SUPPORTING INFORMATION

Palladium-catalyzed formal (5+2) annulation between *ortho*-alkenylanilides and allenes

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GENERAL EXPERIMENTAL PROCEDURES

Reactions were conducted in dry solvents under Argon atmosphere unless otherwise stated. Dry solvents were Aldrich and used without further purification. Dried acetonitrile was also from Aldrich and dried with a solvent system (MBraun, SPS 800 manual), $Pd(OAc)_2$ (98%) [3375-31-3]. 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 or cerium nitrate 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 (300MHz) spectra were recorded at room temperature on a Varian 300MHz or 500 MHz spectrometer in $CDCl_3$* [using $CDCl_3$ (for 1H, δ = 7.26) as internal standard]. ^{13}C NMR (75 MHz) spectra 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 (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestReNova© NMR data processing software (www.mestrelab.com). Mass spectra were acquired using electronic impact (EI) and were recorded at the CACTUS facility of the University of Santiago de Compostela or Amazon SL Bruker using ESI (ion plarity negative and positive).

Allene **2g** (3-methylbuta-1,2-dien-1-yl)benzene) was prepared according to the procedure reported in Rai-Shung Liu et al. *Chem. Commun.*, **2012**, *48*, 6577. Allene **2f** (nona-4,5-diene) was prepared according A. Beauchemin et al *Org. Lett*., **2009**, *11*, 1895. Allene **2h** (2-methyldeca-2,3-diene)was prepared according A. Mohammed et al *Tetrahedron*, **1987**, 43 (3), 513-26. Allene **2e** (4-methylpenta-1,2-dien-3-

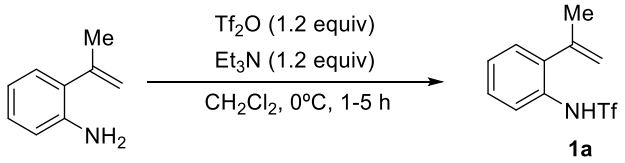
yl)benzene and **2c** propa-1,2-diene-1,1-diyldibenzene were prepared according to the procedure reported in *Org. Lett.*, **2011**, *13*(15), 3864-3867. All the other allenes were purchased from Aldrich.

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

Preparation of *ortho*-alkenylanilines:

All non commercialalkenylanilines were synthesized from the corresponding ketone *via* Wittig reaction, if the ketone was not available, then an addition of the corresponding Grignard reagent was done to the appropriately substituted 2-aminobenzonitrile.[1]Tosyl[2], isopropyl[3] and nosyl[4] protected *o*-alkenylanilines were synthesized as previously described in the literature. All spectral data recorded was in agreement with those in the corresponding communication.

GENERAL PROCEDURE for the synthesis of the triflyl 2-alkenylanilines (1a-1k), exemplified for 1a.

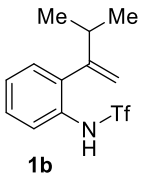


To a solution of *o*-isopropenylaniline (1 mL, 7.34 mmol) in dichloromethane (25 mL) under Ar atmosphere was added triethylamine (1.228 ml, 1.2 equiv) at 0 □C. Then trifluoromethanesulfonic anhydride (1.489 ml, 1.2 equiv) was added dropwise. The reaction was stirred at 0 °C for 1.5 hours and quenched with saturated NH_4Cl aqueous solution. The resulting mixture was extracted with dichloromethane and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification column flash chromatography on silica gel (hexanes:diethylether; 8:2) affording **1,1,1-trifluoro-*N*-(2-(prop-1-en-2-yl)phenyl)methanesulfonamide** (**1a**), (1.84 g, 94%), as a white solid upon freezing. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.49 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.09 (m, 4H), 5.36 (dd, *J* = 2.7, 1.2 Hz, 1H), 4.92 (s, 1H), 2.00 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 142.2

[1] Jana, S.; Ashokan, A.; Kumar, S.; Verma, A.; Kumar, S. *Org. Biomol. Chem* .**2015**, *13*, 8411.
[2]Youn, S. W.; Ko, T. Y.; Jang, M. J.; Jang, S. S. *Adv. Synth. Catal* .**2015**, 357, 227.
[3]Ferguson, J.; Zeng, F.; Alwis, N.; Alper, H. *Org. Lett.* **2013**, *15*, 1998.
[4]Liwosz, T. W.; Chemler, S. R. *Synlett.* **2015**, *26*, 335.

(C), 135.9 (C), 130.8 (C), 128.7 (CH), 128.6 (CH), 126.4 (CH), 121.1 (CH), 119.9 (q, J = 323.4 Hz, C), 118.1 (CH_2), 24.5 (CH_3). **LRMS** (m/z, EI): 132 [$(M\text{-}Tf)^+$,(100], 130 (28), 117 (53). **HRMS** calculated for $C_9H_{10}N$: 132.0813, found 132.0814.

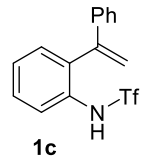
1,1,1-trifluoro-*N*-(2-(3-methylbut-1-en-2-yl)phenyl)methanesulfonamide (**1b**): (615 mg, 76% yield),



1b

white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.61 (d, J = 8.2 Hz, 1H), 7.37 – 7.08 (m, 4H), 5.44 (s, 1H), 5.04 (s, 1H), 2.68 – 2.43 (m, 1H), 1.12 (d, J = 1.7 Hz, 3H), 1.10 (d, J = 1.7 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 152.3 (C), 134.6 (C), 131.9 (C), 129.2 (CH), 128.5 (CH), 125.6 (CH), 119.8 (q, J = 322.8 Hz, C), 119.4 (CH), 115.1 (CH_2), 35.3 (CH), 21.1 (CH_3). **LRMS** (m/z, ESI): $[(M\text{-}H]^{-1}$: 292 (100)

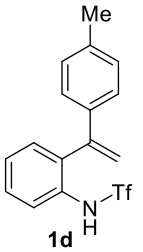
1,1,1-trifluoro-*N*-(2-(1-phenylvinyl)phenyl)methanesulfonamide (**1c**): (620 mg, 85% yield), white



1c

solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.61 (d, J = 8.0 Hz, 1H), 7.53 – 7.26 (m, 8H), 6.47 (brs, 1H), 5.96 (s, 1H), 5.42 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 145.5 (C), 138.7 (C), 135.3 (C), 132.2 (C), 131.2 (CH), 129.5 (CH), 129.4 (CH), 129.3 (CH), 127.3 (CH), 126.7 (CH), 123.0 (CH), 119.7 (q, J = 323.5 Hz, C), 118.3 (CH_2).**LRMS** (m/z, EI): 194 [(M-Tf,100)], 193 (31),165(16).. **HRMS** calculated for $C_{14}H_{12}N$: 194.0970, found 194.0964.

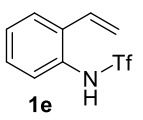
1,1,1-trifluoro-*N*-(2-(1-(p-tolyl)vinyl)phenyl)methanesulfonamide(**1d**): (1.2 g, 87% yield), yellow



1d

liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.58 (d, J = 8.0 Hz, 1H), 7.46 – 7.28 (m, 3H), 7.17 (s, 4H), 6.48 (brs, 1H), 5.88 (s, 1H), 5.33 (s, 1H), 2.37 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 145.3 (C), 139.4 (C), 135.9 (C), 135.6 (C), 132.1 (C), 131.2 (CH), 130.1 (CH), 129.4 (CH), 127.2 (CH), 126.6 (CH), 123.0 (CH), 119.8 (q, J = 323.4 Hz, C), 117.3 (CH_2), 21.2 (CH_3). **HRMS** [ESI] calculated for $C_{16}H_{15}NO_2F_3S$: 342.0770, found 342.0773.

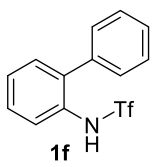
1,1,1-trifluoro-*N*-(2-vinylphenyl)methanesulfonamide(**1e**): (1.439 g, 59% yield), pale yellow solid. **^{1}H**



1e

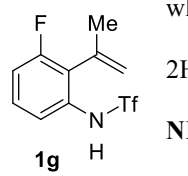
NMR (300 MHz, $CDCl_3$) δ (ppm): 7.49 – 7.37 (m, 1H), 7.35 – 7.10 (m, 3H), 6.79 (dd, J = 17.3, 11.1 Hz, 1H), 6.59 (brs, 1H), 5.63 (d, J = 17.4 Hz, 1H), 5.37 (d, J = 11.0 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 134.4 (C), 131.1 (CH), 130.8 (C), 129.2 (CH), 128.7 (CH), 127.3 (CH), 126.5 (CH), 119.9 (q, J = 322.9 Hz, C), 119.6 (CH_2). **LRMS** (m/z, EI): 251 (9), 118 (100). **HRMS** calculated for $C_9H_8NO_2F_3S$: 251.0228, found 251.0223

***N*-([1,1'-biphenyl]-2-yl)-1,1,1-trifluoromethanesulfonamide** (**1f**): (1.188g, 85% yield), white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.74 – 7.70 (m, 1H), 7.61 – 7.55 (m, 2H), 7.55 – 7.50 (m, 1H), 7.50 – 7.44 (m, 1H), 7.43 – 7.36 (m, 4H), 6.79 (brs, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 137.0 (C), 135.1 (C), 131.8 (C), 131.0 (CH), 129.6 (CH), 129.3 (CH), 129.2 (CH), 128.9 (CH), 126.8 (CH), 121.8 (CH), 119.7 (q, *J* = 323.2 Hz, C). **LRMS** (m/z, EI): 301 (31), 168 (100), 167 (47). **HRMS** calculated for $C_{13}H_{10}NO_2SF_3$: 301.0384, found 301.0394.



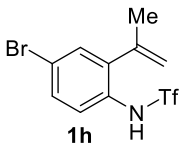
1f

1,1,1-trifluoro-*N*-(3-fluoro-2-(prop-1-en-2-yl)phenyl)methanesulfonamide (**1g**):(468 mg, 69 % yield), white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.46 - 7.39 (m, 1H), 7.31 - 7.21 (m, 2H), 7.02 – 6.90 (m, 1H), 5.59 – 5.56 (s, 1H), 5.09 (s, 1H), 2.06 (d, *J* = 14.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 159.7 (d, *J*=246.6 Hz, C), 137.1 (C), 132.5 (C), 123.9 (CH), 123.8 (d, *J*= 21.1 Hz, C), 120.0 (CH_2), 119.6 (q, J= 322.6 Hz, C) 116.1 (CH), 113.5 (CH), 113.2 (CH), 23.3 (CH_3).**LRMS** (m/z, ESI): 282 [$(M-1)^-$]. **HRMS** calculated for $C_{10}H_8NO_2F_4S$: 282.0216, found 282.0217.



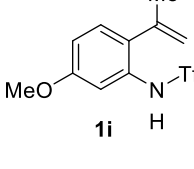
1g

***N*-(4-bromo-2-(prop-1-en-2-yl)phenyl)-1,1,1-trifluoromethanesulfonamide** (**1h**): (390 mg, 62%) yield, yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.50 – 7.33 (m, 3H), 7.13 (brs, 1H), 5.48 (s, 1H), 5.03 (s, 1H), 2.08 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 141.0 (C), 137.8 (C), 131.7 (CH), 131.6 (CH), 130.0 (C), 122.8 (CH), 119.8 (C), 119.8 (q, *J* = 323.4 Hz, C), 119.1 (CH_2), 24.3 (CH_3). **LRMS** (m/z, EI): 209 (100), 131 (100), 130 (68). **HRMS** calculated for $C_{10}H_9NO_2F_3SBr$: 342.9489, found 342.9485.



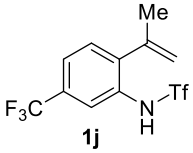
1h

1,1,1-trifluoro-*N*-(5-methoxy-2-(prop-1-en-2-yl)phenyl)methanesulfonamide (**1i**): (730 mg, 53% yield), brown liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.41 (d, *J* = 8.8 Hz, 1H), 7.12 (s, 1H), 6.83-6.78 (m, 1H), 6.78 – 6.73 (m, 1H), 5.38 (s, *J* = 1.0 Hz, 1H), 4.98 (s, 1H), 3.80 (d, *J* = 0.4 Hz, 3H), 2.08 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 158.4 (C), 142.0 (C), 140.1 (C), 126.0 (CH), 124.1 (q, J=322.7 Hz, C), 122.9 (C), 117.6 (CH_2), 114.2 (CH), 113.4 (CH), 55.5 (CH_3), 24.2 (CH_3).**LRMS** (m/z, EI): 295 (21), 162 (100), 147 (66). **HRMS** calculated for $C_{11}H_{12}NO_3F_3S$: 295.0490, found 295.0490.



1i

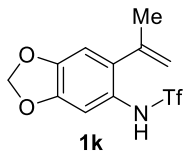
1,1,1-trifluoro-*N*-(2-(prop-1-en-2-yl)-5-(trifluoromethyl)phenyl)methanesulfonamide (**1j**): (810 mg, 56% yield, white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.86 (s, 1H), 7.54 – 7.27 (m, 3H), 5.56 – 5.49 (m, 1H), 5.10 – 5.03 (m, 1H), 2.16 – 2.04 (m, 3H). **^{13}C**



1j

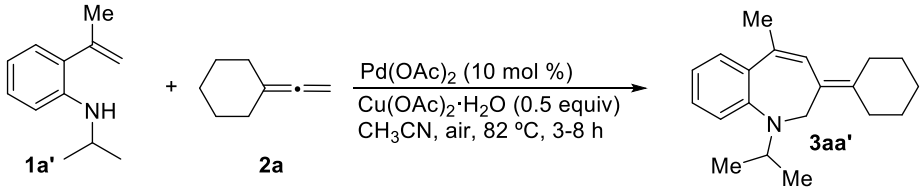
NMR (75 MHz, $CDCl_3$) δ (ppm) 141.1 (C), 139.2 (C) 131.6 (C), 131.1 (q, *J* = 33.2 Hz, C), 129.4 (CH), 123.1 (q, *J* = 3.7 Hz, CH), 119.8 (q, *J* = 323.0 Hz, C) 119.3 (CH_2), 117.9 (q, *J* = 3.8 Hz, CH) 24.2 (CH_3). **LRMS** (m/z, EI): 200 [$(M\text{-}Tf)^+$,100], 198 (27), 180 (25). **HRMS** calculated for $C_{10}H_9NF_3$: 200.0687, found 200.0696.

1,1,1-trifluoro-*N*-(6-(prop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)methanesulfonamide (**1k**): (735 mg, 62% yield), white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.03 (s, 1H), 6.98 (s, 1H), 6.59 (s, 1H), 5.92 (s, 2H), 5.33 (s, 1H), 4.89 (s, 1H), 1.97 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 147.4 (C), 146.4 (C), 142.1 (C), 131.0 (C), 123.8 (C), 119.7 (q, *J* = 321.0 Hz, C), 117.9 (CH), 107.9 (CH_2), 104.1 (CH_2), 102.0 (CH), 24.4 (CH_3).**LRMS** (m/z, ESI):308 [$(M\text{-}1)^-$].). **HRMS** calculated for $C_{11}H_9NO_4F_3S$: 308.0209, found 308.0210.



1k

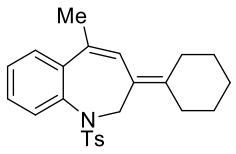
GENERAL PROCEDURE: Pd-catalyzed annulation to give benzazepines 3aa', 3aa'' and 3aa'''. Exemplified for 3aa'.



To a solution of $Pd(OAc)_2$ (2.1 mg, 10 mol %), $Cu(OAc)_2{\bullet}H_2O$ (18.8 mg, 0.5 equiv) and *o*-alkenylaniline**1a'**(33 mg, 0.188 mmol)in CH_3CN (2 mL) under air atmosphere in a Schlenktube was added the allene**2a** (0.188 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 82 °C, stirred until completion followed by TLC and then cooled to room temperature. The mixture was diluted with diethyl ether and adsorbed into a small amount of silica gel, removing the remaining solvents in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes/DCM; 95:5) to yield 53 mg of **3-cyclohexylidene-1-isopropyl-5-methyl-2,3-dihydro-*1H*-benzo[*b*]azepine** (**3aa'**): (23.8 mg, 58% yield, white solid). **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.47 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H),6.96 (s, 1H), 6.94 – 6.82 (m, 2H), 4.01– 3.93 (m, 1H), 3.61 (s, 2H), 2.50 – 2.27 (m, 7H), 1.65 – 1.55 (m, 6H), 1.25 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 152.5 (C), 134.8 (C), 130.5 (C), 130.4 (C), 129.9 (CH), 129.4 (C) 127.9 (CH), 126.7 (CH), 119.0 (CH), 116.3 (CH), 50.7 (CH_2), 45.9

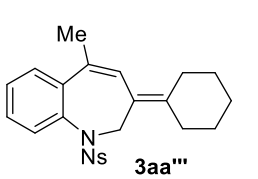
(CH), 30.9 (CH_2), 30.7 (CH_2), 29.1 (CH_3), 28.2 (CH_2), 27.1 (CH_2), 20.7 (CH_3).**LRMS** (m/z, EI): 281 (100), 266 (98), 252 (46).**HRMS** calculated for $C_{20}H_{27}N$: 281.2144, found 281.2137.

3-cyclohexylidene-5-methyl-1-tosyl-2,3-dihydro-*1H*-benzo[*b*]azepine (3aa''): (32 mg, 43% yield, white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.62 – 7.56 (m, 1H), 7.34 – 7.23 (m, 5H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.16 (s, 1H), 2.44 – 2.20 (m, 7H),1.89 – 1.55 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 142.8 (C), 142.0 (C), 139.6 (C), 138.1 (C), 137.5 (C), 130.3 (CH), 128.6 (CH), 128.5 (CH), 128.3 (C), 127.9 (CH), 127.6 (CH), 127.6 (CH), 127.4 (CH), 124.9 (C), 51.9 (CH_2), 31.1 (CH_2), 30.5 (CH_2), 28.2 (CH_2), 28.0 (CH_2), 27.0 (CH_3), 26.7 (CH_2), 21.5 (CH_3). **LRMS** (m/z, EI): 393 (32), 238 (100). **HRMS** calculated for $C_{24}H_{27}NO_2S$: 393.1763, found 393.1761.



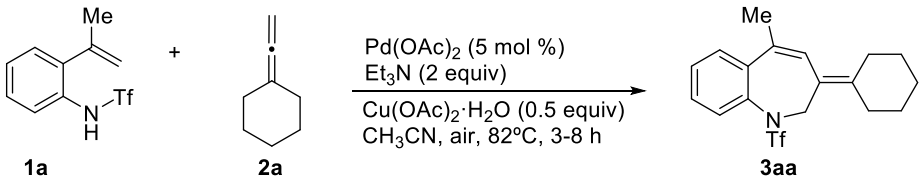
3aa''

3-cyclohexylidene-5-methyl-1-((4-nitrophenyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (3aa'''): (41.4 mg, 51% yield), yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 8.10 (d, *J* = 8.8 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.24 (m, 3H), 6.11 (s, 1H), 5.21 (brs, 1H), 3.68 (brs, 1H), 2.48-2.37 (m, 2H), 2.28-2.20 (m, 2H),1.83 – 1.54 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 149.9 (C), 146.4 (C), 143.4 (C), 138.7 (C), 136.9 (C), 130.3 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.3 (C), 128.0 (CH), 127.6 (CH), 124.2 (C), 123.1 (CH), 51.8 (CH_2), 31.2 (CH_2), 30.4 (CH_2), 28.4 (CH_2), 28.1 (CH_2), 27.1 (CH_3), 26.6 (CH_2).**LRMS** (m/z, EI): 424 (31), 238 (100). **HRMS** calculated for $C_{23}H_{24}N_2O_4S$: 424.1457, found 424.1463.



3aa'''

GENERAL PROCEDURE: Pd-catalyzed annulation to give benzazepines 3 and 6, exemplified for 3aa:

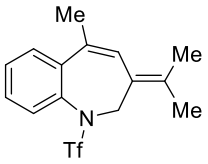


1a **2a** **3aa**

To a solution of $Pd(OAc)_2$ (1.1 mg, 5 mol%), $Cu(OAc)_2$•H_2O (18.8 mg, 0.5 equiv) and *o*-alkenylanilide **1a** (50 mg, 0.188 mmol) in CH_3CN (2 mL) under air atmosphere in a schlenk tube was added the allene **2a** (0.188 mmol) and Et_3N (52 µl, 2 equiv). 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 82 °C, stirred until completion followed by TLC and then cooled to room temperature. The mixture was diluted with diethyl ether and adsorbed into a small amount of silica gel, removing the remaining solvents in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes/DCM; 9.5:0.5) affording **3-cyclohexylidene-5-methyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine**(**3aa**), (57 mg, 82%), as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.46 – 7.32 (m, 3H), 7.30 – 7.19 (m, 1H), 6.77 (s, 1H), 5.26 (brs, 1H), 4.08 (brs, 1H), 2.40 – 2.11 (m, 7H), 1.57 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 141.5 (C), 137.3 (C), 130.2 (C), 129.1 (CH), 128.4 (CH), 128.3 (CH), 127.7 (CH), 127.6 (CH), 123.8 (C), 120.0 (q, *J* = 323.6 Hz, C), 31.1 (CH_2), 31.0 (CH_2), 28.1 (CH_2), 28.0 (CH_2), 26.7 (CH_2), 26.1 (CH_3). **LRMS** (m/z, EI): 371 (58), 238 (100). **HRMS** calculated for $C_{18}H_{20}NO_2SF_3$: 371.1167, found 371.1168.

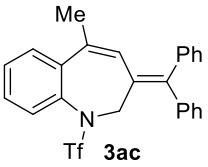
5-methyl-3-(propan-2-ylidene)-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (**3ab**):



3ab

(4.8 mg, 40% yield), transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ(ppm): 7.46-7.40 (m, 3H), 7.31- 7.25 (m, 1H), 6.69 (s, 1H), 5.16 (brs, 1H), 4.11 (brs, 1H), 2.25 (s, 3H), 1.86 (s, 3H), 1.77 (s, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm):145.0 (C), 137.3 (C), 132.6 (C), 129.8 (C), 129.2 (CH), 128.4 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 127.1 (C), 120.1 (q, *J*= 323.4 Hz, C), 26.0 (CH_2), 21.4 (CH_3), 21.1 (CH_3).**LRMS** (m/z, EI): 441 (55), 331 (42), 198 (100), 149 (50). **HRMS** calculated for $C_{15}H_{16}NO_2F_3S$: 331.0854, found 331. 0858

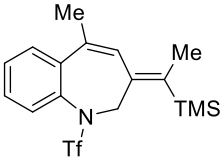
3-(diphenylmethylene)-5-methyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine



3ac

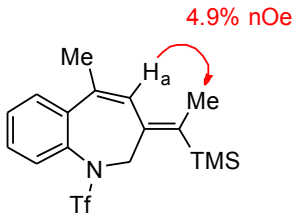
(3ac): (52.3 mg, 61 % yield), transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.50 (d, *J* = 7.5 Hz, 1H), 7.42 – 7.16 (m, 11H), 7.12 (d, *J* = 6.6 Hz, 2H), 6.69 (s, 1H), 5.11 (d, *J* = 17.2 Hz, 1H), 4.07 (d, *J* = 16.8 Hz, 1H), 2.20 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm):142.9 (C), 141.2 (C), 138.0 (C), 131.8 (C), 131.6 (C), 130.2 (CH), 129.8 (CH), 129.5 (CH), 129.0 (CH), 128.7 (CH), 128. 5 (CH), 128.3 (CH), 128.1 (CH), 127.7 (CH), 127.6 (CH), 120.0 (q, *J*=323.4 Hz, C), 56.5 (CH_2), 26.7 (CH_3). **LRMS** (m/z, IE): 455 (73), 322 (100). **HRMS** calculated for $C_{25}H_{20}NO_2F_3S$: 455.1167 found, 407.1166.

(*Z*)-5-methyl-1-((trifluoromethyl)sulfonyl)-3-(1-(trimethylsilyl)ethylidene)-2,3-dihydro-*1H*-benzo[*b*]azepine (3ad): (*Z*/ *E*= >20:1) (38.3 mg, 52% yield), transparent oil. **^{1}H NMR** (300 MHz, $CDCl_2$) δ (ppm: 7.45 – 7.36 (m, 1H), 7.33 (d, *J* = 10.5 Hz, 2H),

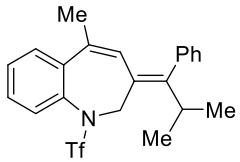


3ad

7.27 – 7.18 (m, 1H), 6.73 (s, 1H), 5.05 (d, *J* = 16.7 Hz, 1H), 4.14 (d, *J* = 16.8 Hz, 1H), 2.19 (d, *J* = 10.4 Hz, 3H), 1.79 (s, 3H), 0.11 (s, 9H).**^{13}C NMR** (75 MHz, $CDCl_2$) δ (ppm):141.7 (C), 137.2 (C), 132.5 (C), 129.7 (CH), 129.0 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 126.5 (C), 122.7 (C), 120. 5 (q, *J*=323.5 Hz, C), 60.5 (CH_2), 26.2 (CH_3), 18.7 (CH_3), 0.3 (3 x CH_3). **LRMS** (m/z, IE): 389 (39), 84 (57), 73 (100). **HRMS** calculated for $C_{17}H_{22}NO_3F_3SSi$: 389.1093 found, 389.1088.The major regioisomer was assigned based by the observation of nOe between the H_a and the methyl.

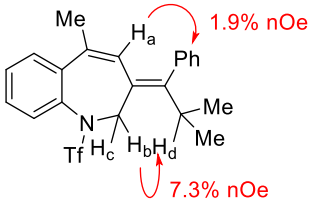


(*E*)-5-methyl-3-(1-phenylethylidene)-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine



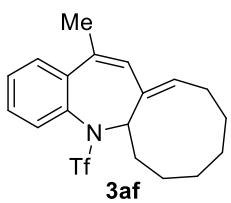
3ae

(3ae): (*Z*/*E*=6.5:1, inseparable mixture): (65.8 mg, 83% yield), transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.52 – 7.20 (m, 8.22H), 7.10 – 6.96 (m, 1.75H), 6.91 (s, 0.14H), 6.10 (s, 0.86H), 5.49 (d, *J* = 16.1 Hz, 0.86H), 4.56 (d, *J* = 17.2 Hz, 0.14H), 4.10 (d, *J* = 16.1 Hz, 0.86H), 3.80 (d, *J* = 16.5 Hz, 0.14H), 3.35 – 3.21 (m, 0.14H), 3.09 – 2.97 (m, 0.86H), 2.33 (s, 0.40H), 2.00 (s, 2.60H), 1.07 – 0.79 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$, *major isomer*) δ (ppm): 148.1 (C), 138.8 (C), 137.6 (C), 130.5 (CH), 129.6 (CH), 129.3 (C), 129.1 (C), 129.0 (C), 128.7 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.1 (CH), 126.9 (CH), 126.6 (CH), 120.0 (q, *J*=323.5 Hz, C), 54.4 (CH_2), 30.4 (CH_3), 26.6 (CH_3), 21.9 (CH_3), 21.2 (CH_3).**LRMS**(m/z, ESI): $[(M+Na]^+$:444.). **HRMS** calculated for $C_{22}H_{23}NO_2F_3S$: 422.1395, found 422.1396.



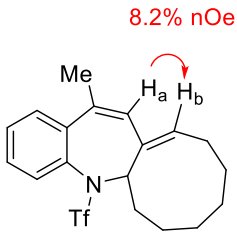
The major regioisomer was assigned based by the observation of nOe between the H_a and the phenyl group, and H_b with H_d

(*Z*)-13-methyl-5-((trifluoromethyl)sulfonyl)-5a,6,7,8,9,10-hexahydro-*5H*-benzo[*b*]cycloocta[*f*]azepine (3af): (43.4 mg**,** 62% yield, white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.48 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.32 – 7.24 (m, 1H), 6.38 (s, 1H), 5.89 – 5.80 (m, 1H), 5.49 – 5.40 (m, 1H), 2.42 – 2.34 (m, 1H), 2.26 (s, 3H), 2.24 – 2.19 (m, 1H), 1.88 – 1.79 (m, 1H), 1.70 – 1.65 (m, 1H), 1.49 – 1.30 (m, 5H), 1.09 – 1.04 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 138.4 (C),

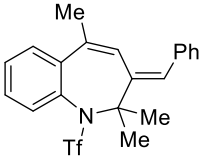


3af

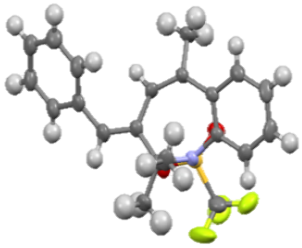
137.8 (C), 135.8 (CH), 133.2 (C), 133.1 (CH), 130.9 (C), 128.8 (CH), 128.1 (CH), 127.5 (CH), 127.3 (CH), 120.1 (q, *J*=324.5 Hz, C), 59.4 (CH_2), 31.9 (CH_2), 27.8 (CH_2), 26.6 (CH_2), 26.3 (CH_3), 25.6 (CH_2), 22.8 (CH_2), 22.7 (CH_2).**LRMS** (m/z, EI): 386 (50), 385 (29), 252 (100).). **HRMS** calculated for $C_{19}H_{23}NO_2F_3S$: 386.1402, found 386.1403. Assignment of stereochemistry based on the HMBC, HSQC, COSY experiments and the observed nOe between the H_a with H_b.



(*E*)-3-benzylidene-2,2,5-trimethyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (6ag): (53.6 mg. 70**%** yield, transparent oil.

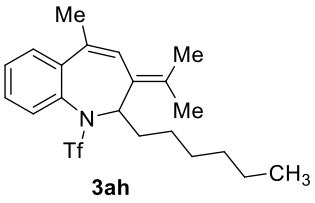


6ag

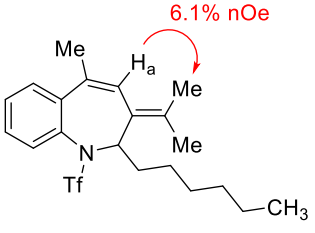


^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.50 – 7.47 (m, 1H), 7.45- 7.41 (m, 1H), 7.39 – 7.34 (m, 2H), 7.33 – 7.26 (m, 5H), 6.79 (s, 1H), 6.55 (s, 1H), 2.28 (d, *J* = 1.2 Hz, 3H), 2.06 (s, 3H), 1.12 (s, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 145.0 (C), 141.1 (C), 137.0 (C), 136.5 (C), 133.1 (C), 130.0 (CH), 129.9 (CH), 129.3 (CH), 128.3 (CH), 128.0 (CH), 127.4 (CH), 127.4 (CH), 127.2 (CH), 126.7 (CH), 117.5 (C), 71.3 (C), 32.8 (CH_3), 28.0 (CH_3), 25.7 (CH_3). **LRMS** (m/z, IE): 407 (77), 274 (100), 273 (38), **HRMS** calculated for $C_{21}H_{20}NO_2F_3S$: 407.1167, found 407.1167. The stereochemistry of **(6ag)** was confirmed by X Ray.

2-hexyl-5-methyl-3-(propan-2-ylidene)-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (3ah): (1:1.1 *r.r* of **3ah** and **6ah**, (42.8 mg, 56% yield) transparent oil). A small fraction of **3ah** was separated from the mixture for characterization. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.47 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.30 – 7.23 (m, 1H), 6.75 (s, 1H), 5.26 (s, 1H), 2.28 (s, 3H), 1.94 (s, 3H), 1.87 (d, *J* = 11.7 Hz, 3H), 1.34 – 0.99 (m, 10H), 0.83 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$)δ (ppm): 138.6 (C), 133.3 (C), 132.8 (C), 132.6 (C), 130.5 (CH), 128.9 (CH), 128.1 (CH), 127.4 (CH), 127.3 (CH), 127.0 (C), 120.2 (C, q, *J*=324.4 Hz), 62.3 (CH), 32.9 (CH_3), 31.6 (CH_2), 28.7 (CH_2), 27.2 (CH_2), 26.0 (CH_2), 22.6 (CH_3), 21.7 (CH_3), 21.4 (CH_2), 14.1 (CH_3). **LRMS** (m/z, IE): 415 (7), 282 (100). **HRMS** calculated for $C_{21}H_{28}NO_2F_3S$: 415. 1793 found, 415.1796.

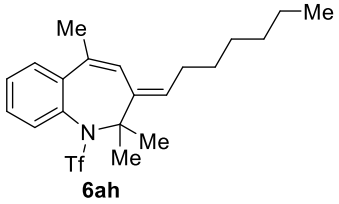


3ah



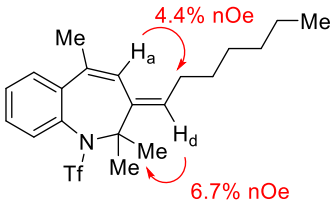
Sterereochemistry **3a** was assigned based by the observation of nOe between the H_a and the methyl group.

(*E*)-3-heptylidene-2,2,5-trimethyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine



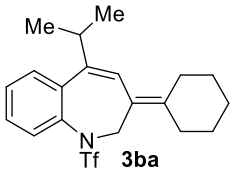
6ah

(6ah): A small fraction of **6ah** was separated for characterization (yellow liquid). yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.46 – 7.43 (m, 1H), 7.41 – 7.35 (m, 1H), 7.27 – 7.22 (m, 2H), 6.67 (s, 1H), 5.47 (t, *J* = 7.4 Hz, 1H), 2.32 (d, *J* = 1.2 Hz, 3H), 2.29 – 2.19 (m, 1H), 2.16 – 2.07 (m, 1H), 1.90 (s, 3H), 1.45 – 1.32 (m, 2H), 1.30 – 1.22 (m, 6H), 1.01 (s, 3H), 0.88 (t, *J* = 4.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 143.1 (C), 140.9 (C), 136.4 (C), 131.3 (C), 130.1 (CH), 128.6 (CH), 128.6 (CH), 127.6 (CH), 127.3 (CH), 126.0 (CH), 119.6 (q, *J*=323.4 Hz, C), 70.9 (C), 32.2 (CH_2), 31.8 (CH_2), 29.6 (CH_2), 29.0 (CH_3), 28.2 (CH_3), 27.7 (CH_2), 25.6 (CH_2), 22.7 (CH_3), 14.2 (CH_3). **LRMS** (m/z, IE): 415 (7), 282 (100). **HRMS** calculated for $C_{21}H_{28}NO_2F_3S$: 415. 1793 found, 415.1796.



The double bond configuration was assigned based by the observation of nOe between H_a and the CH_2, and between H_b and the methyl group.

3-cyclohexylidene-5-isopropyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (3ba):

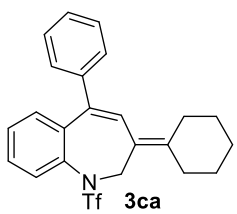


3ba

(67.8 mg, 90% yield), transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.46 – 7.22 (m, 4H), 6.57 (s, 1H), 5.06 (d, *J* = 15.4 Hz, 1H), 4.31 (d, *J* = 15.8 Hz, 1H), 2.93 (dt, *J* = 13.4, 6.7 Hz, 1H), 2.35 – 1.99 (m, 4H), 1.65 – 1.00 (m, 12H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 142.8 (C), 140.1 (C), 137.5 (C), 129.4 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 124.6 (C), 124.5 (CH), 123.0 (C), 120.0 (q, *J* = 322.6 Hz, C) 59.1 (CH_2), 34.1 (CH), 31.5 (CH_2), 30.6 (CH_2), 27.8 (CH_2), 27.7 (CH_2), 26.5 (CH_2), 23.4 (CH_3), 22.5 (CH_3).**LRMS** (m/z, EI): 399 (88), 356 (17), 266 (100). **HRMS** calculated for $C_{20}H_{24}NO_2F_3S$: 399.1480, found 399.1493.

3-cyclohexylidene-5-phenyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (3ca):

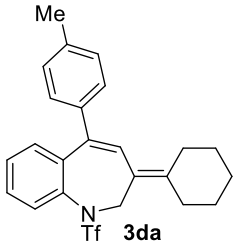
(83.4 mg, 79% yield), white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.47 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.18 (m, 7H), 7.06 – 7.01 (m, 1H), 6.98 (s, 1H), 5.33 (s, 1H), 4.15 (brs, 1H), 2.34 (m, 4H), 1.72-1.49 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 145.2 (C), 143.8 (C), 138.5 (C), 136.8 (C), 131.8 (CH), 129.5 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.3 (CH), 124.0 (C), 119.9 (q, *J* =



3ca

323.6 Hz, C), 57.9 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 28.2 (CH_2), 28.1 (CH_2), 26.6 (CH_2). **LRMS** (m/z, EI): 433 (8), 299 (80), 217 (100). **HRMS** calculated for $C_{23}H_{22}NO_2SF_3$: 433.1393, found 433.1396.

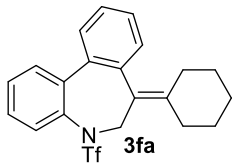
3-cyclohexylidene-5-(p-tolyl)-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (3da):



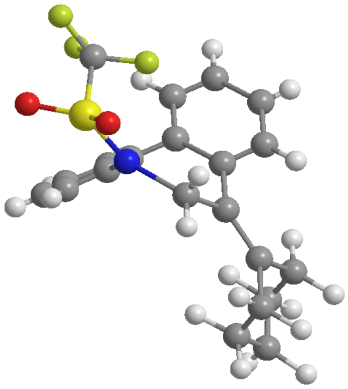
3da

(52.3mg, 62% yield), white solid.**^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.6 Hz, 1H), 7.40-7.22 (m, 6H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 5.41 (brs, 1H), 4.24 (brs, 1H), 2.60 – 2.24 (m, 7H), 1.76-1.60 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 143.7 (C), 143.6 (C), 142.4 (C), 138.5 (C), 137.3 (C), 136.8 (C), 132.0 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.6 (CH), 128.2 (CH), 124.1 (C), 120.0 (q, *J* = 323.5 Hz, C),56.7 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 28.2 (CH_2), 28.1 (CH_2), 26.6 (CH_2), 21.3 (CH_3). **LRMS** (m/z, EI): 447 (77), 314(100). **HRMS** calculated for $C_{24}H_{24}NO_2F_3S$: 447.1480, found 447.1481.

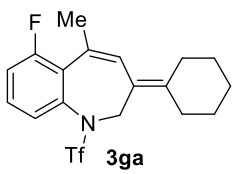
6-cyclohexylidene-5-((trifluoromethyl)sulfonyl)-6,7-dihydro-*5H*-dibenzo[*b,d*]azepine (3fa): (56.8 mg, 70% yield), white solid. **^{1}H NMR** (250 MHz, $CDCl_3$) δ (ppm): 7.55 – 7.32 (m, 6H), 7.26 – 7.15 (m, 2H), 4.93 (d, *J* = 13.8 Hz, 1H), 4.82 (d, *J* = 13.6 Hz, 1H), 2.30 – 2.01 (m, 2H), 1.92 – 1.65 (m, 2H), 1.58 – 1.29 (m, 4H), 1.27 – 0.91 (m, 2H).**^{13}C RMN** (75 MHz, $CDCl_3$) δ (ppm): 143.1 (C), 138.8 (C), 138.5 (C), 134.7 (C), 130.2 (CH), 130.0 (CH), 129.5 (CH), 129.3 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.3 (CH), 124.1 (C), 121.9 (C), 119.9 (q, *J* = 323.8 Hz, C), 60.2 (CH_2), 32.6 (CH_2), 30.4 (CH_2), 28.3 (CH_2), 26.4(CH_2). **LRMS** (m/z, EI): 407 (77), 274 (100), 273 (38). **HRMS** calculated for $C_{21}H_{20}NO_2SF_3$: 407.1167, found 407.1169. The structure of this compound was confirmed by X Ray difraction analysis.



3fa



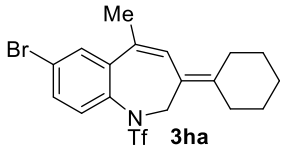
3-cyclohexylidene-6-fluoro-5-methyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (3ga): (54.4 mg, 72% yield), transparent oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.32 – 7.20 (m, 1H), 7.19 – 7.02 (m, 2H), 6.58 (s, 1H), 5.03 (d, *J* = 16.7 Hz, 1H), 4.37 (d, *J* = 16.7 Hz, 1H), 2.35 – 2.11 (m, 5H), 2.13 – 1.91 (m, 2H), 1.74 – 1.33 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 160.1 (d, *J*=251.7 Hz, C), 140.6 (C), 138.1 (C),138.0 (C), 130.5 (C), 130.2 (C), 130.0 (CH), 128.6 (d, *J*=10.1 Hz, CH), 124.5 (CH), 122.2 (C), 121.7 (q, *J*=322.9 Hz, C), 117.5 (d, *J*=23.0 Hz, CH), 59.9 (CH_2) , 31.7 (CH_2), 30.3



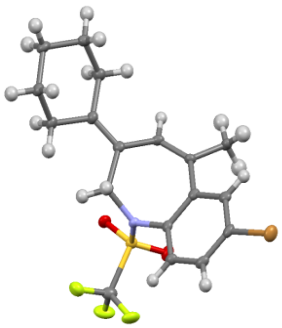
3ga

(CH_2), 27.8 (CH_2), 27.7 (CH_2), 26.4 (CH_2), 23.9 (CH_3). **LRMS** (m/z, IE): 389 (68), 256 (100). **HRMS** calculated for $C_{18}H_{19}NO_2F_4S$: 389.1073, found 389.1078.

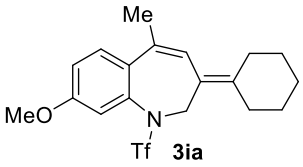
7-bromo-3-cyclohexylidene-5-methyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine(3ha): (83.3 mg, 91% yield), white solid.[1]**H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 2.2 Hz, 1H), 7.37 (ddd, *J* = 8.5, 2.2, 0.6 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.80 (s, 1H), 5.27 (brs, 1H), 4.03 (brs, 1H), 2.40 – 2.15 (m, 7H), 1.62-1.52 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 142.9 (C), 141.0 (C), 136.4 (C), 131.4 (CH), 130.6 (CH), 129.7 (CH), 129.0 (CH), 123.4 (C), 123.2 (C), 119.9 (q, *J* = 323.5 Hz, C), 56.1 (CH_2), 31.1 (CH_2), 31.1 (CH_2), 31.1 (CH_2), 28.1 (CH_2),26.6 (CH_2), 26.1 (CH_3). **LRMS** (m/z, EI): 449 (7), 316 (17), 84 (100). **HRMS** calculated for $C_{18}H_{19}NO_2F_3SBr$: 449.0272, found 449.0268. The structure of this compound was confirmed by X Ray difraction analysis.



3ha

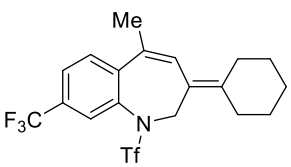


3-cyclohexylidene-8-methoxy-5-methyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (3ia): (34.5 mg, 68% yield), white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.34 – 7.24 (m, 1H), 6.91 (d, *J* = 2.9 Hz, 1H), 6.79 – 6.74 (m, 1H), 5.16 (s, 1H), 4.11 (brs, 1H), 3.82 (brs, 3H), 2.40 -2.06 (m, 7H), 1.69 - 1.45 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 159.9 (C), 141.3 (C), 130.6 (C), 130.0 (C), 129.4 (CH), 127.9 (CH), 123.7 (C), 120.1 (q, *J*=323.7Hz, C), 113.9 (CH), 112.5 (CH), 57.1 (CH_2), 55.6 (CH_3·), 31.2 (CH_2), 30.9 (CH_2), 28.0 (CH_2), 27.9 (CH_2), 26.6 (CH_2), 25.7 (CH_3). **LRMS** (m/z, IE): 401 (18), 269 (18), 268 (100), **HRMS** calculated for $C_{19}H_{22}NO_3F_3S$: 401.1273, found 401.1273.



3ia

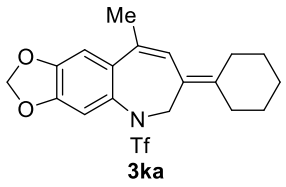
3-cyclohexylidene-5-methyl-8-(trifluoromethyl)-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[*b*]azepine (3ja): (36.2 mg, 92% yield), transparent oil.[1]**H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.71 – 7.59 (m, 2H), 7.59 – 7.48 (m, 1H), 6.89 (s, 1H), 5.30 (brs, 1H), 4.04 (brs, 1H), 2.46 – 2.12 (m, 7H), 1.74 – 0.45 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 143.6 (C), 142.5 (C), 137.7 (C), 129.9 (C, *J* = 30.0 Hz), 129.7 (CH), 129.0 (CH), 125.7 (CH), 125.4 (CH), 123.4 (C), 119.9 (q, *J*= 323.4 Hz, C), 56.0 (CH_2), 31.2(CH_2), 28.1 (CH_2), 28.1 (CH_2), 26.6 (CH_2), 26.2



3ja

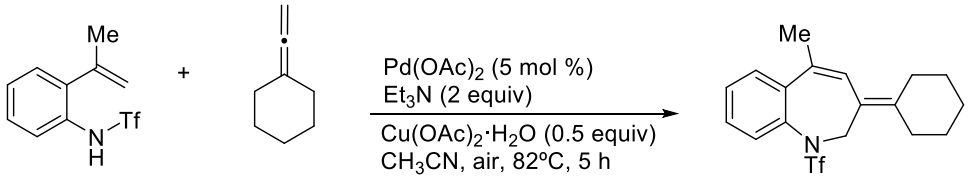
(CH_3). **LRMS** (m/z, IE): 439 (4), 306 (60), 83 (100). **HRMS** calculated for $C_{19}H_{19}NO_2F_6S$: 439.1041, found 439.1042.

7-cyclohexylidene-9-methyl-5-((trifluoromethyl)sulfonyl)-6,7-dihydro-*5H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*b*]azepine (3ka): (36 mg, 52 % yield), white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 6.85-6.80 (m, 2H), 6.64 (s, 1H), 5.99 (s, 2H), 5.16 (d, *J* = 16.7 Hz, 1H), 4.11 (d, *J* = 16.7 Hz, 1H), 2.43-2.01(m, 7H), 1.61-1.49 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 148.2 (C), 146.5 (C), 140.4 (C), 133.8 (C), 130.5 (C), 126.8 (CH), 123.3 (C), 120.0 (q, *J* = 321.8 Hz, C), 108.7 (CH), 107.1 (CH), 101.9 (CH_2), 57.4 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 27.8 (CH_2), 27.7 (CH_2), 26.4 (CH_2), 25.8 (CH_3). **HRMS** calculated for $C_{19}H_{20}F_3NO_4S$: 415.11, found (M+1): 416.1.



3ka

Pd-catalyzed annulation to give benzazepines 3aa scaled to 1 mmol.

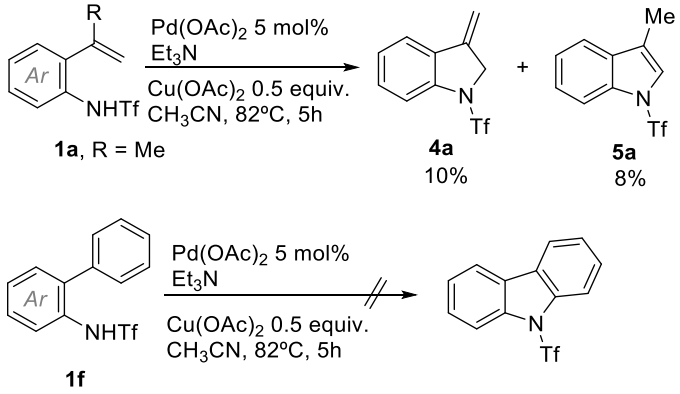


1a **2a** **3aa**

To solution of $Pd(OAc)_2$ (11 mg, 5 mol%) and $Cu(OAc)_2•H_2O$ (99.8 mg, 0.5 equiv) and **1a** (265.3 mg, 1 mmol) in CH_3CN (10.6 mL) under air atmosphere in a schlenk tube was added a solution of the allene **2a** (120.2 mg, 1 equiv) and Et_3N (0.278 mL , 2.0 equiv). 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 82 °C, stirred until completion followed by TLC and then cooled to room temperature. The mixture was diluted with diethyl ether and adsorbed into a small amount of silica gel, removing the remaining solvents *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford **3aa** as white solid (355.7 mg, 75% yield).

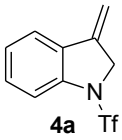
MECHANISTIC EXPERIMENTS

Treatment of 1a and 1f under reaction conditions without allene



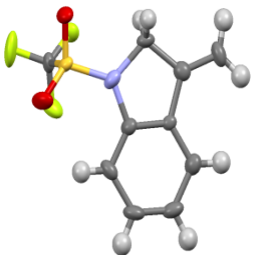
42.3 mg of Trifylanilide**1a** (0.18 mmol), 2.1 mg $Pd(OAc)_2$ (5 mol%), 18 mg $Cu(OAc)_2.H_20$ and 36.4 mg NEt_3 were mixed in a Schlenk tube, dissolved in 2 mL CH_3CN and heated for 5h hours at 82 °C under air atmosphere (balloon). Work up and flash chromatography yielded 4.2 mg of **4a** and 3.5 mg of **5a** (hexanes:DCM 95:5).

3-methylene-1-((trifluoromethyl)sulfonyl)indoline (4a)



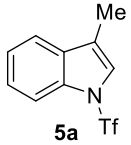
4a

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.7 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.51 (t, *J* = 3.0 Hz, 1H), 5.08 (t, *J* = 2.5 Hz, 1H), 4.72 (d, J = 2.8 Hz, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.3 (s).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.2 (C), 138.5 (C), 130.4 (CH), 129.6 (C), 125.1 (CH), 121.4 (CH), 120.3 (q, $^1J_{CF}$=323.2 Hz, C) 114.7 (CH), 103.8 (CH_2), 55.9 (CH_2). **LRMS** (m/z, IE): 263 (16), 130 (72). **HRMS** calculated for $C_{10}H_8NO_2F_3S$: 263.0228, found :263.0235.



Structure of indoline confirmed by single crystal X Ray diffraction.

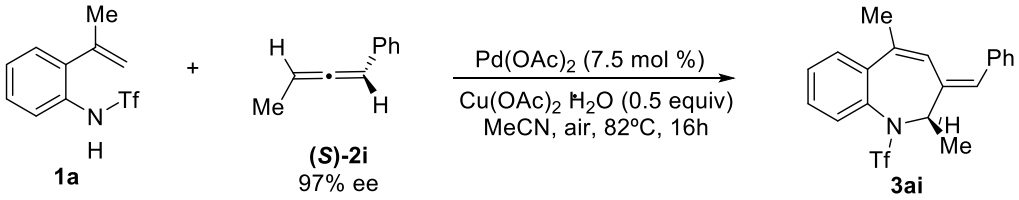
3-methyl-1-((trifluoromethyl)sulfonyl)-*1H*-indole (5a)



5a

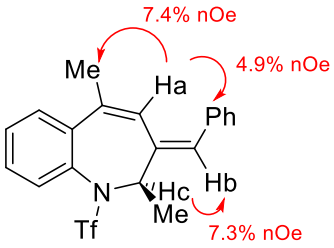
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 1H), 7.61 – 7.53 (m, 1H), 7.47 – 7.33 (m, 2H), 7.14 (d, *J* = 1.6 Hz, 1H), 2.31 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.7 (C), 132.0 (C), 125.8 (CH), 124.7 (CH), 122.7 (CH), 121.1 (C), 120.0 (CH), 119.8 (q, $^1J_{CF}$=325.1 Hz, C), 113.9 (CH), 9.7 (CH_3). **LRMS** (m/z, ESI): 131 (M+1-Tf).

Reaction with an optically active allene



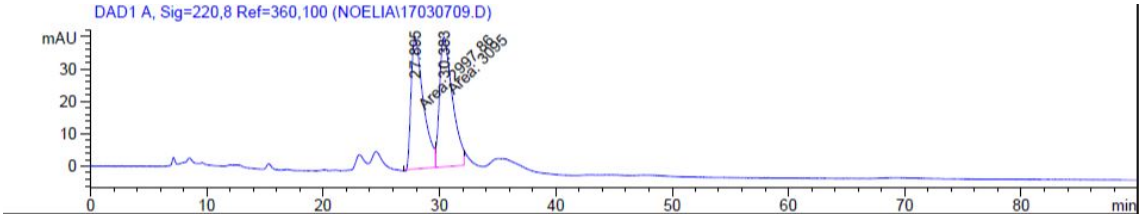
To a solution of $Pd(OAc)_2$ (3.2 mg, 7.5 mol %), $Cu(OAc)_2.H_2O$ (18.8 mg, 0.5 equiv) and o-alkenylanilide **1a** (50 mg, 0.188 mmol) in CH_3CN (2 mL) under air atmosphere in a schlenk tube was added the (*S*)-buta-1,2-dienylbenzene[5] (24.5 mg, 0.188 mmol, 97% ee). The tube was sealed with a rubber septum and an air atmosphere was injected into the flask with a balloon and a needle. The reaction was heated at 82 C, stirred until completion monitored by TLC and the cooled to room temperature. The mixture was diluted with diethyl ether and absorbed into a small amount of silica gel, removing the remaining solvents in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes/ CDM; 95:5) to afford the corresponding benzoazepine (*E*)-3-benzylidene-2,5-dimethyl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-*1H*-benzo[b]azepine (**3ai**) as yellow solid (12 mg, 16% yield, less than 14% ee). 1H NMR (300 MHz, CDCl3) δ (ppm): 7.53 – 7.27 (m, 9H), 6.81 (s, 1H), 6.48 (s, 1H), 5.23 (q, J = 7.1 Hz, 1H), 2.27 (s, 3H), 1.18 (d, J = 7.2 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ (ppm): 139.3 (C), 139.2 (C), 136.5 (C), 132.8 (C), 131.0 (C), 129.7 (CH), 129.3 (CH), 129.2 (CH), 128.5 (CH), 128.2 (CH), 128.2 (CH), 127.6 (CH), 126.4 (CH), 120.13 (q, J = 323.7 Hz, C), 64.4 (CH), 26.3 (CH3), 22.2 (CH3). LRMS (m/z, ESI): 416 (M+Na), 394 (M+1).

Assignment of stereochemistry based on the HMBC, HSQC, COSY experiments and the observed nOe between Ha and the Phenyl group.



<u>Enantioselectivity was determinated by chiral HPLC analysis on Chiralpak at rt, (100% hexane, 0.5 mL/min).</u>

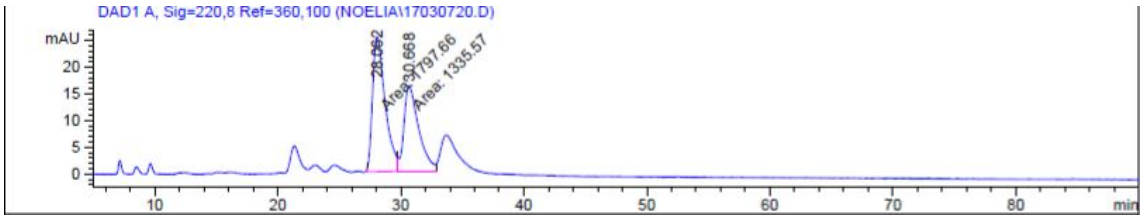
*Racemic sample **3ai** from racemic allene **2i***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.895	MM	1.2265	2997.85522	40.73639	49.2028
2	30.383	MM	1.2897	3094.99829	39.99512	50.7972

[5] This compound was prepared in two steps from commercialiable optically active alkyne (*R*)-but-3-yn-ol (99% ee) as reported by Pu, X., Ready, J.M. *J. Am. Chem. Soc*, **2008**, 130, 33, 10874-10875.

*Sample of **3ai** obtained from the reaction with chiral allene **(S)-2i***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.062	MM	1.1849	1797.66455	25.28577	57.3742
2	30.668	MM	1.3896	1335.56567	16.01805	42.6258

The enantioselectivity of allene (*S*)-2a was determinated by chiral GC analysis on Chiraldex G-TA.[6]

[6] Casanova, N.; Del Rio, P.K.; García-Fandiño, R.; Mascareñas, J.L.; Gulías, M. *ACS Catal.* **2016**, 6, 3349.

DFT CALCULATIONS

Computational methods

Gas-phase calculations were performed with Gaussian 03 and Gaussian 09 at DFT level. [M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, GAUSSIAN 09 (Revision C.01), Gaussian, Inc., Wallingford CT, 2010.] The geometries of all complexes were optimized using the B3LYP hybrid functional.[(a) P. J. Stephens, F. J. Devlin, C. F. Chabalowskiand M. J. Frisch, J. Phys. Chem.,1994, 98, 11623. (b) W. Kohn, A. D. Becke and R. G. Parr, J. Phys. Chem.,1996, 100, 12974. (c) P. J. Hay and W. R. Wadt, J. Chem.Phys., 1985, 82, 270. (d) P. J. Hay and W. R. Wadt, J. Chem.Phys., 1985, 82, 284. (e) P. J. Hay and W. R. Wadt, J. Chem. Phys., 1985, 82, 299] Optimizations were carried out using the standard 6-31G(d) basis set for C, H, O, N, S, F. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt, and employs a split valence (double-zeta) basis set, was used for Pd. [(a) A. D. Becke, J. Chem. Phys., 1993, 98, 5648. (b) A. D. Becke, Phys. Rev. A, 1988, 38,3098. (c) C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785.] Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies (ZPE). The starting approximate geometries for the transition states (TS) were located graphically. Intrinsic reaction coordinate (IRC) studies were performed in ambiguous cases to confirm the relation of the transition states with the corresponding minima. Single-point calculations were performed using the hybrid functional of Truhlar and Zhao M06, [Zhao, Y.; Truhlar, D. G. Theor. Chem. Acc., 2008, 120, 215-41.], 6-311+G(2df,2p) basis set for C, H, O, N, S and F. For Pd, the Stuttgart-Dresden (SDD) ECP was utilised. [Dolg, M.; Wedig, U; Stoll, H.; Preuss, H. J. Chem. Phys.1987, 86, 866] Electronic energy values calculated with the smaller basis set have been corrected using the residual energy at the zero point vibrational energy (ZPE). The evaluation of enthalpy (H) and Gibbs free energy (G) implies the use of the harmonic-oscillator/rigid rotor approximation, which introduces some uncertainty in the calculation of the vibrational entropy. To obtain solvation-corrected relative free-energies, we employed a self-consistent reaction field (SCRF) method using the SMD model [Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. J. Phys. Chem. B 2009, 113, 6378.] to do single-point calculations for all the species studied. Acetonitrile (ε=35.688) was employed as the solvent, corresponding to the experimental conditions.

Atomic Cartesian coordinates and computed energies (atomic units) for the stationary points calculated with basis set [B3LYP/6-31G(d) (C, H, O, N, S, F) and LANL2DZ (Pd)]

INTERMEDIATE I

Zero-point correction= 0.271055 (Hartree/Particle)
Thermal correction to Energy= 0.292447
Thermal correction to Enthalpy= 0.293392
Thermal correction to Gibbs Free Energy= 0.217187
Sum of electronic and zero-point Energies= -1007.662874
Sum of electronic and thermal Energies= -1007.641482
Sum of electronic and thermal Enthalpies= -1007.640538
Sum of electronic and thermal Free Energies= -1007.716742
HF (B3LYP/6-31G(d) and LANL2DZ)= -1007.9339294
HF (M06/6-311+G(2df,2p) and SDD)= -1008.7880074
HF (M06/6-311+G(2df,2p) and SDD, SMD[acetonitrile])= -1008.8146487

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.439820	0.059946	-0.275760
2	8	0	-1.233349	1.158604	-0.695803
3	6	0	-2.432824	0.749152	-0.461442
4	6	0	-2.724996	-0.448854	0.308478
5	6	0	-3.529939	1.570757	-0.864743
6	6	0	-4.035093	-0.608977	0.849536
7	6	0	-4.789567	1.340014	-0.362165
8	6	0	-5.050788	0.255945	0.517569
9	6	0	-1.743024	-1.467793	0.412107
10	6	0	-0.718875	-1.620817	-0.579589
11	6	0	-1.805559	-2.498167	1.509482
12	1	0	-3.312317	2.424887	-1.497645
13	1	0	-4.245653	-1.471858	1.474007
14	1	0	-5.600723	2.013179	-0.629093
15	1	0	-6.054245	0.098265	0.900181
16	1	0	-0.088504	-2.501307	-0.500577
17	1	0	-2.333475	-3.394774	1.155788
18	1	0	-0.790624	-2.812994	1.771724
19	1	0	-2.307699	-2.134635	2.409074
20	8	0	2.153669	-0.921810	0.326006
21	8	0	2.177759	-2.378532	-1.400546
22	6	0	2.697983	-1.880179	-0.415198
23	6	0	4.060776	-2.320102	0.106601
24	1	0	3.977696	-2.659125	1.144839
25	1	0	4.452962	-3.125863	-0.515998
26	1	0	4.760864	-1.476622	0.095409
27	1	0	-1.008640	-1.397306	-1.610042
28	8	0	1.555064	1.987769	-0.076216
29	8	0	3.408249	1.238174	0.975709
30	6	0	2.646223	2.184258	0.472500
31	6	0	3.215728	3.571560	0.618751
32	1	0	2.982239	0.328381	0.800512
33	1	0	3.405363	3.781215	1.676570

34	1	0	4.176813	3.630254	0.097048
35	1	0	2.522800	4.306358	0.208664

TS1

Zero-point correction= 0.266815 (Hartree/Particle)
Thermal correction to Energy= 0.287560
Thermal correction to Enthalpy= 0.288504
Thermal correction to Gibbs Free Energy= 0.214317
Sum of electronic and zero-point Energies= -1007.641394
Sum of electronic and thermal Energies= -1007.620649
Sum of electronic and thermal Enthalpies= -1007.619705
Sum of electronic and thermal Free Energies= -1007.693892
HF (B3LYP/6-31G(d) and LANL2DZ)= -1007.9082088
HF (M06/6-311+G(2df,2p) and SDD)= -1008.7623146
HF (M06/6-311+G(2df,2p) and SDD, SMD[acetonitrile])= -1008.7869639

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-0.536023	0.114824	-0.413870
2	8	0	0.981306	1.397089	-0.453740
3	6	0	2.170450	1.116044	0.005150
4	6	0	2.792431	-0.183340	-0.043001
5	6	0	2.928495	2.206053	0.524662
6	6	0	4.139122	-0.300920	0.400428
7	6	0	4.226827	2.038972	0.955180
8	6	0	4.847213	0.772073	0.898448
9	6	0	2.094389	-1.309710	-0.610107
10	6	0	0.715145	-1.402034	-0.738937
11	6	0	2.912912	-2.498337	-1.082869
12	1	0	2.439690	3.174838	0.553360
13	1	0	4.619940	-1.273308	0.361687
14	1	0	4.777541	2.893064	1.342607
15	1	0	5.867915	0.643808	1.246019
16	1	0	0.362217	-2.103374	-1.504826
17	1	0	3.374779	-3.017448	-0.233519
18	1	0	2.287519	-3.223201	-1.609556
19	1	0	3.723659	-2.182197	-1.748909
20	8	0	-2.164286	-1.250646	-0.092615
21	8	0	-0.797177	-2.704387	0.943007
22	6	0	-1.954126	-2.269835	0.643733
23	6	0	-3.153342	-3.011323	1.186201
24	1	0	-3.781856	-3.342803	0.353123
25	1	0	-2.841057	-3.869914	1.781328
26	1	0	-3.754285	-2.332400	1.800902
27	1	0	0.064724	-2.043549	0.320176
28	8	0	-1.986618	1.851243	-0.118130

29	8	0	-3.958273	0.755703	0.044776
30	6	0	-3.210370	1.851654	-0.000999
31	6	0	-4.014569	3.120682	0.101569
32	1	0	-3.379009	-0.051705	-0.022703
33	1	0	-4.716636	3.178592	-0.737086
34	1	0	-4.606524	3.112374	1.022557
35	1	0	-3.348643	3.983432	0.089713

INTERMEDIATE II

Zero-point correction= 0.271981 (Hartree/Particle)
Thermal correction to Energy= 0.293218
Thermal correction to Enthalpy= 0.294162
Thermal correction to Gibbs Free Energy= 0.218605
Sum of electronic and zero-point Energies= -1007.643427
Sum of electronic and thermal Energies= -1007.622190
Sum of electronic and thermal Enthalpies= -1007.621246
Sum of electronic and thermal Free Energies= -1007.696803
HF (B3LYP/6-31G(d) and LANL2DZ)= -1007.9154083
HF (M06/6-311+G(2df,2p) and SDD)= -1008.7728101
HF (M06/6-311+G(2df,2p) and SDD, SMD[acetonitrile])= -1008.8026731

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.493619	-0.104291	-0.282340
2	8	0	-1.022261	-1.359293	-0.237520
3	6	0	-2.271952	-1.052498	0.054954
4	6	0	-2.858992	0.243678	-0.089884
5	6	0	-3.085760	-2.120698	0.510286
6	6	0	-4.231143	0.390012	0.216931
7	6	0	-4.425874	-1.934131	0.802319
8	6	0	-5.011823	-0.667048	0.659117
9	6	0	-2.072468	1.371676	-0.591150
10	6	0	-0.720488	1.375711	-0.705474
11	6	0	-2.822329	2.620789	-1.028632
12	1	0	-2.614833	-3.093840	0.611602
13	1	0	-4.692706	1.366229	0.106856
14	1	0	-5.022329	-2.776119	1.146396
15	1	0	-6.061669	-0.512723	0.891280
16	1	0	-0.243249	2.190837	-1.258891
17	1	0	-3.335993	3.098032	-0.184451
18	1	0	-2.140375	3.358561	-1.460924
19	1	0	-3.587128	2.380306	-1.776982
20	8	0	2.255844	1.198120	-0.128536
21	8	0	1.142882	2.724549	1.090580
22	6	0	2.240404	2.220136	0.584247
23	6	0	3.489884	2.985933	0.909901

24	1	0	3.512501	3.902008	0.308177
25	1	0	3.484460	3.282120	1.962177
26	1	0	4.373304	2.387722	0.683787
27	1	0	0.349986	2.187977	0.770125
28	8	0	1.936551	-1.886378	0.082606
29	8	0	3.968041	-0.986906	-0.330004
30	6	0	3.146435	-2.006734	-0.068822
31	6	0	3.862672	-3.327469	0.017293
32	1	0	3.443770	-0.151851	-0.352965
33	1	0	4.346300	-3.545243	-0.941026
34	1	0	4.649806	-3.277142	0.776591
35	1	0	3.151822	-4.116388	0.262386

INTERMEDIATE I'

Zero-point correction= 0.298990 (Hartree/Particle)
Thermal correction to Energy= 0.327149
Thermal correction to Enthalpy= 0.328093
Thermal correction to Gibbs Free Energy= 0.238048
Sum of electronic and zero-point Energies= -1873.331182
Sum of electronic and thermal Energies= -1873.303023
Sum of electronic and thermal Enthalpies= -1873.302079
Sum of electronic and thermal Free Energies= -1873.392124
HF (B3LYP/6-31G(d) and LANL2DZ)= -1873.6301717
HF (M06/6-311+G(2df,2p) and SDD)= -1874,470920
HF (M06/6-311+G(2df,2p) and SDD, SMD[acetonitrile])= -1874,500107

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.856845	-0.465231	-0.186196
2	6	0	-2.052626	-0.669762	-0.854140
3	6	0	-1.975919	-1.768019	0.016573
4	6	0	-3.154230	-0.541784	-1.712773
5	6	0	-3.030745	-2.686524	0.081565
6	6	0	-4.195472	-1.464704	-1.642800
7	6	0	-4.145024	-2.531106	-0.741117
8	6	0	-0.717195	-2.012272	0.788566
9	6	0	0.340229	-2.591998	0.109834
10	7	0	-0.972971	0.267912	-0.825989
11	16	0	-1.344940	1.826853	-0.436825
12	8	0	-0.167231	2.680148	-0.575745
13	6	0	-1.655200	1.829882	1.413448
14	8	0	-2.628474	2.224791	-1.013645
15	9	0	-2.632786	0.968544	1.735314
16	9	0	-1.999242	3.051017	1.819917
17	9	0	-0.537051	1.457166	2.068281
18	6	0	-0.755108	-1.931634	2.293434
19	8	0	2.673795	-0.956938	0.659128

20	8	0	3.157610	-2.452800	-0.960688
21	6	0	3.486231	-1.793230	0.010367
22	6	0	4.876752	-1.849354	0.626585
23	1	0	-3.195605	0.291825	-2.401635
24	1	0	-2.965170	-3.536646	0.755954
25	1	0	-5.052519	-1.349598	-2.300354
26	1	0	-4.957545	-3.250195	-0.694209
27	1	0	1.190217	-2.990448	0.650565
28	1	0	0.237823	-2.902809	-0.925916
29	1	0	-1.432806	-2.710221	2.670960
30	1	0	-1.152288	-0.972542	2.631379
31	1	0	0.234001	-2.092674	2.730695
32	1	0	4.812545	-2.085692	1.693638
33	1	0	5.476373	-2.601735	0.112074
34	1	0	5.365550	-0.872120	0.538539
35	8	0	1.916415	1.090928	-1.197256
36	8	0	3.415910	1.557444	0.423827
37	6	0	2.769081	1.835780	-0.686367
38	6	0	3.095351	3.154443	-1.318650
39	1	0	3.179112	0.617920	0.706042
40	1	0	2.247946	3.823028	-1.129230
41	1	0	4.010071	3.581114	-0.905033
42	1	0	3.178040	3.028965	-2.401060

TS1’

Zero-point correction= 0.293615 (Hartree/Particle)
Thermal correction to Energy= 0.321563
Thermal correction to Enthalpy= 0.322507
Thermal correction to Gibbs Free Energy= 0.231658
Sum of electronic and zero-point Energies= -1873.322232
Sum of electronic and thermal Energies= -1873.294285
Sum of electronic and thermal Enthalpies= -1873.293340
Sum of electronic and thermal Free Energies= -1873.384190
HF (B3LYP/6-31G(d) and LANL2DZ)= -1873,615848
HF (M06/6-311+G(2df,2p) and SDD)= -1874,453392
HF (M06/6-311+G(2df,2p) and SDD, SMD[acetonitrile])= -1874,481744

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	1.023150	0.116305	-0.072690
2	6	0	-1.635003	0.507551	1.146242
3	6	0	-1.798351	1.788851	0.541255
4	6	0	-2.288856	0.232543	2.359527
5	6	0	-2.622384	2.739501	1.179756
6	6	0	-3.088099	1.193673	2.966455
7	6	0	-3.250149	2.457223	2.384170
8	6	0	-1.179896	2.059652	-0.756251

9	6	0	0.073878	1.589986	-1.100336
10	7	0	-0.820341	-0.462612	0.531008
11	16	0	-1.413326	-1.900231	0.036962
12	8	0	-0.303056	-2.788387	-0.300122
13	6	0	-2.217326	-1.514247	-1.611204
14	8	0	-2.526515	-2.350217	0.875545
15	9	0	-3.104536	-0.511606	-1.466288
16	9	0	-2.856477	-2.589454	-2.076104
17	9	0	-1.297932	-1.135627	-2.509130
18	6	0	-1.974126	2.859317	-1.761004
19	1	0	-2.163633	-0.747060	2.803298
20	1	0	-2.743641	3.722867	0.736500
21	1	0	-3.582709	0.960380	3.905432
22	1	0	-3.859686	3.212790	2.870815
23	1	0	0.320658	1.631407	-2.166118
24	1	0	-2.339612	3.801902	-1.339203
25	1	0	-2.857926	2.280825	-2.059975
26	1	0	-1.383847	3.084376	-2.652162
27	8	0	2.939442	0.907044	-0.542484
28	8	0	2.173433	3.013088	-0.433997
29	6	0	3.115835	2.174023	-0.506773
30	6	0	4.539283	2.679749	-0.571562
31	1	0	4.995568	2.354796	-1.512708
32	1	0	4.565228	3.767749	-0.504949
33	1	0	5.122232	2.241301	0.244995
34	1	0	1.009890	2.361557	-0.586538
35	8	0	2.040592	-1.500004	1.074968
36	8	0	4.149592	-1.355639	0.272910
37	6	0	3.183046	-1.945441	0.962927
38	6	0	3.605527	-3.237413	1.605983
39	1	0	3.818124	-0.494918	-0.100791
40	1	0	4.509741	-3.084523	2.203157
41	1	0	2.796048	-3.623688	2.224886
42	1	0	3.846605	-3.964523	0.822689

INTERMEDIATE II'

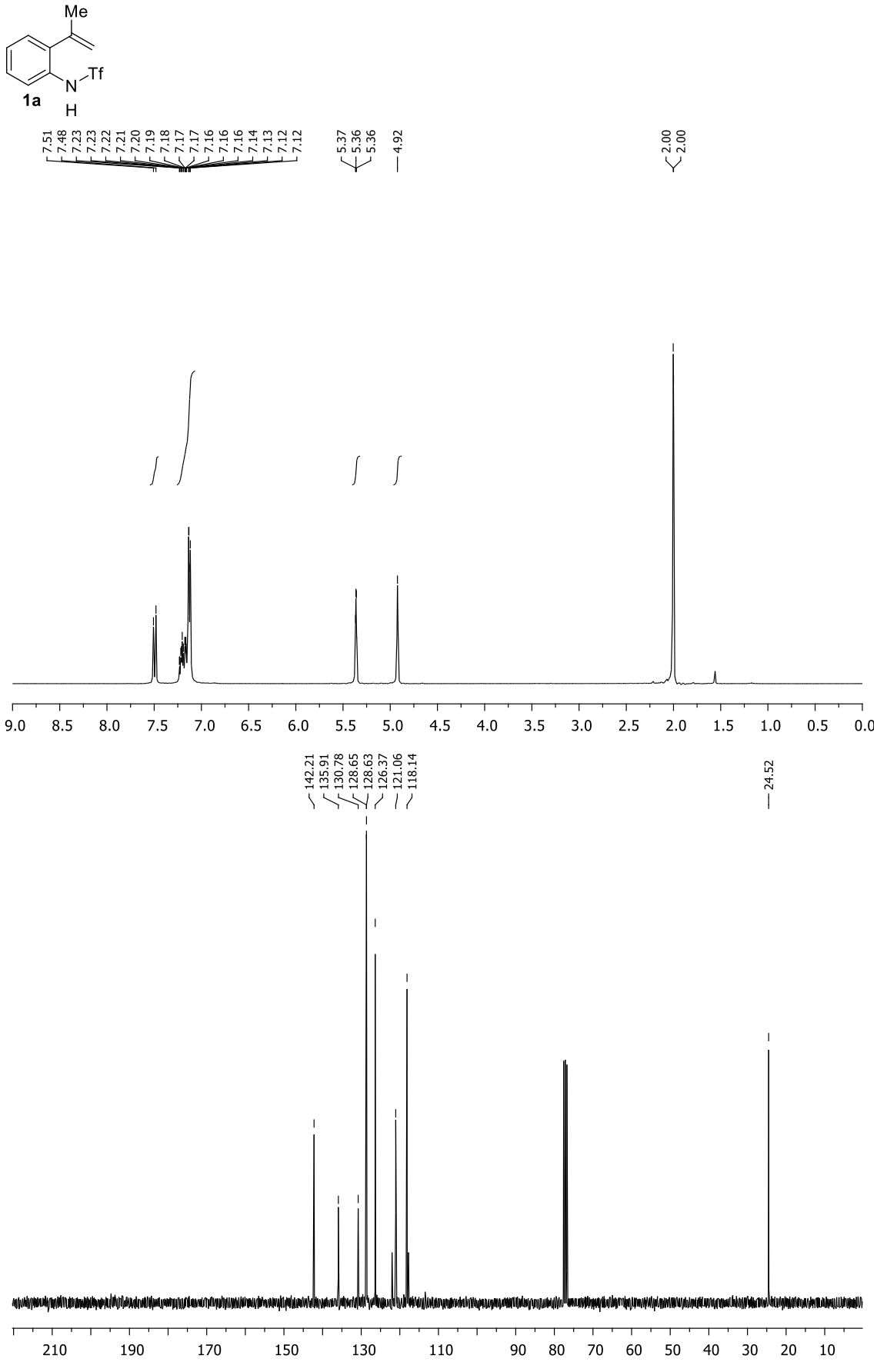
Zero-point correction= 0.299142 (Hartree/Particle)
Thermal correction to Energy= 0.327579
Thermal correction to Enthalpy= 0.328524
Thermal correction to Gibbs Free Energy= 0.236941
Sum of electronic and zero-point Energies= -1873.330659
Sum of electronic and thermal Energies= -1873.302221
Sum of electronic and thermal Enthalpies= -1873.301277
Sum of electronic and thermal Free Energies= -1873.392859

HF (B3LYP/6-31G(d) and LANL2DZ)= -1873,629800
HF (M06/6-311+G(2df,2p) and SDD)= -1874,473361
HF (M06/6-311+G(2df,2p) and SDD, SMD[acetonitrile])= -1874,503320

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	46	0	-1.003558	0.233044	-0.096037
2	6	0	1.826760	0.528485	-1.023498
3	6	0	1.943103	1.793605	-0.388875
4	6	0	2.646118	0.219930	-2.118968
5	6	0	2.903423	2.695407	-0.880086
6	6	0	3.591036	1.133327	-2.579537
7	6	0	3.719319	2.378591	-1.962590
8	6	0	1.113233	2.130201	0.788839
9	6	0	-0.082219	1.553579	1.041551
10	7	0	0.851326	-0.404338	-0.582298
11	16	0	1.277632	-1.880636	-0.029646
12	8	0	0.067000	-2.690418	0.145392
13	6	0	1.896811	-1.606412	1.719833
14	8	0	2.442908	-2.417496	-0.734822
15	9	0	2.837560	-0.650725	1.729056
16	9	0	2.424293	-2.738067	2.196367
17	9	0	0.894027	-1.229058	2.524553
18	6	0	1.662393	3.154990	1.766082
19	1	0	2.537093	-0.748139	-2.591532
20	1	0	3.010749	3.667096	-0.408676
21	1	0	4.219051	0.872530	-3.427081
22	1	0	4.446892	3.100527	-2.322768
23	1	0	-0.574318	1.736322	2.001227
24	1	0	1.743821	4.150309	1.311454
25	1	0	2.666575	2.870890	2.103000
26	1	0	1.016068	3.244649	2.643823
27	8	0	-3.011972	0.967431	0.352829
28	8	0	-2.425930	3.131131	0.180320
29	6	0	-3.314852	2.171446	0.304418
30	6	0	-4.734696	2.649514	0.387802
31	1	0	-1.504461	2.737802	0.198465
32	1	0	-4.853834	3.288004	1.269450
33	1	0	-4.965885	3.259819	-0.491128
34	1	0	-5.417700	1.802138	0.446663
35	8	0	-2.054462	-1.286723	-1.444436
36	8	0	-3.765490	-1.802835	-0.072844
37	6	0	-2.866955	-2.101288	-1.015410
38	6	0	-2.912980	-3.526529	-1.478422
39	1	0	-3.650704	-0.858657	0.174803
40	1	0	-2.056050	-4.035401	-1.021409
41	1	0	-3.838943	-4.022646	-1.184203
42	1	0	-2.778397	-3.561871	-2.562125

NMR SPECTRA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7.16
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7.13
7.12
7.12
5.37
5.36
5.36
4.92
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2.00
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130.78
128.65
128.63
126.37
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150
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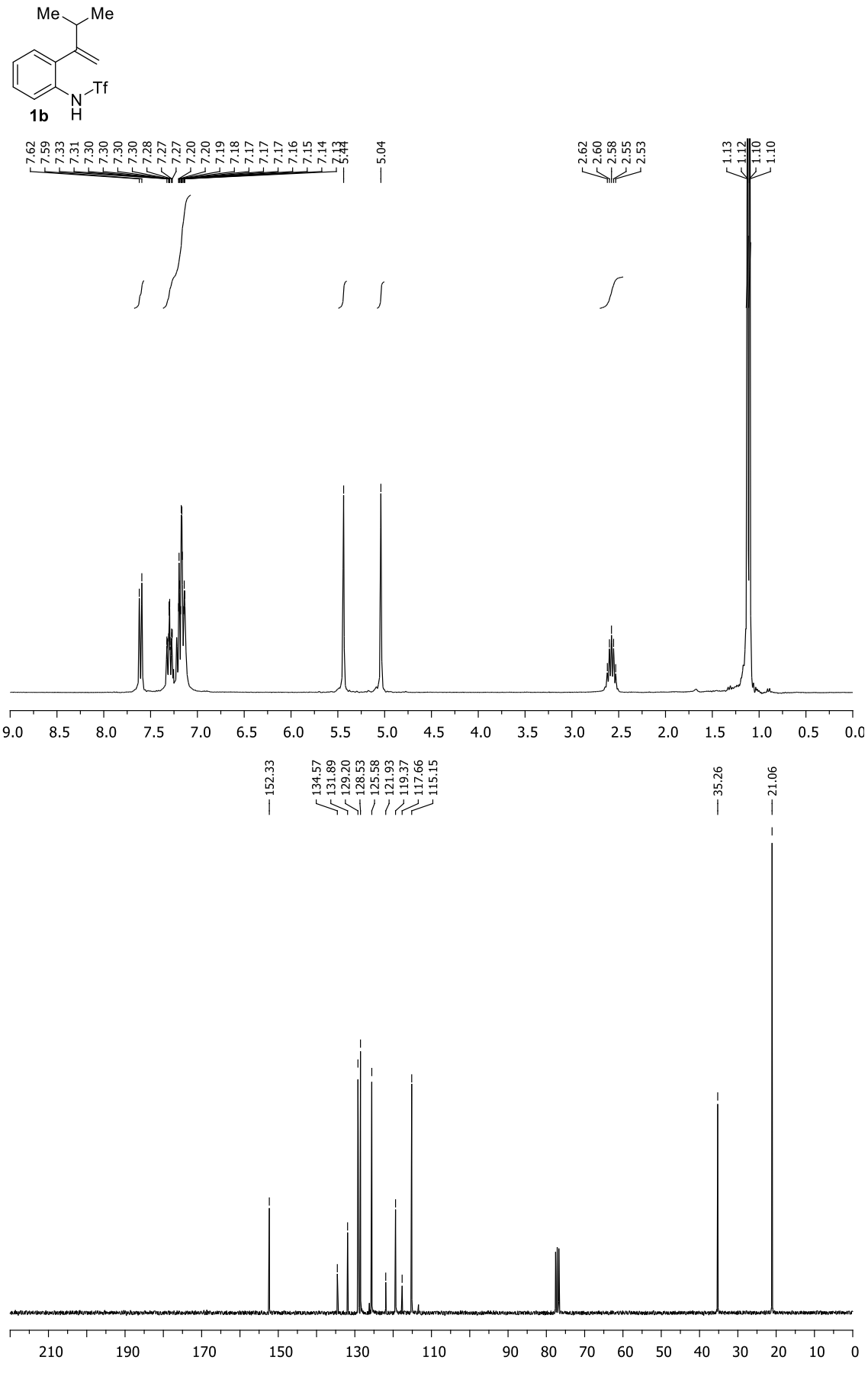
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7.14
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2.58
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2.53
1.13
1.12
1.10
1.10
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8.0
7.5
7.0
6.5
6.0
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3.5
3.0
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2.0
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117.66
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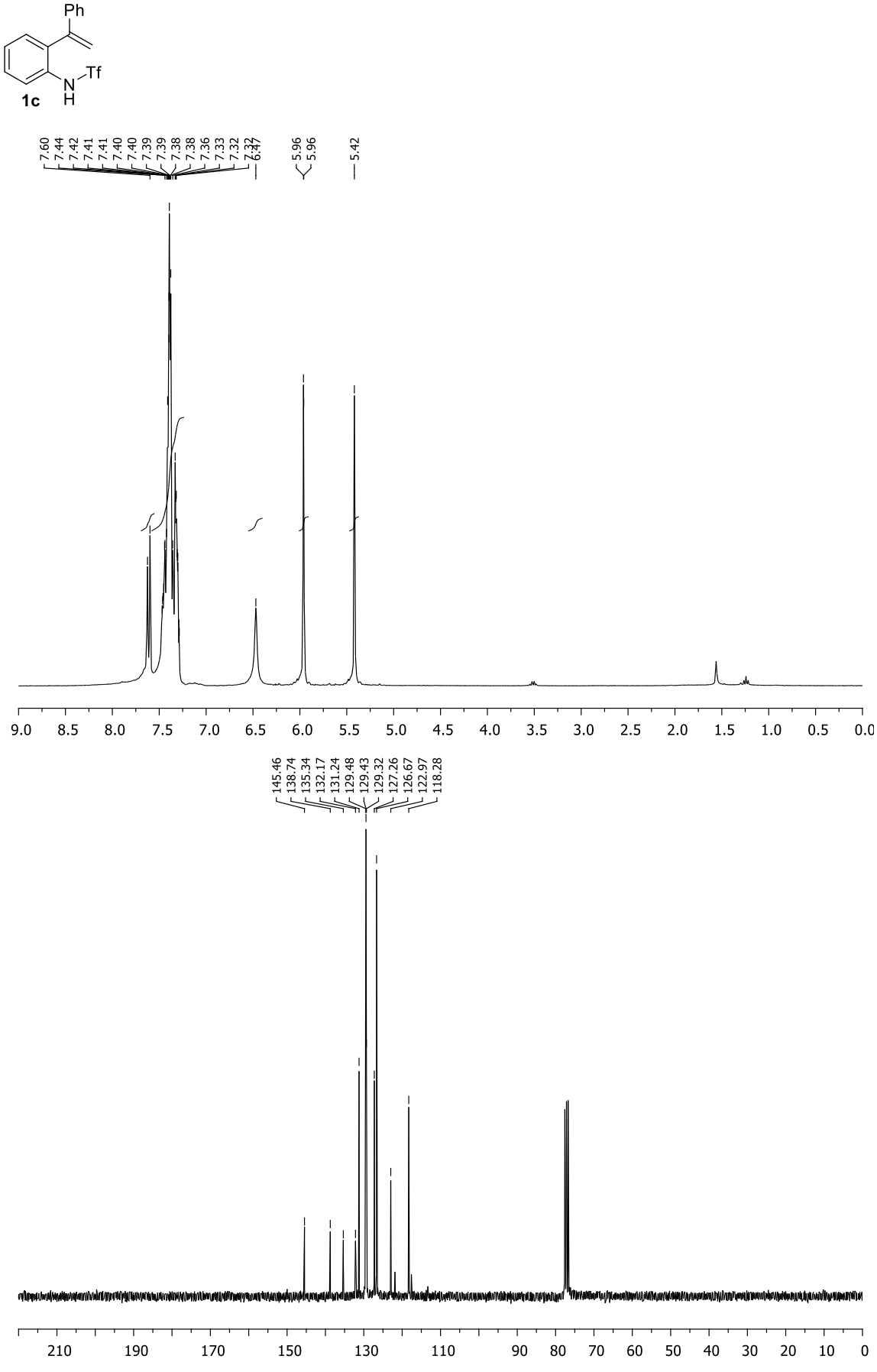
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7.38
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129.32
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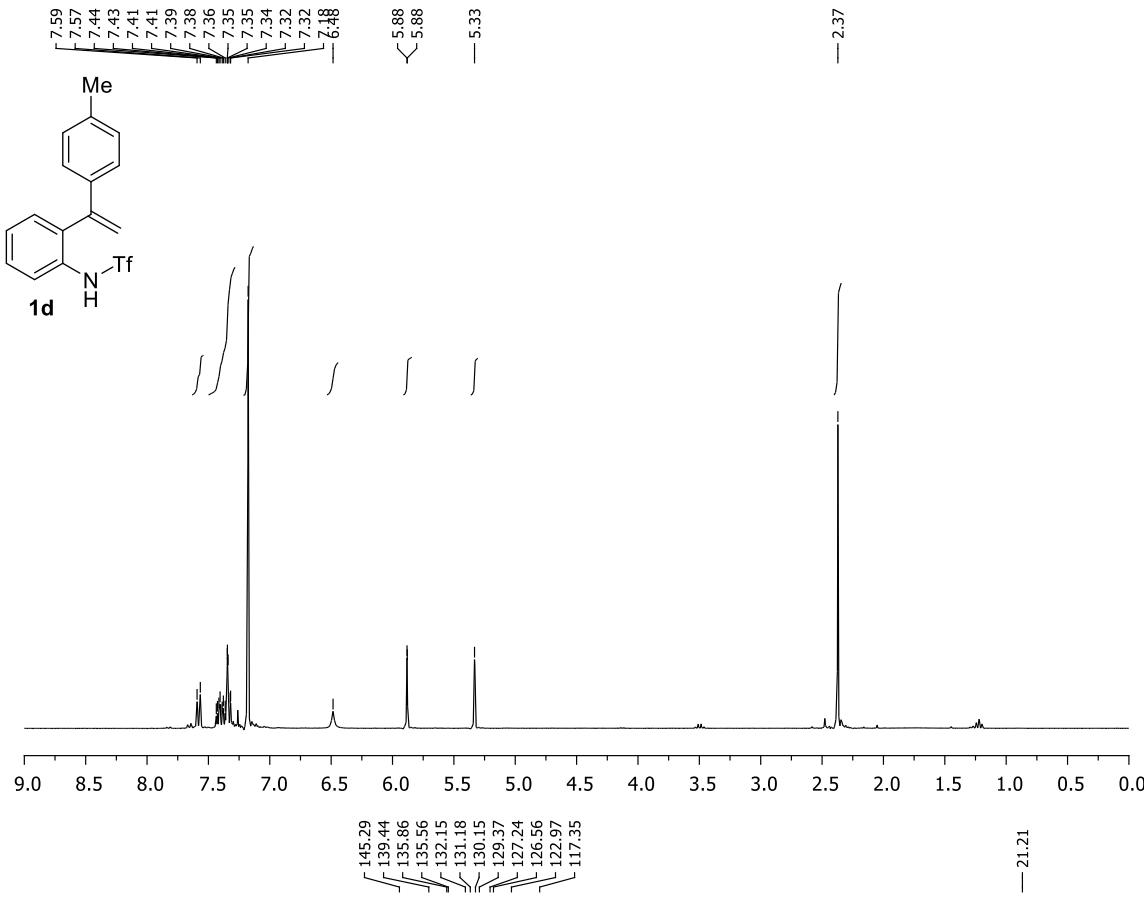
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7.32
7.32
7.18
6.48
5.88
5.88
5.33
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Me
Tf
N
H
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9.0
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8.0
7.5
7.0
6.5
6.0
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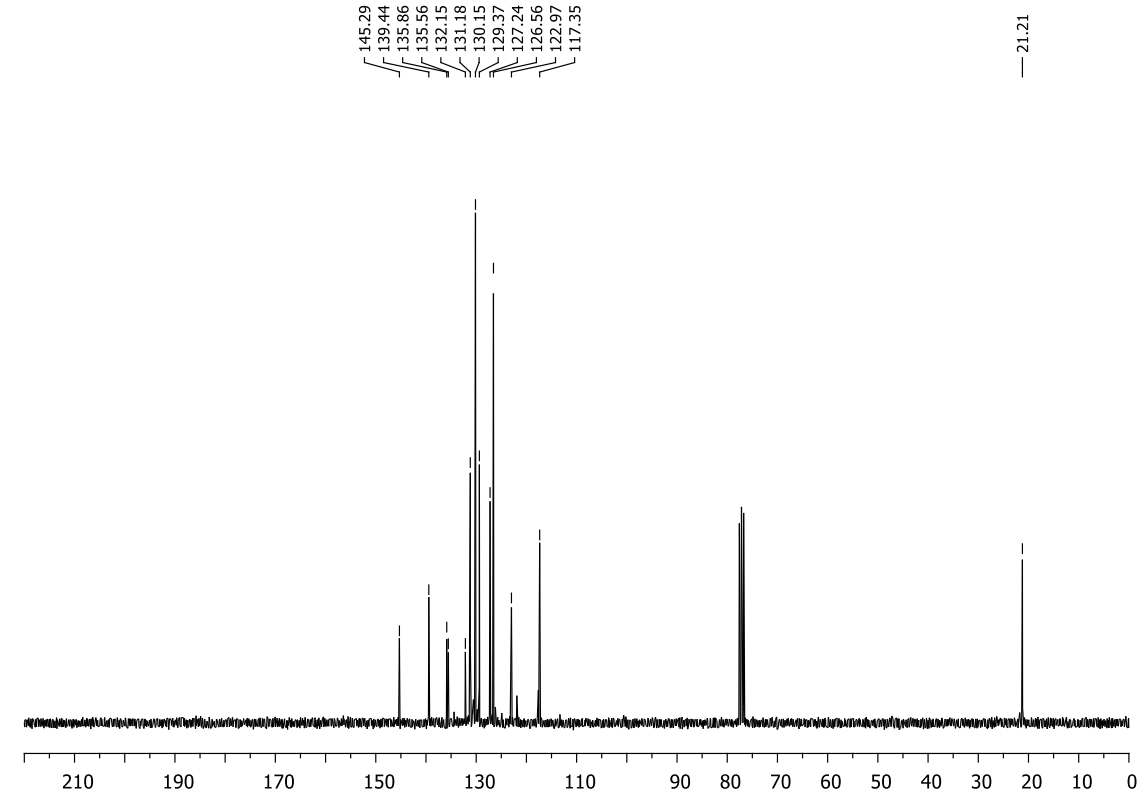
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170
150
130
110
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10
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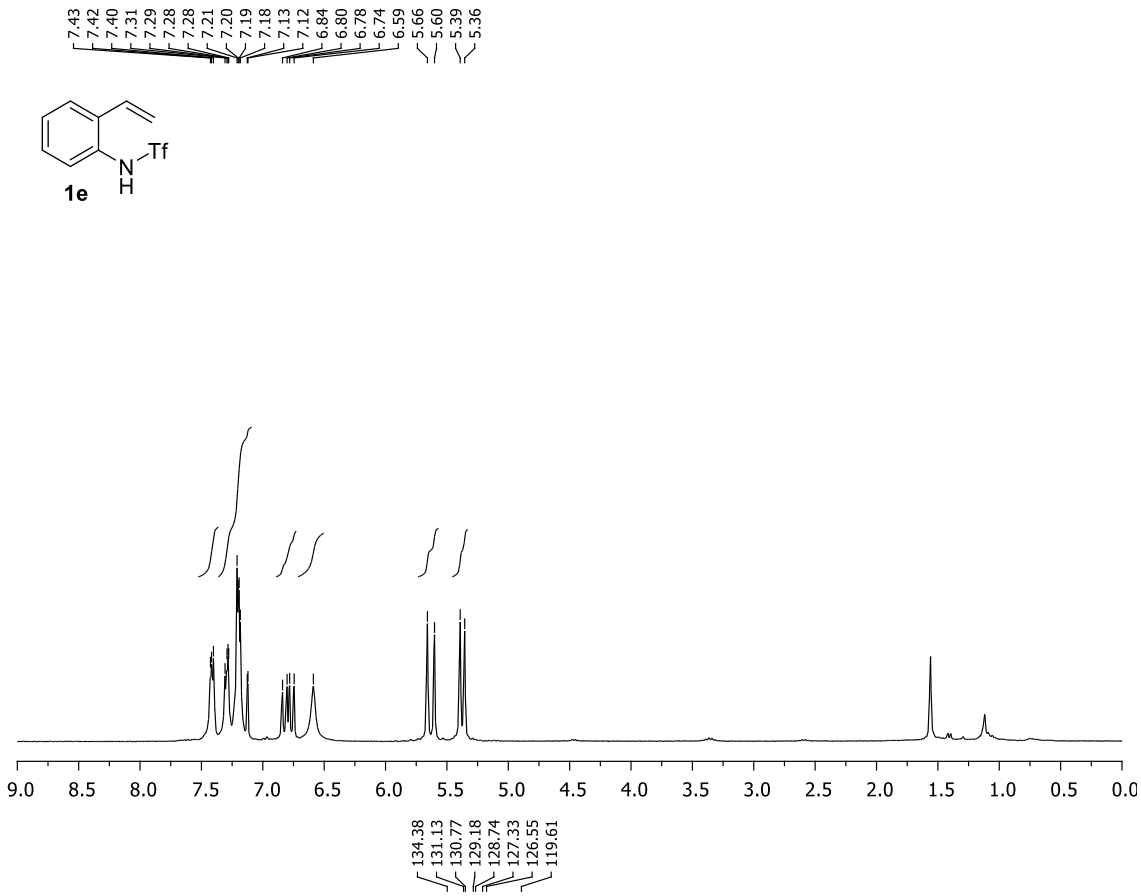
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7.13
7.12
6.84
6.80
6.78
6.74
6.59
5.66
5.60
5.39
5.36
Tf
N
H
1e
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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134.38
131.13
130.77
129.18
128.74
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110
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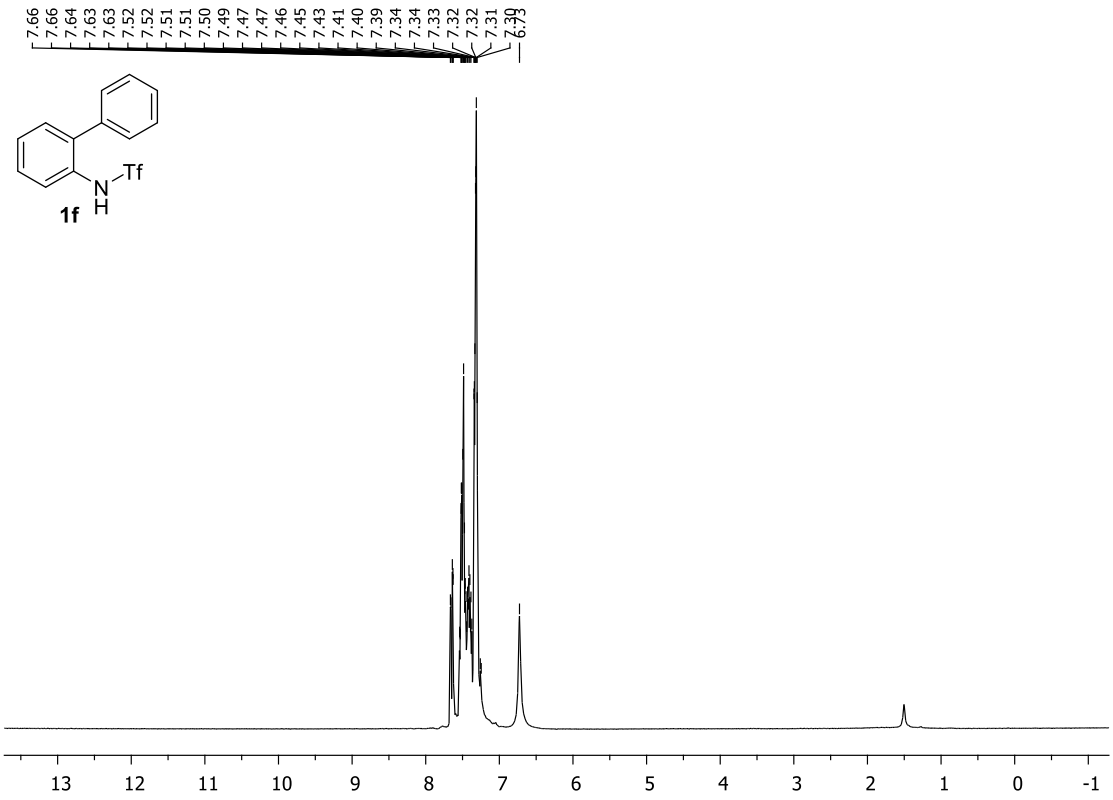
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7.47
7.46
7.45
7.43
7.41
7.40
7.39
7.34
7.34
7.33
7.32
7.32
7.31
7.30
6.73
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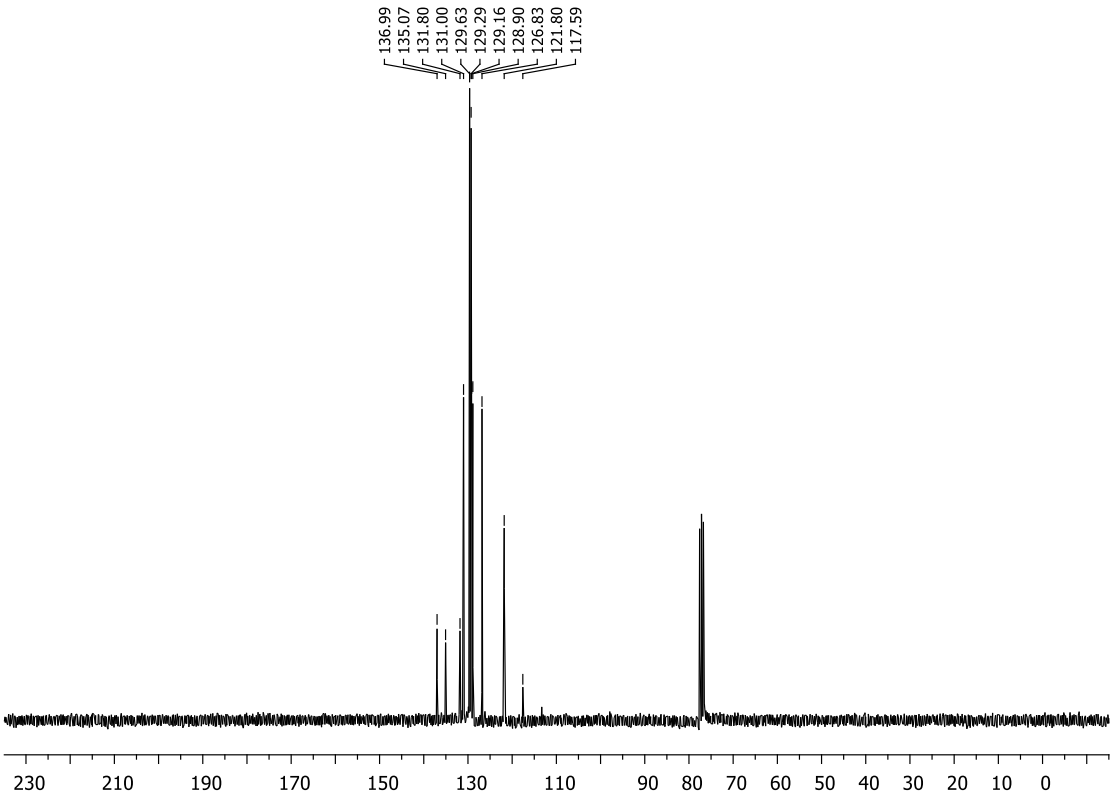
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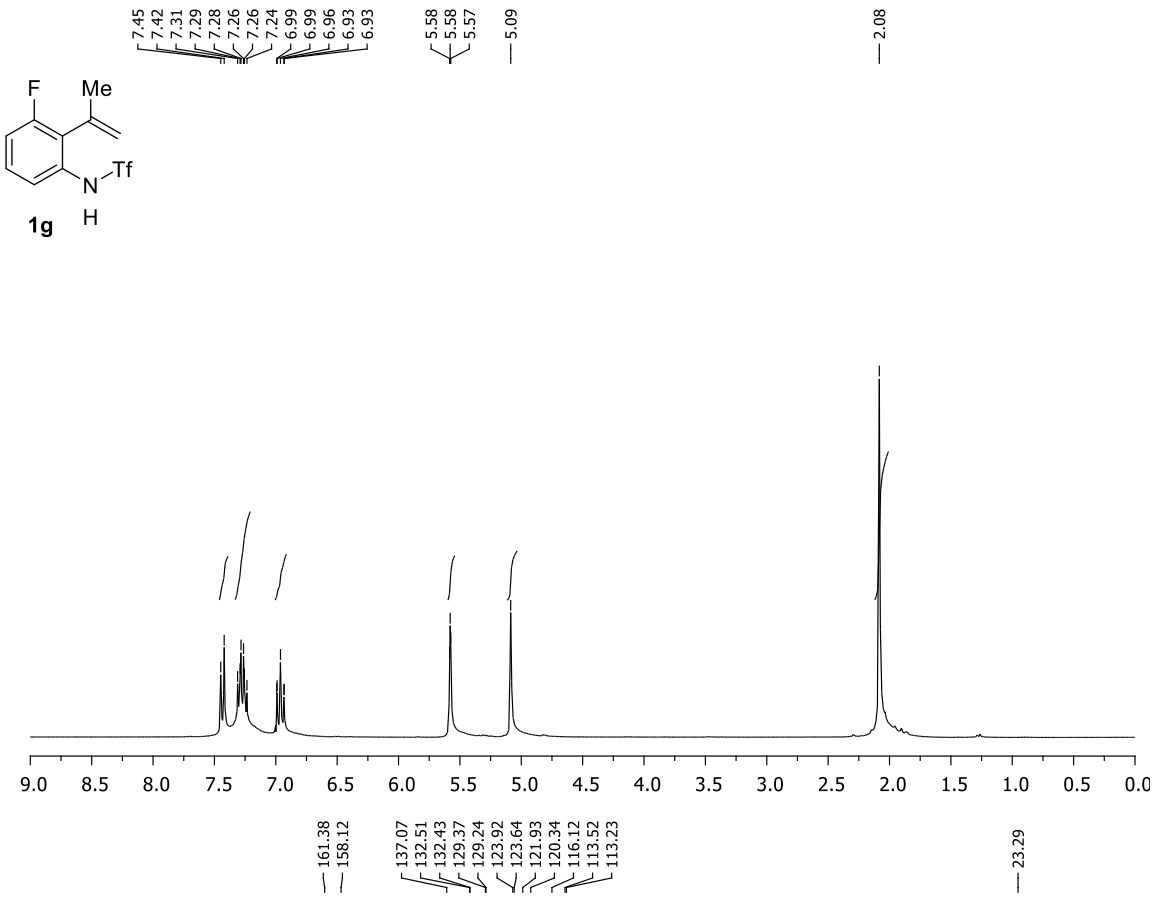
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7.24
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6.99
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6.93
5.58
5.58
5.57
5.09
2.08
F
Me
N
Tf
H
1g
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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2.0
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1.0
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158.12
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116.12
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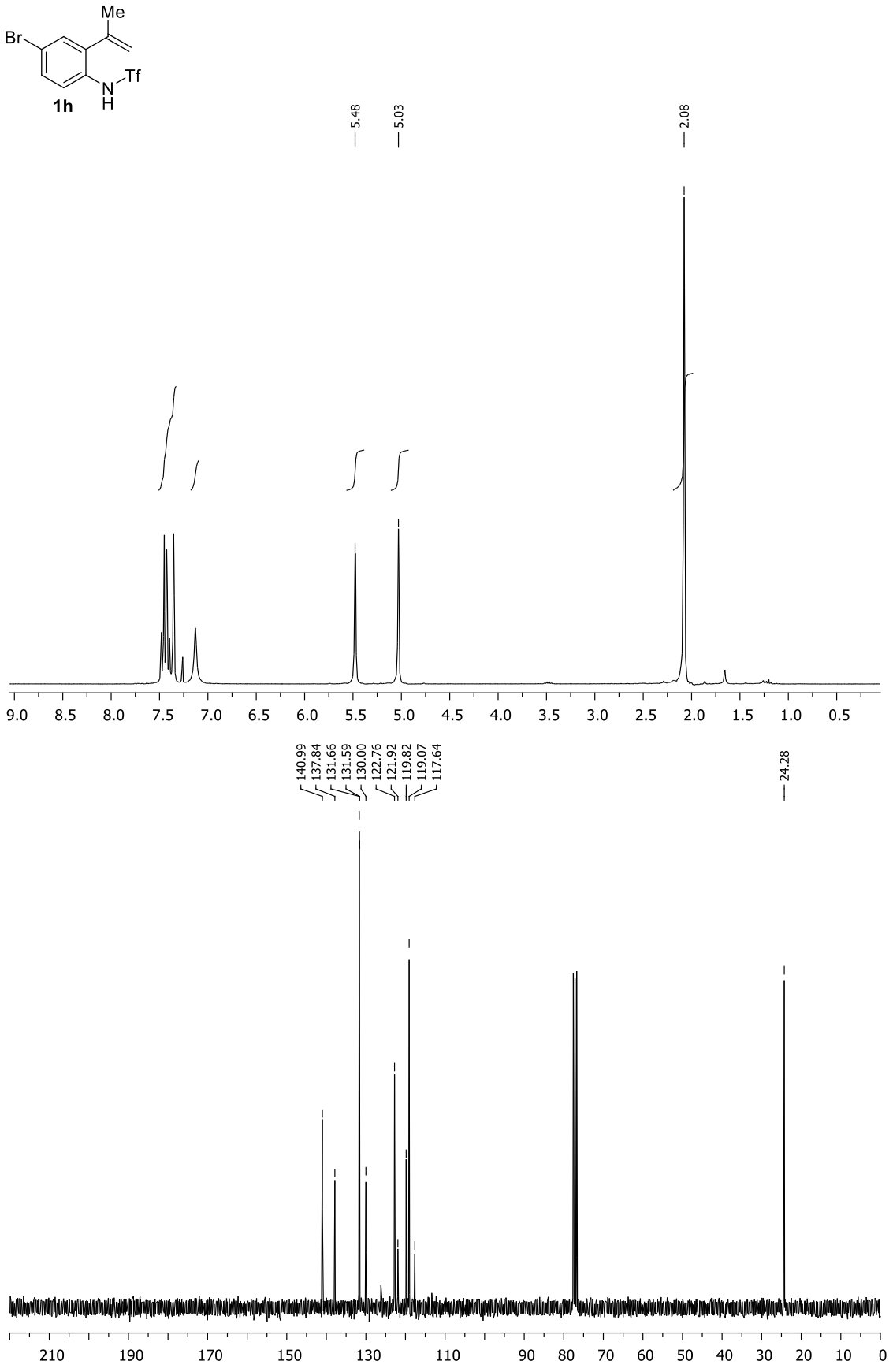
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Br
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H
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121.92
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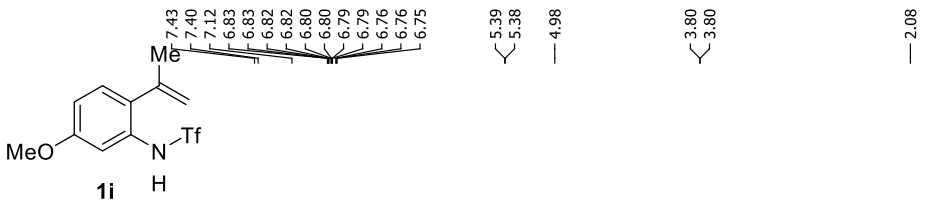
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MeO
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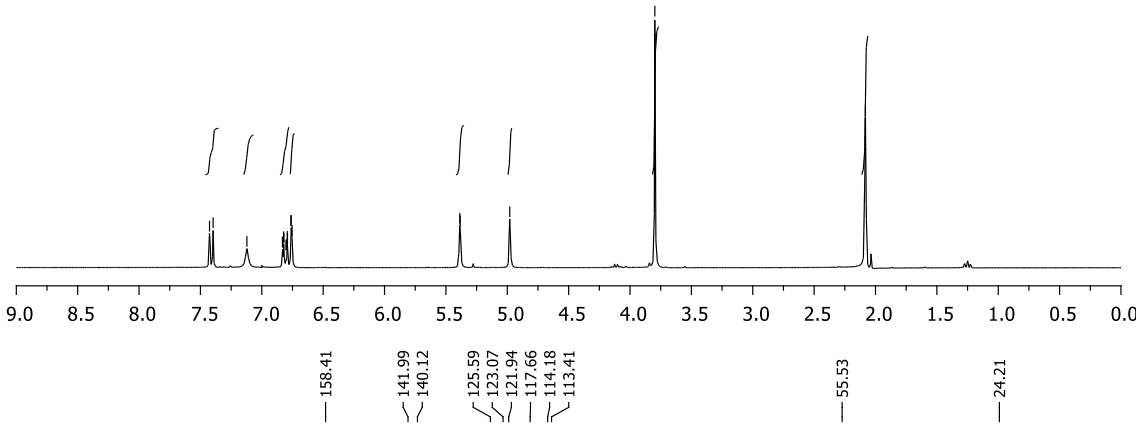
Tf
H

1i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2.0
1.5
1.0
0.5
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140.12
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123.07
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117.66
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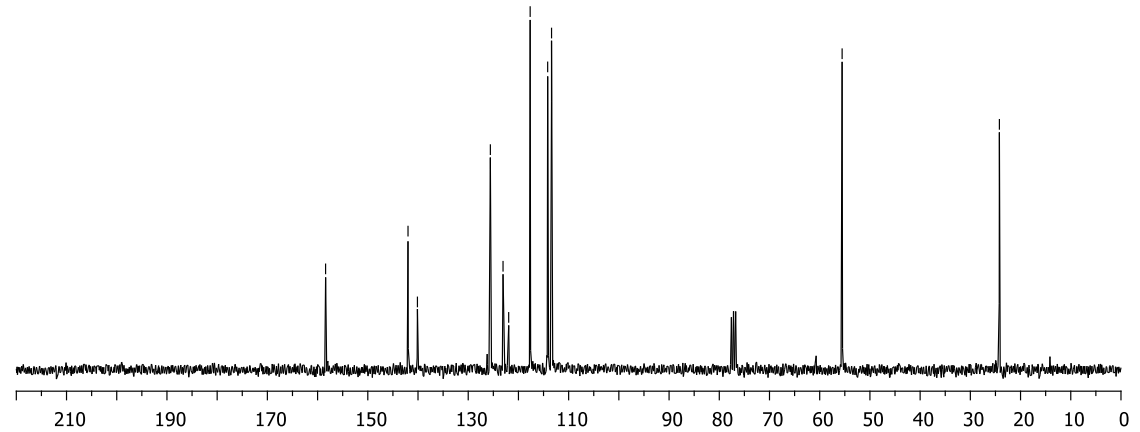
24.21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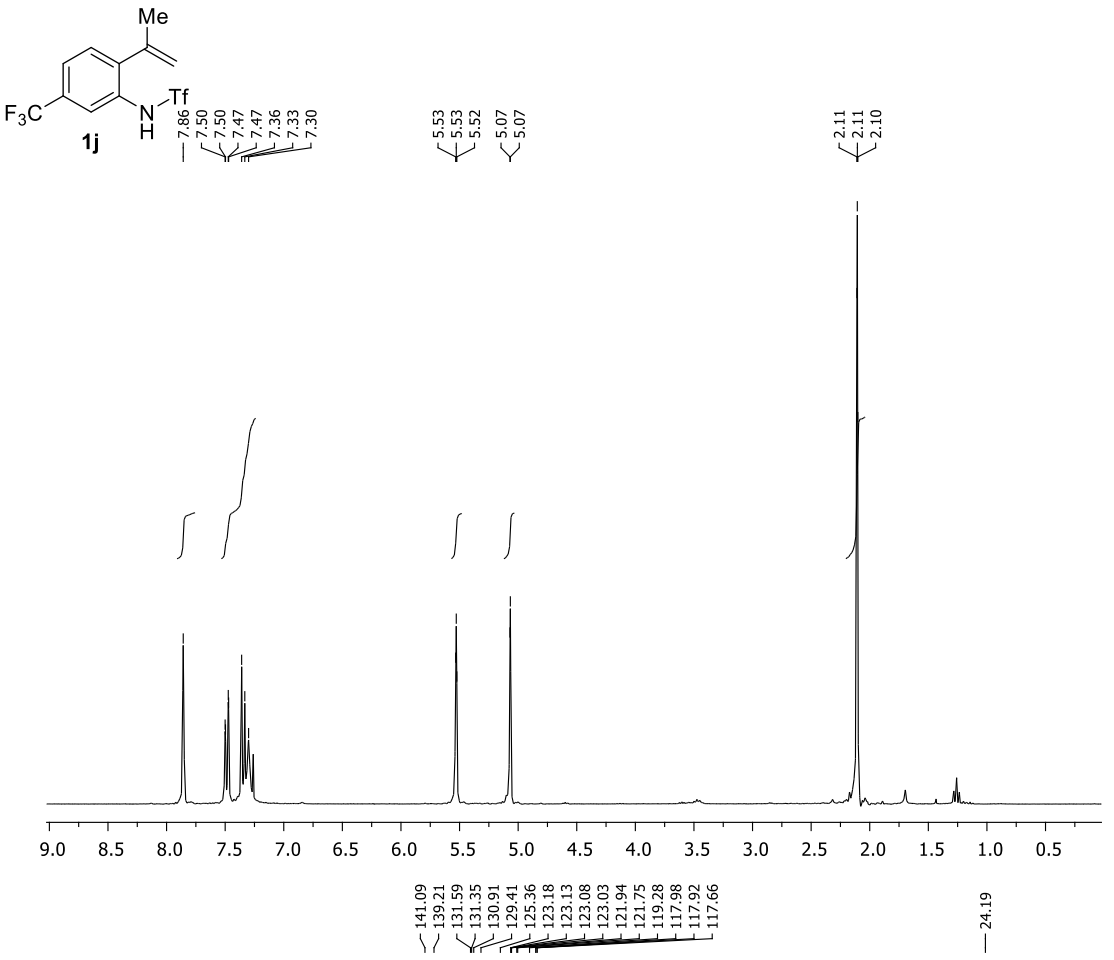
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N
H
Tf
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5.53
5.52
5.07
5.07
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2.11
2.10
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7.0
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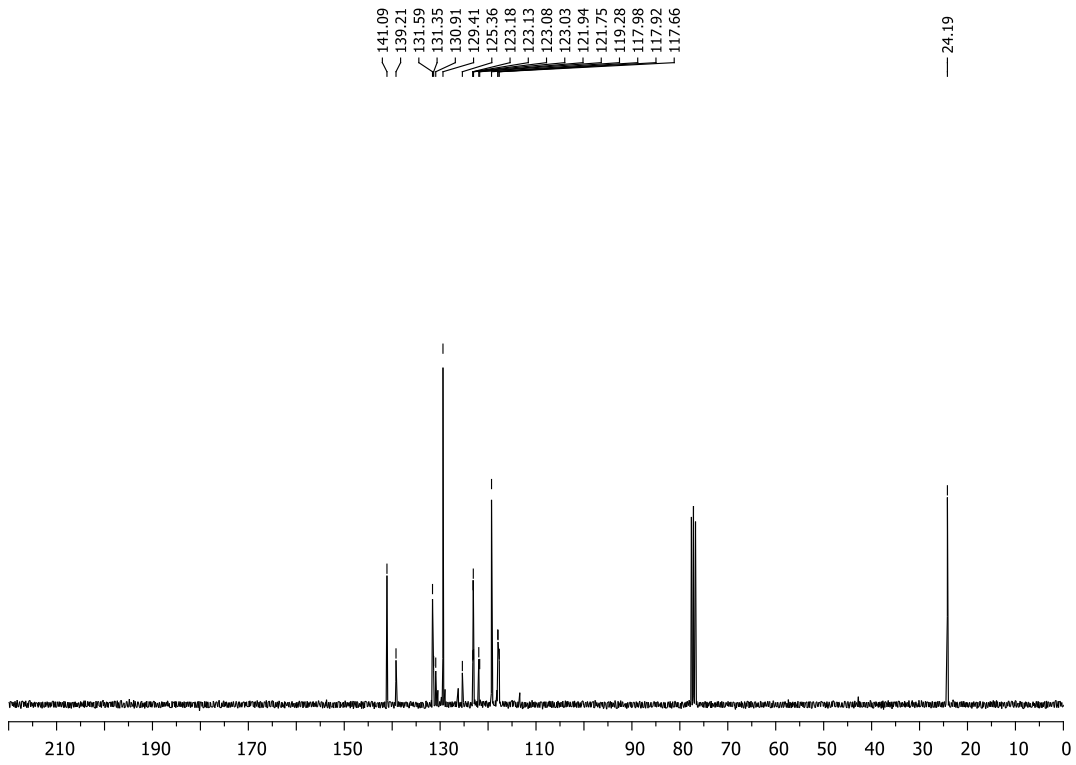
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117.98
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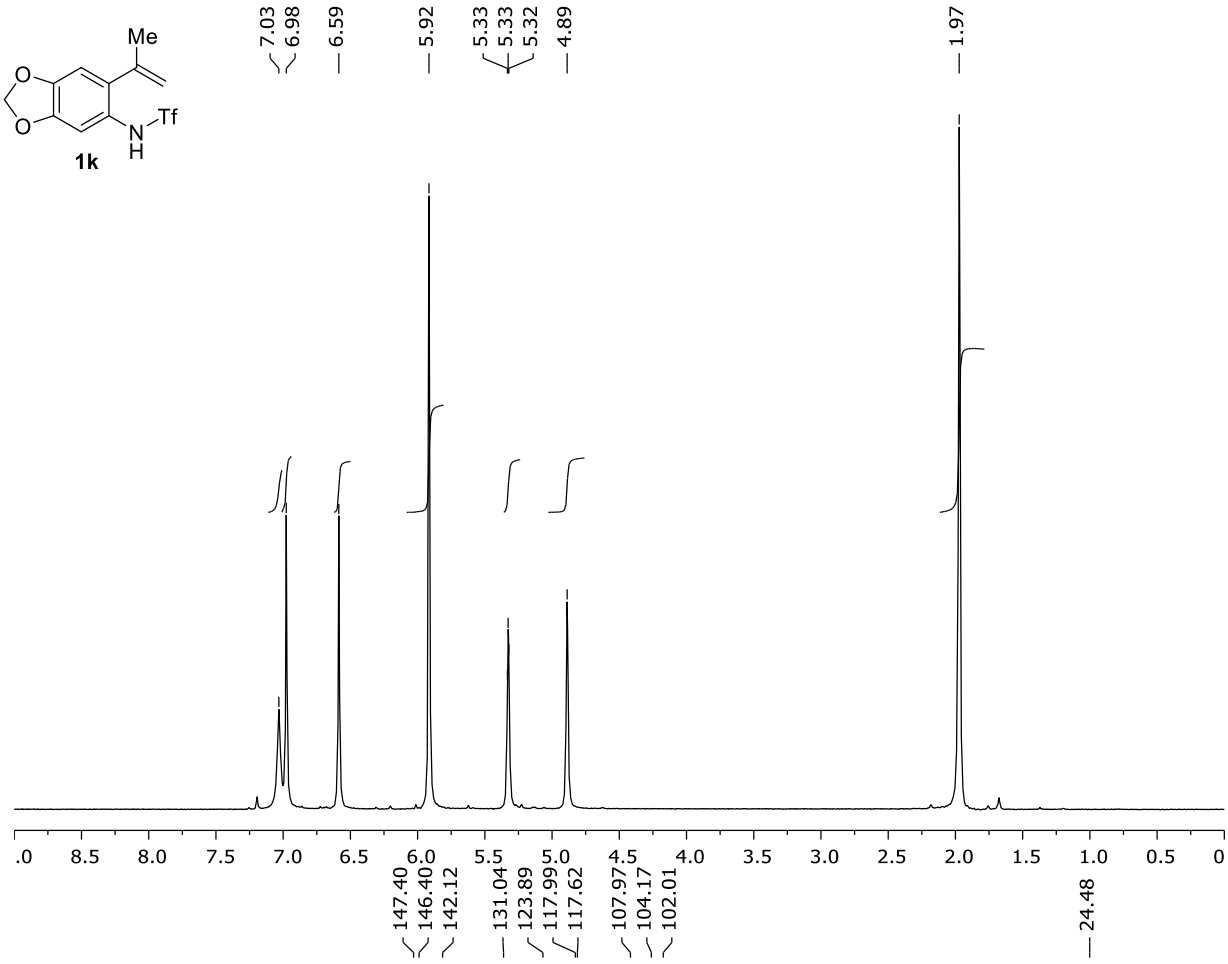
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H
Tf
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5.33
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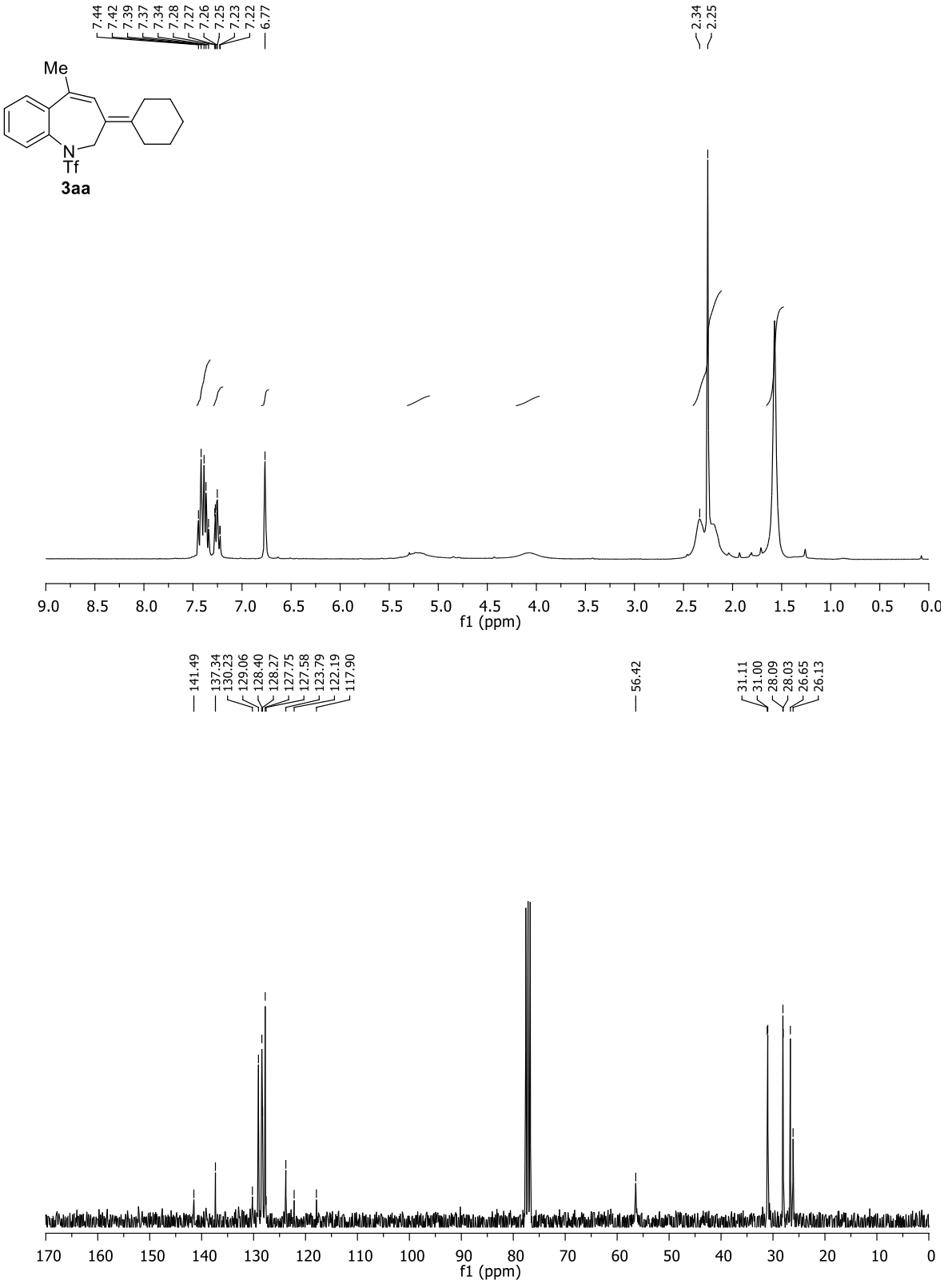
117.62
107.97
104.17
102.01
24.48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7.23
7.22
6.77
2.34
2.25
Me
N
Tf
3aa
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
141.49
137.34
130.23
129.06
128.40
128.27
127.75
127.58
123.79
122.19
117.90
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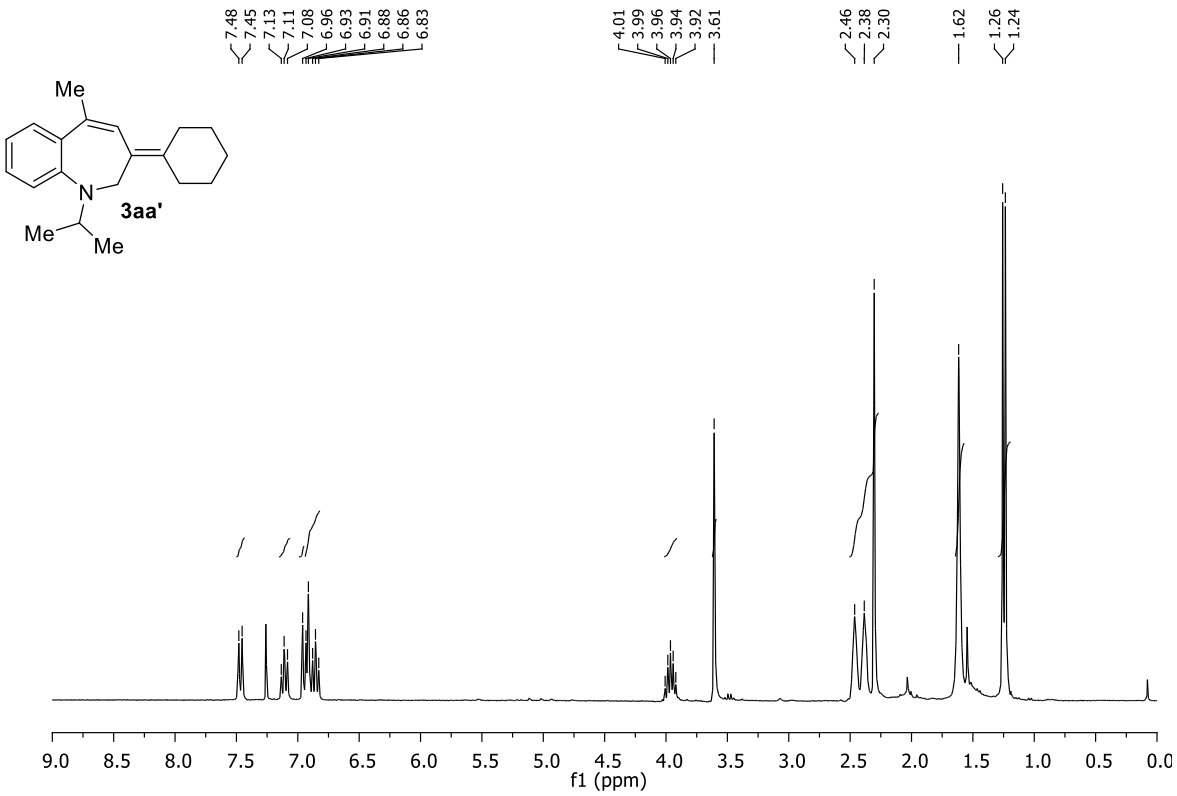
31.11
31.00
28.09
28.03
26.65
26.13
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.83
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3.99
3.96
3.94
3.92
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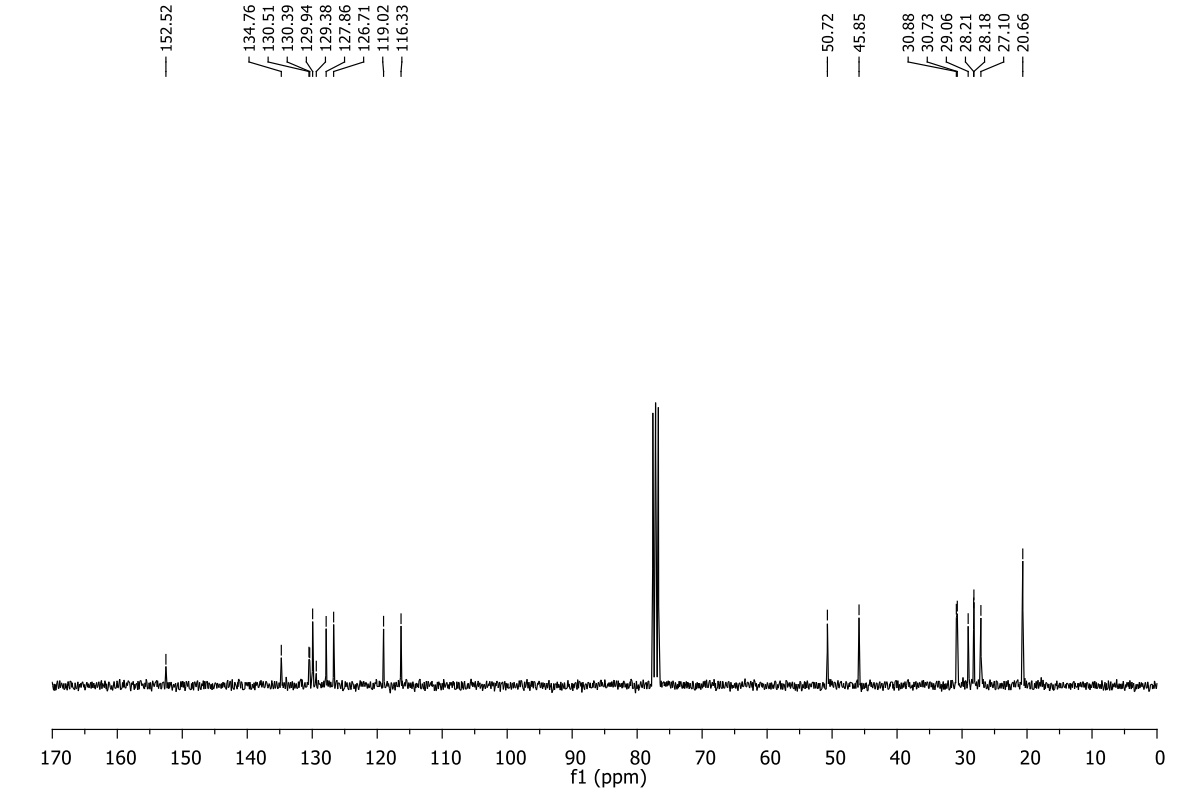
1.26
1.24
Me
N
Me
Me
3aa'
f1 (ppm)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30.73
29.06
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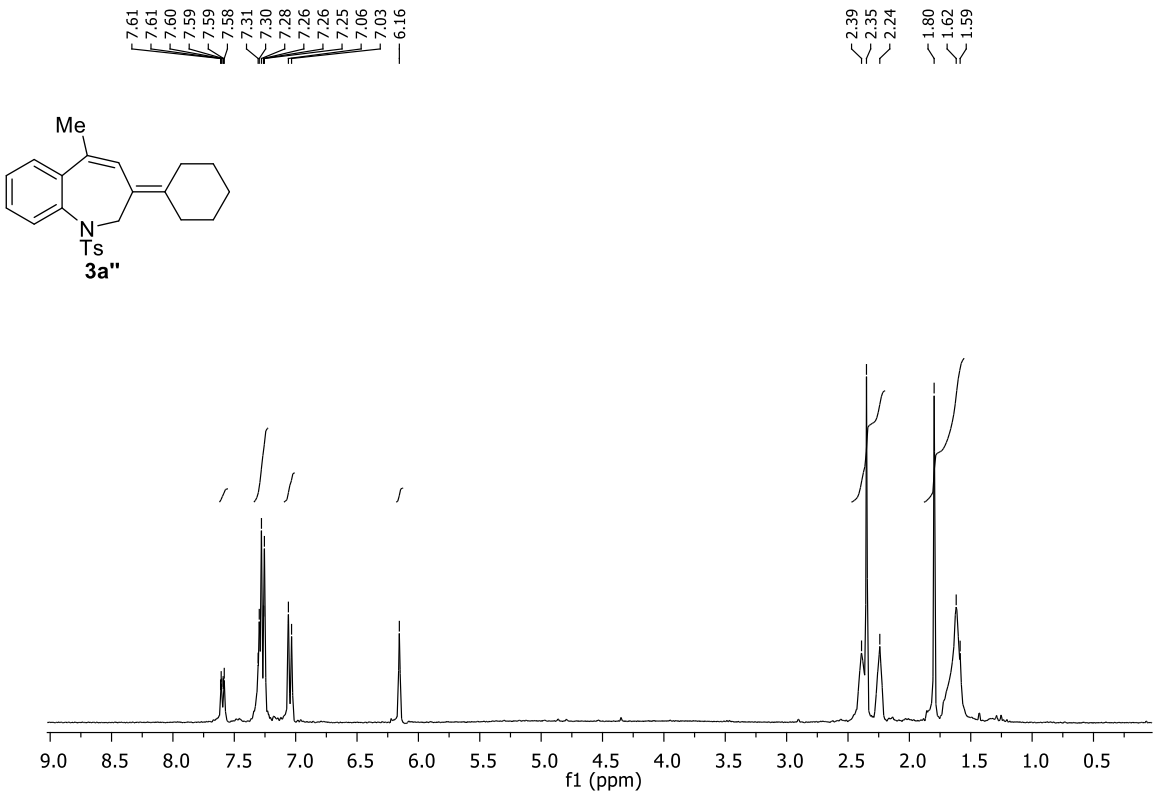
28.18
27.10
20.66
f1 (ppm)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7.26
7.25
7.06
7.03
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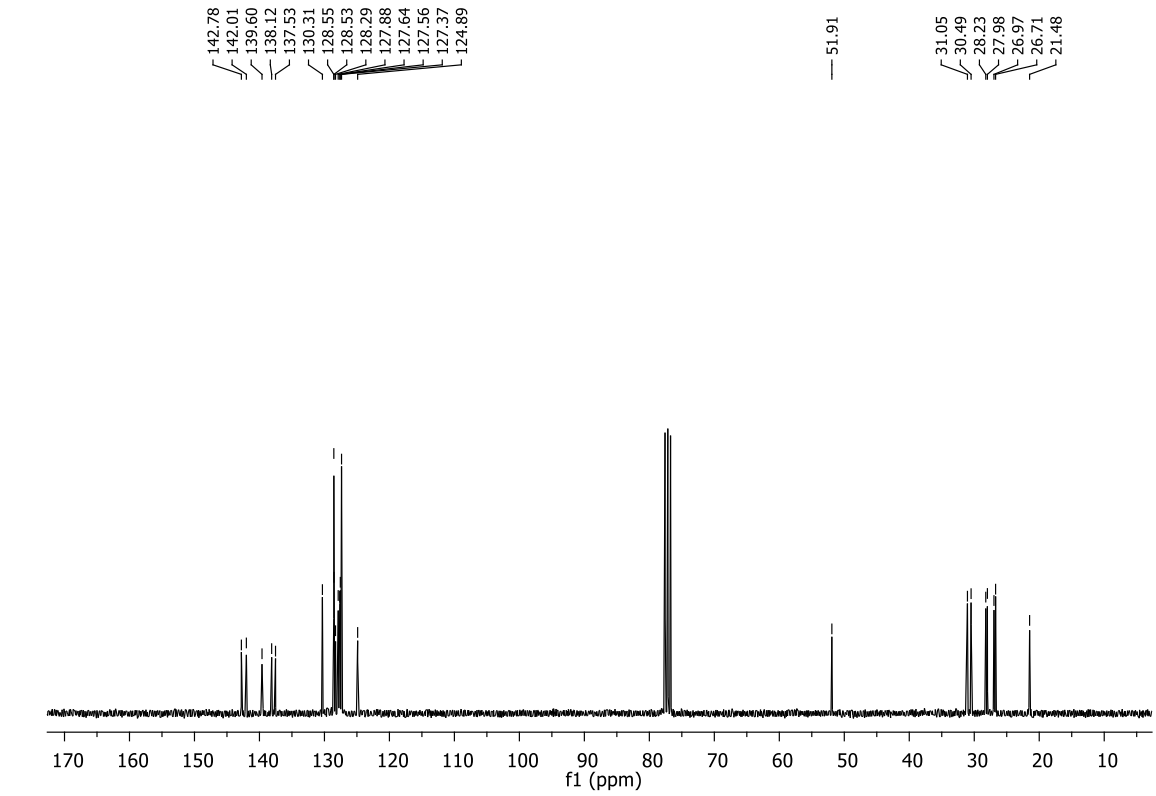
2.35
2.24
1.80
1.62
1.59
Me
N
Ts
3a''
f1 (ppm)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127.88
127.64
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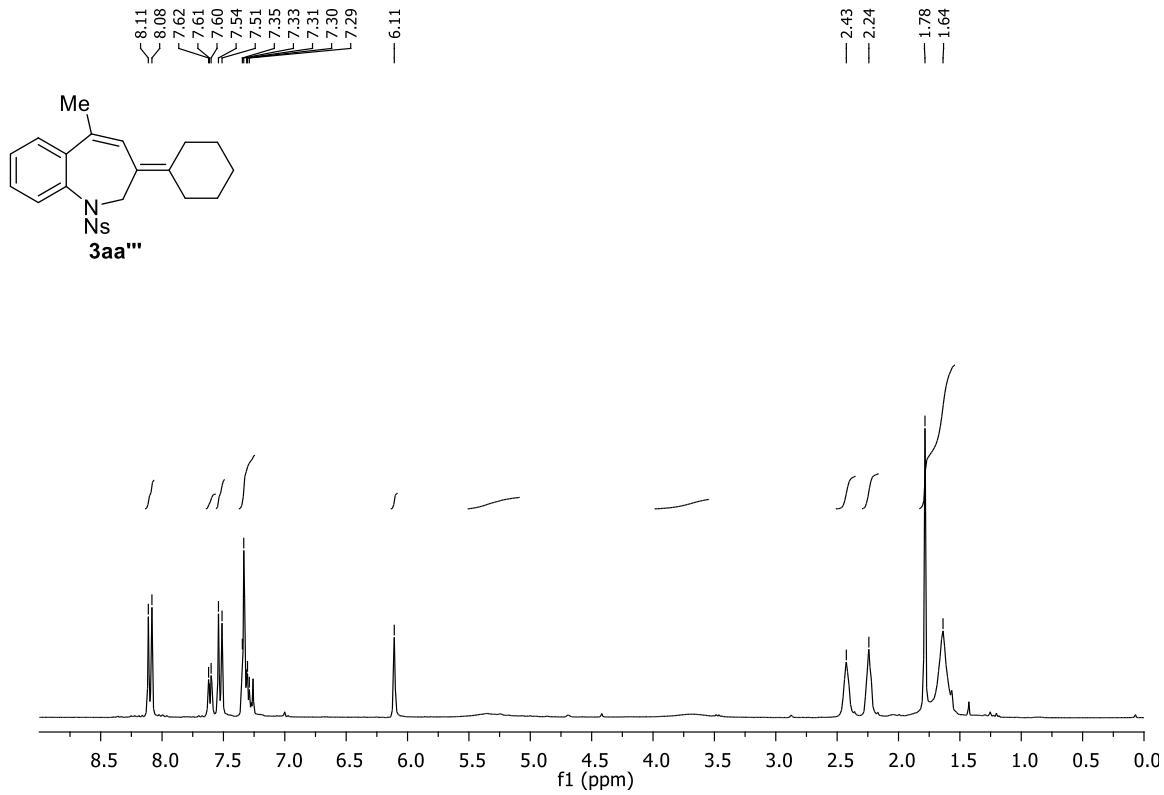
31.05
30.49
28.23
27.98
26.97
26.71
21.48
f1 (ppm)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6.11
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2.24
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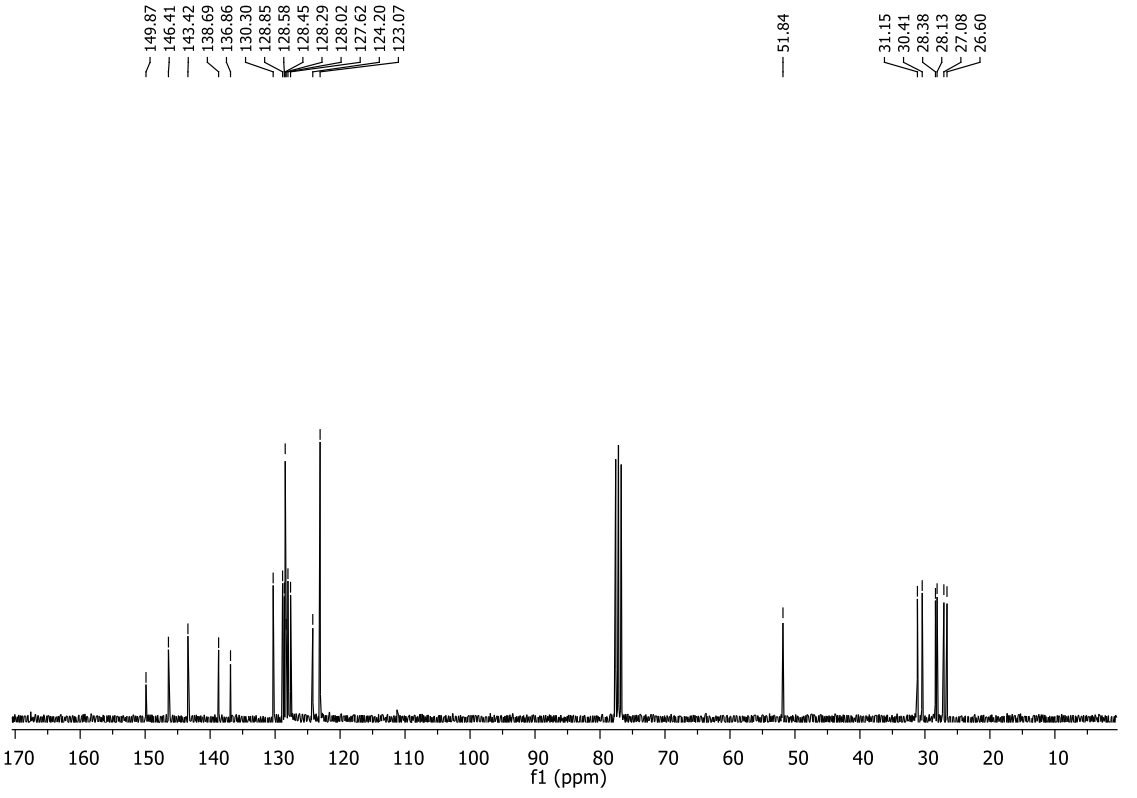
1.64
Me
N
Ns
3aa'''
f1 (ppm)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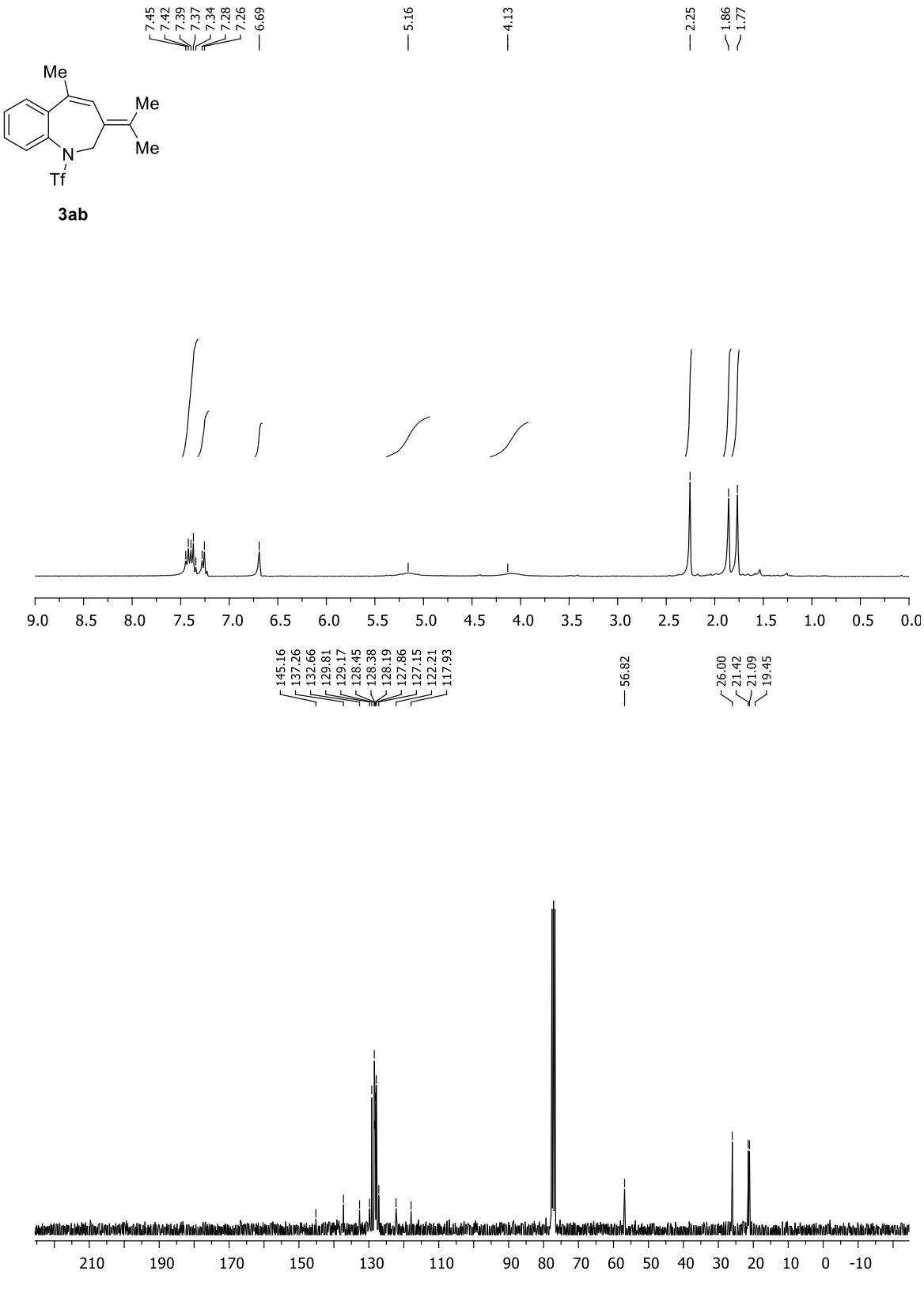
31.15
30.41
28.38
28.13
27.08
26.60
f1 (ppm)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2.25
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1.77
Me
Me
Me
N
Tf
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6.0
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4.5
4.0
3.5
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2.5
2.0
1.5
1.0
0.5
0.0
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127.15
122.21
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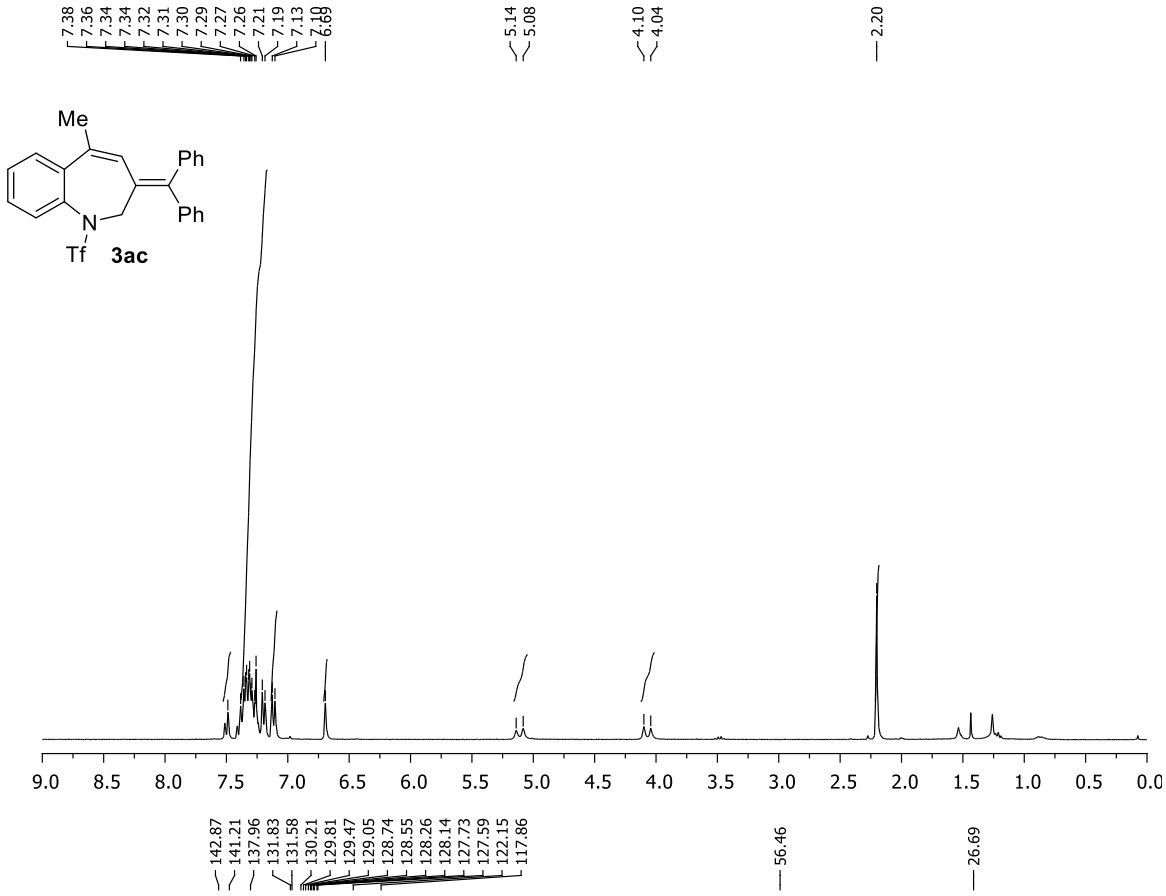
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Ph
Ph
N
Tf
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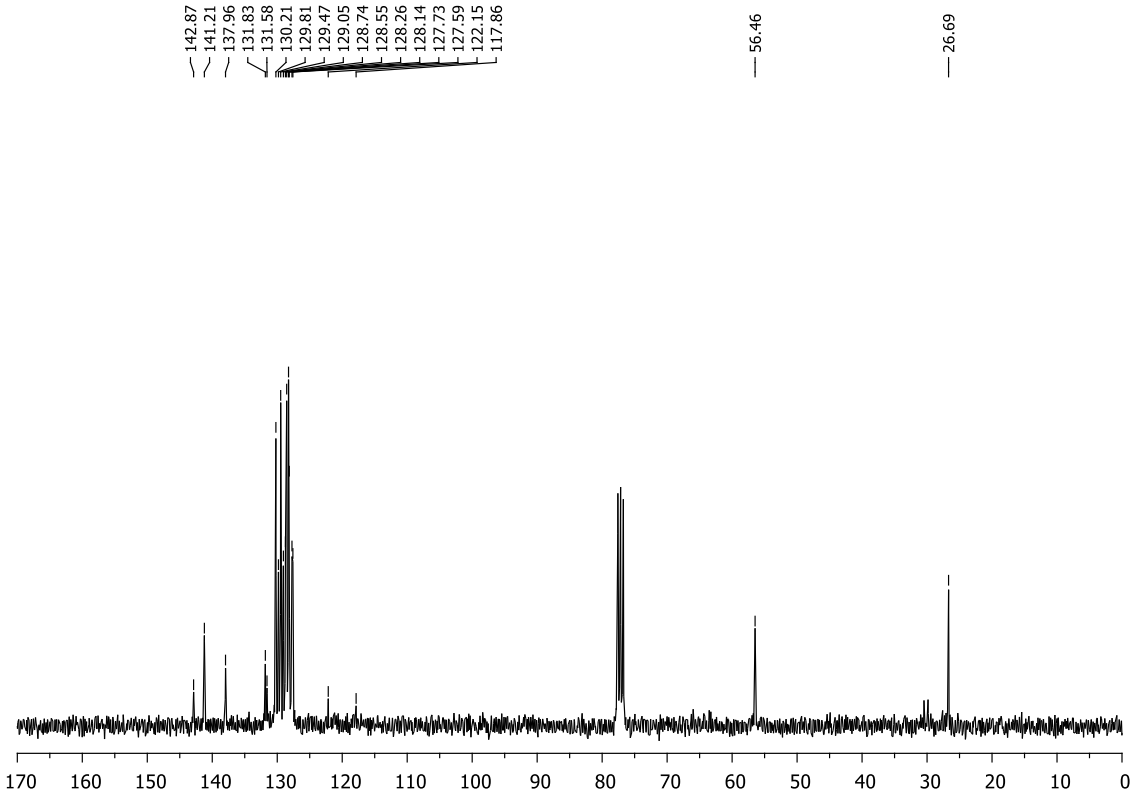
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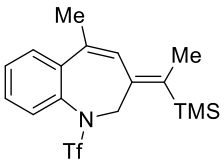
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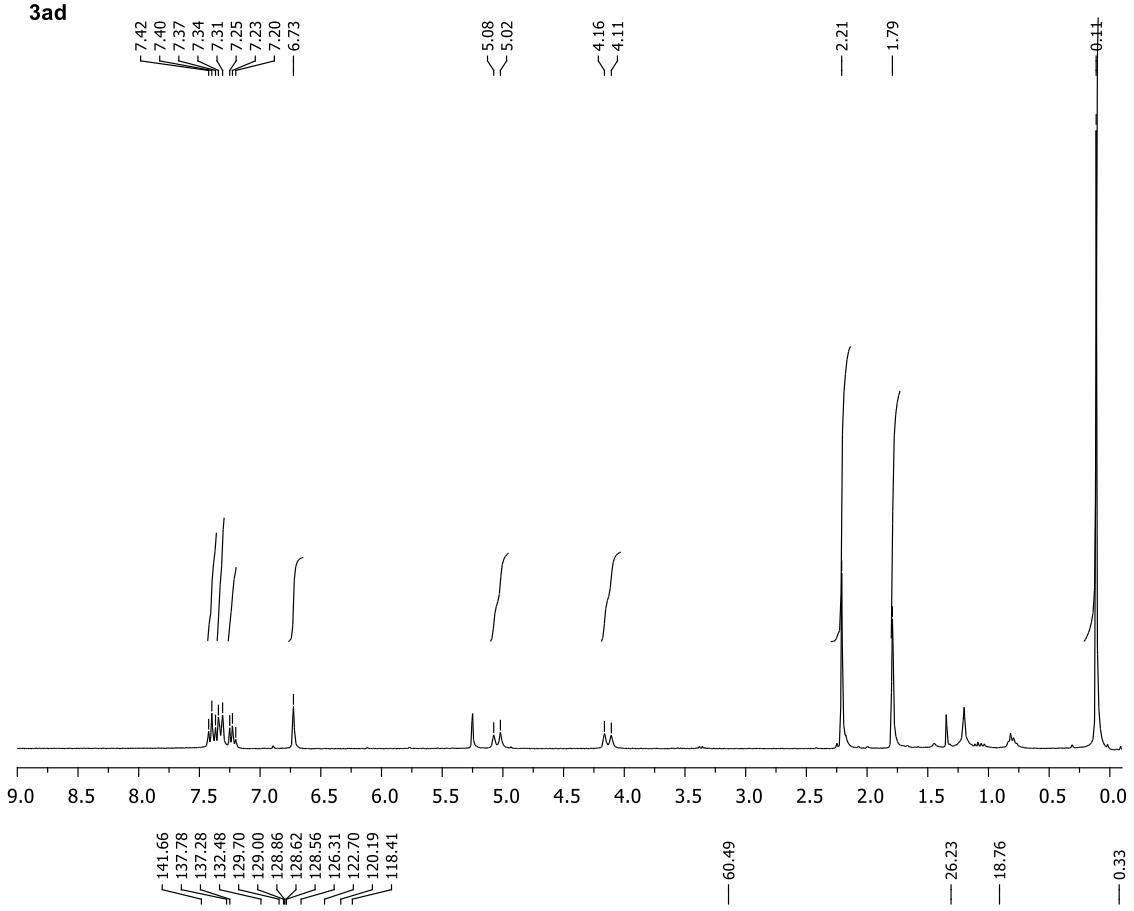
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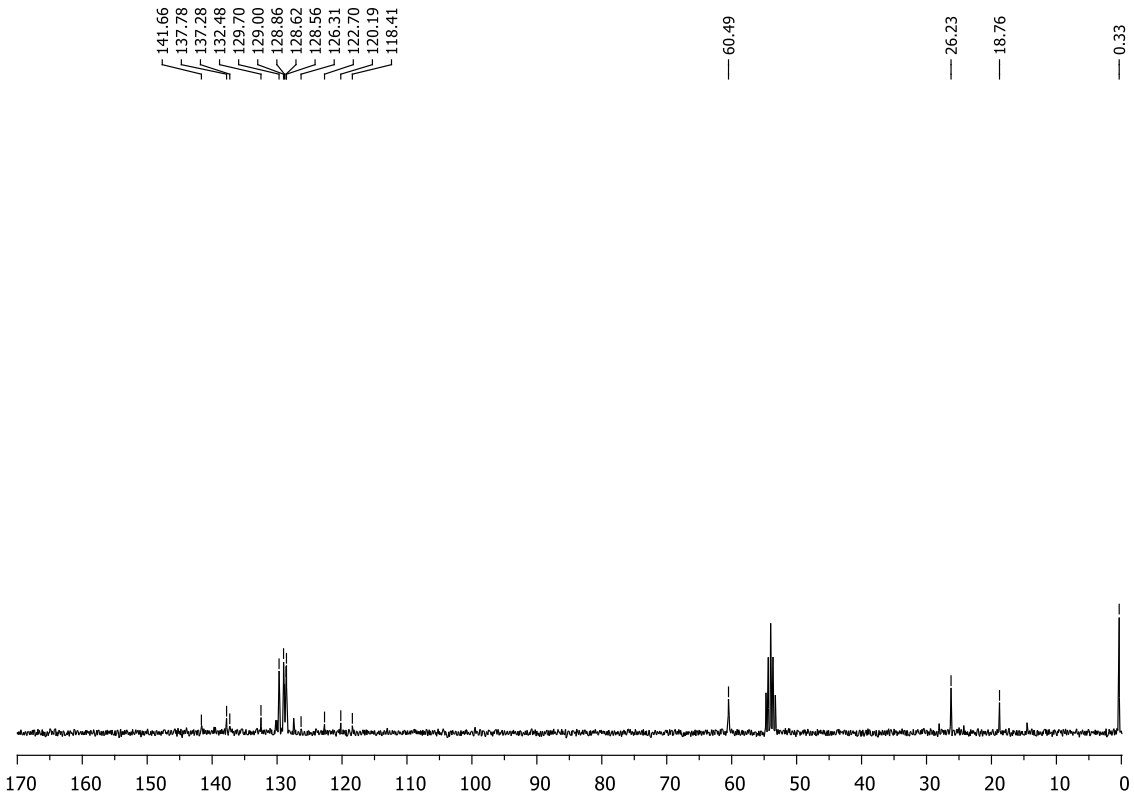
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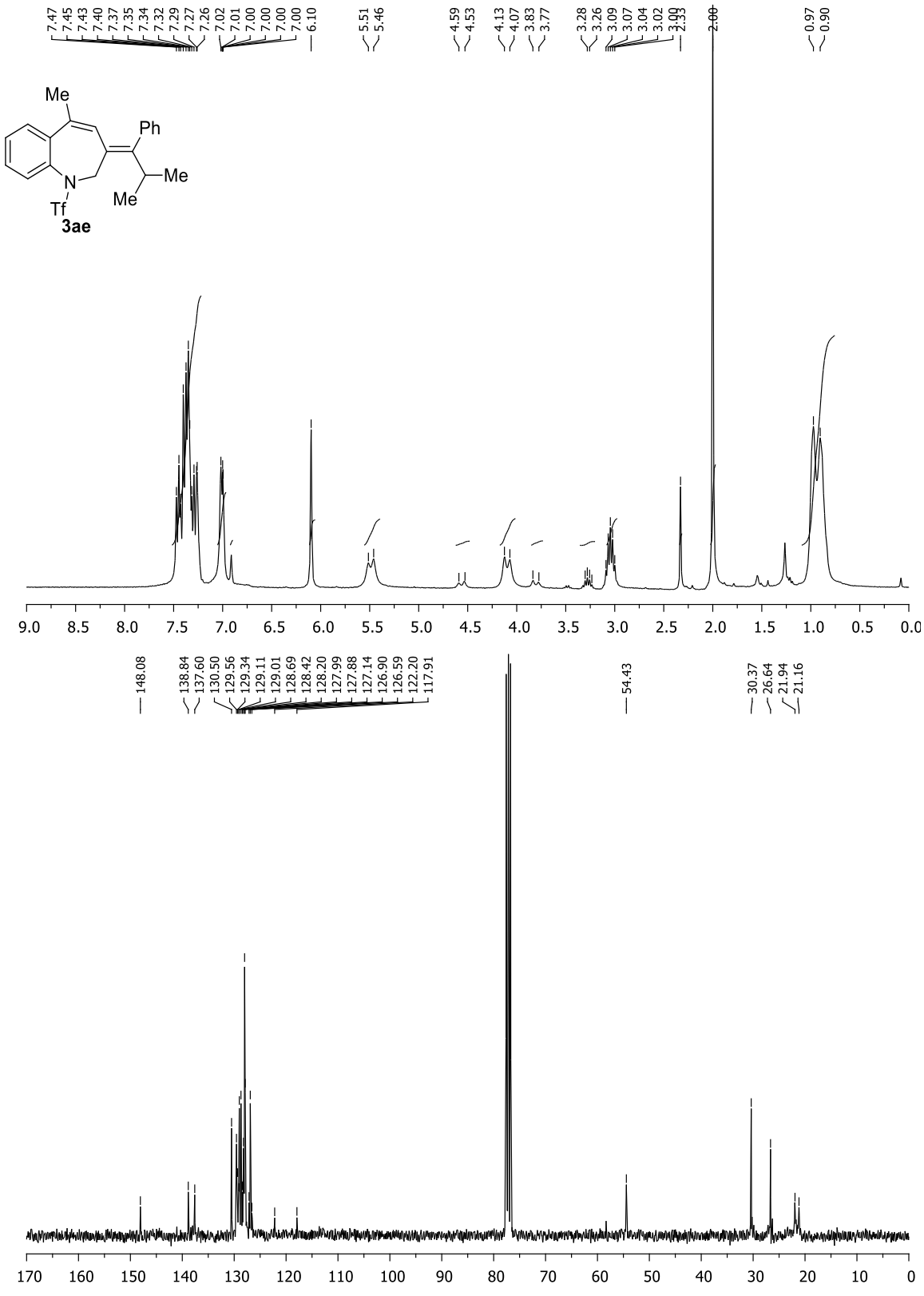
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Ph
Me
Me
N
Tf
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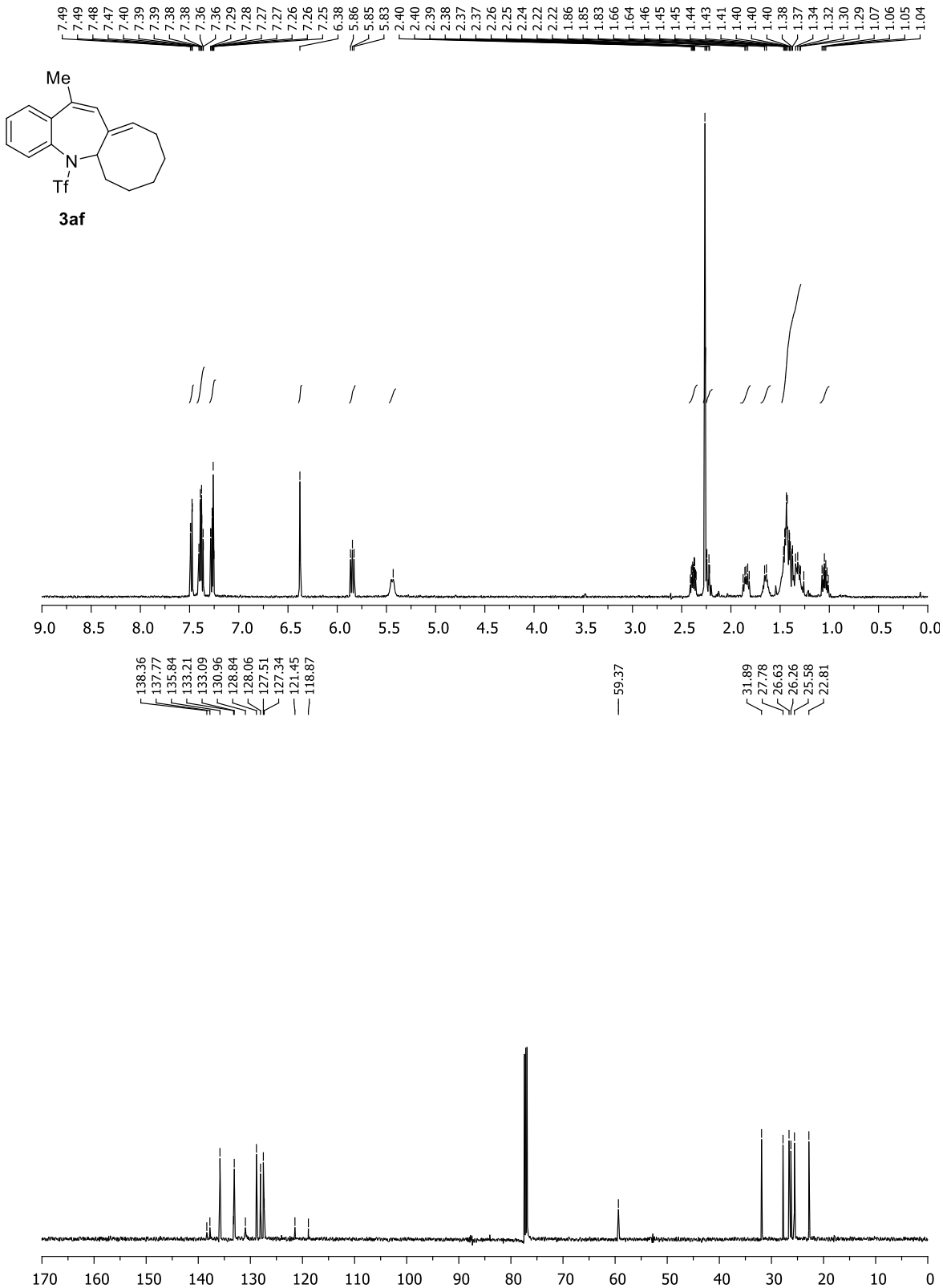
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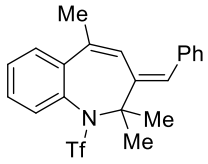
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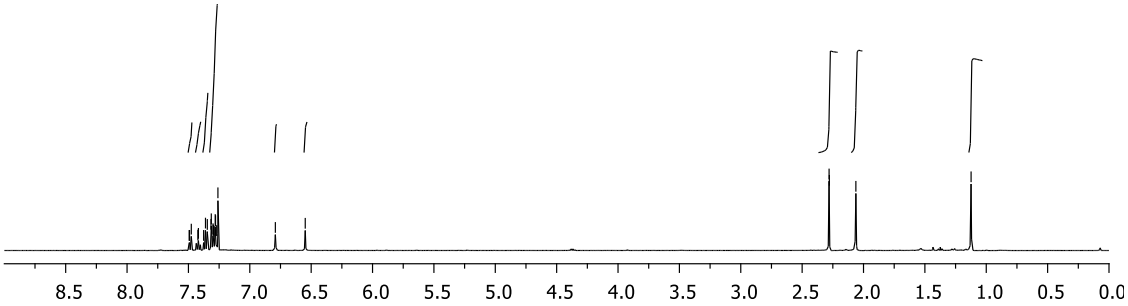
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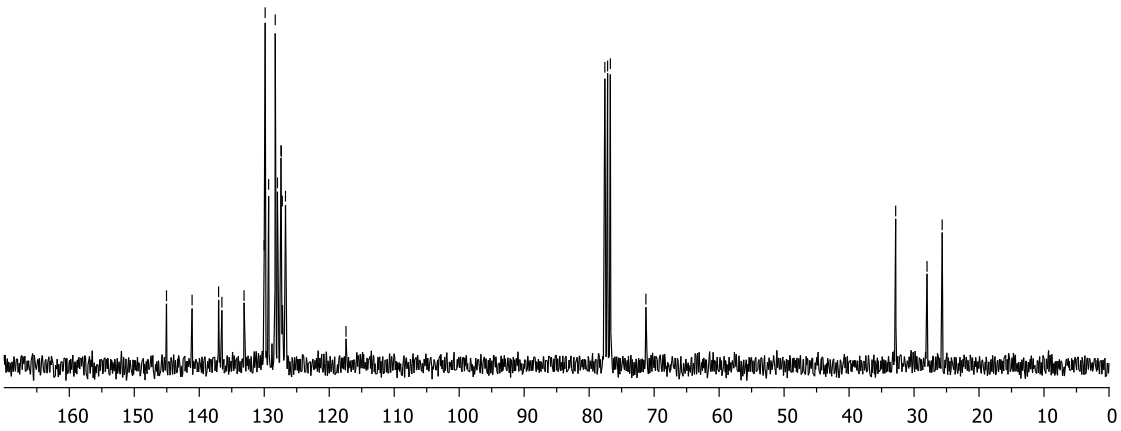
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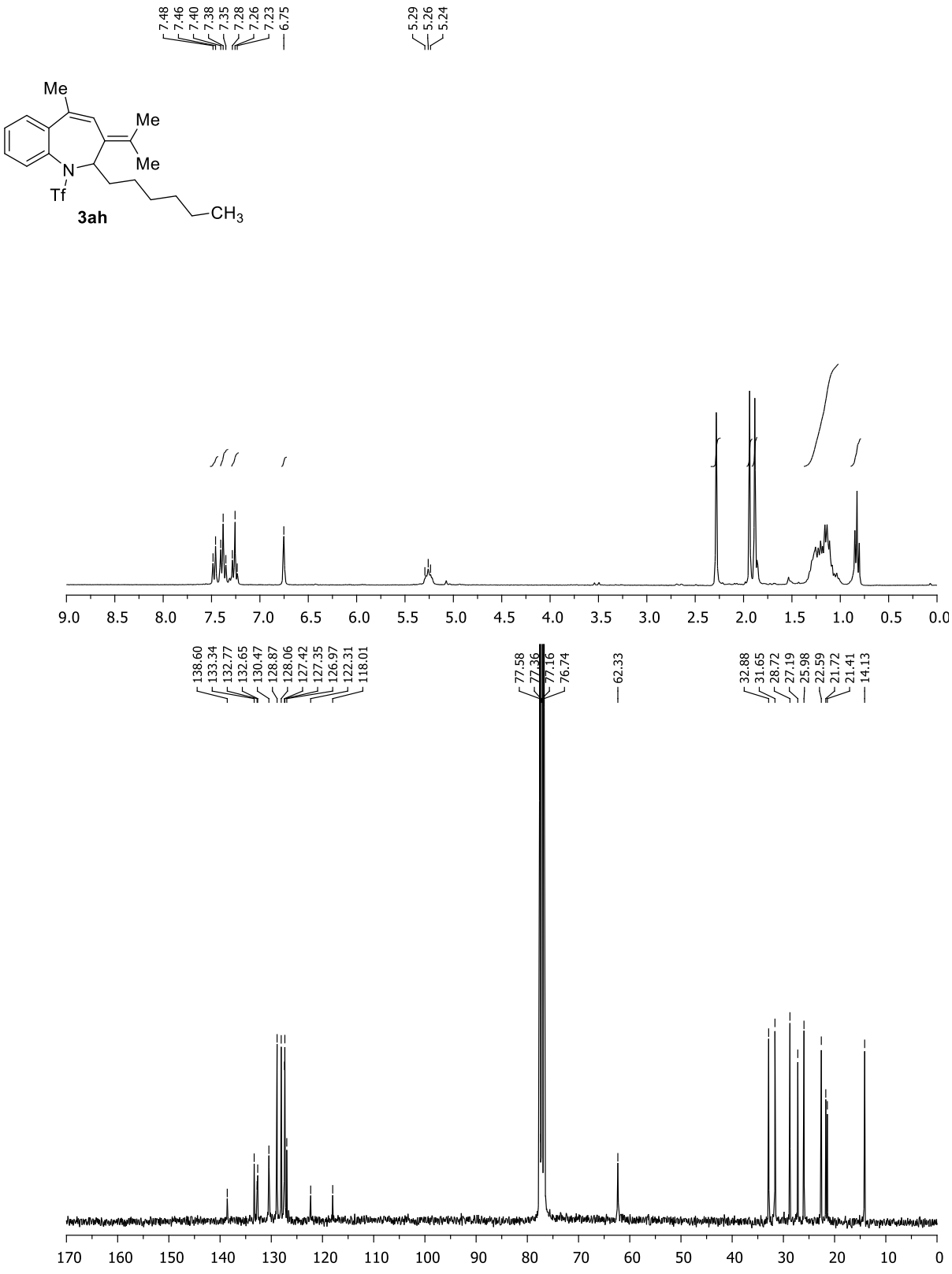
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Me
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Tf
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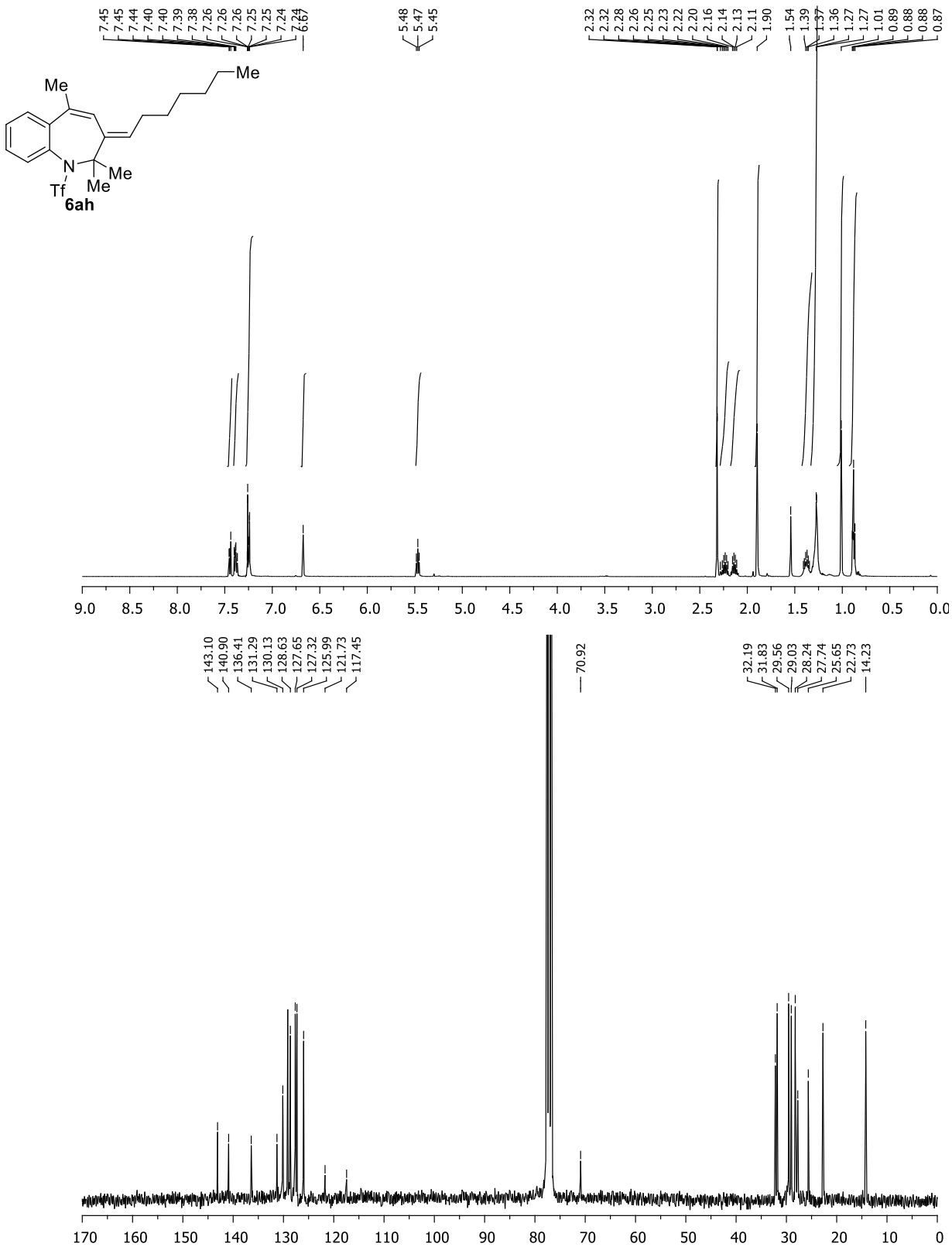
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Me
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Tf
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Me
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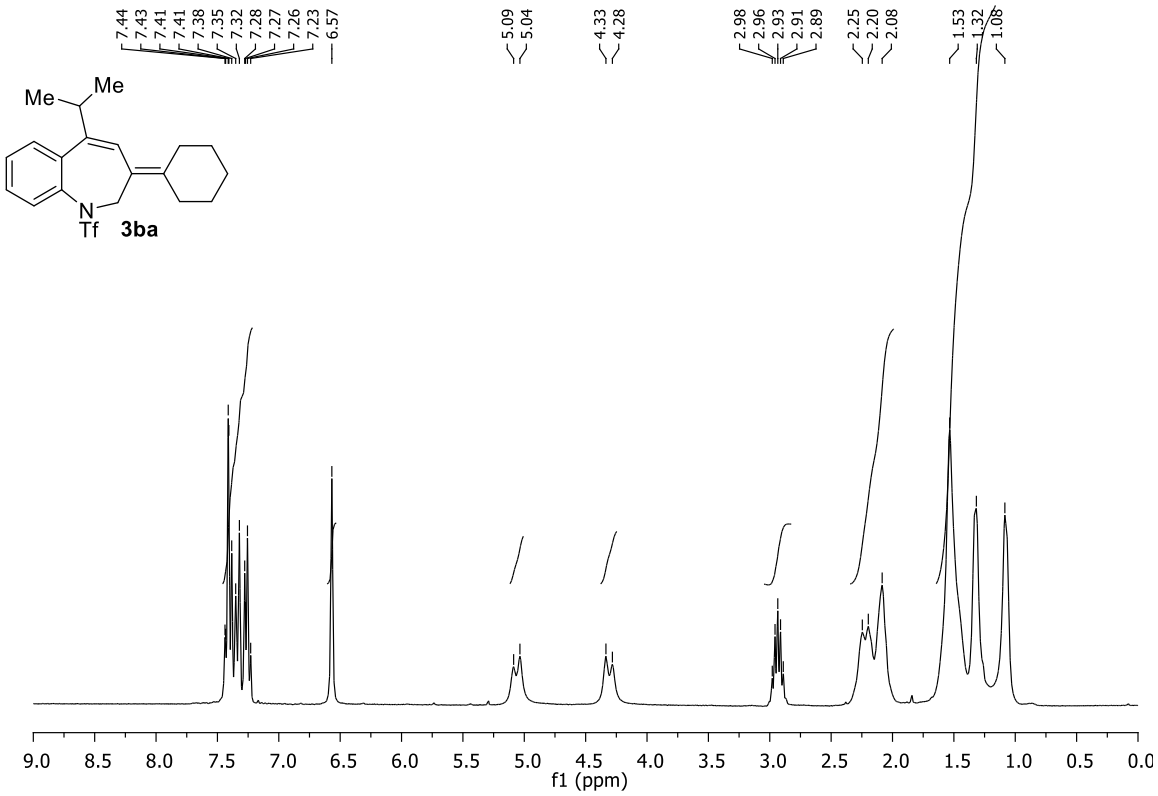
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Me
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Tf
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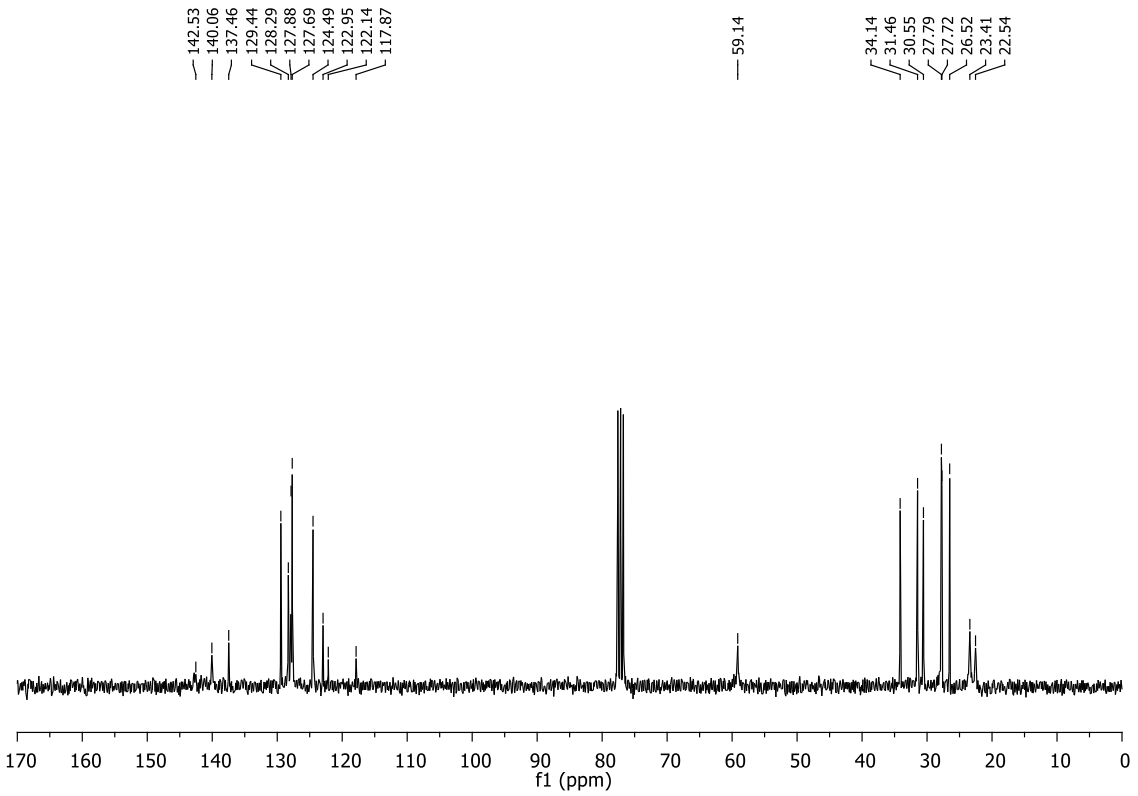
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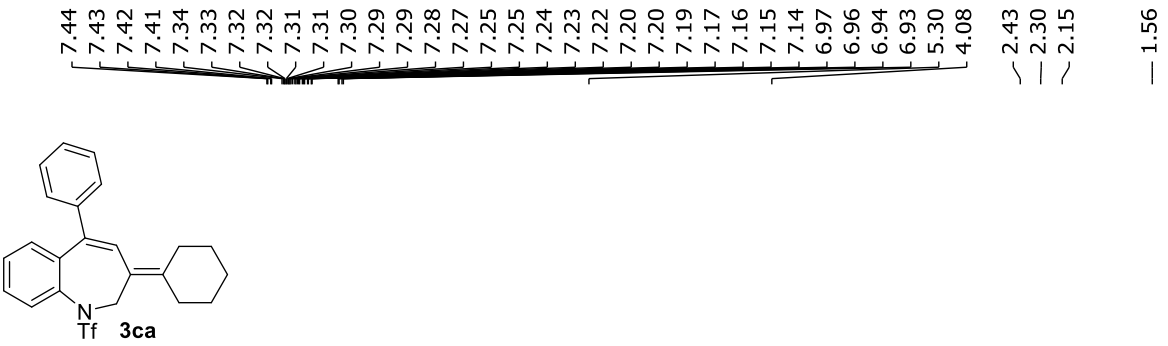
22.54
f1 (ppm)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2.15
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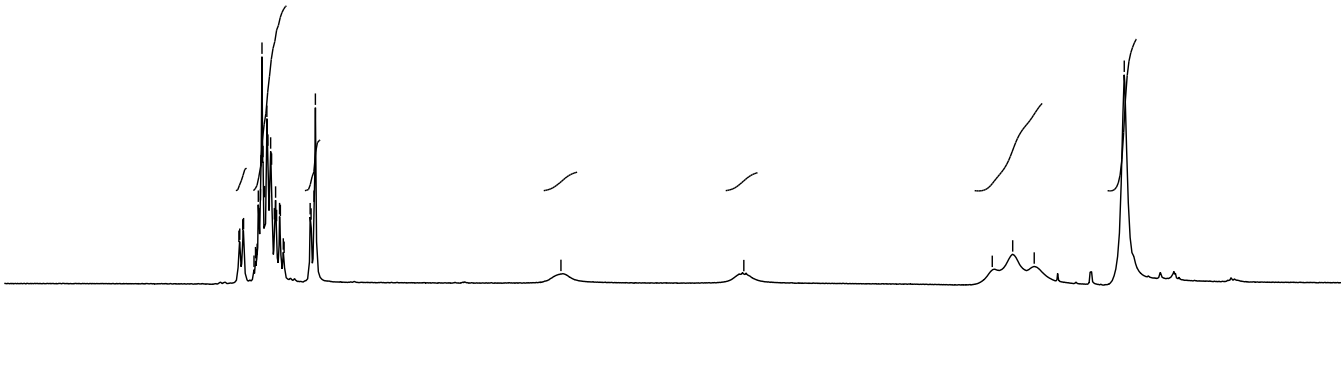
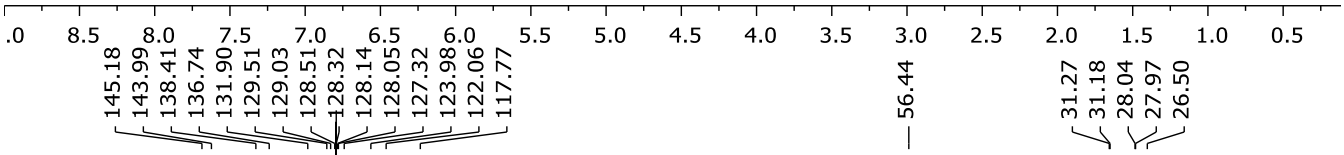
N
Tf

3ca

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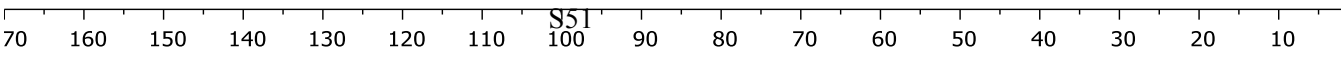
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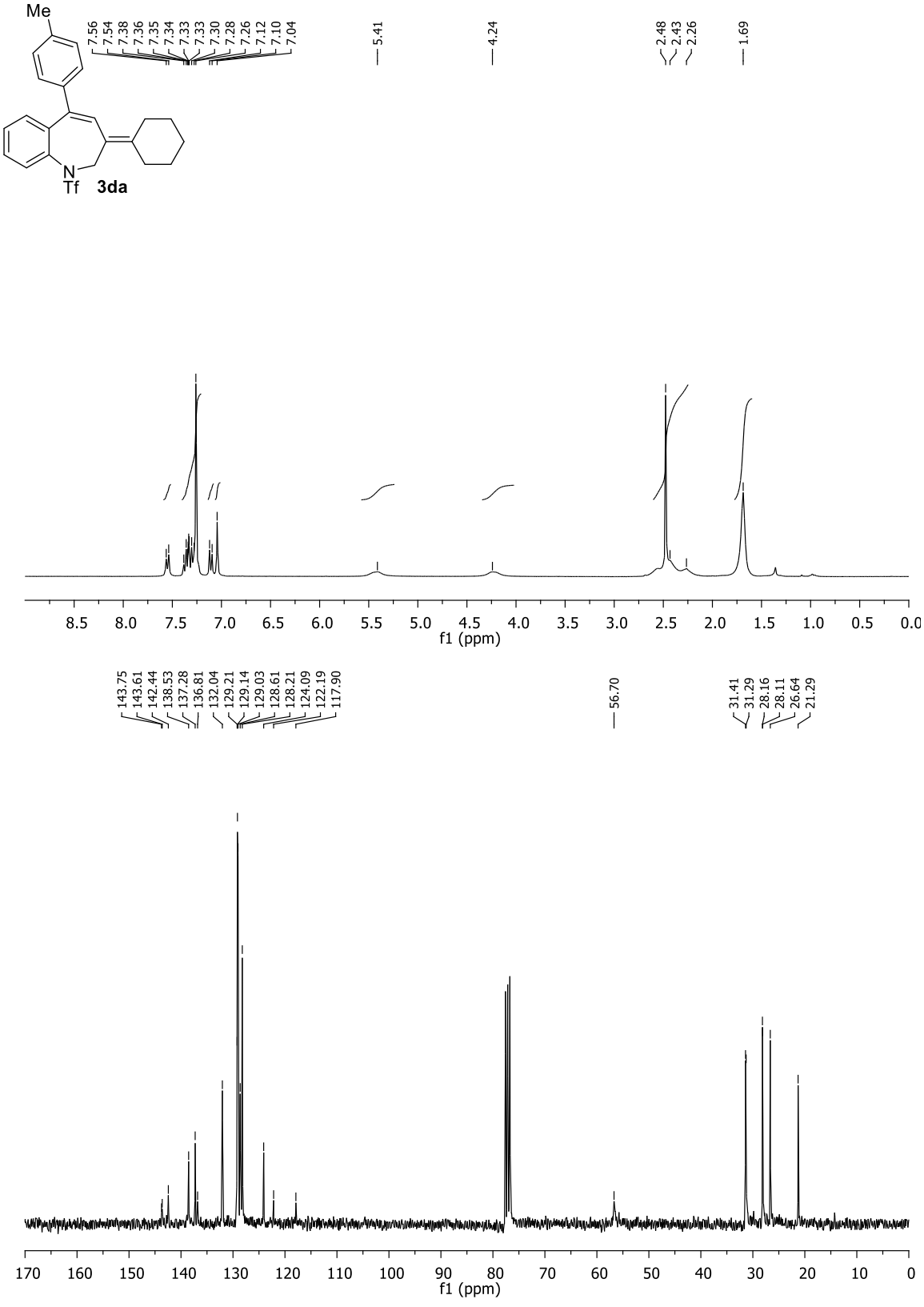
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f1 (ppm)
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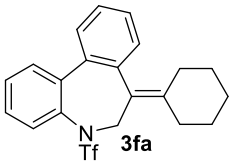
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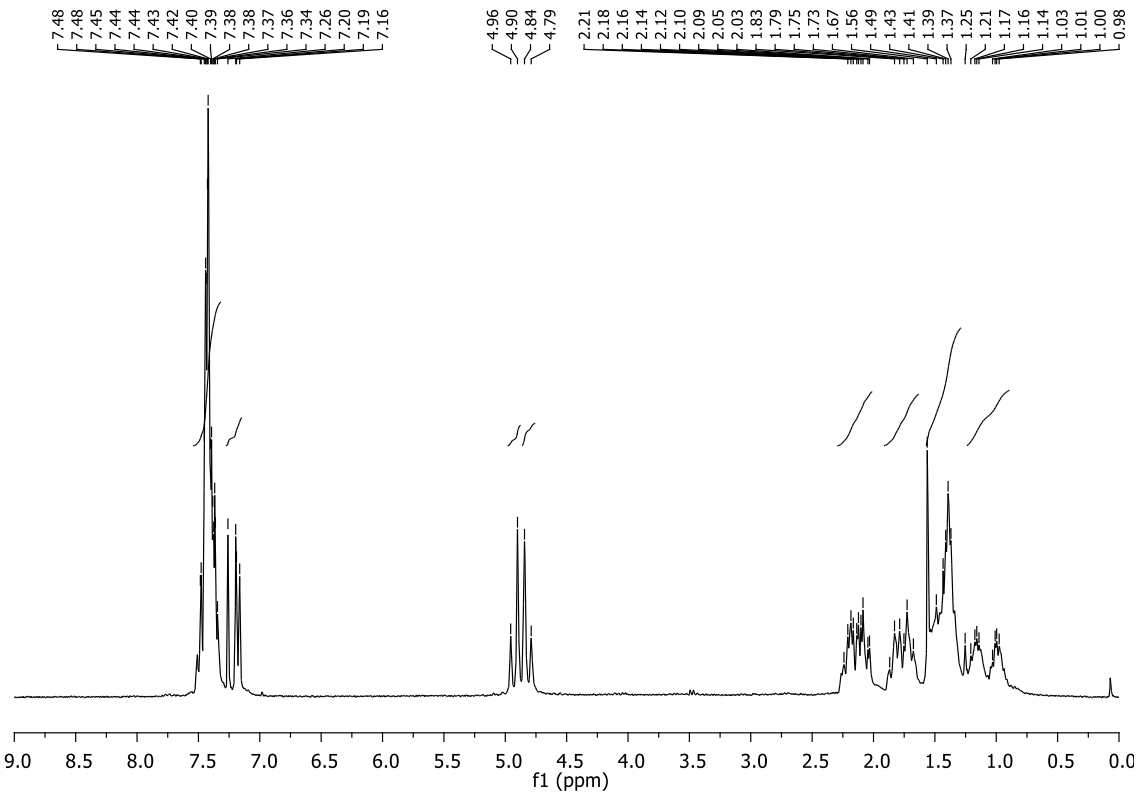
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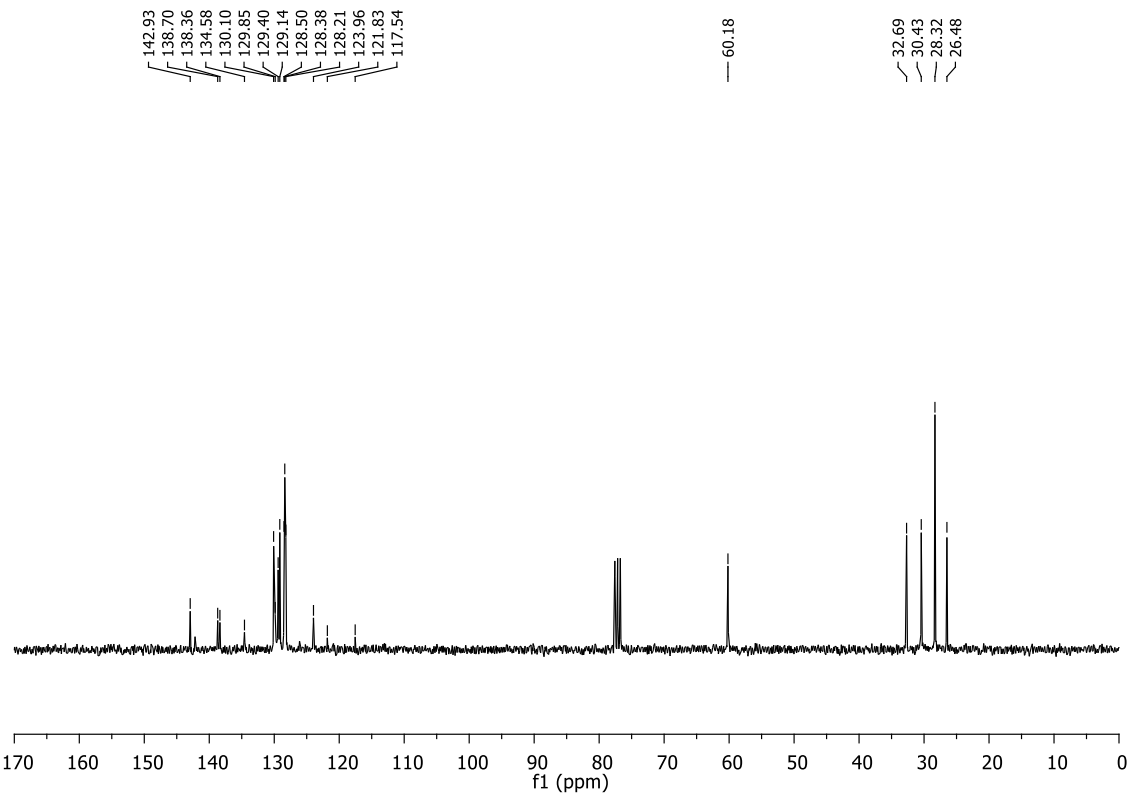
f1 (ppm)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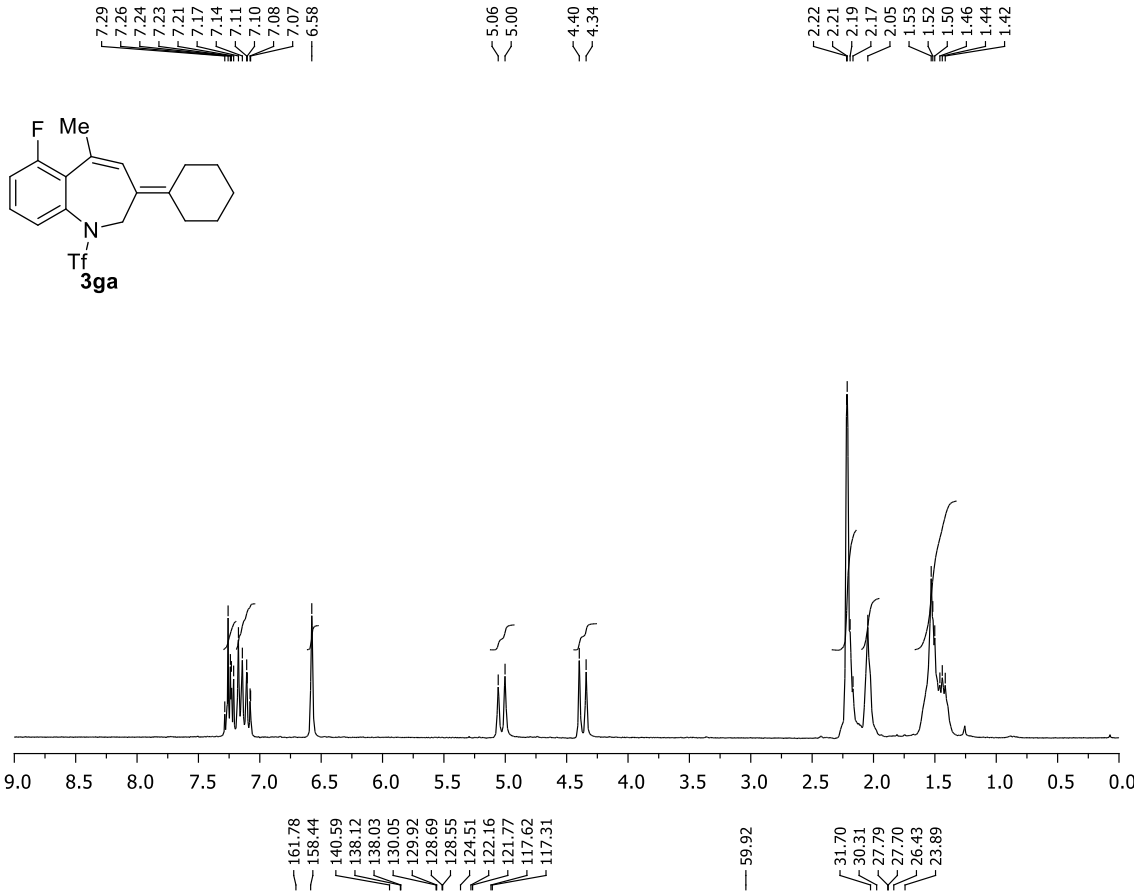
f1 (ppm)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2.17
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Tf
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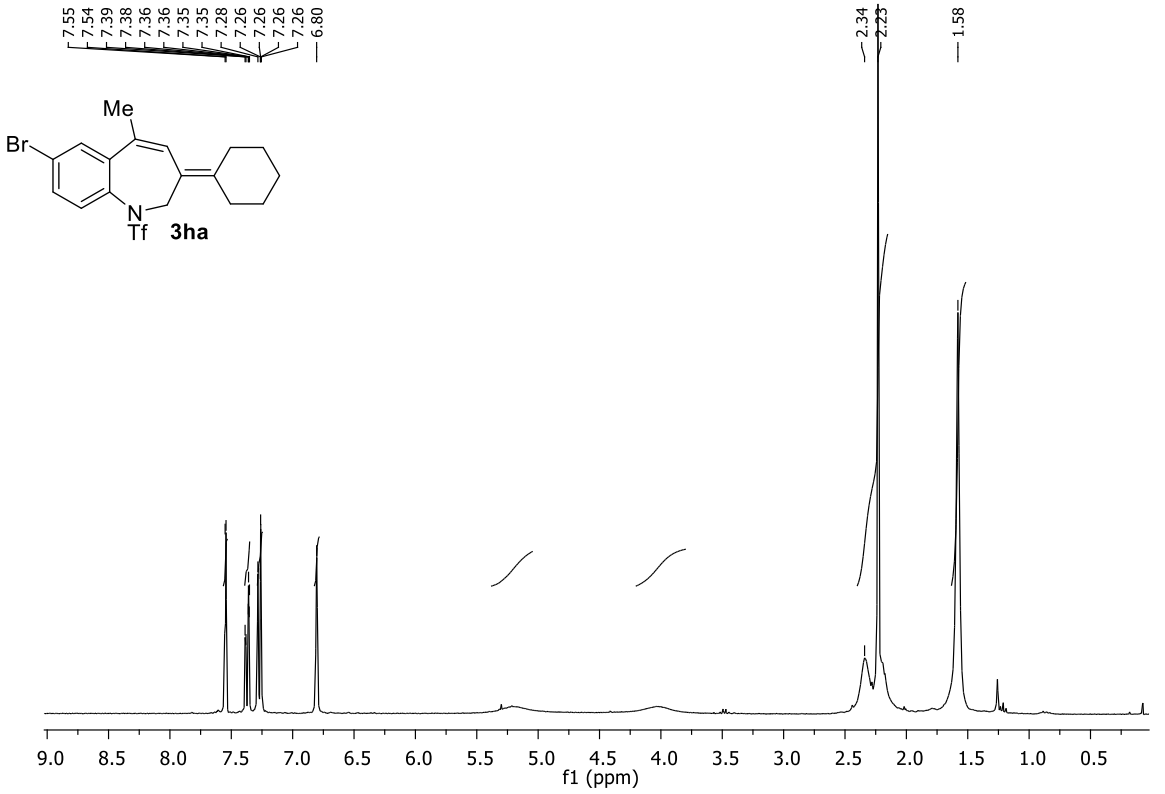
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1.58
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Br
N
Tf
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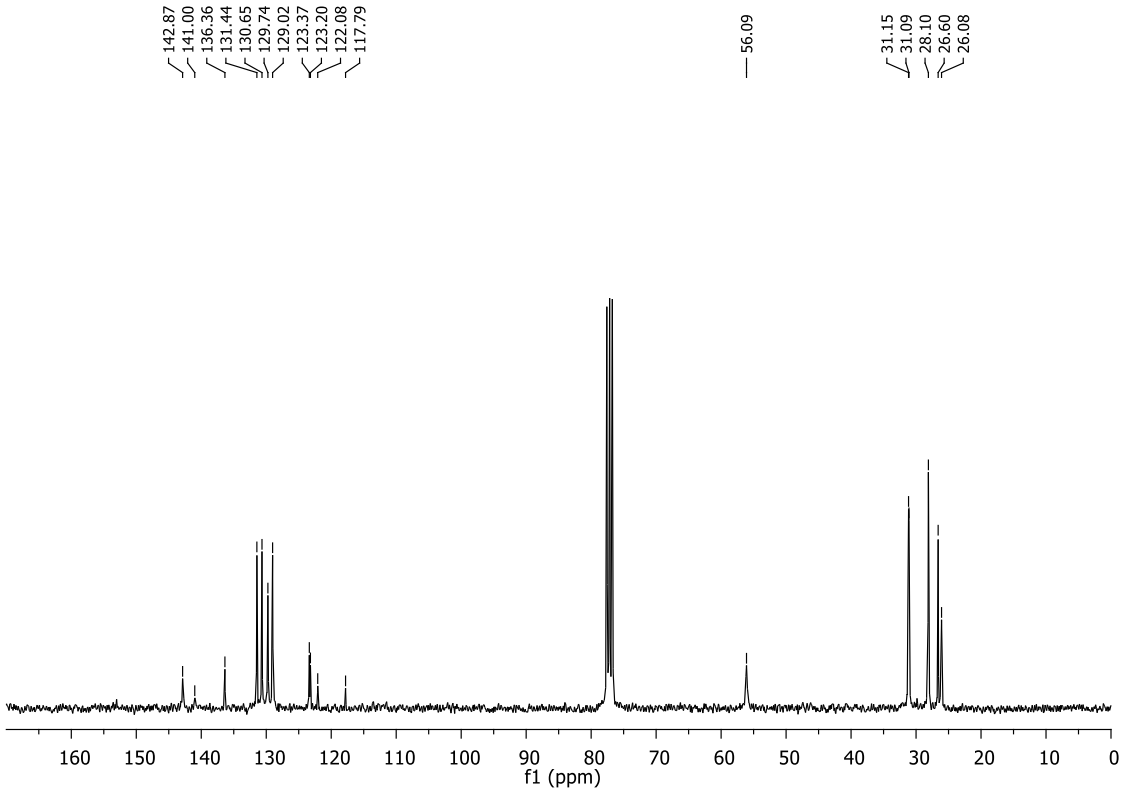
f1 (ppm)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26.60
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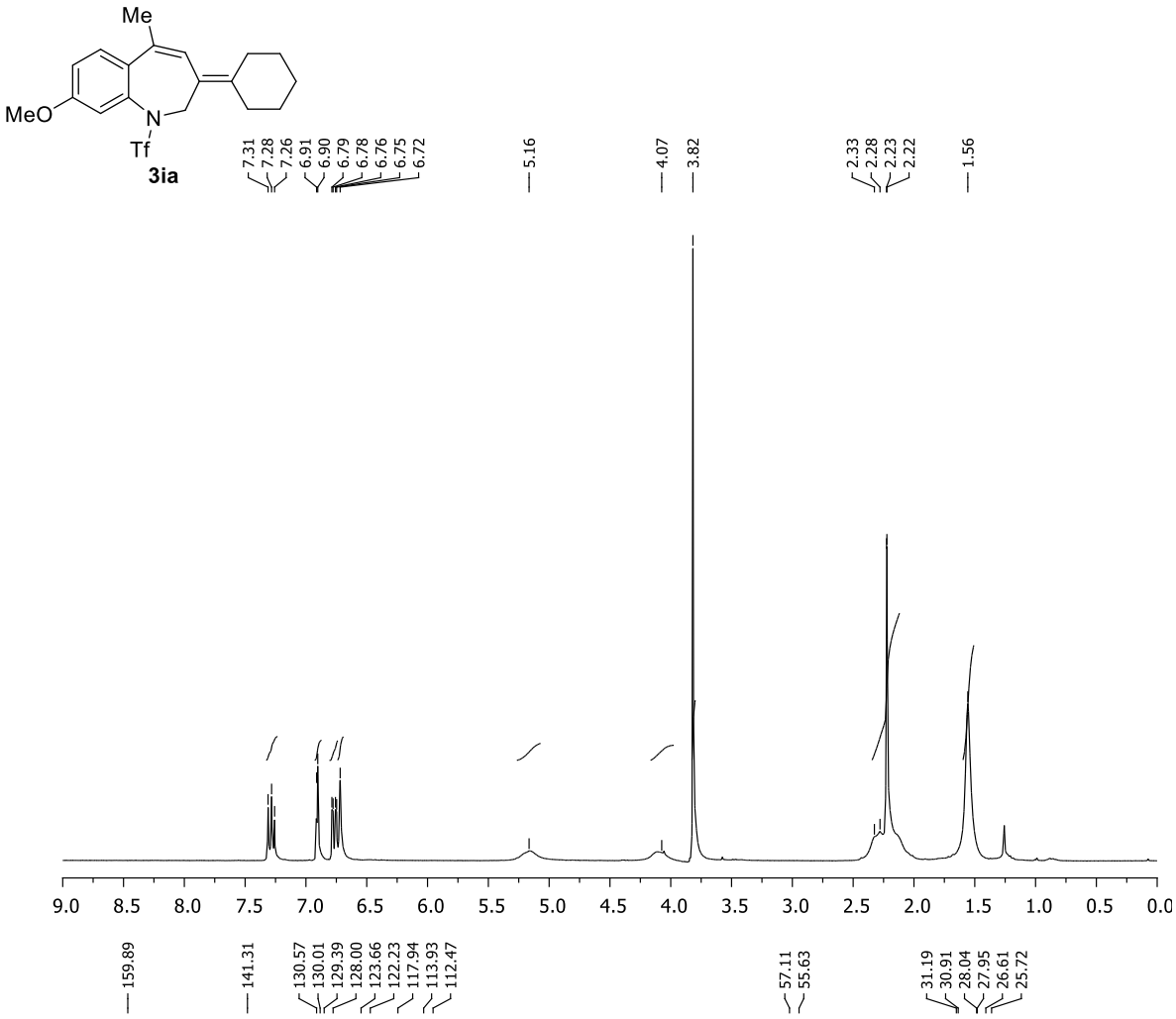
f1 (ppm)


Me
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2.22
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4.5
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
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141.31
130.57
130.01
129.39
128.00
123.66
122.23
117.94
113.93
112.47
57.11
55.63
31.19
30.91
28.04
27.95
26.61
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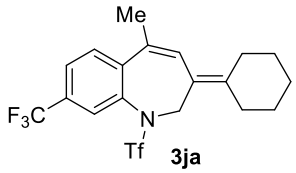
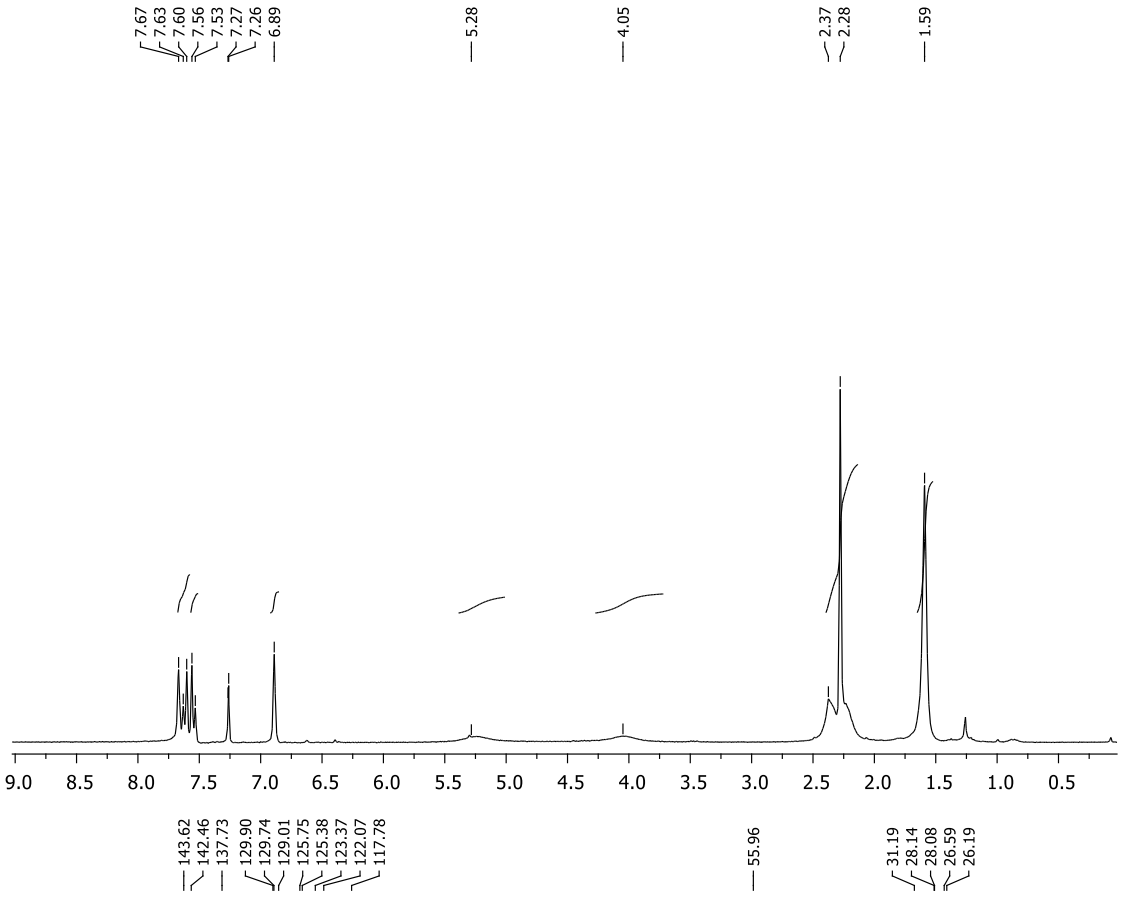

Me
F3C
N
Tf

3ja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7.60
7.56
7.53
7.27
7.26
6.89
5.28
4.05
2.37
2.28
1.59
9.0
8.5
8.0
7.5
7.0
6.5
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3.0
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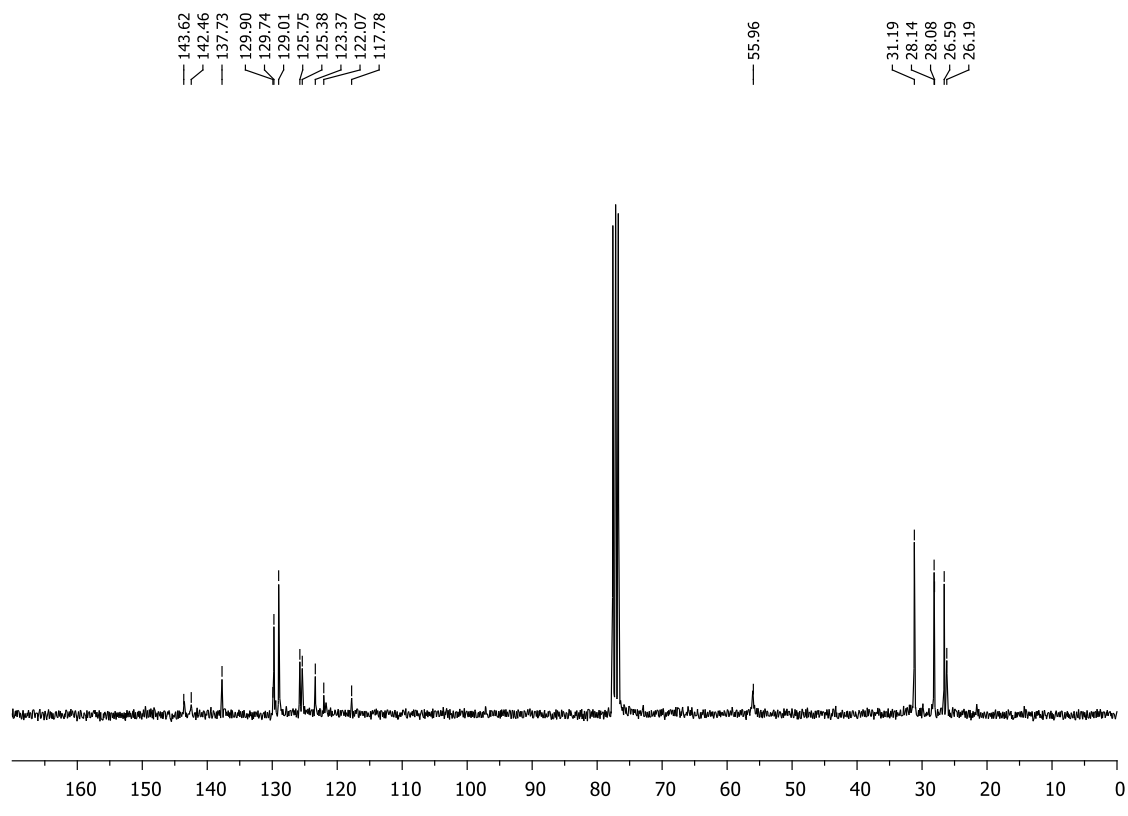
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129.01
125.75
125.38
123.37
122.07
117.78
55.96
31.19
28.14
28.08
26.59
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150
140
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120
110
100
90
80
70
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30
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10
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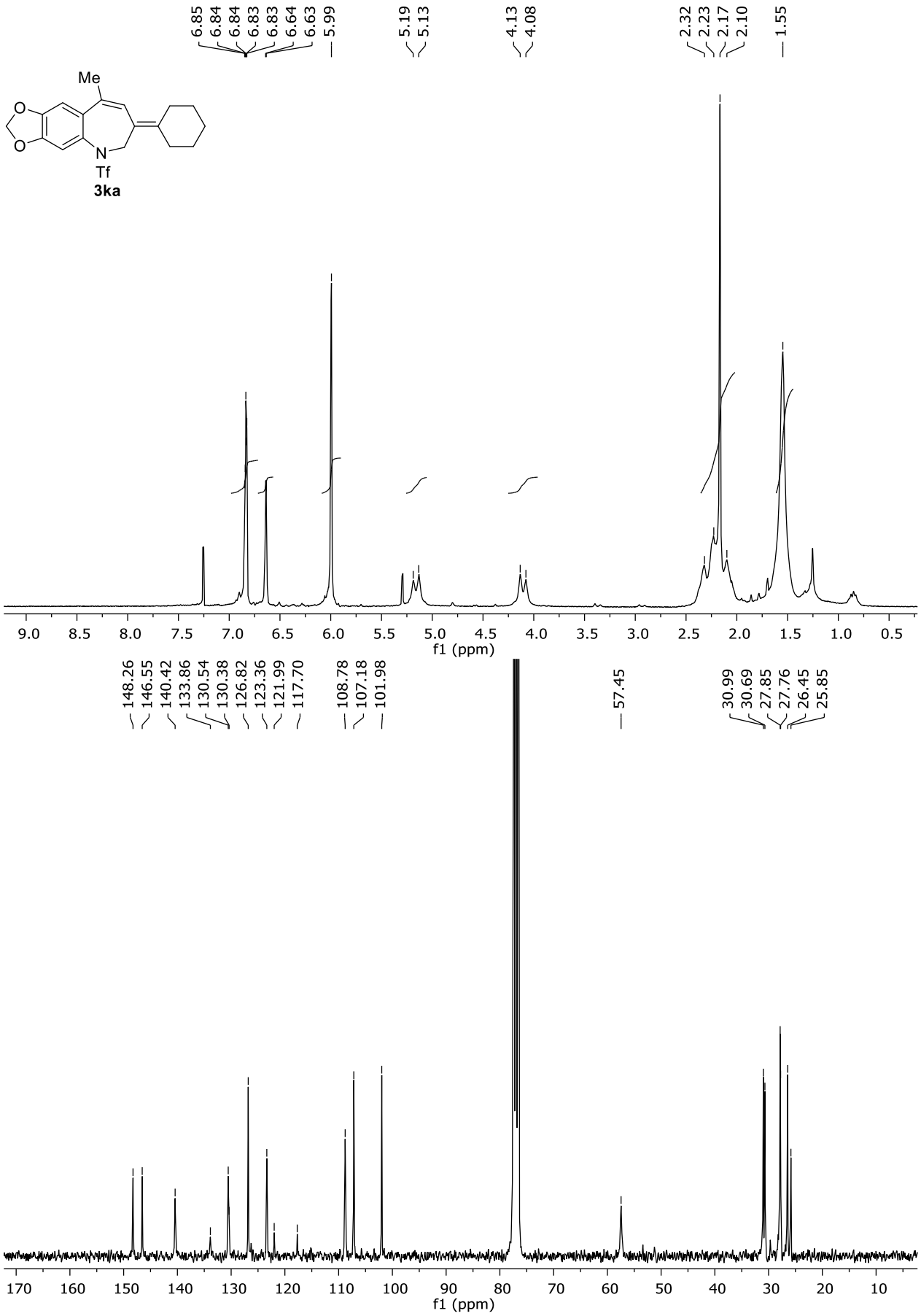
6.85
6.84
6.84
6.83
6.83
6.64
6.63
5.99
5.19
5.13
4.13
4.08
2.32
2.23
2.17
2.10
1.55
Me
O
O
N
Tf
3ka
f1 (ppm)
148.26
146.55
140.42
133.86
130.54
130.38
126.82
123.36
121.99
117.70
108.78
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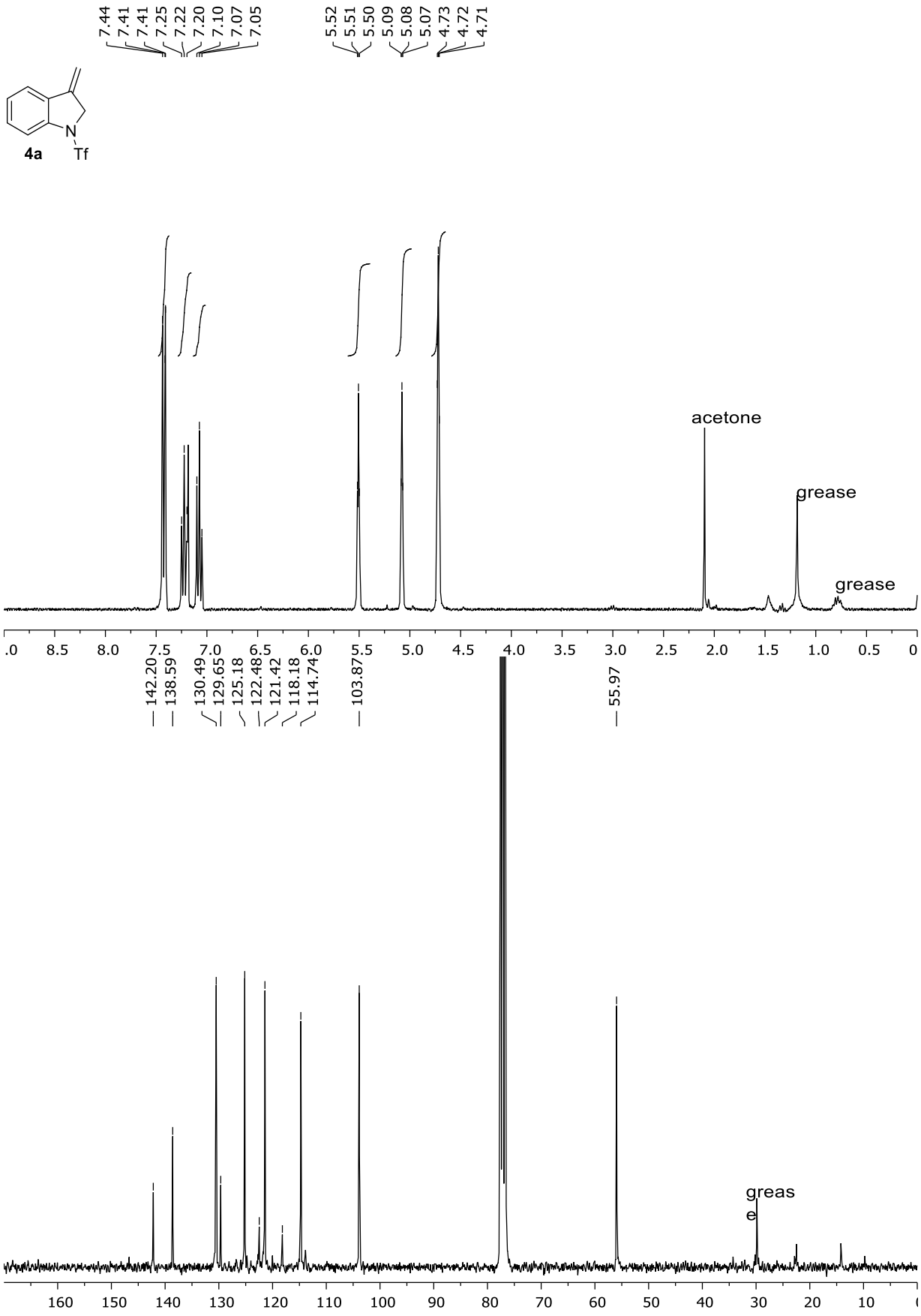
101.98
57.45
30.99
30.69
27.85
27.76
26.45
25.85
f1 (ppm)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7.25
7.22
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7.07
7.05
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5.51
5.50
5.09
5.08
5.07
4.73
4.72
4.71
N
Tf
4a
acetone
grease
grease
142.20
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125.18
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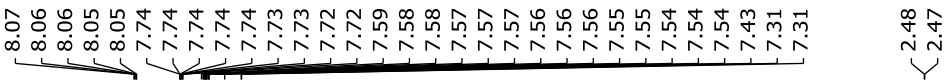
114.74
103.87
55.97
greas
e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8.06
8.05
8.05
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7.74
7.74
7.74
7.74
7.73
7.73
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7.72
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7.58
7.58
7.57
7.57
7.57
7.56
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7.55
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7.54
7.54
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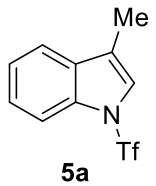
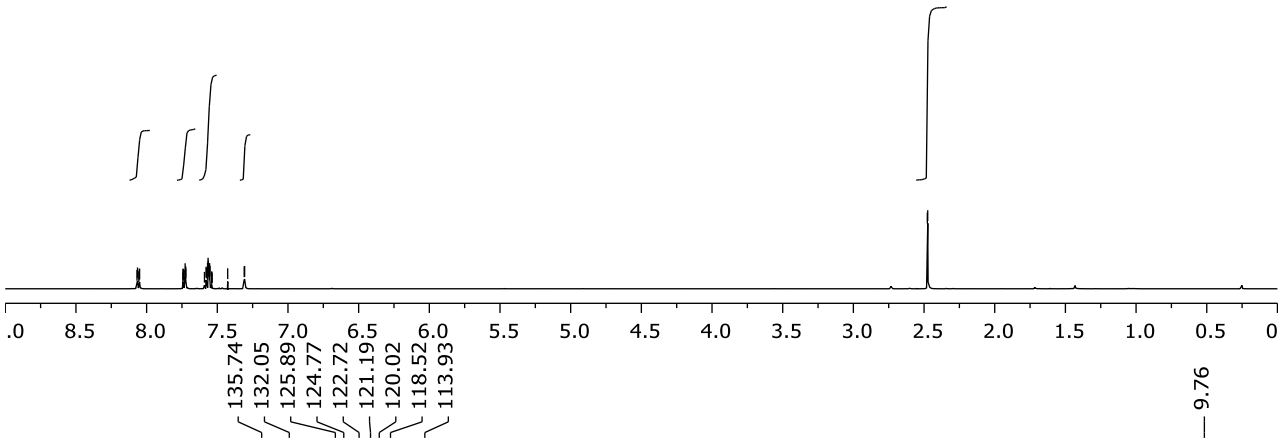
7.31
2.48
2.47


Me
N
Tf

5a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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
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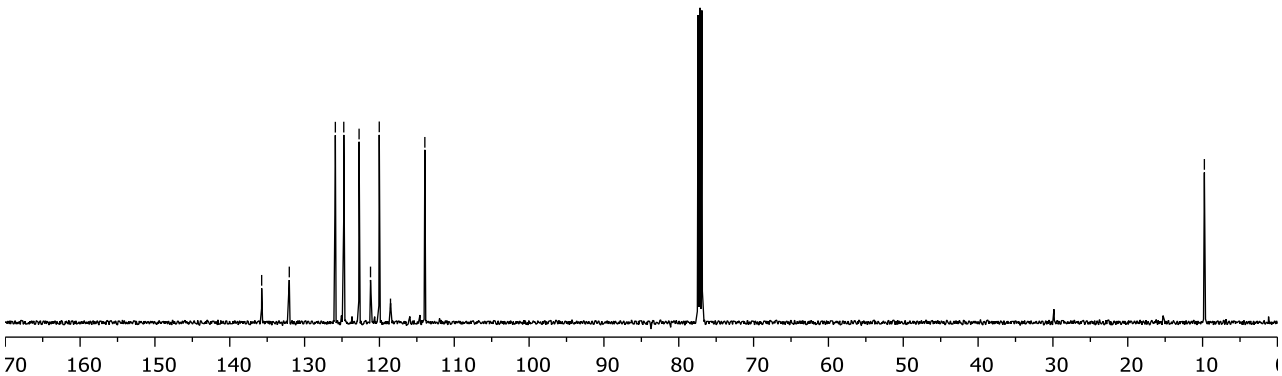
132.05
125.89
124.77
122.72
121.19
120.02
118.52
113.93
9.76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150
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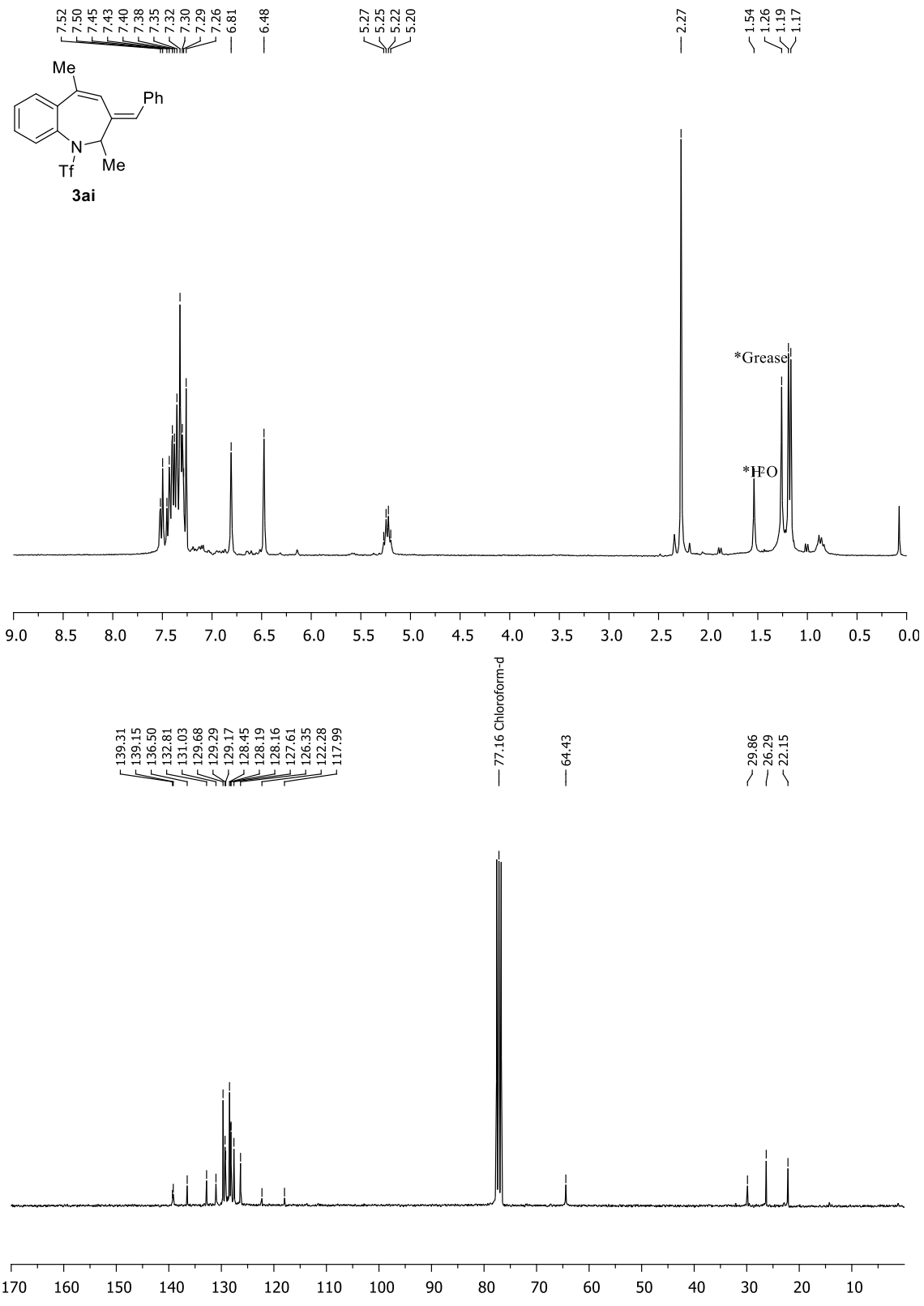
130
120
110
100
90
80
70
60
50
40
30
20
10


7.52
7.50
7.45
7.43
7.40
7.38
7.35
7.32
7.30
7.29
7.26
6.81
6.48
5.27
5.25
5.22
5.20
2.27
1.54
1.26
1.19
1.17
Me
Ph
N
Tf
Me
3ai
*Grease
*H2O
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
139.31
139.15
136.50
132.81
131.03
129.68
129.29
129.17
128.45
128.19
128.16
127.61
126.35
122.28
117.99
77.16 Chloroform-d
64.43
29.86
26.29
22.15
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10