# Ready synthetic access to enantiopure allylic $\alpha_{(F)}$-branched fluoroalkenes.

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# Supporting information

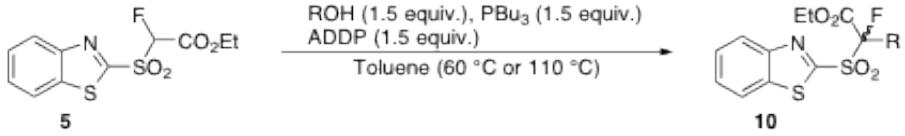
**1.** General conditions

All commercially available reagents were purchased from Aldrich and Alfa Aesar, and used as received. For anhydrous conditions, the glassware was dried in the oven at 120 °C and cooled to room temperature under a continuous nitrogen flow. THF and toluene were dried at a solvent generator from ‘‘Innovative Technologies Inc.’’, which uses an activated alumina column to remove water, or were distilled from Na/benzophenone. DMSO was distilled under $CaH_2$ or 4 Å molecular sieves. Flash column chromatography was realized on silica gel 60 (40-63 µm) from Merck with air pressure and were detected by thin layer chromatography, on which the spots were visualized by UV-irradiation and/or $KMnO_4$ solution. NMR spectra were recorded on a 300 MHz or 400 MHz apparatus in deuterated solvent at 25 °C. $^{19}F$ NMR spectral lines is with respect to the internal references $CFCl_3$. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode. IR spectra were recorded on a Perkin-Elmer ATR IR instrument.

**2.** The Mitsunobu Reaction (Table 1)

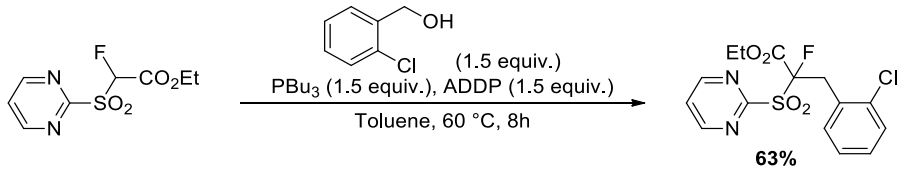
**2.1** General Procedure

**2.1.1** With Benzothiazole (BT)




To fluorosulfone **5**, dissolved in dry toluene (0.08 M), alcohol (1.5 equiv.), $PBu_3$ (1.5 equiv.) and ADDP (1.5 equiv.) were consecutively added. The reaction mixture was stirred at 60 °C or 110 °C, then filtered throught silica and washed with $CH_2Cl_2$. The residue was purified by column chromatography.

**2.1.2** With Pyrimidine

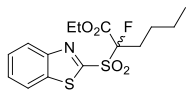



To fluorosulfone (200 mg, 0.81 mmol) dissolved in dry toluene (9.8 mL), 2-chlorobenzyl alcohol (174 mg, 1.22 mmol, 1.5 equiv.), $PBu_3$ (305 µL, 1.22 mmol, 1.5 equiv.) and ADDP (315 mg, 1.22 mmol, 1.5 equiv.) were consecutively added. The reaction mixture was stirred at 60 °C for 8 h, then filtered throught silica and washed with $CH_2Cl_2$. The residue was purified by column chromatography (Petroleum ether/Ethyl acetate (60/40)) to afford the corresponding alkylated sulfone as a white solid (189 mg, 63%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.01 (d, $^3J_{HH}$ 4.6 Hz, 2H), 7.65 (t, $^3J_{HH}$ 4.6 Hz, 1H), 7.38–7.36 (m, 1H), 7.32–7.30 (m, 1H), 7.25–7.17 (m, 2H), 4.32–4.10 (m, 4H), 1.22 (t, $^3J_{HH}$ 7.1 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.3, 162.6 (d, $^2J_{CF}$ 24.9 Hz), 158.8 (2C), 135.3, 131.8 (d, $^4J_{CF}$ 2.2 Hz), 129.9, 129.4, 129.4, 127.0, 124.5, 106.2 (d, $^1J_{CF}$ 237.1 Hz), 63.5, 33.9 (d, $^2J_{CF}$ 19 Hz), 13.7. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –156.04 (dd, $^3J_{HF}$ 12.9 Hz, $^3J_{HF}$ 34.4 Hz).

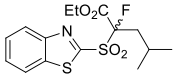
**2.2** Characterisation of the compounds

**2.2.1** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluorohexanoate (**10a**)



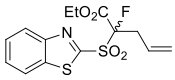
The general procedure was followed with sulfone **5** (330 mg, 1.08 mmol), 1-butanol (149 µL, 1.63 mmol), $PBu_3$ (409 µL, 1.63 mmol), ADDP (425 mg, 1.63 mmol) and toluene (13 mL). The reaction mixture was stirred for 2 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10a** as white crystals (**mp** 106–108 °C): 281 mg, 72%. **$^1$H NMR** (300 MHz, $CDCl_3$) δ 8.27–8.25 (m, 1H), 8.04–8.02 (m, 1H), 7.68–7.60 (m, 2H), 4.42–4.31 (m, 2H), 2.74–2.57 (m, 1H), 2.52–2.42 (m, 1H), 1.66–1.47 (m, 2H), 1.45–1.36 (m, 2H), 1.30 (t, $^3J_{HH}$ 7.0 Hz, 3H), 0.92 (t, $^3J_{HH}$ 7.0 Hz, 3H) ppm. **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 162.7 (d, $^2J_{CF}$ 25.3 Hz), 160.9, 152.6, 137.9, 128.5, 127.8, 125.9, 122.2, 108.1 (d, $^1J_{CF}$ 235.2 Hz), 63.7, 30.3 (d, $^2J_{CF}$ 19.4 Hz), 24.7, 22.2, 13.8, 13.6 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –157.0 (dd, $^3J_{HF}$ 38.7 Hz, $^3J_{HF}$ 12.9 Hz) ppm. NMR spectra correspond to the reported data.[1]

**2.2.2** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-4-methylpentanoate (**10b**)



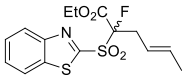
The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), isobutyl alcohol (228 µL, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 2 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10b** as white crystals (**mp** 76 °C): 380 mg, 64%. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.29–8.27 (m, 1H), 8.06–8.03 (m, 1H), 7.69–7.62 (m, 2H), 4.44–4.31 (m, 2H), 2.63 (ddd, $^3J_{HF}$ 40.9 Hz, $^2J_{HH}$ 14.7 Hz, $^3J_{HH}$ 6.8 Hz, 1H), 2.39 (ddd, $^2J_{HH}$ 14.7 Hz, $^3J_{HF}$ 8.2 Hz, $^3J_{HH}$ 6.8 Hz, 1H), 1.88 (tqq, $^3J_{HH}$ 6.8 Hz, $^3J_{HH}$ 6.8 Hz, $^3J_{HH}$ 6.8 Hz, 1H), 1.31 (t, $^3J_{HH}$ 14.3 Hz, 3H), 1.00–0.97 (m, 6H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.0 (d, $^2J_{CF}$ 25.4 Hz), 160.7, 152.6, 137.9, 128.5, 127.8, 126.0, 122.2, 108.3 (d, $^1J_{CF}$ 237.6 Hz), 63.7, 38.0 (d, $^2J_{CF}$ 19.1 Hz), 24.7, 23.0, 22.9 (d, $^4J_{CF}$ 2.2 Hz), 13.8 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –155.3 (dd, $^3J_{HF}$ 40.9 Hz, $^3J_{HF}$ 8.2 Hz) ppm. NMR spectra correspond to the reported data.[1]

**2.2.3** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoropent-4-enoate (**10c**)



The general procedure was followed with sulfone **5** (200 mg, 0.66 mmol), allyl alcohol (68 µL, 0.99 mmol), $PBu_3$ (247 µL, 0.99 mmol), ADDP (257 mg, 0.99 mmol) and toluene (8 mL). The reaction mixture was stirred for 2 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10c** as white crystals (**mp** 84–86 °C): 156 mg, 69%. **$^1$H NMR** (300 MHz, $CDCl_3$) δ 8.30–8.27 (m, 1H), 8.07–8.04 (m, 1H), 7.71–7.62 (m, 2H), 5.75–5.66 (m, 1H), 5.36–5.28 (m, 2H), 4.37 (q, $^3J_{HH}$ 7.3 Hz, 2H), 3.50–3.21 (m, 2H), 1.30 (t, $^3J_{HH}$ 7.3 Hz, 3H) ppm. **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 162.1 (d, $^2J_{CF}$ 25.4 Hz), 160.7, 152.7, 138.0, 128.6, 127.9, 126.7, 126.0, 122.7, 122.3, 106.8 (d, $^1J_{CF}$ 236.6 Hz), 63.8, 35.3 (d, $^2J_{CF}$ 18.8 Hz), 13.9 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –156.1 (dd, $^3J_{HF}$ 34.4 Hz, $^3J_{HF}$ 12.9 Hz) ppm. NMR spectra correspond to the reported data.[2]

**2.2.4** (*E*)-Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluorohex-4-enoate (**10d**)



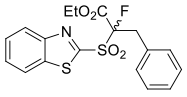
The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), crotyl alcohol (210 µL, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 2 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10d** as white crystals (**mp** 78–80 °C): 418 mg, 68%. **$^1$H NMR** (300 MHz, $CDCl_3$) δ 8.29–8.26 (m, 1H),

[1] Larnaud, F.; Pfund, E.; Linclau, B.; Lequeux, T. *Journal of Fluorine Chem.* **2012**, *134*, 128–135

[2] Calata, C.; Catel, J. M.; Pfund, E.; Lequeux, T. *Tetrahedron* **2009**, *65*, 3967–3973.

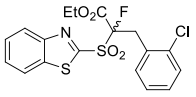
8.06–8.03 (m, 1H), 7.70–7.61 (m, 2H), 5.80–5.69 (m, 1H), 5.37–5.26 (m, 1H), 4.36 (q, $^3J_{HH}$ 7.0 Hz, 2H). 3.43–3.12 (m, 2H), 1.67 (d, $^3J_{HH}$ 5.5 Hz, 3H), 1.30 (t, $^3J_{HH}$ 7.0 Hz, 3H) ppm. **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 162.1 (d, $^2J_{CF}$ 24.6 Hz), 160.8, 152.7, 137.9, 133.8, 128.6, 127.8, 126.0, 122.2, 118.9 (d, $^3J_{CF}$ 2.2 Hz), 106.8 (d, $^1J_{CF}$ 236.0 Hz), 63.7, 34.3 (d, $^2J_{CF}$ 19.9 Hz), 18.1, 13.9 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –156.6 (dd, $^3J_{HF}$ 34.4 Hz, $^3J_{HF}$ 12.9 Hz,) ppm. NMR spectra correspond to the reported data.[1]

**2.2.5** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-phenylpropanoate (**10e**)



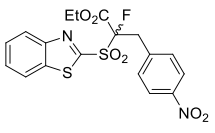
The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), benzyl alcohol (256 µL, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 2 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10e** (**mp** 86−88 °C) as white crystals: 578 mg, 89%. **$^1$H NMR** (300 MHz, $CDCl_3$) δ 8.38−8.16 (m, 1H), 8.13−7.94 (m, 1H), 7.78−7.53 (m, 2H), 7.37−7.10 (m, 5H), 4.08−4.33 (m, 2H), 3.68−4.05 (m, 2H), 1.13 (t, $^3J_{HH}$ 7.1 Hz, 3H) ppm. **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 161.9 (d, $^2J_{CF}$ 25.4 Hz), 160.7, 152.7, 138.0, 130.6, 130.4, 128.7, 128.1, 127.9, 126.0, 122.3, 107.2 (d, $^1J_{CF}$ 238.8 Hz), 63.7, 36.7 (d, $^2J_{CF}$ 25.4 Hz), 13.8 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ −155.1 (dd, $^3J_{HF}$ 38.7 Hz, $^3J_{HF}$ 12.9 Hz) ppm. NMR spectra correspond to the reported data.[2]

**2.2.6** Ethyl-2-(benzothiazol-2-ylsulfonyl)-3-(2-chlorophenyl)-2-fluoropropanoate (**10f**)



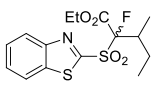
The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), 2-chlorobenzyl alcohol (352 mg, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 2 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10f** (**mp** 76−78 °C) as white crystals: 551 mg, 78%. **IR** (neat) 2982 (w), 2360 (m), 1761 (s), 1463 (m), 1354 (s), 1272 (s), 1161 (s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26–8.34 (m, 1H), 8.10–8.01 (m, 1H), 7.74–7.60 (m, 2H), 7.36 (dd, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.5 Hz, 1H), 7.31–7.26 (m, 3H), 4.40–3.03 (m, 4H), 1.22 (t, $^3J_{HH}$ 7.2 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 161.9 (d, $^2J_{CF}$ 26.3 Hz), 160.8, 152.8, 137.9, 135.3, 131.7, 130.0, 129.5, 129.2, 128.6, 127.9, 127.0, 126.0, 122.3, 105.7 (d, $^1J_{CF}$ 240.0 Hz), 63.9, 33.7 (d, $^2J_{CF}$ 19.0 Hz), 13.7 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –154.5 (dd, $^3J_{HH}$ 34.4 Hz, $^3J_{HH}$ 8.6 Hz) ppm. **MS** (ESI+)(m/z) 428.2 ($(M+H)^+$, 36), 200.1 (39), 182.0 (100). **HRMS** (MS+) for $C_{18}H_{16}FNO_4S_2Cl$ $(M+H)^+$ calcd 428.0193, found 428.0172.

**2.2.7** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-(4-nitrophenyl)propanoate (**10g**)



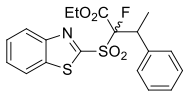
The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), (4-nitrophenyl)methanol (378 mg, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 2 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10g** as white crystals (**mp** 126–128 °C): 449 mg, 62%. **IR** (neat) 2982 (w), 2360 (m), 2328 (m), 1756 (s), 1520 (s), 1346 (s), 1162 (s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.24–8.35 (m, 1H), 8.17 (d, $^3J_{HH}$ 8.4 Hz, 2H), 8.11–8.04 (m, 1H), 7.62–7.76 (m, 2H) 7.45 (d, $^3J_{HH}$ 8.4 H, 2H), 4.32–4.18 (m, 2H), 4.18–3.87 (m, 2H), 1.17 (t, $^3J_{HH}$ 7.1 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 161.6 (d, $^2J_{CF}$ 24.9 Hz), 160.2, 152.7, 147.8, 138.2, 137.9, 131.4, 128.8, 128.1, 126.0, 123.8, 122.3, 106.5 (d, $^1J_{CF}$ 238.6 Hz), 64.1, 36.4 (d, $^2J_{CF}$ 19.0 Hz), 13.8 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –155.3 (dd, $^3J_{HF}$ 25.8 Hz, $^3J_{HF}$ 8.6 Hz) ppm. **MS** (ESI+)(m/z) 439.2 ($(M+H)^+$, 23), 200.1 (25), 182.0 (100). **HRMS** (MS+) for $C_{18}H_{16}FN_2O_6S_2$ (M+H)+ calcd 439.0434, found 439.0415.

**2.2.8** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-methylpentanoate (**10h**)



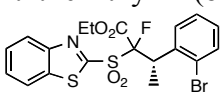
The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), (*S*)-butanol (227 µL, 2.47 mmol) (resp. 2-butanol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 3 h at 110 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10h** as white crystals: 368 mg, 62% (dr 50/50). **IR** (neat) 2360 (s), 2339 (w), 1752 (m), 1349 (m), 1252 (w), 1162 (m) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27–8.24 (m, 2H, Dia 1 & 2), 8.04–8.02 (m, 2H, Dia 1 & 2), 7.68–7.60 (m, 4H, Dia 1 & 2), 4.32–4.21 (m, 4H, Dia 1 & 2), 2.89–2.72 (m, 2H, Dia 1 & 2), 2.17–2.07 (m, 1H, Dia 1), 1.64–1.58 (m, 1H, Dia 2), 1.47–1.36 (m, 2H, Dia 1 & 2), 1.33 (d, $^3J_{HH}$ 7.1 Hz, 3H, Dia 1 or 2), 1.27 (t, $^3J_{HH}$ 7.6 Hz, 3H, Dia 1 or 2), 1.24 (t, $^3J_{HH}$ 7.6 Hz, 3H, Dia 2 or 1), 1.21 (d, $^3J_{HH}$ 7.1 Hz, 3H, Dia 2 or 1), 1.02 (t, $^3J_{HH}$ 7.6 Hz, 3H, Dia 1 or 2), 1.00 (t, $^3J_{HH}$ 7.6 Hz, 3H, Dia 2 or 1) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.3 (d, $^2J_{CF}$ 27.8 Hz, Dia 1 or 2), 163.0 (d, $^2J_{CF}$ 24.9 Hz, Dia 2 or 1), 152.5 (Dia 1 & 2), 137.9 (Dia 1 & 2), 128.5 (Dia 1 & 2), 127.8 (Dia 1 & 2), 125.9 (Dia 1 & 2), 122.2 (Dia 1 & 2), 110.6 (d, $^1J_{CF}$ 241.5 Hz, Dia 1 or 2), 110.2 (d, $^1J_{CF}$ 240.0 Hz, Dia 2 or 1), 63.5 (Dia 1 & 2), 38.2 (d, $^2J_{CF}$ 20.5 Hz, Dia 1 or 2), 37.9 (d, $^2J_{CF}$ 19.0 Hz, Dia 2 or 1), 24.5 (Dia 1 or 2), 23.9 (d, $^3J_{CF}$ 2.9 Hz, Dia 2 or 1), 13.8 (d, $^3J_{CF}$ 4.4 Hz, Dia 1 or 2), 13.4 (Dia 1 or 2), 13.3 (Dia 2 or 1), 12.3 (d, $^3J_{CF}$ 2.9 Hz, Dia 2 or 1), 11.4 (Dia 1 & 2) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –158.4 (d, $^3J_{HF}$ 25.8 Hz, Dia 1 or 2), – 161.6 (d, $^3J_{HF}$ 30.1 Hz, Dia 2 or 1) ppm. **MS** (ESI+)(m/z) 360.2 ($(M+H)^+$, 29), 200.1 (40), 182 (100). **HRMS** (MS+) for $C_{15}H_{19}FNO_4S_2$ (M+H)+ calcd 360.0740, found 360.0742.

**2.2.9** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-phenylbutanoate (**10i**)



The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), 1-phenylethanol (298 µL, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 3 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10i** as white crystals: 531 mg, 79%. **IR** (neat) 2925 (w), 1755 (s), 1461 (m), 1344 (s), 1158 (m), 1146 (m), 1024 (m) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.25–8.23 (m, 1H, *major*), 8.16–8.14 (m, 1H, *minor*), 7.94–7.91 (m, 1H, *minor*), 8.03–8.01 (m, 1H, *major*), 7.67–7.55 (m, 4H, *major & minor*), 7.34–7.30 (m, 2H, *major & minor*), 7.28–7.25 (m, 6H, *major & minor*), 7.21–7.18 (m, 2H, *major & minor*), 4.23 (dq, $^3J_{HF}$ 34.4 Hz, $^3J_{HH}$ 7.1 Hz, 1H, *major*), 4.16 (dq, $^3J_{HF}$ 30.1 Hz, $^3J_{HH}$ 7.1 Hz, 1H, *minor*), 4.42–4.32 (m, 2H, *minor*), 3.96–3.81 (m, 2H, *major*), 1.53 (d, $^3J_{HH}$ 7.1 Hz, 3H, *minor*), 1.73 (d, $^3J_{HH}$ 7.1 Hz, 3H, *major*), 1.31 (t, $^3J_{HH}$ 7.1 Hz, 3H, *minor*), 0.92 (t, $^3J_{HH}$ 7.1 Hz, 3H, *major*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, $^2J_{CF}$ 19.0 Hz) (*major or minor*), 161.7 (d, $^2J_{CF}$ 29.3 Hz) (*minor or major*), 152.4 (*major or minor*), 152.2 (*minor or major*), 138.8, 138.0 (*major or minor*), (137.9, 136.9, 129.5, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6) (*minor or major*), 126.0 (*major*), 125.9 (*minor*), 122.2 (*major*), 122.0 (*minor)*, 109.7 (d, $^1J_{CF}$ 244.4 Hz, *minor & major*), 63.8 (*minor*), 63.2 *(major*), 42.6 (d, $^2J_{CF}$ 19 Hz, *major*), 42.4 (d, $^2J_{CF}$ 19 Hz, *minor*), 17.1 (d, $^2J_{CF}$ 4.4 Hz, *minor*), 16.2 (d, $^2J_{CF}$ 5.9 Hz, *major*), 13.9 (*minor*), 13.4 (*major*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –159.4 (d, $^3J_{HF}$ 30.1 Hz, *minor*), – 164.6 (d, $^3J_{HF}$ 34.4 Hz, *major*) ppm. **MS** (ESI+)(m/z) 408.2 ($(M+H)^+$, 100), 200.1 (20), 182.0 (83). **HRMS** (MS+) for $C_{19}H_{19}FNO_4S_2$ (M+H)+ calcd 408.0740, found 408.0731.

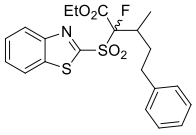
**2.2.10** Ethyl-2-(benzothiazol-2-ylsulfonyl)-3-(2-bromophenyl)-2-fluorobutanoate (**10j**)



The general procedure was followed with sulfone (500 mg, 1.65 mmol), (*R*)-(+)-1-(2-bromophenyl)ethanol (495 mg, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 4 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10j** as yellow oil: 413 mg, 52% (dr 50/50), obtained with 5% of

unknown impurity.[3] **IR** (neat) 3060 (br, w), 2987 (br, w), 2938 (br, w), 2360 (s), 2340 (m), 1760 (s), 1466 (m), 1356 (s), 1256 (br, m), 1165 (br, s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.30–8.24 (m, 1H, *Dia 1 or Dia 2*), 8.21–8.16 (m, 1H, *Dia 2 or Dia 1*), 8.07–8.01 (m, 1H, *Dia 1 or Dia 2*), 7.99–7.92 (m, 1H, *Dia 2 or Dia 1*), 7.72–7.51 (m, 6H, *Dia 1 and Dia 2*), 7.46–7.39 (m, 1H, *Dia 1 and Dia 2*), 7.36–7.30 (m, 1H, *Dia 1 and Dia 2*), 7.29–7.19 (m, 1H, *Dia 1 and Dia 2*), 7.15–7.05 (m, 1H, *Dia 1 and Dia 2*), 7.04–6.94 (m, 2H, *Dia 1 and Dia 2*), 4.99 (dd, $^3J_{HF}$ 32.2 Hz, $^3J_{HH}$ 6.9 Hz, 1H, *Dia 1*), 4.87 (dd, $^3J_{HF}$ 26.7 Hz, $^3J_{HH}$ 6.8 Hz, 1H, *Dia 2*), 4.49–4.34 (m, 2H, *Dia 1*), 4.01–3.83 (m, 2H, *Dia 2*), 1.66 (d, $^3J_{HH}$ 7.1 Hz, 3H, *Dia 2*), 1.49 (d, $^3J_{HH}$ 7.1 Hz, 3H, *Dia 1*), 1.39–1.30 (m, 3H, *Dia 1*), 0.97–0.89 (m, 3H, Dia 2) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.4 (d, $^2J_{CF}$ 26.4 Hz, *Dia 1 or Dia 2*) , 162.3 (d, $^2J_{CF}$ 24.9 Hz, *Dia 2 or Dia 1*), 161.4 (*Dia 1 & Dia 2*), 152.5 (*Dia 1 or Dia 2*), 152.4 (*Dia 2 or Dia 1*), 139.5 (*Dia 1 or Dia 2*), 138.0 (*Dia 1 or Dia 2*), 137.9 (*Dia 1 or Dia 2*), 137.0 (*Dia 1 or Dia 2*), 133.3 (*Dia 1 or Dia 2*), 133.0 (*Dia 1 or Dia 2*), 129.7 (*Dia 1 or Dia 2*), 129.6 (*Dia 1 or Dia 2*), 129.2 (*Dia 1 & Dia 2*), 128.6 (*Dia 1 & Dia 2*), 128.56 (*Dia 1 or Dia 2*), 128.4 (*Dia 1 or Dia 2*), 127.9 (*Dia 1 or Dia 2*), 127.6 (*Dia 1 or Dia 2*), 127.2 (*Dia 1 or Dia 2*), 126.0 (*Dia 1 or Dia 2*), 125.9 (*Dia 1 or Dia 2*), 125.4 (*Dia 1 or Dia 2*), 124.2 (*Dia 1 or Dia 2*), 122.2 (*Dia 1 or Dia 2*), 122.0 (*Dia 1 or Dia 2*), 109.9 (d, $^1J_{CF}$ 244.4 Hz, *Dia 1 or Dia 2*), 109.8 (d, $^1J_{CF}$ 243.0 Hz, *Dia 1 or Dia 2*), 64.0 (*Dia 1*), 63.4 (*Dia 2*), 40.7 (d, $^2J_{CF}$ 17.6 Hz, *Dia 1 or Dia 2*), 40.6 (d, $^2J_{CF}$ 16.1 Hz, *Dia 1 or Dia 2*), 17.6 (d, $^3J_{CF}$ 2.9 Hz, *Dia 1*), 16.3 (d, $^3J_{CF}$ 5.9 Hz, *Dia 2*), 13.9 (*Dia 1*), 13.3 (*Dia 2*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ – 158.2 (d, $^3J_{HF}$ 26.1 Hz, *Dia 1*), – 162.5 (d, $^3J_{HF}$ 32.2 Hz, *Dia 2*) ppm. **MS (ESI+)** (m/z) 442 ((M($^{79}$Br)+H)+, 100), 200.0 (77), 182.0 (100). **HRMS (MS+)** for $C_{19}H_{18}NO_4FS_2{}^{79}Br$ $(M+H)^+$ calcd. 485.9845, found 485.9828.

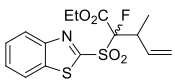
**2.2.11** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-methyl-5-phenylpentanoate (**10k**)




The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), 1-4-phenyl-2-butanol (380 µL, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 3 h at 60 °C. Column chromatography: petroleum ether/DCM, 45:55. Yield of **10k** as colourless oil: 310 mg, 43% (dr 50/50). **IR** (neat) 2969 (br, w), 2932 (br, w), 2361 (m), 2340 (w), 1679 (m), 1486 (m), 1454 (w), 1149 (w), 1009 (m) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.24–8.16 (m, 2H, *Dia 1 & 2*), 8.04–7.92 (d, $^3J_{HH}$ 8.1 Hz, 2H, *Dia 1 & 2*), 7.66–7.52 (m, 4H, *Dia 1 & 2*), 7.30–7.05 (m, 10H, *Dia 1 & 2*), 4.29–4.12 (m, 4H, *Dia 1 & 2*), 2.99–2.74 (m, 4H, *Dia 1 & 2*), 2.67–2.52 (m, 2H, *Dia 1 & 2*), 2.44–2.31 (m, 1H, *Dia 1 or 2* ), 1.89–1.77 (m, 1H, *Dia 2 or 1*), 1.75–1.60 (m, 2H, *Dia 1 & 2*), 1.39 (d, $^3J_{HH}$ 6.6 Hz, 3H, *Dia 1 or 2*), 1.29–1.20 (m, 6H, *Dia 1 & 2*), 1.16 (d, $^3J_{HH}$ 6.6 Hz, 3H, *Dia 2 or 1*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.1 (d, $^2J_{CF}$ 24.9 Hz, *Dia 1 or 2*), 162.9 (d, $^2J_{CF}$ 24.9 Hz, *Dia 2 or 1*), 161.9 (*Dia 1 & 2*), 152.4 (*Dia 1 & 2*), 141.0 (*Dia 1 & 2*), 140.8 (*Dia 1 or 2*), 137.8 (*Dia 1 or 2*), 128.5 (*Dia 1 & 2*), 128.4 (*Dia 1 or 2*), 128.3 (3C, *Dia 1 & 2*) 127.8 (*Dia 1 & 2*), 126.1 (*Dia 1 or 2*), 126.0 (*Dia 1 or 2*) 125.8 (*Dia 1 & 2*), 122.2 (*Dia 1 & 2*), 107.2 (d, $^1J_{CF}$ 238.8 Hz, *Dia 1 & 2*), 63.5 (*Dia 1 & 2*), 36.4 (d, $^2J_{CF}$ 20.5 Hz, *Dia 1 or 2*), 35.9 (d, $^2J_{CF}$ 19 Hz, *Dia 2 or 1*), 33.1 (*Dia 1 or 2*), 32.8 (*Dia 2 or 1*) , 32.7 (*Dia 1 or 2*), 31.5 (d, $^3J_{CF}$ 2.9 Hz, *Dia 1 or 2*), 14.1 (d, $^3J_{CF}$ 4.4 Hz, *Dia 1 or 2*), 13.8 (*Dia 1 or 2*), 13.7 (*Dia 1 or 2*), 12.8 (d, $^3J_{CF}$ 2.9 Hz, *Dia 1 or 2*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –157.7 (d, $^3J_{HF}$ 25.8 Hz, *Dia 1*), –161.7 (d, $^3J_{HF}$ 30.1 Hz, *Dia 2*). **MS** (ESI+) (m/z) 408.2 ($(M+H)^+$, 42), 200.1 (53), 182.0 (100). **HRMS** (MS+) for $C_{21}H_{23}FNO_4S_2$ (M+H)+ calcd 436.1053, found 436.1044.

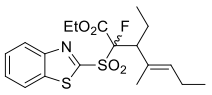
**2.2.12** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-methylpent-4-enoate (**10l**)

[3] Calculated by $^{19}$F NMR



The general procedure was followed with sulfone (500 mg, 1.65 mmol), 3-Buten-2-ol (213 µL, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 3h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10l** as white crystals: 425 mg, 72% (dr 55/45). **IR** (neat) 2987 (w), 1755 (s), 1459 (m), 1350 (s), 1254 (m), 1161 (s), 1147 (s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26–8.23 (m, 2H, *minor & major*), 8.04–8.01 (m, 2H, *minor & major*), 7.67–7.60 (m, 4H, *minor & major*), 5.96 (ddd, $^3J_{HHtrans}$ 17.2 Hz, $^3J_{HHcis}$ 10.6 Hz, $^3J_{HH}$ 8.6 Hz, 1H, *minor*), 5.79 (ddd, $^3J_{HHtrans}$ 17.2 Hz, $^3J_{HHcis}$ 10.1 Hz, $^3J_{HH}$ 9.1 Hz, 1H, *major*), 5.36 (d, $^3J_{HHtrans}$ 17.2 Hz, 1H, *minor*), 5.27 (d, $^3J_{HHcis}$ 10.6 Hz, 1H, *minor*), 5.26 (d, $^3J_{HHtrans}$ 17.2 Hz, 1H, *major*), 5.20 (d, $^3J_{HHcis}$ 10.6 Hz, 1H, *major*), 4.38–4.09 (m, 4H, *minor & major*), 3.68–3.65 (m, 2H, *minor & major*), 1.45 (d, $^3J_{HH}$ 6.6 Hz, 3H, *minor*), 1.28 (d, 3H, $^3J_{HH}$ 7.6 Hz, *major*), 1.26–1.21 (m, 6H, *minor & major*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, $^2J_{CF}$ 24.9 Hz, *minor or major*), 162.6 (d, $^2J_{CF}$ 24.9 Hz, *major or minor*), 161.8, 152.4, 137.8, 134.5 (d, $^3J_{CF}$ 2.9 Hz, *major*), 133.5 (d, $^3J_{CF}$ 2.9 Hz, *minor*), 128.5, 127.8, 125.9, 122.2, 119.4 (*minor*), 119.3 *(major*), 108.8 (d, $^1J_{CF}$ 243.0 Hz, *minor or major*), 108.6 (d, $^1J_{CF}$ 240.0 Hz, *major or minor*), 63.7 (*minor or major*), 63.5 (*major or minor*), 41.5 (d, $^2J_{CF}$ 19.0 Hz, *major*), 40.9 (d, $^2J_{CF}$ 19.0 Hz, *minor*), 15.4 (d, $^3J_{CF}$ 4.4 Hz, *major*), 14.3 (d, $^3J_{CF}$ 2.9 Hz, *minor*), 13.8 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –160.8 (d, $^3J_{HF}$ 25.8 Hz, *minor*), –166.9 (d, $^3J_{HF}$ 25.8 Hz, *major*) ppm. **MS** (ESI+)(m/z) 358.1 ($(M+H)^+$, 72), 330.0 (15), 200.0 (39), 182.0 (100). **HRMS** (MS+) for $C_{15}H_{17}NO_4FS_2$ $(M+H)^+$ calcd 358.0583, found 358.0588.

**2.2.13** (*E*)-Ethyl-2-(benzothiazol-2-ylsulfonyl)-3-ethyl-2-fluoro-4-methylhept-4-enoate (**10m**)



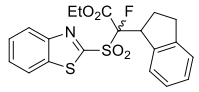
The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), 4-Methyl-4-hepten-3-ol (317 mg, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 3 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10m** as white crystals: 512 mg, 75% (dr 70/30). **IR** (neat) 2966 (m), 2360 (m), 1757 (s), 1463 (m), 1353 (m), 1161 (m) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.25–8.22 (m, 2H, *minor & major*), 8.03–8.00 (m, 2H, *minor & major*), 7.66–7.58 (m, 4H, *minor & major*), 5.59 (t, $^3J_{HH}$ 6.6 Hz, 1H, *minor*), 5.41 (t, $^3J_{HH}$ 6.6 Hz, 1H, *major*), 4.30–4.22 (m, 2H, *minor*), 4.17–4.08 (m, 2H, *major*), 3.39–3.24 (m, 2H, *minor & major*), 2.34–2.24 (m, 2H, *minor*), 2.09–1.95 (m, 4H, *minor & major*), 1.80–1.69 (m, 2H, *major*), 1.61 (s, 3H, *minor*), 1.57 (s, 3H, *major*), 1.22 (t, $^3J_{HH}$ 5.6 Hz, 6H, *minor & major*), 0.99–0.84 (m, 12H, *minor & major*). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.3 (d, $^2J_{CF}$ 24.9 Hz, *minor*), 163.0 (d, $^2J_{CF}$ 24.9 Hz, *major*), 162.5 (*major*), 162.3 (*minor*), 152.4, 137.8, 136.3 (*minor*), 135.3 (*major*), 129.3 (*major*), 128.5, 127.8, 127.7, 127.5 (*minor*), 125.9, 122.2, 111.2 (d, $^1J_{CF}$ 247.4 Hz, *major*), 110.5 (d, $^1J_{CF}$ 243.0 Hz, *minor*), 63.6 (*minor*), 63.1 (*major*), 52.1 (d, $^2J_{CF}$ 17.6 Hz, *major*), 51.8 (d, $^2J_{CF}$ 17.6 Hz, *minor*), 21.3 (*minor*), 21.1 (*major*), 19.0, 13.8 (2C), 13.4–12.9 (m), 11.5 (*major*), 11.4 (*minor*). **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ – 158.8 (d, $^3J_{HF}$ 30.1 Hz, *minor*), –160.6 (d, $^3J_{HF}$ 34.4 Hz, *major*). **MS** (ESI+)(m/z) 414.1 ($(M+H)^+$, 51), 304.1 (27), 215.2 (76), 200.0 (100), 195.2 (88), 182.0 (32). **HRMS** (MS+) for $C_{19}H_{25}NO_4FS_2$ $(M+H)^+$ calcd 414.1209, found 414.1195.

**2.2.14** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-cyclopentyl-2-fluoroacetate (**10n**)

The general procedure was followed with sulfone (500 mg, 1.65 mmol), cyclopentanol (225 µL, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 3 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10n** (**mp** 50−52 °C) as white crystals: 343 mg, 56%. **IR** (neat) 2961 (w), 1750 (s), 1464 (m), 1347 (s), 1258 (m), 1155 (s), 1090 (m), 1020 (m) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.24−8.22 (m, 1H), 8.02−8.00 (m, 1H), 7.65−7.59 (m, 2H),

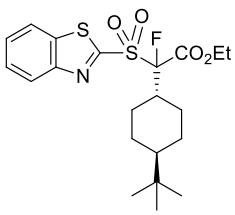
4.28−4.23 (m, 2H), 3.17 (dq, $^{3}J_{HF}$ 29.8 Hz, $^{3}J_{HH}$ 8.4 Hz, 1H), 2.15−2.07 (m, 1H), 1.85−1.56 (m, 7H), 1.23 (t, $^{3}J_{HH}$ 6.9 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.2 (d, $^{2}J_{CF}$ 26.0 Hz), 161.7, 152.5, 137.8, 128.5, 127.8, 125.9, 122.2, 108.8 (d, $^{1}J_{CF}$ 239.4 Hz), 63.5, 41.3 (d, $^{2}J_{CF}$ 20.8 Hz), 27.6 (d, $^{3}J_{CF}$ 2.6 Hz), 26.0 (d, $^{3}J_{CF}$ 3.3 Hz,), 25.9, 24.7, 13.8 ppm. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ −164.5 (d, $^{3}J_{HF}$ 29.8 Hz) ppm. **MS** (ESI+)(m/z) 372.2 ($(M+H)^+$, 100), 182.0 (85), 200.1 (31). **HRMS** (MS+) for $C_{16}H_{19}NO_4FS_2$ $(M+H)^+$ calcd 372.0740, found 372.0737.

**2.2.15** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-(2,3-dihydro-1*H*-inden-1-yl)-2-fluoroacetate (**10o**)



The general procedure was followed with sulfone (500 mg, 1.65 mmol), 1-Indanol (332 mg, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 3 h at 60 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **10o** as white crystals: 547 mg, 79% (dr 58/42). **IR** (neat) 2360 (s), 1748 (m), 1461 (m), 1353 (m), 1158 (m) $cm^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.28–8.26 (m, 2H, *minor & major*), 8.06–8.03 (m, 2H, *minor & major*), 7.69–7.62 (m, 4H, *minor & major*), 7.40–7.06 (m, 8H, *minor & major*), 4.59 (ddd, $^{3}J_{HF}$ 34.4 Hz, $^{3}J_{HH}$ 4.0 Hz, $^{3}J_{HF}$ 8.6 Hz, 1H, *major*), 4.43–4.35 (m, 1H, *minor*), 4.29–4.19 (m, 2H, *major*), 4.19–4.06 (m, 2H, *minor*), 3.19–3.09 (m, 2H), 3.03–2.87 (m, 4H), 2.68–3.09 (m, 1H, *minor*), 2.56–2.46 (m, 1H, *major*), 1.19 (t, $^{3}J_{HH}$ 7.6 Hz, 3H, *major*), 1.04 (t, $^{3}J_{HH}$ 7.1 Hz, 3H, *minor*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.1 (d, $^{2}J_{CF}$ 24.9 Hz, *major*), 162.0 (d, $^{2}J_{CF}$ 24.9 Hz, *minor*), 161.7 (*major or minor*), 161.4 (*major or minor*), 152.6 (*major or minor*),152.5 (*major or minor*),145.9 (*major or minor*),144.9 (*major or minor*),138.1 (*major or minor*), 137.9 (*major & minor*), 137.6 (*major or minor*), 128.6 (*major or minor*), 128.5 (*major or minor*), 128.4 (*major or minor*), 128.3 (*major or minor*), 127.9 (*major or minor*), 127.8 (*major or minor*), 126.4 (*major & minor*), 126.0 (*major & minor*), 125.9 (*major or minor*), 125.1 (*major or minor*), 124.7 (*major & minor*), 122.3 (*major or minor*), 122.2 (*major or minor*), 109.7 (d, $^{1}J_{CF}$ 248.4 Hz, *minor*), 107.9 (d, $^{1}J_{CF}$ 235.7 Hz, *major*), 63.6 (*major)*, 63.3 (*minor),* 48.1 (d, $^{2}J_{CF}$ 17.6 Hz, *minor*), 47.0 (d, $^{2}J_{CF}$ 19.0 Hz, *major),* 31.9 (*major*), 31.8 (*minor*), 26.8 (d, $^{3}J_{CF}$ 2.9 Hz, *major),* 26.3 (d, $^{3}J_{CF}$ 7.3 Hz, *minor),* 13.6 (*major),* 13.5 (*minor*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –143.3 (d, $^{3}J_{HF}$ 17.2 Hz, *minor*), –164.3 (d, $^{3}J_{HF}$ 34.4 Hz, *major*) ppm. **MS** (ESI+)(m/z) 420.3 ($(M+H)^+$, 32), 182.0 (100). **HRMS** (MS+) for $C_{20}H_{19}FNO_4S_2$ $(M+H)^+$ calcd 420.0740, found 420.0735.

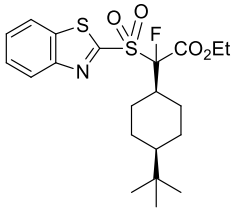
**2.2.16** (*Trans*)-ethyl-2-(benzothiazol-2-ylsulfonyl)-2-(4-*t*butylcyclohexyl)-2-fluoroacetate (**10p**)



The general procedure was followed with sulfone **5** (258 mg, 0.85 mmol), *cis*-4-*tert*-butylcyclohexan-1-ol (200 mg, 1.28 mmol), $PBu_3$ (320 µL, 1.28 mmol), ADDP (332 mg, 1.28 mmol) and toluene (10 mL). The reaction mixture was stirred for 20 h at 110 °C. Column chromatography: petroleum ether/DCM, 40:60. Yield of **10p** as white crystals (**mp** 104–106 °C): 164 mg, 44%. **IR** (neat) 2947 (br, m), 2856 (m), 2361 (br, m), 2364 (br, w), 1756 (s), 1466 (m), 1352 (s), 1264 (m), 1236 (m), 1164 (s), 1148 (m) $cm^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.30–8.21 (m, 1H), 8.08–7.99 (m, 1H), 7.68–7.59 (m, 2H), 4.31–4.20 (m, 2H), 2.70 (dtt, $^{3}J_{HF}$ 25.8 Hz, $^{3}J_{HH}$ 12.1 Hz, $^{3}J_{HH}$ 3.5 Hz, 1H), 2.48–2.37 (m, 1H), 1.96–1.94 (m, 2H), 1.80–1.72 (m, 1H), 1.49–1.33 (m, 2H), 1.25 (t, $^{3}J_{HH}$ 7.1 Hz, 3H), 1.19–1.05 (m, 2H), 1.03–0.97 (m, 1H), 0.85 (s, 9H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.1 (d, $^{2}J_{CF}$ 24.9 Hz), 162.1, 152.4, 137.8, 128.5, 127.8, 125.9, 122.2, 109.9 (d, $^{1}J_{CF}$ 245.9 Hz), 63.5, 47.0, 41.0 (d, $^{2}J_{CF}$ 20.5 Hz), 32.3, 27.4, 27.3 (d, $^{3}J_{CF}$ 2.6 Hz), 26.8, 26.4, 26.2 (d, $^{3}J_{CF}$ 2.9 Hz), 13.8 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –161.4 (d, $^{3}J_{HF}$ 25.8 Hz) ppm. **MS** (ESI+)(m/z) 442

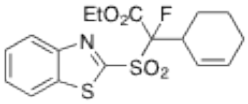
((M+H)$^+$, 25), 200.0 (25), 182.0 (100)**. HRMS** (MS+) for $C_{21}H_{29}NO_4FS_2$ (M+H)$^+$ calcd. 442.1522, found 442.1513.

**2.2.17** (*Cis*)-ethyl-2-(benzothiazol-2-ylsulfonyl)-2-(4-*t*butylcyclohexyl)-2-fluoroacetate (**10q**)



The general procedure was followed with sulfone **5** (500 mg, 1.65 mmol), *trans*-4-*tert*-butylcyclohexan-1-ol (385 mg, 2.47 mmol), $PBu_3$ (617 µL, 2.47 mmol), ADDP (641 mg, 2.47 mmol) and toluene (20 mL). The reaction mixture was stirred for 20 h at 110 °C. Column chromatography: petroleum ether/DCM, 45:55. Yield of **10q** as a yellow oil: 113 mg, 16%, obtained with 3% of unknown impurity.[4] **IR** (neat) 2954 (br, s), 2868 (br, m), 2362 (br, w), 2838 (br, w), 2362, 1761 (s), 1463 (s), 1349 (s) 1251 (s), 1169 (s), 1136 (s) cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.29–8.21 (m, 1H), 8.06–7.99 (m, 1H), 7.70–7.58 (m, 2H), 4.30–4.16 (m, 2H), 3.19–2.98 (m, 1H), 2.74–2.59 (m, 1H), 1.81–1.53 (m, 5H), 1.51–1.37 (m, 1H), 1.34–1.19 (m, $^3J_{HH}$ 7.2 Hz, 4H), 1.14–1.00 (m, 1H), 0.83 (s, 9H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.6 (d, $^2J_{CF}$ 24.9 Hz), 162.2, 152.4, 137.8, 128.5, 127.8, 125.9, 122.2, 112.7 (d, $^1J_{CF}$ 248.8 Hz), 63.6, 46.5, 34.2 (d, $^2J_{CF}$ 17.6 Hz), 32.6, 28.1, 27.5, 26.0, 23.0, 22.8, 13.8. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –155.6 (d, $^3J_{HF}$ 34.4 Hz) ppm. **MS** (ESI+)(m/z) 442 ((M+H)$^+$, 46), 200.0 (64), 182.0 (100). **HRMS** (MS+) for $C_{21}H_{29}NO_4FS_2$ (M+H)$^+$ calcd. 442.1522, found 442.1509.

**2.2.18** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-(cyclohex-2-enyl)-2-fluoroacetate (**10r**)



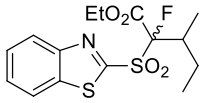
The general procedure was followed with sulfone **5** (350 mg, 1.15 mmol), cyclohex-2-ene-1-ol (169 µL, 1.73 mmol), $PBu_3$ (430 µL, 1.73 mmol), ADDP (446 mg, 1.73 mmol) and toluene (14 mL). The reaction mixture was stirred for 6 h 30 at room temperature. Column chromatography: petroleum ether/DCM, 55:45. Yield of **10r** as white crystals: 362 mg, 82% (dr 45/55). **IR** (neat) 2933 (br, w), 1756 (s), 1465 (m), 1353 (m), 1253 (m), 1162 (s) cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.35–8.16 (m, 2H, *major & minor*), 8.05–7.97 (m, 2H, *major & minor*), 7.68–7.58 (m, 4H, *major & minor*), 6.07–6.01 (m, 1H, *major*), 6.01–5.94 (m, 2H, *major & minor*), 5.57–5.48 (m, 1H, *minor*), 4.34–4.23 (m, 4H, *major & minor*), 3.72–3.48 (m, 2H, *major & minor*), 2.30–2.20 (m, 1H, *major*), 2.11–1.51 (m, 11H, *major & minor*), 1.25 (t, $^3J_{HH}$ 7.1 Hz, 3H, *major or minor*), 1.24 (t, $^3J_{HH}$ 7.1 Hz, 3H, *major or minor*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, $^2J_{CF}$ 24.9 Hz, *major or minor*), 162.6 (d, $^2J_{CF}$ 24.9 Hz, *major or minor*), 161.8 (*major or minor*), 161.7 (*major or minor*), 152.4 (*major & minor*), 137.8 (*major & minor*), 133.0 (*major or minor*), 132.7 (*major or minor*), 128.5 (*major & minor*), 127.8 (*major & minor*), 125.9 (*major & minor*), 122.2 (*major & minor*), 121.6 (d, $^3J_{CF}$ 2.9 Hz, *major or minor*), 121.4 (d, $^3J_{CF}$ 2.9 Hz, *major or minor*), 109.0 (d, $^1J_{CF}$ 238.6 Hz, *major or minor*), 108.9 (d, $^1J_{CF}$ 238.6 Hz, *major or minor*), 63.6 (*major or minor*), 63.5 (*major or minor*), 39.1 (d, $^2J_{CF}$ 20.5 Hz, *major or minor*), 39.0 (d, $^2J_{CF}$ 19.0 Hz, *major or minor*), 24.3 (*major &/or minor*), 23.7 (*major &/or minor*), 22.8 (d, $^3J_{CF}$ 2.9 Hz, *major or minor*), 21.0 (*major &/or minor*), 20.8 (*major &/or minor*), 13.8 (*major or minor*), 13.7 (*major or minor*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –157.6 (d, $^3J_{HF}$ 25.8 Hz, *minor*), –160.0 (d, $^3J_{HF}$ 25.8 Hz, *major*) ppm. **MS** (ESI+)(m/z) 384.1 ((M+H)$^+$, 41), 200.0 (57), 182.0 (100). **HRMS** (MS+) for $C_{17}H_{19}NO_4FS_2$ (M+H)$^+$ calcd. 384.0740, found 384.0730.

[4] Calculated with $^{19}$F NMR

## **2.3** Verification of product enantiopurity

**2.3.1** Mitsunobu reaction with (*S*)-2-butanol (Table 1, entry 8):

a) Racemic ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-methylpentanoate **(*rac*)-10h**




Empower software

RAPPORT HPLC

Reported by User: System Project Name: IC_OBH_ASH2012

**JM6521-53**

**Instrument Method: IC 1mL90% nhep10% prop_20dC**

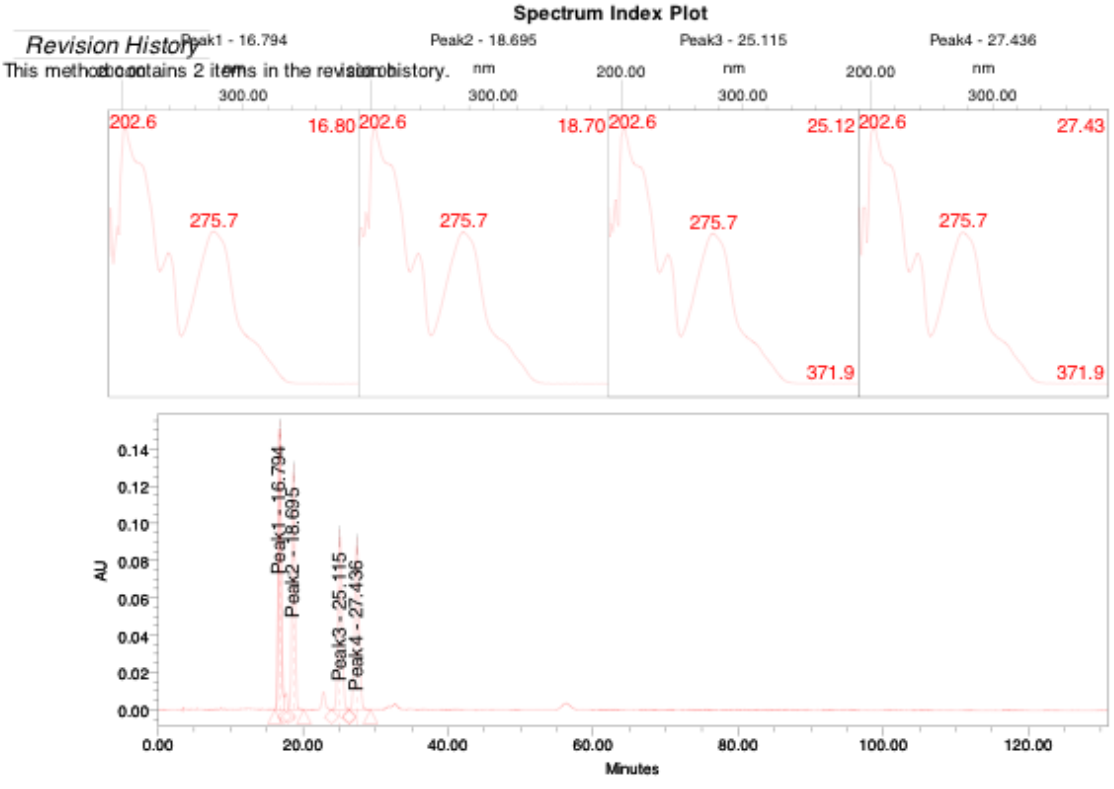
*Stored: 1/18/2012 10:25:00 AM*

*Method Information*

| | |
|---|---|
| Comments | Col. Daicel Chiralpak IC 4,6mmx250mm 5µm 1mL/mn 90%n-heptane10%propanol-2 éch.+col.à 20°C |
| Modified User | System |
| Locked | No |
| Method Id | 1021 |
| Method Version | 1 |
| Edit User | |

*Revision History*

This method contains 2 items in the revision history.



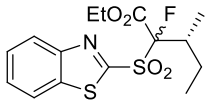

**Peak Results**

| | Name | Retention Time (min) | Area (µV*sec) | % Area |
|---|---|---|---|---|
| 1 | Peak1 | 16.794 | 3904471 | 26.02 |
| 2 | Peak2 | 18.695 | 3643992 | 24.28 |
| 3 | Peak3 | 25.115 | 3648543 | 24.31 |
| 4 | Peak4 | 27.436 | 3811157 | 25.39 |

Processed Channel Descr. PDA 275.0 nm

Report Method: RAPPORT HPLC Printed 4:34:15 PM 10/8/2012 Page: 1 of 1

b) Enantiopure (3*R*)-ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-methylpentanoate **10h** (diastereomers at C2)




Empower software

RAPPORT HPLC

Reported by User: System Project Name: IC_OBH_ASH2012

**JM6521-85**

**Instrument Method: IC 1mL90% nhep10% prop_20dC**

*Stored: 1/18/2012 10:25:00 AM*

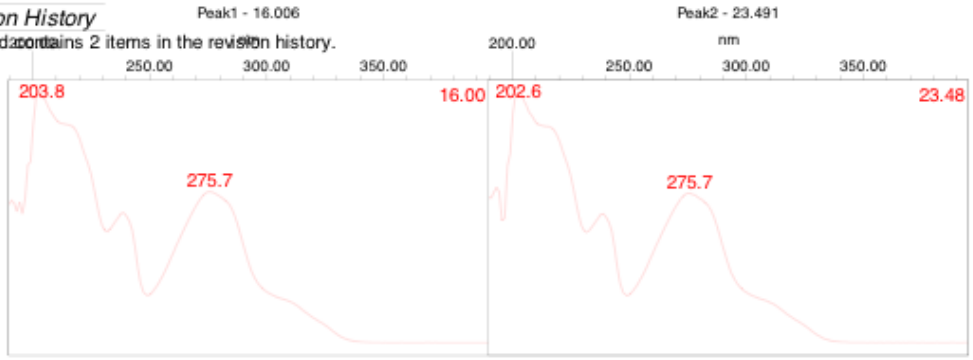
*Method Information*

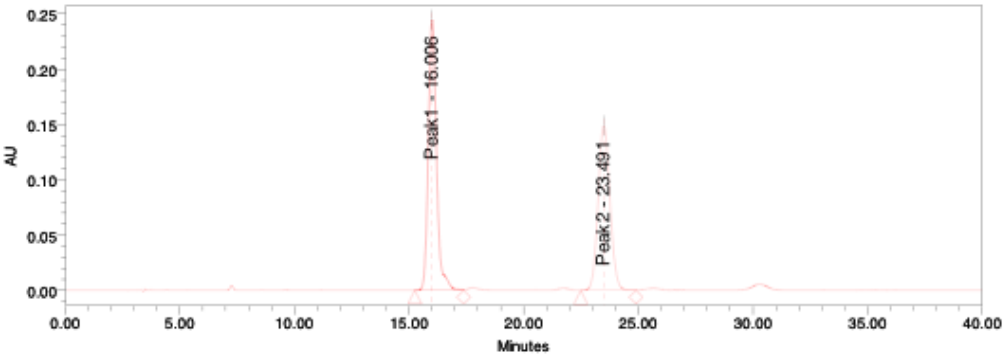
| | |
|---|---|
| Comments | Col. Daicel Chiralpak IC 4,6mmx250mm 5µm 1mL/mn 90%n-heptane10%propanol-2 éch.+col.à 20°C |
| Modified User | System |
| Locked | No |
| Method Id | 1021 |
| Method Version | 1 |
| Edit User | |

*Revision History*

This method contains 2 items in the revision history.

**Spectrum Index Plot**




**Peak Results**

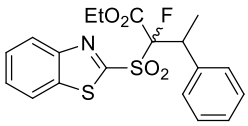
| | Name | Retention Time (min) | Area (µV*sec) | % Area |
|---|---|---|---|---|
| 1 | Peak1 | 16.006 | 6090588 | 53.14 |
| 2 | Peak2 | 23.491 | 5371566 | 46.86 |

Processed Channel Descr. PDA 275.0 nm

Report Method: RAPPORT HPLC Printed 4:34:27 PM 10/8/2012 Page: 1 of 1

**2.3.2** Mitsunobu reaction with (*S*)-1-phenylethanol (Table 1, entry 9)

a) Racemic ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-phenylbutanoate (**10i**)




Empower software

RAPPORT HPLC

Reported by User: System Project Name: IC_OBH_ASH2012

**FL6569-03**

**Instrument Method: IC 1mL70% nhep30% prop_20dC**

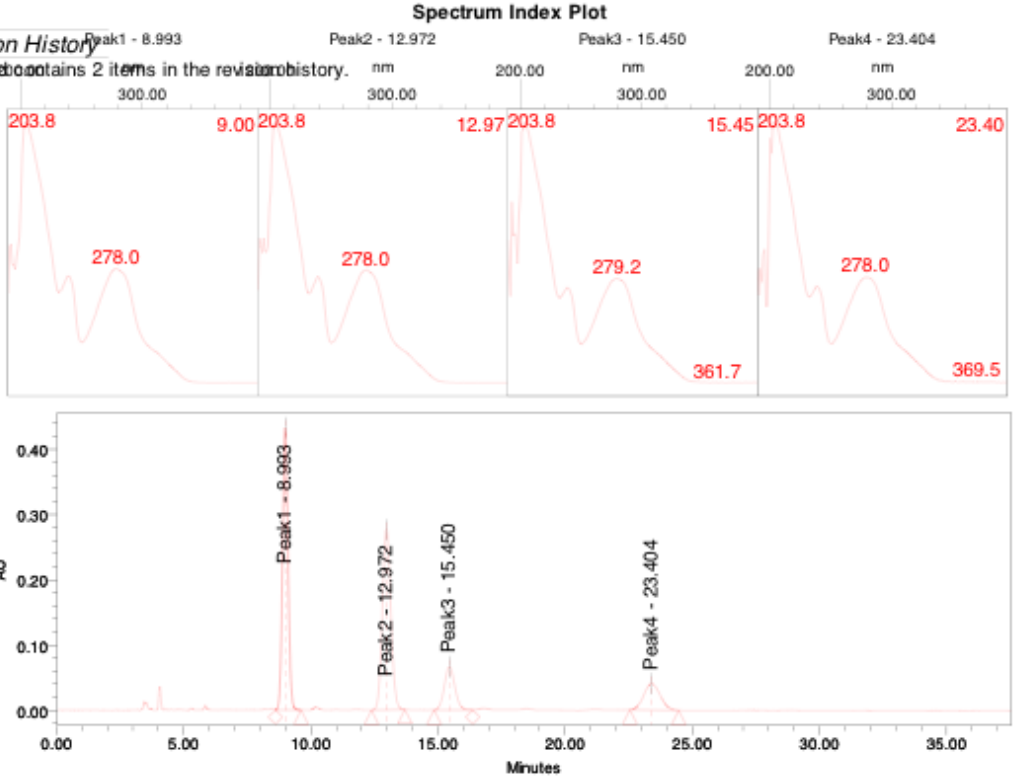
*Stored: 1/18/2012 10:25:00 AM*

*Method Information*

| | |
|---|---|
| Comments | Col. Daicel Chiralpak IC 4,6mmx250mm 5µm 1mL/mn 70%n-heptane30%propanol-2 éch.+col.à 20°C |
| Modified User | System |
| Locked | No |
| Method Id | 1009 |
| Method Version | 1 |
| Edit User | |

*Revision History*

This method contains 2 items in the revision history.







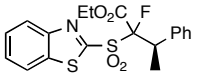
**Peak Results**

| | Name | Retention Time (min) | Area (µV*sec) | % Area |
|---|---|---|---|---|
| 1 | Peak1 | 8.993 | 6511390 | 39.06 |
| 2 | Peak2 | 12.972 | 6435524 | 38.61 |
| 3 | Peak3 | 15.450 | 1907110 | 11.44 |
| 4 | Peak4 | 23.404 | 1814409 | 10.89 |

Processed Channel Descr. PDA 220.0 nm

Report Method: RAPPORT HPLC Printed 4:33:38 PM 10/8/2012 Page: 1 of 1

b) Enantiopure (3*R*)-ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-phenylbutanoate (**10i**)




Empower software

RAPPORT HPLC

Reported by User: System Project Name: IC_OBH_ASH2012

**FLO6521-66**

**Instrument Method: IC 1mL70% nhep30% prop_20dC**

*Stored: 1/18/2012 10:25:00 AM*

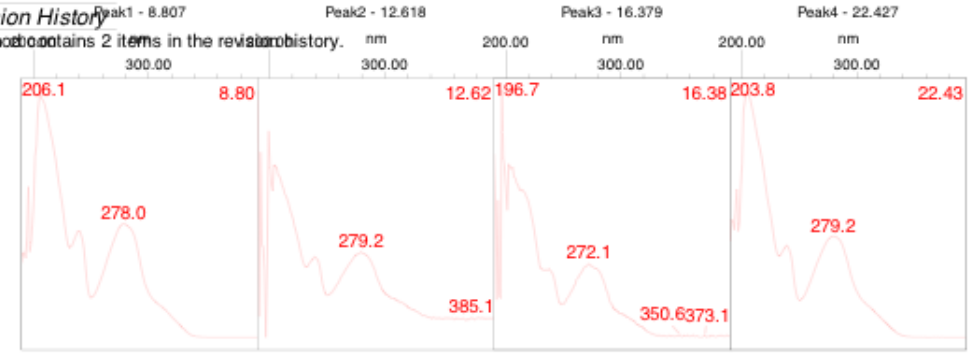
*Method Information*

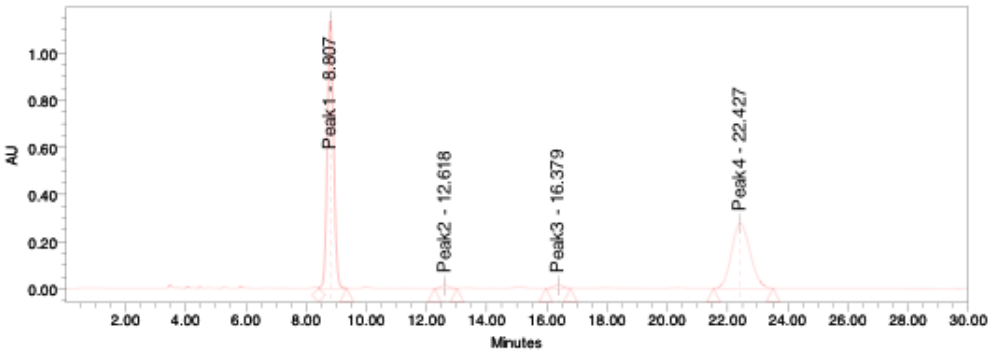
| | |
|---|---|
| Comments | Col. Daicel Chiralpak IC 4,6mmx250mm 5µm 1mL/mn 70%n-heptane30%propanol-2 éch.+col.à 20°C |
| Modified User | System |
| Locked | No |
| Method Id | 1009 |
| Method Version | 1 |
| Edit User | |

*Revision History*

This method contains 2 items in the revision history.

**Spectrum Index Plot**




**Peak Results**

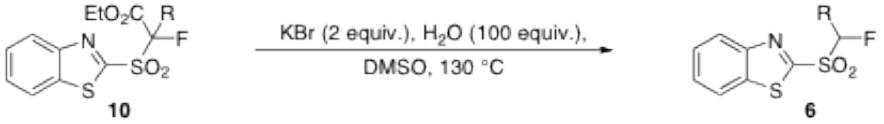
| | Name | Retention Time (min) | Area (µV*sec) | % Area |
|---|---|---|---|---|
| 1 | Peak1 | 8.807 | 16522010 | 57.20 |
| 2 | Peak2 | 12.618 | 240772 | 0.83 |
| 3 | Peak3 | 16.379 | 284788 | 0.99 |
| 4 | Peak4 | 22.427 | 11839141 | 40.98 |

Processed Channel Descr. PDA 220.0 nm

Report Method: RAPPORT HPLC Printed 4:34:00 PM 10/8/2012 Page: 1 of 1

**3** Decarboxylation reaction

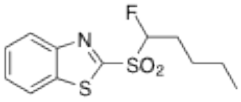
**3.1** General Procedure




The sulfone **10** was dissolved in DMSO (0.15M), then KBr (2 equiv.) and $H_2O$ (100 equiv.) were added. The resulting mixture was stirred for 16 h at 130 °C. The reaction mixture was extracted with $CH_2Cl_2$, then AcOEt. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography.

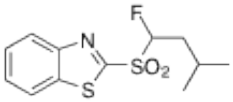
**3.2** Characterisation of the compounds

**3.2.1** 2-(1-Fluoropentylsulfonyl)benzothiazole (**6a**)



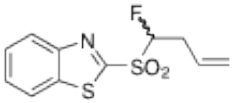
The general procedure was followed with sulfone **10a** (171 mg, 0.48 mmol), KBr (113 mg, 0.96 mmol), $H_2O$ (864 µL, 48 mmol) and DMSO (3.2 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6a** as white crystals (**mp** 84–86 °C): 113 mg, 82%. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.28–8.26 (m, 1H), 8.05–8.03 (m, 1H), 7.68–7.61 (m, 2H), 5.67 (ddd, $^2J_{HF}$ 51.8 Hz, $^3J_{HH}$ 10.0 Hz, $^3J_{HH}$ 3.5 Hz, 1H), 2.39–2.11 (m, 2H), 1.71–1.58 (m, 2H), 1.49–1.40 (m, 2H), 0.96 (t, $^3J_{HH}$ 7.0 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.6, 152.8, 137.4, 128.3, 127.8, 125.7, 122.3, 102.3 (d, $^1J_{CF}$ 221.0 Hz), 26.5 (d, $^2J_{CF}$ 18.5 Hz), 26.4, 22.0, 13.6 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ −178.05 (ddd, $^2J_{HF}$ 51.8 Hz, $^3J_{HF}$ 17.2 Hz, $^3J_{HF}$ 34 Hz) ppm. NMR spectra correspond to the reported data.[1]

**3.2.2** 2-(1-Fluoro-3-methylbutylsulfonyl)benzothiazole (**6b**)



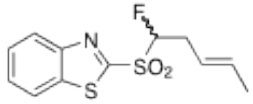
The general procedure was followed with sulfone **10b** (127 mg, 0.35 mmol), KBr (127 mg, 0.70 mmol), $H_2O$ (630 µL, 35 mmol) and DMSO (2.5 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6b** as white crystals (**mp** 50–52 °C): 91 mg, 90%. **IR** (neat) 2960 (w), 2360 (s), 2339 (s), 1467 (w), 1342 (s), 1157 (m) cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.30–8.28 (m, 1H), 8.06–8.04 (m, 1H), 7.70–7.62 (m, 2H), 5.73 (ddd, $^2J_{HF}$ 47.3 Hz, $^3J_{HH}$ 9.6 Hz, $^3J_{HH}$ 2.5 Hz, 1H), 2.18–2.11 (m, 1H), 2.10–1.97 (m, 2H), 1.05 (t, $^3J_{HH}$ 8.2 Hz, 6H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.6, 152.9, 137.5, 128.3, 127.8, 125.8, 122.3, 101.4 (d, $^1J_{CF}$ 222.5 Hz), 34.8 (d, $^2J_{CF}$ 19.0 Hz), 24.6, 22.9, 21.5 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –177.1 (ddd, $^2J_{HF}$ 47.3 Hz, $^3J_{HF}$ 34.4 Hz, $^3J_{HF}$ 22.5 Hz) ppm. **MS** (ESI+)(m/z) 288.2 ($(M+H)^+$, 16), 200.1 (18), 182.0 (100). **HRMS** (MS+) for $C_{12}H_{15}FNO_2S_2$ $(M+H)^+$ calcd 288.0528, found 288.0537.

**3.2.3** 2-(1-Fluorobut-3-enylsulfonyl)benzothiazole (**6c**)



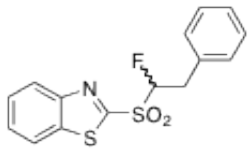
The general procedure was followed with sulfone **10c** (152 mg, 0.44 mmol), KBr (227 mL, 0.88 mmol), $H_2O$ (792 µL, 44 mmol) and DMSO (3 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6c** as white crystals (**mp** 92–94 °C): 108 mg, 90%. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27–8.25 (m, 1H), 8.05-8.03 (m, 1H), 7.68–7.60 (m, 2H), 5.92–5.82 (m, 1H), 5.71 (ddd, $^2J_{HF}$ 48.2 Hz, $^3J_{HH}$ 9.5 Hz, $^3J_{HH}$ 3.5 Hz, 1H), 5.35–5.28 (m, 2H), 3.15–2.86 (m, 2H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.2, 152.8, 137.4, 128.7 ($^3J_{CF}$ 1.9 Hz), 128.4, 127.8, 125.7, 122.3, 120.9, 101.2 ($^1J_{CF}$ 223.5 Hz), 31.5 (d, $^2J_{CF}$ 19.4 Hz) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –178.0 (ddd, $^2J_{HF}$ 48.2 Hz, $^3J_{HF}$ 34.4 Hz, $^3J_{HF}$ 17.2 Hz) ppm. NMR spectra correspond to the reported data.[1]

**3.2.4** (*E*)-2-(1-Fluoropent-3-enylsulfonyl)benzothiazole (**6d**)



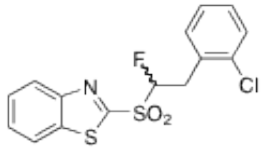
The general procedure was followed with sulfone **10d** (290 mg, 0.78 mmol), KBr (186 mg, 1.56 mmol), $H_2O$ (1.4 mL, 78 mmol) and DMSO (5.3 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6d** as white crystals (**mp** 76–78°C): 204 mg, 92%. **$^1$H NMR** (300 MHz, $CDCl_3$) δ 8.29–8.25 (m, 1H), 8.06–8.03 (m, 1H), 7.70–7.60 (m, 2H), 5.82–5.42 (m, 3H), 3.10–2.79 (m, 2H), 1.70 (dd, $^3J_{HH}$ 6.6 Hz, $^4J_{HH}$ 1.5 Hz, 3H) ppm. **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 162.5, 152.8, 137.5, 132.1, 128.4, 127.8, 125.8, 122.3, 121.1, 101.6 (d, $^1J_{CF}$ 223.4 Hz), 30.5 (d, $^2J_{CF}$ 19.9 Hz), 18.0 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –177.8 (ddd, $^2J_{HF}$ 51.6 Hz, $^3J_{HF}$ 34.4 Hz, $^3J_{HF}$ 17.2 Hz) ppm. NMR spectra correspond to the reported data.[1]

**3.2.5** 2-(1-Fluoro-2-phenylethylsulfonyl)benzothiazole (**6e**)



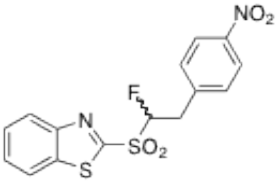
The general procedure was followed with sulfone **10e** (150 mg, 0.38 mmol), KBr (90 mg, 0.76 mmol), $H_2O$ (686 µL, 38 mmol) and DMSO (2.5 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6e** as white crystals (**mp** 106–108 °C): 111 mg, 92%. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.31–8.22 (m, 1H), 8.10–8.01 (m, 1H), 7.72–7.58 (m, 2H), 7.41–7.24 (m, 5H), 5.83 (ddd, $^2J_{HF}$ 47.7 Hz, $^3J_{HH}$ 10.1 Hz, $^3J_{HH}$ 2.0 Hz, 1H), 3.65 (ddd, $^3J_{HF}$ 39.4 Hz, $^2J_{HH}$ 15.2 Hz, $^3J_{HH}$ 2.0 Hz, 1H), 3.42 (ddd, $^3J_{HF}$ 16.2 Hz, $^2J_{HH}$ 15.2 Hz, $^3J_{HH}$ 10.1 Hz, 1H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.3, 152.8, 137.5, 133.1, 129.5, 128.9, 128.4, 127.9, 127.8, 125.8, 122.3, 101.9 (d, $^1J_{CF}$ 225.4 Hz), 33.3 (d, $^2J_{CF}$ 19.0 Hz) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –177.0 (ddd, $^2J_{HF}$ 47.7, $^3J_{HF}$ 39.4, $^3J_{HF}$ 16.2 Hz) ppm. NMR spectra correspond to the reported data.[1]

**3.2.6** 2-(2-(2-Chlorophenyl)-1-fluoroethylsulfonyl)benzothiazole (**6f**)



The general procedure was followed with sulfone **10f** (510 mg, 1.19 mmol), KBr (283 mg, 2.38 mmol), $H_2O$ (2.14 mL, 119 mmol) and DMSO (7.5 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6f** as white crystals (**mp** 108–110 °C): 350 mg, 83%. **IR** (neat) 2960 (w), 2360 (s), 2339 (s), 1467 (w), 1342 (s), 1157 (m) cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, $^3J_{HH}$ 8.1 Hz, 1H), 8.04 (d, $^3J_{HH}$ 8.6 Hz, 1H), 7.71–7.58 (m, 2H), 7.42–7.37 (m, 1H), 7.35–7.39 (m, 1H), 7.28–7.19 (m, 2H), 5.93 (ddd, $^2J_{HF}$ 47.7 Hz, $^3J_{HH}$ 10.1 Hz, $^3J_{HH}$ 2.5 Hz, 1H), 3.91 (ddd, $^3J_{HF}$ 35.4 Hz, $^2J_{HH}$ 14.7 Hz, $^3J_{HH}$ 2.5 Hz, 1H), 3.46 (ddd, $^3J_{HF}$ 12.9 Hz, $^2J_{HH}$ 14.7 Hz, $^3J_{HH}$ 10.1 Hz, 1H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.1, 152.8, 137.5, 134.3, 132.3, 130.7, 129.8, 129.4, 128.5, 127.9, 127.2, 125.8, 122.3, 100.5 (d, $^1J_{CF}$ 229.9 Hz), 31.5 (d, $^2J_{CF}$ 20.5 Hz) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –177.8 (ddd, $^2J_{HF}$ 47.7 Hz, $^3J_{HF}$ 35.4 Hz, $^3J_{HF}$ 12.9 Hz) ppm. **MS** (ESI+)(m/z) 356.0 ((M($^{35}$Cl)+H)$^+$, 100), 182.0 (73). **HRMS** (MS+) for $C_{15}H_{12}NO_2FS_2{}^{35}Cl$ (M+H)$^+$ calcd. 355.9982, found 355.9968.

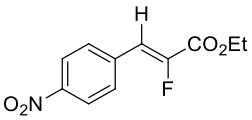
**3.2.7** 2-(1-Fluoro-2-(4-nitrophenyl)ethylsulfonyl)benzothiazole (**6g**)



The general procedure was followed with sulfone **10g** (366 mg, 0.83 mmol), KBr (283 mg, 2.38 mmol), $H_2O$ (2.14 mL, 119 mmol) and DMSO (7.5 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6g** as white crystals (**mp** 170–172 °C): 116 mg, 38% and **JM6521-45** as a colorless oil: 5 mg, 3%**.**

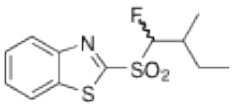
**IR** (neat) 2917 (w), 2360 (s), 2340 (m), 1518 (m), 1467 (m), 1346 (s), 1150 (s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.33–8.16 (m, 3H), 8.06 (d, $^3J_{HH}$ 7.1 Hz, 1H), 7.76–7.59 (m, 2H), 7.51 (d, $^3J_{HH}$ 8.1 Hz, 2H), 5.88 (ddd, $^2J_{HF}$ 47.0 Hz, $^3J_{HH}$ 10.1 Hz, $^3J_{HH}$ 2.2 Hz, 1H), 3.76 (ddd, $^3J_{HF}$ 34.4 Hz, $^2J_{HH}$ 14.1 Hz, $^3J_{HH}$ 2.2 Hz, 1H), 3.58 (ddd, $^3J_{HF}$ 17.2 Hz, $^2J_{HH}$ 14.1 Hz, $^3J_{HH}$ 10.1 Hz, 1H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 161.8, 152.8, 147.7, 140.4, 137.4, 130.6, 128.7, 128.0, 125.8, 124.1, 122.4, 101.2 (d, $^1J_{CF}$ 225.1 Hz), 36.4 (d, $^2J_{CF}$ 20.5 Hz) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –177.0 (ddd, $^2J_{HF}$ 47.0 Hz, $^3J_{HF}$ 34.4 Hz, $^3J_{HF}$ 17.2 Hz) ppm. **MS** (ESI+)(m/z) 367.0 ($(M+H)^+$, 74), 200.0 (18), 182.0 (100). **HRMS** (MS+) for $C_{15}H_{12}N_2O_4FS_2$ $(M+H)^+$ calcd. 367.0223, found 367.0221.

Data for (*Z*)-Ethyl-2-fluoro-3-(4-nitrophenyl)acrylate




**IR** (neat) 2994 (w), 2360 (s), 2339 (s), 1720 (s), 1514 (s), 1345 (s), 1312 (s), 1286 (m) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, $^3J_{HH}$ 9.1 Hz, 2H), 7.80 (d, $^3J_{HH}$ 9.1 Hz, 2H), 6.98 (d, $^3J_{HF\textit{trans}}$ 33.9 Hz, 1H), 4.39 (q, $^3J_{HH}$ 7.1 Hz, 2H), 1.41 (t, $^3J_{HF}$ 7.1 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 160.6 (d, $^2J_{CF}$ 35.1 Hz), 149.1 (d, $^1J_{CF}$ 248.8 Hz), 147.6, 137.3 (d, $^3J_{CF}$ 4.4 Hz), 130.8, 130.7, 124.0, 114.8 (d, $^2J_{CF}$ 4.4 Hz), 62.4, 14.1 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –199.9 (d, $^3J_{HF\textit{trans}}$ 33.9 Hz) ppm. NMR spectra correspond to the reported data.[5]

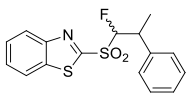
**3.2.8** 2-(1-Fluoro-2-methylbutylsulfonyl)benzothiazole (**6h**)




The general procedure was followed with sulfone **10h** (305 mg, 0.85 mmol), KBr (202 mg, 1.70 mmol), $H_2O$ (1.53 mL, 85 mmol) and DMSO (5.7 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6h** as white crystals: 211 mg, 89% (dr 50/50). **IR** (neat) 2970 (w), 2360 (m), 1467 (m), 1342 (s), 1157 (s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.28–8.26 (m, 2H, *Dia 1 & Dia 2*), 8.05–8.04 (m, 2H, *Dia 1 & Dia 2*), 7.69–7.61 (m, 4H, *Dia 1 & Dia 2*), 5.66 (ddd, $^2J_{HF}$ 47.5 Hz, $^3J_{HH}$ 3.5 Hz, 1H, *Dia 1*), 5.52 (ddd, $^2J_{HF}$ 47.5 Hz, $^3J_{HH}$ 6.6 Hz, 1H, *Dia 2*), 2.62–2.46 (m, 2H, *Dia 1 & Dia 2*), 1.94–1.84 (m, 1H, *Dia 2*), 1.80–1.44 (m, 2H, *Dia 1*), 1.62–1.44 (m, 1H, *Dia 2*), 1.29 (d, $^3J_{HH}$ 7.1 Hz, 3H, *Dia 2*), 1.26 (dd, $^3J_{HH}$ 7.1 Hz, $^4J_{HH}$ 1.5 Hz, 3H, *Dia 1*), 1.04 (t, $^3J_{HH}$ 7.6 Hz, 3H, *Dia 1*), 1.01 (t, $^3J_{HH}$ 7.6 Hz, 3H, *Dia 2*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.8, 152.8, 137.4, 128.3, 127.8, 125.7, 122.3, 105.1 (d, $^1J_{CF}$ 224 Hz, *Dia 2*), 103.9 (d, $^1J_{CF}$ 225.4 Hz, *Dia 1)*, 34.2 (d, $^2J_{CF}$ 14.6 Hz, *Dia 1 or Dia 2),* 34.0 (d, $^2J_{CF}$ 16.1 Hz, *Dia 2 or Dia 1*), 26.5 (*Dia 1 or 2*), 23.9 (d, $^3J_{CF}$ 5.9 Hz, *Dia 1 or 2),* 14.9 (d, $^4J_{CF}$ 4.4 Hz *Dia 1 or 2)*, 13.1 (d, $^4J_{CF}$ 5.9 Hz, *Dia 1 or 2*)11.1 (*Dia 1 or 2)*, 10.6 (*Dia 1 or 2)* ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ – 179.2 (dd, $^2J_{HF}$ 47.5 Hz, $^3J_{HF}$ 17.2 Hz, *Dia 1 or Dia 2*), – 187.4 (dd, $^2J_{HF}$ 47.5 Hz, $^3J_{HF}$ 30.1 Hz, *Dia 2 or Dia 1*) ppm. **MS** (ESI+)(m/z) 288.1 ($(M+H)^+$, 22), 200.1 (29), 182.0 (100). **HRMS** (MS+) for $C_{12}H_{15}FNO_2S_2$ $(M+H)^+$ calcd 288.0528, found 288.0523.

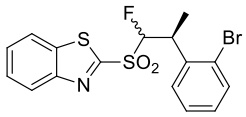
[5] Pfund.E, Lebargy.C, Rouden J., Lequeux T., *J. Org. Chem.* **2007**, *72*, 7871-7877

**3.2.9** 2-((1-Fluoro-2-phenylpropyl)sulfonyl)benzothiazole (**6i**)



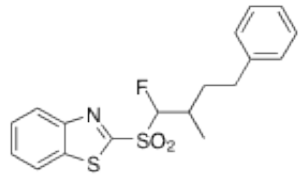
The general procedure was followed with sulfone **10i** (150 mg, 0.37 mmol), KBr (88 mg, 0.74 mmol), $H_2O$ (700 µL, 37 mmol) and DMSO (5.8 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6i** as white crystals: 109 mg, 88% (dr 62/38). **IR** (neat) 2918 (w), 1675 (w), 1468 (w), 1346 (w), 1150 (s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26–8.22 (m, 2H, *major & minor*), 8.04–8.00 (m, 2H, *major & minor*), 7.67–7.60 (m, 4H, *major & minor*), 7.37–7.26 (m, 10H, *major & minor*), 5.87 (dd, $^2J_{HF}$ 47.3 Hz, $^3J_{HH}$ 3.0 Hz, 1H, *major*), 5.75 (dd, $^2J_{HF}$ 47.3 Hz, $^3J_{HH}$ 7.6 Hz, 1H, *minor*), 3.93 (ddq, $^3J_{HF}$ 30.1 Hz, $^3J_{HH}$ 3.0 Hz, $^3J_{HH}$ 7.1 Hz, 1H, *major*), 3.77 (ddq, $^3J_{HF}$ 17.2 Hz, $^3J_{HH}$ 7.6 Hz, $^3J_{HH}$ 7.1 Hz, 1H, *minor*), 1.67 (d, $^3J_{HH}$ 7.1 Hz, 3H, *minor*), 1.63 (d, $^3J_{HH}$ 7.1 Hz, 3H, *major*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.3 (*major*), 163.2 (*minor*), 152.6 (*major & minor*), 140.4 (*major & minor*), 138.7 (*minor*), 137.3 (*major*), , 128.9 (4C, *major & minor*), 128.6 (*major & minor*), 128.24 (*major*), 128.21 (*minor*), 128.1 (*major and minor*), 127.70 (*minor*), 127.65 (3C, *major and minor*), 125.6 (*major & minor*) 122.2 (*major*), 121.2 (*minor*), 104.2 (d, $^1J_{CF}$ 223.9 Hz, *minor*), 104.1 (d, $^1J_{CF}$ 229.8 Hz, *major*), 39.1 (d, $^2J_{CF}$ 17.6 Hz, *minor*), 38.4 (d, $^2J_{CF}$ 19.0 Hz, *major*), 17.8 (d, $^3J_{CF}$ 5.8 Hz, *minor*), 15.2 (d, $^3J_{CF}$ 7.3 Hz, *major*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –174.1 (dd, $^2J_{HF}$ 47.3 Hz, $^3J_{HF}$ 17.2 Hz, *minor*), –186.36 (dd, $^2J_{HF}$ 47.3 Hz, $^3J_{HF}$ 30.1 Hz, *major*) ppm. **MS** (ESI+)(m/z) 336.2 $(M+H)^+$ (42), 182.0 (100). **HRMS** (MS+) for $C_{16}H_{14}FNO_2S_2$ $(M+H)^+$ calcd 336.0528, found 336.0538.

**3.2.10** 2-(((2*S*)-2-(2-Bromophenyl)-1-fluoropropyl)sulfonyl)benzothiazole (**6j**)



The general procedure was followed with sulfone **10j** (234 mg, 0.48 mmol), KBr (114 mg, 0.96 mmol), $H_2O$ (864 µL, 48 mmol) and DMSO (3.2 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6j** as white crystals: 171 mg, 86% (dr 54/46). **IR** (neat) 3056 (br, w), 2913 (br, w), 2354 (br, w), 2337 (br, w), 1471 (s), 1349 (s), 1149 (s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.34–8.19 (m, 2H, *major & minor*), 8.10–7.97 (m, 2H, *major & minor*), 7.72–7.53 (m, 6H, *major & minor*), 7.43–7.36 (m, 2H, *major & minor*), 7.35–7.24 (m, 2H, *major & minor*), 7.20–7.04 (m, 2H, *major & minor*), 5.93 (dd, $^2J_{HF}$ 48.0 Hz, $^3J_{HH}$ 2.8 Hz, 1H, *major*), 5.86 (dd, $^2J_{HF}$ 46.6 Hz, $^3J_{HH}$ 7.1 Hz, 1H, *minor*), 4.54 (dqd, $^3J_{HF}$ 29.6 Hz, $^3J_{HH}$ 7.1 Hz, $^3J_{HH}$ 2.0 Hz, 1H, *major*), 4.46–4.34 (m, 1H, *minor*), 1.71–1.61 (m, 6H, *major & minor*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.4 (*major*), 163.0 (*minor*), 152.8 (*major & minor*), 139.5 (*major*), 138.4 (*minor*), 137.4 (*major & minor*), 133.4 (*minor*), 133.3 (*major*), 129.2 (*major & minor*), 129.1 (*major & minor*), 128.4 (*major & minor*), 128.1 (*major & minor*), 127.8 (*major*), 127.7 (*minor*), 125.8 (*major and minor*), 124.0 (*major*), 122.3 (*major & minor*), 104.1 (d, $^1J_{CF}$ 223.9 Hz, $C_9$, *minor*), 102.8 (d, $^1J_{CF}$ 223.9 Hz, *major*), 38.1–37.9 (m, *minor*), 37.2 (d, $^2J_{CF}$ 19.0 Hz, $C_8$, *major*), 17.4 (d, $^3J_{CF}$ 4.4 Hz, *minor*), 13.9 (d, $^3J_{CF}$ 7.32 Hz, *minor*) ppm. C-Br for minor diastereoisomere not visible. **$^{19}$F NMR** (282 MHz, $CDCl_3$) –174.2 to –172.9 (m, *minor*), –189.8 (dd, $^2J_{HF}$ 47.3, $^3J_{HF}$ 30.1 Hz, *major*) ppm. **MS** (ESI+)(m/z) 414.1 ($(M(^{79}Br)+H)^+$, 100), 200.0 (21), 182.0 (75)**. HRMS** (MS+) for $C_{16}H_{14}NO_2FS_2{}^{79}Br$ $(M+H)^+$ calcd. 413.9633, found 413.9637.

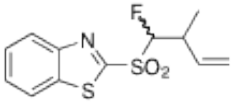
**3.2.11** 2-(1-Fluoro-2-methyl-4-phenylbutylsulfonyl)benzothiazole (**6k**)



The general procedure was followed with sulfone **10k** (241 mg, 0.55 mmol), KBr (131 mg, 1.10 mmol), $H_2O$ (990 µL, 55 mmol) and DMSO (3.7 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6k** as white crystals: 170 mg, 85% (dr 51/49). **IR** (neat) 2961 (w), 2360 (s), 2339 (m), 1467 (m), 1342 (s), 1157 (s) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, $^3J_{HH}$ 8.1 Hz, 2H, *Dia 1 & 2*), 7.98 (d, $^3J_{HH}$ 8.1 Hz, 2H,

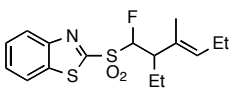
*Dia 1 & 2*), 7.65–7.52 (m, 4H, *Dia 1 & 2*), 7.29–7.10 (m, 10H, *Dia 1 & 2*), 5.65 (dd, $^{2}J_{HF}$ 47.7 Hz, $^{3}J_{HH}$ 3.5 Hz, 1H, *Dia 1 or Dia 2*), 5.51 (dd, $^{2}J_{HF}$ 47.5 Hz, $^{3}J_{HH}$ 6.6 Hz, 1H, *Dia 2 or Dia 1),* 2.81–2.50 (m, 6H, *Dia 1 & 2*), 2.20–2.09 (m, 1H, *Dia 1 or 2*), 2.05–1.93 (m, 1H, *Dia 2 or 1*), 1.85–1.66 (m, 2H, *Dia 1 or 2*), 1.32 (d, $^{3}J_{HH}$ 7.1 Hz, 3H, *Dia 1 or 2*), 1.28 (d, $^{3}J_{HH}$ 7.1 Hz, 3H, *Dia 1 or 2*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.6 (*Dia 1 or 2*), 163.5 (*Dia 1 or 2*), 152.7 (*Dia 1 & 2*), 141.1 (*Dia 1 & 2*), 140.8 (*Dia 1 & 2*), 137.2 (*Dia 1 & 2*), 128.5 (*Dia 1 & 2*), 128.4 (*Dia 1 & 2*), 128.3 (*Dia 1 & 2*), 127.8 (*Dia 1 & 2*), 126.1 (*Dia 1 & 2*), 126.0 (*Dia 1 & 2*), 125.7 (*Dia 1 & 2*), 122.3 (*Dia 1 & 2*), 105.6 (d, $^{1}J_{CF}$ 106.8 Hz, *Dia 1 or 2*), 103.4 (d, $^{1}J_{CF}$ 106.8 Hz, *Dia 2 or 1*), 35.0 (*Dia 1 or 2*) (, 32.8-32.4 (m, $^{2}J_{CF}$ 17.6 Hz, *Dia 1 & 2*), 32.2 (d, $^{2}J_{CF}$ 17.6 Hz, *Dia 2 or 1*), 15.6 (d, $^{3}J_{CF}$ 7.3 Hz, *Dia 1 or 2*), 13.4 (d, $^{3}J_{CF}$ 7.3 Hz, *Dia 2 or 1*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –179.5 (dd, $^{2}J_{HF}$ 47.5 Hz, $^{3}J_{HF}$ 17.2 Hz, *Dia 1 or Dia 2*), – 187.2 (dd, $^{2}J_{HF}$ 47.7 Hz, $^{3}J_{HF}$ 25.8 Hz, *Dia 2 or Dia 1*) ppm. **MS** (ESI+)(m/z) 364.2 ($(M+H)^+$, 13), 200.1 (36), 182.0 (100). **HRMS** (MS+) for $C_{18}H_{19}FNO_2S_2$ $(M+H)^+$ calcd 364.0841, found 364.0853.

**3.2.12** 2-(1-Fluoro-2-methylbut-3-enylsulfonyl)benzothiazole (**6l**)



The general procedure was followed with sulfone **10l** (200 mg, 0.56 mmol), KBr (133 mg, 1.12 mmol), $H_2O$ (1.0 mL, 56 mmol) and DMSO (3.8 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6l** as white crystals: 129 mg, 81% (dr 60/40). **IR** (neat) 2982 (w), 2360 (s), 2340 (m), 1467 (m), 1343 (s), 1153 (s) $cm^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.27–8.25 (m, 2H, *major & minor*), 8.05–8.03 (m, 2H, *major & minor*), 7.69–7.60 (m, 4H, *major & minor*), 5.98–5.87 (m, 2H, *major & minor*), 5.65 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HH}$ 4.6 Hz, 1H, *major*), 5.56 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HH}$ 4.6 Hz, 1H, *minor*), 5.33–5.22 (m, 4H, *major & minor*), 3.39–3.22 (m, 2H, *major & minor*), 1.40 (d, $^{3}J_{HH}$ 7.1 Hz, 3H, *minor*), 1.37 (dd, $^{3}J_{HH}$ 7.1 Hz, $^{4}J_{HH}$ 1.5 Hz, 3H, *major*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.5, 152.8, 137.4, *136.0* (d, $^{3}J_{CF}$ 2.9 Hz, *major*), *134.6* (d, $^{3}J_{CF}$ 4.4 Hz, *minor*), *128.3, 127.8, 125.7, 122.3, 118.4 (minor),* 117.9 (*major),* 103.8 (d, $^{1}J_{CF}$ 223.9 Hz, *minor*), 103.4 (d, $^{1}J_{CF}$ 228.3 Hz, *major*), 37.2 (d, $^{2}J_{CF}$ 17.6 Hz, *minor*), 37.0 (d, $^{2}J_{CF}$ 19.0 Hz, *major*), 16.4 (d, $^{3}J_{CF}$ 4.4 Hz, *minor*), 14.2 (d, $^{3}J_{CF}$ 5.9 Hz, *major*) ppm.**$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –180.3 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HF}$ 21.5 Hz, *minor*), –184.4 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HF}$ 21.5 Hz, *major*). **MS** (ESI+)(m/z) 286.1 ($(M+H)^+$, 8), 200.1 (8), 182.0 (100). **HRMS** (MS+) for $C_{12}H_{13}FNO_2S_2$ $(M+H)^+$ calcd 286.0372, found 286.0380

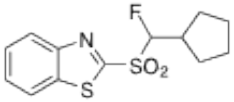
**3.2.13** (*E*)-2-(2-Ethyl-1-fluoro-3-methylhex-3-enylsulfonyl)benzothiazole (**6m**)



The general procedure was followed with sulfone **10m** (241.6 mg, 0.58 mmol), KBr (139 mg, 1.17 mmol), $H_2O$ (1.05 mL, 58 mmol) and DMSO (3.9 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6m** as white crystals: 132 mg, 67% (dr 63/37). **IR** (neat) 2964 (m), 2360 (s), 2339 (m), 1467 (m), 1343 (s), 1155 (m) $cm^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.27–8.25 (m, 2H), 8.04–8.02 (m, 2H), 7.68–7.59 (m, 4H), 5.66 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HH}$ 6.1 Hz, 1H, *major*), 5.64 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HH}$ 7.1 Hz, 1H, *minor*), 5.47 (t, $^{3}J_{HH}$ 7.1 Hz, 1H, *major*), 5.42 (t, $^{3}J_{HH}$ 7.6 Hz, 1H, *minor*), 3.01–2.88 (m, 2H), 2.08–2.00 (m, 4H), 1.96–1.84 (m, 2H), 1.72–1.55 (m, 2H), 1.64 (s, 3H, *major*), 1.62 (s, 3H, *minor*), 0.98 (t, $^{3}J_{HH}$ 7.6 Hz, 3H, *major*), 0.96 (t, $^{3}J_{HH}$ 7.6 Hz, 3H, *minor*), 0.90 (t, $^{3}J_{HH}$ 7.6 Hz, 3H, *major*), 0.88 (t, $^{3}J_{HH}$ 7.6 Hz, 3H, *minor*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.9, 152.8, 137.4, 134.0 (*minor*), 133.8 (*major*), 129.1 (d, $^{3}J_{CF}$ 2.9 Hz, *major*), 128.4 (*minor*), 128.2, 127.7, 125.7, 122.3, 104.0 (d, $^{1}J_{CF}$ 226.9 Hz, *major*), 103.4 (d, $^{1}J_{CF}$ 223.9 Hz, *minor*), 49.0 (d, $^{2}J_{CF}$ 17.6 Hz, *minor*), 48.6 (d, $^{2}J_{CF}$ 17.6 Hz, *major*), 21.6 (d, $^{3}J_{CF}$ 4.4 Hz, *minor*), 21.1 (d, $^{3}J_{CF}$ 2.9 Hz, *major*), 20.0, 13.8, 12.8 (*major*), 12.6 (*minor*), 11.3 (*minor*), 11.2 (*major*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –174.2 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HF}$ 21.5 Hz, *minor*), – 180.7 (dd, $^{2}J_{HF}$

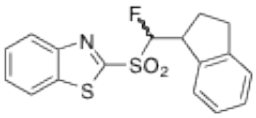
47.3 Hz, $^{3}J_{HF}$ 17.2 Hz, *major*) ppm. **MS** (ESI+)(m/z) 342.2 ((M+H)$^{+}$, 33), 258.2 (68), 200.0 (84), 182.0 (100). **HRMS** (MS+) for $C_{16}H_{21}FNO_2S_2$ (M+H)$^{+}$ calcd 342.0998, found 342.1008.

**3.2.14** 2-(Cyclopentylfluoromethylsulfonyl)benzothiazole (**6n**)



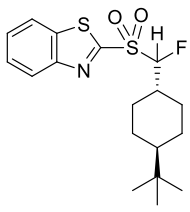
The general procedure was followed with sulfone **10n** (285.8 mg, 0.77 mmol), KBr (183 mg, 0.88 mmol), $H_2O$ (1.38 mL, 77 mmol) and DMSO (5.2 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6n** as white crystals (**mp** 66–68 °C): 219 mg, 95%. **IR** (neat): 2958 (m), 2360 (s), 2340 (m), 1468 (m), 1341 (s), 1151 (s) cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.27–8.24 (m, 1H), 8.04–8.02 (m, 1H), 7.67–7.59 (m, 2H), 5.59 (dd, $^{2}J_{HF}$ 51.6 Hz, $^{3}J_{HH}$ 7.1 Hz, 1H), 2.87–2.72 (m, 1H), 2.12–1.94 (m, 2H), 1.73–1.63 (m, 6H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.3, 152.8, 137.3, 128.2, 127.7, 125.6, 122.3, 104.5 (d, $^{1}J_{CF}$ 222.5 Hz), 37.6 (d, $^{2}J_{CF}$ 17.6 Hz), 28.9 (d, $^{3}J_{CF}$ 4.4 Hz), 27.7 (d, $^{3}J_{CF}$ 4.4 Hz), 25.3, 25.2 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –178.2 (dd, $^{2}J_{HF}$ 51.6 Hz, $^{3}J_{HF}$ 21.5 Hz) ppm. **MS** (ESI+)(m/z) 300.2 ((M+H)$^{+}$, 22), 200.1 (16), 182.0 (100). **HRMS** (MS+) for $C_{13}H_{15}FNO_2S_2$ (M+H)$^{+}$ calcd 300.0528, found 300.0529.

**3.2.15** 2-((2,3-Dihydro-1*H*-inden-1-yl)fluoromethylsulfonyl)benzothiazole (**6o**)



The general procedure was followed with sulfone **10o** (464 mg, 1.11 mmol), KBr (263 mg, 2.22 mmol), $H_2O$ (2.0 mL, 111 mmol) and DMSO (7.5 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 90:10. Yield of **6o** as white crystals: 252 mg, 65% (dr 58/42). **IR** (neat) 2954 (w), 2360 (w), 2336 (w), 1466 (m), 1343 (s), 1316 (m), 1156 (s) cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.30–8.26 (m, 2H, *major & minor*), 8.06–8.04 (m, 2H, *major & minor*), 7.70–7.61 (m, 4H, *major & minor*), 7.40–7.35 (m, 2H, *major & minor*), 7.30–7.15 (m, 6H, *major & minor*), 6.13 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HH}$ 2 Hz, 1H, *major*), 5.62 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HH}$ 9.6 Hz, 1H, *minor*), 4.27 (dt, $^{3}J_{HF}$ 34.4 Hz, $^{3}J_{HH}$ 8.1 Hz, 1H, *major*), 4.13–4.04 (m, 1H, *minor*), 3.16–2.94 (m, 4H, *major & minor*), 2.63–2.40 (m, 4H, *major & minor*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.2, 152.8, 144.7 (*major*), 144.3 (*minor*), *139.7* (minor), 139.5 (*major*), *137.4*, 128.4, 128.2 (*minor*), 128.1 (*major*), 127.8, 126.7 (major), 126.6 (*minor*), 125.8, 125.0 (*major*), 124.8 (*minor*), 123.6, 122.3, 103.4 (d, $^{1}J_{CF}$ 222.5 Hz, *minor*), 102.7 (d, $^{1}J_{CF}$ 228.3 Hz, *major*) 43.3 (d, $^{2}J_{CF}$ 16.1 Hz, *minor*), 43.1 (d, $^{2}J_{CF}$ 20.5 Hz, *major*), 31.9 (*major*), 31.6 (*minor*), 27.6 (d, $^{3}J_{CF}$ 8.8 Hz, *minor*), 25.1 (d, $^{3}J_{CF}$ 4.4 Hz, *major*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –170.8 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HF}$ 12.9 Hz, *minor*), –188.1 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HF}$ 34.4 Hz, *major*) ppm. **MS** (ESI+)(m/z) 348.1 ((M+H)$^{+}$, 11), 264.1 (8), 182.0 (100). **HRMS** (MS+) for $C_{17}H_{15}FNO_2S_2$ (M+H)$^{+}$ calcd 348.0528, found 348.0534.

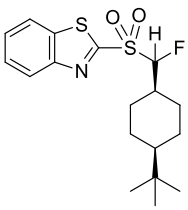
**3.2.16** *Trans*-2-((4-*t*butylcyclohexyl)fluoromethylsulfonyl)benzothiazole (**6p**)



The general procedure was followed with sulfone **10p** (145 mg, 0.33 mmol), KBr (78 mg, 0.66 mmol), $H_2O$ (594 µL, 33 mmol) and DMSO (2.2 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 95:5. Yield of **6p** as white cristals (**mp** 146–148 °C): 100 mg (83%). **IR** (neat) 2948 (br, w), 2862 (w), 2361 (w), 2340 (w), 1467 (w), 1343 (s), 1153 (m) cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.29–8.22 (m, 1H), 8.07–7.99 (m, 1H), 7.70–7.56 (m, 2H), 5.48 (dd, $^{2}J_{HF}$ 47.9 Hz, $^{3}J_{HH}$ 5.4 Hz, 1H), 2.46–2.28 (m, 1H), 2.24–2.07 (m, 2H), 1.96–1.82 (m, 2H), 1.50–1.29 (m, 2H), 1.20–0.96 (m, 3H), 0.86 (s, 9H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.7, 152.8, 137.3, 128.2, 127.7, 125.7, 122.3, 104.6 (d, $^{1}J_{CF}$ 223.9 Hz), 47.2, 37.0 (d, $^{2}J_{CF}$ 19.0 Hz), 32.4, 29.2 (d, $^{3}J_{CF}$ 2.9 Hz), 27.4, 27.0 (d, $^{3}J_{CF}$ 4.4 Hz), 26.5, 26.2 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –182.6 (dd, $^{2}J_{HF}$ 47.9

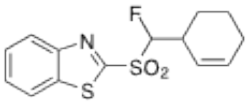
Hz, $^{3}J_{HF}$ 21.5 Hz) ppm. **MS** (ESI+)(m/z) 370.1 ((M+H)$^{+}$, 53), 200.0 (22), 182.0 (100). **HRMS** (MS+) for $C_{18}H_{25}NO_2FS_2$ (M+H)$^{+}$ calcd. 370.1311, found 370.1299.

**3.2.17** *Cis*-2-((4-*t*butylcyclohexyl)fluoromethylsulfonyl)benzothiazole (**6q**)



The general procedure was followed with sulfone **10q** (159 mg, 0.36 mmol), KBr (85 mg, 0.72 mmol), $H_2O$ (648 μL, 36 mmol) and DMSO (2.4 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt: petroleum ether/AcOEt, 95:5. Yield of **6q** as yellow oil: 119 mg (89%), obtained with 4% of unknown impurity.[6] **IR** (neat) 3061 (w), 2962 (w), 2921 (w), 2361 (s), 2326 (m), 1684 (w), 1492 (w) cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.33–8.25 (m, 1H), 8.06–7.99 (m, 1H), 7.71–7.58 (m, 2H), 5.76 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HH}$ 9.8 Hz, 1H), 2.78–2.64 (m, 1H), 2.40–2.29 (m, 1H), 2.17–2.05 (m, 1H), 1.81–1.50 (m, 4H), 1.20–0.96 (m, 3H), 0.86 (s, 9H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.4, 152.9, 137.5, 128.3, 127.8, 125.8, 122.3, 102.6 (d, $^{1}J_{CF}$ 223.9 Hz), 47.7, 32.6, 31.7 (d, $^{2}J_{CF}$ 17.8 Hz), 27.6 (d, $^{3}J_{CF}$ 5.9 Hz), 27.4, 26.7 (d, $^{3}J_{CF}$ 5.9 Hz), 22.5 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –178.3 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HF}$ 8.6 Hz) ppm. **MS** (ESI+)(m/z) 370.3 ((M+H)$^{+}$, 84), 200.1 (52), 182.1 (100). **HRMS** (MS+) for $C_{18}H_{25}NO_2FS_2$ (M+H)$^{+}$ Calcd. 370.1311; Found. 370.1312.

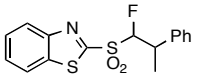
**3.2.18** 2-((Cyclohex-2-enyl)fluoromethylsulfonyl)benzothiazole (**6r**)



The general procedure was followed with sulfone **10r** (222 mg, 0.58 mmol), KBr (138 mg, 1.16 mmol), $H_2O$ (1.05 mL, 58 mmol) and DMSO (3.9 mL). The reaction mixture was stirred for 16 h at 130 °C. Column chromatography: petroleum ether/AcOEt, 95:5. Yield of **6r** as white cristals: 147 mg, 82% (dr 55/45). **IR** (neat) 2933 (br, w), 2360 (m), 2337 (w), 1468 (m), 1341 (s), 1153 (s) cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.30–8.23 (m, 2H, *major and minor*), 8.08–8.00 (m, 2H, *major and minor*), 7.71–7.57 (m, 4H, *major and minor*), 6.04–5.94 (m, 2H, *major and minor*), 5.85–5.74 (m, 2H, *major and minor*), 5.61 (dd, $^{2}J_{HF}$ 44.1 Hz, $^{3}J_{HH}$ 6.4 Hz, 1H, *major or minor*), 5.48 (dd, $^{2}J_{HF}$ 47.5 Hz, $^{3}J_{HH}$ 6.4 Hz, 1H, *major or minor*), 3.32–3.15 (2H, m, *major and minor*), 2.20–1.97 (m, 6H, *major and minor*), 1.91–1.75 (m, 4H, *major and minor*), 1.72–1.57 (m, 2H, *major and minor*) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.4 (*major or minor*), 163.3 (*major or minor*), 152.8 (*major & minor*), 137.4 (*major and minor*), 132.4 (*major or minor*), 132.1 (*major or minor*), 128.3 (*major & minor*), 127.8 (*major and minor*), 125.7 (*major and minor*), 123.2 (d, $^{3}J_{CF}$ 5.9 Hz, *major or minor*), 122.3 (*major and minor*), 122.2 (d, $^{3}J_{CF}$ 5.9 Hz, *major or minor*), 104.0 (d, $^{1}J_{CF}$ 223.9 Hz, *major or minor*), 104.0 (d, $^{1}J_{CF}$ 223.9 Hz, *major or minor*), 34.9 (d, $^{2}J_{CF}$ 19.0 Hz, *major or minor*), 34.7 (d, $^{2}J_{CF}$ 19.0 Hz, *major or minor*), 25.17 (*major &/or minor*), 25.14 (*major &/or minor*), 24.50 (*major &/or minor*), 24.47 (*major &/or minor*), 22.97 (*major &/or minor*), 22.91(*major &/or minor*), 20.6 (*major &/or minor*), 20.2 (*major &/or minor*) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –180.2 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HF}$ 21.5 Hz, *minor*), δ – 181.0 (dd, $^{2}J_{HF}$ 47.3 Hz, $^{3}J_{HF}$ 21.5 Hz, *major*) ppm. **MS** (ESI+)(m/z) 312.0 ((M+H)$^{+}$, 31), 200.0 (18), 182.0 (100). **HRMS** (MS+) for $C_{14}H_{15}NO_2FS_2$ (M+H)$^{+}$ calcd. 312.0528, found 312.0540.

**3.3** Verification of product enantiopurity

**3.3.1** Racemic 2-((1-fluoro-2-phenylpropyl)sulfonyl)benzothiazole (mixture of diastereomers)



6 Calculated by $^{19}$F NMR.

Empower software

RAPPORT HPLC

Reported by User: System Project Name: IC_OBH_ASH2012

**JM6521-78**

# Instrument Method: ASH 1mL90%nhep10%prop_20dC

*Stored: 11/27/2012 2:29:28 PM*

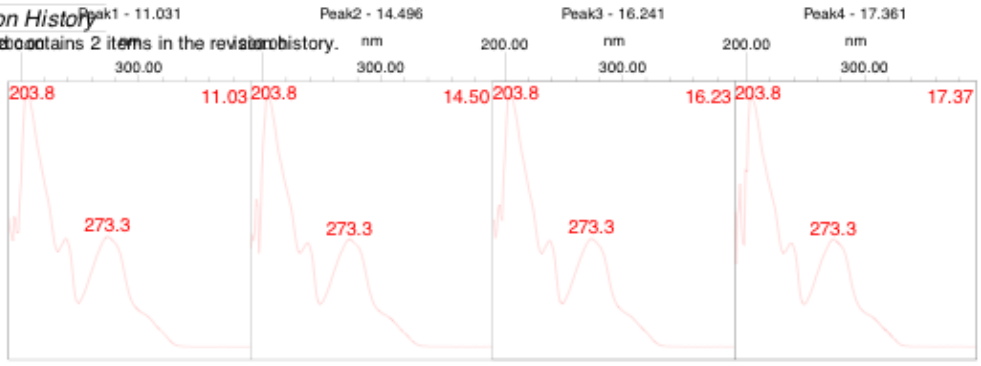
*Method Information*

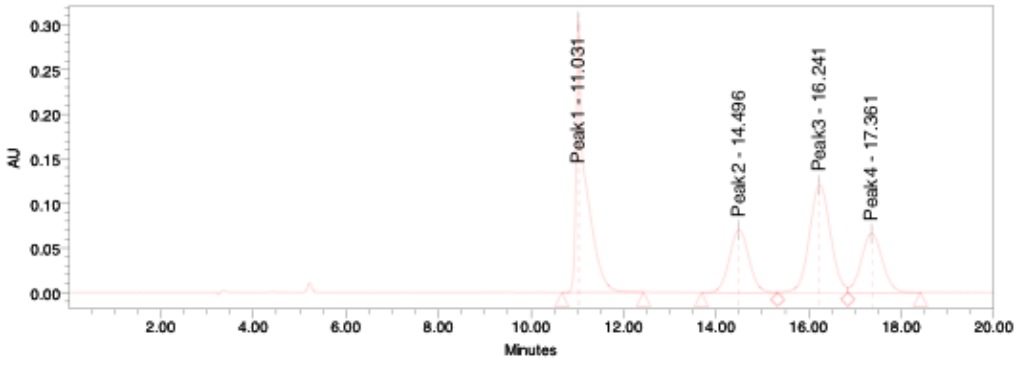
| | |
|---|---|
| Comments | Col. Daicel Chiralpak ASH 4,6mmx250mm 5µm 1mL/mn 90%n-heptane10%propanol-2 éch.+col.à 20°C |
| Modified User | System |
| Locked | No |
| Method Id | 4134 |
| Method Version | 2 |
| Edit User | |

*Revision History*

This method contains 2 items in the revision history.

**Spectrum Index Plot**



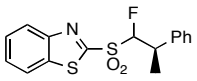

**Peak Results**

| | Name | Retention Time (min) | Area (µV*sec) | % Area |
|---|---|---|---|---|
| 1 | Peak1 | 11.031 | 4307591 | 35.21 |
| 2 | Peak2 | 14.496 | 2063523 | 16.87 |
| 3 | Peak3 | 16.241 | 3784458 | 30.94 |
| 4 | Peak4 | 17.361 | 2077845 | 16.98 |

Processed Channel Descr. PDA 273.0 nm

Report Method: RAPPORT HPLC Printed 4:23:50 PM 11/28/2012 Page: 1 of 1

**3.3.2** Enantiopure 2-((1-fluoro-2-phenylpropyl)sulfonyl)benzothiazole **6i** (mixture of diastereomers)




Empower software

RAPPORT HPLC

Reported by User: System Project Name: IC_OBH_ASH2012

**JM6521-89**

**Instrument Method: ASH 1mL90%nhep10%prop_20dC**

*Stored: 11/27/2012 2:29:28 PM*

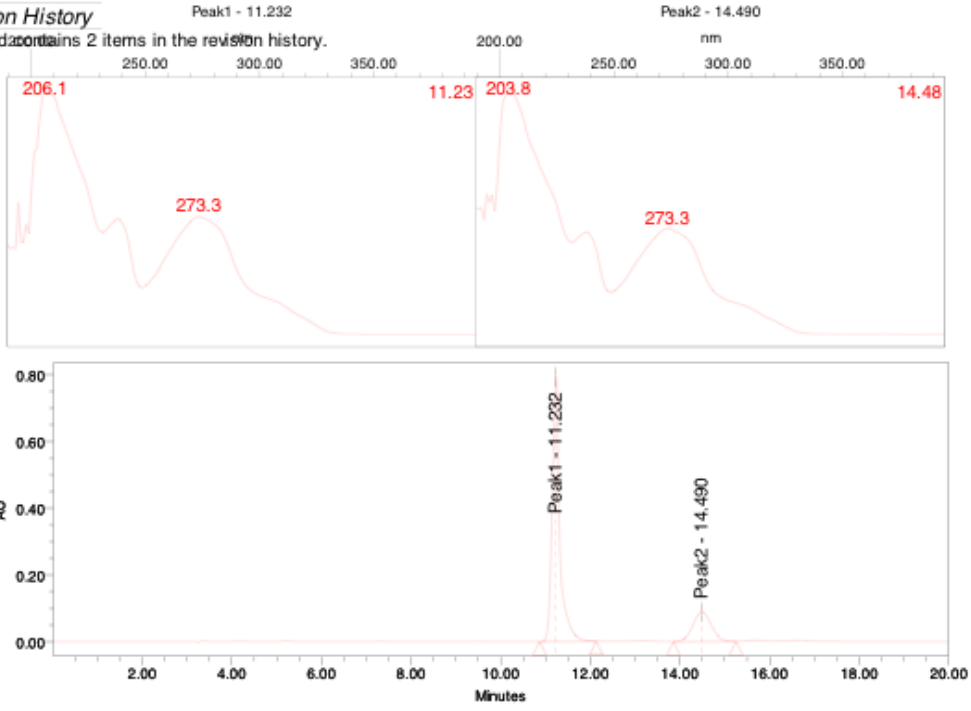
*Method Information*

| | |
|---|---|
| Comments | Col. Daicel Chiralpak ASH 4,6mmx250mm 5µm 1mL/mn 90%n-heptane10%propanol-2 éch.+col.à 20°C |
| Modified User | System |
| Locked | No |
| Method Id | 4134 |
| Method Version | 2 |
| Edit User | |

*Revision History*

This method contains 2 items in the revision history.

**Spectrum Index Plot**



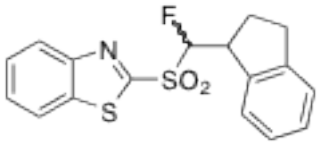

**Peak Results**

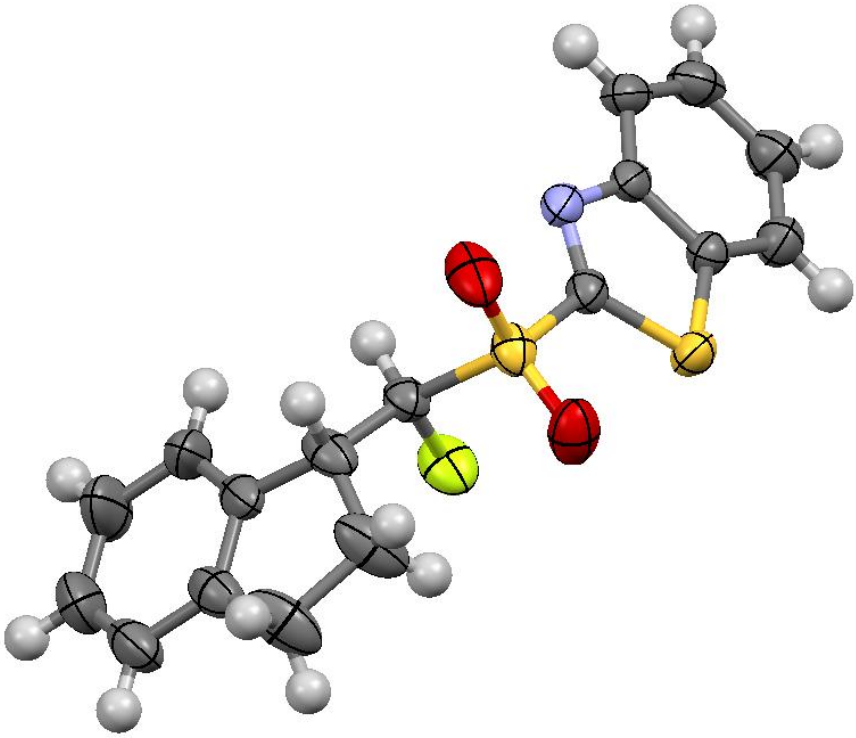
| | Name | Retention Time (min) | Area (µV*sec) | % Area |
|---|---|---|---|---|
| 1 | Peak1 | 11.232 | 9404545 | 78.77 |
| 2 | Peak2 | 14.490 | 2534077 | 21.23 |

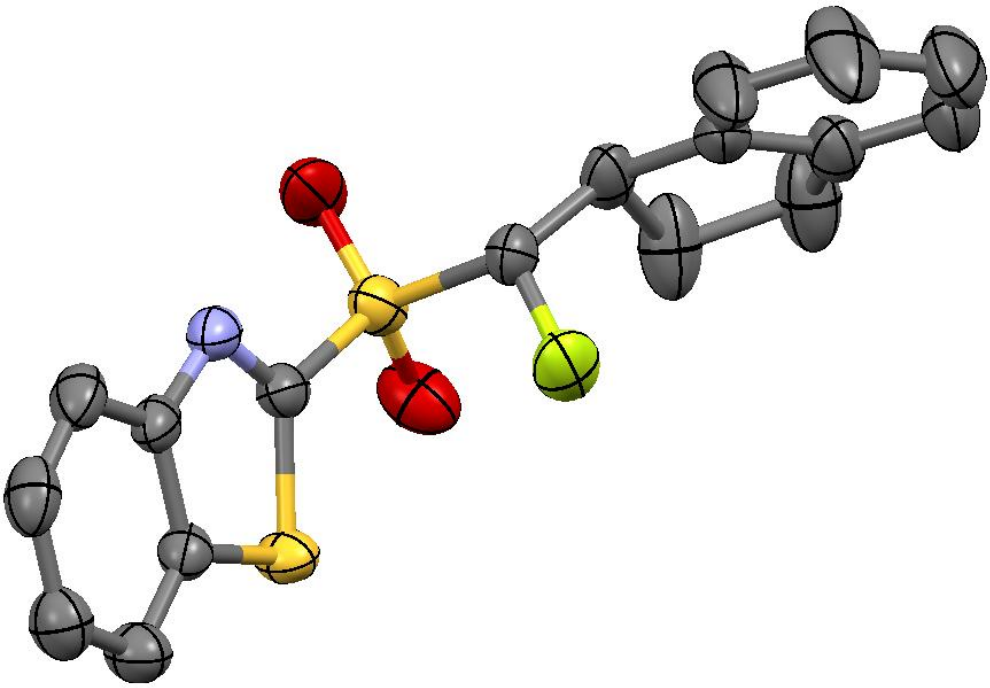
Processed Channel Descr. PDA 273.0 nm

Report Method: RAPPORT HPLC Printed 4:24:00 PM 11/28/2012 Page: 1 of 1

**3.4** X-Ray Structure of **6o**





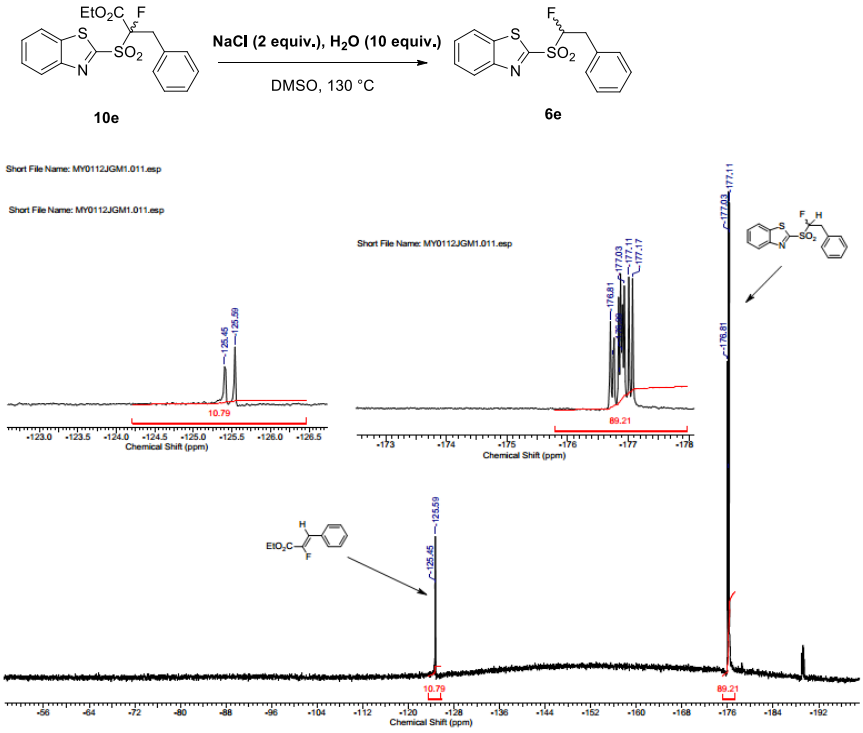
The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 928012

## **3.5** Optimisation of the reaction

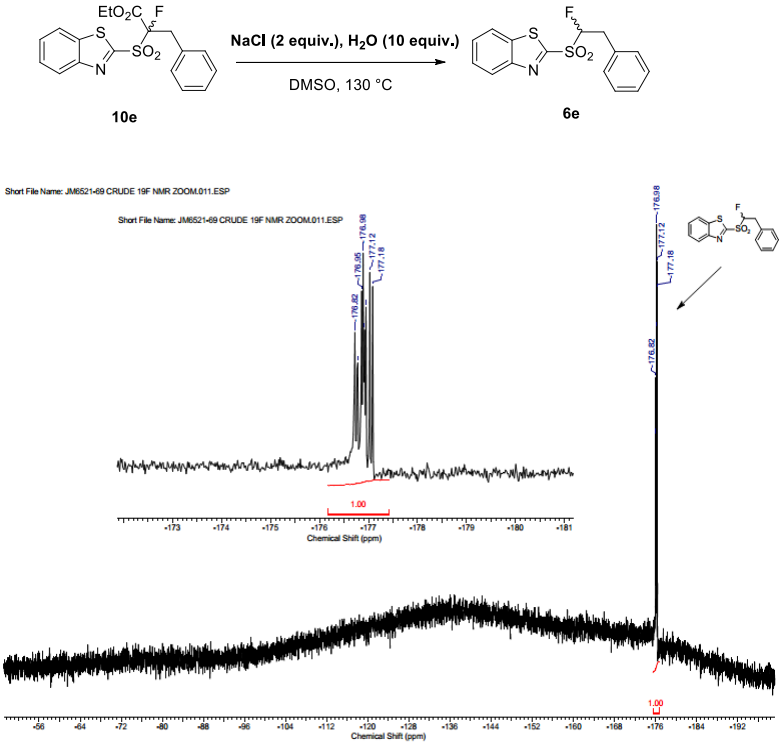
### **3.5.1** Changing NaCl for KBr:

3.5.1.1 For decarboxylation of **10e**

a) Conditions **a (10e)**:

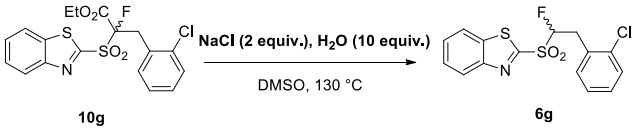



b) Conditions **b (10e):**

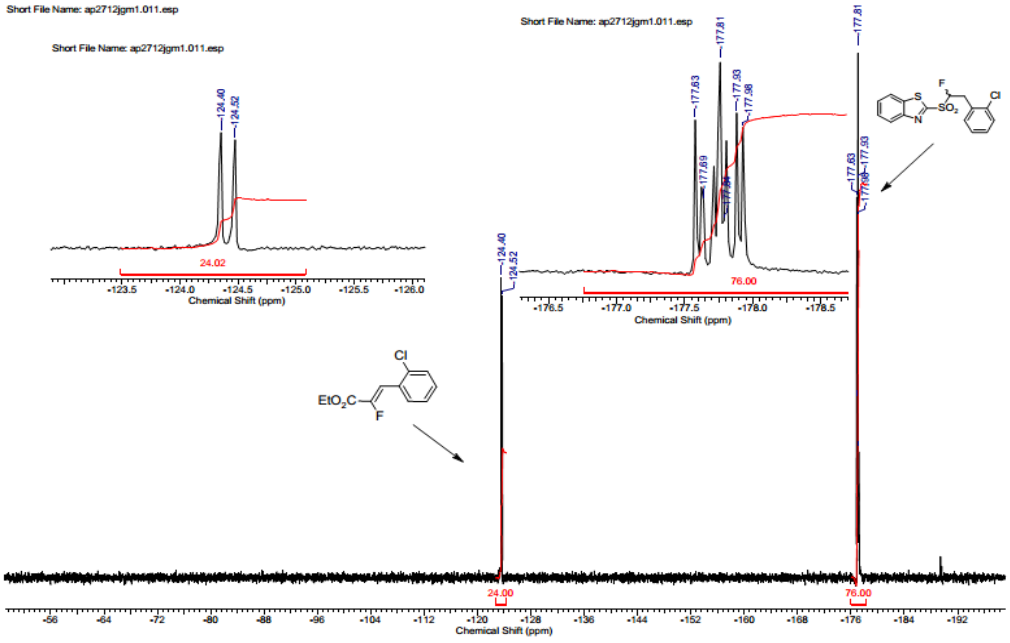


3.5.1.2 For decarboxylation of **10g**

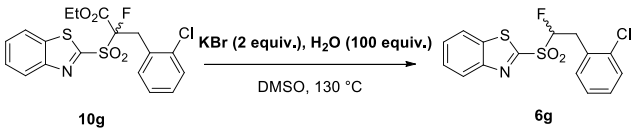
a) Conditions **a (10g)**:



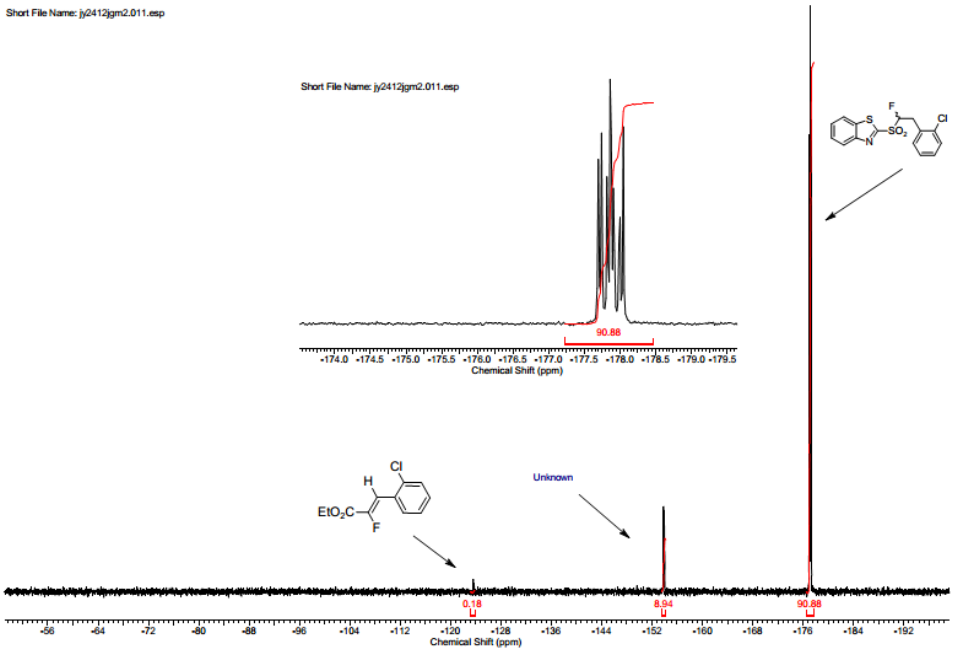

**10g** **6g**




b) Conditions **b (10g):**

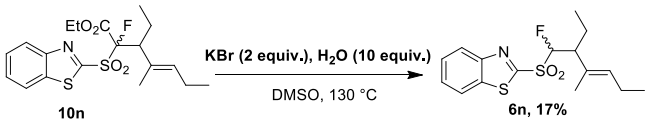


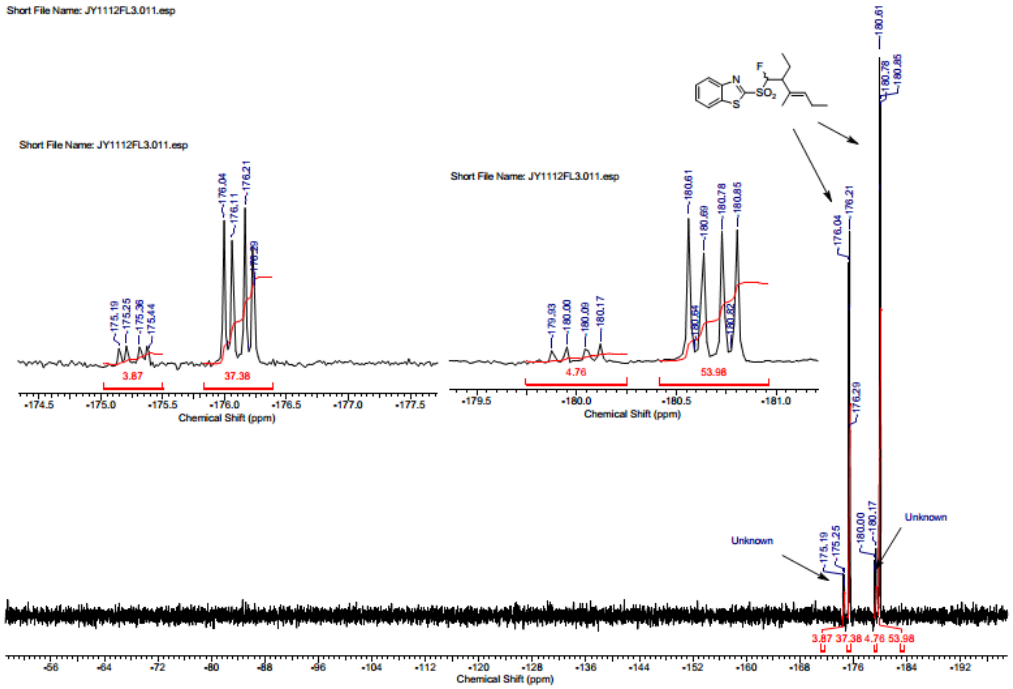

**10g** **6g**



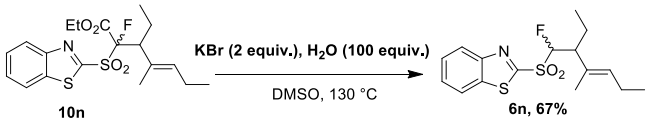
**3.5.2** Effect of the amount of water: Compound **6n** $^{19}F$ NMR (After flash chromatography petroleum ether/EtOAc (90/10))

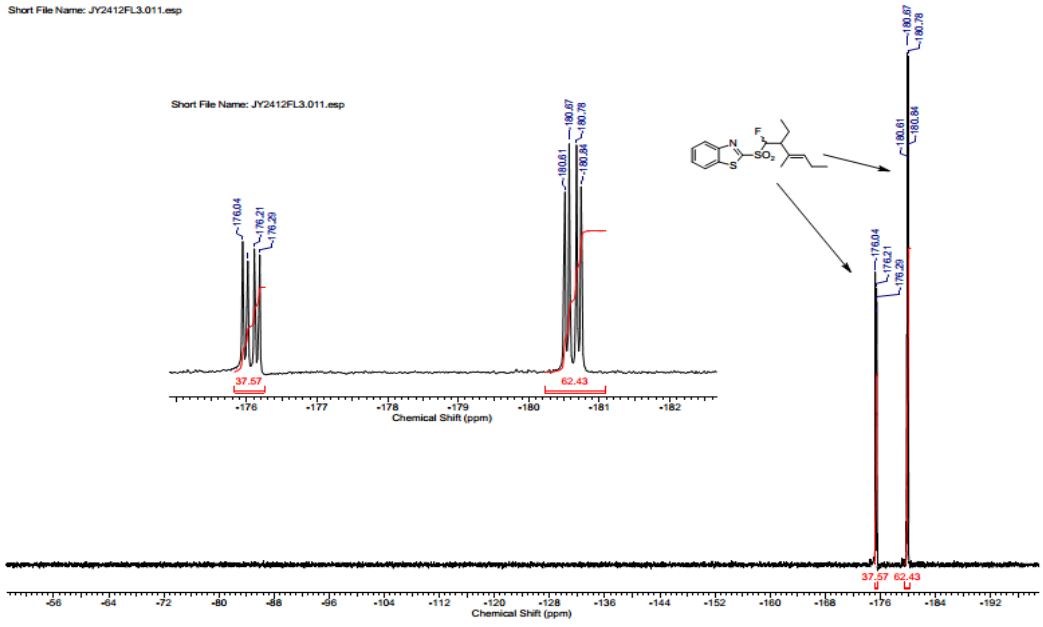
a) Conditions **a** (**10n**):



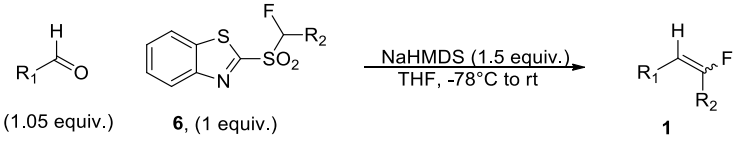

b) Conditions **b** (**10n**)



**4.** Fluoroalkene formation (Table 2)

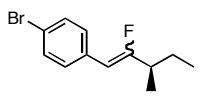
**4.1.** General Procedure




NaHMDS (1.5 equiv, 1M or 2M in THF) was added dropwise to a solution of sulfone **6** (1 equiv) and benzaldehyde (or 4-bromobenzaldehyde) (1.05 equiv) in THF (0.05M) at –78 °C under argon. The mixture was stirred for 30 min at –78 °C, then 3h at room temperature, then was quenched with a saturated solution of $NH_4Cl$ and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by chromatography (silica, pentane/AcOEt 98:2) to afford the corresponding fluoroalkenes.

**4.2.** Characterisation of the compounds

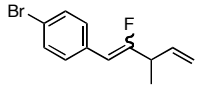
**4.2.1** (*R*)-1-(4-Bromophenyl)-2-fluoro-3-methylpent-1-ene (**1a**)




The general procedure was followed with sulfone **6h** (178.6 mg, 0.62 mmol), 4-bromobenzaldehyde (121 mg, 0.65 mmol), NaHMDS (2M in THF, 465 µL, 0.93 mmol) and THF (13.2 mL). Yield of **1a** as colorless oil: 100 mg (*Z*/*E*: 29/71), 63%.

**IR** (neat) 2965 (m), 2361 (s), 1339 (m), 1679 (m), 1486 (m), 1459 (m) $cm^{-1}$.
(*Z*)-Isomer : **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.73 (m, 2H), 7.37–7.34 (m, 2H), 5.43 (d, $^3J_{HF\,trans}$ 39.4 Hz, 1H), 2.47–2.24 (m, 1H), 1.69–1.38 (m, 2H), 1.19 (d, $^3J_{HH}$ 7.1 Hz, 3H), 0.90 (t, $^3J_{HH}$ 7.6 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.0 (d, $^1J_{CF}$ 270.1 Hz), 132.9, 131.4, 129.9, 129.8, 120.2, 103.9 (d, $^2J_{CF}$ 8.8 Hz), 39.3 (d, $^2J_{CF}$ 24.9 Hz), 26.6, 17.4, 11.6 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –107.7 (dd, $^3J_{HF\,trans}$ 39.4 Hz, $^3J_{HF\,all}$ 25.8 Hz) ppm.
(*E*)-Isomer : **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.73 (m, 2H), 7.07 (d, 2H, $^3J_{HH}$ 8.1 Hz), 6.12 (d, $^3J_{HF\,cis}$ 21.7 Hz, 1H), 2.68 (dsxt, $^3J_{HF\,all}$ 33.9 Hz, $^3J_{HH}$ 7.1 Hz, 1H), 1.69–1.38 (m, 2H), 1.18 (d, $^3J_{HH}$ 7.1 Hz, 3H), 0.90 (t, $^3J_{HH}$ 7.1 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.7 (d, $^1J_{CF}$ 259.1 Hz), 133.3 (d, $^3J_{CF}$ 14.6 Hz), 131.5, 130.2, 120.4, 106.7 (d, $^2J_{CF}$ 30.7 Hz), 34.8 (d, $^2J_{CF}$ 26.4 Hz), 26.4, 17.5, 11.9 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –113.0 (dd, $^3J_{HF\,all}$ 33.9 Hz, $^3J_{HF\,cis}$ 21.7 Hz) ppm. **MS** (EI)(m/z) 256.1 and 258.1 ($(M)^{+\bullet}$, 16, 1:1 ratio), **HRMS** (EI) for $C_{12}H_{14}F^{79}Br$ $M)^{\bullet+}$ calcd 256.02629, found 256.02652.

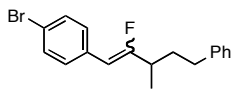
**4.2.2** (*Rac*)-1-(4-bromophenyl)-2-fluoro-3-methylpenta-1,4-diene (**1b**)




The general procedure was followed with sulfone **6l** (1.55 mg, 0.54 mmol), 4-bromobenzaldehyde (106 mg, 0.57 mmol), NaHMDS (2M in THF, 405 µL, 0.81 mmol) and THF (11.7 mL). Yield of **1b** as colorless oil: 93.3 mg (*Z*/*E*: 25/75), 68%.
**IR** (neat) 2977 (m), 2360 (s), 2339 (m), 1680 (m), 1487 (s), 1399 (m), 1152 (s) $cm^{-1}$.
(*Z*)-Isomer : **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.10–7.08 (d, $^3J_{HH}$ 8.1 Hz, 2H), 5.48 (d, $^3J_{HF\,trans}$ 39.4 Hz, 1H), 5.97–5.86 (m, 1H), 5.23–5.14 (m, 2H), 3.20–2.99 (m, 1H), 1.31 (d, $^3J_{HH}$ 7.1 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.4 (d, $^1J_{CF}$ 270.8 Hz), 138.1, 132.6, 131.6 (2C), 130.0, 129.9, 120.5, 115.8, 104.1 (d, $^2J_{CF}$ 8.8 Hz), 41.3 (d, $^2J_{CF}$ 24.9 Hz), 17.0 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –105.4 (dd, $^3J_{HF\,trans}$ 39.4 Hz, $^3J_{HF\,all}$ 12.9 Hz) ppm.
(*E*)-Isomer : **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.36–7.34 (m, 1H), 7.10–7.08 (d, $^3J_{HH}$ 8.1 Hz, 1H), 6.14 (d, $^3J_{HF\,cis}$ 21.2 Hz, 1H), 5.97–5.86 (m, 1H), 5.23–5.14 (m, 2H), 3.47 (ddq, $^3J_{HF}$ 34.4 Hz, $^3J_{HH}$ 7.1 Hz, $^3J_{HH}$ 7.1 Hz, 1H), 1.27 (d, $^3J_{HH}$ 7.1 Hz, 3H). ppm **$^{13}$C**

**NMR** (100 MHz, $CDCl_3$) δ 163.2 (d, $^1J_{CF}$ 259.1 Hz), 138.0, 133.0 (d, $^3J_{CF}$ 14.6 Hz), 131.6 (2C), 131.5, 130.1 (d, $^4J_{CF}$ 2.9 Hz), 120.7, 115.4, 106.9 (d, $^2J_{CF}$ 29.3 Hz), 37.2 (d, $^2J_{CF}$ 26.4 Hz), 17.0 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –110.6 (dd, $^3J_{HFcis}$ 21.2 Hz, $^3J_{HFall}$ 34.4 Hz) ppm. **MS** (EI)(m/z) 254.1, 256.1 (((M)$^{+\bullet}$, 12, 1:1 ratio).. **HRMS** (EI) for $C_{12}H_{12}F^{79}Br$ (M)$^{\bullet+}$calcd 254.01064, found 254.01006.

**4.2.3** (*Rac*)-1-(4-bromo-4-(2-fluoro-3-methyl-5-phenylpent-1-enyl)benzene (**1c**)




The general procedure was followed with sulfone **6k** (121 mg, 0.33 mmol), 4-bromobenzaldehyde (65 mg, 0.35 mmol), NaHMDS (2M in THF, 248 µL, 0.50 mmol) and THF (7 mL). Yield of **1c** as colorless oil: 72 mg (*Z*/*E*: 31/69), 66%.

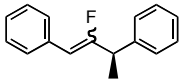
**IR** (neat) 2969 (m), 2932 (m), 2360 (m), 2340 (m), 1678 (s), 1486 (m), 1453 (m), 1150 (m) $cm^{-1}$.

(*Z*)-Isomer : **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.44 (m, 2H), 7.38–7.36 (m, 2H), 7.33–7.29 (m, 2H), 7.25–7.18 (m, 3H), 5.45 (d, $^3J_{HFtrans}$ 39.4 Hz, 1H), 2.49–2.38 (m, 1H), 2.72–2.50 (m, 2H), 2.03–1.91 (m, 1H), 1.81–1.68 (m, 1H), 1.24 (d, $^3J_{HH}$ 6.1 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 164.5 (d, $^1J_{CF}$ 270.8 Hz), 141.8, 132.7, 131.5, 129.9, 128.4, 128.3, 125.9, 120.3, 104.3 (d, $^3J_{CF}$ 8.7 Hz), 37.3 (d, $^2J_{CF}$ 24.9 Hz), 35.3, 33.4, 17.9 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ – 108.8 (dd, $^3J_{HFtrans}$ 39.4 Hz, $^3J_{HFall}$ 25.8 Hz) ppm.

(*E*)-Isomer : **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.25–7.18 (m, 3H), 7.10–7.04 (m, 2H), 6.97 (d, $^3J_{HH}$ 8.1 Hz, 2H), 6.15 (d, $^3J_{HFcis}$ 21.7 Hz, 1H), 2.80 (dsxt, $^3J_{HFall}$ 33.9 Hz, $^3J_{HH}$ 6.6 Hz, 1H), 2.72–2.50 (m, 2H), 2.03–1.91 (m, 1H), 1.81–1.68 (m, 1H), 1.24 (d, $^3J_{HH}$ 6.1 Hz, 1H), 1.23 (d, $^3J_{HH}$ 6.6 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.4 (d, $^1J_{CF}$ 257.6 Hz), 141.6, 133.1 (d, $^3J_{CF}$ 14.6 Hz), 131.5, 130.1, 128.4, 128.3, 125.8, 120.5, 107.0 (d, $^2J_{CF}$ 29.3 Hz), 32.3 (d, $^2J_{CF}$ 26.4 Hz), 35.1, 33.4, 17.8 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –112.9 (dd, $^3J_{HFcis}$ 21.7 Hz, $^3J_{HFall}$ 33.9 Hz) ppm.

**MS** (EI)(m/z) 332.2, 334.2 ((M)$^{+\bullet}$, 28, 1:1 ratio). **HRMS** (EI) for $C_{18}H_{18}F^{79}Br$ (M)$^{\bullet+}$calcd 332.05759, found 332.05738.

**4.2.4** (3*R*)-1,3-Diphenyl-2-fluorobut-1-ene (**1d**)



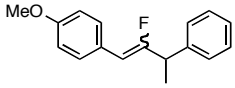

The general procedure was followed with sulfone **6i** (277 mg, 0.82 mmol), benzaldehyde (88 µL, 0.87 mmol), NaHMDS (2M in THF, 615 µL, 1.23 mmol) and THF (19 mL). Yield of **1d** as colorless oil: 133 mg (*Z*/*E*: 36/64), 72%.

**IR** (neat) 3023 (w), 2974 (w), 2360 (s), 2339 (s), 1679 (s), 1493 (m), 1448 (m) $cm^{-1}$.

(*Z*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51–7.47 (d, $^3J_{HH}$ 8.1 Hz, 2H), 7.34–7.20 (m, 8H), 5.59 (d, $^3J_{HFtrans}$ 38.7 Hz, 1H), 3.75 (dq, $^3J_{HFall}$ 17.2 Hz, $^3J_{HH}$ 8.1 Hz, 1H), 1.55–1.24 (m, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.1 (d, $^1J_{CF}$ 269.3 Hz), 142.0, 133.6, 128.6, 128.5, 128.4, 128.3, 127.5, 127.2, 126.9, 105.6 (d, $^2J_{CF}$ 8.8 Hz), 43.3 (d, $^2J_{CF}$ 26.4 Hz), 18.8 (d, $^3J_{CF}$ 4.4 Hz) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –103.7 (dd, $^3J_{HFtrans}$ 38.7 Hz, $^3J_{HFall}$ 17.2 Hz) ppm.

(*E*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.20 (m, 10H), 6.27 (d, $^3J_{HFcis}$ 21.5 Hz, 1H), 4.13 (dq, $^3J_{HFall}$ 30.1 Hz, $^3J_{HH}$ 7.1 Hz, 1H), 1.53 (d, $^3J_{HH}$ 7.1 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.5 (d, $^1J_{CF}$ 257.6 Hz), 142.1 (d, $^3J_{CF}$ 2.9 Hz), 134.0 (d, $^3J_{CF}$ 13.2 Hz), 128.6, 128.5, 127.2, 126.9, 126.7, 108.0 (d, $^2J_{CF}$ 27.8 Hz), 38.6 (d, $^2J_{CF}$ 24.9 Hz), 18.4 (d, $^3J_{CF}$ 4.4 Hz) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –114.6 (dd, $^3J_{HFcis}$ 21.5 Hz, $^3J_{HFall}$ 30.1 Hz) ppm. **MS** (EI)(m/z) 226.1 ((M)$^{+\bullet}$, 61). **HRMS** (EI) for $C_{16}H_{15}F$ (M)$^{\bullet+}$calcd 226.11578, found 226.11583.

**4.2.5** (*Rac*)-2-fluoro-1-(4-methoxyphenyl)-3-phenylbut-1-ene (**1e)**

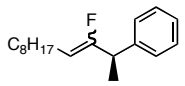


The general procedure was followed with sulfone **(*rac*)-6i** (127 mg, 0.38 mmol), *p*-Anisaldehyde (49 µL, 0.40 mmol), NaHMDS (1M in THF, 570 µL, 0.57 mmol) and THF (11.6 mL). Yield of **1e** as colorless oil: 78.7 mg (*Z*/*E*: 49/51), 57%.

(*Z*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.34 (m, 1H), 7.30–7.26 (m, 4H), 7.21–7.13 (m, 1H), 7.06–7.04 (m, 1H), 6.80–6.76 (m, 2H), 5.46 (d, $^3J_{HF\,trans}$ 39.3 Hz, 1H), 3.71 (s, 3H), 3.66 (dq, $^3J_{HF\,all}$ 15.1 Hz, $^3J_{HH}$ 7.3 Hz, 1H), 1.45 (d, $^3J_{HH}$ 7.3 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, $^1J_{CF}$ 256.0 Hz), 158.5, 142.2, 129.7, 129.6, 128.5 (2C), 127.4 (2C), 127.2 (2C), 126.8, 126.2 (d, $^3J_{CF}$ 6.7 Hz), 113.8, 105.0 (d, $^2J_{CF}$ 9.2 Hz), 55.2, 43.2 (d, $^2J_{CF}$ 27.0 Hz), 18.9 (d, $^3J_{CF}$ 3.9 Hz) ppm. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –106.4 (dd, $^3J_{HF\,trans}$ 39.3 Hz, $^3J_{HF\,all}$ 15.1 Hz) ppm.

(*E*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.34 (m, 1H), 7.30–7.26 (m, 4H), 7.21–7.13 (m, 1H), 7.06–7.04 (m, 1H), 6.80–6.76 (m, 2H), 6.14 (d, $^3J_{HF\,cis}$ 21.0 Hz, 1H), 4.03 (dq, $^3J_{HF\,all}$ 32.9 Hz, $^3J_{HH}$ 7.3 Hz, 1H), 3.72 (s, 3H), 1.45 (d, $^3J_{HH}$ 7.2 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 161.7 (d, $^1J_{CF}$ 266.6 Hz), 158.4 (d, $^3J_{CF}$ 2.6 Hz), 142.2, 129.7 (2C), 128.6 (2C), 127.4 (2C), 127.2 (2C), 126.6, 126.3 (d, $^3J_{CF}$ 4.4 Hz), 113.9, 107.5 (d, $^2J_{CF}$ 28.1 Hz), 55.2, 38. 6 (d, $^3J_{CF}$ 27.0 Hz), 18.4 (d, $^3J_{CF}$ 3.0 Hz) ppm. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ – 111.4 (dd, $^3J_{HF\,cis}$ 21.0 Hz, $^3J_{HF\,all}$ 32.9 Hz) ppm. **MS** 256.2 ($(M)^{+\bullet}$, 100)**.**

**4.2.6** (2*R*)-3-Fluoro-2-phenyl-dodec-3-ene (**1f)**

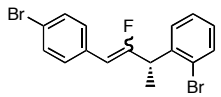


The general procedure was followed with sulfone **6i** (127 mg, 0.40 mmol), nonanal (68 µL, 0.40 mmol), NaHMDS (1M in THF, 570 µL, 0.57 mmol) and THF (8.2 mL). Yield of **1f** as colorless oil: 57.8 mg (*Z*/*E*: 83/17), 58%.

(*Z*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.17 (m, 5H), 4.59 (dt, $^3J_{HF\,cis}$ 38.0 Hz, $^3J_{HH}$ 7.6 Hz, 1H), 3.52 (dq, $^3J_{HF\,all}$ 14.4 Hz, $^3J_{HH}$ 7.2 Hz, 1H), 2.07–1.95 (m, 2H), 1.37 (d, $^3J_{HH}$ 7.2 Hz, 3H), 1.33–1.24 (m, 12H), 0.85 (t, $^3J_{HH}$ 6.8 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 161.7 (d, $^1J_{CF}$ 254 Hz), 142.7, 128.4 (2C), 127.3 (2C), 126.6, 105.2 (d, $^2J_{CF}$ 15.8 Hz), 42.4 (d, $^2J_{CF}$ 26.6 Hz), 31.9, 29.5 (d, $^4J_{CF}$ 1.1 Hz), 29.4, 29.3, 29.2, 23.5 (d, $^3J_{CF}$ 5.4 Hz), 22.7, 19.0 (d, $^3J_{CF}$ 4 Hz), 14.1 ppm. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –112.0 (dd, $^3J_{HF\,trans}$ 38.0 Hz, $^3J_{HF\,all}$ 14.4 Hz) ppm.

(*E*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.17 (m, 5H), 4.99 (dt, $^3J_{HF\,cis}$ 22.8 Hz, $^3J_{HH}$ 8.3 Hz, 1H), 3.89 (dq, $^3J_{HF\,all}$ 31.7 Hz, $^3J_{HH}$ 7.5 Hz, 1H), 2.07–1.95 (m, 2H), 1.45 (d, $^3J_{HH}$ 7.5 Hz, 3H), 1.33–1.24 (m, 12H), 0.85 (t, $^3J_{HH}$ 6.8 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 161.3 (d, $^1J_{CF}$ 251.6 Hz), 142.4 (d, $^3J_{CF}$ 2.5 Hz), 128.4 (2C), 127.3 (2C), 126.5, 105.5 (d, $^2J_{CF}$ 21.4 Hz), 37.8 (d, $^2J_{CF}$ 24.7 Hz), 31.9, 30.0 (d, $^4J_{CF}$ 2 Hz), 29.4, 29.3, 29.2, 29.1, 25.3 (d, $^3J_{CF}$ 8.9 Hz), 22.7, 17.8, 14.1 ppm **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –115.7 (dd, $^3J_{HF\,cis}$ 22.4 Hz, $^3J_{HFall}$ 31.6 Hz) ppm. **MS** (EI)(m/z) 262.3 ($(M)^{+\bullet}$, 14). **HRMS** (EI) for $C_{18}H_{27}F$ $(M)^{\bullet+}$calcd 262.20968, found 262.21043.

**4.2.7** (3*R*)-2-Fluoro-1-(4-bromophenyl)-3-(2-bromophenyl)but-1-ene (**1g**)



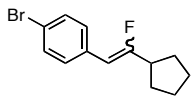
The general procedure was followed with sulfone **6j** (120 mg, 0.28 mmol), 4-Bromobenzaldehyde (56 mg, 0.30 mmol), NaHMDS (2M in THF, 210 µL, 0.42 mmol) and THF (8 mL). Column chromatography: Petroleum Ether 100%. Yield of **1g** as colorless oil: 52 mg (*Z*/*E*: 24/76), 49%.

(Z) Isomer: **IR** (neat) 3061 (w), 2961 (w), 2921 (w), 2361 (s), 2326 (m), 1684 (w), 1492 (w), 1148 (w) $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63–7.56 (m, 1H), 7.51–7.23 (m, 6H), 7.19–7.10 (m, 1H), 5.59 (d, $^3J_{HF\,trans}$ 38.5 Hz, 1H), 4.29 (dq, $^3J_{HF\,all}$ 14.0 Hz, $^3J_{HH}$ 6.9 Hz, 1H), 1.51

(d, $^3J_{HH}$ 7.1 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.4 (d, $^2J_{CF}$ 272.2), 140.8, 133.2, 132.3, 131.6, 130.1 (d, $^4J_{CF}$ 8.8 Hz), 128.6, 128.1, 127.9, 124.6, 120.7, 105.6 (d, $^2J_{CF}$ 8.9), 42.2 (d, $^2J_{CF}$ 26.4), 18.1 (d, $^3J_{CF}$ 4.4 Hz) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –102.7 (dd, $^3J_{FHtrans}$ 38.7 Hz, $^3J_{FH\textit{all}}$ 12.9 Hz). MS (EI) (m/z) 382.0, 383.9, and 386 ($(M)^{+\bullet}$, 46, 1:2:1 ratio). **HRMS** (EI) for $C_{16}H_{13}F^{79}Br_2$ $(M)^{\bullet+}$calcd 381.93680, found 381.93767.

(*E*) Isomer: **IR** (neat) 3060 (br, w), 2970 (w), 2926 (br, w), 2362 (s), 2337 (m), 1671 (m), 1484 (m), 1149 (s) cm$^{-1}$. **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.58 (d, $^3J_{HH}$ 8.1 Hz, 1H), 7.57 (d, $^3J_{HH}$ 8.0 Hz, 1H), 7.44 (d, $^3J_{HH}$ 38.9 Hz, 2H), 7.33 (apparent t, $^3J_{HH}$=7.1 Hz, 1H), 7.13 (apparent td, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 0.8 Hz, 1H), 6.99 (d, $^3J_{HH}$ 8.2 Hz, 2H), 6.22 (d, $^3J_{HFcis}$ 21.7 Hz, 1H), 4.47 (dq, $^3J_{HF}$ 30.4 Hz, $^3J_{HH}$ 7.1 Hz, 1H), 1.50 (d, $^3J_{HH}$ 7.1 Hz, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) 162.7 (d, $^2J_{CF}$ 259.1 Hz), 141.5 (d, $^3J_{CF}$ 2.9 Hz), 133.1, 132.6 (d, $^3J_{CF}$ 13.2 Hz), 131.6 (2C), 130.2 (2C), 128.7 (d, $^4J_{CF}$ 2.9 Hz), 128.5, 128.1, 123.4, 120.9, 107.9 (d, $^2J_{CF}$ 27.8 Hz), 38.2 (d, $^2J_{CF}$ 23.4 Hz), 18.1 (d, $^3J_{CF}$ 4.4 Hz) ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ – 105.2 (dd, $^3J_{HF\textit{all}}$ 30.1 Hz, $^3J_{HF\textit{cis}}$ 21.5 Hz) ppm. MS (EI) (m/z) 382.0, 384.0, and 386.0 ($(M)^{+\bullet}$, 45, 1:2:1 ratio). **HRMS** (EI) for $C_{16}H_{13}F^{79}Br_2$ $(M)^{\bullet+}$calcd 381.93680, found 381.93750.

**4.2.8** 2-(4-Bromophenyl)-1-cyclopentyl-1-fluoroethene (**1h**)



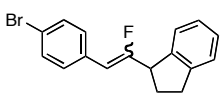
The general procedure was followed with sulfone **6n** (110 mg, 0.37 mmol), 4-Bromobenzaldehyde (72 mg, 0.39 mmol), NaHMDS (2M in THF, 278 µL, 0.56 mmol) and THF (8 mL). Yield of **1h** as colorless oil: 61 mg (*Z*/*E*: 26/74), 87%.

**IR** (neat) 2955 (m), 2360 (w), 1678 (s), 1485 (s), 1168 (m) cm$^{-1}$.

(*Z*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.35–7.33 (m, 2H), 5.46 (d, $^3J_{HF\textit{trans}}$ 38.7 Hz, 1H), 3.12–2.95 (m, 1H), 1.98–1.55 (m, 8H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 164.4 (d, $^1J_{CF}$ 267.9 Hz), 133.0 (d, $^3J_{CF}$ 2.9 Hz), 131.5, 131.4, 129.9, 129.8, 120.1, 103.2 (d, $^2J_{CF}$ 8.9 Hz), 43.1 (d, $^2J_{CF}$ 26.4 Hz), 30.0, 25.5 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –105.5 (dd, $^3J_{HF\textit{trans}}$ 38.7 Hz, $^3J_{HF\textit{all}}$ 21.5 Hz) ppm.

(*E*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.08–7.06 (m, 2H), 6.06 (d, $^3J_{HF\textit{cis}}$ 21.5 Hz, 1H), 2.79–2.66 (m, 1H), 1.98–1.55 (m, 8H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.0 (d, $^1J_{CF}$ 256.1 Hz), 133.5 (d, $^3J_{CF}$ 14.6 Hz), 131.5, 130.2, 120.4, 106.2 (d, $^2J_{CF}$ 30.8 Hz), 38.2 (d, $^2J_{CF}$ 26.4 Hz), 30.2, 26.3 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –97.0 (dd, $^3J_{HF\textit{cis}}$ 21.5 Hz, $^3J_{HF\textit{all}}$ 34.4 Hz) ppm. **MS** (EI)(m/z) 268.1, 270.1 ($(M)^{+\bullet}$, 58, 1:1 ratio). **HRMS** (EI) for $C_{13}H_{14}F^{79}Br$ $(M)^{\bullet+}$calcd 268.02629, found 268.02629.

**4.2.9** 1-(2-(4-bromophenyl)-1-fluorovinyl)-2,3-dihydro-1*H*-indene (**1i**)



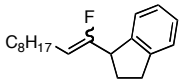
The general procedure was followed with sulfone **6o** (227 mg, 0.65 mmol), 4-bromobenzaldehyde (127 mg, 0.68 mmol), NaHMDS (2M in THF, 500 µL, 1.02 mmol) and THF (14 mL). Yield of **1i** as white crystals: 106 mg (*Z*/*E*: 29/71), 51%.

**IR** (neat) 2946 (m), 2360 (s), 2339 (s), 1677 (s), 1483 (s), 1150 (m), 1133 (m) cm$^{-1}$.

(*Z*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.44 (m, 2H), 7.38–7.21 (m, 6H), 6.38 (d, $^3J_{HF\textit{trans}}$ 38.4 Hz, 1H), 4.06 (dt, $^3J_{HF\textit{all}}$ 22.2 Hz, $^3J_{HH}$ 7.6 Hz, 1H), 3.13–2.91 (m, 2H), 2.47–2.28 (m, 2H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{CF}$ 269.3 Hz), 144.3, 141.7, 132.5, 131.7, 131.5, 130.1, 129.9, 127.5, 126.5, 124.6, 123.6, 120.6, 105.3 (d, $^3J_{CF}$ 8.8 Hz), 49.0 (d, $^2J_{CF}$ 26.4 Hz), 31.4, 30.1 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –106.2 (dd, $^3J_{HF\textit{trans}}$ 38.4 Hz, $^3J_{HF\textit{all}}$ 22.2 Hz) ppm.

(*E*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.44 (m, 2H), 7.38–7.21 (m, 6H), 6.38 (d, $^3J_{HFcis}$ 20.2 Hz, 1H), 4.43 (dt, $^3J_{HFall}$ 32.8 Hz, $^3J_{HH}$ 8.6 Hz, 1H), 3.13–2.91 (m, 2H), 2.47–2.28 (m, 2H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{CF}$ 256.1 Hz), 144.4, 141.7, 133.0 (d, $^3J_{CF}$ 13.2 Hz), 131.7, 131.5, 130.1, 130.0, 127.4, 126.5, 124.8, 123.6, 120.9, 108.7 (d, $^2J_{CF}$ 29.3 Hz), 44.6 (d, $^2J_{CF}$ 27.8 Hz), 31.7, 29.6 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –109.9 (dd, $^3J_{HFcis}$ 20.2 Hz, $^3J_{HFall}$ 32.8 Hz) ppm. **MS** (EI)(m/z) 316.2, 318.2 ($(M)^{+\bullet}$, 97, 1:1 ratio). **HRMS** (EI) for $C_{17}H_{14}F^{79}Br$ $(M)^{\bullet+}$calcd 316.02629, found 268.02693.

**4.2.10** 1-(2-(4-bromophenyl)-1-fluorodec-1-enyl)-2,3-dihydro-1*H*-indene (**1j**)



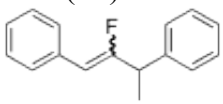

The general procedure was followed with sulfone **6o** (146 mg, 0.42 mmol), nonanal (76 µL, 0.44 mmol), NaHMDS (1M in THF, 630 µL, 0.63 mmol) and THF (9 mL). Yield of **1j** as colorless oil: 58.2 mg (*Z*/*E*: 62/38), 51%.

(*Z*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.19 (m, 4H), 4.61 (dt, $^3J_{HFcis}$ 37.4 Hz, $^3J_{HH}$ 7.4 Hz, 1H), 3.88 (dt, $^3J_{HFall}$ 21.2, $^3J_{HH}$ 7.6 Hz, 1H), 3.08–2.84 (m, 2H), 2.35–2.16 (m, 2H), 2.13–2.06 (m, 2H), 1.46–1.29 (m, 12H), 0.92–0.89 (m, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 160.0 (d, $^1J_{CF}$ 255.8 Hz), 144.2, 142.6 (d, $^3J_{CF}$ 2.2 Hz), 127.1, 126.3, 124.5, 124.4, 106.0 (d, $^2J_{CF}$ 16.0 Hz) 48.1 (d, $^2J_{CF}$ 28.8 Hz), 31.9, 31.3, 29.5 (d, $^3J_{CF}$ 1.2 Hz), 29.4 (2C), 29.3, 29.2, 23.5 (d, $^3J_{CF}$ 4.5 Hz), 22.7, 14.1 ppm. **$^9$F NMR** (376 MHz, $CDCl_3$) δ –116.7 (dd, $^3J_{HFcis}$ 37.4 Hz, $^3J_{HFall}$ 21.2 Hz) ppm.

(*E*)-Isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.19 (m, 4H), 5.22 (dt, $^3J_{HFcis}$ 21.9 Hz, $^3J_{HH}$ 8.3 Hz, 1H), 4.24 (dt, $^3J_{HFall}$ 32.5 Hz, $^3J_{HH}$ 8.6 Hz, 1H), 3.08–2.84 (m, 2H), 2.35–2.16 (m, 2H), 2.13–2.06 (m, 2H), 1.46–1.29 (m, 12H), 0.92–0.89 (m, 3H) ppm. **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 159.6 (d, $^1J_{CF}$ 247.9 Hz), 144.2, 142.4**,** 127.0, 126.3, 124.6, 123.7, 107.1 (d, $^2J_{CF}$ 21.4 Hz), 43.8 (d, $^2J_{CF}$ 28.6 Hz) 31.9 31.8, 30.4 (d, $^3J_{CF}$ 2.0 Hz), 30.0, 29.4, 29.3, 29.1, 25.3 (d, $^3J_{CF}$ 9.0 Hz), 22.7, 14.1 ppm. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –116.6 (dd, $^3J_{HFcis}$ 21.9 Hz, $^3J_{HFall}$ 32.5 Hz) ppm. **MS** (EI)(m/z) 274.3 ($(M)^{+\bullet}$, 30). **HRMS** (EI) for $C_{19}H_{27}F$ $(M)^{\bullet+}$calcd 274.20968, found 274.20988.

## **4.3**. Verification of product enantiopurity

### **4.3.1** (rac)-1,3-Diphenyl-2-fluorobut-1-ene (**1d**)



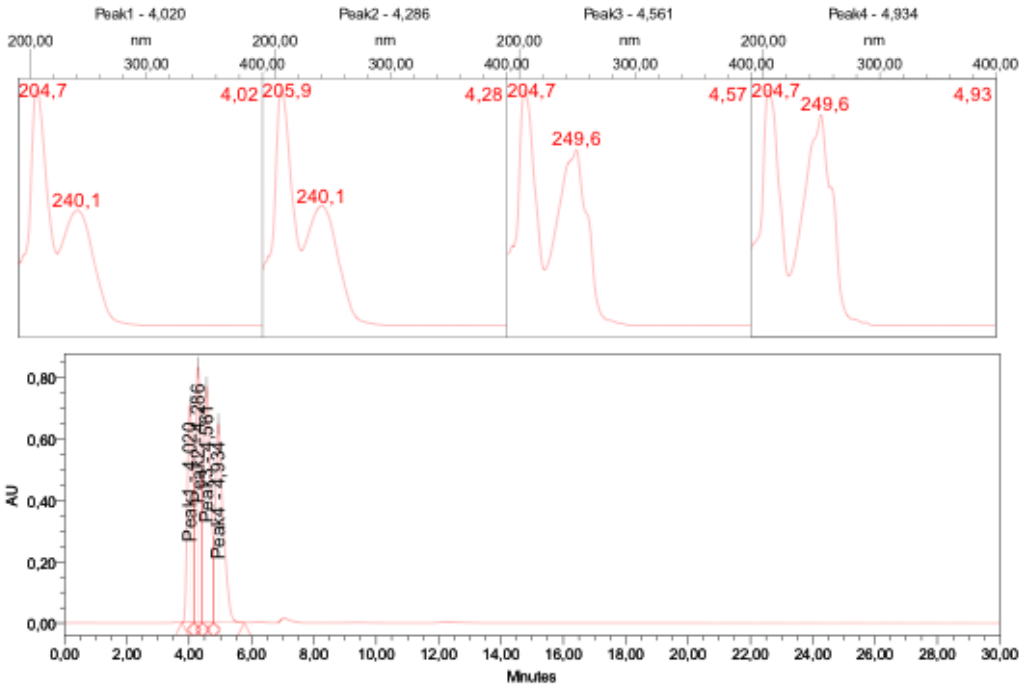



rapport

INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | FL6569-27 | Acquired By: | System |
| Sample Type: | Unknown | Sample Set Name: | Y |
| Vial: | 1 | Acq. Method Set: | PM ODH 1ml 9505 hept_Prop2 |
| Injection #: | 1 | Processing Method: | 3 |
| Injection Volume: | 10,00 ul | Channel Name: | 245,0nm |
| Run Time: | 30,0 Minutes | Proc. Chnl. Descr.: | PDA 245,0 nm |
| Date Acquired: | 13/12/2012 17:22:32 CET | | |
| Date Processed: | 14/12/2012 09:15:47 CET | | |

**Spectrum Index Plot**




SampleName: FL6569-27; Vial: 1; Injection: 1; Date Acquired: 13/12/2012 17:22:32 CET

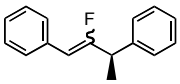
**Peak Results**

| | Name | RT | Area | % Area |
|---|---|---|---|---|
| 1 | Peak1 | 4,020 | 8466383 | 20,08 |
| 2 | Peak2 | 4,286 | 10983234 | 26,05 |
| 3 | Peak3 | 4,561 | 11405752 | 27,06 |
| 4 | Peak4 | 4,934 | 11299007 | 26,80 |

Reported by User: System
Report Method: rapport
Report Method ID 1032
Page: 1 of 1

Project Name: IA-ODH-OJH 2012
Date Printed:
14/12/2012
10:25:40 Europe/Paris

**4.3.2** (3*R*)-1,3-Diphenyl-2-fluorobut-1-ene (**1d**)



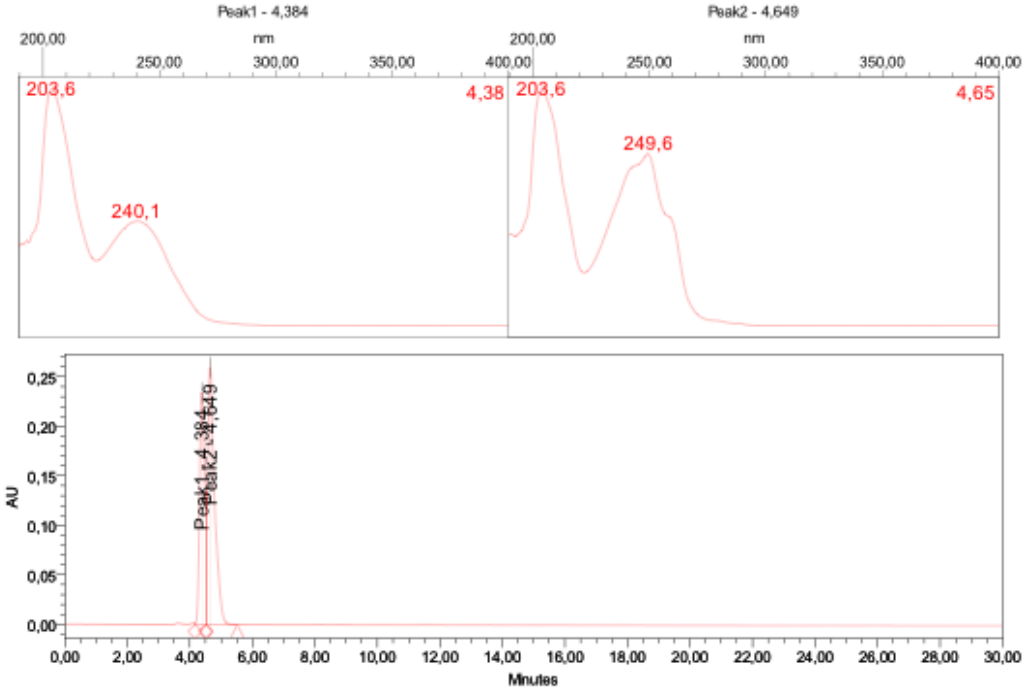



rapport

INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | FL6569-71 | Acquired By: | System |
| Sample Type: | Unknown | Sample Set Name: | GT |
| Vial: | 2 | Acq. Method Set: | PM ODH 1ml 9505 hept_Prop2 |
| Injection #: | 1 | Processing Method: | 3 |
| Injection Volume: | 10,00 ul | Channel Name: | 245,0nm |
| Run Time: | 30,0 Minutes | Proc. Chnl. Descr.: | PDA 245,0 nm |
| Date Acquired: | 14/12/2012 09:24:25 CET | | |
| Date Processed: | 14/12/2012 09:57:13 CET | | |

**Spectrum Index Plot**




SampleName: FL6569-71; Vial: 2; Injection: 1; Date Acquired: 14/12/2012 09:24:25 CET

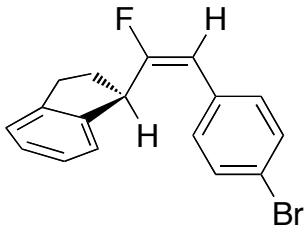
**Peak Results**

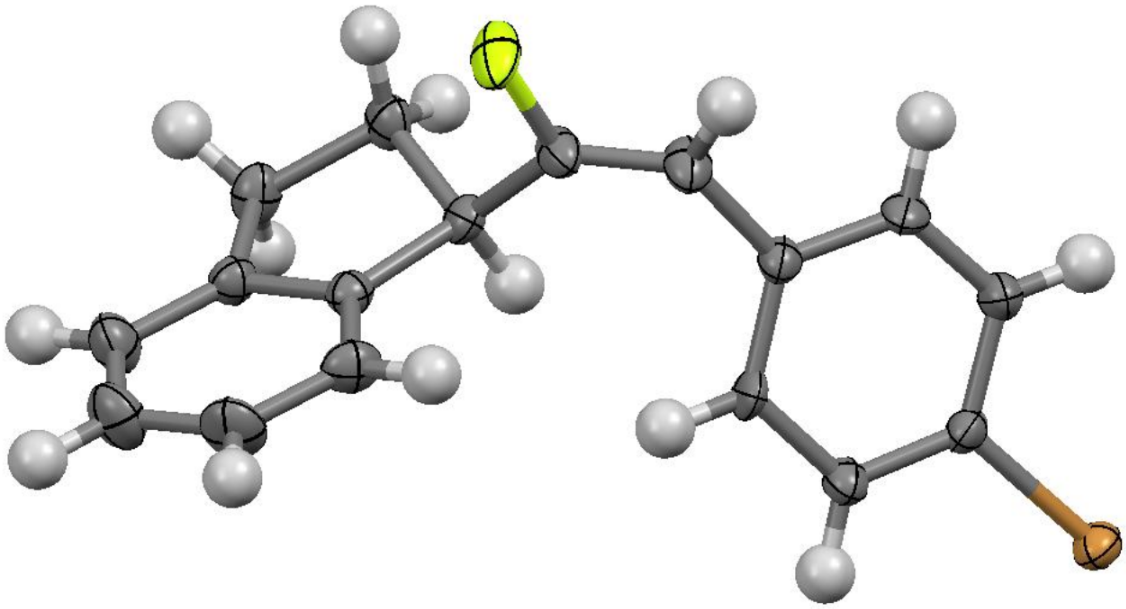
| | Name | RT | Area | % Area |
|---|---|---|---|---|
| 1 | Peak1 | 4,384 | 2619931 | 38,75 |
| 2 | Peak2 | 4,649 | 4141781 | 61,25 |

Reported by User: System
Report Method: rapport
Report Method ID 1032
Page: 1 of 1

Project Name: IA-ODH-OJH 2012
Date Printed:
14/12/2012
10:25:15 Europe/Paris

**4.4.** X-Ray Structure of **1i**



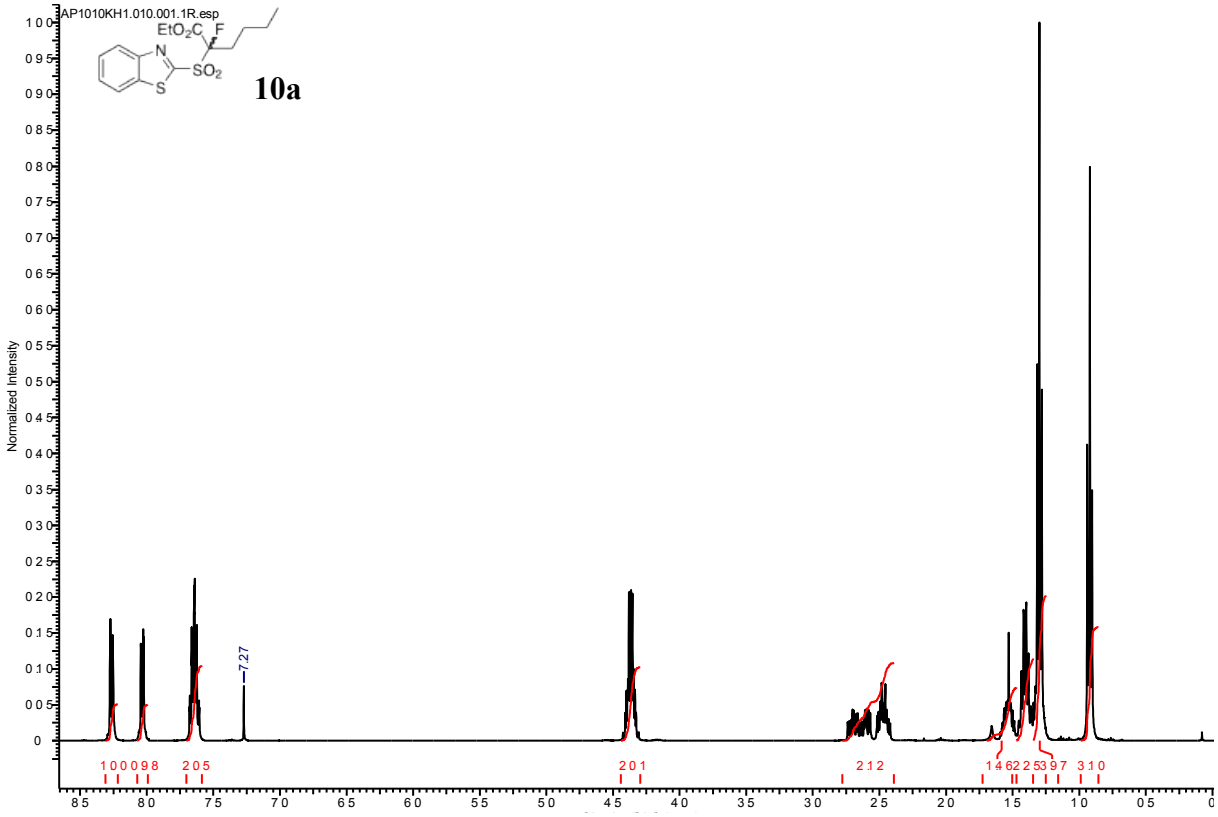



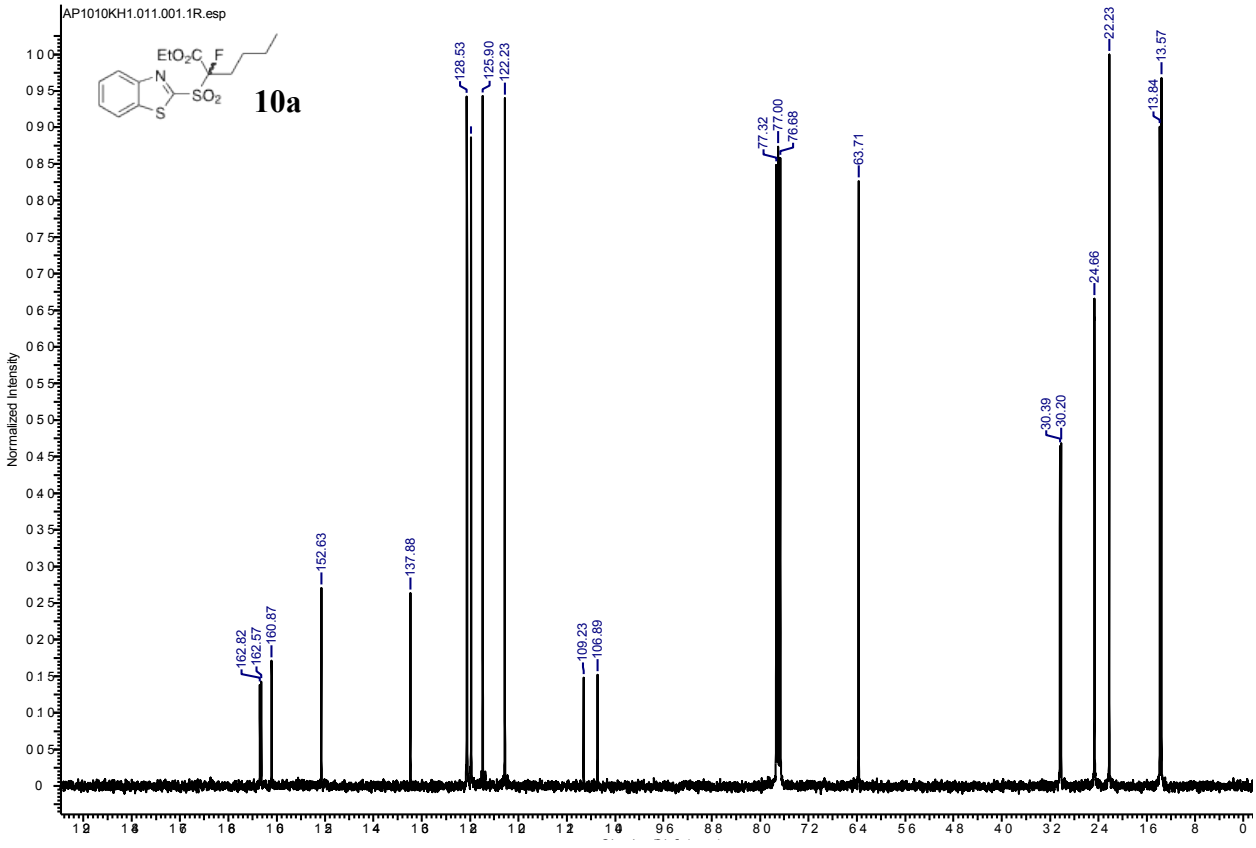
The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 928011

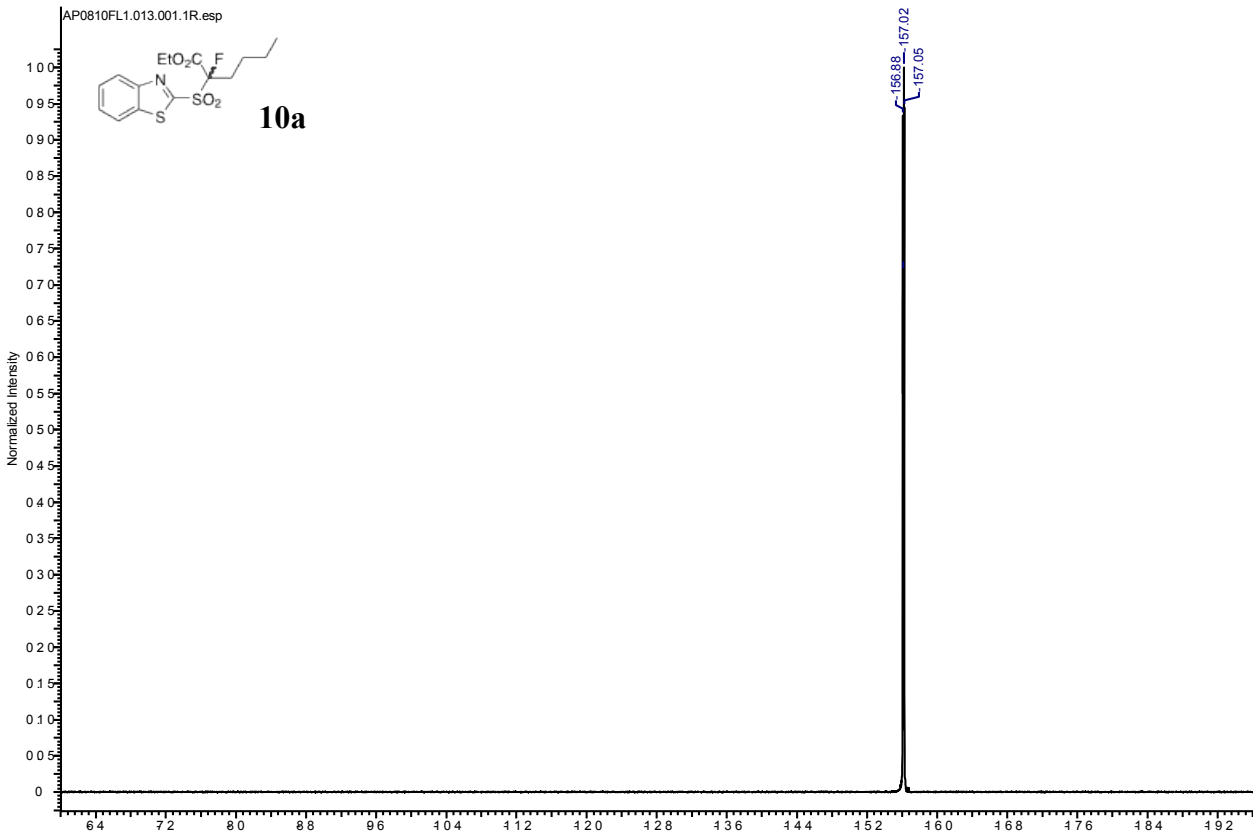
## 5. Copies of spectra

### 5.1 Mitsunobu reaction leading to **10** (Table 1)

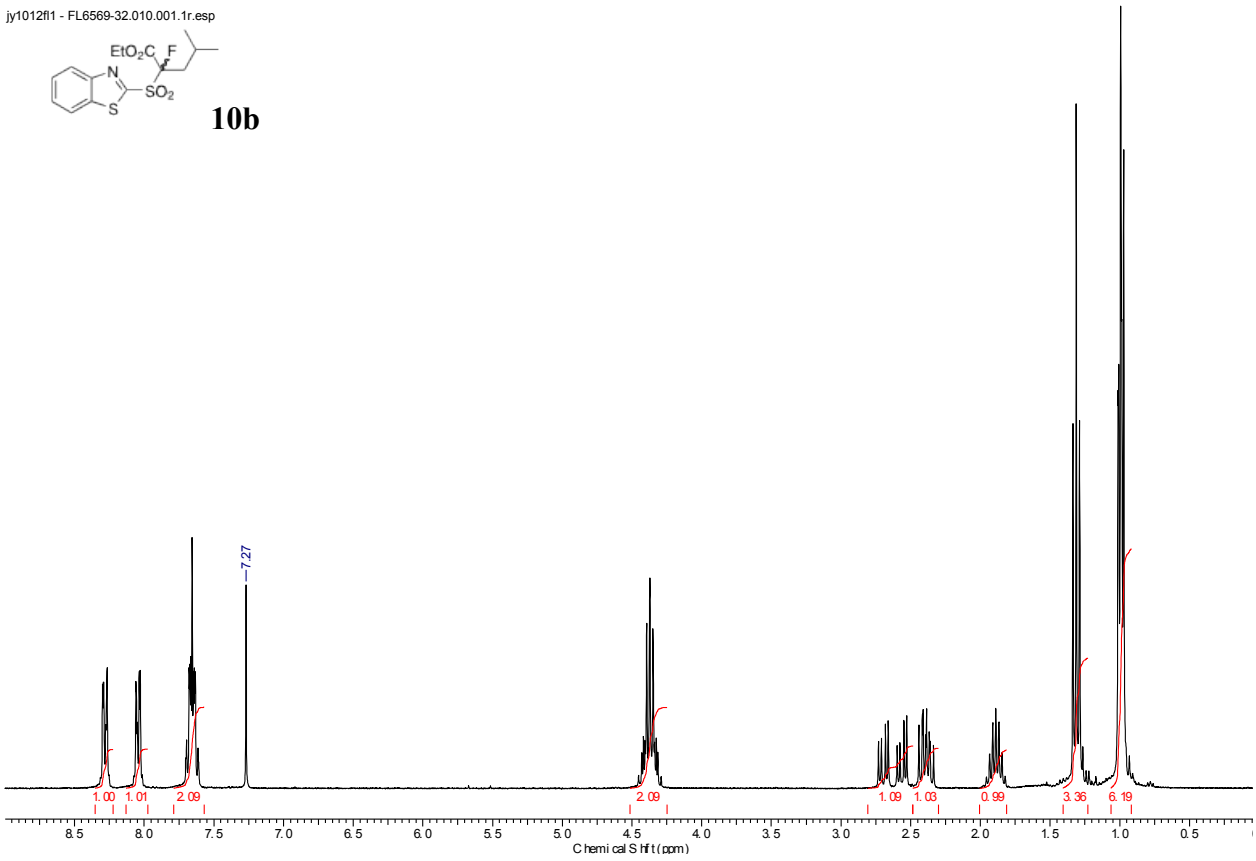
#### 5.1.1 Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluorohexanoate (**10a**)



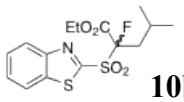






**5.1.2** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-4-methylpentanoate (**10b**)



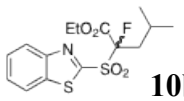
AU1412FL1.010.001.1r.esp



**10b**



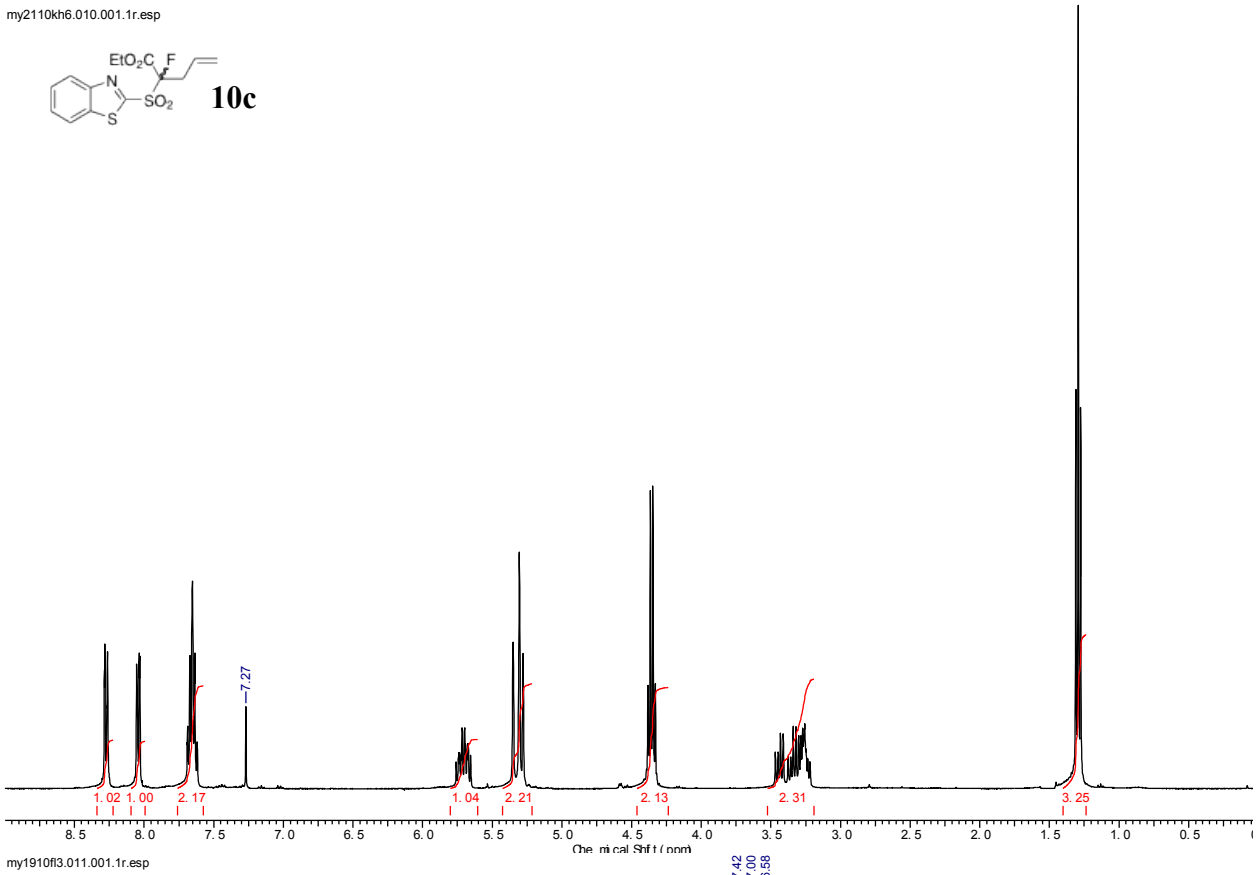

jy1012fl1 - FL6569-32.011.001.1r.esp

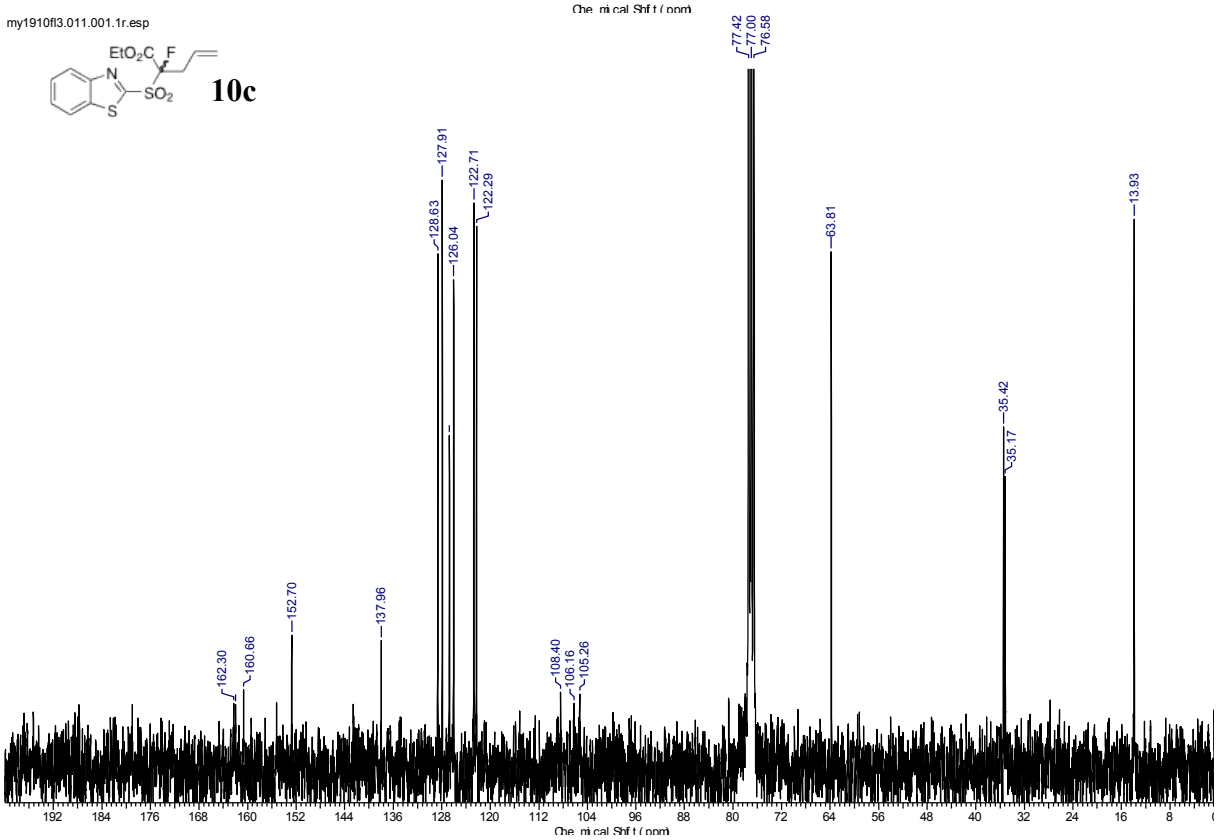


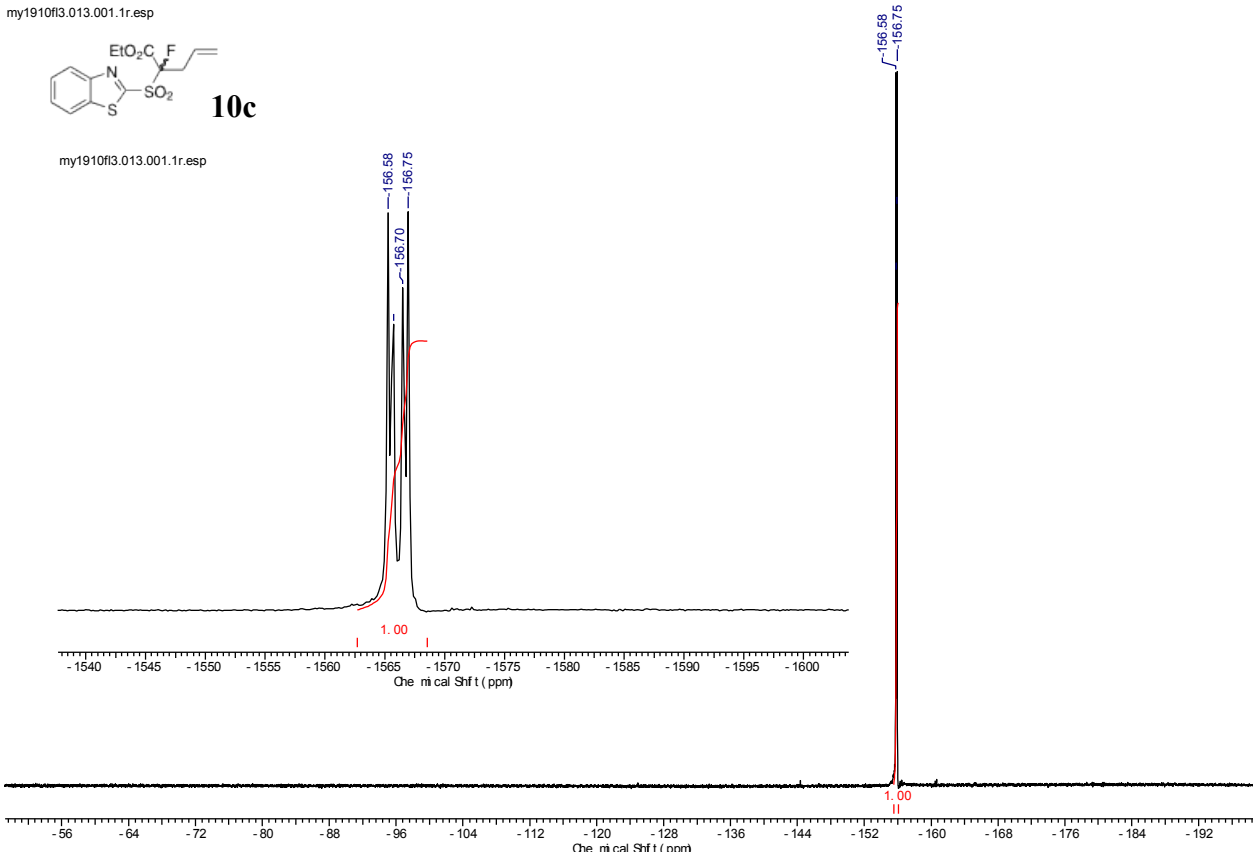
**10b**

jy1012fl1 - FL6569-32.011.001.1r.esp

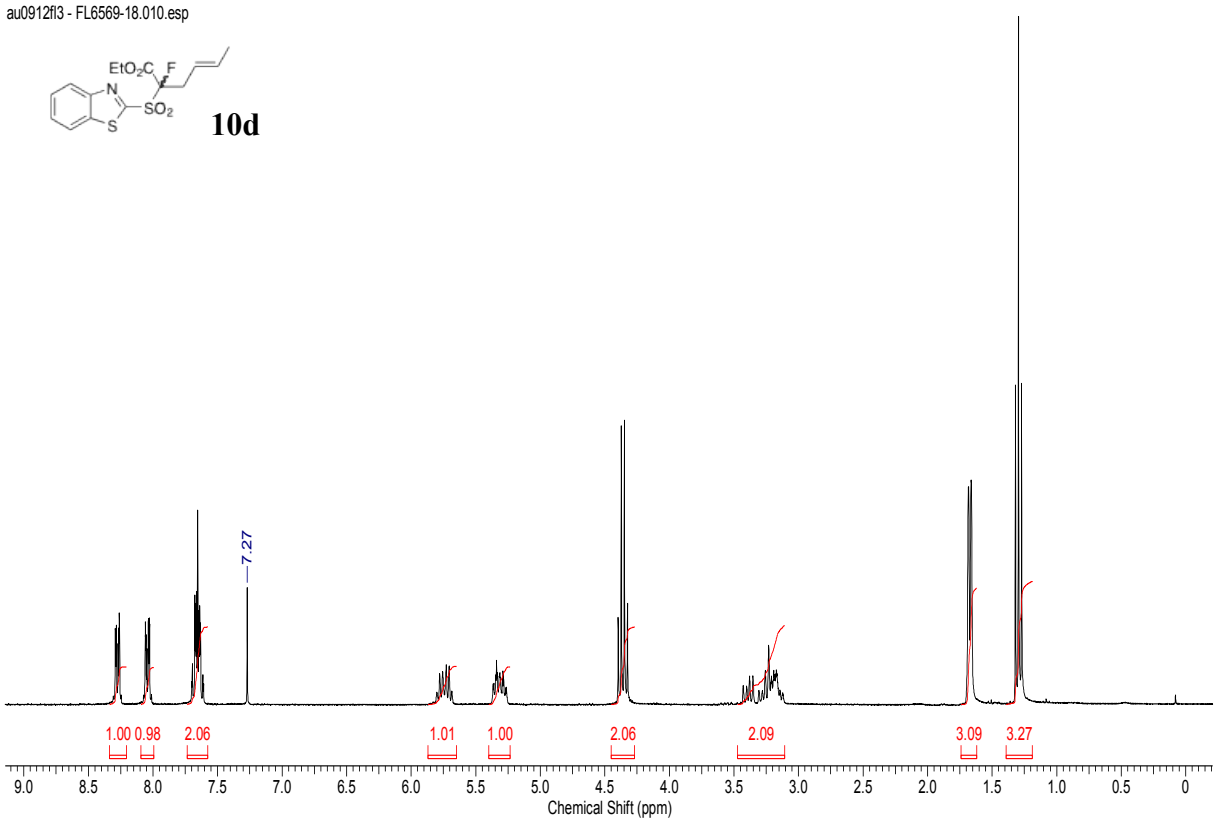
**5.1.3** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoropent-4-enoate (**10c**)

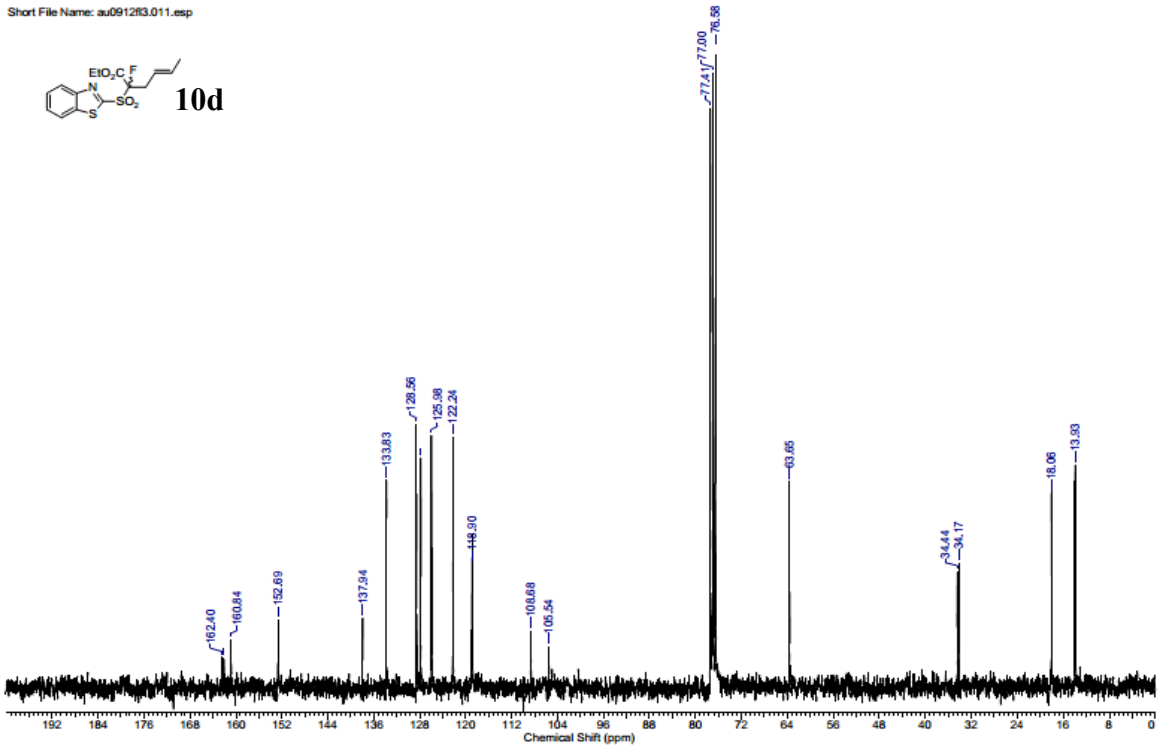


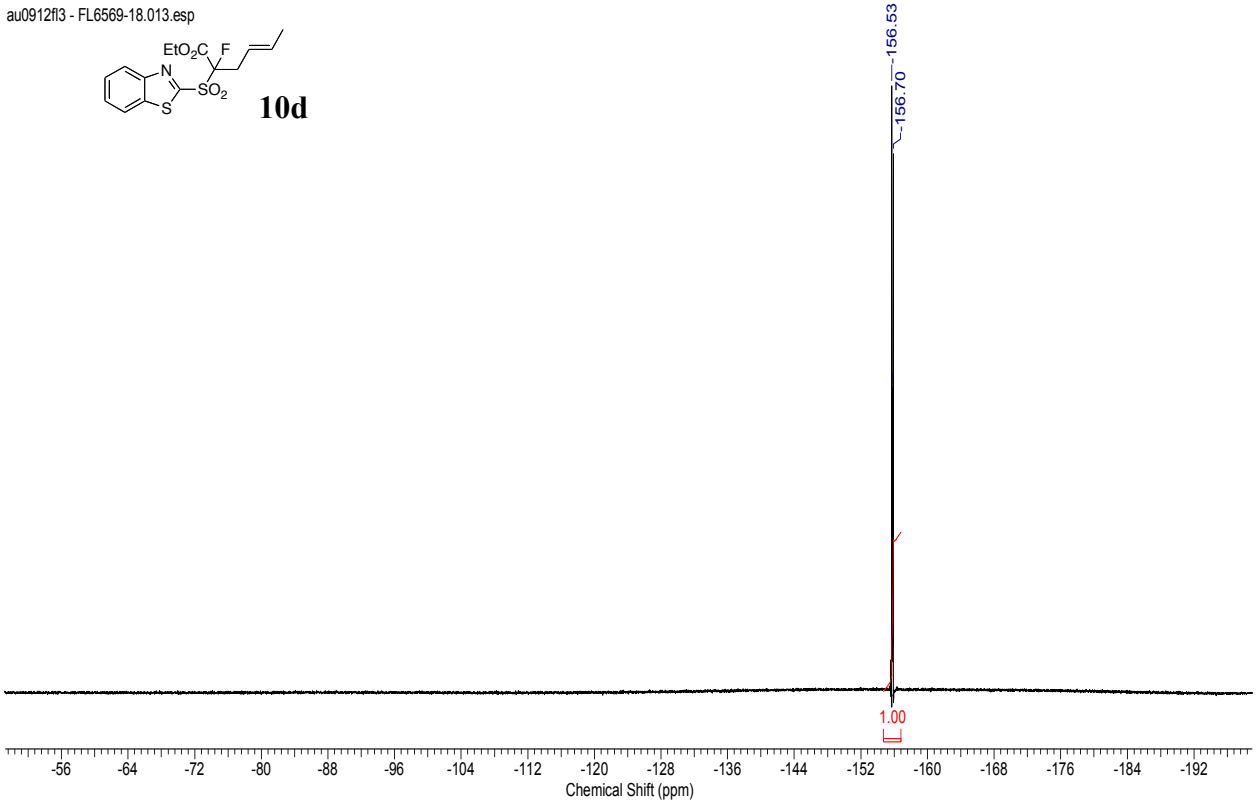





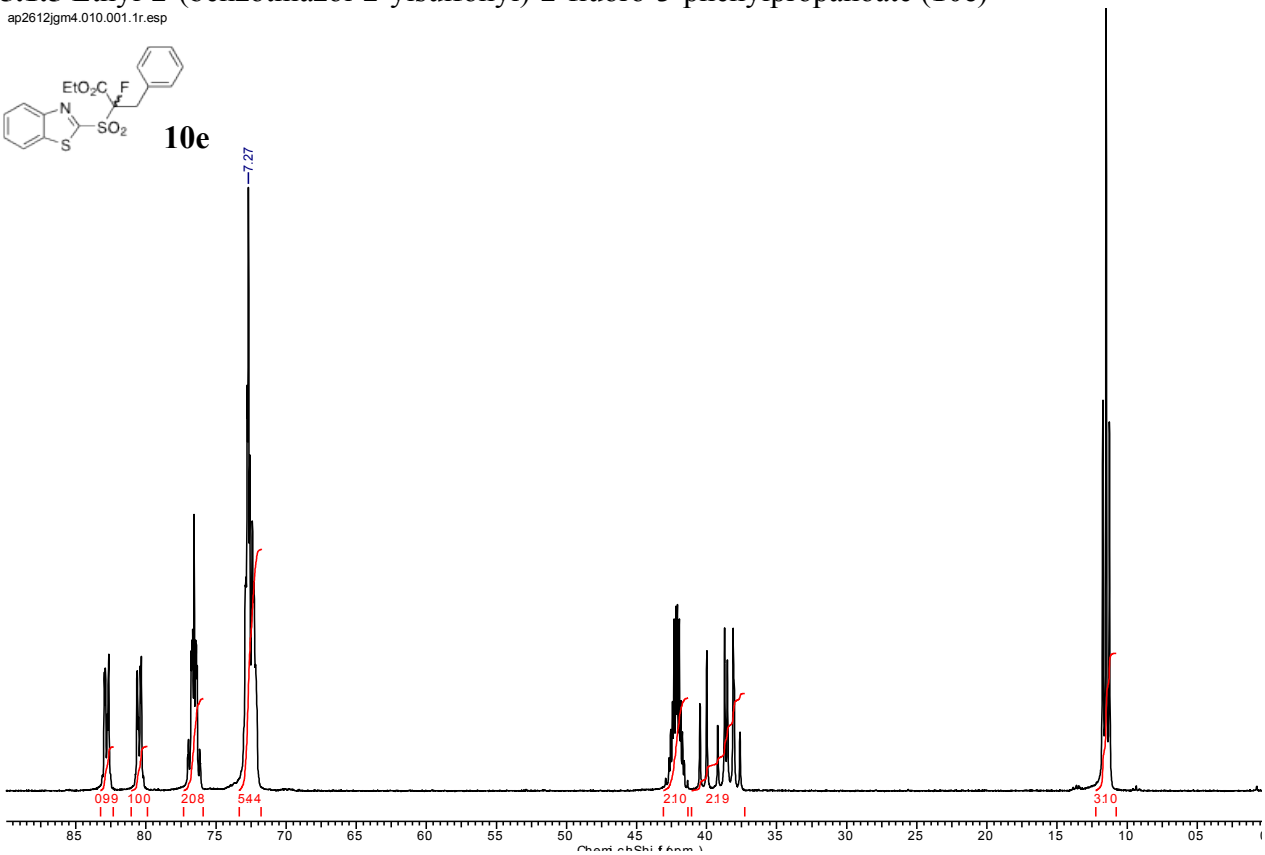

## **5.1.4** (*E*)-Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluorohex-4-enoate (**10d**)

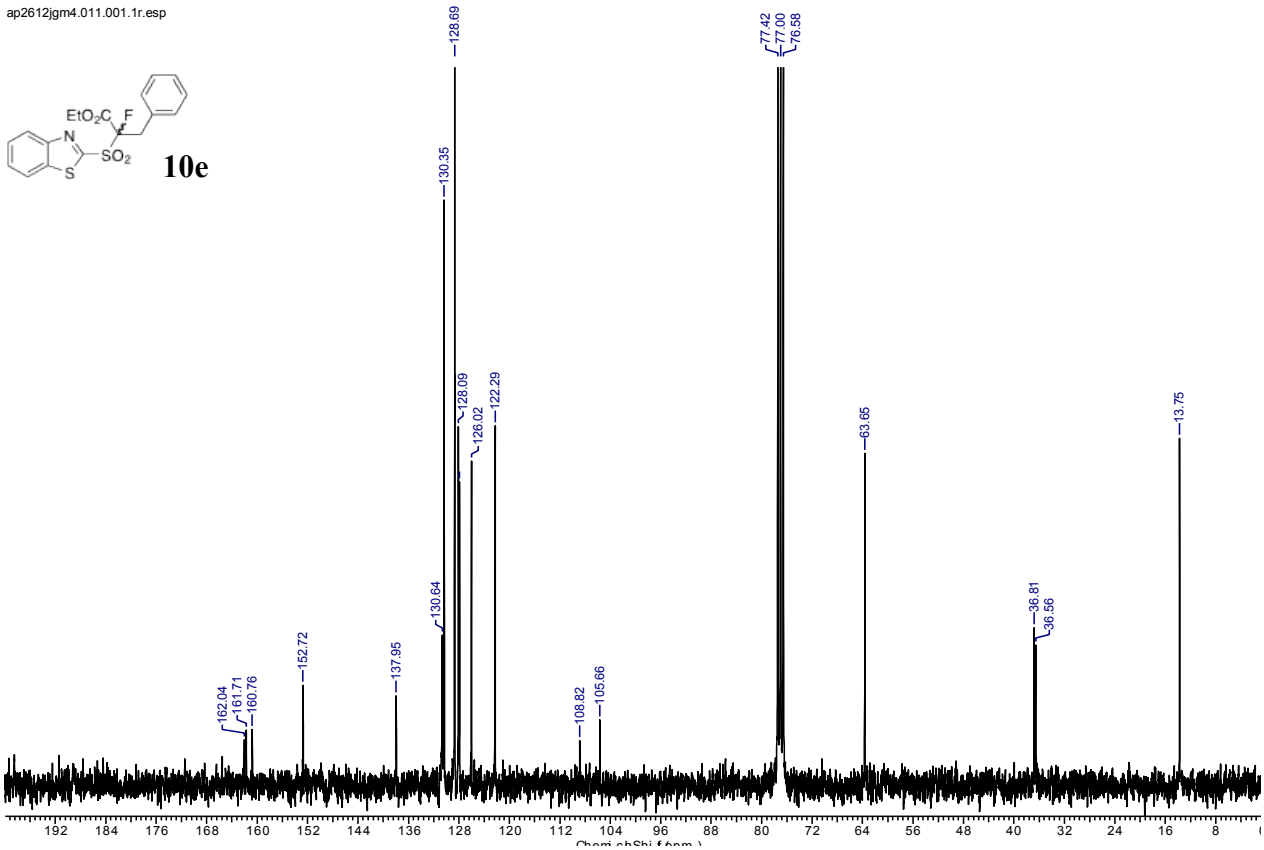


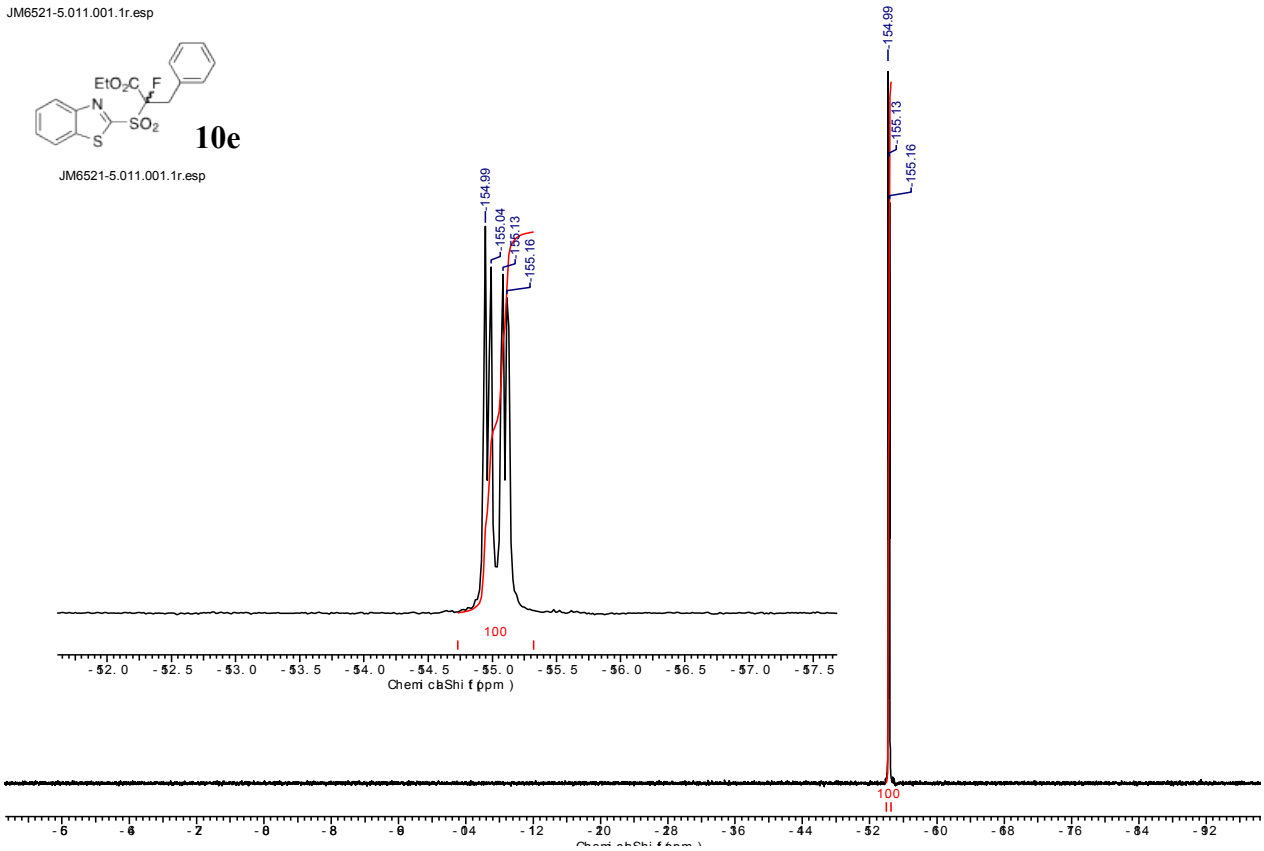

Short File Name: au0912fl3.011.esp
10d
162.40
160.84
152.69
137.94
133.83
129.56
125.98
122.24
118.90
108.68
105.54
77.41
77.00
76.58
63.65
34.44
34.17
18.06
13.93
Chemical Shift (ppm)


au0912fl3 - FL6569-18.013.esp
10d
156.53
156.70
1.00
Chemical Shift (ppm)

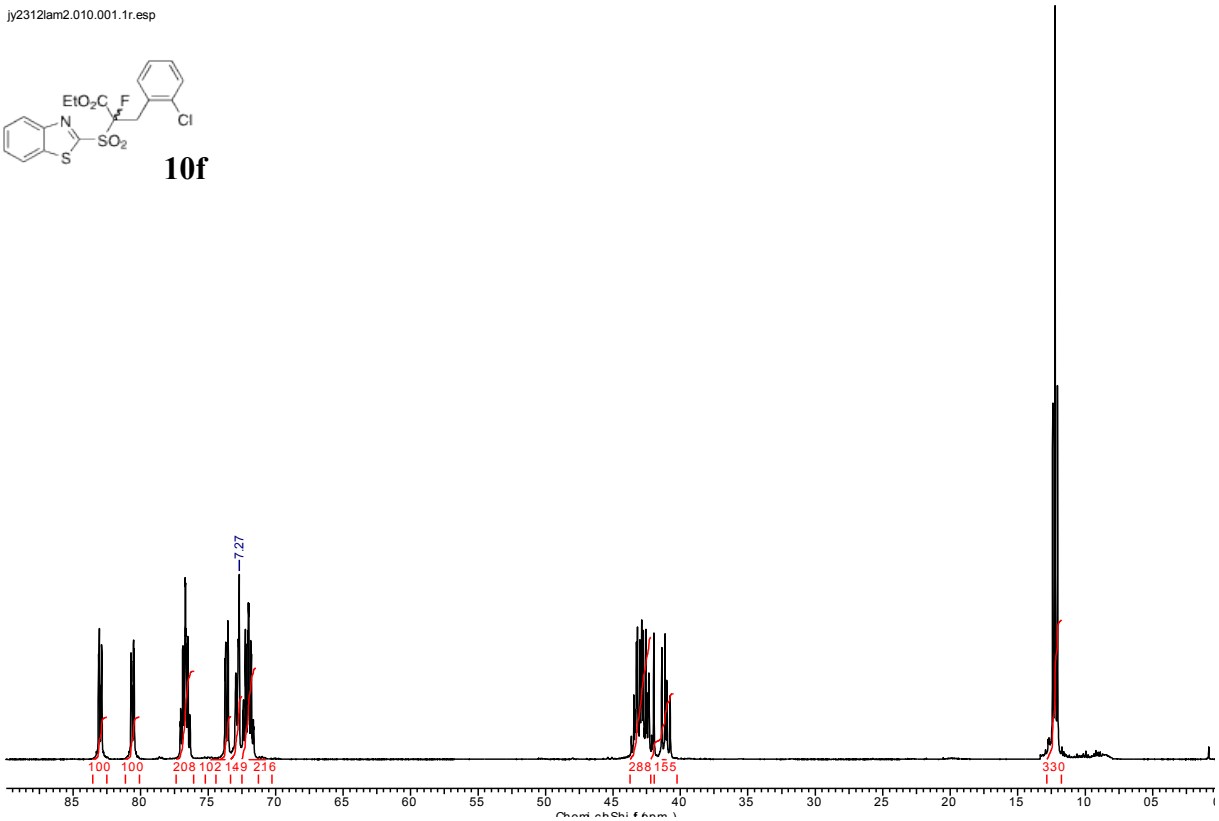
**5.1.5** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-phenylpropanoate (**10e**)



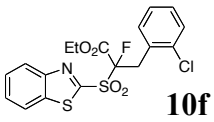






**5.1.6** Ethyl-2-(benzothiazol-2-ylsulfonyl)-3-(2-chlorophenyl)-2-fluoropropanoate (**10f**)



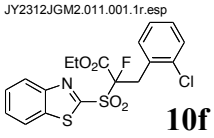
jy2312lam2.011.001.1r.esp




**10f**




JY2312JGM2.011.001.1r.esp

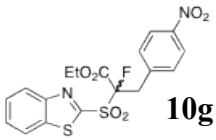



**10f**

JY2312JGM2.011.001.1r.esp

**5.1.7** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-(4-nitrophenyl)propanoate (**10g**)

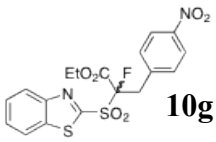
ap1212sbg4.010.001.1r.esp



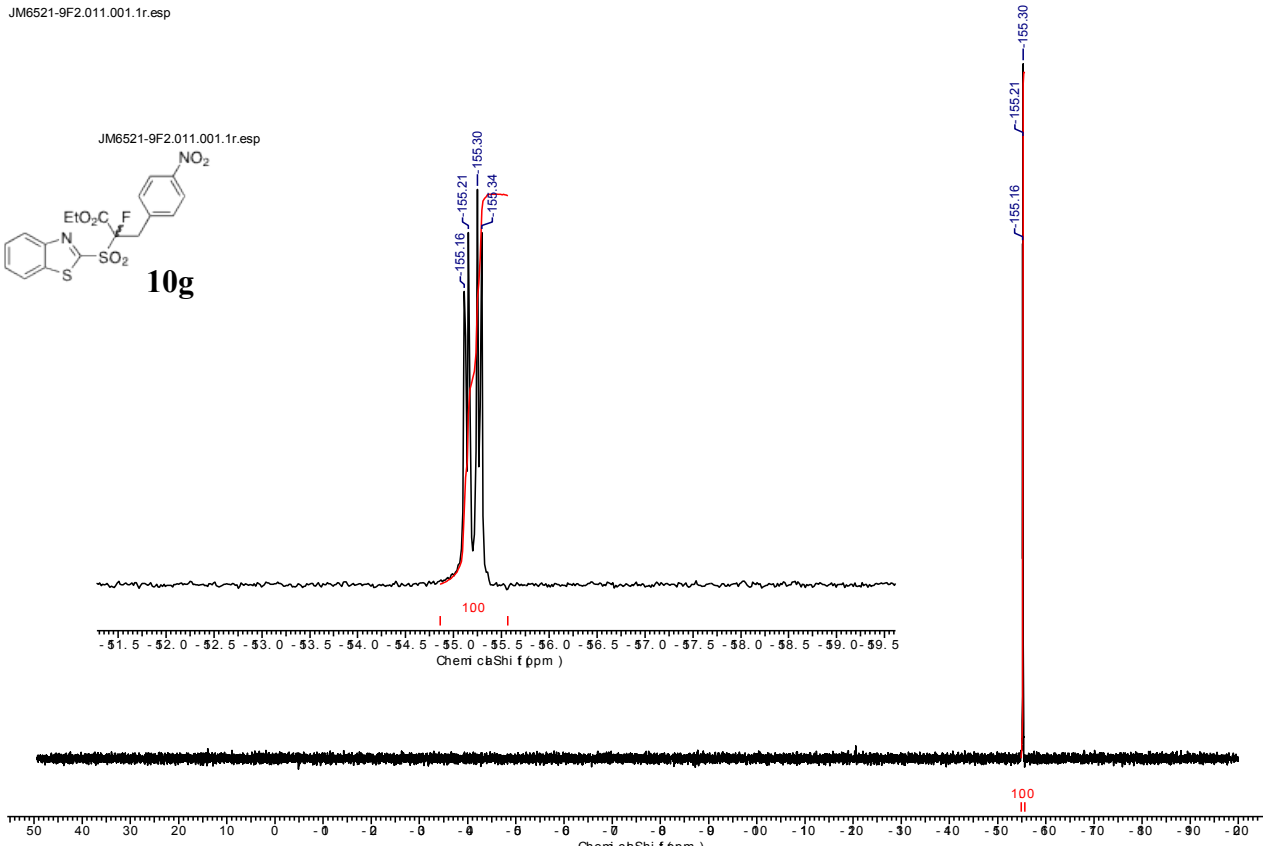

**10g**



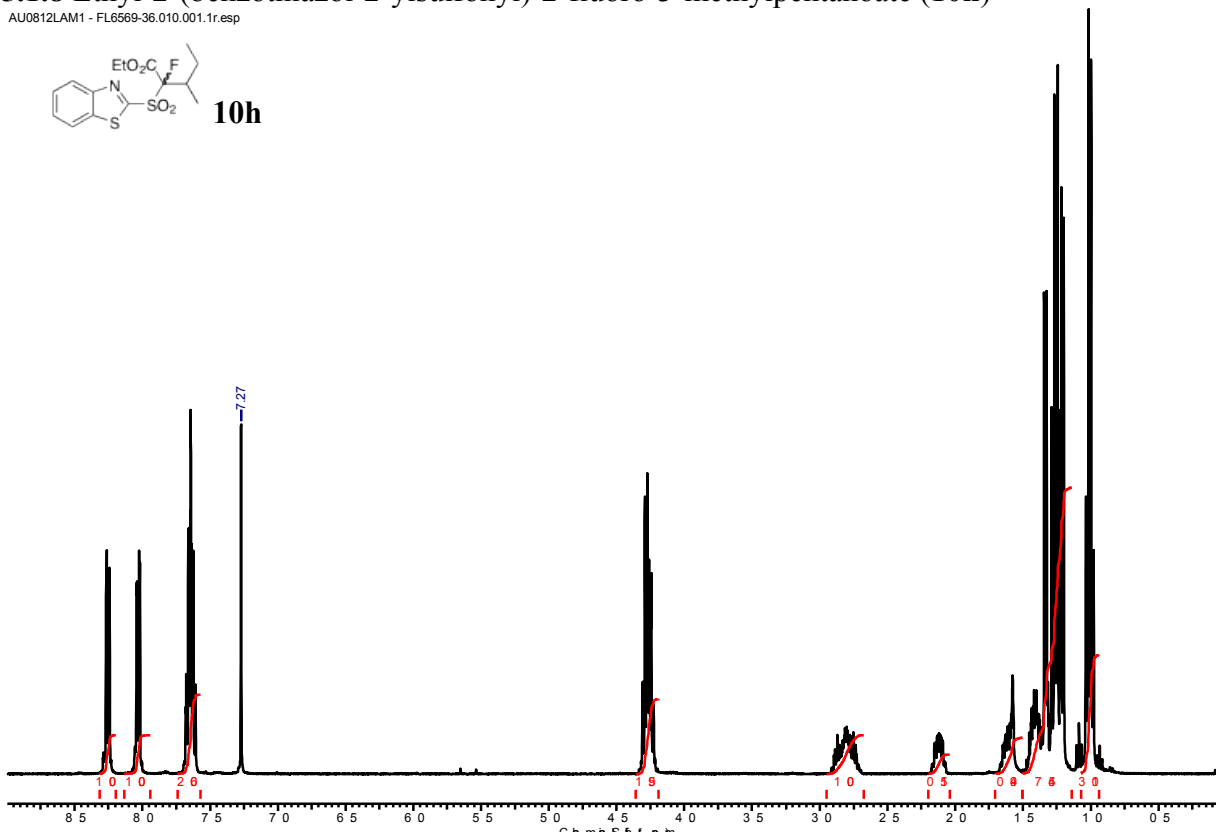

ap1212sbg4.011.001.1r.esp

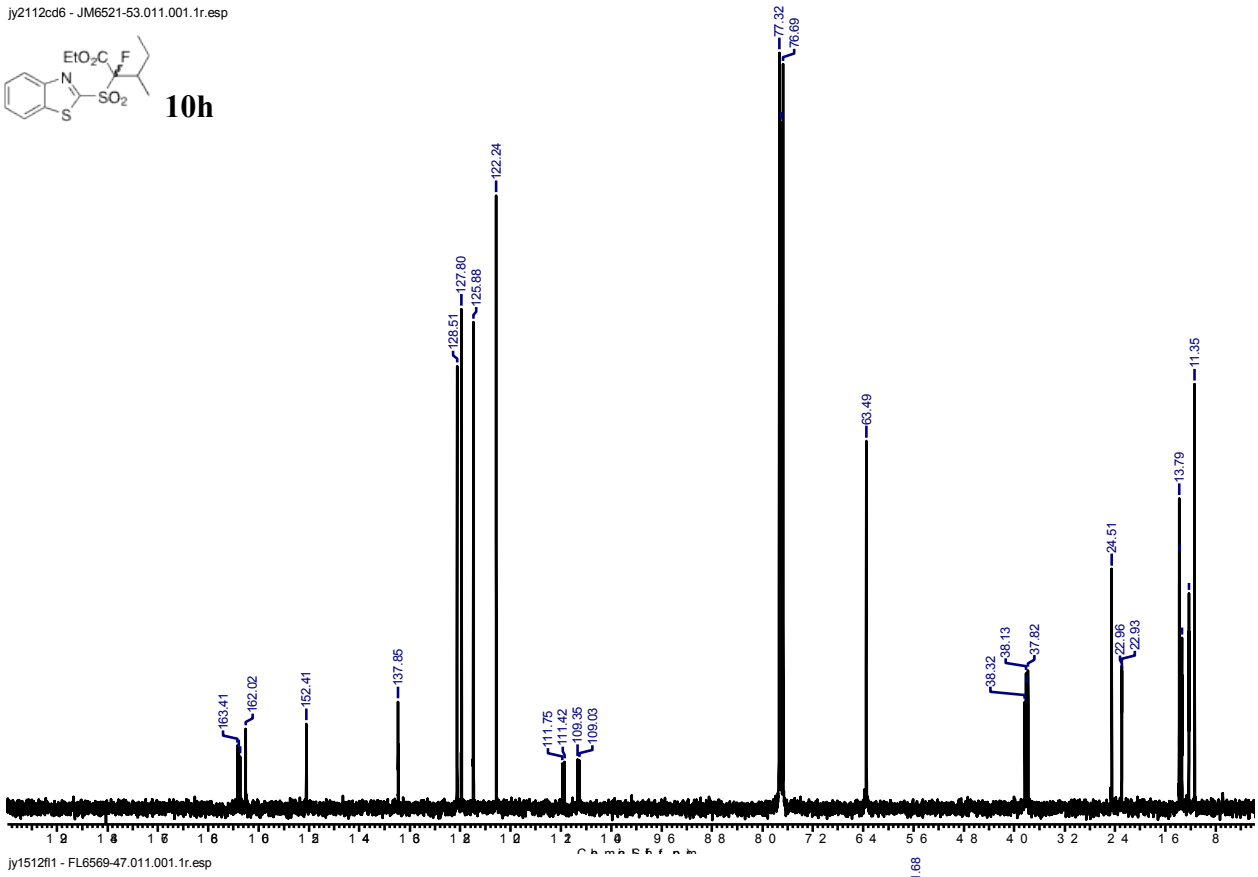


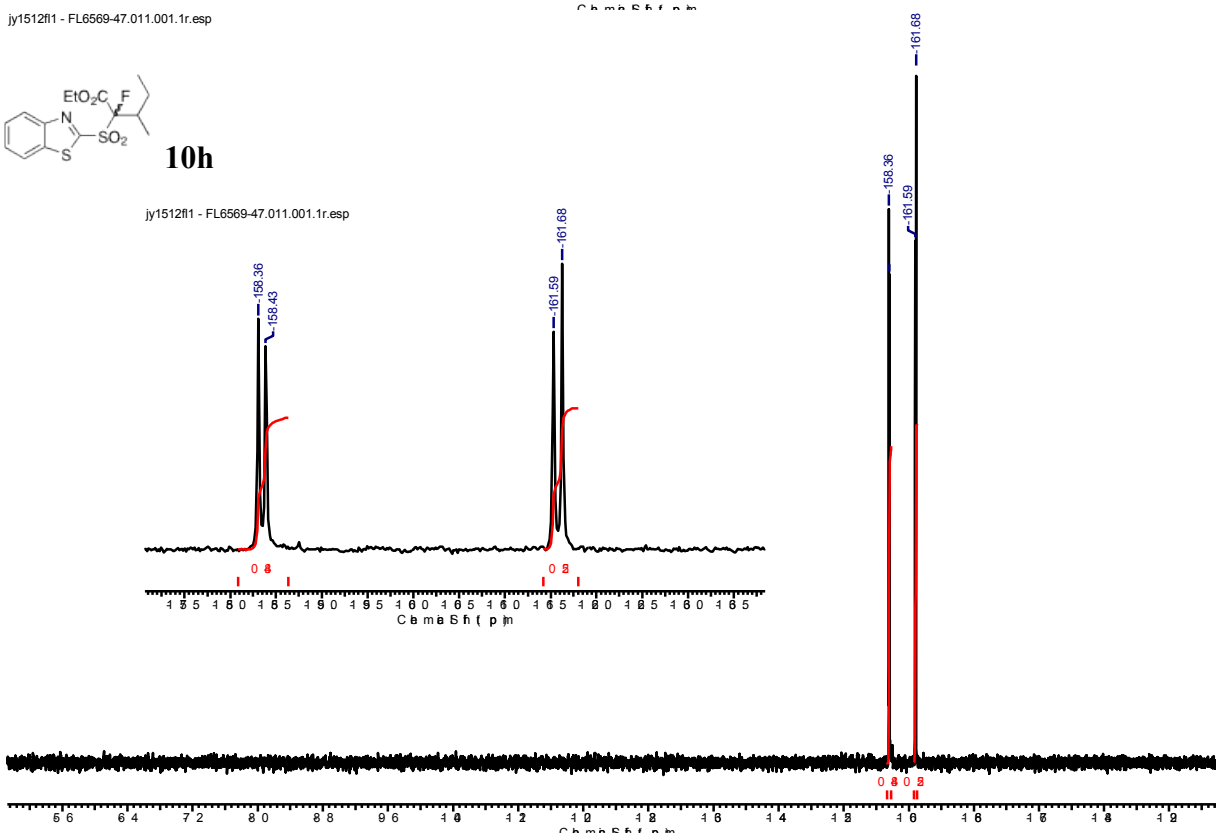

**10g**



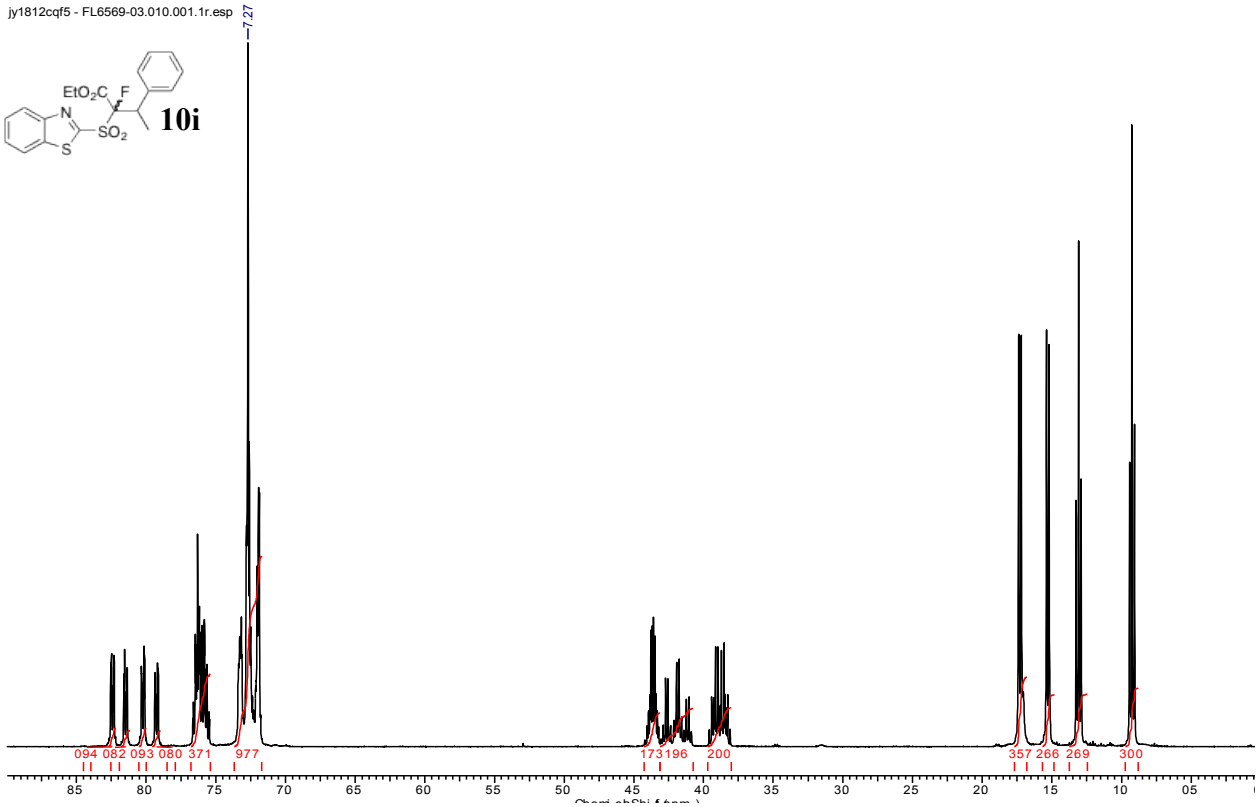

**5.1.8** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-methylpentanoate (**10h**)

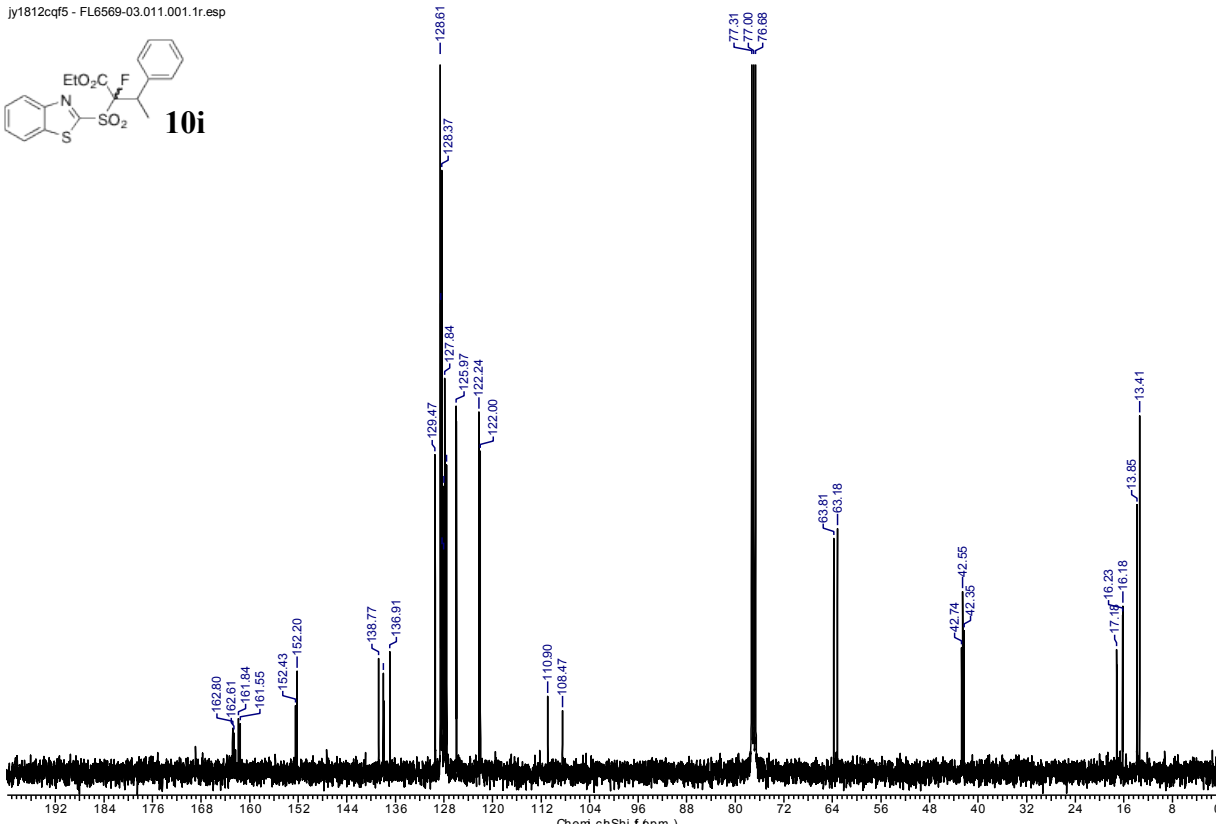


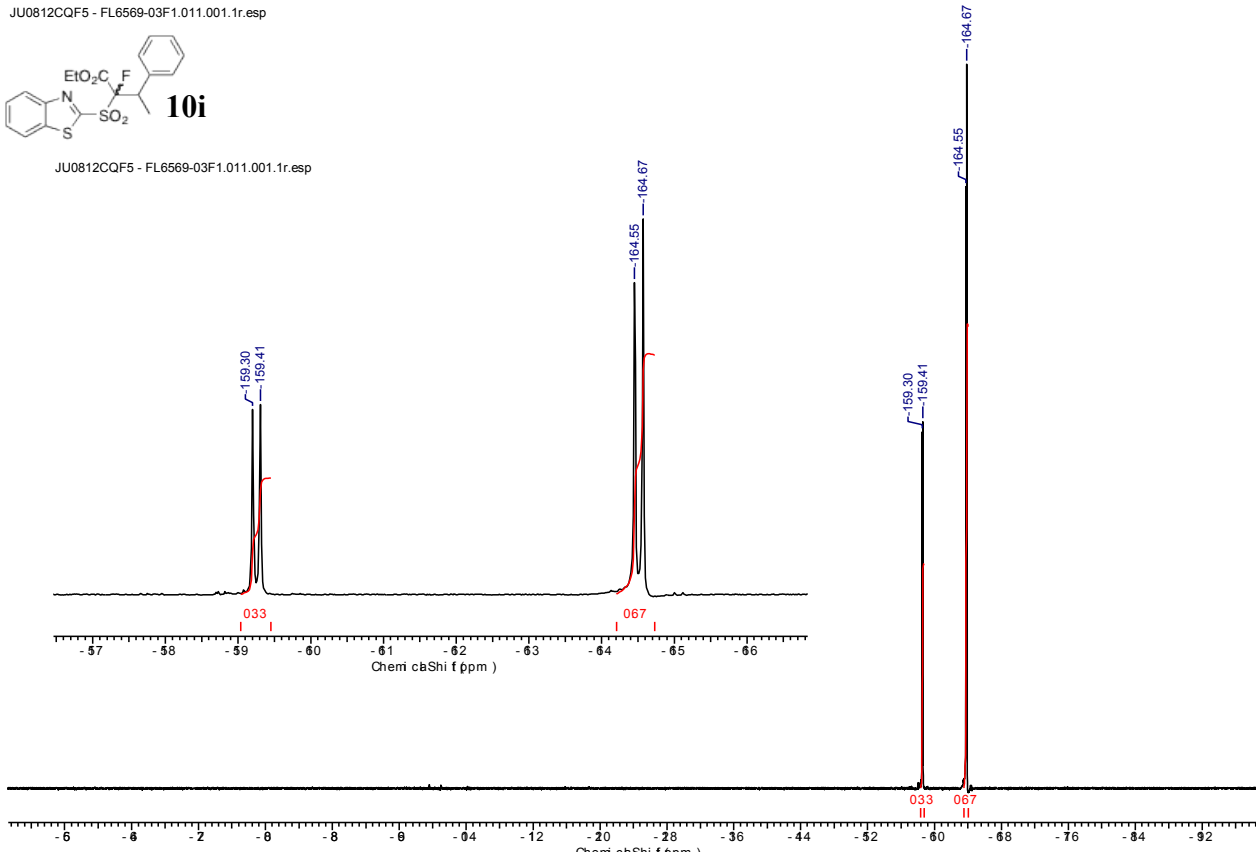

jy2112cd6 - JM6521-53.011.001.1r.esp
10h
77.32
76.69
122.24
127.80
125.88
128.51
63.49
11.35
13.79
24.51
22.96
22.93
38.32
38.13
37.82
137.85
152.41
162.02
163.41
111.75
111.42
109.35
109.03


jy1512fl1 - FL6569-47.011.001.1r.esp
10h
jy1512fl1 - FL6569-47.011.001.1r.esp
161.68
158.36
161.59
158.43
161.59
161.68
158.36
161.59

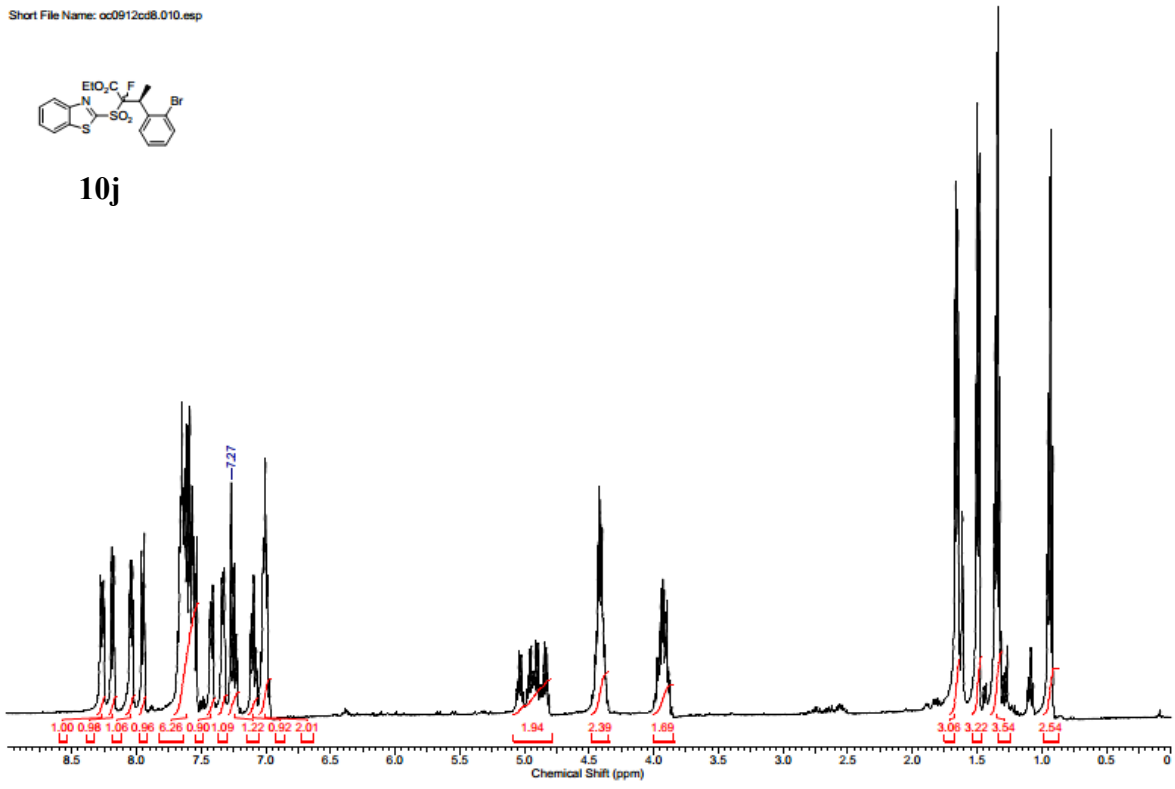
**5.1.9** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-phenylbutanoate (**10i**)

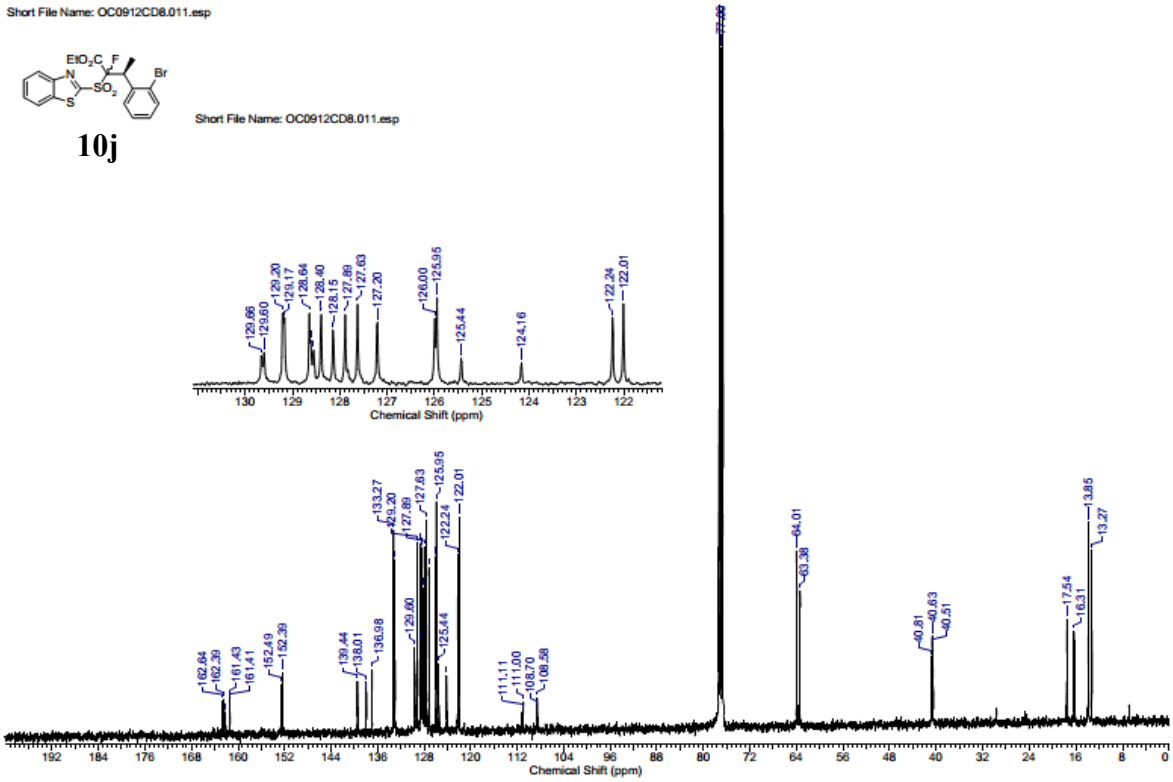


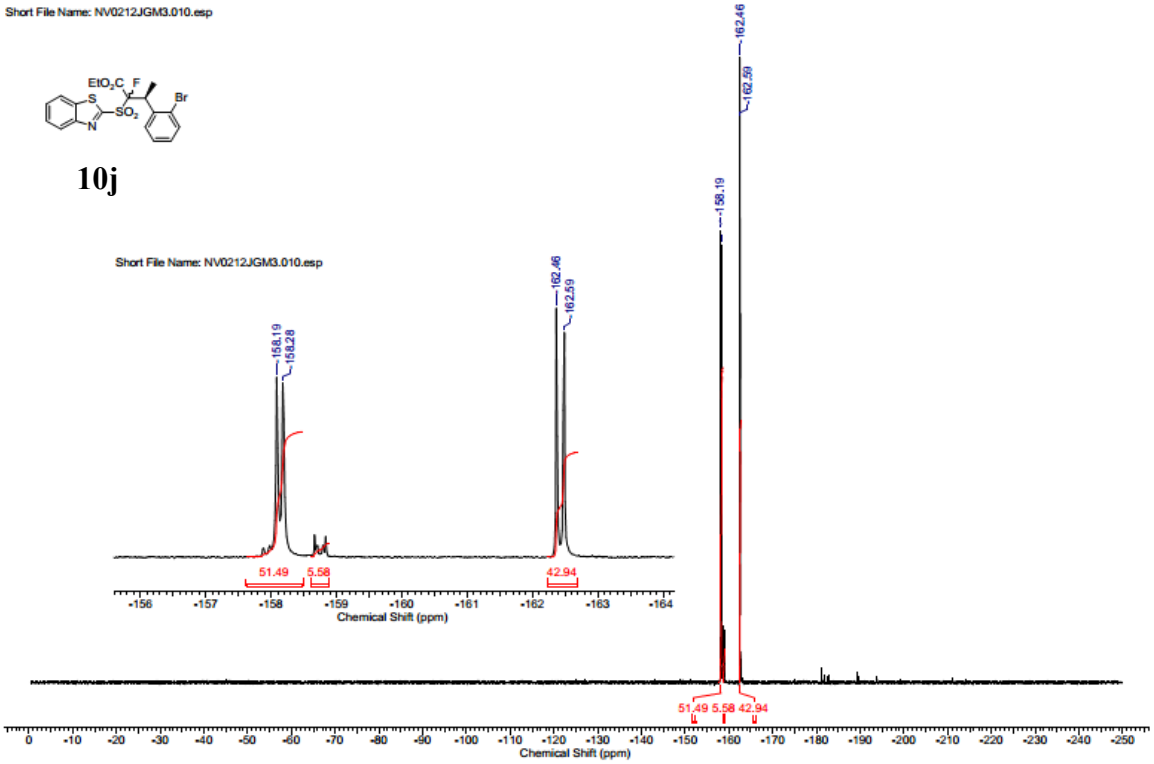



**5.1.10** Ethyl-2-(benzothiazol-2-ylsulfonyl)-3-(2-bromophenyl)-2-fluorobutanoate (**10j**)



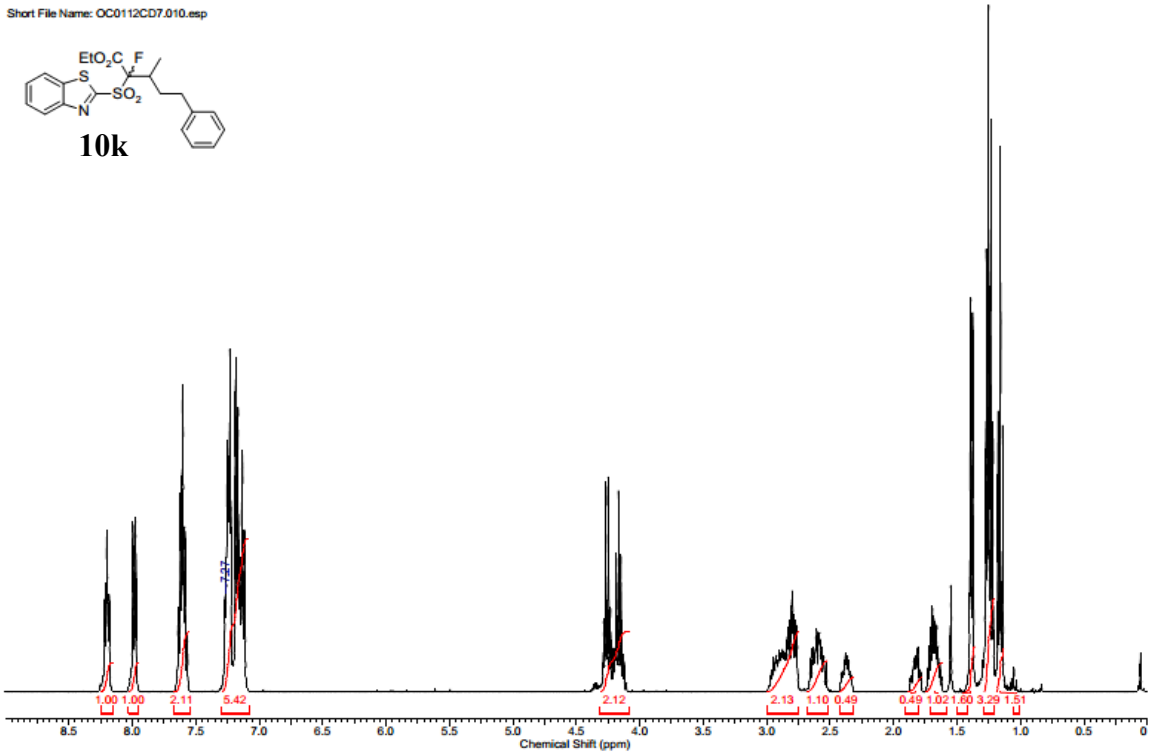

Short File Name: OC0912CD8.011.esp
Short File Name: OC0912CD8.011.esp
Chemical Shift (ppm)
Chemical Shift (ppm)

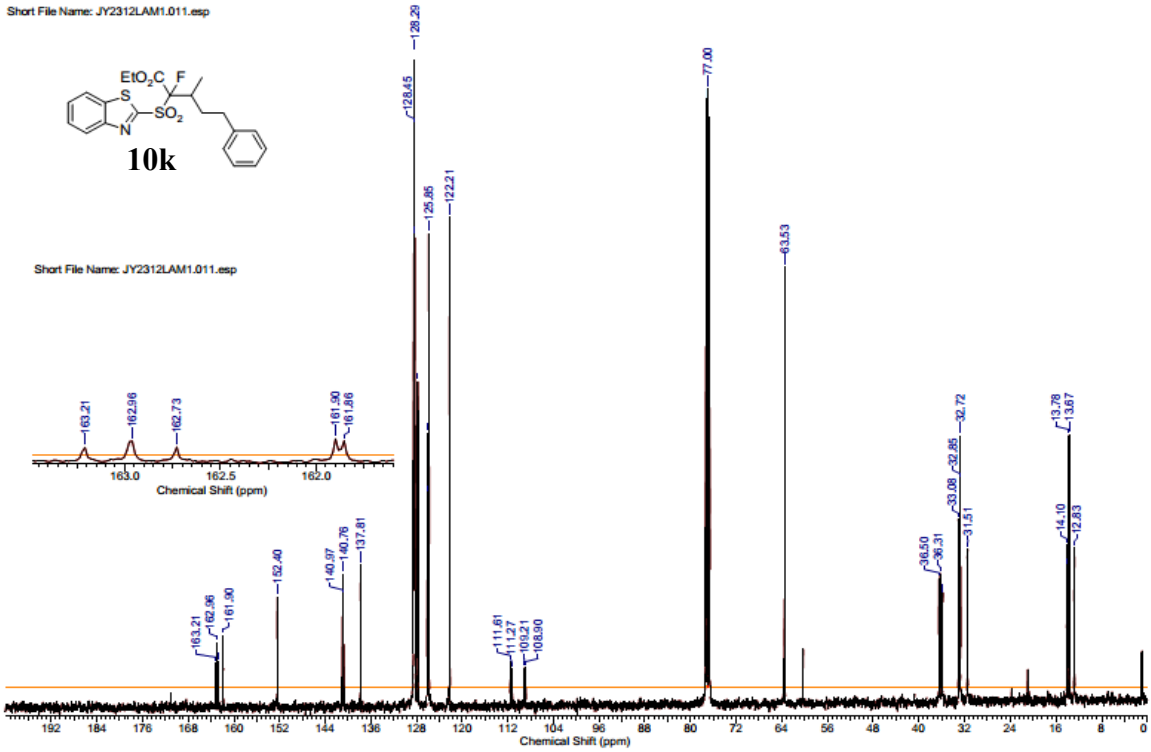
**10j**

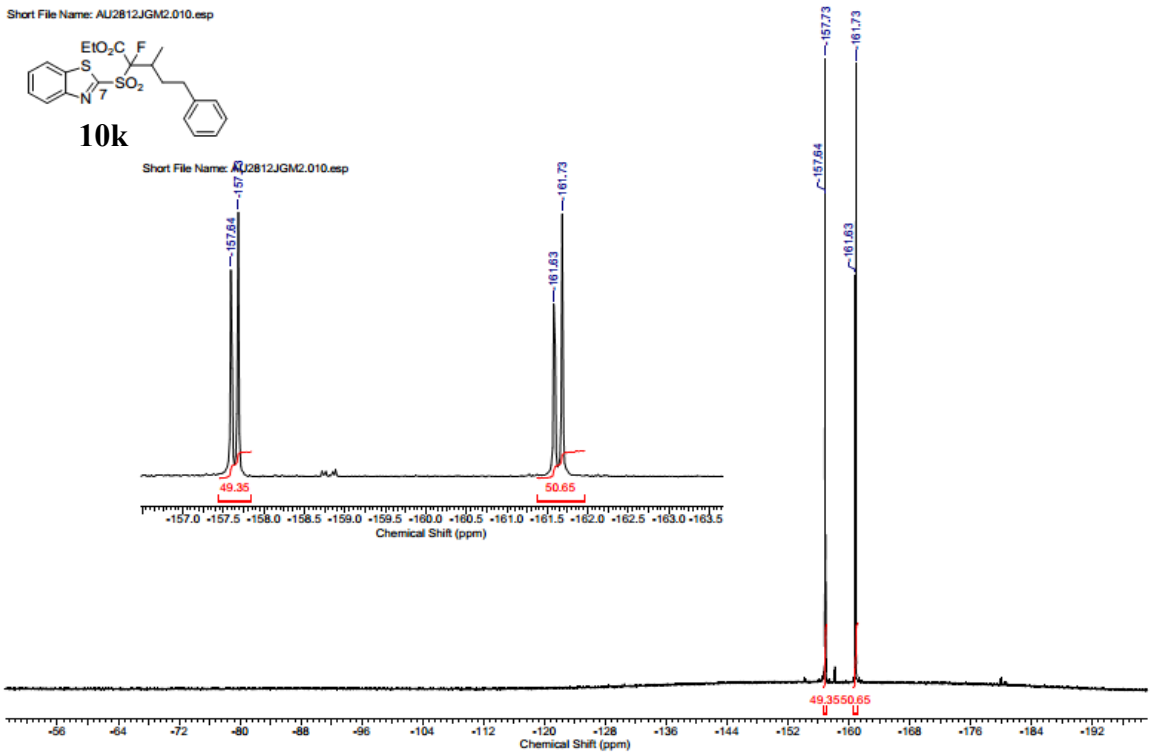

Short File Name: NV0212JGM3.010.esp
Short File Name: NV0212JGM3.010.esp
51.49
5.58
42.94
Chemical Shift (ppm)
51.49 5.58 42.94
Chemical Shift (ppm)

**10j**

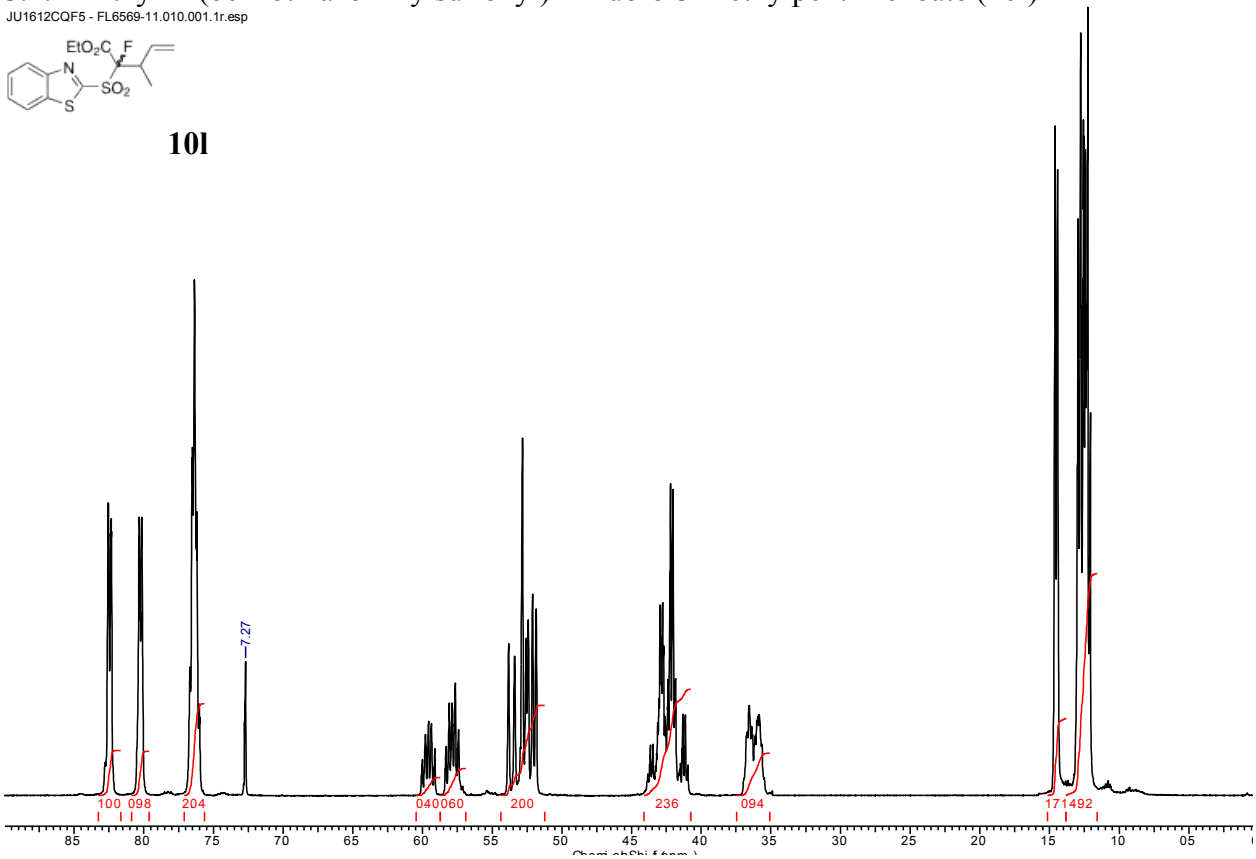
**5.1.11** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-methyl-5-phenylpentanoate (**10k**)



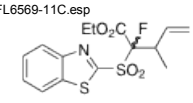






**5.1.12** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-fluoro-3-methylpent-4-enoate (**10l**)



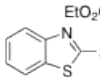
FL6569-11C.esp



**10l**

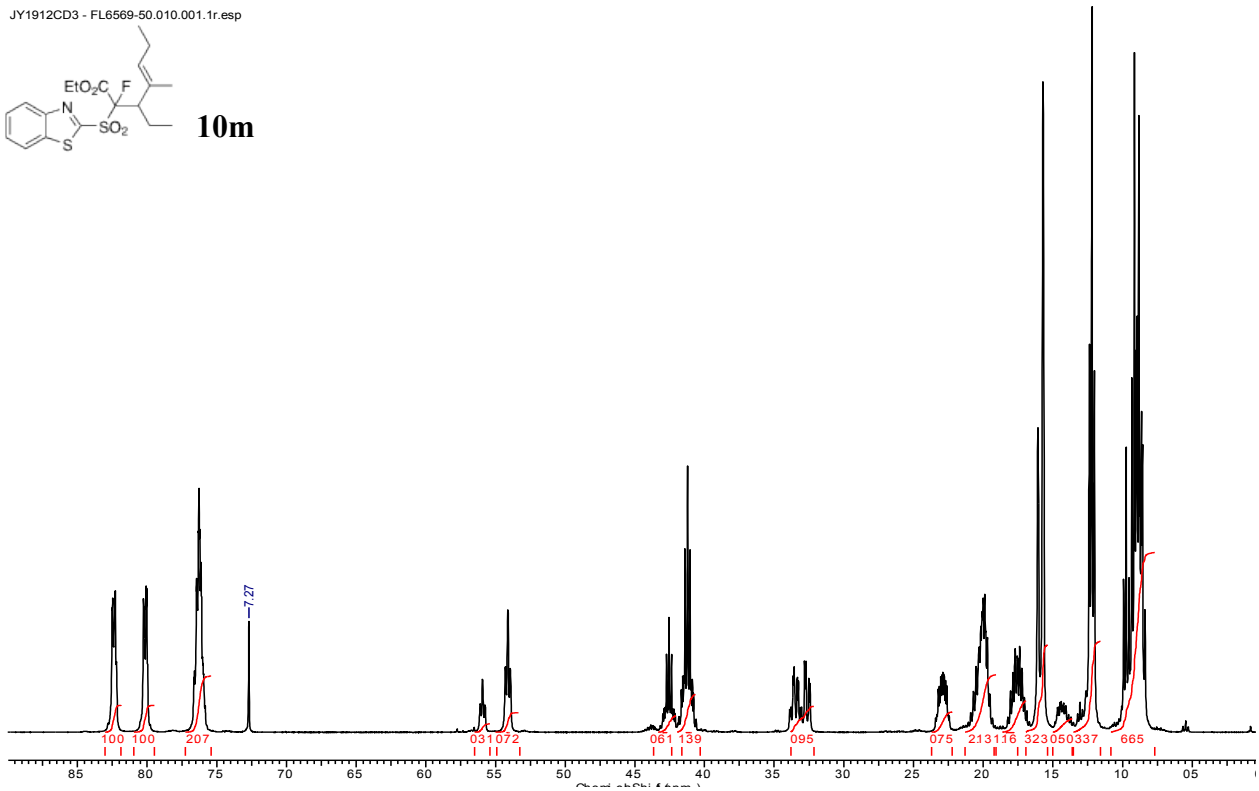


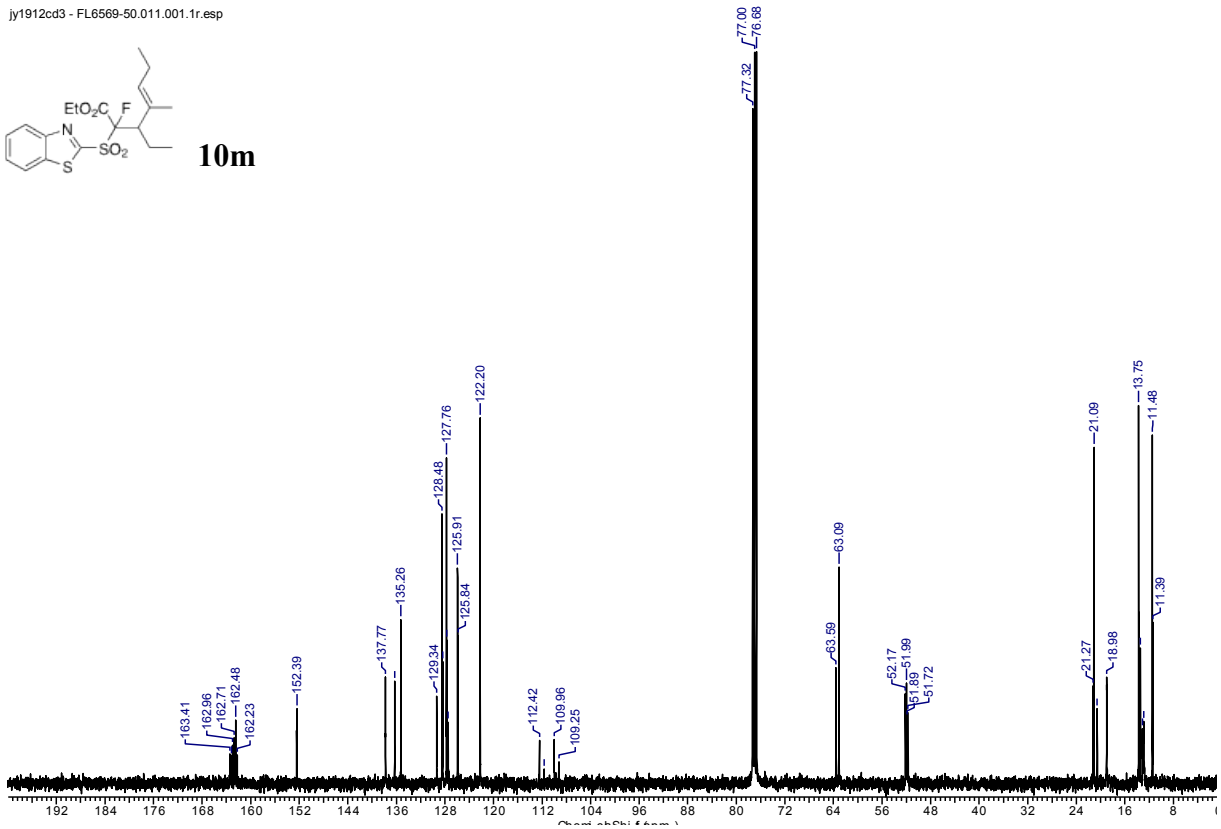

ju1512cqf5 - FL6569-11.011.001.1r.esp

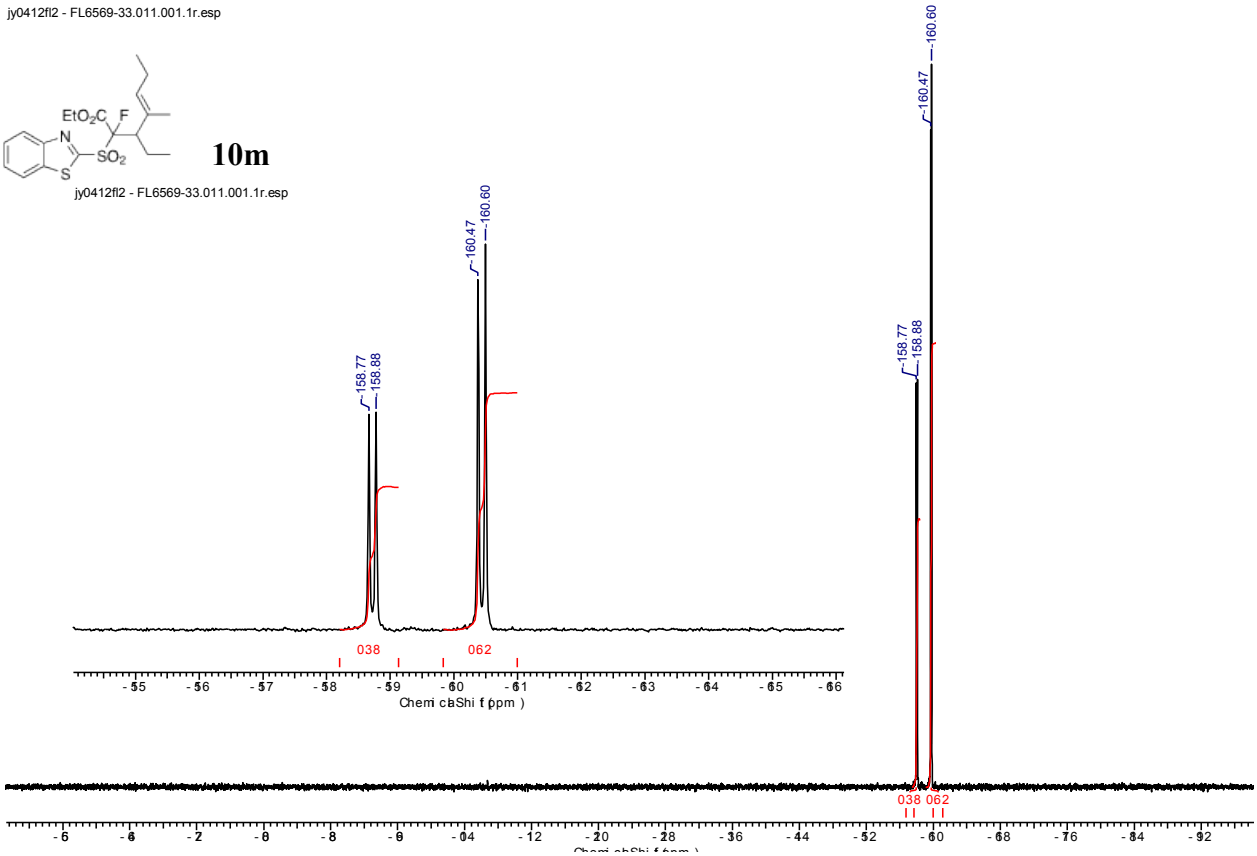


**10l**

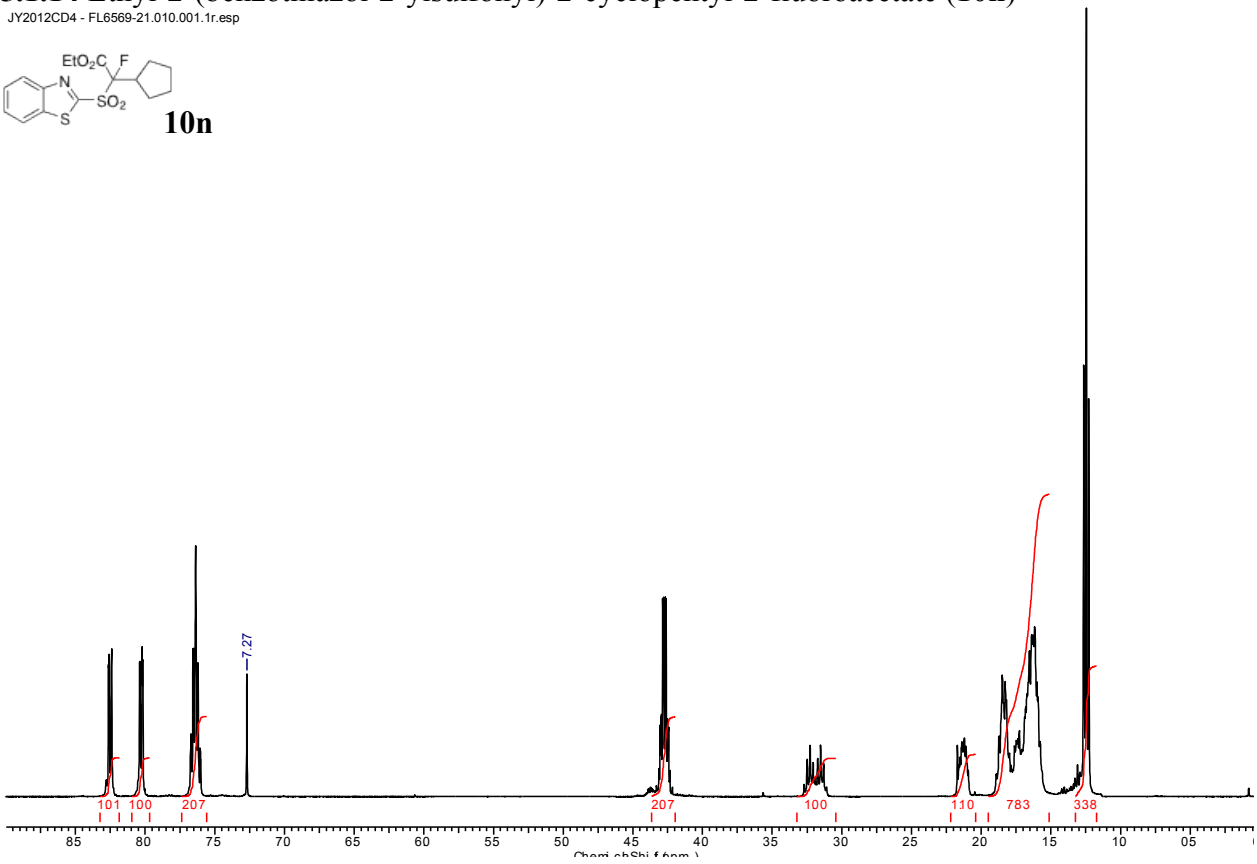
**5.1.13** (*E*)-Ethyl-2-(benzothiazol-2-ylsulfonyl)-3-ethyl-2-fluoro-4-methylhept-4-enoate (**10m**)



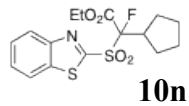






## **5.1.14** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-cyclopentyl-2-fluoroacetate (**10n**)



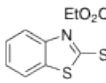
jy2012cd4 - FL6569-21.011.001.1r.esp



**10n**




ju2712fl1 - FL6569-21.011.001.1r.esp

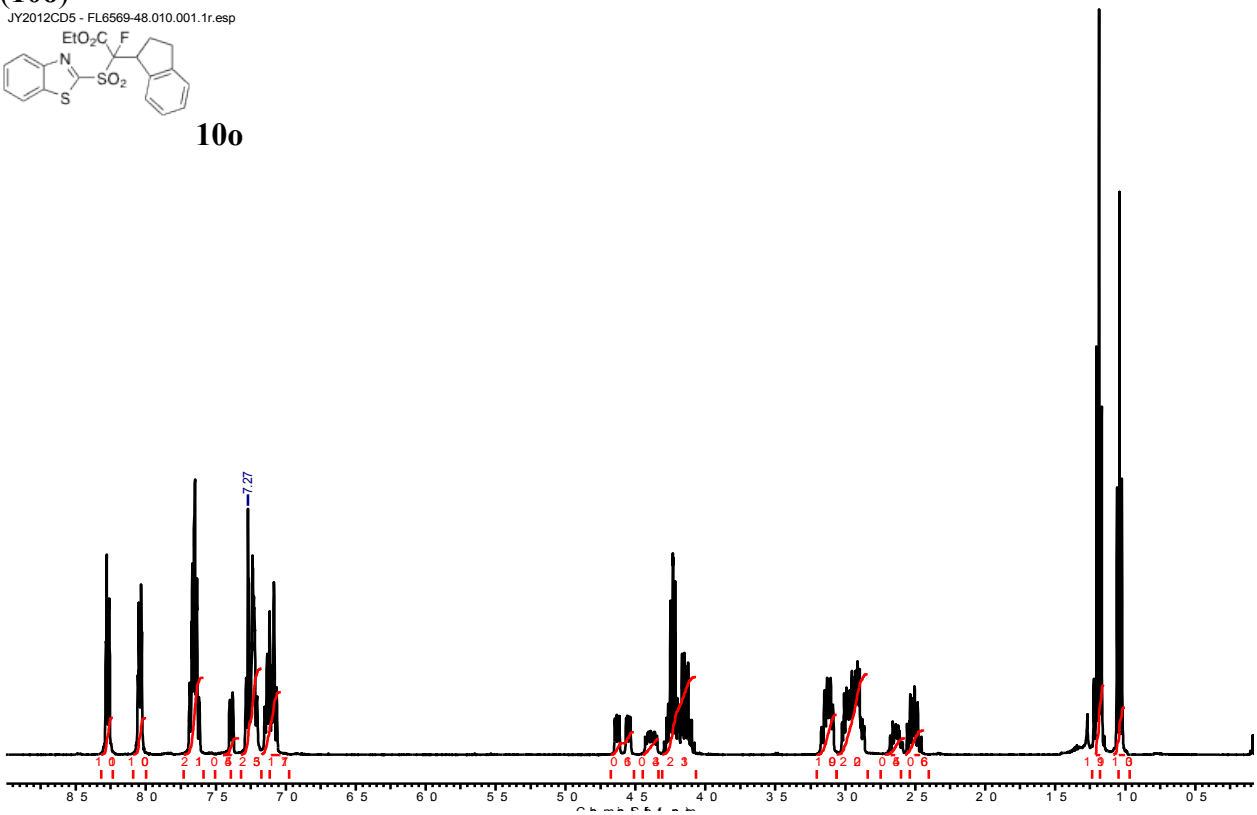


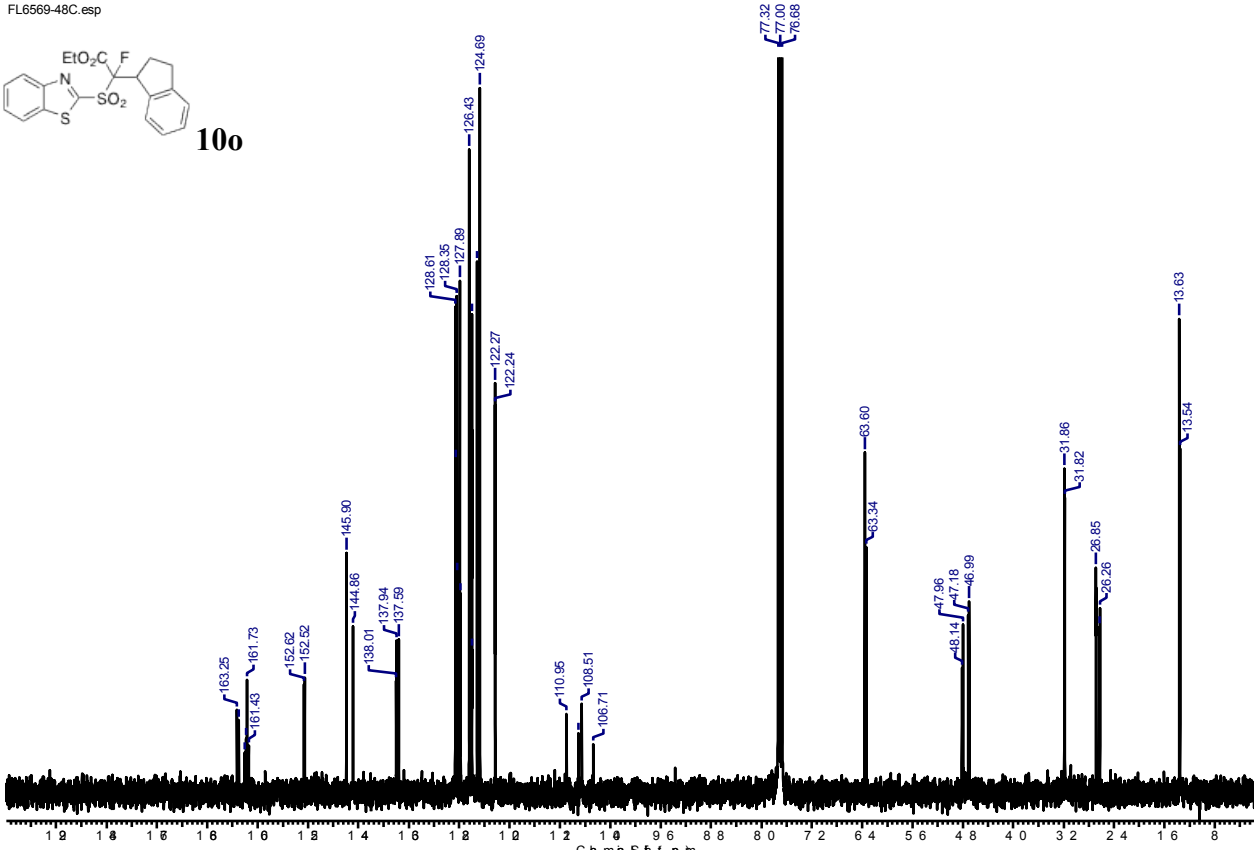
**10n**

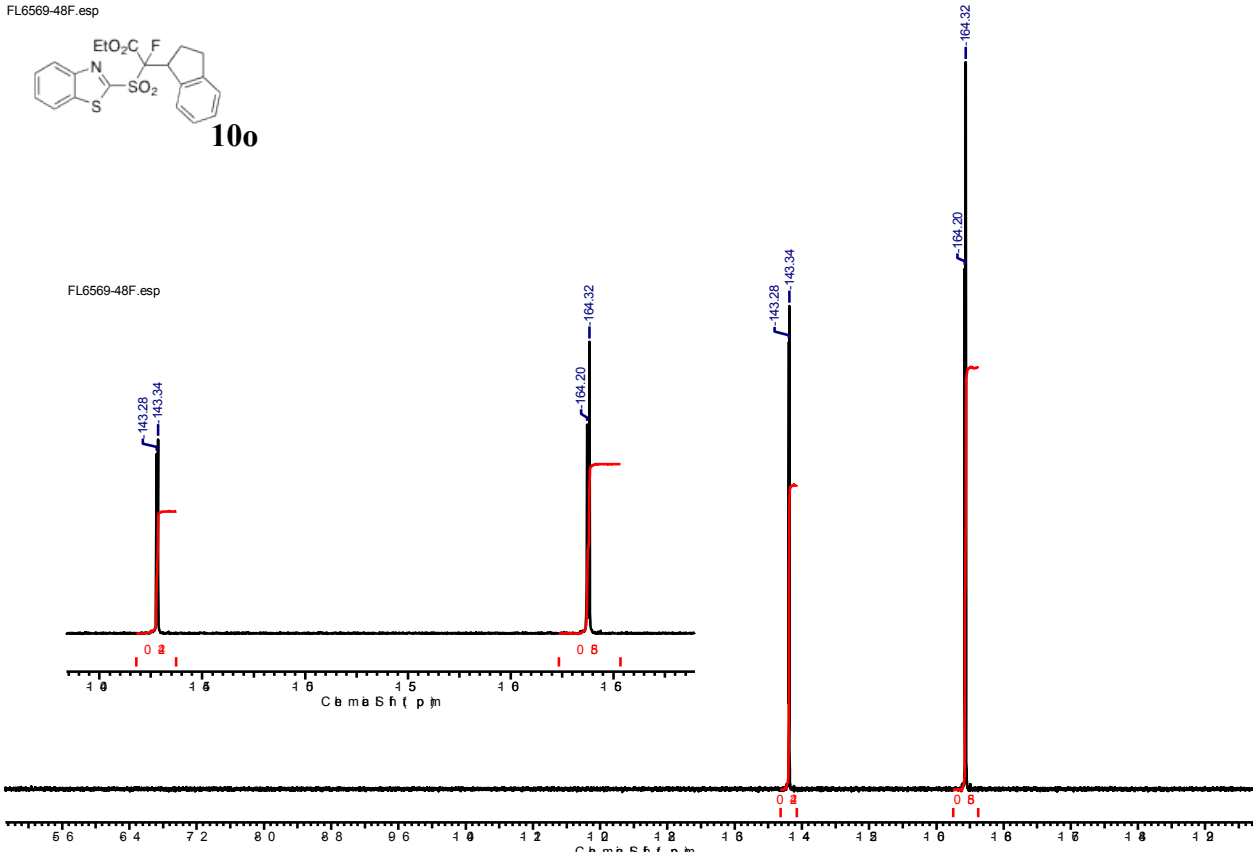



ju2712fl1 - FL6569-21.011.001.1r.esp

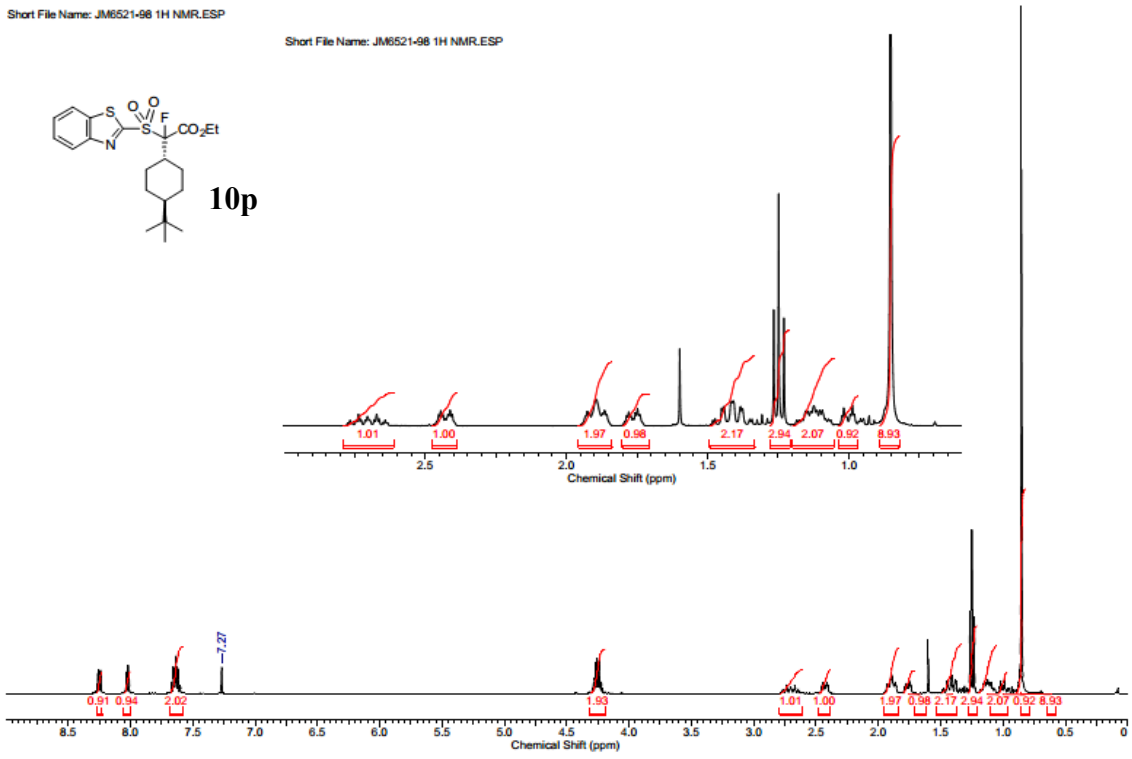
**5.1.15** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-(2,3-dihydro-1*H*-inden-1-yl)-2-fluoroacetate (**10o**)

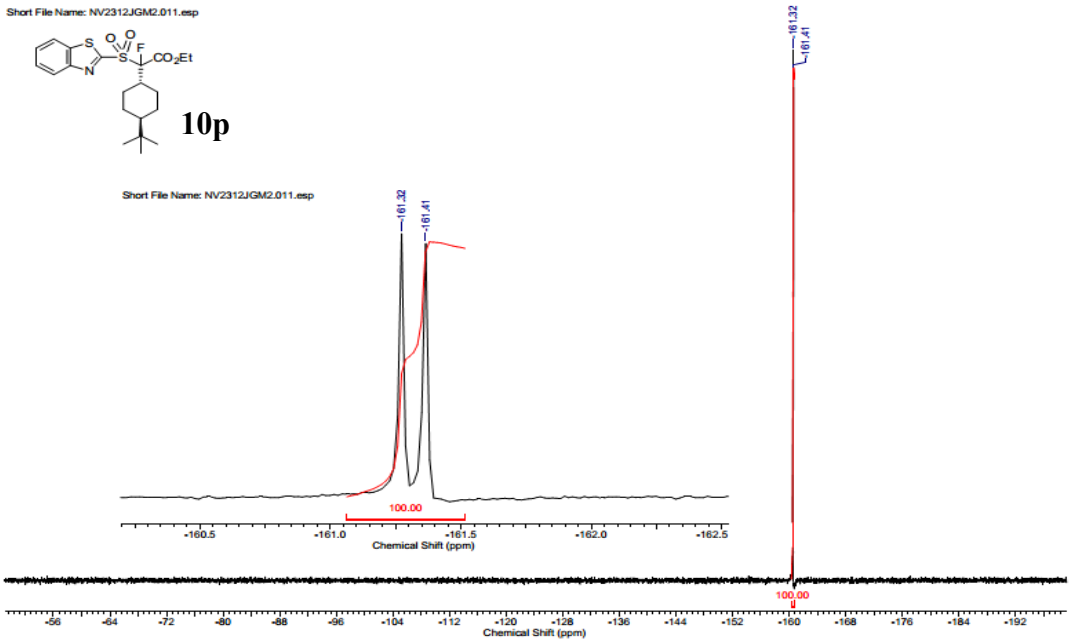


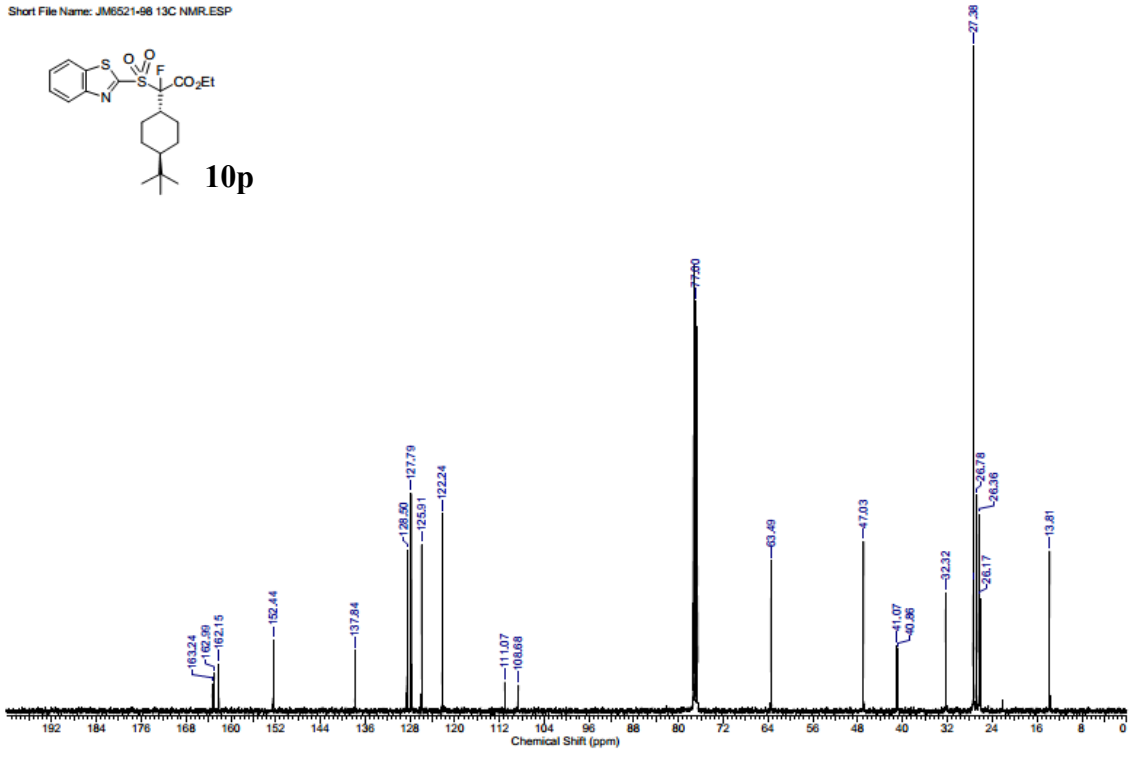





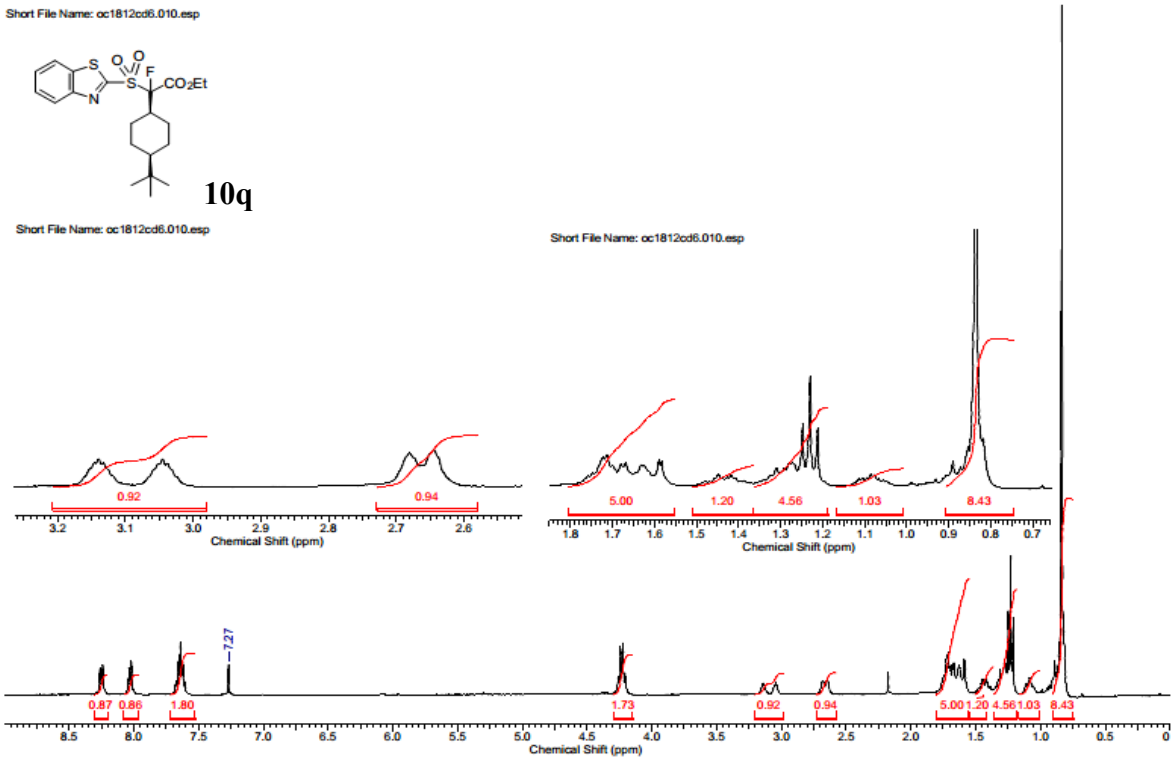

**5.1.16** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-((1*r*,4*r*)-4-*tert*-butylcyclohexyl)-2-fluoroacetate (**10p**)

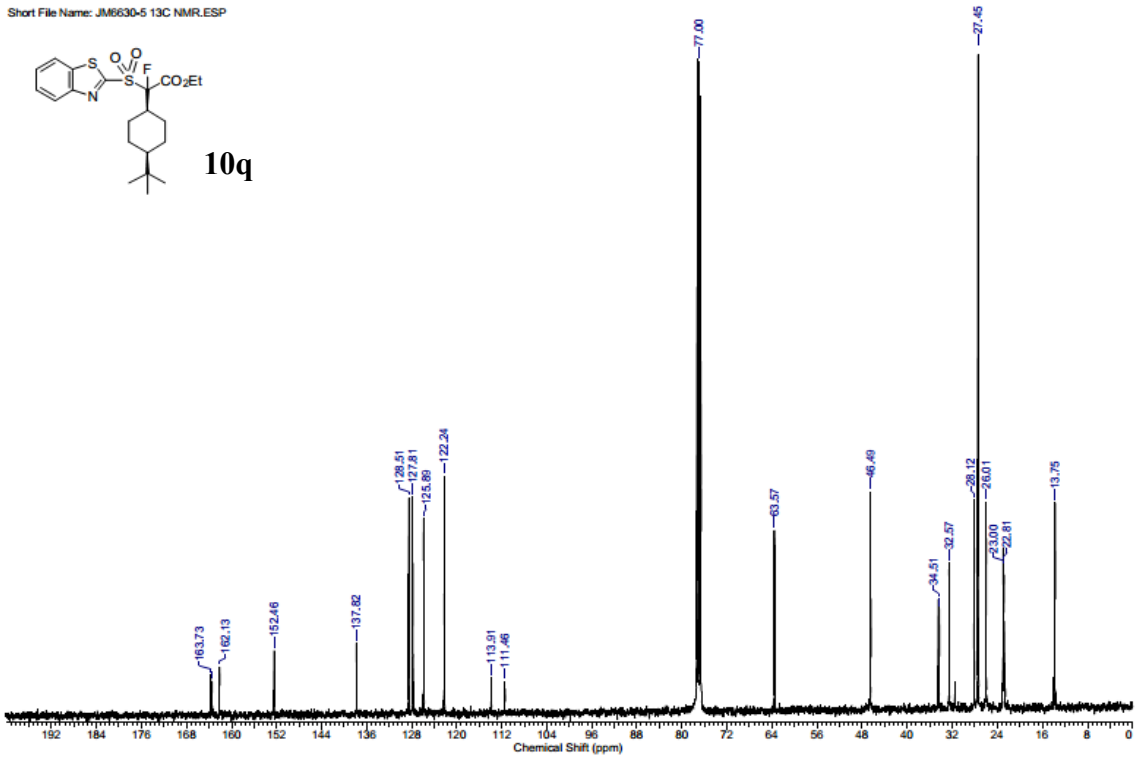


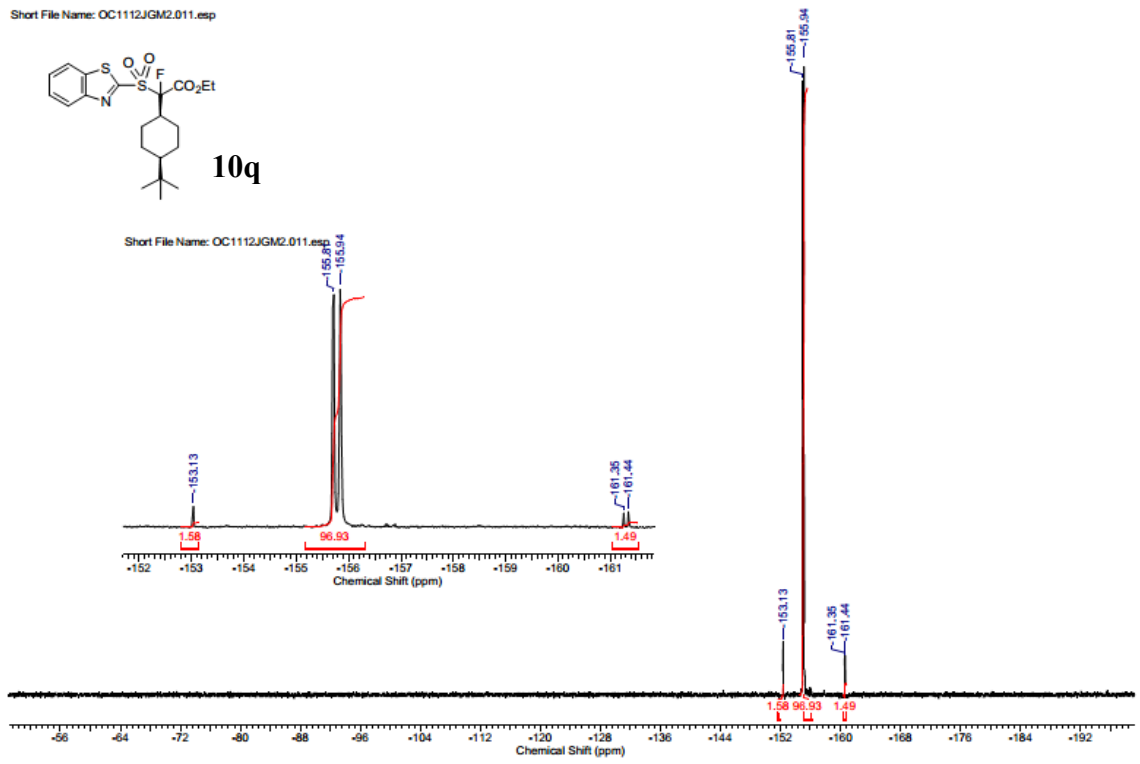

Short File Name: NV2312JGM2.011.esp
10p
Short File Name: NV2312JGM2.011.esp
161.32
161.41
100.00
Chemical Shift (ppm)
100.00
Chemical Shift (ppm)


Short File Name: JM6521-98 13C NMR.ESP
10p
163.24
162.99
162.15
152.44
137.84
128.50
127.79
125.91
122.24
111.07
109.68
77.00
63.49
47.03
41.07
40.86
32.32
27.38
26.78
26.36
26.17
13.81
Chemical Shift (ppm)

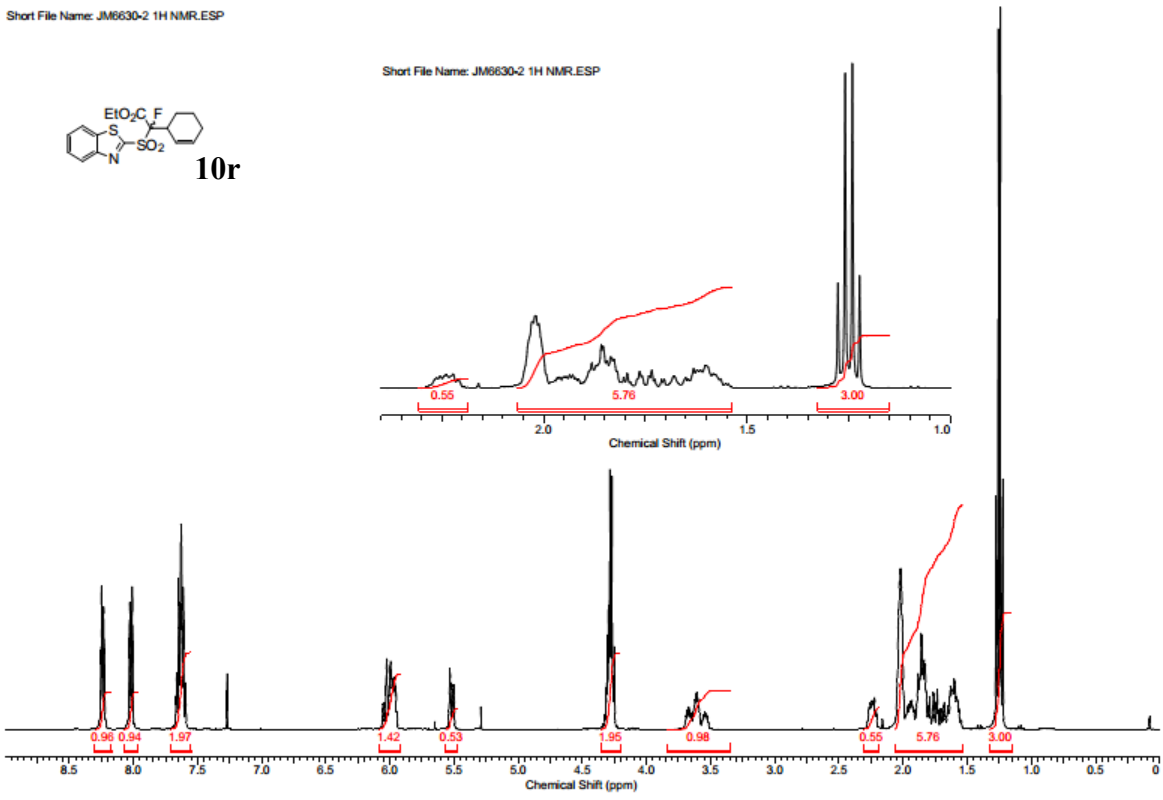
**5.1.17** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-((1*s*,4*s*)-4-*tert*-butylcyclohexyl)-2-fluoroacetate (**10q**)

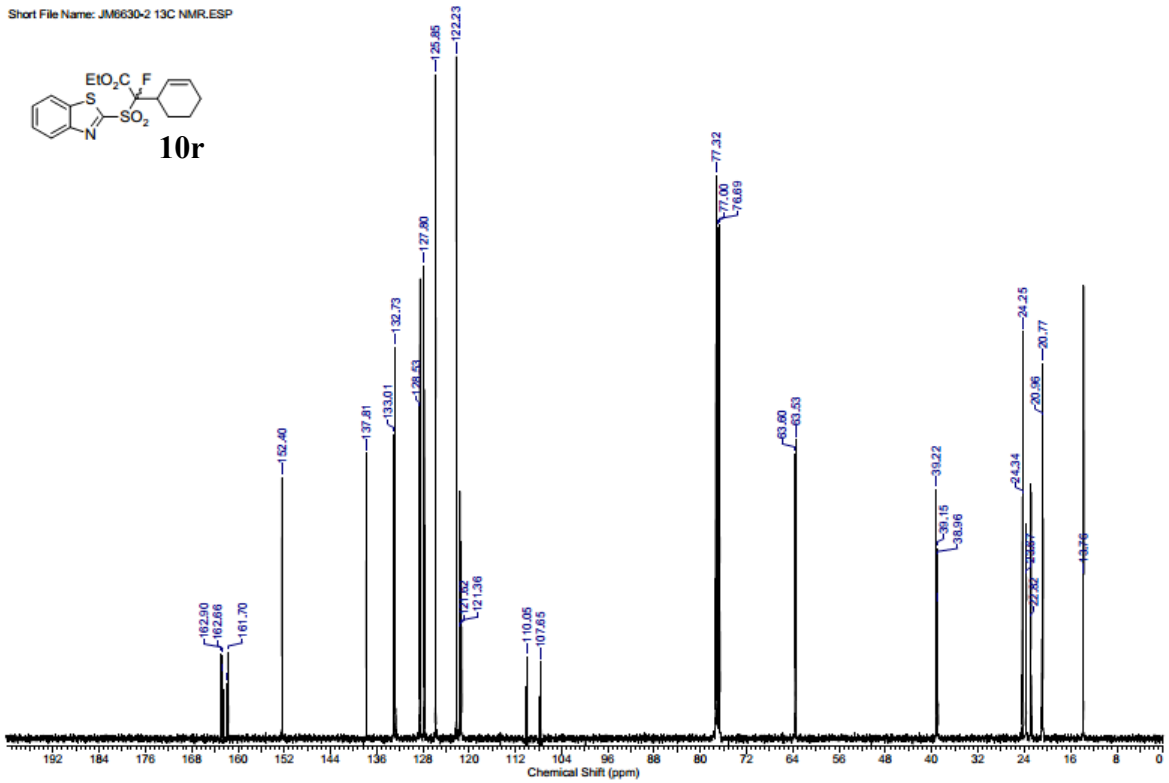


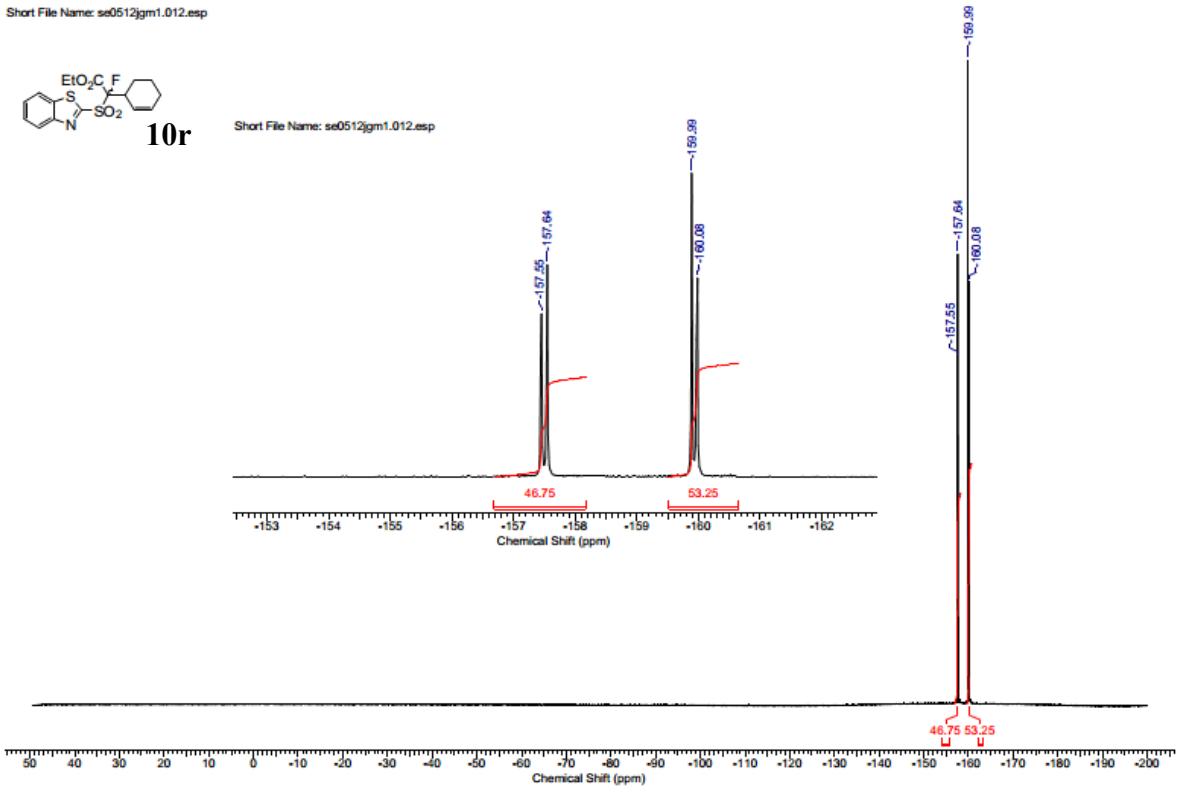






**5.1.18** Ethyl-2-(benzothiazol-2-ylsulfonyl)-2-(cyclohex-2-enyl)-2-fluoroacetate (**10r**)

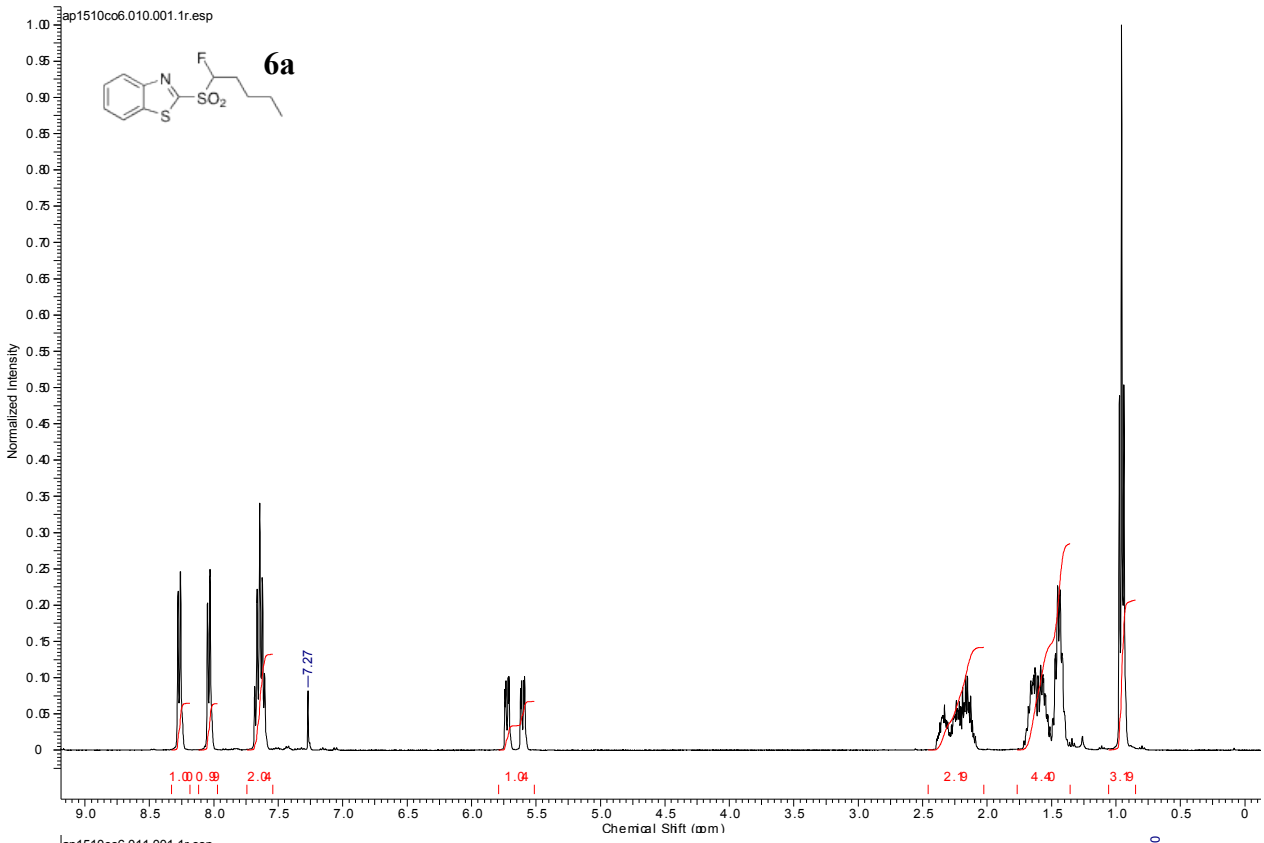


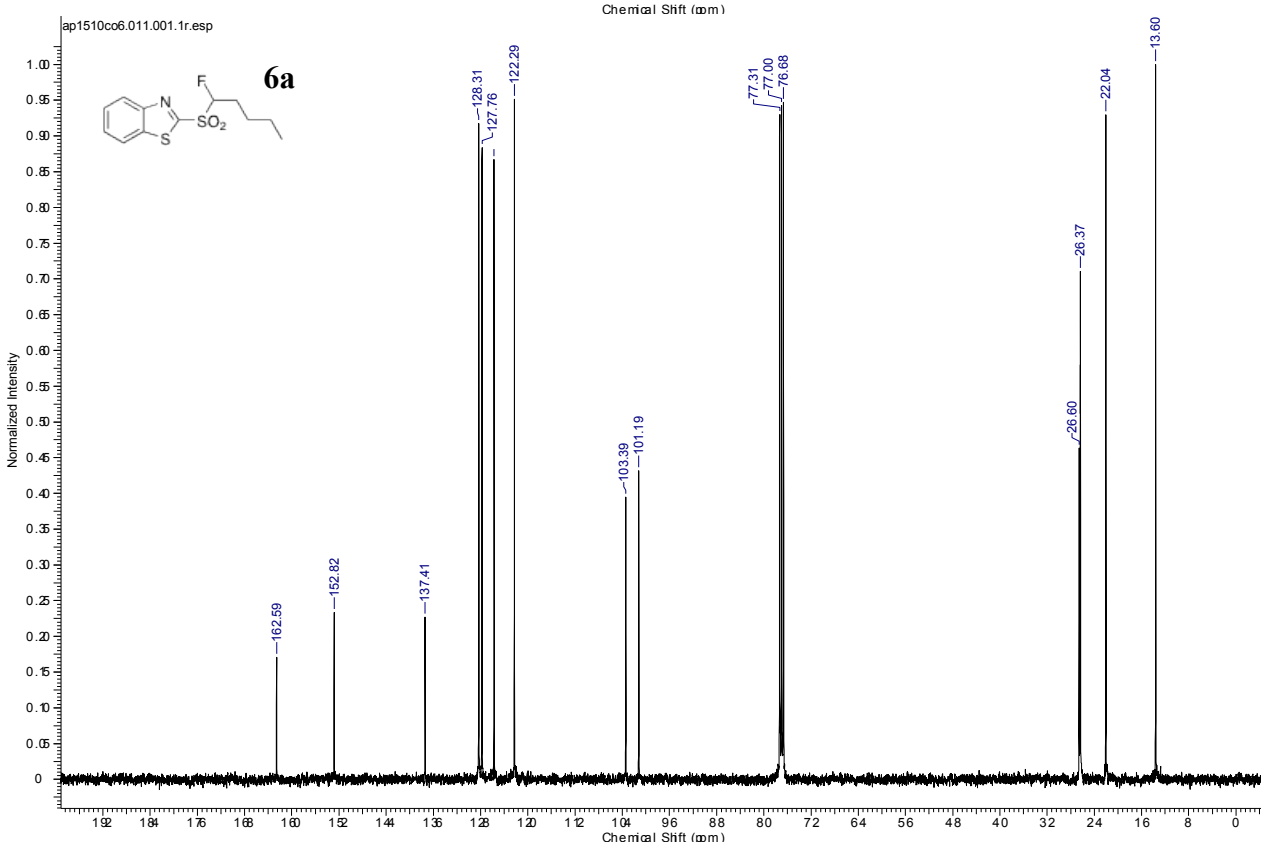

Short File Name: JM6630-2 13C NMR.ESP
10r
Chemical Shift (ppm)

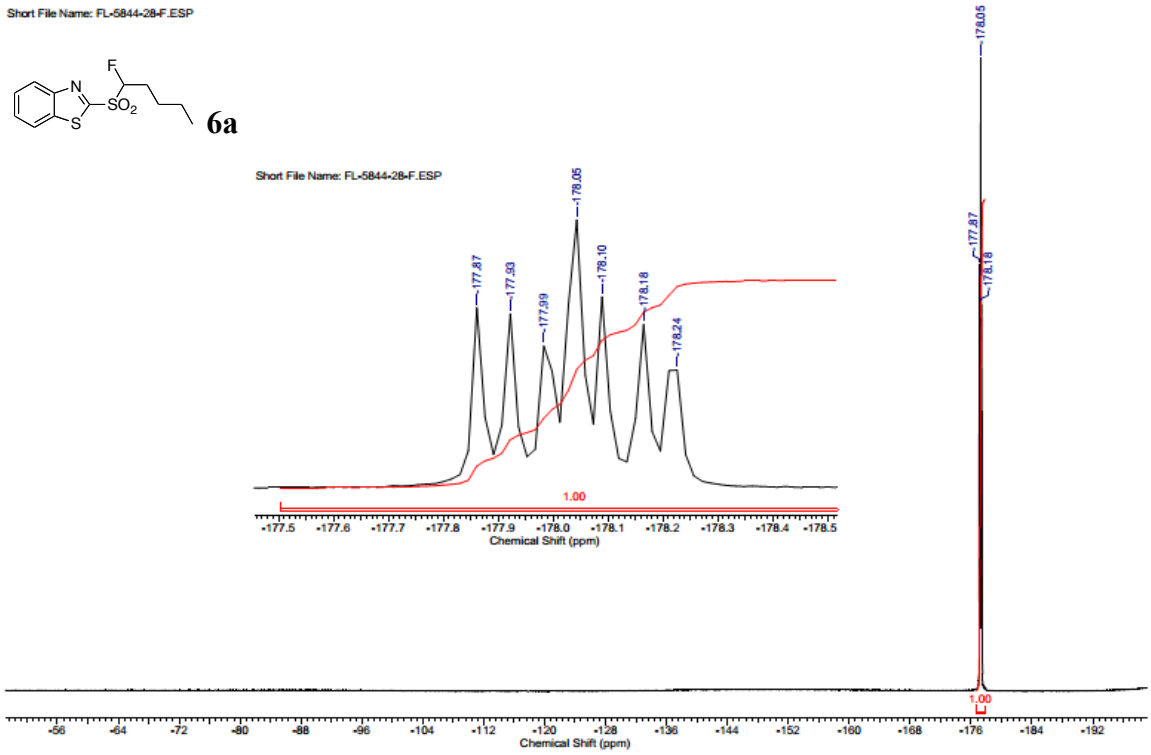

Short File Name: se0512jgm1.012.esp
10r
Short File Name: se0512jgm1.012.esp
46.75
53.25
Chemical Shift (ppm)
46.75 53.25
Chemical Shift (ppm)

**5.2** The Krapcho decarboxylation reaction leading to **6** (Table 1)

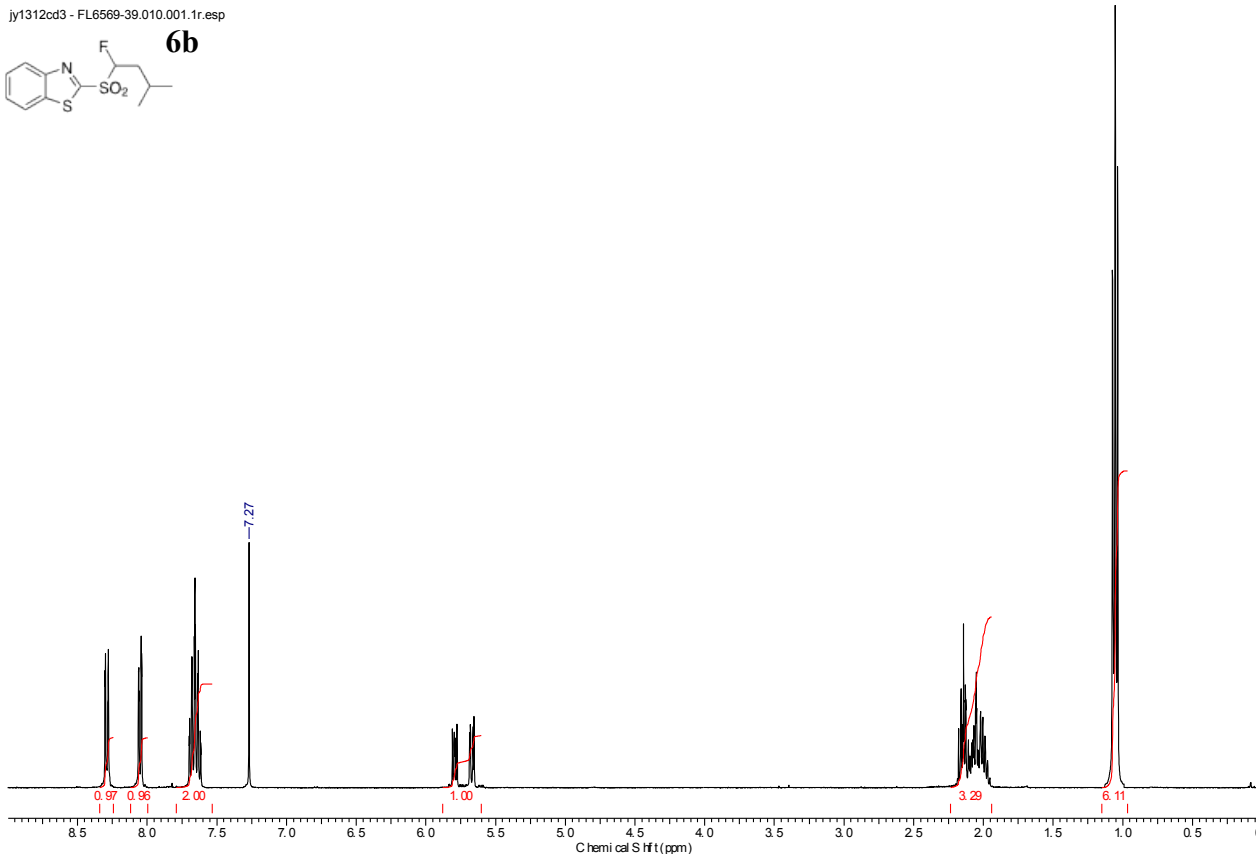
**5.2.1** 2-(1-fluoropentylsulfonyl)benzothiazole (**6a**)



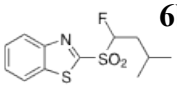



**5.2.2** 2-(1-fluoro-3-methylbutylsulfonyl)benzothiazole (**6b**)



jy1312cd3 - FL6569-39.011.001.1r.esp

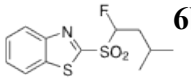
**6b**





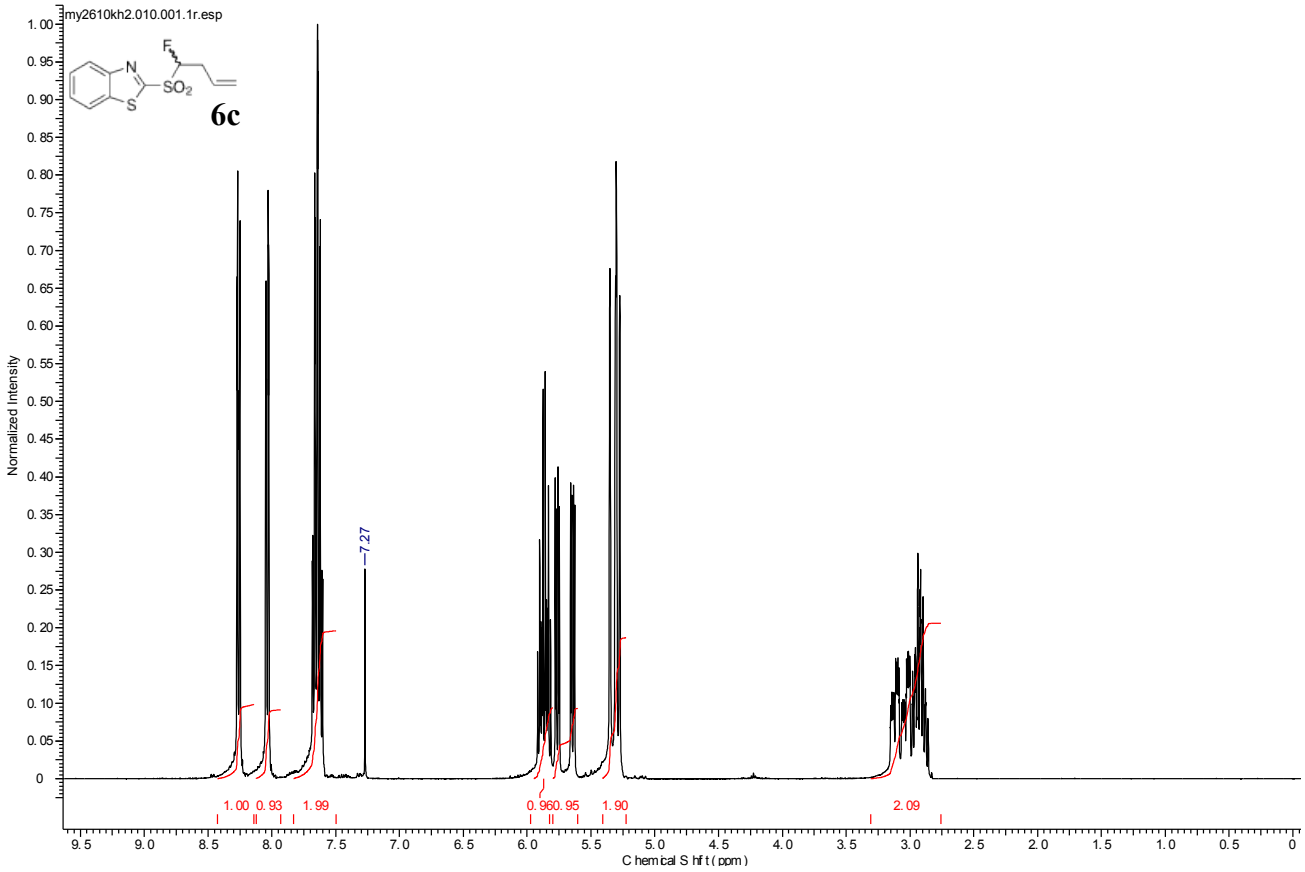

JY1212FL1 - FL6569-39.011.001.1r.esp

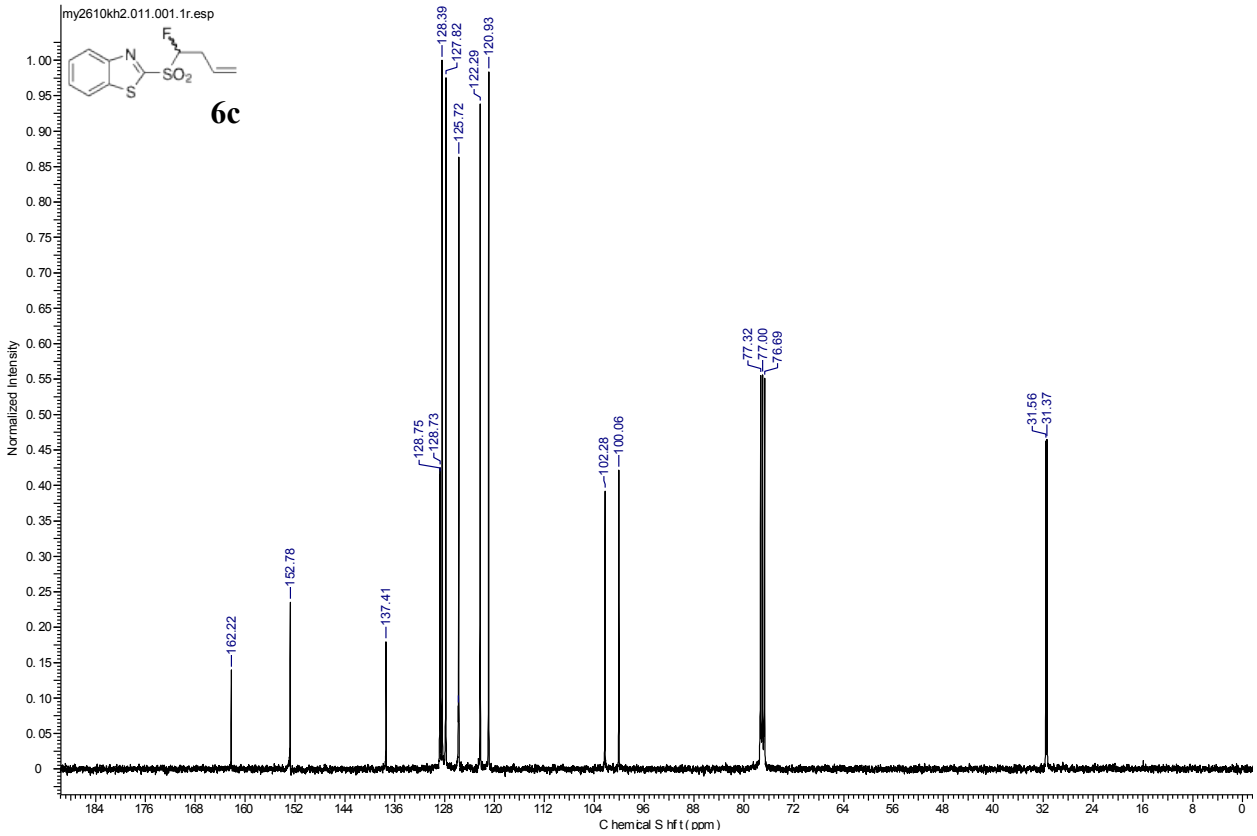
**6b**

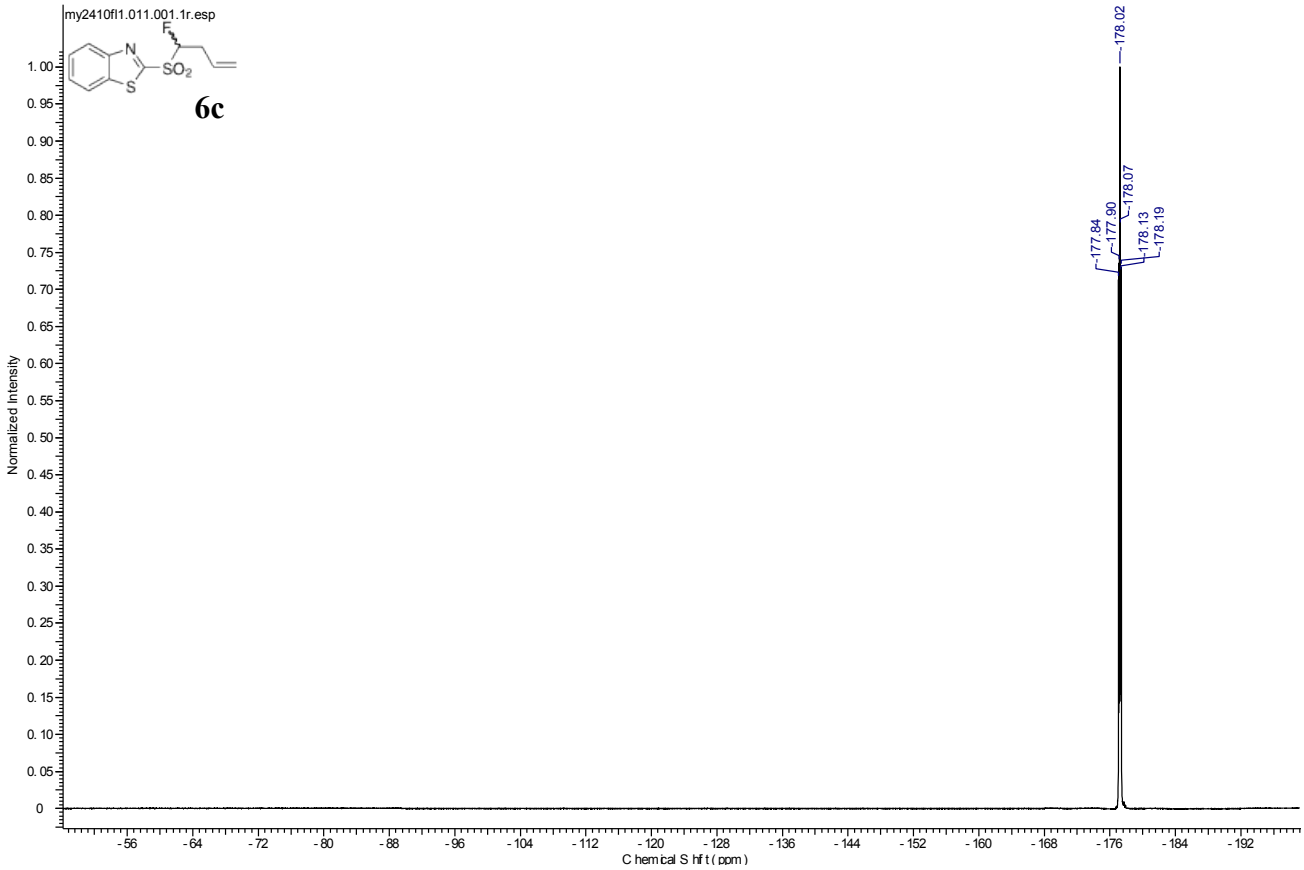


JY1212FL1 - FL6569-39.011.001.1r.esp

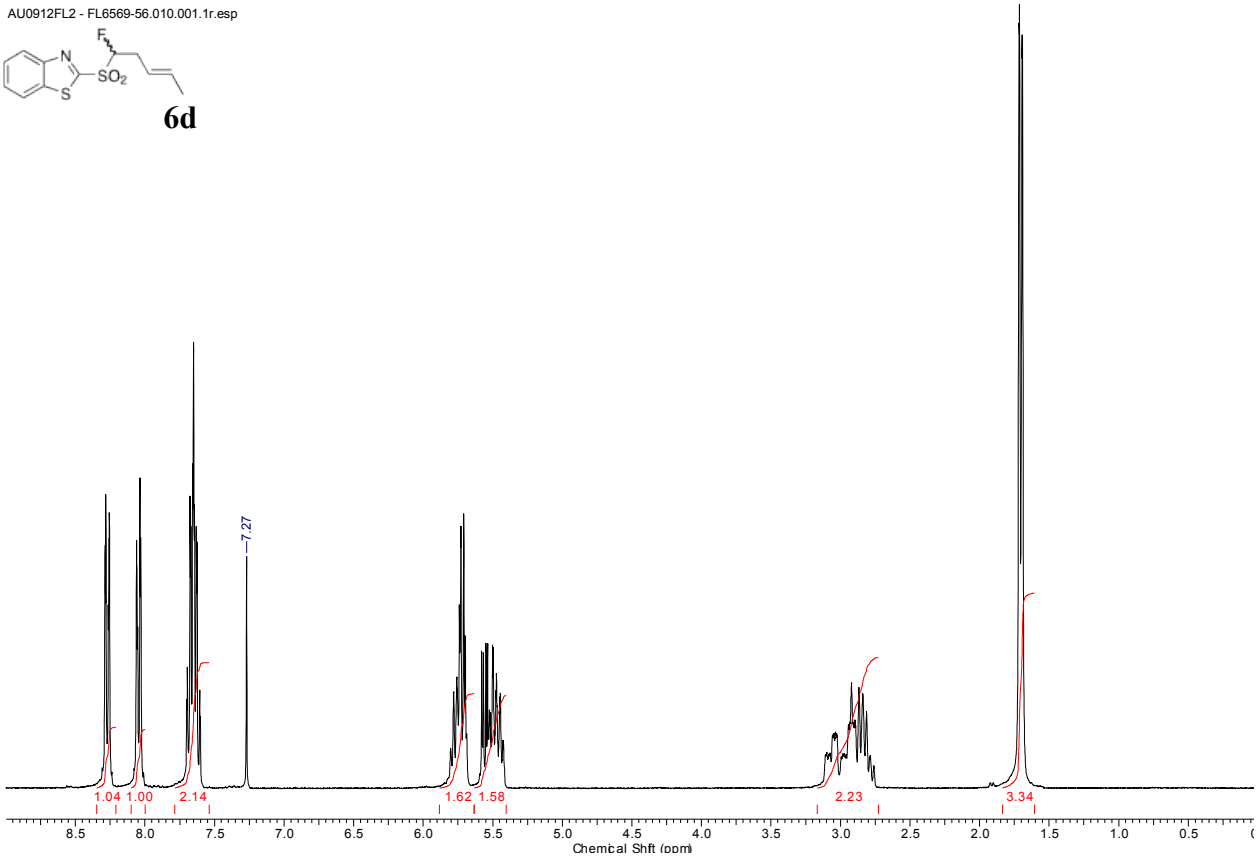
**5.2.3** 2-(1-fluorobut-3-enylsulfonyl)benzothiazole (**6c**)



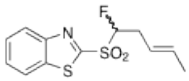






**5.2.4** (*E*)-2-(1-fluoropent-3-enylsulfonyl)benzothiazole (**6d**)



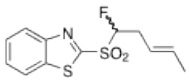
au0912fl2 - FL6569-56.011.001.1r.esp



**6d**



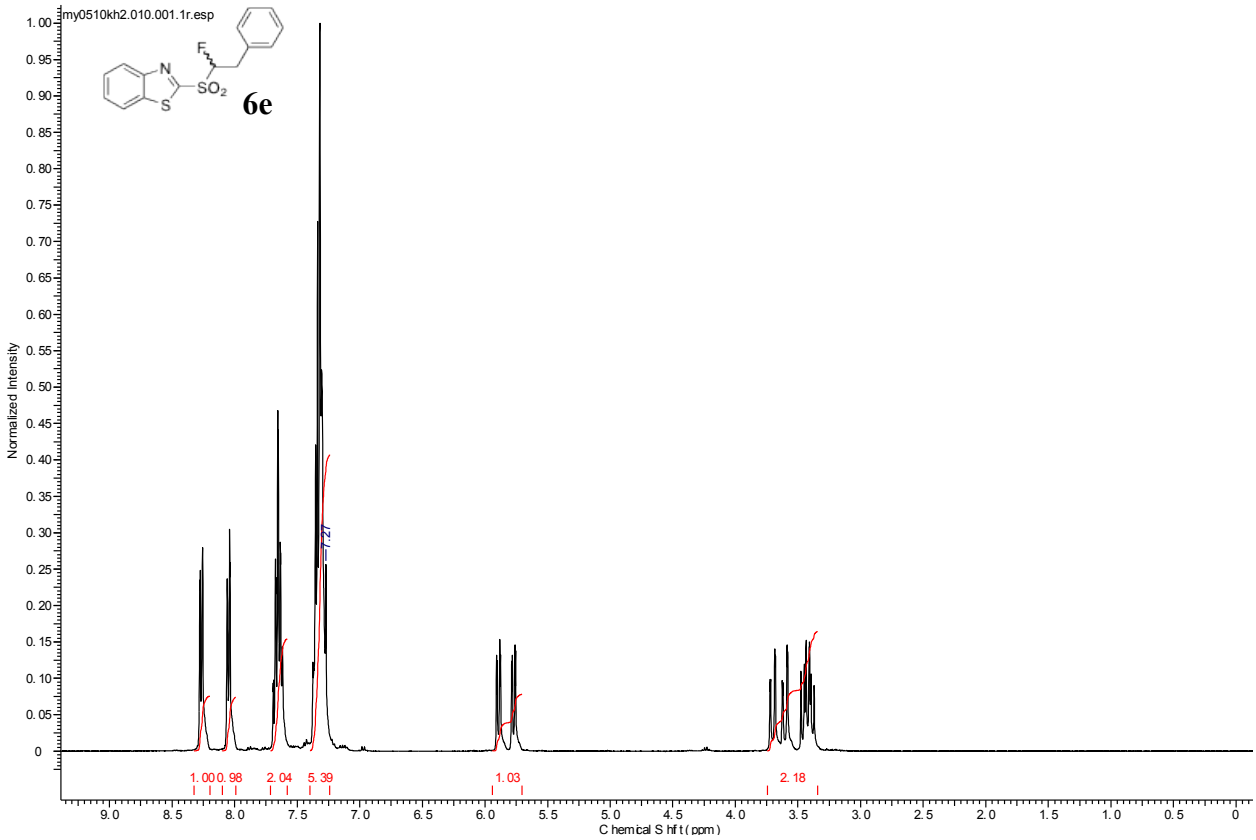

au0912fl2 - FL6569-56.013.001.1r.esp

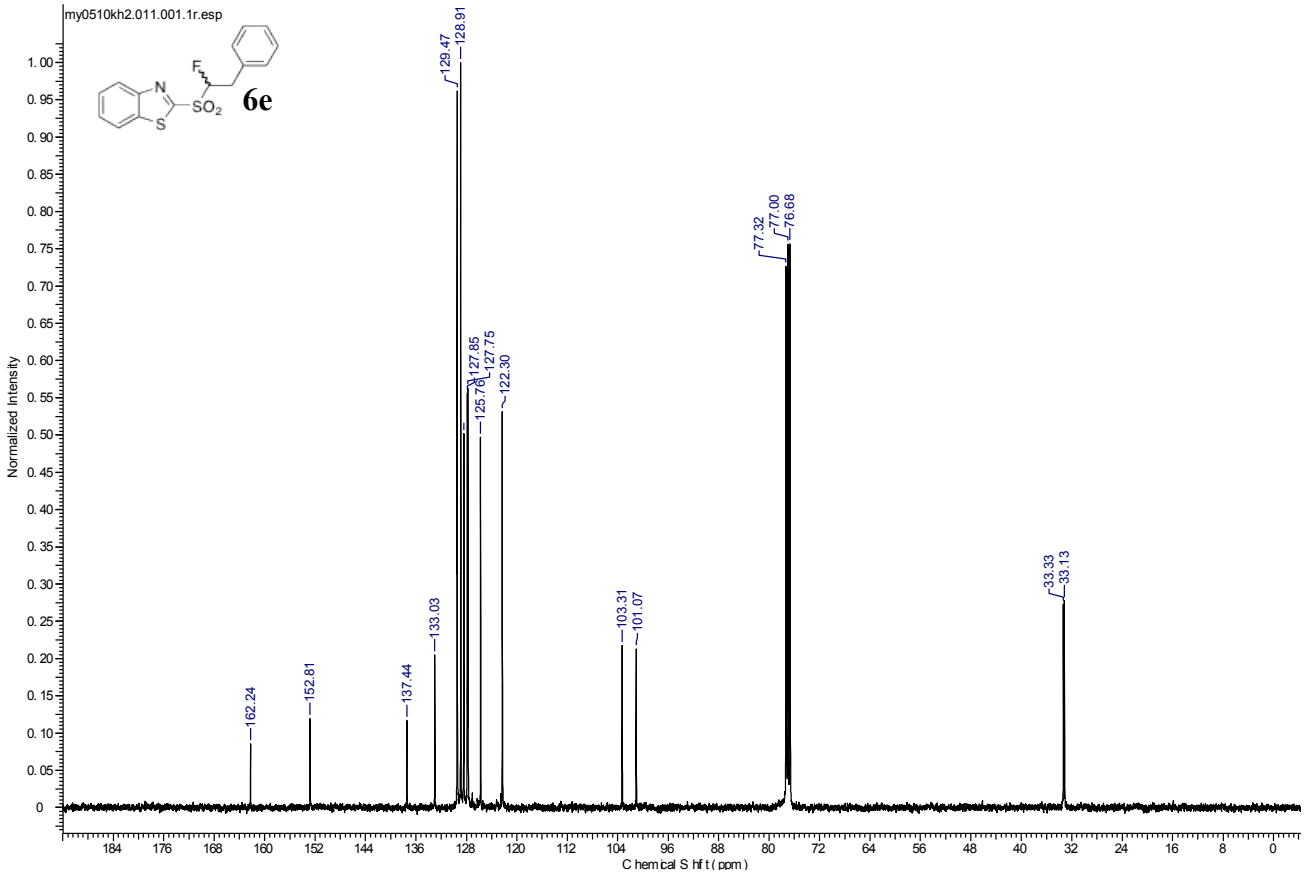


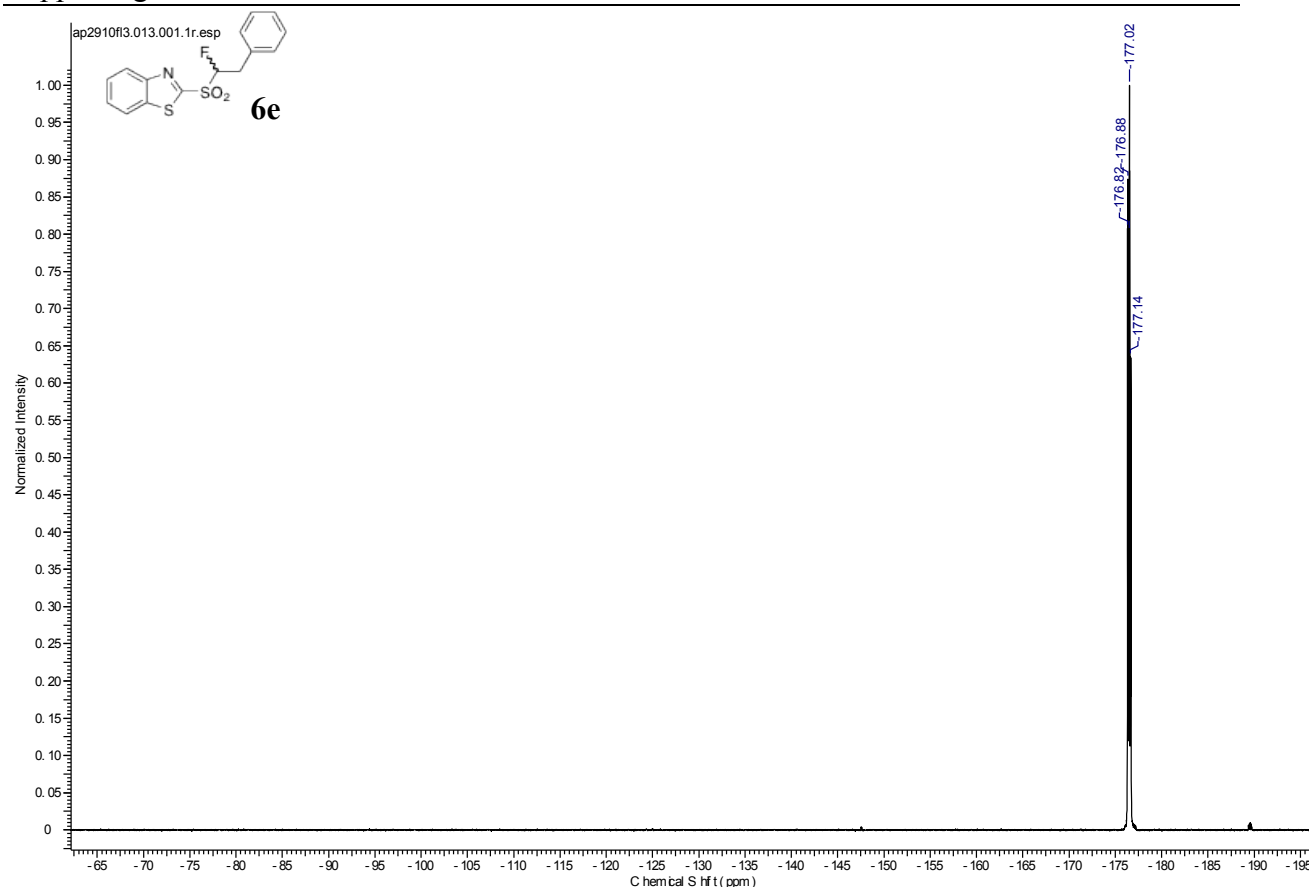
**6d**

au0912fl2 - FL6569-56.013.001.1r.esp

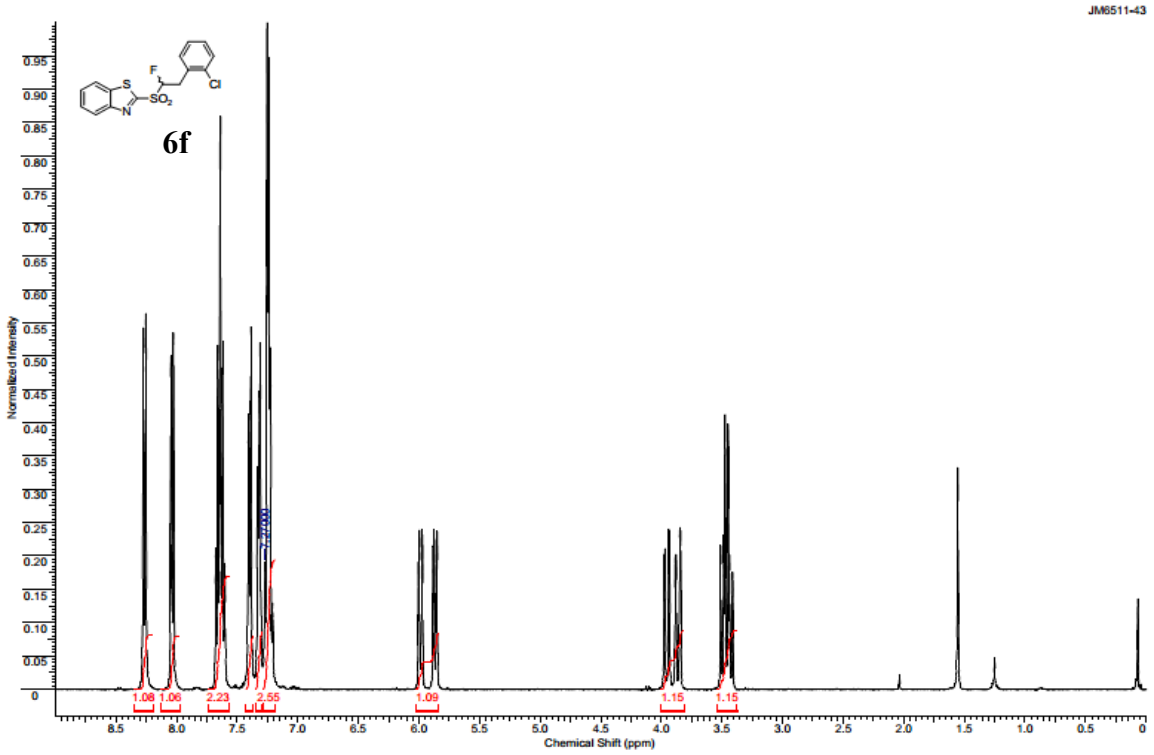
**5.2.5** 2-(1-fluoro-2-phenlethylsulfonyl)benzothiazole (**6e**)

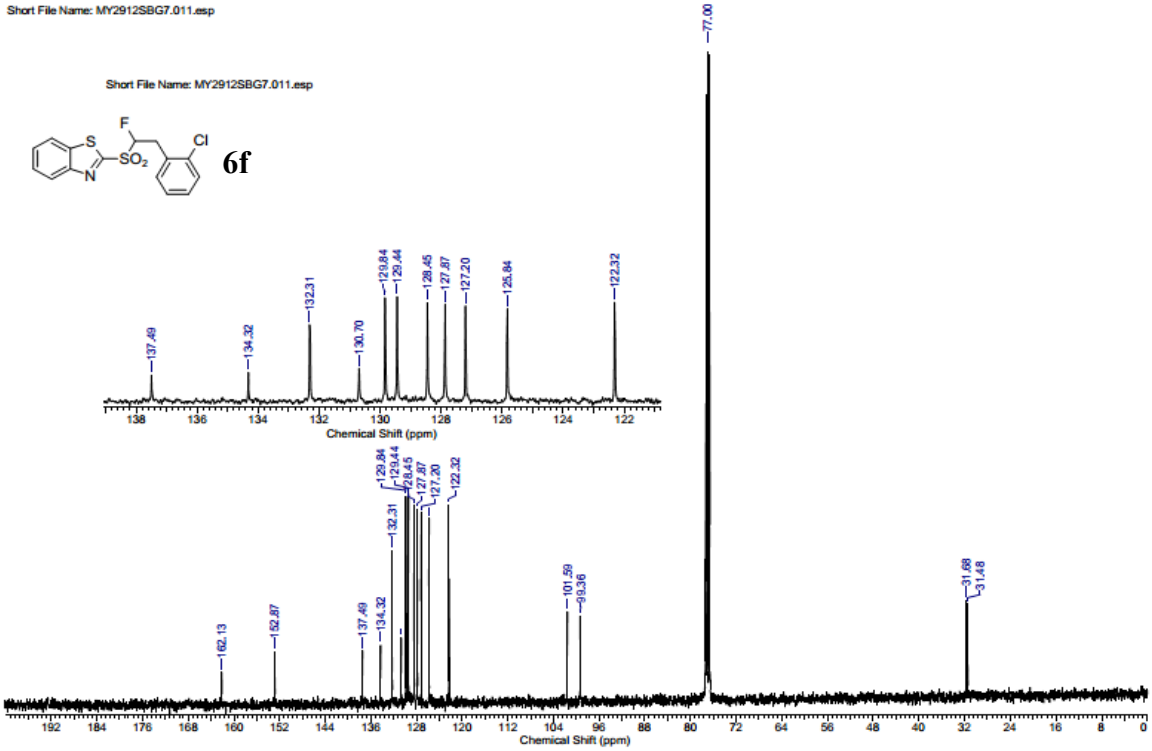





**5.2.6** 2-(2-(2-chlorophenyl)-1-fluoroethylsulfonyl)benzothiazole (**6f**)

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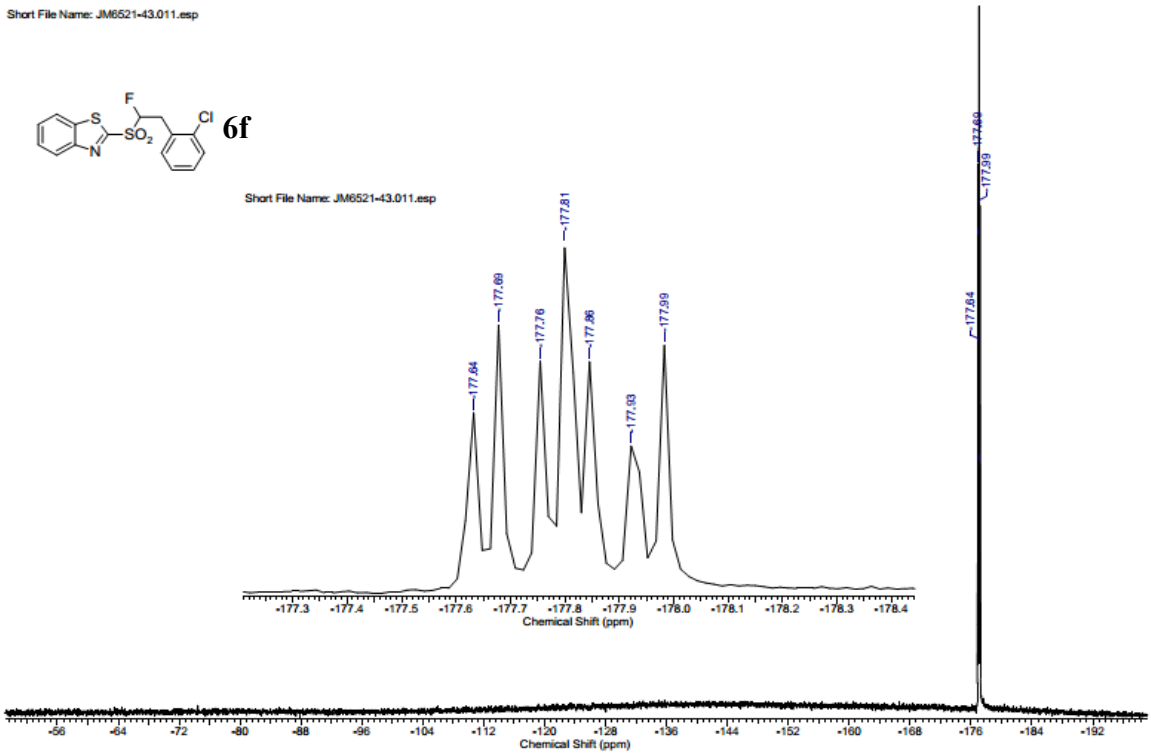
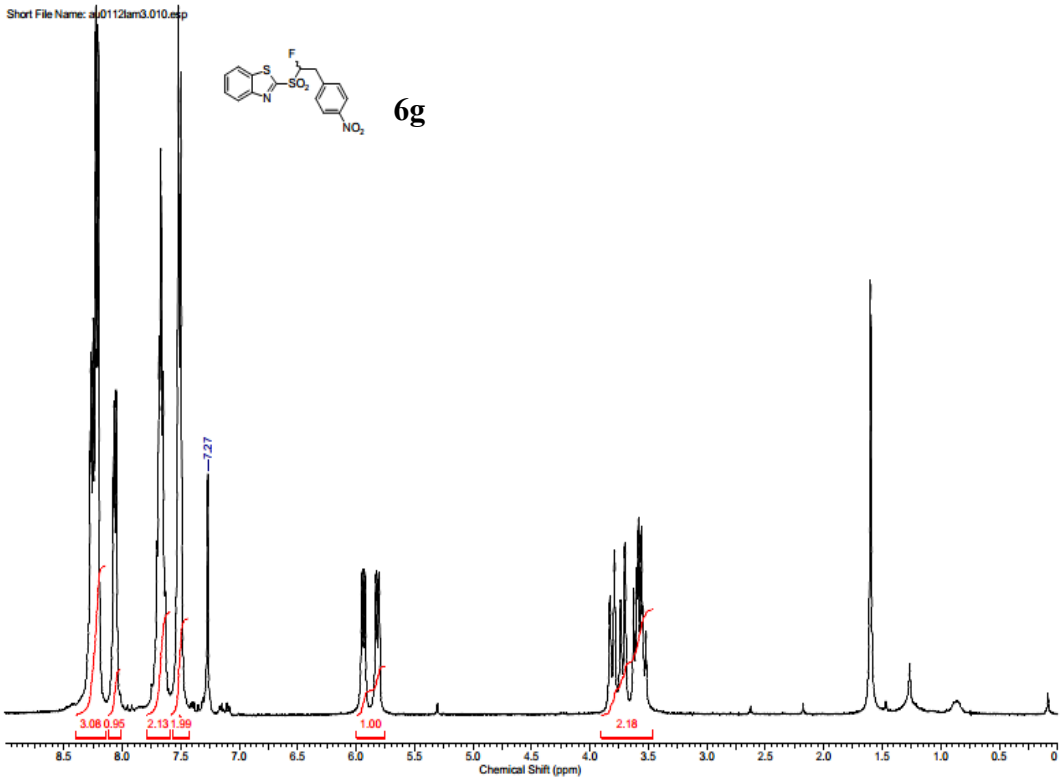
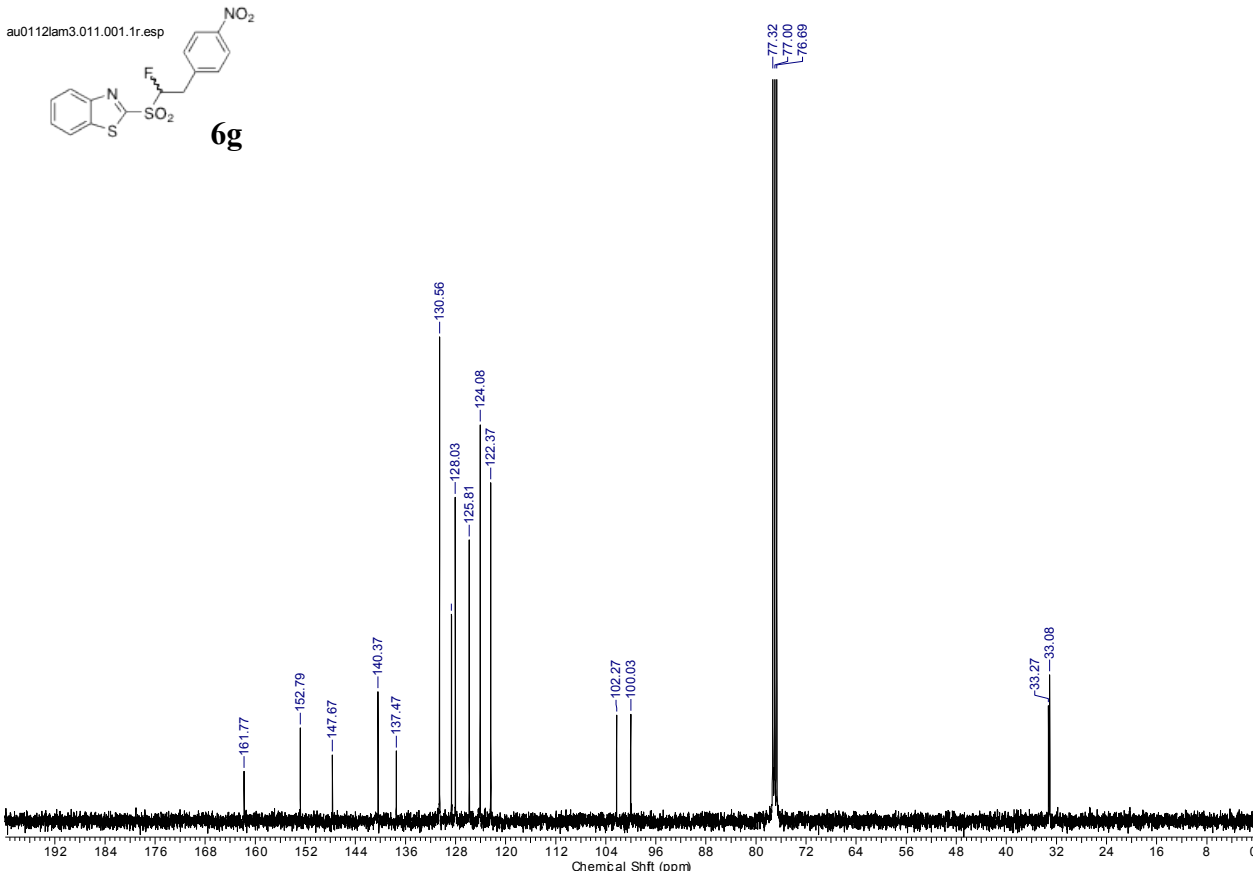
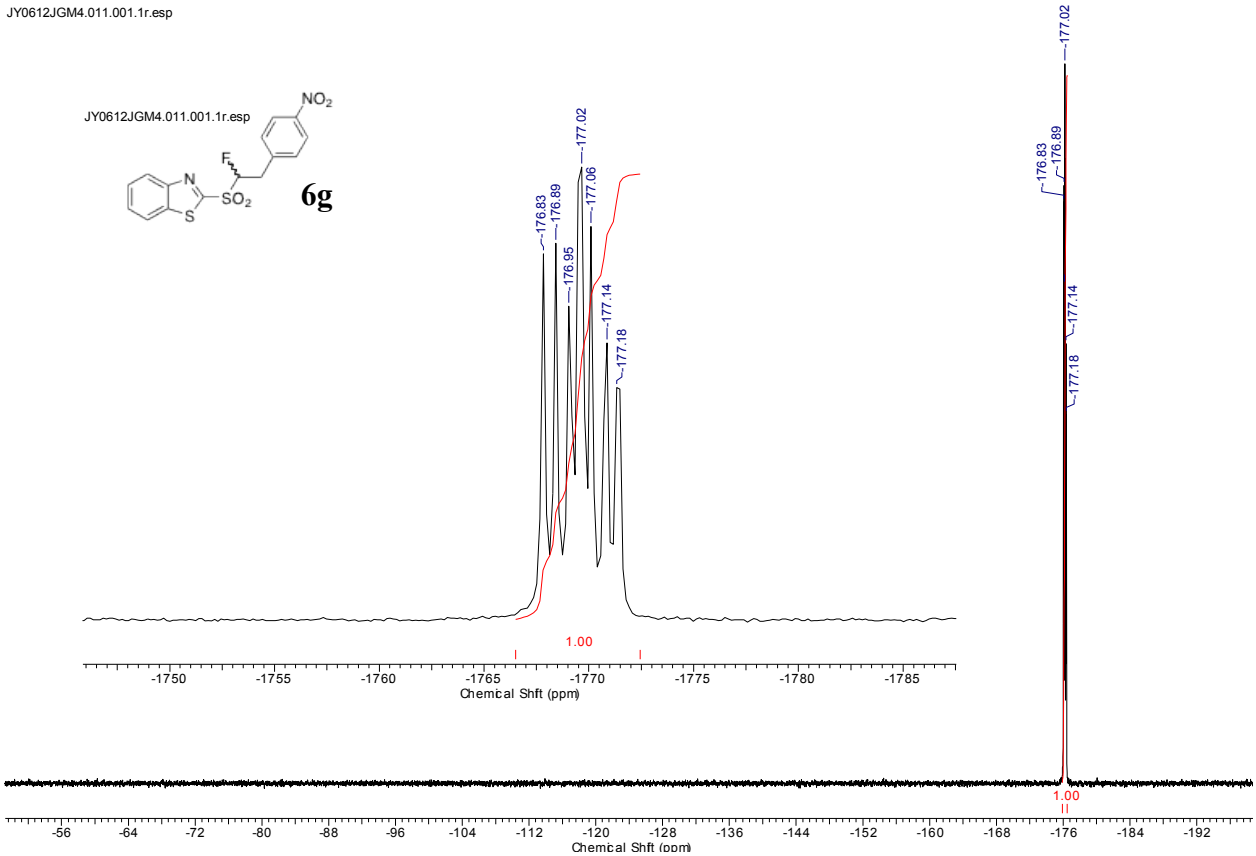
Short File Name: MY2912SBG7.011.esp
6f
Chemical Shift (ppm)
Chemical Shift (ppm)


Short File Name: JM6521-43.011.esp
6f
Short File Name: JM6521-43.011.esp
Chemical Shift (ppm)
Chemical Shift (ppm)

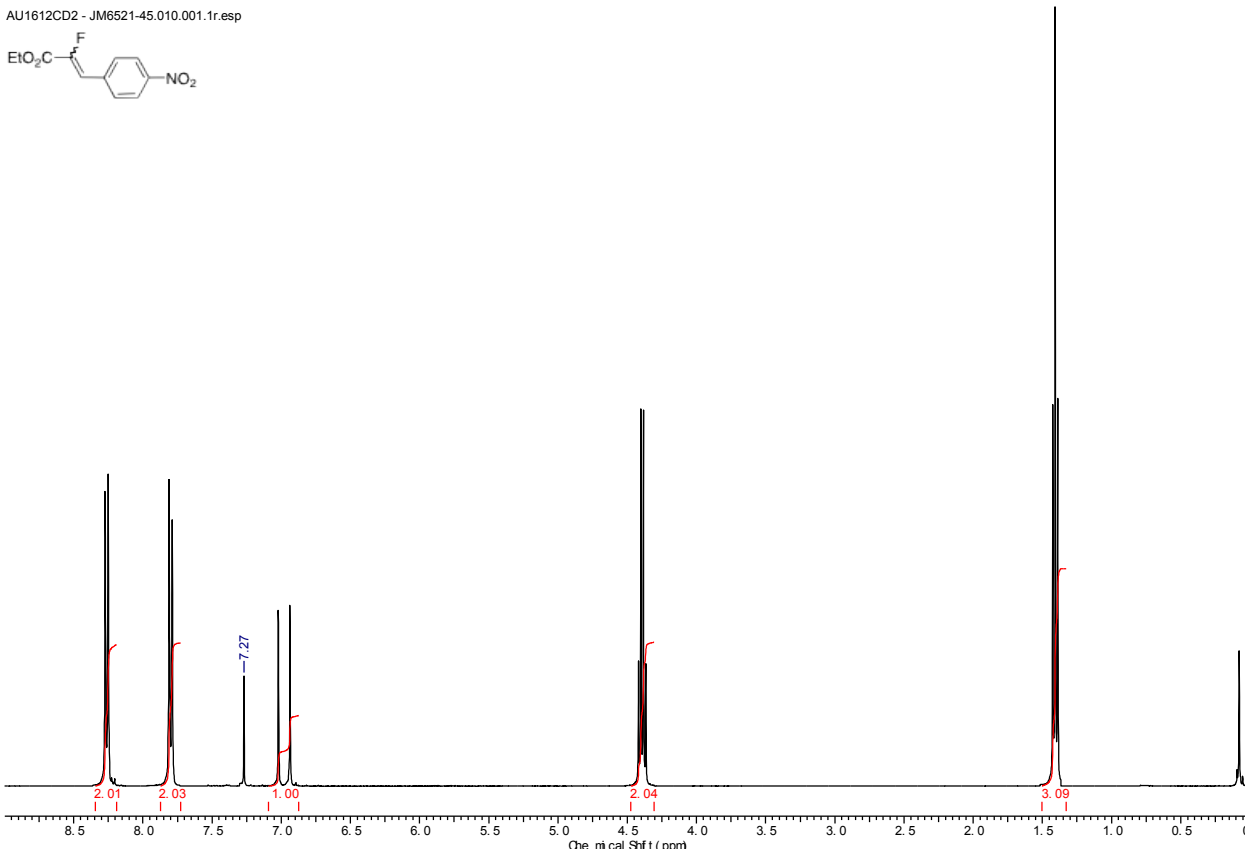
**5.2.7a** 2-(1-fluoro-2-(4-nitrophenyl)ethylsulfonyl)benzothiazole (**6g**)

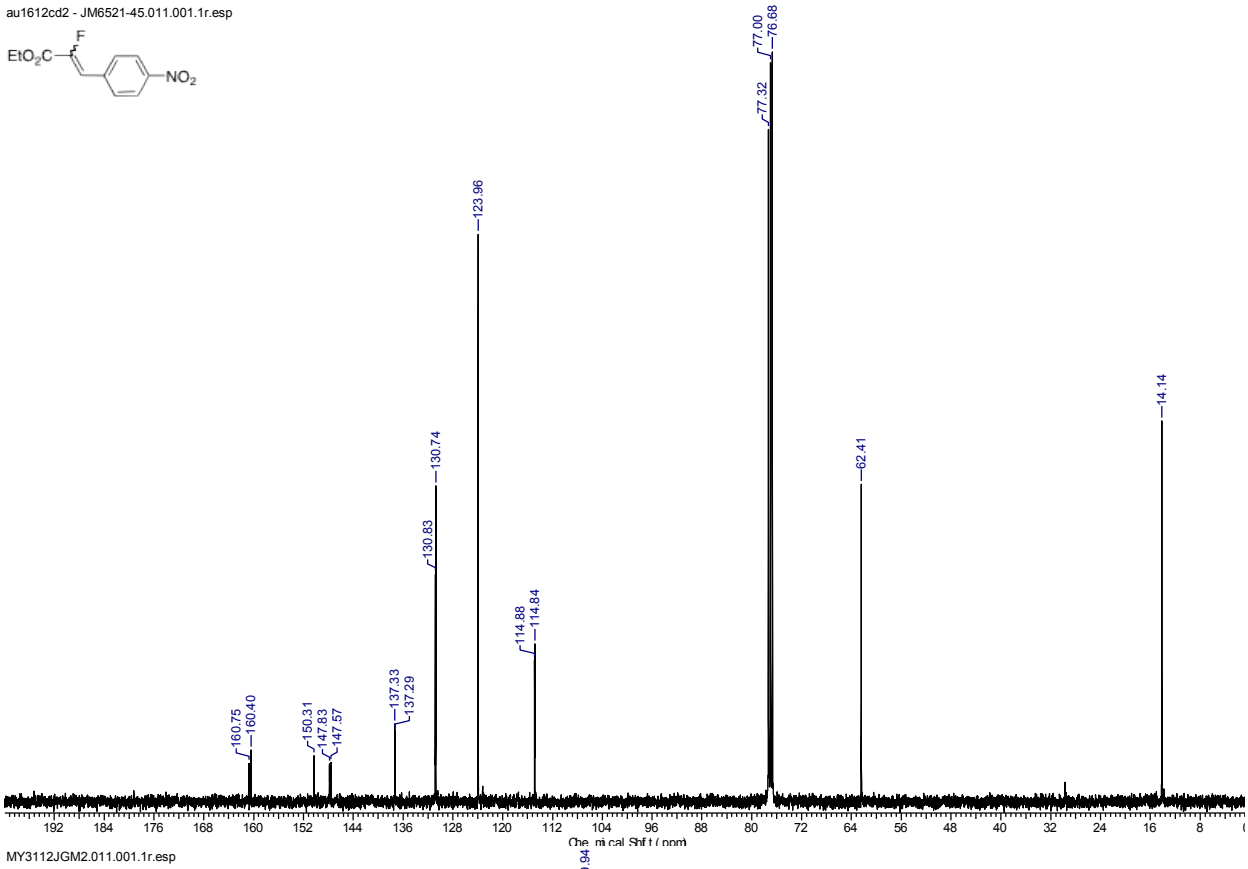


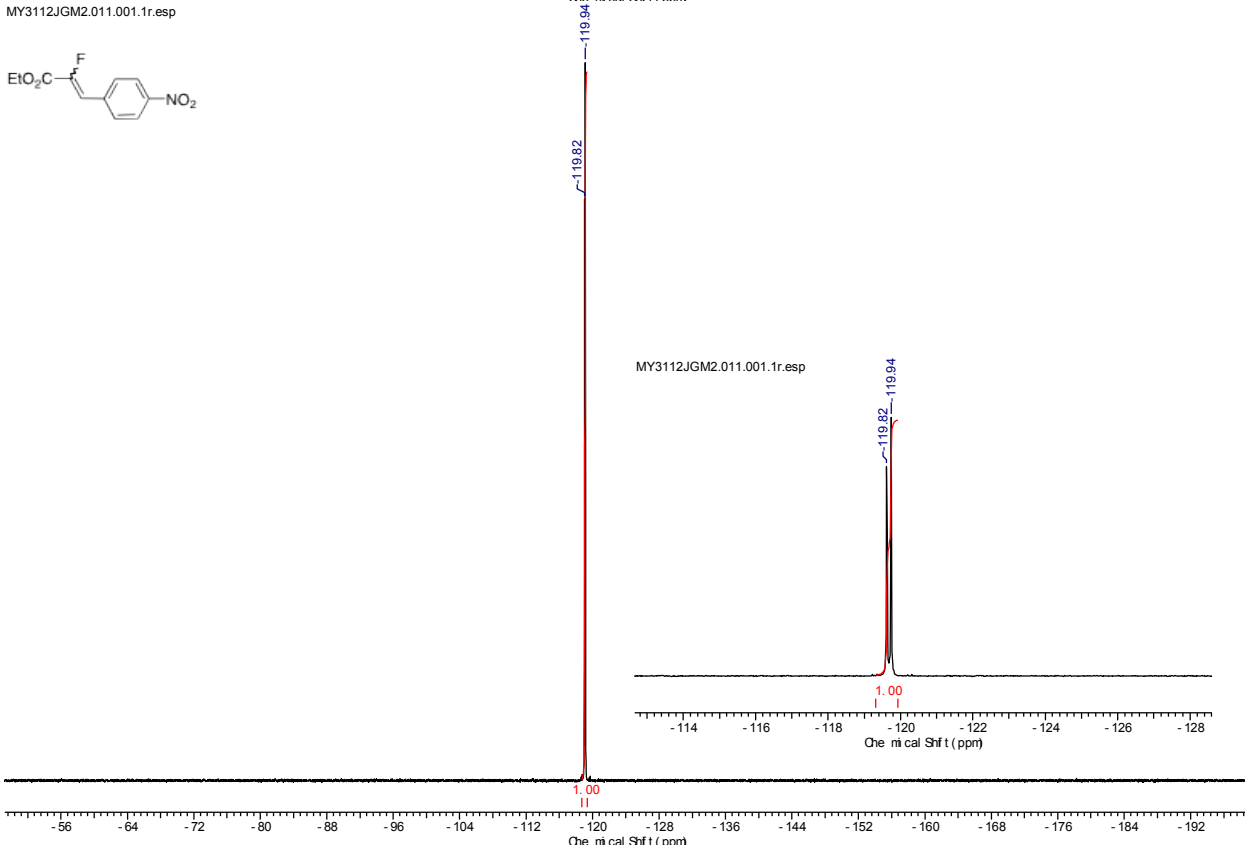





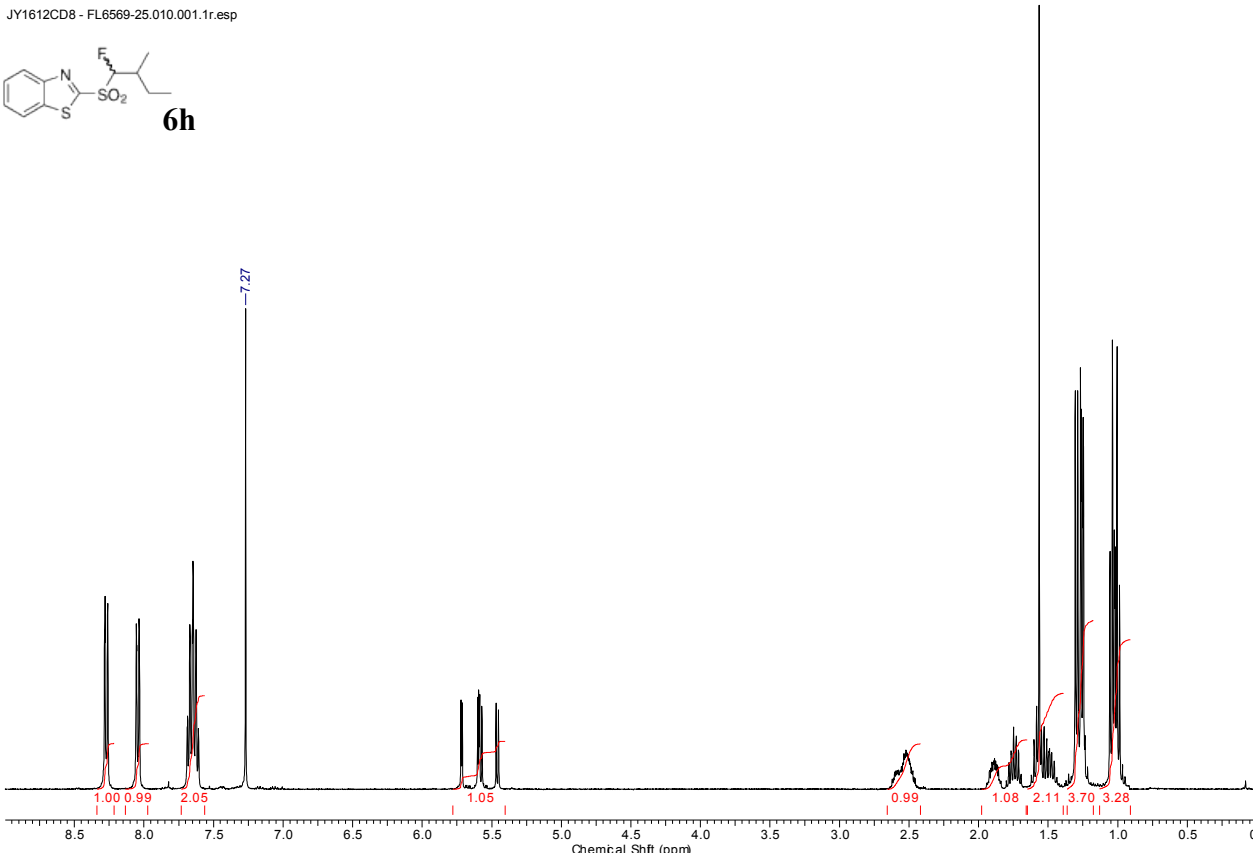

**5.2.7b** Ethyl-2-fluoro-3-(4-nitrophenyl)acrylate ()

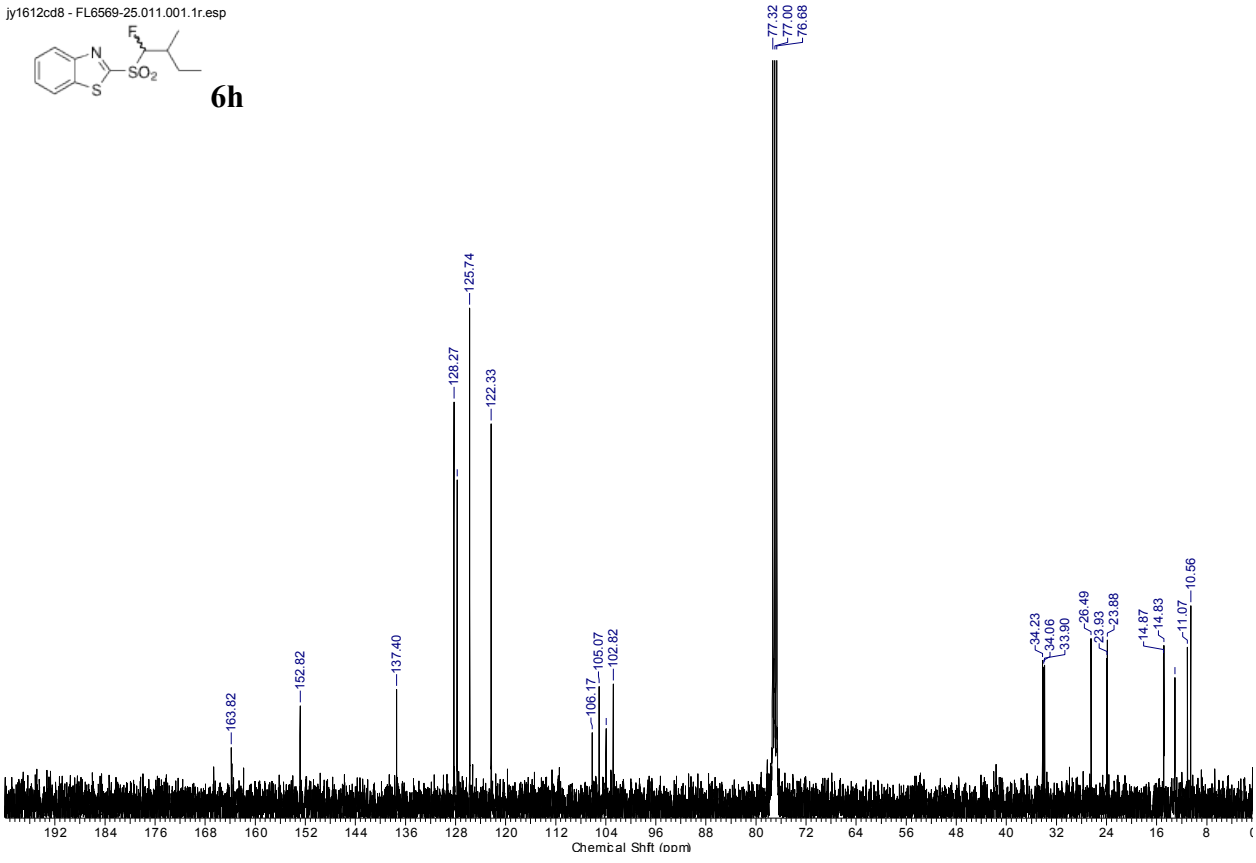


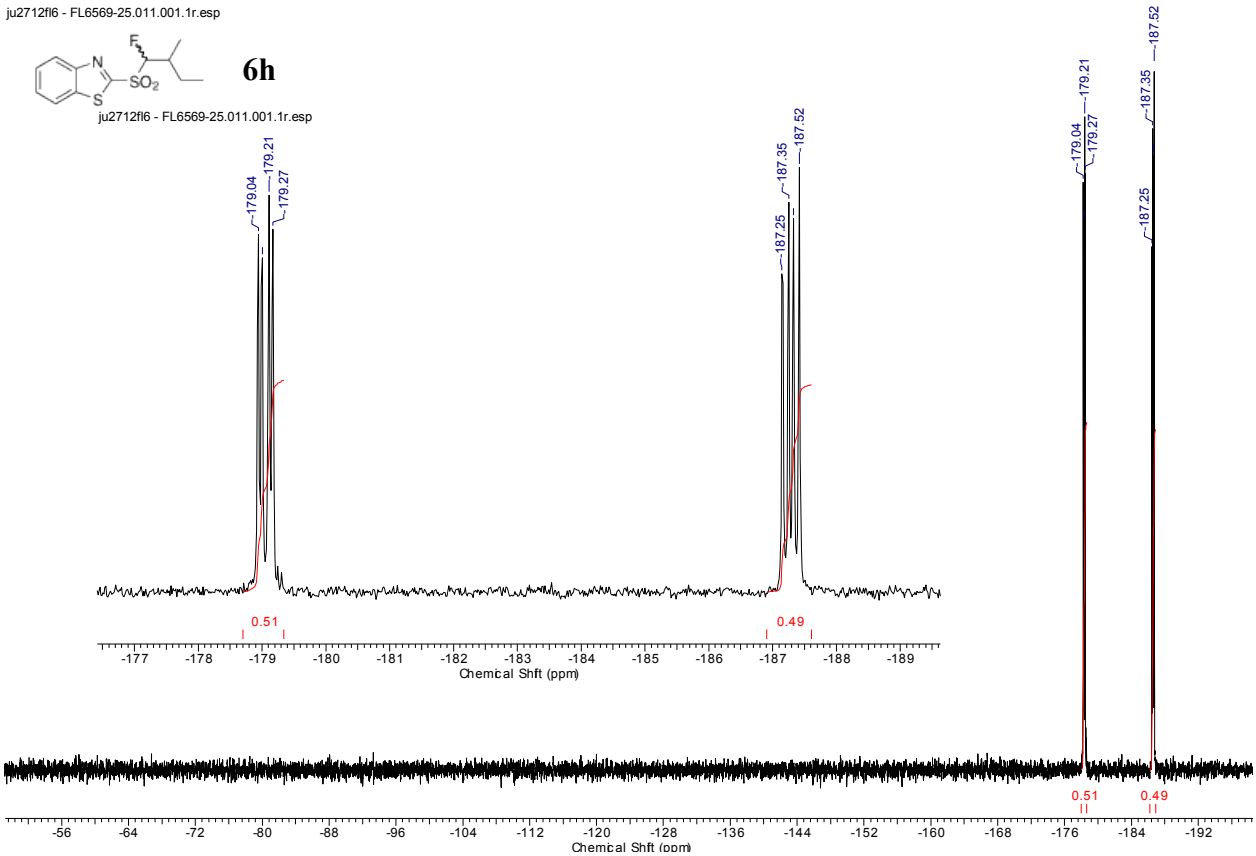

au1612cd2 - JM6521-45.011.001.1r.esp
EtO2C
F
NO2
77.00
76.68
77.32
123.96
130.74
130.83
114.88
114.84
137.33
137.29
160.75
160.40
150.31
147.83
147.57
62.41
14.14
Chemical Shift (ppm)


MY3112JGM2.011.001.1r.esp
EtO2C
F
NO2
119.94
119.82
1.00
MY3112JGM2.011.001.1r.esp
119.94
119.82
1.00
Chemical Shift (ppm)

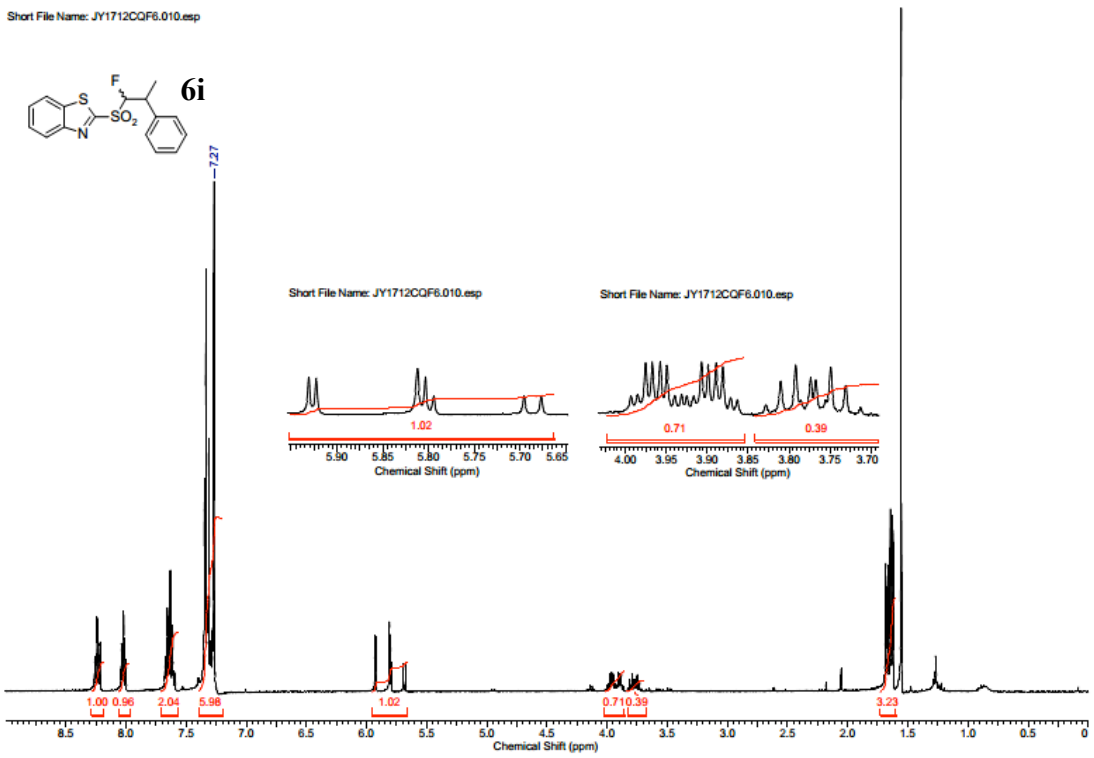
**5.2.8** 2-(1-fluoro-2-methylbutylsulfonyl)benzothiazole (**6h**)

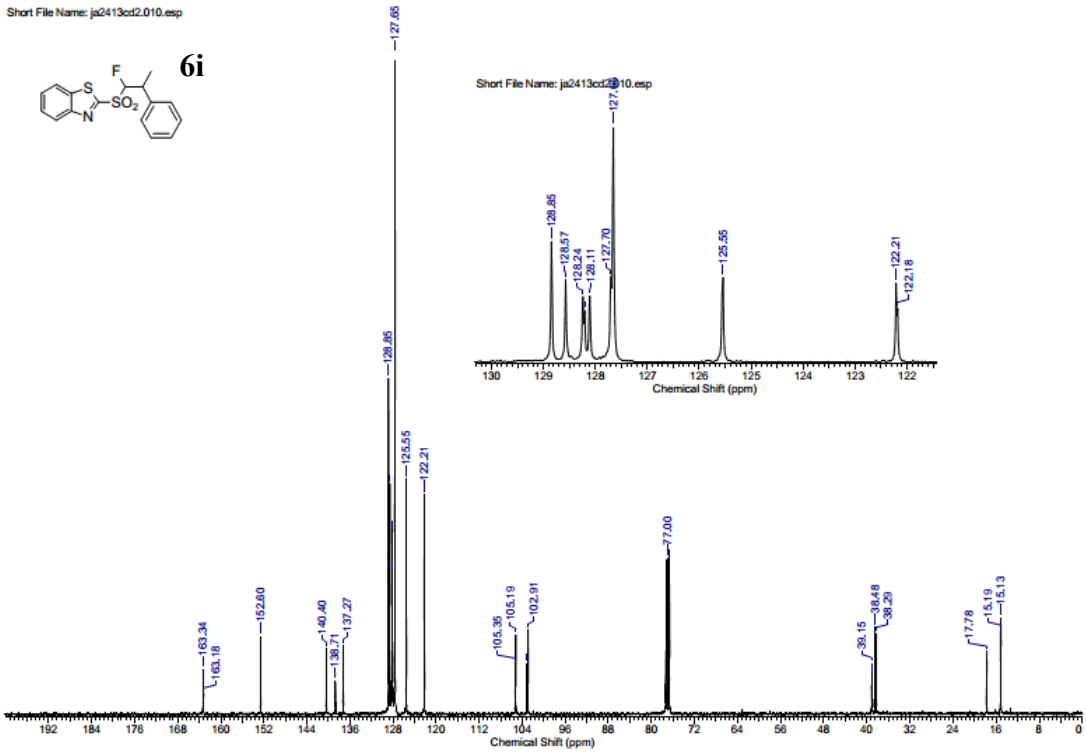





**5.2.9** 2-(1-fluoro-2-phenylpropylsulfonyl)benzothiazole (**6i**)

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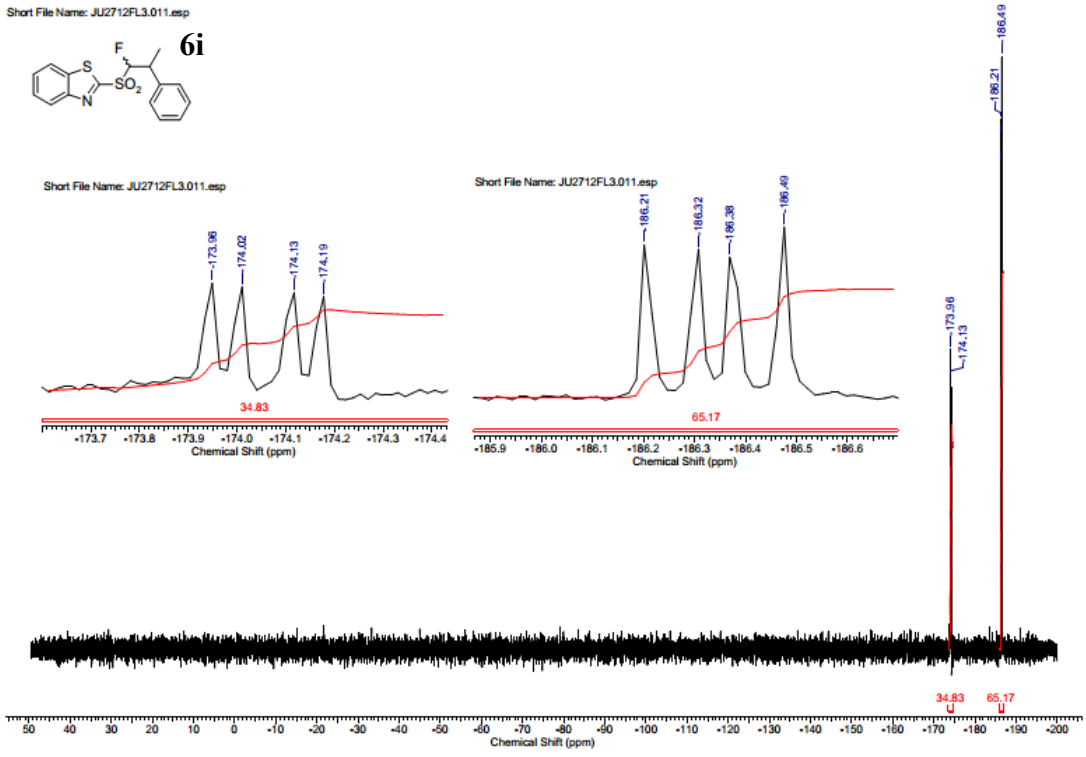
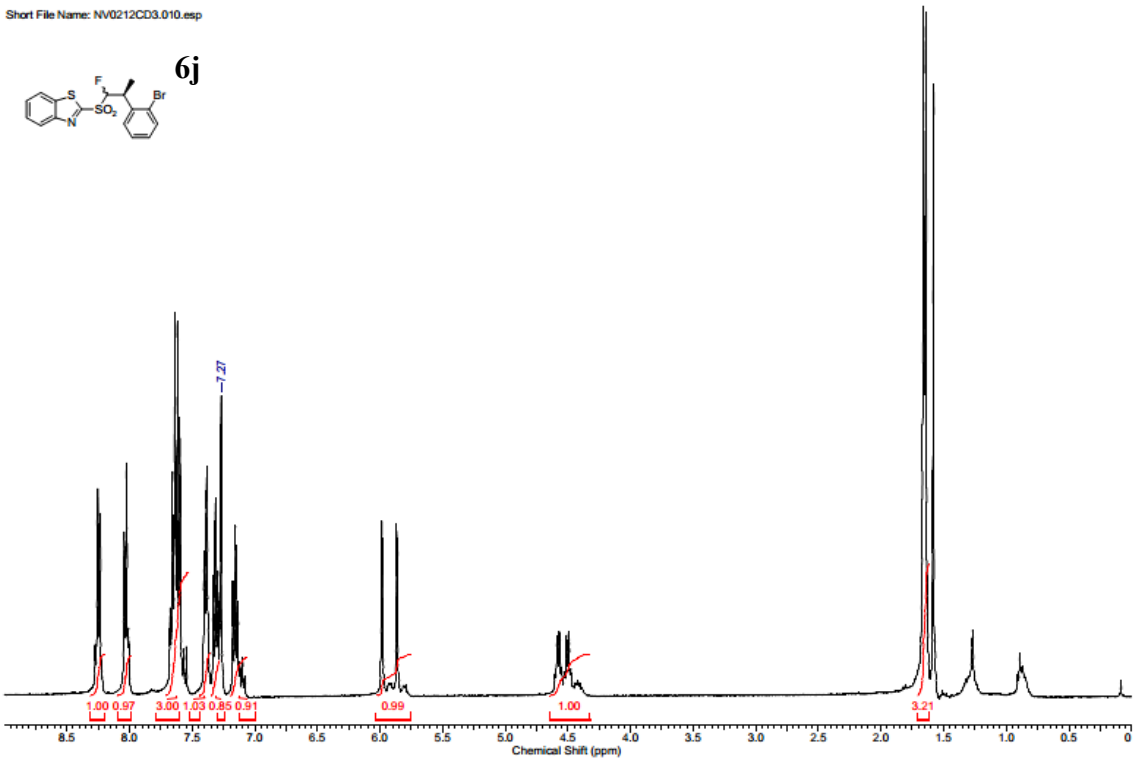
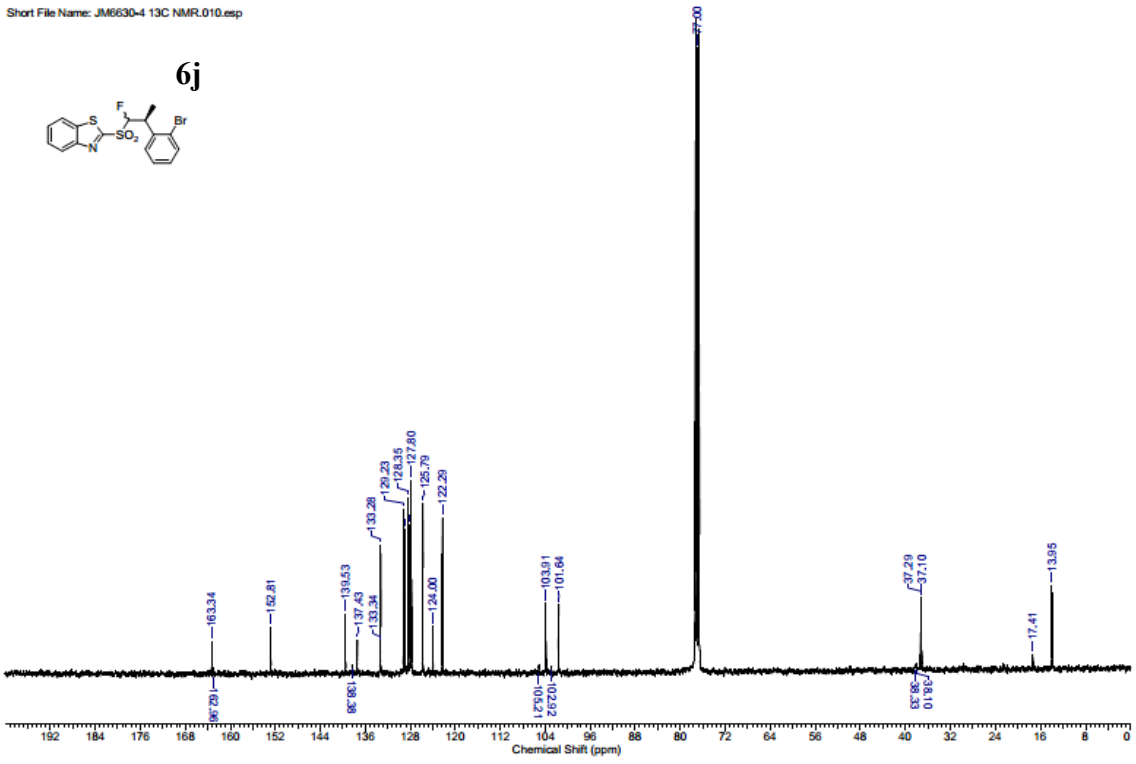
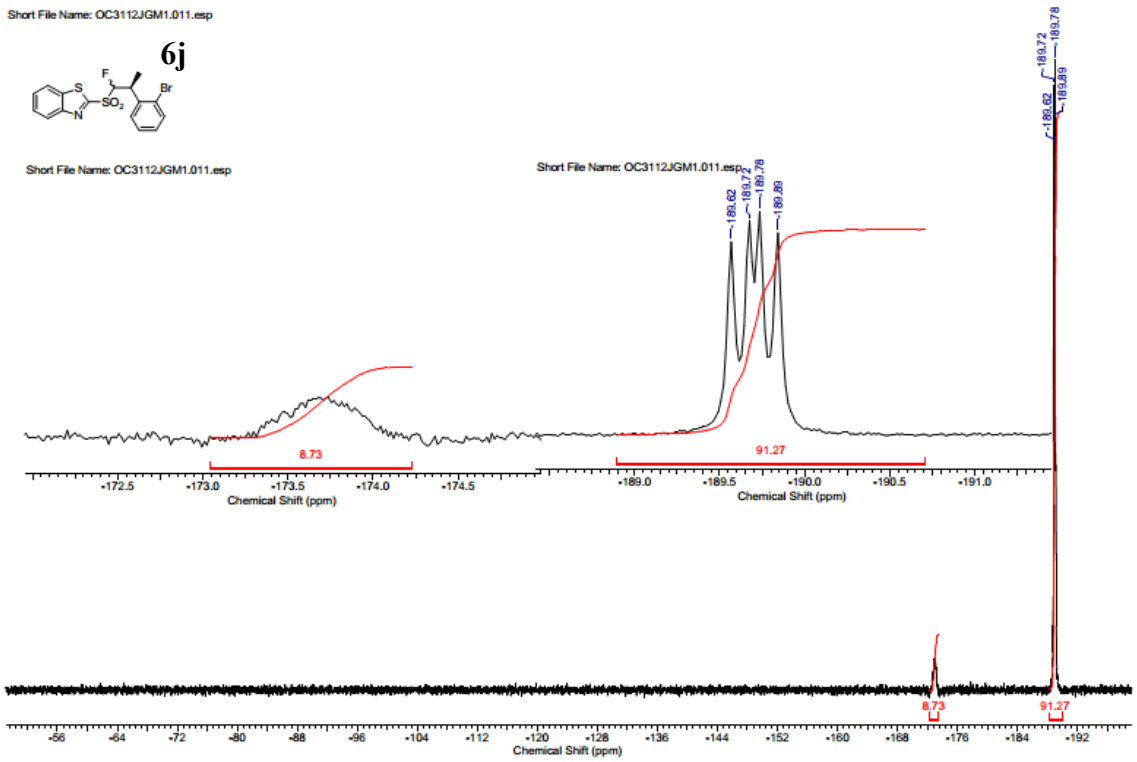
6i
Chemical Shift (ppm)


Short File Name: JU2712FL3.011.esp
6i
34.83
65.17
Chemical Shift (ppm)

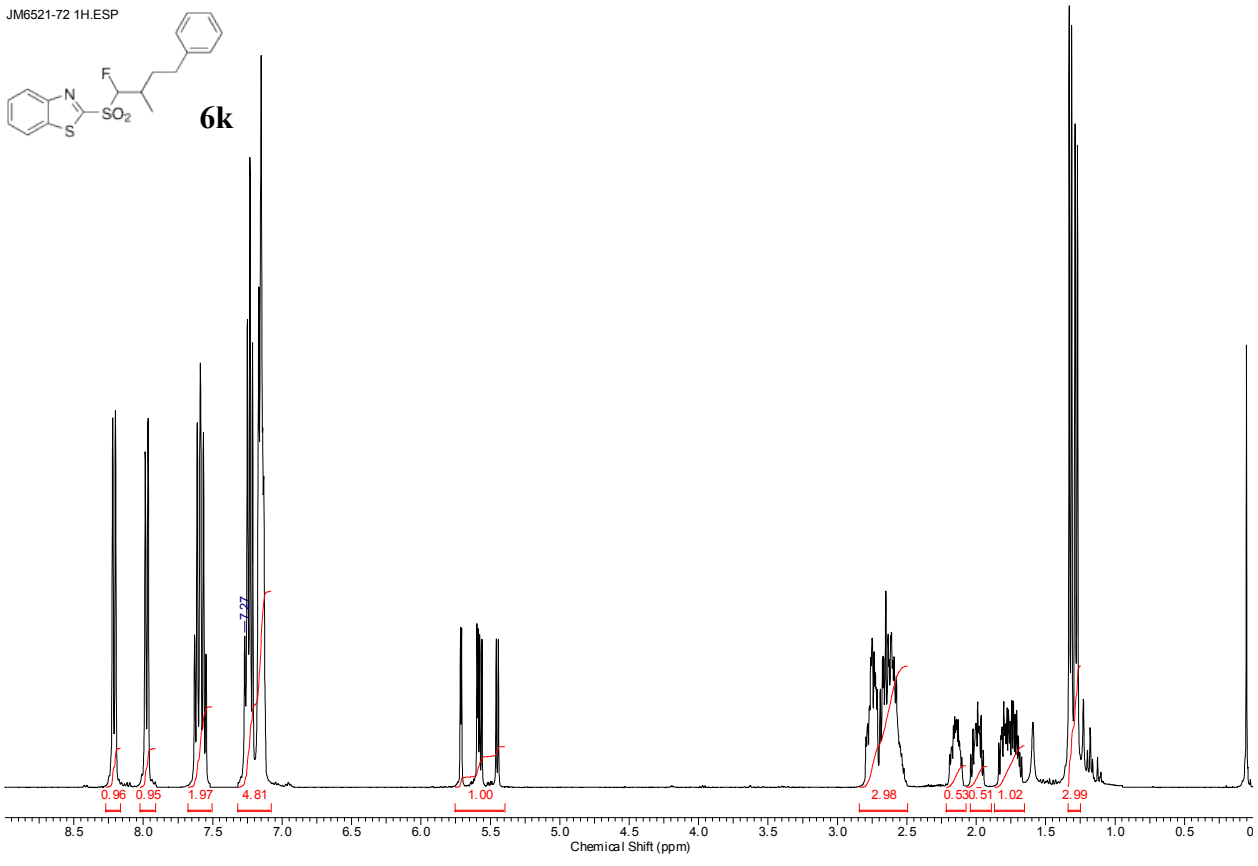
**5.2.10** (R)-2-(2-(2-bromophenyl)-1-fluoropropylsulfonyl)benzothiazole (**6j)**

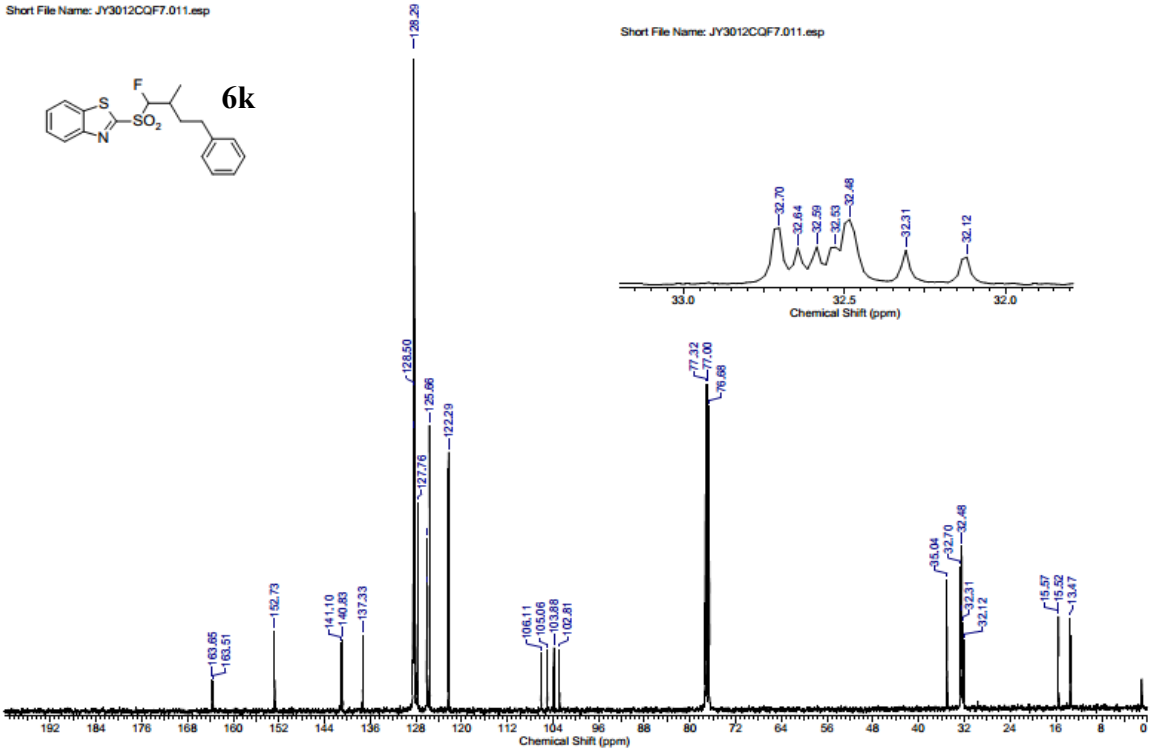





**5.2.11** 2-(1-fluoro-2-methyl-4-phenylbutylsulfonyl)benzothiazole (**6k**)

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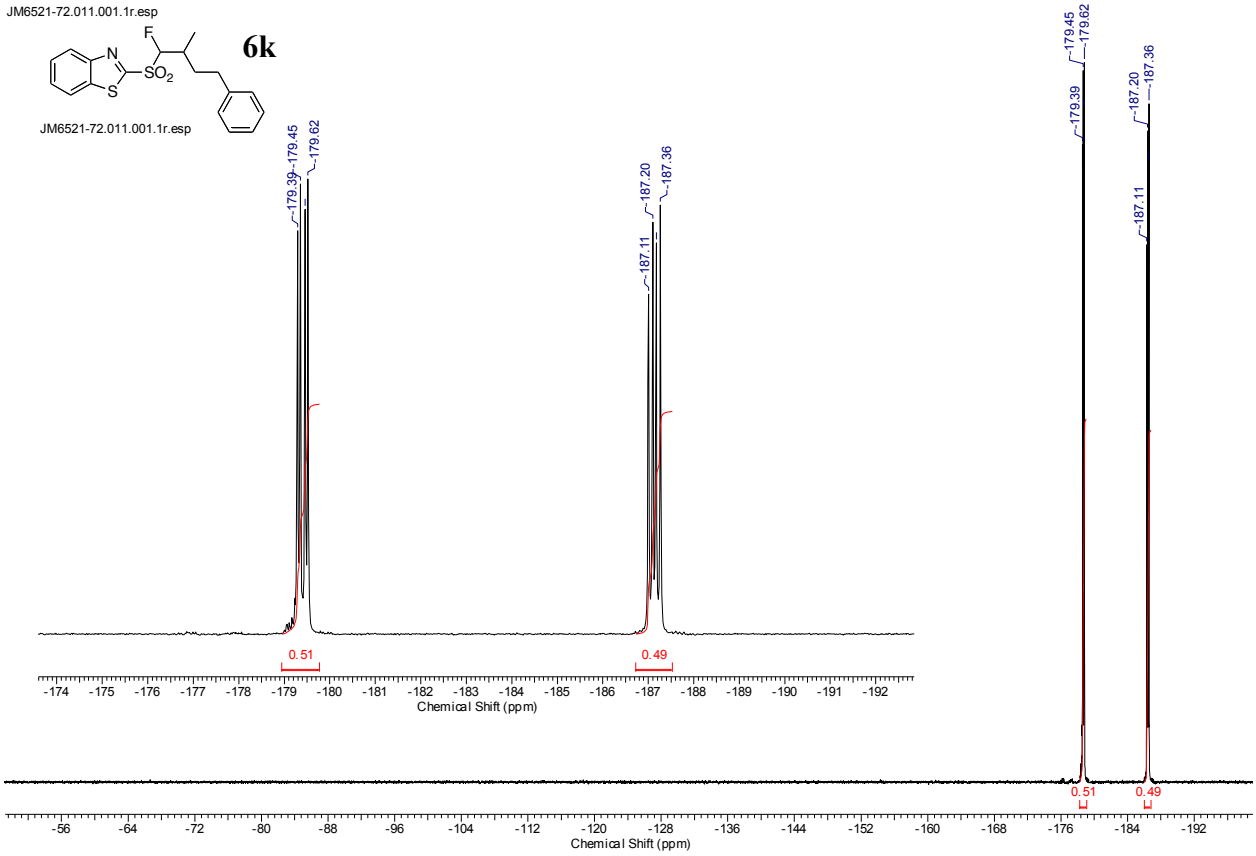
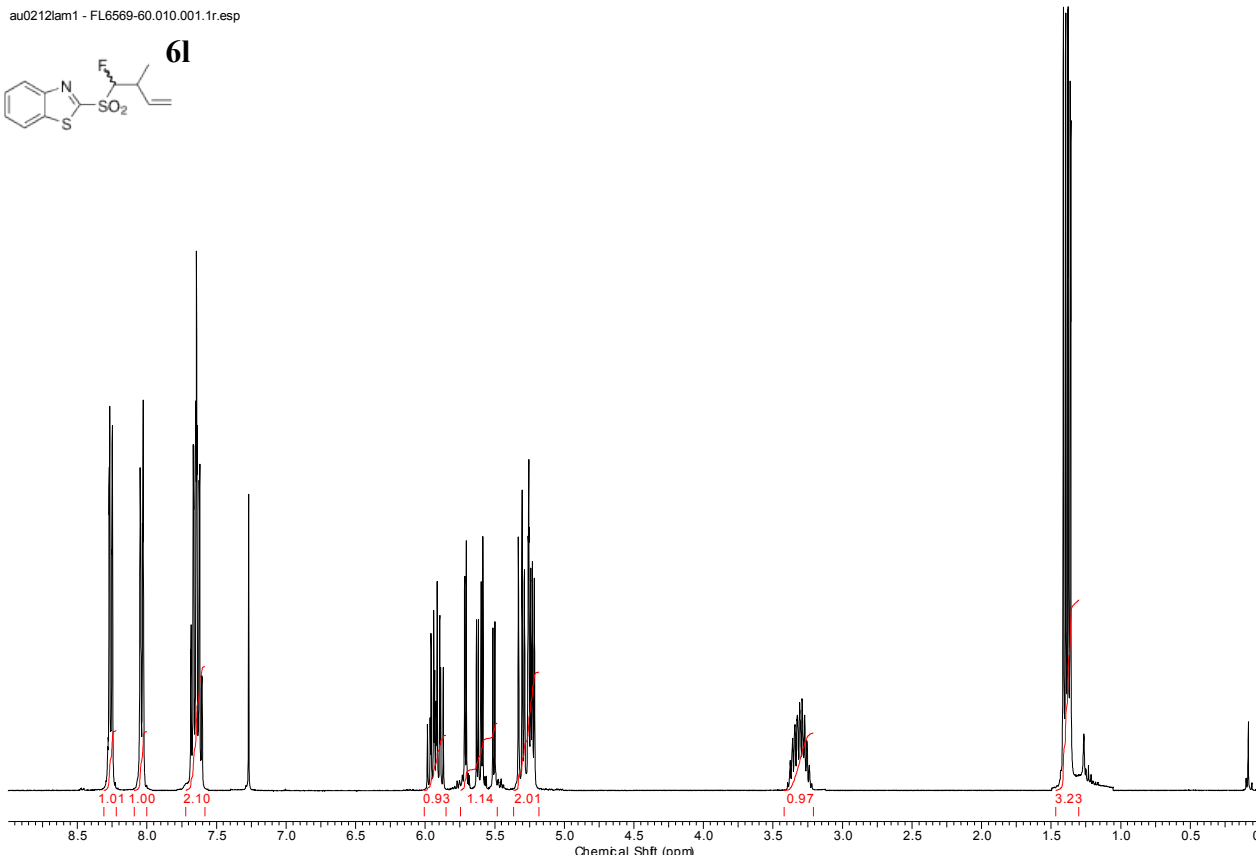
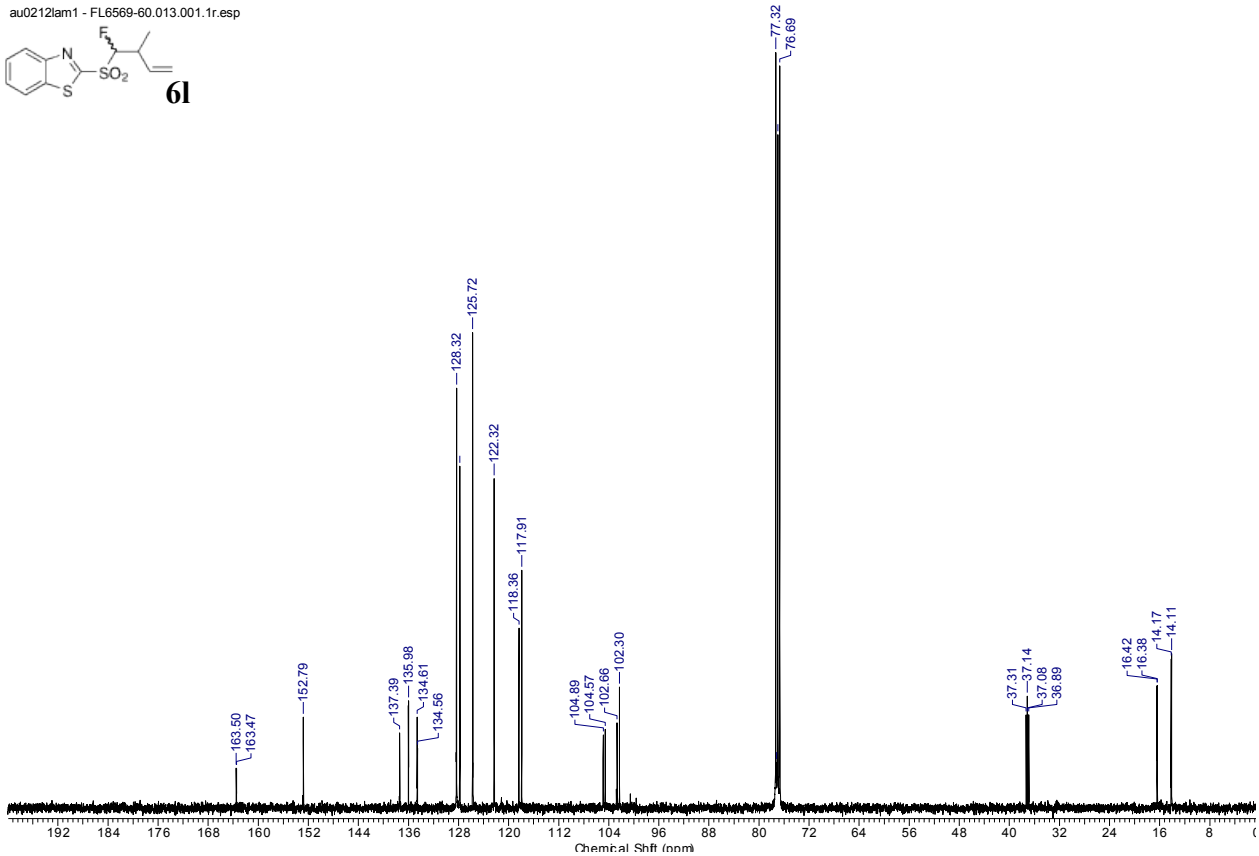
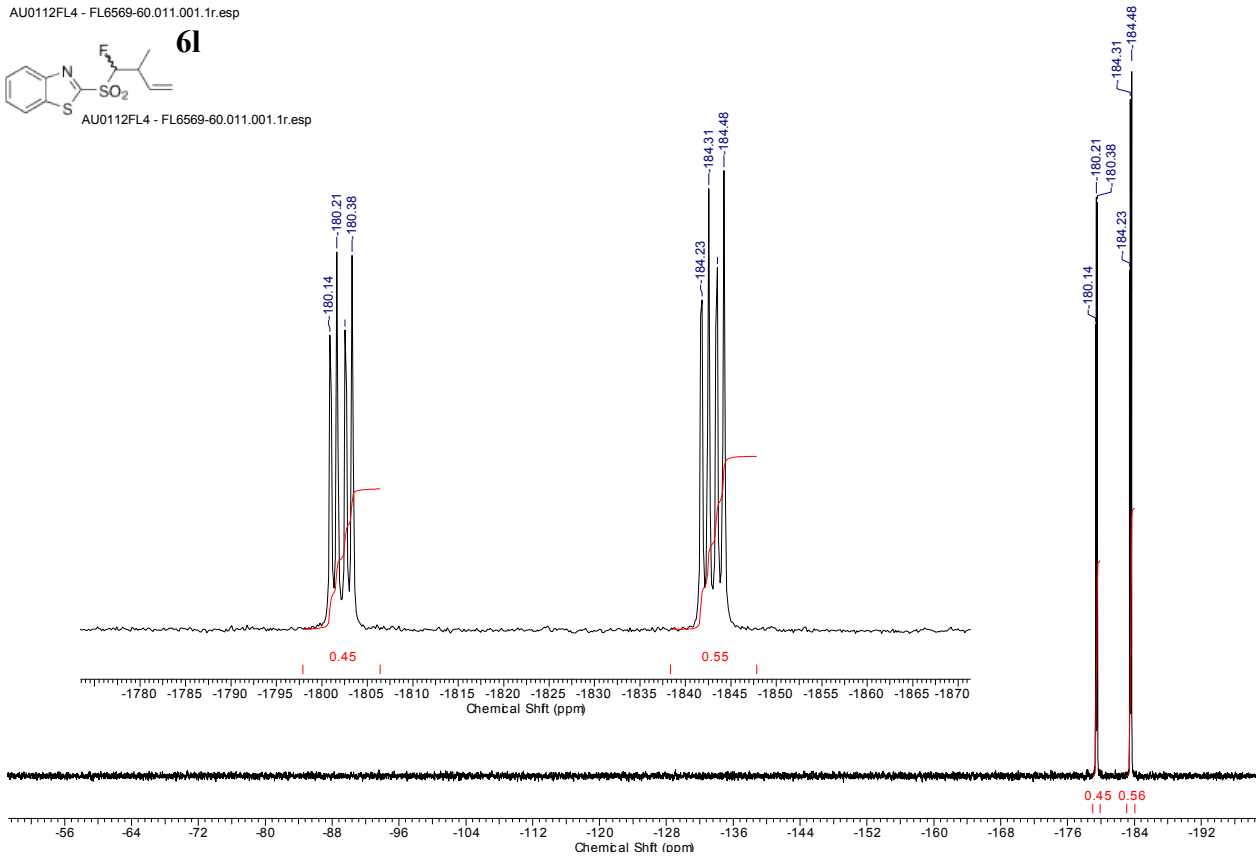
6k
Short File Name: JY3012CQF7.011.esp
Chemical Shift (ppm)
Chemical Shift (ppm)


JM6521-72.011.001.1r.esp
6k
JM6521-72.011.001.1r.esp
0.51
0.49
Chemical Shift (ppm)
0.51
0.49
Chemical Shift (ppm)

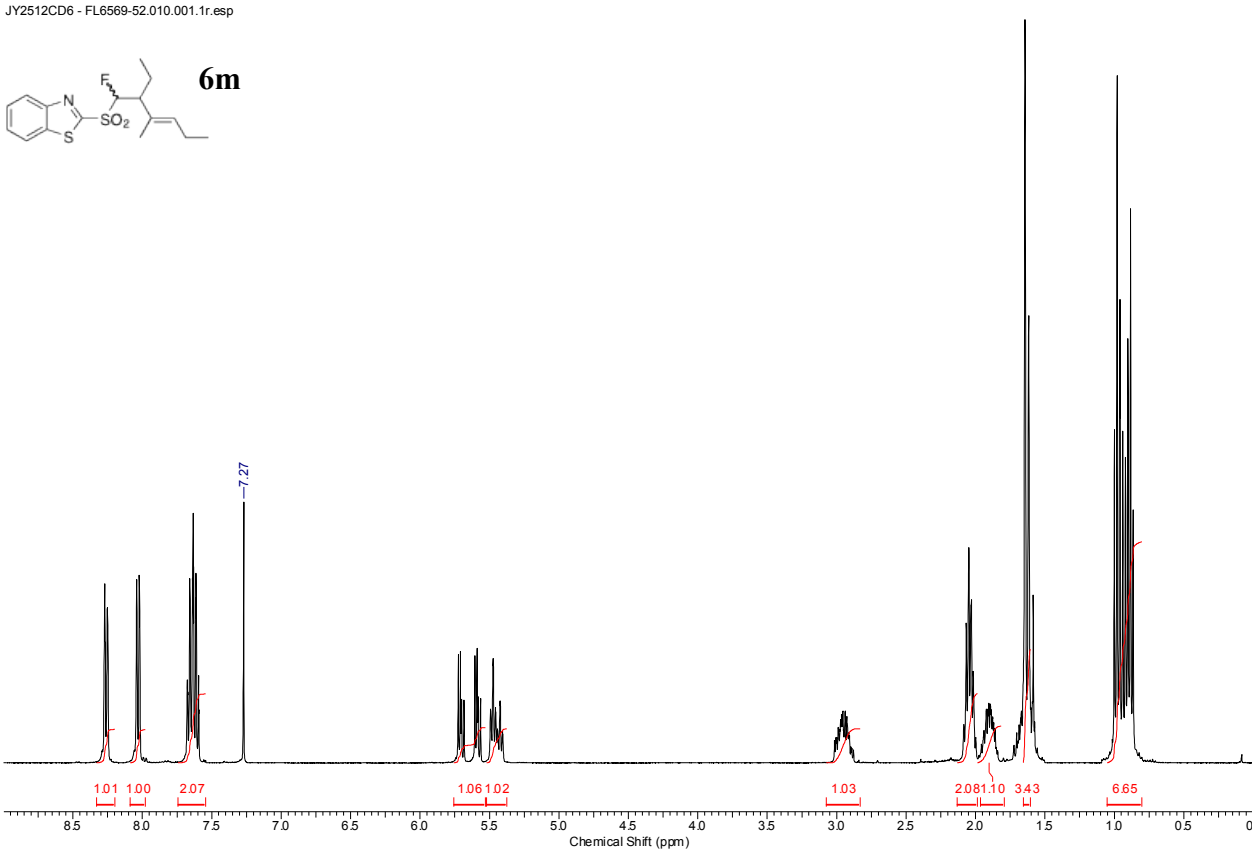
## **5.2.12** 2-(1-fluoro-2-methylbut-3-enylsulfonyl)benzothiazole (**6l**)



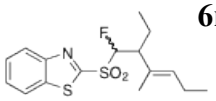






## **5.2.13** (*E*)-2-(2-ethyl-1-fluoro-3-methylhex-3-enylsulfonyl)benzothiazole (**6m**)



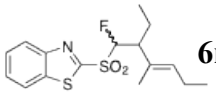
jy2512cd6 - FL6569-52.011.001.1r.esp



**6m**



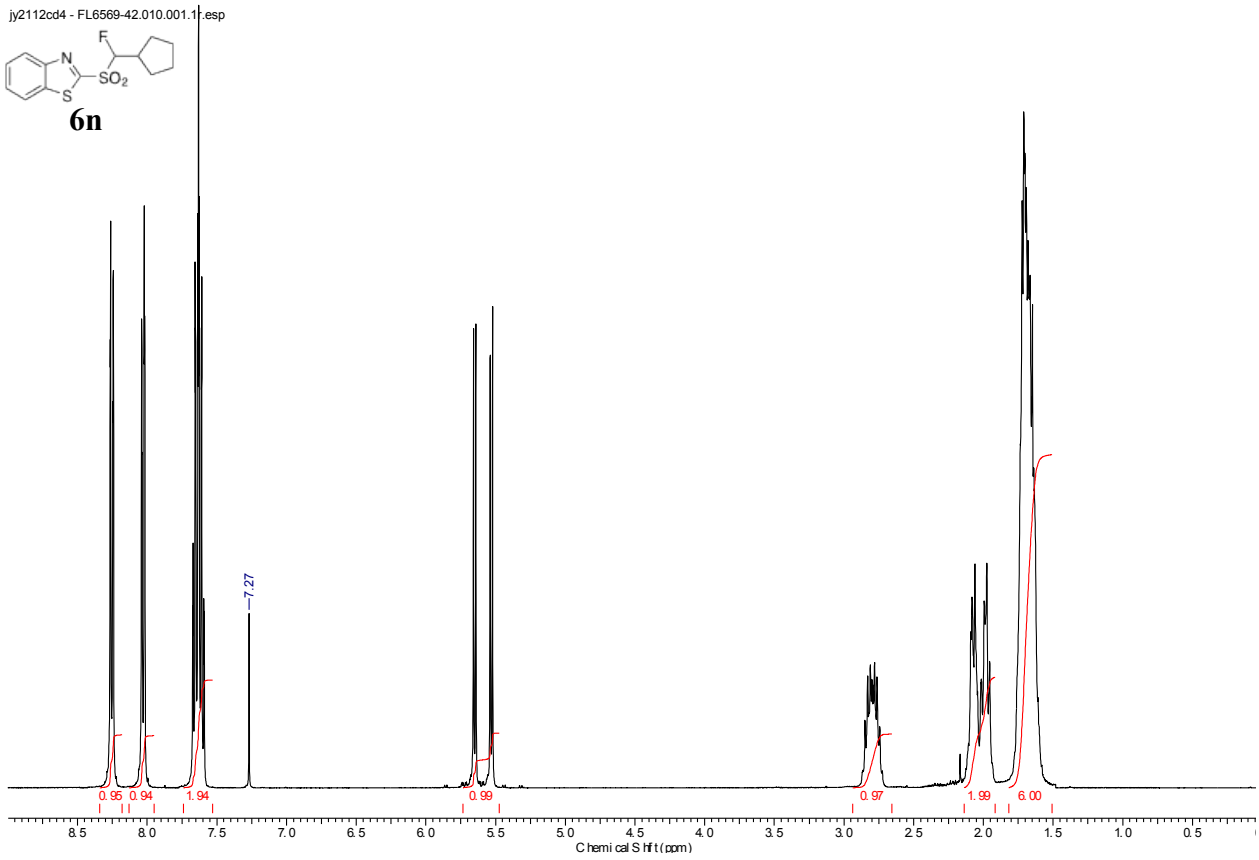

jy2412fl3 - FL6569-52.011.001.1r.esp

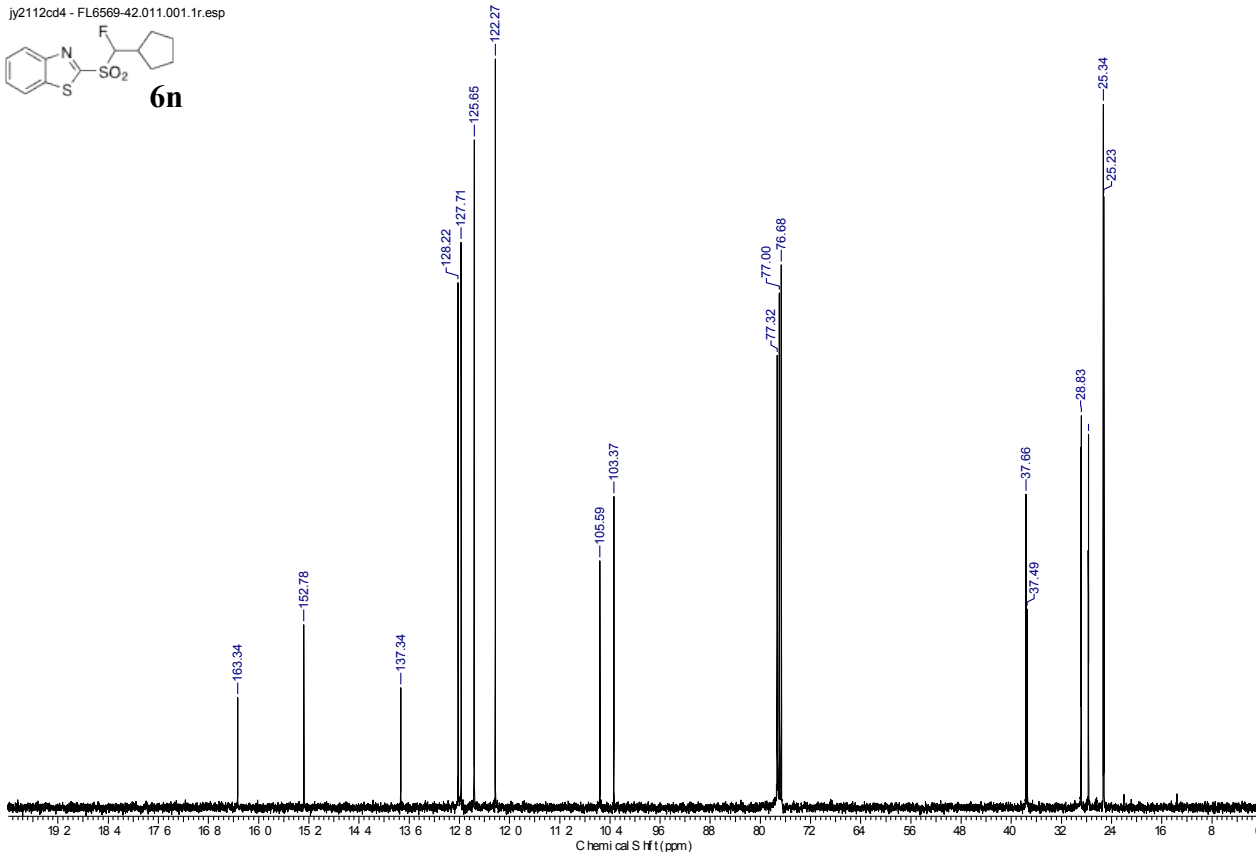


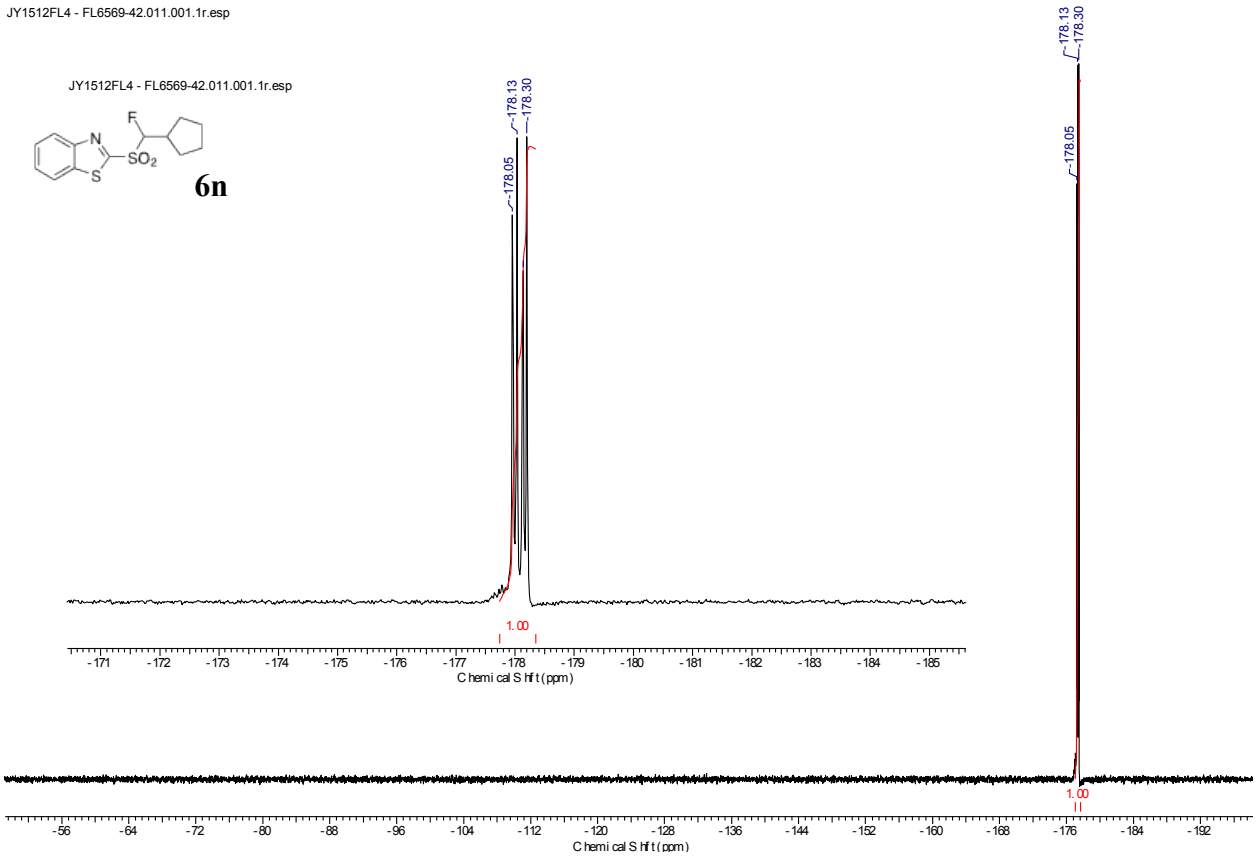
**6m**

jy2412fl3 - FL6569-52.011.001.1r.esp

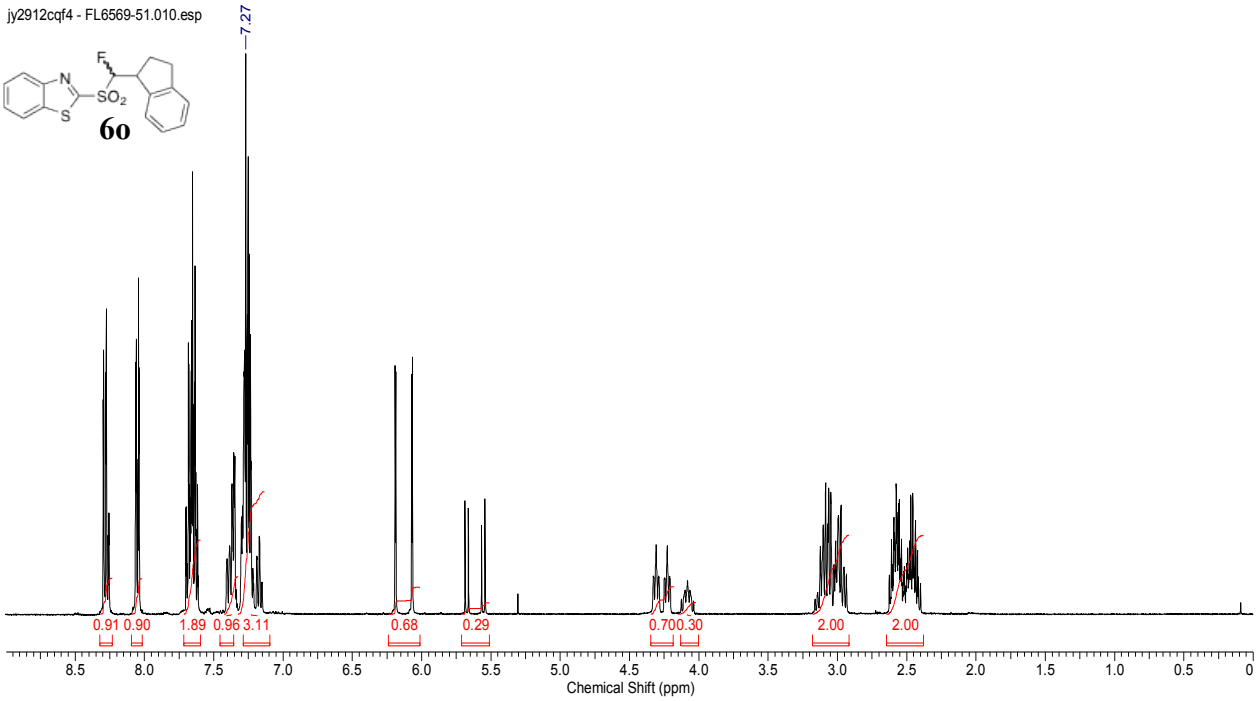
**5.2.14** 2-(cyclopentylfluoromethylsulfonyl)benzothiazole (**6n**)



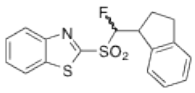






**5.2.15** 2-((2,3-dihydro-1*H*-inden-1-yl)fluoromethylsulfonyl)benzothiazole (**6o**)



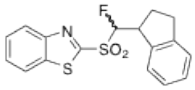
jy2912cqf4 - FL6569-51.011.esp



**6o**

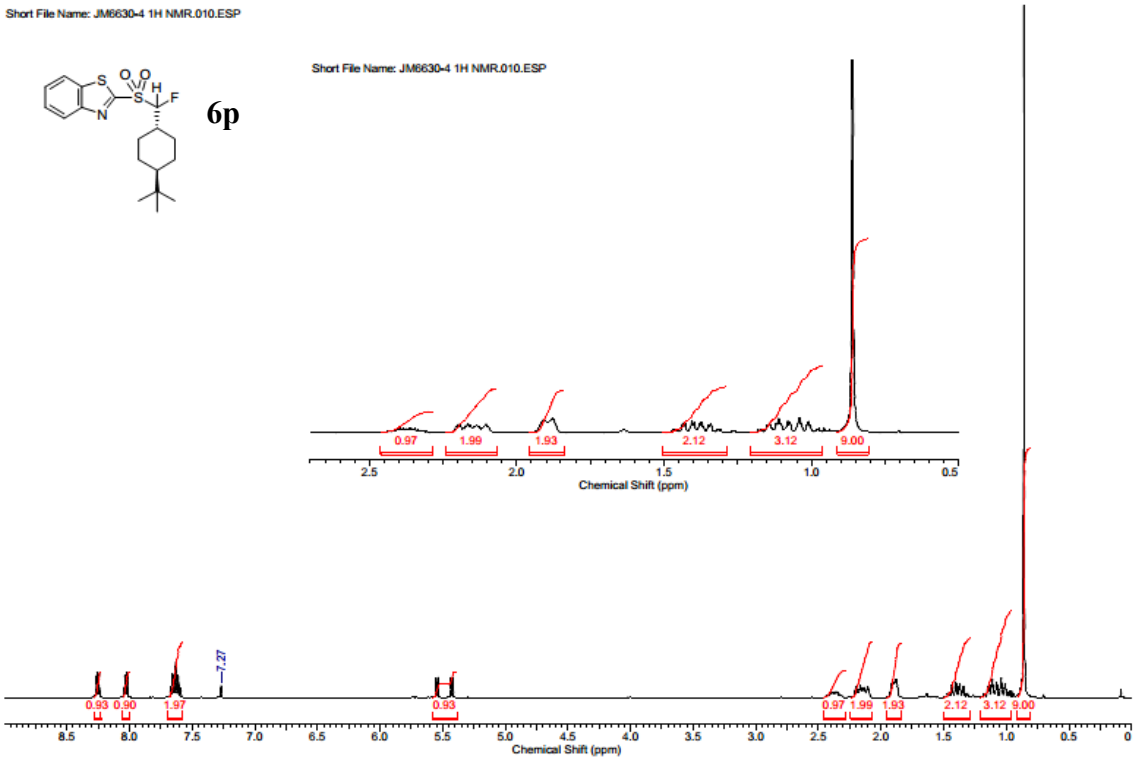


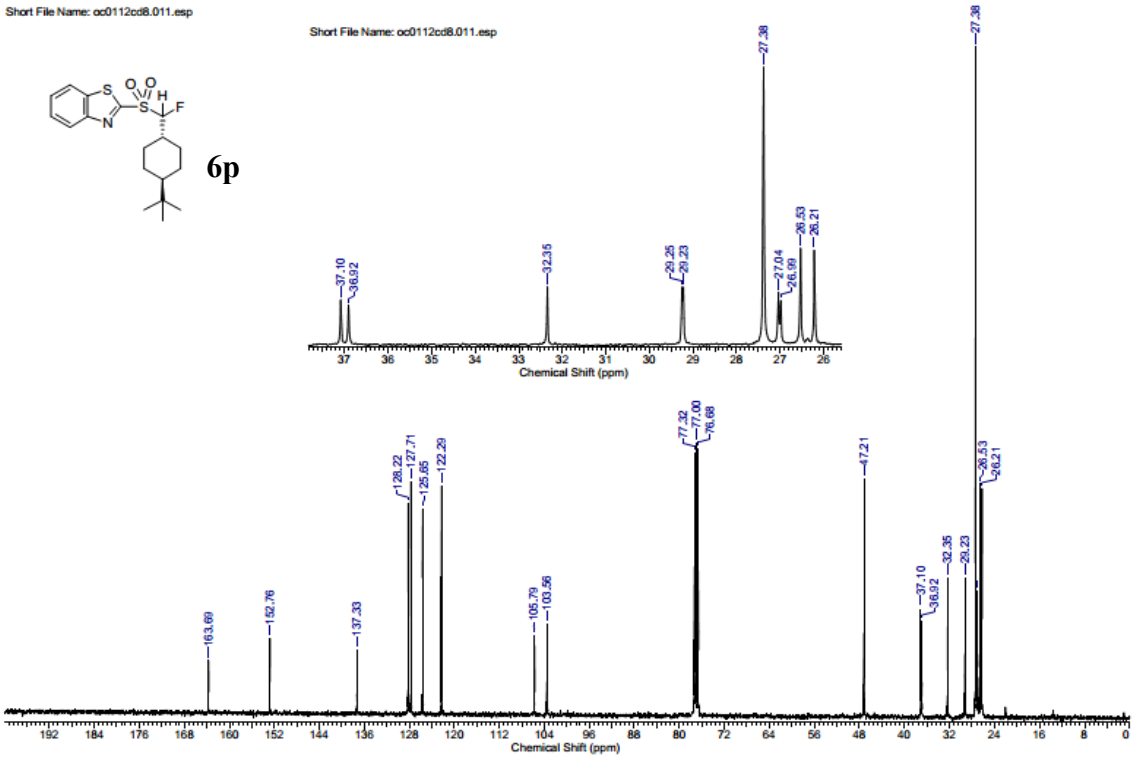

jy2612fl3 - FL6569-51.011.esp

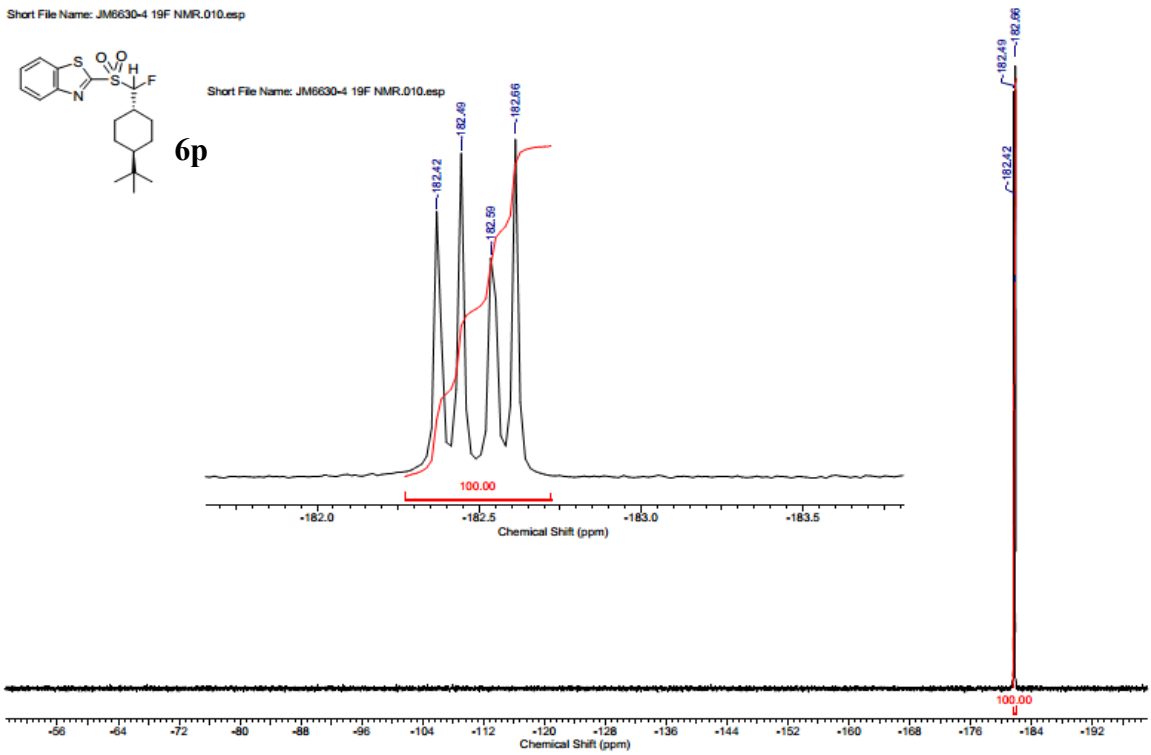


**6o**

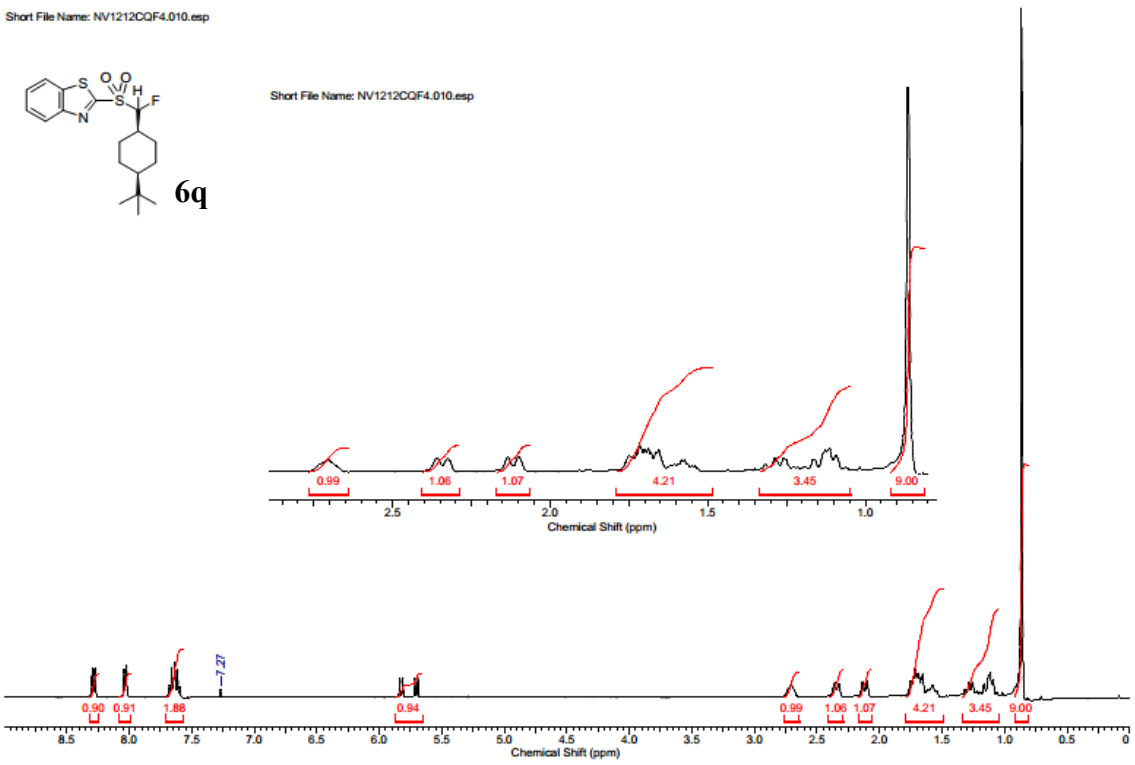
**5.2.16** 2-(((1*r*,4*r*)-4-*tert*-butylcyclohexyl)fluoromethylsulfonyl)benzothiazole (**6p**)

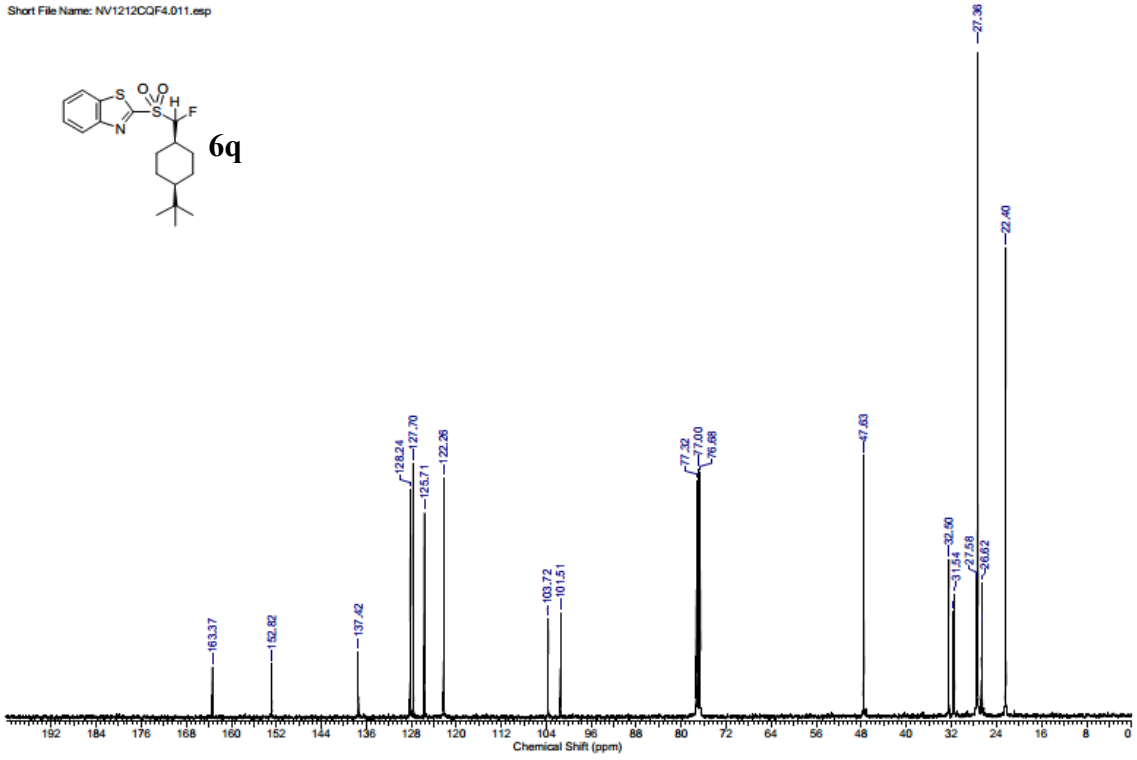


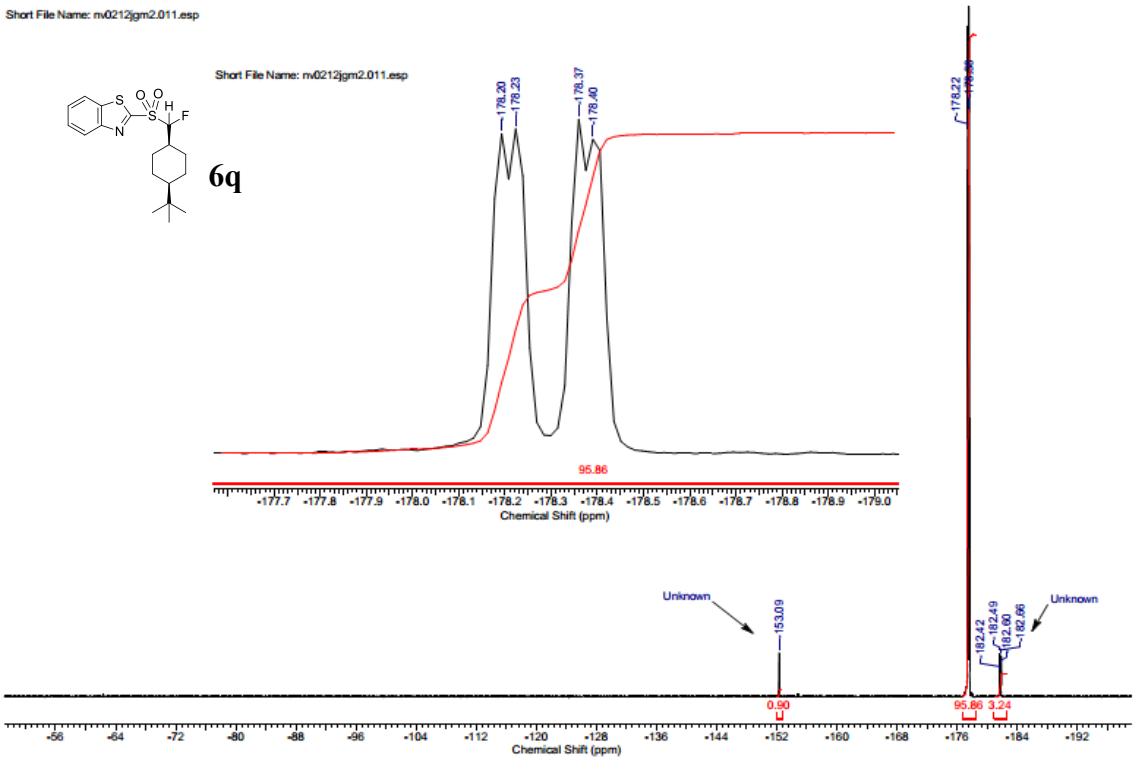





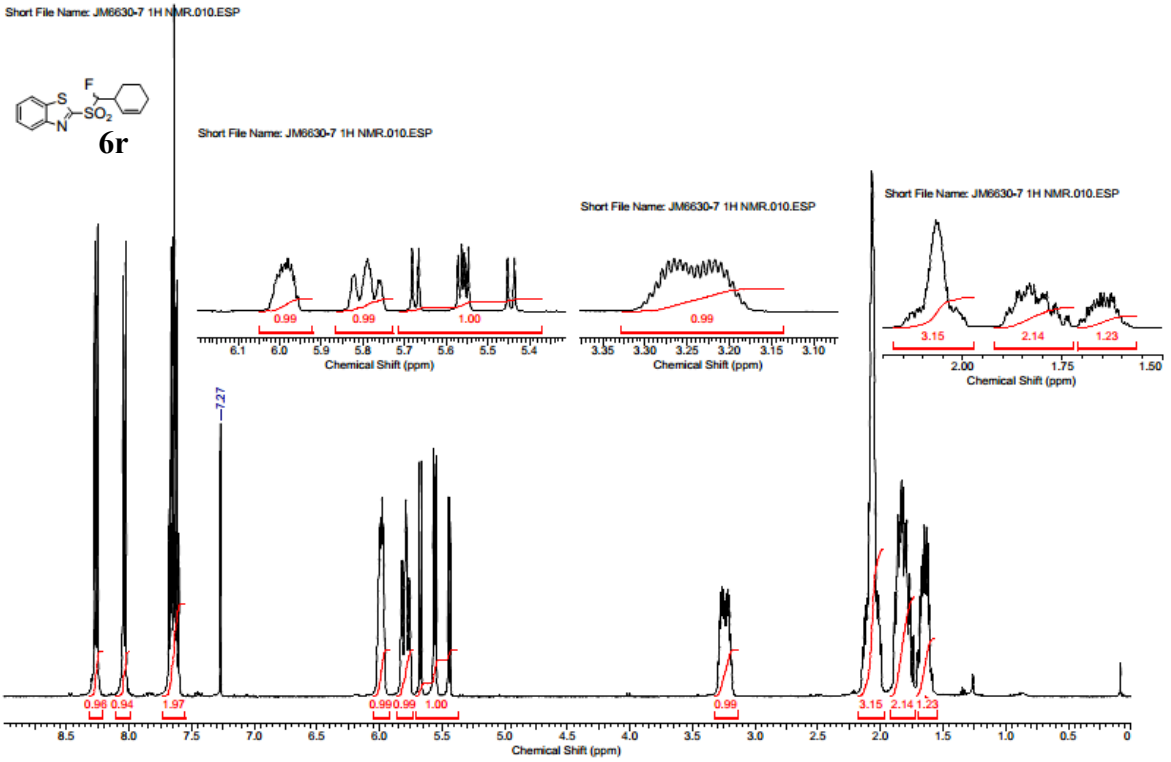

**5.2.17** 2-(((1*s*,4*s*)-4-*tert*-butylcyclohexyl)fluoromethylsulfonyl)benzothiazole (**6q**)

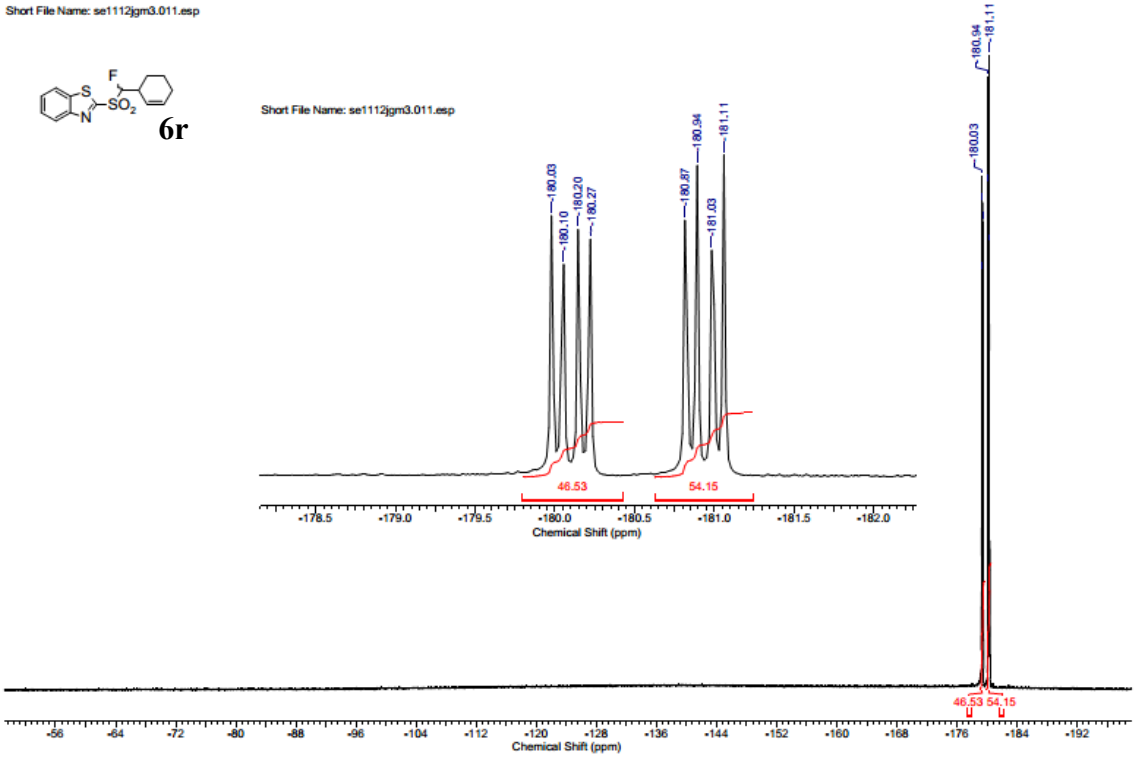



Short File Name: NV1212CQF4.011.esp
6q
Chemical Shift (ppm)


Short File Name: nv0212jgm2.011.esp
Short File Name: nv0212jgm2.011.esp
6q
95.86
Chemical Shift (ppm)
Unknown
Unknown
0.90
95.86
3.24
Chemical Shift (ppm)

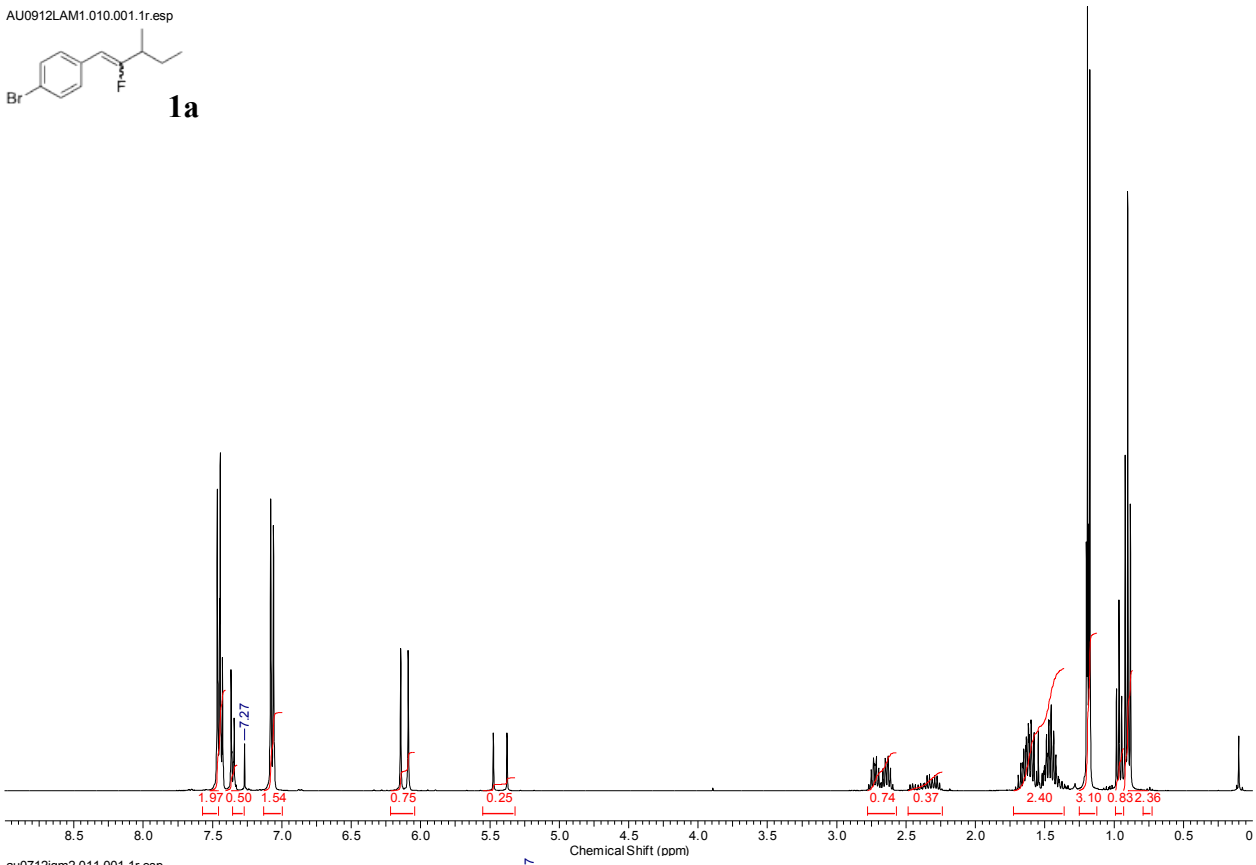
**5.2.18** 2-(cyclohex-2-enylfluoromethylsulfonyl)benzothiazole (**6r**)

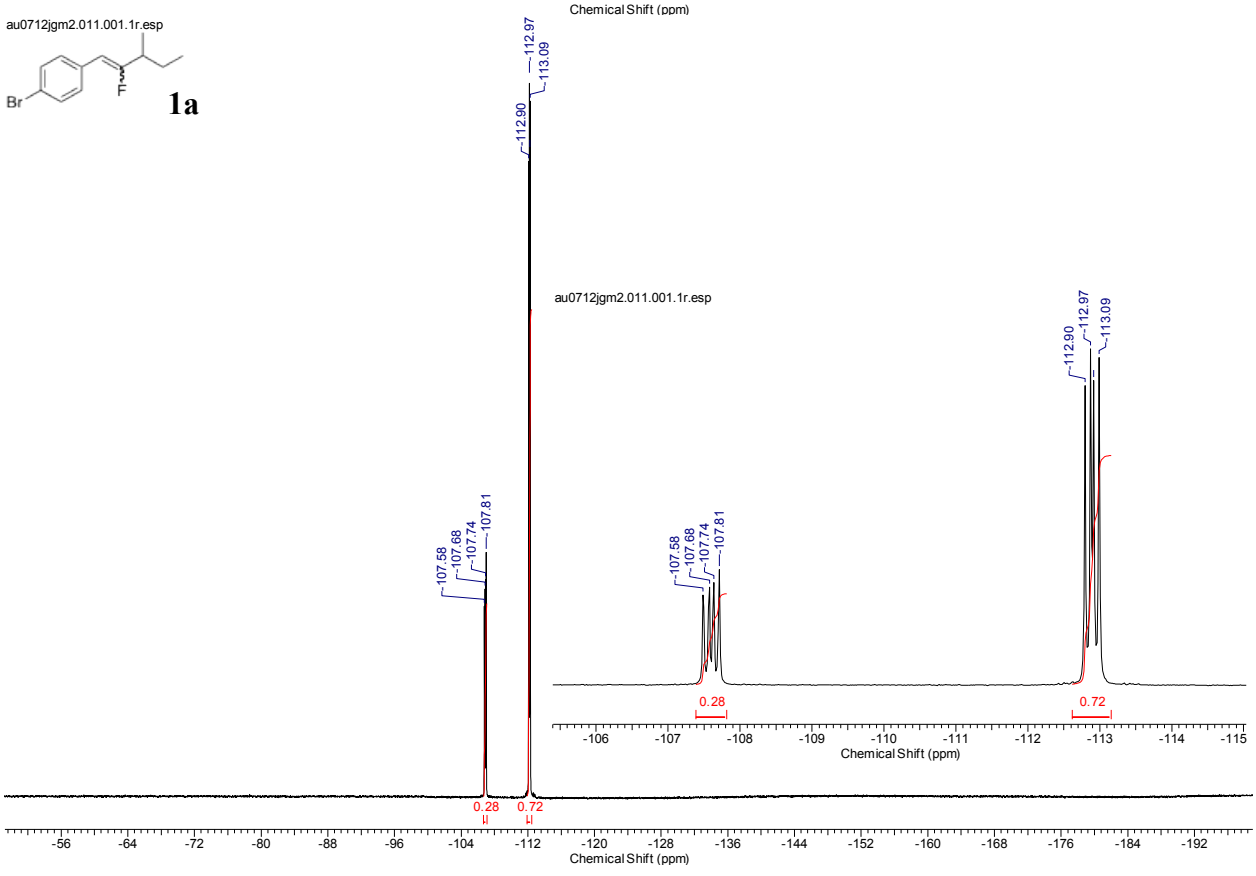


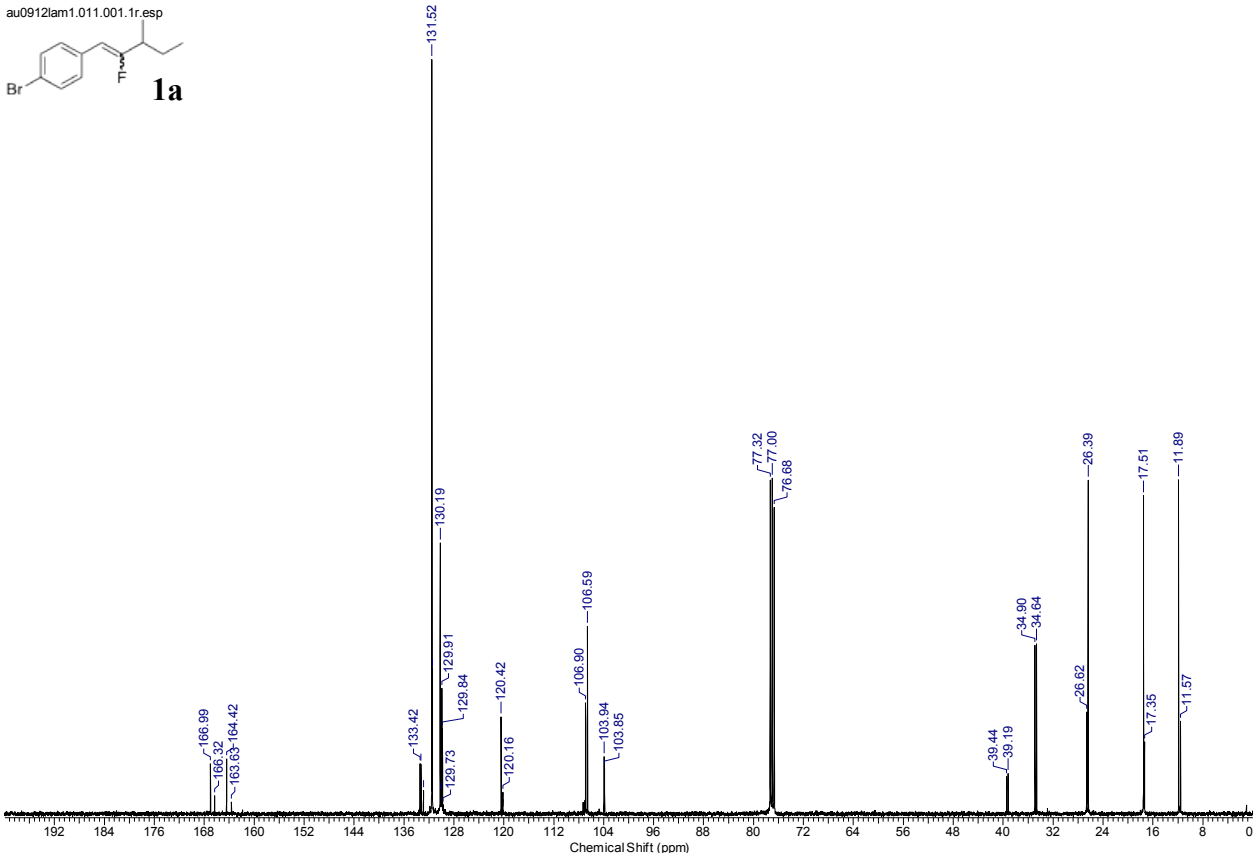



**5.3** Julia-Kocienski reaction to the fluoroalkenes (Table 2)

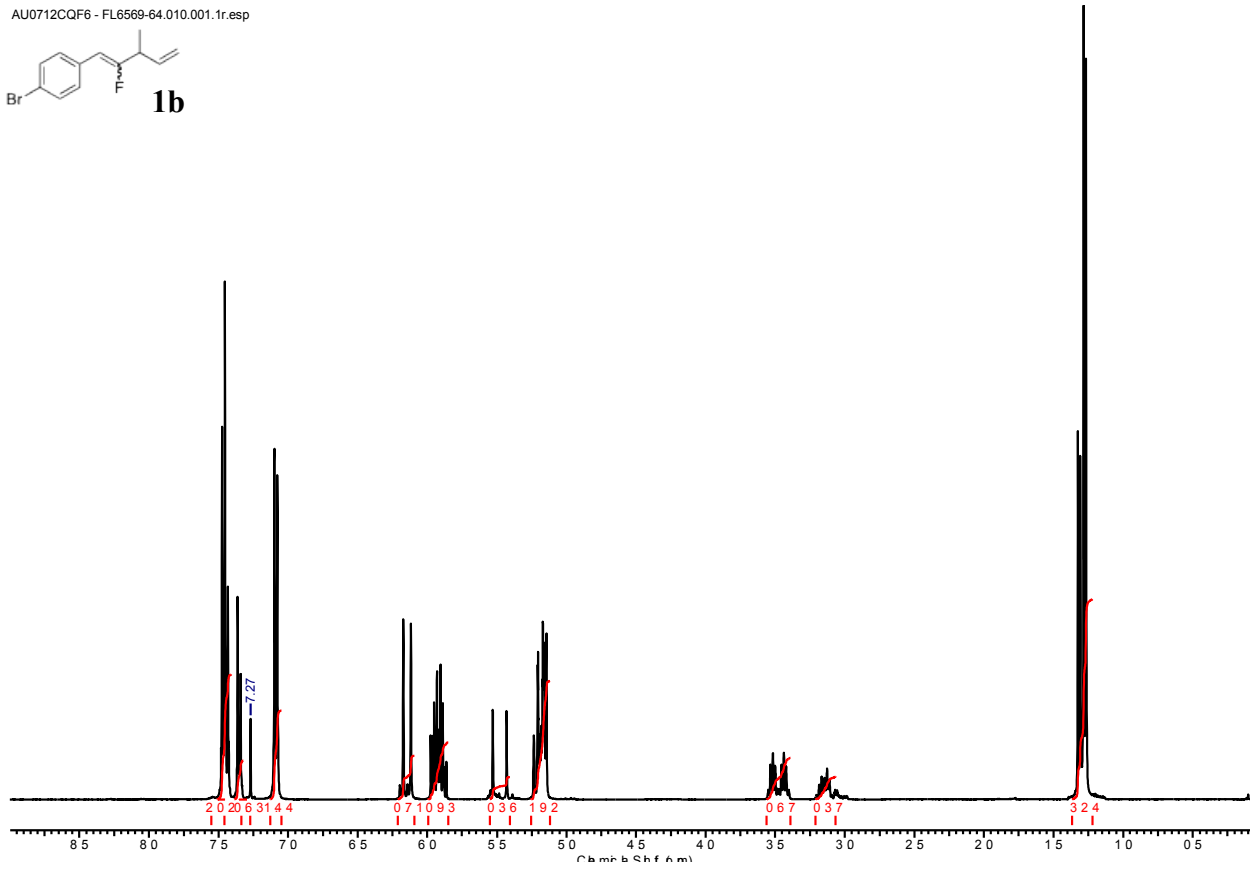
**5.3.1** 1-bromo-4-(2-fluoro-3-methylpent-1-enyl)benzene (**1a**)

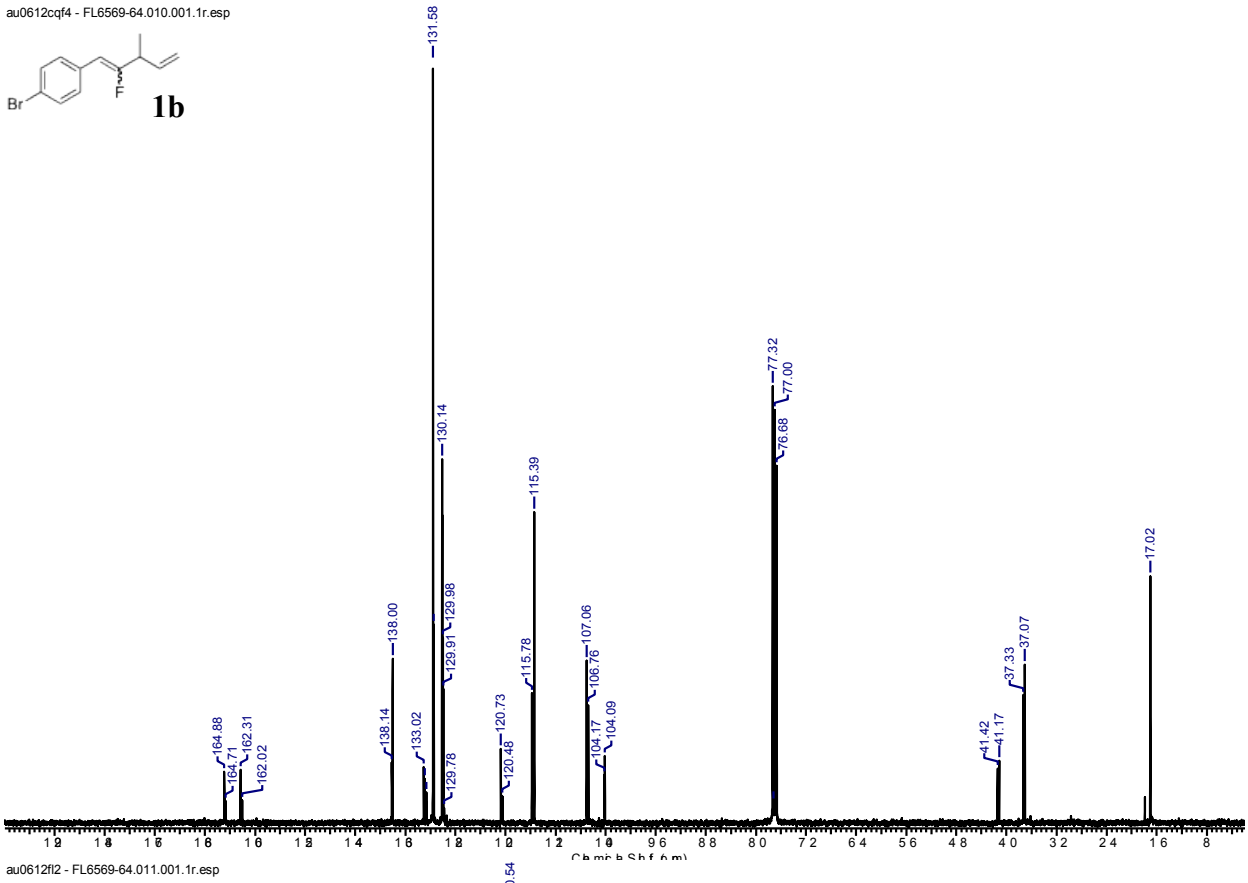


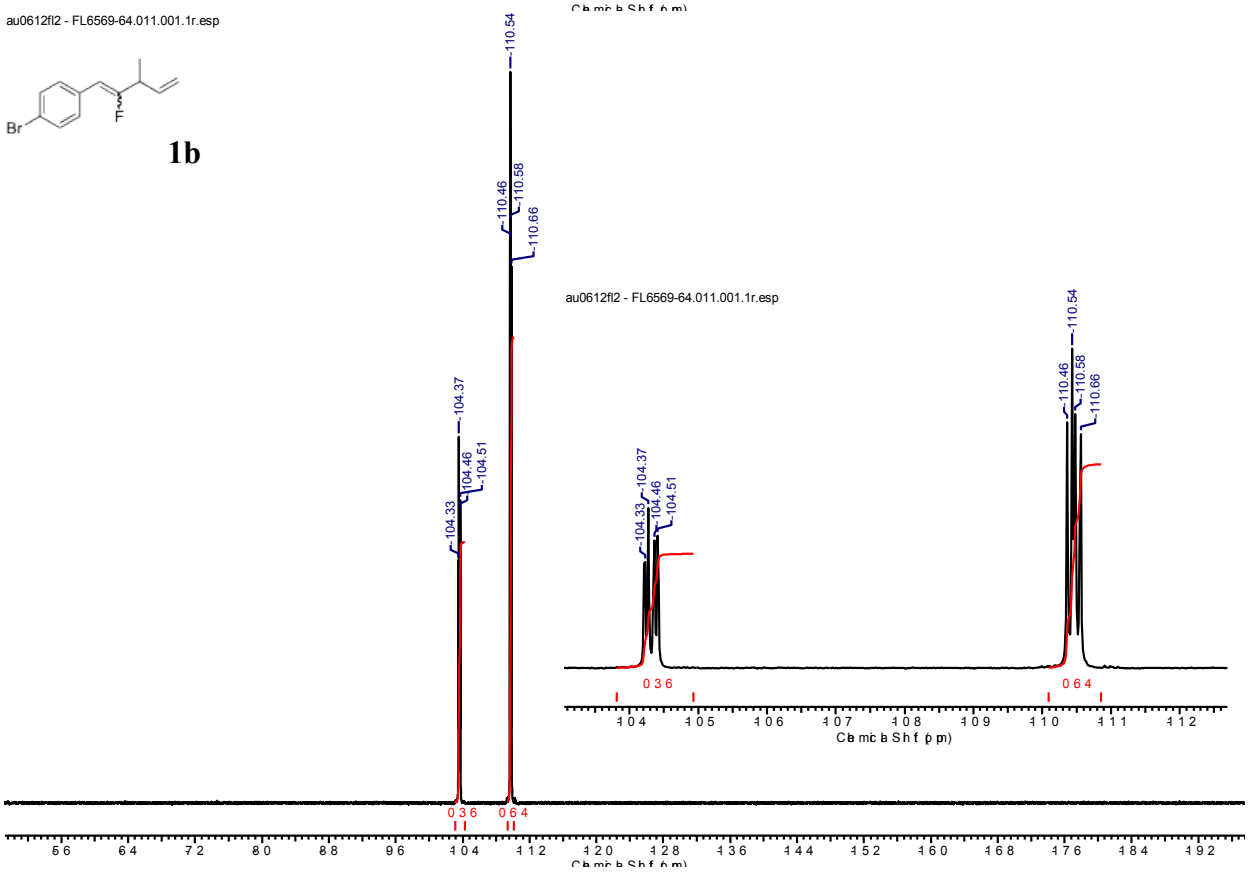





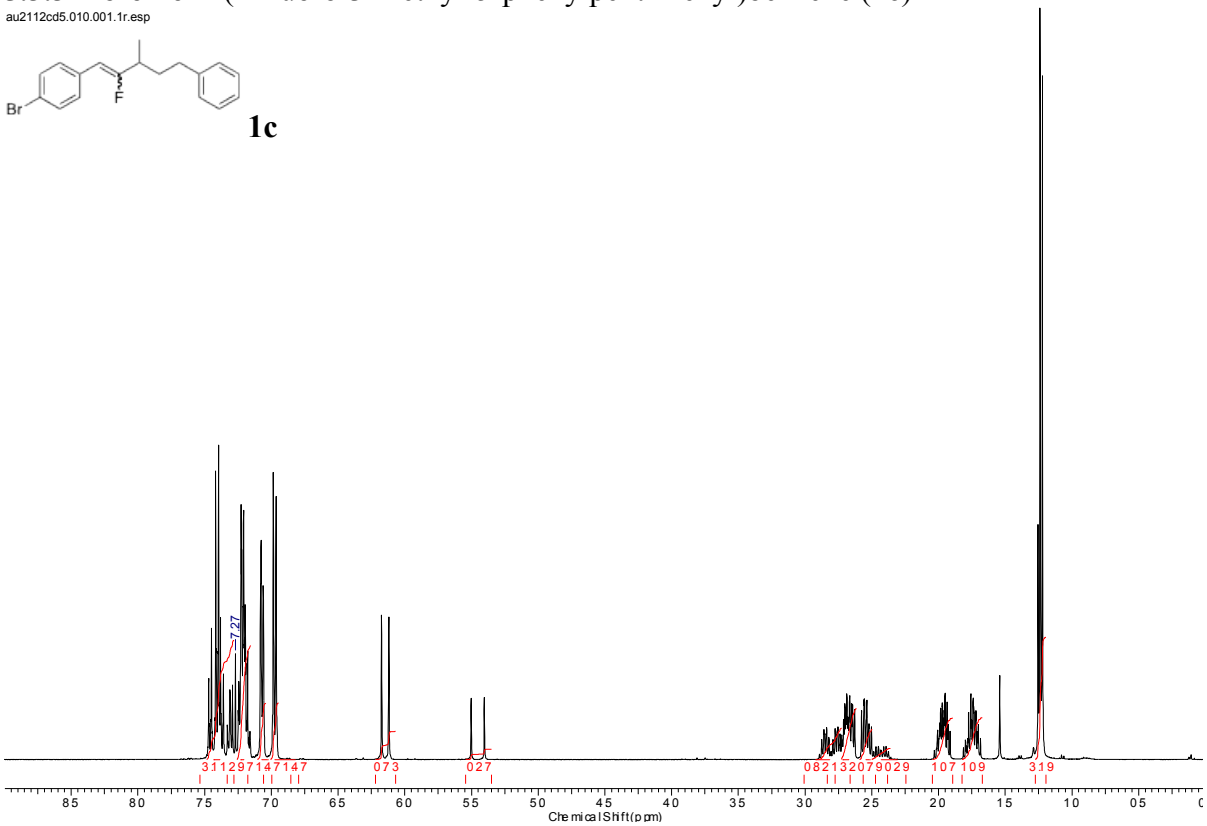

**5.3.2** 1-bromo-4-(2-fluoro-3-methylpenta-1,4-dienyl)benzene (**1b**)

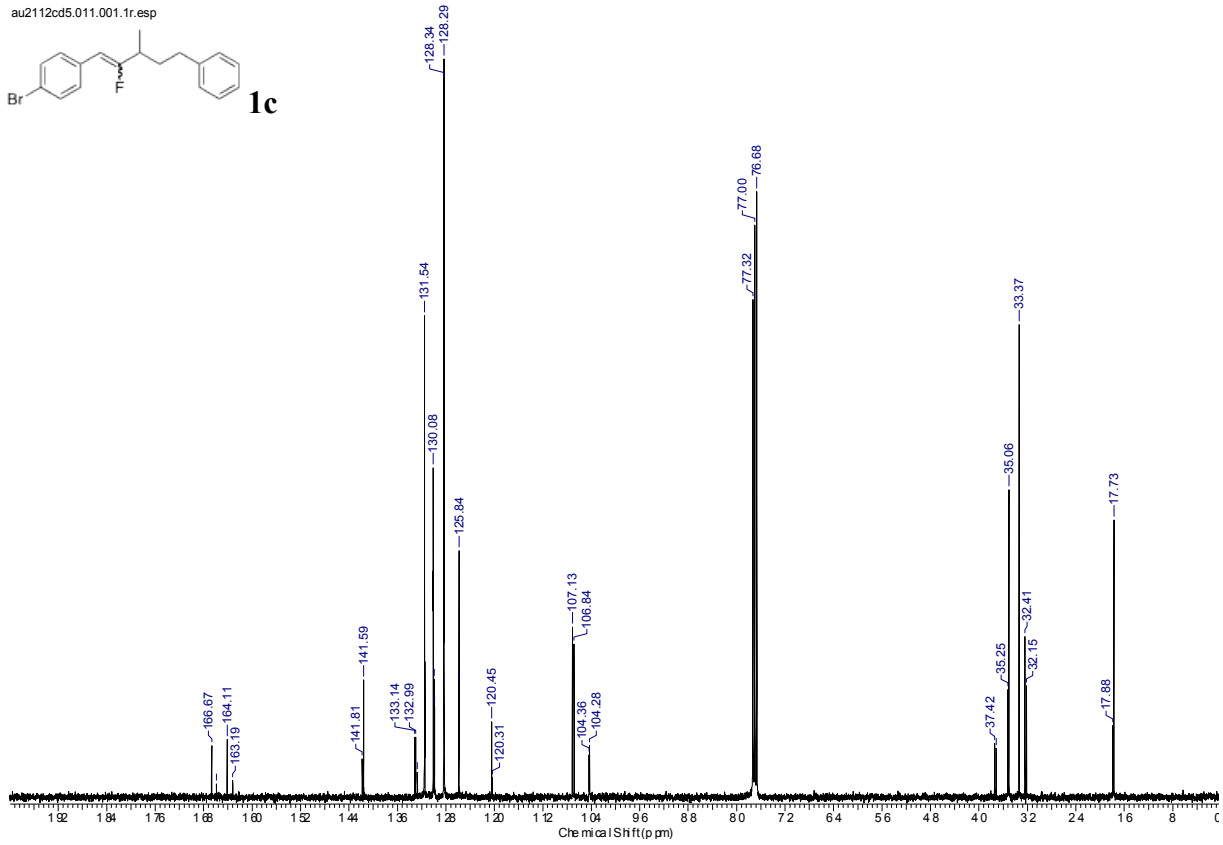


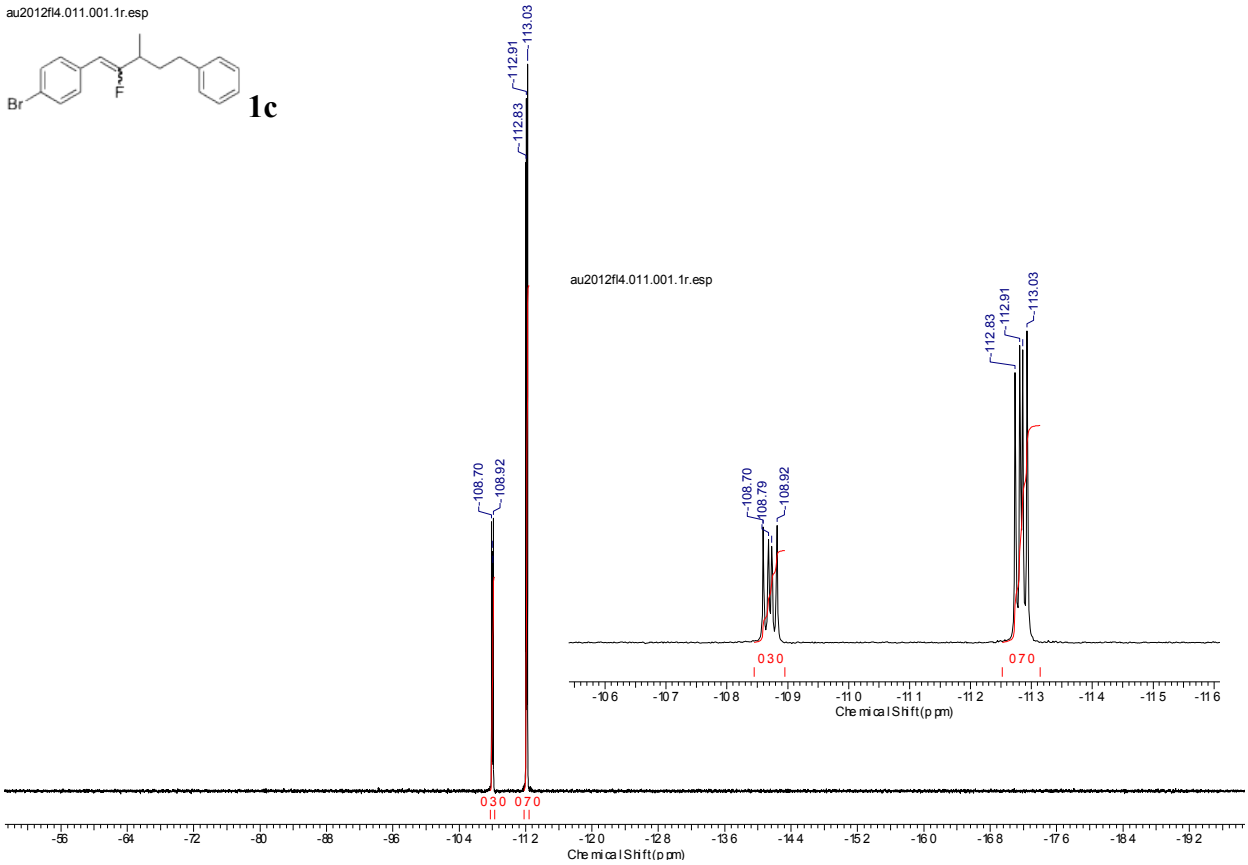

au0612cqf4 - FL6569-64.010.001.1r.esp
Br
F
1b
131.58
130.14
129.98
129.91
129.78
138.00
138.14
133.02
115.39
115.78
120.73
120.48
107.06
106.76
104.17
104.09
77.32
77.00
76.68
164.88
164.71
162.31
162.02
41.42
41.17
37.33
37.07
17.02


au0612fl2 - FL6569-64.011.001.1r.esp
Br
F
1b
110.54
110.46
110.58
110.66
104.37
104.46
104.51
104.33
0.36
0.64
au0612fl2 - FL6569-64.011.001.1r.esp
Chemical Shift (ppm)

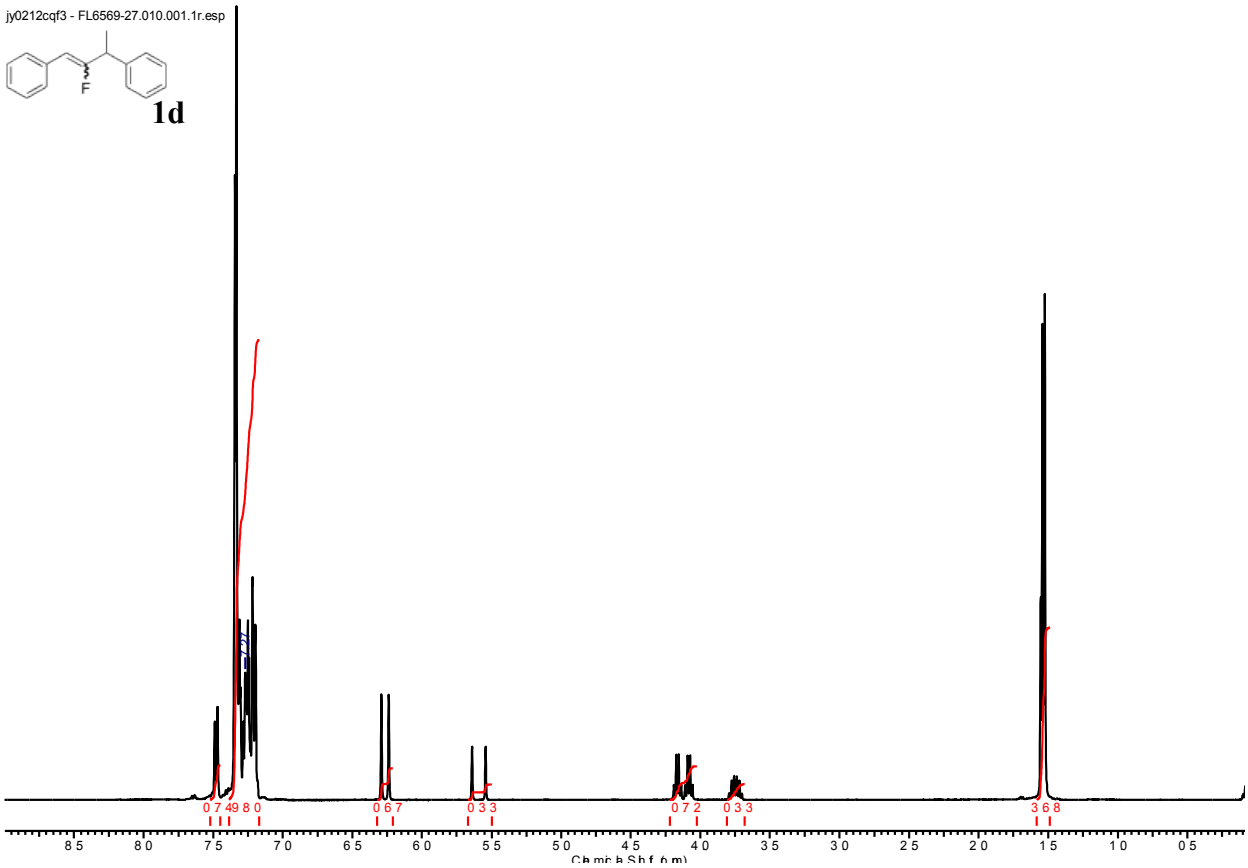
### **5.3.3** 1-bromo-4-(2-fluoro-3-methyl-5-phenylpent-1-enyl)benzene (**1c**)

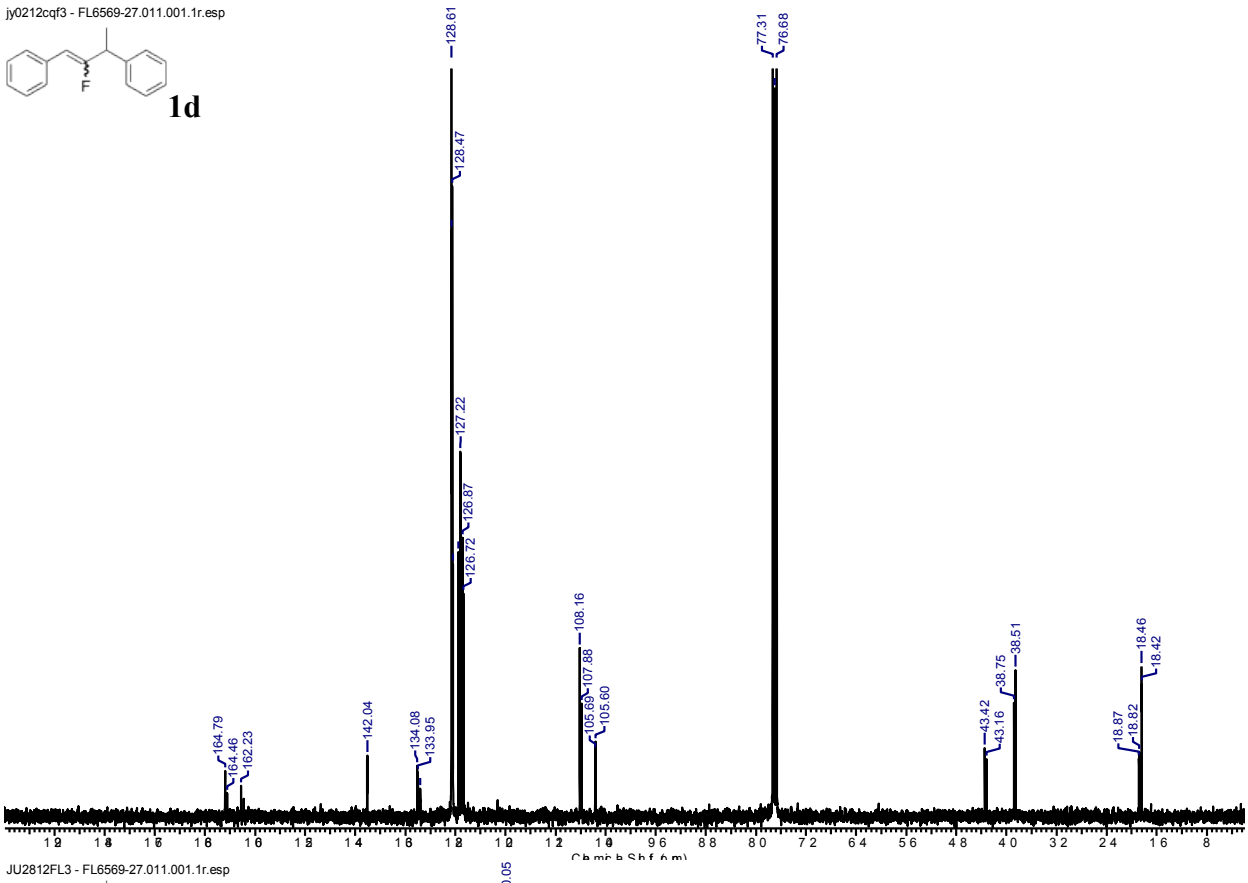


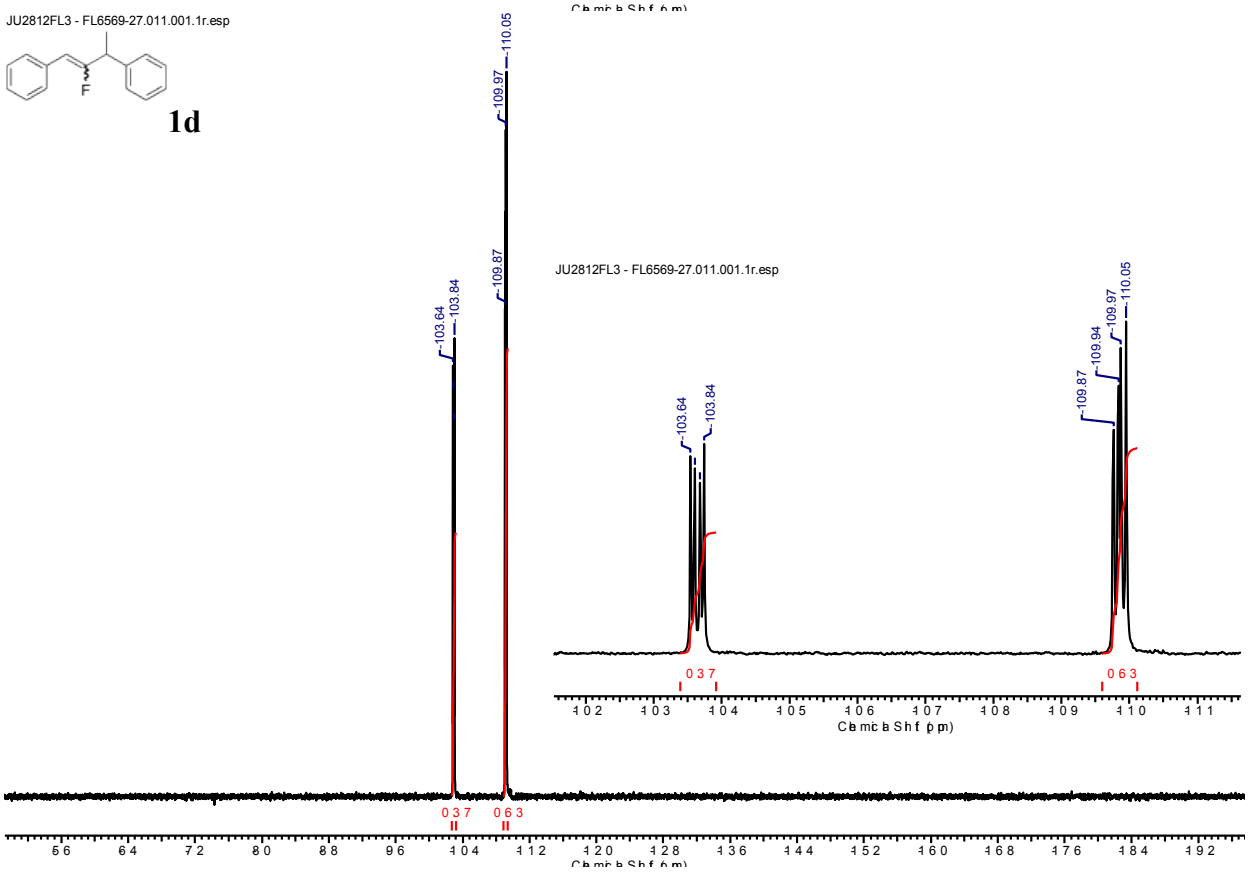





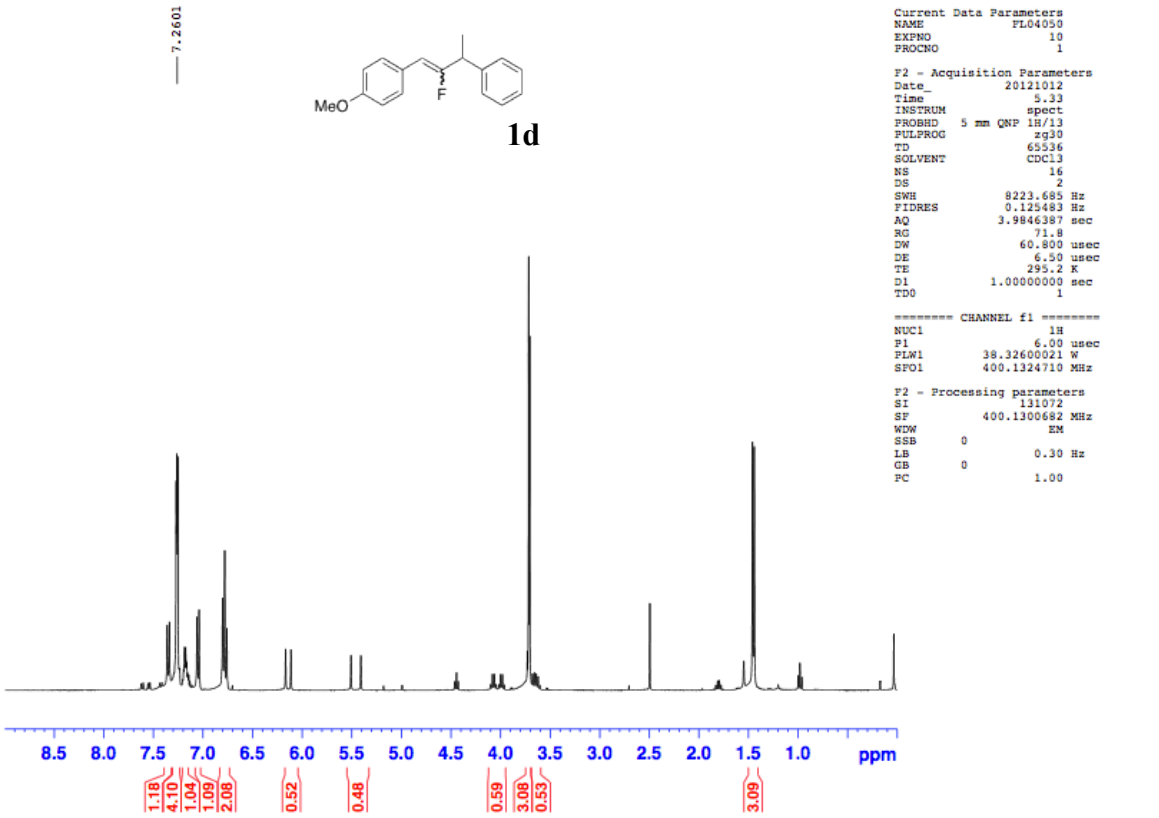

## **5.3.4** (2-fluorobut-1-ene-1,3-diyl)dibenzene (**1d**)

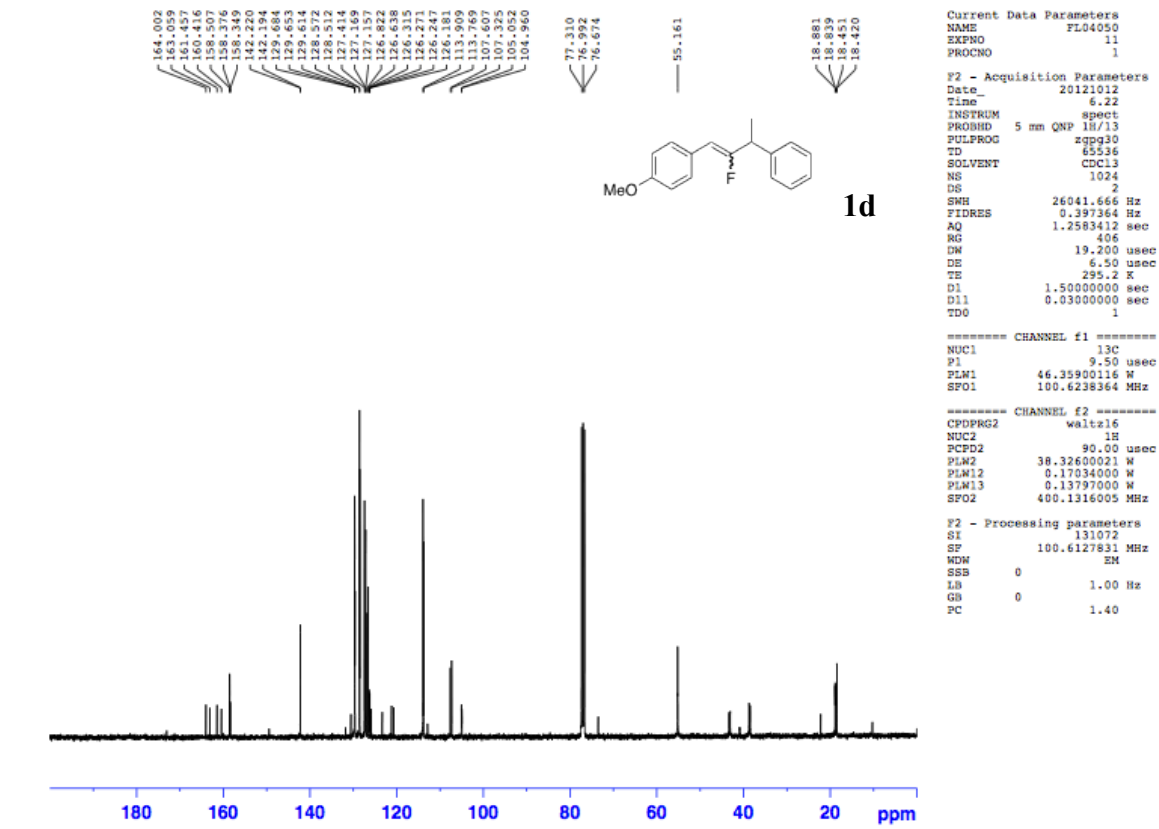


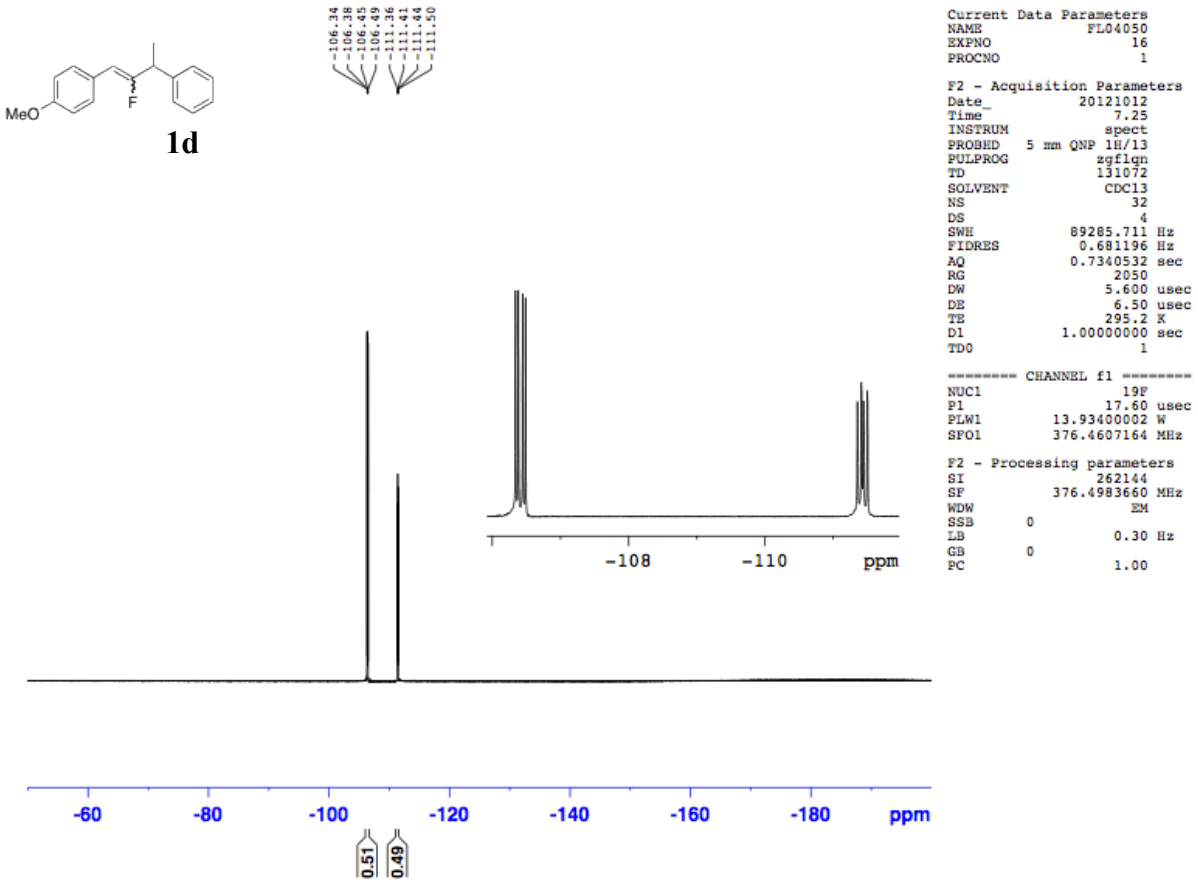

jy0212cqf3 - FL6569-27.011.001.1r.esp
1d
128.61
128.47
127.22
126.87
126.72
108.16
107.88
105.69
105.60
77.31
76.68
164.79
164.46
162.23
142.04
134.08
133.95
43.42
43.16
38.75
38.51
18.87
18.82
18.46
18.42


JU2812FL3 - FL6569-27.011.001.1r.esp
1d
110.05
109.97
109.87
103.84
103.64
0.37
0.63
JU2812FL3 - FL6569-27.011.001.1r.esp
110.05
109.97
109.94
109.87
103.84
103.64
0.37
0.63
Chemical Shift (ppm)

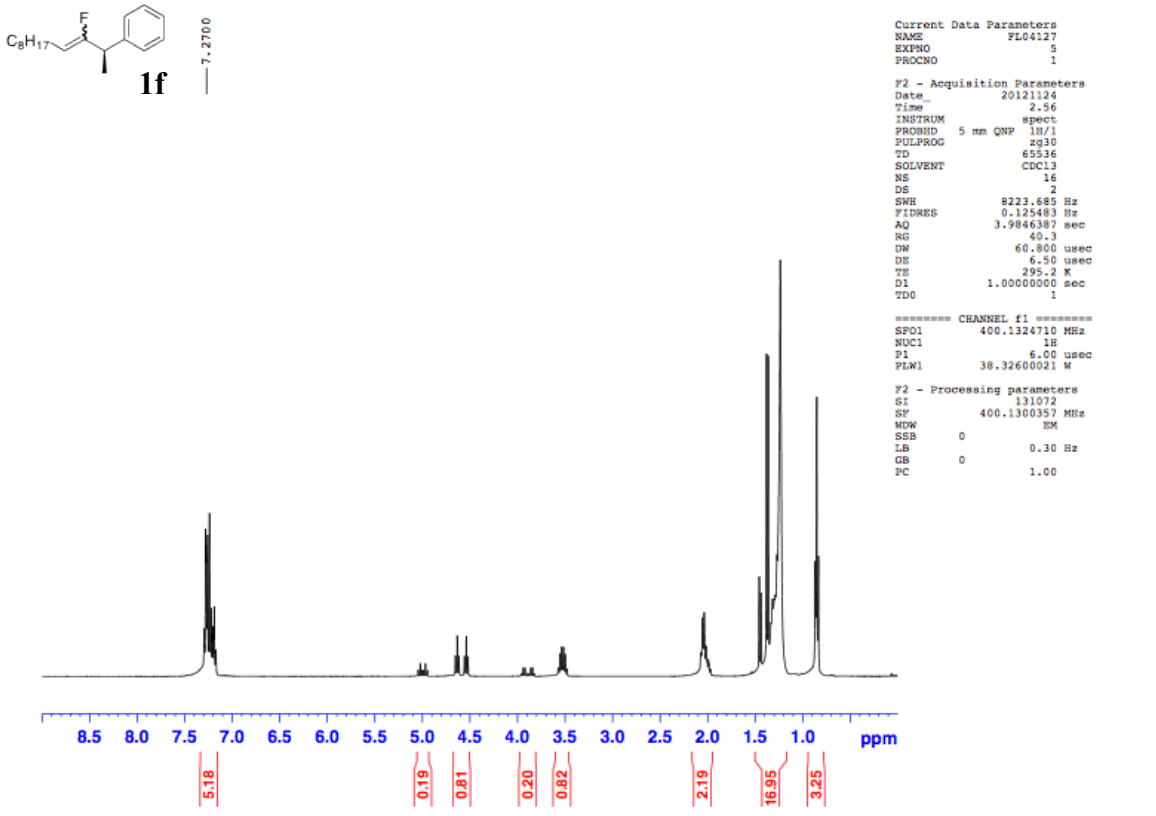
**5.3.5** (*Rac*)-2-fluoro-1-(4-methoxyphenyl)-3-phenylbut-1-ene (**1e**)

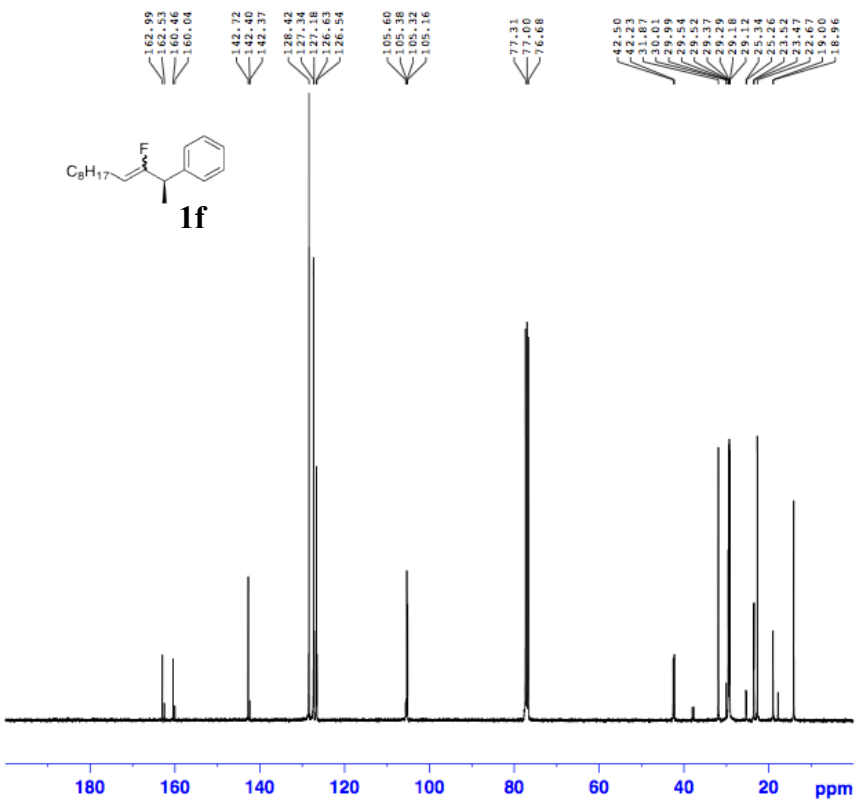





**5.3.6** (2*R*)-3-Fluoro-2-phenyl-dodec-3-ene (**1f**)



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EXPNO                       7
PROCNO                      1

F2 - Acquisition Parameters
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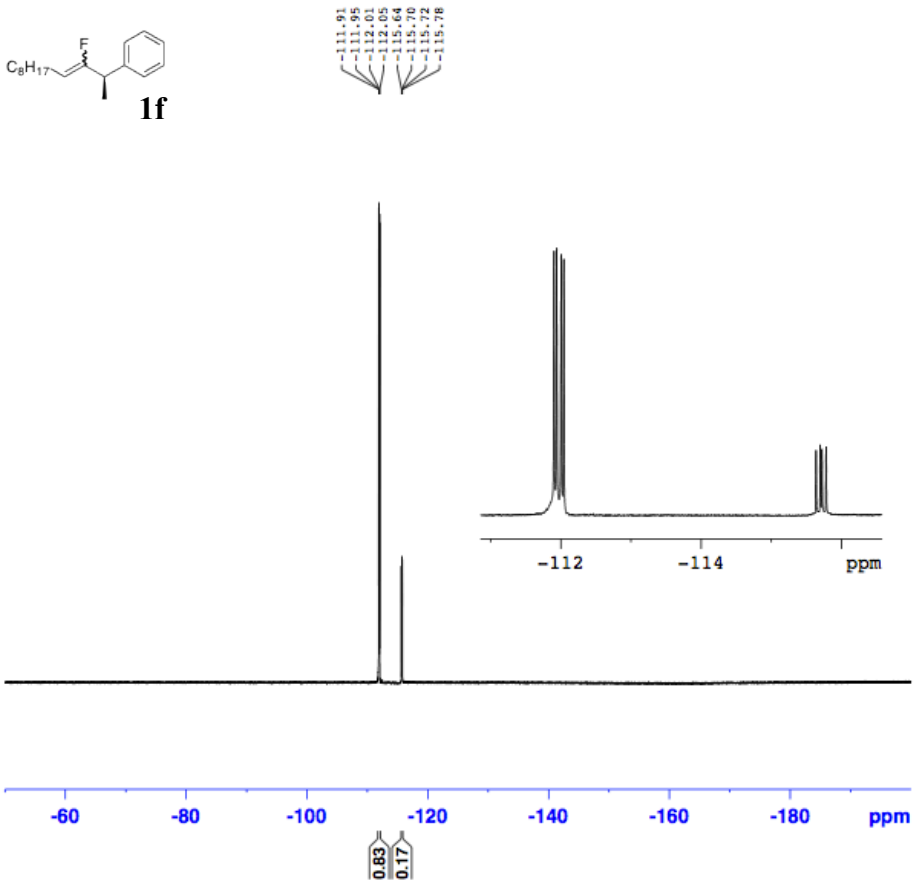
Time                     6.11
INSTRUM                 spect
PROBHD    5 mm QNP  1H/1
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       4096
DS                          2
SWH                 26041.666 Hz
FIDRES                0.397364 Hz
AQ                    1.2583412 sec
RG                        228
DW                       19.200 usec
DE                        6.50 usec
TE                       295.2 K
D1                  1.50000000 sec
d11                 0.03000000 sec
DELTA               1.39999998 sec
TD0                         1
NUC1                      13C
P1                        9.50 usec
PLW1                46.35900116 W
SFO1               100.6238364 MHz
CPDPRG2
NUC2                        1H
PLW2                38.32600021 W
PLW12                0.17034000 W
PLW13                0.13797000 W
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                        131072
SF                 100.6127729 MHz
WDW                           EM
SSB                 0
LB                        1.00 Hz
GB                  0
PC                        1.40
```




```
Current Data Parameters
NAME                  FL04127
EXPNO                       6
PROCNO                      1

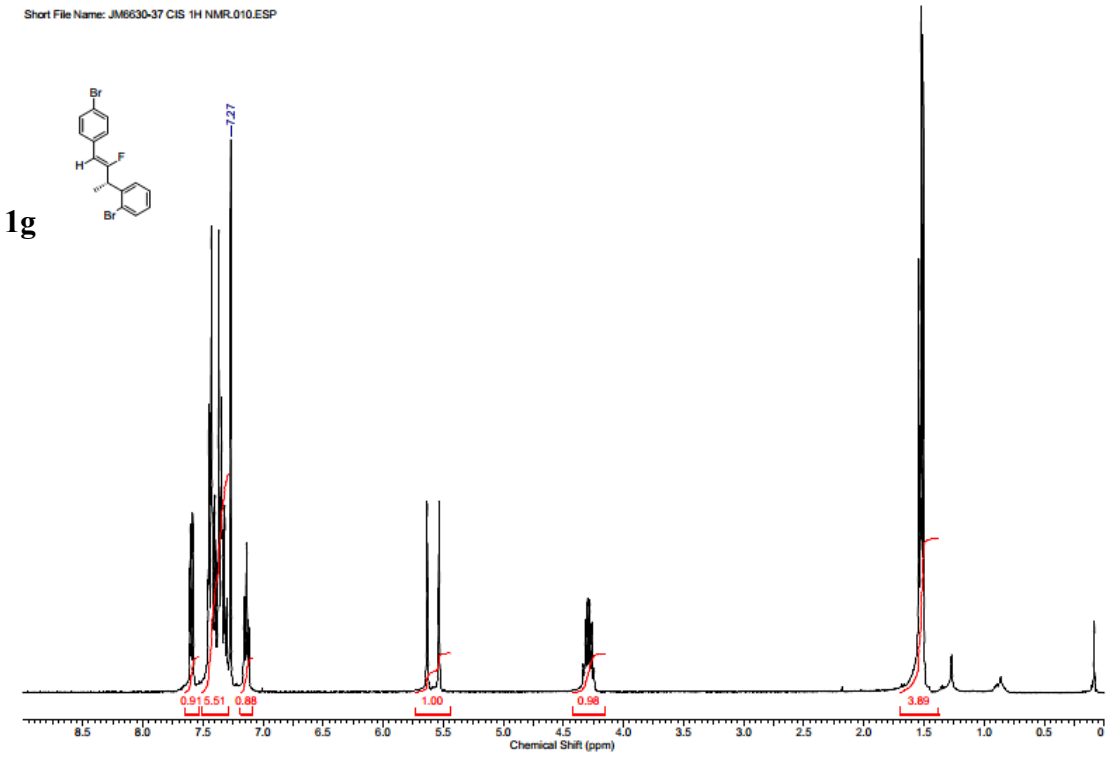
F2 - Acquisition Parameters
Date_                20121124
Time                     2.58
INSTRUM                 spect
PROBHD    5 mm QNP  1H/1
PULPROG                zgflqn
TD                     131072
SOLVENT                 CDCl3
NS                         32
DS                          4
SWH                 89285.711 Hz
FIDRES                0.681196 Hz
AQ                    0.7340532 sec
RG                       2050
DW                       5.600 usec
DE                        6.50 usec
TE                       295.2 K
D1                  1.00000000 sec
TD0                         1

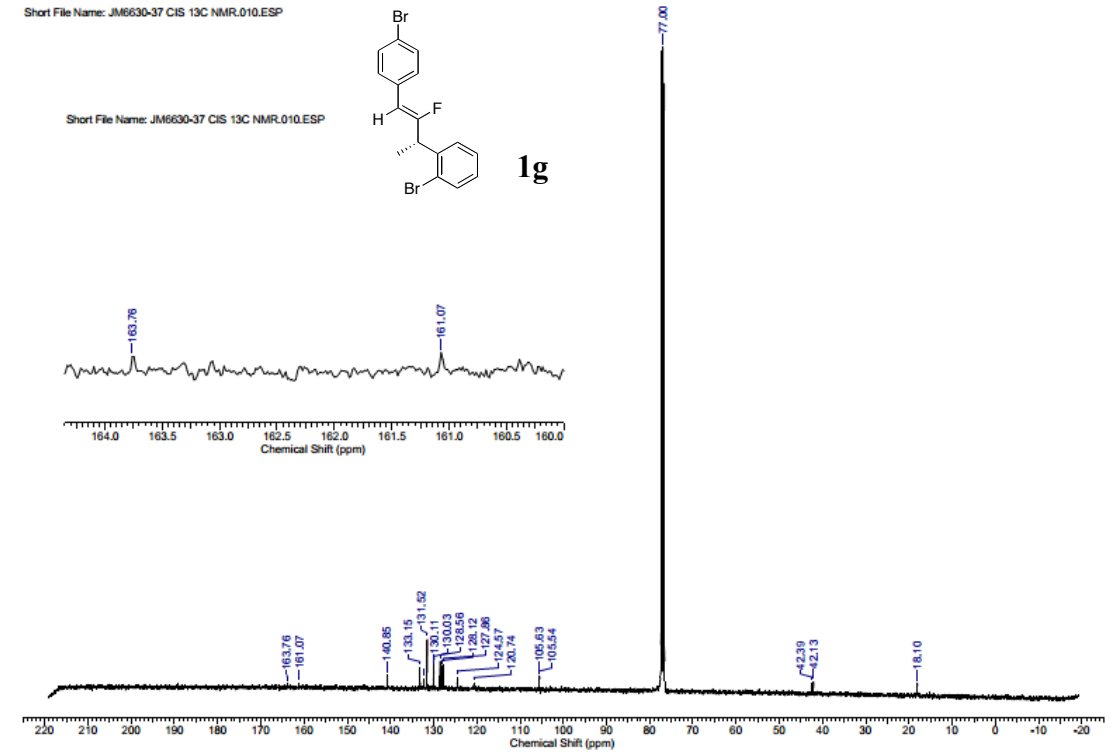
======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       17.60 usec
PLW1                13.93400002 W

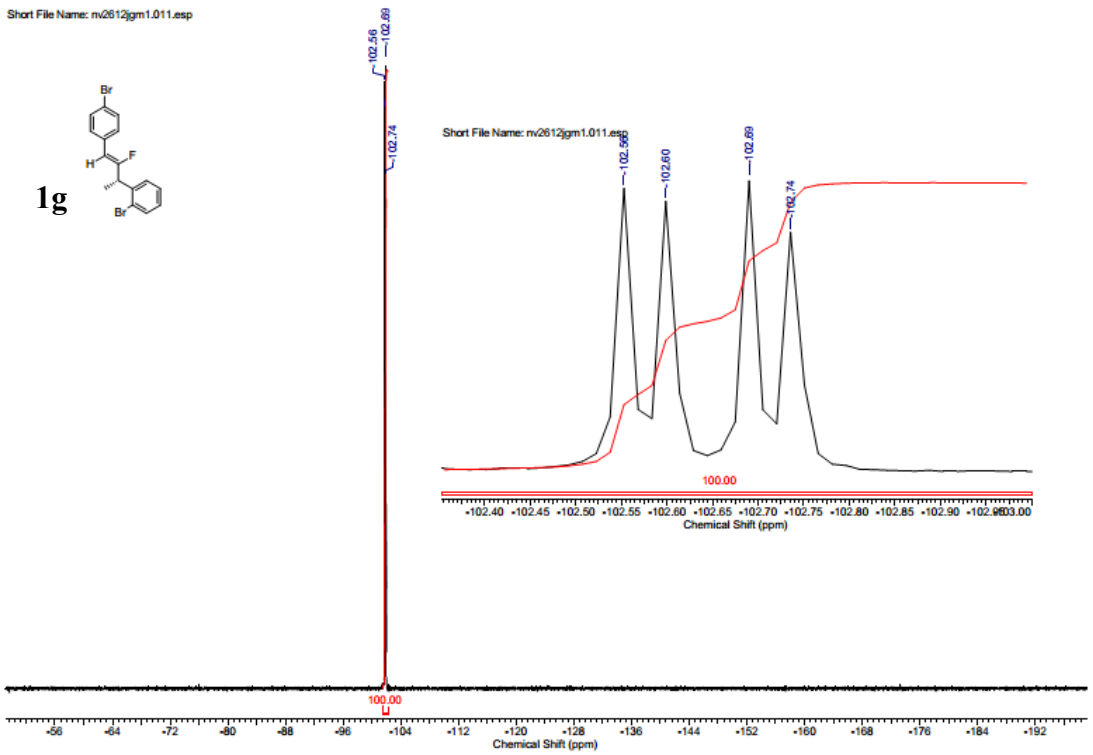
F2 - Processing parameters
SI                        262144
SF                 376.4983660 MHz
WDW                           EM
SSB                 0
LB                        0.30 Hz
GB                  0
PC                        1.00
```

**5.3.7** 1-bromo-2-(4-(4-bromophenyl)-3-fluorobut-3-en-2-yl)benzene (**1g**)

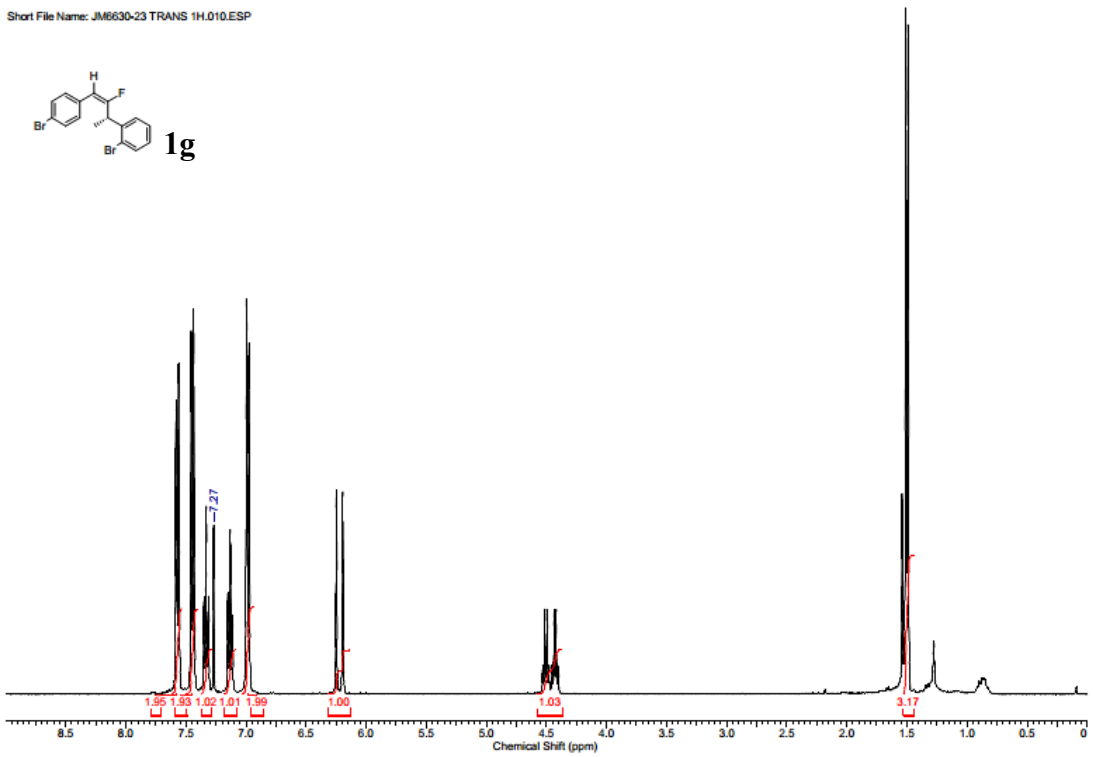
**a)** *cis*-1-bromo-2-(4-(4-bromophenyl)-3-fluorobut-3-en-2-yl)benzene

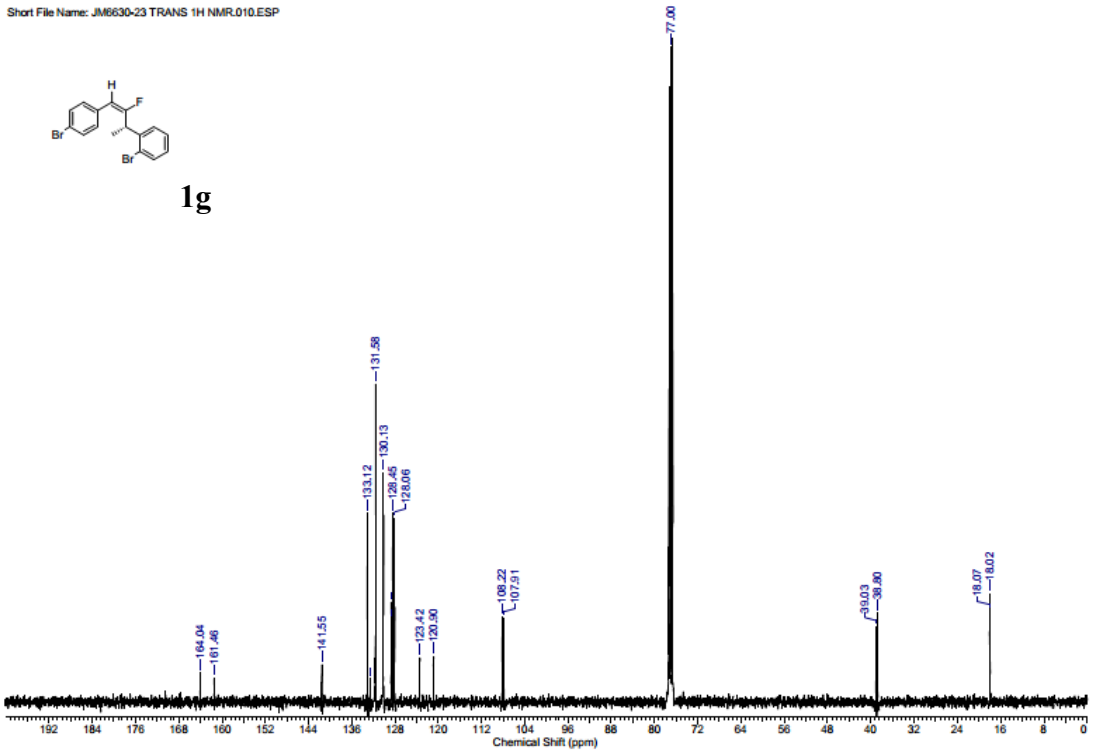


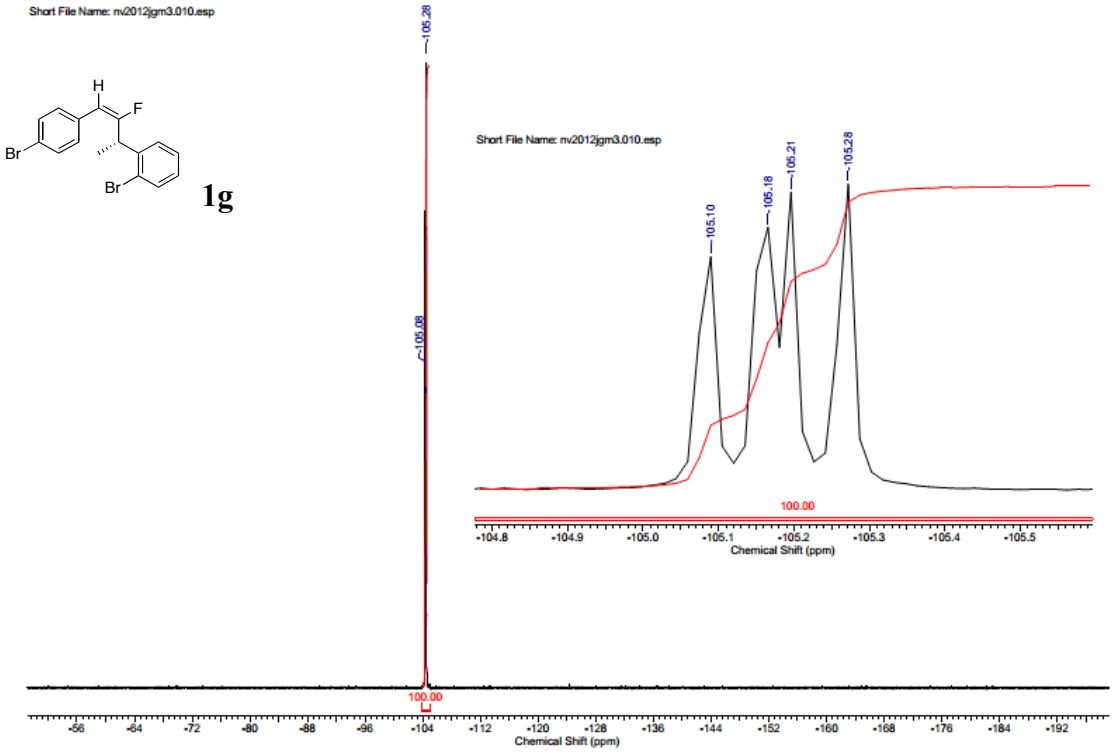






**b)** *trans*-1-bromo-2-(4-(4-bromophenyl)-3-fluorobut-3-en-2-yl)benzene

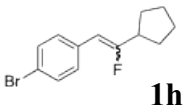





**5.3.8** 1-bromo-4-(2-cyclopentyl-2-fluorovinyl)benzene (**1h**)

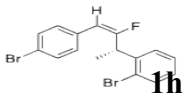
JY2712CQF5 - FL6569-54.010.001.1r.esp



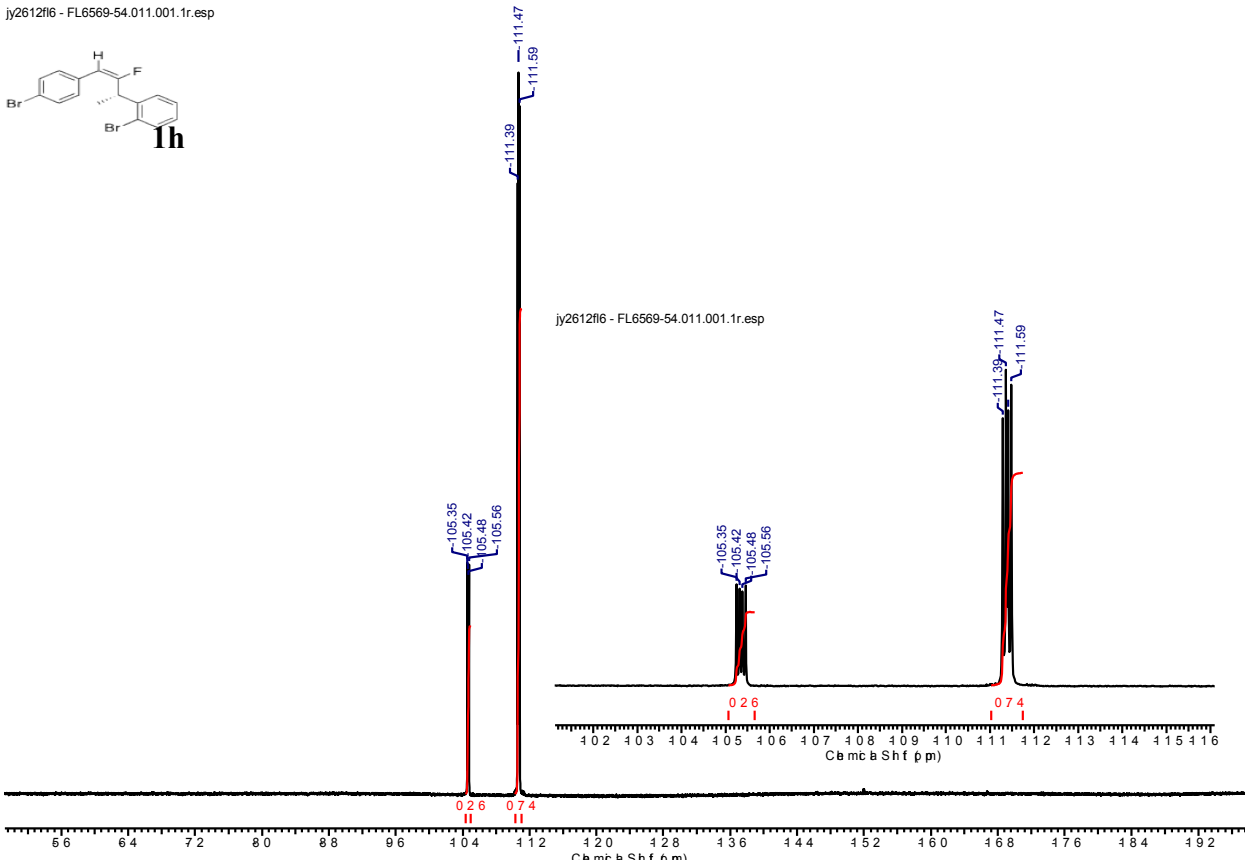

**1h**



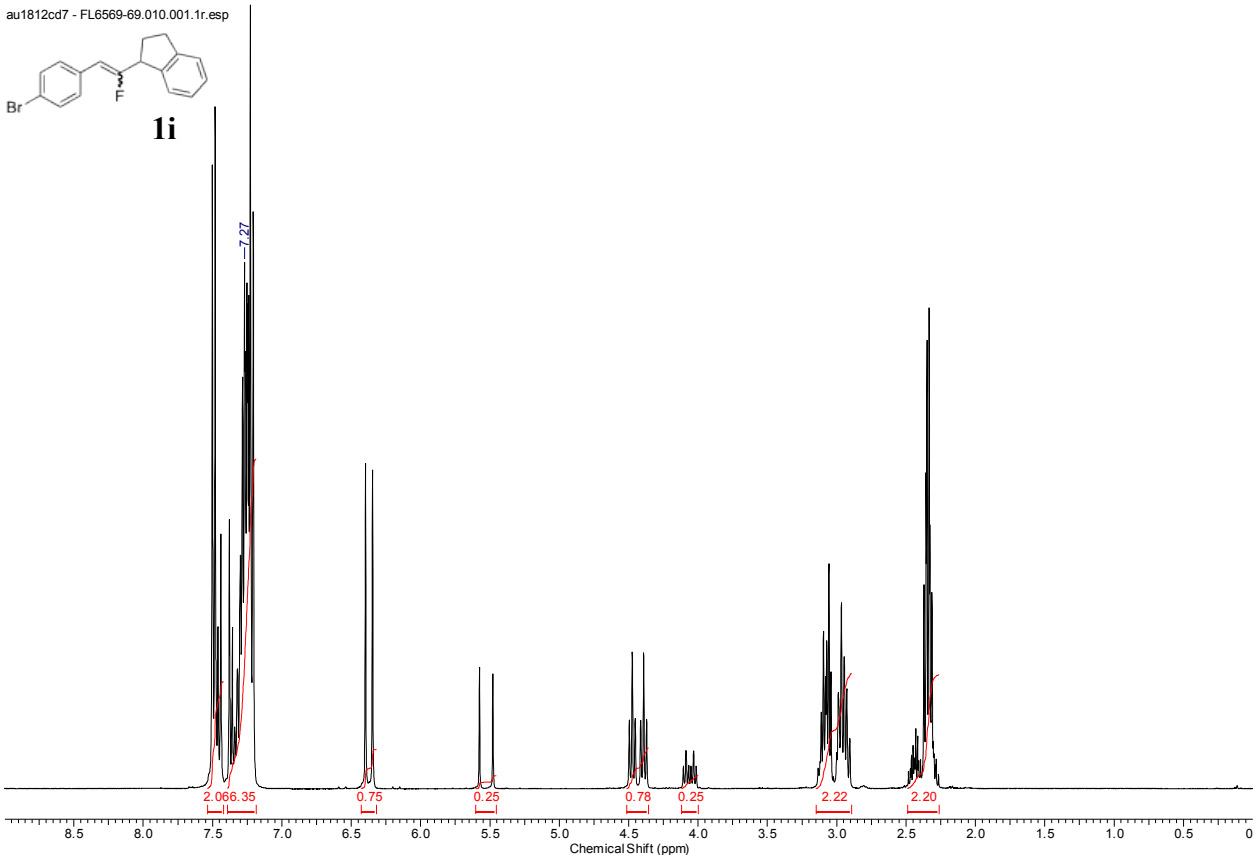

jy2712cqf5 - FL6569-54.011.001.1r.esp



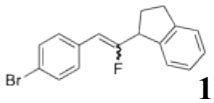

**1h**




## **5.3.9** 1-(2-(4-bromophenyl)-1-fluorovinyl)-2,3-dihydro-1*H*-indene (**1i**)



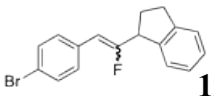
au1812cd7 - FL6569-69.011.001.1r.esp




**1i**




AU1812FL1.011.001.1r.esp

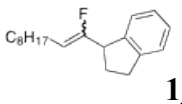



**1i**




AU1812FL1.011.001.1r.esp

**5.3.10** 1-(2-(4-bromophenyl)-1-fluorodec-1-enyl)-2,3-dihydro-1*H*-indene (**1j**)




**1j**




```
Current Data Parameters
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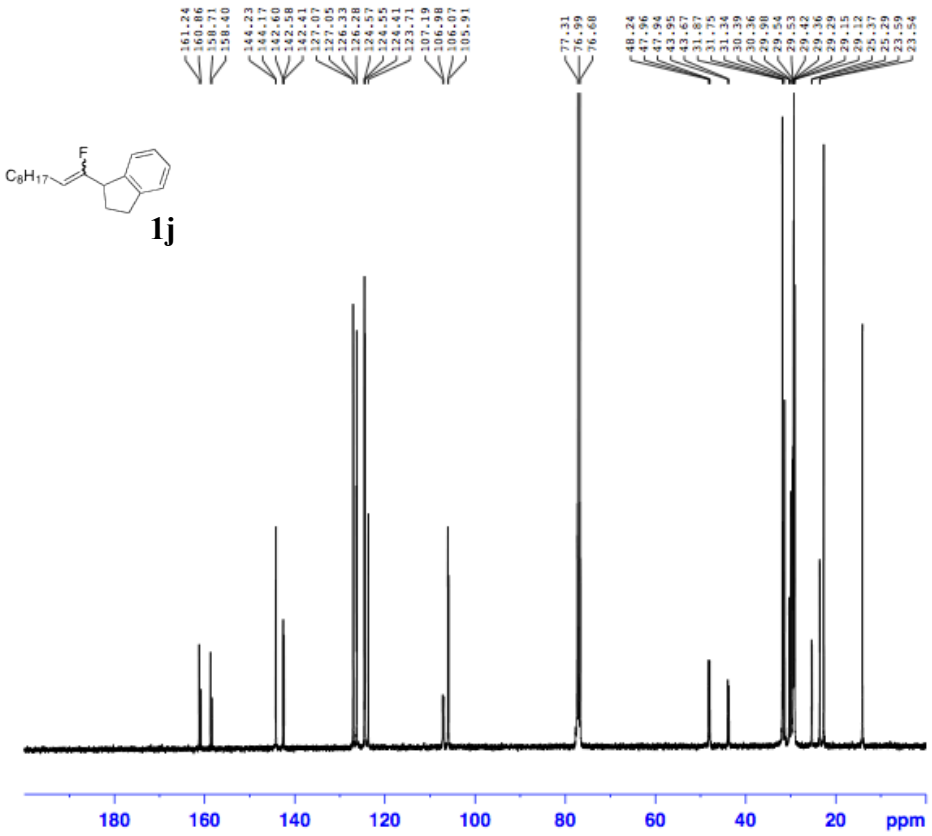
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20121123
Time                  21.40
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      36
DW                 60.800 usec
DE                  6.50 usec
TE                 295.2 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                   6.00 usec
PLW1           38.32600021 W

F2 - Processing parameters
SI                      131072
SF             400.1300206 MHz
WDW                       EM
SSB          0
LB                   0.30 Hz
GB           0
PC                   1.00
```





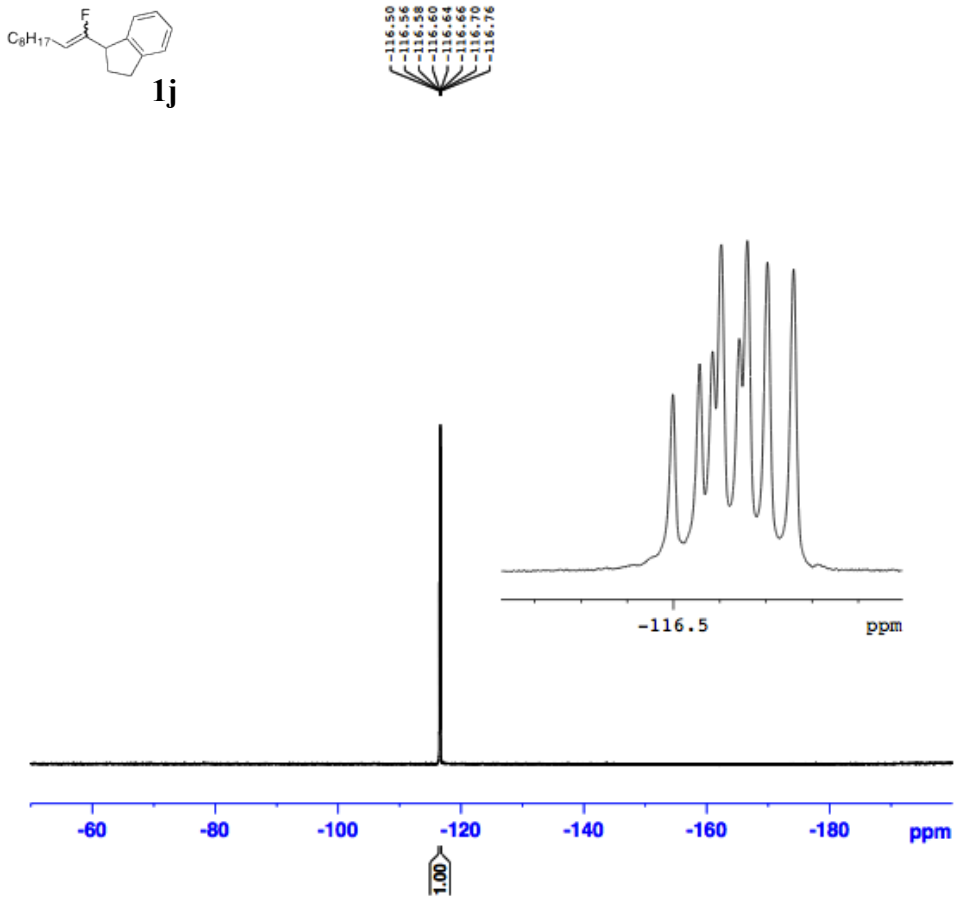


**1j**

```
Current Data Parameters
NAME                  FL04126
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_              20121124
Time                   0.55
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     4096
DS                       2
SWH              26041.666 Hz
FIDRES            0.397364 Hz
AQ                1.2583412 sec
RG                     362
DW                 19.200 usec
DE                  6.50 usec
TE                 295.2 K
D1                1.50000000 sec
d11               0.03000000 sec
DELTA             1.39999998 sec
TD0                         1
NUC1                      13C
P1                   9.50 usec
PLW1           46.35900116 W
SFO1          100.6238364 MHz
CPDPRG2
NUC2                      1H
PLW2           38.32600021 W
PLW12           0.17034000 W
PLW13           0.13797000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                      131072
SF             100.6127750 MHz
WDW                       EM
SSB          0
LB                   1.00 Hz
GB           0
PC                   1.40
```




```
Current Data Parameters
NAME                  FL04126
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20121123
Time                  21.41
INSTRUM                spect
PROBHD    5 mm QNP  1H/1
PULPROG               zgflqn
TD                    131072
SOLVENT                CDCl3
NS                         32
DS                          4
SWH               89285.711 Hz
FIDRES             0.681196 Hz
AQ                0.7340532 sec
RG                       2050
DW                   5.600 usec
DE                    6.50 usec
TE                    295.2 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           376.4607164 MHz
NUC1                    19F
P1                   17.60 usec
PLW1           13.93400002 W

F2 - Processing parameters
SI                     262144
SF             376.4983660 MHz
WDW                        EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```