# Electronic Supplementary Information

## Base-catalyzed diastereodivergent thia-Michael addition to chiral β-trifluoromethyl-α,β-unsaturated *N*-acylated oxazolidin-2-ones

Sasirome Racochote,[a] Phiphob Naweephattana, Panida Surawatanawong,[a] Chutima Kuhakarn,[a] Pawaret Leowanawat,[a] Vichai Reutrakul,[a] and Darunee Soorukram[a]*

[a]Department of Chemistry and Center of Excellence for Innovation in Chemistry (PERCH-CIC), Faculty of Science, Mahidol University, Rama VI Road, Bangkok 10400, Thailand

Fax: 02-354-7151, E-mail: darunee.soo@mahidol.ac.th

### Table of Contents

# EXPERIMENTAL

## *General Methods*

The $^{1}$H NMR spectra were recorded with a Bruker Ascend™ 400 (400 MHz), a Bruker Avance-500 (500 MHz), or a JEOL 400 YH (JMTC-400) (400 MHz) spectrometer in $CDCl_3$ or acetone-$d_6$ or $CD_3OD$ using tetramethylsilane as an internal standard. The $^{13}$C NMR spectra were recorded with a Bruker Ascend™ 400 (100 MHz), a Bruker Avance-500 (125 MHz), or a JEOL 400 YH (JMTC-400) (100 MHz) spectrometer in $CDCl_3$ or acetone-$d_6$ or $CD_3OD$ using residual non-deuterated solvent peaks as an internal standard. The $^{19}$F NMR spectra were recorded with a Bruker Ascend™ 400 (376 MHz) or a Bruker Avance-500 (470 MHz) spectrometer in $CDCl_3$ or acetone-$d_6$ or $CD_3OD$ using hexafluorobenzene as an external standard. The IR spectra were recorded with a Bruker FT-IR spectrometer (ALPHA). The high-resolution mass spectra were recorded with a HR-TOF-MS Micromass model VQ-TOF2 mass spectrometer, a Bruker MicroTOF spectrpmeter, a Bruker UHR-TOF (Ultra High Resolution-TOF), or a Jeol DART™. The mass spectra were recorded with a Thermo Finnigan Polaris Q mass spectrometer, or a Jeol DART™. Melting points were recorded with a Buchi 510 melting Point Apparatus and uncorrected. The specific rotation values were recorded with a Jasco P-1020 polarimeter.

Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl. Dichloromethane ($CH_2Cl_2$), toluene, and ethyl acetate (EtOAc) were distilled over calcium hydride and stored over activated molecular sieves (4 Å). Acetone and acetonitrile (MeCN) were distilled over potassium carbonate and calcium hydride, respectively. Methanol (MeOH) and ethanol (EtOH) were distilled over Mg turnings. Acetone, MeCN, MeOH, and EtOH were stored without using activated molecular sieves. Other common solvents ($CH_2Cl_2$, hexanes, and EtOAc) were distilled before use. All glassware including needles and syringes were oven-dried and kept in a desiccator before use. Column chromatography was performed by using Merck silica gel 60 (Art. 7734). (*R*)-*E*-4-Phenyl-3-(4,4,4-trifluorobut-2-enoyl)oxazolidin-2-one [(*R*)-*E*-**1**] was synthesized according to the literature.[1]

## 1. Synthesis of (*R*,*S*)-3A and (*R*,*R*)-3B

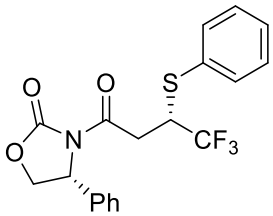
**(*R*)-4-Phenyl-3-[(*S*)-4,4,4-trifluoro-3-(phenylthio)butanoyl]oxazolidin-2-one [(*R*,*S*)-3aA] and (*R*)-4-Phenyl-3-[(*R*)-4,4,4-trifluoro-3-(phenylthio)butanoyl]oxazolidin-2-one [(*R*,*R*)-3aB]**

*Conditions A*: A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with **1** (57.4 mg, 0.20 mmol) and dry acetone (1 mL). The resulting solution was cooled at –78 °C then thiophenol (**2a**, 24 μL, 0.22 mmol) and *N*,*N*-diisopropylethylamine (*i*-$Pr_2NEt$) (2 μL, 0.01 mmol) were added. After stirring at –78 °C for 30 min, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with a saturated aqueous NaCl solution (20 mL) and dried over anhydrous $Na_2SO_4$. After removal of the solvent *in vacuo*, the crude mixture of (*R*,*S*)-**3aA** and (*R*,*R*)-**3aB** (89:11 dr, $^{1}$H NMR analysis) was purified by column chromatography (50% $CH_2Cl_2$ in

hexanes) to afford (*R*,*S*)-**3aA** (58.4 mg, 75% yield) as colorless viscous oil and (*R*,*R*)-**3aB** (8.8 mg, 11% yield) as a white solid.

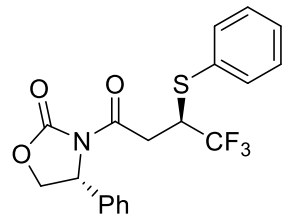
*Conditions B*: A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with **1** (58.0 mg, 0.20 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (2.2 mg, 0.02 mmol), and dry THF (1 mL). The resulting solution was cooled at –78 °C then **2a** (24 μL, 0.22 mmol) was added. After stirring at –78 °C for 30 min, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with a saturated aqueous NaCl solution (20 mL) and dried over anhydrous $Na_2SO_4$. After removal of the solvent *in vacuo*, the crude mixture of (*R*,*S*)-**3aA** and (*R*,*R*)-**3aB** (21:79 dr, $^1$H NMR analysis) was purified by column chromatography (50% $CH_2Cl_2$ in hexanes) to afford (*R*,*S*)-**3aA** (13.0 mg, 17% yield) and (*R*,*R*)-**3aB** (49.0 mg, 62% yield).

*Scale-up synthesis:* According to the *Conditions A*, the reaction of **1** (287 mg, 1 mmol) with **2a** (0.12 mL, 1.1 mmol) and *i*-$Pr_2$NEt (10 μL, 0.05 mmol) in dry acetone (5 mL) afforded (*R*,*S*)-**3aA** (303 mg, 77% yield) and (*R*,*R*)-**3aB** (38.1 mg, 10% yield).



(*R*,*S*)-**3aA**

(*R*,*S*)-**3aA**: $R_f$ 0.30 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{25}$ –61.4 (*c* 0.8, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.60–7.54 (m, 2H, Ar*H*), 7.44–7.34 (m, 3H, Ar*H*), 7.34–7.29 (m, 5H, Ar*H*), 5.50 (dd, *J* = 3.4, 8.8 Hz, 1H, C*H*N), 4.75 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.34 (dd, *J* = 3.4, 8.8 Hz, 1H, CH*H*O), 4.13–4.02 (m, 1H, C*H*$CF_3$), 3.63 (dd, *J* = 10.6, 18.4 Hz, 1H, C*H*H), 3.27 (dd, *J* = 3.1, 18.4 Hz, 1H, CH*H*). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.1 (CO), 153.4 (CO), 138.5 (C), 133.5 (2 × CH), 132.5 (C), 129.3 (2 × CH), 129.1 (2 × CH), 129.0 (CH), 128.7 (CH), 126.3 (q, $^1J_{CF}$ = 277.2 Hz, $CF_3$), 125.9 (2 × CH), 70.3 ($CH_2$), 57.7 (CH), 47.3 (q, $^2J_{CF}$ = 29.8 Hz, CH), 35.2 ($CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.7 ($CF_3$). IR (ATR): $\lambda_{max}$ 1777*s*, 1704*s*, 1494*w*, 1440*s*, 1385*s*, 1313*s*, 1246*s*, 1154*s*, 1096*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 396 [(M+ H)$^+$, 94], 395 [M$^+$, 100], 394 (13), 375 (6), 192 (15), 164 (7), 120 (11), 104 (8), 90 (5). HRMS (ESI-TOF) calcd for $C_{19}H_{16}F_3NO_3SNa^+$ [M + Na]$^+$: 418.0695, found: 418.0693.



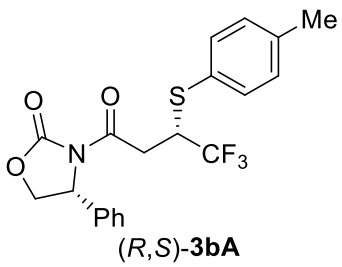
(*R*,*R*)-**3aB**

(*R*,*R*)-**3aB**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); mp 139–141 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{25}$ –110.1 (*c* 0.7, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.43–7.32 (m, 5H, Ar*H*), 7.30–7.17 (m, 5H, Ar*H*), 5.48 (dd, *J* = 4.2, 8.8 Hz, 1H, C*H*N), 4.73 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.32 (dd, *J* = 4.2, 8.8 Hz, 1H, CH*H*O), 4.02–3.88 (m, 1H, C*H*$CF_3$), 3.66 (dd, *J* = 10.4, 17.7 Hz, 1H, C*H*H), 3.27 (dd, *J* = 3.7, 17.7 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.4 (CO), 153.5 (CO), 138.3 (C), 134.1 (2 × CH), 132.2 (C), 129.2 (2 × CH), 129.0 (2 × CH), 128.9 (CH), 128.8 (CH), 126.3 (q, $^1J_{CF}$ = 277.3 Hz, $CF_3$), 126.1 (2 × CH), 70.1 ($CH_2$), 57.9 (CH), 48.2 (q, $^2J_{CF}$ = 29.7 Hz, CH), 35.4 (q, $^3J_{CF}$ = 1.8 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.7 ($CF_3$). IR (ATR): $\lambda_{max}$ 1781*s*, 1713*s*, 1580*m*, 1494*m*,

1386*s*, 1330*s*, 1308*s*, 1236*s*, 1155*s*, 1109*s*, 1075*s*, 1036*s*, 1025*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 396 $[(M+ H)^+$, 72], 395 $[M^+$, 100], 393 (40), 191 (26), 120 (13), 109 (17), 104 (29). HRMS (ESI-TOF) calcd for $C_{19}H_{16}F_3NO_3SNa^+$ $[M + Na]^+$: 418.0695, found: 418.0693.

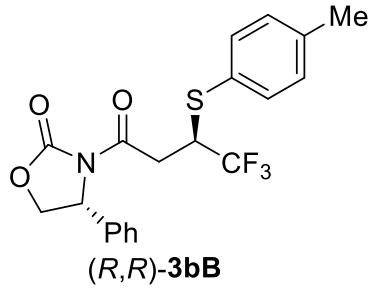
**(*R*)-4-Phenyl-3-[(*S*)-4,4,4-trifluoro-3-(4-methylthio)butanoyl]oxazolidin-2-one [(*R*,*S*)-3bA] and (*R*)-4-Phenyl-3-[(*R*)-4,4,4-trifluoro-3-(4-methylthio)butanoyl]oxazolidin-2-one [(*R*,*R*)-3bB]**

According to the *Conditions A*, the reaction of **1** (57.9 mg, 0.20 mmol) with 4-methylbenzenethiol (28.4 mg, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3bA** and (*R*,*R*)-**3bB** (89:11 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3bA** (59.0 mg, 72% yield) as a colorless viscous oil and (*R*,*R*)-**3bB** (7.4 mg, 9% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (58.1 mg, 0.20 mmol) with 4-methylbenzenethiol (28.4 mg, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3bA** and (*R*,*R*)-**3bB** (24:76 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3bA** (18.4 mg, 23% yield) and (*R*,*R*)-**3bB** (59.0 mg, 72% yield).



(*R*,*S*)-**3bA**

(*R*,*S*)-**3bA**: $R_f$ 0.30 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{25}$ –58.1 (*c* 1.9, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$7.45 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.44–7.29 (m, 5H, Ar*H*), 7.12 (d, *J* = 8.0 Hz, 2H, Ar*H*), 5.50 (dd, *J* = 3.4, 8.6 Hz, 1H, C*H*N), 4.75 (dd, *J* = 8.6, 8.6 Hz, 1H, C*H*HO), 4.34 (dd, *J* = 3.4, 8.6 Hz, 1H, CH*H*O), 4.06–3.94 (m, 1H, C*H*$CF_3$), 3.61 (dd, *J* = 10.6, 18.4 Hz, 1H, C*H*H), 3.24 (dd, *J* = 3.1, 18.4 Hz, 1H, CH*H*), 2.33 (s, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.1 (CO), 153.4 (CO), 139.1 (C), 138.5 (C), 134.1 (2 × CH), 129.9 (2 × CH), 129.3 (2 × CH), 129.0 (CH), 128.7 (C), 126.4 (q, $^1J_{CF}$ = 277.4 Hz, $CF_3$), 125.9 (2 × CH), 70.3 ($CH_2$), 57.7 (CH), 47.5 (q, $^2J_{CF}$ = 29.5 Hz, CH), 35.1 (q, $^3J_{CF}$ = 1.8 Hz, $CH_2$), 21.2 ($CH_3$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.6 ($CF_3$). IR (ATR): $\lambda_{max}$ 1775*s*, 1711*s*, 1493*m*, 1385*s*, 1319*s*, 1244*s*, 1200*s*, 1151*s*, 1096*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 410 $[(M+ H)^+$, 97], 409 $[M^+$, 100], 286 (12), 206 (48), 164 (12), 149 (14), 124 (46), 123 (26), 121 (19), 120 (21), 104 (21), 91 (19), 77 (10). HRMS (ESI-TOF) calcd for $C_{20}H_{18}F_3NO_3SNa^+$ $[M + Na]^+$: 432.0852, found: 432.0857.



(*R*,*R*)-**3bB**

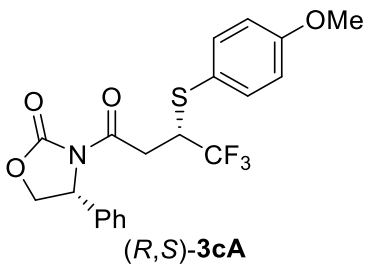
(*R*,*R*)-**3bB**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); mp 160–162 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{29}$ –115.1 (*c* 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$7.45–7.32 (m, 5H, Ar*H*), 7.11 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.00 (d, *J* = 8.1 Hz, 2H, Ar*H*), 5.48 (dd, *J* = 4.2, 8.9 Hz, 1H, C*H*N), 4.72 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.32 (dd, *J* = 4.2, 8.9 Hz, 1H, CH*H*O), 3.95–3.82 (m, 1H, C*H*$CF_3$), 3.63 (dd, *J* = 10.4, 17.7 Hz, 1H, C*H*H), 3.24 (dd, *J* = 3.6, 17.7 Hz, 1H, CH*H*), 2.30 (s, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$168.4 (CO), 153.5 (CO), 139.1 (C), 138.3 (C), 134.5 (2 × CH), 129.8 (2 × CH), 129.2 (2 × CH), 128.9 (CH), 128.5 (C), 126.3 (q, $^1J_{CF}$ = 277.2 Hz, $CF_3$),

126.1 (2 × CH), 70.1 ($CH_2$), 57.9 (CH), 48.4 (q, $^2J_{CF}$ = 29.4 Hz, CH), 35.3 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$), 21.1 ($CH_3$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.6 ($CF_3$). IR (ATR): $\lambda_{max}$ 1783*s*, 1709*s*, 1493*w*, 1411*m*, 1321*s*, 1203*s*, 1155*s*, 1076*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 410 [(M+ H)$^+$, 64], 409 [M$^+$, 100], 389 (17), 206 (41), 164 (29), 104 (11), 91 (14), 77 (19). HRMS (ESI-TOF) calcd for $C_{20}H_{18}F_3NO_3SNa^+$ [M + Na]$^+$: 432.0852, found: 432.0847.

**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(4-methoxyphenyl)thio]butanoyl}oxazolidin-2-one [(*R,S*)-3cA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(4-methoxyphenyl)thio]butanoyl}oxazolidin-2-one [(*R,R*)-3cB]**

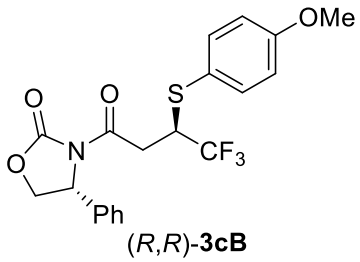
According to the *Conditions A*, the reaction of **1** (58.1 mg, 0.20 mmol) with 4-methoxybenzenethiol (32 μL, 0.22 mmol) gave a crude mixture of (*R,S*)-**3cA** and (*R,R*)-**3cB** (92:8 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) gave (*R,S*)-**3cA** (67.8 mg, 80% yield) as pale-yellow viscous oil and (*R,R*)-**3cB** (5.0 mg, 6% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (58.2 mg, 0.20 mmol) with 4-methoxybenzenethiol (32 μL, 0.22 mmol) gave a crude mixture of (*R,S*)-**3cA** and (*R,R*)-**3cB** (38:62 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R,S*)-**3cA** (26.3 mg, 31% yield) and (*R,R*)-**3cB** (47.2 mg, 55% yield).

*Scale-up synthesis:* According to the *Conditions A*, the reaction of **1** (286 mg, 1.0 mmol) with 4-methoxybenzenethiol (0.16 mL, 1.1 mmol) and *i*-$Pr_2NEt$ (10 μL, 0.05 mmol) in dry acetone (5 mL) gave (*R,S*)-**3cA** (350 mg, 82% yield) and (*R,R*)-**3cB** (17.4 mg, 4% yield). According to the *Conditions B*, the reaction of **1** (286 mg, 1.0 mmol) with 4-methoxybenzenethiol (0.16 mL, 1.1 mmol) and DABCO (11.2 mg, 0.10 mmol) in dry THF (5 mL) gave (*R,S*)-**3cA** (113 mg, 27% yield) and (*R,R*)-**3cB** (255 mg, 60% yield).



(*R,S*)-**3cA**

(*R,S*)-**3cA**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{25}$ –68.8 (*c* 1.8, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.51 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.45–7.29 (m, 5H, Ar*H*), 6.84 (d, *J* = 8.3 Hz, 2H, Ar*H*), 5.49 (dd, *J* = 3.2, 8.7 Hz, 1H, C*H*N), 4.75 (dd, *J* = 8.7, 8.7 Hz, 1H, C*H*HO), 4.33 (dd, *J* = 3.2, 8.7 Hz, 1H, CH*H*O), 3.99–3.84 (m, 1H, C*H*$CF_3$), 3.80 (s, 3H, OC$H_3$), 3.59 (dd, *J* = 11.2, 18.7 Hz, 1H, C*H*H), 3.20 (dd, *J* = 2.8, 18.7 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.2 (CO), 160.5 (C), 153.4 (CO), 138.5 (C), 136.6 (2 × CH), 129.3 (2 × CH), 129.0 (CH), 126.4 (q, $^1J_{CF}$ = 277.0 Hz, $CF_3$), 125.9 (2 × CH), 122.5 (C), 114.6 (2 × CH), 70.3 ($CH_2$), 57.8 (CH), 55.3 ($OCH_3$), 47.9 (q, $^2J_{CF}$ = 29.2 Hz, CH), 35.0 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.5 ($CF_3$). IR (ATR): $\lambda_{max}$ 1775*s*, 1716*s*, 1589*m*, 1491*m*, 1385*s*, 1306*s*, 1238*s*, 1205*m*, 1146*s*, 1090*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 426 [(M+ H)$^+$, 77], 425 [M$^+$, 100], 424(4), 242 (2), 140 (2), 105 (1). HRMS (DART) calcd for $C_{20}H_{19}F_3NO_4S^+$ [M + H]$^+$: 426.0981, found: 426.0983.

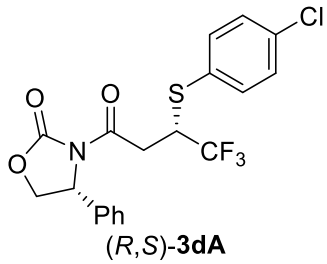


(*R*,*R*)-**3cB**

(*R*,*R*)-**3cB**: $R_f$ 0.18 (50% $CH_2Cl_2$ in hexanes); mp 164–167 ºC (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{28}$ –85.7 (*c* 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.46–7.34 (m, 5H, Ar*H*), 7.17–7.10 (m, 2H, Ar*H*), 6.75–6.68 (m, 2H, Ar*H*), 5.49 (dd, *J* = 4.2, 8.9 Hz, 1H, C*H*N), 4.74 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.34 (dd, *J* = 4.2, 8.9 Hz, 1H, CH*H*O), 3.85–3.74 (m, 4H, C*H*$CF_3$, OC$H_3$), 3.62 (dd, *J* = 10.5, 17.7 Hz, 1H, C*H*H), 3.21 (dd, *J* = 3.4, 17.7 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.5 (CO),160.4 (C), 153.4 (CO), 138.3 (C), 136.8 (2 × CH), 129.2 (2 × CH), 128.9 (CH), 126.4 (q, $^1J_{CF}$ = 277.2 Hz, $CF_3$), 126.2 (2 × CH), 122.4 (C), 114.5 (2 × CH), 70.1 ($CH_2$), 57.9 (CH), 55.3 ($OCH_3$), 48.6 (q, $^2J_{CF}$ = 29.2 Hz, CH), 35.2 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.6 ($CF_3$). IR (ATR): $\lambda_{max}$ 1790*s*, 1696*s*, 1458*m*, 1443*m*, 1330*s*, 1242*s*, 1155*s*, 1075*s*, 1038*s*, 1026*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 426 [(M+ H)$^+$, 63], 425 [M$^+$, 100], 286 (7), 242 (6), 140 (73), 139 (17), 121 (11), 120 (11), 95 (7). HRMS (ESI-TOF) calcd for $C_{20}H_{19}F_3NO_4S^+$ [M + H]$^+$: 426.0981, found: 426.0970.

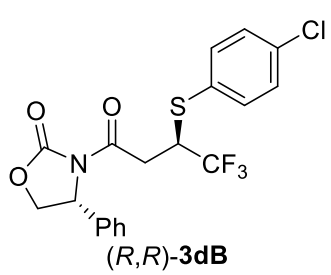
**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(4-chlorophenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*S*)-3dA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(4-chlorophenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*R*)-3dB]**

According to the *Conditions A*, the reaction of **1** (58.2 mg, 0.20 mmol) with 4-chlorobenzenethiol (31.8 mg, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3dA** and (*R*,*R*)-**3dB** (71:29 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) gave (*R*,*S*)-**3dA** (49.3 mg, 58% yield) as a white semi-solid and (*R*,*R*)-**3dB** (20.8 mg, 24% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.8 mg, 0.20 mmol) with 4-chlorobenzenethiol (31.8 mg, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3dA** and (*R*,*R*)-**3dB** (25:75 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) gave (*R*,*S*)-**3dA** (21.6 mg, 25% yield) and (*R*,*R*)-**3dB** (54.0 mg, 63% yield).



(*R*,*S*)-**3dA**

(*R*,*S*)-**3dA**: $R_f$ 0.30 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{24}$ –51.9 (*c* 1.3, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.55–7.48 (m, 2H, Ar*H*), 7.45–7.35 (m, 3H, Ar*H*), 7.35–7.27 (m, 4H, Ar*H*), 5.50 (dd, *J* = 3.4, 8.8 Hz, 1H, C*H*N), 4.77 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.35 (dd, *J* = 3.4, 8.8 Hz, 1H, CH*H*O), 4.06–3.94 (m, 1H, C*H*$CF_3$), 3.62 (dd, *J* = 10.8, 18.5 Hz, 1H, C*H*H), 3.26 (dd, *J* = 2.9, 18.5 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.0 (CO), 153.5 (CO), 138.4 (C), 135.1 (C), 135.0 (2 × CH), 131.0 (C), 129.4 (2 ×CH), 129.3 (2 ×CH), 129.1 (CH), 126.3 (q, $^1J_{CF}$ = 276.6 Hz, $CF_3$), 125.9 (2 × CH), 70.3 ($CH_2$), 57.8 (CH), 47.7 (q, $^2J_{CF}$ = 29.7 Hz, CH), 35.2 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.7 ($CF_3$). IR (ATR): $\lambda_{max}$ 1780*s*, 1706*s*, 1476*m*, 1382*s*, 1305*s*, 1276*s*, 1245*s*, 1202*s*, 1150*s*, 1097*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 430 [(M+ H)$^+$, 76], 429 [M$^+$, 100], 286 (7), 240 (4), 164 (13), 120 (20), 108 (14), 104 (15), 91 (7), 77 (4). HRMS (ESI-TOF) calcd for $C_{19}H_{15}ClF_3NO_3SNa^+$ [M + Na]$^+$: 452.0305, found: 452.0291.



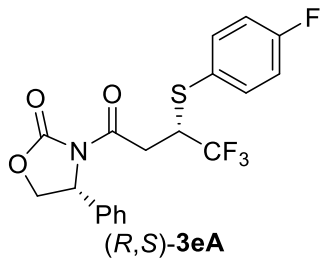
(*R*,*R*)-**3dB**

(*R*,*R*)-**3dB**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); mp 164–166 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{26}$ –116.7 (*c* 1.1, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.45–7.33 (m, 5H, Ar*H*), 7.18–7.10 (m, 4H, Ar*H*), 5.48 (dd, *J* = 4.3, 8.9 Hz, 1H, C*H*N), 4.75 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.34 (dd, *J* = 4.3, 8.9 Hz, 1H, CH*H*O), 3.95–3.82 (m, 1H, C*H*$CF_3$), 3.69 (dd, *J* = 10.7, 17.7 Hz, 1H, C*H*H), 3.23 (dd, *J* = 3.4, 17.7 Hz, 1H, CH*H*). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.3 (CO), 153.4 (CO), 138.2 (C), 135.5 (2 × CH), 135.3 (C), 130.8 (C), 129.2 (4 ×CH), 128.9 (CH), 126.2 (q, $^1J_{CF}$ = 276.9 Hz, $CF_3$), 126.1 (2 × CH), 70.1 ($CH_2$), 57.9 (CH), 48.6 (q, $^2J_{CF}$ = 29.7 Hz, CH), 35.4 ($CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.8 ($CF_3$). IR (ATR): $\lambda_{max}$ 1792*s*, 1694*s*, 1452*m*, 1383*s*, 1312*s*, 1268*m*, 1245*m*, 1209*m*, 1148*s*, 1091*s*, 1039*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 430 [(M+ H)$^+$, 100], 429 [M$^+$, 99], 286 (10), 164 (13), 120 (25), 108 (15), 104 (30), 91 (5), 77 (7). HRMS (ESI-TOF) calcd for $C_{19}H_{15}ClF_3NO_3SNa^+$ [M + Na]$^+$: 452.0305, found: 452.0293.

**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(4-fluorophenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*S*)-3eA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(4-fluorophenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*R*)-3eB]**

According to the *Conditions A*, the reaction of **1** (58.3 mg, 0.20 mmol) with 4-fluorobenzenethiol (24 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3eA** and (*R*,*R*)-**3eB** (85:15 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3eA** (61.1 mg, 74% yield) as a white semi-solid and (*R*,*R*)-**3eB** (12.1 mg, 15% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.9 mg, 0.20 mmol) with 4-fluorobenzenethiol (24 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3eA** and (*R*,*R*)-**3eB** (22:78 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexane) afforded (*R*,*S*)-**3eA** (14.0 mg, 17% yield) and (*R*,*R*)-**3eB** (49.8 mg, 60% yield).

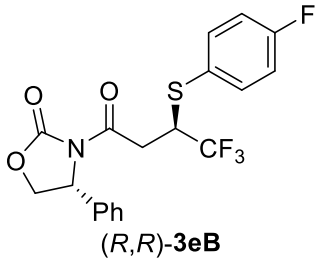
*Scale-up synthesis:* According to the *Conditions A*, the reaction of **1** (1.14 g, 4.0 mmol) with 4-fluorobenzenethiol (0.48 mL, 4.4 mmol) and *i*-$Pr_2NEt$ (36 μL, 0.20 mmol) in dry acetone (20 mL) gave (*R*,*S*)-**3eA** (1.25 g, 76% yield) and (*R*,*R*)-**3eB** (195 mg, 12% yield).



(*R*,*S*)-**3eA**

(*R*,*S*)-**3eA**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{26}$ –61.0 (*c* 1.3, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.57 (dd, *J* = 5.2, 8.7 Hz, 2H, Ar*H*), 7.45–7.30 (m, 5H, Ar*H*), 7.01 (dd, *J* = 8.7, 8.7 Hz, 2H, Ar*H*), 5.51 (dd, *J* = 3.4, 8.8 Hz, 1H, C*H*N), 4.76 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.35 (dd, *J* = 3.4, 8.8 Hz, 1H, CH*H*O), 4.02–3.89 (m, 1H, C*H*$CF_3$), 3.61 (dd, *J* = 10.8, 18.5 Hz, 1H, C*H*H), 3.25 (dd, *J* = 2.9, 18.5 Hz, 1H, CH*H*). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.1 (CO), 163.2 (d, $^1J_{CF}$ = 248.3 Hz, C), 153.4 (CO), 138.4 (C), 136.4 (d, $^3J_{CF}$ = 8.5 Hz, 2 × CH), 129.3 (2 × CH), 129.0 (CH), 127.6 (d, $^4J_{CF}$ = 3.5 Hz, C), 126.3 (q, $^1J_{CF}$ = 277.1 Hz, $CF_3$), 125.9 (2 × CH), 116.3 (d, $^2J_{CF}$ = 21.9 Hz, 2 × CH), 70.3 ($CH_2$), 57.8 (CH), 48.0 (q, $^2J_{CF}$ = 29.5 Hz, CH), 35.2 ($CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.6 ($CF_3$), –111.7 (F). IR (ATR): $\lambda_{max}$ 1778*s*, 1704*s*, 1491*w*, 1384*m*,

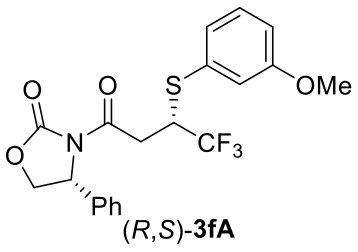
1322*s*, 1307*s*, 1274*s*, 1215*s*, 1199*s*, 1148*s*, 1099*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 414 [(M+ H)$^+$, 99], 413 [M$^+$, 100], 286 (5), 164 (6), 127 (5), 120 (12), 104 (5), 91 (4). HRMS (ESI-TOF) calcd for $C_{19}H_{15}F_4NO_3SNa^+$ [M + Na]$^+$: 436.0601, found: 436.0595.


(*R*,*R*)-**3eB**

(*R*,*R*)-**3eB**: $R_f$ 0.20 (50% $CH_2Cl_2$ in hexanes); mp 154–156 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{26}$ –104.0 (*c* 1.2, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.45–7.34 (m, 5H, Ar*H*), 7.21–7.14 (m, 2H, Ar*H*), 6.91–6.84 (m, 2H, Ar*H*), 5.49 (dd, *J* = 4.3, 8.9 Hz, 1H, C*H*N), 4.75 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.34 (dd, *J* = 4.3, 8.9 Hz, 1H, CH*H*O), 3.90–3.77 (m, 1H, C*H*$CF_3$), 3.67 (dd, *J* = 10.7, 17.7 Hz, 1H, C*H*H), 3.21 (dd, *J* = 3.3, 17.7 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.4 (CO), 163.3 (d, $^1J_{CF}$ = 248.6 Hz, C), 153.4 (CO), 138.3 (C), 136.8 (d, $^3J_{CF}$ = 8.5 Hz, 2 × CH), 129.2 (2 × CH), 128.9 (CH), 127.3 (d, $^4J_{CF}$ = 3.4 Hz, C), 126.3 (q, $^1J_{CF}$ = 276.7 Hz, $CF_3$), 126.2 (2 × CH), 116.1 (d, $^2J_{CF}$ = 21.8 Hz, 2 × CH), 70.1 ($CH_2$), 57.9 (CH), 48.8 (q, $^2J_{CF}$ = 29.8 Hz, CH), 35.3 (q, $^3J_{CF}$ = 1.8 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.7 ($CF_3$), –111.6 (F). IR (ATR): $\lambda_{max}$ 1792*s*, 1697*s*, 1589*m*, 1489*m*, 1384*s*, 1310*s*, 1210*s*, 1146*s*, 1118*s*, 1095*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 414 [(M+ H)$^+$, 98], 413 [M$^+$, 100], 393 (3), 210 (3), 164 (6), 120 (15), 91 (3). HRMS (ESI-TOF) calcd for $C_{19}H_{15}F_4NO_3SNa^+$ [M + Na]$^+$: 436.0601, found: 436.0602.

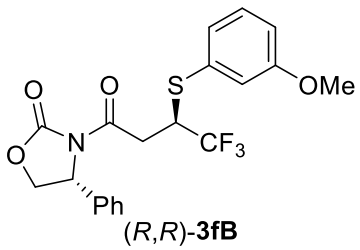
**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(3-methoxyphenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*S*)-3fA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(3-methoxyphenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*R*)-3fB]**

According to the *Conditions A*, the reaction of **1** (57.7 mg, 0.20 mmol) with 3-methoxybenzenethiol (32 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3fA** and (*R*,*R*)-**3fB** (85:15 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3fA** (63.1 mg, 75% yield) as a colorless viscous oil and (*R*,*R*)-**3fB** (10.4 mg, 12% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.6 mg, 0.20 mmol) with 3-methoxybenzenethiol (32 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3fA** and (*R*,*R*)-**3fB** (36:64 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3fA** (28.0 mg, 33%) and (*R*,*R*)-**3fB** (49.1 mg, 60%).


(*R*,*S*)-**3fA**

(*R*,*S*)-**3fA**: $R_f$ 0.20 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{24}$ –50.8 (*c* 1.2, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.45–7.33 (m, 3H, Ar*H*), 7.33–7.29 (m, 2H, Ar*H*), 7.23 (dd, *J* = 8.0, 8.0 Hz, 1H, Ar*H*), 7.15 (ddd, *J* = 0.9, 2.0, 8.0 Hz, 1H, Ar*H*), 7.11 (dd, *J* = 2.0, 2.0 Hz, 1H, Ar*H*), 6.86 (ddd, *J* = 0.9, 2.0, 8.0 Hz, 1H, Ar*H*), 5.48 (dd, *J* = 3.4, 8.8 Hz, 1H, C*H*N), 4.74 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.34 (dd, *J* = 3.4, 8.8 Hz, 1H, CH*H*O), 4.16–4.05 (m, 1H, C*H*$CF_3$), 3.80 (s, 3H, OC*H*$_3$), 3.63 (dd, *J* = 10.6, 18.4 Hz, 1H, C*H*H), 3.27 (dd, *J* = 3.2, 18.4 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.0 (CO), 159.7 (C), 153.4 (CO), 138.5 (C), 133.5 (C), 130.0 (CH),

129.3 (2 × CH), 129.0 (CH), 126.3 (q, $^1J_{CF}$ = 277.3 Hz, $CF_3$), 125.9 (2 × CH), 125.5 (CH), 118.5 (CH), 114.5 (CH), 70.3 ($CH_2$), 57.4 (CH), 55.3 ($OCH_3$), 47.1 (q, $^2J_{CF}$ = 29.7 Hz, CH), 35.2 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –70.7 ($CF_3$). IR (ATR): $\lambda_{max}$ 1776*s*, 1704*s*, 1589*m*, 1478*m*, 1386*s*, 1311*s*, 1245*s*, 1154*s*, 1097*s*, 1037*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 426 [(M+ H)$^+$, 85], 425 [M$^+$, 100], 424 (18), 407 (6), 263 (5), 222 (66), 195 (4), 120 (4). HRMS (ESI-TOF) calcd for $C_{20}H_{19}F_3NO_4S^+$ [M + H]$^+$: 426.0981, found: 426.0987.

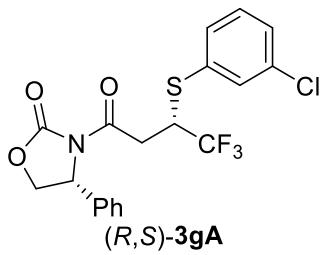


(*R*,*R*)-**3fB**

(*R*,*R*)-**3fB**: $R_f$ 0.15 (50% $CH_2Cl_2$ in hexanes); mp 113–115 ºC (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{23}$ –106.1 (*c* 1.2, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.42–7.30 (m, 5H, Ar*H*), 7.11 (dd, *J* = 8.0, 8.0 Hz, 1H, Ar*H*), 6.89–6.78 (m, 3H, Ar*H*), 5.48 (dd, *J* = 4.3, 8.9 Hz, 1H, C*H*N), 4.73 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.30 (dd, *J* = 4.3, 8.9 Hz, 1H, CH*H*O), 4.05–3.94 (m, 1H, C*H*$CF_3$), 3.73–3.62 (m, 4H, O$CH_3$, C*H*H), 3.29 (dd, *J* = 3.7, 17.8 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.0 (CO), 159.7 (C), 153.5 (CO), 138.3 (C), 133.4 (C), 129.8 (CH), 129.2 (2 × CH), 128.8 (CH), 126.3 (q, $^1J_{CF}$ = 277.2 Hz, $CF_3$), 125.9 (2 × CH), 125.8 (CH), 118.5 (CH), 115.1 (CH), 70.1 ($CH_2$), 57.9 (CH), 55.2 ($OCH_3$), 48.1 (q, $^2J_{CF}$ = 29.8 Hz, CH), 35.5 (q, $^3J_{CF}$ = 1.6 Hz, $CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –70.7 ($CF_3$). IR (ATR): $\lambda_{max}$ 1782*s*, 1706*s*, 1590*m*, 1483*m*, 1379*s*, 1300*s*, 1245*s*, 1155*s*, 1076*s*, 1033*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 426 [(M+ H)$^+$, 77], 425 [M$^+$, 98], 384 (15), 223 (12), 222 (100), 164 (10), 140 (28), 120 (13), 95 (6). HRMS (ESI-TOF) calcd for $C_{20}H_{19}F_3NO_4S^+$ [M + H]$^+$: 426.0981, found: 426.0984.

**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(3-chlorophenyl)thio]butanoyl}oxazolidin-2-one [(*R,S*)-3gA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(3-chlorophenyl)thio]butanoyl}oxazolidin-2-one [(*R,R*)-3gB]**

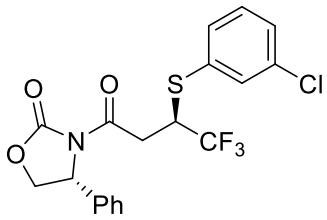
According to the *Conditions A*, the reaction of **1** (58.1 mg, 0.20 mmol) with 3-chlorobenzenethiol (26 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3gA** and (*R*,*R*)-**3gB** (75:25 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3gA**(53.1 mg, 62% yield) as a colorless viscous oil and (*R*,*R*)-**3gB** (19.3 mg, 23% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (58.1 mg, 0.20 mmol) with 3-chlorobenzenethiol (26 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3gA** and (*R*,*R*)-**3gB** (46:54 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3gA** (32.7 mg, 38% yield) and (*R*,*R*)-**3gB** (36.4 mg, 43% yield).



(*R*,*S*)-**3gA**

(*R*,*S*)-**3gA**: $R_f$ 0.33 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{27}$ –53.1 (*c* 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.57–7.54 (m, 1H, Ar*H*), 7.48–7.35 (m, 4H, Ar*H*), 7.35–7.24 (m, 4H, Ar*H*), 5.50 (dd, *J* = 3.4, 8.8 Hz, 1H, C*H*N), 4.77 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.35 (dd, *J* = 3.4, 8.8 Hz, 1H, CH*H*O), 4.15–4.00 (m, 1H, C*H*$CF_3$), 3.62 (dd, *J* = 10.8, 18.6 Hz, 1H, C*H*H), 3.28 (dd, *J* = 3.0, 18.6 Hz, 1H, CH*H*). $^{13}$C NMR

(100 MHz, $CDCl_3$): $\delta$ 167.9 (CO), 153.4 (CO), 138.4 (C), 134.6 (C), 134.5 (C), 132.8 (CH), 131.3 (CH), 130.2 (CH), 129.3 (2 ×CH), 129.0 (CH), 128.9 (CH), 126.2 (q, $^1J_{CF}$ = 277.2 Hz, $CF_3$), 125.9 (2 × CH), 70.4 ($CH_2$), 57.8 (CH), 47.2 (q, $^2J_{CF}$ = 30.0 Hz, CH), 35.1 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.7 ($CF_3$). IR (ATR): $\lambda_{max}$ 1779*s*, 1698*s*, 1605*w*, 1576*w*, 1459*m*, 1363*s*, 1311*s*, 1290*s*, 1257*s*, 1210*s*, 1156*s*, 1102*s*, 1046*s*, 1013*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 430 [(M+ H)$^+$, 100], 429 [M$^+$, 83], 409 (11), 226 (12), 183 (11), 164 (13), 120 (20), 108 (22), 104 (18). HRMS (ESI-TOF) calcd for $C_{19}H_{15}ClF_3NO_3SNa^+$ [M + Na]$^+$: 452.0305, found: 452.0293.

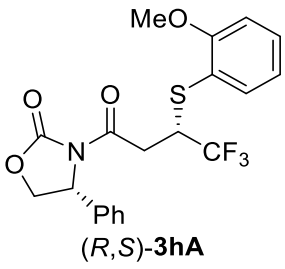


(*R*,*R*)-**3gB**

(*R*,*R*)-**3gB**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); mp 127–130 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{24}$ –113.4 (*c* 1.1, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.45–7.32 (m, 5H, Ar*H*), 7.25–7.20 (m, 2H, Ar*H*), 7.16–7.09 (m, 2H, Ar*H*), 5.49 (dd, *J* = 4.3, 8.9 Hz, 1H, C*H*N), 4.75 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.34 (dd, *J* = 4.3, 8.9 Hz, 1H, CH*H*O), 4.00–3.89 (m, 1H, C*H*$CF_3$), 3.69 (dd, *J* = 10.7, 17.7 Hz, 1H, C*H*H), 3.24 (dd, *J* = 3.4, 17.7 Hz, 1H, CH*H*). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.2 (CO), 153.5 (CO), 138.2 (C), 134.5 (C), 134.3 (C), 133.4 (CH), 131.8 (CH), 130.0 (CH), 129.2 (2 ×CH), 129.0 (CH), 128.9 (CH), 126.2 (q, $^1J_{CF}$ = 276.8 Hz, $CF_3$), 126.1 (2 × CH), 70.2 ($CH_2$), 57.9 (CH), 48.4 (q, $^2J_{CF}$ = 30.0 Hz, CH), 35.4 ($CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.8 ($CF_3$). IR (ATR): $\lambda_{max}$ 1791*s*, 1690*s*, 1573*w*, 1563*w*, 1472*m*, 1386*s*, 1324*s*, 1268*s*, 1247*s*, 1211*s*, 1151*s*, 1100*s*, 1073*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 430 [(M+ H)$^+$, 100], 429 [M$^+$, 79], 409 (32), 389 (18), 286 (17), 226 (19), 211 (12), 183 (15), 121 (10), 120 (23), 108 (13), 104 (69), 91 (7), 77 (6). HRMS (ESI-TOF) calcd for $C_{19}H_{15}ClF_3NO_3SNa^+$ [M + Na]$^+$: 452.0305, found: 452.0301.

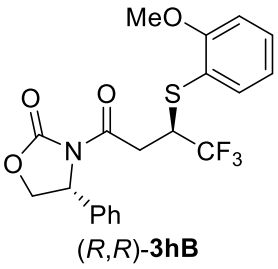
**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(2-methoxyphenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*S*)-3hA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(2-methoxyphenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*R*)-3hB]**

According to the *Conditions A*, the reaction of **1** (57.8 mg, 0.20 mmol) with 2-methoxybenzenethiol (32 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3hA** and (*R*,*R*)-**3hB** (84:16 dr, $^1$H NMR analysis). Purification by column chromatography (30% EtOAc in hexanes) afforded (*R*,*S*)-**3hA** (59.7 mg, 70% yield) as a colorless viscous oil and (*R*,*R*)-**3hB** (13.0 mg, 15% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.5 mg, 0.20 mmol) with 2-methoxybenzenethiol (32 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3hA** and (*R*,*R*)-**3hB** (65:35 dr, $^1$H NMR analysis). Purification by column chromatography (30% EtOAc in hexanes) afforded (*R*,*S*)-**3hA** ( 51.4 mg, 60% yield) and (*R*,*R*)-**3hB** (29.4 mg, 35% yield).



(*R*,*S*)-**3hA**

(*R*,*S*)-**3hA**: $R_f$ 0.18 (30% EtOAc in hexanes); $[\alpha]_D^{23}$ –62.9 (*c* 1.2, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.51 (dd, *J* = 1.6, 7.6 Hz, 1H, Ar*H*), 7.42–7.27 (m, 6H, Ar*H*), 6.95–6.86 (m, 2H, Ar*H*), 5.43 (dd, *J* = 3.6, 8.8 Hz, 1H, C*H*N), 4.70 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.40–4.28 (m, 2H, C*H*HO, C*H*$CF_3$), 3.89 (s, 3H, OC*H*$_3$), 3.60 (dd, *J* = 8.9, 18.2 Hz, 1H, C*H*H), 3.32 (dd, *J* = 4.3, 18.2 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.2 (CO), 159.3 (C), 153.4 (CO), 138.5 (C), 135.3 (CH), 130.5 (CH), 129.2 (2 × CH), 128.9 (CH), 126.3 (q, $^1J_{CF}$ = 277.9 Hz, $CF_3$), 125.9 (2 × CH), 121.0 (CH), 119.5 (C), 111.0 (CH), 70.2 ($CH_2$), 57.8 (CH), 55.8 ($OCH_3$), 44.1 (q, $^2J_{CF}$ = 29.5 Hz, CH), 35.1 (q, $^3J_{CF}$ = 1.8 Hz, $CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –70.2 ($CF_3$). IR (ATR): $\lambda_{max}$ 1777*s*, 1706*s*, 1582*m*, 1476*m*, 1385*s*, 1318*s*, 1242*s*, 1154*s*, 1099*s*, 1066*s*, 1040*s*, 1022*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 426 [(M+ H)$^+$, 89], 425 [M$^+$, 100], 265 (11), 222 (9), 120 (5), 110 (3), 91 (1). HRMS (ESI-TOF) calcd for $C_{20}H_{19}F_3NO_4S^+$ [M + H]$^+$: 426.0981, found: 426.0989.

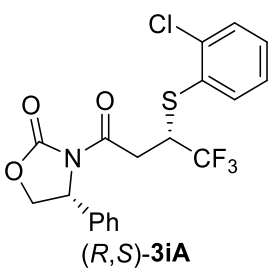


(*R*,*R*)-**3hB**

(*R*,*R*)-**3hB**: $R_f$ 0.20 (30% EtOAc in hexanes); mp 132–134 °C (30% EtOAc in hexanes); $[\alpha]_D^{24}$ –78.3 (*c* 1.2, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.42–7.27 (m, 7H, Ar*H*), 6.87–6.77 (m, 2H, Ar*H*), 5.43 (dd, *J* = 3.8, 8.8 Hz, 1H, C*H*N), 4.70 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.33–4.20 (m, 2H, C*H*HO, C*H*$CF_3$), 3.62–3.53 (m, 4H, OC*H*$_3$, C*H*H), 3.45 (dd, *J* = 5.6, 17.6 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.3 (CO), 159.2 (C), 153.8 (CO), 138.5 (C), 135.4 (CH), 130.5 (CH), 129.2 (2 × CH), 128.8 (CH), 126.4 (q, $^1J_{CF}$ = 277.9 Hz, $CF_3$), 126.0 (2 × CH), 120.8 (CH), 119.8 (C), 111.0 (CH), 70.2 ($CH_2$), 57.8 (CH), 55.4 ($OCH_3$), 44.6 (q, $^2J_{CF}$ = 29.4 Hz, CH), 35.7 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –70.5 (d, *J* = 11.1 Hz, $CF_3$). IR (ATR): $\lambda_{max}$ 1784*s*, 1713*s*, 1585*m*, 1475*m*, 1407*m*, 1317*s*, 1298*s*, 1243*s*, 1183*s*, 1156*s*, 1076*s*, 1057*s*, 1023*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 426 [(M+ H)$^+$, 91], 425 [M$^+$, 100], 286 (6), 265 (28), 222 (23), 164 (8), 140 (41), 120 (13), 104 (10), 77 (10). HRMS (ESI-TOF) calcd for $C_{20}H_{18}F_3NO_4SNa^+$ [M + H]$^+$: 426.0981, found: 426.0978.

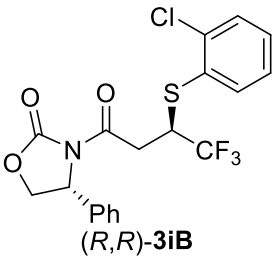
**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(2-chlorophenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*S*)-3iA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(2-chlorophenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*R*)-3iB]**

According to the *Conditions A*, the reaction of **1** (57.9 mg, 0.20 mmol) with 2-chlorobenzenethiol (26 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3iA** and (*R*,*R*)-**3iB** (78:22 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3iA** (61.1 mg, 71% yield) and (*R*,*R*)-**3iB** (17.2 mg, 20% yield) each as a white solid. According to the *Conditions B*, the reaction of **1** (57.9 mg, 0.20 mmol) with 2-chlorobenzenethiol (26 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3iA** and (*R*,*R*)-**3iB** (55:45 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3iA** (38.4 mg, 45% yield) and (*R*,*R*)-**3iB** (31.2 mg, 37% yield).



(*R*,*S*)-**3iA**

(*R*,*S*)-**3iA**: $R_f$ 0.30 (50% $CH_2Cl_2$ in hexanes); mp 136–138 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{27}$ –64.0 (*c* 1.2, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.66–7.60 (m, 1H, Ar*H*), 7.45–7.32 (m, 4H, Ar*H*), 7.32–7.28 (m, 2H, Ar*H*), 7.28–7.19 (m, 2H, Ar*H*), 5.46 (dd, *J* = 3.5, 8.8 Hz, 1H, C*H*N), 4.75 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.33 (dd, *J* = 3.5, 8.8 Hz, 1H, CH*H*O), 4.31–4.21 (m, 1H, C*H*$CF_3$), 3.65 (dd, *J* = 9.5, 18.3 Hz, 1H, C*H*H), 3.37 (dd, *J* = 3.8, 18.3 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 167.9 (CO), 153.5 (CO), 138.4 (C), 136.8 (C), 134.1 (CH), 131.7 (C), 130.1 (CH), 129.5 (CH), 129.3 (2 × CH), 129.0 (CH), 127.5 (CH), 126.0 (2 × CH), 126.1 (q, $^1J_{CF}$ = 277.7 Hz, $CF_3$), 70.3 ($CH_2$), 57.8 (CH), 45.7 (q, $^2J_{CF}$ = 29.9 Hz, CH), 35.1 (q, $^3J_{CF}$ = 1.8 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.4 ($CF_3$). IR (ATR): $\lambda_{max}$ 1788*s*, 1701*s*, 1389*s*, 1301*s*, 1254*s*, 1195*s*, 1139*s*, 1103*s*, 1056*s*, 1033*s*, 1023*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 430 [(M+ H)$^+$, 100], 429 [M$^+$, 74], 426 (10), 425 (19), 409 (16), 286 (11), 183 (11), 120 (26), 108 (21), 104 (54), 91 (8), 77 (6). HRMS (ESI-TOF) calcd for $C_{19}H_{15}ClF_3NO_3SNa^+$ [M + Na]$^+$: 452.0305, found: 452.0317.



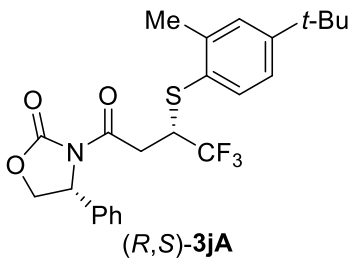
(*R*,*R*)-**3iB**

(*R*,*R*)-**3iB**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); mp 144–146 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{24}$ –79.4 (*c* 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44 (dd, *J* = 1.6, 7.7 Hz, 1H, Ar*H*), 7.40–7.30 (m, 6H, Ar*H*), 7.20 (ddd, *J* = 1.6, 7.7, 7.7 Hz, 1H, Ar*H*), 7.14 (ddd, *J* = 1.6, 7.7, 7.7 Hz, 1H, Ar*H*), 5.46 (dd, *J* = 4.0, 8.9 Hz, 1H, C*H*N), 4.73 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.32 (dd, *J* = 4.0, 8.9 Hz, 1H, CH*H*O), 4.25–4.13 (m, 1H, C*H*$CF_3$), 3.60 (dd, *J* = 8.6, 17.6 Hz, 1H, C*H*H), 3.46 (dd, *J* = 4.7, 17.6 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.0 (CO), 153.5 (CO), 138.2 (C), 137.3 (C), 134.8 (d, *J* = 0.6 Hz, CH), 131.4 (C), 130.0 (CH), 129.7 (CH), 129.2 (2 × CH), 128.9 (CH), 127.4 (CH), 126.1 (q, $^1J_{CF}$ = 277.8 Hz, $CF_3$), 125.9 (2 × CH), 70.2 ($CH_2$), 57.8 (CH), 46.1 (q, $^2J_{CF}$ = 30.0 Hz, CH), 35.4 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –70.4 ($CF_3$). IR (ATR): $\lambda_{max}$ 1796*s*, 1687*s*, 1493*m*, 1384*s*, 1328*s*, 1268*s*, 1148*s*, 1083*s*, 1071*s*, 1036*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 430 [(M+ H)$^+$, 100], 429 [M$^+$, 76], 409 (12), 286 (6), 120 (12), 108 (18), 104 (14), 91 (4). HRMS (ESI-TOF) calcd for $C_{19}H_{15}ClF_3NO_3SNa^+$ [M + Na]$^+$: 452.0305, found: 452.0293.

**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-{[4-(*tert*-butyl)-2-methylphenyl]thio}butanoyl}oxazolidin-2-one [(*R*,*S*)-3jA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-{[4-(*tert*-butyl)-2-methylphenyl]thio}butanoyl}oxazolidin-2-one [(*R*,*R*)-3jB]**

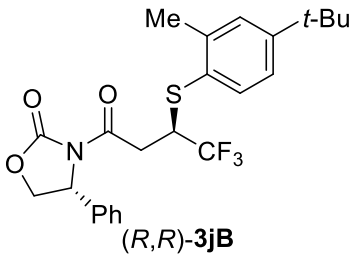
According to the *Conditions A*, the reaction of **1** (59.7 mg, 0.21 mmol) with 4-(*tert*-butyl)-2-methylbenzenethiol (42 μL, 0.23 mmol) gave a crude mixture of (*R*,*S*)-**3jA** and (*R*,*R*)-**3jB** (88:12 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3jA** (83.8 mg, 86% yield) as a colorless viscous oil and (*R*,*R*)-**3jB** (5.9 mg, 6% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.8 mg, 0.20 mmol) with 4-(*tert*-butyl)-2-methylbenzenethiol (40 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3jA** and (*R*,*R*)-**3jB**

(73:27 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexane) afforded (*R*,*S*)-**3jA** (55.8 mg, 60% yield) and (*R*,*R*)-**3jB** (21.1 mg, 23% yield).



(*R*,*S*)-**3jA**

(*R*,*S*)-**3jA**: $R_f$ 0.38 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{25}$ –46.3 (*c* 1.1, $CHCl_3$). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 7.72 (d, *J* = 2.1 Hz, 1H, Ar*H*), 7.40–7.30 (m, 6H, Ar*H*), 7.21 (d, *J* = 8.0 Hz, 1H, Ar*H*), 5.62 (dd, *J* = 3.5, 8.8 Hz, 1H, C*H*N), 4.88 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.31 (dd, *J* = 3.5, 8.8 Hz, 1H, CH*H*O), 4.30–4.19 (m, 1H, C*H*CF$_3$), 3.62 (dd, *J* = 9.4, 18.2 Hz, 1H, C*H*H), 3.48 (dd, *J* = 4.0, 18.2 Hz, 1H, CH*H*), 2.40 (s, 3H, C*H*$_3$), 1.30 (s, 9H, 3 × C*H*$_3$). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 168.7 (CO), 154.8 (CO), 150.7 (C), 140.7 (C), 138.8 (C), 132.3 (C), 132.0 (CH), 131.2 (CH), 129.8 (2 × CH), 129.2 (CH), 127.8 (q, $^1J_{CF}$ = 276.8 Hz, $CF_3$), 127.0 (CH), 126.9 (2 × CH), 71.6 ($CH_2$), 58.6 (CH), 47.4 (q, $^2J_{CF}$ = 29.0 Hz, CH), 35.9 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$), 35.1 (C), 31.5 (3 × $CH_3$), 20.3 ($CH_3$). $^{19}$F NMR (470 MHz, acetone-$d_6$): $\delta$ –71.1 ($CF_3$). IR (ATR): $\lambda_{max}$ 1779*s*, 1706*s*, 1384*m*, 1311*m*, 1199*m*, 1154*s*, 1099*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 466 [(M+ H)$^+$, 100], 465 [M$^+$, 74], 262 (11), 165 (6), 120 (14). HRMS (ESI-TOF) calcd for $C_{24}H_{26}F_3NO_3SNa^+$ [M + Na]$^+$: 488.1478, found: 488.1482.



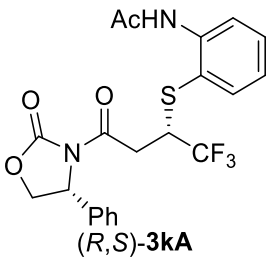
(*R*,*R*)-**3jB**

(*R*,*R*)-**3jB**: $R_f$ 0.20 (50% $CH_2Cl_2$ in hexanes); mp 134–137 ºC (50% $CH_2Cl_2$ in hexanes; $[\alpha]_D^{23}$ –108.9 (*c* 1.1, $CHCl_3$). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 7.54 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.45–7.29 (m, 5H, Ar*H*), 7.27 (dd, *J* = 2.0, 8.0 Hz, 1H, Ar*H*), 7.13 (d, *J* = 8.0 Hz, 1H, Ar*H*), 5.64 (dd, *J* = 4.0, 8.8 Hz, 1H, C*H*N), 4.87 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.31 (dd, *J* = 4.0, 8.8 Hz, 1H, CH*H*O), 4.20–4.06 (m, 1H, C*H*CF$_3$), 3.76 (dd, *J* = 10.0, 17.8 Hz, 1H, C*H*H), 3.34 (dd, *J* = 3.5, 17.8 Hz, 1H, CH*H*), 2.23 (s, 3H, C*H*$_3$), 1.21 (s, 9H, 3 × C*H*$_3$). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 169.0 (CO), 154.9 (CO), 150.7 (C), 140.6 (C), 138.9 (C), 132.6 (C), 132.1 (CH), 131.1 (CH), 129.8 (2 × CH), 129.1 (CH), 127.9 (q, $^1J_{CF}$ = 276.4 Hz, $CF_3$), 127.0 (CH), 126.9 (2 × CH), 71.4 ($CH_2$), 58.7 (CH), 48.5 (q, $^2J_{CF}$ = 29.1 Hz, CH), 35.9 (s, $CH_2$), 35.0 (C), 31.5 (3 × $CH_3$), 20.2 ($CH_3$). $^{19}$F NMR (376 MHz, acetone-$d_6$): $\delta$ –71.3 (d, *J* = 10.9 Hz, $CF_3$). IR (ATR): $\lambda_{max}$ 1789*s*, 1697*s*, 1488*w*, 1442*w*, 1380*s*, 1324*s*, 1263*s*, 1176*s*, 1148*s*, 1105*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 466 [(M+ H)$^+$, 100], 465 [M$^+$, 71], 464 (18), 262 (7), 165 (7), 120 (12). HRMS (ESI-TOF) calcd for $C_{24}H_{26}F_3NO_3SNa^+$ [M + Na]$^+$: 488.1478, found: 488.1481.

**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(2-acetamidophenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*S*)-3kA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(2-acetamidophenyl)thio]butanoyl}oxazolidin-2-one [(*R*,*R*)-3kB]**

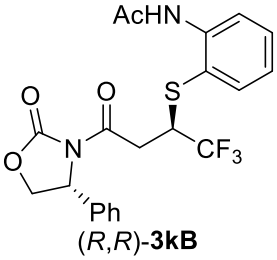
According to the *Conditions A*, the reaction of **1** (57.7 mg, 0.20 mmol) with 2-aminobenzenethiol (24 μL 0.22 mmol) followed by the *N*-acetylation of the obtained crude mixture with acetic anhydride (58 μL, 0.6 mmol) in $CH_2Cl_2$ (1 mL) gave a crude mixture of (*R*,*S*)-**3kA** and (*R*,*R*)-**3kB**

(84:16 dr, $^1$H NMR analysis). Purification by column chromatography (30% EtOAc in hexanes) afforded (*R*,*S*)-**3kA** (67.9 mg, 75% yield) and (*R*,*R*)-**3kB** (9.8 mg, 11% yield) each as a light-brown solid. According to the *Conditions B*, the reaction of **1** (57.6 mg, 0.20 mmol) with 2-aminobenzenethiol (24 μL, 0.22 mmol) followed by the *N*-acetylation of the obtained crude mixture with acetic anhydride (58 μL, 0.6 mmol) in $CH_2Cl_2$ (1 mL) gave a crude mixture of (*R*,*S*)-**3kA** and (*R*,*R*)-**3kB** (60:40 dr, $^1$H NMR analysis). Purification by column chromatography (30% EtOAc in hexanes) afforded (*R*,*S*)-**3kA** (45.5 mg, 50% yield) and (*R*,*R*)-**3kB** (33.9 mg, 38% yield).



(*R*,*S*)-**3kA**

(*R*,*S*)-**3kA**: $R_f$ 0.13 (30% EtOAc in hexanes); mp 141–144 °C (30% EtOAc in hexane); $[\alpha]_D^{23}$ –111.0 (*c* 1.3, $CH_2Cl_2$). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 9.22 (brs, 1H, N*H*), 8.45 (dd, *J* = 1.0, 7.9 Hz, 1H, Ar*H*), 7.62 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.48–7.31 (m, 6H, Ar*H*), 7.05 (ddd, *J* = 1.0, 7.9, 7.9 Hz, 1H, Ar*H*), 5.71 (dd, *J* = 4.0, 8.8 Hz, 1H, C*H*N), 4.93 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.34 (dd, *J* = 4.0, 8.8 Hz, 1H, CH*H*O), 4.07–3.94 (m, 1H, C*H*CF$_3$), 3.59 (dd, *J* = 2.6, 19.1 Hz, 1H, C*H*H), 3.47 (dd, *J* = 11.3, 19.1 Hz, 1H, CH*H*), 2.12 (s, 3H, C*H*$_3$). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 170.2 (CO), 169.7 (CO), 154.7 (CO), 142.8 (C), 140.6 (C), 138.7 (C), 132.0 (CH), 129.8 (2 × CH), 129.2 (CH), 127.8 (q, $^1J_{CF}$ = 277.7 Hz, CF$_3$), 127.1 (2 × CH), 124.2 (CH), 121.5 (CH), 119.5 (C), 71.7 (CH$_2$), 59.0 (CH), 46.4 (q, $^2J_{CF}$ = 28.7 Hz, CH), 34.9 (q, $^3J_{CF}$ = 2.1 Hz, CH$_2$), 24.8 (CH$_3$). $^{19}$F NMR (376 MHz, acetone-$d_6$): $\delta$ –70.5 (CF$_3$). IR (ATR): $\lambda_{max}$ 3307*m*, 1779*s*, 1707*m*, 1682*s*, 1579*m*, 1520*m*, 1400*m*, 1329*s*, 1223*s*, 1181*s*, 1129*s*, 1063*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 453 [(M+ H)$^+$, 100], 452 [M$^+$, 6], 290 (6), 167 (9), 134 (39), 125 (35), 120 (6), 80 (10). HRMS (ESI-TOF) calcd for $C_{21}H_{20}F_3N_2O_4S^+$ [M + H]$^+$: 453.1090, found: 453.1088.

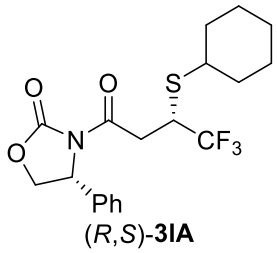


(*R*,*R*)-**3kB**

(*R*,*R*)-**3kB**: $R_f$ 0.10 (30% EtOAc in hexanes); mp 156–159 °C (30% EtOAc in hexane); $[\alpha]_D^{23}$ –85.2 (*c* 1.2, $CH_2Cl_2$). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 8.86 (brs, 1H, N*H*), 8.41 (dd, *J* = 1.1, 7.9 Hz, 1H, Ar*H*), 7.55 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.50–7.33 (m, 6H, Ar*H*), 7.01 (ddd, *J* = 1.1, 7.9, 7.9 Hz, 1H, Ar*H*), 5.72 (dd, *J* = 4.5, 8.8 Hz, 1H, C*H*N), 4.92 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.30 (dd, *J* = 4.5, 8.8 Hz, 1H, CH*H*O), 4.07–3.95 (m, 1H, C*H*CF$_3$), 3.61 (dd, *J* = 10.9, 18.9 Hz, 1H, C*H*H), 3.52 (dd, *J* = 3.0, 18.9 Hz, 1H, CH*H*), 1.75 (s, 3H, C*H*$_3$). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 170.5 (CO), 169.6 (CO), 154.8 (CO), 142.7 (C), 140.4 (C), 138.9 (CH), 132.2 (CH), 130.0 (2 × CH), 129.3 (CH), 127.9 (q, $^1J_{CF}$ = 277.1 Hz, CF$_3$), 126.7 (2 × CH), 124.1 (CH), 121.4 (CH), 119.3 (C), 71.6 (CH$_2$), 58.9 (CH), 46.6 (q, $^2J_{CF}$ = 28.9 Hz, CH), 35.1 (q, $^3J_{CF}$ = 2.2 Hz, CH$_2$), 24.4 (CH$_3$). $^{19}$F NMR (376 MHz, acetone-$d_6$): $\delta$ –70.5 (d, *J* = 8.8 Hz, CF$_3$). IR (ATR): $\lambda_{max}$ 3324*m*, 1781*s*, 1687*s*, 1577*m*, 1517*m*, 1434*m*, 1391*s*, 1249*s*, 1213*s*, 1147*s*, 1098*s* cm$^{-1}$. MS: *m/z* (%) relative intensity intensity 453 [(M+ H)$^+$, 100], 452 [M$^+$, 5], 290 (7), 167 (8), 134 (43), 125 (32), 120 (3), 80 (7).HRMS (ESI-TOF) calcd for $C_{21}H_{20}F_3N_2O_4S^+$ [M + H]$^+$: 453.1090, found: 453.1091.

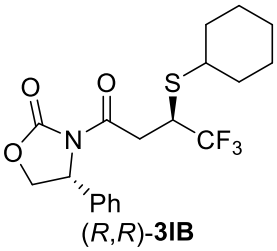
**(*R*)-4-Phenyl-3-[(*S*)-4,4,4-trifluoro-3-(cyclohexylthio)butanoyl]oxazolidin-2-one [(*R*,*S*)-3lA] and (*R*)-4-Phenyl-3-[(*R*)-4,4,4-trifluoro-3-(cyclohexylthio)butanoyl]oxazolidin-2-one [(*R*,*R*)-3lB]**

*Conditions C*: A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with **1** (57.5 mg, 0.20 mmol) and dry THF (1 mL). The resulting solution was cooled at –78 °C then cyclohexanethiol (26 mg, 0.22 mmol) and a solution of $P_2$-*t*-Bu (2.0 M in THF, 10 μL, 10 mol%) were added. After stirring at –78 °C for 30 min., the reaction mixture was quenched with $H_2O$ (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with a saturated aqueous NaCl solution (20 mL) and dried over anhydrous $Na_2SO_4$. After removal of the solvent *in vacuo*, the crude mixture (63:37 dr, $^{19}$F NMR analysis) was purified by column chromatography (50% $CH_2Cl_2$ in hexanes) to afford (*R*,*S*)-**3lA** (43.1 mg, 55% yield) as a white semi-solid and (*R*,*R*)-**3lB** (26.1 mg, 33% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.3 mg, 0.20 mmol) with cyclohexanethiol (26 mg, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3lA** and (*R*,*R*)-**3lB** (7:93 dr, $^{19}$F NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3lA** (4.3 mg, 6% yield) and (*R*,*R*)-**3lB** (67.6 mg, 85% yield).



(*R*,*S*)-**3lA**

(*R*,*S*)-**3lA**: $R_f$ 0.30 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{27}$ –79.7 (*c* 1.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.45–7.28 (m, 5H, Ar*H*), 5.47 (dd, *J* = 3.4, 8.8 Hz, 1H, C*H*N), 4.74 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.32 (dd, *J* = 3.4, 8.8 Hz, 1H, CH*H*O), 3.84–3.72 (m, 1H, C*H*$CF_3$), 3.54 (dd, *J* = 10.5, 18.2 Hz, 1H, C*H*H), 3.24 (dd, *J* = 3.1, 18.2 Hz, 1H, CH*H*), 2.95–2.85 (m, 1H, CH), 2.09–2.00 (m, 1H, C*H*H), 1.95–1.87 (m, 1H, CH*H*), 1.80–1.70 (m, 2H, $CH_2$), 1.35–1.15 (m, 6H, 3 × $CH_2$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.3 (CO), 153.5 (CO), 138.6 (C), 129.3 (2 × CH), 128.9 (CH), 125.8 (2 × CH), 126.7 (q, $^1J_{CF}$ = 276.3 Hz, $CF_3$), 70.2 ($CH_2$), 57.7 (CH), 45.4 (CH), 41.1 (q, $^2J_{CF}$ = 29.7 Hz, CH), 36.2 ($CH_2$), 33.4 ($CH_2$), 33.3 ($CH_2$), 25.8 ($CH_2$), 25.7 ($CH_2$), 25.6 ($CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –72.3 ($CF_3$). IR (ATR): $\lambda_{max}$ 1785*s*, 1702*s*, 1403*m*, 1385*m*, 1317*s*, 1257*m*, 1210*m*, 1153*s*, 1094*s*, 1065*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 402 [(M+ H)$^+$, 100], 401 [M$^+$, 10], 381 (7), 120 (7), 81 (5). HRMS (ESI-TOF) calcd for $C_{19}H_{22}F_3NO_3SNa^+$ [M + Na]$^+$: 424.1165, found: 424.1162.



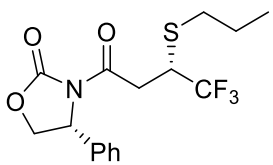
(*R*,*R*)-**3lB**

(*R*,*R*)-**3lB**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); mp 130–133 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{27}$ –77.2 (*c* 1.4, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.42–7.30 (m, 5H, Ar*H*), 5.47 (dd, *J* = 4.3, 8.8 Hz, 1H, C*H*N), 4.72 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.30 (dd, *J* = 4.3, 8.8 Hz, 1H, CH*H*O), 3.78–3.62 (m, 2H, C*H*$CF_3$, C*H*H), 3.24–3.14 (m, 1H, C*H*H), 2.72–2.62 (m, 1H, CH), 1.87–1.77 (m, 1H, C*H*H), 1.70–1.60 (m, 2H, $CH_2$), 1.55–1.45 (m, 2H, $CH_2$), 1.28–1.15 (m, 2H, $CH_2$), 1.15–1.01 (m, 2H, $CH_2$), 0.97–0.85 (m, 1H, CH*H*). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.8 (CO), 153.4 (CO), 138.3 (C), 129.1 (2 × CH), 128.7 (CH), 126.4 (q, $^1J_{CF}$ = 276.6 Hz, $CF_3$), 126.1 (2 × CH), 70.1 ($CH_2$), 57.9 (CH), 45.3 (CH), 41.8 (q, $^2J_{CF}$ = 30.2 Hz, CH) , 36.1 ($CH_2$) , 33.3 ($CH_2$) , 32.7 ($CH_2$), 25.6 ($CH_2$), 25.5 ($CH_2$), 25.4

($CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –72.4 ($CF_3$). IR (ATR): $\lambda_{max}$ 1780*s*, 1700*s*, 1412*m*, 1328*s*, 1265*s* , 1212*s* , 1160*s*, 1088*s*, 1073*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 402 [(M+ H)$^+$, 100], 401 [M$^+$, 17], 400 (9), 381 (8), 120 (8), 81 (7). HRMS (ESI-TOF) calcd for $C_{19}H_{22}F_3NO_3SNa^+$ [M + Na]$^+$: 424.1165, found: 424.1163.

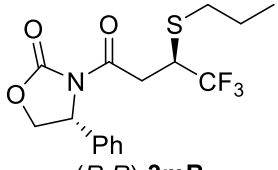
**(*R*)-4-Phenyl-3-[(*S*)-4,4,4-trifluoro-3-(propylthio)butanoyl]oxazolidin-2-one [(*R*,*S*)-3mA] and (*R*)-4-Phenyl-3-[(*R*)-4,4,4-trifluoro-3-(propylthio)butanoyl]oxazolidin-2-one [(*R*,*R*)-3mB]**

According to the *Conditions C*, the reaction of **1** (57.5 mg, 0.20 mmol) with 1-propanethiol (18 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3mA**:(*R*,*R*)-**3mB** (64:36 dr, $^{19}$F NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3mA** (43.4 mg, 60% yield) as a white semi-solid and (*R*,*R*)-**3mB** (23.5 mg, 33% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.0 mg, 0.20 mmol) with 1-propanethiol (18 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3mA** and (*R*,*R*)-**3mB** (3:97 dr, $^{19}$F NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3mA** (2.1 mg, 3% yield) and (*R*,*R*)-**3mB** (63.4 mg, 90% yield).



(*R*,*S*)-**3mA**

(*R*,*S*)-**3mA**: $R_f$ 0.30 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{26}$ –91.9 (*c* 1.3, $CHCl_3$). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 7.44–7.31 (m, 5H, Ar*H*), 5.62 (dd, *J* = 3.7, 8.7 Hz, 1H, C*H*N), 4.89 (dd, *J* = 8.7, 8.7 Hz, 1H, C*H*HO), 4.29 (dd, *J* = 3.7, 8.7 Hz, 1H, CH*H*O), 3.90–3.77 (m, 1H, C*H*CF$_3$), 3.49–3.38 (m, 2H, C*H*$_2$), 2.71 (t, *J* = 7.3, 2H, C*H*$_2$), 1.65–1.54 (m, 2H, C*H*$_2$), 0.95 (t, *J* = 7.3, 3H, C*H*$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.3 (CO), 153.5 (CO), 138.5 (C), 129.3 (2 × CH), 129.0 (CH), 126.7 (q, $^1J_{CF}$ = 277.0 Hz, $CF_3$), 125.9 (2 × CH), 70.3 ($CH_2$), 57.8 (CH), 42.9 (q, $^2J_{CF}$ = 30.0 Hz, CH), 35.9 (q, $^3J_{CF}$ = 2.0 Hz, $CH_2$), 35.4 ($CH_2$), 22.5 ($CH_2$), 13.2 ($CH_3$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –72.1 ($CF_3$). IR (ATR): $\lambda_{max}$ 1794*s*, 1697*s*, 1392*s*, 1340*s*, 1258*s* , 1217*s* , 1153*s* , 1103*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 362 [(M+ H)$^+$, 100], 361 [M$^+$, 6], 343(19), 341(9), 226 (6), 228 (5), 164 (48) , 146 (8) , 120 (27) , 104 (37). HRMS (DART) calcd for $C_{16}H_{19}F_3NO_3^+$ [M +H]$^+$: 362.1032, found: 362.1029.



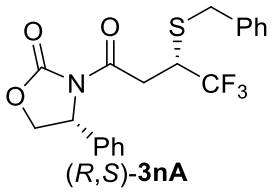
(*R*,*R*)-**3mB**

(*R*,*R*)-**3mB**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); mp 116–118 ºC (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{26}$ –73.1 (*c* 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.43–7.29 (m, 5H, Ar*H*), 5.47 (dd, *J* = 4.2, 8.9 Hz, 1H, C*H*N), 4.73 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.29 (dd, *J* = 4.2, 8.9 Hz, 1H, CH*H*O), 3.74–3.55 (m, 2H, C*H*CF$_3$, C*H*H), 3.25 (dd, *J* = 3.2, 16.9 Hz, 1H, CH*H*), 2.51 (t, *J* = 7.3, 2H, C*H*$_2$), 1.52–1.35 (m, 2H, C*H*$_2$), 0.81 (t, *J* = 7.3, 3H, C*H*$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.5 (CO), 153.5 (CO), 138.3 (C), 129.1 (2 × CH), 128.8 (CH), 126.7 (q, $^1J_{CF}$ = 276.9 Hz, $CF_3$), 125.8 (2 × CH), 70.1 ($CH_2$), 57.8 (CH), 43.2 (q, $^2J_{CF}$ = 30.0 Hz, CH), 35.8 (q, $^3J_{CF}$ = 1.8 Hz, $CH_2$), 35.3 ($CH_2$), 22.3 ($CH_2$), 13.0 ($CH_3$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –72.2 ($CF_3$). IR (ATR): $\lambda_{max}$ 1789*s*, 1696*s*, 1384*s*, 1313*s*, 1210*s*, 1147*s*, 1120*s*, 1097*s*, 1071*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 362 [(M+ H)$^+$, 100], 361 [M$^+$, 6], 343 (17), 266

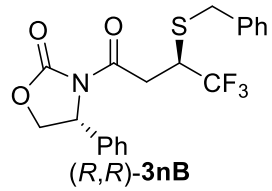
(3), 164 (4), 120 (13). HRMS (ESI-TOF) calcd for $C_{16}H_{19}F_3NO_3^+$ [M +H]$^+$: 362.1032, found: 362.1032.

**(*R*)-4-Phenyl-3-[(*S*)-4,4,4-trifluoro-3-(benzylthio)butanoyl]oxazolidin-2-one [(*R*,*S*)-3nA] and (*R*)-4-Phenyl-3-[(*R*)-4,4,4-trifluoro-3-(benzylthio)butanoyl]oxazolidin-2-one [(*R*,*R*)-3nB]**

According to the *Conditions C*, the reaction of **1** (57.5 mg, 0.20 mmol) with benzylthiol (26 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3nA**:(*R*,*R*)-**3nB** (65:35 dr, $^{19}$F NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3nA** (41.3 mg, 50% yield) as a white semi-solid and (*R*,*R*)-**3nB** (14.1 mg, 17% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.3 mg, 0.20 mmol) with benzylthiol (26 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3nA** and (*R*,*R*)-**3nB** (8:92 dr, $^{19}$F NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3nA** (6.0 mg, 8% yield) and (*R*,*R*)-**3nB** (72.4 mg, 90% yield).


(*R*,*S*)-**3nA**

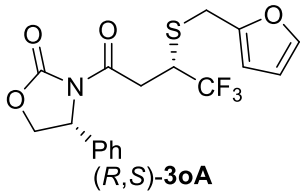
(*R*,*S*)-**3nA**: $R_f$ 0.25 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{26}$ –86.6 (*c* 1.7, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.42–7.32 (m, 3H, Ar*H*), 7.32–7.24 (m, 7H, Ar*H*), 5.41 (dd, *J* = 3.5, 8.9 Hz, 1H, C*H*N), 4.71 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.30 (dd, *J* = 3.5, 8.9 Hz, 1H, C*H*HO), 3.93 (ABq, *J* = 12.5 Hz, 2H, C$H_2$), 3.76–3.67 (m, 1H, C*H*$CF_3$), 3.52 (dd, *J* = 10.3, 18.2 Hz, 1H, C*H*H), 3.26 (dd, *J* = 3.5, 18.2 Hz, 1H, CH*H*). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.0 (CO), 153.4 (CO), 138.5 (C), 136.5 (C), 129.3 (2 × CH), 129.1 (2 × CH), 128.9 (CH), 128.6 (2 × CH), 127.5 (CH), 126.6 (q, $^1J_{CF}$ = 276.9 Hz, $CF_3$), 125.9 (2 × CH), 70.2 ($CH_2$), 57.7 (CH), 42.7 (q, $^2J_{CF}$ = 30.0 Hz, CH), 37.5 ($CH_2$), 35.6 ($CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –71.8 ($CF_3$). IR (ATR): $\lambda_{max}$ 1792*s*, 1694*s*, 1390*m*, 1318*m*, 1263*s* , 1151*s* , 1070*s* , 1026*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 410 [(M+ H)$^+$, 100], 409 [M$^+$, 2], 391 (7), 181 (7), 164 (7), 120 (19), 91 (35). HRMS (ESI-TOF) calcd for $C_{20}H_{18}F_3NO_3SNa^+$ [M + Na]$^+$: 432.0852, found: 432.0851.


(*R*,*R*)-**3nB**

(*R*,*R*)-**3nB**: $R_f$ 0.20 (50% $CH_2Cl_2$ in hexanes); mp 132–134 ºC (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{25}$ –58.4 (*c* 0.9, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.45–7.36 (m, 3H, Ar*H*), 7.35–7.29 (m, 2H, Ar*H*), 7.24–7.16 (m, 3H, Ar*H*), 7.09–7.03 (m, 2H, Ar*H*), 5.41 (dd, *J* = 4.2, 8.9 Hz, 1H, C*H*N), 4.69 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.27 (dd, *J* = 4.2, 8.9 Hz, 1H, C*H*HO), 3.74 (ABq, *J* = 13.2 Hz, 2H, C$H_2$), 3.67–3.49 (m, 2H, C*H*$CF_3$, C*H*H), 3.23 (dd, *J* = 3.2, 16.6 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.2 (CO), 153.4 (CO), 138.4 (C), 136.1 (C), 129.2 (2 × CH), 129.1 (2 × CH), 128.8 (CH), 128.4 (2 × CH), 127.4 (CH), 126.7 (q, $^1J_{CF}$ = 277.2 Hz, $CF_3$), 126.0 (2 × CH), 70.1 ($CH_2$), 57.8 (CH), 42.5 (q, $^2J_{CF}$ = 30.1 Hz, CH), 37.4 ($CH_2$), 35.5 (q, $^3J_{CF}$ = 1.7 Hz, $CH_2$). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ –72.0 ($CF_3$). IR (ATR): $\lambda_{max}$ 1794*s*, 1694*s*, 1493*w*, 1454*w*, 1391*s*, 1318*s*, 1260*s*, 1149*s*, 1104*s*, 1070*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 410 [(M+ H)$^+$, 100], 409 [M$^+$, 2], 391 (14), 228 (6), 164 (15), 120 (25), 91 (27). HRMS (ESI-TOF) calcd for $C_{20}H_{18}F_3NO_3SNa^+$ [M + Na]$^+$: 432.0852, found: 432.0851.

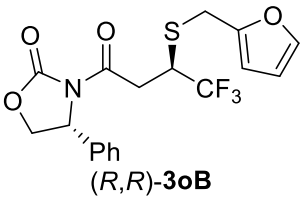
**(*R*)-4-Phenyl-3-{(*S*)-4,4,4-trifluoro-3-[(furan-2-ylmethyl)thio]butanoyl}oxazolidin-2-one [(*R*,*S*)-3oA] and (*R*)-4-Phenyl-3-{(*R*)-4,4,4-trifluoro-3-[(furan-2-ylmethyl)thio]butanoyl}oxazolidin-2-one [(*R*,*R*)-3oB]**

According to the *Conditions C*, the reaction of **1** (57.8 mg, 0.20 mmol) with furan-2-ylethanethiol (24 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3oA**:(*R*,*R*)-**3oB** (60:40 dr, $^1$H NMR analysis). Purification by column chromatography (30% EtOAc in hexanes) afforded (*R*,*S*)-**3oA** (31.1 mg, 39% yield) as a brown viscous oil and (*R*,*R*)-**3oB** (17.6 mg, 22% yield) as a white solid. According to the *Conditions B*, the reaction of **1** (57.6 mg, 0.20 mmol) with furan-2-ylethanethiol (24 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3oA** and (*R*,*R*)-**3oB** (7:93 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3oA** (5.3 mg, 7% yield) and (*R*,*R*)-**3oB** (67.9 mg, 85% yield).



(*R*,*S*)-**3oA**

(*R*,*S*)-**3oA**: $R_f$ 0.38 (30% EtOAc in hexanes); $[\alpha]_D^{24}$ –70.8 (*c* 1.3, $CH_2Cl_2$). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 7.49 (dd, *J* = 0.8, 1.9 Hz, 1H, Ar*H*), 7.44–7.30 (m, 5H, Ar*H*), 6.36 (dd, *J* = 1.9, 3.2 Hz, 1H, Ar*H*), 6.32 (dd, *J* = 0.8, 3.2 Hz, 1H, Ar*H*), 5.60 (dd, *J* = 3.7, 8.8 Hz, 1H, C*H*N), 4.88 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.28 (dd, *J* = 3.7, 8.8 Hz, 1H, CH*H*O), 4.02 (s, 2H, C$H_2$), 4.00–3.90 (m, 1H, C*H*$CF_3$), 3.55–3.39 (m, 2H, C$H_2$). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 168.7 (CO), 154.8 (CO), 151.3 (C), 143.7 (CH), 140.7 (C), 129.4 (2 × CH), 129.1 (CH), 128.0 (q, $^1J_{CF}$ = 277.6 Hz, $CF_3$), 126.9 (2 × CH), 111.4 (CH), 109.4 (CH), 71.5 ($CH_2$), 58.6 (CH), 43.2 (q, $^2J_{CF}$ = 29.6 Hz, CH), 36.6 (q, $^3J_{CF}$ = 1.8 Hz, $CH_2$), 29.7 ($CH_2$). $^{19}$F NMR (470 MHz, acetone-$d_6$): $\delta$ –71.8 ($CF_3$). IR (ATR): $\lambda_{max}$ 1776*s*, 1704*s*, 1495*m*, 1478*m*, 1457*m*, 1387*s*, 1316*s*, 1254*s*, 1200*s*, 1151*s*, 1099*s*, 1068*s* cm$^{-1}$. MS: *m*/*z* (%) relative intensity 400 [(M+ H)$^+$, 48], 399 [M$^+$, 5], 397 (3), 382 (6), 242 (18), 241 (100), 237 (3), 161 (23), 81 (11). HRMS (ESI-TOF) calcd for $C_{18}H_{16}F_3NO_4SNa^+$ [M + Na]$^+$: 422.0644, found: 422.0642.



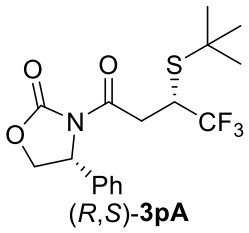
(*R*,*R*)-**3oB**

(*R*,*R*)-**3oB**: $R_f$ 0.35 (30% EtOAc in hexanes); mp 122–124 ºC (30% EtOAc in hexanes); $[\alpha]_D^{24}$ –79.6 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 7.45–7.32 (m, 6H, Ar*H*), 6.29 (dd, *J* = 1.9, 3.2 Hz, 1H, Ar*H*), 6.20 (dd, *J* = 0.6, 3.2 Hz, 1H, Ar*H*), 5.61 (dd, *J* = 3.9, 8.9 Hz, 1H, C*H*N), 4.86 (dd, *J* = 8.9, 8.9 Hz, 1H, C*H*HO), 4.29 (dd, *J* = 3.9, 8.9 Hz, 1H, CH*H*O), 3.94–3.82 (m, 3H, C$H_2$, C*H*$CF_3$), 3.60 (dd, *J* = 9.7, 17.4 Hz, 1H, C*H*H), 3.35 (dd, *J* = 4.1, 17.4 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 168.9 (CO), 154.8 (CO), 151.1 (C), 143.7 (CH), 140.6 (C), 129.8 (2 × CH), 129.0 (CH), 128.0 (q, $^1J_{CF}$ = 276.2 Hz, $CF_3$), 126.9 (2 × CH), 111.4 (CH), 109.3 (CH), 71.4 ($CH_2$), 58.7 (CH), 43.5 (q, $^2J_{CF}$ = 29.7 Hz, CH), 36.5 (q, $^3J_{CF}$ = 1.9 Hz, $CH_2$), 30.0 ($CH_2$). $^{19}$F NMR (470 MHz, acetone-$d_6$): $\delta$ –71.8 ($CF_3$). IR (ATR): $\lambda_{max}$ 1782*s*, 1705*s*, 1558*m*, 1541*m*, 1520*m*, 1474*m*, 1407*m*, 1273*s*, 1245*s*, 1154*s*, 1142*s*, 1093*s*, 1038*s* cm$^{-1}$. MS: *m*/*z* (%) relative intensity 400 [(M+ H)$^+$, 67], 381 (18), 242 (15),

241 (100), 164 (17), 161 (80), 112 (7), 80 (91), 52 (20). HRMS (ESI-TOF) calcd for $C_{18}H_{16}F_3NO_4SNa^+$ $[M + Na]^+$: 422.0644, found: 422.0638.

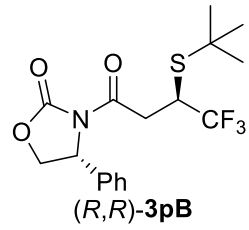
**(*R*)-4-Phenyl-3-[(*S*)-4,4,4-trifluoro-3-(*tert*-butylthio)butanoyl]oxazolidin-2-one [(*R*,*S*)-3pA] and (*R*)-4-Phenyl-3-[(*R*)-4,4,4-trifluoro-3-(*tert*-butylthio)butanoyl]oxazolidin-2-one [(*R*,*R*)-3pB]**

According to the *Conditions C*, the reaction of **1** (57.1 mg, 0.20 mmol) with *tert*-butylthiol (26 μL, 0.22 mmol) gave a crude mixture of (*R*,*S*)-**3pA**:(*R*,*R*)-**3pB** (60:40 dr, $^1$H NMR analysis). Purification by column chromatography (50% $CH_2Cl_2$ in hexanes) afforded (*R*,*S*)-**3pA** (39.0 mg, 52% yield) as a white semi-solid and (*R*,*R*)-**3pB** (21.1 mg, 28% yield) as a white solid.



(*R*,*S*)-**3pA**

(*R*,*S*)-**3pA**: $R_f$ 0.30 (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{25}$ –92.7 (*c* 1.1, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44–7.33 (m, 3H, Ar*H*), 7.33–7.27 (m, 2H, Ar*H*), 5.44 (dd, *J* = 3.6, 8.8 Hz, 1H, C*H*N), 4.73 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.31 (dd, *J* = 3.6, 8.8 Hz, 1H, CH*H*O), 3.88–3.79 (m, 1H, C*H*$CF_3$), 3.53 (dd, *J* = 7.7, 18.0 Hz, 1H, C*H*H), 3.43 (dd, *J* = 5.5, 18.0 Hz, 1H, C*H*H), 1.33 (s, 9H, 3 × C*H*$_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.5 (CO), 153.5 (CO), 138.5 (C), 129.3 (2 × CH), 128.9 (CH), 126.4 (q, $^1J_{CF}$ = 277.0 Hz, $CF_3$), 125.8 (2 × CH), 70.2 ($CH_2$), 57.8 (CH), 44.9 (C), 40.0 (q, $^2J_{CF}$ = 29.7 Hz, CH), 37.6 (q, $^3J_{CF}$ = 2.0 Hz, $CH_2$), 31.1 (3 × $CH_3$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –70.6 (d, *J* = 11.2 Hz, $CF_3$). IR (ATR): $\lambda_{max}$ 1787*s*, 1697*s*, 1455*w*, 1405*s*, 1366*m*, 1300*m*, 1269*m*, 1212*m*, 1180*s*, 1114*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 376 [(M+ H)$^+$, 100], 375 [M$^+$, 58], 320 (27), 275 (14), 242 (10), 151 (9), 120 (33), 119 (27), 104 (9). HRMS (ESI-TOF) calcd for $C_{17}H_{20}F_3NO_3SNa^+$ $[M + Na]^+$: 398.1008, found: 398.1005.

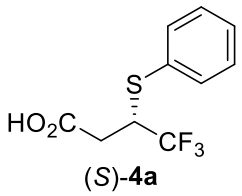


(*R*,*R*)-**3pB**

(*R*,*R*)-**3pB**: $R_f$ 0.20 (50% $CH_2Cl_2$ in hexanes); mp 142–145 °C (50% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{25}$ –105.3 (*c* 0.6, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.41–7.30 (m, 5H, Ar*H*), 5.46 (dd, *J* = 4.2, 8.8 Hz, 1H, C*H*N), 4.72 (dd, *J* = 8.8, 8.8 Hz, 1H, C*H*HO), 4.29 (dd, *J* = 4.2, 8.8 Hz, 1H, CH*H*O), 3.80–3.70 (m, 1H, C*H*$CF_3$), 3.64 (dd, *J* = 9.0, 17.2 Hz, 1H, C*H*H), 3.31 (dd, *J* = 4.7, 17.2 Hz, 1H, CH*H*), 1.11 (s, 9H, 3 × C*H*$_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 168.7 (CO), 153.4 (CO), 138.5 (C), 129.1 (2 × CH), 128.8 (CH), 126.4 (q, $^1J_{CF}$ = 276.1 Hz, $CF_3$), 126.3 (2 × CH), 70.0 ($CH_2$), 57.8 (CH), 44.7 (C), 40.5 (q, $^2J_{CF}$ = 30.1 Hz, CH), 37.0 ($CH_2$), 30.8 (3 × $CH_3$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –70.6 (d, *J* = 11.1 Hz, $CF_3$). IR (ATR): $\lambda_{max}$ 1778*s*, 1703*s*, 1465*m*, 1379*s*, 1310*s*, 1259*s*, 1246*s*, 1210*s*, 1177*s*, 1156*s*, 1116*s*, 1091*s*, 1072*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 376 [(M+ H)$^+$, 100], 375 [M$^+$, 57], 320 (19), 275 (16), 242 (11), 120 (25), 119 (20), 104 (7), 57 (6). HRMS (ESI-TOF) calcd for $C_{17}H_{20}F_3NO_3SNa^+$ $[M + Na]^+$: 398.1008, found: 398.1003.

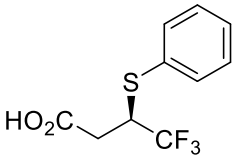
## 2. Synthesis of acids 4

**(*S*)-4,4,4-Trifluoro-3-(phenylthio)butanoic acid [(*S*)-4a]**[2]



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

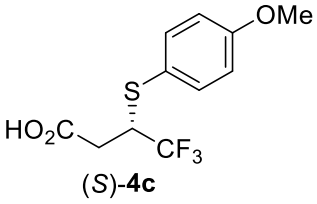
A solution of (*R*,*S*)-**3aA** (298 mg, 0.75 mmol) in THF (8 mL) cooled at 0 °C was treated with an aqueous solution of $H_2O_2$ (30% v/v, 0.44 mL, 3.8 mmol) followed by a dropwise addition of a cooled solution of $LiOH·H_2O$ (51 mg, 1.5 mmol) dissolved in water (4 mL). After stirring at 0 °C for 1 h, two phases of the reaction mixture were separated. To recover the chiral auxiliary, the aqueous phase was further extracted with $CH_2Cl_2$ (3 × 20 mL) then the combined organic phase was washed with a saturated aqueous $NaHCO_3$ solution (2 × 25 mL), dried over anhydrous $Na_2SO_4$, and concentrated *in vacuo*. To collect the acid product, the previously obtained aqueous phase was acidified with 10% HCl and extracted with $CH_2Cl_2$ (3 × 20 mL). The combined $CH_2Cl_2$ phase was dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo* to provide the crude carboxylic acid which was further purified by column chromatography (20% EtOAc in $CH_2Cl_2$) to give (*S*)-**4a** (130 mg, 69% yield) as a yellow liquid. $R_f$ 0.25 (20% EtOAc in $CH_2Cl_2$); $[\alpha]_D^{24}$ +7.6 (*c* 1.1, $CH_2Cl_2$); $[\alpha]_D^{26}$ +7.6 (*c* 1.02, $CHCl_3$) [lit. $[\alpha]_D^{25}$ +8.9 (*c* 1.02, $CHCl_3$)].[2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62–7.54 (m, 2H, Ar*H*), 7.40–7.31 (m, 3H, Ar*H*), 3.97–3.85 (m, 1H, C*H*$CF_3$), 2.98 (dd, *J* = 3.9, 17.1 Hz, 1H, C*H*H), 2.72 (dd, *J* = 10.5, 17.1 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 175.2 (CO), 134.3 (2 × CH), 131.6 (C), 129.3 (2 × CH), 129.1 (CH), 126.0 (q, $^1J_{CF}$ = 277.2 Hz, $CF_3$), 48.2 (q, $^2J_{CF}$ = 29.8 Hz, CH), 34.2 ($CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –70.9 ($CF_3$). IR (ATR): $\lambda_{max}$ 3058*brm*, 1715*s*, 1477*m*, 1439*m*, 1416*m*, 1303*s*, 1247*s*, 1149*s*, 1100*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 250 [$M^+$, 100], 249 [$(M–H)^–$, 2], 233 (27), 229 (45), 209 (29), 165 (77), 135 (25), 109 (21), 65 (11). HRMS (ESI-TOF) calcd for $C_{10}H_8F_3O_2S^–$ [M – H]$^–$: 249.0203, found: 249.0204.



(*R*)-**4b**

**(*R*)-4,4,4-Trifluoro-3-(phenylthio)butanoic acid [(*R*)-4b]** (55.6 mg, 71% yield) was synthesized from (*R*,*R*)-**3aB** (122 mg, 0.31 mmol). $[\alpha]_D^{25}$ –13.3 (*c* 1.1, $CH_2Cl_2$).

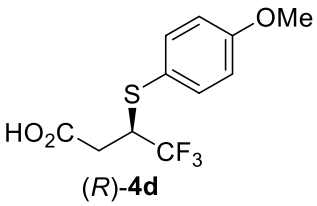
**(*S*)-4,4,4-Trifluoro-3-(4–methoxyphenylthio)butanoic acid [(*S*)-4c]**[2]



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

According to the synthesis of (*S*)-**4a**, hydrolysis of (*R*,*S*)-**3cA** (346 mg, 0.81 mmol) and purification by column chromatography (20% EtOAc in $CH_2Cl_2$) afforded (*S*)-**4c** (152 mg, 67% yield) as a yellow liquid. $R_f$ 0.25 (20% EtOAc in $CH_2Cl_2$); $[\alpha]_D^{25}$ +7.1 (*c* 1.24, $CHCl_3$) [lit. $[\alpha]_D^{25}$ +7.2 (*c* 1.24, $CHCl_3$)].[2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.55–7.49 (m, 2H, Ar*H*), 6.90–6.84 (m, 2H, Ar*H*), 3.81 (s, 3H, O$CH_3$), 3.80–3.70 (m, 1H, C*H*$CF_3$), 2.93 (dd, *J* = 3.9, 17.1 Hz, 1H, C*H*H), 2.68 (dd, *J* = 10.6, 17.1 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 174.8 (q, $^4J_{CF}$ = 2.9 Hz, CO), 160.7 (C), 137.1 (2 × CH), 126.1 (q, $^1J_{CF}$ = 277.4 Hz, $CF_3$), 121.6 (C), 114.7 (2 × CH), 55.3 ($OCH_3$), 48.5 (q, $^2J_{CF}$ = 29.8 Hz, CH), 33.9 (q, $^3J_{CF}$ = 1.9 Hz, $CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ –70.6 ($CF_3$). IR (ATR): $\lambda_{max}$ 3218*brm*, 1729*s*, 1590*m*, 1493*m*, 1354*m*, 1288*s*, 1239*s*, 1222*s*, 1172*s*, 1141*s*, 1096*s*, 1014*s* cm$^{-1}$. MS: *m/z*

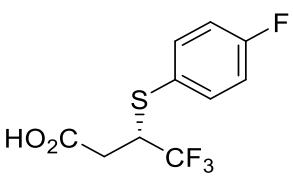
(%) relative intensity 280 [$M^+$, 100], 260 (19), 195 (16), 157 (14), 139 (84), 108 (10), 95 (19), 66 (5). HRMS (ESI-TOF) calcd for $C_{11}H_{10}F_3O_3S^-$ [M – H]$^-$: 279.0308, found: 279.0313.



(*R*)-**4d**

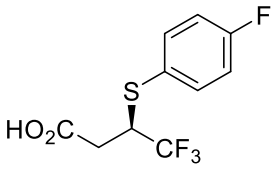
**(*R*)-4,4,4-Trifluoro-3-(4–methoxyphenylthio)butanoic acid [(*R*)-4d]**[3] (90.8 mg, 68% yield) was synthesized from (*R*,*R*)-**3cB** (198 mg, 0.47 mmol). $[\alpha]_D^{25}$ –3.8. (*c* 1.05, $CHCl_3$) [lit. $[\alpha]_D^{25}$ –5.5 (*c* 1.24, $CHCl_3$)].[3]

**(*S*)-4,4,4-Trifluoro-3-(4–fluorophenylthio)butanoic acid [(*S*)-4e]**



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

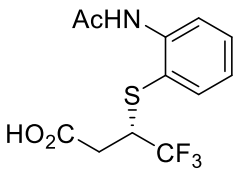
According to the synthesis of (*S*)-**4a**, hydrolysis of (*R*,*S*)-**3eA** (1.25 g, 3.0 mmol) and purification by column chromatography (20% EtOAc in $CH_2Cl_2$) afforded (*S*)-**4e** (533 mg, 66% yield) as a yellow liquid. $R_f$ 0.25 (20% EtOAc in $CH_2Cl_2$); $[\alpha]_D^{23}$ +2.2 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.63–7.54 (m, 2H, Ar*H*), 7.10–7.00 (m, 2H, Ar*H*), 3.87–3.74 (m, 1H, C*H*$CF_3$), 2.97 (dd, *J* = 3.7, 17.1 Hz, 1H, C*H*H), 2.70 (dd, *J* = 10.8, 17.1 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 174.7 (CO), 163.5 (d, $^1J_{CF}$ = 248.9 Hz, C), 137.1 (d, $^3J_{CF}$ = 8.5 Hz, 2 × CH), 126.6 (d, $^4J_{CF}$ = 3.4 Hz, C), 126.0 (q, $^1J_{CF}$ = 277.2 Hz, $CF_3$), 116.5 (d, $^2J_{CF}$ = 21.8 Hz, 2 × CH), 48.6 (q, $^2J_{CF}$ = 29.7 Hz, CH), 34.0 ($CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): –70.8 ($CF_3$), –111.1 (F). IR (ATR): $\lambda_{max}$ 2932*brm*, 1715*s*, 1590*m*, 1490*m*, 1417*m*, 1356*s*, 1228*s*, 1153*s*, 1101*s*, 1014*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 268 [$M^+$, 100], 251 (25), 248 (30), 223 (7), 183 (44), 153 (23), 127 (10). HRMS (ESI-TOF) calcd for $C_{10}H_7F_4O_2S^-$ [M – H]$^-$: 267.0108, found: 267.0112.



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

**(*R*)-4,4,4-Trifluoro-3-(4–fluorophenylthio)butanoic acid [(*R*)-4f]** (65.9 mg, 64% yield) was synthesized from (*R*,*R*)-**3eB** (159 mg, 0.39 mmol). $[\alpha]_D^{23}$ –1.2 (*c* 1.1, $CH_2Cl_2$).

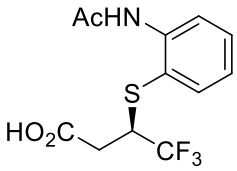
**(*S*)-4,4,4-Trifluoro-3-[(2-acetamidophenyl)thio]butanoic acid [(*S*)-4g]**



(*S*)-**4g**

According to the synthesis of (*S*)-**4a**, hydrolysis of (*R*,*S*)-**3kA** (392 mg, 0.87 mmol) gave (*S*)-**4g** (176 mg, 66% yield) as a white solid. $R_f$ 0.13 (5% MeOH in $CH_2Cl_2$); mp 145–148 °C (5% MeOH in $CH_2Cl_2$); $[\alpha]_D^{21}$ –72.3 (*c* 1.1, acetone). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 9.12 (brs, 1H, N*H*), 8.43 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.64 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.43 (ddd, *J* = 1.3, 8.1, 8.1 Hz, 1H, Ar*H*), 7.08 (ddd, *J* = 1.3, 8.1, 8.1 Hz, 1H, Ar*H*), 4.10–3.90 (m, 1H, C*H*$CF_3$), 3.10 (dd, *J* = 2.9, 17.9 Hz, 1H, C*H*H), 2.71 (dd, *J* = 11.5, 17.9 Hz, 1H, CH*H*), 2.21 (s, 3H, C*H*$_3$). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 172.2 (CO), 169.7 (CO), 142.6 (C), 138.6 (CH), 132.0 (CH), 127.6 (q, $^1J_{CF}$ = 277.0 Hz, $CF_3$), 124.4 (CH), 121.8 (CH), 119.8 (C), 47.6 (q, $^2J_{CF}$ = 29.2 Hz, CH), 33.1 (q, $^3J_{CF}$ = 2.1 Hz, $CH_2$), 24.6 ($CH_3$). $^{19}$F NMR (376 MHz, acetone-$d_6$): $\delta$ –70.8 (d, *J* = 10.3 Hz, $CF_3$). IR (ATR): $\lambda_{max}$ 3298*brm*, 2706*brm*, 2507*brm*, 2345*brm*, 1721*s*, 1637*s*,

1580*s*, 1534*s*, 1438*m*, 1302*s*, 1240*s*, 1149*s*, 1092*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 308 [(M+ H)$^+$, 100], 307 [M$^+$, 1], 306 [(M– H)$^-$, 1], 290 (4), 266 (16), 248 (11), 164 (7). HRMS (DART) calcd for $C_{12}H_{13}F_3NO_3S^+$ [M + H]$^+$: 308.0563, found: 308.0567.

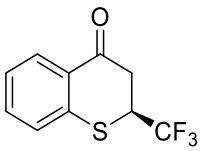


(*R*)-**4h**

**(*R*)-4,4,4-Trifluoro-3--[(2-acetamidophenyl)thio]butanoic acid [(*R*)-4h]** (111 mg, 57% yield) was synthesized from (*R*,*R*)-**3kB** (284 mg, 0.63 mmol). $[\alpha]_D^{24}$ +71.1 (*c* 1.0, acetone).

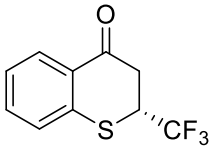
## 3. Synthesis of 5

**(*S*)-2-(Trifluoromethyl)thiochroman-4-one [(*S*)-5a]**[2]



(*S*)-**5a**

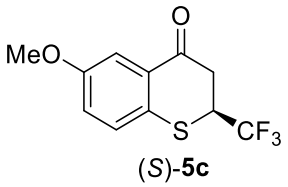
A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with (*S*)-**4a** (46.8 mg, 0.19 mmol) and dry $CH_2Cl_2$ (0.5 mL) followed by the slow addition of thionyl chloride (42 μL, 0.57 mmol). After stirring at room temperature for 3 h, the reaction mixture was concentrated *in vacuo* to give the crude acid chloride which was further dissolved in dry $CH_2Cl_2$ (0.5 mL) under a positive pressure of argon. To a solution was slowly added $AlCl_3$ (76.1 mg, 0.57 mmol) and the reaction mixture was allowed to stir at room temperature for 1 h. The reaction mixture was quenched with $H_2O$ (5 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic phase was washed with a saturated aqueous NaCl solution (10 mL), dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. Purification by column chromatography (40% $CH_2Cl_2$ in hexanes) afforded (*S*)-**5a** (33.9 mg, 79% yield) as a white solid. $R_f$ 0.35 (40% $CH_2Cl_2$ in hexanes); mp 60–63 °C (40% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{24}$ +175.5 (*c* 0.58, $CHCl_3$) [lit. $[\alpha]_D^{25}$ +159.4 (*c* 0.58, $CHCl_3$)].[2] $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 8.02 (dd, *J* = 1.1, 8.0 Hz, 1H, Ar*H*), 7.55 (ddd, *J* = 1.1, 8.0, 8.0 Hz, 1H, Ar*H*), 7.40 (dd, *J* = 1.1, 8.0 Hz, 1H, Ar*H*), 7.30 (ddd, *J* = 1.1, 8.0, 8.0 Hz, 1H, Ar*H*), 4.61–4.50 (m, 1H, C*H*$CF_3$), 3.42 (dd, *J* = 5.3, 17.0 Hz, 1H, C*H*H), 3.18 (dd, *J* = 5.3, 17.0 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 191.1 (CO), 138.6 (C), 135.0 (CH), 131.2 (C), 129.1 (CH), 127.9 (CH), 127.2 (q, $^1J_{CF}$ = 277.9 Hz, $CF_3$), 126.7 (CH), 42.9 (q, $^2J_{CF}$ = 30.6 Hz, CH), 38.4 ($CH_2$). $^{19}$F NMR (376 MHz, acetone-$d_6$): –71.9 (d, *J* = 9.7 Hz, $CF_3$). IR (ATR): $\lambda_{max}$ 1682*s*, 1591*m*, 1437*m*, 1349*m*, 1288*s*, 1180*s*, 1153*s*, 1107*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 233 [(M+ H)$^+$, 12], 232 [M$^+$, 4], 183 (16), 165 (75), 149 (23), 136 (18), 134 (21), 131 (41), 127 (25), 123 (54), 121 (52), 109 (100), 108 (25), 103 (10). HRMS (DART) calcd for $C_{10}H_8F_3OS^+$ [M + H]$^+$: 233.0242, found: 233.0250.



(*R*)-**5b**

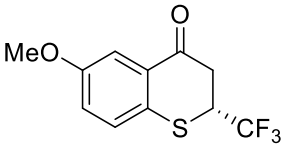
**(*R*)-2-(Trifluoromethyl)thiochroman-4-one [(*R*)-5b]** (41.7 mg, 82% yield) was synthesized from (*R*)-**4b** (55.6 mg, 0.22 mmol) $[\alpha]_D^{24}$ –162.4 (*c* 0.58, $CHCl_3$).

**(*S*)-6-Methoxy-2-(trifluoromethyl)thiochroman-4-one [(*S*)-5c]**[2]



(*S*)-**5c**

According to the synthesis of (*S*)-**5a**, the reaction of (*S*)-**4c** (61.6 mg, 0.22 mmol) and purification by column chromatography (40% $CH_2Cl_2$ in hexanes) afforded (*S*)-**5c** (44.5 mg, 77% yield) as bright yellow liquid. $R_f$ 0.25 (40% $CH_2Cl_2$ in hexanes); $[\alpha]_D^{26}$ +139.6 (*c* 0.6, $CHCl_3$) [lit. $[\alpha]_D^{25}$ +120.4 (*c* 0.6, $CHCl_3$)].[2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.60 (d, *J* = 2.9 Hz, 1H, Ar*H*), 7.19 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.06 (dd, *J* = 2.9, 8.7 Hz, 1H, Ar*H*), 3.98–3.88 (m, 1H, C*H*$CF_3$), 3.83 (s, 3H, OC*H*$_3$), 3.27–3.13 (m, 2H, C*H*$_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 190.7 (CO), 157.9 (C), 130.8 (C), 128.7 (C), 128.4 (CH), 125.3 (q, $^1J_{CF}$ = 278.5 Hz, $CF_3$), 122.8 (CH), 111.3 (CH), 55.6 ($OCH_3$), 42.9 (q, $^2J_{CF}$ = 31.1 Hz, CH), 38.2 ($CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$): –71.1 (d, *J* = 8.3 Hz, $CF_3$). IR (ATR): $\lambda_{max}$ 1680*s*, 1599*m*, 1474*m*, 1404*m*, 1324*m*, 1252*s*, 1219*s*, 1154*s*, 1104*s*, 1024*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 263 [(M+ H)$^+$, 15], 262 [M$^+$, 34], 218 (26), 193 (10), 166 (55), 150 (10), 140 (12), 139 (100), 138 (53), 124 (16), 123 (58). HRMS (ESI-TOF) calcd for $C_{11}H_{10}F_3O_2S^+$ [M + H]$^+$: 263.0348, found: 263.0356.

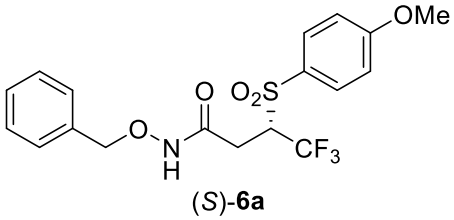


(*R*)-**5d**

**(*R*)-6-Methoxy-2-(trifluoromethyl)thiochroman-4-one [(*R*)-5d]**[3] (26.3 mg, 83% yield) was synthesized from (*R*)-**4d** (34.9 mg, 0.12 mmol). $[\alpha]_D^{25}$ –121.1 (*c* 0.6, $CHCl_3$) [lit. $[\alpha]_D^{25}$ –116.4 (*c* 0.6, $CHCl_3$)].

## 4. Synthesis of 6

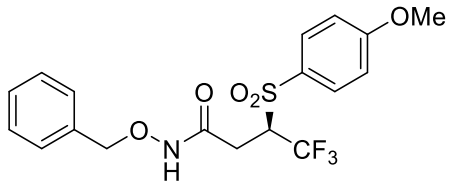
**(*S*)-*N*-(Benzyloxy)-4,4,4-trifluoro-3-[(4-methoxyphenyl)sulfonyl]butanamide [(*S*)-6a]**



(*S*)-**6a**

To a flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum charged with acid (*S*)-**4c** (166 mg, 0.59 mmol) and dry $CH_2Cl_2$ (1.5 mL) was added $SOCl_2$ (0.2 mL, 1.8 mmol). The reaction mixture was stirred at room temperature for 3 h then the resulting acid chloride product was concentrated *in vacuo* and used in the next step without purification. A separated flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with *o*-benzylhydroxylamine hydrochloride (284 mg, 1.8 mmol) and dry $CH_2Cl_2$ (1.8 mL). After stirring for a few minutes at 0 °C, $Et_3N$ (0.25 mL, 1.8 mmol) was added and the reaction was allowed to stir at 0 °C for 1 h. To the resulting mixture, a solution of crude acid chloride in dry $CHCl_2$ (1.5 mL) was slowly added. After stirring at 0 °C for 2 h, the reaction mixture was quenched with $H_2O$ (10 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic phase was washed with 20% aqueous citric acid solution (2 × 20 mL) and a saturated aqueous $NaHCO_3$ solution (2 × 20 mL), dried over anhydrous $Na_2SO_4$, and concentrated *in vacuo*. The obtained crude product was dissolved in dry $CH_2Cl_2$ (2 mL), cooled at 0 °C, and treated with

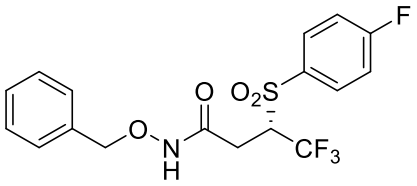
a solution of *m*-CPBA (256 mg, 1.5 mmol) in dry $CH_2Cl_2$ (1.5 mL) under a positive pressure of argon. After stirring at 0 °C for 1 h, the reaction mixture was quenched with $H_2O$ (10 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic phase was washed with a saturated aqueous $NaHCO_3$ solution, dried over anhydrous $Na_2SO_4$, and concentrated *in vacuo*. Purification by column chromatography (40% EtOAc in hexanes) gave (*S*)-**6a** (167 mg, 68% yield) as a white semi-solid. $R_f$ 0.25 (40% EtOAc in hexanes); $[\alpha]_D^{22}$ 26.9 (*c* 1.0, acetone). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 10.49 (s, 1H, N*H*), 7.96–7.86 (m, 2H, Ar*H*), 7.51–7.31 (m, 5H, Ar*H*), 7.22 (d, *J* = 8.8 Hz, 2H, Ar*H*), 4.98–4.82 (m, 2H, C$H_2$), 4.78–4.65 (m, 1H, C*H*$CF_3$), 3.95 (s, 3H, OC$H_3$), 2.96 (dd, *J* = 6.4, 16.5 Hz, 1H, C*H*H), 2.71 (dd, *J* = 5.7, 16.5 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 165.7 (C), 165.5 (CO), 137.0 (C), 132.3 (2 × CH), 130.4 (C), 130.0 (2 × CH), 129.3 (CH), 129.2 (2 × CH), 124.5 (q, $^1J_{CF}$ = 278.2 Hz, $CF_3$), 115.7 (2 × CH), 78.5 ($CH_2$), 63.6 (q, $^2J_{CF}$ = 27.6 Hz, CH), 56.4 ($OCH_3$), 28.6 ($CH_2$). $^{19}$F NMR (376 MHz, acetone-$d_6$): –65.8 ($CF_3$). IR (ATR): $\lambda_{max}$ 3230*m*, 1658*s*, 1593*s*, 1578*m*, 1520*m*, 1496*m*, 1455*m*, 1419*m*, 1344*s*, 1248*s*, 1194*s*, 1142*s*, 1048*s*, 1028*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 418 [(M+ H)$^+$, 50], 375 (19), 295 (29), 246 (23), 203 (8), 181 (9), 155 (100), 124 (9). HRMS (DART) calcd for $C_{18}H_{19}F_3NO_5S^+$ [M + H]$^+$: 418.0931, found: 418.0921.



(*R*)-**6b**

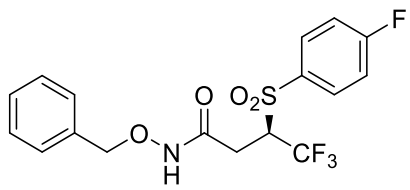
**(*R*)-*N*-(Benzyloxy)-4,4,4-trifluoro-3-[(4-methoxyphenyl)sulfonyl]butanamide [(*R*)-6b]** (89.8 mg, 71% yield) was synthesized from (*R*)-**4d** (88.0 mg, 0.31 mmol). $[\alpha]_D^{22}$ –27.3 (*c* 1.0, acetone).

**(*S*)-*N*-(Benzyloxy)-4,4,4-trifluoro-3-[(4-fluorophenyl)sulfonyl] butanamide [(*S*)-6c]**



(*S*)-**6c**

According to the synthesis of (*S*)-**6a**, the reaction of (*S*)-**4e** (229 mg, 0.86 mmol) and purification by column chromatography (40% EtOAc in hexanes) afforded (*S*)-**6c** (143 mg, 41% yield) as a white solid. $R_f$ 0.38 (40% EtOAc in hexanes); mp 115–118 °C (40% EtOAc in hexanes); $[\alpha]_D^{22}$ +20.8 (*c* 1.0, acetone). $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 10.51 (s, 1H, N*H*), 8.15–8.02 (m, 2H, Ar*H*), 7.52 (dd, *J* = 8.7, 8.7 Hz, 2H, Ar*H*), 7.47–7.32 (m, 5H, Ar*H*), 5.02–4.77 (m, 3H, C$H_2$, C*H*$CF_3$), 3.00 (dd, *J* = 6.8, 16.6 Hz, 1H, C*H*H), 2.76 (dd, *J* = 5.4, 16.6 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 167.4 (d, $^1J_{CF}$ = 253.8 Hz, C), 165.3 (CO), 136.9 (C), 135.5 (C), 133.3 (d, $^3J_{CF}$ = 10.1 Hz, 2 × CH), 130.0 (2 × CH), 129.3 (CH), 129.2 (2 × CH), 124.4 (q, $^1J_{CF}$ = 278.2 Hz, $CF_3$), 117.8 (d, $^2J_{CF}$ = 23.0 Hz, 2 × CH), 78.5 ($CH_2$), 63.6 (q, $^2J_{CF}$ = 27.8 Hz, CH), 28.4 ($CH_2$). $^{19}$F NMR (376 MHz, acetone-$d_6$): –65.8 ($CF_3$), –104.1 (F). IR (ATR): $\lambda_{max}$ 3229*m*, 1661*s*, 1590*s*, 1518*m*, 1493*s*, 1424*m*, 1408*m*, 1345*s*, 1239*s*, 1191*s*, 1144*s*, 1102*s*, 1081*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 406 [(M+ H)$^+$, 100], 386 (13), 363 (38), 283 (8), 203 (19), 181 (33), 143 (13), 124 (10). HRMS (DART) calcd for $C_{17}H_{16}F_4NO_4S^+$ [M + H]$^+$: 406.0731, found: 406.0738.

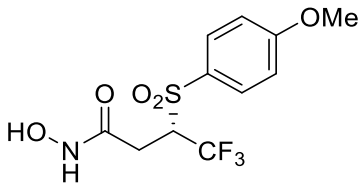


(*R*)-**6d**

**(*R*)-*N*-(Benzyloxy)-4,4,4-trifluoro-3-[(4-fluorophenyl)sulfonyl]butanamide [(*R*)-6d]** (164 mg, 41% yield) was synthesized from (*R*)-**4f** (263 mg, 0.98 mmol). $[\alpha]_D^{22}$ –20.0 (*c* 1.0, acetone).

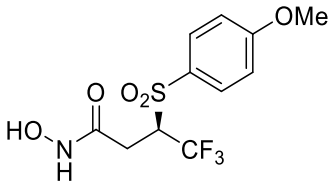
## 5. Synthesis of 7

**(*S*)-4,4,4-Trifluoro-*N*-hydroxy-3-[(4-methoxyphenyl)sulfonyl]butanamide [(*S*)-7a]**[4]



(*S*)-**7a**

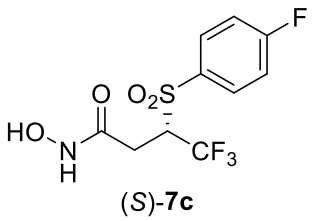
A flame-dried round bottom flask equipped with a magnetic stirring bar, an argon inlet, and a rubber septum was charged with (*S*)-**6a** (59.7 mg, 0.14 mmol), $Pd(OH)_2/C$ (20%wt , 19.7 mg, 0.14 mmol), dry MeOH (2.4 mL), and dry EtOAc (0.6 mL). The argon inlet was replaced by a $H_2$ balloon, and the reaction mixture was stirred at room temperature for 1 h. The resulting mixture was filtered through a celite pad, and the residue was eluted with MeOH (15 mL). After removal of the solvent *in vacuo*, the crude product was purified by column chromatography (5% MeOH in $CH_2Cl_2$) to afford (*S*)-**7a** (32.8 mg, 71% yield) as a white semi-solid. $R_f$ 0.23 (5% MeOH in $CH_2Cl_2$); mp 131–134 °C (5% MeOH in $CH_2Cl_2$); $[\alpha]_D^{25}$ +5.2 (*c* 1.0, EtOH) [lit. $[\alpha]_D^{23}$ +16.1 (*c* 1.1, EtOH)].[4] $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ 7.89 (d, *J* = 10.0 Hz, 2H, Ar*H*), 7.17 (d, *J* = 10.0 Hz, 2H, Ar*H*), 4.70–4.58 (m, 1H, C*H*$CF_3$), 3.92 (s, 3H, OC$H_3$), 2.94 (dd, *J* = 6.2, 16.2 Hz, 1H, C*H*H), 2.65 (dd, *J* = 6.2, 16.2 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ 167.1 (CO), 166.5 (C), 132.6 (2 × CH), 130.4 (C), 124.8 (q, $^1J_{CF}$ = 278.2 Hz, $CF_3$), 115.9 (2 × CH), 64.2 (q, $^2J_{CF}$ = 27.7 Hz, CH), 56.6 ($OCH_3$), 28.7 ($CH_2$). $^{19}$F NMR (376 MHz, $CD_3OD$): –66.7 (d, *J* = 10.6 Hz, $CF_3$). IR (ATR): $\lambda_{max}$ 3312*brm*, 1659*s*, 1593*s*, 1497*s*, 1345*s*, 1320*m*, 1251*s*, 1194*s*, 1143*s*, 1082*s*, 1014*s* $cm^{-1}$. MS: *m/z* (%) relative intensity 328 [(M+ H)$^+$, 14], 327 ($M^+$, 3), 312 (18), 310 (5), 295 (18), 284 (9), 278 (26), 247 (18), 246 (100), 189 (8), 171 (11), 155 (26). HRMS (DART) calcd for $C_{11}H_{13}F_3NO_5S^+$ $[M + H]^+$: 328.0461, found: 328.0470.



(*R*)-**7b**

**(*R*)-4,4,4-Trifluoro-*N*-hydroxy-3-[(4-methoxyphenyl)sulfonyl] butanamide [(*R*)-7b]**[4] (40.4 mg, 71% yield) was synthesized from (*R*)-**6b** (70.9 mg, 0.17 mmol). $[\alpha]_D^{25}$ –3.3 (*c* 0.88, EtOH) [lit. $[\alpha]_D^{23}$ –16.9 (*c* 0.88, EtOH)].

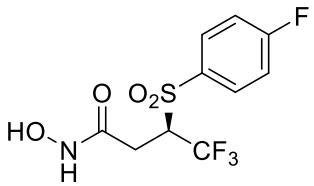
**(*S*)-4,4,4-Trifluoro-*N*-hydroxy-3-[(4-fluorophenyl)sulfonyl]butanamide [(*S*)-7c]**



(*S*)-**7c**

According to the synthesis of (*S*)-**7a**, the reaction of (*R*)-**6c** (154 mg, 0.38 mmol) and purification by column chromatography (60% EtOAc in hexanes) gave (*R*)-**7c** (85.4 mg, 71% yield) as a white solid. $R_f$ 0.25 (60% EtOAc in hexanes); $[\alpha]_D^{24}$ +3.9 (*c* 1.1, EtOH). $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ 8.09–8.01 (m, 2H, Ar*H*), 7.46–7.38 (m, 2H, Ar*H*),

4.82–4.71 (m, 1H, C*H*$CF_3$), 2.97 (dd, *J* = 6.2, 16.3 Hz, 1H, C*H*H), 2.69 (dd, *J* = 6.2, 16.3 Hz, 1H, CH*H*). $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ 168.1 (d, $^1J_{CF}$ = 254.6 Hz, C), 166.9 (CO), 135.7 (C), 133.6 (d, $^3J_{CF}$ = 10.1 Hz, 2 × CH), 124.7 (q, $^1J_{CF}$ = 278.2 Hz, $CF_3$), 118.0 (d, $^2J_{CF}$ = 23.1 Hz, 2 × CH), 64.1 (q, $^2J_{CF}$ = 28.0 Hz, CH), 28.5 ($CH_2$). $^{19}$F NMR (376 MHz, $CD_3OD$): –66.6 (d, *J* = 10.2 Hz, $CF_3$), –104.1 (F). IR (ATR): $\lambda_{max}$ 3365*brm*, 3151*brm*, 1672*s*, 1590*s*, 1494*s*, 1344*s*, 1240*s*, 1147*s*, 1081*s* cm$^{-1}$. MS: *m/z* (%) relative intensity 316 [(M+ H)$^+$, 91], 315 (M$^+$, 3), 313 (3), 302 (4), 300 (56), 298 (91), 284 (12), 283 (100), 256 (7), 177 (39), 158 (16). HRMS (DART) calcd for $C_{10}H_{10}F_4NO_4S^+$ [M + H]$^+$: 316.0261, found: 316.0254.



(*R*)-**7d**

**(*R*)-4,4,4-Trifluoro-*N*-hydroxy-3-[(4-fluorophenyl)sulfonyl]butan amide [(*R*)-7d]** (86.5 mg, 69% yield) was synthesized from (*R*)-**6d** (159 mg, 0.39 mmol). $[\alpha]_D^{24}$ –3.2 (*c* 1.1, EtOH).

**References:**

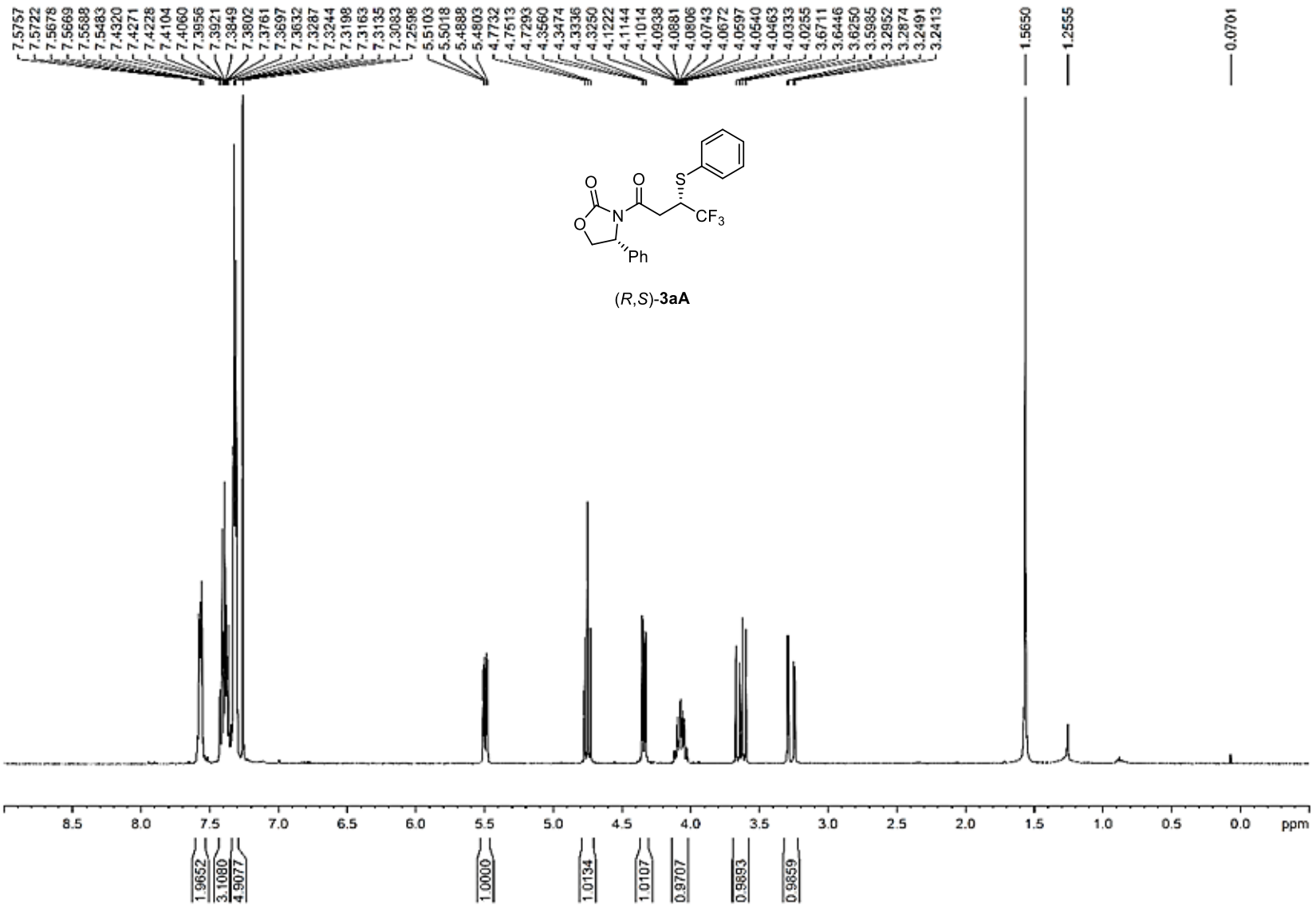
[1] Racochote, S.; Pohmakotr, M.; Kuhakarn, C.; Leowanawat, P.; Reutrakul, V.; Soorukram, D. *Eur. J. Org. Chem*. **2019**, *12*, 2212–2223

[2] Dong, X-O.; Fang, X.; Tao, H-Y.; Zhou, X.; Wang, C-J. *Adv. Synth. Catal*. **2012**, *354*, 1141–1147

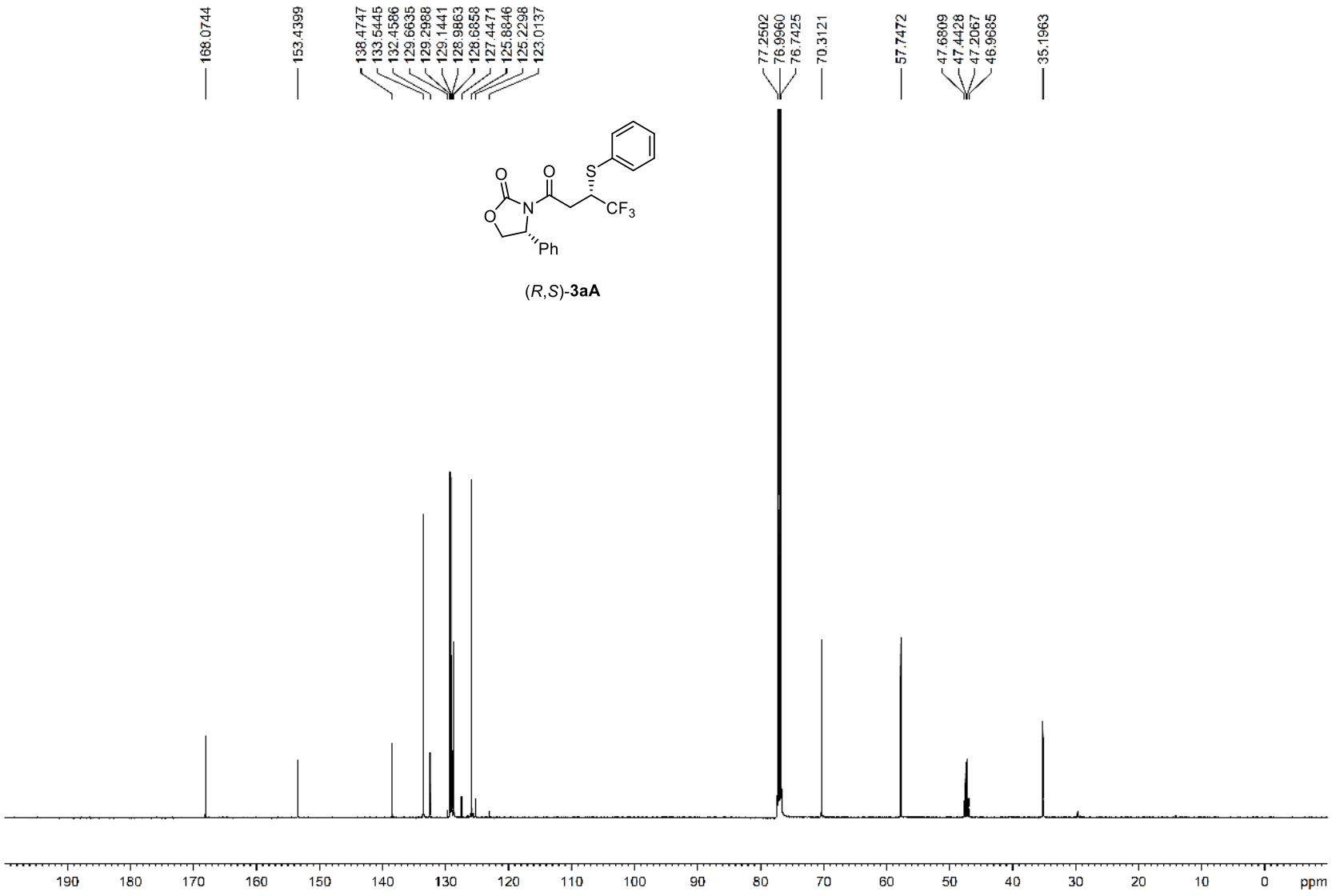
[3] Dong, X-O.; Fang, X.; Wang, C-J. *Org. Lett*. **2011**, *13*, 4426─4429

[4] Sani, M.; Candiani, G.; Pecker, F.; Malpezzia, L.; Zanda, M. *Tetrahedron Letters* **2005**, *46*, 2393–2396.

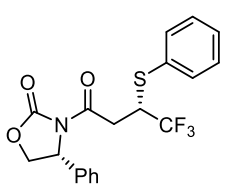
$^{1}$H NMR Spectrum of (*R*,*S*)-**3aA** (400 MHz, $CDCl_3$)



$^{13}$C NMR Spectrum of (*R*,*S*)-**3aA** (125 MHz, $CDCl_3$)

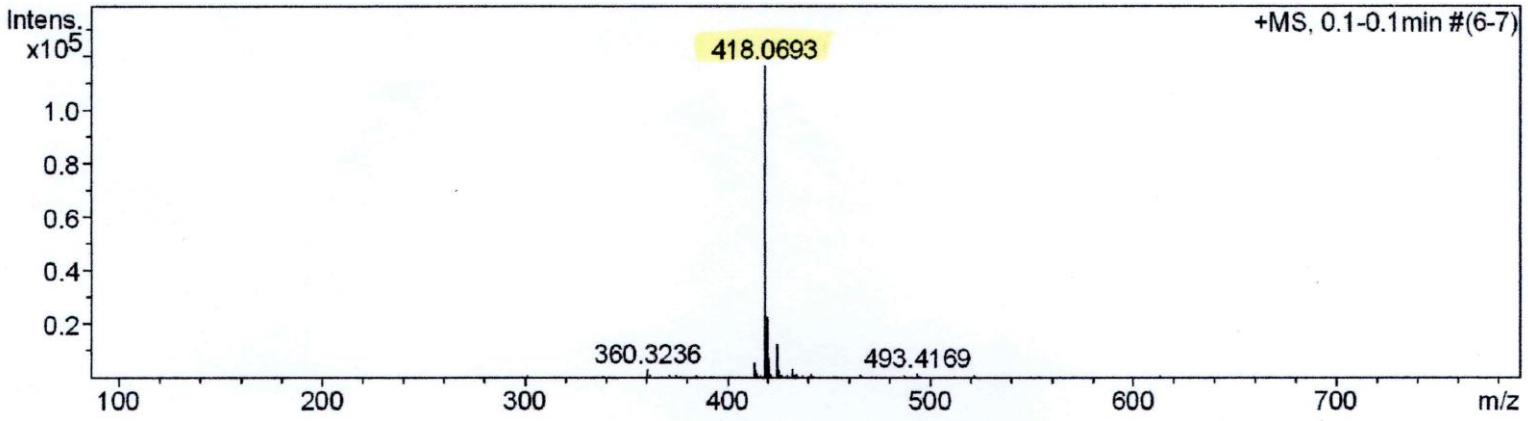


$^{19}$F NMR Spectrum of (*R*,*S*)-**3aA** (470 MHz, $CDCl_3$)




(*R*,*S*)-**3aA**

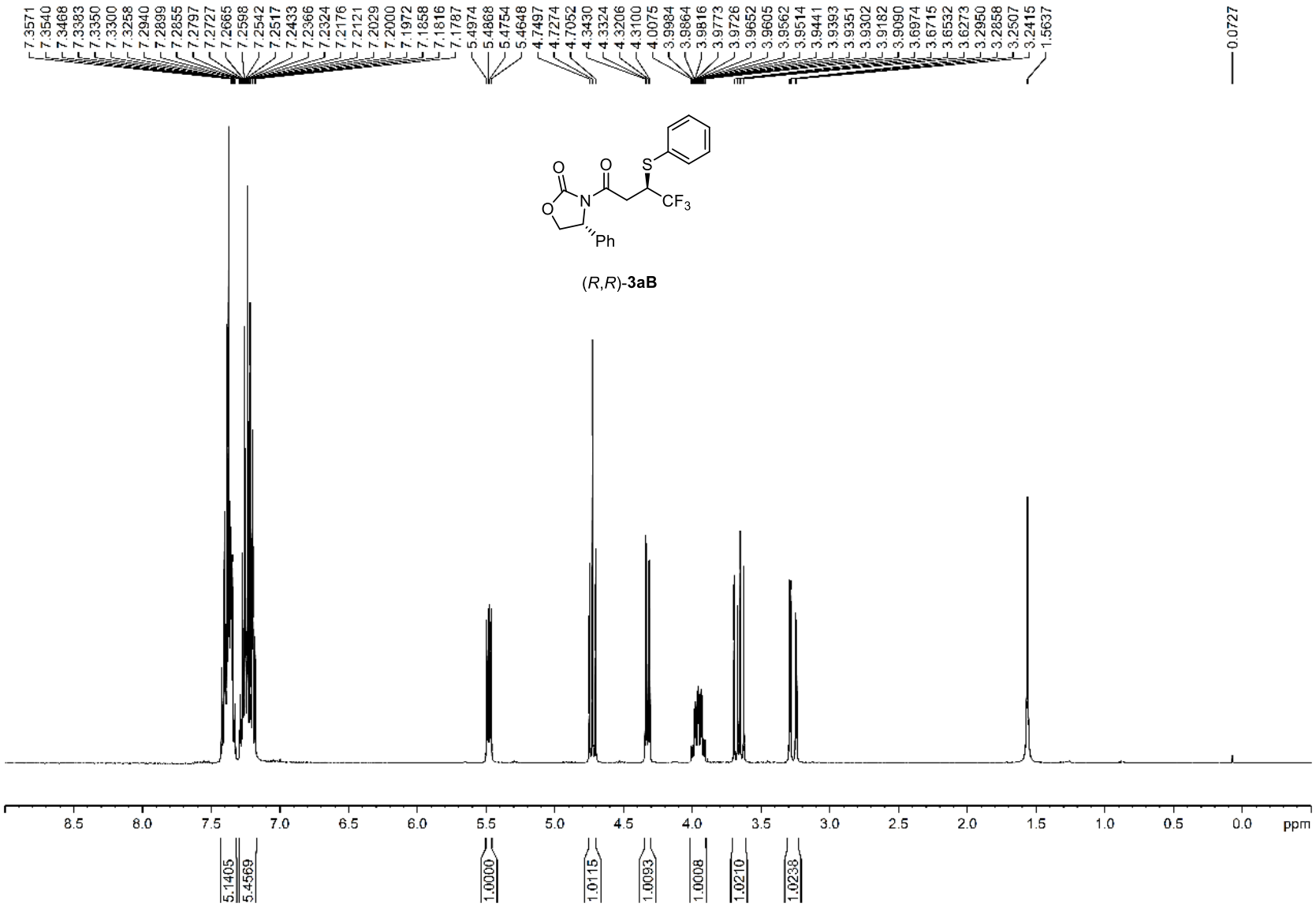
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3aA**



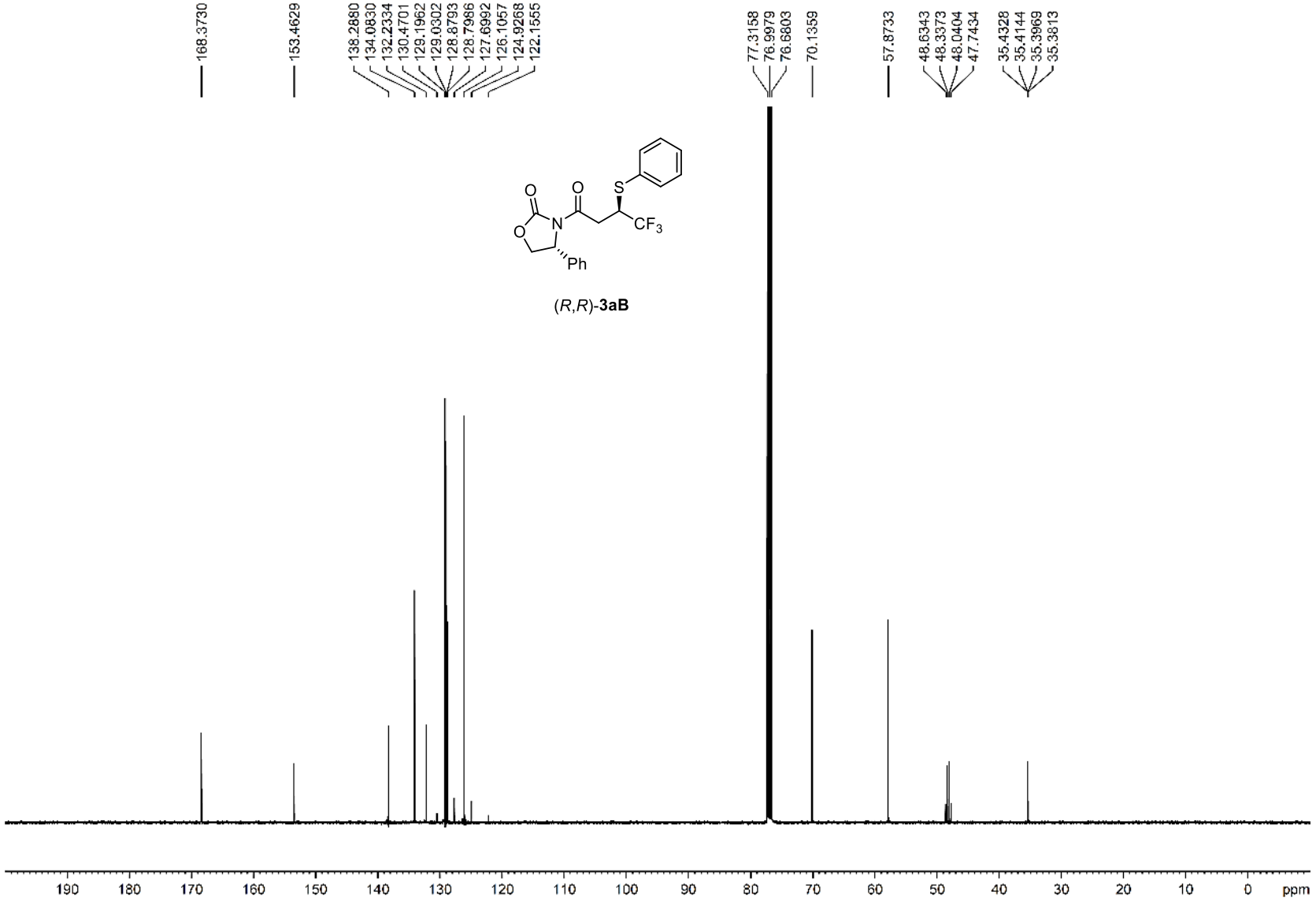

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.8300 w/v% |
| Factor | 1.0000 |
| Blank | -0.0018 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -61.3735 |
| S.D. | 1.6533 |
| C.V. | -2.6938 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 624( 1/ 5) | -62.651 | 25.0 |
| 2 | 624( 2/ 5) | -59.639 | 25.0 |
| 3 | 624( 3/ 5) | -59.639 | 25.0 |
| 4 | 624( 4/ 5) | -63.133 | 25.0 |
| 5 | 624( 5/ 5) | -61.807 | 25.0 |

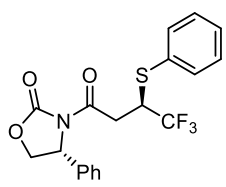
$^1$H NMR Spectrum of (*R*,*R*)-**3aB** (400 MHz, $CDCl_3$)



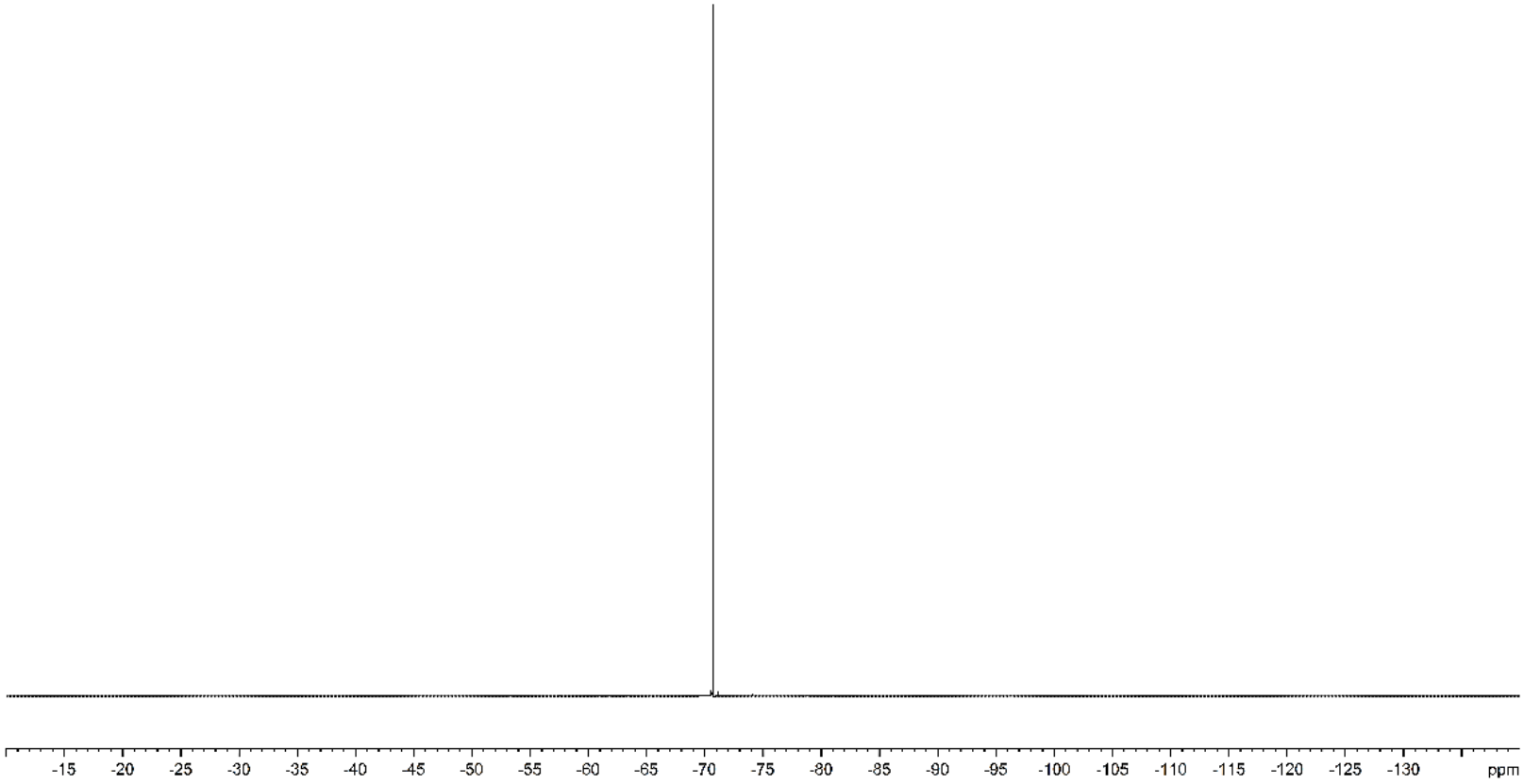
$^{13}$C NMR Spectrum of (*R*,*R*)-**3aB** (100 MHz, $CDCl_3$)



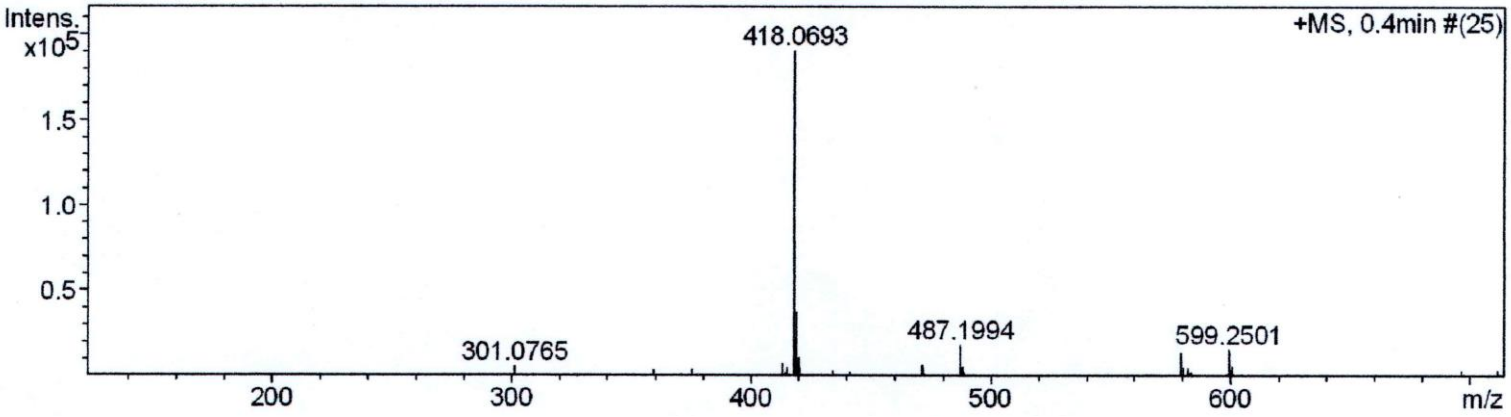
$^{19}$F NMR Spectrum of (*R*,*R*)-**3aB** (470 MHz, $CDCl_3$)




(*R*,*R*)-**3aB**



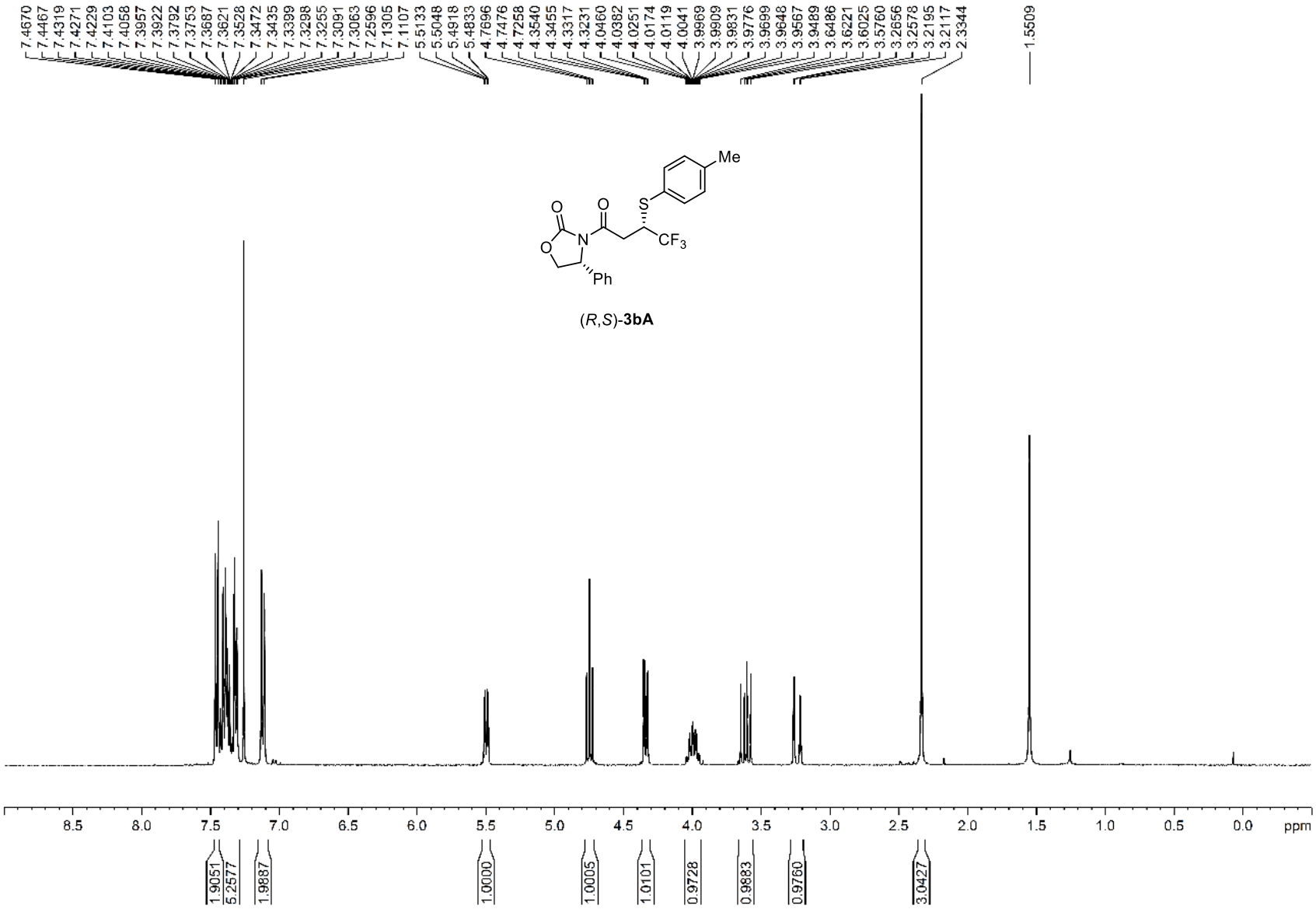
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3aB**



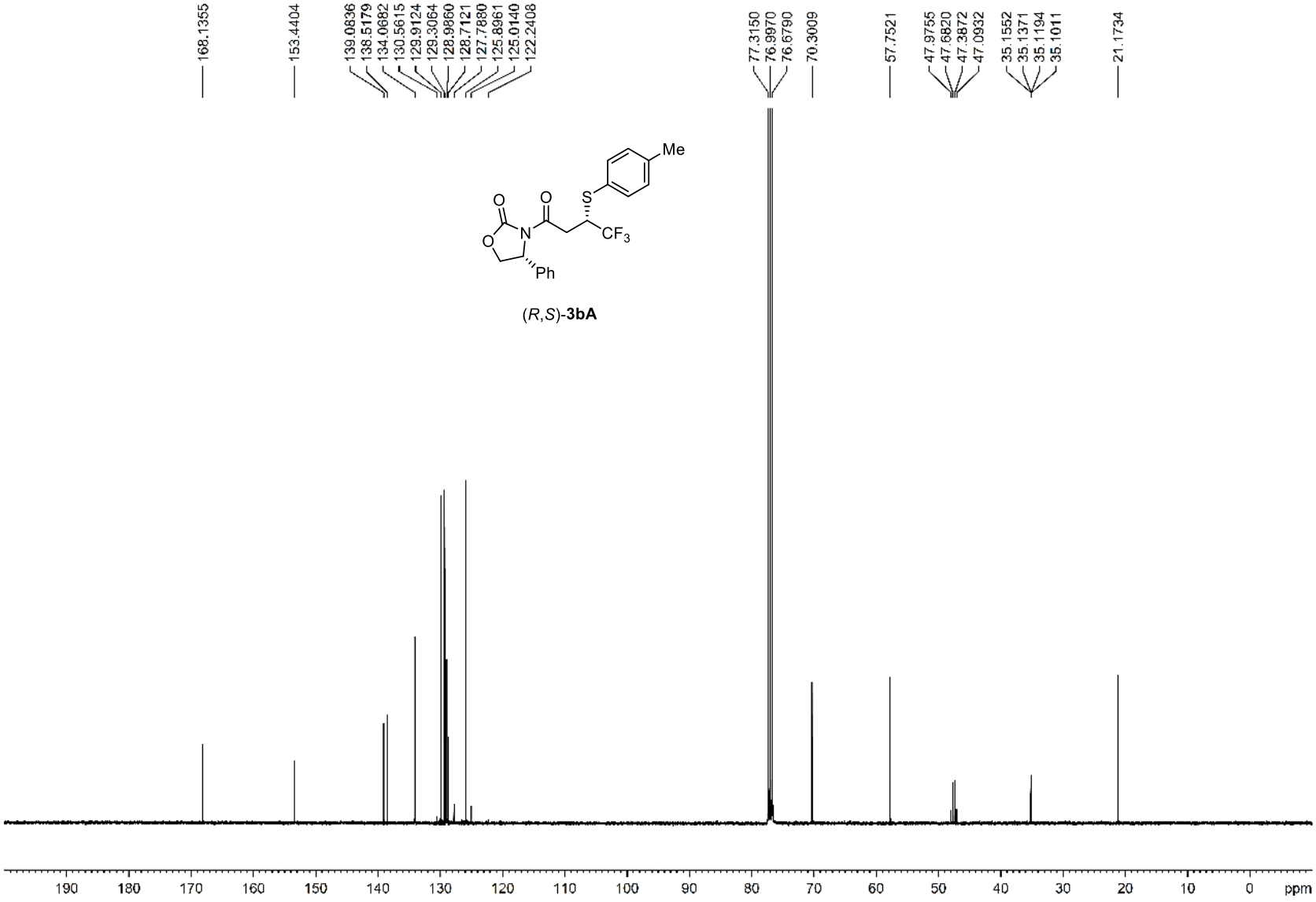

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.7100 w/v% |
| Factor | 1.0000 |
| Blank | -0.0018 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -110.0845 |
| S.D. | 0.8830 |
| C.V. | -0.8021 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 625( 1/ 5) | -110.845 | 24.6 |
| 2 | 625( 2/ 5) | -109.577 | 24.6 |
| 3 | 625( 3/ 5) | -110.986 | 24.6 |
| 4 | 625( 4/ 5) | -110.141 | 24.6 |
| 5 | 625( 5/ 5) | -108.873 | 24.6 |

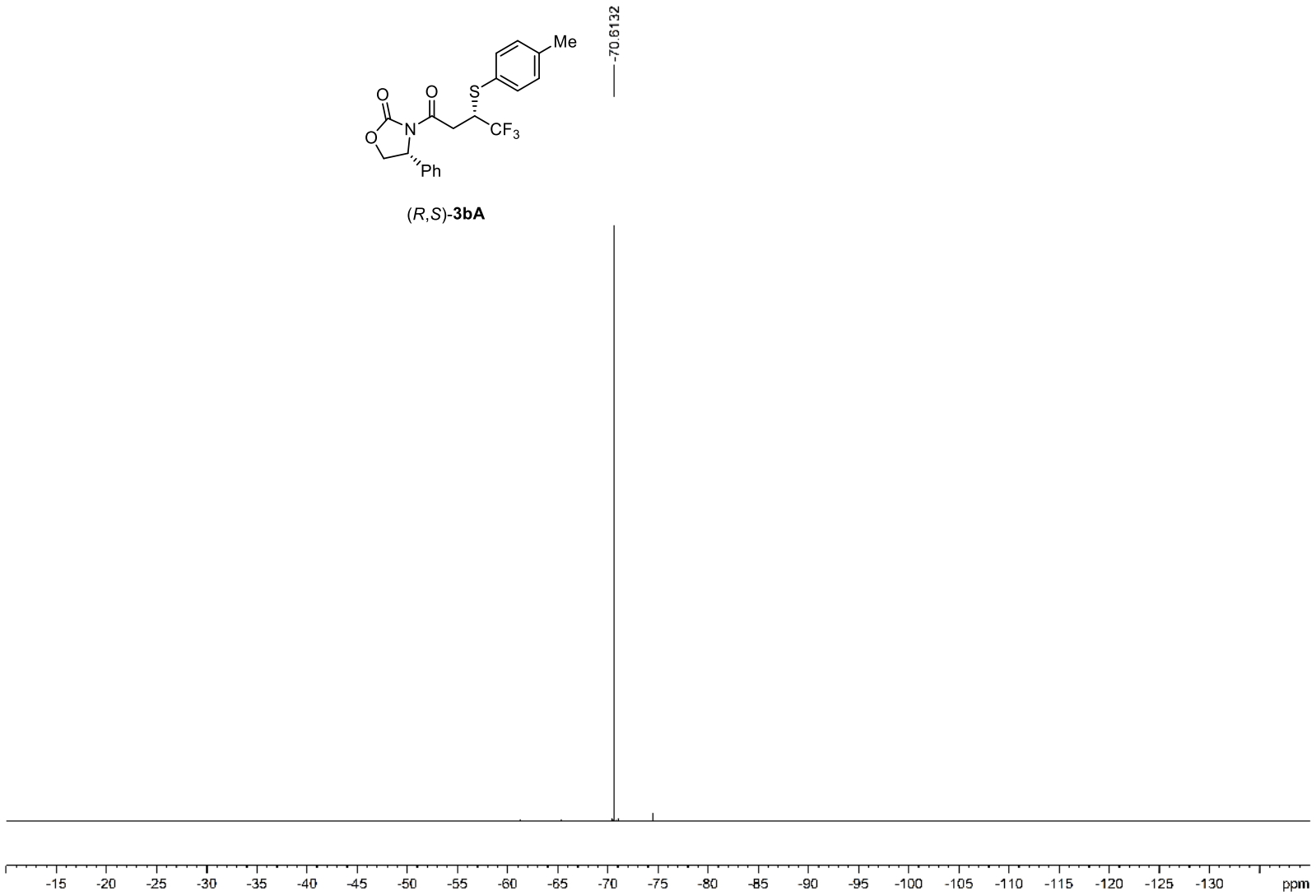
$^1$H NMR Spectrum of (*R*,*S*)-**3bA** (400 MHz, $CDCl_3$)



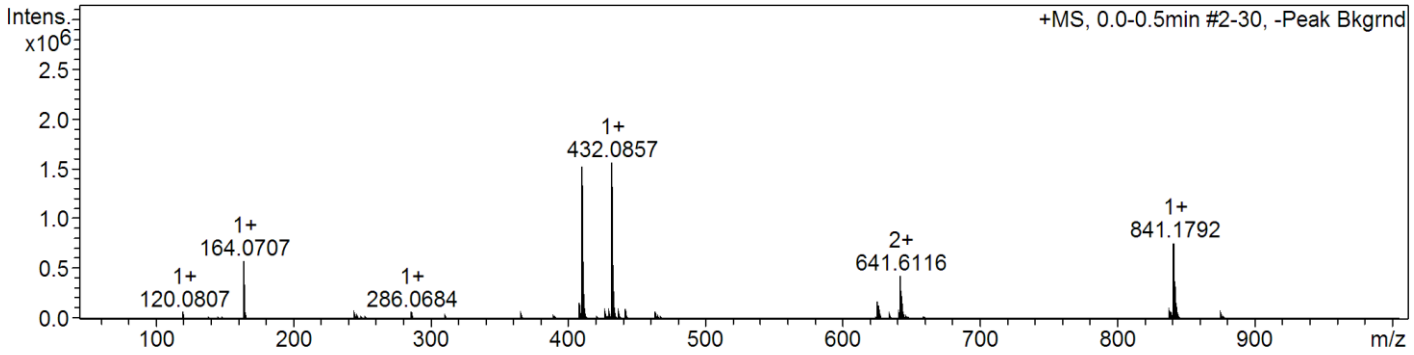
$^{13}$C NMR Spectrum of (*R*,*S*)-**3bA** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3bA** (470 MHz, $CDCl_3$)



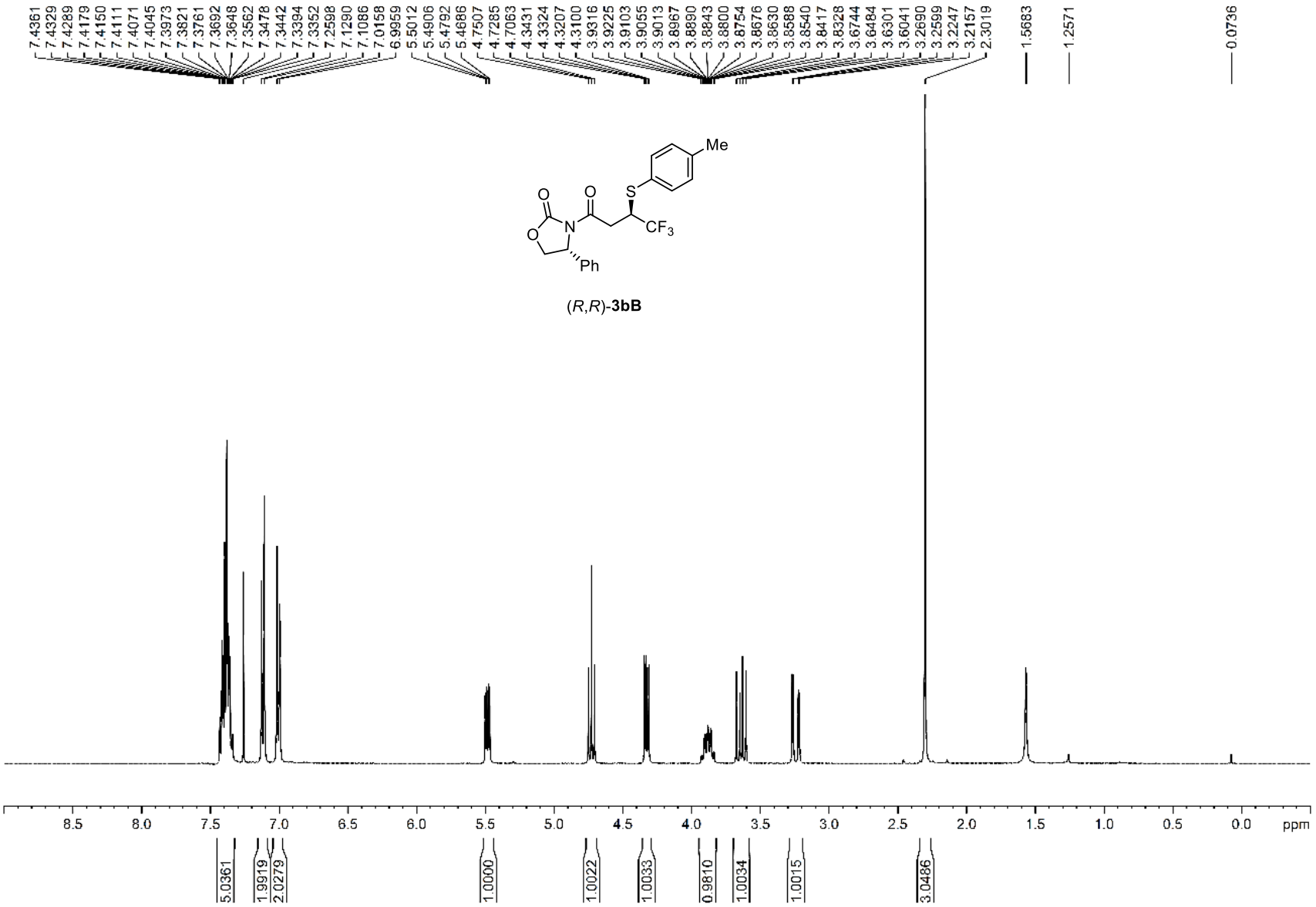
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3bA**




| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.8500 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -58.0973 |
| S.D. | 0.6468 |
| C.V. | -1.1134 % |

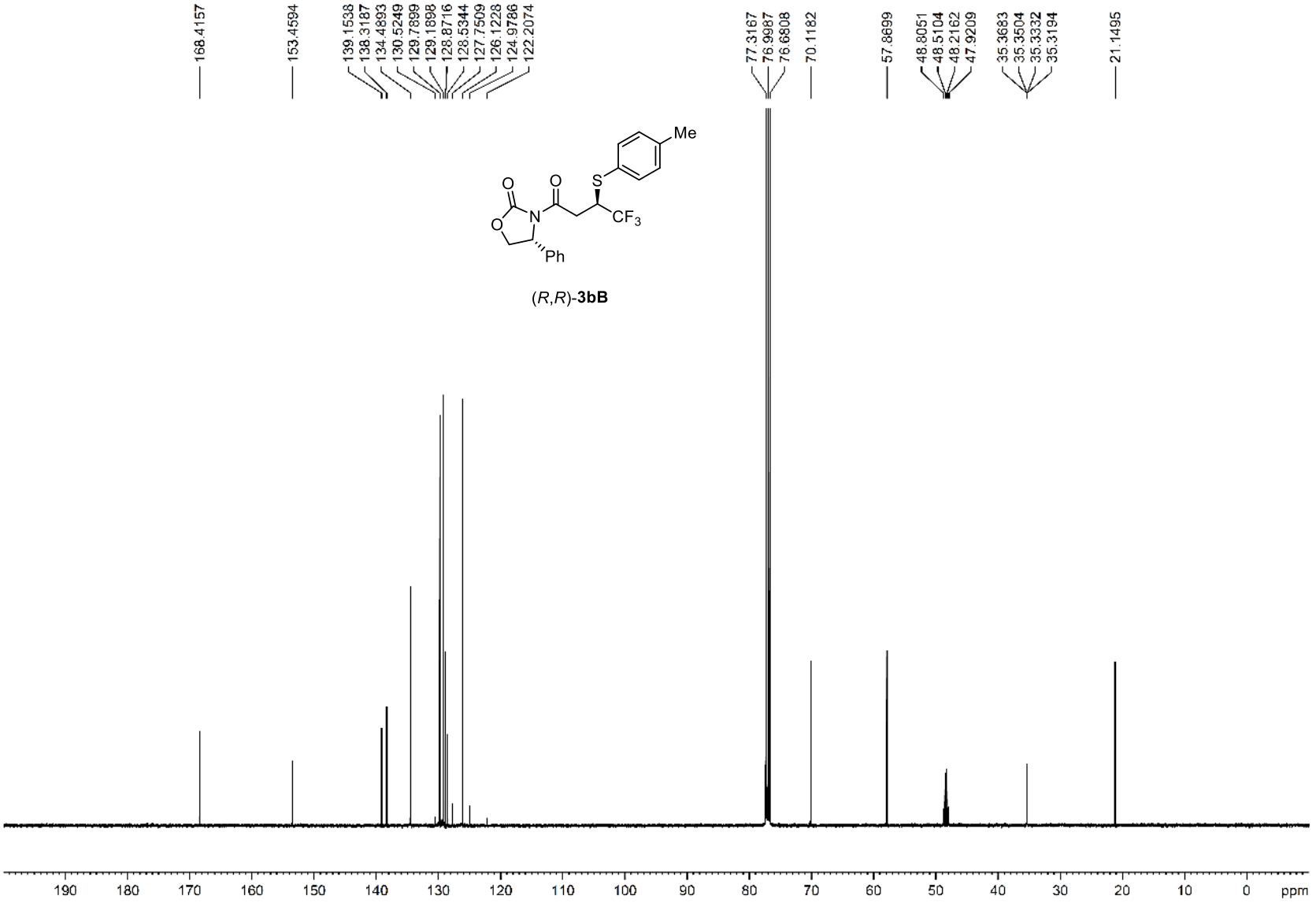
| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 110( 1/ 5) | -57.946 | 25.4 |
| 2 | 110( 2/ 5) | -58.432 | 25.4 |
| 3 | 110( 3/ 5) | -58.541 | 25.3 |
| 4 | 110( 4/ 5) | -57.027 | 25.3 |
| 5 | 110( 5/ 5) | -58.541 | 25.3 |

$^1$H NMR Spectrum of (*R*,*R*)-**3bB** (400 MHz, $CDCl_3$)

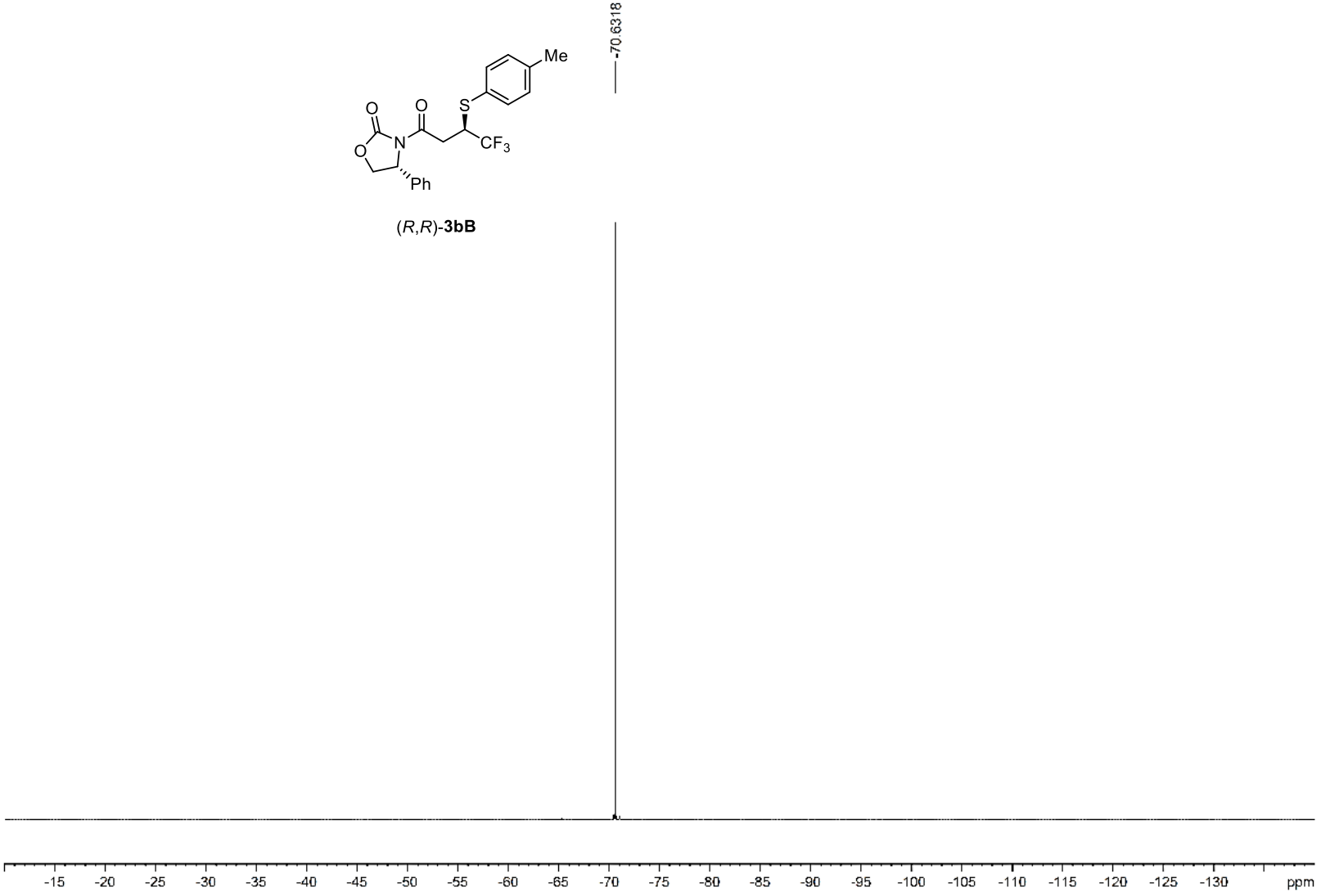



(*R*,*R*)-**3bB**

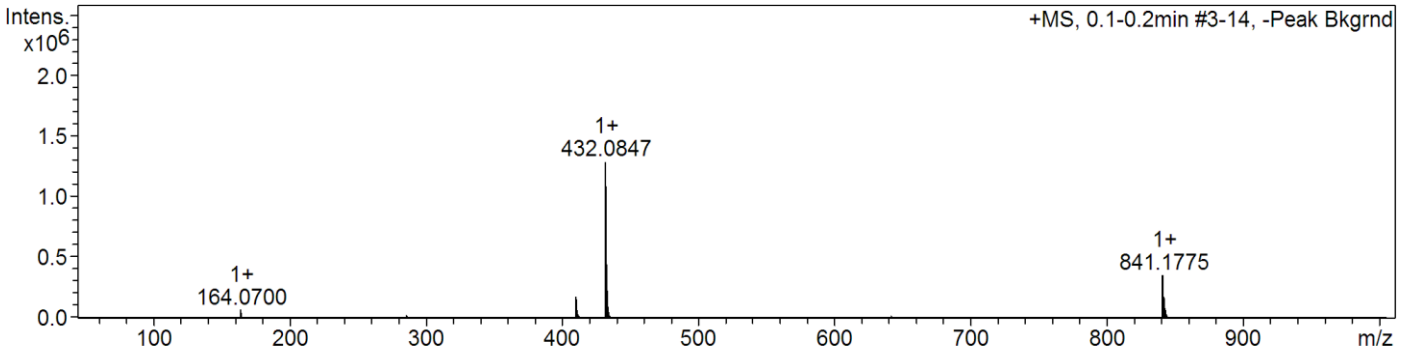
$^{13}$C NMR Spectrum of (*R*,*R*)-**3bB** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3bB** (470 MHz, $CDCl_3$)



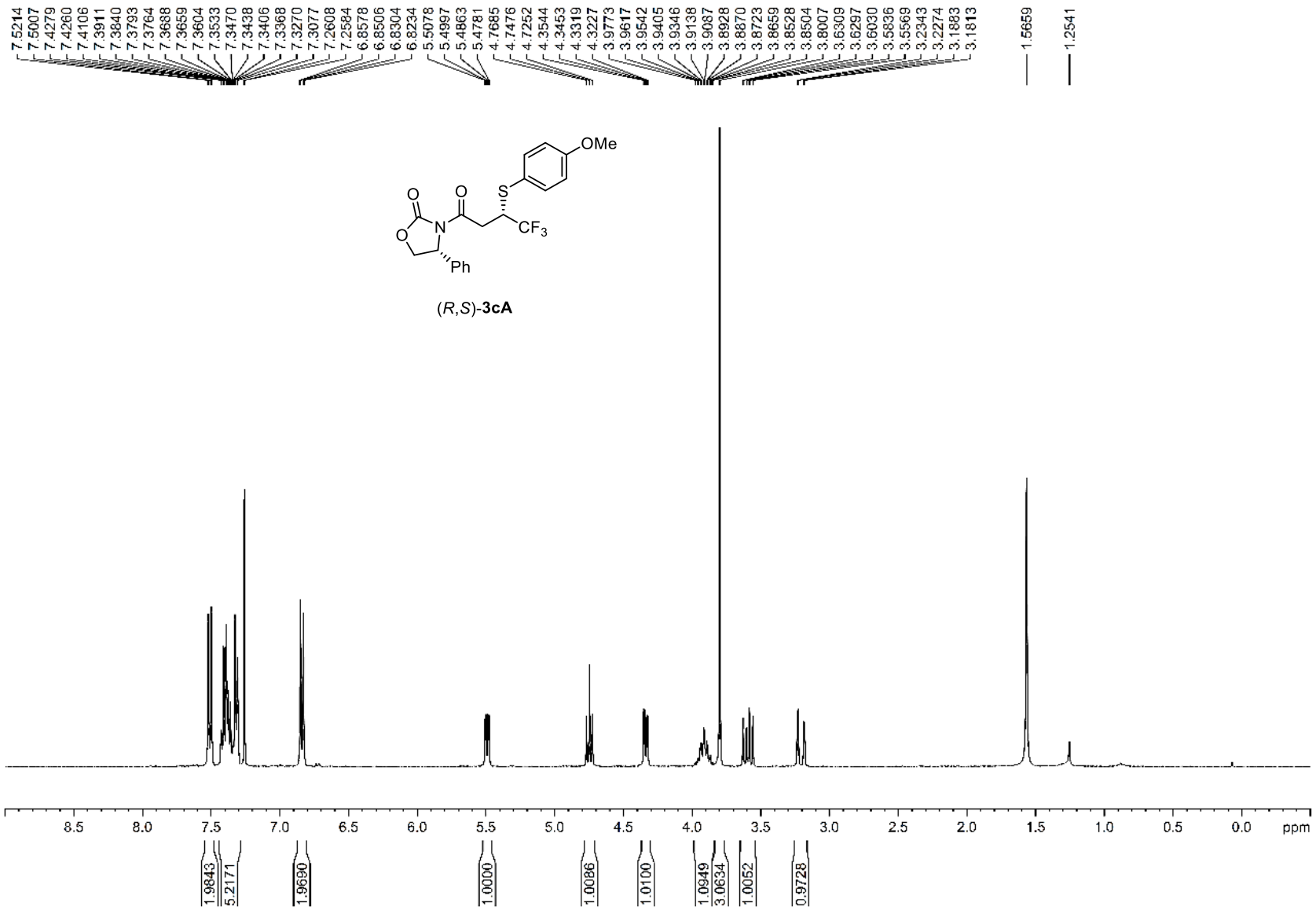
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3bB**



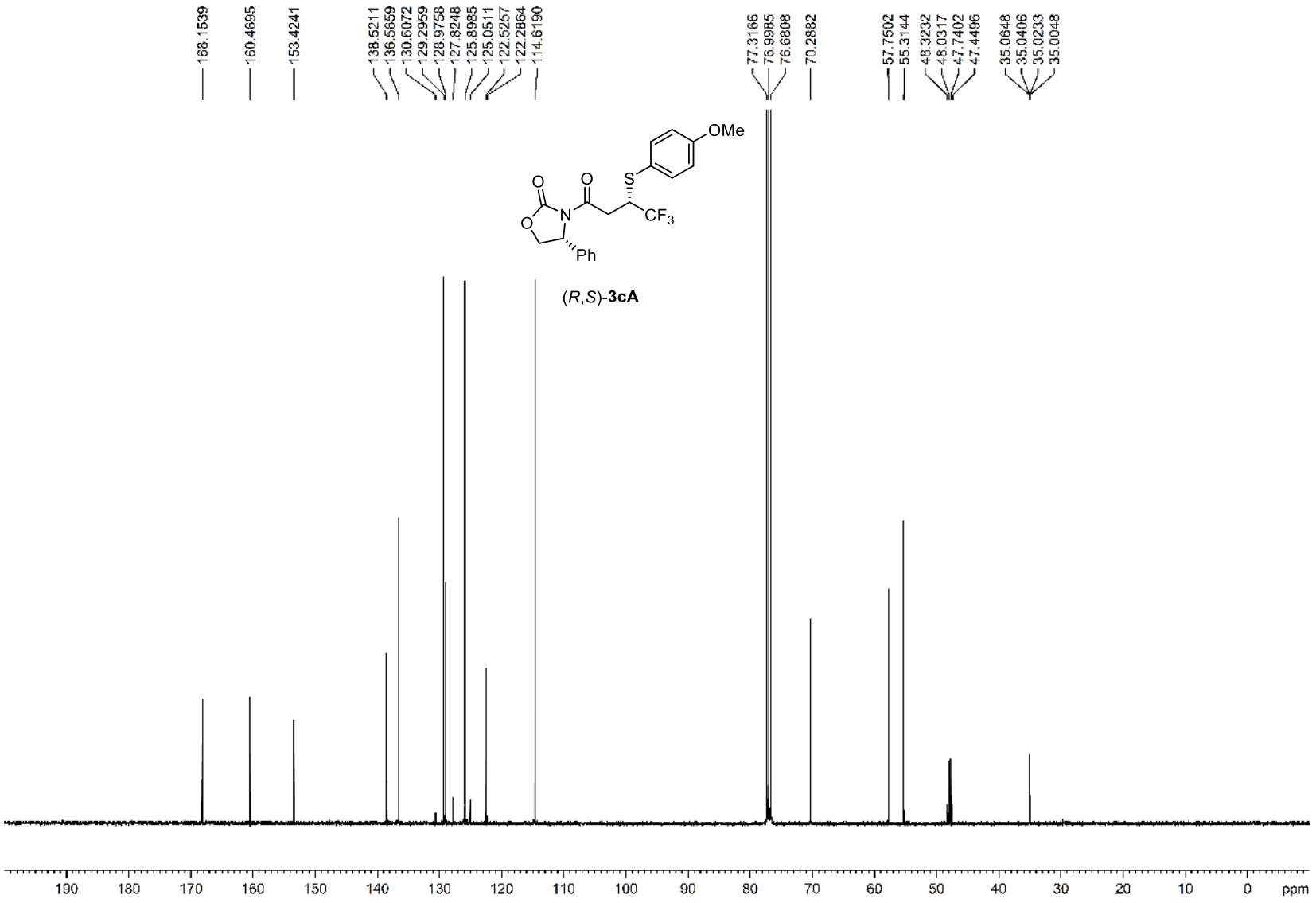

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0333 w/v% |
| Factor | 1.0000 |
| Blank | -0.0007 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -115.1069 |
| S.D. | 0.3529 |
| C.V. | -0.3066 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 3( 1/ 5) | -115.649 | 29.2 |
| 2 | 3( 2/ 5) | -115.165 | 29.2 |
| 3 | 3( 3/ 5) | -114.971 | 29.2 |
| 4 | 3( 4/ 5) | -114.681 | 29.2 |
| 5 | 3( 5/ 5) | -115.068 | 29.2 |

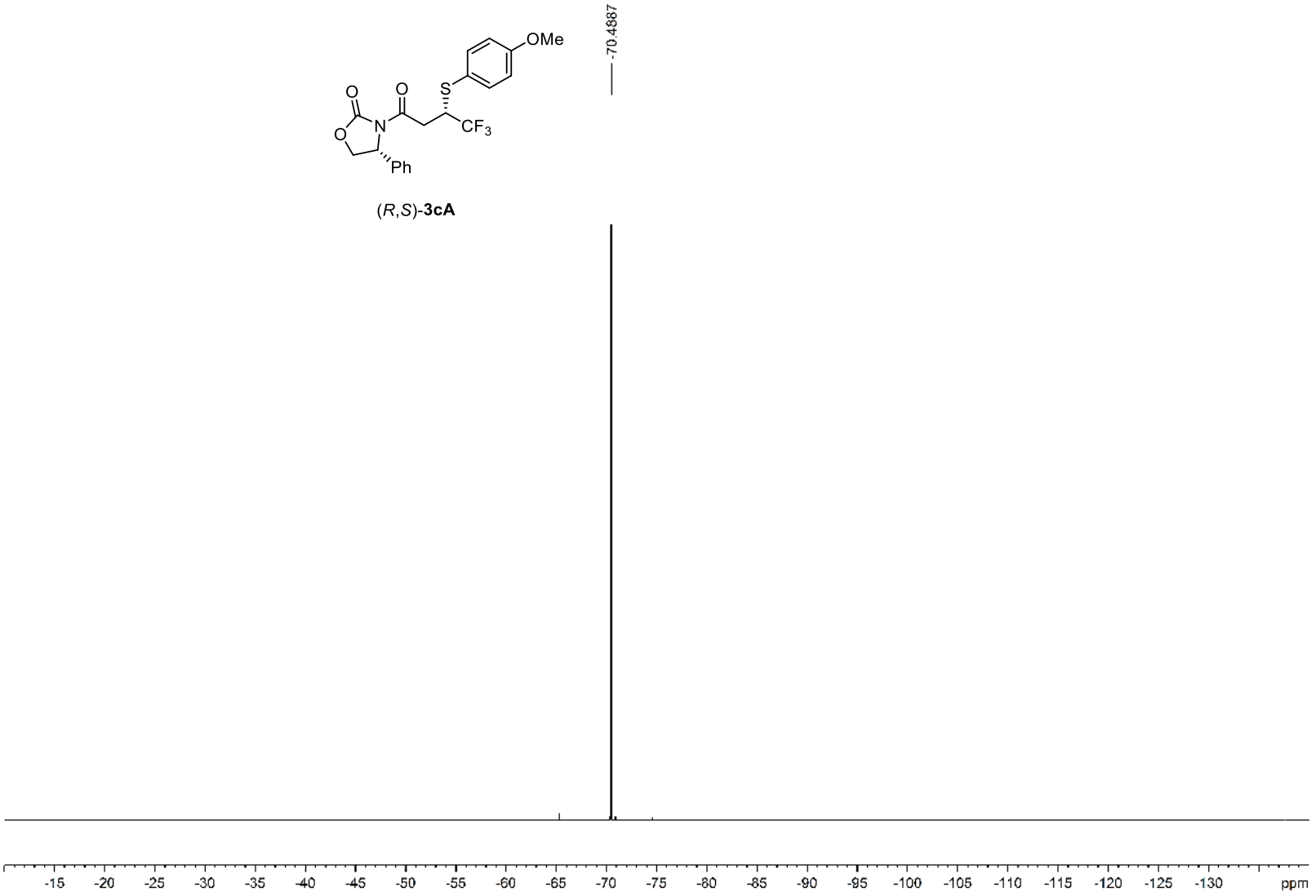
$^1$H NMR Spectrum of (*R*,*S*)-**3cA** (400 MHz, $CDCl_3$)



$^{13}$C NMR Spectrum of (*R*,*S*)-**3cA** (100 MHz, $CDCl_3$)

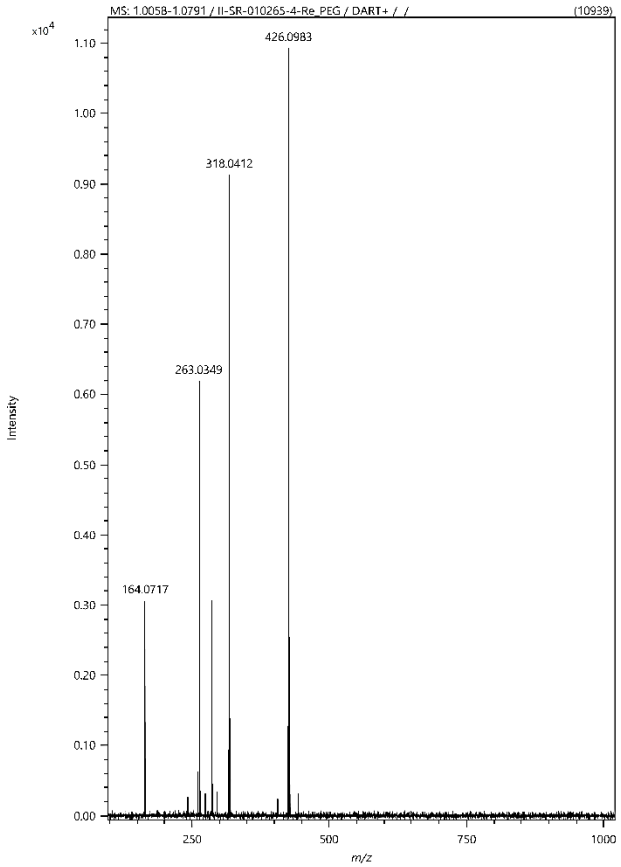


$^{19}$F NMR Spectrum of (*R*,*S*)-**3cA** (470 MHz, $CDCl_3$)




(*R*,*S*)-**3cA**

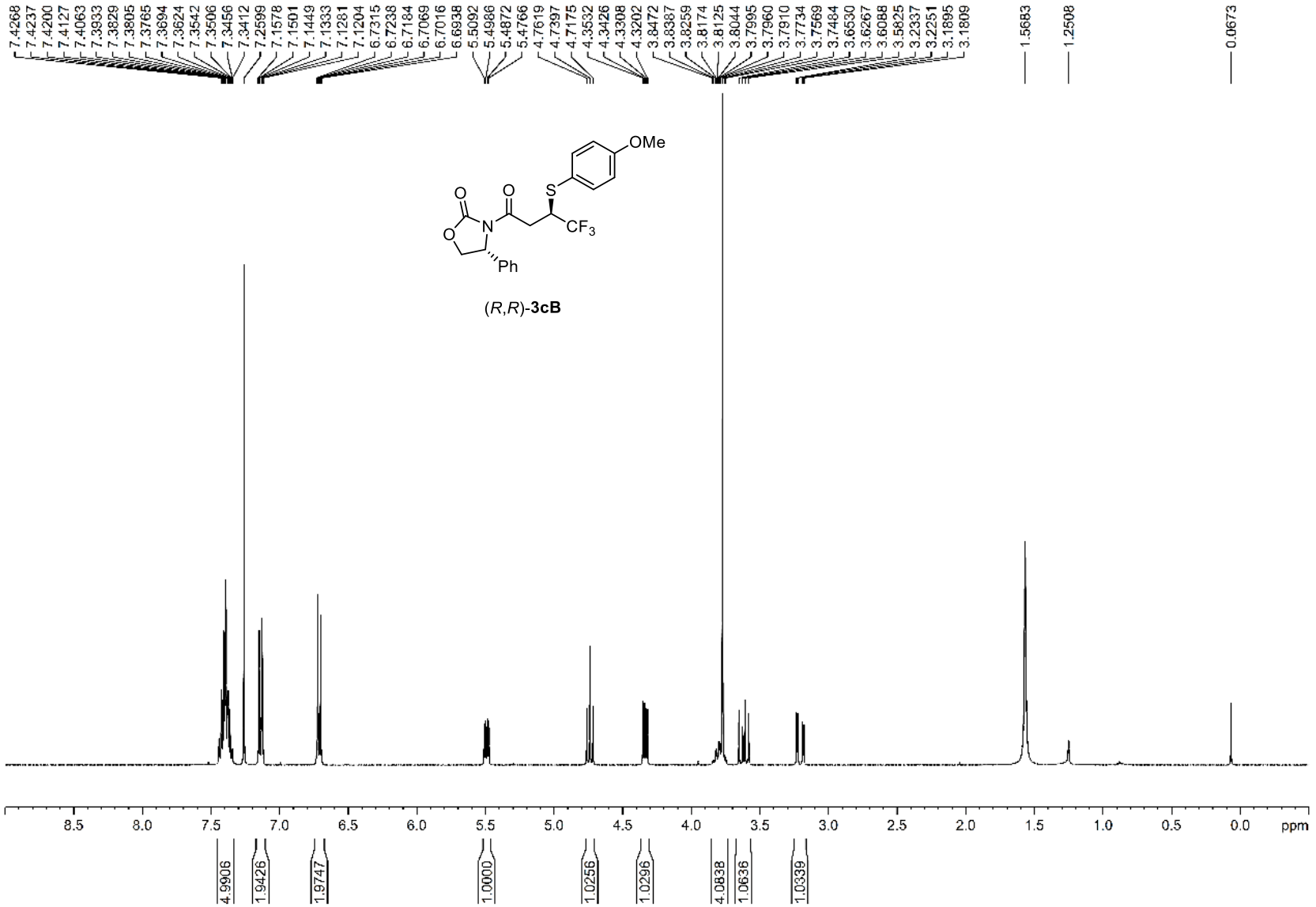
HRMS (DART) and Specific rotation of (*R*,*S*)-**3cA**



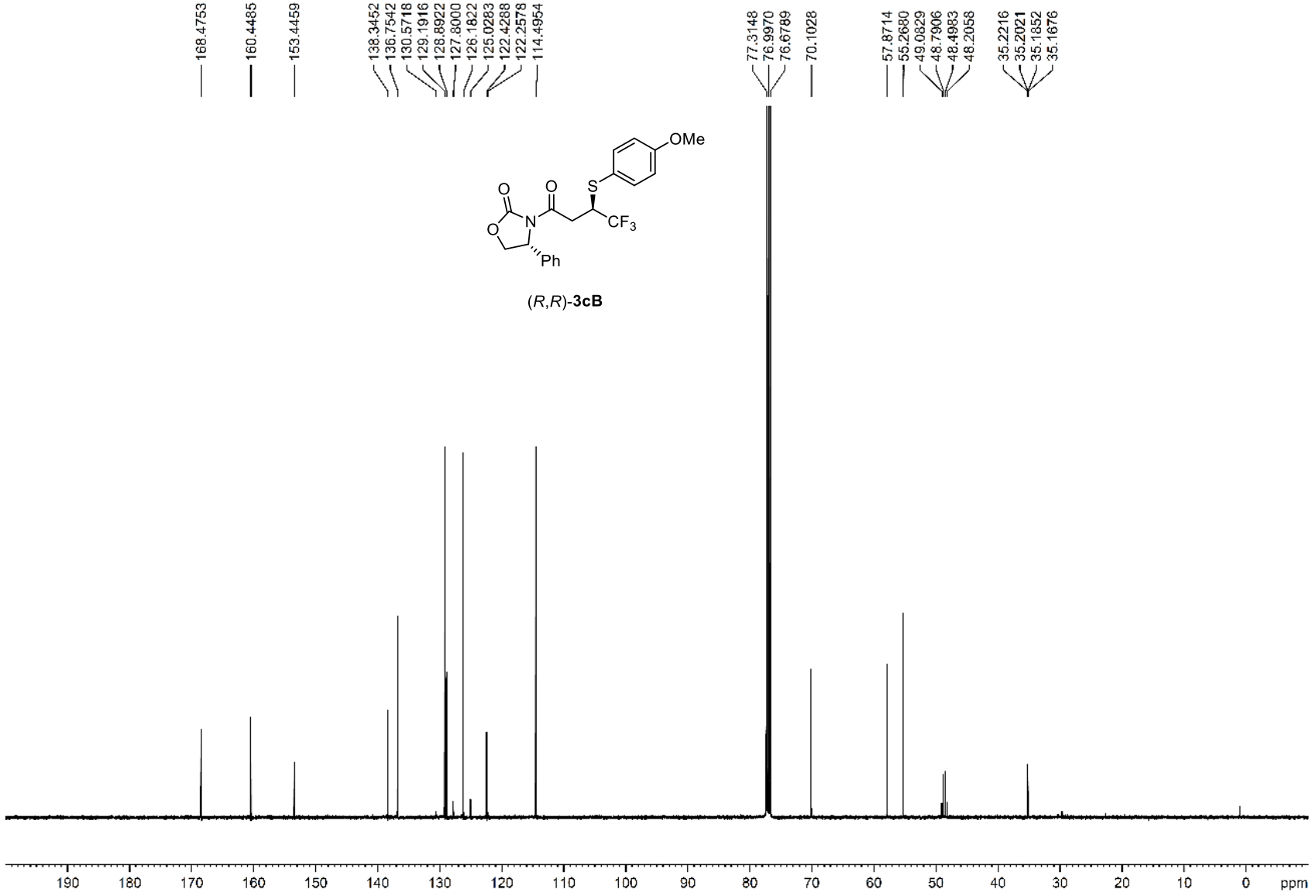

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.7700 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -68.8023 |
| S.D. | 0.5276 |
| C.V. | -0.7668 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 117( 1/ 5) | -68.362 | 25.4 |
| 2 | 117( 2/ 5) | -68.814 | 25.4 |
| 3 | 117( 3/ 5) | -69.040 | 25.4 |
| 4 | 117( 4/ 5) | -68.249 | 25.3 |
| 5 | 117( 5/ 5) | -69.548 | 25.3 |

$^1$H NMR Spectrum of (*R*,*R*)-**3cB** (400 MHz, $CDCl_3$)

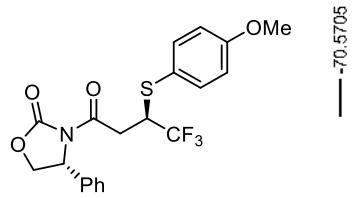


$^{13}$C NMR Spectrum of (*R*,*R*)-**3cB** (100 MHz, $CDCl_3$)

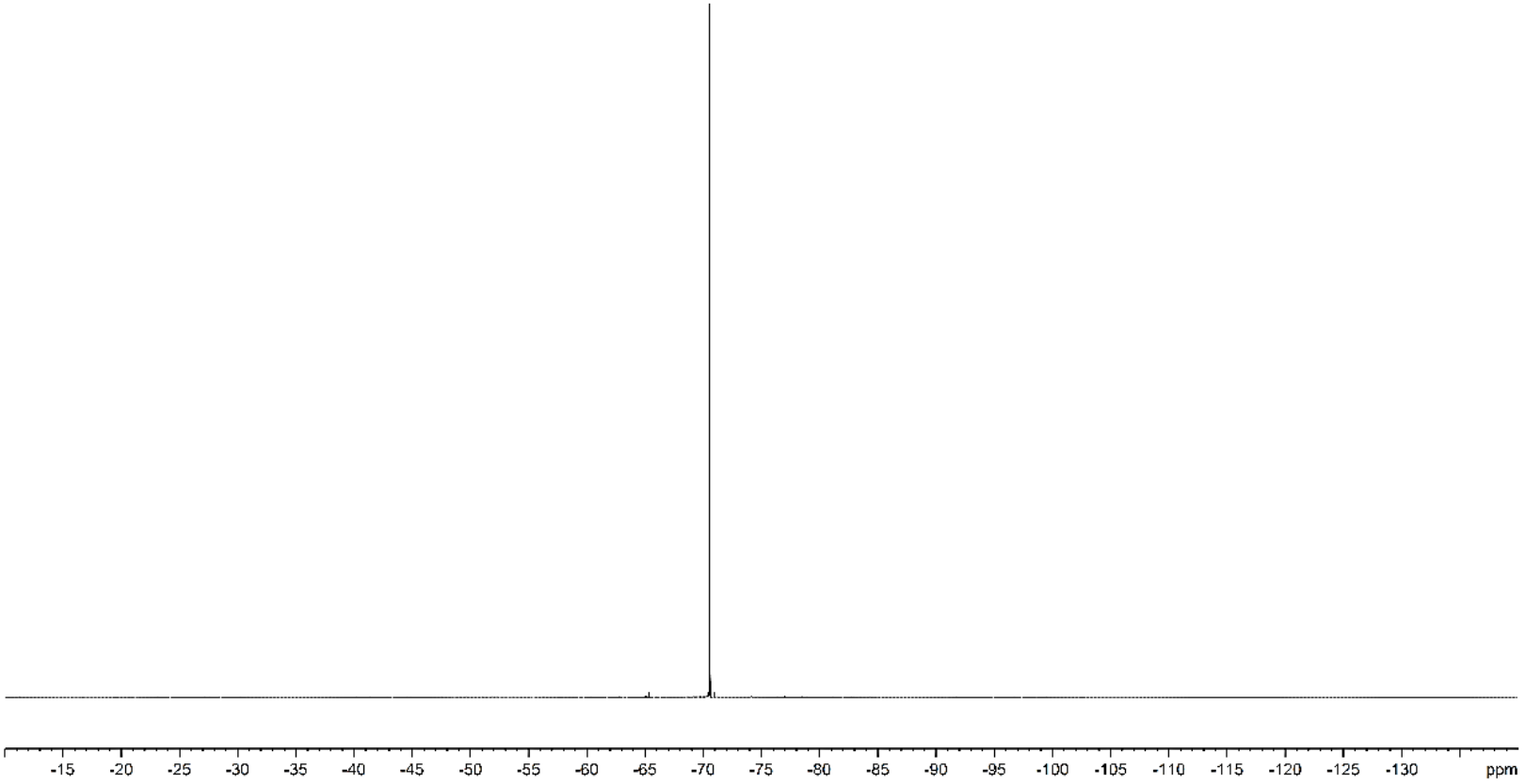



(*R*,*R*)-**3cB**

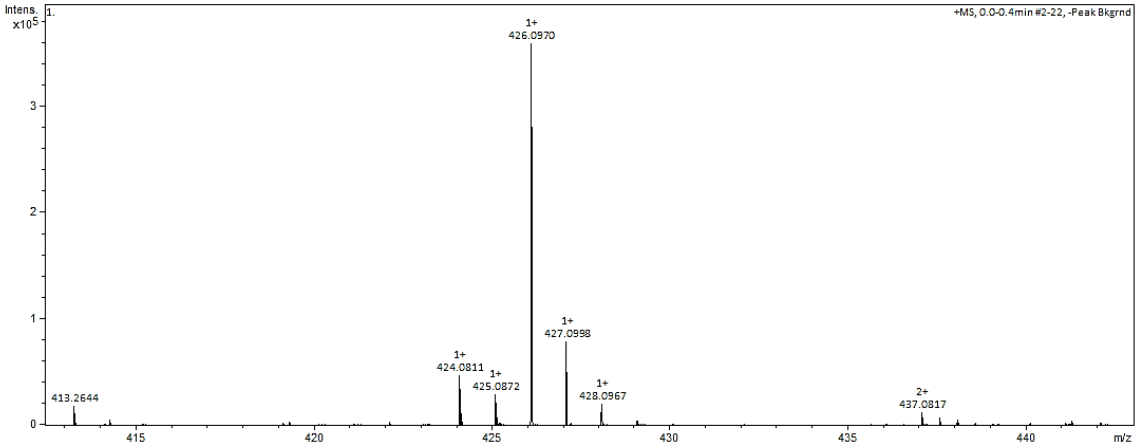
$^{19}$F NMR Spectrum of (*R*,*R*)-**3cB** (470 MHz, $CDCl_3$)




(*R*,*R*)-**3cB**



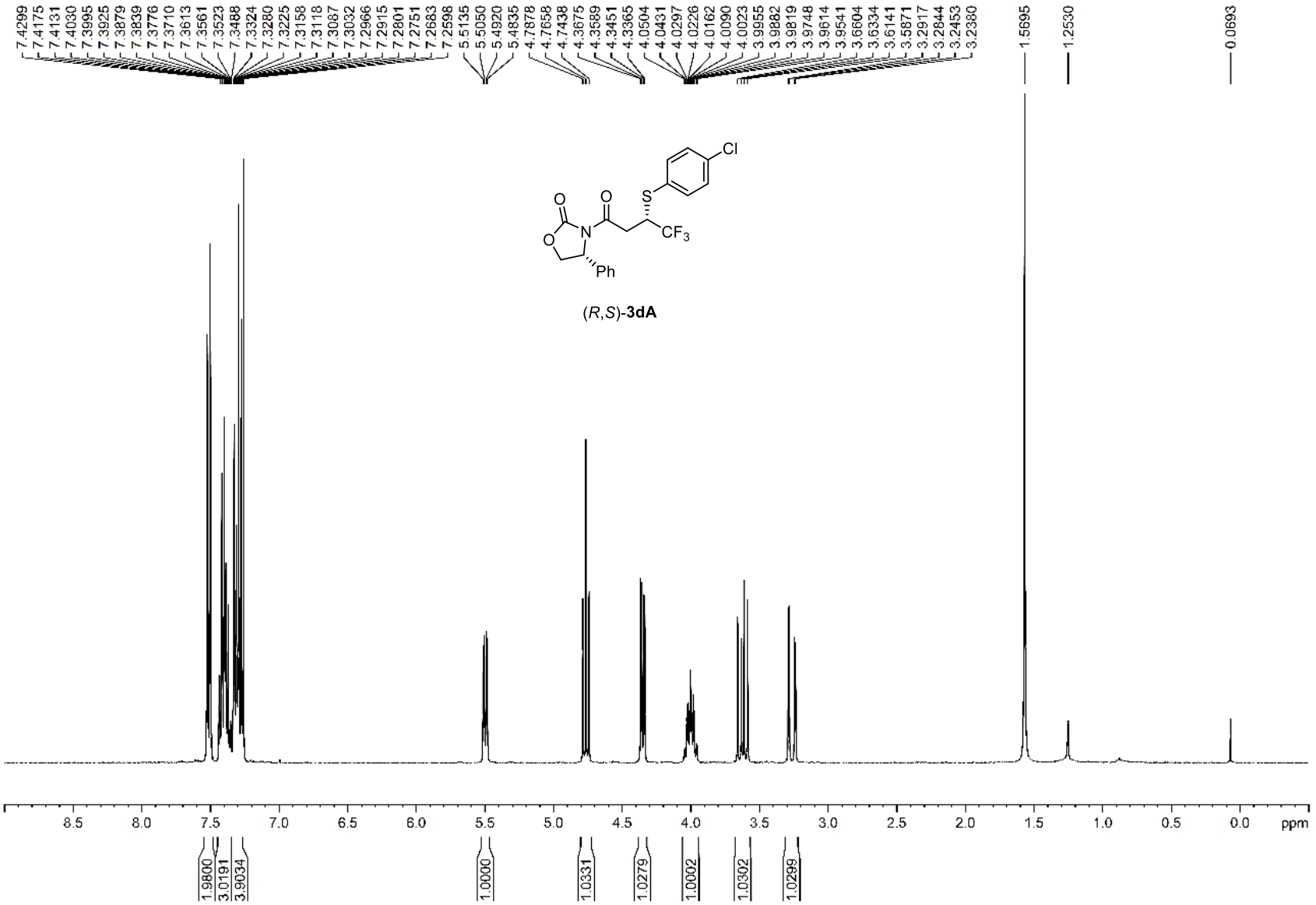
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3cB**



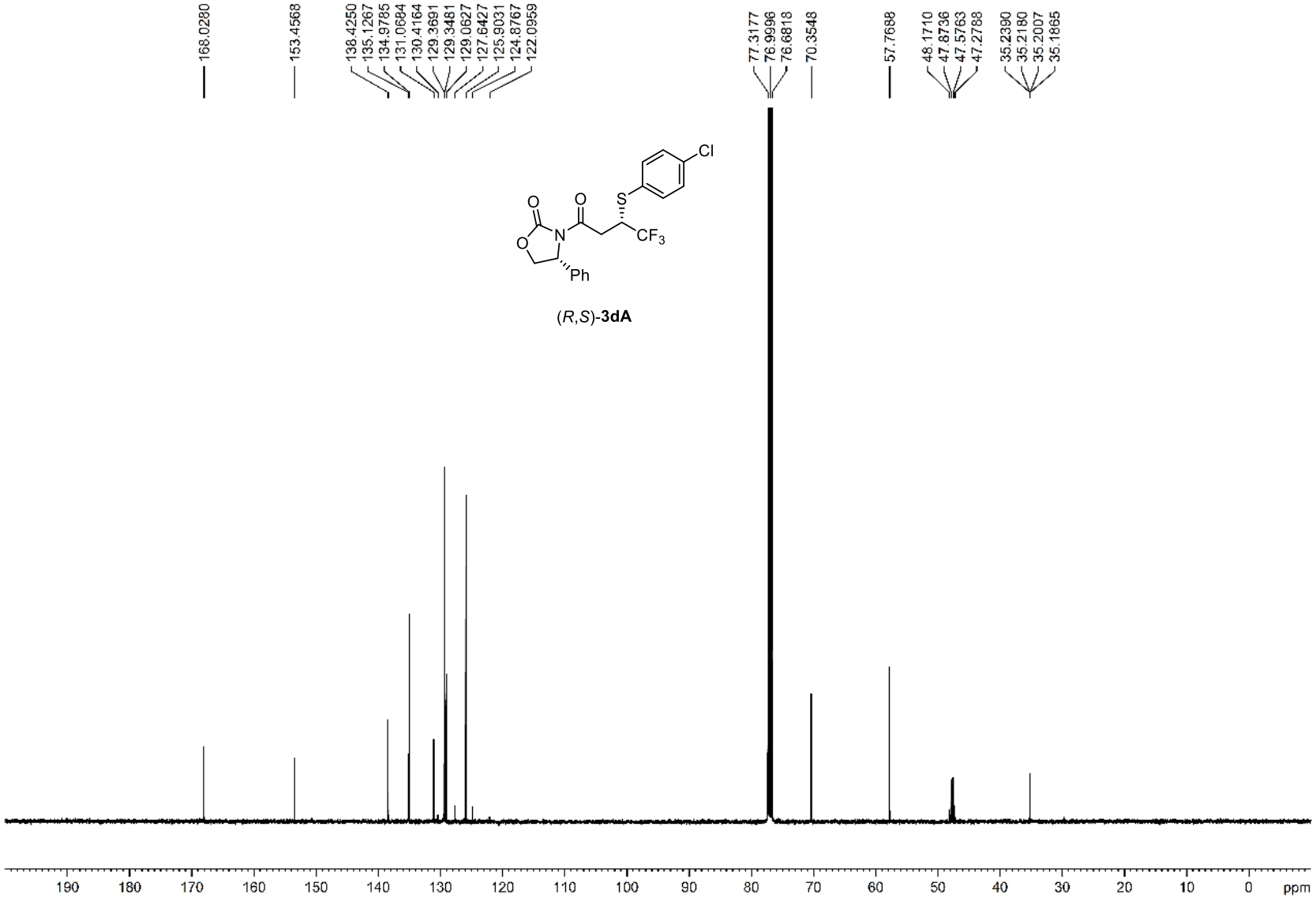

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.9650 w/v% |
| Factor | 1.0000 |
| Blank | -0.0007 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -85.7202 |
| S.D. | 0.7487 |
| C.V. | -0.8734 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 13( 1/ 5) | -84.456 | 27.5 |
| 2 | 13( 2/ 5) | -85.907 | 27.6 |
| 3 | 13( 3/ 5) | -85.699 | 27.5 |
| 4 | 13( 4/ 5) | -86.321 | 27.6 |
| 5 | 13( 5/ 5) | -86.218 | 27.5 |

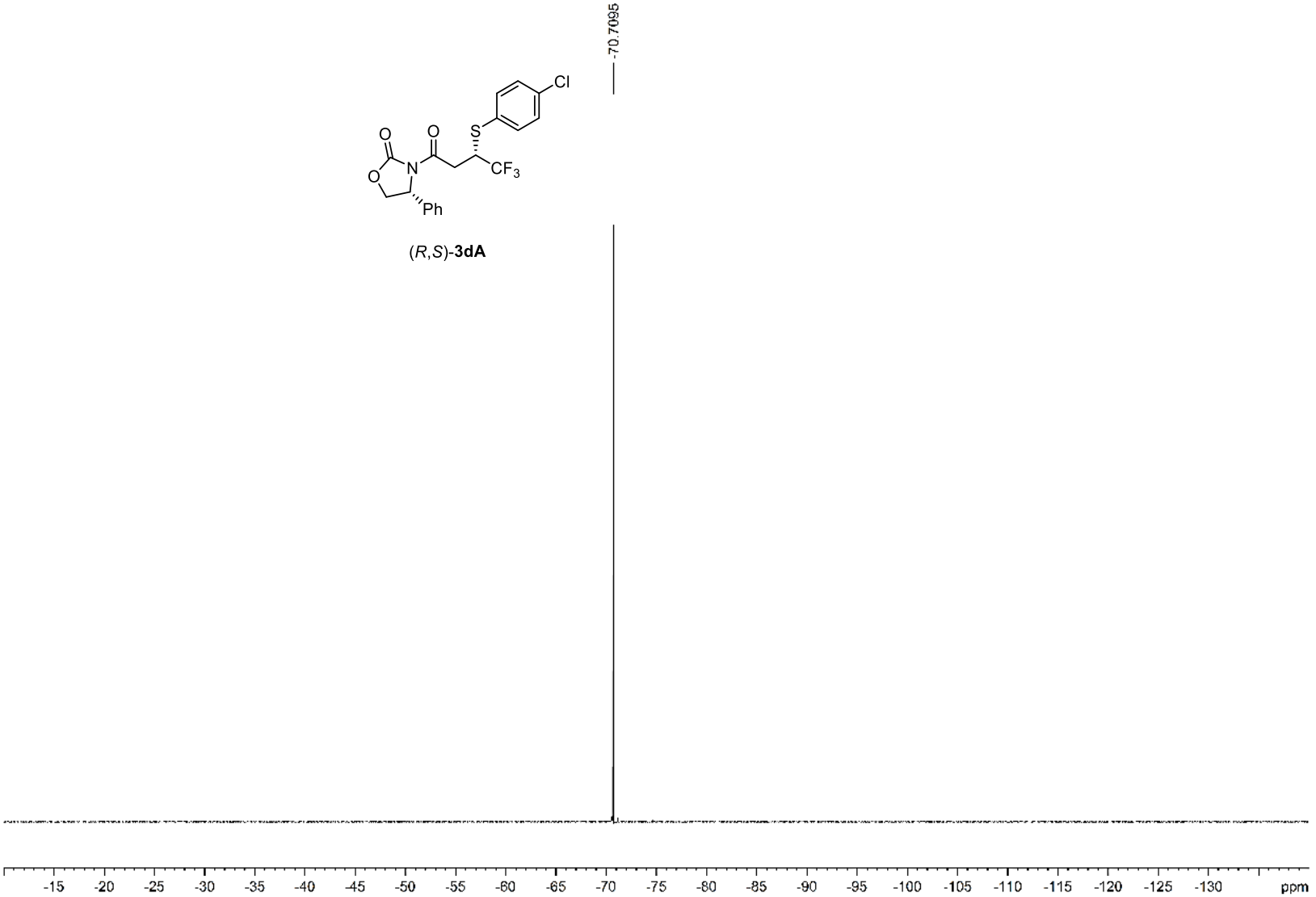
$^1$H NMR Spectrum of (*R*,*S*)-**3dA** (400 MHz, $CDCl_3$)



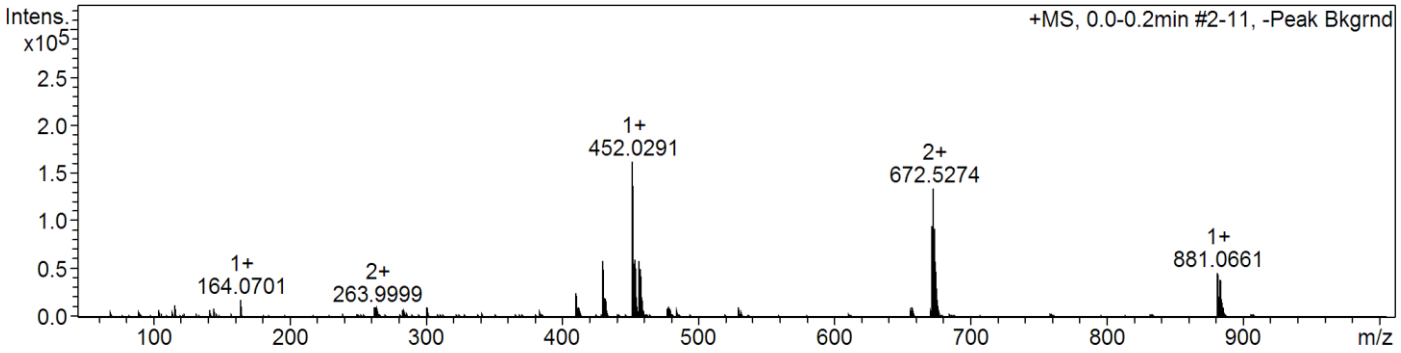
$^{13}$C NMR Spectrum of (*R*,*S*)-**3dA** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3dA** (470 MHz, $CDCl_3$)



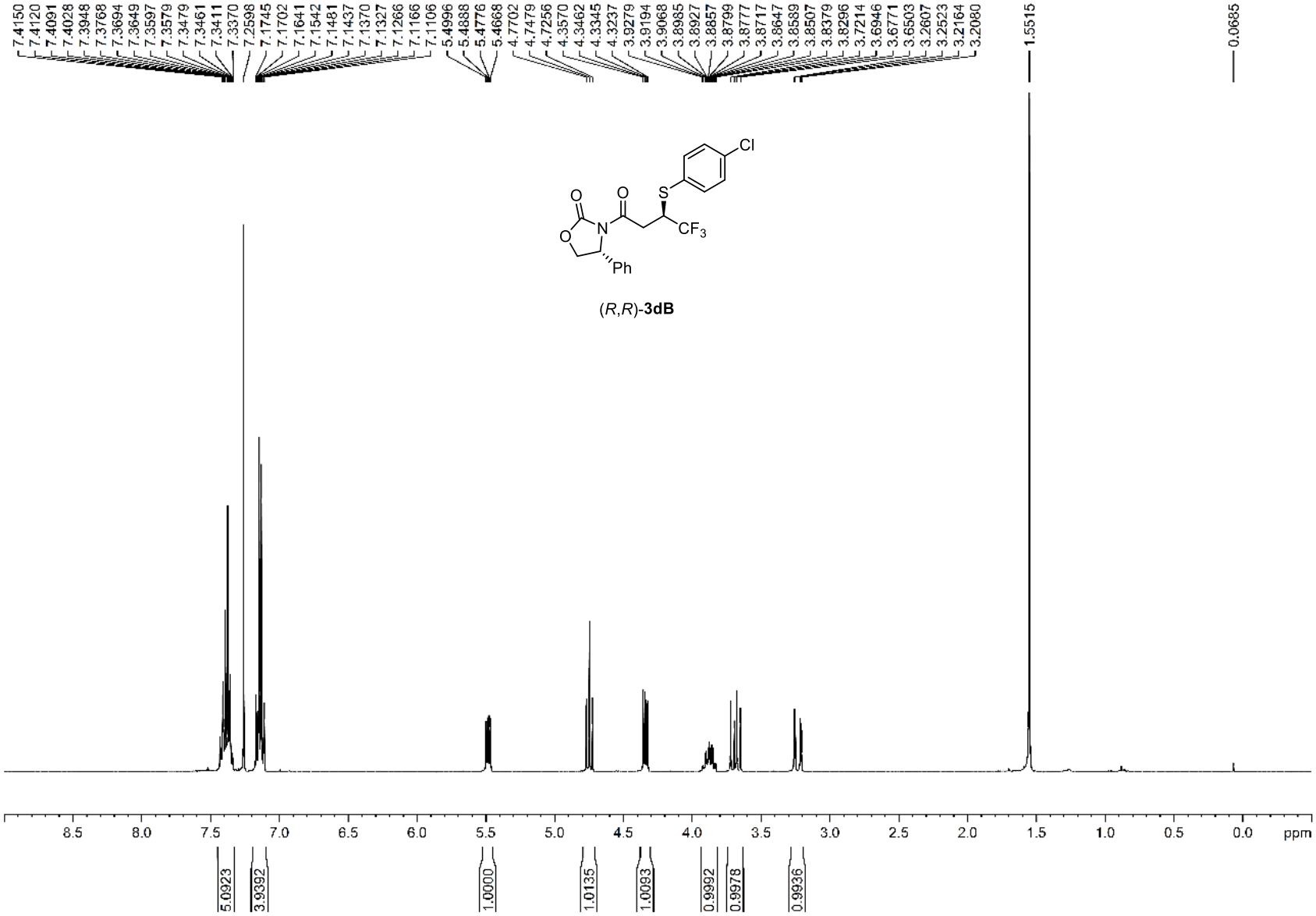
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3dA**



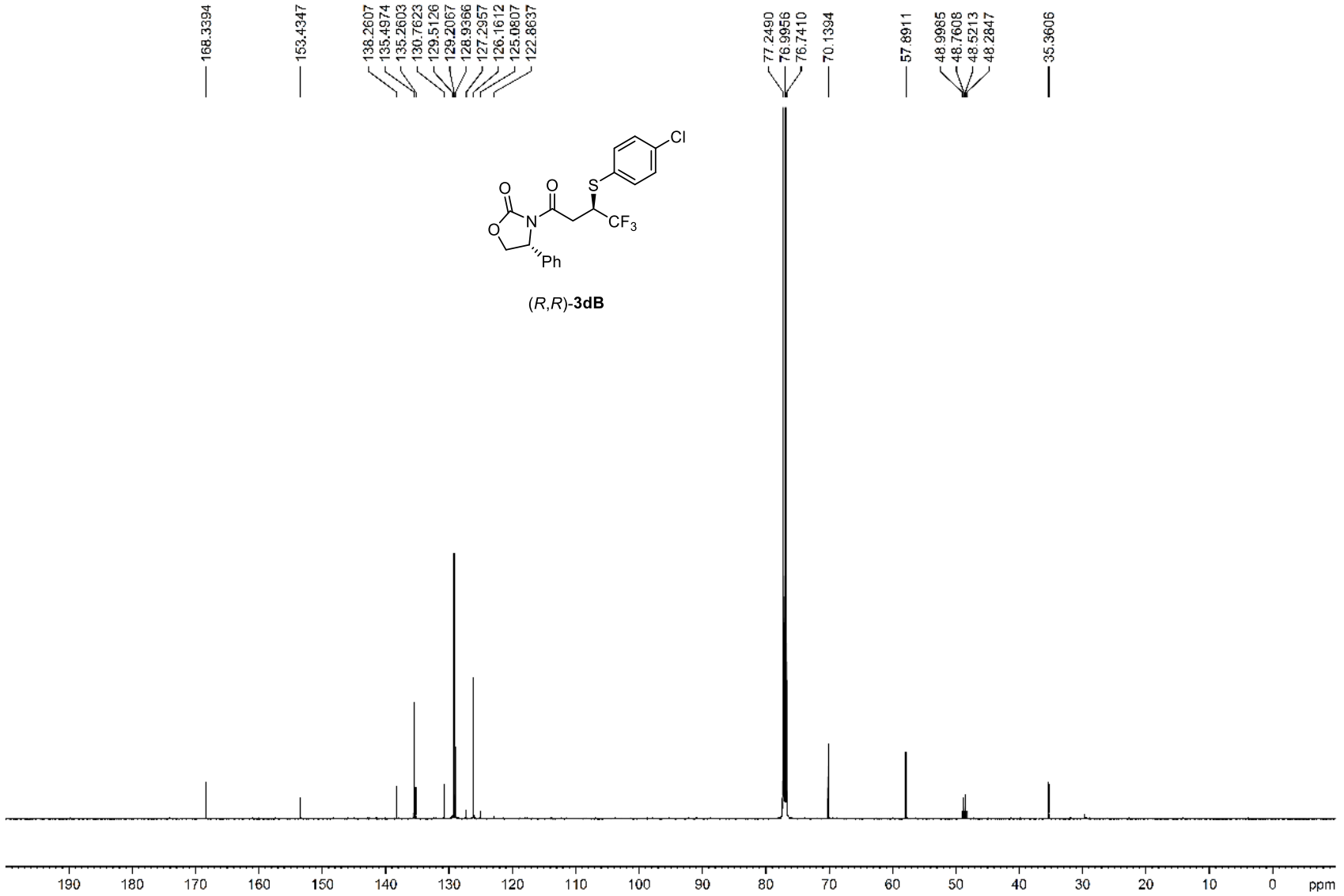

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.3300 w/v% |
| Factor | 1.0000 |
| Blank | -0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -51.9098 |
| S.D. | 0.6632 |
| C.V. | -1.2776 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 27( 1/ 5) | -52.105 | 24.4 |
| 2 | 27( 2/ 5) | -50.902 | 24.4 |
| 3 | 27( 3/ 5) | -51.729 | 24.4 |
| 4 | 27( 4/ 5) | -52.105 | 24.4 |
| 5 | 27( 5/ 5) | -52.707 | 24.4 |

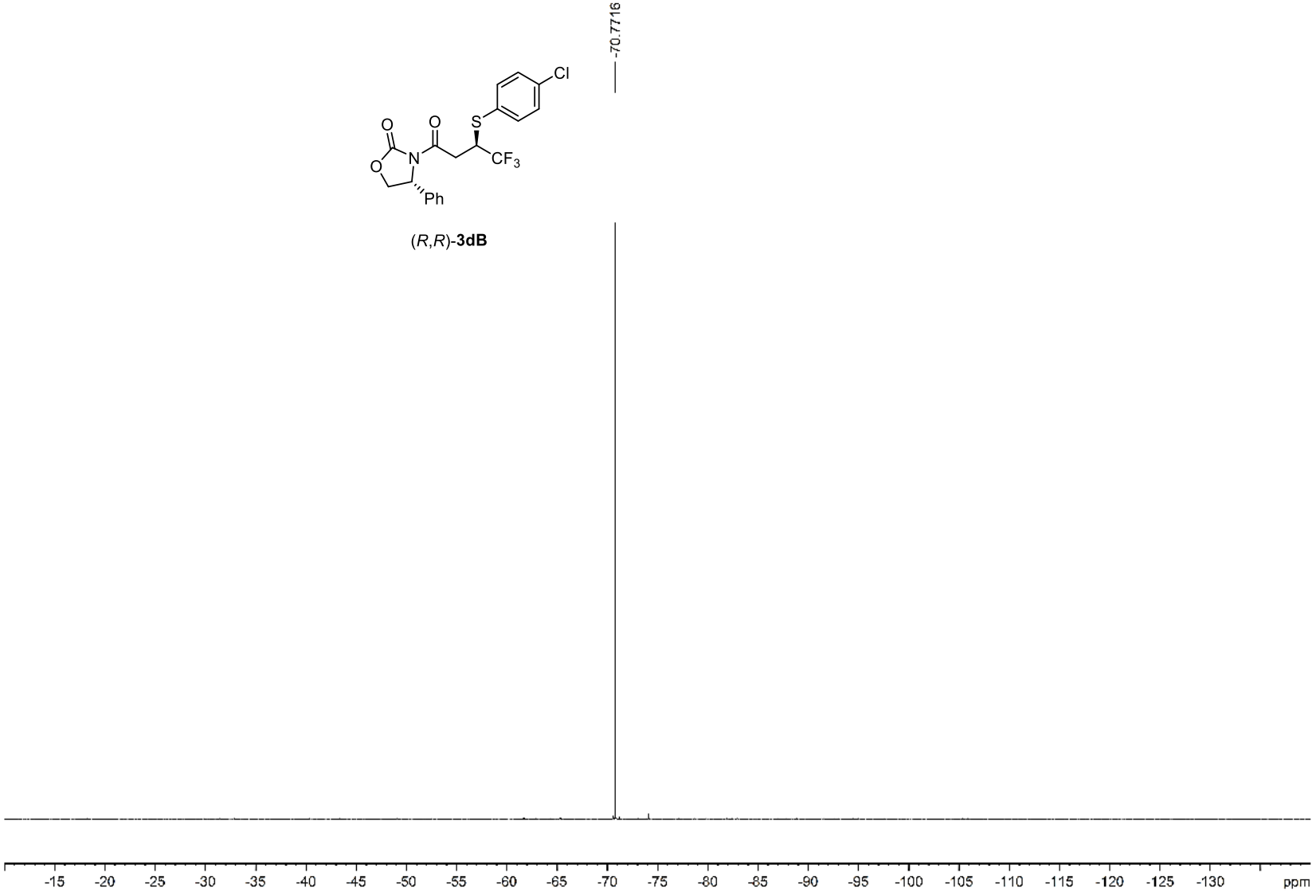
$^1$H NMR Spectrum of (*R*,*R*)-**3dB** (400 MHz, $CDCl_3$)



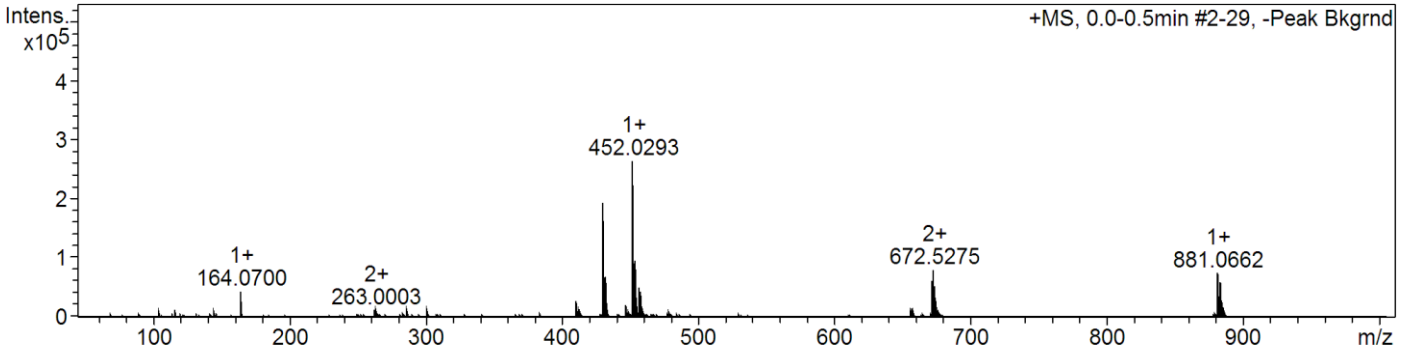
$^{13}$C NMR Spectrum of (*R*,*R*)-**3dB** (125 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3dB** (470 MHz, $CDCl_3$)



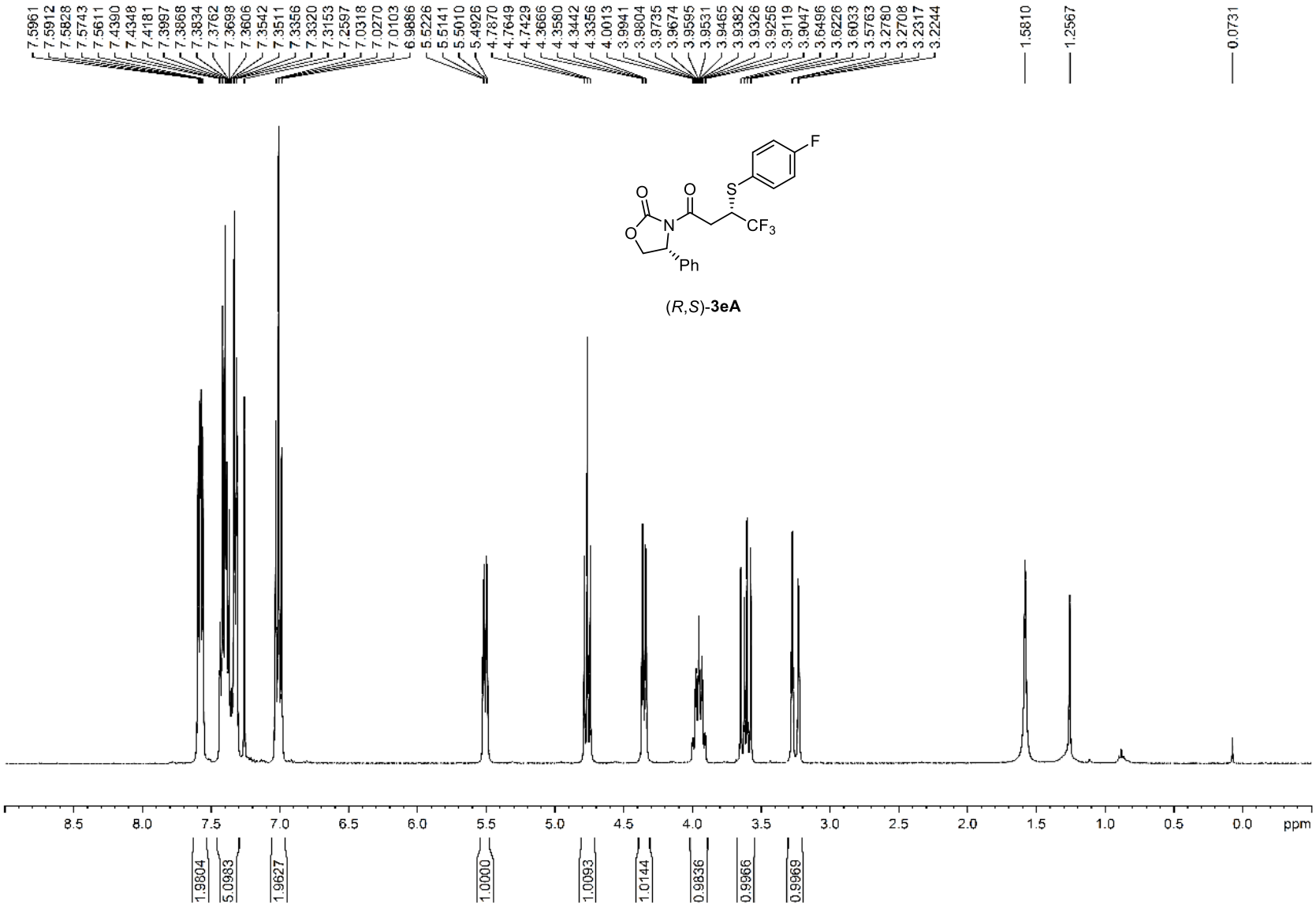
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3dB**



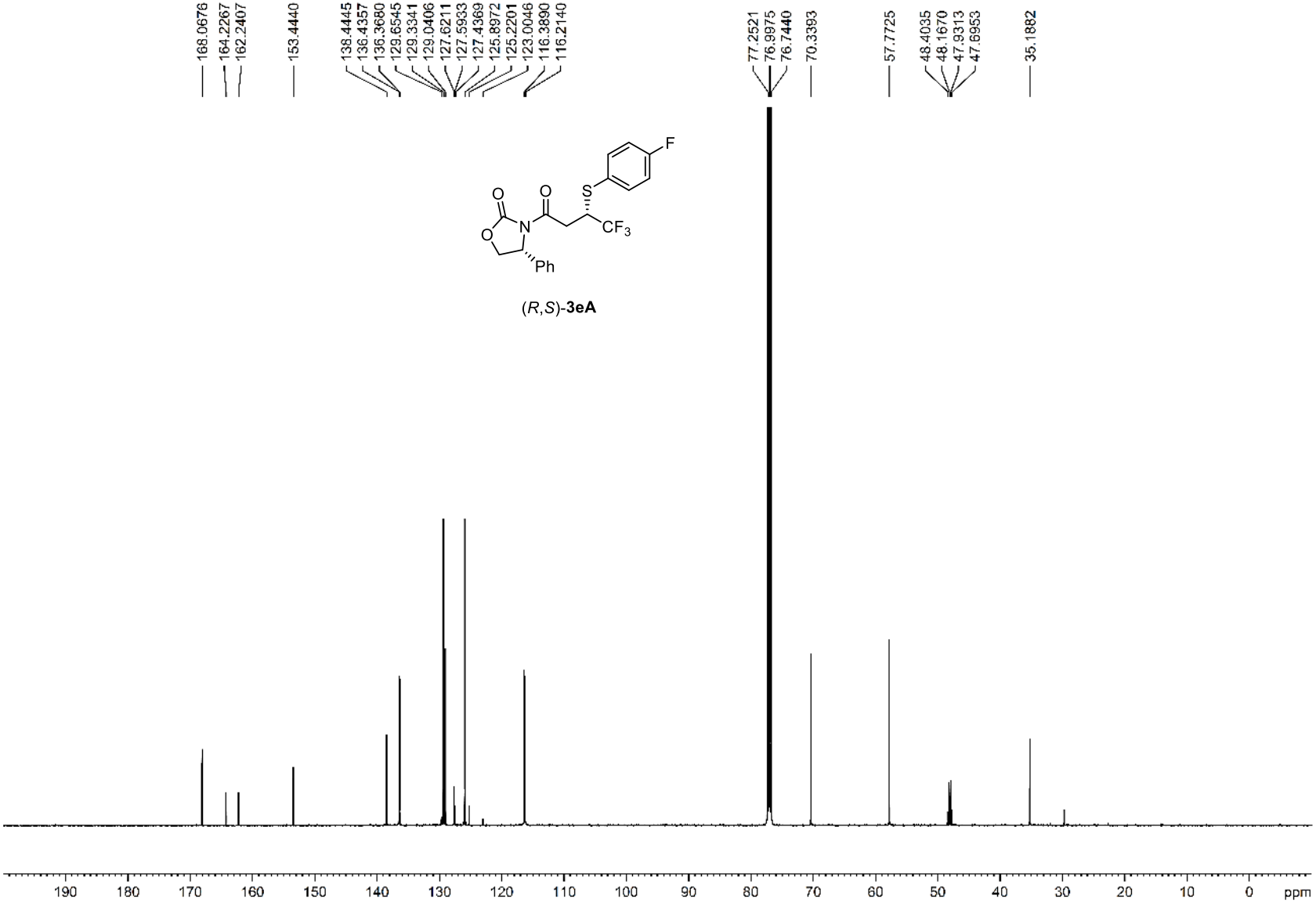

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0900 w/v% |
| Factor | 1.0000 |
| Blank | 0.0002 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -116.6972 |
| S.D. | 0.5505 |
| C.V. | -0.4717 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 3( 1/ 5) | -116.147 | 25.7 |
| 2 | 3( 2/ 5) | -117.248 | 25.7 |
| 3 | 3( 3/ 5) | -116.147 | 25.7 |
| 4 | 3( 4/ 5) | -116.697 | 25.7 |
| 5 | 3( 5/ 5) | -117.248 | 25.7 |

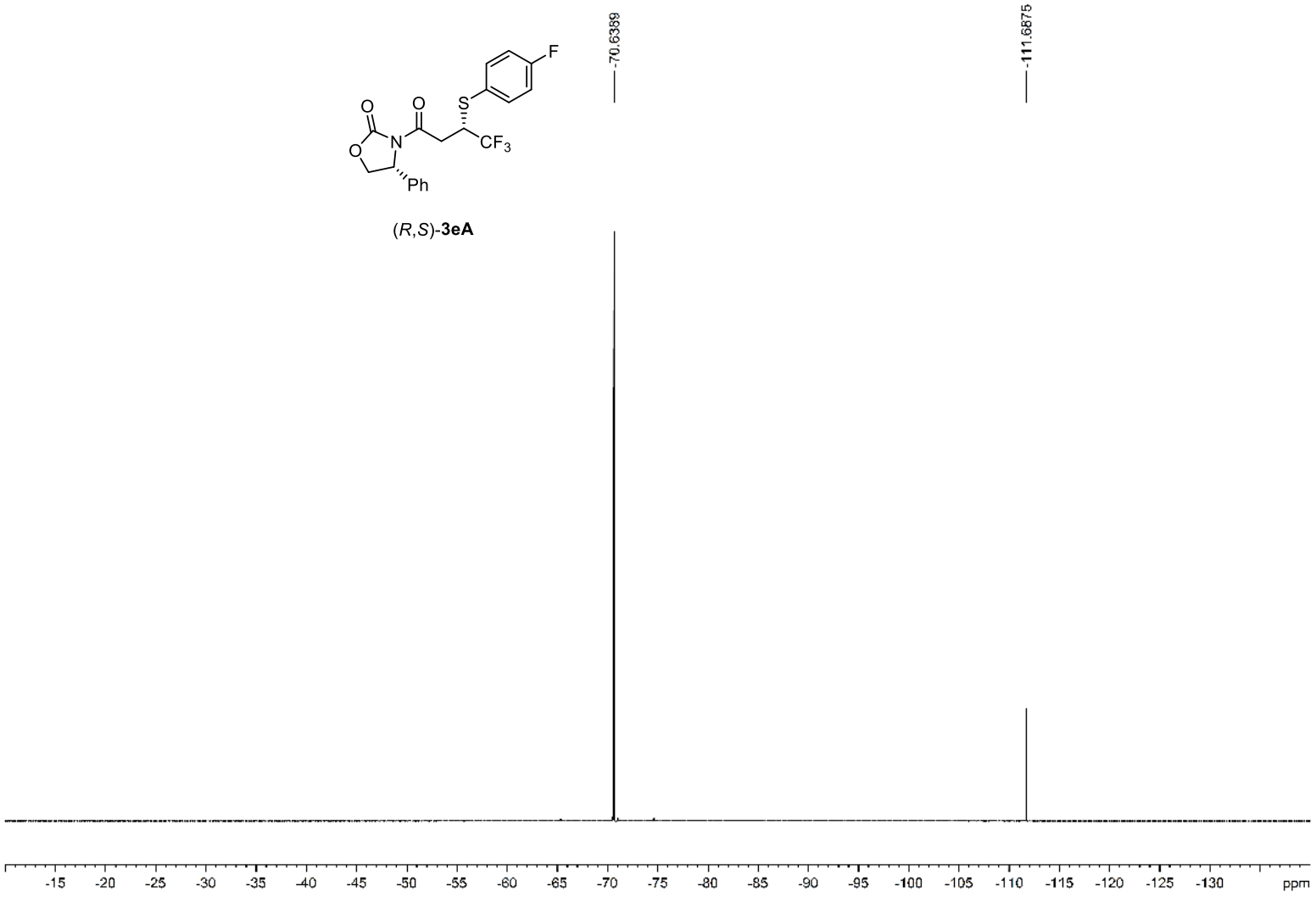
$^1$H NMR Spectrum of (*R*,*S*)-**3eA** (400 MHz, $CDCl_3$)



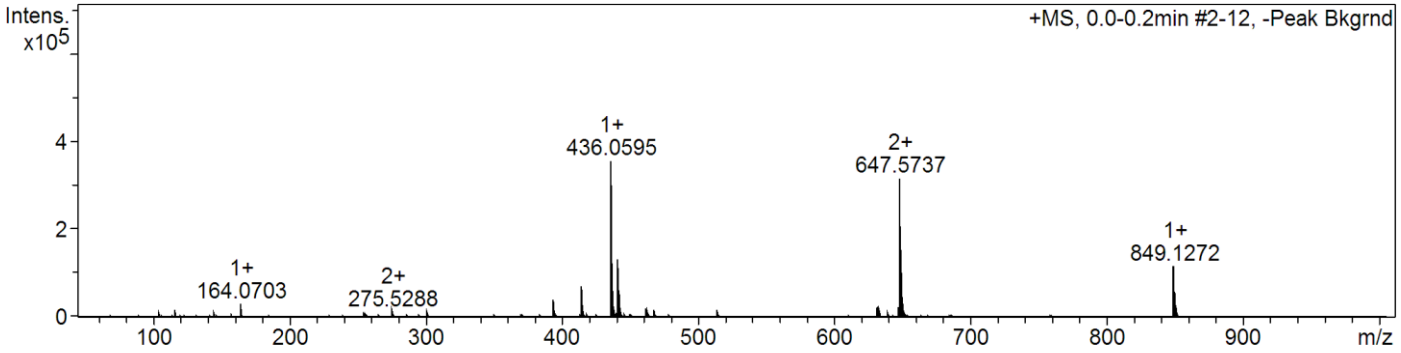
$^{13}$C NMR Spectrum of (*R*,*S*)-**3eA** (125 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3eA** (470 MHz, $CDCl_3$)



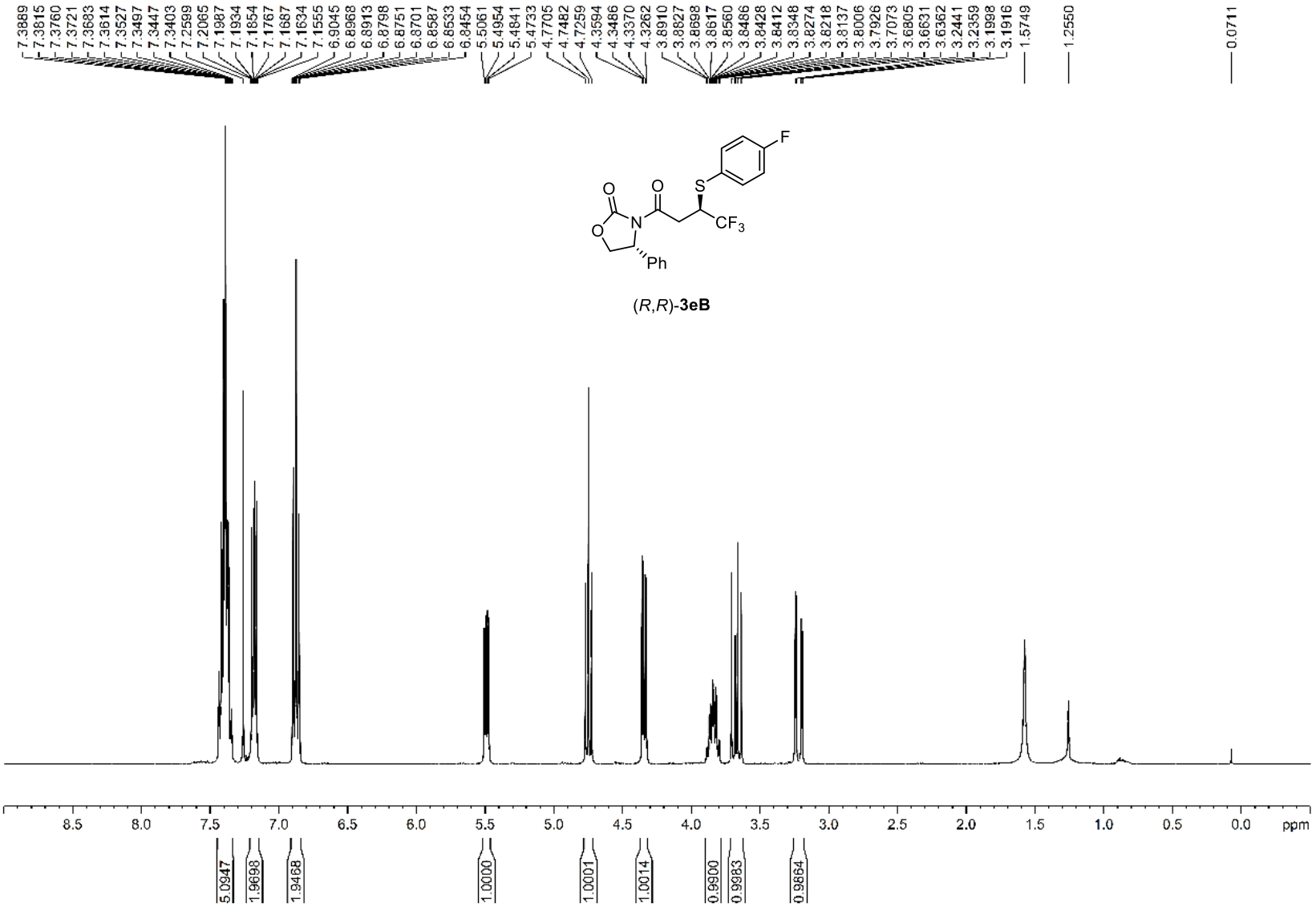
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3eA**



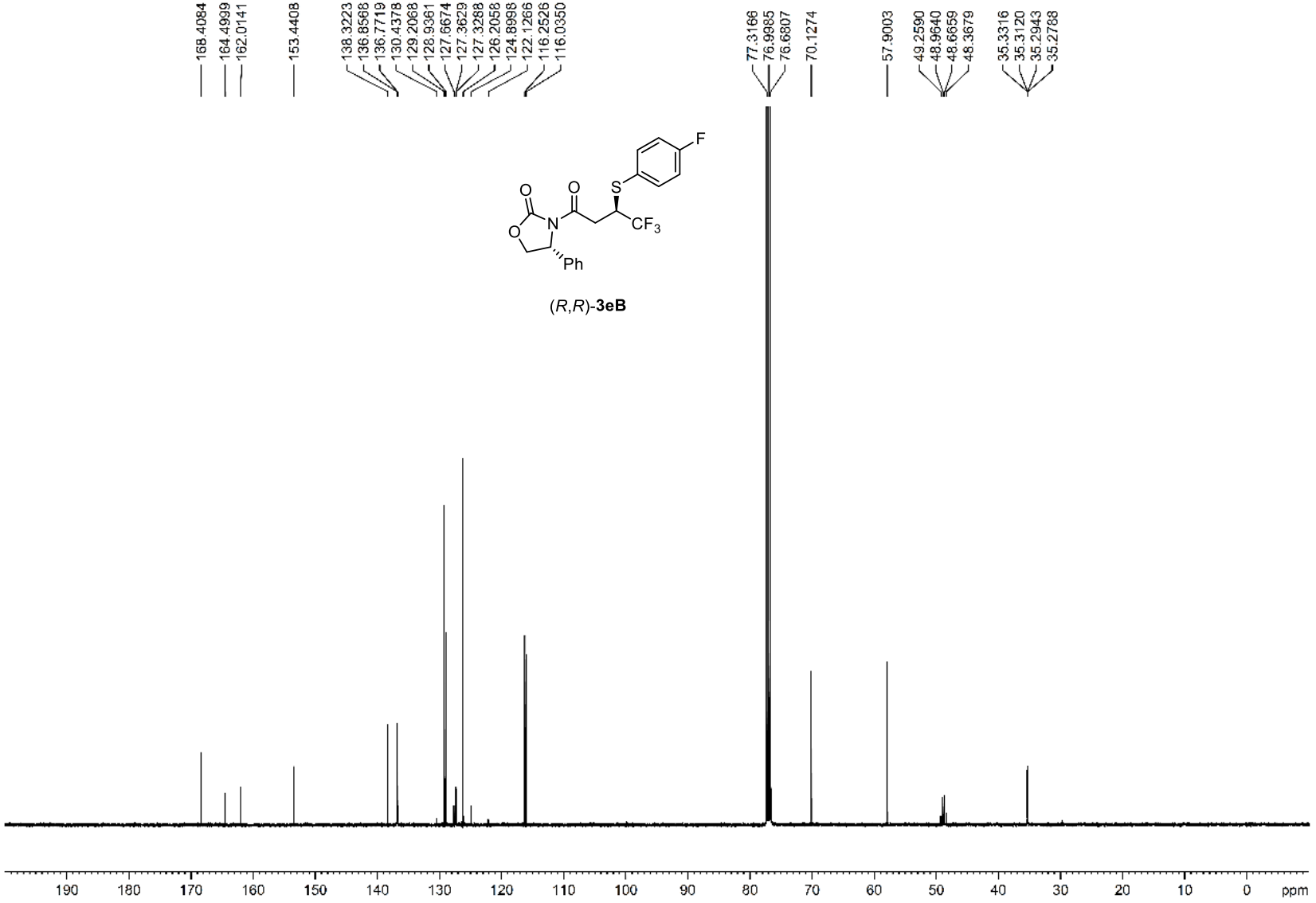

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.2667 w/v% |
| Factor | 1.0000 |
| Blank | 0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -60.9616 |
| S.D. | 0.4117 |
| C.V. | -0.6754 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 73( 1/ 5) | -61.262 | 26.1 |
| 2 | 73( 2/ 5) | -61.183 | 26.1 |
| 3 | 73( 3/ 5) | -60.314 | 26.1 |
| 4 | 73( 4/ 5) | -60.788 | 26.0 |
| 5 | 73( 5/ 5) | -61.262 | 26.1 |

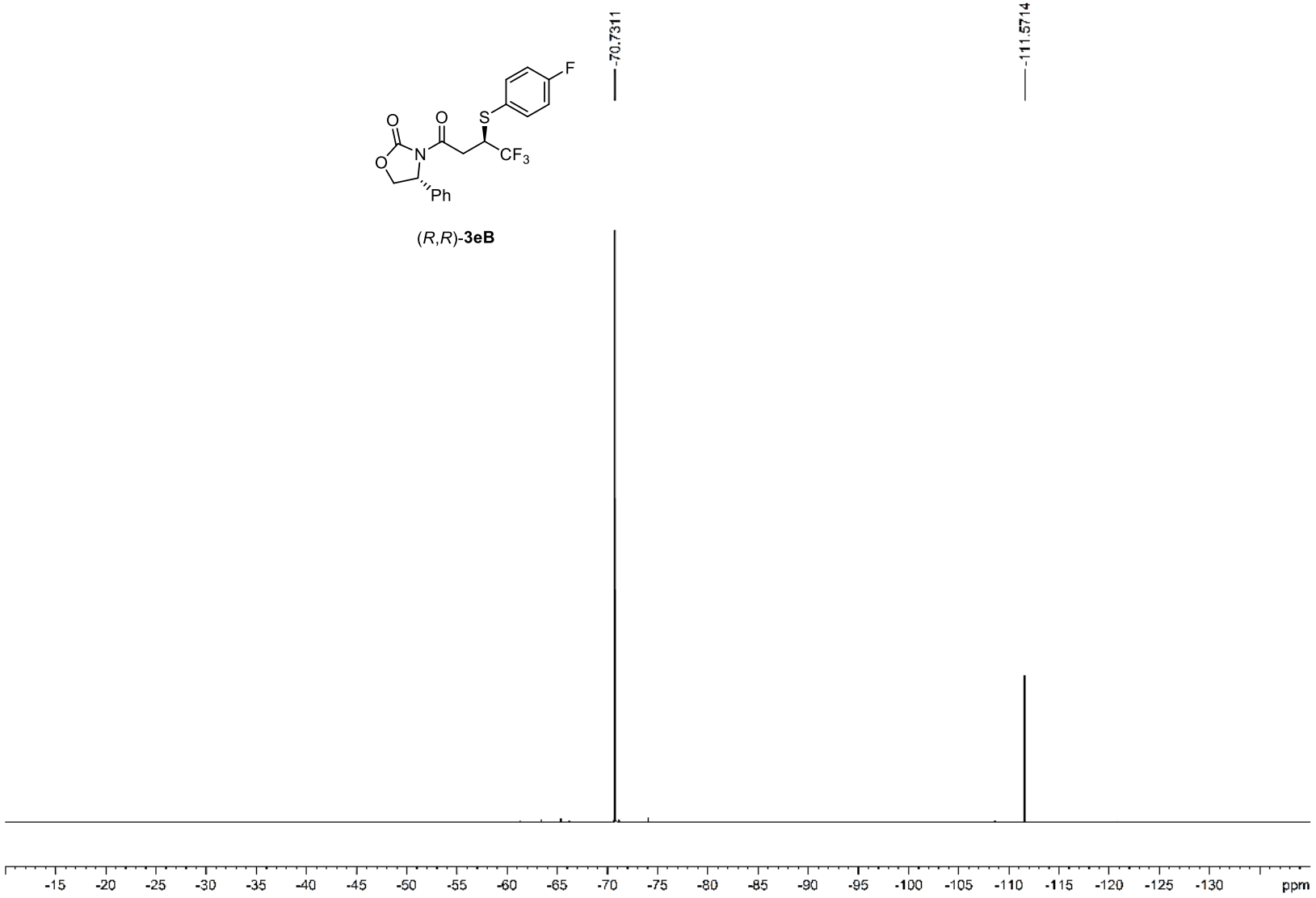
$^1$H NMR Spectrum of (*R*,*R*)-**3eB** (400 MHz, $CDCl_3$)



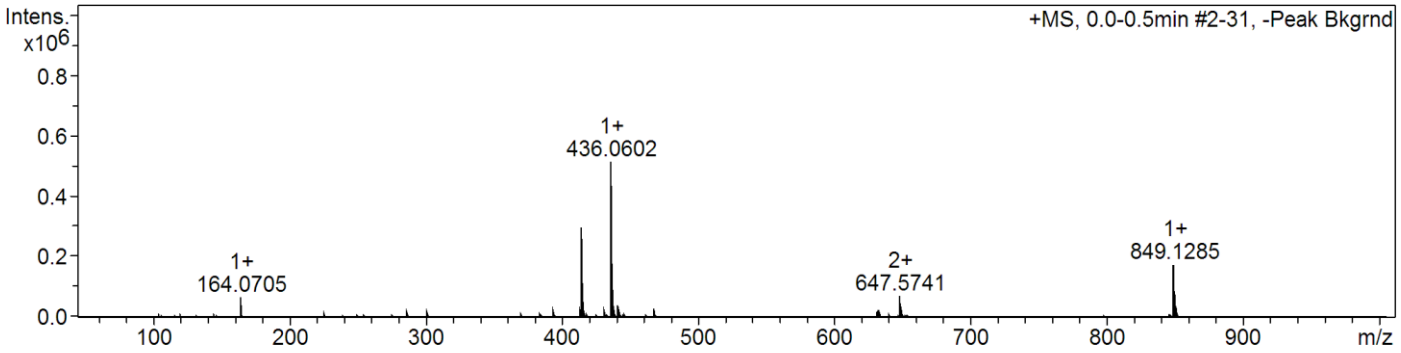
$^{13}$C NMR Spectrum of (*R*,*R*)-**3eB** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3eB** (470 MHz, $CDCl_3$)



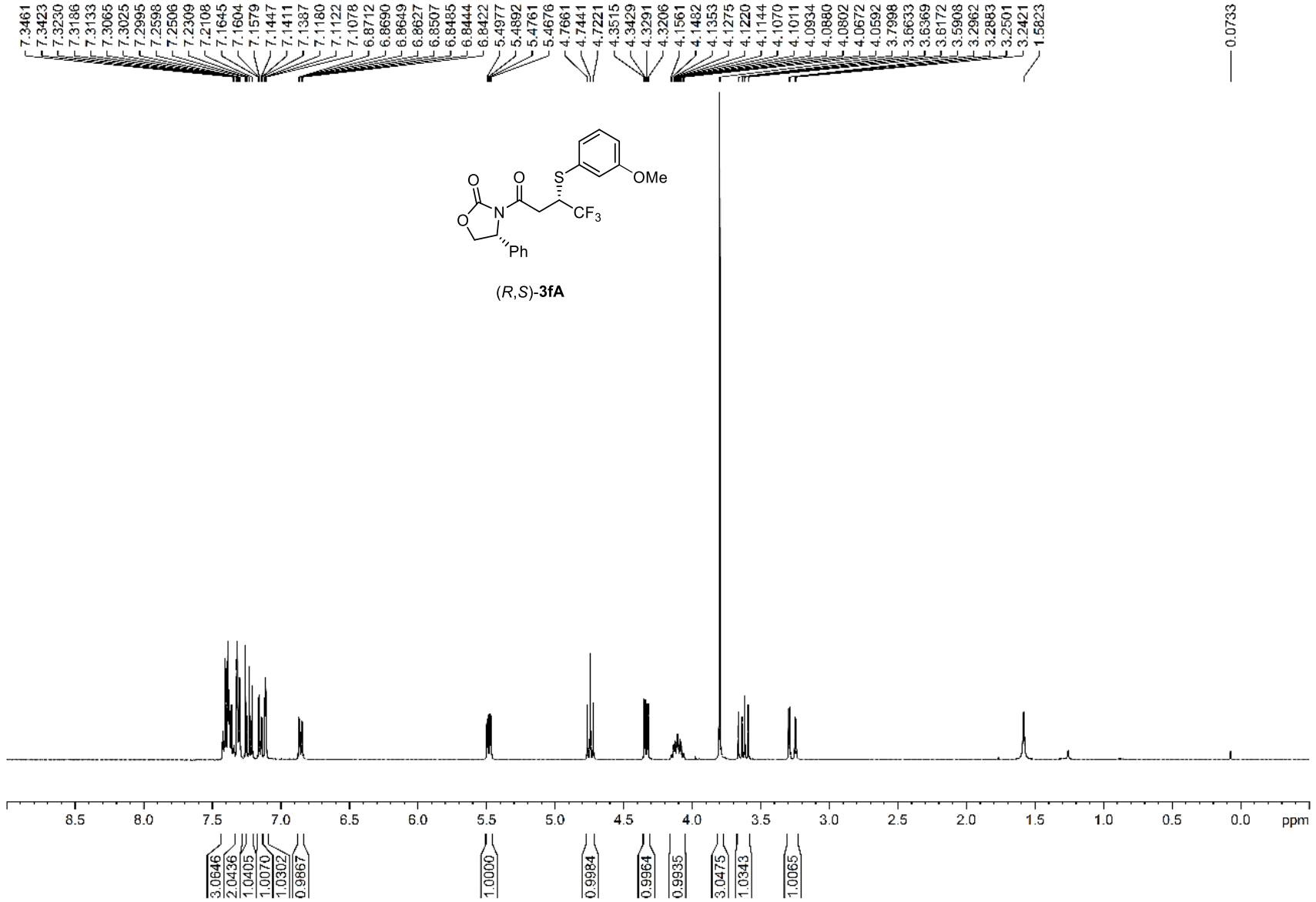
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3eB**



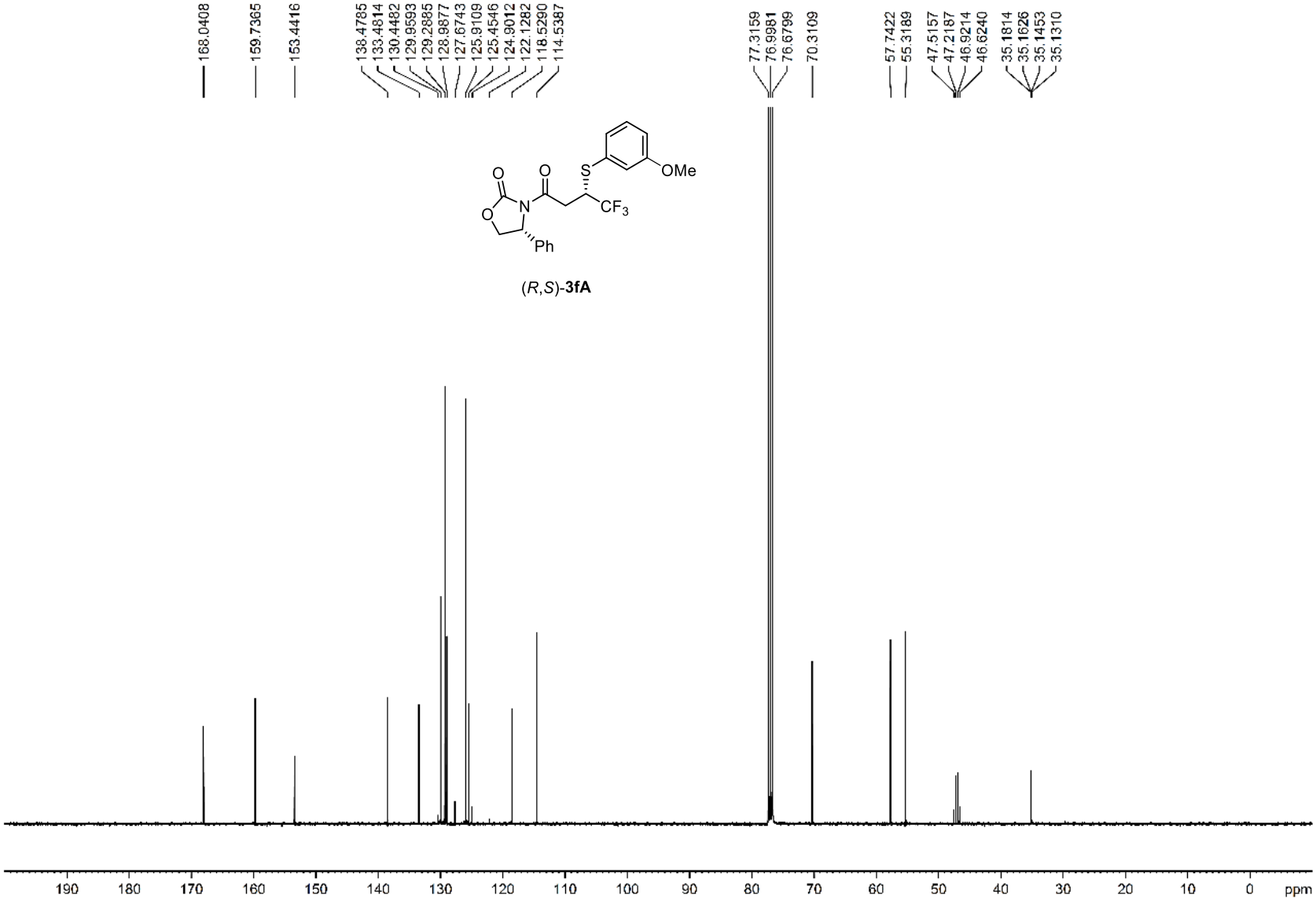

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.2400 w/v% |
| Factor | 1.0000 |
| Blank | 0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -103.9677 |
| S.D. | 0.3296 |
| C.V. | -0.3170 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 77( 1/ 5) | -103.548 | 25.8 |
| 2 | 77( 2/ 5) | -103.710 | 25.8 |
| 3 | 77( 3/ 5) | -104.274 | 25.8 |
| 4 | 77( 4/ 5) | -104.274 | 25.8 |
| 5 | 77( 5/ 5) | -104.032 | 25.8 |

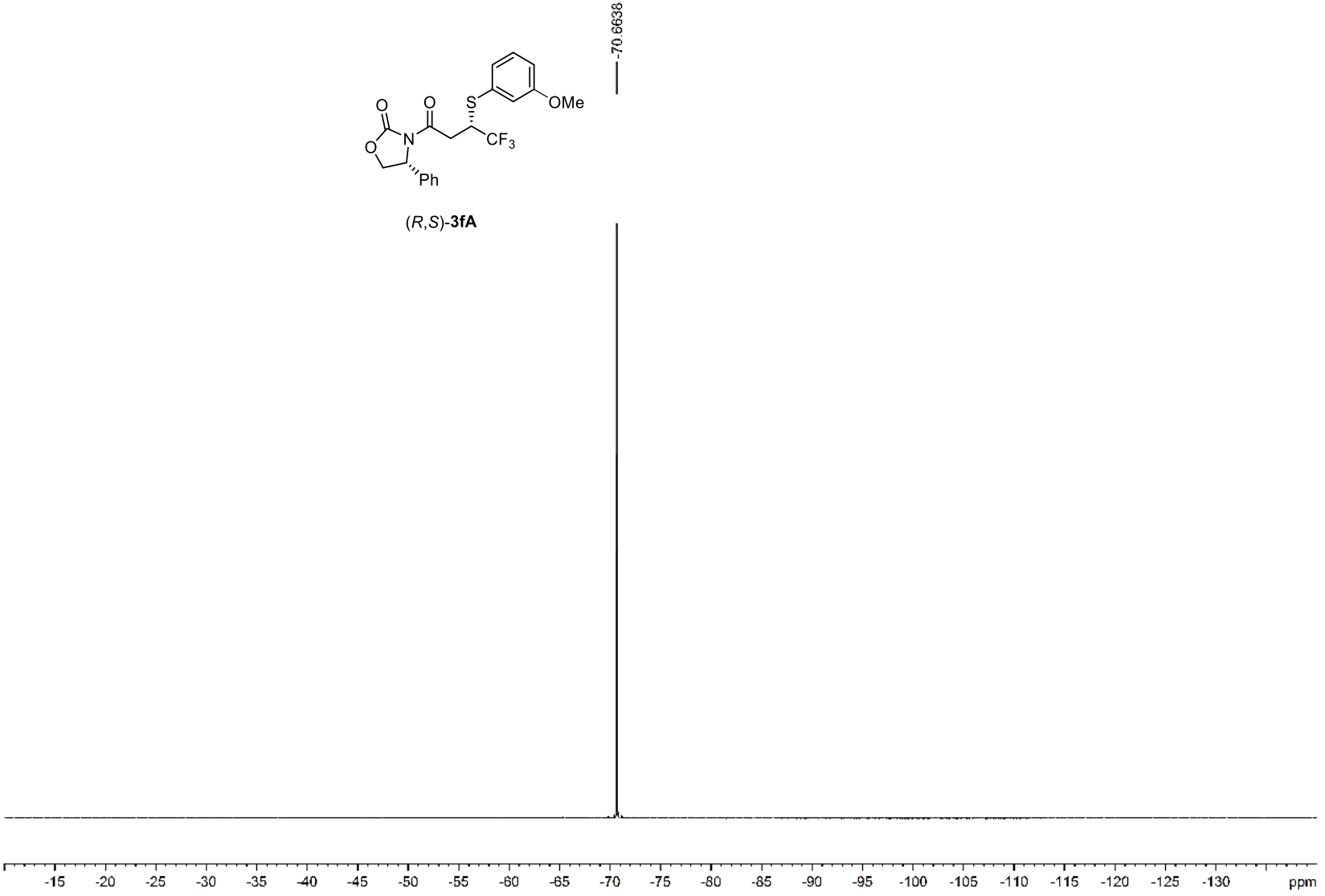
$^1$H NMR Spectrum of (*R*,*S*)-**3fA** (400 MHz, $CDCl_3$)



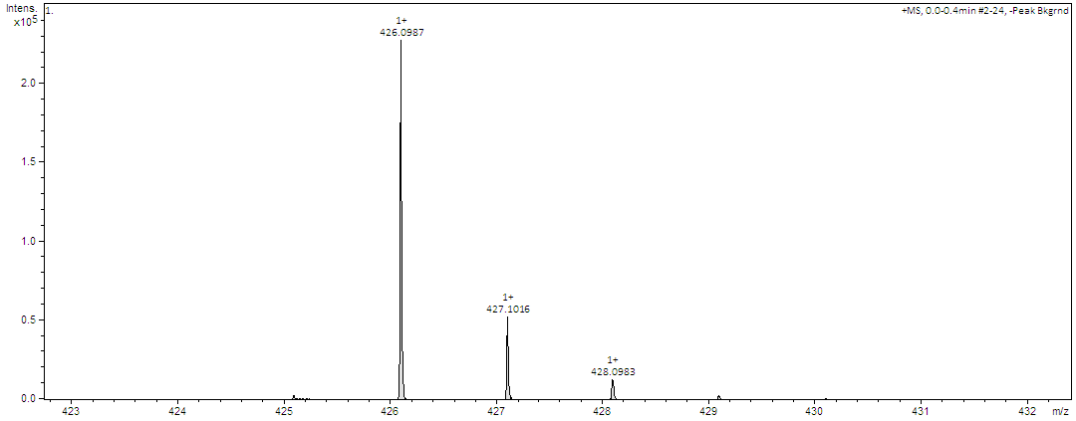
$^{13}$C NMR Spectrum of (*R*,*S*)-**3fA** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3fA** (376 MHz, $CDCl_3$)



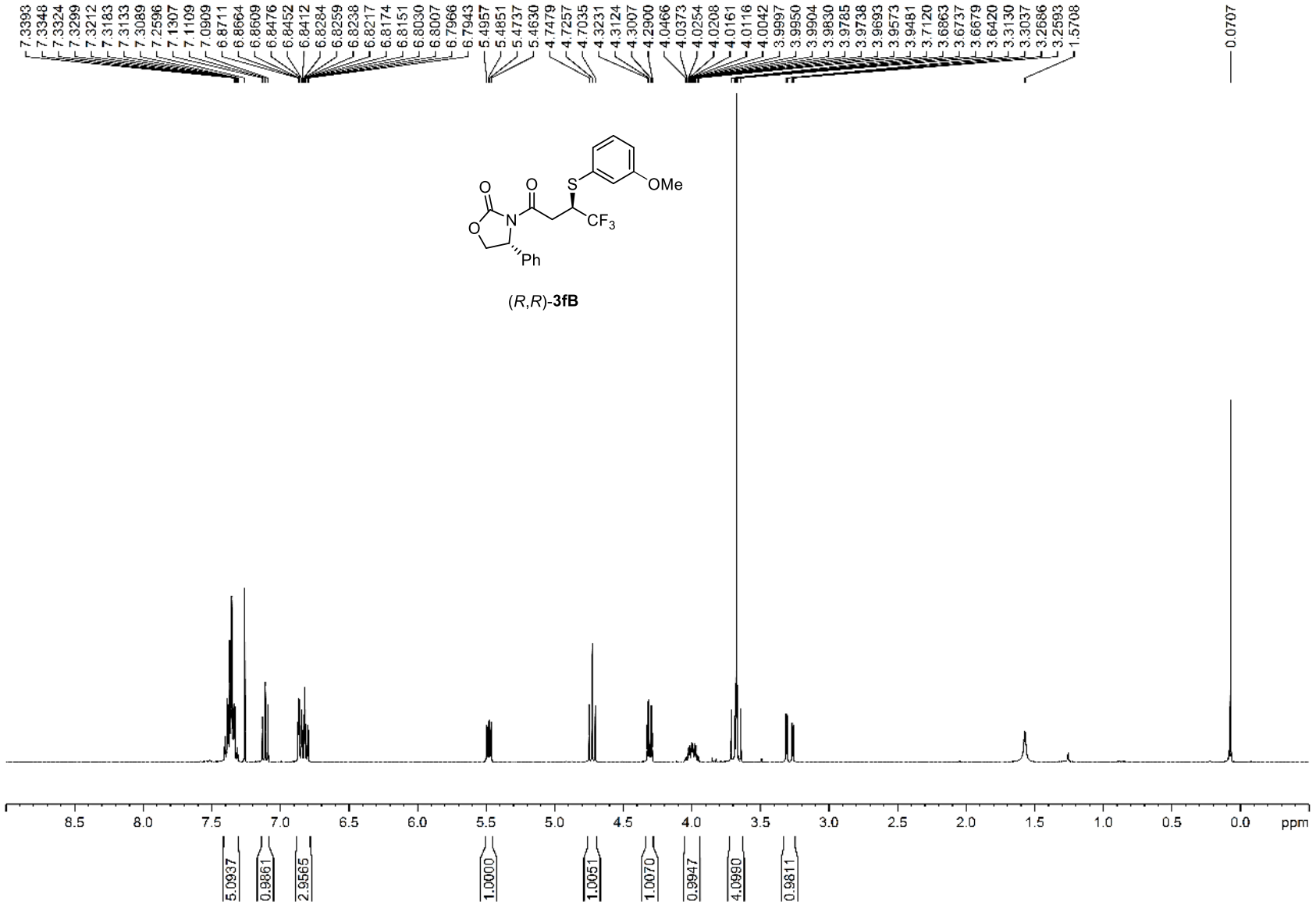
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3fA**



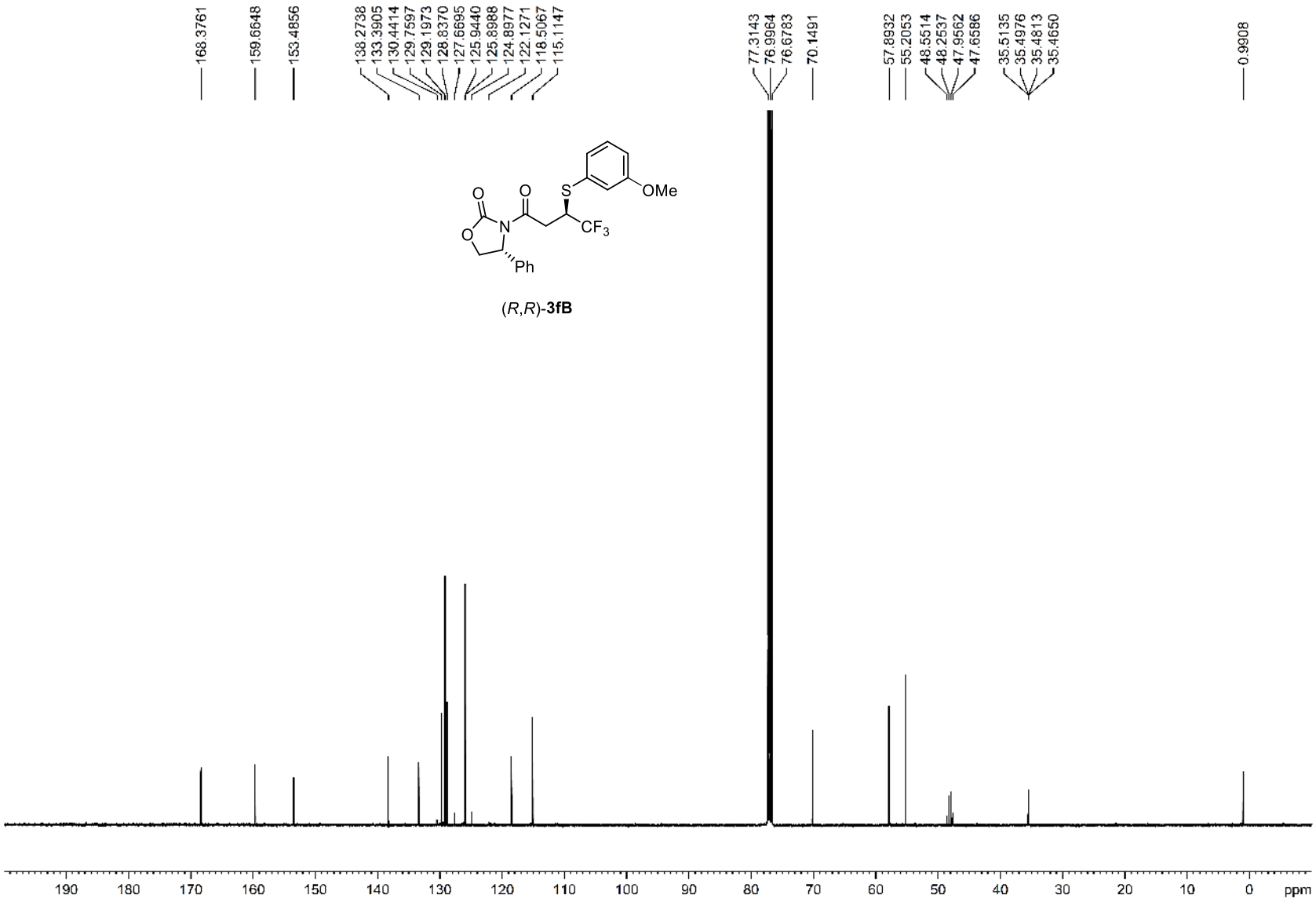

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.1667 w/v% |
| Factor | 1.0000 |
| Blank | 0.0002 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -50.7585 |
| S.D. | 0.7258 |
| C.V. | -1.4299 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 44( 1/ 5) | -51.341 | 24.0 |
| 2 | 44( 2/ 5) | -51.341 | 24.0 |
| 3 | 44( 3/ 5) | -50.056 | 24.0 |
| 4 | 44( 4/ 5) | -51.170 | 24.0 |
| 5 | 44( 5/ 5) | -49.884 | 24.0 |

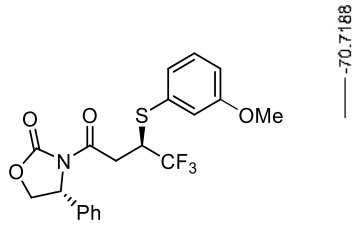
$^1$H NMR Spectrum of (*R*,*R*)-**3fB** (400 MHz, $CDCl_3$)



$^{13}$C NMR Spectrum of (*R*,*R*)-**3fB** (100 MHz, $CDCl_3$)

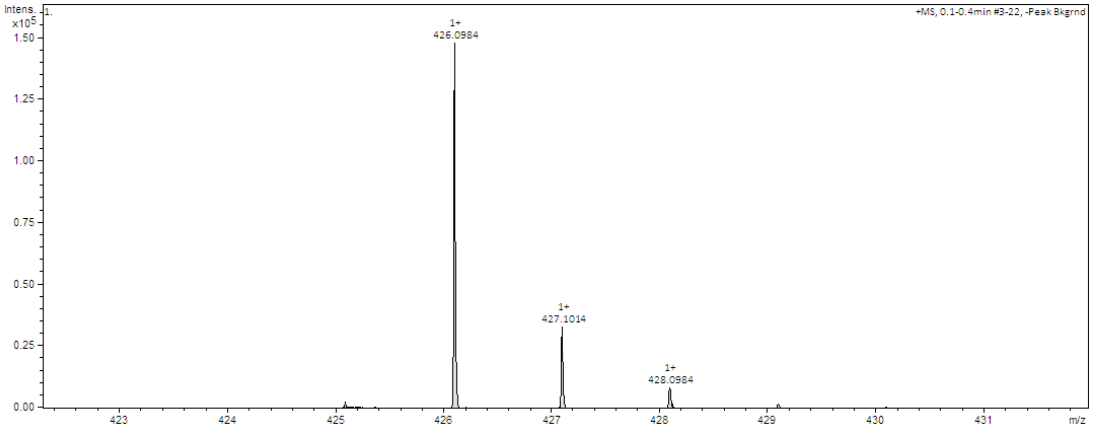


$^{19}$F NMR Spectrum of (*R*,*R*)-**3fB** (376 MHz, $CDCl_3$)




(*R*,*R*)-**3fB**

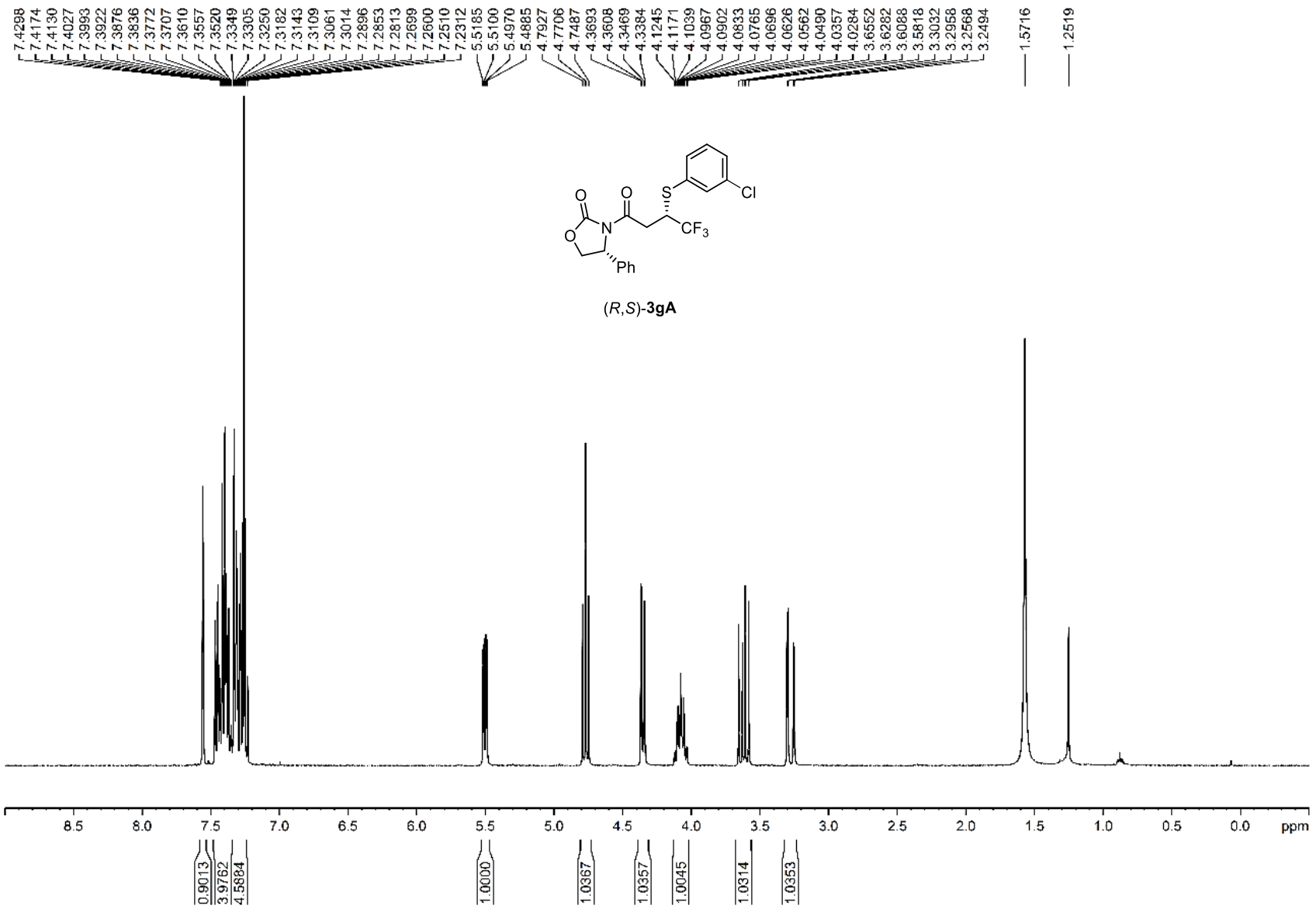
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3fB**



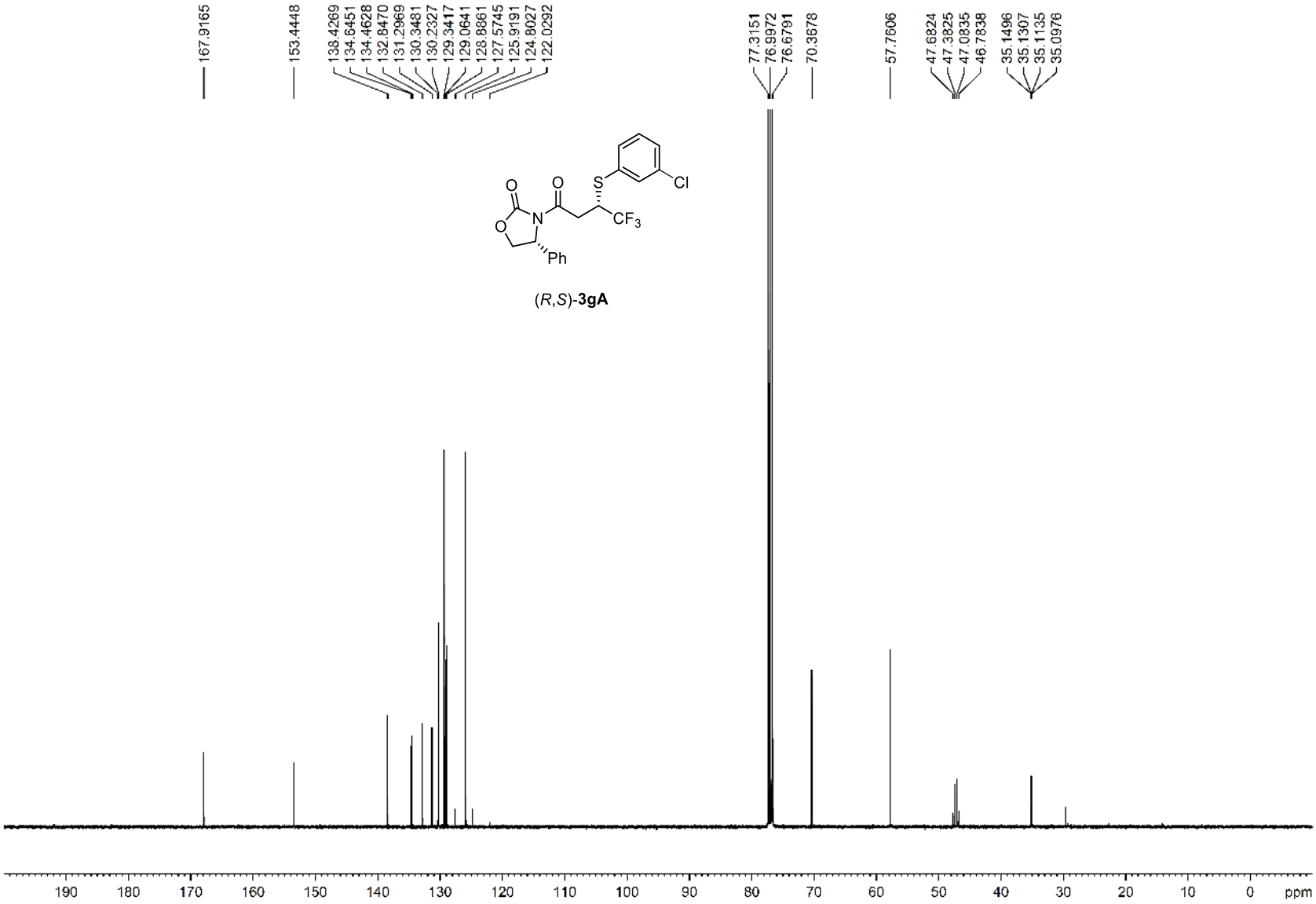

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.1750 w/v% |
| Factor | 1.0000 |
| Blank | 0.0002 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -106.0766 |
| S.D. | 0.5469 |
| C.V. | -0.5156 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 76( 1/ 5) | -106.809 | 23.3 |
| 2 | 76( 2/ 5) | -105.362 | 23.3 |
| 3 | 76( 3/ 5) | -105.872 | 23.3 |
| 4 | 76( 4/ 5) | -106.383 | 23.3 |
| 5 | 76( 5/ 5) | -105.957 | 23.3 |

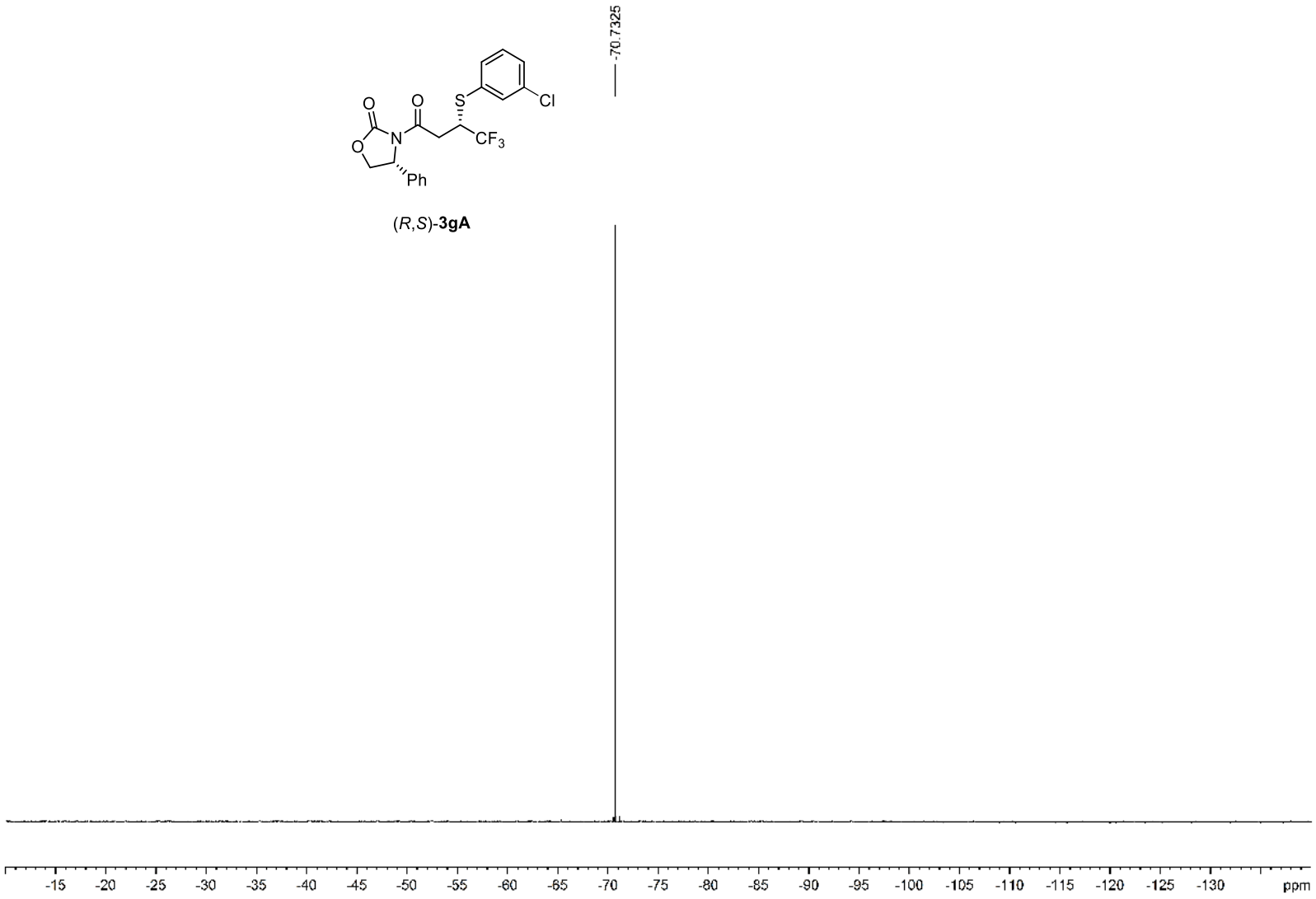
$^1$H NMR Spectrum of (*R*,*S*)-**3gA** (400 MHz, $CDCl_3$)



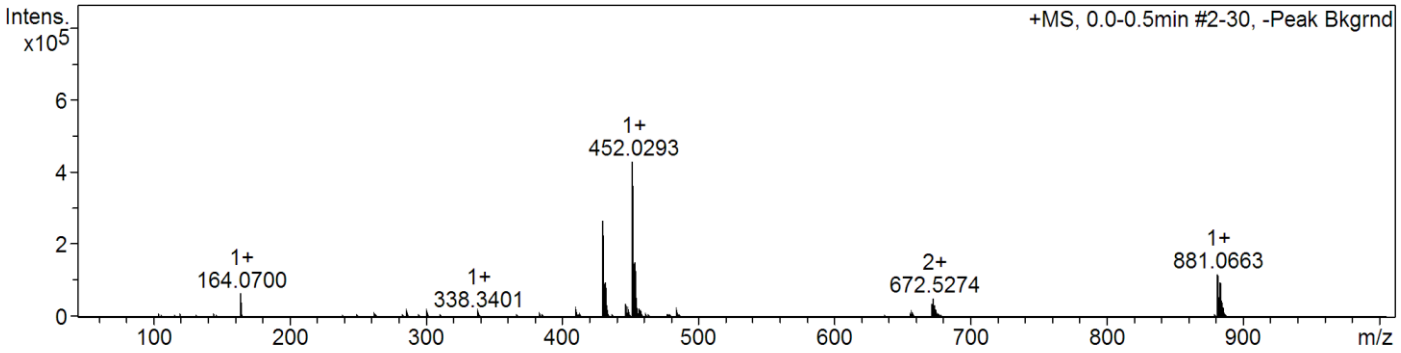
$^{13}$C NMR Spectrum of (*R*,*S*)-**3gA** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3gA** (470 MHz, $CDCl_3$)



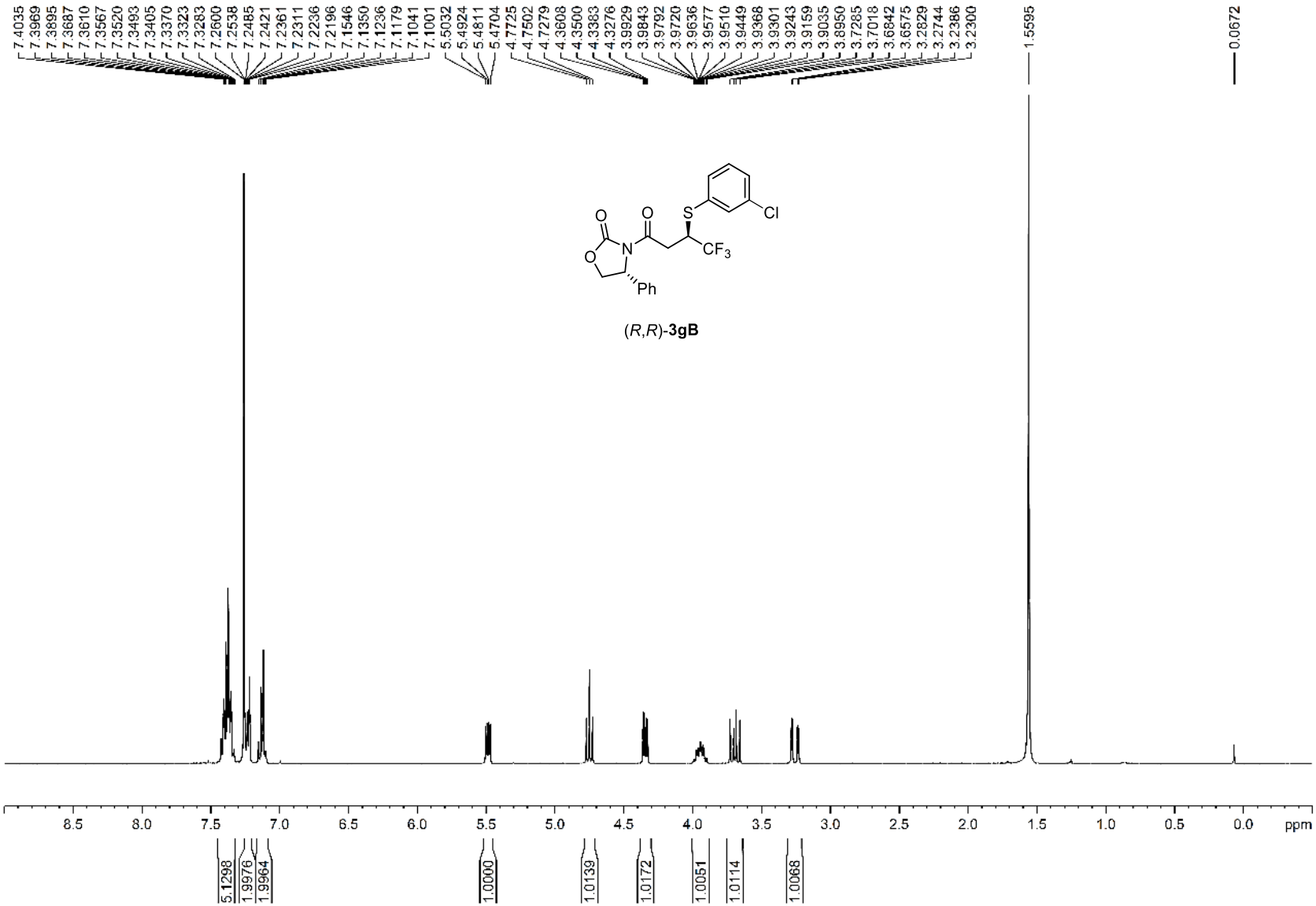
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3gA**




| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.9933 w/v% |
| Factor | 1.0000 |
| Blank | 0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -53.0756 |
| S.D. | 0.7239 |
| C.V. | -1.3639 % |

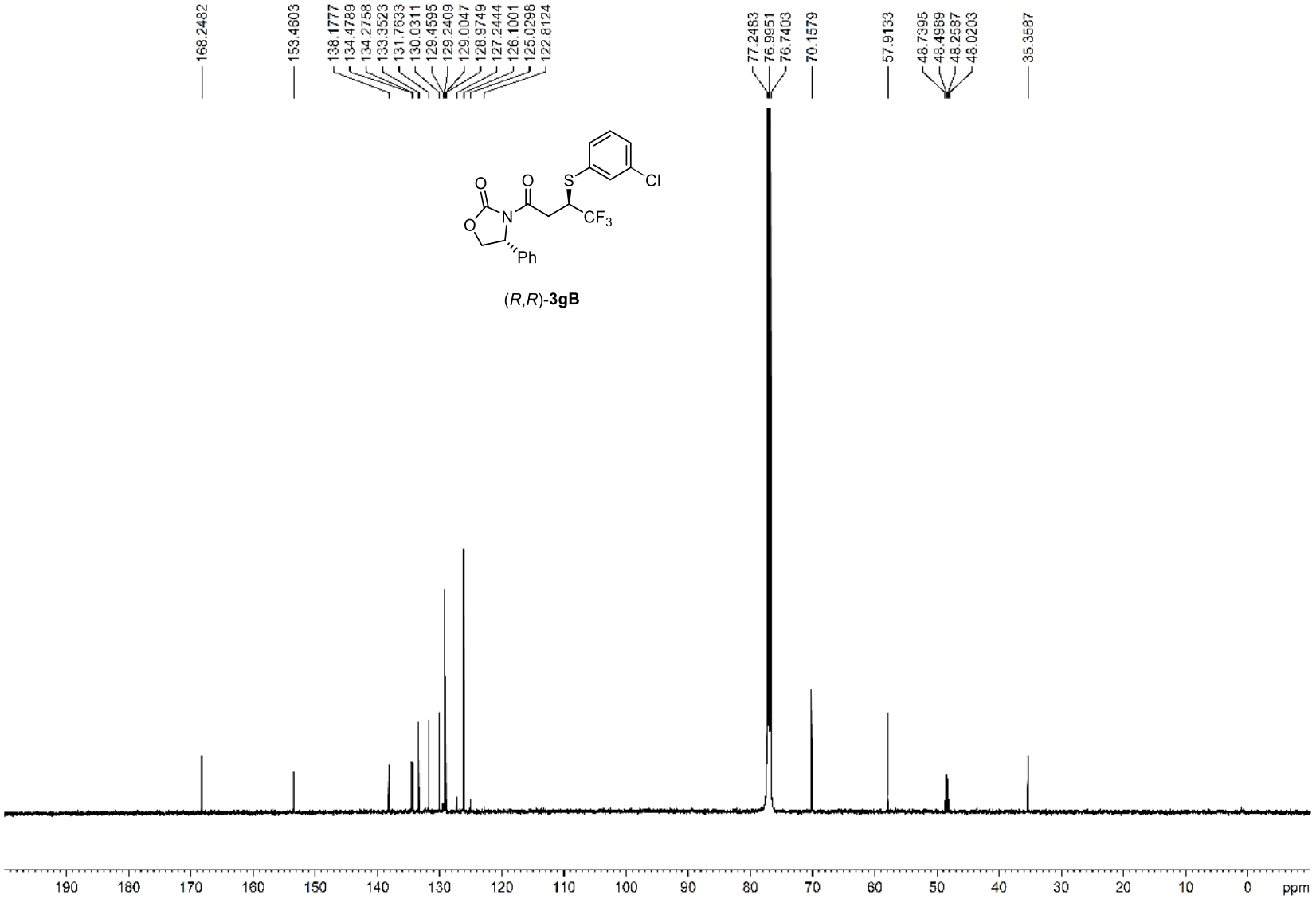
| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 65( 1/ 5) | -52.552 | 26.6 |
| 2 | 65( 2/ 5) | -53.962 | 26.6 |
| 3 | 65( 3/ 5) | -52.451 | 26.6 |
| 4 | 65( 4/ 5) | -52.653 | 26.6 |
| 5 | 65( 5/ 5) | -53.760 | 26.6 |

$^1$H NMR Spectrum of (*R*,*R*)-**3gB** (400 MHz, $CDCl_3$)

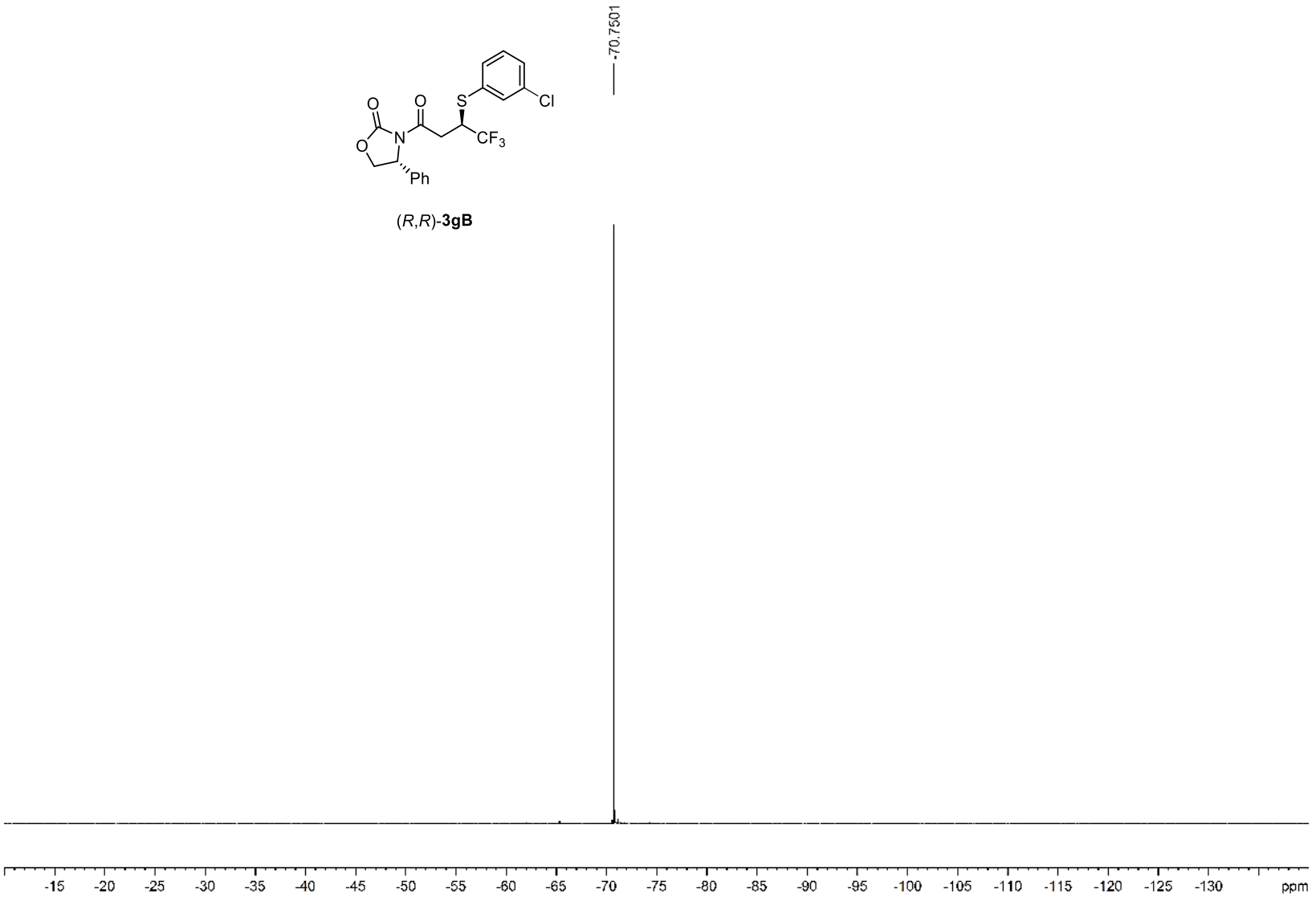



(*R*,*R*)-**3gB**

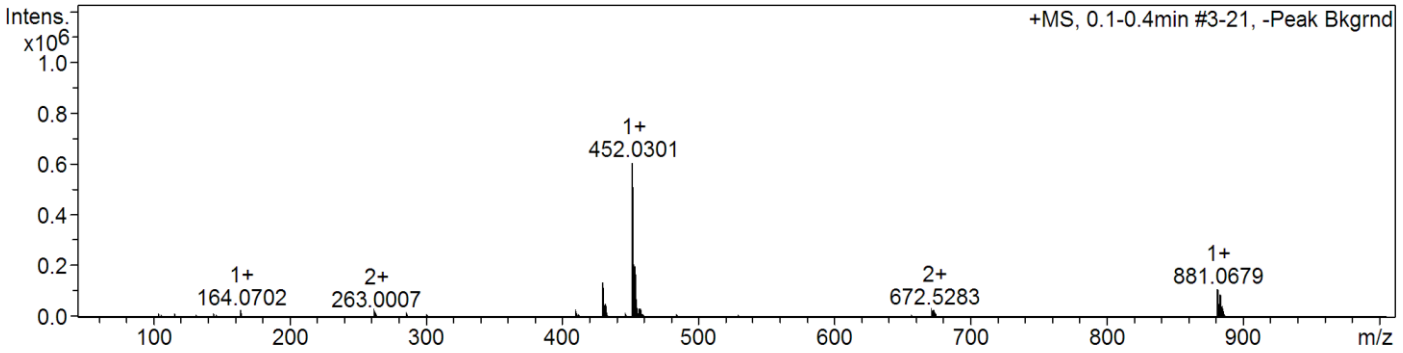
$^{13}$C NMR Spectrum of (*R*,*R*)-**3gB** (125 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3gB** (470 MHz, $CDCl_3$)



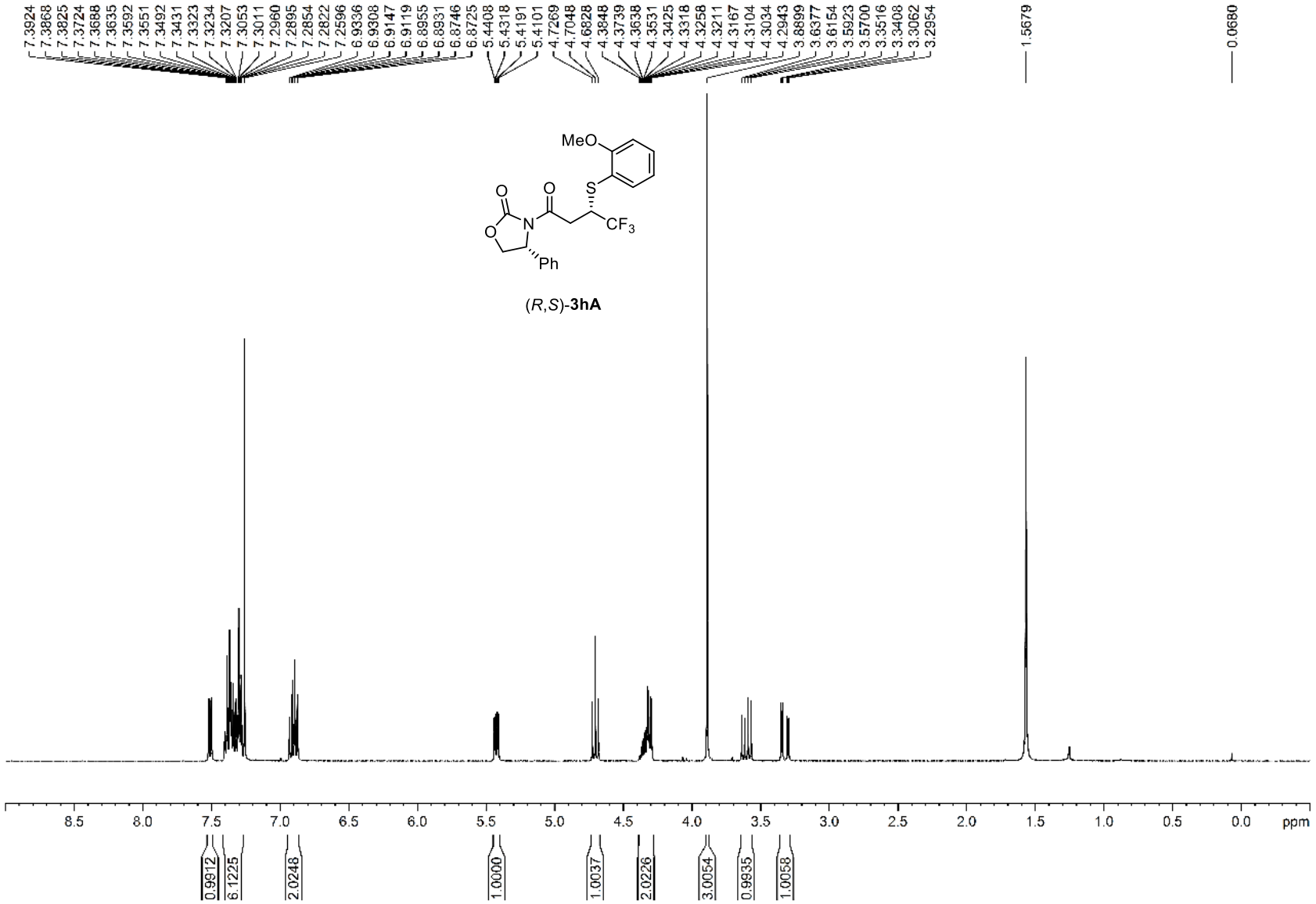
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3gB**



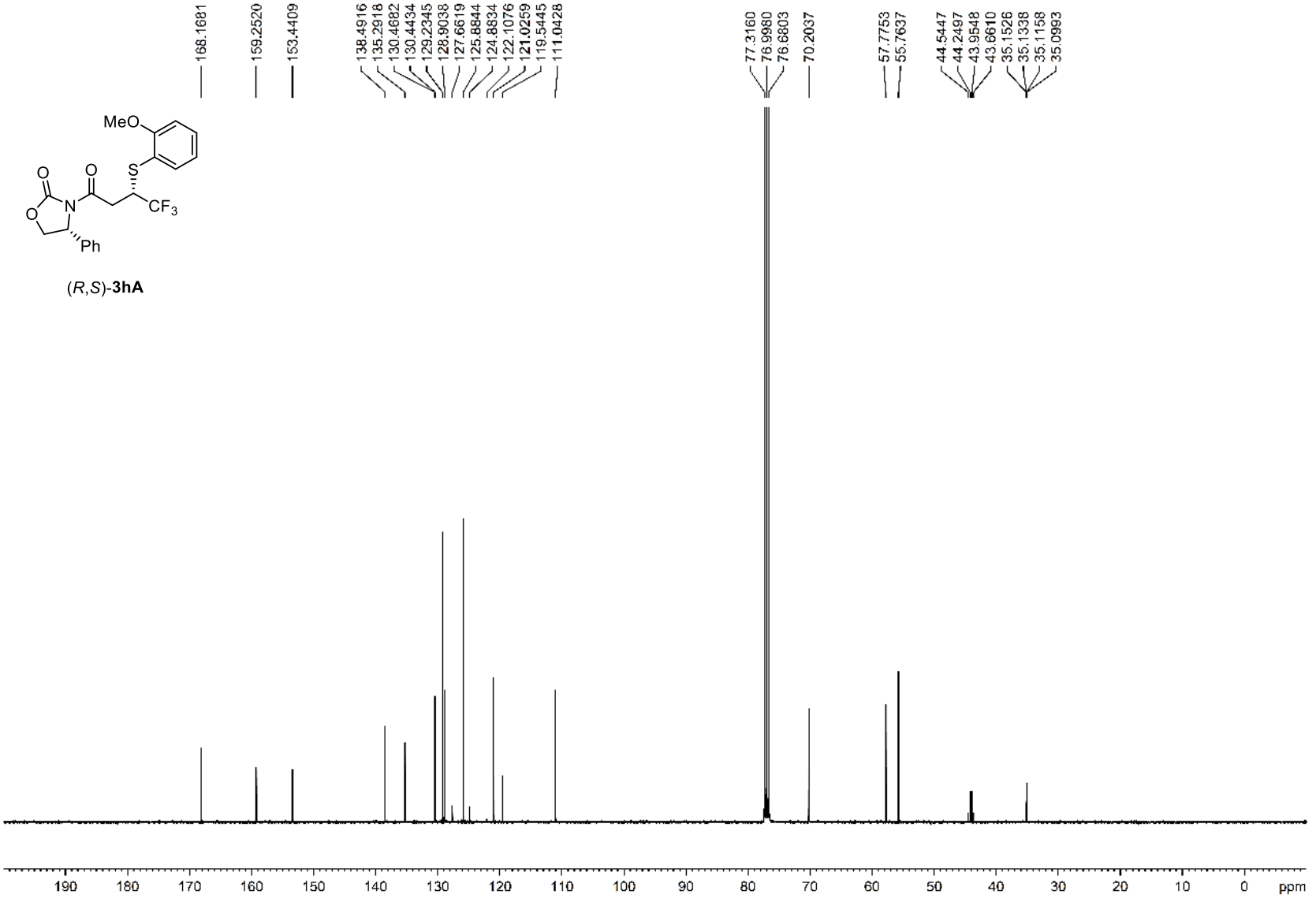

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0800 w/v% |
| Factor | 1.0000 |
| Blank | 0.0002 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -113.4259 |
| S.D. | 0.7938 |
| C.V. | -0.6999 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 24( 1/ 5) | -112.593 | 24.2 |
| 2 | 24( 2/ 5) | -112.593 | 24.2 |
| 3 | 24( 3/ 5) | -114.167 | 24.2 |
| 4 | 24( 4/ 5) | -113.611 | 24.2 |
| 5 | 24( 5/ 5) | -114.167 | 24.2 |

$^1$H NMR Spectrum of (*R*,*S*)-**3hA** (400 MHz, $CDCl_3$)



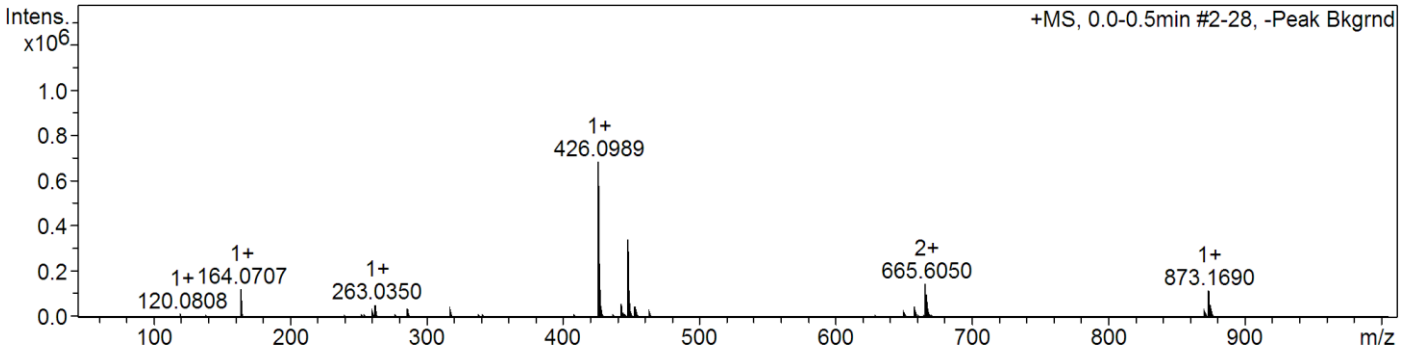
$^{13}$C NMR Spectrum of (*R*,*S*)-**3hA** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3hA** (376 MHz, $CDCl_3$)


(*R*,*S*)-**3hA**

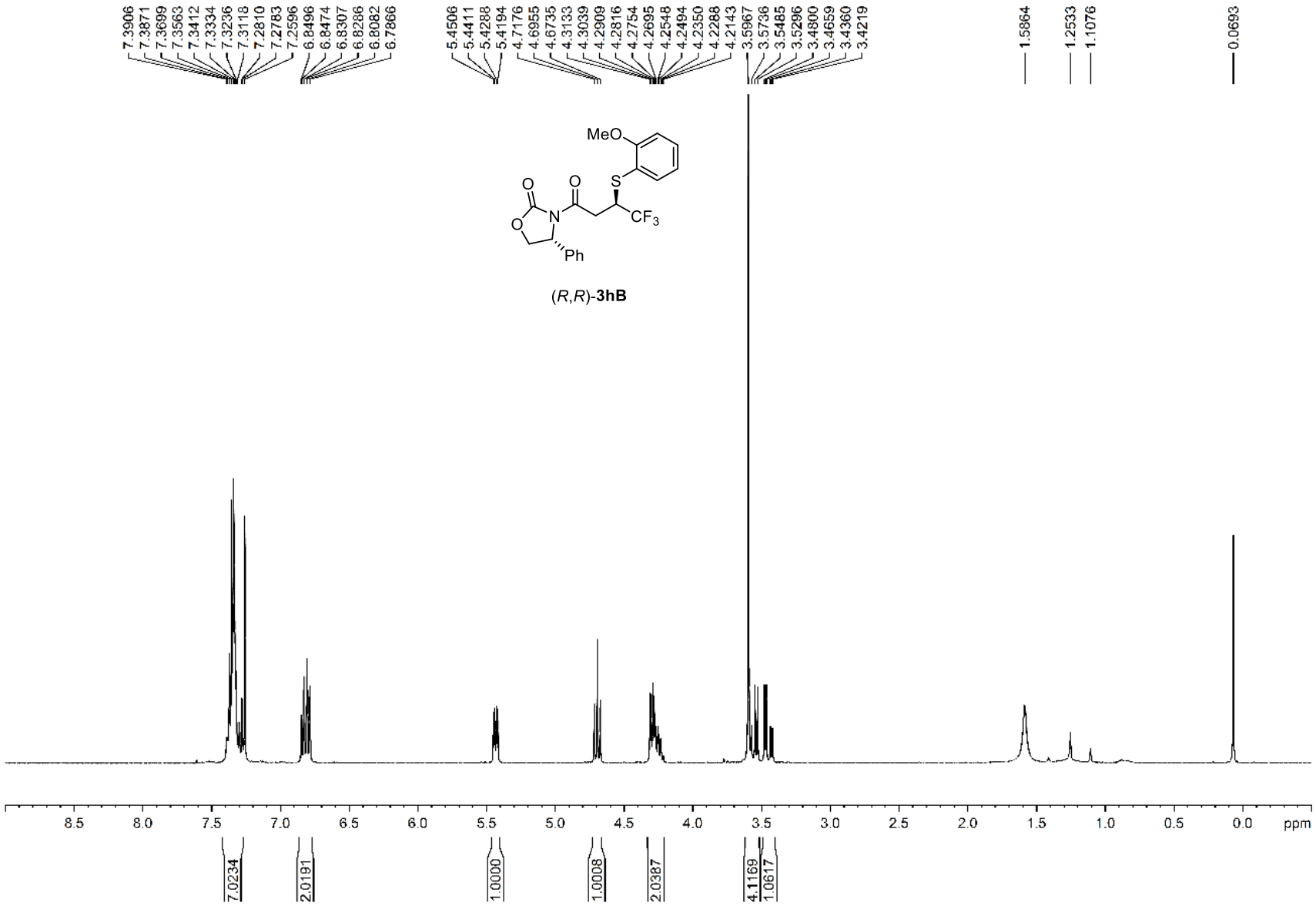
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3hA**



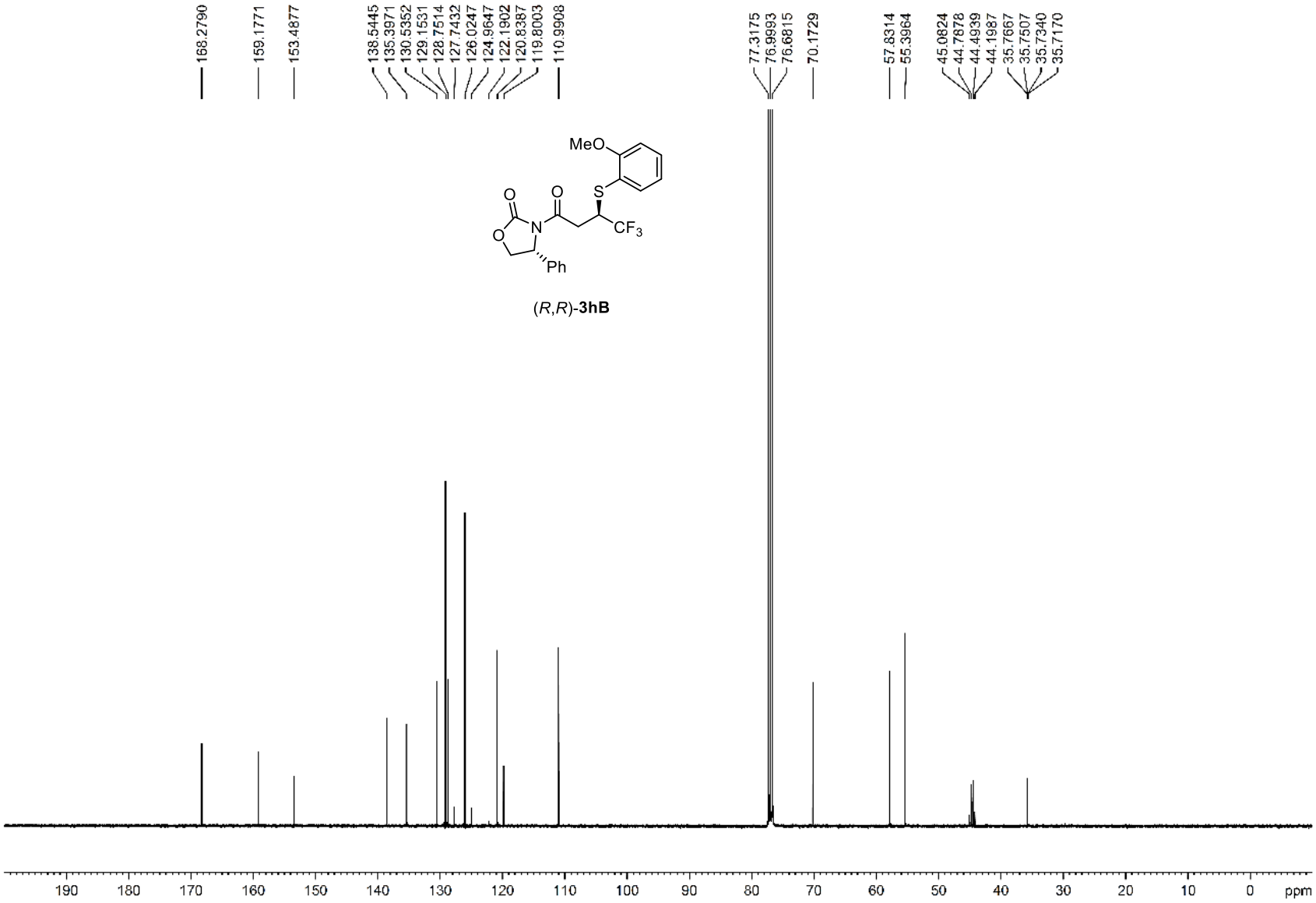

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.2083 w/v% |
| Factor | 1.0000 |
| Blank | 0.0002 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -62.9148 |
| S.D. | 0.7617 |
| C.V. | -1.2106 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 86( 1/ 5) | -62.319 | 23.2 |
| 2 | 86( 2/ 5) | -63.726 | 23.2 |
| 3 | 86( 3/ 5) | -62.153 | 23.2 |
| 4 | 86( 4/ 5) | -62.650 | 23.2 |
| 5 | 86( 5/ 5) | -63.726 | 23.2 |

$^1$H NMR Spectrum of (*R*,*R*)-**3hB** (400 MHz, $CDCl_3$)



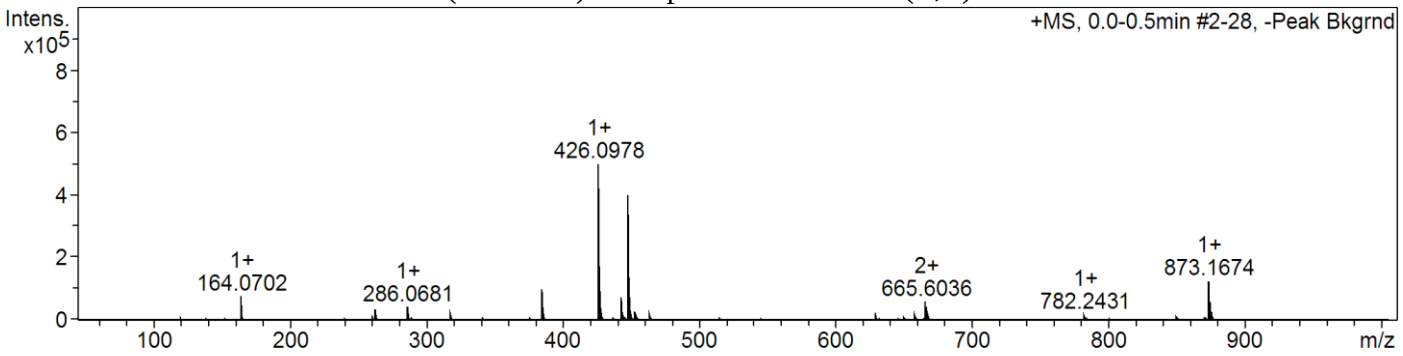
$^{13}$C NMR Spectrum of (*R*,*R*)-**3hB** (100 MHz, $CDCl_3$)




(*R*,*R*)-**3hB**

$^{19}$F NMR Spectrum of (*R*,*R*)-**3hB** (376 MHz, $CDCl_3$)

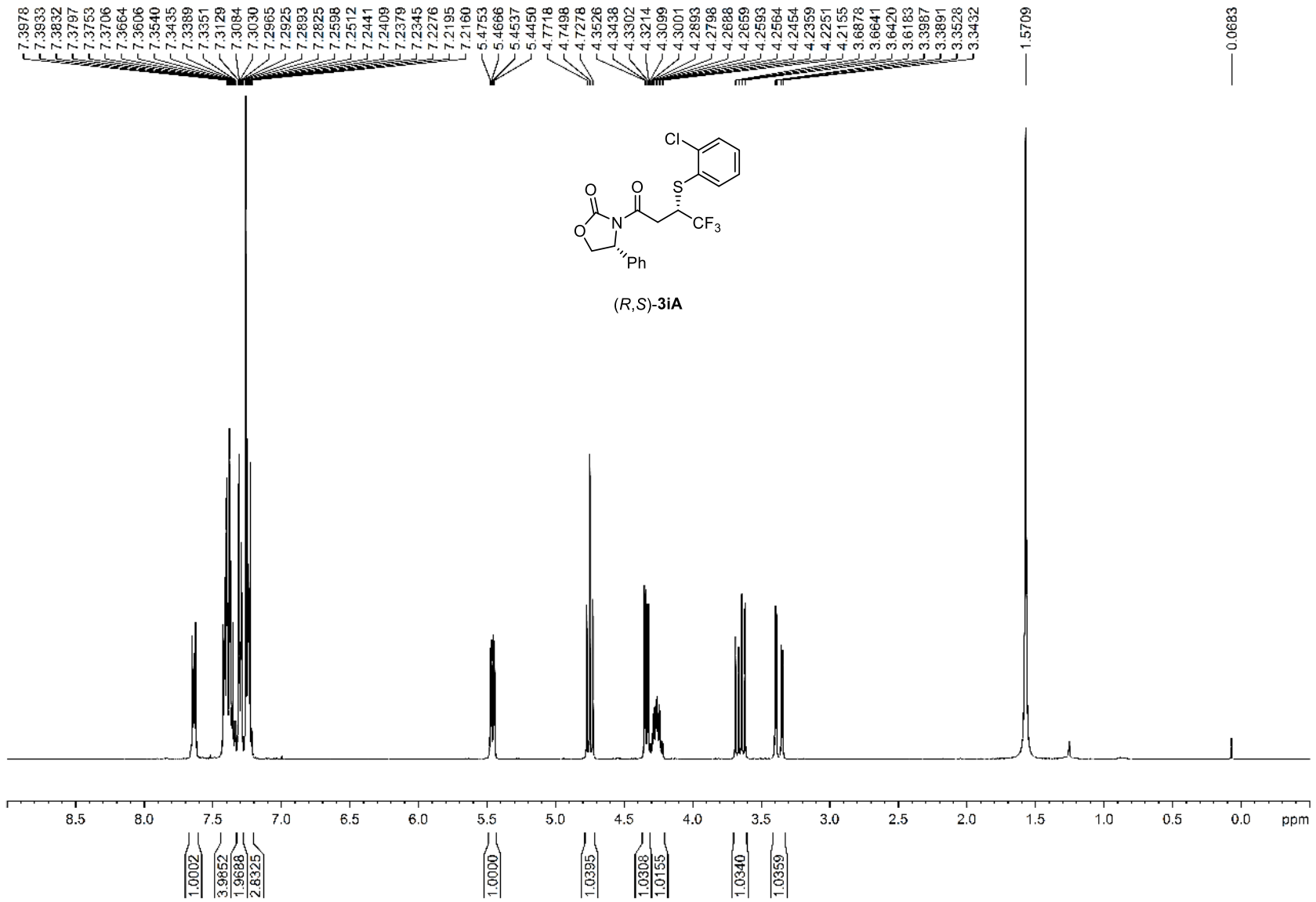
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3hB**



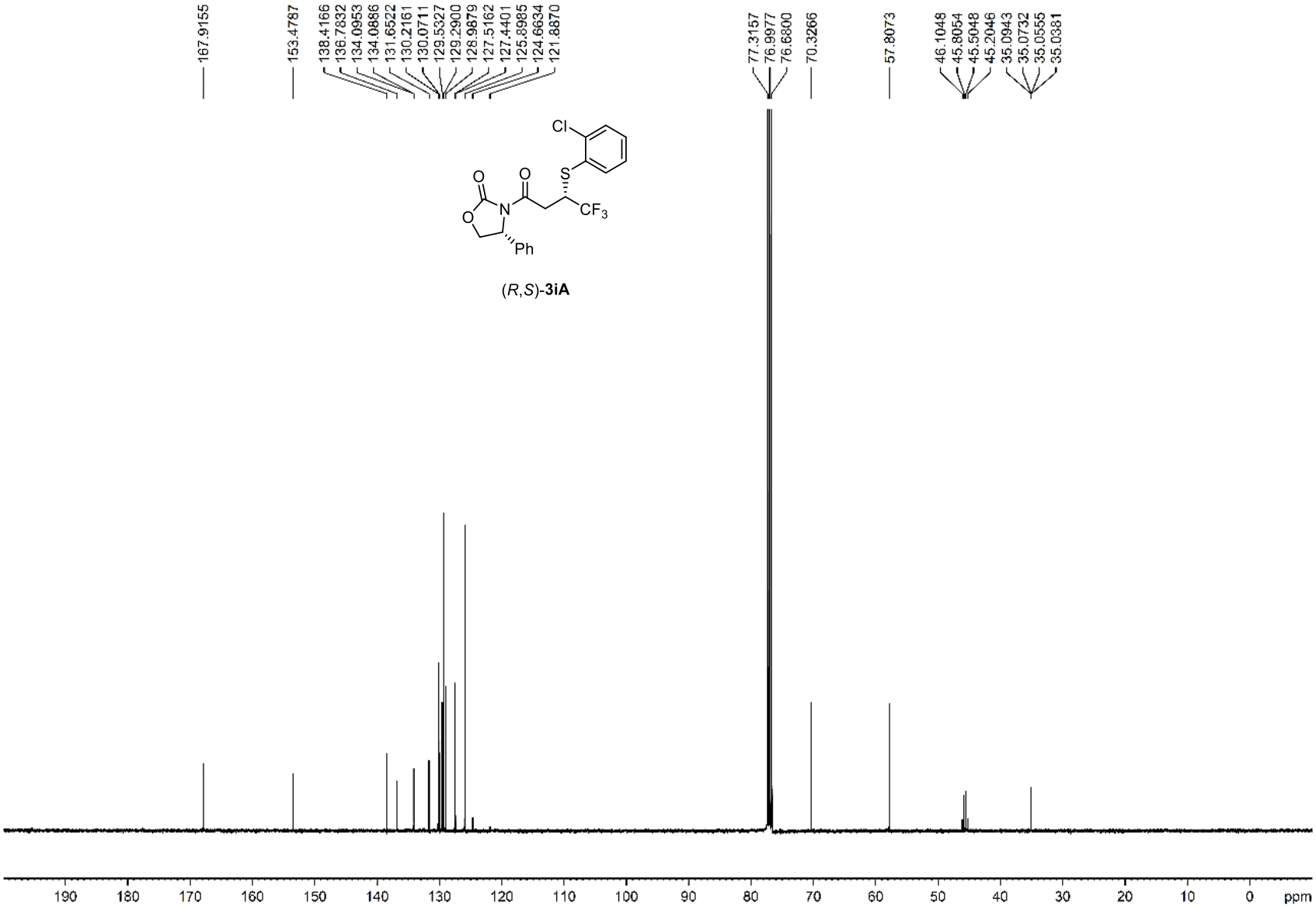

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.1800 w/v% |
| Factor | 1.0000 |
| Blank | 0.0002 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -78.2712 |
| S.D. | 0.7688 |
| C.V. | -0.9822 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 96( 1/ 5) | -78.136 | 23.7 |
| 2 | 96( 2/ 5) | -77.034 | 23.7 |
| 3 | 96( 3/ 5) | -78.390 | 23.7 |
| 4 | 96( 4/ 5) | -78.983 | 23.7 |
| 5 | 96( 5/ 5) | -78.814 | 23.7 |

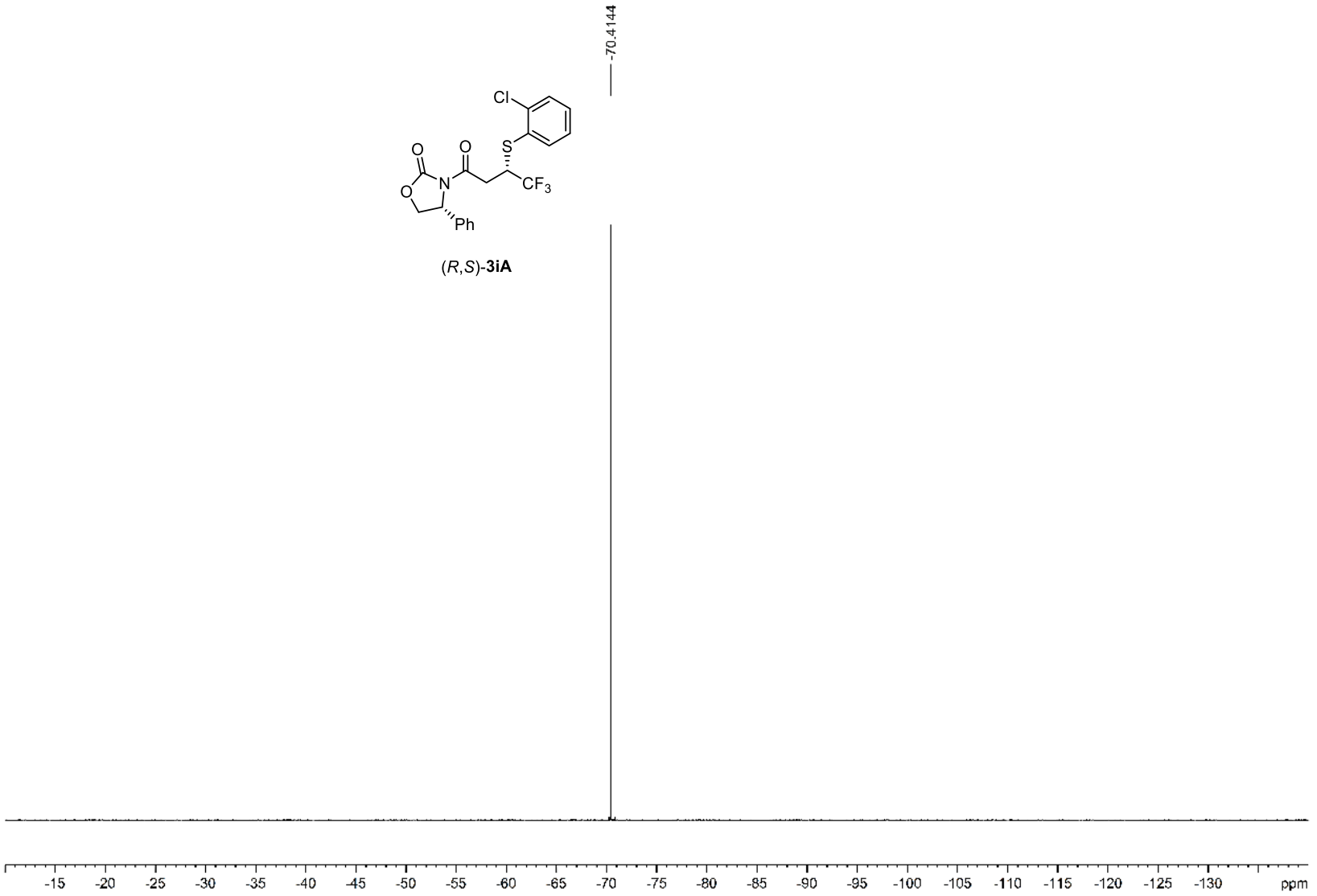
$^1$H NMR Spectrum of (*R*,*S*)-**3iA** (400 MHz, $CDCl_3$)



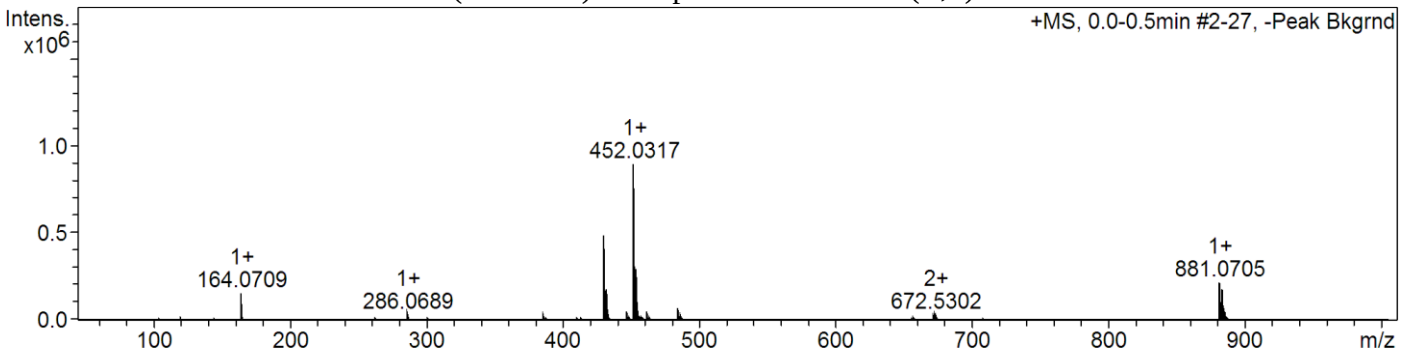
$^{13}$C NMR Spectrum of (*R*,*S*)-**3iA** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3iA** (470 MHz, $CDCl_3$)



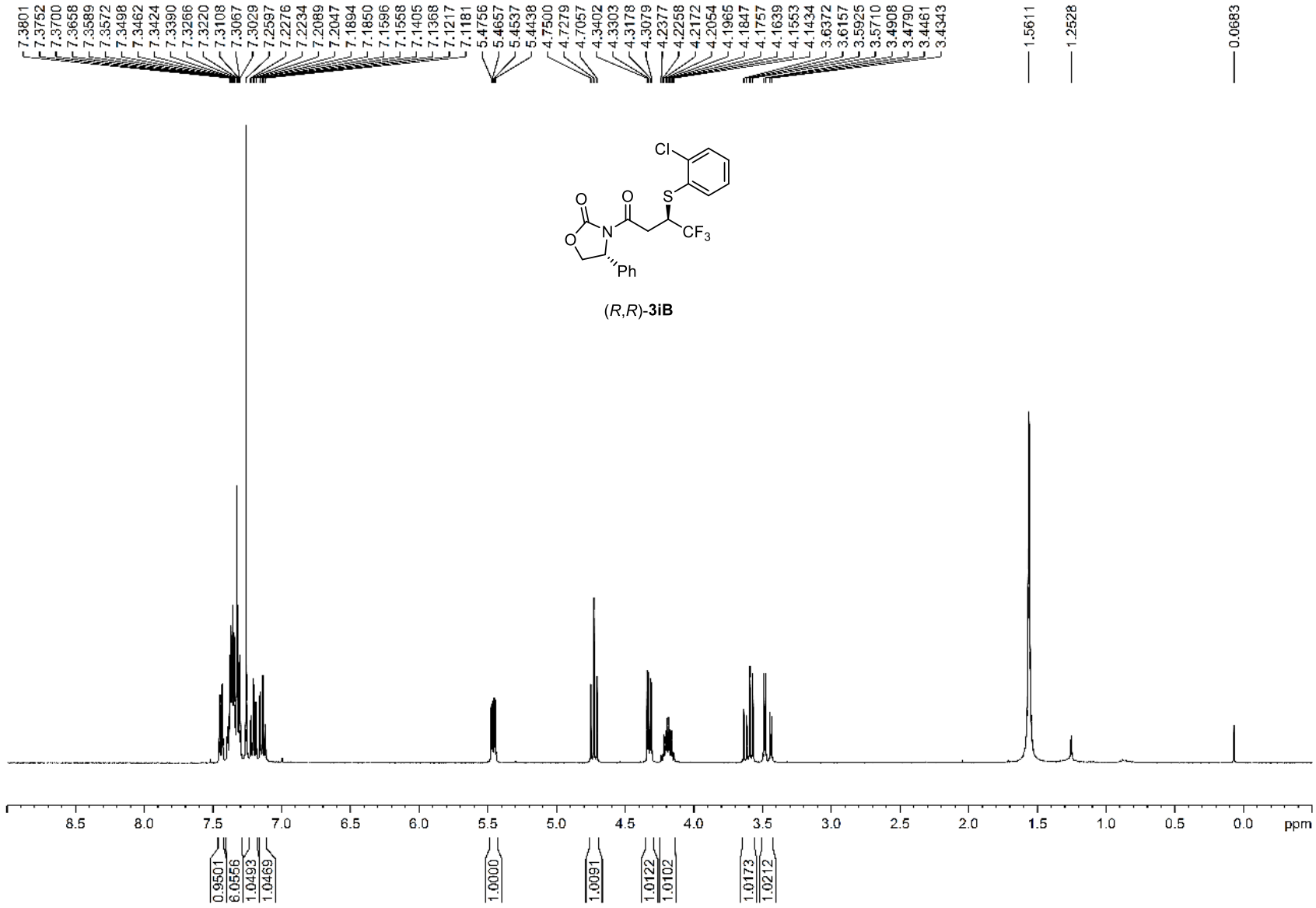
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3iA**




| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.1600 w/v% |
| Factor | 1.0000 |
| Blank | 0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -63.9828 |
| S.D. | 0.4413 |
| C.V. | -0.6897 % |

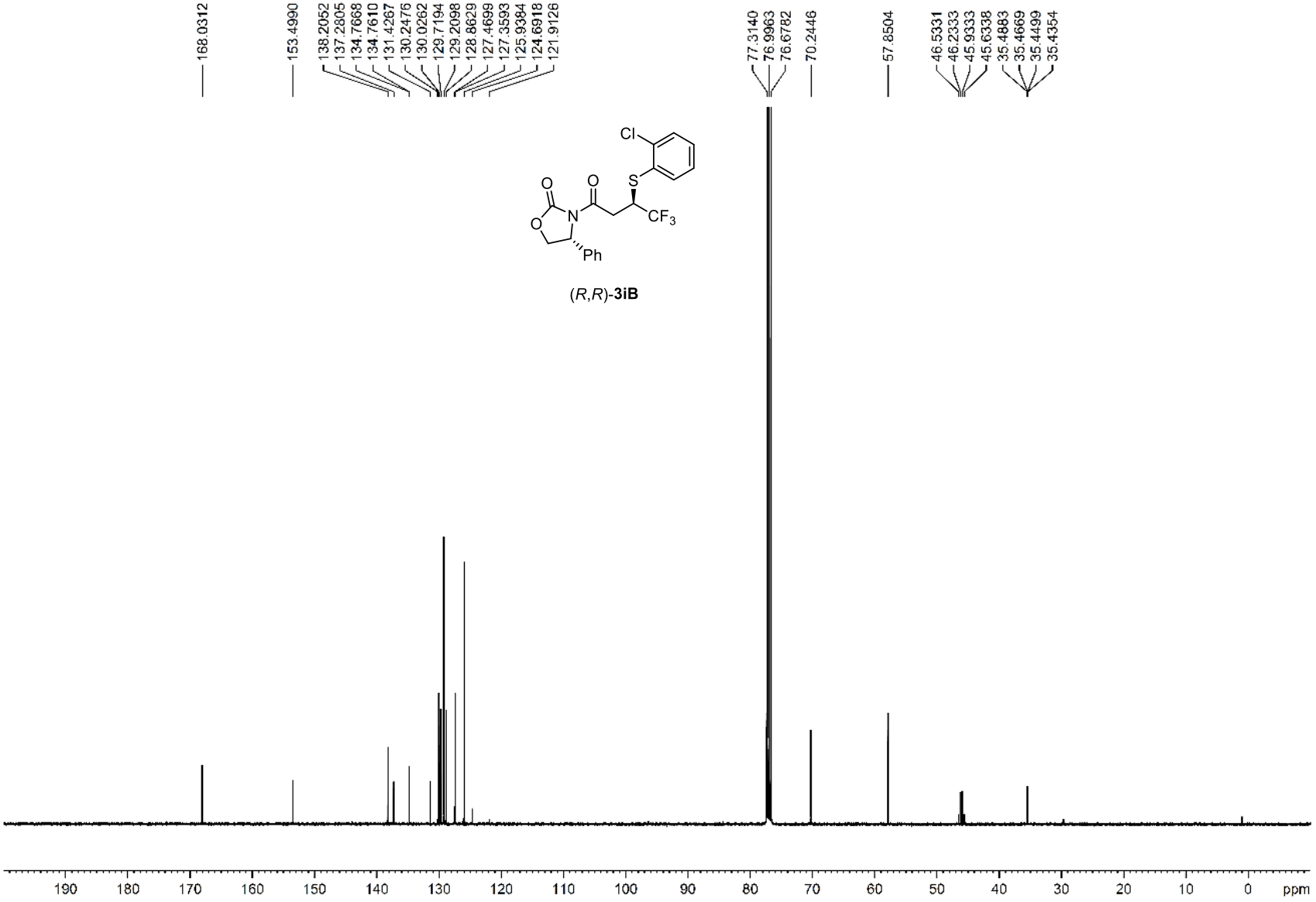
| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 45( 1/ 5) | -64.310 | 26.8 |
| 2 | 45( 2/ 5) | -63.362 | 26.8 |
| 3 | 45( 3/ 5) | -63.793 | 26.8 |
| 4 | 45( 4/ 5) | -64.483 | 26.8 |
| 5 | 45( 5/ 5) | -63.966 | 26.8 |

$^1$H NMR Spectrum of (*R*,*R*)-**3iB** (400 MHz, $CDCl_3$)

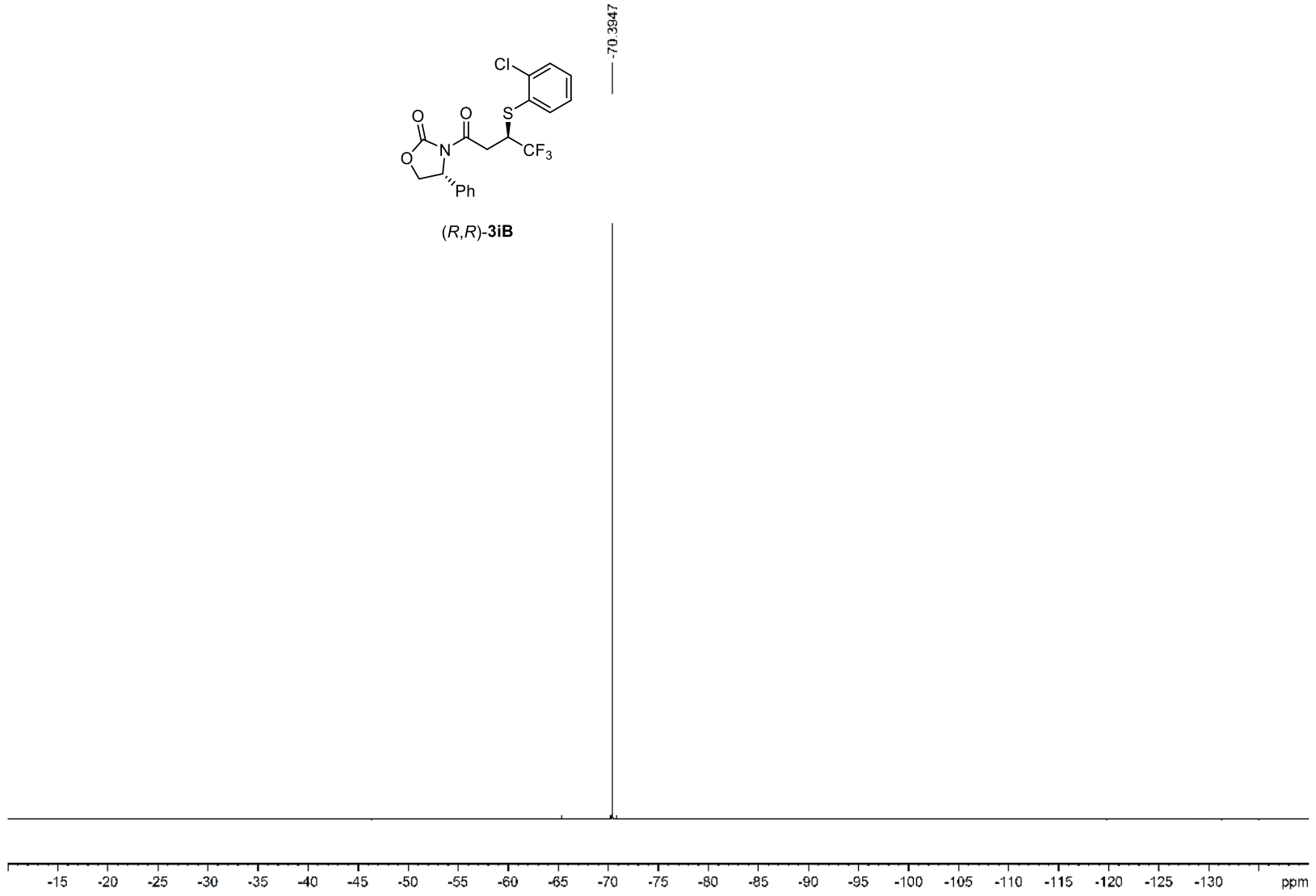



(*R*,*R*)-**3iB**

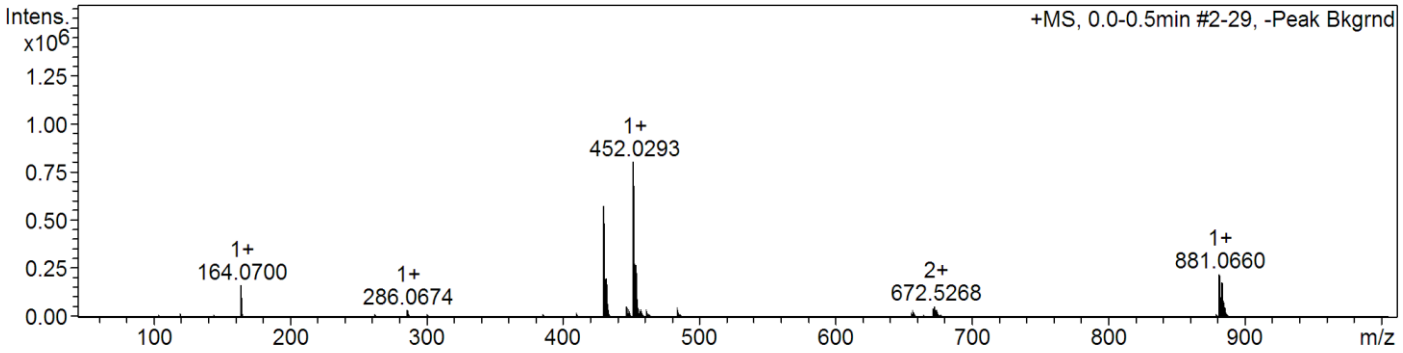
$^{13}$C NMR Spectrum of (*R*,*R*)-**3iB** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3iB** (470 MHz, $CDCl_3$)



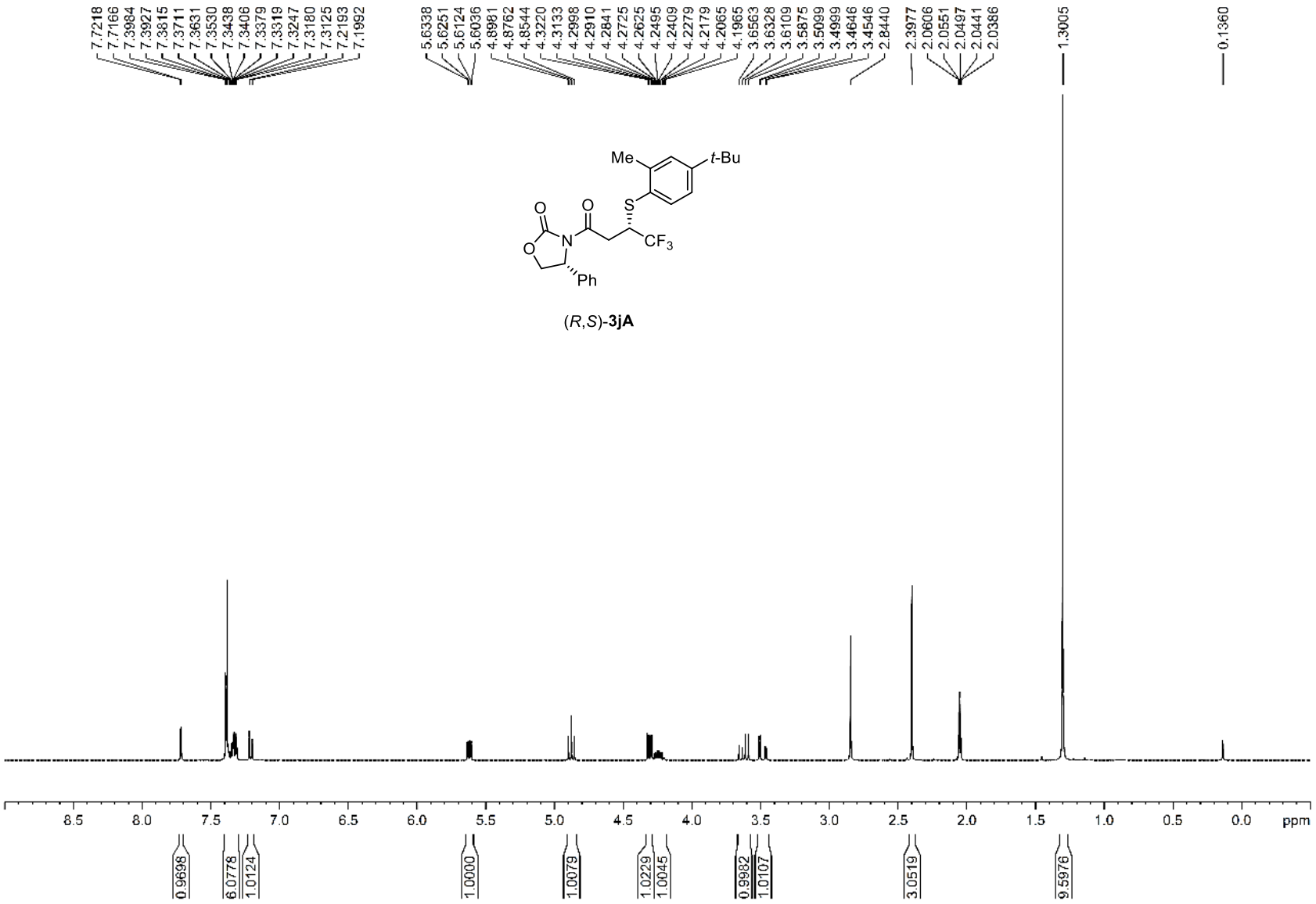
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3iB**




| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0455 w/v% |
| Factor | 1.0000 |
| Blank | 0.0002 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -79.3687 |
| S.D. | 0.7202 |
| C.V. | -0.9074 % |

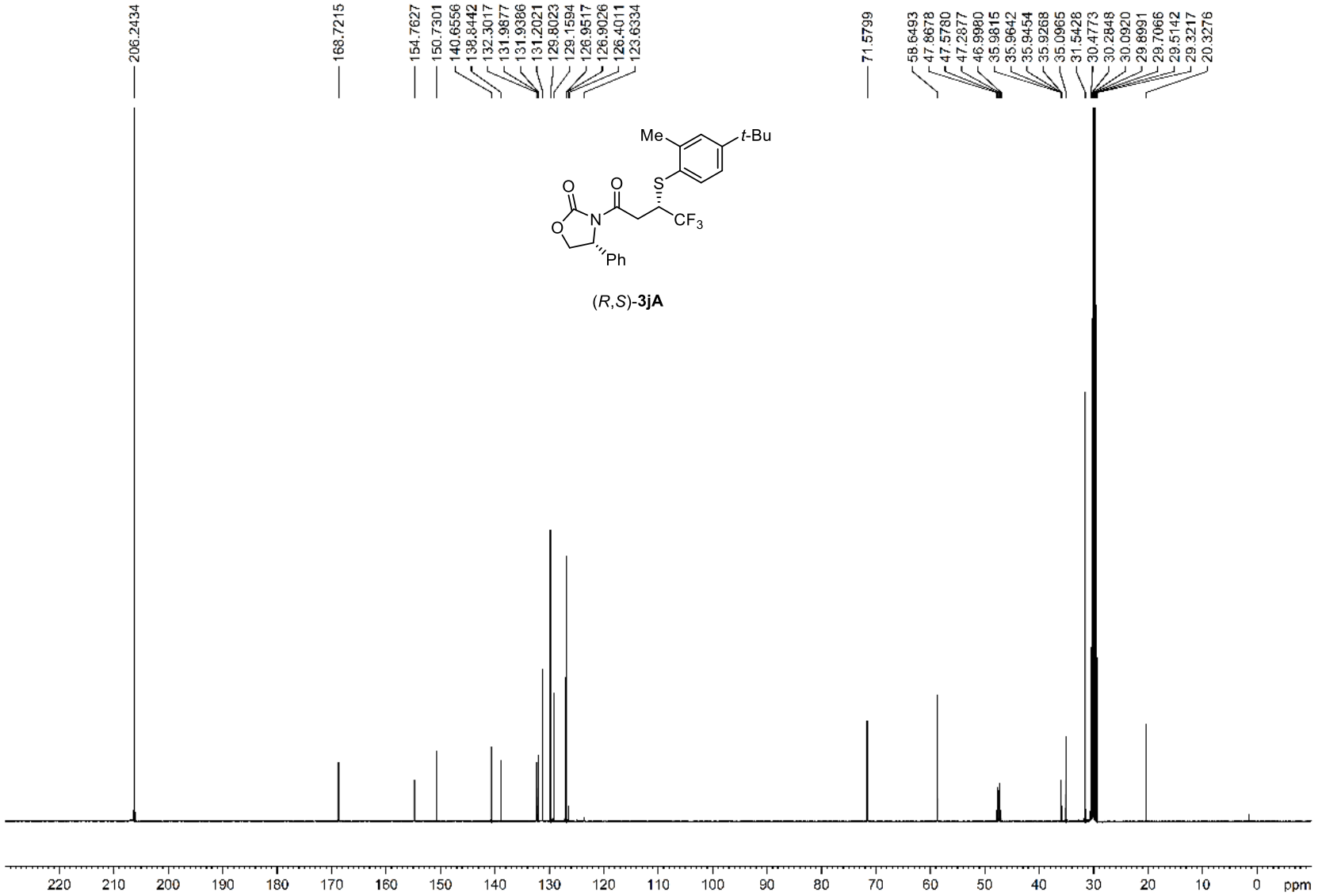
| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 37( 1/ 5) | -79.484 | 24.0 |
| 2 | 37( 2/ 5) | -78.336 | 24.0 |
| 3 | 37( 3/ 5) | -79.866 | 24.0 |
| 4 | 37( 4/ 5) | -80.153 | 24.0 |
| 5 | 37( 5/ 5) | -79.005 | 24.0 |

$^1$H NMR Spectrum of (*R*,*S*)-**3jA** (400 MHz, acetone-$d_6$)

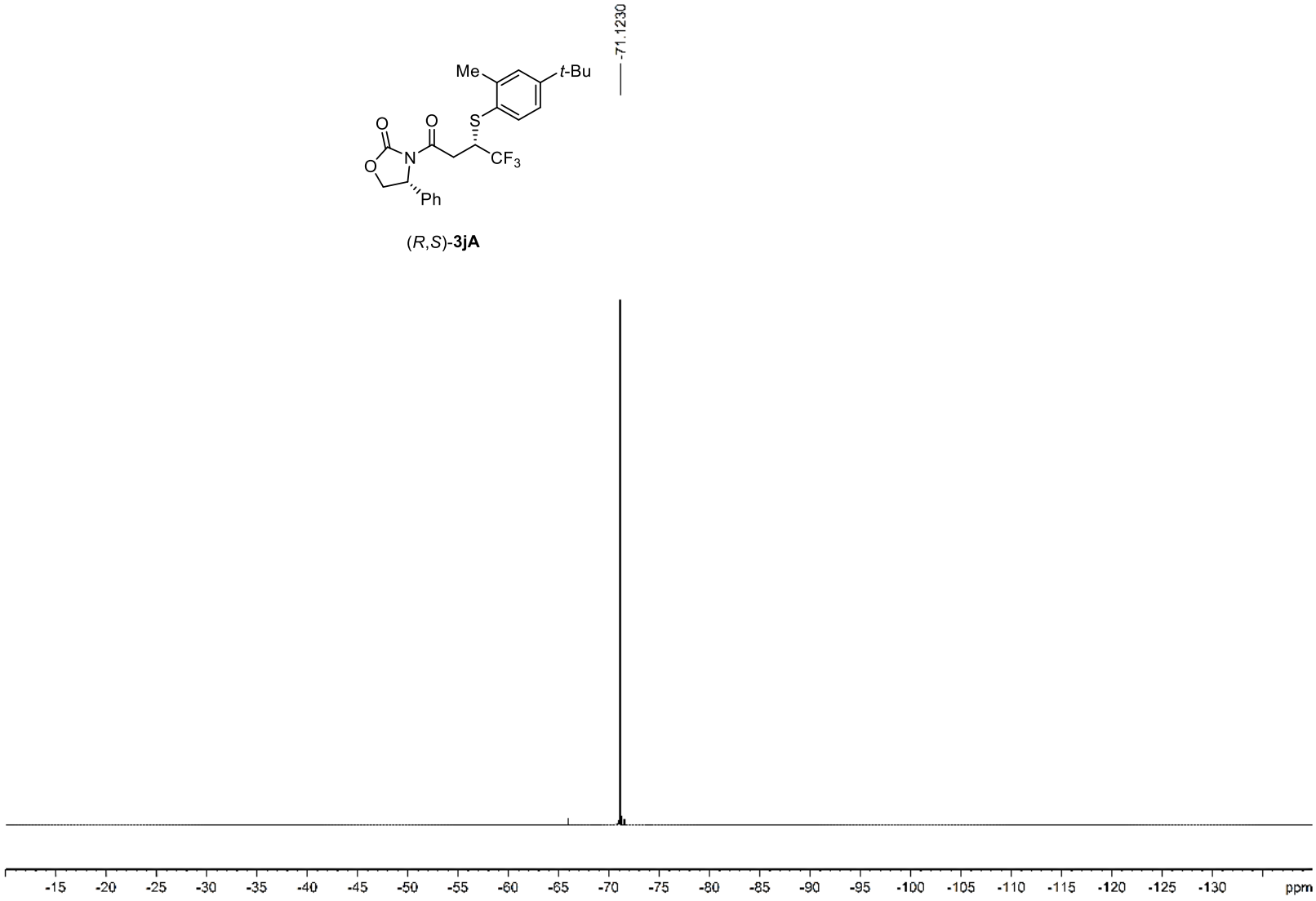



(*R*,*S*)-**3jA**

$^{13}$C NMR Spectrum of (*R*,*S*)-**3jA** (100 MHz, acetone-$d_6$)

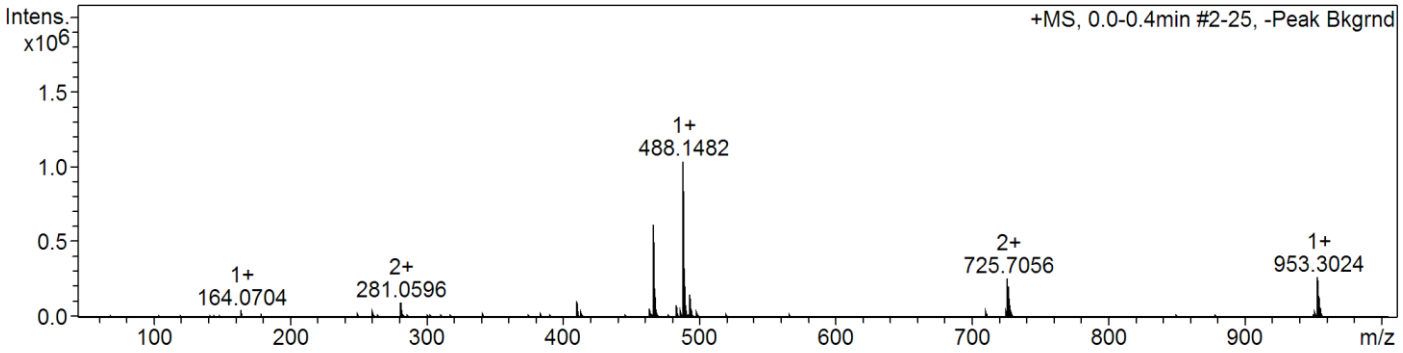


$^{19}$F NMR Spectrum of (*R*,*S*)-**3jA** (470 MHz, acetone-$d_6$)




(*R*,*S*)-**3jA**

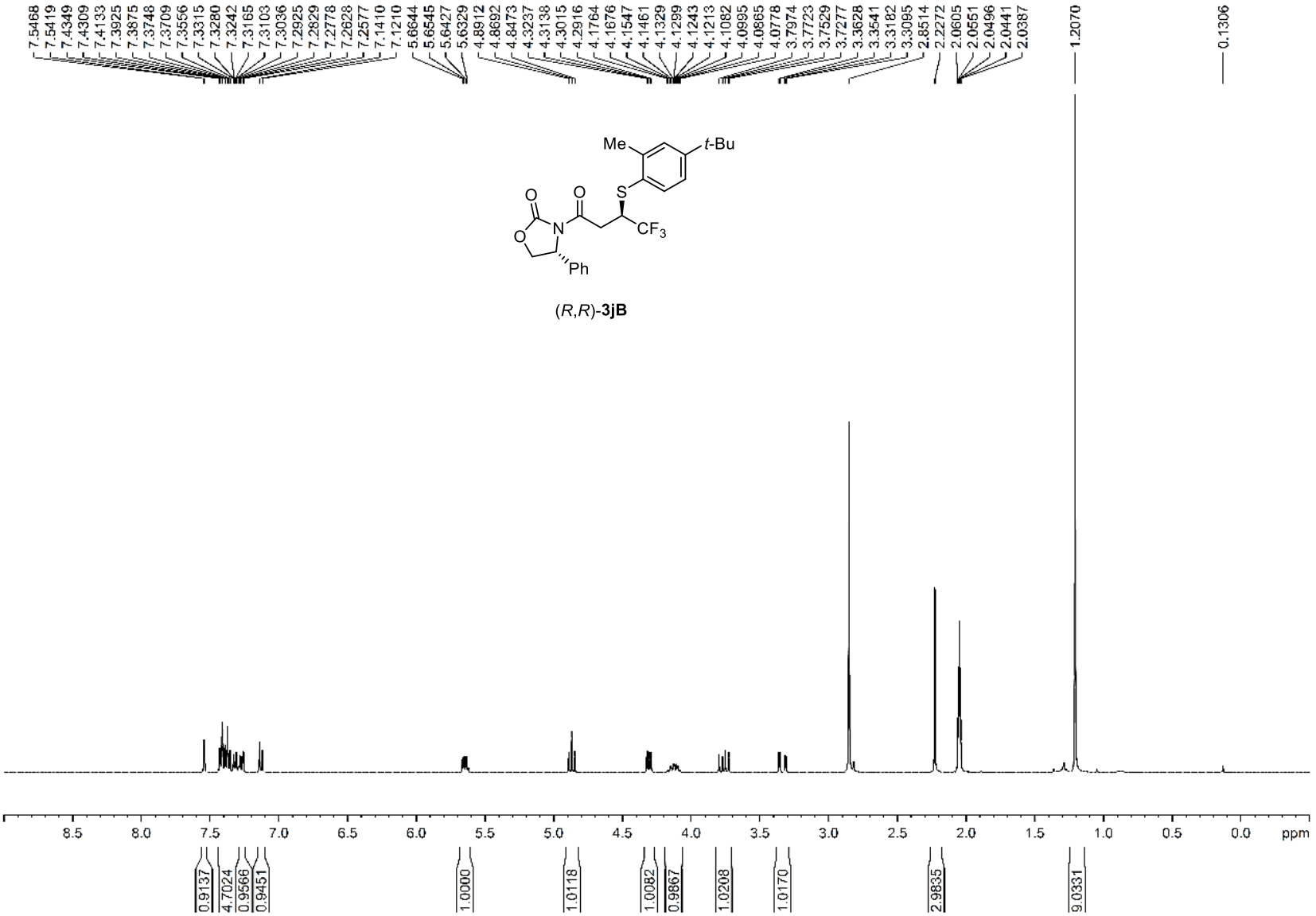
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3jA**



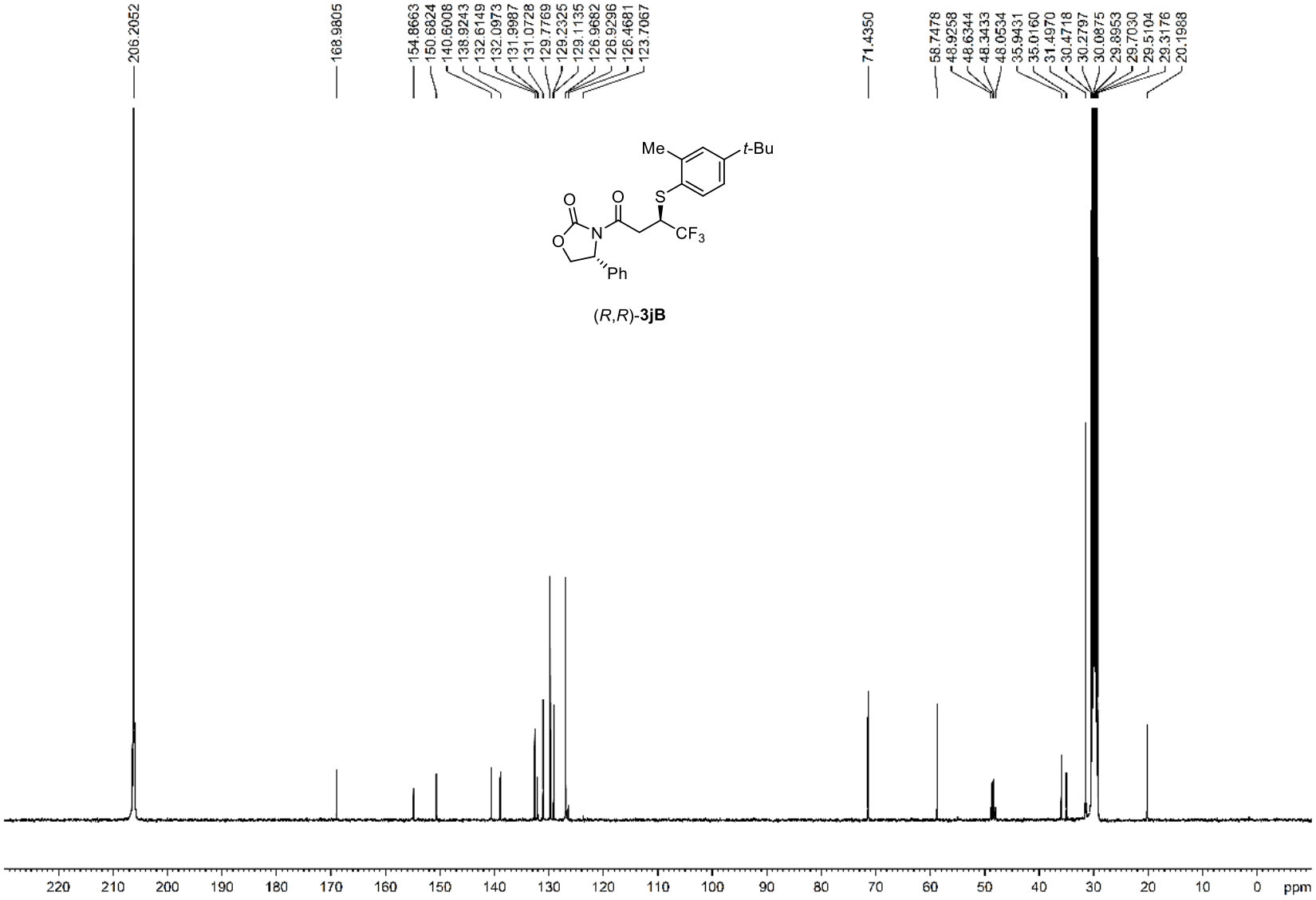

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.1200 w/v% |
| Factor | 1.0000 |
| Blank | -0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -46.3393 |
| S.D. | 0.6469 |
| C.V. | -1.3961 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 78( 1/ 5) | -46.875 | 24.6 |
| 2 | 78( 2/ 5) | -47.054 | 24.6 |
| 3 | 78( 3/ 5) | -46.250 | 24.6 |
| 4 | 78( 4/ 5) | -45.446 | 24.6 |
| 5 | 78( 5/ 5) | -46.071 | 24.6 |

$^1$H NMR Spectrum of (*R*,*R*)-**3jB** (400 MHz, acetone-$d_6$)

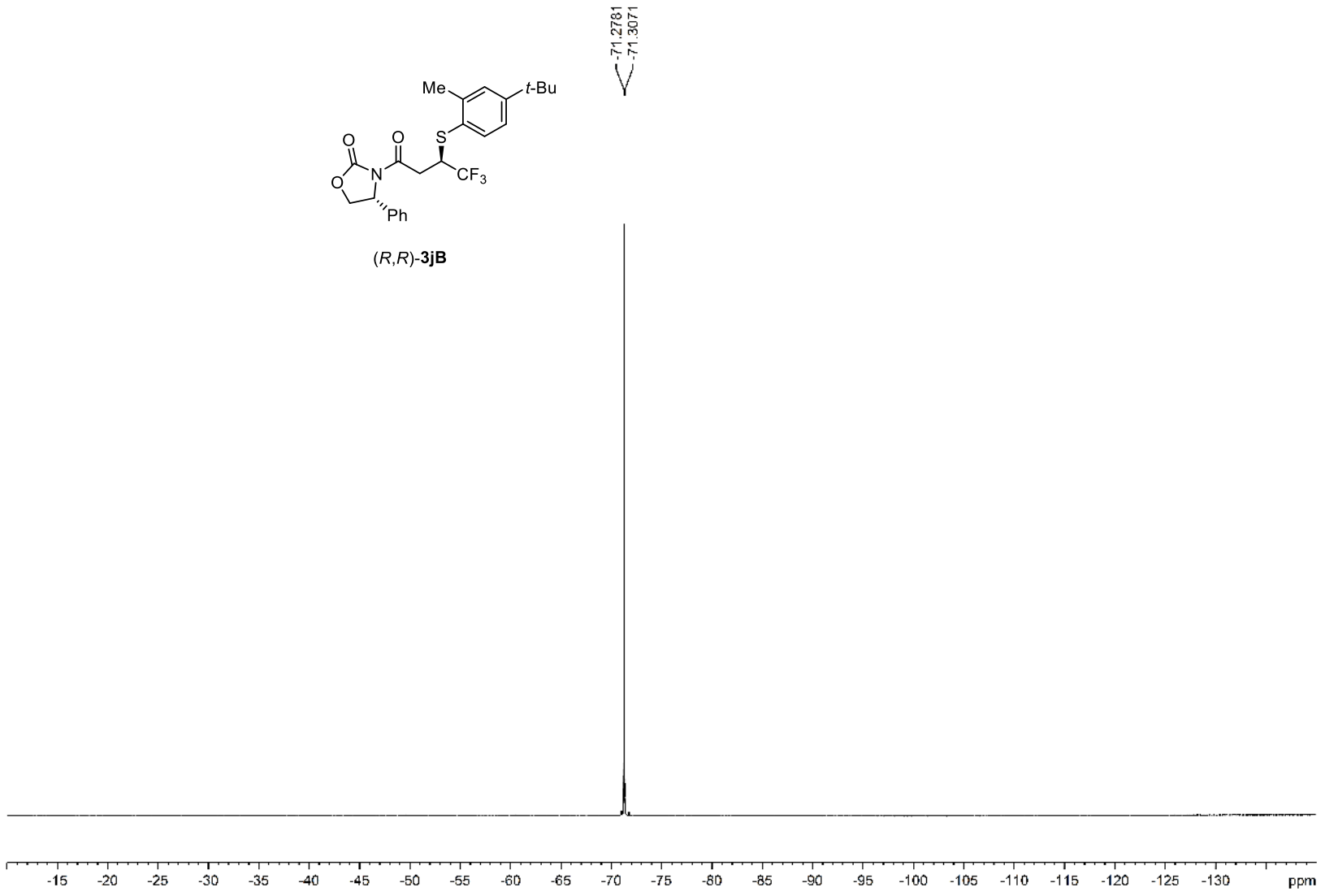


$^{13}$C NMR Spectrum of (*R*,*R*)-**3jB** (100 MHz, acetone-$d_6$)

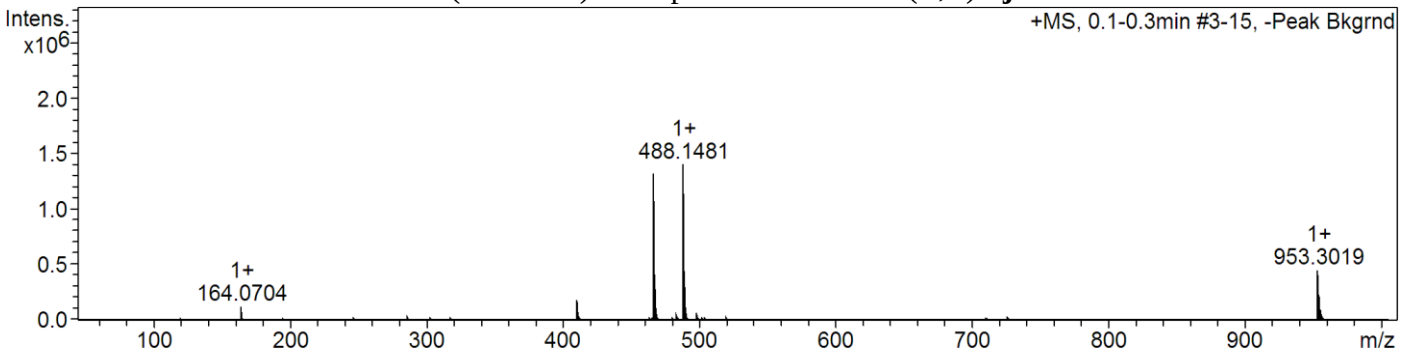



(*R*,*R*)-**3jB**

$^{19}$F NMR Spectrum of (*R*,*R*)-**3jB** (376 MHz, acetone-$d_6$)



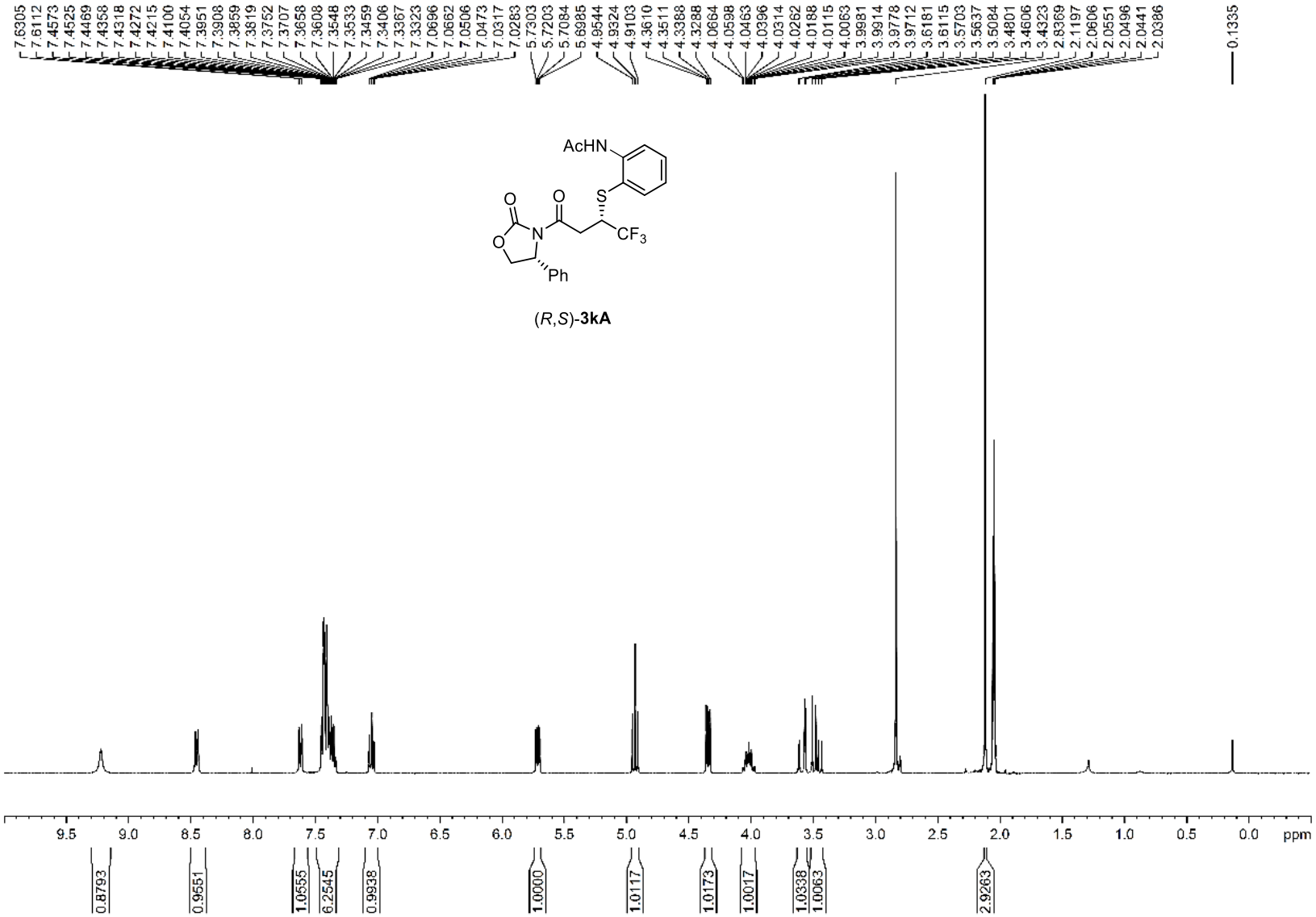
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3jB**



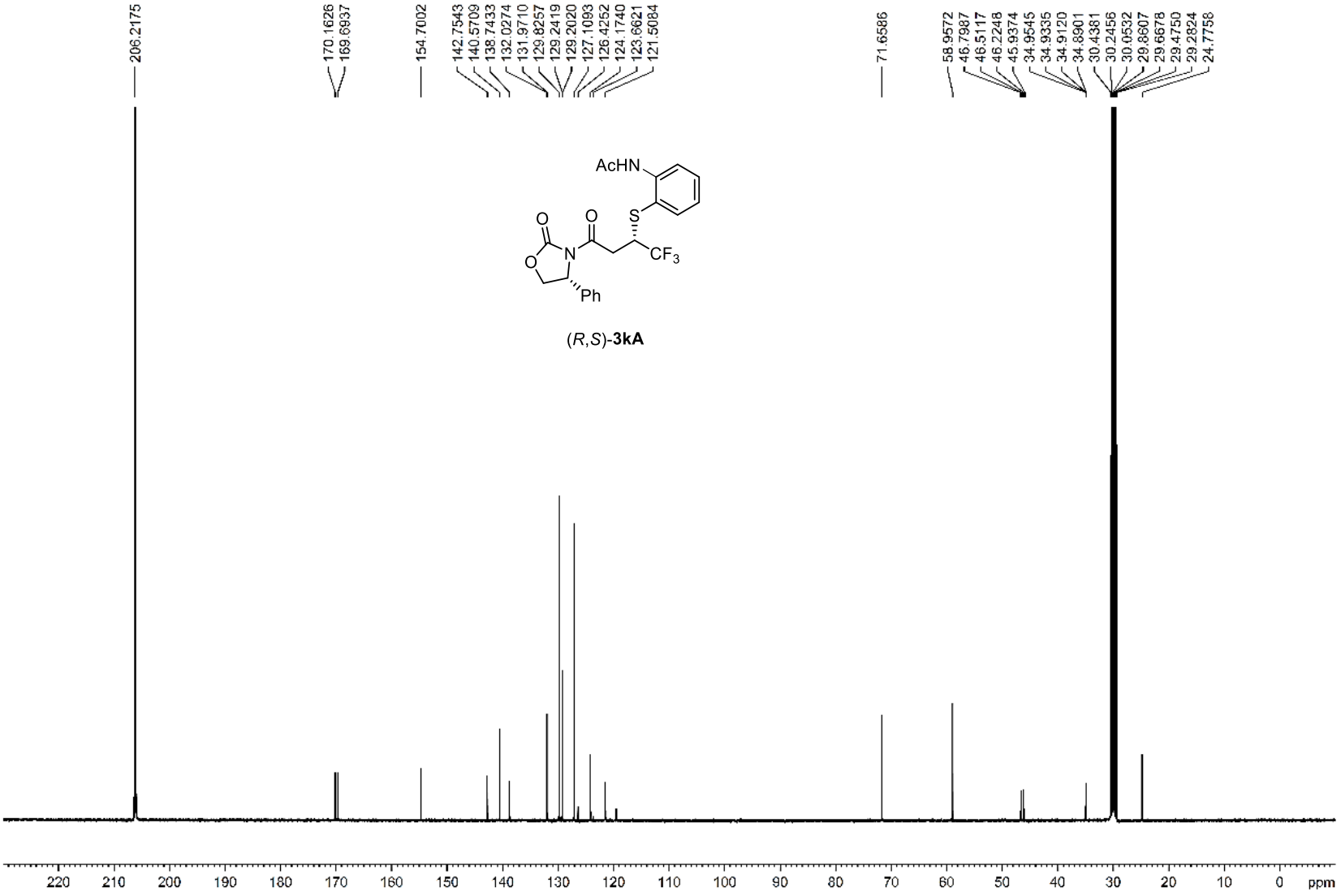

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0800 w/v% |
| Factor | 1.0000 |
| Blank | 0.0007 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -108.8704 |
| S.D. | 0.7619 |
| C.V. | -0.6998 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 109( 1/ 5) | -108.056 | 22.7 |
| 2 | 109( 2/ 5) | -109.630 | 22.7 |
| 3 | 109( 3/ 5) | -108.333 | 22.7 |
| 4 | 109( 4/ 5) | -108.611 | 22.7 |
| 5 | 109( 5/ 5) | -109.722 | 22.6 |

$^1$H NMR Spectrum of (*R*,*S*)-**3kA** (400 MHz, acetone-$d_6$)

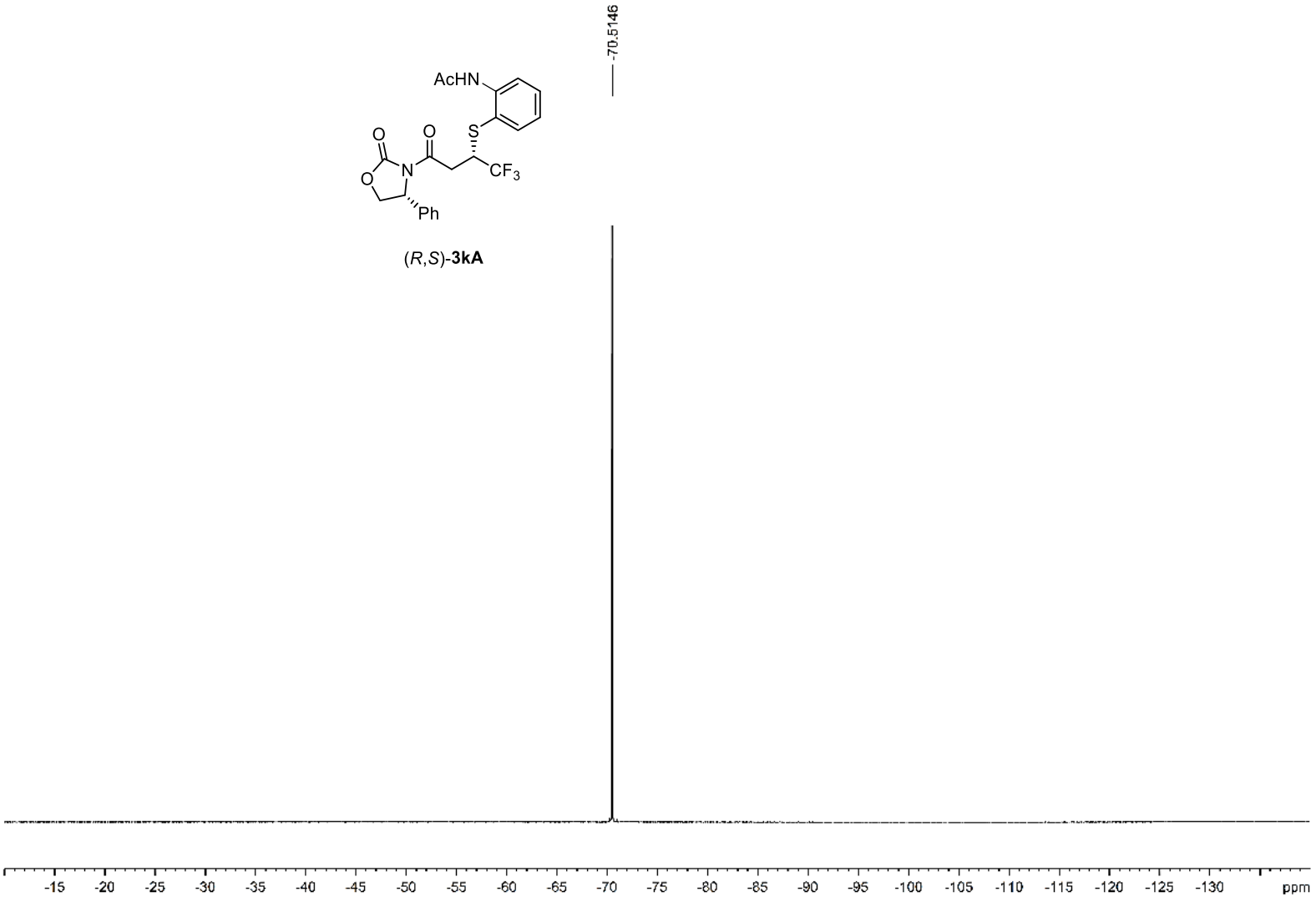


$^{13}$C NMR Spectrum of (*R*,*S*)-**3kA** (100 MHz, acetone-$d_6$)

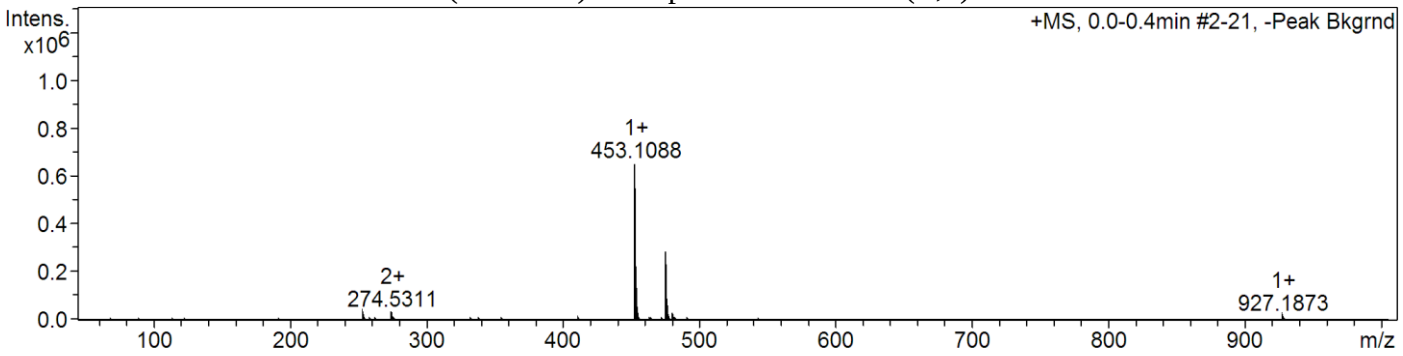



(*R*,*S*)-**3kA**

$^{19}$F NMR Spectrum of (*R*,*S*)-**3kA** (376 MHz, acetone-$d_6$)



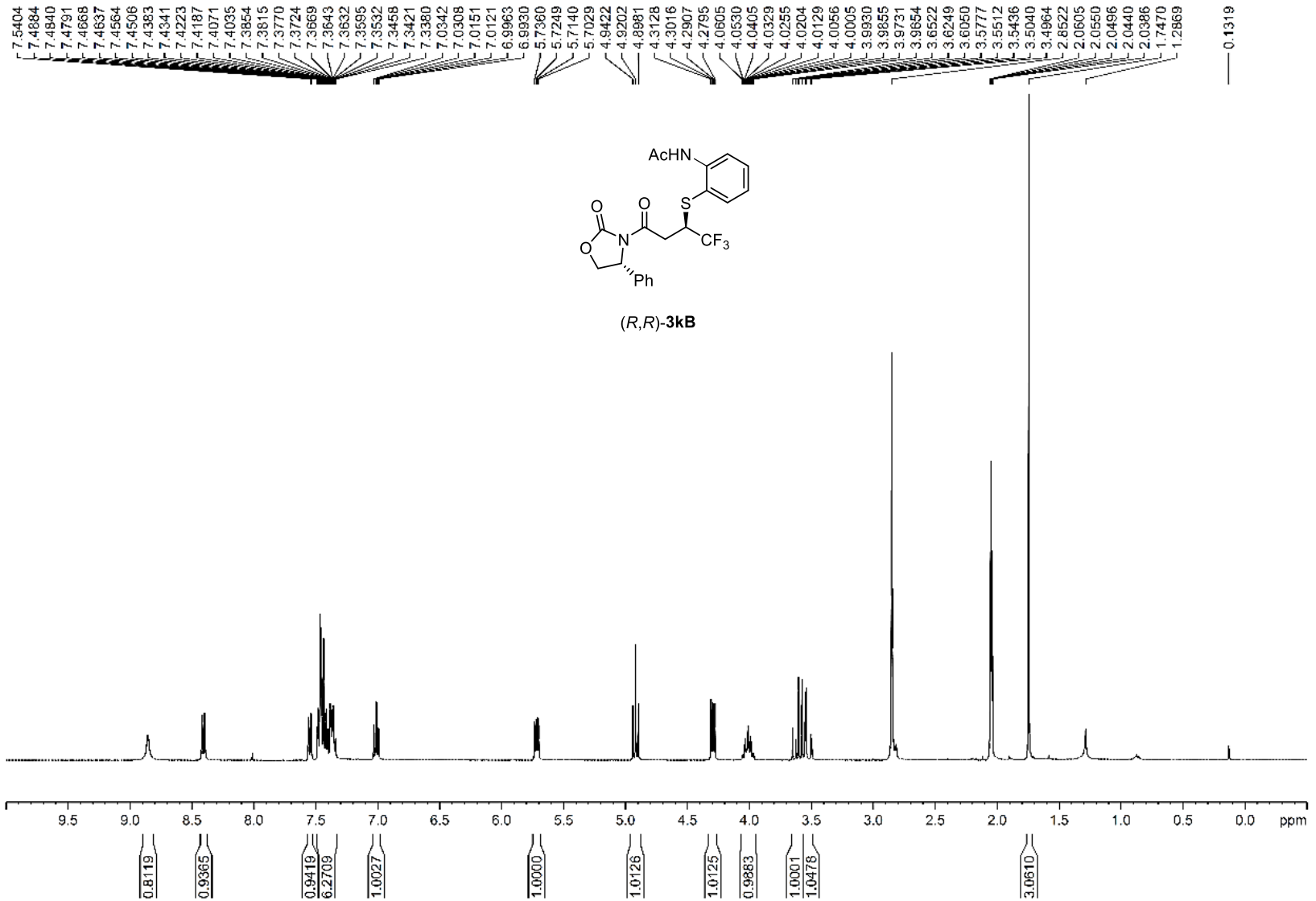
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3kA**



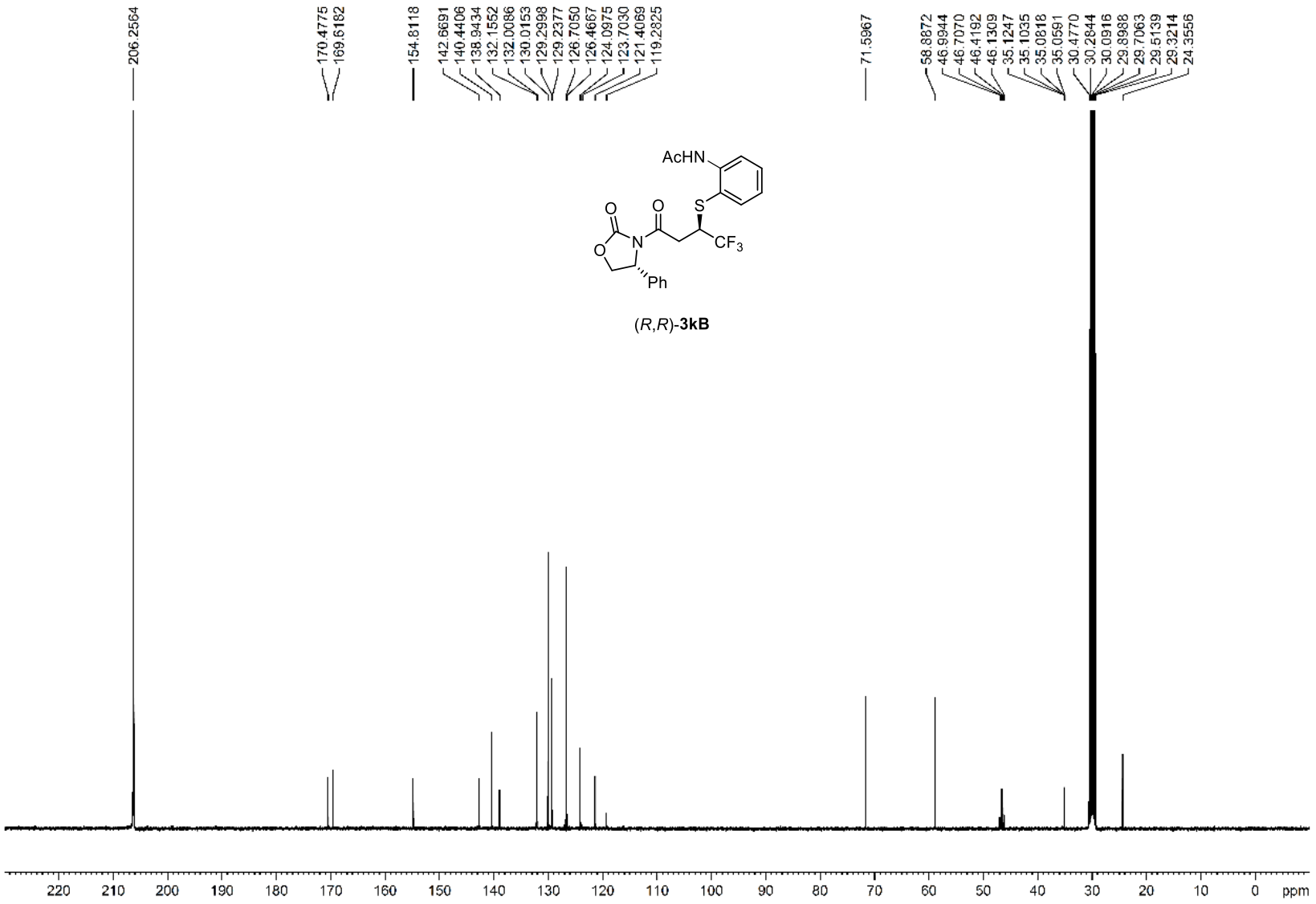

| | |
|---|---|
| Comment | CH2Cl2 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.2500 w/v% |
| Factor | 1.0000 |
| Blank | 0.0005 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -111.0080 |
| S.D. | 0.3129 |
| C.V. | -0.2819 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 104( 1/ 5) | -111.440 | 22.7 |
| 2 | 104( 2/ 5) | -111.200 | 22.8 |
| 3 | 104( 3/ 5) | -110.960 | 22.8 |
| 4 | 104( 4/ 5) | -110.720 | 22.7 |
| 5 | 104( 5/ 5) | -110.720 | 22.7 |

$^1$H NMR Spectrum of (*R*,*R*)-**3kB** (400 MHz, acetone-$d_6$)

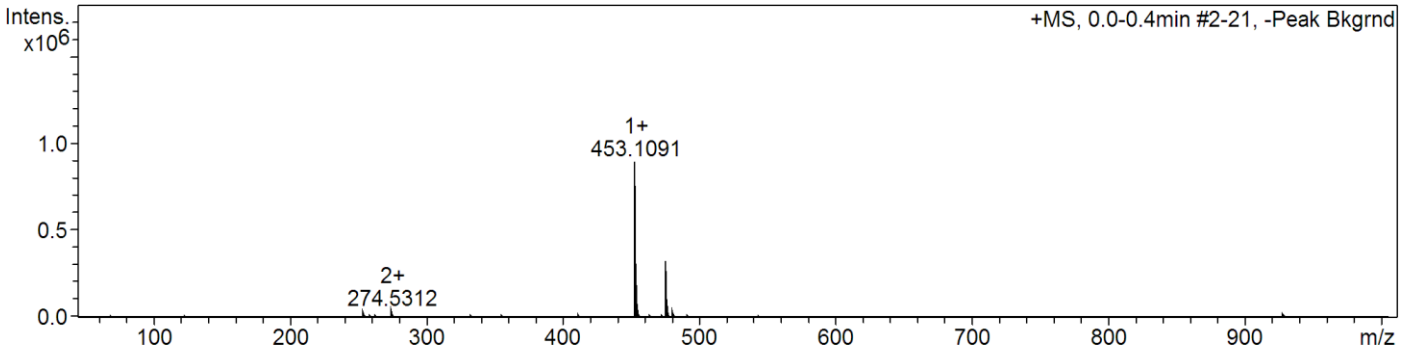


$^{13}$C NMR Spectrum of (*R*,*R*)-**3kB** (100 MHz, acetone-$d_6$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3kB** (376 MHz, acetone-$d_6$)

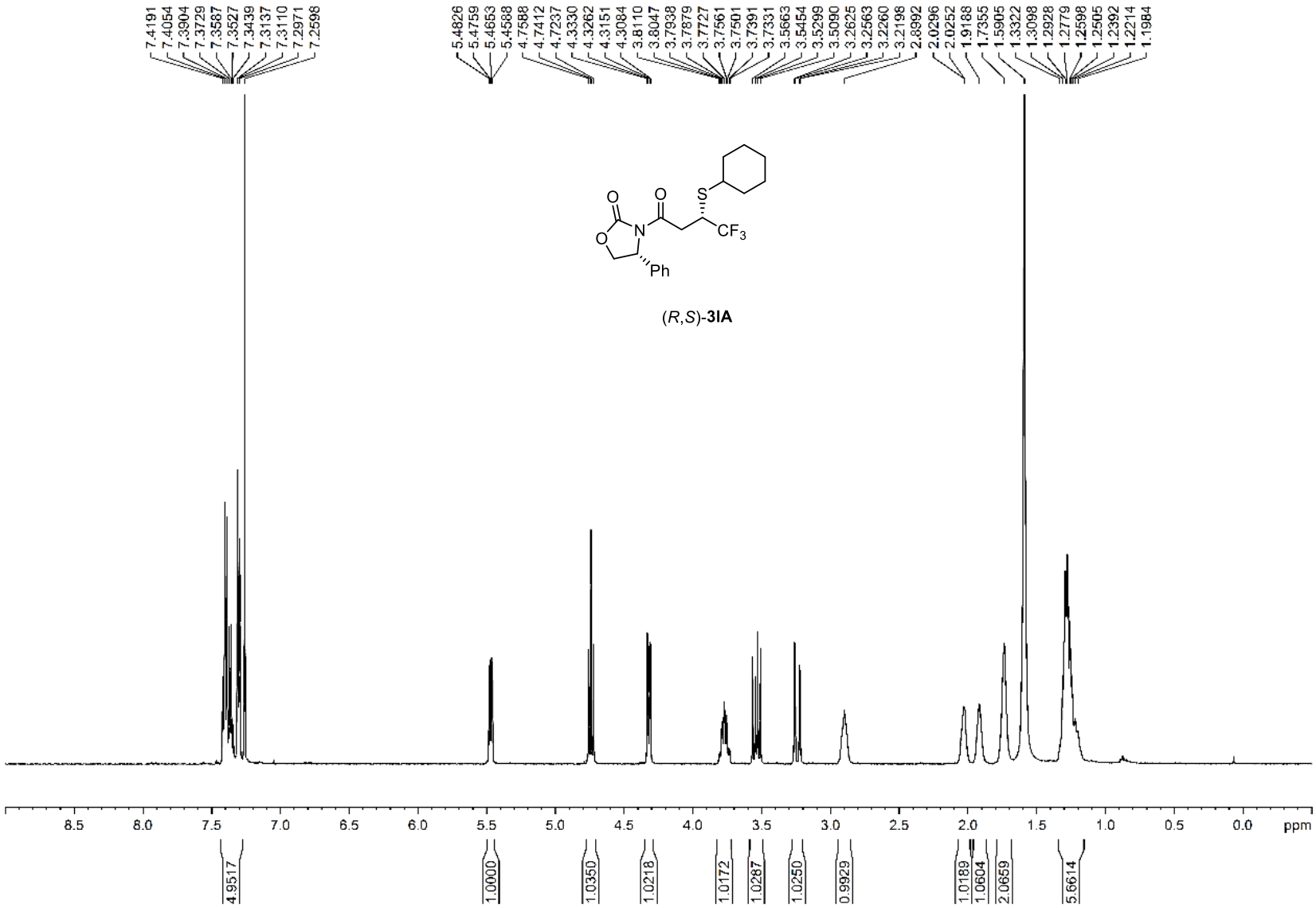
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3kB**



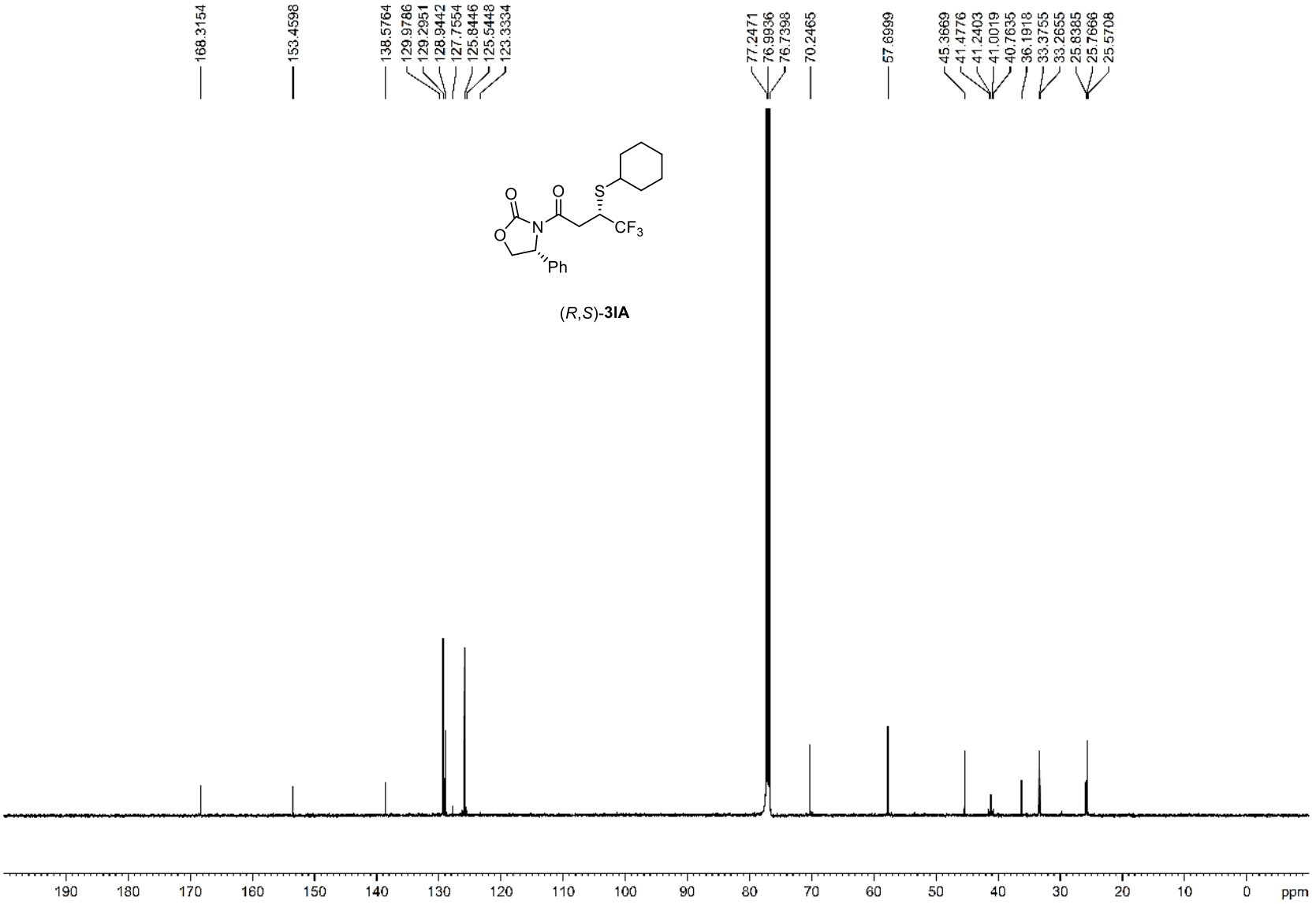

| | |
|---|---|
| Comment | CH2Cl2 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.2308 w/v% |
| Factor | 1.0000 |
| Blank | 0.0005 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -85.2454 |
| S.D. | 0.2895 |
| C.V. | -0.3397 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 112( 1/ 5) | -85.067 | 23.4 |
| 2 | 112( 2/ 5) | -85.635 | 23.4 |
| 3 | 112( 3/ 5) | -85.067 | 23.4 |
| 4 | 112( 4/ 5) | -84.985 | 23.4 |
| 5 | 112( 5/ 5) | -85.473 | 23.4 |

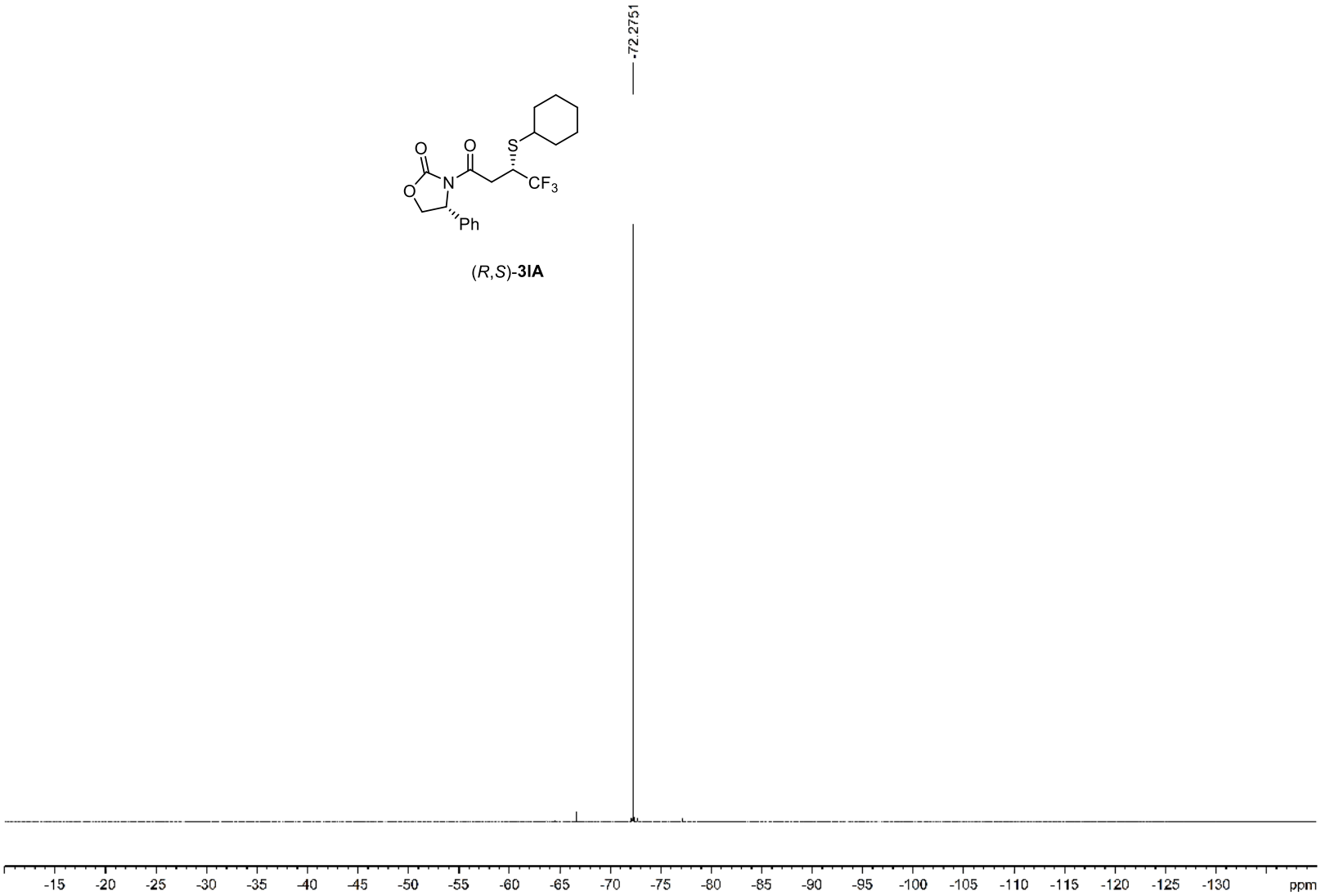
$^1$H NMR Spectrum of (*R*,*S*)-**3lA** (500 MHz, $CDCl_3$)



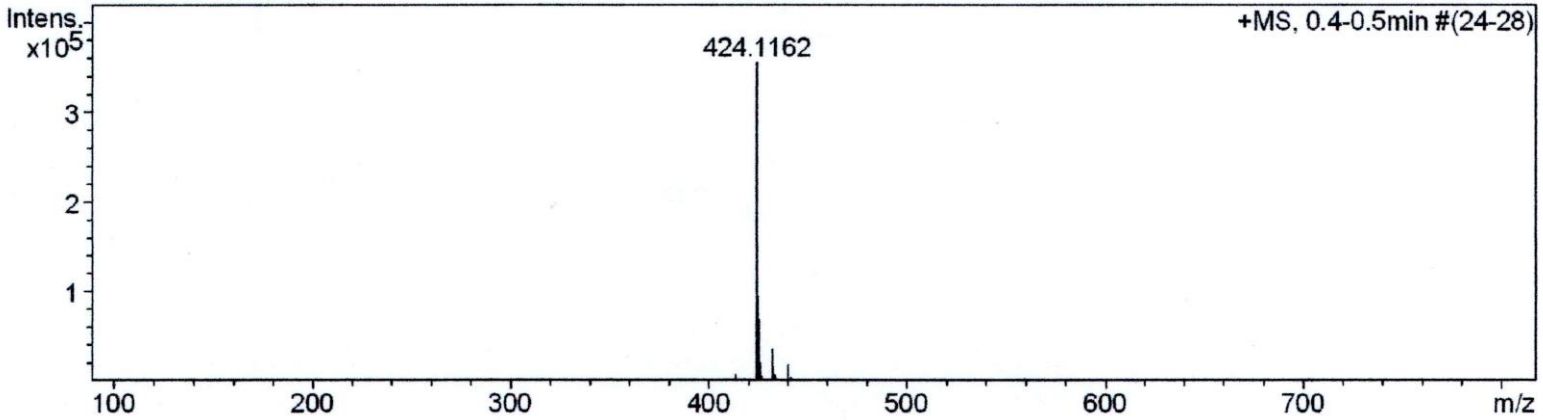
$^{13}$C NMR Spectrum of (*R*,*S*)-**3IA** (125 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3lA** (470 MHz, $CDCl_3$)



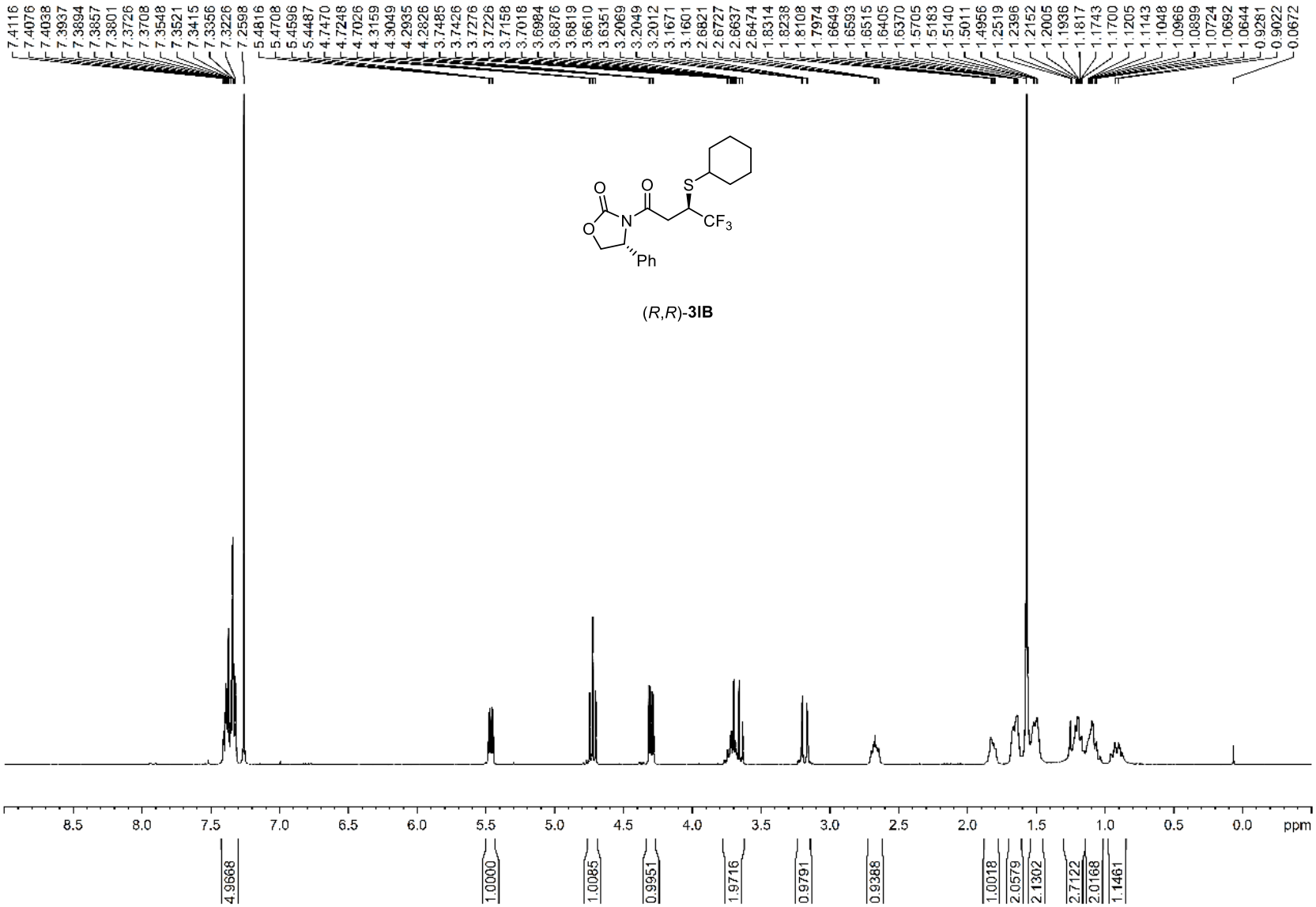
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3lA**




| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.5400 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -79.6753 |
| S.D. | 0.8986 |
| C.V. | -1.1278 % |

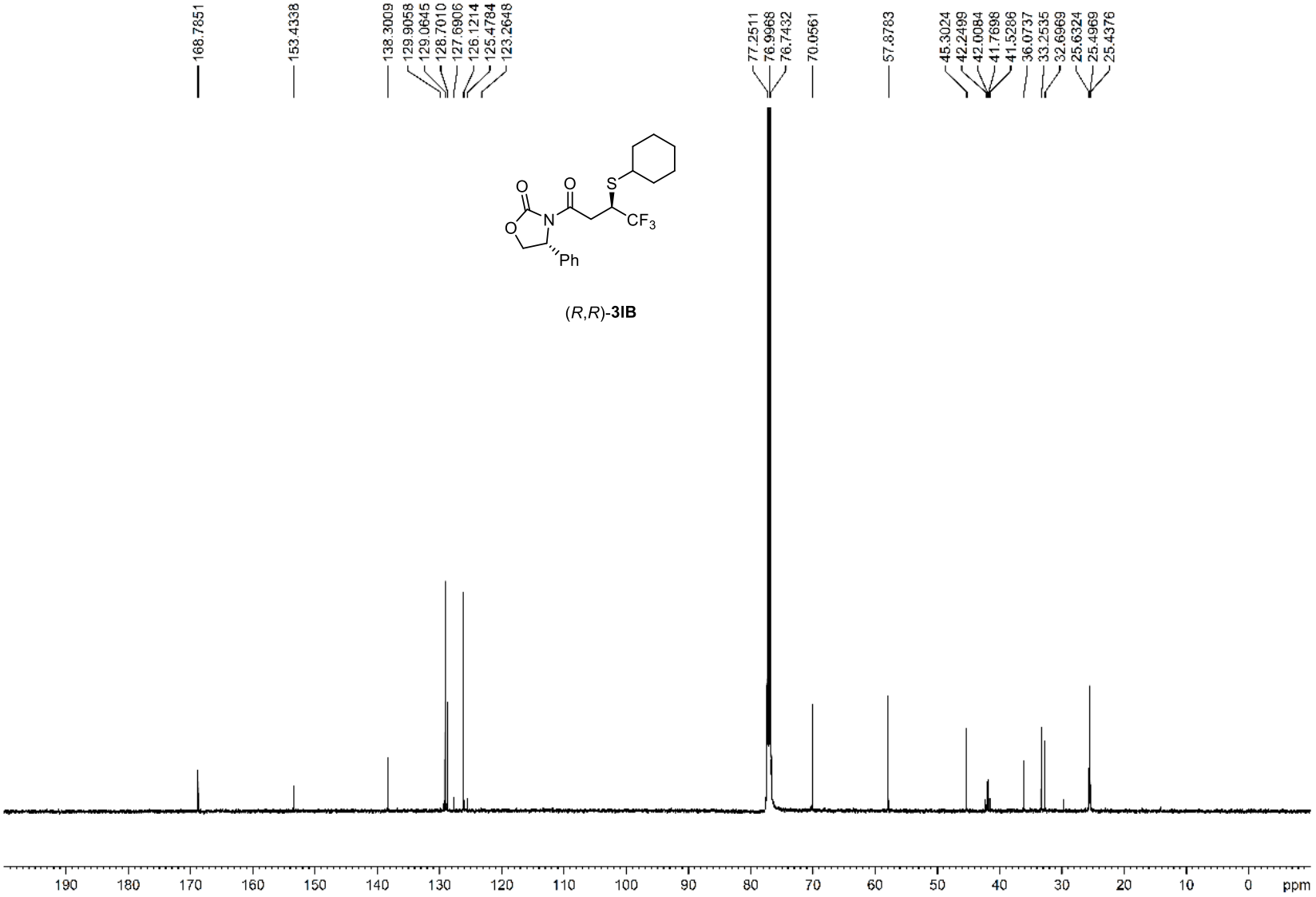
| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 11( 1/ 5) | -80.584 | 26.7 |
| 2 | 11( 2/ 5) | -79.610 | 26.7 |
| 3 | 11( 3/ 5) | -78.377 | 26.7 |
| 4 | 11( 4/ 5) | -80.455 | 26.7 |
| 5 | 11( 5/ 5) | -79.351 | 26.7 |

$^1$H NMR Spectrum of (*R*,*R*)-**3lB** (400 MHz, $CDCl_3$)

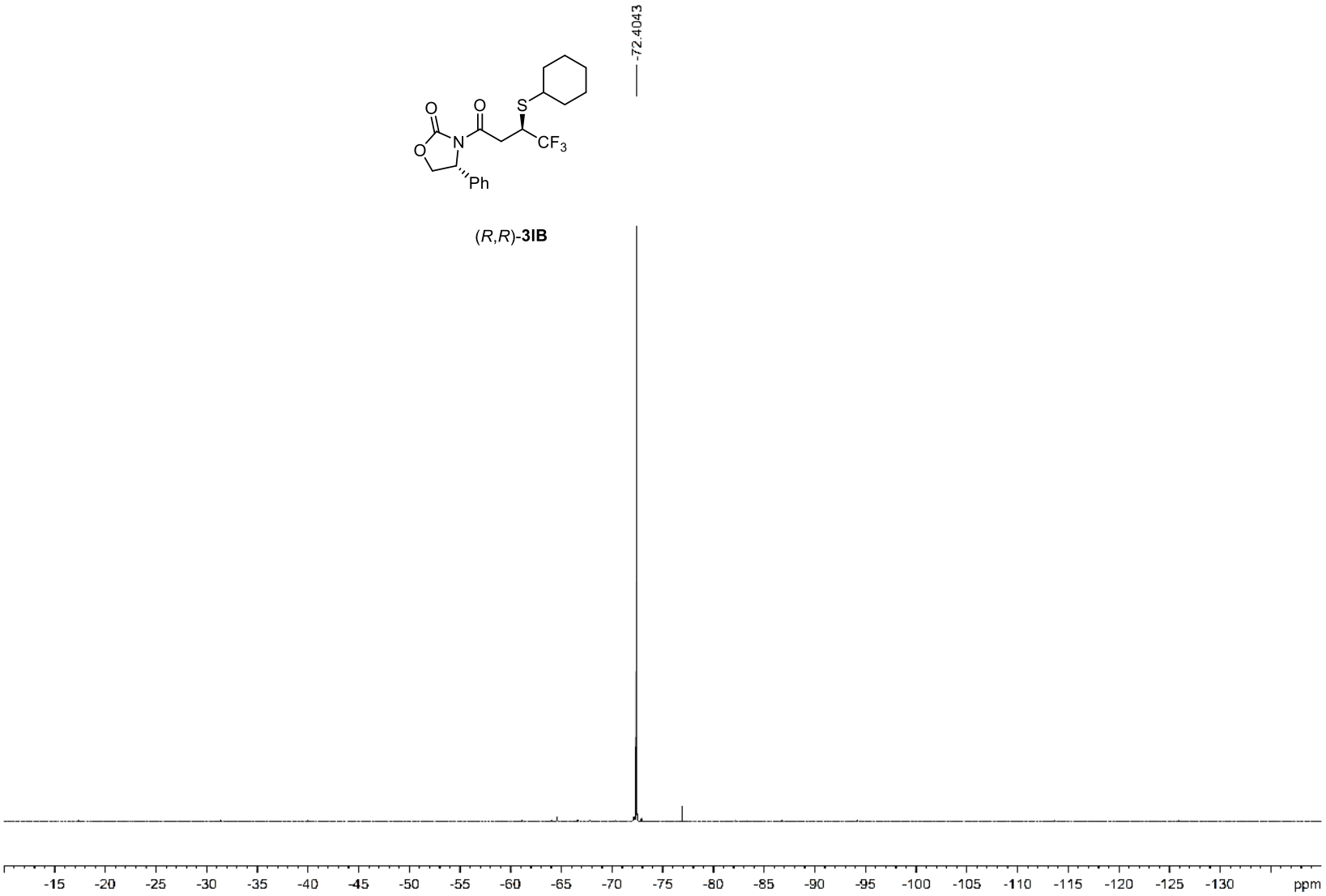



(*R*,*R*)-**3lB**

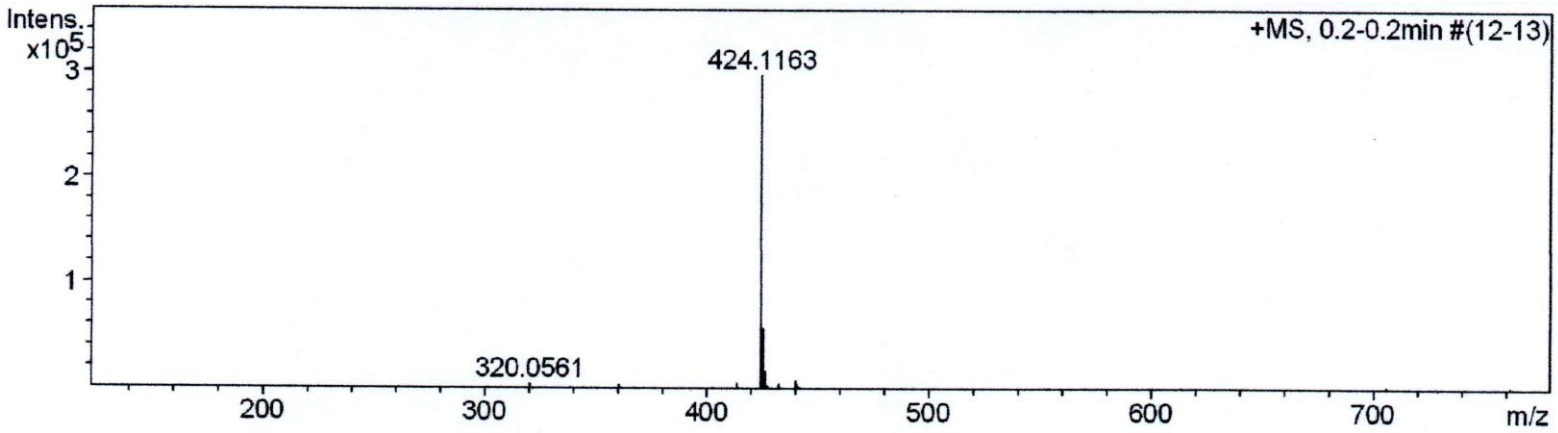
$^{13}$C NMR Spectrum of (*R*,*R*)-**3lB** (125 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3lB** (376 MHz, $CDCl_3$)



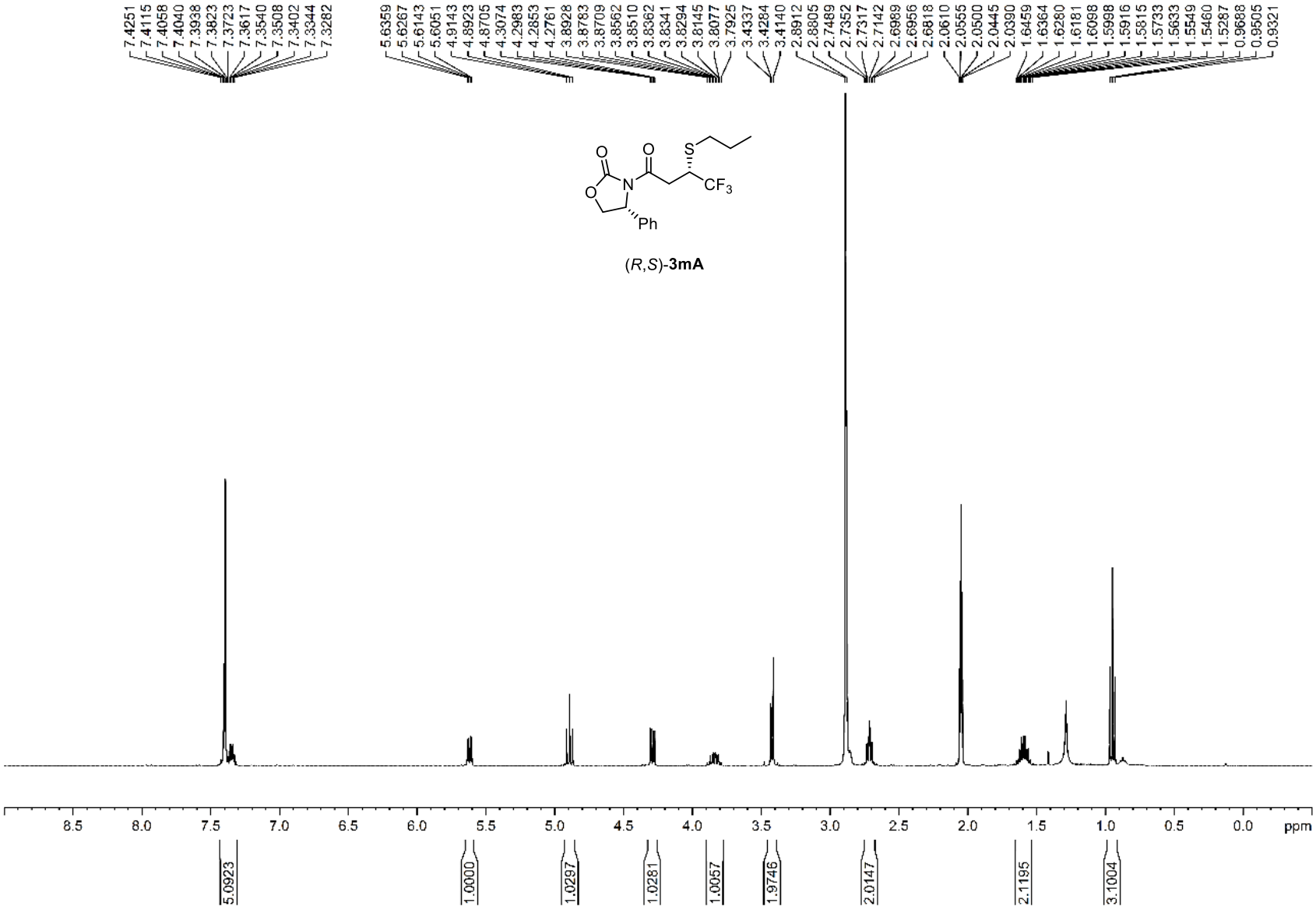
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3lB**



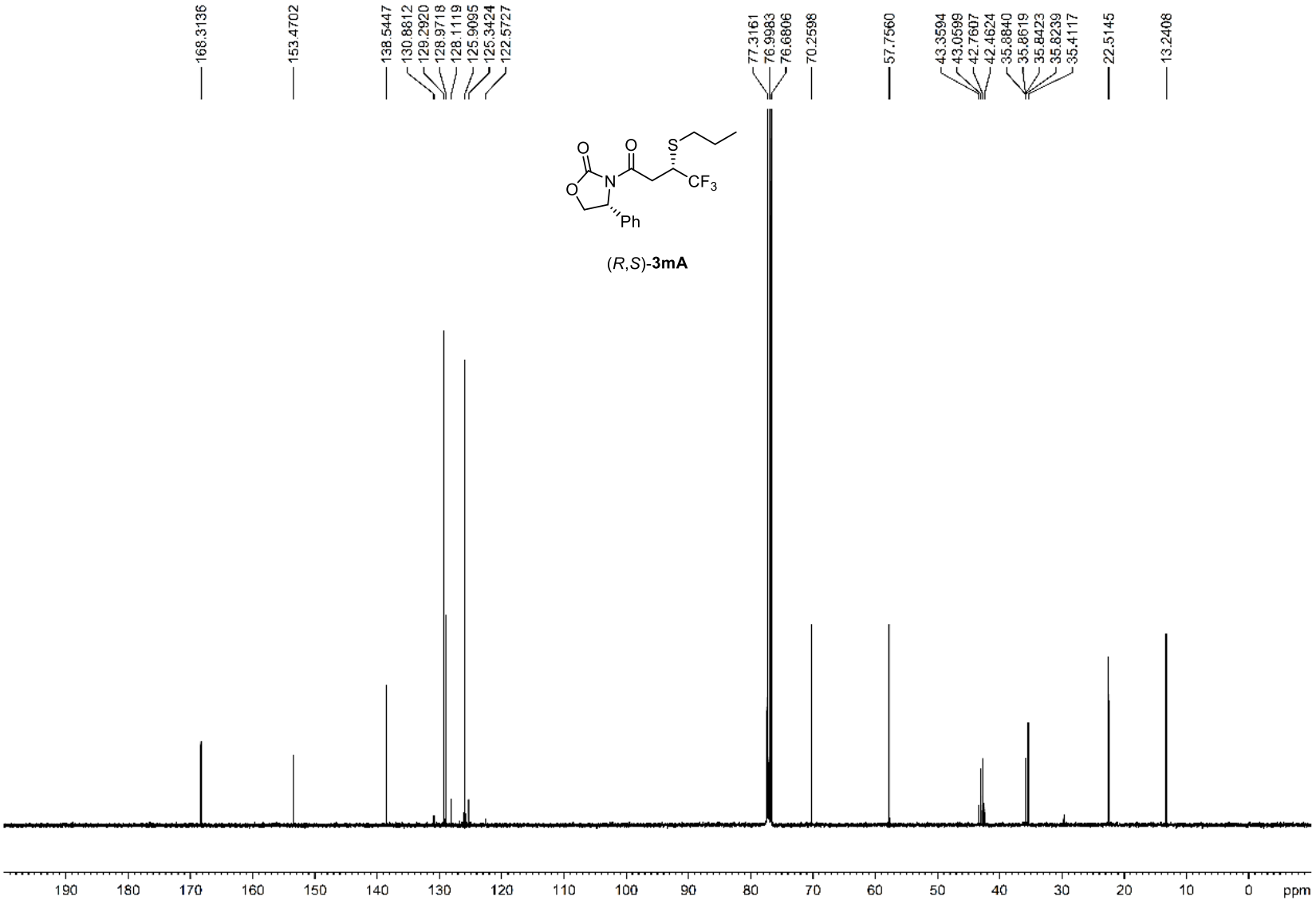

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.4300 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -77.1888 |
| S.D. | 0.7424 |
| C.V. | -0.9618 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 28( 1/ 5) | -76.294 | 26.9 |
| 2 | 28( 2/ 5) | -77.273 | 26.9 |
| 3 | 28( 3/ 5) | -78.322 | 26.9 |
| 4 | 28( 4/ 5) | -77.203 | 26.9 |
| 5 | 28( 5/ 5) | -76.853 | 26.9 |

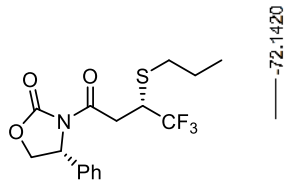
$^{1}$H NMR Spectrum of (*R*,*S*)-**3mA** (400 MHz, acetone-$d_6$)



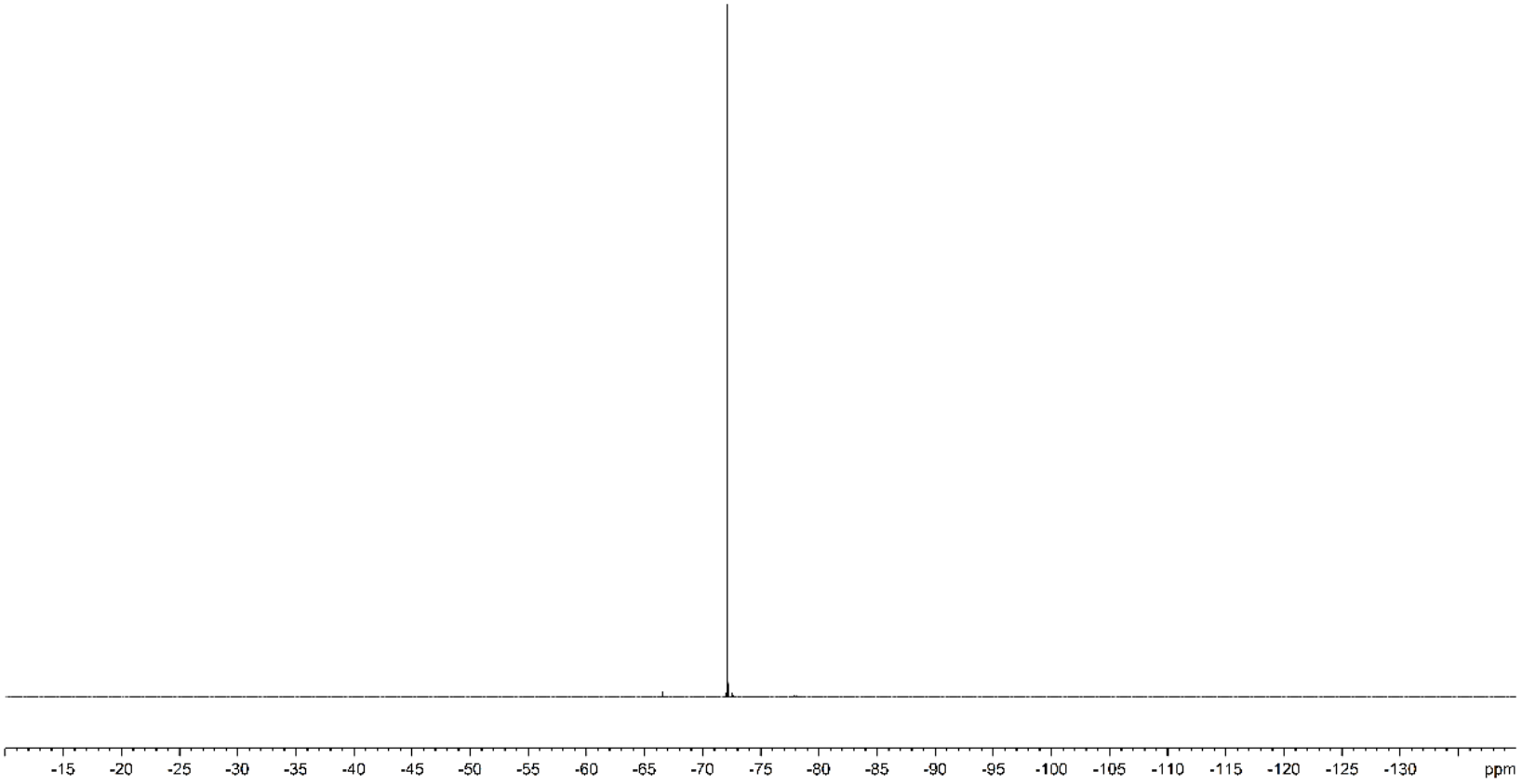
$^{13}$C NMR Spectrum of (*R*,*S*)-**3mA** (100 MHz, $CDCl_3$)



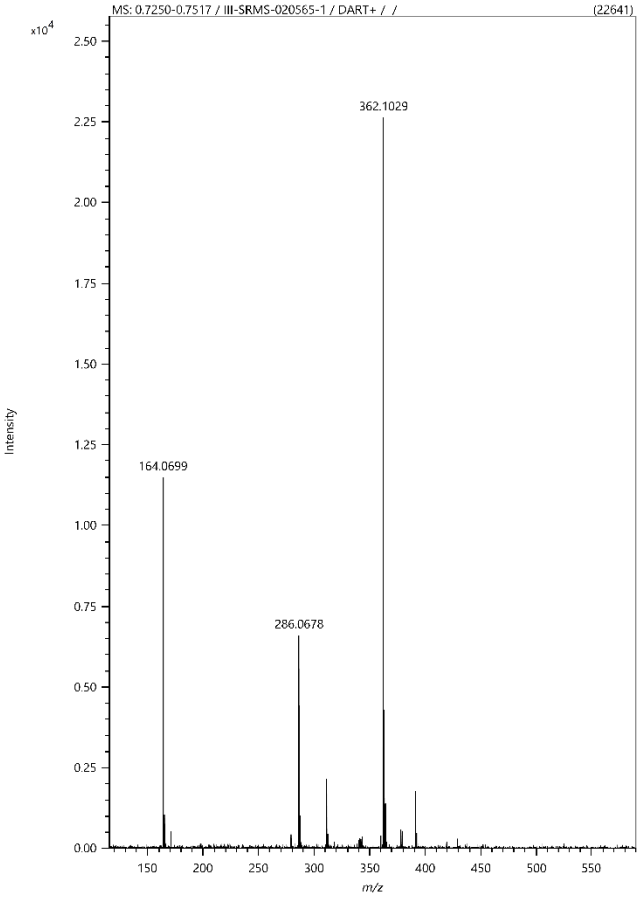
$^{19}$F NMR Spectrum of (*R*,*S*)-**3mA** (470 MHz, $CDCl_3$)




(*R*,*S*)-**3mA**



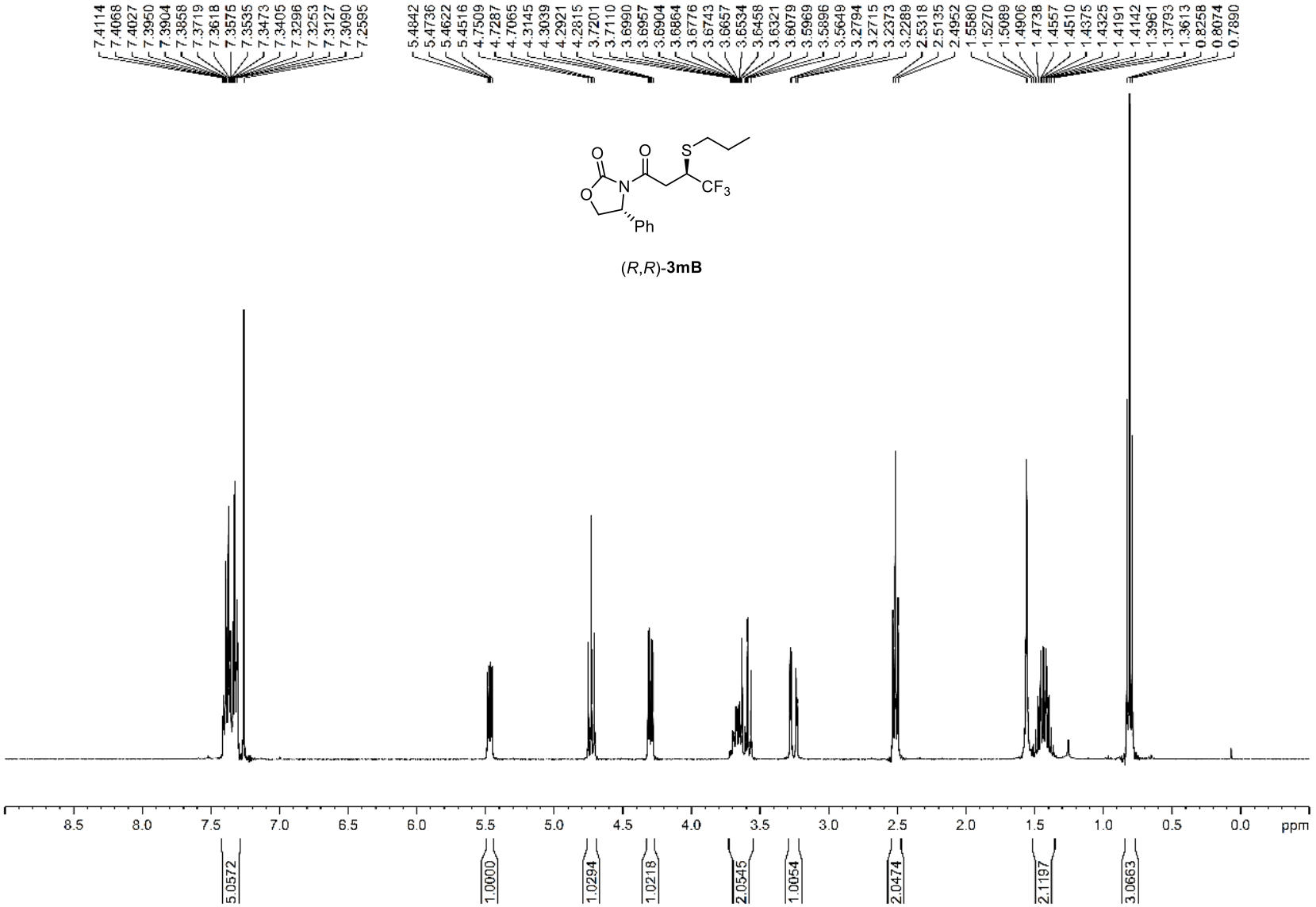
HRMS (DART) and Specific rotation of (*R*,*S*)-**3mA**



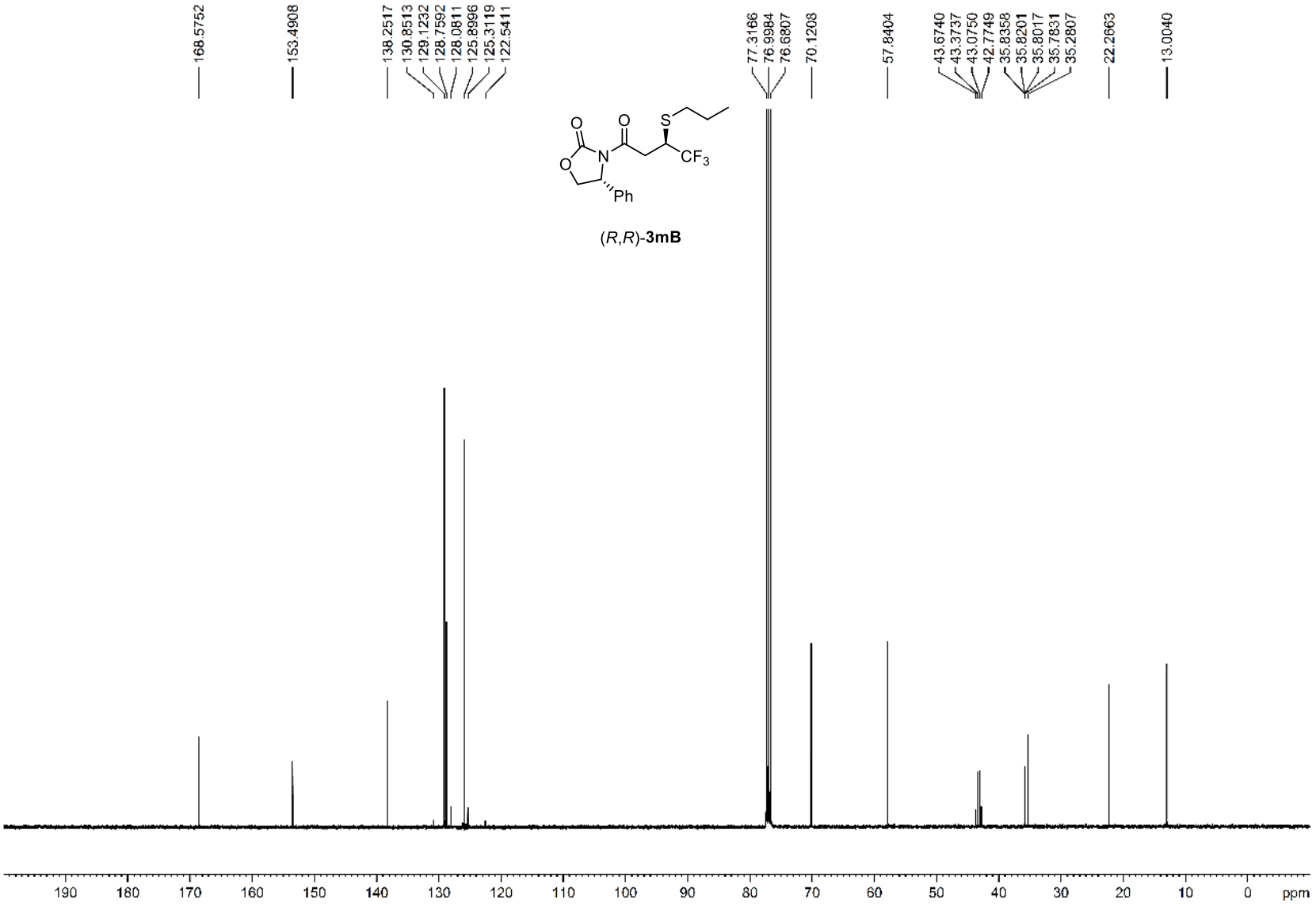

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.3000 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -91.8615 |
| S.D. | 0.5818 |
| C.V. | -0.6333 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 45( 1/ 5) | -92.692 | 25.9 |
| 2 | 45( 2/ 5) | -91.923 | 25.9 |
| 3 | 45( 3/ 5) | -91.308 | 25.9 |
| 4 | 45( 4/ 5) | -91.308 | 25.9 |
| 5 | 45( 5/ 5) | -92.077 | 25.9 |

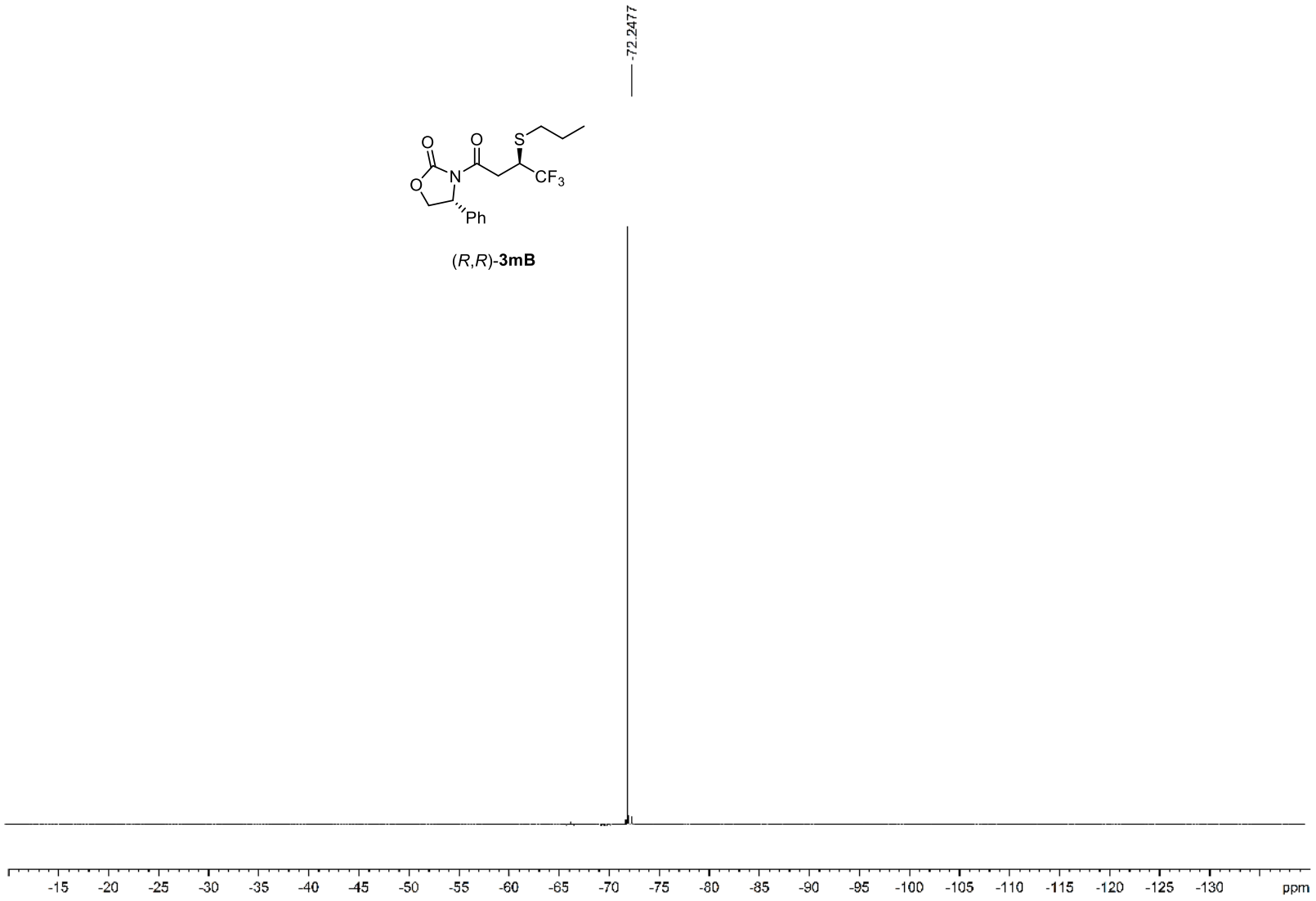
$^1$H NMR Spectrum of (*R*,*R*)-**3mB** (400 MHz, $CDCl_3$)



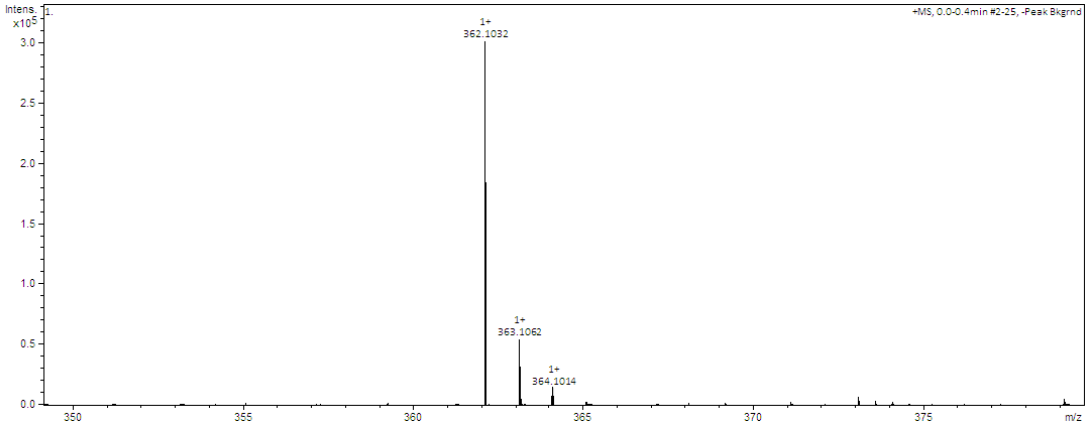
$^{13}$C NMR Spectrum of (*R*,*R*)-**3mB** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3mB** (470 MHz, $CDCl_3$)



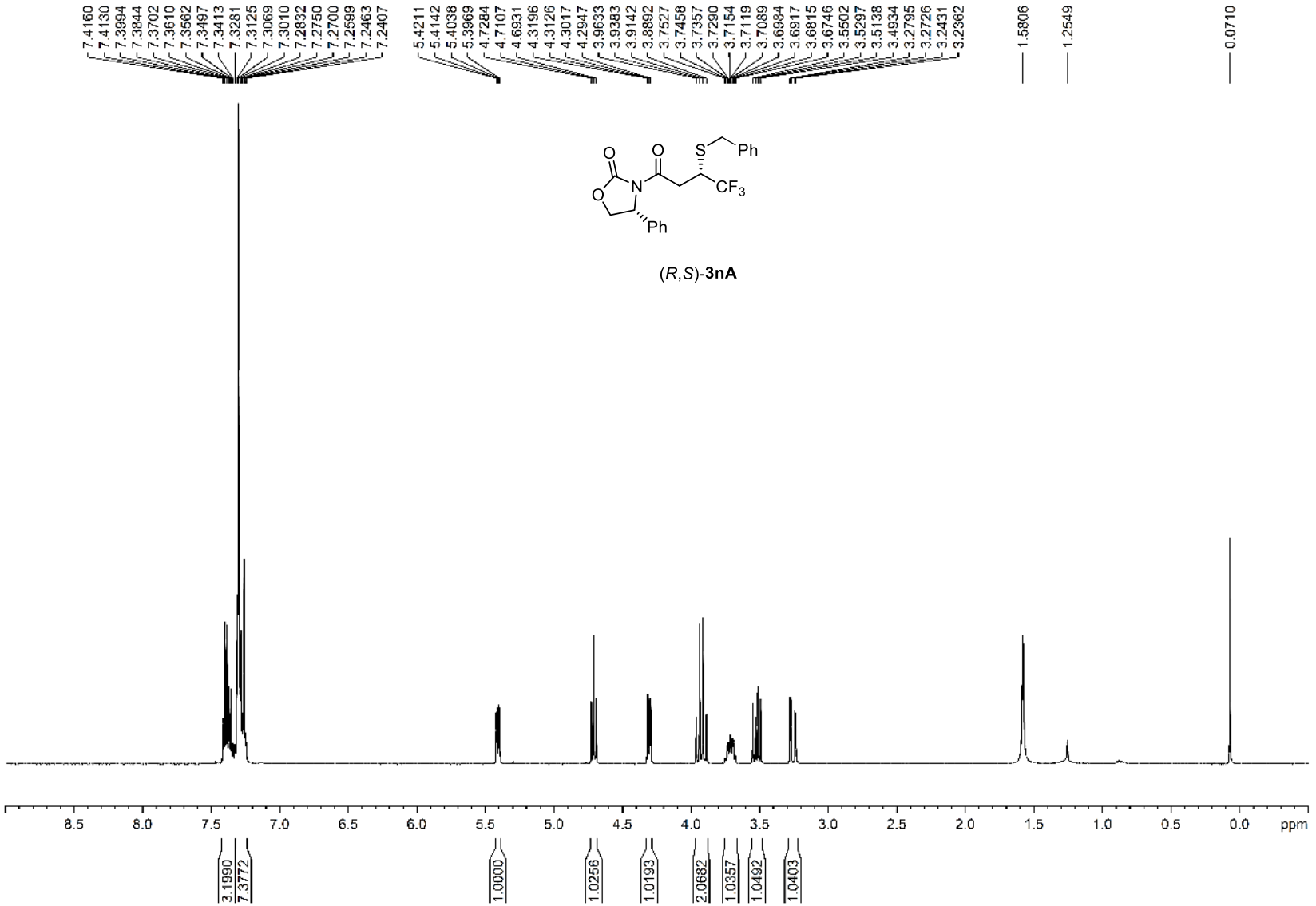
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3mB**



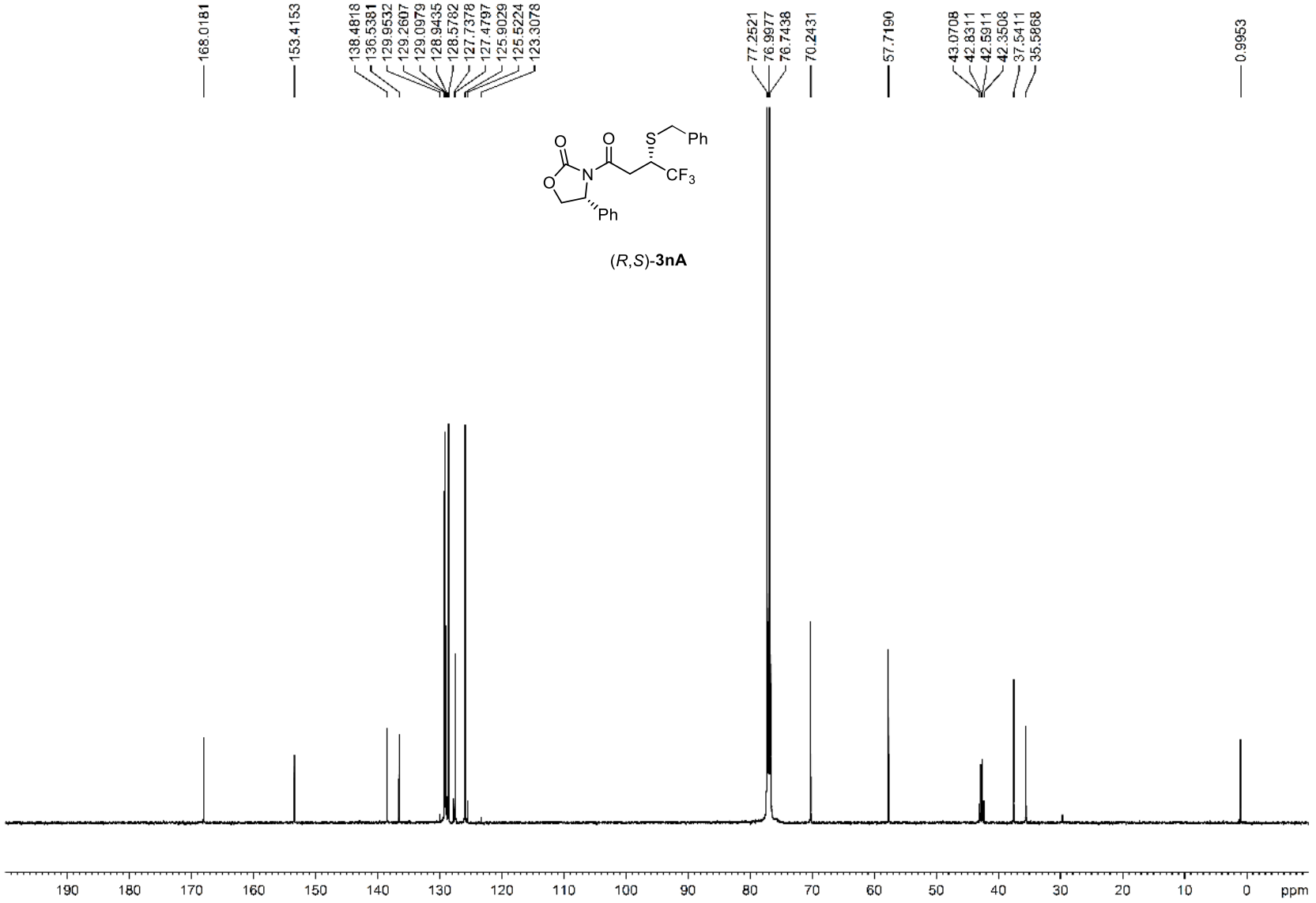

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0067 w/v% |
| Factor | 1.0000 |
| Blank | 0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -73.0506 |
| S.D. | 0.5775 |
| C.V. | -0.7906 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 89( 1/ 5) | -73.309 | 26.2 |
| 2 | 89( 2/ 5) | -73.607 | 26.2 |
| 3 | 89( 3/ 5) | -72.117 | 26.2 |
| 4 | 89( 4/ 5) | -73.309 | 26.2 |
| 5 | 89( 5/ 5) | -72.911 | 26.2 |

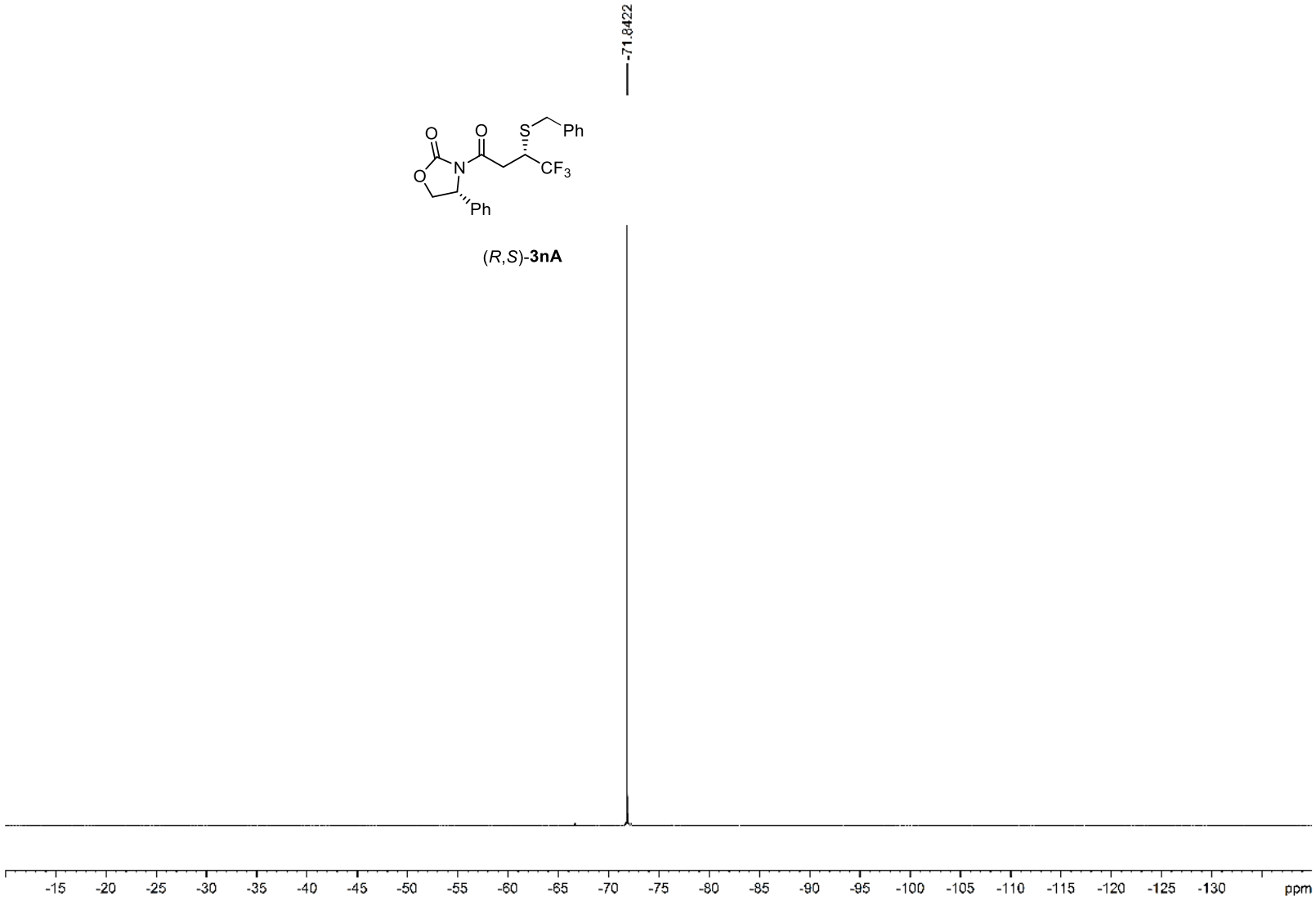
$^1$H NMR Spectrum of (*R*,*S*)-**3nA** (400 MHz, $CDCl_3$)



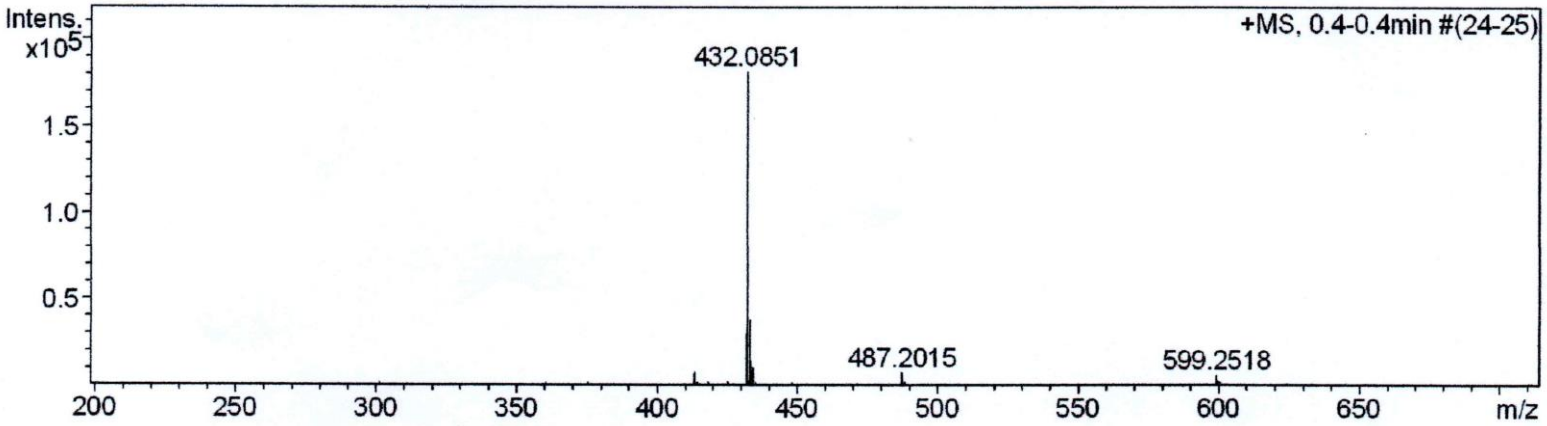
$^{13}$C NMR Spectrum of (*R*,*S*)-**3nA** (125 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3nA** (470 MHz, $CDCl_3$)



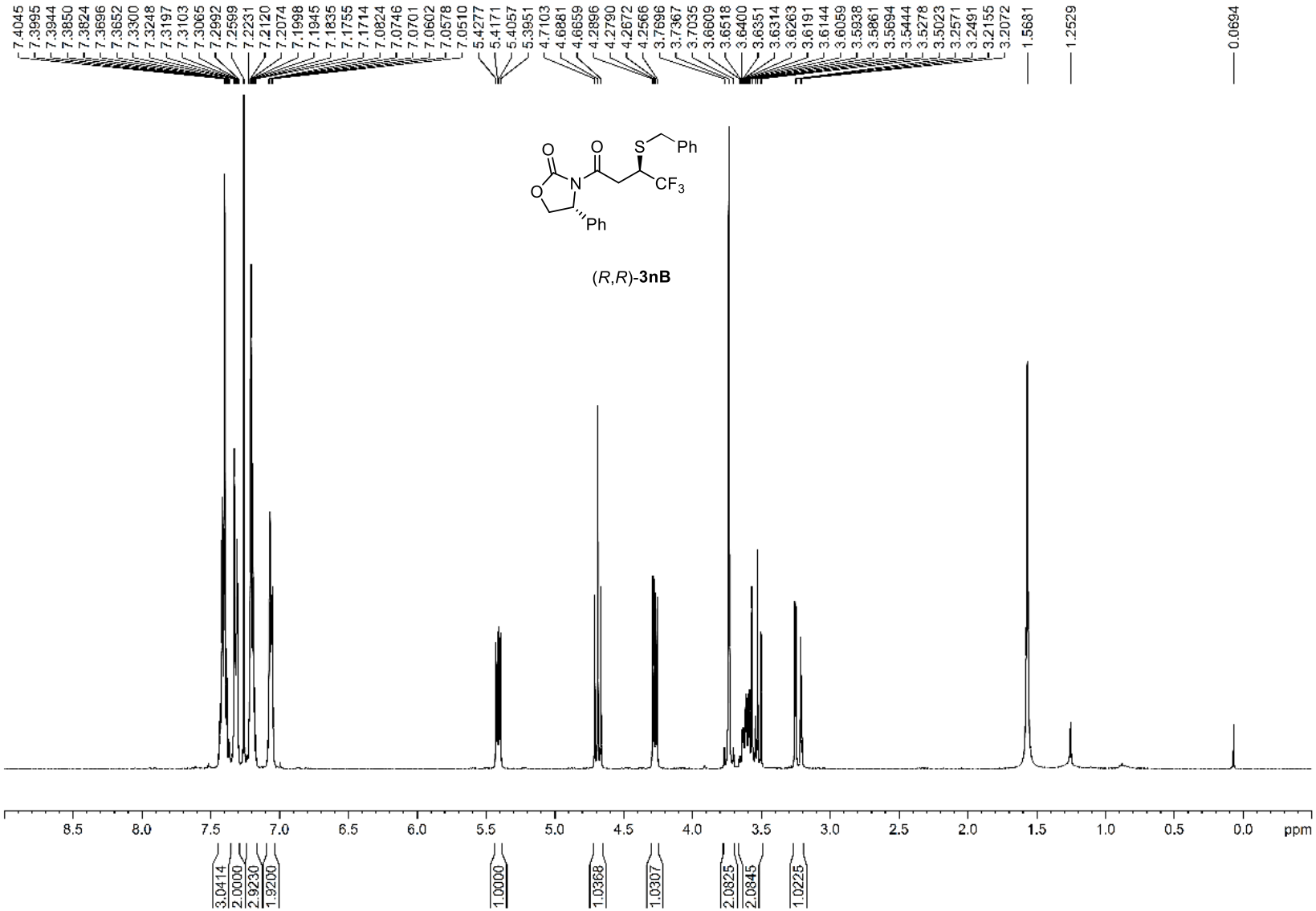
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3nA**



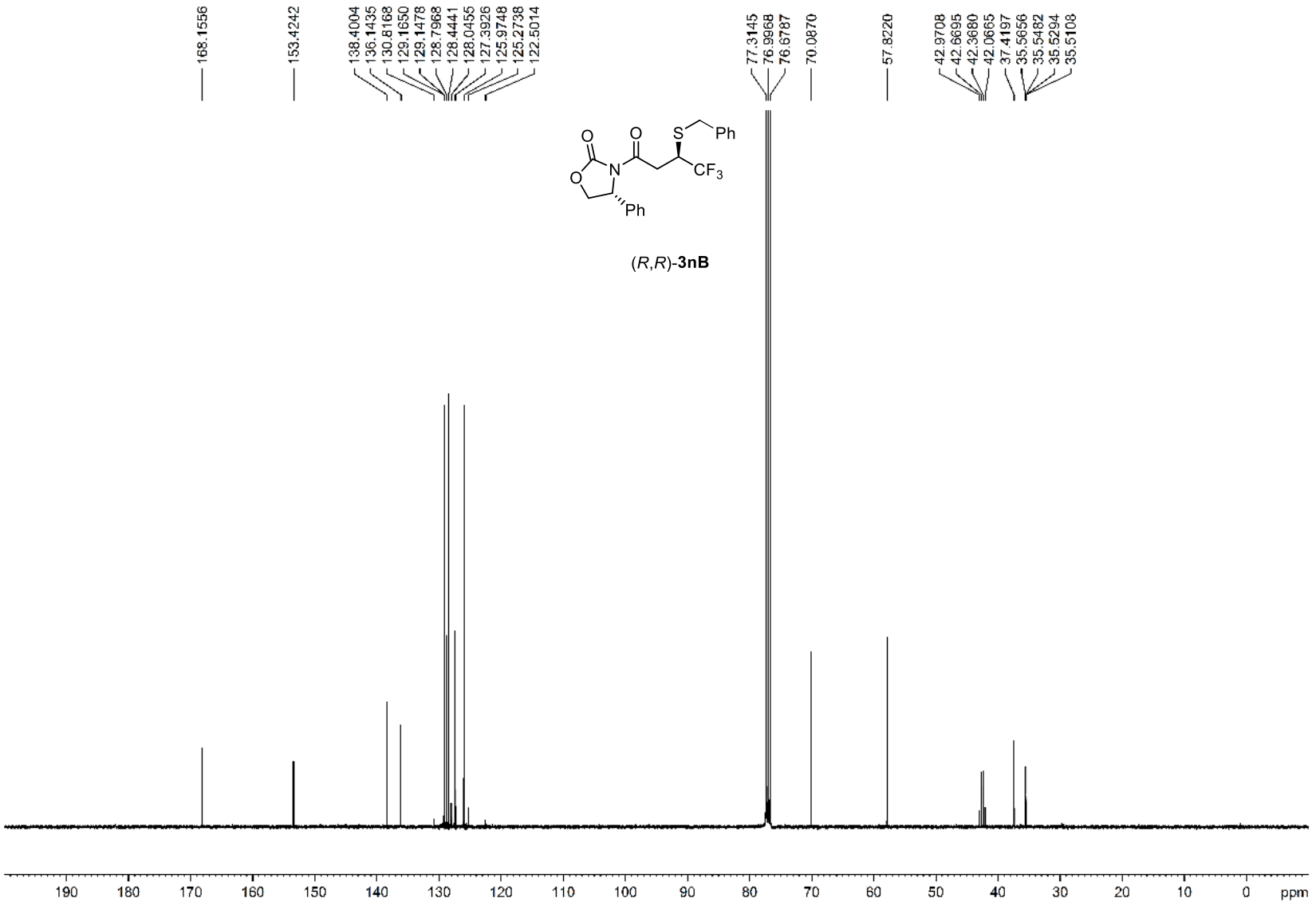

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.7100 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -86.5614 |
| S.D. | 0.5984 |
| C.V. | -0.6913 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 33( 1/ 5) | -86.842 | 25.9 |
| 2 | 33( 2/ 5) | -86.316 | 25.9 |
| 3 | 33( 3/ 5) | -86.374 | 25.9 |
| 4 | 33( 4/ 5) | -87.427 | 25.9 |
| 5 | 33( 5/ 5) | -85.848 | 25.9 |

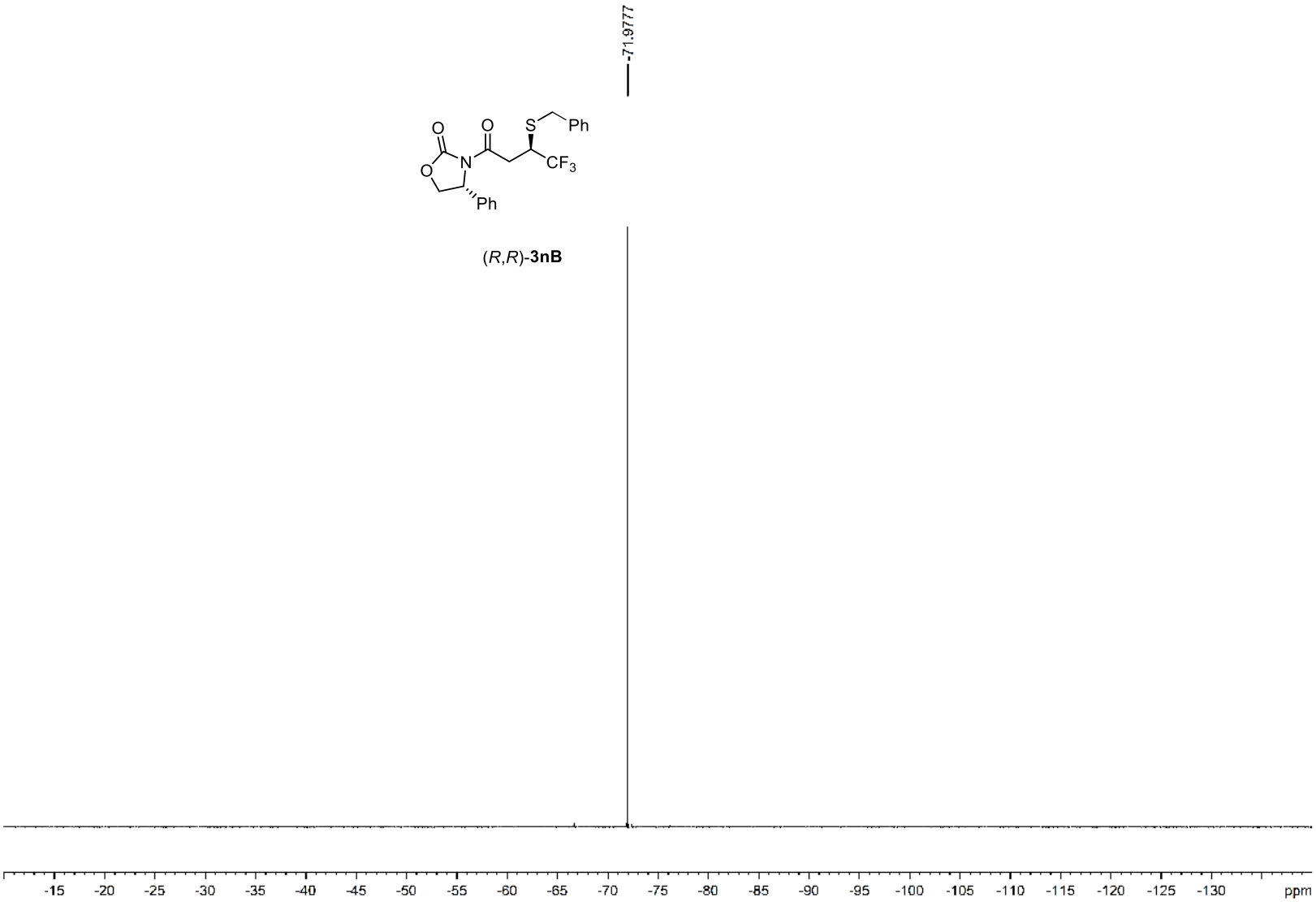
$^1$H NMR Spectrum of (*R*,*R*)-**3nB** (400 MHz, $CDCl_3$)



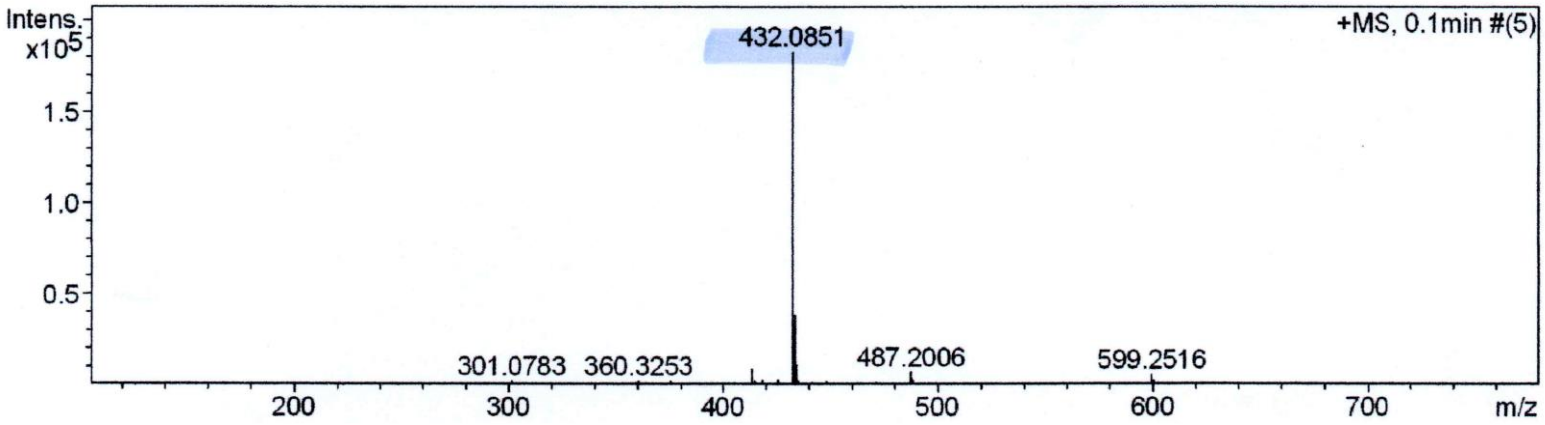
$^{13}$C NMR Spectrum of (*R*,*R*)-**3nB** (100 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3nB** (470 MHz, $CDCl_3$)



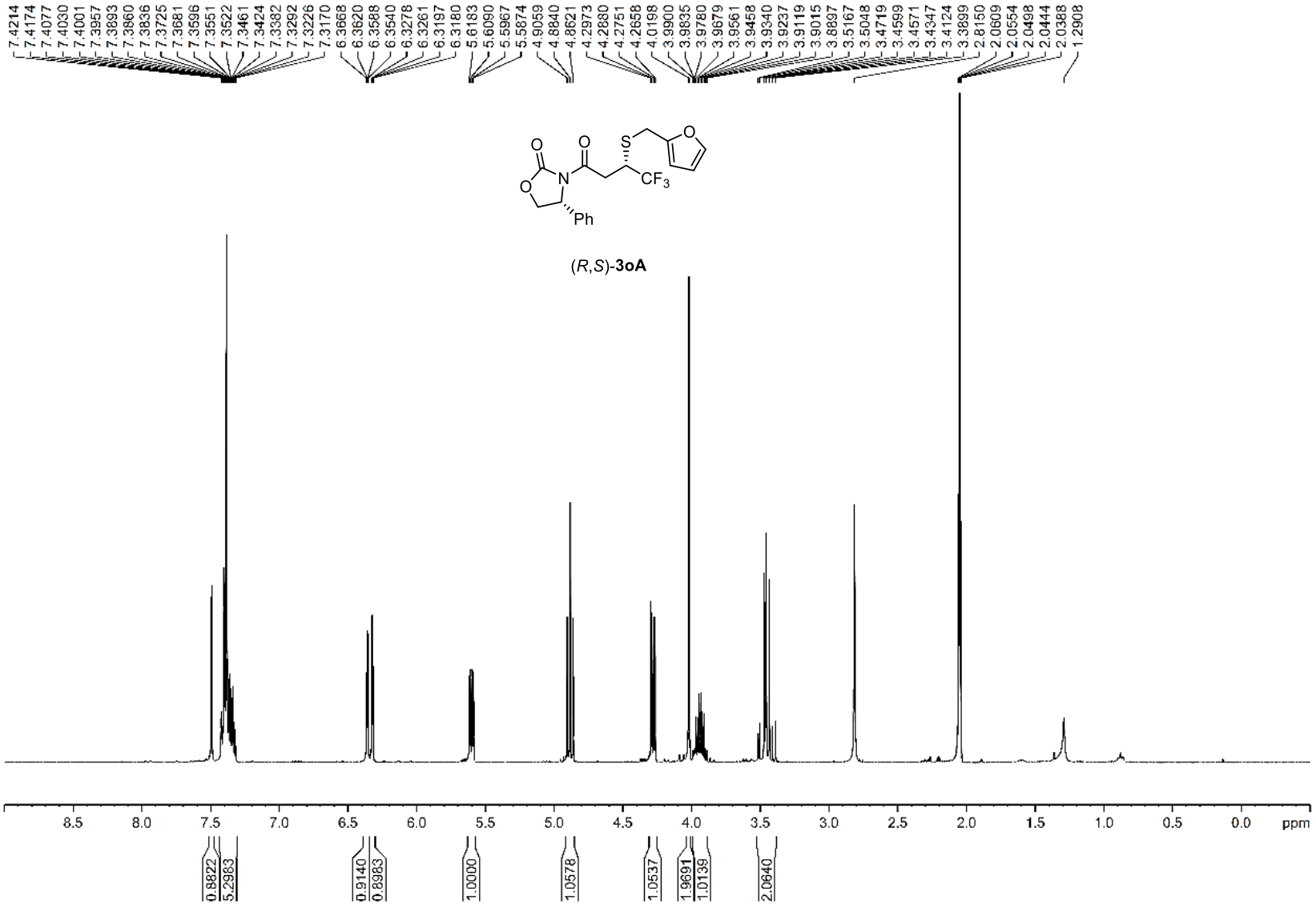
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3nB**



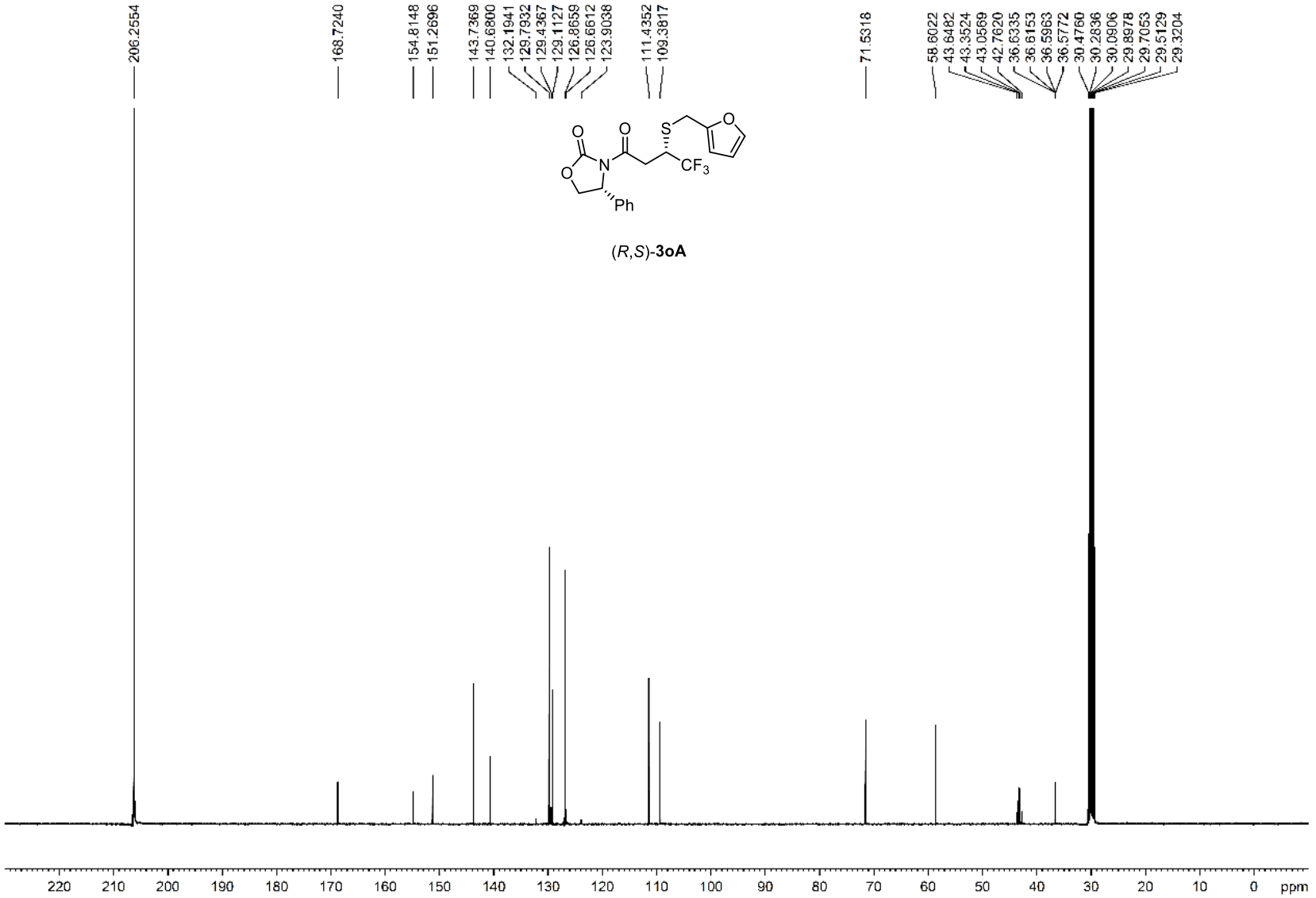

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.8700 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -58.3908 |
| S.D. | 0.7493 |
| C.V. | -1.2833 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 38( 1/ 5) | -58.736 | 25.4 |
| 2 | 38( 2/ 5) | -57.471 | 25.4 |
| 3 | 38( 3/ 5) | -59.080 | 25.4 |
| 4 | 38( 4/ 5) | -57.701 | 25.4 |
| 5 | 38( 5/ 5) | -58.966 | 25.4 |

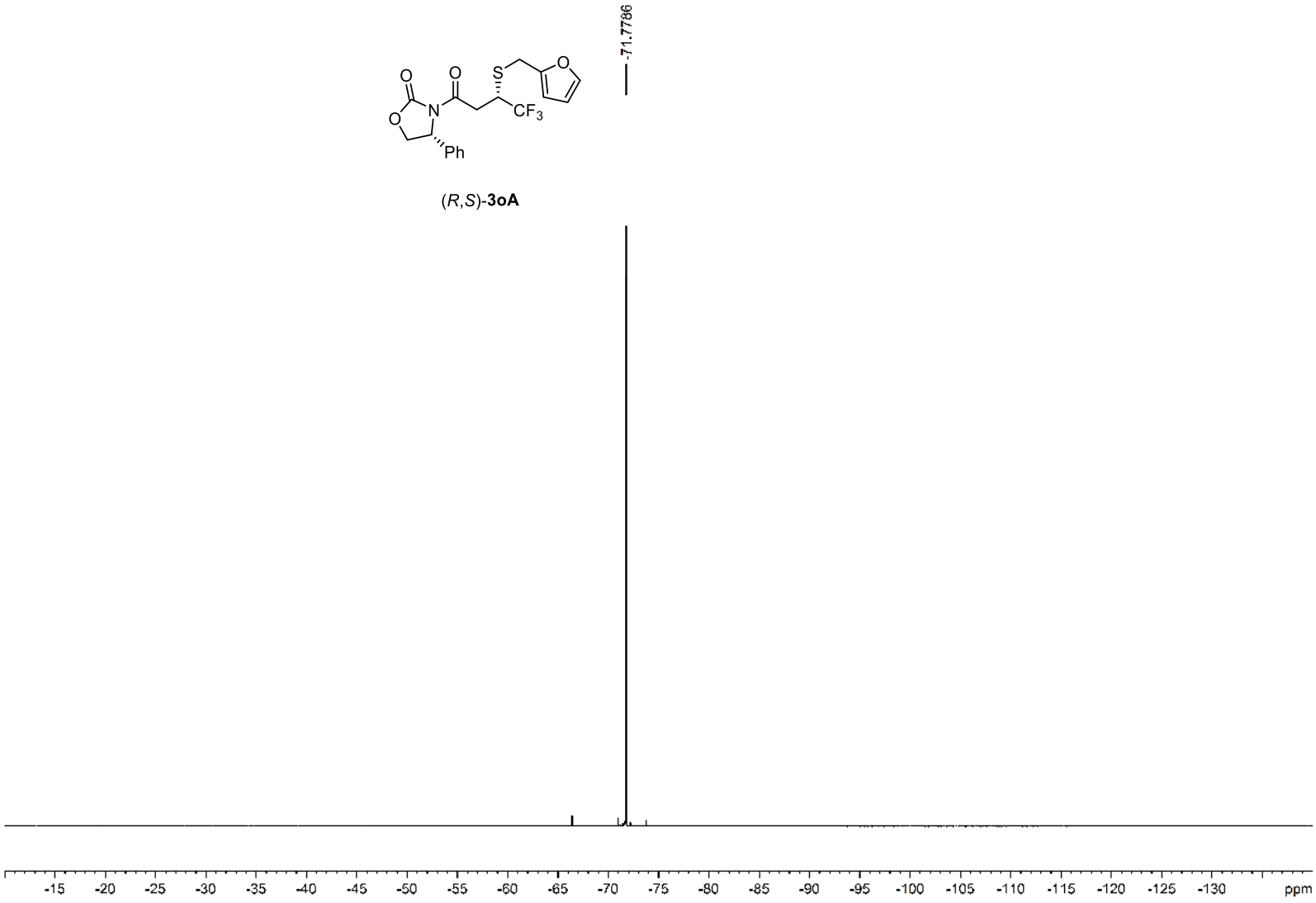
$^1$H NMR Spectrum of (*R*,*S*)-**3oA** (400 MHz, acetone-$d_6$)



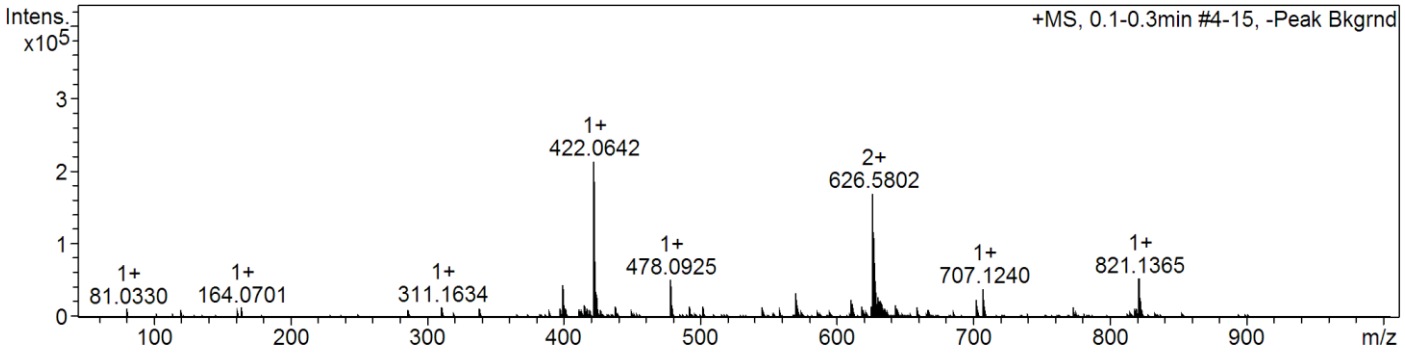
$^{13}$C NMR Spectrum of (*R*,*S*)-**3oA** (100 MHz, acetone-$d_6$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3oA** (470 MHz, acetone-$d_6$)



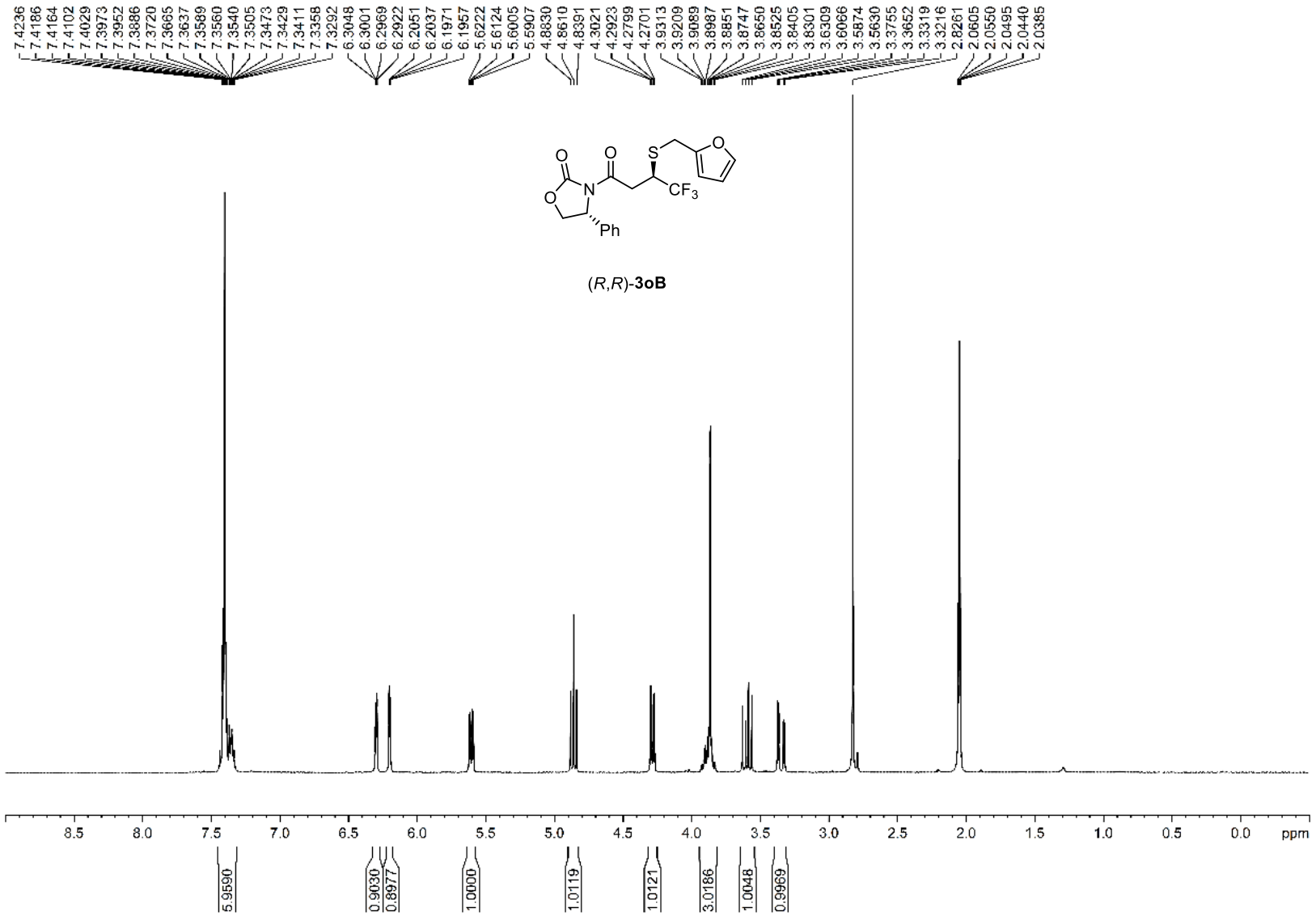
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3oA**



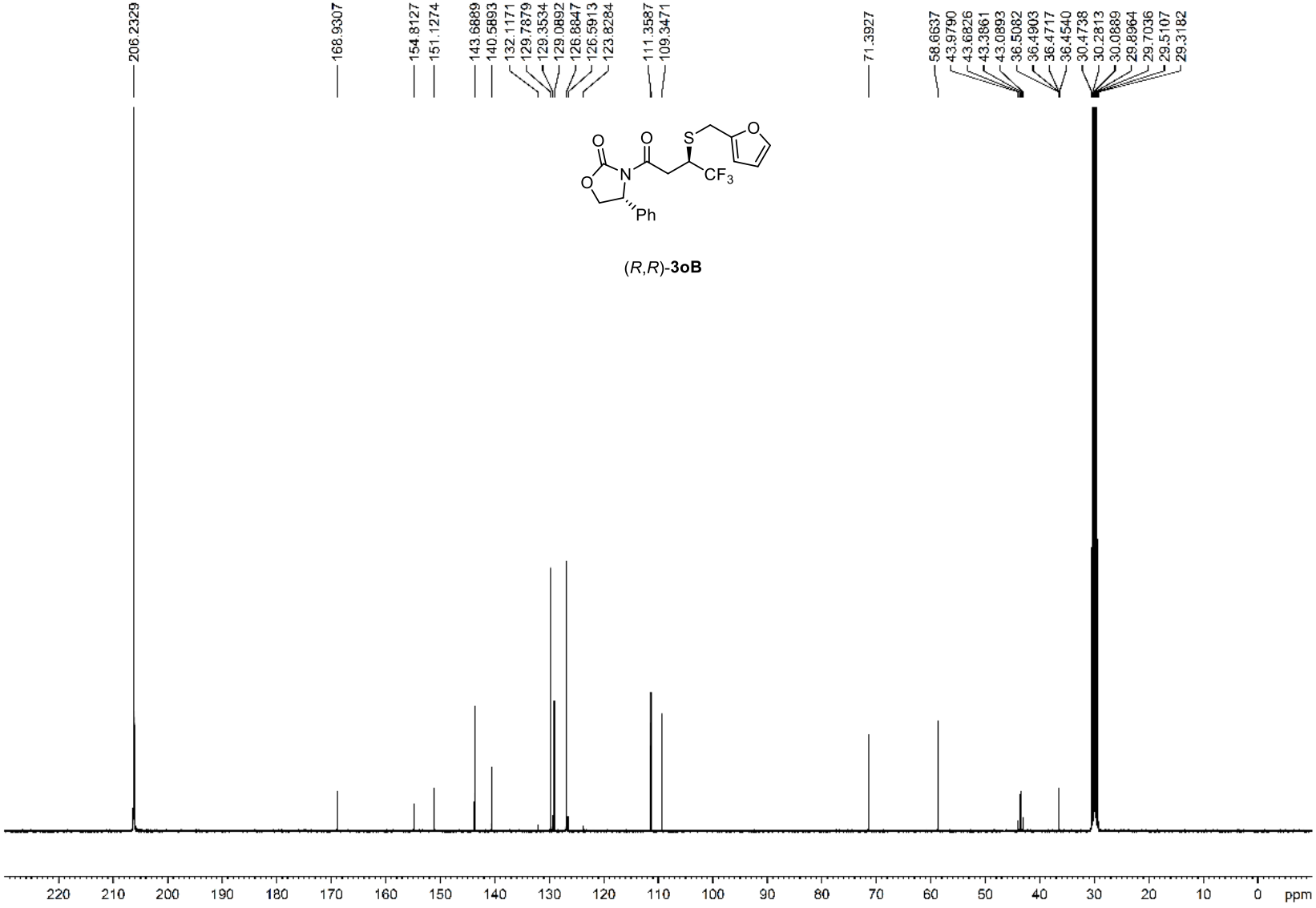

| | |
|---|---|
| Comment | CH2Cl2 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.2500 w/v% |
| Factor | 1.0000 |
| Blank | -0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -70.7680 |
| S.D. | 0.5502 |
| C.V. | -0.7775 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 3( 1/ 5) | -71.200 | 23.6 |
| 2 | 3( 2/ 5) | -70.160 | 23.6 |
| 3 | 3( 3/ 5) | -70.320 | 23.6 |
| 4 | 3( 4/ 5) | -70.720 | 23.6 |
| 5 | 3( 5/ 5) | -71.440 | 23.6 |

$^1$H NMR Spectrum of (*R*,*R*)-**3oB** (400 MHz, acetone-$d_6$)

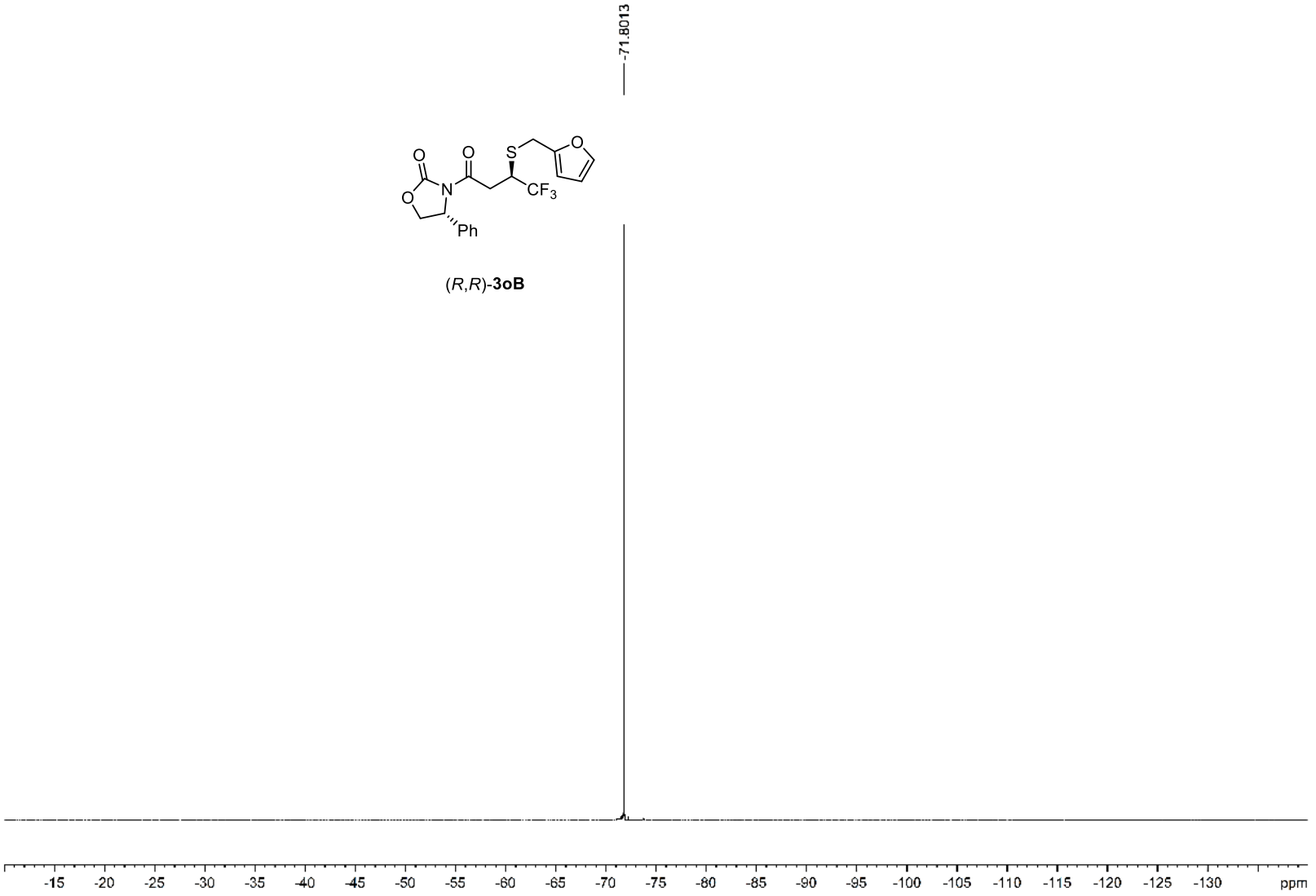


$^{13}$C NMR Spectrum of (*R*,*R*)-**3oB** (100 MHz, acetone-$d_6$)

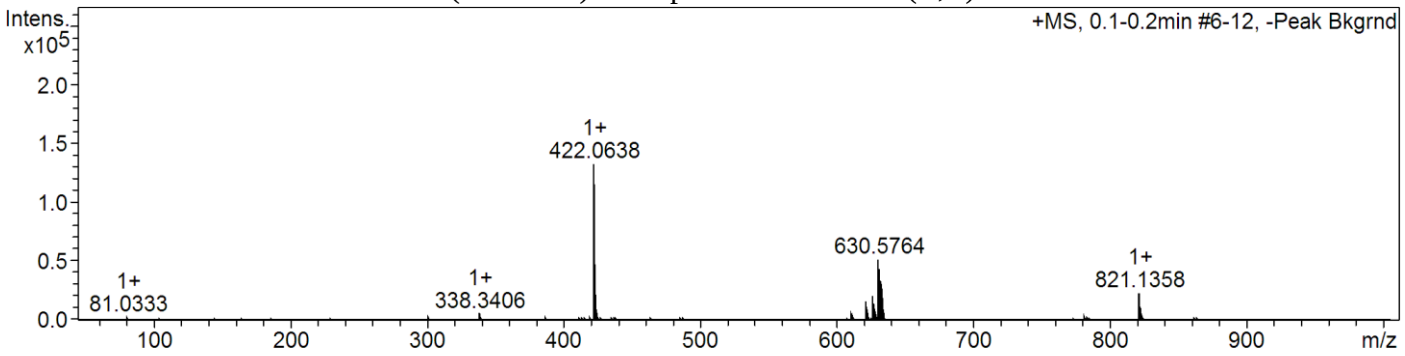



(*R*,*R*)-**3oB**

$^{19}$F NMR Spectrum of (*R*,*R*)-**3oB** (470 MHz, acetone-$d_6$)



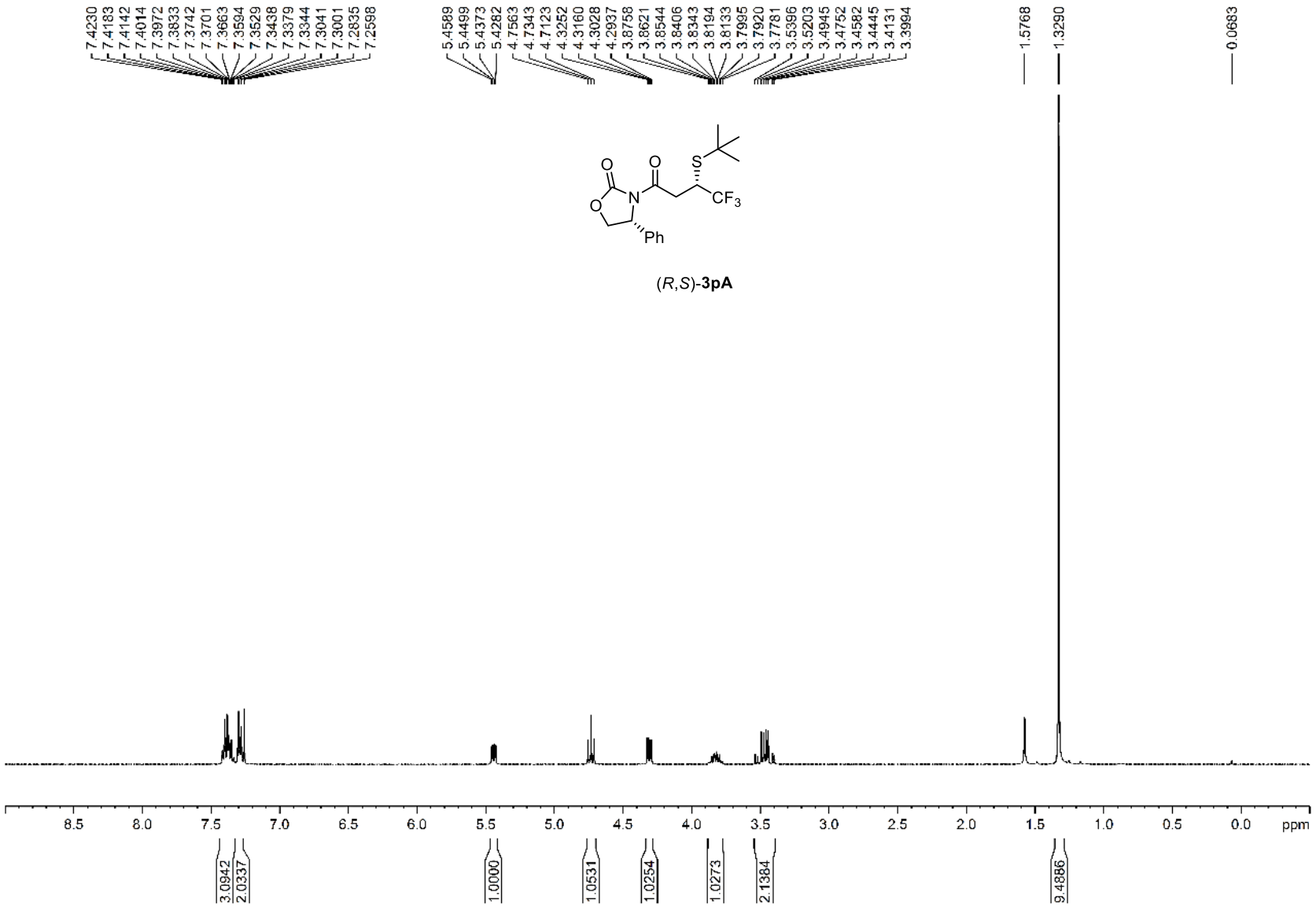
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3oB**



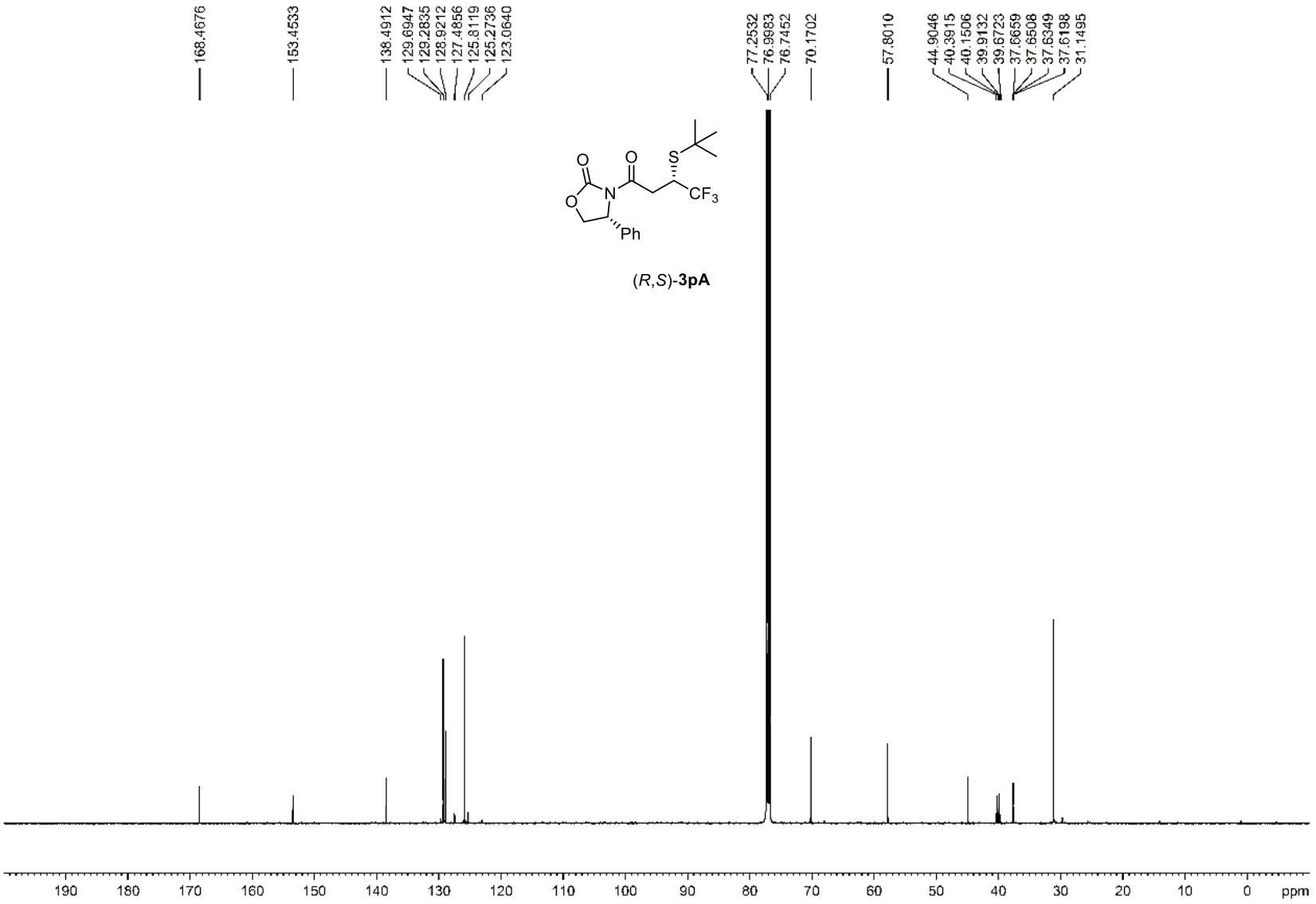

| | |
|---|---|
| Comment | CH2Cl2 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.9714 w/v% |
| Factor | 1.0000 |
| Blank | -0.0006 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -79.5553 |
| S.D. | 0.5219 |
| C.V. | -0.6560 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 19( 1/ 5) | -79.885 | 24.3 |
| 2 | 19( 2/ 5) | -79.576 | 24.4 |
| 3 | 19( 3/ 5) | -79.782 | 24.3 |
| 4 | 19( 4/ 5) | -78.649 | 24.3 |
| 5 | 19( 5/ 5) | -79.885 | 24.3 |

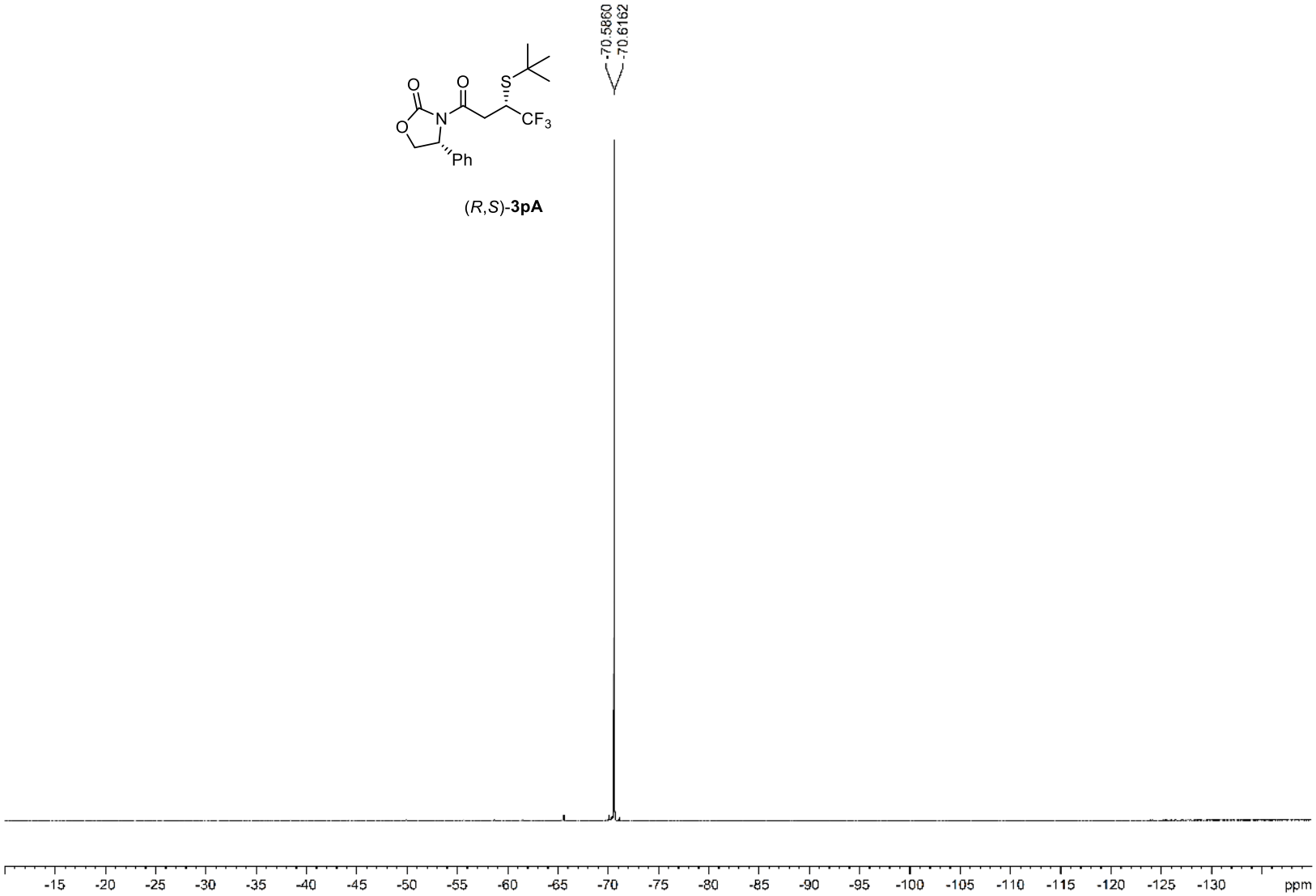
$^1$H NMR Spectrum of (*R*,*S*)-**3pA** (400 MHz, $CDCl_3$)



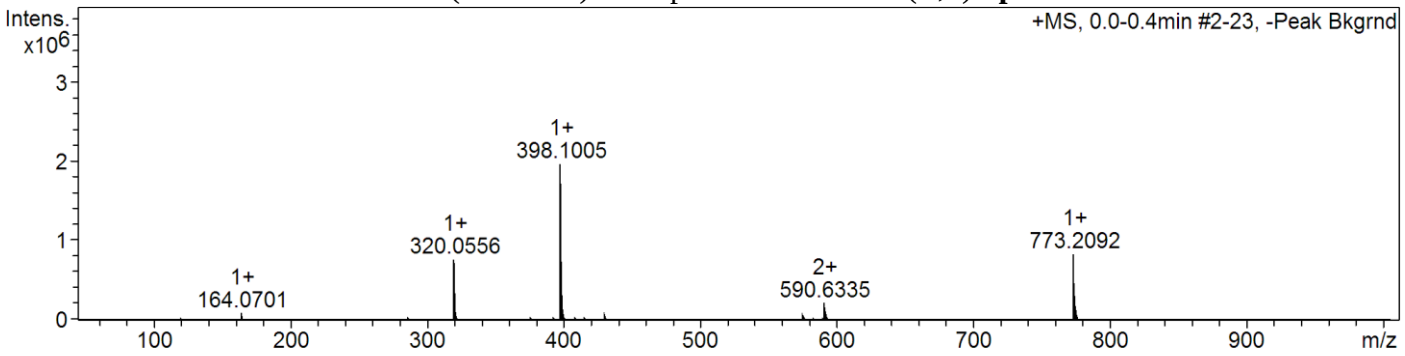
$^{13}$C NMR Spectrum of (*R*,*S*)-**3pA** (125 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*S*)-**3pA** (376 MHz, $CDCl_3$)



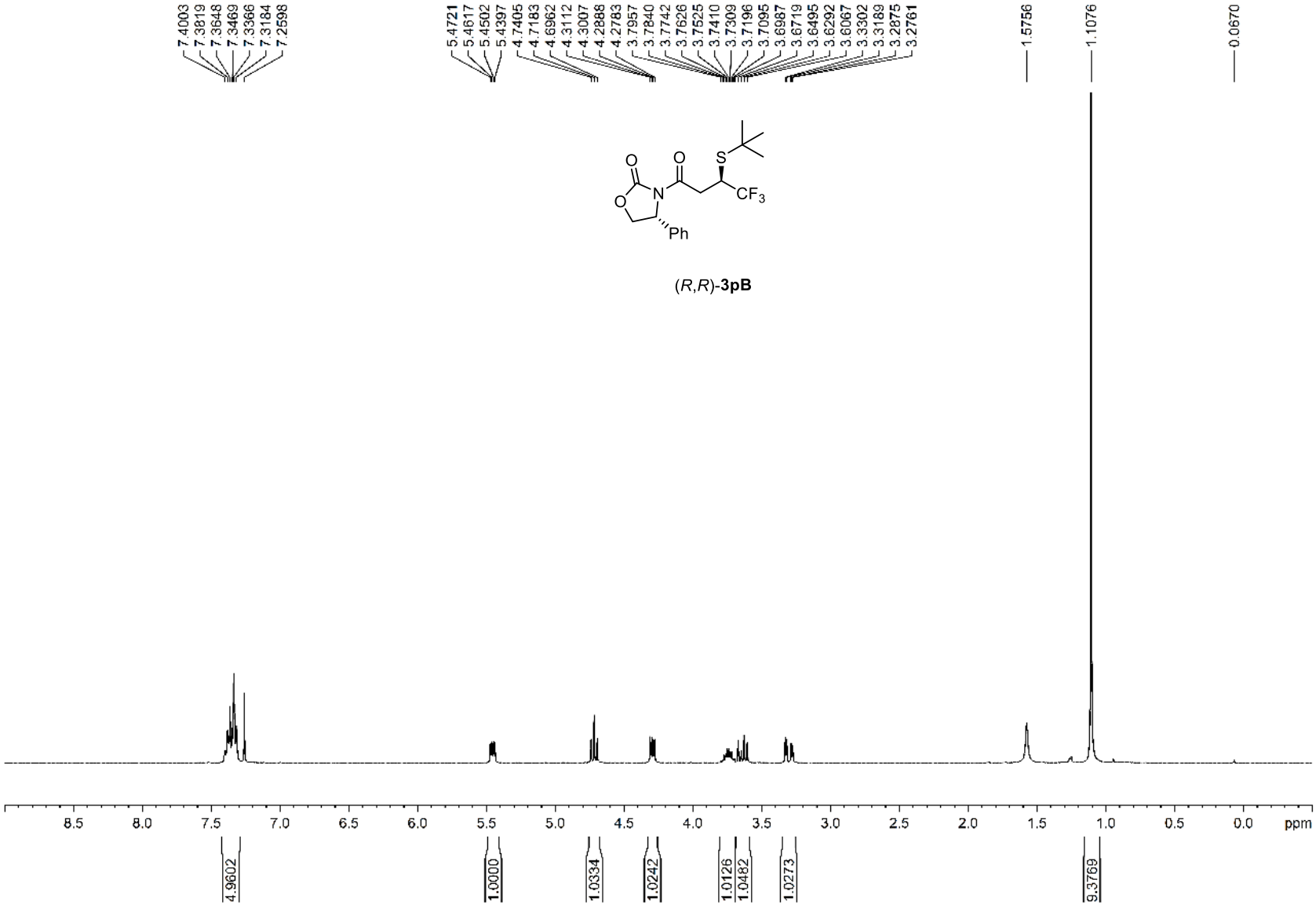
HRMS (ESI-TOF) and Specific rotation of (*R*,*S*)-**3pA**




| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.1300 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -92.6903 |
| S.D. | 0.7831 |
| C.V. | -0.8448 % |

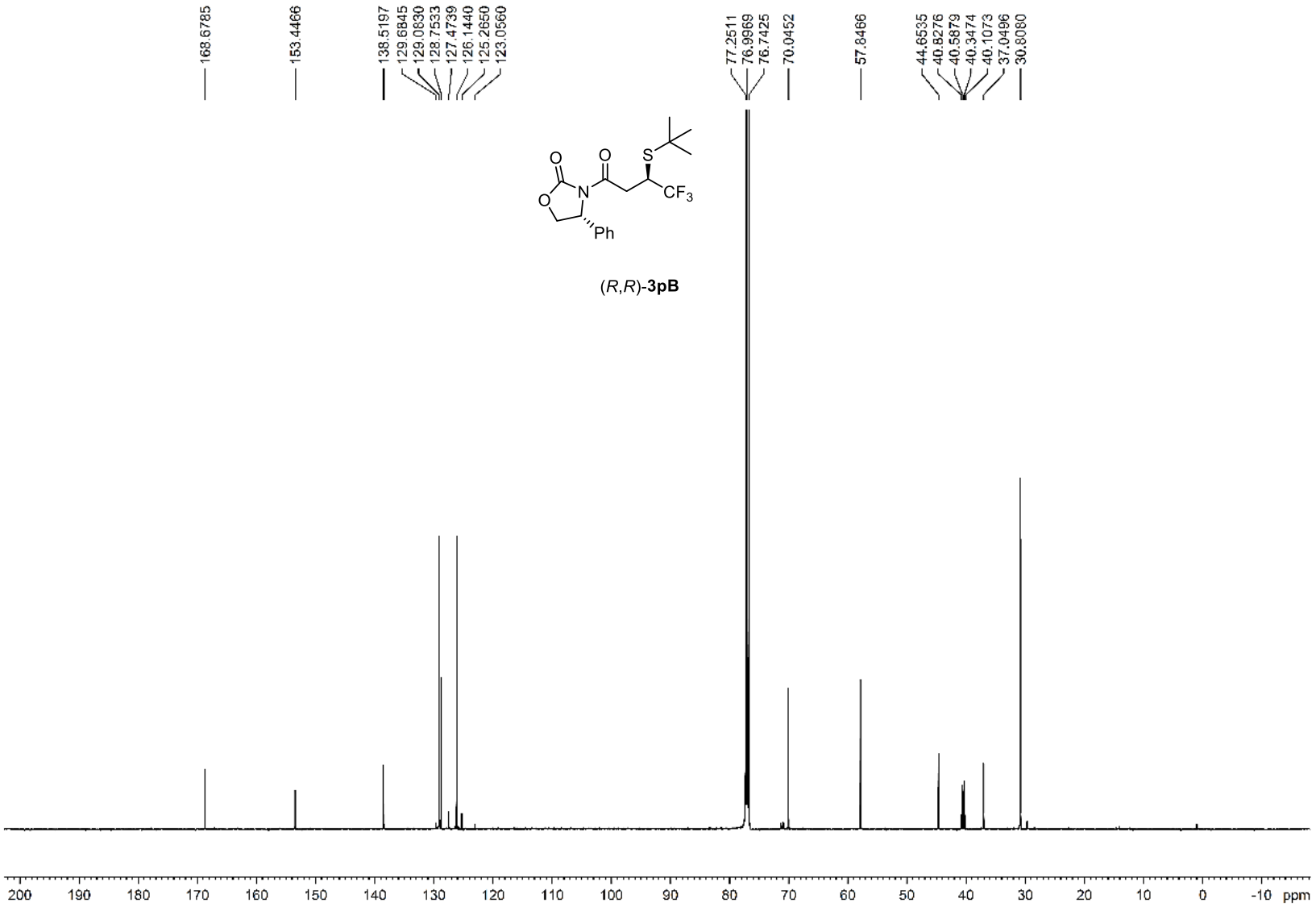
| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 62( 1/ 5) | -92.832 | 25.4 |
| 2 | 62( 2/ 5) | -92.832 | 25.4 |
| 3 | 62( 3/ 5) | -91.681 | 25.4 |
| 4 | 62( 4/ 5) | -93.805 | 25.4 |
| 5 | 62( 5/ 5) | -92.301 | 25.4 |

$^1$H NMR Spectrum of (*R*,*R*)-**3pB** (400 MHz, $CDCl_3$)

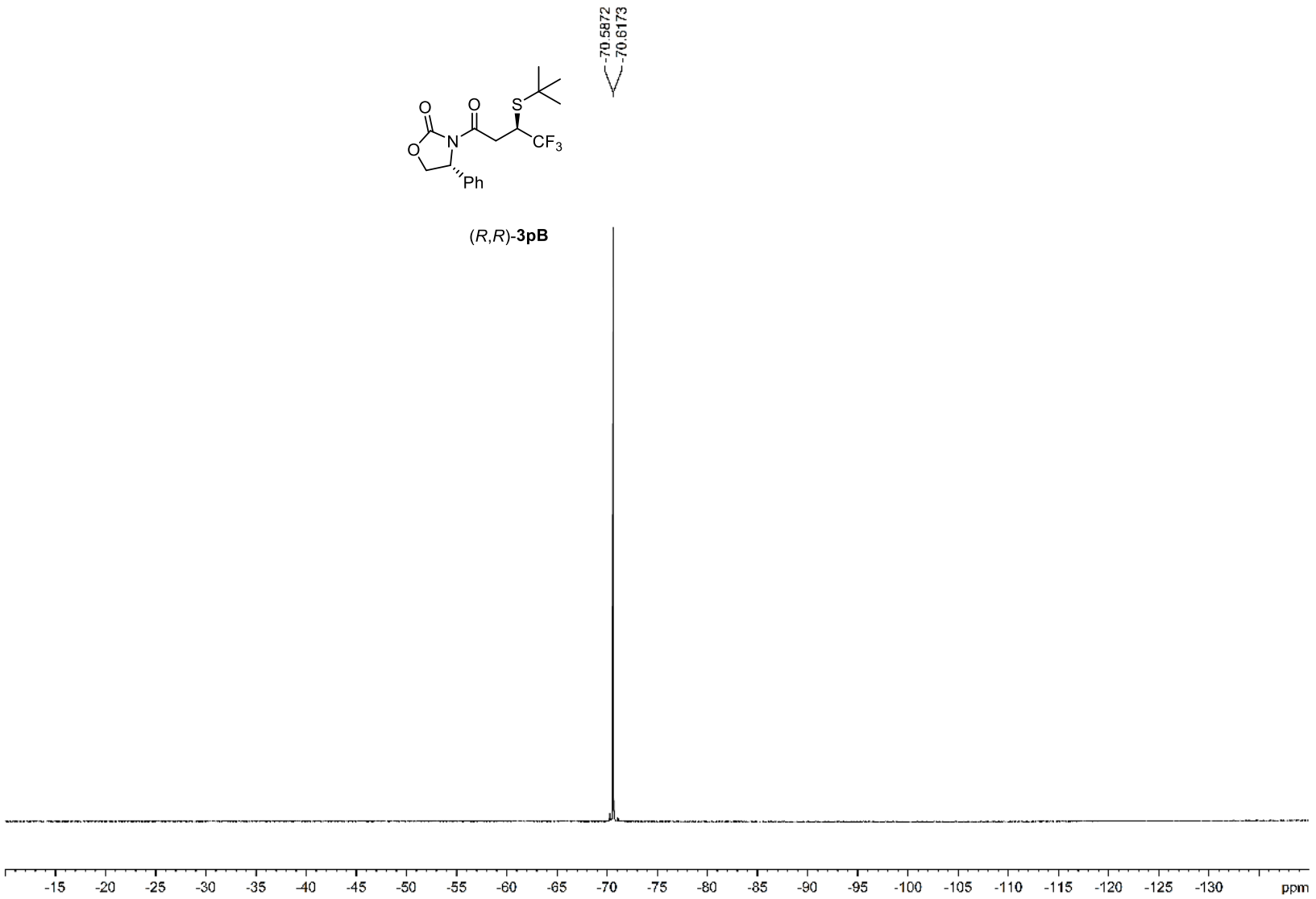



(*R*,*R*)-**3pB**

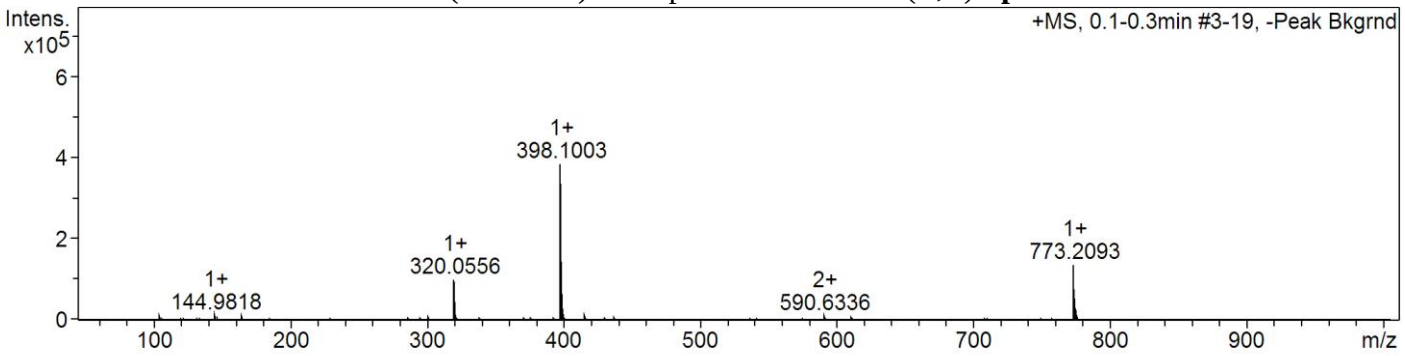
$^{13}$C NMR Spectrum of (*R*,*R*)-**3pB** (125 MHz, $CDCl_3$)



$^{19}$F NMR Spectrum of (*R*,*R*)-**3pB** (376 MHz, $CDCl_3$)



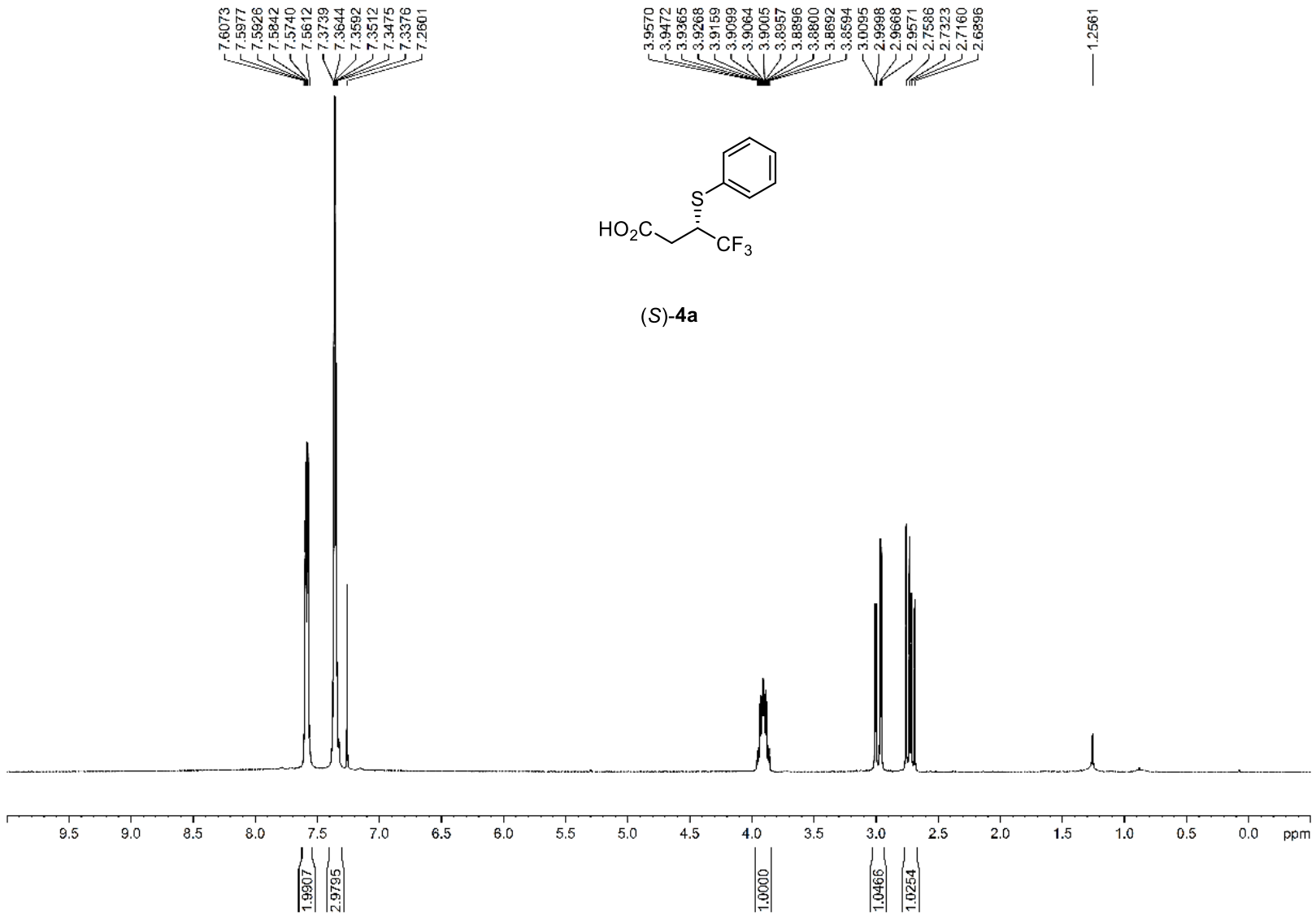
HRMS (ESI-TOF) and Specific rotation of (*R*,*R*)-**3pB**




| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.6000 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -105.3000 |
| S.D. | 1.2769 |
| C.V. | -1.2127 % |

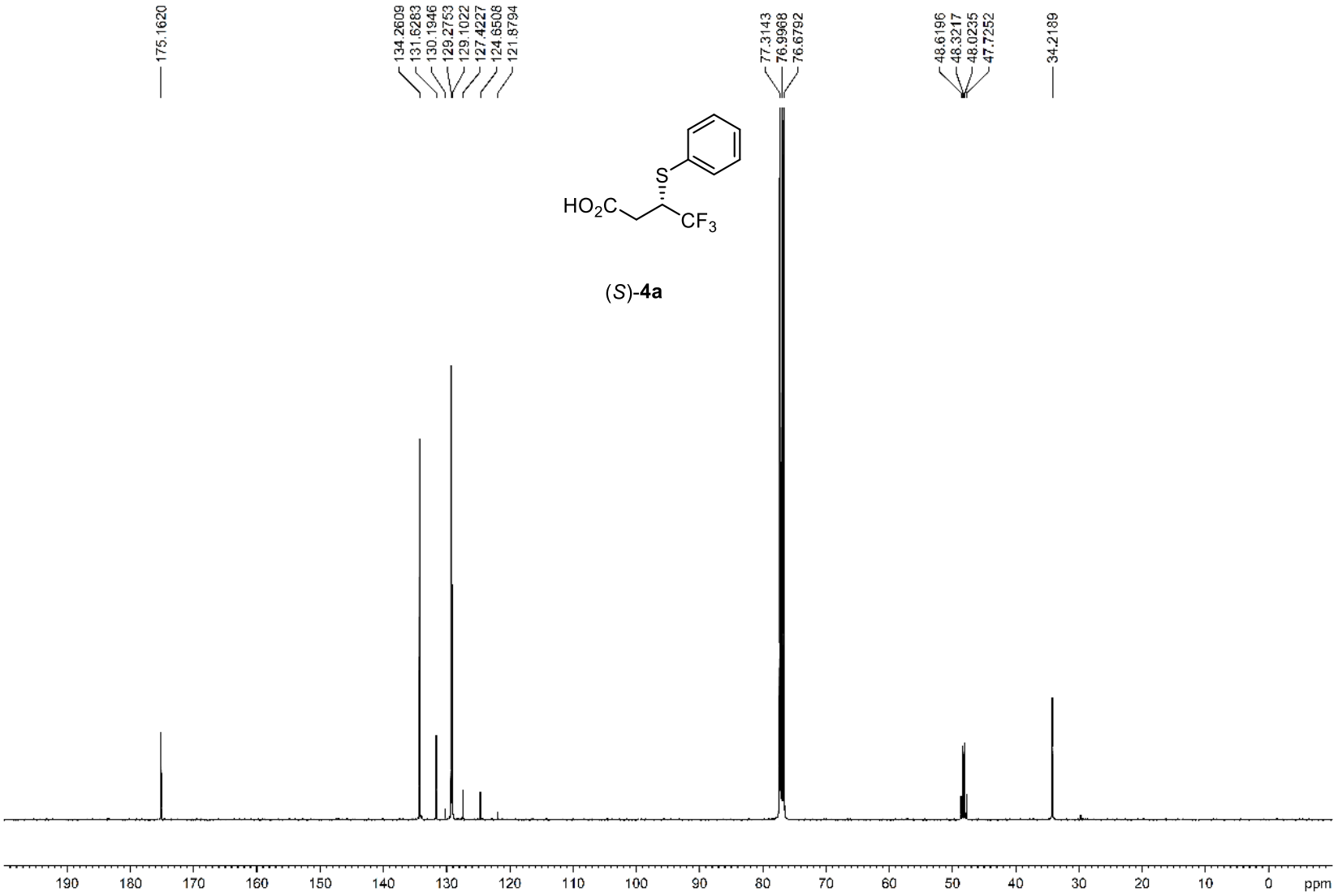
| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 83( 1/ 5) | -105.833 | 25.2 |
| 2 | 83( 2/ 5) | -106.833 | 25.2 |
| 3 | 83( 3/ 5) | -105.333 | 25.2 |
| 4 | 83( 4/ 5) | -103.333 | 25.2 |
| 5 | 83( 5/ 5) | -105.167 | 25.2 |

$^1$H NMR Spectrum of (*S*)-**4a** (400 MHz, $CDCl_3$)

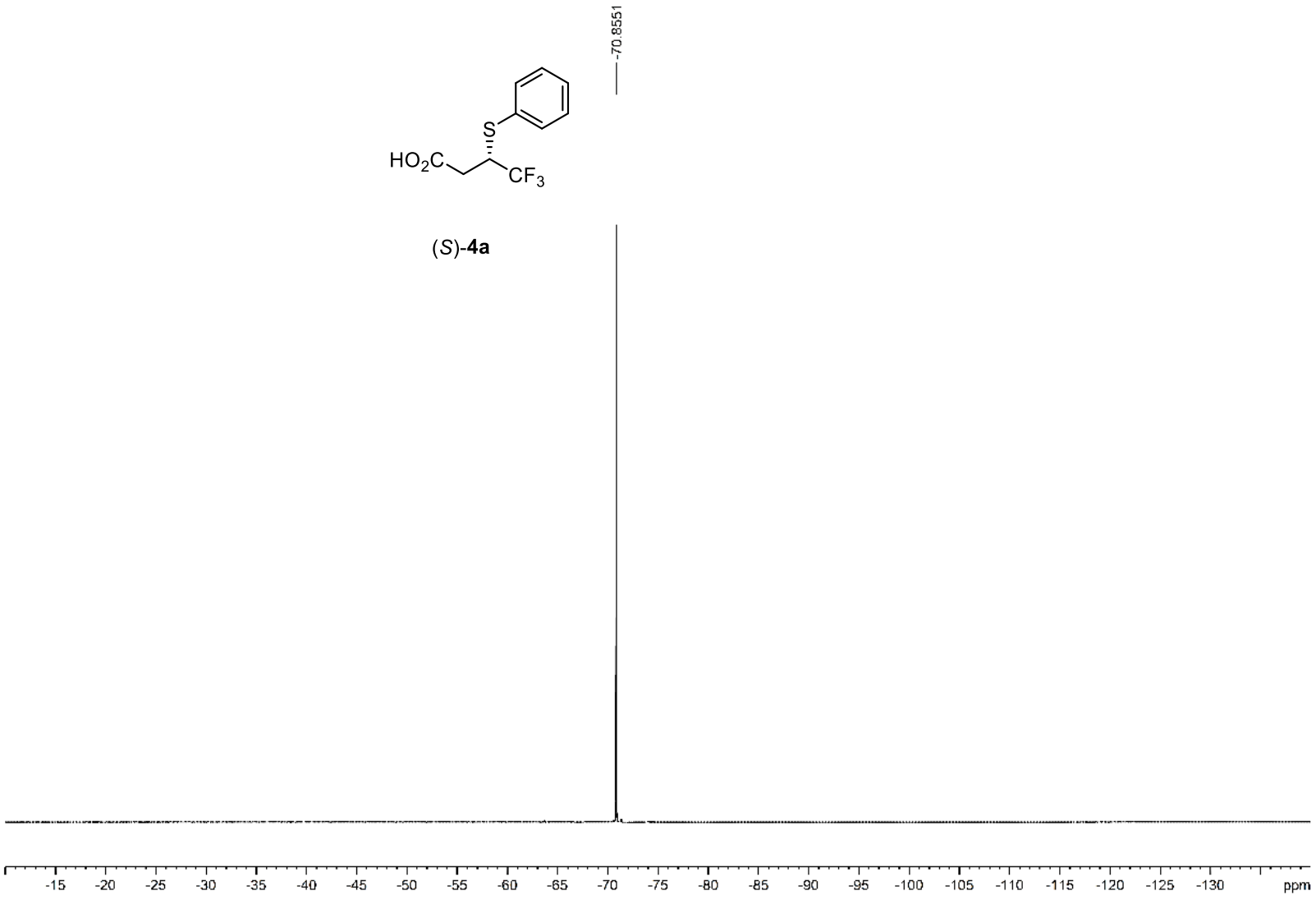



(*S*)-**4a**

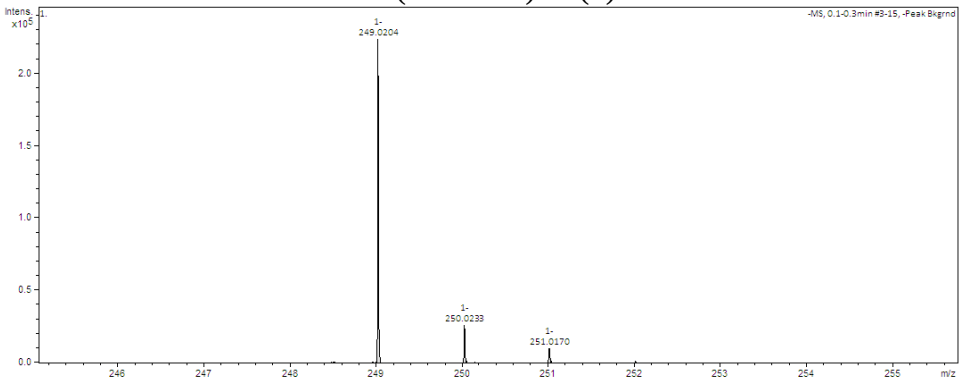
$^{13}$C NMR Spectrum of (*S*)-**4a** (100 MHz, $CDCl_3$)



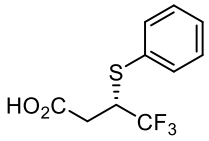
$^{19}$F NMR Spectrum of (*S*)-**4a** (376 MHz, $CDCl_3$)



HRMS (ESI-TOF) of (*S*)-**4a**



Specific rotations of (*S*)-**4a** and (*R*)-**4b**



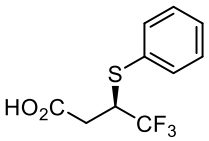

(*S*)-**4a**

| Comment | CH2Cl2 |
|---|---|
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0900 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 7.5596 |
| S.D. | 0.7908 |
| C.V. | 10.4609 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 38( 1/ 5) | 7.339 | 24.1 |
| 2 | 38( 2/ 5) | 6.789 | 24.1 |
| 3 | 38( 3/ 5) | 7.982 | 24.1 |
| 4 | 38( 4/ 5) | 8.716 | 24.1 |
| 5 | 38( 5/ 5) | 6.972 | 24.1 |

| Comment | CHCl3 |
|---|---|
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0167 w/v% |
| Factor | 1.0000 |
| Blank | 0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 7.5539 |
| S.D. | 0.5752 |
| C.V. | 7.6147 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 5( 1/ 5) | 7.377 | 25.9 |
| 2 | 5( 2/ 5) | 8.164 | 25.9 |
| 3 | 5( 3/ 5) | 7.967 | 26.0 |
| 4 | 5( 4/ 5) | 6.688 | 26.0 |
| 5 | 5( 5/ 5) | 7.574 | 26.0 |

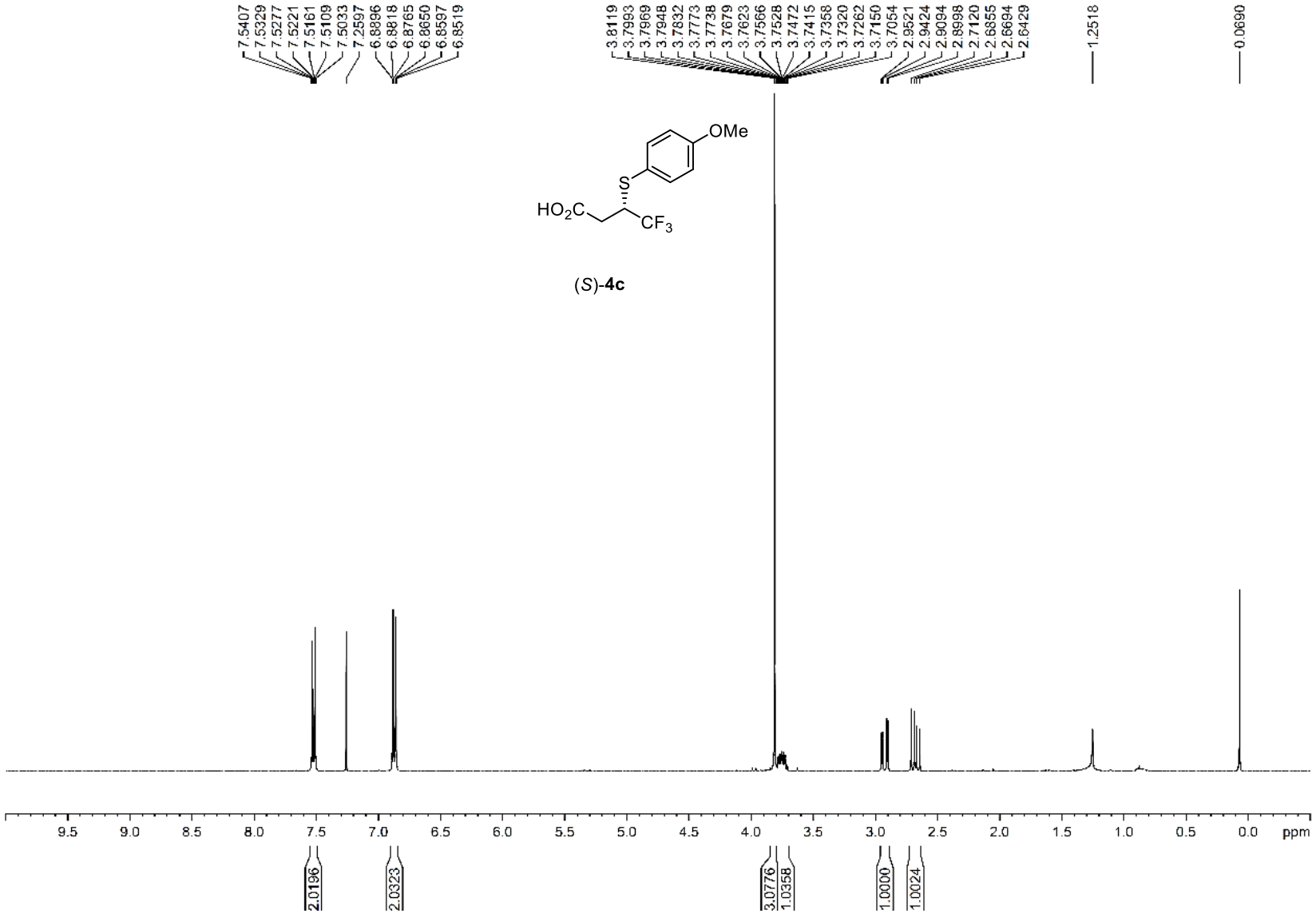



(*R*)-**4b**

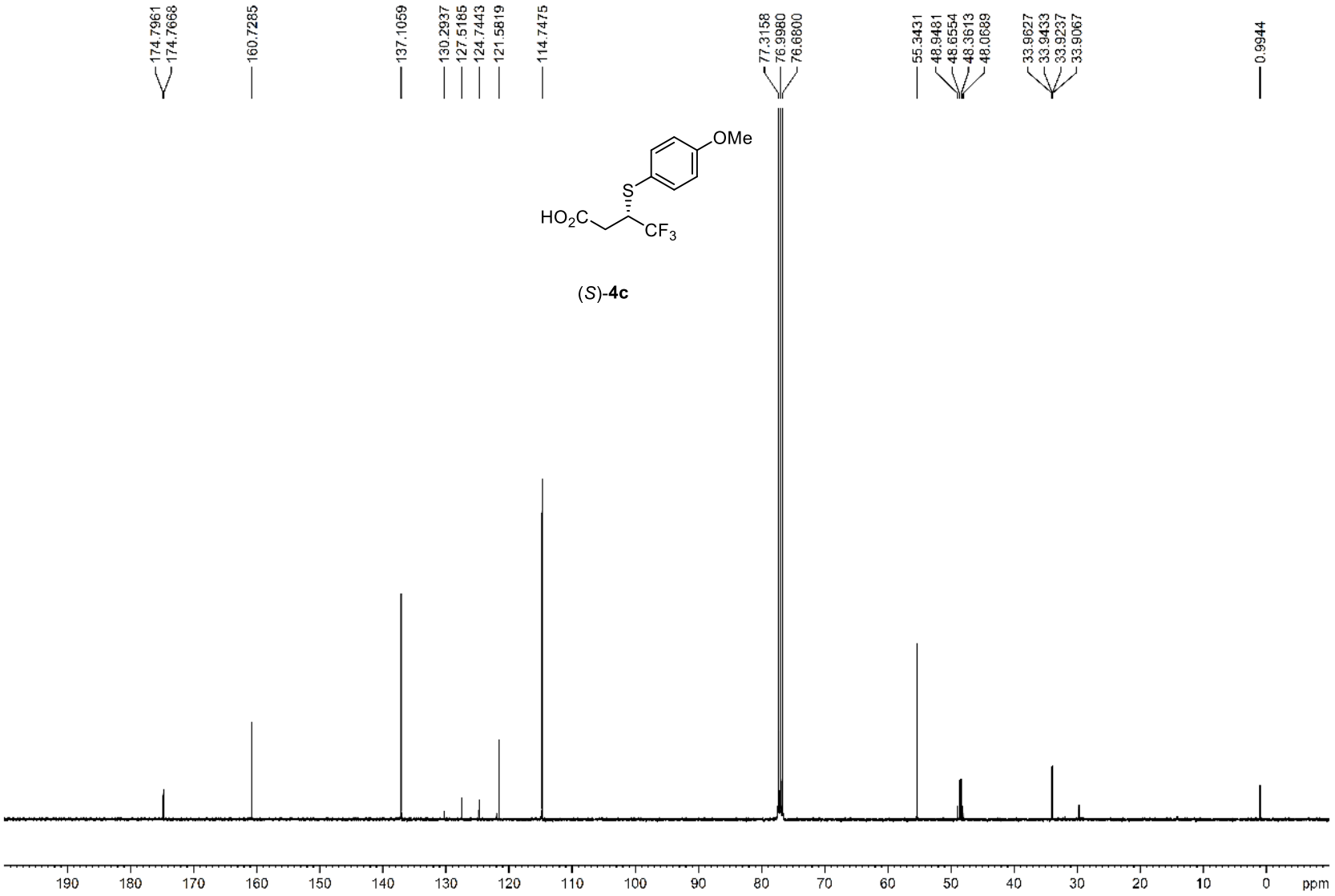
| Comment | CH2Cl2 |
|---|---|
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0727 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -13.3122 |
| S.D. | 0.8630 |
| C.V. | -6.4828 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 10( 1/ 5) | -13.051 | 25.2 |
| 2 | 10( 2/ 5) | -11.933 | 25.2 |
| 3 | 10( 3/ 5) | -14.077 | 25.2 |
| 4 | 10( 4/ 5) | -13.611 | 25.2 |
| 5 | 10( 5/ 5) | -13.890 | 25.2 |

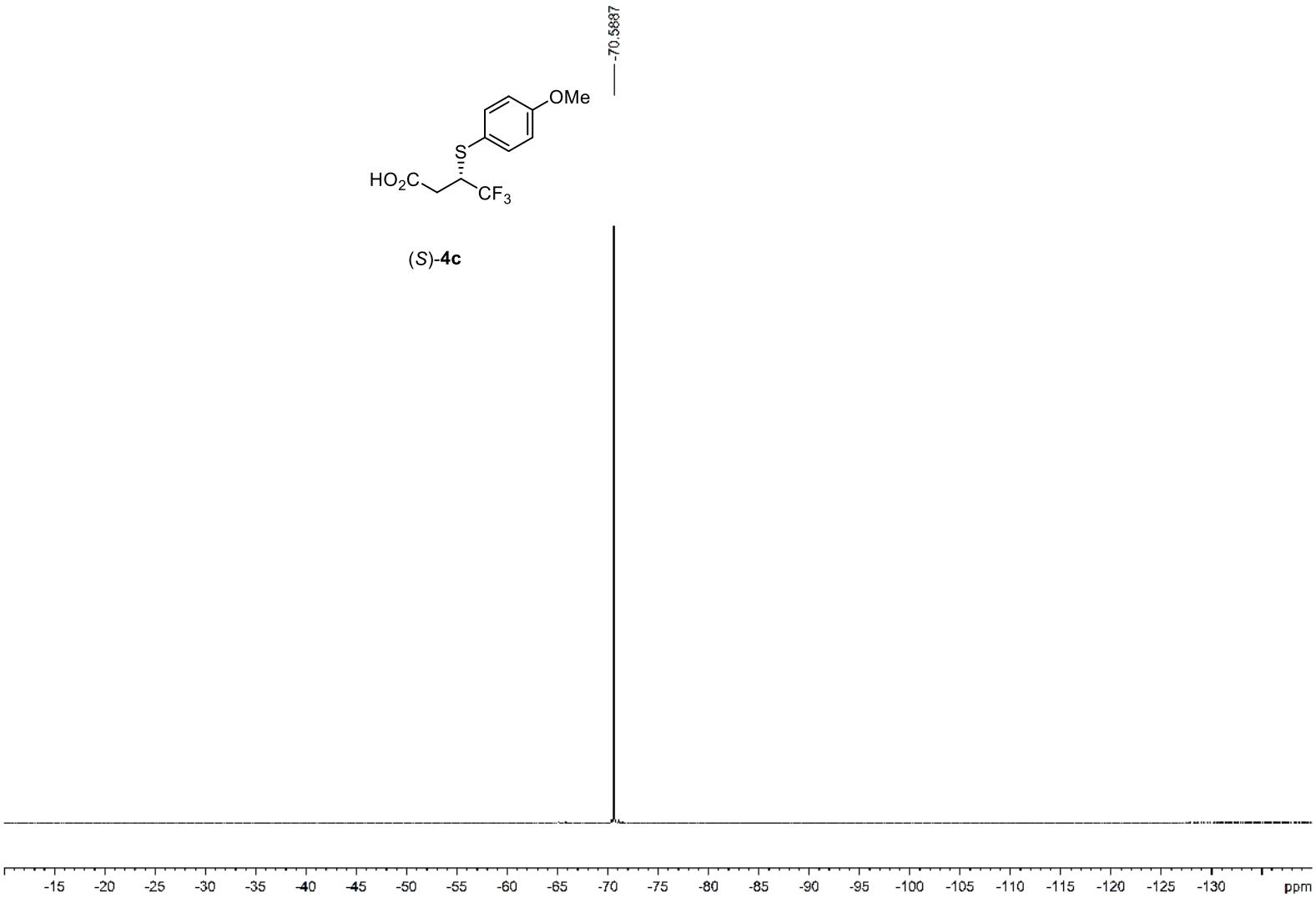
$^1$H NMR Spectrum of (*S*)-**4c** (400 MHz, $CDCl_3$)



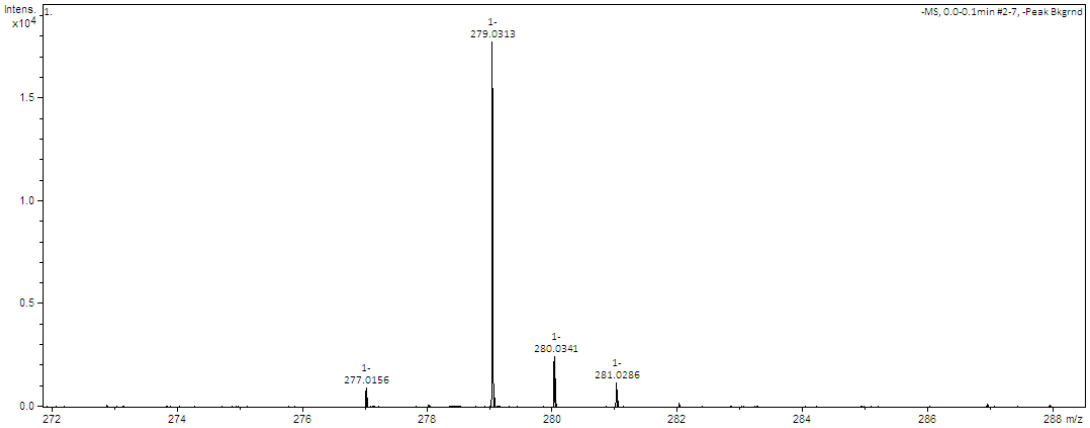
$^{13}$C NMR Spectrum of (*S*)-**4c** (100 MHz, $CDCl_3$)



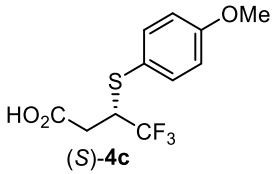
$^{19}$F NMR Spectrum of (*S*)-**4c** (376 MHz, $CDCl_3$)



HRMS (ESI-TOF) of (*S*)-**4c**



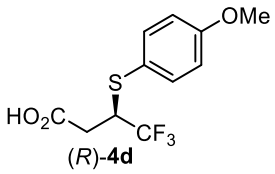
Specific rotations of (*S*)-**4c** and (*R*)-**4d**



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

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.2385 w/v% |
| Factor | 1.0000 |
| Blank | 0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 7.1377 |
| S.D. | 0.4295 |
| C.V. | 6.0178 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 26( 1/ 5) | 7.105 | 25.1 |
| 2 | 26( 2/ 5) | 7.832 | 25.1 |
| 3 | 26( 3/ 5) | 6.782 | 25.1 |
| 4 | 26( 4/ 5) | 7.186 | 25.1 |
| 5 | 26( 5/ 5) | 6.782 | 25.1 |

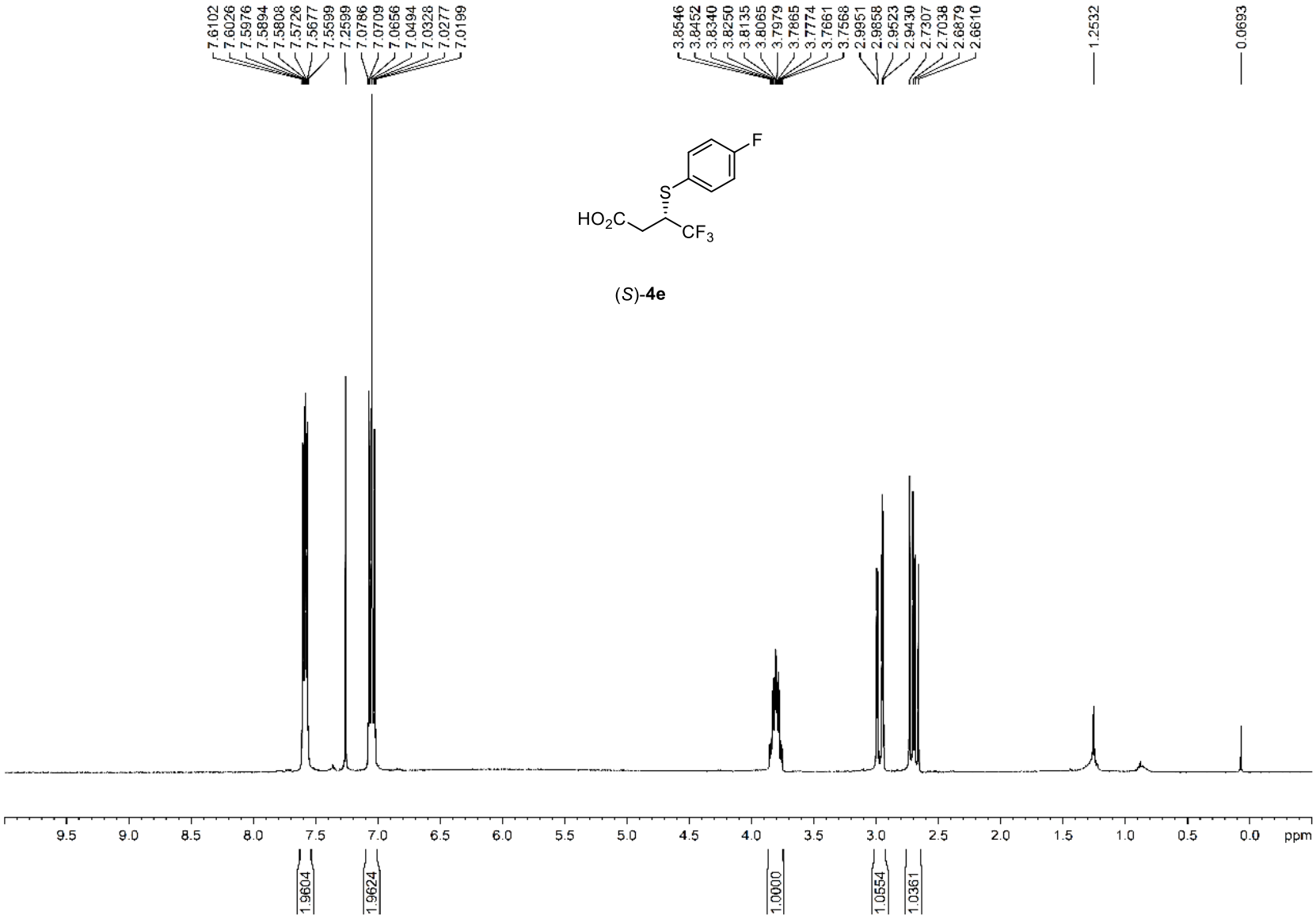


(*R*)-**4d**

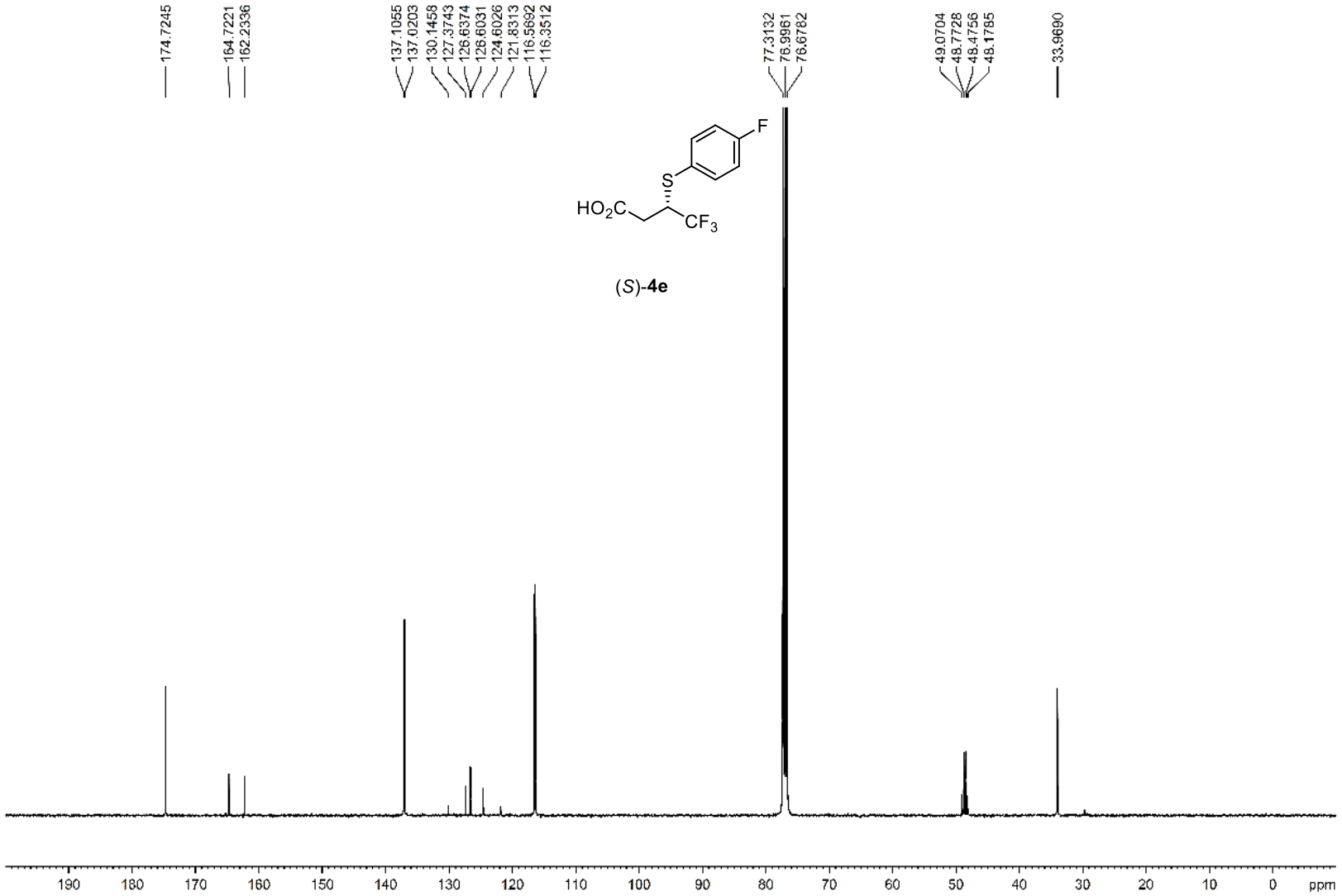
| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0500 w/v% |
| Factor | 1.0000 |
| Blank | -0.0004 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -3.8286 |
| S.D. | 1.3759 |
| C.V. | -35.9364 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 72( 1/ 5) | -5.143 | 25.2 |
| 2 | 72( 2/ 5) | -2.000 | 25.3 |
| 3 | 72( 3/ 5) | -2.952 | 25.3 |
| 4 | 72( 4/ 5) | -5.143 | 25.2 |
| 5 | 72( 5/ 5) | -3.905 | 25.2 |

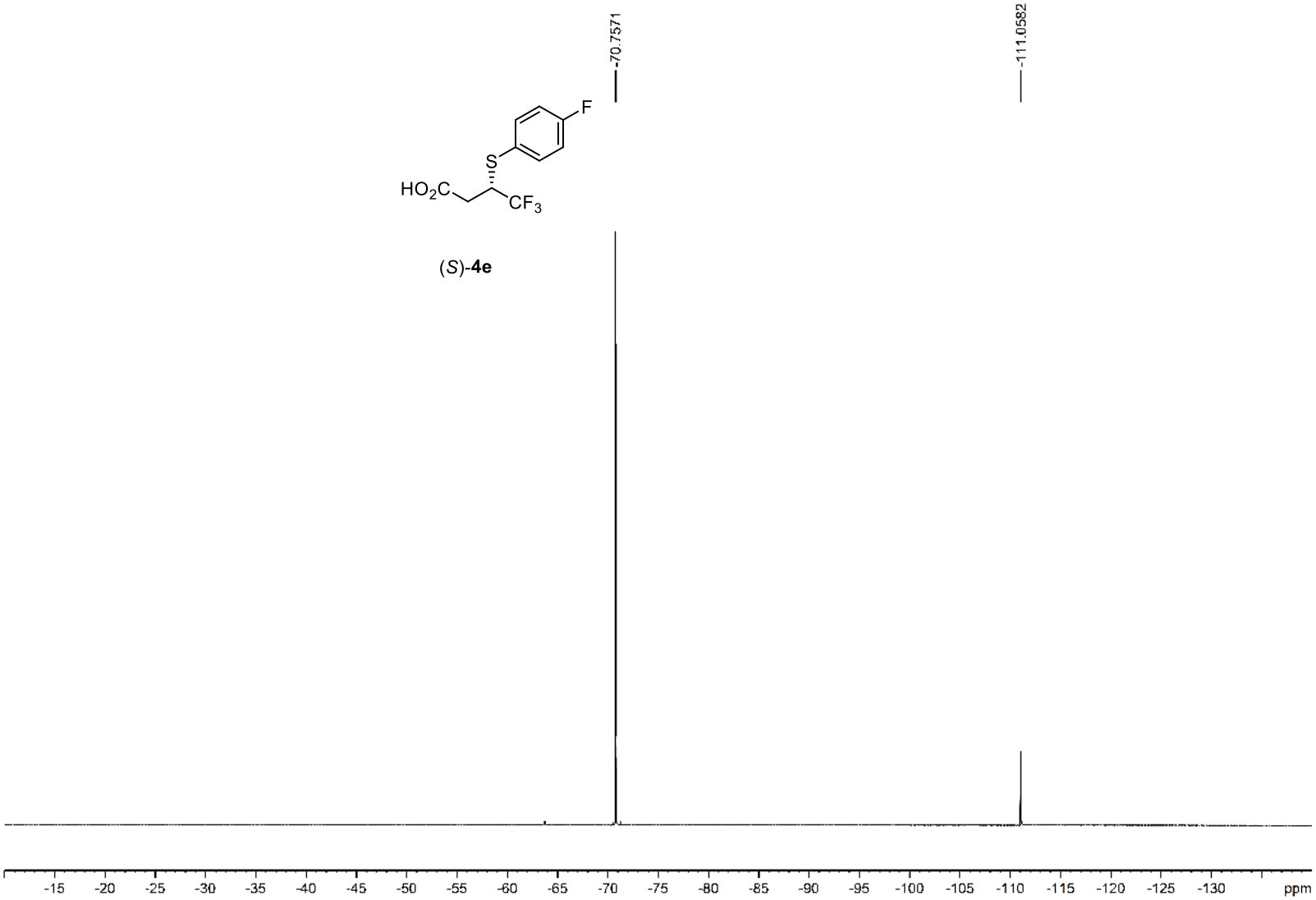
$^1$H NMR Spectrum of (*S*)-**4e** (400 MHz, $CDCl_3$)



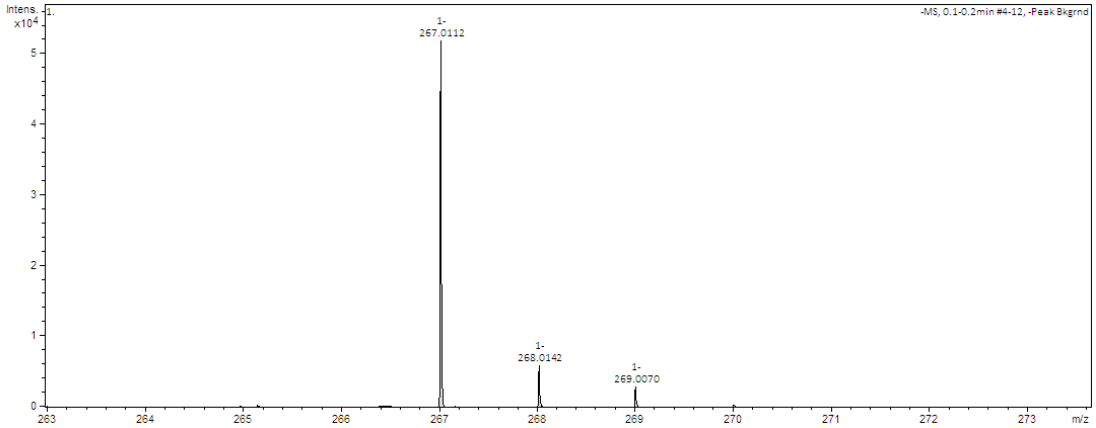
$^{13}$C NMR Spectrum of (*S*)-**4e** (100 MHz, $CDCl_3$)



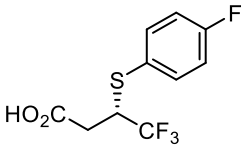
$^{19}$F NMR Spectrum of (*S*)-**4e** (376 MHz, $CDCl_3$)



HRMS (ESI-TOF) of (*S*)-**4e**



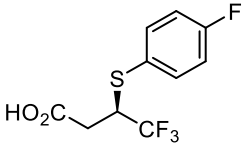
Specific rotations of (*S*)-**4e** and (*R*)-**4f**



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

| | |
|---|---|
| Comment | CH2Cl2 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0167 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 2.2032 |
| S.D. | 0.5044 |
| C.V. | 22.8944 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 100( 1/ 5) | 2.459 | 22.9 |
| 2 | 100( 2/ 5) | 1.672 | 22.9 |
| 3 | 100( 3/ 5) | 2.951 | 22.9 |
| 4 | 100( 4/ 5) | 1.967 | 22.9 |
| 5 | 100( 5/ 5) | 1.967 | 22.9 |

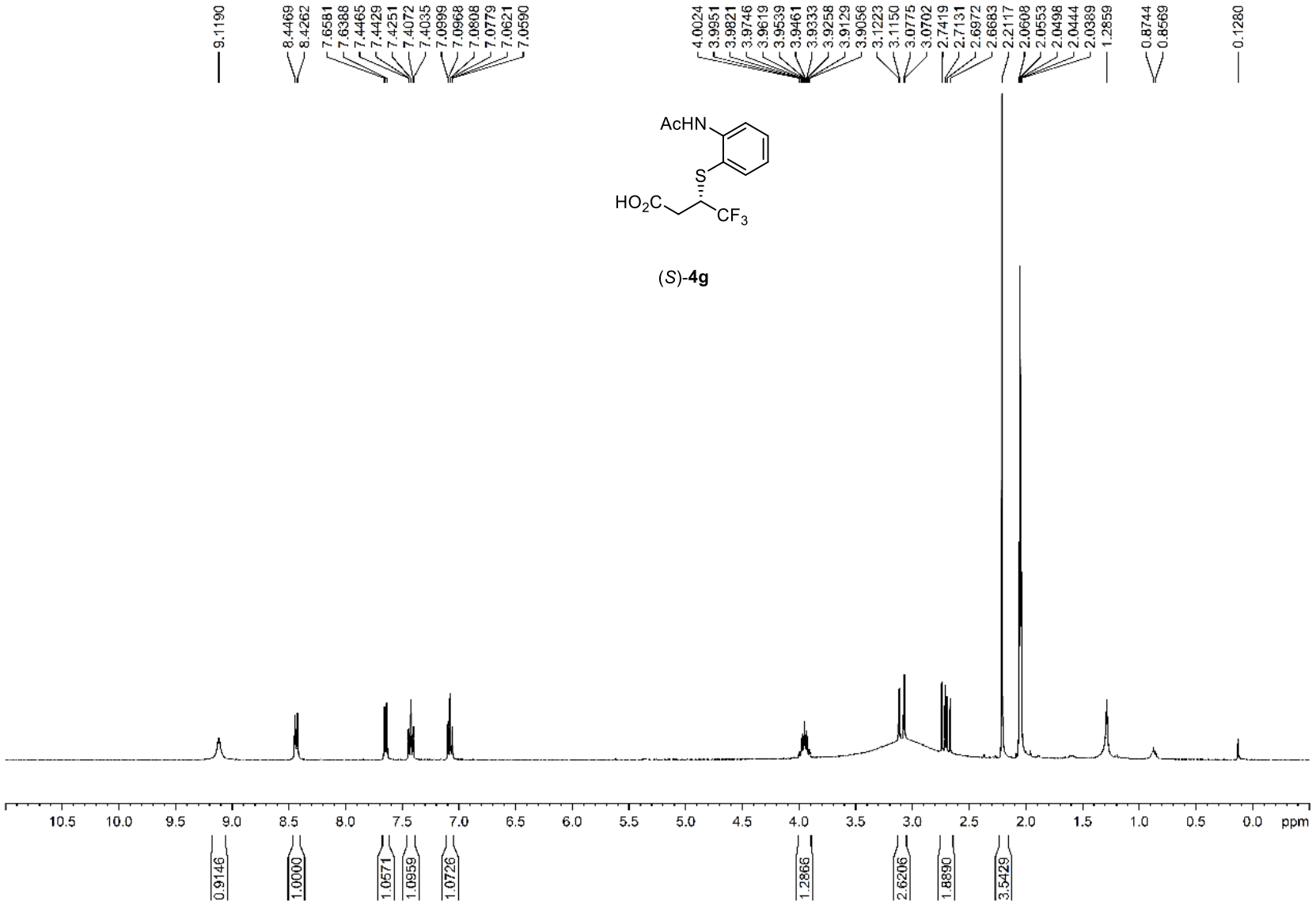


(*R*)-**4f**

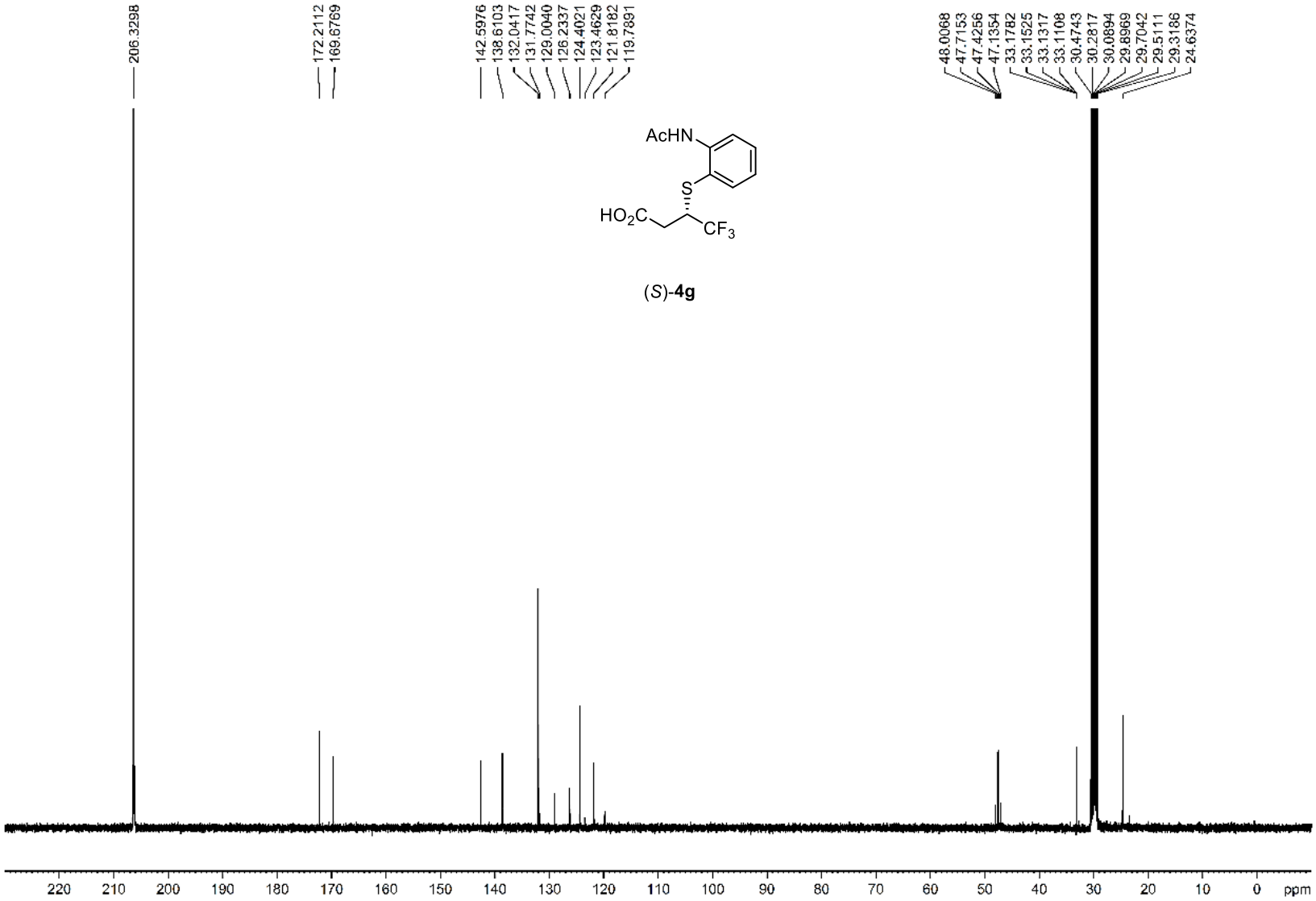
| | |
|---|---|
| Comment | CH2Cl2 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0923 w/v% |
| Factor | 1.0000 |
| Blank | -0.0001 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -1.2451 |
| S.D. | 0.7482 |
| C.V. | -60.0965 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 135( 1/ 5) | -1.556 | 23.4 |
| 2 | 135( 2/ 5) | -1.556 | 23.3 |
| 3 | 135( 3/ 5) | 0.092 | 23.4 |
| 4 | 135( 4/ 5) | -1.648 | 23.4 |
| 5 | 135( 5/ 5) | -1.556 | 23.4 |

$^1$H NMR Spectrum of (*S*)-**4g** (400 MHz, acetone-$d_6$)



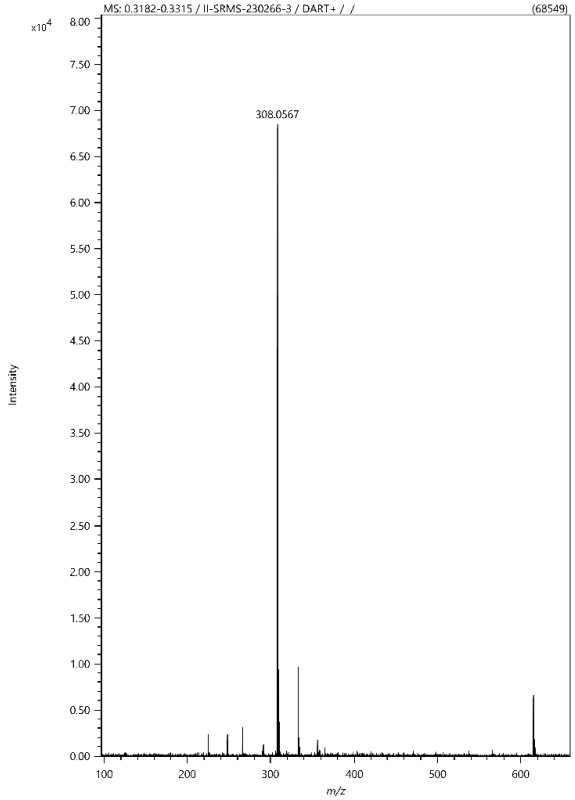
$^{13}$C NMR Spectrum of (*S*)-**4g** (100 MHz, acetone-$d_6$)



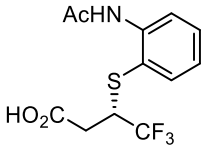

(*S*)-**4g**

$^{19}$F NMR Spectrum of (*S*)-**4g** (376 MHz, acetone-$d_6$)

# HRMS (DART) of (*S*)-**4g**



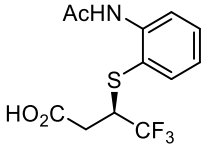
# Specific rotations of (*S*)-**4g** and (*R*)-**4h**




(*S*)-**4g**

| | |
|---|---|
| Comment | Acetone |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0538 w/v% |
| Factor | 1.0000 |
| Blank | -0.0005 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -72.2718 |
| S.D. | 0.3712 |
| C.V. | -0.5136 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 56( 1/ 5) | -72.310 | 21.0 |
| 2 | 56( 2/ 5) | -72.310 | 21.0 |
| 3 | 56( 3/ 5) | -72.784 | 21.0 |
| 4 | 56( 4/ 5) | -72.215 | 21.0 |
| 5 | 56( 5/ 5) | -71.740 | 21.0 |

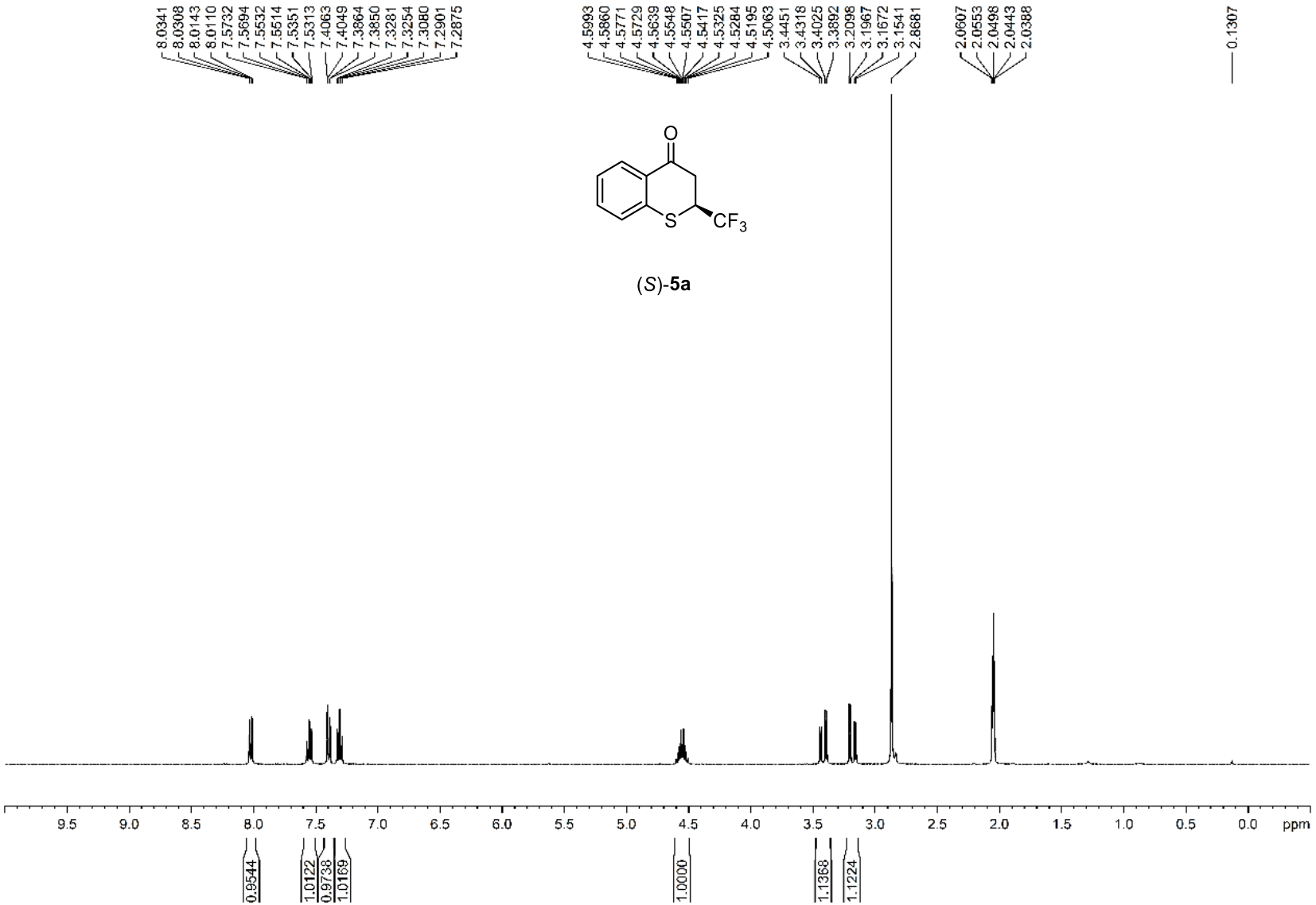



(*R*)-**4h**

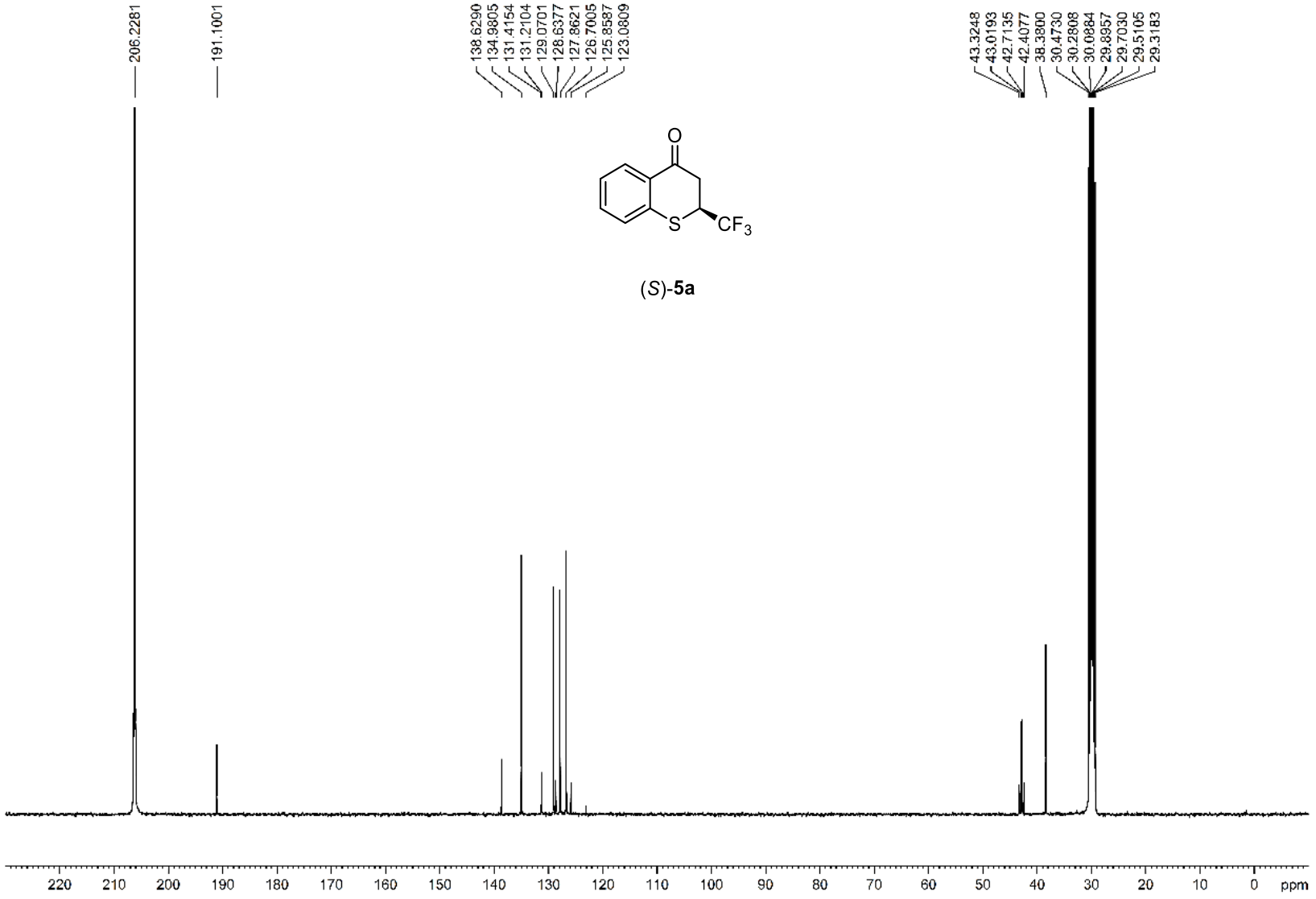
| | |
|---|---|
| Comment | Acetone |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0000 w/v% |
| Factor | 1.0000 |
| Blank | -0.0002 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 71.0600 |
| S.D. | 0.7369 |
| C.V. | 1.0370 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 66( 1/ 5) | 70.500 | 24.2 |
| 2 | 66( 2/ 5) | 71.700 | 24.2 |
| 3 | 66( 3/ 5) | 71.900 | 24.2 |
| 4 | 66( 4/ 5) | 70.200 | 24.2 |
| 5 | 66( 5/ 5) | 71.000 | 24.2 |

$^1$H NMR Spectrum of (*S*)-**5a** (400 MHz, acetone-$d_6$)

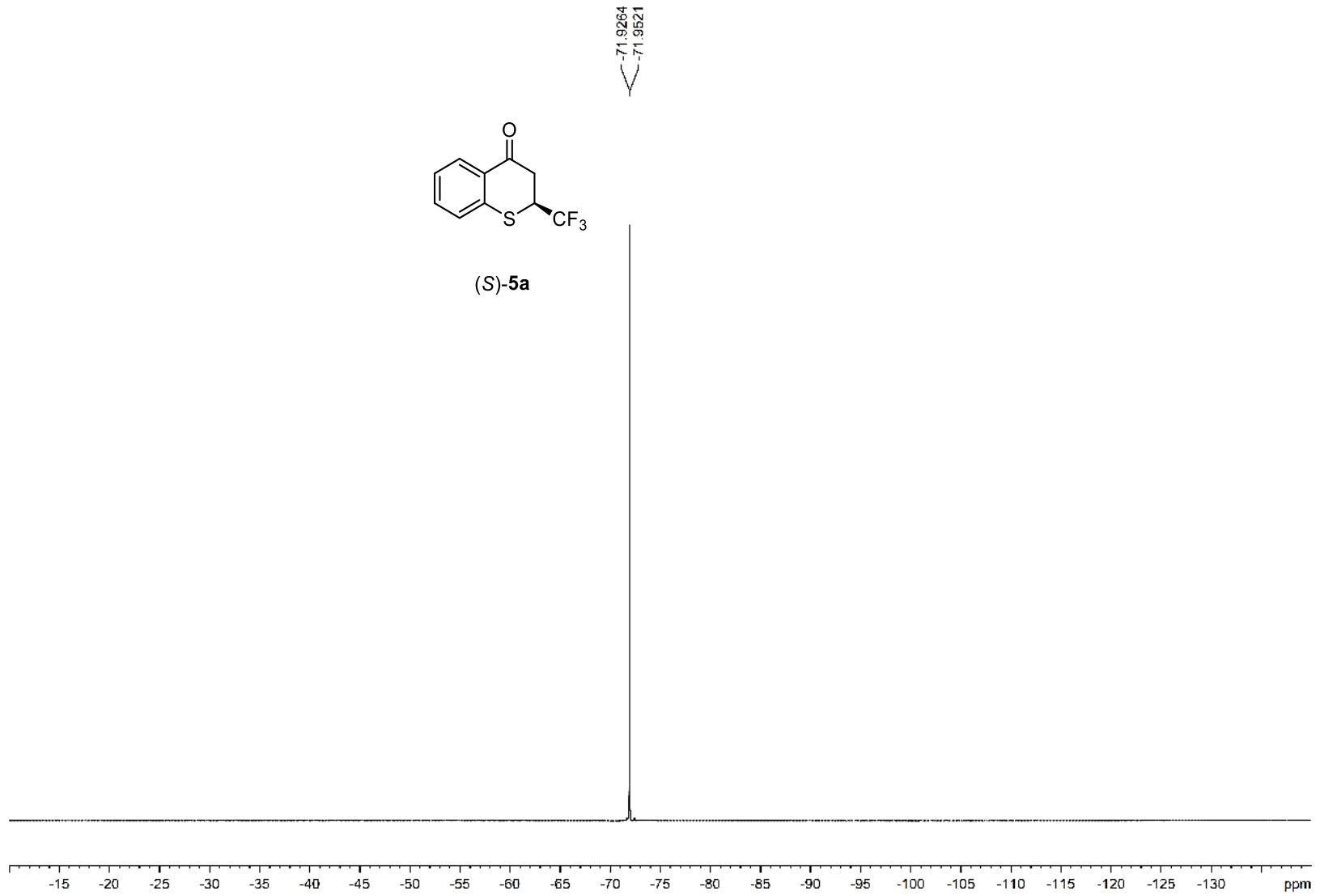


$^{13}$C NMR Spectrum of (*S*)-**5a** (100 MHz, acetone-$d_6$)

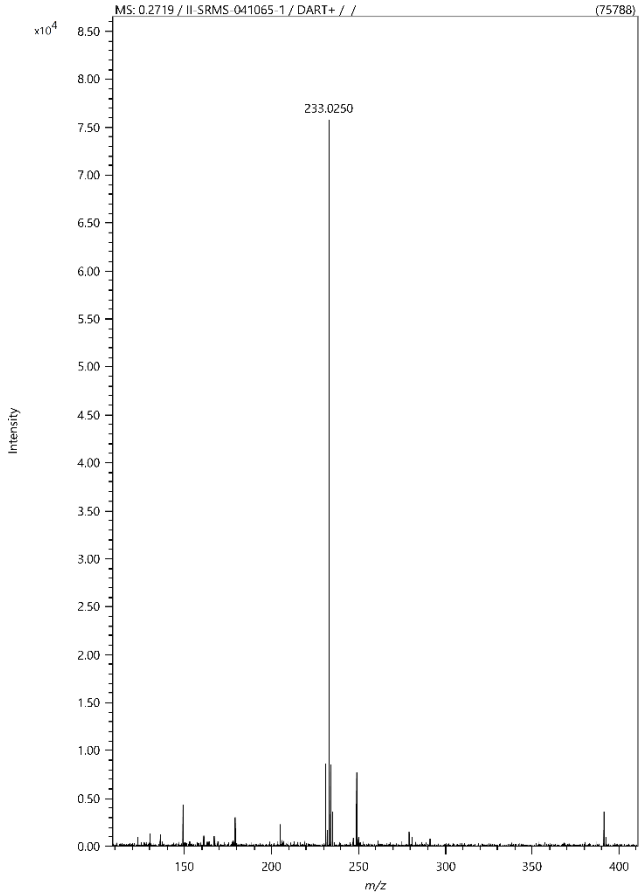



(*S*)-**5a**

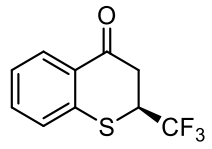
$^{19}$F NMR Spectrum of (*S*)-**5a** (376 MHz, acetone-$d_6$)



HRMS (DART) of (*S*)-**5a**



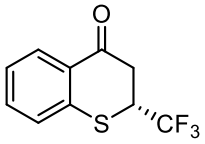
Specific rotations of (*S*)-**5a** and (*R*)-**5b**



(*S*)-**5a**

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.5800 w/v% |
| Factor | 1.0000 |
| Blank | -0.0007 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 175.5172 |
| S.D. | 1.0416 |
| C.V. | 0.5935 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 56( 1/ 5) | 174.655 | 23.8 |
| 2 | 56( 2/ 5) | 175.690 | 23.8 |
| 3 | 56( 3/ 5) | 177.241 | 23.8 |
| 4 | 56( 4/ 5) | 174.828 | 23.8 |
| 5 | 56( 5/ 5) | 175.172 | 23.8 |

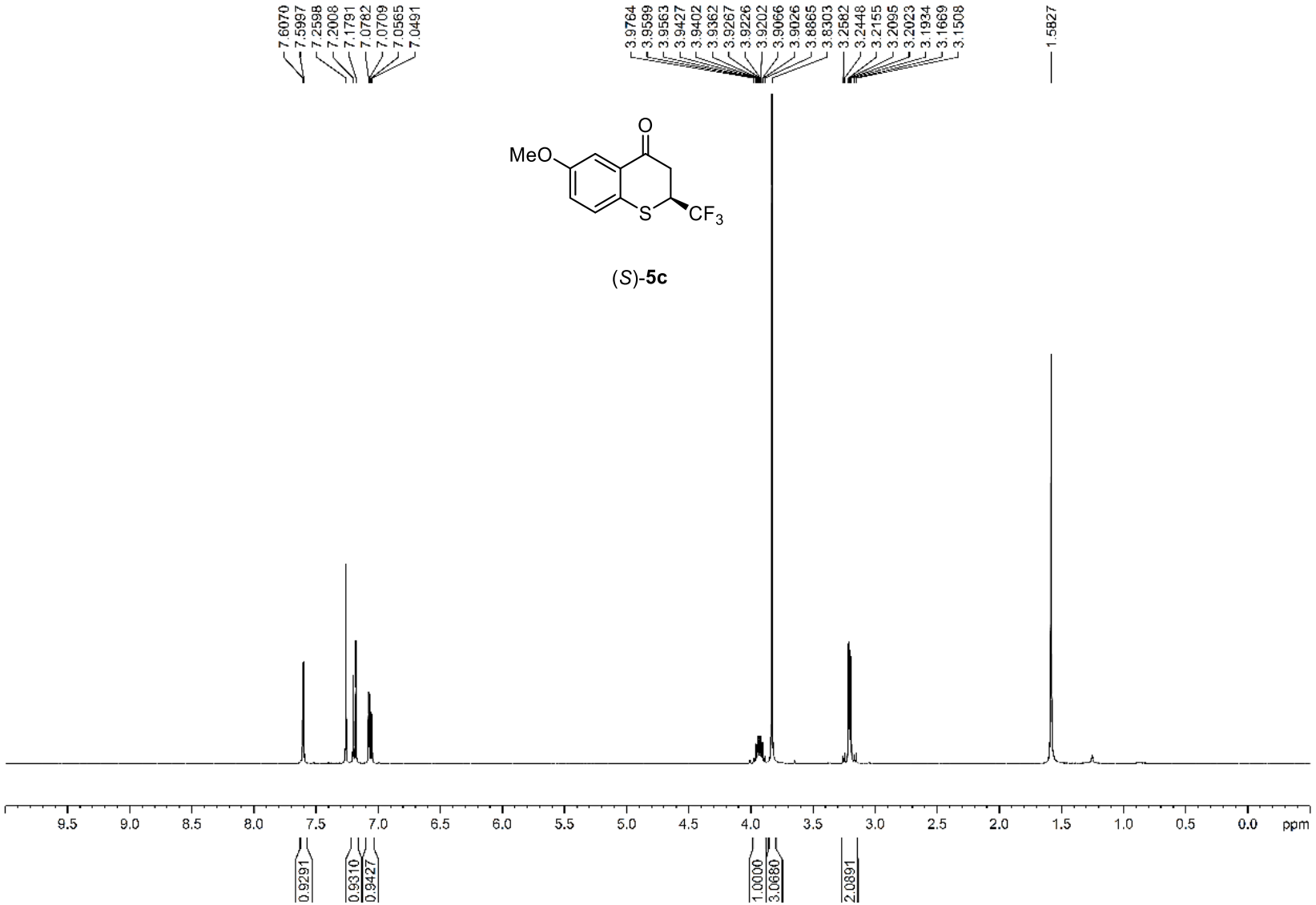


(*R*)-**5b**

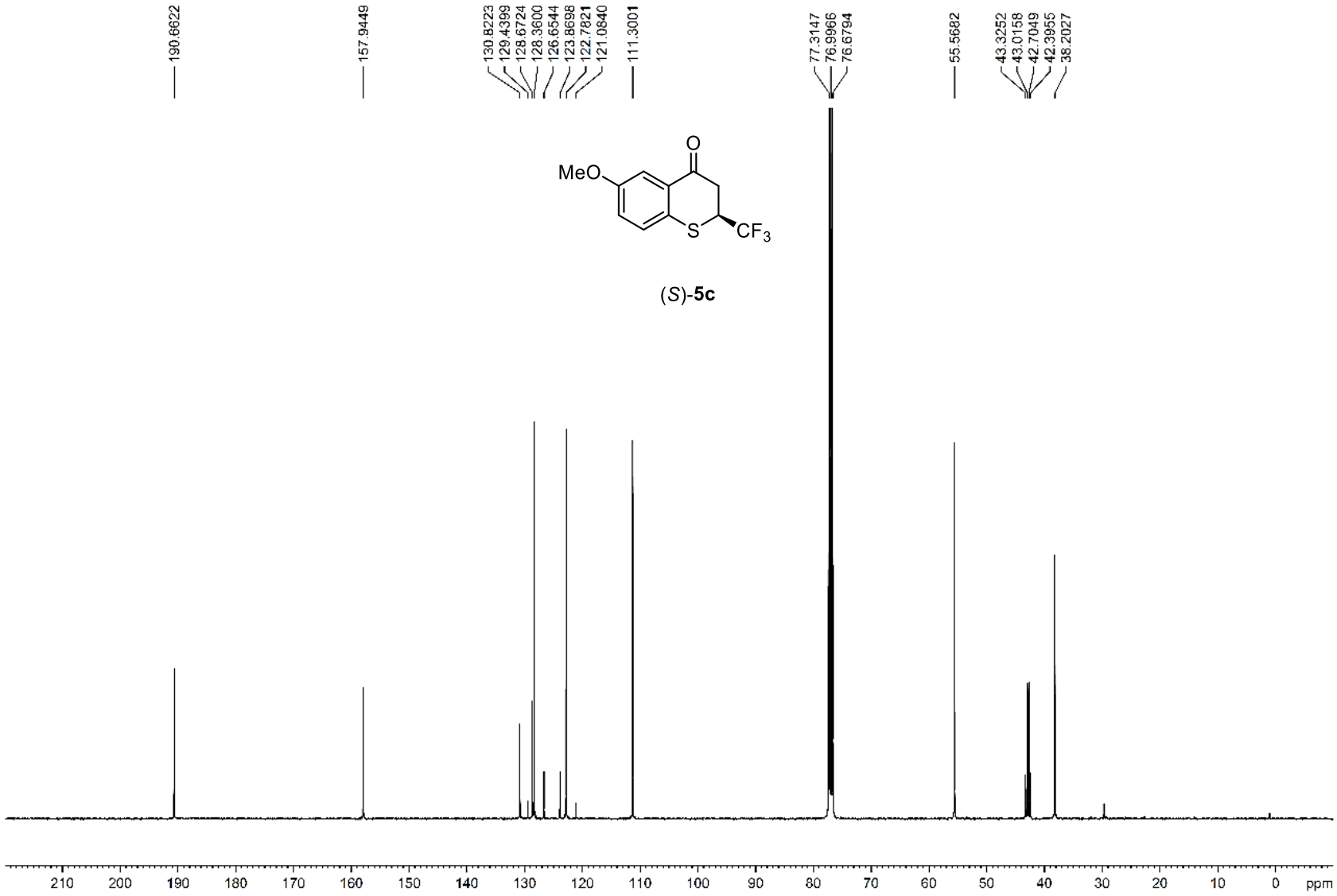
| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.5800 w/v% |
| Factor | 1.0000 |
| Blank | -0.0007 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -162.3793 |
| S.D. | 0.7653 |
| C.V. | -0.4713 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 93( 1/ 5) | -162.069 | 24.0 |
| 2 | 93( 2/ 5) | -161.552 | 24.0 |
| 3 | 93( 3/ 5) | -163.103 | 24.0 |
| 4 | 93( 4/ 5) | -161.897 | 24.0 |
| 5 | 93( 5/ 5) | -163.276 | 24.0 |

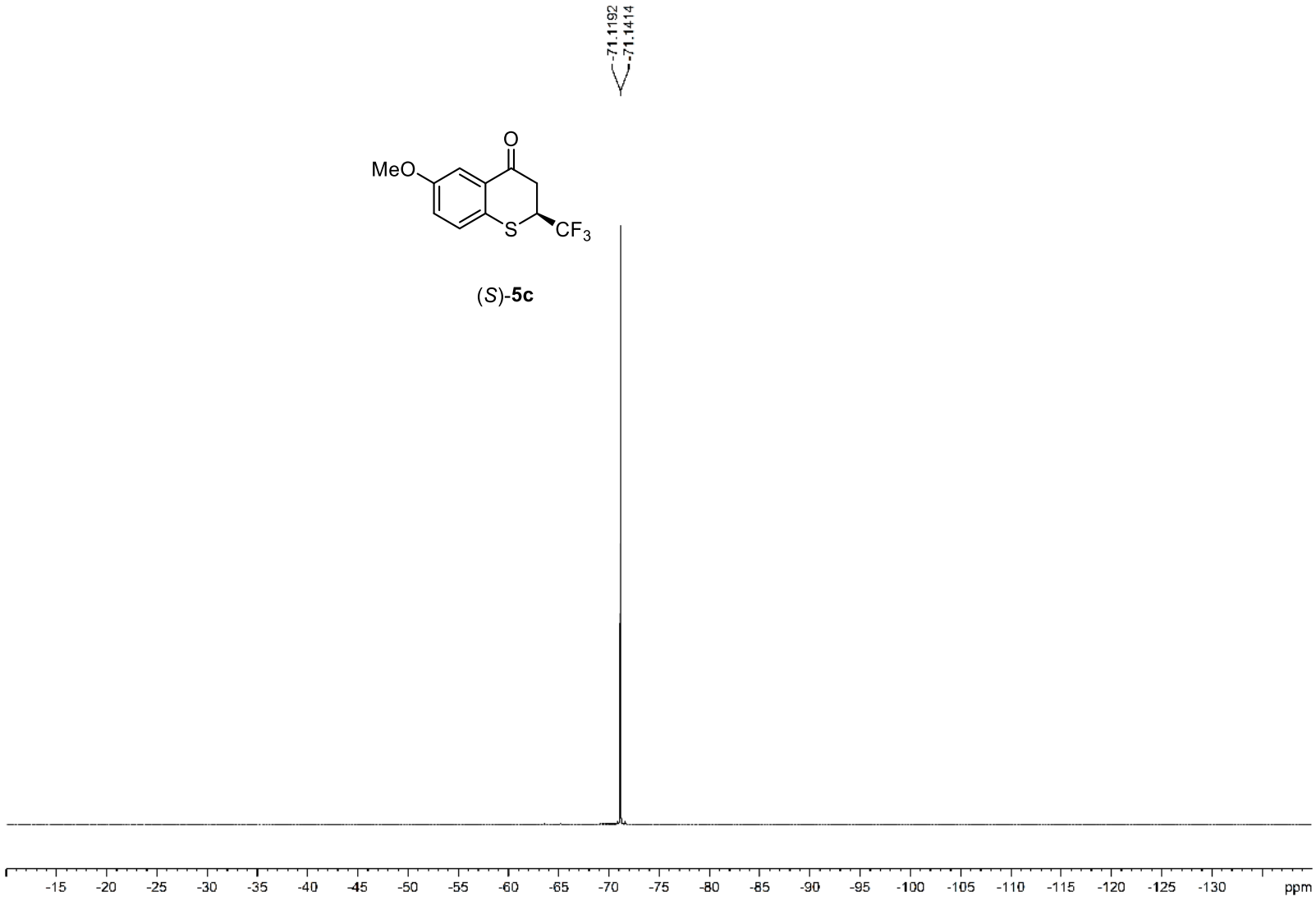
$^1$H NMR Spectrum of (*S*)-**5c** (400 MHz, $CDCl_3$)



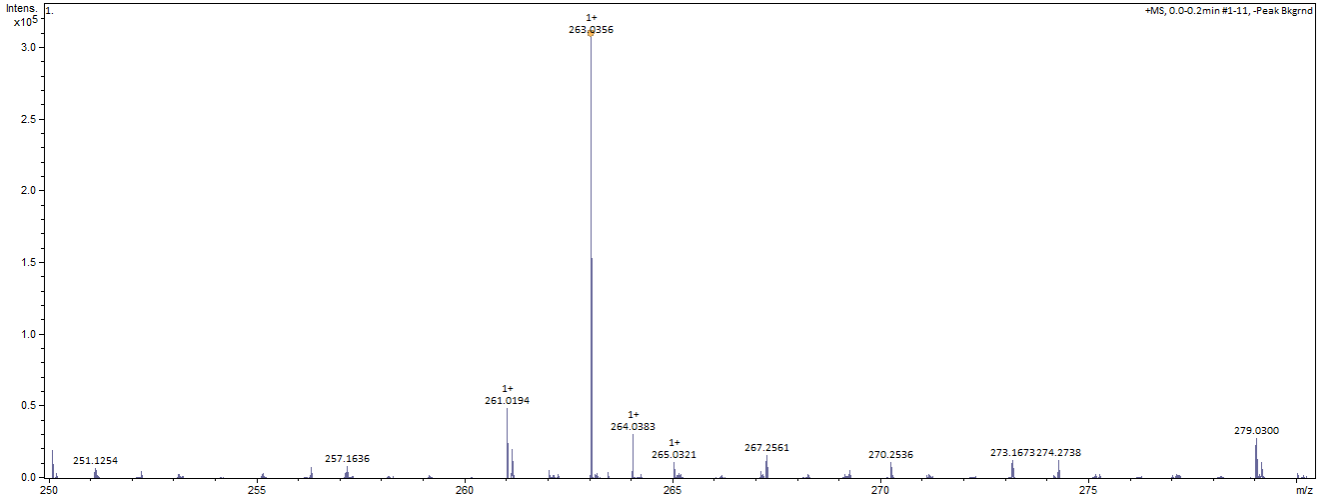
$^{13}$C NMR Spectrum of (*S*)-**5c** (100 MHz, $CDCl_3$)



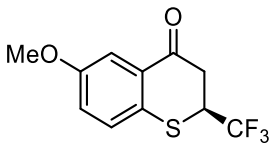
$^{19}$F NMR Spectrum of (*S*)-**5c** (376 MHz, $CDCl_3$)



HRMS (ESI-TOF) of (*S*)-**5c**



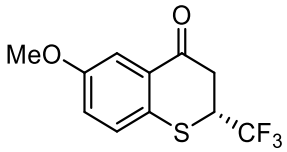
Specific rotations of (*S*)-**5c** and (*R*)-**5d**




(*S*)-**5c**

| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.6300 w/v% |
| Factor | 1.0000 |
| Blank | -0.0004 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 139.5873 |
| S.D. | 0.6002 |
| C.V. | 0.4300 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 27( 1/ 5) | 140.159 | 25.8 |
| 2 | 27( 2/ 5) | 140.159 | 25.8 |
| 3 | 27( 3/ 5) | 138.730 | 25.8 |
| 4 | 27( 4/ 5) | 139.524 | 25.7 |
| 5 | 27( 5/ 5) | 139.365 | 25.8 |

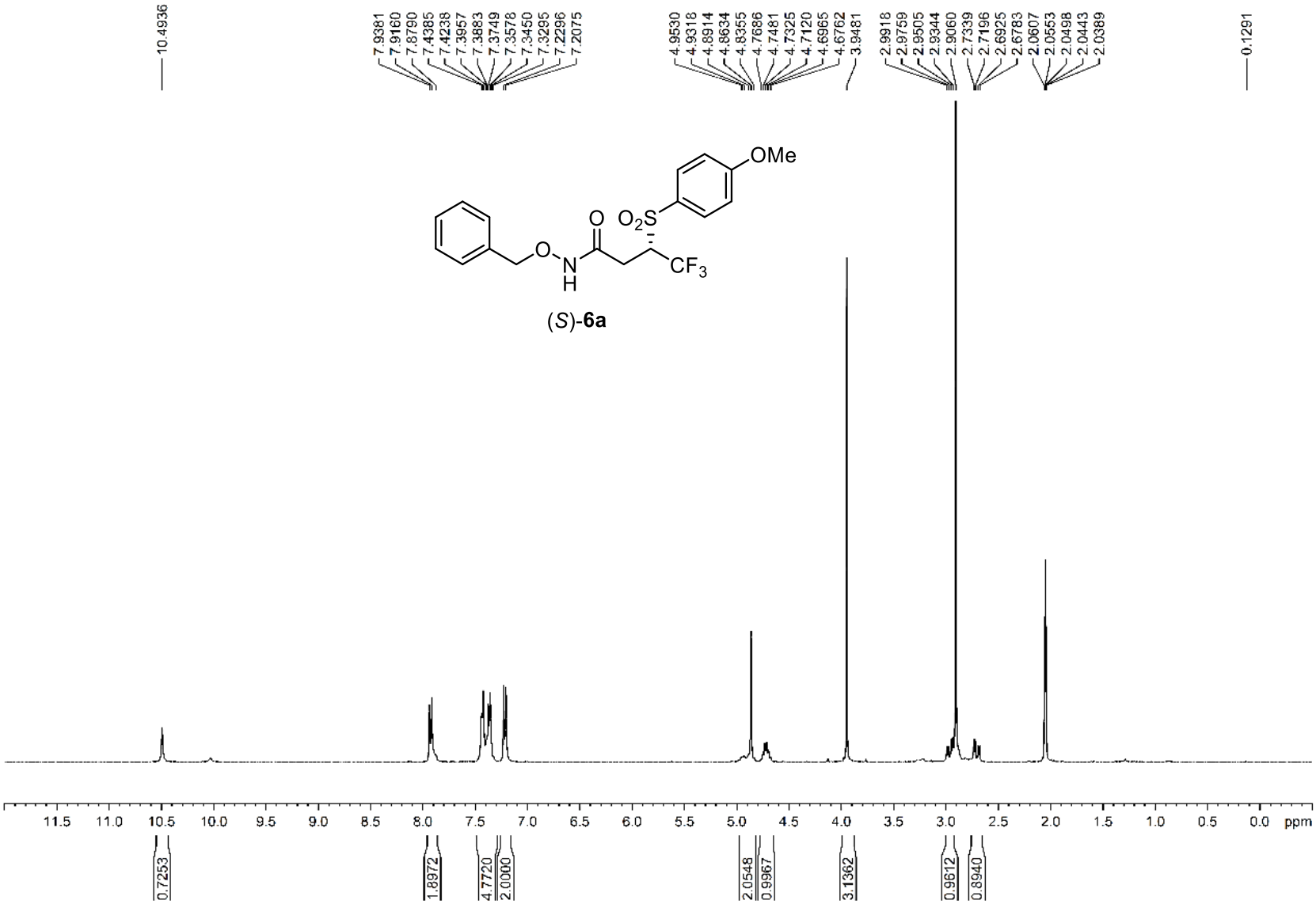



(*R*)-**5d**

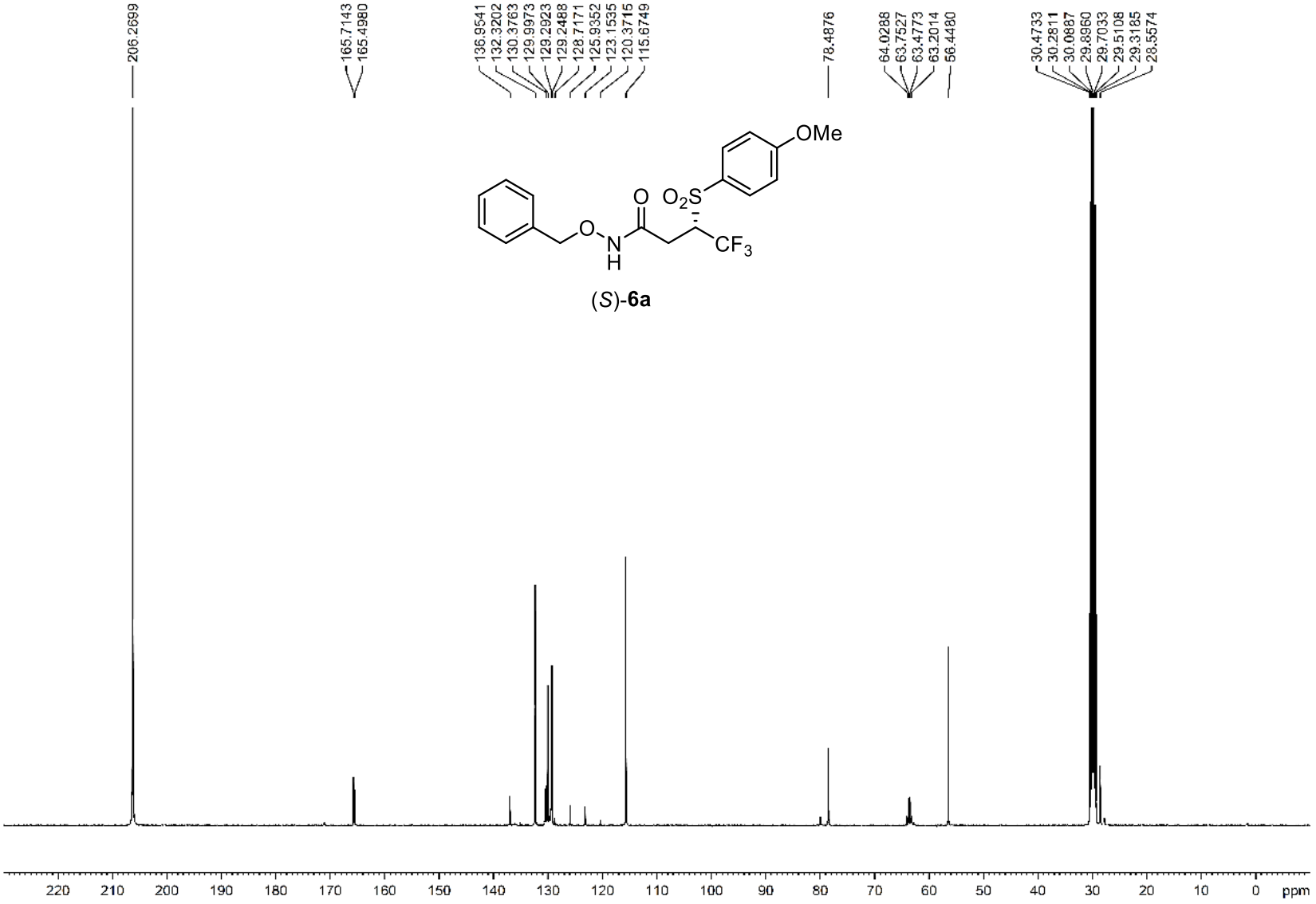
| | |
|---|---|
| Comment | CHCl3 |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.6100 w/v% |
| Factor | 1.0000 |
| Blank | -0.0025 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -121.0492 |
| S.D. | 0.8487 |
| C.V. | -0.7011 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 157( 1/ 5) | -121.803 | 25.4 |
| 2 | 157( 2/ 5) | -122.131 | 25.4 |
| 3 | 157( 3/ 5) | -120.328 | 25.4 |
| 4 | 157( 4/ 5) | -120.492 | 25.4 |
| 5 | 157( 5/ 5) | -120.492 | 25.4 |

$^1$H NMR Spectrum of (*S*)-**6a** (400 MHz, acetone-$d_6$)

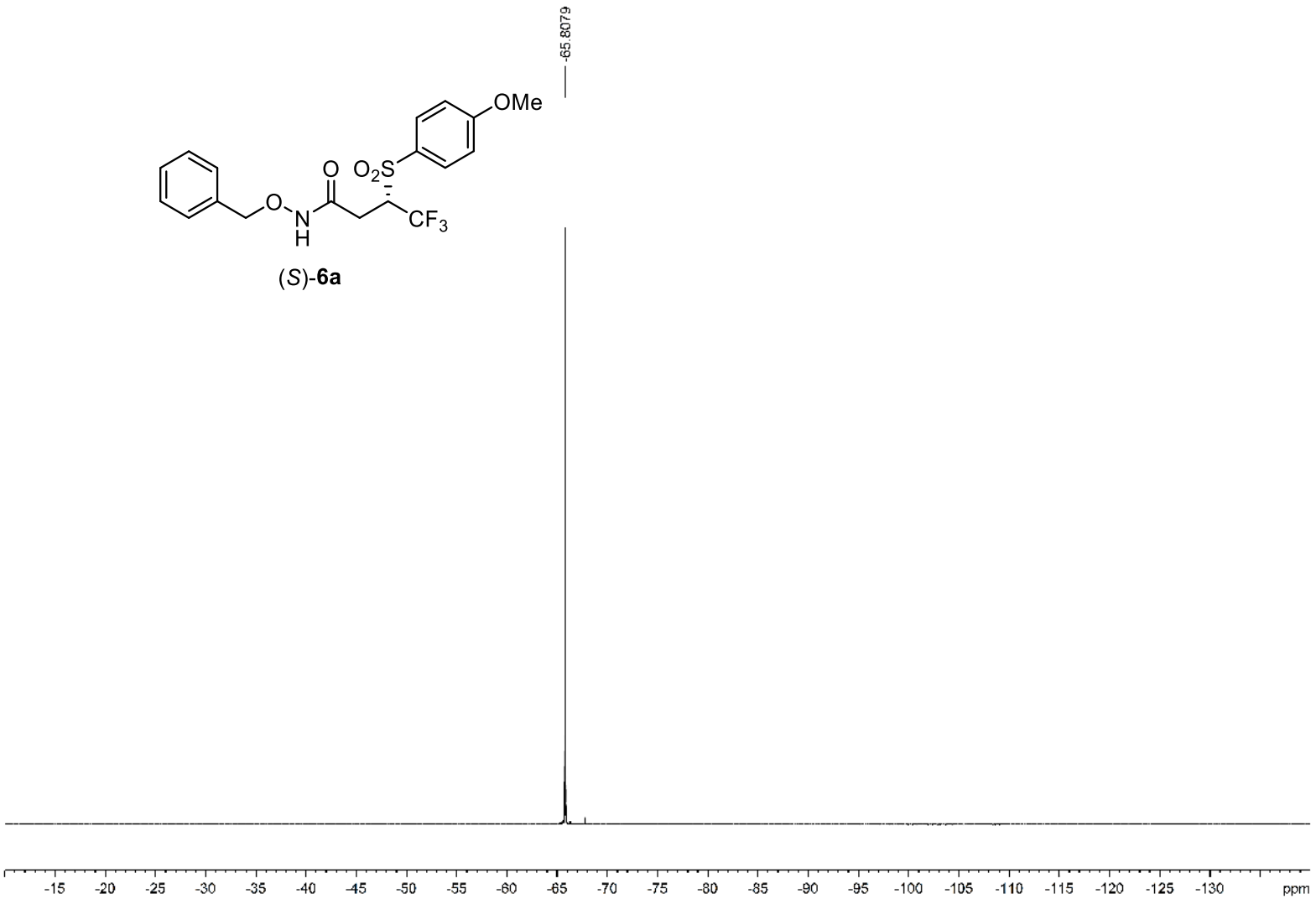


$^{13}$C NMR Spectrum of (*S*)-**6a** (100 MHz, acetone-$d_6$)

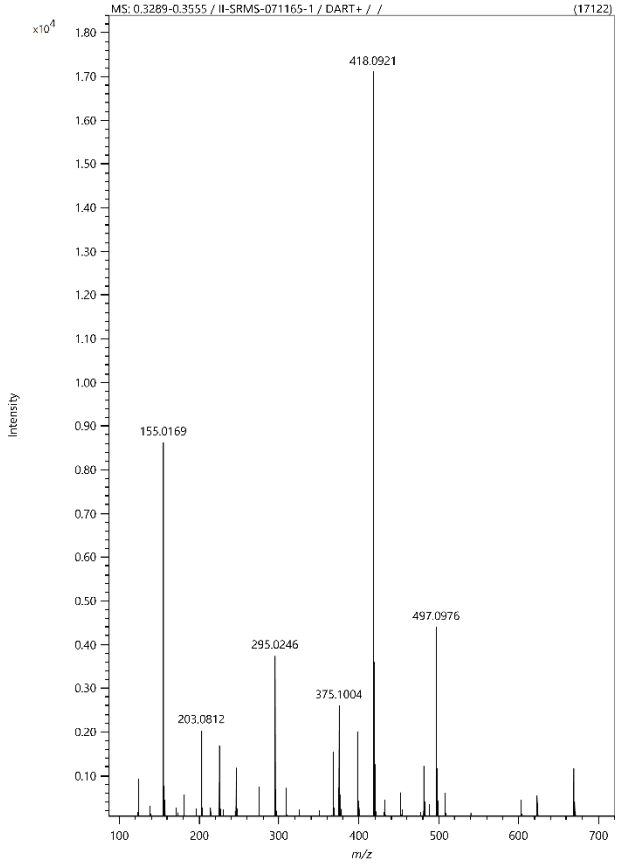



(*S*)-**6a**

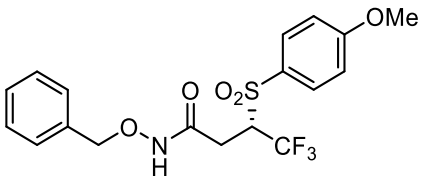
$^{19}$F NMR Spectrum of (*S*)-**6a** (376 MHz, acetone-$d_6$)



HRMS (DART) of (*S*)-**6a**



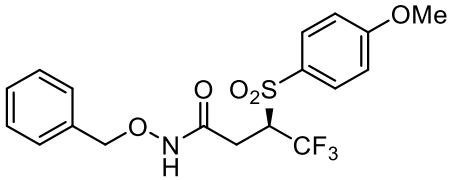
Specific rotations of (*S*)-**6a** and (*R*)-**6b**




(*S*)-**6a**

| | |
|---|---|
| Comment | Acetone |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0455 w/v% |
| Factor | 1.0000 |
| Blank | -0.0005 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 26.8580 |
| S.D. | 0.5675 |
| C.V. | 2.1129 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 4( 1/ 5) | 26.495 | 21.9 |
| 2 | 4( 2/ 5) | 26.208 | 21.9 |
| 3 | 4( 3/ 5) | 27.451 | 21.9 |
| 4 | 4( 4/ 5) | 26.686 | 21.9 |
| 5 | 4( 5/ 5) | 27.451 | 21.9 |

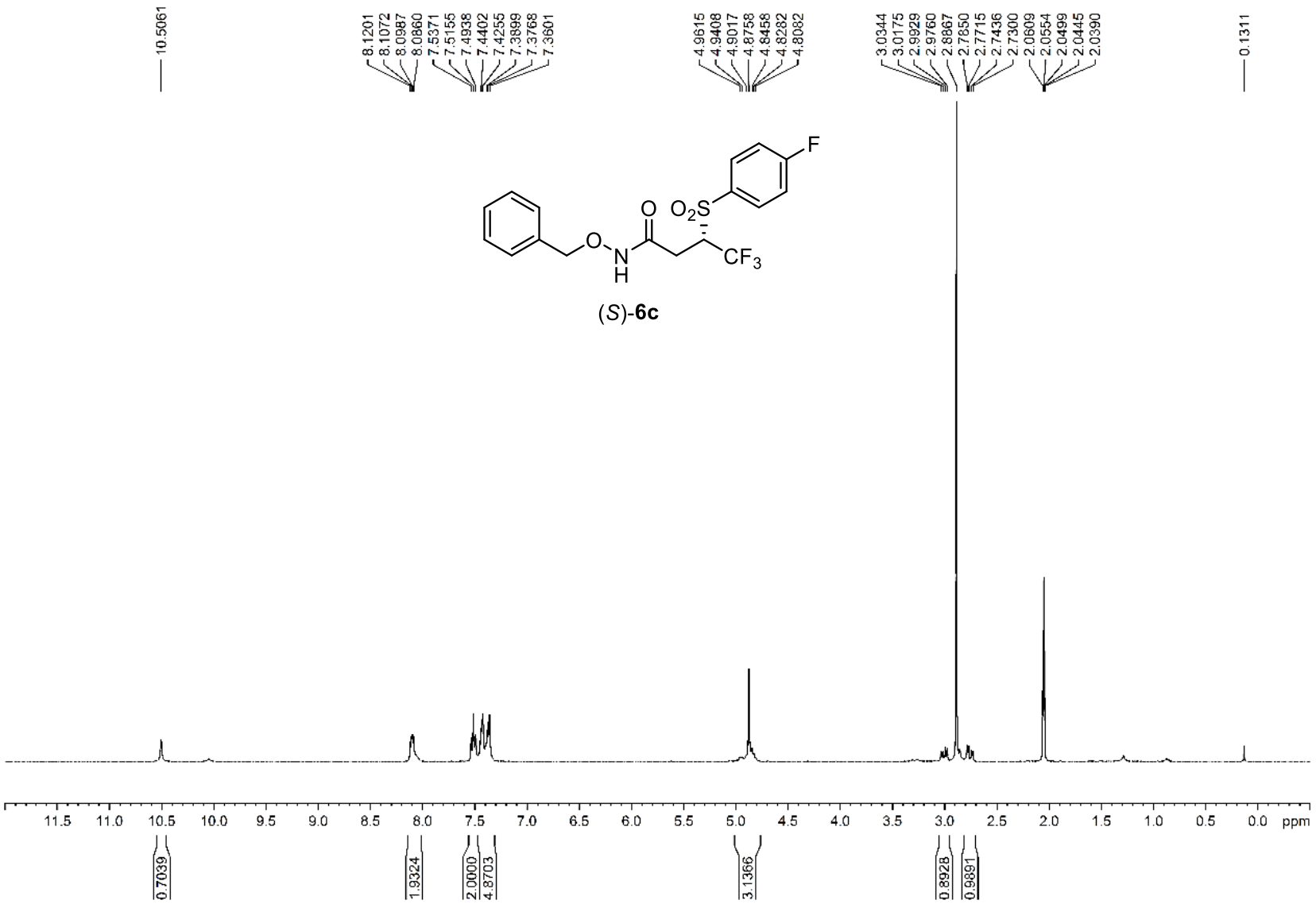



(*R*)-**6b**

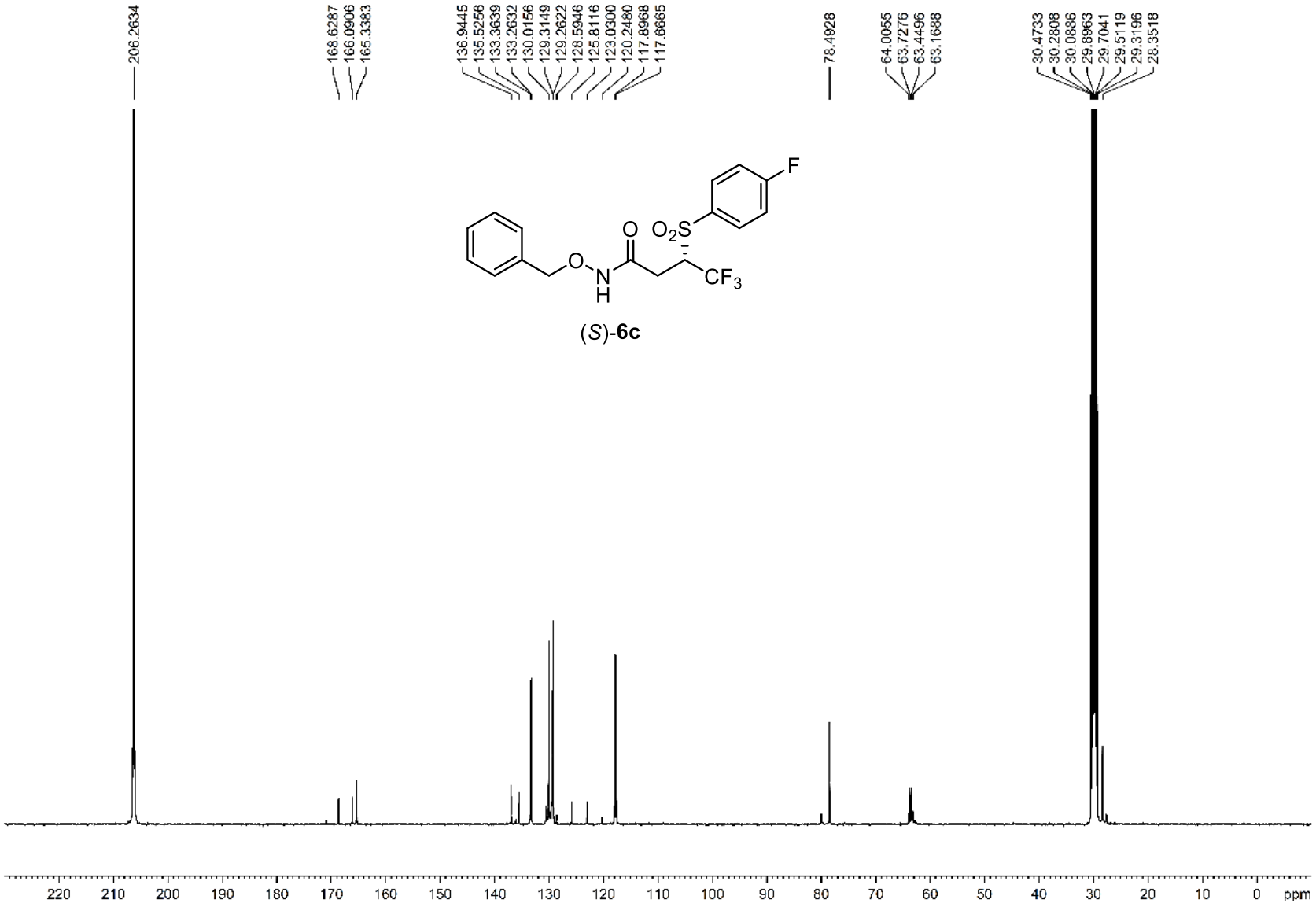
| | |
|---|---|
| Comment | Acetone |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0063 w/v% |
| Factor | 1.0000 |
| Blank | -0.0005 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -27.3278 |
| S.D. | 0.5067 |
| C.V. | -1.8542 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 7( 1/ 5) | -27.030 | 22.0 |
| 2 | 7( 2/ 5) | -27.626 | 22.0 |
| 3 | 7( 3/ 5) | -26.732 | 22.0 |
| 4 | 7( 4/ 5) | -28.023 | 22.0 |
| 5 | 7( 5/ 5) | -27.228 | 22.0 |

$^1$H NMR Spectrum of (*S*)-**6c** (400 MHz, acetone-$d_6$)

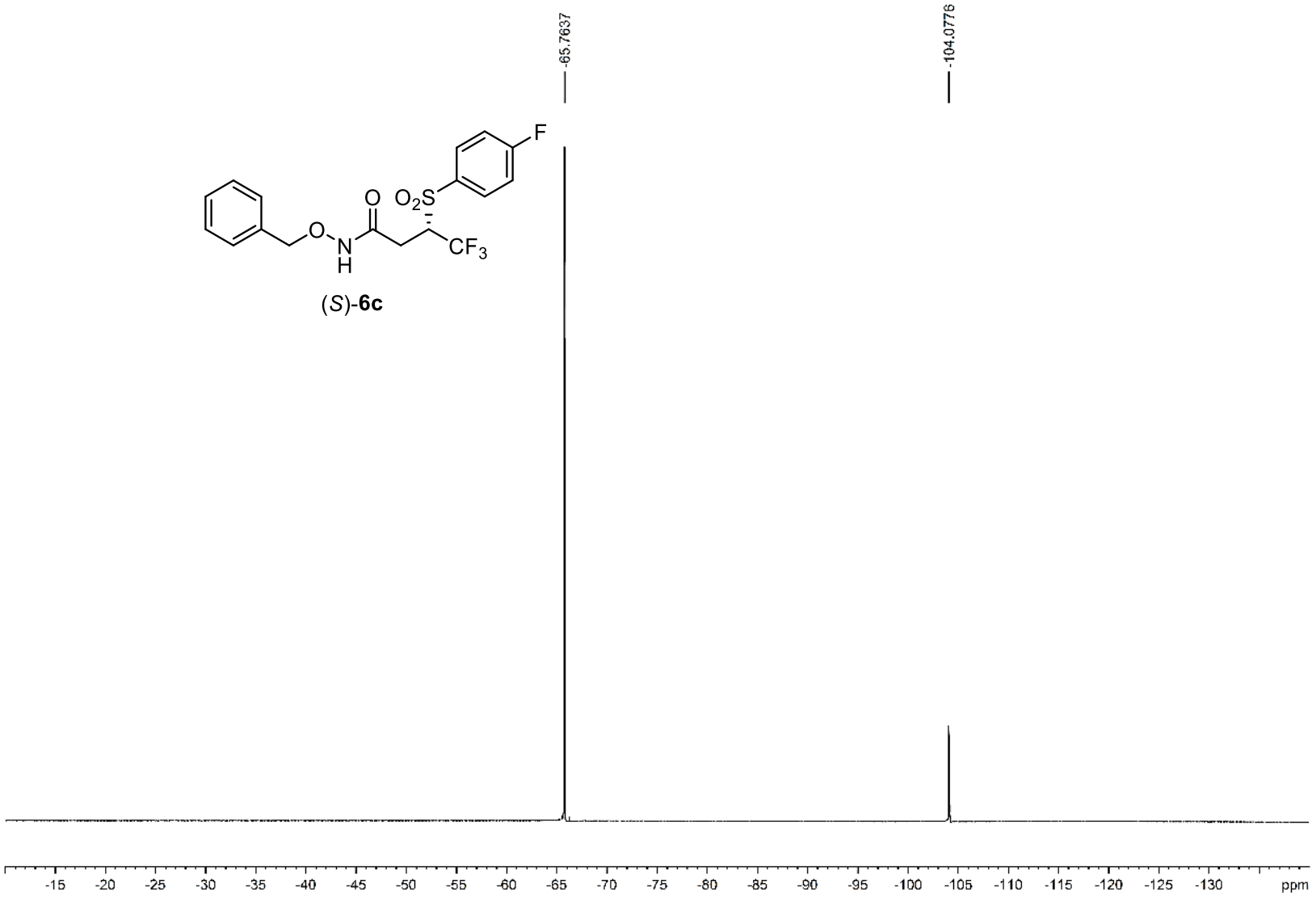


$^{13}$C NMR Spectrum of (*S*)-**6c** (100 MHz, acetone-$d_6$)

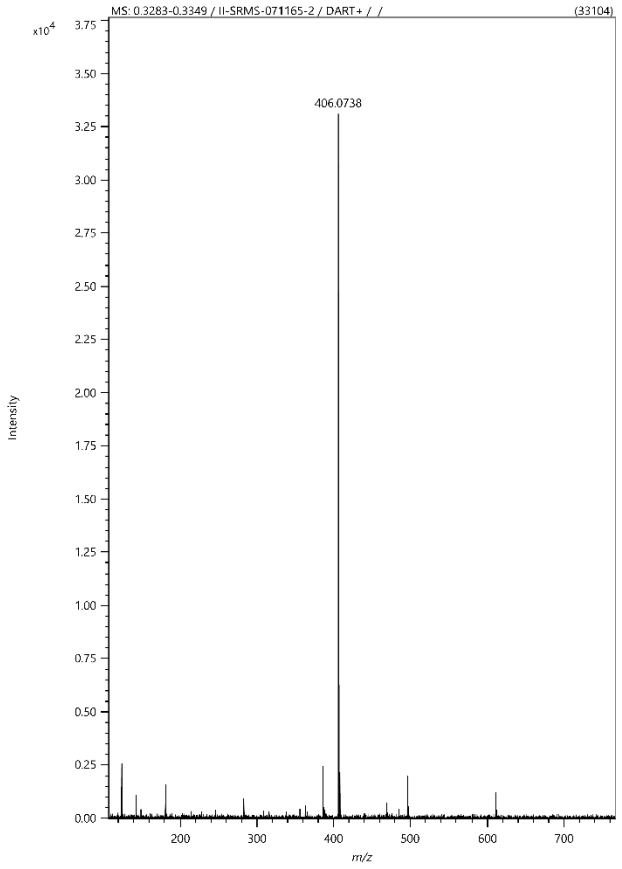



(*S*)-**6c**

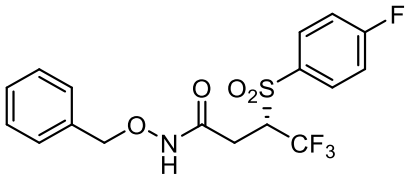
$^{19}$F NMR Spectrum of (*S*)-**6c** (376 MHz, acetone-$d_6$)



HRMS (DART) of (*S*)-**6c**



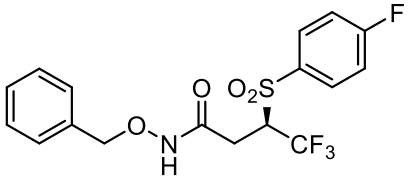
Specific rotations of (*S*)-**6c** and (*R*)-**6d**



(*S*)-**6c**

| | |
|---|---|
| Comment | Acetone |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0333 w/v% |
| Factor | 1.0000 |
| Blank | -0.0005 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 20.7684 |
| S.D. | 0.8672 |
| C.V. | 4.1757 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 17( 1/ 5) | 21.388 | 22.3 |
| 2 | 17( 2/ 5) | 20.904 | 22.3 |
| 3 | 17( 3/ 5) | 21.291 | 22.3 |
| 4 | 17( 4/ 5) | 19.259 | 22.3 |
| 5 | 17( 5/ 5) | 21.001 | 22.3 |

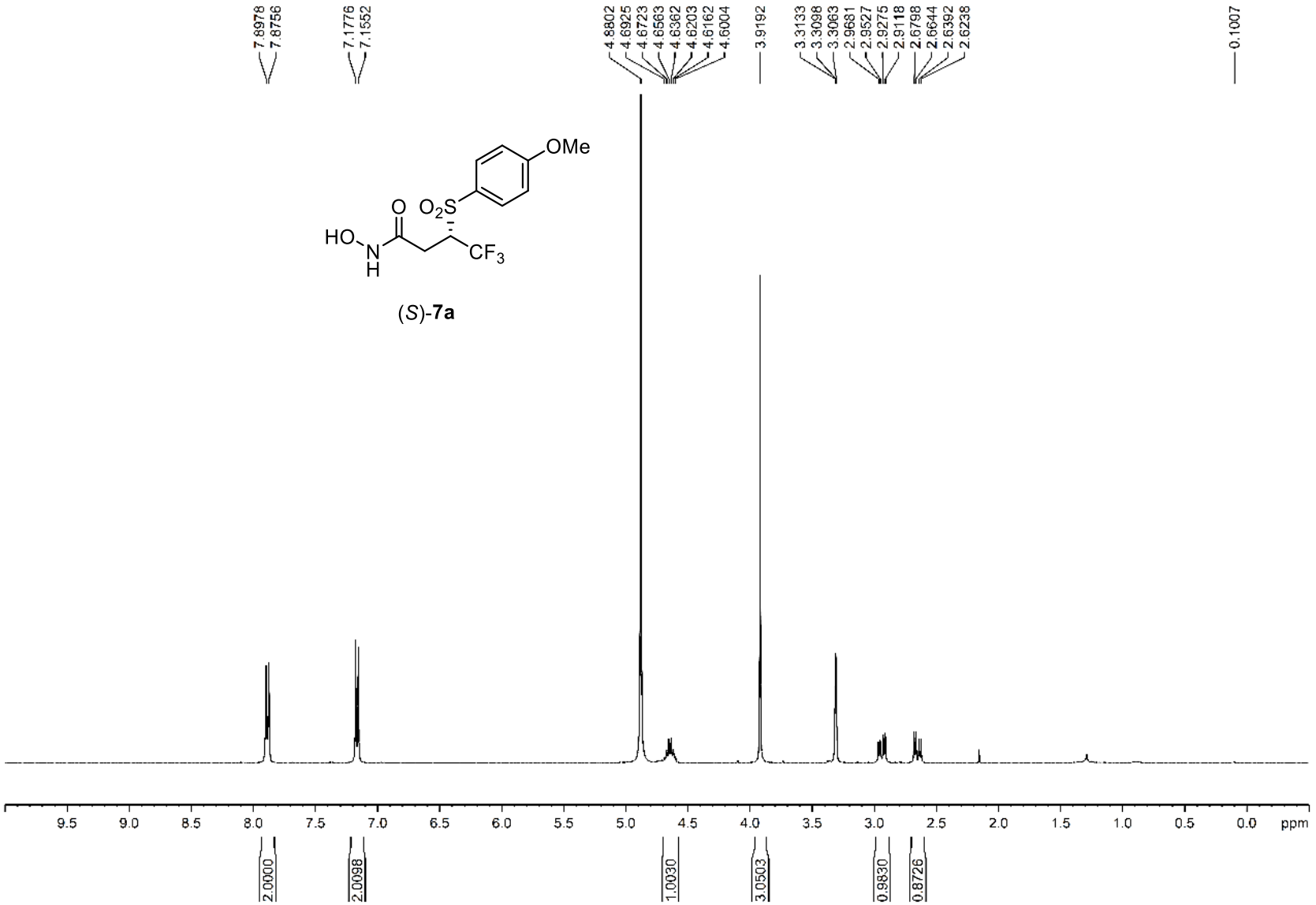


(*R*)-**6d**

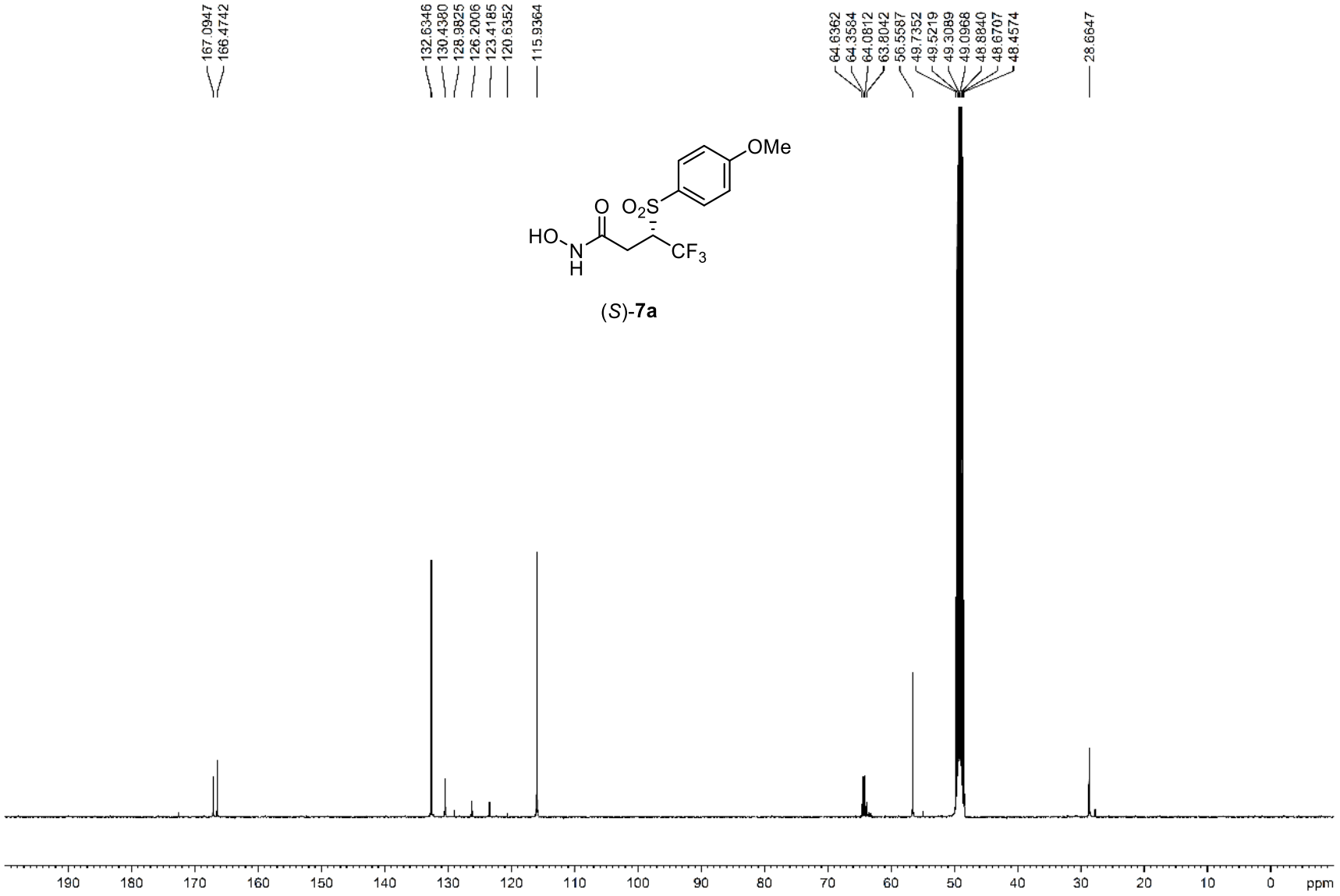
| | |
|---|---|
| Comment | Acetone |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0308 w/v% |
| Factor | 1.0000 |
| Blank | -0.0005 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -20.0427 |
| S.D. | 0.3471 |
| C.V. | -1.7317 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 46( 1/ 5) | -20.081 | 21.9 |
| 2 | 46( 2/ 5) | -19.596 | 21.9 |
| 3 | 46( 3/ 5) | -20.373 | 21.9 |
| 4 | 46( 4/ 5) | -19.790 | 21.9 |
| 5 | 46( 5/ 5) | -20.373 | 21.9 |

$^1$H NMR Spectrum of (*S*)-**7a** (400 MHz, $CD_3OD$)

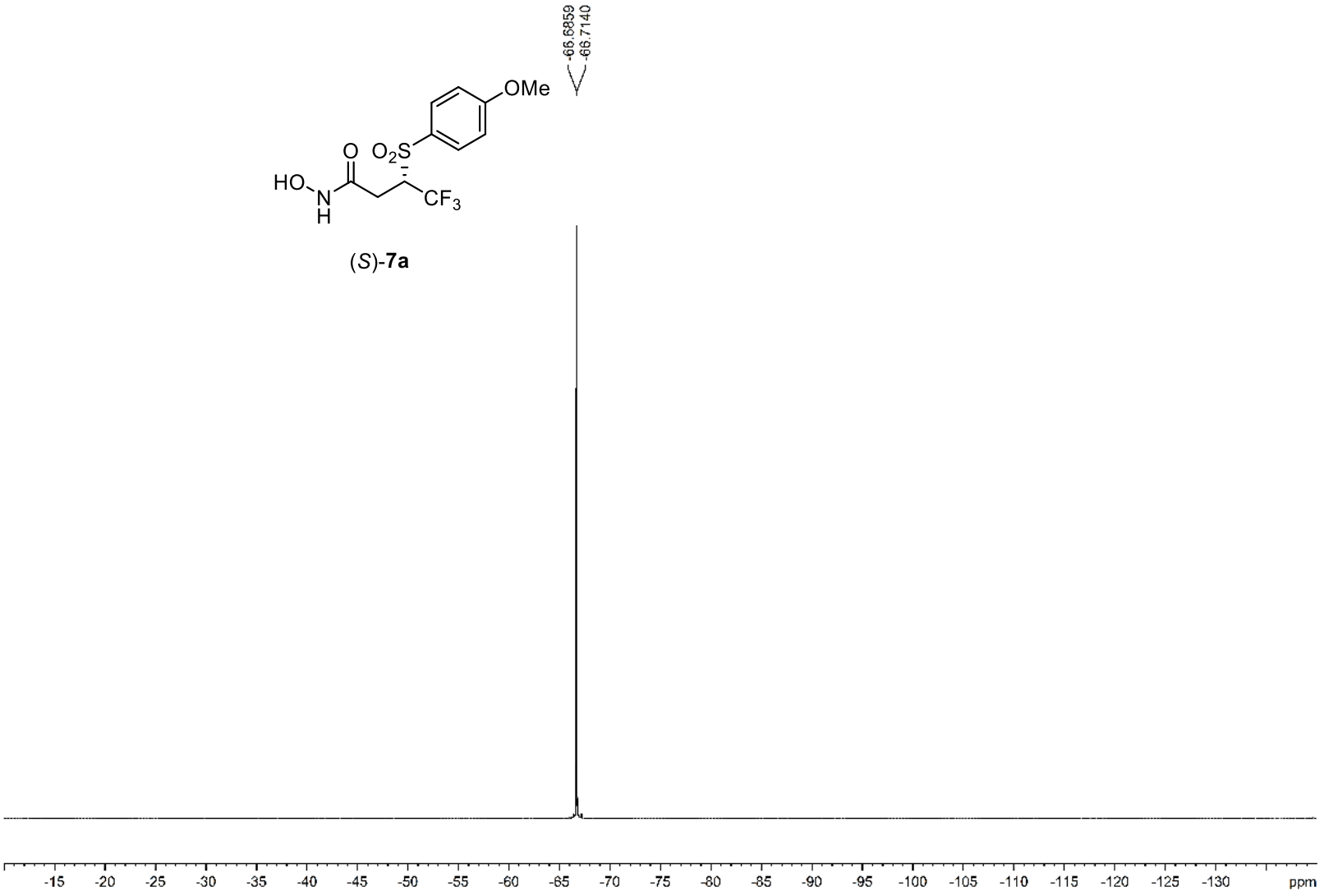


$^{13}$C NMR Spectrum of (*S*)-**7a** (100 MHz, $CD_3OD$)

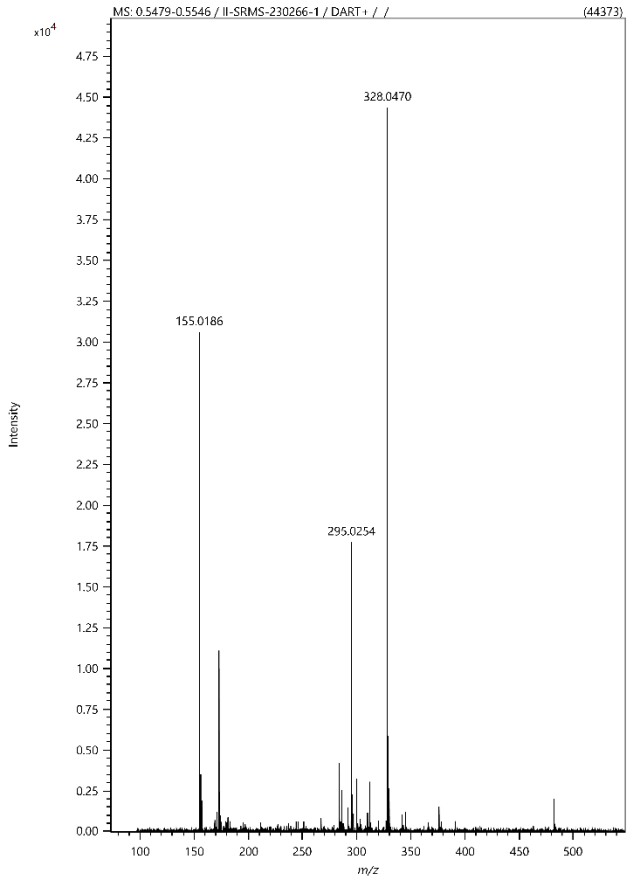



(*S*)-**7a**

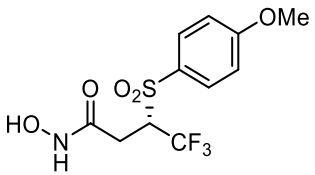
$^{19}$F NMR Spectrum of (*S*)-**7a** (376 MHz, $CD_3OD$)



HRMS (DART) of (*S*)-**7a**



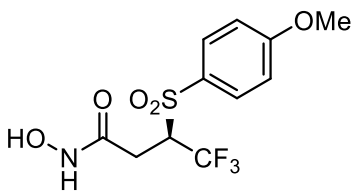
Specific rotations of (*S*)-**7a** and (*R*)-**7b**




(*S*)-**7a**

| | |
|---|---|
| Comment | EtOH |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0500 w/v% |
| Factor | 1.0000 |
| Blank | -0.0024 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 5.2000 |
| S.D. | 0.7842 |
| C.V. | 15.0807 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 89( 1/ 5) | 4.571 | 25.0 |
| 2 | 89( 2/ 5) | 4.190 | 25.1 |
| 3 | 89( 3/ 5) | 5.905 | 25.1 |
| 4 | 89( 4/ 5) | 5.429 | 25.1 |
| 5 | 89( 5/ 5) | 5.905 | 25.1 |

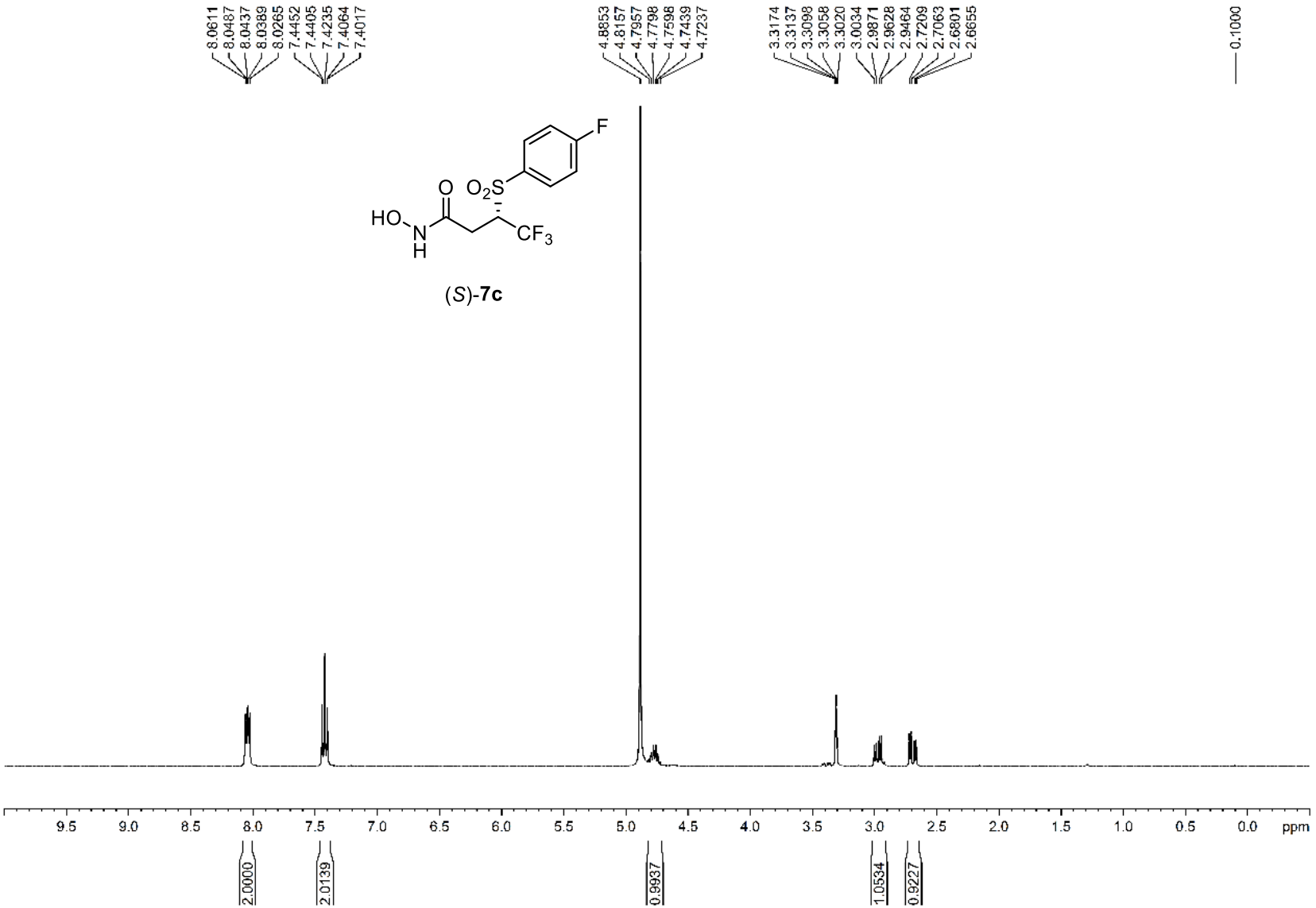



(*R*)-**7b**

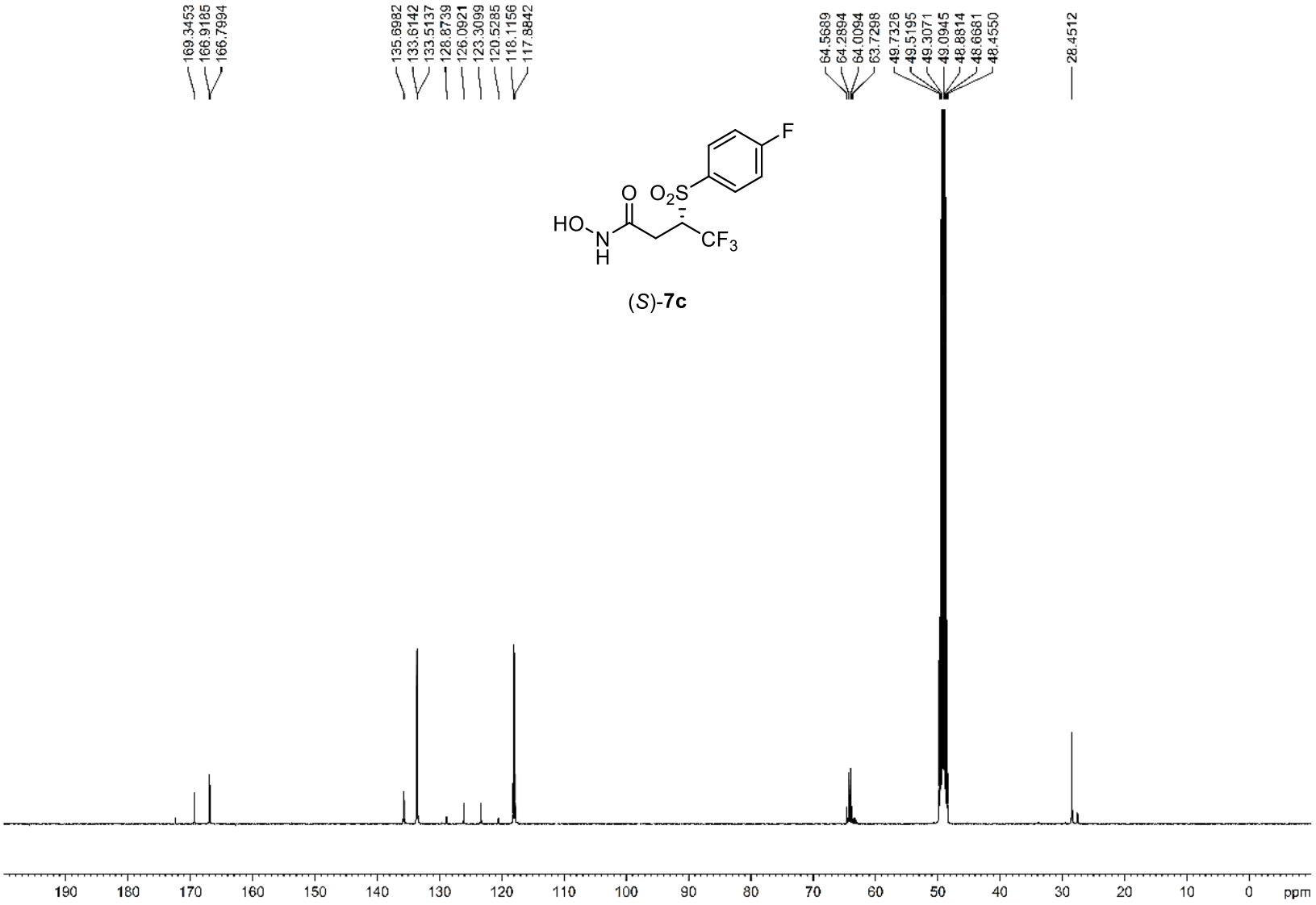
| | |
|---|---|
| Comment | EtOH |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 0.8800 w/v% |
| Factor | 1.0000 |
| Blank | -0.0024 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -3.2955 |
| S.D. | 0.4754 |
| C.V. | -14.4252 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 107( 1/ 5) | -3.523 | 24.7 |
| 2 | 107( 2/ 5) | -3.295 | 24.7 |
| 3 | 107( 3/ 5) | -3.750 | 24.7 |
| 4 | 107( 4/ 5) | -3.409 | 24.7 |
| 5 | 107( 5/ 5) | -2.500 | 24.7 |

$^1$H NMR Spectrum of (*S*)-**7c** (400 MHz, $CD_3OD$)

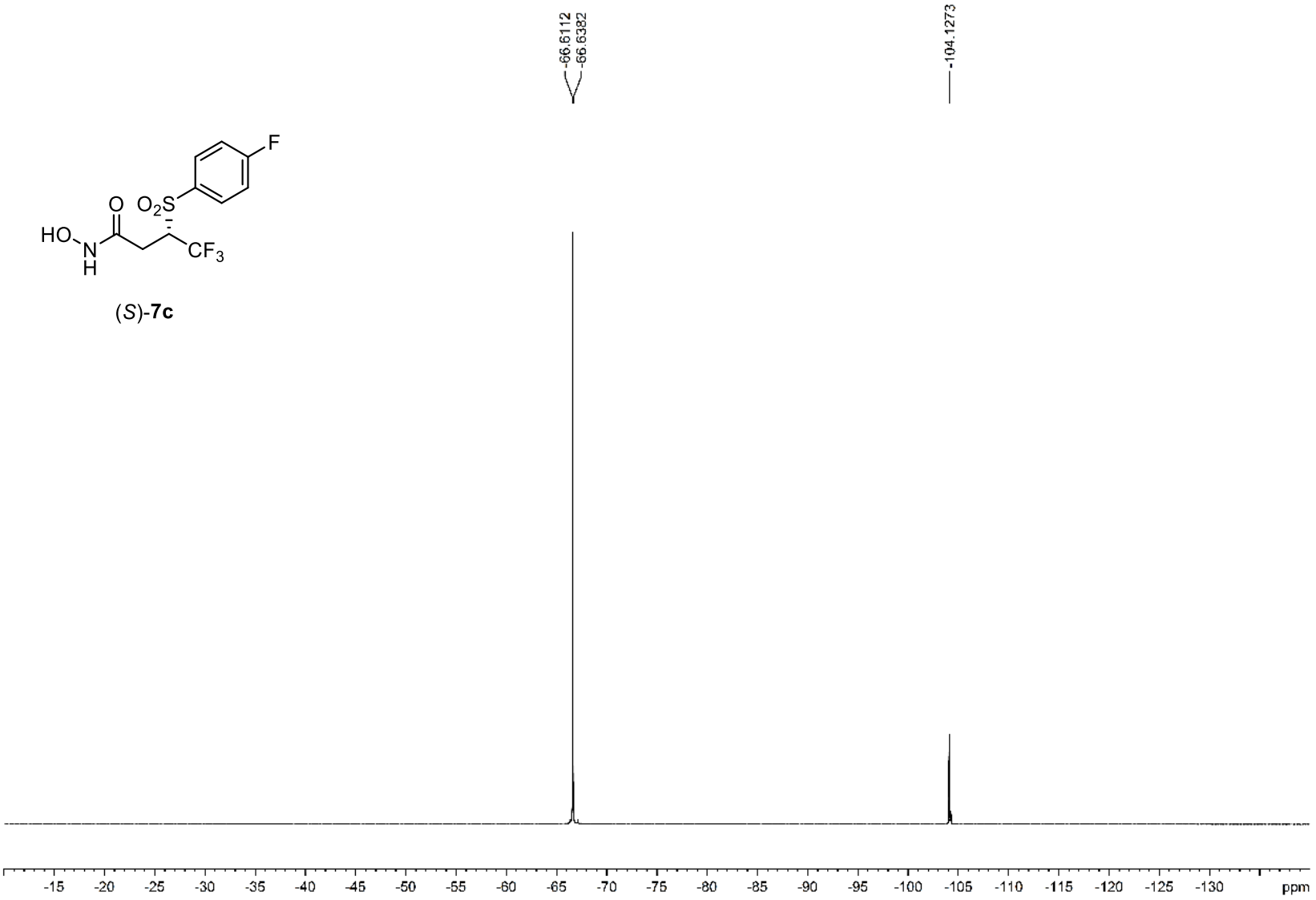


$^{13}$C NMR Spectrum of (*S*)-**7c** (100 MHz, $CD_3OD$)

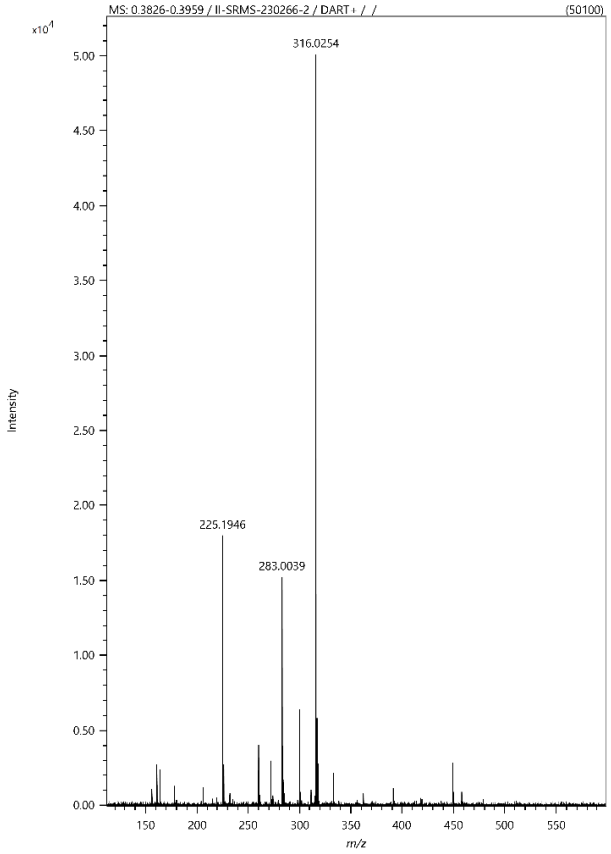



(*S*)-**7c**

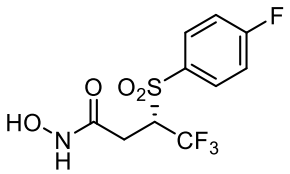
$^{19}$F NMR Spectrum of (*S*)-**7c** (376 MHz, $CD_3OD$)



HRMS (DART) of (*S*)-**7c**



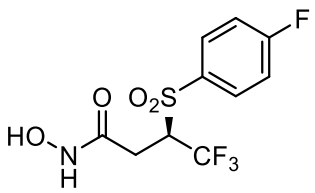
Specific rotations of (*S*)-**7c** and (*R*)-**7d**



(*S*)-**7c**

| | |
|---|---|
| Comment | EtOH |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0900 w/v% |
| Factor | 1.0000 |
| Blank | -0.0003 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | 3.9266 |
| S.D. | 0.7929 |
| C.V. | 20.1937 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 225( 1/ 5) | 4.220 | 23.6 |
| 2 | 225( 2/ 5) | 2.569 | 23.6 |
| 3 | 225( 3/ 5) | 4.312 | 23.6 |
| 4 | 225( 4/ 5) | 3.945 | 23.6 |
| 5 | 225( 5/ 5) | 4.587 | 23.6 |



(*R*)-**7d**

| | |
|---|---|
| Comment | EtOH |
| Mode | Specific O.R. |
| Light | Na |
| Wavelength | 589nm |
| Cell path | 10.00 mm |
| Concentration | 1.0800 w/v% |
| Factor | 1.0000 |
| Blank | -0.0003 deg |
| Interval | 1 sec |
| Integration | 1 sec |
| Average | -3.2037 |
| S.D. | 0.7220 |
| C.V. | -22.5359 % |

| No. | Sample No | Data | Temp. |
|---|---|---|---|
| 1 | 202( 1/ 5) | -2.407 | 24.4 |
| 2 | 202( 2/ 5) | -3.889 | 24.5 |
| 3 | 202( 3/ 5) | -3.148 | 24.5 |
| 4 | 202( 4/ 5) | -3.981 | 24.4 |
| 5 | 202( 5/ 5) | -2.593 | 24.5 |

**The information of the crystal measurement**

Crystallographic data of (*R*,*R*)-**3aB** and (*R*,*R*)-**3pB** (CCDC: 2257377 and 2257378) were collected on D8 VENTURE Bruker diffractometer. The crystals were kept at 273.15 K during data collection. Using Olex2[1], Both structures were solved with the olex2.solve[2] structure program using Charge Flipping and refine with the XL[3] refinement package using Least Squares minimization.

[1] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.

[2] Bourhis, L. J.;Dolomanov, O. V.;Gildea, R. J.;Howard, J. A. K.;Puschmann, H. *Acta Cryst*. **2015**, *A71*, 59-75.

[3] Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112-122.

**The description of the sample preparation**

The crystals used in X-ray diffraction data collection were obtained by slow evaporation technique, for (*R*,*R*)-**3aB** using total 25% $CH_2Cl_2$ in hexanes and for (*R*,*R*)-**3pB** using total 10% $CH_2Cl_2$ in methanol, in vials. Each compound was dissolved using the minimum amount of $CH_2Cl_2$ then hexanes [for (*R*,*R*)-**3aB**] or methanol [for (*R*,*R*)-**3pB**] was added dropwise until the clear solution turned cloudy. $CH_2Cl_2$ was then added dropwise to the cloudy solution until it appeared as a clear solution again. Each vial was let stand undisturbed at room temperature (35 °C).

**X-ray diffraction analysis of compound (*R*,*R*)-3aB (CCDC 2257377)**

**Crystal data**

| | |
|---|---|
| Chemical formula | $C_{19}H_{16}F_3NO_3S$ |
| $M_r$ | 395.39 |
| Crystal system, space group | Monoclinic, *C*2 |
| Temperature (K) | 273 |
| *a*, *b*, *c* (Å) | 21.0440 (12), 5.1578 (3), 19.5025 (11) |
| $\beta$ (º) | 119.164 (2) |
| $V$ (Å$^3$) | 1848.46 (19) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 2.01 |
| Crystal size (mm$^3$) | 0.3 × 0.1 × 0.1 |

**Data collection**

| | |
|---|---|
| Diffractometer | BRUKER D8 VENTURE |
| Absorption correction | – |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 10969, 3389, 3082 |
| $R_{int}$ | 0.035 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.619 |

**Refinement**

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.042, 0.120, 1.05 |
| No. of reflections | 3389 |
| No. of parameters | 244 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.14, –0.29 |
| Absolute structure | Flack x determined using 1155 quotients [(I+)-(I-)]/[(I+)+(I-)] [Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259]. |
| Absolute structure parameter | 0.124 (11) |

Computer programs: *SAINT* V8.40B (2016), olex2.solve 1.3 (Bourhis *et al*., 2015), XL (Sheldrick, 2008), Olex2 1.3 (Dolomanov *et al*., 2009).

**References**

1. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Acta Cryst*. **2015**, *A71*, 59-75.

2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.

3. Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112-122.

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) iisrx02rt3_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: iisrx02rt3_0m_a

---

```
Bond precision:   C-C = 0.0067 A          Wavelength=1.54178

Cell:             a=21.0440(12)    b=5.1578(3)         c=19.5025(11)
                  alpha=90         beta=119.164(2)     gamma=90
Temperature:      273 K

                  Calculated                Reported
Volume            1848.46(19)               1848.46(19)
Space group       C 2                       C 1 2 1
Hall group        C 2y                      C 2y
Moiety formula    C19 H16 F3 N O3 S         C19 H16 F3 N O3 S
Sum formula       C19 H16 F3 N O3 S         C19 H16 F3 N O3 S
Mr                395.39                    395.39
Dx,g cm-3         1.421                     1.421
Z                 4                         4
Mu (mm-1)         2.005                     2.005
F000              816.0                     816.0
F000'             820.20
h,k,lmax          26,6,24                   25,6,24
Nref              3681[ 2056]               3389
Tmin,Tmax         0.786,0.818               0.555,0.753
Tmin'             0.548

Correction method= # Reported T Limits: Tmin=0.555 Tmax=0.753
AbsCorr = NONE

Data completeness= 1.65/0.92        Theta(max)= 72.527

R(reflections)= 0.0417( 3082)                wR2(reflections)=
                                             0.1197( 3389)
S = 1.047                  Npar= 244
```

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

### Alert level C

```
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .      0.973 Why?
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of       S001 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         C9 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C15 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         C3 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         C5 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C11 Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00671 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        49 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....         8 Note
PLAT987_ALERT_1_C The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

### Alert level G

```
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.124 Note
PLAT128_ALERT_4_G Alternate Setting for Input Space Group  C2             I2 Note
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)       273 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)       273 Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of         C4 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  O1'      ..C2'             2.96 Ang.
                                      3/2-x,-1/2+y,1-z  =      4_646 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........         3 Note
PLAT791_ALERT_4_G Model has Chirality at C3          (Sohnke SpGr)        R Verify
PLAT791_ALERT_4_G Model has Chirality at C4'         (Sohnke SpGr)        R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).        1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600       22 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...        1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        1 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 11 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 13 ALERT level G = General information/check it is not something unexpected

  3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 10 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
  6 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

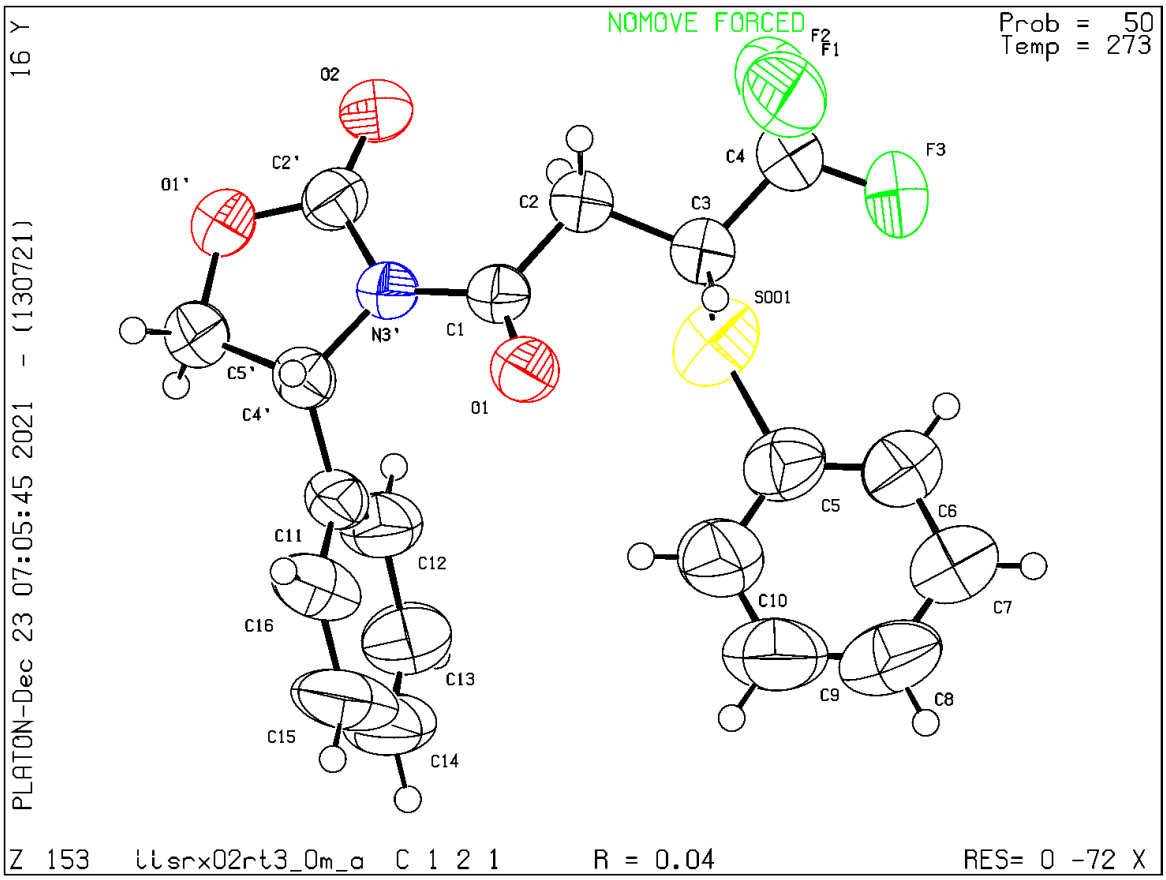
**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

---

**PLATON version of 13/07/2021; check.def file version of 13/07/2021**

**ORTEP plot of (*R*,*R*)-3aB (CCDC 2257377)**



**X-ray diffraction analysis of compound (*R*,*R*)-3pB (CCDC 2257378)**

**Crystal data**

| | |
|---|---|
| Chemical formula | $C_{17}H_{20}F_3NO_3S$ |
| $M_r$ | 375.40 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 273 |
| *a*, *b*, *c* (Å) | 5.4848 (3), 11.8755 (7), 32.4602 (19) |
| *V* (Å$^3$) | 2114.3 (2) |
| *Z* | 4 |
| Radiation type | Cu *Kα* |
| $\mu$ (mm$^{-1}$) | 1.72 |
| Crystal size (mm$^3$) | 0.1 × 0.1 × 0.1 |

**Data collection**

| | |
|---|---|
| Diffractometer | BRUKER D8 VENTURE |
| Absorption correction | – |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 19206, 3668, 3356 |
| $R_{int}$ | 0.054 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.603 |

**Refinement**

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.073, 0.214, 1.09 |
| No. of reflections | 3668 |
| No. of parameters | 229 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.95, –0.28 |
| Absolute structure | Flack x determined using 1279 quotients [(I+)-(I-)]/[(I+)+(I-)] [Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259]. |
| Absolute structure parameter | 0.092 (8) |

Computer programs: *SAINT* V8.40B (2016), olex2.solve 1.3 (Bourhis *et al*., 2015), XL (Sheldrick, 2008), Olex2 1.3 (Dolomanov *et al*., 2009).

**References**

1. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Acta Cryst*.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.
3. Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112-122.

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ii_sr_xrd_03_rt_2_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: ii_sr_xrd_03_rt_2_0m_a

---

```
Bond precision:   C-C = 0.0076 A          Wavelength=1.54178

Cell:              a=5.4848(3)      b=11.8755(7)      c=32.4602(19)
                   alpha=90         beta=90           gamma=90
Temperature:       273 K

                  Calculated                Reported
Volume            2114.3(2)                 2114.3(2)
Space group       P 21 21 21                P 21 21 21
Hall group        P 2ac 2ab                 P 2ac 2ab
Moiety formula    C17 H20 F3 N O3 S         C17 H20 F3 N O3 S
Sum formula       C17 H20 F3 N O3 S         C17 H20 F3 N O3 S
Mr                375.40                    375.40
Dx,g cm-3         1.179                     1.179
Z                 4                         4
Mu (mm-1)         1.720                     1.720
F000              784.0                     784.0
F000'             788.06
h,k,lmax          6,14,39                   6,14,39
Nref              3899[ 2295]               3668
Tmin,Tmax         0.842,0.842               0.519,0.753
Tmin'             0.842

Correction method= # Reported T Limits: Tmin=0.519 Tmax=0.753
AbsCorr = NONE

Data completeness= 1.60/0.94        Theta(max)= 68.294

R(reflections)= 0.0726( 3356)                wR2(reflections)=
                                             0.2141( 3668)
S = 1.091                  Npar= 229
```

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

**Alert level B**

```
PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low .      0.945 Why?
PLAT601_ALERT_2_B Unit Cell Contains Solvent Accessible VOIDS of .        179 Ang**3
```

**Alert level C**

```
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       3.44 Report
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         C3 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C14 Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00764 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.393 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        124 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          2 Check
PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S .      12.39 Check
PLAT987_ALERT_1_C The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

**Alert level G**

```
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.092 Note
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.18 Report
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        273 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        273 Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of         C4 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  O2       ..C6       .       2.98 Ang.
                                      -1/2+x,3/2-y,1-z  =      4_466 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          1 Note
PLAT791_ALERT_4_G Model has Chirality at C3          (Sohnke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C7          (Sohnke SpGr)          R Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          3 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          3 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          3 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   2 ALERT level B = A potentially serious problem, consider carefully
   9 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   9 ALERT type 2 Indicator that the structure model may be wrong or deficient
   7 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

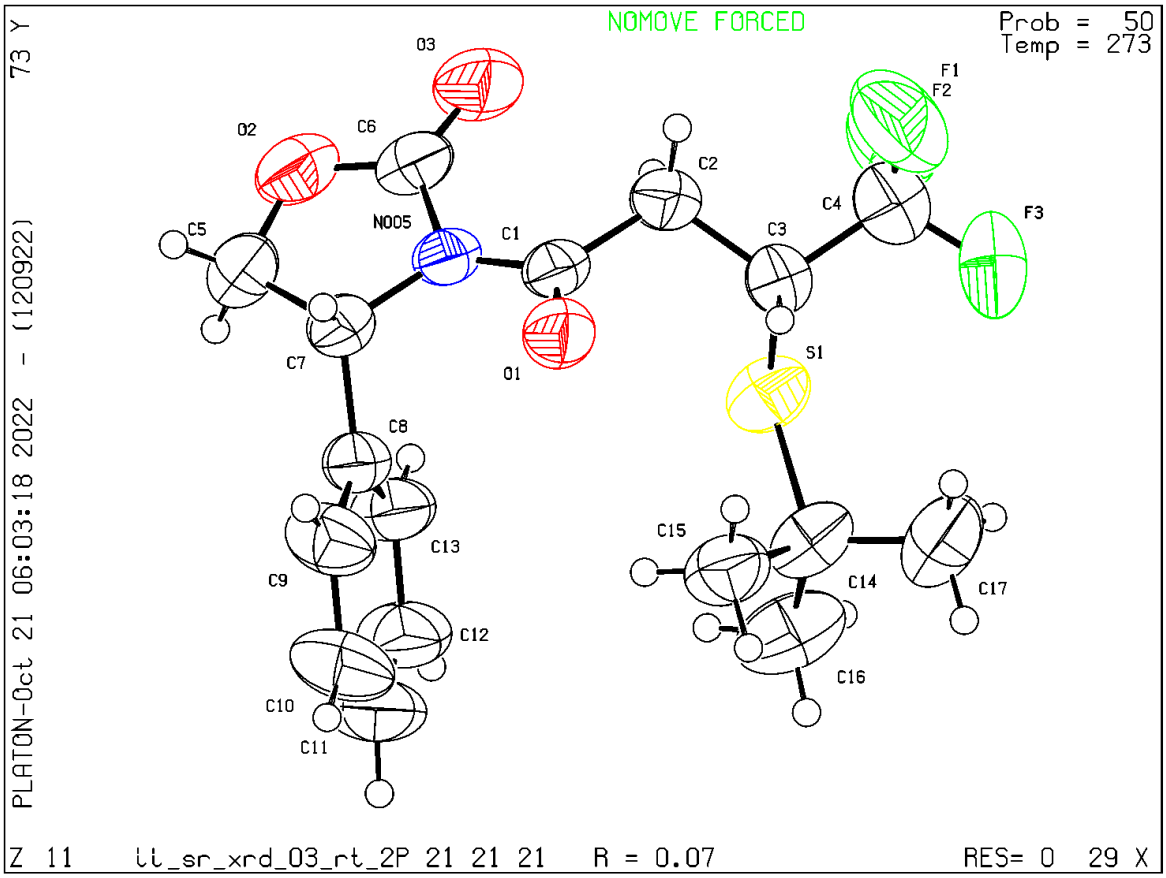
**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

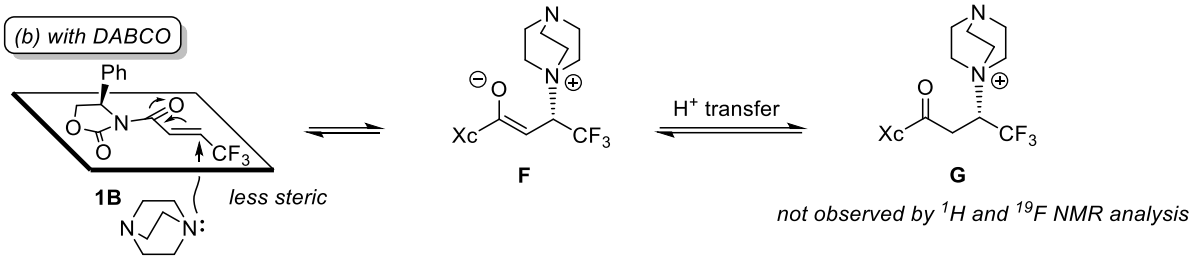
---

**PLATON version of 12/09/2022; check.def file version of 09/08/2022**

**ORTEP plot of (*R*,*R*)-3pB (CCDC 2257378)**



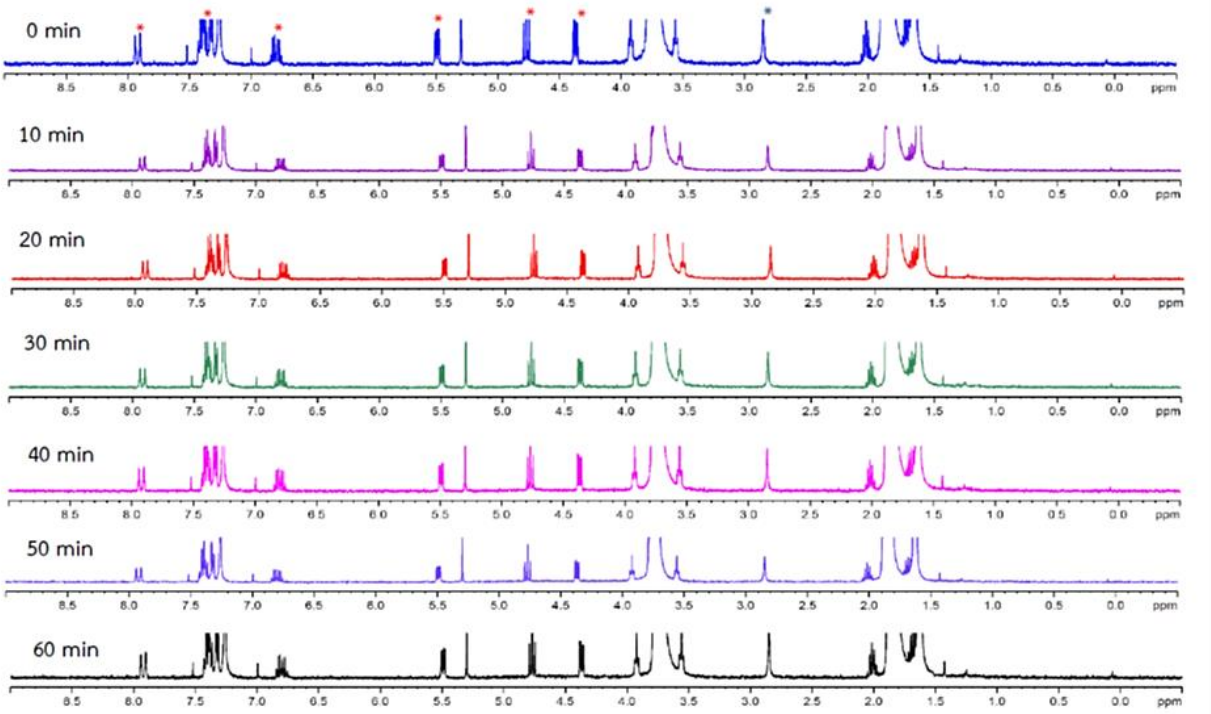
Attempts to record $^{1}H$ and $^{19}F$ NMR spectra of the intermediate **G**



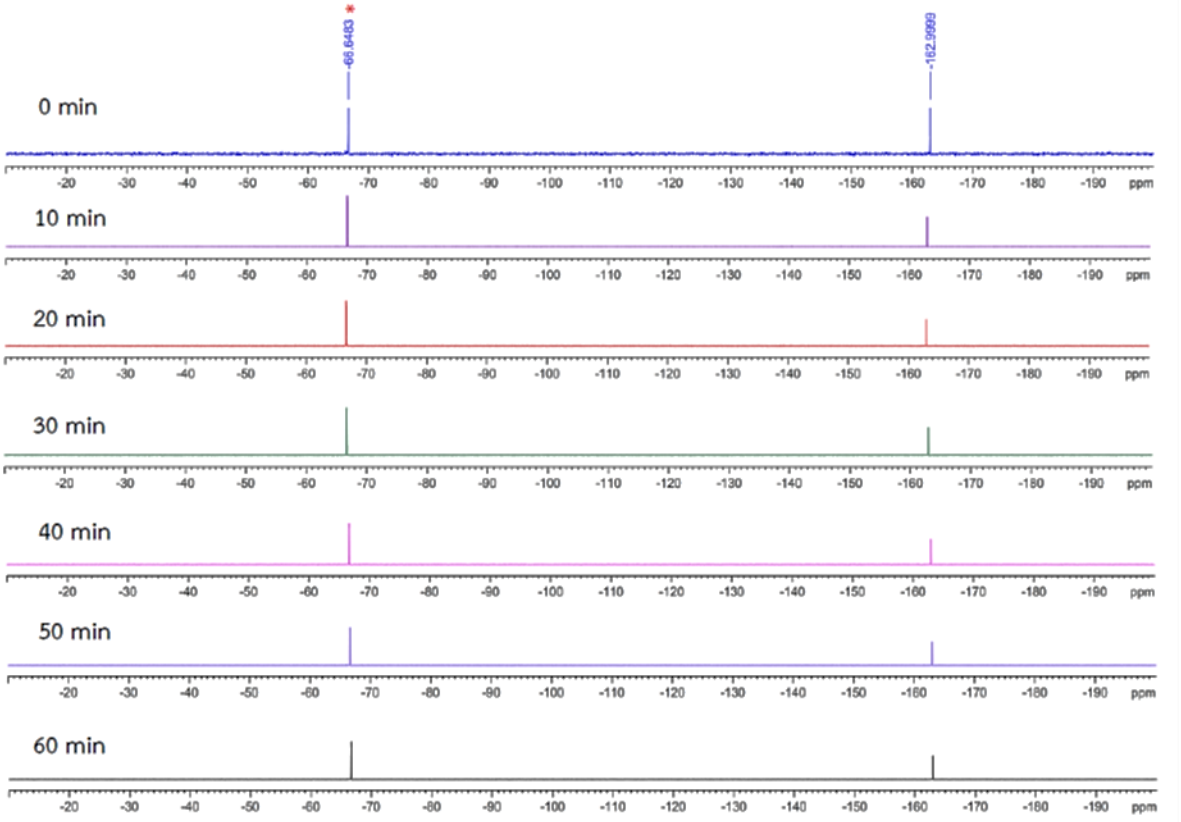

**$^{1}H$ NMR** (400 MHz, $CDCl_3$)

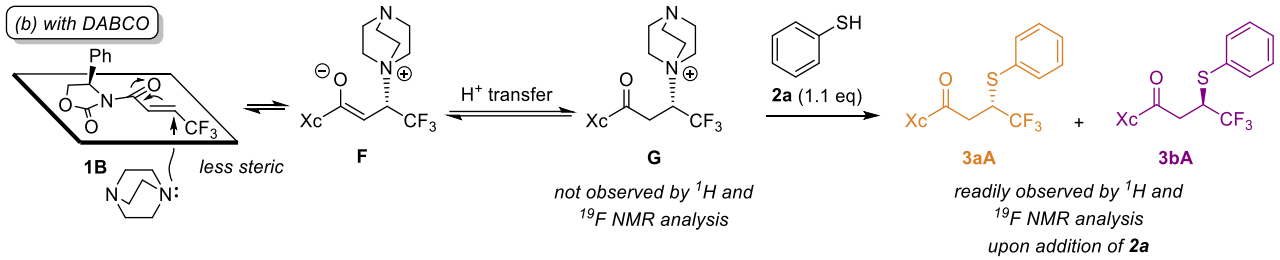
(7 sections/ 10 min per section)

the starting material **1** (marked as a red *) and DABCO (marked as a blue *)



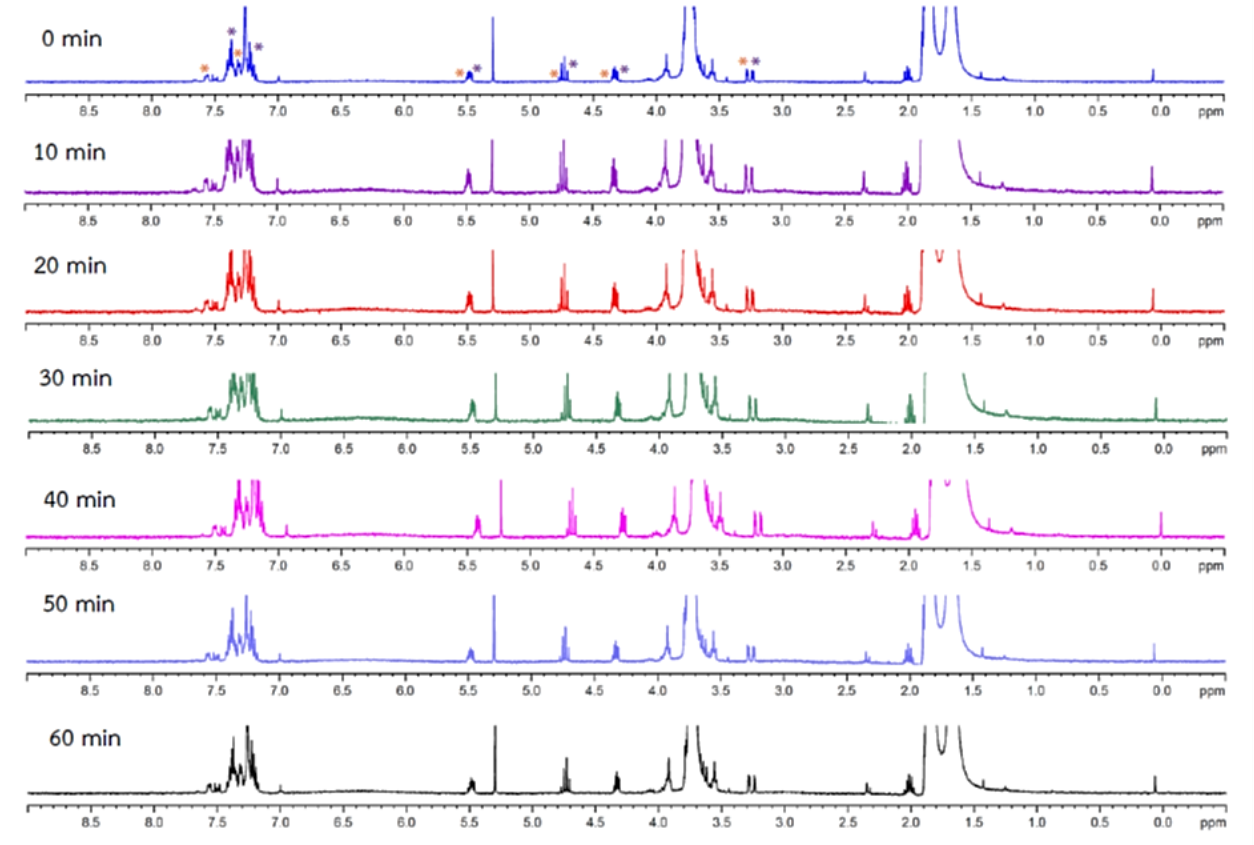
**$^{19}$F NMR** (470 MHz, $CDCl_3$ with $C_6F_6$ as an int. standard)
(7 sections/ 10 min per section)






**$^1$H NMR** (400 MHz, $CDCl_3$)
(7 sections/ 10 min per section)

(*R*,*S*)-**3aA(*)** and (*R*,*R*)-**3bA(*)**



**$^{19}$F NMR** (470 MHz, $CDCl_3$ with $C_6F_6$ as an int. standard)
(7 sections/ 10 min per section)