Electronic Supplementary Information

Iron porphyrin catalysed light driven C-H bond amination and alkene aziridination with organic azides

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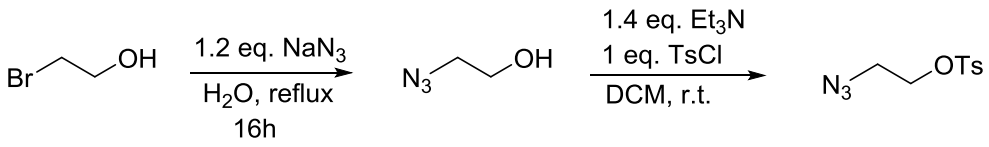
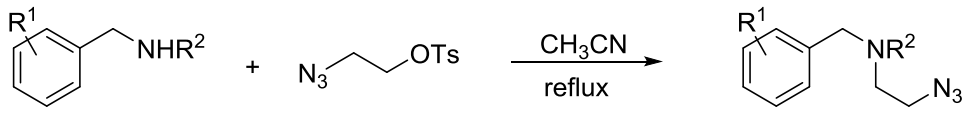
General information

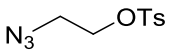
All reactions were performed using the standard Schlenk technique under an argon atmosphere. Reagents obtained commercially were used without further purification unless indicated otherwise. The substrates,[1,2,3] aryl azides,[4,5,6] alkyl azides,[7] and $Fe^{III}(TF_4DMAP)Cl$[8] were prepared following literature procedures or were obtained commercially. All solvents used in the reaction were dried and freshly distilled. Flash chromatography was performed using Merck silica gel 60 and a gradient solvent system (Et_2O / *n*-hexane or EtOAc / *n*-hexane as eluent). ^1H, ^{19}F and ^{13}C NMR spectra were measured on a Bruker DPX-500, DPX-400 or DPX-300 spectrometer. ^1H NMR chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. ^{13}C NMR chemical shifts were determined relative to $CDCl_3$ at δ 77.16. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad), coupling constant (Hz), integration. ^{13}C NMR spectra were reported as chemical shifts in ppm and multiplicity where appropriate. GC-MS analysis was performed by Agilent Technologies 7890B GC system with 5977A MS detector. Positive-ion mode electron-impact (EI) mass spectra were recorded on a Thermo Scientific DFS high resolution magnetic sector MS. Low-resolution and high-resolution ESI-MS (positive-ion mode) measurements were recorded on a Finnigan LCQ quadrupole ion trap mass spectrometer and a Waters Micromass Q-Tof Premier quadrupole time-of-flight tandem mass spectrometer, respectively. All absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Nanosecond time-resolved emission measurements were performed on a LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd., Livingston, UK). The excitation source was the 355 nm output (third harmonic) of a Nd:YAG laser (Spectra-Physics Quanta-Ray Lab-130 Pulsed Nd:YAG Laser). The signals were processed by a PC plug-in controller with L900 software. The blue LED used for photochemical reaction has an emission maximum at 469 nm with full width at half maximum (FWHM) of 25 nm. The power of the blue LED is 16 W. Upon light irradiation, the temperature of the reaction mixture was found to increase from 25 to 35 ^oC. A 300 W Xe lamp (Asahi Spectra) with a band-pass filter at 420 nm (FWHM at 420 nm = 10 nm) was used for photochemical quantum yield measurements.

Synthesis and characterizations of substrates



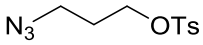


Scheme S1 Synthesis of alkyl azides**.**



The azide was synthesized according to literature. [9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.78 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.17 (t, *J* = 5.1 Hz, 2H), 3.49 (t, *J* = 5.1 Hz, 2H), 2.46 (s, 3H). For detailed characterizations, see ref. 9.

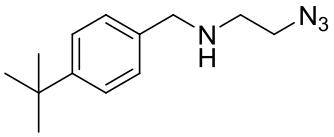


The azide was synthesized according to literature. [9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.76 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.10 (t, *J* = 5.9 Hz, 2H), 3.38 (t, *J* = 6.5 Hz, 2H), 2.45 (s, 3H), 1.88 (p, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 132.8, 130.1, 128.0, 67.1, 47.4, 28.6, 21.8.

General procedure for the synthesis of alkyl azides: [10]

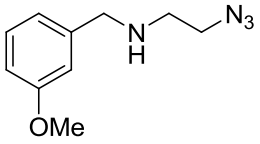
To a solution of 2-azidoethyl 4-methylbenzenesulfonate (0.615 g, 2.55 mmol) in acetonitrile (15.0 mL) was added benzylamine (6.0 mmol). The stirred mixture was heated at reflux temperature for 16 h. After cooling to room temperature, solvent was removed under vacuum and the crude product was purified by silica gel column chromatography.



7a

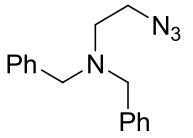
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 2H), 7.28 – 7.21 (m, 2H), 3.78 (s, 2H), 3.42 (t, *J* = 4.0 Hz, 2H), 2.82 (t, *J* = 4.0 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 137.0, 127.9, 125.5, 53.3, 51.6, 48.1, 34.6, 31.5; EI-MS: *m/z* 232 (M^+); EI-HRMS for $[C_{13}H_{20}N_4]^+$

(M^+): *m/z* Calcd. 232.1682, Found: 232.1677.



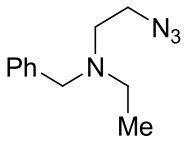
7b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.21 (m, 1H), 6.92 – 6.87 (m, 2H), 6.82 – 6.79 (m 1H), 3.81 (s, 3H), 3.80 (s, 2H), 3.43 (td, *J* = 5.6, 1.1 Hz, 2H), 2.82 (td, *J* = 5.6, 1.1 Hz, 2H), 1.61 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 141.7, 129.6, 120.4, 113.6, 112.8, 55.3, 53.6, 51.6, 48.1; EI-MS: *m/z* 206 (M^+); EI-HRMS for $[C_{10}H_{14}N_4O]^+$ (M^+): *m/z* Calcd. 206.1162, Found: 206.1154.



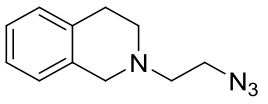
7c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.35 (m, 4H), 7.35 – 7.29 (m, 4H), 7.28 – 7.21 (m, 2H), 3.63 (s, 4H), 3.24 (t, *J* = 6.1 Hz, 2H), 2.70 (t, *J* = 6.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.1, 128.9, 128.5, 127.3, 59.0, 53.1, 49.4; EI-MS: *m/z* 266 (M^+); EI-HRMS for $[C_{16}H_{18}N_4]^+$ (M^+): *m/z* Calcd. 266.1526, Found: 266.1534.



7d

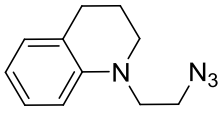
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 4H), 7.27 – 7.21 (m, 1H), 3.63 (s, 2H), 3.23 (t, *J* = 6.1 Hz, 2H), 2.69 (t, *J* = 6.1 Hz, 2H), 2.58 (q, *J* = 7.1 Hz, 2H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 128.9, 128.4, 127.1, 58.6, 52.9, 49.5, 48.0, 11.9; EI-MS: *m/z* 204 (M^+); EI-HRMS for $[C_{11}H_{16}N_4]^+$ (M^+): *m/z* Calcd. 204.1369, Found: 204.1374.



7e

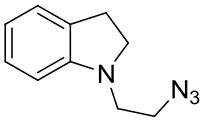
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 – 7.06 (m, 3H), 7.05 – 6.97 (m, 1H), 3.70 (s, 2H), 3.46 (td, *J* = 6.2, 1.3 Hz, 2H), 2.91 (t, *J* = 5.9 Hz, 2H), 2.83 – 2.79 (m, 2H), 2.77 (td, *J* = 6.2, 1.3 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 134.4, 134.3, 128.8, 126.6, 126.3, 125.8, 56.9, 56.2, 51.0, 48.9, 29.1; EI-MS: *m/z* 202 (M^+); EI-HRMS for $[C_{11}H_{14}N_4]^+$ (M^+): *m/z* Calcd. 202.1213, Found: 202.1208.



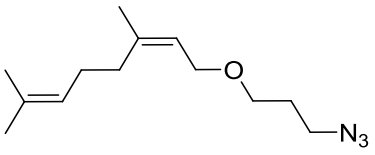
7f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 8.2 Hz, 1H), 3.52 – 3.45 (m, 4H), 3.37 (t, *J* = 4.0 Hz, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.03 – 1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 129.6, 127.3, 122.9, 116.5, 110.4, 51.0, 50.5, 48.6, 28.2, 22.3; EI-MS: *m/z* 202 (M^+); EI-HRMS for $[C_{11}H_{14}N_4]^+$ (M^+): *m/z* Calcd. 202.1213, Found: 202.1220.



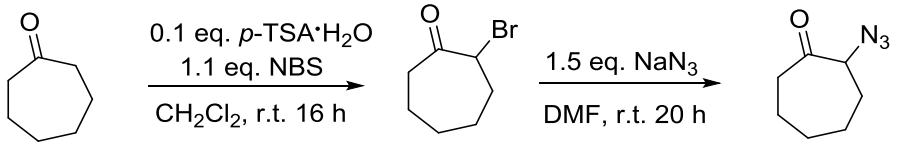
7g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 – 7.05 (m, 2H), 6.68 (td, *J* = 7.4, 1.0 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 1H), 3.47 (t, *J* = 6.1 Hz, 2H), 3.43 (t, *J* = 8.3 Hz, 2H), 3.29 (t, *J* = 6.1 Hz, 2H), 3.00 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 129.9, 127.5, 124.7, 118.1, 106.8, 53.8, 49.5, 49.2, 28.8; EI-MS: *m/z* 188 (M^+); EI-HRMS for $[C_{10}H_{12}N_4]^+$ (M^+): *m/z* Calcd. 188.1056, Found: 188.1051.



7h

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.35 (td, *J* = 6.9, 1.5 Hz, 1H), 5.13 – 5.06 (m, 1H), 3.95 (dd, *J* = 7.0, 1.1 Hz, 2H), 3.49 (t, *J* = 6.1 Hz, 2H), 3.39 (t, *J* = 6.7 Hz, 2H), 2.11 – 2.02 (m, 4H), 1.85 (p, *J* = 6.4 Hz, 2H), 1.76 (d, *J* = 1.1 Hz, 3H), 1.69 (s, 3H), 1.61 (s, 3H)； ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 132.1, 123.9, 121.8, 67.3, 66.8, 48.7, 32.4, 29.5, 26.8, 25.8, 23.6, 17.8; EI-MS: *m/z* 209 $[M\text{-}N_2]^+$; EI-HRMS for $[C_{13}H_{23}NO]^+$ ($[M\text{-}N_2]^+$): *m/z* Calcd. 209.1774, Found: 209.1768.

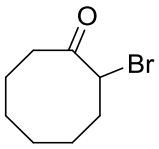


Scheme 2 Synthesis of α-azidoketones.

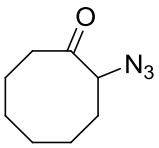
General procedure for the synthesis of α-azidoketones:

Step 1: To a solution of cycloheptanone (5.0 g, 44.6 mmol, 1.0 eq) in CH_2Cl_2 (50 mL) was added *p*-toluenesulfonic acid monohydrate (84 mg, 0.446 mmol, 0.1 eq). The reaction was cooled down with an ice bath and NBS (8.7 g, 49.1 mmol, 1.1 eq) was added. The reaction was stirred for 16 h and quenched with 20 mL of aqueous saturated solution of $Na_2S_2O_3$. The organic phase was extracted with CH_2Cl_2 and washed with aqueous saturated solution of $NaHCO_3$ and brine. The solvent was removed under vacuum. The pure product was obtained as yellow oil by silica gel column chromatography. The characterization data of the compound are consistent with literature.[7]

Step 2: A mixture of α-bromo cycloheptanone (9.8 g, 44.6 mmol) and sodium azide (4.35 g, 66.9 mmol) in DMF (120 mL) was stirred at room temperature for 24 h; the mixture was poured into water and extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$, After filtration, the solvent was removed under vacuum. The crude product was purified using silica gel column chromatography. The characterization data of the compound are consistent with literature.[7]

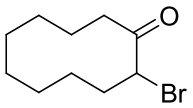


^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (dd, *J* = 11.2, 4.1 Hz, 1H), 2.87 (td, *J* = 12.1, 3.7 Hz, 1H), 2.44 – 2.24 (m, 3H), 1.92 (ddq, *J* = 13.8, 6.7, 4.1, 3.3 Hz, 1H), 1.82 – 1.62 (m, 3H), 1.62 – 1.50 (m, 2H), 1.46 – 1.35 (m, 1H), 1.22 – 1.10 (m, 1H).

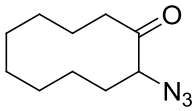


9b

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 (dd, *J* = 8.3, 3.5 Hz, 1H), 2.58 (ddd, *J* = 13.5, 9.5, 4.0 Hz, 1H), 2.43 (ddd, *J* = 13.2, 7.9, 4.0 Hz, 1H), 2.28 (ddt, *J* = 14.6, 9.9, 3.6 Hz, 1H), 2.01 – 1.84 (m, 3H), 1.84 – 1.72 (m, 1H), 1.71 – 1.56 (m, 2H), 1.53 – 1.40 (m, 2H), 1.23 – 1.09 (m, 1H); EI-MS: *m/z* 167 (M^+); EI-HRMS for $[C_8H_{13}N_3O]^+$ (M^+): *m/z* Calcd. 167.1053, Found: 167.1046.

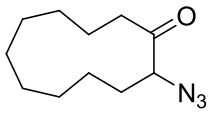


^{1}H NMR (400 MHz, $CDCl_3$): δ 4.58 (dd, *J* = 11.7, 3.8 Hz, 1H), 2.85 – 2.69 (m, 2H), 2.43 (dddt, *J* = 15.2, 11.5, 7.6, 3.6 Hz, 1H), 2.13 (ddt, *J* = 13.2, 8.4, 3.9 Hz, 1H), 2.02 – 1.90 (m, 1H), 1.84 – 1.72 (m, 1H), 1.71 – 1.60 (m, 1H), 1.57 – 1.41 (m, 4H), 1.40 – 1.21 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.5, 51.9, 37.2, 33.9, 25.4, 24.9, 24.63, 24.57, 24.48, 23.4.



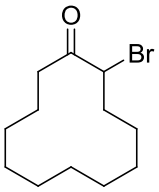
9c

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00 (dd, *J* = 8.1, 3.6 Hz, 1H), 2.71 (ddd, *J* = 17.2, 9.5, 3.7 Hz, 1H), 2.56 (ddd, *J* = 17.3, 7.8, 3.9 Hz, 1H), 2.14 – 2.04 (m, 1H), 1.93 (ddtt, *J* = 28.5, 14.3, 7.4, 3.7 Hz, 2H), 1.72 (dtt, *J* = 14.9, 8.1, 3.7 Hz, 1H), 1.60 (tp, *J* = 10.6, 5.6, 5.1 Hz, 1H), 1.49 (dt, *J* = 8.6, 3.8 Hz, 1H), 1.46 – 1.14 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 67.6, 37.7, 29.1, 25.1, 24.6, 24.2, 23.6, 22.6, 21.5; EI-MS: *m/z* 195 (M^+); EI-HRMS for $[C_{10}H_{17}N_3O]^+$ (M^+): *m/z* Calcd. 195.1367, Found: 195.1365.

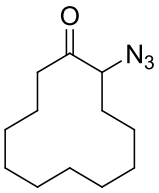


9d

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.97 (dd, *J* = 7.4, 4.2 Hz, 1H), 2.67 (ddd, *J* = 17.4, 8.6, 3.4 Hz, 1H), 2.60 (ddd, *J* = 17.4, 8.6, 3.4 Hz, 1H), 2.05 – 1.98 (m, 2H), 1.85 – 1.78 (m, 1H), 1.76 – 1.69 (m, 1H), 1.57 – 1.37 (m, 5H), 1.36 – 1.27 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.2, 68.0, 39.0, 28.7, 26.1, 26.0, 25.6, 25.3, 23.9, 22.6, 22.0; EI-MS: *m/z* 209 (M^+); EI-HRMS for $[C_{11}H_{19}N_3O]^+$ (M^+): *m/z* Calcd. 209.1523, Found: 209.1515.

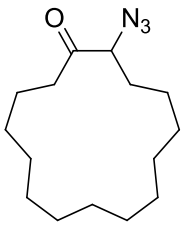


^{1}H NMR (400 MHz, $CDCl_3$): δ 4.38 (dd, *J* = 11.7, 3.7 Hz, 1H), 2.80 (ddd, *J* = 16.4, 6.5, 3.7 Hz, 1H), 2.71 (ddd, *J* = 16.5, 11.0, 3.5 Hz, 1H), 2.31 (dddd, *J* = 13.9, 11.8, 8.3, 4.0 Hz, 1H), 2.03 – 1.83 (m, 2H), 1.63 – 1.47 (m, 1H, overlapped with signal of H_2O), 1.45 – 1.18 (m, 14H).



9e

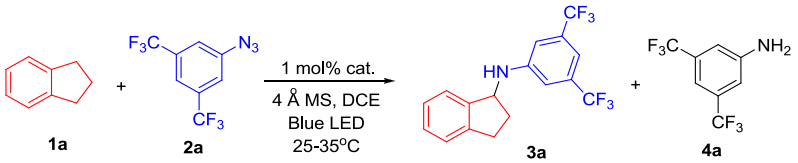
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (dd, *J* = 7.8, 4.0 Hz, 1H), 2.70 (ddd, *J* = 17.8, 9.2, 3.4 Hz, 1H), 2.48 (ddd, *J* = 17.8, 8.1, 3.5 Hz, 1H), 2.00 – 1.80 (m, 3H), 1.71 – 1.59 (m, 1H), 1.48 – 1.13 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 68.1, 35.6, 29.0, 26.02, 26.00, 23.8, 23.0, 22.5, 22.2, 21.4, 20.4; EI-MS: *m/z* 223 (M^+); EI-HRMS for $[C_{12}H_{21}N_3O]^+$ (M^+): *m/z* Calcd. 223.1679, Found: 223.1678.



9f

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (t, *J* = 6.2 Hz, 1H), 2.52 (t, *J* = 6.9 Hz, 2H), 1.82 (dpd, *J* = 13.8, 8.7, 4.2 Hz, 2H), 1.66 (dh, *J* = 13.6, 6.8 Hz, 2H), 1.45 – 1.19 (m, 20H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.1, 67.6, 39.0, 30.5, 27.4, 27.0, 26.70, 26.65, 26.56, 26.52, 26.36, 26.26, 26.1, 23.9, 22.4; EI-MS: *m/z* 265 (M^+); EI-HRMS for $[C_{15}H_{27}N_3O]^+$ (M^+): *m/z* Calcd. 265.2149, Found: 265.2146.

Table S1. Reaction conditions optimization [a]



1a 2a 3a 4a

Entry	Catalyst	Time (h)	Conversion (%)	**3a** (%)	**4a** (%)
1	Fe(TTP)Cl	24	50	12	35
2	Fe(*p*-Cl-TPP)Cl	24	35	20	10
3	Fe(*p*-F-TPP)Cl	24	100	93	trace
4	Fe(TMP)Cl	24	80	70	8
5	Fe(TDCPP)Cl	24	100	92	trace
6	Fe(TDCDMAP)Cl	24	100	92	trace
7	Fe(F_{20}TPP)Cl	24	100	99	trace
8	Fe(TF_4DMAP)Cl	24	100	99	trace
9	Fe(TF_4DMAP)Cl	15	100	93	trace
10	Ru(F_{20}TPP)CO	24	92	80	10
11	Ru(TF_4DMAP)CO	24	90	77	8
12	Mn(F_{20}TPP)Cl	24	50	15	30
13	Co(F_{20}TPP)	24	100	43	55
14	Ir(TTP)Me	24	100	42	50
15	Co(Pc)	24	trace	trace	trace
16[b]	Fe^{II}(BQCN)$(OTf)_2$	24	trace	trace	N.D.
17[b]	Fe^{II}(Qp)$(H_2O)_2(ClO_4)_2$	36	trace	trace	N.D.
18[b]	Fe^{II}(qpy)$(CH_3CN)_2(ClO_4)_2$	36	trace	trace	N.D.
19	-	24	trace	N.D.	N.D.
20[c]	Fe(TF_4DMAP)Cl	24	trace	N.D.	N.D.
21	H_2TF_4DMAP	24	20	10	10
22	H_2F_{20}TPP	24	42	trace	32
23	$Rh_2(OAc)_4$	24	trace	N.D.	N.D.
24[b]	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$	24	50	15	30
25[d]	Fe(TF_4DMAP)Cl	18	100	90	trace
26[e]	Fe(TF_4DMAP)Cl	36	40	25	10
27[f]	Fe^{II}(F_{20}TPP)(Ad)	24	100	98	trace
28	[Fe(F_{20}TPP)]$_2$(μ-O)	24	100	96	trace

[a] Reactions were performed under argon with 0.5 mmol of the azide and 5.0 mmol of indane, 5×10^{-3} mmol of the catalyst (1 mol% with respect to the azide) and 120 mg 4Å MS in 2.0 mL of anhydrous $ClCH_2CH_2Cl$ in 10.0 mL sealed tube. The tube was irradiated with blue LED (469 nm) at 25-35°C for 18-36 h. The yield was determined by ^1H NMR spectroscopy with PhTMS as internal standard. BQCN = N^1,N^2-dimethyl-N^1,N^2-bis(2-methylquinolin-8-yl)cyclohexane-1,2-diamine; Qp = 2,2':6',2":6",2"'-quaterpyridine; qpy = 2,2':6',2":6",2"':6"',2""-quinquepyridine. [b] 2 mol% catalyst was used. [c] No light, room temperature. [d] Reaction temperature = 120 °C. [e] Green LED. [f] Ad stands for 2-adamantylidene.

Mechanistic study

Photo-stability of iron porphyrin complexes

Deaerated DCE solutions of Fe(TF_4DMAP)Cl, Fe(F_{20}TPP)Cl (both at a concentration of 2.5 × 10^{-5} M) and [Fe(F_{20}TPP)]$_2$(μ-O) (concentration at 1.5 × 10^{-5} M) were subjected to blue LED (469 nm) irradiation and their UV-vis absorption spectra were recorded at indicated time intervals as shown in Fig. S1, Fig. S2 and Fig. S3 respectively.

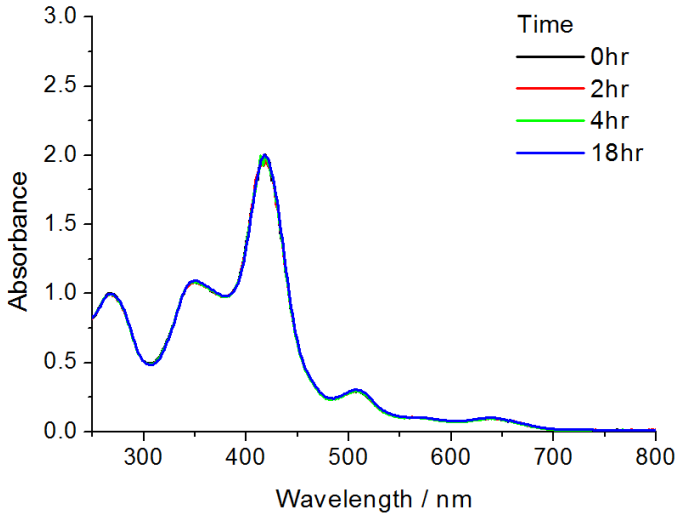


Fig. S1. UV-vis absorption spectral change of Fe(TF_4DMAP)Cl in DCE upon blue LED irradiation at room temperature.

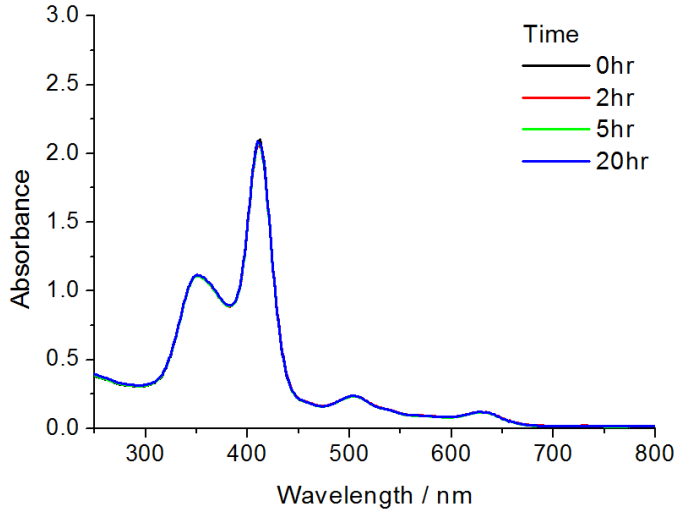


Fig. S2. UV-vis absorption spectral change of Fe(F_{20}TPP)Cl in DCE upon blue LED irradiation at room temperature.

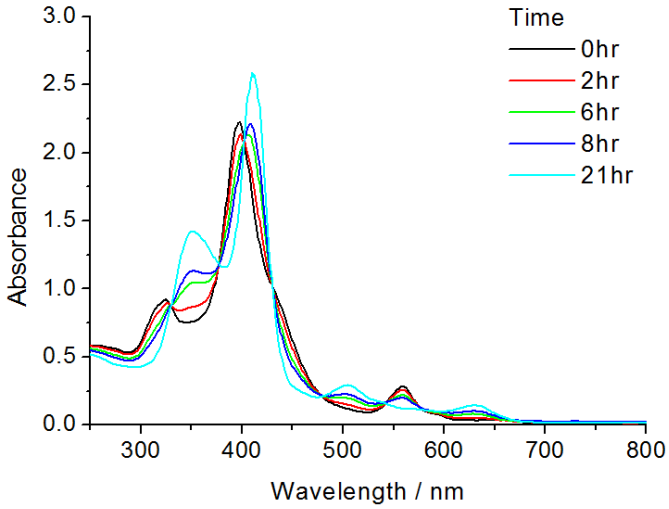
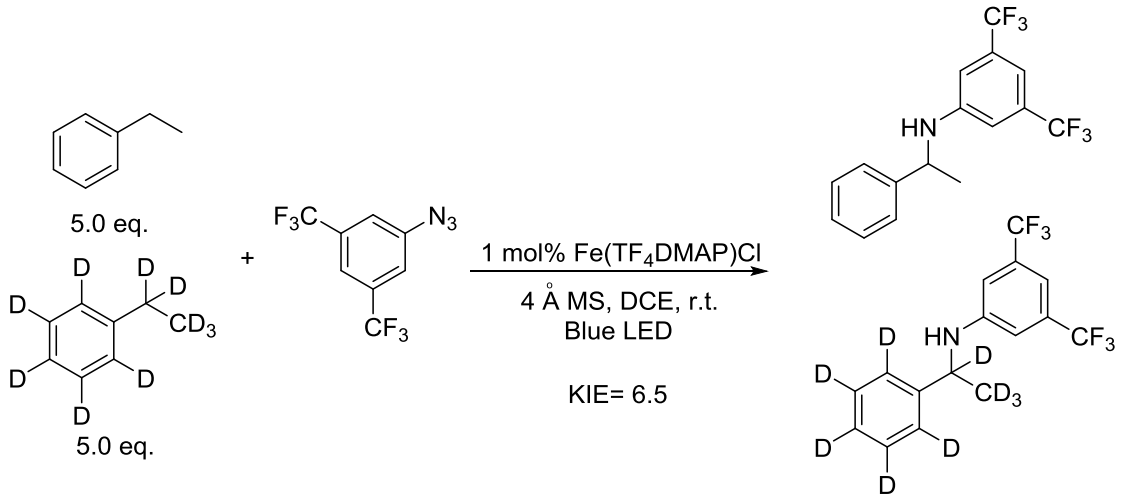
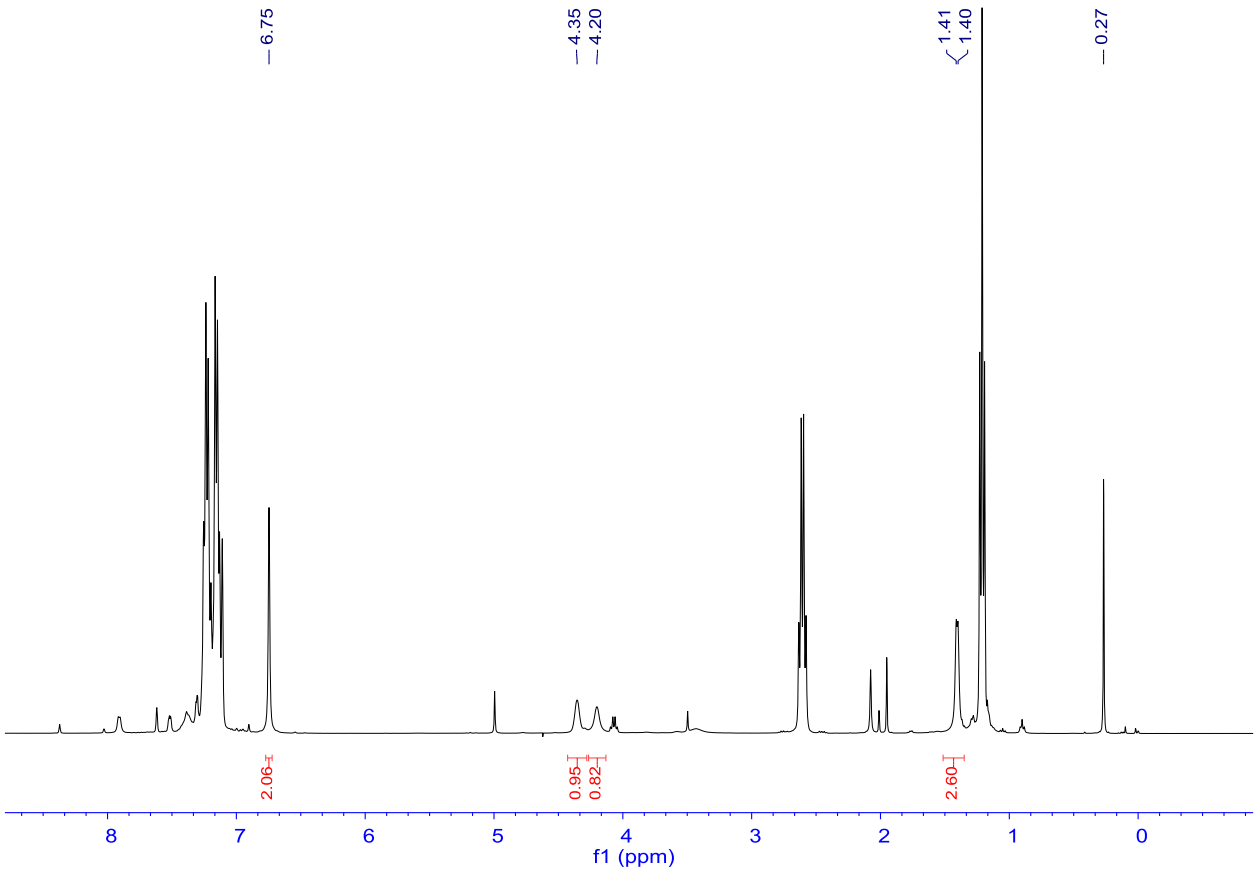


Fig. S3. UV-vis absorption spectral change of $[Fe(F_{20}TPP)]_2(\mu\text{-}O)$ in DCE upon blue LED irradiation at room temperature. The spectrum recorded after 21 hours of light irradiation is identical to that of $Fe(F_{20}TPP)Cl$.

KIE experiment

An oven-dried 10-mL sealed tube was charged with 3,5-bis-(trifluoromethyl)phenyl azide (127.6 mg, 0.5 mmol), ethylbenzene (5 eq., 2.5 mmol), d_{10}-ethylbenzene (5 eq., 2.5 mmol), catalyst (1 mol%), 4Å molecular sieves (120 mg) and dry $ClCH_2CH_2Cl$ (2.0 mL) under argon. The tube was irradiated with blue LED at 25-35°C for 16 h. Then the reaction mixture was filtered through a short pad of celite and washed with CH_2Cl_2, the filtrate was concentrated, and the crude residue was analyzed by ^1H NMR with PhTMS as internal standard (KIE = 6.5).





Determination of quantum yield

The quantum yield was calculated using eq 1.

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot t \cdot f} \qquad (1)$$

Determination of fraction of light absorbed at 420 nm for the reaction mixture was measured, f = 1.

An oven-dried 10-mL sealed tube was charged with 3,5-bis-(trifluoromethyl)phenyl azide (51.0 mg, 0.2 mmol), styrene (3 eq., 0.6 mmol), Fe(TF_4DMAP)Cl (1 mol%), 4Å molecular sieves (60 mg) and dry DCE (1.0 mL) under argon. The tube was then irradiated with a commercial 420 nm laser (intensity: $1.83*10^{-8}$ einstein s^{-1}) for 4 h. ^{1}H NMR analysis revealed that the yield was 15.72%.

Φ= (0.1572*0.2*10^{-3} mol)/($1.83*10^{-8}$ einstein s^{-1}•4*60*60 s•1) = 12%.

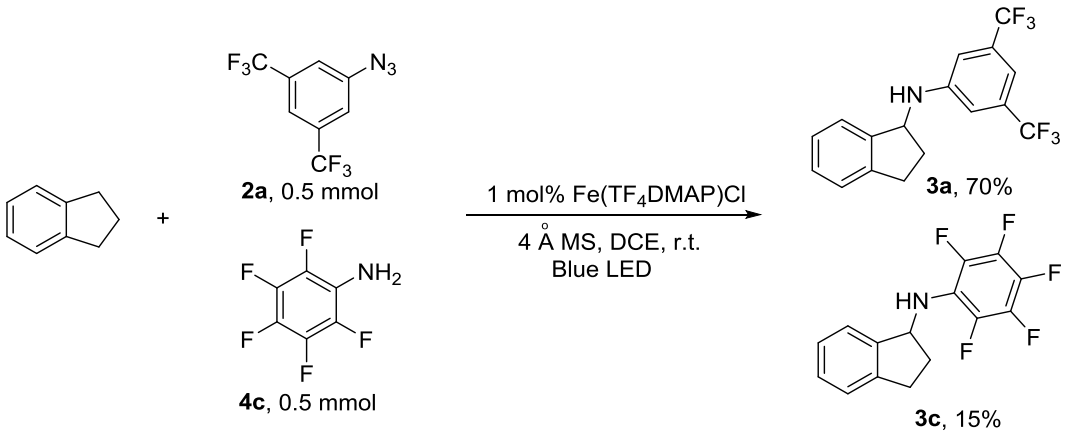
An oven-dried 10-mL sealed tube was charged with 3,5-bis-(trifluoromethyl)phenyl azide (127.6 mg, 0.5 mmol), indane (10 eq., 5.0 mmol), catalyst (1 mol%), 4Å molecular sieves (120 mg) and dry DCE (2.0 mL) under argon. The tube was then irradiated with a commercial 420 nm laser (intensity: $1.83*10^{-8}$ einstein s^{-1}) for 5 h for Fe(TF_4DMAP)Cl for which ^{1}H NMR analysis revealed that the yield was 3.63% while for Fe(3,5-Di^{t}Bu-Chenphyrin)Cl for 6 h with a yield of 2.77%.

Φ= ($0.0363*0.5*10^{-3}$ mol)/($1.83*10^{-8}$ einstein s^{-1}•5*60*60 s•1) = 5.5% for Fe(TF_4DMAP)Cl.

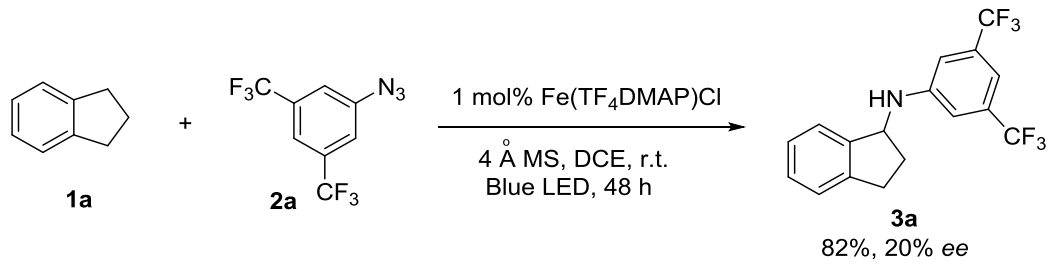
Φ= ($0.0277*0.5*10^{-3}$ mol)/($1.83*10^{-8}$ einstein s^{-1}•6*60*60 s•1) = 3.5% for Fe(3,5-Di^{t}Bu-Chenphyrin)Cl

Crossover experiment

An oven-dried 10-mL sealed tube was charged with aryl azide **2a** (0.5 mmol), 2,3,4,5,6-pentafluoroaniline **4c** (0.5 mmol), indane (10 equiv, 5.0 mmol), Fe(TF_4DMAP)Cl (1 mol%), 4 Å molecular sieves (120 mg) and dry $ClCH_2CH_2Cl$ (2.0 mL). The tube was irradiated with blue LED at 25-35^{o}C for 16 h. Then the reaction mixture was filtered through a short pad of celite and washed with CH_2Cl_2, the filtrate was concentrated, and the residue was purified by silica gel column chromatography to give the corresponding products.



Enantioselective photo-induced C-H amination and alkene aziridination catalysed Fe(TF$_4$DMAP)Cl



1a + **2a** → **3a**

82%, 20% *ee*

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Additional Info : Peak(s) manually integrated
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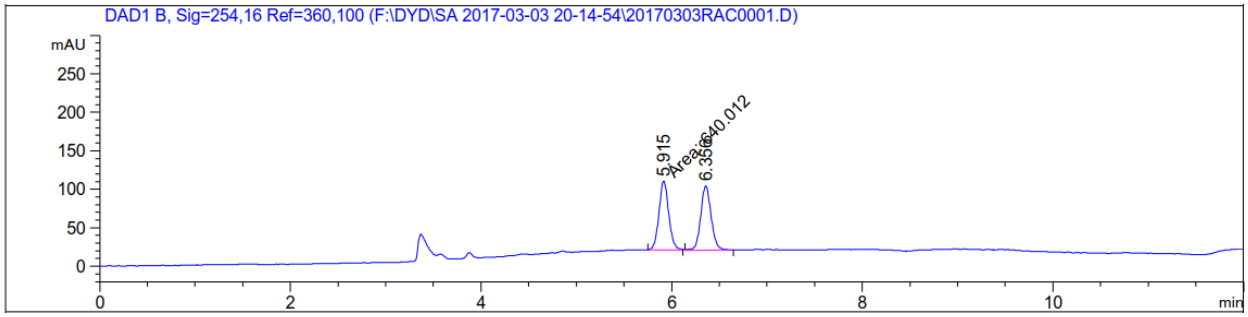

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.915	MM	0.1191	640.01202	89.57922	49.9319
2	6.356	VB	0.1177	641.75885	83.51464	50.0681

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Additional Info : Peak(s) manually integrated
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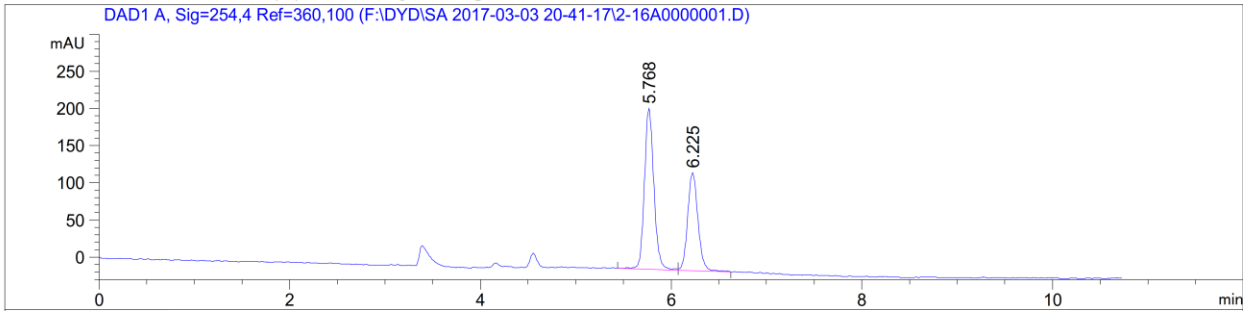

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.768	VV R	0.1067	1500.15967	216.13806	59.9984
2	6.225	VV R	0.1165	1000.17297	131.84363	40.0016

11d

49%, 34% *ee*

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                                              Inj Volume : 7.0 µl
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Additional Info : Peak(s) manually integrated
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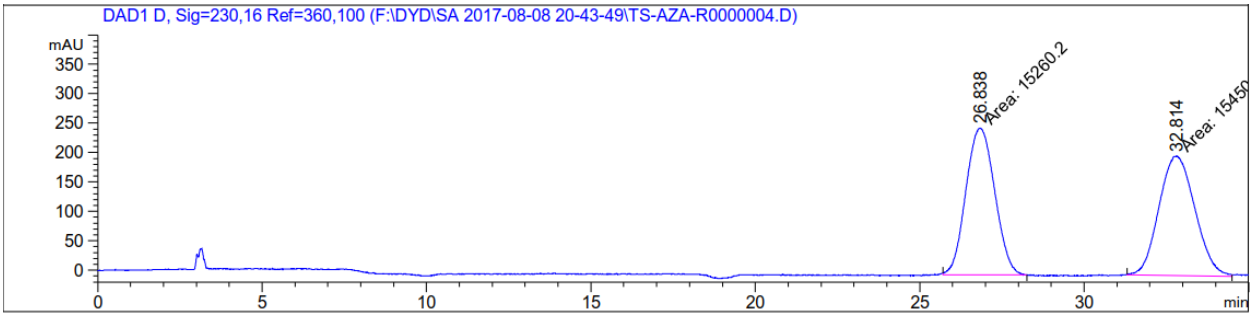

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.838	MM	1.0184	1.52602e4	249.73022	49.6910
2	32.814	MM	1.2686	1.54500e4	202.98251	50.3090

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Additional Info : Peak(s) manually integrated
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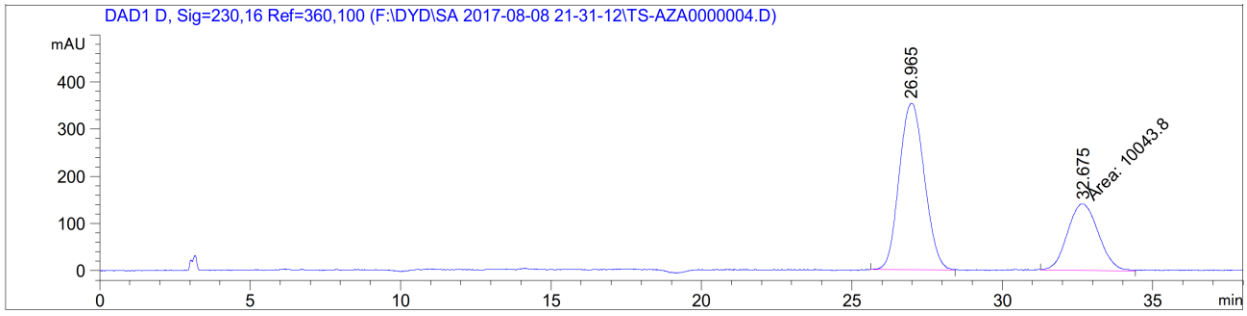

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.965	VV R	0.6928	2.05462e4	352.10623	67.1663
2	32.675	MM	1.1889	1.00438e4	140.79974	32.8337

44%, 42% ee

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Inj Volume : 7.0 µl

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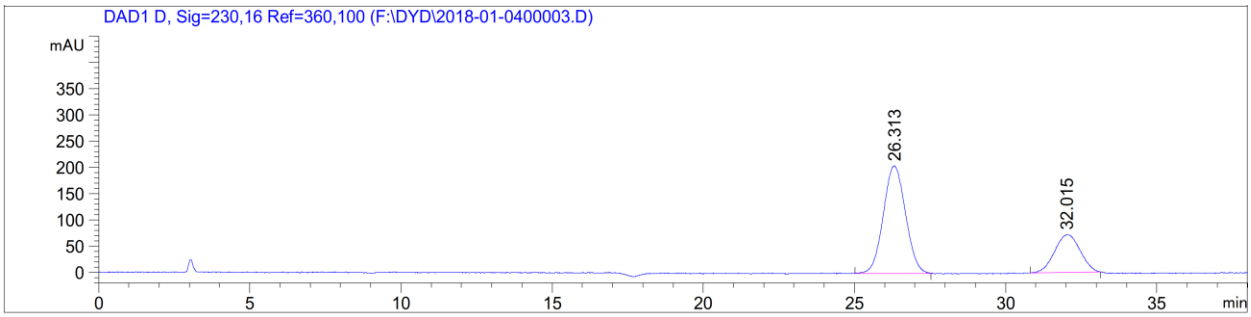
Sample Info : AS-H, Hex:IPA=90:10; 1.0 ml/min

Additional Info : Peak(s) manually integrated



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.313	VV R	0.6495	1.04547e4	204.67041	71.1253
2	32.015	VV R	0.6976	4244.28174	72.22841	28.8747

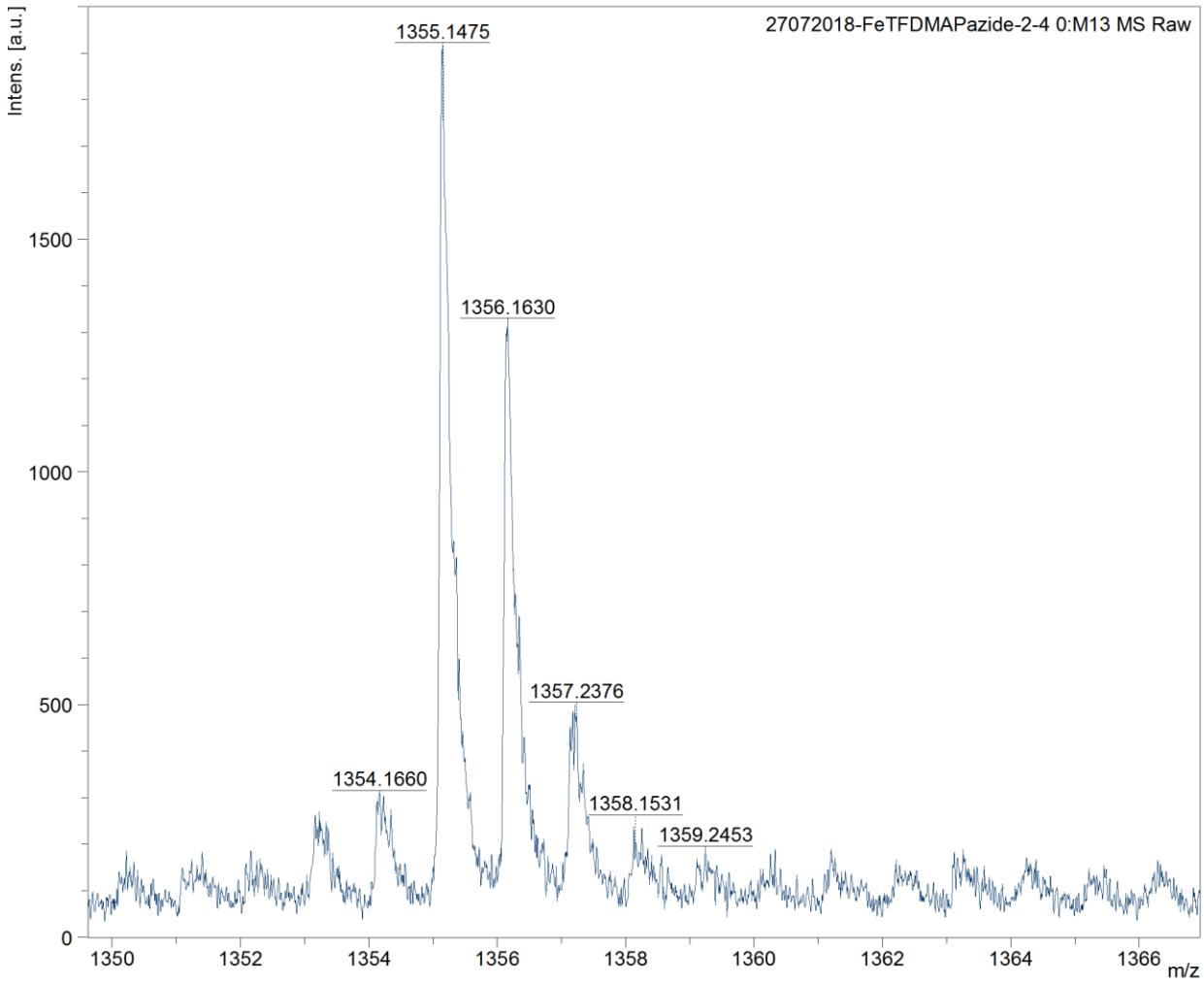


Fig. S4. MALDI-MS analysis of stoichiometric reaction of Fe(TF_4DMAP)Cl and azide **2a**.

Typical procedure of screening catalyst for C-H amination of indane under photocatalytic condition (Table S1)

An oven-dried 10-mL sealed tube was charged with 3,5-bis-(trifluoromethyl)phenyl azide (127.6 mg, 0.5 mmol), indane (10 eq., 5.0 mmol), catalyst (1 mol%), 4Å molecular sieves (120 mg) and dry $ClCH_2CH_2Cl$ (2.0 mL) under argon. The tube was irradiated with blue LED at 25-35^oC for 18-36 h. The conversion of the azide and product yield were determined by ^1H NMR with PhTMS as internal standard.

General procedure for Fe(TF_4DMAP)Cl-catalysed intermolecular C-H amination with organic azide under photocatalytic condition (Table 1-2)

An oven-dried 10-ml sealed tube was charged with organic azide (0.5 mmol), C–H substrate (5.0 mmol), Fe(TF_4DMAP)Cl (1 mol%), 4 Å molecular sieves (120 mg) and dry $ClCH_2CH_2Cl$ (2.0 mL). The tube was irradiated with blue LED at 25-35^oC for 16-24 h (monitor the reaction by GC-MS until azide was consumed completely). Then the reaction mixture was filtered through a short pad of celite and washed with CH_2Cl_2, the filtrate was concentrated, and the residue was purified by silica gel column chromatography to give the corresponding products.

General procedure for Fe(TF_4DMAP)Cl-catalysed intramolecular C-H amination of N-containing alkyl azides under photocatalytic condition (Table 3)

An oven-dried Schlenk tube was charged with alkyl azide (0.3 mmol), Boc_2O (0.36 mmol), Fe(TF_4DMAP)Cl (1 mol%), 4 Å molecular sieves (120 mg) and dry $ClCH_2CH_2Cl$ (2.0 mL). The tube was irradiated with blue LED at 25-35^oC for 10 h (monitor the reaction by GC-MS until azide was consumed completely). The reaction mixture was filtered through a short pad of celite and washed with CH_2Cl_2, the filtrate was concentrated, and the residue was purified by silica gel column chromatography to give the corresponding products.

General procedure for Fe(TF_4DMAP)Cl-catalysed intramolecular C-H amination of α-azidoketones under photocatalytic condition (Table 4)

An oven-dried Schlenk tube was charged with α-azidoketone (0.3 mmol), Boc_2O (0.36 mmol), Fe(TF_4DMAP)Cl (3 mol%), 4 Å molecular sieves (120 mg) and dry $ClCH_2CH_2Cl$ (2.0 mL). The tube was irradiated with blue LED at 25-35^oC for 10 h (monitor the reaction by GC-MS until

azide was consumed completely). The reaction mixture was filtered through a short pad of celite and washed with CH_2Cl_2, the filtrate was concentrated, and the residue was purified by silica gel column chromatography to give the corresponding products.

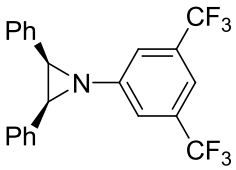
General procedure for Fe(TF_4DMAP)Cl-catalysed alkene aziridination with organic azides under photocatalytic condition

An oven-dried Schlenk tube was charged with azide (0.2 mmol), alkene (0.6 mmol), Fe(TF_4DMAP)Cl (1 mol%), 4 Å molecular sieves (60 mg) and dry $ClCH_2CH_2Cl$ (1.0 mL). The tube was irradiated with blue LED at 25-35^oC for 4 - 10 h (monitor the reaction by GC-MS until azide was consumed completely). The reaction mixture was filtered through a short pad of celite and washed with CH_2Cl_2, the filtrate was concentrated, and the residue was purified by silica gel column chromatography to give the corresponding products.

General procedure for Fe(TF_4DMAP)Cl-catalysed C-H amination of natural products under photocatalytic condition (Scheme 6)

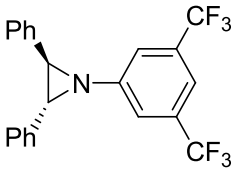
An oven-dried Schlenk tube was charged with aryl azide (0.30 mmol, 1.5 equiv), natural product (0.2 mmol), Fe(TF_4DMAP)Cl (2 mol%), 4 Å molecular sieves (120 mg) and dry $ClCH_2CH_2Cl$ (1.0 mL). The tube was irradiated with blue LED at 25-35^oC for 24 h (monitored by TLC). The reaction mixture was filtered and washed with CH_2Cl_2, the filtrate was concentrated, and the residue was purified by silica gel column chromatography to give the corresponding products.

Characterization of products



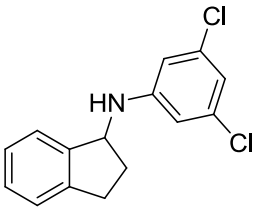
12

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.52 (m, 3H), 7.29 – 7.27 (m, 4H), 7.24 – 7.17 (m, 6H), 3.77 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.89; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 134.5, 132.79 (q, *J* = 33.0 Hz), 128.2, 127.8, 127.7, 123.32 (q, *J* = 271.0 Hz), 120.27 – 120.19 (m), 116.48 – 116.33 (m), 49.7; ESI-MS: *m/z* 408 $[M+H]^+$; ESI-HRMS for $[C_{22}H_{16}F_6N]^+$ ($[M+H]^+$): *m/z* Calcd. 408.1181, Found: 408.1163.



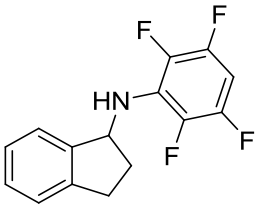
13

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 7H), 7.20 – 7.16 (m, 4H), 7.05– 7.02 (m, 2H), 3.75 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.10; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 134.9, 132.01 (q, *J* = 33.0 Hz), 128.7, 128.4, 127.4, 123.28 (q, *J* = 271.0 Hz), 121.02 – 120.91 (m), 115.43 – 115.27 (m), 50.4; ESI-MS: *m/z* 408 $[M+H]^+$; ESI-HRMS for $[C_{22}H_{16}F_6N]^+$ ($[M+H]^+$): *m/z* Calcd. 408.1181, Found: 408.1163.



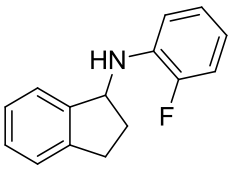
3b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.14 (m, 4H), 6.65 (t, *J* = 1.8 Hz, 1H), 6.51 (d, *J* = 1.7 Hz, 2H), 4.89 (q, *J* = 7.0 Hz, 1H), 4.02 (d, *J* = 7.6 Hz, 1H), 3.00 (ddd, *J* = 16.1, 8.6, 4.4 Hz, 1H), 2.87 (dt, *J* = 15.9, 7.8 Hz, 1H), 2.54 (dddd, *J* = 12.8, 8.2, 7.0, 4.5 Hz, 1H), 1.84 (dddd, *J* = 12.9, 8.7, 7.4, 6.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 143.6, 143.5, 135.6, 128.4, 126.9, 125.1, 124.2, 117.0, 111.2, 58.5, 33.7, 30.3; ESI-MS: *m/z* 278 $[M+H]^+$; ESI-HRMS for $[C_{15}H_{14}Cl_2N]^+$ ($[M+H]^+$): *m/z* Calcd. 278.0497, Found: 278.0481.



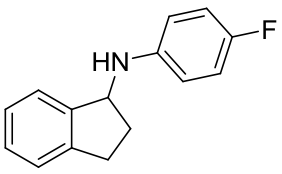
3d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.1 Hz, 1H), 7.29 – 7.17 (m, 3H), 6.46 – 6.32 (m, 1H), 5.28 (q, *J* = 7.8 Hz, 1H), 3.97 (d, *J* = 9.3 Hz, 1H), 3.02 (ddd, *J* = 16.5, 8.7, 4.5 Hz, 1H), 2.86 (dt, *J* = 16.0, 7.9 Hz, 1H), 2.56 (dt, *J* = 11.5, 4.0 Hz, 1H), 1.90 (dd, *J* = 13.6, 7.0 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -140.90 – -141.15 (m, 2F), -159.19 (m, 2F). ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8 (ddt, *J* = 242, 12.8, 3.4 Hz), 144.0, 143.45, 137.5 (dtd, *J* = 238, 15.9, 4.2 Hz), 128.4, 128.23 (m), 127.0, 125.1, 124.3, 93.6 (t, *J* = 23.0 Hz), 60.89 (t, *J* = 5.0 Hz), 35.3, 30.1; ESI-MS: *m/z* 282 $[M+H]^+$; ESI-HRMS for $[C_{15}H_{12}F_4N]^+$ ($[M+H]^+$): *m/z* Calcd. 282.0900, Found: 282.0886.



3e

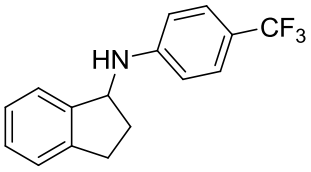
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.30 – 7.18 (m, 3H), 7.05 – 6.94 (m, 2H), 6.88 (td, *J* = 8.4, 1.6 Hz, 1H), 6.63 (tdd, *J* = 7.8, 4.9, 1.6 Hz, 1H), 5.02 (d, *J* = 7.1 Hz, 1H), 4.15 (s, 1H), 3.03 (ddd, *J* = 15.9, 8.7, 4.3 Hz, 1H), 2.89 (dt, *J* = 15.9, 7.9 Hz, 1H), 2.59 (dddd, *J* = 12.6, 8.1, 7.0, 4.3 Hz, 1H), 1.91 (dtd, *J* = 12.7, 8.3, 6.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -136.09 – -136.15 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (d, *J* = 237 Hz), 144.2, 143.7, 136.4 (d, *J* = 11.4 Hz), 128.2, 126.9, 125.0, 124.7 (d, *J* = 3.5 Hz), 124.3, 116.7 (d, *J* = 6.9 Hz), 114.7 (d, *J* = 18 Hz), 112.7 (d, *J* = 3.1 Hz) 58.5, 34.1, 30.4; ESI-MS: *m/z* 228 $[M+H]^+$; ESI-HRMS for $[C_{15}H_{15}FN]^+$ ($[M+H]^+$): *m/z* Calcd. 228.1183, Found: 228.1178.



3f

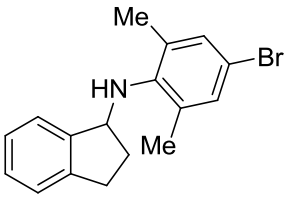
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.2 Hz, 1H), 7.29 – 7.16 (m, 3H), 6.94 – 6.87 (m,

2H), 6.67 – 6.61 (m, 2H), 4.94 (t, *J* = 6.7 Hz, 1H), 3.76 (br, s, 1H), 3.01 (ddd, *J* = 16.1, 8.7, 4.4 Hz, 1H), 2.89 (dt, *J* = 15.9, 7.8 Hz, 1H), 2.62 – 2.51 (m, 1H), 1.94 – 1.82 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -128.00; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.90 (d, *J* = 233.0 Hz), 144.5, 144.2, 143.7, 128.1, 126.8, 125.0, 124.3, 115.88 (d, *J* = 22.0 Hz), 114.14 (d, *J* = 7.0 Hz), 59.4, 33.9, 30.3; EI-MS: *m/z* 227 (M^+); EI-HRMS for $[C_{15}H_{14}FN]^+$: *m/z* Calcd. 227.1110, Found: 227.1105.



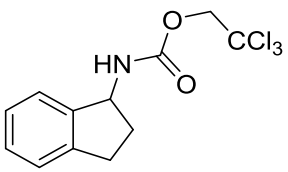
3g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.23 – 7.17 (m, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.02 (q, *J* = 7.1 Hz, 1H), 4.22 (d, *J* = 7.6 Hz, 1H), 3.03 (ddd, *J* = 16.1, 8.7, 4.4 Hz, 1H), 2.91 (dt, *J* = 15.9, 7.8 Hz, 1H), 2.59 (dtd, *J* = 12.5, 7.6, 4.4 Hz, 1H), 1.90 (dtd, *J* = 13.0, 8.4, 6.8 Hz, 1H)); ^{19}F NMR (376 MHz, $CDCl_3$): δ -60.85; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 143.8, 143.7, 128.3, 126.9, 126.85 (q, *J* = 4.0 Hz), 125.15, 125.13 (q, *J* = 268.0 Hz), 124.3, 118.92 (q, *J* = 32.0 Hz), 112.3, 58.4, 33.8, 30.4; EI-MS: *m/z* 277 (M^+); EI-HRMS for $[C_{16}H_{14}F_3N]^+$: *m/z* Calcd. 277.1078, Found: 277.1074.



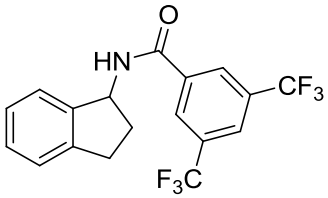
3h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.20 (m, 3H), 7.20 – 7.15 (m, 1H), 7.13 (s, 2H), 4.74 (t, *J* = 6.7 Hz, 1H), 3.21 (s, 1H), 3.02 (ddd, *J* = 15.9, 8.4, 4.8 Hz, 1H), 2.81 (dt, J = 15.8, 7.6 Hz, 1H), 2.46 – 2.34 (m, 2H), 2.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 144.4, 143.1, 131.5, 131.2, 127.9, 126.7, 125.0, 124.3, 113.8, 62.4, 34.9, 30.2, 18.9; ESI-MS: *m/z* 316 $[M+H]^+$; ESI-HRMS for $[C_{17}H_{19}BrN]^+$ ($[M+H]^+$): *m/z* Calcd. 316.0695, Found: 316.0682.



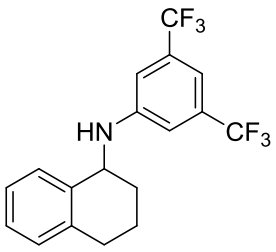
3j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.30 (m, 1H), 7.27 – 7.16 (m, 3H), 5.29-5.25 (m, 1H), 5.25 – 5.20 (m, 1H), 4.80 – 4.71 (m, 2H), 2.98 (ddd, *J* = 16.0, 8.8, 3.9 Hz, 1H), 2.85 (dt, *J* = 16.0, 8.1 Hz, 1H), 2.59 (dtd, *J* = 15.7, 7.7, 3.8 Hz, 1H), 1.91 – 1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 143.3, 142.6, 128.3, 126.9, 125.0, 124.1, 95.8, 74.6, 56.8, 34.1, 30.2.



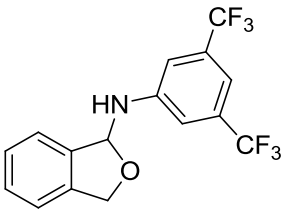
3k

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.55 (s, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 6.88 (br, s, 1H), 6.25 (dd, *J* = 6.9, 3.3 Hz, 1H), 3.14 (ddd, *J* = 15.4, 8.3, 6.7 Hz, 1H), 2.93 (ddd, *J* = 16.2, 8.6, 4.3 Hz, 1H), 2.56 (ddt, *J* = 13.7, 8.7, 6.8 Hz, 1H), 2.21 (dddd, *J* = 14.2, 8.1, 4.4, 3.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.04; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 144.7, 140.4, 139.6, 132.61 (q, *J* = 33.0 Hz), 129.6, 127.0, 125.7, 125.1, 123.22 (q, *J* = 271.0 Hz), 118.3, 116.88 – 116.73 (m), 80.4, 32.5, 30.3; EI-MS: *m/z* 373 (M^+); EI-HRMS for $[C_{18}H_{13}F_6NO]^+$ (M^+): *m/z* Calcd. 373.0896, Found: 373.0854.



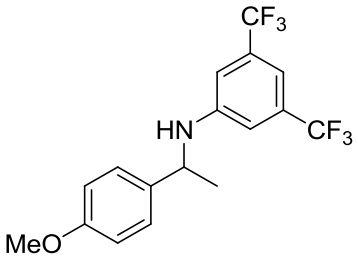
5a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.24 – 7.11 (m, 3H), 7.14 (s, 1H), 6.97 (s, 2H), 4.66 (dt, *J* = 7.8, 5.0 Hz, 1H), 4.30 (d, *J* = 7.8 Hz, 1H), 2.90 – 2.71 (m, 2H), 2.01 – 1.95 (m, 2H), 1.91 – 1.79 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.16; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 137.8, 136.7, 132.76 (q, *J* = 32.0 Hz), 129.5, 129.2, 127.8, 126.5, 123.78 (q, *J* = 271.0 Hz), 111.94 – 111.87 (m), 110.16 – 109.94 (m), 51.2, 29.3, 28.5, 19.4. For detailed characterizations, see Table S2.



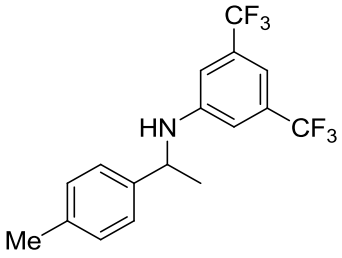
5f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.41 (m, 1H), 7.39 – 7.37 (m, 2H), 7.32 – 7.30 (m, 2H) , 7.24 (s, 2H), 6.63 (dd, *J* = 9.4, 2.4 Hz, 1H), 5.20 – 5.08 (m, 2H), 4.90 (d, *J* = 9.5 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.11; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.7, 140.3, 137.5, 132.71 (q, *J* = 33.0 Hz), 129.7, 128.2, 123.58 (q, *J* = 271.0 Hz), 122.7, 121.6, 114.17 – 114.10 (m), 112.65 – 112.49 (m), 88.7, 71.8; ^{13}C-dept-135 NMR (100 MHz, $CDCl_3$): δ 129.5 (CH), 128.0 (CH), 122.6 (CH), 121.5 (CH), 113.98 – 113.94 (m, CH), 112.48 – 112.33 (m, CH), 88.6 (CH), 71.7 (CH_2); ESI-MS: *m/z* 348 $[M+H]^+$; ESI-HRMS for $[C_{16}H_{12}F_6NO]^+$ ($[M+H]^+$): *m/z* Calcd. 348.0817, Found: 348.0803.



5g

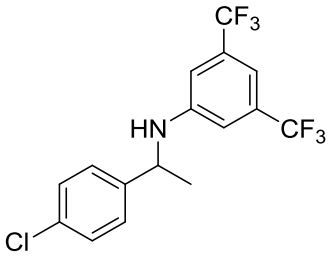
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.23 (m, 2H), 7.09 (s, 1H), 6.89 – 6.86 (m, 1H), 6.87 – 6.85 (m, 3H), 4.51 – 4.44 (m, 2H), 3.78 (s, 3H), 1.52 (d, *J* = 8.0 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.21; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 147.9, 135.5, 132.32 (q, *J* = 33.0 Hz), 127.0, 123.68 (q, *J* = 271.0 Hz), 114.4, 112.61 – 112.49 (m), 110.27 – 110.11 (m), 55.4, 52.9, 24.6; ESI-MS: *m/z* 364 $[M+H]^+$; ESI-HRMS for $[C_{17}H_{16}F_6NO]^+$ ($[M+H]^+$): *m/z* Calcd. 364.1130, Found: 364.1113.



5h

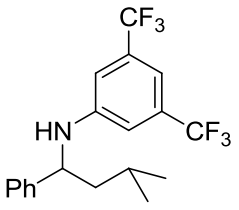
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.19 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 6.86

(s, 2H), 4.50 – 4.43 (m, 2H), 2.31 (s, 3H), 1.52 (d, J = 6.5 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.20; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 140.5, 137.3, 132.35 (q, J = 33.0 Hz), 129.8, 125.8, 123.71 (q, J = 271.0 Hz), 112.57 – 112.53 (m), 110.29 – 110.14 (m), 53.3, 24.6, 21.1; ESI-MS: *m/z* 348 $[M+H]^+$; ESI-HRMS for $[C_{17}H_{16}F_6N]^+$ ($[M+H]^+$): *m/z* Calcd. 348.1181, Found: 348.1166.



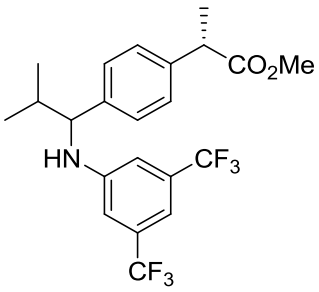
5j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 4H), 7.11 (s, 1H), 6.83 (s, 2H), 4.53 – 4.46 (m, 2H), 1.55 (d, J = 6.5 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.25; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 142.1, 133.2, 132.43 (q, J = 33.0 Hz), 129.2, 127.2, 123.60 (q, J = 271.0 Hz), 112.59 – 112.55 (m), 110.68 – 110.50 (m), 53.0, 24.6. For detailed characterizations, see Table S2.



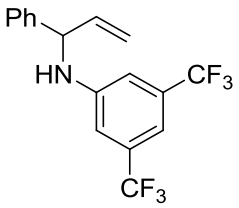
5k

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 7.08 (s, 1H), 6.87 (s, 2H), 4.47 (d, J = 5.9 Hz, 1H), 4.39 (q, J = 6.6 Hz, 1H), 1.74 – 1.61 (m, 3H), 0.99 (d, J = 8.0 Hz, 3H), 0.93 (d, J = 5.7 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.22; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 142.9, 132.38 (q, J = 33.0 Hz), 129.1, 127.6, 126.3, 123.72 (q, J = 271.0 Hz), 112.57 – 112.45 (m), 110.30 – 110.14 (m), 56.4, 48.2, 25.1, 22.9, 22.4; ESI-MS: *m/z* 376 $[M+H]^+$; ESI-HRMS for $[C_{19}H_{20}F_6N]^+$ ($[M+H]^+$): *m/z* Calcd. 376.1494, Found: 376.1479.



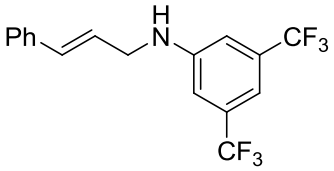
5l

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.24 (m, 2H), 7.22 – 7.18 (m, 2H), 7.05 (s, 1H), 6.83 (s, 2H), 4.60 (d, *J* = 5.5 Hz, 1H), 4.11 (t, *J* = 6.2 Hz, 1H), 3.71 (q, *J* = 7.2 Hz, 1H), 3.64 (s, 3H), 2.04 (h, *J* = 6.7 Hz, 1H), 1.48 (dd, *J* = 7.2, 1.9 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.32; ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.1, 148.3, 139.80, 139.75, 132.27 (q, *J* = 33.0 Hz), 127.8, 127.4, 123.65 (q, *J* = 271.0 Hz), 112.56 – 112.49 (m), 110.15 – 110.03(m), 63.7, 52.1, 45.2, 34.8, 19.7, 18.9, 18.6; ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 127.6, 127.3, 112.40 – 112.36 (m), 109.99 – 109.87(m), 63.5, 52.0, 45.0, 34.7, 19.6, 18.7, 18.4; EI-MS: *m/z* 447 (M^+); EI-HRMS for $[C_{22}H_{23}F_6NO_2]^+$: *m/z* Calcd. 447.1627, Found: 447.1623.



5na

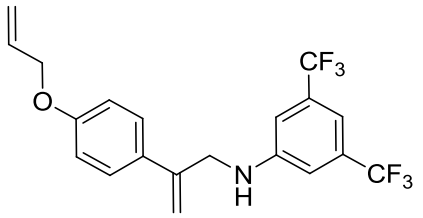
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.34 (m, 4H), 7.33 – 7.29 (m, 1H), 7.15 (s, 1H), 6.94 (s, 2H), 6.06 – 5.98 (m, 1H), 5.33 – 5.28 (m, 2H), 4.96 (t, *J* = 5.5 Hz, 1H), 4.45 (d, *J* = 5.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.19; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 140.4, 137.4, 132.38 (q, *J* = 33.0 Hz), 129.2, 128.3, 127.3, 123.66 (q, *J* = 271.0 Hz), 117.1, 112.84 – 112.80 (m), 110.76 – 110.60 (m), 60.7; ESI-MS: *m/z* 346 $[M+H]^+$; ESI-HRMS for $[C_{17}H_{14}F_6N]^+$ ($[M+H]^+$): *m/z* Calcd. 346.1024, Found: 346.1008.



5nb

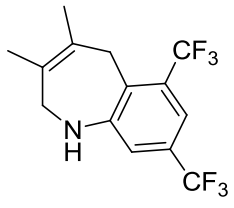
^{1}H NMR (400 MHz, $CDCl_3$): δ 7. 39 – 7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 7.17 (s, 1H), 6.99 (s,

2H), 6.64 (dt, J = 15.9, 1.5 Hz, 1H), 6.26 (dtd, J = 15.9, 5.8, 1.2 Hz, 1H), 4.31 (t, J = 5.9 Hz, 1H), 3.99 (td, J = 5.8, 1.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.15; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 136.5, 132.8, 132.56 (q, J = 33.0 Hz), 128.8, 128.1, 126.5, 125.0, 122.3, 112.22 – 112.18 (m), 110.63 – 110.48 (m), 45.9; ESI-MS: *m/z* 346 $[M+H]^+$; ESI-HRMS for $[C_{17}H_{14}F_6N]^+$ ($[M+H]^+$): *m/z* Calcd. 346.1024, Found: 346.1006.



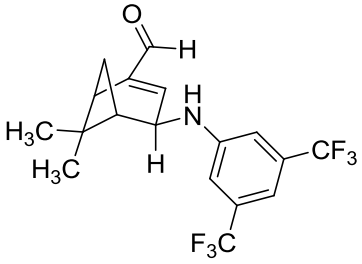
5o

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.34 (m, 2H), 7.15 (s, 1H), 6.94 (s, 2H), 6.93 – 6.89 (m, 2H), 6.06 (ddt, J = 17.2, 10.6, 5.3 Hz, 1H), 5.44 (d, J = 1.3 Hz, 1H), 5.41 (dq, J = 10.5, 1.4 Hz, 1H), 5.30 (dq, J = 10.5, 1.4 Hz, 1H), 5.24 (q, J = 1.2 Hz, 1H), 4.55 (dt, J = 5.3, 1.6 Hz, 2H), 4.30 (t, J = 5.5 Hz, 1H), 4.21 – 4.12 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.19; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 148.6, 142.8, 133.2, 132.52 (q, J = 32.5 Hz), 131.1, 127.4, 123.70 (q, J = 271.0 Hz), 118.0, 115.0, 113.2, 112.12 – 112.09 (m), 110.54 – 110.42 (m), 69.0, 48.0; ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 133.1, 127.2, 117.9 (CH_2), 114.8, 113.0 (CH_2), 111.97 – 111.95 (m), 110.40 – 110.27 (m), 68.9 (CH_2), 47.8 (CH_2); EI-MS: *m/z* 401 (M^+); EI-HRMS for $[C_{20}H_{17}F_6NO]^+$: *m/z* Calcd. 401.1214, Found: 401.1215.



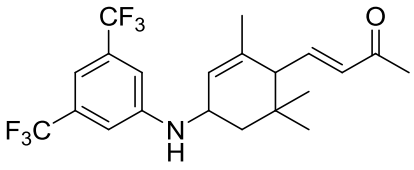
5p

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (s, 1H), 6.94 (s, 1H), 3.98 (br, s, 1H), 3.84 (s, 2H), 3.64 (s, 2H), 1.81 (s, 3H), 1.65 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.47 (3F), -63.02 (3F); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 131.6, 129.01, 129.00 (q, J = 30.0 Hz), 128.93 (q, J = 32.5 Hz), 125.9, 124.02 (q, J = 272.5 Hz), 123.70 (q, J = 270.0 Hz), 118.11 – 118.08 (m), 113.48 – 113.30 (m), 50.9, 33.0, 19.7, 18.5; ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 117.96 – 117.93 (m), 113.27 – 113.14 (m), 50.7 (CH_2), 32.8 (CH_2), 19.5 (CH_3), 18.3 (CH_3); EI-MS: *m/z* 309 (M^+); EI-HRMS for $[C_{14}H_{13}F_6N]^+$: *m/z* Calcd. 309.0952, Found: 309.0951.



5q

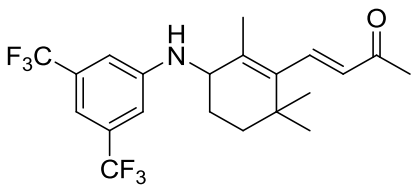
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 7.20 (s, 1H), 7.01 (s, 2H), 6.63 – 6.61 (m, 1H), 4.45 (dt, *J* = 9.2, 2.9 Hz, 1H), 4.32 (d, *J* = 9.1 Hz, 1H), 2.97 (t, *J* = 5.6 Hz, 1H), 2.50 (dt, *J* = 10.2, 5.5 Hz, 1H), 2.36 (tt, *J* = 5.6, 2.4 Hz, 1H), 1.44 (s, 3H), 1.15 (d, *J* = 9.8 Hz, 1H), 0.93 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.17; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 152.5, 147.2, 142.4, 132.88 (q, *J* = 33.0 Hz), 123.56 (q, *J* = 271.0 Hz), 112.41 – 112.38 (m), 111.12 – 111.00 (m), 52.9, 44.9, 44.5, 38.9, 28.8, 26.0, 20.7; EI-MS: *m/z* 377 (M^+); EI-HRMS for $[C_{18}H_{17}F_6NO]^+$: *m/z* Calcd. 377.1214, Found: 377.1205.



5r *dr* = 2.6:1

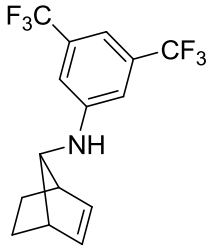
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (s, 1H), 6.97 (s, 0.50H), 6.94 (s, 1.38H), 6.65 (dd, *J* = 15.9, 9.5 Hz, 0.26H), 6.60 (dd, *J* = 15.8, 10.2 Hz, 0.70H), 6.17 – 6.13 (m, 0.69H), 6.11 (dd, *J* = 15.8, 0.8 Hz, 0.27H), 5.57 (tt, *J* = 3.0, 1.5 Hz, 1H), 4.19 (d, *J* = 8.5 Hz, 1H), 4.14 – 4.05 (m, 1H), 2.60 – 2.55 (m, 0.72H), 2.37 (d, *J* = 9.3 Hz, 0.26H), 2.30 (s, 2.02H), 2.28 (s, 0.77H), 1.93 – 1.87 (m, 1H), 1.75 (ddt, *J* = 13.2, 6.1, 1.3 Hz, 0.30H), 1.41 – 1.36 (m, 0.86H), 1.10 (s, 0.79H), 1.02 (s, 2.08H), 0.98 (s, 2.03H), 0.92 (s, 0.82H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.22; ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.3 (minor), 198.1, 148.1 (minor), 147.9, 147.3 (minor), 146.8, 136.47, 136.36 (minor), 134.1, 132.59 (q, *J* = 32.5 Hz), 123.68 (q, *J* = 271.0 Hz), 123.2 (minor), 122.95, 112.33 –112.30 (m, minor), 112.18 – 112.09 (m), 110.10 – 109.95 (m), 54.3, 54.1 (minor), 48.2 (minor), 47.5, 41.4, 38.0 (minor), 34.5 (minor), 34.0, 29.3, 29.0 (minor), 27.3 (minor), 27.2, 27.0 (minor), 24.1, 22.8, 22.6 (minor); ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 147.2 (minor), 146.8, 134.0, 132.6 (minor), 123.1 (minor), 122.8, 112.20 – 112.18 (m, minor), 112.03 – 111.99 (m), 109.97 – 109.82 (m), 54.2, 53.96 (minor), 48.1 (minor), 47.4, 41.3 (CH_2), 37.9 (CH_2, minor), 29.2, 28.9 (minor), 27.2 (minor), 27.1, 26.8 (minor), 23.95, 22.7, 22.5 (minor); EI-MS: *m/z* 419

(M^+); EI-HRMS for $[C_{21}H_{23}F_6NO]^+$: *m/z* Calcd. 419.1684, Found: 419.1684.



5s

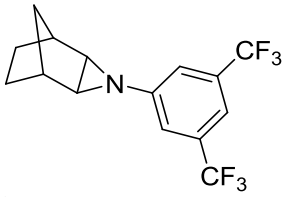
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, *J* = 16.4 Hz, 1H), 7.12 (s, 1H), 6.97 (s, 2H), 6.14 (d, *J* = 16.4 Hz, 1H), 4.32 (t, *J* = 6.8 Hz, 1H), 3.89 (dt, *J* = 8.4, 4.1 Hz, 1H), 2.33 (s, 3H), 1.91 – 1.77 (m, 2H), 1.82 (s, 3H), 1.62 (td, *J* = 12.7, 12.0, 3.3 Hz, 1H), 1.50 (ddd, *J* = 13.6, 5.8, 3.2 Hz, 1H), 1.10 (d, *J* = 2.8 Hz, 6H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.24; ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.3, 148.3, 142.3, 141.2, 133.5, 132.68 (q, *J* = 32.5 Hz), 131.4, 123.70 (q, *J* = 271.0 Hz), 112.01 – 111.98 (m), 110.03 – 109.96 (m), 53.2, 34.8, 34.6, 29.3, 27.6, 27.3, 24.1, 19.6; ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 142.2 (CH), 133.4 (CH), 111.86 – 111.83 (m), 109.87 – 109.84 (m), 53.1, 34.6 (CH_2), 29.2, 27.5, 27.2, 23.9 (CH_2), 19.5; EI-MS: *m/z* 419 (M^+); EI-HRMS for $[C_{21}H_{23}F_6NO]^+$: *m/z* Calcd. 419.1684, Found: 419.1676.



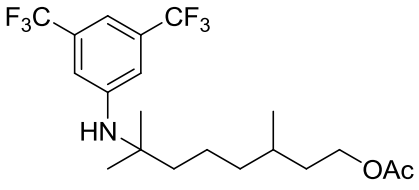
5t, *endo*: *exo* = 3: 1

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, *J* = 4.1 Hz, 1H), 6.91 (d, *J* = 1.4 Hz, 1H), 6.84 (d, *J* = 1.5 Hz, 2H), 6.04 (td, *J* = 1.9, 0.9 Hz, 2H), 4.47 (d, *J* = 8.8 Hz, 0.79H), 4.22 (d, *J* = 6.5 Hz, 0.26H), 3.46 (dt, *J* = 8.8, 1.3 Hz, 0.83H), 3.37 (dt, *J* = 6.6, 1.7 Hz, 0.28H), 2.93 (h, *J* = 1.7 Hz, 2H), 2.11 – 2.07 (m, 0.27H), 1.92 – 1.82 (m, 1.74H), 1.58 – 1.52 (m, 0.5H), 1.39 (dt, *J* = 10.6, 1.6 Hz, 0.28H), 1.32 – 1.24 (m, 1H), 1.18 (tt, *J* = 5.3, 1.3 Hz, 0.30H), 1.12 – 1.00 (m, 1.75H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.21, -63.23; ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.1, 148.5 (minor), 132.9, 132.50 (q, *J* = 32.5 Hz), 132.46 (q, *J* = 32.5 Hz, minor), 123.76 (q, *J* = 271.2 Hz, minor), 123.74 (q, *J* = 271.2 Hz), 112.24 – 112.21, 111.97 – 111.95 (minor), 110.04 – 109.92 (m), 109.84 – 109.72 (m, minor), 70.0, 58.9, 45.5, 32.7, 31.9, 29.6, 23.4, 15.1, 12.2, 10.7; ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 132.74, 112.05-111.8, 109.9-109.6, 69.9, 58.7, 45.3, 32.6, 31.8 (CH_2), 29.4

(CH_2), 23.2 (CH_2), 15.0, 12.0, 10.5;. EI-MS: *m/z* 321 (M^+); EI-HRMS for $[C_{15}H_{13}F_6N]^+$: *m/z* Calcd. 321.0952, Found: 321.0951.

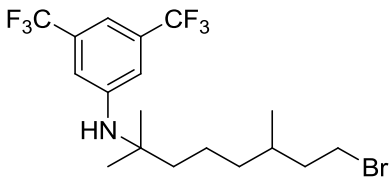


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (s, 2H), 7.48 (s, 1H), 4.70 (d, *J* = 9.0 Hz, 1H), 3.73 (dd, *J* = 9.0, 1.5 Hz, 1H), 2.88 – 2.81 (m, 1H), 2.63 (d, *J* = 3.5 Hz, 1H), 1.73 – 1.63 (m, 2H), 1.41 (tdd, *J* = 14.0, 11.3, 5.6 Hz, 2H), 1.27 – 1.20 (m, 1H), 1.12 – 1.05 (m, 1H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.10; ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.6, 132.94 (q, *J* = 33.0 Hz), 123.35 (q, *J* = 271.0 Hz), 114.91 – 114.79 (m), 113.46 – 113.42 (m), 87.8, 59.8, 41.1, 39.7, 32.2, 25.6, 24.9; ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 114.76 – 114.64 (m), 113.31 – 113.29 (m), 87.7, 59.7, 41.0, 39.5, 32.1 (CH_2), 25.4 (CH_2), 24.8 (CH_2); EI-MS: *m/z* 321 (M^+); EI-HRMS for $[C_{15}H_{13}F_6N]^+$: *m/z* Calcd. 321.0952, Found: 321.0951.



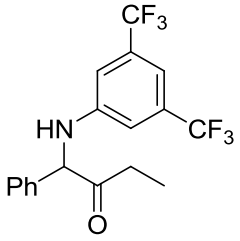
6h (mixture with ratio of C7:C3=5.3:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 1H), 7.02 (s, 2H), 4.18– 4.03 (m, 3H), 2.03 (s, 3H), 1.71 – 1.59 (m, 3H), 1. 57 – 1.48 (m, 1H), 1.45 – 1.26 (m, 10H), 1.18 – 1.12 (m, 1H), 0.87 (d, *J* = 6.5 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.29; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 147.8, 147.5 (minor), 132.23 (q, *J* = 33.0 Hz), 123.74 (q, *J* =271.0 Hz), 114.12 – 114.05 (m), 109.82 – 109.67 (m), 63.0, 60.9 (minor), 55.7 (minor), 54.1, 41.4, 40.1 (minor), 39.2 (minor), 37.4 (minor), 37.2, 35.5, 29.7, 27.96 (d, *J* = 4.0 Hz), 27.8 (minor), 26.0 (minor), 22.54 (d, *J* = 8.0 Hz, minor), 21.25, 21.19 (minor), 21.0, 20.9 (minor), 19.4; ^{13}C-dept-135 NMR (100 MHz, $CDCl_3$) δ 113.97 – 113.93 (CH, m), 109.66 – 109.51 (CH, m), 62.9 (CH_2), 60.7 (CH_2, minor), 41.3 (CH_2), 40.0 (CH_2, minor), 39.0 (CH_2, minor), 37.3 (CH_2, minor), 37.0 (CH_2), 35.3 (CH_2), 29.6, 27.81 (d, *J* = 4.0 Hz), 27.7 (minor), 25.8 (minor), 22.39 (d, *J* = 8.0 Hz, minor), 21.1 (CH_2), 21.0 (CH_2, minor), 20.9, 20.7 (minor), 19.2; ESI-MS: *m/z* 428 $[M+H]^+$; ESI-HRMS for $[C_{20}H_{28}F_6NO_2]^+$ ($[M+H]^+$): *m/z* Calcd. 428.2019, Found: 428.2005.



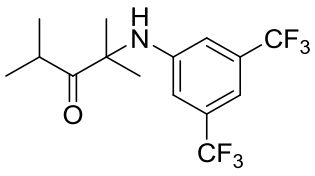
6i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 7.00 (s, 2H), 4.00 (br, s, 1H), 3.47 – 3.34 (m, 2H), 1.88 – 1.79 (m, 1H), 1.72 – 1.59 (m, 5H), 1.35 (s, 6H), 1.34 – 1.26 (m, 2H), 1.19 – 1.09 (m, 1H), 0.85 (d, *J* = 6.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.23; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 132.29 (q, *J* = 33.0 Hz), 123.73 (q, *J* = 271.0 Hz), 114.18-114.14 (m), 110.01-109.85 (m), 54.2, 41.4, 40.0, 36.8, 32.1, 31.5, 28.06 (d, *J* = 4.0 Hz), 21.3, 18.9; ^{13}C-dept-135 NMR (100 MHz, $CDCl_3$) δ 114.01 – 113.97 (CH, m), 109.85 – 109.69 (CH, m), 41.2 (CH_2), 39.9 (CH_2), 36.7 (CH_2), 32.0 (CH_2), 31.4, 27.90 (d, *J* = 4.0 Hz), 27.9, 21.1 (CH_2), 18.7; ESI-MS: *m/z* 448 $[M+H]^+$; ESI-HRMS for $[C_{18}H_{25}BrF_6N]^+$ ($[M+H]^+$): *m/z* Calcd. 448.1069, Found: 448.1052.



6l

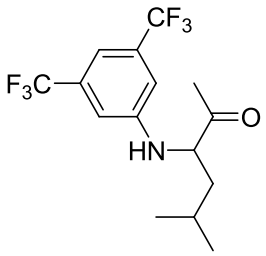
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.37 (m, 4H), 7.36–7.32 (m, 1H), 7.09 (s, 1H), 6.90 (s, 2H), 6.04 (d, *J* = 4.5 Hz, 1H), 5.04 (d, *J* = 4.5 Hz, 1H), 2.47 (qd, *J* = 7.3, 4.1 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.30; ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7, 146.5, 136.8, 132.39 (q, *J* = 33.0 Hz), 129.7, 129.1, 127.8, 123.56 (q, *J* = 271.0 Hz), 112.75–112.72 (m), 110.73–110.58 (m), 66.8, 32.7, 8.0. ESI-MS: *m/z* 376 $[M+H]^+$; ESI-HRMS for $[C_{18}H_{16}F_6NO]^+$ ($[M+H]^+$): *m/z* Calcd. 376.1130, Found: 376.1116.



6m

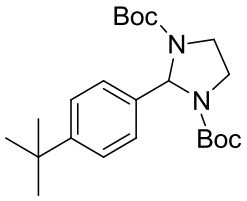
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, 1H), 6.86 (s, 2H), 4.90 (s, 1H), 3.28 (p, *J* = 6.7 Hz, 1H), 1.54 (s, 6H), 1.06 (d, *J* = 6.6 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.34; ^{13}C NMR (100 MHz, $CDCl_3$): δ217.9, 146.5, 132.44 (q, *J* = 33.0 Hz), 123.53 (q, *J* = 271.0 Hz), 113.67–113.62

(m), 110.80–110.65 (m), 62.4, 33.9, 24.1, 20.6; ESI-MS: *m/z* 342 $[M+H]^+$; ESI-HRMS for $[C_{15}H_{18}F_6NO]^+$ ($[M+H]^+$): *m/z* Calcd. 342.1287, Found: 342.1276.



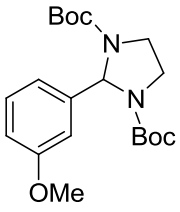
6n

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 1H), 6.90 (s, 2H), 4.65 (d, *J* = 7.4 Hz, 1H), 4.09 (td, *J* = 7.9, 4.7 Hz, 1H), 2.23 (s, 3H), 1.78 (dq, *J* = 8.4, 6.3 Hz, 1H), 1.70 (ddd, *J* = 13.2, 8.2, 4.7 Hz, 1H), 1.60 – 1.53 (m, 1H), 0.98 (t, *J* = 6.4 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.23; ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.9, 147.8, 132.80 (q, *J* = 33.0 Hz), 123.53 (q, *J* = 271.0 Hz), 112.35 – 112.23 (m), 111.25 – 111.10 (m), 61.7, 40.9, 26.6, 25.1, 23.3, 22.3; ESI-MS: *m/z* 342 $[M+H]^+$; ESI-HRMS for $[C_{15}H_{18}F_6NO]^+$ ($[M+H]^+$): *m/z* Calcd. 342.1287, Found: 342.1268.



8a, two rotamers.

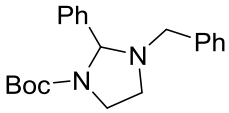
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.12 (m, 4H), 6.21 (s, 0.53H), 5.96 (s, 0.28H), 3.83 (s, 2H), 3.65 (s, 2H), 1.63 – 1.17 (m, 27H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.0, 150.8, 137.9, 126.2, 125.0, 80.5, 72.3, 43.7, 34.6, 31.4, 28.3; EI-MS: *m/z* 404 (M^+); EI-HRMS for $[C_{23}H_{36}N_2O_4]^+$: *m/z* Calcd. 404.2670, Found: 404.2671.



8b

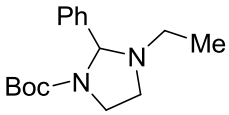
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.9 Hz, 1H), 7.04 – 6.73 (m, 3H), 6.21 – 5.89 (m, 1H), 3.97 – 3.82 (m, 2H), 3.79 (s, 3H), 3.63 (br, 2H), 1.50 – 1.19 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 152.9, 142.8, 129.2, 118.9, 113.4, 80.7, 72.2, 55.3, 43.6, 28.5, 28.3; EI-MS: *m/z*

378 (M^+); EI-HRMS for $[C_{20}H_{30}N_2O_5]^+$: *m/z* Calcd. 378.2149, Found: 378.2153.



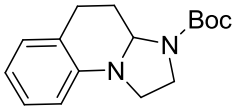
8c, two rotamers.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.36 (m, 2H), 7.34–7.16 (m, 8H), 5.10 (s, 0.21H), 4.84 (s, 0.65H), 3.73 (d, *J* = 13.0 Hz, 2H), 3.61–3.46 (m, 1H), 3.44–3.30 (m, 1H), 3.07–3.02 (m, 1H), 2.70–2.55 (m, 1H), 1.43 (s, 2.33H), 1.18 (s, 6.79H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 141.5, 138.3, 128.8, 128.3, 128.0, 128.0, 127.9, 127.2, 80.2, 79.9, 56.1, 49.9, 45.0, 28.5, 28.2; EI-MS: *m/z* 338 (M^+); EI-HRMS for $[C_{21}H_{26}N_2O_2]^+$: *m/z* Calcd. 338.1989, Found: 338.1993.



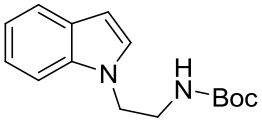
8d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.25 (m, 5H), 4.97 – 4.65 (m, 1H), 3.80 – 3.50 (m, 2H), 3.30 – 3.24 (m, 2H), 2.63 – 2.54 (m, 2H), 2.36 – 2.29 (m, 1H), 1.49 (s, 3H), 1.14 (s, 6H), 1.02 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 141.9, 128.0, 127.9, 127.6, 80.9, 79.8, 49.9, 46.0, 45.2, 28.52, 28.49, 28.2, 13.3; EI-MS: *m/z* 276 (M^+); EI-HRMS for $[C_{16}H_{24}N_2O_2]^+$: *m/z* Calcd. 276.1838, Found: 276.1843.



8f

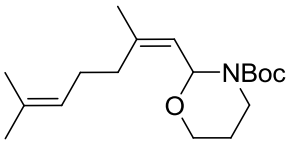
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (td, *J* = 7.8, 1.5 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.73 – 6.66 (m, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 4.68 (d, *J* = 10.1 Hz, 1H), 3.74 (s, 1H), 3.53 – 3.40 (m, 4H), 2.89 (ddd, *J* = 18.1, 12.8, 5.5 Hz, 1H), 2.78 (ddd, *J* = 16.8, 5.3, 2.4 Hz, 1H), 2.59 (s, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 143.8, 128.9, 127.1, 122.5, 117.8, 113.1, 80.1, 71.2, 46.2, 44.3, 28.6, 26.3, 26.03; EI-MS: *m/z* 274 (M^+); EI-HRMS for $[C_{16}H_{22}N_2O_2]^+$: *m/z* Calcd. 274.1681, Found: 274.1676.



8g

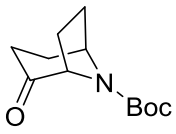
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.19 (t, *J* = 7.4

Hz, 1H), 7.13 – 7.07 (m, 1H), 7.04 (d, *J* = 3.2 Hz, 1H), 6.49 (d, *J* = 3.1 Hz, 1H), 4.58 (t, *J* = 6.3 Hz, 1H), 4.22 (t, *J* = 6.0 Hz, 2H), 3.43 (q, *J* = 6.1 Hz, 2H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 136.1, 128.7, 128.0, 121.8, 121.1, 119.6, 109.4, 101.7, 79.7, 45.9, 41.0, 28.4; ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 128.0 (CH), 121.7 (CH), 121.0 (CH), 119.6 (CH), 109.4 (CH), 101.7 (CH), 45.9 (CH_2), 40.9 (CH_2), 28.4 (CH_3); EI-MS: *m/z* 260 (M^+); EI-HRMS for $[C_{15}H_{20}N_2O_2]^+$: *m/z* Calcd. 260.1525, Found: 260.1525.



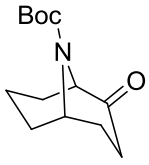
8h, rotamers

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17 (d, *J* = 6.5 Hz, 1H), 5.61 – 5.53 (m, 1H), 5.09 (tdd, *J* = 6.6, 3.3, 1.9 Hz, 1H), 4.06 – 3.90 (m, 2H), 3.73 – 3.66 (m, 1H), 3.18 (tdd, *J* = 13.1, 10.6, 3.3 Hz, 1H), 2.23 – 2.03 (m, 5H), 1.99 – 1.84 (m, 1H), 1.78 (t, *J* = 1.2 Hz, 1H), 1.73 (d, *J* = 1.3 Hz, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.46 (d, *J* = 1.7 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.93, 153.91, 142.2, 132.0, 131.9, 124.1, 124.0, 123.9, 121.6, 120.3, 119.6, 80.24, 80.22, 79.1, 78.7, 67.5, 63.7, 60.3, 60.2, 44.1, 39.9, 37.84, 37.77, 32.6, 32.4, 28.55, 28.53, 26.8, 26.6, 26.4, 25.9, 25.8, 23.6, 17.9, 17.8, 16.9. EI-MS: *m/z* 309 (M^+); EI-HRMS for $[C_{18}H_{31}NO_3]^+$: *m/z* Calcd. 309.2304, Found: 309.2311.



10a

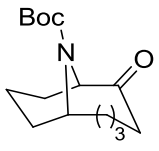
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (s, 1H), 4.04 (s, 1H), 2.65 (dd, *J* = 18.0, 7.5 Hz, 1H), 2.20 (d, *J* = 18.0 Hz, 1H), 1.96 (s, 1H), 1.86 – 1.74 (m, 2H), 1.73 – 1.61 (m, 2H), 1.60 – 1.52 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.3, 153.3, 80.4, 61.5, 51.8, 42.9, 28.6, 28.2, 17.1; For detailed characterizations, see Table S2.



10b, two rotamers with a ratio of 3: 2

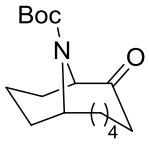
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70 (ddd, *J* = 9.0, 4.3, 1.9 Hz, 0.6H), 4.70 (ddd, *J* = 9.0, 4.3, 1.9 Hz, 0.4H), 4.13 (d, *J* = 8.4 Hz, 0.4H), 4.03 (d, *J* = 8.4 Hz, 0.6H), 2.77 (td, *J* = 17.3, 8.7 Hz, 1H),

2.45 – 2.32 (m, 0.4H), 2.30 – 2.20 (m, 0.6H), 2.14 (dt, *J* = 18.0, 1.7 Hz, 1H), 2.04 – 1.92 (m, 1H), 1.91 – 1.67 (m, 3H), 1.66 – 1.55 (m, 1H), 1.52 (s, 3.6H), 1.49 (s, 5.4H), 1.28 (dtd, *J* = 13.3, 11.5, 6.5 Hz, 1H), 1.04 (dtd, *J* = 15.2, 12.0, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.0, 216.5 (minor), 153.8, 153.5 (minor), 79.90, 79.86 (minor), 61.4, 60.8 (minor), 53.3 (minor), 52.5, 42.8 (minor), 42.4, 34.7 (minor), 33.7, 31.0, 30.2 (minor), 28.50 (minor), 28.47, 24.4, 22.31 (minor), 22.27; ^{13}C- dept-135 NMR (125 MHz, $CDCl_3$): δ 61.3 (CH), 60.8 (CH, minor), 53.2 (CH, minor), 52.4 (CH), 42.7 (CH_2, minor), 42.4 (CH_2), 34.6 (CH_2, minor), 33.6 (CH_2), 30.9 (CH_2), 30.1 (CH_2, minor), 28.41 (CH_3, minor), 28.38 (CH_3), 24.3 (CH_2), 22.22 (CH_2, minor), 22.18 (CH_2); EI-MS: *m/z* 239 (M^+); EI-HRMS for $[C_{13}H_{21}NO_3]^+$: *m/z* Calcd. 239.1521, Found: 239.1516.



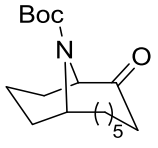
10c, two rotamers with a ratio of 5: 4

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.80 – 4.57 (m, 1H), 4.54 – 4.10 (m, 1H), 2.67 – 2.49 (m, 1H), 2.35 – 2.28 (m, 1H), 2.25 – 2.17 (m, 1H), 1.96 – 1.75 (m, 3H), 1.72 – 1.55 (m, 4H), 1.54 – 1.52 (m, 9H), 1.45 – 1.23 (m, 4H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.5, 215.2, 213.0, 156.0, 155.6, 155.3, 80.43, 80.39, 80.2, 67.7, 67.2, 59.6, 58.0, 57.6, 57.4, 51.7, 50.2, 40.7, 40.6, 40.23, 40.16, 31.6, 31.5, 31.1, 30.4, 30.2, 28.8, 28.7, 28.61, 28.58, 28.55, 28.4, 28.1, 27.62, 25.1, 24.60, 24.57, 24.2, 22.9, 22.4, 21.9, 21.8, 15.0; EI-MS: *m/z* 267 (M^+); EI-HRMS for $[C_{15}H_{25}NO_3]^+$: *m/z* Calcd. 267.1829, Found: 267.1825.



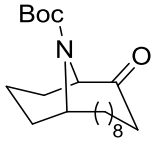
10d, two rotamers with a ratio of 5: 3

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.53 – 4.35 (m, 1H), 4.23 – 4.07 (m, 1H), 3.18 – 3.05 (m, 1H), 2.50 – 2.41 (m, 1H), 2.05 (ddd, *J* = 14.3, 8.1, 4.1 Hz, 1H), 1.99 – 1.80 (m, 3H), 1.77 – 1.65 (m, 2H), 1.64 – 1.56 (m, 2H), 1.55 – 1.48 (m, 9H), 1.46 – 1.29 (m, 5H), 1.28 – 1.12 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.2, 156.25, 155.23, 80.5, 80.4, 67.6, 67.1, 58.6, 58.4, 35.3, 35.25, 30.20, 29.5, 29.0, 28.6, 26.0, 24.9, 24.4, 22.9, 21.7; EI-MS: *m/z* 281 (M^+); EI-HRMS for $[C_{16}H_{27}NO_3]^+$: *m/z* Calcd. 281.1985, Found: 281.1986.



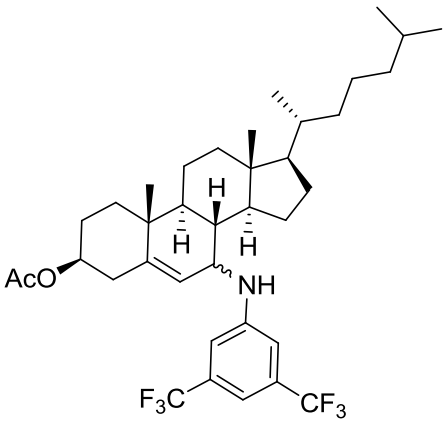
10e, two rotamers with a ratio of 2: 1

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.48 – 4.28 (m, 1H), 4.16 – 3.98 (m, 1H), 3.30 – 2.98 (m, 1H), 2.54 – 2.39 (m, 1H), 2.30 – 2.13 (m, 1H), 2.09 – 1.98 (m, 1H), 1.94 – 1.85 (m, 1H), 1.82 –1.65 (m, 3H), 1.61 – 1.44 (m, 1H), 1.52 – 1.50 (m, 9H), 1.46-1.42 (m, 2H), 1.42 – 1.15 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 156.3, 80.3, 67.4, 66.2, 59.0, 37.1, 36.0, 30.1, 29.8, 29.4, 28.6, 27.3, 27.1, 24.2, 24.0, 23.5, 23.2, 22.2, 21.1; EI-MS: *m/z* 295 (M^+); EI-HRMS for $[C_{17}H_{29}NO_3]^+$: *m/z* Calcd. 295.2142, Found: 295.2144.



10f, rotamers

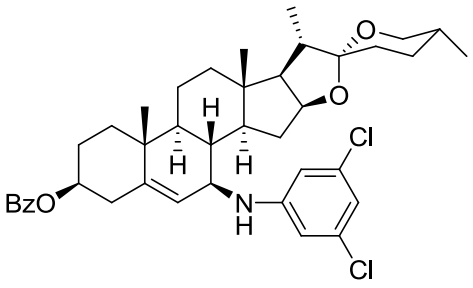
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.21 – 4.01 (m, 2H), 2.78 – 2.66 (m, 1H), 2.44 – 2.35 (m, 1H), 2.15 – 2.03 (m, 1H), 1.97 – 1.84 (m, 2H), 1.66 – 1.57 (m, 2H), 1.51 – 1.37 (m, 15H), 1.34– 1.11 (m, 11H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.6, 212.6, 212.2, 156.1, 155.7, 155.2, 80.3, 80.2, 68.3, 67.3, 58.9, 43.7, 38.6, 36.6, 35.9, 35.7, 35.6, 33.4, 31.5, 30.9, 28.5, 28.4, 28.2, 27.6, 27.1, 27.0, 26.7, 26.4, 26.1, 26.0, 25.85, 25.4, 25.1, 25.0, 24.2, 23.78, 23.5, 22.5, 21.9; EI-MS: *m/z* 337 (M^+); EI-HRMS for $[C_{20}H_{35}NO_3]^+$: *m/z* Calcd. 337.2611, Found: 337.2617.



15, two isomers with a ratio of 5: 1

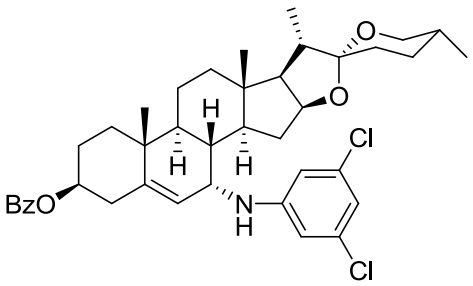
^{1}H NMR (400 MHz, $CDCl_3$): δ7.08 (s, 1H), 6.96 (s, 0.34H), 6.86 (s, 1.66H), 5.58 (s, 0.17H), 5.26 (s, 0.83H), 4.67 – 4.59 (m, 1H), 3.89 – 3.65 (m, 2H), 2.31 (d, *J* = 7.6 Hz, 2H), 2.03 – 2.02 (m, 4H), 1.94 – 1.89 (m, 2H), 1. 82 – 1.75 (m, 1H), 1. 67 – 1.06 (m, 23H), 0.92 (d, *J* = 6.5 Hz, 3H),

0.85 (d, J = 6.5 Hz, 6H), 0.71 – 0.70 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.11 (s, 4.84 F), -63.15 (s, 1.16 F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 148.5 (minor), 147.8, 143.2 (minor), 142.7, 132.69 (q, J = 33.0 Hz), 123.72 (q, J = 271.0 Hz), 123.2, 122.7 (minor), 111.88 – 111.86 (m), 109.75 – 109.67 (m), 73.4,73.3 (minor), 56.5, 56.0 (minor), 55.42 (d, J = 5.0 Hz), 50.6 (minor), 49.4, 48.5 (minor), 44.0 (minor), 43.3, 42.4 (minor), 39.6, 39.2 (minor), 38.7, 38.0 (minor), 37.7, 37.5 (minor), 37.0 (minor), 36.8, 36.5, 36.2, 35.9 (minor), 35.8, 28.6, 28.2 (minor), 28.1, 27.8, 27.6, 26.5, 24.4 (minor), 23.9, 22.9, 22.7, 21.5, 21.3, 21.0 (minor), 19.1, 18.92, 18.88 (minor), 18.6, 12.1, 11.9 (minor); ESI-MS: *m/z* 656 $[M+H]^+$; ESI-HRMS for $[C_{37}H_{52}F_6NO_2]^+$ $[M+H]^+$: *m/z* Calcd. 656.3897, Found: 656.3857.



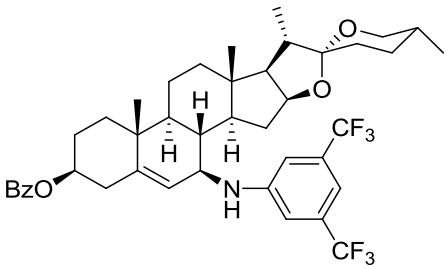
16a

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.5 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 6.63 (s, 1H), 6.49 (s, 2H), 5.59 (d, J = 4.7 Hz, 1H), 4.87 (tt, J = 10.9, 4.8 Hz, 1H), 4.35 (q, J = 7.5 Hz, 1H), 3.71 (dt, J = 10.8, 5.1 Hz, 1H), 3.44 (ddd, J = 12.2, 8.9, 2.9 Hz, 2H), 3.33 (td, J = 10.9, 1.6 Hz, 1H), 2.56 – 2.41 (m, 2H), 2.08 – 2.00 (m, 1H), 1.99 – 1.83 (m, 4H), 1.82 – 1.71 (m, 3H), 1.68 – 1.54 (m, 5H), 1.53 – 1.35 (m, 3H), 1.33 – 1.15 (m, 4H), 1.11 (s, 3H), 0.97 (d, J = 7.0 Hz, 3H), 0.82 (s, 3H), 0.77 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 149.4, 142.8, 135.8, 133.0, 130.70 129.7, 128.4, 123.4, 117.1, 111.3, 109.4, 80.7, 73.9, 67.0, 62.1, 50.3, 48.8, 44.0, 41.8, 40.3, 39.3, 38.1, 37.6, 37.1, 35.6, 32.0, 31.5, 30.4, 28.9, 27.8, 20.9, 18.7, 17.2, 16.4, 14.7; EI-MS: *m/z* 677 (M^+); EI-HRMS for $[C_{40}H_{49}Cl_2NO_4]^+$: *m/z* Calcd. 677.3039, Found: 677.3037.



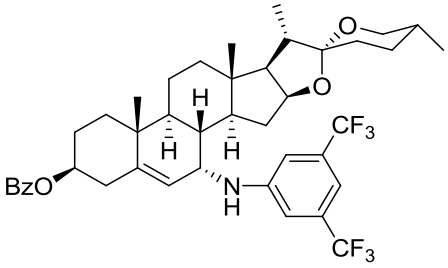
16b

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 – 7.99 (m, 2H), 7.57 – 7.52 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.61 (t, *J* = 1.8 Hz, 1H), 6.38 (d, *J* = 1.8 Hz, 2H), 5.32 (s, 1H), 4.87 (tdd, *J* = 10.8, 6.7, 4.5 Hz, 1H), 4.40 – 4.32 (m, 1H), 3.63 – 3.52 (m, 2H), 3.45 (ddd, *J* = 11.0, 4.5, 2.2 Hz, 1H), 3.32 (t, *J* = 11.0 Hz, 1H), 2.49 – 2.38 (m, 2H), 2.08 – 1.99 (m, 2H), 1.95 (dt, *J* = 13.5, 3.6 Hz, 1H), 1.87 (p, *J* = 6.9 Hz, 1H), 1.81 – 1.72 (m, 3H), 1.72 – 1.61 (m, 4H), 1.57 – 1.47 (m, 3H), 1.42 (ddd, *J* = 13.7, 8.7, 5.3 Hz, 2H), 1.34 (ddd, *J* = 13.4, 10.4, 5.3 Hz, 1H), 1.23 (dtd, *J* = 18.0, 9.5, 7.4, 4.2 Hz, 3H), 1.13 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.82 (s, 3H), 0.76 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 148.5, 142.1, 135.8, 133.0, 130.7, 129.7, 128.4, 123.5, 116.7, 111.0, 109.4, 81.1, 74.0, 67.0, 61.6, 56.0, 54.8, 49.4, 41.9, 41.2, 39.8, 38.7, 37.9, 36.9, 36.7, 34.1, 31.5, 30.4, 28.9, 27.9, 21.2, 19.4, 17.2, 16.5, 14.7; EI-MS: *m/z* 677 (M^+); EI-HRMS for $[C_{40}H_{49}Cl_2NO_4]^+$: *m/z* Calcd. 677.3039, Found: 677.3037.



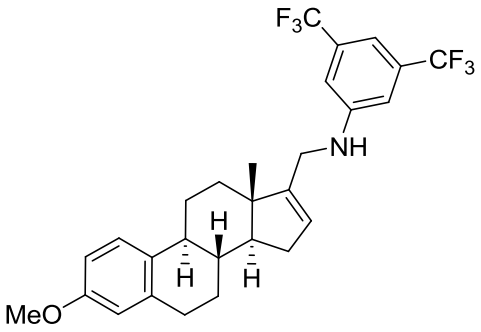
17a

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.98 (m, 2H), 7.58 – 7.51 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.11 (s, 1H), 6.98 (s, 2H), 5.61 (d, *J* = 4.2 Hz, 1H), 4.88 (tt, *J* = 10.9, 5.2 Hz, 1H), 4.34 (q, *J* = 7.4 Hz, 1H), 3.90 – 3.75 (m, 2H), 3.45 – 3.37 (m, 1H), 3.31 (t, *J* = 10.9 Hz, 1H), 2.57 – 2.42 (m, 2H), 2.00 (dtd, *J* = 16.8, 9.8, 7.9, 4.7 Hz, 3H), 1.91 – 1.71 (m, 5H), 1.68 – 1.54 (m, 6H), 1.51 – 1.38 (m, 2H), 1.36 – 1.15 (m, 4H), 1.13 (s, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.83 (s, 3H), 0.76 (d, *J* = 6.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.13; ^{13}C NMR (100 MHz, $CDCl_3$):) δ 166.1, 148.4, 143.3, 133.0, 132.78 (q, *J* = 33.0 Hz), 130.6, 129.7, 128.5, 123.69 (q, *J* = 271.0 Hz), 122.8, 112.08 – 112.05 (m), 110.31 – 110.20 (m), 109.4, 80.6, 73.8, 66.9, 62.2, 50.3, 48.6, 44.0, 41.8, 40.4, 39.3, 38.1, 37.7, 37.1, 35.5, 31.9, 31.5, 30.4, 28.9, 27.8, 20.9, 18.7, 17.2, 16.3, 14.7; EI-MS: *m/z* 745 (M^+); EI-HRMS for $[C_{42}H_{49}F_6NO_4]^+$: *m/z* Calcd. 745.3566, Found: 745.3560.



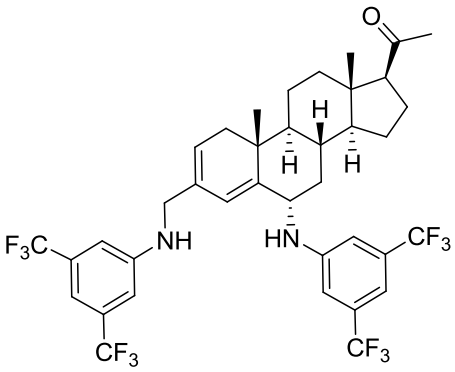
17b

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.02 (s, 1H), 6.86 (s, 2H), 5.26 (s, 1H), 4.95 – 4.82 (m, 1H), 4.38 (dt, *J* = 21.7, 8.5 Hz, 2H), 3.68 (t, *J* = 9.3 Hz, 1H), 3.43 (dd, *J* = 11.3, 4.3 Hz, 1H), 3.23 (t, *J* = 11.1 Hz, 1H), 2.49 – 2.37 (m, 2H), 2.11 – 1.92 (m, 3H), 1.91 – 1.72 (m, 4H), 1.71 – 1.61 (m, 3H), 1.60 – 1.45 (m, 5H), 1.42 – 1.19 (m, 5H), 1.14 (s, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.86 (s, 3H), 0.62 (d, *J* = 6.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.26; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 147.6, 142.5, 133.0, 132.56 (q, *J* = 33.0 Hz), 130.7, 129.7, 128.5, 123.68 (q, *J* = 271.0 Hz), 123.4, 111.58 – 118.38 (m), 109.6, 109.54 – 109.46 (m), 81.0, 73.9, 66.8, 61.5, 56.0, 54.5, 49.2, 41.9, 41.2, 39.6, 38.8, 37.8, 36.9, 36.7, 33.8, 31.1, 30.1, 29.0, 27.9, 21.1, 19.2, 17.1, 16.8, 14.6; EI-MS: *m/z* 745 (M^+); EI-HRMS for $[C_{42}H_{49}F_6NO_4]^+$: *m/z* Calcd. 745.3566, Found: 745.3547.



18

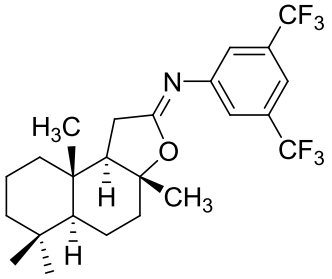
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.8 Hz, 1H), 7.15 (s, 1H), 7.00 (s, 2H), 6.97 (d, *J* = 2.8 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.8 Hz, 1H), 4.82 (td, *J* = 10.1, 6.5 Hz, 1H), 4.69 (s, 2H), 4.34 (d, *J* = 9.1 Hz, 1H), 3.74 (s, 3H), 2.56 (ddd, *J* = 17.5, 10.1, 2.4 Hz, 1H), 2.43 – 2.24 (m, 4H), 1.81 – 1.76 (m, 1H), 1.66 (q, *J* = 11.2 Hz, 1H), 1.54 – 1.28 (m, 6H), 0.86 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.22; ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.3, 158.3, 148.6, 138.7, 133.2, 132.79 (q, *J* = 32.5 Hz), 127.0, 123.70 (q, *J* = 271.2 Hz), 113.5, 112.5, 112.07 – 112.05 (m), 110.29 – 110.17 (m), 101.3, 55.4, 53.3, 53.0, 44.4, 38.6, 35.8, 35.6, 29.9, 29.5, 26.8, 23.9, 18.7; EI-MS: *m/z* 509 (M^+); EI-HRMS for $[C_{28}H_{29}F_6NO]^+$: *m/z* Calcd. 509.2153, Found: 509.2147.



19

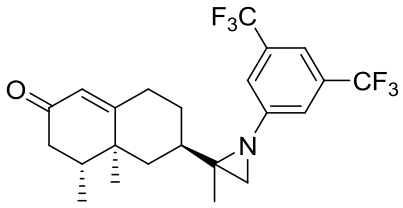
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (s, 1H), 7.13 (s, 1H), 7.03 (s, 2H), 6.94 (s, 2H), 5.57 (d, *J* = 6.3 Hz, 1H), 5.50 (t, *J* = 2.0 Hz, 1H), 4.25 (t, *J* = 5.5 Hz, 1H), 4.15 – 4.03 (m, 2H), 3.73 (t, *J* = 3.3 Hz, 2H), 2.53 (t, *J* = 9.1 Hz, 1H), 2.34 – 2.25 (m, 3H), 2.23 – 2.14 (m, 3H), 2.12 (s, 3H), 2.08 (s, 1H), 2.05 – 2.02 (m, 1H), 1.79 – 1.61 (m, 5H), 1.55 – 1.51 (m, 2H), 0.90 (s, 3H), 0.64 (s, 3H); ^{19}F NMR (470 MHz, , $CDCl_3$): δ -63.21, -63.27; ^{13}C NMR (125 MHz, , $CDCl_3$): δ 209.7, 149.0, 148.3, 147.5, 132.43 (q, *J* = 32.5 Hz), 132.40 (q, *J* = 32.5 Hz), 130.7, 123.74 (q, *J* = 271.2 Hz), 123.54 (q, *J* = 271.2 Hz), 119.8, 117.6, 114.31 – 114.29 (m), 112.16 – 112.14 (m), 111.75 – 111.63 (m), 110.23 – 110.12 (m), 63.9, 56.4, 54.9, 47.9, 44.2, 39.2, 38.3, 37.9, 36.4, 31.7, 31.54

(d, J = 3.7 Hz), 29.9, 24.7, 23.0, 21.8, 17.3, 13.5; EI-MS: *m/z* 766 (M^+); EI-HRMS for $[C_{38}H_{38}F_{12}N_2O]^+$: *m/z* Calcd. 766.2793, Found: 766.2787.



20

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 0.25H), 7.52 (s, 0.86H), 7.45 (s, 1.60H), 7.27 (s, 0.39H), 2.66 (dd, J = 16.0, 14.4 Hz, 1H), 2.51 (dd, J = 16.0, 6.5 Hz, 1H), 2.04 (dt, J = 11.8, 3.3 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.77 – 1.61 (m, 2H), 1. 51– 1.43 (m, 4H), 1.33 (s, 3H), 1.26 –1.03 (m, 3H, overlapped with hexane residue), 0.94 (s, 3H), 0.89 (s, 3H, overlapped with hexane residue), 0.85 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.83 (s, 1.28F), -62.88 (s, 4.72F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 148.7, 131.8 (q, J = 33.0 Hz) , 126.29 (q, J = 271.0 Hz), 123.33 – 123.30 (m), 117.04 – 116.97 (m), 89.0, 59.2 (minor), 58.9, 56.9, 42.4, 42.3, 39.7, 39.6 (minor), 38.9 (minor), 38.8, 36.4, 33.4, 33.2, 29.9 (minor), 29.8, 25.7 (minor), 21.81, 21.78 (minor), 21.1, 20.9, 20.8 (minor), 18.3, 18.2 (minor), 15.3; ESI-MS: *m/z* 462 $[M+H]^+$; ESI-HRMS for $[C_{24}H_{30}F_6NO]^+$ ($[M+H]^+$): *m/z* Calcd. 462.2226, Found: 462.2210.

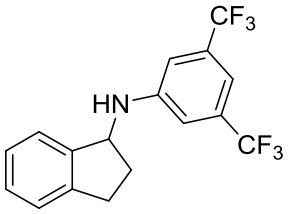
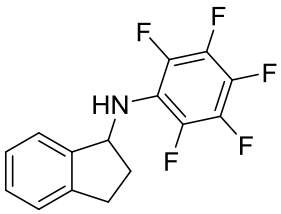
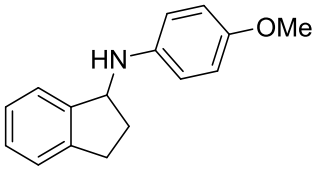
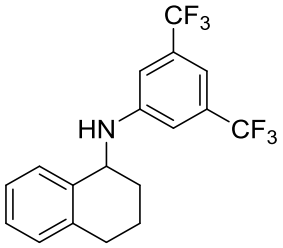
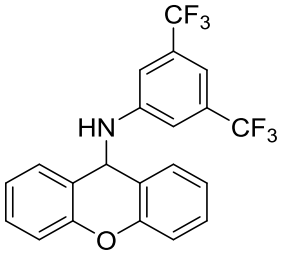
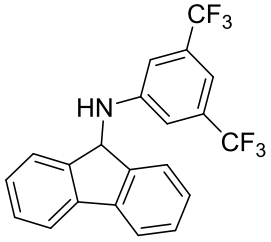


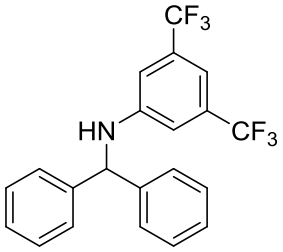
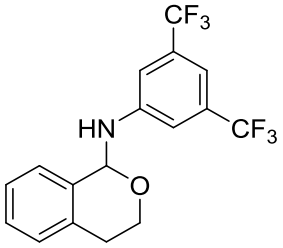
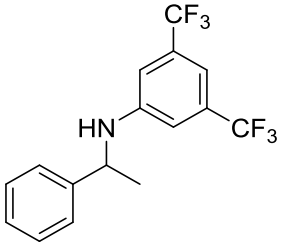
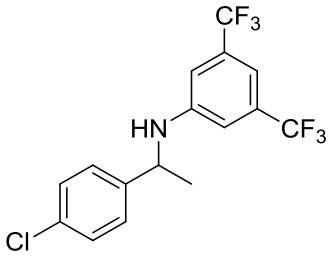
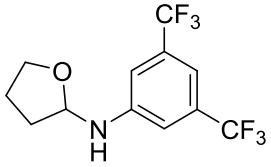
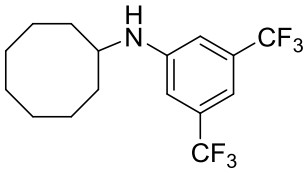
21

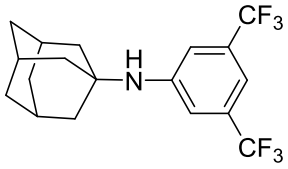
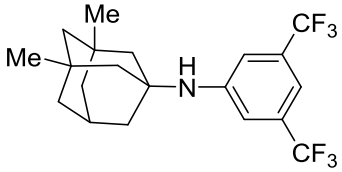
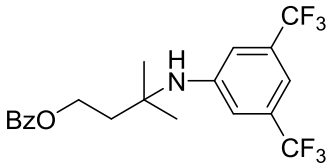
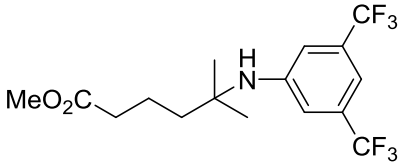
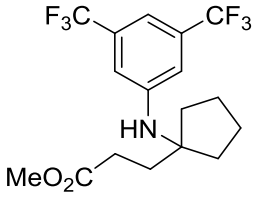
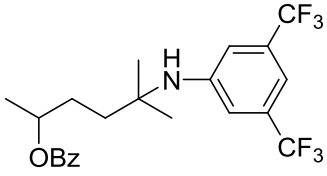
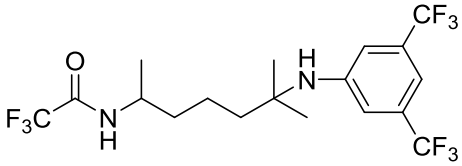
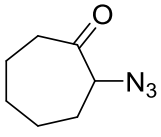
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.21 (s, 2H), 5.81 (s, 1H), 2.57 – 2.44 (m, 2H), 2.43 (s, 1H), 2.35 – 2.22 (m, 2H), 2.12 – 1.98 (m, 4H), 1.97 (s, 1H), 1.69 – 1.64 (m, 1H), 1.48 (qd, J = 12.6, 4.6 Hz, 1H), 1.11 (s, 3H), 1.01 (d, J = 6.8 Hz, 3H), 0.94 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -63.02; ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5, 169.6, 152.1, 132.40 (q, J = 32.5 Hz), 125.2, 123.40 (q, J = 271.0 Hz), 120.60 – 120.58 (m), 115.49 – 115.41 (m), 46.4, 42.2, 41.2, 40.9, 40.7, 39.9, 39.3, 32.6, 29.2, 17.0, 15.2, 15.1; ^{13}C-dept-135 NMR (125 MHz, $CDCl_3$): δ 125.0 (CH), 120.46 – 120.44 (m), 115.33 – 115.30 (m), 42.0 (CH_2), 41.0 (CH_2), 40.8, 40.6, 39.8 (CH_2),

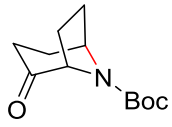
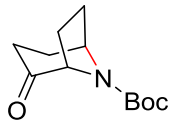
32.5 (CH_2), 29.0 (CH_2), 16.9, 15.05, 14.96; EI-MS: *m/z* 445 (M^+); EI-HRMS for $[C_{23}H_{25}F_6NO]^+$: *m/z* Calcd. 445.1835, Found: 445.1835.

Table S2 References for the characterization of known compounds

 **3a**	Ref. 11
 **3c**	Ref. 11
 **3i**	Ref. 12
 **5a**	Ref. 13
 **5b**	Ref. 11
 **5c**	Ref. 11

 **5d**	Ref. 14
 **5e**	Ref. 11
 **5i**	Ref. 11
 **5j**	Ref. 15
 **6a**	Ref. 11
 **6b**	Ref. 16

 **6c**	Ref. 11
 **6d**	Ref. 11
 **6e**	Ref. 11
 **6f**	Ref. 11
 **6g**	Ref. 11
 **6j**	Ref. 11
 **6k**	Ref. 11
 **9a**	Ref. 17

 **10a**	Ref. 7
 **14**	Ref. 18

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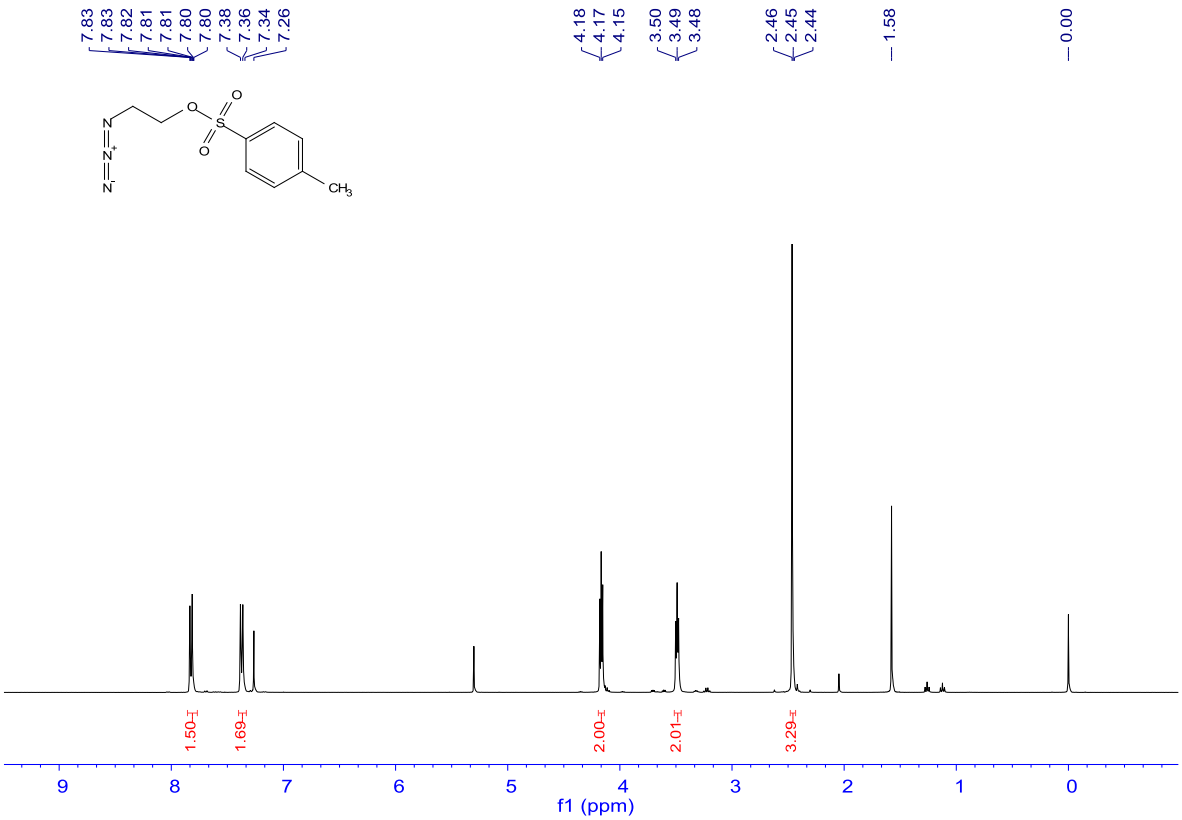
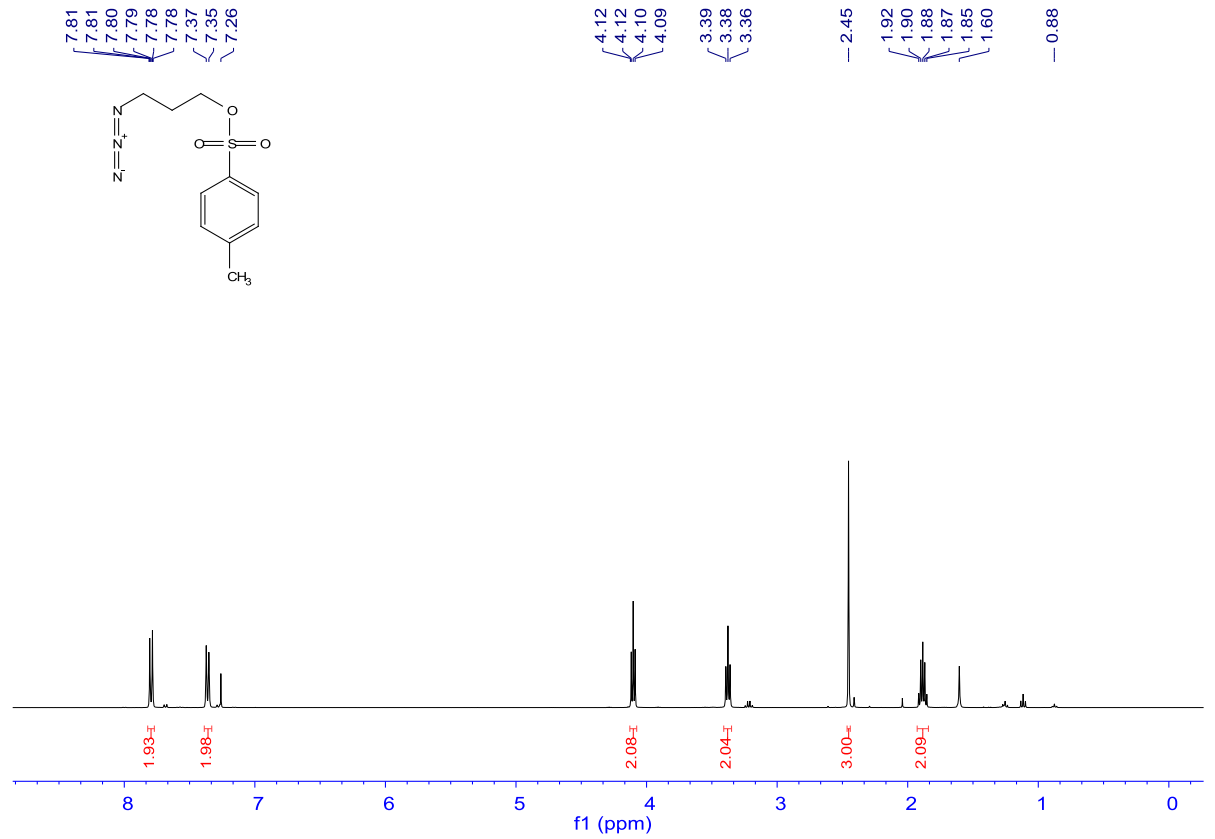
NMR spectra of substrates and products

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3.38
3.36
2.45
1.92
1.90
1.88
1.87
1.85
1.60
0.88
1.93
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5
4
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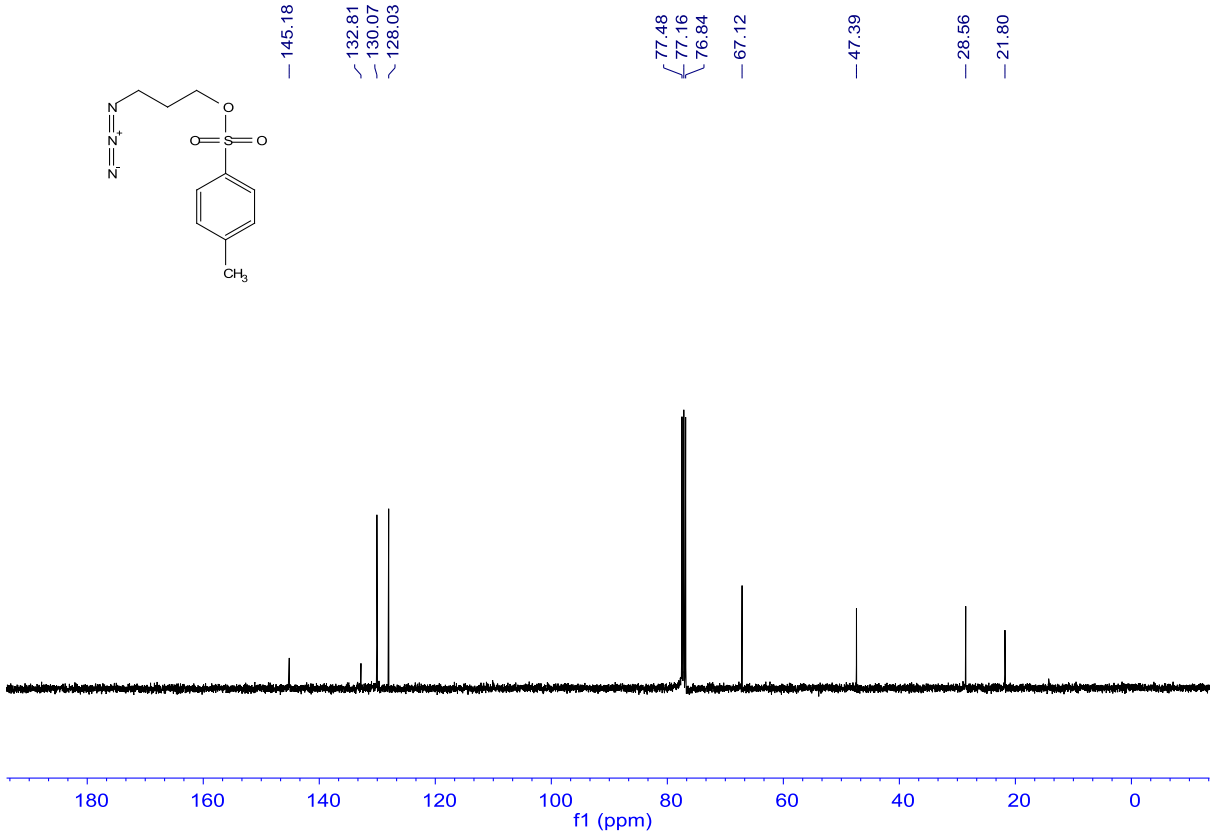
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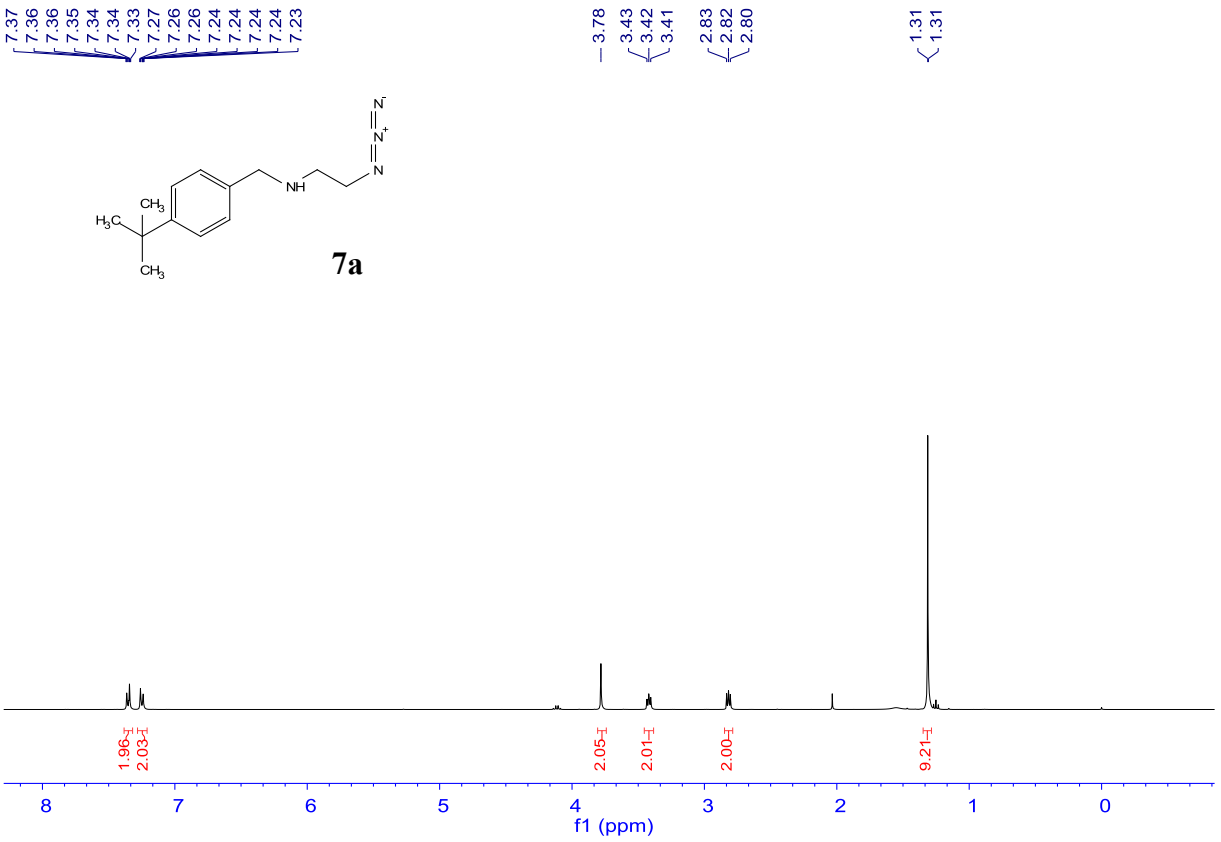
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7.24
7.24
7.23
3.78
3.43
3.42
3.41
2.83
2.82
2.80
1.31
1.31
NH
CH3
H3C
CH3
1.96
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4
3
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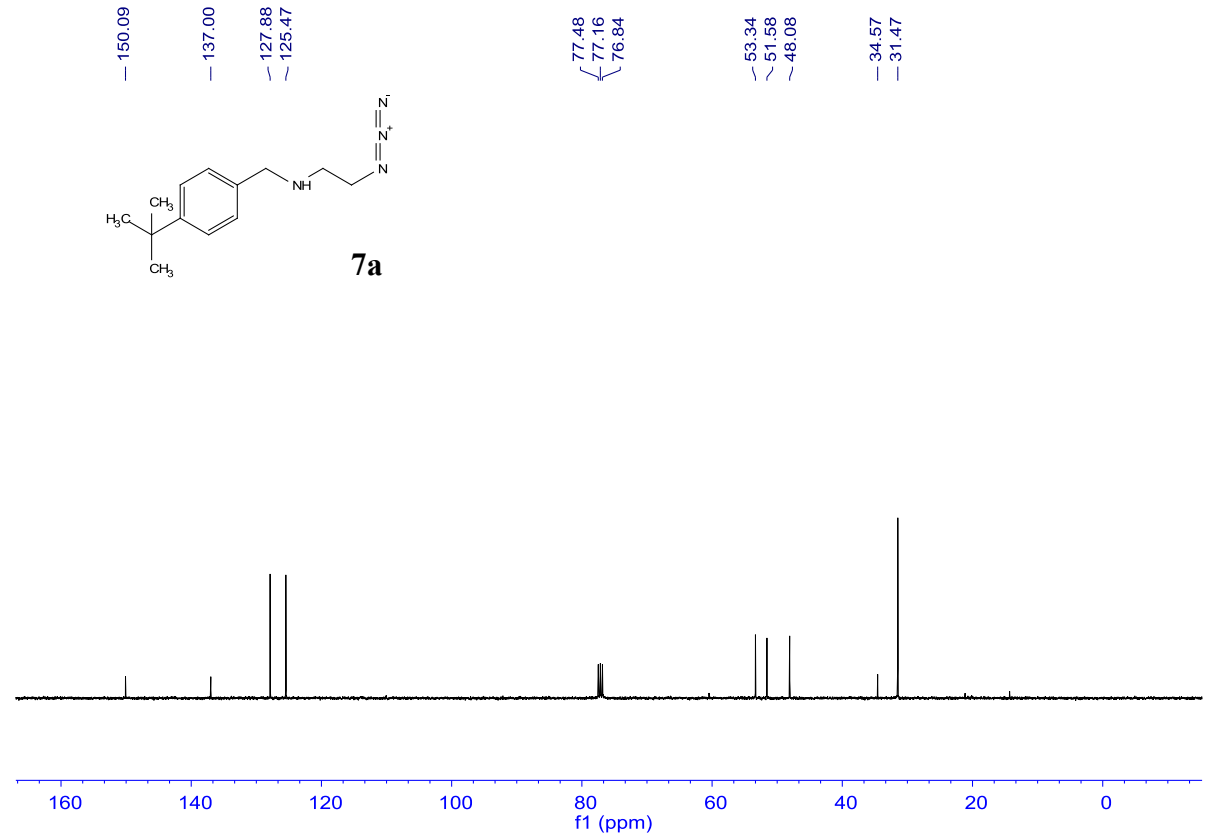
0
f1 (ppm)

7a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80
60
40
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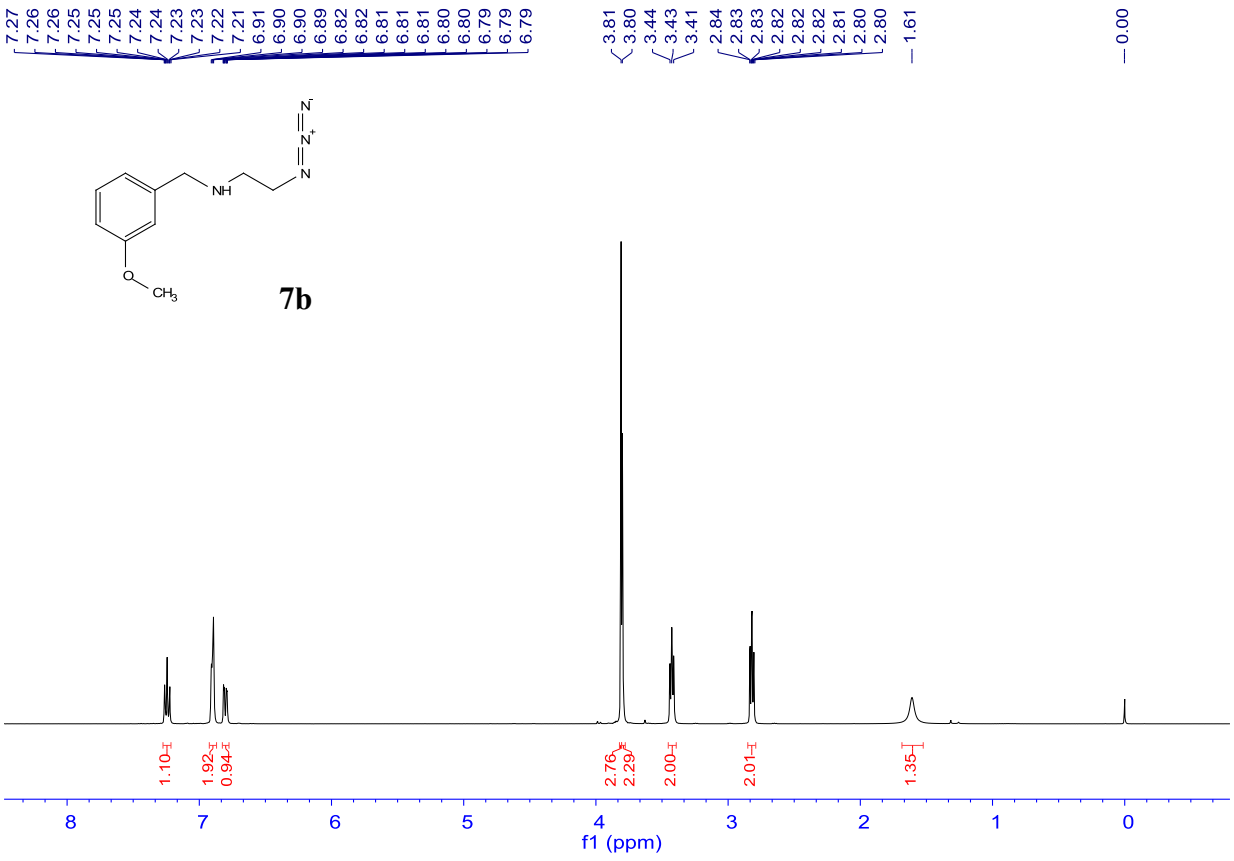
0
f1 (ppm)

7a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3.81 3.80 3.44 3.43 3.41
2.84 2.83 2.83 2.82 2.82 2.82 2.81 2.80 2.80
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7b
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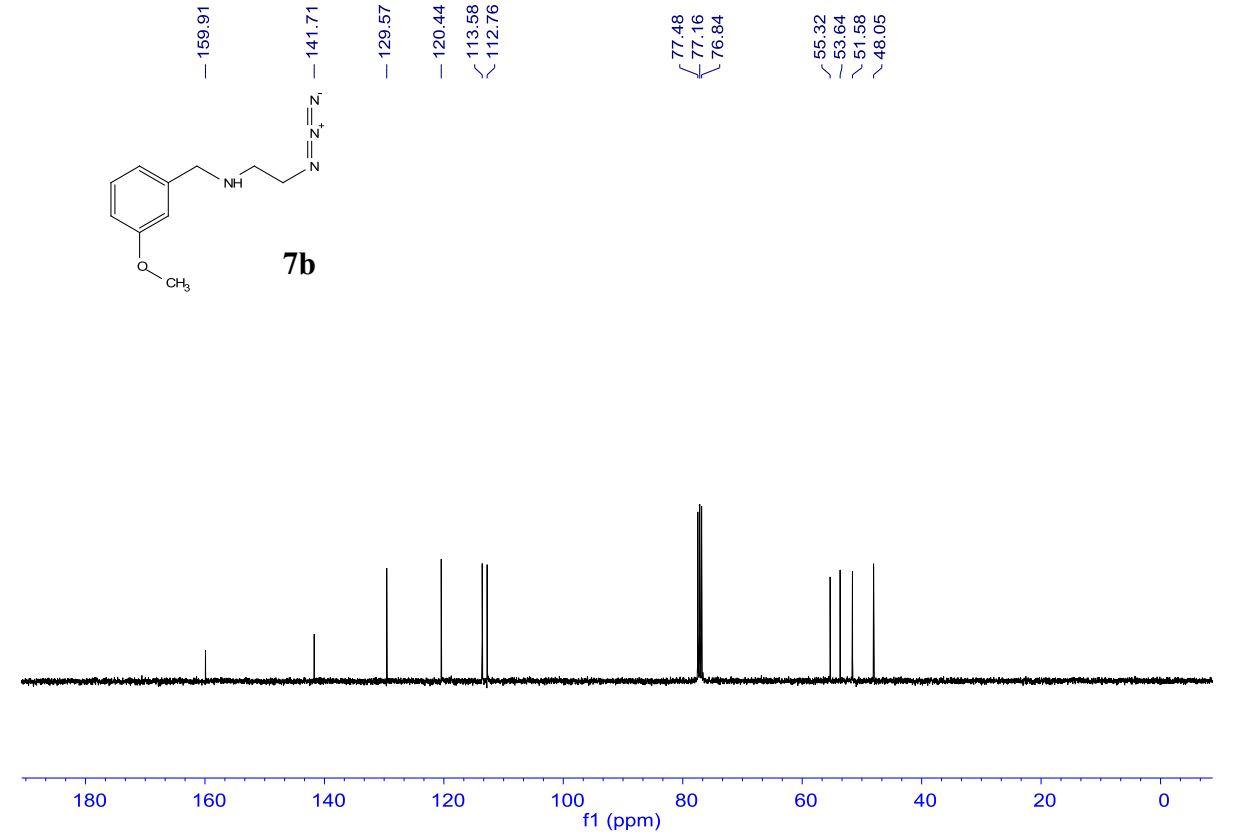
f1 (ppm)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7b
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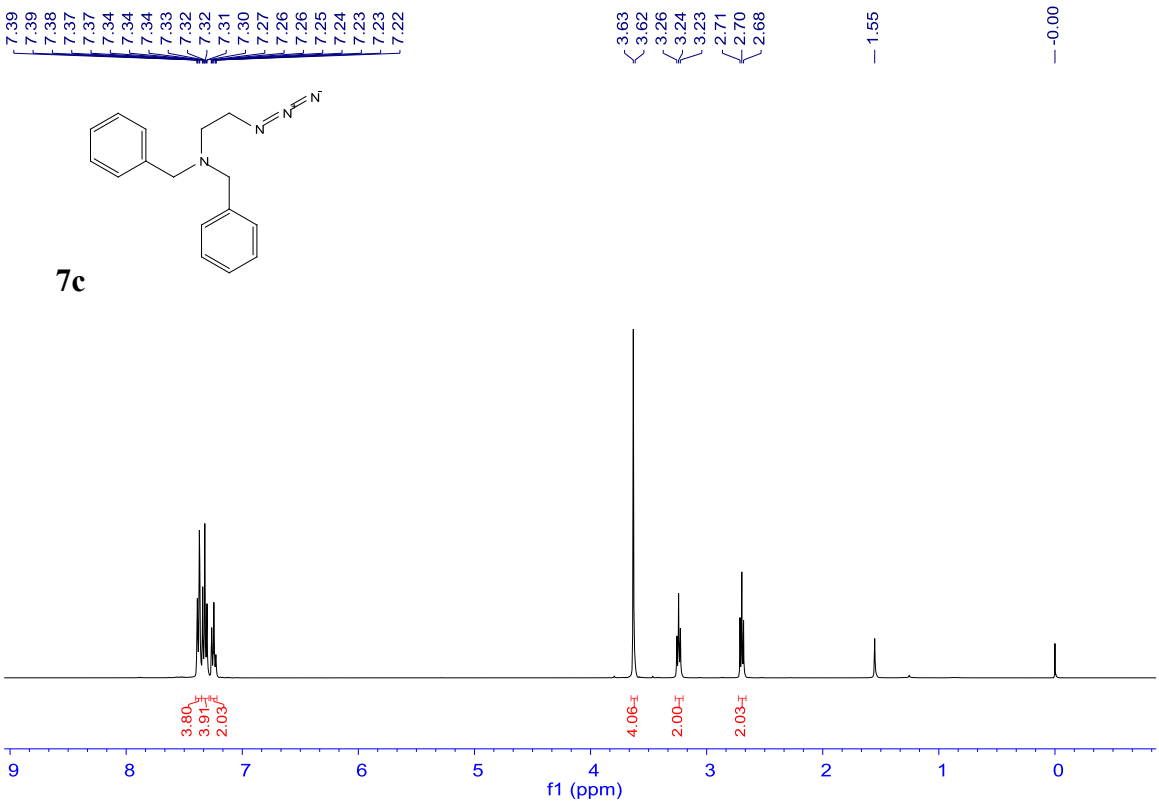
f1 (ppm)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7.30
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.22
3.63
3.62
3.26
3.24
3.23
2.71
2.70
2.68
1.55
0.00
7c
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7
6
5
4
3
2
1
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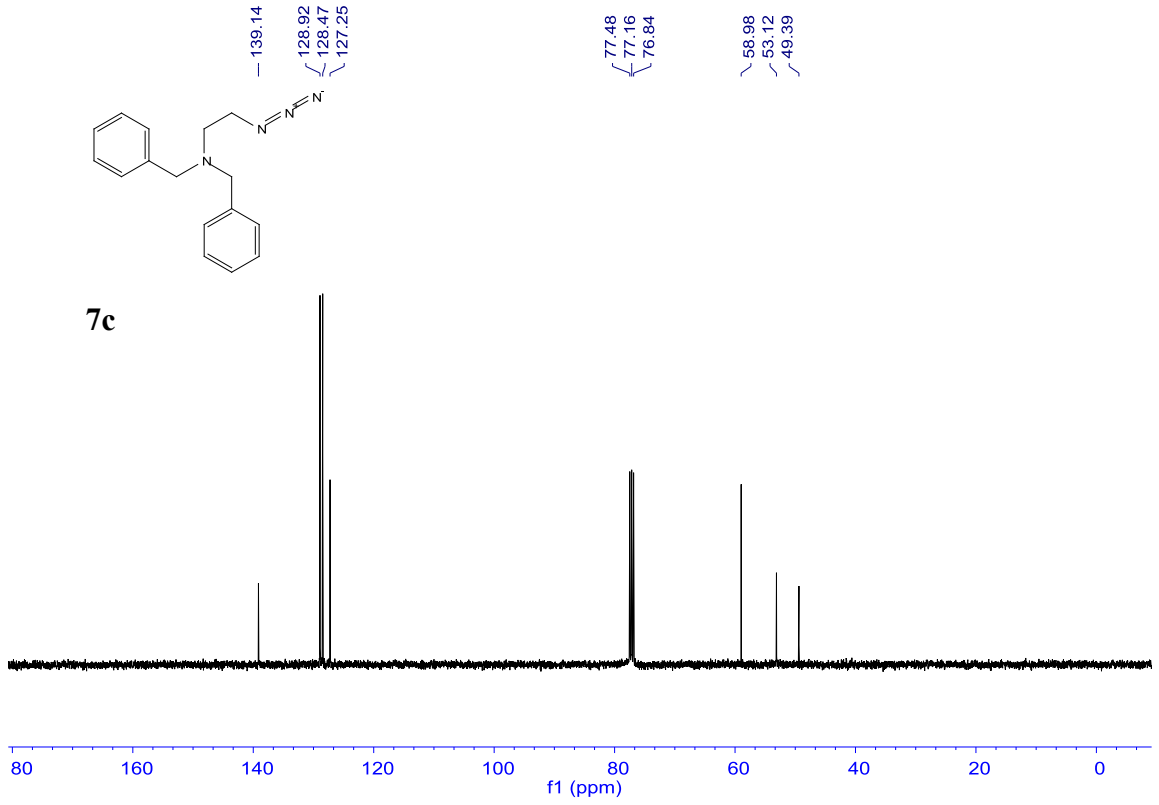
f1 (ppm)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100
80
60
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20
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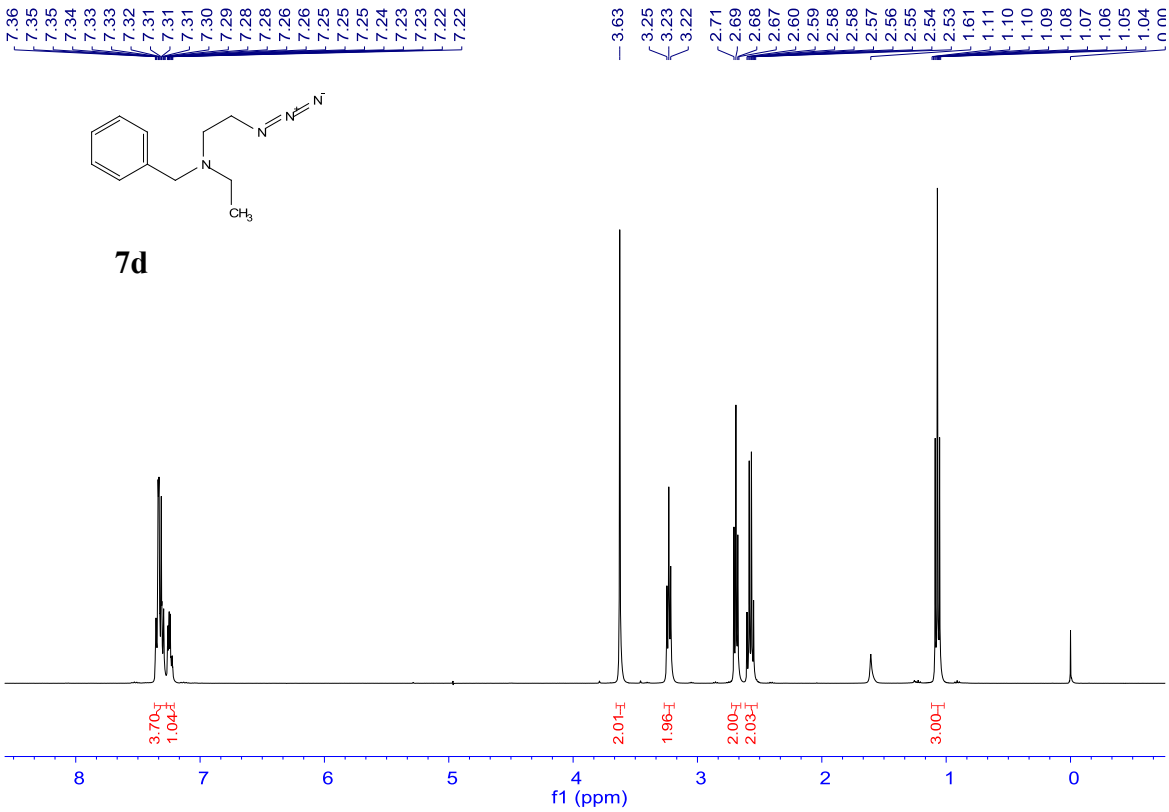
f1 (ppm)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3.63 3.25 3.23 3.22
2.71 2.69 2.68 2.67 2.60 2.59 2.58 2.58 2.57 2.56 2.55 2.54 2.53 1.61 1.11 1.10 1.10 1.09 1.08 1.07 1.06 1.05 1.04
N
N
N
N
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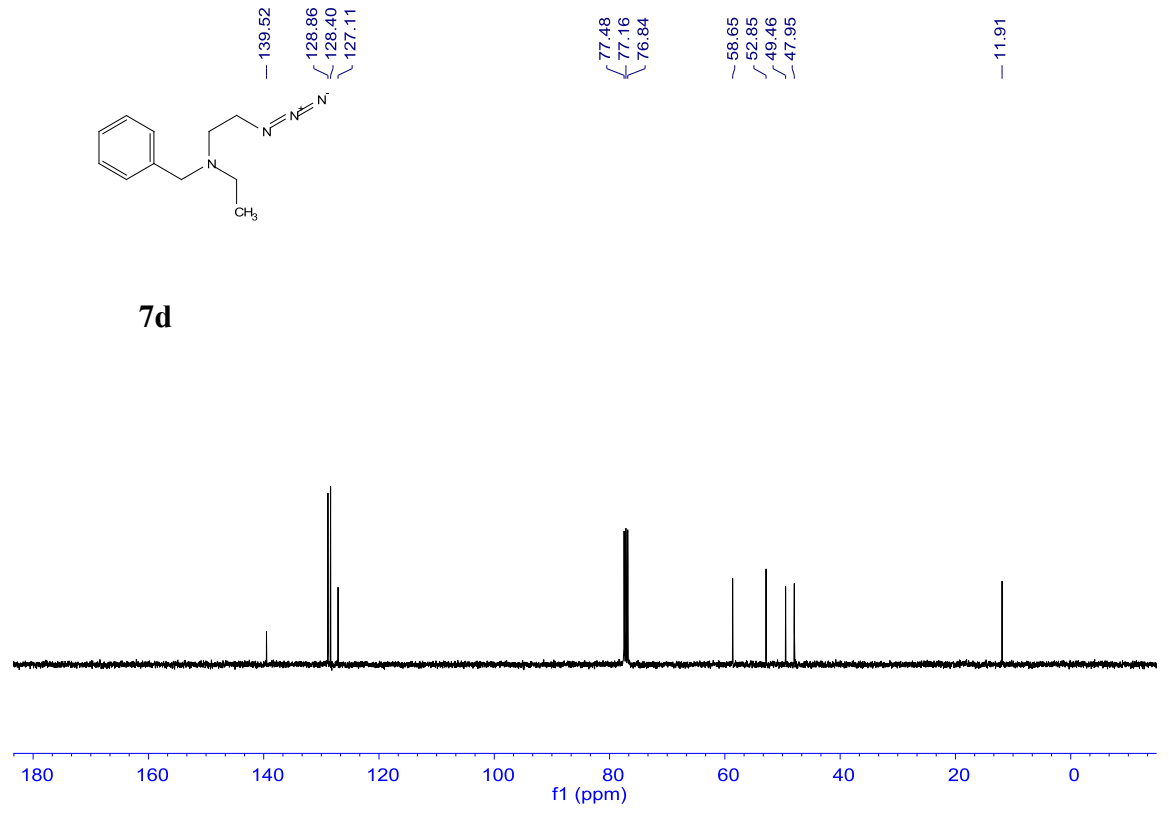
3.00
8 7 6 5 4 3 2 1 0
f1 (ppm)

7d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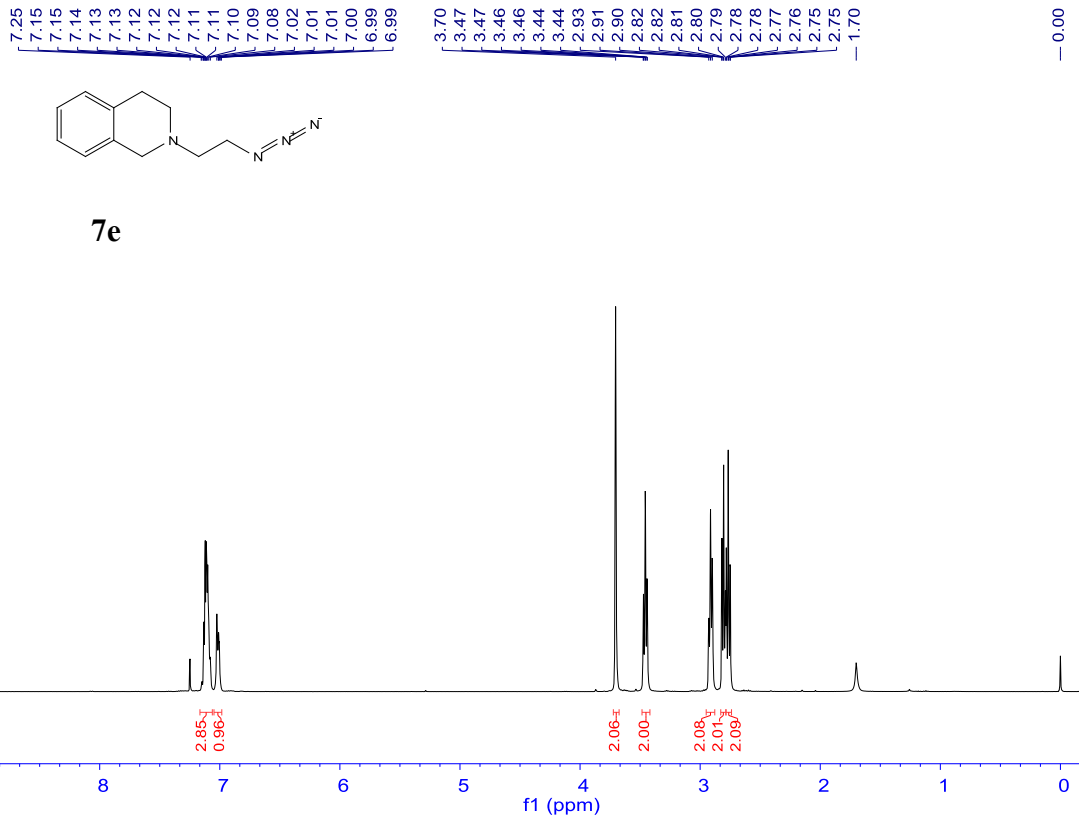
f1 (ppm)

7d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7.02
7.01
7.01
7.00
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6.99
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3.47
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2.91
2.90
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2.82
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2.80
2.79
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2.78
2.77
2.76
2.75
2.75
1.70
0.00
N
N
N
N

7e

2.85
0.96
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2.00
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2.01
2.09
9
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7
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5
4
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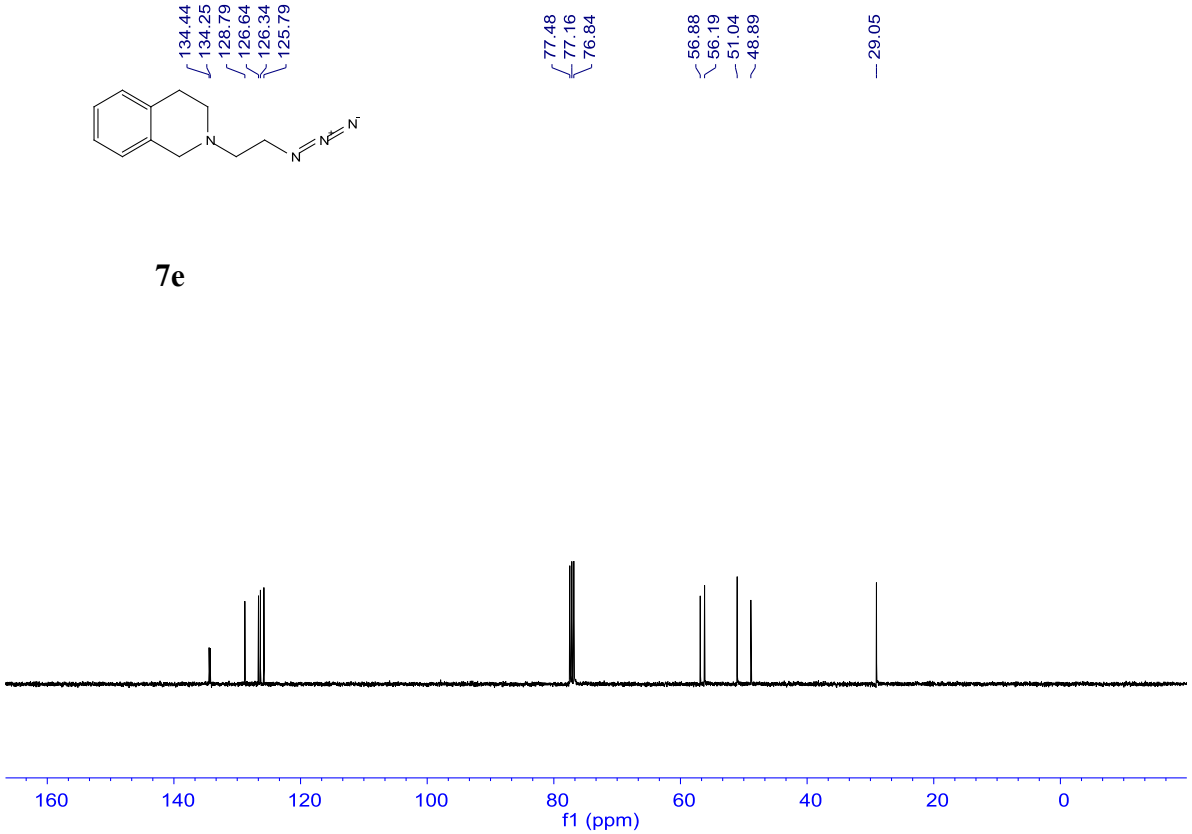
f1 (ppm)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N
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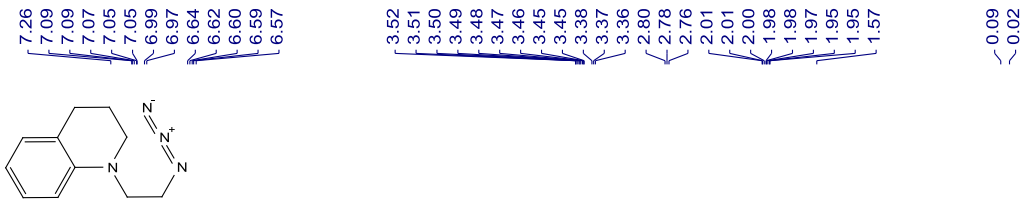
80
60
40
20
0
f1 (ppm)

7e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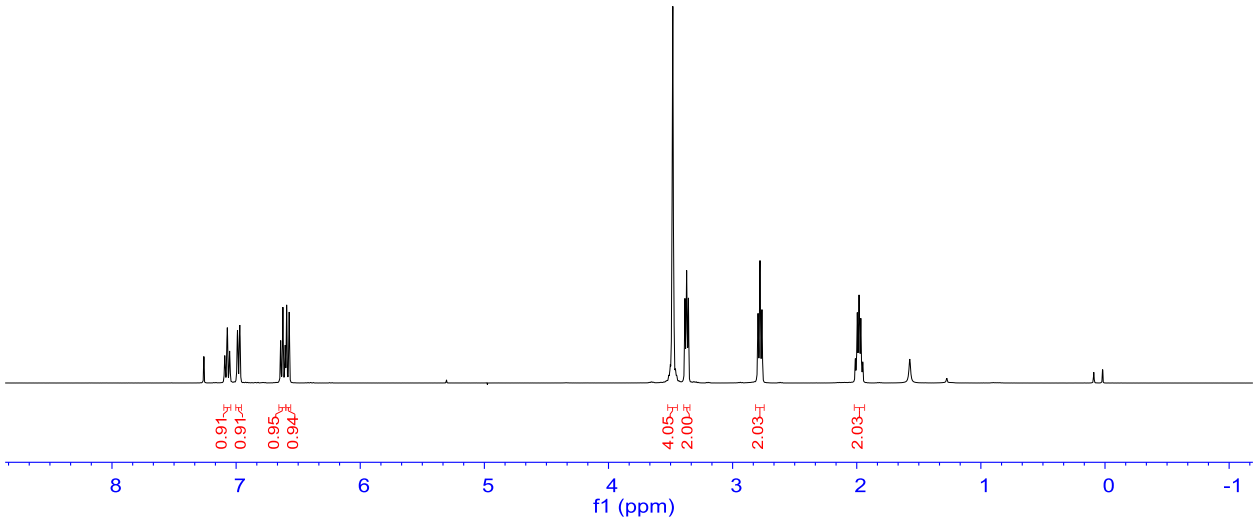
7f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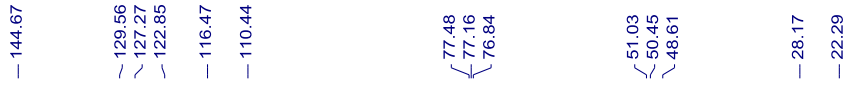
0
-1
f1 (ppm)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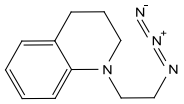
22.29



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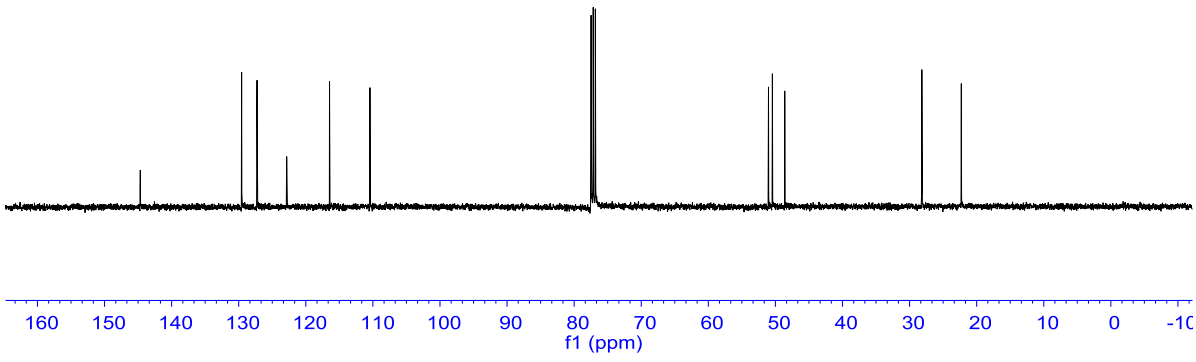
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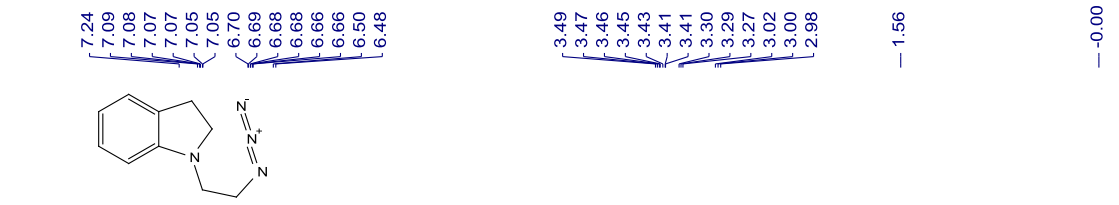
f1 (ppm)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6.48
3.49
3.47
3.46
3.45
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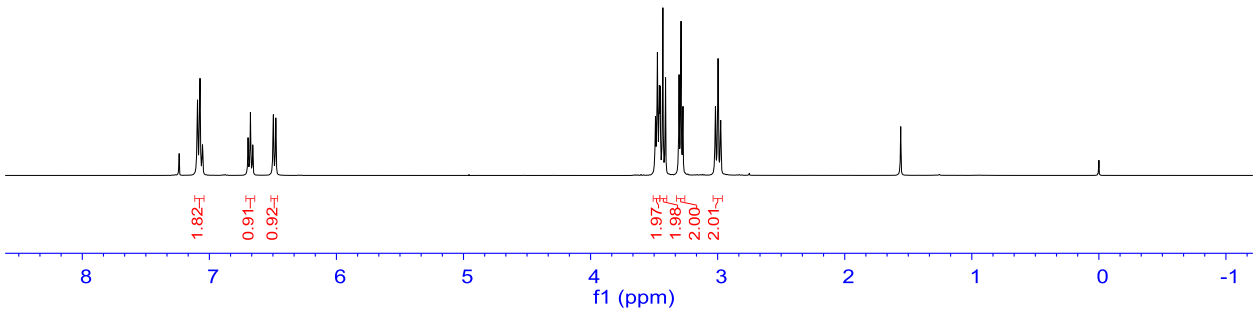
7g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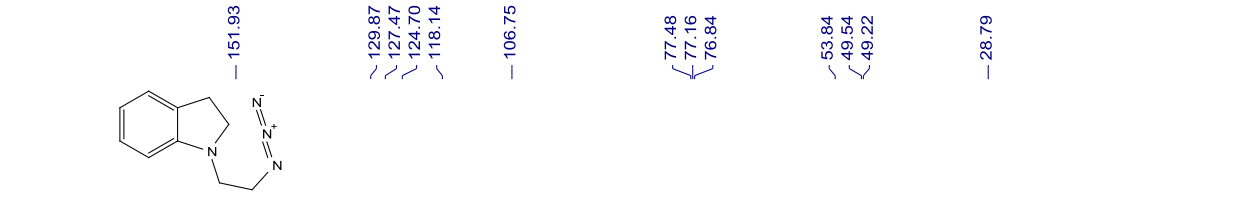
f1 (ppm)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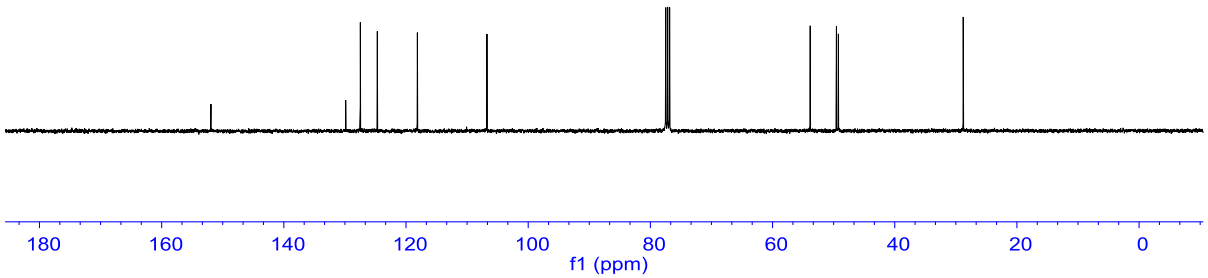
7g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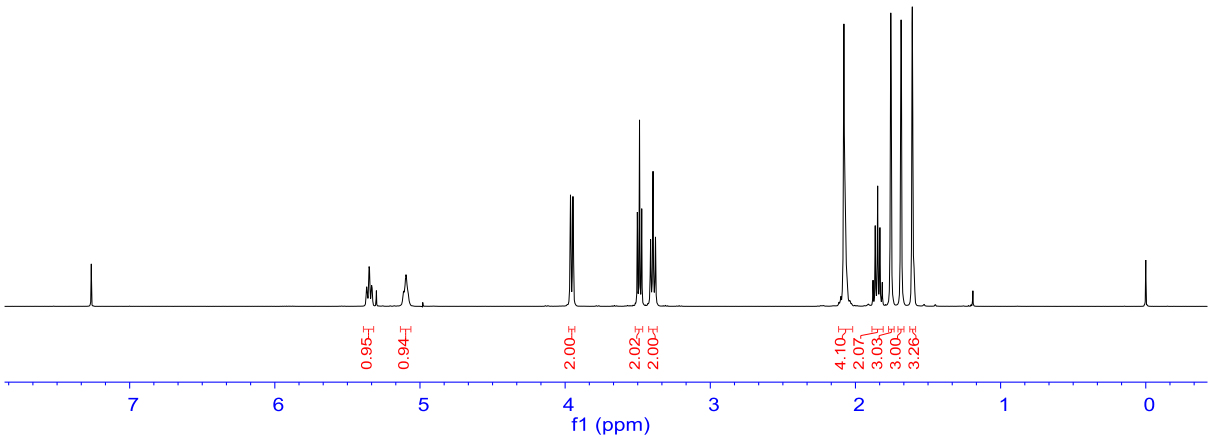
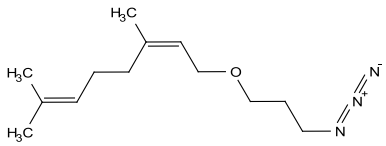
f1 (ppm)

7h





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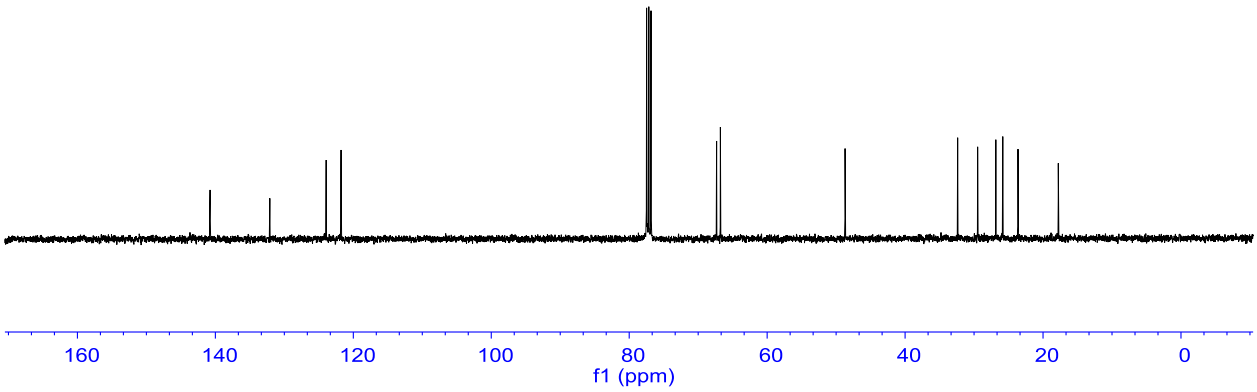

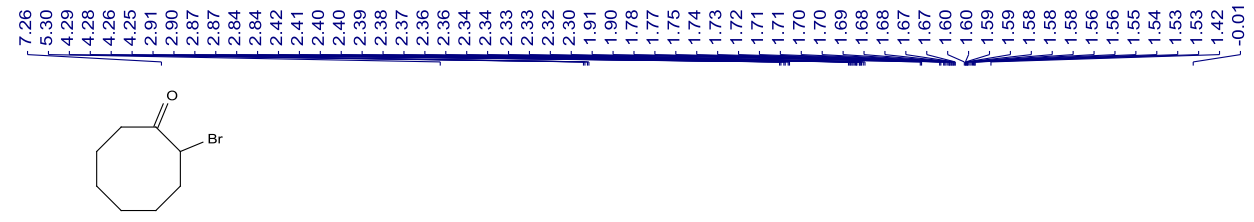
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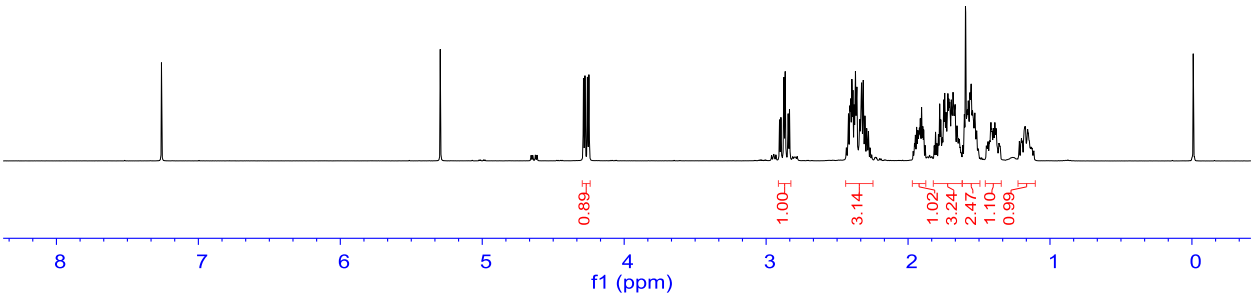
Br

9b

9b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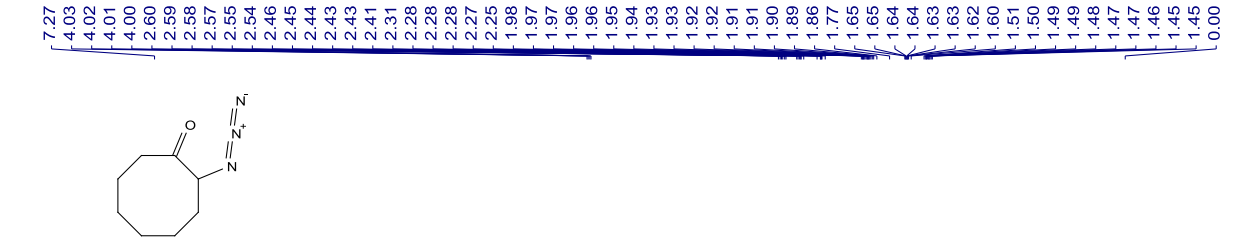
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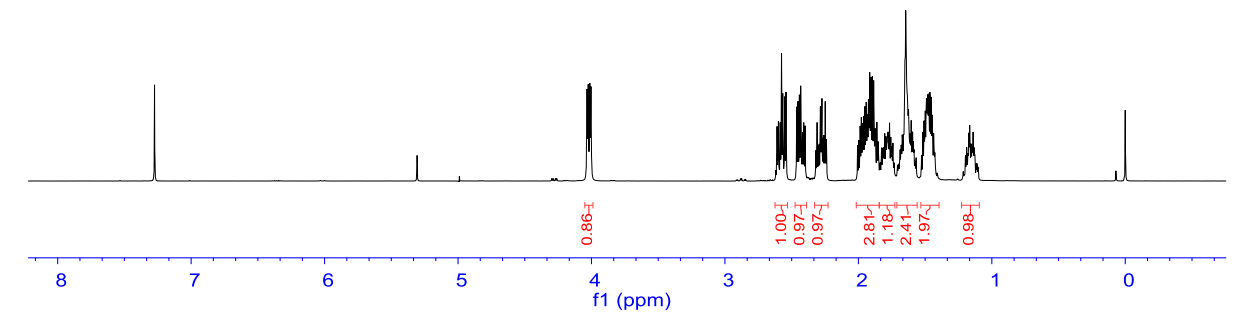
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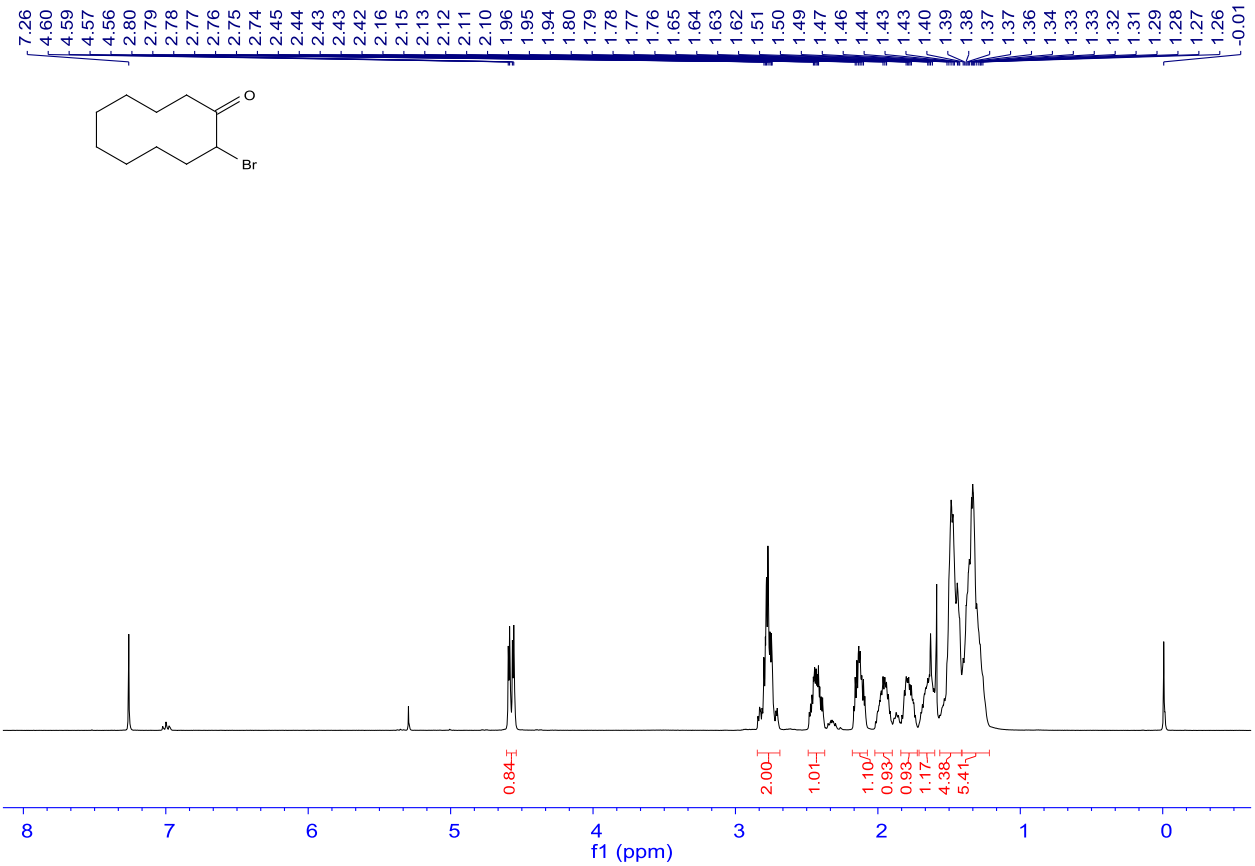
f1 (ppm)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1.64
1.63
1.62
1.51
1.50
1.49
1.47
1.46
1.44
1.43
1.43
1.40
1.39
1.38
1.37
1.37
1.36
1.34
1.33
1.33
1.32
1.31
1.29
1.28
1.27
1.26
-0.01
O
Br
0.84
2.00
1.01
1.10
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0.93
1.17
4.38
5.41
8
7
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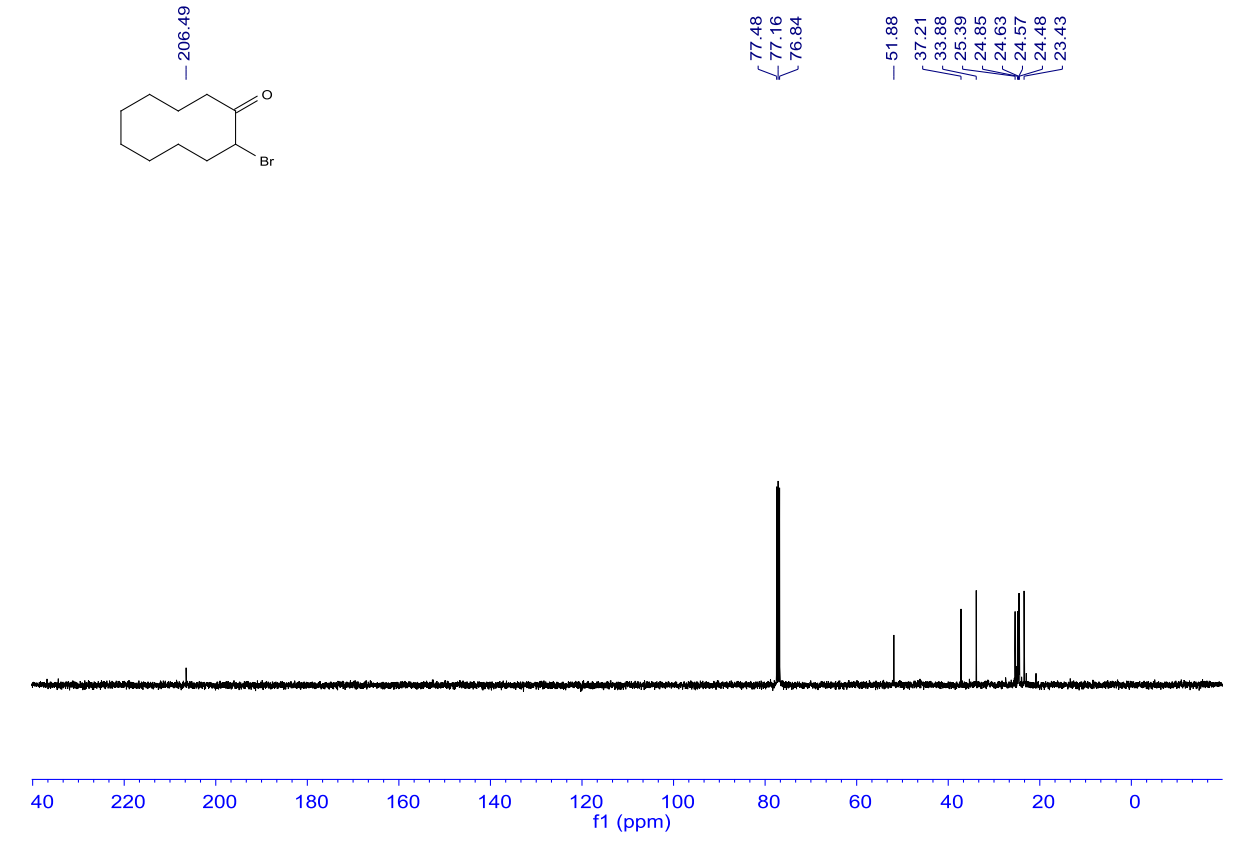
5
4
3
2
1
0
f1 (ppm)


206.49
O
Br
77.48
77.16
76.84
51.88
37.21
33.88
25.39
24.85
24.63
24.57
24.48
23.43
40
220
200
180
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140
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100
80
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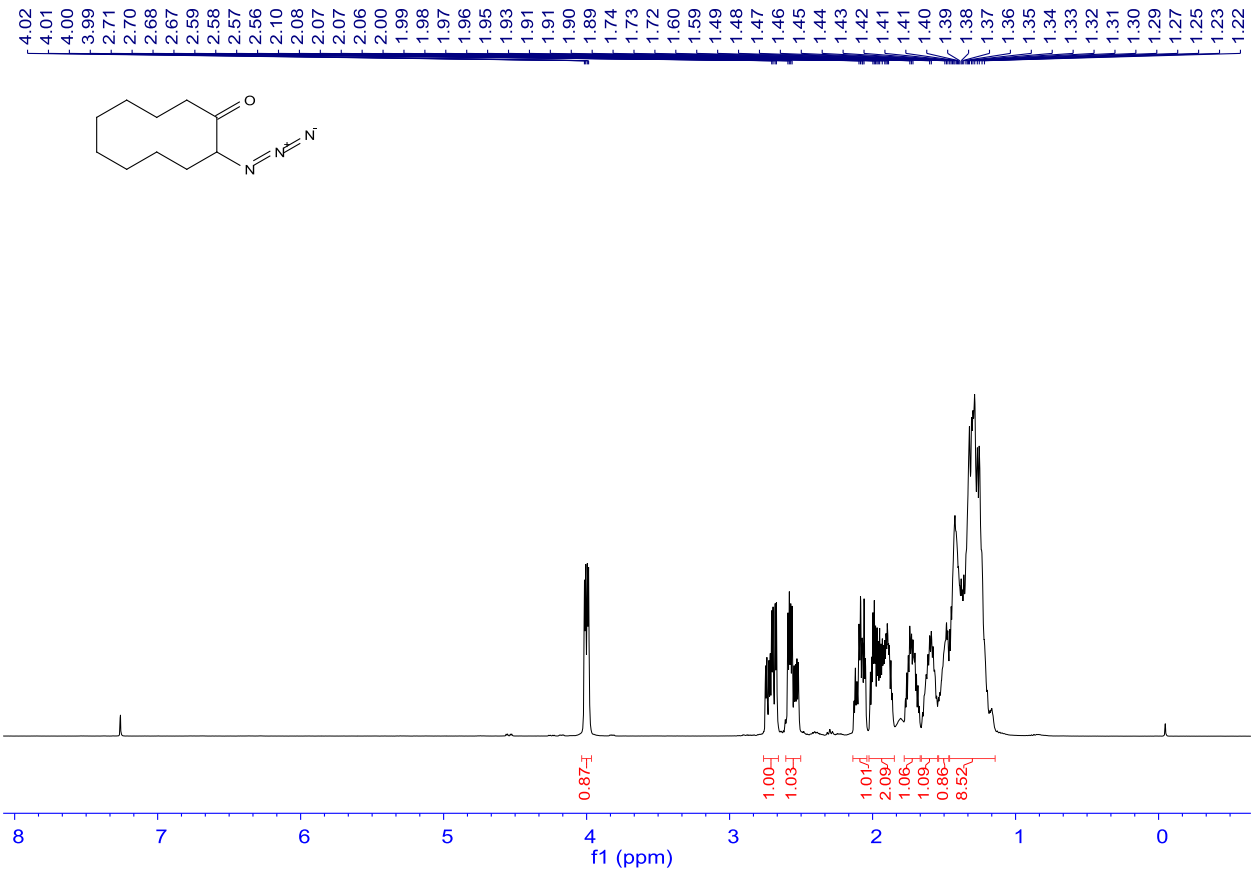
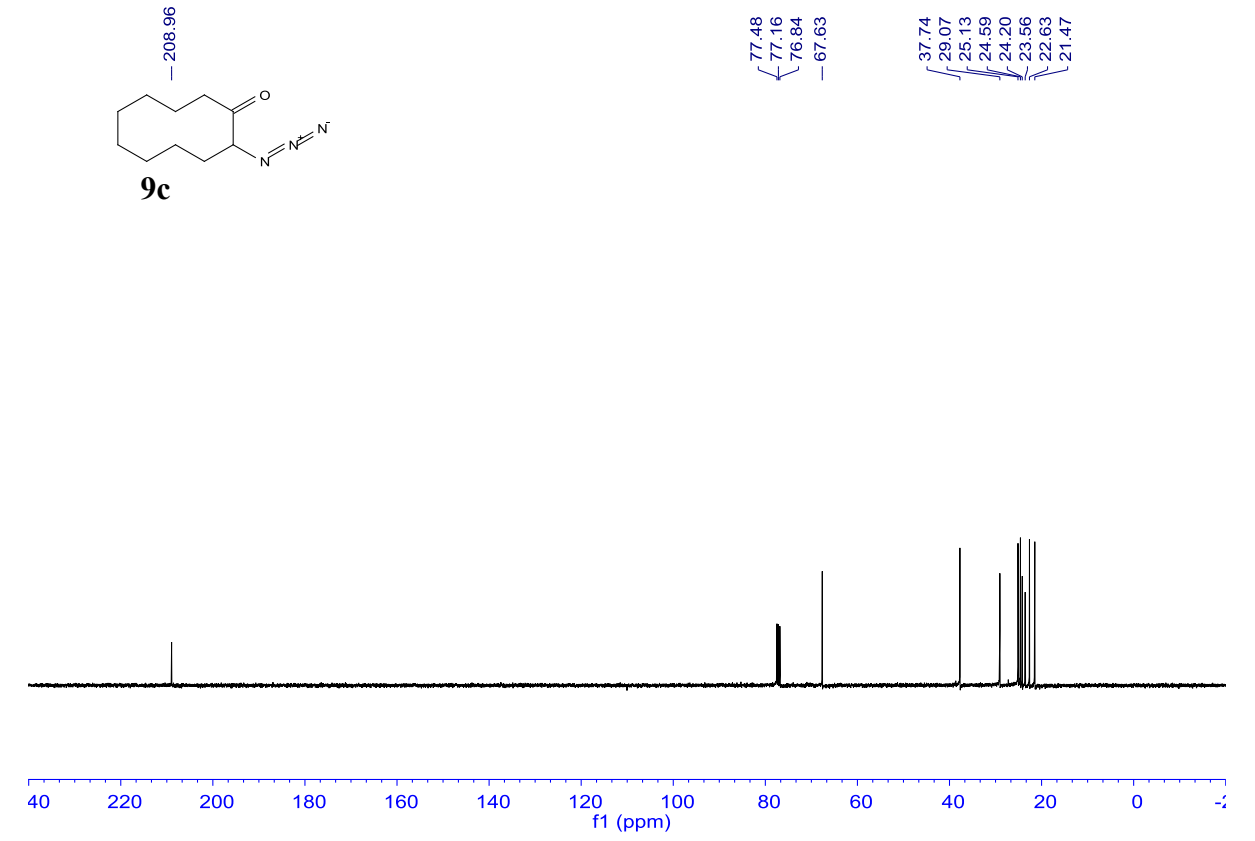
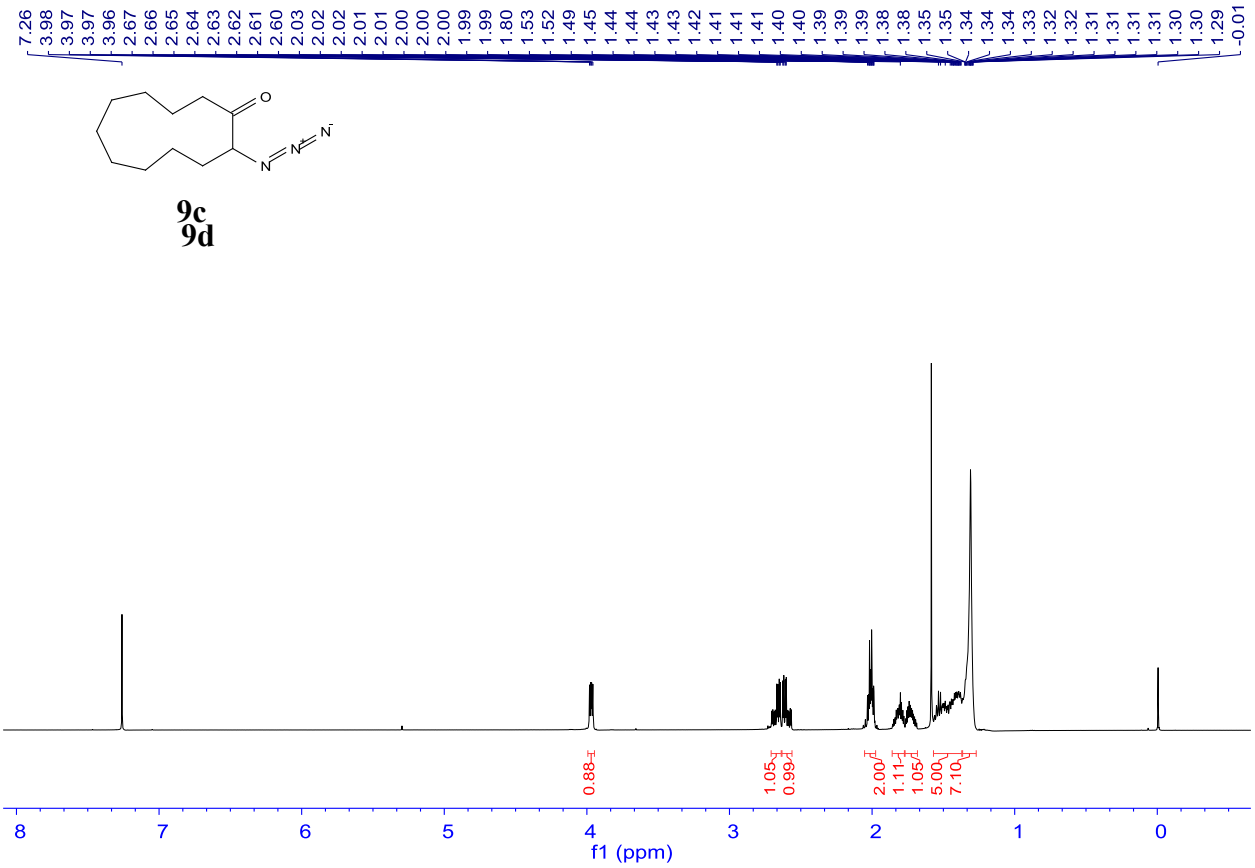
40
20
0
f1 (ppm)


4.02 4.01 4.00 3.99 2.71 2.70 2.68 2.67 2.59 2.58 2.57 2.56 2.10 2.08 2.07 2.07 2.06 2.00 1.99 1.98 1.97 1.96 1.95 1.93 1.91 1.91 1.90 1.89 1.74 1.73 1.72 1.60 1.59 1.49 1.48 1.47 1.46 1.45 1.44 1.43 1.42 1.41 1.41 1.40 1.39 1.38 1.37 1.36 1.35 1.34 1.33 1.32 1.31 1.30 1.29 1.27 1.25 1.23 1.22
O
N
N
N
0.87
1.00
1.03
1.01
2.09
1.06
1.09
0.86
8.52
8 7 6 5 4 3 2 1 0
f1 (ppm)


208.96
O
N
N
N
77.48
77.16
76.84
67.63
37.74
29.07
25.13
24.59
24.20
23.56
22.63
21.47
40 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

9c


7.26 3.98 3.97 3.97 3.96 2.67 2.66 2.65 2.64 2.63 2.62 2.61 2.60 2.03 2.02 2.02 2.01 2.01 2.00 2.00 2.00 1.99 1.99 1.80 1.53 1.52 1.49 1.45 1.44 1.44 1.43 1.43 1.42 1.41 1.41 1.41 1.40 1.40 1.39 1.39 1.39 1.38 1.38 1.35 1.35 1.34 1.34 1.34 1.33 1.32 1.32 1.31 1.31 1.31 1.30 1.30 1.29 -0.01
O
N
N
N
9c
9d
0.88
1.05
0.99
2.00
1.11
1.05
5.00
7.10
8
7
6
5
4
3
2
1
0
f1 (ppm)
209.24
O
N
N
N
9d
77.42
77.16
76.91
67.97
38.96
28.68
26.13
26.04
25.57
25.32
23.91
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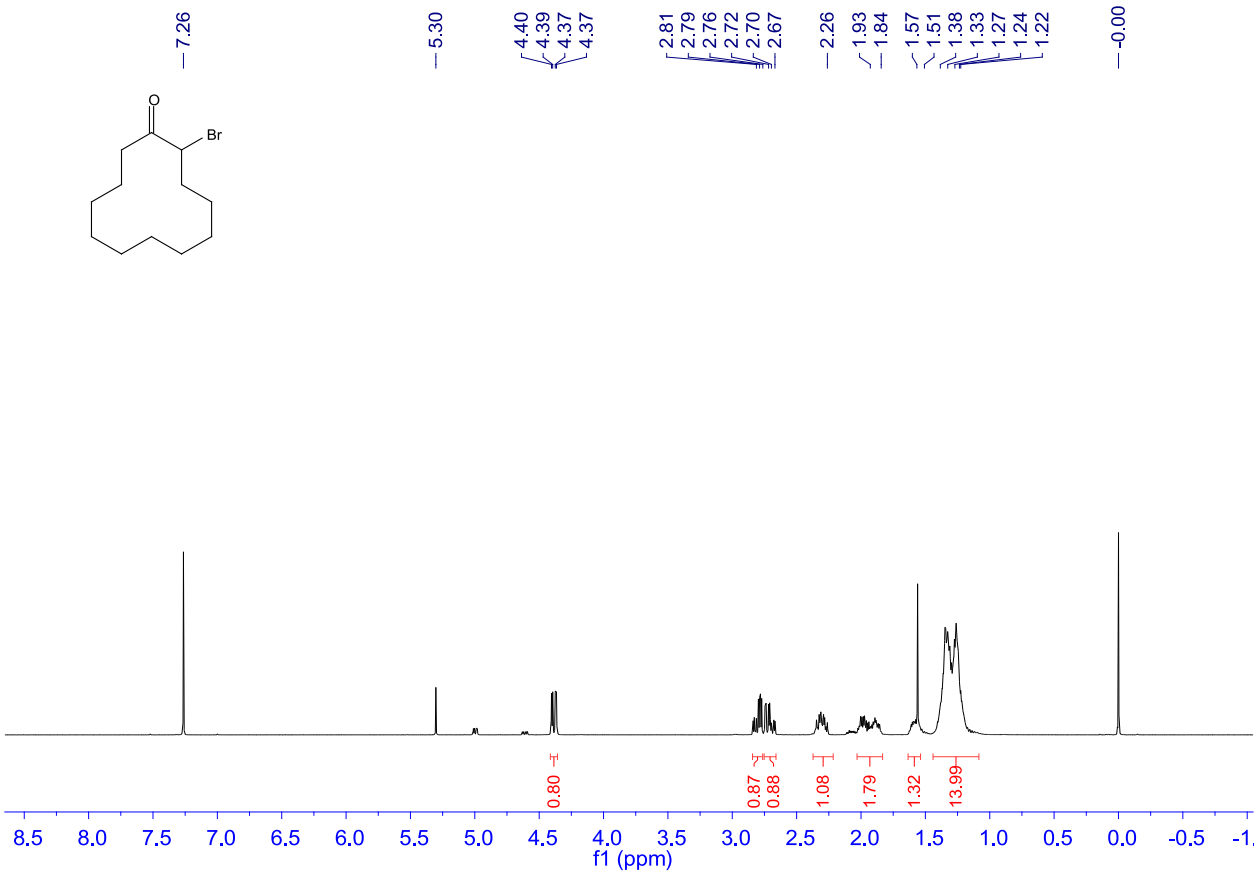
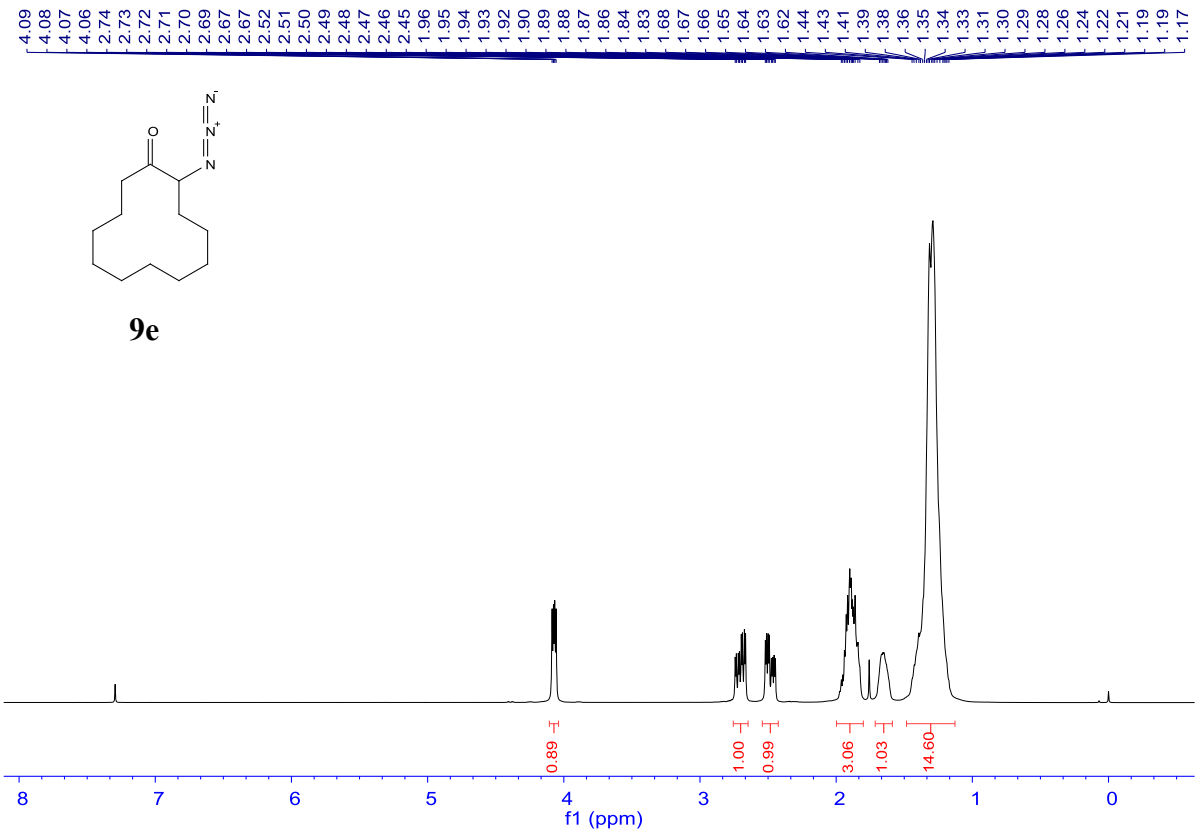
22.03
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.26
5.30
4.40
4.39
4.37
4.37
2.81
2.79
2.76
2.72
2.70
2.67
2.26
1.93
1.84
1.57
1.51
1.38
1.33
1.27
1.24
1.22
0.00
O
Br
0.80
0.87
0.88
1.08
1.79
1.32
13.99
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
-0.5
f1 (ppm)


4.09 4.08 4.07 4.06 2.74 2.73 2.72 2.71 2.70 2.69 2.67 2.67 2.52 2.51 2.50 2.49 2.48 2.47 2.46 2.45 1.96 1.95 1.94 1.93 1.92 1.90 1.89 1.88 1.87 1.86 1.84 1.83 1.68 1.67 1.66 1.65 1.64 1.63 1.62 1.44 1.43 1.41 1.39 1.38 1.36 1.35 1.34 1.33 1.31 1.30 1.29 1.28 1.26 1.24 1.22 1.21 1.19 1.19 1.17
O
N
N
N
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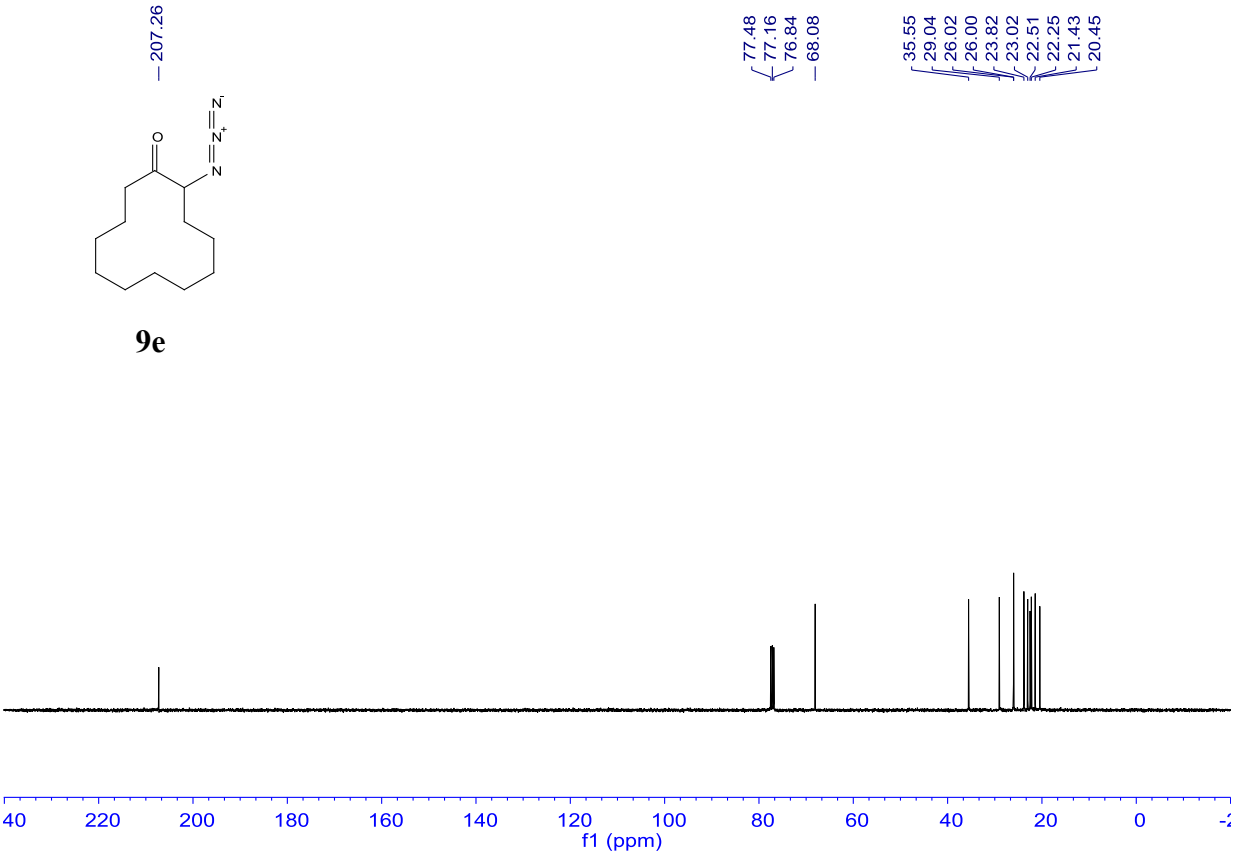
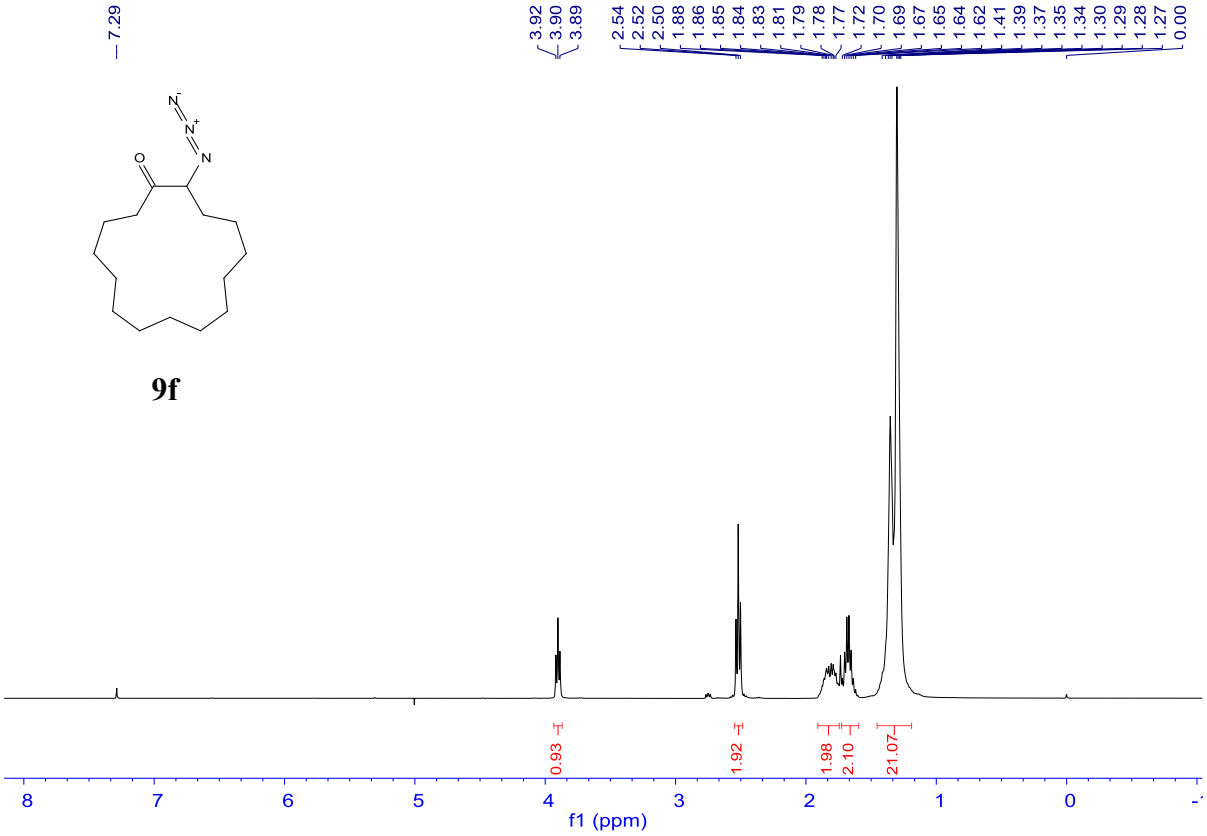
1.00
0.99
3.06
1.03
14.60
8 7 6 5 4 3 2 1 0
f1 (ppm)

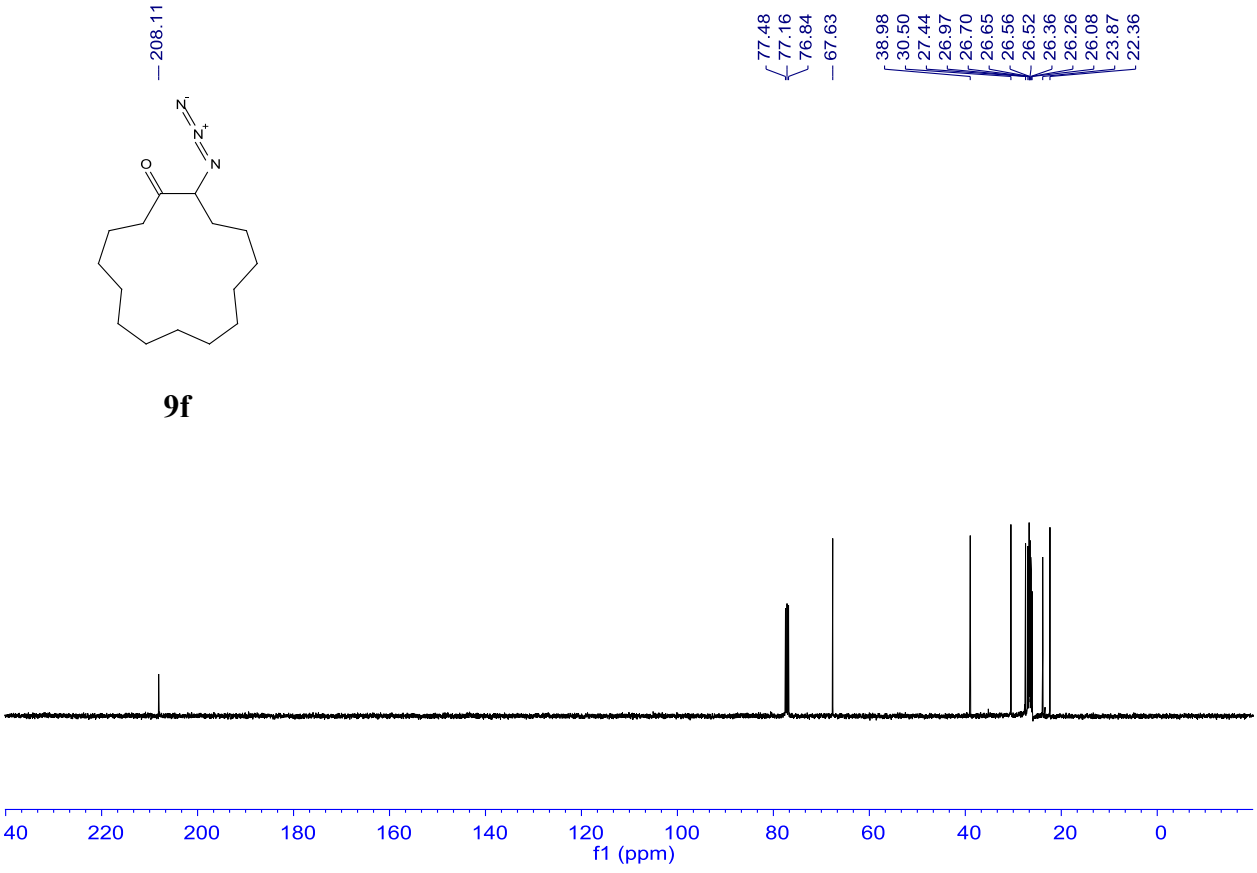
9e


207.26
77.48
77.16
76.84
68.08
35.55
29.04
26.02
26.00
23.82
23.02
22.51
22.25
21.43
20.45
O
N
N
N
40 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

9e


7.29
3.92
3.90
3.89
2.54
2.52
2.50
1.88
1.86
1.85
1.84
1.83
1.81
1.79
1.78
1.77
1.72
1.70
1.69
1.67
1.65
1.64
1.62
1.41
1.39
1.37
1.35
1.34
1.30
1.29
1.28
1.27
0.00
0.93
1.92
1.98
2.10
21.07
8
7
6
5
4
3
2
1
0
f1 (ppm)

9f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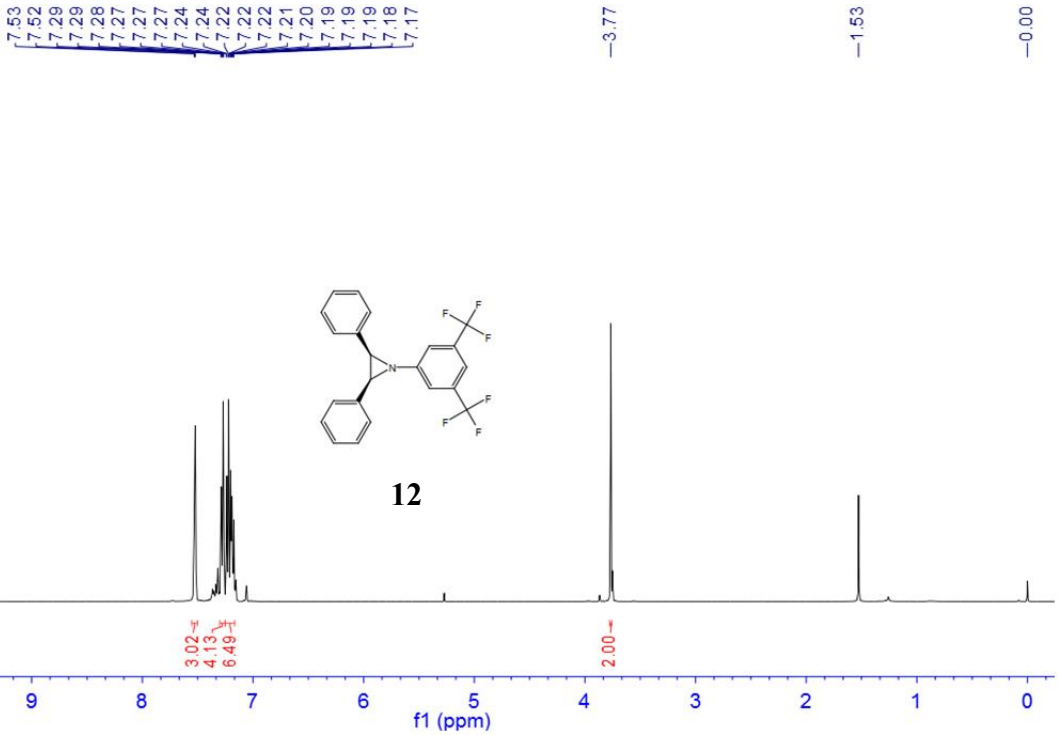
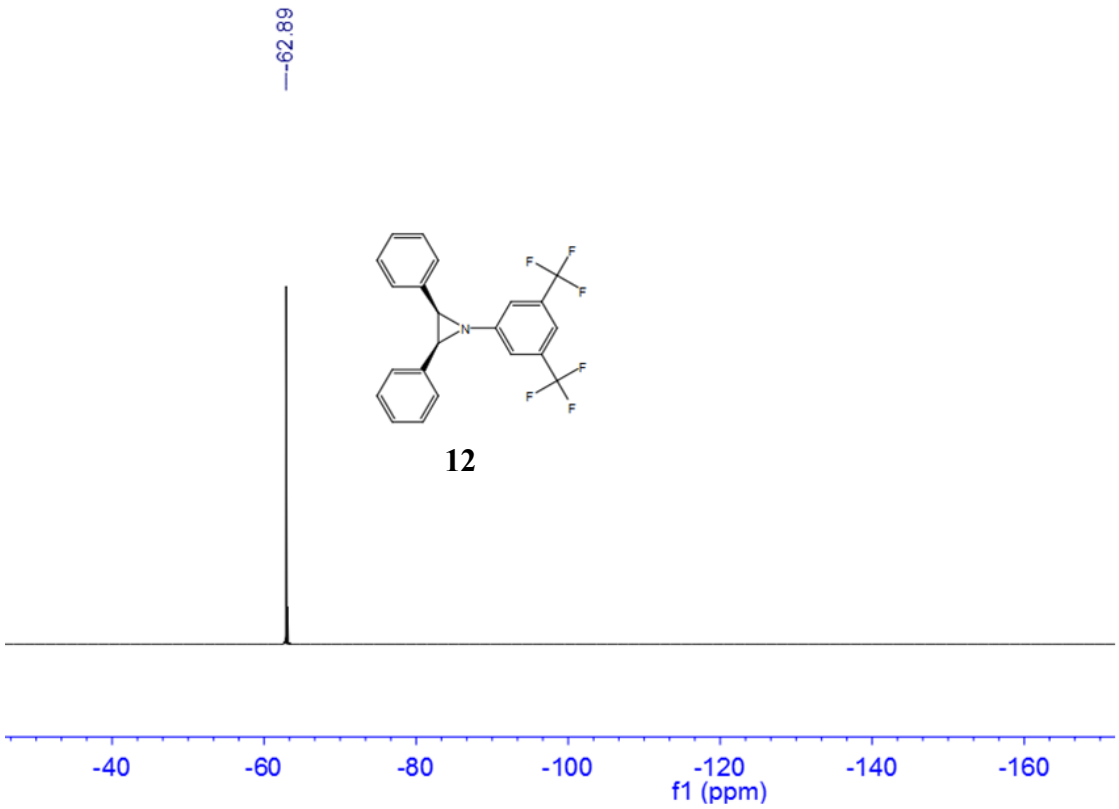
77.16
76.84
67.63
38.98
30.50
27.44
26.97
26.70
26.65
26.56
26.52
26.36
26.26
26.08
23.87
22.36
40
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

9f


7.53
7.52
7.29
7.29
7.28
7.27
7.27
7.27
7.24
7.24
7.22
7.22
7.22
7.21
7.20
7.19
7.19
7.19
7.18
7.17
3.77
1.53
0.00
12
3.02
4.13
6.49
2.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


62.89
12
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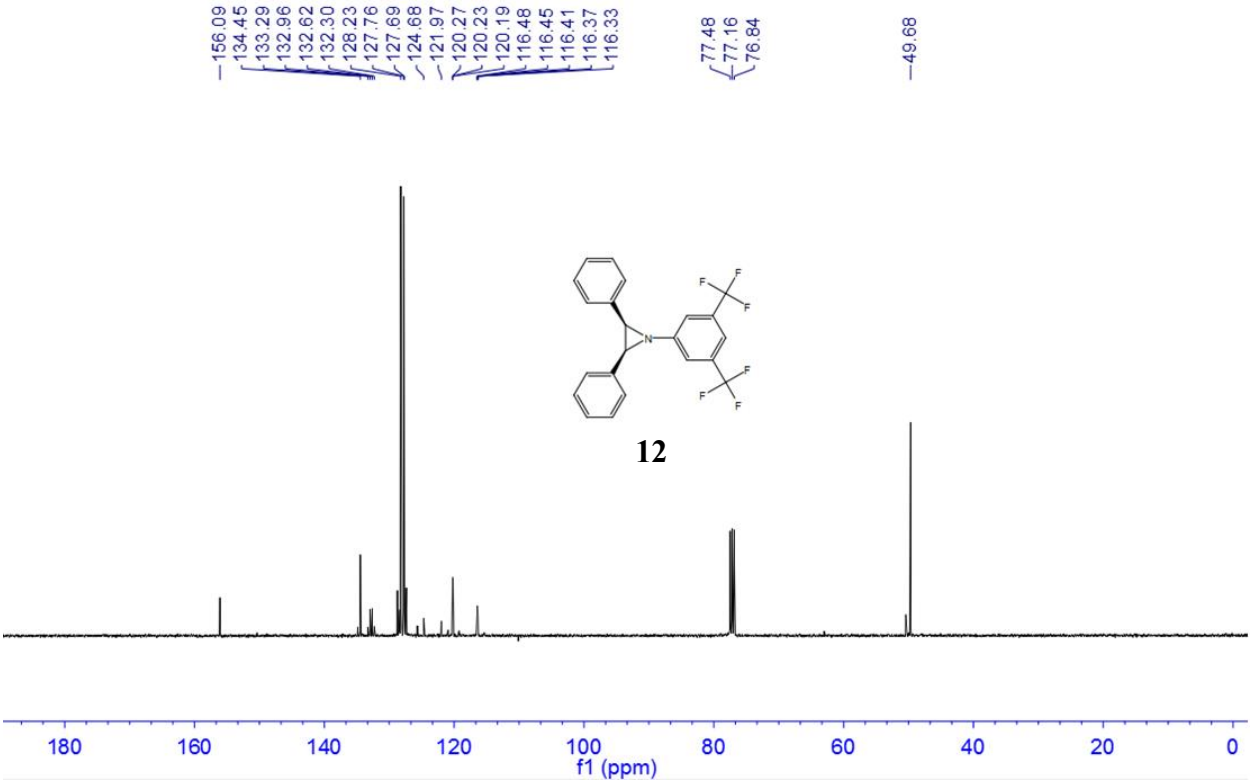
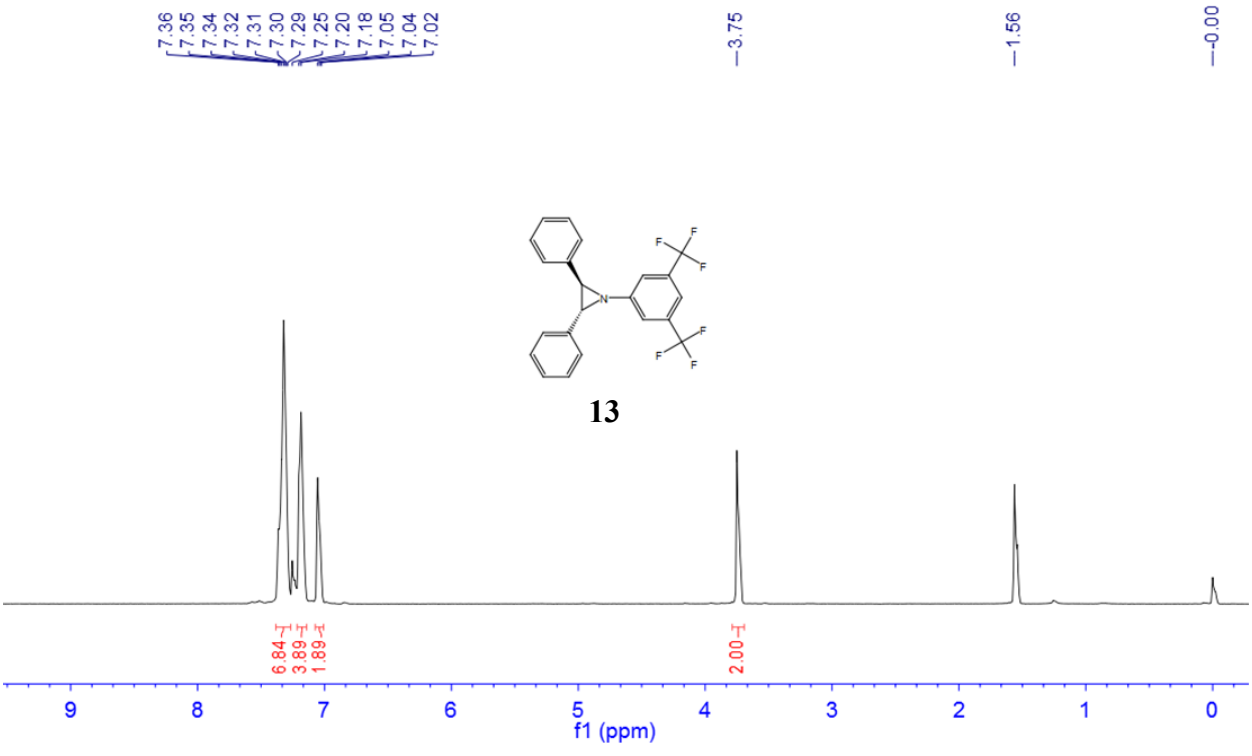
-60
-80
-100
-120
-140
-160
f1 (ppm)


156.09
134.45
133.29
132.96
132.62
132.30
128.23
127.76
127.69
124.68
121.97
120.27
120.23
120.19
116.48
116.45
116.41
116.37
116.33
77.48
77.16
76.84
49.68
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

12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7.35
7.34
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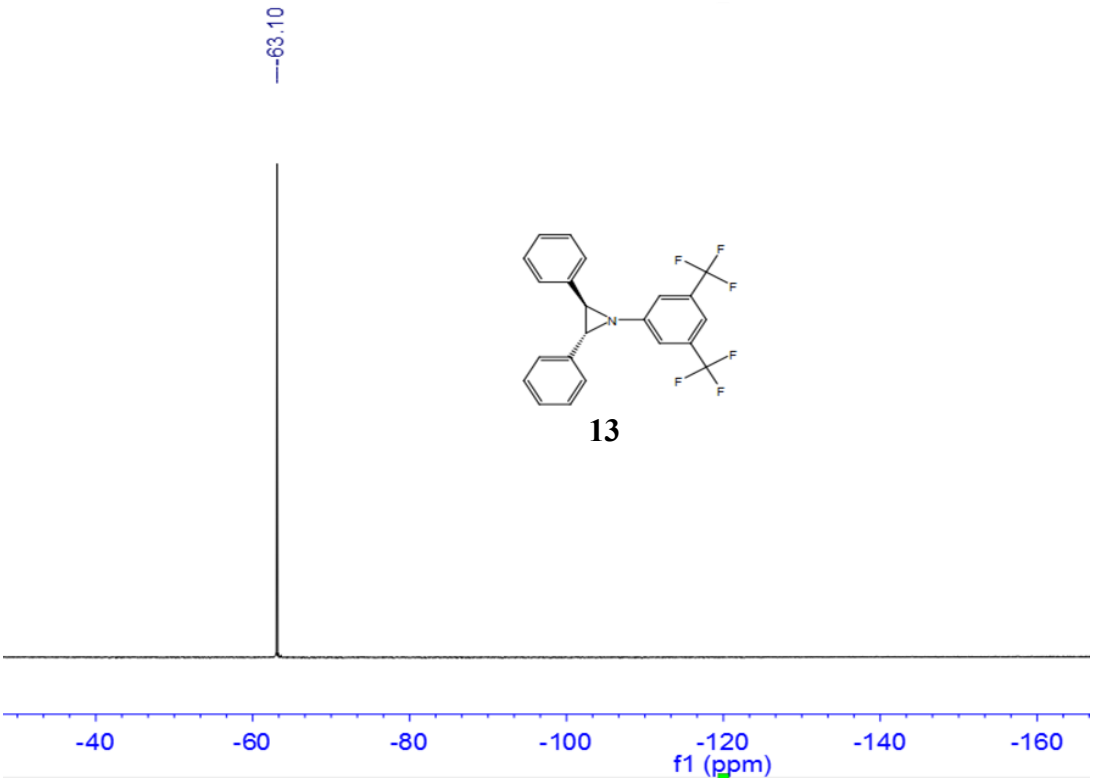
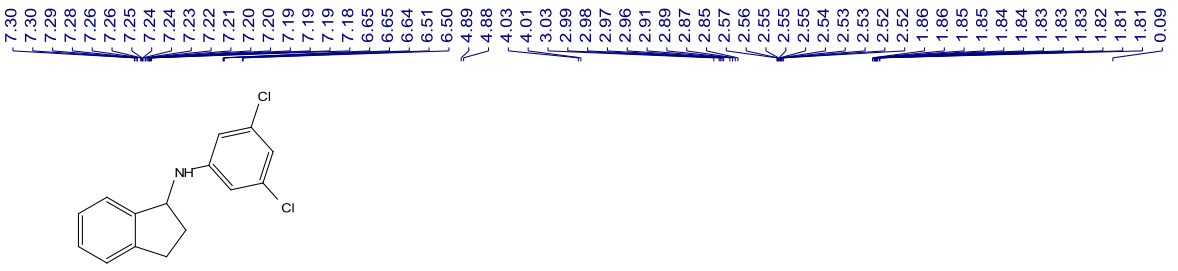
7.31
7.30
7.29
7.25
7.20
7.18
7.05
7.04
7.02
3.75
1.56
0.00
6.84
3.89
1.89
2.00
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

13

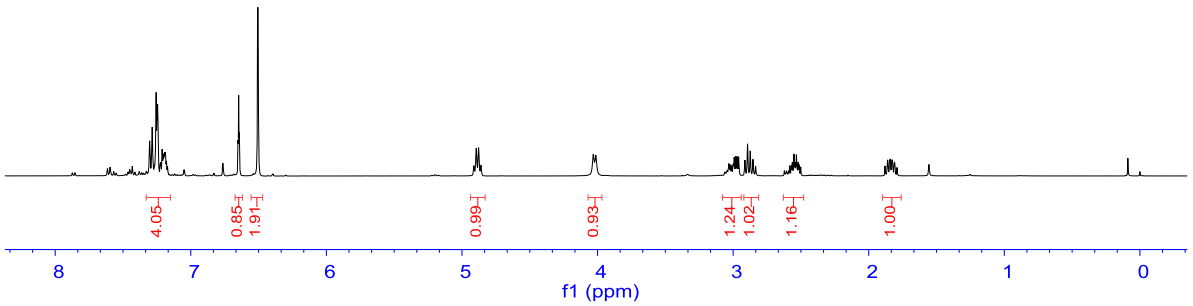


13


7.30
7.30
7.29
7.28
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.19
7.19
7.18
6.65
6.65
6.64
6.51
6.50
4.89
4.88
4.03
4.01
3.03
2.99
2.98
2.97
2.96
2.91
2.89
2.87
2.85
2.57
2.56
2.55
2.55
2.55
2.54
2.53
2.53
2.52
2.52
1.86
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.83
1.82
1.81
1.81
0.09

Cl
NH
Cl

3b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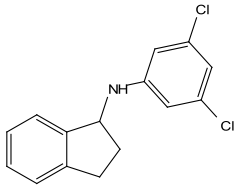
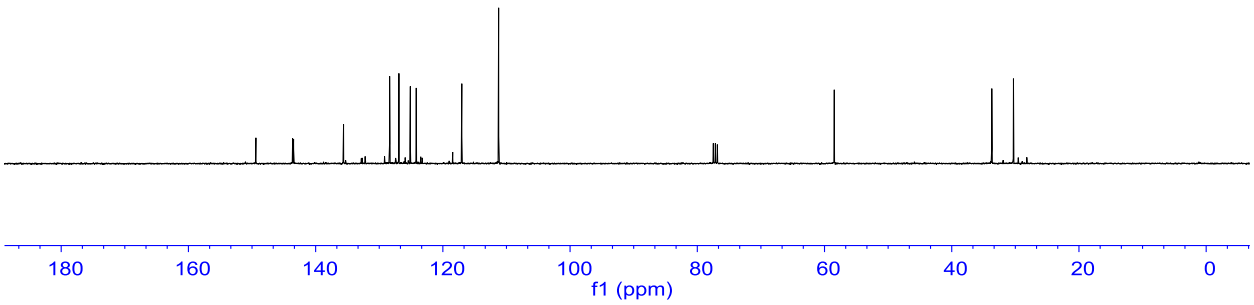
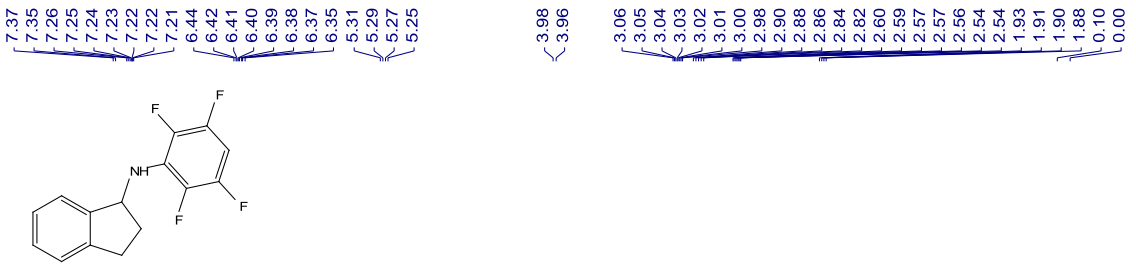
0.85
1.91
0.99
0.93
1.24
1.02
1.16
1.00
8
7
6
5
4
3
2
1
0
f1 (ppm)


149.39
143.61
143.47
135.62
128.37
126.91
125.11
124.18
117.02
111.23
77.48
77.16
76.84
58.47
33.70
30.29

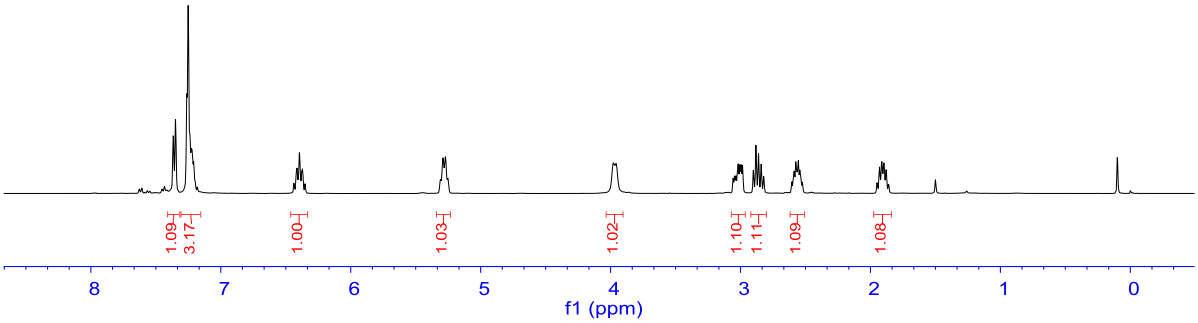

Cl
NH
Cl

3b


180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.37
7.35
7.26
7.25
7.24
7.23
7.22
7.22
7.21
6.44
6.42
6.41
6.40
6.39
6.38
6.37
6.35
5.31
5.29
5.27
5.25
3.98
3.96
3.06
3.05
3.04
3.03
3.02
3.01
3.00
2.98
2.90
2.88
2.86
2.84
2.82
2.60
2.59
2.57
2.57
2.56
2.54
2.54
1.93
1.91
1.90
1.88
0.10
0.00
F
F
NH
F
F

3d


1.09
3.17
1.00
1.03
1.02
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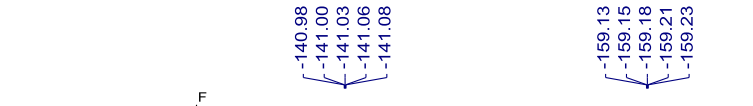
1.11
1.09
1.08
8
7
6
5
4
3
2
1
0
f1 (ppm)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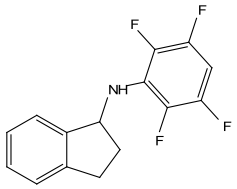
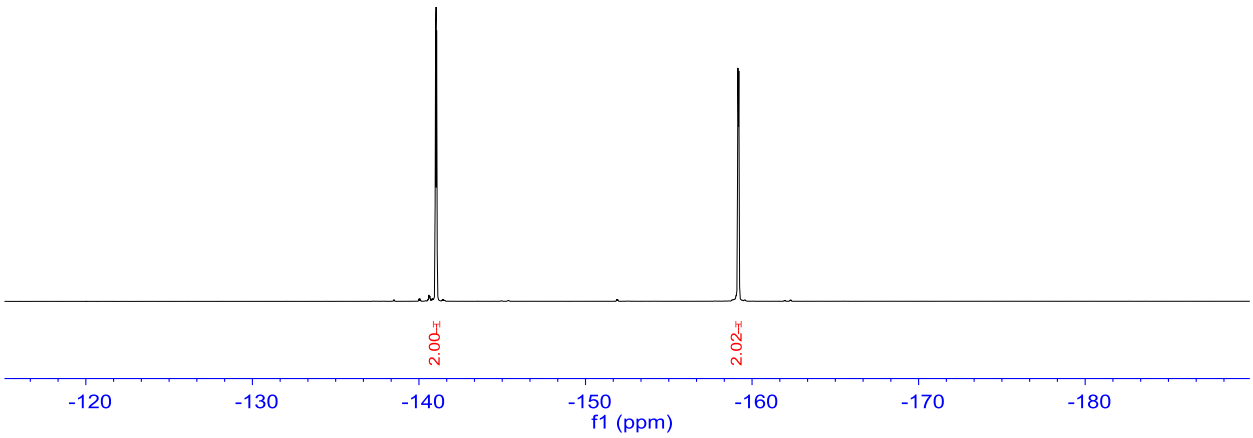
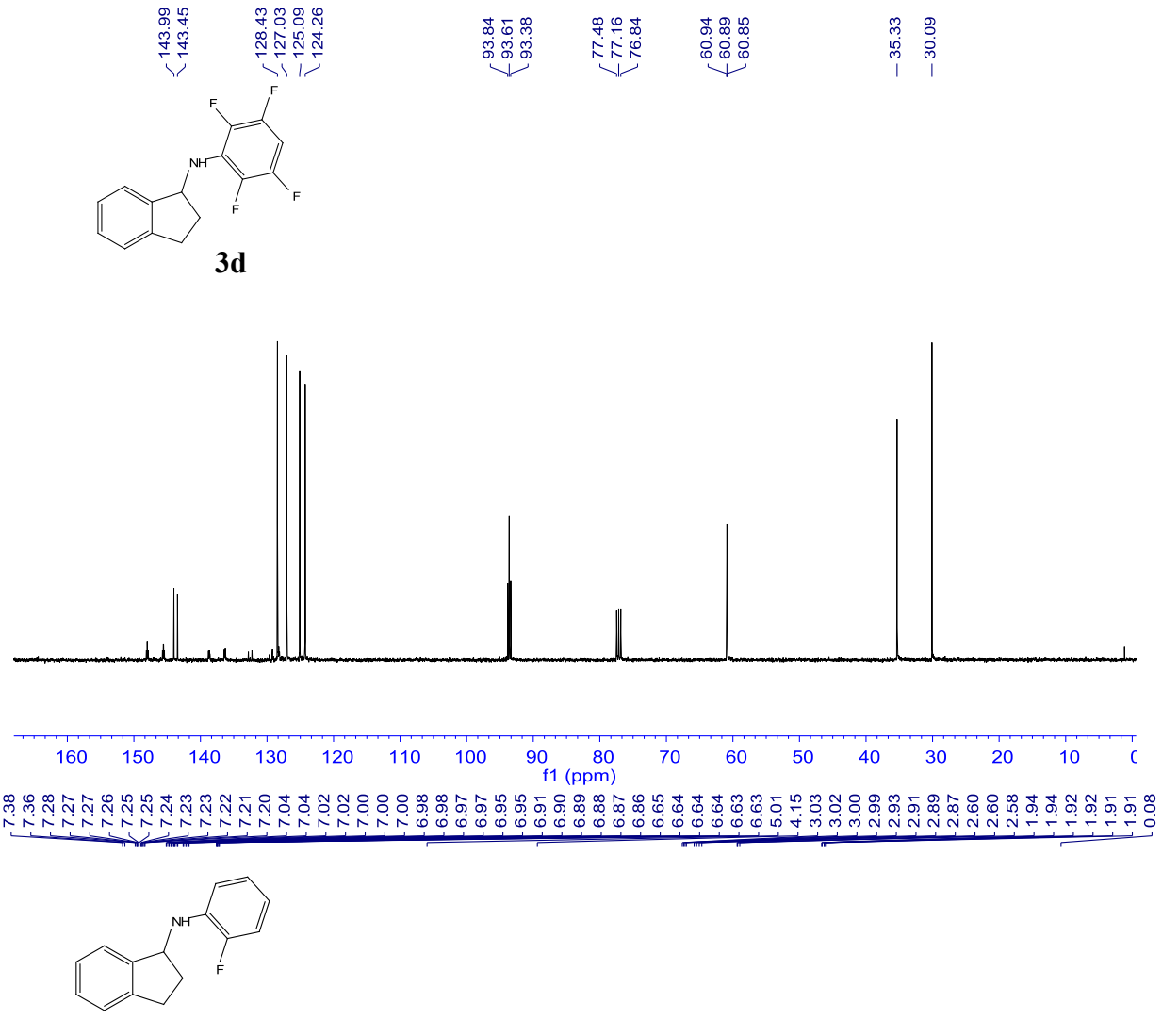
-141.00
-141.03
-141.06
-141.08
-159.13
-159.15
-159.18
-159.21
-159.23


F
F
NH
F
F

3d

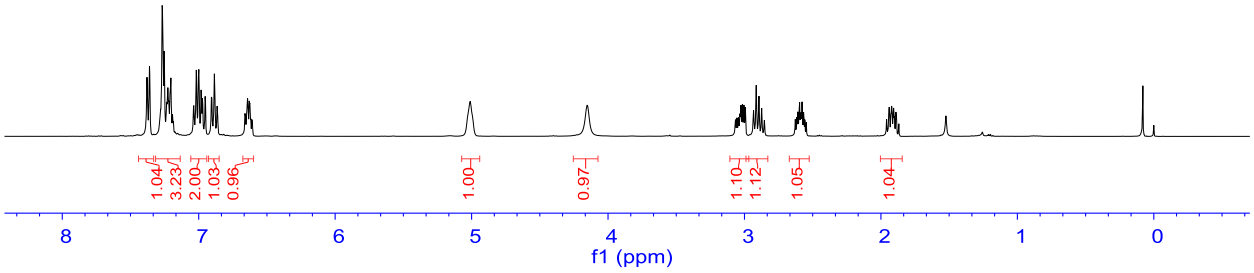

2.00
2.02
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)


143.99
143.45
128.43
127.03
125.09
124.26
93.84
93.61
93.38
77.48
77.16
76.84
60.94
60.89
60.85
35.33
30.09
F
F
NH
F
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
7.38
7.36
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.04
7.04
7.02
7.02
7.00
7.00
7.00
6.98
6.98
6.97
6.97
6.95
6.95
6.91
6.90
6.89
6.88
6.87
6.86
6.65
6.64
6.64
6.64
6.63
6.63
5.01
4.15
3.03
3.02
3.00
2.99
2.93
2.91
2.89
2.87
2.60
2.60
2.58
1.94
1.94
1.92
1.92
1.91
1.91
0.08

3d

NH
F

3e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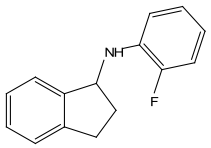
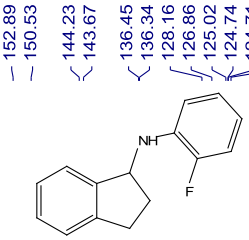
3.23
2.00
1.03
0.96
1.00
0.97
1.10
1.12
1.05
1.04
8
7
6
5
4
3
2
1
0
f1 (ppm)


NH
F

3e

-136.09
-136.12
-136.15
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


152.89
150.53
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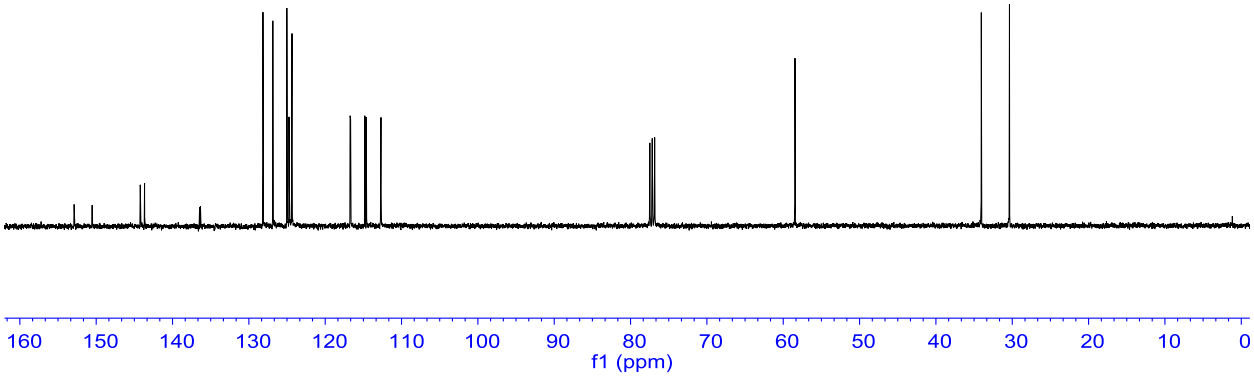
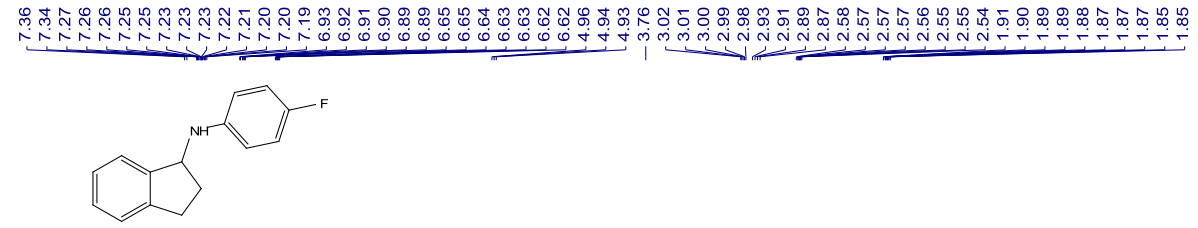
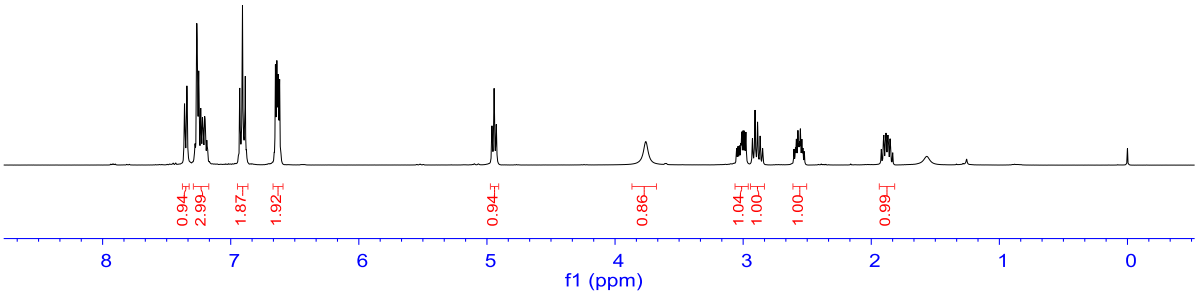
143.67
136.45
136.34
128.16
126.86
125.02
124.74
124.71
124.35
116.74
116.67
114.81
114.62
112.73
112.69
77.48
77.16
76.84
58.46
34.05
30.37
NH
F

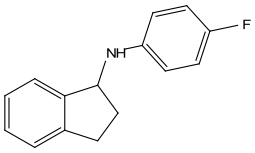
3e


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

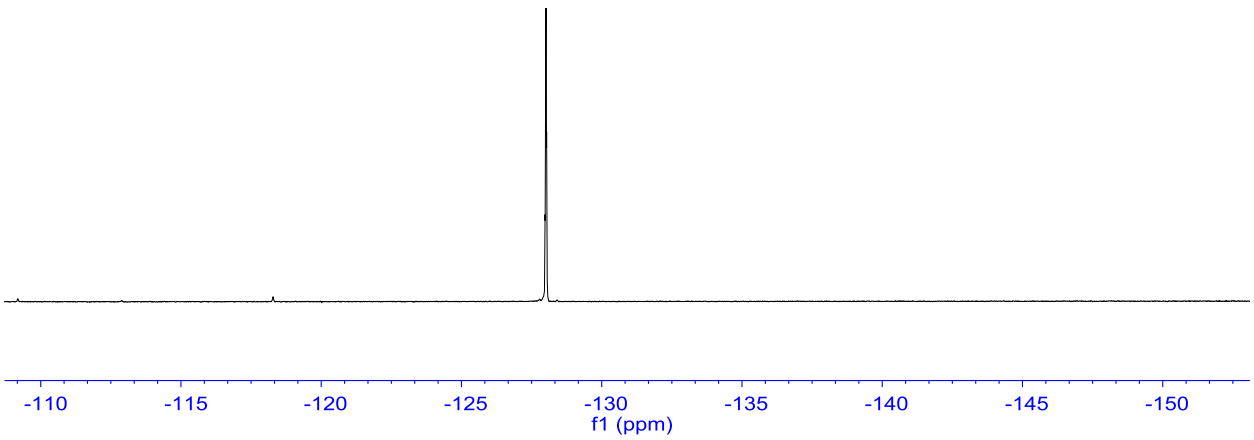

7.36
7.34
7.27
7.26
7.26
7.25
7.25
7.23
7.23
7.23
7.22
7.21
7.20
7.20
7.19
6.93
6.92
6.91
6.90
6.89
6.89
6.65
6.65
6.64
6.63
6.63
6.62
6.62
4.96
4.94
4.93
3.76
3.02
3.01
3.00
2.99
2.98
2.93
2.91
2.89
2.87
2.58
2.57
2.57
2.57
2.56
2.55
2.55
2.54
1.91
1.90
1.89
1.89
1.88
1.87
1.87
1.87
1.85
1.85
NH
F

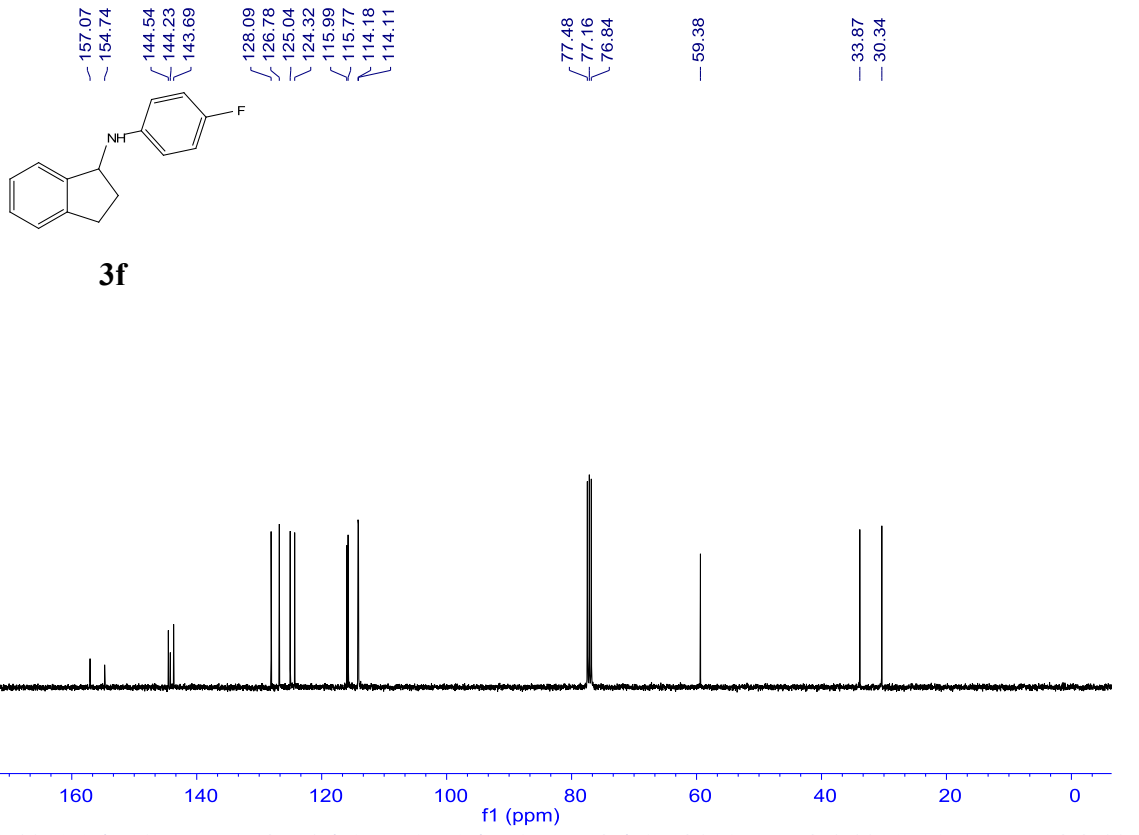
3f


0.94
2.99
1.87
1.92
0.94
0.86
1.04
1.00
1.00
0.99
8
7
6
5
4
3
2
1
0
f1 (ppm)

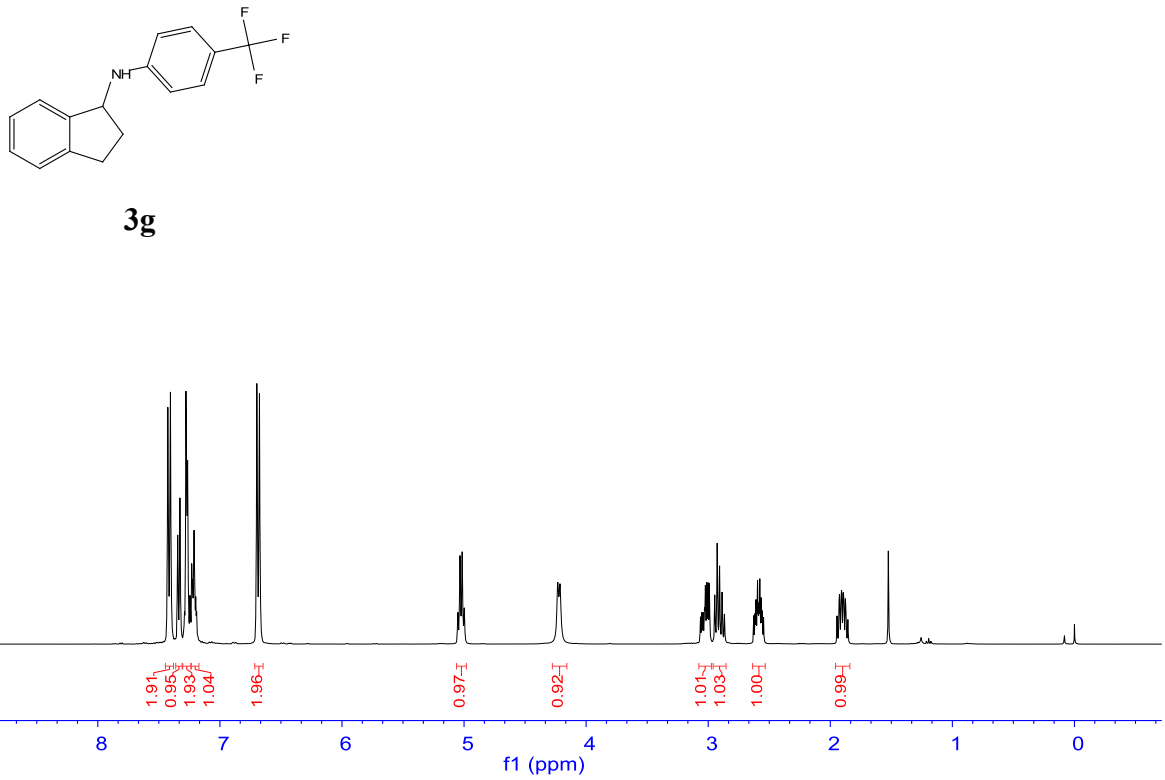

NH
F

3f

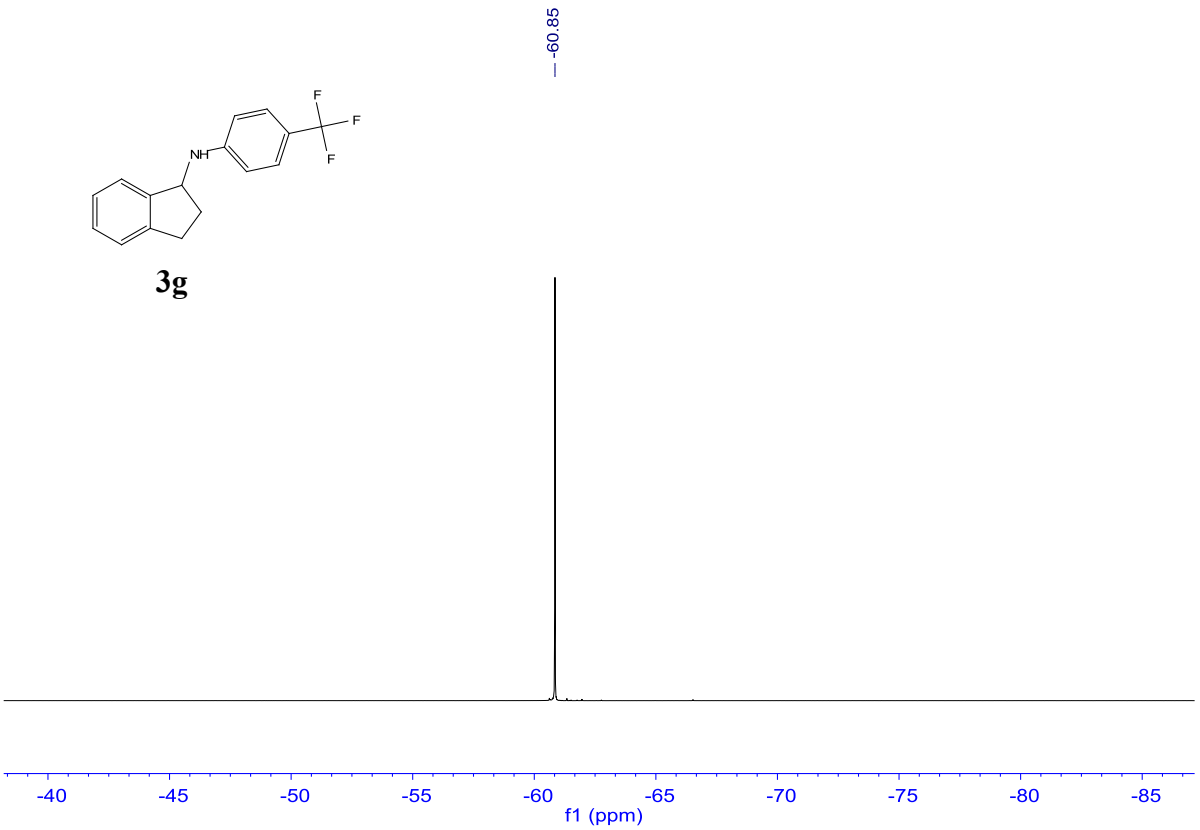

-128.00
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)

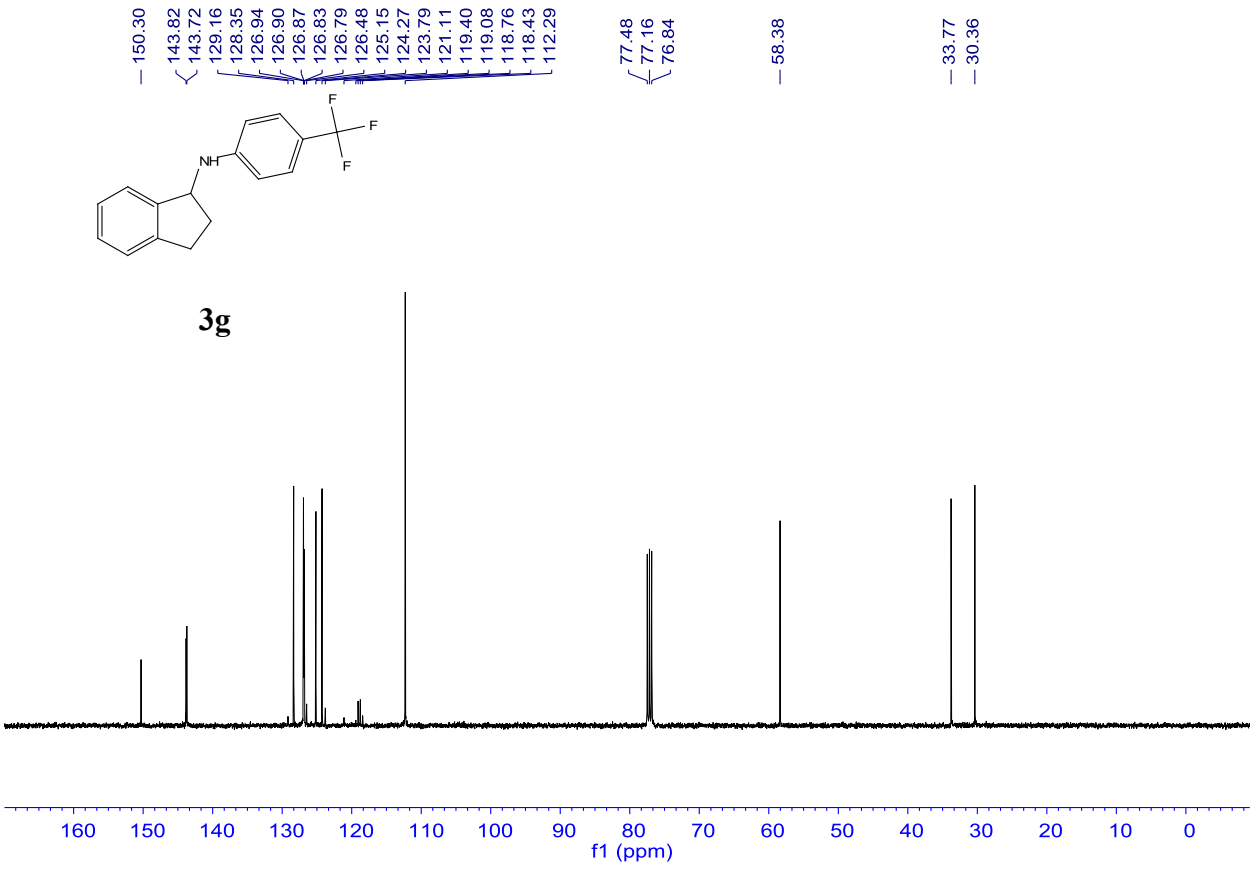

157.07
154.74
144.54
144.23
143.69
128.09
126.78
125.04
124.32
115.99
115.77
114.18
114.11
77.48
77.16
76.84
59.38
33.87
30.34
NH
F
180
160
140
120
100
80
60
40
20
0
f1 (ppm)
7.43
7.41
7.35
7.33
7.29
7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.19
6.70
6.68
5.05
5.03
5.02
5.00
4.23
4.21
3.06
3.05
3.04
3.03
3.02
3.01
3.00
2.99
2.95
2.93
2.91
2.89
2.87
2.63
2.62
2.61
2.60
2.59
2.58
2.58
2.57
2.56
1.94
1.93
1.92
1.91
1.91
1.90
1.90
1.89
1.89
1.88
1.87

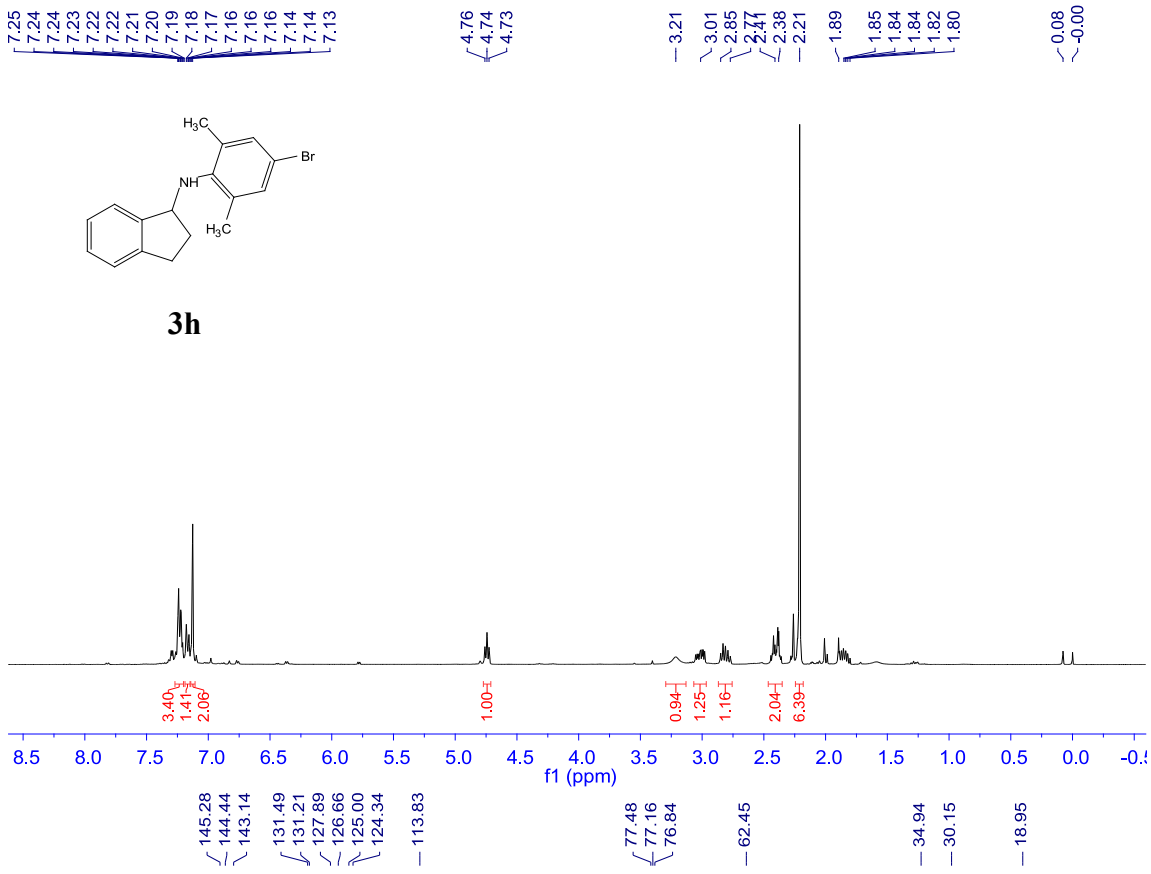
3f


F
F
F
NH
1.91
0.95
1.93
1.04
1.96
0.97
0.92
1.01
1.03
1.00
0.99
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

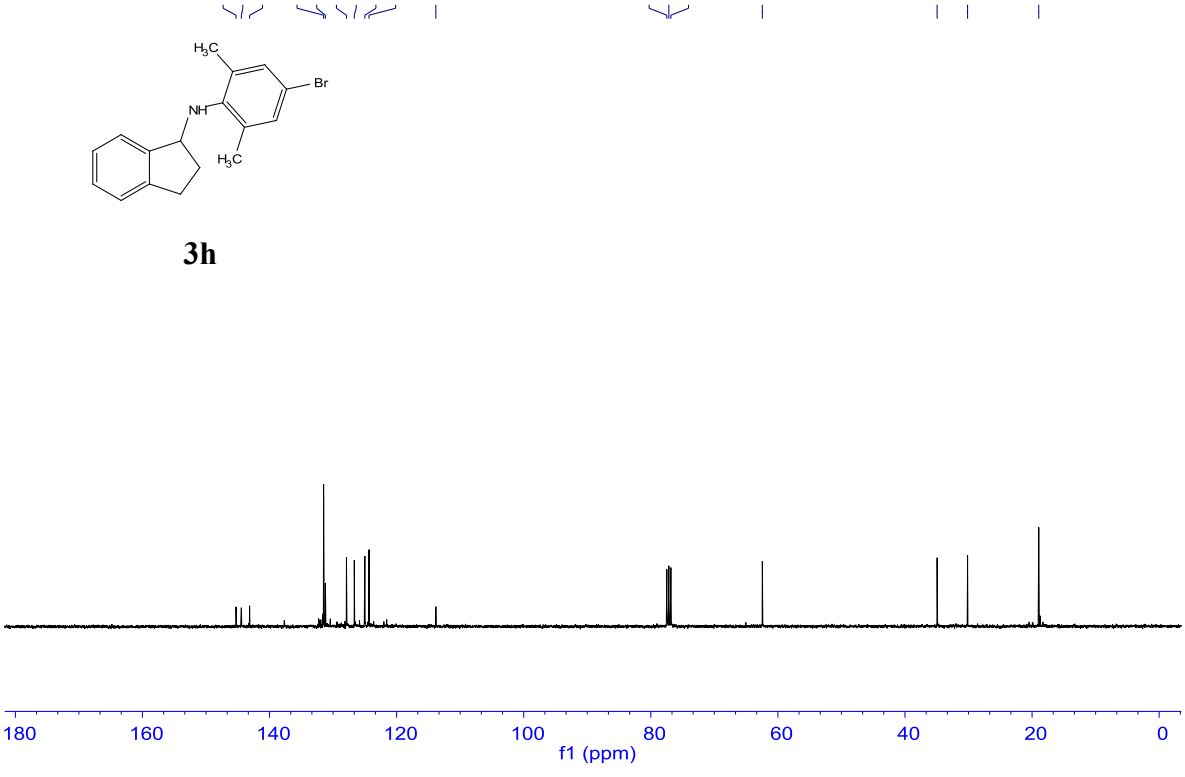
3g


-60.85
F
F
F
NH
3g
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
f1 (ppm)

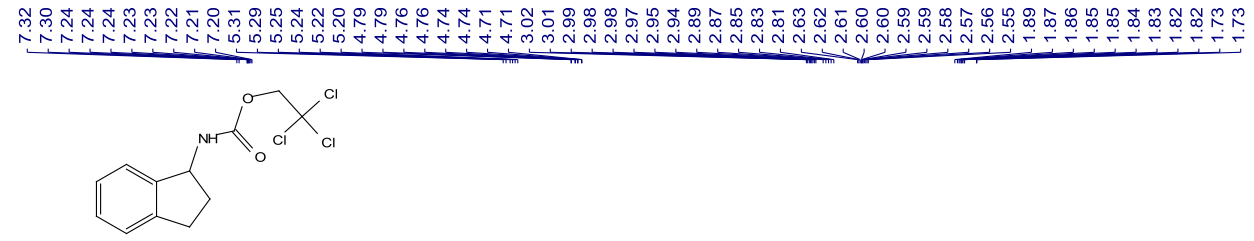

150.30
143.82
143.72
129.16
128.35
126.94
126.90
126.87
126.83
126.79
126.48
125.15
124.27
123.79
121.11
119.40
119.08
118.76
118.43
112.29
77.48
77.16
76.84
58.38
33.77
30.36
F
F
F
NH
3g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.18
7.17
7.16
7.16
7.16
7.14
7.14
7.13
4.76
4.74
4.73
3.21
3.01
2.85
2.77
2.41
2.38
2.21
1.89
1.85
1.84
1.84
1.82
1.80
0.08
-0.00
H3C
Br
NH
H3C
3.40
1.41
2.06
1.00
0.94
1.25
1.16
2.04
6.39
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)

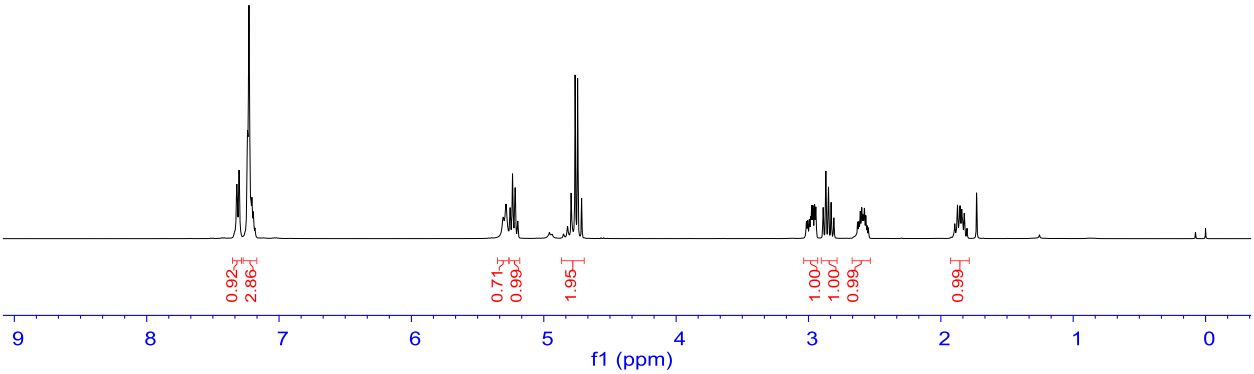
3h


145.28
144.44
143.14
131.49
131.21
127.89
126.66
125.00
124.34
113.83
77.48
77.16
76.84
62.45
34.94
30.15
18.95
H3C
Br
NH
H3C
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

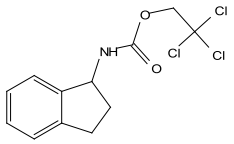
3h


7.32 7.30 7.24 7.24 7.24 7.23 7.23 7.22 7.21 7.20 5.31 5.29 5.25 5.24 5.22 5.20 4.79 4.79 4.76 4.76 4.74 4.74 4.71 4.71 3.02 3.01 2.99 2.98 2.98 2.97 2.95 2.94 2.89 2.87 2.85 2.83 2.81 2.63 2.62 2.61 2.60 2.60 2.59 2.59 2.58 2.57 2.56 2.55 1.89 1.87 1.86 1.85 1.85 1.84 1.83 1.82 1.82 1.73 1.73
O
NH
O
Cl
Cl
Cl

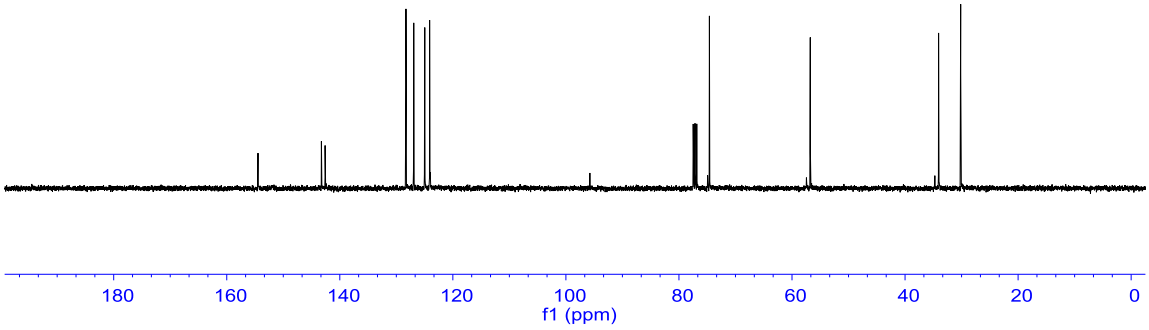
3j

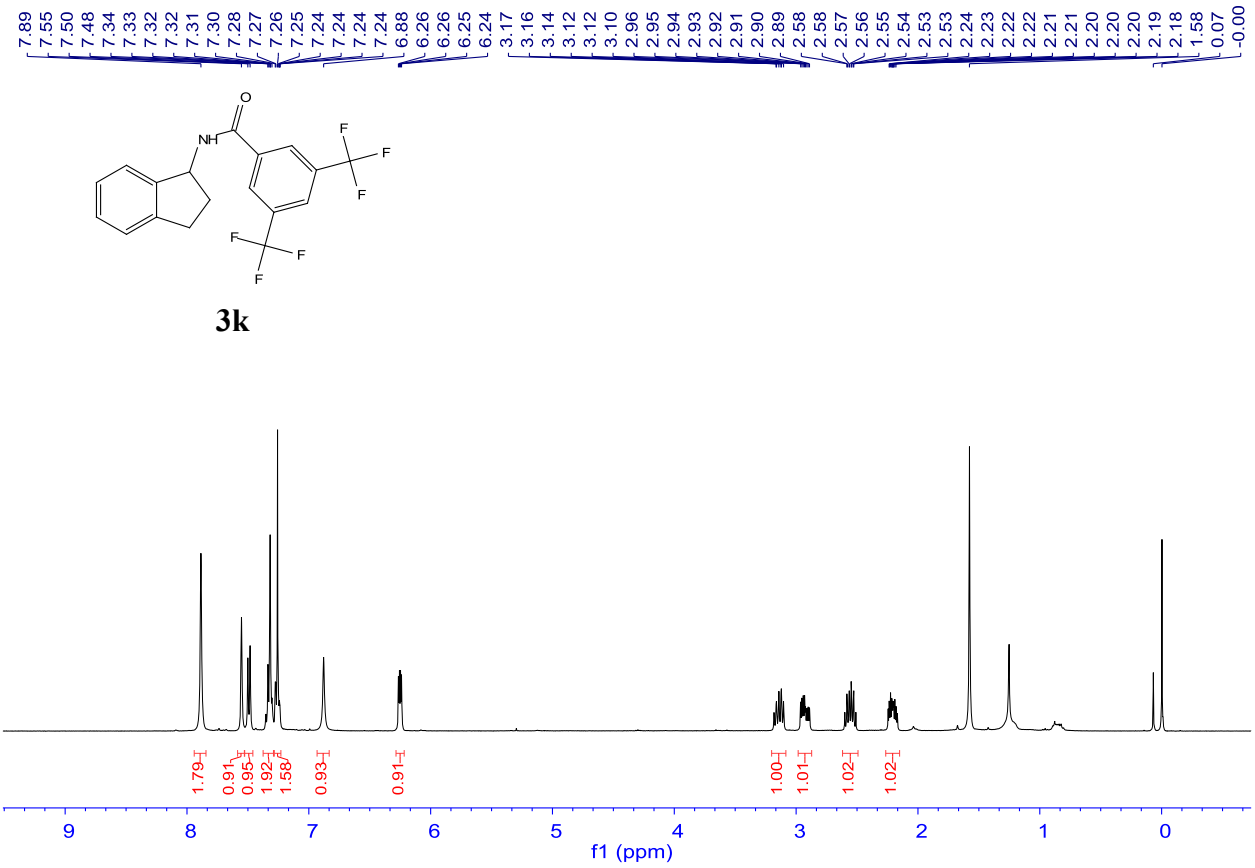

0.92
2.86
0.71
0.99
1.95
1.00
1.00
0.99
0.99
9 8 7 6 5 4 3 2 1 0
f1 (ppm)

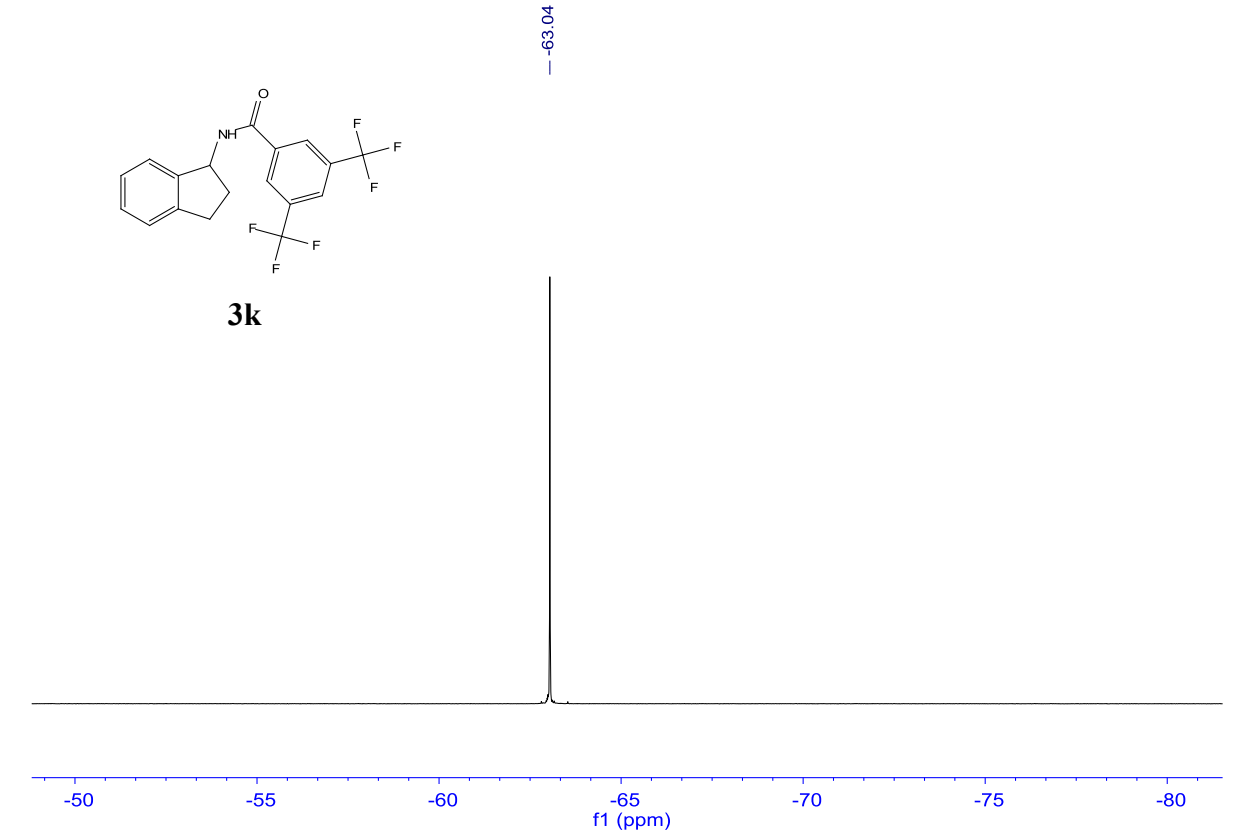

154.47
143.26
142.60
128.30
126.92
124.97
124.11
95.76
77.48
77.16
76.84
74.61
56.77
34.06
30.16

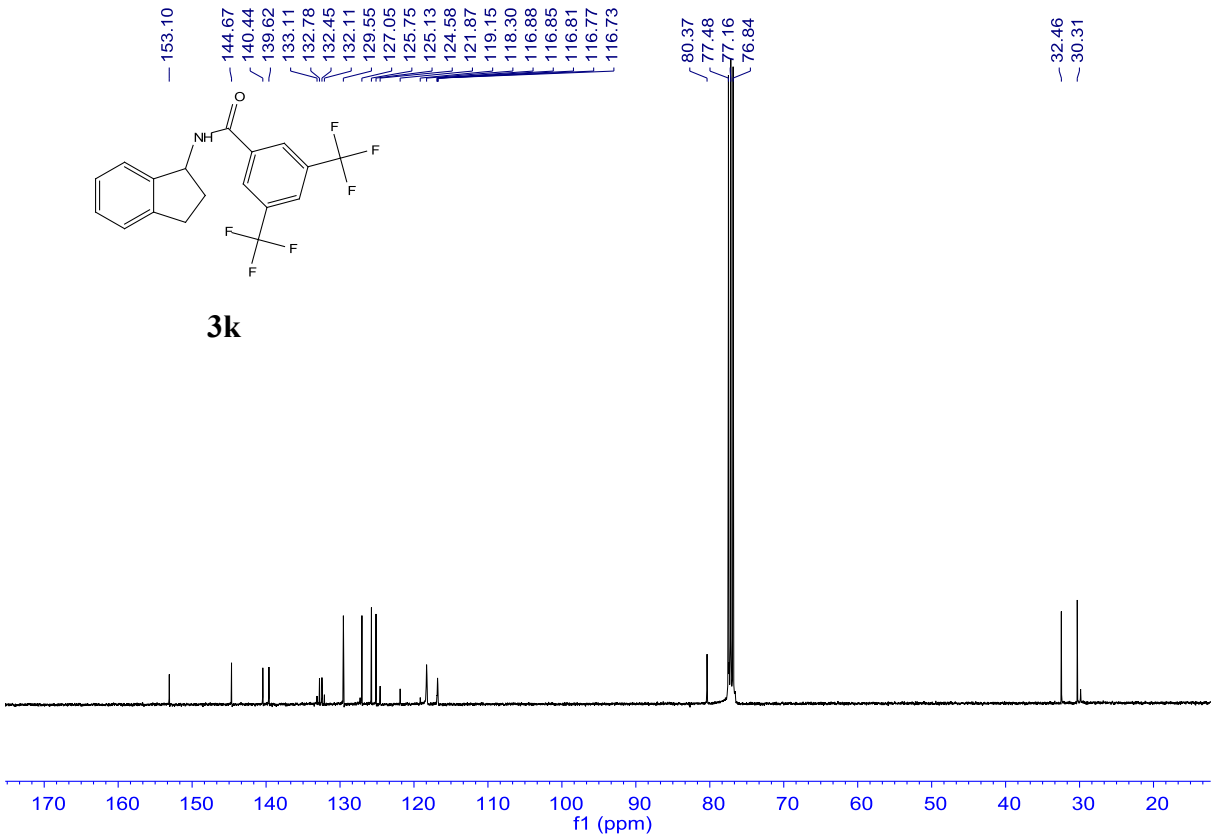

O
NH
O
Cl
Cl
Cl

3j

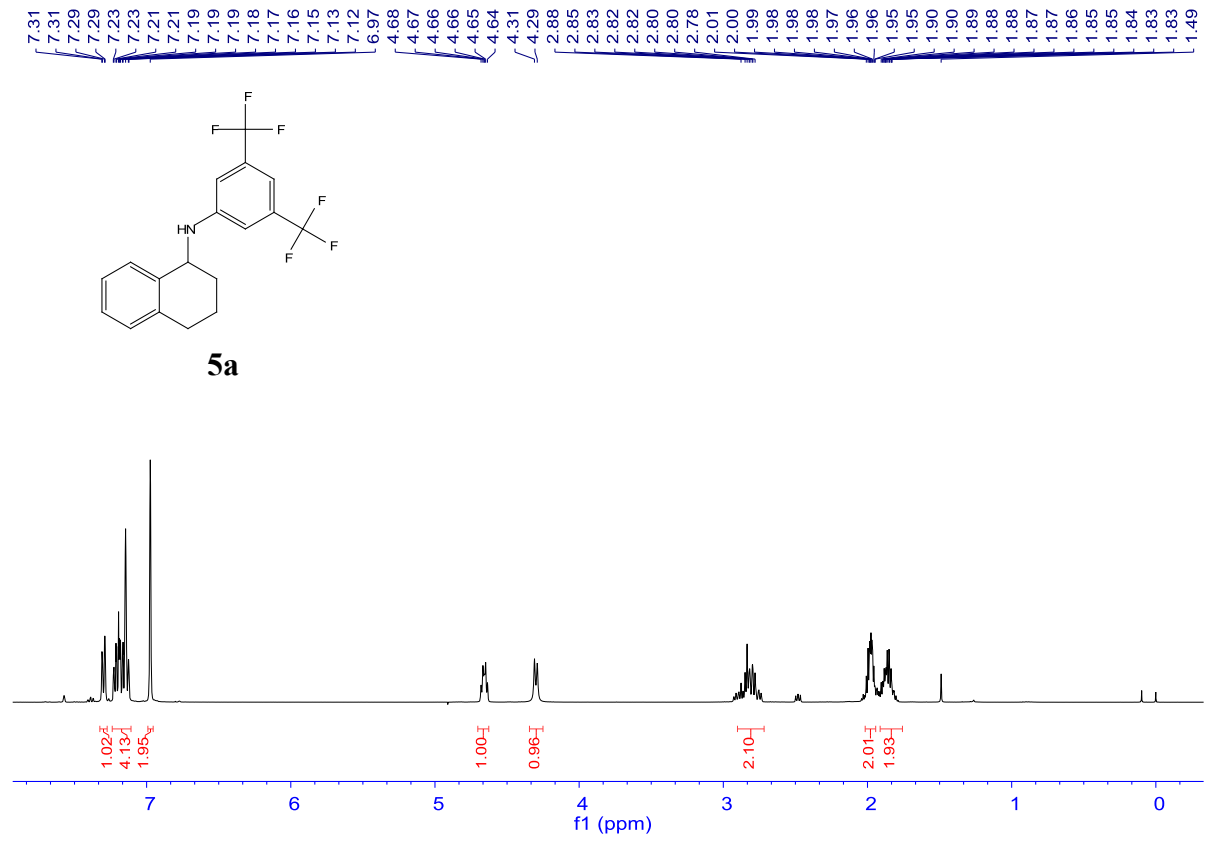

180 160 140 120 100 80 60 40 20 0
f1 (ppm)


7.89 7.55 7.50 7.48 7.34 7.33 7.32 7.32 7.31 7.30 7.28 7.27 7.26 7.25 7.24 7.24 7.24 7.24 6.88 6.26 6.26 6.25 6.24 3.17 3.16 3.14 3.12 3.12 3.10 2.96 2.95 2.94 2.93 2.92 2.91 2.90 2.89 2.58 2.58 2.57 2.56 2.55 2.54 2.53 2.53 2.24 2.23 2.22 2.22 2.21 2.21 2.20 2.20 2.20 2.19 2.18 1.58 0.07 -0.00
O
NH
F
F
F
F
F
F
3k
1.79
0.91
0.95
1.92
1.58
0.93
0.91
1.00
1.01
1.02
1.02
9 8 7 6 5 4 3 2 1 0
f1 (ppm)

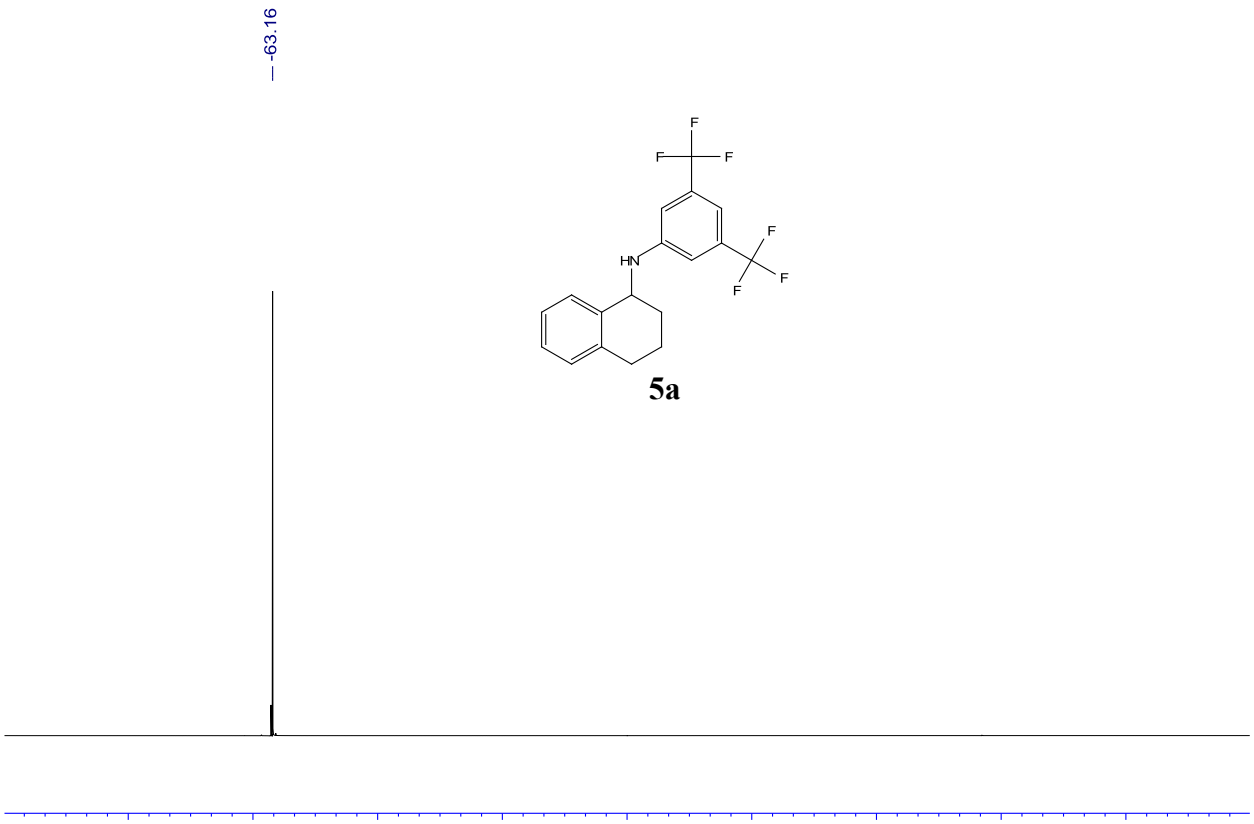

-63.04
O
NH
F
F
F
F
F
F
3k
-50 -55 -60 -65 -70 -75 -80
f1 (ppm)


153.10
144.67
140.44
139.62
133.11
132.78
132.45
132.11
129.55
127.05
125.75
125.13
124.58
121.87
119.15
118.30
116.88
116.85
116.81
116.77
116.73
80.37
77.48
77.16
76.84
32.46
30.31
O
NH
F
F
F
F
F
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

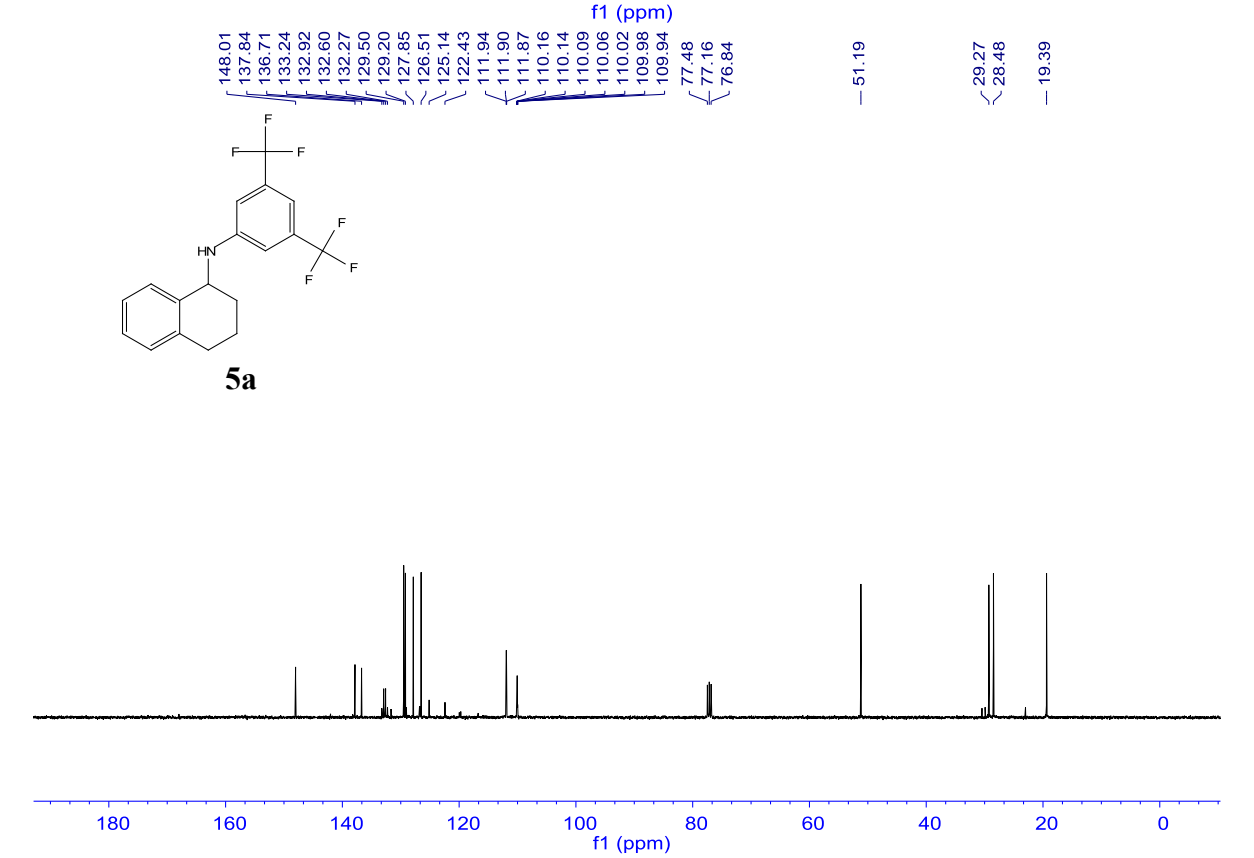
3k


7.31
7.31
7.29
7.29
7.23
7.23
7.21
7.21
7.19
7.19
7.19
7.18
7.17
7.16
7.15
7.13
7.12
6.97
4.68
4.67
4.66
4.66
4.65
4.64
4.31
4.29
2.88
2.85
2.83
2.82
2.82
2.80
2.80
2.78
2.01
2.00
1.99
1.98
1.98
1.98
1.97
1.96
1.96
1.95
1.95
1.90
1.90
1.89
1.88
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.83
1.83
1.49
F
F
F
F
F
F
HN
1.02
4.13
1.95
1.00
0.96
2.10
2.01
1.93
7
6
5
4
3
2
1
0
f1 (ppm)

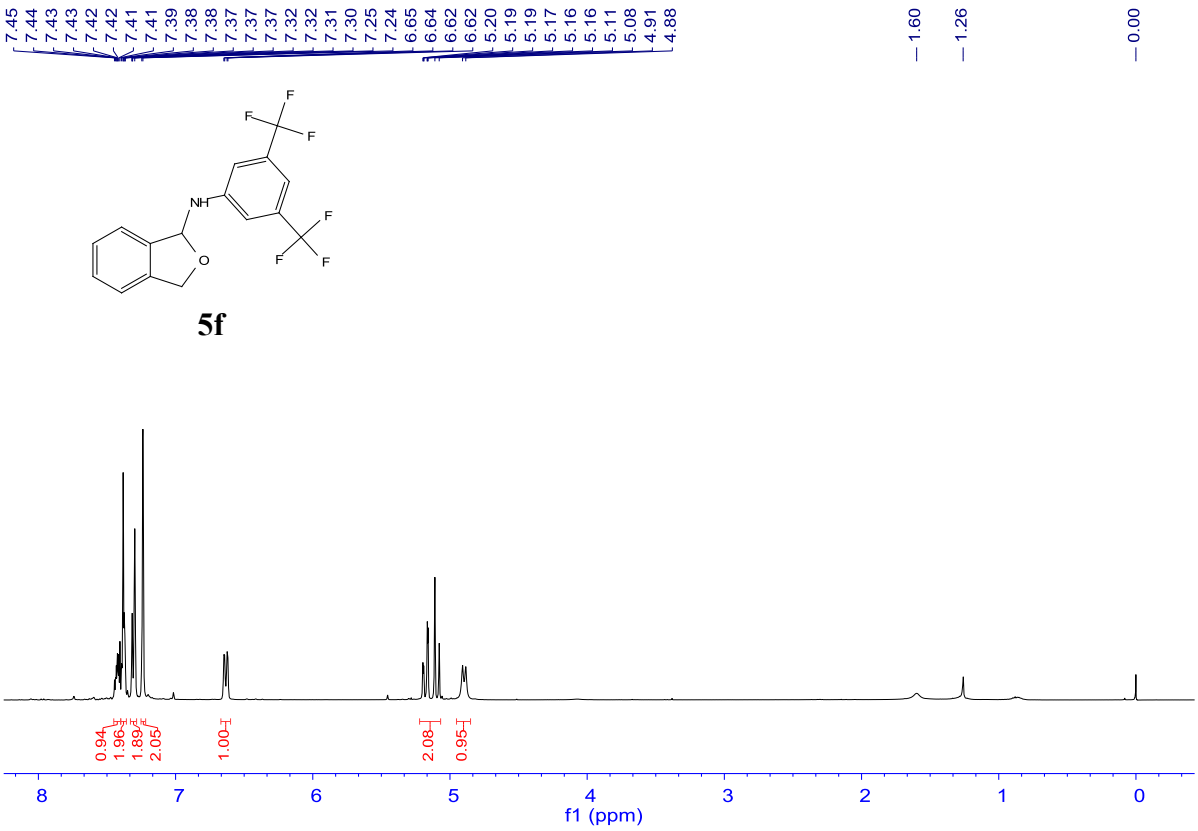
5a


-63.16
F
F
F
F
F
F
HN
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

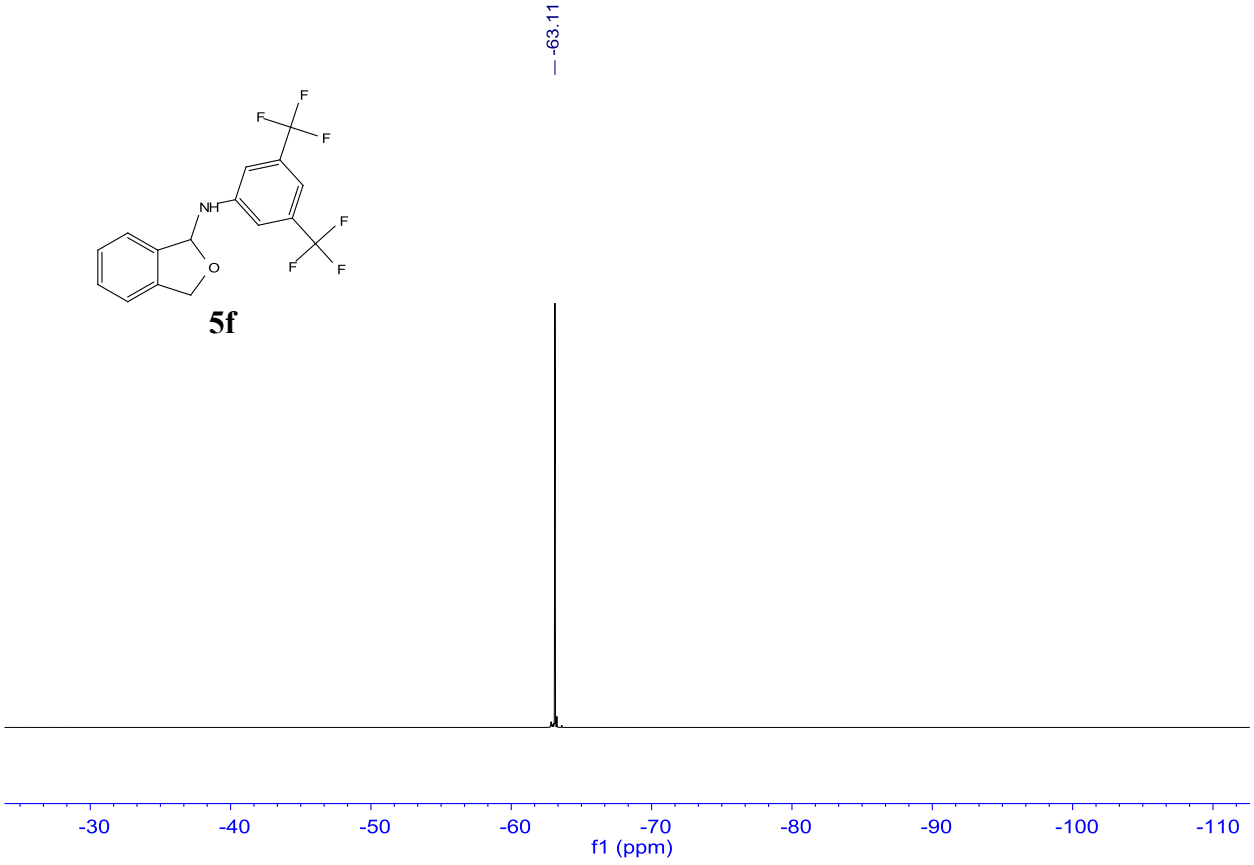
5a


148.01
137.84
136.71
133.24
132.92
132.60
132.27
129.50
129.20
127.85
126.51
125.14
122.43
111.94
111.90
111.87
110.16
110.14
110.09
110.06
110.02
109.98
109.94
77.48
77.16
76.84
51.19
29.27
28.48
19.39
F
F
F
F
F
F
HN
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

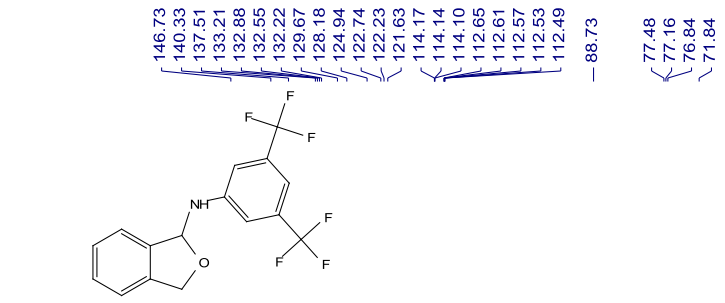
5a


7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.39
7.38
7.38
7.37
7.37
7.37
7.32
7.32
7.31
7.30
7.25
7.24
6.65
6.64
6.62
6.62
5.20
5.19
5.19
5.17
5.16
5.16
5.11
5.08
4.91
4.88
1.60
1.26
0.00
F
F
F
NH
O
F
F
F
0.94
1.96
1.89
2.05
1.00
2.08
0.95
8
7
6
5
4
3
2
1
0
f1 (ppm)

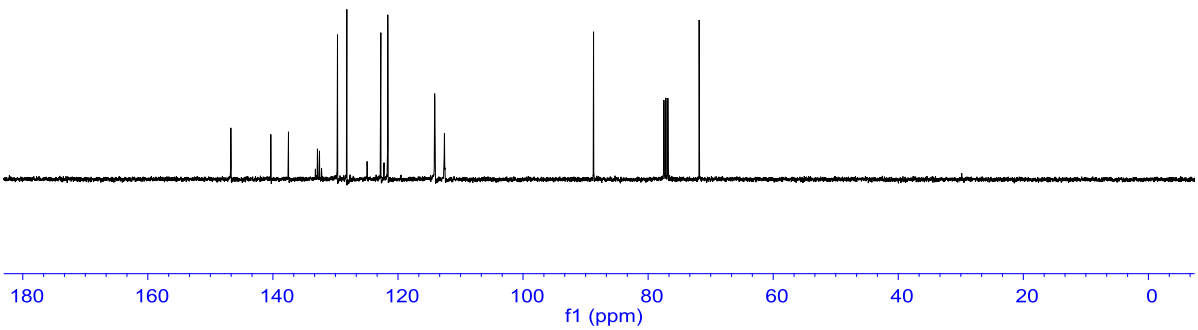
5f

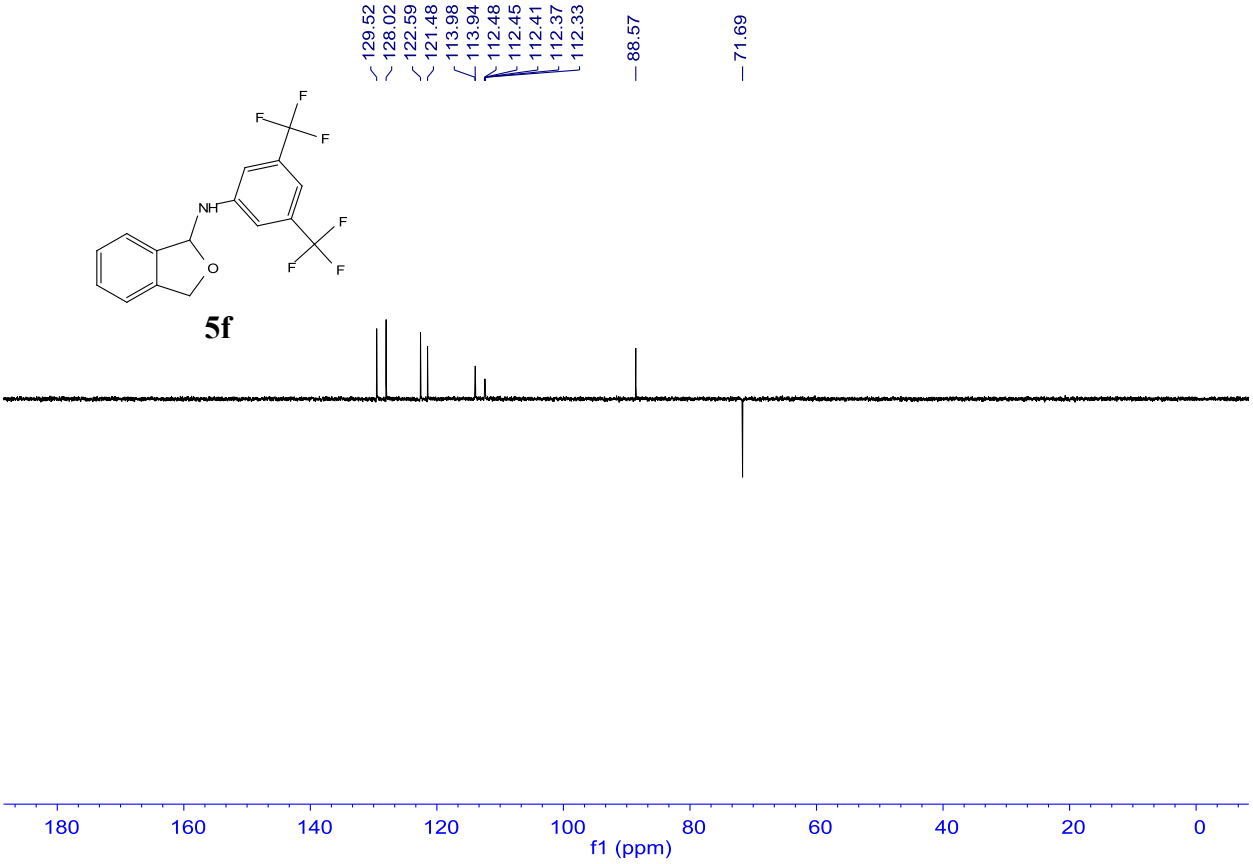

-63.11
F
F
F
NH
O
F
F
F
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

5f

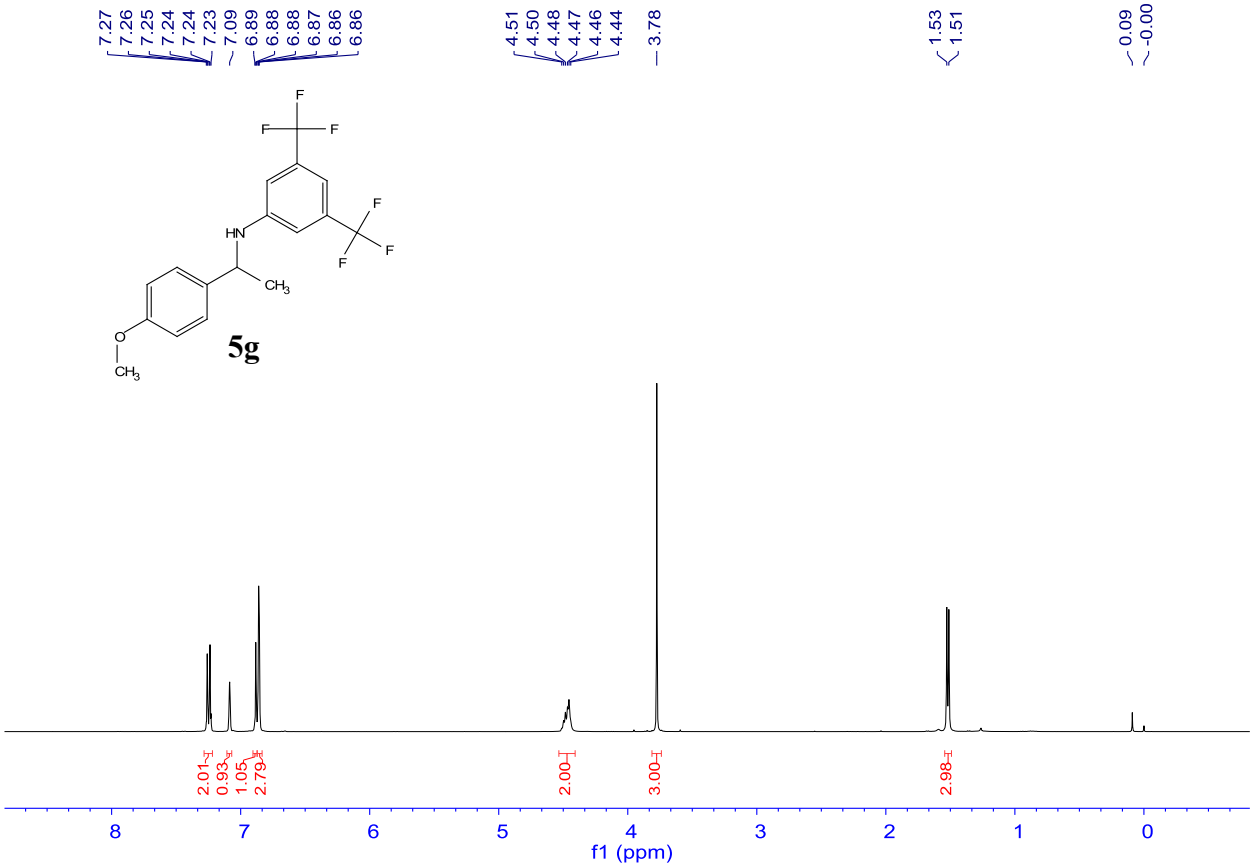

146.73
140.33
137.51
133.21
132.88
132.55
132.22
129.67
128.18
124.94
122.74
122.23
121.63
114.17
114.14
114.10
112.65
112.61
112.57
112.53
112.49
88.73
77.48
77.16
76.84
71.84
F
F
F
NH
O
F
F
F

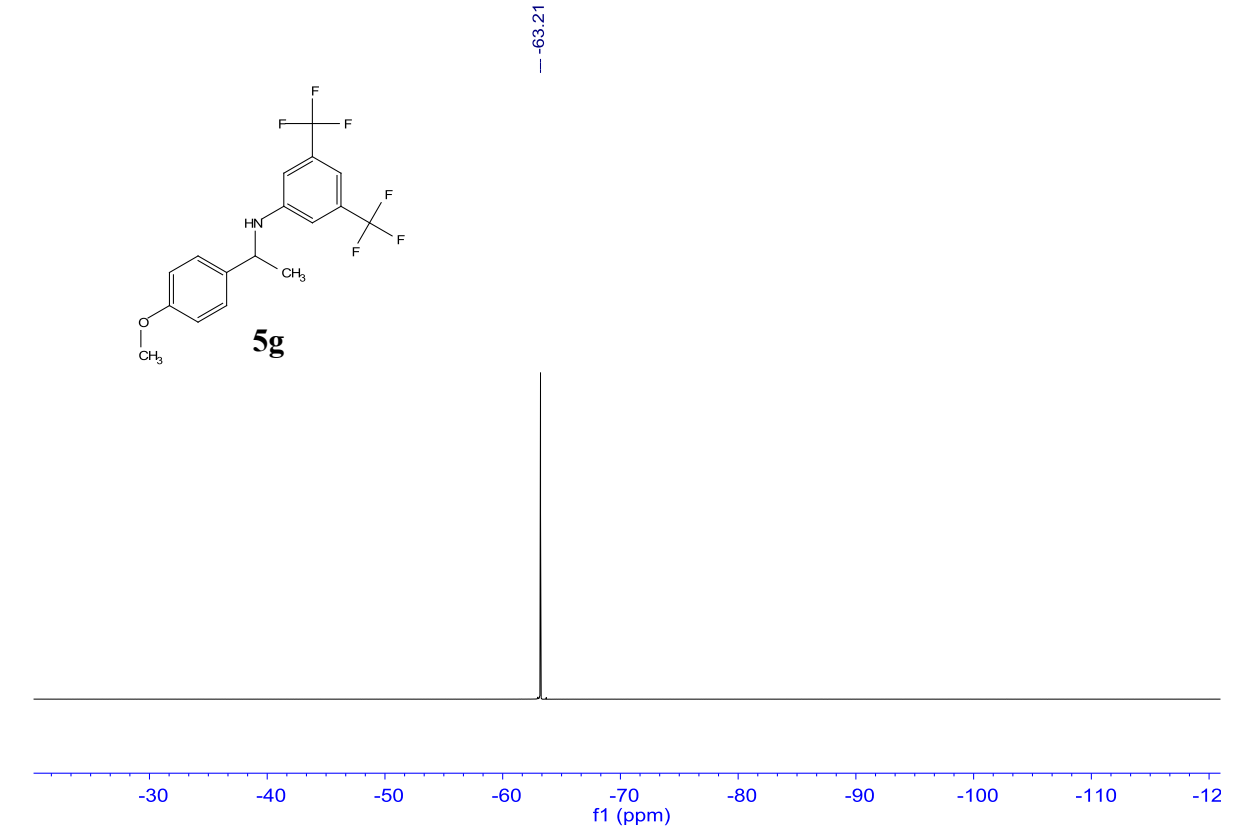
5f

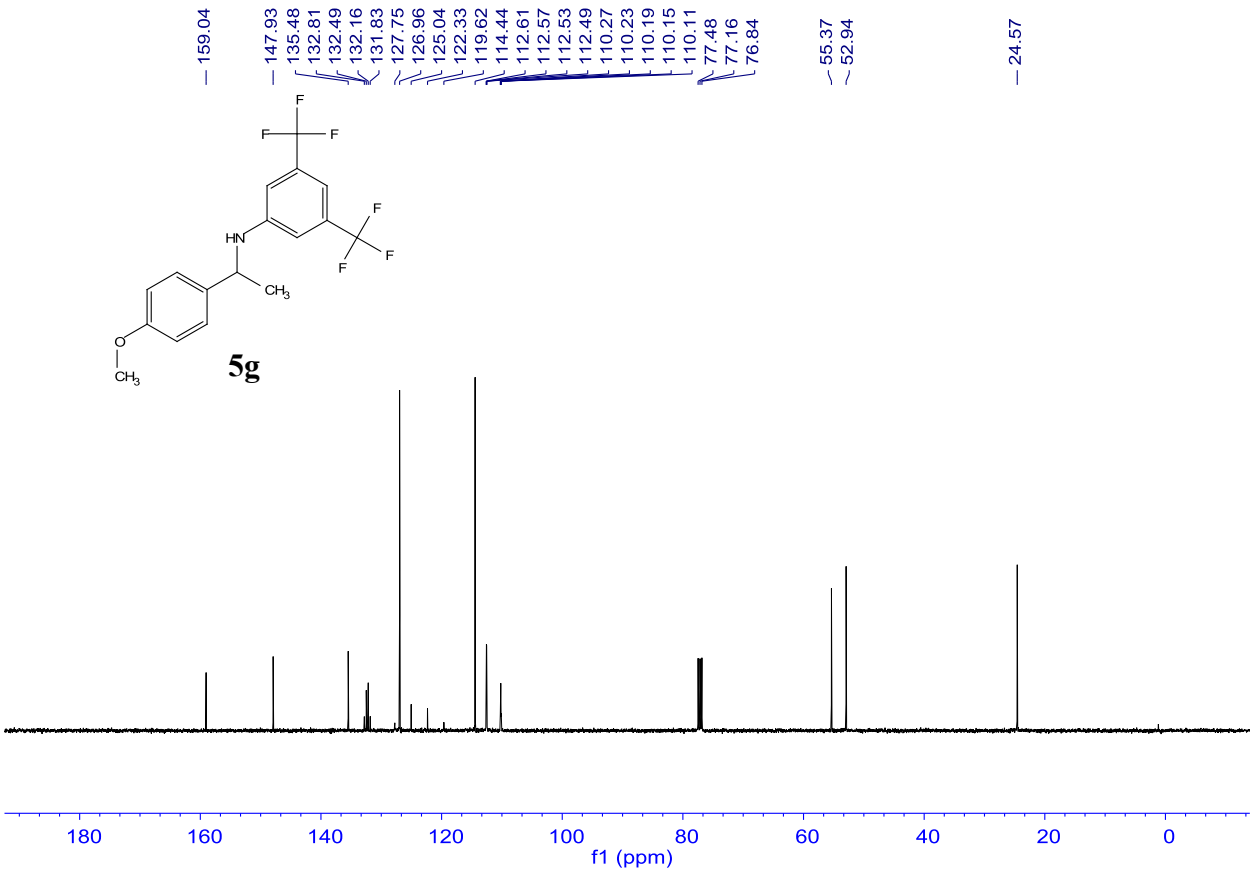

180
160
140
120
100
80
60
40
20
0
f1 (ppm)


129.52
128.02
122.59
121.48
113.98
113.94
112.48
112.45
112.41
112.37
112.33
88.57
71.69
F
F
F
NH
O
F
F
F
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

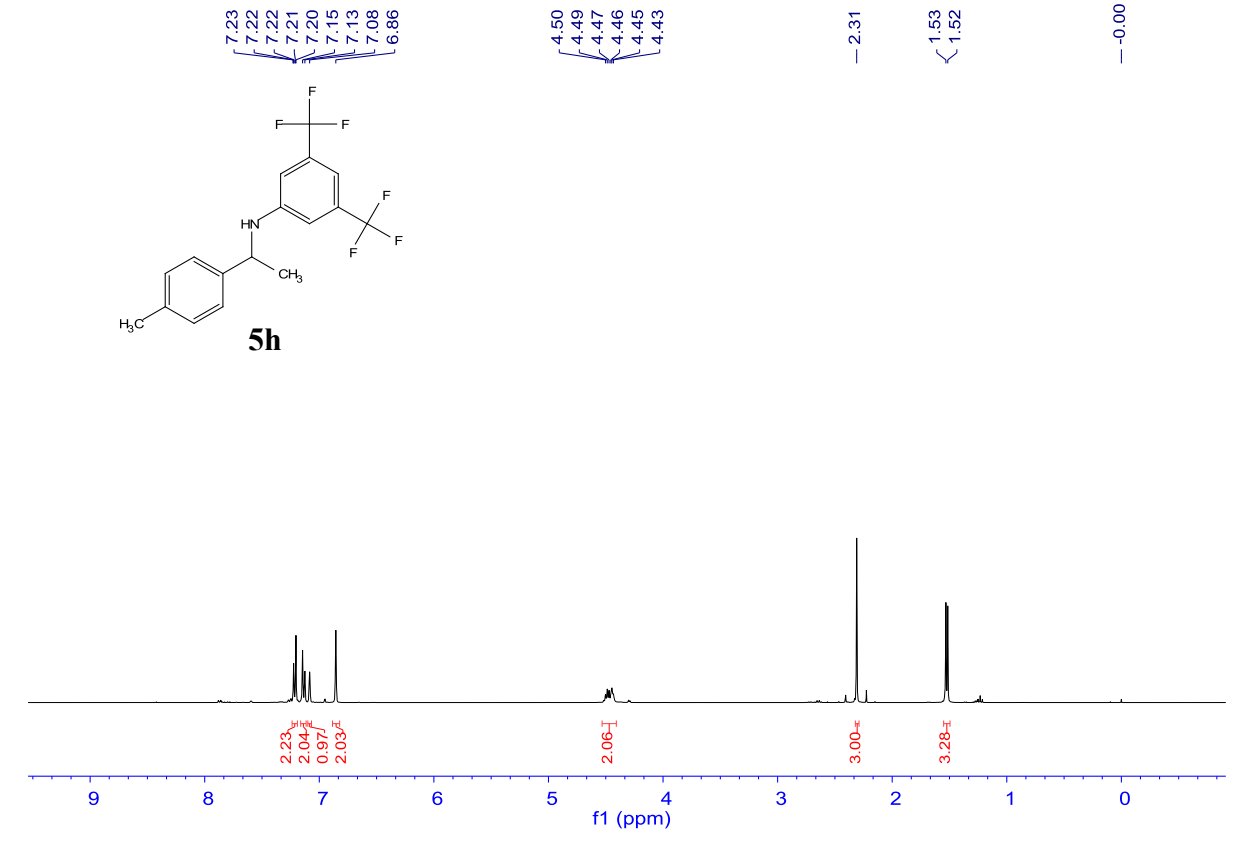
5f


7.27
7.26
7.25
7.24
7.24
7.23
7.09
6.89
6.88
6.88
6.87
6.86
6.86
4.51
4.50
4.48
4.47
4.46
4.44
3.78
1.53
1.51
0.09
-0.00
F
F
F
HN
F
F
F
CH3
O
CH3
5g
2.01
0.93
1.05
2.79
2.00
3.00
2.98
8
7
6
5
4
3
2
1
0
f1 (ppm)

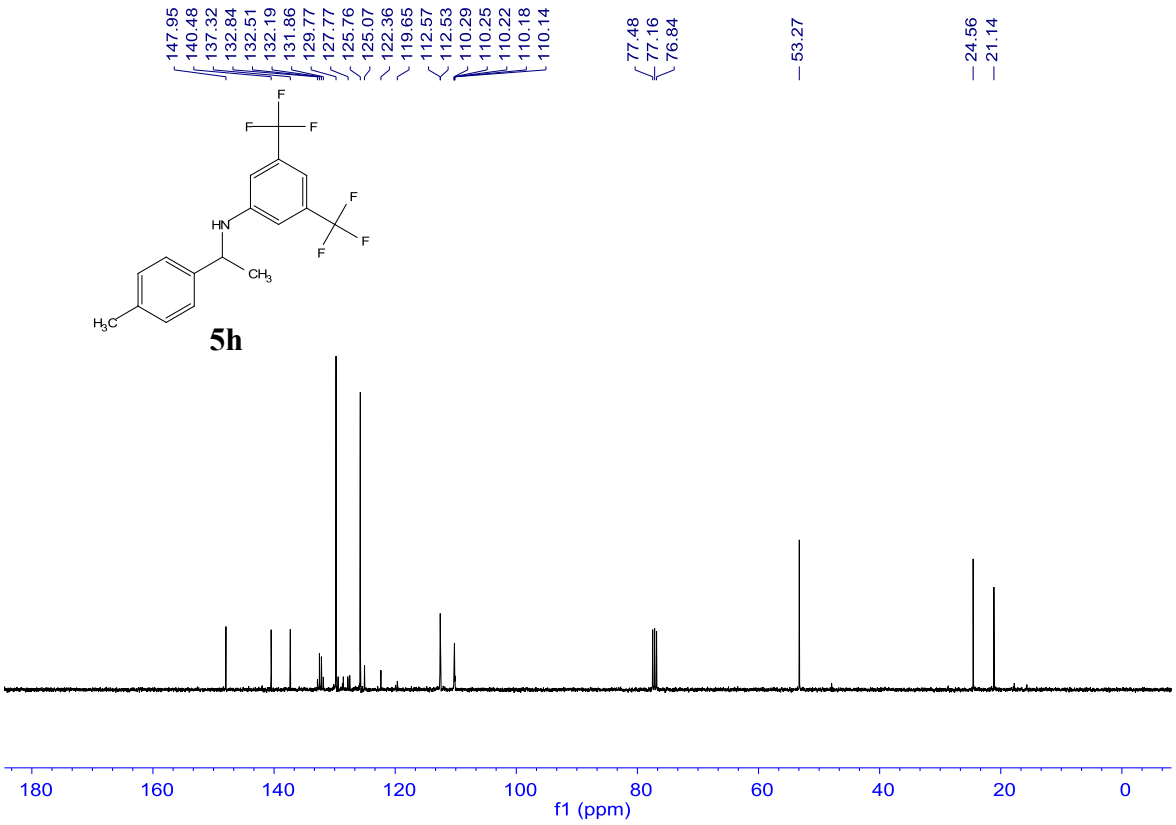

-63.21
F
F
F
HN
F
F
F
CH3
O
CH3
5g
-30
-40
-50
-60
-70
-80
-90
-100
-110
-12
f1 (ppm)


159.04
147.93
135.48
132.81
132.49
132.16
131.83
127.75
126.96
125.04
122.33
119.62
114.44
112.61
112.57
112.53
112.49
110.27
110.23
110.19
110.15
110.11
77.48
77.16
76.84
55.37
52.94
24.57
F
F
F
HN
F
F
F
CH3
O
CH3
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

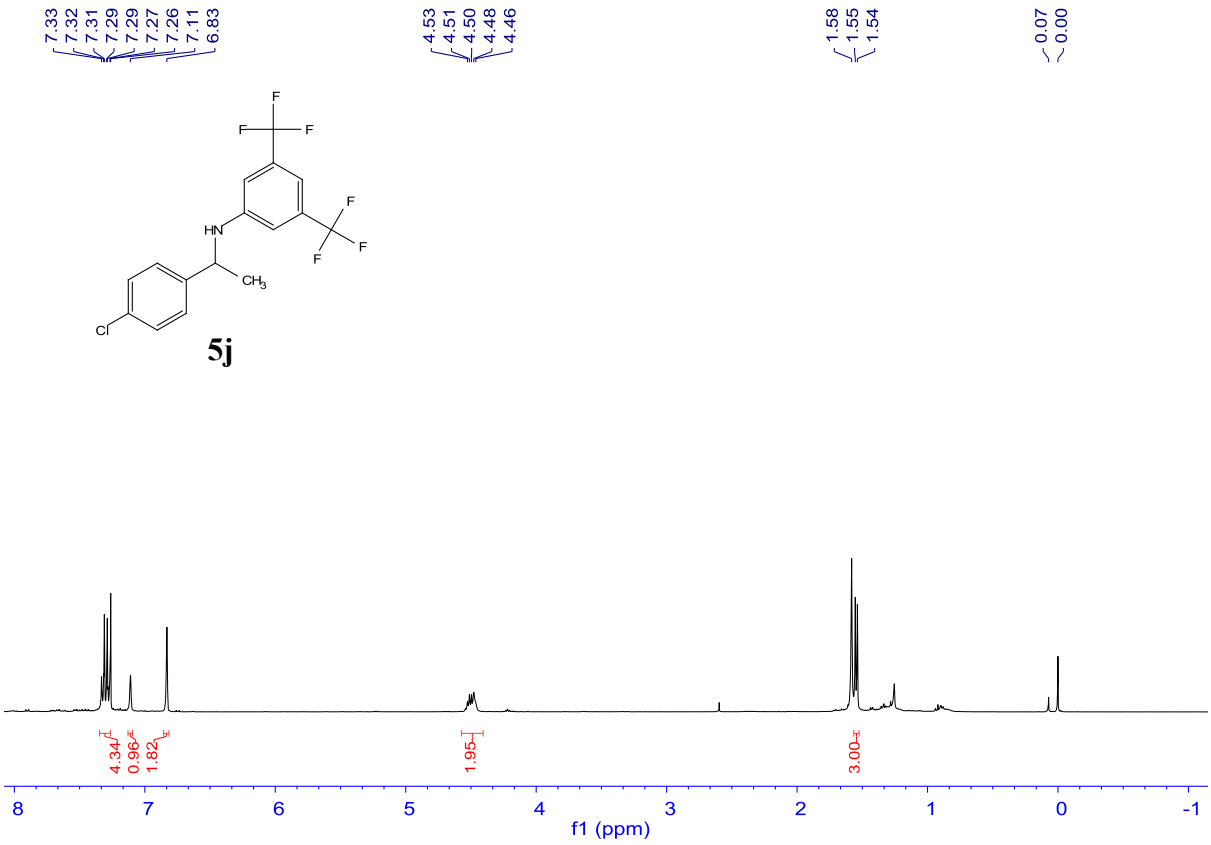
5g


7.23
7.22
7.22
7.21
7.20
7.15
7.13
7.08
6.86
4.50
4.49
4.47
4.46
4.45
4.43
2.31
1.53
1.52
-0.00
F
F
F
HN
F
F
F
CH3
H3C
2.23
2.04
0.97
2.03
2.06
3.00
3.28
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

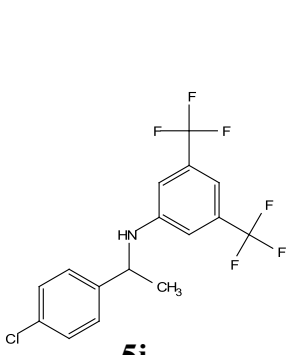
5h


147.95
140.48
137.32
132.84
132.51
132.19
131.86
129.77
127.77
125.76
125.07
122.36
119.65
112.57
112.53
110.29
110.25
110.22
110.18
110.14
77.48
77.16
76.84
53.27
24.56
21.14
F
F
F
F
F
HN
CH3
H3C
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

5h


7.33
7.32
7.31
7.29
7.29
7.27
7.26
7.11
6.83
4.53
4.51
4.50
4.48
4.46
1.58
1.55
1.54
0.07
0.00
F
F
F
F
F
HN
CH3
Cl
4.34
0.96
1.82
1.95
3.00
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

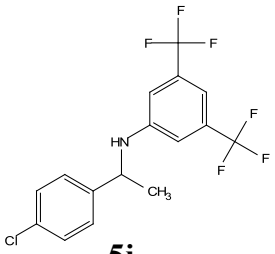
5j


F
F
F
HN
F
F
F
CH3
Cl

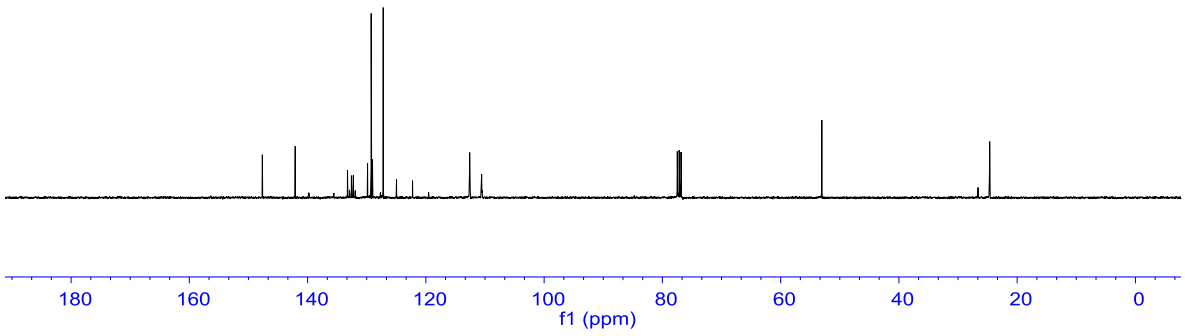
5j

-63.25
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

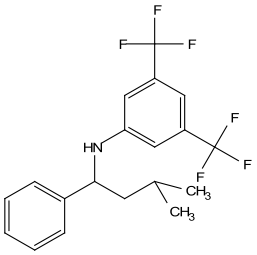

147.65
142.10
133.25
132.92
132.59
132.27
131.94
129.25
127.67
127.21
124.96
122.25
119.54
112.59
112.55
110.68
110.65
110.61
110.57
110.53
110.50
77.48
77.16
76.84
53.04
24.65


F
F
F
HN
F
F
F
CH3
Cl

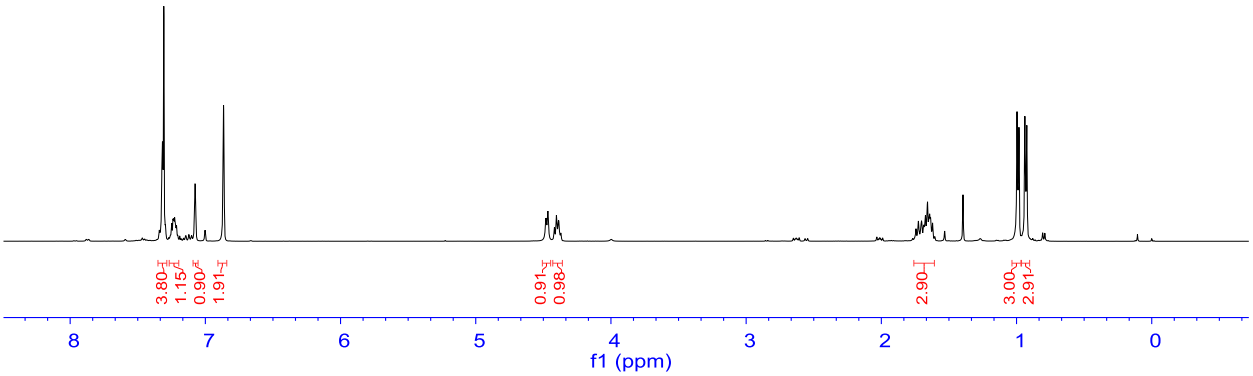
5j


180
160
140
120
100
80
60
40
20
0
f1 (ppm)

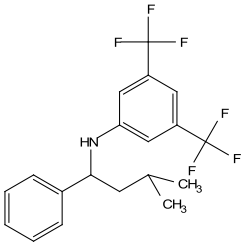

7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.29
7.26
7.25
7.25
7.25
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.08
6.87
4.48
4.47
4.42
4.40
4.39
4.37
1.74
1.73
1.71
1.70
1.69
1.67
1.66
1.65
1.64
1.64
1.62
1.61
1.40
1.39
1.00
0.98
0.94
0.92
0.11
0.00


F
F
F
HN
F
F
F
CH3
CH3

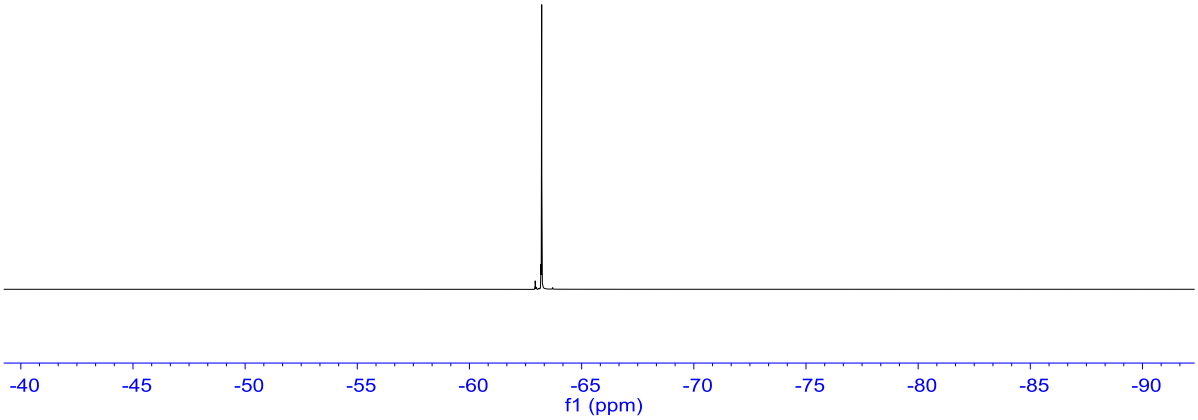
5k

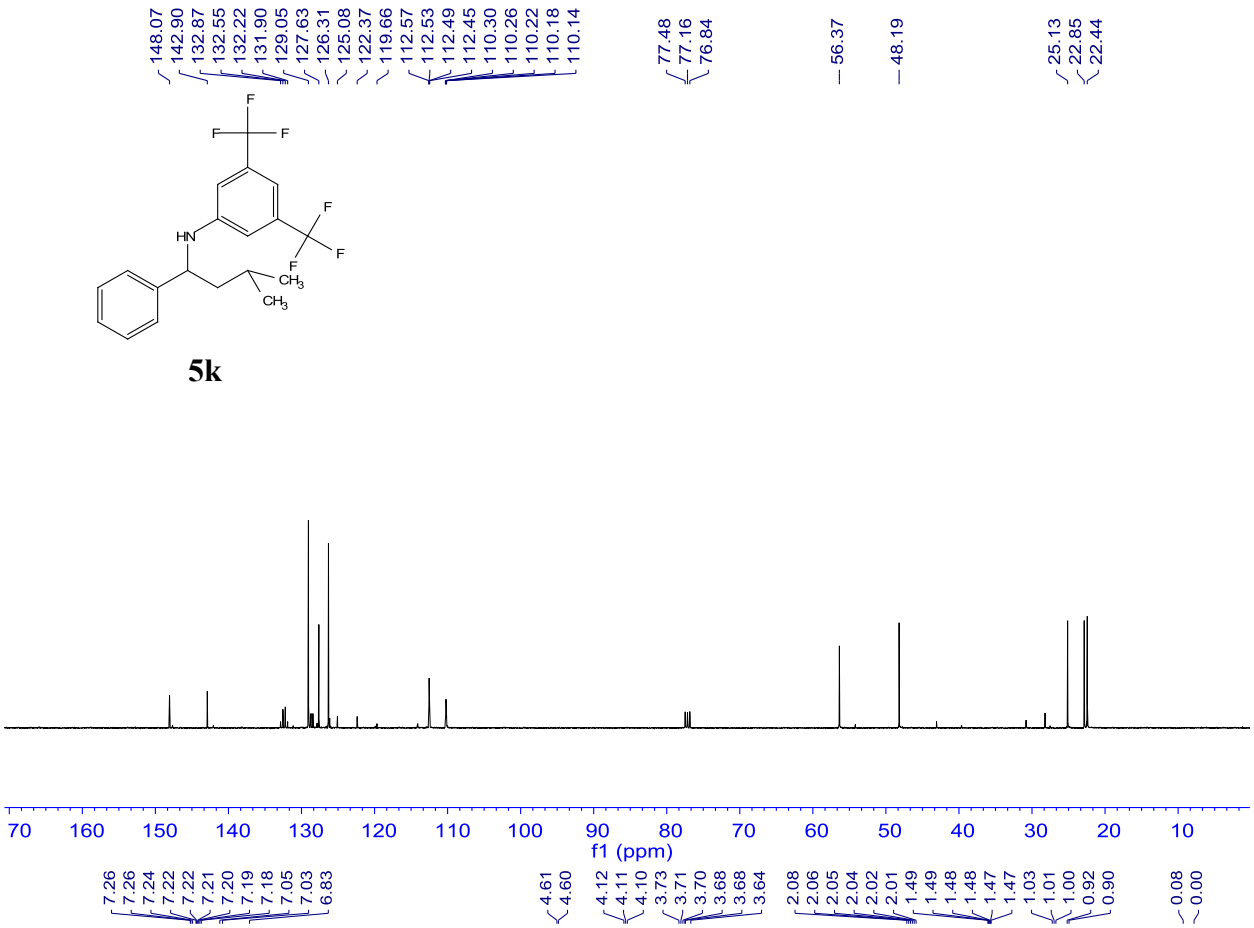

3.80
1.15
0.90
1.91
0.91
0.98
2.90
3.00
2.91
8
7
6
5
4
3
2
1
0
f1 (ppm)


-63.22

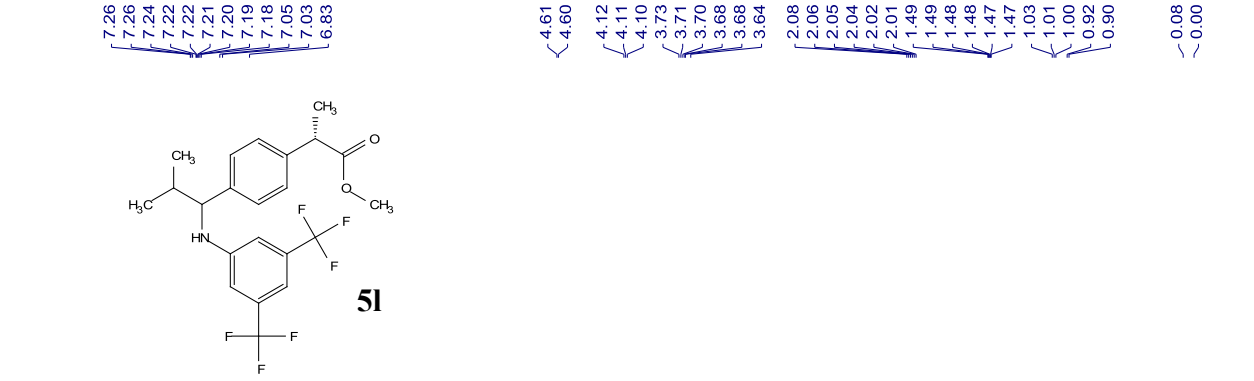

F
F
F
HN
F
F
F
CH3
CH3

5k


-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)

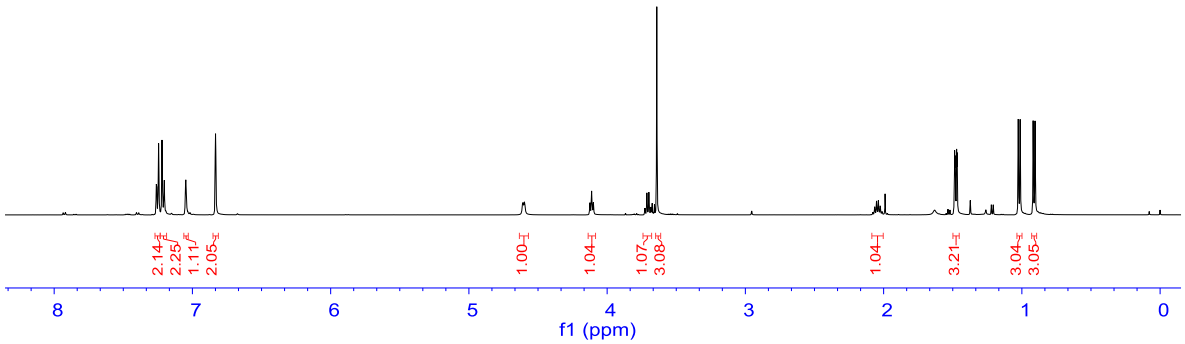

148.07
142.90
132.87
132.55
132.22
131.90
129.05
127.63
126.31
125.08
122.37
119.66
112.57
112.53
112.49
112.45
110.30
110.26
110.22
110.18
110.14
77.48
77.16
76.84
56.37
48.19
25.13
22.85
22.44
F
F
F
HN
F
F
F
CH3
CH3
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

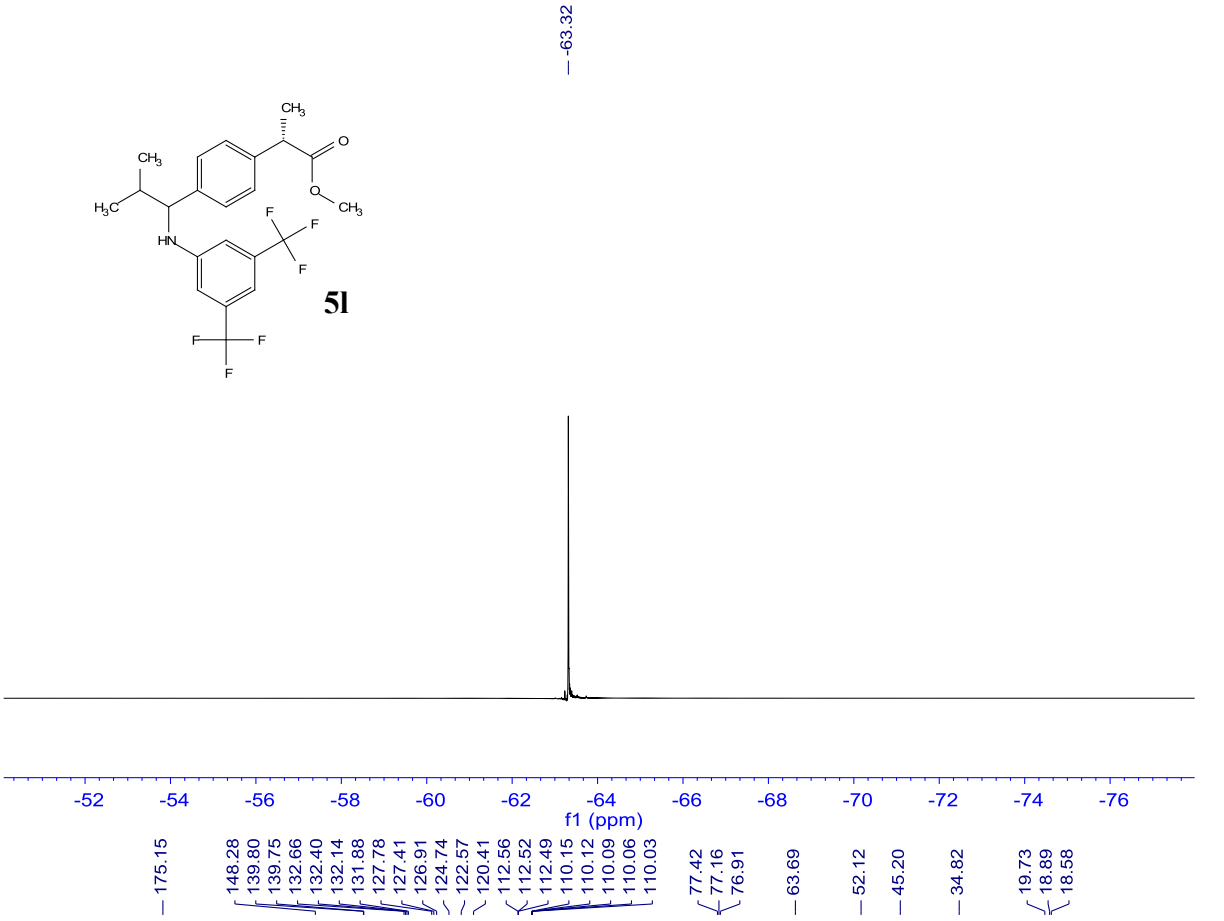
5k

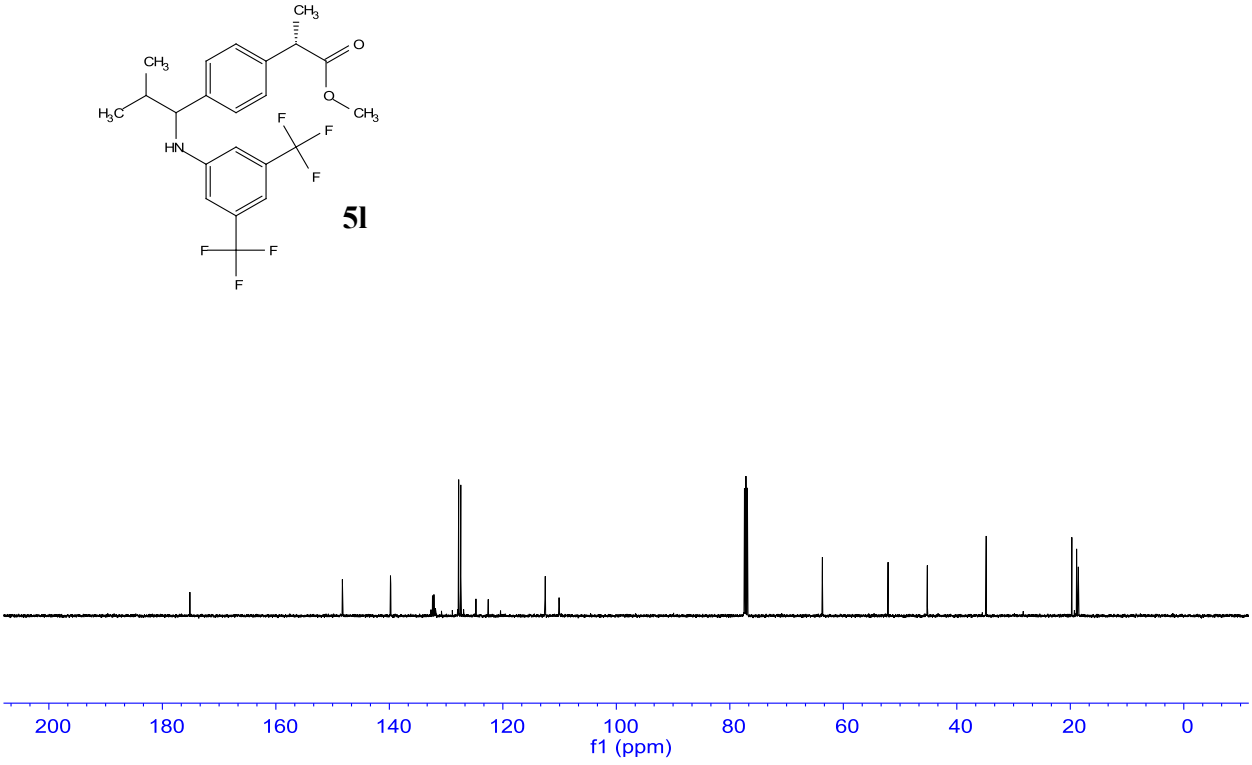

7.26
7.26
7.24
7.22
7.22
7.21
7.20
7.19
7.18
7.05
7.03
6.83
4.61
4.60
4.12
4.11
4.10
3.73
3.71
3.70
3.68
3.64
2.08
2.06
2.05
2.04
2.02
2.01
1.49
1.49
1.48
1.48
1.47
1.47
1.03
1.01
1.00
0.92
0.90
0.08
0.00

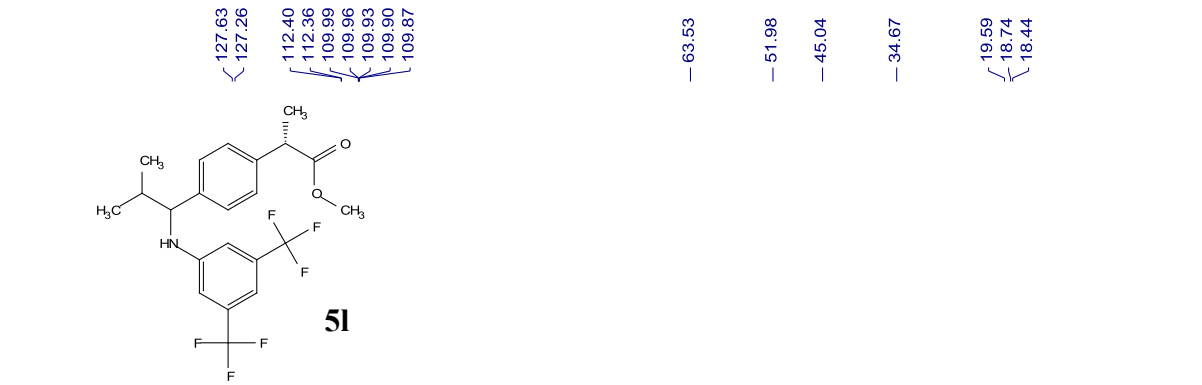
CH3
O
O
CH3
CH3
H3C
HN
F
F
F
F
F
F

5l

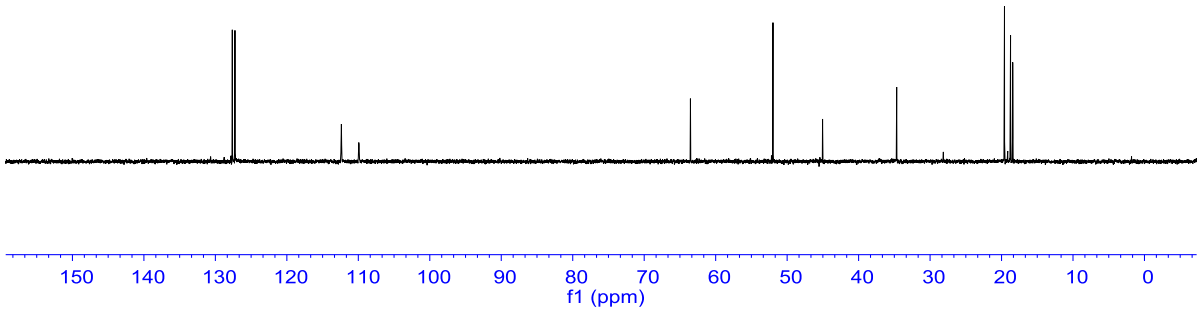

2.14
2.25
1.11
2.05
1.00
1.04
1.07
3.08
1.04
3.21
3.04
3.05
8
7
6
5
4
3
2
1
0
f1 (ppm)


-63.32
5l
f1 (ppm)

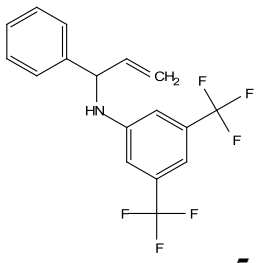

175.15
148.28
139.80
139.75
132.66
132.40
132.14
131.88
127.78
127.41
126.91
124.74
122.57
120.41
112.56
112.52
112.49
110.15
110.12
110.09
110.06
110.03
77.42
77.16
76.91
63.69
52.12
45.20
34.82
19.73
18.89
18.58
5l
f1 (ppm)


127.63
127.26
112.40
112.36
109.99
109.96
109.93
109.90
109.87
63.53
51.98
45.04
34.67
19.59
18.74
18.44
CH3
O
O
CH3
H3C
CH3
HN
F
F
F
F
F
F

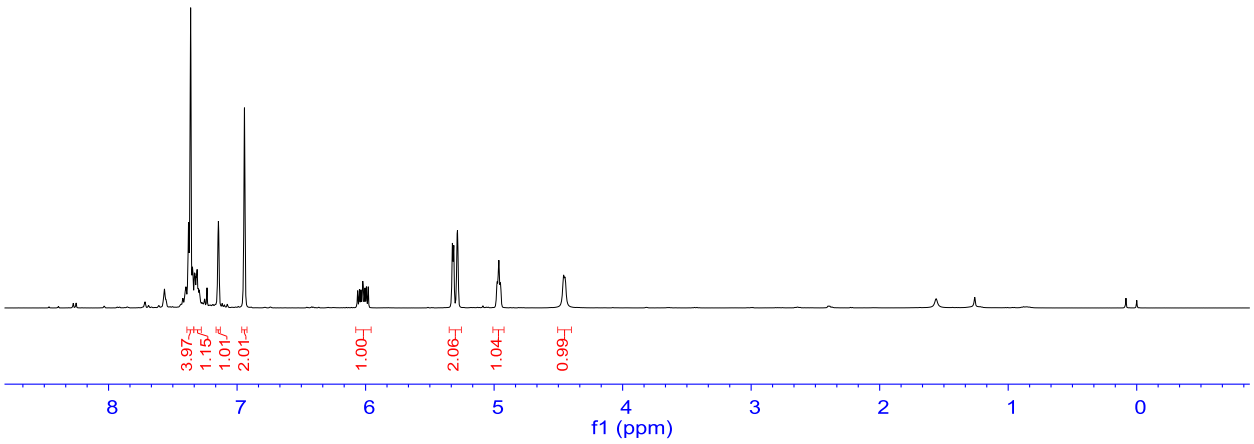
5l

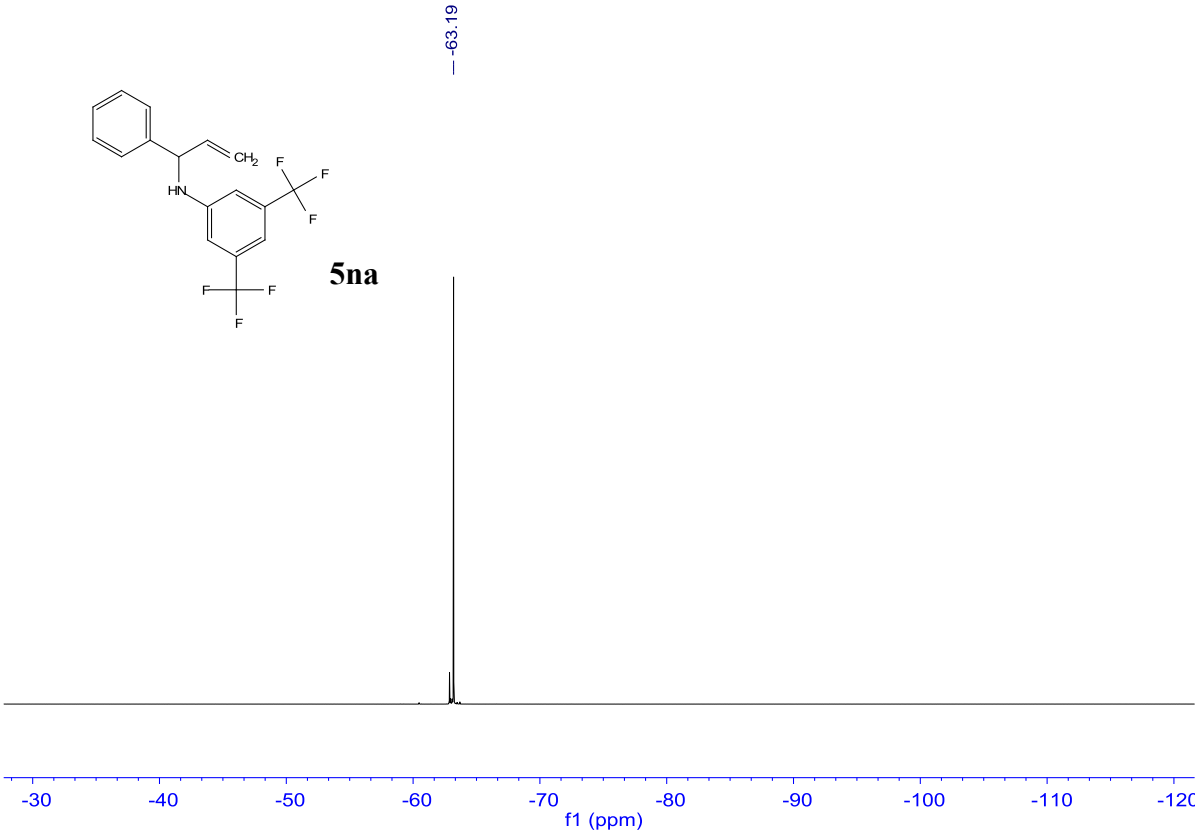

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

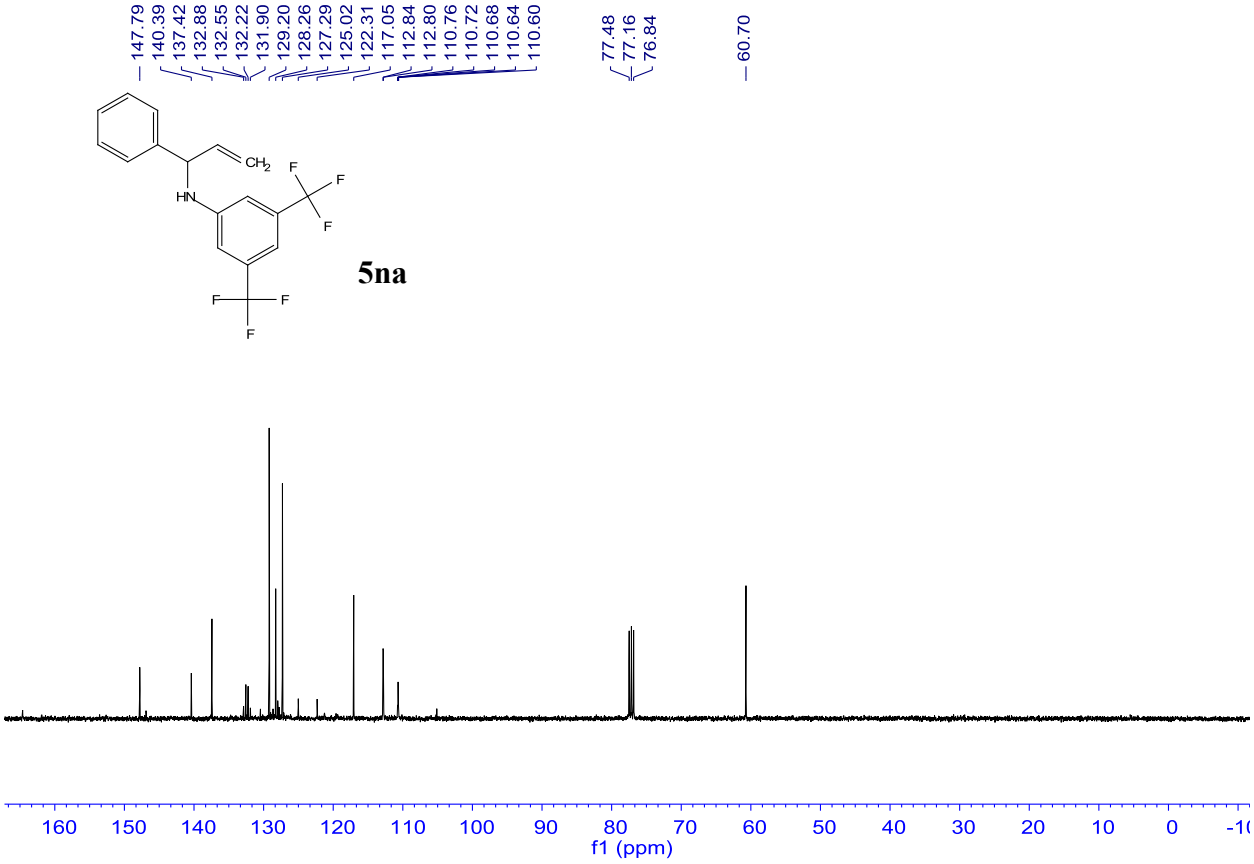

7.38
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.29
7.15
6.94
6.06
6.06
6.05
6.05
6.04
6.02
6.02
6.00
5.99
5.98
5.98
5.33
5.32
5.32
5.31
5.29
5.29
5.28
5.28
4.98
4.96
4.95
4.46
4.45
1.56
1.26
0.08
0.00
-0.00

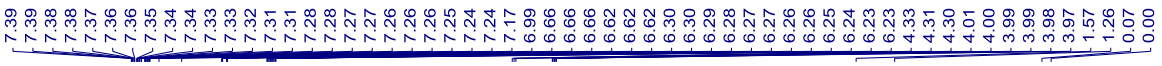

CH2
HN
F
F
F
F
F
F

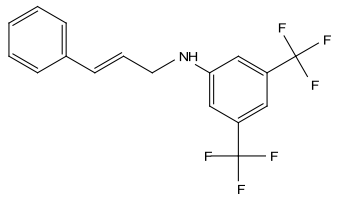
5na


3.97
1.15
1.01
2.01
1.00
2.06
1.04
0.99
8
7
6
5
4
3
2
1
0
f1 (ppm)

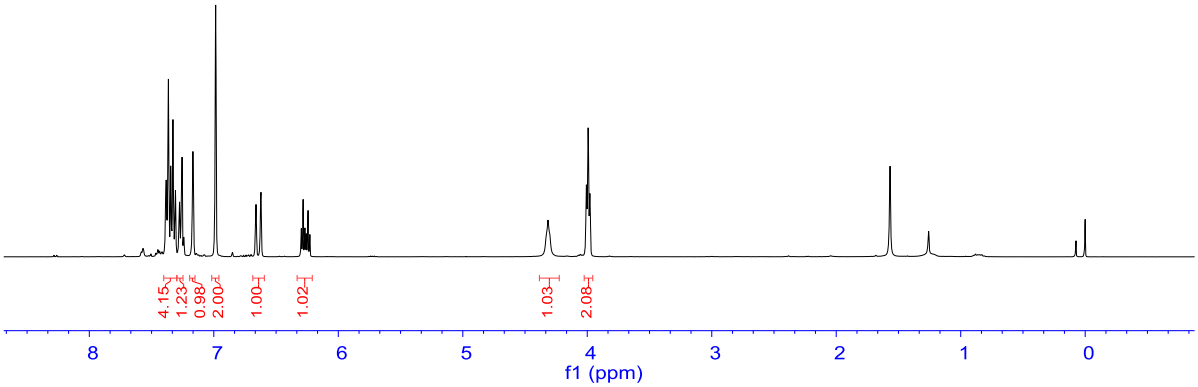

-63.19
CH2
HN
F
F
F
F
F
F
5na
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
f1 (ppm)

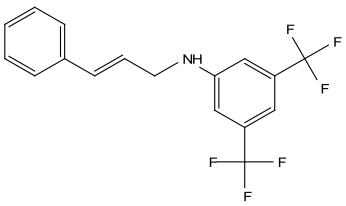

147.79
140.39
137.42
132.88
132.55
132.22
131.90
129.20
128.26
127.29
125.02
122.31
117.05
112.84
112.80
110.76
110.72
110.68
110.64
110.60
77.48
77.16
76.84
60.70
CH2
HN
F
F
F
F
F
F
5na
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.24
7.24
7.17
6.99
6.66
6.66
6.62
6.62
6.62
6.30
6.30
6.29
6.28
6.27
6.27
6.26
6.26
6.25
6.24
6.23
6.23
4.33
4.31
4.30
4.01
4.00
3.99
3.99
3.98
3.97
1.57
1.26
0.07
0.00


NH
F
F
F
F
F
F

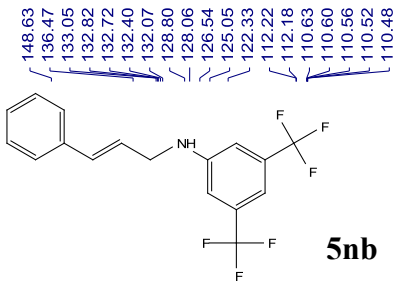
5nb


4.15
1.23
0.98
2.00
1.00
1.02
1.03
2.08
8
7
6
5
4
3
2
1
0
f1 (ppm)

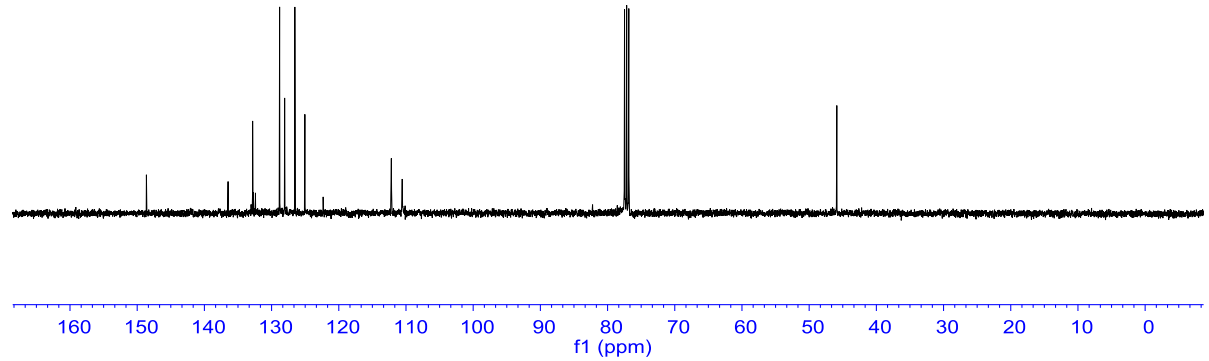

NH
F
F
F
F
F
F

5nb

-63.15
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)


148.63
136.47
133.05
132.82
132.72
132.40
132.07
128.80
128.06
126.54
125.05
122.33
112.22
112.18
110.63
110.60
110.56
110.52
110.48
77.48
77.16
76.84
45.89
NH
F
F
F
F
F
F

5nb


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.38
7.37
7.37
7.36
7.36
7.35
7.25
7.15
6.94
6.94
6.93
6.92
6.92
6.91
6.91
6.90
6.08
6.07
6.06
6.05
6.05
6.04
6.03
5.44
5.44
5.43
5.41
5.41
5.40
5.40
5.31
5.31
5.31
5.31
5.29
5.29
5.29
5.29
5.24
5.24
5.24
5.23
4.56
4.56
4.56
4.55
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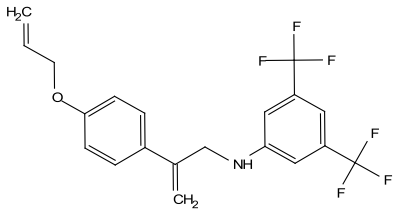
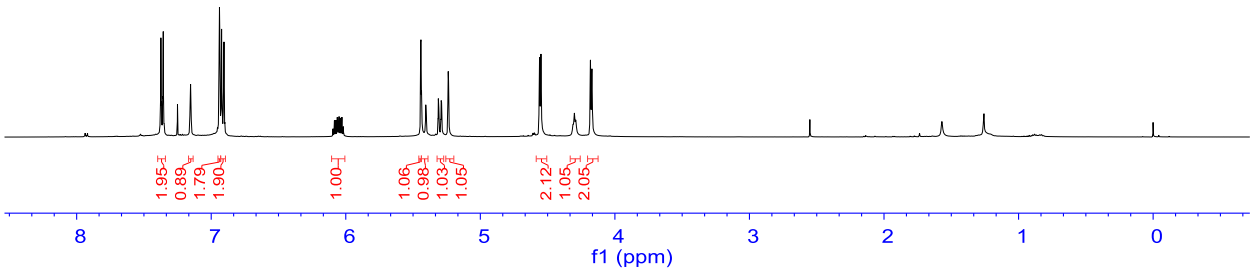
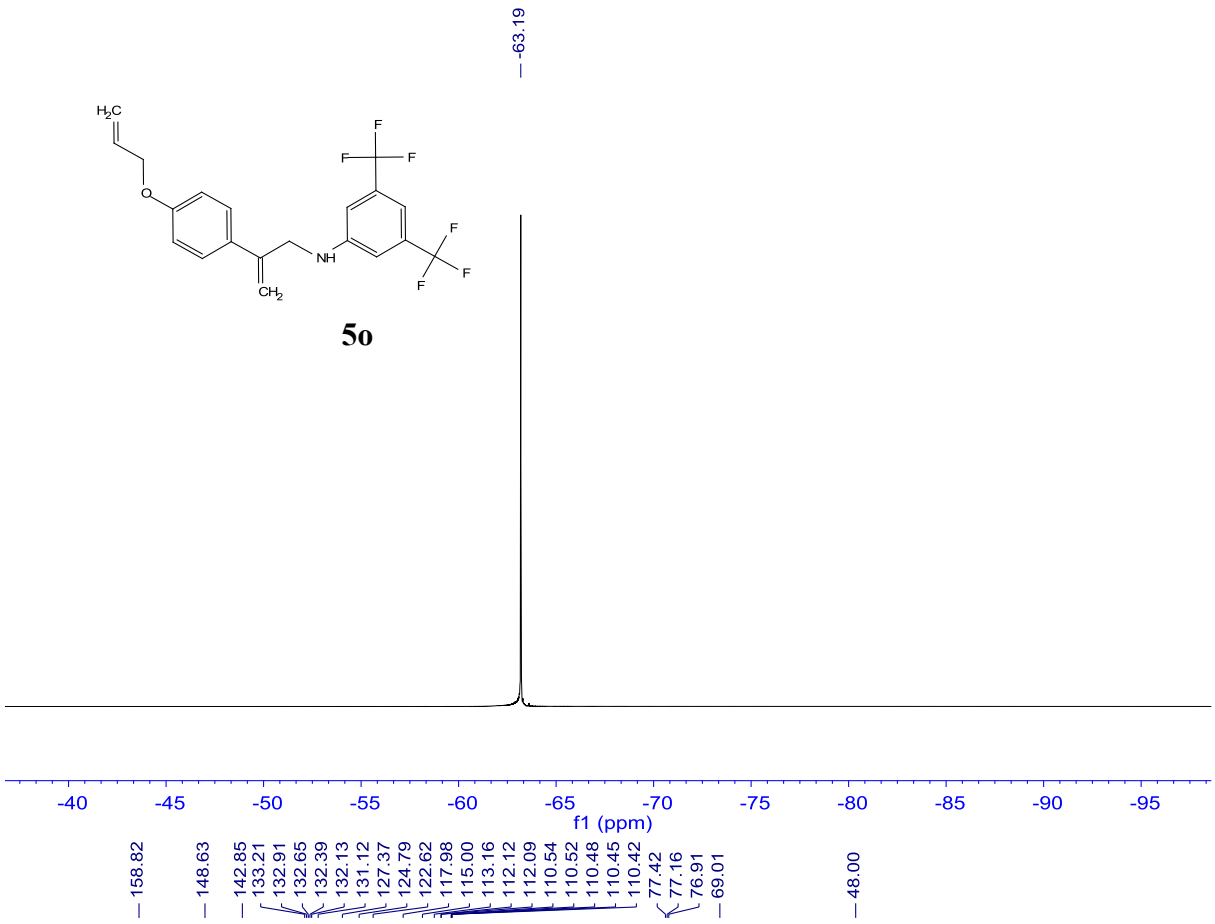
4.18
4.18
4.17
1.57
1.26
0.00

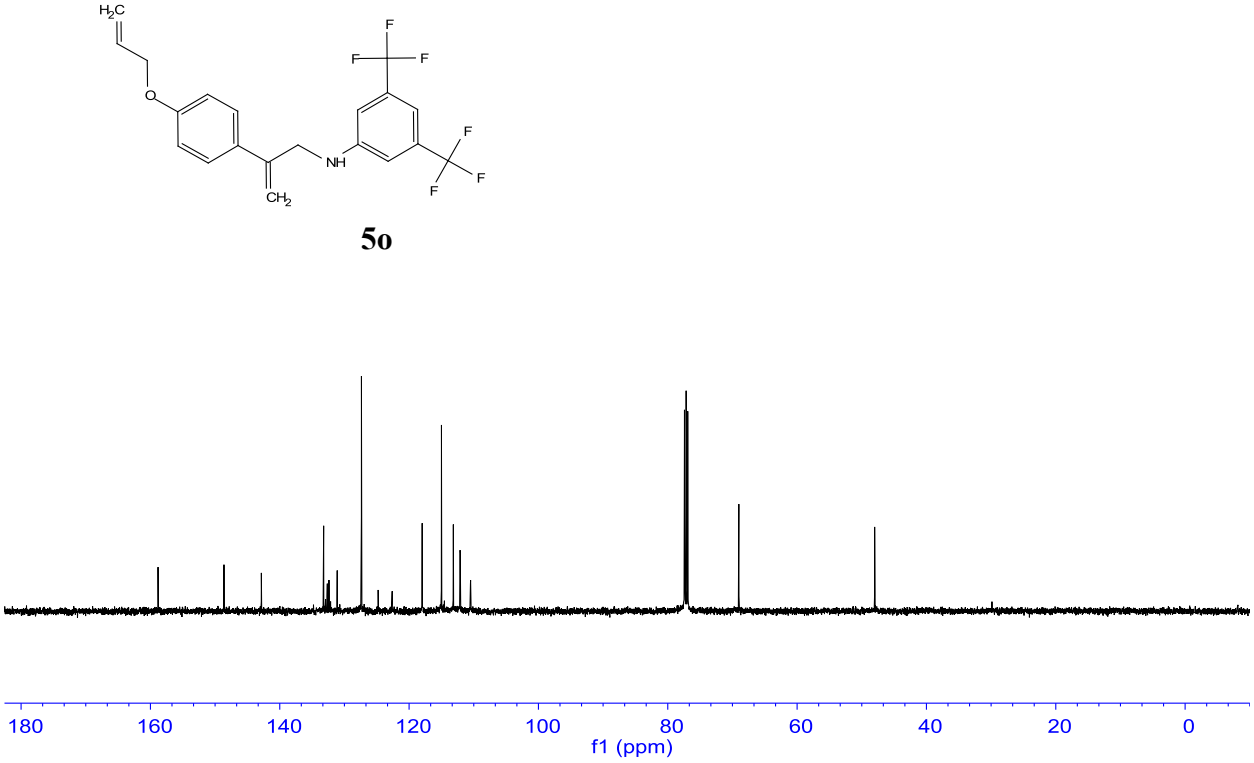

H2C
O
NH
CH2
F
F
F
F
F
F

5o

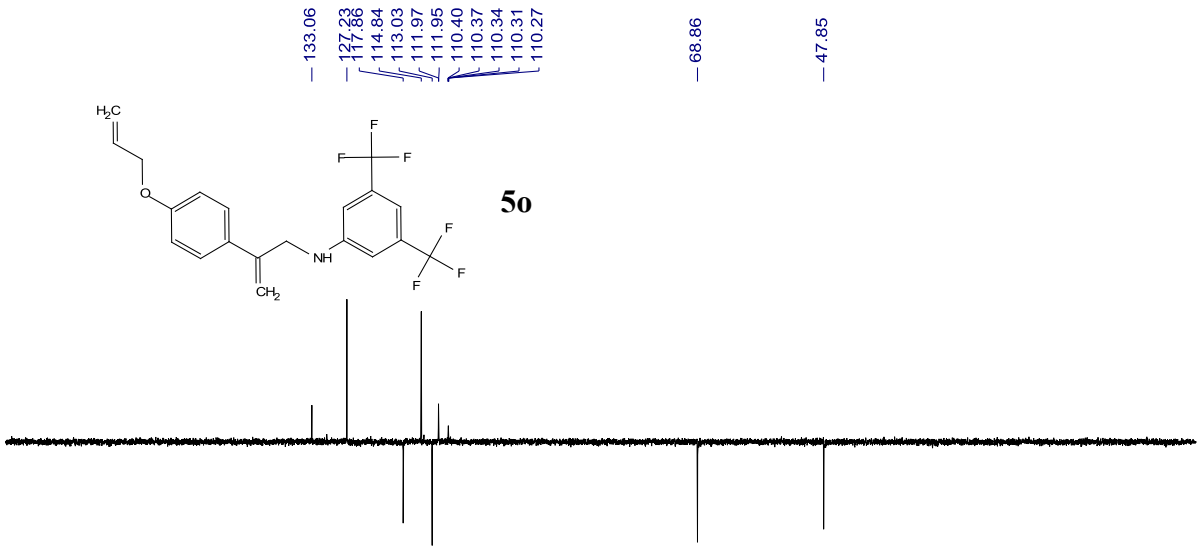

1.95
0.89
1.79
1.90
1.00
1.06
0.98
1.03
1.05
2.12
1.05
2.05
8
7
6
5
4
3
2
1
0
f1 (ppm)

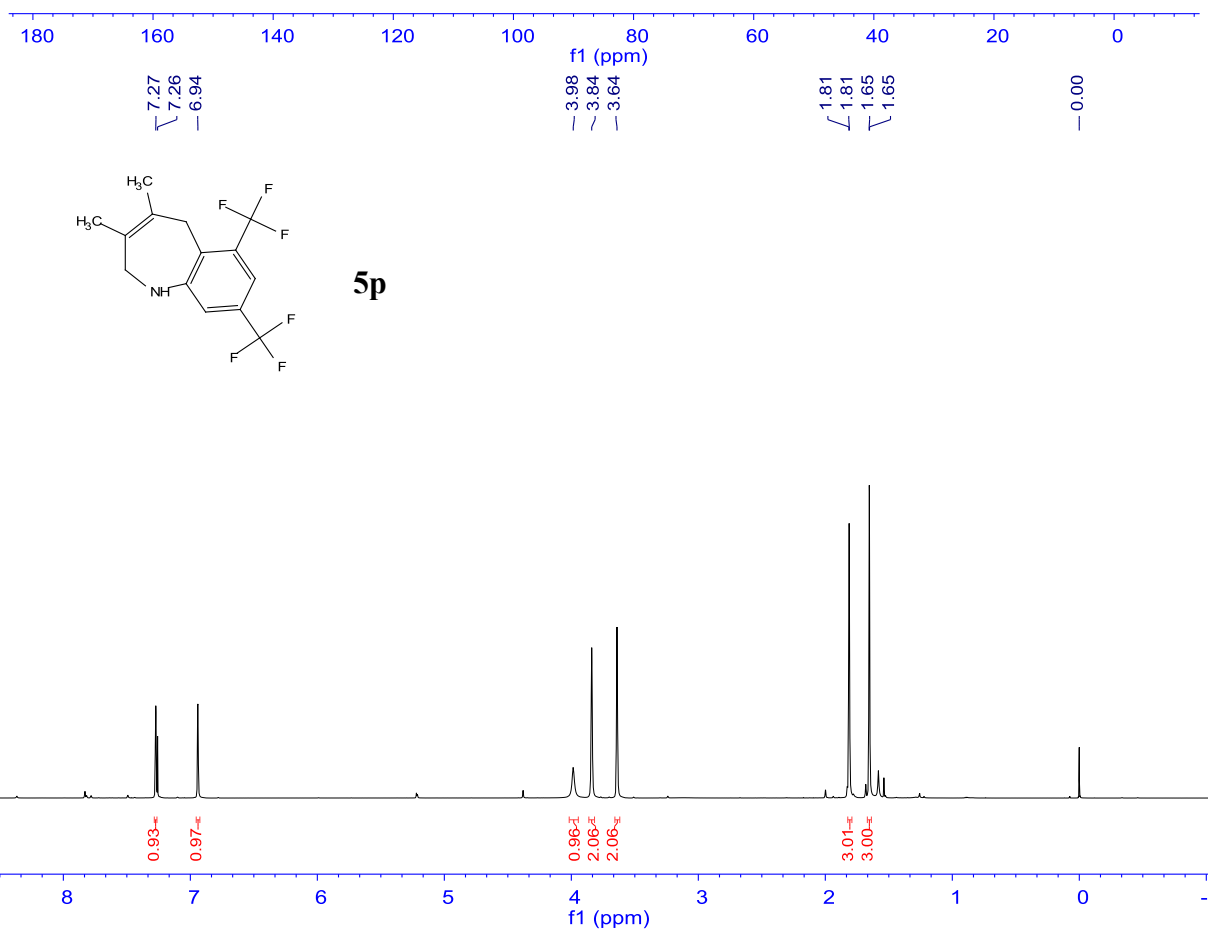

-63.19
H2C
O
NH
CH2
F
F
F
F
F
F
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

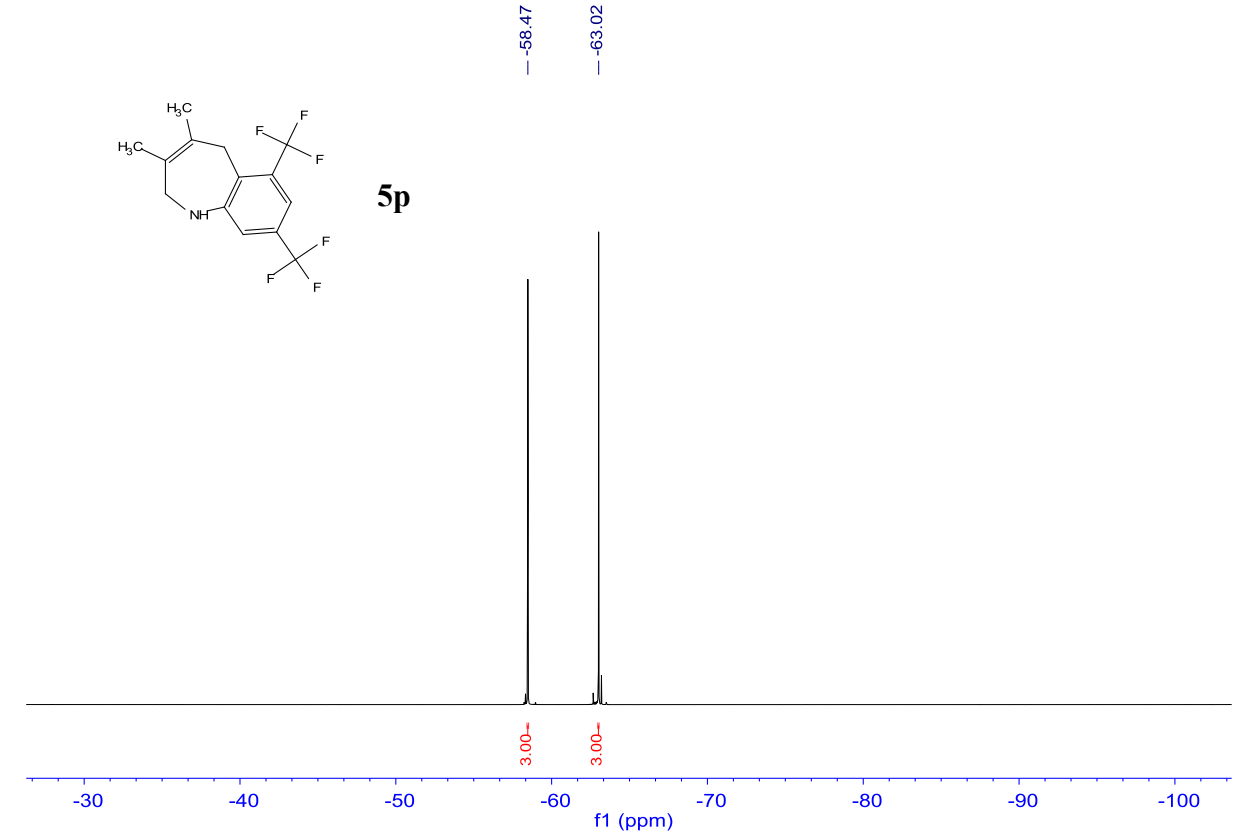
5o


158.82
148.63
142.85
133.21
132.91
132.65
132.39
132.13
131.12
127.37
124.79
122.62
117.98
115.00
113.16
112.12
112.09
110.54
110.52
110.48
110.45
110.42
77.42
77.16
76.91
69.01
48.00
H2C
O
NH
CH2
F
F
F
F
F
F
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

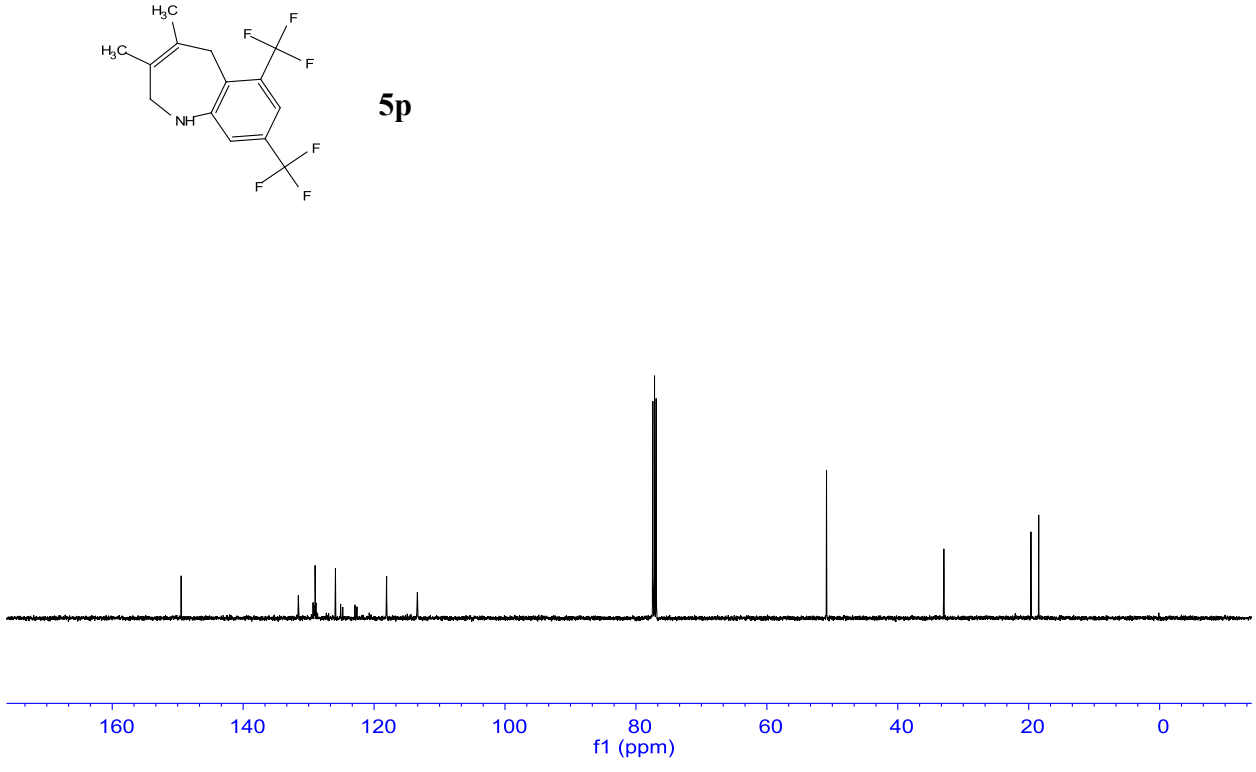
5o

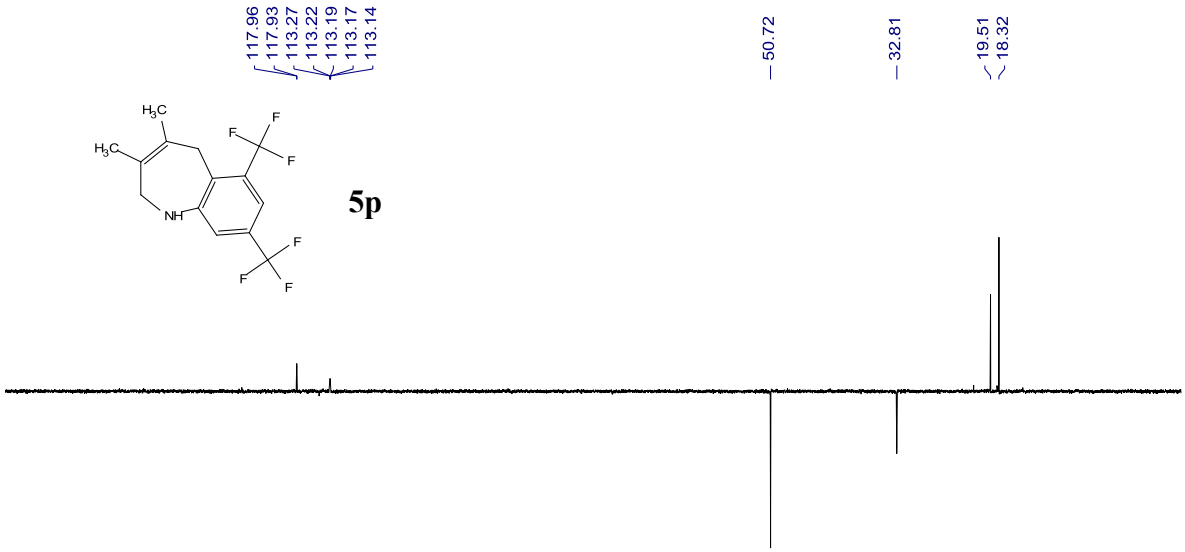

133.06
127.23
117.86
114.84
113.03
111.97
111.95
110.40
110.37
110.34
110.31
110.27
68.86
47.85
5o
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

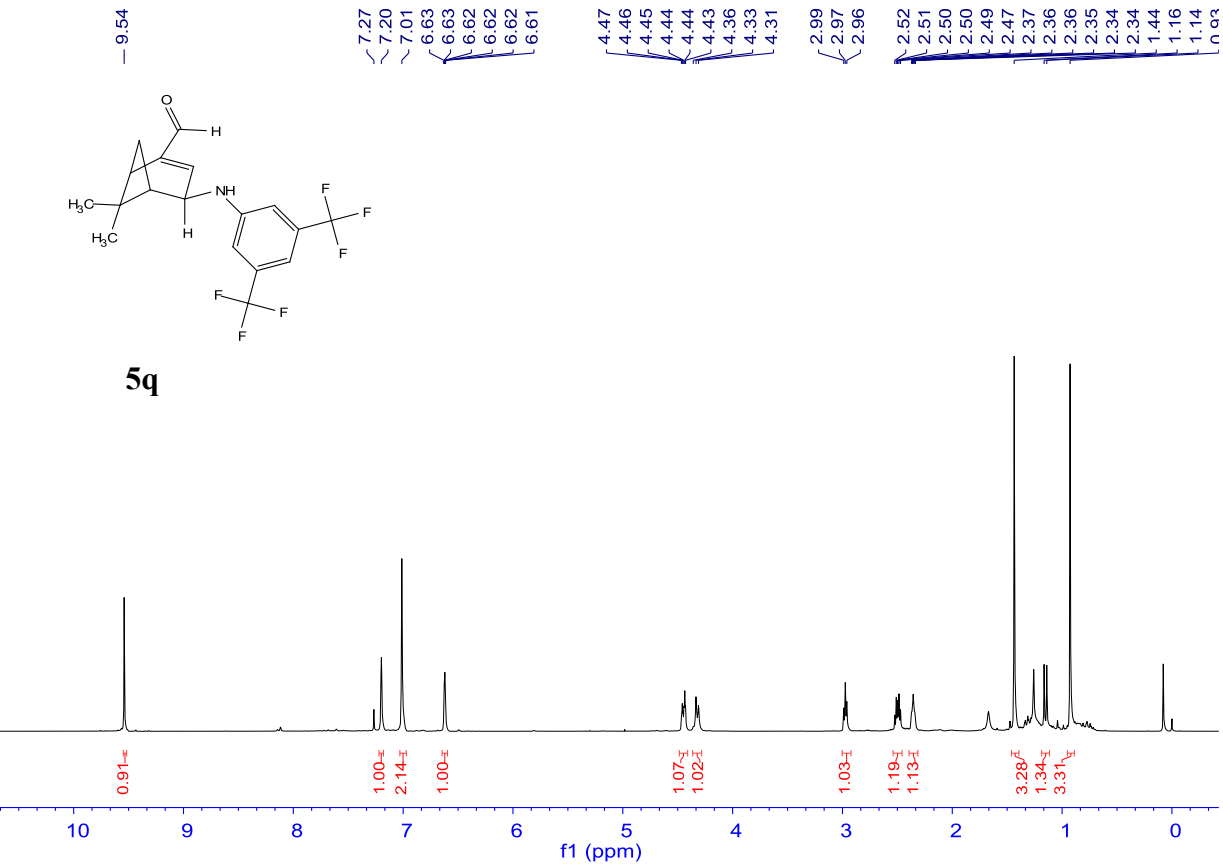

7.27
7.26
6.94
3.98
3.84
3.64
1.81
1.81
1.65
1.65
0.00
5p
0.93
0.97
0.96
2.06
2.06
3.01
3.00
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

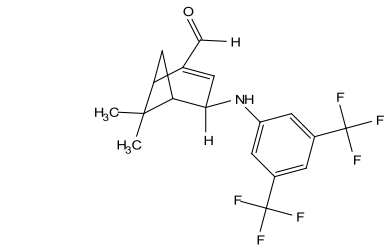

-58.47
-63.02
5p
3.00
3.00
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)


149.47
131.57
129.36
129.32
129.12
129.06
129.01
128.88
128.80
128.65
128.58
127.29
126.95
125.89
125.11
124.79
122.93
122.62
120.75
120.46
118.11
118.08
113.48
113.45
113.43
113.40
113.35
113.32
113.30
77.42
77.16
76.91
50.89
32.96
19.66
18.47


5p
160
140
120
100
80
60
40
20
0
f1 (ppm)

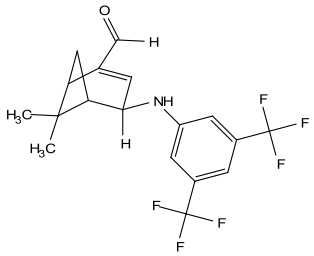

117.96
117.93
113.27
113.22
113.19
113.17
113.14
50.72
32.81
19.51
18.32
5p
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.54
7.27
7.20
7.01
6.63
6.63
6.62
6.62
6.62
6.61
4.47
4.46
4.45
4.44
4.44
4.43
4.36
4.33
4.31
2.99
2.97
2.96
2.52
2.51
2.50
2.50
2.49
2.47
2.37
2.36
2.36
2.35
2.34
2.34
1.44
1.16
1.14
5q
0.91
1.00
2.14
1.00
1.07
1.02
1.03
1.19
1.13
3.28
1.34
3.31
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)



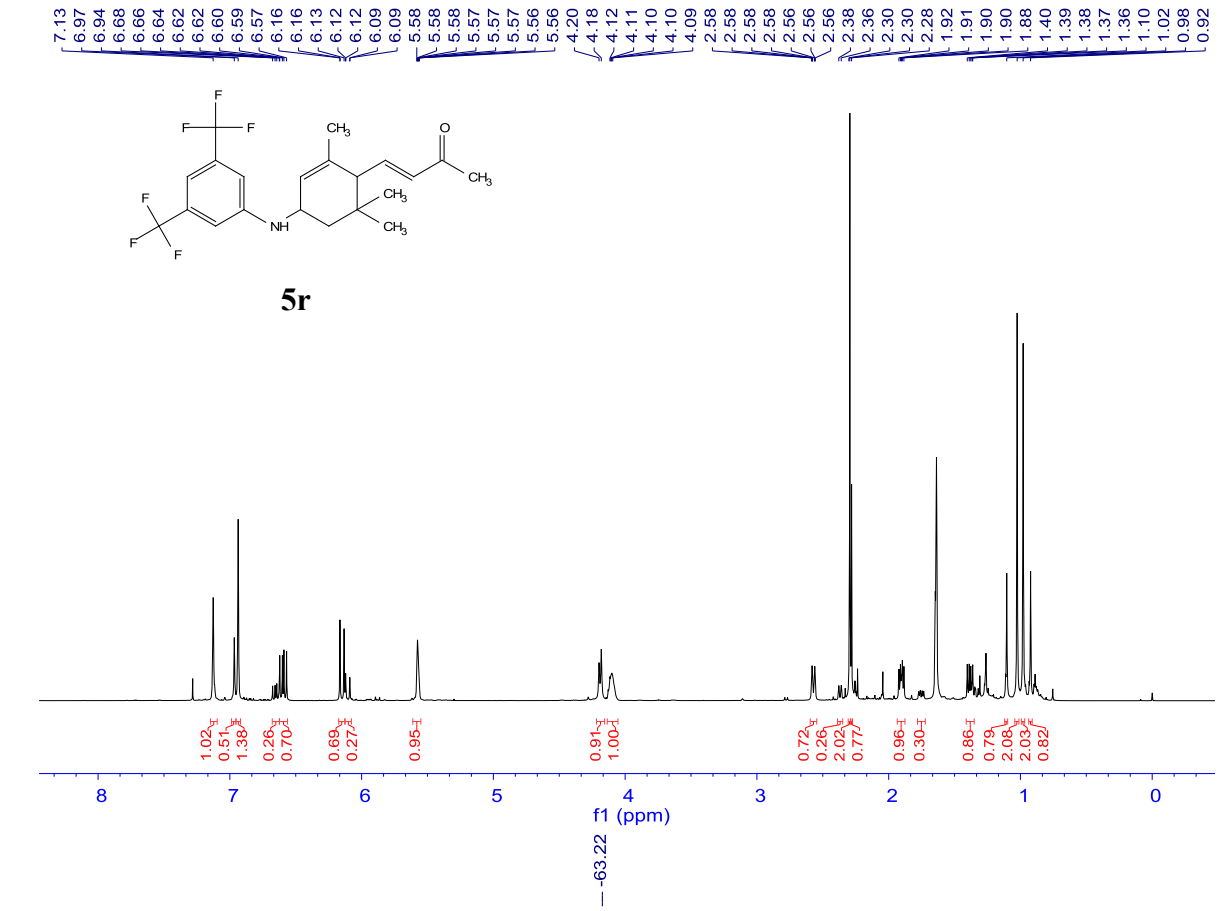
5q

-63.17
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
f1 (ppm)

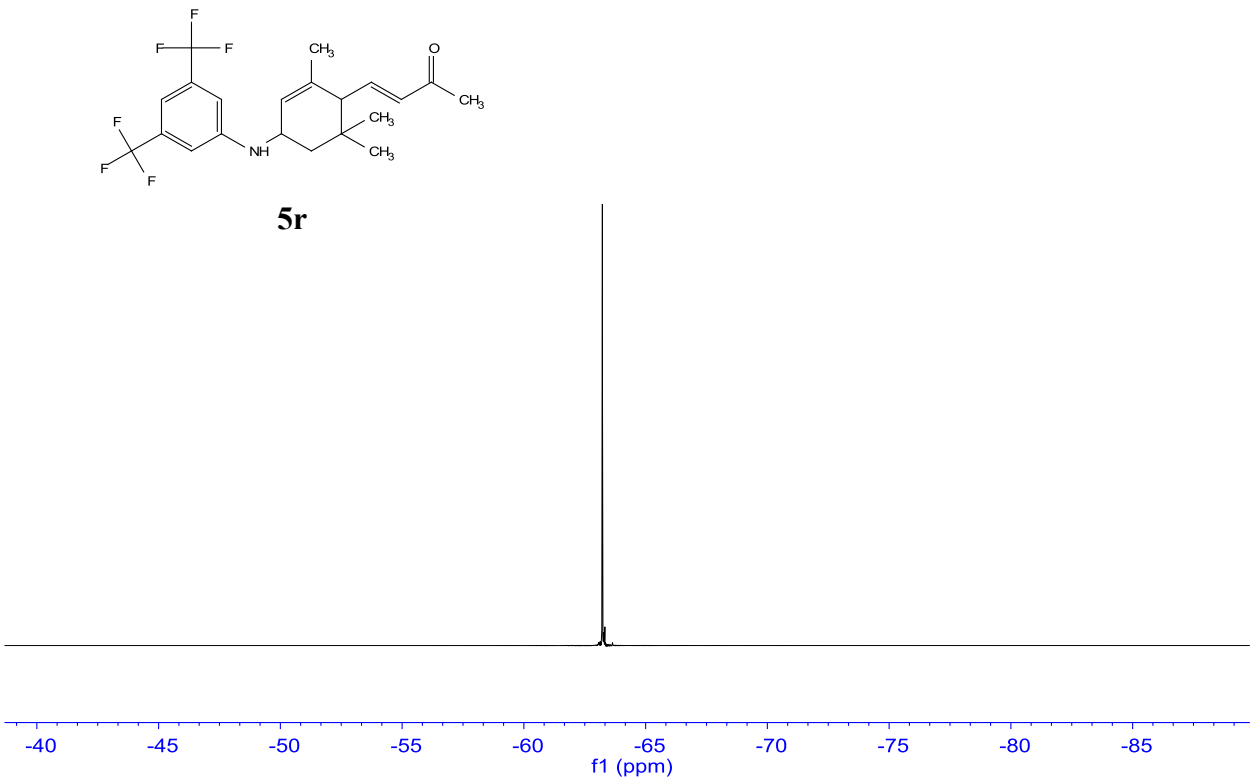


5q

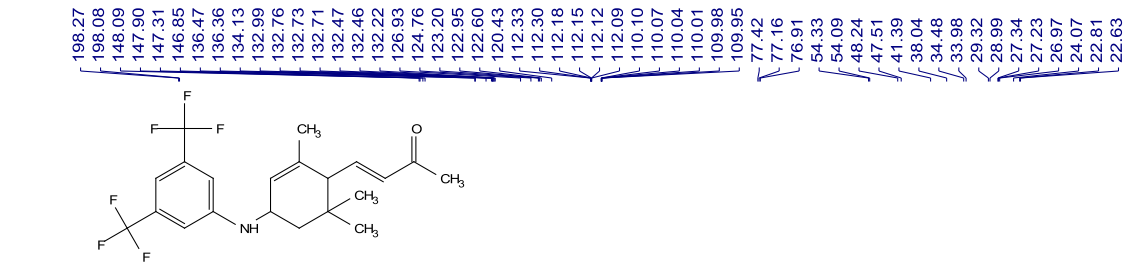
191.38
152.52
147.24
142.43
133.37
133.05
132.72
132.40
127.63
124.92
122.21
119.42
112.41
112.38
111.12
111.08
111.04
111.00
77.48
77.16
76.84
52.89
44.93
44.52
38.89
28.85
26.03
20.75
40
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.13 6.97 6.94 6.68 6.66 6.64 6.62 6.62 6.60 6.59 6.57 6.16 6.16 6.13 6.12 6.12 6.09 6.09 5.58 5.58 5.58 5.57 5.57 5.57 5.56 5.56 4.20 4.18 4.12 4.11 4.10 4.10 4.09 2.58 2.58 2.58 2.58 2.56 2.56 2.56 2.38 2.36 2.30 2.30 2.28 1.92 1.91 1.90 1.90 1.88 1.40 1.39 1.38 1.37 1.36 1.10 1.02 0.98 0.92
F
F
F
CH3
O
CH3
CH3
F
F
F
NH
CH3
1.02 0.51 1.38 0.26 0.70 0.69 0.27 0.95 0.91 1.00 0.72 0.26 2.02 0.77 0.96 0.30 0.86 0.79 2.08 2.03 0.82
8 7 6 5 4 3 2 1 0
f1 (ppm)

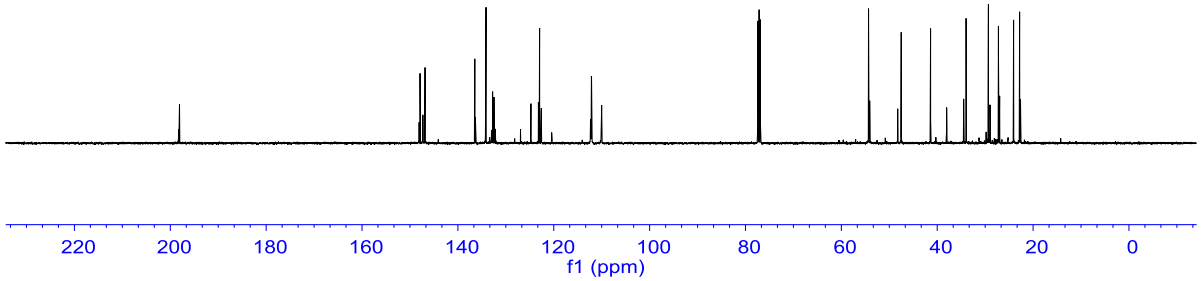
5r


-63.22
F
F
F
CH3
O
CH3
CH3
F
F
F
NH
CH3
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85
f1 (ppm)

5r

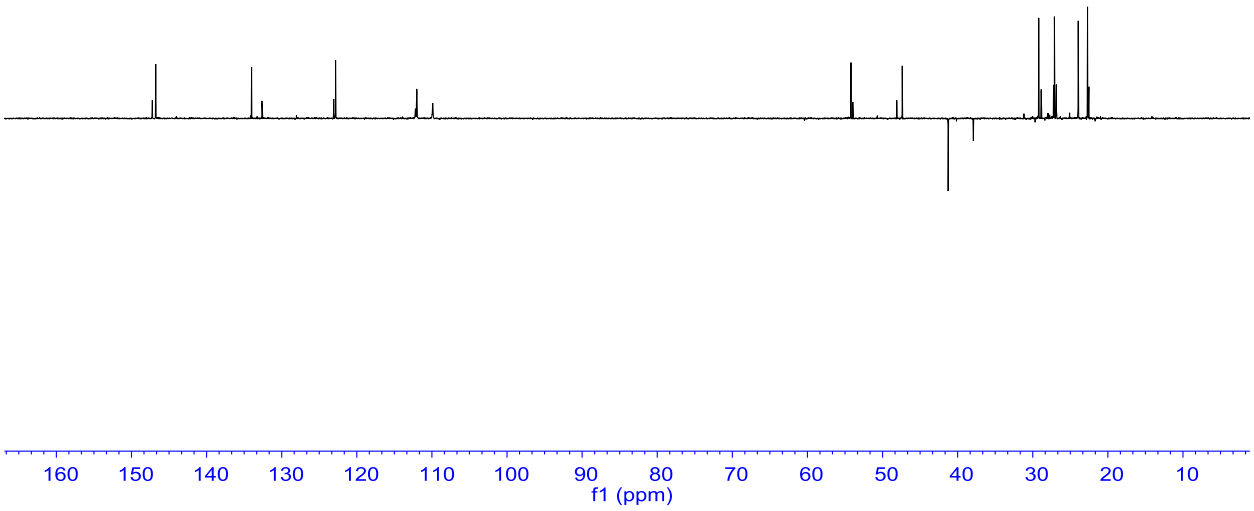

198.27
198.08
148.09
147.90
147.31
146.85
136.47
136.36
134.13
132.99
132.76
132.73
132.71
132.47
132.46
132.22
126.93
124.76
123.20
122.95
122.60
120.43
112.33
112.30
112.18
112.15
112.12
112.09
110.10
110.07
110.04
110.01
109.98
109.95
77.42
77.16
76.91
54.33
54.09
48.24
47.51
41.39
38.04
34.48
33.98
29.32
28.99
27.34
27.23
26.97
24.07
22.81
22.63
F
F
F
CH3
O
CH3
CH3
F
F
F
NH
CH3

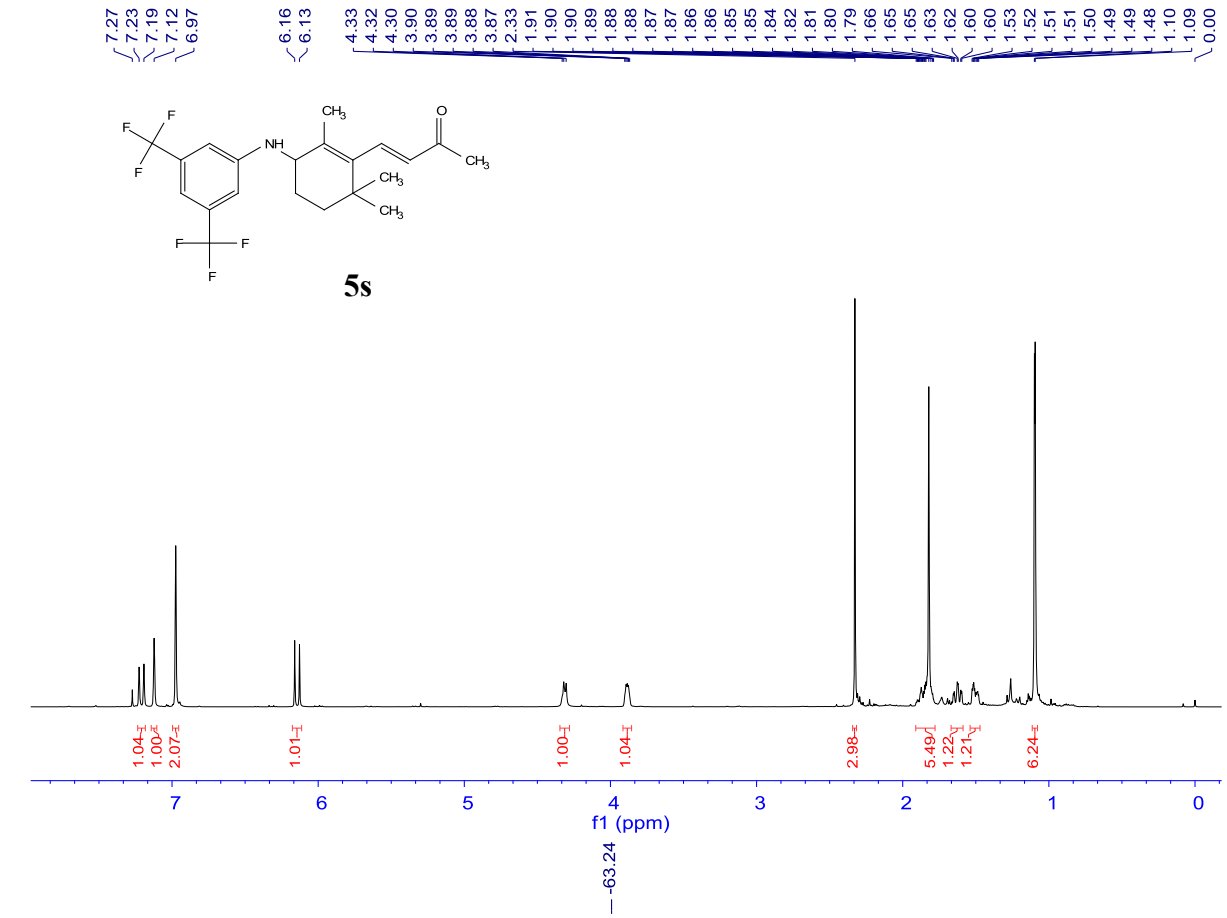
5r


220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

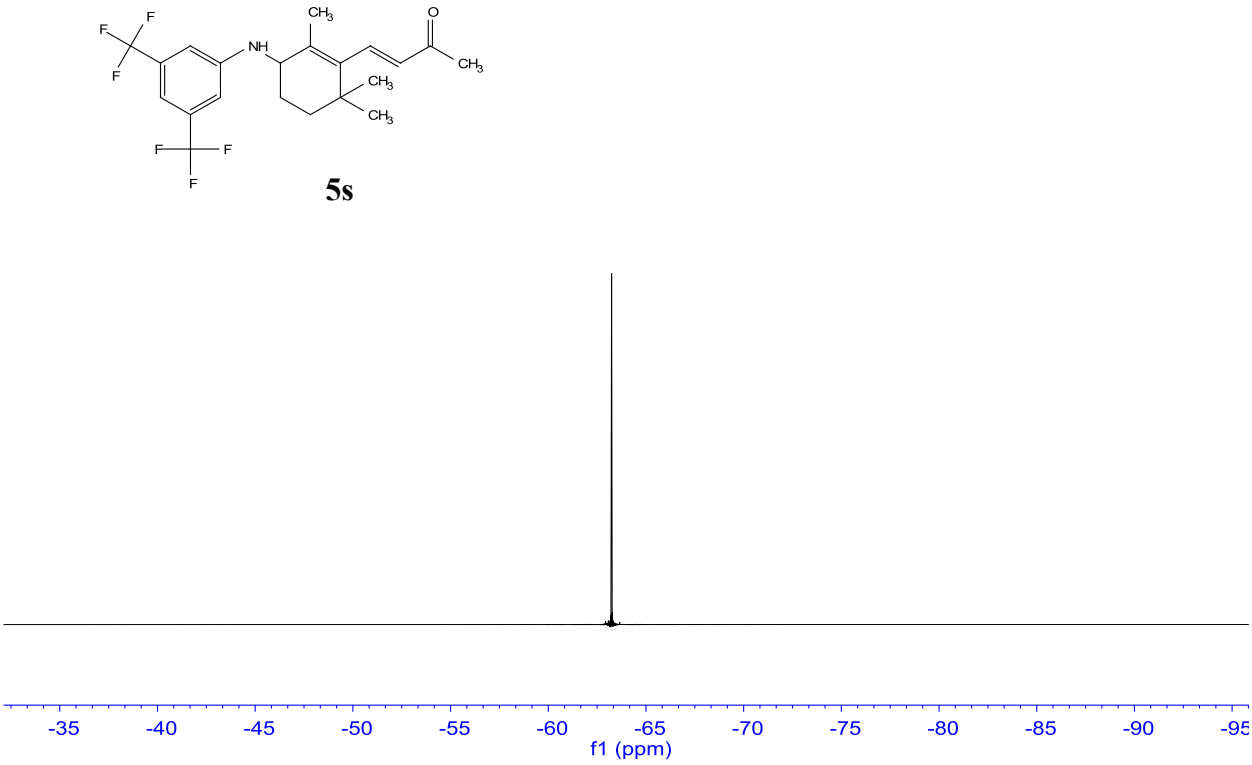

147.23
146.77
134.01
132.64
123.08
122.82
112.20
112.18
112.03
111.99
109.97
109.94
109.91
109.88
109.85
109.82
54.20
53.96
48.11
47.38
41.27
37.90
29.20
28.88
27.23
27.12
26.85
23.95
22.70
22.52
F
F
F
CH3
O
CH3
CH3
F
F
F
NH
CH3

5r

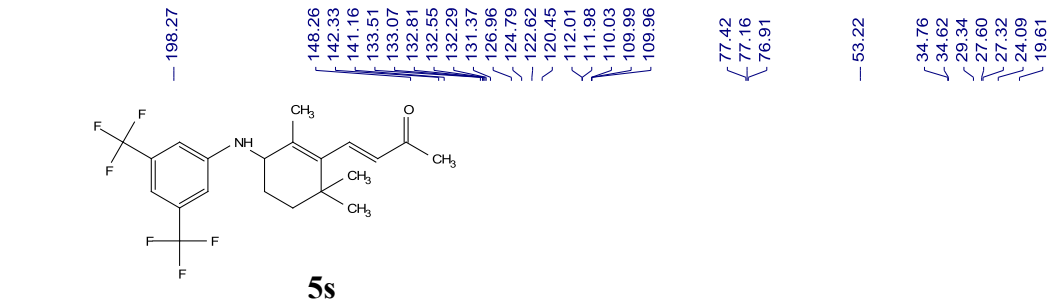

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.27
7.23
7.19
7.12
6.97
6.16
6.13
4.33
4.32
4.30
3.90
3.89
3.89
3.88
3.87
2.33
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.85
1.84
1.82
1.81
1.80
1.79
1.66
1.65
1.65
1.63
1.62
1.60
1.60
1.53
1.52
1.51
1.51
1.50
1.49
1.49
1.48
1.10
1.09
0.00
F
F
F
NH
CH3
O
CH3
CH3
CH3
F
F
F
1.04
1.00
2.07
1.01
1.00
1.04
2.98
5.49
1.22
1.21
6.24
7
6
5
4
3
2
1
0
f1 (ppm)

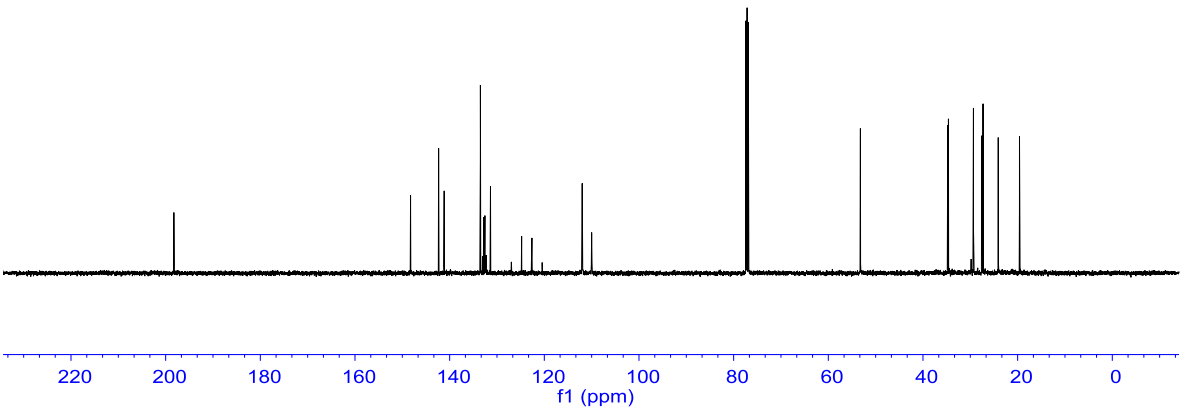
5s

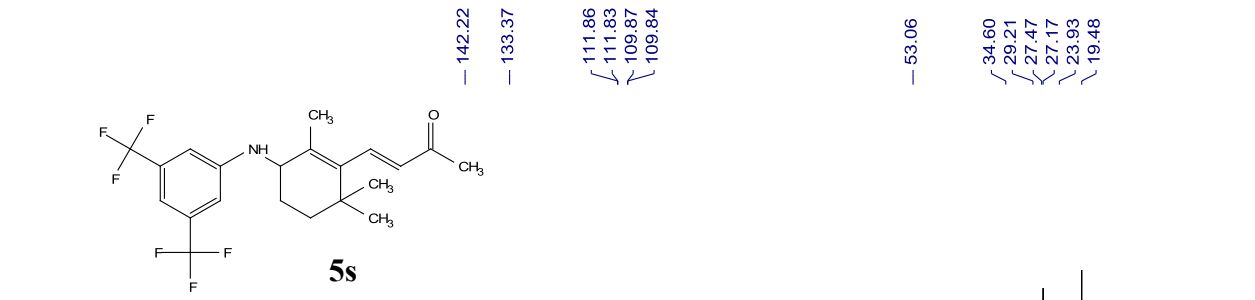

-63.24
F
F
F
NH
CH3
O
CH3
CH3
CH3
F
F
F
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

5s

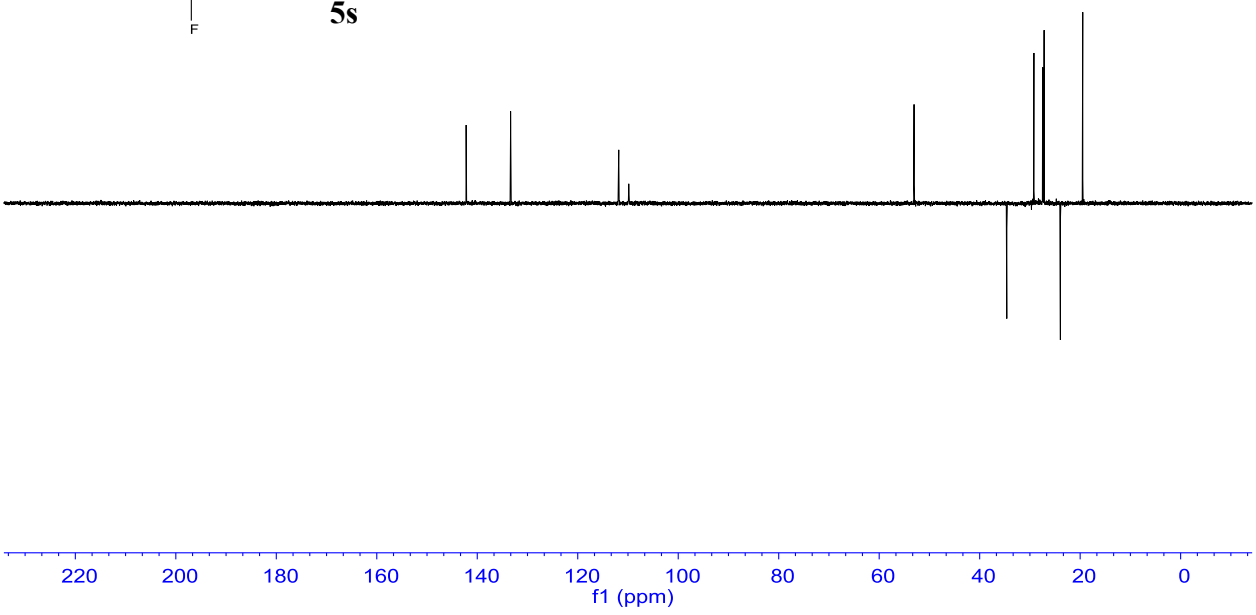

198.27
148.26
142.33
141.16
133.51
133.07
132.81
132.55
132.29
131.37
126.96
124.79
122.62
120.45
112.01
111.98
110.03
109.99
109.96
77.42
77.16
76.91
53.22
34.76
34.62
29.34
27.60
27.32
24.09
19.61
NH
O
CH3
CH3
CH3
CH3
F
F
F
F
F
F

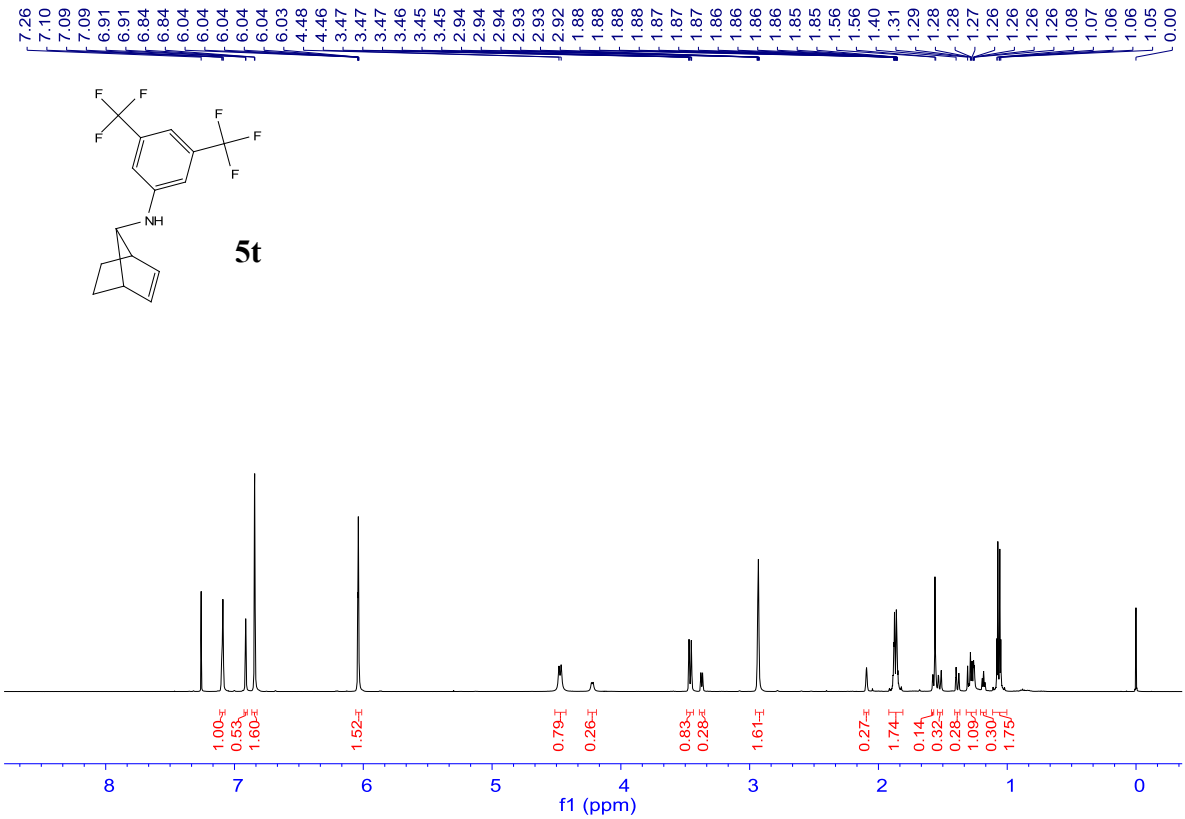
5s

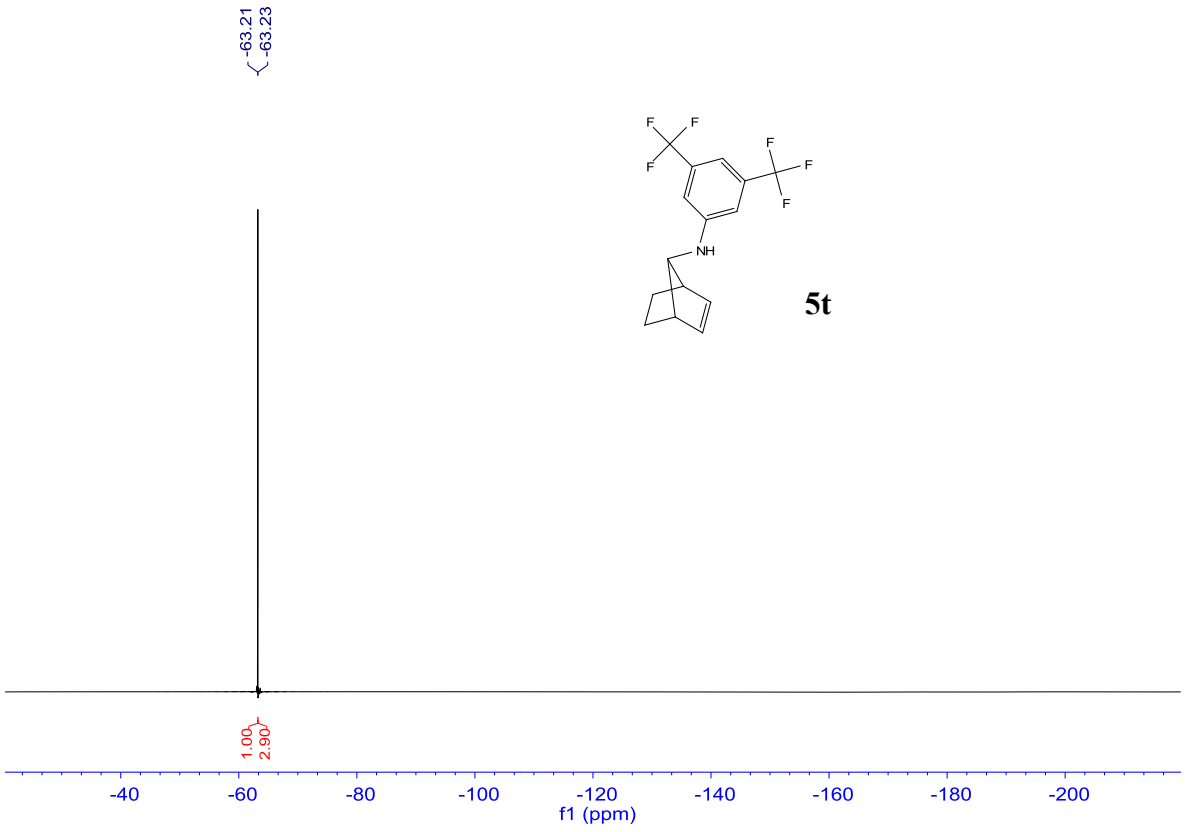

220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

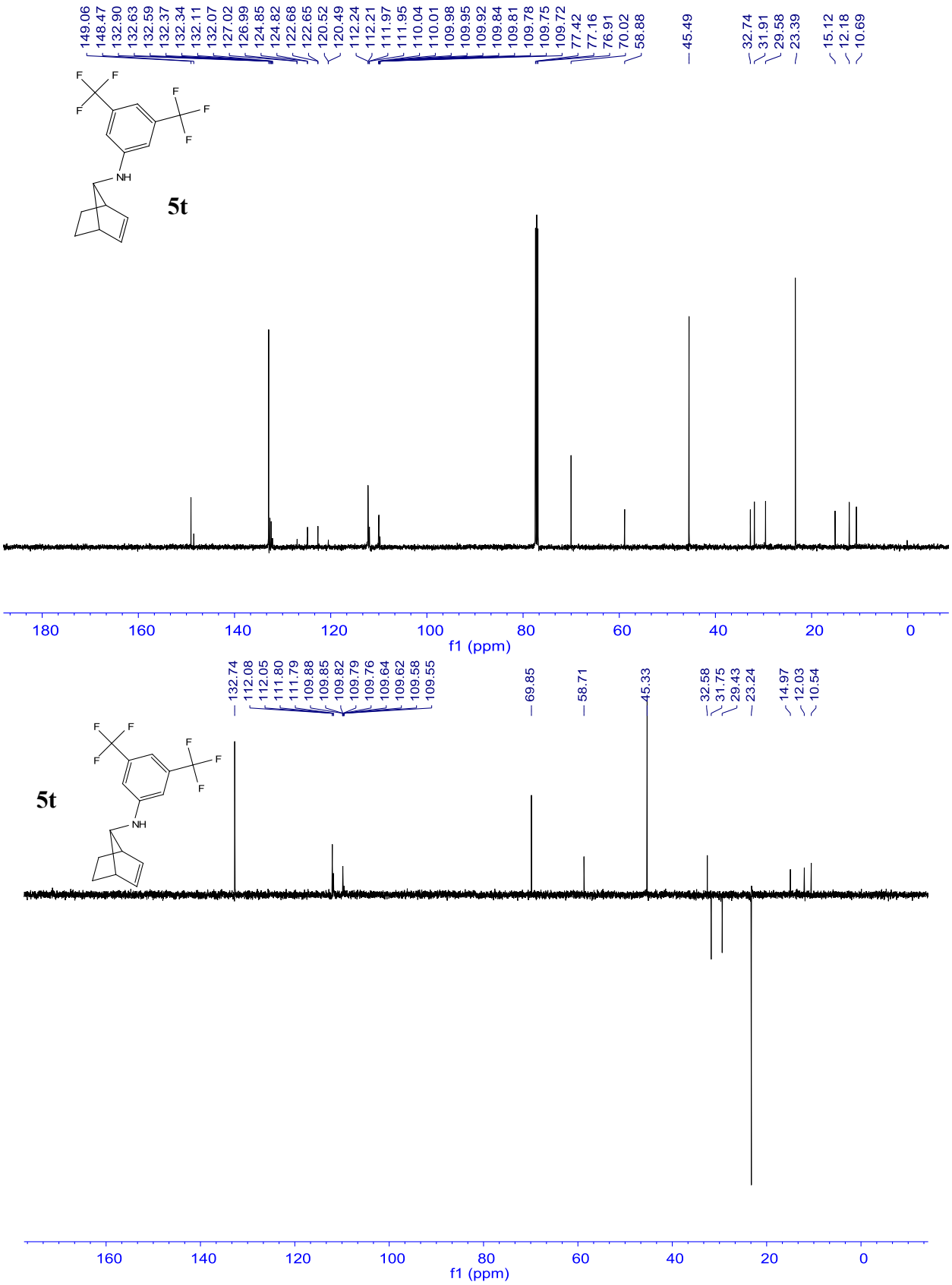

142.22
133.37
111.86
111.83
109.87
109.84
53.06
34.60
29.21
27.47
27.17
23.93
19.48
NH
O
CH3
CH3
CH3
CH3
F
F
F
F
F
F

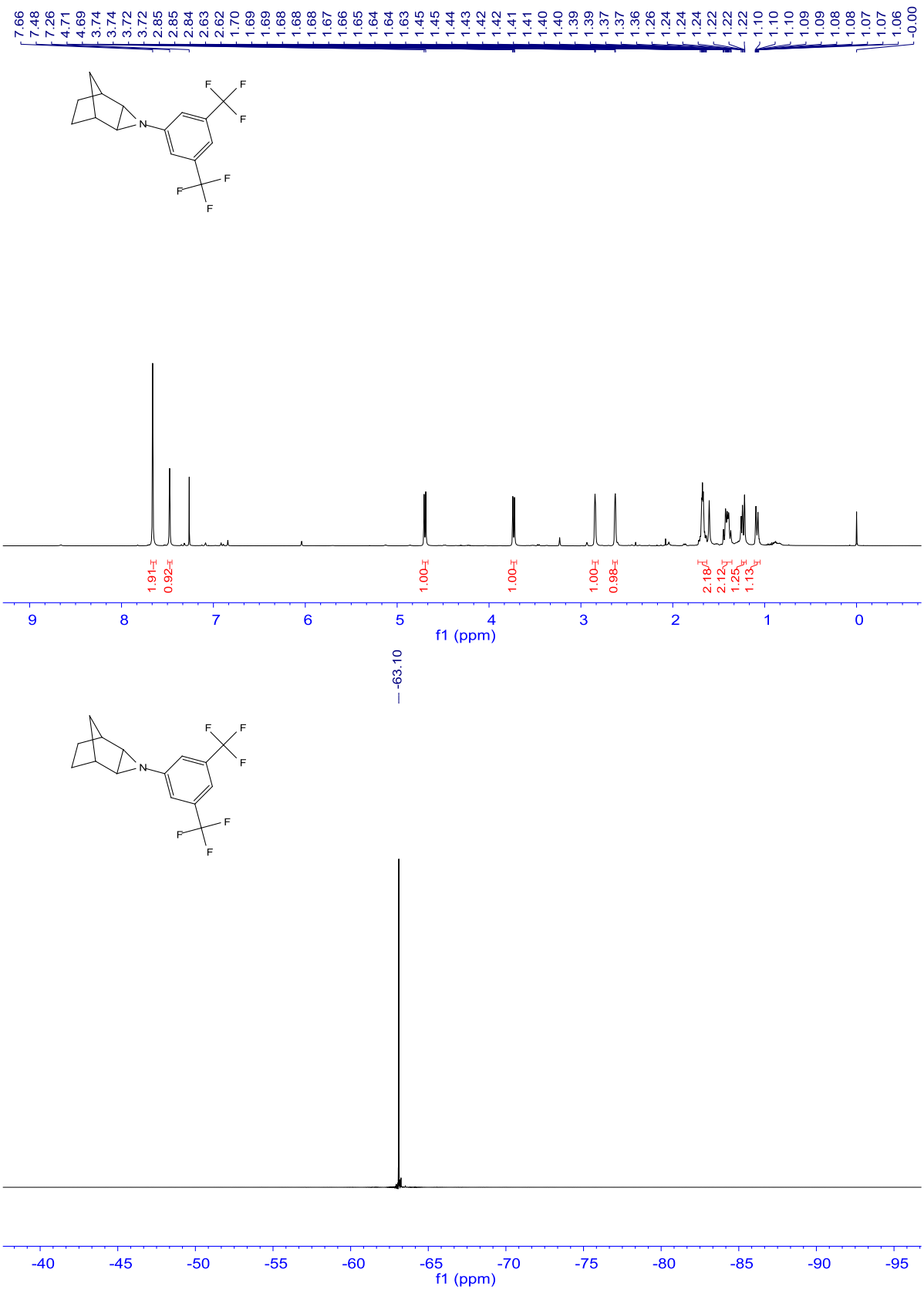
5s

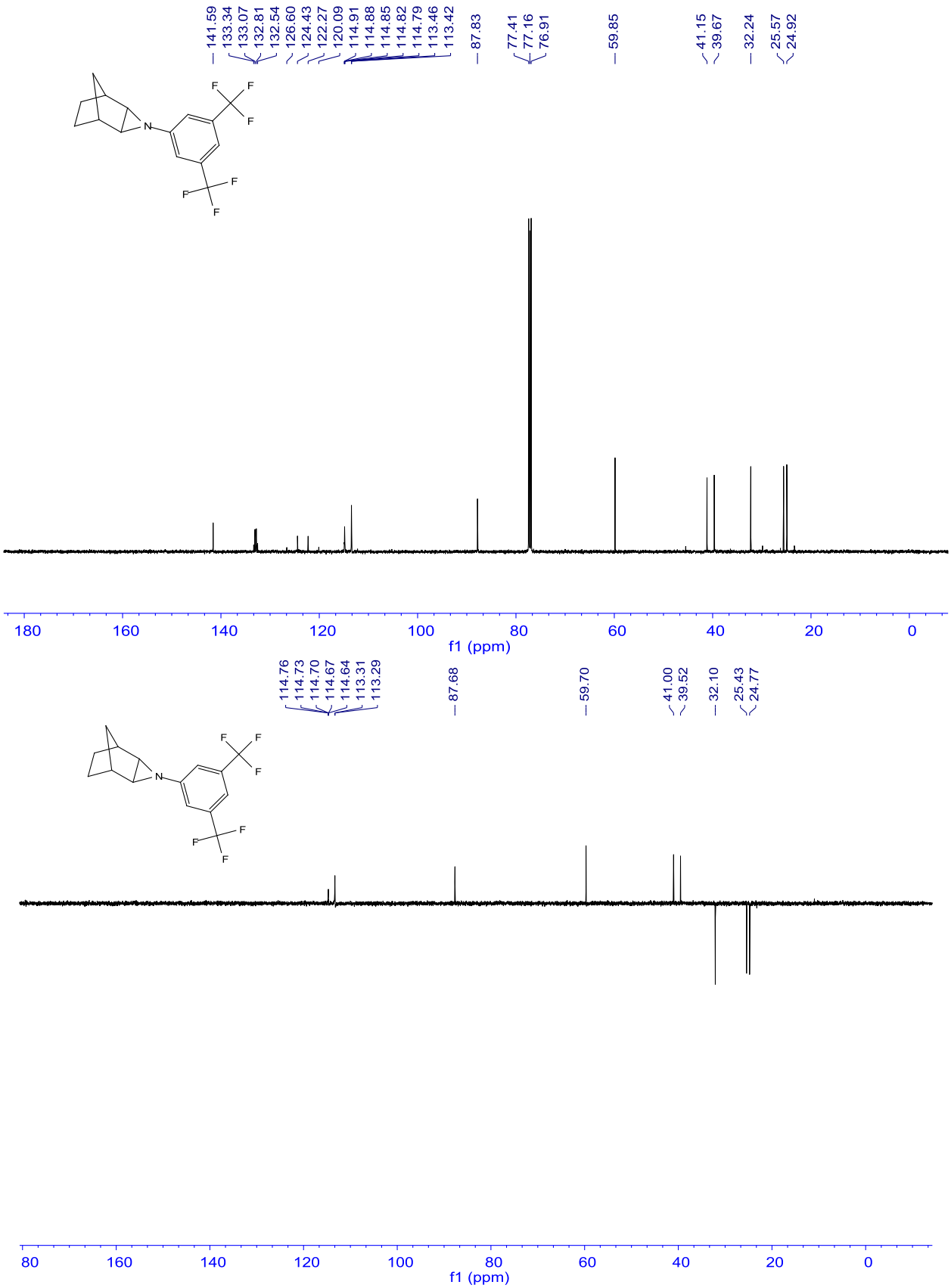

220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

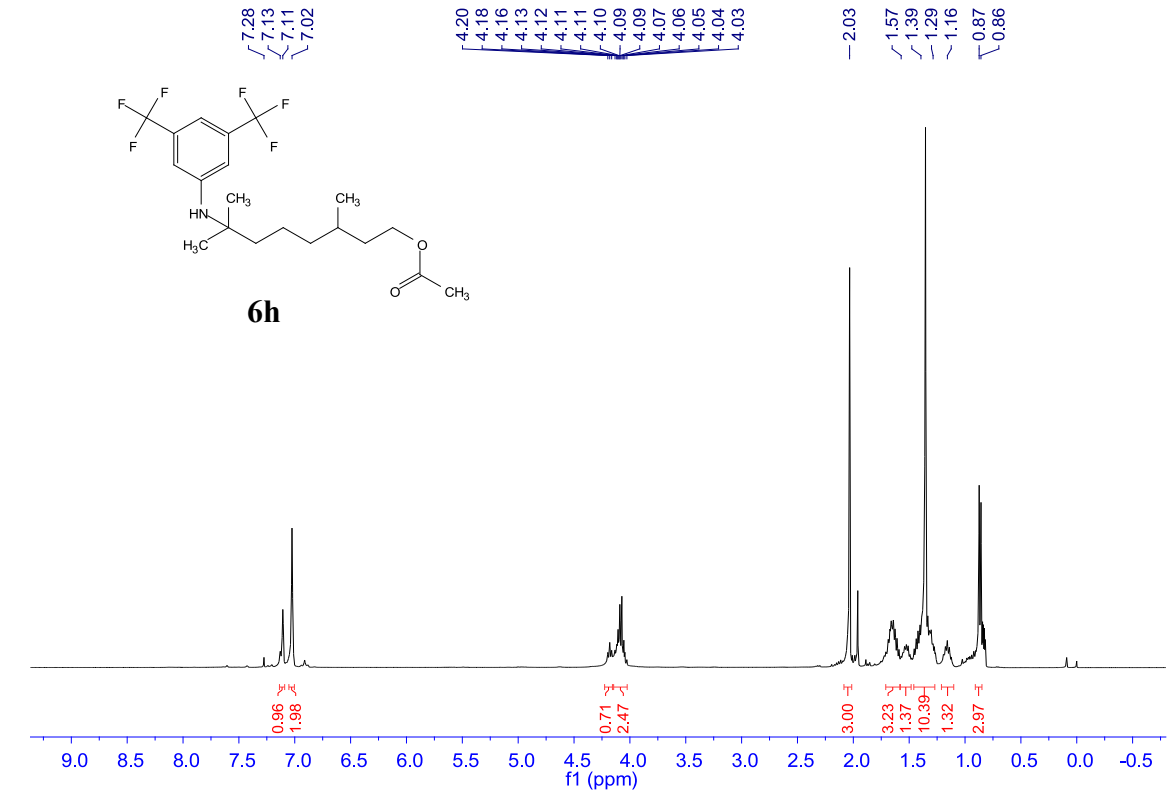

7.26 7.10 7.09 7.09 6.91 6.91 6.84 6.84 6.04 6.04 6.04 6.04 6.04 6.03 4.48 4.46 3.47 3.47 3.47 3.46 3.45 3.45 2.94 2.94 2.93 2.92 1.88 1.88 1.88 1.87 1.87 1.87 1.86 1.86 1.86 1.86 1.85 1.56 1.56 1.40 1.31 1.29 1.28 1.28 1.27 1.26 1.26 1.26 1.26 1.08 1.07 1.06 1.06 1.05 0.00
F F F F F F NH
5t
1.00 0.53 1.60 1.52 0.79 0.26 0.83 0.28 1.61 0.27 1.74 0.14 0.32 0.28 1.09 0.30 1.75
8 7 6 5 4 3 2 1 0
f1 (ppm)


-63.21 -63.23
F F F F F F NH
5t
1.00 2.90
-40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

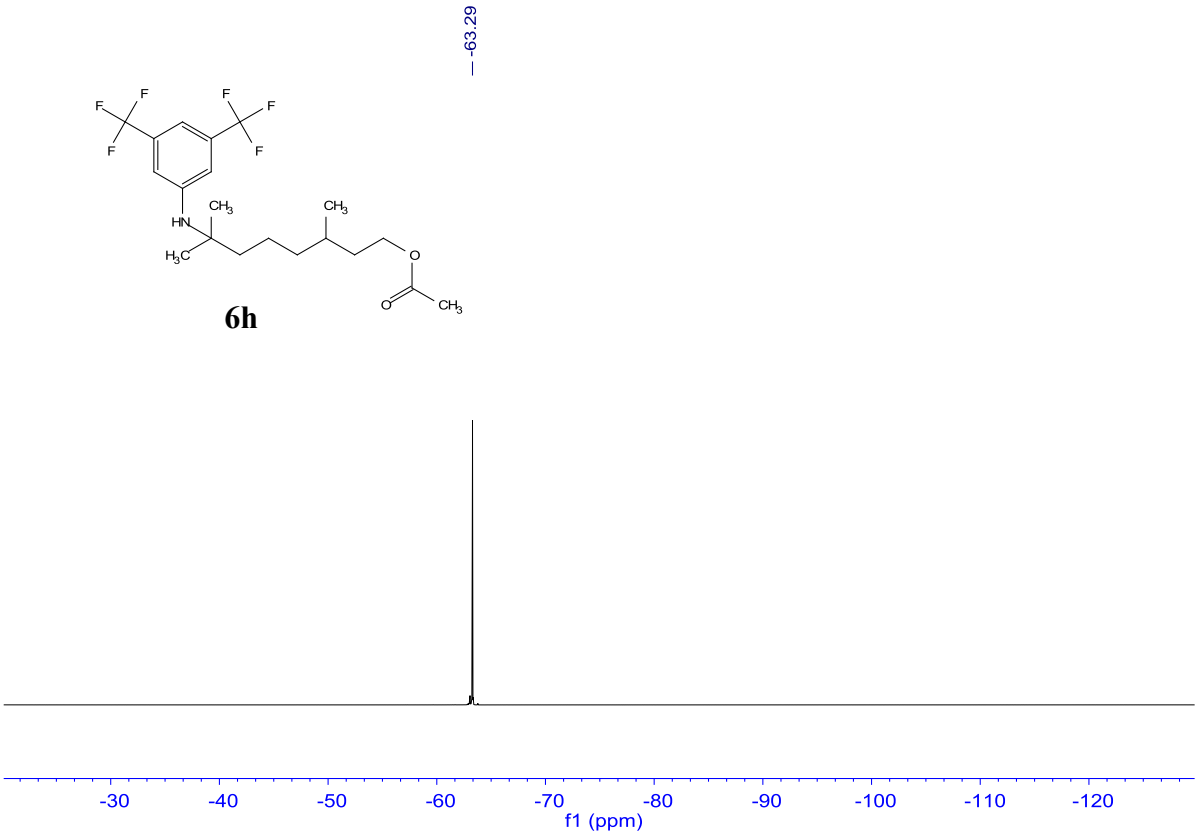

149.06
148.47
132.90
132.63
132.59
132.37
132.34
132.11
132.07
127.02
126.99
124.85
124.82
122.68
122.65
120.52
120.49
112.24
112.21
111.97
111.95
110.04
110.01
109.98
109.95
109.92
109.84
109.81
109.78
109.75
109.72
77.42
77.16
76.91
70.02
58.88
45.49
32.74
31.91
29.58
23.39
15.12
12.18
10.69
F
F
F
F
F
NH
5t
180
160
140
120
100
80
60
40
20
0
f1 (ppm)
132.74
112.08
112.05
111.80
111.79
109.88
109.85
109.82
109.79
109.76
109.64
109.62
109.58
109.55
69.85
58.71
45.33
32.58
31.75
29.43
23.24
14.97
12.03
10.54
5t
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.66 7.48 7.26 4.71 4.69 3.74 3.74 3.72 3.72 2.85 2.85 2.84 2.63 2.62 1.70 1.69 1.69 1.68 1.68 1.68 1.67 1.66 1.65 1.64 1.64 1.63 1.45 1.45 1.44 1.43 1.42 1.42 1.41 1.41 1.40 1.40 1.39 1.39 1.37 1.37 1.36 1.26 1.24 1.24 1.24 1.22 1.22 1.22 1.10 1.10 1.10 1.09 1.09 1.08 1.08 1.07 1.07 1.06 -0.00
F F F F F F N
1.91 0.92 1.00 1.00 1.00 0.98 2.18 2.12 1.25 1.13
9 8 7 6 5 4 3 2 1 0
f1 (ppm)
-63.10
F F F F F F N
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)

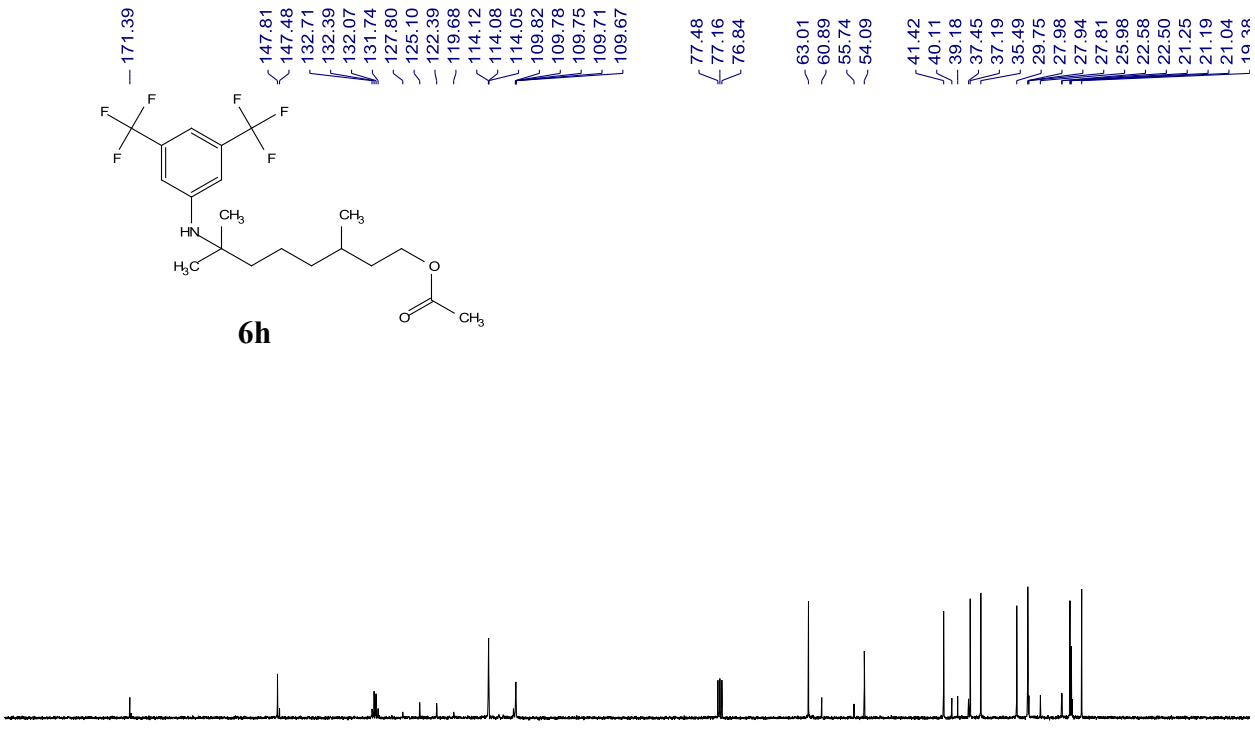

141.59
133.34
133.07
132.81
132.54
126.60
124.43
122.27
120.09
114.91
114.88
114.85
114.82
114.79
113.46
113.42
87.83
77.41
77.16
76.91
59.85
41.15
39.67
32.24
25.57
24.92
F
F
F
F
F
F
N
180
160
140
120
100
80
60
40
20
0
f1 (ppm)
114.76
114.73
114.70
114.67
114.64
113.31
113.29
87.68
59.70
41.00
39.52
32.10
25.43
24.77
F
F
F
F
F
F
N
80
160
140
120
100
80
60
40
20
0
f1 (ppm)

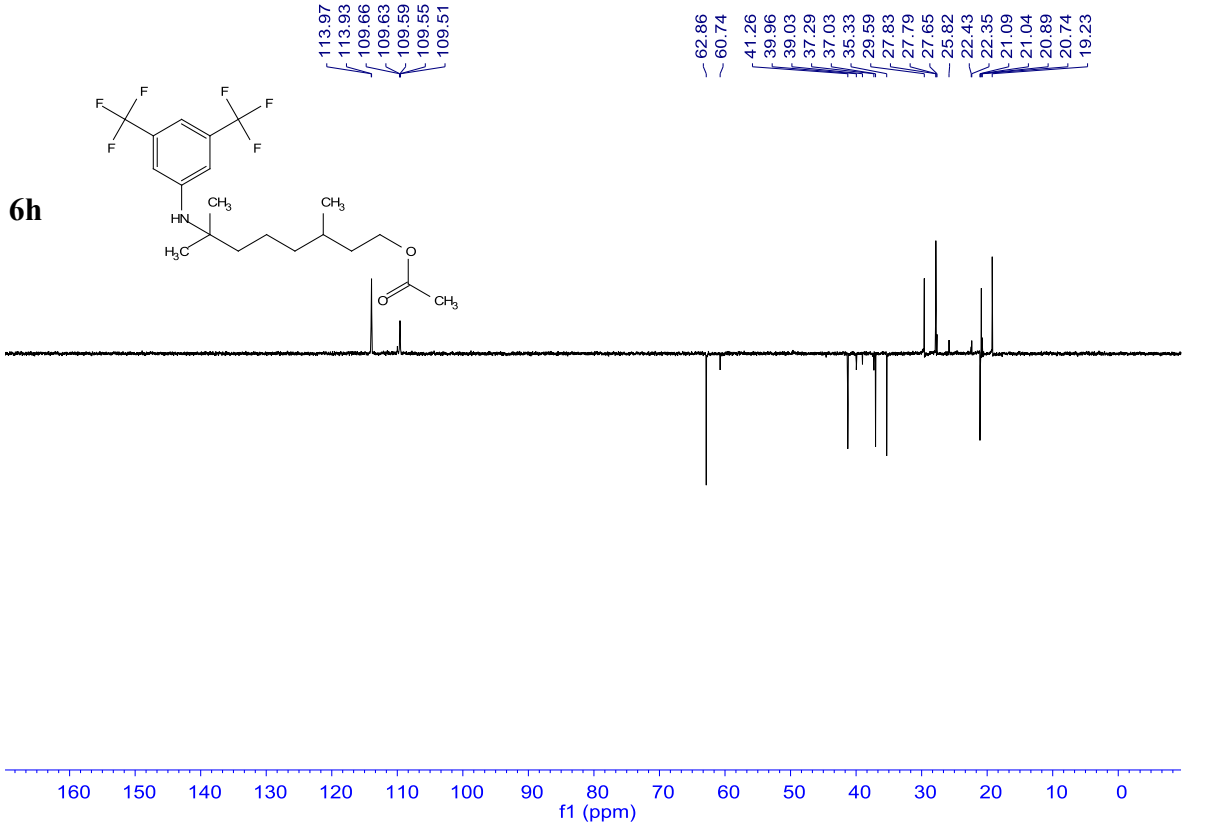

7.28
7.13
7.11
7.02
4.20
4.18
4.16
4.13
4.12
4.11
4.11
4.10
4.09
4.09
4.07
4.06
4.05
4.04
4.03
2.03
1.57
1.39
1.29
1.16
0.87
0.86
F
F
F
F
F
F
CH3
CH3
HN
H3C
O
O
CH3
0.96
1.98
0.71
2.47
3.00
3.23
1.37
10.39
1.32
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

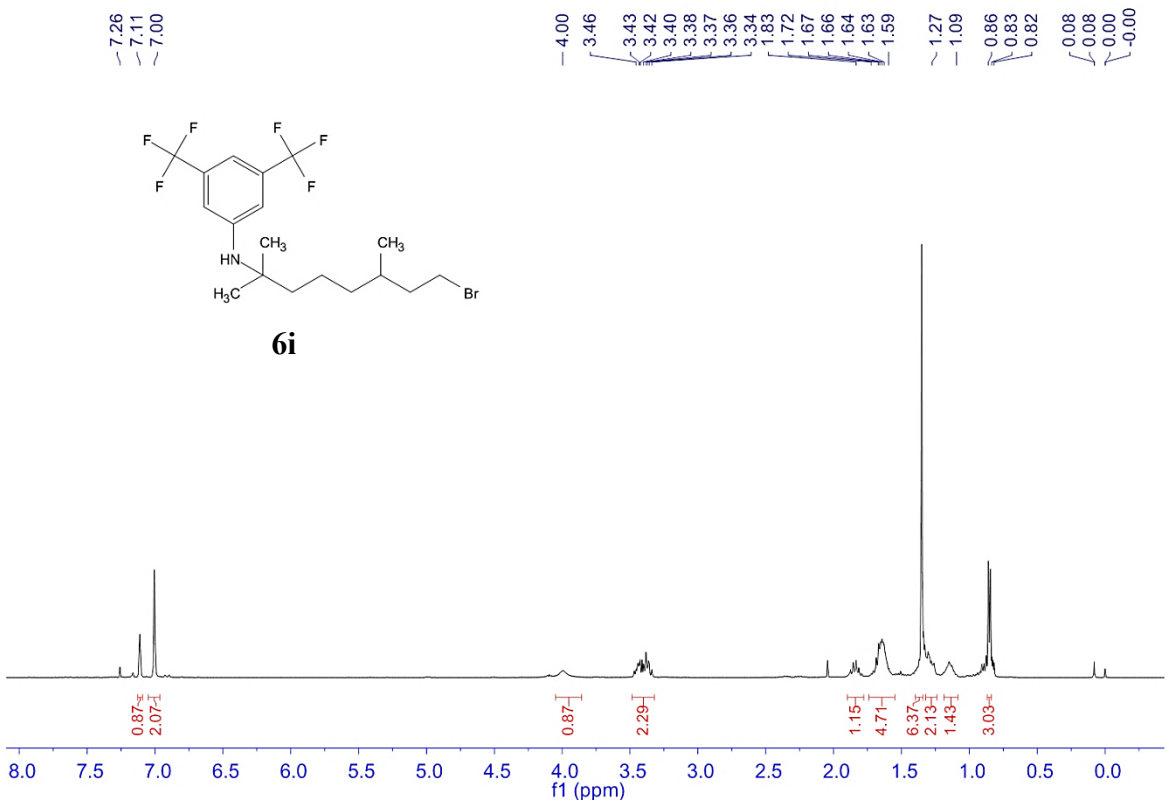
6h


-63.29
F
F
F
F
F
F
CH3
CH3
HN
H3C
O
O
CH3
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
f1 (ppm)

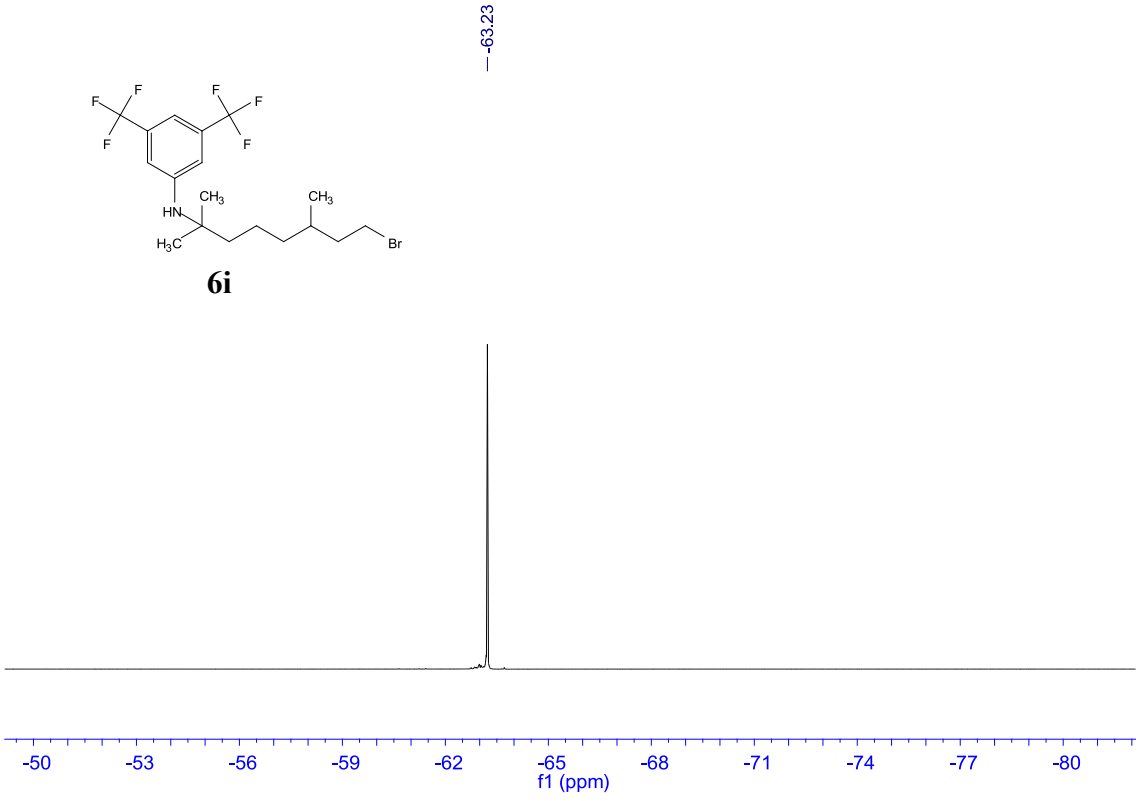
6h


171.39
147.81
147.48
132.71
132.39
132.07
131.74
127.80
125.10
122.39
119.68
114.12
114.08
114.05
109.82
109.78
109.75
109.71
109.67
77.48
77.16
76.84
63.01
60.89
55.74
54.09
41.42
40.11
39.18
37.45
37.19
35.49
29.75
27.98
27.94
27.81
25.98
22.58
22.50
21.25
21.19
21.04
19.38
F
F
F
F
F
F
HN
CH3
CH3
H3C
O
O
CH3
6h
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

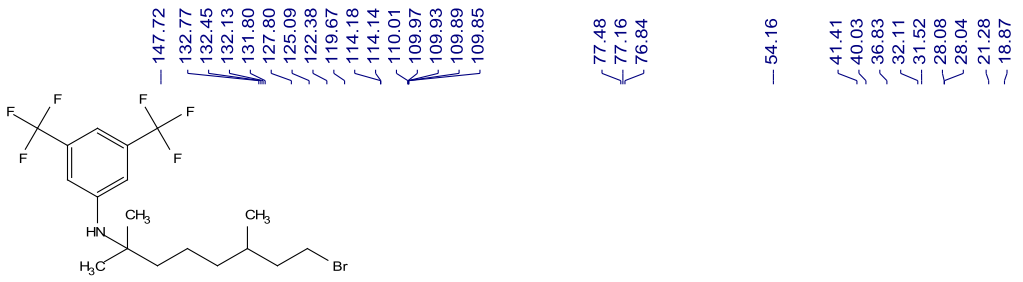

113.97
113.93
109.66
109.63
109.59
109.55
109.51
62.86
60.74
41.26
39.96
39.03
37.29
37.03
35.33
29.59
27.83
27.79
27.65
25.82
22.43
22.35
21.09
21.04
20.89
20.74
19.23
6h
F
F
F
F
F
F
HN
CH3
CH3
H3C
O
O
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
7.11
7.00
4.00
3.46
3.43
3.42
3.40
3.38
3.37
3.36
3.34
1.83
1.72
1.67
1.66
1.64
1.63
1.59
1.27
1.09
0.86
0.83
0.82
0.08
0.08
0.00
-0.00
F
F
F
F
F
F
HN
CH3
CH3
H3C
Br
0.87
2.07
0.87
2.29
1.15
4.71
6.37
2.13
1.43
3.03
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)

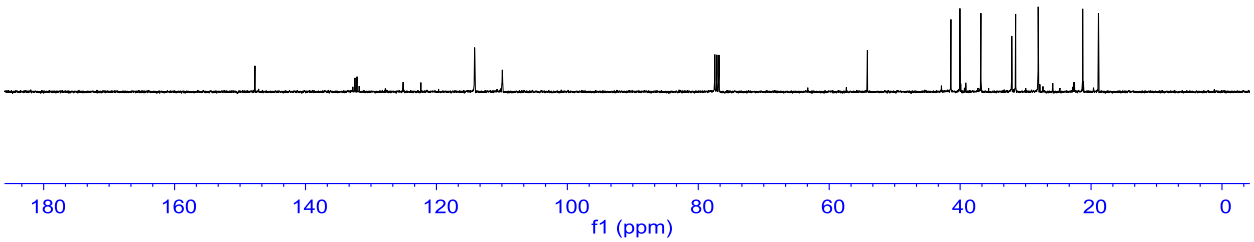
6i

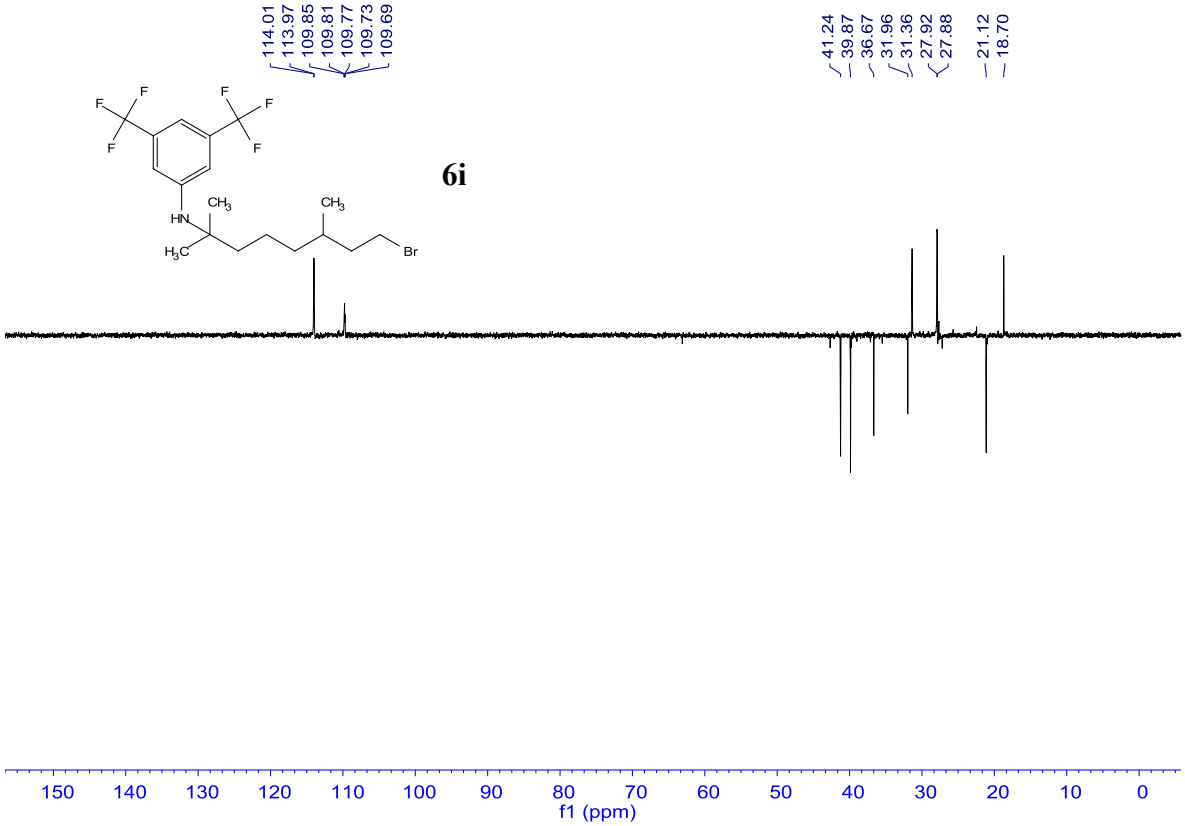

-63.23
F
F
F
F
F
F
HN
CH3
CH3
H3C
Br
-50
-53
-56
-59
-62
-65
-68
-71
-74
-77
-80
f1 (ppm)

6i

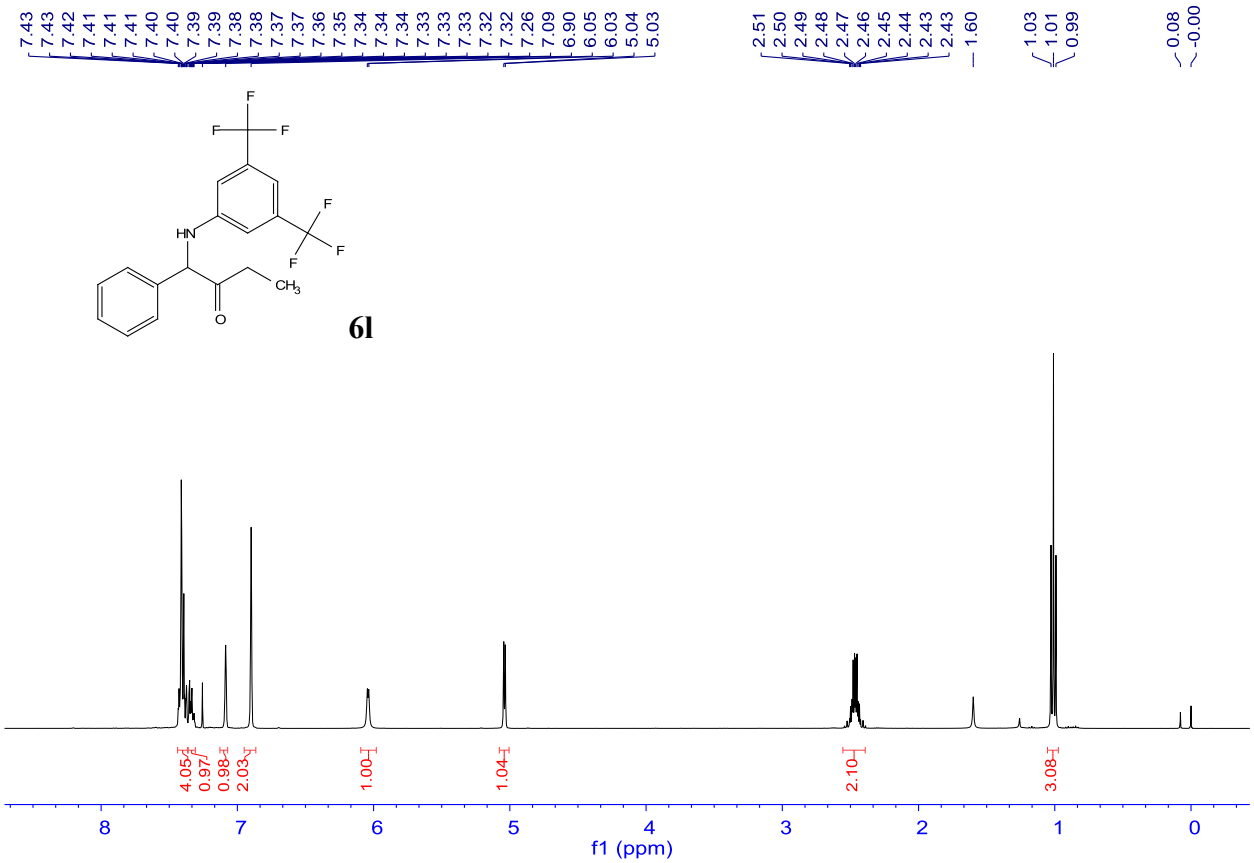

147.72
132.77
132.45
132.13
131.80
127.80
125.09
122.38
119.67
114.18
114.14
110.01
109.97
109.93
109.89
109.85
77.48
77.16
76.84
54.16
41.41
40.03
36.83
32.11
31.52
28.08
28.04
21.28
18.87
F
F
F
F
F
F
HN
CH3
CH3
H3C
Br

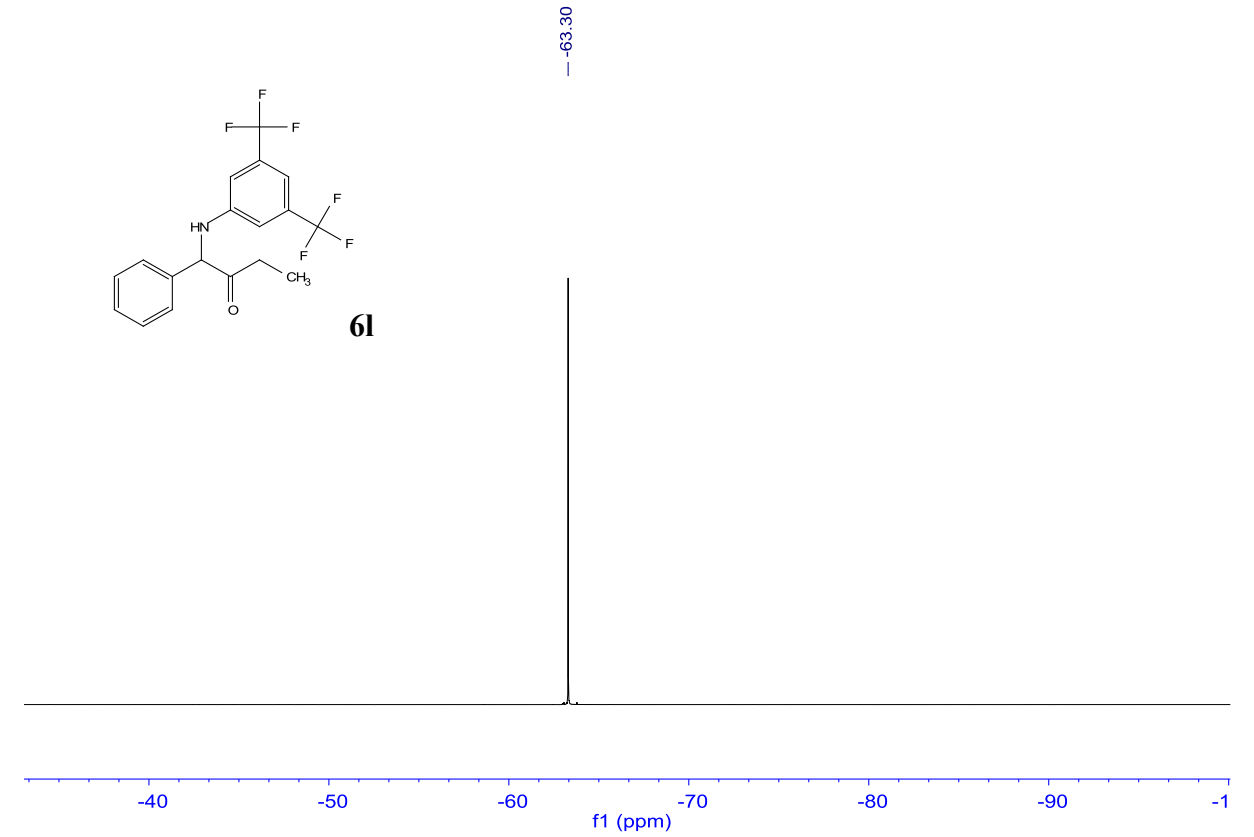
6i

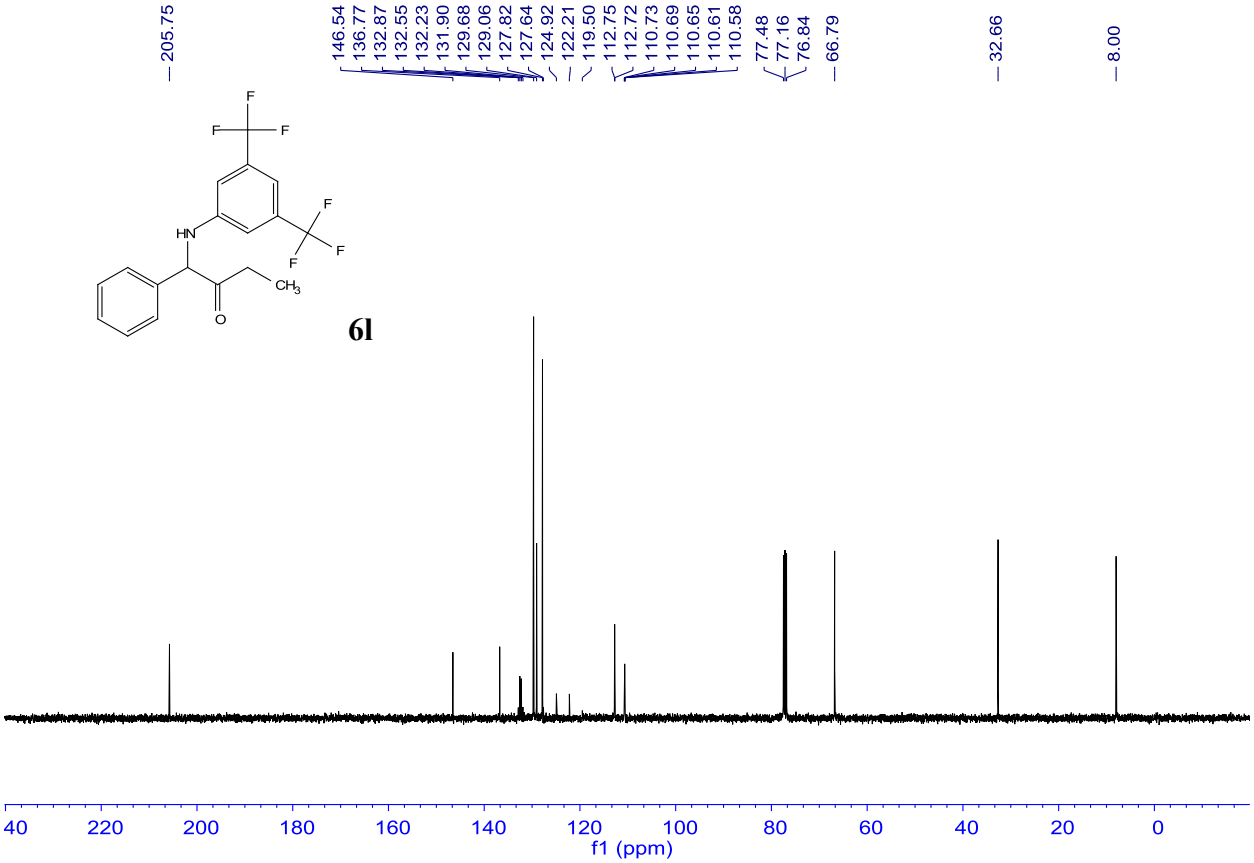

180
160
140
120
100
80
60
40
20
0
f1 (ppm)


114.01
113.97
109.85
109.81
109.77
109.73
109.69
41.24
39.87
36.67
31.96
31.36
27.92
27.88
21.12
18.70
F
F
F
F
F
F
HN
CH3
CH3
H3C
Br
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

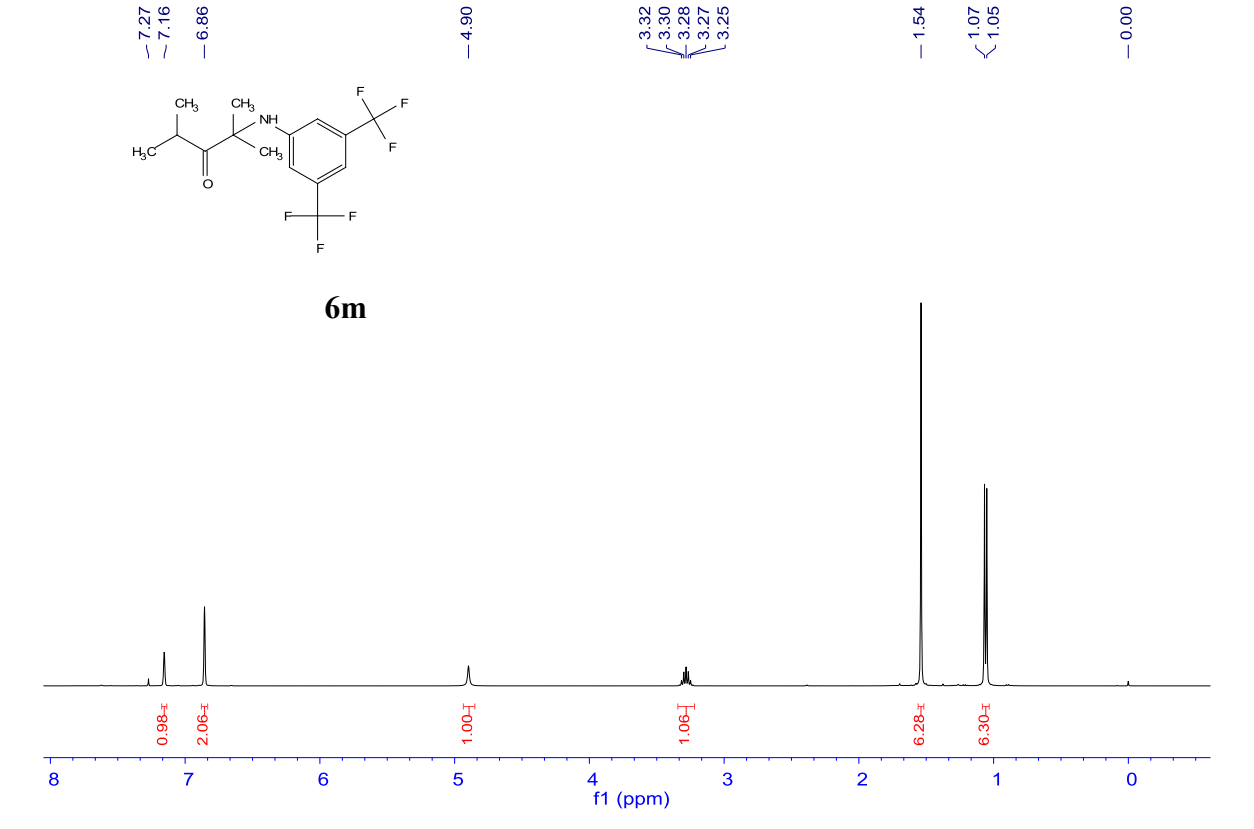
6i


7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.26 7.09 6.90 6.05 6.03 5.04 5.03
2.51 2.50 2.49 2.48 2.47 2.46 2.45 2.44 2.43 2.43 1.60
1.03 1.01 0.99
0.08 -0.00
F F F F F F HN CH3 O
6l
4.05 0.97 0.98 2.03 1.00 1.04 2.10 3.08
8 7 6 5 4 3 2 1 0
f1 (ppm)

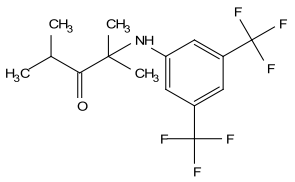

-63.30
F F F F F F HN CH3 O
6l
-40 -50 -60 -70 -80 -90 -1
f1 (ppm)


205.75
146.54
136.77
132.87
132.55
132.23
131.90
129.68
129.06
127.82
127.64
124.92
122.21
119.50
112.75
112.72
110.73
110.69
110.65
110.61
110.58
77.48
77.16
76.84
66.79
32.66
8.00
F
F
F
F
F
HN
CH3
O
40
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

6l

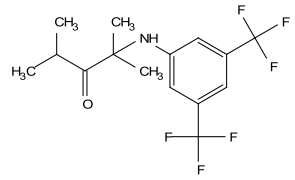

7.27
7.16
6.86
4.90
3.32
3.30
3.28
3.27
3.25
1.54
1.07
1.05
0.00
CH3
CH3
NH
H3C
CH3
O
F
F
F
F
F
F
0.98
2.06
1.00
1.06
6.28
6.30
8
7
6
5
4
3
2
1
0
f1 (ppm)

6m



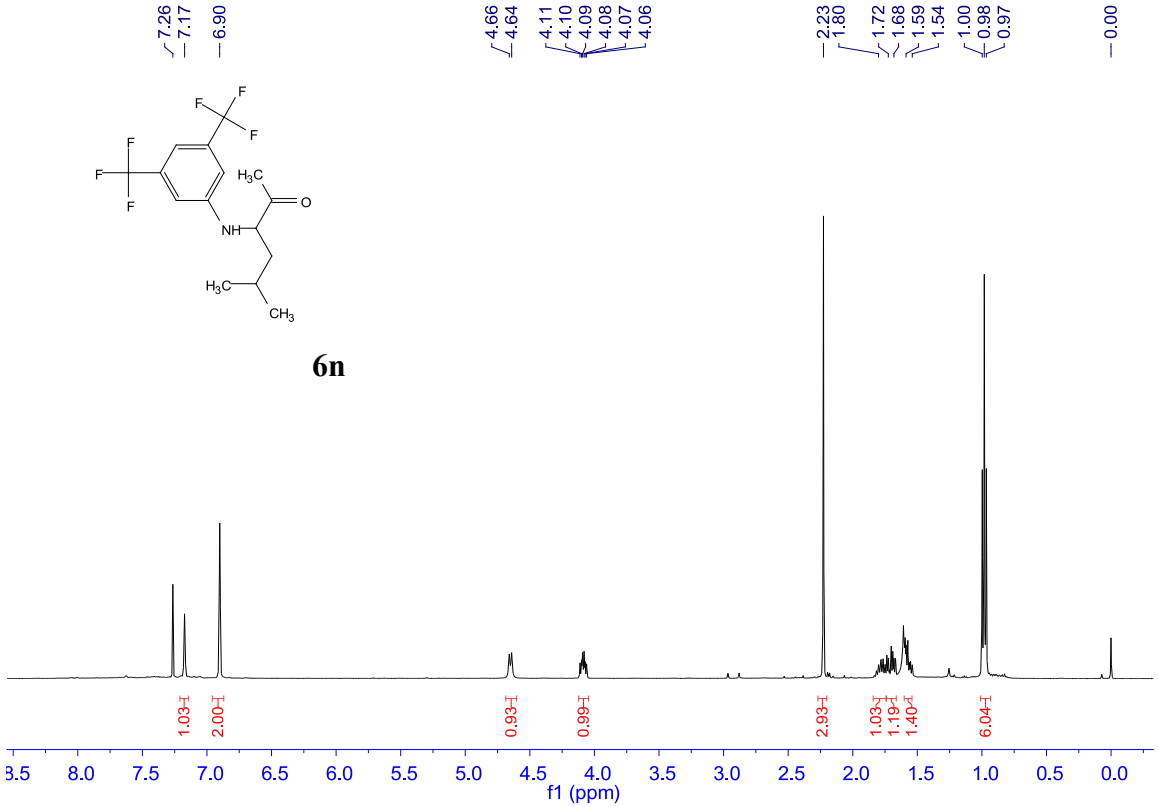
6m

-63.34
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

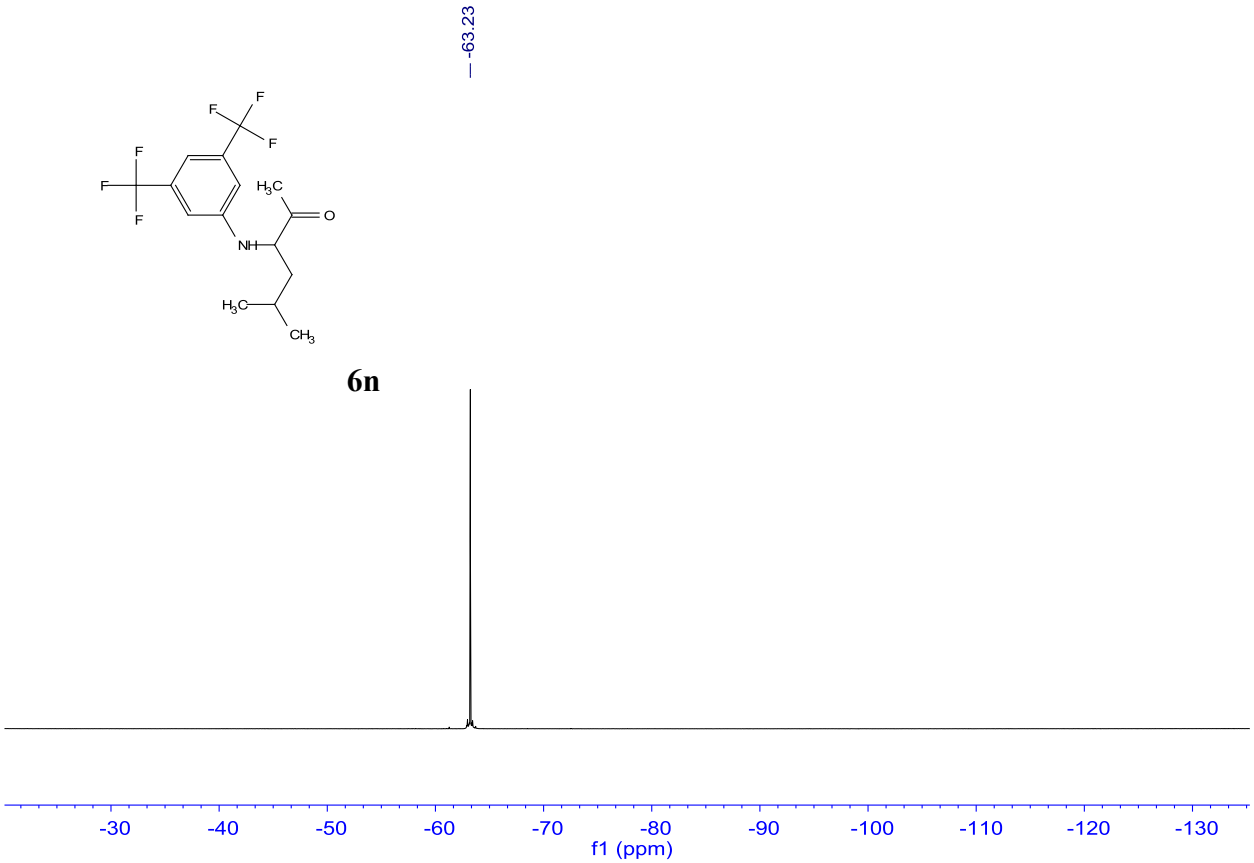


6m

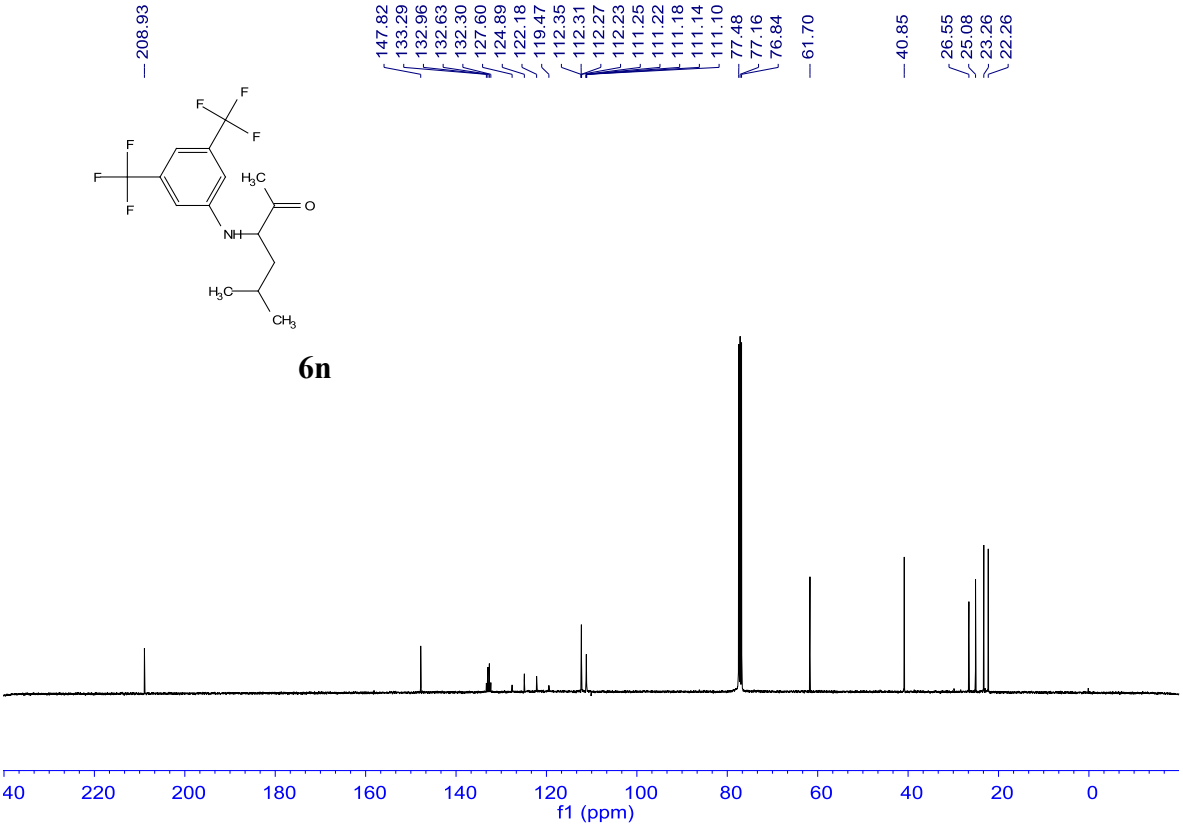
217.86
146.50
132.93
132.60
132.28
131.95
127.60
124.89
122.18
119.47
113.67
113.62
110.80
110.77
110.73
110.69
110.65
77.48
77.16
76.84
62.38
33.85
24.10
20.63
40
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.26
7.17
6.90
4.66
4.64
4.11
4.10
4.09
4.08
4.07
4.06
2.23
1.80
1.72
1.68
1.59
1.54
1.00
0.98
0.97
0.00
1.03
2.00
0.93
0.99
2.93
1.03
1.19
1.40
6.04
f1 (ppm)

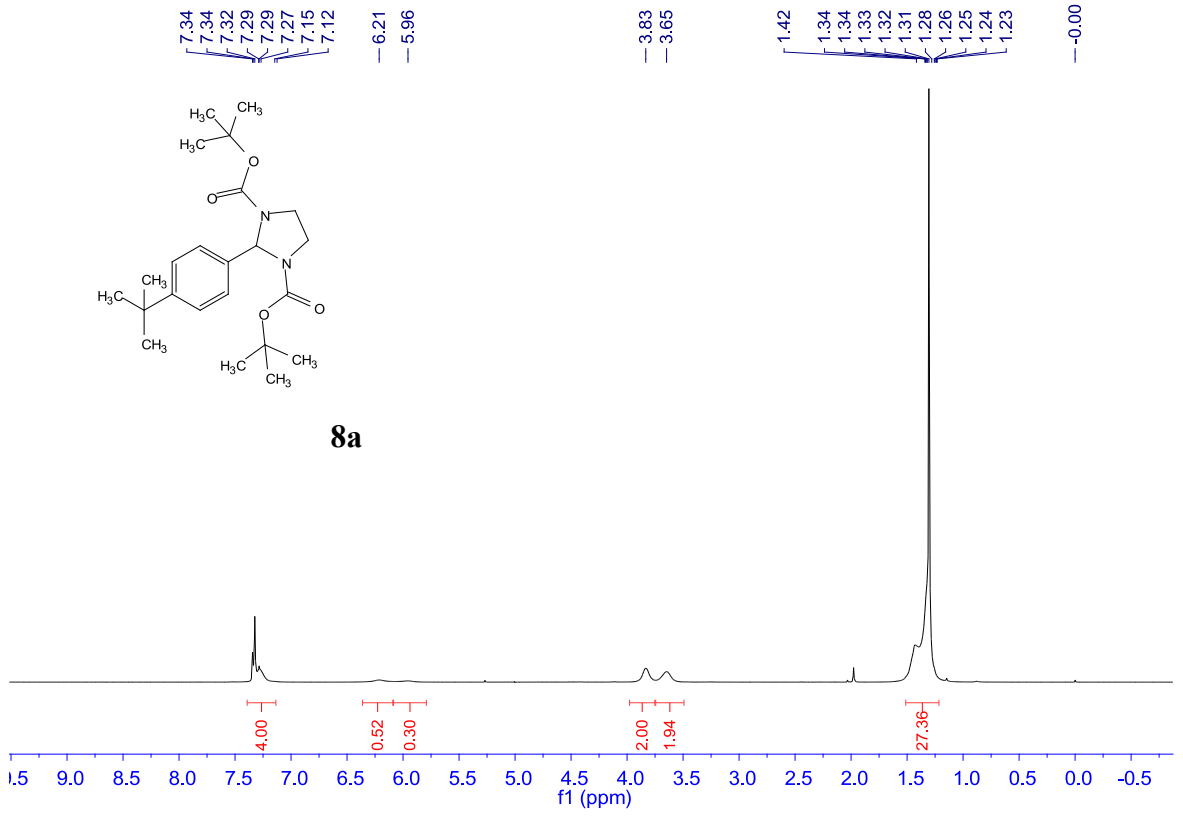
6n


-63.23
f1 (ppm)

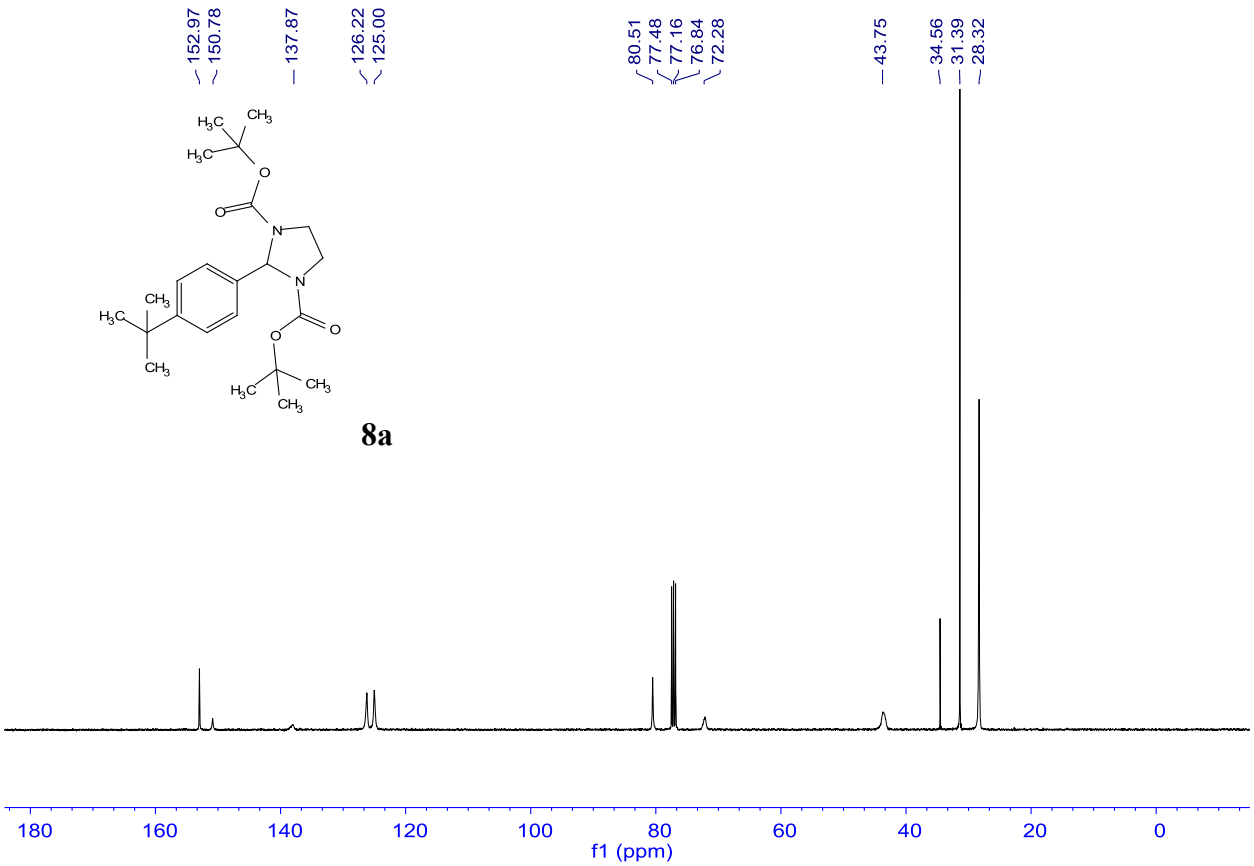
6n

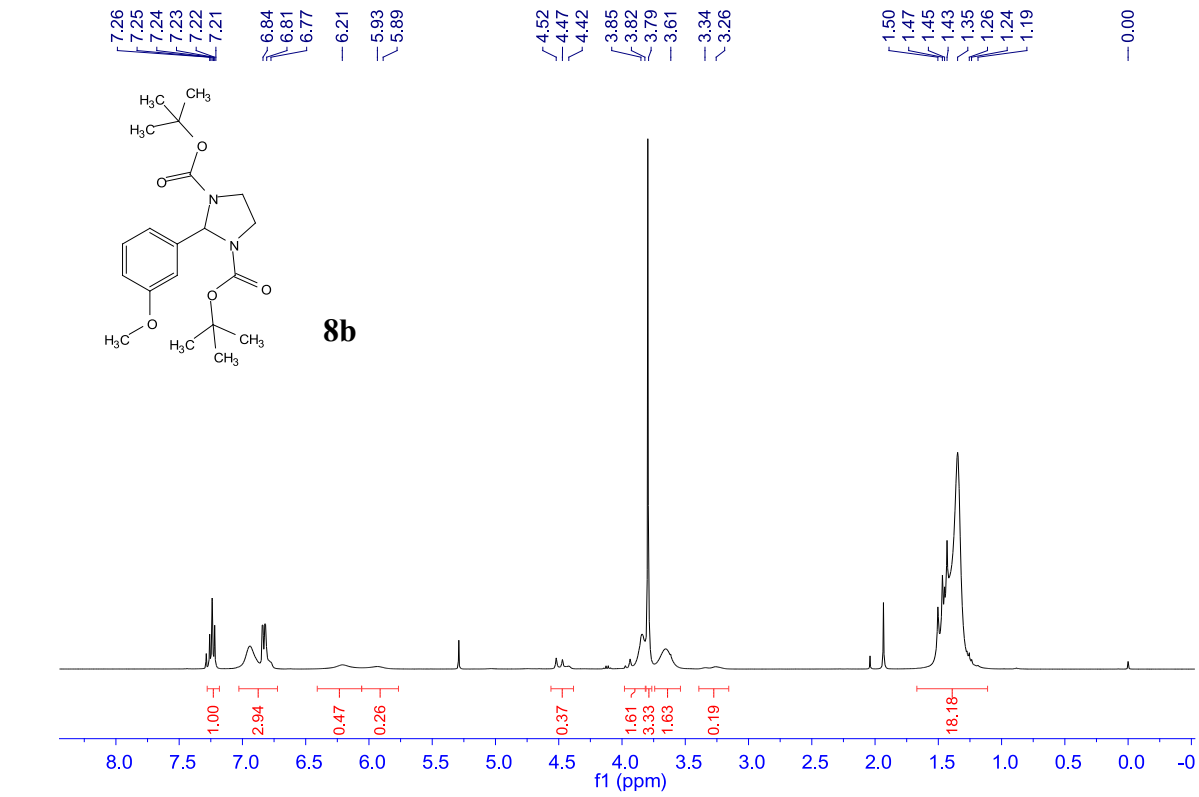

208.93
147.82
133.29
132.96
132.63
132.30
127.60
124.89
122.18
119.47
112.35
112.31
112.27
112.23
111.25
111.22
111.18
111.14
111.10
77.48
77.16
76.84
61.70
40.85
26.55
25.08
23.26
22.26
F
F
F
F
F
H3C
O
NH
H3C
CH3
40
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

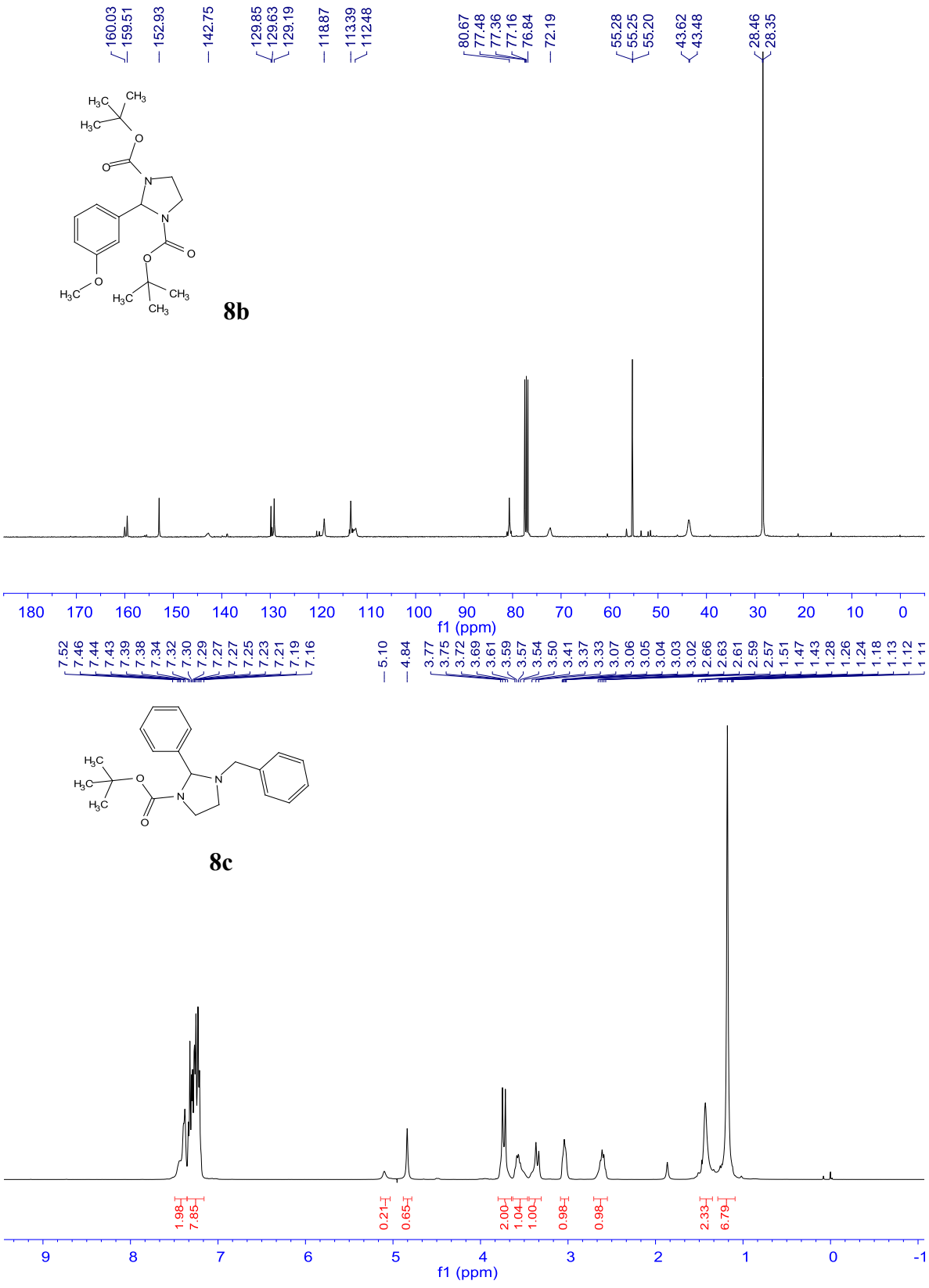
6n

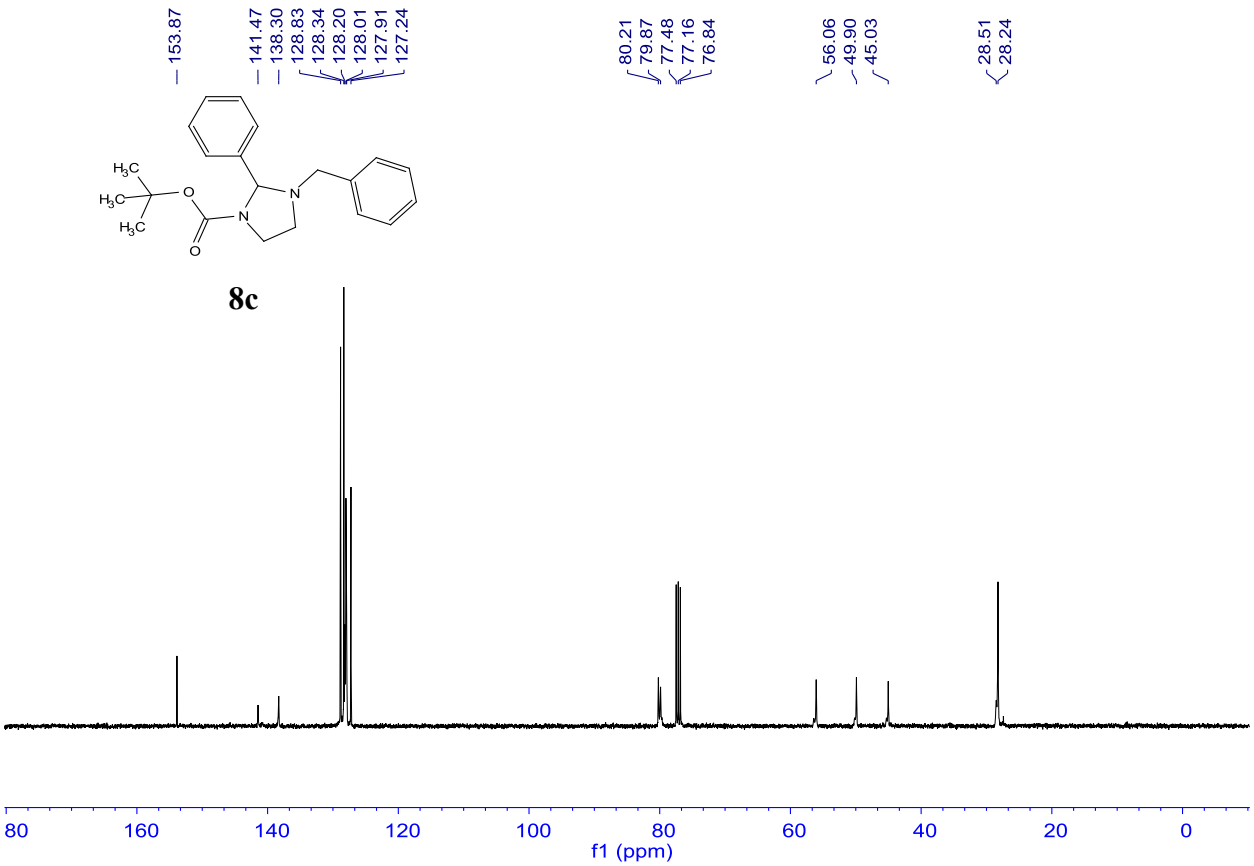

7.34
7.34
7.32
7.29
7.29
7.27
7.15
7.12
6.21
5.96
3.83
3.65
1.42
1.34
1.34
1.33
1.32
1.31
1.28
1.26
1.25
1.24
1.23
-0.00
H3C
CH3
H3C
O
O
N
N
O
O
H3C
CH3
CH3
H3C
CH3
CH3
4.00
0.52
0.30
2.00
1.94
27.36
f1 (ppm)

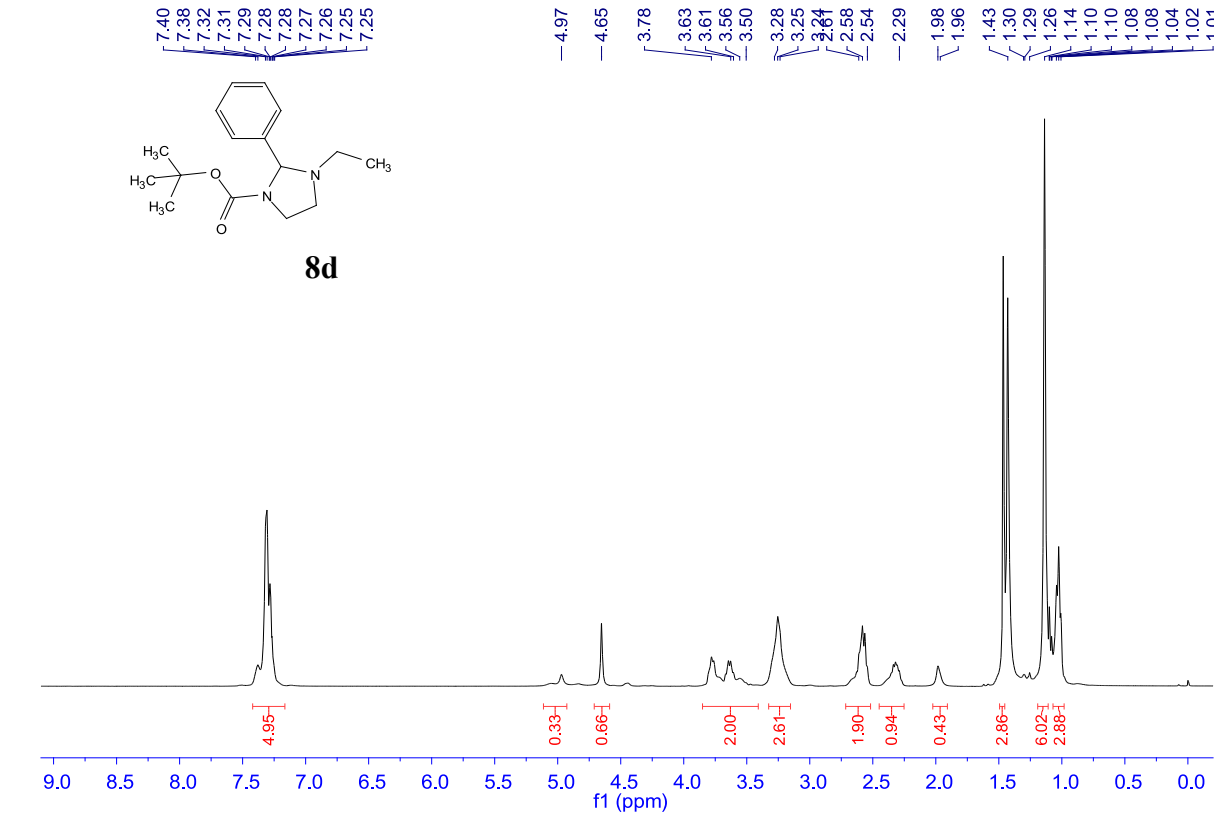
8a

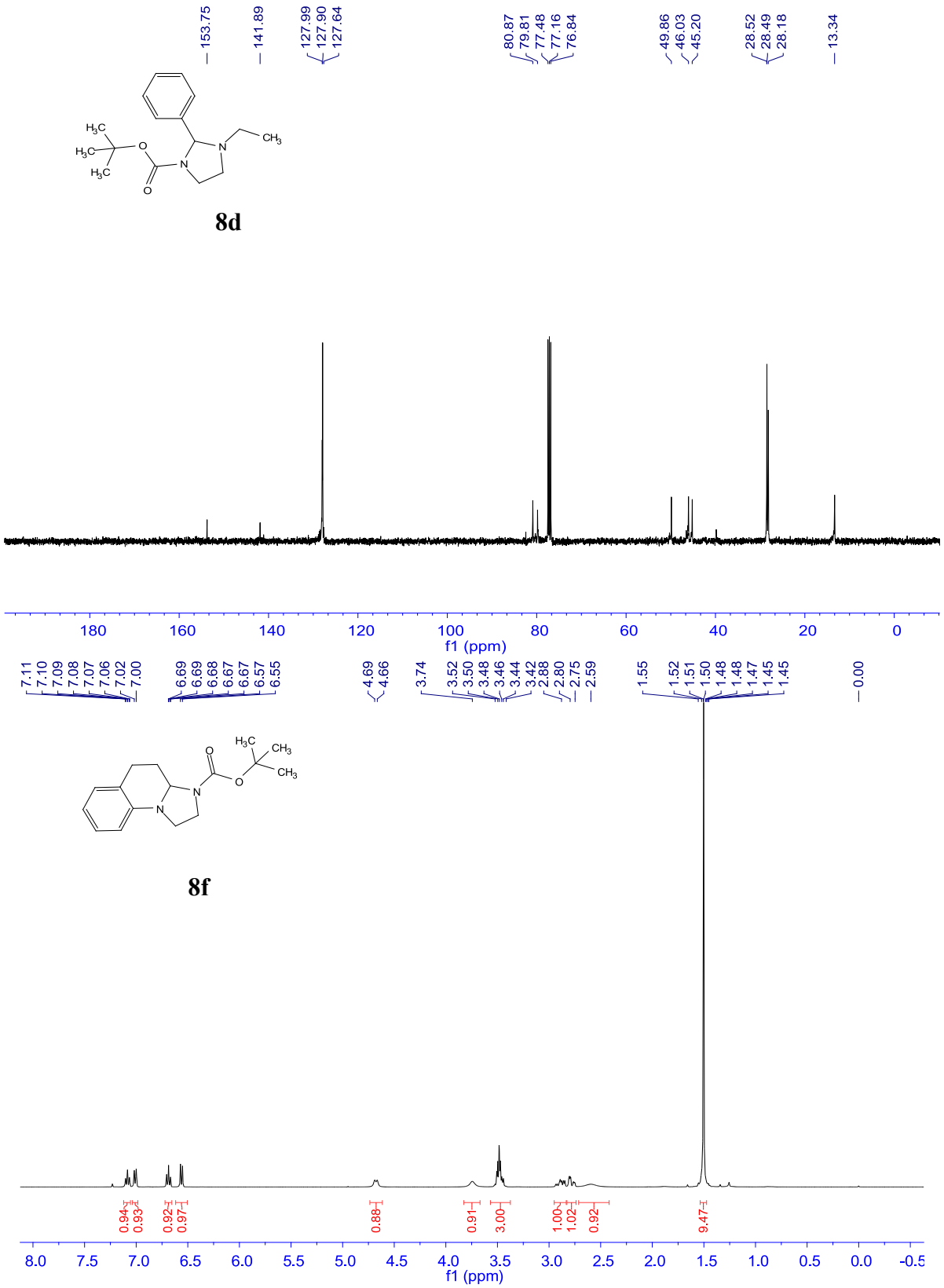

152.97
150.78
137.87
126.22
125.00
80.51
77.48
77.16
76.84
72.28
43.75
34.56
31.39
28.32
8a
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

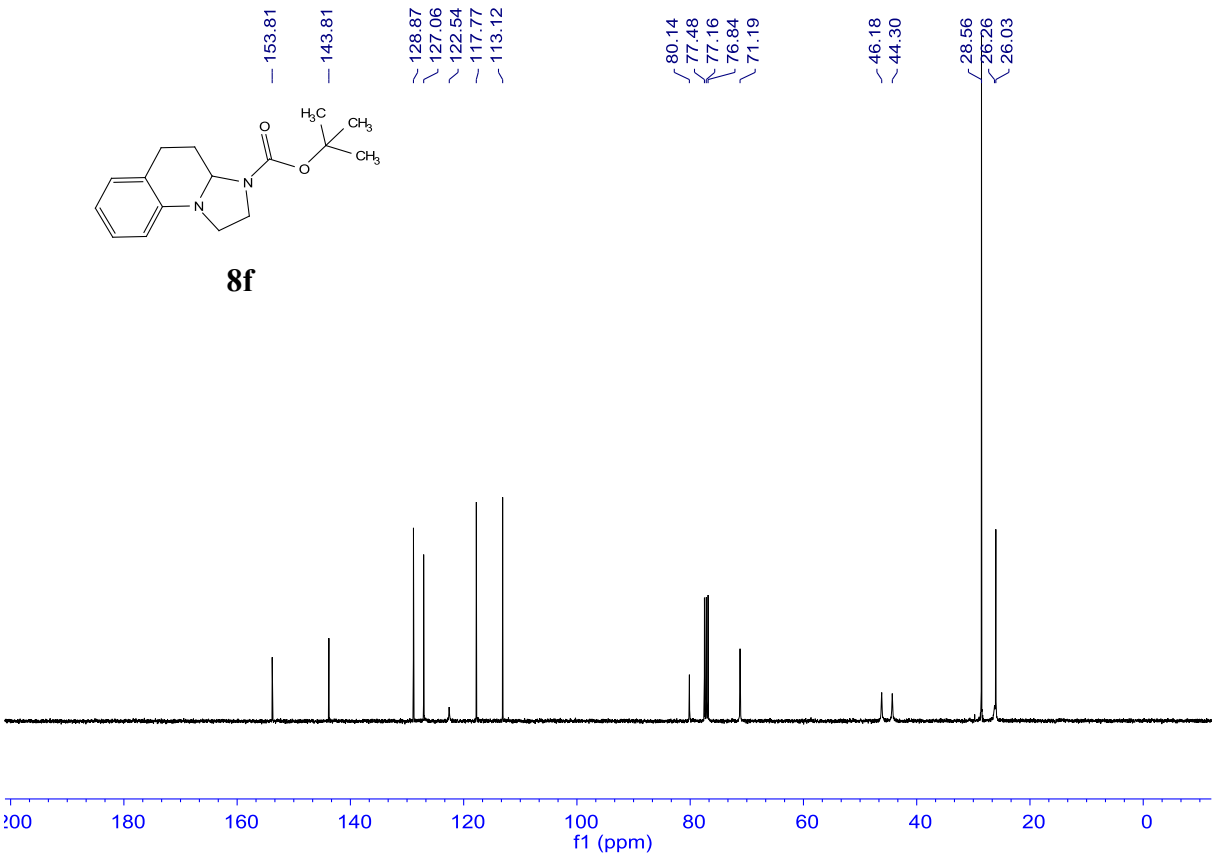

7.26
7.25
7.24
7.23
7.22
7.21
6.84
6.81
6.77
6.21
5.93
5.89
4.52
4.47
4.42
3.85
3.82
3.79
3.61
3.34
3.26
1.50
1.47
1.45
1.43
1.35
1.26
1.24
1.19
0.00
8b
1.00
2.94
0.47
0.26
0.37
1.61
3.33
1.63
0.19
18.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


160.03
159.51
152.93
142.75
129.85
129.63
129.19
118.87
113.39
112.48
80.67
77.48
77.36
77.16
76.84
72.19
55.28
55.25
55.20
43.62
43.48
28.46
28.35
8b
f1 (ppm)
7.52
7.46
7.44
7.43
7.39
7.38
7.34
7.32
7.30
7.29
7.27
7.27
7.25
7.23
7.21
7.19
7.16
5.10
4.84
3.77
3.75
3.72
3.69
3.61
3.59
3.57
3.54
3.50
3.41
3.37
3.33
3.07
3.06
3.05
3.04
3.03
3.02
2.66
2.63
2.61
2.59
2.57
1.51
1.47
1.43
1.28
1.26
1.24
1.18
1.13
1.12
1.11
8c
1.98
7.85
0.21
0.65
2.00
1.04
1.00
0.98
0.98
2.33
6.79
f1 (ppm)

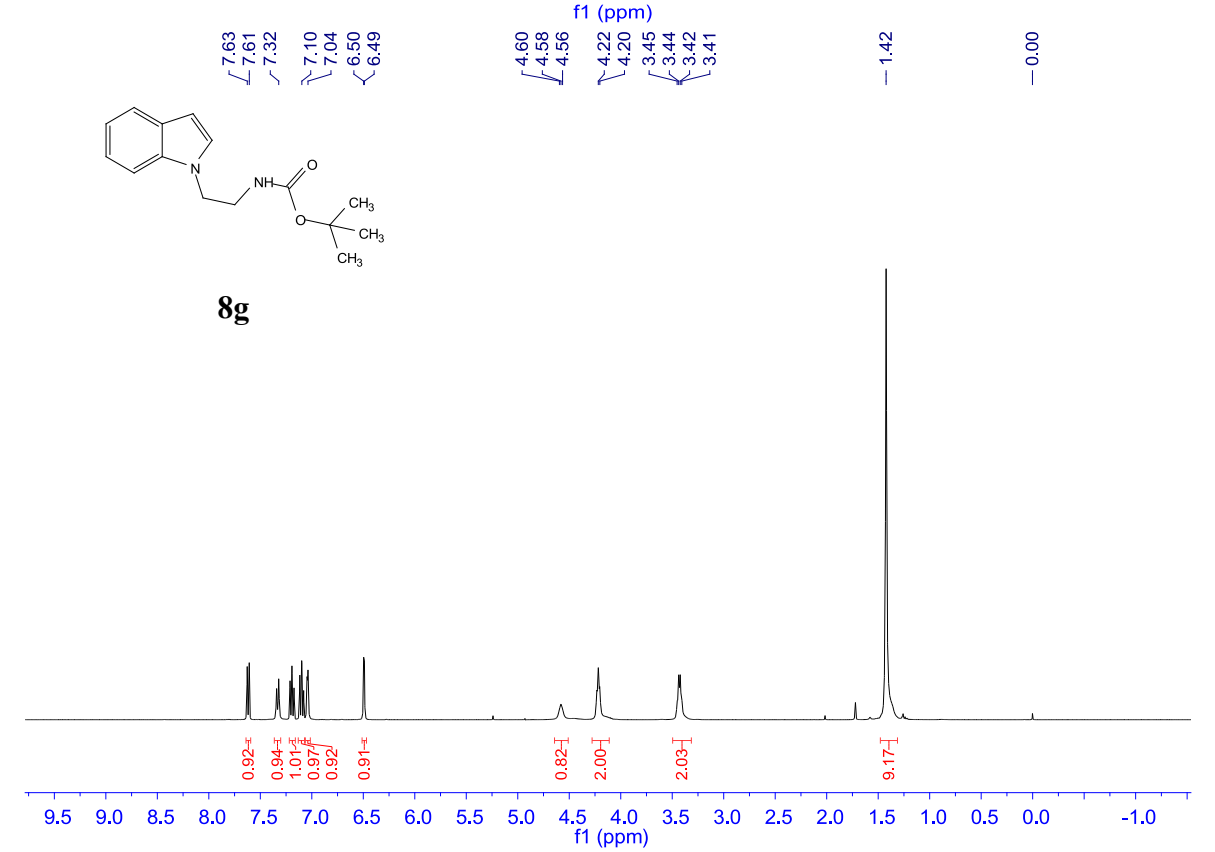

153.87
141.47
138.30
128.83
128.34
128.20
128.01
127.91
127.24
80.21
79.87
77.48
77.16
76.84
56.06
49.90
45.03
28.51
28.24
8c
80
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.40
7.38
7.32
7.31
7.29
7.28
7.28
7.27
7.26
7.25
7.25
4.97
4.65
3.78
3.63
3.61
3.56
3.50
3.28
3.25
2.58
2.54
2.29
1.98
1.96
1.43
1.30
1.29
1.26
1.14
1.10
1.10
1.08
1.08
1.04
1.02
8d
4.95
0.33
0.66
2.00
2.61
1.90
0.94
0.43
2.86
6.02
2.88
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)

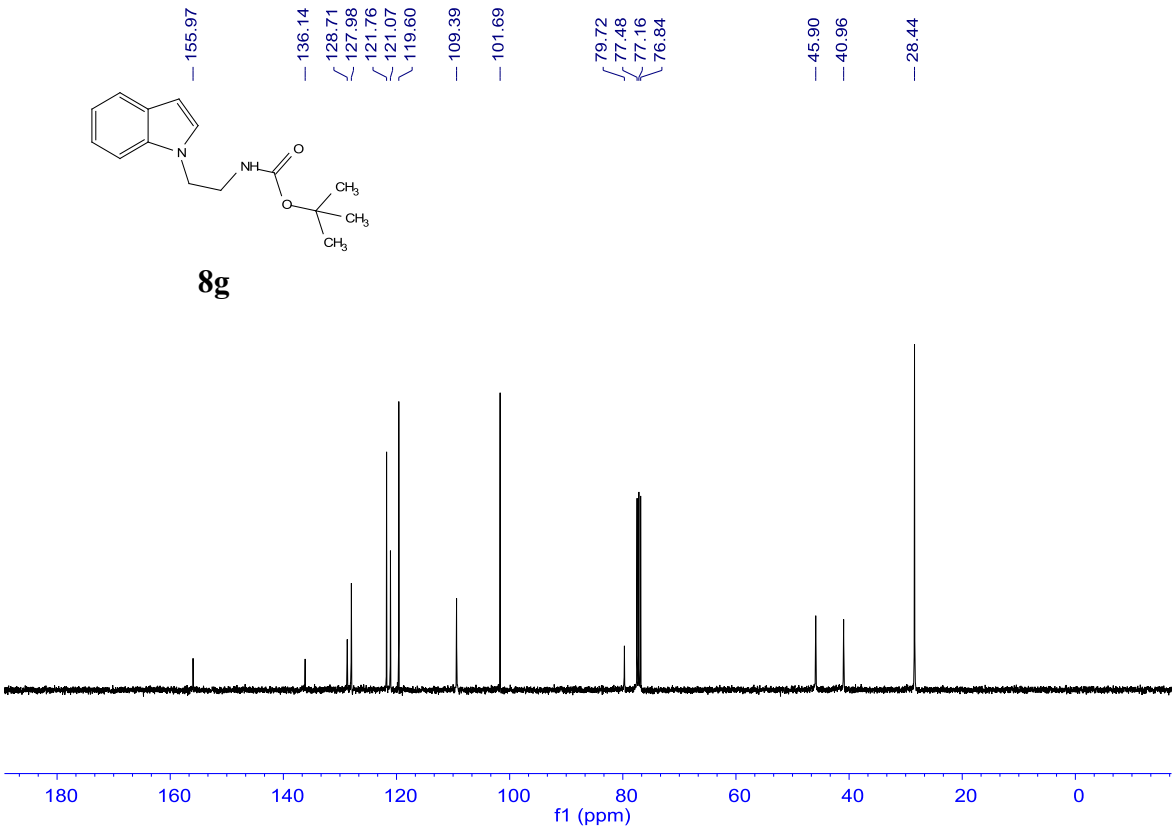

153.75
141.89
127.99
127.90
127.64
80.87
79.81
77.48
77.16
76.84
49.86
46.03
45.20
28.52
28.49
28.18
13.34
8d
180
160
140
120
100
80
60
40
20
0
f1 (ppm)
7.11
7.10
7.09
7.08
7.07
7.06
7.02
7.00
6.69
6.69
6.68
6.67
6.67
6.57
6.55
4.69
4.66
3.74
3.52
3.50
3.48
3.46
3.44
3.42
2.88
2.80
2.75
2.59
1.55
1.52
1.51
1.50
1.48
1.48
1.47
1.45
1.45
0.00
8f
0.94
0.93
0.92
0.97
0.88
0.91
3.00
1.00
1.02
0.92
9.47
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
-0.5
f1 (ppm)


153.81
143.81
128.87
127.06
122.54
117.77
113.12
80.14
77.48
77.16
76.84
71.19
46.18
44.30
28.56
26.26
26.03
f1 (ppm)

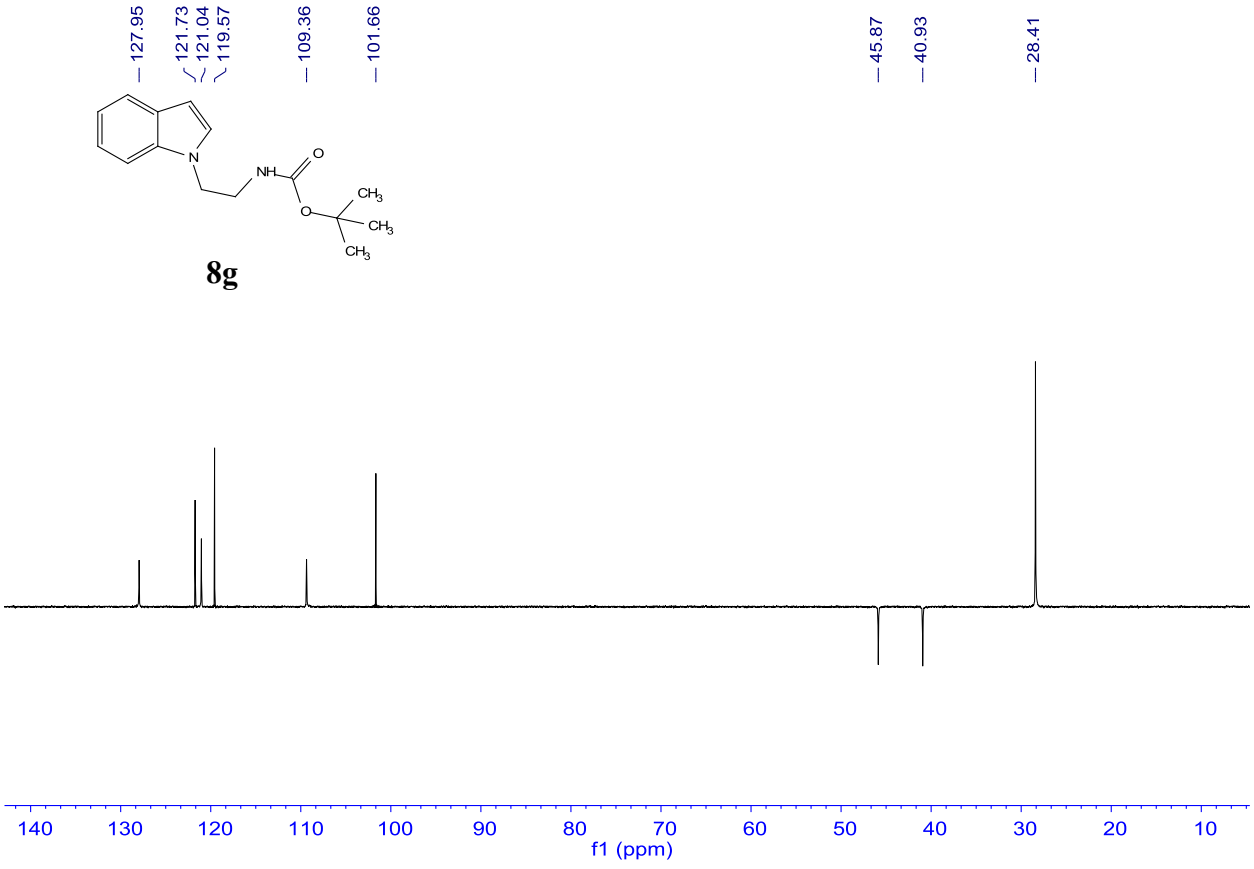
8f


7.63
7.61
7.32
7.10
7.04
6.50
6.49
4.60
4.58
4.56
4.22
4.20
3.45
3.44
3.42
3.41
1.42
0.00
0.92
0.94
1.01
0.97
0.92
0.91
0.82
2.00
2.03
9.17
f1 (ppm)

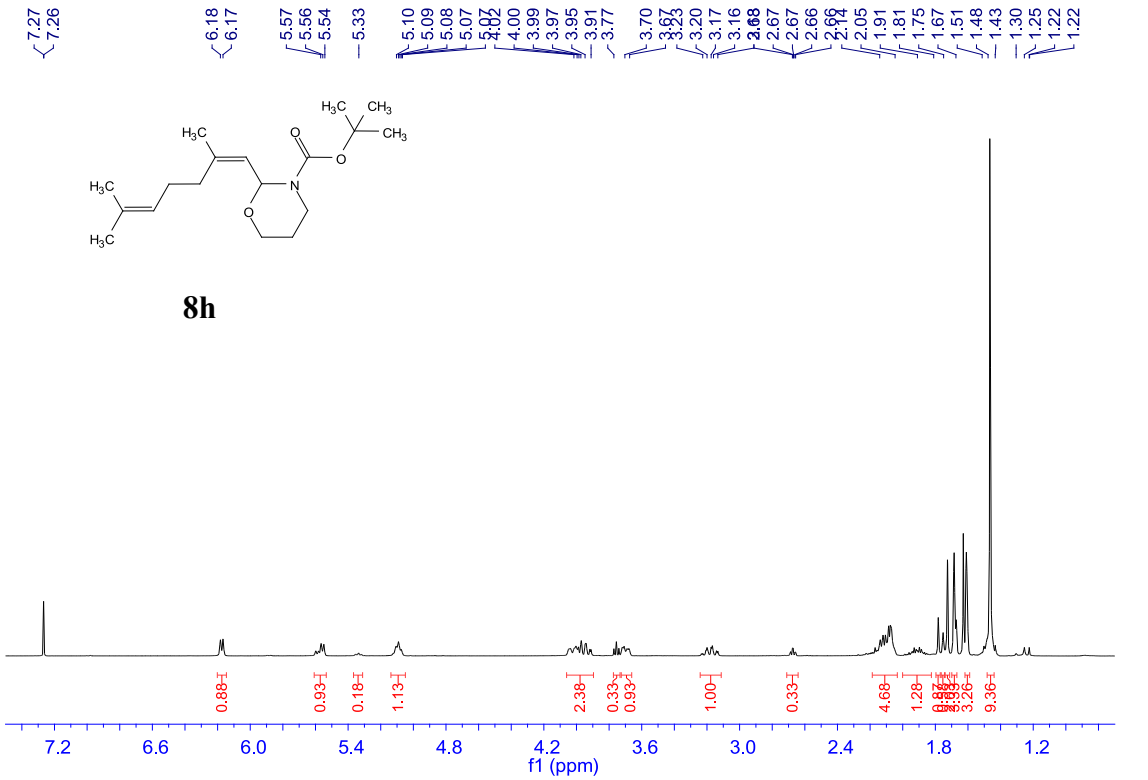
8g


155.97
136.14
128.71
127.98
121.76
121.07
119.60
109.39
101.69
79.72
77.48
77.16
76.84
45.90
40.96
28.44
NH
O
O
CH3
CH3
CH3
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

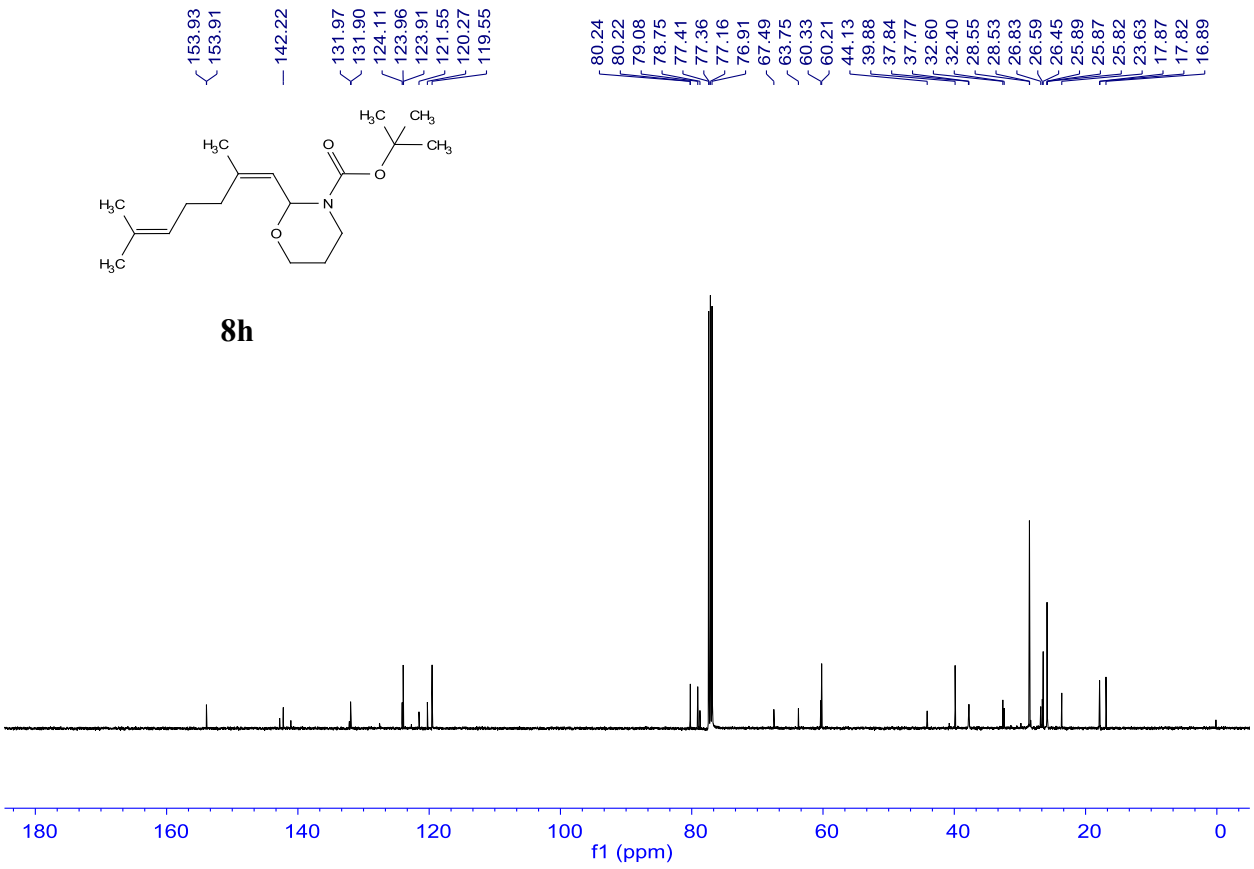
8g


127.95
121.73
121.04
119.57
109.36
101.66
45.87
40.93
28.41
NH
O
O
CH3
CH3
CH3
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

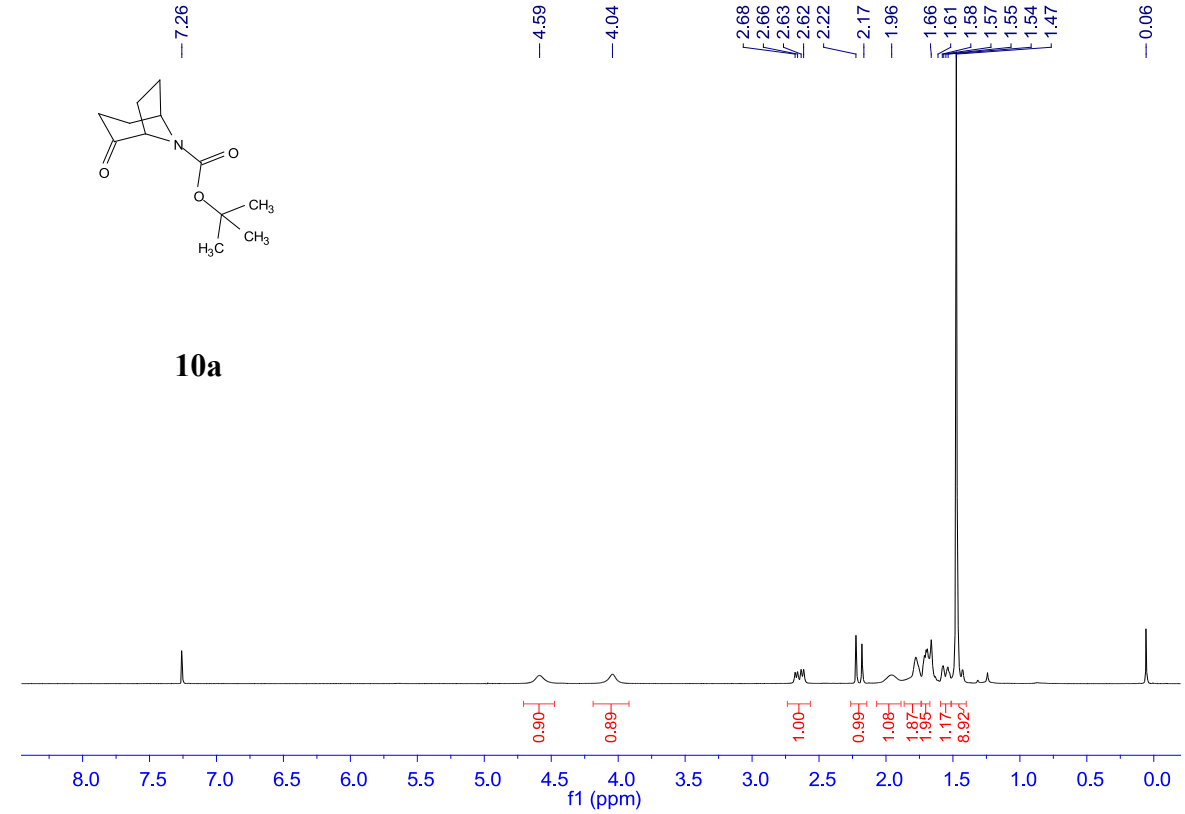
8g


7.27
7.26
6.18
6.17
5.57
5.56
5.54
5.33
5.10
5.09
5.08
5.07
4.00
3.99
3.97
3.95
3.91
3.77
3.70
3.67
3.23
3.20
3.17
3.16
2.67
2.67
2.66
2.66
2.14
2.05
1.91
1.81
1.75
1.67
1.51
1.48
1.43
1.30
1.25
1.22
1.22
H3C
CH3
CH3
H3C
O
O
N
O
H3C
H3C
0.88
0.93
0.18
1.13
2.38
0.33
0.93
1.00
0.33
4.68
1.28
3.26
9.36
7.2
6.6
6.0
5.4
4.8
4.2
3.6
3.0
2.4
1.8
1.2
f1 (ppm)

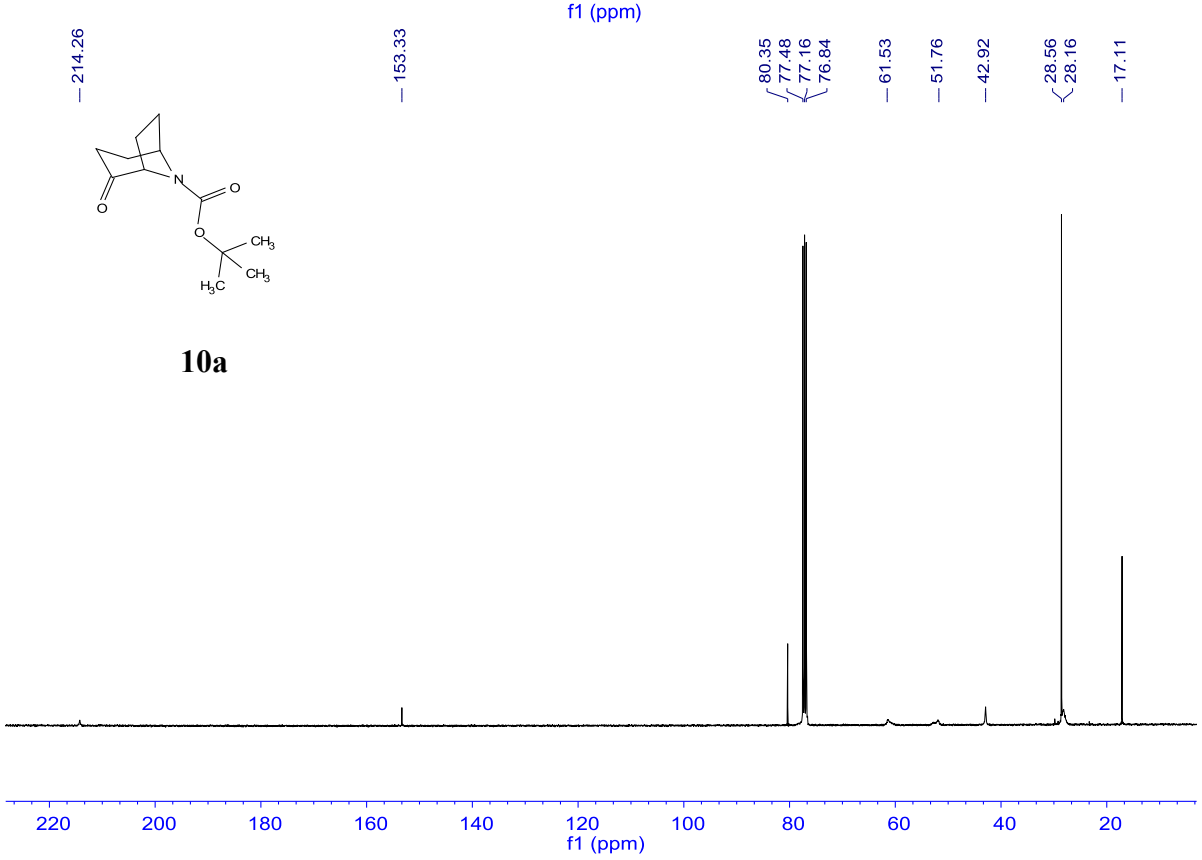
8h


153.93
153.91
142.22
131.97
131.90
124.11
123.96
123.91
121.55
120.27
119.55
80.24
80.22
79.08
78.75
77.41
77.36
77.16
76.91
67.49
63.75
60.33
60.21
44.13
39.88
37.84
37.77
32.60
32.40
28.55
28.53
26.83
26.59
26.45
25.89
25.87
25.82
23.63
17.87
17.82
16.89
H3C
CH3
CH3
H3C
O
O
N
O
H3C
H3C
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

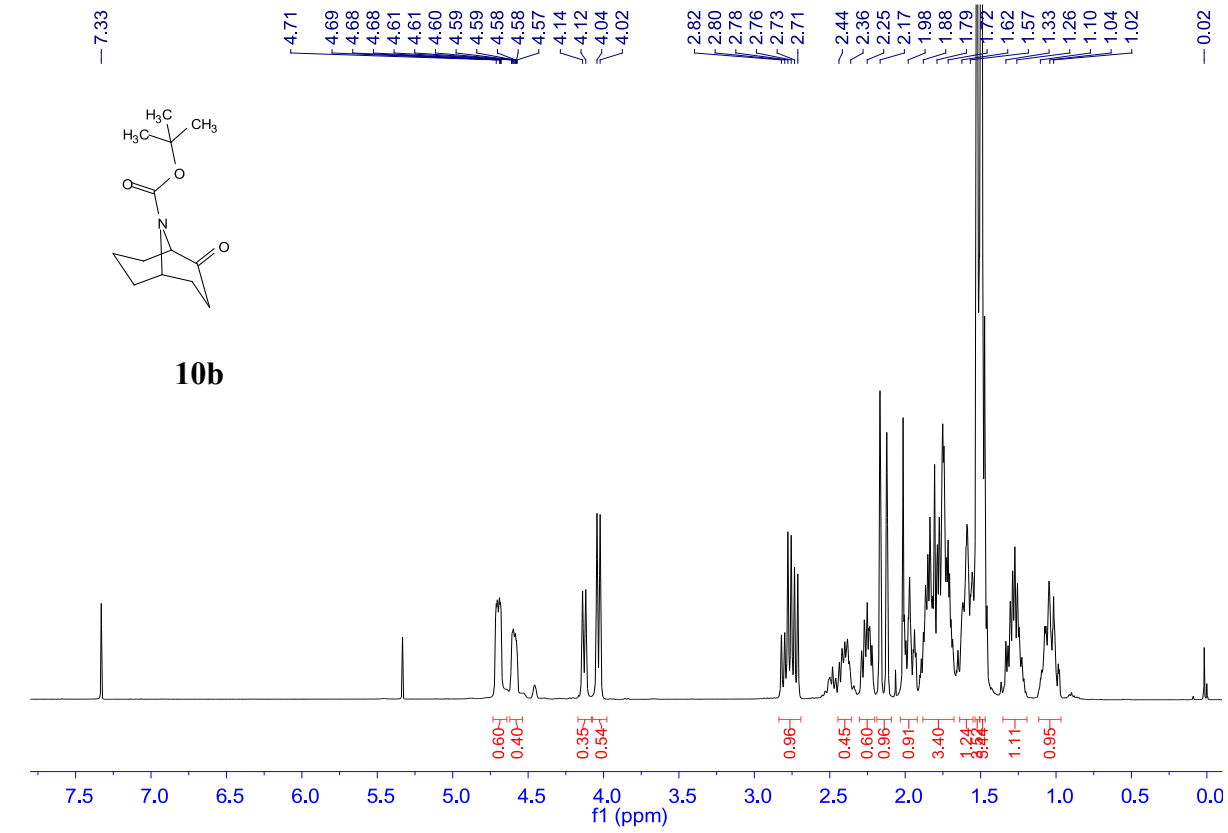
8h


7.26
4.59
4.04
2.68
2.66
2.63
2.62
2.22
2.17
1.96
1.66
1.61
1.58
1.57
1.55
1.54
1.47
0.06
0.90
0.89
1.00
0.99
1.08
1.87
1.95
1.17
8.92
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)

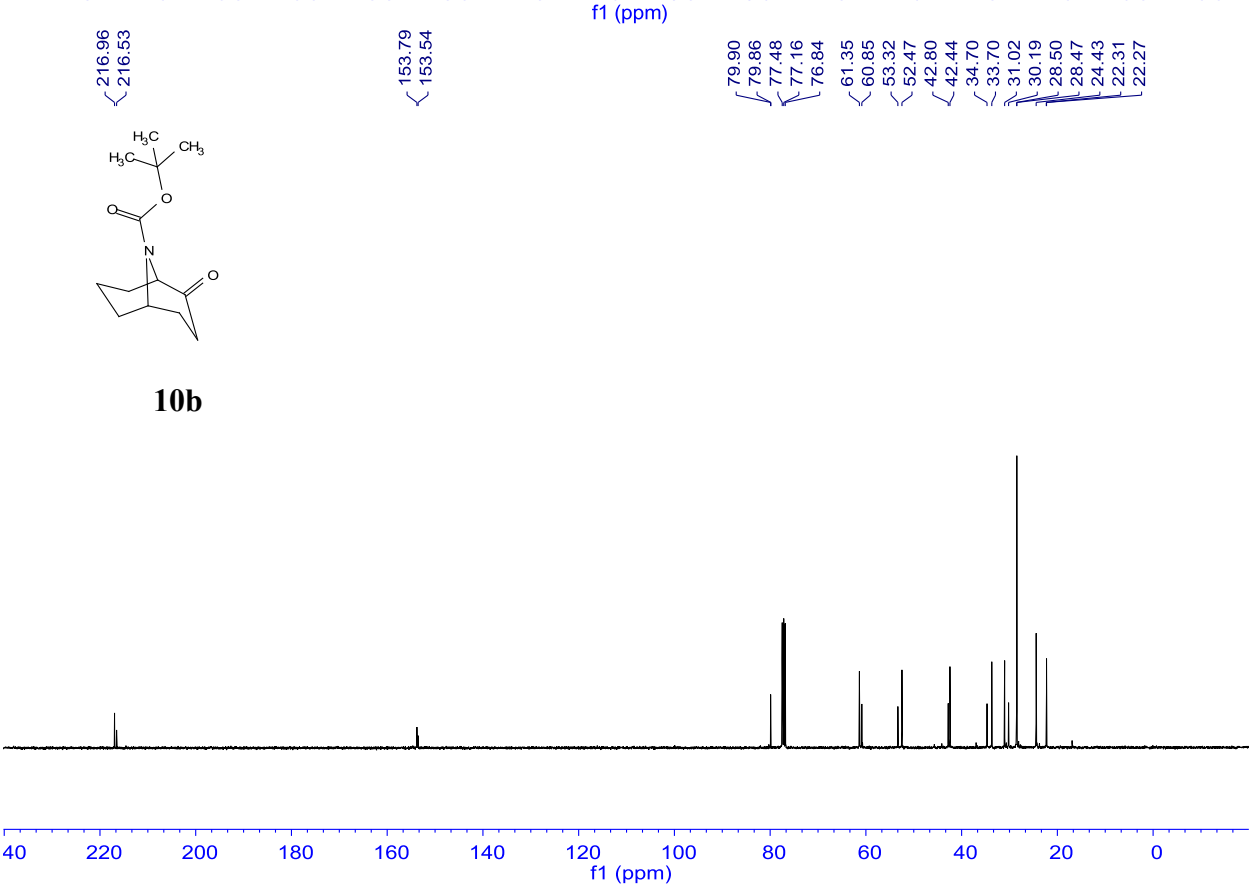
10a


214.26
153.33
80.35
77.48
77.16
76.84
61.53
51.76
42.92
28.56
28.16
17.11
220
200
180
160
140
120
100
80
60
40
20
f1 (ppm)

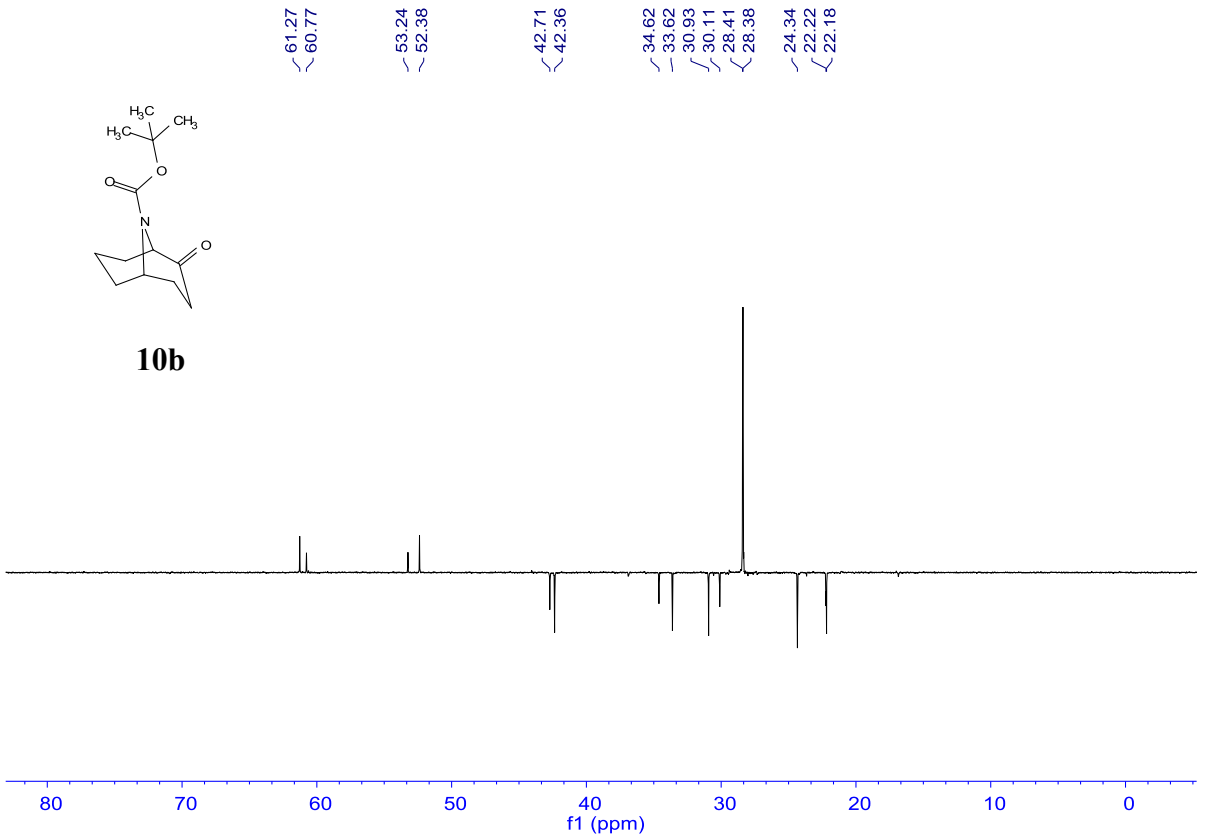
10a


7.33
4.71
4.69
4.68
4.68
4.61
4.61
4.60
4.59
4.59
4.58
4.58
4.57
4.14
4.12
4.04
4.02
2.82
2.80
2.78
2.76
2.73
2.71
2.44
2.36
2.25
2.17
1.98
1.88
1.79
1.72
1.62
1.57
1.33
1.26
1.10
1.04
1.02
0.02
0.60
0.40
0.35
0.54
0.96
0.45
0.60
0.96
0.91
3.40
1.24
1.11
0.95
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)

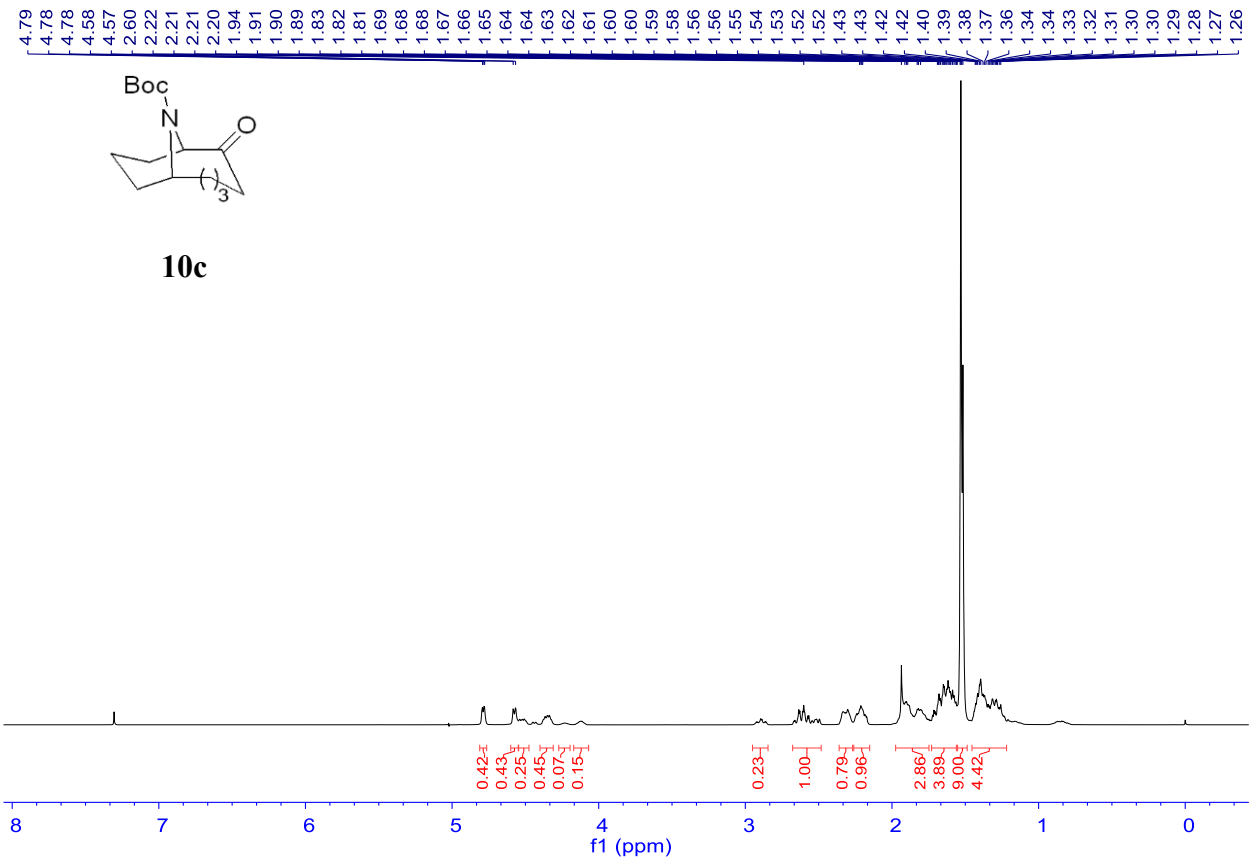
10b


216.96
216.53
153.79
153.54
79.90
79.86
77.48
77.16
76.84
61.35
60.85
53.32
52.47
42.80
42.44
34.70
33.70
31.02
30.19
28.50
28.47
24.43
22.31
22.27
40
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

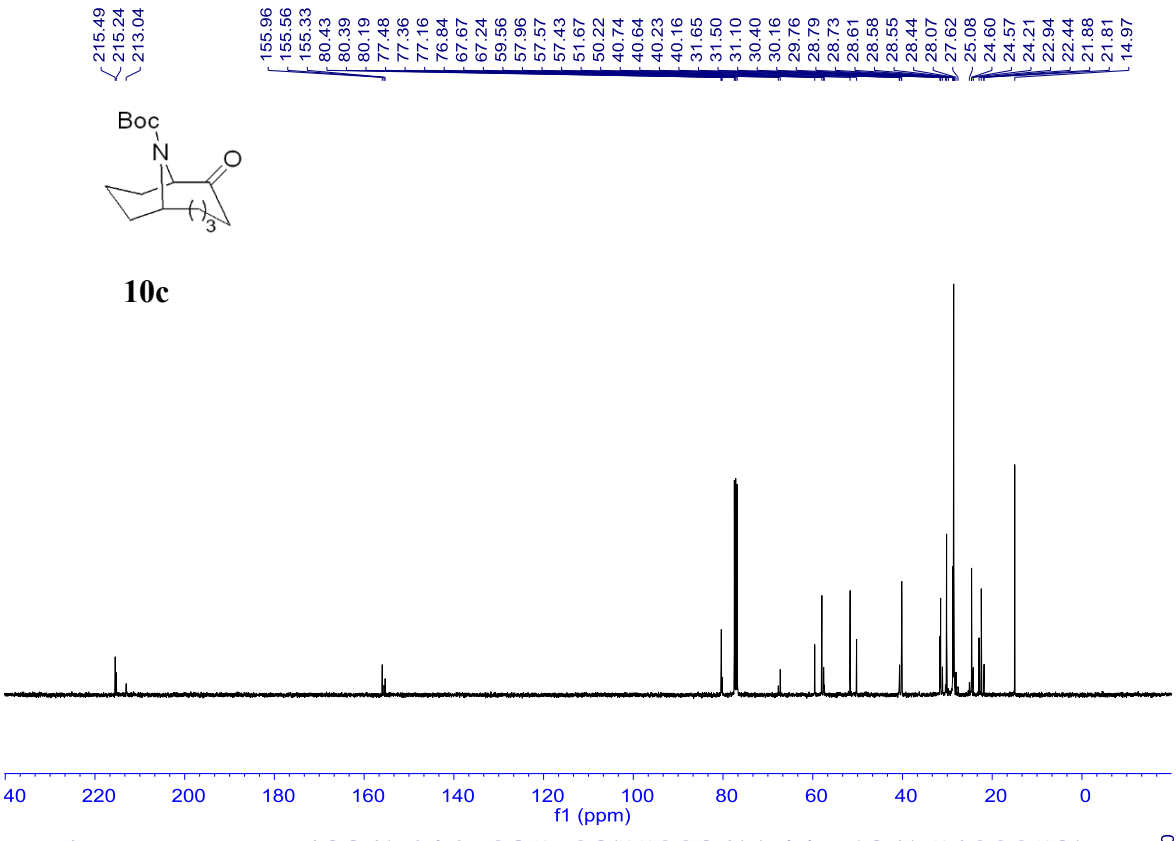
10b

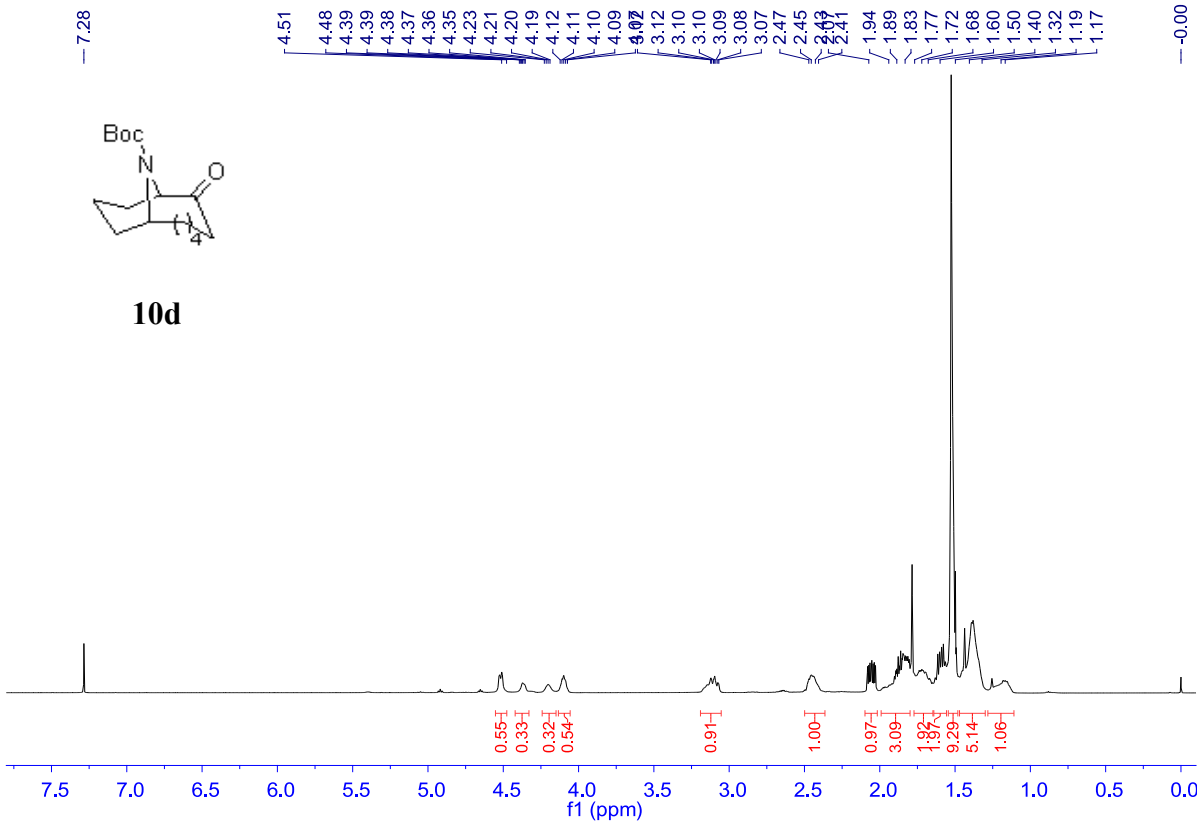

61.27
60.77
53.24
52.38
42.71
42.36
34.62
33.62
30.93
30.11
28.41
28.38
24.34
22.22
22.18
80
70
60
50
40
30
20
10
0
f1 (ppm)

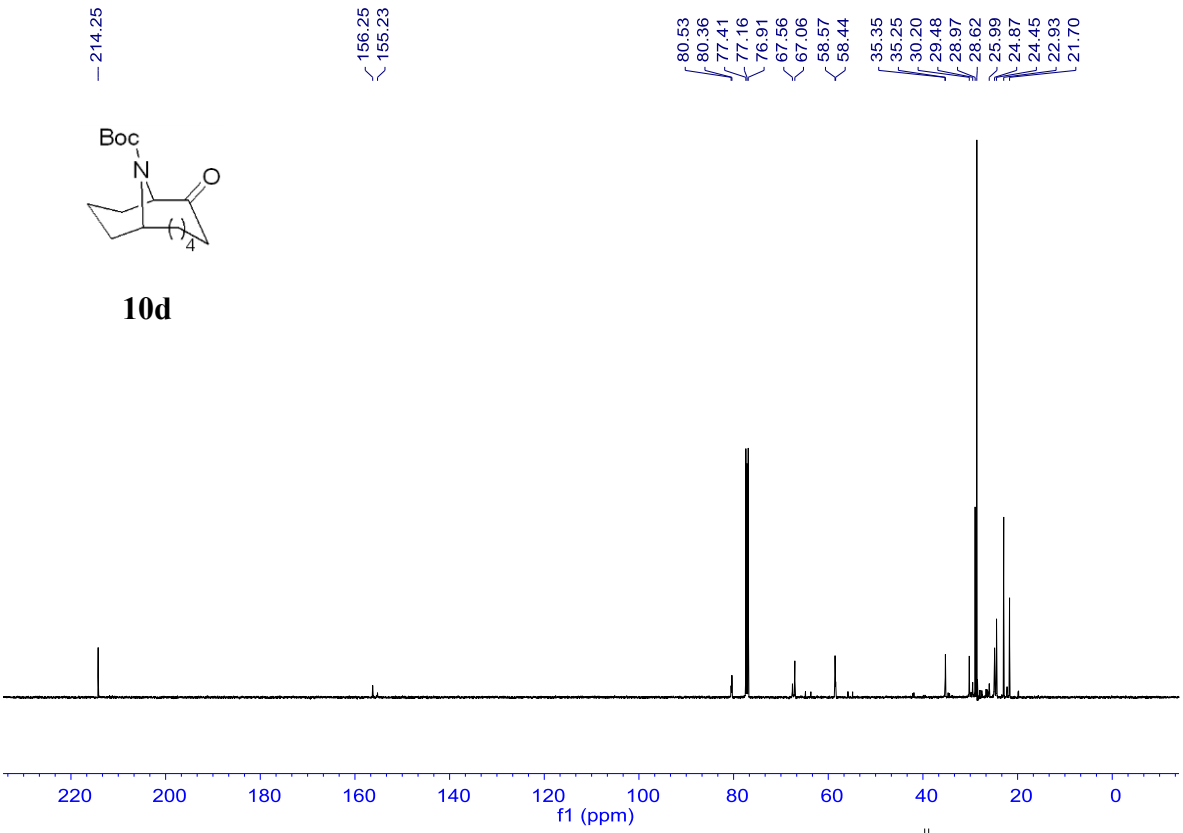
10b


4.79
4.78
4.78
4.58
4.57
2.60
2.22
2.21
2.21
2.20
1.94
1.91
1.90
1.89
1.83
1.82
1.81
1.69
1.68
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.60
1.60
1.59
1.58
1.56
1.56
1.55
1.54
1.53
1.52
1.52
1.43
1.43
1.42
1.42
1.40
1.39
1.38
1.37
1.36
1.34
1.34
1.33
1.32
1.31
1.30
1.30
1.29
1.28
1.27
1.26
0.42
0.43
0.25
0.45
0.07
0.15
0.23
1.00
0.79
0.96
2.86
3.89
9.00
4.42
8
7
6
5
4
3
2
1
0
f1 (ppm)

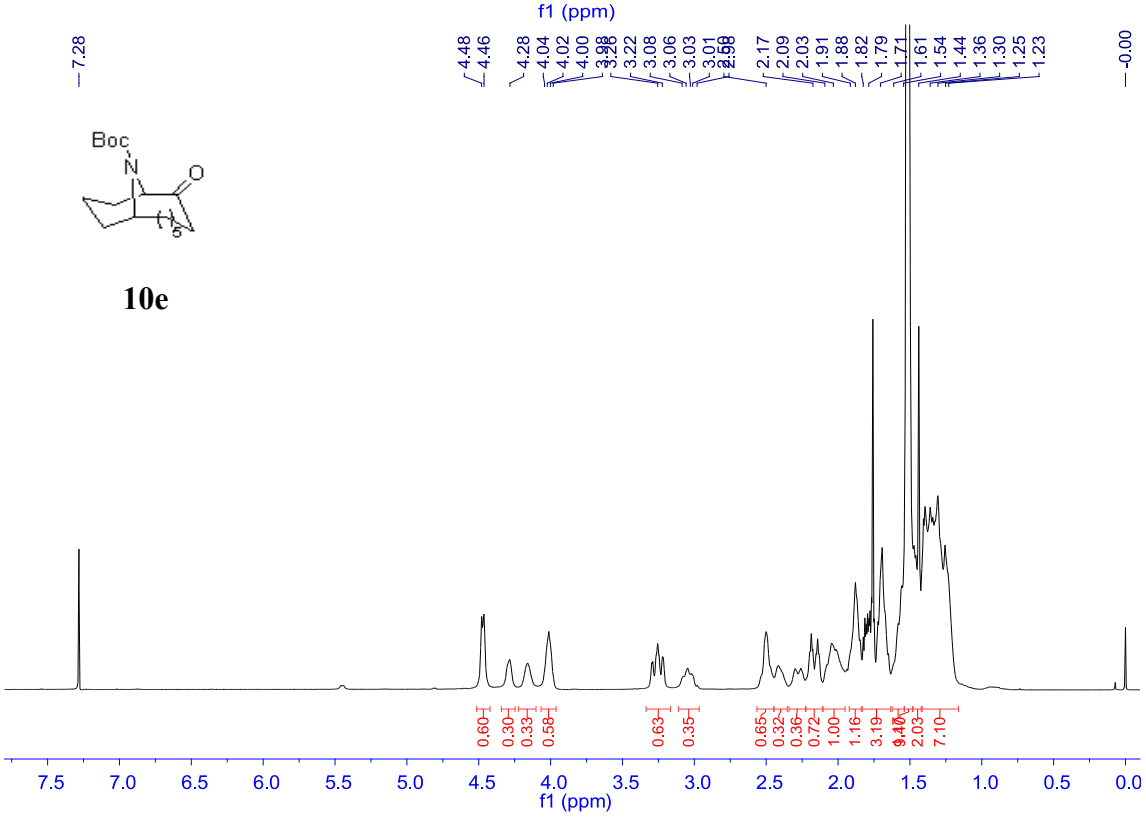
10c


215.49
215.24
213.04
155.96
155.56
155.33
80.43
80.39
80.19
77.48
77.36
77.16
76.84
67.67
67.24
59.56
57.96
57.57
57.43
51.67
50.22
40.74
40.64
40.23
40.16
31.65
31.50
31.10
30.40
30.16
29.76
28.79
28.73
28.61
28.58
28.55
28.44
28.07
27.62
25.08
24.60
24.57
24.21
22.94
22.44
21.88
21.81
14.97
Boc
N
O
3
10c
40
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

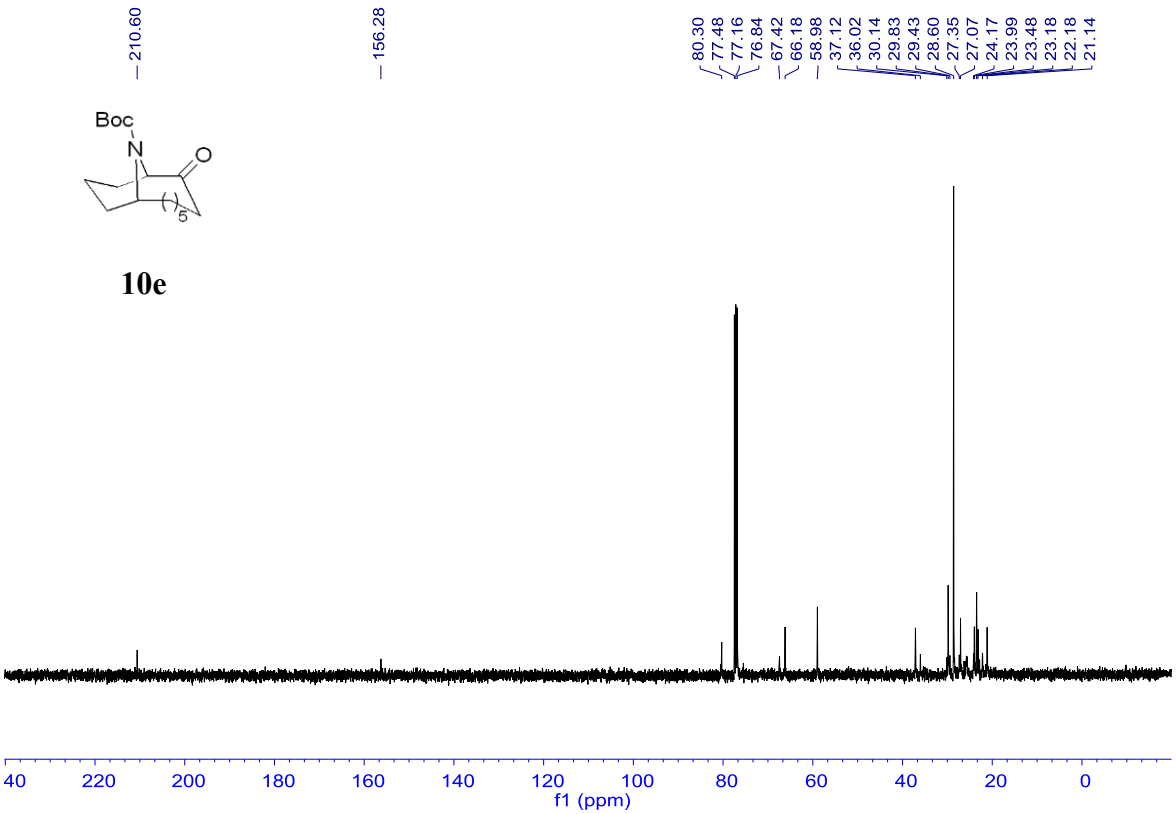

7.28
4.51
4.48
4.39
4.39
4.38
4.37
4.36
4.35
4.23
4.21
4.20
4.19
4.12
4.11
4.10
4.09
3.12
3.10
3.10
3.09
3.08
3.07
2.47
2.45
1.94
1.89
1.83
1.77
1.72
1.68
1.60
1.50
1.40
1.32
1.19
1.17
-0.00
Boc
N
O
4
10d
0.55
0.33
0.32
0.54
0.91
1.00
0.97
3.09
1.92
1.97
9.29
5.14
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


214.25
156.25
155.23
80.53
80.36
77.41
77.16
76.91
67.56
67.06
58.57
58.44
35.35
35.25
30.20
29.48
28.97
28.62
25.99
24.87
24.45
22.93
21.70
Boc
N
O
4
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

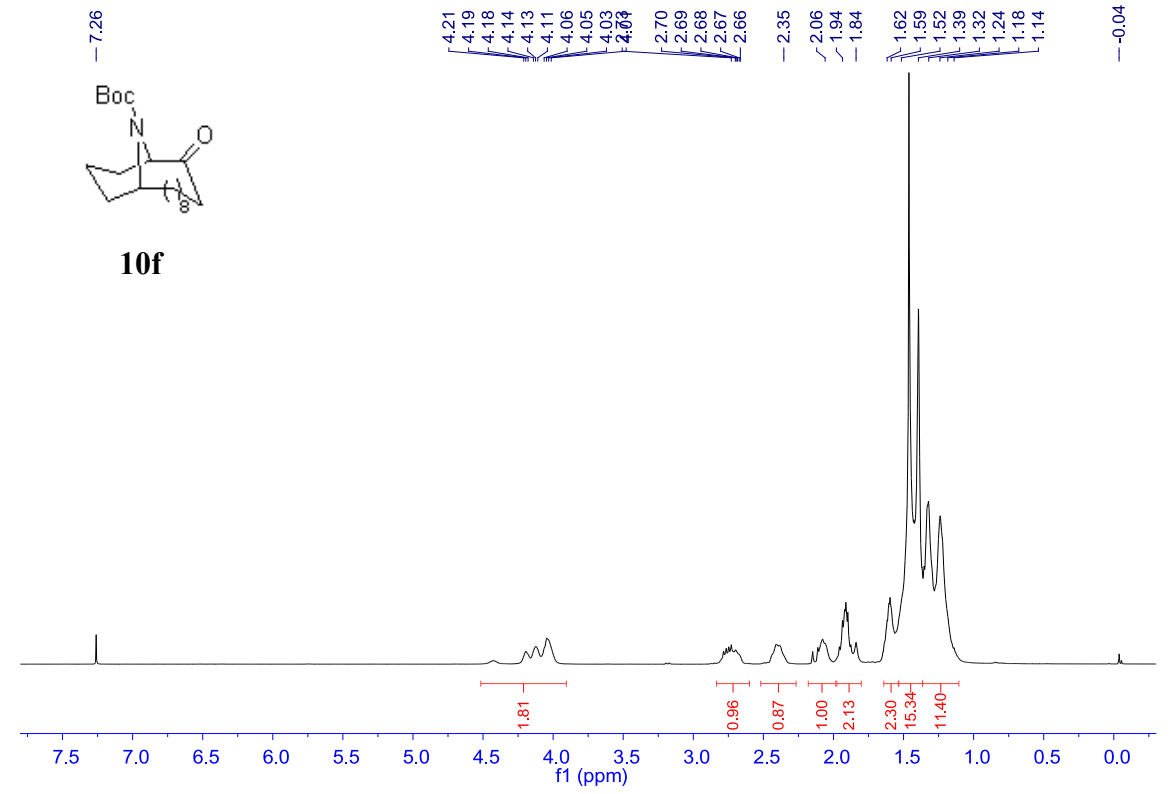
10d


7.28
4.48
4.46
4.28
4.04
4.02
4.00
3.98
3.22
3.08
3.06
3.03
3.01
2.17
2.09
2.03
1.91
1.88
1.82
1.79
1.71
1.61
1.54
1.44
1.36
1.30
1.25
1.23
0.00
Boc
N
O
5
0.60
0.30
0.33
0.58
0.63
0.35
0.65
0.32
0.36
0.72
1.00
1.16
3.19
2.03
7.10
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)

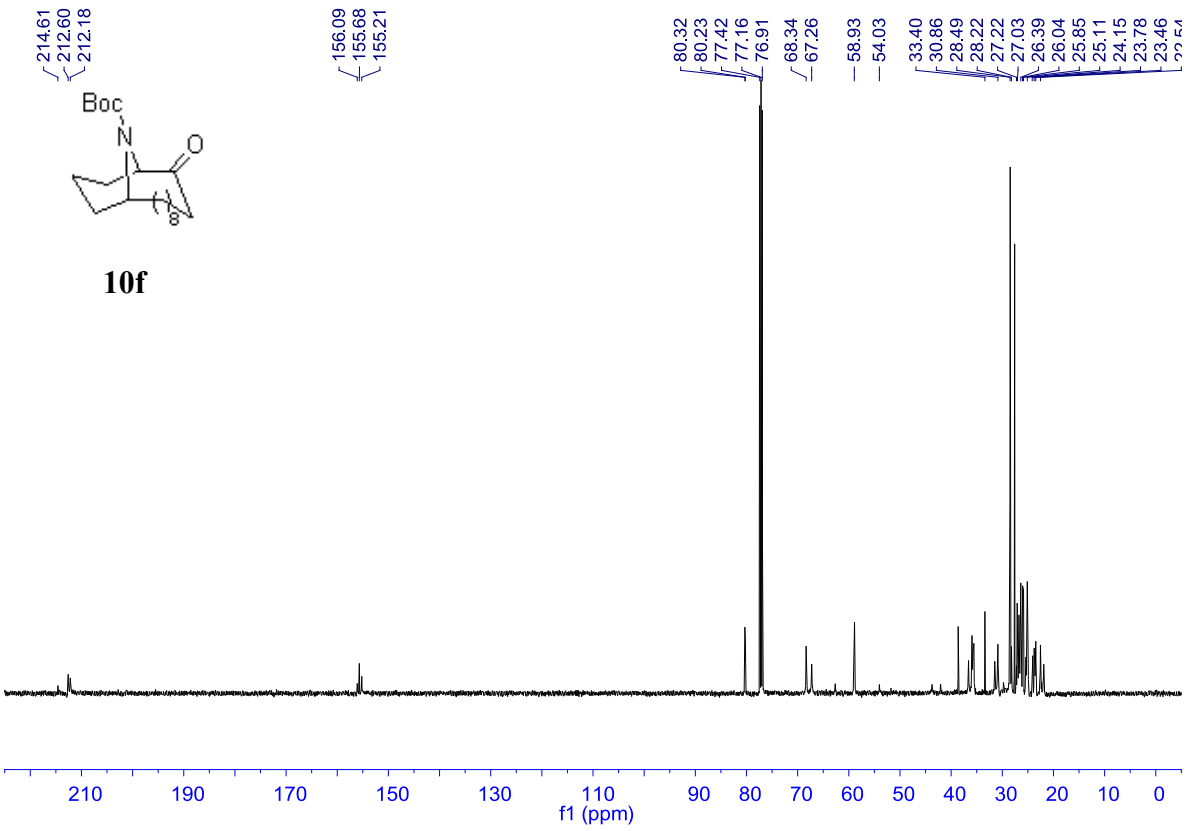
10e


210.60
156.28
80.30
77.48
77.16
76.84
67.42
66.18
58.98
37.12
36.02
30.14
29.83
29.43
28.60
27.35
27.07
24.17
23.99
23.48
23.18
22.18
21.14
Boc
N
O
5
40
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

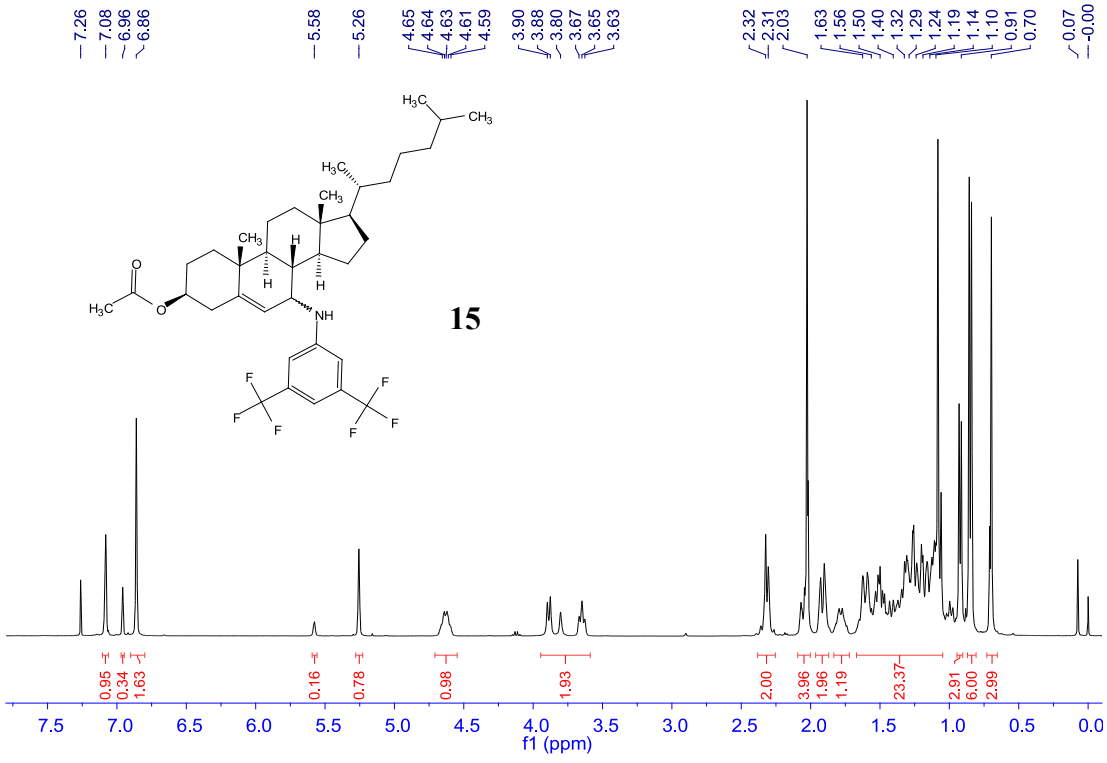
10e


7.26
4.21
4.19
4.18
4.14
4.13
4.11
4.06
4.05
4.03
2.70
2.69
2.68
2.67
2.66
2.35
2.06
1.94
1.84
1.62
1.59
1.52
1.39
1.32
1.24
1.18
1.14
-0.04
Boc
N
O
8
1.81
0.96
0.87
1.00
2.13
2.30
15.34
11.40
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)

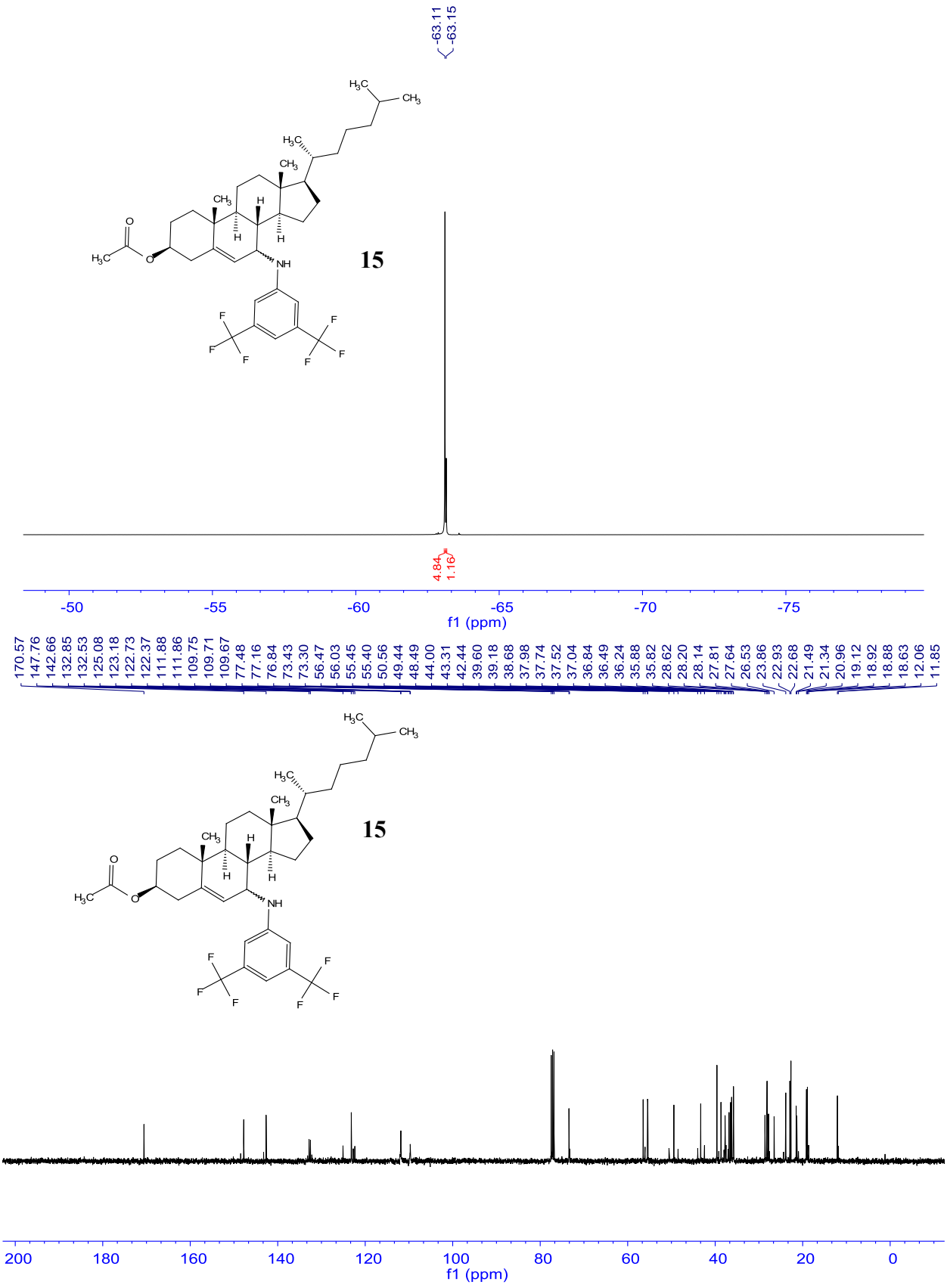
10f

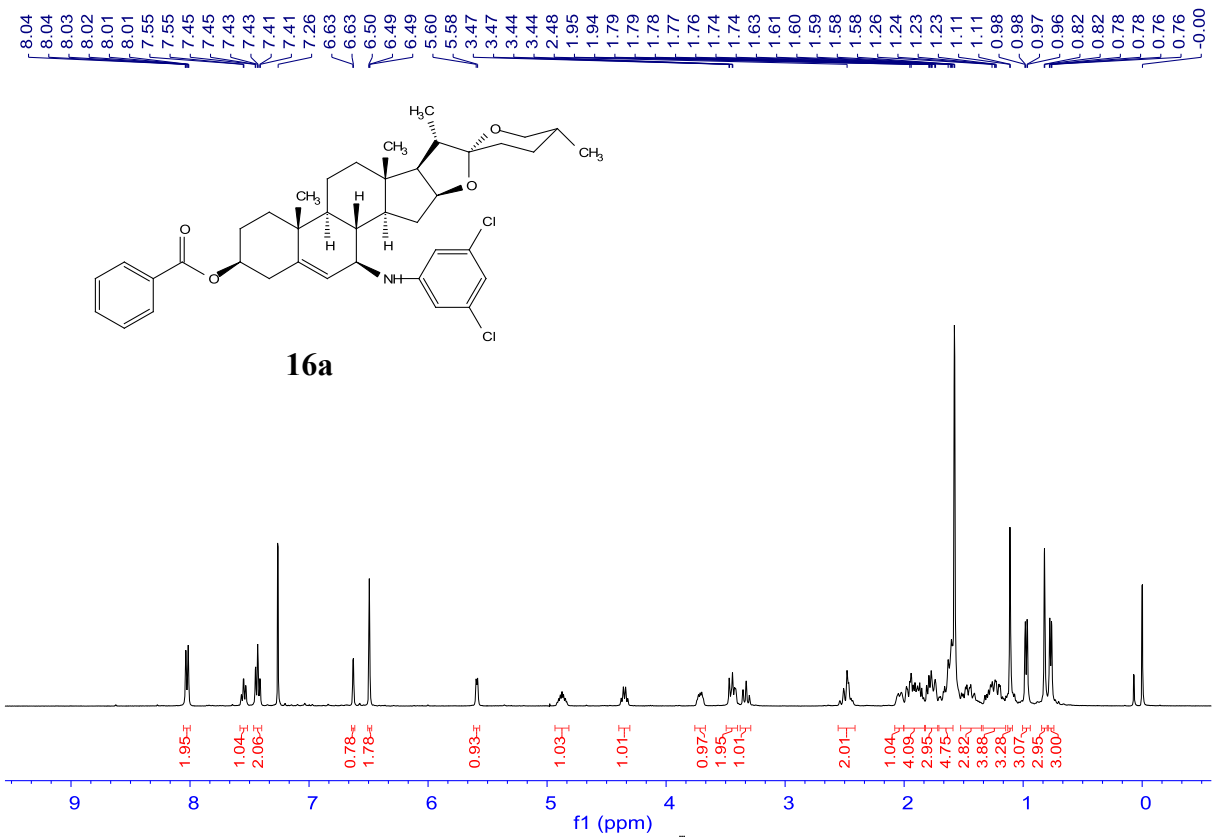

214.61
212.60
212.18
156.09
155.68
155.21
80.32
80.23
77.42
77.16
76.91
68.34
67.26
58.93
54.03
33.40
30.86
28.49
28.22
27.22
27.03
26.39
26.04
25.85
25.11
24.15
23.78
23.46
Boc
N
O
8
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

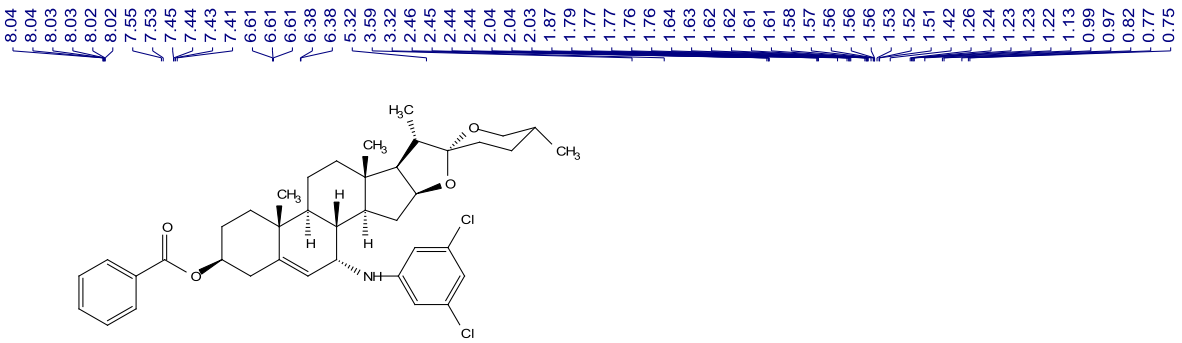
10f


7.26
7.08
6.96
6.86
5.58
5.26
4.65
4.64
4.63
4.61
4.59
3.90
3.88
3.80
3.67
3.65
3.63
2.32
2.31
2.03
1.63
1.56
1.50
1.40
1.32
1.29
1.24
1.19
1.14
1.10
0.91
0.70
0.07
-0.00
H3C
CH3
H3C
CH3
CH3
H
H
H
O
H3C
O
NH
F
F
F
F
F
F
0.95
0.34
1.63
0.16
0.78
0.98
1.93
2.00
3.96
1.96
1.19
23.37
2.91
6.00
2.99
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)

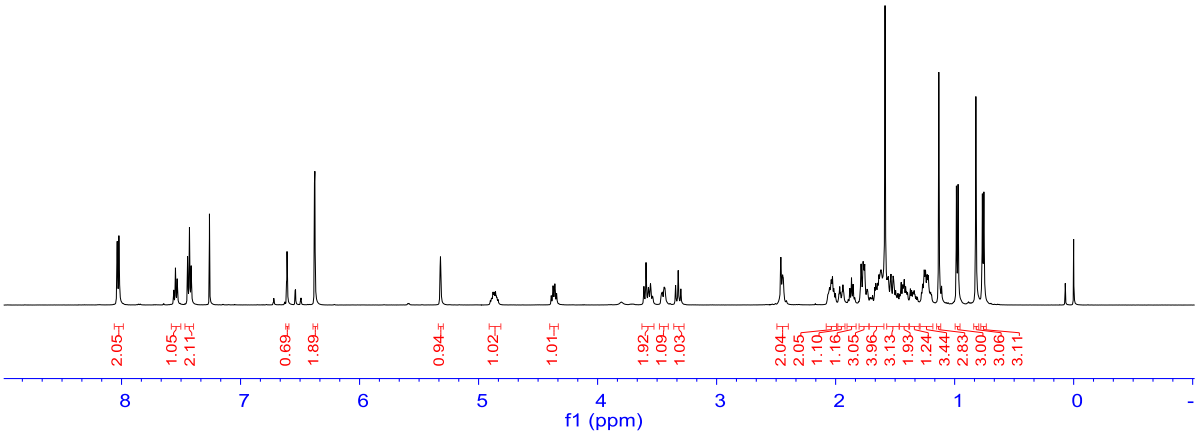
15

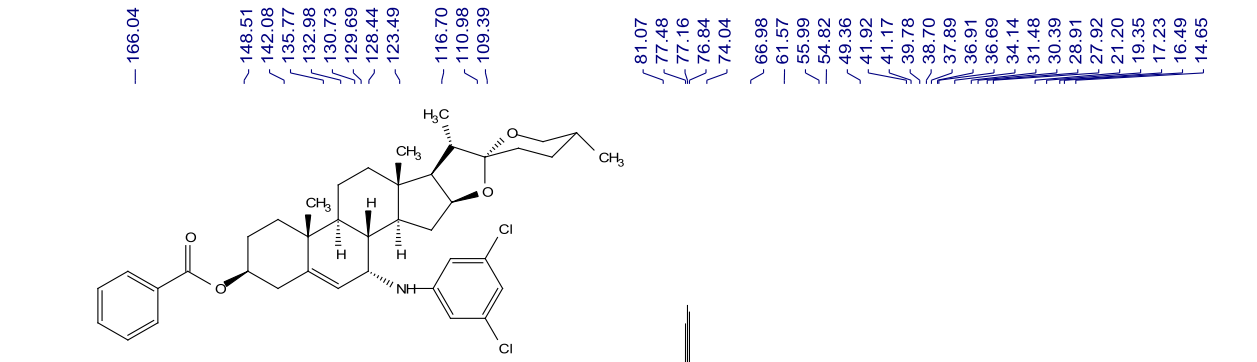

-63.11
-63.15
15
4.84
1.16
-50
-55
-60
-65
-70
-75
f1 (ppm)
170.57
147.76
142.66
132.85
132.53
125.08
123.18
122.73
122.37
111.88
111.86
109.75
109.71
109.67
77.48
77.16
76.84
73.43
73.30
56.47
56.03
55.45
55.40
50.56
49.44
48.49
44.00
43.31
42.44
39.60
39.18
38.68
37.98
37.74
37.52
37.04
36.84
36.49
36.24
35.88
35.82
28.62
28.20
28.14
27.81
27.64
26.53
23.86
22.93
22.68
21.49
21.34
20.96
19.12
18.92
18.88
18.63
12.06
11.85
15
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.04 8.04 8.03 8.02 8.01 8.01 7.55 7.55 7.45 7.45 7.43 7.43 7.41 7.41 7.26 6.63 6.63 6.50 6.49 6.49 5.60 5.58 3.47 3.47 3.44 3.44 2.48 1.95 1.94 1.79 1.79 1.78 1.77 1.76 1.74 1.74 1.63 1.61 1.60 1.59 1.58 1.58 1.26 1.24 1.23 1.23 1.11 1.11 0.98 0.98 0.97 0.96 0.82 0.82 0.78 0.78 0.76 0.76 -0.00
H3C
CH3
O
CH3
O
CH3
H
O
H
H
Cl
O
NH
Cl
16a
1.95 1.04 2.06 0.78 1.78 0.93 1.03 1.01 0.97 1.95 1.01 2.01 1.04 4.09 2.95 4.75 2.82 3.88 3.28 3.07 2.95 3.00
9 8 7 6 5 4 3 2 1 0
f1 (ppm)
166.02 149.42 142.79 135.79 133.00 130.70 129.69 128.45 123.41 117.09 111.28 109.38
80.69 77.48 77.16 76.84 73.87 66.96 62.14 50.32 48.84 44.03 41.81 40.35 39.33 38.07 37.60 37.10 35.59 31.98 31.54 30.43 28.94 27.78 20.88 18.73 17.25 16.37 14.71
H3C
CH3
O
CH3
O
CH3
H
O
H
H
Cl
O
NH
Cl
16a
180 160 140 120 100 80 60 40 20 0
f1 (ppm)

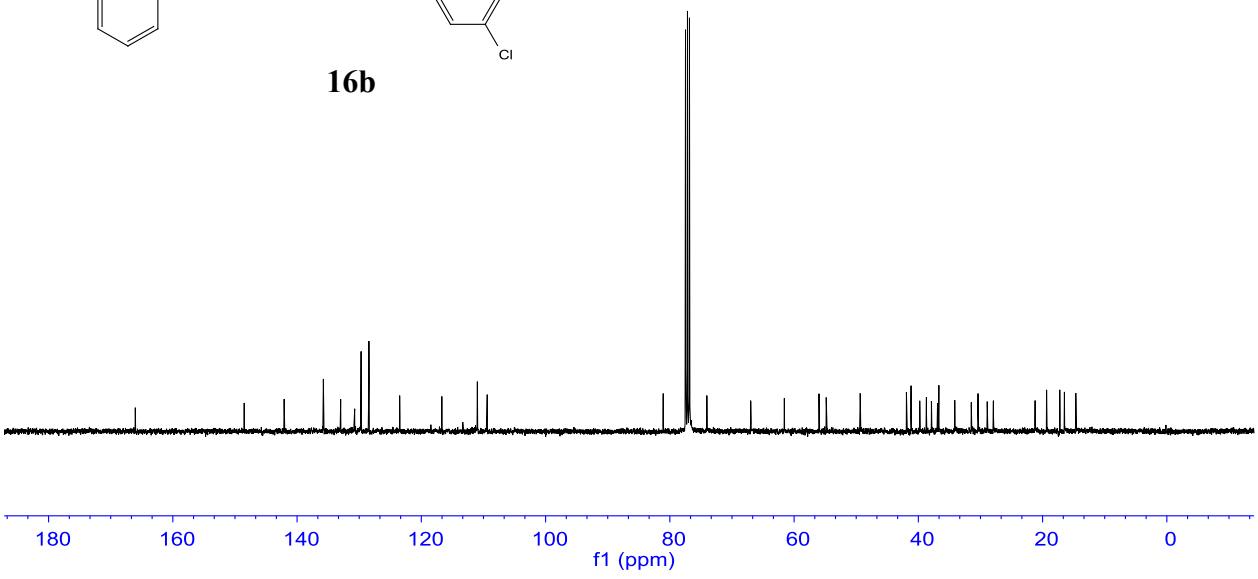


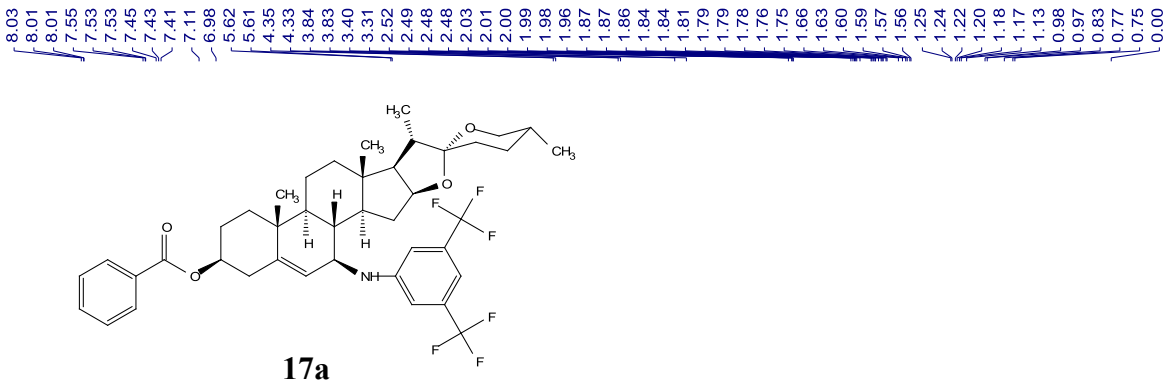
16b





16b





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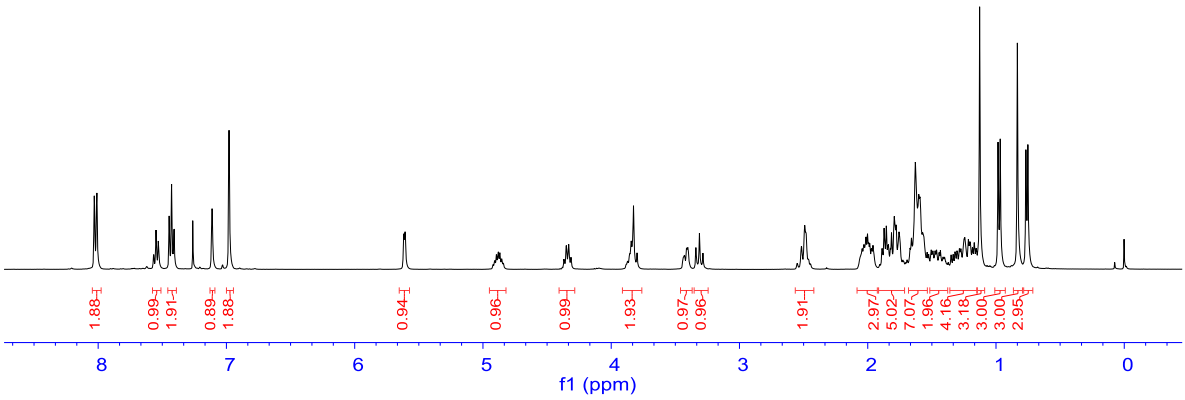
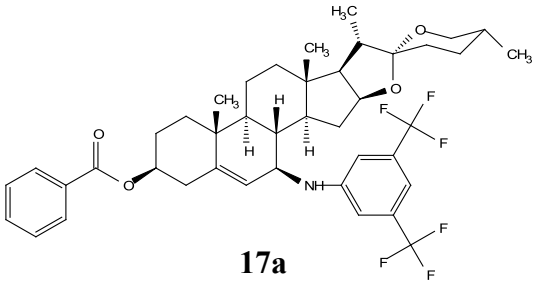
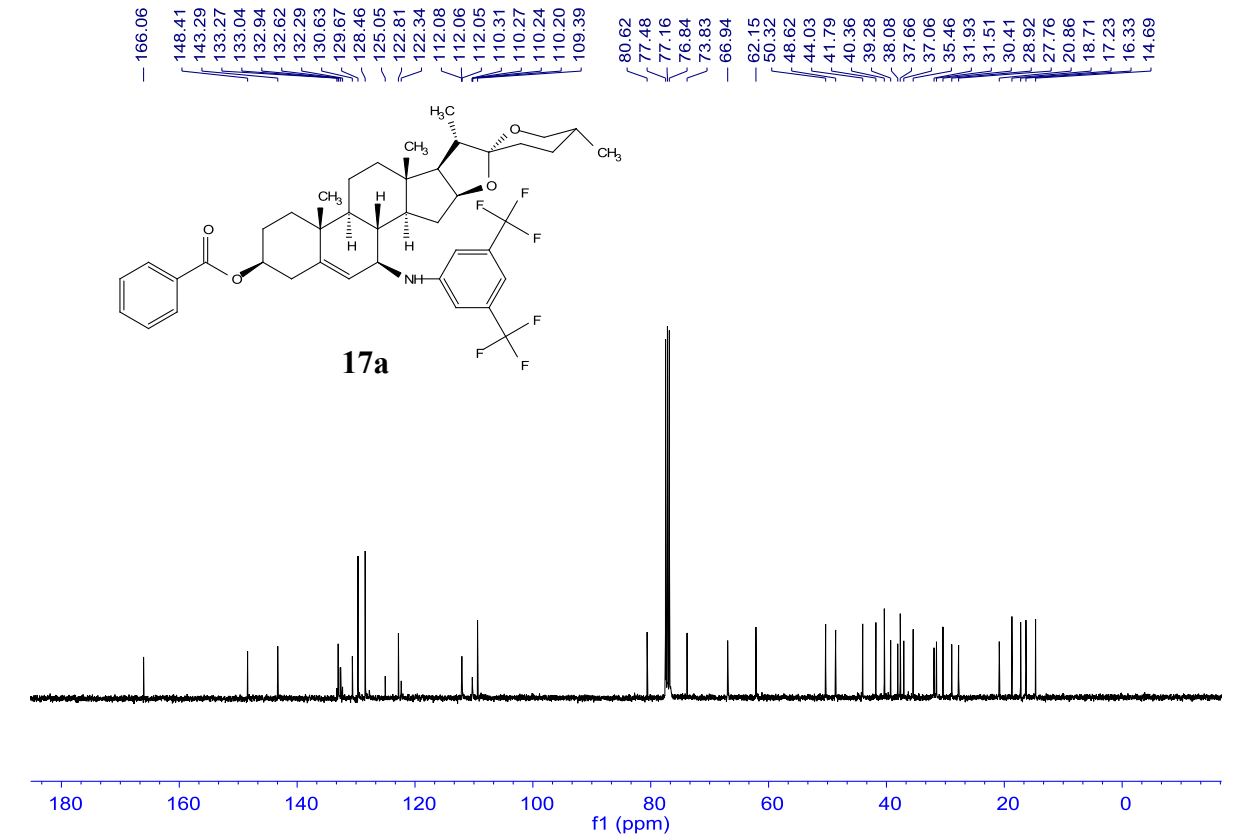
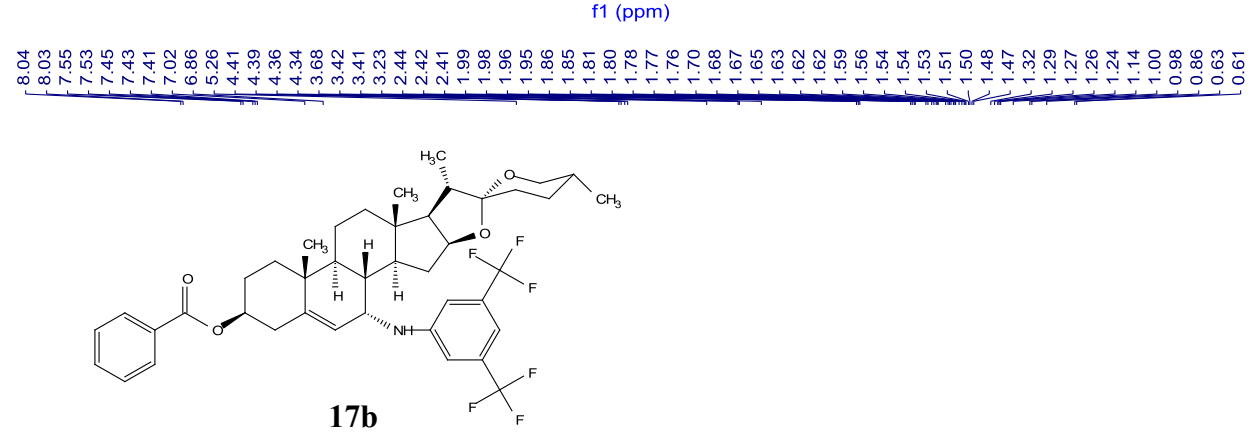




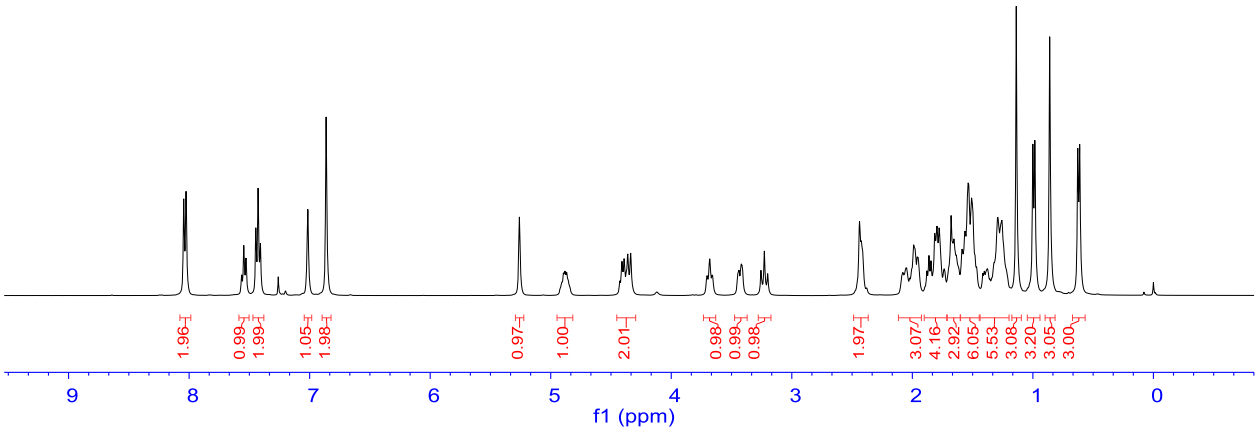
17a

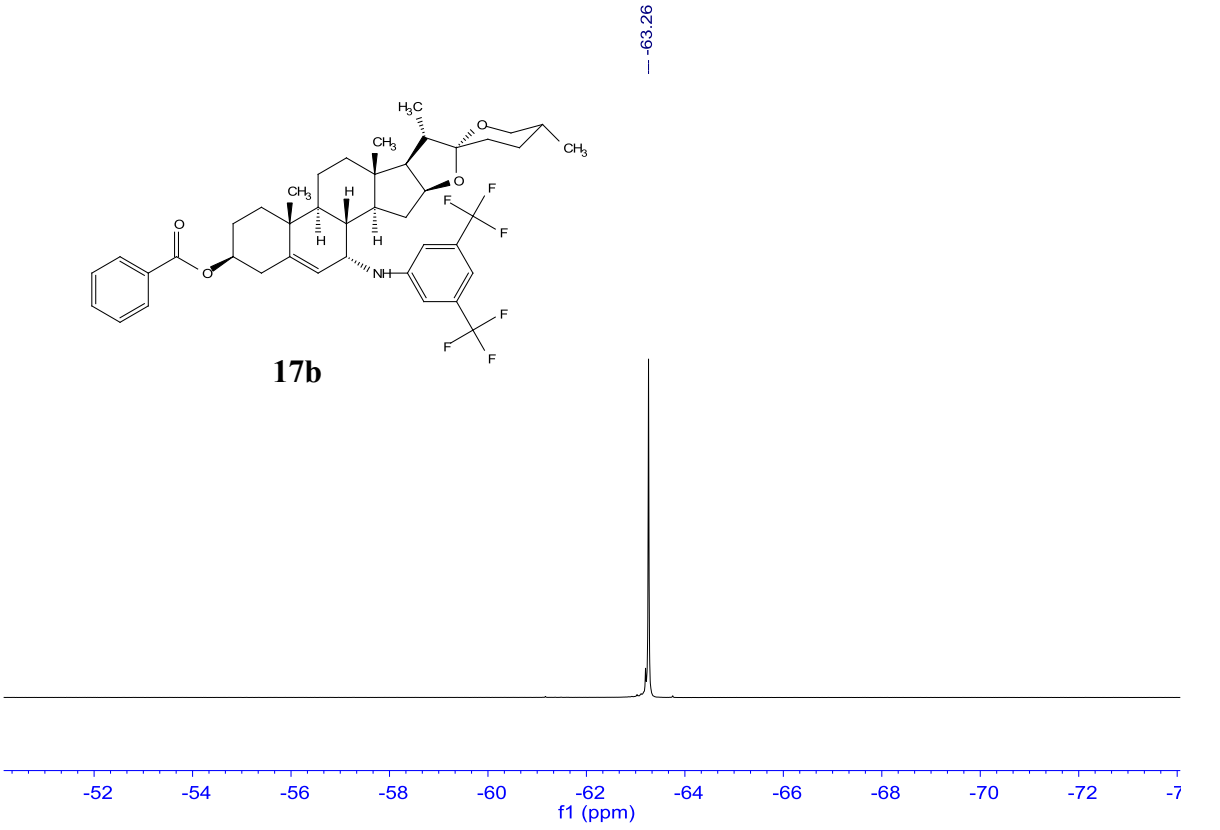

166.06
148.41
143.29
133.27
133.04
132.94
132.62
132.29
130.63
129.67
128.46
125.05
122.81
122.34
112.08
112.06
112.05
110.31
110.27
110.24
110.20
109.39
80.62
77.48
77.16
76.84
73.83
66.94
62.15
50.32
48.62
44.03
41.79
40.36
39.28
38.08
37.66
37.06
35.46
31.93
31.51
30.41
28.92
27.76
20.86
18.71
17.23
16.33
14.69
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

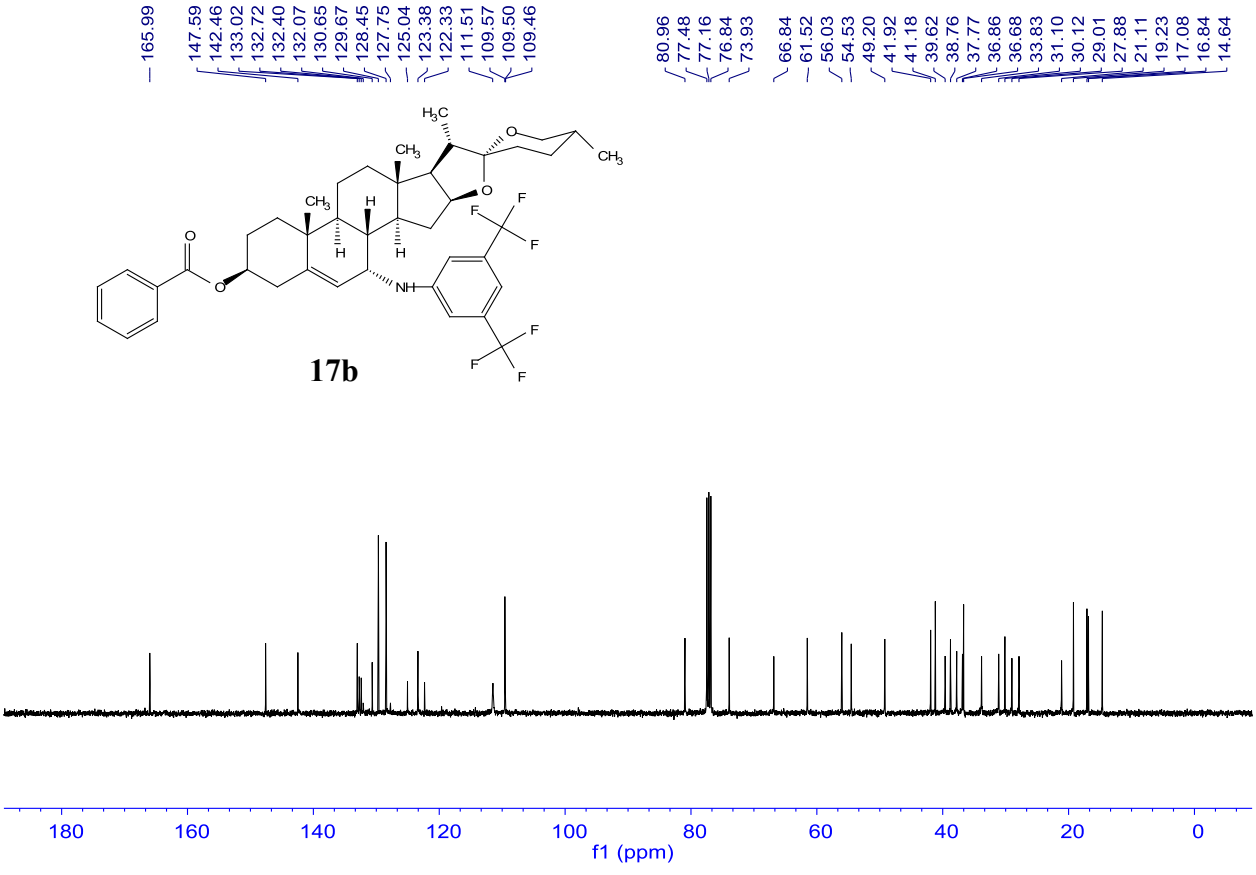
17a

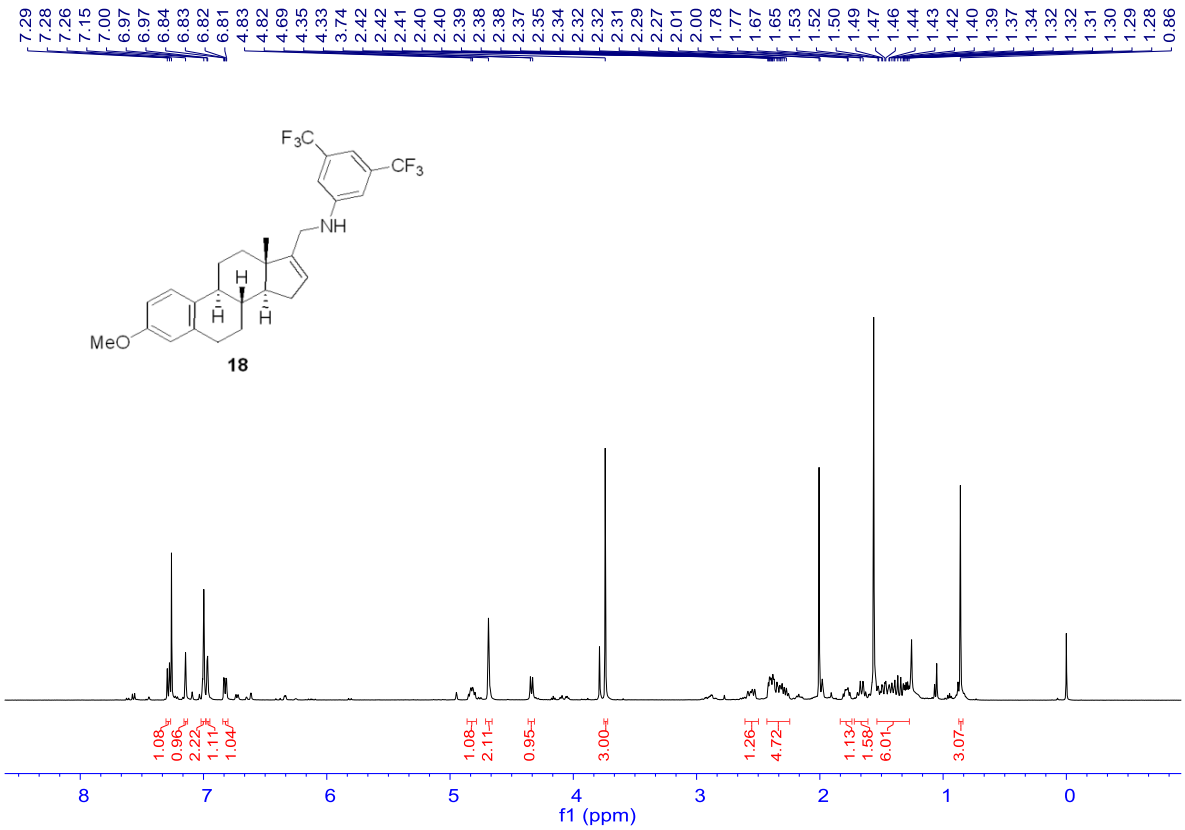

8.04
8.03
7.55
7.53
7.45
7.43
7.41
7.02
6.86
5.26
4.41
4.39
4.36
4.34
3.68
3.42
3.41
3.23
2.44
2.42
2.41
1.99
1.98
1.96
1.95
1.86
1.85
1.81
1.80
1.78
1.77
1.76
1.70
1.68
1.67
1.65
1.63
1.62
1.62
1.59
1.56
1.54
1.54
1.53
1.51
1.50
1.48
1.47
1.32
1.29
1.27
1.26
1.24
1.14
1.00
0.98
0.86
0.63
0.61

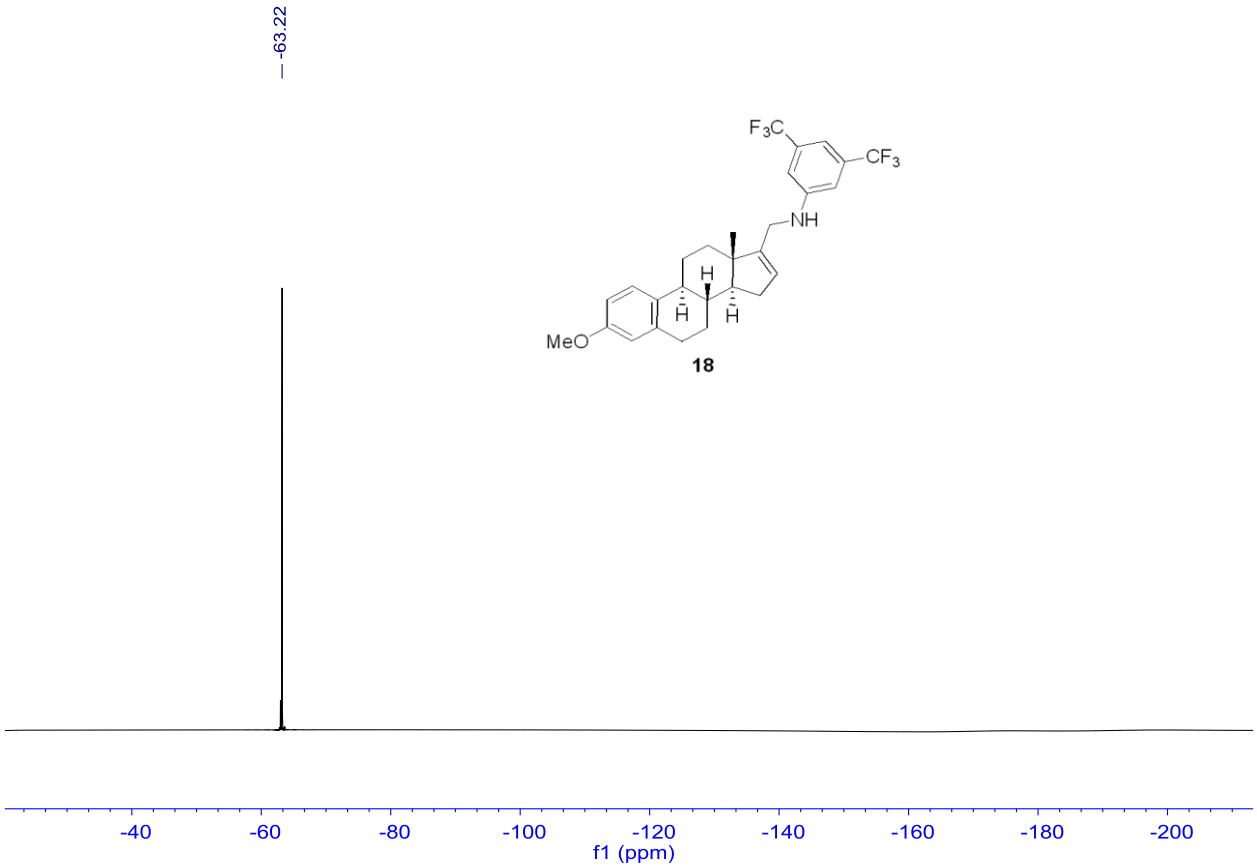
17b

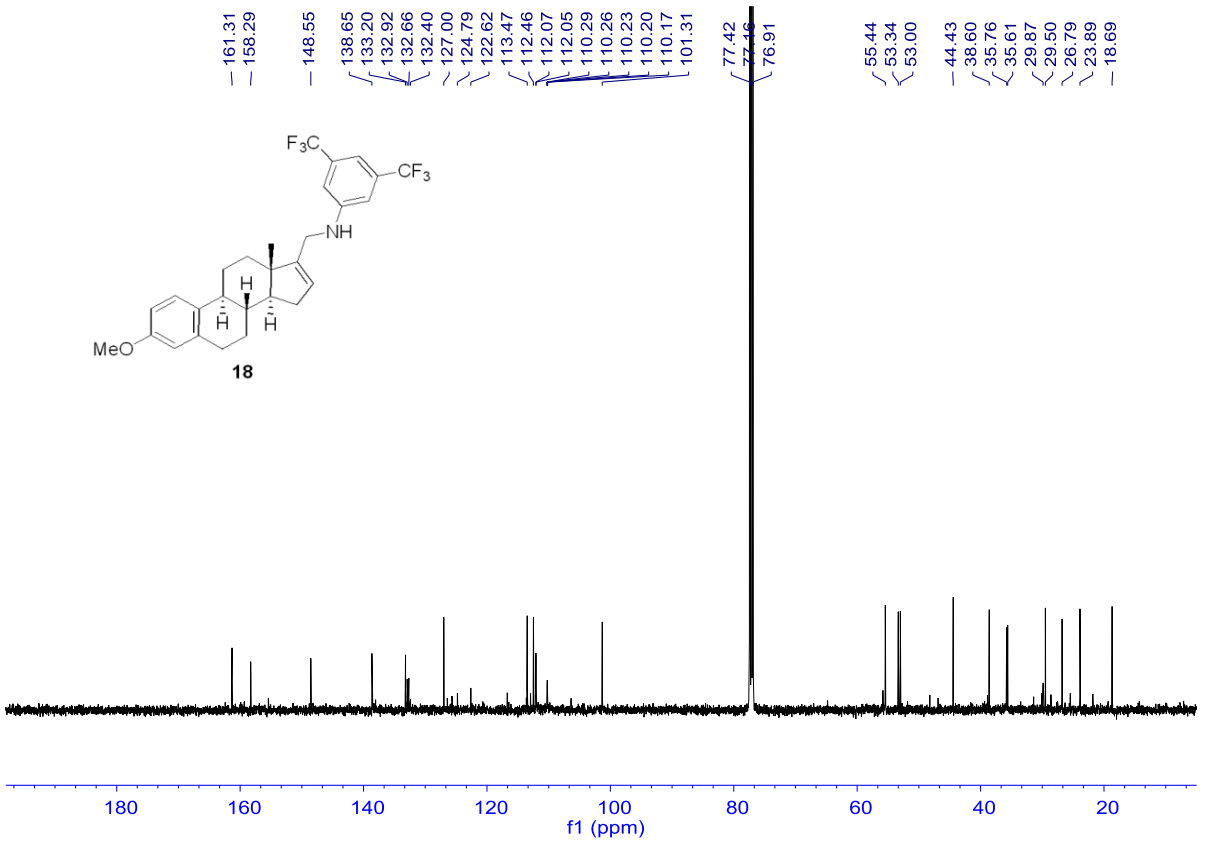

1.96
0.99
1.99
1.05
1.98
0.97
1.00
2.01
0.98
0.99
0.98
1.97
3.07
4.16
2.92
6.05
5.53
3.08
3.20
3.05
3.00
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


-63.26
17b
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-7
f1 (ppm)

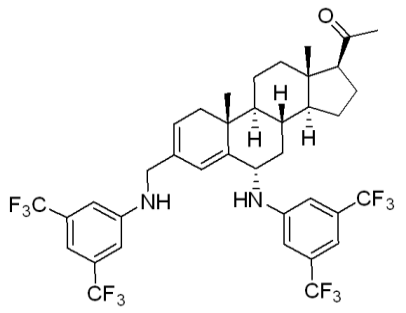

165.99
147.59
142.46
133.02
132.72
132.40
132.07
130.65
129.67
128.45
127.75
125.04
123.38
122.33
111.51
109.57
109.50
109.46
80.96
77.48
77.16
76.84
73.93
66.84
61.52
56.03
54.53
49.20
41.92
41.18
39.62
38.76
37.77
36.86
36.68
33.83
31.10
30.12
29.01
27.88
21.11
19.23
17.08
16.84
14.64
17b
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

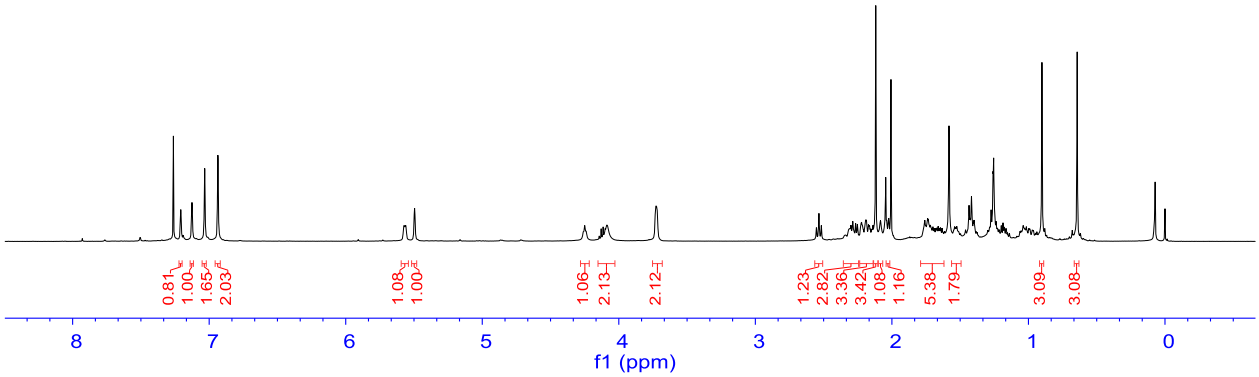

7.29 7.28 7.26 7.15 7.00 6.97 6.97 6.84 6.83 6.82 6.81 4.83 4.82 4.69 4.35 4.33 3.74 2.42 2.42 2.41 2.40 2.40 2.39 2.38 2.38 2.37 2.35 2.34 2.32 2.32 2.31 2.29 2.27 2.01 2.00 1.78 1.77 1.67 1.65 1.53 1.52 1.50 1.49 1.47 1.46 1.44 1.43 1.42 1.40 1.39 1.37 1.34 1.32 1.32 1.31 1.30 1.29 1.28 0.86
F3C
CF3
NH
H
H
H
MeO
18
1.08 0.96 2.22 1.11 1.04 1.08 2.11 0.95 3.00 1.26 4.72 1.13 1.58 6.01 3.07
8 7 6 5 4 3 2 1 0
f1 (ppm)

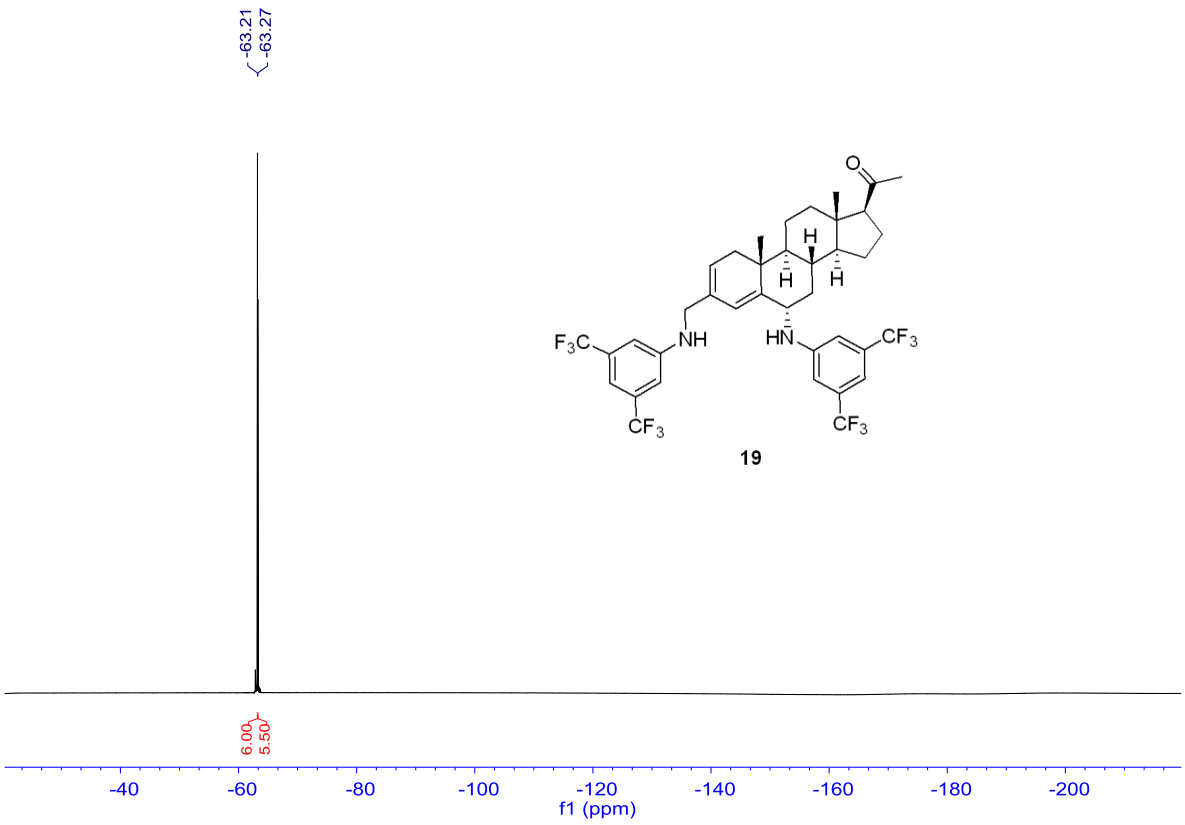

-63.22
F3C
CF3
NH
H
H
H
MeO
18
-40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

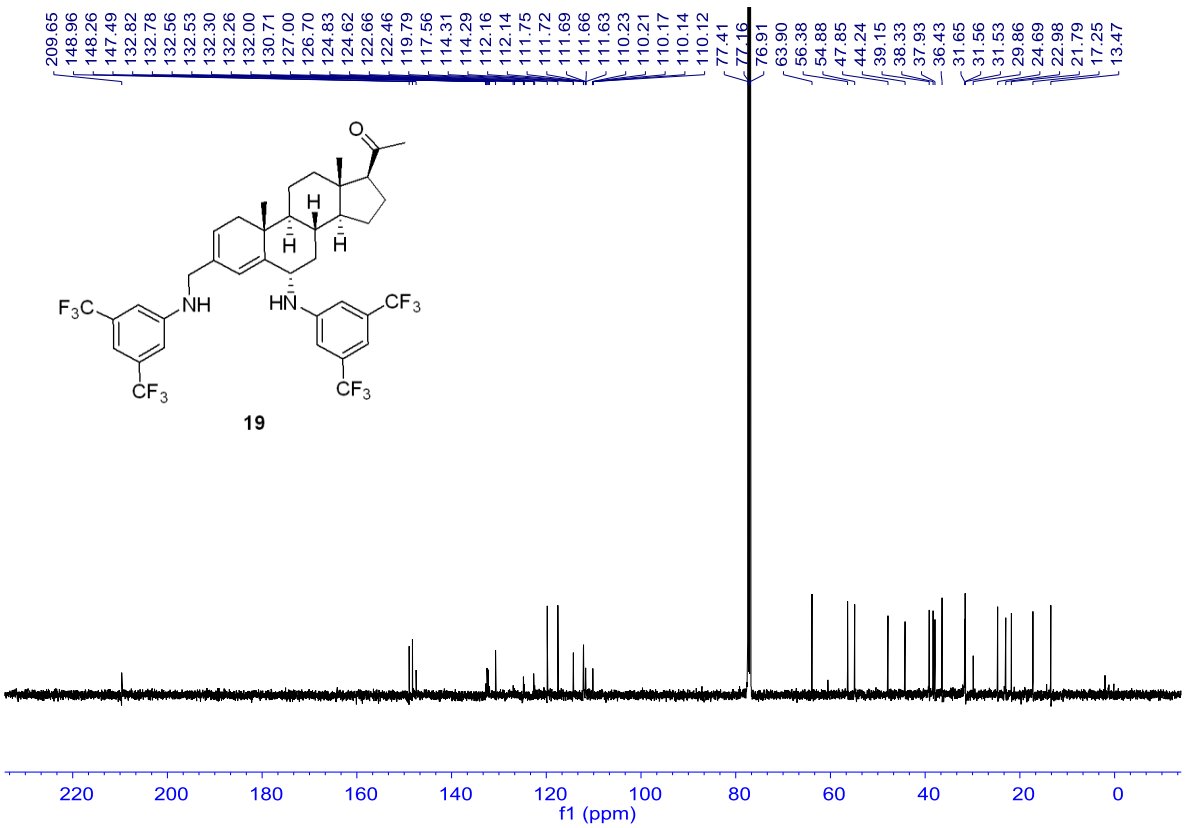

161.31
158.29
148.55
138.65
133.20
132.92
132.66
132.40
127.00
124.79
122.62
113.47
112.46
112.07
112.05
110.29
110.26
110.23
110.20
110.17
101.31
77.42
77.16
76.91
55.44
53.34
53.00
44.43
38.60
35.76
35.61
29.87
29.50
26.79
23.89
18.69
F3C
CF3
NH
H
H
H
MeO
18
180
160
140
120
100
80
60
40
20
f1 (ppm)

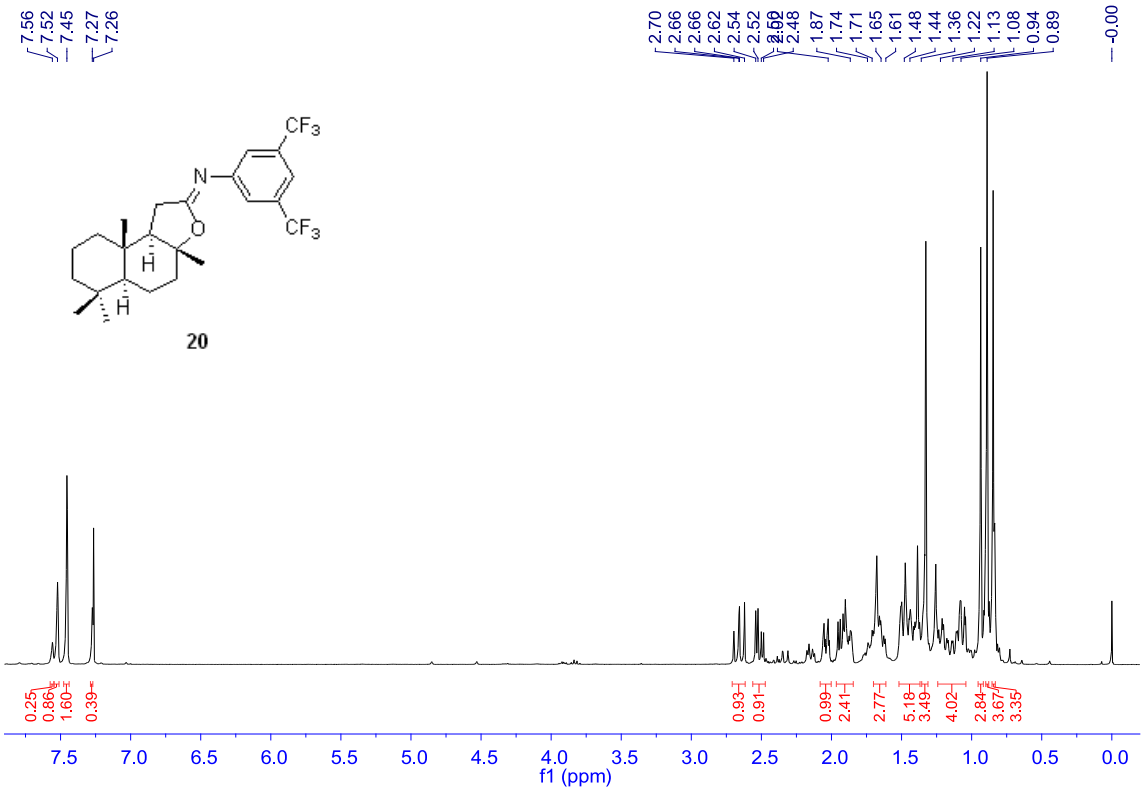

7.26
7.21
7.13
7.03
6.94
5.56
5.50
5.50
5.49
4.09
3.73
3.73
3.72
2.53
2.30
2.29
2.27
2.25
2.22
2.22
2.22
2.19
2.19
2.19
2.17
2.13
2.12
2.08
2.05
2.05
2.04
2.03
2.02
2.01
1.76
1.76
1.74
1.74
1.73
1.73
1.72
1.58
1.44
1.43
1.42
1.40
1.40
1.27
1.26
1.25
1.25
1.25
1.24
1.19
0.90
0.64
0.08
0.07
-0.00

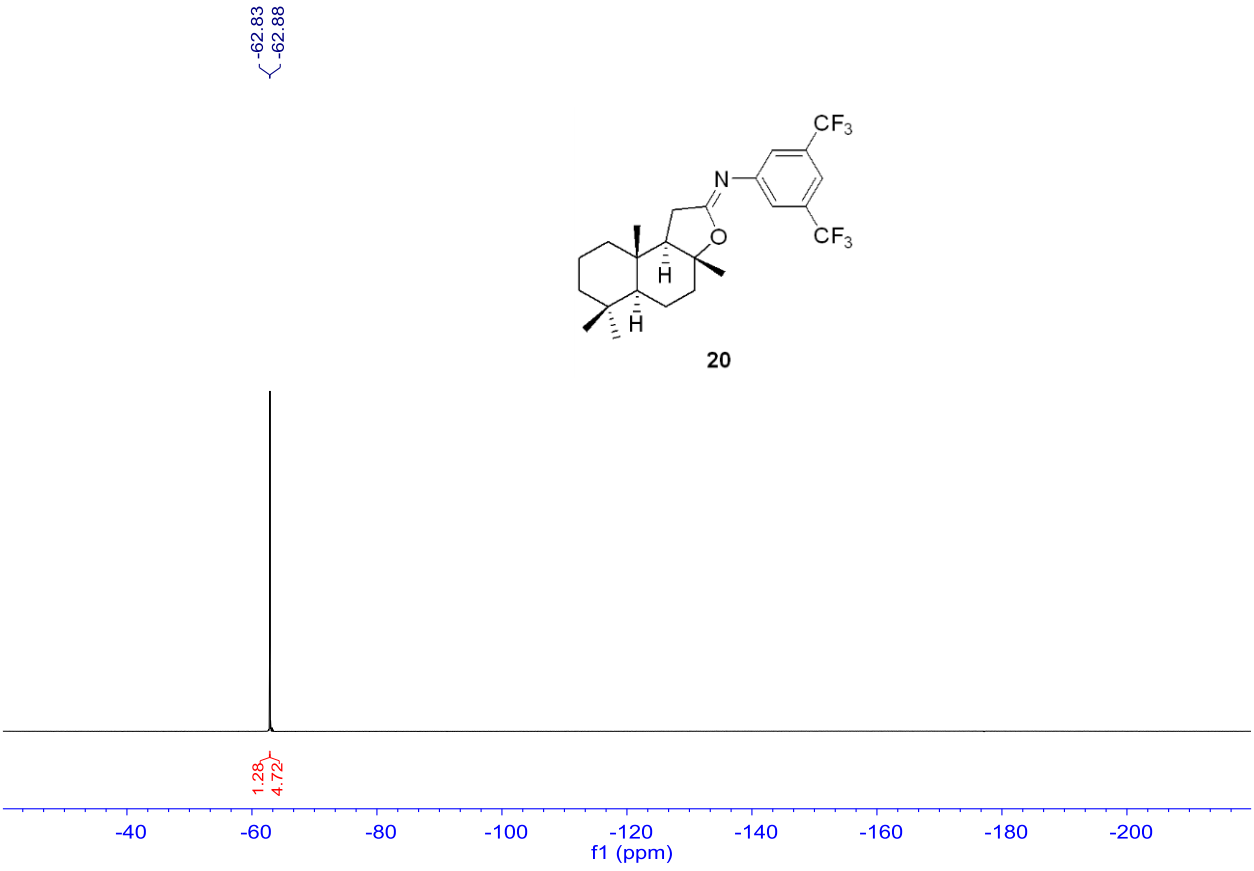

O
H
H
H
F3C
NH
HN
CF3
CF3
CF3
19


0.81
1.00
1.65
2.03
1.08
1.00
1.06
2.13
2.12
1.23
2.82
3.36
3.42
1.08
1.16
5.38
1.79
3.09
3.08
8
7
6
5
4
3
2
1
0
f1 (ppm)


-63.21
-63.27
6.00
5.50
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)
F3C
NH
HN
CF3
CF3
CF3
O
H
H
H
19


209.65
148.96
148.26
147.49
132.82
132.78
132.56
132.53
132.30
132.26
132.00
130.71
127.00
126.70
124.83
124.62
122.66
122.46
119.79
117.56
114.31
114.29
112.16
112.14
111.75
111.72
111.69
111.66
111.63
110.23
110.21
110.17
110.14
110.12
77.41
77.16
76.91
63.90
56.38
54.88
47.85
44.24
39.15
38.33
37.93
36.43
31.65
31.56
31.53
29.86
24.69
22.98
21.79
17.25
13.47
F3C
NH
HN
CF3
CF3
CF3
O
H
H
H
19
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.56
7.52
7.45
7.27
7.26
2.70
2.66
2.66
2.62
2.54
2.52
2.48
1.87
1.74
1.71
1.65
1.61
1.48
1.44
1.36
1.22
1.13
1.08
0.94
0.89
0.00
CF3
CF3
N
O
H
H
20
0.25
0.86
1.60
0.39
0.93
0.91
0.99
2.41
2.77
5.18
3.49
4.02
2.84
3.67
3.35
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)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-62.88
CF3
CF3
N
O
H
H
20
1.28
4.72
-40
-60
-80
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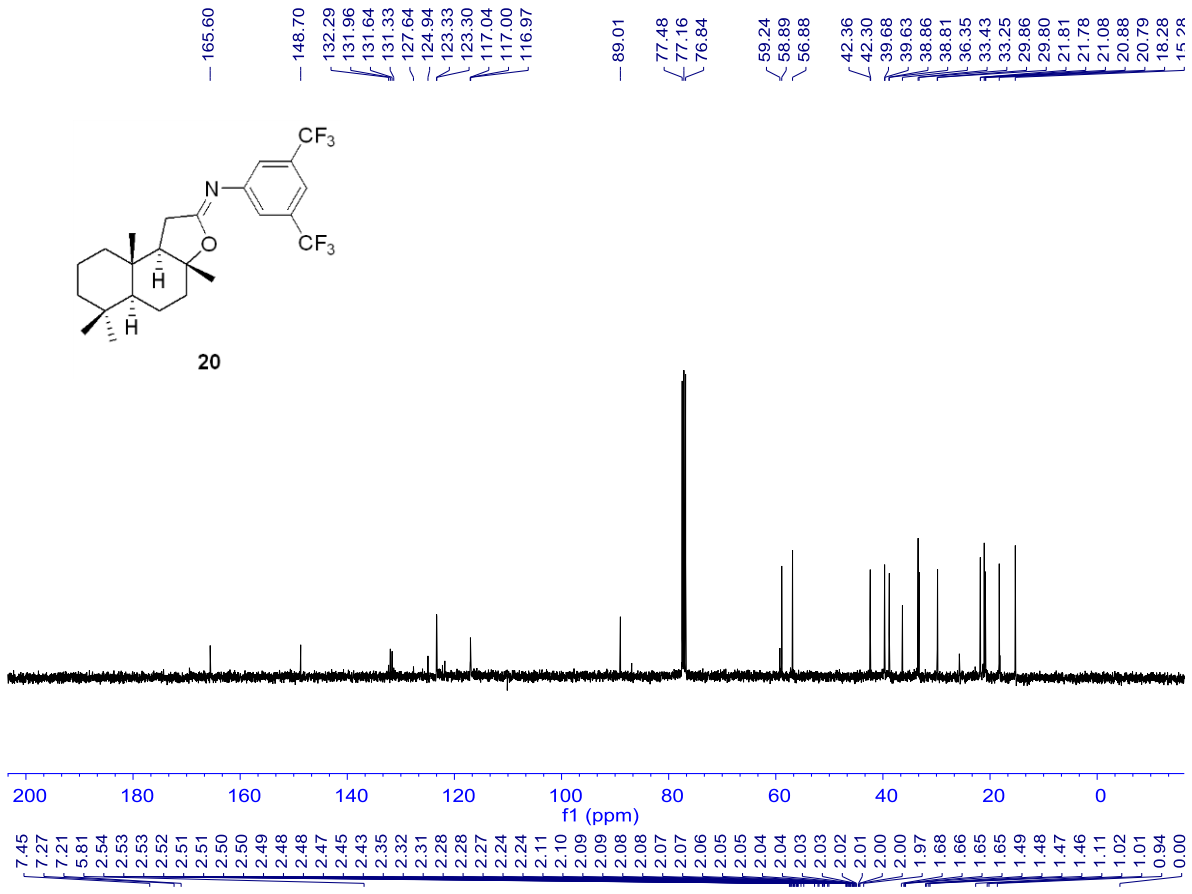
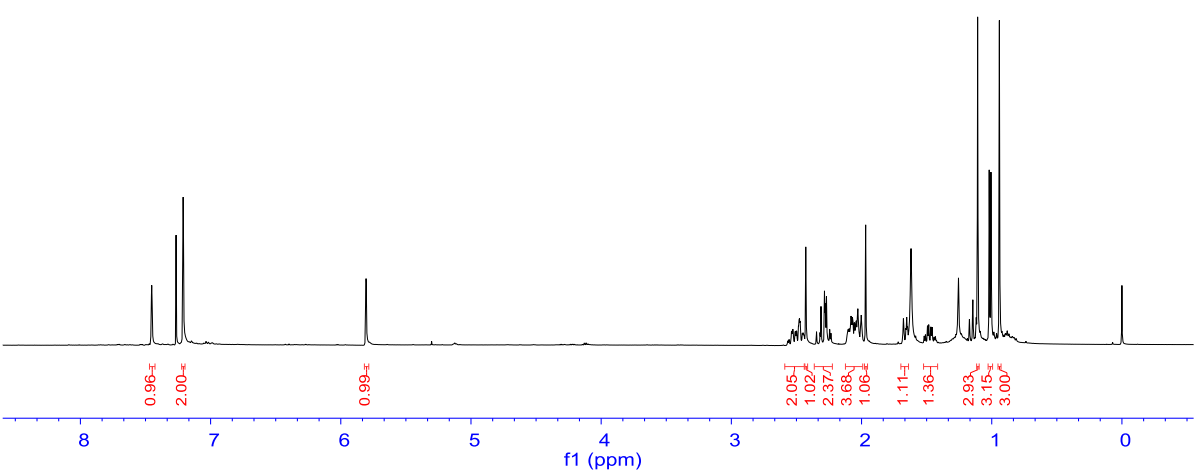
-120
-140
-160
-180
-200
f1 (ppm)


165.60
148.70
132.29
131.96
131.64
131.33
127.64
124.94
123.33
123.30
117.04
117.00
116.97
89.01
77.48
77.16
76.84
59.24
58.89
56.88
42.36
42.30
39.68
39.63
38.86
38.81
36.35
33.43
33.25
29.86
29.80
21.81
21.78
21.08
20.88
20.79
18.28
CF3
CF3
N
O
H
H
20
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.27
7.21
5.81
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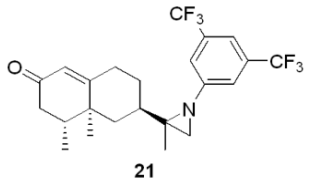
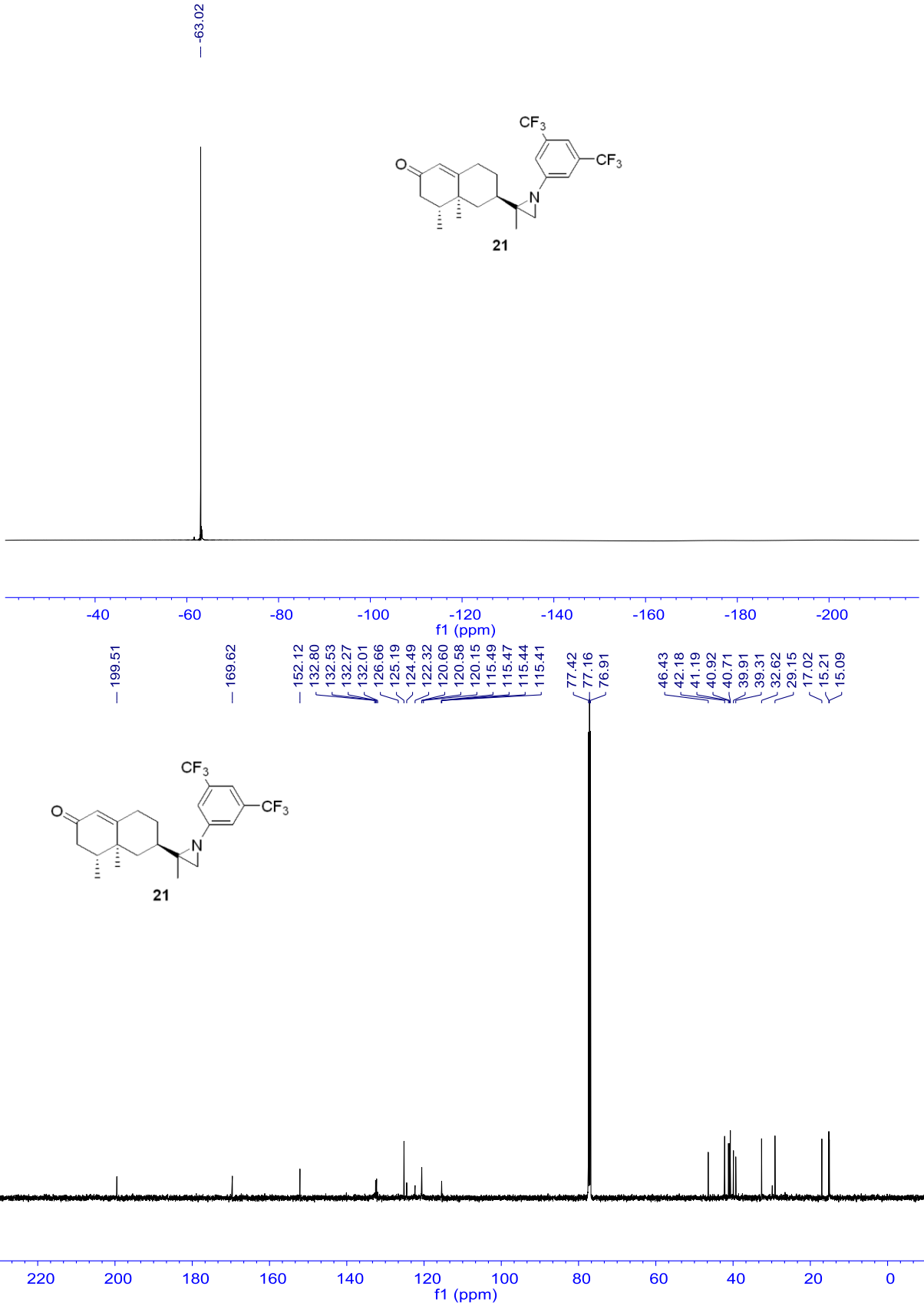
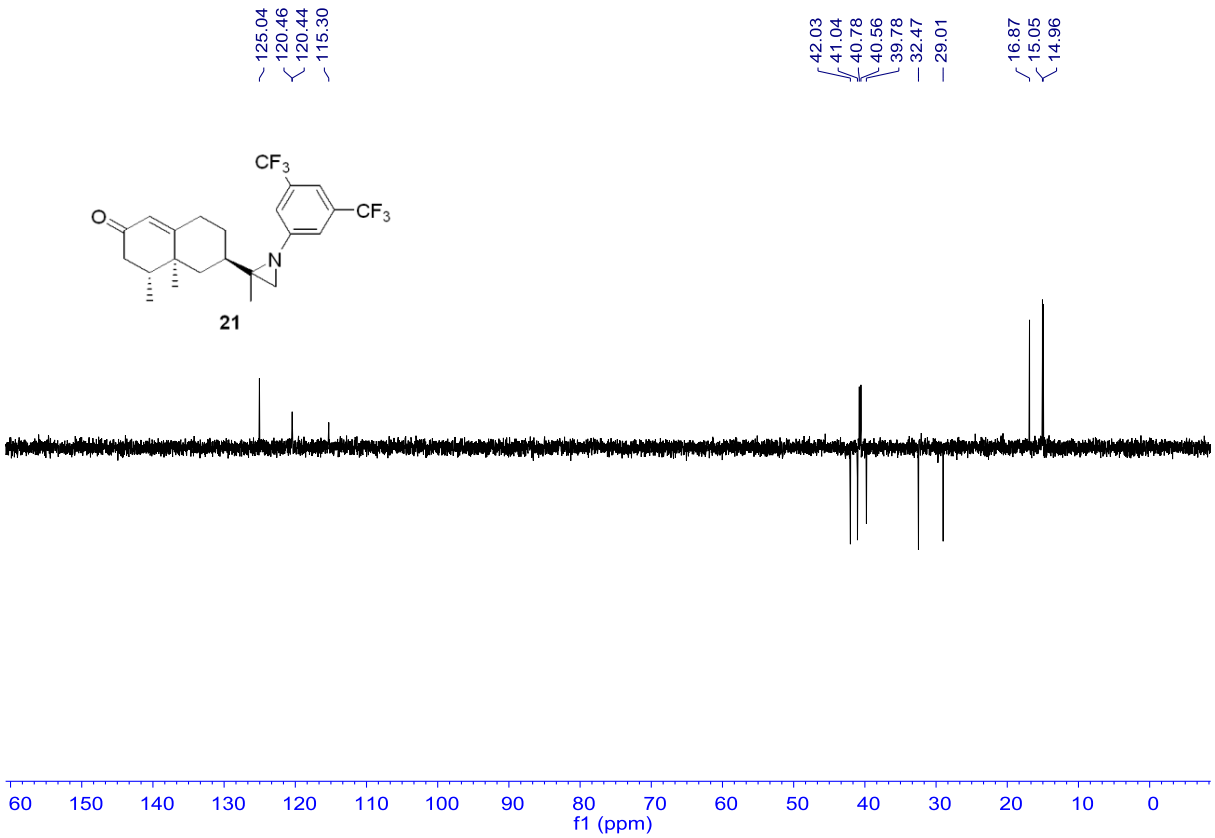
2.53
2.53
2.52
2.51
2.51
2.50
2.50
2.49
2.48
2.48
2.47
2.45
2.43
2.35
2.32
2.31
2.28
2.28
2.27
2.24
2.24
2.11
2.10
2.09
2.09
2.08
2.08
2.07
2.07
2.06
2.05
2.05
2.04
2.04
2.03
2.03
2.02
2.01
2.00
2.00
1.97
1.68
1.66
1.65
1.65
1.49
1.48
1.47
1.46
1.11
1.02
1.01
0.94
0.00


CF3
CF3
O
N
21

0.96
2.00
0.99
2.05
1.02
2.37
3.68
1.06
1.11
1.36
2.93
3.15
3.00
8
7
6
5
4
3
2
1
0
f1 (ppm)


-63.02
CF3
CF3
O
N
21
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)
199.51
169.62
152.12
132.80
132.53
132.27
132.01
126.66
125.19
124.49
122.32
120.60
120.58
120.15
115.49
115.47
115.44
115.41
77.42
77.16
76.91
46.43
42.18
41.19
40.92
40.71
39.91
39.31
32.62
29.15
17.02
15.21
15.09
CF3
CF3
O
N
21
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


125.04
120.46
120.44
115.30
42.03
41.04
40.78
40.56
39.78
32.47
29.01
16.87
15.05
14.96
CF3
CF3
O
N
21
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)