Supporting information for

Catalytic Enantioselective Intramolecular 1,3-Dipolar Cycloaddition of Azomethine Ylides with Fluorinated Dipolarophiles

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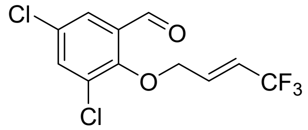
1. General methods

All anaerobic and moisture-sensitive manipulations were carried out in anhydrous solvents and under nitrogen. Dichloromethane, toluene, and tetrahydrofuran were dried over the PureSolv MD purification system. Melting points were taken in open-end capillary tubes. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (230-400 mesh). Flash column chromatographies were performed using silica gel (230-400 mesh). NMR spectra were recorded on AU-300 MHz instrument and calibrated using residual undeuterated solvent ($CDCl_3$) as internal reference. MS spectra were recorded on a VG *AutoSpec* mass spectrometer. The HPLC chromatograms of the racemic and enantiomerically enriched cycloadducts are also included. α-Iminoesters (**1a-j, 6b-f, 10, 12, 14 and 15**) were prepared by condensation of aminoesters hydrochlorides with the corresponding aldehydes, according to literature procedures.[1] The aldehydes needed for the preparation of α-iminoesters (**1a-f**, **2g**, **2h**, **2j**, **6b-f and 14**) were previously reported.[2] Starting imine **15** were previously described.[3]

2. Typical procedure for the synthesis of aldehyde precursors

[1]. S. Cabrera, R. Gómez Arrayás, J. C. Carretero, *J. Am. Chem. Soc.* 2005, **127**, 16394.
[2] a) F. Rabasa Alcañiz, D. Hammerl, A. Sánchez-Merino, T. Tejero, P. Merino, S. Fustero, C. del Pozo, *Org. Chem. Front*. 2019, **6**, 2916; b) B. Wang, L. Huang, Y. Lou, S. Lan, J. Chen, *Org. Lett.* 2018, **20**, 6012.
[3] R. Stohler, F. Wahl and A. Pfaltz, *Synthesis*, 2005, 1431

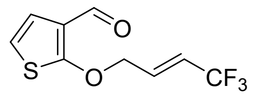
Typical procedure 1: (*E*)-3,5-Dichloro-2-((4,4,4-trifluorobut-2-en-1-yl)oxy)benzaldehyde.



This procedure was adapted from the literature procedure.[4] A solution of the 4,5-dichloro-2-hydroxybenzaldehyde (148 mg, 0.78 mmol) and K_2CO_3 (98 mg, 0.71 mmol) in dry acetonitrile (2 mL) was heated in a pressure vial at 60 °C for 10 min. A solution of (*E*)-4,4,4-trifluorobut-2-en-1-yl 4-methylbenzenesulfonate (199 mg, 0.71 mmol) in dry acetonitrile (2 mL) was added and the resulting mixture was heated at the same temperature for 16 h. Water (4 mL) was added to quench the reaction and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were washed with brine (30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel to afford starting fluorinated aldehyde (254 mg, 77%, yellowish solid).

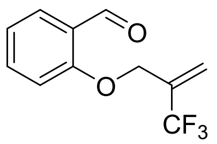
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.73 (d, *J* = 2.6 Hz, 1H), 7.65 (d, *J* = 2.6 Hz, 1H), 6.66 – 6.49 (m, 1H), 6.26 – 6.08 (m, 1H), 4.75 – 4.67 (m, 2H).
^{19}F NMR (282 MHz, $CDCl_3$) δ -64.57.
^{13}C NMR (75 MHz, $CDCl_3$) δ 187.2, 155.6, 136.0, 133.7 (q, *J* = 6.5 Hz), 131.5, 131.4, 130.0, 127.5, 122.8 (q, *J* = 269.6 Hz), 120.7 (q, *J* = 34.6 Hz), 72.9.

(*E*)-2-((4,4,4-Trifluorobut-2-en-1-yl)oxy)thiophene-3-carbaldehyde.



Following the typical procedure 1, the reaction of 2-hydroxythiophene-3-carbaldehyde (198 mg, 1.55 mmol) and (*E*)-4,4,4-trifluorobut-2-en-1-yl 4-methylbenzenesulfonate (392 mg, 1.40 mmol) afforded the corresponding aldehyde (276 mg, 83%, white solid).
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.05 (d, *J* = 1.2 Hz, 1H), 7.66 (dd, *J* = 5.4, 1.2 Hz, 1H), 6.82 (d, *J* = 5.5 Hz, 1H), 6.62 – 6.48 (m, 1H), 6.14 – 5.97 (m, 1H), 4.88 – 4.76 (m, 2H).
^{19}F NMR (282 MHz, $CDCl_3$) δ -64.58.
^{13}C NMR (75 MHz, $CDCl_3$) δ 181.04, 162.68, 135.41, 133.81 (q, *J* = 6.4 Hz), 122.55, 122.68 (d, *J* = 269.5 Hz), 120.53 (q, *J* = 34.7 Hz), 116.22, 69.10.

2-((2-(Trifluoromethyl)allyl)oxy)benzaldehyde.

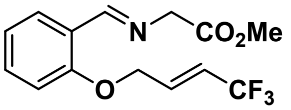


Folowing the typical procedure 1, the reaction of salicylaldehyde (95.1 mg, 0.78 mmol) and 2-(trifluoromethyl)allyl 4-methylbenzenesulfonate[5] (199 mg, 0.71 mmol) afforded the corresponding aldehyde (64 mg, 39%, light yellow oil).
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.52 (d, *J* = 0.7 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.4, 1.9 Hz, 1H), 7.17 – 7.06 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.00 (q, *J* = 1.3 Hz, 1H), 5.86 (q, *J* = 1.4 Hz, 1H), 4.79 (s, 2H).
^{19}F NMR (282 MHz, $CDCl_3$) δ -67.42 (s, 3F).
^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 160.1, 136.1, 132.1 (q, *J* = 282.4 Hz, CF_3), 129.1, 128.0, 125.4, 121.9, 121.3 (q, *J* = 5.4 Hz), 112.6, 65.1 (q, *J* = 1.4 Hz).

3. Typical procedure for the synthesis of iminoesteres

4. E. Forcellini, R. Hemelaere, J. Desroches, J.-F. Paquin, *J. Fluorine Chem.* 2015, **180**, 216.
5. V. De Matteis, F. L. van Delft, H. Jakobi, S. Lindell, J. Tiebes, F. P. J. T Rutjes,. *J. Org. Chem.* 2006, **71**, 7527.

Typical procedure 2: Methyl 2-(2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1a)

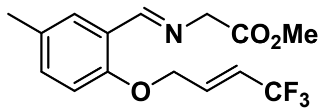


crude **1a**

To a suspension of 2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (40 mg, 0.17 mmol), glycine methyl ester hydrochloride (43 mg, 0.34 mmol) and anhydrous $MgSO_4$ (excess) in dry dichloromethane (4.0 mL), Et_3N (48 µL, 0.34 mmol) was added. The mixture was stirred at room temperature for 12 hours and water (10 mL) was added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (10mL). The combined organic layers were dried over $MgSO_4$, and evaporated under reduced pressure to afford **1a** (44.5 mg, 87%, yellow oil), which was used without further purification in the next reaction step.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.03 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.41 (td, *J* = 7.6, 2.1 Hz, 1H), 7.05 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.0, 0.9 Hz, 1H), 6.66 – 6.53 (m, 1H), 6.12 – 5.97 (m, 1H), 4.76 – 4.69 (m, 2H), 4.45 (d, *J* = 1.3 Hz, 2H), 3.78 (s, 3H).

Methyl 2-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1b)

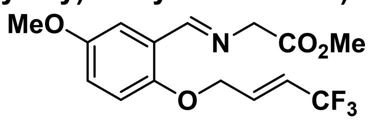


crude **1b**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (50 mg, 0.40 mmol), $MgSO_4$ (excess), Et_3N (56 μL, 0.40 mmol) and 5-methyl-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (50 mg, 0.20 mmol) in dichloromethane (5 mL) afforded **1b** (49 mg, 77%, colorless oil).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 7.12 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.57 – 6.44 (m, 1H), 6.05 – 5.89 (m, 1H), 4.66 – 4.53 (m, 2H), 4.37 (d, *J* = 1.4 Hz, 2H), 3.71 (s, 3H), 2.22 (s, 3H).

Methyl 2-(5-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1c)

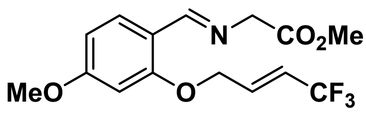


crude **1c**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (48 mg, 0.38 mmol), $MgSO_4$ (excess), Et_3N (53 μL, 0.38 mmol) and 5-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (50 mg, 0.19 mmol) in dichloromethane (5 mL) afforded **1c** (60 mg, 96%, colorless oil).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 6.59 – 6.45 (m, 2H), 6.33 (d, *J* = 2.3 Hz, 1H), 6.09 – 5.91 (m, 1H), 4.65 – 4.57 (m, 2H), 4.35 (d, *J* = 1.4 Hz, 2H), 3.77 (s, 3H), 3.72 (s, 3H).

Methyl 2-(4-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1d)

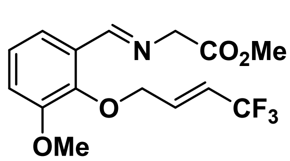


crude **1d**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (95 mg, 0.76 mmol), $MgSO_4$ (excess), Et_3N (106 µL, 0.76 mmol) and 4-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (100 mg, 0.38 mmol) in dichloromethane (7 mL) afforded **1d** (117 mg, 99%, colorless oil).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.05 – 7.90 (m, 1H), 6.55 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.35 (d, *J* = 2.3 Hz, 1H), 6.14 – 5.97 (m, 1H), 4.65 (s, 2H), 4.38 (s, 2H), 3.80 (s, 3H), 3.75 (s, 3H).

Methyl 2-(3-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1e)

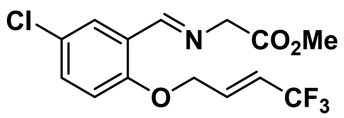


crude **1e**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (48 mg, 0.38 mmol), $MgSO_4$ (excess), Et_3N

(53 μL, 0.38 mmol) and 3-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (50 mg, 0.19 mmol) in dichloromethane (5 mL) afforded **1e** (58 mg, 99%, colorless oil).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.61 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.61 – 6.50 (m, 1H), 6.17 – 6.00 (m, 1H), 4.68 – 4.62 (m, 2H), 4.43 (d, *J* = 1.3 Hz, 2H), 3.87 (s, 3H), 3.77 (s, 3H).

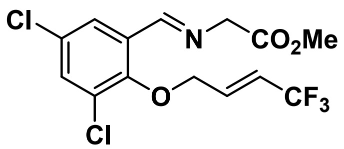
Methyl 2-(5-chloro-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1f)



crude **1f**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (48 mg, 0.38 mmol), $MgSO_4$ (excess), Et_3N (53 μL, 0.38 mmol) and 5-chloro-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (50 mg, 0.19 mmol) in dichloromethane (5 mL) afforded **1f** (51 mg, 80 %, yellow oil).
^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.94 (d, *J* = 2.7 Hz, 1H), 7.27 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 1H), 6.57 – 6.46 (m, 1H), 6.04 – 5.89 (m, 1H), 4.70 – 4.56 (m, 2H), 4.39 (d, *J* = 1.4 Hz, 2H), 3.73 (s, 3H).

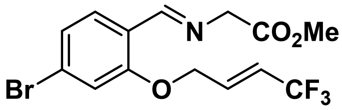
Methyl 2-(3,5-dichloro-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1g)



crude **1g**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (125 mg, 1.00 mmol), $MgSO_4$ (excess), Et_3N (140 µL, 1.00 mmol) and 3,5-dichloro-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (150 mg, 0.50 mmol) in dichloromethane (7 mL) afforded **1g** (201 mg, 99%, yellow oil).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.89 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 2.6 Hz, 1H), 6.60 – 6.44 (m, 1H), 6.19 – 6.04 (m, 1H), 4.60 – 4.54 (m, 2H), 4.41 (d, *J* = 1.4 Hz, 2H), 3.74 (s, 3H).

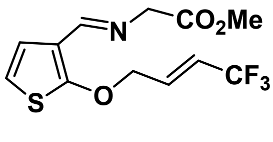
Methyl 2-(4-bromo-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1h)



crude **1h**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (40 mg, 0.32 mmol), $MgSO_4$ (excess), Et_3N (45 µL, 0.32 mmol) and 4-bromo-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (50 mg, 0.16 mmol) in dichloromethane (7 mL) afforded **1h** (48 mg, 82%, yellow oil).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 6.63 – 6.51 (m, 1H), 6.12 – 5.97 (m, 1H), 4.72 – 4.66 (m, 2H), 4.43 (d, *J* = 1.4 Hz, 2H), 3.78 (s, 3H).

Methyl 2-(2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)thiophen-3-ylmethyleneamino)acetate (1i)

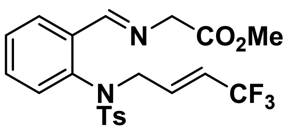


crude **1i**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (107 mg, 0.85 mmol), $MgSO_4$ (excess), Et_3N (119 µL, 0.85 mmol) and 2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)thiophene-3-carbaldehyde (20 mg, 0.085 mmol) in dichloromethane (5 mL) afforded **1i** (26 mg, 99%, yellow oil).

^{1}**H NMR (300 MHz, CDCl$_3$)** δ 8.47 (s, 1H), 7.36 (d, *J* = 5.5 Hz, 1H), 6.76 (d, *J* = 5.5 Hz, 1H), 6.60 – 6.46 (m, 1H), 6.11 – 5.94 (m, 1H), 4.77 – 4.69 (m, 2H), 4.36 (d, *J* = 1.2 Hz, 2H), 3.76 (s, 3H).

Methyl 2-(2-(4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6a)

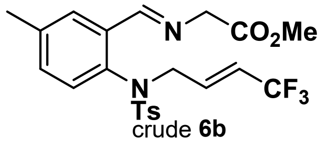


crude **6a**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (65 mg, 0.52 mmol), $MgSO_4$ (excess), Et_3N (73 μL, 0.52 mmol) and *N*-(2-formylphenyl)-4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide (100 mg, 0.26 mmol) in dichloromethane (5 mL) afforded **6a** (135 mg, 99%, yellow oil).

^{1}**H NMR (300 MHz, CDCl$_3$)** δ 8.47 (s, 1H), 8.15 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.32 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.70 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.36 – 6.23 (m, 1H), 5.72 – 5.58 (m, 1H), 4.44 – 4.05 (m, 4H), 3.77 (s, 3H), 2.44 (s, 3H).

Methyl 2-(5-methyl-2-(4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6b)

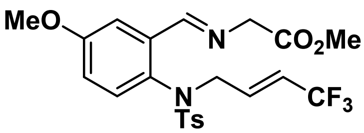


crude **6b**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (19 mg, 0.15 mmol), $MgSO_4$ (excess), Et_3N (21 μL, 0.15 mmol) and *N*-(2-formyl-4-methylphenyl)-4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide (30 mg, 0.075 mmol) in dichloromethane (4 mL) afforded **6b** (42 mg, 99%, yellow oil).

^{1}**H NMR (300 MHz, CDCl$_3$)** δ 8.44 (s, 1H), 7.96 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 1H), 6.36 – 6.22 (m, 1H), 5.71 – 5.58 (m, 1H), 4.45 – 3.94 (m, 4H), 3.77 (s, 3H), 2.44 (s, 3H), 2.36 (s, 3H).

Methyl 2-(5-methoxy-2-(4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6c)

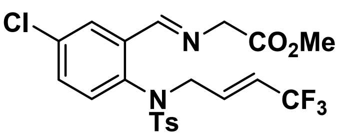


crude **6c**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (18 mg, 0.15 mmol), $MgSO_4$ (excess), Et_3N (20 μL, 0.15 mmol) and *N*-(2-formyl-4-methoxyphenyl)-4-methyl-*N*-((E)-4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide (30 mg, 0.073 mmol) in dichloromethane (4 mL) afforded **6c** (32 mg, 90%, yellow oil).

^{1}**H NMR (300 MHz, CDCl$_3$)** δ 8.43 (s, 1H), 7.63 (d, *J* = 3.0 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.86 (dd, *J* = 9.0, 3.3 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 6.36 – 6.22 (m, 1H), 5.74 – 5.58 (m, 1H), 4.46 – 3.98 (m, 4H), 3.85 (s, 3H), 3.77 (s, 3H), 2.44 (s, 3H).

Methyl 2-(5-chloro-2-(4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6d)

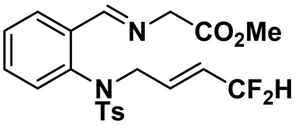


crude **6d**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (18 mg, 0.14 mmol), $MgSO_4$ (excess), Et_3N (20 μL, 0.15 mmol) and *N*-(2-formyl-4-chlorophenyl)-4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide (30 mg, 0.072 mmol) in

dichloromethane (4 mL) afforded **6d** (40 mg, 99%, yellow oil).
¹H NMR (300 MHz, CDCl$_3$) δ 8.41 (s, 1H), 8.16 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 3H), 6.62 (d, *J* = 8.5 Hz, 1H), 6.35 – 6.21 (m, 1H), 5.73 – 5.58 (m, 1H), 4.47 – 3.98 (m, 4H), 3.78 (s, 3H), 2.45 (s, 3H).

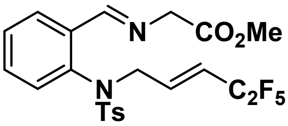
Methyl 2-(2-(*N*-((*E*)-4,4-difluorobut-2-en-1-yl)-4-methylphenylsulfonamido)benzylideneamino)acetate (6e)



crude **6e**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (14 mg, 0.11 mmol), MgSO$_4$ (excess), Et$_3$N (16 μL, 0.11 mmol) and *N*-((*E*)-4,4-difluorobut-2-en-1-yl)-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide (20 mg, 0.055 mmol) in dichloromethane (4 mL) afforded **6e** (36 mg, 99%, colorless oil).
¹H-NMR (300 MHz, CDCl$_3$) δ 8.53 (s, 1H), 8.14 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.23 (m, 4H), 6.64 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.06 – 5.96 (m, 1H), 5.69 – 5.53 (m, 1H), 4.49–3.89 (m, 4H), 3.76 (s, 3H), 2.43 (s, 3H).

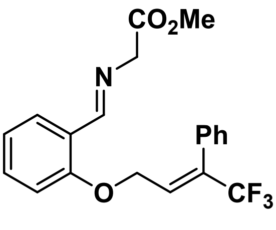
Methyl 2-(2-(4-methyl-*N*-((*E*)-4,4,5,5,5-pentafluoropent-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6f)



crude **6f**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (18 mg, 0.14 mmol), MgSO$_4$ (excess), Et$_3$N (20 μL, 0.14 mmol) and *N*-(2-formylphenyl)-4-methyl-*N*-((*E*)-4,4,5,5,5-pentafluoropent-2-en-1-yl)benzenesulfonamide (30 mg, 0.070 mmol) in dichloromethane (4.0 mL) afforded **6f** (34 mg, 96%, colorless oil).
¹H NMR (300 MHz, CDCl$_3$) δ 8.49 (s, 1H), 8.18 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.55 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.47 – 7.35 (m, 2H), 7.32 (dd, *J* = 8.3, 1.4 Hz, 2H), 6.71 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.42 – 6.29 (m, 1H), 5.73 – 5.55 (m, 1H), 4.48 – 4.10 (m, 4H), 3.79 (s, 3H), 2.47 (s, 3H).

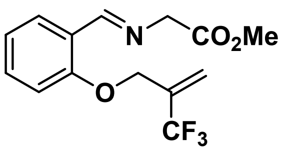
Methyl 2-(2-((*E*)-4,4,4-trifluoro-3-phenylbut-2-en-1-yloxy)benzylideneamino)acetate (10)



crude **10**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (25 mg, 0.20 mmol), MgSO$_4$ (excess), Et$_3$N (28 μL, 0.20 mmol) and 2-((*E*)-4,4,4-trifluoro-3-phenylbut-2-en-1-yloxy)benzaldehyde[4b] (30 mg, 0.098 mmol) in dichloromethane (5 mL) afforded **10** (52 mg, 99%, yellow oil).
¹H NMR (300 MHz, CDCl$_3$) δ 8.53 (s, 1H), 7.85 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.16 – 7.09 (m, 3H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.55 – 6.48 (m, 2H), 4.43 – 4.37 (m, 1H), 4.28 (d, *J* = 1.4 Hz, 2H), 3.62 (s, 3H).

Methyl 2-(2-(2-trifluoromethylallyloxy)benzylideneamino)acetate (12)

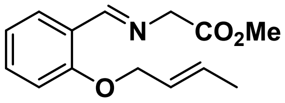


crude **12**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (33 mg, 0.26 mmol), MgSO$_4$ (excess), Et$_3$N (36 μL, 0.26 mmol) and 2-(2-trifluoromethylallyloxy)benzaldehyde (30 mg, 0.13 mmol) in dichloromethane (5 mL) afforded **12** (36 mg, 92%, yellow oil).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.03 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.39 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.87 (dd, *J* = 8.4, 1.0 Hz, 1H), 5.95 (q, *J* = 1.0 Hz, 1H), 5.78 (q, *J* = 1.5 Hz, 1H), 4.72 (s, 2H), 4.42 (d, *J* = 1.3 Hz, 2H), 3.76 (s, 3H).

Methyl-2-(-2-((*E*)-2-butenyloxy)benzylideneamino)acetate (14)

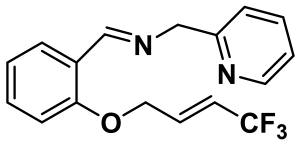


crude **14**

Following the typical procedure 2, the reaction of glycine methyl ester hydrochloride (33 mg, 0.26 mmol), $MgSO_4$ (excess), Et_3N (36 µL, 0.26 mmol) and (E)-2-(butenyloxy)benzaldehyde (23 mg, 0.13 mmol) in dichloromethane (5 mL) afforded **14** (35 mg, 92%, yellow oil).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.04 – 7.97 (m, 1H), 7.41 – 7.33 (m, 1H), 7.02 – 6.86 (m, 2H), 5.93 – 5.63 (m, 2H), 4.42 (s, 2H), 3.76 (s, 3H), 1.76 (d, *J* = 6.1 Hz, 3H).

Typical procedure 3: *N*-(pyridin-2-ylmethyl)-1-((*E*)-2-(4,4,4-trifluorobut-2-en-1-yloxy)phenyl)methanimine (16)

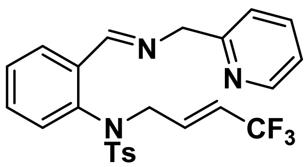


crude **16**

To a suspension of 2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzaldehyde (10 mg, 0.04 mmol) and $MgSO_4$ in anhydrous dichloromethane (3 mL), 2-Picolylamine (8 µL, 0.078 mmol) (5 µL, 0.04 mmol) was added. The mixture was stirred at room temperature for 12 h and filtered to remove the $MgSO_4$. The solvent was evaporated under reduced pressure to afford **16** (12.6 mg, 98%, yellow oil), which is used without purification in the next step.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.58 (d, *J* = 5.6 Hz, 1H), 8.07 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.18 (dd, *J* = 7.3, 4.9 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.64 – 6.52 (m, 1H), 6.12 – 5.97 (m, 1H), 4.99 (s, 2H), 4.73 (s, 2H).

Typical procedure 4: 4-methyl-*N*-(2-(pyridin-2-ylmethyl)iminomethylphenyl)-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide (18)



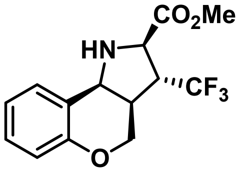
crude **18**

To a suspension of *N*-(2-formylphenyl)-4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide (30 mg, 0.078 mmol), and molecular sieves 4Å, in dichloromethane (5 mL), 2-Picolylamine (8 µL, 0.078 mmol) was added. The mixture was stirred at room temperature for 12 h and filtered to remove de sieves. The solvent was evaporated under reduced pressure to afford**18** (49 mg, 99%, yellow oil), which was used without further purification in the next reaction step.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.19 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.69 – 7.61 (m, 1H), 7.57 – 7.50 (m, 2H), 7.44 – 7.28 (m, 4H), 7.23 – 7.12 (m, 3H), 6.77 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.41 – 6.24 (m, 1H), 5.70 – 5.60 (m, 1H), 4.87 (s, 2H), 4.19 (s, 2H), 2.40 (s, 3H).

4. Typical procedure for the asymmetric [3+2] cycloaddition of azomethine ylides

Typical Procedure 5: Methyl (2*R*,3*R*,3a*R*,9b*S*)-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2a)



2a

To a suspension of $[Cu(CH_3CN)_4]PF_6$ (2.5 mg, $6.7\cdot10^{-3}$ mmol), (*R*)-Segphos (**3**, 4.5 mg, $7.4\cdot10^{-3}$ mmol) and **1a** (20 mg, 0.067 mmol) in anhydrous dichloromethane (4 mL) under argon atmosphere, a solution of KO^{t}Bu (20 µL, 0.020 mmol, 1 M in THF) was added. The resulting mixture was stirred at room temperature for 12 h, filtered over celite® and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography, (heptane:AcOEt 4:1) to afford **2a** (16 mg, 80%, white solid).

M.p.: 103-105ºC.

$[\alpha]_D^{25}$:+49.5 (c =1.0 , CH_2Cl_2), 93% *ee*.

HPLC: Chiralpak IB, hexane/ ^{i}PrOH 97/3 in 40 min, flow rate 1 mL/min (λ = 210 nm), t_R: 11.43 min (*2R,3R,3aR,9bS*)-**2a** and 15.21 min (*2S,3S,3aS,9bR*)-**2a**.

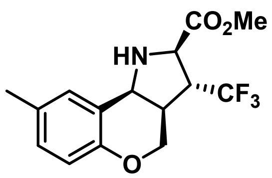
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.20 (td, *J* = 7.5, 1.7 Hz, 1H), 6.96 (td, *J* = 7.5, 1.2 Hz, 1H), 6.89 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.28 (d, *J* = 6.3 Hz, 1H), 4.16 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.97 (d, *J* = 5.9 Hz, 1H), 3.78 (t, *J* = 9.5 Hz, 1H), 3.67 (s, 3H), 2.96 – 2.81 (m, 1H), 2.77 – 2.68 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 154.6, 130.3, 129.2, 126.9 (q, *J*=277.9 Hz, CF_3), 121.4, 121.4, 117.2, 64.5, 59.6 (d, *J* = 2.6 Hz), 55.9, 52.8, 49.4 (q, *J* = 27.3 Hz), 38.6.

Coupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.6 (d, *J* = 9.4 Hz).

HRMS (ESI+): Calculated for $C_{14}H_{15}F_3NO_3$, 302.0999; found, 302.0992.

Methyl (2*R*,3*R*,3a*R*,9b*S*)-8-methyl-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2b)



2b

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (5.6 mg, 0.015 mmol), (*R*)-Segphos (**3**, 10.4 mg, 0.017 mmol), **1b** (49 mg, 0.15 mmol) and KO^{t}Bu (46 µL, 0.046 mmol) in dichloromethane (5 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 6:1) the cycloadduct **2b** (37 mg, 75%, white solid).

M.p.: 170-172ºC.

$[\alpha]_D^{25}$:+51.0 (c = 0.45, CH_2Cl_2), 99% *ee*.

SFC: Chiralpak IC, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ = 280 nm) t_R: 1.58 min (*2S,3S,3aS,9bR*)-**2b** and 1.74 min (*2R,3R,3aR,9bS*)-**2b**.

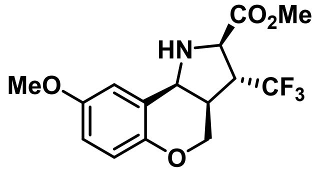
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.27 (d, *J* = 6.4 Hz, 1H), 4.17 (dd, *J* = 11.2, 4.5 Hz, 1H), 4.00 (d, *J* = 5.3 Hz, 1H), 3.79 (d, *J* = 10.3 Hz, 1H), 3.73 (s, 3H), 2.99 – 2.82 (m, 1H), 2.81 – 2.66 (m, 1H), 2.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 152.4, 130.8, 130.5, 129.9, 126.9 (q, *J* = 277.7 Hz, CF_3). 120.9, 116.9, 64.6, 59.65 (d, *J* = 1.9 Hz), 56.0, 52.8, 49.5 (q, *J* = 27.3 Hz), 38.7, 20.5.

Coupled ^{19}F RMN (471 MHz, $CDCl_3$) δ -69.6 (d, *J* = 9.8 Hz).

HRMS (ESI+): Calculated for $C_{15}H_{17}F_3NO_2$, 316.1161; found, 316.1173.

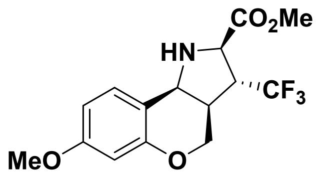
Methyl (2*R*,3*R*,3a*R*,9b*S*)-8-methoxy-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2c)



2c

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (6.7 mg, 0.018 mmol), (*R*)-Segphos (**3**, 12.2 mg, 0.020 mmol), **1c** (60 mg, 0.18 mmol) and KO^{t}Bu (54 µL, 0.054 mmol) in dichloromethane (6 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **2c** (39 mg, 65%, brown solid).
M.p.: 177-179ºC.
$[\alpha]_D^{25}$:-25.0 (c = 0.40, CH_2Cl_2), 98% *ee*.
HPLC: Chiralpak IB, hexane/^{i}PrOH 97/3 in 40 min, flow rate 1 mL/min (λ = 280 nm), t_R: 15.67 min (*2R,3R,3aR,9bS*)-**2c** and 17.50 min (*2S,3S,3aS,9bR*)-**2c**.
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.88 – 6.77 (m, 3H), 4.27 (d, *J* = 6.3 Hz, 1H), 4.14 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.99 (d, *J* = 6.0 Hz, 1H), 3.79 (s, 3H), 3.76 – 3.69 (m, 4H), 2.95 – 2.81 (m, 1H), 2.80 – 2.67 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 154.1, 148.5, 126.8 (q, *J* = 278.0 Hz, CF_3), 121.7, 118.0, 116.2, 113.7, 64.7, 59.6, 56.3, 55.8, 52.9, 49.6 (q, *J* = 27.1 Hz), 38.8.
Coupled ^{19}F RMN (471 MHz, $CDCl_3$) δ -69.6 (d, *J* = 9.8 Hz).
HRMS (ESI+): Calculated for $C_{15}H_{17}F_3NO_4$, 332.1110; found, 332.1080.

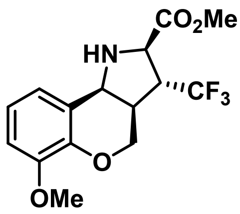
Methyl (2*R*,3*R*,3a*R*,9b*S*)-7-methoxy-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2d)



2d

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (2.2 mg, $6.0\cdot10^{-3}$ mmol), (*R*)-Segphos (**3**, 4.0 mg, $6.6\cdot10^{-3}$ mmol), **1d** (20 mg, 0.060 mmol) and KO^{t}Bu (18 µL, 0.018 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **2d** (14 mg, 72%, brown solid).
M.p.: 174-176ºC.
$[\alpha]_D^{25}$:+188.5 (c= 0.20 CH_2Cl_2), 98% *ee*.
HPLC: Chiralpak IC, hexane/^{i}PrOH 95/5 in 30 min, flow rate 1 mL/min (λ = 230 nm), t_R: 11.89 min (*2S,3S,3aS,9bR*)-**2d** and 14.14 min (*2R,3R,3aR,9bS*)-**2d**.
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 1H), 6.56 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.42 (d, *J* = 2.5 Hz, 1H), 4.27 (d, *J* = 6.4 Hz, 1H), 4.14 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.99 (d, *J* = 5.8 Hz, 1H), 3.82 – 3.73 (m, 4H), 3.69 (s, 3H), 2.96 – 2.79 (m, 1H), 2.78 – 2.66 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 160.5, 155.7, 131.2, 127.0 (q, *J* = 277.9 Hz, CF_3), 113.7, 109.0, 101.6, 64.7, 59.8 (d, *J* = 2.6 Hz), 55.8, 55.5, 53.0, 49.5 (q, *J* = 27.5 Hz), 38.8.
Coupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.6 (d, *J* = 9.8 Hz).
HRMS (ESI+): Calculated for $C_{15}H_{17}F_3NO_4$, 332.1110; found, 332.1111.

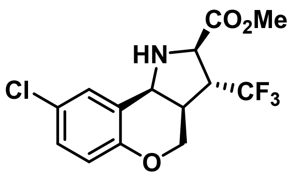
Methyl (2*R*,3*R*,3a*R*,9b*S*)-6-methoxy-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2e)



2e

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (4.5 mg, 0.012 mmol), (*R*)-Segphos (**3**, 8,1 mg, 0.013 mmol), **1e** (40 mg, 0.12 mmol) and KO*t*Bu (36 µL, 0.036 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **2e** (31 mg, 78%, white solid).
M.p.: 179-181ºC.
$[\alpha]_D^{25}$:+119.3 (c= 0.3 CH_2Cl_2), 86% *ee.*
SFC: Chiralpak IB, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ=280 nm) t_R: 2.34 min (*2S,3S,3aS,9bR*)-**2e** and 2.96 min (*2R,3R,3aR,9bS*)-**2e**.
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.94 – 6.90 (m, 2H), 6.82 – 6.77 (m, 1H), 4.32 – 4.21 (m, 2H), 3.97 (d, *J* = 5.9 Hz, 1H), 3.87 (s, 3H), 3.84 (t, *J* = 10.9 Hz, 1H), 3.67 (s, 3H), 2.97 – 2.83 (m, 1H), 2.78 – 2.68 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 148.6, 144.2, 126.9 (q, *J* = 277.8 Hz, CF_3), 122.3, 121.9, 121.3, 110.9, 65.0, 59.6, 56.1, 55.9, 52.9, 49.3 (q, *J* = 27.1 Hz), 38.6.
Coupled ^{19}F RMN (471 MHz, $CDCl_3$) δ -69.6 (d, *J* = 9.5 Hz).
HRMS (ESI+): Calculated for $C_{15}H_{17}F_3NO_4$, 332.1110; found, 332.1069.

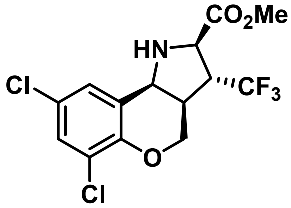
Methyl (2*R*,3*R*,3a*R*,9b*S*)-8-chloro-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2f)



2f

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (3.4 mg, $9.0 \cdot 10^{-3}$ mmol), (*R*)-Segphos (**3**, 6.0 mg, 0.01 mmol), **1f** (30 mg, 0.090 mmol) and KO*t*Bu (27 µL, 0.027 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **2f** (21 mg, 70%, yellow solid).
M.p.: 174-176ºC.
$[\alpha]_D^{25}$:+480.0 (c = 0.50, CH_2Cl_2), 97% *ee*.
HPLC: Chiralpak IB, hexane/ *i*PrOH 98/2 in 60 min, flow rate 0.5 mL/min (λ = 280 nm), t_R: 22.9 min (*2S,3S,3aS,9bR*)-**2f** and 38.1 min (*2R,3R,3aR,9bS*)-**2f**.
^{1}H-NMR (75 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 1H), 7.15 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 4.32 (d, *J* = 6.6 Hz, 1H), 4.16 (dd, *J* = 11.3, 4.3 Hz, 1H), 4.02 (d, *J* = 5.9 Hz, 1H), 3.84 (t, *J* = 10.1 Hz, 1H), 3.68 (s, 3H), 3.06 – 2.89 (m, 1H), 2.81 – 2.68 (m, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.6, 153.2, 129.9, 129.4, 126.6 (q, *J* = 276.8 Hz, CF_3), 126.3, 122.7, 118.7, 64.6, 59.5, 55.7, 52.9, 48.8 (q, *J* = 27.7 Hz), 38.4.
Coupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.7 (d, *J* = 9.2 Hz).
HRMS (ESI+): Calculated for $C_{14}H_{14}ClF_3NO_3$, 336.0609; found, 336.0609.

Methyl (2*R*,3*R*,3a*R*,9b*S*)-6,8-dichloro-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2g)



2g

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (10.1 mg, 0.027 mmol), (*R*)-Segphos (**3**, 18.3 mg, 0.030 mmol), **1g** (100 mg, 0.27 mmol) and KO^{t}Bu (81 µL, 0.081 mmol) in dichloromethane (7 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **2g** (71 mg, 71%, yellow solid).

M.p.: 195-197ºC.

$[\alpha]_D^{25}$:+120.0 (c = 0.2, CH_2Cl_2), 99% *ee.*

HPLC: Chiralpak IB, hexane/ ^{i}PrOH 97/3 in 40 min, flow rate 1 mL/min (λ = 210 nm), t_R: 11.83 min (*2S,3S,3aS,9bR*)-**2g** and 20.68 min (*2R,3R,3aR,9bS*)-**2g**.

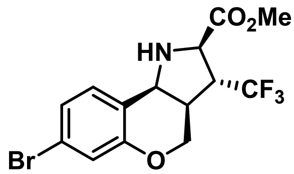
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.4 Hz, 1H), 7.22 (d, *J* = 2.3 Hz, 1H), 4.31 – 4.24 (m, 2H), 3.98 (d, *J* = 5.8 Hz, 1H), 3.88 (t, *J* = 9.7 Hz, 1H), 3.69 (s, 3H), 3.01 – 2.86 (m, 1H), 2.79 – 2.68 (m, 1H), 2.56 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 149.3, 129.6, 128.5, 126.7 (q, *J* = 277.7 Hz, CF_3), 126.1, 124.4, 123.0, 65.3, 59.6 (d, *J* = 2.5 Hz), 55.7, 53.0, 48.9 (q, *J* = 27.6 Hz), 38.3.

Coupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.7 (d, *J* = 9.3 Hz).

HRMS (ESI+): Calculated for $C_{14}H_{13}Cl_2F_3NO_3$, 370.0219; found, 370.0206.

Methyl (2*R*,3*R*,3a*R*,9b*S*)-7-bromo-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2h)



2h

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (5.2 mg, 0.014 mmol), (*R*)-Segphos (**3**, 9.2 mg, 0.015 mmol), **1h** (52 mg, 0.14 mmol) and KO^{t}Bu (42 µL, 0.042 mmol) in dichloromethane (5 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **2h** (36 mg, 69%, white solid).

M.p.: 178-180ºC.

$[\alpha]_D^{25}$:+122.0 (c = 0.2, CH_2Cl_2), 82% *ee.*

HPLC: Chiralpak IB, hexane/ ^{i}PrOH 97/3 in 40 min, flow rate 1 mL/min (λ = 280 nm), t_R: 9.30 min (*2S,3S,3aS,9bR*)-**2h** and 12.91 min (*2R,3R,3aR,9bS*)-**2h.**

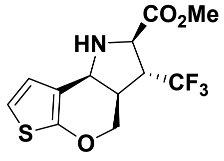
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 1H), 7.09 (d, *J* = 1.8 Hz, 1H), 7.07 (d, *J* = 1.2 Hz, 1H), 4.22 (d, *J* = 6.3 Hz, 1H), 4.15 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.96 (d, *J* = 5.8 Hz, 1H), 3.77 (t, *J* = 10.1 Hz, 1H), 3.68 (s, 3H), 2.95 – 2.80 (m, 1H), 2.75 – 2.64 (m, 1H), 2.39 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 155.3, 131.6, 126.8 (q, *J* = 278.0 Hz, CF_3), 124.7, 122.2, 120.5, 120.4, 64.6, 59.5 (d, *J* = 2.8 Hz), 55.5, 52.9, 49.2 (q, *J* = 27.3 Hz), 38.3.

Coupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.6 (d, *J* = 9.8 Hz).

HRMS (ESI+): Calculated for $C_{14}H_{14}BrF_3NO_3$, 380.0104; found, 380.0087.

Methyl (2R,3R,3aR,8bS)-3-trifluoromethyl-1,2,3,3a,4,8b-hexahydrothieno[3',2':5,6]pyrano[4,3-*b*]pyrrolo-2-carboxylate (2i)



2i

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (3.0 mg, $8.1{\cdot}10^{-3}$ mmol), (*R*)-Segphos (**3**, 5.4 mg, $8.9{\cdot}10^{-3}$ mmol), **1i** (25 mg, 0.081 mmol) and KO*^t^*Bu (24 μL, 0.024 mmol) in dichloromethane (5 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **2i** (14 mg, 57%, yellow oil).

$[\alpha]_D^{25}$:+100.4 (c = 1.4, CH_2Cl_2), 99% *ee.*

HPLC: Chiralpak IC, hexane/ ^{i}PrOH 95/5 in 30 min, flow rate 1 mL/min (λ = 254 nm), t_R: 9.36 min (*2S,3S,3aS,9bR*)-**2i** and 10.79 min (*2R,3R,3aR,9bS*)-**2i.**

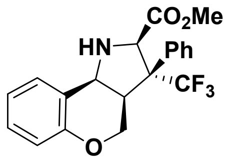
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.4 Hz, 1H), 6.65 (d, *J* = 5.4 Hz, 1H), 4.46 (s, 1H), 4.29 – 4.14 (m, 1H), 4.08 – 3.91 (m, 2H), 3.71 (s, 3H), 3.19 – 2.99 (m, 1H), 2.87 – 2.72 (m, 1H), 2.47 (s, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 181.0, 172.0, 153.3, 127.2 (q, *J* = 277.9 Hz), 124.6, 118.2, 66.1, 60.5, 54.4, 52.9, 48.0 (q, *J* = 27.6 Hz), 40.1.

Coupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.8 (d, *J* = 9.5 Hz).

HRMS (ESI+): Calculated for $C_{12}H_{12}F_3NO_3S$, 307.0490; found, 307.0484.

Methyl (2*R*,3*S*,3a*R*,9b*S*)-3-phenyl-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (11)



11

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (2.9 mg, $7.8{\cdot}10^{-3}$ mmol), (*R*)-Segphos (**3**, 5.2 mg, $8.6{\cdot}10^{-3}$ mmol), **10** (29 mg, 0.078 mmol) and KO*^t^*Bu (23 μL, 0.023 mmol) in dichloromethane (5 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **11** (18 mg, 53%, white solid).

M.p.: 138-140ºC.

$[\alpha]_D^{25}$:+61.3 (c = 0.4, CH_2Cl_2), 55% *ee.*

SFC: Chiralpak IA, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ=280 nm) t_R: 2.82 min (*2S,3R,3aS,9bR*)-**11** and 3.18 min (*2R,3S,3aR,9bS*)-**11**.

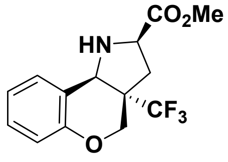
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.51 – 7.38 (m, 4H), 7.21 (td, *J* = 7.9, 1.9 Hz, 1H), 6.96 (td, *J* = 7.5, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.89 (s, 1H), 4.53 (dd, *J* = 10.2, 3.9 Hz, 1H), 4.04 (d, *J* = 11.8 Hz, 1H), 3.82 (s, 3H), 3.73 (t, *J* = 10.9 Hz, 1H), 2.59 (td, *J* = 11.6, 3.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 152.6, 132.9, 128.7 (2C), 128.6 (2C), 128.3, 127.5 (q, *J* = 2.0 Hz), 127.0 (d, *J* = 284.6 Hz, CF_3), 124.7, 123.8, 120.2, 115.9, 69.6, 67.9, 62.8 (q, *J* = 28.2 Hz), 57.5, 52.4, 49.1.

Coupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -65.2 (s).

HRMS (ESI+): Calculated for $C_{20}H_{18}F_3NO_3$, 377.1239; found, 377.1234.

Methyl (2*R*,3a*S*,9b*R*)-3a-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (13)



13

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (3.7 mg, $9.8\cdot10^{-3}$ mmol), (*R*)-Segphos (**3**, 6.7 mg, 0.011 mmol), **12** (29 mg, 0.098 mmol) and KO^{t}Bu (29 µL, 0.029 mmol) in dichloromethane (3 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 5:1) the cycloadduct **13** (16 mg, 54%, brown oil).

$[\alpha]_D^{25}$:+0.259 (c=0.9, CH_2Cl_2), 70% *ee.*

SFC: Chiralpak IA, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ=280 nm) tR: 2.05 min (*2S,3aR,9bS*)-**13** and 3.07 min (*2R,3aS,9bR*)-**13**.

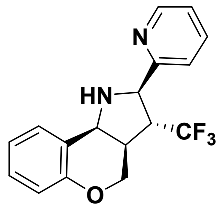
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.26 – 7.19 (m, 1H), 6.99 (td, *J* = 7.5, 1.2 Hz, 1H), 6.94 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.37 (dd, *J* = 12.0, 1.4 Hz, 1H), 4.27 (s, 1H), 3.97 (t, *J* = 8.6 Hz, 1H), 2.70 – 2.51 (m, 2H), 1.72 (dd, *J* = 14.0, 8.6 Hz, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 172.7, 153.7, 130.2, 129.2, 127.2 (q, *J* = 281.5 Hz, CF_3), 121.8, 121.0, 117.3, 65.0, 58.3, 56.6, 52.6, 49.3 (q, *J* = 24.3 Hz), 36.0.

Decoupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.6 (s).

HRMS (ESI+): Calculated for $C_{14}H_{15}F_3NO_3$, 302.0999; found, 302.0988.

(2*R*,3*R*,3a*R*,9b*S*)-2-(pyridin-2-yl)-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole (17)



17

Following the typical procedure 5, the reaction of $Cu(CH_3CN)_4PF_6$ (1.5 mg, $4.0\cdot10^{-3}$ mmol), (*R*)-Segphos (**3**, 2.7 mg, $4.4\cdot10^{-3}$ mmol), **16** (13 mg, 0.04 mmol) and KO^{t}Bu (12 µL, 0.012 mmol) in dichloromethane (3 mL) afforded, after purification by silica gel flash chromatography (heptane-AcOEt 4:1) the cycloadduct **17** (8 mg, 62%, yellow oil).

$[\alpha]_D^{25}$:+17,2 (c=1,3, CH_2Cl_2), 53% *ee.*

SFC: Chiralpak IG, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 2 mL/min (λ=280 nm) t_R: 3.21 min (*2S,3S,3aS,9bR*)-**17** and 4.31 min (*2R,3R,3aR,9bS*)-**17**.

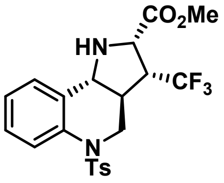
^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.7 Hz, 1H), 7.69 (tt, *J* = 7.4, 2.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.19 (m, 2H), 6.99 (td, *J* = 7.6, 1.4 Hz, 2H), 4.49 (d, *J* = 7.0 Hz, 1H), 4.32 (d, *J* = 6.1 Hz, 1H), 4.26 (dd, *J* = 11.1, 5.5 Hz, 1H), 3.94 (t, *J* = 11.6 Hz, 1H), 2.90 – 2.76 (m, 1H), 2.75 – 2.60 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 154.9, 149.9, 137.0, 131.1, 129.1, 127.5 (d, *J* = 278.4 Hz, CF_3), 123.5, 123.3, 121.4 (d, *J* = 2.6 Hz), 117.3, 64.8, 64.0 (q, *J* = 2.4 Hz), 56.9, 53.9 (q, *J* = 25.5 Hz), 39.6.

Coupled ^{19}F NMR (471 MHz, $CDCl_3$) δ -68.6 (d, *J* = 9.9 Hz).

HRMS (ESI+): Calculated for $C_{17}H_{16}F_3N_2O$, 321.1209; found, 321.1200.

Typical procedure 6: Methyl (2*S*,3*R*,3a*S*,9b*R*)-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7a)



7a

To a suspension of $[Cu(CH_3CN)_4]PF_6$ (4.1 mg, 0.011 mmol), ^{t}Bu-Ferrocenyl-PHOX (**8**, 5.9 mg, 0.012 mmol) and **6a** (48 mg, 0.11 mmol) in anhydrous dichloromethane (4 mL), under argon atmosphere, KO^{t}Bu (32 µL, 0,032 mmol, 1 M in THF) was added. The resulting mixture was stirred at room temperature for 12 h, filtered over celite® and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography, (cyclohexane:AcOEt 4:1) to afford **7a** (30 mg, 63%, yellow oil).

$[\alpha]_D^{25}$:+0.316 (c=1.3, CH_2Cl_2), 85% *ee*.

SFC: Chiralpak IB, CO_2/MeOH from 95/5 to 70/30 in 8 min, flow rate 2 mL/min (λ=280 nm) t_R: 1.48 min (2*S*,3*S*,3a*S*,9b*R*)-**7a** and 1.62 min (2*R*,3*R*,3a*R*,9b*S*)-**7a**.

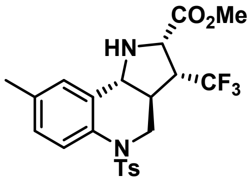
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.24-7.20 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.17 – 4.06 (m, 2H), 3.75 (s, 3H), 3.57 (t, *J* = 11.8 Hz, 1H), 2.96 – 2.75 (m, 2H), 2.37 (s, 3H), 1.91 – 1.75 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 144.2, 135.2, 134.6, 133.2, 129.9 (2C), 128.2, 127.0 (2C), 126.0, 125.9, 125.7 (q, *J* = 278.7 Hz, CF_3), 122.4, 60.6, 60.4, 53.0, 52.6 (q, *J* = 28.7 Hz), 49.5, 46.2, 21.7.

Coupled ^{19}F-RMN (471 MHz, $CDCl_3$) δ -65.6 (d, *J*=8.8 Hz).

HRMS (ESI+): Calculated for $C_{21}H_{22}F_3N_2O_4S$, 455.1247; found, 455.1237.

Methyl (2*S*,3*R*,3a*S*,9b*R*)-8-methyl-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7b)



7b

Following the typical procedure 6, the reaction of $Cu(CH_3CN)_4PF_6$ (2.8 mg, $7.5\cdot10^{-3}$ mmol), ^{t}Bu-Ferrocenyl-PHOX (**8**, 4.1 mg, $8.2\cdot10^{-3}$ mmol), **16b** (35 mg, 0.075 mmol) and KO^{t}Bu (22 µL, 0.022 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (cyclohexane-AcOEt 4:1) the cycloadduct **7b** (22 mg, 63%, colorless solid).

M.p. 187-189ºC.

$[\alpha]_D^{25}$:-0.127 (c=1.5, CH_2Cl_2), 94% *ee.*

SFC: Chiralpak IA, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ=254 nm) t_R: 3.09 min (2*S*,3*S*,3a*S*,9b*R*)-**7b** and 4.38 min (2*R*,3*R*,3a*R*,9b*S*)-**7b**.

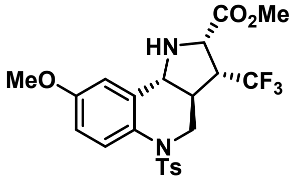
^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.13 (m, 3H), 7.07 – 7.01 (m, 1H), 4.19 – 4.08 (m, 2H), 3.79 (s, 3H), 3.55 (t, *J* = 11.8 Hz, 1H), 2.95 – 2.80 (m, 1H), 2.74 (d, *J* = 11.0 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 1.89 – 1.73 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 144.1, 135.9, 135.2, 133.1, 131.9, 129.8 (2C), 128.8, 127.0 (2C), 126.0, 125.7 (q, *J* = 278.6 Hz, CF_3), 123.0, 60.6, 60.4, 53.0, 52.6 (q, *J* = 28.7 Hz), 49.4, 46.3, 21.7, 21.1.

Coupled ^{19}F-RMN (471 MHz, $CDCl_3$) δ -65.6 (d, *J* = 9.1 Hz).

HRMS (ESI+): Calculated for $C_{22}H_{24}F_3N_2O_4S$, 469.1403; found, 469.1404.

Methyl (2*S*,3*R*,3a*S*,9b*R*)-8-methoxy-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7c)



7c

Following the typical procedure 6, the reaction of $Cu(CH_3CN)_4PF_6$ (2.4 mg, $6.5{\cdot}10^{-3}$ mmol), *t*Bu-Ferrocenyl-PHOX (**8**, 3.6 mg, $7.2{\cdot}10^{-3}$ mmol), **6c** (32 mg, 0.065 mmol) and KO*t*Bu (20 µL, 0.020 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (cyclohexane-AcOEt 4:1) the cycloadduct **7c** (18 mg, 58%, yellow oil).

$[\alpha]_D^{25}$:+0.161 (c=1.3, CH_2Cl_2), 80% *ee.*

SFC: Chiralpak IC, CO_2/MeOH from 95/5 to 70/30 in 8 min, flow rate 2 mL/min (λ=254 nm) t_R: 5.49 min (2*S*,3*S*,3a*S*,9b*R*)-**7c** and 5.69 min (2*R*,3*R*,3a*R*,9b*S*)-**7c.**

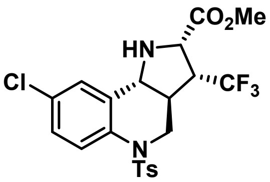
^{1}H-RMN (300 MHz, $CDCl_3$) *δ* δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.87 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.74 (d, *J* = 3.1 Hz, 1H), 4.16 – 4.02 (m, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 3.53 (t, *J* = 11.8 Hz, 1H), 2.89 – 2.75 (m, 1H), 2.61 (d, *J* = 10.8 Hz, 1H), 2.38 (s, 3H), 1.84 – 1.73 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 170.8, 157.9, 144.1, 135.2, 134.9, 129.9, 128.1, 127.2, 127.0, 125.7 (q, *J* = 278.8 Hz, CF_3). 113.0, 108.2, 60.6, 60.4, 55.7, 53.0, 52.7 (q, *J* = 28.7 Hz), 49.2, 46.5, 21.7.

Coupled ^{19}F-RMN (471 MHz, $CDCl_3$) *δ* -65.6 (d, *J* = 8.9 Hz).

HRMS (ESI+): Calculated for $C_{22}H_{24}F_3N_2O_5S$, 489.0857; found, 489.0847.

Methyl (2*S*,3*R*,3a*S*,9b*R*)-8-chloro-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7d)



7d

Following the typical procedure 6, the reaction of $Cu(CH_3CN)_4PF_6$ (2.7 mg, $7.2{\cdot}10^{-3}$ mmol), ^{t}Bu-Ferrocenyl-PHOX (**8**, 3.9 mg, $7.9{\cdot}10^{-3}$ mmol), **6d** (35 mg, 0.072 mmol) and KO^{t}Bu (22 µL, 0.022 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (yclohexane-AcOEt 4:1) the cycloadduct **7d** (18 mg, 52%, colorless solid).

M.p. 159-161ºC

$[\alpha]_D^{25}$:+0.102 (c=1.8, CH_2Cl_2), 81% *ee.*

SFC: Chiralpak IA, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ=254 nm) t_R: 3.44 min (2*S*,3*S*,3a*S*,9b*R*)-**7d** and 5.80 min (2*R*,3*R*,3a*R*,9b*S*)-**7d**.

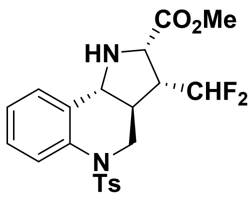
^{1}H-RMN (300 MHz, $CDCl_3$) *δ* 7.77 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.23 – 7.19 (m, 3H), 4.17 – 4.06 (m, 2H), 3.76 (s, 3H), 3.53 (t, *J* = 11.8 Hz, 1H), 2.95 – 2.73 (m, 1H), 2.39 (s, 3H), 1.94 – 1.76 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 170.7, 144.5, 134.9, 134.8, 133.2, 131.5, 130.0 (2C), 128.2, 127.2, 127.0 (2C), 125.5 (d, *J* = 278.7 Hz, CF_3), 122.9, 60.4, 60.1, 53.0, 52.4 (q, *J* = 28.9 Hz), 49.4, 45.6, 21.7.

Coupled ^{19}F-RMN (471 MHz, $CDCl_3$) *δ* -65.6 (d, *J* = 8.8 Hz).

HRMS (ESI+): Calculated for $C_{21}H_{21}ClF_3N_2O_4S$, 489.0857; found, 489.0847.

Methyl (2*S*,3*R*,3a*S*,9b*R*)-3-difluoromethyl-5-tosyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7e)



7e

Following the typical procedure 6, the reaction of $Cu(CH_3CN)_4PF_6$ (2.1 mg, $5.5 \cdot 10^{-3}$ mmol), *t*Bu-Ferrocenyl-PHOX (**8**, 3.0 mg, $6.0 \cdot 10^{-3}$ mmol), **6e** (24 mg, 0.055 mmol) and KO*t*Bu (17 µL, 0.017 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (cyclohexane-AcOEt 2:1) the cycloadduct **7e** (14 mg, 57%, yellow oil).

$[\alpha]_D^{25}$:+0.293 (c=1.4, CH_2Cl_2), 89% *ee.*

SFC: Chiralpak IA, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ=254 nm) t_R: 4.04 min (2*S*,3*S*,3a*S*,9b*R*)-**7e** and 4.69 min (2*R*,3*R*,3a*R*,9b*S*)-**7e**.

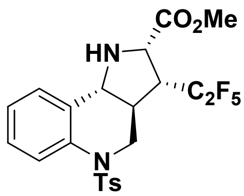
^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.25 (m, 1H), 7.22 – 7.13 (m, 4H), 5.95 (td, *J* = 55.9, 4.2 Hz, 1H), 4.18 – 4.05 (m, 2H), 3.75 (s, 3H), 3.54 (t, *J* = 11.8 Hz, 1H), 2.81 (d, *J* = 11.0 Hz, 1H), 2.69 – 2.49 (m, 1H), 2.37 (s, 3H), 2.25 (s, 1H, NH), 1.92 – 1.77 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 144.1, 135.4, 134.7, 133.6, 129.8 (2C), 128.1, 127.0 (2C), 125.9, 125.7, 122.4, 115.6 (t, *J* = 241.1 Hz, CF_2H), 60.8 (t, *J* = 4.4 Hz), 60.5, 52.9, 51.3 (t, *J* = 21.5 Hz), 49.9, 44.8 (t, *J* = 2.7 Hz), 21.7.

Coupled ^{19}F-RMN (471 MHz, $CDCl_3$) : δ -115.3 (ddd, *J* = 289.6, 55.5, 7.1 Hz, 1F), -123.7 (ddd, *J* = 289.7, 56.2, 22.3 Hz, 1F).

HRMS (ESI+): Calculated for $C_{21}H_{23}F_2N_2O_4S$, 437.1341; found, 437.1339.

Methyl (2*S*,3*R*,3a*S*,9b*R*)-3-perfluoroethyl-5-tosyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7f)



7f

Following the typical procedure 6, the reaction of $Cu(CH_3CN)_4PF_6$ (2.5 mg, $6.7 \cdot 10^{-3}$ mmol), *t*Bu-Ferrocenyl-PHOX (**8**, 3.7 mg, $7.4 \cdot 10^{-3}$ mmol), **6f** (34 mg, 0.067 mmol) and KO*t*Bu (20 µL, 0.020 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (cyclohexane-AcOEt 4:1) the cycloadduct **7f** (21 mg, 61%, yellow oil).

$[\alpha]_D^{25}$: +0.221, (c=1.4, CH_2Cl_2) 92% *ee.*

SFC: Chiralpak IA, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ=210 nm) t_R: 2.61 min (2*S*,3*S*,3a*S*,9b*R*)-**7f** and 3.02 min (2*R*,3*R*,3a*R*,9b*S*)-**7f**.

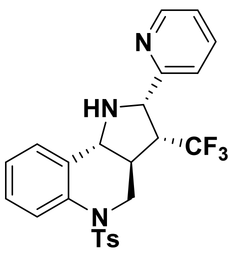
^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.23 – 7.20 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.12 (dd, *J* = 11.2, 6.3 Hz, 2H), 3.74 (s, 3H), 3.56 (t, *J* = 11.7 Hz, 1H), 2.92 – 2.71 (m, 2H), 2.37 (s, 3H), 2.11 – 1.93 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 144.2, 135.4, 134.4, 133.6, 129.9 (2C), 128.2, 127.0 (2C), 125.9, 125.9, 122.2, 120.8 – 115.2 (m, C_2F_5), 61.8, 61.2, 52.8, 50.4 – 49.7 (m), 49.6, 45.6, 21.7.

Coupled ^{19}F-RMN (471 MHz, $CDCl_3$) δ -83.3 (s, 3F), -113.8 (dd, *J* = 275.7, 12.4 Hz, 1F), -117.3 (dd, *J* = 275.8, 19.4 Hz, 1F).

HRMS (ESI+): Calculated for $C_{22}H_{22}F_5N_2O_4S$, 505.1215; found, 505.1215.

(2*S*,3*R*,3a*S*,9b*R*)-2-(pyridin-2-yl)-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline (19)



19

Following the typical procedure 6, the reaction of $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.010 mmol), ^{t}Bu-Ferrocenyl-PHOX (**8**, 5.5 mg, 0.011 mmol), **18** (49 mg, 0.10 mmol) and KO^{t}Bu (30 μL, 0.030 mmol) in dichloromethane (4 mL) afforded, after purification by silica gel flash chromatography (cyclohexane-AcOEt 2:1) the cycloadduct **19** (28 mg, 56%, yellow oil).

$[\alpha]_D^{25}$:+0.380 (c=0.5, CH_2Cl_2), 56% *ee.*

SFC: Chiralpak IA, CO_2/MeOH from 95/5 to 60/40 in 8 min, flow rate 3 mL/min (λ=210 nm) t_R: 4.42 min (2*S*,3*S*,3a*S*,9b*R*)-**19** and 4.50 min (2*R*,3*R*,3a*R*,9b*S*)-**19**.

^{1}H-RMN (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.3 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.25 – 7.16 (m, 3H), 4.79 (d, *J* = 9.6 Hz, 1H), 4.13 (dd, *J* = 11.8, 6.1 Hz, 1H), 3.60 (t, *J* = 11.9 Hz, 1H), 3.02 – 2.84 (m, 2H), 2.39 (s, 3H), 2.15 – 1.99 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 148.7, 144.1, 136.3, 135.3, 134.8, 134.2, 129.8 (2C), 127.9, 127.0 (2C), 126.0 (q, *J* = 278.7 Hz, CF_3), 126.0, 125.7, 124.3, 123.2, 122.70, 63.9, 60.2, 53.6 (q, *J* = 26.9 Hz), 49.9, 45.6, 21.7.

Coupled ^{19}F-RMN (471 MHz, $CDCl_3$) δ -63.7 (d, *J* = 9.4 Hz).

HRMS (ESI+): Calculated for $C_{24}H_{23}F_3N_3O_2S$, 474.1458; found, 474.1452.

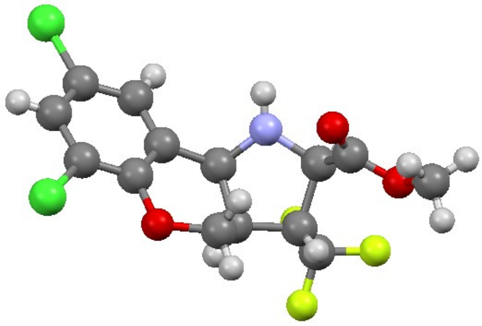
4. Preparation of racemic products for HPLC analysis.

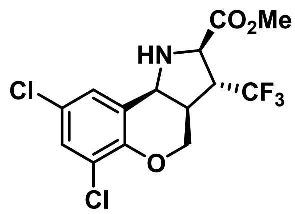
The racemic pyrrolidines were prepared according to the general procedure, but using PPh_3 as ligand. The samples for HPLC analysis were dissolved in isopropyl alcohol and used as quickly as possible to minimize the formation of decomposition products.

5. Stereochemical assignment

The relative and absolute configuration of compounds **2g** and **7b** was established by X-ray crystal structure analysis.

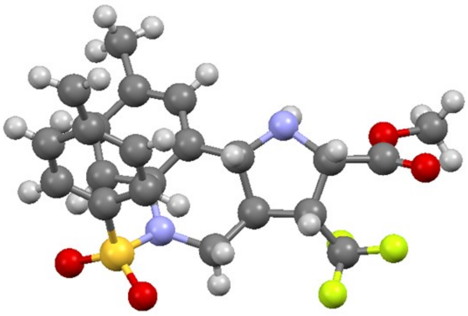
X-ray structure of 2g

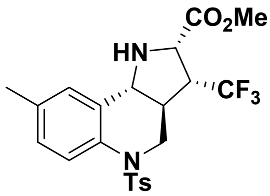




(+) 2g

X-ray structure of 7b





(-) 7b

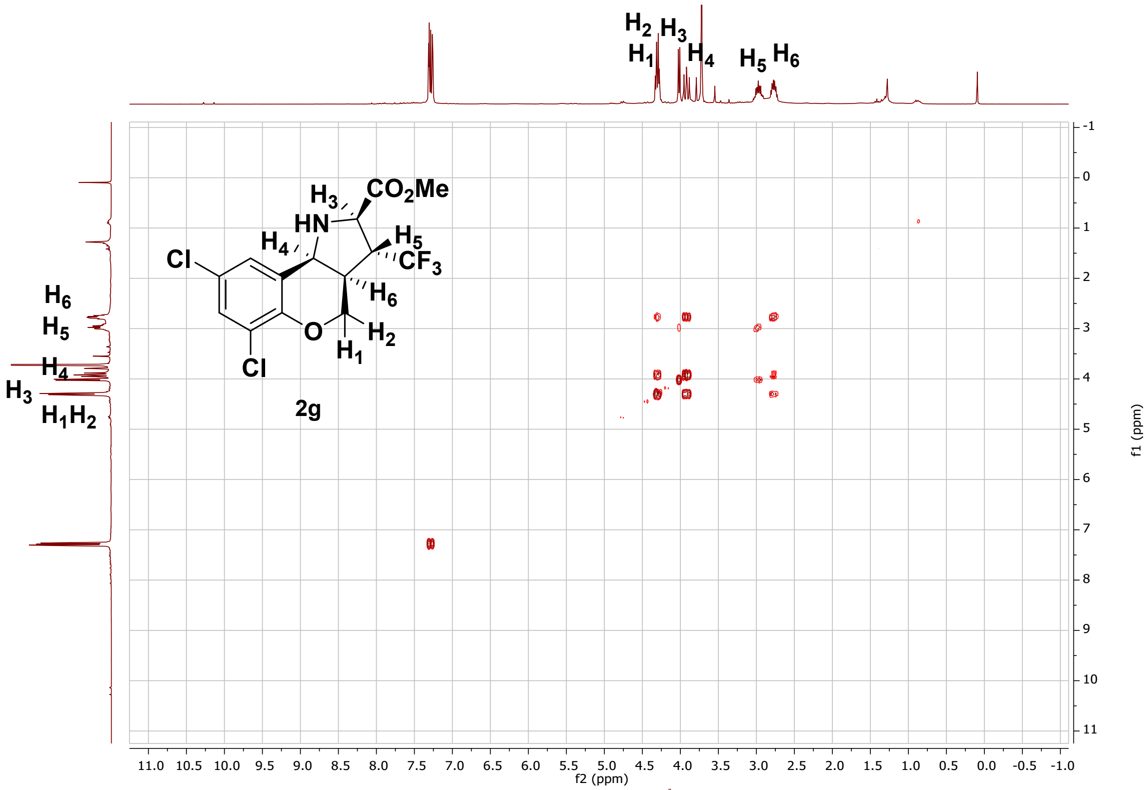
In the case of compound **7b**, four complete data sets from different crystals have been collected. In all cases the crystals are single domains of good quality and the data collected can be integrated without problems, but there is an area of the molecule with extraordinarily high disorder. It has been tried to lower the symmetry of the system to better localise the atomic positions in this area, but it has not been possible.

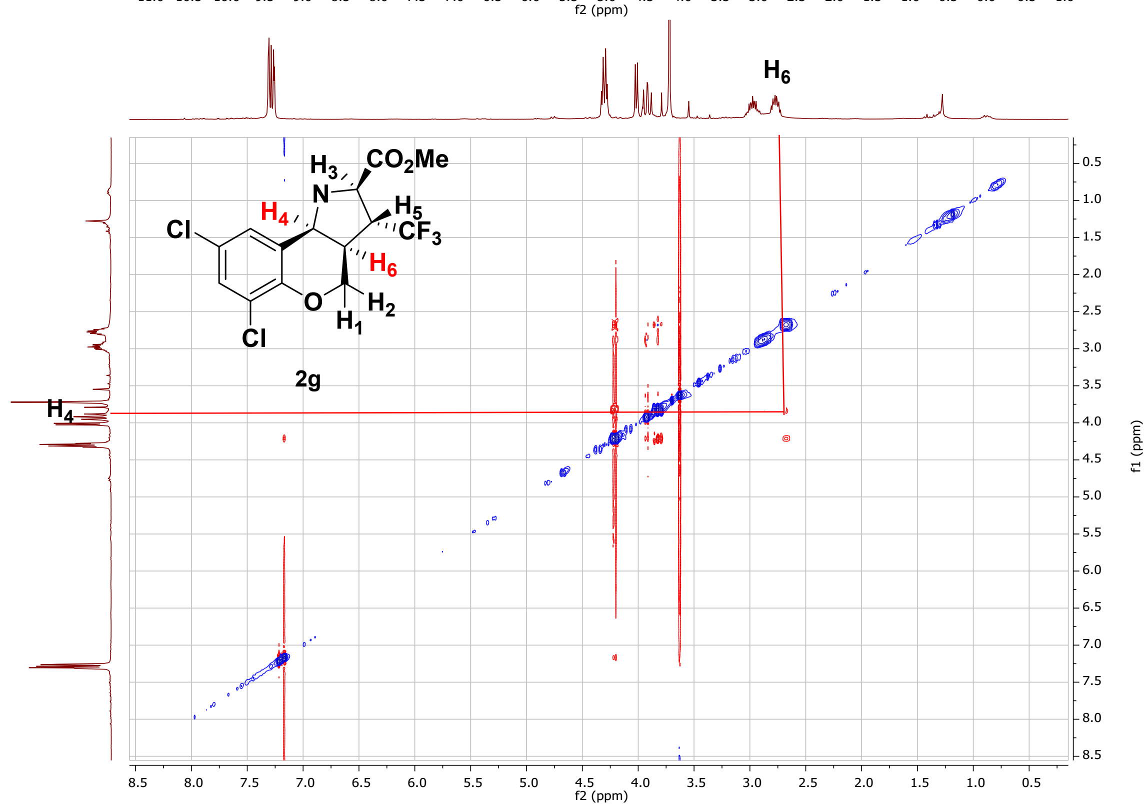
In order to refine this model, the -CF_3 and -$COOCH_3$ fragments have been fixed with geometrical restrictions. However only partial electron densities of these substituents have been located. The atoms C13, C14 and C15, O1, O2, F1, F2, F3 and H14A, H14B and H14C have been isotropically refined with 50% occupancy in the model positions.

6. NMR experiments

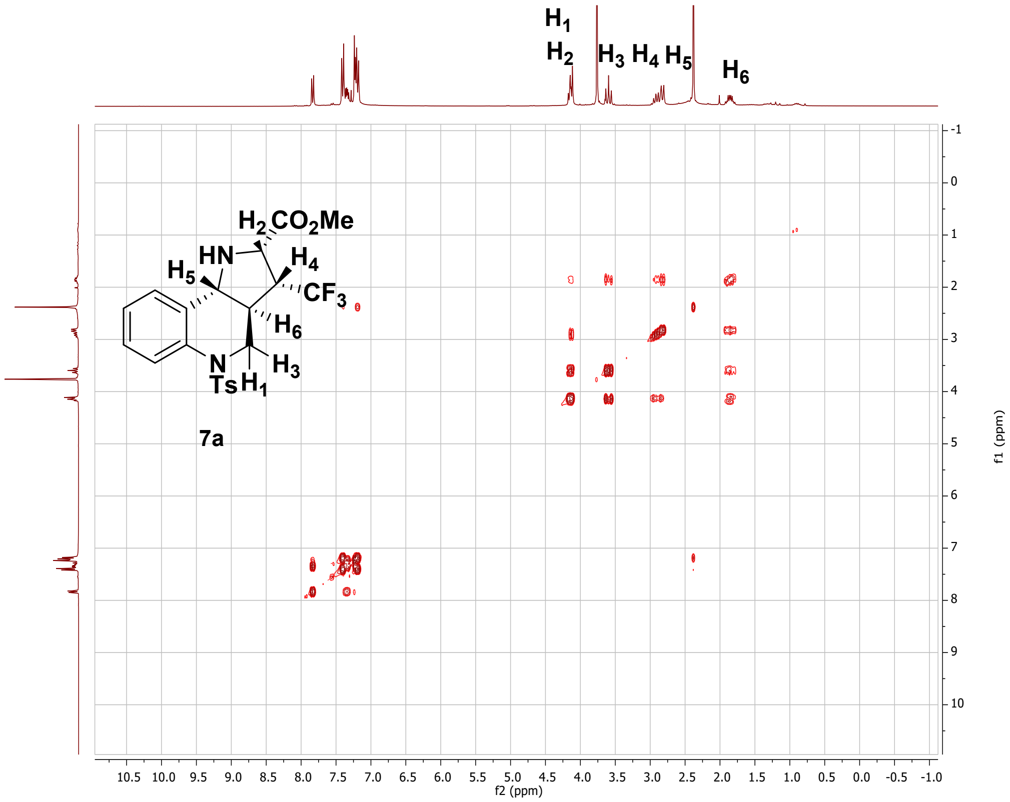
In addition COSY and NOESY experiments were performed on compounds **2g** and **7a**.

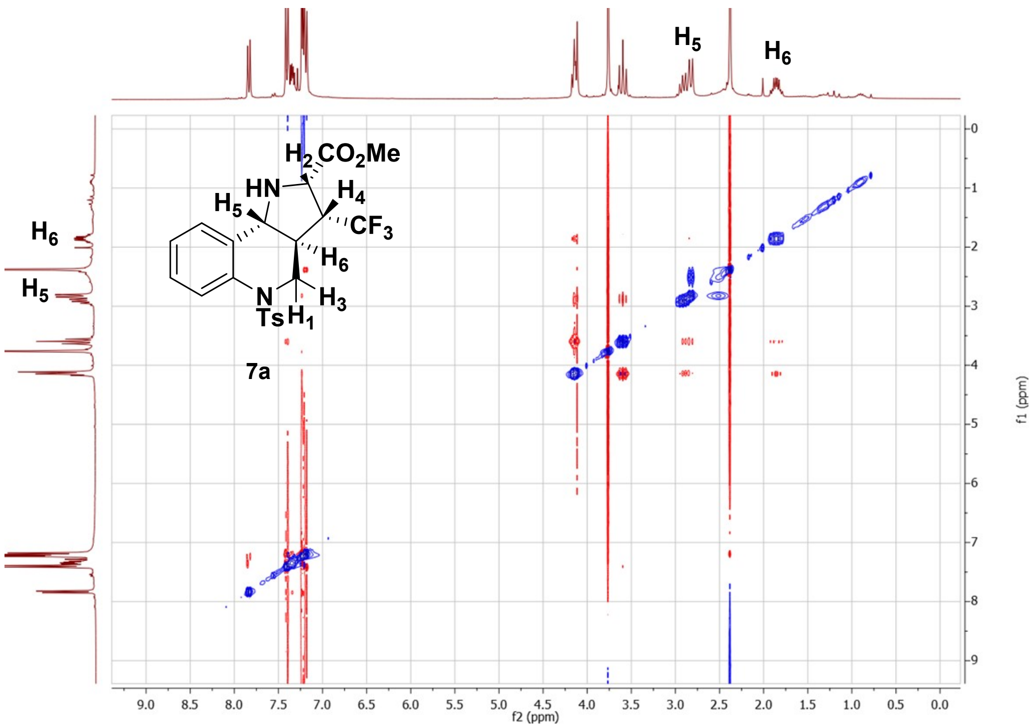
Compound 2g-COSY and NOESY spectra





Compound 7a-COSY and NOESY spectra





The NOESY spectrum of adduct **2g** shows a correlation between H_4 and H_6 suggesting that those protons are in *cis* configuration. This correlation was not observed in compound **7g** (protons H_5-H_6 in *trans* relationship)

7. Theoretical calculations

1. Computational details

Theoretical calculations were performed with Gaussian 09[6]. Geometries were optimized using the B3LYP-D3[7] functional in the gas phase. A mixed basis set of LANL2DZ(f) for Cu with 6-31G(d) for all other atoms was used in geometry optimizations (basis set 1). The LANL2DZ basis set was supplemented with an f-type polarization function (exponent 3.525) for Cu.[8] Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies (ZPE). Single points were calculated with the M06 functional[9] and a mixed basis set of LANL2TZ(f) for Cu[10] with 6-311++G(d,p) for all other atoms (basis set 2). Solvation was introduced implicitly in all cases through the SMD[11] model, with dichloromethane as the solvent. The reported free energies include zero-point energies and thermal corrections calculated at 298 K with B3LYP-D3/BS1.

In the case of TS-*endo* **2a** y TS-*exo* **2a**, additional calculations were carried out with the B97D3 functional[12] in the gas phase for geometry optimization with basis set 1. In these cases single point energies were calculated with the same functional and basis set 2. Solvation was introduced implicitly in all cases through the SMD model, with dichloromethane as the solvent. The reported free energies include zero-point energies and thermal corrections calculated at 298 K with B97D3/BS1.

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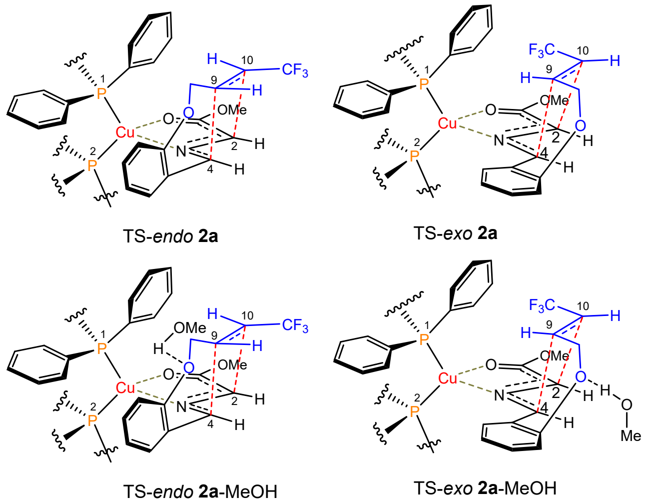
2. **Model structures for the study of *endo*/*exo* diastereoselectivity in the formation of compound 2a.**

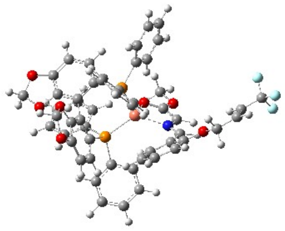


Structure	θ(N-C-C-C$_O$)	Rel. ΔG‡	*endo/exo*(%)
TS-*endo* **2a** (1)	-130.3	0	82
TS-*exo* **2a** (1)	-158.5	0.9	18
TS-*endo* **2a** (2)	-127.5	0	80
TS-*exo* **2a** (2)	-154.6	0.8	20
TS-*endo* **2a**-MeOH (2)	-122.6	0	99
TS-*exo* **2a**-MeOH (2)	-159.1	2.6	1

(1) M06$_{SMD}$/BS2//B3LYP-D3/BS1
(2) B97D3$_{SMD}$/BS2//B97D3/BS1

Figure S1. Simplified structures of the transition states for the *endo* and *exo* approaches to give compound **2a** by reaction through the less hindered (2*Re*, 4*Si*) face. The increase in dihedral angle would be related to a slight distortion of the ligand aryl rings arrangement with the lack of stabilizing p-stacking interactions.

3. **Cartesian coordinates (Å) and energies (hartrees) of all the optimized structures (cartesian coordinates obtained with B3LYP-D3 except for TS *endo*-2a-MeOH and TS *exo*-2a-MeOH for which B97D3 method was used).**



modIa

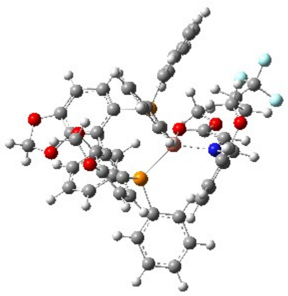
E(B3LYPD3/BS1) = -3766.02924642
H(correction)= 0.878217
G(correction)= 0.716344
E(M06/BS2)$_{CH2Cl2}$ = -3764.89027861

E(B97D3/BS1) = -3764.60751204
H(correction)= 0.860897
G(correction)= 0.696327
E(B97D3/BS2)$_{CH2Cl2}$ = -3765.56276956

Imaginary frequencies: 0

6	0	3.01996	2.57531	-0.97622
6	0	2.76949	1.27413	-0.58045
6	0	2.8778	3.01932	-2.2905
8	0	3.45845	3.61127	-0.18894
6	0	2.37882	0.36946	-1.61904
6	0	3.02698	0.89301	0.84335
6	0	2.49862	2.16303	-3.30047
8	0	3.20772	4.34772	-2.37042
6	0	3.38371	4.77935	-1.01369
6	0	2.2467	0.8273	-2.93492
15	0	1.80952	-1.3137	-1.14033
6	0	2.04168	0.71208	1.86269
6	0	4.3421	0.72483	1.23873
1	0	2.39845	2.50222	-4.32566
1	0	2.51874	5.38281	-0.70898
1	0	4.31807	5.34113	-0.93012
1	0	1.92769	0.13785	-3.70818
29	0	-0.15858	-1.04735	0.06937
6	0	1.64967	-2.27744	-2.69648
6	0	3.24667	-2.06368	-0.27378
6	0	2.43034	0.34998	3.15763
15	0	0.25147	0.79737	1.41702
6	0	4.71356	0.3462	2.52588
8	0	5.46186	0.85781	0.45583
7	0	-2.06399	-1.72554	-0.53013
6	0	0.44064	-2.9674	-2.87812
6	0	2.65884	-2.39664	-3.66682
6	0	2.98843	-2.78406	0.9024
6	0	4.56566	-1.92967	-0.73172
6	0	3.77568	0.14986	3.5153
1	0	1.67138	0.2101	3.91853
6	0	-0.62354	0.68033	3.03264
6	0	0.01155	2.54292	0.89907
8	0	6.07615	0.22221	2.60159
6	0	6.57645	0.5395	1.2961
6	0	-2.97523	-1.10206	-1.2331
6	0	-2.31919	-2.91389	0.08993
6	0	0.24181	-3.75589	-4.0141
1	0	-0.33901	-2.88676	-2.1247
6	0	2.45559	-3.18032	-4.80148
1	0	3.60059	-1.87111	-3.54109
6	0	4.04554	-3.35857	1.61173
1	0	1.96501	-2.88359	1.2536
6	0	5.61447	-2.52047	-0.02774
1	0	4.77804	-1.33495	-1.61496
1	0	4.06159	-0.14215	4.51957
6	0	-0.94501	1.79066	3.82731
6	0	-0.9866	-0.60659	3.46676
6	0	-0.99012	2.8272	-0.03946
6	0	0.7695	3.59503	1.43778
1	0	7.09883	-0.33251	0.88877
1	0	7.2424	1.40843	1.36156
6	0	-2.71222	0.11146	-1.9926
1	0	-3.99385	-1.49513	-1.25497
6	0	-1.3458	-3.44079	0.94825
1	0	-3.26712	-3.42808	-0.04989
6	0	1.24587	-3.86064	-4.97696
1	0	-0.69855	-4.28473	-4.14283
1	0	3.24061	-3.26311	-5.54863
6	0	5.35668	-3.22976	1.14957
1	0	3.84293	-3.90388	2.52964
1	0	6.63353	-2.42421	-0.3947
6	0	-1.61634	1.61657	5.03875
1	0	-0.68178	2.79136	3.49956
6	0	-1.64789	-0.77429	4.68425
1	0	-0.74657	-1.46978	2.85038
6	0	-1.2347	4.14485	-0.43037
1	0	-1.56924	2.01926	-0.47299
6	0	0.51605	4.9118	1.05209
1	0	1.56173	3.38232	2.14878
6	0	-3.74508	1.07083	-2.16643
6	0	-1.47035	0.3865	-2.59226
8	0	-0.2437	-2.89009	1.24647
8	0	-1.66733	-4.64903	1.4978
1	0	1.09074	-4.47155	-5.86234
1	0	6.17702	-3.67735	1.70447
6	0	-1.96694	0.33523	5.47059
1	0	-1.86744	2.48374	5.64412
1	0	-1.92499	-1.77327	5.01071
6	0	-0.48491	5.18861	0.1153
1	0	-2.00556	4.34347	-1.1684
1	0	1.10025	5.7212	1.48324
6	0	-3.52653	2.2451	-2.88894
8	0	-4.93359	0.75986	-1.55637
6	0	-1.24167	1.56358	-3.30422
1	0	-0.68382	-0.35403	-2.5058
6	0	-0.69746	-5.20094	2.3847
1	0	-2.49256	0.20339	6.41278
1	0	-0.677	6.21474	-0.18789
6	0	-2.2695	2.49126	-3.45607
1	0	-4.31883	2.97455	-3.01308
6	0	-6.00876	1.67135	-1.63001
1	0	-0.26466	1.74953	-3.73604

1	0	-0.5154	-4.54034	3.2401
1	0	-1.11812	-6.1486	2.7278
1	0	0.25602	-5.37701	1.87431
1	0	-2.10671	3.40855	-4.01516
1	0	-5.71225	2.6574	-1.23417
1	0	-6.31883	1.82823	-2.67679
6	0	-7.16501	1.14596	-0.83608
6	0	-7.14451	0.02337	-0.12198
1	0	-8.06535	1.75524	-0.86671
1	0	-6.2636	-0.60662	-0.06406
6	0	-8.32487	-0.46139	0.65337
9	0	-9.38927	0.36956	0.56917
9	0	-8.72875	-1.67809	0.21619
9	0	-8.02385	-0.60001	1.96576



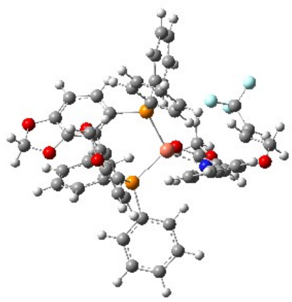
TS *endo*-**2a**

E(B3LYPD3/BS1) = -3766.0190927
H(correction)= 0.877234
G(correction)= 0.723963
$E(M06/BS2)_{CH2Cl2}$ = -3764.87320683
Imaginary frequencies: 1 (-340.5644 cm^{-1})

E(B97D3/BS1) = -3764.60601334
H(correction)= 0.860190
G(correction)= 0.705236
$E(B97D3/BS2)_{CH2Cl2}$ = -3765.55277115
Imaginary frequencies: 1 (-308.1047 cm^{-1})

6	0	-3.41629	1.90202	-0.6053
6	0	-2.78491	0.7094	-0.30088
6	0	-3.62219	2.9194	0.32328
8	0	-3.89383	2.29184	-1.83032
6	0	-2.40026	0.53715	1.06569
6	0	-2.57397	-0.27528	-1.40644
6	0	-3.2209	2.78644	1.63443
8	0	-4.2347	3.98531	-0.28138
6	0	-4.34556	3.64118	-1.67033
6	0	-2.60751	1.57082	1.9868
15	0	-1.37062	-0.91637	1.52228
6	0	-1.34559	-0.46993	-2.11365
6	0	-3.65452	-1.00805	-1.85965
1	0	-3.36125	3.58315	2.35617
1	0	-3.70525	4.30695	-2.2599
1	0	-5.39407	3.71239	-1.97901
1	0	-2.26823	1.44708	3.00795
29	0	0.71552	-0.48991	0.61397
6	0	-1.46368	-1.08288	3.34891
6	0	-2.30069	-2.37348	0.89273
6	0	-1.28498	-1.3725	-3.18001
15	0	0.16702	0.37769	-1.47728
6	0	-3.57546	-1.92078	-2.90883
8	0	-4.9349	-0.98026	-1.36737
7	0	2.47417	-0.36438	1.64188
6	0	-0.26231	-1.41516	3.99537
6	0	-2.63749	-0.95328	4.10834
6	0	-1.59448	-3.30925	0.12256
6	0	-3.66627	-2.57165	1.14272
6	0	-2.39979	-2.12292	-3.59776
1	0	-0.35042	-1.50603	-3.71208
6	0	1.51131	0.03994	-2.68317
6	0	-0.24304	2.15432	-1.6606
8	0	-4.7987	-2.50408	-3.11177
6	0	-5.65875	-1.98285	-2.08885
6	0	3.08246	0.77803	2.029
6	0	3.3047	-1.38436	1.35135
6	0	-0.23655	-1.61851	5.37707
1	0	0.65069	-1.49557	3.40876
6	0	-2.60725	-1.14931	5.48867
1	0	-3.57052	-0.68017	3.6248
6	0	-2.25336	-4.42434	-0.39928
1	0	-0.5372	-3.15369	-0.0693
6	0	-4.31533	-3.69652	0.63521
1	0	-4.22842	-1.84004	1.71452
1	0	-2.33868	-2.82267	-4.42376
6	0	2.18764	1.05844	-3.37044
6	0	2.01917	-1.27245	-2.73951
6	0	-0.11261	2.98616	-0.54077
6	0	-0.73021	2.68538	-2.86594
1	0	-5.93529	-2.79241	-1.40373
1	0	-6.54232	-1.53066	-2.55198
6	0	2.22926	1.97102	2.28922
1	0	3.95251	0.69047	2.68775
6	0	2.74607	-2.52799	0.66767
1	0	4.25053	-1.5221	1.86987
6	0	-1.4077	-1.48487	6.12444
1	0	0.69951	-1.87234	5.8669
1	0	-3.51945	-1.04097	6.06954
6	0	-3.61196	-4.62056	-0.14442
1	0	-1.70454	-5.13749	-1.00836
1	0	-5.37134	-3.85049	0.84362
6	0	3.34852	0.77032	-4.0933
1	0	1.82796	2.08094	-3.32476
6	0	3.16969	-1.55562	-3.47301
1	0	1.55029	-2.05574	-2.15377
6	0	-0.44907	4.33824	-0.62894
1	0	0.23221	2.57399	0.40208
6	0	-1.0516	4.03917	-2.95513
1	0	-0.85994	2.03706	-3.72818
6	0	2.53315	3.22061	1.71642
6	0	1.109	1.8877	3.13301
8	0	1.6317	-2.54899	0.11445
8	0	3.56863	-3.59265	0.64208
1	0	-1.3878	-1.63671	7.20031
1	0	-4.12315	-5.48961	-0.55005

6	0	3.84369	-0.53281	-4.14566
1	0	3.87241	1.57288	-4.6054
1	0	3.56517	-2.56727	-3.48275
6	0	-0.91184	4.86674	-1.8348
1	0	-0.34791	4.96653	0.24946
1	0	-1.41577	4.44793	-3.89434
6	0	1.79525	4.36039	2.06385
8	0	3.52279	3.39006	0.79131
6	0	0.34836	3.01154	3.45156
1	0	0.85226	0.92057	3.55077
6	0	3.17856	-4.66726	-0.21743
1	0	4.75877	-0.74814	-4.68958
1	0	-1.16893	5.92065	-1.90328
6	0	0.71239	4.25892	2.93352
1	0	2.07307	5.3057	1.60789
6	0	3.68391	2.31724	-0.16116
1	0	-0.5051	2.91887	4.11731
1	0	3.1464	-4.3291	-1.25868
1	0	3.94609	-5.43263	-0.09657
1	0	2.19677	-5.06034	0.06293
1	0	0.14174	5.14799	3.19013
1	0	2.70392	2.03712	-0.57141
1	0	4.27044	2.77558	-0.96544
6	0	4.3819	1.11241	0.40779
6	0	4.38096	-0.09957	-0.29532
1	0	5.29966	1.36354	0.94094
1	0	3.6408	-0.26315	-1.06771
6	0	5.61441	-0.88295	-0.50024
9	0	6.34183	-1.03575	0.6404
9	0	5.35169	-2.12852	-0.98657
9	0	6.47264	-0.3203	-1.4087



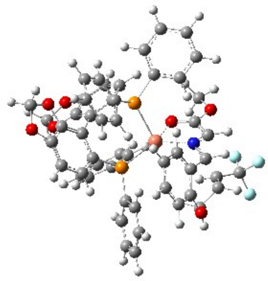
TS *exo*-**2a**

E(B3LYPD3/BS1) = -3766.01530655
H(correction)= 0.877066
G(correction)= 0.720783
E(M06/BS2)$_{CH2Cl2}$ = -3764.8686453
Imaginary frequencies: 1 (-382.2543 cm^{-1})

E(B97D3/BS1) = -3764.59722564
H(correction)= 0.859781
G(correction)= 0.699688
E(B97D3/BS2)$_{CH2Cl2}$ = -3765.54583204
Imaginary frequencies: 1 (-434.6027 cm^{-1})

6	0	-2.95116	1.95405	-1.49218
6	0	-2.54406	1.0026	-0.57504
6	0	-2.89684	3.32672	-1.25082
8	0	-3.50109	1.73081	-2.7314
6	0	-2.05821	1.50477	0.67333
6	0	-2.79373	-0.4381	-0.88541
6	0	-2.45712	3.82602	-0.04434
8	0	-3.38716	4.00749	-2.33551
6	0	-3.54233	3.01612	-3.36086
6	0	-2.02761	2.8848	0.90985
15	0	-1.20122	0.35605	1.83273
6	0	-1.8345	-1.40373	-1.31135
6	0	-4.09734	-0.88841	-0.77142
1	0	-2.43515	4.89125	0.15725
1	0	-2.71085	3.09543	-4.07432
1	0	-4.51044	3.14893	-3.84994
1	0	-1.64448	3.25301	1.85482
29	0	0.75794	-0.30417	0.67943
6	0	-0.99602	1.33181	3.3776
6	0	-2.4282	-0.94425	2.24254
6	0	-2.23607	-2.72288	-1.56108
15	0	-0.04688	-0.94436	-1.40224
6	0	-4.47775	-2.20695	-0.99921
8	0	-5.18778	-0.15902	-0.36149
7	0	2.53439	0.43521	1.47404
6	0	0.29991	1.77682	3.68085
6	0	-2.05498	1.66397	4.238
6	0	-1.94355	-2.25413	2.37786
6	0	-3.80073	-0.69455	2.39374
6	0	-3.56385	-3.15563	-1.40173
1	0	-1.50016	-3.44811	-1.88544
6	0	0.72178	-2.45716	-2.10639
6	0	0.03566	0.30445	-2.7422
8	0	-5.81571	-2.35873	-0.74149
6	0	-6.30723	-1.04789	-0.43534
6	0	3.31195	1.49549	1.14724
6	0	3.19887	-0.52049	2.14443
6	0	0.52968	2.55554	4.81748
1	0	1.12322	1.50445	3.02744
6	0	-1.82063	2.43623	5.37492
1	0	-3.0602	1.3141	4.02626
6	0	-2.82415	-3.29825	2.6689
1	0	-0.88274	-2.44836	2.23845
6	0	-4.67526	-1.74089	2.68535
1	0	-4.19086	0.30605	2.23378
1	0	-3.85352	-4.18458	-1.58303
6	0	0.83592	-2.69366	-3.48288
6	0	1.19533	-3.41725	-1.19826
6	0	1.06542	1.25295	-2.67353
6	0	-0.87242	0.34842	-3.81116
1	0	-6.81683	-1.07016	0.53307
1	0	-6.98671	-0.71573	-1.23176
6	0	2.82406	2.6518	0.37911
1	0	4.09373	1.7586	1.8703
6	0	2.56385	-1.80675	2.31356
1	0	4.03791	-0.28679	2.79514
6	0	-0.52866	2.88688	5.6643
1	0	1.53686	2.89779	5.03962
1	0	-2.64572	2.68665	6.03663

6	0	-4.18851	-3.04399	2.82264
1	0	-2.44507	-4.31231	2.76368
1	0	-5.73794	-1.54178	2.79983
6	0	1.4139	-3.87774	-3.94463
1	0	0.48435	-1.9533	-4.19475
6	0	1.76269	-4.60214	-1.66441
1	0	1.15415	-3.21376	-0.13293
6	0	1.19387	2.23149	-3.65971
1	0	1.74862	1.24019	-1.8309
6	0	-0.73749	1.32238	-4.80185
1	0	-1.69044	-0.36391	-3.85706
6	0	3.81891	3.41533	-0.26973
6	0	1.48377	3.01486	0.20619
8	0	1.48064	-2.13669	1.79948
8	0	3.27287	-2.6553	3.07953
1	0	-0.35009	3.49023	6.55049
1	0	-4.8736	-3.8592	3.03945
6	0	1.87426	-4.83458	-3.03739
1	0	1.50719	-4.05026	-5.01367
1	0	2.13973	-5.33321	-0.95417
6	0	0.2932	2.26535	-4.72654
1	0	1.98228	2.97296	-3.57476
1	0	-1.43931	1.34617	-5.63202
6	0	3.4709	4.51905	-1.05296
8	0	5.14927	3.14436	-0.10527
6	0	1.13195	4.11557	-0.57513
1	0	0.71267	2.42597	0.68987
6	0	2.81634	-4.01251	3.08683
1	0	2.32896	-5.75284	-3.39977
1	0	0.38929	3.02697	-5.49615
6	0	2.12794	4.87251	-1.19759
1	0	4.26459	5.08271	-1.53368
6	0	5.64498	1.77802	-0.15344
1	0	0.08511	4.37192	-0.69762
1	0	2.86528	-4.4271	2.07514
1	0	3.49843	-4.5475	3.74888
1	0	1.78968	-4.08097	3.45846
1	0	1.86093	5.73345	-1.80513
1	0	6.23439	1.70682	-1.07693
1	0	6.33385	1.68441	0.69384
6	0	4.61391	0.67869	-0.12065
6	0	4.95555	-0.5878	0.38778
1	0	3.96779	0.6651	-0.99661
1	0	5.83343	-0.72612	1.01213
6	0	4.53126	-1.7955	-0.34585
9	0	4.406	-2.90734	0.4379
9	0	3.33694	-1.61249	-0.97111
9	0	5.40918	-2.16865	-1.33014



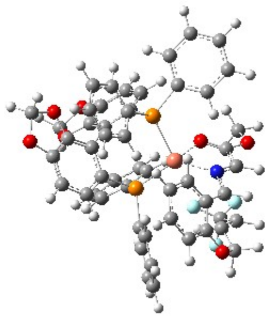
TS *endo* **ent-2a**

E(B3LYPD3/BS1) = -3766.01264509
H(correction)= 0.877177
G(correction)= 0.722488
E(M06/BS2)$_{CH2Cl2}$ = -3764.86837278
Imaginary frequencies: 1 (-338.8548 cm^{-1})

E(B97D3/BS1) = -3764.5992416
H(correction)= 0.860168
G(correction)= 0.703646
E(B97D3/BS2)$_{CH2Cl2}$ = -3765.54751467
Imaginary frequencies: 1 (-284.9258 cm^{-1})

6	0	-4.084	1.18992	-0.11319
6	0	-2.89733	0.72011	0.41712
6	0	-4.30774	2.52815	-0.42562
8	0	-5.19345	0.44926	-0.43405
6	0	-1.88955	1.70318	0.67127
6	0	-2.78334	-0.73206	0.74542
6	0	-3.35211	3.48966	-0.18194
8	0	-5.55985	2.67924	-0.96017
6	0	-6.10921	1.35685	-1.05629
6	0	-2.13839	3.04827	0.37665
15	0	-0.21916	1.14368	1.24609
6	0	-2.05839	-1.70175	-0.011
6	0	-3.42969	-1.20193	1.87521
1	0	-3.52578	4.53507	-0.41125
1	0	-6.22197	1.08901	-2.11345
1	0	-7.06894	1.32326	-0.52982
1	0	-1.37513	3.78947	0.57995
29	0	0.82064	-0.16137	-0.36502
6	0	0.65897	2.69065	1.70905
6	0	-0.58855	0.30292	2.83612
6	0	-1.95711	-3.01882	0.45464
15	0	-1.03274	-1.14652	-1.43437
6	0	-3.33314	-2.51727	2.31863
8	0	-4.20888	-0.47742	2.74238
7	0	2.67801	-0.51663	-1.13341
6	0	1.13548	3.50087	0.66289
6	0	0.94511	3.05239	3.03351
6	0	0.00692	-0.93935	3.09566
6	0	-1.46817	0.86262	3.77706
6	0	-2.59084	-3.4536	1.63147
1	0	-1.3552	-3.73106	-0.09633
6	0	-0.7041	-2.65248	-2.42971
6	0	-2.1508	-0.12443	-2.48003
8	0	-4.04526	-2.67235	3.47962
6	0	-4.58023	-1.37848	3.79135
6	0	3.51931	0.40383	-1.64666

6	0	3.26196	-1.64647	-0.69071
6	0	1.84842	4.66601	0.94085
1	0	0.96831	3.21249	-0.37174
6	0	1.68023	4.20842	3.30565
1	0	0.60425	2.43226	3.85521
6	0	-0.27369	-1.61033	4.28809
1	0	0.65336	-1.39369	2.35154
6	0	-1.7281	0.19739	4.97469
1	0	-1.95422	1.81077	3.56533
1	0	-2.49782	-4.47448	1.9848
6	0	-1.66471	-3.62945	-2.73925
6	0	0.60321	-2.7985	-2.91767
6	0	-1.73171	1.18627	-2.74992
6	0	-3.37444	-0.57225	-2.99783
1	0	-4.14941	-1.02901	4.73599
1	0	-5.67314	-1.43987	3.84762
6	0	2.93759	1.69053	-2.11437
1	0	4.36303	0.04237	-2.24302
6	0	2.43524	-2.56794	0.05597
1	0	4.16143	-2.04277	-1.15469
6	0	2.12515	5.02167	2.26283
1	0	2.20843	5.2768	0.12047
1	0	1.90317	4.47111	4.33638
6	0	-1.13511	-1.04387	5.22916
1	0	0.17715	-2.58082	4.47628
1	0	-2.39888	0.64294	5.70509
6	0	-1.32258	-4.72708	-3.52806
1	0	-2.67113	-3.54778	-2.33987
6	0	0.94251	-3.89773	-3.70979
1	0	1.35282	-2.05644	-2.65818
6	0	-2.52144	2.03898	-3.52162
1	0	-0.79575	1.54129	-2.33029
6	0	-4.15819	0.27663	-3.77988
1	0	-3.72312	-1.57718	-2.78379
6	0	3.4596	2.92346	-1.68259
6	0	1.86953	1.70532	-3.02671
8	0	1.31701	-2.29802	0.52422
8	0	2.99285	-3.78266	0.21789
1	0	2.69667	5.92073	2.47654
1	0	-1.34896	-1.56789	6.15702
6	0	-0.019	-4.86139	-4.01665
1	0	-2.07138	-5.48014	-3.75955
1	0	1.95987	-4.00289	-4.07669
6	0	-3.73596	1.58476	-4.03955
1	0	-2.19049	3.05693	-3.70782
1	0	-5.10079	-0.08166	-4.18653
6	0	2.99955	4.12166	-2.24855
8	0	4.40223	3.02953	-0.70269
6	0	1.36711	2.89786	-3.54684
1	0	1.4448	0.75219	-3.33019
6	0	2.25875	-4.69814	1.037
1	0	0.2451	-5.7195	-4.62907
1	0	-4.35382	2.24599	-4.64115
6	0	1.96032	4.10989	-3.17507
1	0	3.45778	5.05019	-1.92197
6	0	4.33353	2.06175	0.37066
1	0	0.54151	2.87785	-4.25284
1	0	1.27034	-4.89569	0.61045
1	0	2.85461	-5.61133	1.06197
1	0	2.13453	-4.29807	2.04846
1	0	1.60355	5.04681	-3.595
1	0	4.96302	2.50856	1.14811
1	0	3.30554	2.00513	0.75046
6	0	4.82739	0.69793	-0.02598
6	0	4.62098	-0.41254	0.80168
1	0	5.77483	0.7251	-0.56434
1	0	3.88318	-0.37542	1.59837
6	0	5.69378	-1.40543	1.02077
9	0	6.67435	-0.97532	1.87383
9	0	5.22348	-2.55821	1.56414
9	0	6.33853	-1.73453	-0.13508



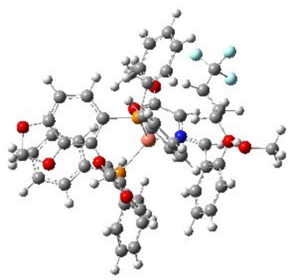
TS *exo* **ent-2a**

E(B3LYPD3/BS1) = -3766.02074809
H(correction)= 0.876981
G(correction)= 0.724065
$E(M06/BS2)_{CH2Cl2}$ = -3764.8725154
Imaginary frequencies: 1 (-379.6645 cm^{-1})

E(B97D3/BS1) = -3764.60438467
H(correction)= 0.859717
G(correction)= 0.703442
$E(B97D3/BS2)_{CH2Cl2}$ = -3765.54954375
Imaginary frequencies: 1 (-440.9579 cm^{-1})

6	0	3.57635	1.31285	-1.53863
6	0	2.4991	0.48541	-1.28411
6	0	3.48919	2.47218	-2.30506
8	0	4.86192	1.15535	-1.08469
6	0	1.25632	0.86972	-1.882
6	0	2.72909	-0.76437	-0.497
6	0	2.30509	2.85172	-2.89745
8	0	4.71249	3.08852	-2.358
6	0	5.57202	2.32767	-1.49684
6	0	1.18952	2.02363	-2.67004
15	0	-0.25677	-0.10602	-1.45571
6	0	2.37365	-0.97734	0.86997
6	0	3.35373	-1.82331	-1.13187
1	0	2.23524	3.74514	-3.50793
1	0	5.82154	2.92801	-0.61349
1	0	6.47052	2.03372	-2.04915
1	0	0.24909	2.30113	-3.13089
29	0	-0.72693	0.02135	0.81362

6	0	-1.60946	0.53085	-2.52253
6	0	0.15143	-1.77191	-2.11133
6	0	2.58684	-2.22755	1.46335
15	0	1.38978	0.30484	1.74899
6	0	3.57278	-3.05736	-0.52635
8	0	3.81208	-1.8549	-2.42461
7	0	-2.51179	0.20088	1.82911
6	0	-2.09183	1.83276	-2.29204
6	0	-2.30057	-0.30039	-3.41645
6	0	-0.0107	-2.88657	-1.27677
6	0	0.66589	-1.94104	-3.40604
6	0	3.19069	-3.29549	0.77603
1	0	2.26096	-2.39299	2.48329
6	0	1.51118	-0.09582	3.53543
6	0	2.33453	1.8698	1.5182
8	0	4.17611	-3.91125	-1.41234
6	0	4.28452	-3.18783	-2.64702
6	0	-3.46847	1.11727	1.56609
6	0	-2.95656	-0.95875	2.33069
6	0	-3.21118	2.30256	-2.97859
1	0	-1.61869	2.47339	-1.55249
6	0	-3.43657	0.16613	-4.08002
1	0	-1.97257	-1.32124	-3.57566
6	0	0.33619	-4.15703	-1.73916
1	0	-0.38999	-2.7542	-0.26945
6	0	0.99271	-3.21525	-3.8695
1	0	0.81605	-1.07543	-4.04538
1	0	3.34419	-4.26082	1.24536
6	0	2.70252	-0.40308	4.21323
6	0	0.30344	-0.07441	4.25028
6	0	1.6738	2.90923	0.8479
6	0	3.66103	2.06078	1.93028
1	0	3.65698	-3.67052	-3.40431
1	0	5.33509	-3.15394	-2.95671
6	0	-3.11321	2.45639	1.06176
1	0	-4.35438	1.09873	2.21173
6	0	-2.06298	-2.09073	2.29902
1	0	-3.85723	-1.02331	2.93442
6	0	-3.88919	1.46968	-3.8715
1	0	-3.56925	3.3074	-2.78209
1	0	-3.97071	-0.49697	-4.75501
6	0	0.83187	-4.3254	-3.03363
1	0	0.2215	-5.01572	-1.08338
1	0	1.37898	-3.34113	-4.87793
6	0	2.68617	-0.66448	5.58278
1	0	3.6383	-0.46911	3.66667
6	0	0.29035	-0.3327	5.62263
1	0	-0.6234	0.13052	3.72109
6	0	2.32063	4.11887	0.59553
1	0	0.66202	2.75192	0.49141
6	0	4.30448	3.27573	1.69047
1	0	4.19986	1.26279	2.42953
6	0	-4.0375	3.12999	0.23969
6	0	-1.88664	3.07625	1.33895
8	0	-0.94788	-2.09757	1.75247
8	0	-2.56223	-3.18271	2.91182
1	0	-4.77477	1.8304	-4.38769
1	0	1.09592	-5.31748	-3.39097
6	0	1.48065	-0.62425	6.29037
1	0	3.61284	-0.90319	6.09814
1	0	-0.65109	-0.31355	6.16496
6	0	3.63708	4.30649	1.02085
1	0	1.79936	4.90455	0.05584
1	0	5.33004	3.41709	2.02262
6	0	-3.73451	4.40505	-0.25784
8	0	-5.24808	2.62675	-0.12747
6	0	-1.57437	4.33715	0.82978
1	0	-1.18378	2.54908	1.97753
6	0	-1.8325	-4.39572	2.6974
1	0	1.47113	-0.82847	7.35779
1	0	4.14455	5.24764	0.8268
6	0	-2.51146	5.00502	0.03453
1	0	-4.47243	4.89799	-0.88357
6	0	-5.57153	1.21553	-0.0796
1	0	-0.62316	4.80081	1.07415
1	0	-0.80025	-4.30218	3.0473
1	0	-2.36189	-5.16104	3.2668
1	0	-1.83347	-4.64781	1.63219
1	0	-2.2917	5.99384	-0.35944
1	0	-6.27366	1.06167	0.75086
1	0	-6.11552	1.04375	-1.01508
6	0	-4.41592	0.25251	0.02041
6	0	-4.65394	-1.07976	0.38183
1	0	-3.65403	0.40815	-0.73882
1	0	-5.5572	-1.36327	0.91522
6	0	-4.01945	-2.18897	-0.34964
9	0	-2.73952	-1.90928	-0.73583
9	0	-3.96962	-3.34729	0.36734
9	0	-4.6695	-2.52417	-1.51243



TS *endo*-**2a-MeOH**

E(B97D3/BS1) = -3880.26894186

H(correction)= 0.917835

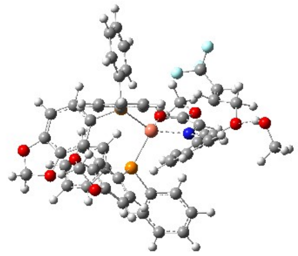
G(correction)= 0.751053

$E(B97D3/BS2)_{CH2Cl2}$ = -3881.26337672

Imaginary frequencies: 1 (-307.2688 cm^{-1})

6	0	-3.0239	2.27928	-1.02786
6	0	-2.67665	1.03133	-0.51974
6	0	-2.8948	3.4668	-0.30031
8	0	-3.47061	2.55807	-2.29977
6	0	-2.25522	1.01009	0.85052
6	0	-2.7096	-0.14908	-1.43359
6	0	-2.41943	3.4683	1.00052

8	0	-3.25987	4.53926	-1.08023
6	0	-3.57272	3.99264	-2.37862
6	0	-2.10878	2.21332	1.56351
15	0	-1.64539	-0.55862	1.59029
6	0	-1.53741	-0.73137	-2.02523
6	0	-3.92376	-0.69092	-1.83343
1	0	-2.27426	4.392	1.55715
1	0	-2.84213	4.36454	-3.11202
1	0	-4.60271	4.26787	-2.64904
1	0	-1.71382	2.18749	2.57548
29	0	0.48063	-0.81013	0.76627
6	0	-1.89675	-0.39544	3.40556
6	0	-2.8988	-1.82455	1.11502
6	0	-1.65443	-1.79668	-2.93078
15	0	0.10838	-0.12007	-1.45042
6	0	-4.02679	-1.76834	-2.72058
8	0	-5.18067	-0.29094	-1.43772
7	0	2.23198	-1.01093	1.77424
6	0	-0.97585	-1.08387	4.2195
6	0	-2.94781	0.32049	4.00912
6	0	-2.456	-2.97561	0.4373
6	0	-4.26492	-1.67395	1.41361
6	0	-2.90517	-2.3416	-3.29581
1	0	-0.75663	-2.21555	-3.38028
6	0	1.36894	-0.84288	-2.57872
6	0	0.05467	1.65585	-1.90989
8	0	-5.35004	-2.09581	-2.91043
6	0	-6.0981	-1.22411	-2.03724
6	0	3.02521	0.04413	2.10979
6	0	2.90031	-2.15115	1.48003
6	0	-1.10221	-1.0543	5.61419
1	0	-0.152	-1.62404	3.74897
6	0	-3.06496	0.3583	5.40416
1	0	-3.65872	0.86753	3.39086
6	0	-3.37789	-3.95358	0.04336
1	0	-1.39798	-3.09057	0.20827
6	0	-5.17952	-2.66274	1.03428
1	0	-4.6149	-0.78294	1.9333
1	0	-2.98354	-3.1688	-3.99898
6	0	2.24285	-0.03539	-3.33244
6	0	1.61712	-2.23171	-2.50456
6	0	0.39037	2.62212	-0.94681
6	0	-0.30717	2.06259	-3.20871
1	0	-6.57018	-1.8262	-1.24586
1	0	-6.84257	-0.67125	-2.628
6	0	2.33359	1.34008	2.37825
1	0	3.8788	-0.16186	2.77368
6	0	2.12005	-3.22477	0.88742
1	0	3.81499	-2.42669	2.00915
6	0	-2.14359	-0.32816	6.2089
1	0	-0.38026	-1.58696	6.23483
1	0	-3.87727	0.92387	5.86363
6	0	-4.73913	-3.80054	0.34025
1	0	-3.03184	-4.83367	-0.5003
1	0	-6.23703	-2.54483	1.27814
6	0	3.34088	-0.60526	-3.99183
1	0	2.08306	1.03995	-3.38604
6	0	2.70565	-2.79551	-3.17785
1	0	0.99578	-2.85511	-1.86519
6	0	0.40108	3.98036	-1.28461
1	0	0.62099	2.31274	0.07021
6	0	-0.29169	3.4211	-3.5458
1	0	-0.59236	1.31439	-3.94887
6	0	2.63631	2.51652	1.66172
6	0	1.35252	1.41864	3.38773
8	0	0.968	-3.09961	0.423
8	0	2.77713	-4.41165	0.86185
1	0	-2.2361	-0.29421	7.29537
1	0	-5.45528	-4.5648	0.03446
6	0	3.57723	-1.98335	-3.91767
1	0	4.01996	0.03642	-4.5551
1	0	2.89727	-3.8657	-3.09182
6	0	0.07066	4.38027	-2.58589
1	0	0.68403	4.72031	-0.53895
1	0	-0.5547	3.73087	-4.55894
6	0	2.02579	3.74083	1.9961
8	0	3.52421	2.54246	0.60547
6	0	0.72047	2.62267	3.71089
1	0	1.10166	0.50882	3.92908
6	0	2.10381	-5.48166	0.17759
1	0	4.44508	-2.41911	-4.41327
1	0	0.09569	5.43773	-2.85163
6	0	1.07411	3.79117	3.01763
1	0	2.28379	4.62584	1.41608
6	0	3.60145	1.34452	-0.22587
1	0	3.40565	4.1613	-0.40325
1	0	-0.0297	2.64719	4.5027
1	0	1.95417	-5.22996	-0.88145
1	0	2.76815	-6.34666	0.27098
1	0	1.12907	-5.69029	0.63874
1	0	0.5996	4.74345	3.26082
1	0	2.58865	1.07899	-0.55911
1	0	4.17396	1.69077	-1.09864
6	0	4.2489	0.17266	0.4562
8	0	3.43471	5.10337	-0.67453
6	0	4.1553	-1.1002	-0.16368
1	0	5.20727	0.41508	0.92583
6	0	4.64697	5.6249	-0.14354
1	0	3.4226	-1.24901	-0.95162
6	0	5.34633	-1.96742	-0.29778
1	0	5.54254	5.14787	-0.58536
1	0	4.67467	6.69618	-0.38715
1	0	4.70996	5.51779	0.95596
9	0	6.05599	-2.0781	0.87264
9	0	5.02352	-3.23515	-0.69875
9	0	6.25513	-1.5112	-1.23491

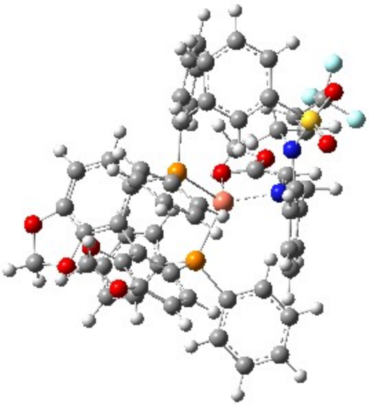


TS *exo*-**2a-MeOH**

E(B97D3/BS1) = -3880.25764319
H(correction)= 0.917402
G(correction)= 0.747658
$E(B97D3/BS2)_{CH2Cl2}$ = -3881.2557757
Imaginary frequencies: 1 (-430.5482cm^{-1})

6	0	-2.36635	3.05079	-0.49692
6	0	-2.3282	1.74426	-0.02477
6	0	-1.88561	4.14764	0.23201
8	0	-2.90166	3.49208	-1.68939
6	0	-1.77576	1.5723	1.29008
6	0	-3.00279	0.6636	-0.80676
6	0	-1.37755	3.99812	1.51183
8	0	-2.0646	5.30551	-0.49341
6	0	-2.47183	4.86105	-1.8049
6	0	-1.32473	2.68317	2.02258
15	0	-1.3988	-0.13677	1.8698
6	0	-2.36485	-0.34373	-1.59896
6	0	-4.39366	0.62899	-0.78841
1	0	-1.023	4.84896	2.09047
1	0	-1.60988	4.91211	-2.49153
1	0	-3.31217	5.47504	-2.15016
1	0	-0.89815	2.528	3.01152
6	0	-0.98577	0.05947	3.65298
6	0	-3.01939	-0.9973	1.84205
6	0	-3.13658	-1.30904	-2.26956
15	0	-0.52057	-0.42916	-1.65855
6	0	-5.14835	-0.35047	-1.44081
8	0	-5.2331	1.48522	-0.10735
6	0	0.36468	0.31437	3.97248
6	0	-1.93034	-0.03934	4.69174
6	0	-3.05035	-2.31822	1.35775
6	0	-4.21512	-0.37602	2.25046
6	0	-4.54439	-1.34168	-2.19492
1	0	-2.63576	-2.06435	-2.86949
29	0	0.34287	-0.81442	0.42697
6	0	-0.22752	-1.79307	-2.85718
6	0	-0.03133	1.08128	-2.58126
8	0	-6.48837	-0.15595	-1.19528
6	0	-6.57129	1.0448	-0.40176
6	0	0.75273	0.50066	5.30482
1	0	1.10848	0.34709	3.17786
6	0	-1.53401	0.13256	6.0243
1	0	-2.9711	-0.26226	4.46255
6	0	-4.26775	-3.00733	1.28029
1	0	-2.1219	-2.79052	1.03488
6	0	-5.42576	-1.07526	2.18664
1	0	-4.19822	0.6618	2.58285
1	0	-5.12587	-2.10585	-2.70727
7	0	2.16751	-0.88853	1.35031
6	0	-0.08381	-1.57029	-4.2383
6	0	-0.18001	-3.10805	-2.35379
6	0	1.29431	1.53422	-2.45046
6	0	-0.91912	1.76732	-3.43107
1	0	-7.0933	0.81991	0.53869
1	0	-7.09437	1.82662	-0.97591
6	0	-0.19523	0.41102	6.33379
1	0	1.79918	0.70359	5.53761
1	0	-2.27395	0.04902	6.82203
6	0	-5.45525	-2.38909	1.69532
1	0	-4.28945	-4.02488	0.88748
1	0	-6.34879	-0.59311	2.51368
6	0	3.23324	-0.04189	1.28829
6	0	2.50694	-2.13619	1.73684
6	0	0.10254	-2.65361	-5.10698
1	0	-0.11416	-0.55476	-4.63172
6	0	-0.0063	-4.18644	-3.22811
1	0	-0.24578	-3.27738	-1.2799
6	0	1.72994	2.6592	-3.16051
1	0	1.9751	1.02056	-1.77387
6	0	-0.48123	2.89477	-4.13767
1	0	-1.94819	1.42501	-3.52875
1	0	0.10895	0.54726	7.37269
1	0	-6.40309	-2.92503	1.62936
6	0	3.11565	1.35401	0.83528
1	0	4.00487	-0.18365	2.06223
6	0	1.52137	-3.18982	1.57127
1	0	3.31549	-2.30862	2.45085
6	0	0.13658	-3.96208	-4.60501
1	0	0.22235	-2.47437	-6.17667
1	0	0.04029	-5.20137	-2.83035
6	0	0.84206	3.34299	-4.00279
1	0	2.7539	3.00896	-3.03314
1	0	-1.17326	3.41998	-4.79878
6	0	4.31584	1.95712	0.38894
6	0	1.92769	2.09949	0.75712
8	0	0.44138	-3.06948	0.95807
8	0	1.89675	-4.35889	2.14616
1	0	0.28567	-4.80338	-5.2836
1	0	1.17918	4.22329	-4.55259
6	0	4.33178	3.27013	-0.10183
8	0	5.51728	1.28245	0.49521
6	0	1.93314	3.4137	0.27587
1	0	0.99229	1.64528	1.07793
6	0	1.04449	-5.48372	1.86293
6	0	3.13544	3.9995	-0.14406
1	0	5.27827	3.69674	-0.43376
6	0	5.62052	-0.12143	0.05099
1	0	6.99779	2.39511	0.09513
1	0	0.99895	3.96992	0.22602
1	0	1.02321	-5.67674	0.7822
1	0	1.49499	-6.32811	2.39441
1	0	0.02324	-5.30092	2.22282
1	0	3.1452	5.02346	-0.52093
1	0	6.18823	-0.08935	-0.89204
1	0	6.243	-0.6067	0.81535

6	0	4.3225	-0.86026	-0.1391
8	0	7.63142	3.13774	0.00021
6	0	4.28588	-2.26415	0.06888
1	0	3.74641	-0.51059	-0.99961
6	0	7.73555	3.72433	1.29014
1	0	5.06506	-2.75068	0.65734
6	0	3.67252	-3.1369	-0.95566
1	0	8.16435	3.03151	2.04039
1	0	8.40838	4.58907	1.20226
1	0	6.76109	4.08276	1.67449
9	0	3.31064	-4.37141	-0.47777
9	0	2.55711	-2.57432	-1.51496
9	0	4.51976	-3.40694	-2.01555

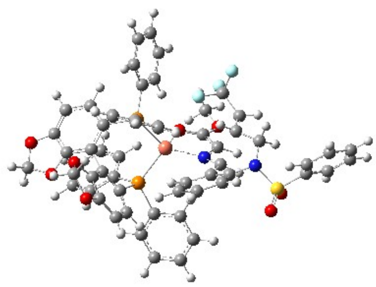


TS *endo* **7a**

E(B3LYPD3/BS1) = -4525.79276737
H(correction)= 0.989597
G(correction)= 0.819963
E(M06/BS2)$_{CH2Cl2}$ = -4524.48599154
Imaginary frequencies: 1 (-366.1169 cm^{-1})

6	0	3.04595	-2.96633	0.61191
6	0	2.93287	-1.62959	0.27315
6	0	2.94009	-3.438	1.91736
8	0	3.21395	-4.02135	-0.24842
6	0	2.77364	-0.71993	1.36535
6	0	2.97641	-1.2621	-1.17554
6	0	2.73315	-2.5806	2.97586
8	0	3.03769	-4.8049	1.92894
6	0	3.22448	-5.20093	0.56284
6	0	2.65585	-1.20924	2.67233
15	0	2.47784	1.05918	1.00212
6	0	1.83666	-0.92822	-1.97461
6	0	4.1862	-1.31106	-1.84237
1	0	2.62816	-2.94587	3.99126
1	0	2.3985	-5.85358	0.26073
1	0	4.19221	-5.70627	0.45862
1	0	2.48725	-0.5148	3.48707
29	0	0.30815	1.20724	0.15128
6	0	2.80305	1.97556	2.56065
6	0	3.87525	1.5338	-0.09972
6	0	1.98964	-0.64045	-3.33416
15	0	0.20397	-0.72684	-1.13656
6	0	4.32797	-1.00672	-3.19436
8	0	5.40858	-1.6356	-1.31145
7	0	-1.09168	2.46369	0.95514
8	0	0.4007	2.96206	-1.33398
6	0	1.90947	3.01773	2.85491
6	0	3.88811	1.74	3.42048
6	0	3.56817	2.22228	-1.28287
6	0	5.21115	1.22209	0.19233
6	0	3.2431	-0.66803	-3.97319
1	0	1.11722	-0.38664	-3.92561
6	0	-1.06461	-0.5785	-2.45729
6	0	-0.06548	-2.37075	-0.37113
8	0	5.64269	-1.12264	-3.56195
6	0	6.36193	-1.43754	-2.36142
6	0	-2.13824	2.09661	1.72643
6	0	-1.25063	3.6052	0.25689
6	0	-0.3481	3.83099	-0.84399
6	0	2.09902	3.81158	3.98867
1	0	1.05984	3.18936	2.19837
6	0	4.07038	2.52938	4.55552
1	0	4.57929	0.92823	3.21524
6	0	4.58841	2.5863	-2.16416
1	0	2.53363	2.45836	-1.51148
6	0	6.22804	1.60398	-0.68201
1	0	5.45713	0.6616	1.08874
1	0	3.35047	-0.43956	-5.02766
6	0	-2.04238	-1.55253	-2.7026
6	0	-1.15887	0.66608	-3.10859
6	0	-0.37627	-2.42449	0.9927
6	0	0.08835	-3.56466	-1.09425
1	0	7.0155	-0.59701	-2.10165
1	0	6.93353	-2.35963	-2.51131
6	0	-1.97937	0.84419	2.53269
1	0	-2.70567	2.88952	2.22419
1	0	-1.80921	4.45067	0.64857
8	0	-0.39914	5.07726	-1.34891
6	0	3.17751	3.56742	4.8402
1	0	1.39953	4.61387	4.20717
1	0	4.90969	2.336	5.21839
6	0	5.91762	2.28038	-1.86615
1	0	4.34231	3.10469	-3.08699
1	0	7.26222	1.36823	-0.44302
6	0	-3.09029	-1.29174	-3.5889
1	0	-2.01947	-2.50138	-2.1807
6	0	-2.1924	0.91086	-4.01188
1	0	-0.45083	1.4546	-2.86761
6	0	-0.54299	-3.65714	1.62699
1	0	-0.46254	-1.50485	1.56081
6	0	-0.0939	-4.79449	-0.46254
1	0	0.36223	-3.52843	-2.14487
6	0	-2.79395	-0.29897	2.36947
6	0	-0.95841	0.80679	3.49878
6	0	0.37718	5.30856	-2.52868
1	0	3.32268	4.18065	5.72554
1	0	6.71025	2.56674	-2.55246
6	0	-3.16455	-0.06542	-4.25036
1	0	-3.85467	-2.04797	-3.742

1	0	-2.25717	1.8772	-4.50482
6	0	-0.40732	-4.84219	0.90112
1	0	-0.77219	-3.68127	2.68709
1	0	0.01926	-5.71536	-1.02943
6	0	-2.62274	-1.39521	3.2364
7	0	-3.67745	-0.37432	1.25706
6	0	-0.77429	-0.28912	4.33604
1	0	-0.3134	1.67425	3.59127
1	0	0.05779	4.64543	-3.33925
1	0	0.19491	6.34936	-2.79878
1	0	1.44193	5.14459	-2.33463
1	0	-3.98487	0.13852	-4.93296
1	0	-0.53533	-5.80094	1.39649
6	0	-1.6376	-1.38119	4.21754
1	0	-3.26178	-2.26111	3.13296
6	0	-3.39147	0.41994	0.04598
16	0	-5.21995	-1.06146	1.28671
1	0	0.01615	-0.2822	5.08142
1	0	-1.53145	-2.24071	4.87462
1	0	-2.35411	0.22389	-0.23621
1	0	-4.0156	0.02805	-0.76341
6	0	-3.59961	1.89745	0.25207
8	0	-5.42474	-1.68875	2.59363
8	0	-6.1924	-0.09475	0.76833
6	0	-5.03015	-2.34067	0.03042
6	0	-3.24071	2.78934	-0.76255
1	0	-4.47213	2.14349	0.85375
6	0	-3.954	-3.22724	0.11427
6	0	-5.96826	-2.42668	-0.99737
1	0	-2.72673	2.43825	-1.65032
6	0	-3.97776	4.05737	-0.94206
6	0	-3.81935	-4.22193	-0.85278
1	0	-3.21456	-3.12646	0.90096
6	0	-5.82497	-3.42859	-1.96072
1	0	-6.7811	-1.70985	-1.04021
9	0	-4.24648	4.66454	0.24934
9	0	-3.28487	4.94841	-1.70016
9	0	-5.1865	3.91286	-1.56286
6	0	-4.7541	-4.32281	-1.88925
1	0	-2.97624	-4.90381	-0.7997
1	0	-6.54818	-3.50564	-2.76776
1	0	-4.64427	-5.09745	-2.64346

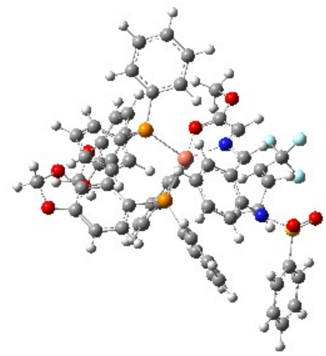


TS *exo* **7a**

E(B3LYPD3/BS1) = -4525.78359043
H(correction)= 0.989114
G(correction)= 0.814031
$E(M06/BS2)_{CH2Cl2}$ = -4524.48143675
Imaginary frequencies: 1 (-390.093 cm^{-1})

6	0	3.2383	-2.41383	-1.91953
6	0	3.12607	-1.59522	-0.81046
6	0	2.64702	-3.67373	-2.0077
8	0	3.95406	-2.16496	-3.06627
6	0	2.3661	-2.1229	0.28145
6	0	3.92459	-0.33209	-0.77188
6	0	1.92732	-4.20406	-0.95901
8	0	2.95319	-4.24607	-3.21617
6	0	3.58064	-3.20488	-3.97696
6	0	1.79256	-3.39704	0.18594
15	0	1.90635	-1.01686	1.68409
6	0	3.44218	0.99892	-0.94749
6	0	5.28564	-0.45826	-0.55488
1	0	1.48262	-5.19144	-1.01461
1	0	2.86447	-2.80561	-4.708
1	0	4.47649	-3.59972	-4.46267
1	0	1.20837	-3.77874	1.01563
29	0	0.45971	0.58772	0.7258
6	0	1.20426	-2.15025	2.94884
6	0	3.49401	-0.41702	2.37725
6	0	4.33015	2.07981	-0.86183
15	0	1.63189	1.30784	-1.13823
6	0	6.15232	0.62502	-0.45118
8	0	5.9789	-1.62485	-0.33869
7	0	-1.52101	0.41478	1.32454
8	0	0.36593	2.28574	2.22218
6	0	-0.19567	-2.19737	3.04327
6	0	1.97611	-2.97229	3.78534
6	0	3.5427	0.92501	2.78377
6	0	4.644	-1.2148	2.48145
6	0	5.70172	1.91798	-0.60144
1	0	3.95287	3.08628	-0.99442
6	0	1.55573	3.11061	-1.48534
6	0	1.18928	0.51222	-2.73058
8	0	7.41839	0.18441	-0.16422
6	0	7.35208	-1.24673	-0.19834
6	0	-2.61754	-0.19822	0.8044
6	0	-1.84811	1.39677	2.17732
6	0	-0.80763	2.29531	2.63006
6	0	-0.81453	-3.06776	3.94274
1	0	-0.7943	-1.54236	2.41903
6	0	1.35488	-3.83296	4.68999
1	0	3.05962	-2.93503	3.73984
6	0	4.72801	1.45731	3.2953
1	0	2.65656	1.54707	2.68045
6	0	5.82386	-0.67891	2.99688
1	0	4.62905	-2.2374	2.11615
1	0	6.37059	2.76736	-0.51989
6	0	1.75398	3.65	-2.76428
6	0	1.29828	3.96896	-0.40565
6	0	-0.14852	0.1286	-2.89952
6	0	2.10823	0.28307	-3.76503
1	0	7.74522	-1.64894	0.74045
1	0	7.92417	-1.61993	-1.05856

6	0	-2.54516	-1.26275	-0.21187
1	0	-3.45996	-0.32097	1.49207
1	0	-2.76479	1.36506	2.76103
8	0	-1.23537	3.18527	3.54166
6	0	-0.0404	-3.88685	4.76603
1	0	-1.89917	-3.09786	3.99996
1	0	1.96017	-4.463	5.33661
6	0	5.86759	0.65786	3.40352
1	0	4.76362	2.50024	3.59858
1	0	6.7119	-1.30124	3.07536
6	0	1.69936	5.03096	-2.95885
1	0	1.94175	2.99491	-3.60958
6	0	1.25025	5.34848	-0.60437
1	0	1.1039	3.55203	0.57709
6	0	-0.56672	-0.47833	-4.08366
1	0	-0.8541	0.2881	-2.09079
6	0	1.68609	-0.31585	-4.95343
1	0	3.15103	0.55406	-3.63358
6	0	-3.74628	-1.52566	-0.90705
6	0	-1.39123	-1.95583	-0.59407
6	0	-0.31341	4.23096	3.87047
1	0	-0.52025	-4.56168	5.46996
1	0	6.79154	1.07635	3.79349
6	0	1.45015	5.88209	-1.87938
1	0	1.84675	5.44121	-3.9545
1	0	1.03345	6.00427	0.2346
6	0	0.35089	-0.70024	-5.11309
1	0	-1.60032	-0.79483	-4.18628
1	0	2.40137	-0.48253	-5.75525
6	0	-3.78732	-2.46978	-1.93319
7	0	-4.93875	-0.80218	-0.55668
6	0	-1.43267	-2.90329	-1.6163
1	0	-0.45483	-1.75372	-0.08815
1	0	-0.09969	4.83307	2.98175
1	0	-0.81481	4.83634	4.62656
1	0	0.6212	3.82152	4.26477
1	0	1.40107	6.95671	-2.03468
1	0	0.0289	-1.17473	-6.03647
6	0	-2.63079	-3.16698	-2.28488
1	0	-4.73059	-2.65498	-2.43576
6	0	-4.88008	0.6839	-0.36475
16	0	-6.00272	-1.60878	0.49745
1	0	-0.52227	-3.42726	-1.89
1	0	-2.66514	-3.90843	-3.07825
1	0	-5.37799	1.13658	-1.23046
1	0	-5.46681	0.93779	0.52266
6	0	-3.48435	1.25461	-0.21432
8	0	-5.97276	-3.02605	0.12881
8	0	-5.7792	-1.21203	1.89978
6	0	-7.56609	-0.88505	-0.01051
6	0	-3.2945	2.45602	0.49895
1	0	-2.8892	1.16341	-1.12082
6	0	-7.96064	-0.9858	-1.34691
6	0	-8.37317	-0.27059	0.94619
1	0	-4.06073	2.85222	1.15792
6	0	-2.37058	3.46786	-0.04894
6	0	-9.18952	-0.45173	-1.72955
1	0	-7.3072	-1.4643	-2.06901
6	0	-9.60402	0.25848	0.55153
1	0	-8.03083	-0.20895	1.97352
9	0	-2.96371	4.32917	-0.93408
9	0	-1.811	4.28303	0.89531
9	0	-1.34281	2.89068	-0.73299
6	0	-10.01006	0.16882	-0.78135
1	0	-9.50761	-0.51786	-2.7661
1	0	-10.24222	0.74224	1.28541
1	0	-10.96671	0.58502	-1.08494

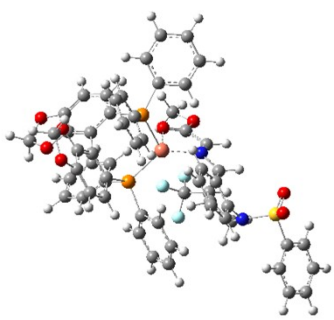


TS *endo* **ent-7a**

E(B3LYPD3/BS1) = -4525.78438157
H(correction)= 0.989273
G(correction)= 0.817706
E(M06/BS2)$_{CH2Cl2}$ = -4524.48218943
Imaginary frequencies: 1 (-356.7888 cm^{-1})

6	0	3.86107	-2.90387	0.11047
6	0	3.0256	-1.89216	0.5448
6	0	3.41752	-4.18837	-0.19314
8	0	5.21341	-2.81992	-0.1048
6	0	1.64703	-2.23954	0.70122
6	0	3.62958	-0.56906	0.88667
6	0	2.0961	-4.54422	-0.03764
8	0	4.46893	-4.95699	-0.61715
6	0	5.60803	-4.08457	-0.64717
6	0	1.22028	-3.54199	0.41924
15	0	0.44757	-0.89919	1.14
6	0	3.59724	0.60039	0.06772
6	0	4.31088	-0.45292	2.08534
1	0	1.74766	-5.54731	-0.25683
1	0	5.93044	-3.94828	-1.68603
1	0	6.40805	-4.51058	-0.03236
1	0	0.17829	-3.80462	0.55412
29	0	0.38555	0.75608	-0.48765
6	0	-1.15109	-1.75549	1.4442
6	0	1.01679	-0.36382	2.80152
6	0	4.1761	1.79072	0.52384
15	0	2.53114	0.6089	-1.43077
6	0	4.88814	0.7355	2.52383
8	0	4.51059	-1.43653	3.02176
7	0	-1.00263	2.05201	-1.25832
6	0	-1.82016	-2.32671	0.34557
6	0	-1.79497	-1.73011	2.6905

6	0	1.1344	1.00753	3.06623
6	0	1.34729	-1.29592	3.7984
6	0	4.83448	1.88321	1.7624
1	0	4.09924	2.68416	-0.08347
6	0	3.06543	2.05658	-2.42291
6	0	3.03244	-0.87153	-2.40143
8	0	5.47099	0.54628	3.74989
6	0	5.15869	-0.80161	4.12989
6	0	-2.21266	1.6898	-1.7421
6	0	-0.96059	3.27886	-0.70345
6	0	-3.08168	-2.89653	0.50697
1	0	-1.37173	-2.29961	-0.64435
6	0	-3.0743	-2.27183	2.83594
1	0	-1.30884	-1.27552	3.54664
6	0	1.57003	1.44029	4.32075
1	0	0.92185	1.72737	2.28233
6	0	1.76445	-0.85797	5.0547
1	0	1.28079	-2.35941	3.58681
1	0	5.27471	2.81291	2.10535
6	0	4.4008	2.36729	-2.72827
6	0	2.04194	2.88897	-2.90138
6	0	2.01103	-1.7742	-2.73104
6	0	4.34802	-1.15333	-2.797
1	0	4.4749	-0.78672	4.98651
1	0	6.08513	-1.33681	4.36356
6	0	-2.32472	0.31507	-2.30362
1	0	-2.80208	2.44223	-2.2751
6	0	0.24082	3.63524	0.02478
1	0	-1.56657	4.09728	-1.08675
6	0	-3.71795	-2.86395	1.74941
1	0	-3.58399	-3.33278	-0.34912
1	0	-3.56769	-2.22689	3.80329
6	0	1.87871	0.51203	5.31657
1	0	1.67084	2.50431	4.51614
1	0	2.0065	-1.58371	5.8271
6	0	4.70295	3.48425	-3.50629
1	0	5.20636	1.75424	-2.3359
6	0	2.34744	4.00624	-3.68189
1	0	1.01008	2.66498	-2.64456
6	0	2.29546	-2.93976	-3.44288
1	0	0.99699	-1.56811	-2.40292
6	0	4.62998	-2.31189	-3.52141
1	0	5.15634	-0.48202	-2.52648
6	0	-3.42062	-0.5175	-2.00945
6	0	-1.31788	-0.18346	-3.14984
8	0	1.07665	2.82167	0.44714
8	0	0.37082	4.95681	0.23449
1	0	-4.71609	-3.27509	1.85826
1	0	2.21187	0.85198	6.29375
6	0	3.67635	4.3038	-3.98647
1	0	5.73928	3.71852	-3.73532
1	0	1.54626	4.64533	-4.04294
6	0	3.60619	-3.20981	-3.84102
1	0	1.49577	-3.63756	-3.67562
1	0	5.65078	-2.51709	-3.83459
6	0	-3.54024	-1.76766	-2.63462
7	0	-4.31804	-0.12755	-0.97721
6	0	-1.42308	-1.43713	-3.7476
1	0	-0.45453	0.44622	-3.34301
6	0	1.4457	5.34552	1.09689
1	0	3.91539	5.17476	-4.59097
1	0	3.83213	-4.11688	-4.39504
6	0	-2.55742	-2.22038	-3.50818
1	0	-4.40205	-2.38542	-2.41571
6	0	-3.76435	0.56642	0.20938
16	0	-5.98412	-0.06675	-1.20282
1	0	-0.63647	-1.78996	-4.40901
1	0	2.40858	5.02145	0.69081
1	0	1.39816	6.43366	1.15167
1	0	1.31299	4.90934	2.09217
1	0	-2.66698	-3.19071	-3.98488
1	0	-4.50321	0.46433	1.01161
1	0	-2.88181	0.00439	0.5201
6	0	-3.41758	2.01122	-0.03865
8	0	-6.47321	1.21653	-0.68958
8	0	-6.26018	-0.50988	-2.57034
6	0	-6.59301	-1.33241	-0.0761
6	0	-2.57663	2.71954	0.83408
1	0	-4.2429	2.57701	-0.46812
6	0	-6.7091	-2.64892	-0.52792
6	0	-6.93356	-0.98067	1.23129
1	0	-1.91985	2.17473	1.50922
6	0	-2.94929	4.06061	1.33437
6	0	-7.15477	-3.63312	0.3544
1	0	-6.48221	-2.88481	-1.56219
6	0	-7.37438	-1.97432	2.1076
1	0	-6.8749	0.0568	1.54188
9	0	-3.92642	4.03175	2.29147
9	0	-1.8961	4.6977	1.91875
9	0	-3.42042	4.87305	0.3512
6	0	-7.48239	-3.29755	1.6724
1	0	-7.25725	-4.65869	0.01109
1	0	-7.64341	-1.7113	3.1266
1	0	-7.83239	-4.06638	2.35575



TS-*exo* **ent-7a**

E(B3LYPD3/BS1) = -4525.78727356

H(correction)= 0.989017

G(correction)= 0.815829

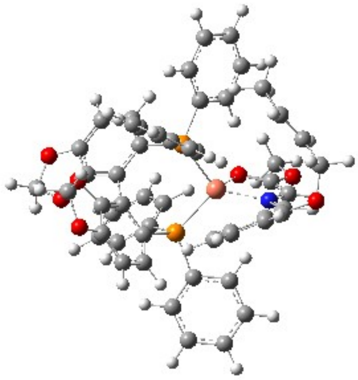
E(M06/BS2)$_{CH2Cl2}$ = -4524.48219957

Imaginary frequencies: 1 (-387.5971 cm^{-1})

6	0	-4.29392	-1.68108	-1.89344

6	0	-3.44673	-0.69312	-1.42904
6	0	-3.95756	-2.55833	-2.92173
8	0	-5.55301	-1.97303	-1.43206
6	0	-2.17976	-0.59071	-2.08685
6	0	-3.9433	0.2327	-0.36571
6	0	-2.75051	-2.46319	-3.57857
8	0	-4.98621	-3.43771	-3.13797
6	0	-5.94959	-3.17071	-2.1077
6	0	-1.86824	-1.45751	-3.13959
15	0	-0.9473	0.60725	-1.40464
6	0	-3.60261	0.1886	1.02098
6	0	-4.82597	1.22947	-0.7418
1	0	-2.49208	-3.13158	-4.39241
1	0	-5.95501	-4.00318	-1.39318
1	0	-6.93421	-3.02336	-2.56196
1	0	-0.91496	-1.361	-3.64518
29	0	-0.36937	0.10126	0.79045
6	0	0.50618	0.57224	-2.52812
6	0	-1.76732	2.22467	-1.69523
6	0	-4.09702	1.16481	1.89462
15	0	-2.28778	-0.9702	1.58274
6	0	-5.32213	2.18554	0.1399
8	0	-5.31565	1.46386	-2.0014
7	0	1.44236	0.16521	1.78965
6	0	1.26587	-0.60944	-2.61501
6	0	1.00672	1.74365	-3.11522
6	0	-1.90771	3.11302	-0.62002
6	0	-2.29524	2.56314	-2.95059
6	0	-4.96863	2.18436	1.4718
1	0	-3.78546	1.15531	2.93213
6	0	-2.42434	-1.06065	3.40884
6	0	-2.80021	-2.62687	0.95775
8	0	-6.14266	3.05555	-0.52905
6	0	-6.09194	2.66377	-1.90906
6	0	2.60949	-0.37621	1.35576
6	0	1.59078	1.27512	2.52099
6	0	2.47202	-0.62576	-3.31441
1	0	0.93808	-1.51329	-2.11003
6	0	2.22911	1.72902	-3.78934
1	0	0.46397	2.6767	-3.01712
6	0	-2.56087	4.33236	-0.80577
1	0	-1.51545	2.84408	0.35454
6	0	-2.93191	3.79041	-3.13533
1	0	-2.20982	1.8653	-3.77916
1	0	-5.33882	2.93757	2.15836
6	0	-3.62483	-1.21936	4.12064
6	0	-1.21489	-0.97169	4.11605
6	0	-1.95025	-3.23599	0.02299
6	0	-3.98216	-3.28403	1.32913
1	0	-5.60419	3.45367	-2.49116
1	0	-7.10824	2.46731	-2.26759
6	0	2.60746	-1.61321	0.55468
1	0	3.48154	-0.27321	2.00882
6	0	0.42499	2.10785	2.72553
1	0	2.46575	1.44964	3.14033
6	0	2.95959	0.54492	-3.90076
1	0	3.04226	-1.54758	-3.36471
1	0	2.61195	2.65039	-4.21922
6	0	-3.06652	4.6765	-2.06107
1	0	-2.67552	5.0126	0.03364
1	0	-3.32706	4.05294	-4.11347
6	0	-3.6115	-1.30687	5.51224
1	0	-4.57212	-1.24232	3.59042
6	0	-1.20416	-1.06464	5.50942
1	0	-0.28884	-0.81486	3.56863
6	0	-2.27143	-4.47314	-0.53447
1	0	-1.05595	-2.71411	-0.29754
6	0	-4.29819	-4.52848	0.78171
1	0	-4.66239	-2.82955	2.04136
6	0	3.73839	-1.86696	-0.24378
6	0	1.54172	-2.52224	0.51237
8	0	-0.67706	1.92704	2.18469
8	0	0.65121	3.14375	3.55453
1	0	3.91074	0.53665	-4.42646
1	0	-3.56774	5.63056	-2.20353
6	0	-2.40043	-1.23537	6.20784
1	0	-4.54548	-1.4269	6.05495
1	0	-0.26193	-0.99519	6.04608
6	0	-3.44593	-5.12459	-0.15322
1	0	-1.61233	-4.91733	-1.27509
1	0	-5.21272	-5.03285	1.08372
6	0	3.79735	-2.99872	-1.05911
7	0	4.84254	-0.95239	-0.21304
6	0	1.59909	-3.65331	-0.30251
1	0	0.68353	-2.34908	1.15341
6	0	-0.37685	4.14047	3.5921
1	0	-2.39306	-1.30388	7.29245
1	0	-3.69961	-6.08938	-0.5841
6	0	2.72798	-3.89354	-1.09293
1	0	4.6909	-3.16986	-1.65011
6	0	4.59055	0.52068	-0.30663
16	0	6.11778	-1.38556	0.82897
1	0	0.77231	-4.35854	-0.3002
1	0	-1.33456	3.70764	3.89505
1	0	-0.04195	4.87952	4.32114
1	0	-0.48157	4.60231	2.60527
1	0	2.78139	-4.77913	-1.71982
1	0	5.33094	1.02203	0.32053
1	0	4.78947	0.80644	-1.34571
6	0	3.20234	1.01202	0.06908
8	0	6.01746	-0.68773	2.12256
8	0	6.21682	-2.84658	0.79022
6	0	7.50985	-0.6674	-0.05075
6	0	3.07539	2.26324	0.70022
1	0	2.45923	0.8095	-0.6969
6	0	8.3472	0.22726	0.61435
6	0	7.7496	-1.05062	-1.37263
1	0	3.9014	2.67767	1.27187
6	0	2.13694	3.28039	0.20293
6	0	9.4491	0.75264	-0.06459
1	0	8.12662	0.50299	1.6399
6	0	8.85067	-0.5188	-2.04047
1	0	7.0762	-1.74422	-1.86535
9	0	0.94547	2.75383	-0.20978

9	0	1.84235	4.23709	1.12787
9	0	2.60045	3.97751	-0.88853
6	0	9.69934	0.38143	-1.38695
1	0	10.10846	1.45286	0.44017
1	0	9.04769	-0.80456	-3.06986
1	0	10.55589	0.79461	-1.91248

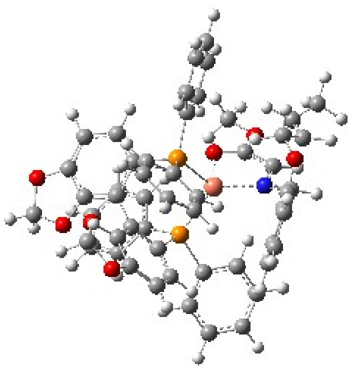


mod14

E(B3LYPD3/BS1) = -3468.31785551
H(correction)= 0.899447
G(correction)= 0.747147
E(M06/BS2)$_{CH2Cl2}$ = -3467.15195646
Imaginary frequencies: 0

6	0	-1.86175	-2.23241	-2.14535
6	0	-1.88647	-1.18901	-1.23816
6	0	-1.61783	-2.06088	-3.50769
8	0	-2.09626	-3.56183	-1.88818
6	0	-1.66843	0.11712	-1.78212
6	0	-2.26421	-1.4813	0.17974
6	0	-1.40931	-0.81106	-4.04777
8	0	-1.67661	-3.27318	-4.14621
6	0	-1.75801	-4.24855	-3.09832
6	0	-1.43189	0.27534	-3.15283
15	0	-1.44649	1.53043	-0.62285
6	0	-1.3795	-1.56949	1.29801
6	0	-3.59987	-1.72645	0.44619
1	0	-1.23313	-0.67154	-5.10867
1	0	-0.78082	-4.73485	-2.97745
1	0	-2.54278	-4.97154	-3.33548
1	0	-1.24542	1.26704	-3.54873
29	0	0.50051	1.12781	0.59256
6	0	-1.44088	3.04137	-1.66818
6	0	-3.01614	1.61852	0.32566
6	0	-1.88744	-1.85177	2.57232
15	0	0.39962	-1.12665	1.09487
6	0	-4.09298	-1.99159	1.72054
8	0	-4.63528	-1.716	-0.45562
6	0	-0.31249	3.86988	-1.57108
6	0	-2.49592	3.41426	-2.51753
6	0	-2.91843	1.90856	1.69527
6	0	-4.27649	1.40383	-0.25173
6	0	-3.25668	-2.06204	2.81279
1	0	-1.20636	-1.90673	3.41339
6	0	1.15243	-1.54036	2.72327
6	0	1.08363	-2.4134	-0.02164
8	0	-5.45217	-2.15748	1.67104
6	0	-5.82392	-1.97745	0.29821
6	0	-0.23626	5.04705	-2.31968
1	0	0.49896	3.59135	-0.90473
6	0	-2.4159	4.58824	-3.26438
1	0	-3.37835	2.78698	-2.59746
6	0	-4.07525	1.9828	2.47457
1	0	-1.93841	2.06686	2.13911
6	0	-5.42827	1.49543	0.52946
1	0	-4.35573	1.1253	-1.2982
1	0	-3.63601	-2.26996	3.80697
6	0	1.49958	-2.84775	3.09609
6	0	1.40402	-0.48024	3.6085
6	0	2.26227	-2.10433	-0.71606
6	0	0.51371	-3.6878	-0.16485
1	0	-6.49994	-1.11953	0.21757
1	0	-6.29716	-2.89362	-0.07488
6	0	-1.28449	5.40553	-3.16745
1	0	0.64313	5.67972	-2.23687
1	0	-3.23574	4.86838	-3.9207
6	0	-5.32908	1.77951	1.89511
1	0	-3.99443	2.19605	3.53716
1	0	-6.40383	1.34297	0.07397
6	0	2.09951	-3.09041	4.33177
1	0	1.31825	-3.67339	2.4145
6	0	2.00071	-0.7295	4.84679
1	0	1.12278	0.53132	3.32675
6	0	2.86639	-3.05624	-1.53877
1	0	2.70964	-1.12129	-0.6176
6	0	1.12326	-4.63895	-0.9852
1	0	-0.41057	-3.93076	0.34968
1	0	-1.2252	6.32064	-3.75082
1	0	-6.22754	1.83781	2.50388
6	0	2.35462	-2.03118	5.20763
1	0	2.37398	-4.10503	4.60853
1	0	2.19631	0.09774	5.524
6	0	2.29905	-4.32486	-1.67428
1	0	3.76901	-2.79016	-2.07998
1	0	0.68189	-5.62814	-1.08129
1	0	2.82922	-2.2216	6.16674
1	0	2.76784	-5.06658	-2.31588
7	0	2.2316	2.31978	0.4003
6	0	3.22778	2.24936	-0.44618
6	0	2.2514	3.20225	1.44503
6	0	3.25913	1.38275	-1.61387
1	0	4.12027	2.85058	-0.26553
6	0	1.21527	3.15676	2.38366
1	0	3.06104	3.92005	1.55316
6	0	4.51045	0.96434	-2.12689
6	0	2.10604	0.93632	-2.29203
8	0	0.25178	2.33071	2.38953
8	0	1.30155	4.09673	3.37253
6	0	4.59521	0.11712	-3.23091
8	0	5.66531	1.43106	-1.52864
6	0	2.1874	0.08014	-3.38585

1	0	1.13575	1.27489	-1.94891
6	0	0.25697	4.06931	4.34138
6	0	3.43404	-0.33539	-3.86182
1	0	5.57915	-0.17283	-3.58933
6	0	6.3833	0.46894	-0.73076
1	0	1.27533	-0.25965	-3.86526
1	0	0.21991	3.1067	4.8642
1	0	0.4895	4.86935	5.04766
1	0	-0.72068	4.24995	3.88031
1	0	3.5034	-0.99644	-4.72149
1	0	6.71235	-0.37295	-1.3583
1	0	7.27529	1.01685	-0.40596
6	0	5.59797	-0.03161	0.44687
6	0	5.39438	-1.32686	0.70397
1	0	5.1899	0.72973	1.11095
1	0	5.80076	-2.06602	0.00965
6	0	4.65374	-1.87673	1.88626
1	0	5.31964	-2.46724	2.53087
1	0	3.85134	-2.54821	1.5617
1	0	4.20175	-1.08655	2.49406



TS-*endo* **14**

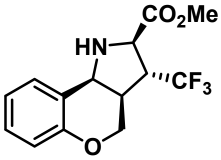
E(B3LYPD3/BS1) = -3468.28642713
H(correction)= 0.898178
G(correction)= 0.749660
E(M06/BS2)$_{CH2Cl2}$ = -3467.11589772
Imaginary frequencies: 1 (-423.7807 cm^{-1})

6	0	-3.19024	1.94447	0.57088
6	0	-2.51435	0.76372	0.31952
6	0	-3.23427	2.55041	1.8237
8	0	-3.86999	2.71488	-0.33852
6	0	-1.91122	0.13653	1.4544
6	0	-2.47564	0.25007	-1.0841
6	0	-2.61135	1.98788	2.91629
8	0	-3.94159	3.7221	1.75109
6	0	-4.32891	3.86629	0.37756
6	0	-1.95236	0.76339	2.70588
15	0	-0.88137	-1.3655	1.19572
6	0	-1.35152	0.34151	-1.96601
6	0	-3.62047	-0.30692	-1.623
1	0	-2.62655	2.46731	3.8886
1	0	-3.85447	4.76189	-0.0379
1	0	-5.42159	3.92393	0.31125
1	0	-1.45304	0.30013	3.54886
29	0	1.07617	-0.65103	0.14306
6	0	-0.6718	-2.14455	2.84728
6	0	-1.98842	-2.52558	0.28984
6	0	-1.44017	-0.15314	-3.27108
15	0	0.25283	0.96876	-1.29703
6	0	-3.69056	-0.8098	-2.91977
8	0	-4.82992	-0.4756	-0.99688
7	0	2.89654	-1.10413	0.90752
6	0	0.61879	-2.60797	3.14897
6	0	-1.70605	-2.34384	3.77648
6	0	-1.46712	-3.16775	-0.84326
6	0	-3.31265	-2.77572	0.67857
6	0	-2.61217	-0.74708	-3.77462
1	0	-0.5792	-0.08192	-3.92599
6	0	1.34076	1.21663	-2.75961
6	0	-0.18052	2.64668	-0.70304
8	0	-4.9413	-1.31878	-3.15557
6	0	-5.65851	-1.18974	-1.92024
6	0	3.72067	-0.26272	1.56027
6	0	3.52995	-2.11818	0.25983
6	0	0.86847	-3.26123	4.35874
1	0	1.42367	-2.43914	2.43712
6	0	-1.452	-2.99132	4.9849
1	0	-2.70609	-1.97753	3.5656
6	0	-2.26695	-4.04526	-1.57855
1	0	-0.44429	-2.96735	-1.14782
6	0	-4.1011	-3.66723	-0.048
1	0	-3.73788	-2.25662	1.53175
1	0	-2.66698	-1.13149	-4.78702
6	0	1.61684	2.46369	-3.33739
6	0	2.00459	0.07488	-3.24487
6	0	0.24483	3.03001	0.57531
6	0	-0.96084	3.52932	-1.4679
1	0	-5.86864	-2.18813	-1.51972
1	0	-6.58089	-0.62444	-2.0924
6	0	3.12368	0.93673	2.21792
1	0	4.56829	-0.69793	2.10259
6	0	2.79479	-2.80855	-0.75756
1	0	4.38628	-2.62763	0.69984
6	0	-0.16448	-3.45293	5.27711
1	0	1.87197	-3.6132	4.58248
1	0	-2.25803	-3.13661	5.69948
6	0	-3.58166	-4.29848	-1.18291
1	0	-1.86233	-4.52728	-2.46456
1	0	-5.12301	-3.86458	0.26688
6	0	2.52974	2.56465	-4.39016
1	0	1.13795	3.36047	-2.95945
6	0	2.90207	0.17963	-4.30694
1	0	1.83411	-0.8866	-2.76776
6	0	-0.0977	4.28595	1.07916
1	0	0.82315	2.34133	1.18177
6	0	-1.28352	4.79063	-0.96953
1	0	-1.32755	3.22051	-2.44273
6	0	3.50216	2.2432	1.85008
6	0	2.18421	0.78705	3.25264
8	0	1.69127	-2.45081	-1.21927
8	0	3.44273	-3.88845	-1.26489

1	0	0.03026	-3.95732	6.21992
1	0	-4.20169	-4.98325	-1.75569
6	0	3.16875	1.42521	-4.88173
1	0	2.74236	3.5385	-4.82338
1	0	3.40955	-0.71015	-4.67051
6	0	-0.85672	5.16782	0.30848
1	0	0.23083	4.56337	2.07508
1	0	-1.87602	5.47443	-1.57242
6	0	3.02836	3.34611	2.5778
8	0	4.31825	2.52984	0.79799
6	0	1.67889	1.88311	3.95011
1	0	1.86501	-0.21708	3.51478
6	0	2.79657	-4.54008	-2.36191
1	0	3.87993	1.5086	-5.69921
1	0	-1.12079	6.14575	0.70261
6	0	2.132	3.167	3.62701
1	0	3.35593	4.33518	2.273

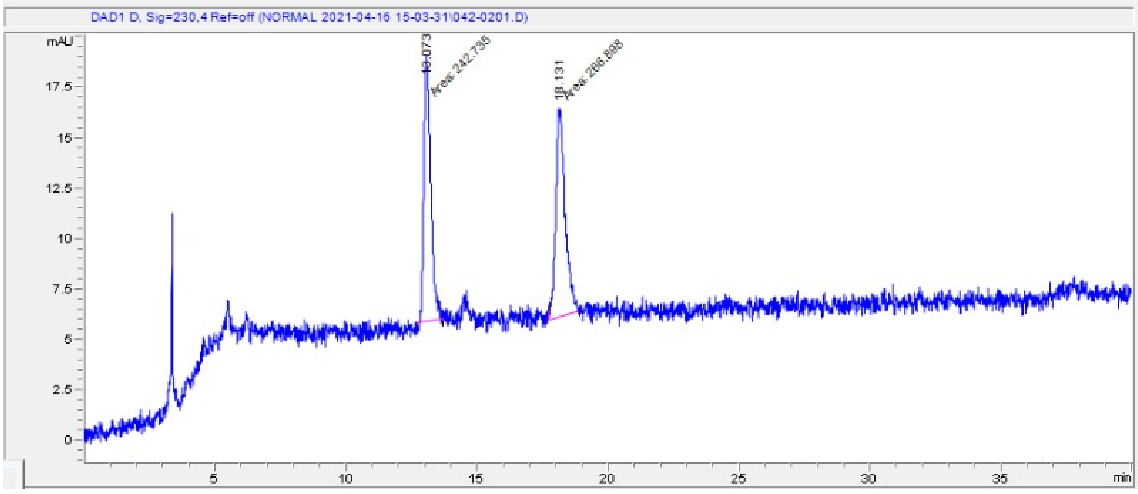
6	0	4.31288	1.61204	-0.31783
1	0	0.95725	1.73609	4.74892
1	0	2.67389	-3.85678	-3.20893
1	0	3.45104	-5.36853	-2.63776
1	0	1.81089	-4.91557	-2.06919
1	0	1.76962	4.03148	4.17825
1	0	3.27849	1.42779	-0.64049
1	0	4.8189	2.17907	-1.10797
6	0	4.99868	0.30918	-0.00923
6	0	4.94798	-0.75943	-0.9206
1	0	5.92951	0.43525	0.54781
1	0	4.25632	-0.66911	-1.7566
6	0	6.11918	-1.68267	-1.14291
1	0	6.81218	-1.29245	-1.90476
1	0	6.69844	-1.81163	-0.21941
1	0	5.79154	-2.67585	-1.47406

8. HPLC chart



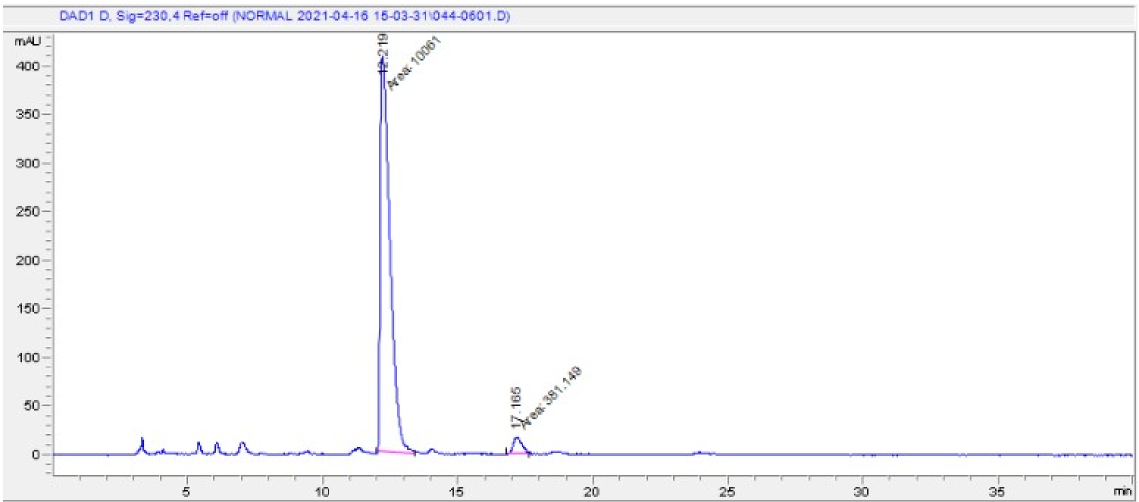
2a

(±)-**2a**

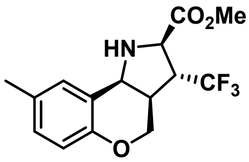


#	Time	Area	Height	Width	Area%	Symmetry
1	13.073	242.7	13.3	0.3053	47.629	0.634
2	18.131	266.9	10.4	0.4259	52.371	0.519

(+)-**2a**; 93% *ee*

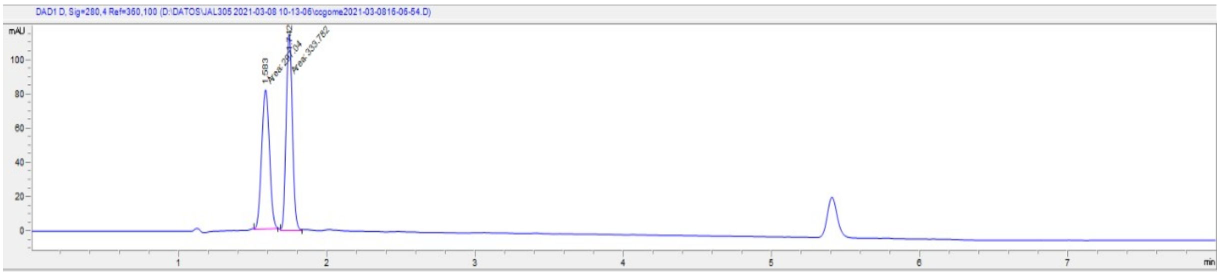


#	Time	Area	Height	Width	Area%	Symmetry
1	12.219	10061	409.5	0.4095	96.350	0.288
2	17.165	381.1	17.1	0.3707	3.650	0.572



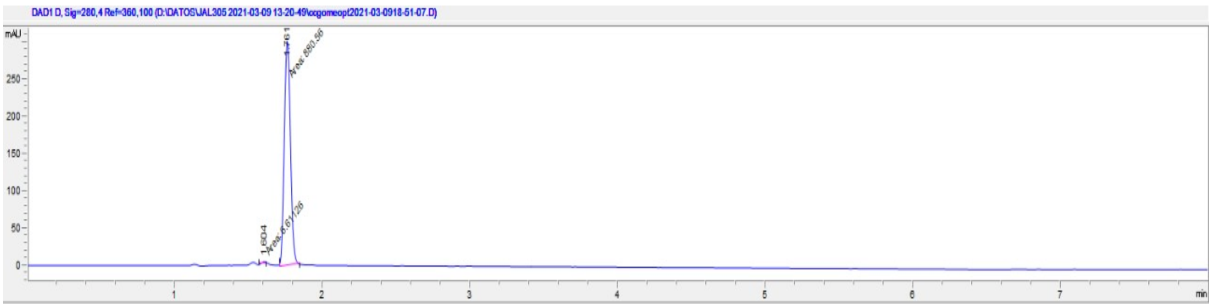
2b

(±)-**2b**

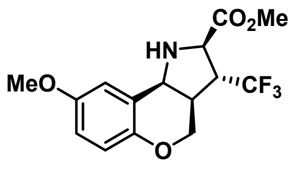


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.583	MM	297	81.6	0.0607	47.088	0.988
2	1.742	MM	333.8	115.1	0.0483	52.912	0.933

(+)-**2b**; 99% *ee*

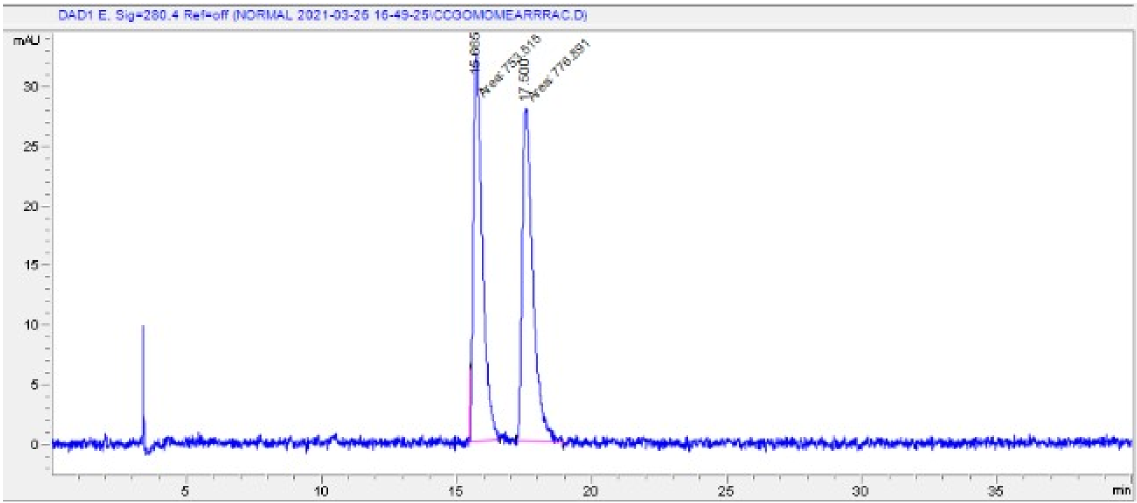


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.604	MM	6.6	3.2	0.0344	0.745	1.053
2	1.761	MM	880.6	306.4	0.0479	99.255	0.938



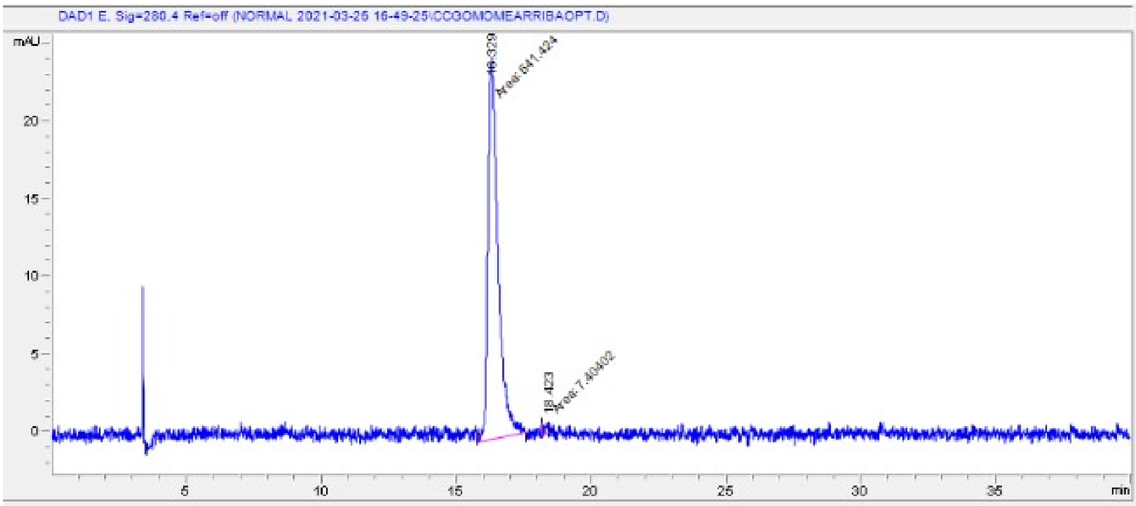
2c

(±)-**2c**

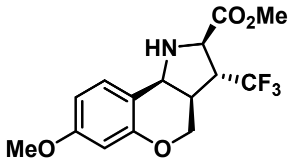


#	Time	Area	Height	Width	Area%	Symmetry
1	15.665	753.5	32.7	0.3844	49.236	0.392
2	17.5	776.9	28	0.462	50.764	0.462

(-)-**2c**; 98% *ee*

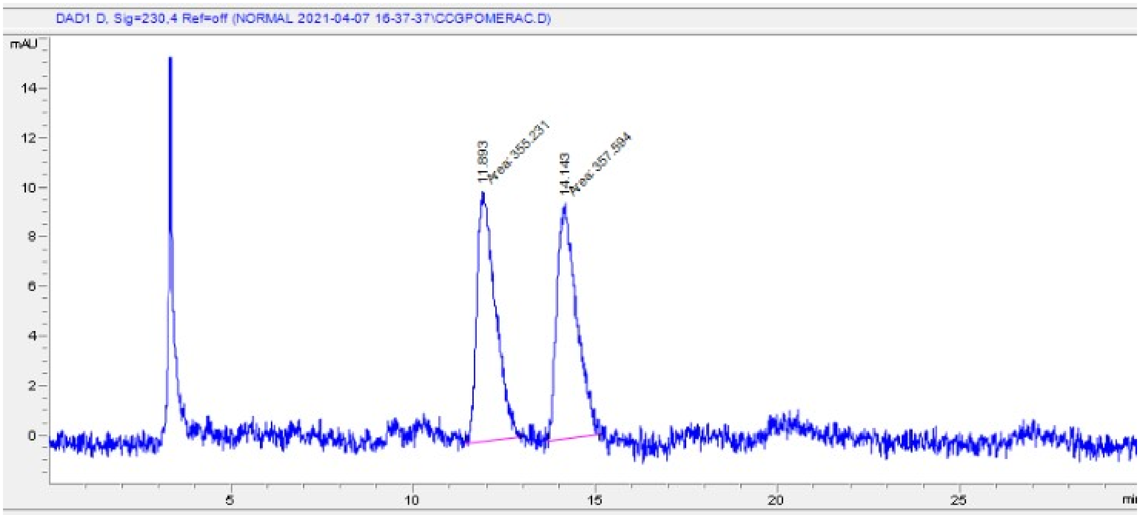


#	Time	Area	Height	Width	Area%	Symmetry
1	16.329	641.4	24.8	0.4313	98.859	0.597
2	18.423	7.4	8E-1	0.1536	1.141	5.093



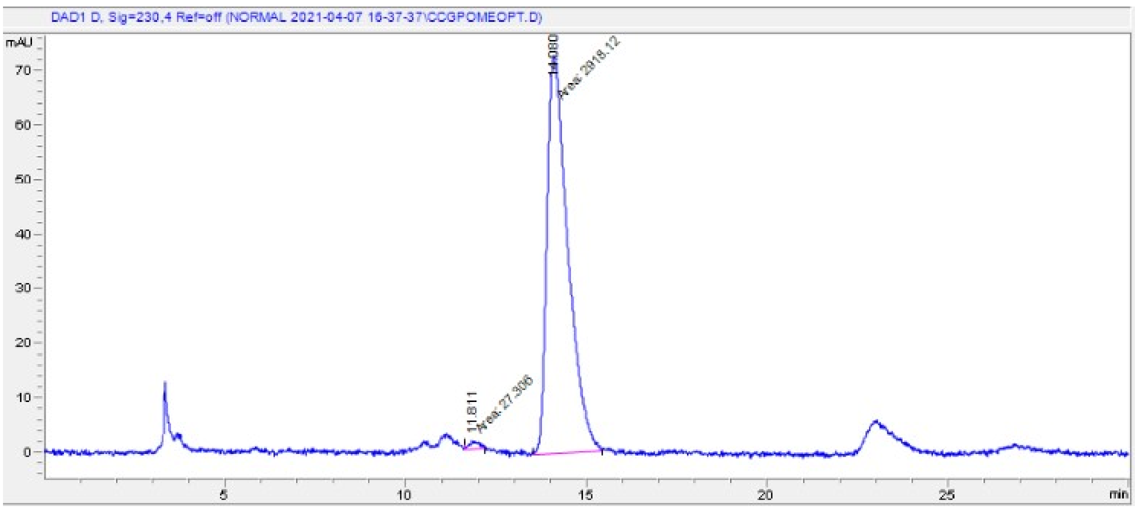
2d

(±)-**2d**

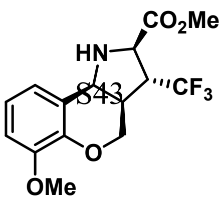


#	Time	Area	Height	Width	Area%	Symmetry
1	11.893	355.2	10.1	0.5863	49.834	0.472
2	14.143	357.6	9.6	0.6231	50.166	0.647

(+)-**2d**; 98% *ee*

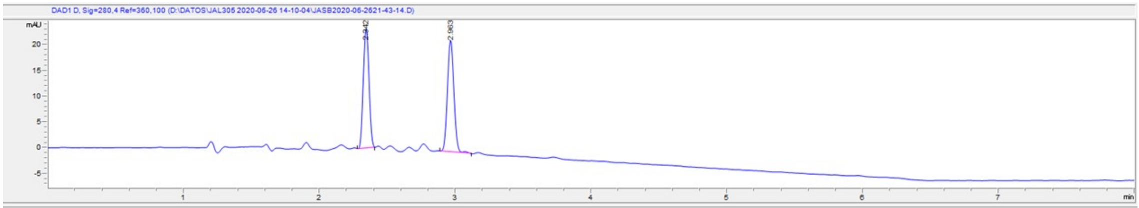


#	Time	Area	Height	Width	Area%	Symmetry
1	11.811	27.3	1.6	0.2881	0.927	0.416
2	14.08	2918.1	73.1	0.6651	99.073	0.476



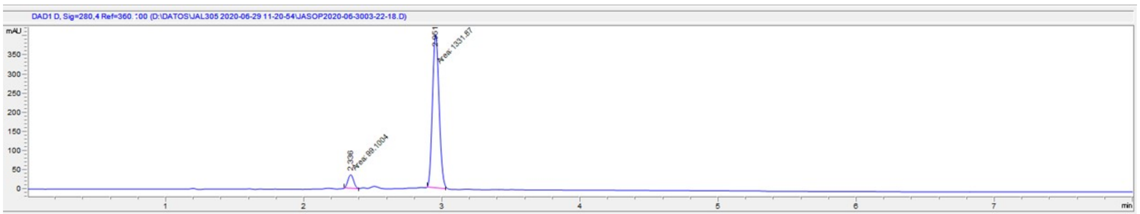
2e

(±)-**2e**

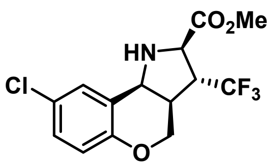


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.342	BB	67.7	23.2	0.048	48.436	0.946
2	2.963	BB	72.1	21.8	0.0526	51.564	0.894

(+)-**2e**; 86% *ee*

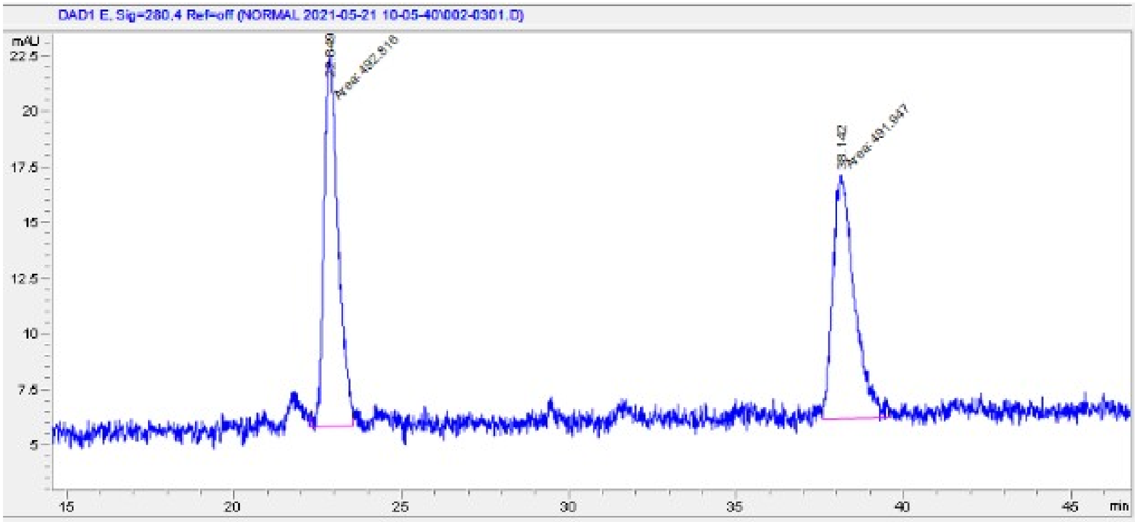


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.336	MM	99.1	35.3	0.0468	6.925	0.918
2	2.951	MM	1331.9	402.1	0.0552	93.075	0.885



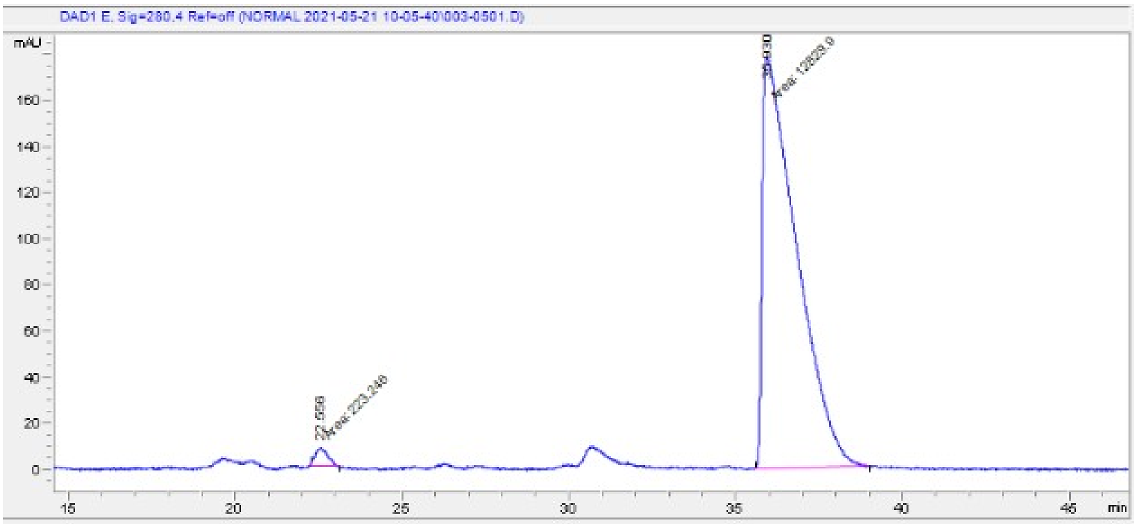
2f

(±)-**2f**

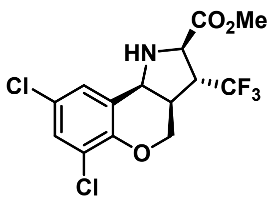


#	Time	Area	Height	Width	Area%	Symmetry
1	22.849	492.8	16.7	0.4929	50.044	0.698
2	38.142	491.9	10.9	0.7525	49.956	0.627

(+)-**2f**; 97% *ee*

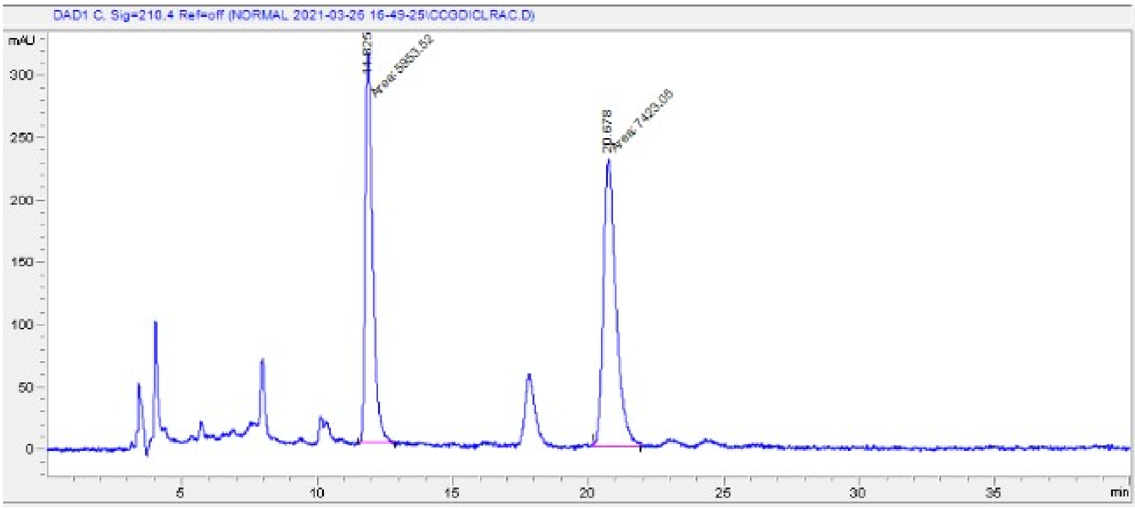


#	Time	Area	Height	Width	Area%	Symmetry
1	22.556	223.2	8.5	0.4391	1.710	0.793
2	35.93	12829.9	178.9	1.1952	98.290	0.153



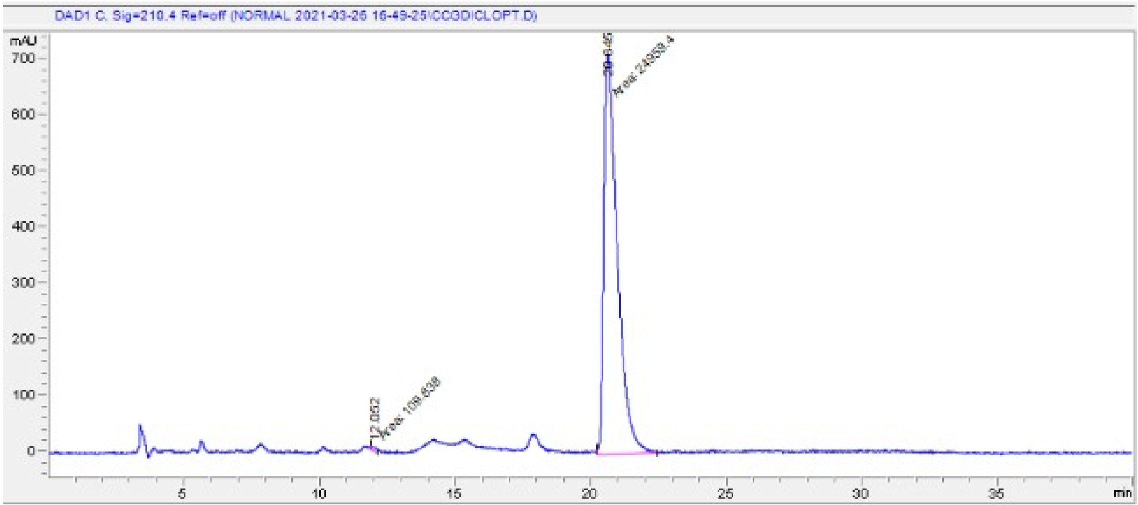
2g

(±)-**2g**

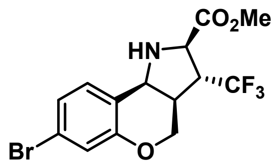


#	Time	Area	Height	Width	Area%	Symmetry
1	11.825	5953.5	313.1	0.3169	44.507	0.543
2	20.678	7423	230	0.5379	55.493	0.61

(+)-**2g**; 99% *ee*

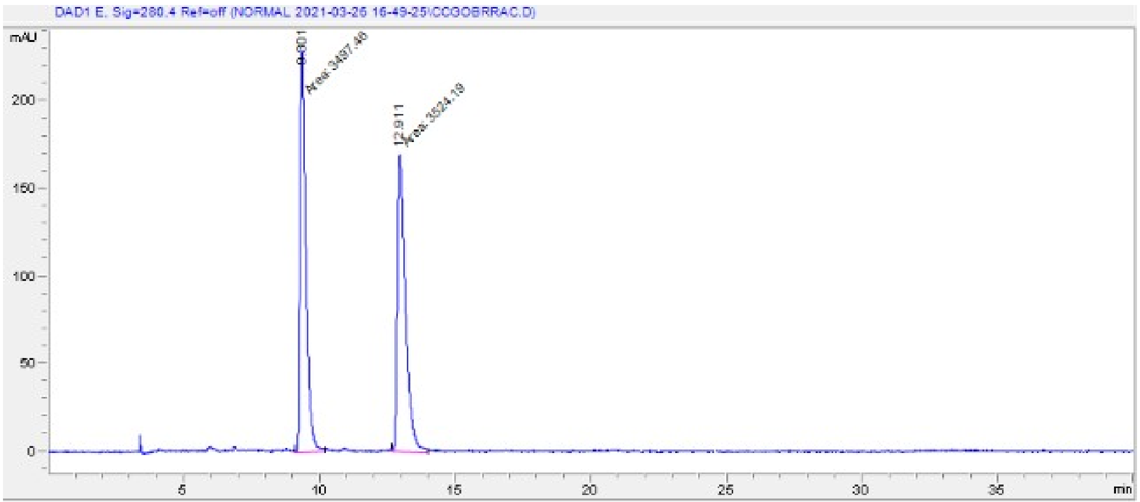


#	Time	Area	Height	Width	Area%	Symmetry
1	12.052	109.8	8.8	0.2073	0.438	1.35
2	20.645	24959.4	713.6	0.5829	99.562	0.403



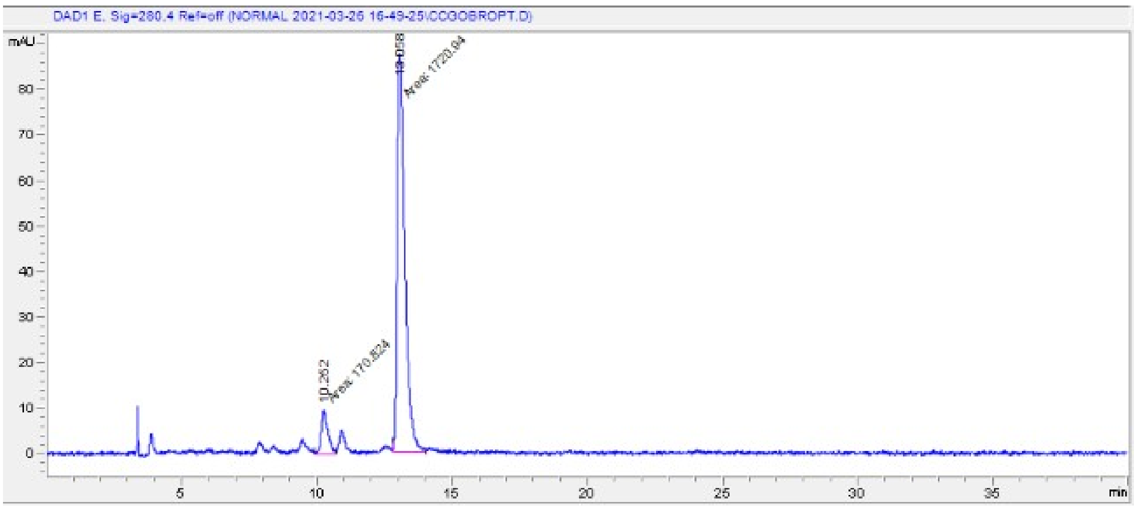
2h

(±)-**2h**

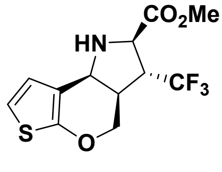


#	Time	Area	Height	Width	Area%	Symmetry
1	9.301	3497.5	229.5	0.254	49.810	0.421
2	12.911	3524.2	169.5	0.3464	50.190	0.399

(+)-**2h**; 82% *ee*

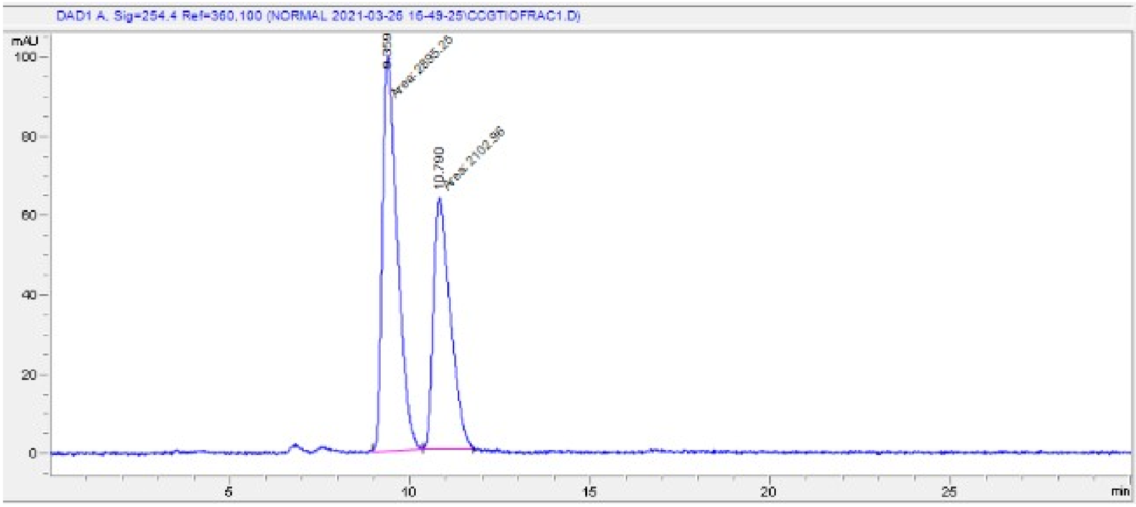


#	Time	Area	Height	Width	Area%	Symmetry
1	10.252	170.8	9.8	0.2911	9.030	0.597
2	13.058	1720.9	87.2	0.3288	90.970	0.44



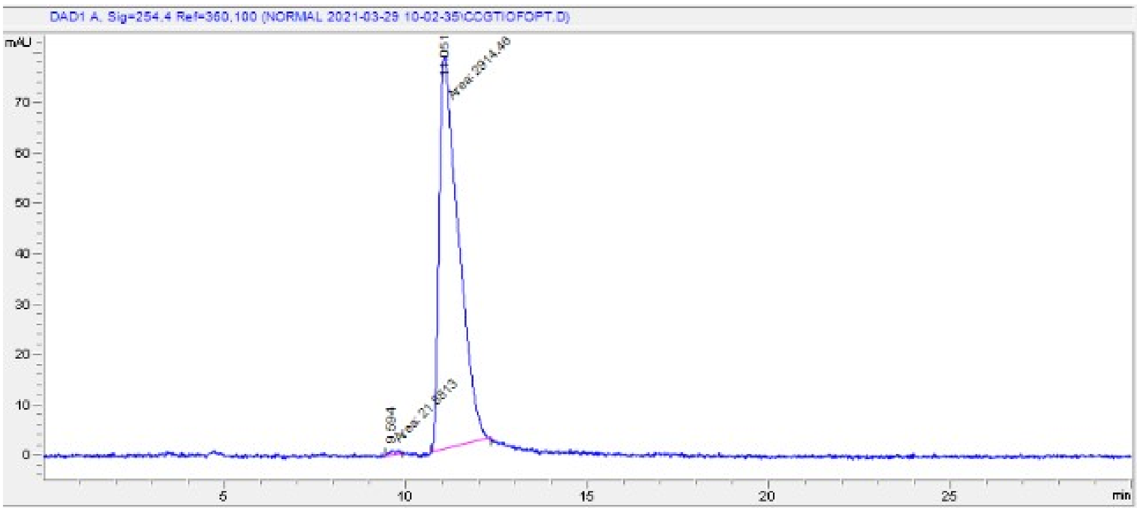
2i

(±)-**2i**

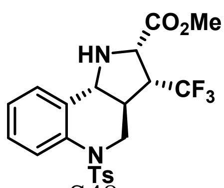


#	Time	Area	Height	Width	Area%	Symmetry
1	9.359	2895.2	100.3	0.4812	57.926	0.544
2	10.79	2103	63.9	0.5489	42.074	0.524

(+)-**2i**; 99% *ee*

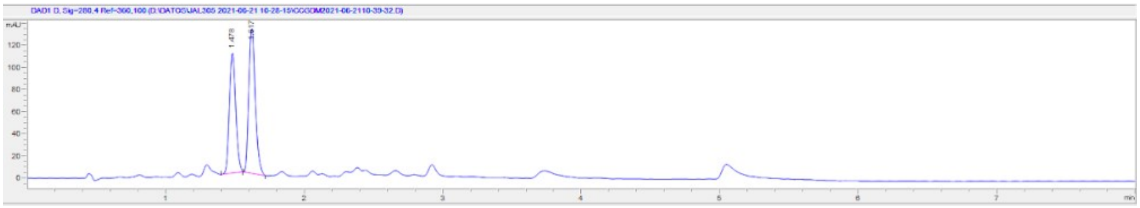


#	Time	Area	Height	Width	Area%	Symmetry
1	9.594	21.9	1.3	0.2851	0.745	0.639
2	11.051	2914.5	78.4	0.6195	99.255	0.407



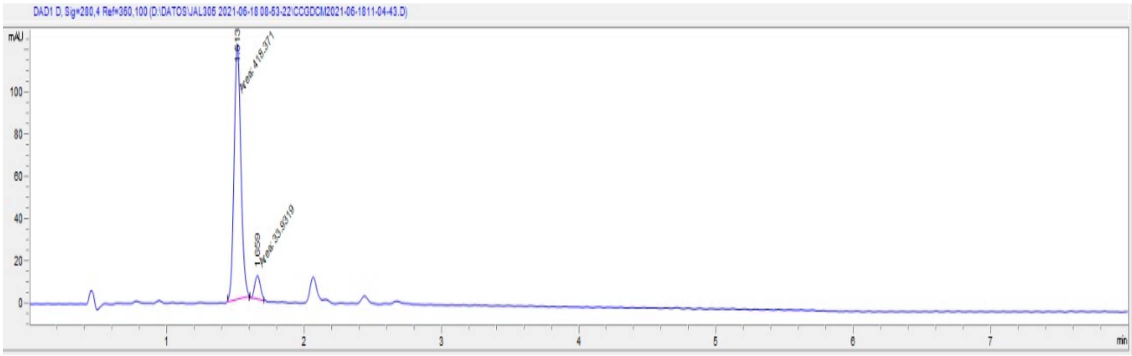
7a

(±)-**7a**

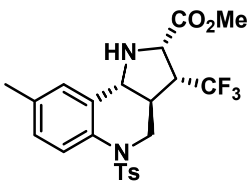


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.478	BB	349.1	109.5	0.0492	44.819	0.878
2	1.617	BB	429.9	132.2	0.0499	55.181	0.791

(**+**)-**7a;** 85% *ee*

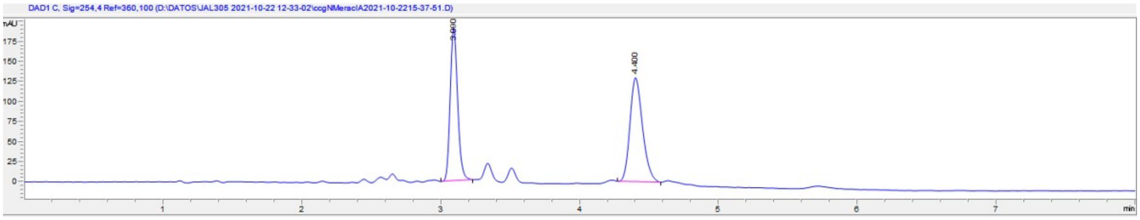


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.513	MM	418.4	122.8	0.0568	92.498	0.901
2	1.659	MM	33.9	11.6	0.0489	7.502	0.911



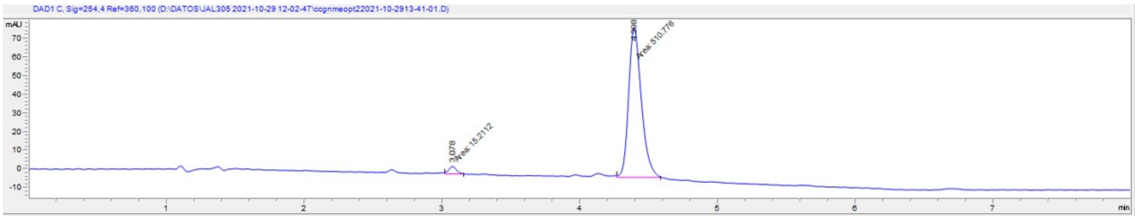
7b

(±)-**7b**

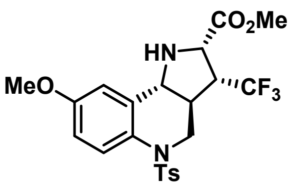


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.09	BB	713.8	191.5	0.0575	46.631	0.823
2	4.4	BB	817	129.8	0.0974	53.369	0.756

(-)-**7b**; 94% *ee*

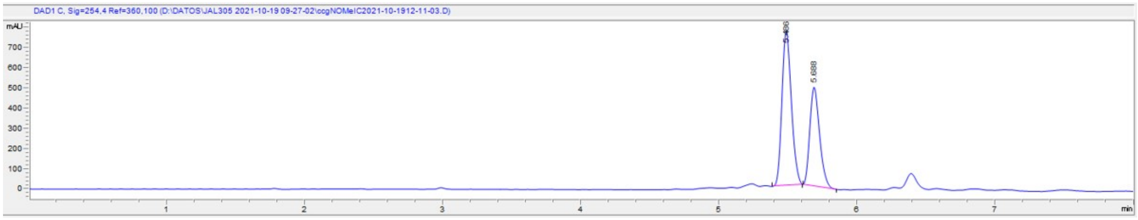


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.078	MM	15.2	4	0.0638	2.892	0.864
2	4.398	MM	510.8	79.9	0.1066	97.108	0.748



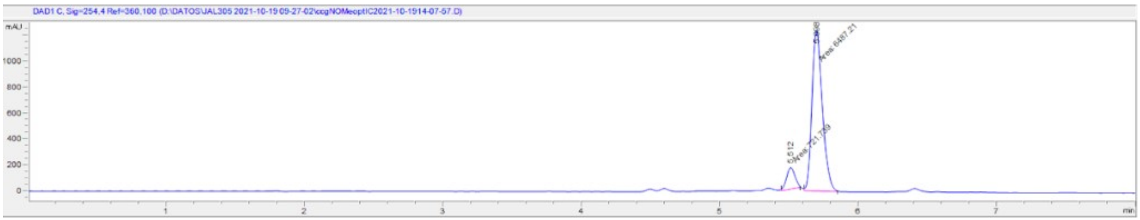
7c

(±)-**7c**

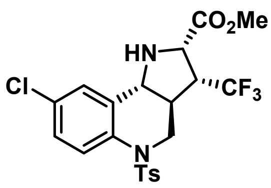


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.486	BB	3646.9	769.2	0.0733	60.069	0.786
2	5.688	BB	2424.3	493.2	0.0753	39.931	0.737

(+)-7c; 80% *ee*

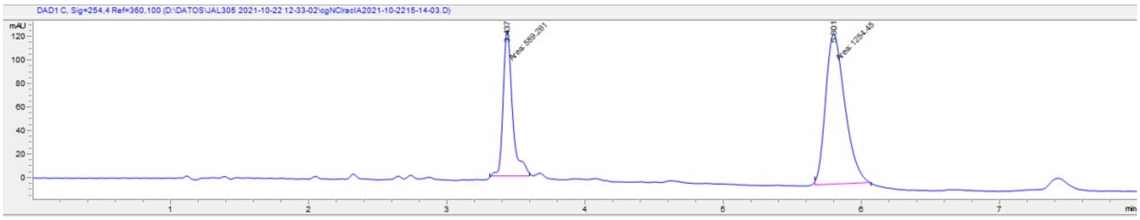


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.512	MM	721.7	167.2	0.0719	10.012	0.944
2	5.698	MM	6487.2	1237.2	0.0874	89.988	0.729



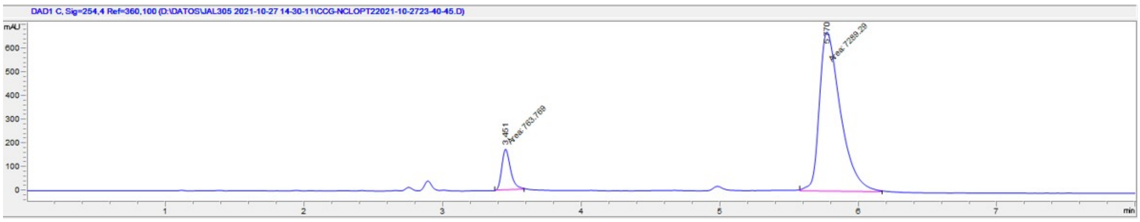
7d

(±)-**7d**

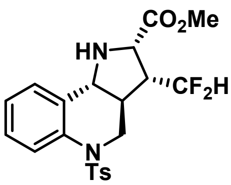


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.437	MM	589.3	125.2	0.0784	31.961	0.73
2	5.801	MM	1254.5	128.4	0.1629	68.039	0.683

(+)-**7d**; 81 % *ee*

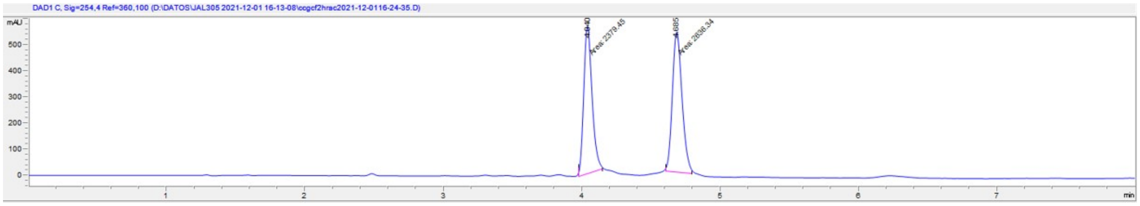


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.451	MM	763.8	173.5	0.0734	9.484	0.729
2	5.77	MM	7289.3	681.3	0.1783	90.516	0.548



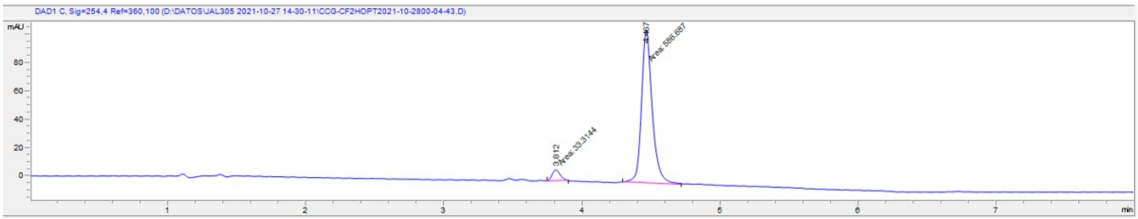
7e

(±)-**7e**

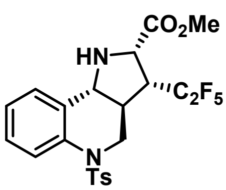


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.04	MM	2379.5	571.6	0.0694	47.439	0.769
2	4.685	MM	2636.3	541.6	0.0811	52.561	0.787

(+)-7e; 89% ee

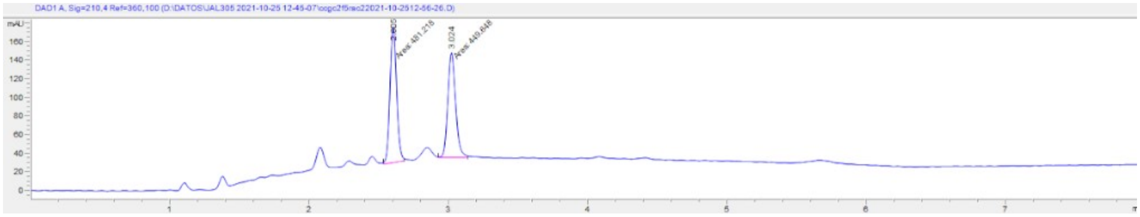


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.812	MM	33.3	8.1	0.0685	5.373	0.879
2	4.467	MM	586.7	107.9	0.0906	94.627	0.782



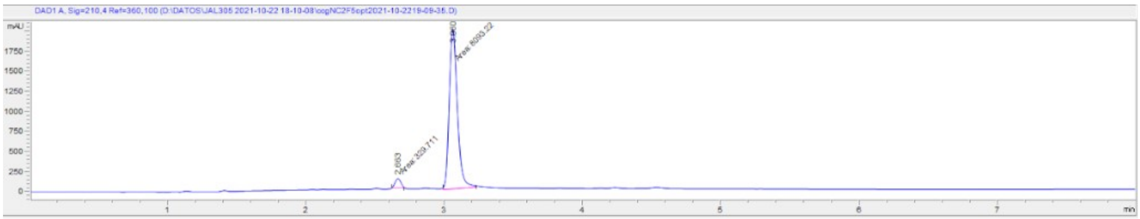
7f

(±)-**7f**

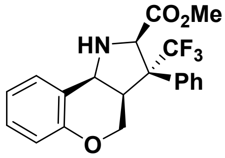


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.605	MM	481.2	145.6	0.0551	51.696	0.924
2	3.024	MM	449.6	113.4	0.0661	48.304	0.858

(+)-7f; 92% *ee*

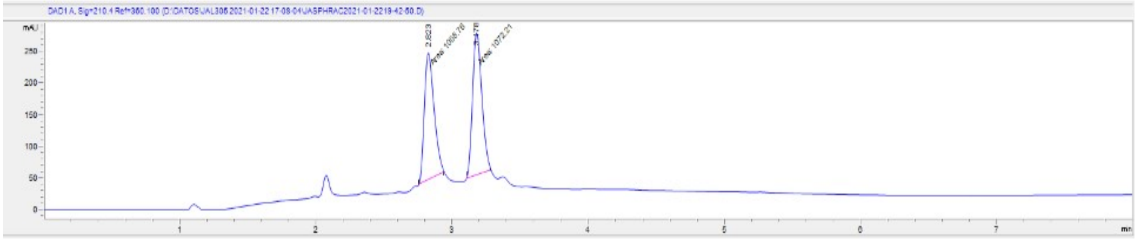


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.663	MM	329.7	115.6	0.0476	3.914	0.955
2	3.06	MM	8093.2	1984.3	0.068	96.086	0.766



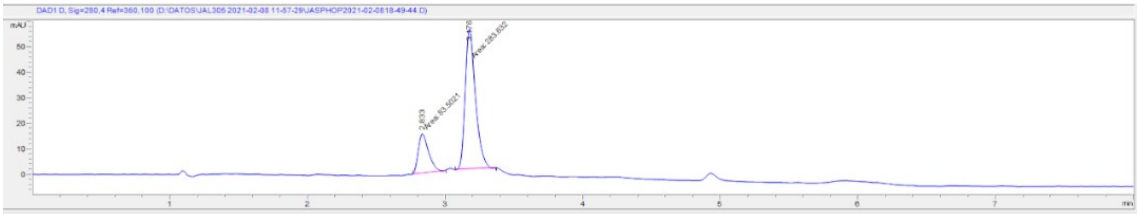
11

(±)-**11**

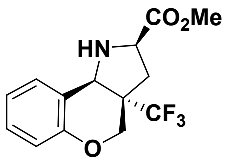


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.823	MM	1008.8	203.1	0.0828	48.476	0.679
2	3.178	MM	1072.2	227.3	0.0786	51.524	0.786

(+)-**11**; 55% *ee*

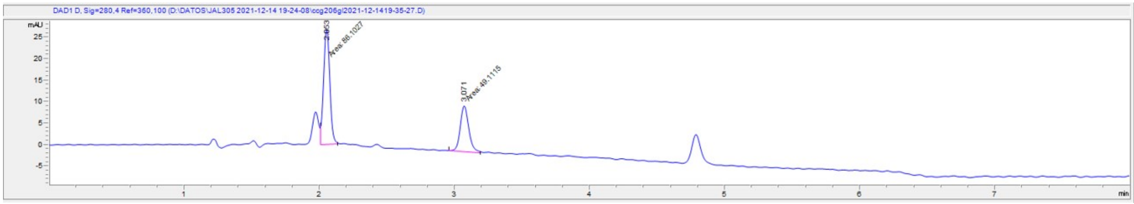


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.833	MM	83.5	15.6	0.0895	22.744	0.625
2	3.176	MM	283.6	54.9	0.0861	77.256	0.686



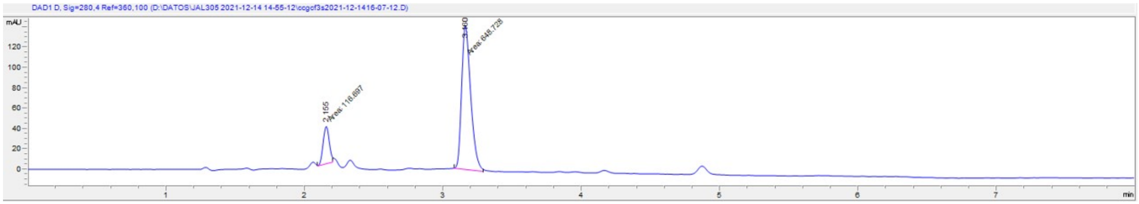
13

(±)-**13**

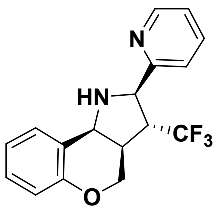


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.053	FM	86.1	27.4	0.0523	63.679	0.92
2	3.071	MM	49.1	10.9	0.0752	36.321	0.815

(+)-13; 70% *ee*

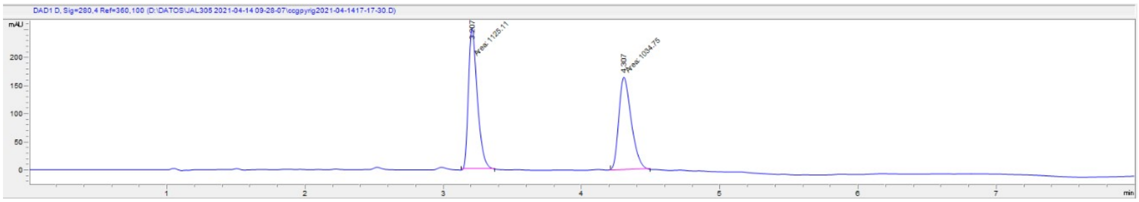


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.155	MM	116.7	37.3	0.0521	15.246	0.969
2	3.16	MM	648.7	142.5	0.0759	84.754	0.684



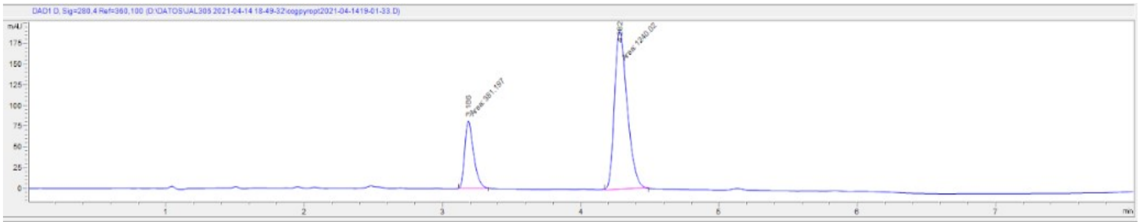
17

(±)-**17**

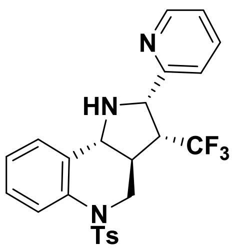


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.207	MM	1125.1	251.7	0.0745	52.092	0.656
2	4.307	MM	1034.7	165	0.1045	47.908	0.681

(+)-**17**; 53% *ee*

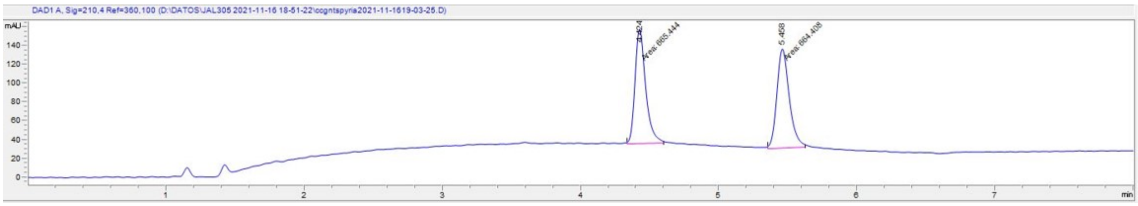


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.186	MM	381.2	83.4	0.0761	23.513	0.659
2	4.282	MM	1240	193.2	0.107	76.487	0.672



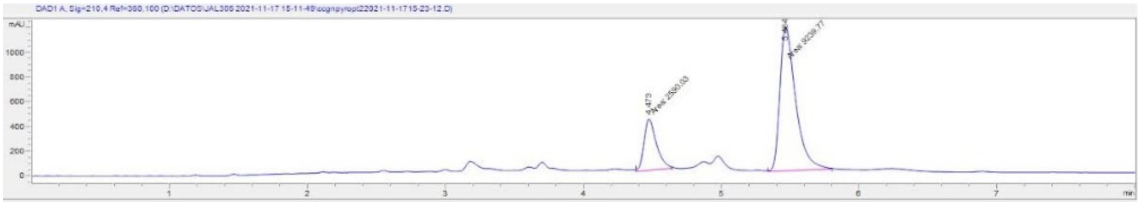
19

(±)-**19**



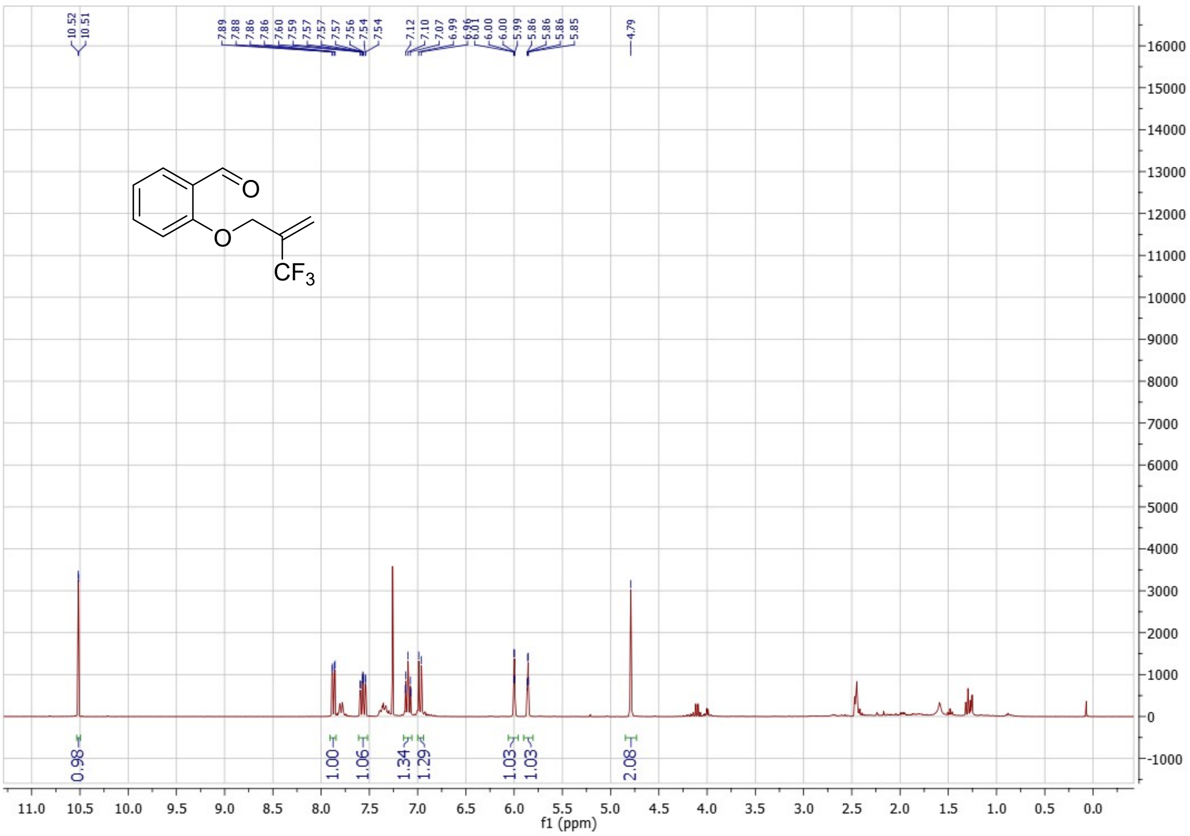
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.424	MM	665.4	123.2	0.09	50.039	0.706
2	5.458	MM	664.4	106.4	0.1041	49.961	0.782

(+)-**19**; 56% *ee*

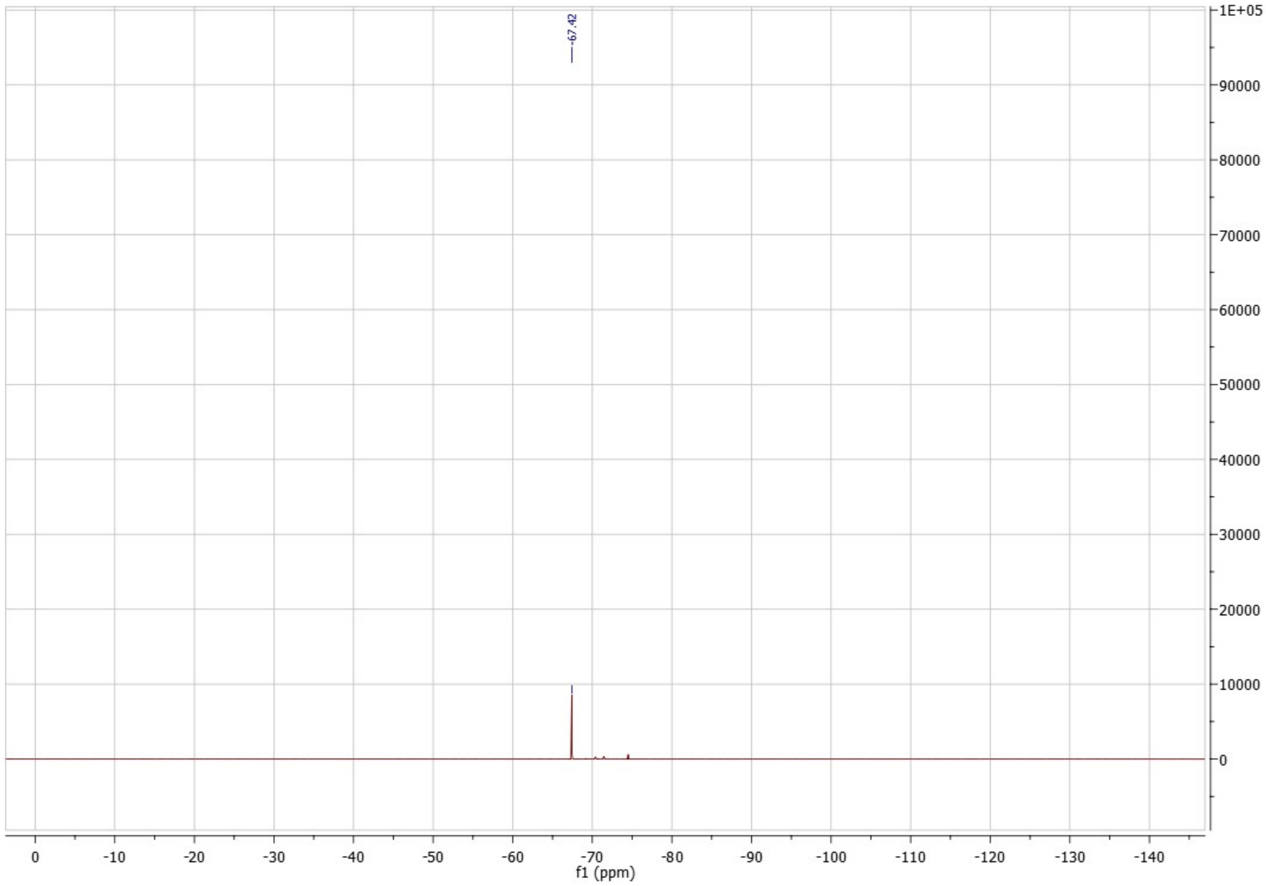


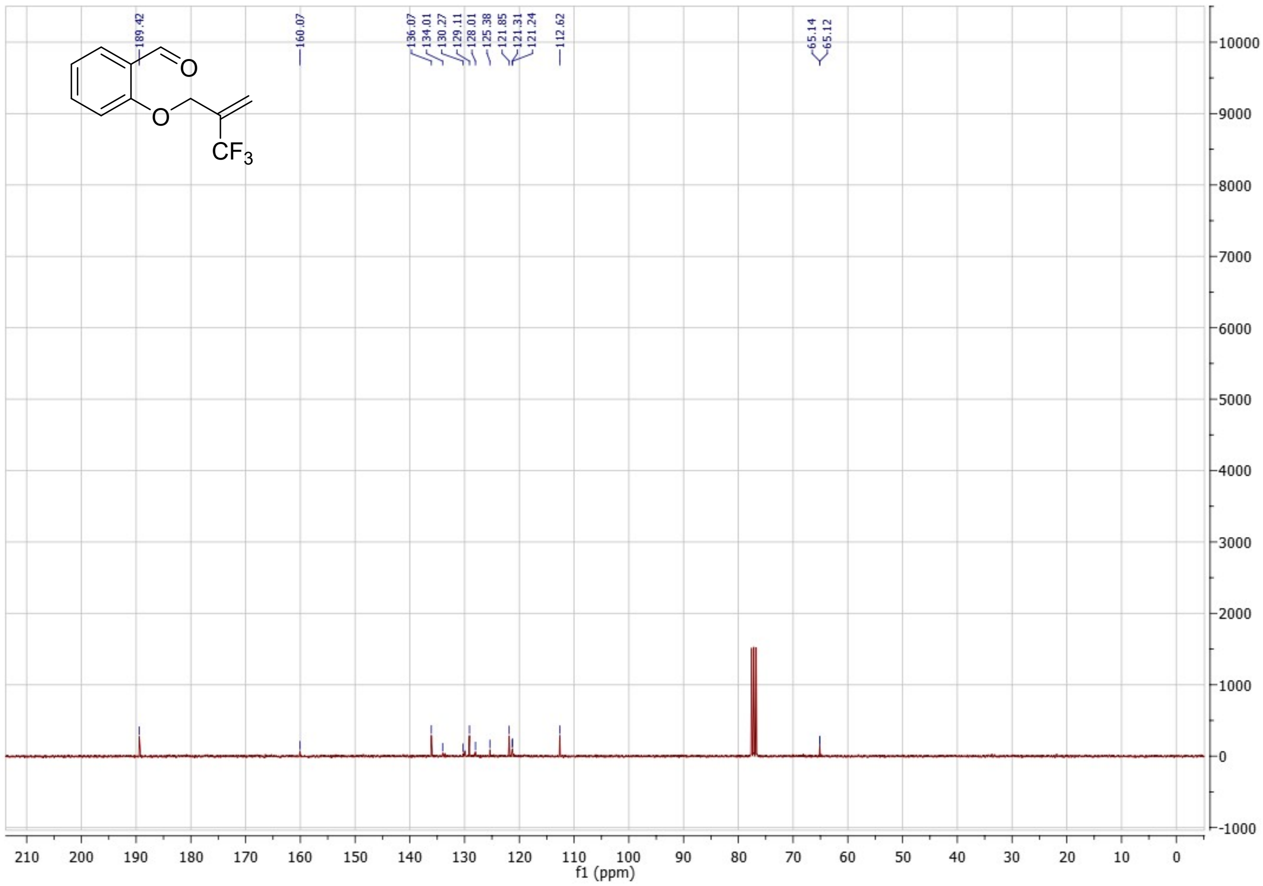
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.473	MM	2590	414.4	0.1042	21.894	0.646
2	5.464	MM	9239.8	1163.8	0.1323	78.106	0.565

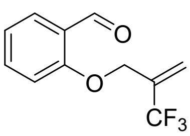
9. NMR Spectra collection



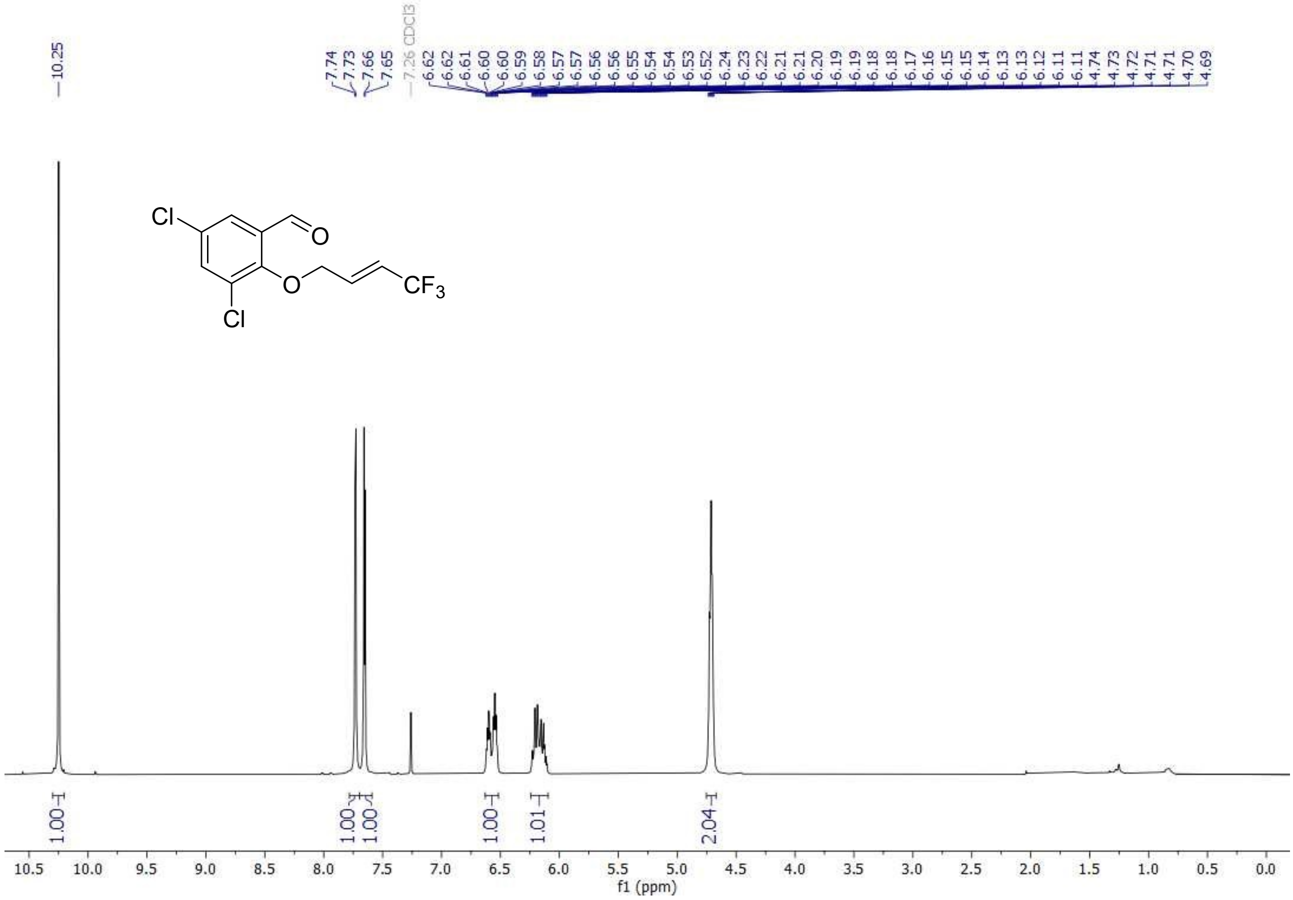
2-((2-(Trifluoromethyl)allyl)oxy)benzaldehyde:

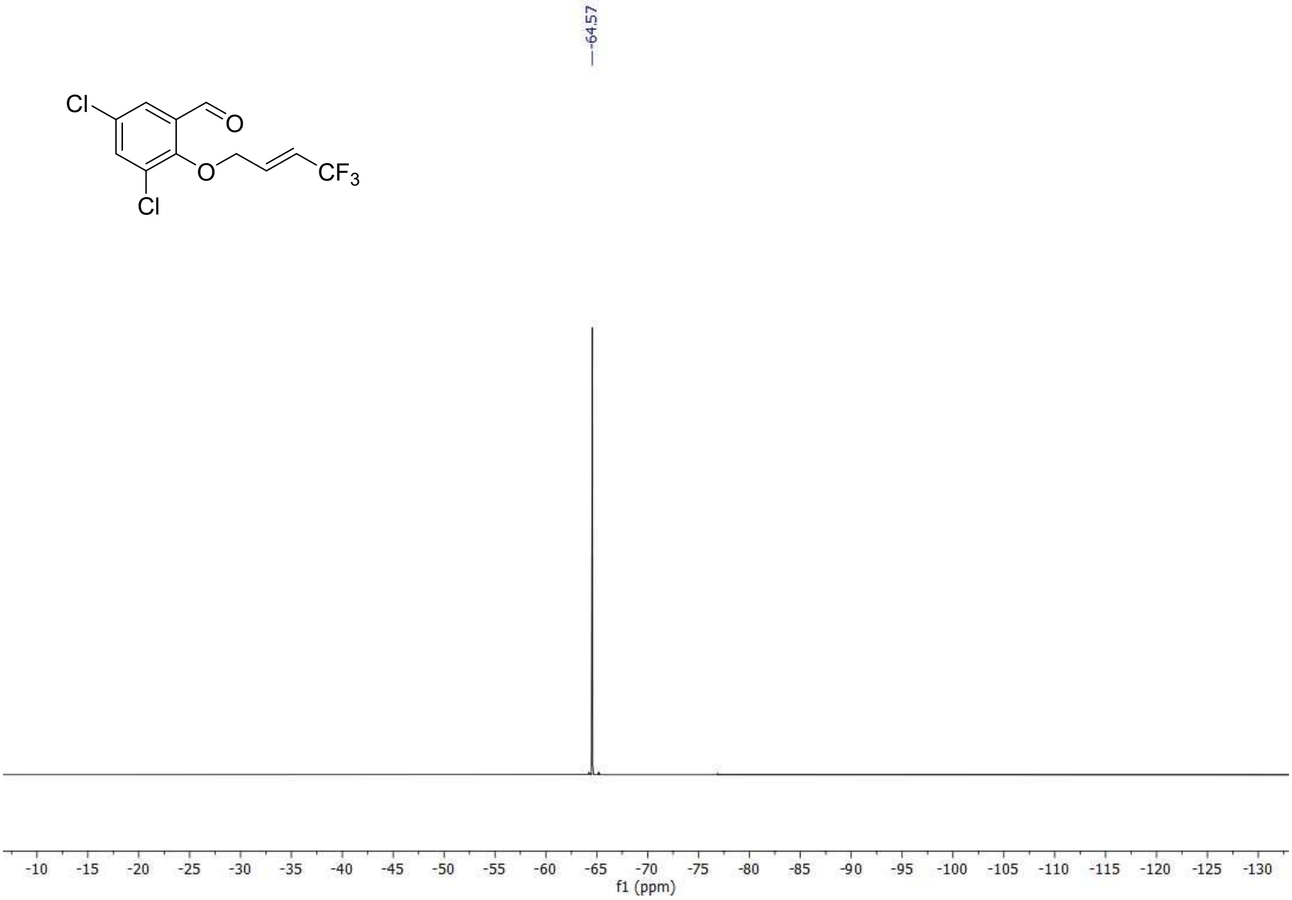

-67.42
f1 (ppm)

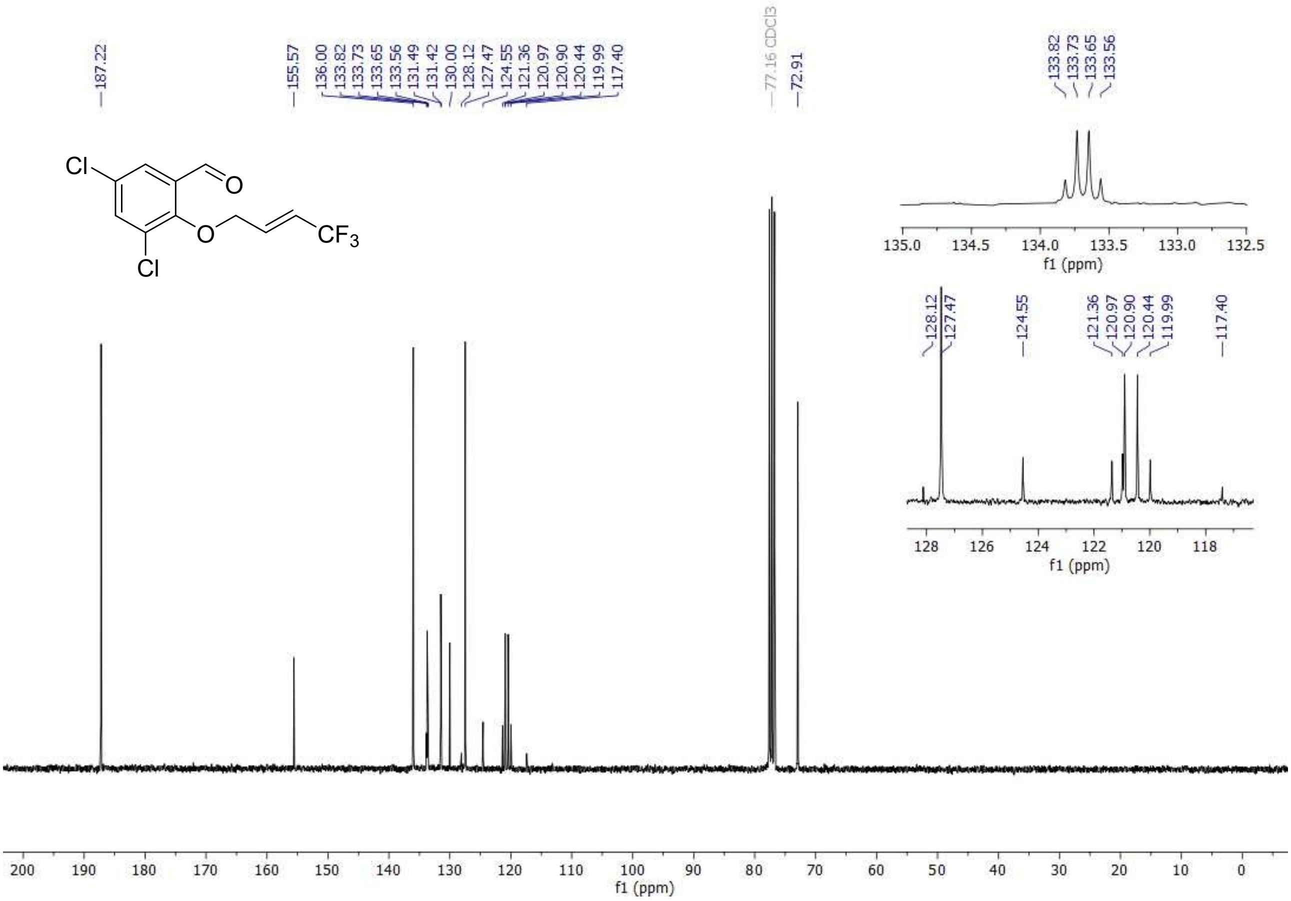

189.42
160.07
136.07
134.01
130.27
129.11
128.01
125.38
121.85
121.31
121.24
112.62
65.14
65.12
O
O
CF3
f1 (ppm)


O
O
CF3

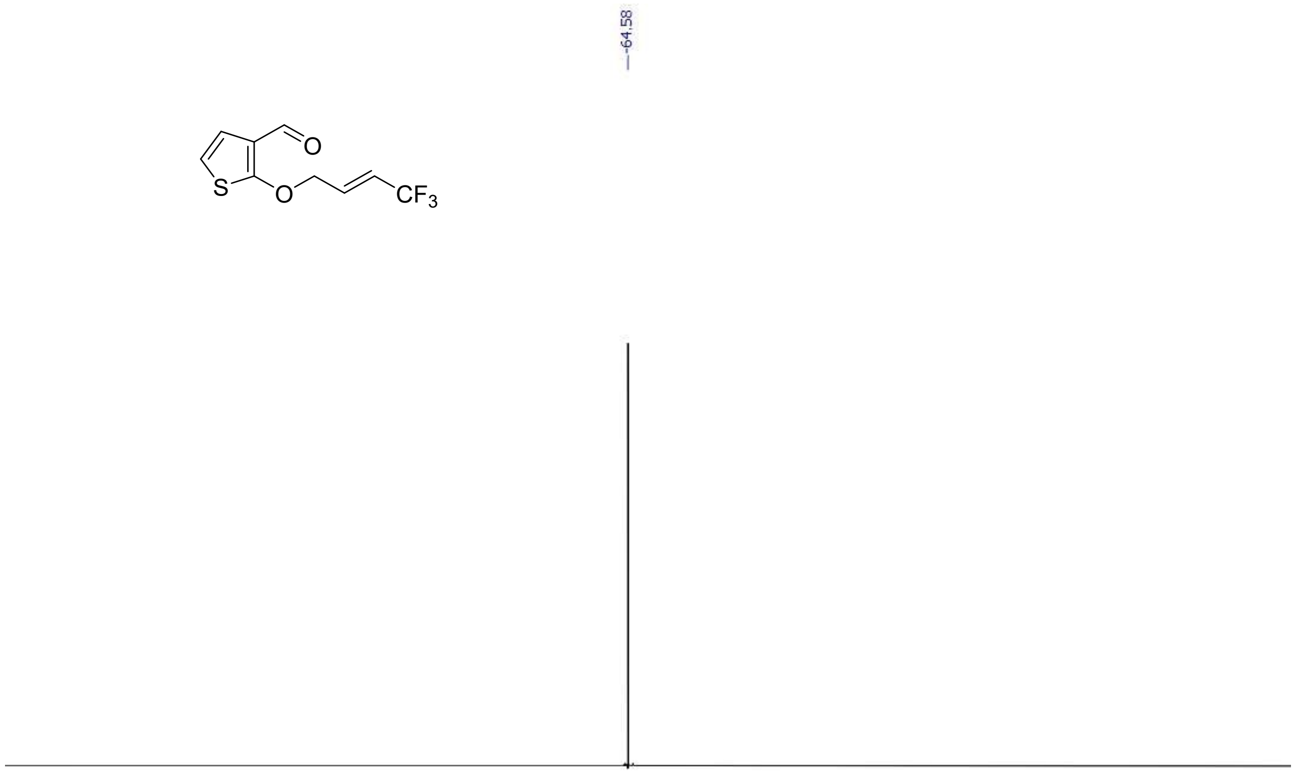
(E)-3,5-dichloro-2-((4,4,4-trifluorobut-2-en-1-yl)oxy)benzaldehyde

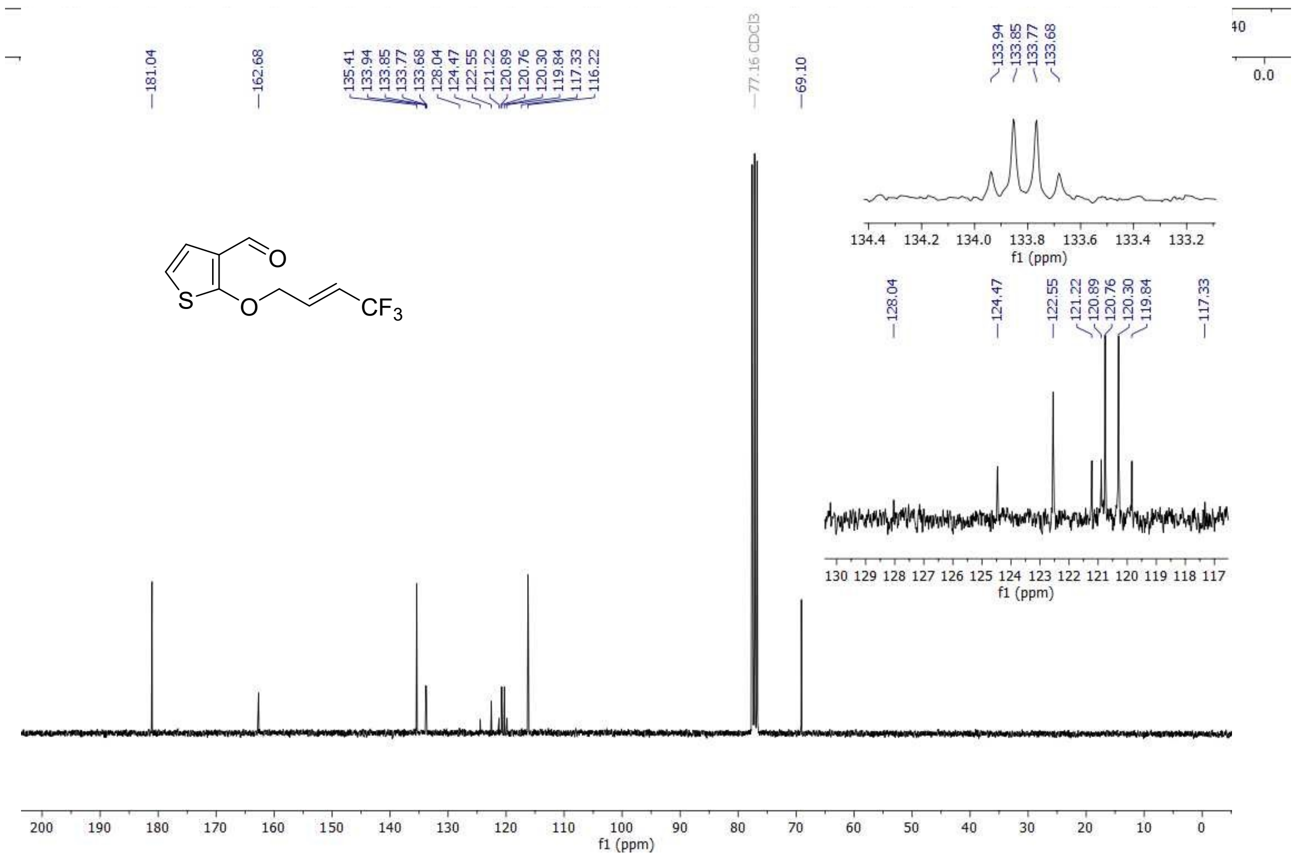



-64.57
Cl
O
O
CF3
Cl
f1 (ppm)

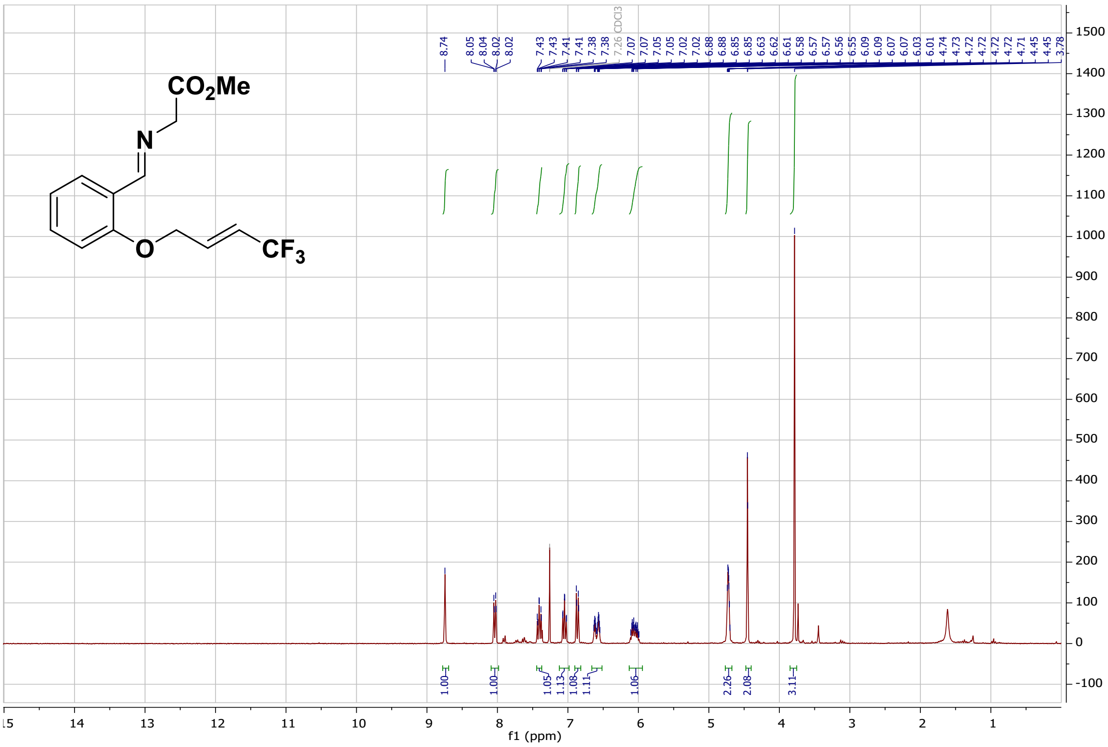

187.22
155.57
136.00
133.82
133.73
133.65
133.56
131.49
131.42
130.00
128.12
127.47
124.55
121.36
120.97
120.90
120.44
119.99
117.40
77.16 CDCl3
72.91
Cl
O
O
CF3
Cl
f1 (ppm)

(E)-2-((4,4,4-trifluorobut-2-en-1-yl)oxy)thiophene-3-carbaldehyde:

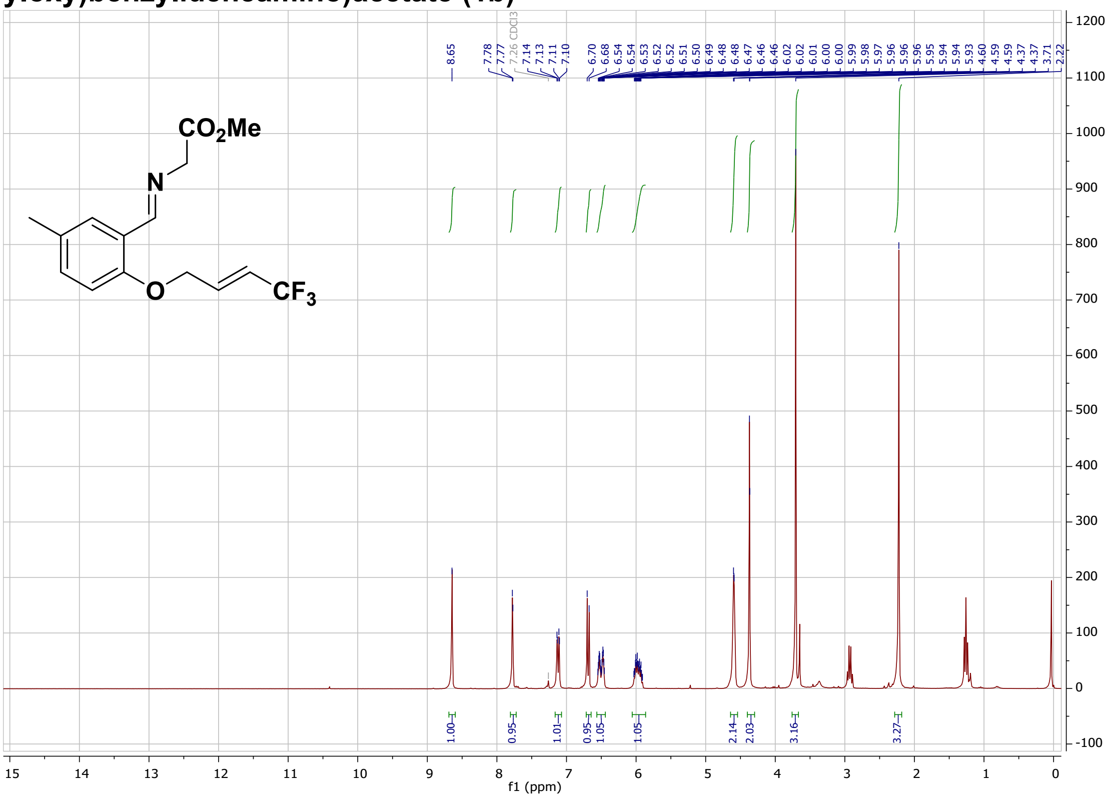




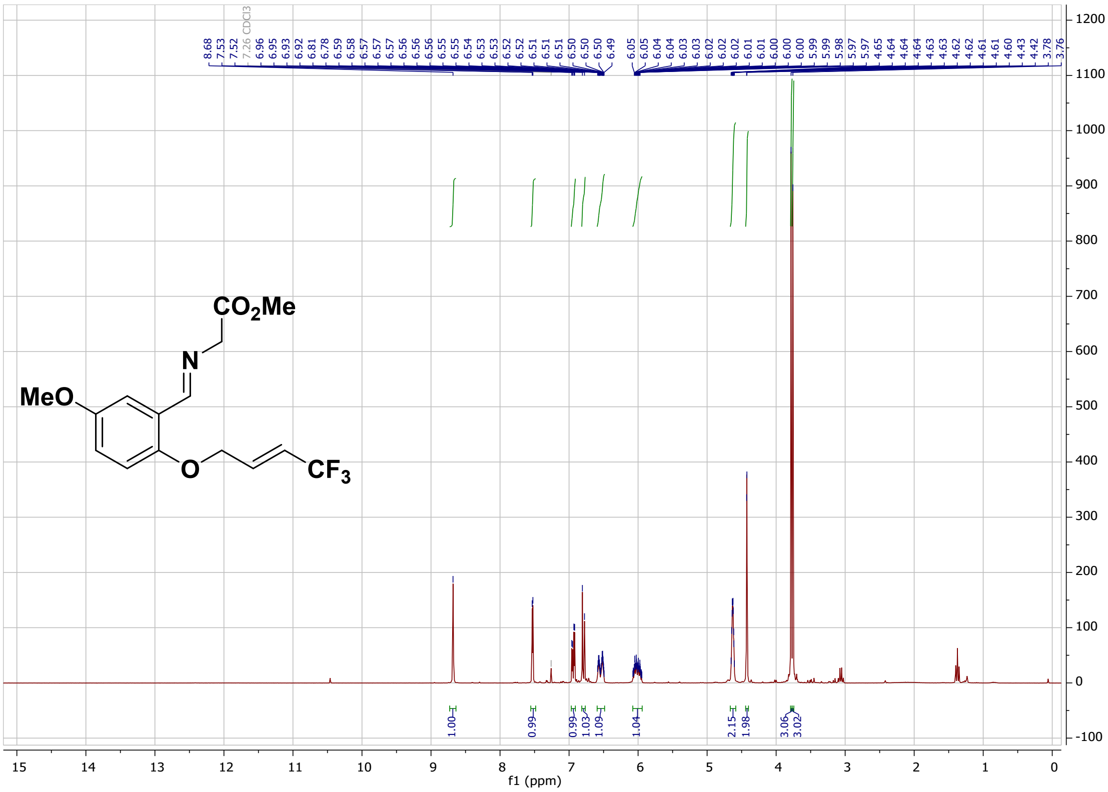
Methyl 2-(2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1a)



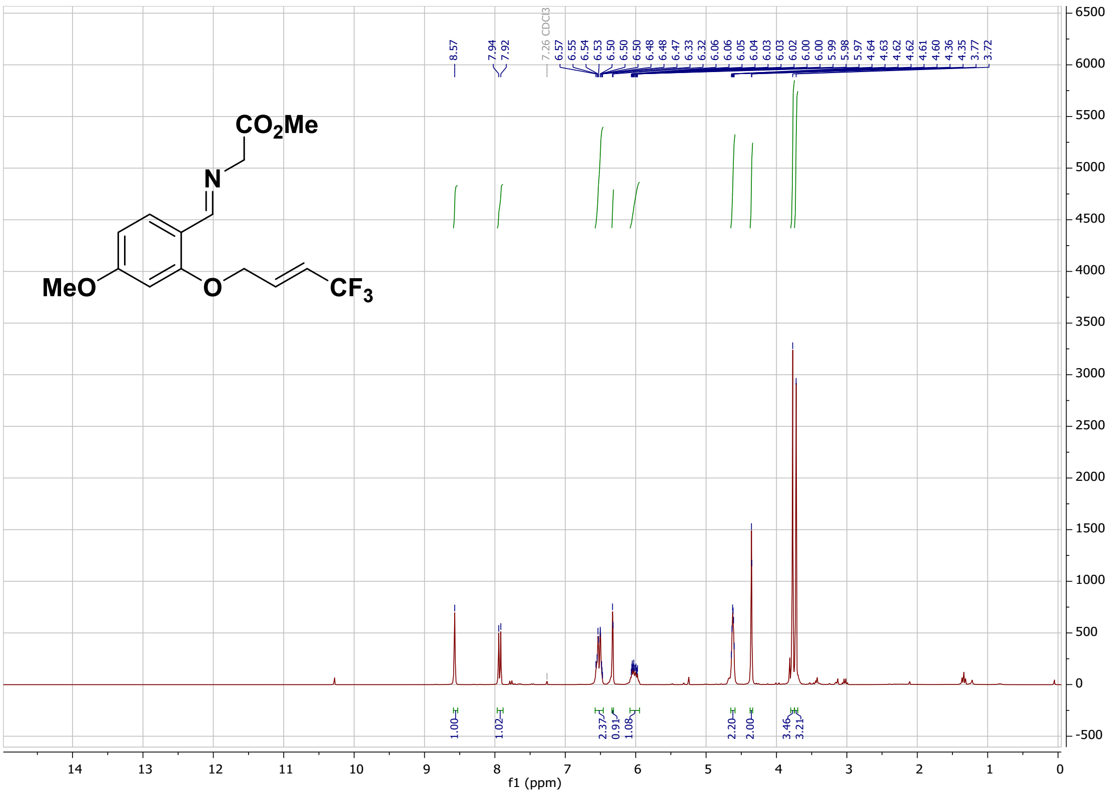
Methyl 2-(5-methyl-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1b)



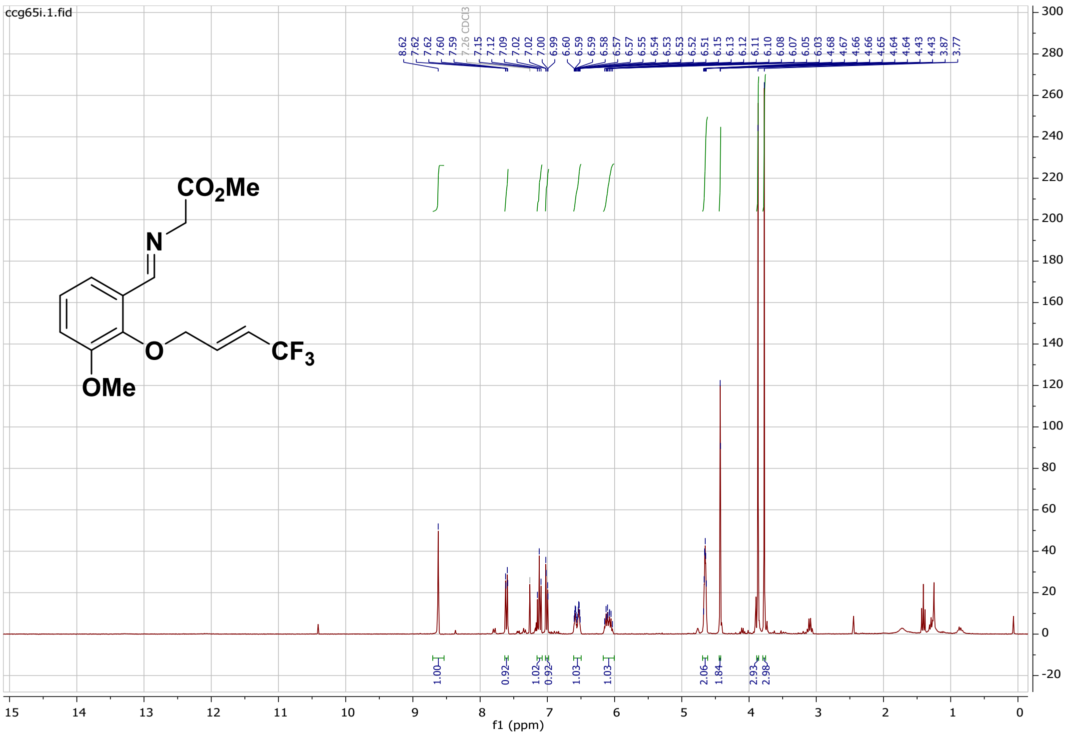
Methyl 2-(5-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1c)



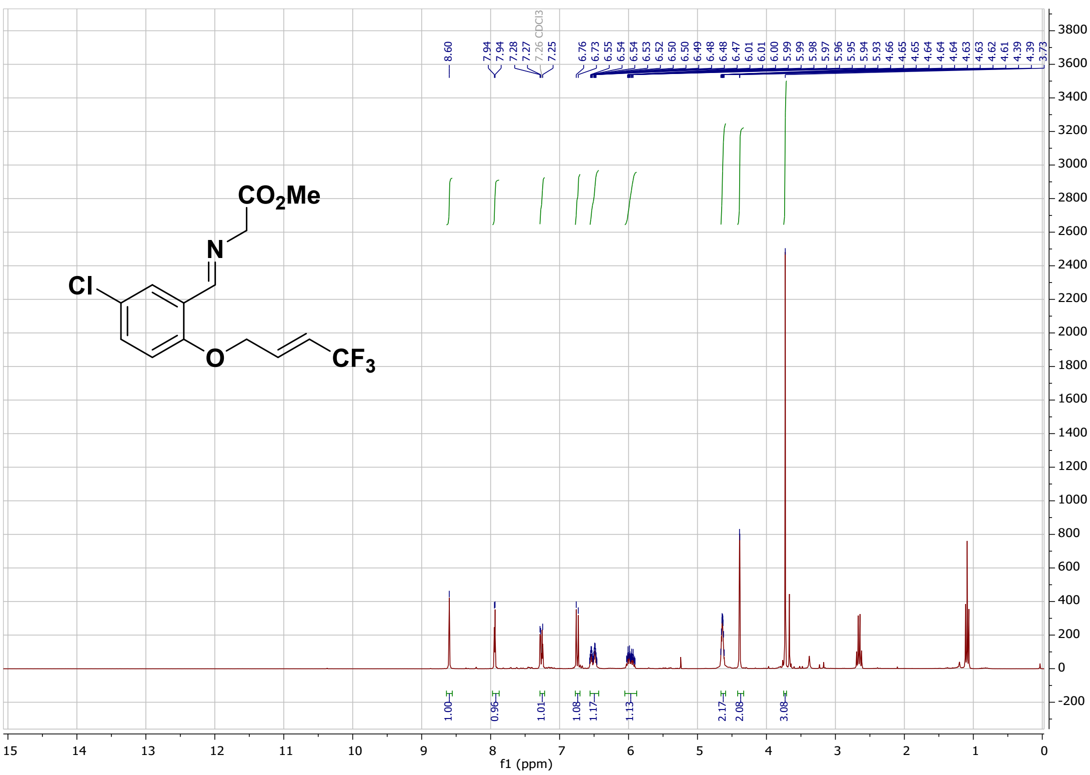
Methyl 2-(4-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1d)



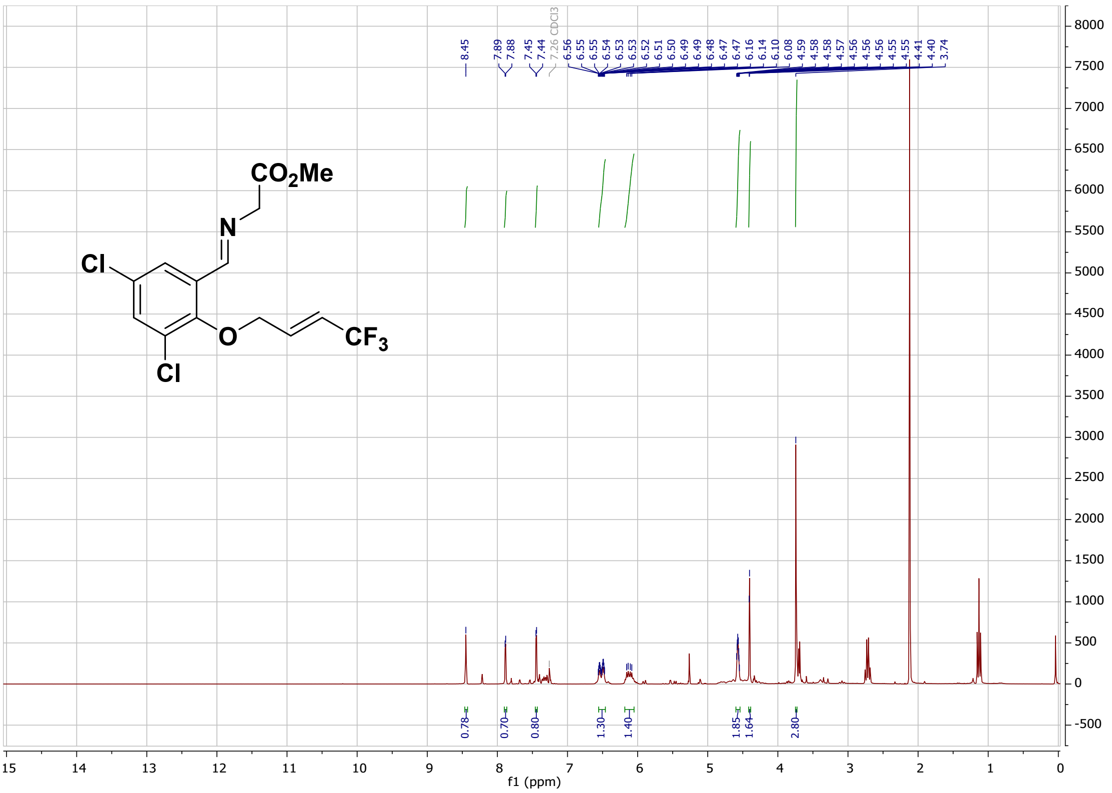
Methyl 2-(3-methoxy-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1e)



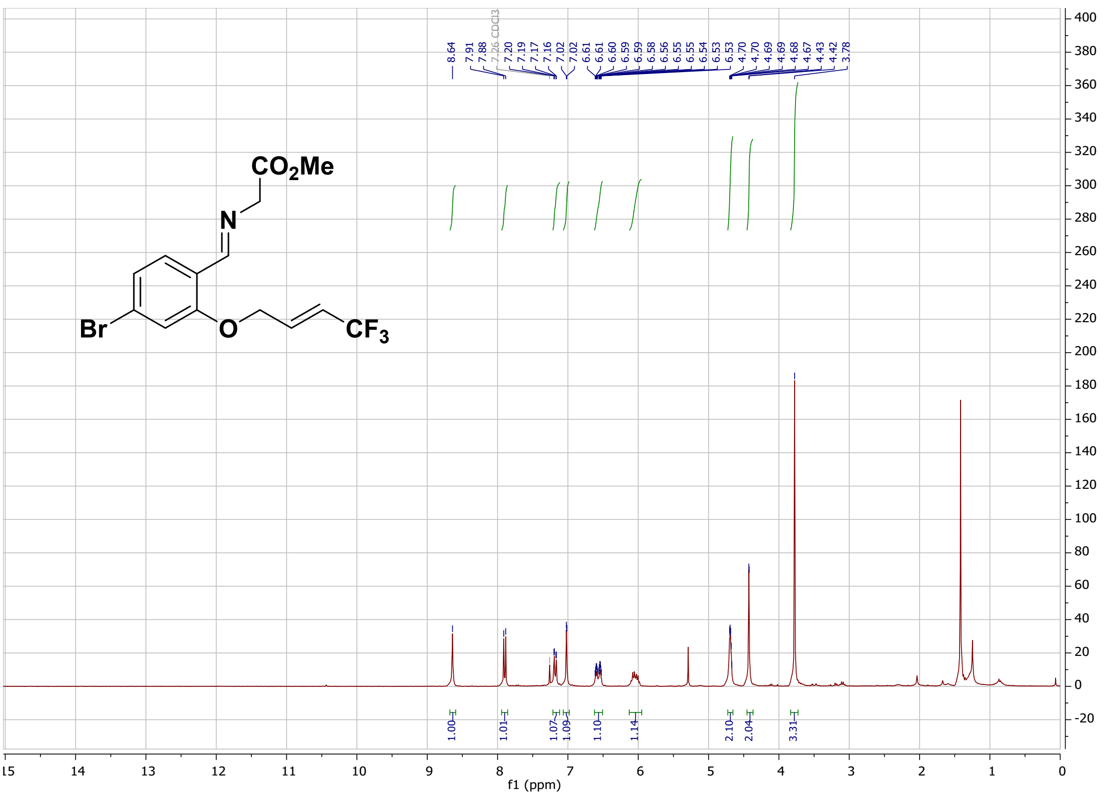
Methyl 2-(5-chloro-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1f)



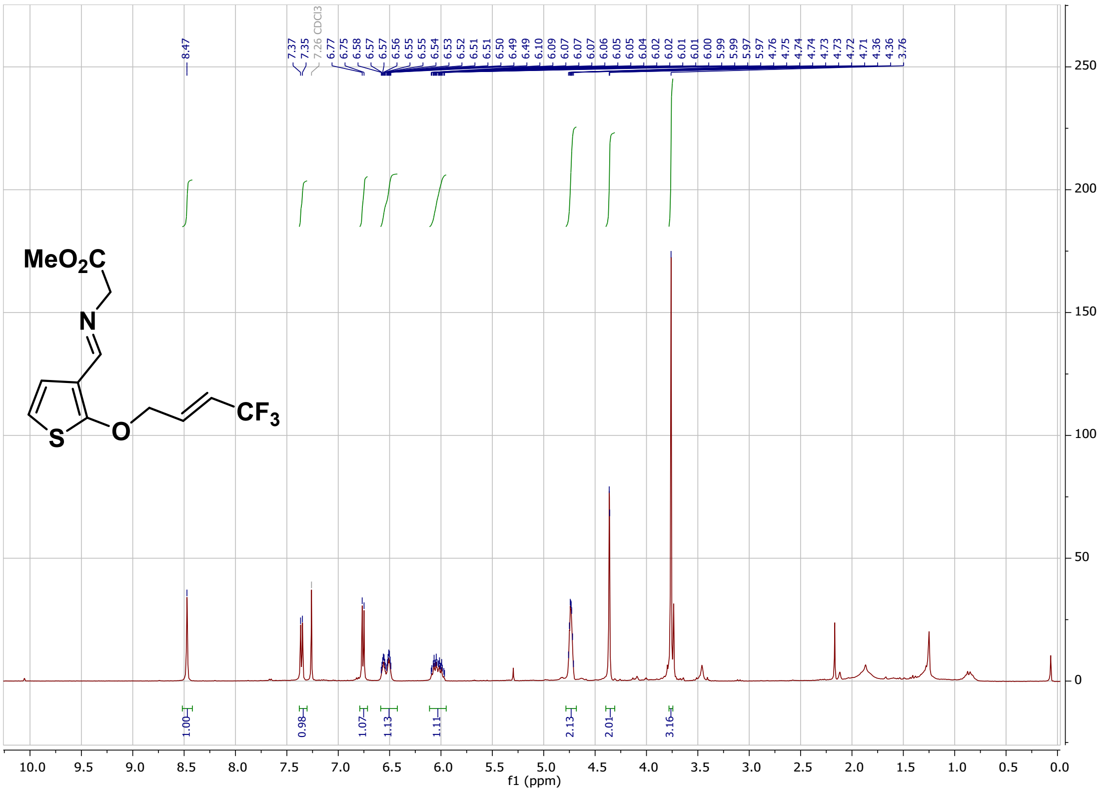
Methyl 2-(3,5-dichloro-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1g)



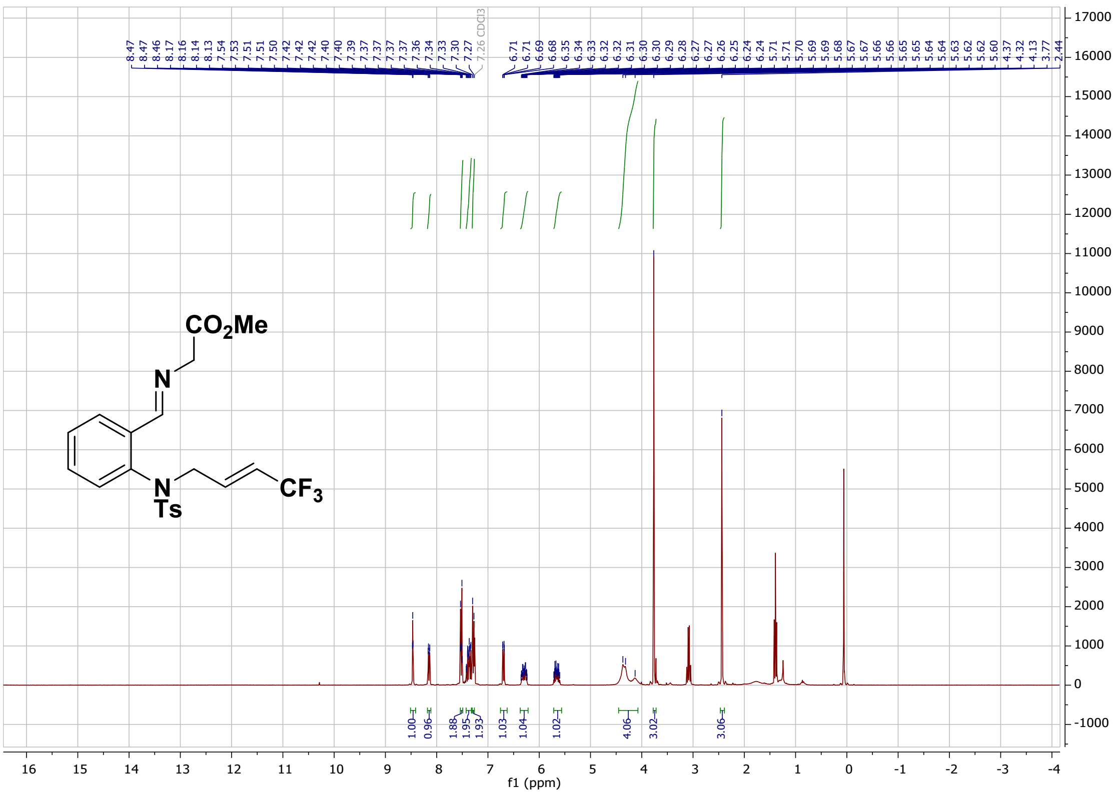
Methyl 2-(4-bromo-2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)benzylideneamino)acetate (1h)



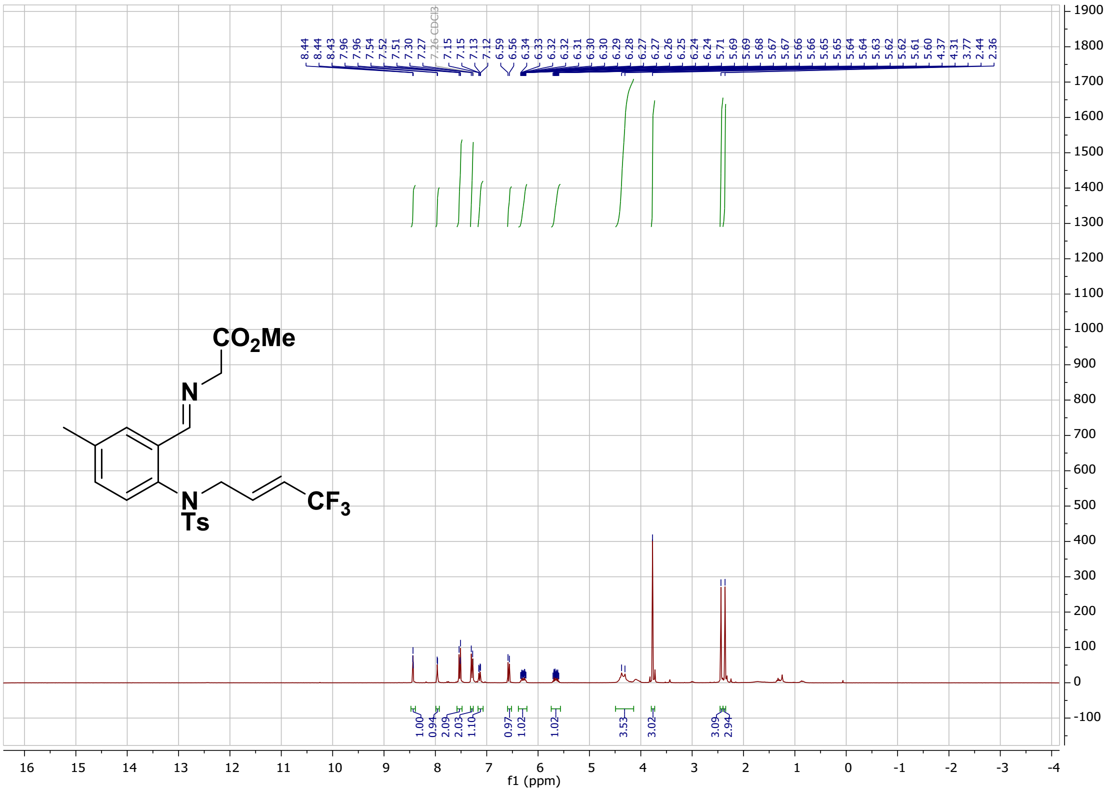
Methyl 2-(2-((*E*)-4,4,4-trifluorobut-2-en-1-yloxy)thiophen-3-ylmethyleneamino)acetate (1i)



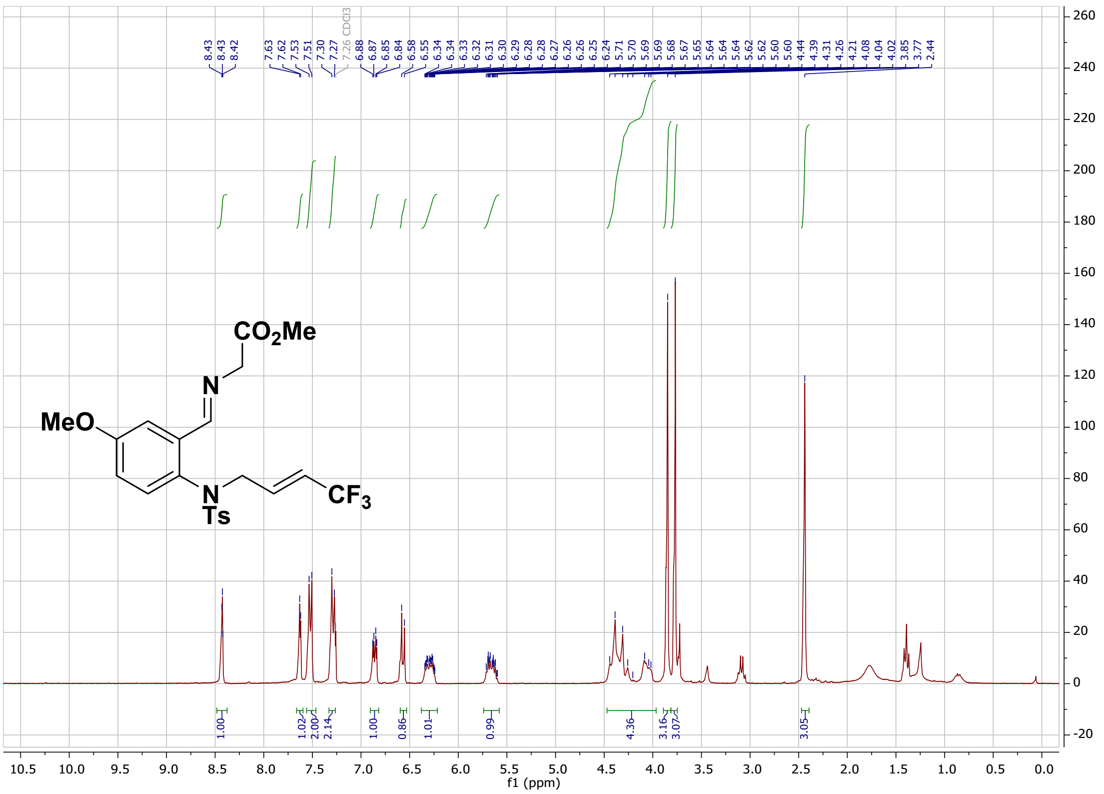
Methyl 2-(2-(4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6a)



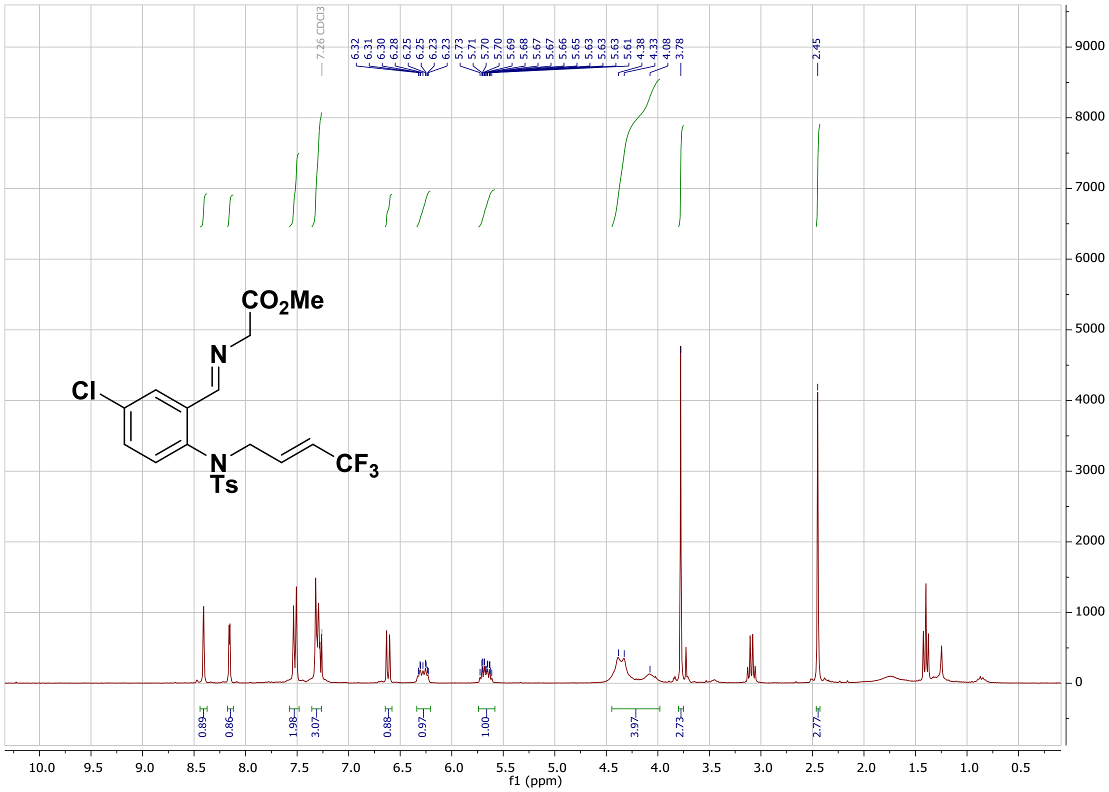
Methyl 2-(5-methyl-2-(4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6b)



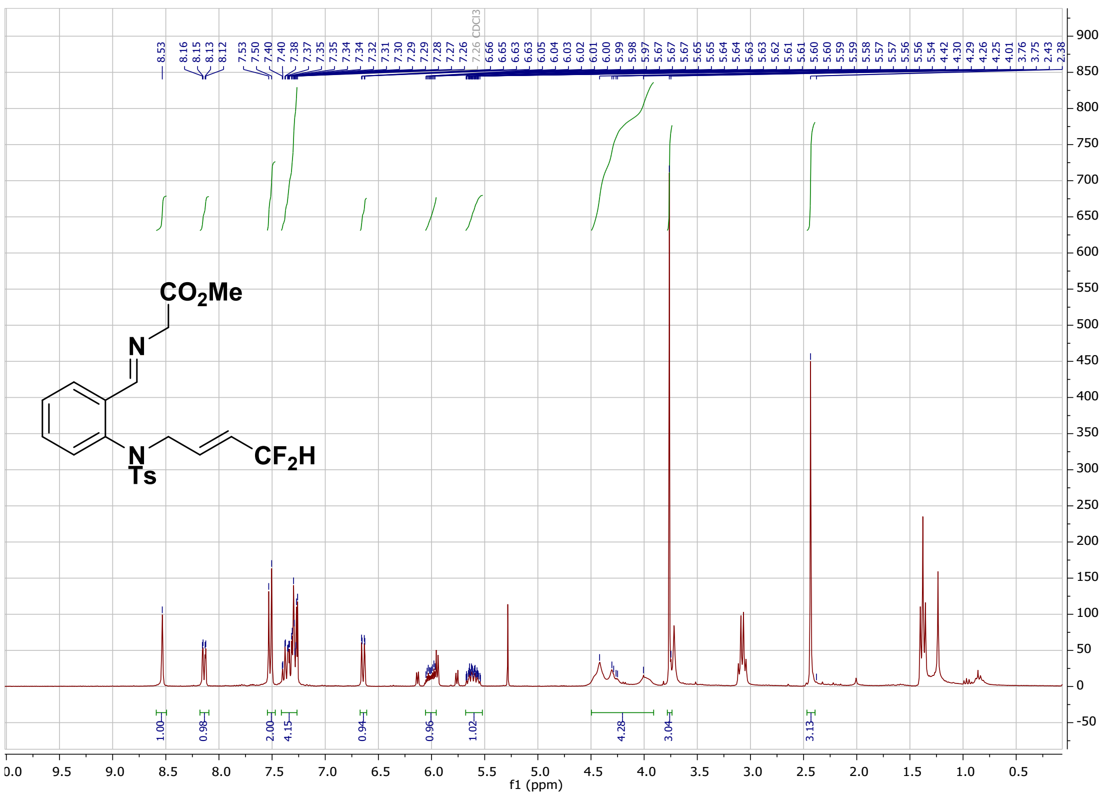
Methyl 2-(5-methoxy-2-(4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6c)



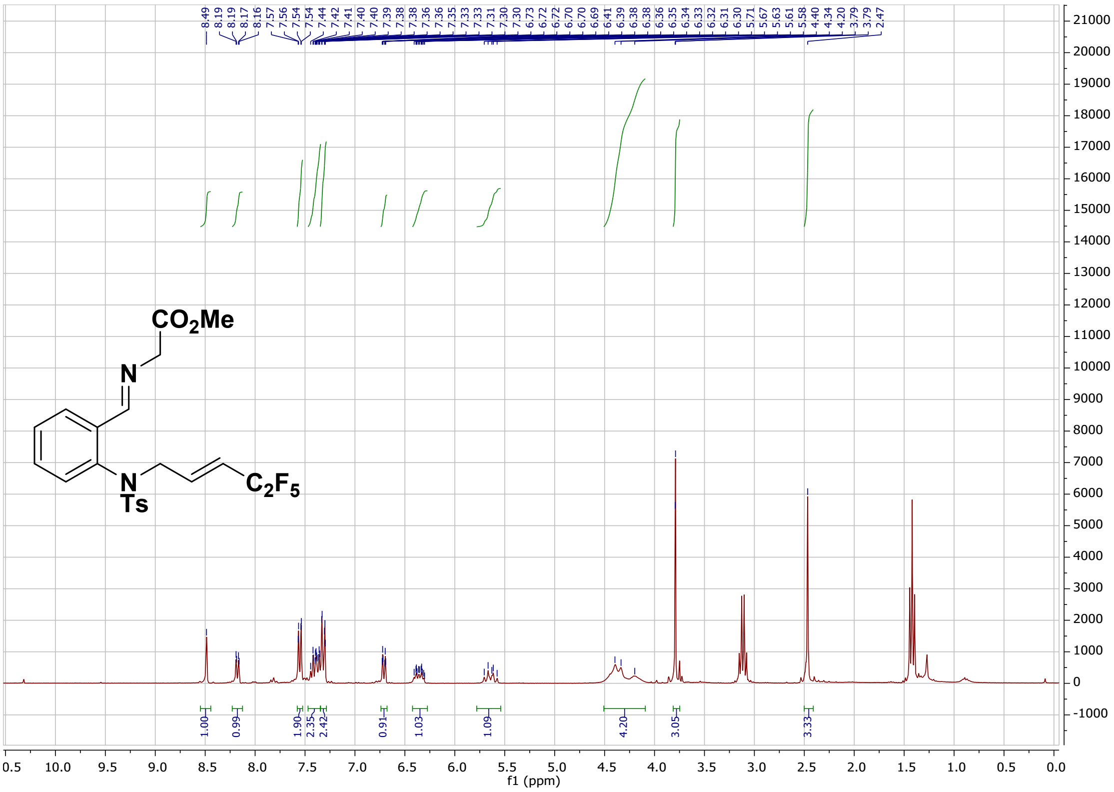
Methyl 2-(5-chloro-2-(4-methyl-*N*-((*E*)-4,4,4-trifluorobut-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6d)



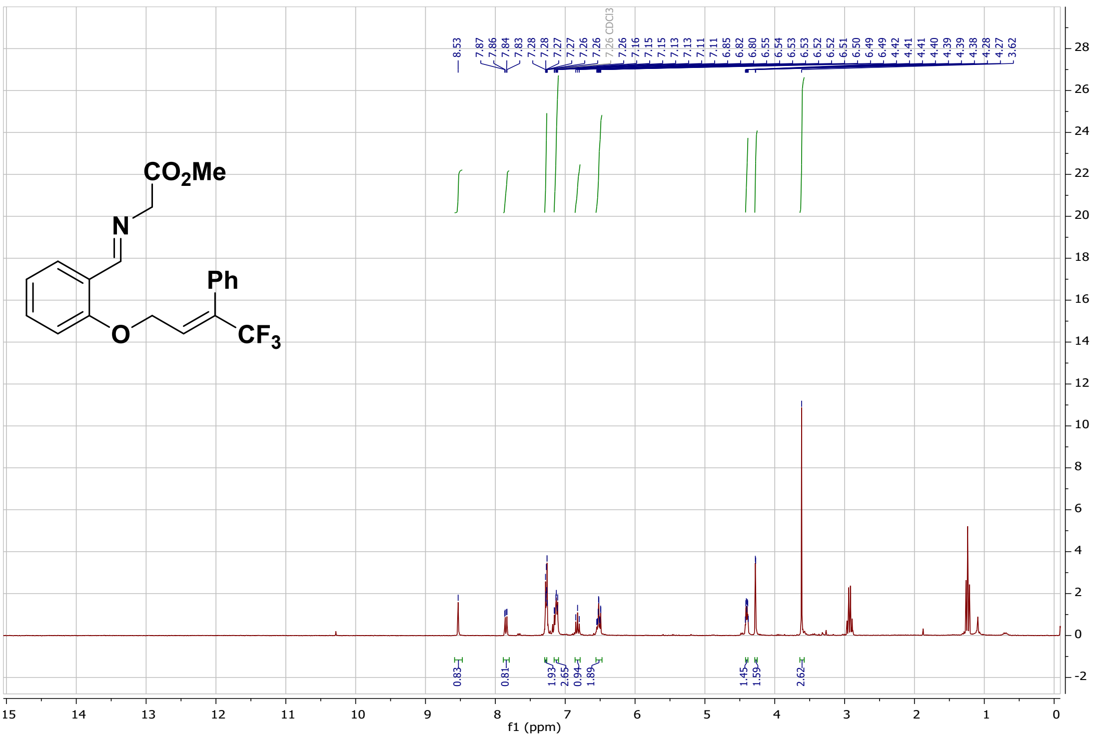
Methyl 2-(2-(*N*-((*E*)-4,4-difluorobut-2-en-1-yl)-4-methylphenylsulfonamido)benzylideneamino)acetate (6e)



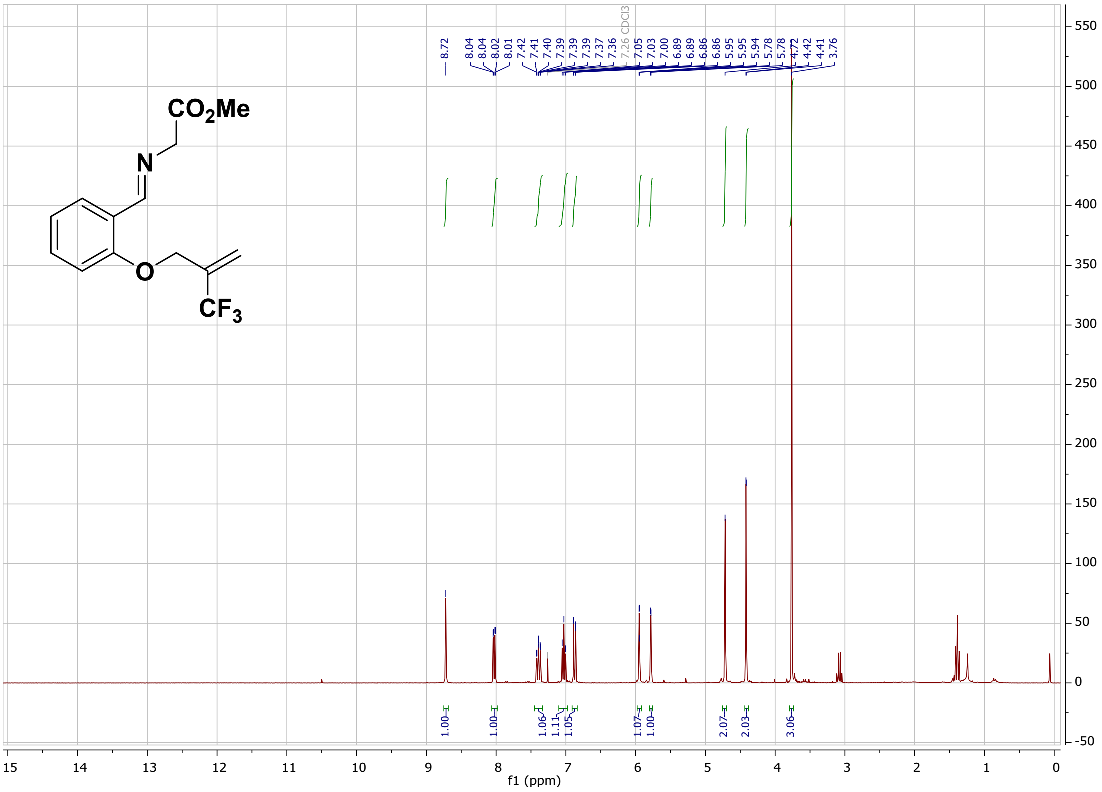
Methyl 2-(2-(4-methyl-N-((E)-4,4,5,5,5-pentafluoropent-2-en-1-yl)phenylsulfonamido)benzylideneamino)acetate (6f)



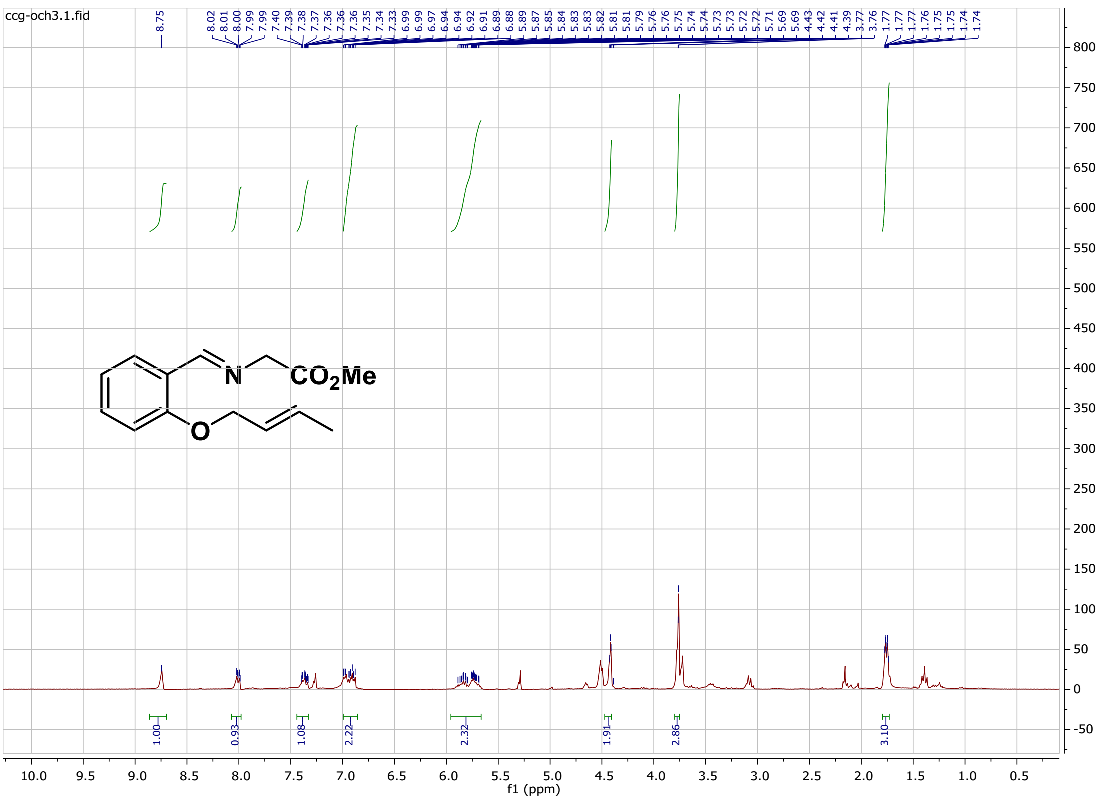
Methyl 2-(2-((*E*)-4,4,4-trifluoro-3-phenylbut-2-en-1-yloxy)benzylideneamino)acetate (10)



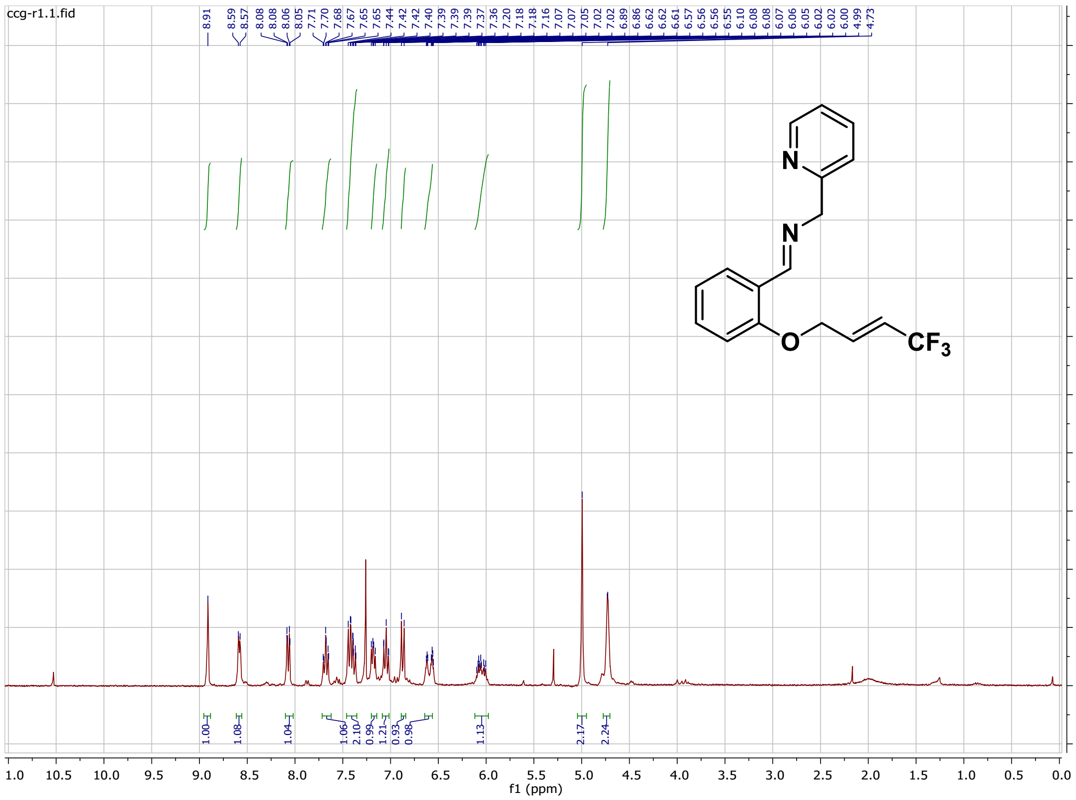
Methyl 2-(2-(2-trifluoromethylallyloxy)benzylideneamino)acetate (12)



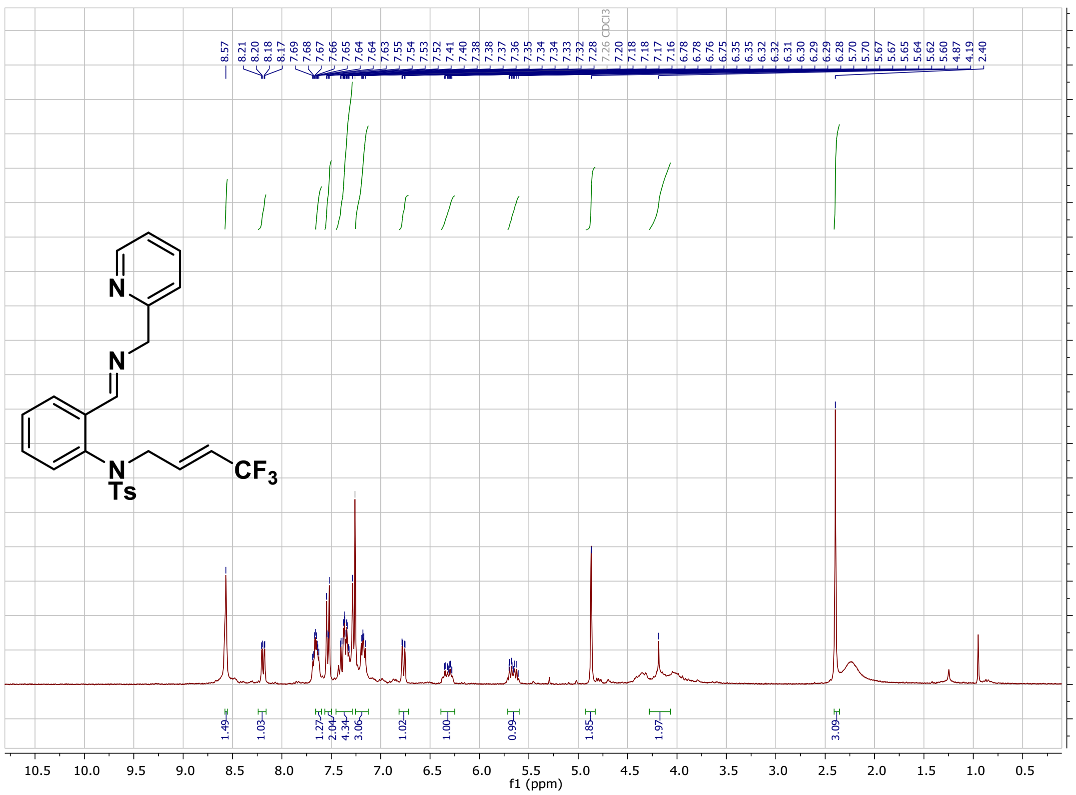
Methyl-2-(-2-((*E*)-2-butenyloxy)benzylideneamino)acetate (14)



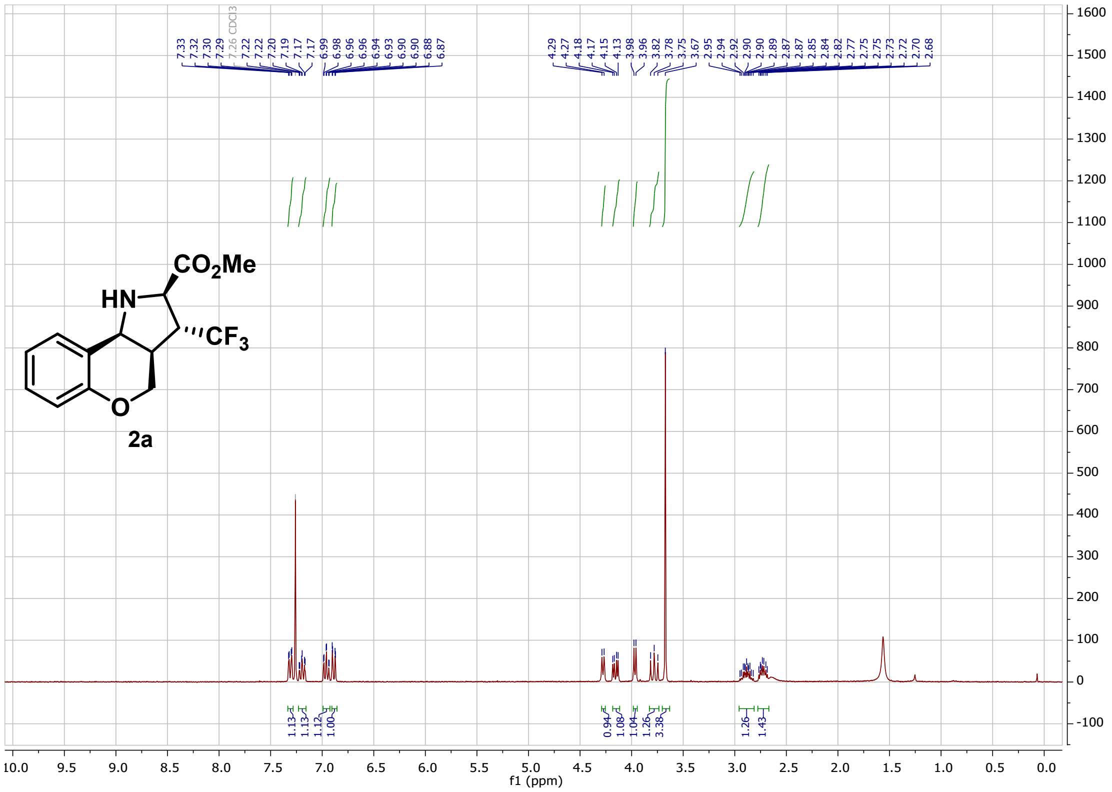
N-(pyridin-2-ylmethyl)-1-(2-(4,4,4-trifluorobut-2-en-1-yloxy)phenyl)methanimine (16)

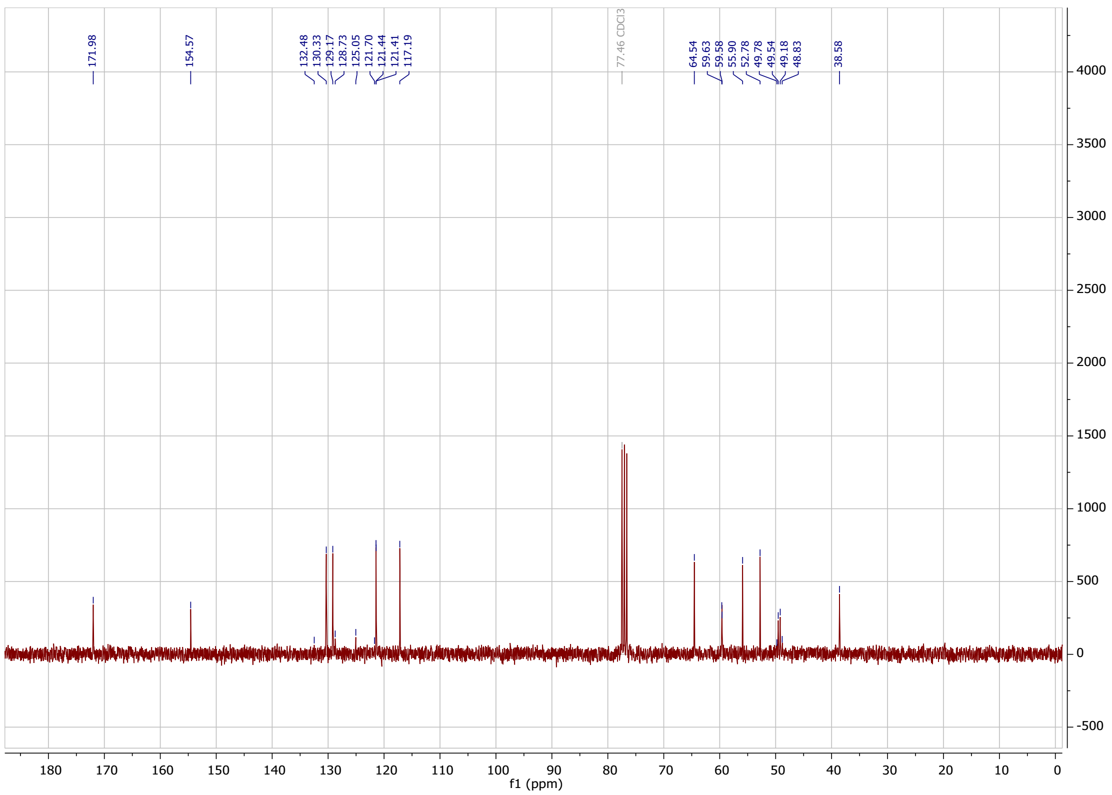


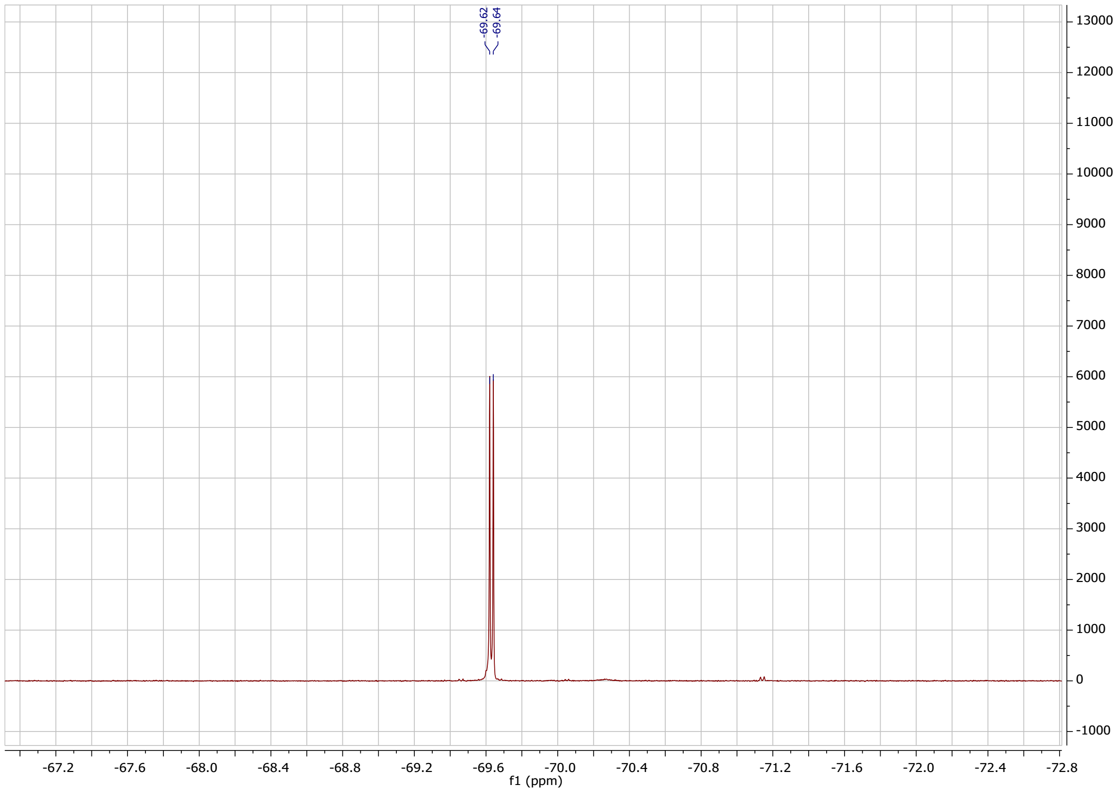
4-methyl-N-(2-(pyridin-2-ylmethyl)iminomethylphenyl)-N-((E)-4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide (18)



Methyl (2*R*,3*R*,3a*R*,9b*S*)-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2a)

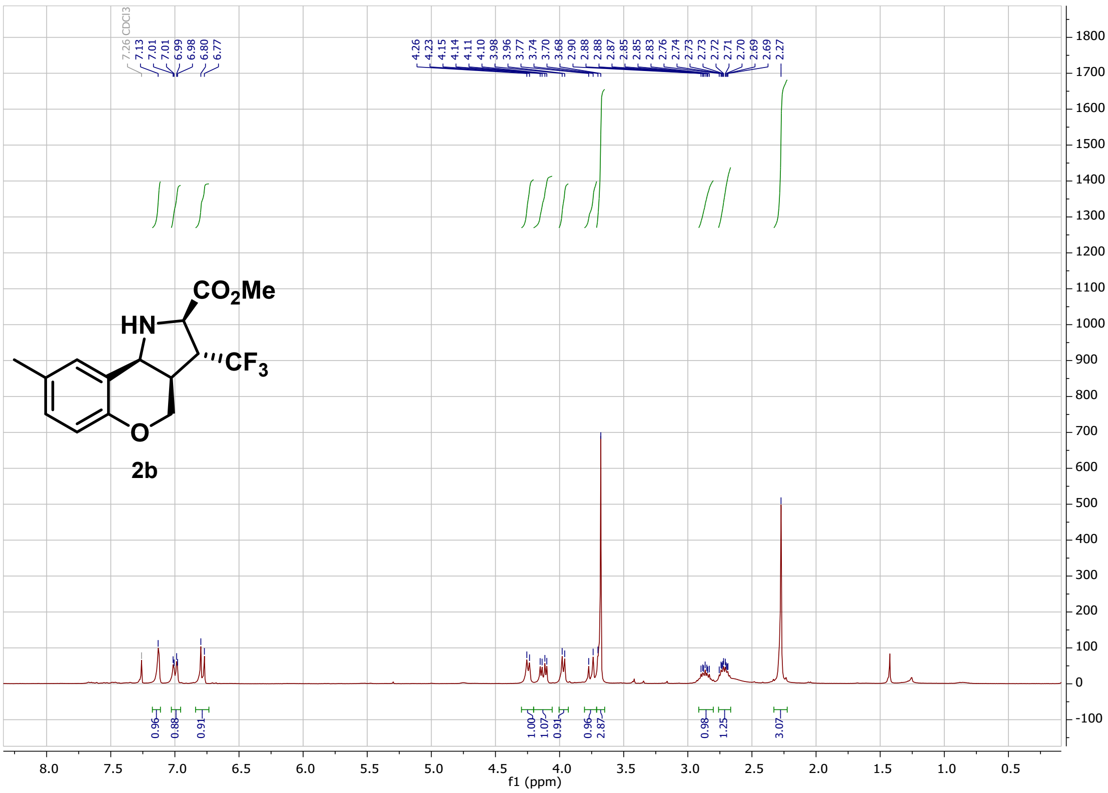


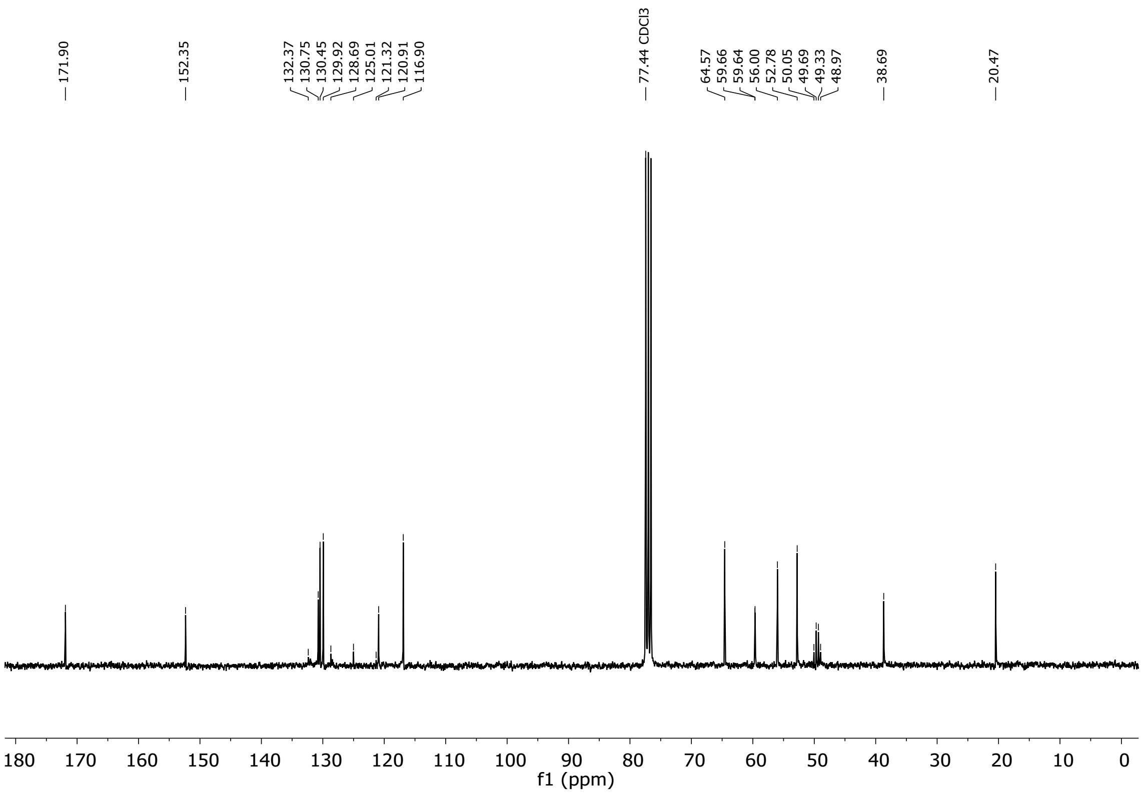


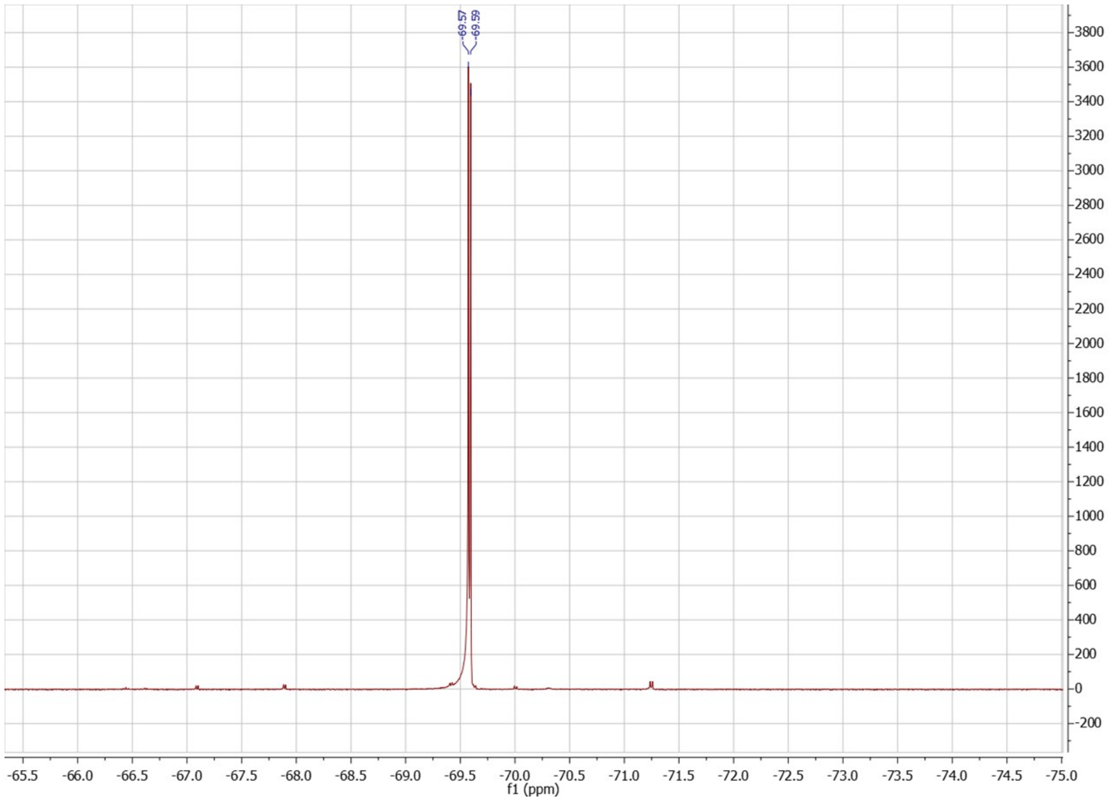


-69.62
-69.64
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-67.2
-67.6
-68.0
-68.4
-68.8
-69.2
-69.6
-70.0
-70.4
-70.8
-71.2
-71.6
-72.0
-72.4
-72.8
f1 (ppm)

Methyl (2*R*,3*R*,3a*R*,9b*S*)-8-methyl-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2b)

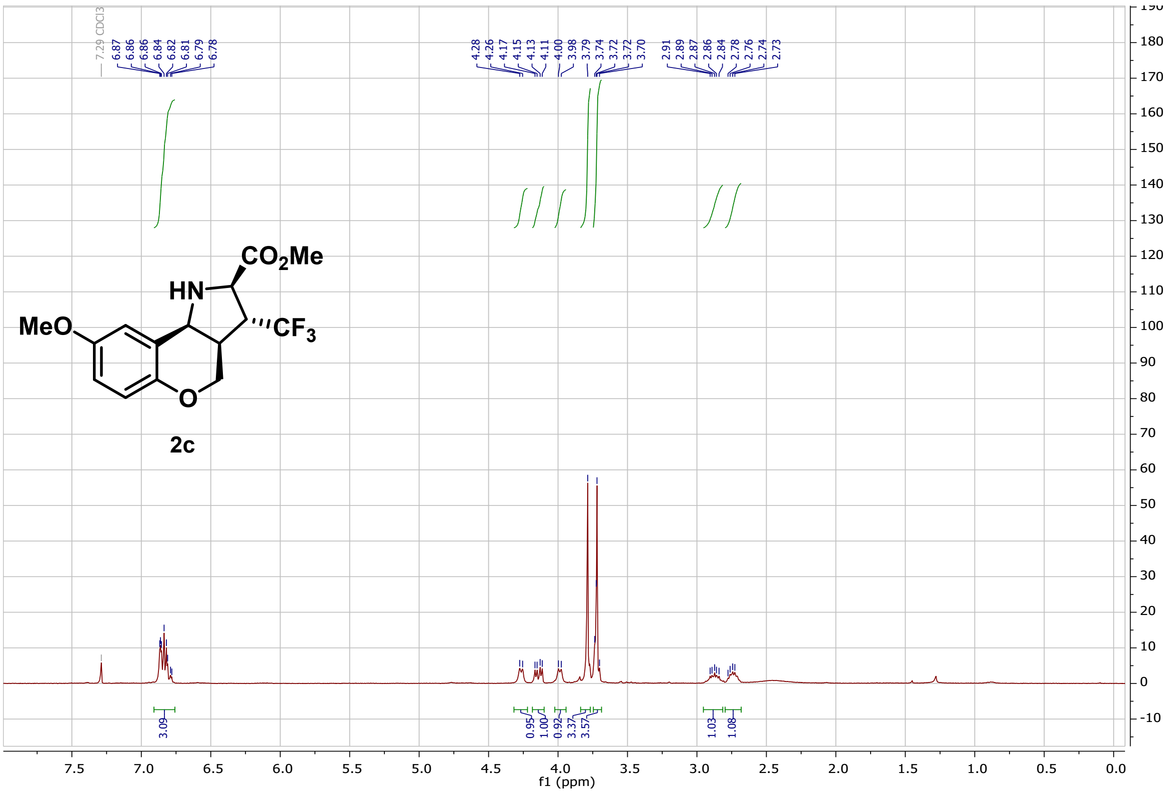


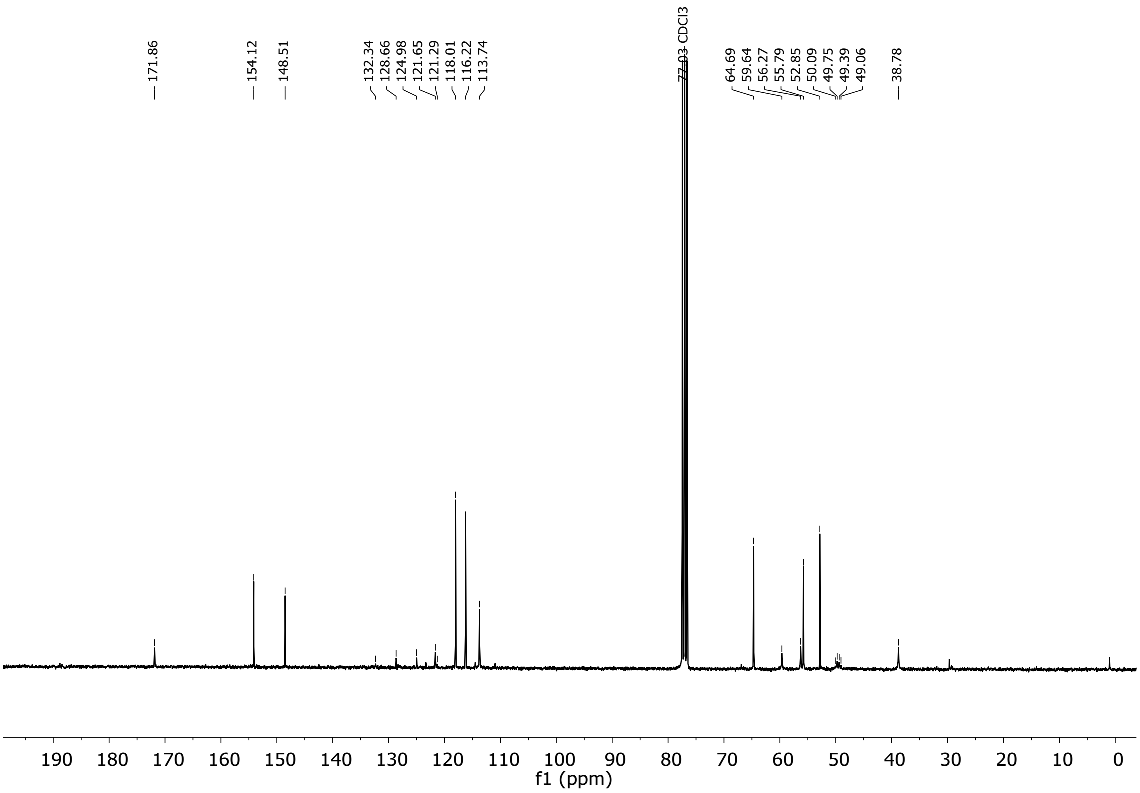


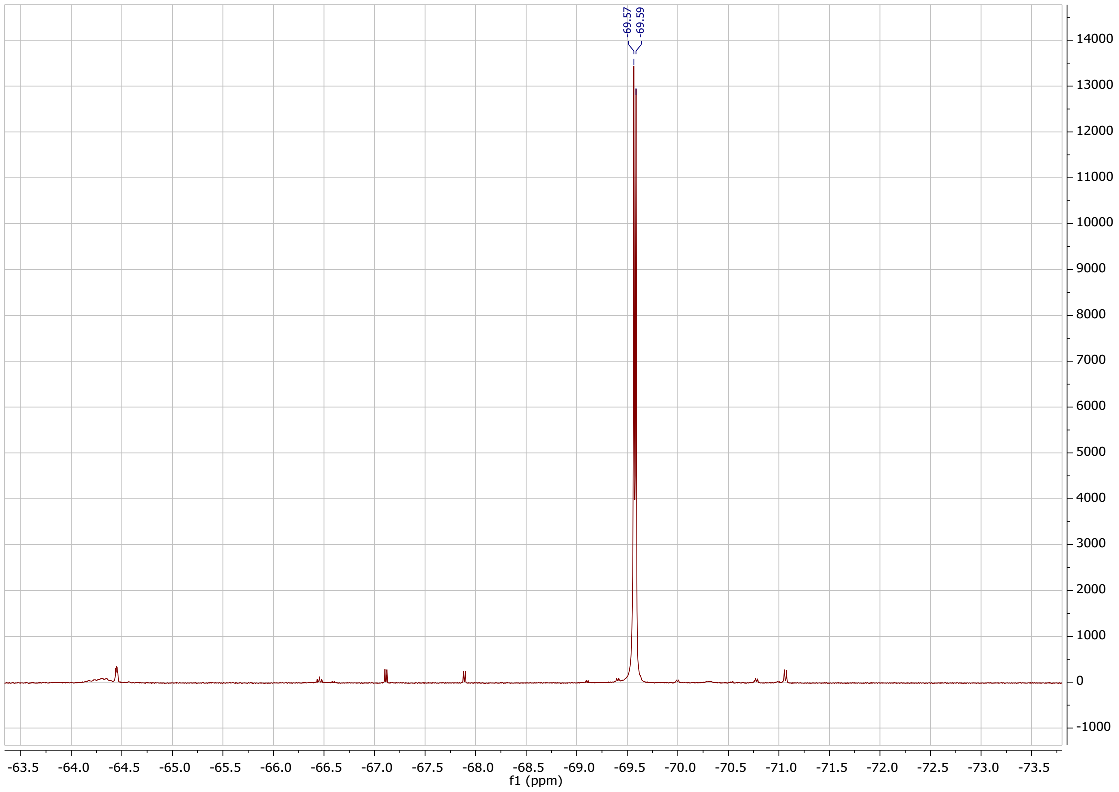


-69.57
-69.59
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0 -70.5 -71.0 -71.5 -72.0 -72.5 -73.0 -73.5 -74.0 -74.5 -75.0
f1 (ppm)

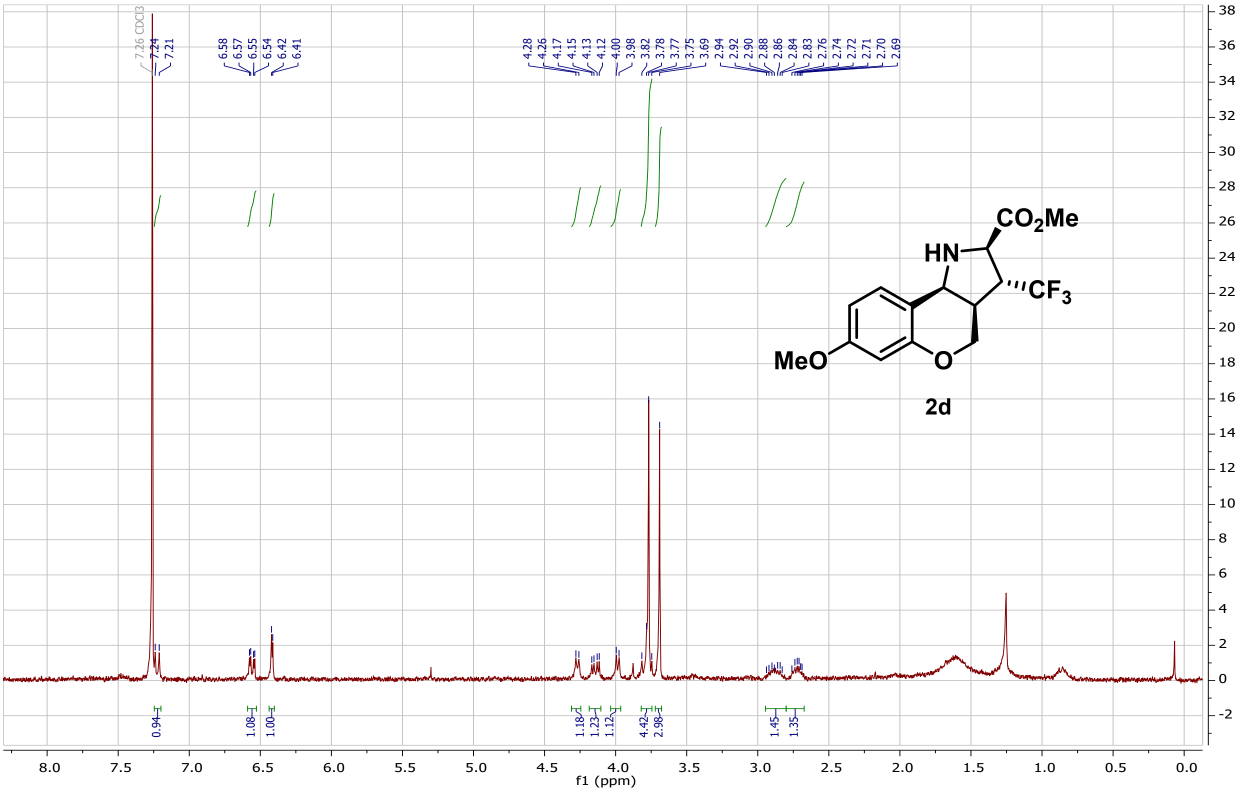
Methyl (2*R*,3*R*,3a*R*,9b*S*)-8-methoxy-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2c)

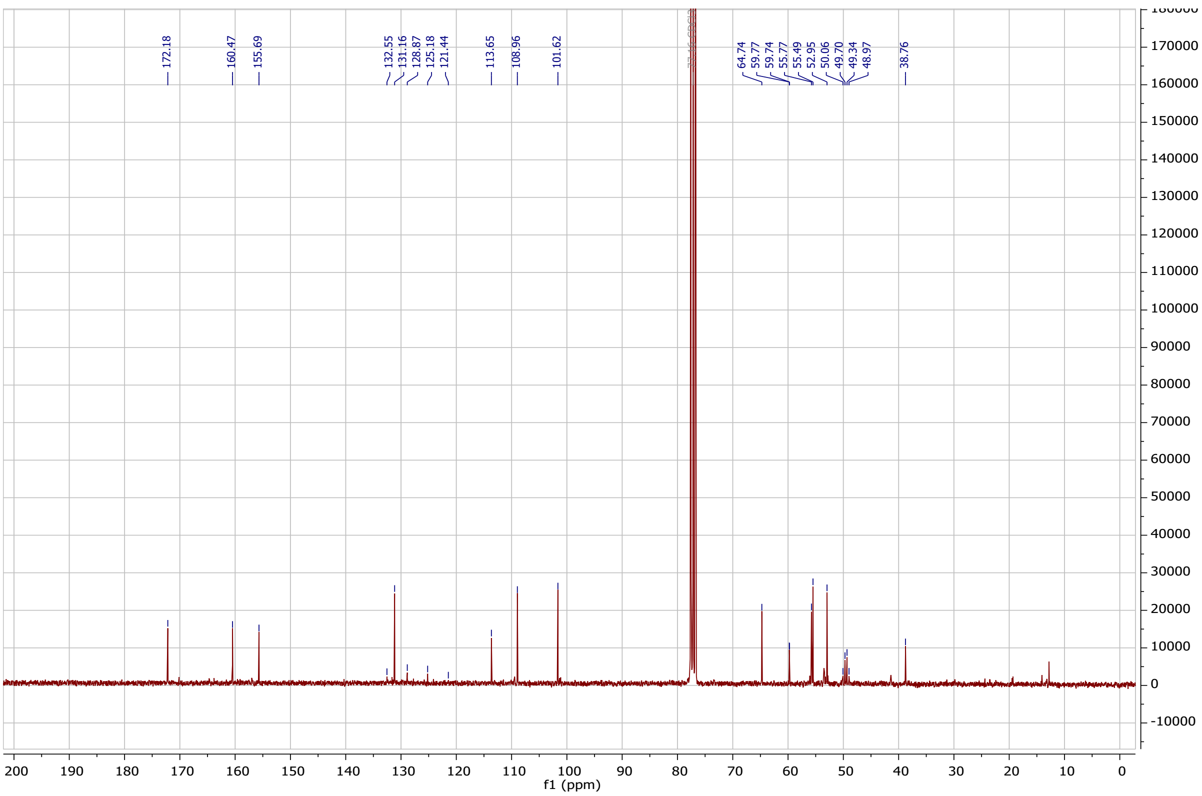


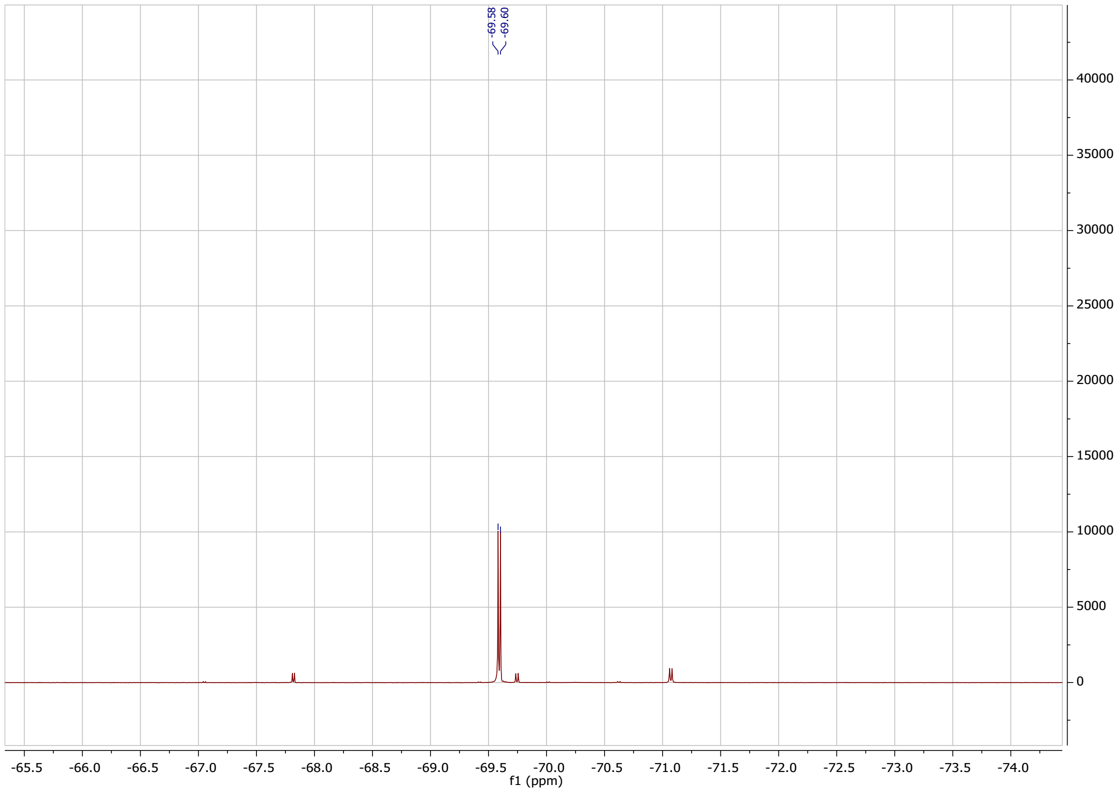



-69.57
-69.59
f1 (ppm)

Methyl (2*R*,3*R*,3a*R*,9b*S*)-7-methoxy-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2d)

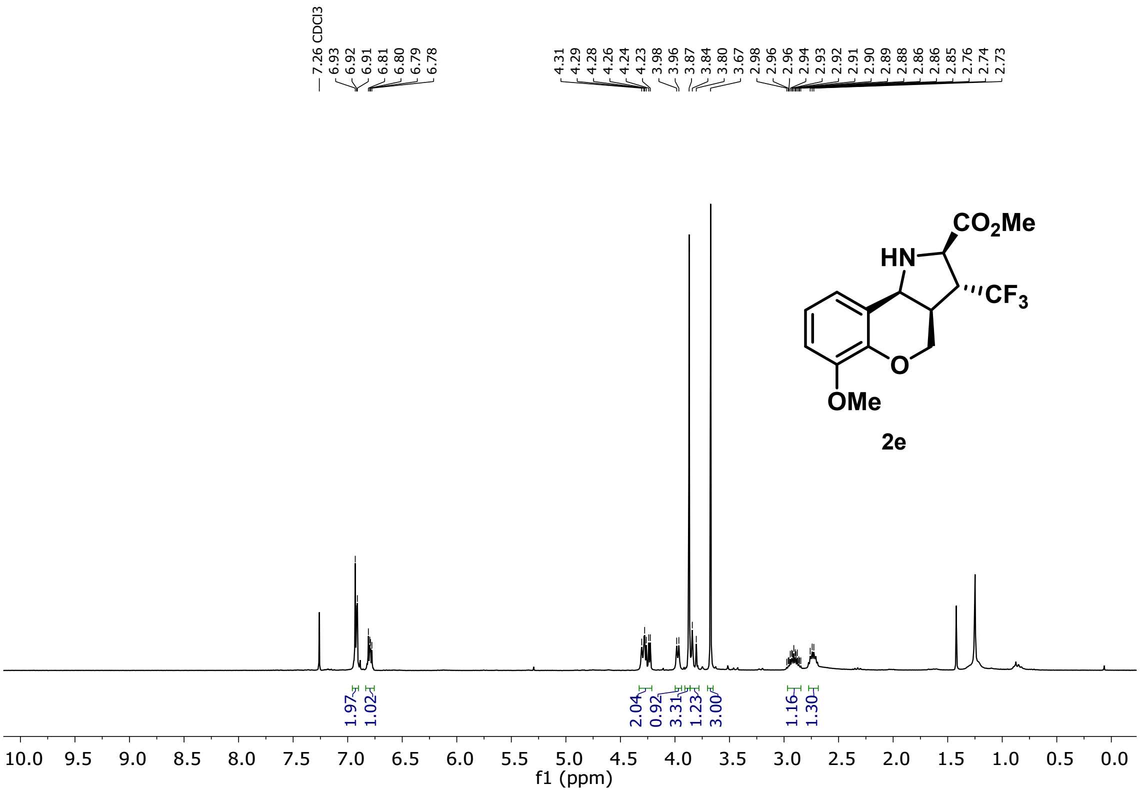


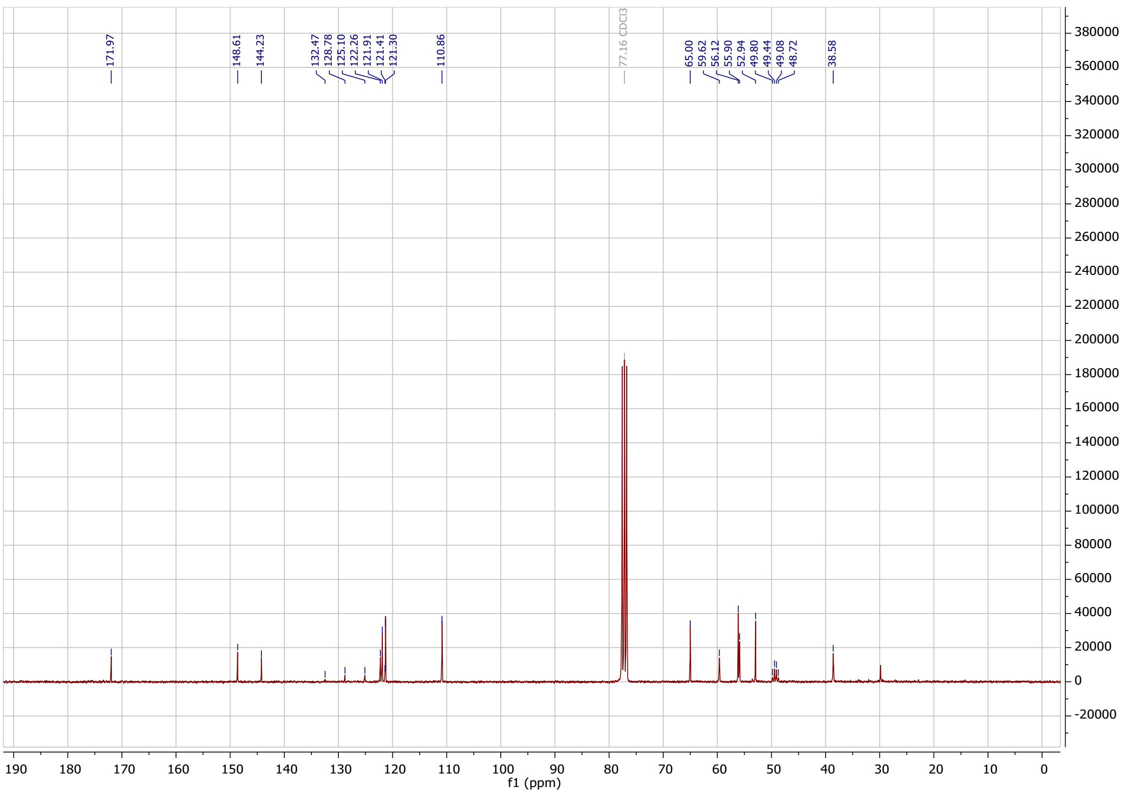


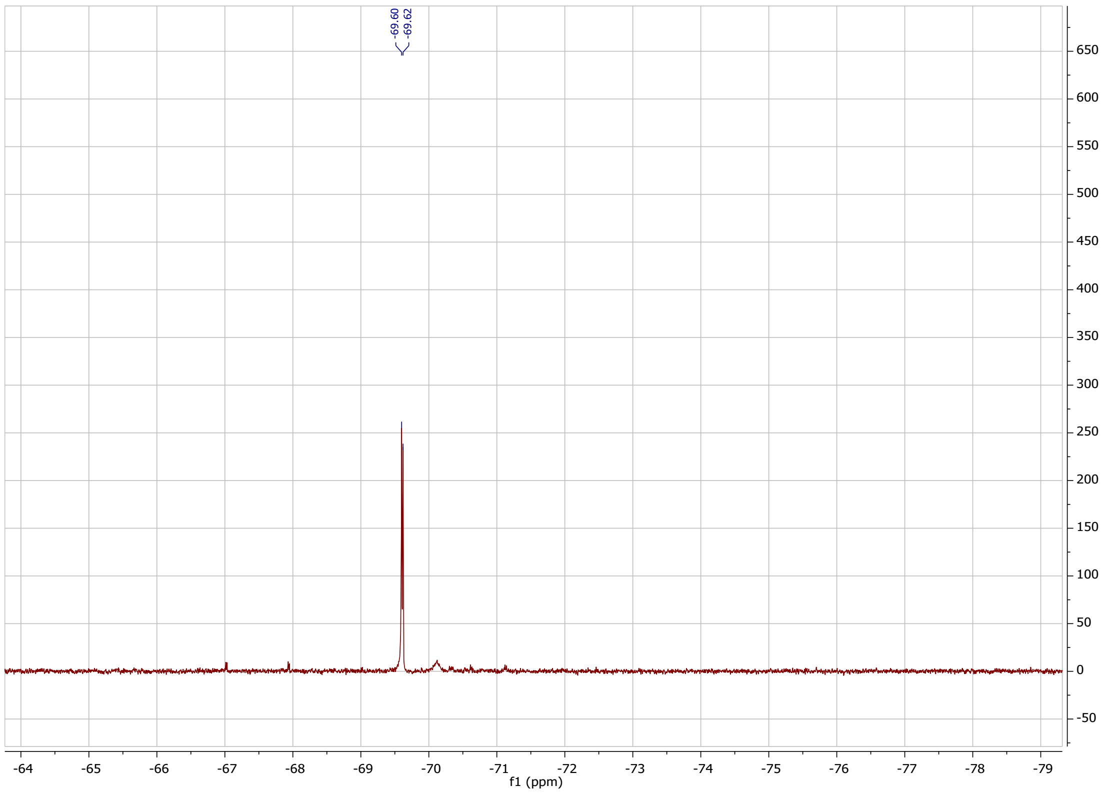


-69.58
-69.60
40000
35000
30000
25000
20000
15000
10000
5000
0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
-70.5
-71.0
-71.5
-72.0
-72.5
-73.0
-73.5
-74.0
f1 (ppm)

Methyl (2*R*,3*R*,3a*R*,9b*S*)-6-methoxy-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2e)

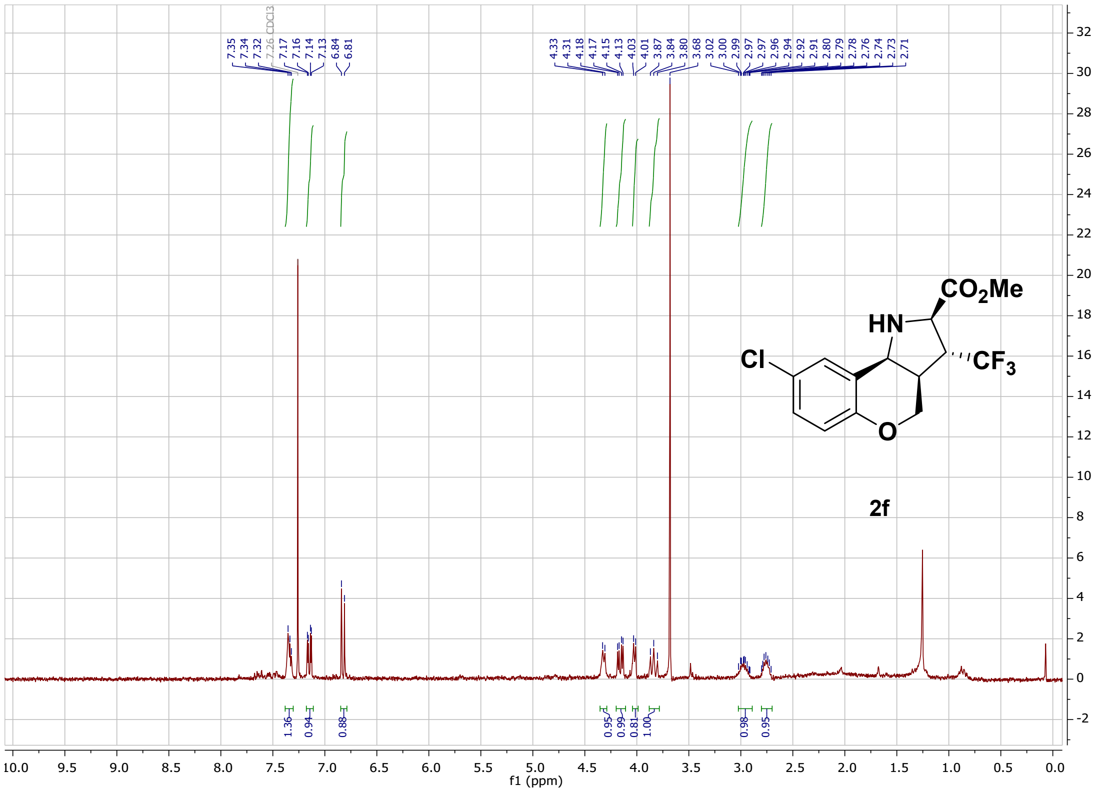


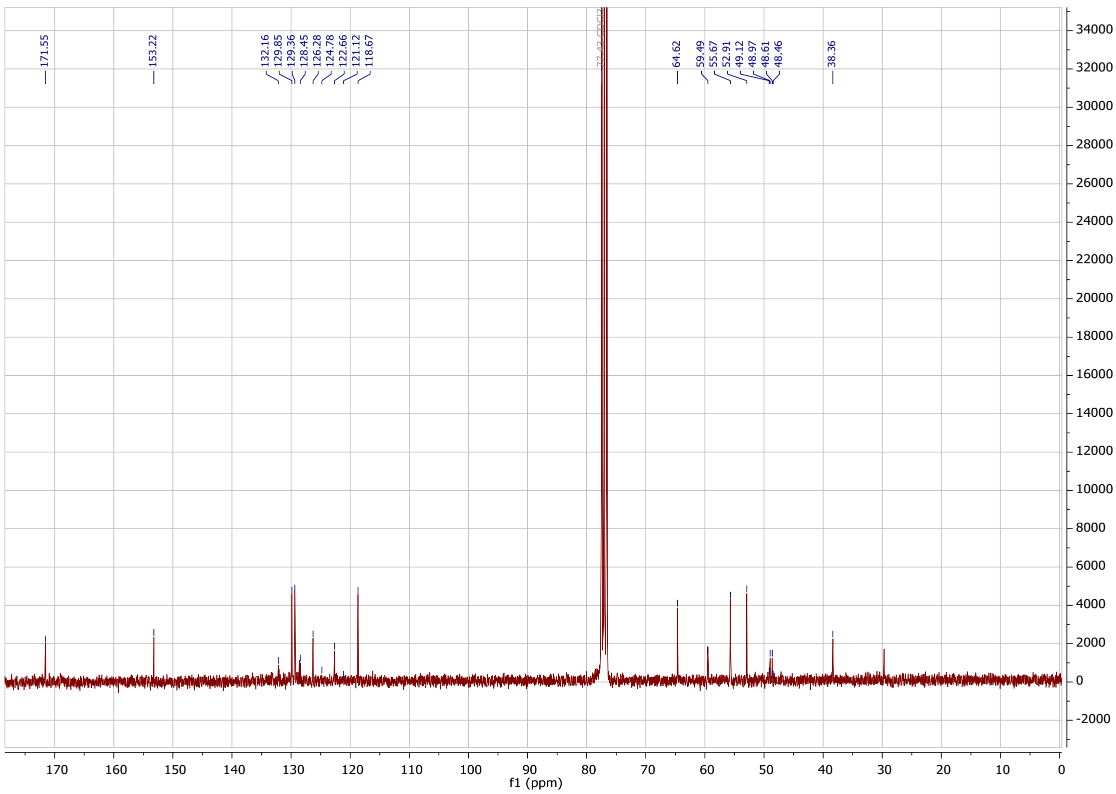


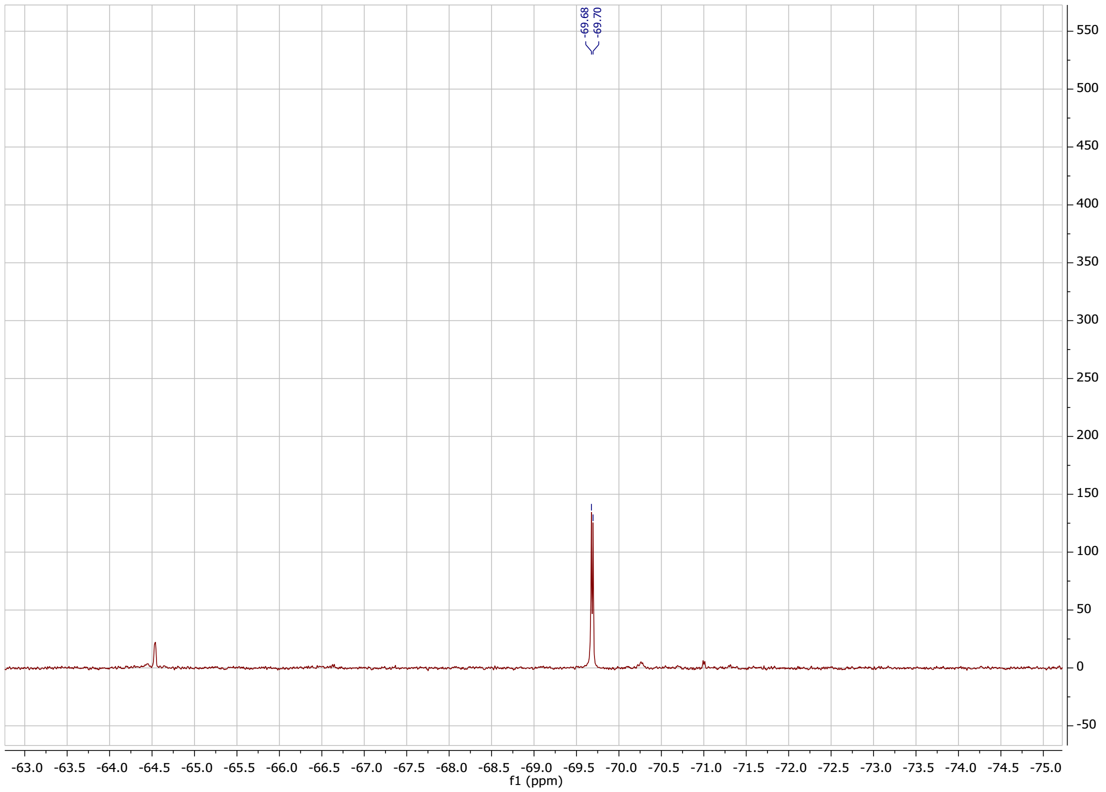


-69.60
-69.62
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
f1 (ppm)

Methyl (2*R*,3*R*,3a*R*,9b*S*)-8-chloro-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2f)



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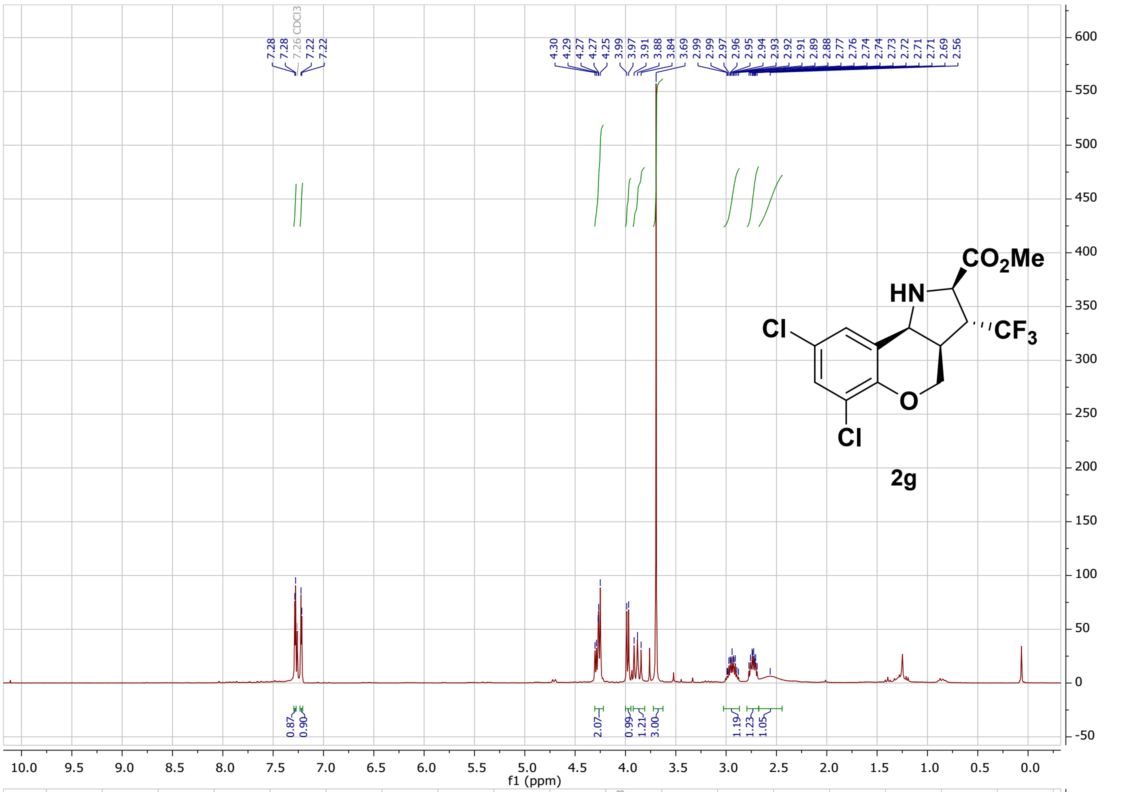
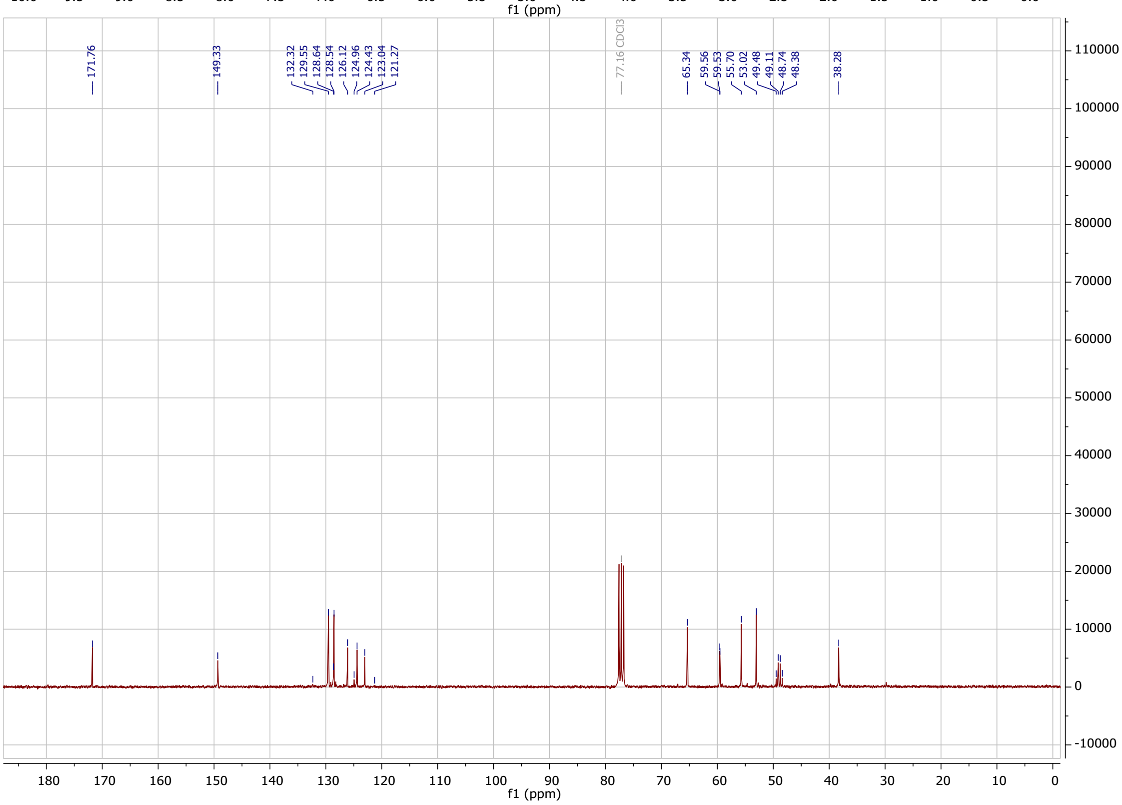
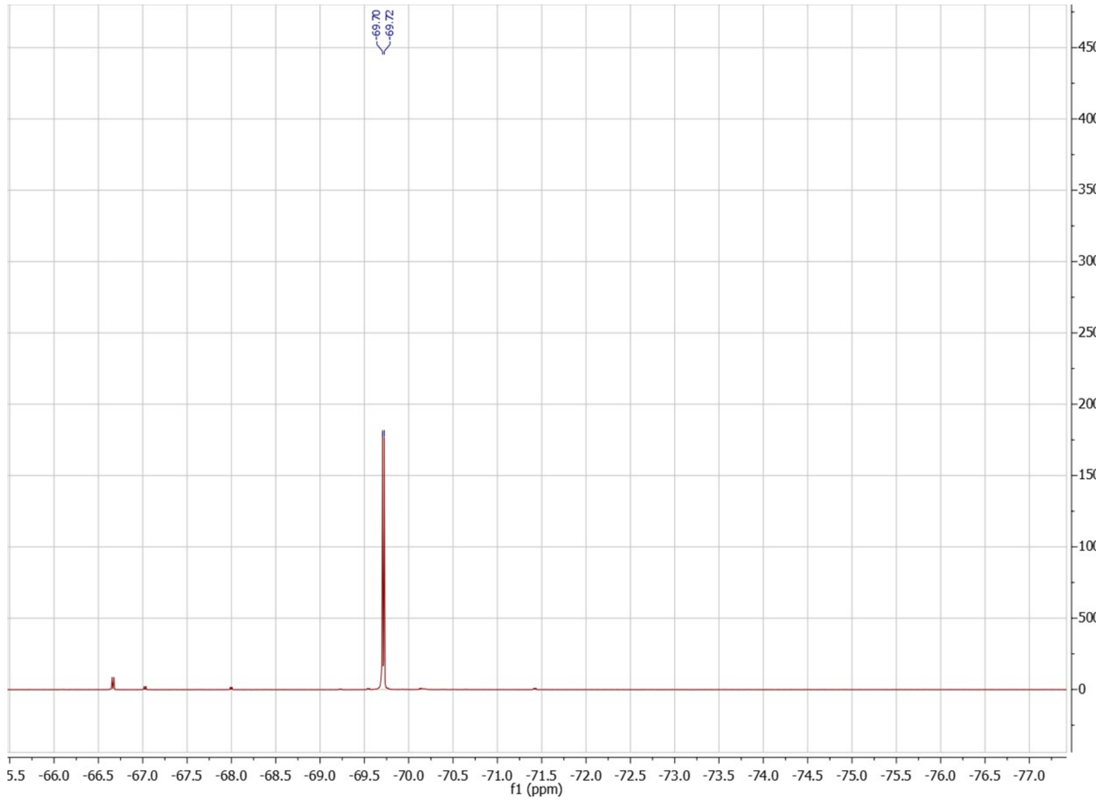
-69.70
550
500
450
400
350
300
250
200
150
100
50
0
-50
-63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0 -70.5 -71.0 -71.5 -72.0 -72.5 -73.0 -73.5 -74.0 -74.5 -75.0
f1 (ppm)

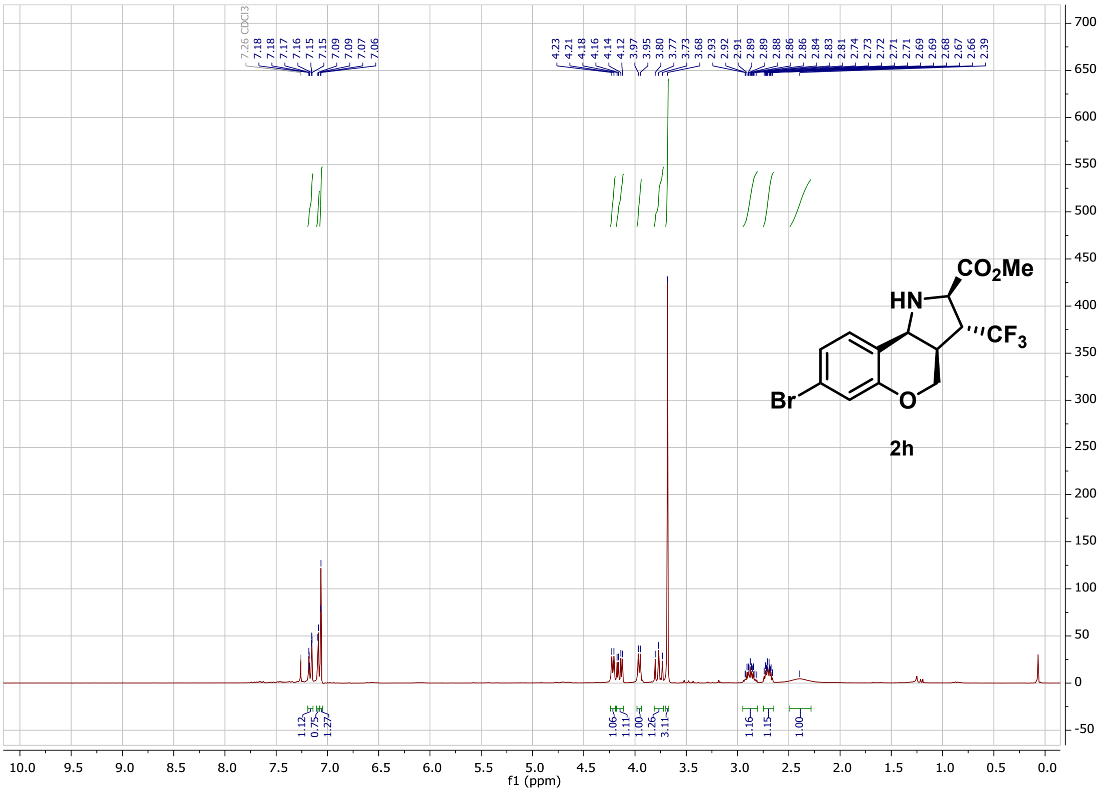
Methyl (2*R*,3*R*,3a*R*,9b*S*)-6,8-dichloro-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2g)

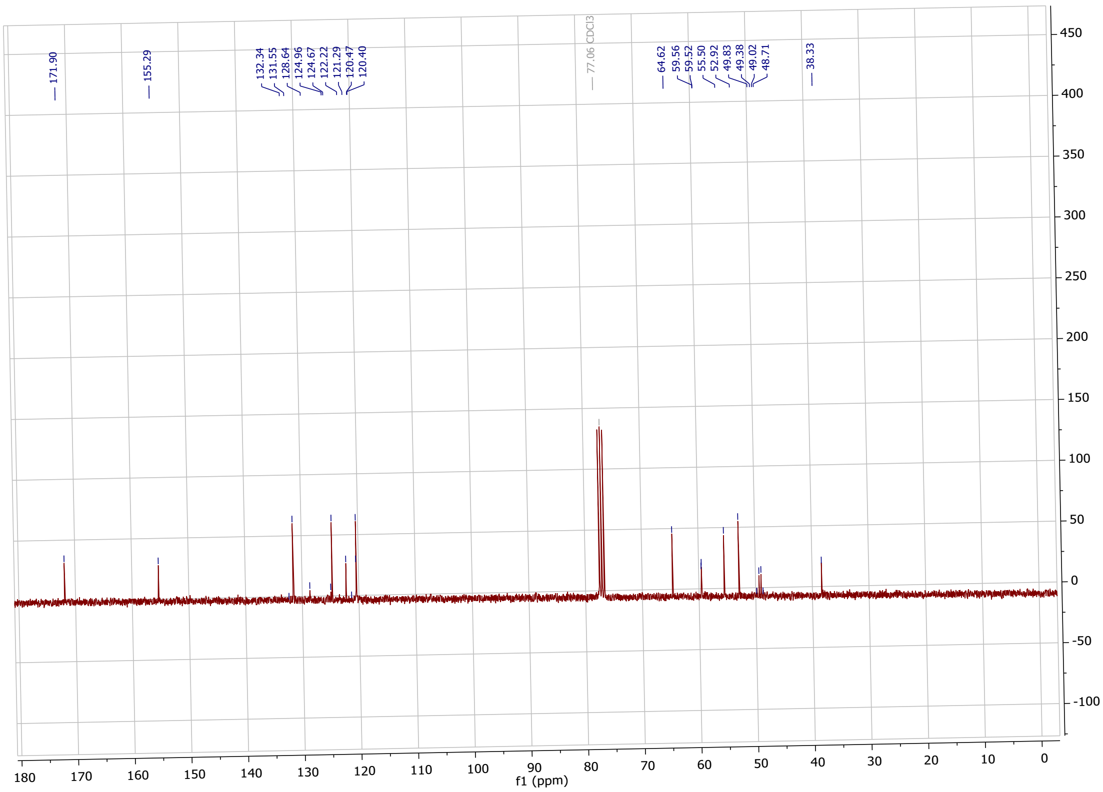


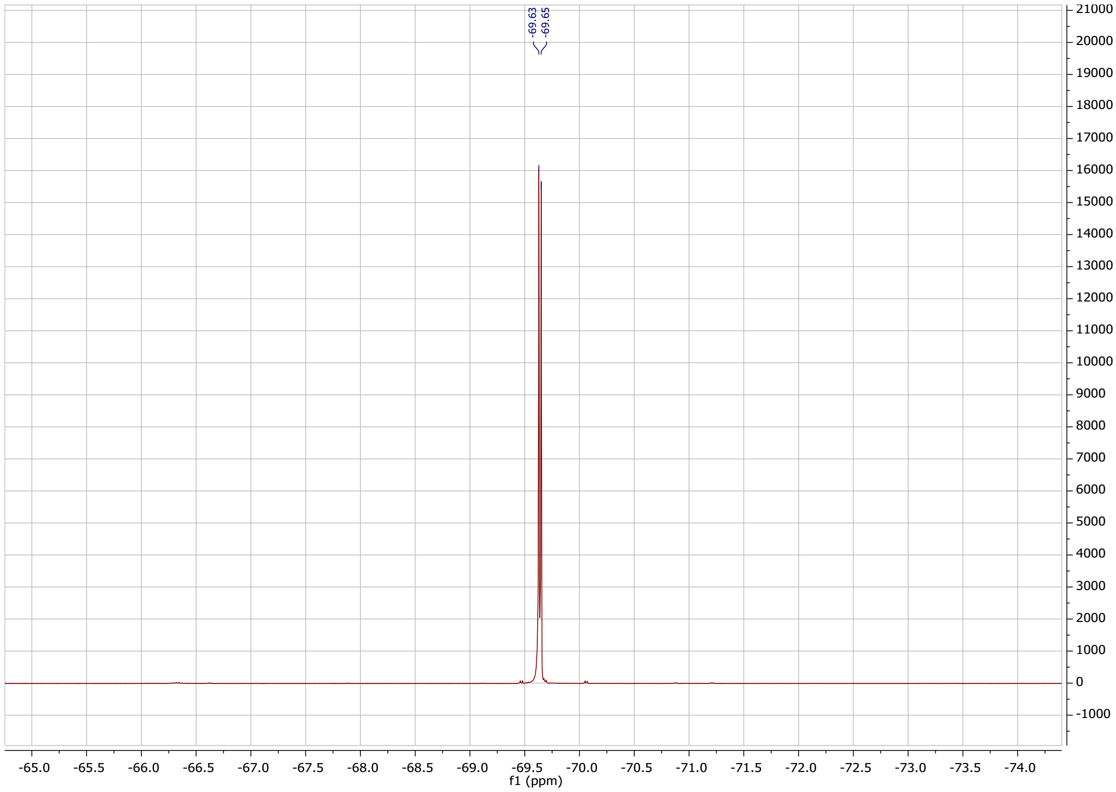



-69.70
-69.72
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
5.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0 -70.5 -71.0 -71.5 -72.0 -72.5 -73.0 -73.5 -74.0 -74.5 -75.0 -75.5 -76.0 -76.5 -77.0
f1 (ppm)

Methyl (2*R*,3*R*,3a*R*,9b*S*)-7-bromo-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (2h)

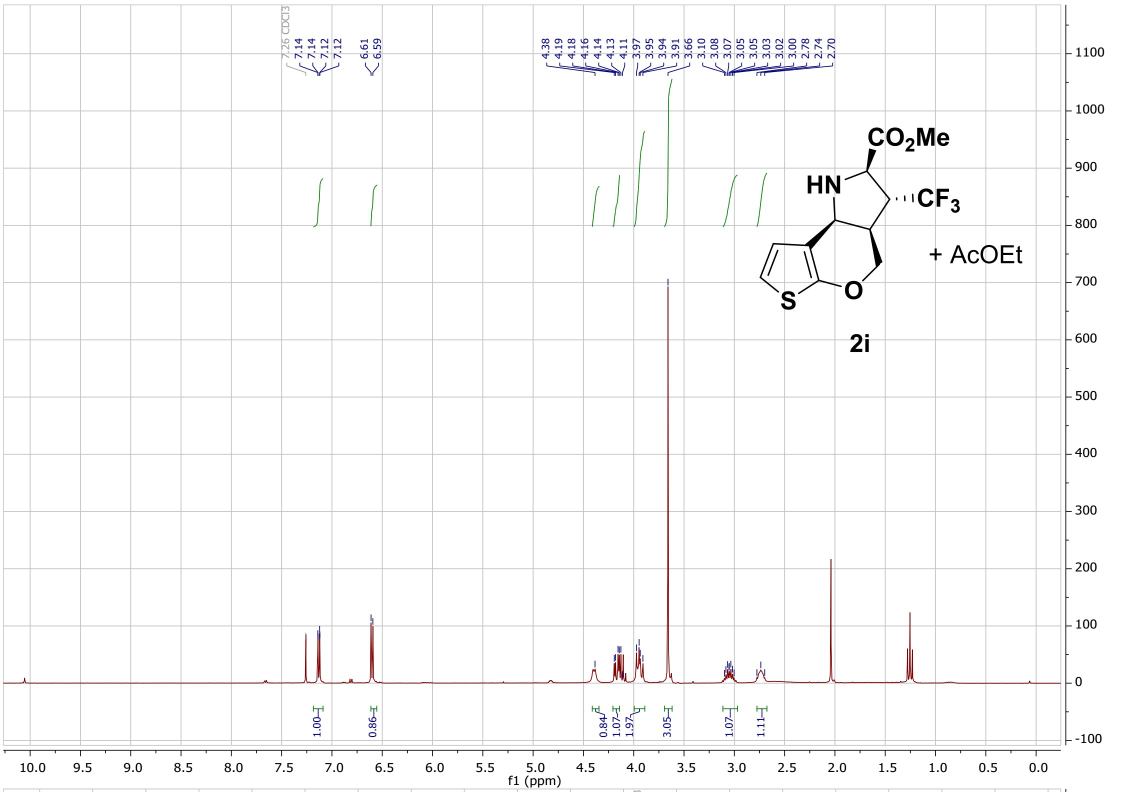


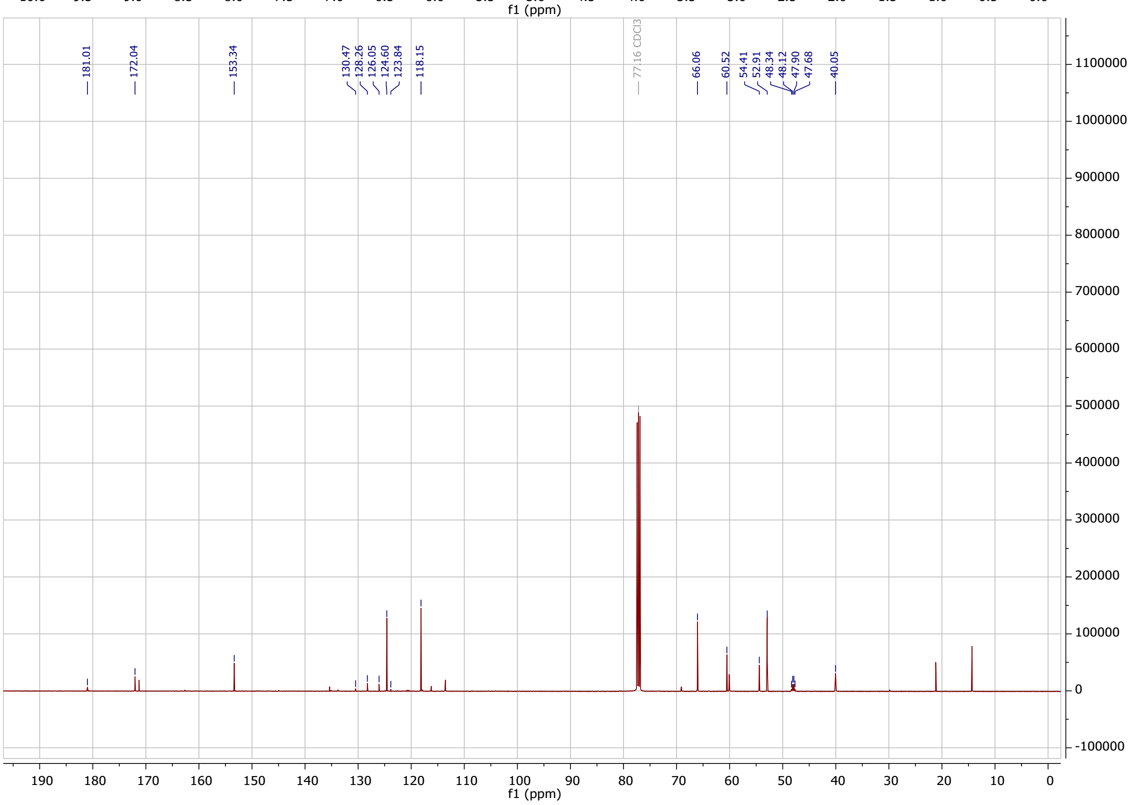


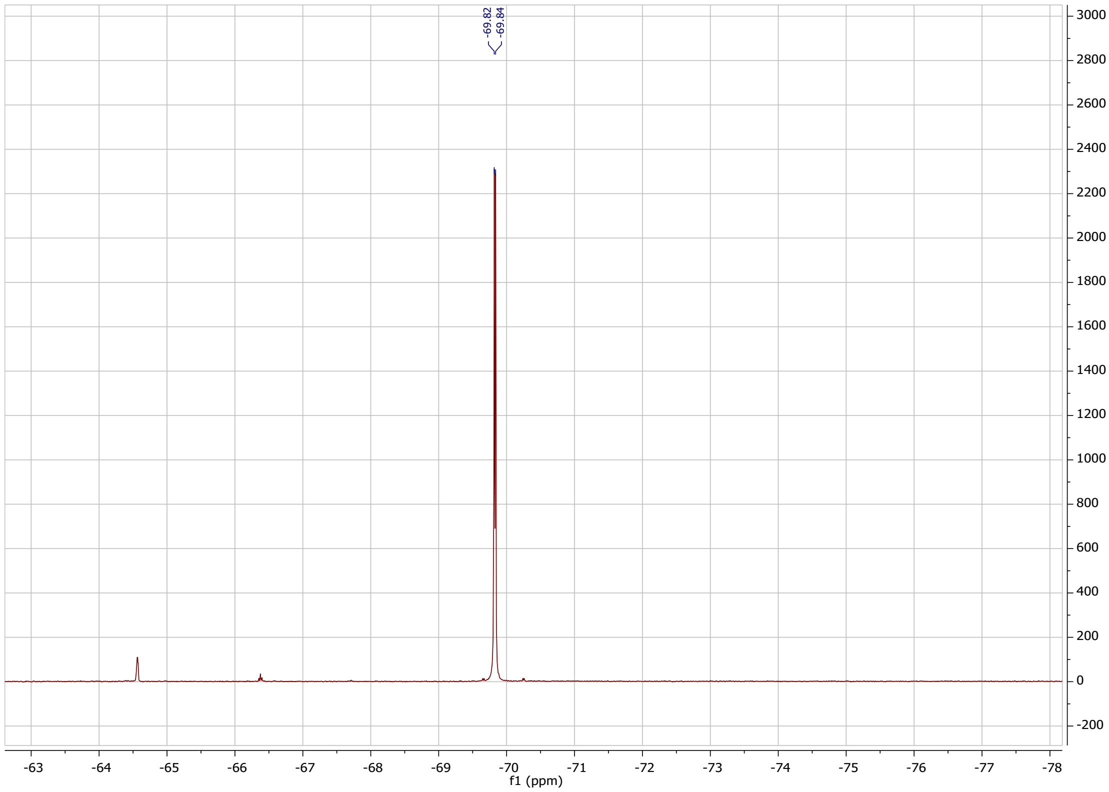


-69.63
-69.65
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
-70.5
-71.0
-71.5
-72.0
-72.5
-73.0
-73.5
-74.0
f1 (ppm)

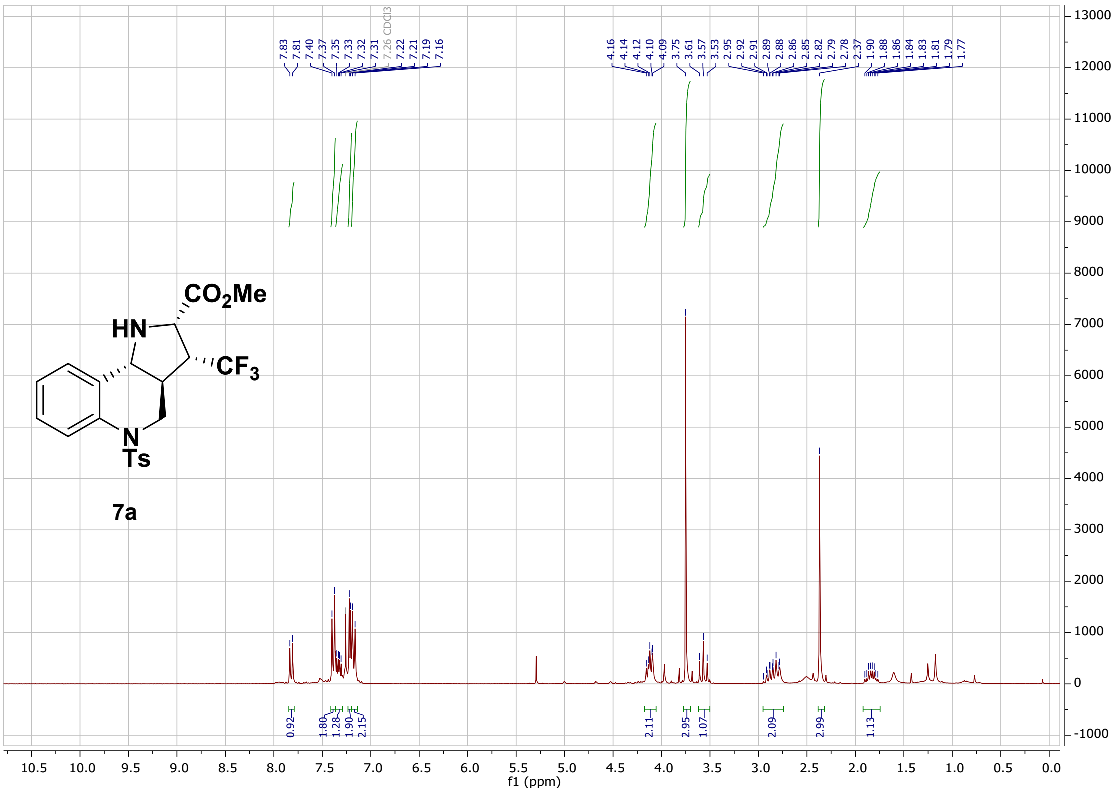
Methyl (2R,3R,3aR,8bS)-3-trifluoromethyl-1,2,3,3a,4,8b-hexahydrothieno[3',2':5,6]pyrano[4,3-*b*]pyrrolo-2-carboxylate (2i)

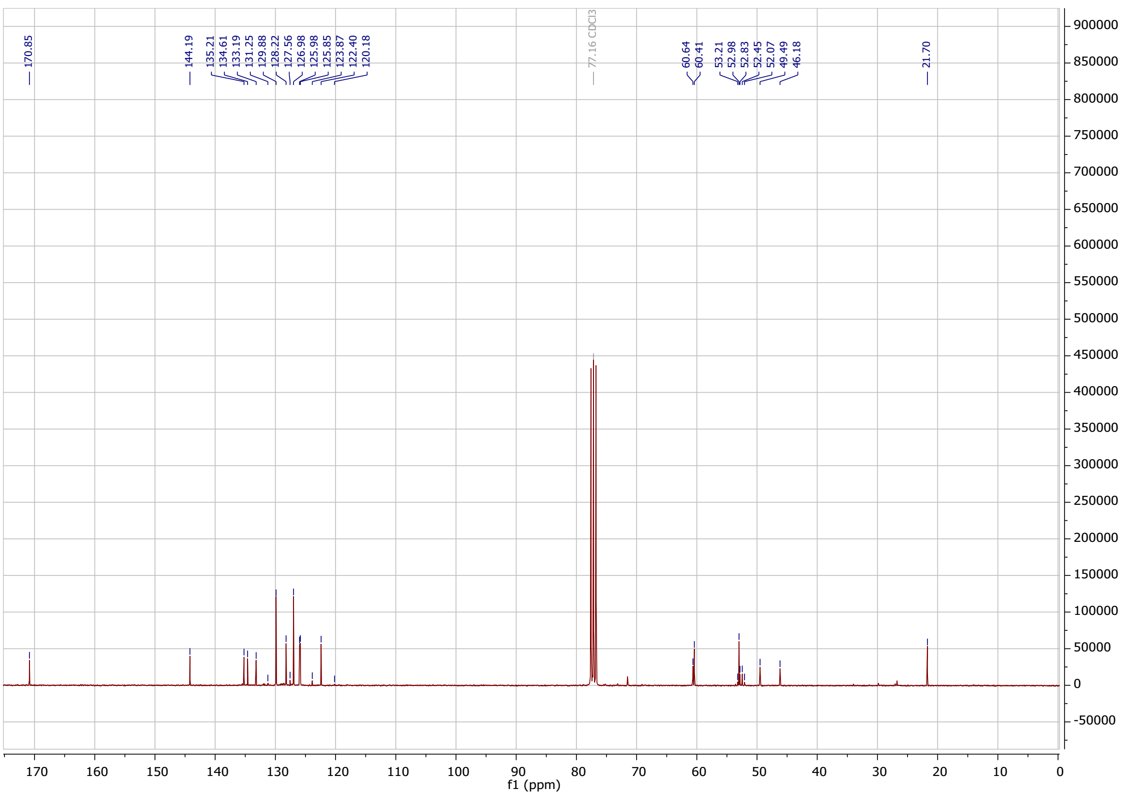


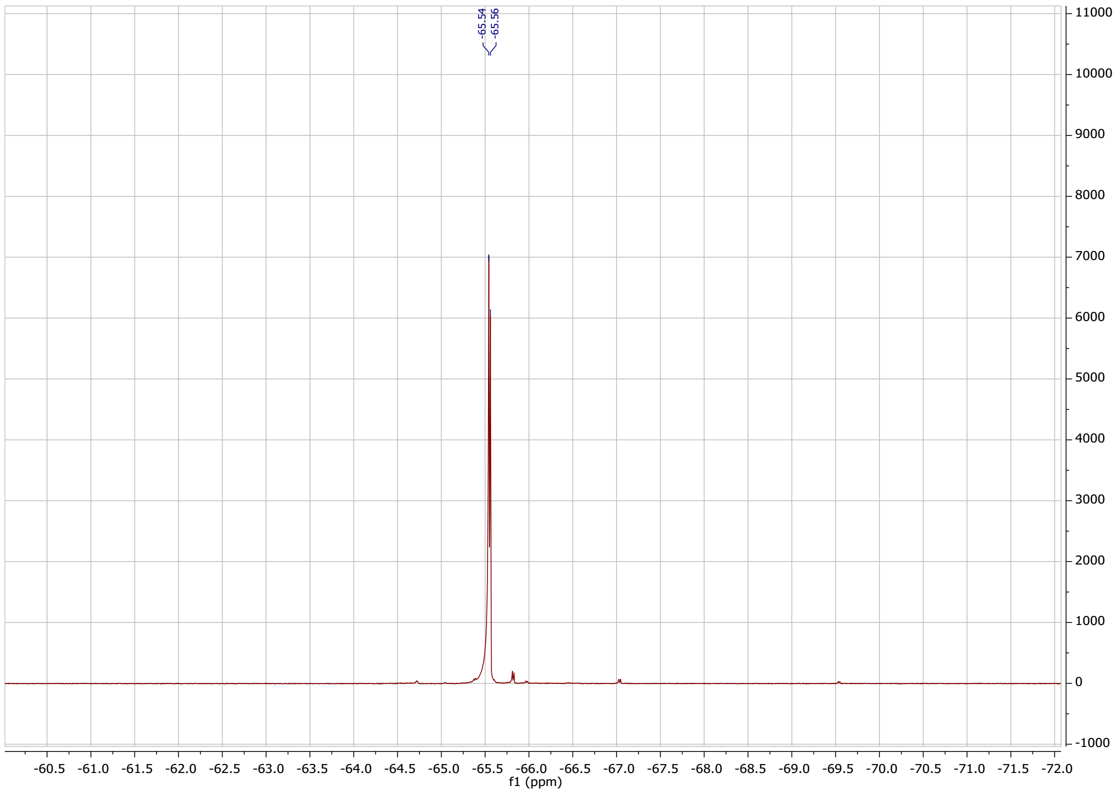



-69.82
-69.84
f1 (ppm)

Methyl (2*S*,3*R*,3a*S*,9b*R*)-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7a)

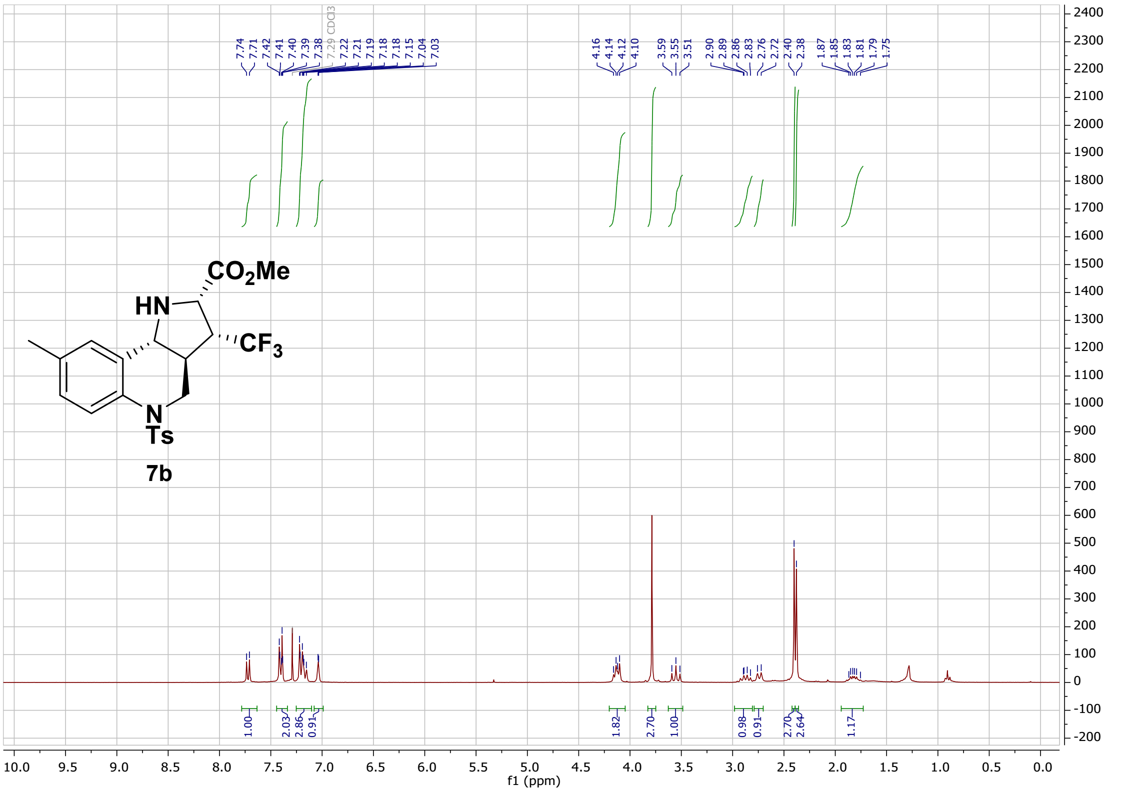


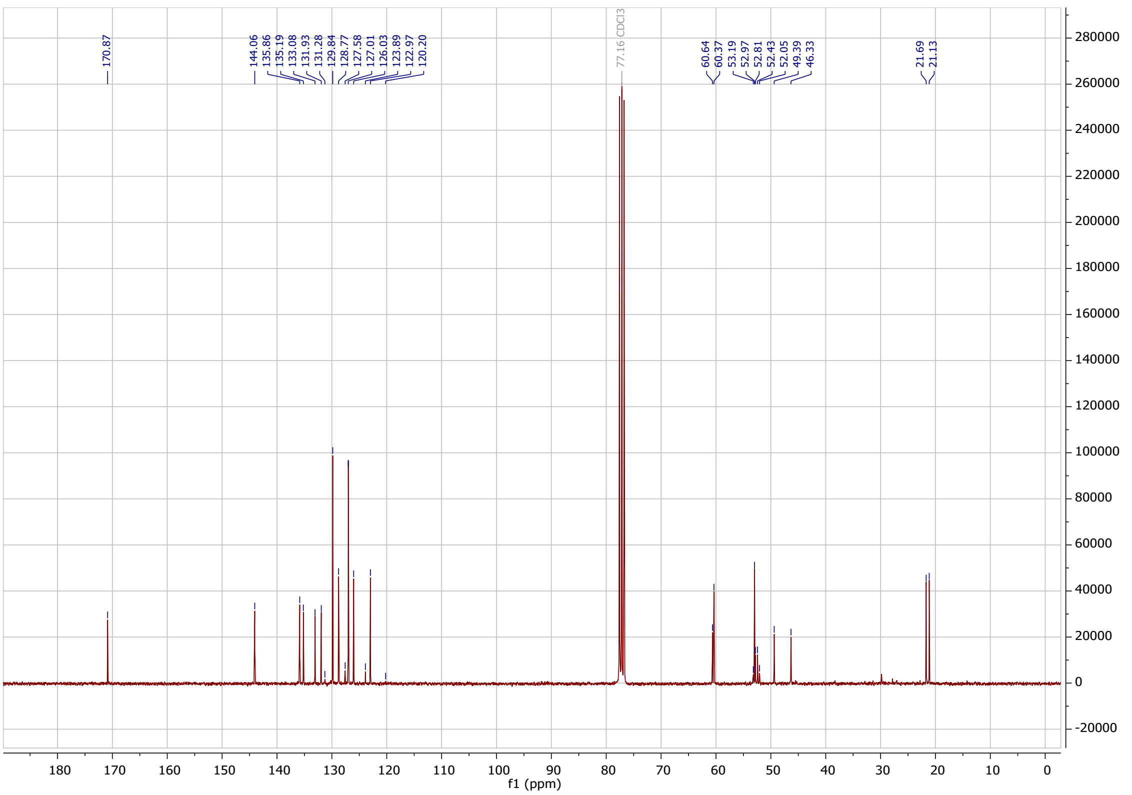


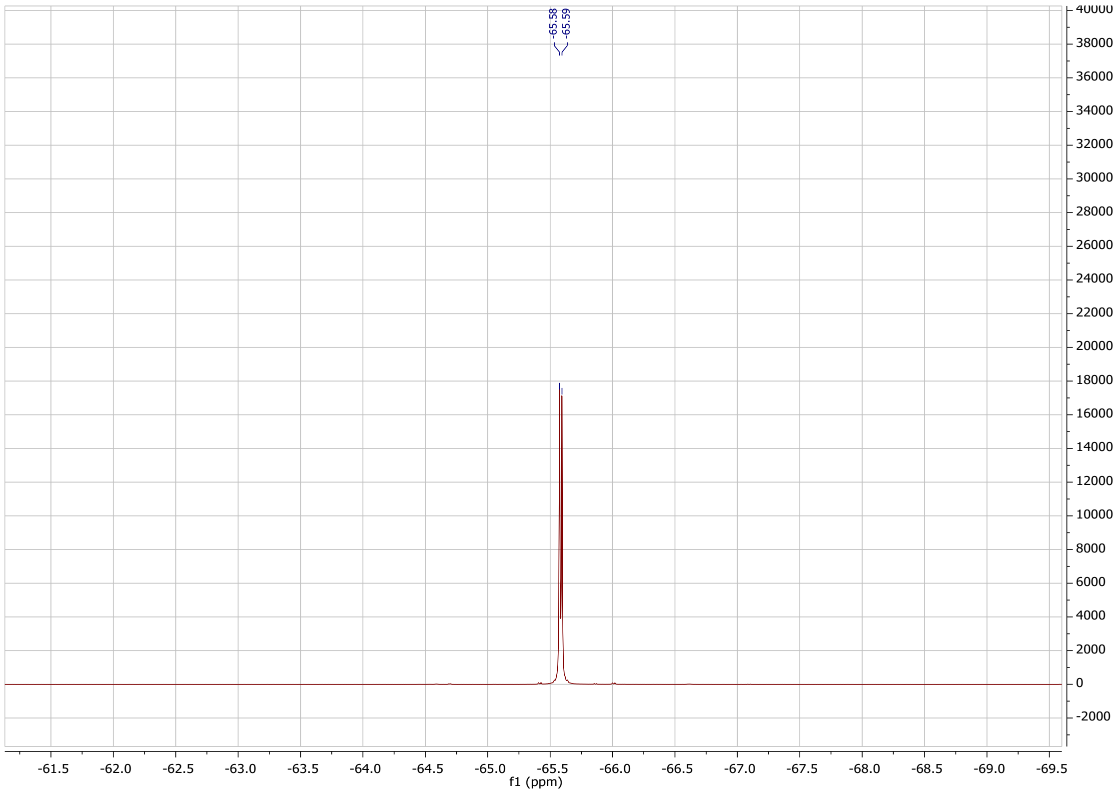


-65.54
-65.56
f1 (ppm)

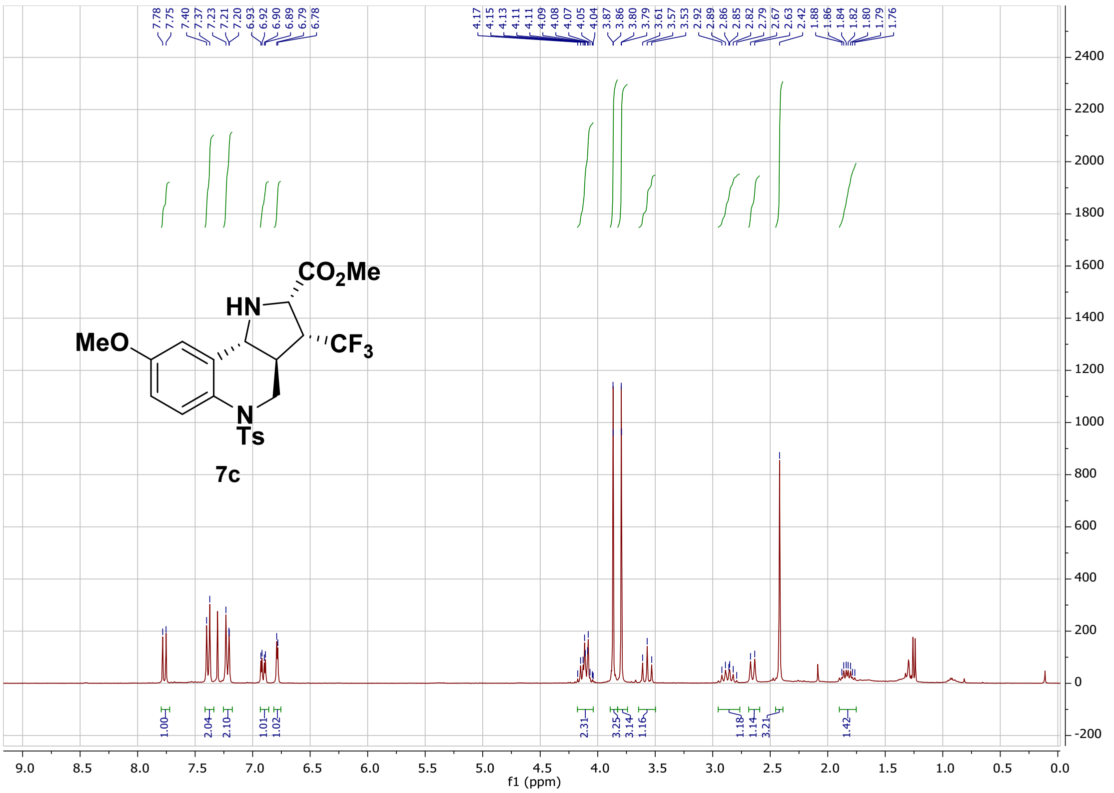
Methyl (2S,3R,3aS,9bR)-8-methyl-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[3,2-c]quinoline-2-carboxylate (7b)

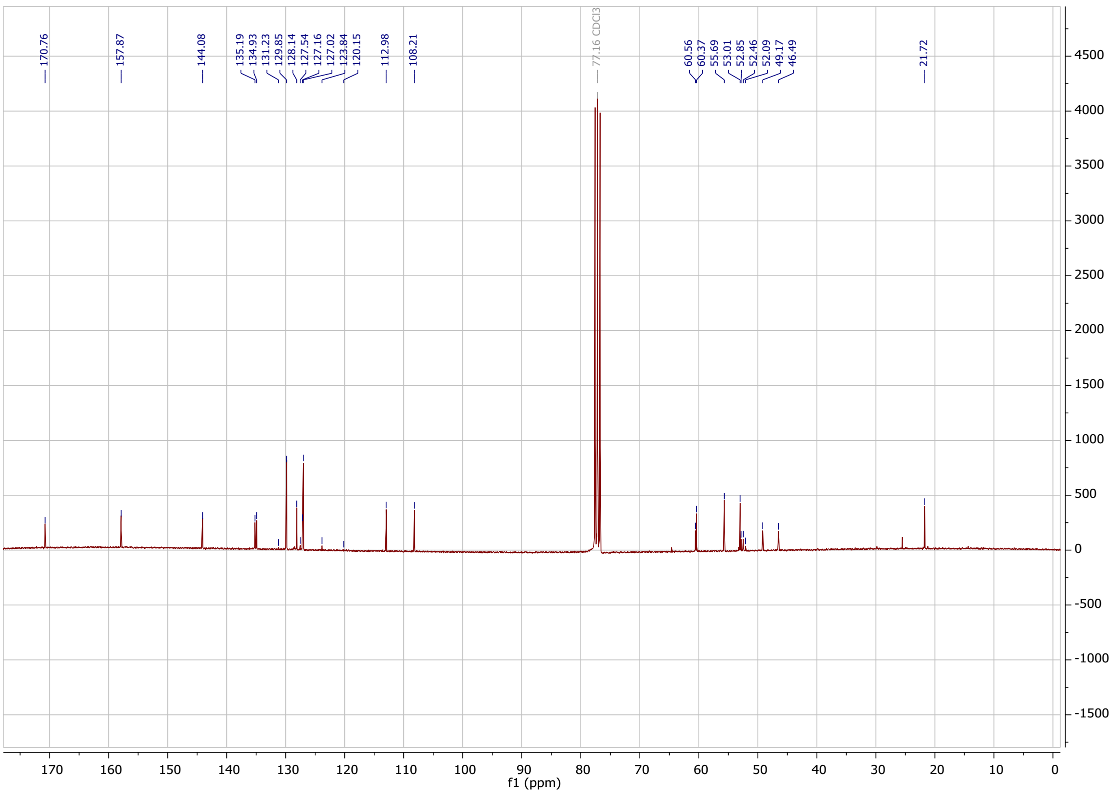


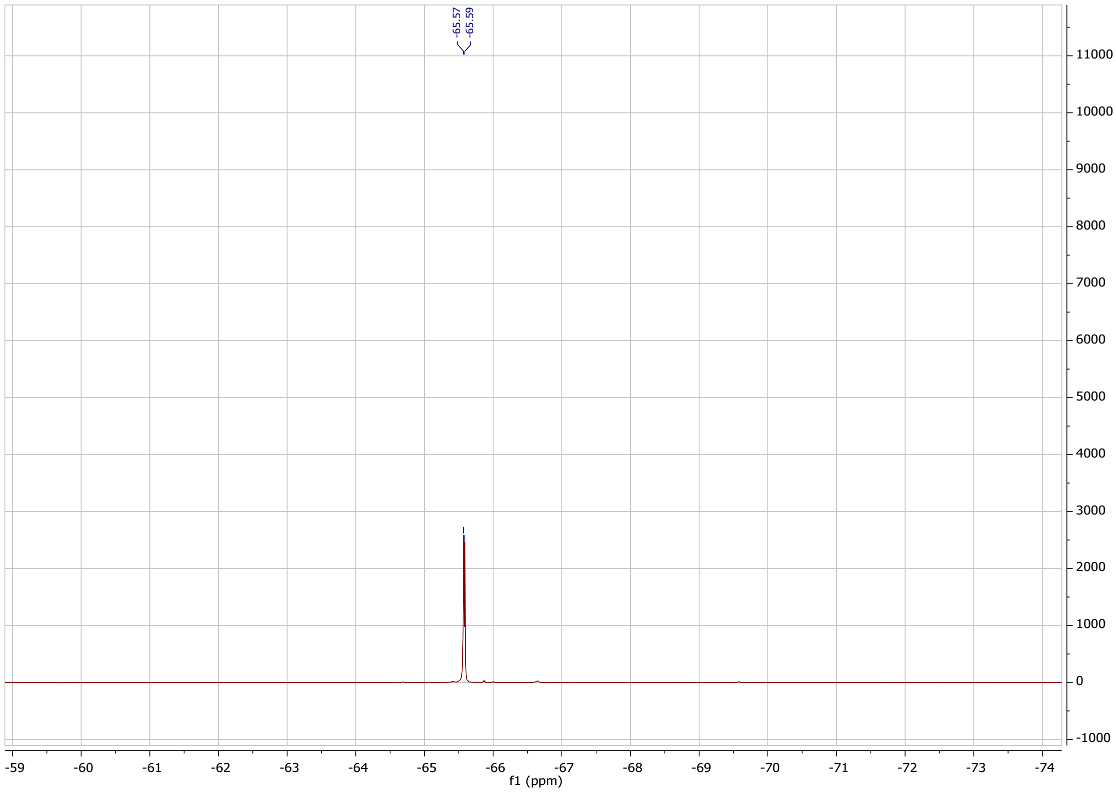



-65.58
-65.59
f1 (ppm)

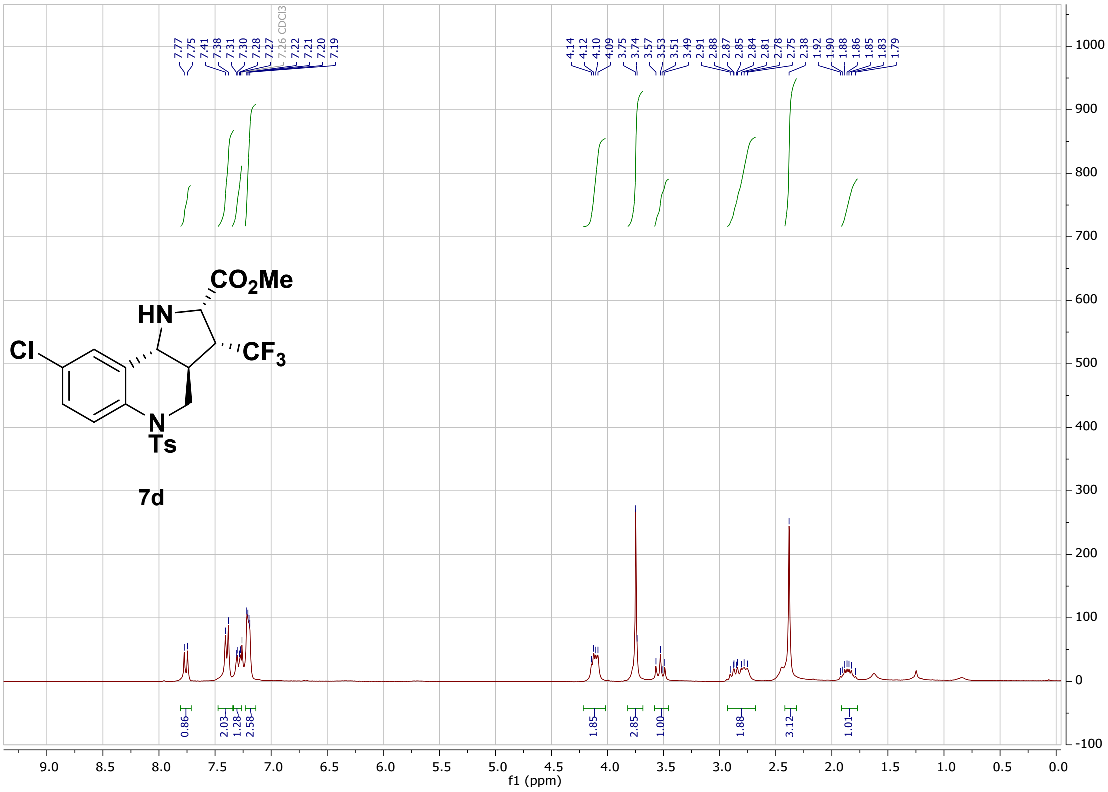
Methyl (2*S*,3*R*,3a*S*,9b*R*)-8-methoxy-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7c)

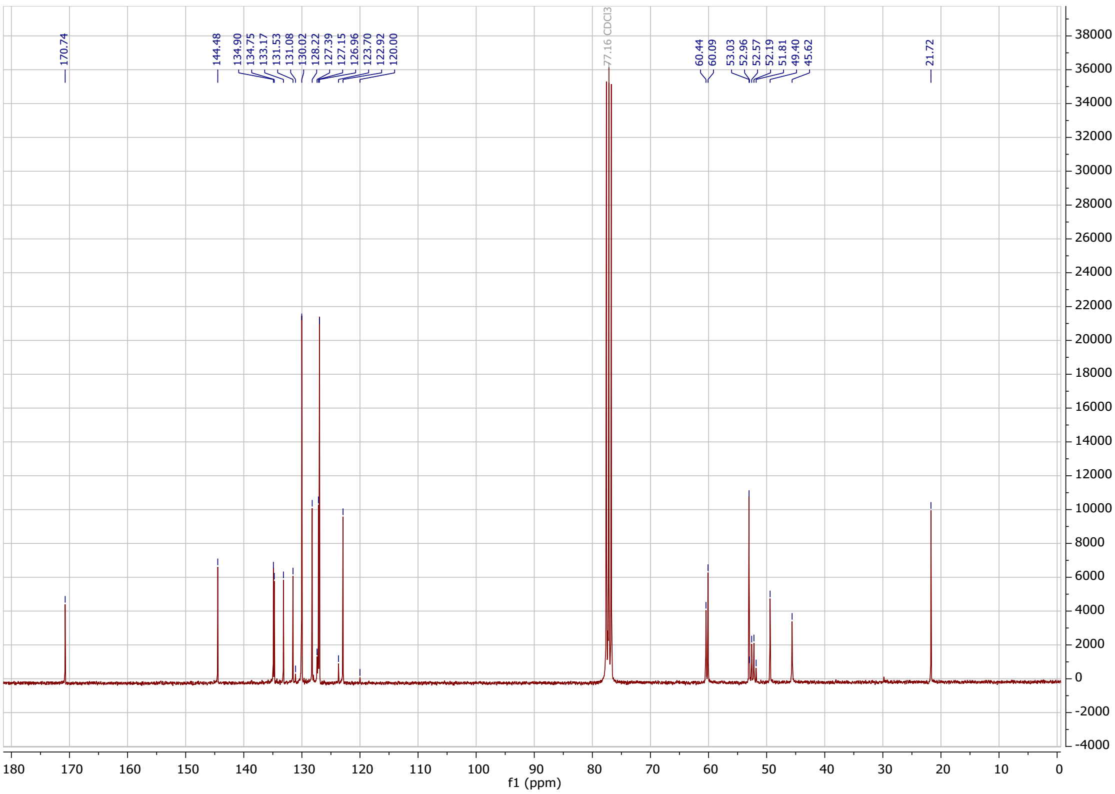


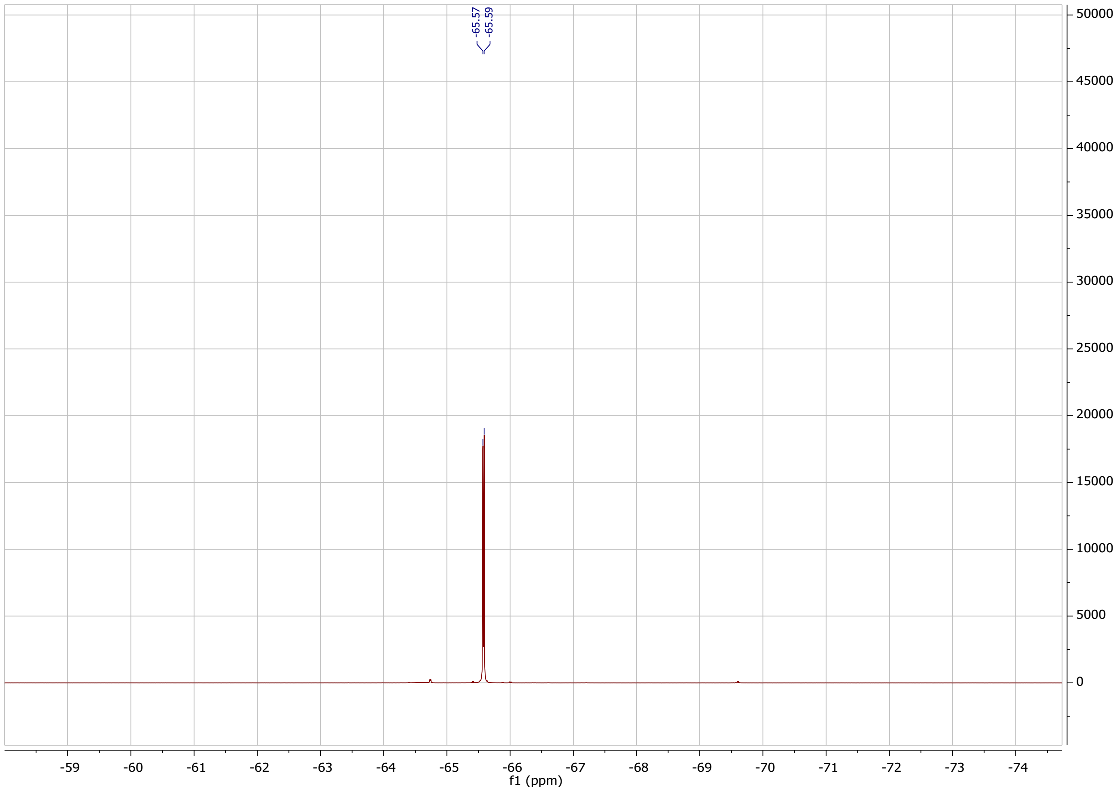



-65.57
-65.59
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
f1 (ppm)

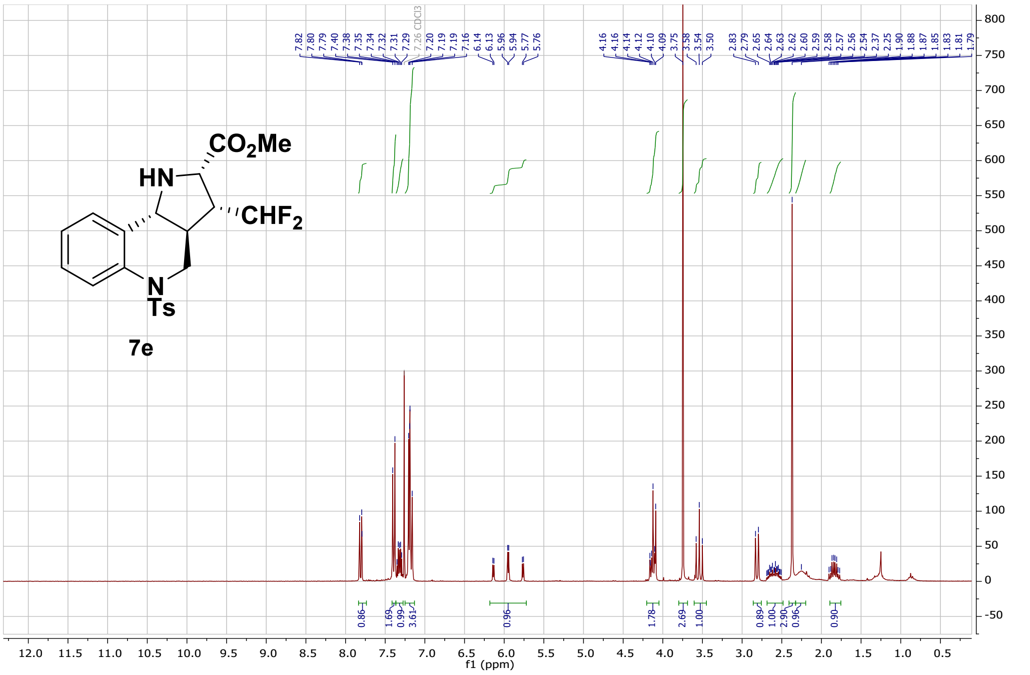
Methyl (2*S*,3*R*,3a*S*,9b*R*)-8-chloro-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7d)

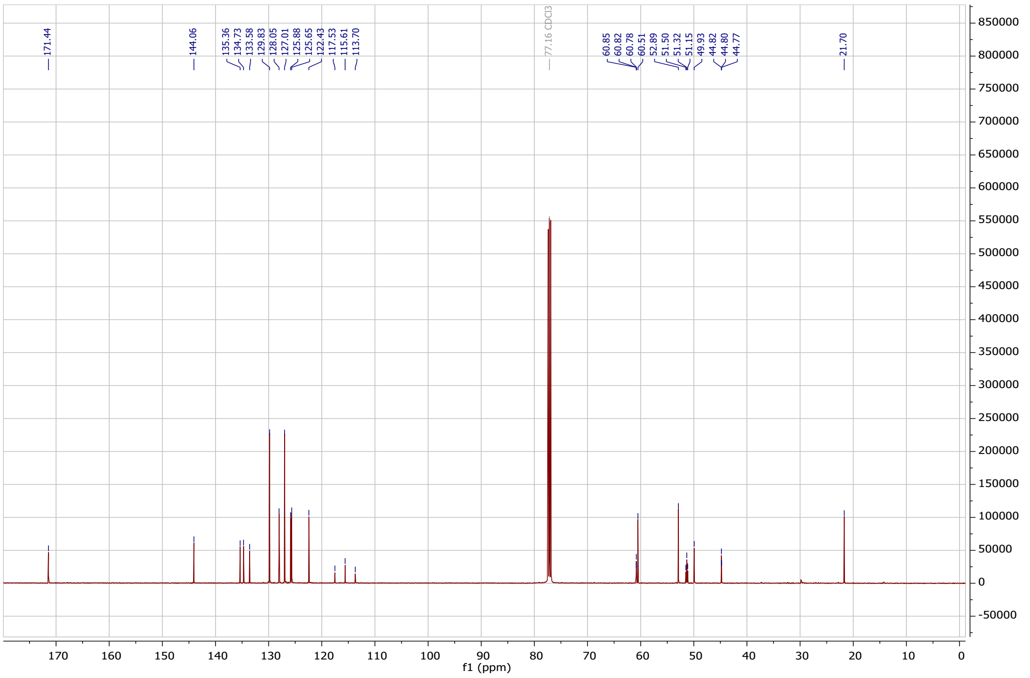


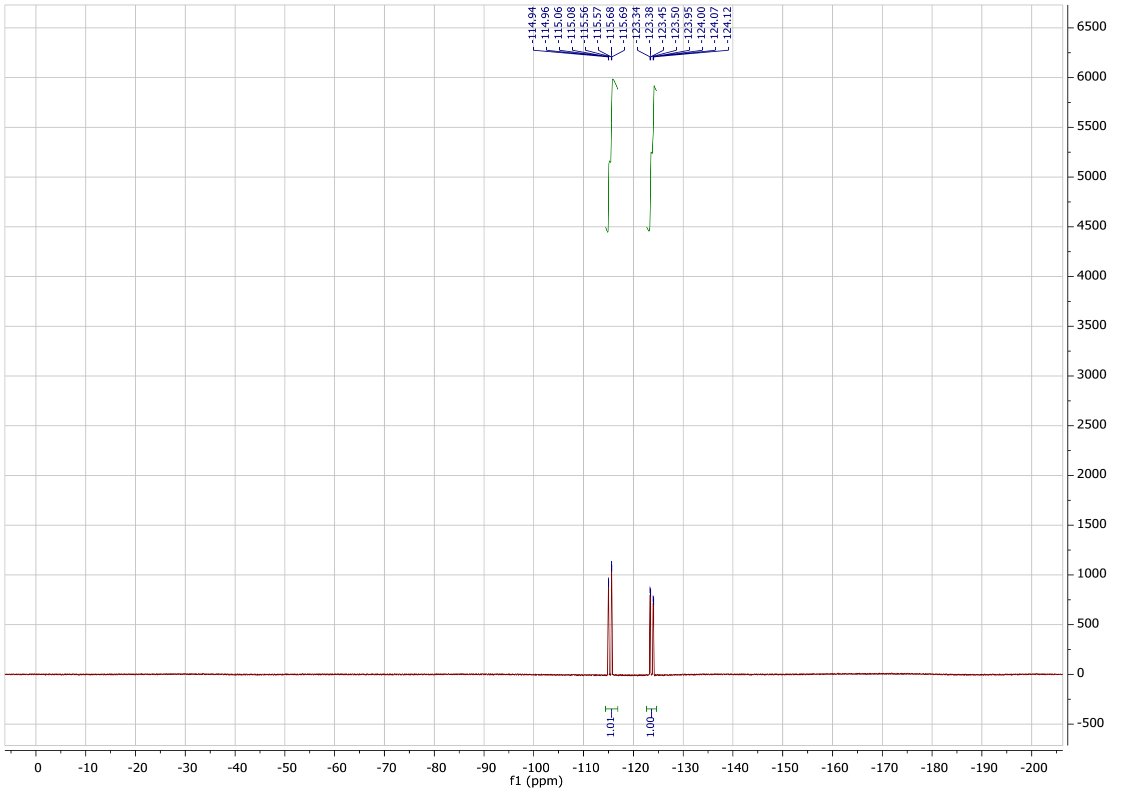



-65.57
-65.59
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
f1 (ppm)

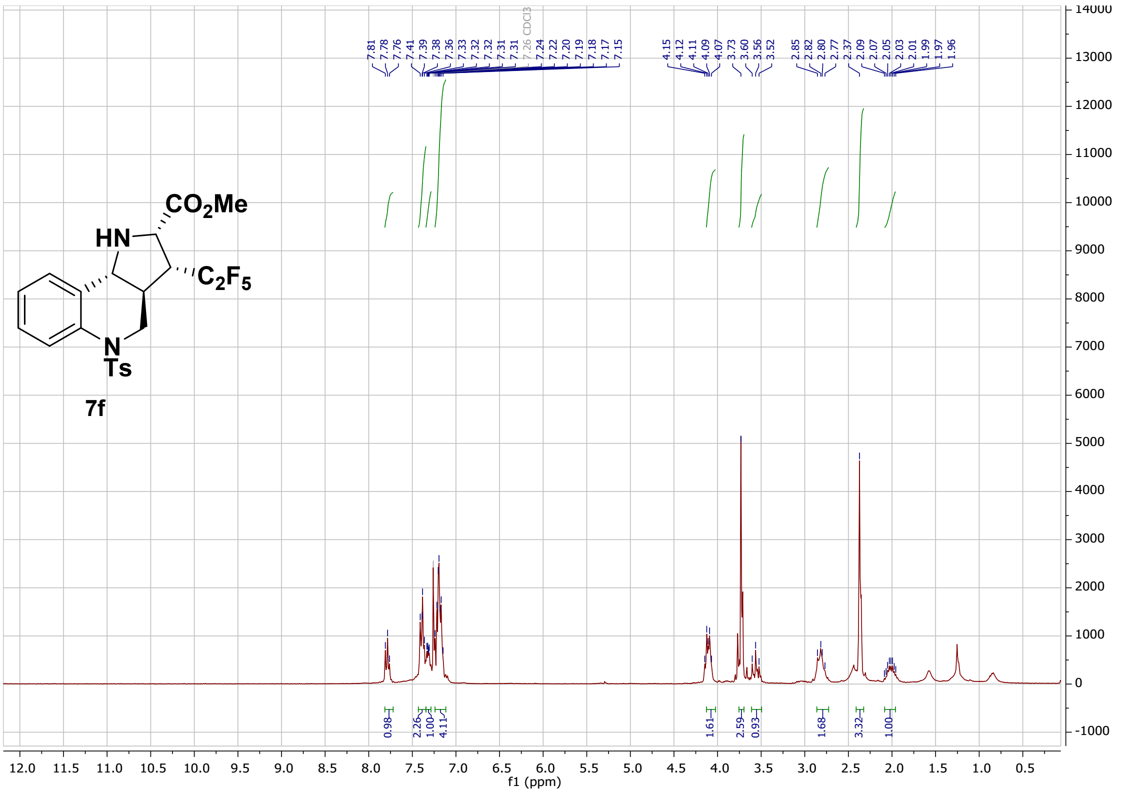
Methyl (2*S*,3*R*,3a*S*,9b*R*)-3-difluoromethyl-5-tosyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7e)

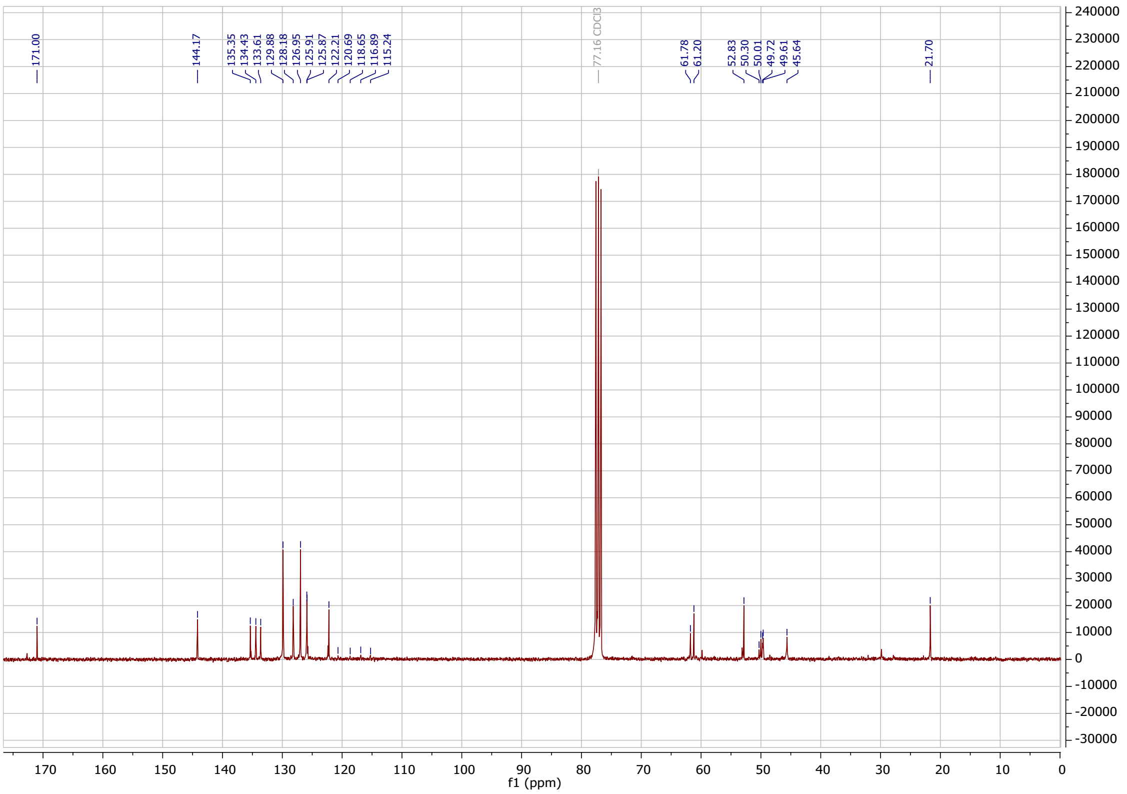


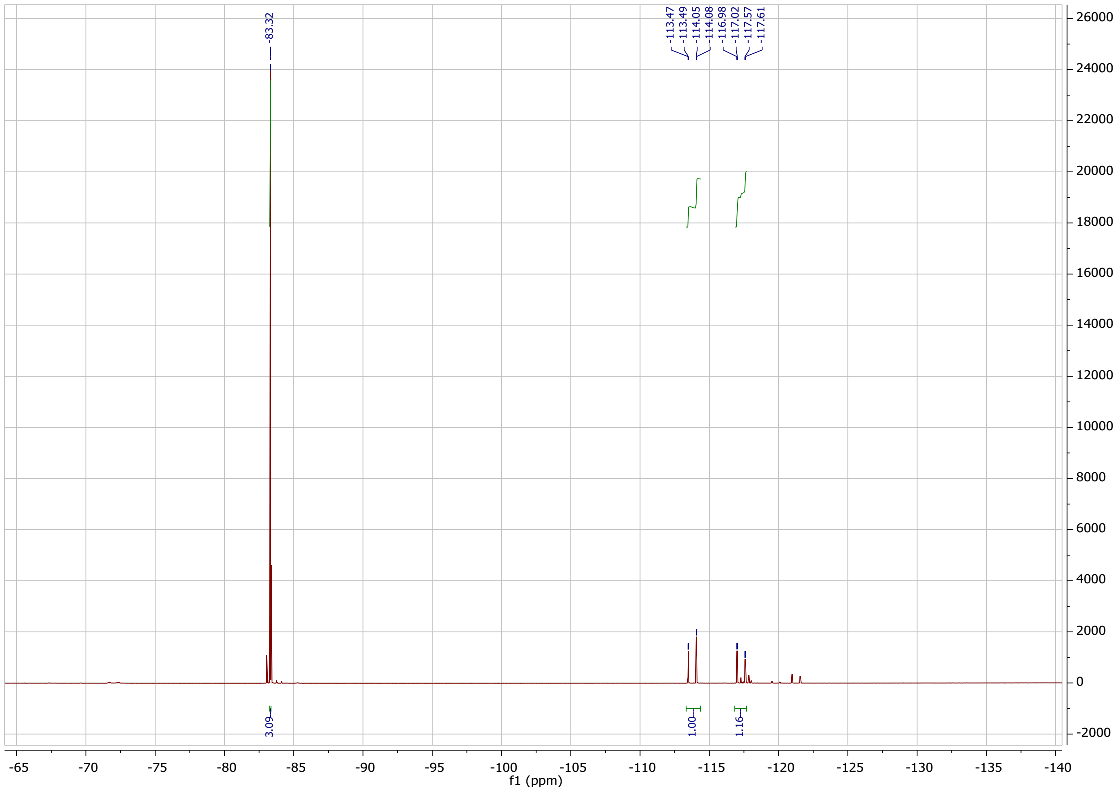



-114.94
-114.96
-115.06
-115.08
-115.56
-115.57
-115.68
-115.69
-123.34
-123.38
-123.45
-123.50
-123.95
-124.00
-124.07
-124.12
1.01
1.00
f1 (ppm)

Methyl (2*S*,3*R*,3a*S*,9b*R*)-3-perfluoroethyl-5-tosyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (7f)

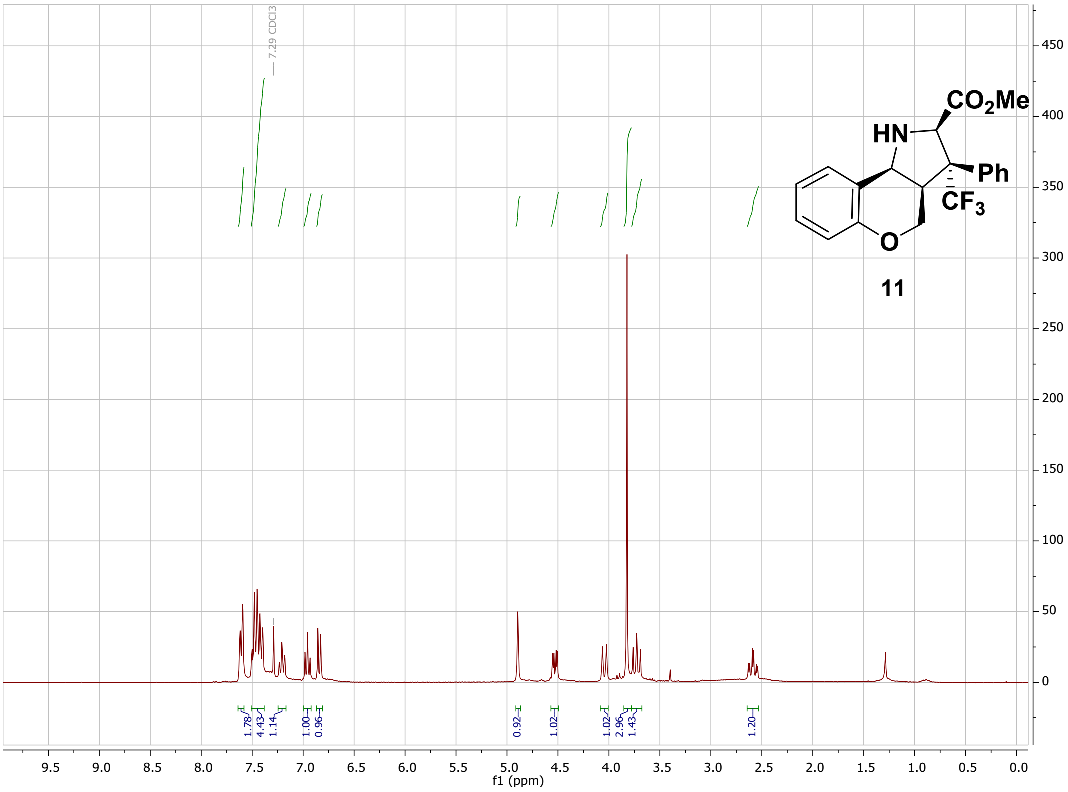


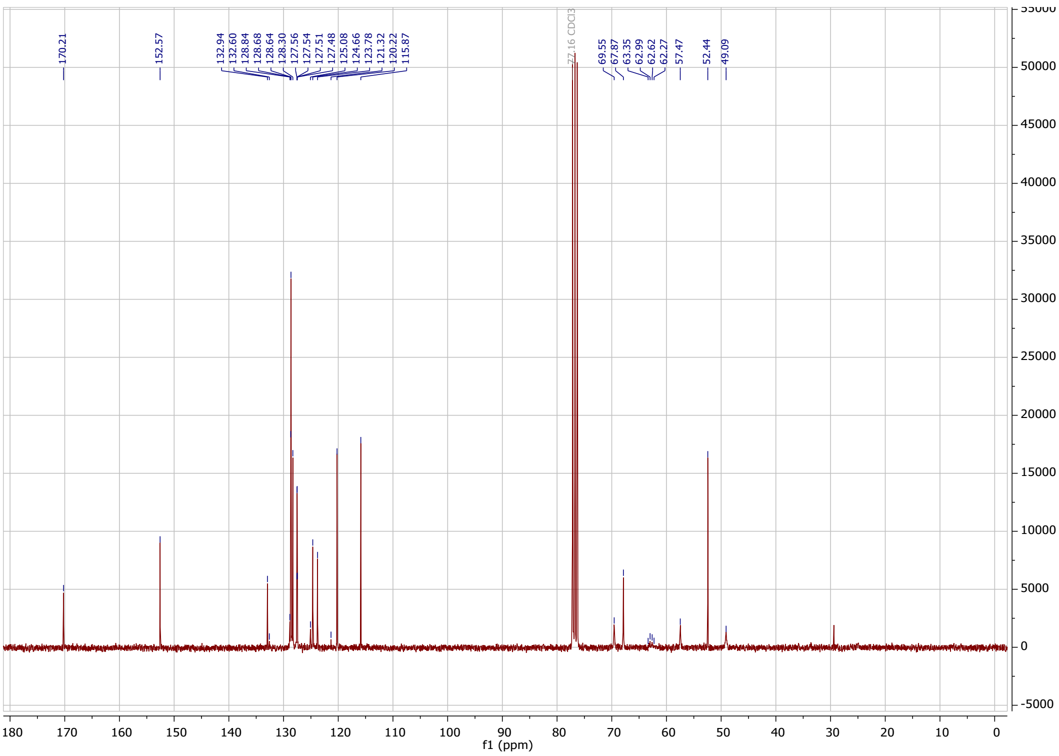


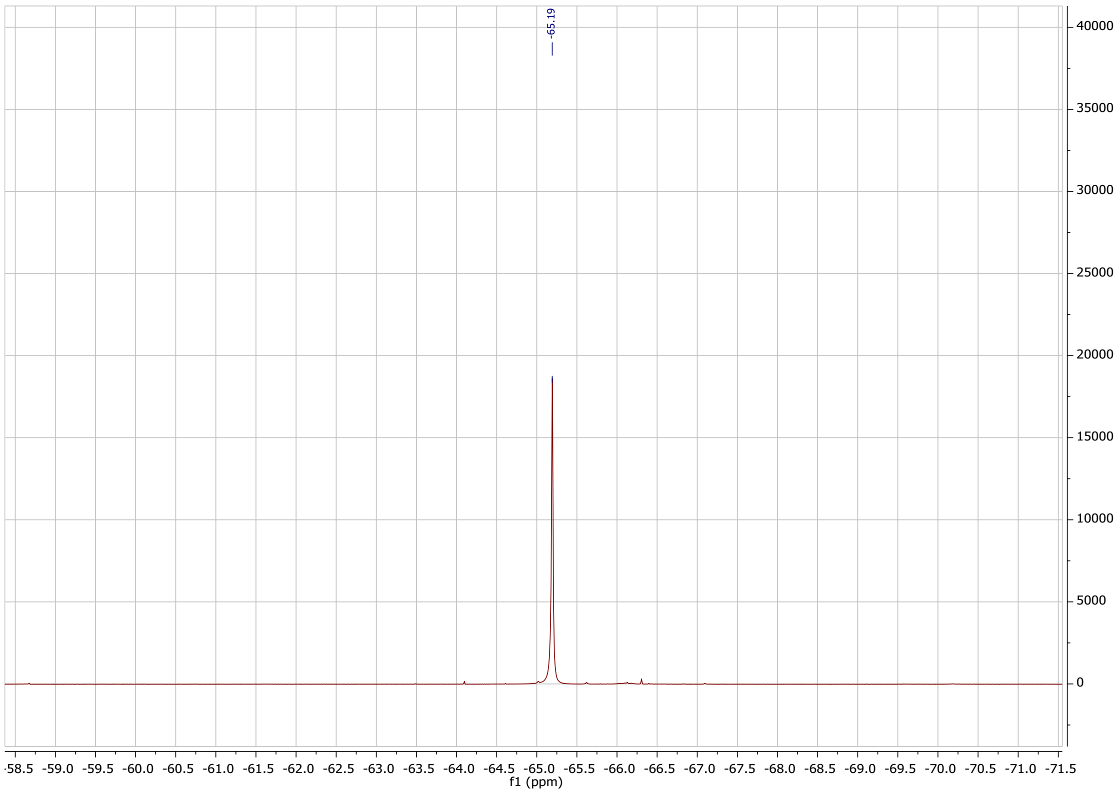


-83.32
-113.47
-113.49
-114.05
-114.08
-116.98
-117.02
-117.57
-117.61
3.09
1.00
1.16
f1 (ppm)

Methyl (2*R*,3*S*,3a*R*,9b*S*)-3-phenyl-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (11)






-65.19
40000
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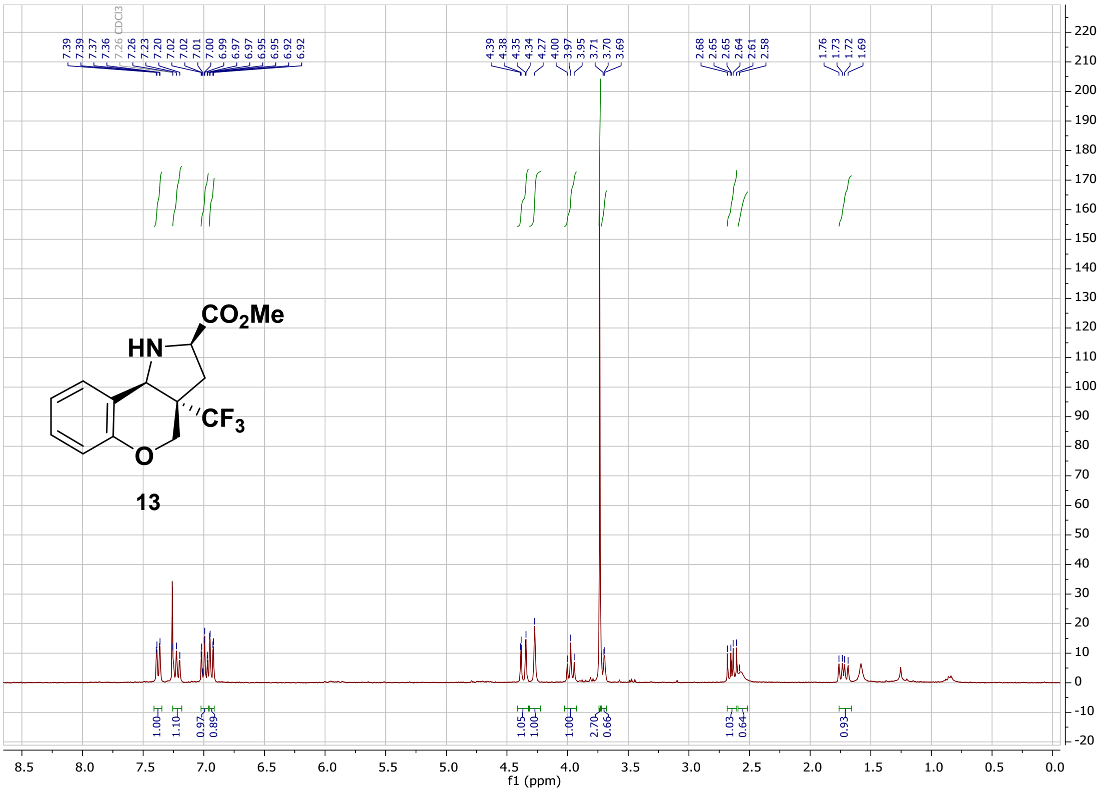
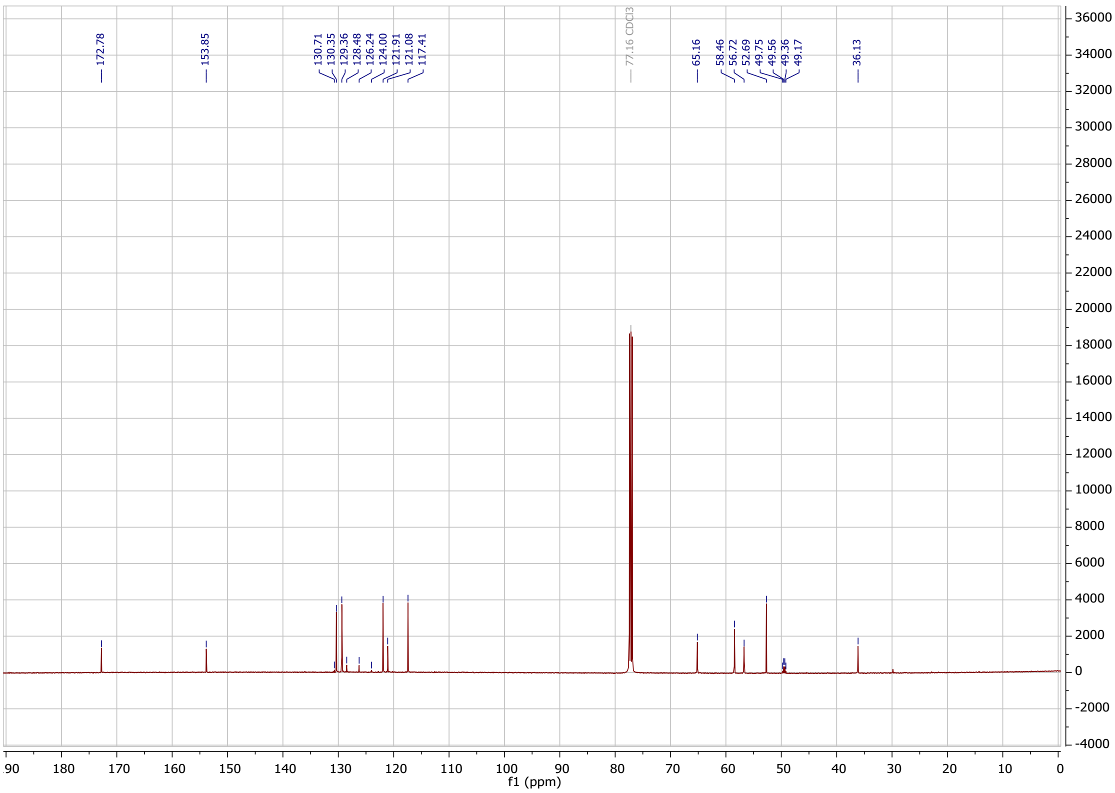
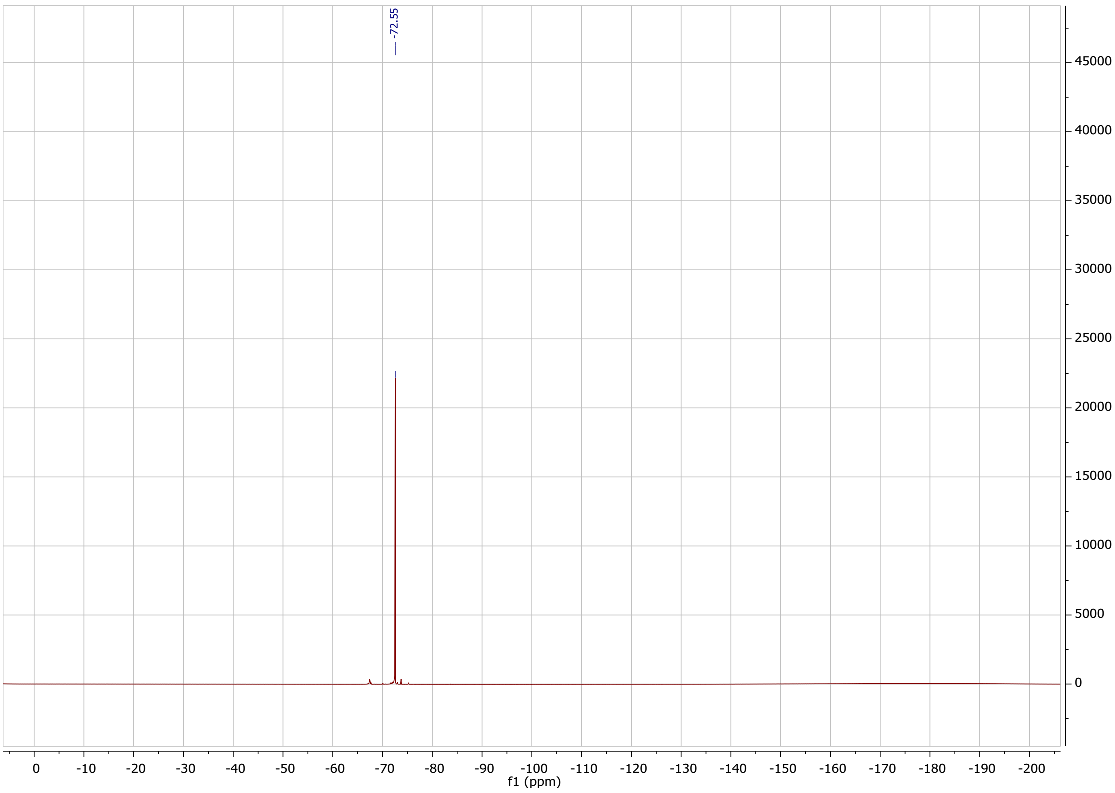
30000
25000
20000
15000
10000
5000
0
-58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0 -70.5 -71.0 -71.5
f1 (ppm)

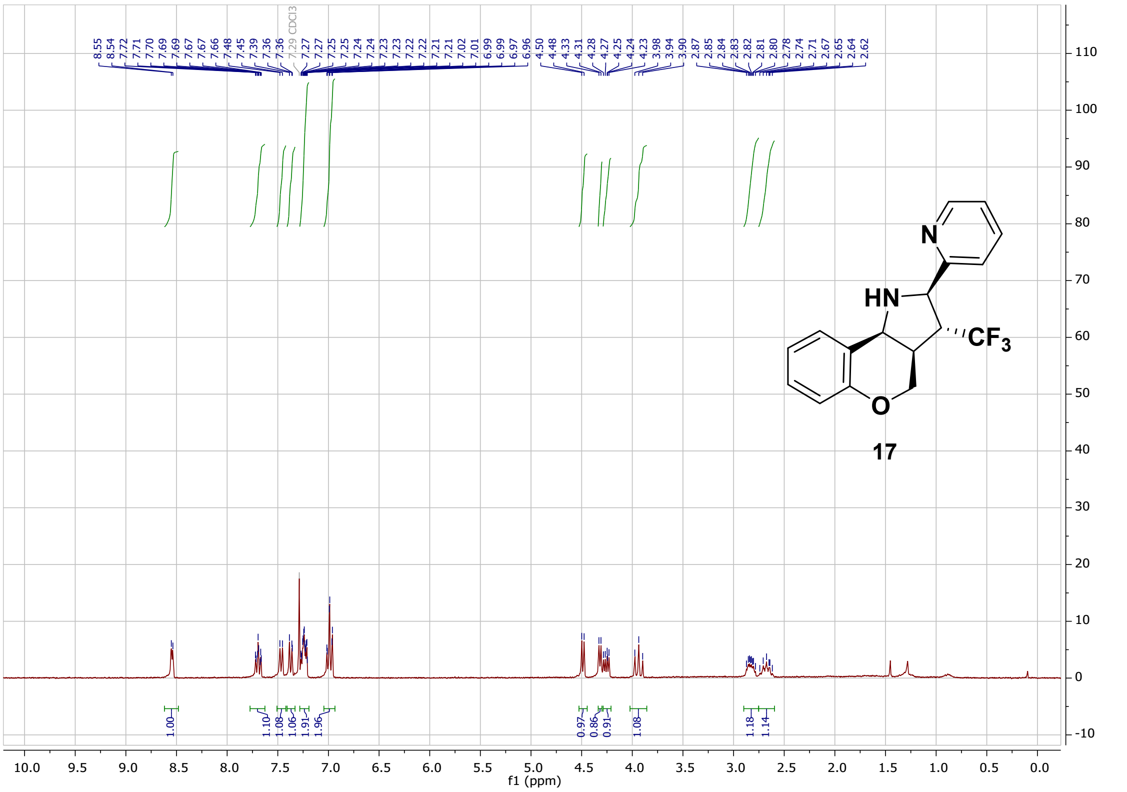
Methyl (2*R*,3a*S*,9b*R*)-3a-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole-2-carboxylate (13)

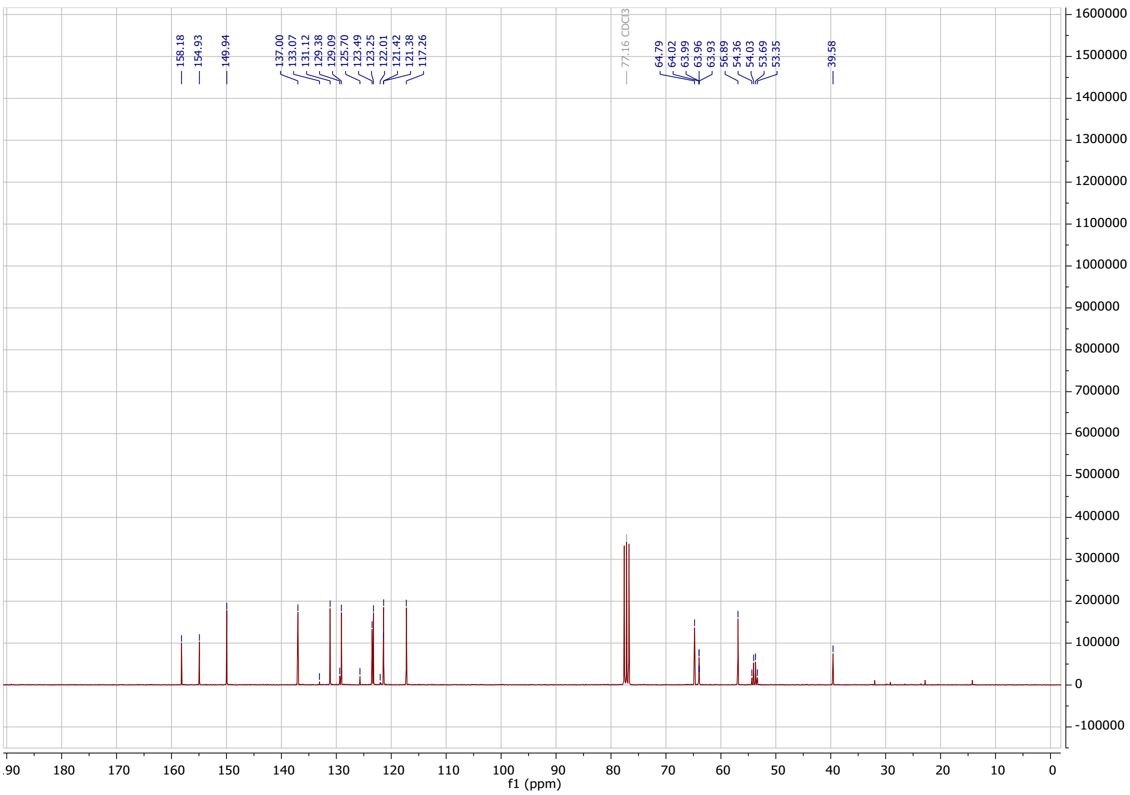


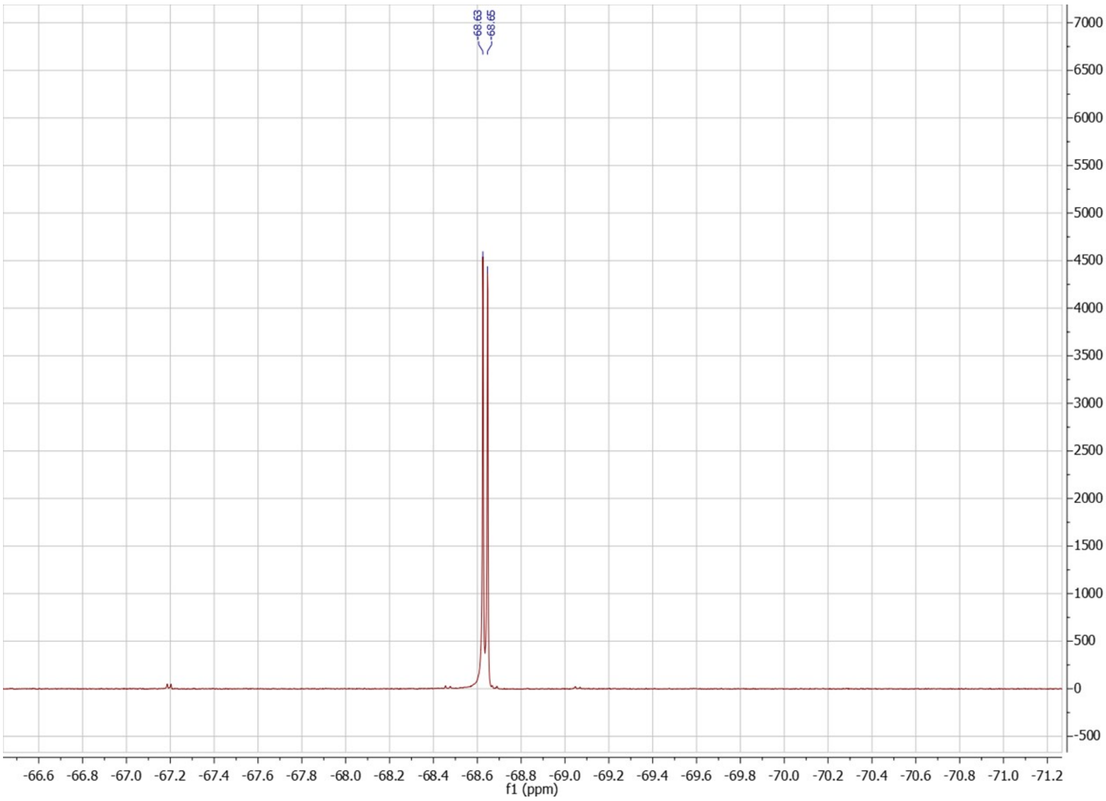



-72.55
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

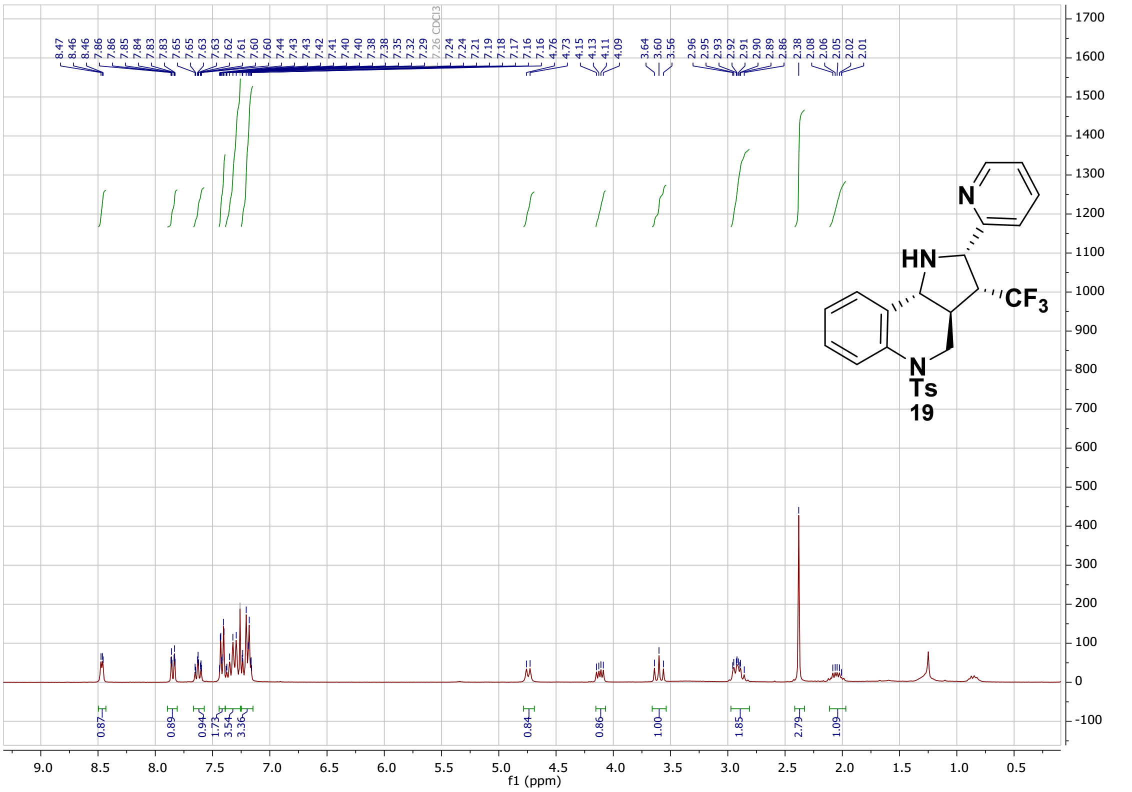
(2*R*,3*R*,3a*R*,9b*S*)-2-(pyridin-2-yl)-3-trifluoromethyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole (17)

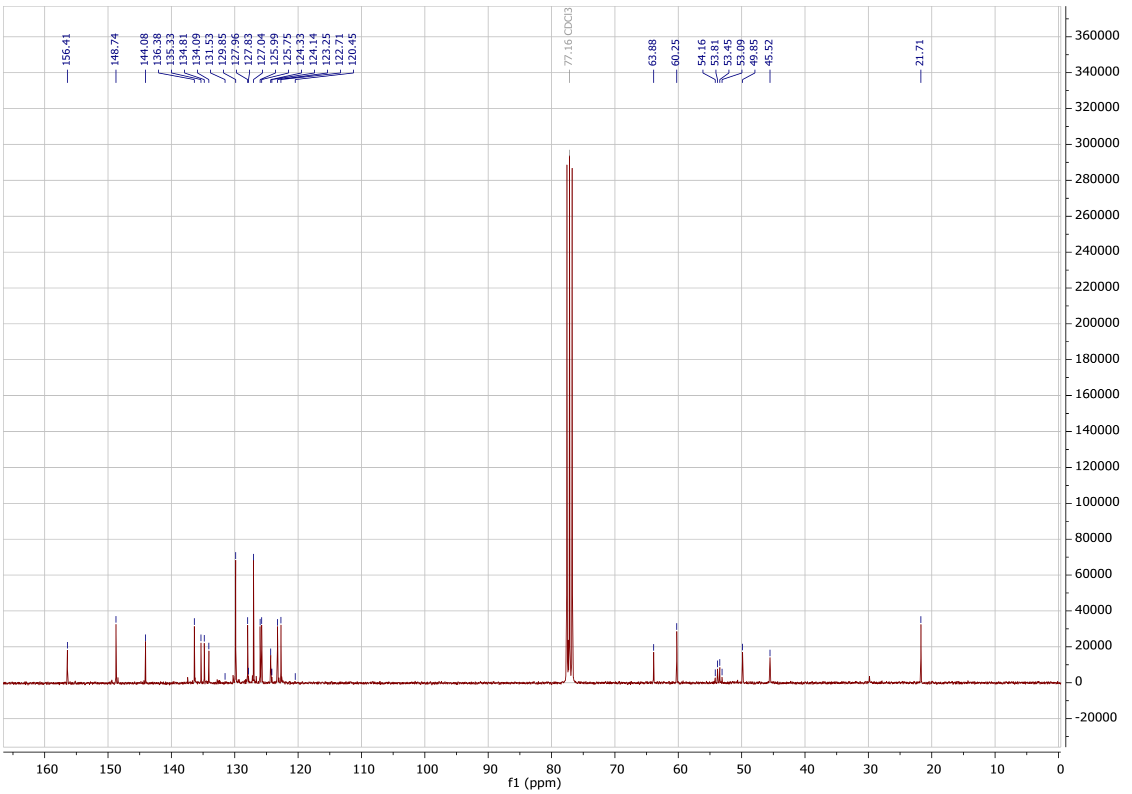


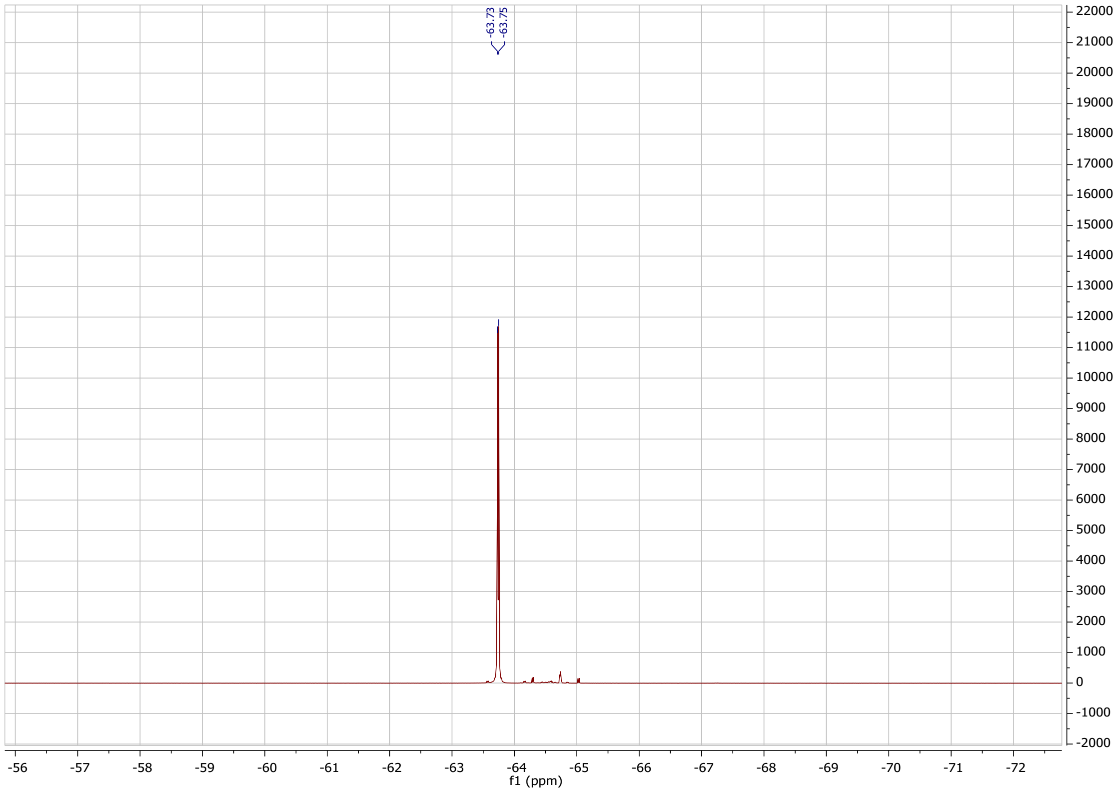



-68.63
-68.65
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-66.6 -66.8 -67.0 -67.2 -67.4 -67.6 -67.8 -68.0 -68.2 -68.4 -68.6 -68.8 -69.0 -69.2 -69.4 -69.6 -69.8 -70.0 -70.2 -70.4 -70.6 -70.8 -71.0 -71.2
f1 (ppm)

(2*S*,3*R*,3a*S*,9b*R*)-2-(pyridin-2-yl)-5-tosyl-3-trifluoromethyl-2,3,3a,4,5,9b-hexahydro-*1H*-pyrrolo[3,2-*c*]quinoline **(19)**






-63.73
-63.75
f1 (ppm)