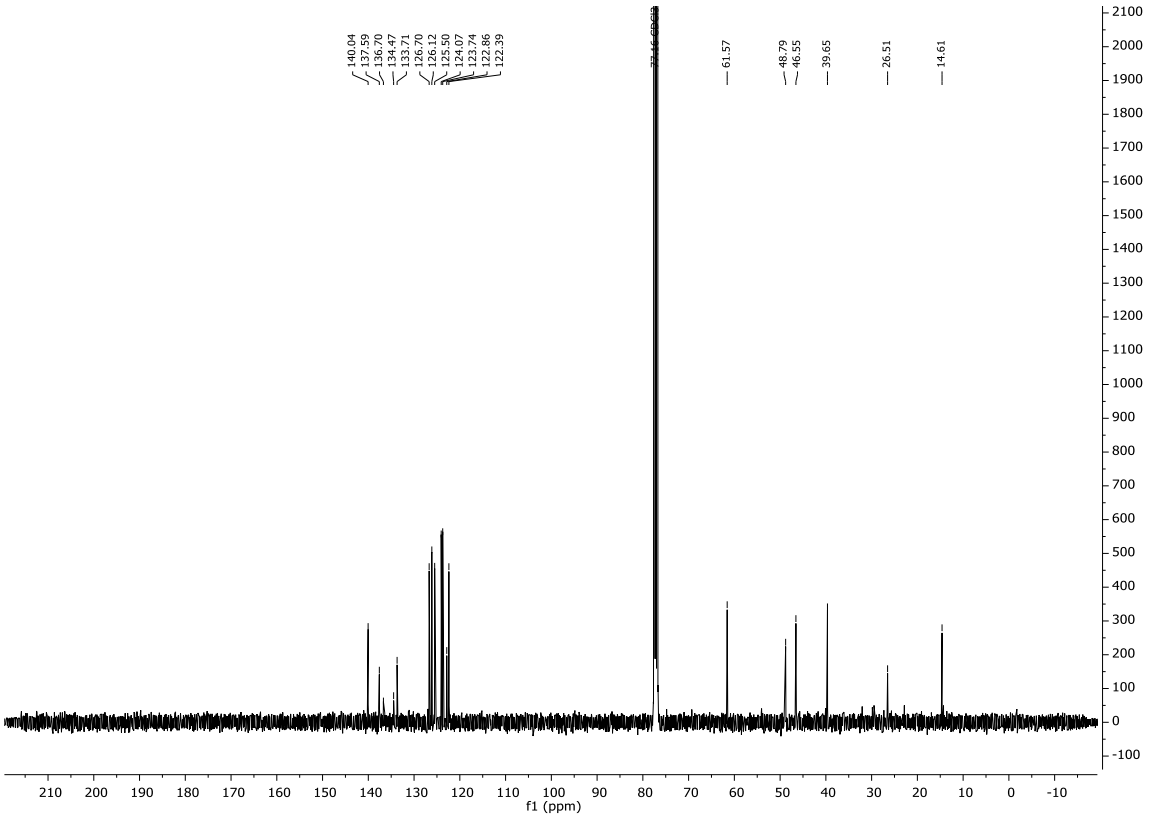

147.51
145.68
134.68
122.15
109.72
108.12
100.86
72.72
59.59
59.02
50.74
39.60
15.02
f1 (ppm)

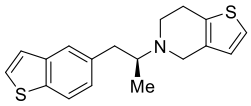

S
N
Me
CO2t-Bu
(R)-8e
7.83
7.83
7.82
7.81
7.81
7.81
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.33
7.31
7.31
7.26 CDCl3
7.08
7.07
6.91
6.76
6.74
3.76
3.76
3.14
3.12
3.10
3.10
3.09
3.08
3.08
3.07
3.06
3.05
2.95
2.95
2.94
2.94
2.93
2.93
2.92
2.92
2.91
2.90
2.61
2.59
2.58
2.56
2.56
2.55
1.59
1.05
1.04
2.00
2.08
0.97
1.01
1.95
2.07
4.03
1.03
9.33
3.15
f1 (ppm)
166.08
140.72
134.39
133.68
133.53
132.15
130.25
128.30
127.25
125.48
122.84
81.12
77.16 CDCl3
61.08
48.74
46.39
39.52
28.34
26.45
14.47
f1 (ppm)


S
N
Me
S

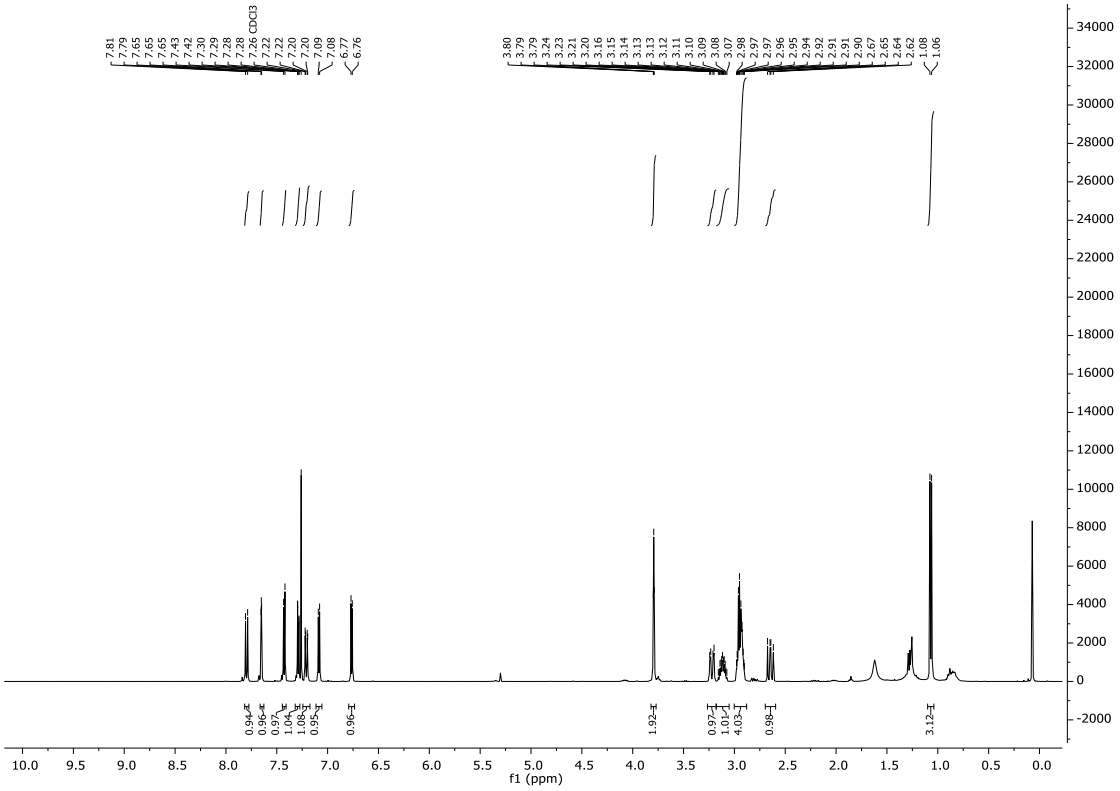
(*R*)-**8f**

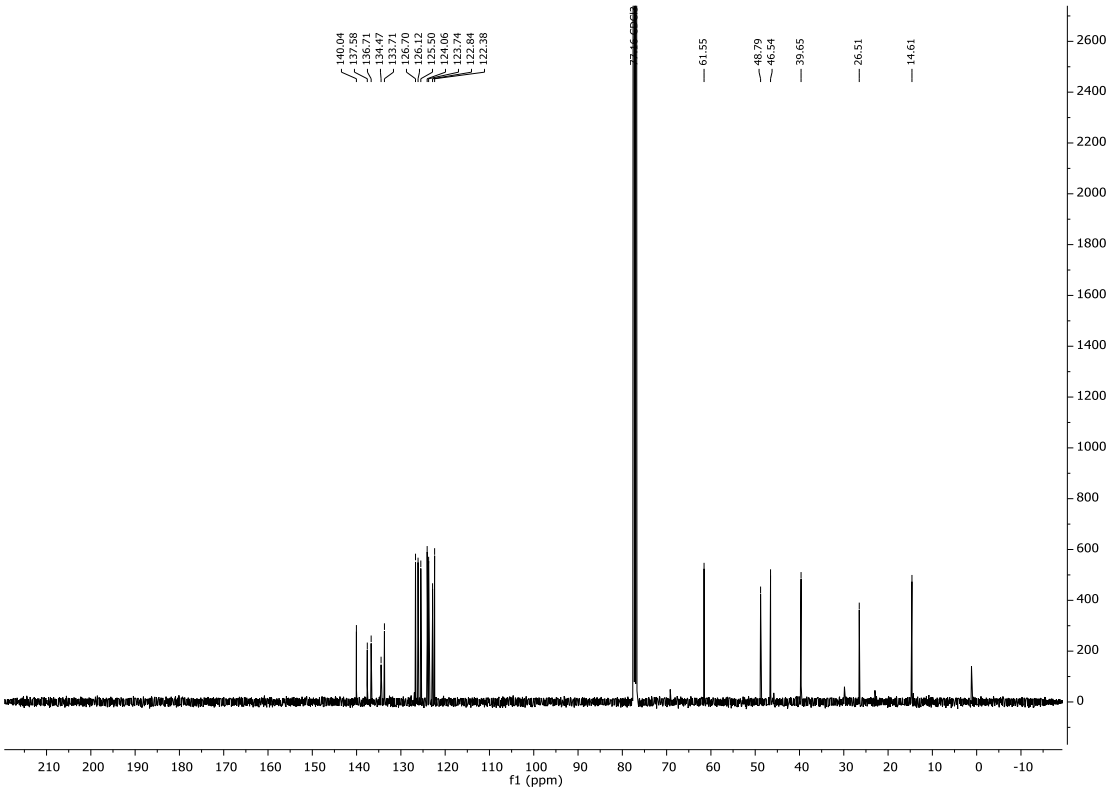

7.81
7.81
7.80
7.79
7.79
7.78
7.65
7.65
7.43
7.42
7.30
7.29
7.28
7.28
7.26 CDCl3
7.22
7.22
7.20
7.20
7.09
7.08
6.77
6.76
3.80
3.24
3.23
3.21
3.20
3.16
3.14
3.13
3.13
3.12
3.11
3.10
3.10
3.08
2.98
2.96
2.95
2.94
2.93
2.91
2.68
2.65
2.64
2.62
1.08
1.06
1.00
1.00
1.00
1.00
1.03
1.00
1.00
1.94
1.00
1.00
4.00
1.00
3.00
f1 (ppm)

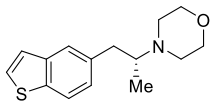

140.04
137.59
136.70
134.47
133.71
126.70
126.12
125.50
124.07
123.74
122.86
122.39
61.57
48.79
46.55
39.65
26.51
14.61
f1 (ppm)


S
N
Me
S

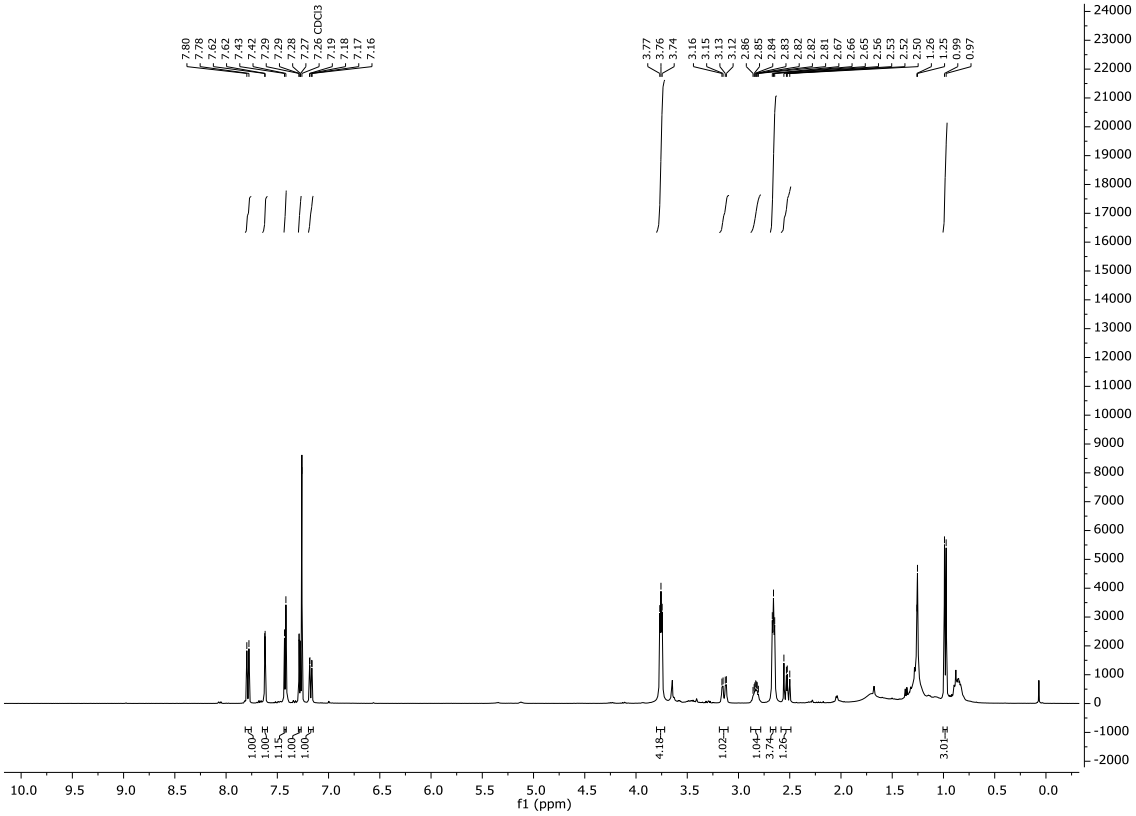
(*S*)-**8f**

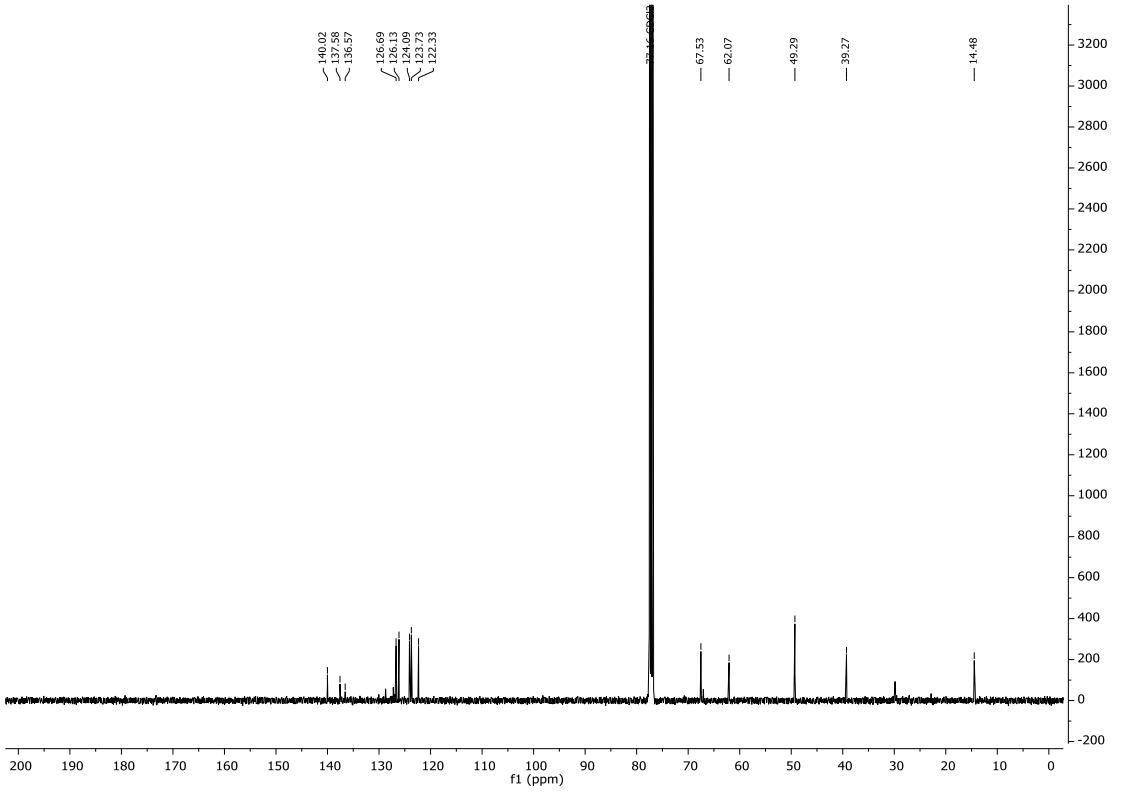

7.81
7.79
7.65
7.65
7.65
7.43
7.42
7.30
7.29
7.28
7.28
7.26 CDCl3
7.22
7.22
7.20
7.20
7.09
7.08
6.77
6.76
3.80
3.79
3.79
3.24
3.23
3.21
3.20
3.16
3.15
3.14
3.13
3.13
3.12
3.11
3.10
3.09
3.08
3.07
2.98
2.97
2.97
2.96
2.95
2.94
2.92
2.91
2.91
2.90
2.67
2.65
2.64
2.62
1.08
1.06
0.94
0.96
0.97
1.04
1.08
0.95
0.96
1.92
0.97
1.01
4.03
0.98
3.12
f1 (ppm)

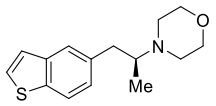

140.04
137.58
136.71
134.47
133.71
126.70
126.12
125.50
124.06
123.74
122.84
122.38
77.16 CDCl3
61.55
48.79
46.54
39.65
26.51
14.61
f1 (ppm)


O
N
Me
S

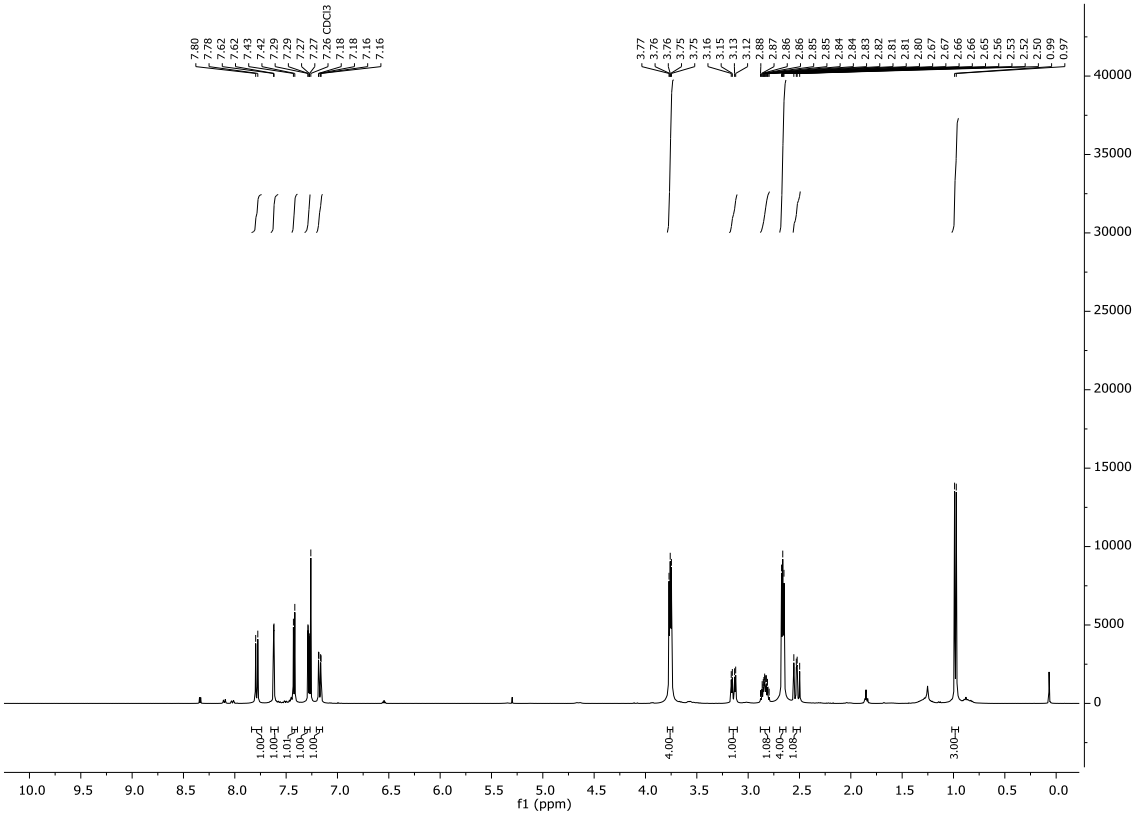
(*R*)-**8g**

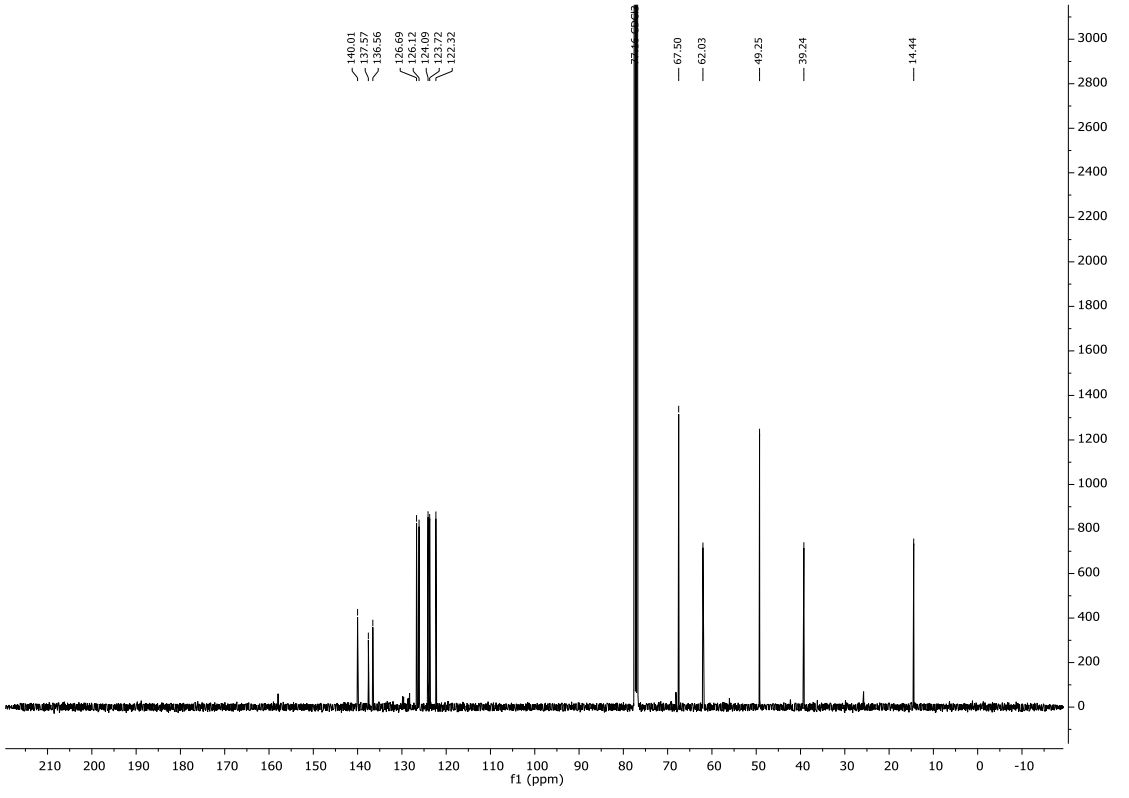

7.80
7.78
7.62
7.62
7.43
7.42
7.29
7.29
7.28
7.27
CDCl3
7.26
7.19
7.18
7.17
7.16
3.77
3.76
3.74
3.16
3.15
3.13
3.12
2.86
2.85
2.84
2.83
2.82
2.82
2.81
2.67
2.66
2.65
2.55
2.53
2.52
2.50
1.26
1.25
0.99
0.97
1.00
1.00
1.15
1.00
1.00
4.18
1.02
1.04
3.74
1.26
3.01
f1 (ppm)

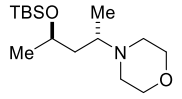

140.02
137.58
136.57
126.69
126.13
124.09
123.73
122.33
77.42
77.00
76.58
67.53
62.07
49.29
39.27
14.48
f1 (ppm)


O
N
Me
S

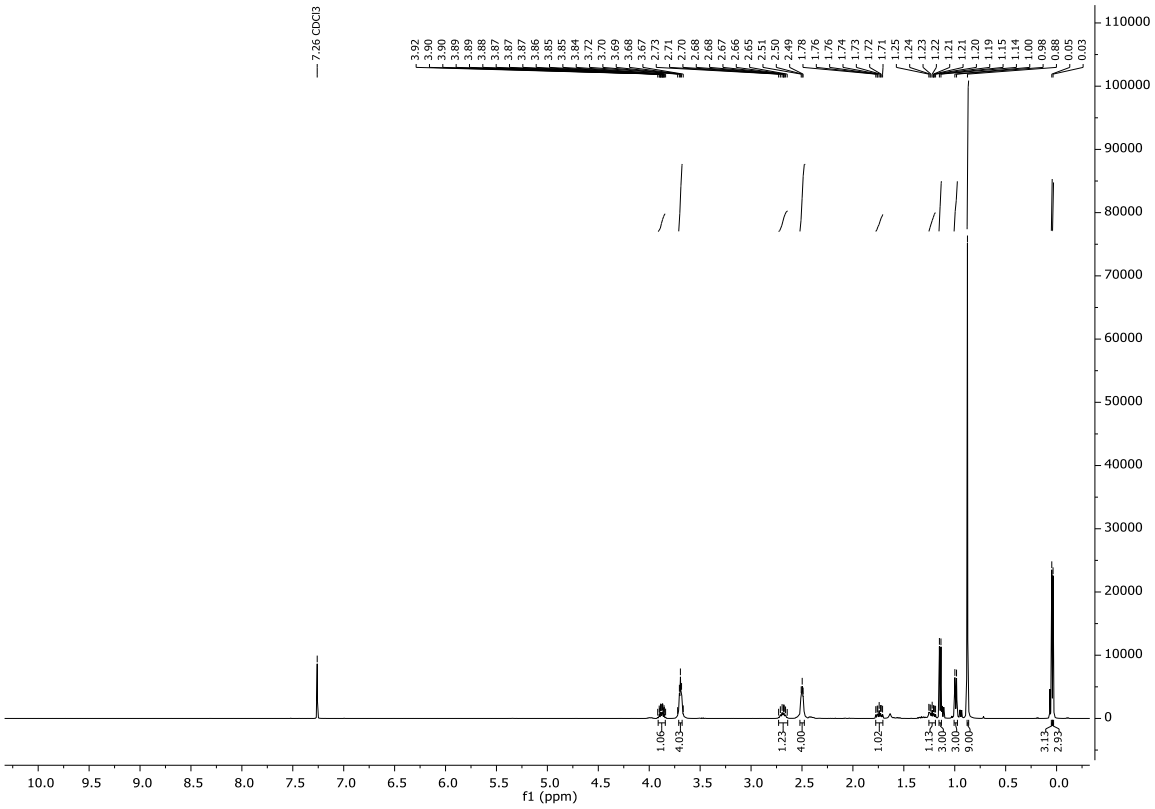
(*S*)-**8g**

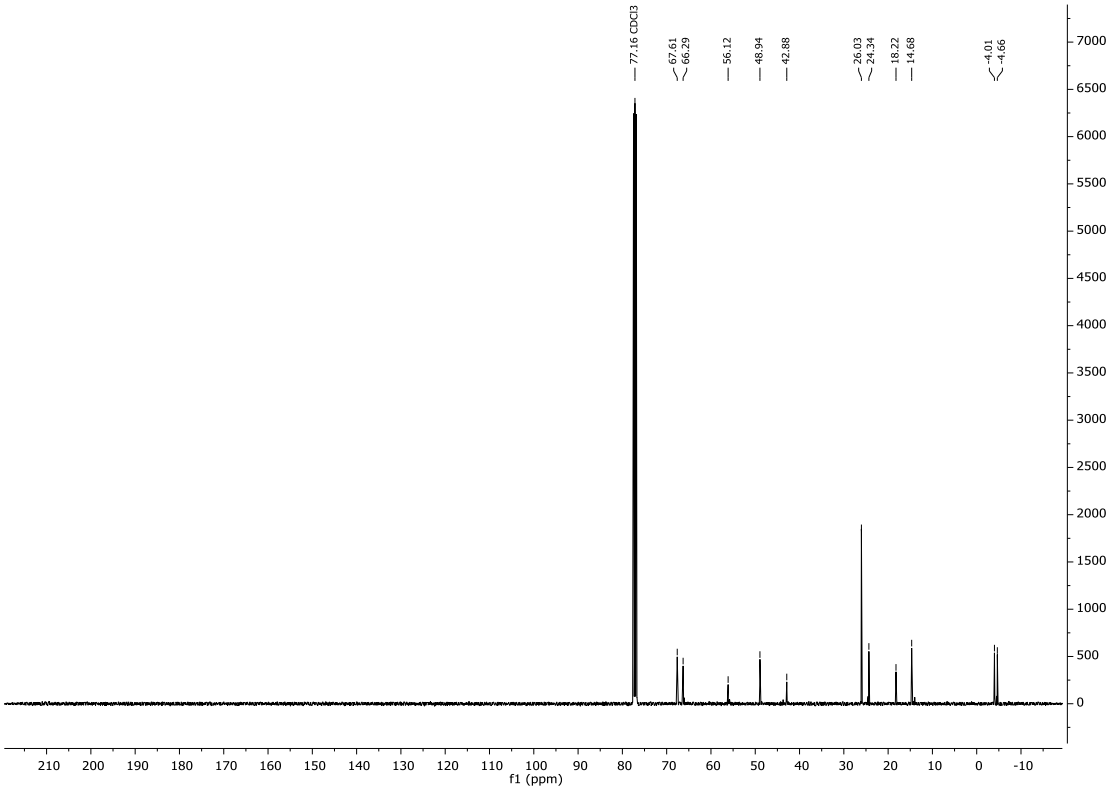

7.80
7.78
7.62
7.62
7.43
7.42
7.29
7.29
7.27
7.27
7.26 CDCl3
7.18
7.18
7.16
7.16
3.77
3.76
3.76
3.75
3.75
3.16
3.15
3.13
3.12
2.88
2.87
2.86
2.86
2.85
2.85
2.84
2.84
2.83
2.82
2.81
2.81
2.80
2.67
2.67
2.66
2.66
2.65
2.56
2.53
2.52
2.50
0.99
0.97
1.00
1.00
1.01
1.00
1.00
4.00
1.00
1.08
4.00
1.08
3.00
f1 (ppm)

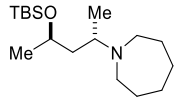

140.01
137.57
136.56
126.69
126.12
124.09
123.72
122.32
77.16 CDCl3
67.50
62.03
49.25
39.24
14.44
f1 (ppm)


TBSO
Me
Me
N
O

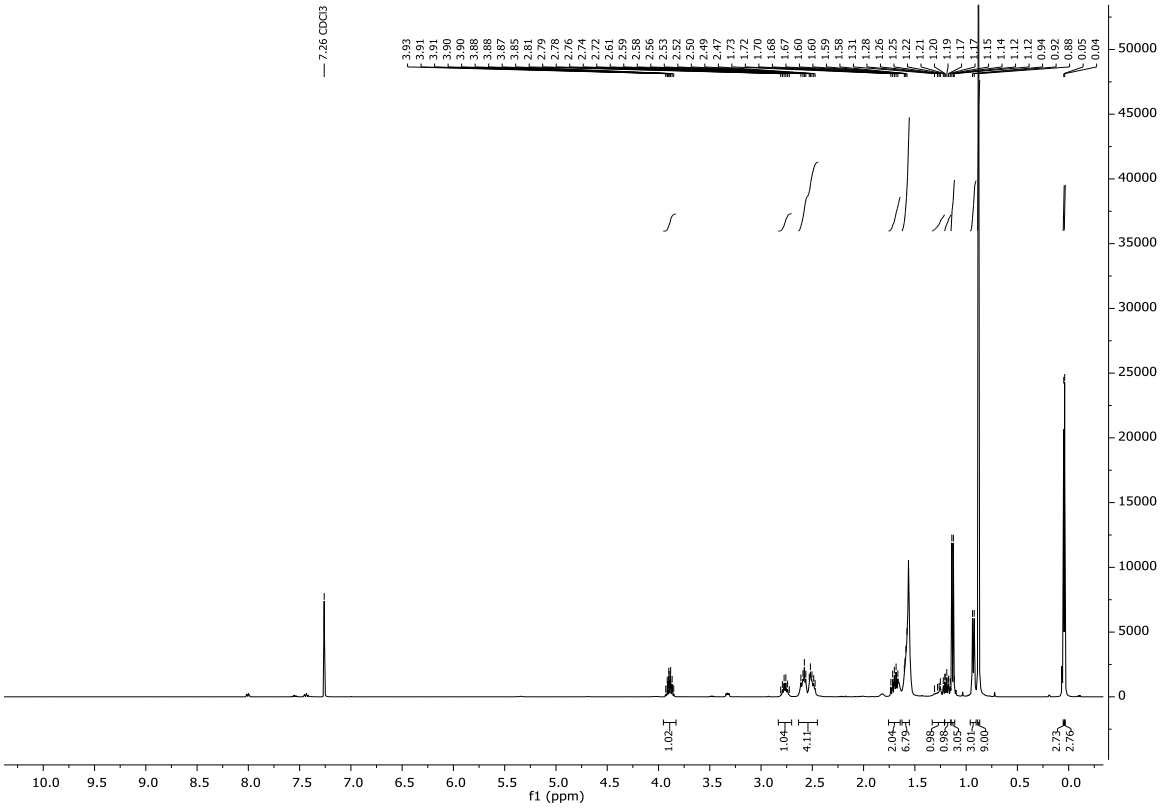
anti-**8h**

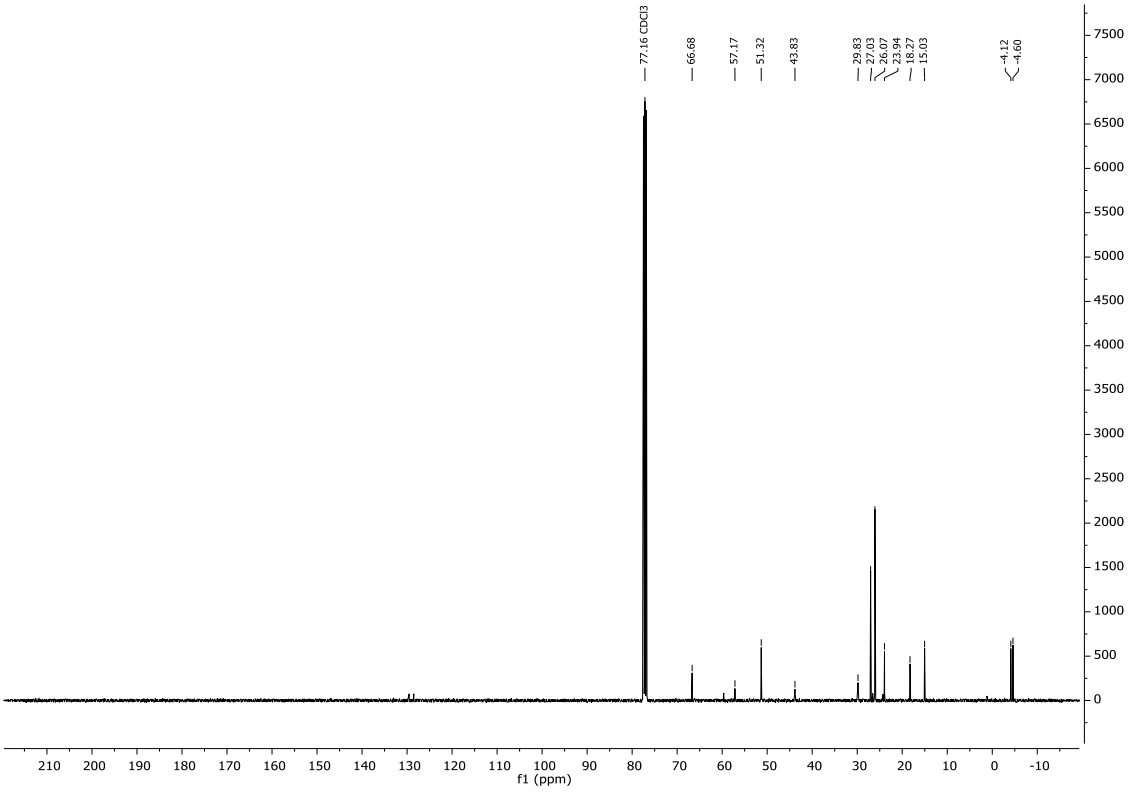

7.26 CDCl3
3.92
3.90
3.90
3.89
3.89
3.88
3.87
3.87
3.87
3.86
3.85
3.85
3.84
3.72
3.70
3.69
3.68
3.67
2.73
2.71
2.70
2.68
2.68
2.67
2.66
2.65
2.51
2.50
2.49
1.78
1.76
1.76
1.74
1.73
1.72
1.71
1.25
1.24
1.23
1.22
1.21
1.21
1.20
1.19
1.15
1.14
1.00
0.98
0.88
0.05
0.03
1.06
4.03
1.23
4.00
1.02
1.13
3.00
3.00
9.00
3.13
2.93
f1 (ppm)

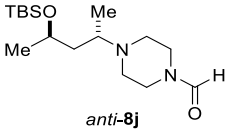

77.16 CDCl3
67.61
66.29
56.12
48.94
42.88
26.03
24.34
18.22
14.68
-4.01
-4.66
f1 (ppm)


TBSO
Me
Me
N

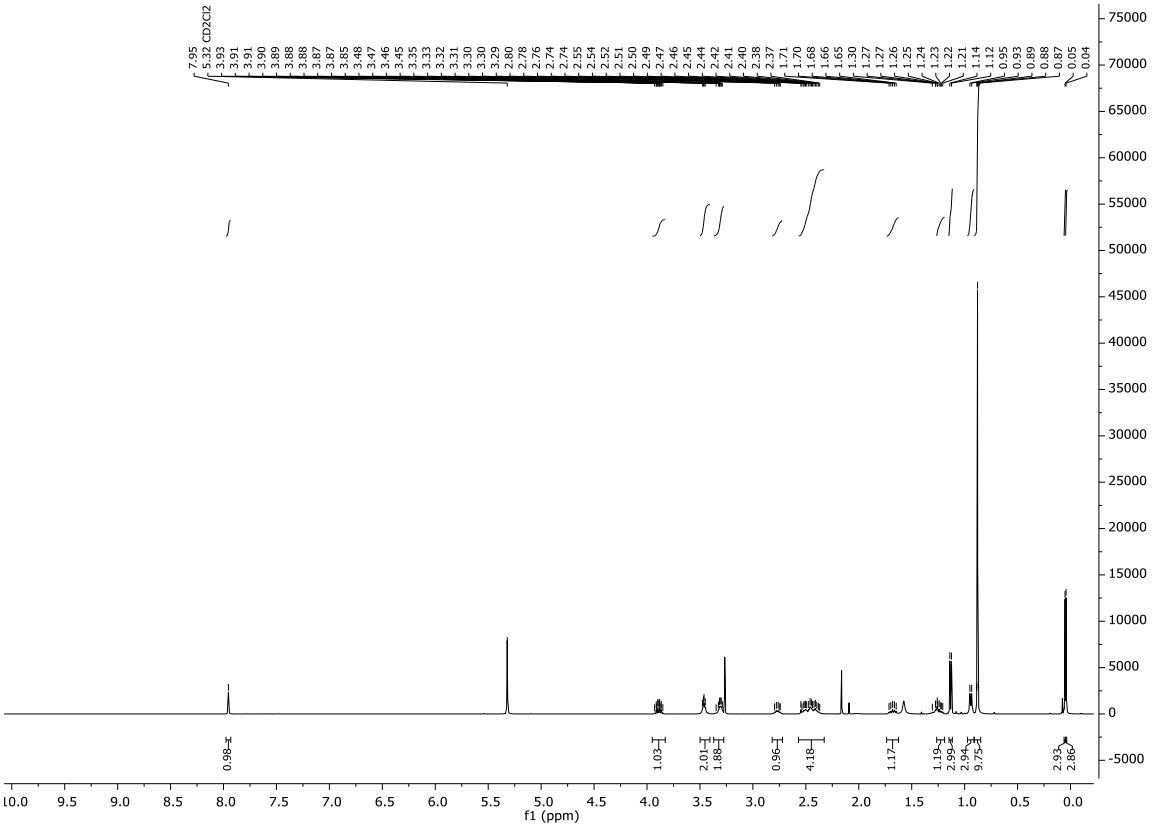
anti-**8i**

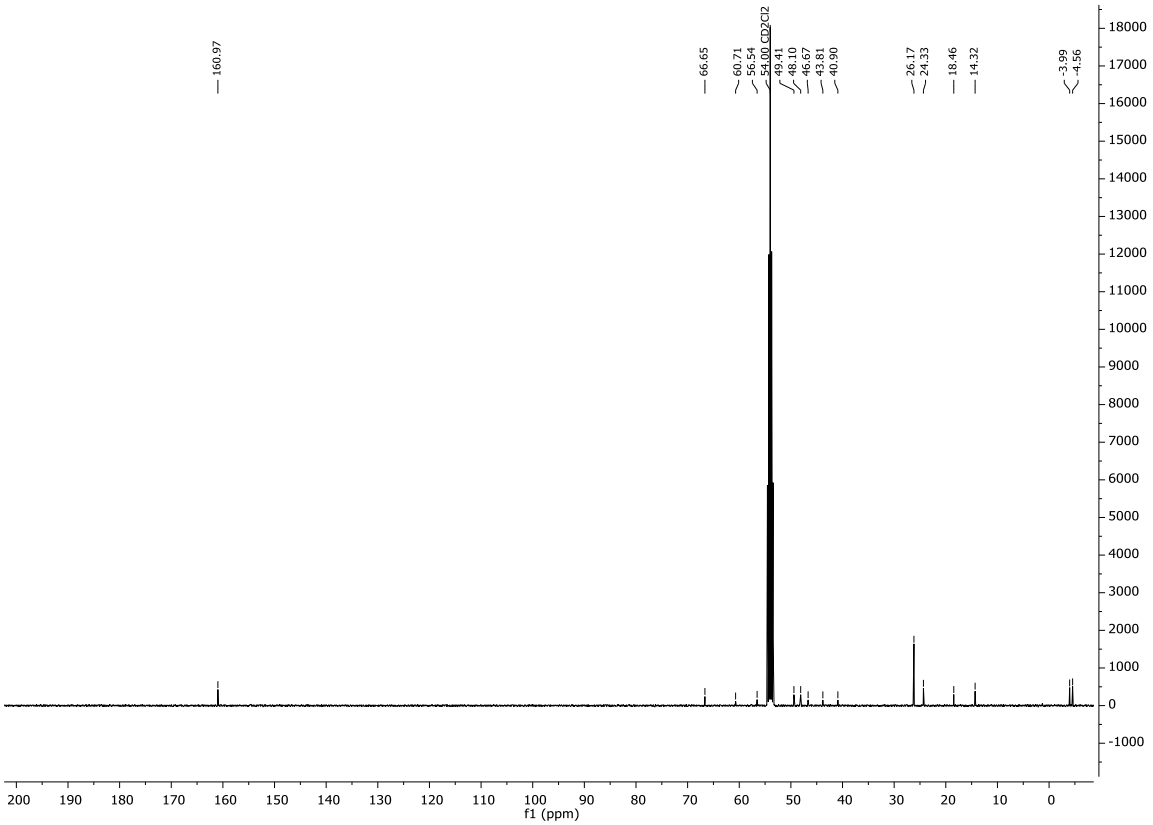

7.26 CDCl3
3.93
3.91
3.91
3.90
3.90
3.88
3.88
3.87
3.85
2.81
2.79
2.78
2.76
2.74
2.72
2.61
2.59
2.58
2.56
2.53
2.52
2.50
2.49
2.47
1.73
1.72
1.70
1.68
1.67
1.60
1.60
1.59
1.58
1.31
1.28
1.26
1.25
1.22
1.21
1.20
1.19
1.17
1.17
1.15
1.14
1.12
1.12
0.94
0.92
0.88
0.05
0.04
1.02
1.04
4.11
2.04
6.79
0.98
0.98
3.05
3.01
9.00
2.73
2.76
f1 (ppm)


77.16 CDCl3
66.68
57.17
51.32
43.83
29.83
27.03
26.07
23.94
18.27
15.03
-4.12
-4.60
f1 (ppm)


TBSO
Me
Me
N
N
H
O

anti-**8j**


7.95
5.32 CD2Cl2
3.93
3.91
3.91
3.90
3.89
3.88
3.88
3.87
3.87
3.85
3.48
3.47
3.46
3.45
3.35
3.33
3.32
3.31
3.30
3.30
3.29
2.80
2.78
2.76
2.74
2.74
2.55
2.54
2.52
2.51
2.50
2.49
2.47
2.46
2.45
2.44
2.42
2.41
2.40
2.38
2.37
1.71
1.70
1.68
1.66
1.65
1.30
1.27
1.27
1.26
1.25
1.24
1.23
1.22
1.21
1.14
1.12
0.95
0.93
0.89
0.88
0.87
0.05
0.04
0.98
1.03
2.01
1.88
0.96
4.18
1.17
1.19
2.99
2.94
9.75
2.93
2.86
f1 (ppm)


160.97
66.65
60.71
56.54
54.00 CD2Cl2
49.41
48.10
46.67
43.81
40.90
26.17
24.33
18.46
14.32
-3.99
-4.56
f1 (ppm)

8 Chiral chromatograms for the determination of the enantiomeric excess

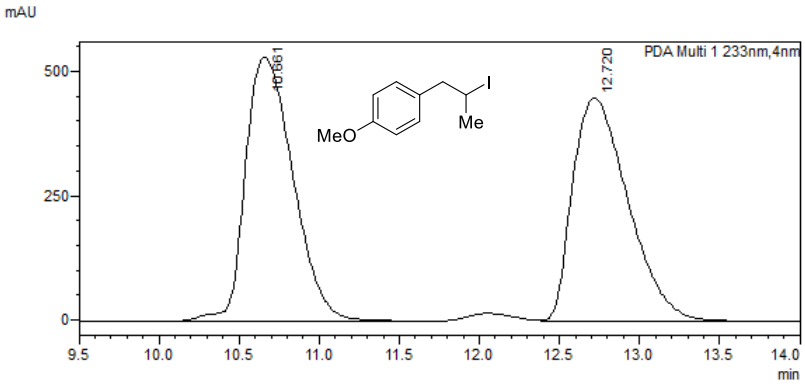
8.1 Analysis of optically enriched secondary alkyl iodides

8.1.1 (*R*)- and (*S*)-1a

The enantiomeric excess of (*R*)- and (*S*)-**1a** was determined by chiral HPLC analysis.

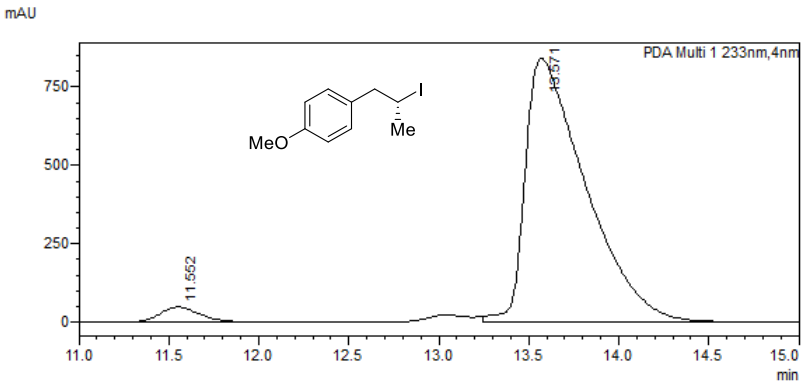
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.9:0.1, 1 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	10.661	11065561	531348	50.458
2	12.720	10864627	449040	49.542
Total		21930188	980388	100.000

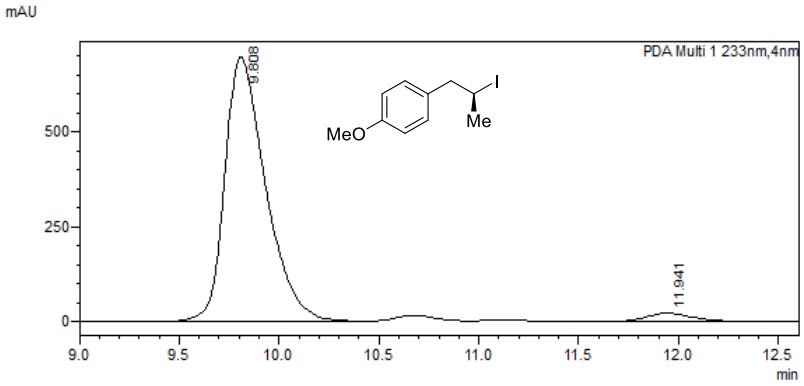
(*R*)-Enantiomer: t_R (min) = 11.6 ((*S*)-enantiomer, minor), 13.6 ((*R*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	11.552	674295	46262	3.322
2	13.571	19625958	840123	96.678
Total		20300252	886385	100.000

The enantiomeric excess of (*R*)-**1a** was determined 94%.

(*S*)-Enantiomer: t_R (min) = 9.8 ((*S*)-enantiomer, major), 11.9 ((*R*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	9.808	9866016	697209	96.726
2	11.941	333951	21630	3.274
Total		10199967	718839	100.000

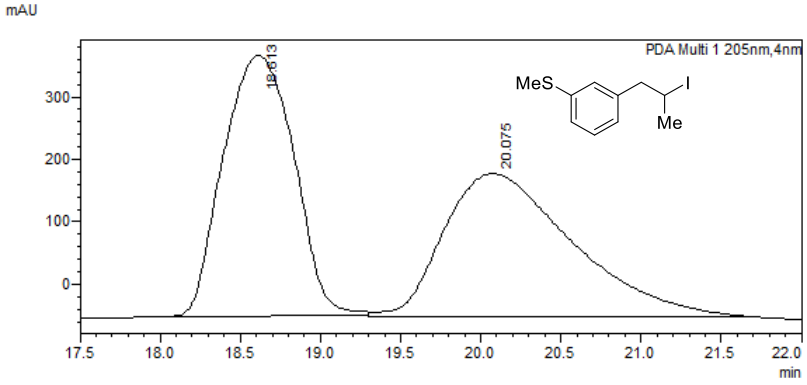
The enantiomeric excess of (*S*)-**1a** was determined 94%.

8.1.2 (*S*)-1b

The enantiomeric excess of (*S*)-**1b** was determined by chiral HPLC analysis.

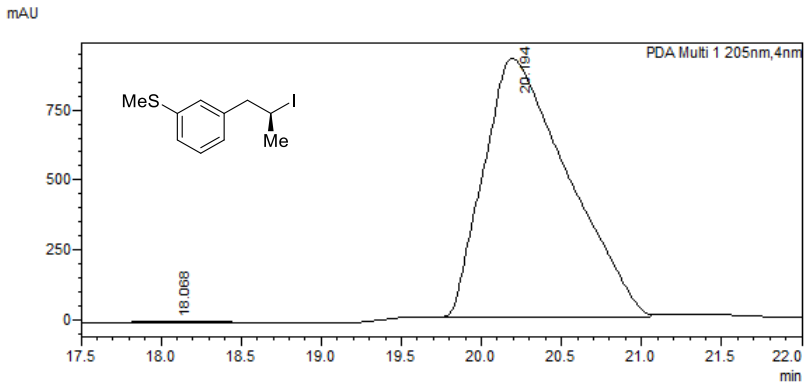
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.9:01, 1 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	18.613	12815406	417724	50.188
2	20.075	12719460	228430	49.812
Total		25534866	646154	100.000

(*S*)-Enantiomer: t_R (min) = 18.1 ((*R*)-enantiomer, minor), 20.2 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	18.068	144998	4140	0.424
2	20.194	34035369	928103	99.576
Total		34180367	932243	100.000

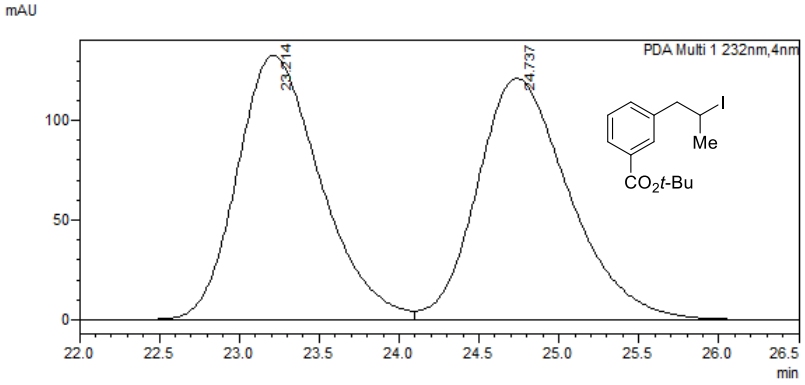
The enantiomeric excess of (*S*)-**1b** was determined to 99%.

8.1.3 (*R*)- and (*S*)-1e

The enantiomeric excess of (*R*)- and (*S*)-**1e** was determined by chiral HPLC analysis.

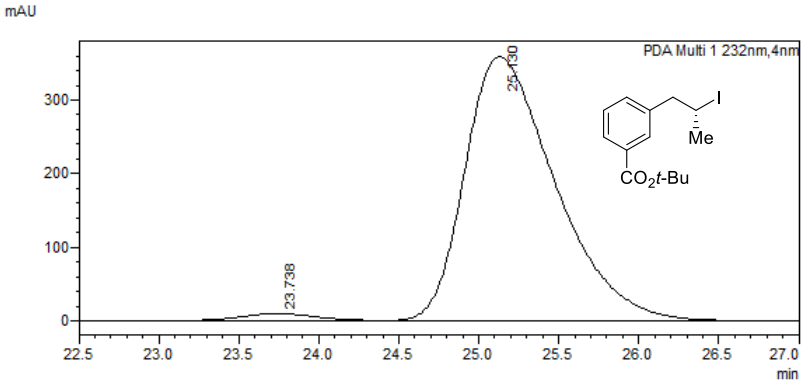
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.9:0.1, 0.5 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	23.214	4828903	132734	49.743
2	24.737	4878869	121420	50.257
Total		9707771	254154	100.000

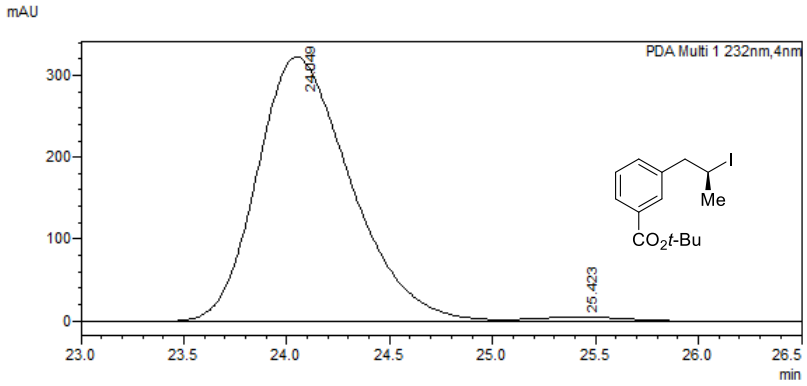
(*R*)-Enantiomer: t_R (min) = 23.7 ((*S*)-enantiomer, minor), 25.1 ((*R*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	23.738	271665	8925	1.898
2	25.130	14039051	358807	98.102
Total		14310716	367731	100.000

The enantiomeric excess of (*R*)-**1e** was determined to 96%.

(*S*)-Enantiomer: t_R (min) = 24.1 ((*S*)-enantiomer, major), 25.4 ((*R*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	24.049	10197771	322555	98.329
2	25.423	173315	5340	1.671
Total		10371086	327894	100.000

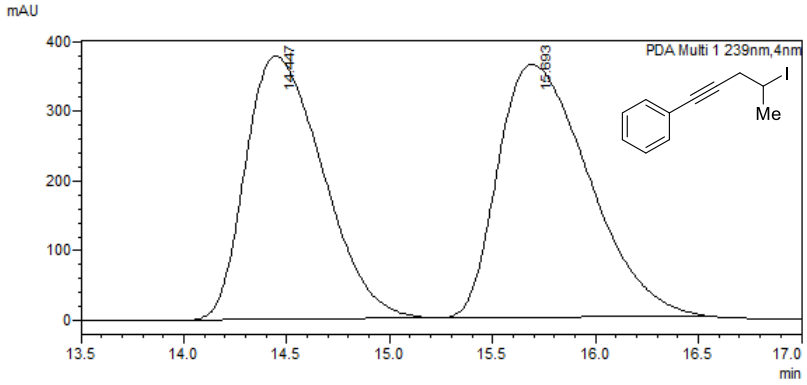
The enantiomeric excess of (*S*)-**1e** was determined to 97%.

8.1.4 (*R*)-1f

The enantiomeric excess of (*R*)-**1f** was determined by chiral HPLC analysis.

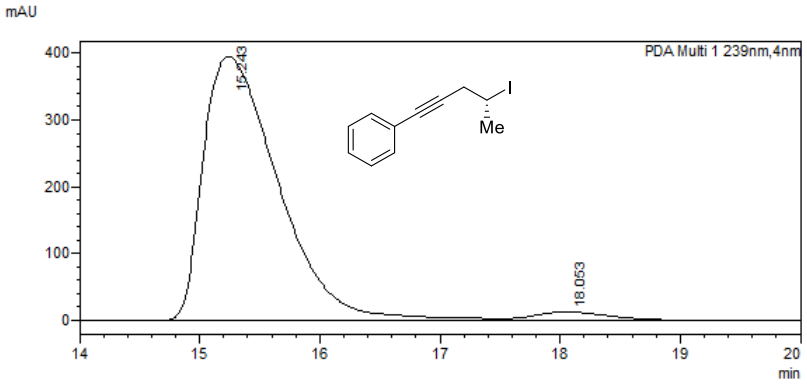
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.9:0.1, 1 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	14.447	9864264	377571	47.019
2	15.693	11114852	361927	52.981
Total		20979117	739498	100.000

(*S*)-Enantiomer: t_R (min) = 15.2 ((*R*)-enantiomer, major), 18.1 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	15.243	17202309	394597	96.747
2	18.053	578371	13081	3.253
Total		17780680	407678	100.000

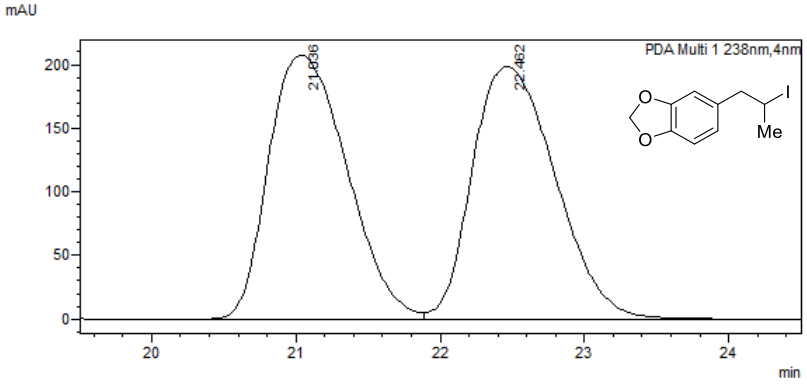
The enantiomeric excess of (*R*)-**1f** was determined to 94%.

8.1.5 (*R*)- and (*S*)-1g

The enantiomeric excess of (*R*)- and (*S*)-**1g** was determined by chiral HPLC analysis.

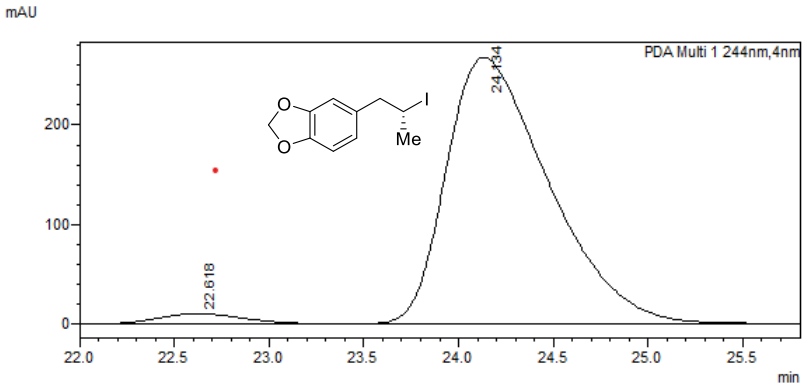
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.8:0.2, 0.5 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	21.036	7834897	207201	49.691
2	22.462	7932212	198494	50.309
Total		15767110	405695	100.000

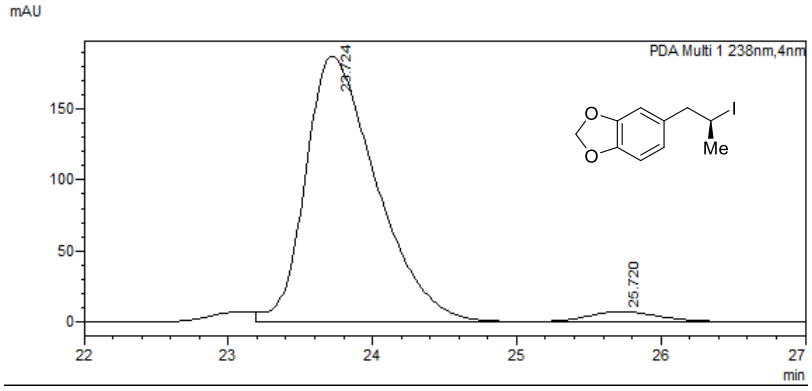
(*R*)-Enantiomer: t_R (min) = 22.6 ((*S*)-enantiomer, minor), 24.1 ((*R*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	22.618	292104	9839	2.818
2	24.134	10072633	267478	97.182
Total		10364736	277316	100.000

The enantiomeric excess of (*R*)-**1g** was determined to 95%.

(*S*)-Enantiomer: t_R (min) = 23.7 ((*S*)-enantiomer, major), 25.7 ((*R*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	23.724	6385689	186446	96.660
2	25.720	220628	6962	3.340
Total		6606317	193408	100.000

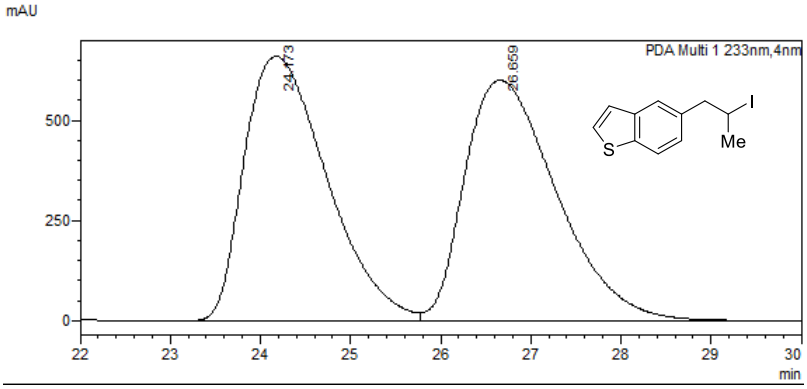
The enantiomeric excess of (*S*)-**1g** was determined to 94%.

8.1.6 (*S*)- and (*R*)-1h

The enantiomeric excess of (*R*)- and (*S*)-**1k** was determined by chiral HPLC analysis.

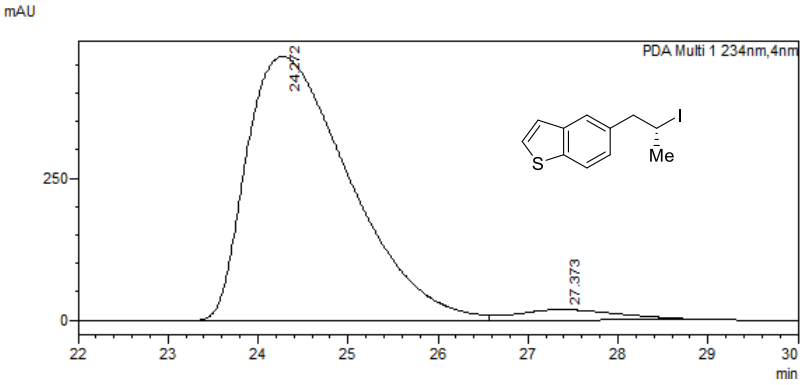
HPLC (column: OJ-H; *n*-heptane/2-propanol = 99.9:0.1, 1 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	24.173	42209021	660675	49.815
2	26.659	42523330	600084	50.185
Total		84732352	1260760	100.000

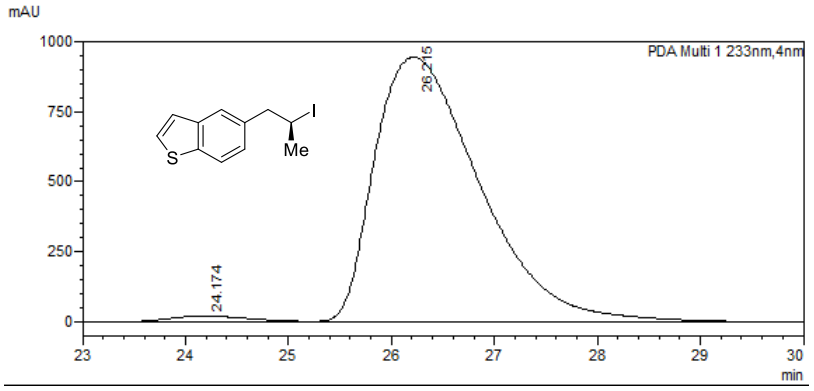
(*R*)-Enantiomer: t_R (min) = 24.3 ((*R*)-enantiomer, major), 27.4 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	24.272	37028289	465067	96.258
2	27.373	1439359	18151	3.742
Total		38467648	483218	100.000

The enantiomeric excess of (*R*)-**1h** was determined to 93%.

(*S*)-Enantiomer: t_R (min) = 24.2 ((*R*)-enantiomer, minor), 26.2 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	24.174	1203977	21662	1.758
2	26.215	67282608	943929	98.242
Total		68486585	965591	100.000

The enantiomeric excess of (*S*)-**1h** was determined to 97%.

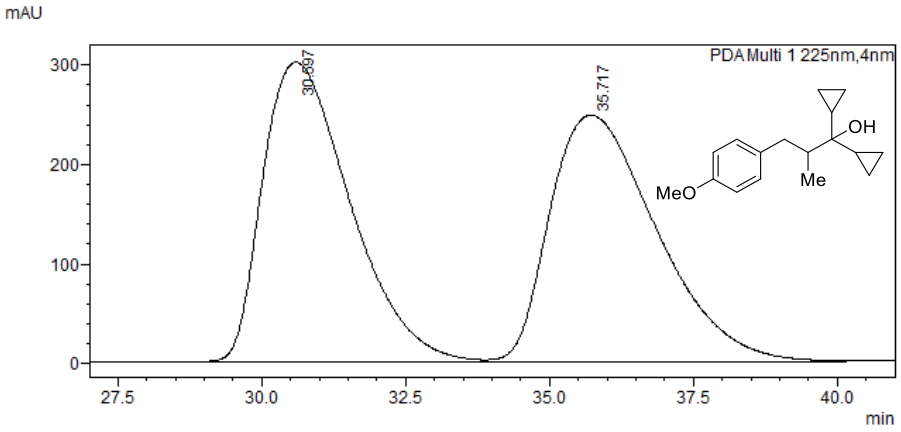
8.2 Analysis of optically enriched products

8.2.1 (*R*)- and (S)-4a

The enantiomeric excess of (*R*)- and (*S*)-**4a** was determined by chiral HPLC analysis.

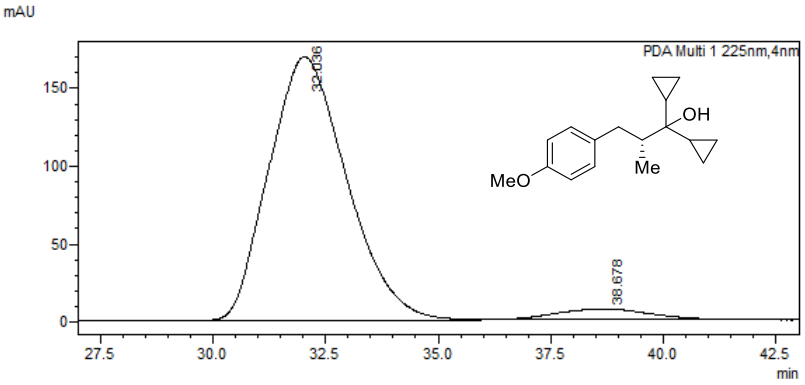
HPLC (column: OJ-H; *n*-heptane/2-propanol = 99:1, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	30.597	31717245	300745	49.856
2	35.717	31900167	247589	50.144
Total		63617412	548334	100.000

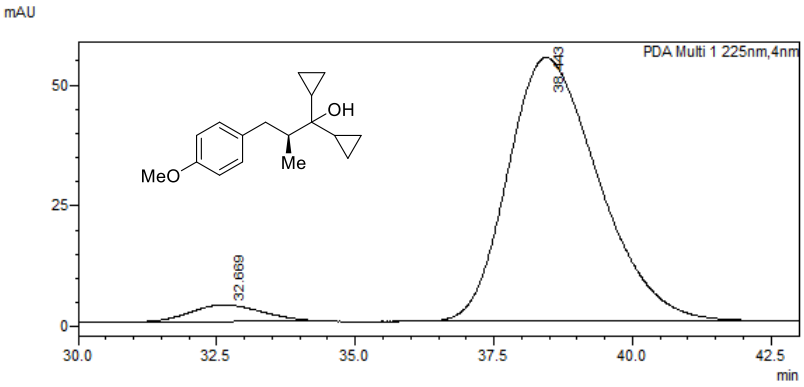
(*R*)-Enantiomer: t_R (min) = 32.0 ((*R*)-enantiomer, major), 38.7 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	32.036	20354365	169281	95.558
2	38.678	946215	6756	4.442
Total		21300581	176037	100.000

The enantiomeric excess of (*R*)-**4a** was determined to 91%.

(*S*)-Enantiomer: t_R (min) = 32.7 ((*R*)-enantiomer, minor), 38.4 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	32.669	316010	3447	4.835
2	38.443	6219453	54567	95.165
Total		6535463	58014	100.000

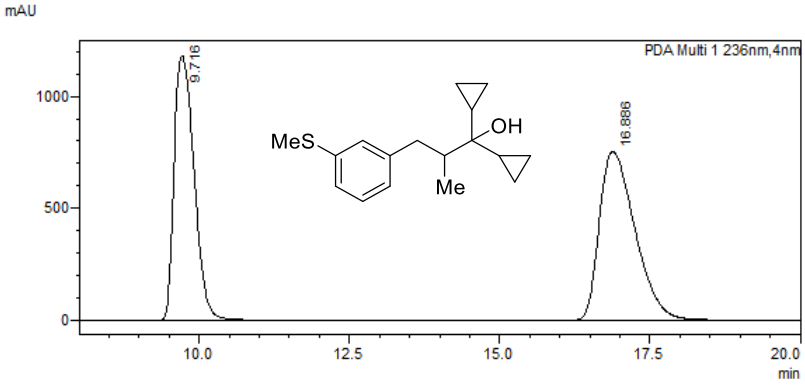
The enantiomeric excess of (*S*)-**4a** was determined to 90%.

8.2.2 (*R*)-4b

The enantiomeric excess of (*R*)-**4b** was determined by chiral HPLC analysis.

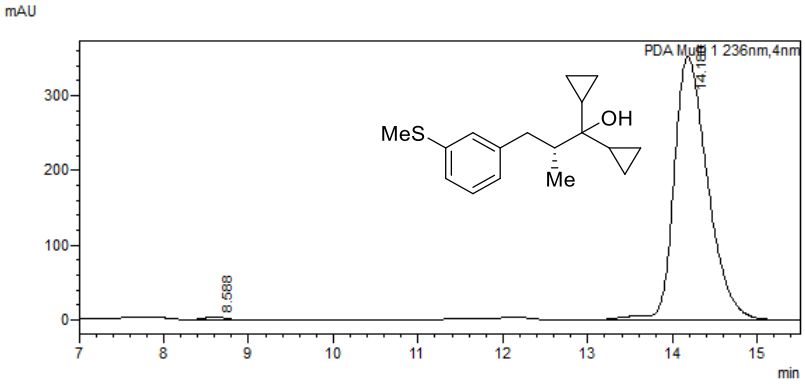
HPLC (column: OD-H; *n*-heptane/2-propanol = 98:2, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	9.716	27326583	1178811	46.684
2	16.886	31209135	752704	53.316
Total		58535718	1931516	100.000

(*R*)-Enantiomer: t_R (min) = 8.6 ((*S*)-enantiomer, minor), 14.2 ((*R*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	8.588	70829	4459	0.722
2	14.180	9732780	352539	99.278
Total		9803609	356998	100.000

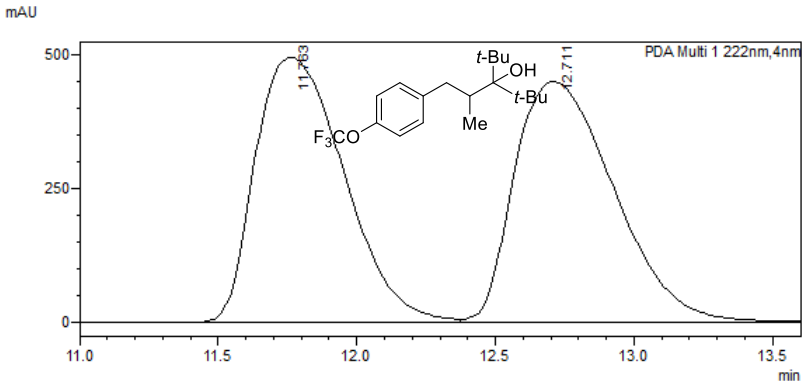
The enantiomeric excess of (*R*)-**4b** was determined to 99%.

8.2.3 (*S*)-4c

The enantiomeric excess of (*S*)-**4c** was determined by chiral HPLC analysis.

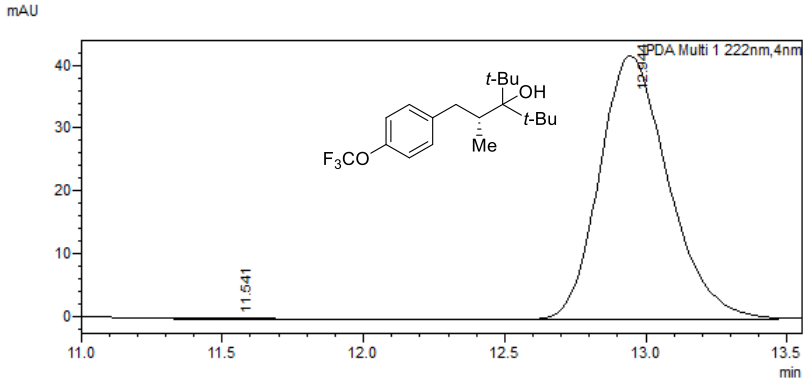
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.8:0.2, 0.5 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	11.763	11073574	495854	49.485
2	12.711	11304212	450112	50.515
Total		22377786	945966	100.000

(*S*)-Enantiomer: t_R (min) = 11.5 ((*R*)-enantiomer, minor), 12.9 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	11.541	6368	255	0.884
2	12.944	713886	41976	99.116
Total		720254	42231	100.000

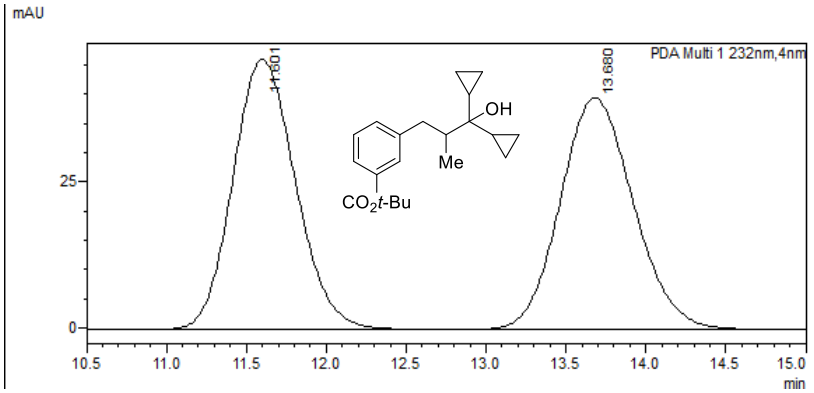
The enantiomeric excess of (*S*)-**4c** was determined to 98%.

8.2.4 (*R*)- and (*S*)-4e

The enantiomeric excess of (*R*)- and (*S*)-**4e** was determined by chiral HPLC analysis.

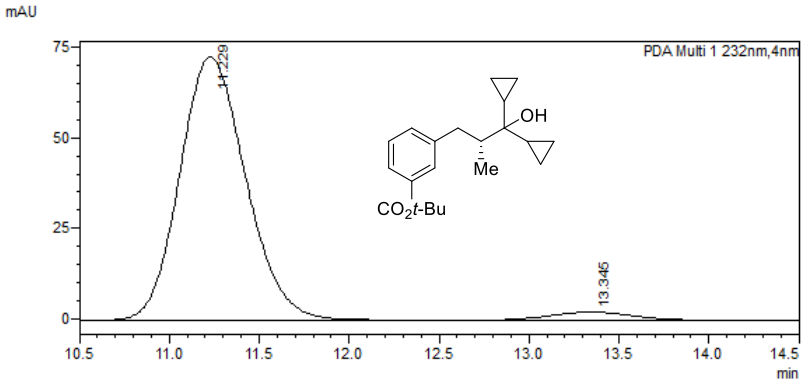
HPLC (column: OD-H; *n*-heptane/2-propanol = 99:1, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	11.601	1254758	46187	49.917
2	13.680	1258918	39559	50.083
Total		2513675	85746	100.000

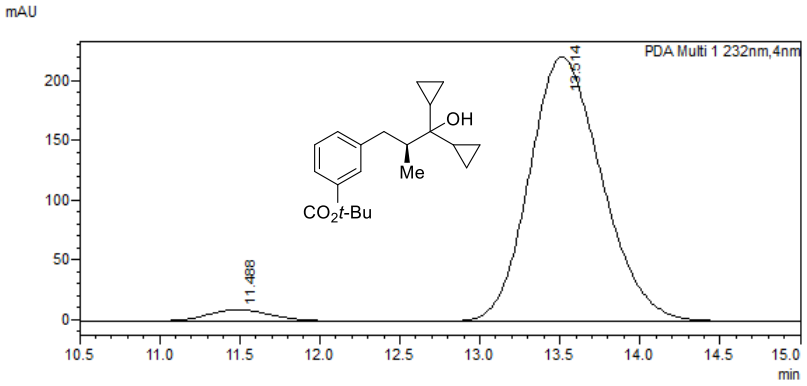
(*R*)-Enantiomer: t_R (min) = 11.3 ((*R*)-enantiomer, major), 13.5 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	11.229	1846325	72683	96.455
2	13.345	67851	2229	3.545
Total		1914176	74912	100.000

The enantiomeric excess of (*R*)-**4e** was determined to 93%.

(*S*)-Enantiomer: t_R (min) = 11.5 ((*R*)-enantiomer, minor), 13.5 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	11.488	241642	9377	3.362
2	13.514	6945710	221138	96.638
Total		7187352	230515	100.000

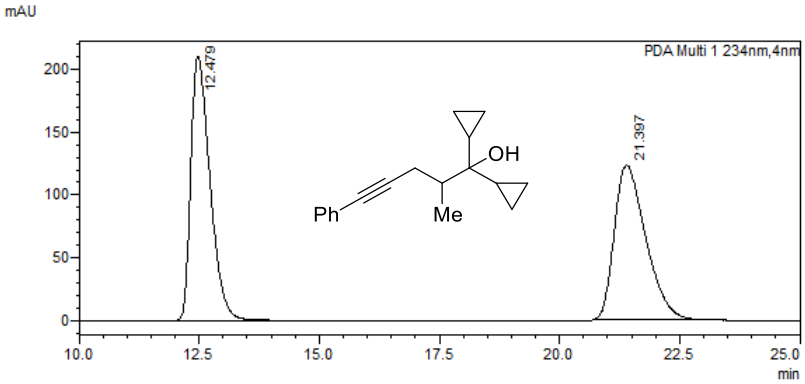
The enantiomeric excess of (*S*)-**4e** was determined to 93%.

8.2.5 (*R*)-4f

The enantiomeric excess of (*R*)-**4f** was determined by chiral HPLC analysis.

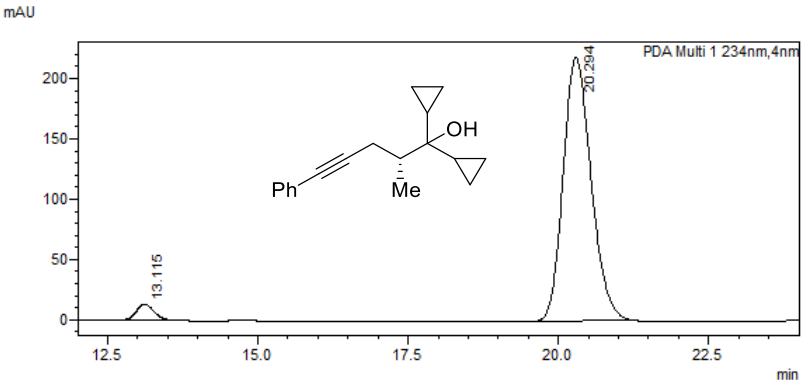
HPLC (column: OD-H; *n*-heptane/2-propanol = 98:2, 0.5 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	12.479	5828381	209942	51.048
2	21.397	5589133	122684	48.952
Total		11417514	332626	100.000

(*R*)-Enantiomer: t_R (min) = 13.1 ((*S*)-enantiomer, minor), 20.3 ((*R*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	13.115	253101	12925	3.459
2	20.294	7064039	218350	96.541
Total		7317140	231275	100.000

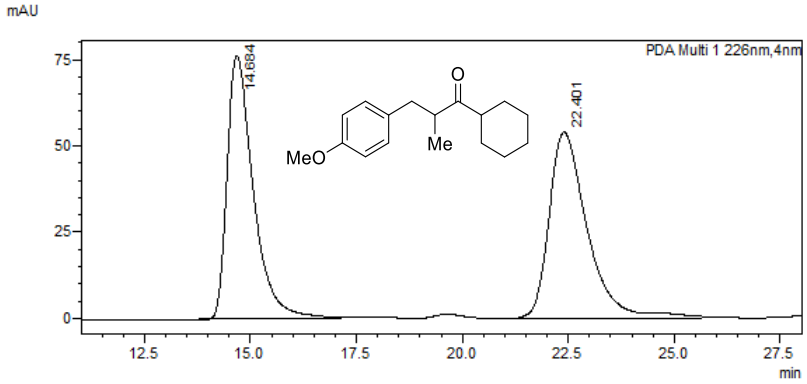
The enantiomeric excess of (*R*)-**4f** was determined to 93%.

8.2.6 (*R*)-4g

The enantiomeric excess of (*R*)-**4g** was determined by chiral HPLC analysis.

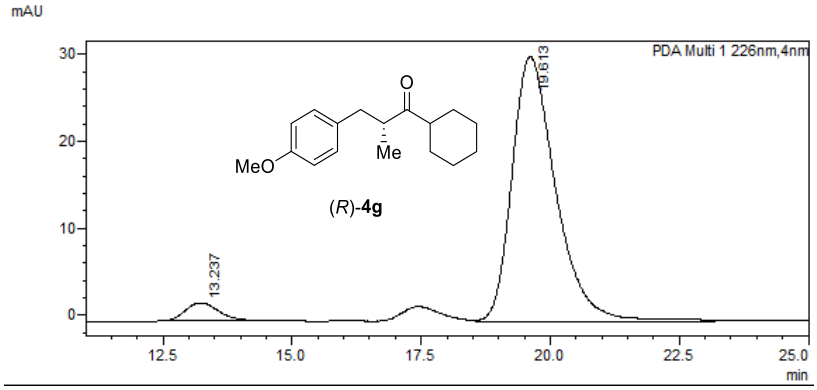
HPLC (column: OJ-H; *n*-heptane/2-propanol = 99.7:0.3, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	14.684	3282438	76146	48.896
2	22.401	3430708	54100	51.104
Total		6713146	130245	100.000

(*R*)-Enantiomer: t_R (min) = 13.2 ((*S*)-enantiomer, minor), 19.6 ((*R*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	13.237	91998	2055	4.805
2	19.613	1822524	30530	95.195
Total		1914522	32586	100.000

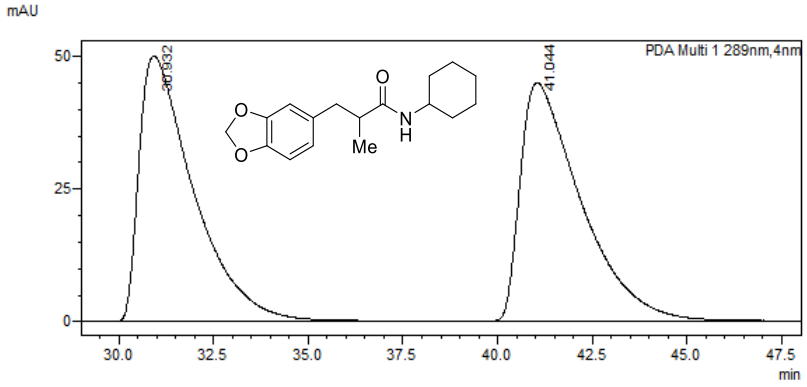
The enantiomeric excess of (*R*)-**4g** was determined to 90%.

8.2.7 (*R*)- and (*S*)-4l

The enantiomeric excess of (*R*)- and (*S*)-**4l** was determined by chiral HPLC analysis.

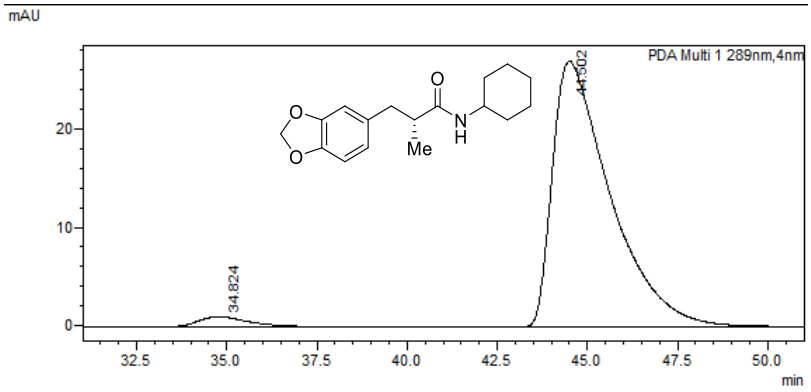
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.0:1.0, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	30.932	5017068	49987	49.872
2	41.044	5042728	44983	50.128
Total		10059796	94970	100.000

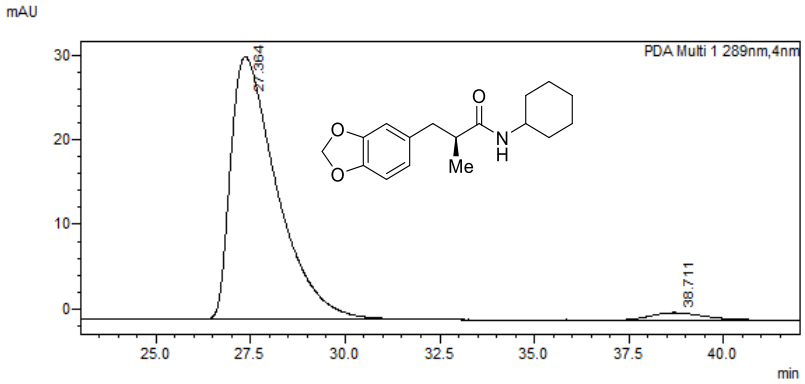
(*R*)-Enantiomer: t_R (min) = 34.8 ((*S*)-enantiomer, minor), 44.5 ((*R*)-enantiomer, major).



1	34.824	97782	1017	3.141
2	44.502	3015744	26934	96.859
Total		3113526	27951	100.000

The enantiomeric excess of (*R*)-**4l** was determined to 94%.

(*S*)-Enantiomer: t_R (min) = 27.3 ((*S*)-enantiomer, major), 38.7 ((*R*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	27.364	2627520	31029	96.719
2	38.711	89145	890	3.281
Total		2716666	31918	100.000

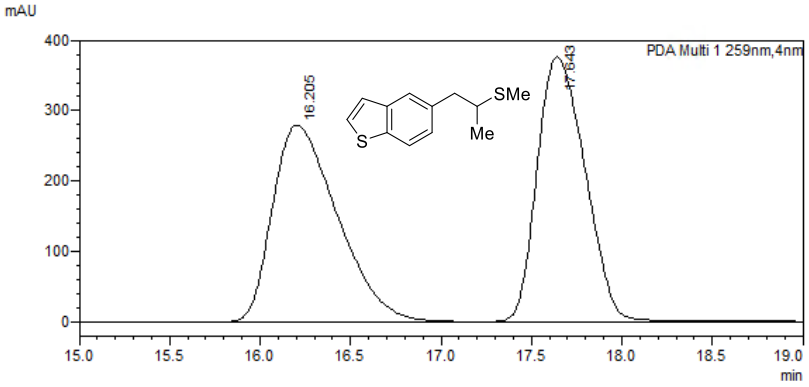
The enantiomeric excess of (*S*)-**4l** was determined to 94%.

8.2.8 (*R*)- and (*S*)-4o

The enantiomeric excess of (*R*) and (*S*)-**4o** was determined by chiral HPLC analysis.

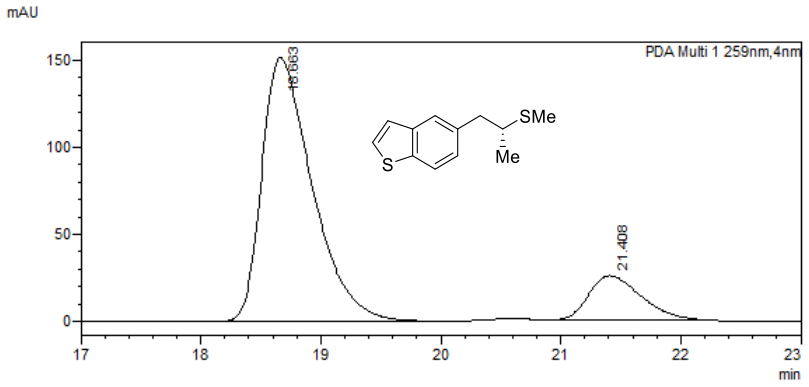
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.9:0.1, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	16.205	6992471	279140	50.083
2	17.643	6969380	376542	49.917
Total		13961851	655682	100.000

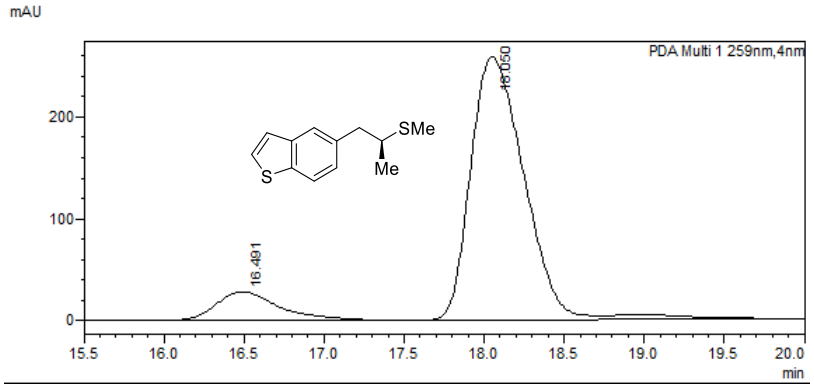
(*R*)-Enantiomer: t_R (min) = 18.6 ((*R*)-enantiomer, major), 21.4 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	18.663	4437119	151599	85.226
2	21.408	769185	25469	14.774
Total		5206304	177068	100.000

The enantiomeric excess of (*R*)-**4o** was determined to 70%

(*S*)-Enantiomer: t_R (min) = 16.5 ((*R*)-enantiomer, minor), 18.1 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	16.491	741404	27825	10.859
2	18.050	6086252	258725	89.141
Total		6827656	286550	100.000

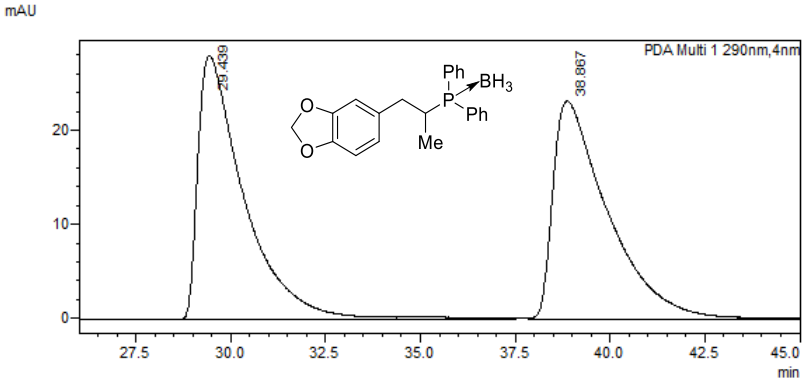
The enantiomeric excess of (*S*)-**4o** was determined to 78%

8.2.9 (*R*)- and (*S*)-4q

The enantiomeric excess of (*R*)- and (*S*)-**4q** was determined by chiral HPLC analysis.

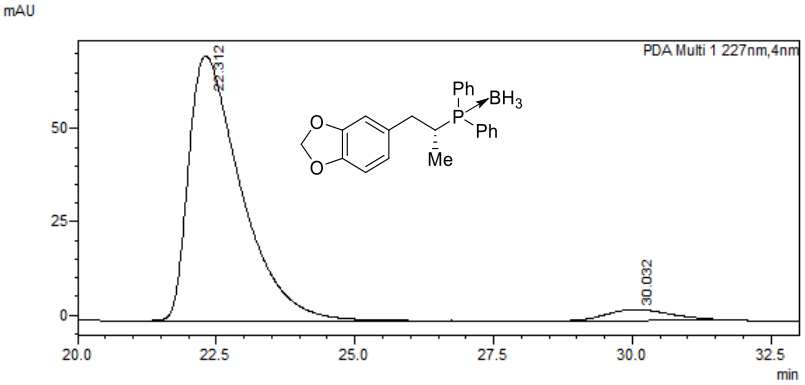
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.7:0.3, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	29.439	2408738	28058	50.330
2	38.867	2377128	23242	49.670
Total		4785867	51300	100.000

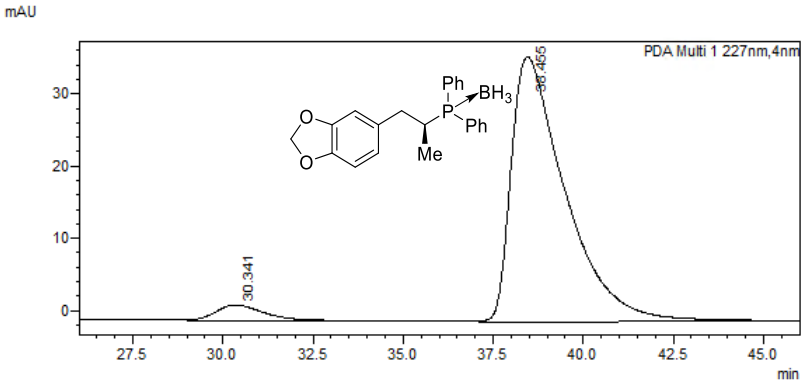
(*R*)-Enantiomer: t_R (min) = 22.3 ((*R*)-enantiomer, major), 30.0 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	22.312	4723819	71146	95.135
2	30.032	241547	2990	4.865
Total		4965367	74136	100.000

The enantiomeric excess of (*R*)-**4q** was determined to 90%.

(*S*)-Enantiomer: t_R (min) = 30.3 ((*R*)-enantiomer, minor), 38.5 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	30.341	202878	2186	5.005
2	38.455	3850935	36707	94.995
Total		4053813	38893	100.000

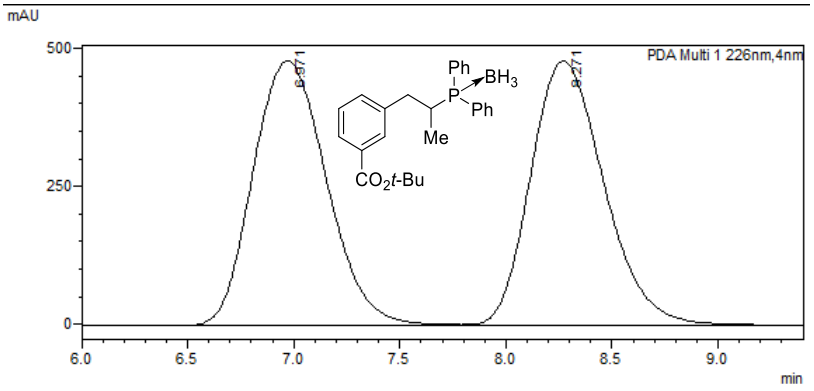
The enantiomeric excess of (*S*)-**4q** was determined to 90%.

8.2.10 (*R*)-4r

The enantiomeric excess of (*R*)-**4r** was determined by chiral HPLC analysis.

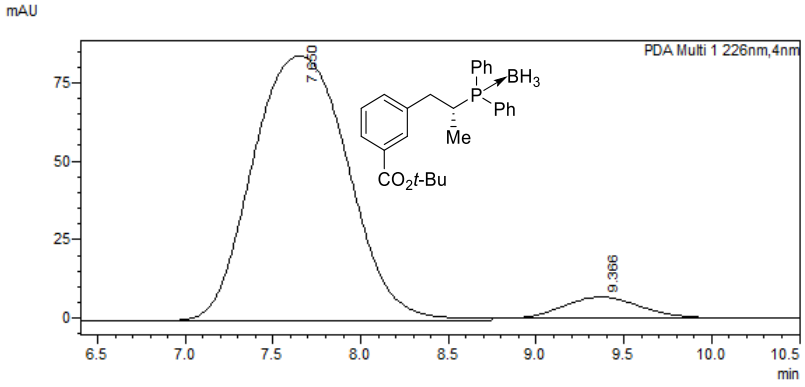
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.0:1.0, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	6.971	11576004	479470	50.018
2	8.271	11567654	479898	49.982
Total		23143659	959369	100.000

(*R*)-Enantiomer: t_R (min) = 7.7 ((*R*)-enantiomer, major), 9.4 ((S)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	7.650	3194589	84277	93.914
2	9.366	207022	6778	6.086
Total		3401611	91055	100.000

The enantiomeric excess of (*R*)-**4r** was determined to 88%.

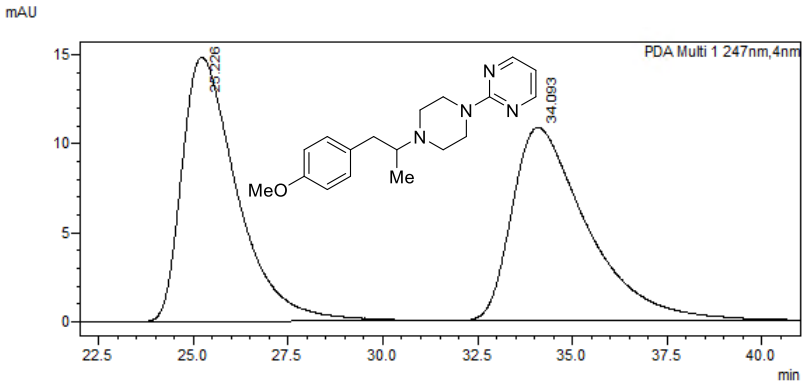
8.3 Analysis of optically enriched tertiary amines

8.3.1 (*R*)- and (*S*)-8a

The enantiomeric excess of (*R*)- and (*S*)-**8a** was determined by chiral HPLC analysis.

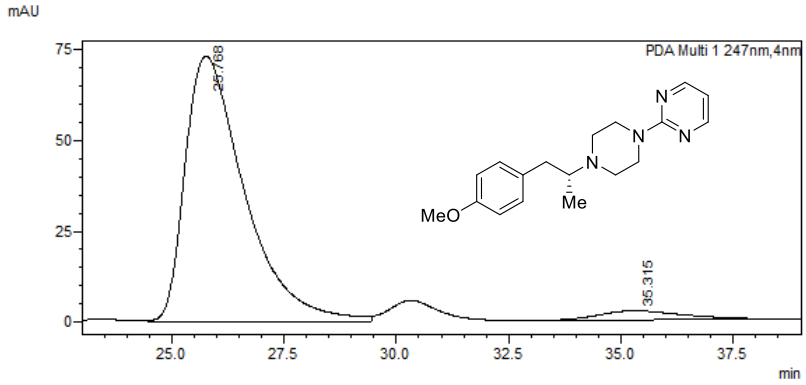
HPLC (column: OJ-H; *n*-heptane/2-propanol = 98.0:2.0, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	25.226	1507633	14852	50.044
2	34.093	1504959	10857	49.956
Total		3012592	25709	100.000

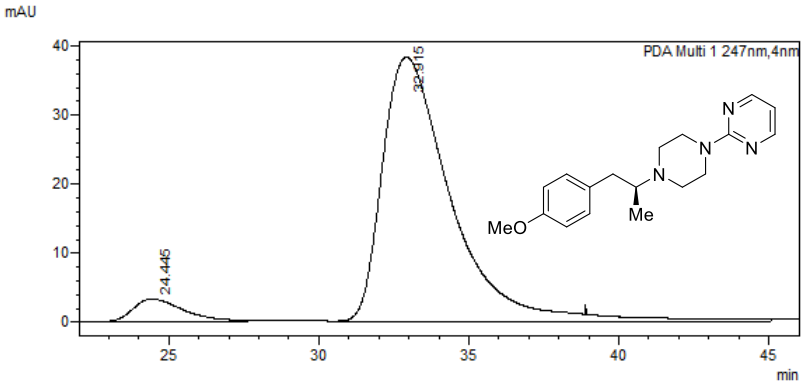
(*R*)-Enantiomer: t_R (min) = 25.8 ((*R*)-enantiomer, major), 35.3 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	25.768	6715045	72849	95.466
2	35.315	318885	2485	4.534
Total		7033929	75334	100.000

The enantiomeric excess of (*R*)-**8a** was determined to 91%.

(*S*)-Enantiomer: t_R (min) = 24.5 ((*R*)-enantiomer, minor), 32.9 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	24.445	392946	3308	6.015
2	32.915	6139817	38292	93.985
Total		6532763	41600	100.000

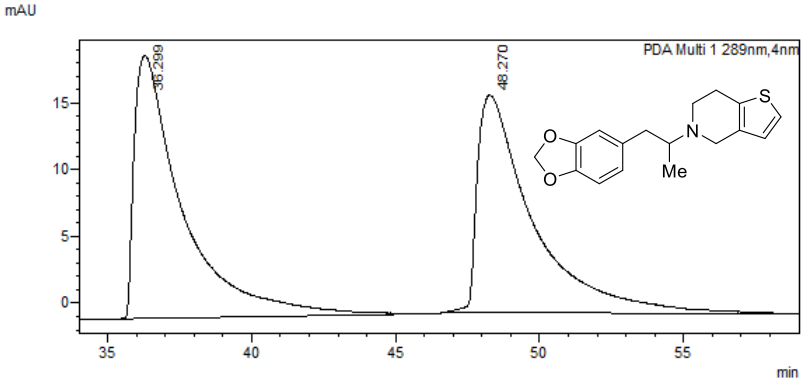
The enantiomeric excess of (*S*)-**8a** was determined to 88%.

8.3.2 (*R*)- and (*S*)-8c

The enantiomeric excess of (*R*)- and (*S*)-**8c** was determined by chiral HPLC analysis.

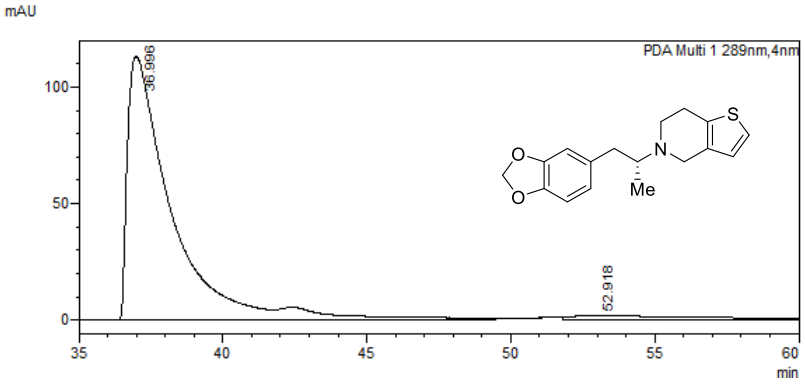
HPLC (column: OD-H; *n*-heptane/2-propanol = 99.5:0.5, 0.5 mL/min): t_R (min) = 36.3 ((*R*)-enantiomer, major), 52.9 ((*S*)-enantiomer, minor).

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	36.299	2286647	19680	51.045
2	48.270	2192981	16293	48.955
Total		4479628	35972	100.000

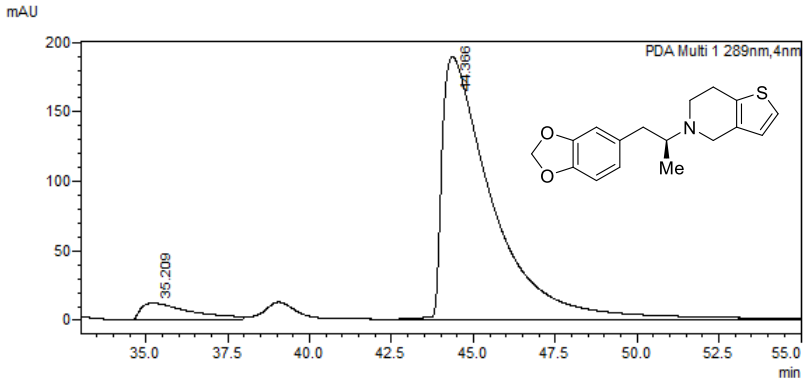
(*R*)-Enantiomer: t_R (min) = 37.0 ((*R*)-enantiomer, major), 52.9 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	36.996	12239819	113204	93.422
2	52.918	861890	1940	6.578
Total		13101709	115144	100.000

The enantiomeric excess of (*R*)-**8c** was determined to 87%.

(*S*)-Enantiomer: t_R (min) = 35.2 ((*R*)-enantiomer, minor), 44.4 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	35.209	1339039	12239	5.973
2	44.366	21078107	189469	94.027
Total		22417146	201707	100.000

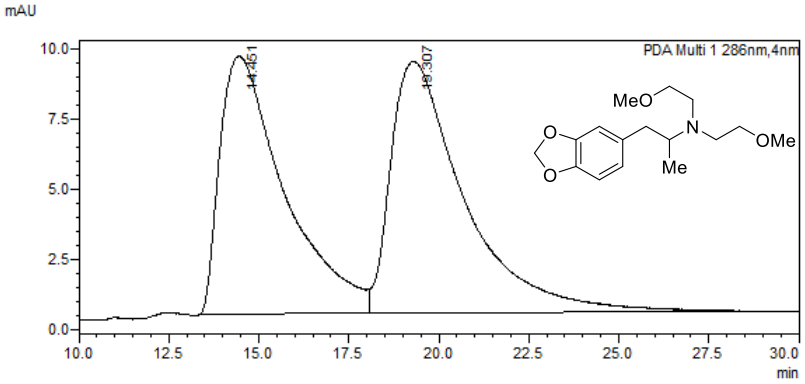
The enantiomeric excess of (*S*)-**8c** was determined to 88%.

8.3.3 (*R*)- and (*S*)-8d

The enantiomeric excess of (*R*)- and (*S*)-**8d** was determined by chiral HPLC analysis.

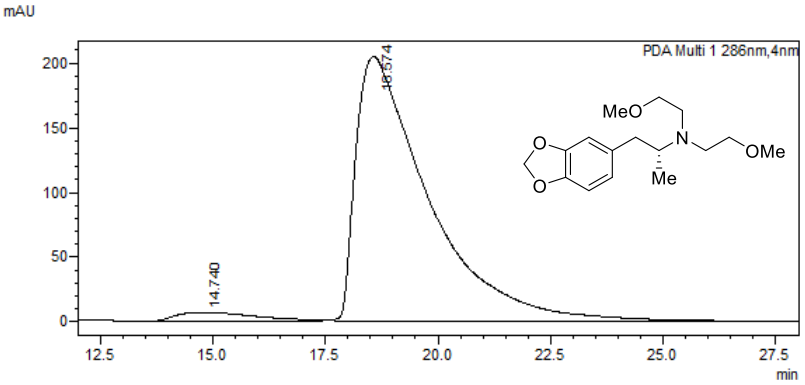
HPLC (column: OJ-H; *n*-heptane/2-propanol = 99.0:1.0, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	14.451	1139197	9177	47.241
2	19.307	1272242	8961	52.759
Total		2411439	18138	100.000

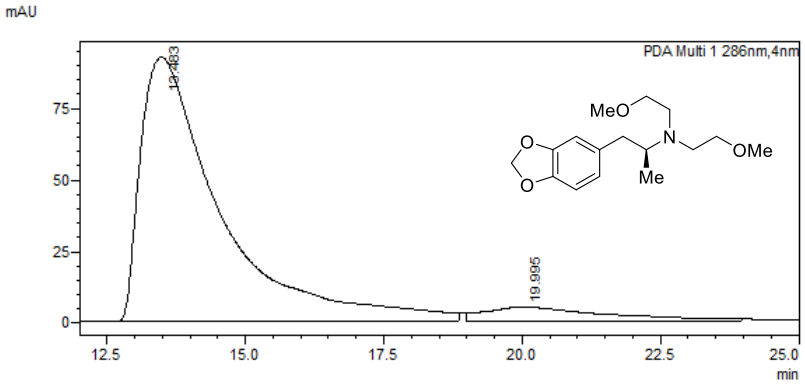
(*R*)-Enantiomer: t_R (min) = 14.7 ((*S*)-enantiomer, minor), 18.6 ((*R*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	14.740	875442	6935	3.662
2	18.574	23032019	204681	96.338
Total		23907461	211616	100.000

The enantiomeric excess of (*R*)-**8d** was determined to 93%.

(*S*)-Enantiomer: 13.5 ((*S*)-enantiomer, major), 20.0 ((*R*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	13.483	9266843	92307	92.065
2	19.995	798689	5029	7.935
Total		10065532	97336	100.000

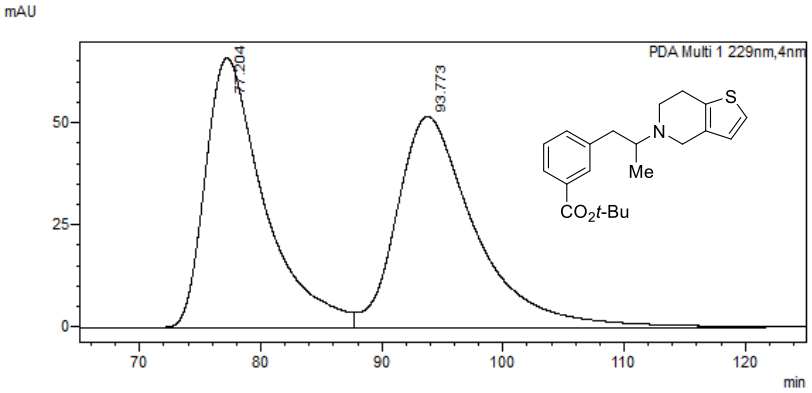
The enantiomeric excess of (*S*)-**8c** was determined to 84 %

8.3.4 (*R*)-8e

The enantiomeric excess of (*R*)-**8e** was determined by chiral HPLC analysis.

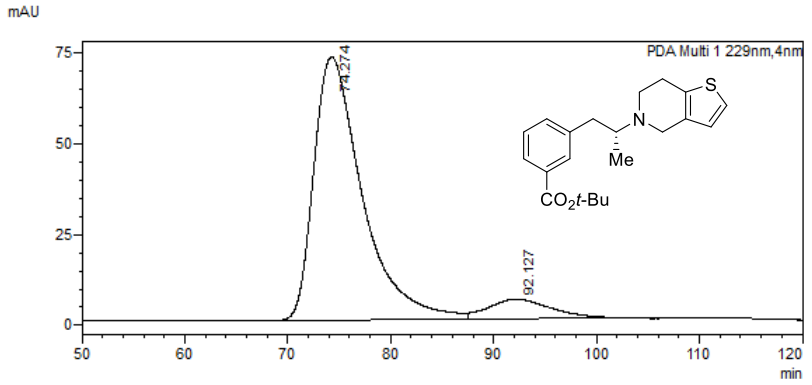
HPLC (column: OJ-H; *n*-heptane/2-propanol = 99.5:0.5, 0.25 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	77.204	22217014	65965	48.646
2	93.773	23453753	51671	51.354
Total		45670767	117635	100.000

(*R*)-Enantiomer: t_R (min) = 74.3 ((*R*)-enantiomer, major), 92.2 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	74.274	23728923	72461	91.506
2	92.127	2202713	5300	8.494
Total		25931636	77761	100.000

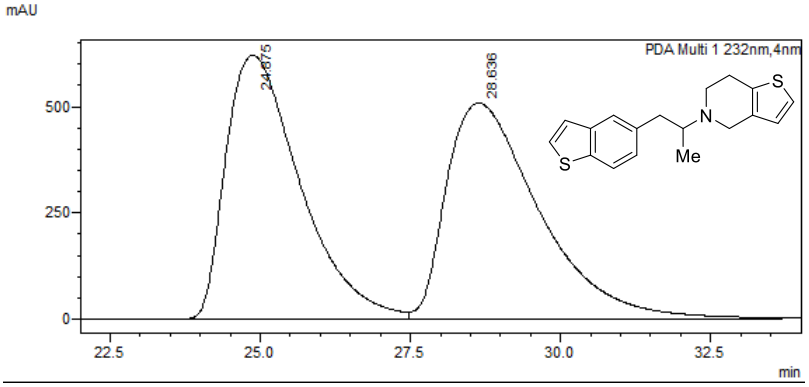
The enantiomeric excess of (*R*)-**8e** was determined to 83%.

8.3.5 (*R*)- and (*S*)-8f

The enantiomeric excess of (*R*)- and (*S*)-**8f** was determined by chiral HPLC analysis.

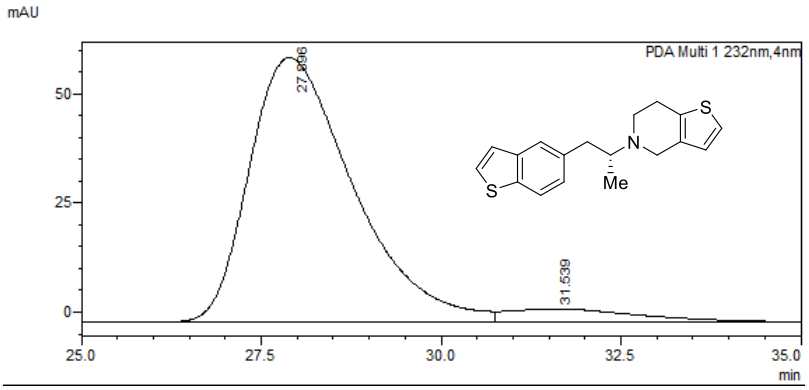
HPLC (column: OJ-H; *n*-heptane/2-propanol = 98.0:2.0, 1.0 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	24.875	53428670	620346	49.335
2	28.636	54869965	508120	50.665
Total		108298635	1128466	100.000

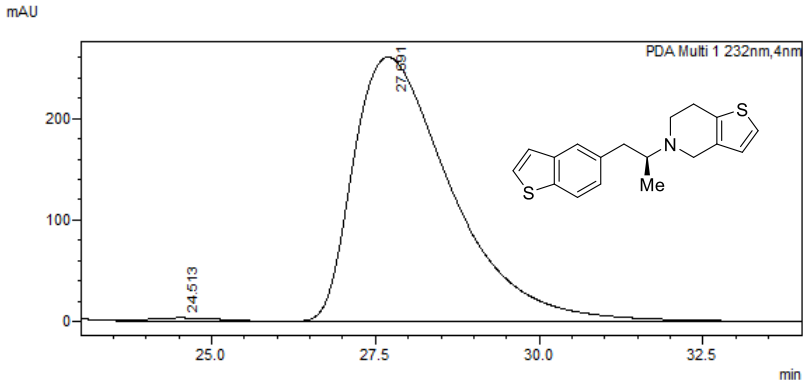
(*R*)-Enantiomer: t_R (min) = 27.9 ((*R*)-enantiomer, major), 31.5 ((*S*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	27.896	6097529	60542	94.037
2	31.539	386647	3052	5.963
Total		6484176	63594	100.000

The enantiomeric excess of (*R*)-**8f** was determined to 88%.

(*S*)-Enantiomer: t_R (min) = 24.5 ((*R*)-enantiomer, minor), 27.7 ((*S*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	24.513	306019	3694	1.112
2	27.691	27214904	260851	98.888
Total		27520924	264545	100.000

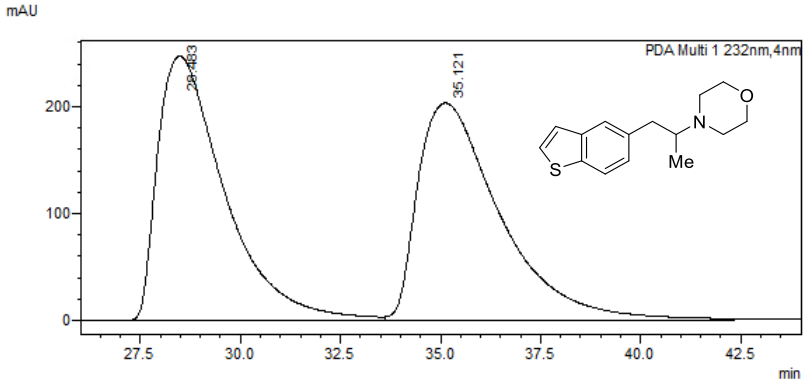
The enantiomeric excess of (*S*)-**8f** was determined to 97%.

8.3.6 (*R*)- and (*S*)-8g

The enantiomeric excess of (*R*)- and (*S*)-**8g** was determined by chiral HPLC analysis.

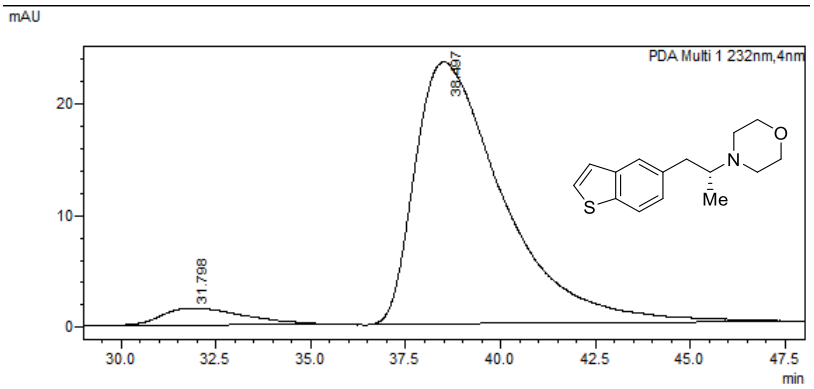
HPLC (column: OJ-H; *n*-heptane/2-propanol = 99.3:0.7, 1.25 mL/min):

Racemate:



Peak#	Ret. Time	Area	Height	Area%
1	28.483	28872265	247432	49.594
2	35.121	29344801	203583	50.406
Total		58217066	451015	100.000

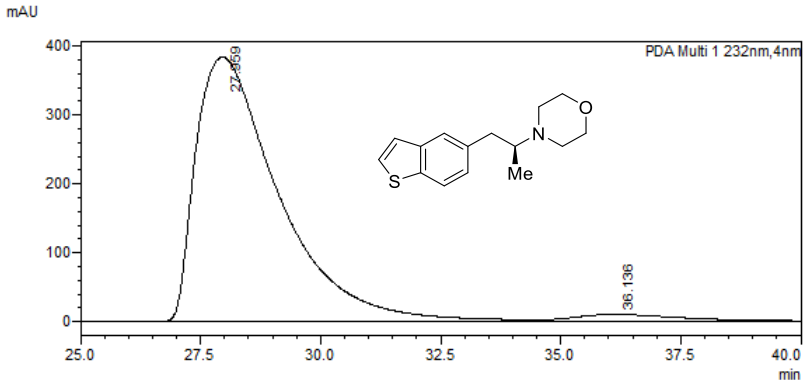
(*R*)-Enantiomer: t_R (min) = 31.8 ((*S*)-enantiomer, minor), 38.5 ((*R*)-enantiomer, major).



Peak#	Ret. Time	Area	Height	Area%
1	31.798	229991	1482	5.728
2	38.497	3785273	23435	94.272
Total		4015263	24916	100.000

The enantiomeric excess of (*R*)-**8g** was determined to 89%.

(*S*)-Enantiomer: t_R (min) = 28.0 ((*S*)-enantiomer, major), 36.1 ((*R*)-enantiomer, minor).



Peak#	Ret. Time	Area	Height	Area%
1	27.959	46032973	383821	96.908
2	36.136	1468773	9662	3.092
Total		47501746	393483	100.000

The enantiomeric excess of (*S*)-**8g** was determined to 94%.

9 References

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