Supporting Information

Palladium-catalyzed, enantioselective annulation of benzyltriflimides with allenes: Straight access to enantioenriched isoquinolines

Xandro Vidal, José L. Mascareñas,* Moisés Gulías*

e-mail: moises.gulias@usc.es; joseluis.mascarenas@usc.es

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.

Contents

General experimental procedures

Reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. Dry solvents were obtained from Aldrich and used without further purification. Toluene HPLC grade used for catalysis was obtained from Fisher Chemical. $Pd(OAc)_2$ (98%) [3375-31-3] was obtained from Strem. All other chemicals were purchased in Aldrich and used without further purification.

The abbreviation "rt" refers to reactions carried out at a temperature between 21-25 ºC. Reaction mixtures were stirred using Teflon-coated magnetic stir bars. High reaction temperatures were maintained using Thermowatch-controlled heating blocks. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, and/or by treating the plates with *p*-anisaldehyde, ninhydrin, phospomolybdic or potassium permanganate solutions, followed by heating. Flash chromatography was carried out on silica gel. Dryings were performed with anhydrous Na_2SO_4.

Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator followed by high vacuum.

All palladium-catalyzed reactions were carried out without particular precautions to extrude moisture or oxygen.

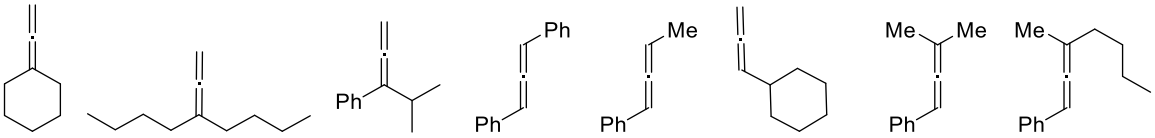
^{1}H-NMR spectra were recorded at room temperature on a Varian 300 MHz or 500 MHz spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{1}H, δ = 7.26) as internal standard]. ^{19}F-NMR (282 MHz) spectra were recorded at room temperature on a Varian 300 MHz spectrometer in $CDCl_3$. ^{13}C NMR spectra were recorded at room temperature on a Varian spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, δ = 77.160) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Carbon types and structure assignments were determined from DEPT-NMR and two dimensional experiments (HSQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestReNova© NMR data processing software (www.mestrelab.com). Mass spectra were acquired using electrospray ionization (ESI, ion polarity positive) or atmospheric pressure chemical ionization (APCI) and were recorded at the CACTUS facility of the University of Santiago de Compostela on Bruker micrOTOF. Melting points were measured on a Büchi Melting Point B-560 apparatus.

Enantiomeric ratios (er) were determined on an Agilent HPLC 1100 Series or on a Jasco SFC 4000 series using commercially available chiral colums. All racemic products were prepared under the same procedure than the chiral products but with the employment of a racemic amino acid.

X-ray crystallographic analysis of **3ga** and **3ba** was performed at the CACTUS facility of the University of Santiago de Compostela.

Amounts of isolated products are indicated independently of the scale used.

Allene **2a** (vinylidenecyclohexane) and allene **2f** (propa-1,2-dien-1-ylcyclohexane) were purchased from Aldrich. Allene **2b** (5-vinylidenenonane), allene **2c** ((4-methylpenta-1,2-dien-3-yl)benzene), allene **2d** (1,3-diphenylpropa-1,2-diene), allene **2e** (buta-1,2-dien-1-ylbenzene), allene **2g** ((3-methylbuta-1,2-dien-1-yl)benzene) and allene **2h** ((3-methylhepta-1,2-dien-1-yl)benzene) were prepared according procedures reported in the literature[1].

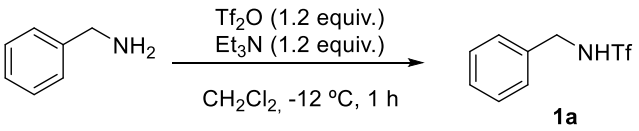


2a **2b** **2c** **2d** **2e** **2f** **2g** **2h**

General procedure for the synthesis of benzylamines:

Benzylamine, 1-phenylpropan-1-amine, diphenylmethanamine, bis(4-methoxyphenyl)methanamine, bis(3-methoxyphenyl)methanamine and 2-(cyclohex-1-en-1-yl)ethan-1-amine were commercially available. All non-commercial benzylamines were synthesized with a method previously reported in literature.[2] All spectral data recorded for known compounds were in agreement with those in the corresponding literature[3].

General procedure for the synthesis of the trifyl benzylamines (1a-1b, 1f-1m) and triflyl allylamines (1e and 1l), from the precursor amines, exemplified for 1a



1a

To a solution of benzylamine (2 mL, 18.31 mmol) in dichloromethane (36.6 mL) under argon atmosphere was added triethylamine (2.55 mL, 18.31 mmol) at -12ºC. After the solution was stirred 5 minutes at that temperature, trifluoromethanesulfonic anhydride (3.23 mL, 19.22 mmol) was added dropwise. The reaction was stirred for 1 h at that temperature before being quenched with water. The organic layer was separated and the aqueous layer extracted with dichloromethane. The combined organic phase was washed with brine and then dried over Na_2SO_4. Evaporation and column chromatography on silica gel (hexanes:diethylether; 80:20) afforded **N-benzyl-1,1,1-trifluoromethanesulfonamide** (**1a**) as a white solid (3.97g, 91%). Mp: 43-44 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 – 7.18 (m, 5H), 5.10 (brs, 1H), 4.33 (d, *J* = 5.8 Hz, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.64. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 135.3 (C), 129.2 (CH), 128.8 (CH), 128.0 (CH), 119.8 (q, *J* = 320.9 Hz, C), 48.3 (CH_2). **HRMS** [APCI]: *m/z* calculated for $C_8H_7F_3NO_2S$ $[M+H]^+$: 238.0144, found 238.0145.

1,1,1-trifluoro-*N*-(1-phenylpropyl)methanesulfonamide (1b)

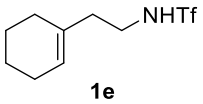
[1] Allene **2b**: Kippo, T.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2011**, *13*, 3864–3867. Allene **2c** and **2d**: Zhao, Z.; Racicot, L.; Murphy, G. K. *Angew. Chemie - Int. Ed.* **2017**, *56*, 11620–11623. Allene **2e**: Zhao, Z.; Racicot, L.; Murphy, G. K. *Angew. Chemie - Int. Ed.* **2017**, *56*, 11620–11623. Allene **2g** and **2h**: Ting, C.-H.; Hsu, Y.-L.; Liu, R.-S., *Chem. Commun.* **2012**, *48*, 6577-6579.

[2] Zhang, Y.; Lu, Z.; Desai, A.; Wulff, W. D. *Org. Lett.* **2008**, *10*, 5429–5432.

[3] For di-*o*-tolylmethanamine and di-*p*-tolylmethanamine: Zhang, Y.; Lu, Z.; Desai, A.; Wulff, W. D. *Org. Lett.* **2008**, *10*, 5429–5432. For bis(4-chlorophenyl)methanamine: Huang, H.; Chen, W.; Xu, Y.; Li, J. *Green Chem.* **2015**, *17,* 4715-4719.

(836 mg, 84% yield), obtained as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 3H), 7.19 – 7.12 (m, 2H), 5.50 (d, *J* = 8.8 Hz, 1H), 4.40 (q, *J* = 7.7 Hz, 1H), 1.91 – 1.70 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.03. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.2 (C), 129.1 (CH), 128.4 (CH), 126.3 (CH), 120.0 (d, *J* = 320.9 Hz, C), 61.6 (CH), 31.0 (CH_2), 10.6 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{10}H_{12}F_3NNaO_2S$ [M+Na]$^+$: 290.0433, found 290.0433. Data in agreement with those reported in literature.[4]

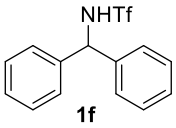
***N*-(2-(cyclohex-1-en-1-yl)ethyl)-1,1,1-trifluoromethanesulfonamide (1e)**



1e

(433 mg, 84% yield), obtained as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.46 (brs, 1H), 5.03 (brs, 1H), 3.28 (q, *J* = 6.3 Hz, 2H), 2.14 (t, *J* = 13.5 Hz, 2H), 2.06 – 1.97 (m, 2H), 1.93 – 1.83 (m, 2H), 1.70 – 1.49 (m, 4H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.00. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 132.8 (C), 125.7 (CH), 119.8 (q, *J* = 321.2 Hz, C), 42.1 (CH_2), 38.2 (CH_2), 27.7 (CH_2), 25.2 (CH_2), 22.7 (CH_2), 22.2 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_9H_{15}F_3NO_2S$ [M+H]$^+$: 258.0770, found 258.0769.

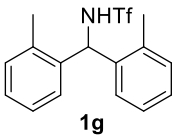
***N*-benzhydryl-1,1,1-trifluoromethanesulfonamide (1f)**



1f

(1.62 g, 63% yield), obtained as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 10H), 5.77 (d, *J* = 8.9 Hz, 1H), 5.68 (d, *J* = 9.0 Hz, 1H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.31. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.7 (C), 129.1 (CH), 128.4 (CH), 127.3 (CH), 119.5 (q, *J* = 321.1 Hz, CF_3) 62.5 (CH). **HRMS** [ESI]: *m/z* calculated for $C_{14}H_{12}F_3NNaO_2S$ [M+Na]$^+$: 338.0443, found 338.0440. Data in agreement with those reported in literature.[5]

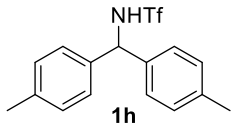
***N*-(di-*o*-tolylmethyl)-1,1,1-trifluoromethanesulfonamide (1g)**



1g

(2.60 g, 80% yield), obtained as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.17 – 7.02 (m, 8H), 6.09 (d, *J* = 8.2 Hz, 1H), 5.27 (d, *J* = 8.2 Hz, 1H), 2.21 (s, 6H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.42. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.2 (C), 136.0 (C), 131.2 (CH), 128.5 (CH), 127.0 (CH), 126.5 (CH, 119.4 (q, *J* = 321.2 Hz, C), 56.7 (CH), 19.1 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{16}H_{16}F_3NNaO_2S$ [M+Na]$^+$: 366.0746, found 336.0749. Data in agreement with those reported in literature.[5]

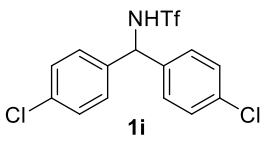
***N*-(di-*p*-tolylmethyl)-1,1,1-trifluoromethanesulfonamide (1h)**



1h

(1.95 g, 70% yield), obtained as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.09 – 6.97 (m, 8H), 5.75 – 5.54 (m, 2H), 2.22 (s, 6H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.69. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.2 (C), 137.1 (C), 129.7 (CH), 127.1 (CH), 119.6 (d, *J* = 321.0 Hz, C), 62.2 (CH), 21.2 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{16}H_{16}F_3NNaO_2S$ [M+Na]$^+$: 366.0746, found 336.0743. Data in agreement with those reported in literature.[5]

***N*-(bis(4-chlorophenyl)methyl)-1,1,1-trifluoromethanesulfonamide (1i)**

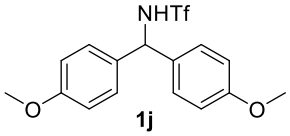


1i

(2.92 g, 74% yield), obtained as a white solid. Mp: 105-107 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.12 – 7.04 (m, 4H), 5.73 (d, *J* = 8.8 Hz, 1H), 5.64 (d, *J* = 8.9 Hz, 1H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.64. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.7 (C), 134.8 (C), 129.5 (CH), 128.6 (CH), 119.5 (q, *J* = 321.0 Hz, C), 61.4 (CH). **HRMS** [ESI]: *m/z* calculated for $C_{14}H_{10}Cl_2F_3NNaO_2S$ [M+Na]$^+$: 405.9654, found 405.9656.

[4] Miyamoto, K.; Hoque, M. M.; Ogasa, S. *J. Org. Chem.* **2012**, *77*, 8317–8320.
[5] Chu, L.; Wang, X. C.; Moore, C. E.; Rheingold, A. L.; Yu, J. Q. *J. Am. Chem. Soc.* **2013**, *135*, 16344–16347.

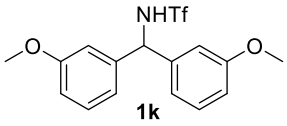
***N*-(bis(4-methoxyphenyl)methyl)-1,1,1-trifluoromethanesulfonamide (1j)**



1j

(302 mg, 24% yield), obtained as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.09 – 7.02 (m, 4H), 6.81 – 6.73 (m, 4H), 5.69 (s, 2H), 3.70 (s, 6H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.90. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.5 (C), 132.2 (C), 128.5 (CH), 119.6 (d, *J* = 321.1 Hz, C), 114.4 (C), 61.67 (C), 55.5 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{16}H_{16}F_3NNaO_4S$ $[M+Na]^+$: 398.0644, found 398.0641. Data in agreement with those reported in literature. [5]

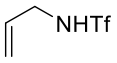
***N*-(bis(3-methoxyphenyl)methyl)-1,1,1-trifluoromethanesulfonamide (1k)**



1k

(325 mg, 84% yield), obtained as a white solid. Mp: 86-87 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 3H), 6.78 – 6.65 (m, 5H), 6.00 (d, *J* = 9.0 Hz, 1H), 5.68 (d, *J* = 8.8 Hz, 1H), 3.63 (s, 6H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.82. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.0 (C), 141.2 (C), 130.1 (CH), 119.6 (d, *J* = 321.1 Hz), 119.6 (CH), 113.6 (CH), 113.2 (CH), 62.3 (CH), 55.4 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{16}H_{17}F_3NO_4S$ $[M+H]^+$: 376.0825, found 376.0825.

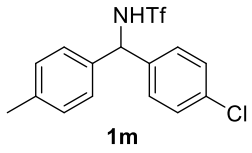
***N*-allyl-1,1,1-trifluoromethanesulfonamide (1l)**



1l

(1.35 g, 82% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.86 (ddt, *J* = 17.1, 10.2, 5.8 Hz, 1H), 5.38 – 5.25 (m, 2H), 5.04 (brs, 1H), 3.97 – 3.86 (m, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.02 (d, *J* = 16.6 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 132.16 (CH), 119.72 (q, *J* = 320.8 Hz, C), 118.87 (CH_2), 46.71 (CH_2).

***N*-((4-chlorophenyl)(*p*-tolyl)methyl)-1,1,1-trifluoromethanesulfonamide (1m)**

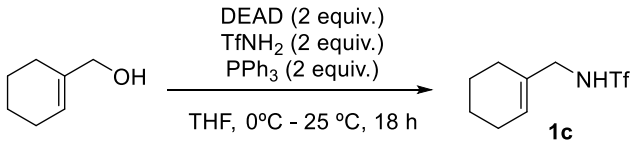


1m

(0.57 g, 72% yield), obtained as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 – 7.03 (m, 8H), 5.82 (d, *J* = 7.2 Hz, 1H), 5.36 (d, *J* = 8.3 Hz, 1H), 2.36 (s, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ 77.67. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.7 (C), 138.5 (C), 136.3 (C), 134.3 (C), 129.9 (CH), 129.2 (CH), 128.6 (CH), 127.1 (CH), 119.5 (d, *J* = 321.1 Hz, C), 61.8 (CH), 21.2 (CH_3).

General procedure for the synthesis of the triflyl alken-amines 1c-1d from the corresponding alcohols, exemplified for 1c.

2-methylprop-2-en-1-ol was commercially available. Cyclohex-1-en-1-ylmethanol was synthesized with a method previously reported in literature.[6] All spectral data recorded agreed with those in the corresponding literature[7].



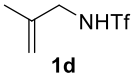
1c

To a solution of cyclohex-1-en-1-ylmethanol (801.4 mg, 7.145 mmol), trifluoromethane sulfonamide (2.13 g, 2 equiv.), and triphenylphosphine (3.75 g, 2 equiv.) in THF (25 mL) at 0 °C was added DEAD (5.6 mL, 40% in toluene, 2 equiv.). The reaction mixture was stirred at room temperature overnight, and was quenched with water, then diluted with ethyl acetate. The combined organic phases were washed with brine and then dried over Na_2SO_4. Evaporation and column

[5] Chu, L.; Wang, X. C.; Moore, C. E.; Rheingold, A. L.; Yu, J. Q. *J. Am. Chem. Soc.* **2013**, *135*, 16344–16347.
[6] Karaki, F.; Ohgane, K.; Fukuda, H.; Nakamura, M.; Dodo, K.; Hashimoto, Y. *Bioorganic Med. Chem.* **2014**, *22*, 3587–3609.
[7] Hanessian, S.; Szychowski, J.; Pablo Maianti, J. *Org. Lett.* **2009**, *11*, 429–432.

chromatography on silica gel (hexanes:diethylether; 90:10) afforded ***N*-(cyclohex-1-en-1-ylmethyl)-1,1,1-trifluoromethanesulfonamide 1c** as a yellow oil (0.80 g, 46%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.65 (brs, 1H), 4.98 (brs, 1H), 3.67 (d, *J* = 5.9 Hz, 2H), 2.01 – 1.86 (m, 4H), 1.66 – 1.44 (m, 4H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.84. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 132.2 (C), 126.9 (CH), 119.8 (q, *J* = 321.2 Hz, C), 50.8 (CH_2), 26.0 (CH_2), 25.1 (CH_2), 22.4 (CH_2), 22.1 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_8H_{12}F_3NNaO_2S$ $[M+Na]^+$: 266.0433, found 266.0432.

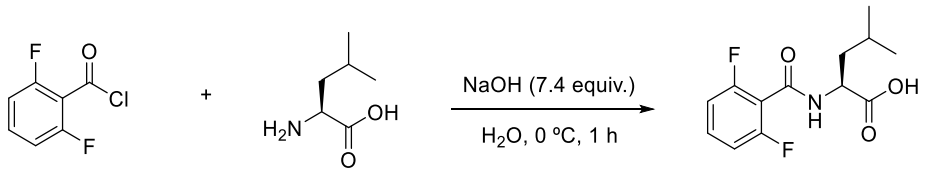
1,1,1-trifluoro-*N*-(2-methylallyl)methanesulfonamide (1d)



1d

(0.94 g, 33% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.01 (brs, 1H), 4.94 – 4.90 (m, 2H), 3.74 (d, *J* = 6.1 Hz, 2H), 1.72 (s, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.83. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.6 (C), 119.8 (d, *J* = 321.2 Hz, C), 113.9 (CH_2), 50.1 (CH_2), 19.8 (CH_3). **HRMS** [ESI]: *m/z* calculated $C_5H_9F_3NO_2S$ $[M+H]^+$: 204.0301, found 204.0300.

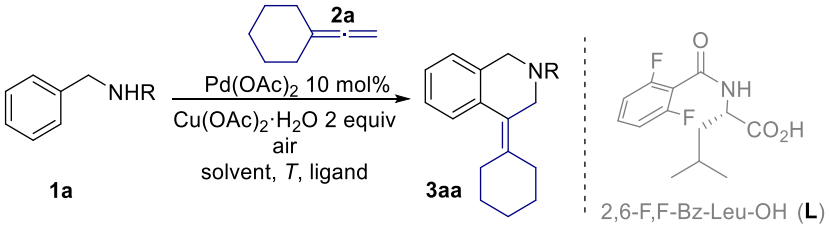
Procedure for the synthesis of N-(2,6-difluorobenzoyl)-L-leucine[8]



To a 25 mL round bottom flask with stir bar was added L-leucine (1.11 g, 8.496 mmol), sodium hydroxide (2.52 g, 7.4 equiv), and water (15.5 mL). The mixture was stirred at room temperature until homogeneous before cooling to 0 °C in an ice bath. Upon cooling, 2,6- difluorobenzoyl chloride (1.07 mL, 8.496 mmol) was added dropwise to the mixture. After 1 hour, the reaction mixture was allowed to warm to room temperature and pH adjusted to ~3.0 with hydrochloric acid (36% w/w). The precipitate was filtered and washed with cold water and then dried with a high-vacuum pump to give ***N*-(2,6-difluorobenzoyl)-L-leucine** as a white solid (2.10 g, 91 % yield). Spectral data recorded were in agreement with those in the corresponding literature.[8] **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.63 (brs, 1H), 8.97 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.38 (m, 1H), 7.38 – 7.02 (m, 2H), 4.52 – 4.27 (m, 1H), 1.92 – 1.41 (m, 3H), 0.89 (t, *J* = 6.0 Hz, 6H).

[8] Plata, R. E.; Hill, D. E.; Haines, B. E.; Musaev, D. G.; Chu, L.; Hickey, D. P.; Sigman, M. S.; Yu, J. Q.; Blackmond, D. G. *J. Am. Chem. Soc.* **2017**, *139*, 9238–9245.

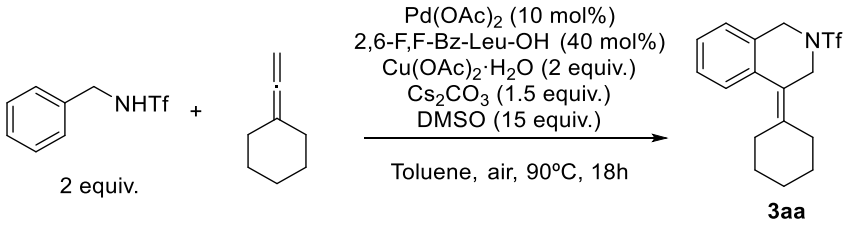
Optimization of the conditions for the annulation of 1a and 2a [a]



Entry	R	Solvent	Base	Temp	Ligand **L**[b]	Yield[c]
1	Tf	t-AmyOH	Cs_2CO_3 (1.5 equiv)	80 ºC	-	15%
2	Tf	Dioxane	Cs_2CO_3 (1.5 equiv)	80 ºC	-	23%
3	Tf	DCE	Cs_2CO_3 (1.5 equiv)	80 ºC		24%
4	Tf	CH_3CN	Cs_2CO_3 (1.5 equiv)	80 ºC	-	9%
5	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90ºC	-	25%
6[d]	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90ºC	-	34%
7	Tf	Toluene	-	90 ºC	-	28%
8	Tf	Toluene	Et_3N (2 equiv.)	90 ºC	-	35%
9	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90 ºC	Boc-Ala-OH	58%
10	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90 ºC	Boc-Val-OH	69%
11	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90ºC	Boc-Leu-NHOMe	37%
12	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90ºC	Boc-Phe-NHOMe	31%
13	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90ºC	2,6-F,F-Bz-Leu-OH	85%
14[d]	Tf	**Toluene**	Cs_2CO_3 (1.5 equiv)	**90ºC**	**2,6-F,F-Bz-Leu-OH**	**95%[e]**
15[d]	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90ºC	2,6-F,F-Bz-Leu-OH	86%[e,f]
16[d]	Ac	Toluene	Cs_2CO_3 (1.5 equiv)	90 ºC	2,6-F,F-Bz-Leu-OH	No reaction
17[d]	Me	Toluene	Cs_2CO_3 (1.5 equiv)	90 ºC	2,6-F,F-Bz-Leu-OH	No reaction
18[d]	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90ºC	2,6-F,F-Bz-Leu-OH	95%[g]
19	Tf	Toluene	Cs_2CO_3 (1.5 equiv)	90ºC	2,6-F,F-Bz-Leu-OH	31%[g]

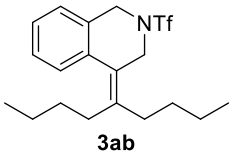
[a] Conditions: 0.333 mmol **1a**, 0.167 mmol of allene **2a**, 2 mL of solvent, under air, 16h. [b] 40% of ligand. [c] Yields calculated by using an internal standard. [d] 15 equiv of DMSO added [e] Isolated yield based on **2a**. [f] 0.5 equiv. of $Cu(OAc)_2 \cdot H_2O$. [g] Reaction performed during 40 minutes.

General procedure for the Pd-catalyzed annulation of benzylamines, alkenyl and allylamines with allenes, exemplified for 3aa:



To a solution of $Pd(OAc)_2$ (3.7 mg, 10 mol%), 2,6-F,F-Bz-Leu-OH (18.1 mg, 40 mol%), $Cu(OAc)_2•H_2O$ (66.7 mg, 2 equiv.), Cs_2CO_3 (81.6 mg, 1.5 equiv.) and **1a** (79.9 mg, 0.333 mmol, 2 equiv.) in toluene (2 mL), under air atmosphere, in a Schlenk tube was added the allene **2a** (18.0 mg, 0.167 mmol).The tube was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 90 °C, stirred during 18 h and then cooled to room temperature. Evaporation and column cromatography on silica gel (hexanes:diethylether; 99:1) afforded **4-cyclohexylidene-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline** (**3aa**) as a white solid (54.8 mg, 95% yield) Mp: 66-67 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.28 – 7.04 (m, 4H), 4.44 (s, 2H), 4.22 (s, 2H), 2.45 – 2.34 (m, 2H), 2.32 – 2.24 (m, 2H), 1.66 – 1.49 (m, 6H).**^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.78. **^{13}C NMR** (75 MHz, $CDCl_3$**)** δ 141.7 (C), 135.9 (C), 133.3 (C), 129.0 (CH), 127.3 (CH), 126.1 (CH), 120.4 (C), 120.3 (d, *J* = 324.0 Hz, C), 48.2 (CH_2), 46.8 (CH_2), 32.1 (CH_2), 31.3 (CH_2), 28.6 (CH_2), 28.3 (CH_2), 26.7 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{16}H_{19}F_3NO_2S$ $[M+H]^+$: 346.1083, found 346.1085.

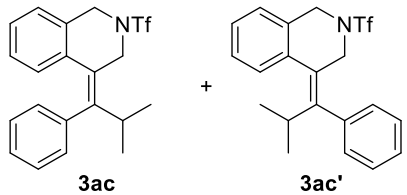
4-(nonan-5-ylidene)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ab)



3ab

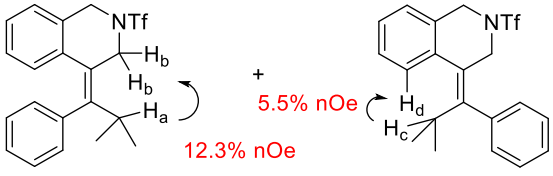
(55.3 mg, 85% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26 – 7.07 (m, 4H), 4.38 (s, 2H), 4.18 (s, 2H), 2.35 – 2.06 (m, 4H), 1.53 – 1.09 (m, 8H), 0.94 – 0.85 (m, 3H), 0.85 – 0.76 (m, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.22. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 143.1 (C), 136.1 (C), 133.4 (C), 128.3 (CH), 127.5 (CH), 127.3 (CH), 126.1 (CH), 123.6 (C), 120.4 (d, *J* = 324.2 Hz, C), 48.2 (CH_2), 47.2 (CH_2), 33.1 (CH_2), 31.8 (CH_2), 31.6 (CH_2), 31.2 (CH_2), 23.1 (CH_2), 22.8 (CH_2), 14.1 (CH_3), 14.0 (CH_3). **HRMS** [ESI]: *m/z* calculated $C_{19}H_{27}F_3NO_2S$ $[M+H]^+$: 390.1709, found 390.1711.

4-(2-methyl-1-phenylpropylidene)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ac and 3ac')

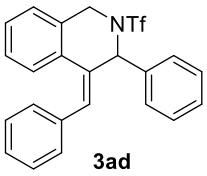


3ac **3ac'**

(3.3:1 E/Z ratio of **3ac** and **3ac'**, inseparable mixture (56.8 mg, 86% yield, white solid. Mp: 79-81 ºC)). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 0.23H), 7.36 – 7.22 (m, 1.15H), 7.21 – 7.13 (m, 2.54H), 7.03 – 6.98 (m, 0.45H), 6.99 – 6.89 (m, 3.08H), 6.74 – 6.66 (m, 0.77H), 6.54 (d, *J* = 8.1 Hz, 0.77H), 4.55 (s, 1.54H), 4.42 (s, 2.00H), 3.75 (s, 0.46H), 3.35 (hept, *J* = 6.8 Hz, 0.23H), 3.16 (hept, *J* = 6.9 Hz, 0.77H), 0.97 (d, *J* = 6.9 Hz, 4.62H), 0.92 (d, *J* = 6.8 Hz, 1.38H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -75.50, -75.72. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.0 (C), 147.4 (C), 139.3 (C), 137.1 (C), 135.3 (C), 135.2 (C), 134.0 (C), 132.4 (C), 130.0 (CH), 129.9 (CH), 129.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 127.1 (CH), 126.9 (CH), 126.6 (CH), 126.3 (CH), 125.5 (CH), 124.66 (C), 124.46 (C), 120.29 (d, *J* = 324.1 Hz, C), 48.80 (CH_2), 48.49 (CH_2), 48.23 (CH_2), 46.42 (CH_2), 30.98 (CH), 30.60 (CH), 21.82 (CH_3), 21.71 (CH_3). **HRMS** [ESI]: *m/z* calculated $C_{20}H_{20}F_3NNaO_2S$ $[M+Na]^+$: 418.1059, found 418.1056. Assignment of stereochemistry based on the observed nOe between the H_a (3.16 ppm, 100%) with H_b (4.42 ppm, 12.3%) and between the H_c (3.35 ppm, 100%) with H_d (7.44 ppm, 5.5%).

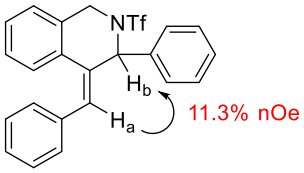


(*E*)-4-benzylidene-3-phenyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ad)

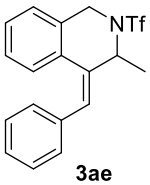


3ad

(57.9 mg, 80% yield), obtained as a white solid. Mp: 100-102 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.28 – 6.98 (m, 12H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.75 (s, 1H), 5.74 (s, 1H), 4.85 (d, *J* = 17.3 Hz, 1H), 4.30 (d, *J* = 17.3 Hz, 1H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.65. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.4 (C), 136.1 (C), 131.2 (C), 130.9 (CH), 130.7 (C), 130.5 (C), 129.8 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 127.2 (CH), 126.7 (CH), 125.8 (CH), 120.2 (d, J = 323.5 Hz, C), 64.9 (CH), 45.8 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{23}H_{18}F_3NNaO_2S$ $[M+Na]^+$: 452.0903, found 452.0901. Assignment of stereochemistry based on the observed nOe between the H_a (6.75 ppm, 100%) with H_b (5.74 ppm, 11.3%).

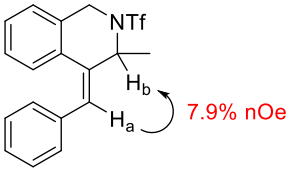


(*E*)-4-benzylidene-3-methyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline

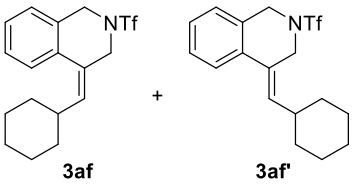


3ae

(46.2 mg, 74% yield), obtained as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 6.85 (m, 9H), 6.58 (s, 1H), 4.98 – 4.42 (m, 3H), 1.27 (d, *J* = 6.8 Hz, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.16. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.4 (C), 133.7 (C), 131.0 (C), 130.2 (C), 130.0 (CH), 129.0 (CH), 128.6 (CH), 128.4 (CH), 127.7 (CH), 127.5 (CH), 126.8 (CH), 125.9 (CH), 120.2 (d, *J* = 323.6 Hz, C), 58.8 (CH), 45.3 (CH_2), 19.7 (CH_3, brs identified by HSQC experiment). **HRMS** [ESI]: *m/z* calculated for $C_{18}H_{16}F_3NNaO_2S$ $[M+Na]^+$: 390.0746, found 390.0745. Assignment of stereochemistry based on the observed nOe between the H_a (6.58 ppm, 100%) with H_b (4.94 – 4.88 ppm, 7.9%).

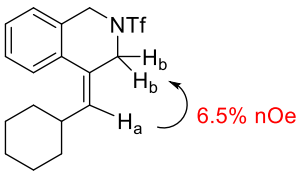


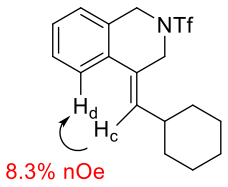
4-(cyclohexylmethylene)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3af and 3af')



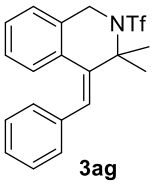
3af **3af'**

(1.1:1 E/Z r.r. of **3af** and **3af'**, inseparable mixture (50.8 mg, 85% yield, transparent oil)) **^{1}H NMR** (300 %MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 0.47H), 7.36 – 7.06 (m, 3.06H), 7.05 – 6.95 (m, 0.47H), 5.95 (d, *J* = 9.6 Hz, 0.47H), 5.46 (d, *J* = 10.3 Hz, 0.53H), 4.65 – 4.50 (m, 2H), 4.33 (s, 0.94H), 4.05 (s, 1.06H), 2.60 – 2.44 (m, 0.47H), 2.35 – 2.16 (m, 0.53H), 1.74 – 1.55 (m, 5H), 1.32 – 0.99 (m, 5H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.81, -76.20. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.1 (CH), 133.6 (C), 133.4 (CH), 133.1 (C), 132.2 (C), 130.3 (C), 128.0 (CH), 127.93 (CH), 127.87 (CH), 127.6 (CH), 127.5 (CH), 126.12 (CH), 126.05 (CH), 125.8 (C), 125.4 (C), 124.0 (CH), 120.13 (d, *J* = 332.4 Hz, C), 120.12 (d, *J* = 315.2 Hz, C), 52.9 (CH_2), 48.5 (CH_2), 48.3 (CH_2), 45.7 (CH_2), 37.4 (CH), 37.22 (CH), 33.15 (CH_2), 33.0 (CH_2), 26.0 (CH_2), 25.8 (CH_2), 25.6 (CH_2). **HRMS** [ESI]: *m/z* calculated $C_{17}H_{21}F_3NO_2S$ $[M+H]^+$: 360.1240, found 360.1238. Assignment of stereochemistry based on the observed nOe between the H_a (5.46 ppm, 100%) with H_b (4.05 ppm, 6.5%) and between the H_c (5.95 ppm, 100%) with H_d (7.58 – 7.47, 8.3%).



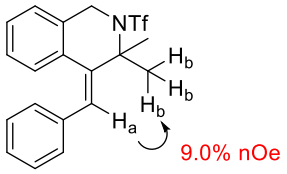


(*E*)-4-benzylidene-3,3-dimethyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ag)



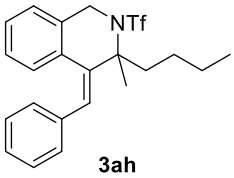
3ag

(50.7 mg, 80% yield), obtained as a white solid. Mp: 91-92 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.22 – 6.87 (m, 9H), 6.74 (s, 1H), 4.45 (s, 2H), 1.69 (s, 6H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -76.10. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.8 (C), 136.3 (C), 135.0 (C), 134.8 (C), 129.5 (CH), 129.4 (CH), 128.29 (CH), 128.26 (CH), 128.0 (CH), 127.5 (CH), 125.7 (CH), 125.5 (CH), 119.7 (d, *J* = 324.4 Hz, C), 67.6 (C), 49.4 (CH_2), 27.9 (CH_3, brs). **HRMS** [ESI]:



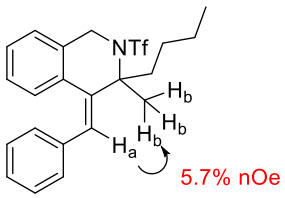
m/z calculated for $C_{19}H_{19}F_3NO_2S$ $[M+H]^+$: 382.1083, found 382.1085. Assignment of stereochemistry based on the observed nOe between the H_a (6.74 ppm 100%) with H_b (1.69 ppm, 9.0%).

(*E*)-4-benzylidene-3-butyl-3-methyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ah)

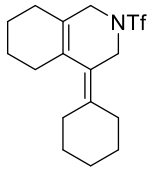


3ah

(63.8 mg, 90% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.23 – 6.83 (m, 9H), 6.67 (s, 1H), 4.46 (s, 2H), 2.15 – 1.97 (m, 1H), 1.70 (s, 3H), 1.36 – 1.07 (m, 4H), 0.77 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.93. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.9 (C), 136.4 (C), 135.2 (C), 134.6 (C), 129.5 (CH), 129.2 (CH), 128.7 (CH), 128.3 (CH), 128.0 (CH), 127.5 (CH), 127.3 (CH), 125.4 (CH), 119.8 (d, *J* = 324.9 Hz, C), 71.2 (C), 50.2 (CH_2), 26.8 (CH_2), 25.0 (CH_3, brs), 22.8 (CH_2), 14.0 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{22}H_{25}F_3NO_2S$ $[M+H]^+$: 424.1553, found 424.1553. Assignment of stereochemistry based on the observed nOe between the H_a (6.67 ppm, 100%) with H_b (0.77 ppm, 5.7%).



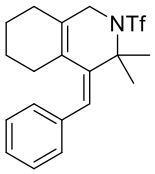
4-cyclohexylidene-2-((trifluoromethyl)sulfonyl)-1,2,3,4,5,6,7,8-octahydroisoquinoline (3ca)



3ca

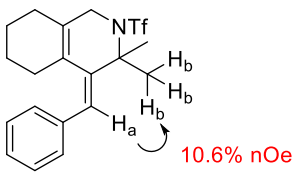
Reaction performed at 105 ºC. (41.5 mg, 71% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.03 (s, 2H), 3.84 (s, 2H), 2.36 – 2.17 (m, 6H), 2.09 – 1.97 (m, 2H), 1.78 – 1.65 (m, 2H), 1.65 – 1.51 (m, 8H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -76.01. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.6 (C), 132.0 (C), 128.4 (C), 123.0 (C), 120.3 (d, *J* = 324.0 Hz, C), 49.3 (CH_2), 46.4 (CH_2), 33.4 (CH_2), 32.1 (CH_2), 31.4 (CH_2), 28.33 (CH_2), 28.28 (CH_2), 27.8 (CH_2), 26.7 (CH_2), 23.7 (CH_2), 22.4 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{16}H_{23}F_3NO_2S$ $[M+H]^+$: 350.1396, found 350.1399.

(*E*)-4-benzylidene-3,3-dimethyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4,5,6,7,8-octahydroisoquinoline (3cg)

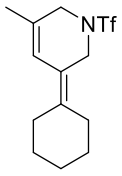


3cg

(58.2 mg, 90% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.27 – 7.10 (m, 5H), 6.48 (s, 1H), 3.84 (s, 2H), 2.12 – 2.02 (m, 2H), 1.73 – 1.65 (m, 2H), 1.64 (s, 6H), 1.62 – 1.52 (m, 2H), 1.46 – 1.35 (m, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.94. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.6 (C), 137.7 (C), 132.7 (C), 132.5 (C), 129.0 (CH), 128.2 (CH), 127.4 (CH), 123.2 (CH), 120.0 (d, *J* = 325.1 Hz, C), 65.8 (C), 49.9 (CH_2), 28.0 (CH_2), 27.6 (CH_2), 27.3 (brs, CH_3), 22.8 (CH_2), 22.4 (CH_2). **HRMS** [APCI]: *m/z* calculated for $C_{19}H_{22}F_3NO_2S$ $[M+H]^+$: 386.1396, found 386.1395. Assignment of stereochemistry based on the observed nOe between the H_a (6.48 ppm, 100%) with H_b (1.64 ppm).



3-cyclohexylidene-5-methyl-1-((trifluoromethyl)sulfonyl)-1,2,3,6-tetrahydropyridine (3da)

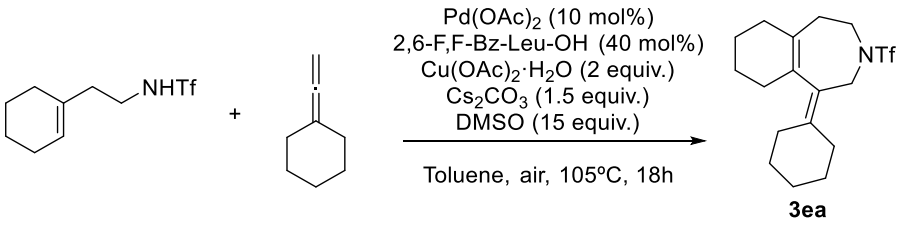


3da

(45.7 mg, 88% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.33 – 6.28 (m, 1H), 4.10 (s, 2H), 3.88 (s, 2H), 2.32 – 2.08 (m, 4H), 1.74 (s, 3H), 1.55 – 1.43 (m, 6H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -76.34. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.4 (C), 129.3 (C), 120.6 (CH), 120.2 (d, *J* = 324.0 Hz, C), 118.6 (C), 49.1 (CH_2), 44.9 (CH_2), 30.7 (CH_2), 29.7 (CH_2), 28.11 (CH_2), 28.08 (CH_2), 26.8 (CH_2), 20.8 (CH_2). **HRMS** [APCI]: *m/z* calculated for $C_{13}H_{19}F_3NO_2S$ $[M+H]^+$: 310.1083, found 310.1083.

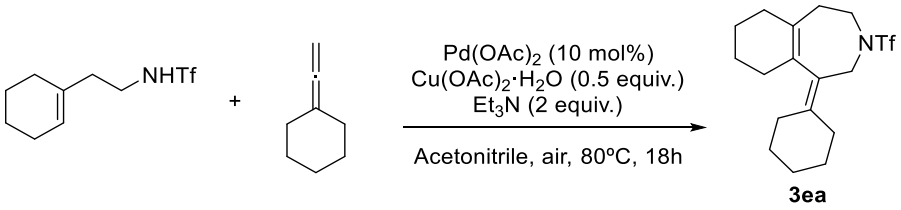
Procedure for the synthesis of 1-cyclohexylidene-3-((trifluoromethyl)sulfonyl)-2,3,4,5,6,7,8,9-octahydro-1*H*-benzo[*d*]azepine 3ea

Method A



To a solution of $Pd(OAc)_2$ (3.7 mg, 10 mol%), 2,6-F,F-Bz-Leu-OH (18.1 mg, 40 mol%), $Cu(OAc)_2$•H_2O (66.7 mg, 2 equiv.), Cs_2CO_3 (81.6 mg, 1.5 equiv.) and triflimide **1e** (43.0 mg, 0.167 mmol, 1 equiv.) in toluene (2 mL) under air atmosphere in a Schlenk tube was added the allene **2a** (18.0 mg, 0.167 mmol).The tube was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 105 °C, stirred during 18 h and then cooled to room temperature. Evaporation and column cromatography on silica gel (hexanes:diethylether; 99:1) afforded **1-cyclohexylidene-3-((trifluoromethyl)sulfonyl)-2,3,4,5,6,7,8,9-octahydro-1*H*-benzo[*d*]azepine 3ea** as a yellow oil (50.4 mg, 83% yield). NMR characterization performed at 110 ºC due to the presence of conformers. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 3.68 (s, 2H), 3.09 (t, *J* = 6.2 Hz, 2H), 1.87 – 1.76 (m, 4H), 1.69 (t, *J* = 6.3 Hz, 2H), 1.66 – 1.55 (m, 4H), 1.24 – 1.09 (m, 10H). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -76.03. **^{13}C NMR** (126 MHz, DMSO-*d*6) δ 139.6 (C), 132.5 (C), 130.2 (C), 125.8 (C), 119.4 (q, *J* = 324.7 Hz, C), 48.2 (CH_2), 44.4 (CH_2), 33.6 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 28.7 (CH_2), 27.1 (CH_2), 26.6 (CH_2), 25.3 (CH_2), 21.9 (CH_2), 21.8 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{17}H_{25}F_3NO_2S$ $[M+H]^+$: 364.1553, found 364.1549.

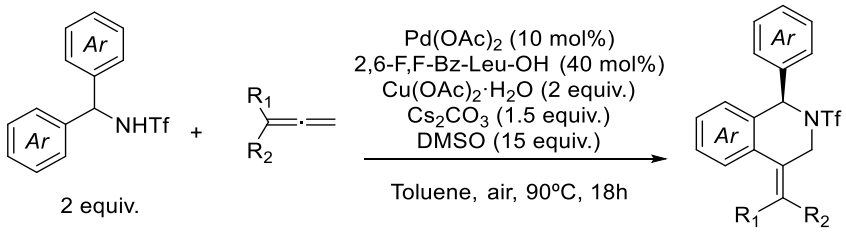
Method B



To a solution of $Pd(OAc)_2$ (3.7 mg, 10 mol%), $Cu(OAc)_2$•H_2O (16.7 mg, 0.5 equiv.), Et_3N (46 µL, 2 equiv.) and **1e** (43.0 mg, 0.167 mmol, 1 equiv.) in acetonitrile (2 mL) under air atmosphere in a Schlenk tube was added the allene **2a** (18.0 mg, 0.167 mmol).The tube was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 80 °C, stirred during 18 h and then cooled to room temperature. Evaporation and column cromatography on silica gel (hexanes:diethylether; 99:1) afforded **1-cyclohexylidene-3-((trifluoromethyl)sulfonyl)-2,3,4,5,6,7,8,9-octahydro-1*H*-benzo[*d*]azepine 3ea** as a yellow oil (37.8 mg, 62% yield).

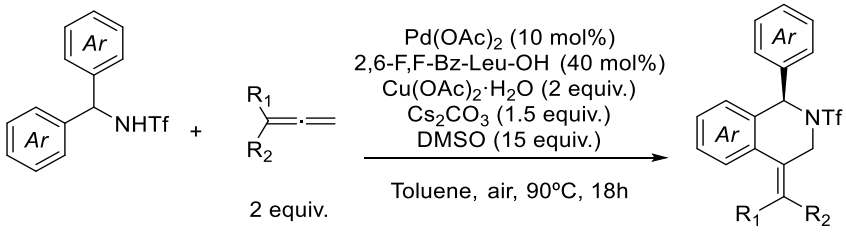
Procedure for the Pd-catalyzed desymmetrization of benzylamides with allenes 2

Method A (using excess of amide)



To a solution of $Pd(OAc)_2$ (3.7 mg, 10 mol%), 2,6-F,F-Bz-Leu-OH (18.1 mg, 40 mol%), $Cu(OAc)_2•H_2O$ (66.7 mg, 2 equiv.), Cs_2CO_3 (81.6 mg, 1.5 equiv.) and triflimides **1** (0.333 mmol, 2 equiv.) in toluene (2 mL) under air atmosphere in a Schlenk tube was added the allene **2** (0.167 mmol).The tube was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 90 °C, stirred during 18 h and then cooled to room temperature. Evaporation and column cromatography on silica gel (hexanes:diethylether; 99:1) afforded adducts **3**.

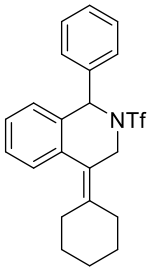
Method B (using excess of allene)



To a solution of $Pd(OAc)_2$ (3.7 mg, 10 mol%), 2,6-F,F-Bz-Leu-OH (18.1 mg, 40 mol%), $Cu(OAc)_2•H_2O$ (66.7 mg, 2 equiv.), Cs_2CO_3 (81.6 mg, 1.5 equiv.) and **1** (0.167 mmol, 2 equiv.) in toluene (2 mL) under air atmosphere in a Schlenk tube was added the allene **2** (0.333 mmol).The tube was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 90 °C, stirred during 18 h and then cooled to room temperature. Evaporation and column cromatography on silica gel (hexanes:diethylether; 99:1) afforded compounds **3**.

Racemic products were obtained using the racemic 2,6-F,F-Bz-Leu-OH

4-cyclohexylidene-1-phenyl-2-((trifluoromethyl) sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3fa)

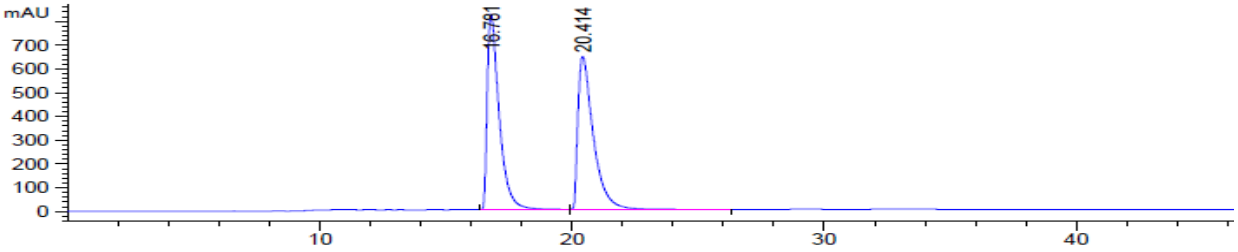


3fa

Method A: (60.1 mg, 85% yield), obtained as a white solid. Mp: 97-99 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 – 7.05 (m, 9H), 5.92 (s, 1H), 4.40 (d, *J* = 13.6 Hz, 1H), 4.10 (d, *J* = 13.4 Hz, 1H), 2.38 – 2.25 (m, 1H), 2.18 – 2.02 (m, 2H), 1.96 – 1.79 (m, 1H), 1.50 – 1.28 (m, 4H), 1.00 – 0.75 (m, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.18. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.9 (C), 138.5 (C), 137.3(C), 135.2(C), 129.8 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.31 (CH), 127.26 (CH), 127.2 (CH), 120.1 (q, *J* = 324.4 Hz, C), 119.7 (C), 62.4 (CH), 46.5 (CH_2), 31.9 (CH_2), 30.6 (CH_2), 27.8 (CH_2), 27.2 (CH_2), 26.4 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{22}H_{23}F_3NO_2S$ $[M+H]^+$: 422.1396, found 422.1386.

Enantioselectivity was determined by chiral HPLC analysis on Chiralpak IB at rt (Hexane, 0.5 mL/min).

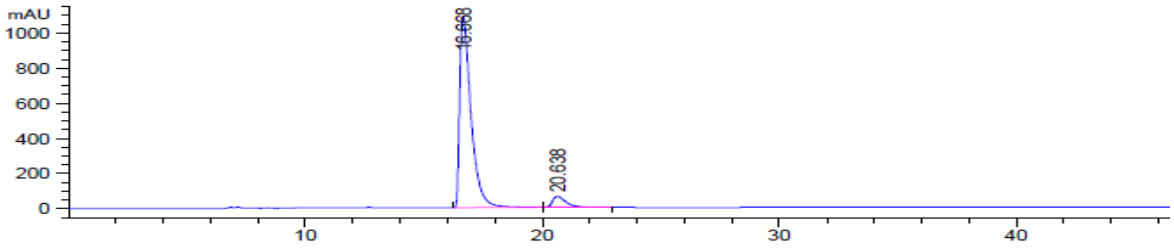
Racemic sample



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.781	BB	0.4998	2.72435e4	823.86963	49.7619
2	20.414	BB	0.6477	2.75042e4	644.70233	50.2381
Totals :				5.47478e4	1468.57196	

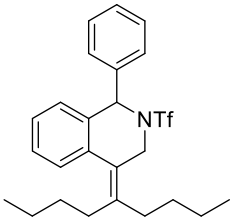
Asymmetric sample (94 : 6 e.r.)



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.668	BB	0.5091	3.63547e4	1090.09351	93.6232
2	20.638	BB	0.5843	2476.17505	63.03621	6.3768
Totals :				3.88308e4	1153.12972	

4-(nonan-5-ylidene)-1-phenyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3fb)

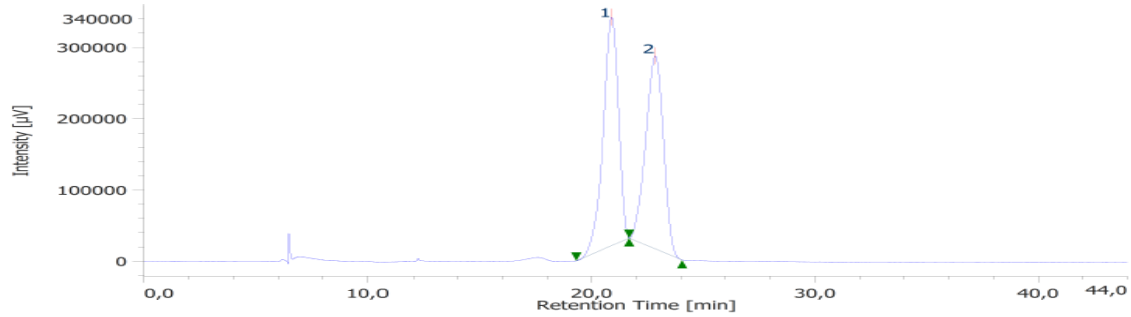


3fb

Method A: (73.2 mg, 94% yield), obtained as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.02 (m, 10H), 5.90 (s, 1H), 4.29 (d, *J* = 13.8 Hz, 1H), 4.11 (d, *J* = 13.9 Hz, 1H), 2.16 – 1.99 (m, 1H), 1.92 – 1.75 (m, 3H), 1.25 – 0.82 (m, 8H), 0.80 – 0.68 (m, 6H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.62. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.9 (C), 138.2 (C), 136.8 (C), 135.3 (C), 129.1 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 122.5 (C), 120.1 (d, *J* = 324.4 Hz, C), 62.3 (CH), 46.7 (CH_2), 32.9 (CH_2), 31.2 (CH_2), 31.0 (CH_2), 29.7 (CH_2), 23.03 (CH_2), 22.97 (CH_2), 14.13 (CH_3), 14.07 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{25}H_{31}F_3NO_2S$ $[M+H]^+$: 466.2022, found 466.2015.

Enantioselectivity was determined by chiral SFC analysis on Phenomenex i-Cellulose-5 at 40 ºC (CO_2 : MeOH = 98:02, 0.5 mL/min).

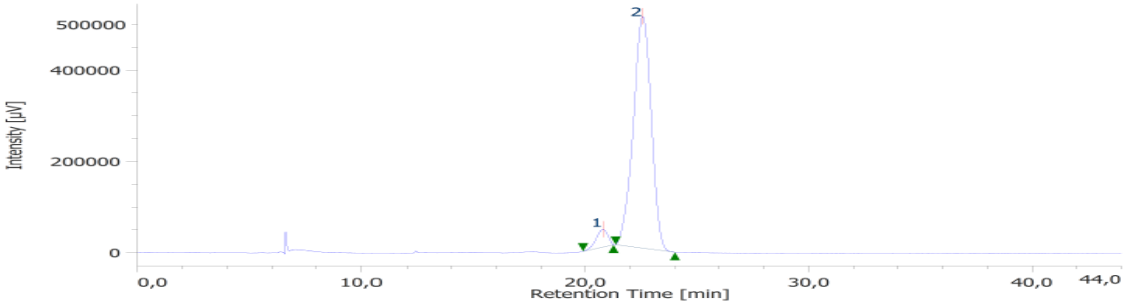
Racemic sample



Channel Name 222,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	20,887	15244033	319865	50,484	54,195	N/A	4537	1,436	0,826	
2	Unknown	9	22,833	14951856	270352	49,516	45,805	N/A	3821	N/A	0,909	

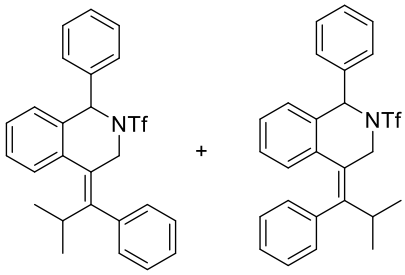
Asymmetric sample (95 : 5 e.r.)



Channel Name 222,0nm Sampling Interval 200 [msec]

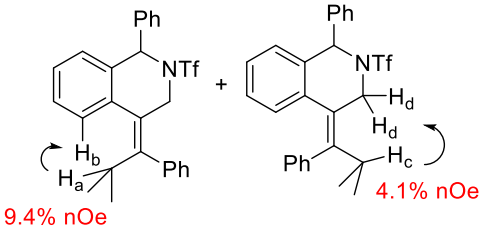
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	20,790	1419800	38483	4,739	7,048	N/A	6876	1,423	0,786	
2	Unknown	9	22,560	28540687	507501	95,261	92,952	N/A	3665	N/A	0,922	

4-(2-methyl-1-phenylpropylidene)-1-phenyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline



3fc **3fc'**

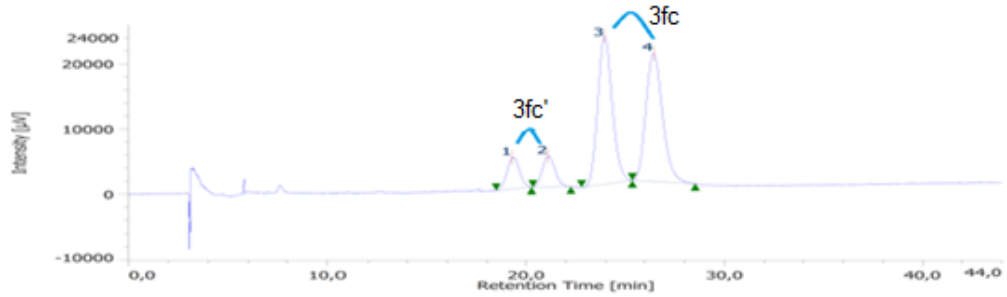
Method A performed at 70 ºC over 72h: (1:4.9 E/Z r.r. of **3fc** and **3fc'**, inseparable mixture (51.8 mg, 66% yield, white solid, Mp: 143-145 ºC)). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46 – 6.57 (m, 14H), 5.98 – 5.86 (m, 2H), 4.58 – 4.32 (m, 0.34 H), 3.76 (s, 1.66H), 3.09 (hept, *J* = 6.8 Hz, 0.83H), 2.81 (hept, *J* = 7.0 Hz, 0.17H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.41 (d, *J* = 6.8 Hz, 0.51H), 0.30 (d, *J* = 6.7 Hz, 2.49H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.34. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.5 (C), 138.5 (C), 137.0 (C), 134.6 (C), 130.6 (C), 129.8 (C), 129.2 (CH), 128.64 (CH), 128.55 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 123.8 (C), 120.1 (d, *J* = 324.3 Hz, C), 62.4 (CH), 62.2 (CH), 48.3 (CH_2), 45.7 (CH_2), 30.5 (CH), 22.3 (CH_3), 21.5 (CH_3), 20.1 (CH_3), 19.9 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{26}H_{25}F_3NO_2S$ $[M+H]^+$: 472.1555, found 472.1549.



Assignment of stereochemistry based on the observed nOe between the H_a (3.09 ppm, 100%) with H_b (7.45 – 7.28 ppm, 9.4%) and the H_c (2.81 ppm, 100%) with the H_d (4.58 – 4.32 ppm, 4.1%).

Enantioselectivity was determined by chiral SFC analysis on Phenomenex Cellulose-2 at 40 ºC (CO_2 : MeOH = 98:02, 1 mL/min).

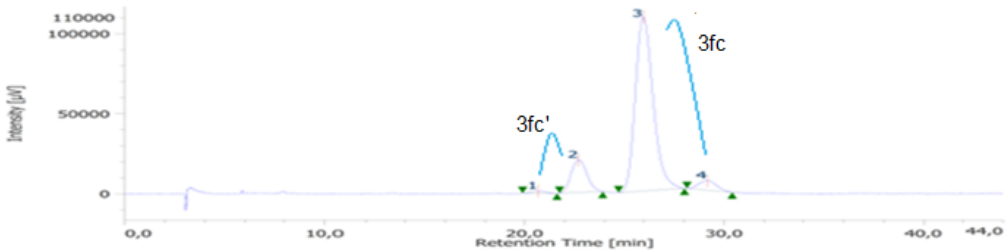
Racemic sample



Channel Name 254,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	19.283	210552	4866	7.704	9.360	N/A	4391	1.550	1.087	
2	Unknown	11	21.100	207639	4747	7.598	9.132	N/A	5065	2.240	1.126	
3	Unknown	11	23.933	1165726	22705	42.656	43.678	N/A	5023	1.728	1.176	
4	Unknown	11	26.410	1148947	19664	42.042	37.829	N/A	4808	N/A	1.208	

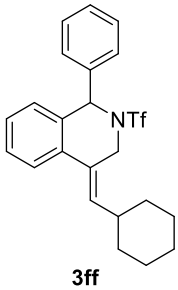
Asymmetric sample (**3fc**, 95 : 5 e.r., **3fc**', 94 : 6 e.r.)



Channel Name 254,0nm Sampling Interval 200 [msec]

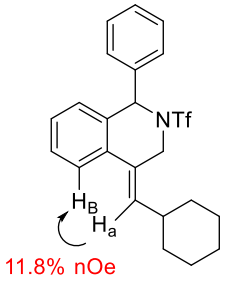
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	20.670	70695	1474	0.846	1.081	N/A	3968	1.455	1.069	
2	Unknown	11	22.703	1117247	20266	13.362	14.862	N/A	3715	2.079	1.107	
3	Unknown	11	25.937	6805087	108729	81.388	79.732	N/A	4059	1.910	1.266	
4	Unknown	11	29.137	368302	5898	4.405	4.325	N/A	4529	N/A	1.108	

(*Z*)-4-(cyclohexylmethylene)-1-phenyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ff)



3ff

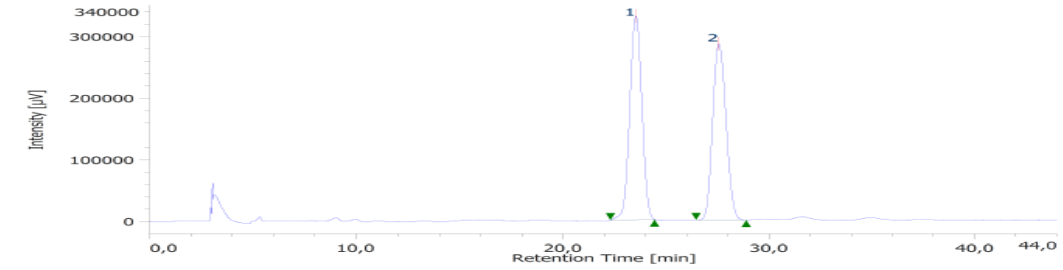
Method A: (58.9 mg, 81% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.09 (m, 7H), 6.98 (d, *J* = 7.1 Hz, 1H), 6.07 (s, 1H), 5.97 (d, *J* = 9.6 Hz, 1H), 4.60 (d, *J* = 16.6 Hz, 1H), 3.80 (d, *J* = 16.6 Hz, 1H), 2.23 – 2.01 (m, 1H), 1.76 – 0.89 (m, 10H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -76.64. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.3 (C), 133.2 (C), 132.9 (CH), 128.83 (CH), 128.76 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 127.4 (CH), 125.0 (C), 123.9 (CH), 119.8 (q, *J* = 323.2 Hz, C), 61.2 (CH), 42.3 (CH_2), 37.1 (CH), 32.7 (CH_2), 32.6 (CH_2), 26.0 (CH_2), 25.8 (CH_2), 25.8 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{23}H_{25}F_3NO_2S$ $[M+H]^+$: 436.1553, found 436.1550.



Assignment of stereochemistry based on the observed nOe between the H_a (5.97 ppm, 100%) with H_b (7.65 ppm, 11.8%).

Enantioselectivity was determined by chiral SFC analysis on Phenomenex Cellulose-1 at 40 ºC (CO_2 : MeOH = 98:02, 1 mL/min).

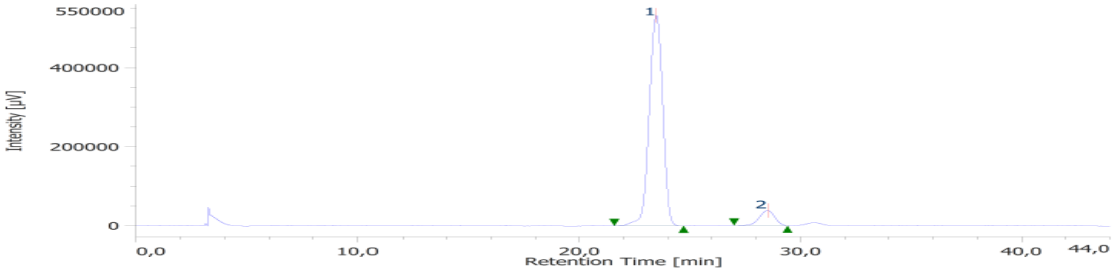
Racemic sample



Channel Name 210,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	23.537	13523659	330453	51.207	53.629	N/A	7432	3.505	0.995	
2	Unknown	5	27.570	12886049	285726	48.793	46.371	N/A	8227	N/A	1.115	

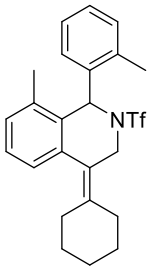
Asymmetric sample (93 : 7 e.r.)



Channel Name 210,0nm Sampling Interval 200 [msec]

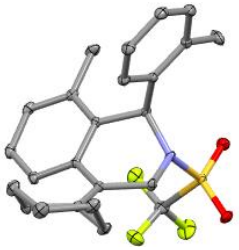
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	23.467	22591968	532175	92.535	93.358	N/A	6934	4.194	0.959	
2	Unknown	5	28.507	1822624	37862	7.465	6.642	N/A	7906	N/A	0.912	

4-cyclohexylidene-8-methyl-1-(*o*-tolyl)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ga)



3ga

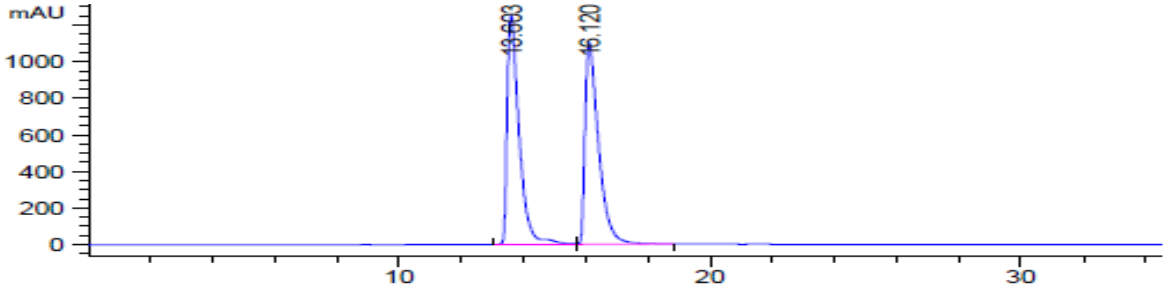
Method B: (44.9 mg, 66% yield), obtained as a white solid. Mp: 145-147 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20 – 7.08 (m, 4H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.88 (t, *J* = 7.0 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 4.41 (d, *J* = 16.4 Hz, 1H), 3.84 (d, *J* = 16.4 Hz, 1H), 2.55 (s, 3H), 2.28 (t, *J* = 11.7 Hz, 1H), 2.15 (s, 3H), 2.04 – 1.75 (m, 2H), 1.65 – 1.26 (m, 7H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.78. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.7 (C), 136.5 (C), 134.4 (C), 134.1 (C), 131.9 (C), 131.5 (CH), 130.0 (CH), 128.9 (CH), 128.5 (CH), 128.2 (CH), 127.3 (CH), 125.6 (CH), 121.0 (C), 119.6 (d, *J* = 325.2 Hz, C), 57.9 (CH), 46.2 (CH_2), 32.4 (CH_2), 30.8 (CH_2), 28.1 (CH_2), 26.9 (CH_2), 26.6 (CH_2), 20.5 (CH_3), 18.6 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{24}H_{27}F_3NO_2S$ $[M+H]^+$: 450.1709, found 450.1715.



The structure of this compound (**3ga**) was confirmed by X-Ray diffraction analysis (CCDC: 1877409).

Enantioselectivity was determined by chiral HPLC analysis on Chiralpak IB at rt (Hexane, 0.5 mL/min).

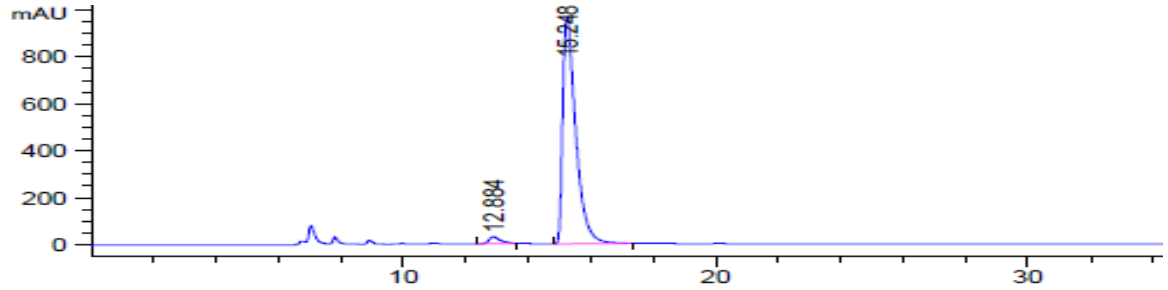
Racemic sample



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.603	BV R	0.3945	3.35972e4	1252.76074	50.2071
2	16.120	VB	0.4492	3.33200e4	1100.64124	49.7929
Totals :				6.69172e4	2353.40198	

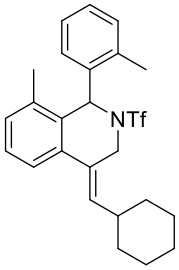
Asymmetric sample (97 : 3 e.r.)



Signal 2: DAD1 B, Sig=254,4 Ref=off

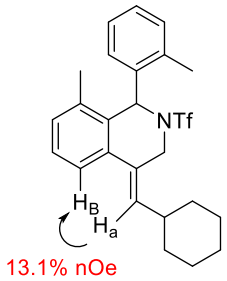
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.884	BB	0.3744	776.70538	30.16767	2.7075
2	15.248	BB	0.4320	2.79104e4	969.03998	97.2925
Totals :				2.86871e4	999.20765	

(*Z*)-4-(cyclohexylmethylene)-8-methyl-1-(*o*-tolyl)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3gf)



3gf

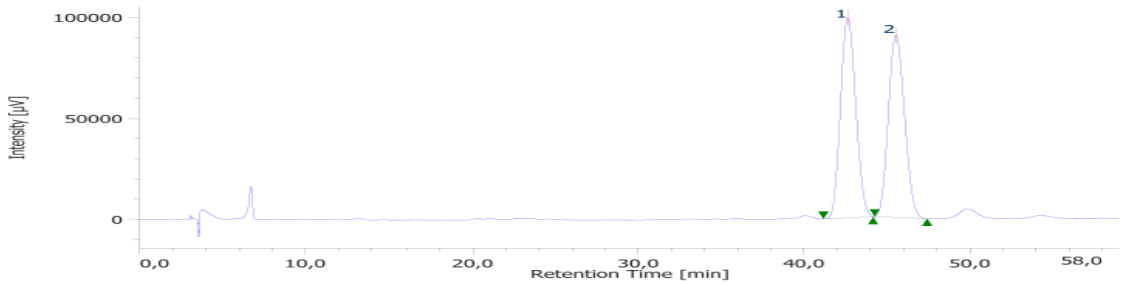
Method B: (73.5 mg, 95% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.07 (m, 3H), 7.03 – 6.83 (m, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.30 (s, 1H), 5.97 (d, *J* = 9.7 Hz, 1H), 4.61 (d, *J* = 17.6 Hz, 1H), 3.88 (d, *J* = 17.6 Hz, 1H), 2.57 (s, 3H), 2.05 (m, 1H), 1.98 (s, 3H), 1.77 – 1.53 (m, 4H), 1.49 – 1.38 (m, 1H), 1.24 – 1.01 (m, 5H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.74. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.4 (C), 134.3 (C), 133.6 (C), 133.4 (C), 132.9 (C), 132.6 (CH), 131.7 (CH), 129.7 (CH), 129.3 (CH), 129.0 (CH), 128.1 (CH), 125.9 (C), 125.8 (CH), 121.5 (CH), 119.7 (d, *J* = 324.8 Hz, C), 56.5 (CH), 42.9 (CH_2), 37.2 (CH), 32.6 (CH_2), 32.3 (CH_2), 26.0 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 20.0 (CH_3), 18.7 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{25}H_{29}F_3NO_2S$ $[M+H]^+$: 464.1866, found 464.1862.



Assignment of stereochemistry based on the observed nOe between the H_a (5.97 ppm, 100%) with H_b (7.52 ppm, 13.1%).

Enantioselectivity was determined by chiral SFC analysis on Phenomenex Cellulose-1 at 40 ºC (CO_2 : MeOH = 99:01, 1 mL/min).

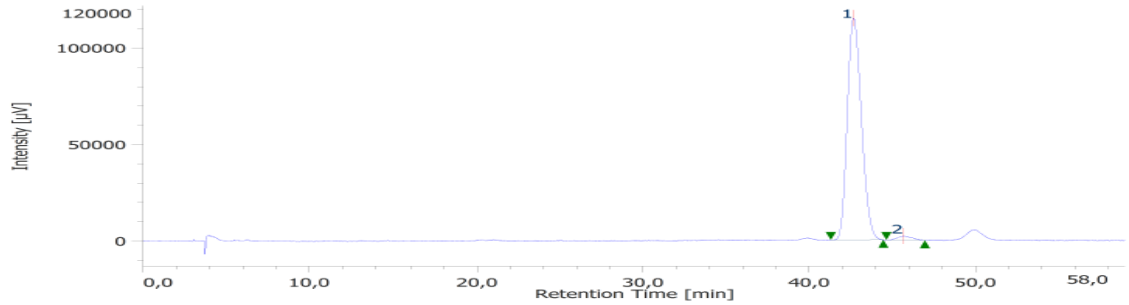
Racemic sample



Channel Name 222,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	42.633	6308646	98969	50.828	52.326	N/A	9955	1.647	1.094	
2	Unknown	10	45.530	6103049	90169	49.172	47.674	N/A	10037	N/A	1.121	

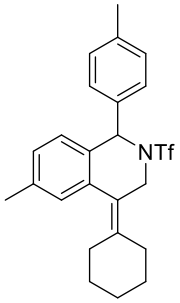
Asymmetric sample (98 : 2 e.r.)



Channel Name 222,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	42.663	6737805	114745	98.233	98.191	N/A	11900	1.881	1.194	
2	Unknown	10	45.673	121172	2115	1.767	1.809	N/A	12349	N/A	1.267	

4-cyclohexylidene-6-methyl-1-(*p*-tolyl)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ha)

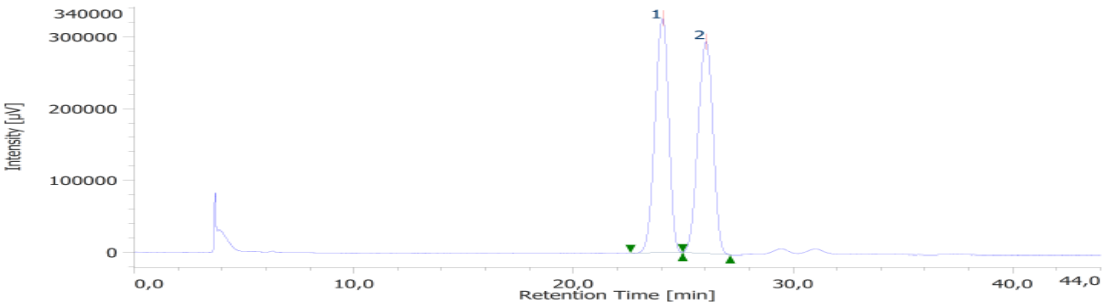


3ha

Method A: (71.2 mg, 95% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.22 – 6.87 (m, 7H), 5.85 (s, 1H), 4.35 (d, *J* = 13.5 Hz, 1H), 4.08 (d, *J* = 14.0 Hz, 1H), 2.31 (s, 4H), 2.24 (s, 3H), 2.12 (d, *J* = 13.0 Hz, 2H), 1.90 (t, *J* = 11.6 Hz, 1H), 1.53 – 1.28 (m, 4H), 0.96 (brs, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.16. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.4 (C), 137.4 (C), 137.4 (C), 135.9 (C), 134.9 (C), 134.5 (C), 130.3 (CH), 129.0 (CH), 127.8 (CH), 127.4 (CH), 127.1 (CH), 120.2 (d, *J* = 324.2 Hz, C), 120.0 (C), 62.1 (CH), 46.3 (CH_2), 32.0 (CH_2), 30.7 (CH_2), 27.9 (CH_2), 27.3 (CH_2), 26.5 (CH_2), 21.6 (CH_3), 21.1 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{24}H_{27}F_3NO_2S$ $[M+H]^+$: 450.1709, found 450.1707.

Enantioselectivity was determined by chiral SFC analysis on Phenomenex Cellulose-1 at 40 ºC (CO_2 : MeOH = 98:02, 1 mL/min).

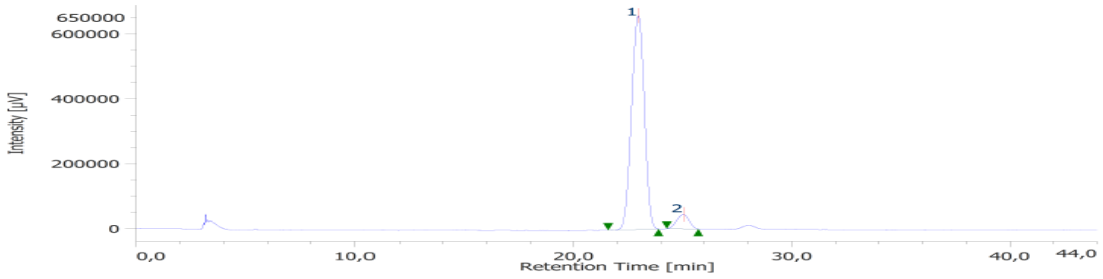
Racemic sample



Channel Name 210,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	24,047	14221311	326263	50,358	52,512	N/A	6651	1,611	0,913	
2	Unknown	5	26,030	14019082	295054	49,642	47,488	N/A	6526	N/A	0,935	

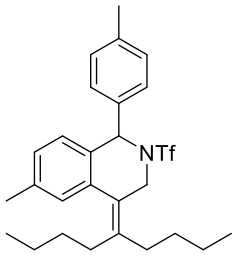
Asymmetric sample (94 : 6 e.r.)



Channel Name 210,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	22,953	26775063	657766	93,968	93,772	N/A	6934	1,893	0,955	
2	Unknown	5	25,017	1718772	43685	6,032	6,228	N/A	8536	N/A	0,941	

6-methyl-4-(nonan-5-ylidene)-1-(p-tolyl)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3hb)

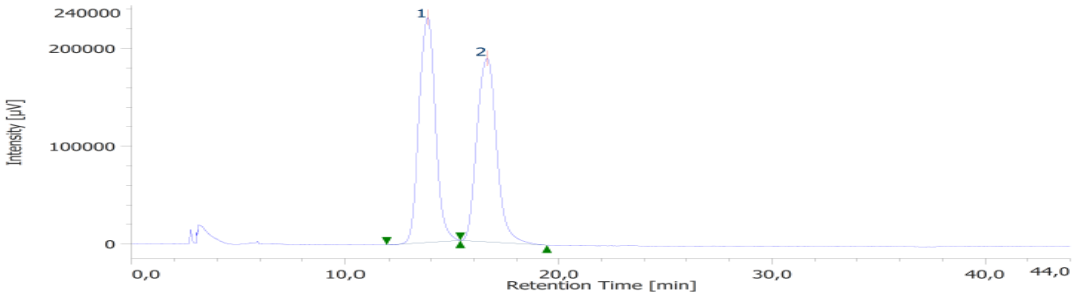


3hb

Method A: (76.2 mg, 92% yield), obtained as a white solid. Mp: 56-58 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20 – 6.89 (m, 7H), 5.84 (s, 1H), 4.25 (d, *J* = 13.8 Hz, 1H), 4.08 (d, *J* = 14.0 Hz, 1H), 2.32 (s, 3H), 2.20 (s, 3H), 1.91 – 1.76 (m, 3H), 1.31 – 1.11 (m, 7H), 1.11 – 0.97 (m, 2H), 0.80 (t, *J* = 6.9 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.52. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.4 (C), 137.50 (C), 137.46 (C), 135.4 (C), 135.0 (C), 134.1 (C) 129.7 (CH), 129.0 (CH), 127.7 (CH), 127.4 (CH), 127.0 (CH), 122.7 (C), 120.1 (d, *J* = 324.4 Hz, C), 62.0 (CH), 46.6 (CH_2), 32.9 (CH_2), 31.2 (CH_2), 31.1 (CH_2), 29.7 (CH_2), 23.00 (CH_2), 22.97 (CH_2), 21.6 (CH_3), 21.1 (CH_3), 14.2 (CH_3), 14.1 (CH_3). **HRMS** [ESI]: calculated for $C_{27}H_{35}F_3NO_2S$ $[M+H]^+$: 494.2335, found 494.2337.

Enantioselectivity was determined by chiral SFC analysis on Phenomenex Cellulose-2 at 40 ºC (CO_2 : MeOH = 98:02, 1 mL/min).

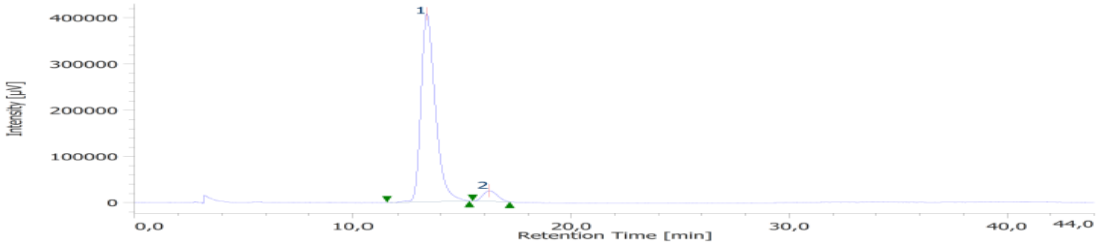
Racemic sample



Channel Name 210,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	13,827	12282853	229944	50,397	55,069	N/A	1512	1,783	1,054	
2	Unknown	5	16,610	12089469	187611	49,603	44,931	N/A	1512	N/A	1,130	

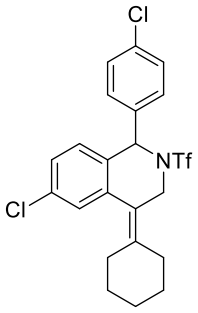
Asymmetric sample (95 : 5 e.r.)



Channel Name 210,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	13,347	18751014	406458	94,741	94,670	N/A	2063	2,378	1,411	
2	Unknown	5	16,220	1040795	22882	5,259	5,330	N/A	2705	N/A	1,149	

6-chloro-1-(4-chlorophenyl)-4-cyclohexylidene-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline

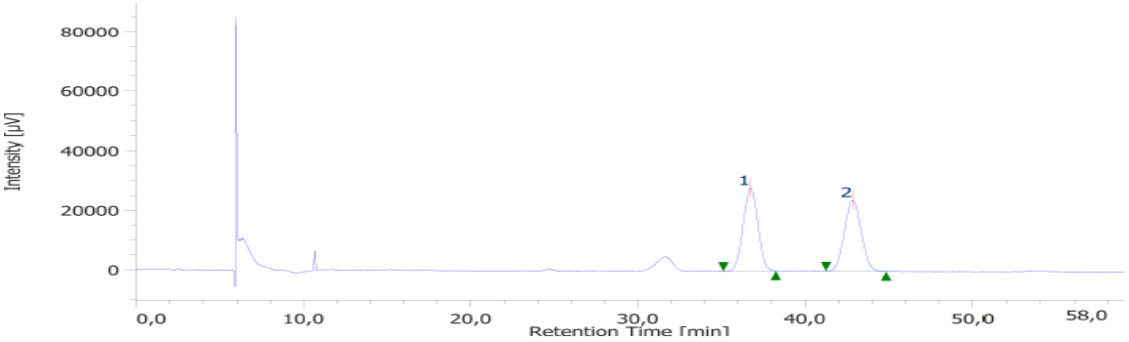


3ia

Method A: (75.9 mg, 93% yield), obtained as a white solid. Mp: 47-49 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.27 – 6.97 (m, 7H), 5.86 (s, 1H), 4.36 (d, *J* = 13.5 Hz, 1H), 4.07 (d, *J* = 13.8 Hz, 1H), 2.39 – 2.22 (m, 1H), 2.22 – 2.03 (m, 2H), 2.03 – 1.84 (m, 1H), 1.56 – 1.30 (m, 4H), 1.08 – 0.84 (m, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.38. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.7 (C), 136.8 (C), 135.2 (C), 134.1 (C), 134.0 (C), 129.8 (CH), 128.70 (CH), 128.65 (CH), 128.5 (CH), 127.4 (CH), 120.0 (q, *J* = 324.0 Hz, C), 118.7 (C), 77.4 (CH), 61.2 (CH_2), 46.1 (CH_2), 31.9 (CH_2), 30.7 (CH_2), 27.9 (CH_2), 27.3 (CH_2), 26.2 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{22}H_{21}Cl_2F_3NO_2S$ $[M+H]^+$: 490.0617, found 490.0616.

Enantioselectivity was determined by chiral SFC analysis on Phenomenex i-Cellulose-5 at 40 ºC (CO_2 : MeOH = 97:03, 0.5 mL/min).

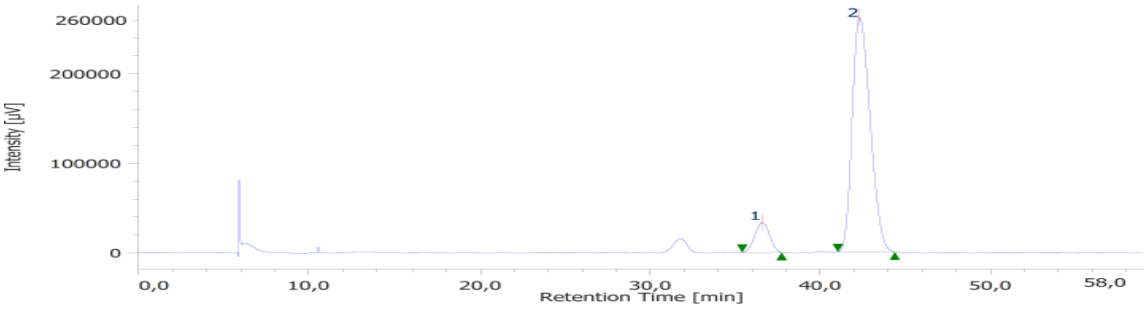
Racemic sample



Channel Name 254,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	36,737	1718634	27961	50,611	53,843	N/A	7956	3,486	1,000	
2	Unknown	11	42,853	1677171	23970	49,389	46,157	N/A	8392	N/A	1,024	

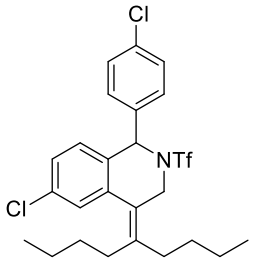
Asymmetric sample (91 : 9 e.r.)



Channel Name 254,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	11	36,557	2014371	33391	9,462	11,308	N/A	7997	3,192	1,018	
2	Unknown	11	42,313	19274230	261900	90,538	88,692	N/A	7299	N/A	1,258	

6-chloro-1-(4-chlorophenyl)-4-(nonan-5-ylidene)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ib)

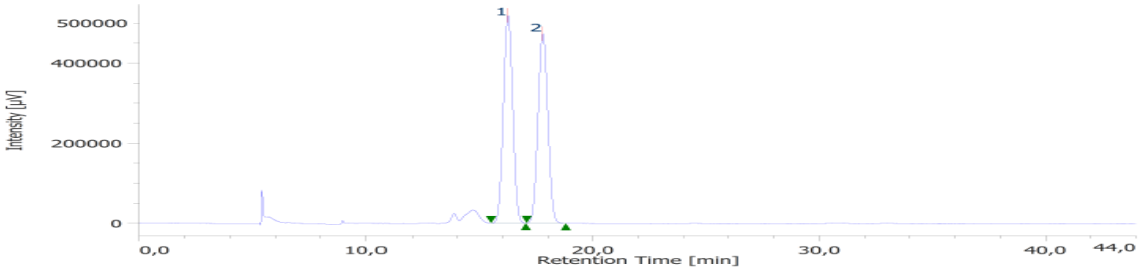


3ib

Method A: (76.8 mg, 86% yield), obtained as a transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 5H), 7.01 – 6.94 (m, 2H), 5.84 (s, 1H), 4.26 (d, *J* = 14.0 Hz, 1H), 4.08 (d, *J* = 14.0 Hz, 1H), 2.17 – 2.00 (m, 1H), 1.93 – 1.78 (m, 3H), 1.26 – 0.87 (m, 8H), 0.86 – 0.69 (m, 6H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.39. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.9 (C), 136.9 (C), 136.4 (C), 134.8 (C), 134.2 (C), 134.1 (C), 129.3 (CH), 128.7 (CH), 128.7 (CH), 128.4 (CH), 127.4 (CH), 121.4 (C), 120.1 (d, *J* = 324.4 Hz, C), 61.2 (CH), 46.3 (CH_2), 32.9 (CH_2), 31.4 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 22.95 (CH_2), 22.92 (CH_2), 14.1 (CH_3), 14.0 (CH_3). **HRMS** [ESI]: *m/z* calculated for $C_{25}H_{29}Cl_2F_3NO_2S$ $[M+H]^+$: 534.1243, found 534.1237.

Enantioselectivity was determined by chiral SFC analysis on Phenomenex i-Cellulose-5 at 40 ºC (CO_2 : MeOH = 96:04, 0.5 mL/min).

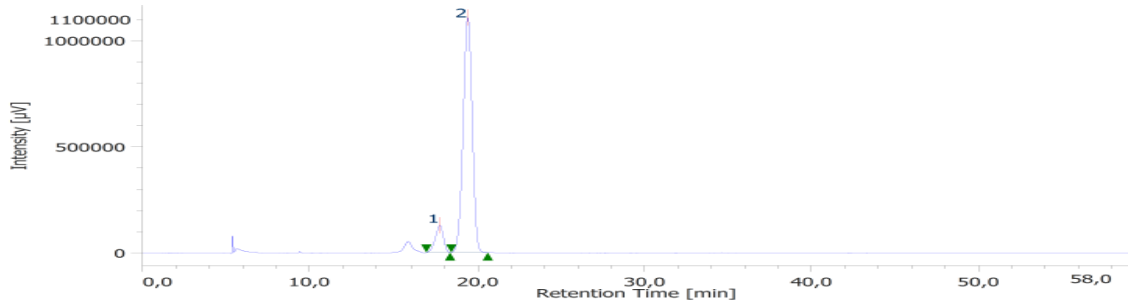
Racemic sample



Channel Name 220,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	16.227	14829939	517718	50.967	52.294	N/A	7113	1.955	1.014	
2	Unknown	5	17.767	14266975	472301	49.033	47.706	N/A	7697	N/A	1.039	

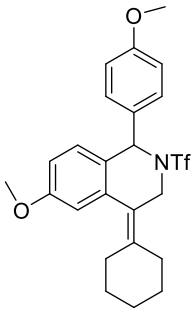
Asymmetric sample (91 : 9 e.r.)



Channel Name 220,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	17.717	4367855	127345	9.485	10.328	N/A	6027	1.751	0.866	
2	Unknown	5	19.387	41683416	1105637	90.515	89.672	N/A	6021	N/A	0.959	

4-cyclohexylidene-6-methoxy-1-(4-methoxyphenyl)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ja)

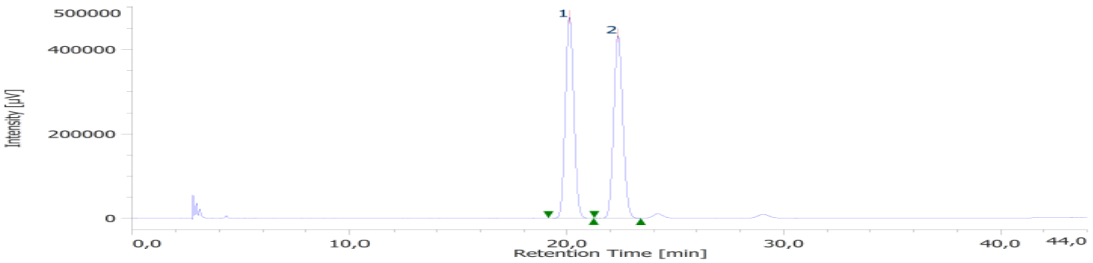


3ja

Method A: (74.8 mg, 93% yield), obtained as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 1H), 7.03 – 6.98 (m, 2H), 6.78 – 6.68 (m, 4H), 5.85 (s, 1H), 4.30 (d, *J* = 13.7 Hz, 1H), 4.10 (d, *J* = 13.8 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 2.53 – 1.78 (m, 4H), 1.56 – 1.31 (m, 4H), 1.13 – 0.95 (m, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.59. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.2 (C), 158.9 (C), 140.8 (C), 136.2 (C), 131.0 (C), 129.8 (C), 128.8 (CH), 128.2 (CH), 120.1 (d, *J* = 324.0 Hz, C), 120.0 (C), 115.6 (CH), 113.7 (CH), 112.1 (CH), 61.5 (CH), 55.5 (CH_3), 55.4 (CH_3), 46.0 (CH_2), 32.0 (CH_2), 30.8 (CH_2), 27.9 (CH_2), 27.4 (CH_2), 26.4 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{24}H_{27}F_3NO_4S$ $[M+H]^+$: 482.1607, found 482.1612.

Enantioselectivity was determined by chiral SFC analysis on Phenomenex Cellulose-1 at 40 ºC (CO_2 : MeOH = 95:05, 1 mL/min).

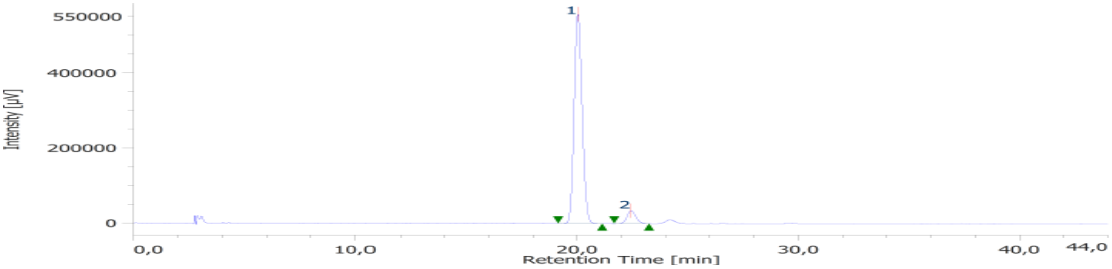
Racemic sample



Channel Name 222,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	20,093	12979419	476051	50,142	52,401	N/A	12311	2,976	1,087	
2	Unknown	10	22,343	12905703	432425	49,858	47,599	N/A	12735	N/A	1,088	

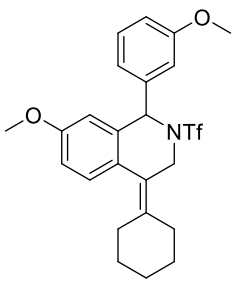
Asymmetric sample (94 : 6 e.r.)



Channel Name 222,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	20,017	13956839	557304	93,685	94,256	N/A	14680	3,483	1,127	
2	Unknown	10	22,437	940851	33965	6,315	5,744	N/A	15014	N/A	1,098	

4-cyclohexylidene-7-methoxy-1-(3-methoxyphenyl)-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (3ka)

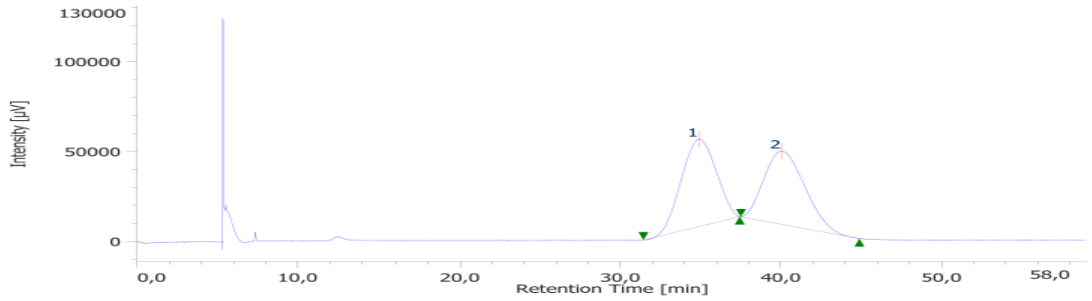


3ka

Method A: (72.4 mg, 90% yield), obtained as a white solid. Mp: 125-127 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 1H), 7.11 – 7.08 (m, 1H), 6.82 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.75 (d, *J* = 2.7 Hz, 1H), 6.72 – 6.70 (m, 1H), 6.70 – 6.68 (m, 1H), 6.68 – 6.65 (m, 1H), 5.83 (s, 1H), 4.34 (d, *J* = 13.6 Hz, 1H), 4.11 (d, *J* = 12.7 Hz, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 2.43 – 2.22 (m, 1H), 2.18 – 2.01 (m, 2H), 2.01 – 1.77 (m, 1H), 1.52 – 1.28 (m, 4H), 1.05 – 0.85 (m, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -75.58. **^{13}C NMR** (76 MHz, $CDCl_3$) δ 159.8 (C), 158.6 (C), 139.9 (C), 139.4 (C), 138.3 (C), 131.0 (CH), 129.5 (CH), 127.4 (C), 120.1 (d, *J* = 323.9 Hz, C), 119.9 (CH), 119.2 (C), 113.7 (CH), 113.4 (CH), 112.8 (CH), 112.6 (CH), 62.3 (CH), 55.5 (CH_3), 55.4 (CH_3), 46.6 (CH_2), 32.0 (CH_2), 30.6 (CH_2), 27.8 (CH_2), 27.3 (CH_2), 26.5 (CH_2). **HRMS** [ESI]: *m/z* calculated for $C_{24}H_{27}F_3NO_4S$ $[M+H]^+$: 482.1607, found 482.1619.

Enantioselectivity was determined by chiral SFC analysis on Phenomenex Amylose-2 at 40 ºC (CO_2 : MeOH = 96:04, 0.5 mL/min).

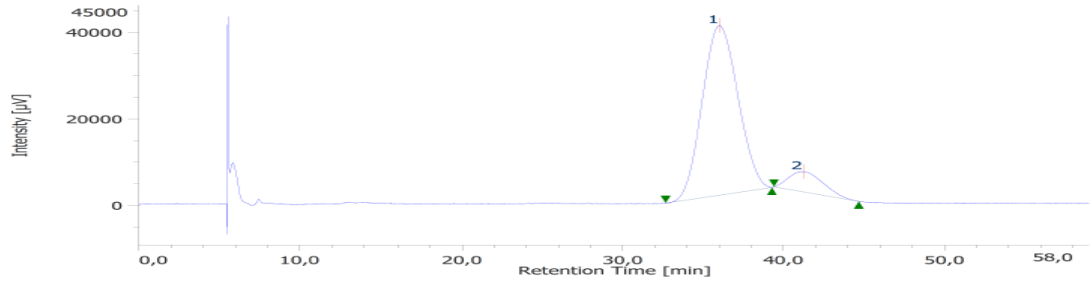
Racemic sample



Channel Name 254,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	34,880	7340802	48615	50,471	54,400	N/A	1114	1,148	0,986	
2	Unknown	5	40,047	7203868	40750	49,529	45,600	N/A	1094	N/A	1,233	

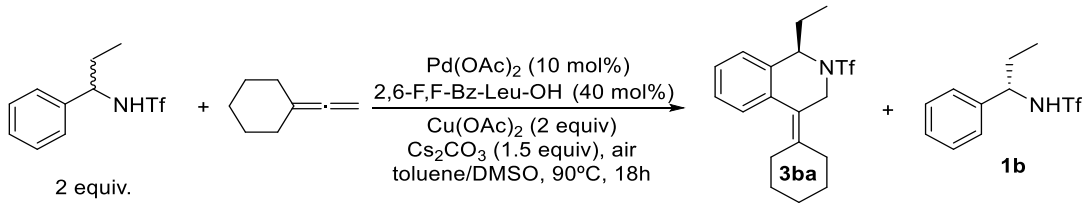
Asymmetric sample (90 :10 e.r.)



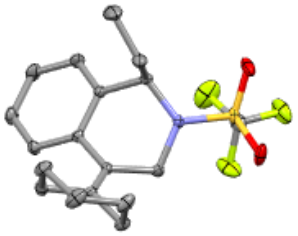
Channel Name 254,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	36,020	6055247	39232	89,702	89,352	N/A	1185	1,251	1,061	
2	Unknown	5	41,210	695179	4675	10,298	10,648	N/A	1589	N/A	1,321	

Procedure for the kinetic resolution of benzylamides with allenes

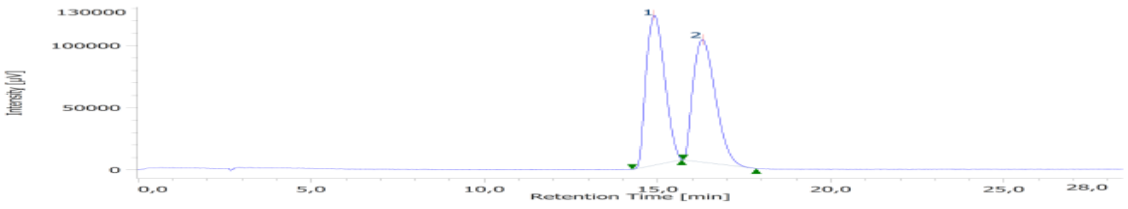


To a solution of $Pd(OAc)_2$ (3.7 mg, 10 mol%), 2,6-F,F-Bz-Leu-OH (18.1 mg, 40 mol%), $Cu(OAc)_2•H_2O$ (66.7 mg, 2 equiv.), Cs_2CO_3 (81.6 mg, 1.5 equiv.) and **1b** (89.3 mg, 0.333 mmol, 2 equiv.) in toluene (2 mL) under air atmosphere in a Schlenk tube was added the allene **2a** (18.0 mg, 0.167 mmol).The tube was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 90 °C, stirred during 22 h and then cooled to room temperature. Evaporation and column cromatography on silica gel (hexanes:diethylether; 99:1) afforded **4-cyclohexylidene-1-ethyl-2-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline** (**3ba**) as a white solid (56.6 mg, 91% yield, Mp: 88-90 ºC) and remaining **1b** as a white solid (39.0 mg, 40% yield based on the starting benzylamide, 80% recovered based on reaction yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.28 – 7.10 (m, 3H), 7.03 (d, J = 7.3 Hz, 1H), 4.62 – 4.44 (m, 2H), 4.07 (d, *J* = 13.4 Hz, 1H), 2.45 – 2.34 (m, 2H), 2.34 – 2.11 (m, 2H), 1.92 – 1.37 (m, 9H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.54. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.5 (C), 137.8 (C), 133.9 (C), 129.5 (CH), 127.4 (CH), 127.0 (CH), 126.6 (CH), 120.2 (d, *J* = 324.4 Hz, C), 119.8 (C), 62.3 (CH), 46.3 (CH_2), 32.2 (CH_2), 31.0 (CH_2), 28.5 (CH_2), 28.0 (CH_2), 26.7 (CH_2), 11.2 (CH). **HRMS** [ESI]: *m/z* calculated for $C_{18}H_{23}F_3NO_2S$ $[M+H]^+$: 374.1396, found 374.1398. The structure of **3ba** was confirmed by X-Ray diffraction analysis (CCDC: 1880116, hydrogens omitted for clarity).



Enantioselectivity was determined by chiral SFC analysis on Chiralpak IF-3 at 40 ºC (CO_2, 2 mL/min).

Racemic sample



Channel Name 254,0nm Sampling Interval 200 [msec]

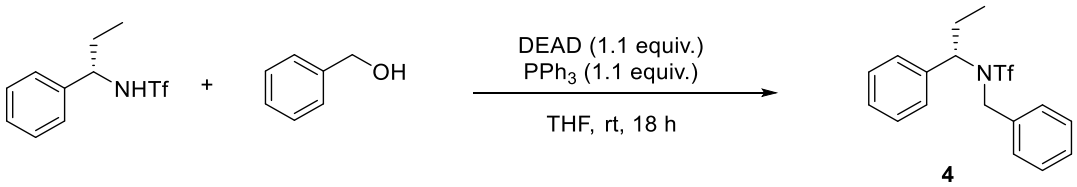
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	14.907	4535366	120606	50.574	54.988	N/A	3234	1.214	1.259	
2	Unknown	5	16.287	4432385	98727	49.426	45.012	N/A	2804	N/A	1.445	

Asymmetric sample (93 :7 e.r.)

Channel Name 254,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	16.320	2467749	52800	93.060	92.707	N/A	2635	1.376	1.288	
2	Unknown	9	18.030	184031	4154	6.940	7.293	N/A	3487	N/A	1.353	

Procedure for the derivatization[9] of recovered triflimide 1b to measure the enantiomeric ratio



4

To a solution of recovered **1,1,1-trifluoro-N-(1-phenylpropyl)methanesulfonamide** (**1b**, 39.0 mg, 0.146 mmol), benzyl alcohol (15.8 mg, 1 equiv.), and triphenylphosphine (42.1 mg, 1.1 equiv.) in THF (0.15 mL) was added DEAD (63 µL, 40% in toluene, 1.1 equiv.). The reaction mixture was stirred at room temperature overnight. Evaporation of the solvent and column chromatography on silica gel (hexanes:diethylether; 90:10) afforded **N-benzyl-1,1,1-trifluoro-N-(1-phenylpropyl)methanesulfonamide (4**) as a transparent oil (22.8 mg, 44%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.36 – 6.99 (m, 10H), 4.87 (t, J = 7.9 Hz, 1H), 4.46 (d, J = 16.1 Hz, 1H), 3.92 (brs, 1H), 1.77 (d, J = 10.4 Hz, 2H), 0.69 (t, J = 7.3 Hz, 3H). **HRMS** [ESI]: *m/z* calculated for $C_{17}H_{18}F_3NO_2S$ $[M+H]^+$: 357.1005, found 357.1001.

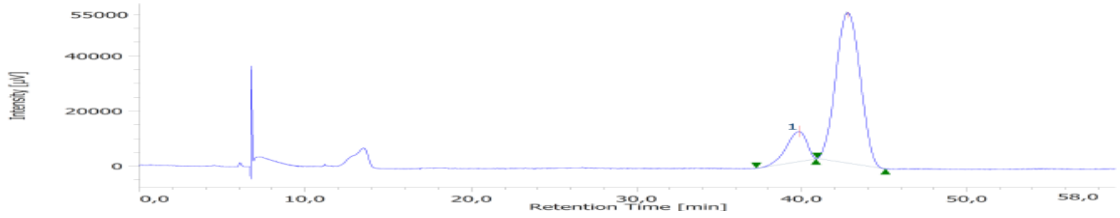
Enantioselectivity was determined by chiral SFC analysis on Phenomenex Cellulose-1 at 40 ºC (CO_2 : MeOH = 99:01, 0.5 mL/min).

Racemic sample

Channel Name 222,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	40.423	3235516	32453	50.331	51.475	N/A	3633	1.208	0.818	
2	Unknown	10	43.773	3192986	30593	49.669	48.525	N/A	3705	N/A	1.010	

Asymmetric sample (86 :14 e.r.)

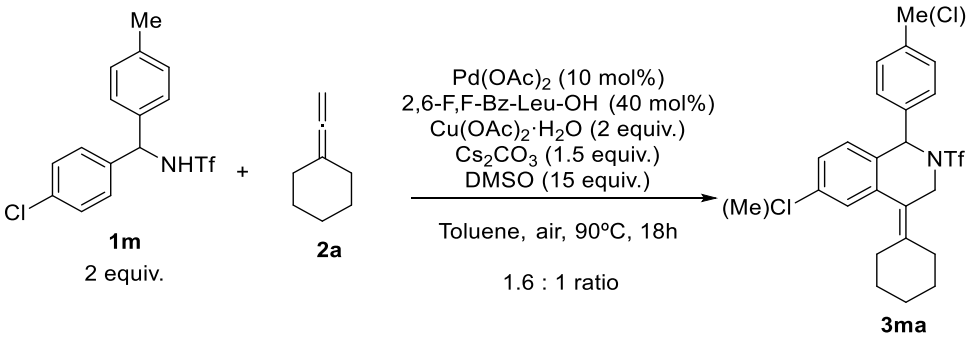


Channel Name 222,0nm Sampling Interval 200 [msec]

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	39.810	938742	10978	14.309	16.707	N/A	4680	1.175	0.767	
2	Unknown	10	42.817	5621613	54731	85.691	83.293	N/A	3734	N/A	0.998	

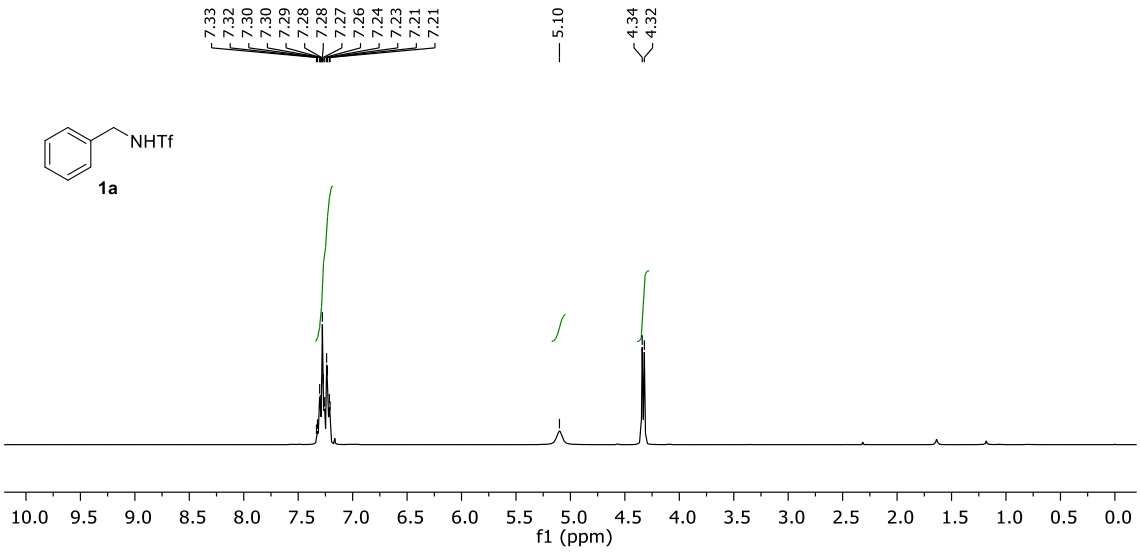
[9] Bell, E.; Knight, D. W.; Uk, N. G. Z. R. D.; Gravestock, B. *Org. Lett.* **1995**, *36*, 8681–8684.

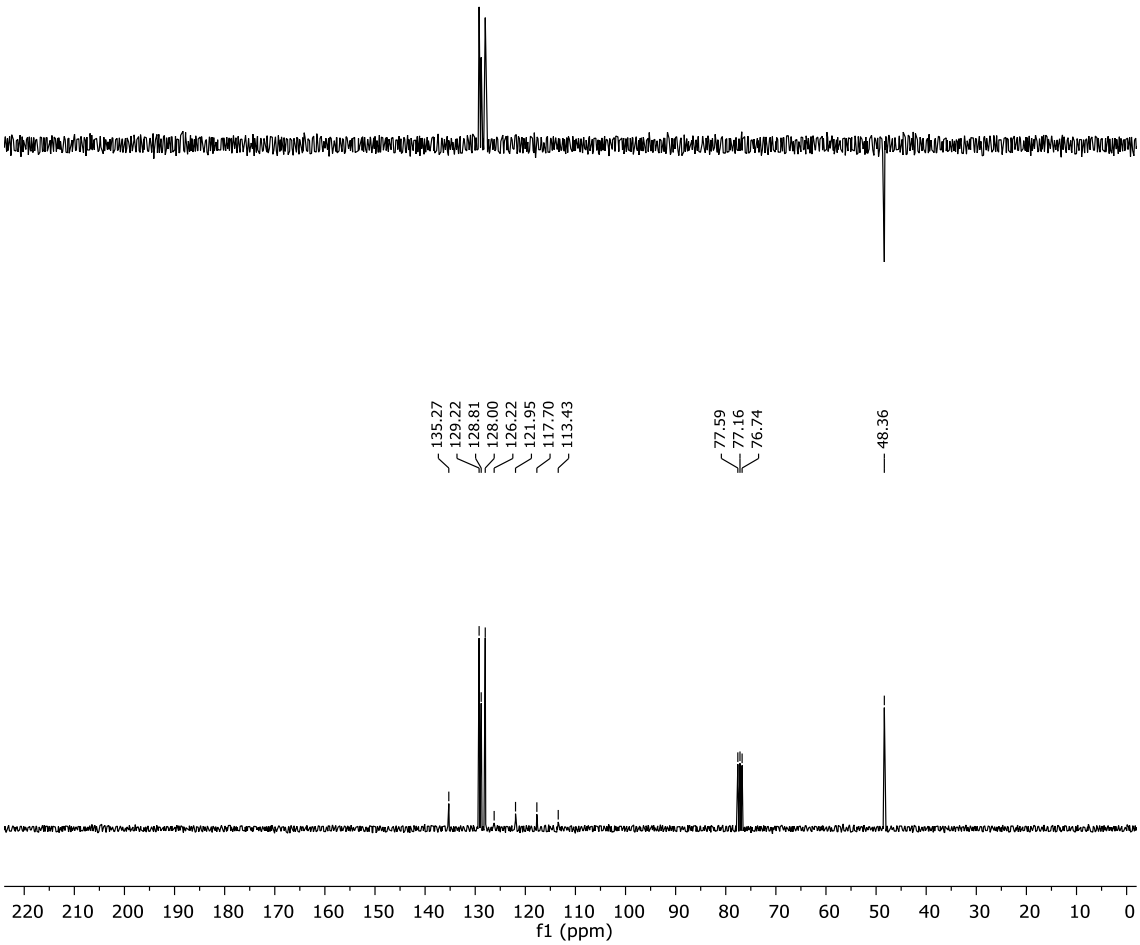
Pd-catalyzed annulation of a triflamide 1m (with two different aryl rings) with allene 2a

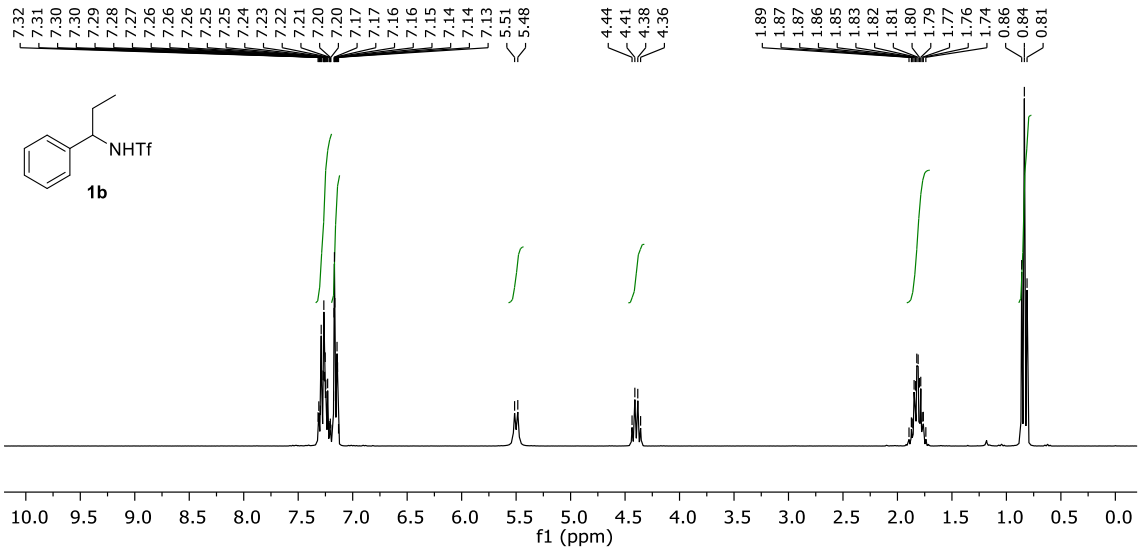


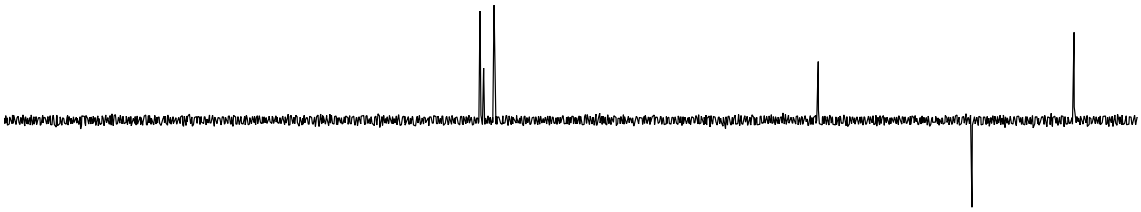
To a solution of $Pd(OAc)_2$ (3.7 mg, 10 mol%), 2,6-F,F-Bz-Leu-OH (18.1 mg, 40 mol%), $Cu(OAc)_2•H_2O$ (66.7 mg, 2 equiv.), Cs_2CO_3 (81.6 mg, 1.5 equiv.) and **1m** (121.5 mg, 0.333 mmol, 2 equiv.) in toluene (2 mL), under air atmosphere, in a Schlenk tube was added the allene **2a** (18.0 mg, 0.167 mmol).The tube was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 90 °C, stirred during 18 h and then cooled to room temperature. Evaporation and column cromatography on silica gel (hexanes:diethylether; 99:1). Obtained as a 1.6:1 inseparable mixture (70.4 mg, 90% yield, white solid). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 6.87 (m, 7H), 5.88 (s, 0.39H), 5.83 (s, 0.61H), 4.52 – 3.88 (m, 2H), 2.41 – 2.03 (m, 6H), 1.98 – 1.82 (m, 1H), 1.54 – 1.25 (m, 4H), 1.10 – 0.69 (m, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.42. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.0 (C), 140.6 (C), 137.9 (C), 137.8 (C), 137.7 (C), 135.0 (C), 133.8 (C), 133.7 (C), 133.5 (C), 130.4 (CH) 129.8 (C), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.0 (C), 127.8 (C), 127.6 (C), 127.4 (CH), 127.38 (CH), 127.11 (CH), 127.06 (CH), 118.76 (d, *J* = 125.7 Hz, C), 61.7 (CH), 61.6 (CH), 46.5 (CH_2), 46.0 (CH_2), 31.94 (CH_2), 31.89 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 27.9 (CH_2), 27.8 (CH_2), 27.4 (CH_2), 27.2 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 21.6 (CH_3), 21.1 (CH_3).

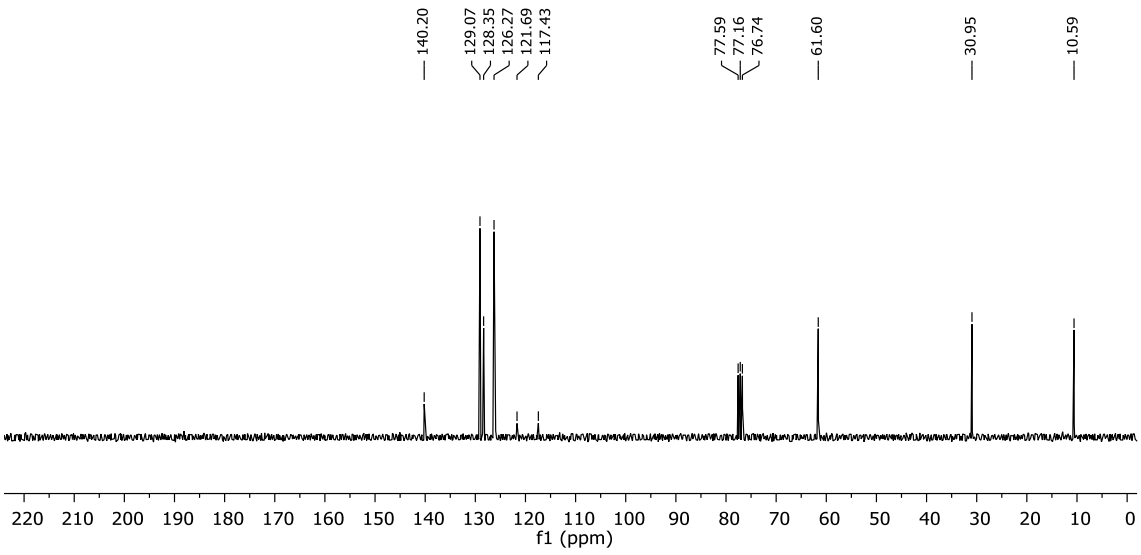
NMR SPECTRA

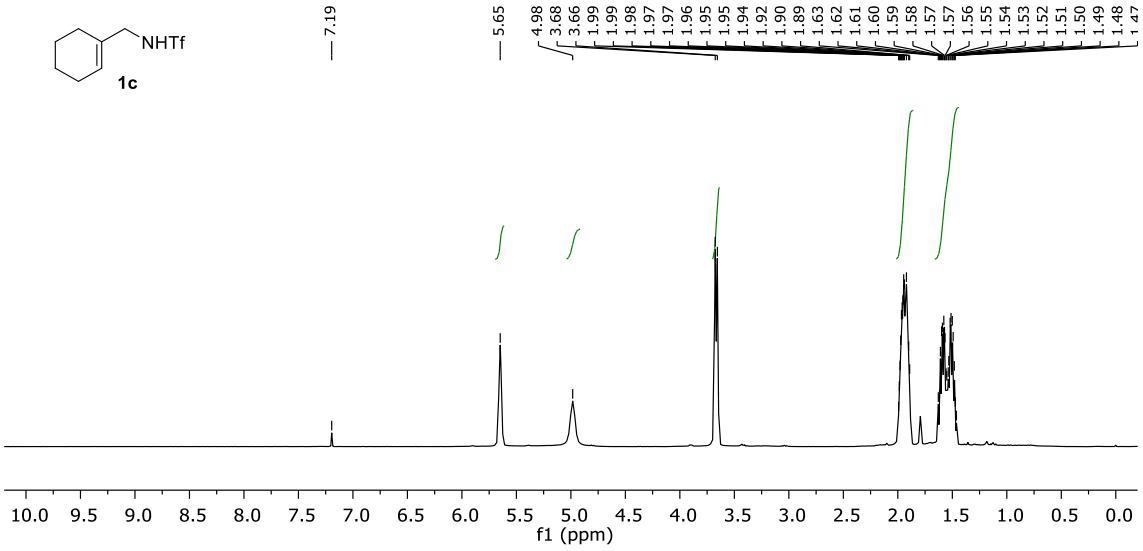

7.33
7.32
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.24
7.23
7.21
7.21
5.10
4.34
4.32
NHTf
1a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

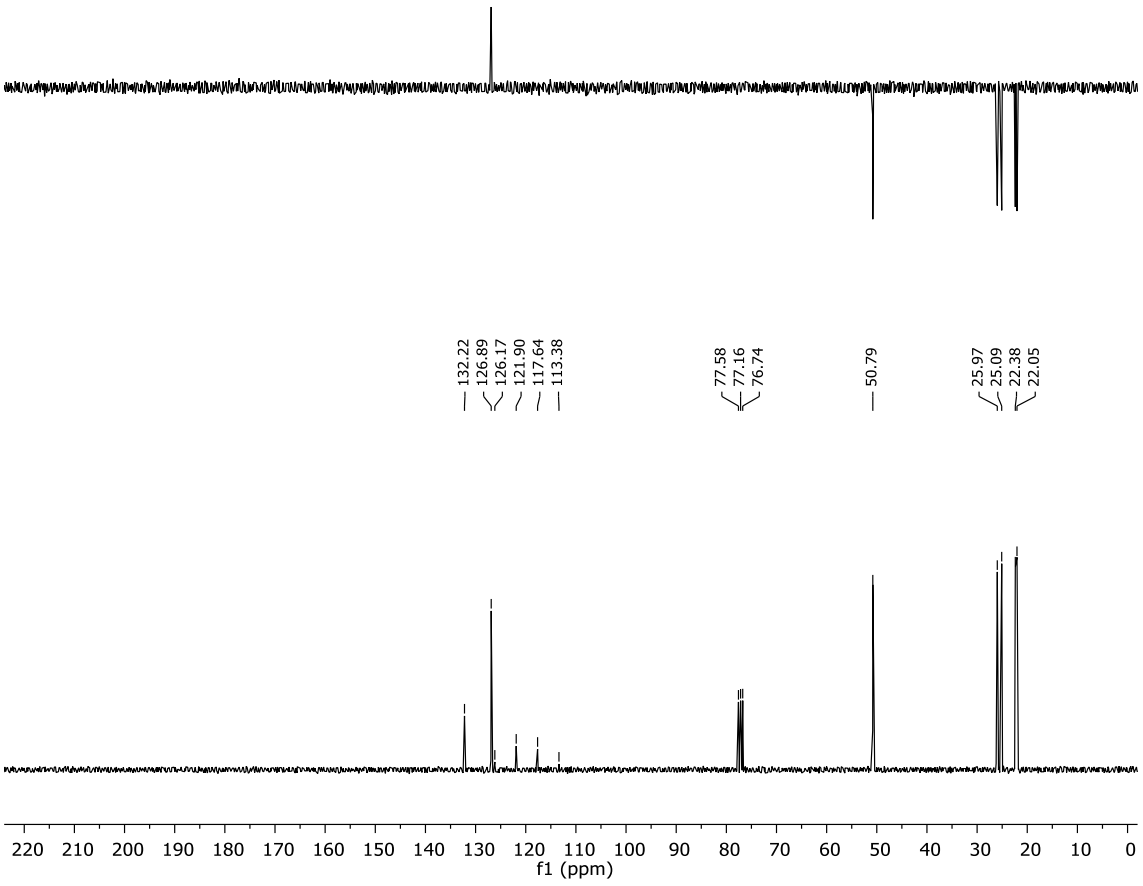

135.27
129.22
128.81
128.00
126.22
121.95
117.70
113.43
77.59
77.16
76.74
48.36
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

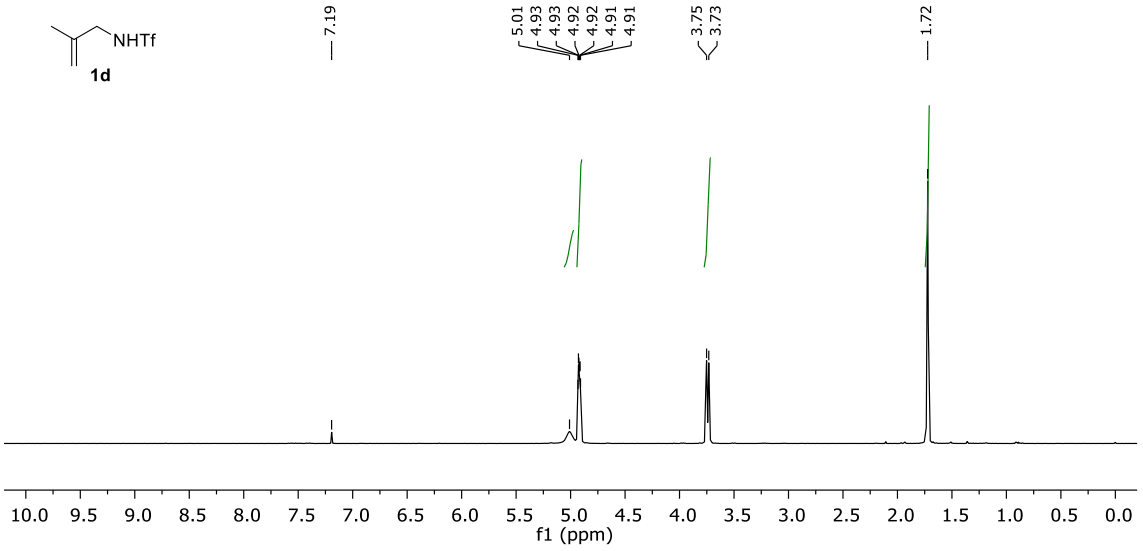

7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.20
7.20
7.17
7.17
7.16
7.16
7.15
7.14
7.14
7.13
5.51
5.48
4.44
4.41
4.38
4.36
1.89
1.87
1.87
1.86
1.85
1.83
1.82
1.81
1.80
1.79
1.77
1.76
1.74
0.86
0.84
0.81
NHTf
1b
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

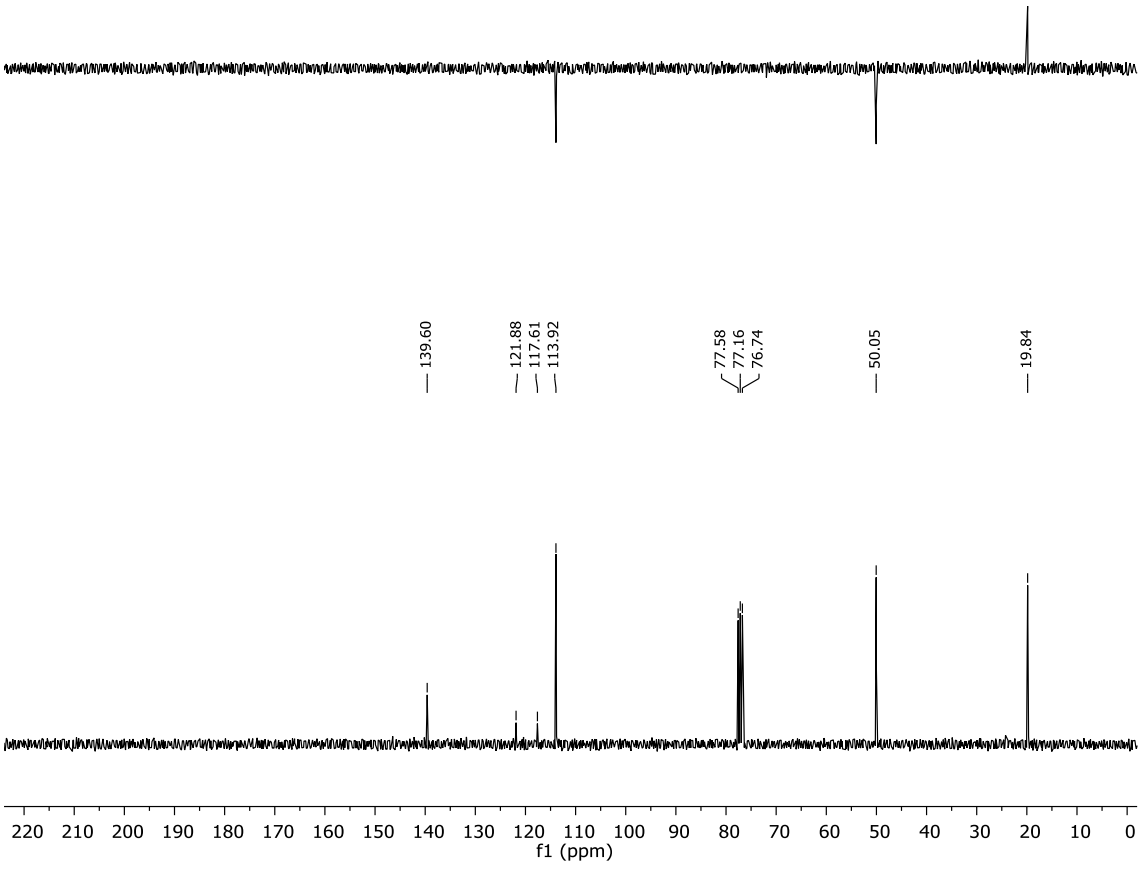


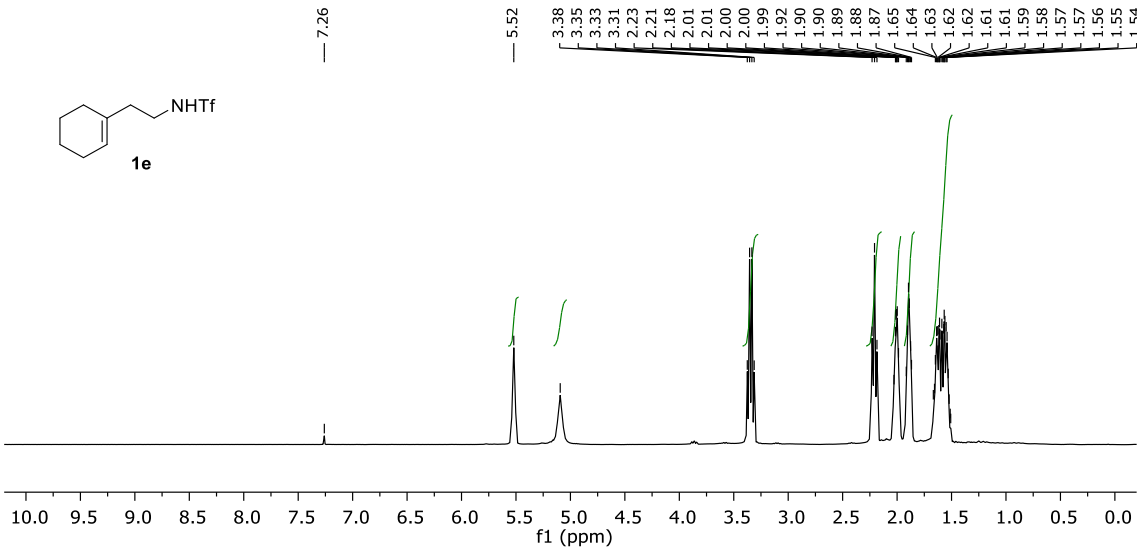

140.20
129.07
128.35
126.27
121.69
117.43
77.59
77.16
76.74
61.60
30.95
10.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

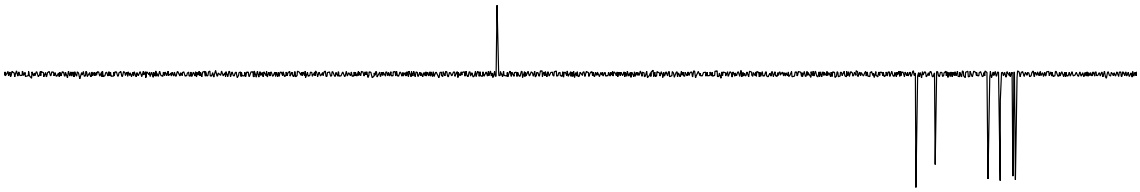

NHTf
1c
7.19
5.65
4.98
3.68
3.66
1.99
1.99
1.98
1.97
1.97
1.96
1.95
1.95
1.94
1.92
1.90
1.89
1.63
1.62
1.61
1.60
1.59
1.58
1.57
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.49
1.48
1.47
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

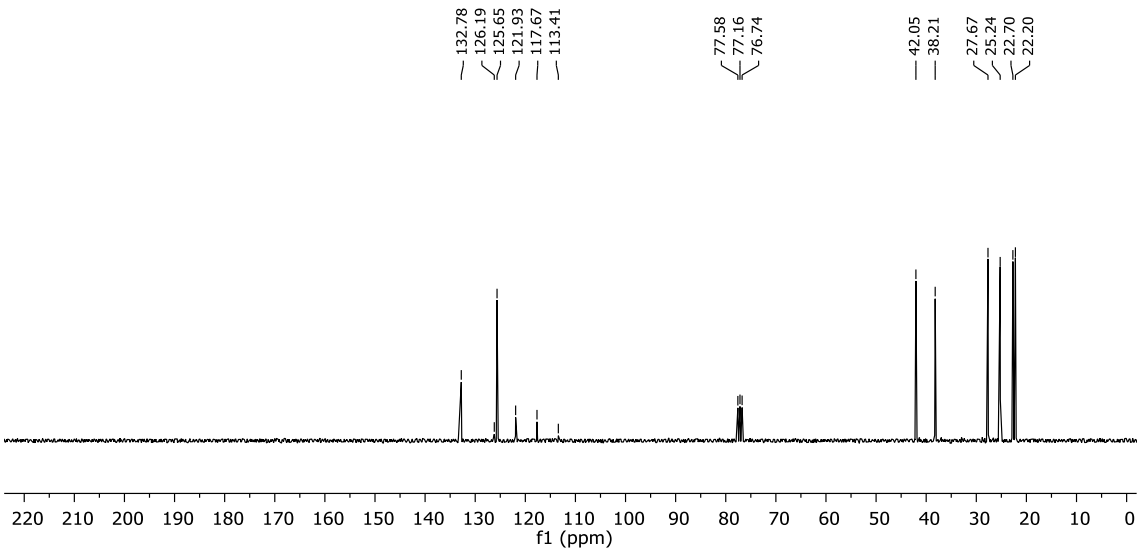

132.22
126.89
126.17
121.90
117.64
113.38
77.58
77.16
76.74
50.79
25.97
25.09
22.38
22.05
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

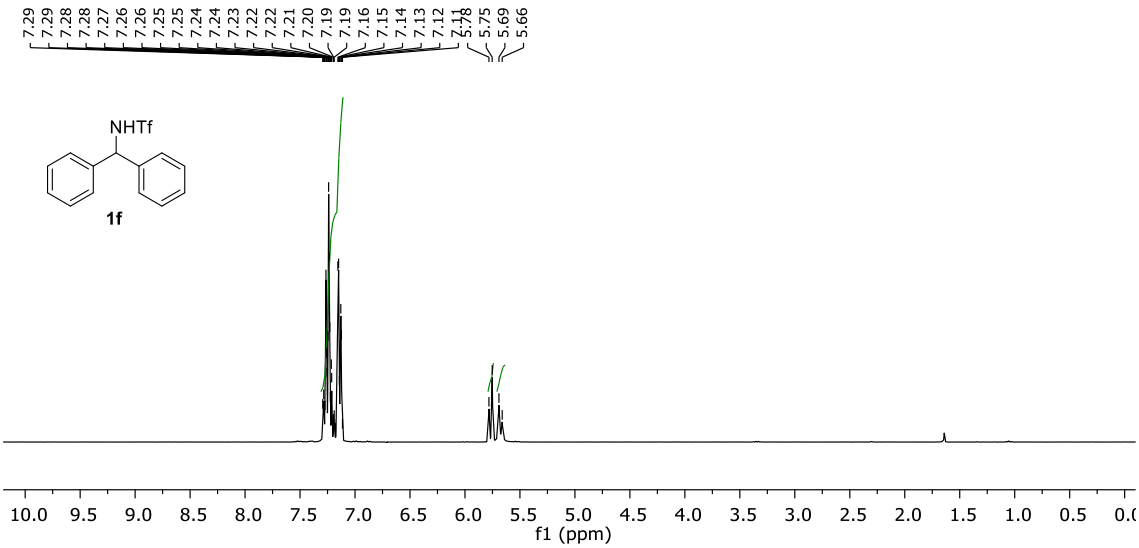

NHTf
1d
7.19
5.01
4.93
4.93
4.92
4.92
4.91
4.91
3.75
3.73
1.72
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

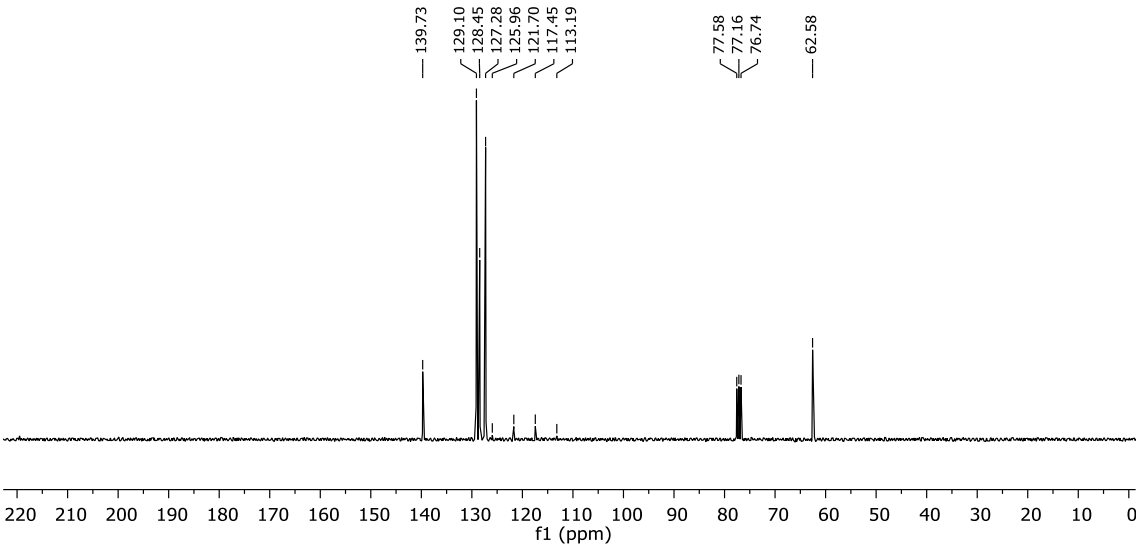

139.60
121.88
117.61
113.92
77.58
77.16
76.74
50.05
19.84
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

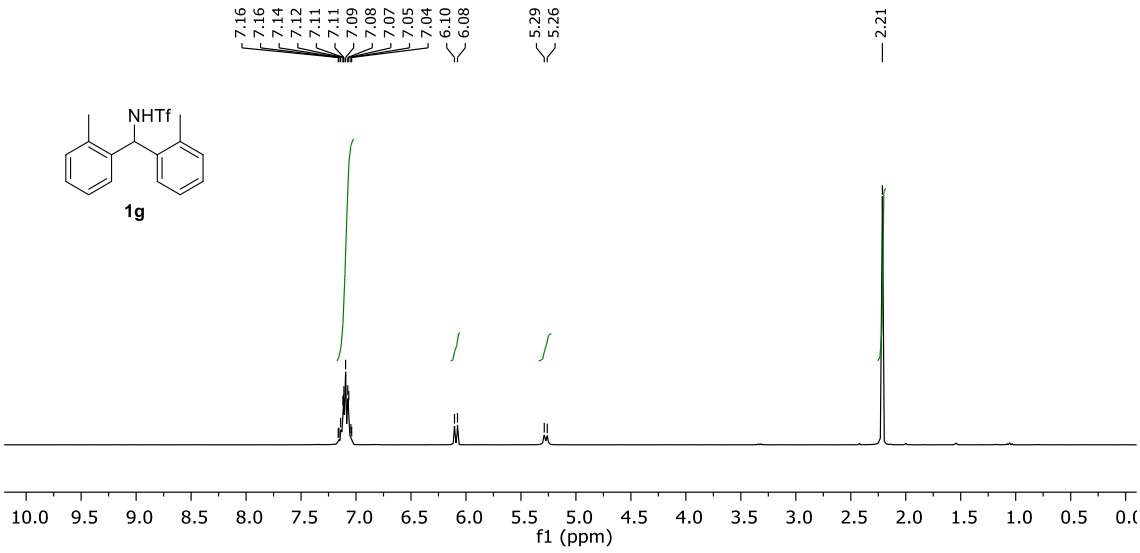

7.26
5.52
3.38
3.35
3.33
3.31
2.23
2.21
2.18
2.01
2.01
2.00
2.00
1.99
1.92
1.90
1.90
1.89
1.88
1.87
1.65
1.64
1.63
1.62
1.62
1.61
1.61
1.59
1.58
1.57
1.57
1.56
1.55
NHTf
1e
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

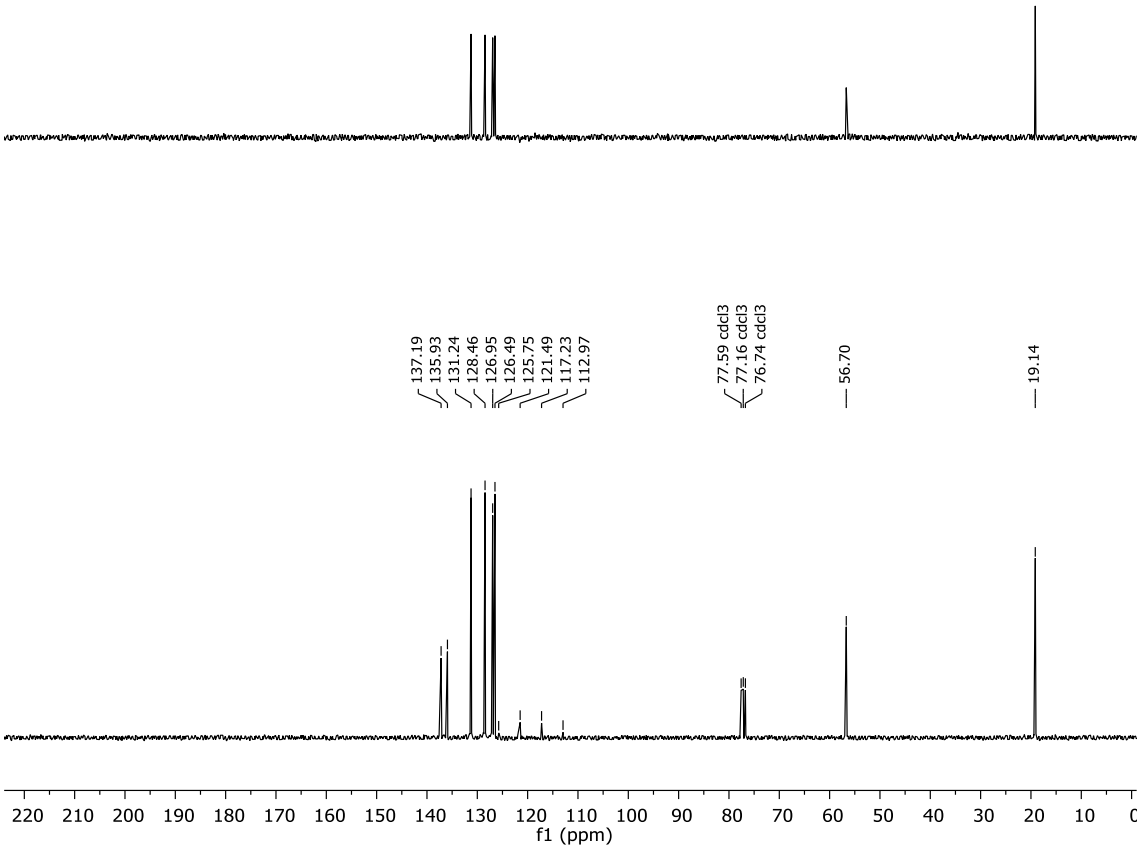


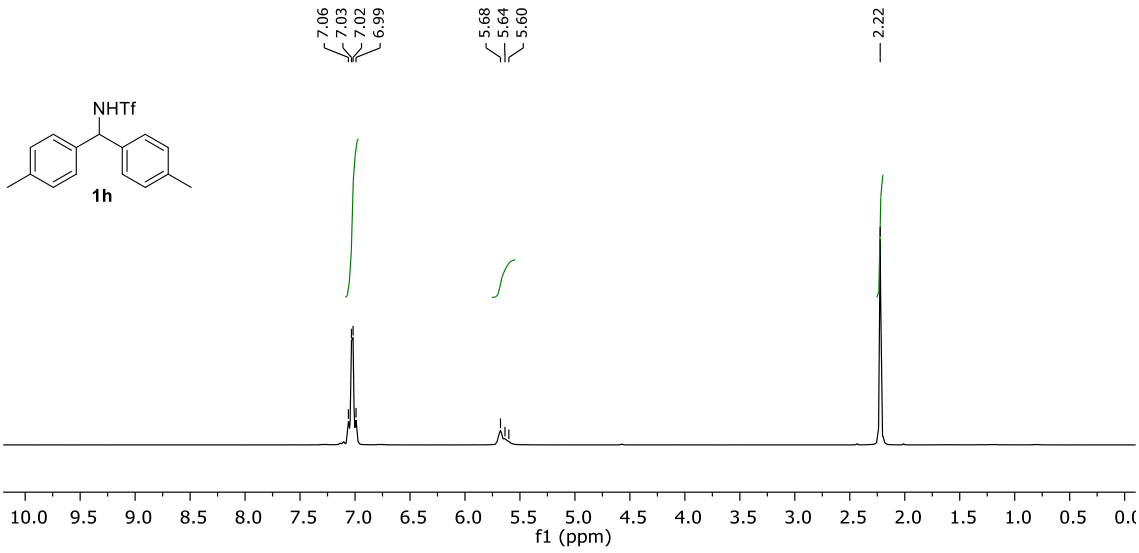

132.78
126.19
125.65
121.93
117.67
113.41
77.58
77.16
76.74
42.05
38.21
27.67
25.24
22.70
22.20
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

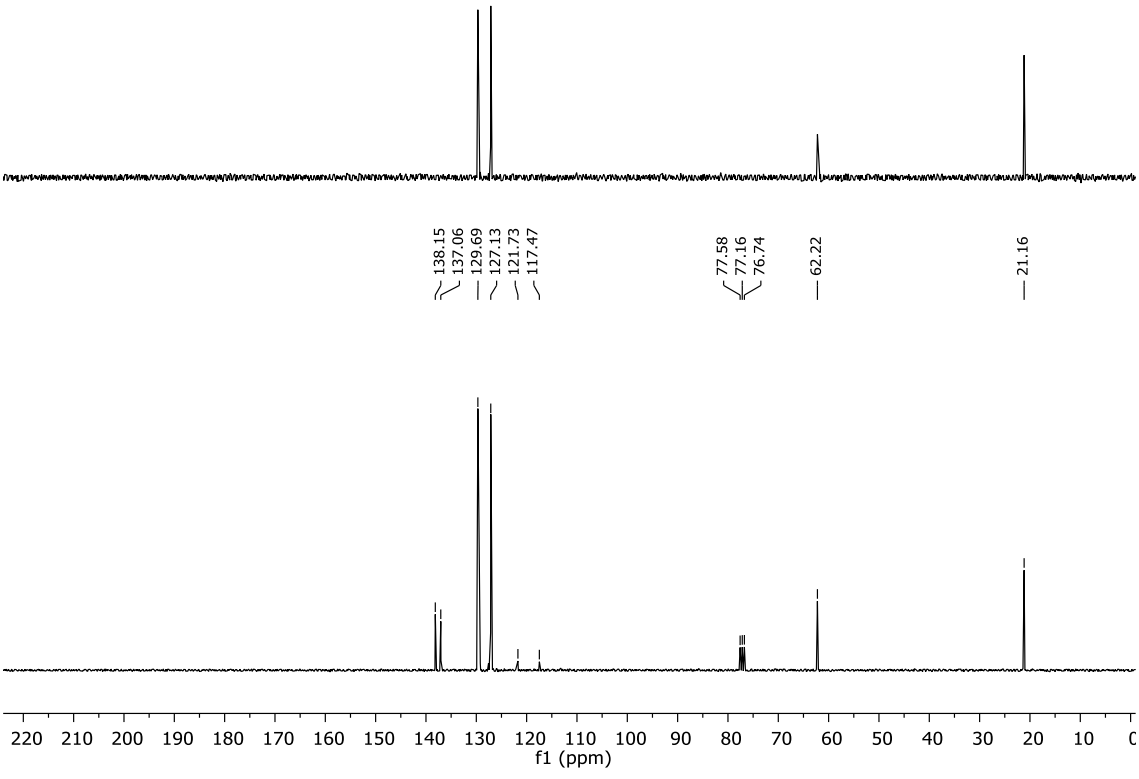

7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.19
7.16
7.15
7.14
7.13
7.12
5.78
5.75
5.69
5.66
NHTf
1f
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

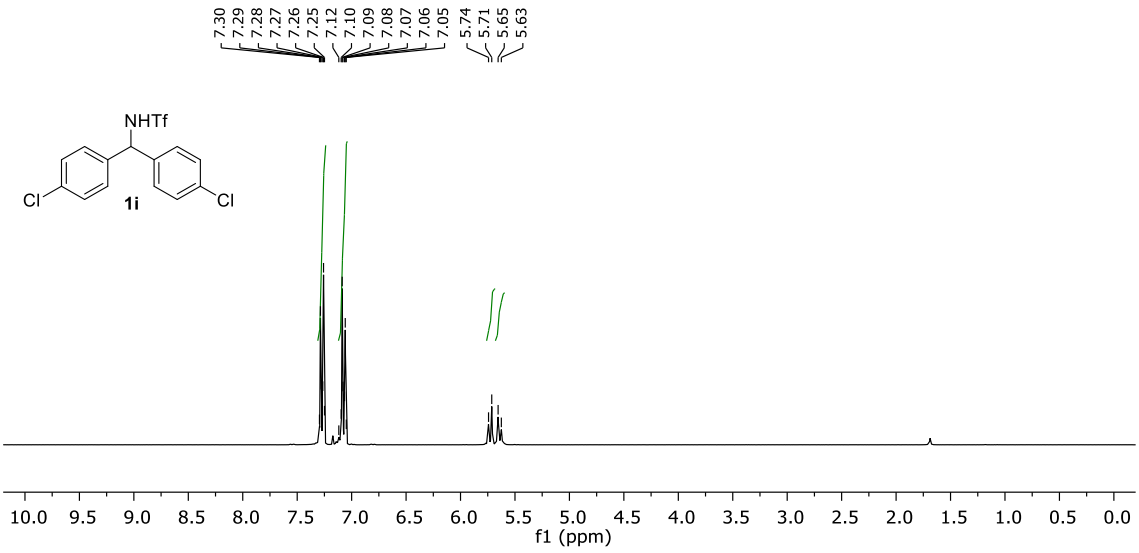

139.73
129.10
128.45
127.28
125.96
121.70
117.45
113.19
77.58
77.16
76.74
62.58
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

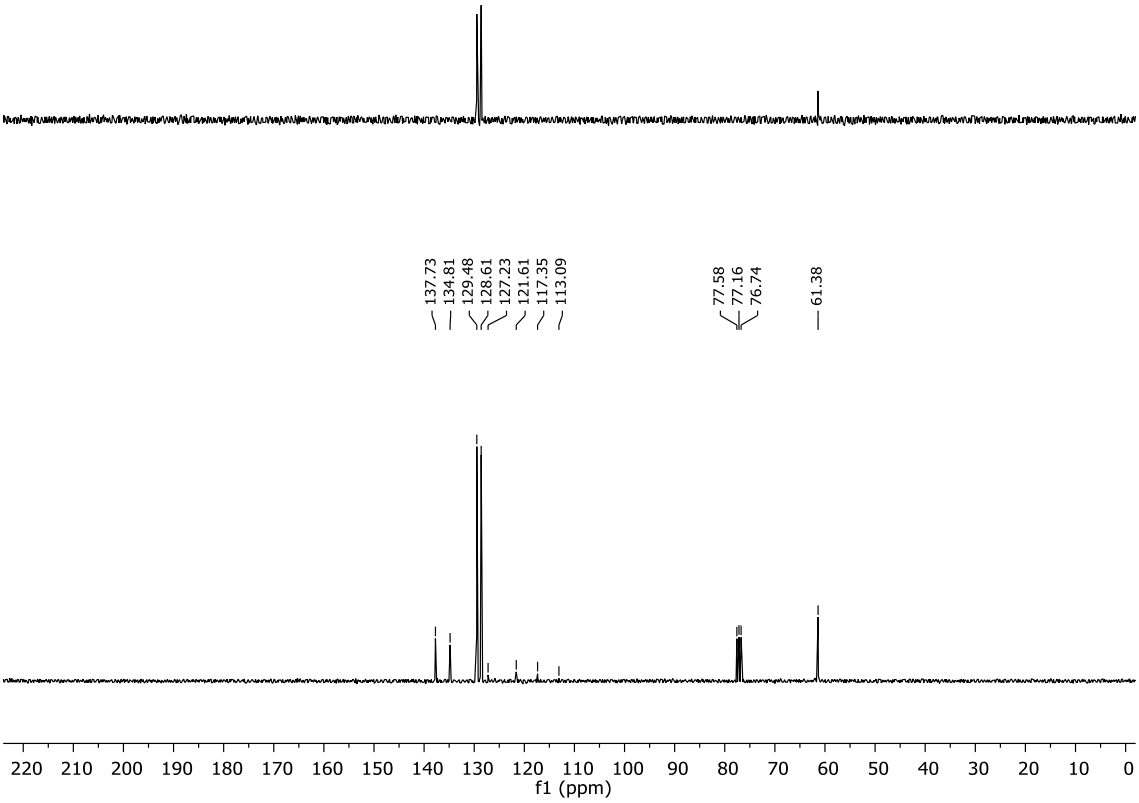

7.16
7.16
7.14
7.12
7.11
7.11
7.09
7.08
7.07
7.05
7.04
6.10
6.08
5.29
5.26
2.21
NHTf
1g
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

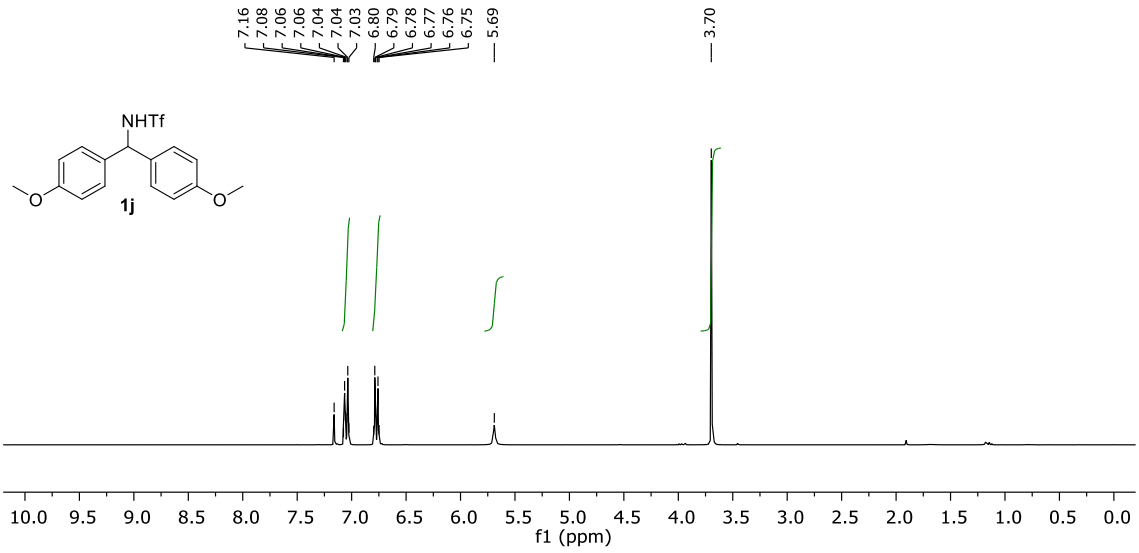

137.19
135.93
131.24
128.46
126.95
126.49
125.75
121.49
117.23
112.97
77.59 cdcl3
77.16 cdcl3
76.74 cdcl3
56.70
19.14
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

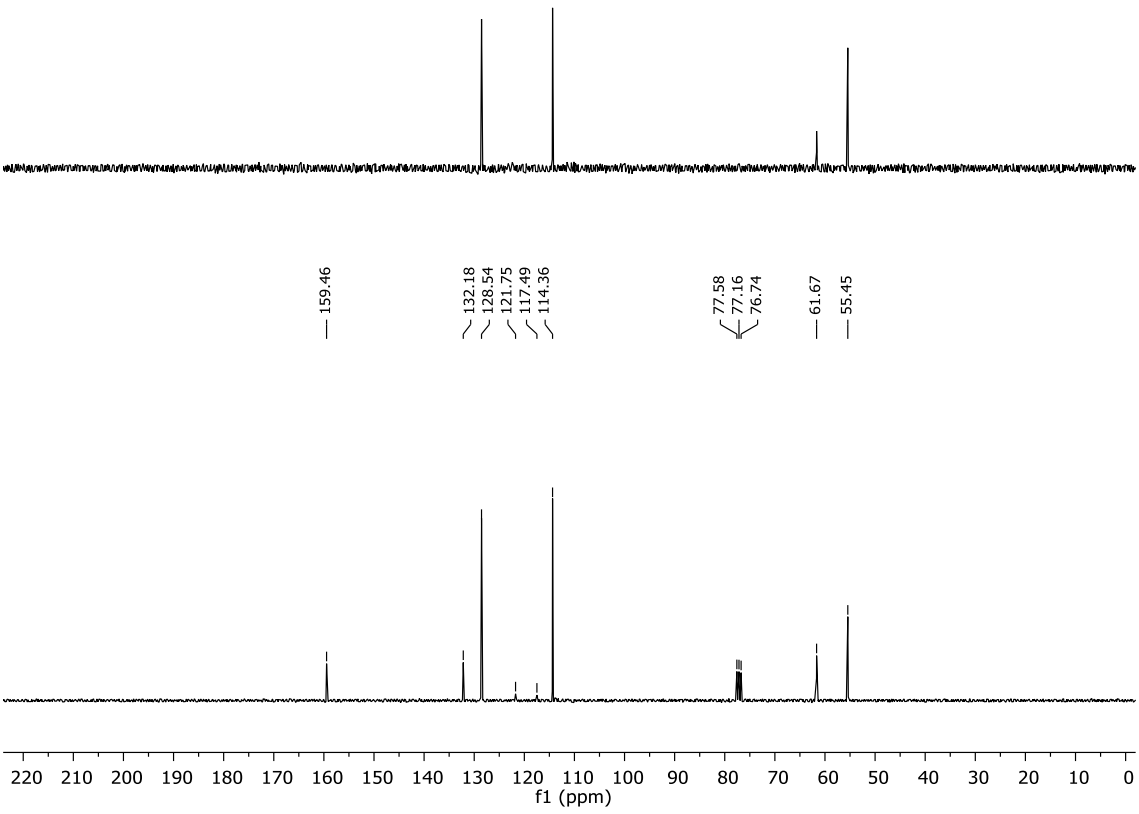

7.06
7.03
7.02
6.99
5.68
5.64
5.60
2.22
NHTf
1h
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

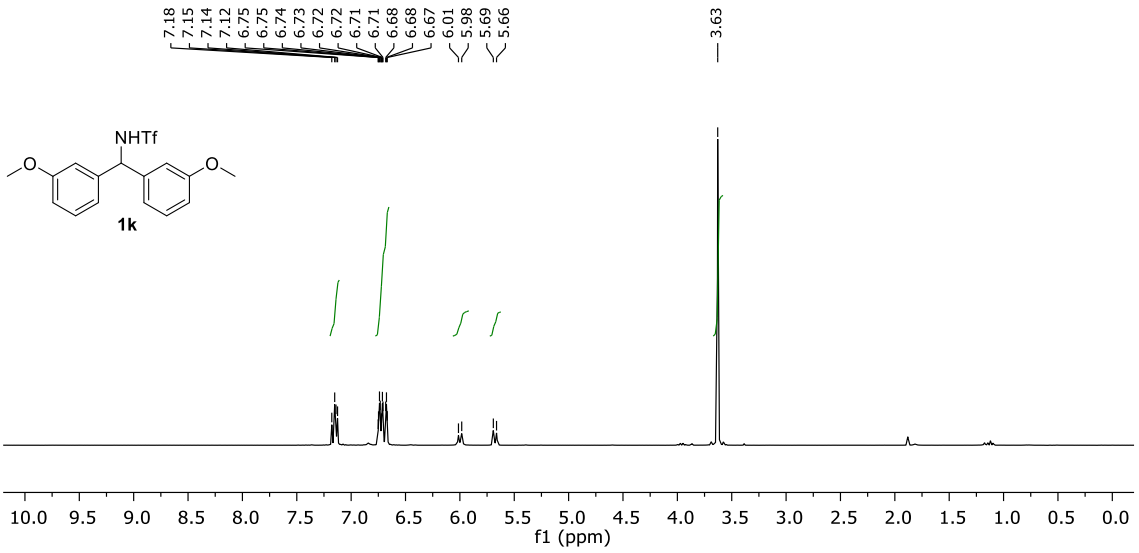

138.15
137.06
129.69
127.13
121.73
117.47
77.58
77.16
76.74
62.22
21.16
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

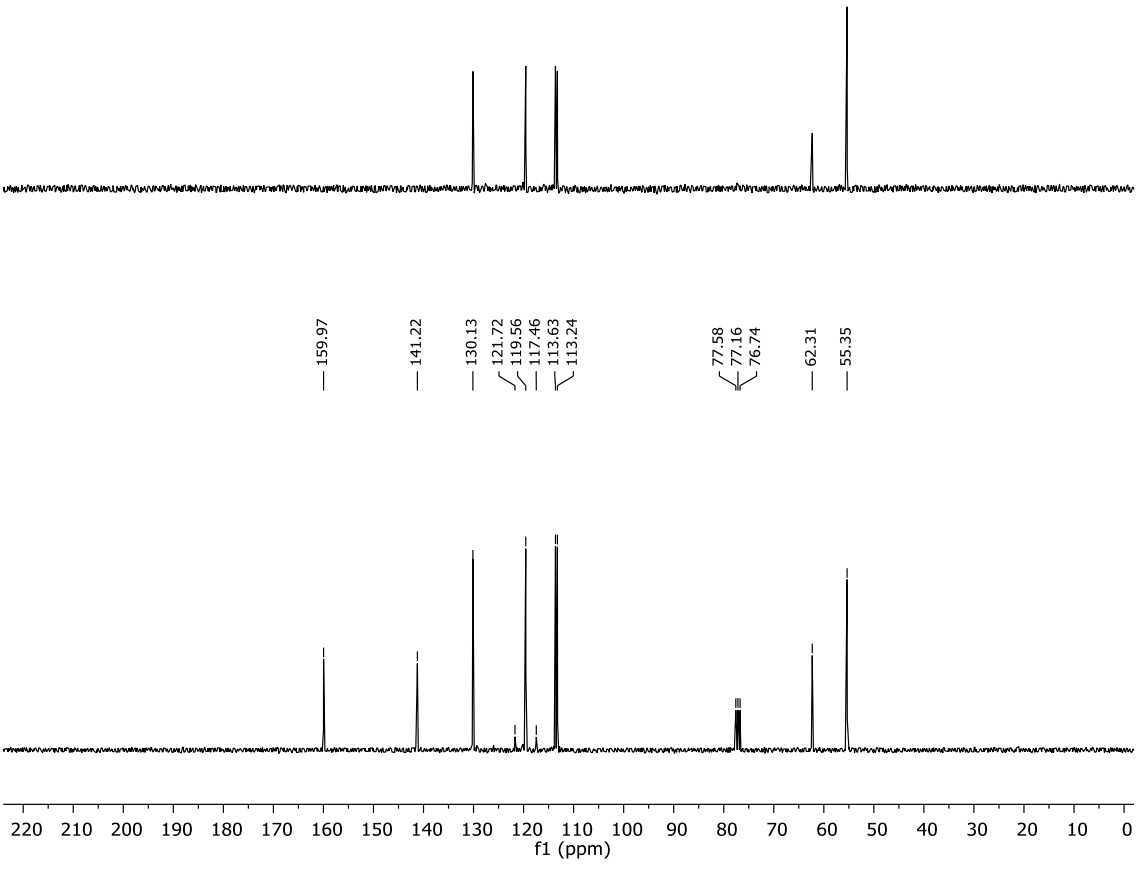

7.30
7.29
7.28
7.27
7.26
7.25
7.12
7.10
7.09
7.08
7.07
7.06
7.05
5.74
5.71
5.65
5.63
NHTf
Cl
Cl
1i
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

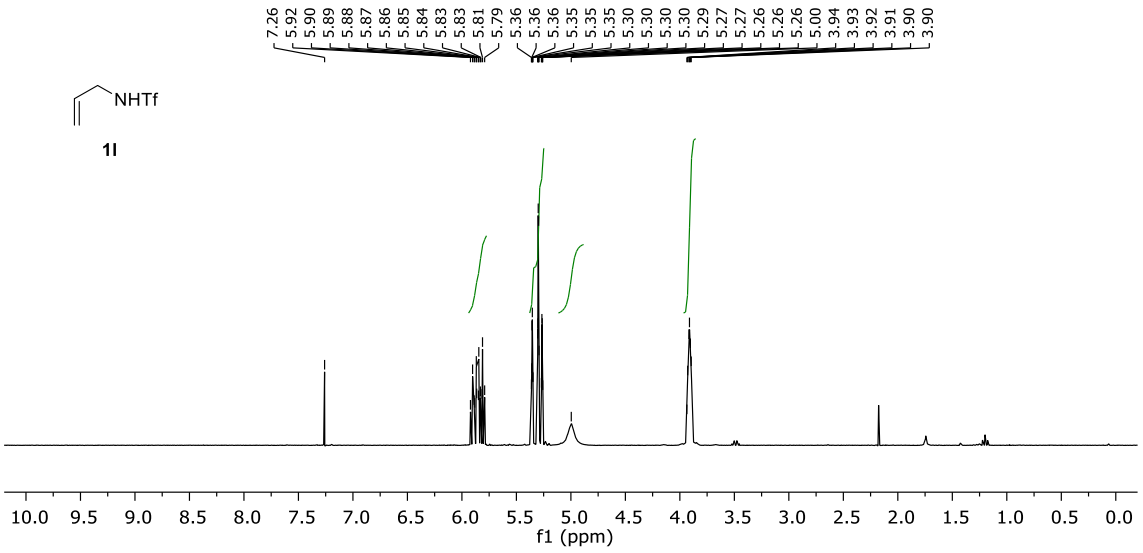

137.73
134.81
129.48
128.61
127.23
121.61
117.35
113.09
77.58
77.16
76.74
61.38
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

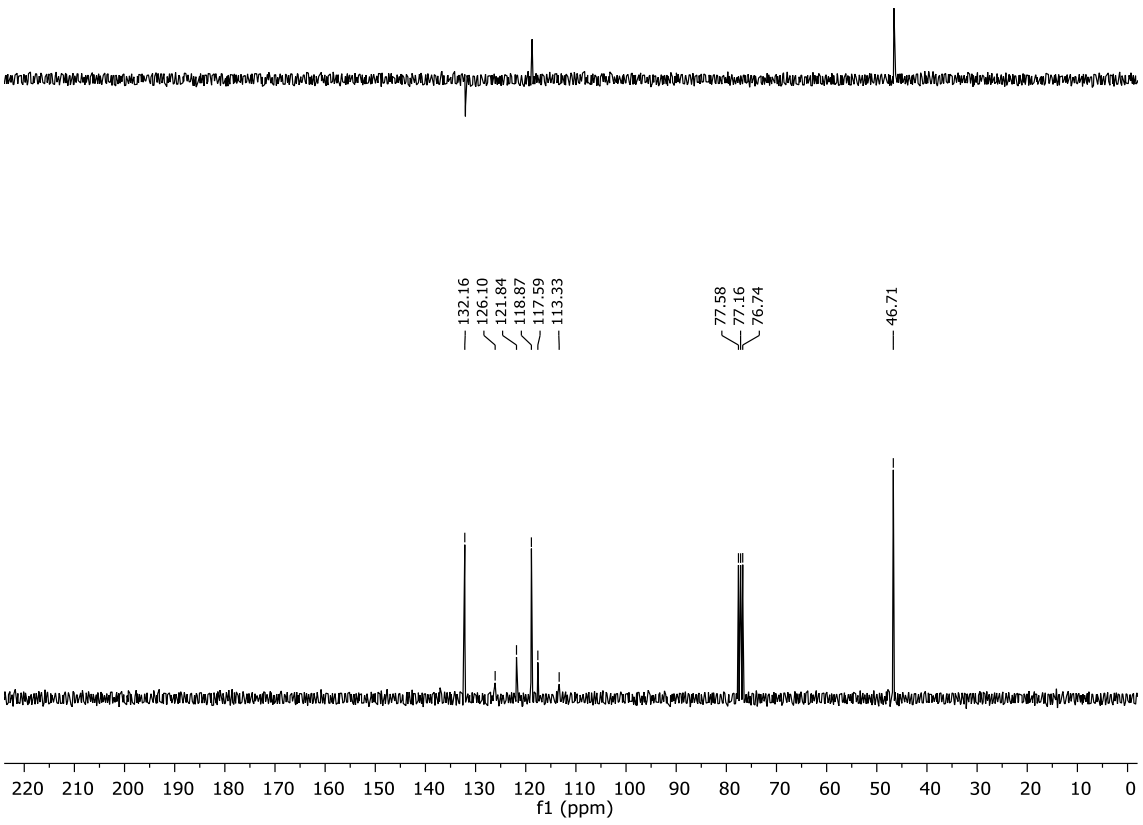

7.16
7.08
7.06
7.06
7.04
7.04
7.03
6.80
6.79
6.78
6.77
6.76
6.75
5.69
3.70
NHTf
O
O
1j
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

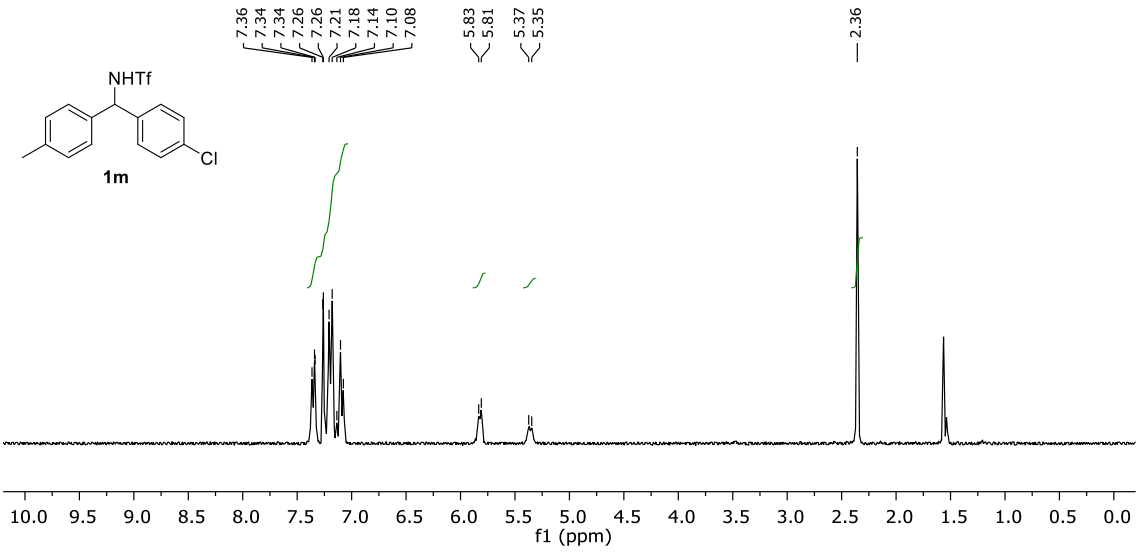

159.46
132.18
128.54
121.75
117.49
114.36
77.58
77.16
76.74
61.67
55.45
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

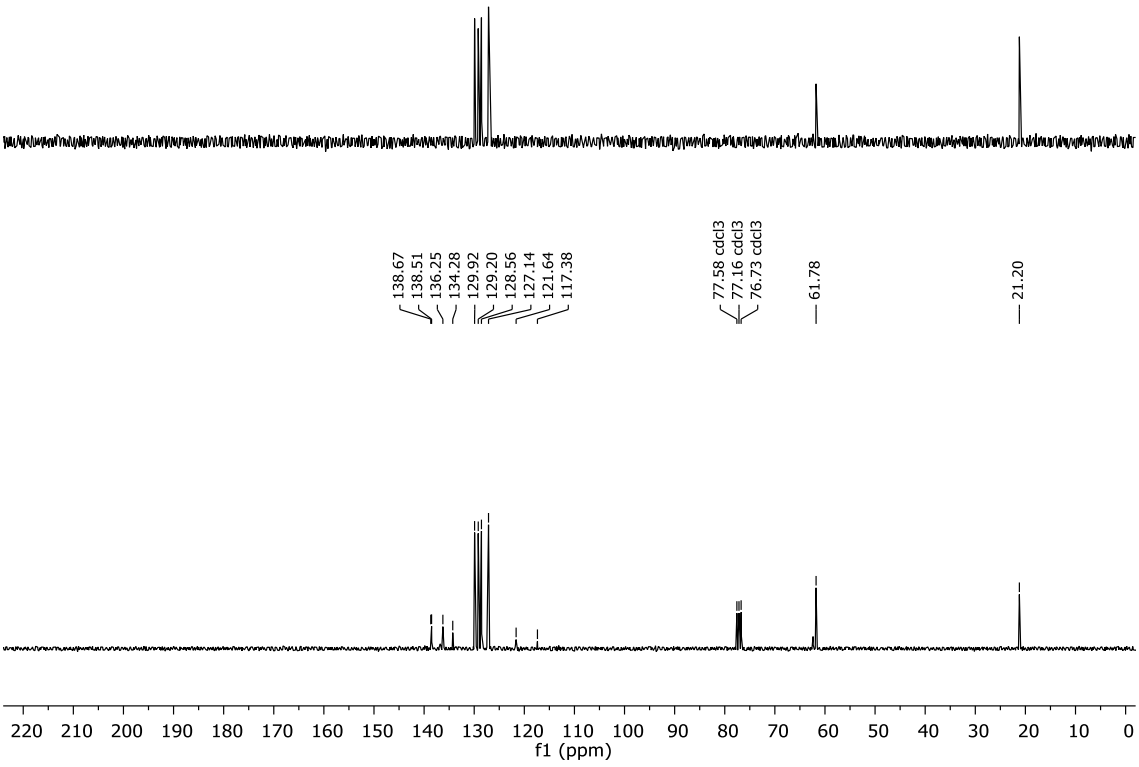

7.18
7.15
7.14
7.12
6.75
6.75
6.74
6.73
6.72
6.72
6.71
6.71
6.68
6.68
6.67
6.01
5.98
5.69
5.66
3.63
NHTf
O
O
1k
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

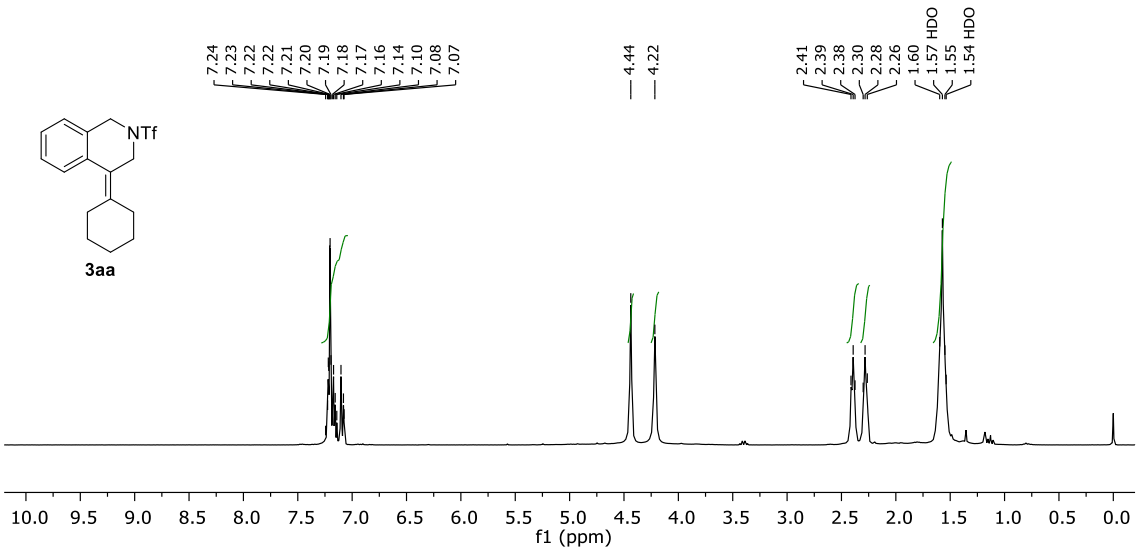

159.97
141.22
130.13
121.72
119.56
117.46
113.63
113.24
77.58
77.16
76.74
62.31
55.35
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

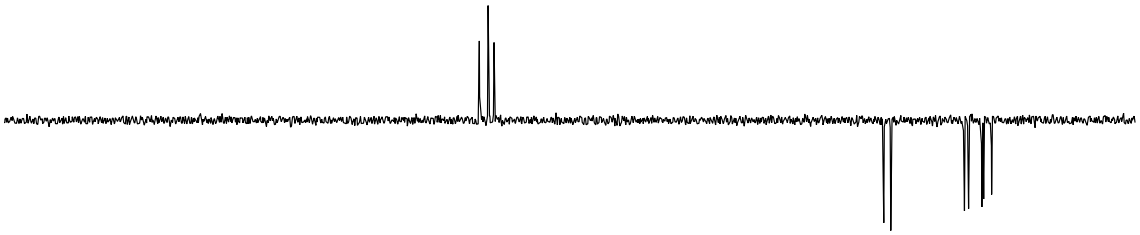

7.26
5.92
5.90
5.89
5.88
5.87
5.86
5.85
5.84
5.83
5.83
5.81
5.79
5.36
5.36
5.36
5.35
5.35
5.30
5.30
5.30
5.30
5.29
5.27
5.27
5.26
5.26
5.26
5.00
3.94
3.93
3.92
3.91
3.90
3.90
NHTf
1l
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

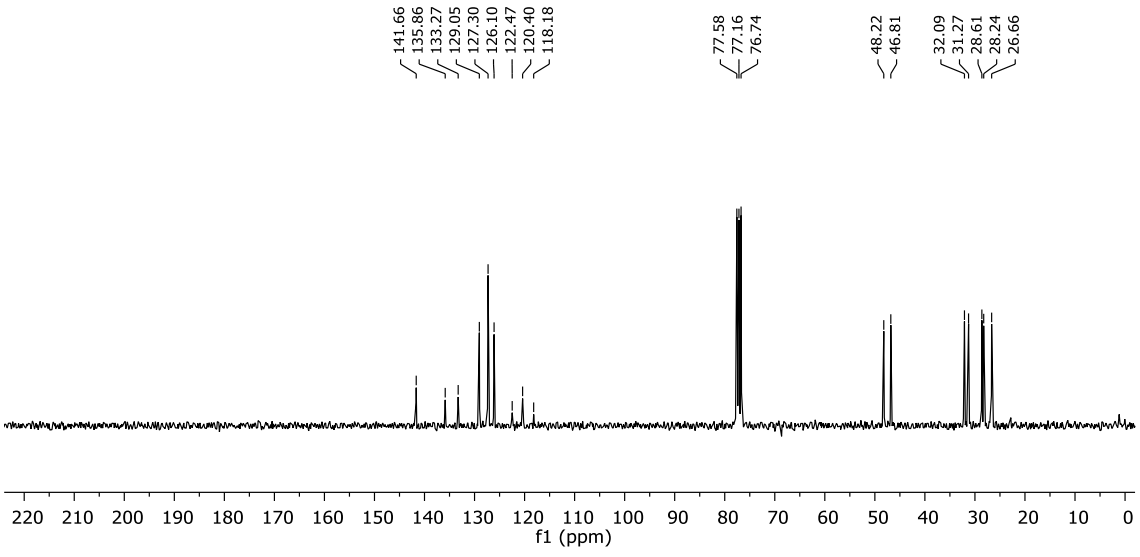

132.16
126.10
121.84
118.87
117.59
113.33
77.58
77.16
76.74
46.71
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

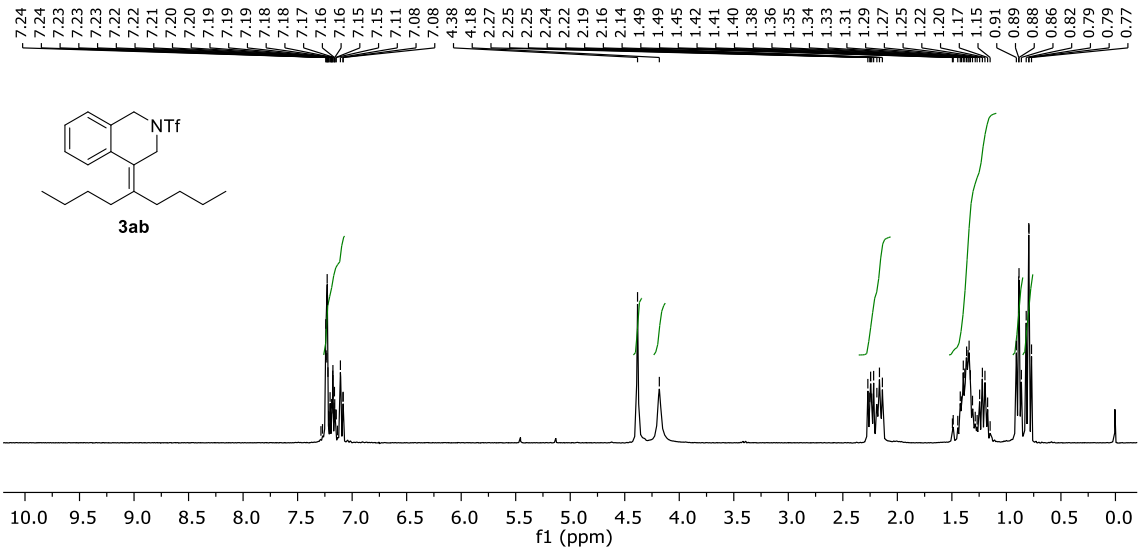

7.36
7.34
7.34
7.26
7.26
7.21
7.18
7.14
7.10
7.08
5.83
5.81
5.37
5.35
2.36
NHTf
Cl
1m
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

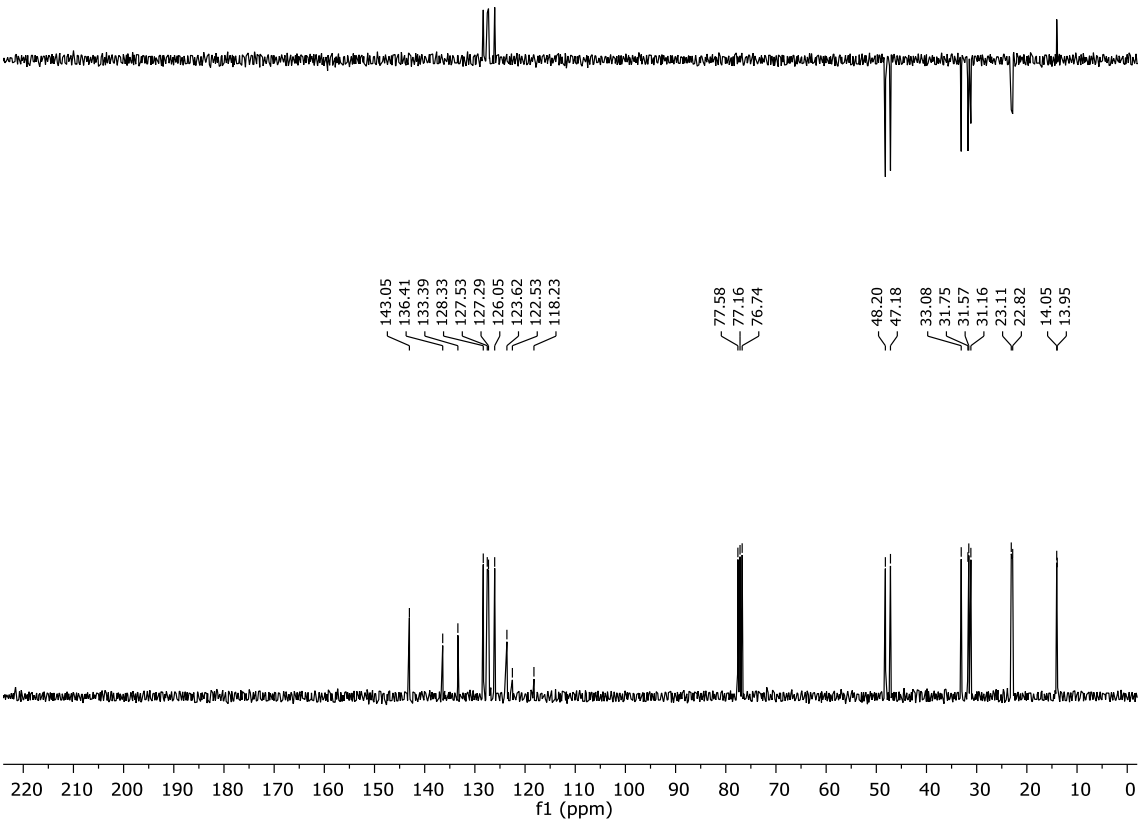

138.67
138.51
136.25
134.28
129.92
129.20
128.56
127.14
121.64
117.38
77.58 cdcl3
77.16 cdcl3
76.73 cdcl3
61.78
21.20
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

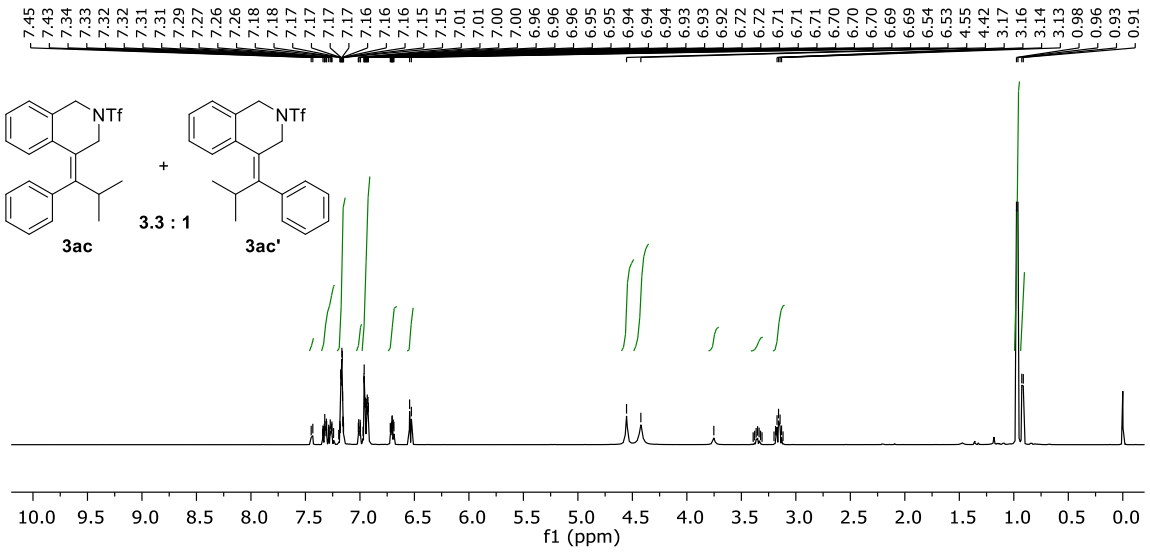

7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.18
7.17
7.16
7.14
7.10
7.08
7.07
4.44
4.22
2.41
2.39
2.38
2.30
2.28
2.26
1.60
1.57 HDO
1.55
1.54 HDO
NTf
3aa
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

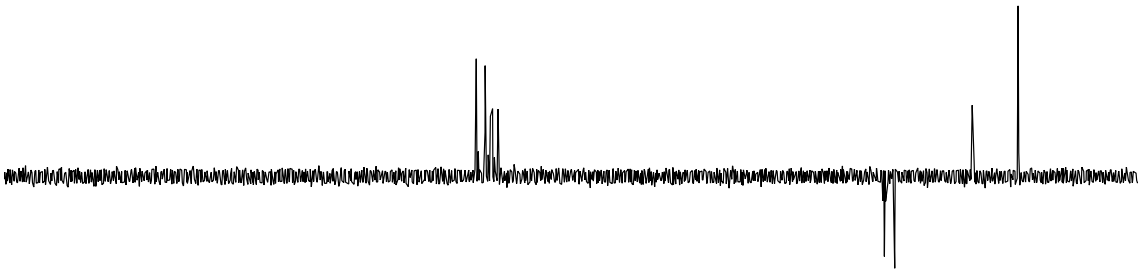


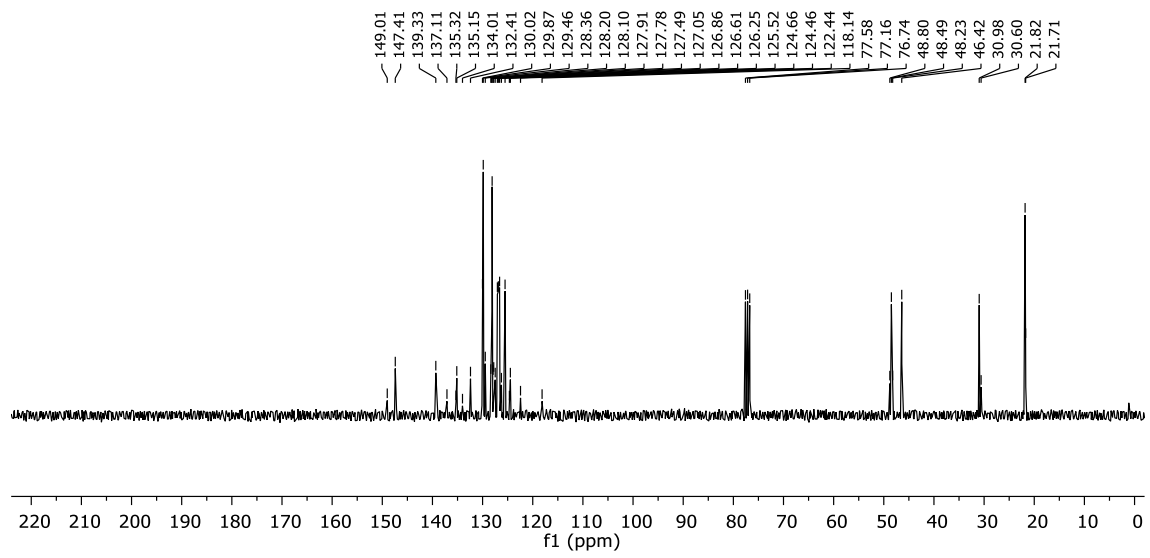

141.66
135.86
133.27
129.05
127.30
126.10
122.47
120.40
118.18
77.58
77.16
76.74
48.22
46.81
32.09
31.27
28.61
28.24
26.66
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

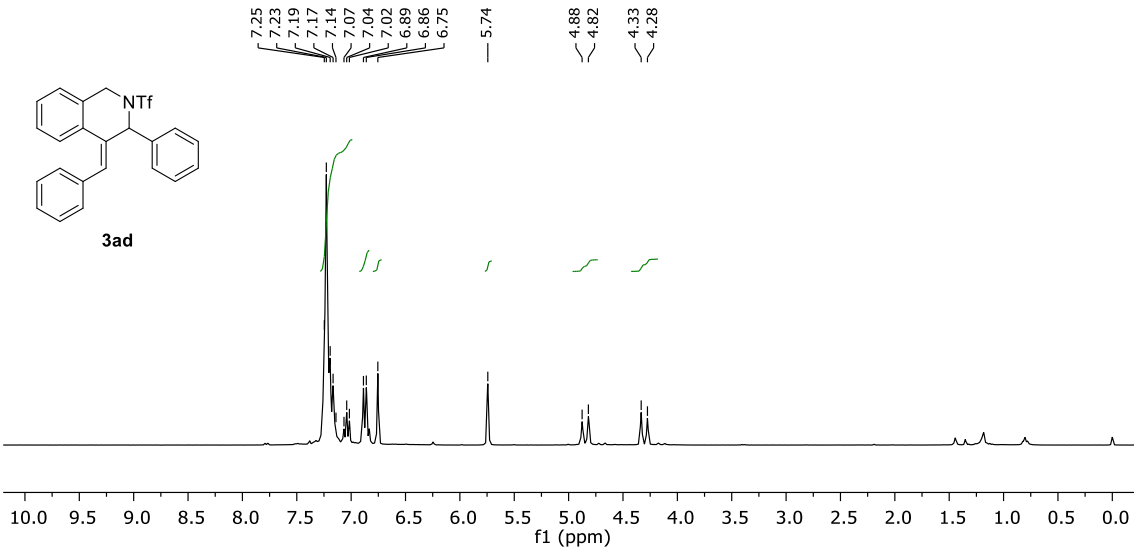

7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.19 7.19 7.18 7.18 7.17 7.16 7.16 7.15 7.15 7.11 7.08 7.08
4.38 4.18 2.27 2.25 2.24 2.22 2.19 2.16 2.14 1.49 1.49 1.45 1.42 1.41 1.40 1.38 1.36 1.35 1.34 1.33 1.31 1.29 1.27 1.25 1.22 1.20 1.17 1.15 0.91 0.89 0.88 0.86 0.82 0.79 0.79 0.77
NTf
3ab
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

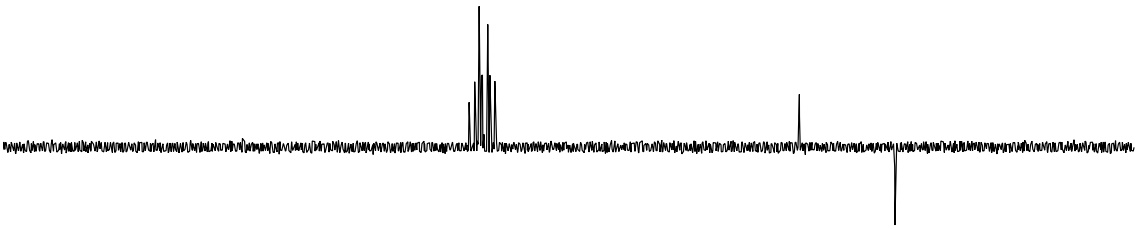

143.05 136.41 133.39 128.33 127.53 127.29 126.05 123.62 122.53 118.23
77.58 77.16 76.74
48.20 47.18
33.08 31.75 31.57 31.16 23.11 22.82 14.05 13.95
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

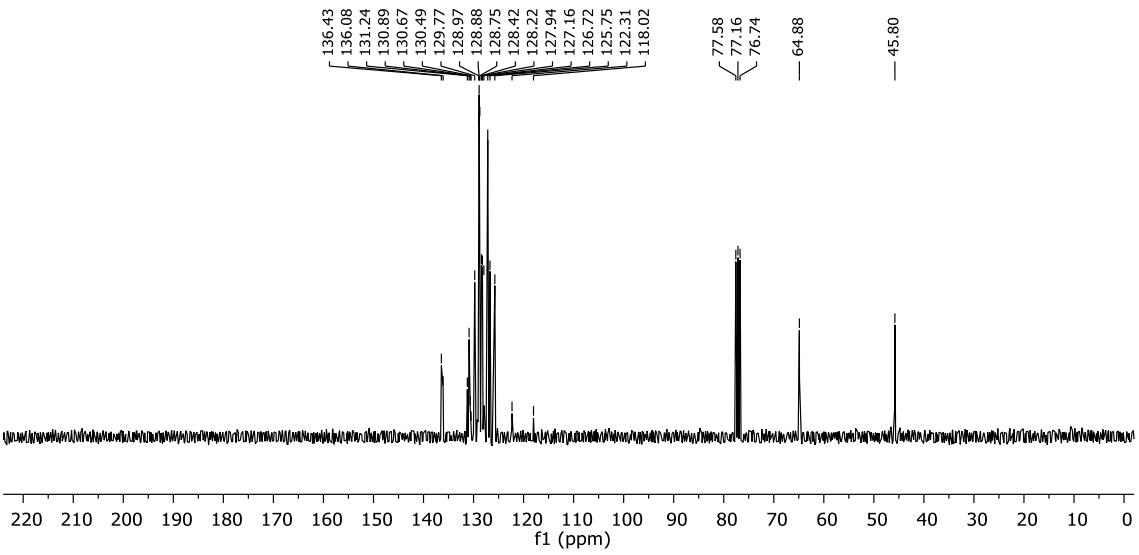

7.45 7.43 7.34 7.33 7.32 7.32 7.31 7.31 7.29 7.27 7.26 7.26 7.18 7.18 7.17 7.17 7.17 7.17 7.16 7.16 7.16 7.15 7.15 7.01 7.01 7.00 7.00 6.96 6.96 6.96 6.95 6.95 6.94 6.94 6.94 6.93 6.93 6.92 6.72 6.72 6.71 6.71 6.71 6.70 6.70 6.70 6.69 6.69 6.54 6.53 4.55 4.42 3.17 3.16 3.14 3.13 0.98 0.96 0.93 0.91
NTf
NTf
+
3.3 : 1
3ac
3ac'
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

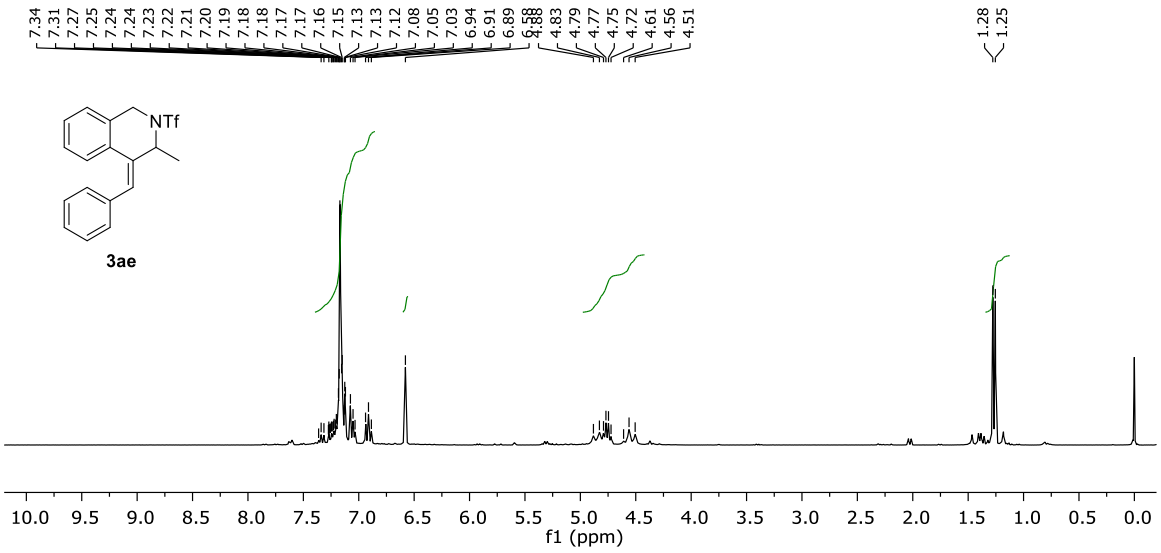


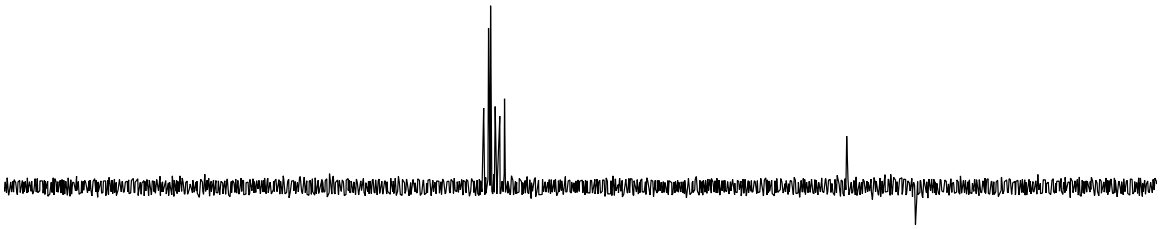

149.01 147.41 139.33 137.11 135.32 135.15 134.01 132.41 130.02 129.87 129.46 128.36 128.20 128.10 127.91 127.78 127.49 127.05 126.86 126.61 126.25 125.52 124.66 124.46 122.44 118.14 77.58 77.16 76.74 48.80 48.49 48.23 46.42 30.98 30.60 21.82 21.71
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

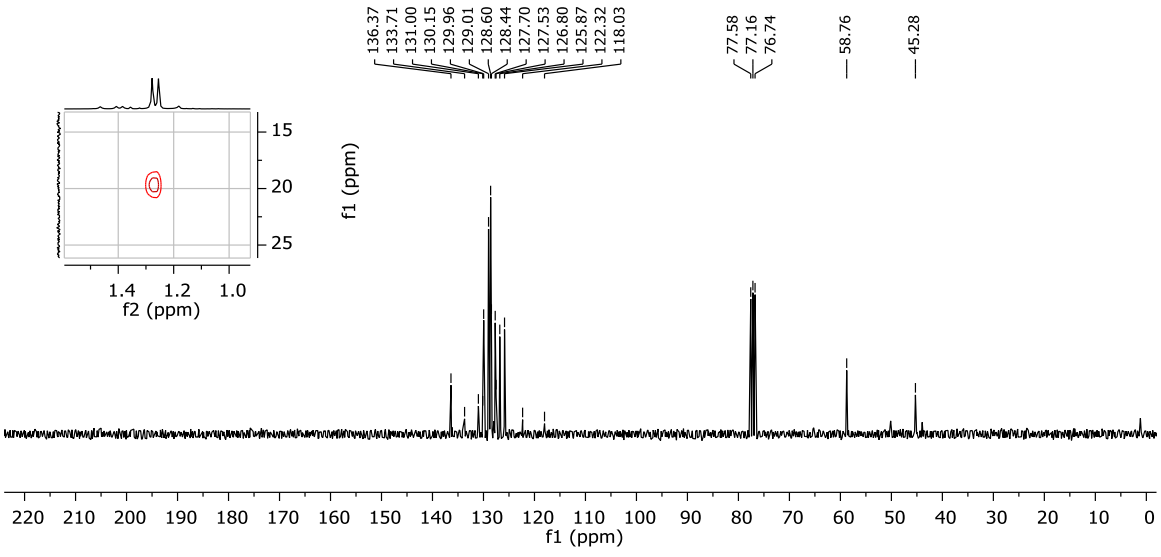

7.25
7.23
7.19
7.17
7.14
7.07
7.04
7.02
6.89
6.86
6.75
5.74
4.88
4.82
4.33
4.28
NTf
3ad
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

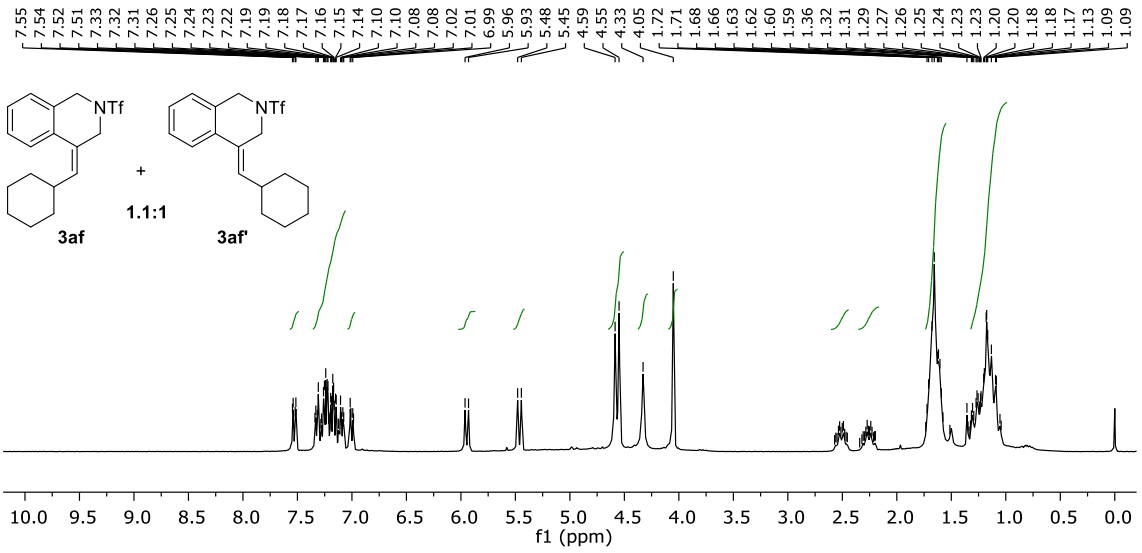


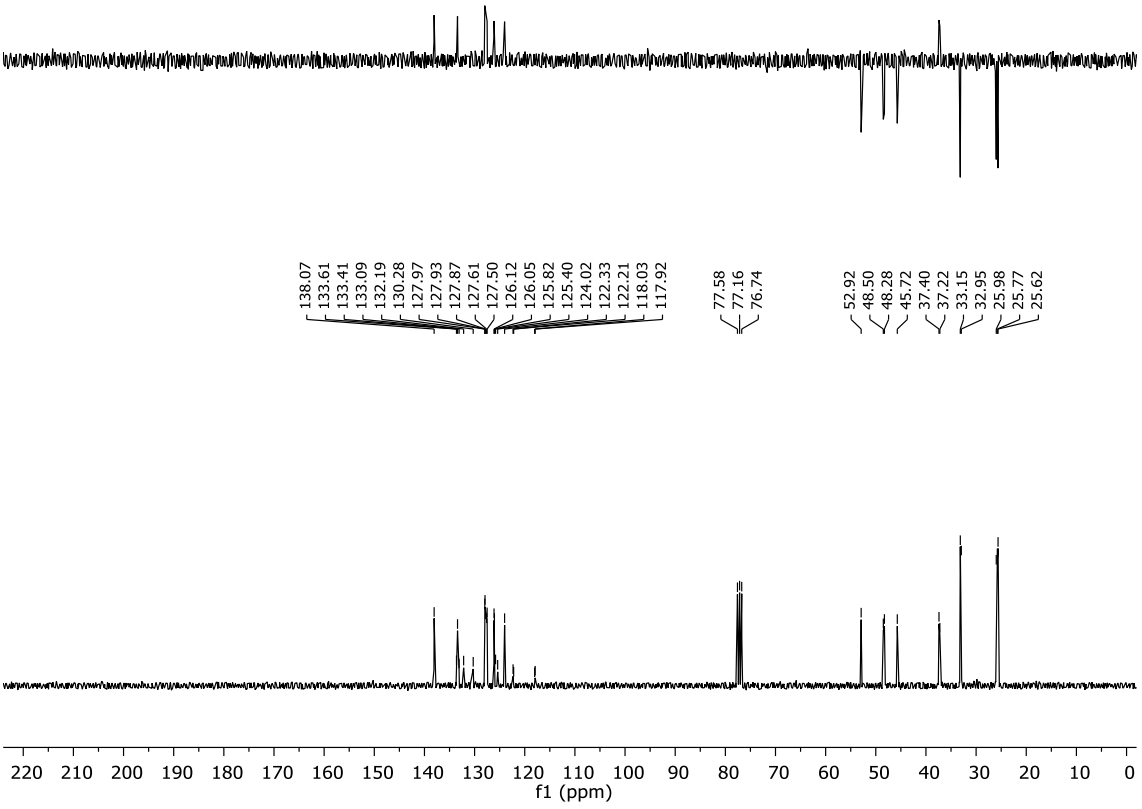

136.43
136.08
131.24
130.89
130.67
130.49
129.77
128.97
128.88
128.75
128.42
128.22
127.94
127.16
126.72
125.75
122.31
118.02
77.58
77.16
76.74
64.88
45.80
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

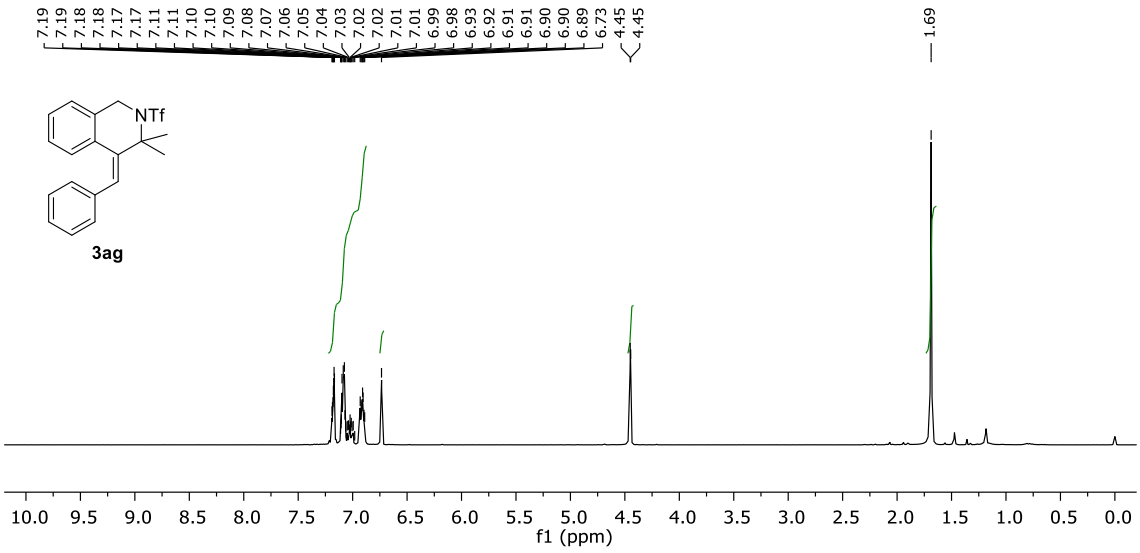

7.34
7.31
7.27
7.25
7.24
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.15
7.13
7.13
7.12
7.08
7.05
7.03
6.94
6.91
6.89
4.83
4.79
4.77
4.75
4.72
4.61
4.56
4.51
1.28
1.25
NTf
3ae
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

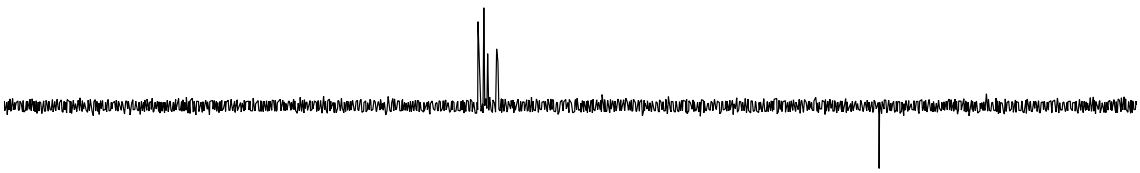


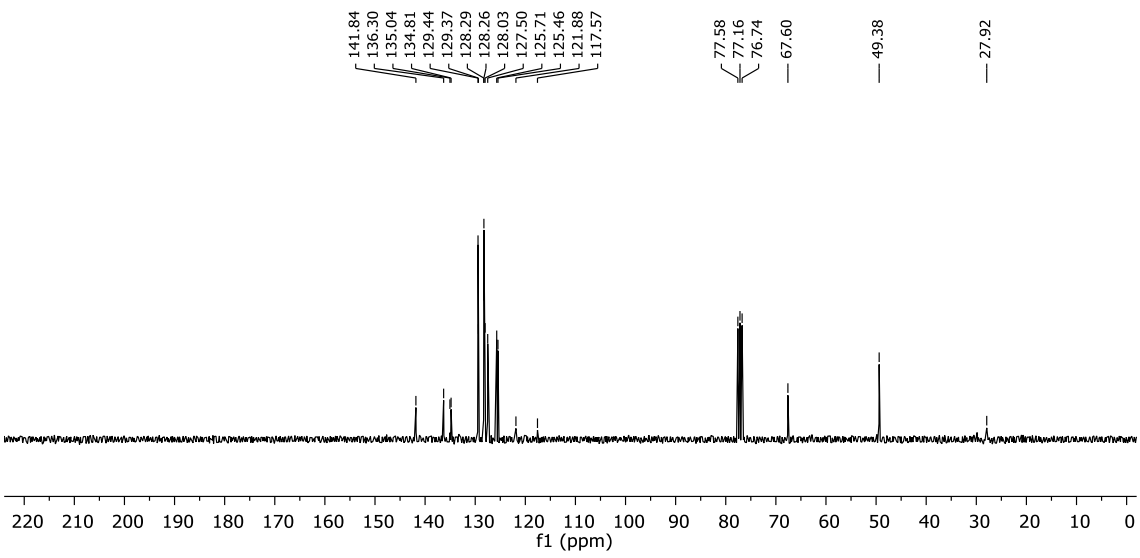

136.37
133.71
131.00
130.15
129.96
129.01
128.60
128.44
127.70
127.53
126.80
125.87
122.32
118.03
77.58
77.16
76.74
58.76
45.28
15
20
25
1.4 1.2 1.0
f2 (ppm)
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

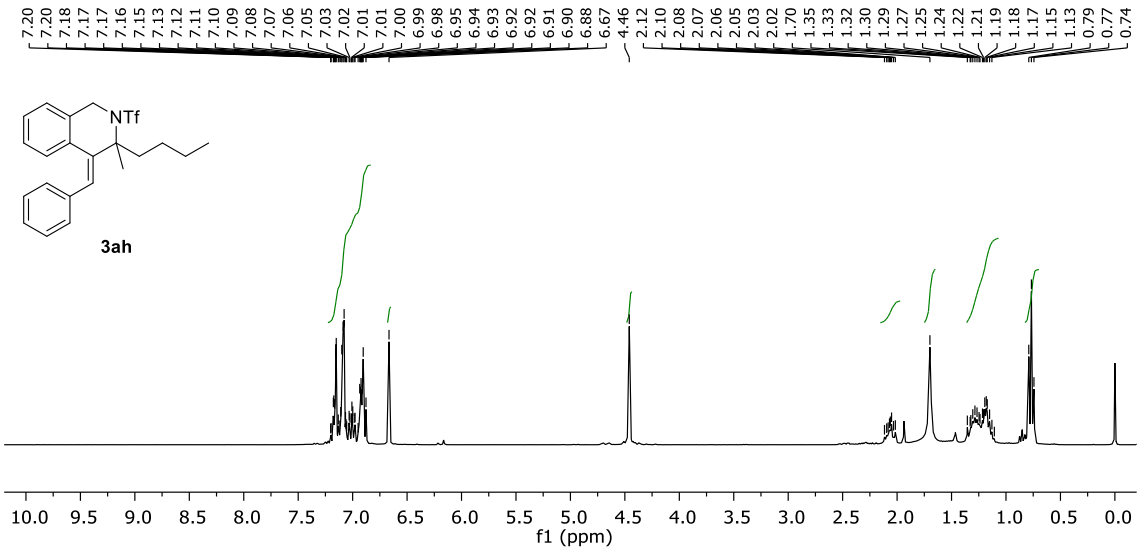

7.55 7.54 7.52 7.51 7.33 7.32 7.31 7.26 7.25 7.24 7.23 7.22 7.19 7.19 7.18 7.17 7.16 7.15 7.14 7.10 7.10 7.08 7.08 7.02 7.01 6.99 5.96 5.93 5.48 5.45 4.59 4.55 4.33 4.05 1.72 1.71 1.68 1.66 1.63 1.62 1.60 1.59 1.36 1.32 1.31 1.29 1.27 1.26 1.25 1.24 1.23 1.23 1.20 1.20 1.18 1.17 1.13 1.09 1.09
NTf
NTf
+
1.1:1
3af
3af'
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

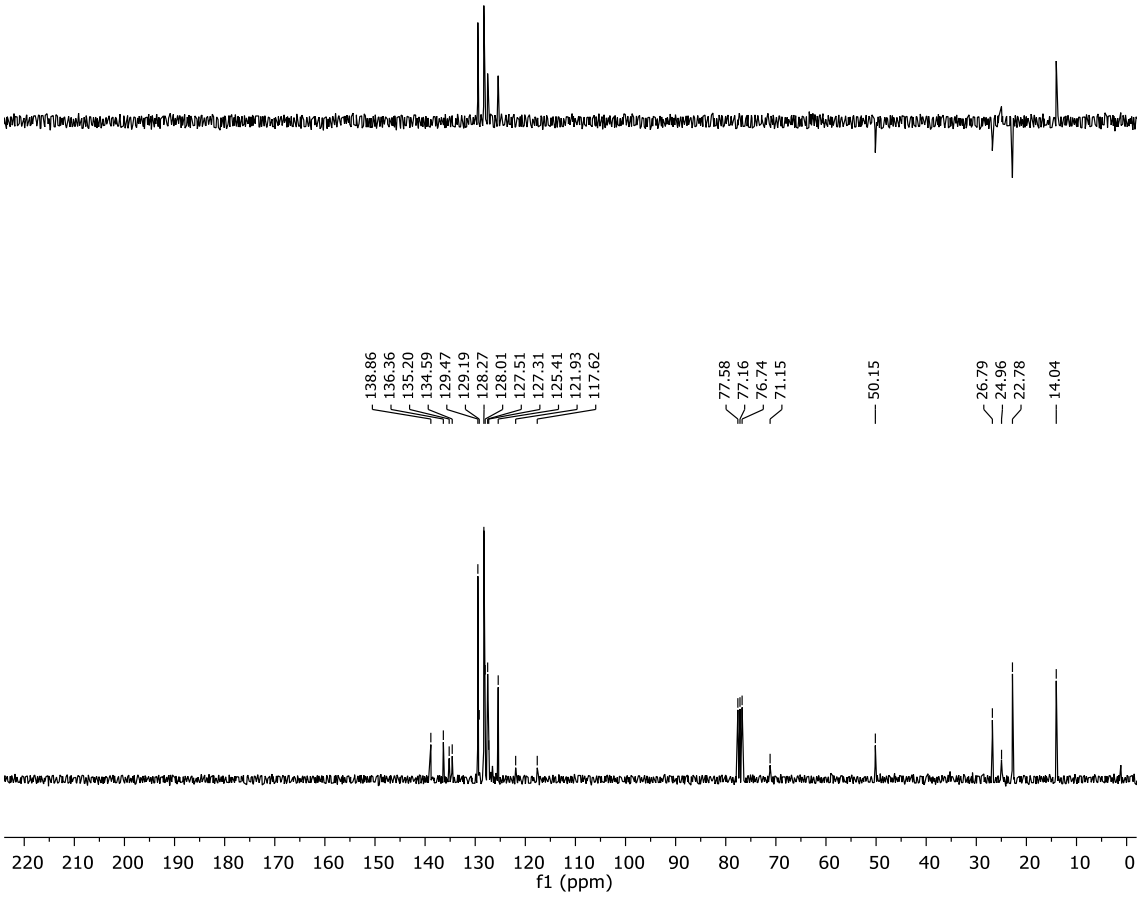

138.07 133.61 133.41 133.09 132.19 130.28 127.97 127.93 127.87 127.61 127.50 126.12 126.05 125.82 125.40 124.02 122.33 122.21 118.03 117.92
77.58 77.16 76.74
52.92 48.50 48.28 45.72 37.40 37.22 33.15 32.95 25.98 25.77 25.62
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

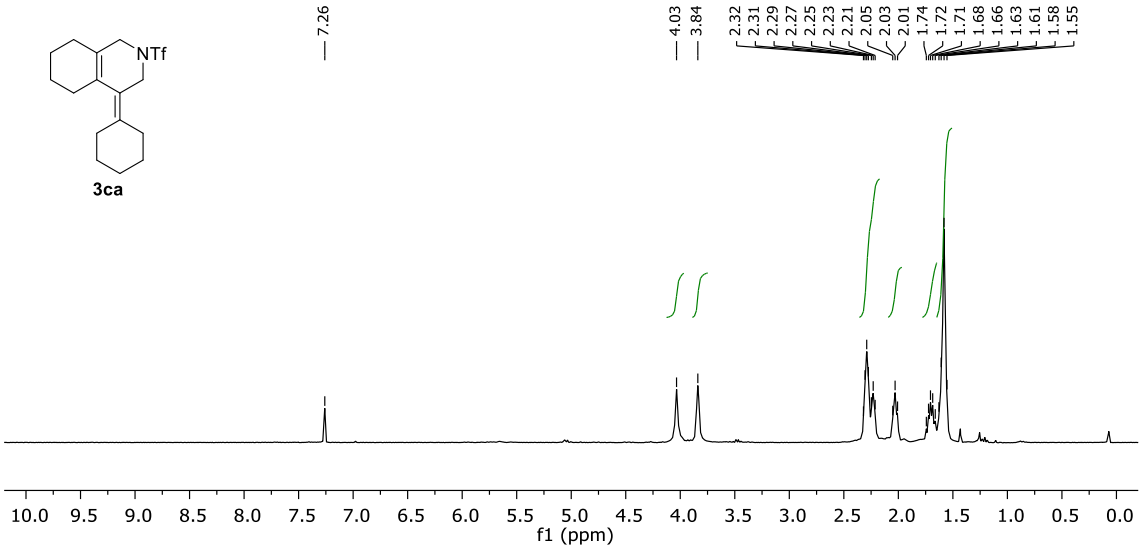

7.19
7.19
7.18
7.18
7.17
7.17
7.11
7.11
7.10
7.10
7.09
7.08
7.07
7.06
7.05
7.04
7.03
7.02
7.02
7.01
7.01
6.99
6.98
6.93
6.92
6.91
6.91
6.90
6.90
6.89
6.73
4.45
4.45
1.69
NTf
3ag
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

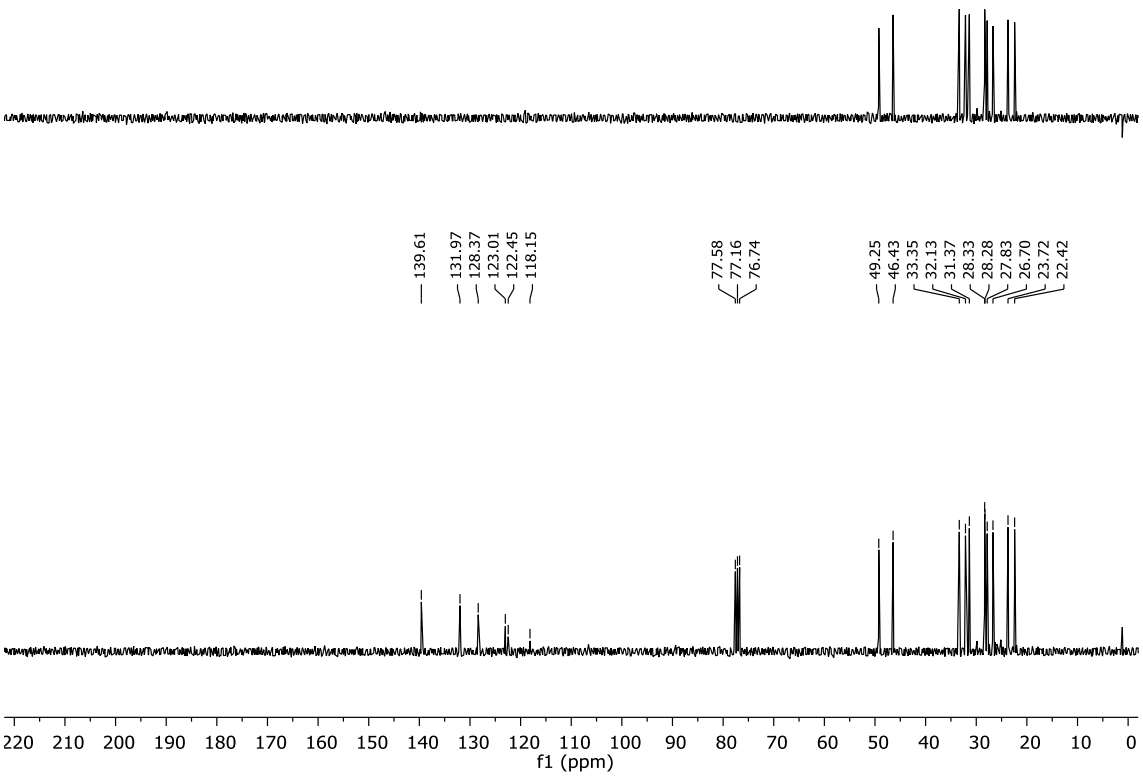


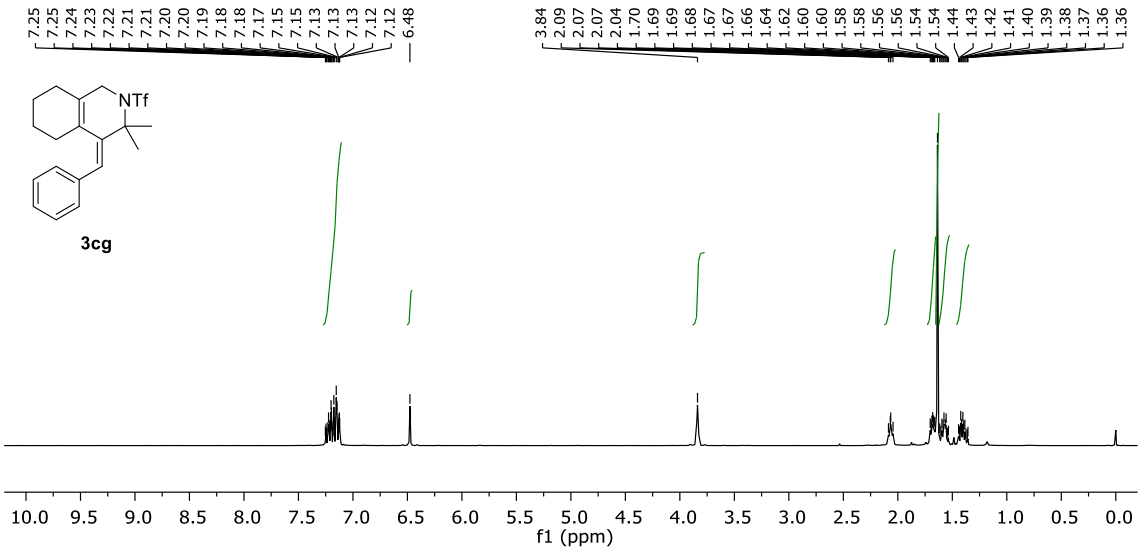

141.84
136.30
135.04
134.81
129.44
129.37
128.29
128.26
128.03
127.50
125.71
125.46
121.88
117.57
77.58
77.16
76.74
67.60
49.38
27.92
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

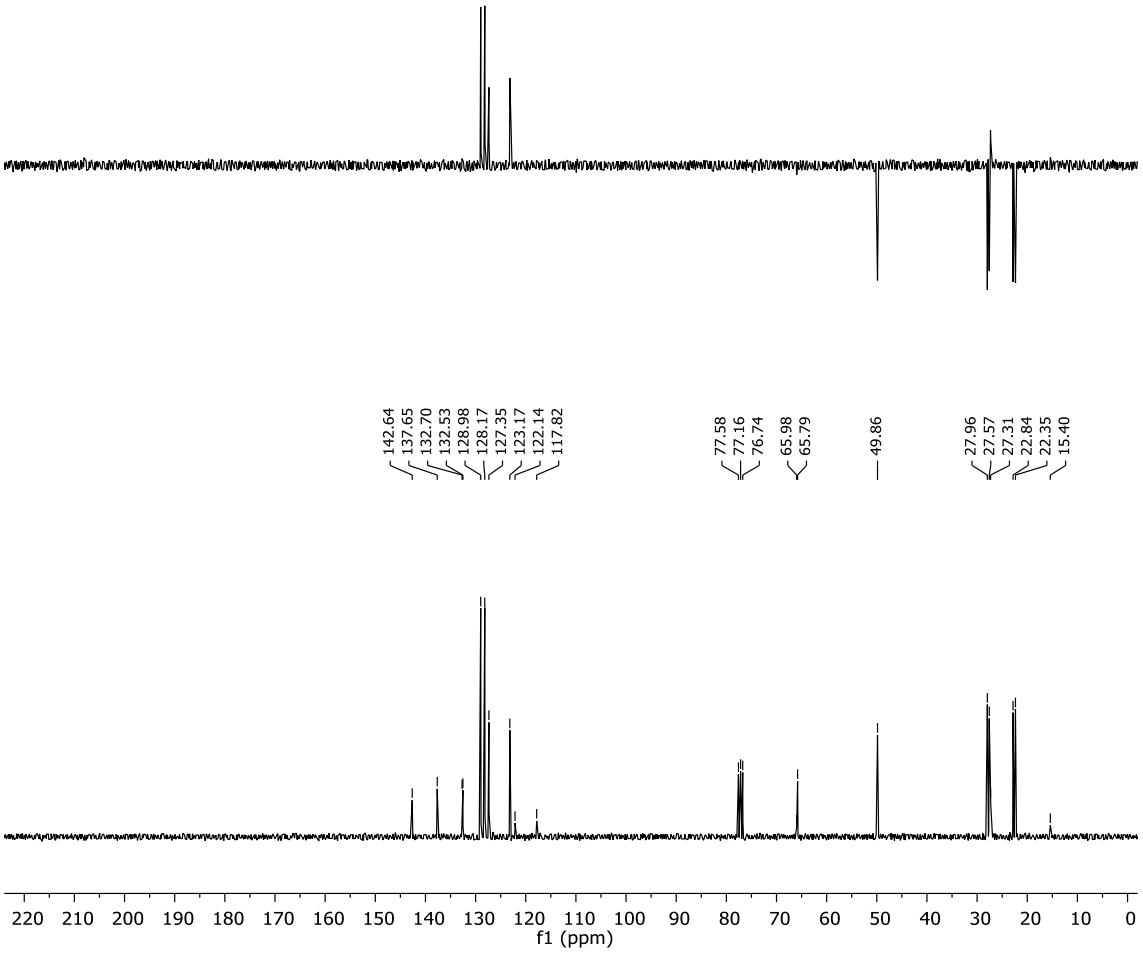

7.20 7.20 7.18 7.17 7.17 7.16 7.15 7.13 7.12 7.11 7.10 7.09 7.08 7.07 7.06 7.05 7.03 7.02 7.01 7.01 7.00 6.99 6.98 6.95 6.94 6.93 6.92 6.92 6.91 6.90 6.88 6.67 4.46 2.12 2.10 2.08 2.07 2.06 2.05 2.03 2.02 1.70 1.35 1.33 1.32 1.30 1.29 1.27 1.25 1.24 1.22 1.21 1.19 1.18 1.17 1.15 1.13 0.79 0.77 0.74
NTf
3ah
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

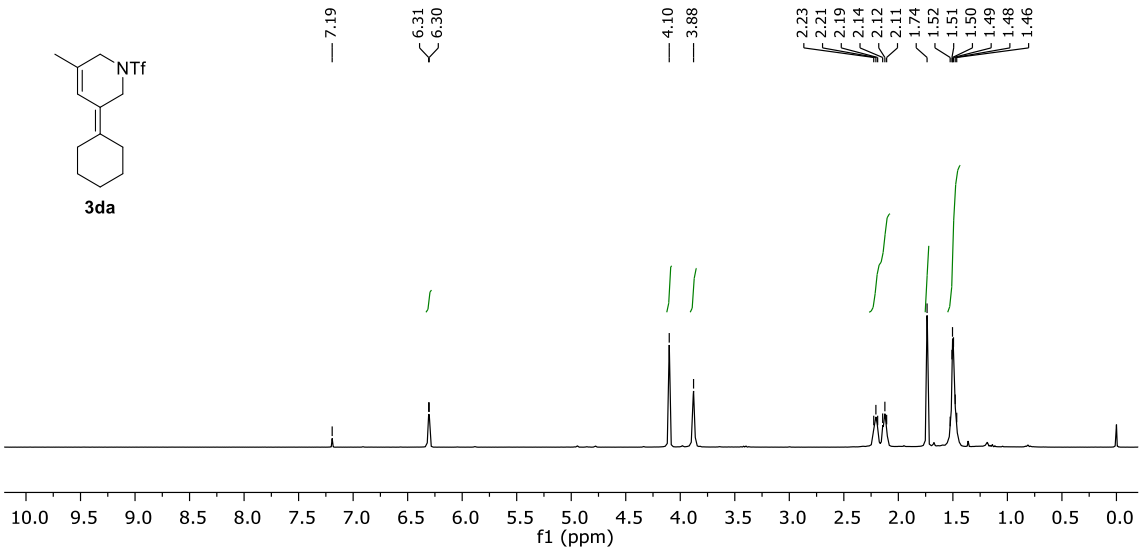

138.86 136.36 135.20 134.59 129.47 129.19 128.27 128.01 127.51 127.31 125.41 121.93 117.62
77.58 77.16 76.74 71.15
50.15
26.79 24.96 22.78
14.04
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

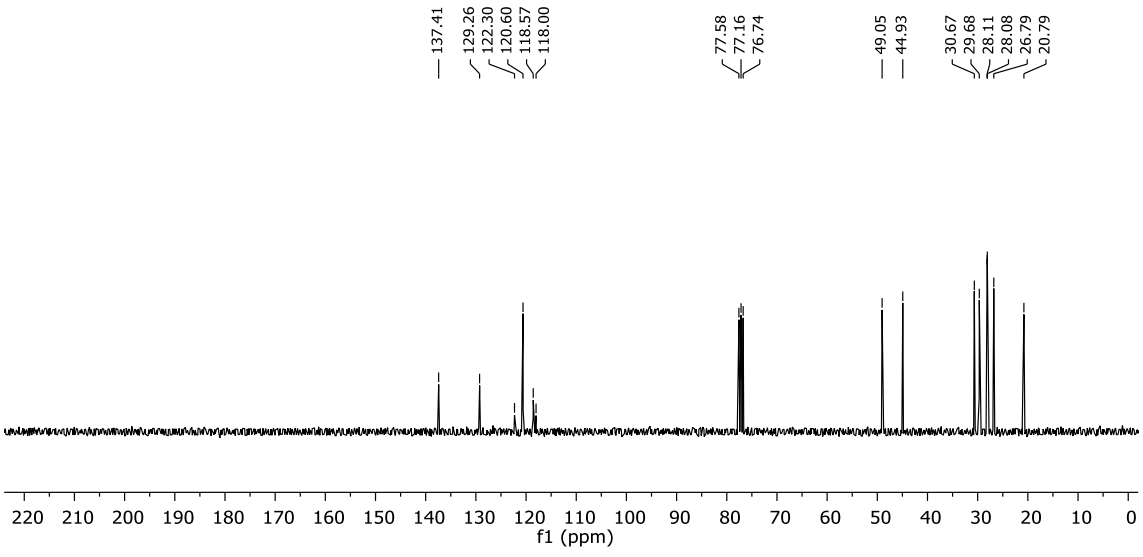

NTf
3ca
7.26
4.03
3.84
2.32
2.31
2.29
2.27
2.25
2.23
2.21
2.05
2.03
2.01
1.74
1.72
1.71
1.68
1.66
1.63
1.61
1.58
1.55
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

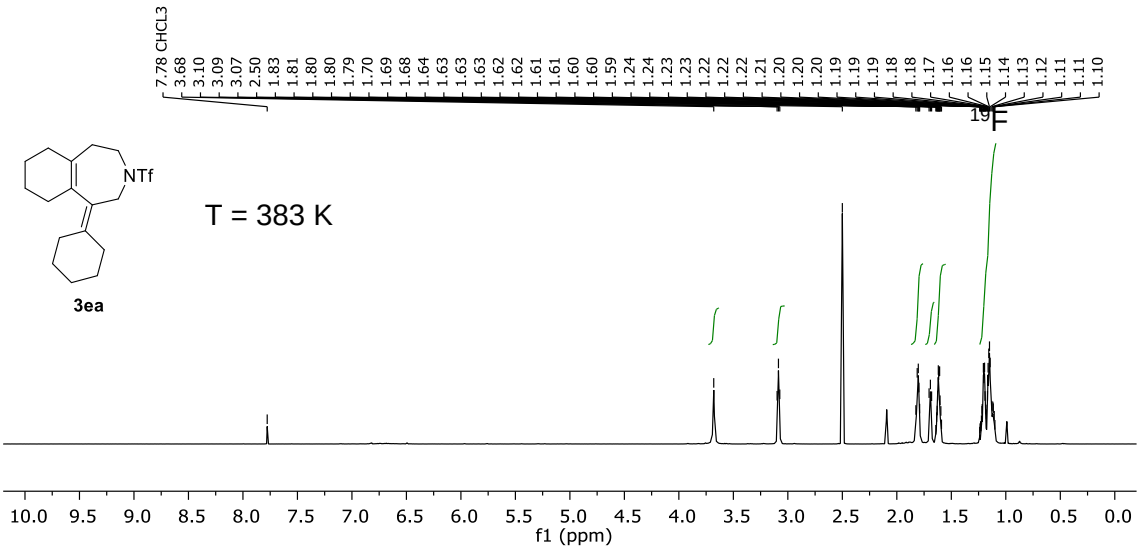

139.61
131.97
128.37
123.01
122.45
118.15
77.58
77.16
76.74
49.25
46.43
33.35
32.13
31.37
28.33
28.28
27.83
26.70
23.72
22.42
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

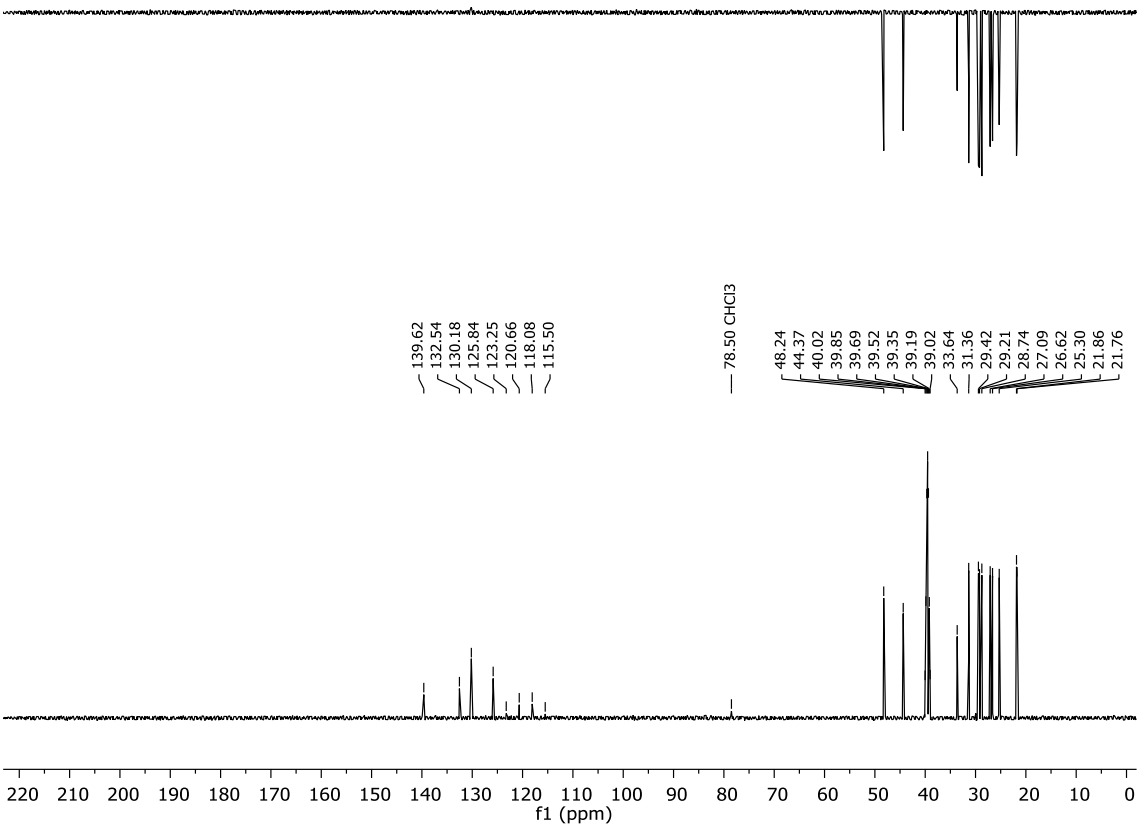

7.25 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.18 7.17 7.15 7.15 7.13 7.13 7.13 7.12 7.12 6.48
3.84 2.09 2.07 2.07 2.04 1.70 1.69 1.69 1.68 1.67 1.67 1.66 1.64 1.62 1.60 1.60 1.58 1.58 1.56 1.56 1.54 1.54 1.44 1.43 1.42 1.41 1.40 1.39 1.38 1.37 1.36 1.36
NTf
3cg
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

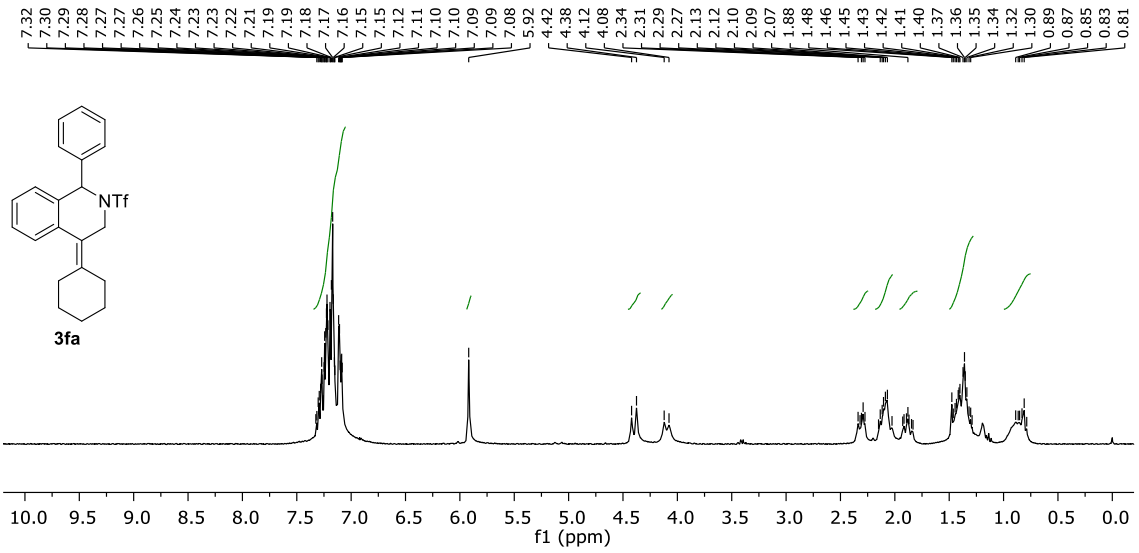

142.64 137.65 132.70 132.53 128.98 128.17 127.35 123.17 122.14 117.82
77.58 77.16 76.74 65.98 65.79 49.86 27.96 27.57 27.31 22.84 22.35 15.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

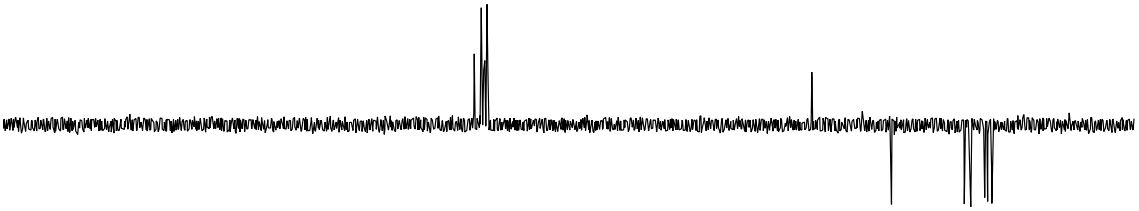

NTf
3da
7.19
6.31
6.30
4.10
3.88
2.23
2.21
2.19
2.14
2.12
2.11
1.74
1.52
1.51
1.50
1.49
1.48
1.46
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

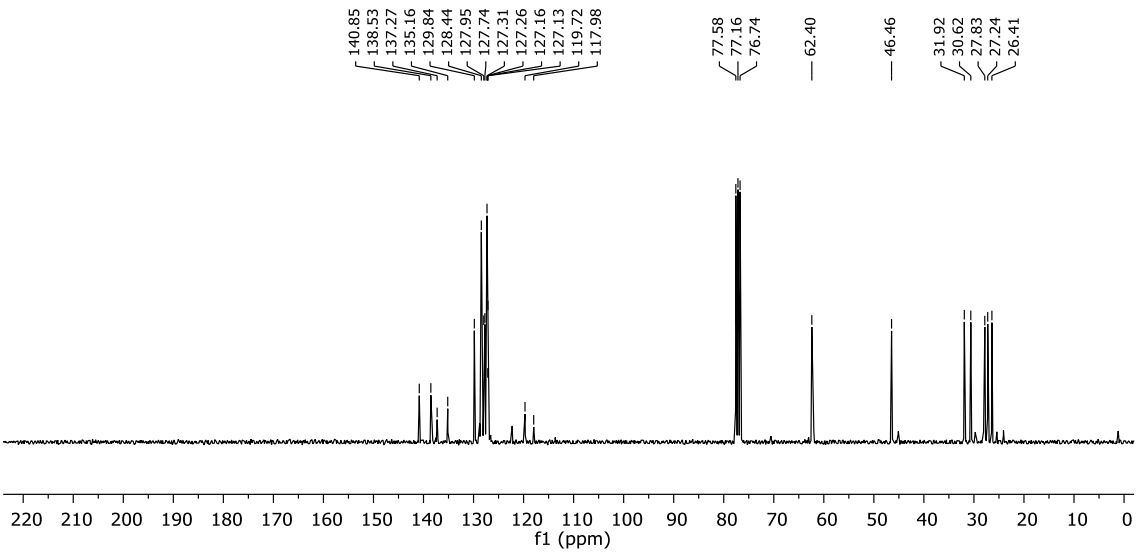

137.41
129.26
122.30
120.60
118.57
118.00
77.58
77.16
76.74
49.05
44.93
30.67
29.68
28.11
28.08
26.79
20.79
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

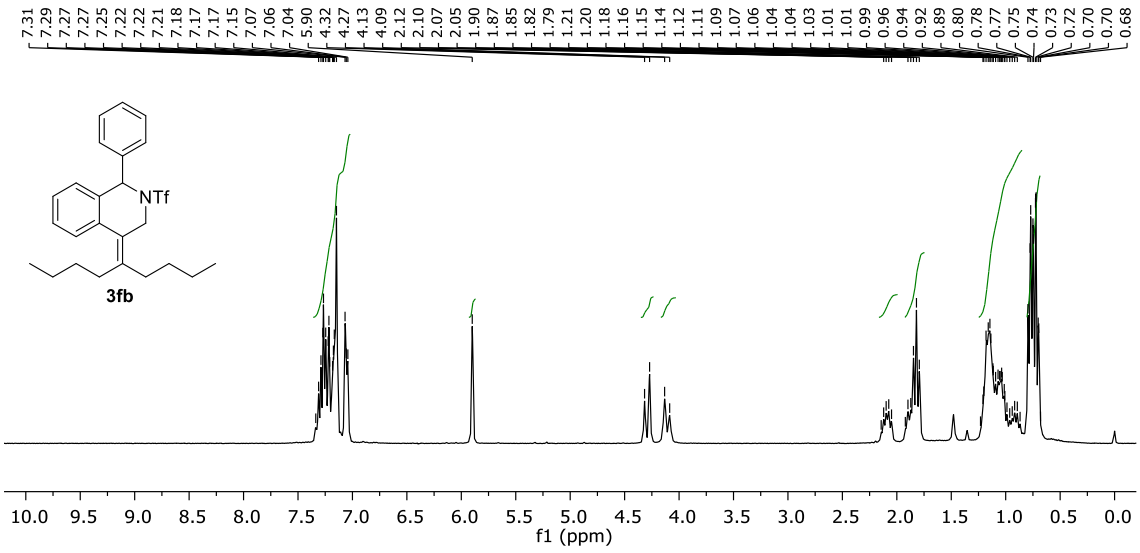

7.78 CHCL3
3.68
3.10
3.09
3.07
2.50
1.83
1.81
1.80
1.80
1.79
1.70
1.69
1.68
1.64
1.63
1.63
1.63
1.62
1.62
1.61
1.61
1.60
1.60
1.59
1.24
1.24
1.23
1.23
1.22
1.22
1.22
1.21
1.20
1.20
1.20
1.19
1.19
1.19
1.18
1.18
1.17
1.16
1.16
1.15
1.14
1.13
1.12
1.11
1.11
1.10
19F
NTf
T = 383 K
3ea
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

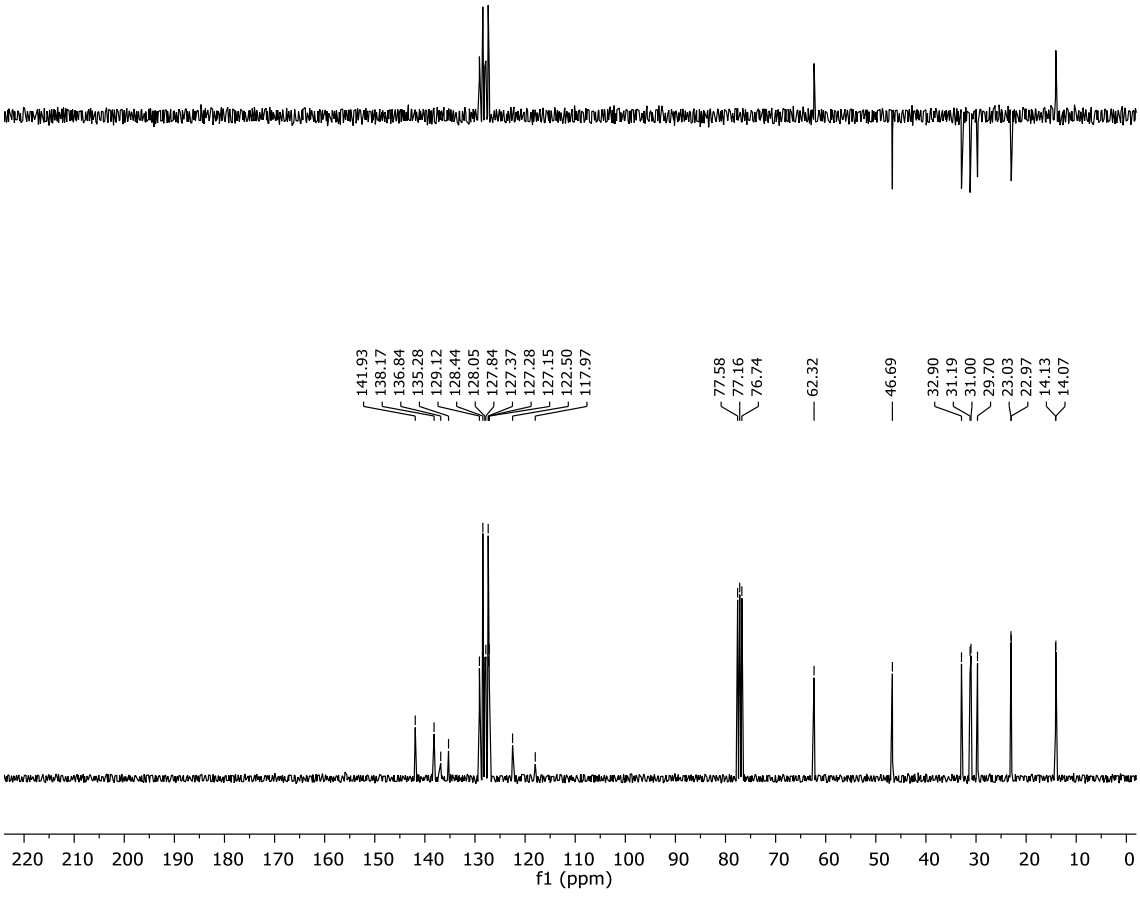

139.62
132.54
130.18
125.84
123.25
120.66
118.08
115.50
78.50 CHCl3
48.24
44.37
40.02
39.85
39.69
39.52
39.35
39.19
39.02
33.64
31.36
29.42
29.21
28.74
27.09
26.62
25.30
21.86
21.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

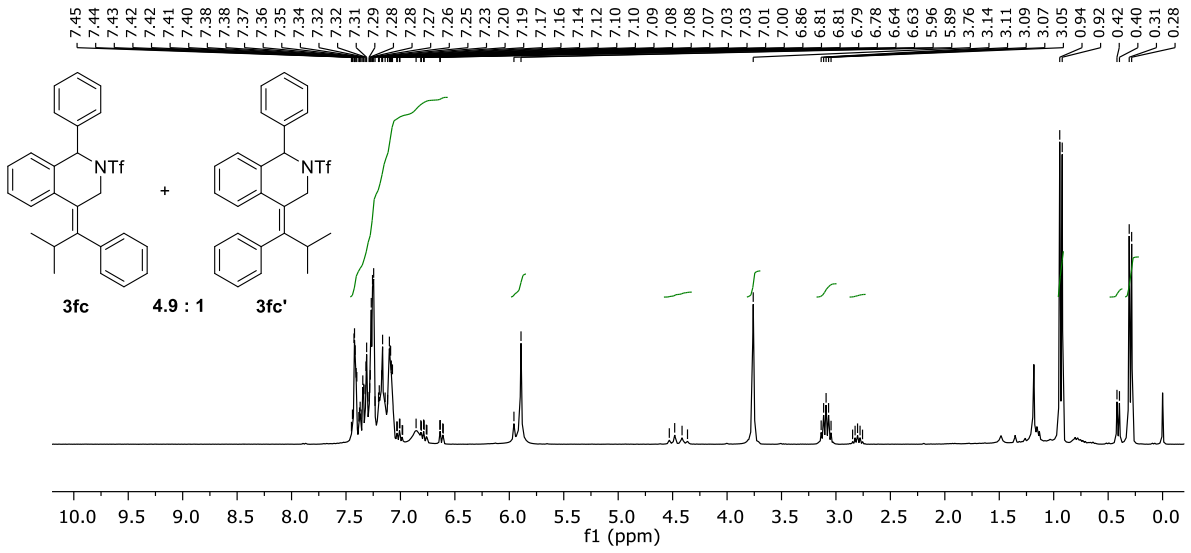

7.32 7.30 7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.23 7.22 7.21 7.19 7.19 7.18 7.17 7.16 7.15 7.15 7.12 7.11 7.10 7.10 7.09 7.09 7.08 5.92 4.42 4.38 4.12 4.08 2.34 2.31 2.29 2.27 2.13 2.12 2.10 2.09 2.07 1.88 1.48 1.46 1.45 1.43 1.42 1.41 1.40 1.37 1.36 1.35 1.34 1.32 1.30 0.89 0.87 0.85 0.83 0.81
NTf
3fa
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

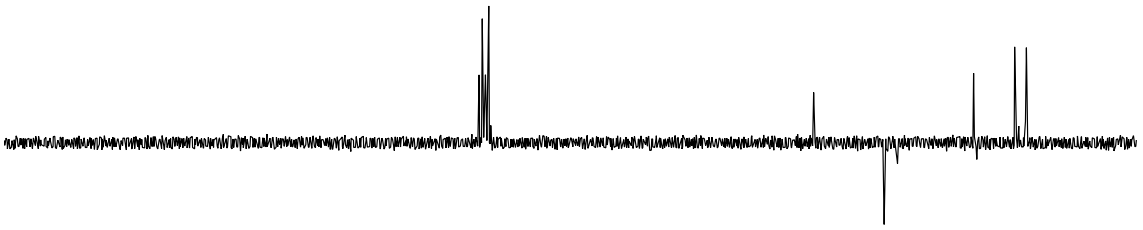


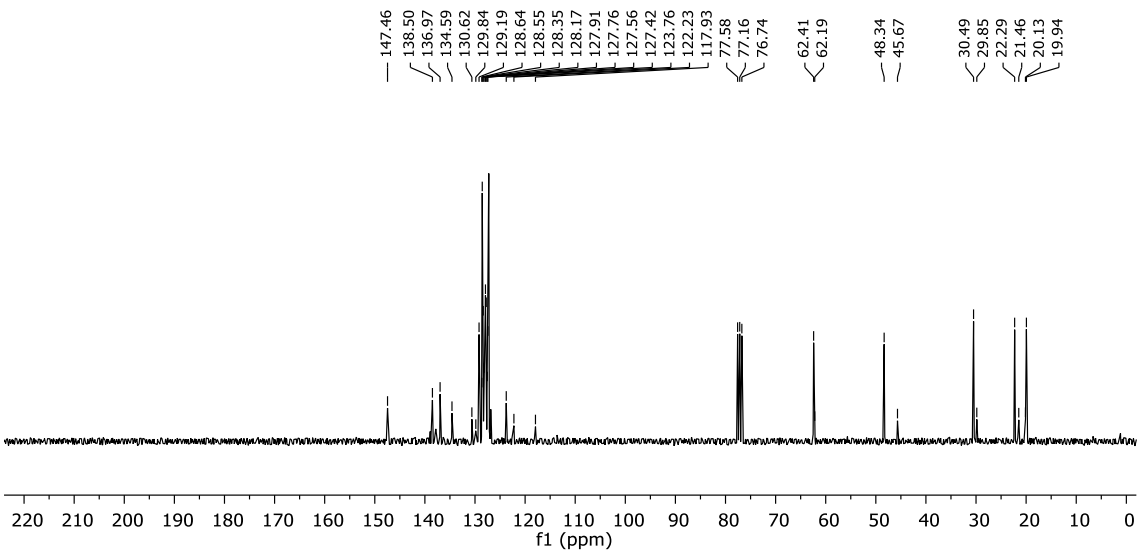

140.85 138.53 137.27 135.16 129.84 128.44 127.95 127.74 127.31 127.26 127.16 127.13 119.72 117.98
77.58 77.16 76.74
62.40
46.46
31.92 30.62 27.83 27.24 26.41
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

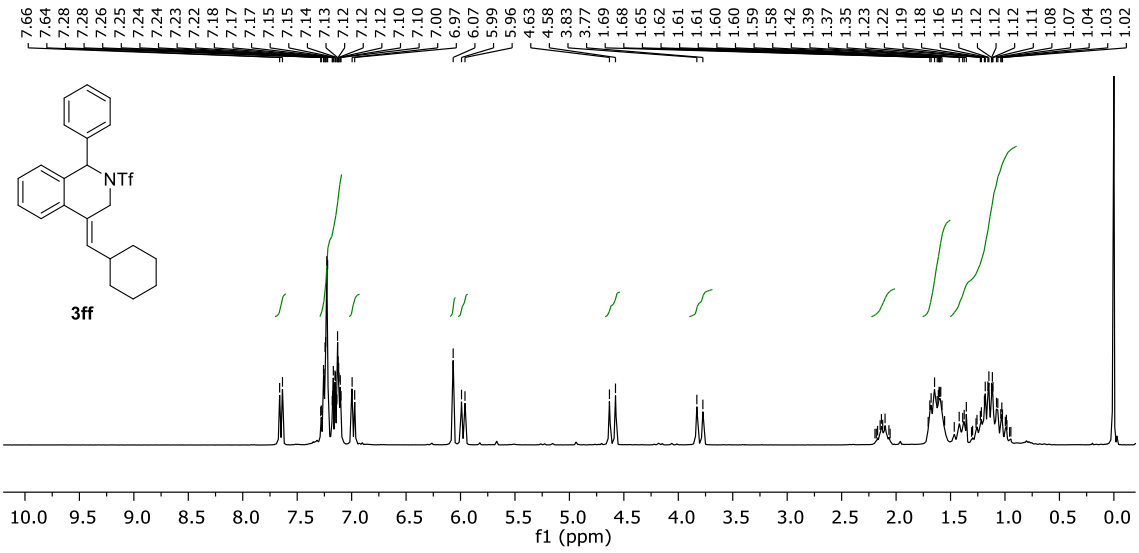

7.31
7.29
7.27
7.27
7.25
7.22
7.21
7.18
7.17
7.17
7.15
7.07
7.06
7.04
5.90
4.32
4.27
4.13
4.09
2.12
2.10
2.07
2.05
1.90
1.87
1.85
1.82
1.79
1.21
1.20
1.18
1.16
1.15
1.14
1.12
1.11
1.09
1.07
1.06
1.04
1.04
1.03
1.01
1.01
0.99
0.96
0.94
0.92
0.89
0.80
0.78
0.77
0.75
0.74
0.73
0.72
0.70
0.70
0.68
NTf
3fb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

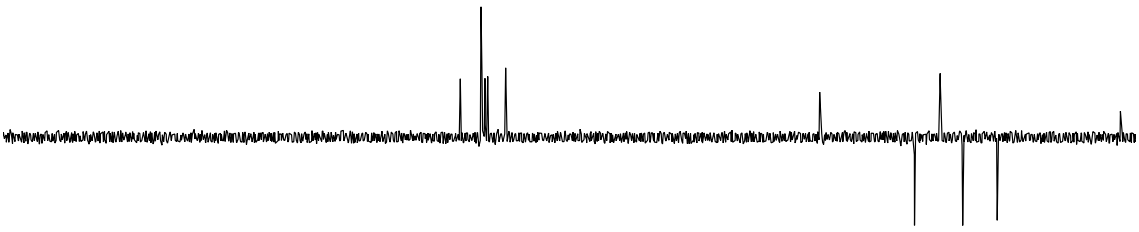

141.93
138.17
136.84
135.28
129.12
128.44
128.05
127.84
127.37
127.28
127.15
122.50
117.97
77.58
77.16
76.74
62.32
46.69
32.90
31.19
31.00
29.70
23.03
22.97
14.13
14.07
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

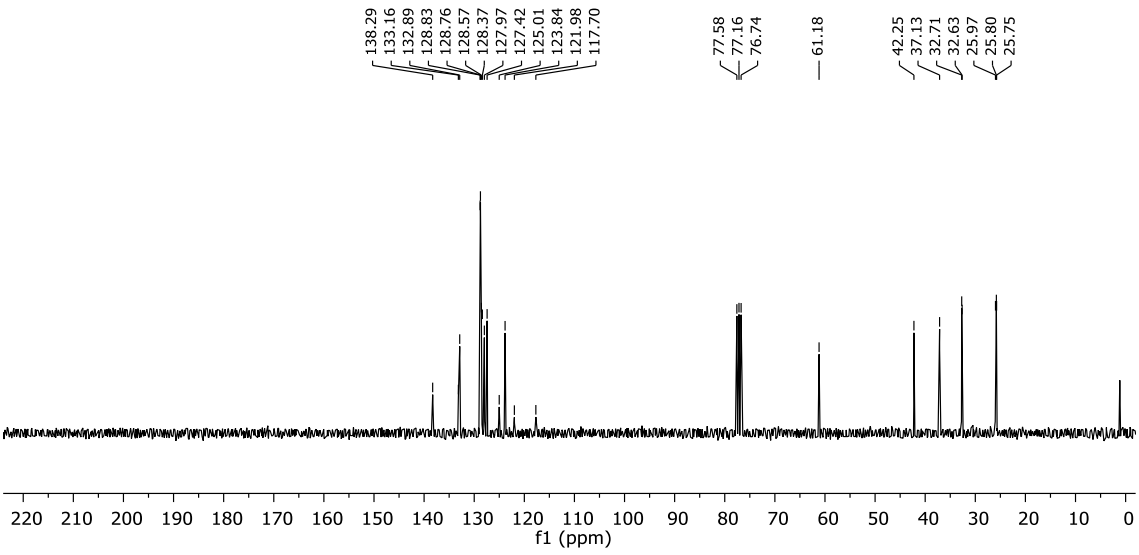

7.45 7.44 7.43 7.42 7.42 7.41 7.40 7.38 7.38 7.37 7.36 7.35 7.34 7.32 7.32 7.31 7.29 7.28 7.28 7.27 7.26 7.25 7.23 7.20 7.19 7.17 7.16 7.14 7.12 7.10 7.10 7.09 7.08 7.08 7.07 7.03 7.03 7.01 7.00 6.86 6.81 6.81 6.79 6.78 6.64 6.63 5.96 5.89 3.76 3.14 3.11 3.09 3.07 3.05 0.94 0.92 0.42 0.40 0.31 0.28
NTf
+
NTf
3fc
4.9 : 1
3fc'
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

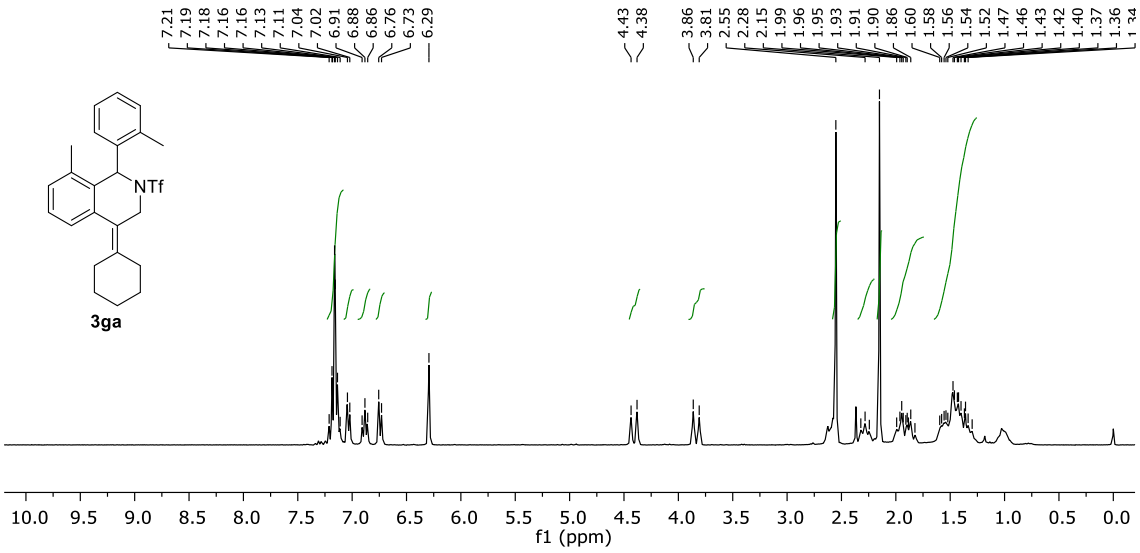


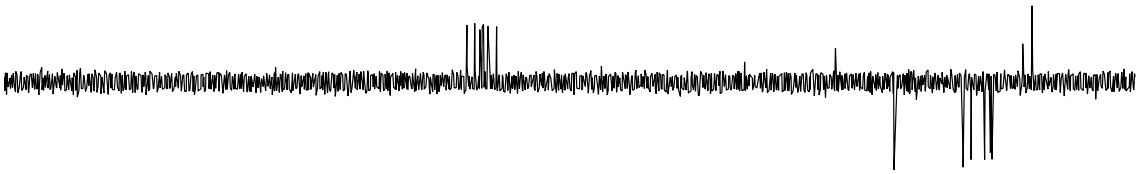

147.46 138.50 136.97 134.59 130.62 129.84 129.19 128.64 128.55 128.35 128.17 127.91 127.76 127.56 127.42 123.76 122.23 117.93 77.58 77.16 76.74 62.41 62.19 48.34 45.67 30.49 29.85 22.29 21.46 20.13 19.94
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

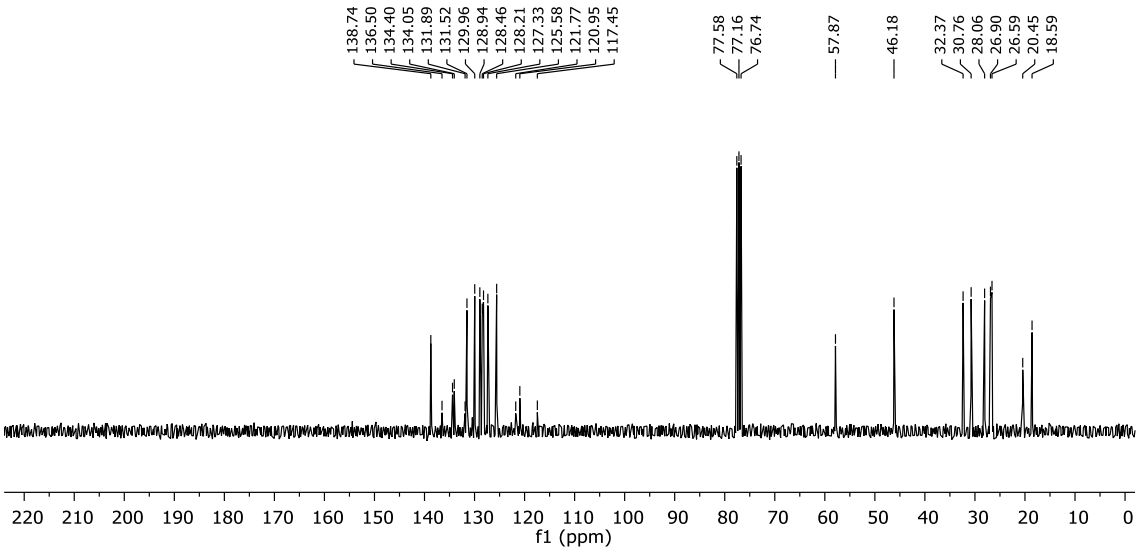

7.66 7.64 7.28 7.28 7.26 7.25 7.24 7.24 7.23 7.22 7.18 7.17 7.17 7.15 7.15 7.14 7.13 7.12 7.12 7.12 7.10 7.10 7.00 6.97 6.07 5.99 5.96 4.63 4.58 3.83 3.77 1.69 1.68 1.65 1.62 1.61 1.61 1.60 1.60 1.59 1.58 1.42 1.39 1.37 1.35 1.23 1.22 1.19 1.18 1.16 1.15 1.12 1.12 1.12 1.11 1.08 1.07 1.04 1.03 1.02
NTf
3ff
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

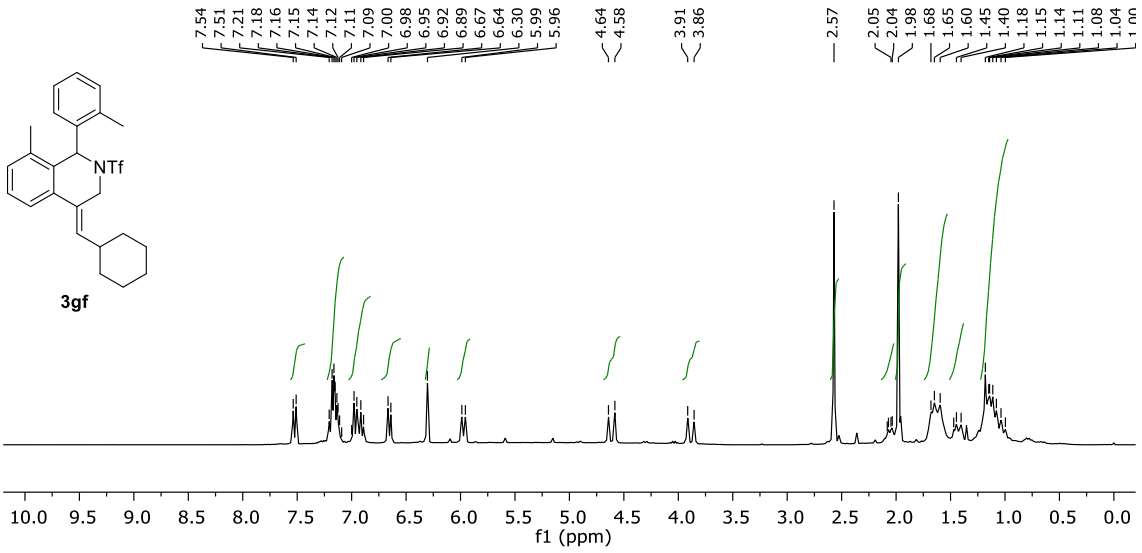


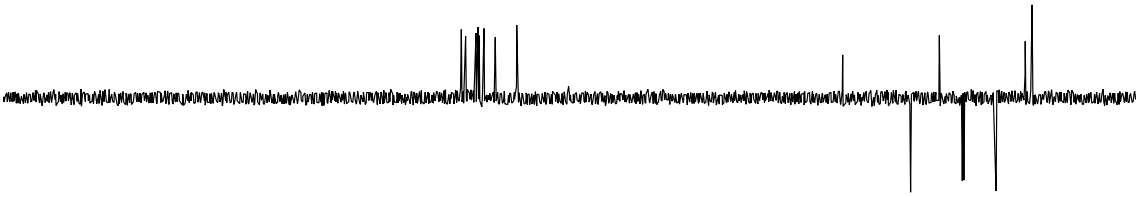

138.29 133.16 132.89 128.83 128.76 128.57 128.37 127.97 127.42 125.01 123.84 121.98 117.70
77.58 77.16 76.74
61.18
42.25 37.13 32.71 32.63 25.97 25.80 25.75
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

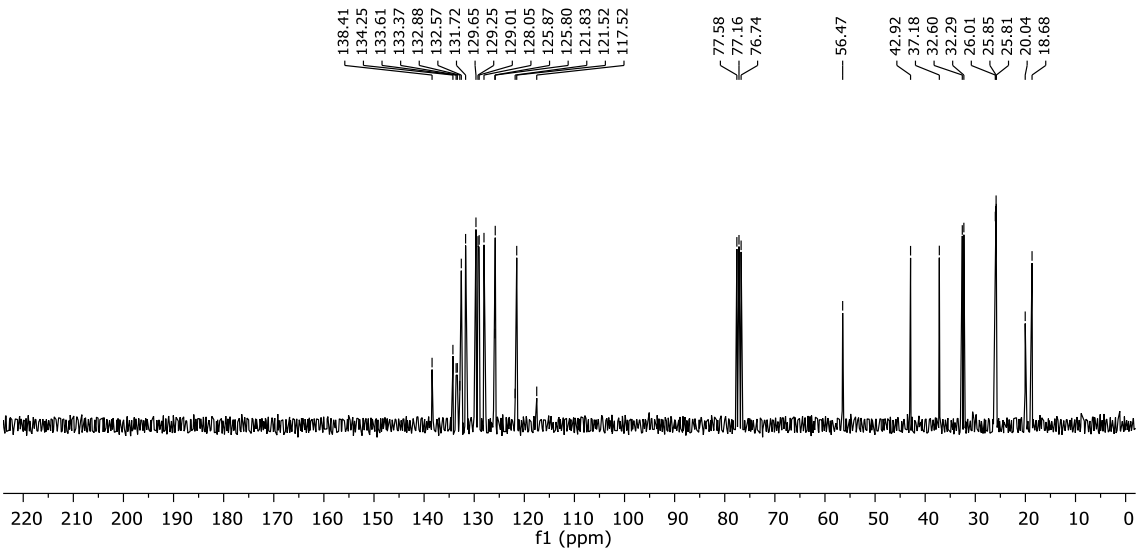

7.21
7.19
7.18
7.16
7.16
7.13
7.11
7.04
7.02
6.91
6.88
6.86
6.76
6.73
6.29
4.43
4.38
3.86
3.81
2.55
2.28
2.15
1.99
1.96
1.95
1.93
1.91
1.90
1.86
1.60
1.58
1.56
1.54
1.52
1.47
1.46
1.43
1.42
1.40
1.37
1.36
NTf
3ga
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

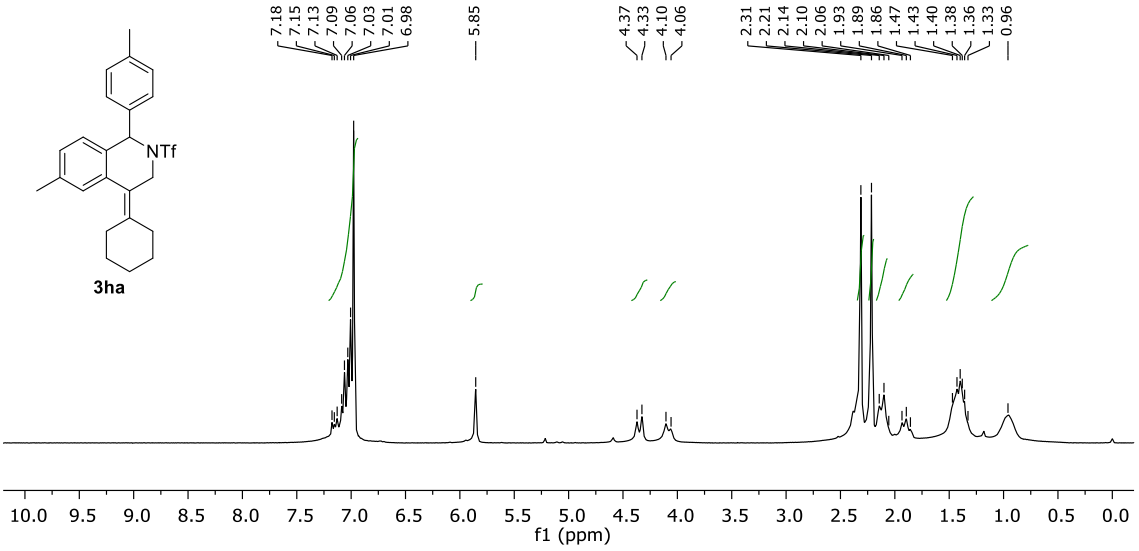


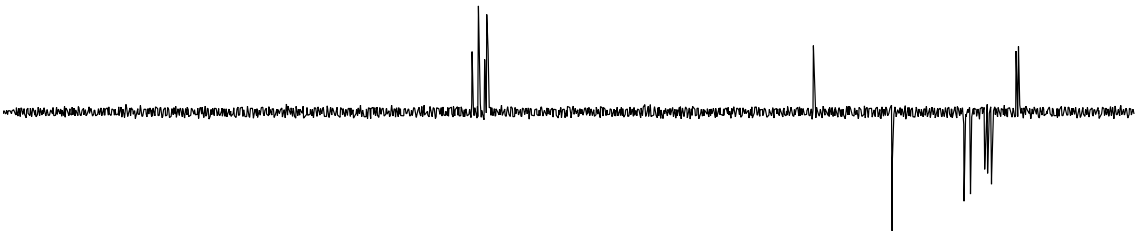

138.74
136.50
134.40
134.05
131.89
131.52
129.96
128.94
128.46
128.21
127.33
125.58
121.77
120.95
117.45
77.58
77.16
76.74
57.87
46.18
32.37
30.76
28.06
26.90
26.59
20.45
18.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

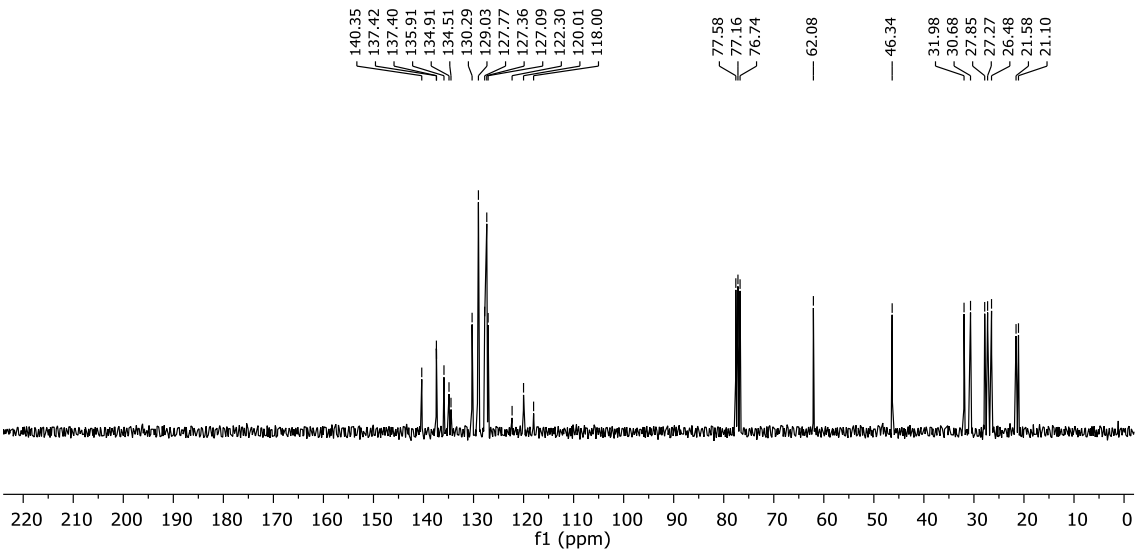

7.54
7.51
7.21
7.18
7.16
7.15
7.14
7.12
7.11
7.09
7.00
6.98
6.95
6.92
6.89
6.67
6.64
6.30
5.99
5.96
4.64
4.58
3.91
3.86
2.57
2.05
2.04
1.98
1.68
1.65
1.60
1.45
1.40
1.18
1.15
1.14
1.11
1.08
1.04
NTf
3gf
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

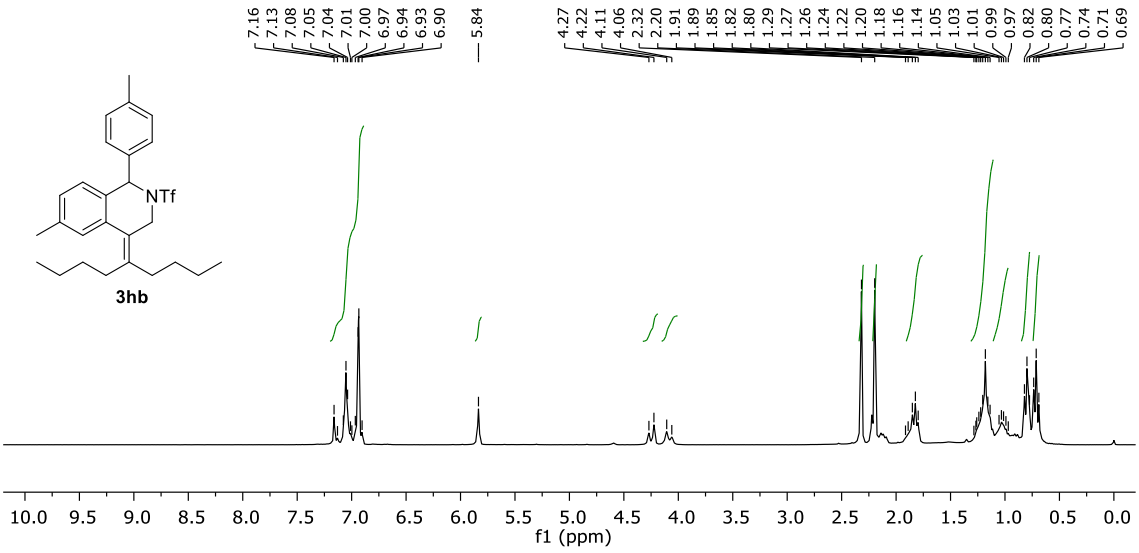


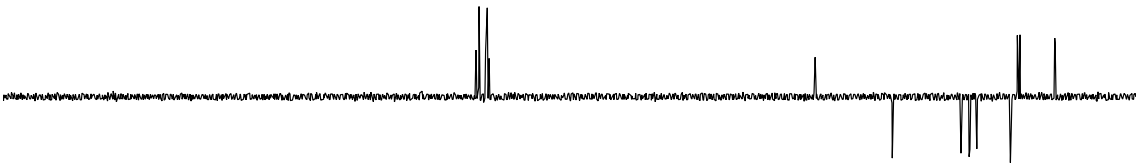

138.41
134.25
133.61
133.37
132.88
132.57
131.72
129.65
129.25
129.01
128.05
125.87
125.80
121.83
121.52
117.52
77.58
77.16
76.74
56.47
42.92
37.18
32.60
32.29
26.01
25.85
25.81
20.04
18.68
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

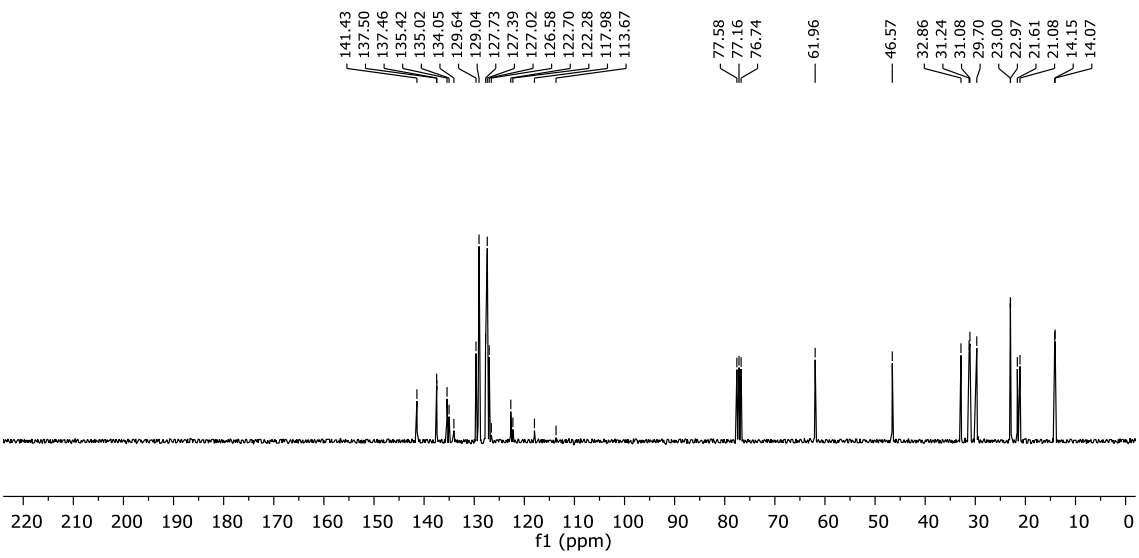

7.18
7.15
7.13
7.09
7.06
7.03
7.01
6.98
5.85
4.37
4.33
4.10
4.06
2.31
2.21
2.14
2.10
2.06
1.93
1.89
1.86
1.47
1.43
1.40
1.38
1.36
1.33
0.96
NTf
3ha
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

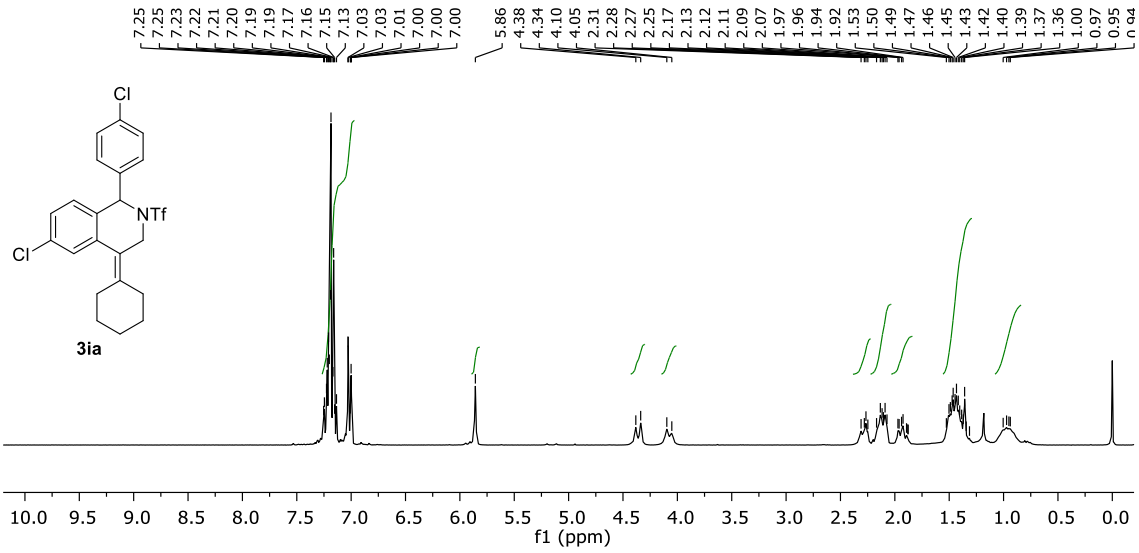


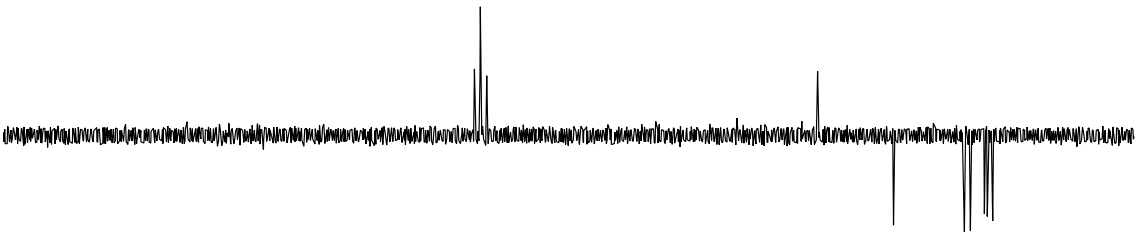

140.35
137.42
137.40
135.91
134.91
134.51
130.29
129.03
127.77
127.36
127.09
122.30
120.01
118.00
77.58
77.16
76.74
62.08
46.34
31.98
30.68
27.85
27.27
26.48
21.58
21.10
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

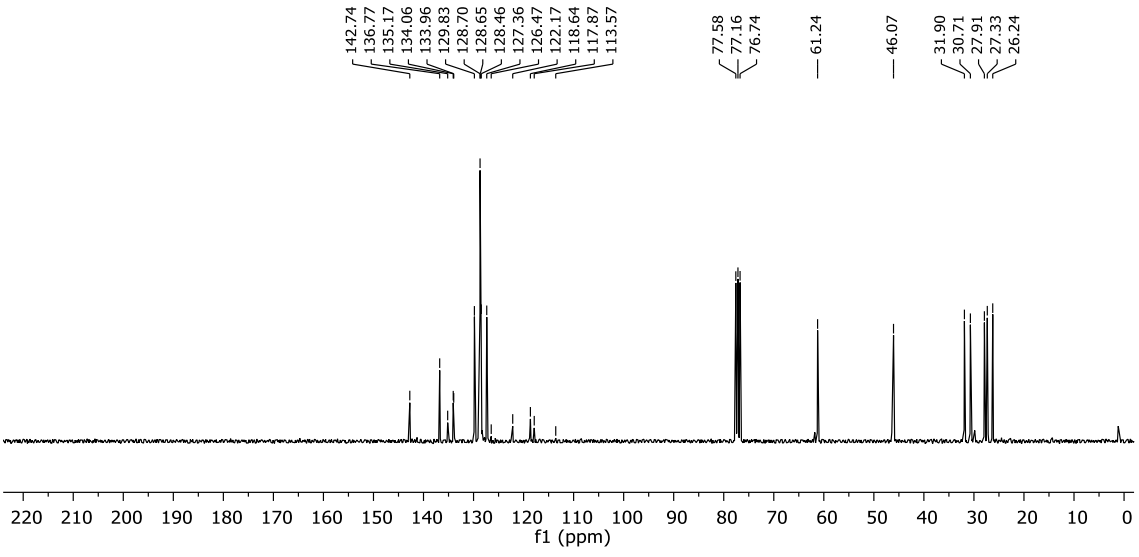

7.16
7.13
7.08
7.05
7.04
7.01
7.00
6.97
6.94
6.93
6.90
5.84
4.27
4.22
4.11
4.06
2.32
2.20
1.91
1.89
1.85
1.82
1.80
1.29
1.27
1.26
1.24
1.22
1.20
1.18
1.16
1.14
1.05
1.03
1.01
0.99
0.97
0.82
0.80
0.77
0.74
0.71
0.69
NTf
3hb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

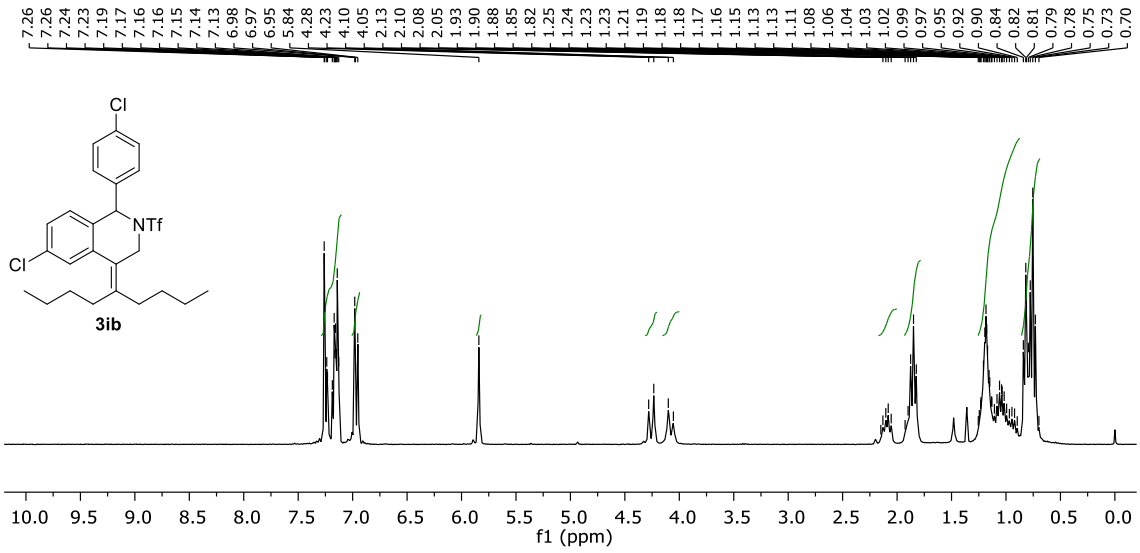


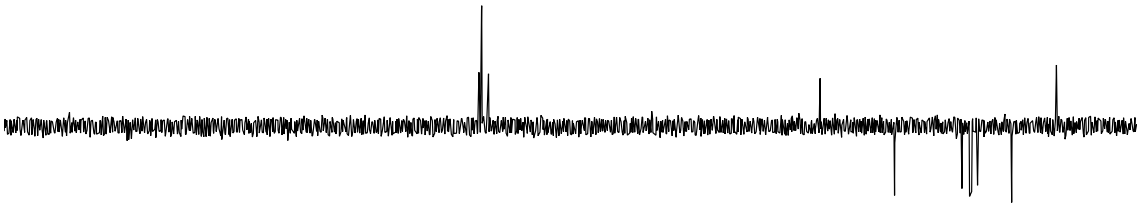

141.43
137.50
137.46
135.42
135.02
134.05
129.64
129.04
127.73
127.39
127.02
126.58
122.70
122.28
117.98
113.67
77.58
77.16
76.74
61.96
46.57
32.86
31.24
31.08
29.70
23.00
22.97
21.61
21.08
14.15
14.07
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

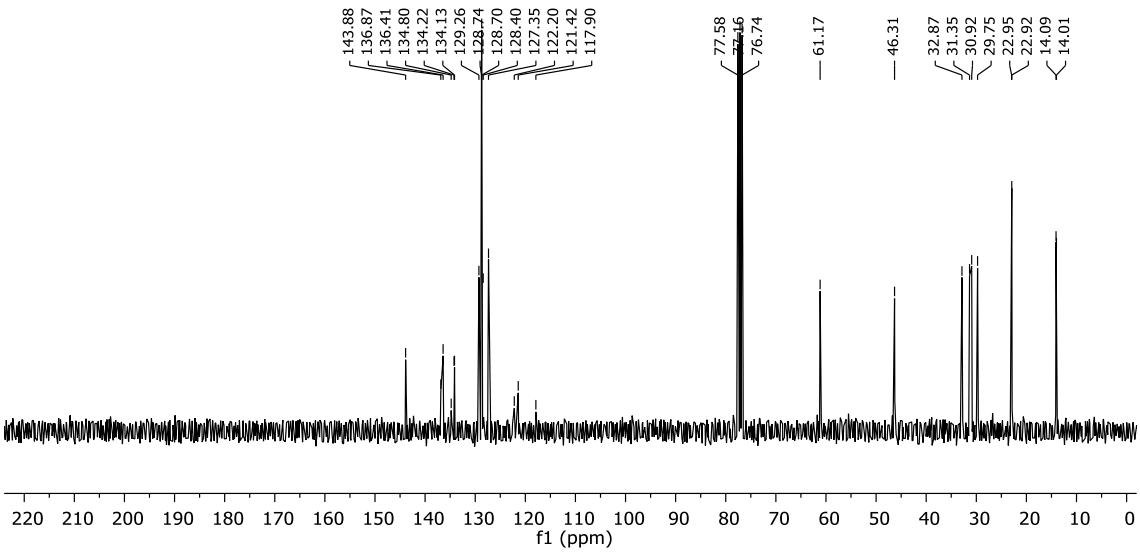

7.25 7.25 7.23 7.22 7.21 7.20 7.19 7.19 7.17 7.16 7.15 7.13 7.03 7.03 7.01 7.00 7.00 7.00
5.86
4.38 4.34 4.10 4.05 2.31 2.28 2.27 2.25 2.17 2.13 2.12 2.11 2.09 2.07 1.97 1.96 1.94 1.92 1.53 1.50 1.49 1.47 1.46 1.45 1.43 1.42 1.40 1.39 1.37 1.36 1.00 0.97 0.95
Cl
NTf
Cl
3ia
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

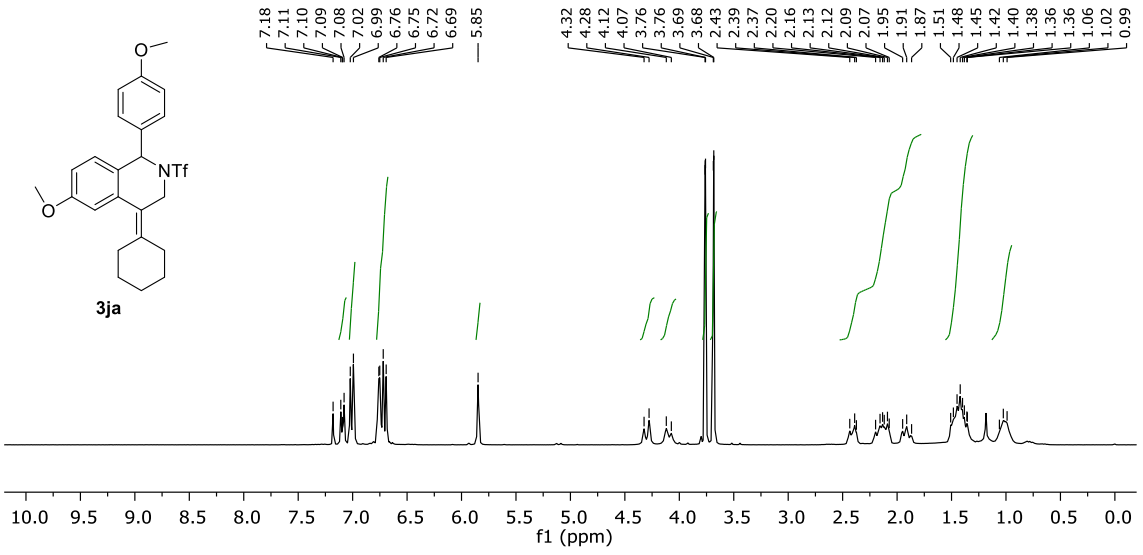


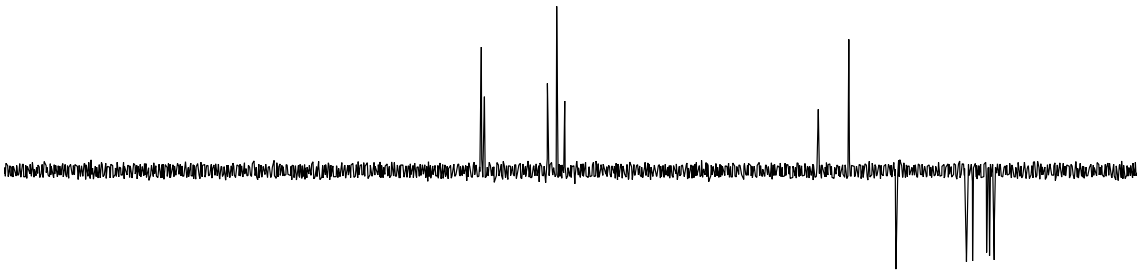

142.74 136.77 135.17 134.06 133.96 129.83 128.70 128.65 128.46 127.36 126.47 122.17 118.64 117.87 113.57
77.58 77.16 76.74
61.24
46.07
31.90 30.71 27.91 27.33 26.24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

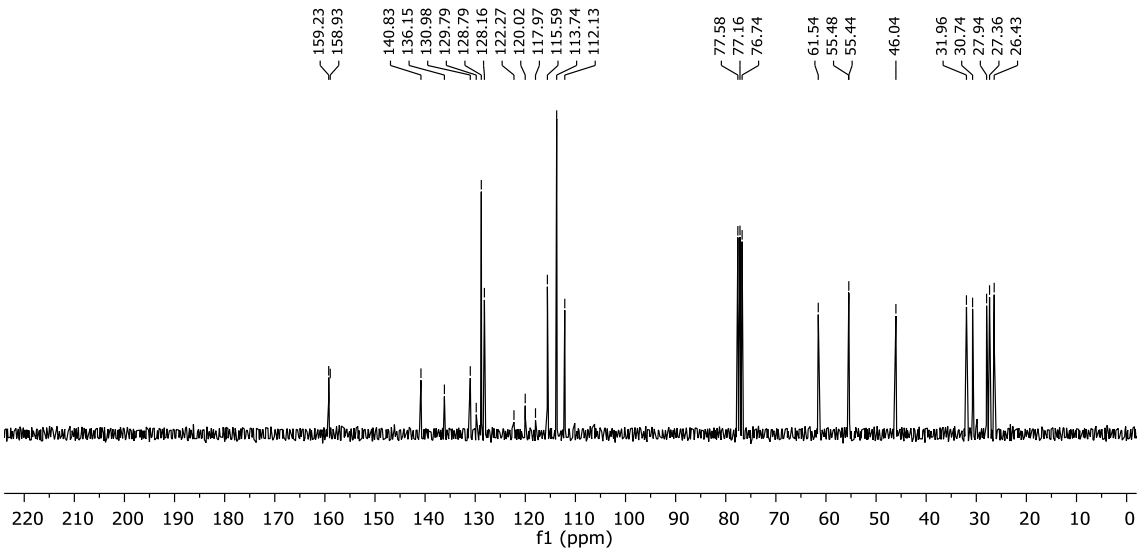

7.26 7.26 7.24 7.23 7.19 7.17 7.16 7.16 7.15 7.14 7.13 6.98 6.97 6.95 5.84 4.28 4.23 4.10 4.05 2.13 2.10 2.08 2.05 1.93 1.90 1.88 1.85 1.82 1.25 1.24 1.23 1.23 1.21 1.19 1.18 1.18 1.17 1.16 1.15 1.13 1.13 1.11 1.08 1.06 1.04 1.03 1.02 0.99 0.97 0.95 0.92 0.90 0.84 0.82 0.81 0.79 0.78 0.75 0.73 0.70
Cl
NTf
Cl
3ib
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

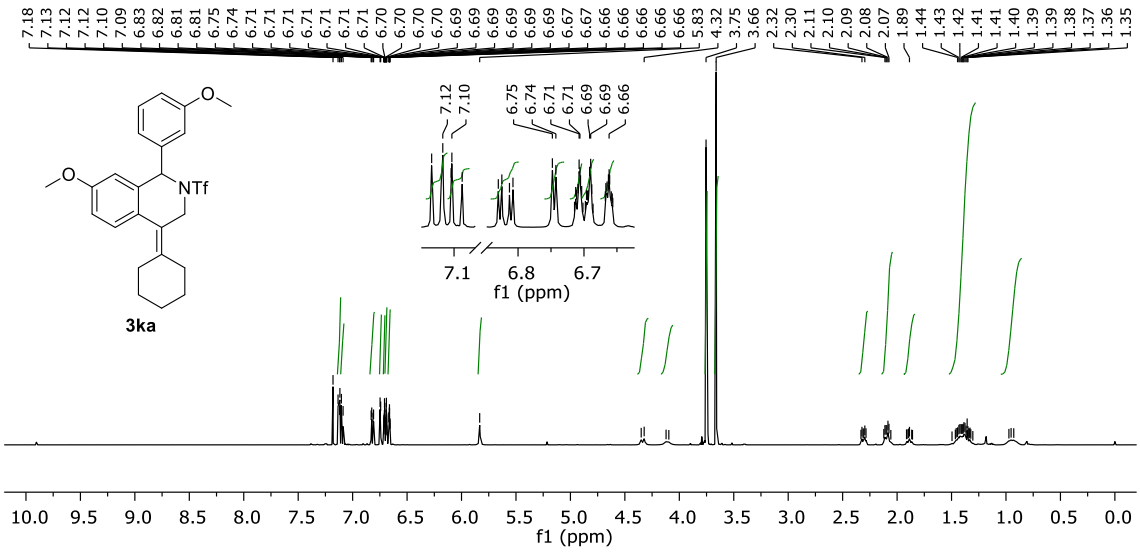


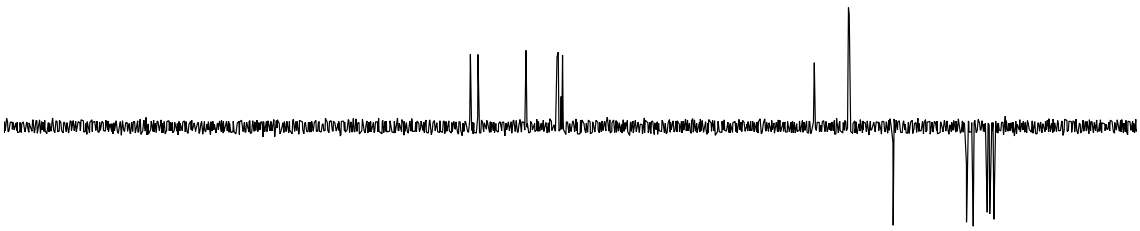

143.88 136.87 136.41 134.80 134.22 134.13 129.26 128.74 128.70 128.40 127.35 122.20 121.42 117.90
77.58 77.16 76.74
61.17
46.31
32.87 31.35 30.92 29.75 22.95 22.92 14.09 14.01
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

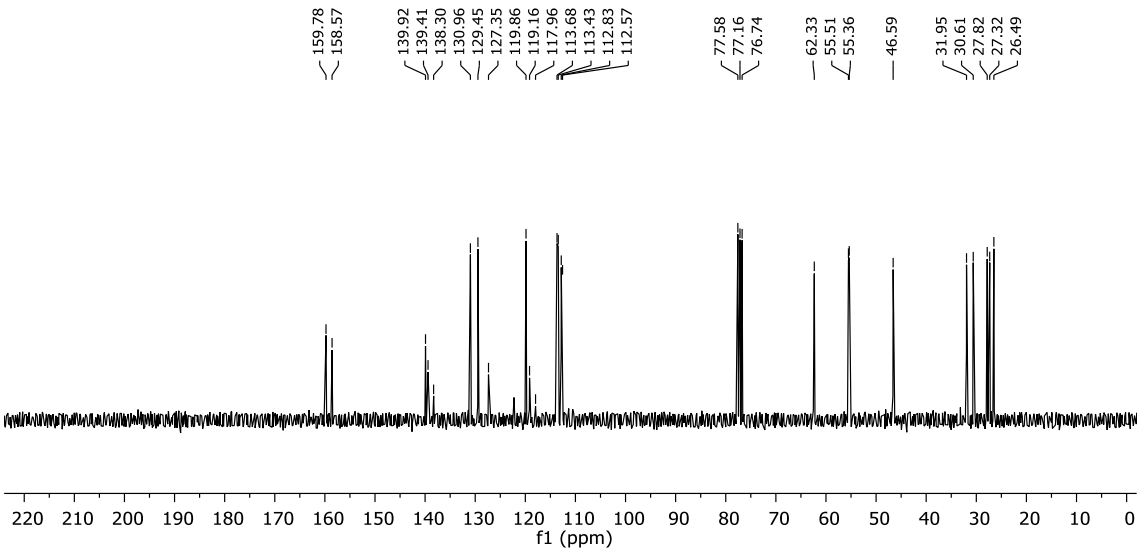

7.18
7.11
7.10
7.09
7.08
7.02
6.99
6.76
6.75
6.72
6.69
5.85
4.32
4.28
4.12
4.07
3.76
3.76
3.69
3.68
2.43
2.39
2.37
2.20
2.16
2.13
2.12
2.09
2.07
1.95
1.91
1.87
1.51
1.48
1.45
1.42
1.40
1.38
1.36
1.36
1.06
1.02
0.99
O
NTf
O
3ja
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

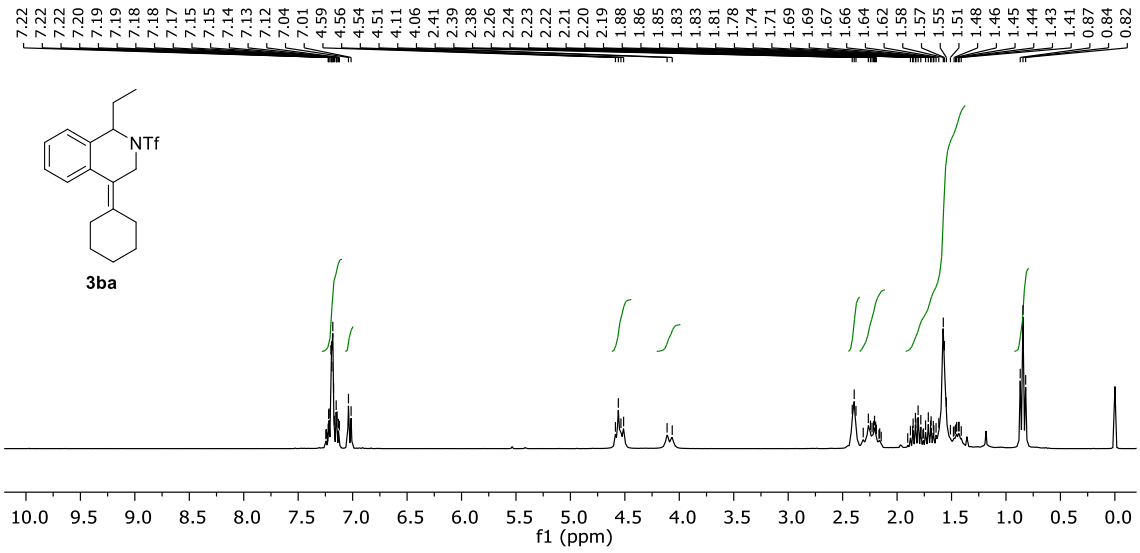


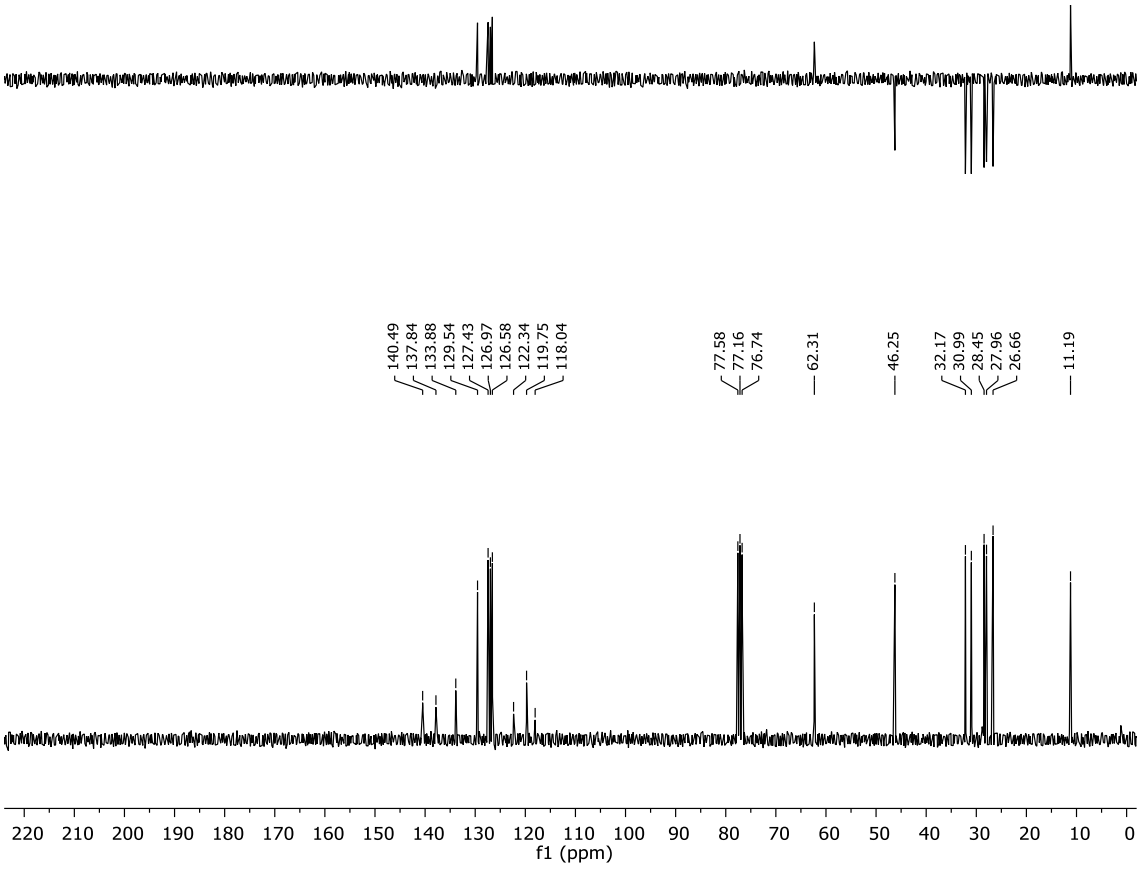

159.23
158.93
140.83
136.15
130.98
129.79
128.79
128.16
122.27
120.02
117.97
115.59
113.74
112.13
77.58
77.16
76.74
61.54
55.48
55.44
46.04
31.96
30.74
27.94
27.36
26.43
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

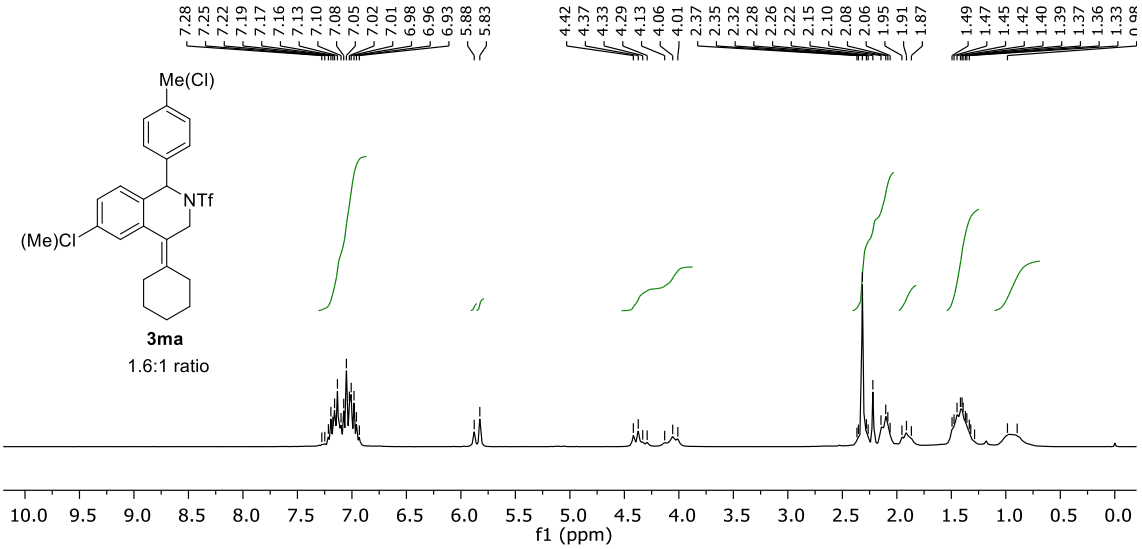

7.18 7.13 7.12 7.12 7.10 7.09 6.83 6.82 6.81 6.81 6.75 6.74 6.71 6.71 6.71 6.71 6.71 6.71 6.70 6.70 6.70 6.70 6.69 6.69 6.69 6.69 6.69 6.67 6.67 6.66 6.66 6.66 6.66 6.66 5.83 4.32 3.75 3.66 2.32 2.30 2.11 2.10 2.09 2.08 2.07 1.89 1.44 1.43 1.42 1.41 1.41 1.40 1.39 1.39 1.38 1.37 1.36 1.35
O
O
NTf
3ka
7.12 7.10 6.75 6.74 6.71 6.71 6.69 6.69 6.66
7.1 6.8 6.7
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

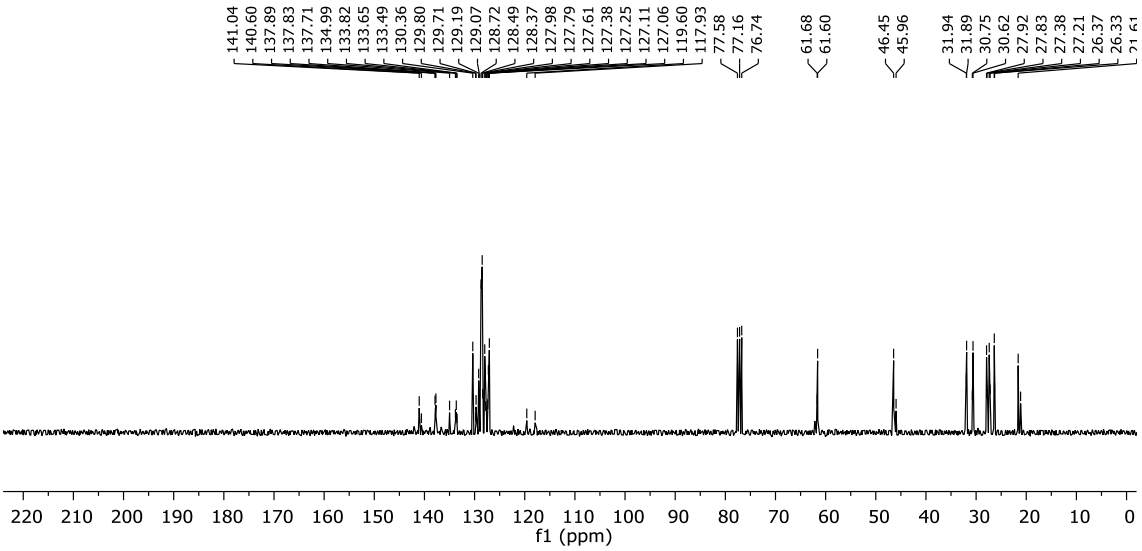



159.78 158.57 139.92 139.41 138.30 130.96 129.45 127.35 119.86 119.16 117.96 113.68 113.43 112.83 112.57 77.58 77.16 76.74 62.33 55.51 55.36 46.59 31.95 30.61 27.82 27.32 26.49
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.22 7.22 7.22 7.20 7.19 7.19 7.18 7.18 7.17 7.15 7.15 7.14 7.13 7.12 7.04 7.01 4.59 4.56 4.54 4.51 4.11 4.06 2.41 2.39 2.38 2.26 2.24 2.23 2.22 2.21 2.20 2.19 1.88 1.86 1.85 1.83 1.81 1.78 1.74 1.71 1.69 1.69 1.67 1.66 1.64 1.62 1.58 1.57 1.55 1.51 1.48 1.46 1.45 1.44 1.43 1.41 0.87 0.84 0.82
NTf
3ba
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.49 137.84 133.88 129.54 127.43 126.97 126.58 122.34 119.75 118.04
77.58 77.16 76.74
62.31
46.25
32.17 30.99 28.45 27.96 26.66
11.19
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me(Cl)
NTf
(Me)Cl
3ma
1.6:1 ratio
f1 (ppm)


f1 (ppm)