Supporting Information

Heterocyclic Group Transfer Reactions with I(III) *N*-HVI Reagents: Diverse Pyridinium Salts via Metal-Free Olefin Aminolactonization

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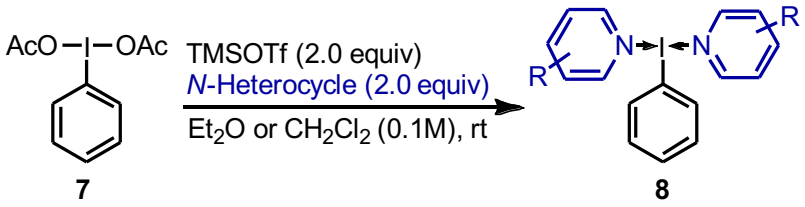
Section A. Instrumentation and General Considerations

^{1}H and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz on a Bruker Advance 500, 500 MHz and 125 MHz on a Bruker Advance III HD, or 400 MHz and 100 MHz on a Bruker Advance 400. ^{1}H NMR chemical shifts were reported in part per million (ppm) from the solvent resonance ($CDCl_3$ 7.26 ppm, CD_3CN 1.96 ppm). The data was reported as follows: chemical shift number, multiplicity (s = singlet, d = doublet, t = triplet, sept = septet, dd = doublet of doublets, td = triplet of doublets, m = multiplet, br = broad signal). Proton decoupled attached proton test (APT) ^{13}C NMR shifts were reported in ppm from the solvent resonance [$CDCl_3$ 77.16 ppm, CD_3CN 1.32 ppm (CD_3CN)]. The reaction solvents used were anhydrous (HPLC-grade solvent passed through an activated-alumina column), unless otherwise noted.

Septum sealed bottles of anhydrous pyridine and *n*-BuLi were purchased from Sigma-Aldrich and Acros, respectively, and used without any further purification. Diisopropylamine [(iPr)$_2$NH] was purchased from Oakwood Chemical and freshly distilled over CaH_2 directly before use. *N*-bromosuccinimide (NBS) was purchased from Oakwood Chemical and recrystallized directly before use. All deuterated solvents were purchased from Cambridge Isotope Laboratories (CIL) and stored over activated 5 Å molecular sieves. All other reagents were purchased from Sigma-Aldrich (now Millipore Sigma), Fisher Chemical, Oakwood Chemical, and used without further purification.

Flash chromatography was carried out using Sorbent Technologies silica gel 60 Å (40–63 μm) in the solvent system listed in the individual experiments. The reactions were monitored using analytical thin-layer chromatography (TLC) on Merck silica gel (60 F254) plates. Accurate masses for derivatized products were conducted on an Agilent 6520 Accurate-Mass Q-TOF LC/MS. Samples were taken up in a suitable solvent for analysis. The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LCMS. Waters software calibrates the instruments, and reports measurements, by use of neutral atomic masses. The mass of the electron is not included. Infrared spectra were obtained using a Thermo Nicolet iS5 FTIR spectrometer with an iD5 ATR accessory. Melting points were obtained on a Standford Research Systems MPA100 OptiMelt Automated Melting Point System and are uncorrected.

Section B. Synthesis and Isolation of *N*-HVI Reagents



General Procedure A: Synthesis of *N*-HVIs with neutral or electron-rich heterocycles (N-HVIs 9, SI-1)

Reaction procedures are consistent with those previously reported by Weiss[1] and our laboratory.[2] A flame dried round-bottom flask is charged with (diacetoxyiodo)benzene (**7**) (1.0 equiv.) and fitted with a rubber septum followed by Et_2O (0.1 M) to generate a white suspension. Trimethylsilyl trifluoromethanesulfonate (2.0 equiv.) is then added over 10 seconds and the mixture stirred for 10 minutes to generate a clear, gray solution. The heterocycle (24 mmol, 2.0 equiv.) is then added at room temperature over 20 seconds and the mixture is allowed to stir for 15 minutes, over which the desired *N*-HVI forms as a white precipitate. The white solids are then collected via vacuum filtration on a Buchner funnel, the flask is rinsed with Et_2O, the solids are washed two times with Et_2O and quickly transferred to a pre-tared, flame-dried vial.

Notes: The synthesis and stability of individual N-HVI can vary slightly depending on the heterocycle used.

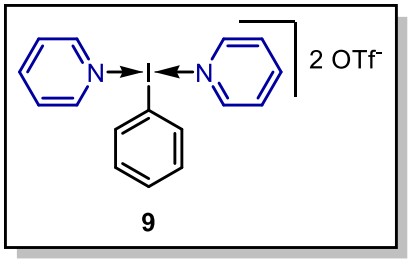
- *If the white precipitate is not observed after 15 minutes of stirring, allow to stir an additional 15 minutes. If no precipitate is formed cool the reaction down to 0 °C. Lastly, if no precipitate forms after cooling the reaction, evaporate approximately ¼ volume of the solvent off on high vacuum.*
- *The N-HVIs can be moisture sensitive. Filtrations can be performed on the bench however they should be performed quickly. If significant yellowing of the solid occurs, the reagent has likely formed an oxo-bridged dimer and should be remade.*
- *Our laboratory has found Et_2O to more reliably give clean N-HVIs, however if the N-HVI should be synthesized in CH_2Cl_2 as byproducts or incomplete conversion can result from incomplete solubilization.*

General Procedure B: Synthesis of *N*-HVIs with sterically hindered or electron-deficient heterocycles (*N*-HVI SI-2)

Reaction procedure is modified from that reported by Weiss, with only changes to the isolation procedure.[2] A flame dried round-bottomed flask is charged with (diacetoxyiodo)benzene (**7**) (1.0 equiv.) and fitted with a rubber septum, followed by CH_2Cl_2 (0.1 M) to generate a white suspension. Trimethylsilyl trifluoromethanesulfonate (2.0 equiv.) is then added over 10 seconds and the mixture stirred for 10 minutes to generate a clear, gray solution. The heterocycle (2.0 equiv.) is then added at room temperature over 20 seconds, the mixture stirred for 15 minutes.

The septa is taped with electrical tape and the reaction flask is transferred to a glovebox for filtration using a 4-5M glass fritted filter. The solid is then transferred to pre-weighed, single neck (24/40) 100 mL round bottom flask for drying. The flask is left under constant vacuum for one hour to give a free-flowing powder. The product can be transferred to a flame-dried 20 mL vial for storage in the glovebox.

1,1'-(phenyl-λ^3-iodanediyl)bis(pyridinium) trifluoromethanesulfonate (*Py*-HVI, 9).

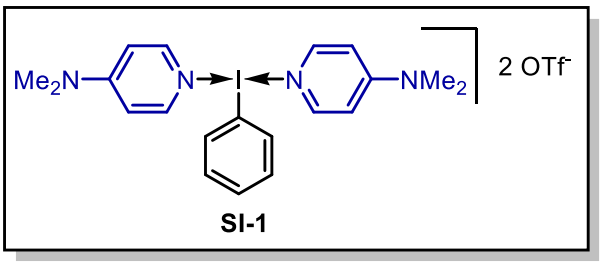


9

Prepared according to General Procedure A to give **9** (5.07 g, 62%) as a white solid after filtration. **^{1}H NMR** (500 MHz, 1:20 TFA:Chloroform-*d*) δ 8.85 (t, *J* = 6.7, 1.6 Hz, 4H), 8.62 (t, *J* = 7.9, 1.6 Hz, 2H), 8.24 – 8.21 (m, 2H), 8.09 (t, *J* = 8.1, 6.4, 1.5 Hz, 4H), 7.77 (t, 1H), 7.64 (t, 2H). **^{13}C NMR** (126 MHz, 1:20 TFA:Chloroform-*d*) δ 161.48 (q, TFA), 148.07, 141.79, 135.76, 134.56, 132.55, 128.16, 122.89, 120.94, 118.43, 114.58 (q, TFA). **^{13}C NMR** (126 MHz, CD_3CN) δ 148.5, 146.1, 136.7, 136.1, 134.3, 129.8, 124.6. Elemental Analysis: calc'd; C: 32.74, H: 2.29, N: 4.24, Found; C: 31.95, H: 2.38, N: 4.06.

Note: Original spectral data from Weiss[1] was reported in CD_3CN. We get poor resolution in 1H NMR spectra in this solvent, possibly due to transient solvent coordination. We report 13C NMR in two solvent systems here to show the effect of solvent on spectral data. The 13C data reported in CD_3CN matches that reported by Weiss, whereas the use of TFA:$CDCl_3$ leads to desymmetrization and appearance of 16 unique carbon signals.

1,1'-(phenyl-λ^3-iodanediyl)bis(4-(N,N-dimethylamino)pyridin-1-ium) trifluoromethanesulfonate (*DMAP*-HVI, SI-1).

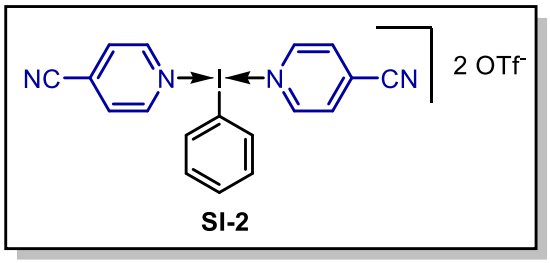


SI-1

Prepared according to General Procedure A with the following modification: solvent used was CH_2Cl_2. **SI-1** was obtained (3.17 g, 85%) as a white solid after filtration. **^{1}H NMR** [500 MHz, $CDCl_3$:TFA (20:1)] δ 8.24–8.17 (m, 2H), 8.17–8.10 (m, 4H), 7.76 (tt, *J*= 7.4, 1.0 Hz, 1H), 7.67–7.59 (m, 2H), 6.81–6.74 (m, 4H), 3.28 (s, 12H). **^{13}C NMR** [125 MHz, $CDCl_3$:TFA(20:1)] δ 161.48 (q, TFA), 157.8, 139.1, 135.6, 134.3, 132.4, 122.8, 120.8, 118.3, 114.58 (q, TFA), 107.1, 40.2. **^{13}C NMR** (126 MHz, CD_3CN) δ ^{13}C NMR (126 MHz, CD_3CN) δ 157.16, 145.96, 135.18, 134.86, 133.75, 123.26, 120.71, 109.65, 40.26.

Note: Original spectral data from Weiss[1] was reported in CD_3CN. We get poor resolution in 1H NMR spectra in this solvent, possibly due to transient solvent coordination. We report 13C NMR in two solvent systems here to show the effect of solvent on spectral data. The 13C data reported in CD_3CN matches that reported by Weiss, whereas the use of TFA:$CDCl_3$ leads to desymmetrization and appearance of 16 unique carbon signals.

1,1'-(phenyl-λ^3-iodanediyl)bis(4-cyanopyridin-1-ium) trifluoromethanesulfonate (4-CN-Py-HVI, SI-2).



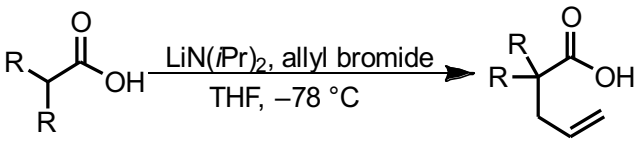
SI-2

Prepared according to General Procedure B with the following modification: solvent used was CH_2Cl_2. **SI-2** was obtained (329 mg, 46%) as a white solid after filtration in a glovebox. **^{1}H NMR** [500 MHz, CD_3CN)] δ 8.88–8.82 (m, 4H), 8.18–8.12 (m, 4H), 7.96 (d, *J*= 7.9 Hz, 2H), 7.64 (t, *J*= 7.5 Hz, 1H), 7.42 (t, *J*= 7.9 Hz, 2H). **^{13}C NMR** [125 MHz, $CDCl_3$:TFA(20:1)] δ 143.91, 143.30, 135.38, 133.98, 132.27, 130.66, 130.29, 122.89, 113.31.Elemental Analysis: calc'd; C: 30.17, H: 1.65, N: 3.52. Found; C: 29.65, H: 1.66, N: 3.21. Due to inherent instability, melting point was not determined.

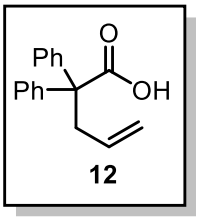
Section C. Substrate Syntheses

Section C.1 Synthesis of Alkenoic Acids

General Procedure C: Allylation of acetic acid derivatives



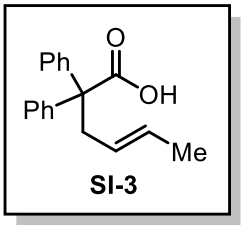
Alkylations were according to published procedure.[3] *n*-BuLi (1.2 equiv.) was added slowly to freshly distilled diisopropylamine (1.2 equiv.) in dry THF (1.05 M, respective to (iPr)$_2$NH) at –78 °C in a flame dried round bottom flask under argon and let stir for 1 h. A solution of acetic acid derivative (1.0 equiv.) in dry THF (0.33 M, respective to the acetic acid derivative) was then added dropwise and the reaction stirred at –78 °C for 1 h then transferred to an ice bath and stirred at 0 °C for an additional 1 h. Allyl bromide (1.2 equiv.) was added dropwise and the reaction was allowed to stir and reach room temperature as the ice melted, and monitored by TLC. Once the reaction was complete (17 h), it was quenched with 1 M HCl (aq.) and acidified to pH= 1. The resulting aqueous solution was extracted with Et_2O (3x). The combined organic layers were washed with brine and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude materials were then purified by flash chromatography (15% EtOAc:Hexanes).



12

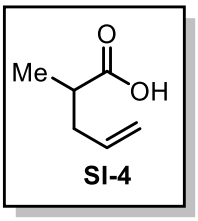
2,2-diphenylpent-4-enoic acid (12). General procedure C was followed using 2,2-diphenylacetic acid (2.00 g, 9.42 mmol) and allyl bromide (980 µL, 11.3 mmol) to give the desired product **12** (2.10 g, 88%) as a white solid. Except for not observing the exchangeable carboxylic acid proton, –CO_2**H**, the spectral data is consistent with that previously reported.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.19 (m, 10H), 5.56 (ddt, *J*= 16.4, 11.3, 7.0 Hz, 1H), 4.93–4.90 (m, 1H), 4.89–4.88 (m, 1H), 3.13 (dt, *J*= 7.1, 1.3 Hz, 2H).



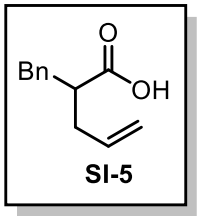
SI-3

(E)-2,2-diphenylhex-4-enoic acid (SI-13). Modified version of General procedure C was followed using 2,2-diphenylacetic acid (810 mg, 3.7 mmol) and crotyl bromide (885 mg, 4.44 mmol) to give desired product **SI-3** (532 mg, 54%) as a white solid. Spectral data is consistent with that previously reported.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32–7.22 (m, 10H), 5,31–5.21 (m, 2H), 3.08 (d, 2H, *J*=6.4 Hz,), 1.50 (dd, 3H, *J*= 0.9 Hz).



SI-4

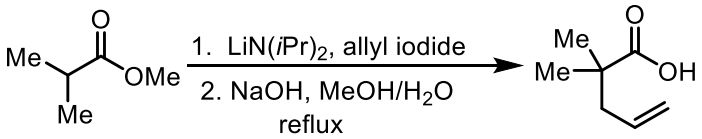
2-methylpent-4-enoic acid (SI-4). General procedure C was followed using propionic acid (750 µL, 10.0 mmol) and allyl bromide (2.2 mL, 25 mmol) to give desired product **SI-4** (749 mg, 65%) as a colorless liquid. Except for not observing the exchangeable carboxylic acid proton, –CO_2**H**, the spectral data is consistent with that previously reported.[3] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.77 (ddt, *J*= 17.1, 10.1, 7.0 Hz, 1H), 5.12–5.03 (m, 2H), 2.56 (d, *J*= 7.0 Hz, 1H), 2.45 (dtt, *J*= 15.0, 6.8, 1.4 Hz, 1H), 2.21 (dtt, *J*= 14.2, 7.2, 1.3 Hz, 1H), 1.19 (d, *J*= 7.0 Hz, 3H).



SI-5

2-benzylpent-4-enoic acid (SI-5). General procedure C was followed using hydrocinnamic acid (15.0 g, 100.0 mmol) and allyl bromide (30.0 mL, 210 mmol) to give desired product **SI-5** (12.92 g, 68%) as colorless liquid. With the exception of not observing the exchangeable carboxylic acid proton, –CO_2**H**, the spectral data is consistent with that previously reported.[5] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37–7.19 (m, 5H), 5.91–5.76 (ddt, *J*= 17.1Hz, 10.2Hz, 6.9Hz, 1H), 5.21–5.07 (m, 2), 3.08–2.98 (m, 1H), 2.89–2.76 (m, 2H) 2.51–2.39 (m, 1H), 2.38–2.30 (dddt, *J*= 13.8Hz, 6.7Hz, 5.4Hz, 1.4Hz, 1H).

<u>Synthesis of 2,2-dimethylpent-4-enoic acid (SI-6)</u>



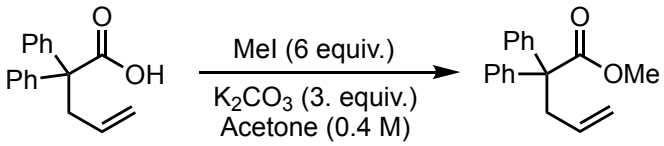
SI-5 **SI-6**

2,2-dimethylpen-4-enoic acid (SI-6). Alkylation and saponification were performed according to published procedures.[6] *n*-BuLi (1.1 equiv.) was added dropwise to freshly distilled diisopropylamine (755 µL, 5.39 mmol, 1.1 equiv.) in THF (1.7 mL, 3.1 M, respective to $(iPr)_2NH$) at –78 °C in a flame dried round bottom flask under argon and let stir for 30 min. Methyl isobutyrate (560 µL, 4.90 mmol) in THF (1.7 mL, 2.8 M, respective to methyl isobutyrate) was added dropwise

over 30 min and the solution was allowed to stir for an additional 1 h. Allyl iodide (500 µL, 5.39 mmol) in THF (1.7 mL, 3.2 M, respective to allyl bromide) was added dropwise and the solution was allowed to stir for 1 h at –78 °C. Once the reaction was complete (7 h), NH_4Cl was added at –78 °C to quench the reaction and the mixture was diluted with Et_2O. The organic layer was washed with brine and the combined aqueous layers were extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The methyl ester was dissolved in (25 mL) MeOH and (12 mL) water. NaOH (2.0 equiv.) was added neat and the solution was heated to 80 °C overnight. After cooling to room temperature, the MeOH was removed. The aqueous layer was acidified with 10% H_2SO_4 and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield 2,2-dimethylpent-4-enoic acid (**SI-6**) (430 mg, 70%). Except for not observing the exchangeable carboxylic acid proton, $–CO_2\mathbf{H}$, the spectral data is consistent with that previously reported.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82–5.72 (m, 1H), 5.11–5.05 (m, 2H), 2.31 (dt, *J*= 7.4, 1.2 Hz, 2H), 1.20 (s, 6H).

Synthesis of methyl 2,2-diphenylpent-4-enoate (68)

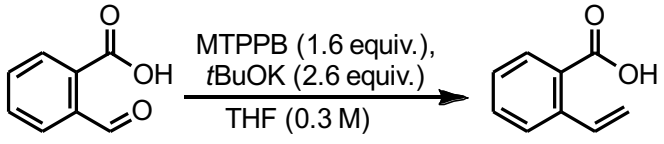


12 **68**

2,2-diphenylpent-4-enoate (68). Esterification was performed according to published procedure.[7] 2,2-diphenylpent-4-enoic acid (**12**) was dissolved in acetone (5 mL, 0.4 M) then K_2CO_3 (830 mg, 6.0 mmol, 3.0 equiv.) was added in one portion, the reaction stirred for 20 min. Iodomethane (750 µL, 12.0 mmol, 6.0 equiv.) was then added to the mixture and stirred overnight. After the reaction was complete (18 h), it was diluted with H_2O and the aqueous layer was extracted with EtOAc (2 x 10 mL). The organic layer was then washed with brine (1x), dried over Na_2SO_4, then concentrated *in vacuo* to yield **68** (518 mg, 97%) as a yellow oil. No further purification was necessary. Spectral data is consistent with that previously reported.[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.28 (m, 10H), 5.75–5.56 (m, 1H), 5.01–4.94 (m, 2H), 3.74 (s, 3H), 3.21 (dt, *J*= 7.0, 1.4 Hz, 2H).

Synthesis of 2-vinylbenzoic acid (SI-8).

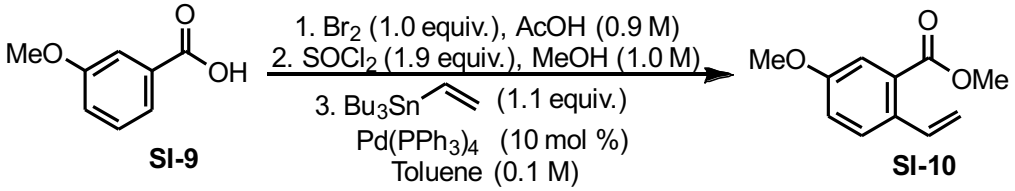


SI-7 **SI-8**

2-vinylbenzoic acid (SI-8). Olefination reaction was performed according to published procedure.[8] A flame, dried round bottom was charged with *t*-BuOK (589 mg, 5.2 mmol, 2.6 equiv.) followed by dry THF (2.5 mL, 2.1 M). The base solution was added to a suspension of methyltriphenylphosphonium bromide (MTPPB, 1.15 g, 3.2 mmol, 1.6 equiv.) in dry THF (4.5 mL, 0.4 M) and stirred for 1.5 h at room temperature. 2-Carboxybenzaldehyde (**SI-7**) (304 mg, 2.0 mmol, 1.0 equiv.) was added and the mixture was refluxed overnight. Once the reaction was complete (17 h) it was cooled to room temperature and quenched with acetic acid followed by EtOAc, the organic layer was washed with $NaHCO_3$ (sat. aq.) (3 x 5.0 mL). The combined organic layers were washed with H_2O and brine sequentially, dried over Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (25% EtOAc:Hexanes) to **SI-8** (245 mg, 48%) as a white solid. The spectral data is consistent with that previously reported.[9]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J*= 8.1, 1.4 Hz, 1H), 7.63–7.53 (m, 3H), 7.37 (td, *J*= 7.6, 1.4 Hz, 1H), 5.68 (dd, *J*= 17.4, 1.3 Hz, 1H), 5.39 (dd, *J*= 11.0, 1.3 Hz, 1H).

Synthesis 5-Methoxy-2-vinylbenzoic acid (SI-10)

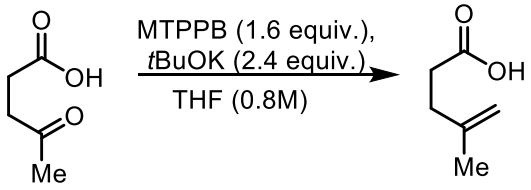


5-Methoxy-2-vinylbenzoic acid (SI-10). Vinylation and esterification were performed according to published procedures.[10-12] 3-methoxy benzoic acid (**SI-9**) (1.00 g, 6.57 mmol, 1.0 equiv.) was dissolved in AcOH (6.5 mL, 0.9 M). Br_2 (336 µL, 6.57 mmol, 1.0 equiv.) was added dropwise and the solution was heated to 110 °C for 10 h. After the reaction was complete by TLC it was poured over ice, forming a white precipitate. The white solid was filtered and washed with 1:1 H_2O:Pentane mixture and dried on high vacuum, yielding (746 mg, 46%). The product was dissolved in HPLC grade MeOH (3.0 mL, 1.0 M) and placed at 0 °C. Thionyl chloride (445 mL, 6.10 mmol, 1.9 equiv.) was added dropwise over 5 min to the solution, and upon complete addition the reaction was heated to reflux at 80 °C. Once the reaction was complete (2 h) it was concentrated to remove MeOH and excess SO_2Cl_2. It was then taken up in EtOAc and washed with H_2O (2x) and $NaHCO_3$ (sat. aq.). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to yield the methyl ester (715 mg, 90%). Next, the methyl ester (715 mg, 2.92 mmol, 1.0 equiv.) was dissolved in dry toluene (29 mL, 0.1 M) and degassed for 45 min. Vinyl tributyl tin (940 µL, 3.21 mmol, 1.1 equiv.) and $Pd(PPh_3)_4$ (337 mg, 10 mol %) was added, backfilled with argon, capped and heated to 100 °C. Once the reaction was complete (18 h) it was filtered through a celite plug and concentrated *in vacuo* to give an oil. The crude material was purified by

flash column chromatography (10% EtOAc:Hexanes) to give **SI-10** as a yellow oil (512 mg, 91%). The spectral data is consistent with that previously reported.[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J*= 8.7 Hz, 1H), 7.41–7.34 (m, 2H), 7.04 (ddd, *J*= 8.6, 2.8, 0.7 Hz, 1H), 5.56 (dd, *J*= 17.4, 1.4 Hz, 1H), 5.30 (d, *J*= 0.7 Hz, 2H), 5.28–5.22 (m, 1H), 3.91 (d, *J*= 0.6 Hz, 3H), 3.84 (d, *J*= 0.8 Hz, 3H).

Synthesis of 4-methylpent-4-enoic acid (SI-12)

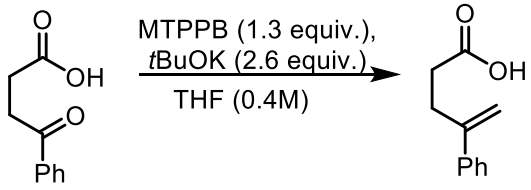


SI-11 **SI-12**

4-methylpent-4-enoic acid (SI-12). Olefination reaction was performed according to published procedures.[13] A flame dried round bottom was charged with *t*-BuOK (11.6 g, 103 mmol, 2.4 equiv.) and methyltriphenylphosphonium bromide (MTPPB, 24.6 g, 69 mmol, 1.6 equiv.) followed by dry THF (54 mL, 0.8M). The suspension was stirred for 1.5 h before the addition of 4-oxopentanoic acid (**SI-11**) (5 g, 43 mmol, 1.0 equiv.), the reaction was refluxed overnight. Once the reaction was complete (17 h) the reaction was quenched with glacial acetic acid then filtered through celite, then concentrated. The material was diluted with EtOAc, the organic layer was extracted with $NaHCO_3$ (3 x 100mL). The combined aqueous layers were acidified to pH of 1 with 1M HCl then extracted with EtOAc (3 x 100 mL). The organic layer was washed with H_2O and brine sequentially, dried over Na_2SO_4, and concentrated *in vacuo.* The crude material was purified by flash column chromatography (10-15% EtOAc:Hexanes) to yield **SI-12** as a colorless oil. Spectral data is consistent with that previously reported.[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.26 (br s, 1H, 4.77–4.75 (m, 1H), 4.72–4.70 (m, 1H), 2.51 (dd, *J*= 8.8, 6.8 Hz, 2H), 2.37–2.31 (m, 2H), 1.77–1.74 (s, 3H).

Synthesis of 4-phenylpent-4-enoic acid (SI-14)



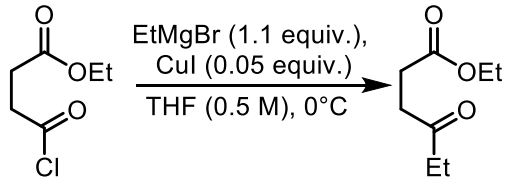
SI-13 **SI-14**

4-phenylpent-4-enoic acid (SI-14). Olefination reaction was performed according to published procedures.[13] A flame dried round bottom was charged with *t*-BuOK (8.2 g, 73 mmol, 2.6 equiv.) and methyltriphenylphosphonium bromide (MTPPB, 12.9 g, 36 mmol, 1.3 equiv.) followed by dry THF (67 mL, 0.4M). The suspension was stirred for 30 min before the addition of 3-

benzoylpropionic acid (**SI-13**) (5 g, 28 mmol, 1.0 equiv.), the reaction was allowed to stir overnight. Once the reaction was complete (13h) the reaction was concentrated in *vacuo* then diluted with CH_2Cl_2 and NaOH (1M in H_2O). The aqueous layer was separated then washed with CH_2Cl_2 and acidified to pH of 1 with 1M HCl. The content was filtered via buchner funnel. The crude material was purified by flash column chromatography (0-15% EtOAc:Hexanes) to yield **SI-14** as a white solid. Spectral data is consistent with that previously reported.[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J*= 8.0 Hz, 2H), 7.36 (dd, *J*= 8.0, 7.2 Hz, 2H), 7.30 (t, *J*= 7.2 Hz, 1H), 5.35 (s, 1H), 5.13 (s, 1H), 2.87 (t, *J*= 7.6 Hz, 2H), 2.58 (t, *J*= 7.6 Hz, 2H).

Synthesis of ethyl-4-oxohexanoate (SI-16)

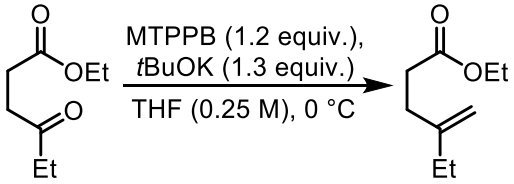


SI-15 **SI-16**

Ethyl-4-oxohexanoate (SI-16). Grignard reaction was performed according to modified published procedures.[14] A flame dried flask under argon was charged with ethyl succinyl chloride (**SI-15**) (4.3 mL, 30. 4 mmol, 1.0 equiv.), CuI (289 mg, 1.52 mmol, 0.05 equiv.) in dry THF (60 mL, 0.5 M) at 0 °C. 1 M solution of EtMgBr (11.15 mL, 33.44 mmol, 1.1 equiv.) was added dropwise over 1 h. Once the reaction was complete (1 h), the reaction was concentrated then diluted with CH_2Cl_2, the solution was then filtered through a celite pad. The organic solution was washed with NH_4Cl (sat. aq.), the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with H_2O and brine sequentially, dried over Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (5% EtOAc:Hexanes) to yield **SI-16** (3.2 g, 66%) as a colorless oil. Spectral data is consistent with that previously reported.[15]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.10 (q, *J*= 7.1 Hz, 2H) 2.69 (t, *J*= 6.5 Hz, 2H), 2.56 (t, *J*= 6.5 Hz, 2H), 2.45 (q, *J*= 7.2 Hz, 2H), 1.23 (t, *J*= 7.1 Hz, 3H), 1.05 (t, *J*= 7.3 Hz, 3H).

Synthesis of ethyl 4-methylenehexenoate (SI-17)



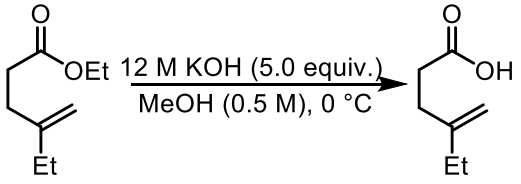
SI-16 **SI-17**

4-methylenehexenoate (SI-17). A flame dried round bottom under argon was charged with (methyltriphenylphosphonium bromide (MTPPB, 8.68 g, 24, 30 mmol, 1.2 equiv.) and *t*-BuOK (2.95 g, 25.30 mmol, 1.3 equiv.) in dry THF (61 mL, 0.4 M, respective to MTPPB) at 0 °C and was

allowed to stir for 1 h. Ethyl-4-oxohexanoate (**SI-16**) (3.2 g, 20.23 mmol, 1.0 equiv.) was added as a solution in dry THF (20 mL, 1 M, respective to SI-16). The reaction was allowed to stir and reach room temperature as the ice bath melted. Once the reaction was complete (16 h), it was quenched with NH_4Cl (sat. aq.) (100 mL), extracted with Et_2O (3 x 150 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography (2% EtOAc:Hexanes) to yield **SI-17** (1.8 g, 62%) as a colorless oil. Spectral data is consistent with that previously reported.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77–4.68 (m, 2H), 4.13 (q, *J*= 7.1 Hz, 2H), 2.48–2.41 (m, 1H), 2.38–2.32 (m, 1H), 2.04 (qdd, *J*= 7.5, 1.5, 0.7 Hz, 1H), 1.25 (t, *J*= 7.1 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 2H).

Synthesis of 4-methylenehexanoic acid (SI-18)

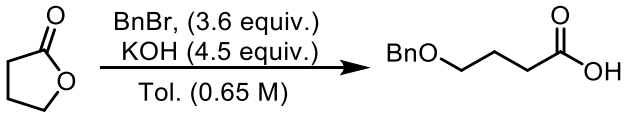


SI-17 **SI-18**

4-methylenenehexenoic acid (SI-18). Saponification was performed according to modified published procedures.[17] A solution of KOH (539 mg, 9.6 mmol, 5.0 equiv.) in H_2O (800 µL) was added to a solution of 4-methylenehexenoate (**SI-17**) (300 mg, 1.92 mmol, 1.0 equiv.) in MeOH (4 mL, 0.5 M) at 0 °C. After stirring for 2 hr at room temperature, the reaction was quenched with 1 M HCl (5 mL). The solution was extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield **SI-18** (223 mg, 82%) as a yellow oil. No further purification was necessary. Spectral data is consistent with that previously reported.[18]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.75 (dp, *J*= 25.4, 1.1 Hz, 2H), 2.57–2.49 (m, 2H), 2.40–2.32 (m, 2H), 2.05 (qdd, *J*= 7.4, 1.8, 0.9 Hz, 2H), 1.04 (t, *J*= 7.4 Hz, 3H).

Synthesis of 4-(benzyloxy)butanoic acid (SI-20)



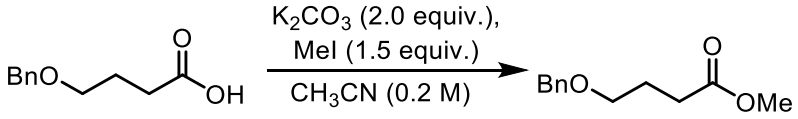
SI-19 **SI-20**

4-(benzyloxyl)butanoic acid (SI-20). Reaction was performed according to published procedures.[19] KOH (14.7 g, 261.5 mmol, 4.5 equiv.) was added to a solution of γ-Butyrolactone (**SI-19**) (5.0 g, 58.1 equiv., 1.0 equiv.) and benzyl bromide (25 mL, 209.2 mmol, 3.6 equiv.) in dry toluene (90 mL, 0.65 M) at room temperature, then the temperature was raised to reflux. Once the reaction reached completion (48 h), the reaction was cooled to room temperature. The solution was diluted with Et_2O (100 mL) and H_2O (100 mL) the aqueous layer was extracted with

Et_2O (3 x 100 mL). The aqueous phase was cooled to 0 ℃ and acidified with 6 N sulfuric acid. The solution was extracted with Et_2O (3 x 100 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield **SI-20** (4.3 g, 38%) as a colorless oil. Spectral data is consistent with that previously reported.[19]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.17 (m, 5H), 4.44 (s, 2H), 3.46 (t, J= 6.1 Hz, 2H), 2.42 (t, J= 7.3 Hz, 2H), 1.88 (tt, J= 7.3, 6.1 Hz, 2H).

Synthesis of methyl 4-(benzyloxy)butanoate (SI-21)

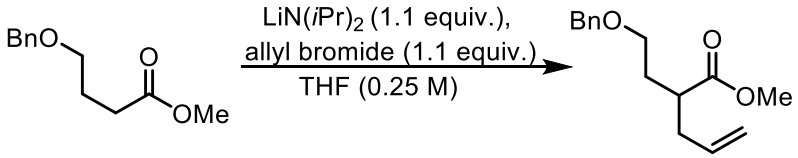


SI-20 **SI-21**

Methyl 4-(benzyloxy)butanoate (SI-21). Esterification was performed according to modified published procedure.[7] 4-(benzyloxyl)butanoic acid (**SI-20**) (4.2 g, 20.2 mmol, 1.0 equiv.) was dissolved in CH_3CN (100 mL, 0.2 M) then K_2CO_3 (7.4 g, 40.3 mmol, 2.0 equiv.) was added in one portion, the reaction stirred for 30 min. Iodomethane (1.89 mL, 30.3 mmol, 1.5 equiv.) was then added to the mixture and stirred overnight. After the reaction was complete (15 h), it was diluted with H_2O and the aqueous layer was extracted with EtOAc (3 x 200 mL). The organic layer was washed with brine (1x), dried over Na_2SO_4, then concentrated *in vacuo.* The crude material was purified by flash column chromatography (10% EtoAc:Hexanes) to yield **SI-21** (10 g, 93%) as a light brown solid. Spectral data is consistent with that previously reported.[20]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 5H), 4.43 (s, 2H), 3.58 (s, 2H), 3.44 (t, *J* = 6.2 Hz, 2H), 2.37 (t, *J* = 7.4 Hz, 2H).

Synthesis of methyl 2-(2-(benzyloxy)ethyl)pent-4-enoate (SI-22)

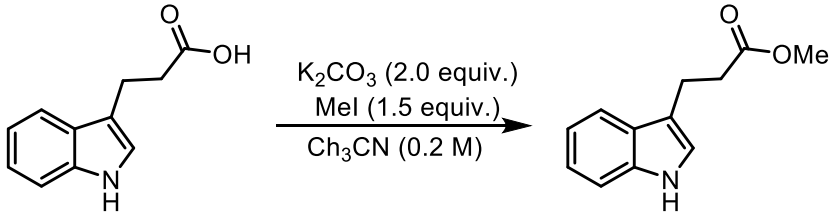


SI-21 **SI-22**

Methyl 2-(2-(benzyloxy)ethyl)pent-4-enoate (SI-22). Alkylation and saponification were performed according to published procedures.[6] In a flame dried round bottom flask, *n*-BuLi (5.06 mL, 12.65, 1.1 equiv.) was added dropwise to freshly distilled diisopropylamine (1.78 mL, 12.65 mmol, 1.1 equiv.) in THF (42 mL, 0.3 M, respective to $(iPr)_2NH$) at –78 °C in a flame dried round bottom flask under argon and let stir for 30 min. Methyl 4-(benzyloxy)butanoate (**SI-21**) (2.4 g, 11.5 mmol, 1.0 equiv.) in THF (4 mL, 2.8 M, respective to Methyl 4-(benzyloxy)butanoate) was added dropwise over 30 min and the solution was allowed to stir for an additional 1 h. Allyl bromide (1.1 mL, 12.65 mmol, 1.1 equiv.) was added dropwise over 5 min and the solution was allowed to reach room temperature as the ice melted. Once the reaction was complete (15 h),

NH_4Cl was added to quench the reaction and the mixture was diluted with Et_2O. The aqueous solution was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with Brine and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (10% EtoAc:Hexanes) to yield **SI-22** (1 g, 35%) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 5.79–5.69 (m, 1H), 5.10–4.99 (m, 2H), 4.48 (s, 2H), 3.62 (s, 3H), 3.53–3.44 (m, 2H), 2.66 (dddd, *J*= 9.2, 7.9, 6.2, 4.9 Hz, 1H), 2.37 (dddt, *J*= 13.9, 8.1, 7.0, 1.3 Hz, 1H), 2.30–2.21 (m, 1H), 2.02–1.93 (m, 1H), 1.79 (dddd, *J*= 14.0, 7.1, 5.9, 5.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.7, 138.4, 135.2, 128.3, 127.6, 127.5, 72.9, 68.0, 51.4, 42.3, 36.5, 31.7. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{15}H_{21}O_3$, 249.1491; found 249.1483.

Synthesis of methyl 3-(1*H*-indol-3-yl)propanoate (SI-24)

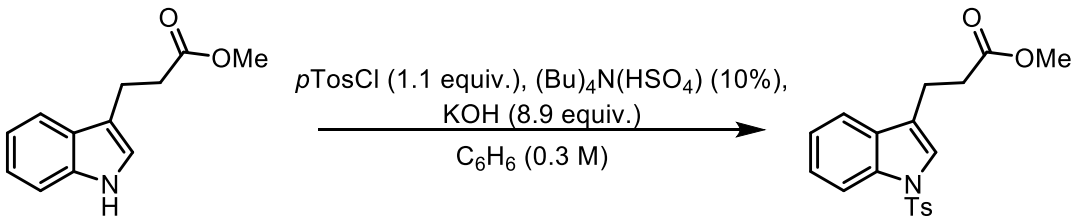


SI-23 **SI-24**

Methyl 3-(1*H*-indol-3-yl)propanoate (SI-24). Esterification was performed according to published procedures.[21] 3-indolepropionic acid (**SI-23**) (10.0 g, 53.0 mmol, 1.0 equiv.) was dissolved in CH_3CN (265 mL, 0.2 M) then K_2CO_3 (11 g, 79.5 mmol, 1.5 equiv.) was added in one portion, the reaction stirred for 30 min. Iodomethane (4.95 mL, 79.5 mmol, 1.5 equiv.) was then added to the mixture and stirred overnight. After the reaction was complete (15 h), it was diluted with H_2O and the aqueous layer was extracted with EtOAc (3 x 200 mL). The organic layer was washed with brine (1x), dried over Na_2SO_4, then concentrated *in vacuo.* The crude material was purified by flash column chromatography (10% EtoAc:Hexanes) to yield **SI-24** (10 g, 93%) as a light brown solid. Spectral data is consistent with that previously reported.[21]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.61 (dq, *J*= 7.9, 0.9 Hz, 1H), 7.36 (dt, *J*= 8.1, 1.0 Hz, 1H), 7.20 (ddd, *J*= 8.2, 7.0, 1.2 Hz, 1H), 7.13 (ddd, *J*= 8.0, 7.0, 1.0 Hz, 1H), 7.02 (dd, *J*= 2.3, 1.1 Hz, 1H), 3.68 (s, 3H), 3.11 (td, *J*= 7.6, 1.0 Hz, 2H), 2.73 (dd, *J*= 8.4, 7.1 Hz, 2H).

Synthesis of methyl 3-(1-tosyl-1*H*-indol-3-yl)propanoate (SI-25)

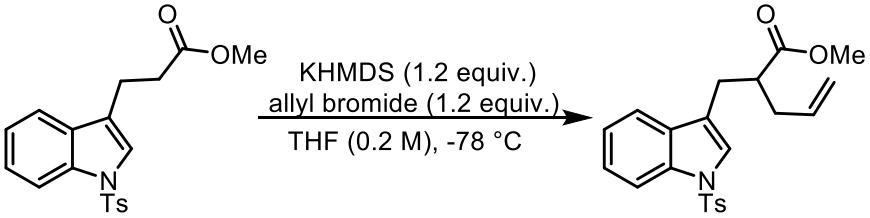


SI-24 **SI-25**

Methyl 3-1(Tosyl-1*H*-indol-3-yl)propanoate (SI-25). Tosyl protection was performed according to published procedures.[22] An aqueous KOH solution (50%, 11.8 g, 210.0 mmol was added dropwise for 20 min to a solution of 3-(1*H*-indol-3-yl)propanoate (**SI-24**) (4.8 g, 23.6 mmol, 1.0 equiv.), tetrabutylammoniumhydrogensulfate (801 mg, 2.36 mmol, 0.1 equiv.) in benzene (79 mL, 0.3M). The solution was stirred vigorously at room temperature for 3 h. Once the reaction was complete it was diluted with water (100 mL). The resulting mixture was extracted with EtOAc (3 x 100 mL), the combined organic layers were washed with brine, dried over Na2SO4, concentrated in vacuo. The crude material was purified by flash column chromatography (5% EtOAc:Hexanes) to yield **SI-25** (7.2 g, 85%) as a yellow solid. Spectral data is consistent with that previously reported.[22]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J*= 8.3, 0.8 Hz, 1H), 7.73 (d, *J*= 8.5 Hz, 2H), 7.48 (dt, *J*= 7.7, 0.9 Hz, 1H), 7.34 (d, *J*= 1.2 Hz, 1H), 7.31 (ddd, *J*= 8.3, 7.2, 1.3 Hz, 1H), 7.25–7.22 (m, 1H), 7.20 (d, *J*= 8.1 Hz, 2H), 3.68 (s, 3H), 3.00 (ddd, *J*= 7.9, 7.0, 1.2 Hz, 2H), 2.69 (dd, *J*= 8.5, 6.8 Hz, 2H), 2.33 (s, 3H).

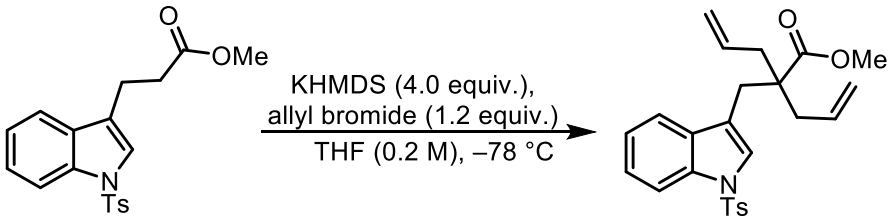
Synthesis of methyl 2-((1-tosyl-1*H*-indol-3-yl)propanoate (SI-26)



SI-25 **SI-26**

Methyl 2-((1-tosyl-1*H*-indol-3-yl)propanoate (SI-26). 1 M solution of KHMDS in THF (2.52 mL, 2.52 mmol, 1.2 equiv.) was added dropwise over 5 min to a solution of 3-1(Tosyl-1*H*-indol-3-yl)propanoate (**SI-25**) (750 mg, 2.1 mmol, 1.0 equiv.) in dry THF (11 mL, 0.2 M) at –78 °C. After stirring for 30 min, allyl bromide (218 µL, 2.52 mmol, 1.2 equiv.) was added to the solution. The solution was allowed to reach room temperature as the ice melted. After the reaction was complete (21 h) it was quenched with NaH_4Cl (sat. aq.) (5 mL), extracted with EtOAc (3 x 20 mL). The organic layer was dried over $MgSO_4$, filtered the concentrated *in vacuo*. The crude material was purified by flash column chromatography (5% EtoAc:Hexanes) to yield **SI-26** (512 mg, 61%) as a colorless viscous oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dt, *J*= 8.2, 0.9 Hz, 1H), 7.72 (d, *J*= 8.5 Hz, 2H), 7.48–7.44 (m, 1H), 7.35 (d, *J*= 1.0 Hz, 1H), 7.31 (ddd, *J*= 8.3, 7.2, 1.3 Hz, 1H), 7.25–7.21 (m, 1H), 7.21–7.18 (m, 2H), 5.75 (ddt, *J*= 16.3, 10.7, 6.9 Hz, 1H), 5.10–5.04 (m, 2H), 3.57 (s, 3H), 3.05–2.98 (m, 1H), 2.86–2.79 (m, 2H), 2.46–2.36 (m, 1H), 2.32 (s, 3H), 2.31–2.25 (m, 1H). **^{13}C NMR** δ 175.2, 144.9, 135.4, 134.9, 130.9, 129.9, 126.8, 124.9, 123.9, 123.2, 120.3, 119.4, 117.5, 113.9, 51.7, 45.3, 36.4, 26.9, 21.7. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{22}H_{24}NO_4S$, 398.1426; found 398.1424.

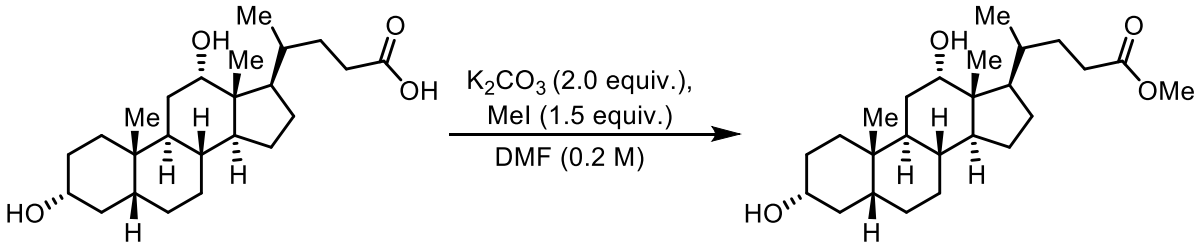
Synthesis of methyl 2-allyl-2-((1-tosyl-1H-indol-3-yl)methyl)pent-4-enoate (SI-27)



SI-25 **SI-27**

Methyl 2-((1*H*-indol-3-yl)-2-allylpent-4-enoate (SI-27). 1 M solution of KHMDS in THF (1.2 mL, 4.0 equiv.) was added dropwise over 5 min to a solution of 3-1(Tosyl-1*H*-indol-3-yl)propanoate (**SI-25**) (100 mg, 0.3 mmol, 1.0 equiv.) in dry THF (3.0 mL, 0.2 M) at –78 °C. After stirring for 30 min allyl bromide (31 µL, 1.2 equiv.) was added to the solution. The solution was allowed to reach room temperature as the ice melted. After the reaction was complete (12 h) it was quenched with NaH_4Cl (sat. aq.) (5 mL), extracted with EtOAc (3 x 20 mL). The organic layer was dried over $MgSO_4$, filtered the concentrated *in vacuo*. The crude material was purified by flash column chromatography (10% EtOAc:Hexanes) to yield **SI-27** (22 mg, 30%) as a brown solid.
^{1}H NMR (500 MHz, CD_3CN) δ 7.94 (dt, *J*= 8.3, 0.9 Hz, 1H), 7.77–7.71 (m, 2H), 7.48 (dt, *J*= 7.8, 1.0 Hz, 1H), 7.39–7.21 (m, 6H), 5.81 (ddt, *J*= 16.8, 10.3, 7.3 Hz, 2H), 5.12–5.03 (m, 4H), 3.49 (s, 3H), 2.95 (d, *J*= 1.0 Hz, 2H), 2.40 (ddt, *J*= 14.3, 7.1, 1.3 Hz, 2H), 2.35–2.27 (m, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 176.0, 146.4, 135.0, 134.2, 130.5, 127.2, 125.4, 123.9, 120.5, 118.7, 114.1, 51.8, 50.4, 39.0, 31.1, 21.1. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{25}H_{28}NO_4S$, 438.1739; found 438.1749.

Synthesis of methyl deoxycholate (SI-29)

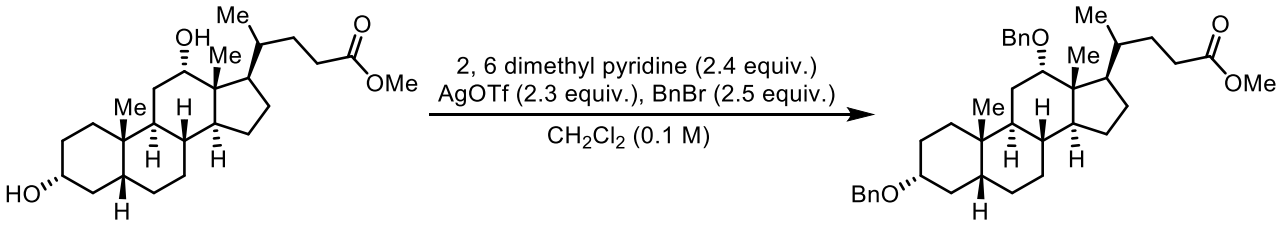


SI-28 **SI-29**

Methyl deoxycholate (SI-29). Esterification was performed according to published procedures.[23] Deoxycholic acid (SI-28) (10.0 g, 25.5 mmol, 1.0 equiv.) was dissolved in DMF (102 mL, 0.25 M) then K_2CO_3 (7.04 g, 51 mmol, 2.0 equiv.) was added in one portion, the reaction stirred for 30 min. Iodomethane (2.4 mL, 38.25 mmol, 1.5 equiv.) was then added to the mixture and stirred overnight. After the reaction was complete (15 h), it was diluted with EtOAc (50 mL) and washed with H_2O (150 mL). The organic layer was washed with brine (1x), dried over $MgSO_4$, then concentrated *in vacuo.* The crude material was purified by flash column chromatography (10% EtOAc:Hexanes) to yield **SI-29** (9.01 g, 87%) as a light brown solid. Spectral data is consistent with that previously reported.[23]

^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.98 (t, *J*= 2.8 Hz, 1H), 3.66 (s, 3H), 3.65–3.57 (m, 1H), 2.41–1.01 (m, 28H), 0.97 (d, *J*= 6.4 Hz, 3H), 0.91 (s, 3H, 19), 0.68 (s, 3H).

Synthesis of methyl 3α, 12α-bis(benzyloxy)-5β-cholan-24-oate (SI-30)

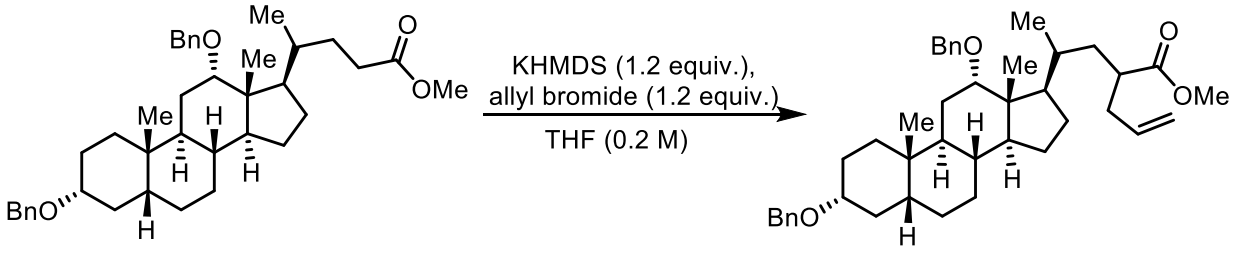


SI-29 **SI-30**

Methyl 3α, 12α-bis(benzyloxy)-5β-cholan-24-oate (SI-30). Benzyl protection was performed according to a modification to published procedures.[24] A solution of benzyl bromide (6.6 mL, 55.33 mmol, 2.5 equiv.) in 50 mL of dry CH_2Cl_2 was added dropwise over 10 min. to a suspension of methyl deoxycholate (**SI-29**) (9.0 g, 22.13 mmol, 1.0 equiv.), 2,6-dimethyl pyridine (6.2 mL, 53.11 mmol, 2.4 equiv.) and AgOTf (13.1 g, 50.9 mmol, 2.3 equiv.) in dry CH_2Cl_2 (148 mL, 0.15 M relative to deoxycholate). The mixture was refluxed for 3 h, allowed to cool to room temperature, and filtered. The precipitate was washed with CH_2Cl_2 (100 mL). The combined organic layer was washed with 5 M HCl (3 x 100 mL), H_2O (3 x 100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography (2% EtOAc:Hexanes) to yield **SI-30** (6.0 g, 46%) as a yellow oil. Spectral data is consistent with that previously reported.[24]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.27 (m, 10H), 4.53 (d, *J*= 1.0 Hz, 2H), 4.28 (d, *J*= 11.5 Hz, 2H), 3.66 (s, 3H), 3.35 (td, *J*= 10.9, 5.4 Hz, 1H), 2.36 (ddd, *J*= 14.9, 10.2, 4.6 Hz, 1H), 2.20 (ddd, *J*= 15.5, 9.5, 6.4 Hz, 2H), 2.03 (q, *J*= 9.6 Hz, 1H), 1.92–1.66 (m, 10H), 1.66–1.52 (m, 2H), 1.49–1.00 (m, 13H), 0.92 (s, 3H), 0.70 (s, 3H).

Synthesis of methyl 2-((R)-2-((3R,5R,8R,9S,10S,12S,13R,14S,17R)-3,12-bis(benzyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)propyl)pent-4-enoate (SI-31)

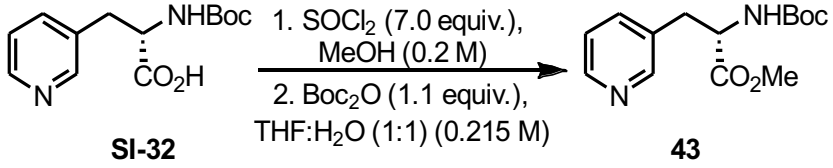


SI-30 **SI-31**

Methyl 2-((R)-2-((3R,5R,8R,9S,10S,12S,13R,14S,17R)-3,12-bis(benzyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)propyl)pent-4-enoate (SI-31). 1 M solution of KHMDS in THF (3.96 mL, 3.96 mmol, 1.2 equiv.) was added dropwise over 5 min to a solution of methyl 3α, 12α-bis(benzyloxy)-5β-cholan-24-oate (**SI-30**) (3.3 g, 3.3 mmol, 1.0 equiv.) in dry THF (17 mL, 0.2 M) at –78 °C. After stirring for 30 min, allyl bromide (342 µL, 3.96 mmol, 1.2 equiv.) was added to the solution. The solution was allowed to reach room temperature as the ice melted. After the reaction was complete (21 h) it was quenched with NaH_4Cl (sat. aq.) (5 mL), extracted with EtOAc (3 x 20 mL). The organic layer was dried over $MgSO_4$, filtered the concentrated *in vacuo*. The crude material was purified by flash column chromatography (5% EtoAc:Hexanes) to yield **SI-31** (1.9 g, 92%) as a colorless viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43–7.28 (m, 10H), 5.72 (ddq, *J*= 17.1, 10.2, 6.8 Hz, 1H), 5.10–4.97 (m, 2H), 4.60 (dd, *J*= 11.7, 3.9 Hz, 1H), 4.53 (d, *J*= 1.6 Hz, 2H), 4.29 (dd, *J*= 11.5, 1.7 Hz, 1H), 3.70–3.63 (m, 3H), 3.35 (dt, *J*= 11.1, 7.1 Hz, 1H), 2.61–2.09 (m, 3H), 2.08–1.92 (m, 1H), 1.91–1.74 (m, 8H), 1.70 (tt, *J*= 11.4, 3.4 Hz, 1H), 1.66–1.49 (m, 2H), 1.48–1.10 (m, 8H), 1.09–0.81 (m, 10H), 0.73–0.65 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.85, 176.45, 139.41, 135.75, 128.40, 127.60, 127.38, 116.74, 81.09, 81.00, 51.55, 51.39, 48.90, 47.27, 47.16, 46.83, 46.73, 43.19, 42.99, 38.87, 38.10, 36.23, 35.87, 35.46, 34.67, 34.59, 34.23, 33.90, 33.40, 27.96, 27.79, 27.52, 27.39, 26.16, 23.87, 23.52, 23.18, 17.92, 12.89. **HRMS** (m/z): $[M]^+$ calcd. For $C_{42}H_{59}O_4$, 627. 4413; found 627.4426.

Section C.2 Synthesis of Nitrogen Heterocycles

Synthesis of Methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(pyridin-3-yl)propanoate (43).

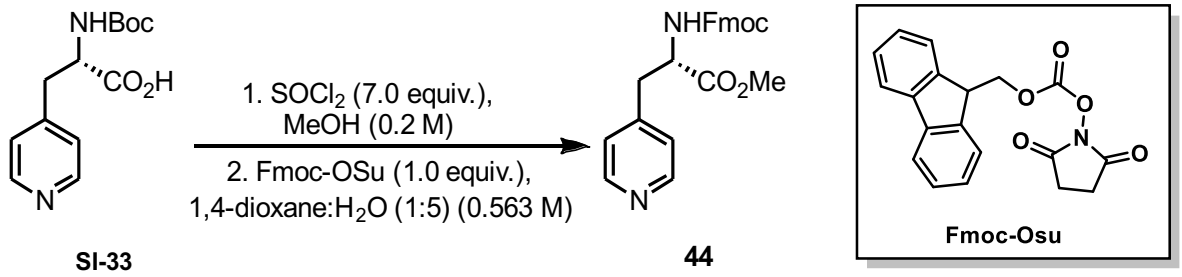


SI-32 **43**

Methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(pyridin-3-yl)propanoate (43). Thionyl chloride (550 µL, 7.56 mmol, 7.0 equiv.) was added dropwise to a solution of N-(*t*-butoxycarbonyl)-3-(3-pyridyl)alanine (**SI-32**) (288 mg, 1.08 mmol, 1.0 equiv.) in HPLC grade MeOH (5.4 mL, 0.20 M) at 0 °C and allowed to reach room temperature overnight as the ice melted. The reaction was then concentrated *in vacuo* and dried on high vacuum for 1 h. The resulting white precipitate was taken up in a 1:1 (v:v) mixture of THF:H_2O (2.50 mL:2.50 mL, 0.215 M) and Boc_2O (260 mg, 1.19 mmol, 1.1 equiv.) and Na_2CO_3 (115 mg, 1.08 mmol, 1.0 equiv.) were added sequentially. The reaction was stirred at room temperature overnight open to air. Once completion was reached (12 h), the reaction was diluted with EtOAc, and the organic layer was washed with $NaHCO_3$ (sat. aq.) (2 x 3.0 mL) followed by brine. The organic layer was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was then purified by flash chromatography (60% EtOAc:hexanes) to give **43** as a colorless oil (182 mg, 60%). Spectral data is consistent with that previously reported.[25]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, *J*= 4.9, 1.6 Hz, 1H), 8.39 (s, 1H), 7.47 (dt, *J*= 7.8, 2.0 Hz, 1H), 7.25–7.21 (m, 1H), 5.04 (s, 1H), 4.61 (q, *J*= 6.6 Hz, 1H), 3.73 (d, *J*= 0.9 Hz, 3H), 3.16 (dd, *J*= 13.9, 5.7 Hz, 1H), 3.03 (dd, *J*= 14.2, 6.1 Hz, 1H), 1.41 (s, 9H).

Synthesis of Methyl (S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(pyridin-4-yl)propanoate (44).

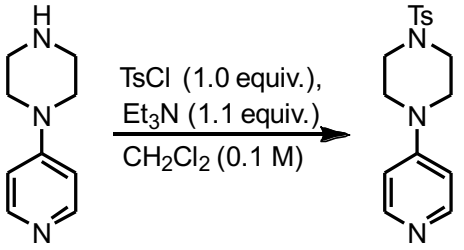


SI-33 **44**

Methyl (S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(pyridin-4-yl)propanoate (44). Thionyl chloride (570 µL, 7.88 mmol, 7.0 equiv.) was added dropwise to a solution of (S)-2-((tert-butoxycarbonyl)amino)-3-(pyridin-4-yl)propanoic acid (**SI-33**) (300 mg, 1.13 mmol, 1.0 equiv.) in HPLC grade MeOH (5.6 mL, 0.20 M) at 0 °C then the reaction was allowed to reach room temperature overnight as the ice melted. The reaction was then concentrated *in vacuo* and dried on high vacuum for 1 h. The crude reaction was taken up in 1:5 (v:v) mixture of 1,4-dioxane:H_2O (0.40 mL: 1.60 mL, 0.563 M) and solid Na_2CO_3 (190 mg, 2.25 mmol, 2.0 equiv.) was added at room temperature and stirred for 15 min. A slurry of Fmoc N-hydroxysuccunimide ester (Fmoc-OSu) (380 mg, 1.13 mmol, 1.0 equiv.) in 1,4-dioxane (1.0 mL) was added and the reaction stirred overnight at room temperature and open to air. Once completion was reached (18 h) the reaction was diluted with H_2O and extracted with EtOAc (2 x 5.0 mL). The combined organic layers were washed with H_2O and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated to yield **44** as a white foam (183 mg, 40%). Spectral data is consistent with that previously reported.[26]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (br s, 2H), 7.78 (d, *J*= 7.6 Hz, 2H), 7.56 (d, *J*= 7.5 Hz, 2H), 7.44–7.38 (m, 2H), 7.35–7.30 (m, 2H), 7.00 (br s, 2H), 5.26 (d, *J*= 7.9 Hz, 1H), 4.69 (q, *J*= 6.5 Hz, 1H), 4.45 (ddd, *J*= 52.3, 10.7, 6.9 Hz, 2H), 4.21 (t, *J*= 6.7 Hz, 1H), 3.74 (s, 3H), 3.11 (ddd, *J*= 49.2, 13.9, 5.9 Hz, 2H).

Synthesis of 1-(pyridin-4-yl)-4-tosylpiperazine (SI-35)



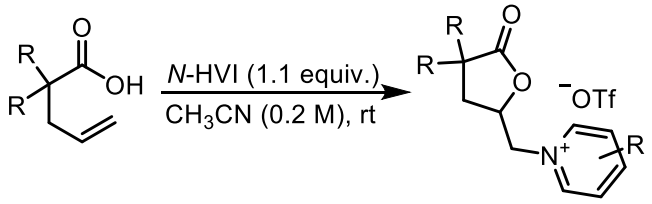
SI-34 **SI-35**

1-(pyridin-4-yl)-4-tosylpiperazine (SI-35). Tosyl protection was performed according to published procedures.[27] 1-(pyridin-4-yl)piperazine (**SI-34**) (1.0 g, 6.16 mmol, 1.0 equiv.) and Et_3N (1.28 mL, 6.80 mmol, 1.1 equiv.) were dissolved in dry CH_2Cl_2 (60 mL, 0.1 M). TsCl (1.30 g, 6.80 mmol, 1.1 equiv.) was then added in small portions at room temperature. The reaction stirred at room temperature overnight (15 h). Once completion was reached, the reaction was washed with $NaHCO_3$ (sat. aq.) and brine sequentially. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield **SI-35** as a yellow solid (1.6 g, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ8.24 (d, *J*= 5.7 Hz, 2H), 7.70–7.54 (m, 2H), 7.32 (d, *J*= 8.0 Hz, 2H), 6.65–6.52 (m, 2H), 3.42–3.34 (m, 4H), 3.14–3.03 (m, 4H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.3, 150.5, 144.2, 132.1, 129.9, 127.8, 108.8, 45.7, 45.5, 21.6. **HRMS** (m/z): $[M]^+$ calcd. For $C_{16}H_{20}N_3O_2S^+$, 318.1276; found 318.1277.

Section D. *N*-HVI Mediated Aminolactonization of Alkenoic Acids

<u>General Procedure D: Aminolactonization with Pre-formed, Isolated *N*-HVI</u>

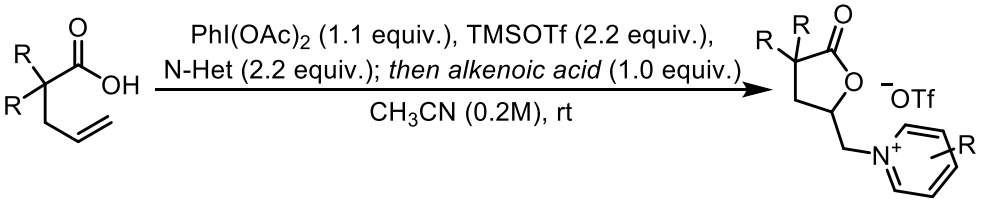


In a flame dried flask under argon, the desired alkenoic acid (0.30 mmol, 1.0 equiv.) was added to a suspension of *N*-HVI (0.33 mmol, 1.1 equiv.) in CH_3CN (1.5 mL, 0.20 M) at room temperature. The reaction was monitored by TLC and, once completion was reached (typically 20 min–6 h), the reaction was diluted with 3 mL of EtOAc and washed with $Na_2S_2O_3$ (sat. aq.) (1 x 2.0 mL) and $NaHCO_3$ (sat. aq.) (1 x 2.0 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Trituration with Et_2O and decanting the Et_2O yields the pure pyridinium lactone salts as solids. The solids are then dried under high vacuum.

Note: In some cases, trituration with Et_2O does not fully purify desired pyridinium lactones away from other heterocyclic salts and this can be seen on ^{1}H-NMR. In these cases, purification via flash chromatography with MeOH:CH_2Cl_2 can be performed to achieve pure products. Specific

substrates where this was required, and their chromatography conditions, are indicated in characterization data.

General Procedure E: Aminolactonization with *in situ* Formation of N-HVI

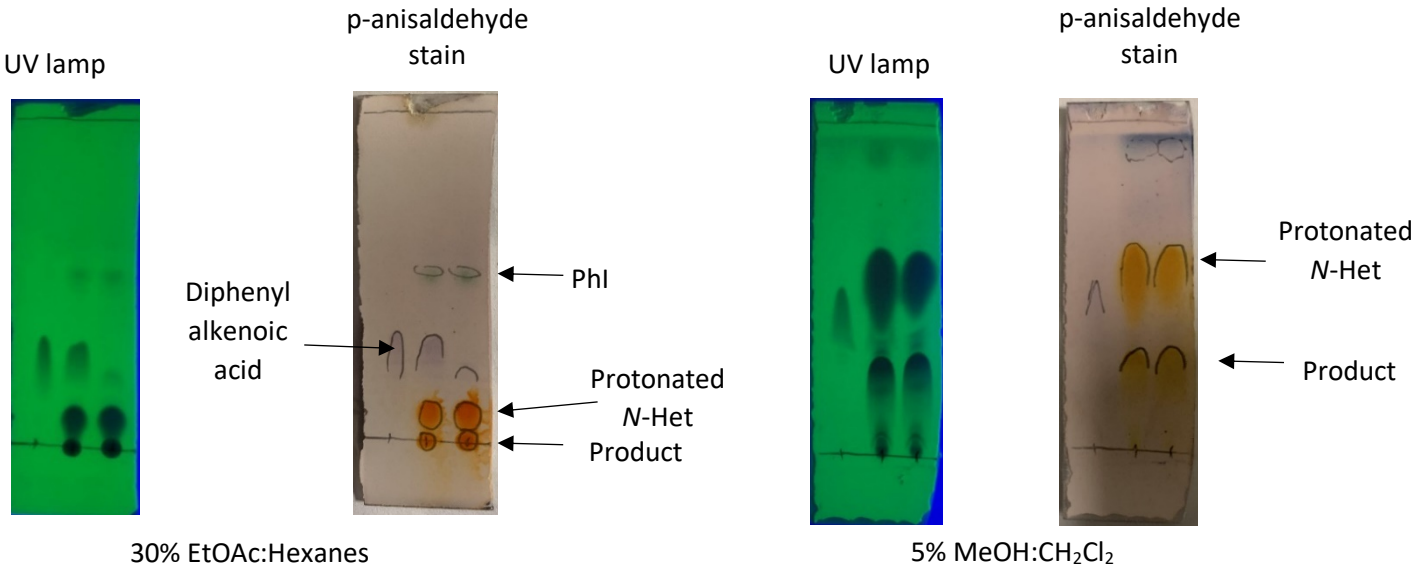


In a flame dried flask under argon, trimethylsilyl trifluoromethanesulfonate (2.2 equiv.) was added to a suspension of (diacetoxyiodo)benzene (**7**) (1.1 equiv.) in dry CH_3CN (1.5 mL, 0.2 M) at room temperature. After stirring for 15 minutes, the N-heterocycle (0.660 mmol, 2.2 equiv.) was added at room temperature and the reaction was allowed to stir for an additional 30 minutes. *Note: Unlike isolated N-HVI preparation described in General Procedure A, no precipitate will form in these cases as N-HVIs are soluble in CH_3CN.* The desired alkenoic acid (1.0 equiv.) was then added in one portion and the reaction stirred at room temperature and monitored by TLC (see representative TLC plates below). Once completion was reached (20 min–6 h) the reaction was diluted with 3 mL of EtOAc and washed with $Na_2S_2O_3$ (sat. aq.) (1 x 2.0 mL) and $NaHCO_3$ (sat. aq.) (1 x 2.0 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Trituration with Et_2O and decanting the Et_2O yields the pure pyridinium lactone salts as solids, and the solids are dried under high vacuum.

Note: "Precaution Free" aminolactonization was performed according to General Procedure E with the exception that glassware was not flame dried and reaction was left open to air.

Representative TLC of aminolactonization

TLC of the aminolactonization at completion



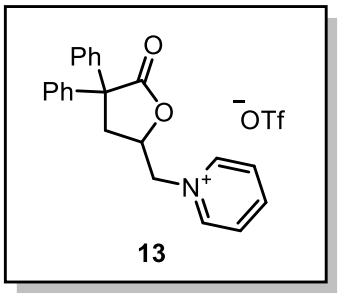
Note: When analyzing the reaction, using 30% EtOAc:Hexanes as solvent system, the consumption of starting material is evident, the top spot is PhI a byproduct of the reaction, the spot above the baseline is protonated N-Heterocycle, the formation of a pyridinium salt (product) at the baseline is also present. Using 5% MeOH:CH_2Cl_2 allows to visualize the product formation off the baseline.

General Procedure F: Aminolactonization with *N*-heterocycles containing more than one heteroatom (Representative of Substrates 40-42, Table 1).

In a flame dried flask under argon, trimethylsilyl trifluoromethanesulfonate (2.2 equiv.) was added to a suspension of (diacetoxyiodo)benzene (**7**) (1.1 equiv.) in dry CH_3CN (0.2 M) at room temperature. After stirring for 15 minutes, the N-heterocycle (2.2 equiv.) was added at room temperature and the reaction stirred for an additional 30 minutes. The solution was added in one portion to a preheated (50 °C) suspension of the alkenoic acid (1.0 equiv.) in dry CH_3CN (0.60 M) and the reaction stirred at 50 °C. Once completion was reached (2 h-8 h) the reaction was diluted with 3 mL of EtOAc and washed with $Na_2S_2O_3$ (sat. aq.) (1 x 2 mL) and $NaHCO_3$ (sat. aq.) (1 x 2 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Trituration with Et_2O and decanting the Et_2O yields the pure pyridinium lactone salts as solids, and the solids are dried under high vacuum.

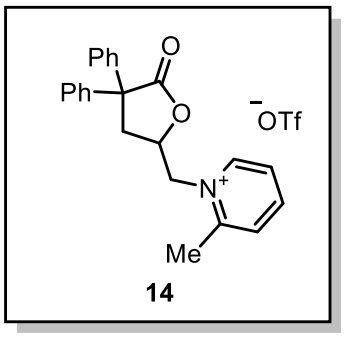
General Procedure G: "Dummy Ligand" Aminolactonization Protocol with *2,6-Lut*-HVI

In a flame dried flask under argon, trimethylsilyl trifluoromethanesulfonate (2.2 equiv.) was added to a suspension of (diacetoxyiodo)benzene (**7**) (1.1 equiv.) in dry CH_3CN (0.2 M) at room temperature. After stirring for 15 minutes, 2,6-lutidine (2.2 equiv.) was added and the reaction stirred for 15 minutes. The resulting solution of *2,6-lut-HVI* was added dropwise to a solution of the desired alkenoic acid (1.0 equiv.) and the desired N-heterocycle (1.1 equiv.) in dry CH_3CN (0.60 M) at room temperature, and the reaction was stirred at room temperature. Once completion was reached (30 min) the reaction was diluted with 3 mL of EtOAc and washed with $Na_2S_2O_3$ (sat. aq.) (1 x 2 mL) and with $NaHCO_3$ (sat. aq.) (1 x 2 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Trituration with Et_2O and decanting the Et_2O yields the pure pyridinium lactone salts as solids, and the solids are dried under high vacuum.



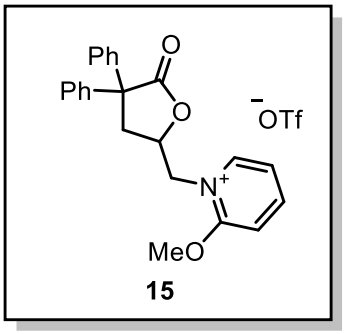
13

1-((5-oxo-4,4-dipenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (13). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and pyridine. Purification: Trituration with Et_2O to give **13** as a white solid. **Yield:** 692 mg, 96%. Alternatively, **13** could be accessed using Precaution Free procedure (**Yield:** 131 mg, 91%). **MP:** 127–129 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.75–8.72 (m, 2H), 8.55 (tt, *J*= 7.9, 1.4, Hz, 1H), 8.10–8.03 (m, 2H), 7.44–7.27 (m, 10H), 4.98–4.93 (m, 1H), 4.84–4.73 (m, 2H), 3.37 (dd, *J*= 13.3, 4.8 Hz, 1H), 2.87 (m, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.6, 147.7, 146.1, 142.5, 140.0, 130.0, 129.5, 129.4, 129.0, 128.7, 128.5, 128.2, 76.3, 64.5, 58.6, 40.3. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{22}H_{20}NO_2^+$,330.1489; found 330.1485.



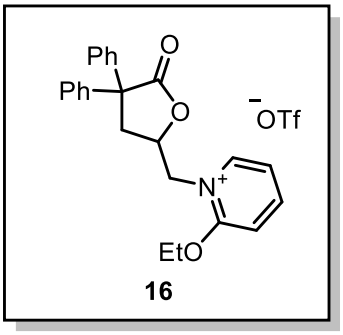
14

2-methyl-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (14). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 2-Me-pyridine. Purification: Trituration with Et_2O to give **14** as a light brown solid. **Yield:** 131 mg, 89%. Alternatively, **14**, could also be accessed using General Procedure D (**Yield:** 18 mg, 74%). **MP**: 142–144 °C. **^{1}H NMR** (400 MHz, CD_3CN): δ 8.64 (dd, *J*= 6.4, 1.5 Hz, 1H), 8.38 (td, *J*= 7.9, 1.5 Hz, 1H), 7.87 (ddd, *J*= 14.1, 7.9, 1.5, Hz, 2H), 7.43–7.27 (m, 10H), 4.91–4.70 (m, 3H), 3.39 (dd, *J*= 13.2, 4.8 Hz, 1H), 2.94 (dd, *J*= 13.3, 10.1 Hz, 1H), 2.81 (s, 3H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.4, 157.2, 146.9, 146.6, 142.2, 139.9, 131.1, 129.8, 129.2, 128.8, 128.4, 128.2, 127.9, 126.6, 75.6, 60.5, 58.2, 40.2, 21.1. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{23}H_{22}NO_3^+$, 344.1651; found 344.1656.



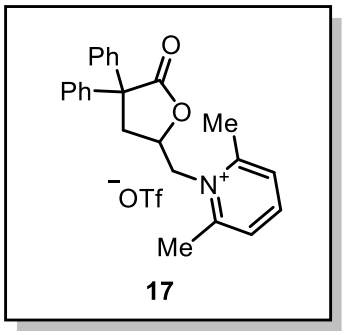
15

2-methoxy-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (15). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 2-OMe-pyridine. Purification: Trituration with Et_2O to give **15** as a white solid. **Yield:** 128 mg, 84%. **MP**: 182–183 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.43 (ddd, *J*= 9.0, 7.3, 1.8 Hz, 1H), 8.31 (dd, *J*= 6.4, 1.8 Hz, 1H), 7.55–7.46 (m, 2H), 7.42–7.28 (m, 10H), 4.88 (dd, *J*= 14.2, 2.4 Hz, 1H), 4.74 (ddt, *J*=14.8, 7.5, 2.5 Hz, 1H), 4.52 (dd, *J*=14.2, 9.3 Hz, 1H), 4.20 (s, 3H), 3.34 (dd, *J*= 13.3, 5.1 Hz, 1H), 2.87 (dd, *J*= 13.3, 10.4 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.8, 161.6, 149.8, 144.2, 142.6, 140.4, 130.0, 129.4, 129.0, 128.7. 128.4, 128.2, 119.8, 112.7, 74.6, 60.4, 58.6, 57.6, 40.6. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{23}H_{22}NO_3^+$, 360.1594; found 360.1622.



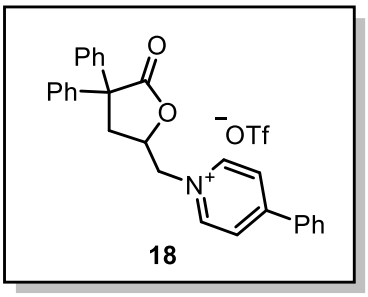
16

2-ethoxy-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (16). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 2-OEt-pyridine. Purification: Trituration with Et_2O to give **16** as a white solid. **Yield:** 64 mg, 61%. **MP:** 178–180 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.39 (ddd, *J*= 8.9, 7.6, 1.8 Hz, 1H), 8.28 (dd, *J*= 6.9, 1.8 Hz, 1H), 7.48–7.44 (m, 2H), 7.43–7.28 (m, 10H), 4.85 (dd, *J*= 14.3, 2.5 Hz, 1H), 4.75 (dddd, *J*= 10.4, 9.0, 5.1, 2.4 Hz, 1H), 4.56–4.46 (m, 3H), 3.34 (dd, *J*= 13.3, 5.1 Hz, 1H), 2.86 (dd, *J*= 13.3, 10.4 Hz, 1H), 1.47 (t, *J*= 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.8, 149.7, 144.1, 142.6, 140.3, 130.0, 129.4, 129.0, 128.6, 128.4, 128.1, 119.6, 113.1, 74.7, 70.7, 57.5, 40.5, 14.2. **HRMS** (m/z): $[M\text{-OTf}]^+$ calcd. For $C_{24}H_{24}NO_3^+$, 374.1756; found 374.1742.



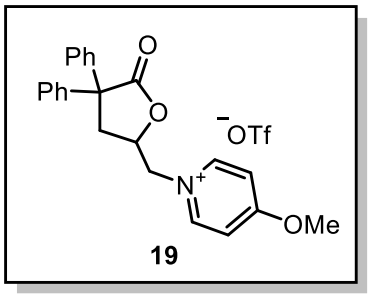
17

2,6-dimethyl-1-((5-oxo-4,4,-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (17). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 2,6-lutidine. Purification: trituration with Et_2O to give **17** as a light-brown solid. **Yield:** 30 mg, 21%. **MP:** 100–102 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.22 (t, *J*= 7.9 Hz, 1H), 7.73 (d, *J*= 7.9 Hz, 2H), 7.43–7.27 (m, 10H), 4.65–4.61 (m, 1H), 4.58 (ddd, *J*= 10.8, 5.4, 2.4 Hz, 1H), 4.35 (dd, *J*= 12.3, 5.6 Hz, 1H), 3.12 (dd, *J*= 13.3, 5.2 Hz, 1H), 2.80–2.74 (m, 1H), 2.71 (s, 6H). **^{13}C NMR** (126 MHz, CD_3CN): ^{13}C NMR (126 MHz, CD_3CN) δ 177.35, 165.63, 157.65, 147.06, 142.79, 129.98, 129.34, 128.83, 128.61, 128.32, 128.06, 75.31, 67.13, 54.55, 38.76, 21.92, 1.79. **HRMS** (m/z): $[M\text{-OTf}]^+$ calcd. oi 358.1810; found 358.1802



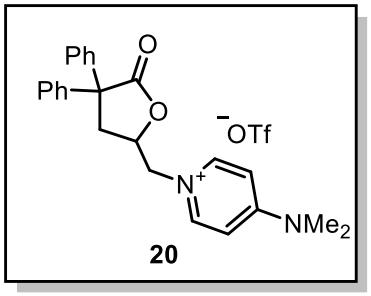
18

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-4-phenylpyridin-1-ium trifluoromethanesulfonate (18). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 4-Ph-pyridine. Purification: trituration with Et_2O to give **18** as a white solid. **Yield:** 159 mg, 95%. **MP:** 168–169 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.73 (d, *J*= 7.1 Hz, 2H), 8.28 (d, *J*= 7.0 Hz, 2H), 7.95-7.89 (m, 2H), 7.69–7.59 (m, 3H), 7.42–7.27 (m, 10H), 5.01–4.91 (m, 1H), 4.84–4.74 (m, 2H), 3.43–3.36 (m, 1H), 2.92–2.83 (m, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.7, 158.1, 146.0, 142.6, 140.0, 134.7, 133.5, 130.8, 130.1, 129.4, 129.2, 129.1, 128.7, 128.4, 128.2, 126.2, 76.4, 63.7, 58.6, 40.3. **HRMS** (m/z): $[M\text{-OTf}]^+$ calcd. For $C_{28}H_{24}NO_2^+$, 406.1802; found 406.1834.



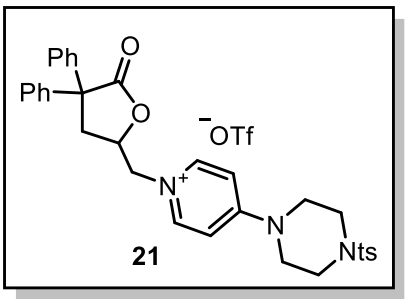
19

4-methoxy-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (19). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 4-OMe-pyridine. Purification: trituration with Et_2O to give **19** as a white solid. **Yield:** 135 mg, 88%. **MP:** 144–146 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.50 (d, *J*= 7.6 Hz, 1.5H), 7.43–7.26 (m, 12.5H), 4.78 (dd, *J*= 14.2, 2.2 Hz, 1H), 4.71 (dddd, *J*= 10.6, 9.0, 4.9, 2.2 Hz, 1H), 4.61 (dd, *J*= 14.2, 9.0 Hz, 1H), 4.08 (s, 3H), 3.34 (dd, *J*= 13.3, 5.0 Hz, 1H), 2.81 (dd, *J*= 13.4, 10.5 Hz, 1H) **^{13}C NMR** (126 MHz, CD_3CN): δ 176.7, 172.9, 147.3, 142.6, 140.1, 130.0, 129.4, 129.0, 128.7, 128.4, 128.2, 114.6, 76.4, 62.6, 59.1, 58.6, 40.2. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{23}H_{22}NO_3^+$, 360.1594; found 360.1612.



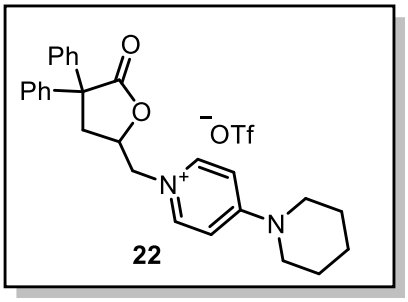
20

4-(dimethylamino-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (20). General Procedure D was followed using 2,2-Diphenylpent-4-enoic acid (**12**) and 4-(dimethylamino)-pyridine. Purification: trituration with Et_2O to give **20** as a white solid. **Yield:** 144 mg, 92%. Alternatively, **20**, could also be accessed using General Procedure E (**Yield:** 114 mg, 73%). **MP**: 117–119 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 7.95 (d, *J*= 8.0 Hz, 2H), 7.45–7.25 (m, 10H), 6.85 (d, *J*= 8.0 Hz, 2H), 4.64 (dddd, *J*= 8.0, 6.2, 5.1, 2.5, Hz, 1H), 4.50 (dd, *J*= 14.8, 2.5 Hz, 1H), 4.32 (dd, *J*= 14.8, 8.8 Hz, 1H), 3.28, (dd, *J*= 13.3, 5.1 Hz, 1H), 3.17 (s, 6H), 2.75 (dd, *J*= 13.3, 10.5 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.9, 157.6, 143.1, 142.7, 140.3, 130.0, 129.4, 129.0, 128.6, 128.4, 128.2, 108.7, 76.7, 60.6, 58.6, 40.7, 40.2. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{24}H_{25}N_2O_2^+$, 373.1911; found 373.1937.



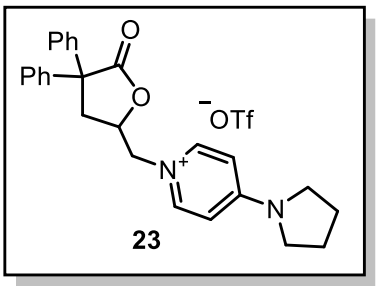
21

4-(4-tosylpiperazin-1-yl)-1-((5-oxo-4,4-dipenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (21). General Procedure F was followed using 2,2-Diphenylpent-4-enoic acid (**12**) and **1**-(pyridin-4-yl)-4-tosylpiperazine (**SI-35**). Modifications to General Procedure: reaction time: 4 days. Purification: flash column chromatography (0–2% MeOH:CH_2Cl_2) to give **21** as a white solid. **Yield:** 83mg, 70%. **MP:** 148–150 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.14 (d, *J*= 7.0 Hz, 2H), 7.57 (d, *J*= 8.5 Hz, 2H), 7.35–7.25 (m, 7H), 7.23–7.15 (m, 5H), 6.91 (d, *J*= 7.5 Hz, 2H), 4.72 (dd, *J*= 15.0, 2.5 Hz, 1H), 4.64–4.56 (m, 1H), 4.32 (dd, *J*= 14.5, 8.5 Hz, 1H), 3.68 (t, *J*= 5.0 Hz, 4H), 3.37 (dd, *J*= 13.5, 5.0 Hz, 1H), 3.08 (t, *J*= 5.0 Hz, 4H), 2.55 (dd, *J*= 13.5, 10.5 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 176.3, 156.0, 144.7, 143.5, 141.7, 138.0, 131.9, 130.2, 129.3, 128.6, 128.3, 127.78, 127.77, 127.6, 127.4, 120.8 (q, *J*= 319.0 Hz), 108.8, 76.1, 60.4, 57.7, 46.1, 45.5, 39.8, 21.7. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{33}H_{34}N_3O_4S^+$, 568.2270; found 568.2280.



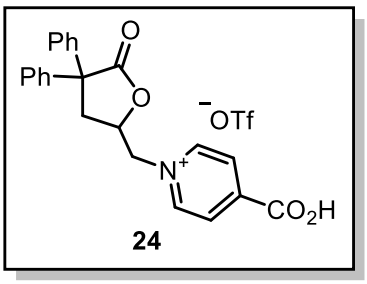
22

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-4-(piperidin-1-yl)pyridin-1-ium trifluoromethanesulfonate (22). General Procedure F was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 4-piperidinylpyridine. Modifications to General Procedure: two washes with $NaHCO_3$ (sat. aq.). Purification: trituration with Et_2O to give **22** as a brown solid. **Yield:** 57 mg, 41%. **MP:** 192–194 °C. **^{1}H NMR** (500 MHz, CH_3CN): δ 7.92–7.87 (d, *J*= 7.9 Hz, 2H), 7.43–7.27 (m, 10H), 6.95 (d, *J*= 8.0 Hz, 2H), 4.62 (dddd, *J*= 10.8, 8.7, 5.1, 2.5 Hz, 1H), 4.46 (dd, *J*= 14.8, 2.5 Hz, 1H), 4.28 (dd, *J*= 14.8, 8.7 Hz, 1H), 3.61 (dd, *J*= 6.6, 4.4 Hz, 4H), 3.26 (dd, *J*= 13.3, 5.1 Hz, 1H), 2.75 (dd, *J*= 13.3, 10.6 Hz, 1H), 1.76–1.69 (m, 2H), 1.69–1.63 (m, 4H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.84, 156.40, 143.47, 142.63, 140.32, 129.99, 129.37, 128.94, 128.59, 128.37, 128.13, 108.80, 76.64, 71.53, 60.38, 58.60, 48.87, 40.20, 26.16, 24.37. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{27}H_{29}N_2O_2^+$, 413.2229; found 413.2230.



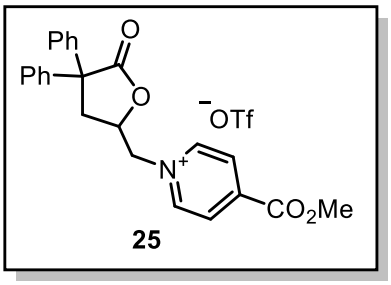
23

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-4-(pyrrolidin-1-yl)pyridin-1-ium trifluoromethanesulfonate (23). General Procedure F was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 4-pyrrolidin-1-ylpyridine. Purification: trituration with Et_2O to give **23** as a white solid. **Yield:** 105 mg, 64%. **MP:** 198–200 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 7.91 (d, *J*= 7.7 Hz, 2H), 7.42–7.26 (m, 10H), 6.71 (d, *J*= 7.7 Hz, 2H), 4.63 (dddd, *J*= 10.6, 8.7, 5.1, 2.5 Hz, 1 H), 4.48 (dd, *J*= 14.8, 2.5 Hz, 1H) 4.30 (dd, *J*= 14.8, 8.7 Hz, 1H), 3.51–3.44 (m, 4H), 3.27 (dd, *J*= 13.3, 5.2 Hz, 1H), 2.75 (dd, *J*= 13.3, 10.5 Hz, 1H), 2.08–2.03 (m, 4H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.9, 154.7, 143.0, 142.7, 140.4, 130.0, 129.4, 129.0, 128.6, 128.4, 128.2, 109.2, 76.7, 60.6, 58.6, 49.6, 47.9, 40.2, 25.7. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{26}H_{27}N_2O_2^+$, 399.2067; found 399.2098.



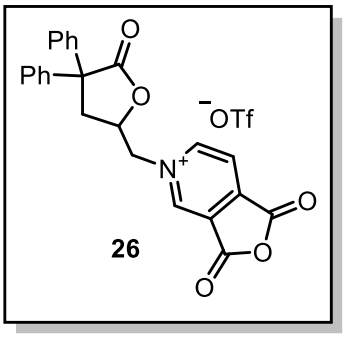
24

4-carboxy-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (24). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and isonicotinic acid. Purification: trituration with Et_2O to give **24** as a white solid. **Yield:** 11 mg, 21%. **MP:** 136–138 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.90–8.85 (m, 2H), 8.46–8.42 (m, 2H), 7.45–7.28 (m, 10H), 5.00 (dd, *J*= 14.0, 2.1 Hz, 1H), 4.86 (dd, *J*= 14.0, 9.3 Hz, 1H), 4.80–4.72 (m, 1H), 3.36 (dd, *J*= 13.3, 5.0 Hz, 1H), 2.89 (dd, *J*= 13.3, 10.5 Hz, 1H).); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.45, 147.58, 146.64, 142.34, 139.96, 130.03, 129.40, 129.05, 128.74, 128.60, 128.47, 128.10, 76.01, 64.86, 58.52, 54.70, 40.21. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{22}H_{20}NO_4^+$, 374.1392; found 374.1394.



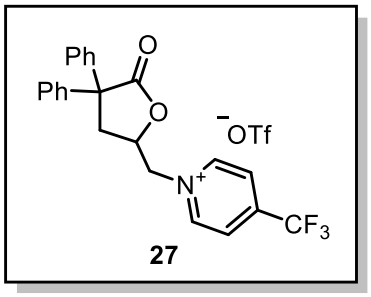
25

4-(methoxycarbonyl)-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (25). General Procedure E was followed using 2,2-Diphenylpent-4-enoic acid (**12**) and methyl isonicotinate. Purification: trituration with Et_2O to give **25** as an off-white solid. **Yield:** 140 mg, 87%. **MP:** 128–130 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.88 (td, *J*= 6.3, 3.1 Hz, 2H), 8.48–8.42 (m, 2H), 7.43–7.28 (m, 10H), 5.01 (d, *J*= 13.9 Hz, 1H), 4.93–4.82 (m, 1H), 4.78 (dddt, *J*= 8.8, 5.1, 3.5, 1.6 Hz, 1H), 4.01 (s, 3H), 3.39–3.32 (m, 1H), 2.89 (dd, *J*= 13.3, 10.6 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ ^{13}C NMR (126 MHz, CD_3CN) δ 176.5, 163.2, 147.6, 146.6, 142.4, 140.0, 130.0, 129.0, 128.7, 128.6, 128.5, 128.1, 76.1, 64.9, 58.5, 54.7, 40.2. **HRMS** (m/z): $[M\text{-OTf}]^+$ calcd. For $C_{24}H_{22}NO_4^+$, 388.1546; found 388.1543.



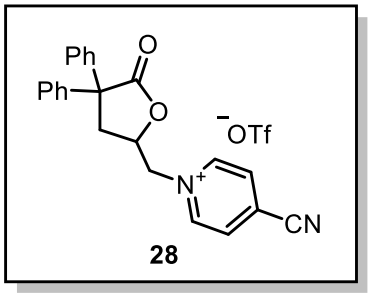
26

1,3-dioxo-5-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-1,3-dihydrofuro[3,4-c]pyridin-5-ium trifluoromethanesulfonate (26) General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and pyridine-2,3-dicarboxylic anhydride. Modifications to General Procedure: instead of doing a $Na_2S_2O_3$ and $NaHCO_3$ wash, do one wash with DI H_2O Purification: trituration with Et_2O to give **26** as an off-white solid. **Yield:** 27 mg, 43%. **MP:** 102–104 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.23 (s, 1H), 8.94 (dd, *J*= 6.3, 1.4 Hz, 1H), 8.22 (d, *J*= 6.4 Hz, 1H), 7.47–7.26 (m, 10H), 4.99 (dd, *J*= 14.0, 2.3 Hz, 1H), 4.87 (dd, *J*= 14.1, 9.2 Hz, 1H), 4.77 (tdd, *J*= 9.1, 4.8, 2.2 Hz, 1H), 3.33 (dd, *J*= 13.2, 5.0 Hz, 1H), 2.89 (dd, *J*= 13.3, 10.6 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 201.73, 176.41, 164.77, 150.32, 142.36, 139.95, 130.04, 129.41, 129.07, 128.64, 128.48, 75.84, 64.96, 58.53, 40.19 **HRMS** (m/z): $[M\text{-OTf}]^+$ calcd. For $C_{24}H_{18}NO_5^+$, 400.1179; found 418.1291 [addition of H_2O during analysis. $[M\text{-OTf} + H_2O]^+$ calcd. 418.1285].

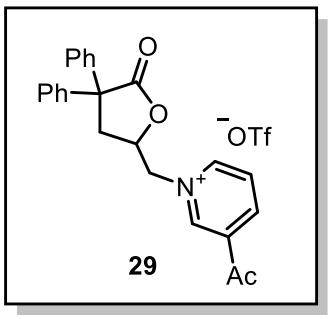


27

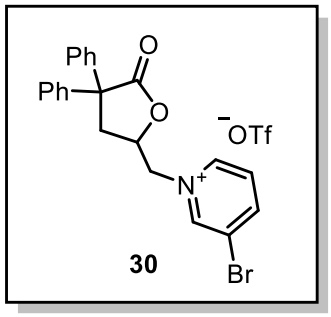
1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-4-(trifluoromethyl)pyridin-1-ium trifluoromethanesulfonate (27). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 4-trifluoromethylpyridine. Purification: trituration with Et_2O to give **27** as a white solid. **Yield:** 133 mg, 81%. **MP:** 195–196 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.07 (d, *J*= 6.5 Hz, 2H), 8.40 (d, *J*= 6.3 Hz, 2H), 7.49–7.29 (m, 10H), 5.12 (dd, *J*= 14.1, 2.3 Hz, 1H), 4.97 (dd, *J*= 14.1, 9.2 Hz, 1H), 4.85–4.76 (m, 1H), 3.42 (dd, *J*= 13.3, 5.0 Hz, 1H), 2.93 (dd, *J*= 13.3, 10.7 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 175.2, 147.2, 141.1, 138.6, 128.8, 128.1, 127.8, 127.4, 127.2, 126.9, 125.2, 74.7, 64.0, 57.3, 38.9. **^{19}F NMR** (470 MHz, CD_3CN): δ –66.01, –79.36. **HRMS** (m/z): $[M\text{-OTf}]^+$ calcd. For $C_{23}H_{19}F_3NO_2^+$, 398.1362; found 398.1382.



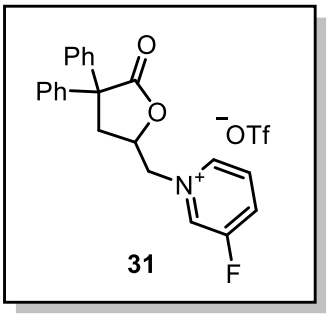
4-cyano-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (28). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 4-cyanopyridine. Purification: trituration with Et_2O to give **28** as an off-white solid. **Yield:** 138 mg, 91%. Alternatively, **28** could also be accessed using Precaution Free procedure. **Yield:** 61 mg, 53%. **MP:** 169–170 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.93 (d, *J*= 7.0 Hz, 2H), 8.38 (d, *J*= 6.9 Hz, 2H), 7.43–7.29 (m, 10H), 5.02 (dd, *J*= 14.1, 2.2 Hz, 1H), 4.87 (dd, *J*= 14.0, 9.2 Hz, 1H), 4.75 (dddd, *J*= 10.7, 9.2, 5.0, 2.2 Hz, 1H), 3.36 (dd, *J*= 13.3, 5.0 Hz, 1H), 2.89 (dd, *J*= 13.3, 10.6 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.0, 147.3, 141.9, 139.5, 132.1, 129.7, 129.0, 128.7, 128.2, 128.1, 127.7, 114.5, 75.5, 65.1, 58.2, 39.8. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{23}H_{19}N_2O_2^+$, 355.1441; found 355.1461.



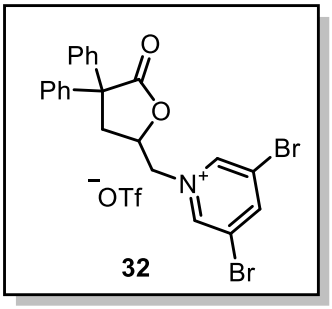
3-acetyl-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (29). General Procedure E was followed using 2,2-Diphenylpent-4-enoic acid (**12**) and 3-acetylpyridine. Purification: trituration with Et_2O to give **29** as an orange solid. **Yield:** 102 mg, 66%. **MP:** 186–188 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.18 (d, *J*= 1.7 Hz, 1H), 8.95 (d, *J*= 8.2 Hz, 1H), 8.85 (dd, *J*= 6.1, 1.1 Hz, 1H), 8.21–8.16 (m, 1H), 7.43–7.28 (m, 10H), 5.01 (dd, *J*= 13.9, 2.0 Hz, 1H), 4.87 (dd, *J*= 13.9, 9.4 Hz, 1H), 4.80 (dddd, *J*= 10.5, 9.3, 4.8, 2.0 Hz, 1H), 3.37 (dd, *J*= 13.3, 4.9 Hz, 1H), 2.90 (dd, *J*= 13.3, 10.5 Hz, 1H), 2.68 (s, 3H). δ **^{13}C NMR** (126 MHz, CD_3CN): δ 194.2, 176.5, 148.7, 146.6, 146.2, 142.6, 139.9, 137.2, 130.0, 129.8, 129.4, 129.1, 128.7, 128.4, 128.2, 76.2, 71.5, 64.9, 58.6, 40.3, 27.4. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{24}H_{22}NO_3^+$, 372.1594; found 372.1594.



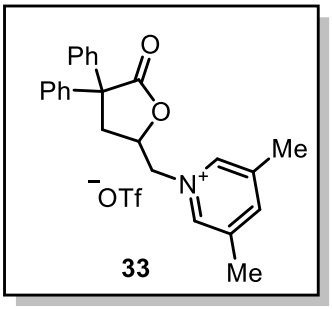
3-bromo-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (30). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 3-bromopyridine. Purification: trituration with Et_2O to give **30** as an off-white solid. **Yield:** 137 mg, 83%. **MP:** 148–149 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.97–8.95 (m, 1H), 8.75 (dq, *J*= 6.2, 1.5 Hz, 1H), 8.70 (ddd, *J*= 8.5, 2.0, 1.1 Hz, 1H), 7.98 (dd, *J*= 8.4, 6.1 Hz, 1H), 7.44–7.28 (m, 10H), 4.98–4.90 (m, 1H), 4.82–4.74 (m, 2H), 3.39–3.33 (m, 1H), 2.91–2.84 (m, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.5, 150.2, 147.3, 145.2, 142.5, 140.0, 130.2, 130.1, 129.4, 129.1, 128.7, 128.5, 128.2, 123.9, 76.0, 64.8, 58.6, 40.3. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{22}H_{19}BrNO_2^+$, 408.0594; found 408.0594.



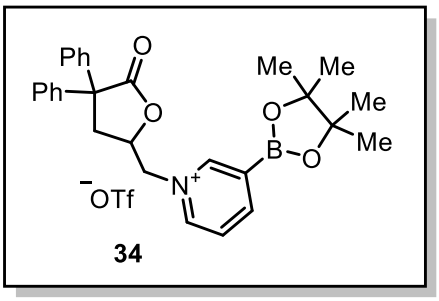
3-fluoro-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (31). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 3-fluoropyridine. Purification: trituration with Et_2O to give **31** as a white solid. **Yield:** 71 mg, 71%. **MP:** 152–154 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.78 (d, *J*= 2.2 Hz, 1H), 8.67–8.60 (m, 1H), 8.43–8.37 (m, 1H), 8.12 (dt, *J*= 8.7, 5.7 Hz, 1H), 7.44–7.26 (m, 10H), 5.00–4.89 (m, 1H), 4.86–4.73 (m, 2H), 3.34 (dd, *J*= 13.2, 4.8 Hz, 1H), 2.89 (dd, *J*= 13.1, 10.3 Hz, 1H).**^{13}C NMR** (126 MHz, CD_3CN) δ 176.49, 162.58, 160.55, 143.55, 142.51, 139.99, 136.37, 135.37, 131.06, 131.00, 130.07, 129.45, 129.09, 128.66, 128.49, 128.19, 75.99, 65.10, 60.95, 58.56, 40.28. **^{19}F NMR** (470 MHz, CD_3CN): δ –79.34, –116.08. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{22}H_{19}FNO_2^+$, 348.1394; found 348.1373.



3,5-dibromo-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (32). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 3,5-dibromopyridine. Purification: trituration with Et_2O to give **32** as a white solid. **Yield:** 135 mg, 71%. **MP:** 200–202 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.02–8.90 (m, 3H), 7.44–7.26 (m, 10H), 5.01–4.91 (m, 1H), 4.83–4.73 (m, 2H), 3.41–3.32 (m, 1H), 2.91–2.84 (m, 1H); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.5, 152.3, 146.5, 142.5, 139.9, 130.1, 129.4, 129.1, 128.7, 128.5, 128.2, 124.0, 75.8, 65.0, 58.6, 40.2. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{22}H_{18}Br_2NO_2^+$, 485.9699; found 485.9704.

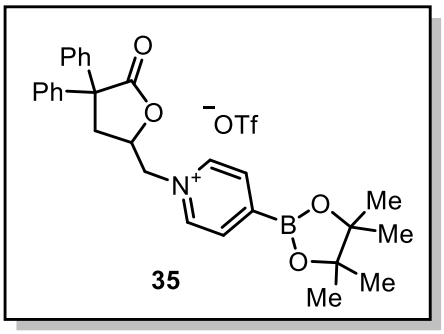


3,5-dimethyl-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (33). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 3,5-dimethylpyridine. Purification: trituration with Et_2O to give **33** as an off-white solid. **Yield:** 99 mg, 65%. **MP:** 142–143 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.45 (d, *J*= 1.6 Hz, 2H), 8.23–8.19 (m, 1H), 7.46–7.30 (m, 10H), 4.90 (dd, *J*= 14.0, 2.2 Hz, 1H), 4.84–4.76 (m, 1H), 4.71 (dd, *J*= 13.9, 9.1 Hz, 1H), 3.40 (dd, *J*= 13.3, 5.0 Hz, 1H), 2.89 (dd, *J*= 13.3, 10.5 Hz, 1H), 2.50 (s, 6H).**^{13}C NMR** (125 MHz, CD_3CN): δ 176.6, 148.5, 142.8, 142.6, 140.1, 130.0, 129.4, 129.0, 128.6, 128.4, 76.3, 71.5, 64.3, 58.5, 40.3, 18.3. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. $C_{24}H_{24}NO_2^+$, 358.1801; found 358.1801.



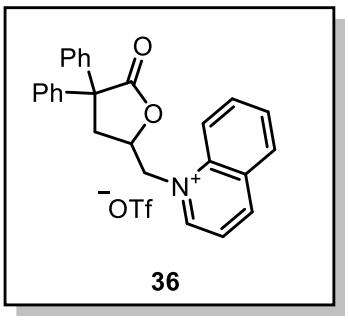
34

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-1-ium trifluoromethanesulfonate (34). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 3-Bpin-pyridine. Modifications to General Procedure: In place of washing with $NaHCO_3$, one wash with 1 M HCl was performed. Purification: trituration with Et_2O to give **34** as an off-white foam. **Yield:** 127 mg, 68%. **MP:** 118–119 °C. **^{1}H NMR** (500 MHz, CD_3CN) δ 8.74 (dd, *J*= 5.0, 1.5 Hz, 2H), 8.20 (dd, *J*= 5.0, 1.5 Hz, 2H), 7.40–7.28 (m, 10H), 4.99 (dd, *J*= 13.5, 2.0 Hz, 1H), 4.85–4.74 (m, 2H), 3.38 (dd, *J*= 13.5, 5.0 Hz, 1H), 2.86 (dd, *J*= 13.0, 5.0 Hz, 1H)), 1.37 (s, 12H); **^{13}C NMR** (125 MHz, CD_3CN) δ 176.5, 144.9, 142.5, 139.9, 133.6, 130.0, 129.4, 129.0, 128.6, 128.4, 128.1, 124.5 (q, *J*= 322.4 Hz), 87.0, 76.2, 64.5, 40.2, 25.0. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. for $C_{28}H_{31}BNO_4^+$, 456.2341; found 374.1558 [due to hydrolysis of boronic ester to boronic acid during analysis. $[M\text{-}OTf\text{-}C_6H_{12}]^+$: 374.1558.]



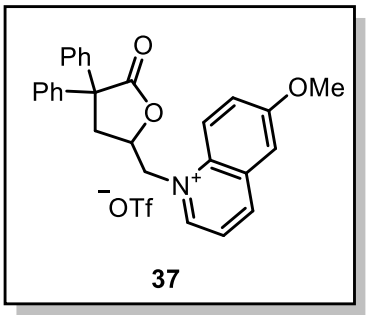
35

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-1-ium trifluromethanesulfonate (35). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 4-Bpin-pyridine. Modifications to General Procedure: instead of doing a $NaHCO_3$ wash, do one was with DI H_2O. Purification: trituration with Et_2O to give **35** as a white solid. **Yield:** 131 mg, 72%. **MP**: 91–93 °C. **^{1}H NMR** (500 MHz, CD_3CN) δ 8.74 (dd, *J*= 5.0, 1.5 Hz, 2H), 8.20 (dd, *J*= 5.0, 1.5 Hz, 2H), 7.40–7.28 (m, 10H), 4.99 (dd, *J*= 13.5, 2.0 Hz, 1H), 4.85–4.74 (m, 2H), 3.38 (dd, *J*= 13.5, 5.0 Hz, 1H), 2.86 (dd, *J*= 13.0, 5.0 Hz, 1H)), 1.37 (s, 12H); **^{13}C NMR** (125 MHz, CD_3CN) δ 176.5, 144.9, 142.5, 139.9, 133.6, 130.0, 129.4, 129.0, 128.6, 128.4, 128.1, 124.5 (q, *J*= 322.4 Hz), 87.0, 76.2, 64.5, 40.2, 25.0. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{28}H_{31}BNO_4^+$, 456.2346; found 456.2348.



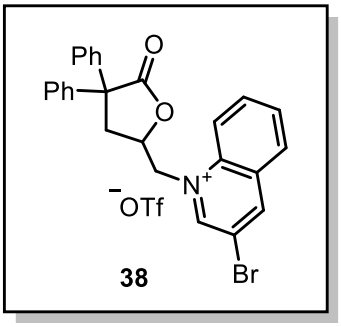
36

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)quinolin-1-ium trifluoromethanesulfonate (36). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and quinoline. Purification: trituration with Et_2O to give **36** as a light orange solid. **Yield:** 63 mg, 40%. **MP:** 196–197 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.18–9.13 (m, 2H), 8.49 (d, *J*= 9.0 Hz, 1H), 8.38 (dd, *J*= 8.3, 1.4 Hz, 1H), 8.23 (ddd, *J*= 8.8, 7.0, 1.4 Hz, 1H), 8.06 (dd, *J*= 8.4, 5.8 Hz, 1H), 8.01 (t, *J*= 7.6 Hz, 1H), 7.42–7.27 (m, 10H), 5.43 (dd, *J*= 15.1, 2.3 Hz, 1H), 5.20 (dd, *J*= 15.1, 9.4 Hz, 1H), 4.88–4.80 (m, 1H), 3.51 (dd, *J*= 13.3, 5.0 Hz, 1H), 3.04 (dd, *J*= 13.3, 10.6 Hz, 1H); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.6, 150.8, 149.8, 142.5, 140.2, 139.6, 137.2, 131.9, 131.4, 131.3, 130.0, 129.4, 129.0, 128.7, 128.5, 128.2, 123.0, 119.7, 75.6, 60.6, 58.7, 40.6. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. for $C_{26}H_{22}NO_2^+$, 380.1645; found 380.1676.



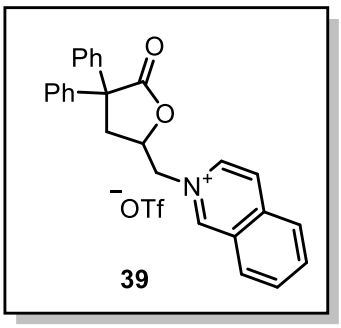
37

6-methoxy-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)quinolin-1-ium trifluoromethanesulfonate (37). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 6-methoxyquinoline. Purification: trituration with Et_2O to give **37** as a brown solid. **Yield:** 117 mg, 70%. **MP:** 176–178 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.00–8.94 (m, 2H), 8.39 (d, *J*= 9.7 Hz, 1H), 7.98 (dd, *J*= 8.4, 5.8 Hz, 1H), 7.82 (dd, *J*= 9.7, 2.9 Hz, 1H), 7.70 (d, *J*= 2.9 Hz, 1H), 7.40–7.28 (m, 10H), 5.35 (dd, *J*= 15.1, 2.3 Hz, 1H), 5.15 (dd, *J*= 15.1, 9.4 Hz, 1H), 4.81 (dddd, *J*= 10.5, 9.3, 5.0, 2.3 Hz, 1H), 4.01 (s, 3H), 3.48 (dd, *J*= 13.3, 5.0 Hz, 1H), 3.02 (dd, *J*= 13.3, 10.5 Hz, 1H); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.6, 161.0, 147.7, 147.6, 142.5, 140.3, 135.3, 133.5, 130.0, 129.4, 129.0, 128.7, 128.5, 128.2, 123.3, 121.3, 109.1, 75.7, 60.7, 58.7, 57.3, 40.6. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{27}H_{24}NO^+$, 410.1756; found 410.1782.



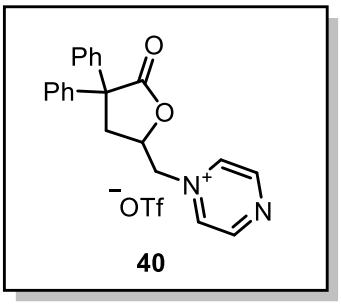
38

3-bromo-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)quinolin-1-ium trifluoromethanesulfonate (38). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 3-bromoquinoline. Purification: trituration with Et_2O to give **38** as a light yellow solid. **Yield:** 65 mg, 35%. **MP:** 171–172 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.34 (s, 2H), 8.48 (d, *J*= 9.1 Hz, 1H), 8.32–8.23 (m, 2H), 8.05 (t, *J*= 7.6 Hz, 1H), 7.41–7.27 (m, 10H), 5.32 (dd, *J*= 15.1, 2.5 Hz, 1H), 5.23 (dd, *J*= 15.1, 9.2 Hz, 1H), 4.85 (dddd, *J*= 10.9, 9.1, 5.1, 2.4 Hz, 1H), 3.46 (dd, *J*= 13.3, 5.0 Hz, 1H), 3.06 (dd, *J*= 13.3, 10.7 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.4, 151.6, 151.1, 142.3, 140.1, 138.5, 137.4, 131.7, 131.0, 130.0, 129.4, 129.0, 128.6, 128.5, 128.1, 119.9, 75.8, 60.7, 40.5. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{26}H_{21}BrNO_2^+$, 458.0756; found 458.0760.



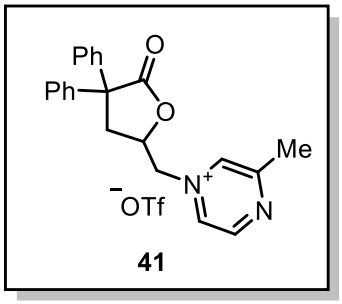
39

2-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)isoquinolin-2-ium trifluoromethanesulfonate (39). General Procedure E was followed using 2,2-diphenylpent-4-enoic acid (**12**) and isoquinoline. Purification: trituration with Et_2O to give **39** as a light orange solid. **Yield:** 132 mg, 83%. **MP**: 166–167 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.67–9.58 (m, 1H), 8.48–8.40 (m, 3H), 8.29–8.21 (m, 2H), 8.07–8.02 (m, 1H), 7.42–7.26 (m, 10H), 5.10 (dd, *J*= 14.0, 2.2 Hz, 1H), 4.93 (dd, *J*= 14.0, 9.1 Hz, 1H), 4.87 (dddd, *J*= 11.0, 9.1, 4.9, 2.0 Hz, 1H), 3.42 (dd, *J*= 13.2, 4.9 Hz, 1H), 2.93 (dd, *J*= 13.3, 10.4 Hz, 1H); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.7, 151.2, 142.6, 140.1, 139.0, 138.7, 136.0, 132.7, 131.5, 130.0, 129.4, 129.0, 128.6, 128.4, 128.4, 128.2, 127.5, 76.5, 64.4, 58.6, 40.4. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{26}H_{22}NO_2^+$, 380.1645; found 380.1676.



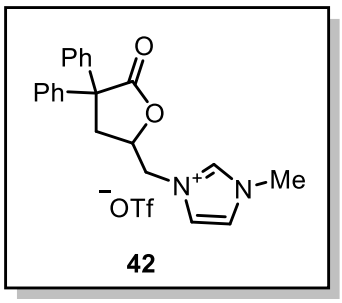
40

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyrazin-1-ium trifluoromethanesulfonate (40). General Procedure F was followed using 2,2-diphenylpent-4-enoic acid (**12**) and pyrazine. Purification: trituration with Et_2O to give **40** as a brown solid. **Yield:** 88 mg, 59%. **MP:** 98–100 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.44 (qd, *J*= 2.8, 1.5 Hz, 2H), 8.78 (dt, *J*= 2.8, 1.2 Hz, 2H), 7.43–7.28 (m, 10H), 5.01 (dd, *J*= 13.9, 1.9 Hz, 1H), 4.88 (dd, *J*= 13.9, 9.2 Hz, 1H), 4.80–4.72 (m, 1H), 3.38 (dd, *J*= 13.3, 4.9 Hz, 1H), 2.91 (dd, *J*= 13.3, 10.7 Hz, 1H); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.4, 152.5, 142.3, 139.9, 138.1, 130.1, 129.4, 129.1, 128.7, 128.5, 128.1, 75.7, 65.3, 58.5, 40.2. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{21}H_{19}N_2O_2^+$, 331.1441; found 331.1447.



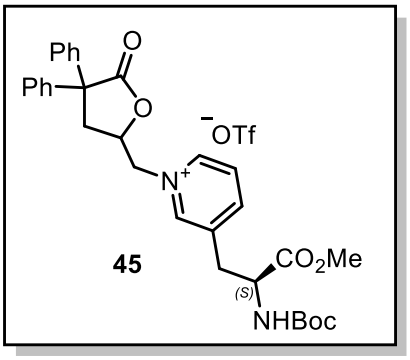
41

3-methyl-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyrazin-1-ium trifluoromethanesulfonate (41). General Procedure F was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 2-Methylpyrazine. Modification: reaction temperature was run at room temperature. Purification: trituration with Et_2O to give **41** as a brown solid. **Yield:** 66 mg, 60%. **MP:** 101–103 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 9.28 (d, *J*= 2.9 Hz, 1H), 8.69–8.62 (m, 1H), 8.60–8.54 (m, 1H), 7.43–7.27 (m, 10H), 4.95 (t, *J*= 12.8 Hz, 1H), 4.79 (ddt, *J*= 19.7, 10.3, 5.5 Hz, 2H), 3.38 (ddd, *J*= 12.9, 6.6, 4.7 Hz, 1H), 2.90 (dd, *J*= 13.2, 10.4 Hz, 1H), 2.79 (s, 3H). **^{13}C NMR** (126 MHz, CD_3CN): δ 176.4, 163.4, 151.3, 142.3, 139.9, 137.4, 134.8, 130.0, 129.4, 129.1, 128.6, 128.5, 128.1, 75.7, 71.5, 65.0, 58.5, 40.2, 22.7. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{22}H_{21}N_2O_2^+$, 345.1598; found 345.1628.

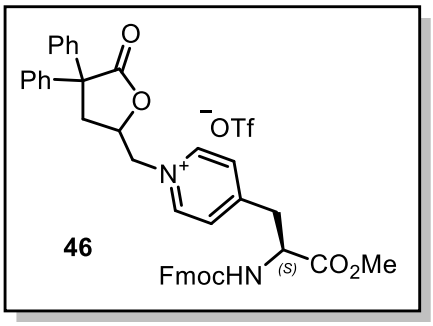


42

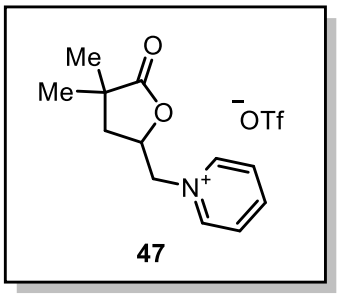
1-methyl-3-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-1H-imidazol-3-ium trifluoromethanesulfonate (42). General Procedure F was followed using 2,2-diphenylpent-4-enoic acid (**12**) and 1-methylimidazole. Purification: trituration with Et_2O to give **42** as a white solid. **Yield:** 120 mg, 83%. **MP:** 97–99 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.56 (s, 1H), 7.55–7.14 (m, 12H), 4.64 (dddd, *J*= 10.7, 8.3, 5.0, 2.6 Hz, 1H), 4.58 (dd, *J*= 14.9, 2.6 Hz, 1H), 4.43 (dd, *J*= 14.9, 8.4 Hz, 1H), 3.82 (s, 3H), 3.28 (dd, *J*= 13.3, 5.0 Hz, 1H), 2.74 (dd, *J*= 13.3, 10.6 Hz, 1H); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.9, 142.7, 140.2, 130.0, 129.4, 129.0, 128.65, 128.4, 128.2, 124.8, 124.0, 76.2, 58.7, 52.8, 40.1, 37.0. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{21}H_{21}N_2O_2^+$, 333.1603; found 333.1625.



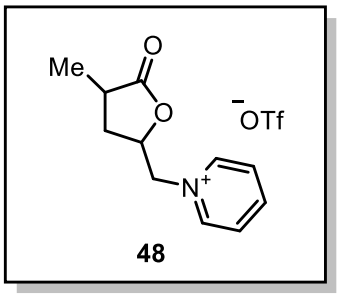
3-((S)-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (45). General Procedure G was followed using 2,2-diphenylpent-4-enoic acid (**12**) and methyl (*S*)-2-((tert-butoxycarbonyl)amino)-3-(pyridin-3-yl)propanoate (**43**). Purification: trituration with Et_2O to give **45** as a light-yellow foam. **Yield:** 146 mg, 71%. **MP:** 104–106 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.69 (d, *J*= 15.6 Hz, 1H), 8.62 (t, *J*= 5.0 Hz, 1H), 8.40 (dd, *J*= 14.3, 8.1 Hz, 1H), 8.01–7.95 (m, 1H), 7.43–7.25 (m, 10H), 5.85–5.76 (m, 1H), 4.99–4.86 (m, 1H), 4.82–4.69 (m, 2H), 4.56–4.45 (m, 1H), 3.69 (d, C**H$_3$** of methyl ester, splitting due to rotomers, 3H), 3.43–3.33 (m, 2H), 3.18–3.09 (m, 1H), 2.91–2.84 (m, 1H), 1.27 (d, C**H$_3$** of Boc, splitting due to rotomers, 9H); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.6, 172.1, 171.9, 148.4, 146.4, 146.1, 144.4, 144.3, 142.6, 140.6, 140.5, 140.0, 130.1, 129.4, 129.1, 128.8, 128.7, 128.4, 128.2, 80.5, 76.3, 64.6, 64.5, 58.5, 54.4, 53.2, 40.3, 35.5, 35.2, 28.4. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{31}H_{35}N_2O_6^+$, 531.2495; found 531.2482.



4-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-methoxy-3-oxopropyl)-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (46). General Procedure G was followed using 2,2-diphenylpent-4-enoic acid (**12**) and methyl (*S*)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(pyridin-4-yl)propanoate (**44**). Purification: trituration with Et_2O to give **46** as a white solid. **Yield:** 66 mg, 41%. **MP:** 126–128 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.55 (d, *J*= 6.2 Hz, 2H), 7.89–7.80 (m, 4H), 7.64–7.56 (m, 2H), 7.46–7.28 (m, 15H), 6.13 (t, *J*= 8.8 Hz, 1H), 4.89–4.80 (m, 1H), 4.75–4.65 (m, 2H), 4.64–4.56 (m, 1H), 4.39–4.26 (m, 2H), 4.25–4.14 (m, 1H), 3.71 (s, 3H), 3.52–3.43 (m, 1H), 3.37–3.21 (m, 2H), 2.90–2.79 (m, 1H); **^{13}C NMR** (126 MHz, CD_3CN): δ 176.57, 160.54, 145.27, 144.94, 142.45, 142.19, 140.06, 130.08, 129.46, 129.09, 128.76, 128.65, 128.51, 128.15, 126.08, 121.04, 76.22, 67.34, 63.96, 54.54, 53.40, 47.98, 40.27, 37.77. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{41}H_{37}N_2O_6^+$, 653.2652; found 653.2643.

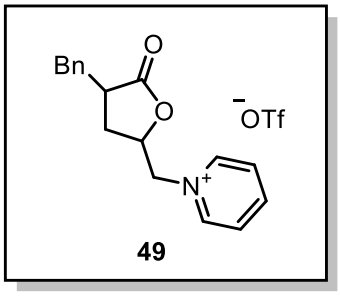


1-((4,4-dimethyl-5-oxotetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (47). General Procedure E was followed using 2,2-dimethylpent-4-enoic acid (**SI-6**) and pyridine. Purification: trituration with Et_2O to give **47** as a yellow-white solid. **Yield:** 85 mg, 80%. **MP:** 113–115 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.77–8.71 (m, 2H), 8.58 (tt, *J*= 7.9, 1.4 Hz, 1H), 8.12–8.06 (m, 2H), 4.93–4.83 (m, 2H), 4.65 (ddd, *J*= 14.3, 9.6, 1.9 Hz, 1H), 2.40 – 2.34 (m, 1H), 1.26 (s, 3H), 1.22 (s, 3H) 4; **^{13}C NMR** (125 MHz, CD_3CN): δ 181.2, 147.6, 146.0, 129.4, 75.7, 65.0, 40.8, 39.9, 24.6, 24.4. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{12}H_{16}NO^+$, 206.1175; found 206.1181.



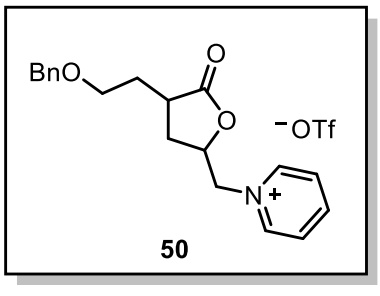
48

1-((4-methyl-5-oxotetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (48). General Procedure E was followed using 2-methylpent-4-enoic acid (**SI-3**) and pyridine to give **48** as a 3:1 ratio of diastereomers, the mixture of which could not be separated. Purification: trituration with Et_2O to give a yellow-white solid. **Yield:** 82 mg, 81%. **MP:** 90–92 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.75 (dt, *J*= 6.6, 1.6 Hz, 2H), 8.57 (ddt, *J*= 7.9, 6.8, 1.3 Hz, 1H), 8.11–8.06 (m, 2H), 4.90 (dd, *J*= 14.1, 2.3 Hz, 1H, major), 4.84 (d, *J*= 2.7 Hz, 0.12H, minor), 4.82–4.74 (m, 1H), 4.66 (ddd, *J*= 14.1, 9.5, 5.9 Hz, 1H), 2.87–2.75 (m, 1H), 2.68 (ddd, *J*= 12.5, 8.8, 5.8 Hz, 1H), 2.35 (ddd, *J*= 13.8, 9.4, 4.5 Hz, 0.2H, minor), 1.67 (td, *J*= 12.2, 10.3 Hz, 0.85H, minor), 1.23 (d, *J*= 7.3 Hz, 0.85H, minor), 1.21 (d, *J*= 7.1 Hz, 2.50H, major). **^{13}C NMR** (126 MHz, CD_3CN) δ 178.8, 147.6, 146.0, 129.4, 123.2, 120.7, 76.6, 71.5, 64.9, 35.8, 34.1, 33.9, 32.6, 15.7, 14.9. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{11}H_{14}NO_2^+$, 192.1019; found 192.1025.



49

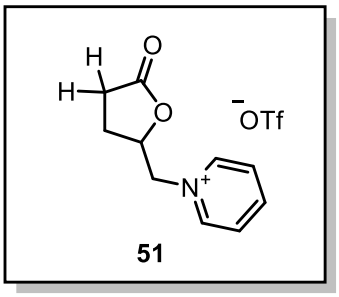
1-((4-benzyl-5-oxotetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (49). General Procedure E was followed 2-benzylpent-4-enoic acid (**SI-4**) and pyridine to give **49** as a 4:1 ratio of diastereomers, the mixture of which could not be separated. Purification: flash column chromatography (0–5% MeOH:CH_2Cl_2) to give a white solid. **Yield:** 138 mg, 82%. **MP:** 105–107 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.65–8.62 (m, 0.56H, minor), 8.62–8.58 (m, 2H, major), 8.46 (tt, *J*= 7.9, 1.4 Hz, 1H), 8.00–7.98 (m, 0.49H, minor), 7.98–7.93 (m, 2H, majot), 7.27–7.10 (m, 6H), 4.78 (dd, *J*= 14.2, 2.4 Hz, 1H), 4.73–4.66 (m, 1H), 4.56 (dd, *J*= 14.4, 10.3 Hz, 0.34H, minor), 4.46 (dd, *J*= 14.2, 8.5 Hz, 1H), 3.04 (dddd, *J*= 13.3, 11.5, 6.8, 3.2 Hz, 3H), 2.77–2.65 (m, 3H), 2.37–2.30 (m, 1H, major), 2.20 (dt, *J* = 13.8, 7.6 Hz, 0.36H, minor), 2.07 (ddd, *J* = 13.9, 9.2, 4.9 Hz, 0.35H, minor), 1.62 (ddd, *J* = 12.6, 11.5, 10.3 Hz, 1H, major v). **^{13}C NMR** (126 MHz, CD_3CN) δ 177.5, 147.6, 146.0, 139.4, 129.8, 129.5, 129.3, 127.5, 122.9, 120.4, 77.1, 76.7, 64.4, 64.5, 42.2, 41.0, 36.6, 36.0, 31.1, 30.1. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{17}H_{18}NO_2^+$, 268.1332; found 268.1339.



50

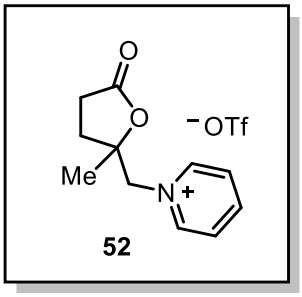
1-((4-(2-(benzyloxy)ethyl)-5-oxotetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (50). General Procedure E was followed using methyl 2-(2-(benzyloxy)ethyl)pent-4-enoate (**SI-22**) and pyridine to give **50** as a 4:1 ratio of diastereomers. Purification: flash column chromatography (0–5% MeOH:CH_2Cl_2) to give a brown solid. **Yield:** 123 mg, 67%. **MP:** 111–112 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.75–8.56 (m, 2.8H), 8.52–8.41 (m, 1.25H), 8.04–7.91 (m, 2.43H), 7.41–7.16 (m, 5H), 4.82 (dd, *J*= 14.2, 2.4 Hz, 0.71H, major), 4.79–4.75 (m, 0.25H, minor), 4.71 (dddd, *J*= 10.2, 8.6, 6.0, 2.7 Hz, 0.89H, major), 4.63–4.58 (m, 0.33H, minor), 4.54 (dd, *J*= 14.1, 8.9 Hz, 0.79H, major), 4.40 (d, *J*= 1.9 Hz, 2H), 3.59–3.50 (m, 1H), 3.49–3.43 (m, 1H), 2.82 (dtd, *J*= 11.6, 8.8, 4.8 Hz, 1H), 2.56 (ddd, *J*= 12.7, 9.0, 6.0 Hz, 0.76H, major), 2.26–2.12 (m,

0.73H, major), 1.98 (dddt, *J*= 28.5, 14.3, 6.9, 5.2 Hz, 1H), 1.78–1.60 (m, 2H). **^{13}C NMR** (126 MHz, CD_3CN) δ 179.27, 178.24, 147.56, 145.98, 139.71, 130.77, 130.39, 130.07, 129.51, 129.41, 129.27, 129.22, 128.54, 128.43, 77.16, 76.95, 73.33, 71.48, 68.25, 64.85, 38.36, 36.74, 31.88, 31.22, 30.70, 30.50. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{19}H_{22}NO_3^+$, 312.1600; found 312.1590.



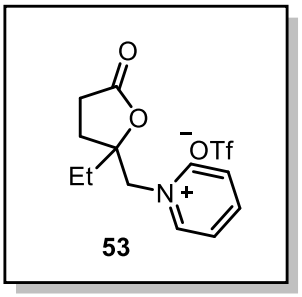
51

1-((5-oxotetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (51). General Procedure E was followed using pent-4-enoic acid as purchased and pyridine. Purification: trituration with Et_2O to give **51** as a white solid. **Yield:** 21 mg, 81%. **MP:** 107–109 °C. **^{1}H NMR** (500 MHz, CD_3CN): 8.81–8.76 (m, 2H), 8.60 (tt, *J*= 7.9, 1.4 Hz, 1H), 8.15–8.07 (m, 2H), 4.98–4.88 (m, 2H), 4.72 (dd, *J*= 14.4, 9.6 Hz, 1H), 2.69–2.57 (m, 2H), 2.57–2.49 (m, 1H), 2.14–2.02 (m, 1H). **^{13}C NMR** (126 MHz, CD_3CN) δ 176.8, 147.6, 146.0, 129.4, 78.8, 64.9, 28.4, 25.1. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{10}H_{12}NO_2^+$, 178.0868; found 178.0858.



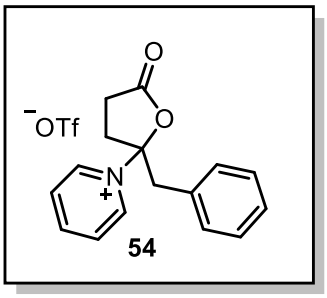
52

1-((2-methyl-5-oxotetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (52). General Procedure E was followed using Synthesis of 4-methylpent-4-enoic acid (**SI-12**) and pyridine. Purification: column chromatography (0–5% MeOH:CH_2Cl_2) to give **52** as a white solid. **Yield** 84 mg, 87%. **MP:** 190–191 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.77–8.71 (m, 2H), 8.60 (tt, *J*= 7.9, 1.4 Hz, 1H), 8.14–8.06 (m, 2H), 4.89–4.75 (m, 2H), 2.70 (ddd, *J*= 18.1, 9.8, 8.4 Hz, 1H), 2.53 (ddd, *J*= 18.2, 9.8, 5.4 Hz, 1H), 2.27–2.13 (m, 2H), 1.33 (s, 3H).**^{13}C NMR** (126 MHz, CD_3CN) δ 176.1, 147.7, 146.7, 129.2, 83.8, 67.9, 60.9, 31.1, 28.7, 23.0. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{11}H_{14}NO_2^+$, 192.1025; found 192.1023.

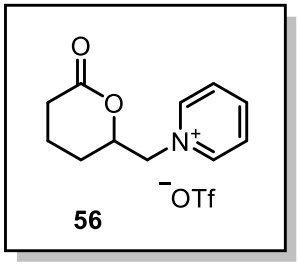


53

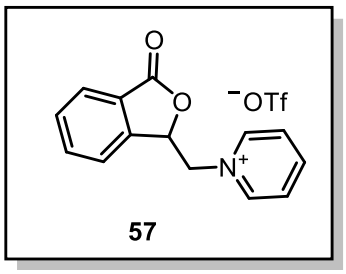
1-((2-ethyl-5-oxotetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (53). General Procedures E was followed using 4-methylenehexenoate (**SI-18**) and pyridine. Purification: Column chromatography (0-5% MeOH:CH_2Cl_2) to give **53** as a yellow solid. Yield 115 mg, 81%. **MP:** 195–197 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.75–8.67 (m, 2H), 8.60 (tt, *J*= 7.8, 1.4 Hz, 1H), 8.09 (dd, *J*= 7.9, 6.5 Hz, 2H), 4.82 (d, *J*= 1.3 Hz, 2H), 2.61 (ddd, *J*= 18.1, 10.5, 7.4 Hz, 1H), 2.44 (ddd, *J*= 18.4, 10.6, 5.7 Hz, 1H), 2.31 (ddd, *J*= 13.7, 10.5, 5.7 Hz, 1H), 2.06 (ddd, *J*= 13.8, 10.6, 7.4 Hz, 1H), 1.71 (dq, *J*= 14.9, 7.5 Hz, 1H), 1.60 (dq, *J*= 14.7, 7.5 Hz, 1H), 0.94 (t, *J*= 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, CD_3CN) δ 176.2, 147.8, 146.8., 129.3, 86.1, 66.6, 29.6, 28.9, 27.8, 7.4. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{12}H_{16}NO_2^+$, 206.1181; found 206.1179.



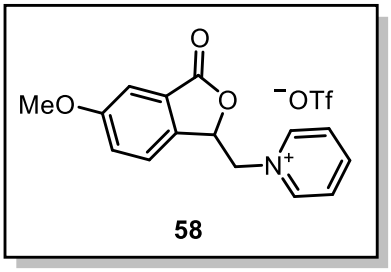
1-(2-benzyl-5-oxotetrahydrofuran-2-yl)pyridin-1-ium trifluoromethanesulfonate (54). General Procedure E was followed using Synthesis of 4-phenylpent-4-enoic acid (**SI-14**) and pyridine. Purification: column chromatography (0–5% MeOH:CH_2Cl_2) to give **54** as a yellow solid. **Yield** 99 mg, 82%. **MP:** 112–114 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.80 (dq, *J*= 6.4, 1.1 Hz, 2H), 8.56 (tt, *J*= 7.7, 1.3 Hz, 1H), 8.09–7.97 (m, 2H), 7.37–7.23 (m, 3H), 7.02–6.98 (m, 2H), 3.66 (d, *J*= 14.6 Hz, 1H), 3.56 (d, *J*= 14.7 Hz, 1H), 3.15 (ddd, *J*= 14.3, 9.9, 7.4 Hz, 1H), 3.02 (ddd, *J*= 14.2, 9.4, 6.2 Hz, 1H), 2.74–2.56 (m, 2H). **^{13}C NMR** (126 MHz, CD_3CN) δ 173.3, 148.3, 141.5, 131.0, 129.7, 129.2, 104.1, 47.7, 34.1, 27.9. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{16}H_{16}NO_2^+$, 254.1181; found 254.1178.



1-((6-oxotetrahydro-2H-pyran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (56). General Procedure E was followed using 5-hexenoic acid as purchased and pyridine. Modifications: After the addition of the alkenoic acid, the temperature was raised to 40 °C. Purification: flash column chromatography (0–5% MeOH:CH_2Cl_2) to give **56** as a white solid. **Yield:** 72 mg, 52%. **MP**:111–113 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ δ 8.73 (d, *J*= 5.9 Hz, 2H), 8.57 (tt, *J*= 7.8, 1.4 Hz, 1H), 8.08 (t, *J*= 7.1 Hz, 2H), 4.83 (dt, *J*= 13.7, 3.2 Hz, 1H), 4.76 (tt, *J*= 8.8, 2.7 Hz, 1H), 4.64 (ddd, *J*= 14.0, 8.6, 2.9 Hz, 1H), 2.52 (dt, *J*= 17.7, 6.1 Hz, 1H), 2.41 (ddd, *J* = 17.7, 8.8, 7.2 Hz, 2H), 2.18–2.04 (m, 1H), 1.92–1.84 (m, 1H), 1.59 (dtd, *J*= 13.7, 10.5, 6.4 Hz, 1H).**^{13}C NMR** δ 170.4, 147.6, 146.2, 129.2, 78.6, 65.2, 29.9, 25.0, 18.6. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{11}H_{14}NO_2^+$, 192.1019; found 192.1025.

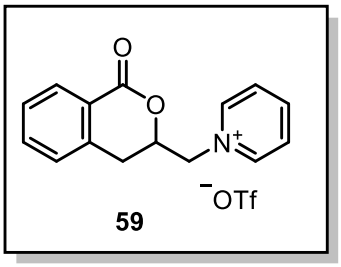


1-((3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (57). General Procedure E was followed using 2-vinylbenzoic acid (**SI-8**) and pyridine. Purification: trituration with Et_2O to give **57** as a white solid. **Yield:** 70 mg, 62%. **MP:** 130–131 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.68 (d, *J*= 6.2 Hz, 2H), 8.57 (t, *J*= 7.7 Hz, 1H), 8.31–8.24 (m, 1H), 8.06 (t, *J*= 7.0 Hz, 2H), 7.91–7.76 (m, 2H), 7.64 (d, *J*= 7.6 Hz, 1H), 6.29 (t, *J*= 2.5 Hz, 1H), 5.11 (dd, *J*= 13.5, 3.5 Hz, 1H), 4.94 (dt, *J*= 13.6, 1.6 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN) δ 163.6, 148.1, 144.7, 136.6, 136.0, 133.1, 132.2, 131.7, 130.7, 129.9, 129.4, 127.1, 126.6, 124.2, 79.2, 71.1, 65.1. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{14}H_{12}NO_2^+$, 226.0868; found 226.0859.



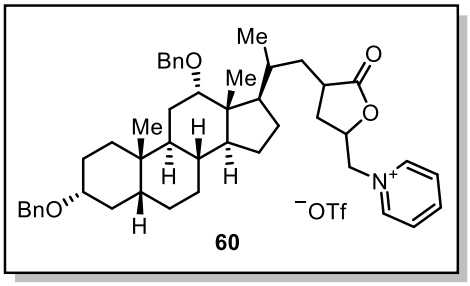
58

1-((5-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (58). General Procedure E was followed using 5-Methoxy-2-vinylbenzoic acid (**SI-10**) and pyridine. Purification: trituration with Et_2O to give **58** as a light brown solid. **Yield:** 88 mg, 73%. **MP:** 125–126 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.67 (d, *J*= 6.1 Hz, 2H), 8.57 (t, *J*= 7.8 Hz, 1H), 8.05 (t, *J*= 7.1 Hz, 2H), 7.76 (d, *J*= 2.4 Hz, 1H), 7.59 (d, *J*= 8.5 Hz, 1H), 7.39 (dd, *J*= 8.6, 2.5 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (125 MHz, CD_3CN) δ 163.5, 163.1, 147.9, 144.5, 132.5, 129.8, 128.6, 123.9, 123.0, 115.3, 71.4, 64.9, 56.7. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{15}H_{14}NO_3^+$, 256.0974; found 256.0961.



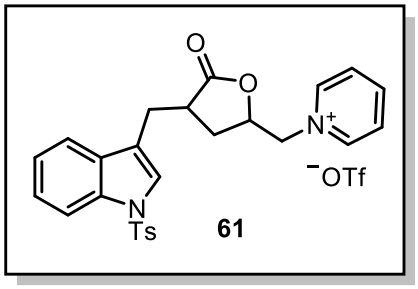
59

1-((1-oxoisochroman-3-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (59). General Procedure E was followed using2-(2-propenyl)benzoic acid as purchased and pyridine. Purification: trituration with Et_2O to give **59** as a white solid. **Yield:** 118 mg, 58%. **MP:** 123–125 °C. **^{1}H NMR** (400 MHz, CD_3CN): δ 8.92–8.83 (m, 2H), 8.59 (t, *J*= 7.8 Hz, 1H), 8.11 (t, *J*= 7.1 Hz, 1H), 7.96–7.90 (m, 1H), 7.62 (td, *J*= 7.6, 1.4 Hz, 1H), 7.46–7.35 (m, 2H), 5.05 (dq, *J*= 11.9, 2.9 Hz, 2H), 4.90 (dd, *J*= 14.5, 9.1 Hz, 0H), 3.23 (dd, *J*= 16.3, 3.0 Hz, 1H), 3.10 (dd, *J*= 16.3, 11.7 Hz, 1H). **^{13}C NMR** (101 MHz, CD_3CN): δ 164.3, 147.5, 146.3, 139.1, 135.1, 130.6, 128.7, 125.2, 123.3, 120.1, 118.3, 77.1, 64.2, 30.1. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{15}H_{14}NO_2^+$, 240.1025; found 240.1035.

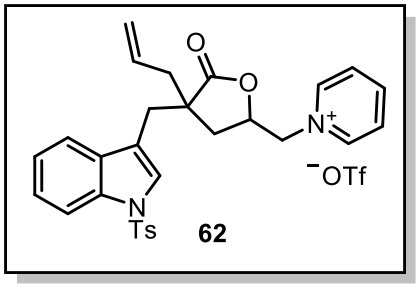


60

1-((4-((R)-2-((3R,5R,8R,9S,10S,12S,13R,14S,17R)-3,12-bis(benzyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)propyl)-5-oxotetrahydrofuran-2-yl)methyl)pyridin-1-ium (60). General Procedure E was followed using methyl General Procedure E was followed using methyl 2-((R)-2-((3R,5R,8R,9S,10S,12S,13R,14S,17R)-3,12-bis(benzyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)propyl)pent-4-enoate (**SI-31**) and pyridine. Purification: trituration with Et_2O to give **60** as orange solid. **Yield:** 112mg, 59%. **MP:** 205–207 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.69–8.58 (m, 2H), 8.49 (ddd, *J*= 9.3, 7.2, 1.6 Hz, 1H), 8.00 (t, *J*= 7.2 Hz, 2H), 7.63–6.98 (m, 10H), 4.89–4.74 (m, 1H), 4.73–4.60 (m, 1H), 4.60–4.47 (m, 2H), 4.40 (d, *J*= 2.2 Hz, 1H), 4.30–4.19 (m, 1H), 3.74–3.63 (m, 1H), 3.42–3.22 (m, 1H), 2.83–2.40 (m, 2H), 2.35–2.04 (m, 2H), 1.80–1.67 (m, 6H), 1.66–1.36 (m, 14H), 1.29 (tdd, *J*= 14.5, 6.1, 2.7 Hz, 6H), 1.25–1.10 (m, 4H), 1.10–0.94 (m, 6H), 0.93–0.83 (m, 6H). **^{13}C NMR** (126 MHz, CD_3CN) δ 178.9, 147.6, 146.0, 133.8, 130.1, 129.5, 129.3, 129.1, 128.5, 128.3, 128.2, 128.1, 118.3, 81.7, 79.2, 76.8, 70.8, 70.0, 64.9, 50.1, 47.9, 42.8, 38.4, 37.8, 36.8, 34.8, 34.7, 34.0, 32.6, 28.5, 28.2, 27.9, 30.0, 24.3, 23.6, 17.7, 13.1. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{46}H_{60}NO_4^+$, 690.4522; found 690.4526.

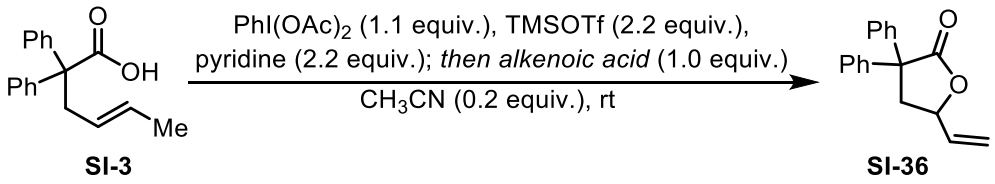


1-((5-oxo-4-((1-tosyl-1H-indol-3-yl)methyl)tetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (61). General Procedure E was followed using methyl 2-((1-tosyl-1*H*-indol-3-yl)propanoate (**SI-26**) and pyridine to give **61** as a 2:1 ratio of diastereomers. Purification: flash column chromatography (0–5% MeOH:CH_2Cl_2) to give a brown solid. **Yield** 100 mg, 54%. **MP:** 172–175 °C. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.74–8.67 (m, 3H), 8.65–8.59 (m, 2H), 8.60 4–8.49 (m, 2H), 8.46 (tt, *J*= 7.8, 1.4 Hz, 1H), 8.02 (dt, *J*= 13.9, 6.6 Hz, 3H), 7.95–7.88 (m, 3H), 7.73 (dd, *J*= 8.4, 3.0 Hz, 3H), 7.54–7.46 (m, 2H), 7.44 (s, 1H), 7.30 (dddd, *J*= 8.4, 7.2, 3.7, 1.2 Hz, 2H), 7.27–7.19 (m, 5H), 4.90–4.72 (m, 3H), 4.65 (dd, *J* = 14.0, 10.0 Hz, 0.54H, minor), 4.57 (dd, *J*= 14.2, 8.1 Hz, 1H, major), 3.23–3.05 (m, 3H), 2.92–2.79 (m, 2H), 2.45 (ddd, *J*= 12.7, 8.7, 5.8 Hz, 1H), 2.34–2.14 (m, 6H), 1.61 (td, *J*= 12.2, 10.4 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN) δ 177.94, 177.32, 147.63, 146.82, 145.97, 135.82, 135.40, 131.65, 131.24, 130.98, 129.50, 129.21, 128.00, 127.70, 125.98, 125.95, 125.51, 124.47, 120.68, 118.26, 114.58, 77.06, 76.55, 64.86, 64.30, 40.92, 39.32, 31.31, 30.59, 26.14, 25.27, 21.50, 14.46. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{26}H_{25}N_2O_4S^+$, 461.1535; found 461.1528.



1-((4-allyl-5-oxo-4-((1-tosyl-1H-indol-3-yl)methyl)tetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (61). General Procedure E was followed using methyl 2-allyl-2-((1-tosyl-1H-indol-3-yl)methyl)pent-4-enoate (**SI-27**) and pyridine to give **62** as a 1:1 ratio of diastereomers. Purification: trituration with Et_2O to give a brown solid. **Yield:** 26 mg, 57%. **MP:** 201–203 °C**. ^{1}H NMR** (500 MHz, CD_3CN): δ 8.62 (dt, *J*= 6.9, 1.7 Hz, 2H), 8.5–8.53 (m, 1H), 8.40–8.34 (m, 3H), 8.04 (dd, *J*= 7.9, 6.5 Hz, 2H), 7.94 (t, *J*= 8.5 Hz, 2H), 7.81–7.75 (m, 4H), 7.74–7.70 (m, 2H), 7.57–7.52 (m, 2H), 7.48 (d, *J*= 7.9 Hz, 1H), 7.38 (ddd, *J*= 8.4, 7.2, 1.2 Hz, 1H), 7.36–7.21 (m, 9H), 5.86 (ddt, *J*= 17.6, 10.2, 7.5 Hz, 1H), 5.59 (dddd, *J*= 16.6, 10.1, 8.6, 6.1 Hz, 1H), 5.27–5.18 (m, 2H), 5.14–5.05 (m, 2H), 4.85 (ddt, *J*= 9.5, 6.6, 3.3 Hz, 1H), 4.76 (dt, *J*= 14.2, 2.1 Hz, 2H), 4.50 (ddd, *J*= 14.4, 8.1, 2.2 Hz, 1H), 4.34 (dq, *J*= 6.8, 4.8, 3.5 Hz, 1H), 4.26 (ddd, *J*= 14.6, 6.3, 2.2 Hz, 1H), 3.06–2.93 (m, 3H), 2.88 (d, *J*= 14.6 Hz, 1H), 2.54–2.39 (m, 4H), 2.39–2.26 (m, 9H), 1.65 (ddd, *J*= 13.7, 10.1, 1.6 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN) δ 179.37, 179.17, 147.78, 147.55, 146.90, 146.15, 145.79, 135.74, 135.44, 133.43, 133.16, 132.07, 131.06, 129.47, 128.65, 127.77, 126.76, 126.01, 124.64, 124.47, 120.88, 114.61, 75.69, 75.17, 64.63, 63.51, 50.53, 49.57, 42.08, 41.54, 33.48, 33.15, 32.42, 30.76, 21.51. **HRMS** (m/z): $[M\text{-}OTf]^+$ calcd. For $C_{29}H_{29}N_2O_4S^+$, 501.1848; found 501.1851.

Aminolactonization with Internal Olefin



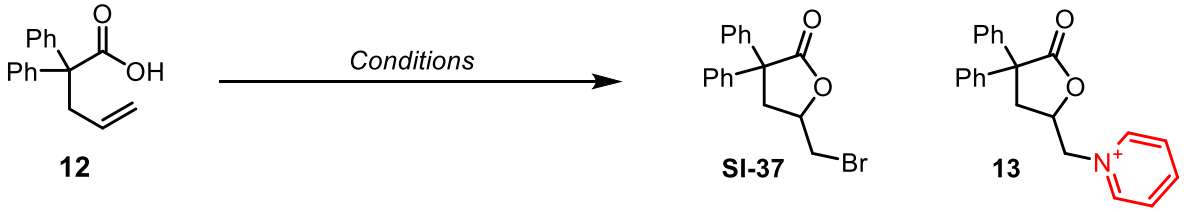
SI-3 **SI-36**

3,3-diphenyl-5-vinyldihydrofuran-2(3H)-one (SI-36). General Procedure E was followed using **SI-3**. Purification: column chromatography (0–5% MeOH:CH_2Cl_2) to give **SI-36** as a colorless oil. **Yield:** 20 mg, 25%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.09 (m, 9H), 5.85 (ddd, *J*= 17.1, 10.5, 6.7 Hz, 1H), 5.34 (dt, *J*= 17.1, 1.1 Hz, 1H), 5.23 (dt, *J*= 10.5, 1.0 Hz, 1H), 4.75–4.63 (m, 1H), 3.03 (dd, *J*= 13.0, 5.0 Hz, 1H), 2.68 (dd, *J*= 13.0, 10.5 Hz, 1H). Spectral data is consistent with that previously reported.[28]

Section F. Mechanistic Investigations of Aminolactonization

Control Reactions (as discussed in Manuscript Figure 2a):

Pyridinium Lactone formation using NBS as Activator



12 **SI-37** **13**

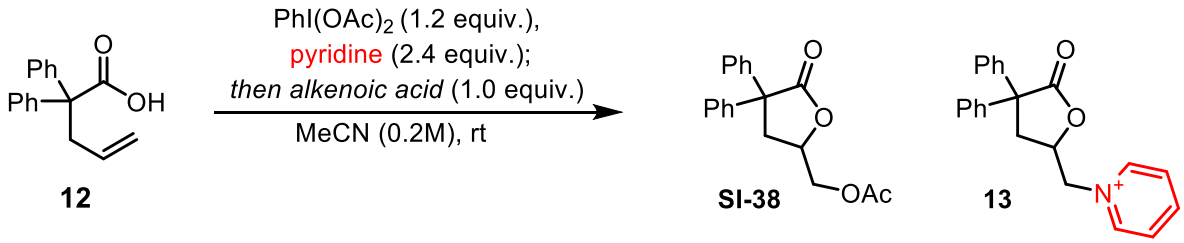
Standard Conditions NBS (1.2 equiv.), pyridine (4.0 equiv.); *then alkenoic acid* (1.0 equiv.) CH_2Cl_2 (0.2M), rt	Only product	Not observed
Forcing Conditions NBS (1.2 equiv.), pyridine (4.0 equiv.); *then alkenoic acid* (1.0 equiv.) DCE (0.2M), 80 °C	Only product	Not observed

5-(bromomethyl)-3,3-diphenyldihydrofuran-2(3H)-one (SI-37). In a flame dried flask under argon, *N*-bromosuccinimide (NBS) (11 mg, 0.060 mmol, 1.2 equiv.) and pyridine (16 µL, 0.20 mmol, 4.0 equiv.) were dissolved in dry CH_2Cl_2 (250 µL, 0.2M). 2,2-diphenyl-4-pentenoic acid **12** (13 mg, 0.050 mmol, 1.0 equiv.) was added to the solution in one portion and the reaction stirred at room temperature and monitored by TLC. Upon completion (2 h), the reaction was concentrated *in vacuo* and the crude reaction mixture was analyzed by ^{1}H NMR. The ^{1}H NMR showed exclusively bromolactone **SI-37** and no incorporation of pyridine to form the pyridinium lactone **13**. Bromolactone **SI-37**: **^{1}H NMR** (500 MHz, $CDCl_3$) ^{1}H NMR δ 7.39–7.13 (m, 10H), 4.50 (ddt, *J*= 10.0, 6.5, 5.0 Hz, 1H), 3.56 (dd, *J*= 10.8, 4.7 Hz, 1H), 3.46 (dd, *J*= 10.8, 6.5 Hz, 1H), 3.12 (dd, *J*= 13.2, 5.2 Hz, 1H), 2.77 (dd, *J*= 13.2, 9.9 Hz, 1H). Spectral data is consistent with that previously reported.[29]

Pyridinium Lactone formation using NBS as activator and with forcing conditions

5-(bromomethyl)-3,3-diphenyldihydrofuran-2(3H)-one (SI-37). In a flame dried flask under argon, NBS (11 mg, 0.060 mmol, 1.2 equiv) and pyridine (16 µL, 0.20 mmol, 4.0 equiv.) were dissolved in dry 1,2-dichloroethane (250 µL, 0.2M). 2,2-diphenyl-4-pentenoic acid **12** (13 mg, 0.050 mmol, 1.0 equiv.) was added to the solution and stirred at 80 °C and was monitored by TLC. Upon completion (2 h), the reaction was concentrated *in vacuo* and the crude reaction mixture was analyzed by ^{1}H NMR to determine whether the pyridine can displace the primary bromide. The ^{1}H NMR showed no incorporation of pyridine to form the pyridinium lactone. **^{1}H NMR** (500 MHz, CD_3CN) δ 7.45–7.25 (m, 10H), 4.55 (dtd, *J*= 9.9, 5.4, 4.3 Hz, 1H), 3.74 (dd, *J*= 11.3, 4.4 Hz, 1H), 3.65 (dd, *J*= 11.2, 5.6 Hz, 1H), 3.21 (dd, *J*= 13.3, 5.2 Hz, 1H), 2.81 (dd, *J*= 13.3, 10.1 Hz, 1H) is consistent with bromolactone **SI-37**.

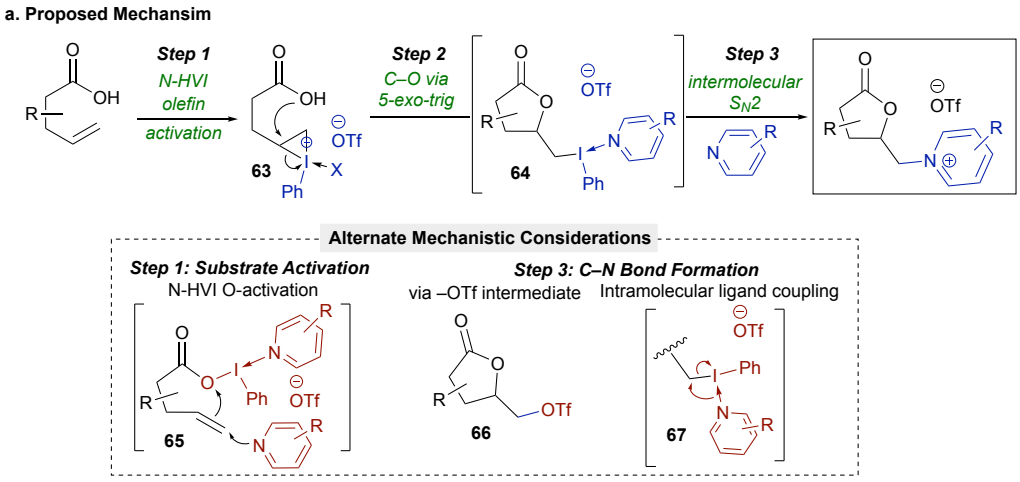
Pyridinium Lactone formation using $PhI(OAc)_2$ as Activator



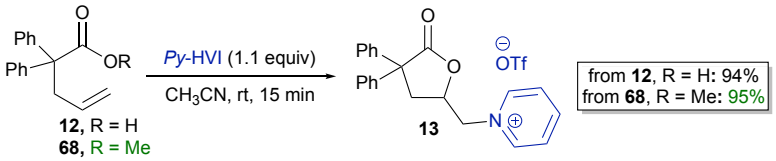
In a flame dried flask under argon, (diacetoxyiodo)benzene (19 mg, 0.60 mmol, 1.2 equiv.) and pyridine (10 µL, 0.12 mmol, 2.4 equiv.) were dissolved with CH_3CN (250 µL, 0.2M). 2,2-diphenyl-4-pentenoic acid **12** (126 mg, 0.50 mmol, 1.2 equiv.) was then added in one portion and stirred overnight. After 19 h the reaction was diluted with 2.0 mL of CH_2Cl_2, then washed with $Na_2S_2O_3$ (sat. aq.) (1 x 2 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo.*

*Reaction gave no conversion to pyridinium lactone **13** and less than 5% conversion to –OAc lactone **SI-38** was observed.*

Proposed Mechanistic Pathways *(Figure 5)*



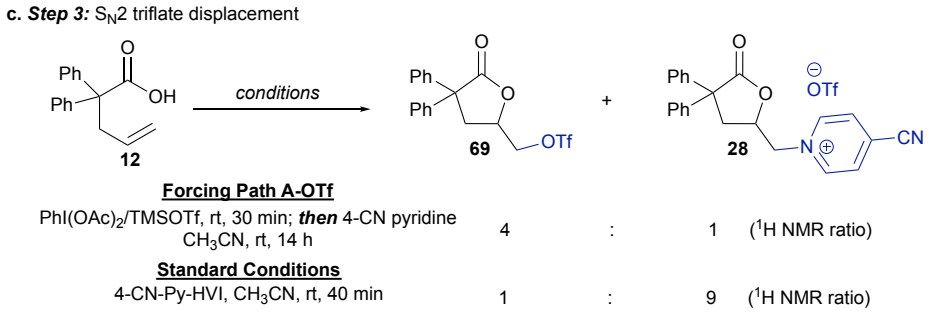
Probing Step 1: O-Activation (Figure 5b)



In a flame dried flask under argon, a solution of methyl 2,2-diphenylpent-4-enoate **68** (13.3 mg, 0.05 mmol, 1.0 equiv.) in 50 µL of dry CH_3CN was added in one portion to a solution of *Py*-HVI (66 mg, 0.10 mmol, 2.0 equiv.) in dry CH_3CN (200 µL, 0.5 M). The reaction stirred at room temperature and was monitored by TLC. Once the reaction was complete (20 min.) the solution was diluted with 3 mL of CH_2Cl_2 and washed with $Na_2S_2O_3$ (sat. aq.) (1 x 2mL), dried over Na_2SO_4, and concentrated *in vacuo* to yield **13** as a white solid (22 mg, 95%).

*Reaction was found to proceed with equal efficiency to give desired product **68** using methyl ester as with alkenoic acid **12**, indicating that in Step 1, O-activation was unlikely to be operative.*

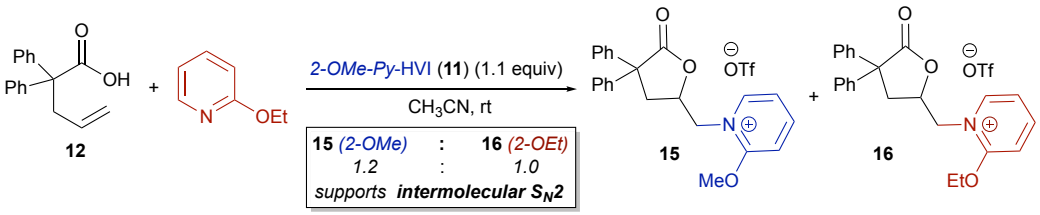
Probing Step 3, via –OTf Intermediate 66: Pyridine displacement of OTf lactone 69 (*Figure 5c*)



Forcing Step 3, –OTf Conditions. In a flame dried flask under argon, trimethyl silyl trifluoromethanesulfonate (40 µL, 0.22 mmol, 2.2 equiv.) was added to a suspension of (diacetoxyiodo)benzene (35 mg, 0.11 mmol, 1.1 equiv.) in dry CH_2Cl_2 (500 µL, 0.2 M). 2,2-diphenyl-4-pentenoic acid (25 mg, 0.10 mmol, 1.0 equiv.) was added in one portion and the reaction stirred at room temperature. Once full consumption of 2,2-diphenyl-4-pentenoic acid **12** (30 min) by TLC, 4-cyanopyridine (42 mg, 0.40 mmol, 2.2 equiv.) was added. Once completion was reached (14 h) the reaction was diluted with CH_2Cl_2, washed with $Na_2S_2O_3$ (sat. aq.) (1 x 2 mL) and with H_2O (1 x 2 mL). the organic layer was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was analyzed by ^1H NMR to determine the ratio of **69** and **28**.

Standard in situ conditions. Performed according to General Procedure E using diphenyl alkenoic acid **12** (75 mg, 0.33 mmol, 1.0 equiv.), (diacetoxyiodo)benzene (106 mg, 0.33 mmol, 1.1 equiv.), trimethylsilyl trifluoromethanesulfonate (120 µL, 0.66 mmol, 2.2 equiv.) and 4-CN-pyridine (69 mg, 0.66 mmol, 2.2 equiv.).

Probing Step 3, Ligand Coupling vs S_N2: Crossover Experiment (*Figure 5d*)

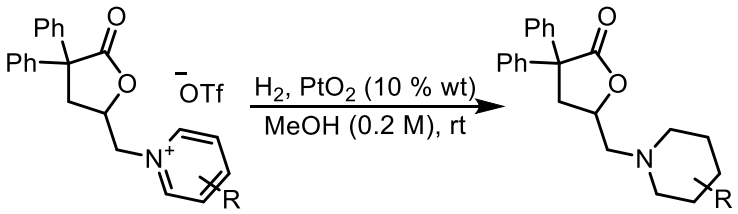


In a flame dried flask under argon, 2-*OMe-Py*-HVI (100 mg, 0.14 mmol, 1.1 equiv.) was dissolved in dry CH_3CN (700 µL, 0.2M). A solution of 2-OEt-pyridine (17 µL, 0.14 mmol, 1.1 equiv.) and 2,2-diphenyl-4-pentenoic acid (33 mg, 0.13 mmol, 1.0 equiv.) in dry CH_3CN (250 µL, 0.5 M) was added to the 2-*OMe-Py*-HVI solution in one portion and the reaction stirred overnight. Once completion was reached (18 h) the reaction was diluted with 3 mL of EtOAc and washed with $Na_2S_2O_3$ (sat. aq.) (1 x 2 mL) and with $NaHCO_3$ (sat. aq.) (1 x 2 mL). the organic layer was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. Trituration with Et_2O and decanting the Et_2O yields the pure pyridinium lactone salts as solids which were dried on high vacuum. ^1H NMR analysis of the pyridinium salt products revealed a 1.2:1.0 ratio of **15**:**16**, in 55% and 45% respectively.

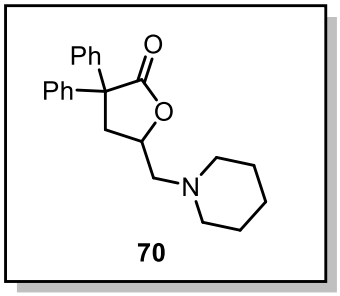
This is supportive of intermolecular S_N2 rather than ligand coupling, as originally proposed in Figure 5a.

Section F. Derivatizations of Pyridinium Lactones

General Procedure H: Hydrogenation of Pyridinium Lactones (*Figure 6a*)

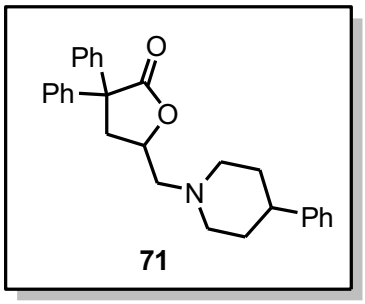


A flame dried flask under argon, was charged with desired pyridinium lactone (0.1 mmol, 1.0 equiv.) and dissolved with dry MeOH (1 mL, 0.1 M). PtO_2 (10% wt.) was added in one portion at room temperature. An H_2 balloon was used to bubble through the solution using a vent needle. The vent needle was removed and H_2 balloon was placed in the reaction septum and the reaction was stirred overnight. Once completion (18 h) was reached the reaction was filtered through a celite plug and concentrated *in vacuo.* The crude product was dissolved in EtOAc and stirred with solid $NaHCO_3$ for 30 min then wash with H_2O 3x, the organic layer was dried over Na_2SO_4, and concentrated *in vacuo.* The Crude material is purified by flash column chromatography.



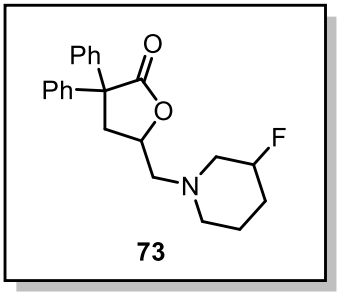
70

3,3-diphenyl-5-(piperidin-1-ylmethyl)dihydrofuran-2(3H)-one (70). General Procedure H was followed using **13**. Purification: flash column chromatography (1–5% MeOH:CH_2Cl_2) to give **70** as a colorless oil. **Yield:** 62 mg, 88%. **^{1}H NMR** (500 MHz, CD_3CN) δ 7.46–7.25 (m, 10H), 4.55 (dq, *J*= 10.4, 5.2 Hz, 1H), 3.14 (dd, *J*= 13.2, 5.1 Hz, 1H), 2.81–2.69 (m, 3H), 2.59 (s, 4H), 1.60 (p, *J*= 5.6 Hz, 4H), 1.46 (t, *J*= 6.0 Hz, 2H). **^{13}C NMR** (126 MHz, CD_3CN) δ177.8, 143.4, 140.8, 129.9. 129.2, 128.7, 128.2, 128.1, 75.9, 62.3, 60.9, 58.3, 55.4, 41.7, 32.3, 25.9, 24.1, 14.. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{22}H_{26}NO_2^+$, 336.1964; found 336.1957.



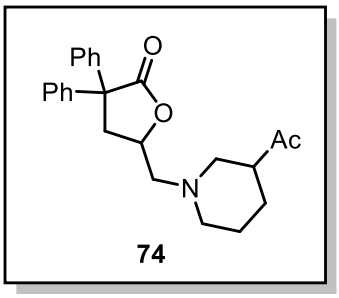
71

3,3-diphenyl-5-((4-phenylpiperidin-1-yl)methyl)dihydrofuran-2(3H)-one (71). General Procedure H was followed using **18** to give **63** as a 10:1 ratio of diastereomers, for which the major and minor isomers could not be assigned. Purification: flash column chromatography (1–5% MeOH:CH_2Cl_2) to give **71** as a yellow oil. **Yield:** 29 mg, 81%. **^{1}H NMR** (500 MHz, CD_3CN) δ 7.45–7.15 (m, 17H), 4.51 (dddd, *J*= 10.3, 6.5, 5.1, 4.0 Hz, 1H, major), 4.37–4.30 (m, 0.08H, minor), 3.13 (dd, *J*= 13.2, 5.1 Hz, 1H, major), 3.08 (d, *J*= 5.1 Hz, 0.10H, minor), 3.03–2.97 (m, 2H), 2.92–2.87 (m, 0.21H, minor), 2.79–2.67 (m, 3H, major), 2.67–2.59 (m, 0.45H, minor), 2.51 (tt, *J*= 12.0, 4.0 Hz, 1H, major), 2.45–2.39 (m, 0.15H, minor), 2.21 (dtd, *J*= 16.7, 11.6, 2.7 Hz, 2H), 1.77 (dddd, *J*= 8.7, 6.3, 4.5, 3.0 Hz, 2H), 1.74–1.65 (m, 2H). **^{13}C NMR** (126 MHz, CD_3CN) 178.12, 147.67, 143.69, 141.31, 129.91, 129.38, 129.27, 128.79, 128.68, 128.35, 128.10, 127.79, 127.04, 118.26, 76.99, 62.51, 58.65, 55.74, 43.03, 41.89, 34.40. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{28}H_{30}NO_2^+$, 412.2277; found 412.2271.



73

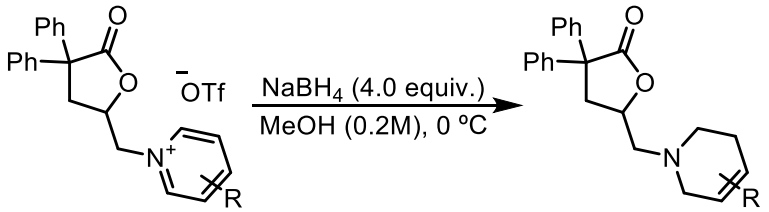
5-((3-fluoropiperidin-1-yl)methyl)-3,3-diphenyldihydrofuran-2(3H)-one (73). General Procedure H was followed using **31** to give **6** as a 10:1 ratio of diastereomers, for which the major and minor isomers could not be assigned. Purification: flash column chromatography (1–5% MeOH:CH_2Cl_2) to give **73** as a yellow oil. **Yield:** 28 mg, 84%. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50–7.24 (m, 10H), 4.79 (dddd, *J*= 10.8, 7.9, 5.1, 2.6 Hz, 1H, major), 4.66 (dddd, *J* = 10.8, 8.2, 5.1, 2.6 Hz, 0.10H, minor), 3.65–3.58 (m, 1H), 3.54–3.41 (m, 3H), 3.27 (dd, *J*= 13.3, 5.0 Hz, 1H), 3.23 (d, *J*= 5.1 Hz, 0.10H), 3.02 (tdt, *J*= 12.5, 9.4, 4.9 Hz, 2H), 2.76–2.69 (m, 1H), 1.91 (dt, *J*= 14.7, 3.5 Hz, 2H), 1.78 (dtt, *J*= 16.2, 6.8, 3.9 Hz, 3H). **^{13}C NMR** ^{13}C NMR (126 MHz, CD_3CN) δ 177.98, 143.53, 141.08, 129.87, 129.22, 128.72, 128.66, 128.28, 128.07, 76.45, 62.66, 55.70, 41.77, 26.44, 24.54. ^{19}F NMR (471 MHz, CD3CN) δ -79.11. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{22}H_{25}FNO_2^+$, 354.1869; found 354.1857.



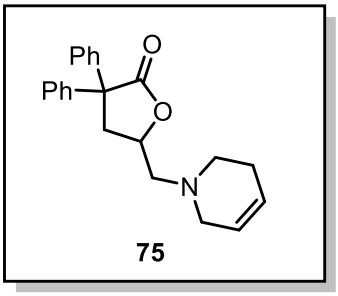
74

5-((3-acetylpiperidin-1-yl)methyl)-3,3-diphenyldihydrofuran-2(3H)-one (74). General Procedure H was followed using **29** to give **74** as a ratio of approximately 1:1 of diastereomers, for which the major and minor isomers could not be assigned or separated. Purification: flash column chromatography (1–5% MeOH:CH_2Cl_2) to give **66** as a colorless oil. **Yield:** 38 mg, 76%. **^{1}H NMR** ^{1}H NMR (500 MHz, CD_3CN) 7.45–7.25 (m, 10H), 4.50 (ddq, *J*= 9.2, 6.6, 4.0 Hz, 1H), 3.11 (ddd, *J*= 13.2, 5.1, 3.3 Hz, 1H), 2.99–2.89 (m, 1H), 2.80–2.64 (m, 4H), 2.59 (tq, *J*= 8.4, 3.9 Hz, 1H), 2.39–2.23 (m, 1H), 2.23–2.13 (m, 1H), 2.10 (d, *J*= 1.8 Hz, 3H), 1.91–1.79 (m, 1H), 1.68 (dtd, *J*= 13.2, 4.5, 3.2 Hz, 1H), 1.60–1.47 (m, 1H), 1.35 (d, *J*= 20.7 Hz, 1H). **^{13}C NMR** (126 MHz, CD_3CN) δ 210.30, 177.62, 143.14, 140.69, 129.47, 128.80, 128.32, 127.87, 127.67, 76.23, 62.05, 58.11, 55.86, 54.65, 49.61, 41.27, 29.92, 28.01, 26.46, 24.87. **HRMS** (m/z): $[M+H]^+$ calcd. For $H_{24}H_{28}NO_3^+$, 378.2096; found 378.2068.

General Procedure I: Partial Reduction of Pyridinium Lactones (*Figure 6b*)

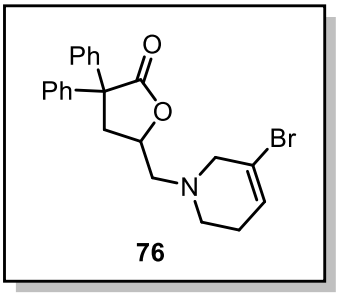


A flame dried flask under argon was charged with desired pyridinium lactone (0.1 mmol, 1.0 equiv.) and dissolved with dry MeOH (1 mL, 0.1M) and cooled to 0 °C. $NaBH_4$ (0.4 mmol, 4.0 equiv.) was added in one portion and the reaction was stirred overnight and allowed to reach room temperature as the ice melted. Once complete by TLC (12 h) the reaction was quenched with H_2O (20 mL), extracted with EtOAc (3x 10 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield the desired product.



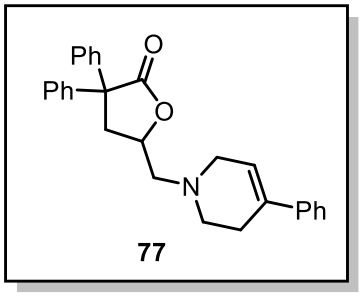
75

5-((3,6-dihydropyridin-1(2H)-yl)methyl)-3,3-diphenyldihydrofuran-2(3H)-one (75). General Procedure I was followed using **13**. Purification: flash column chromatography (10–30% EtOAc:Hexanes) to give **75** as a colorless oil. **Yield:** 40 mg, 90%. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40–7.27 (m, 10H), 5.74 (ddt, *J*= 7.5, 3.7, 1.9 Hz, 1H), 5.64 (ddt, *J*= 10.1, 3.3, 1.4 Hz, 1H), 4.57 (ddt, *J*= 10.7, 6.0, 4.7 Hz, 1H), 3.14 (dt, *J*= 16.3, 2.8 Hz, 1H), 2.78 (dd, *J*= 5.1, 1.9 Hz, 2H), 2.75–2.68 (m, 2H), 2.63 (dt, *J*= 11.2, 5.6 Hz, 1H), 2.21–2.14 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.9, 142.8, 140.4, 129.8, 129.3, 128.6, 128.2, 128.1, 126.0, 125.8, 62.8, 61.3, 56.0, 54.1, 51.5, 42.8, 26.8. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{22}H_{24}NO_2^+$, 334.1807; found 334.1780.



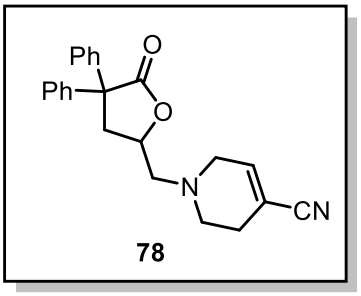
76

5-((5-bromo-3,6-dihydropyridin-1(2H)-yl)methyl)-3,3-diphenyldihydrofuran-2(3H)-one (76). General Procedure I was followed using **30**. Purification: flash column chromatography (10–30% EtOAc:Hexanes) to give **76** as a colorless oil. **Yield:** 14 mg, 81%. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.38–7.29 (m, 10H), 6.08 (dt, *J*= 4.1, 2.2 Hz, 1H), 4.52 (dq, *J*= 10.3, 5.0 Hz, 1H), 3.36–3.24 (m, 3H), 3.02 (dd, *J*=13.0, 5.0 Hz, 1H), 2.81 (d, *J*= 5.2 Hz, 2H), 2.80–2.72 (m, 1H), 2.72–2.65 (m, 2H), 2.25–2.17 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.05, 129.07, 128.51, 127.88, 127.81, 127.44, 127.37, 126.93, 118.30, 76.14, 70.67, 60.90, 59.80, 57.72, 49.19, 41.74, 27.39. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{22}H_{23}BrNO_2^+$, 412.0912; found 412.0905.



77

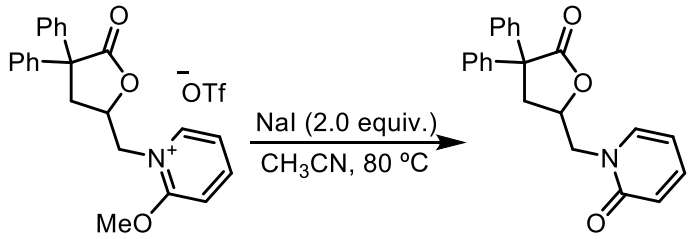
3,3-diphenyl-5-((4-phenyl-3,6-dihydropyridin-1(2H)-yl)methyl)dihydrofuran-2(3H)-one (77). General Procedure I was followed using **18**. Purification: flash column chromatography (10–30% EtOAc:Hexanes) to give **77** as a colorless oil. **Yield:** 11 mg, 81%. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.42–7.28 (m, 15H), 6.03 (tt, *J*= 3.5, 1.5 Hz, 1H), 4.64 (ddt, *J*= 10.8, 7.8, 3.8 Hz, 1H), 3.44–3.26 (m, 2H), 3.10 (dd, *J*= 13.0, 5.0 Hz, 1H), 2.97–2.81 (m, 4H), 2.73 (dd, *J*= 13.0, 10.6 Hz, 1H), 2.60 (d, *J*= 6.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.07, 141.98, 140.70, 139.68, 134.96, 128.98, 128.43, 128.34, 127.77, 127.39, 127.27, 127.11, 124.93, 121.50, 77.34, 77.09, 76.40, 61.68, 57.70, 53.80, 51.06, 41.94, 27.98. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{28}H_{28}NO_2^+$, 410.2120; found 410.2110.



78

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)-1,2,3,6-tetrahydropyridine-4-carbonitrile (78). General Procedure I was followed using **28.** Modification: The reducing agent used was $NaCNBH_3$. Purification: No purification was needed, giving **78** as a gray solid. **Yield:** 32 mg, 89%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32–7.18 (m, 10H), 6.49-6.47 (m, 1H), 4.50–4.43 (m, 1H), 3.21 (qq, *J*= 58.0, 19.5, 6.5, 3.5 Hz, 2H), 2.96 (dd, *J*= 13.0, 5.0 Hz, 1H), 2.78 (dd, *J*= 14.0, 3.0 Hz, 1H), 2.74-2.61 (m, 4H), 2.35-2.26 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.9, 141.9, 141.8, 139.6, 129.1, 128.5, 128.0, 127.8, 127.5, 127.4, 118.6, 1 10.8, 76.1, 61.1, 57.6, 53.0, 49.4, 41.6, 27.5. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{23}H_{23}N_{22}O_2^+$, 359.1683; found 359.1772.

Aryl Ether Demethylation (*Figure 6c*)

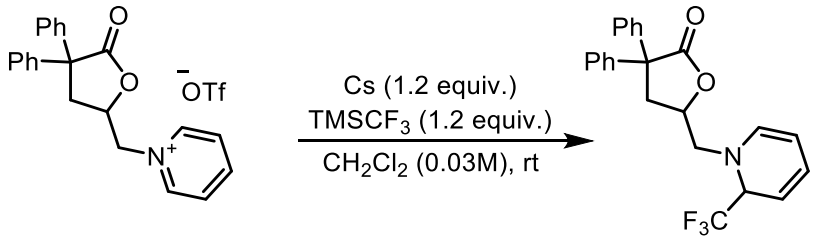


15 **79**

1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-2(1H)-one (79). in a flame dried flask, 2-methoxy-1-((5-oxo-4,4-diphenyltetrahydrofuran-2-yl)methyl)pyridin-1-ium trifluoromethanesulfonate (**15**) (25 mg, 0.05 mmol, 1.0 equiv.) was dissolved in dry CH_3CN (300 µL, 0.17 M) at room temperature. Sodium iodide (15 mg, 0.10 mmol, 2.0 equiv.) was then added, and the reaction was refluxed to 80 °C. Once completion was reached (21 h), the reaction was cooled to room temperature and concentrated *in vacuo.* The crude product was purified by filtering over a silica plug (80% EtOAc:pentane) to yield **79** as a light yellow foam. (16 mg, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.34–7.16 (m, 12H), 6.49 (d, *J*= 9.1 Hz, 1H), 6.12 (td, *J*= 6.7, 1.3 Hz, 1H), 4.64 (dddd, *J*= 10.3, 7.4, 5.0, 2.3 Hz, 1H), 4.54 (dd, *J*= 14.1, 2.3 Hz, 1H), 3.80 (dd, *J*= 14.1, 7.5 Hz, 1H), 3.11 (dd, *J*= 13.2, 5.1 Hz, 1H), 2.58 (dd, *J*= 13.2, 10.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.5, 162.8, 141.6, 140.4, 139.1, 138.7, 129.2, 128.6, 128.1, 127.7, 127.6, 127.4, 120.9, 106.4, 75.4, 58.0, 52.3, 40.6, 29.9. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{22}H_{20}NO_3^+$, 346.1443; found 346.1451.

Addition of C-nucleophiles to give 1,2- and 1,4-dihydropyridines (*Figure 6d*)

1,2-Addition of CF_3 to give 1,2-dihydropyridine

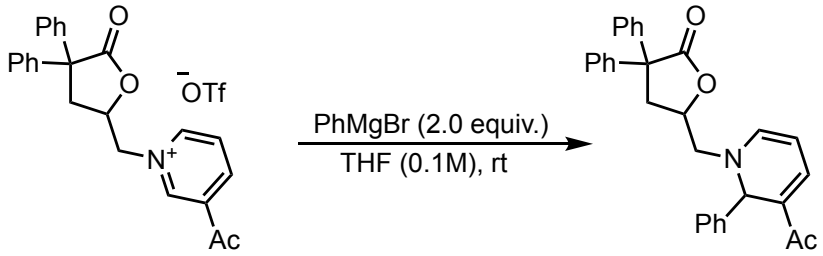


13 **80**

3,3-diphenyl-5-((2-(trifluoromethyl)pyridin-1(2*H*)-yl)methyl)dihydrofuran-2(3*H*)-one (80). Reaction was performed according to literature procedure[30]. A flame dried flask was charged with pyridinium lactone **13** (47.9 mg, 0.1 mmol) and CsF (18.2 mg, 0.12 mmol,1.2 equiv.) in dry CH_2Cl_2 (3.0 mL, 0.03M). $TMSCF_3$ (18 µL, 0.12 mmol, 1.2 equiv.) was added dropwise at room temperature under Argon. After stirring for 18 h, the mixture was concentrated and purified via flash chromatography

(10-30% EtOAc:Hexane; R_f = 0.5, 30% EtOAc/Hexane) to give **80** as a yellow oil in a 1.1:1 mixture of diastereomers (21.2 mg, 53%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.10 (m, 19H), 6.16 (dd, *J*= 9.5, 5.5 Hz, 1H, major), 6.12 (dd, *J*= 9.5, 6.0 Hz, 0.9H, minor), 6.05 (d, *J*= 7.0 Hz, 1H, major), 6.02 (d, *J*= 7.0 Hz, 0.9H minor), 5.01–4.93 (m, 1.9H), 4.90 (dt, *J*= 6.0, 1.5 Hz, 1H, major), 4.86 (dt, *J*= 6.5, 1.5 Hz, 0.9H, minor), 4.61–4.53 (m, 1.8H, minor), 4.43–4.35 (m, 2H, major), vb 3.5.'/67 (dd, *J*= 15.5, 3.0 Hz, 1H, major), 3.39 (d, *J* = 1.5, 1H, major), 3.38 (s, *J*= 3.5 Hz, 0.9H, minor), 3.24 (dd, *J*= 16.0, 5.0 Hz, 0.9H, minor), 2.94 (dd, *J*= 13.0, 5.5 Hz, 0.9H, minor), 2.84 (dd, *J*= 13.0, 5.0 Hz, 1H, major), 2.73 (dd, *J*= 13.0, 11.0 Hz, 1H, major), 2.57 (dd, *J*= 13.0, 10.0 Hz, 0.9H, minor); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.8, 176.7, 141.92, 141.88, 139.0, 138.9, 136.5, 135.3, 129.20, 129.19, 128.8, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.6, 127.6 (q, *J* = 288.4 Hz), 127.54, 127.52, 127.5, 127.5 (q, *J* = 288.1 Hz), 104.8, 104.6, 98.1, 97.9, 77.4, 77.2, 77.16, 77.1, 76.9, 70.7, 59.7 (q, *J* = 30.5 Hz), 58.9 (q, *J* = 30.6 Hz), 58.0, 56.3, 40.5, 39.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ –79.9, –80.2. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{23}H_{21}F_3NO_2^+$, 400.1519; found 400.1510.

1,2-Addition of aryl Grignard to give 1,2-dihydropyridine (Conditions A)



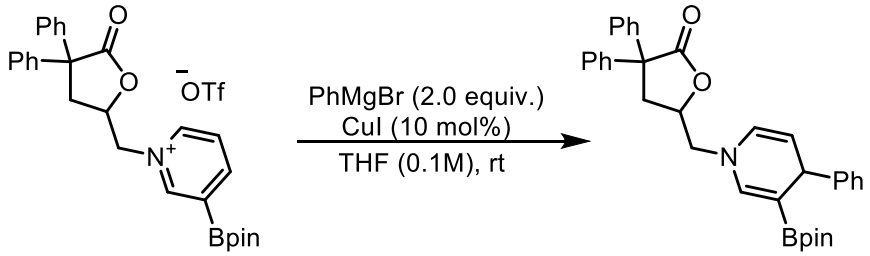
29 **81**

5-((3-acetyl-2-phenyl-2,3-dihydro-1λ^4-pyridin-1-yl)methyl)-3,3diphenyldihydrofuran-2(3*H*)-one (81). To a flame dried Schlenk tube with pyridinium lactone **29** (53.8 mg, 0.1 mmol, 1.0 equiv.)and copper iodide (1.9 mg, 0.01 mmol, 10 mol %) in dry THF. (1.0 mL, 0.1 M) Phenyl magnesium bromide (67 µL, 2.0 equiv., 3 M in diethyl ether) was added dropwise at room temperature under argon. The mixture was stirred for 2h, quenched by NH_4Cl (sat. aq.) (10 mL), extracted by EtOAc (3x 10 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified byflash chromatography (10-30% EtOAc/Hexane; R_f = 0.6, 30% EtOAc:Hexane) to give **81** as a yellow oil in a 10:1 mixture of diastereomers. **Yield:** 56 mg, 62%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.15 (m, 17H), 7.09 (d, *J*= 6.5 Hz, 0.15H, minor), 7.06 (d, *J*= 6.5 Hz, 1H, major), 6.79–6.75 (m, 0.16H, minor), 6.74–6.70 (m, 1H, major), 5.76 (dd, *J*= 6.4, 1.3 Hz, 1H), 5.00 (t, *J*= 6.6 Hz, 0.15H, minor), 4.91 (t, *J*= 6.6 Hz, 1H, major), 4.51 (tdd, *J*= 8.7, 4.6, 2.5 Hz, 1H), 4.25 (ddd, *J* = 10.3, 5.2, 3.1 Hz, 0.15H, minor), 3.60 (dd, *J* = 15.3, 3.1 Hz, 0.17H, minor), 3.53 (dd, *J*= 15.4, 5.2 Hz, 0.16H, minor), 3.47 (dd, *J*= 15.0, 3.7 Hz, 1H, major), 3.37 (dd, *J*= 15.0, 7.8 Hz, 1H, major), 2.96 (dd, *J*= 13.0, 5.1 Hz, 1H, major), 2.88 (dd, *J*= 12.8, 4.9 Hz, 0.16H, minor), 2.67 (dd, *J*= 12.9, 10.7 Hz, 0.17H, minor), 2.50 (dd, *J*= 13.1, 10.3 Hz, 1H, major), 2.22 (s, 0.45H, minor), 2.21 (s, 3H, major). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.14, 194.99, 176.5, 176.4, 144.5, 144.2, 142.5, 142.4, 141.8, 141.6, 139.3, 139.1, 136.0, 129.2,

129.1, 128.7, 128.64, 128.59, 128.5, 128.11, 128.10, 128.0, 127.9, 127.8, 127.7, 127.54, 127.50, 127.34, 127.33, 126.8, 126.5, 121.8, 121.0, 95.3, 94.2, 75.8, 74.9, 60.5, 60.3, 59.3, 58.3, 57.4, 40.9, 39.9. **LRMS** (m/z): $[M+H]^+$ calcd. For $C_{30}H_{28}NO_3^+$, 450.2069; found 450.31.

Note: Low resolution mass was obtained due to stability issues that resulted in decomposition en route to off-site HRMS facility or elemental analysis.

1,4-Addition of aryl cuprate to give 1,4-dihydropyridine (Conditions B)



34 **82**

3,3-diphenyl-5-((4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-1(4*H*)-yl)methyl)dihydrofuran-2(3*H*)-one (82). A flame dried Schlenk tube under argon was charged with pyridinium lactone **34** (60.5 mg, 0.1 mmol, 1.0 equiv.) and copper iodide (1.9 mg, 0.01 mmol, 10 mol%) in dry THF (1.0 mL, 0.1 M). Phenyl magnesium bromide (67 µL, 2.0 equiv., 3 M in diethyl ether) was added dropwise at room temperature. The mixture was stirred for 3 h, quenched with NH_4Cl (sat. aq.) (10 mL), extracted with EtOAc (3 x 10mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by flash chromatography (gradient, 10–30% EtOAc/Hexane; R_f = 0.3-0.4, 10% EtOAc/Hexane) to give **82** as a light brown oil in a 4:1 ratio of diastereomers. **Yield:** 20 mg, 46%. (Major diastereomer) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39–7.18 (m, 15H), 6.55 (t, *J*= 1.5 Hz, 1H), 6.02 (ddd, *J*= 15.0, 8.0, 1.5 Hz, 1H), 4.76 (ddd, *J*= 8.0, 5.0, 1.5 Hz, 1H), 4.46–4.40 (m, 1H), 4.23 (dd, *J*= 4.5, 1.5 Hz, 1H), 3.53–3.41 (m, 2H), 2.98 (td, *J*= 13.0, 5.0 Hz, 1H), 2.75–2.66 (m, 1H), 1.17 (s, 6H), 1.07 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.8, 149.5, 141.8, 140.5, 140.4, 139.3, 129.2, 128.7, 128.2, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.5, 125.8, 125.8, 105.4, 105.4, 82.8, 76.38, 76.37, 57.0, 56.5, 40.9, 40.5, 38.4, 25.2, 24.7. **HRMS** (m/z): $[M+H]^+$ calcd. For $C_{34}H_{37}BNO_4^+$, 534.2810; found 406.1767 [due to loss of boronic ester during analysis. $[M-C_6H_{12}]^+$: 406.1807]

Section G. References

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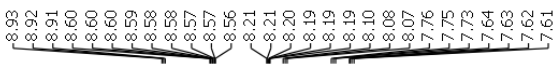

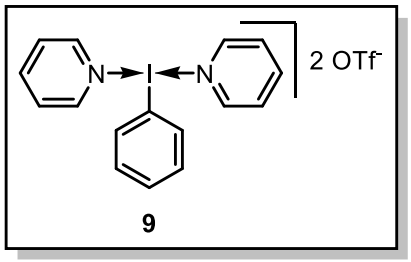

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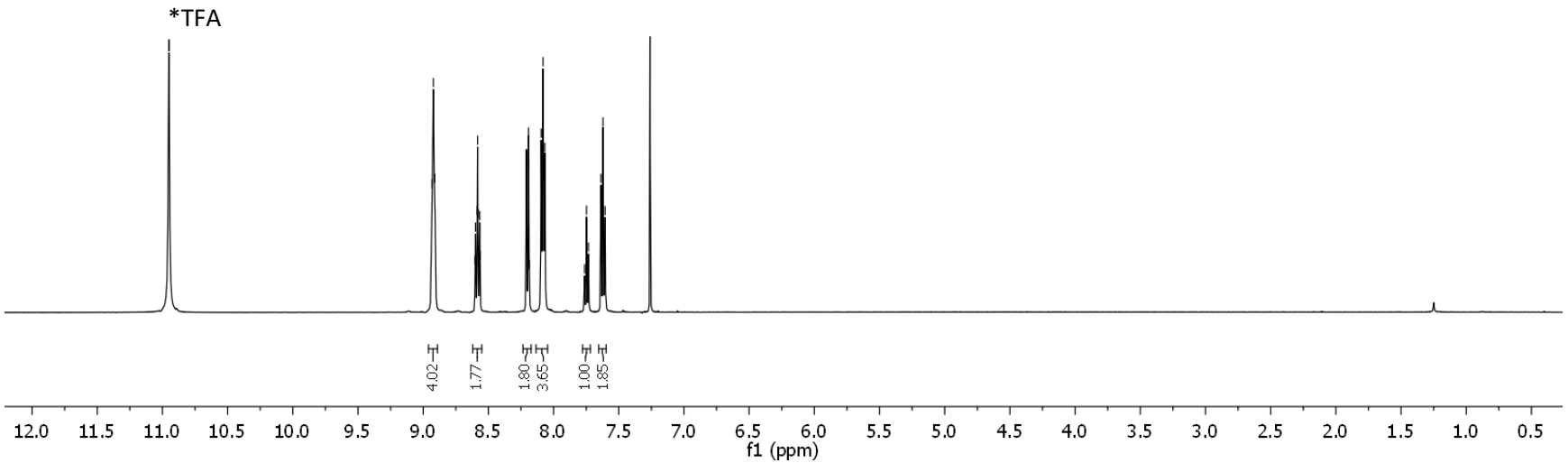

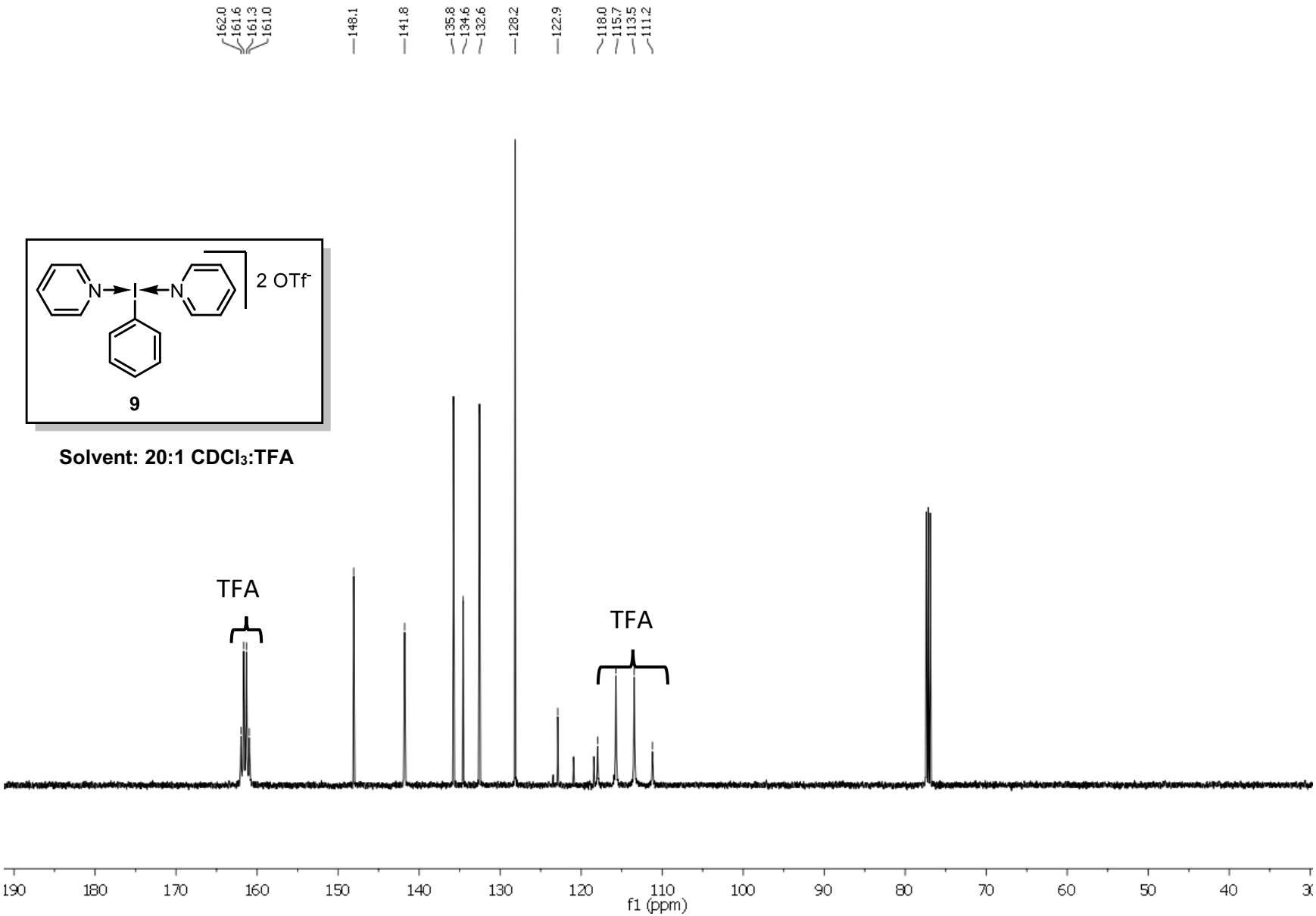
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113.5
111.2
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I
N
2 OTf-
9
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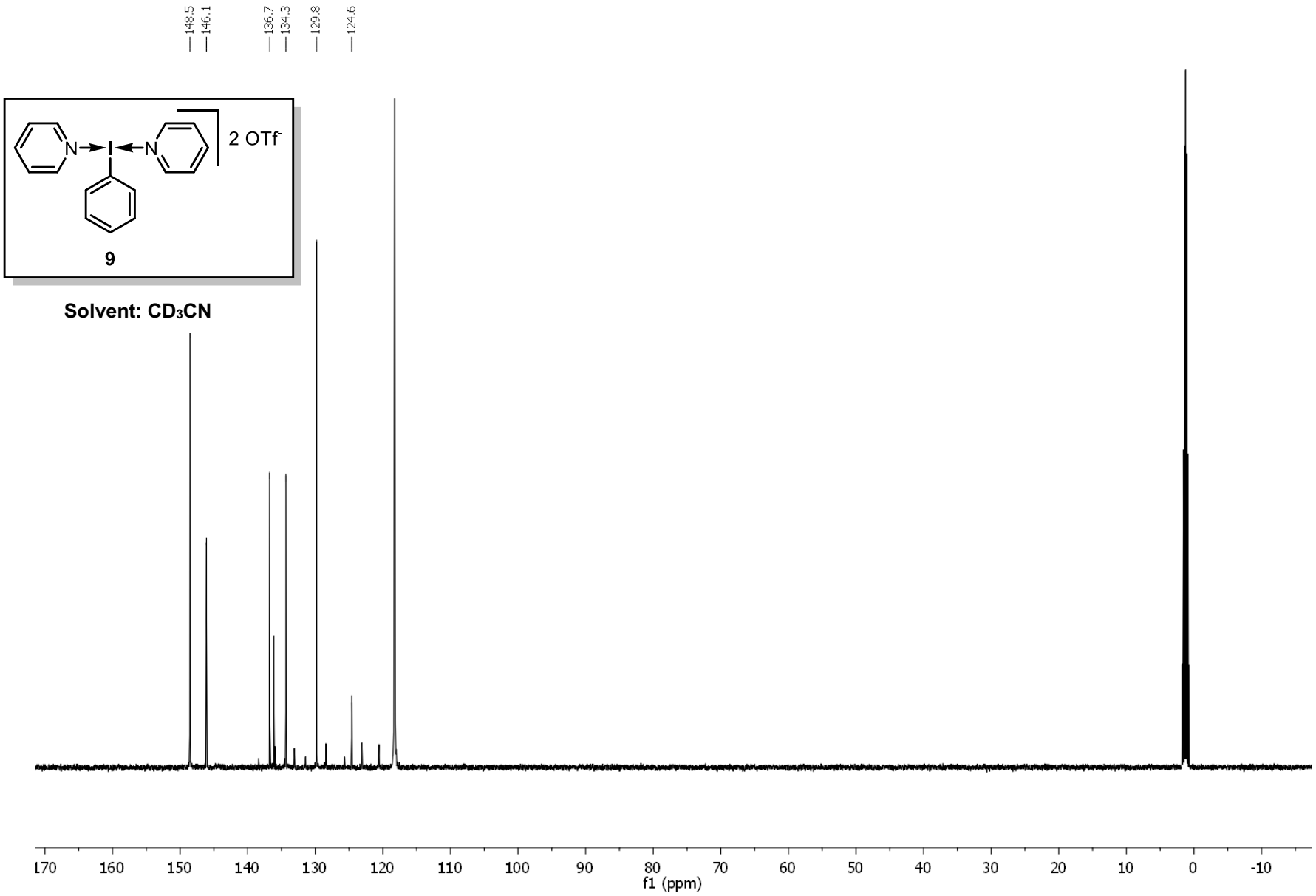
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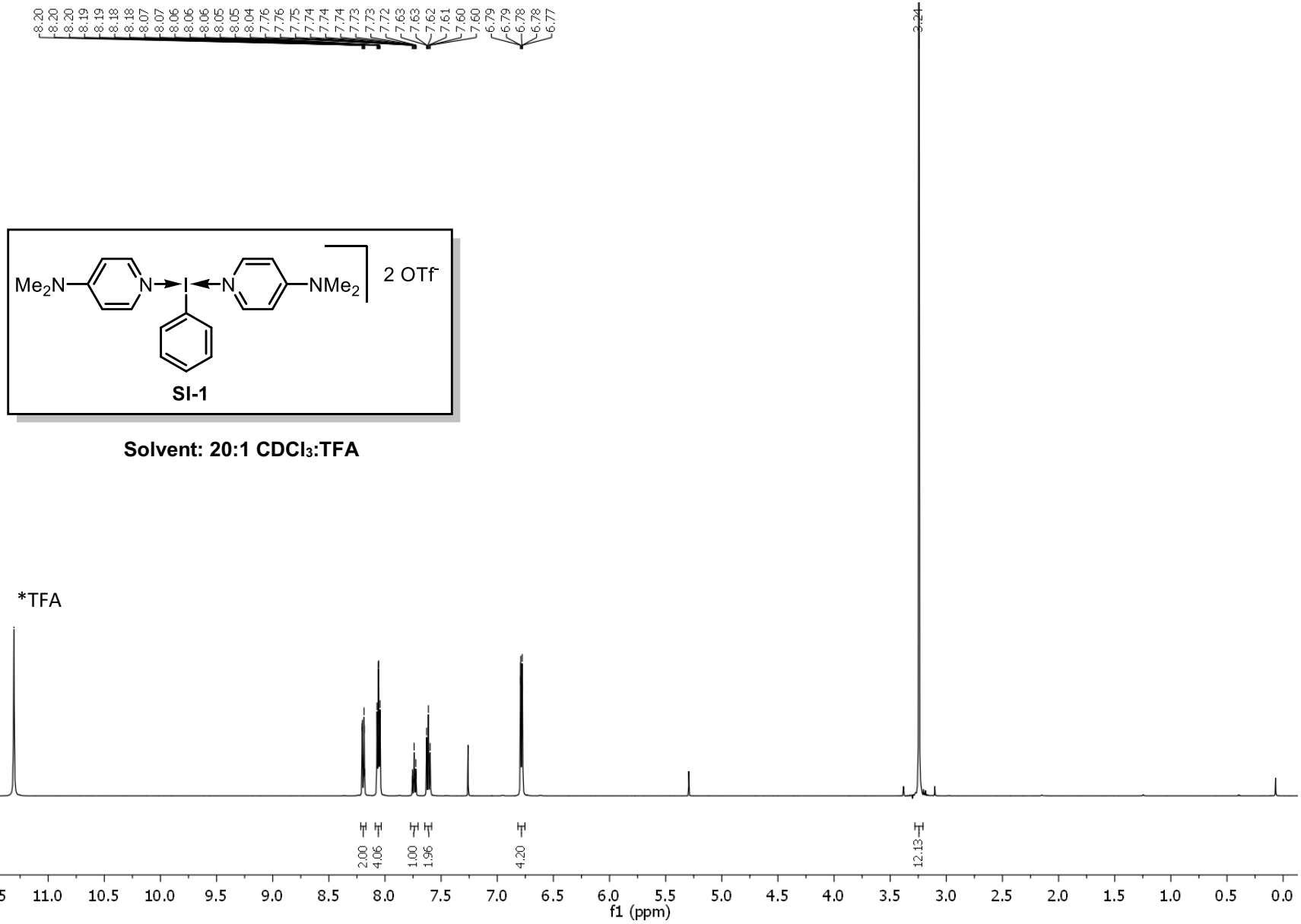
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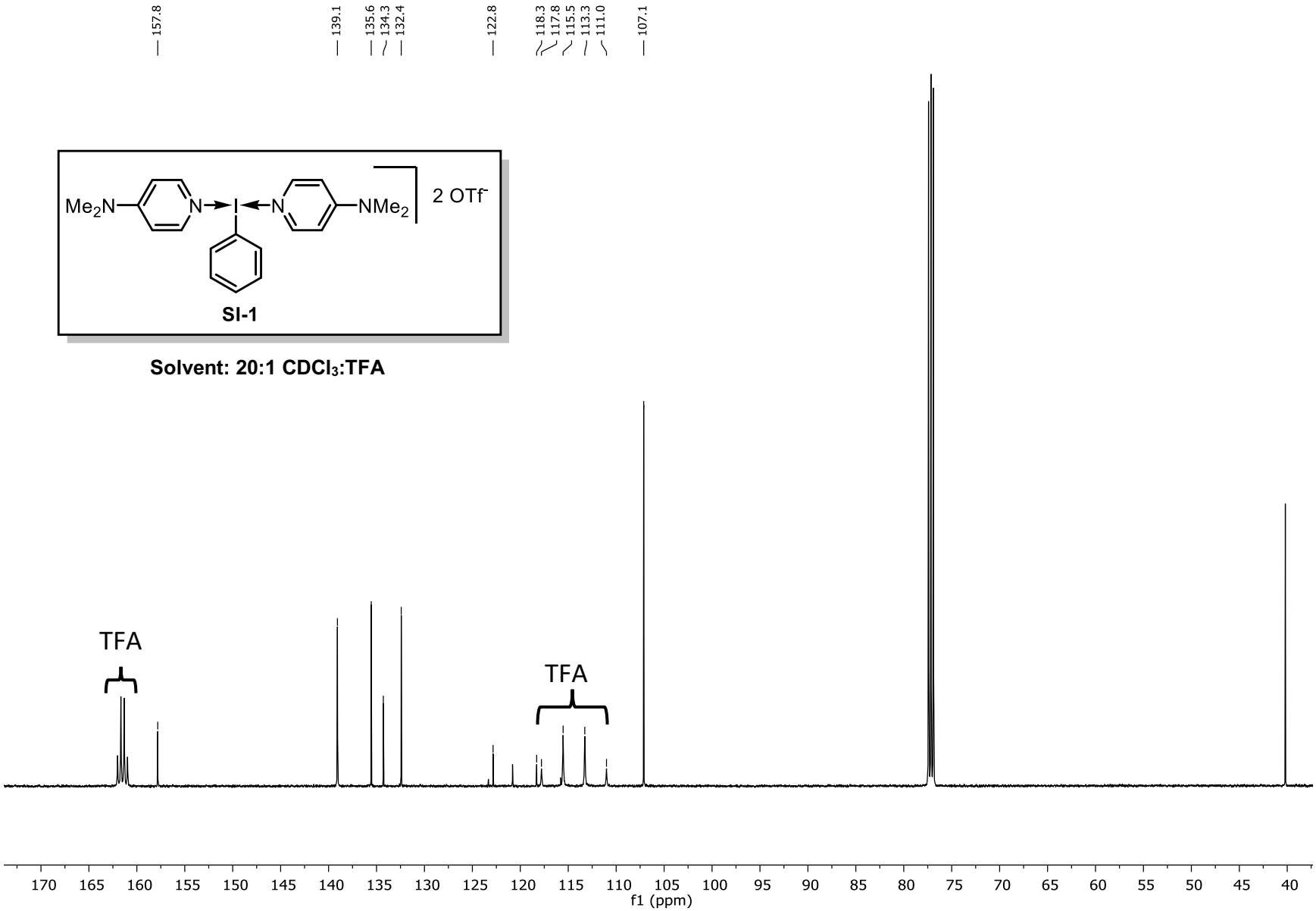
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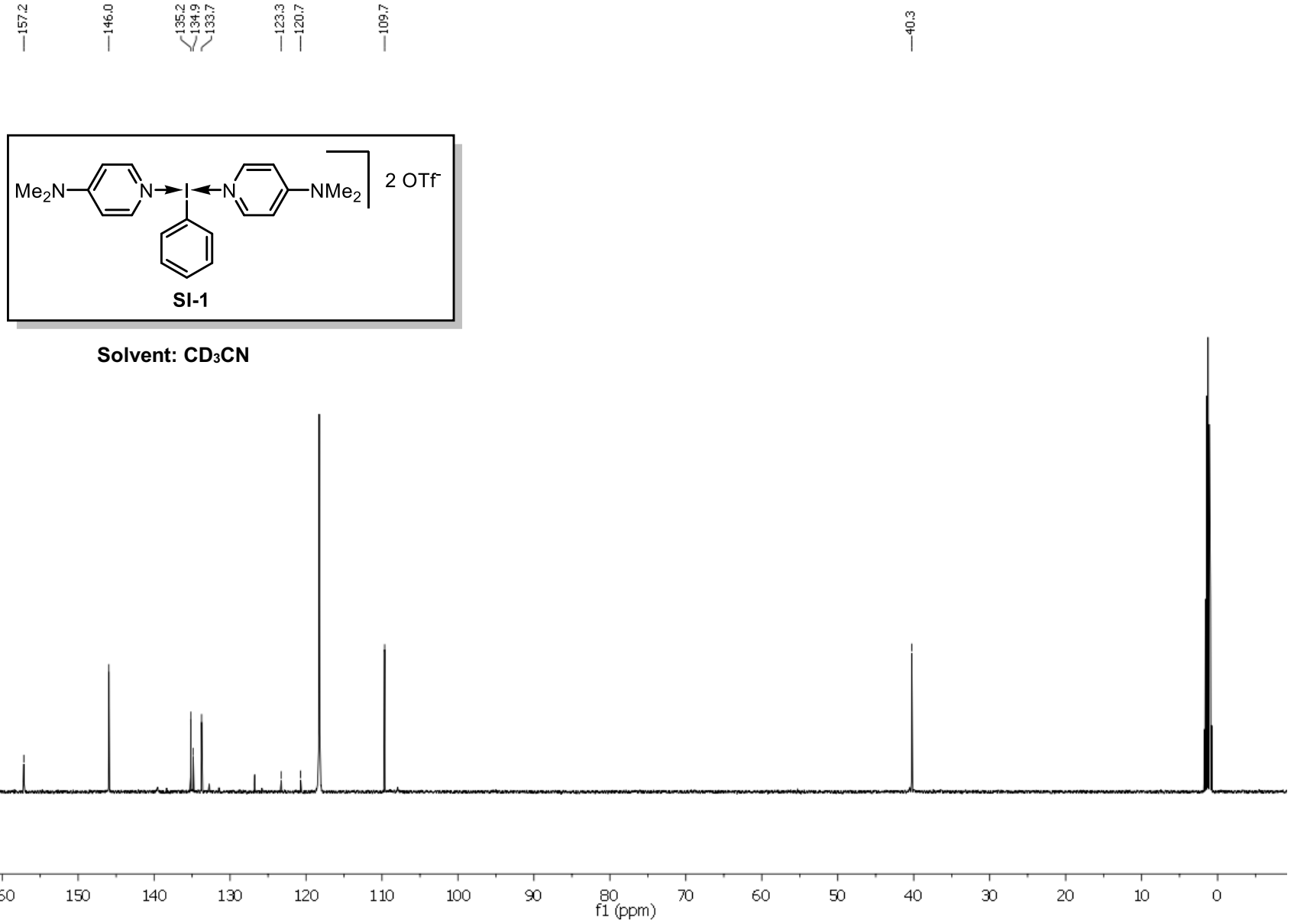
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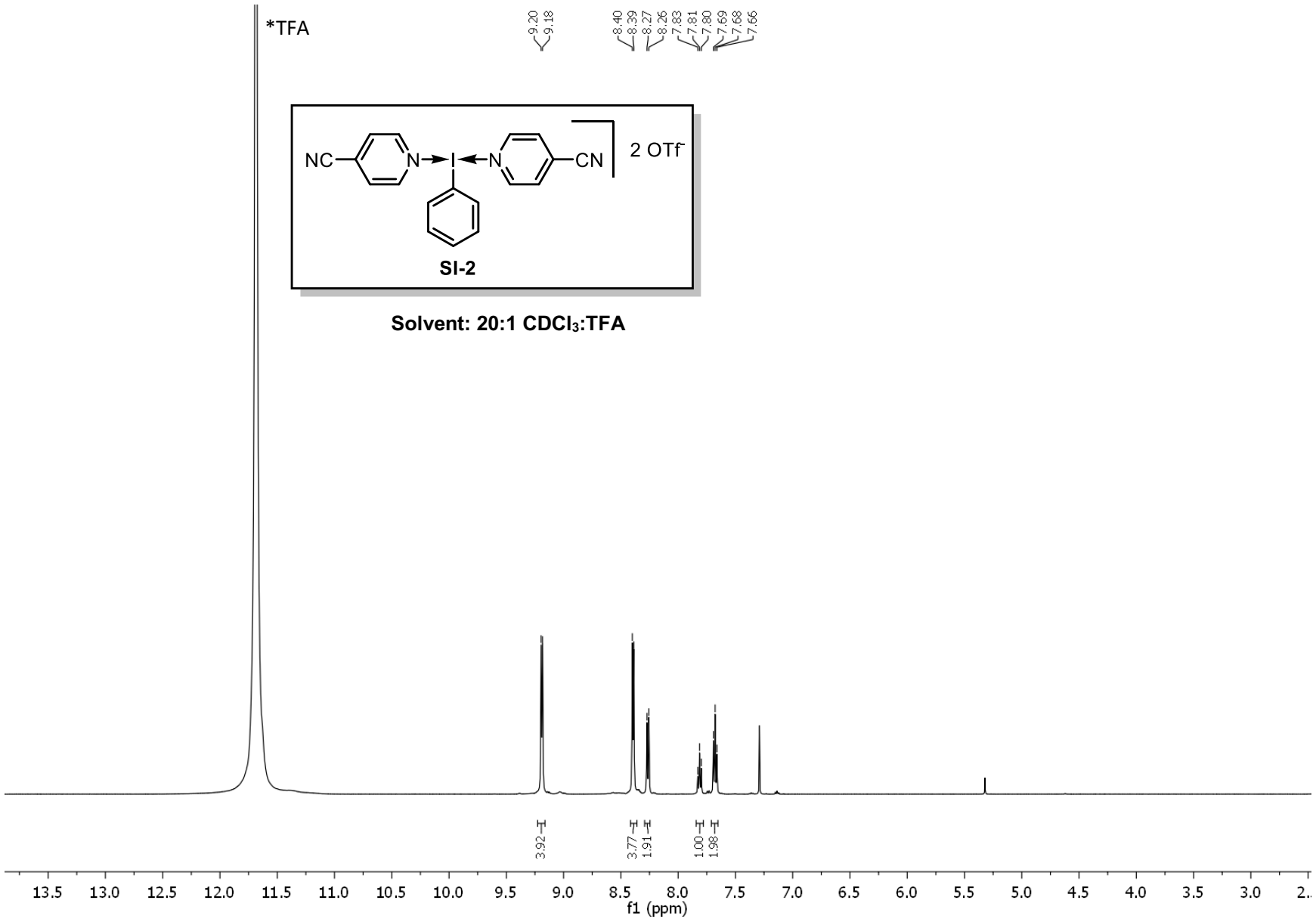
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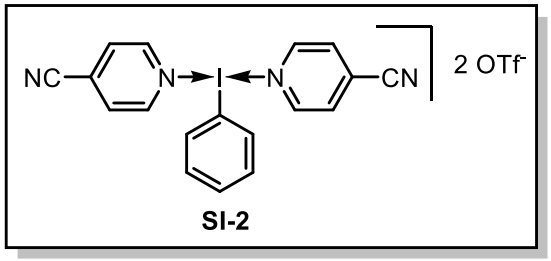

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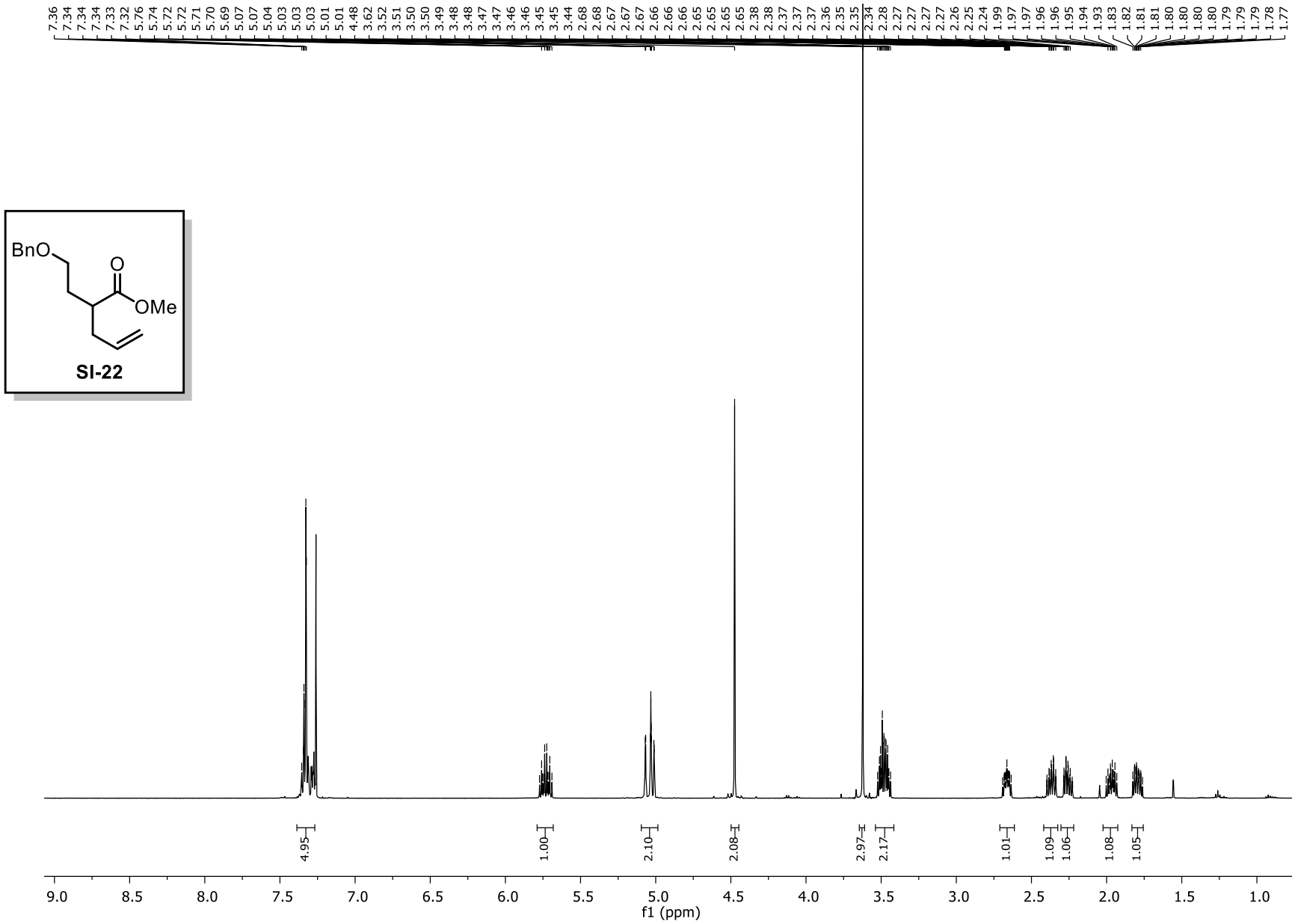
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1.06
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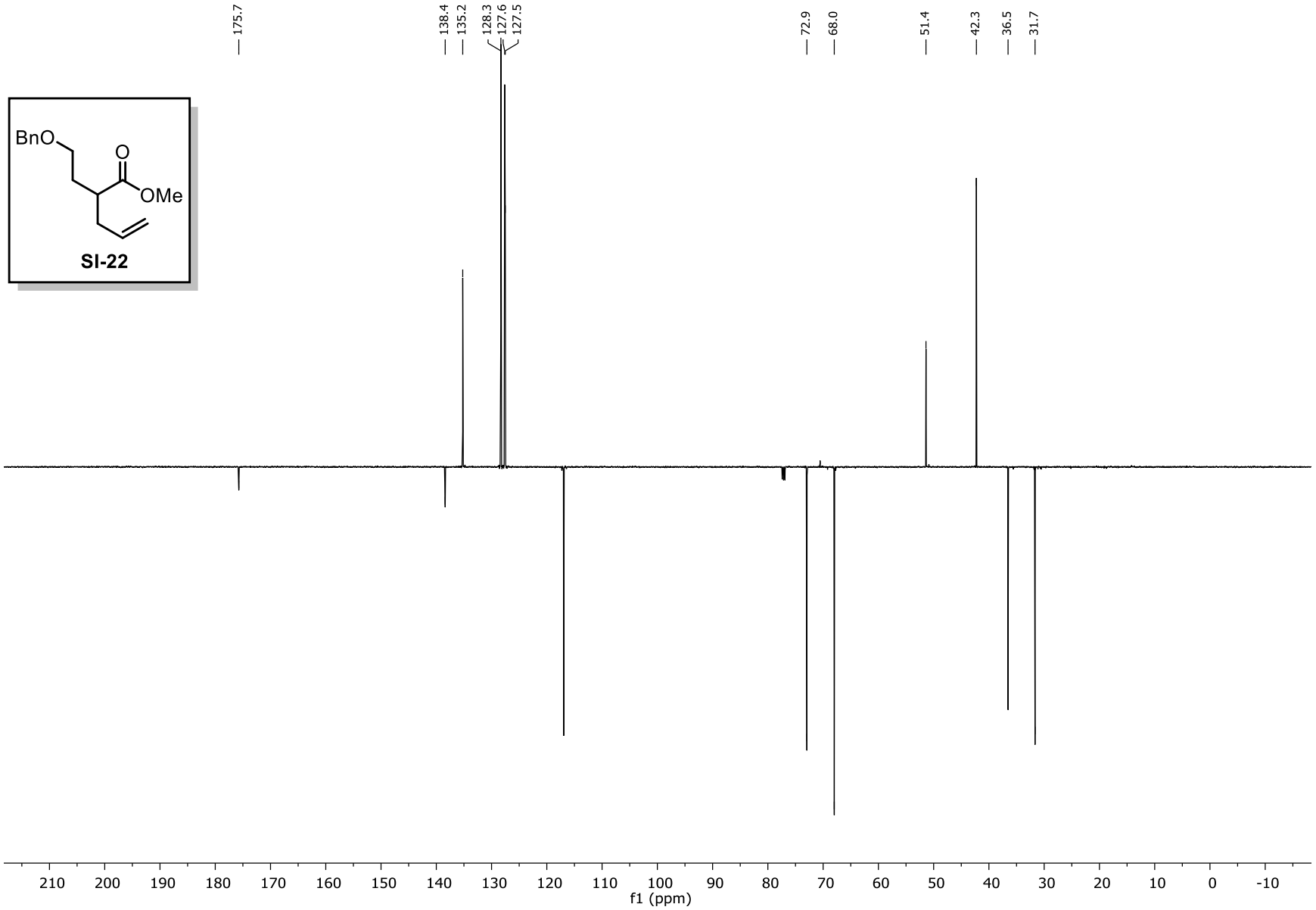
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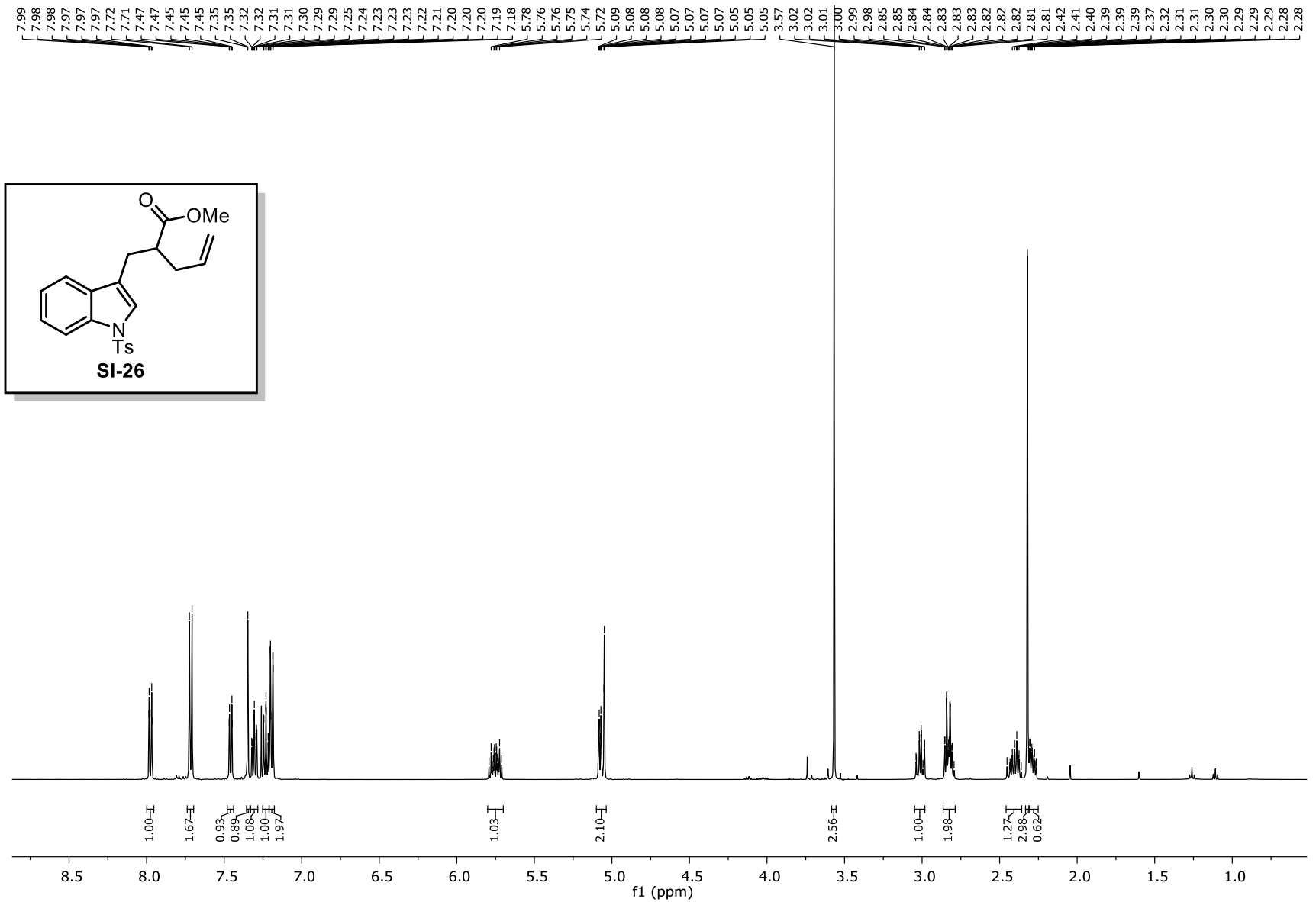
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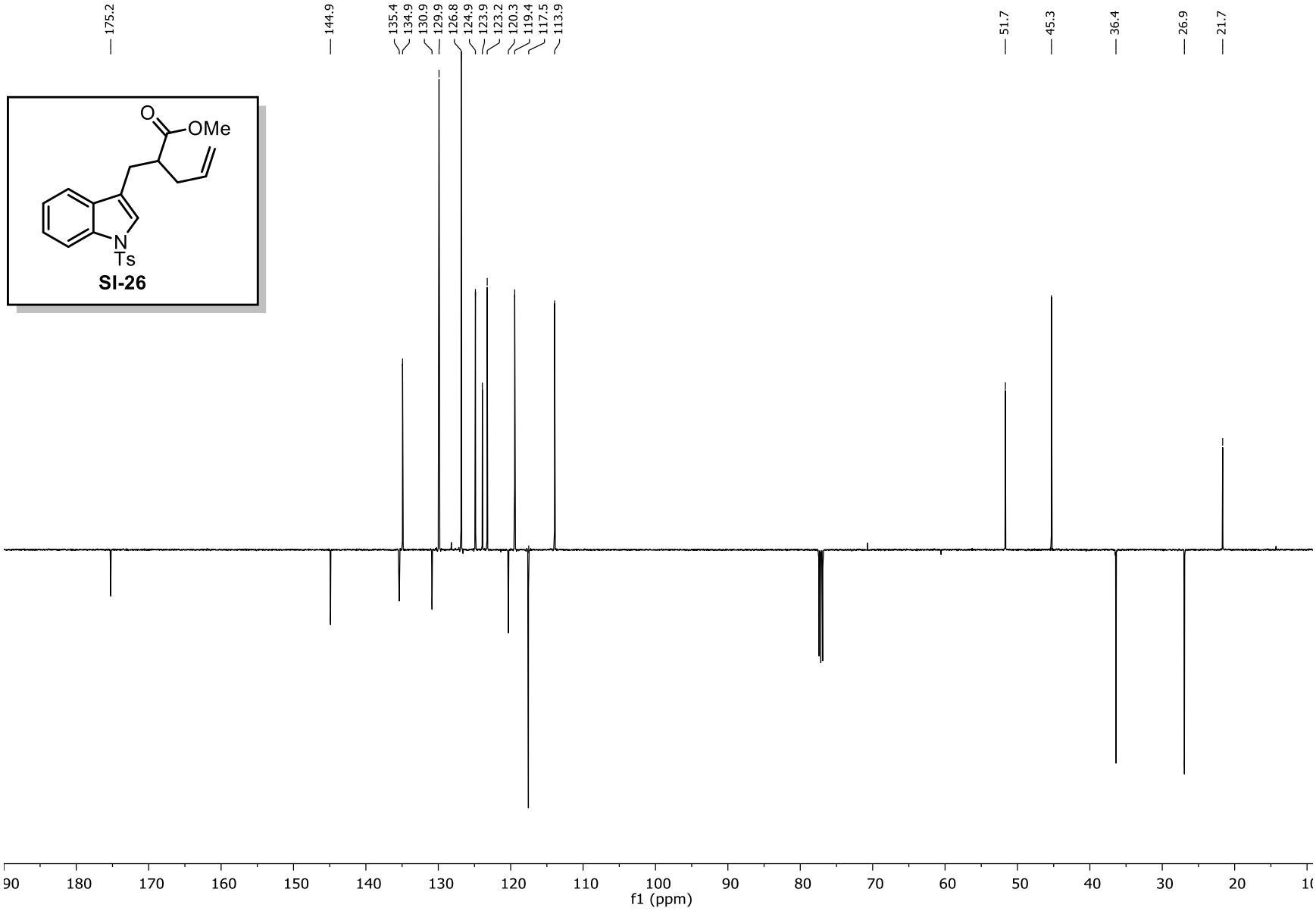
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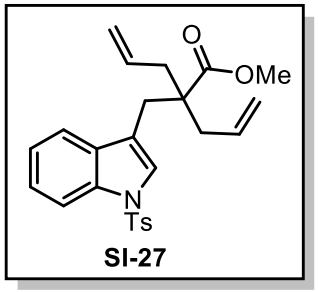
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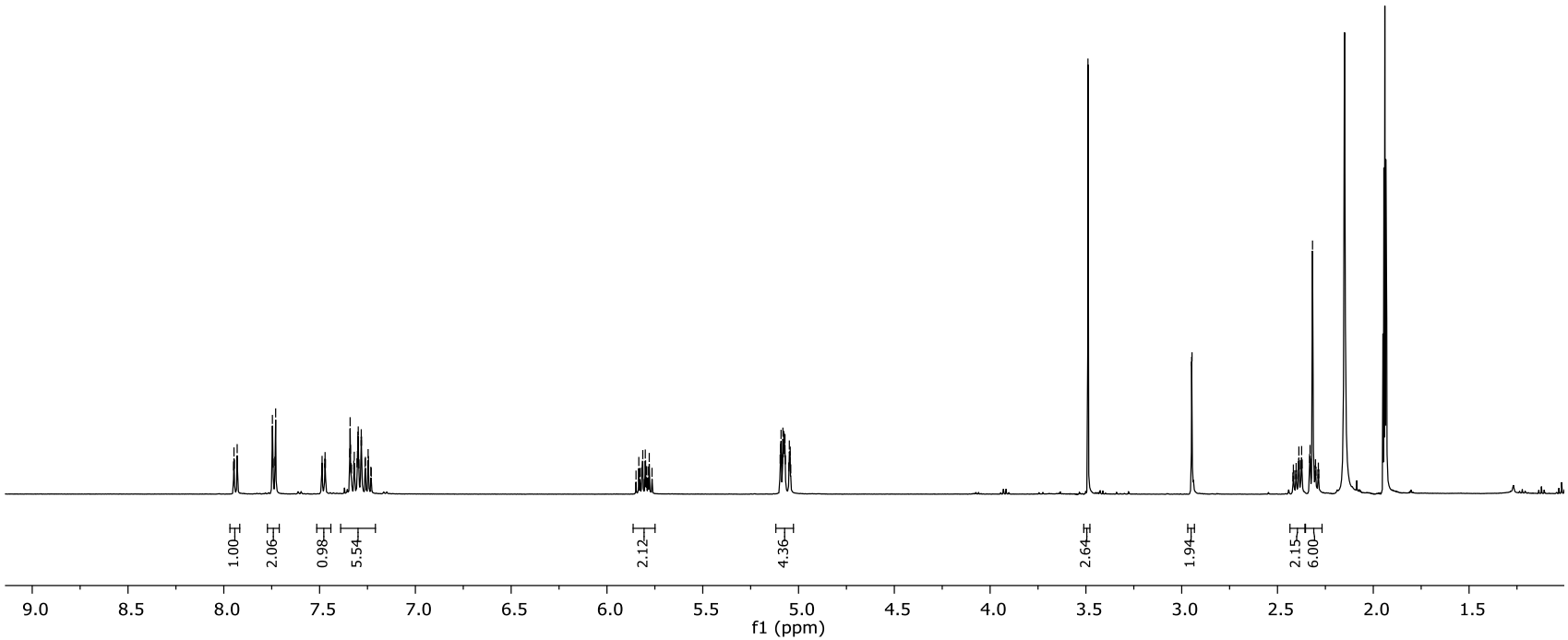
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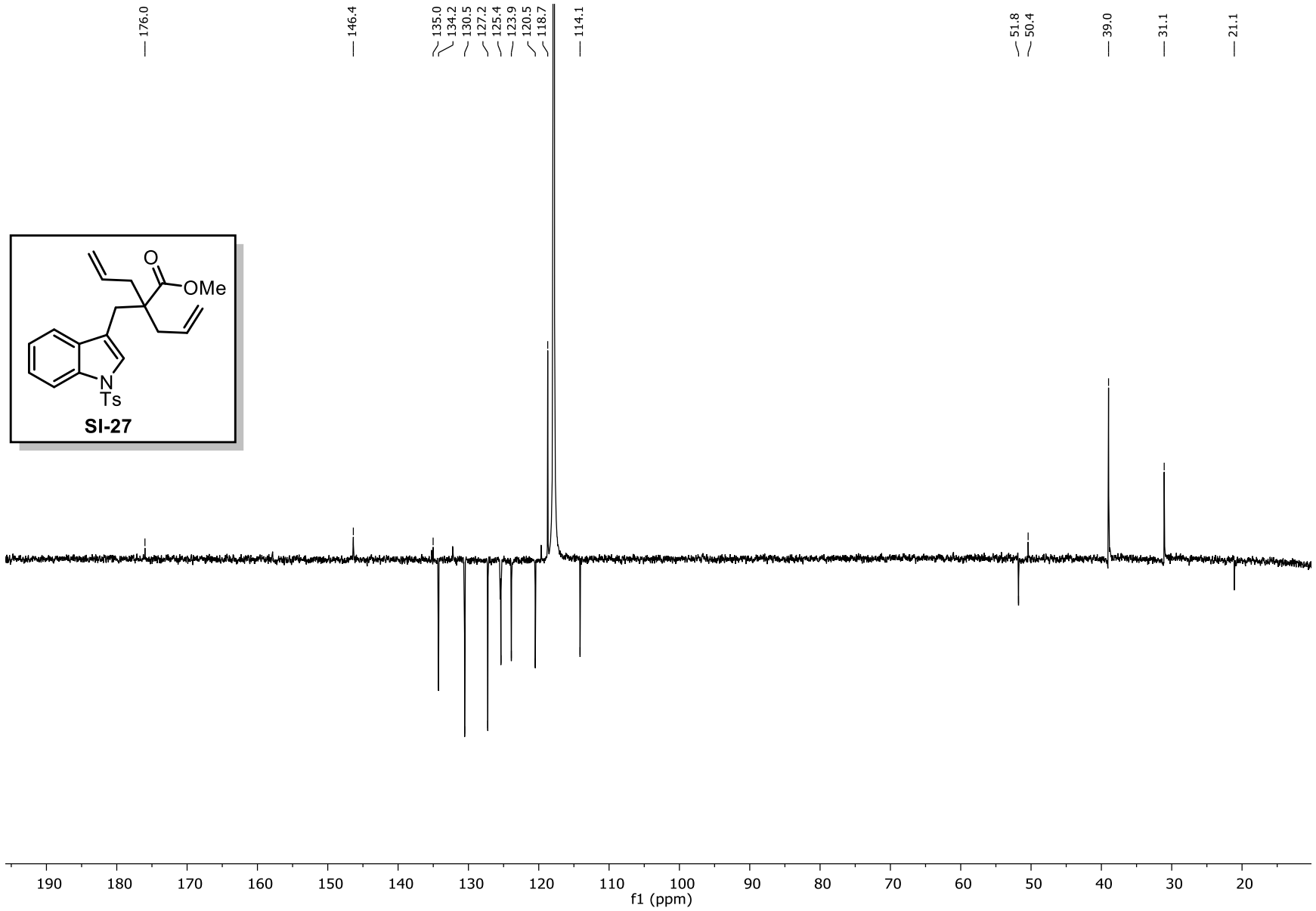
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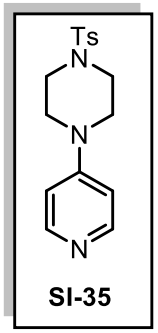
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SI-35

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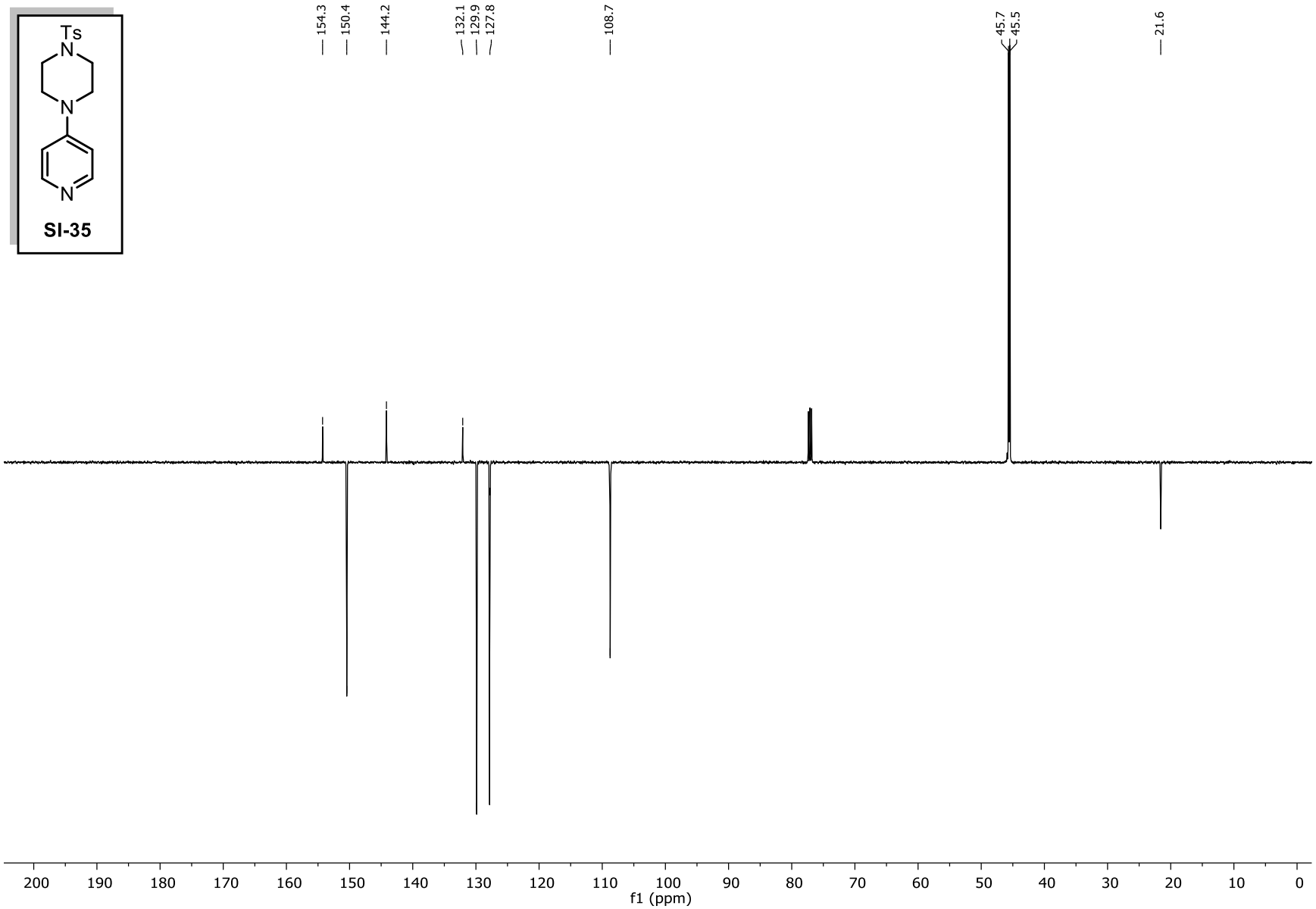
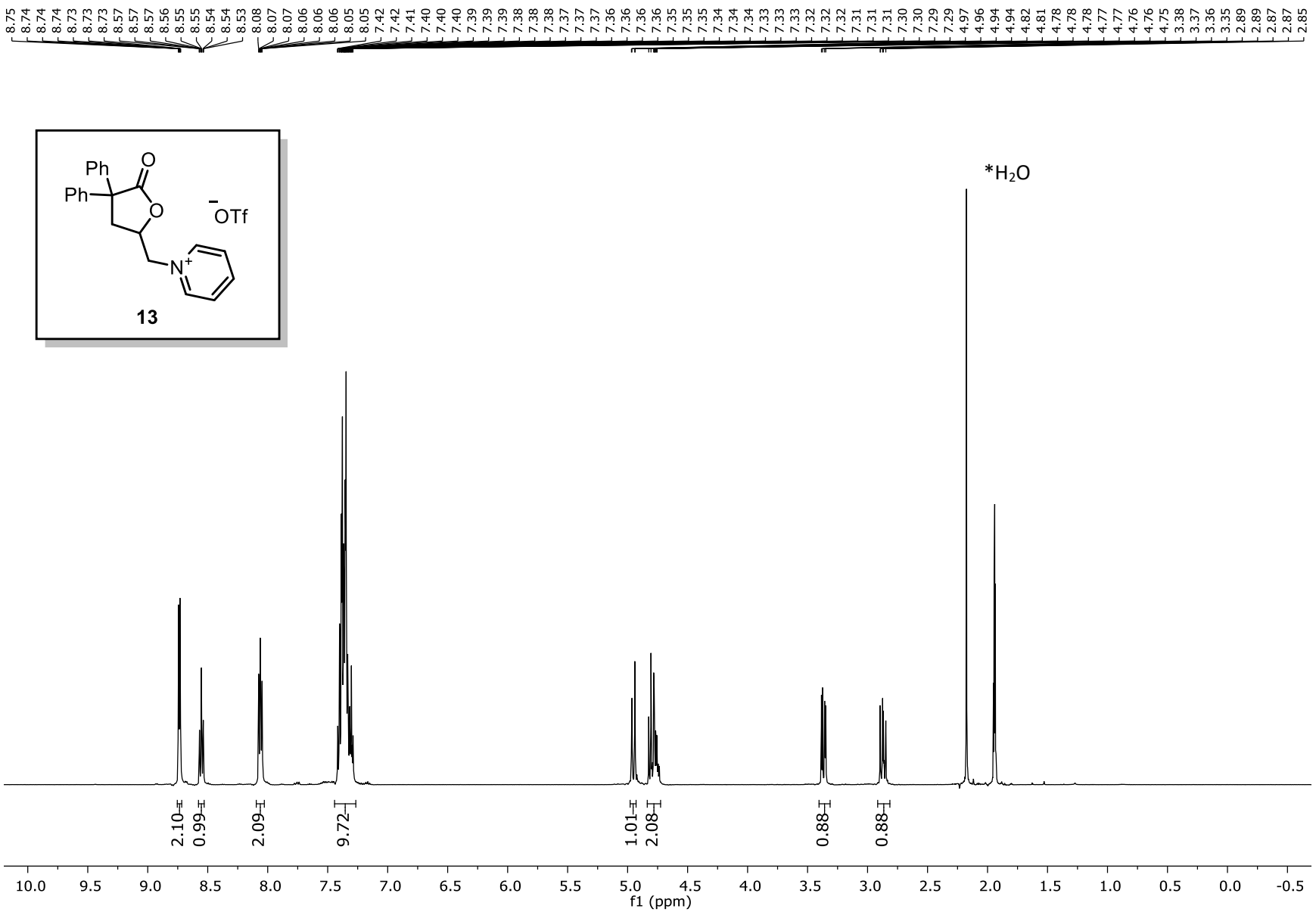
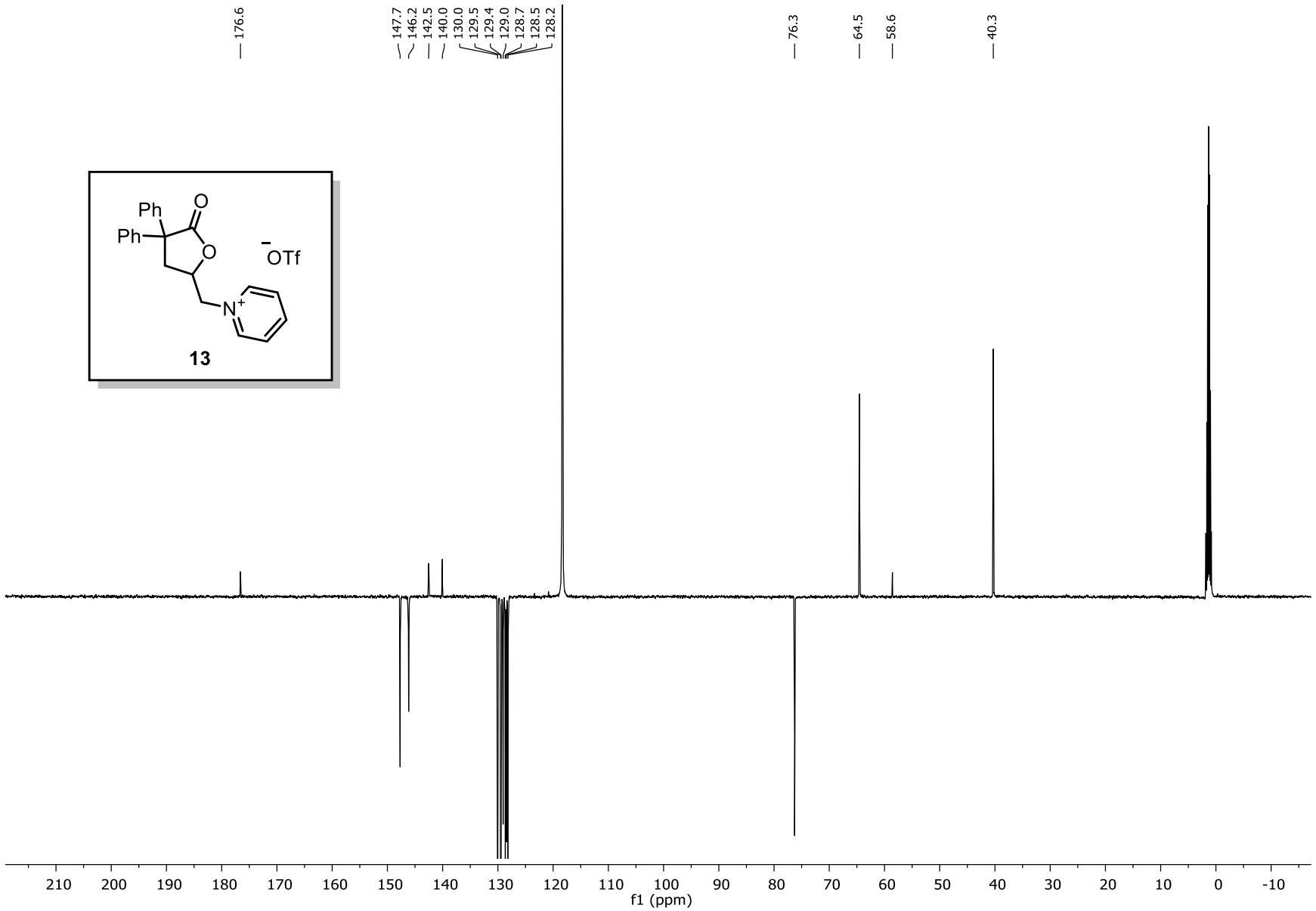
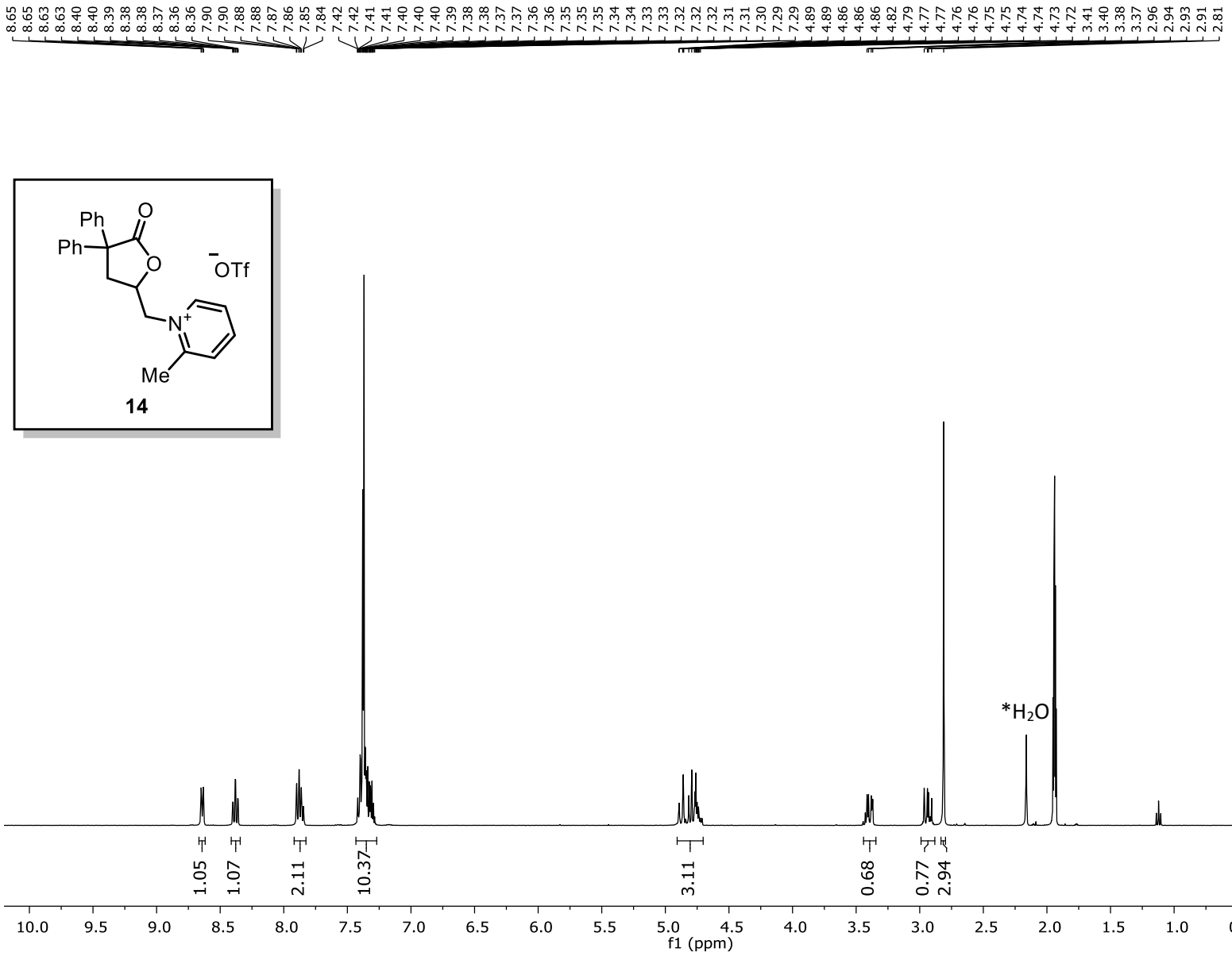
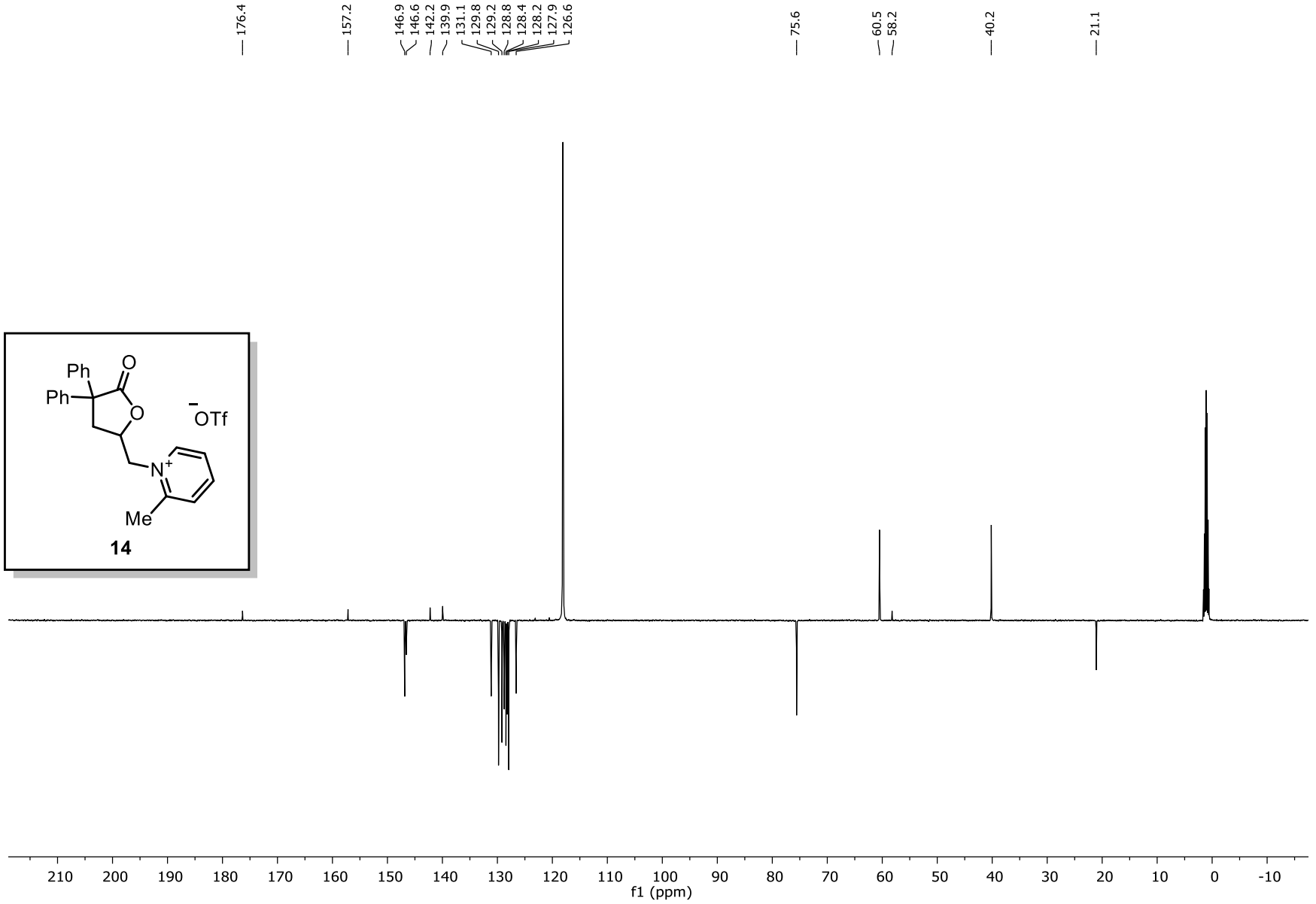
3.38
3.10
3.09
3.08
2.41
1.99
1.97
2.00
2.03
3.96
4.05
3.01
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

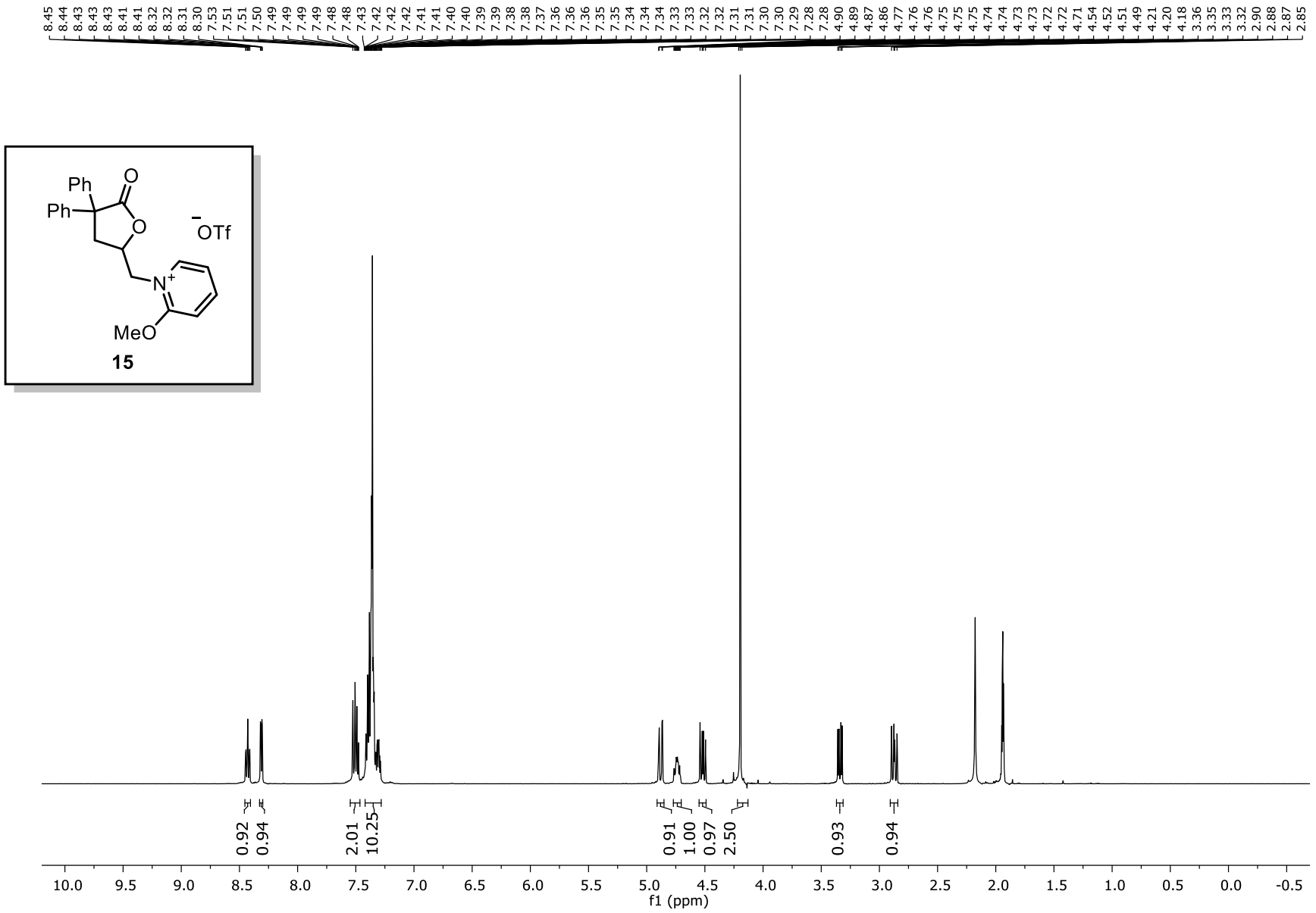

Ts
N
N
N
SI-35
154.3
150.4
144.2
132.1
129.9
127.8
108.7
45.7
45.5
21.6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

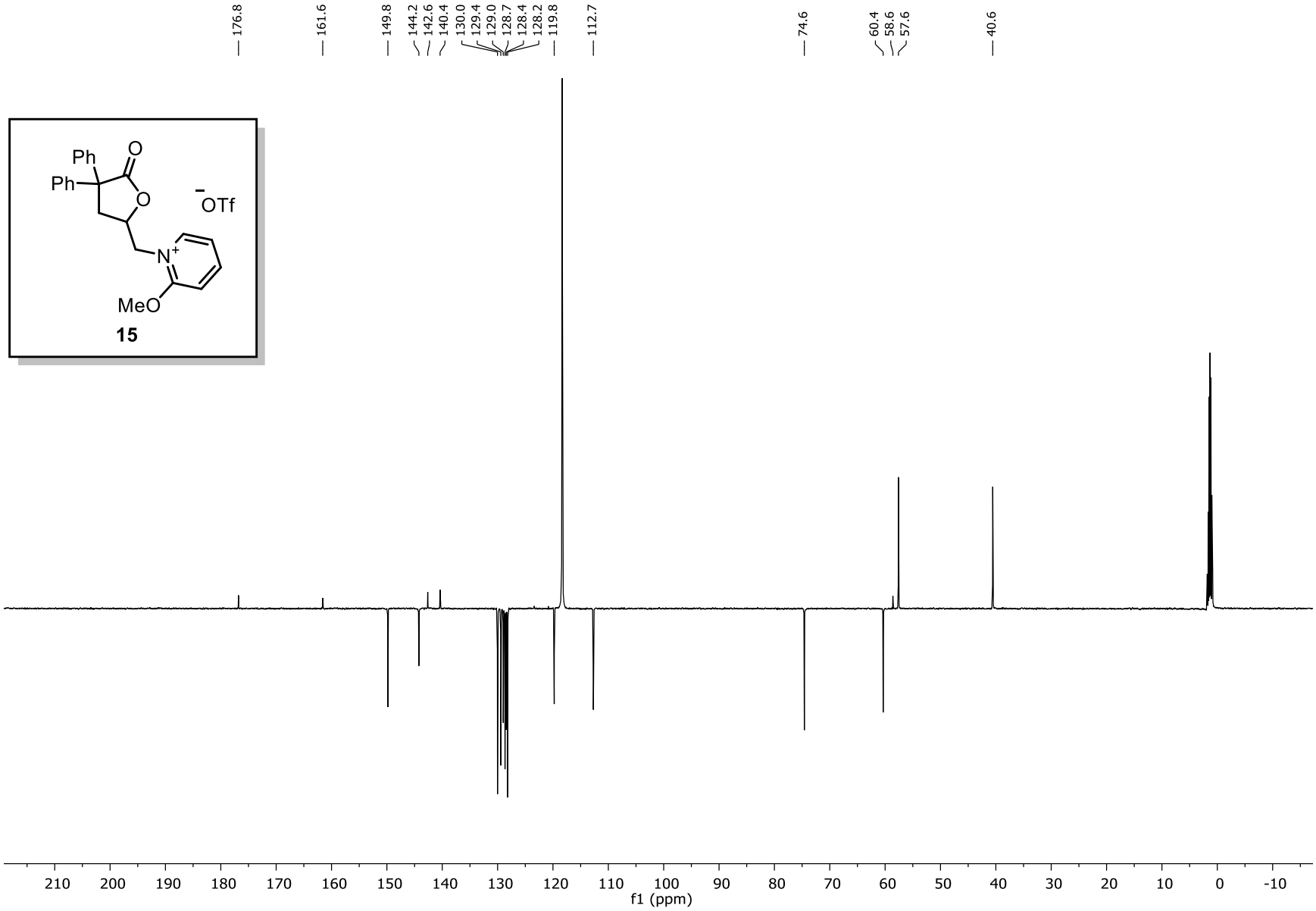

8.75 8.74 8.74 8.74 8.73 8.73 8.73 8.57 8.57 8.57 8.56 8.55 8.55 8.54 8.54 8.53
8.08 8.07 8.07 8.06 8.06 8.06 8.05 8.05 7.42 7.42 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 4.97 4.96 4.94 4.94 4.82 4.81 4.78 4.78 4.78 4.77 4.77 4.76 4.76 4.75 3.38 3.37 3.36 3.35 2.89 2.89 2.87 2.87 2.85
Ph
Ph
O
O
OTf
N+
13
*H2O
2.10
0.99
2.09
9.72
1.01
2.08
0.88
0.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

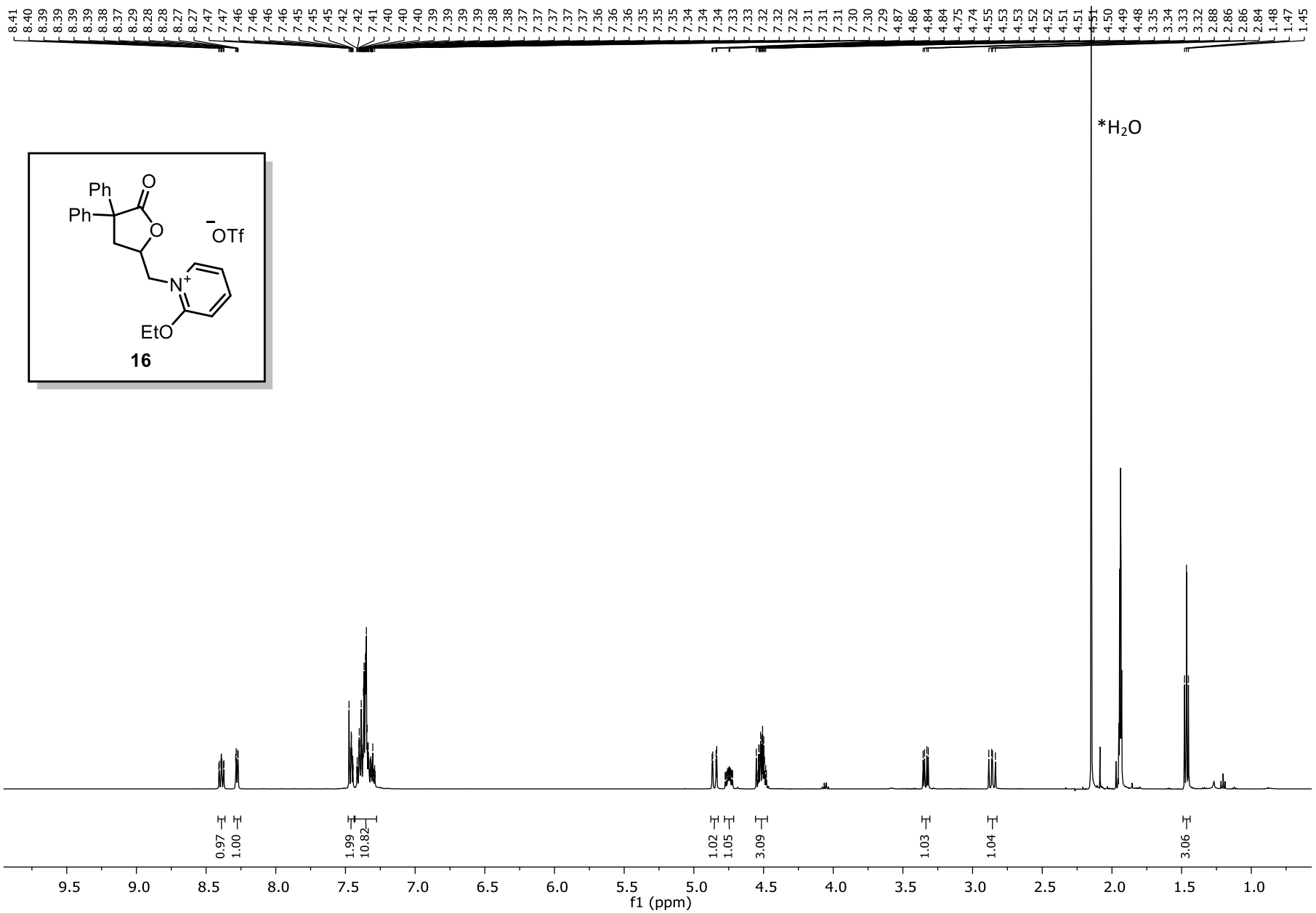

176.6
147.7
146.2
142.5
140.0
130.0
129.5
129.4
129.0
128.7
128.5
128.2
76.3
64.5
58.6
40.3
Ph
Ph
O
O
OTf
N+
13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

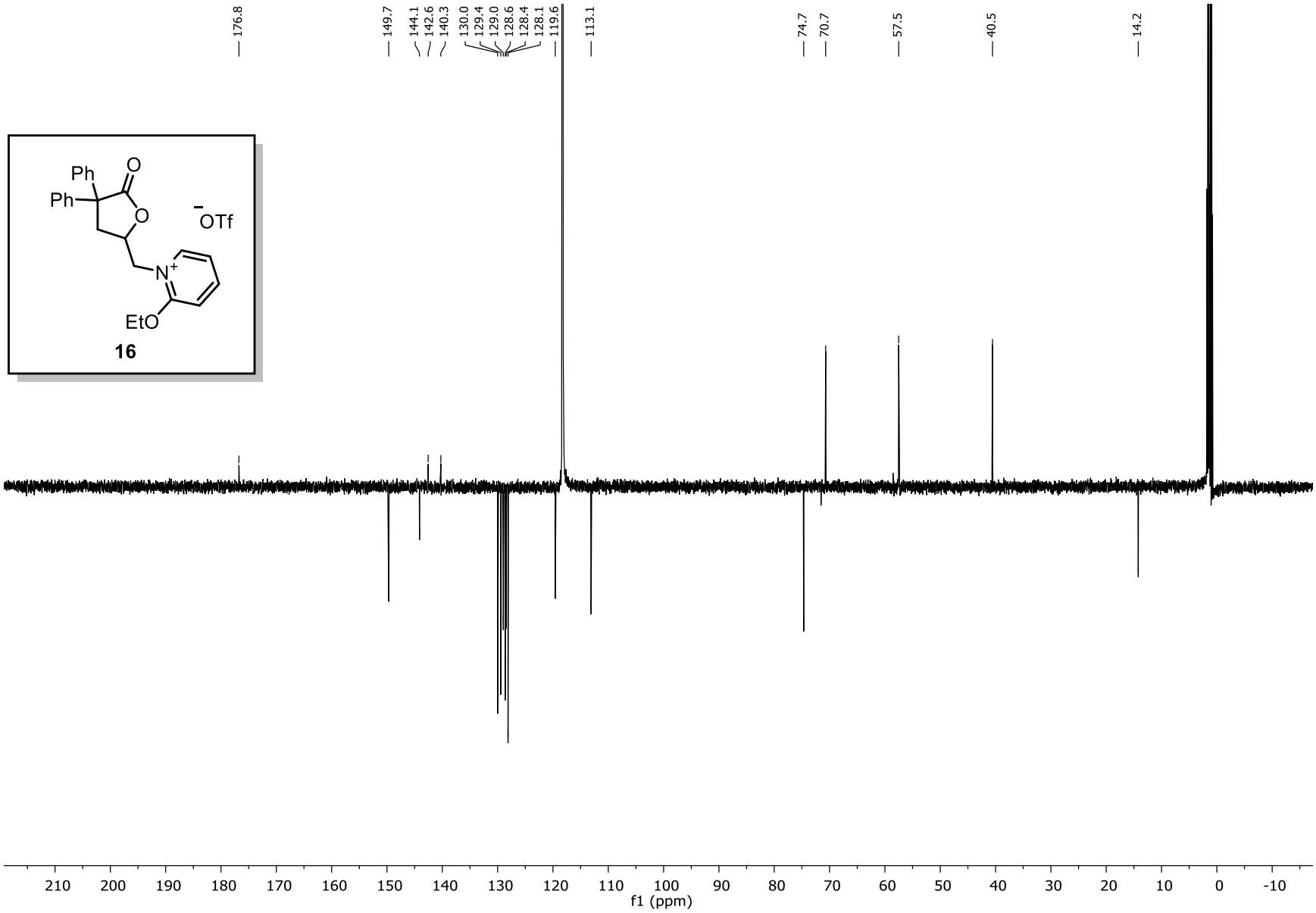

8.65 8.65 8.63 8.63 8.40 8.40 8.39 8.38 8.38 8.37 8.36 8.36 7.90 7.90 7.88 7.88 7.87 7.86 7.85 7.84
7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.29 7.29 4.89 4.89 4.86 4.86 4.86 4.82 4.79 4.77 4.77 4.76 4.76 4.75 4.75 4.74 4.74 4.73 4.72 3.41 3.40 3.38 3.37 2.96 2.94 2.93 2.91 2.81
Ph
Ph
O
O
OTf
N+
Me
14
*H2O
1.05
1.07
2.11
10.37
3.11
0.68
0.77
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

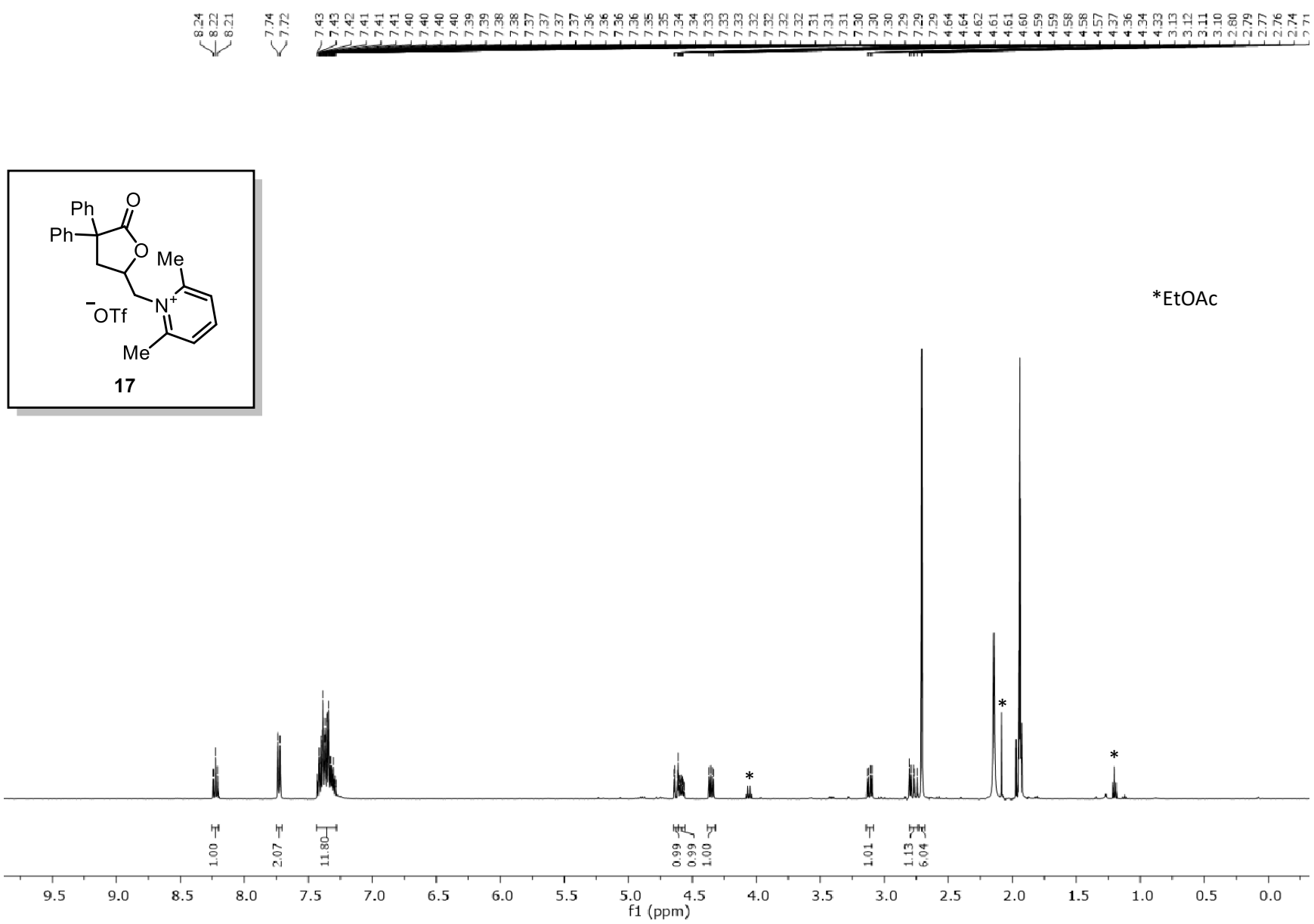

176.4
157.2
146.9
146.6
142.2
139.9
131.1
129.8
129.2
128.8
128.4
128.2
127.9
126.6
75.6
60.5
58.2
40.2
21.1
Ph
Ph
O
O
OTf
N+
Me
14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

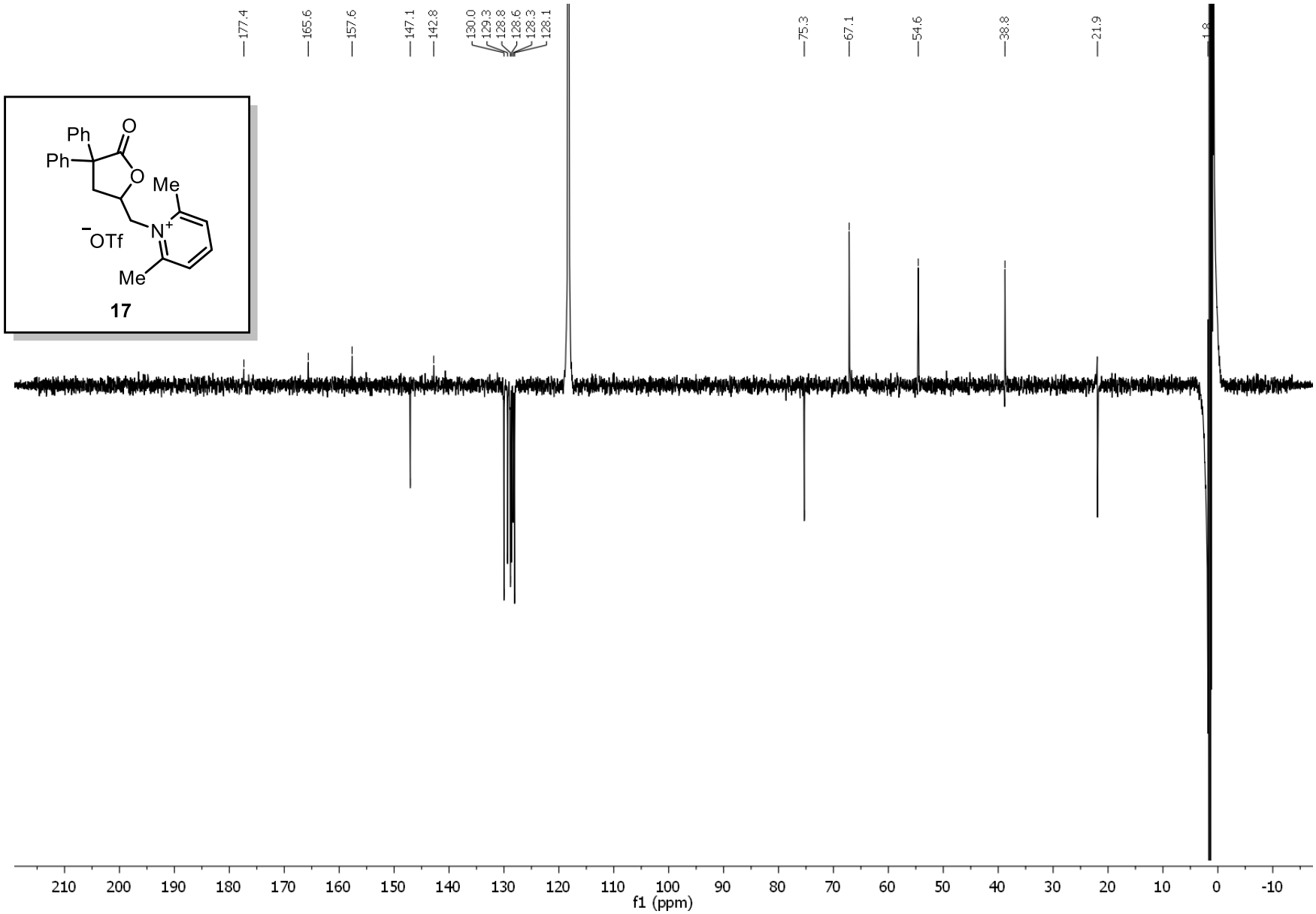

Ph
Ph
O
O
OTf
N+
MeO
15
f1 (ppm)

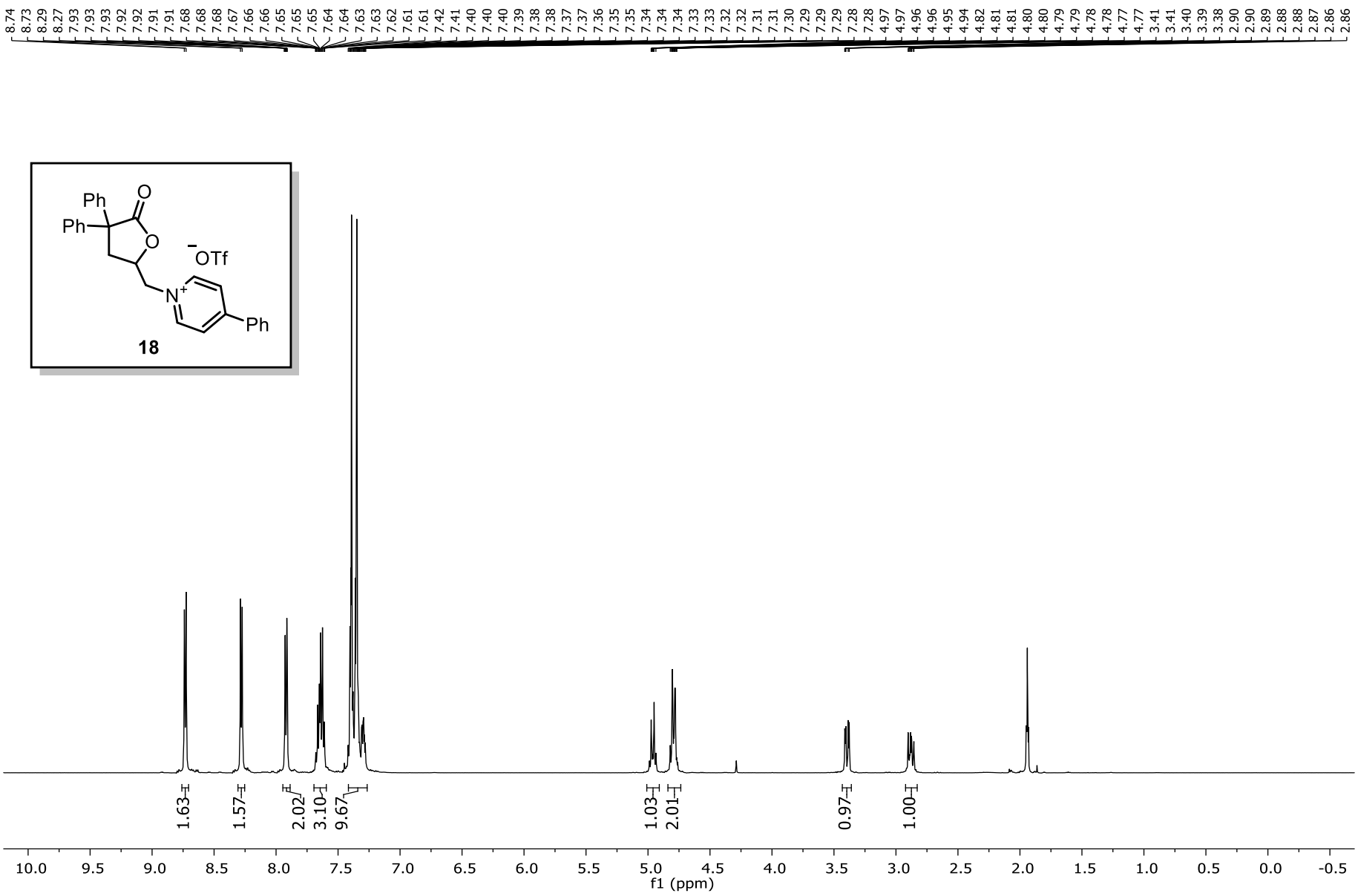

176.8
161.6
149.8
144.2
142.6
140.4
130.0
129.4
129.0
128.7
128.4
128.2
119.8
112.7
74.6
60.4
58.6
57.6
40.6
Ph
Ph
O
O
OTf
N+
MeO
15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

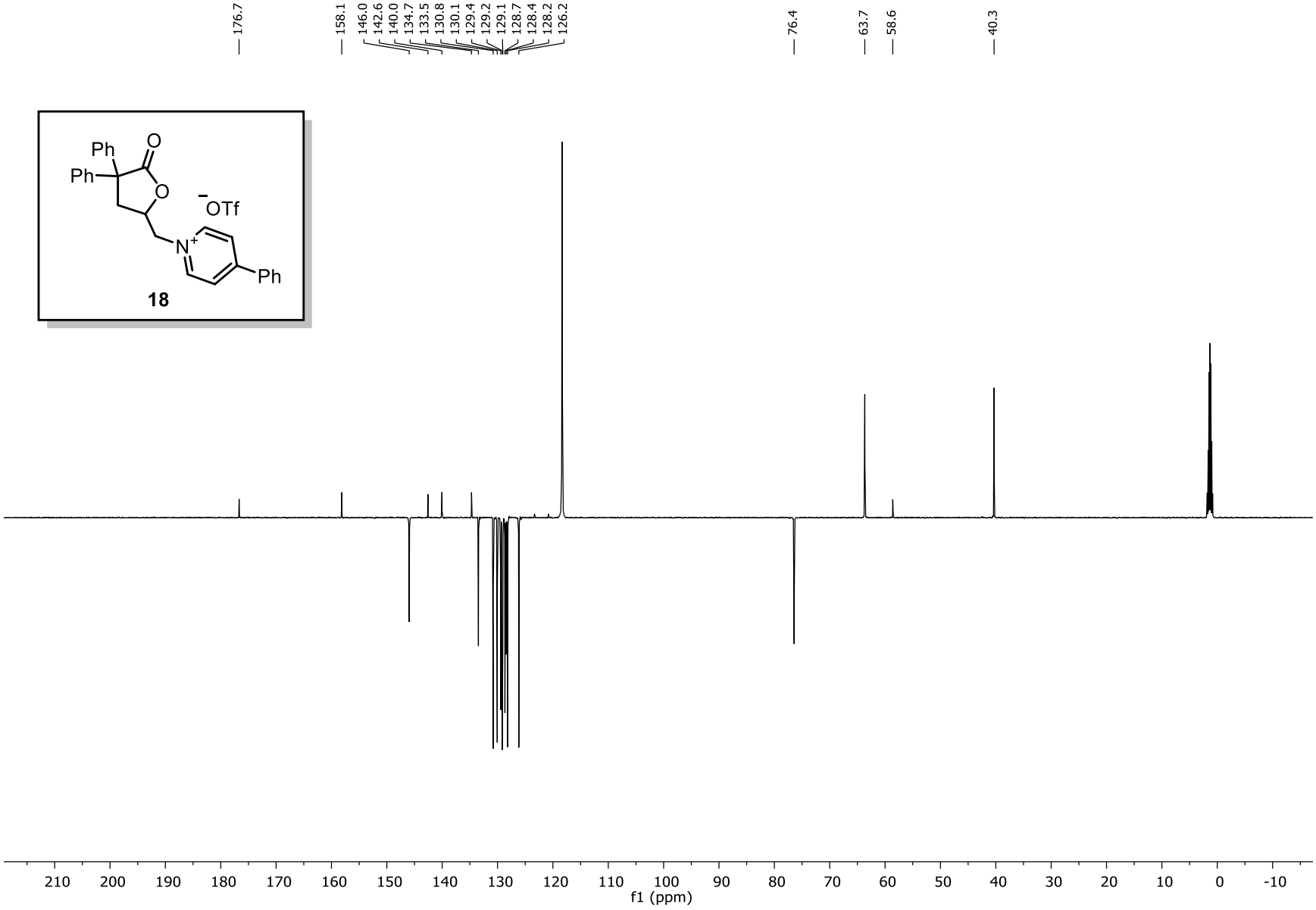

*H2O
Ph
Ph
O
O
OTf
N+
EtO
16
0.97
1.00
1.99
10.82
1.02
1.05
3.09
1.03
1.04
3.06
f1 (ppm)

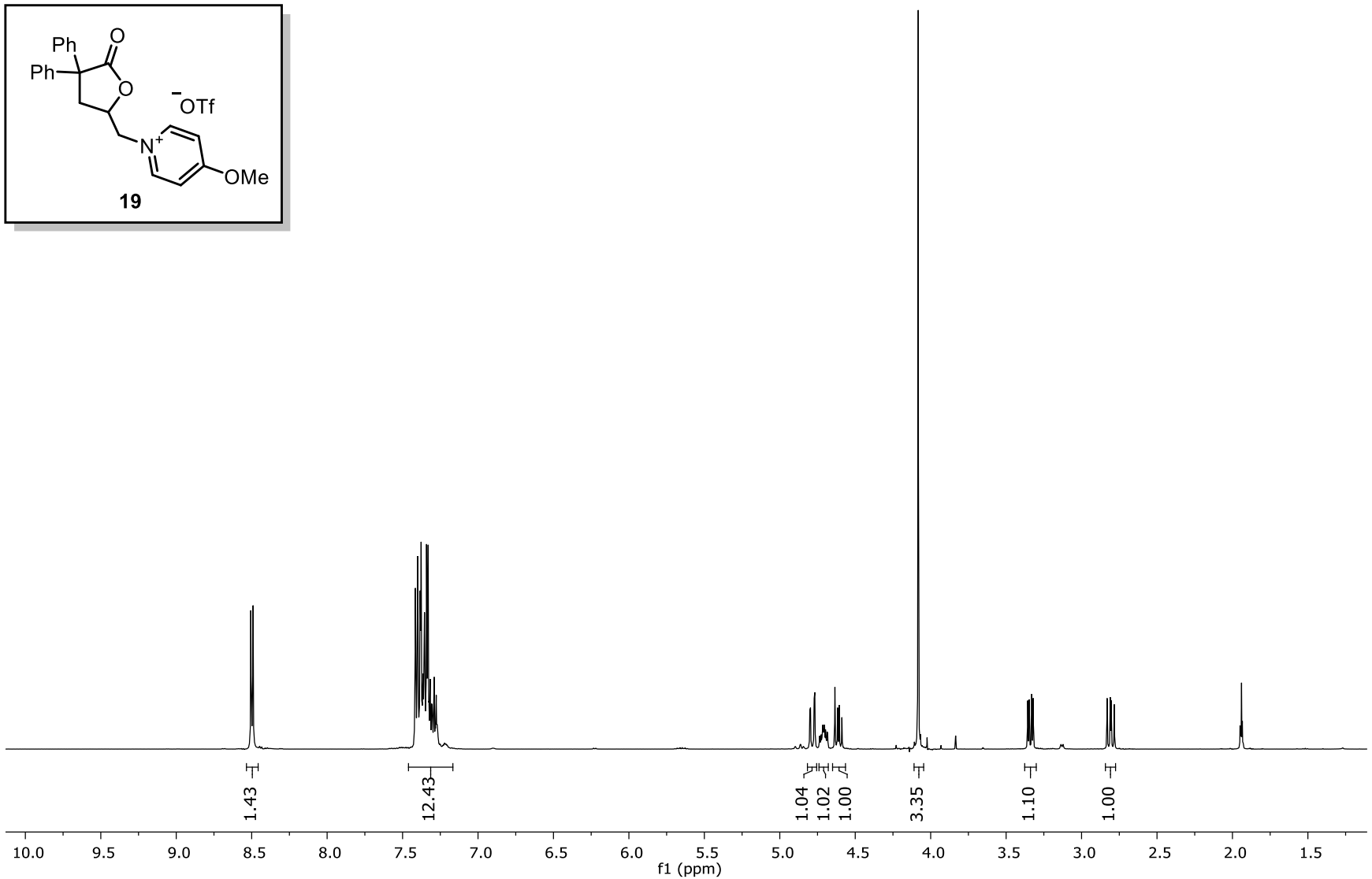

176.8
149.7
144.1
142.6
140.3
130.0
129.4
129.0
128.6
128.4
128.1
119.6
113.1
74.7
70.7
57.5
40.5
14.2
Ph
Ph
O
O
OTf
N+
EtO
16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

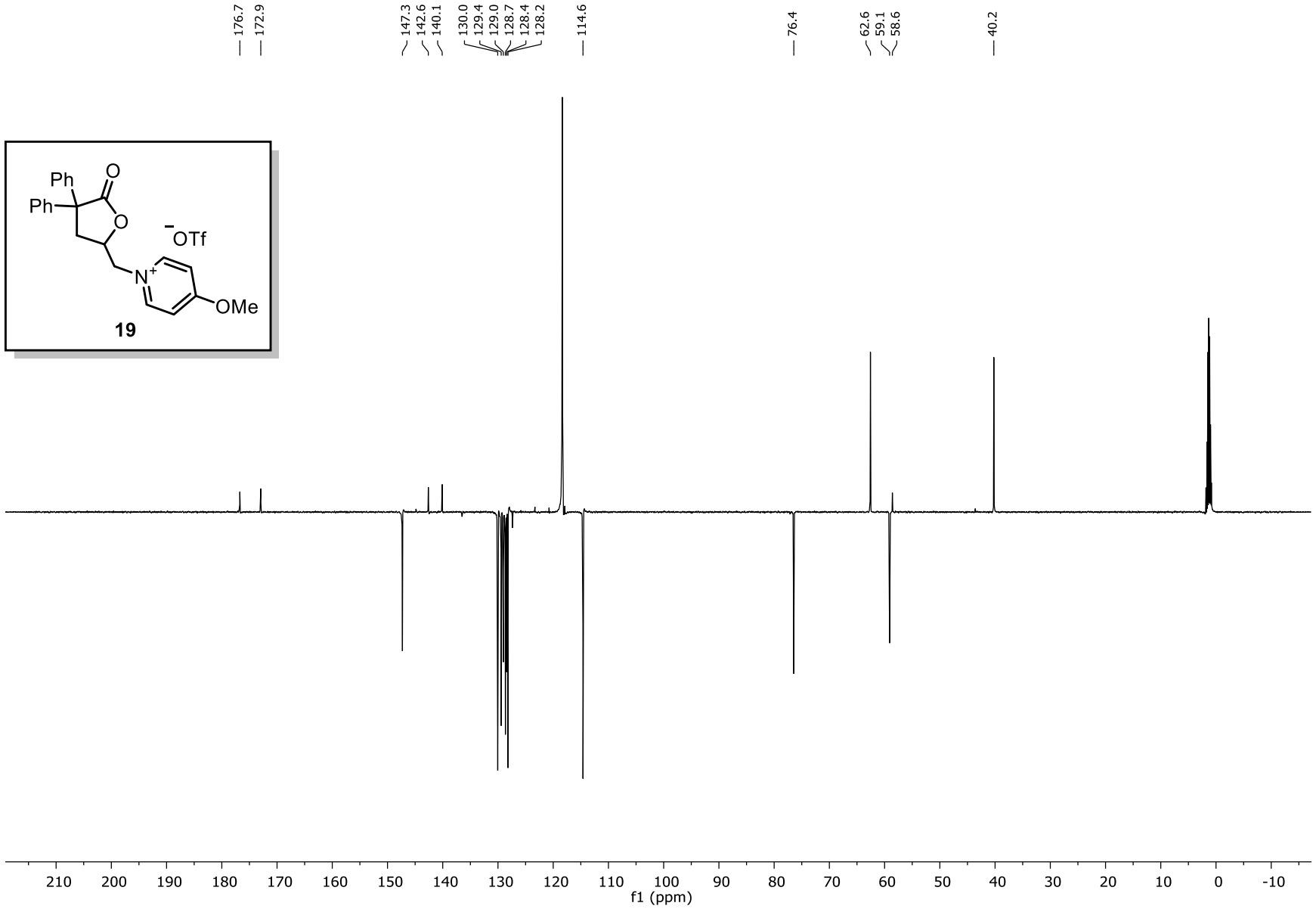

Ph
Ph
O
O
Me
N+
OTf
Me
17
*EtOAc
*
*
*
1.00
2.07
11.80
0.99
0.99
1.00
1.01
1.13
6.04
f1 (ppm)

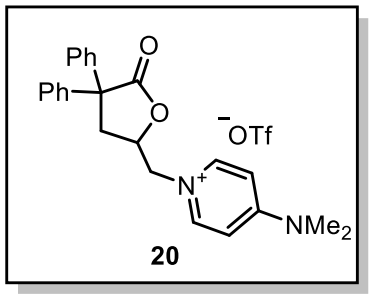

177.4
165.6
157.6
147.1
142.8
130.0
129.3
128.8
128.6
128.3
128.1
75.3
67.1
54.6
38.8
21.9
1.8
Ph
Ph
O
O
Me
N+
−OTf
Me
17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.74 8.73 8.29 8.27 7.93 7.93 7.93 7.92 7.92 7.91 7.91 7.68 7.68 7.68 7.67 7.66 7.66 7.65 7.65 7.65 7.64 7.64 7.63 7.63 7.62 7.61 7.61 7.42 7.41 7.40 7.40 7.40 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.28 4.97 4.97 4.96 4.96 4.95 4.94 4.82 4.81 4.81 4.80 4.80 4.79 4.79 4.78 4.78 4.77 4.77 3.41 3.41 3.40 3.39 3.38 2.90 2.90 2.89 2.88 2.88 2.87 2.86 2.86
Ph
Ph
O
O
OTf
N+
Ph
18
1.63
1.57
2.02
3.10
9.67
1.03
2.01
0.97
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


176.7
158.1
146.0
142.6
140.0
134.7
133.5
130.8
130.1
129.4
129.2
129.1
128.7
128.4
128.2
126.2
76.4
63.7
58.6
40.3
Ph
Ph
O
O
OTf
N+
Ph
18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

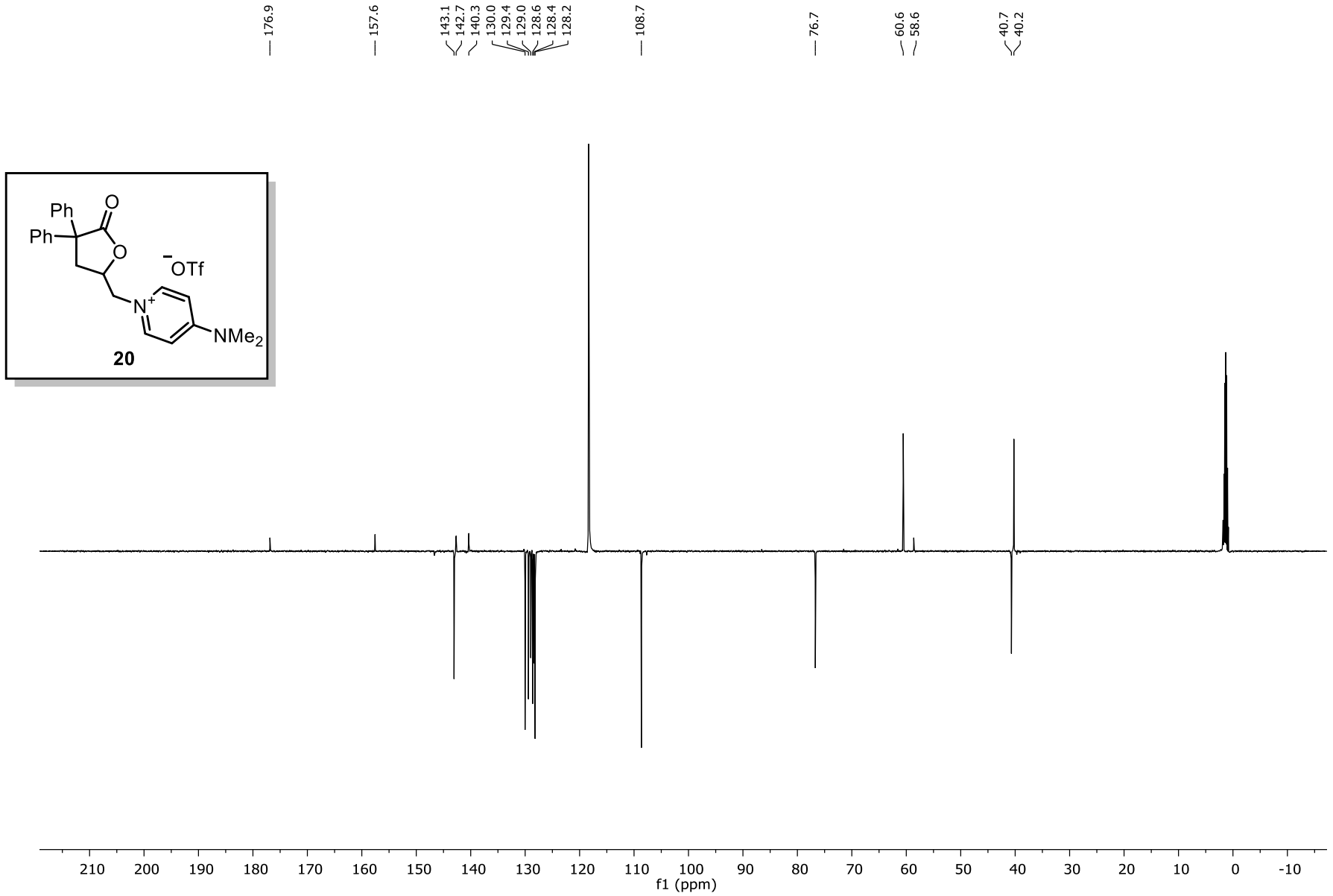

Ph
Ph
O
O
OTf
N+
OMe
19
1.43
12.43
1.04
1.02
1.00
3.35
1.10
1.00
f1 (ppm)

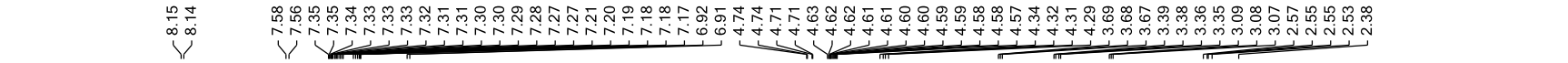

176.7
172.9
147.3
142.6
140.1
130.0
129.4
129.0
128.7
128.4
128.2
114.6
76.4
62.6
59.1
58.6
40.2
Ph
Ph
O
O
OTf
N+
OMe
19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

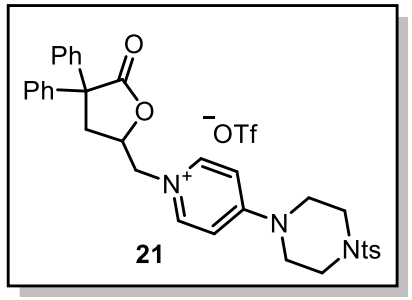

Ph
Ph
O
O
OTf
N+
NMe2

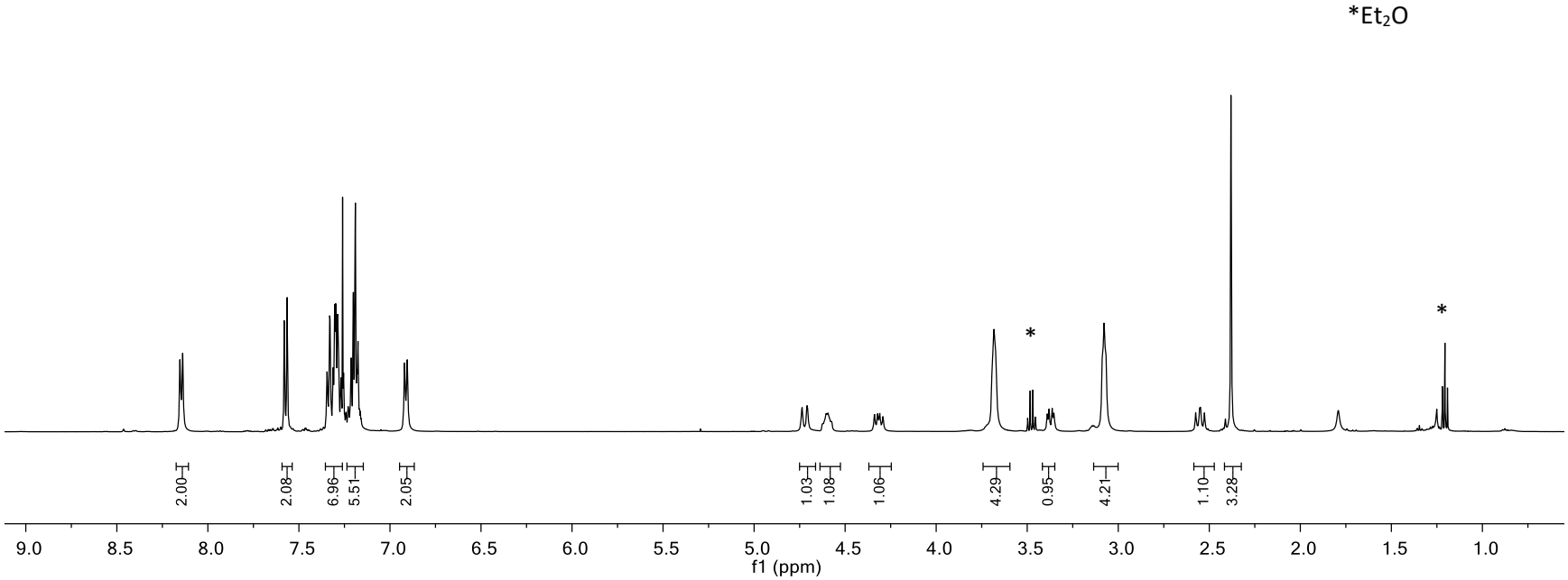
20

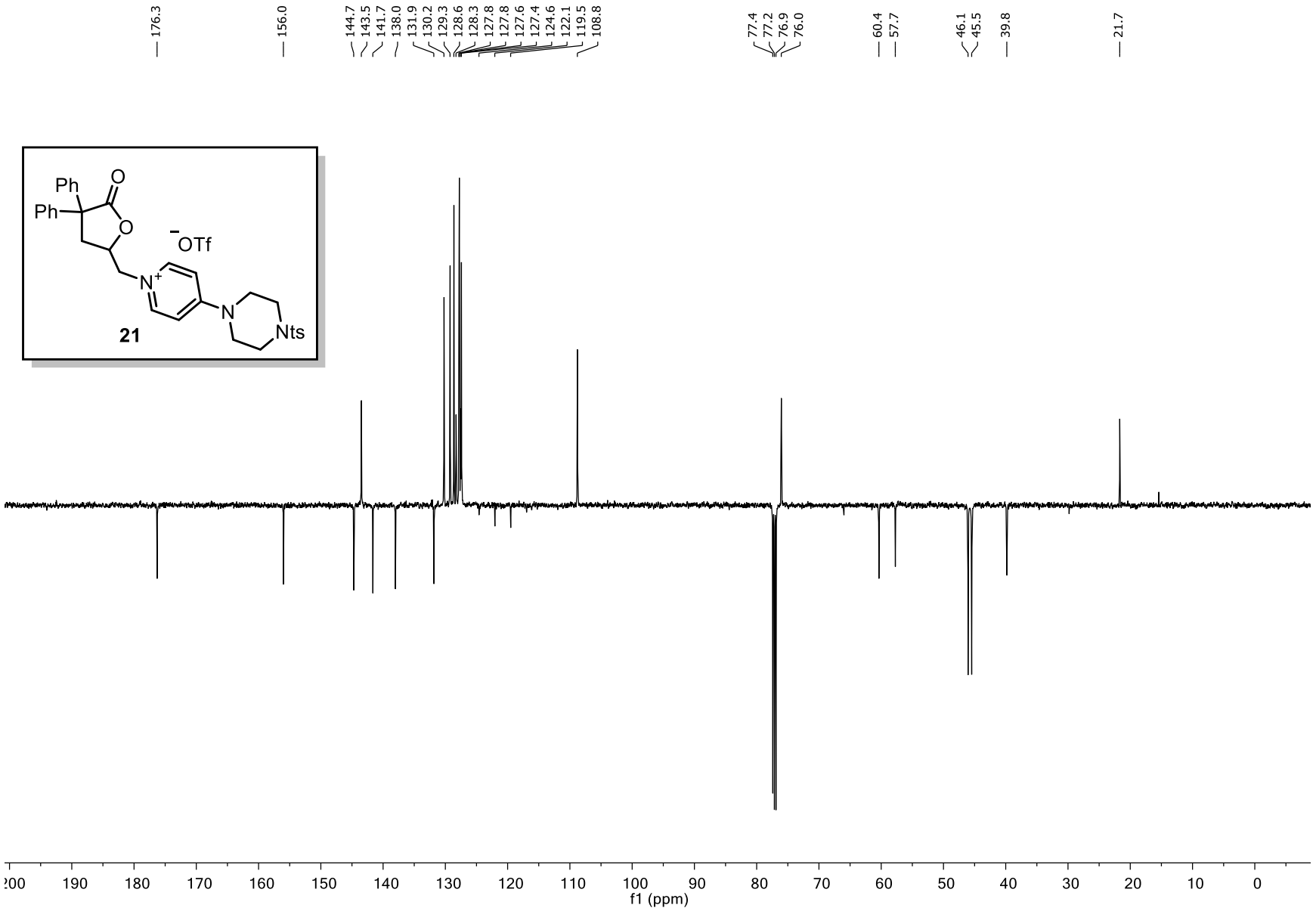
7.96 7.95 7.95 7.94 7.93 7.93 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.27 6.86 6.86 6.85 6.84 6.84 6.83 4.66 4.66 4.65 4.65 4.64 4.64 4.64 4.64 4.63 4.63 4.63 4.62 4.62 4.62 4.61 4.52 4.51 4.48 4.48 4.34 4.32 4.31 4.29 3.30 3.29 3.27 3.25 3.18 3.17 2.78 2.75 2.75 2.72
1.98
10.39
1.98
1.44
1.13
1.07
1.11
6.09
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

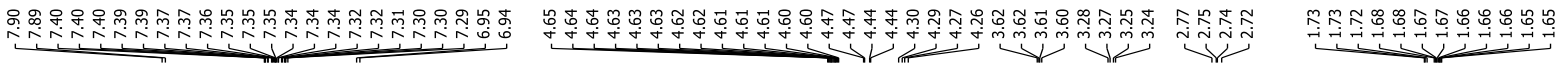

176.9
157.6
143.1
142.7
140.3
130.0
129.4
129.0
128.6
128.4
128.2
108.7
76.7
60.6
58.6
40.7
40.2
Ph
Ph
O
O
OTf
N+
NMe2
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

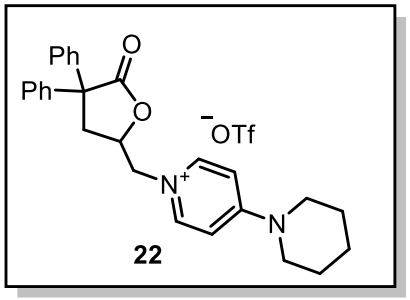

8.15
8.14
7.58
7.56
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.21
7.20
7.19
7.18
7.18
7.17
6.92
6.91
4.74
4.74
4.71
4.71
4.63
4.62
4.62
4.61
4.61
4.60
4.60
4.59
4.59
4.58
4.58
4.57
4.34
4.32
4.31
4.29
3.69
3.68
3.67
3.39
3.38
3.36
3.35
3.09
3.08
3.07
2.57
2.55
2.55
2.53
2.38


Ph
Ph
O
O
OTf
N+
N
Nts
21

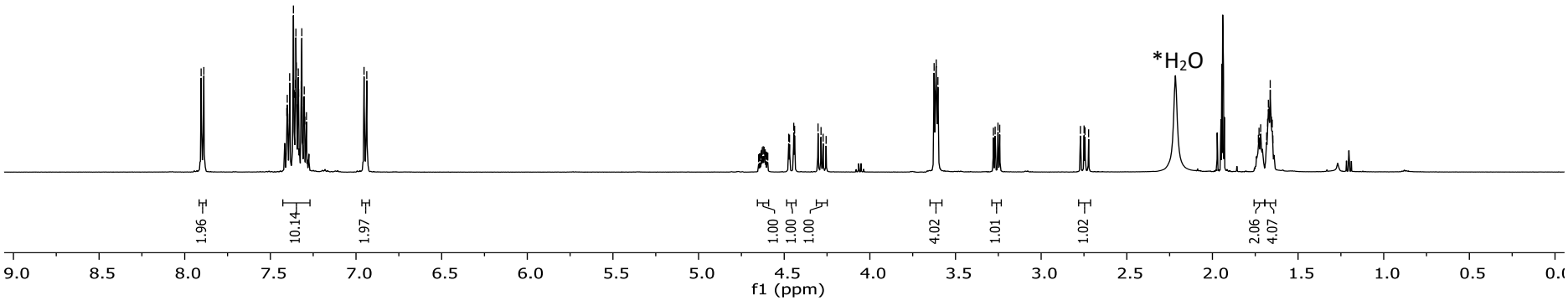

*Et2O
*
*
2.00
2.08
6.96
5.51
2.05
1.03
1.08
1.06
4.29
0.95
4.21
1.10
3.28
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

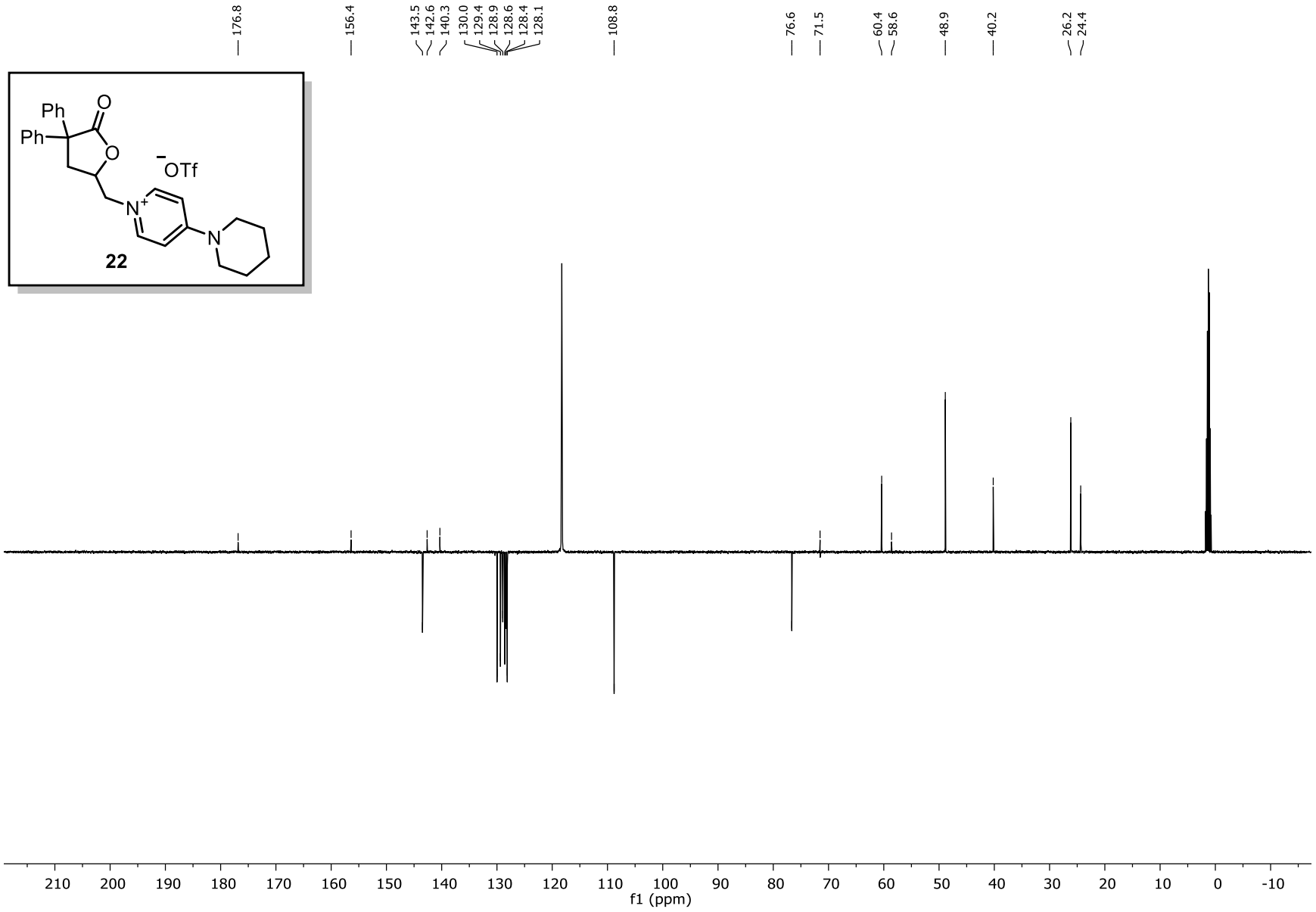

176.3
156.0
144.7
143.5
141.7
138.0
131.9
130.2
129.3
128.6
128.3
127.8
127.8
127.6
127.4
124.6
122.1
119.5
108.8
77.4
77.2
76.9
76.0
60.4
57.7
46.1
45.5
39.8
21.7
Ph
Ph
O
O
OTf
N+
N
Nts
21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

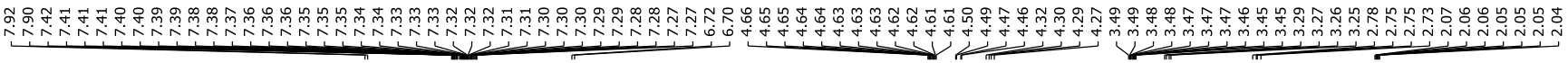

7.90 7.89 7.40 7.40 7.40 7.39 7.39 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.32 7.32 7.31 7.30 7.30 7.29 6.95 6.94
4.65 4.64 4.64 4.63 4.63 4.63 4.62 4.62 4.61 4.61 4.61 4.60 4.60 4.47 4.47 4.44 4.44 4.30 4.29 4.27 4.26
3.62 3.62 3.61 3.60 3.28 3.27 3.25 3.24
2.77 2.75 2.74 2.72
1.73 1.73 1.72 1.68 1.68 1.67 1.67 1.66 1.66 1.66 1.65 1.65

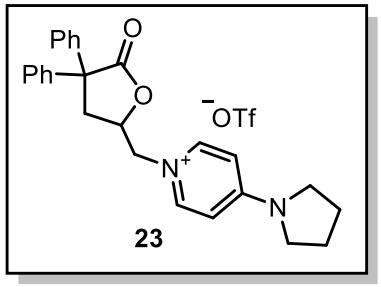

Ph
Ph
O
O
OTf
N+
N

22

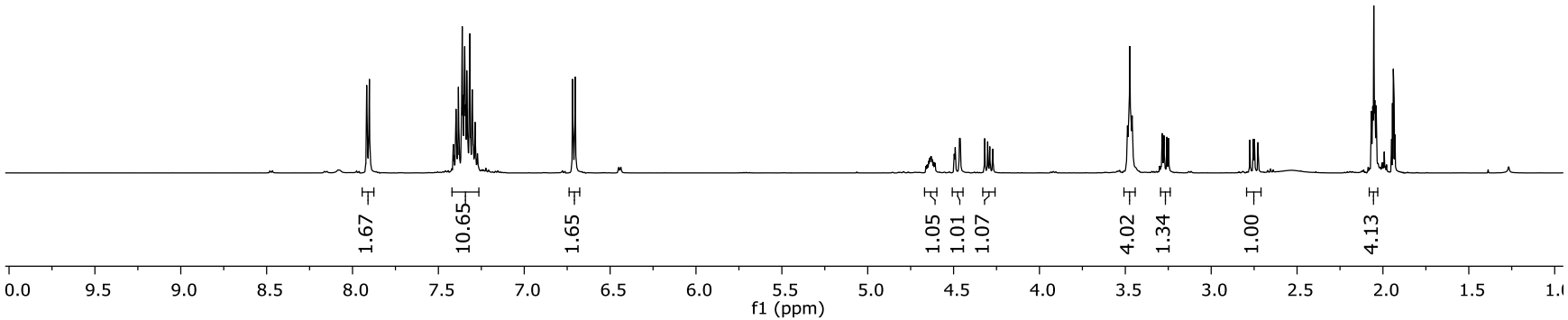

*H2O
1.96
10.14
1.97
1.00
1.00
1.00
4.02
1.01
1.02
2.06
4.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

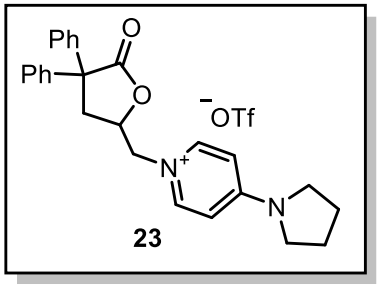

176.8
156.4
143.5
142.6
140.3
130.0
129.4
128.9
128.6
128.4
128.1
108.8
76.6
71.5
60.4
58.6
48.9
40.2
26.2
24.4
Ph
Ph
O
O
OTf
N+
N
22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.92 7.90 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 6.72 6.70
4.66 4.65 4.65 4.64 4.64 4.63 4.63 4.63 4.62 4.62 4.61 4.61 4.50 4.49 4.47 4.46 4.32 4.30 4.29 4.27
3.49 3.49 3.48 3.48 3.47 3.47 3.47 3.46 3.45 3.45 3.29 3.27 3.26 3.25 2.78 2.75 2.75 2.73 2.07 2.06 2.06 2.05 2.05 2.05 2.04


Ph
Ph
O
O
OTf
N+
N

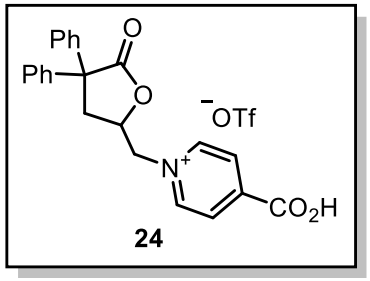
23


1.67
10.65
1.65
1.05
1.01
1.07
4.02
1.34
1.00
4.13
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

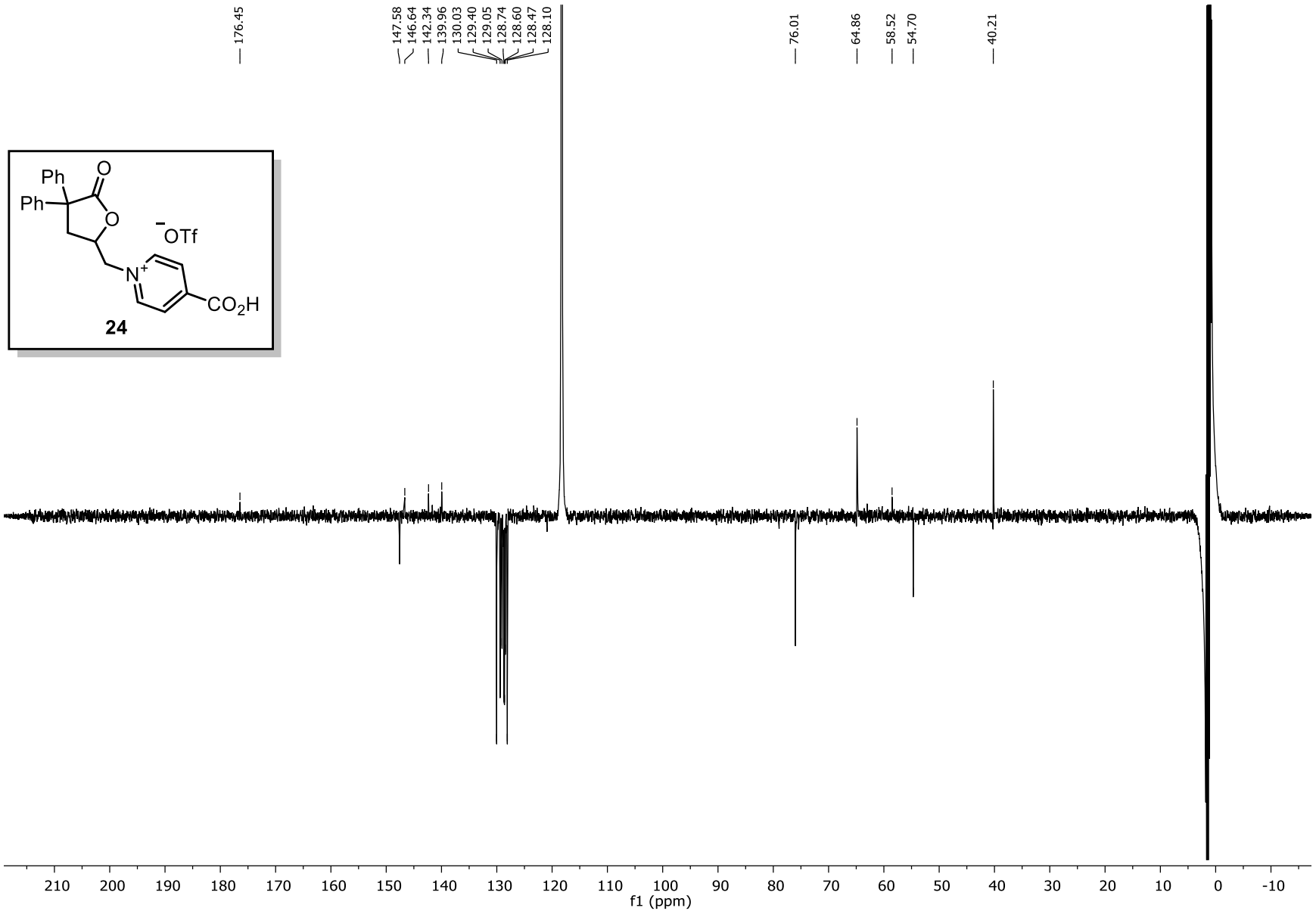

Ph
Ph
O
O
OTf
N+
N

23

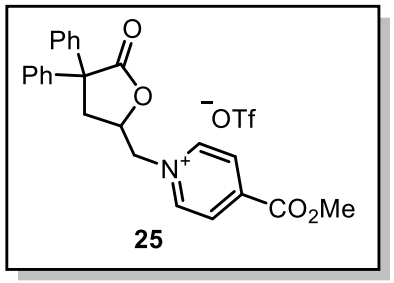
176.9
154.7
143.0
142.7
140.4
130.0
129.4
129.0
128.6
128.4
128.2
109.2
76.7
60.6
58.6
49.6
47.9
40.2
25.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



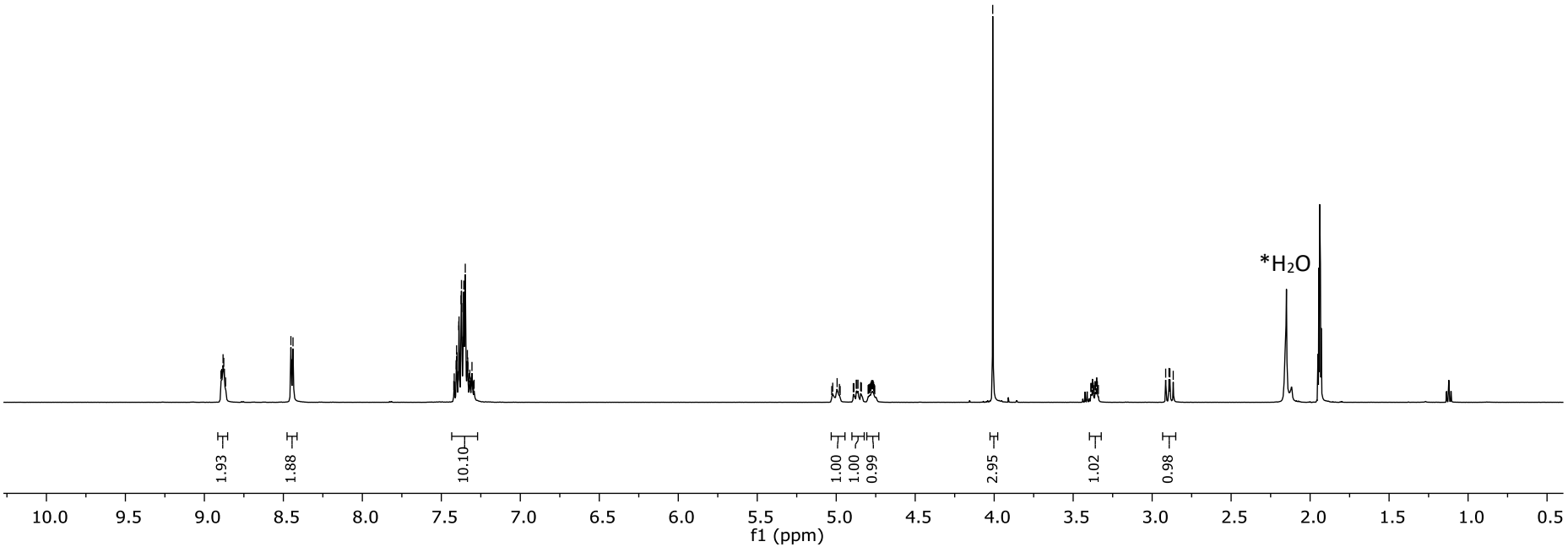
24

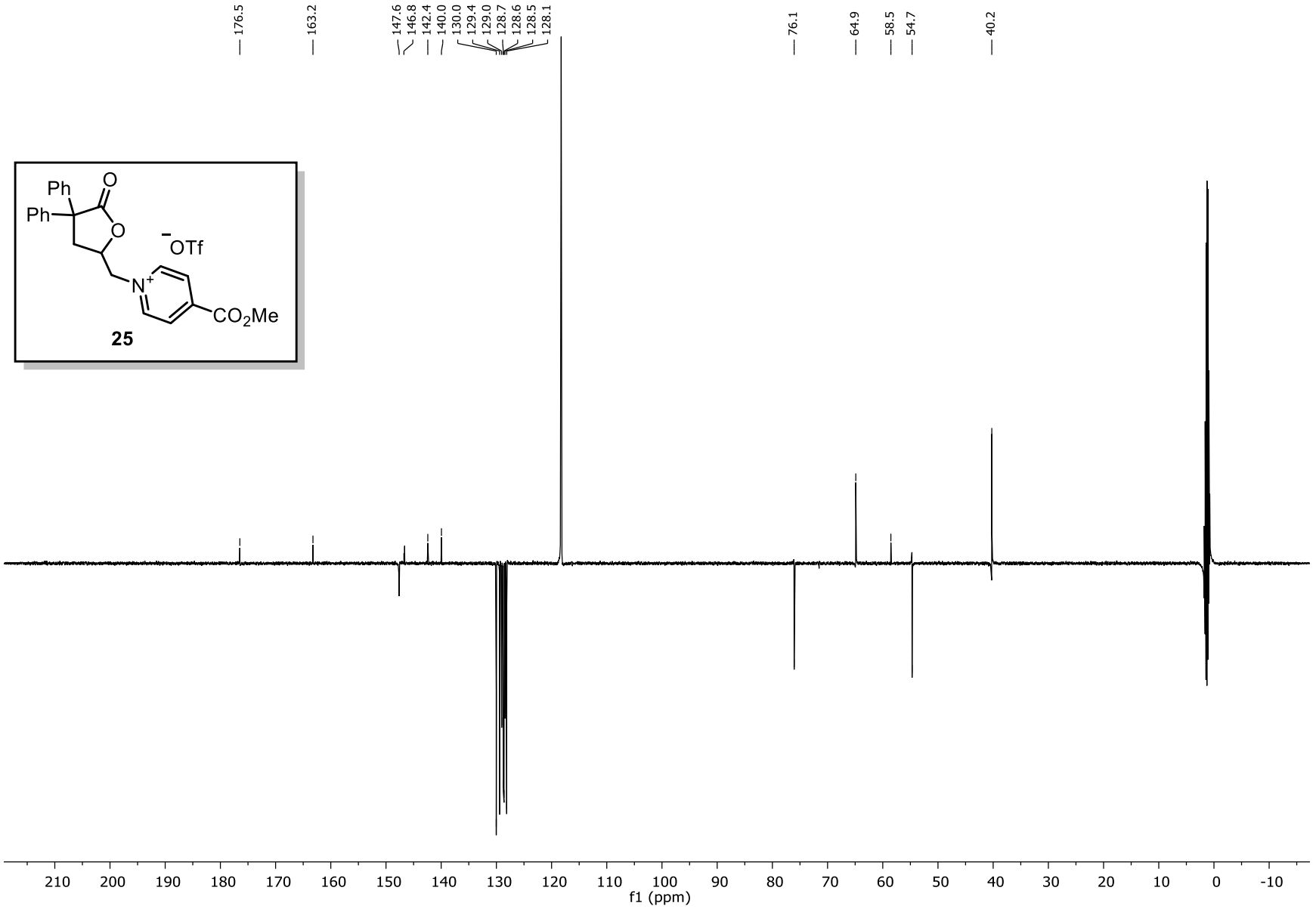

176.45
147.58
146.64
142.34
139.96
130.03
129.40
129.05
128.74
128.60
128.47
128.10
76.01
64.86
58.52
54.70
40.21
Ph
Ph
O
O
OTf
N+
CO2H
24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

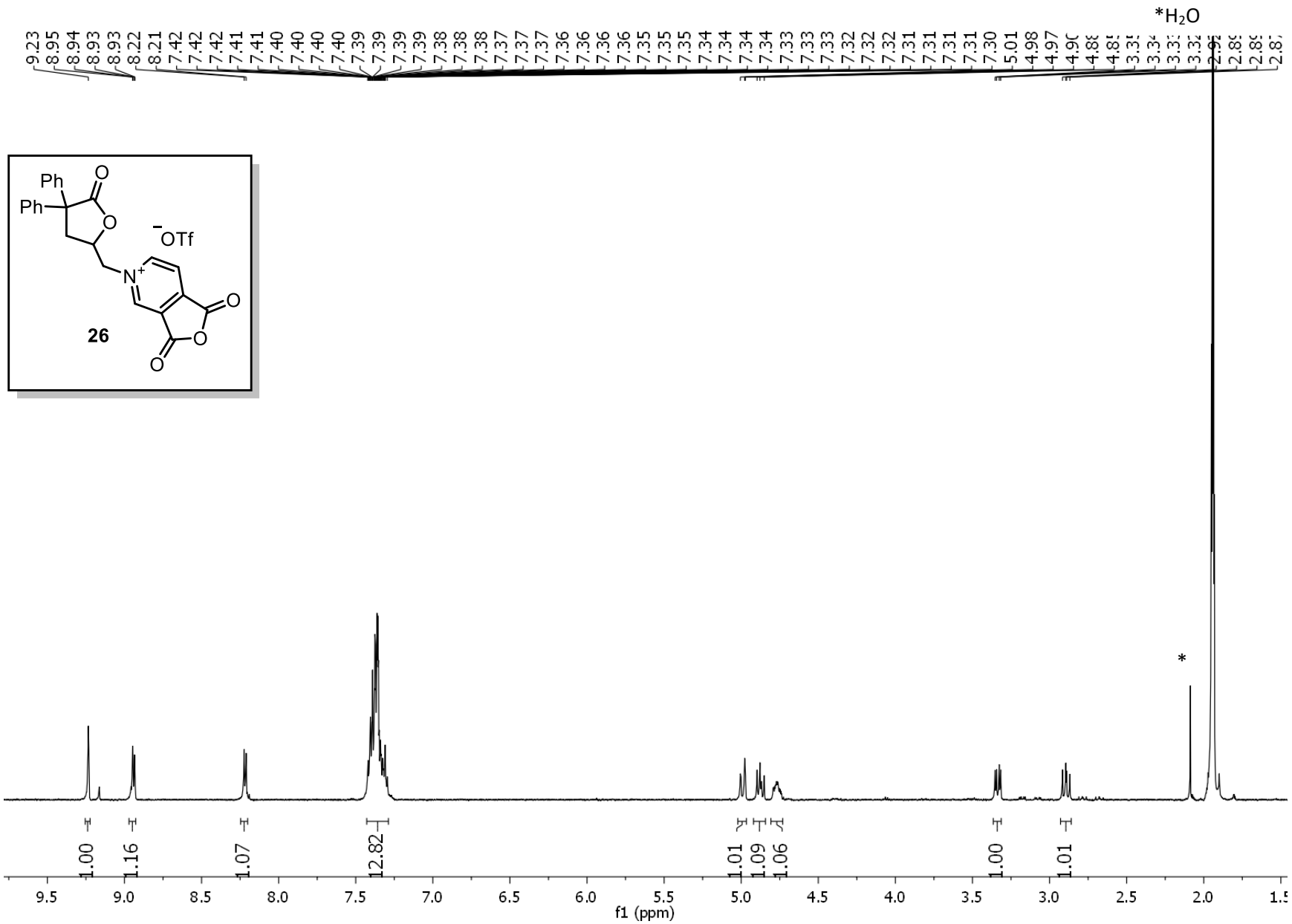

8.90 8.89 8.88 8.88 8.87 8.87 8.45 8.45 8.44 8.44
7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 5.02 4.99 4.98 4.89 4.89 4.87 4.87 4.86 4.85 4.84 4.80 4.80 4.79 4.79 4.79 4.78 4.78 4.77 4.77 4.77 4.76 4.76 4.01 3.39 3.38 3.38 3.38 3.37 3.36 3.36 3.35 3.35 3.35 3.34 2.91 2.89 2.89

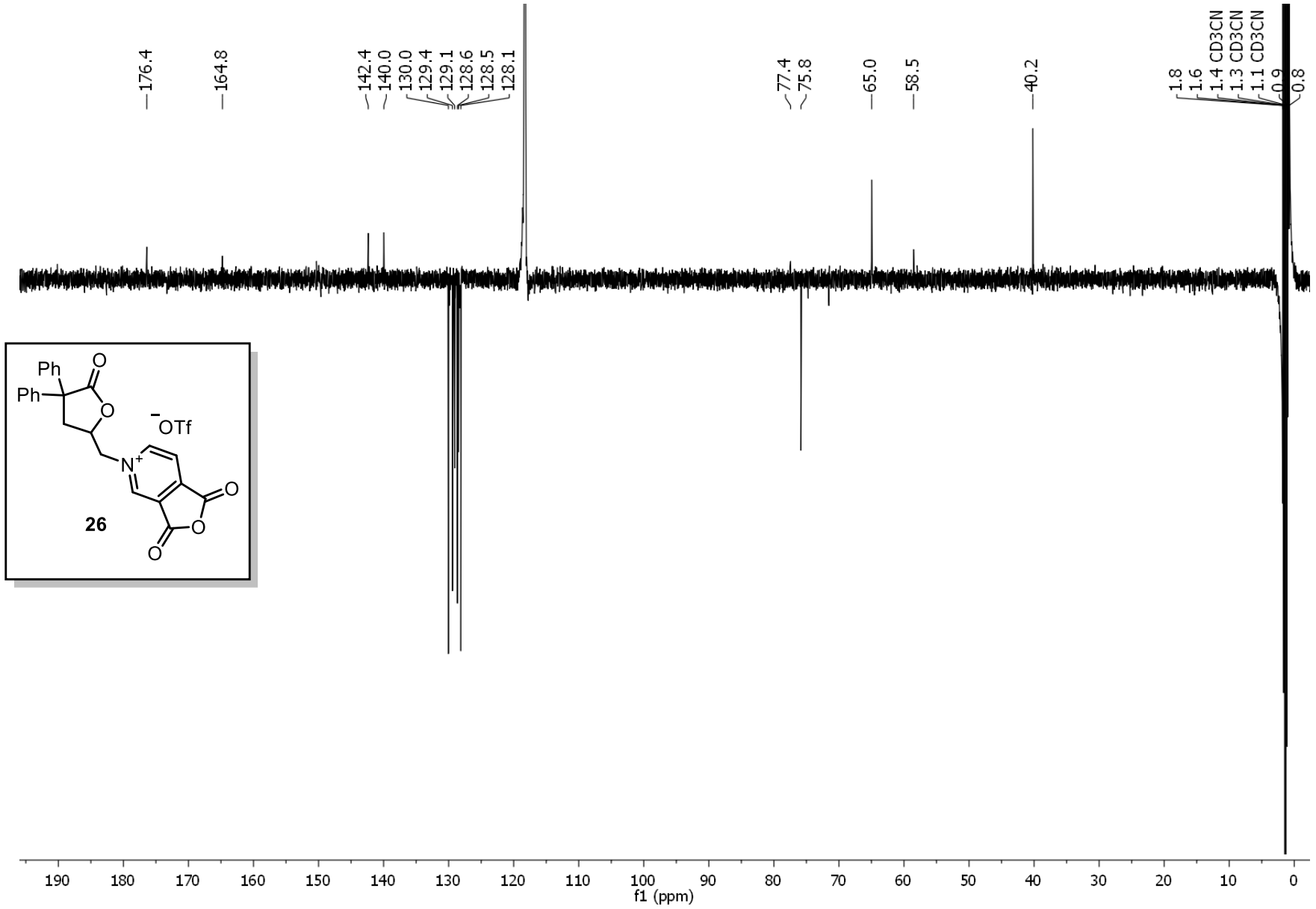

Ph
Ph
O
O
OTf
N+
CO2Me

25

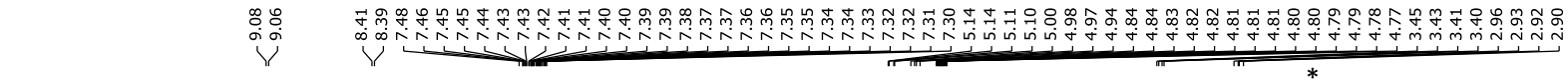

*H2O
1.93
1.88
10.10
1.00
1.00
0.99
2.95
1.02
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

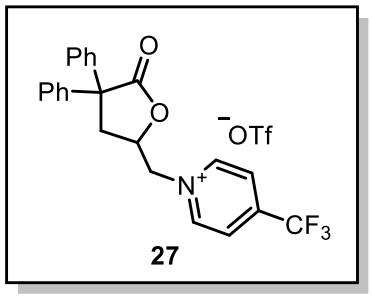

176.5
163.2
147.6
146.8
142.4
140.0
130.0
129.4
129.0
128.7
128.6
128.5
128.1
76.1
64.9
58.5
54.7
40.2
Ph
Ph
O
O
OTf
N+
CO2Me
25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


*H2O
Ph
Ph
O
O
OTf
N+
O
O
O
26
*
1.00
1.16
1.07
12.82
1.01
1.09
1.06
1.00
1.01
f1 (ppm)

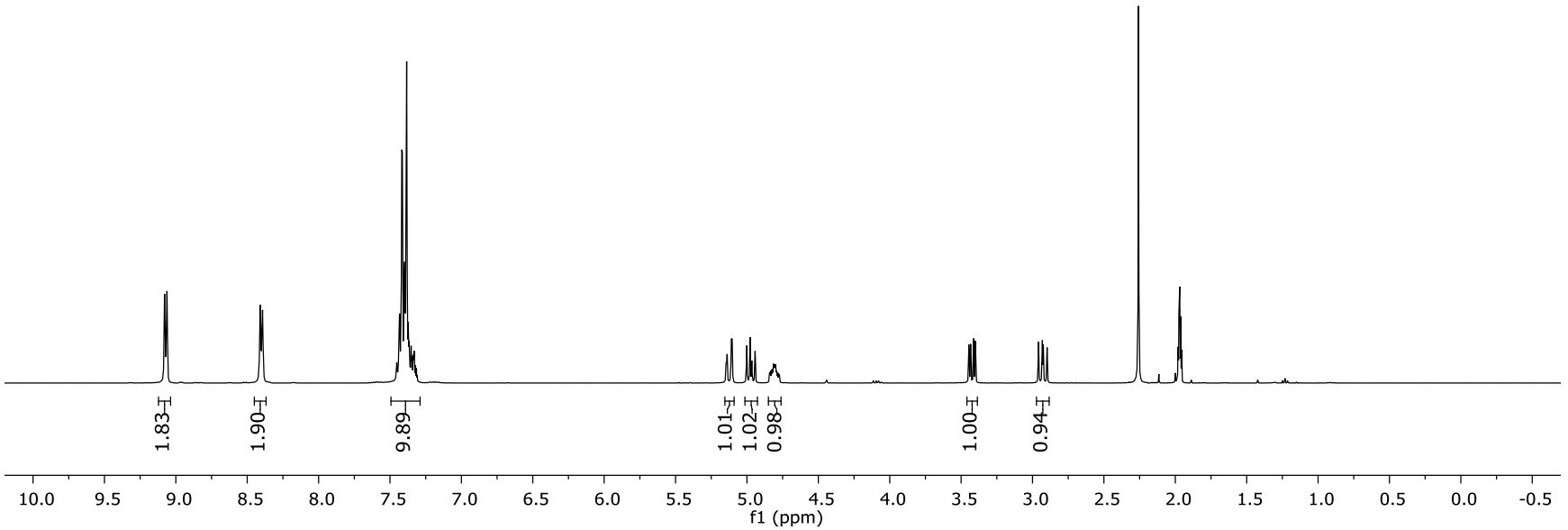

176.4
164.8
142.4
140.0
130.0
129.4
129.1
128.6
128.5
128.1
77.4
75.8
65.0
58.5
40.2
1.8
1.6
1.4 CD3CN
1.3 CD3CN
1.1 CD3CN
0.9
0.8
Ph
Ph
O
O
OTf
N+
O
O
O
26
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

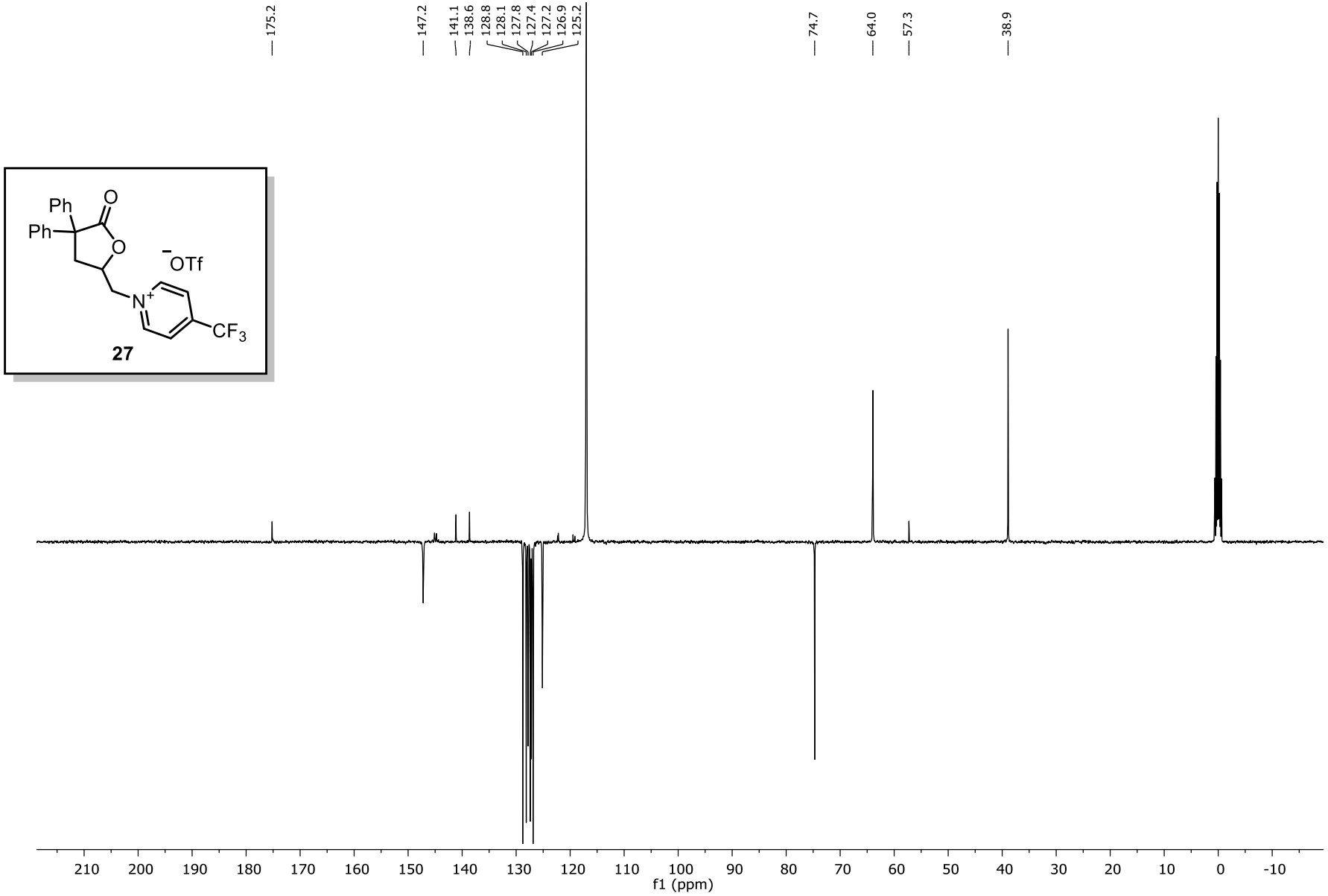
*H_2O

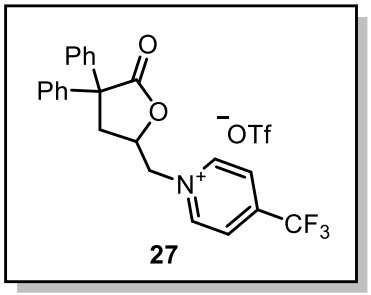

9.08
9.06
8.41
8.39
7.48
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
5.14
5.14
5.11
5.10
5.00
4.98
4.97
4.94
4.84
4.84
4.83
4.82
4.82
4.81
4.81
4.81
4.80
4.80
4.79
4.79
4.78
4.77
3.45
3.43
3.41
3.40
2.96
2.93
2.92
2.90
*


Ph
Ph
O
O
OTf
N+
CF3

27

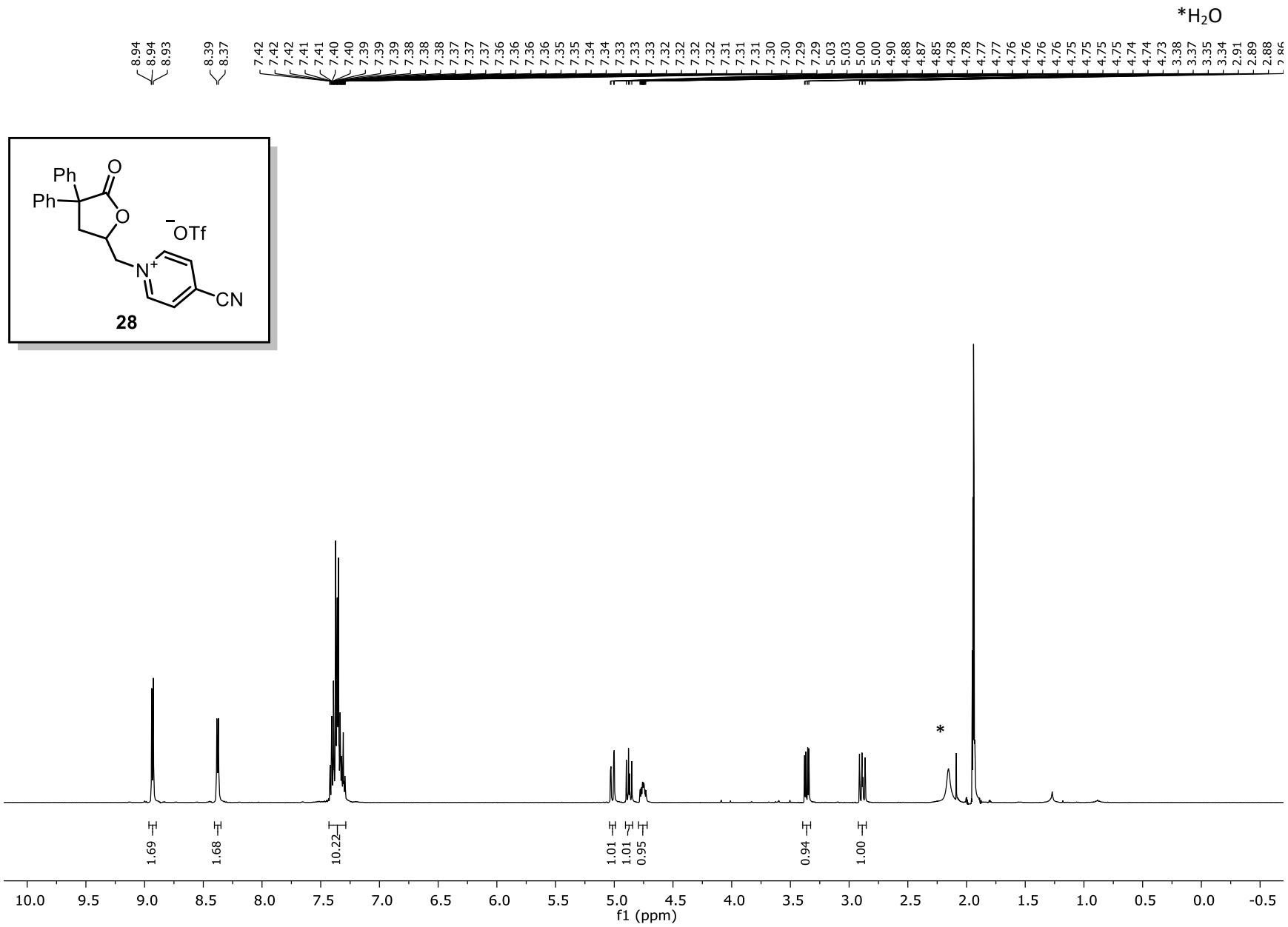

1.83
1.90
9.89
1.01
1.02
0.98
1.00
0.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

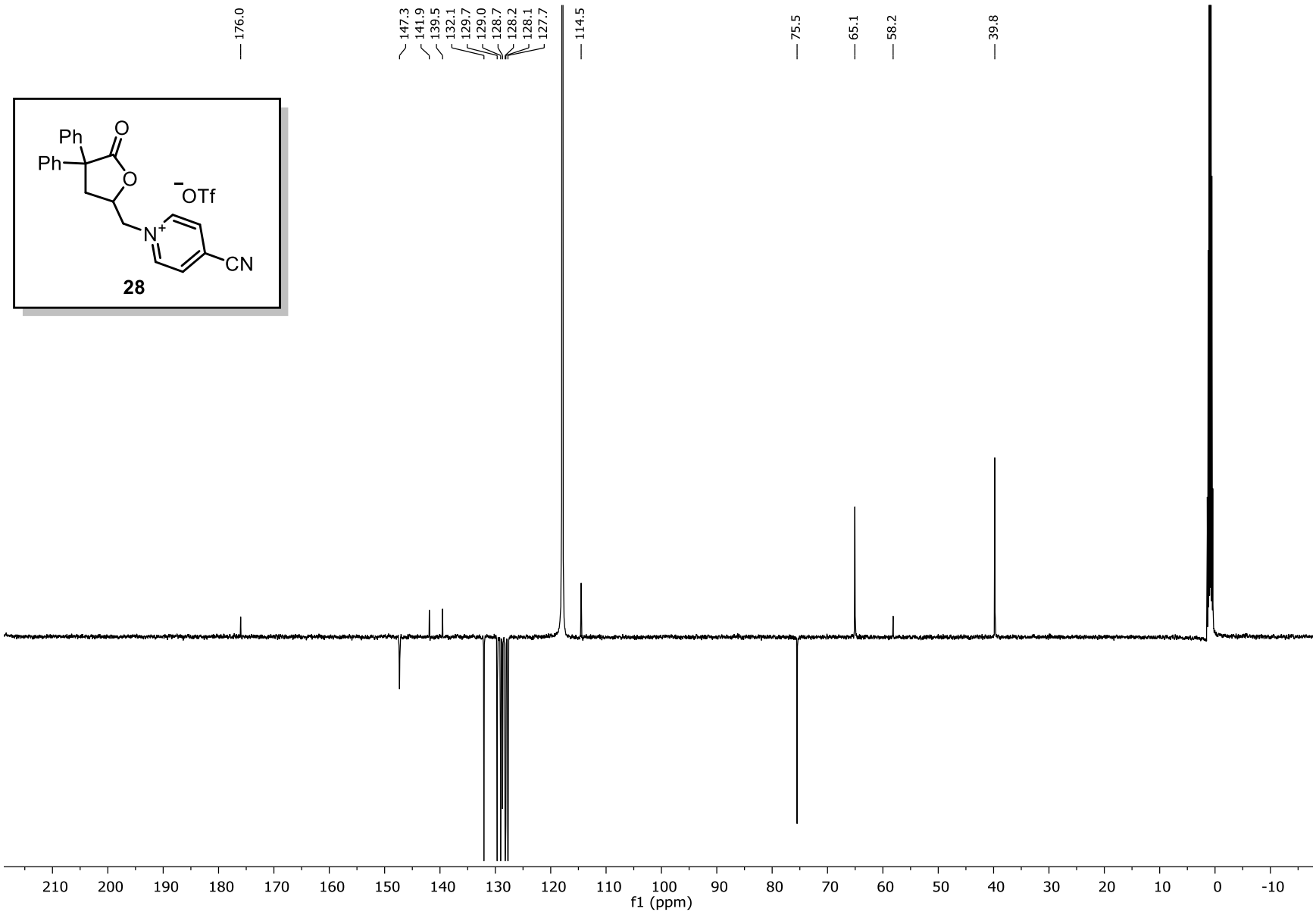

175.2
147.2
141.1
138.6
128.8
128.1
127.8
127.4
127.2
126.9
125.2
74.7
64.0
57.3
38.9
Ph
Ph
O
O
OTf
N+
CF3
27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

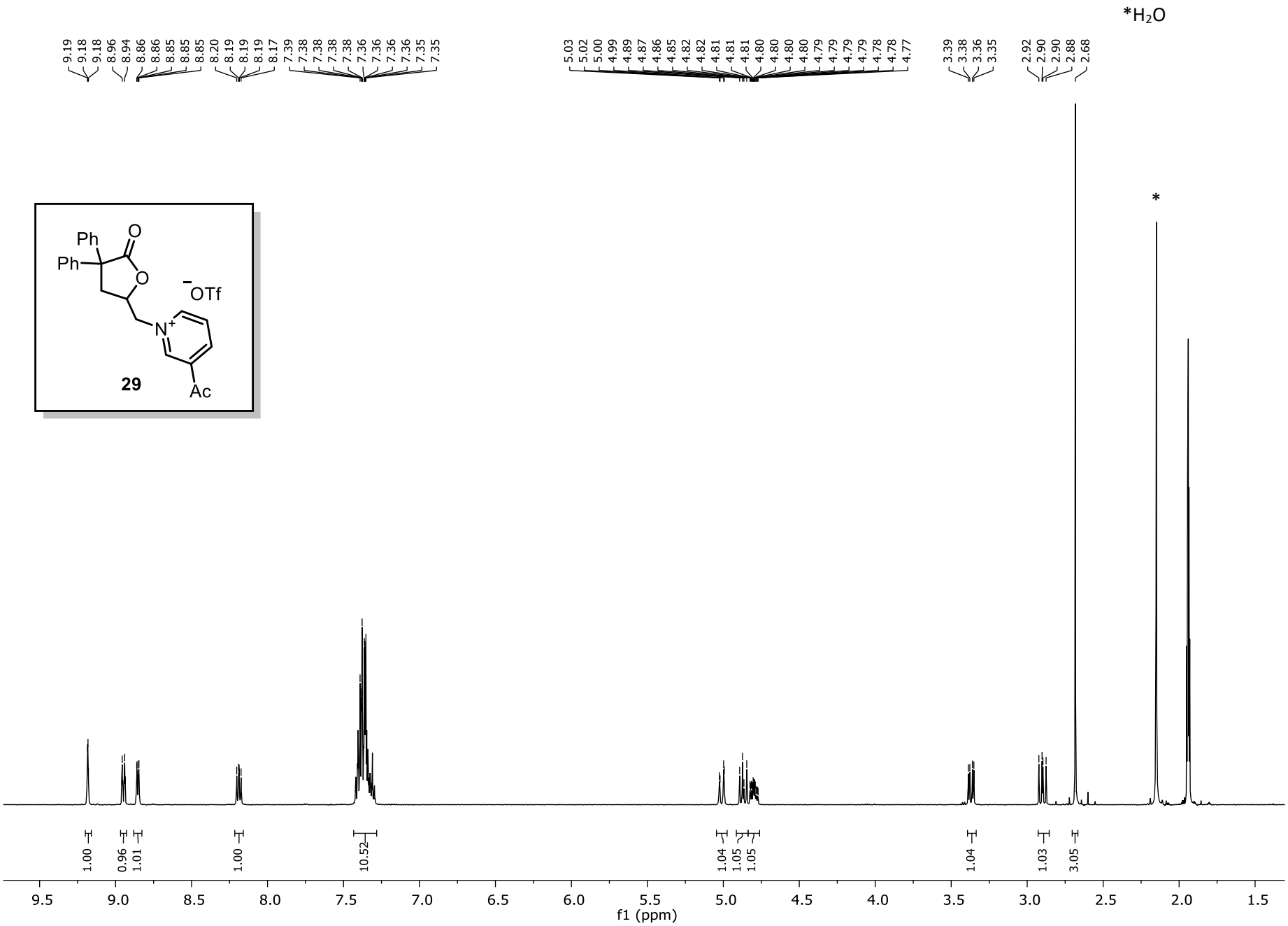

Ph
Ph
O
O
OTf
N+
CF3

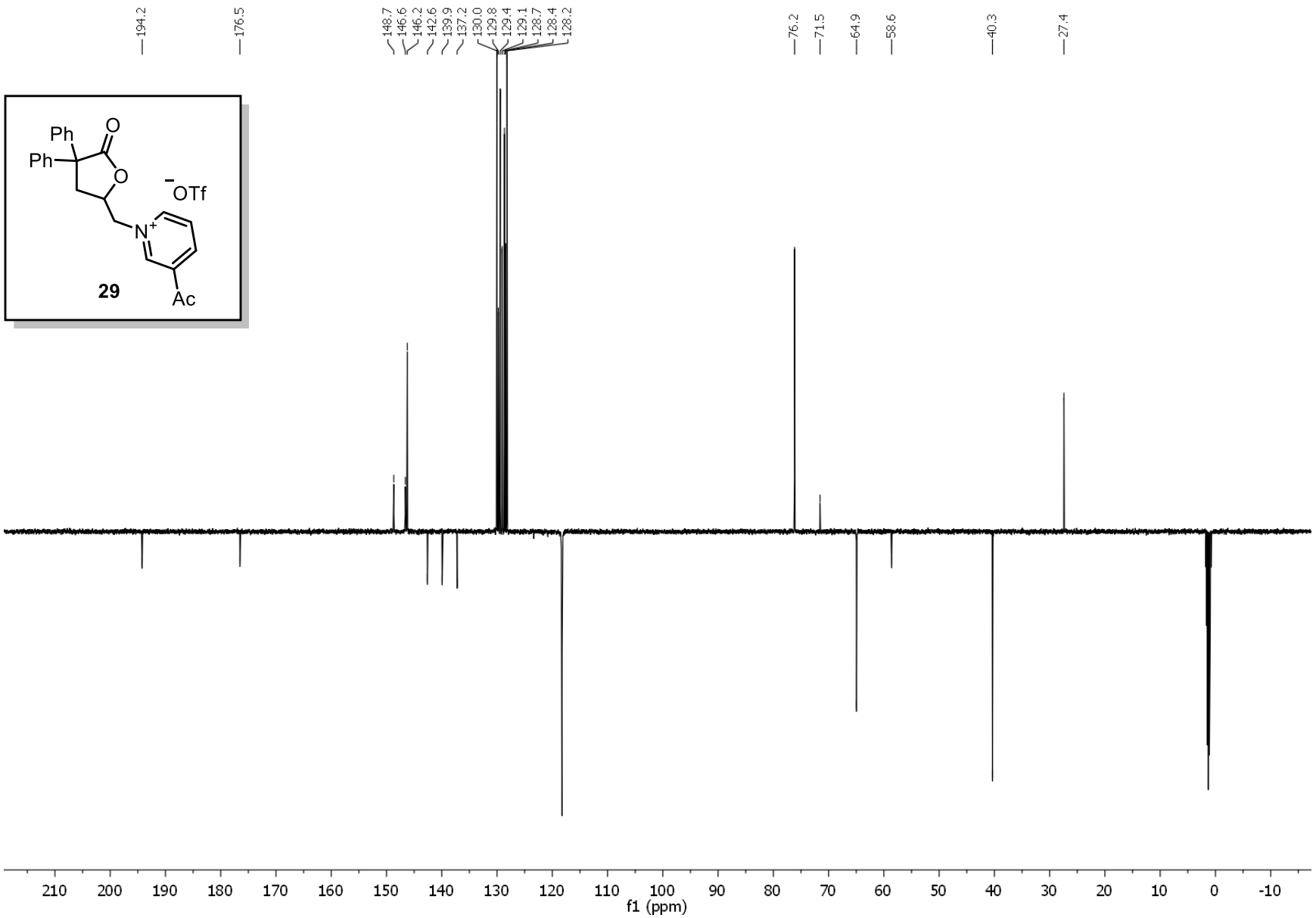
27

-66.01
-79.36
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

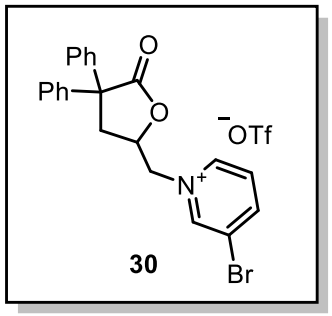

*H2O
8.94 8.94 8.93 8.39 8.37
7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 5.03 5.03 5.00 5.00 4.90 4.88 4.87 4.85 4.78 4.78 4.77 4.77 4.76 4.76 4.76 4.76 4.75 4.75 4.75 4.74 4.74 4.73 3.38 3.37 3.35 3.34 2.91 2.89 2.88
Ph
Ph
O
O
OTf
N+
CN
28
*
1.69
1.68
10.22
1.01
1.01
0.95
0.94
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


176.0
147.3
141.9
139.5
132.1
129.7
129.0
128.7
128.2
128.1
127.7
114.5
75.5
65.1
58.2
39.8
Ph
Ph
O
O
OTf
N+
CN
28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

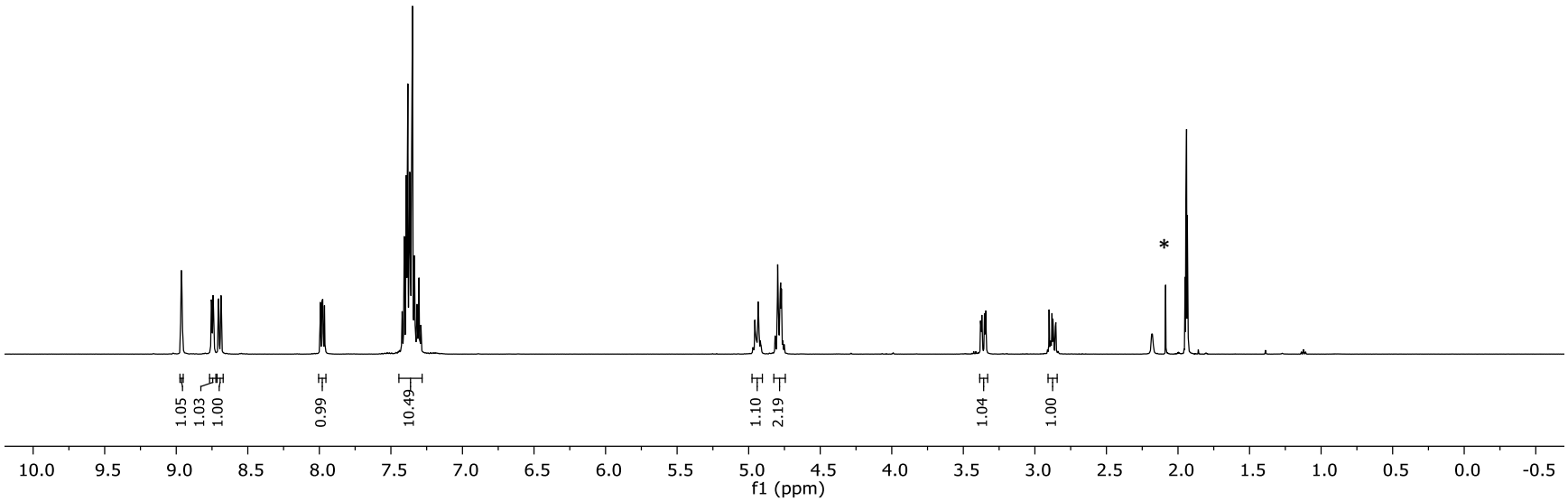

*H2O
9.19
9.18
9.18
8.96
8.94
8.86
8.86
8.85
8.85
8.85
8.20
8.19
8.19
8.19
8.17
7.39
7.38
7.38
7.38
7.38
7.36
7.36
7.36
7.36
7.35
7.35
5.03
5.02
5.00
4.99
4.89
4.87
4.86
4.85
4.82
4.82
4.81
4.81
4.81
4.80
4.80
4.80
4.80
4.79
4.79
4.79
4.79
4.78
4.78
4.77
3.39
3.38
3.36
3.35
2.92
2.90
2.90
2.88
2.68
*
Ph
Ph
O
O
OTf
N+
Ac
29
1.00
0.96
1.01
1.00
10.52
1.04
1.05
1.05
1.04
1.03
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

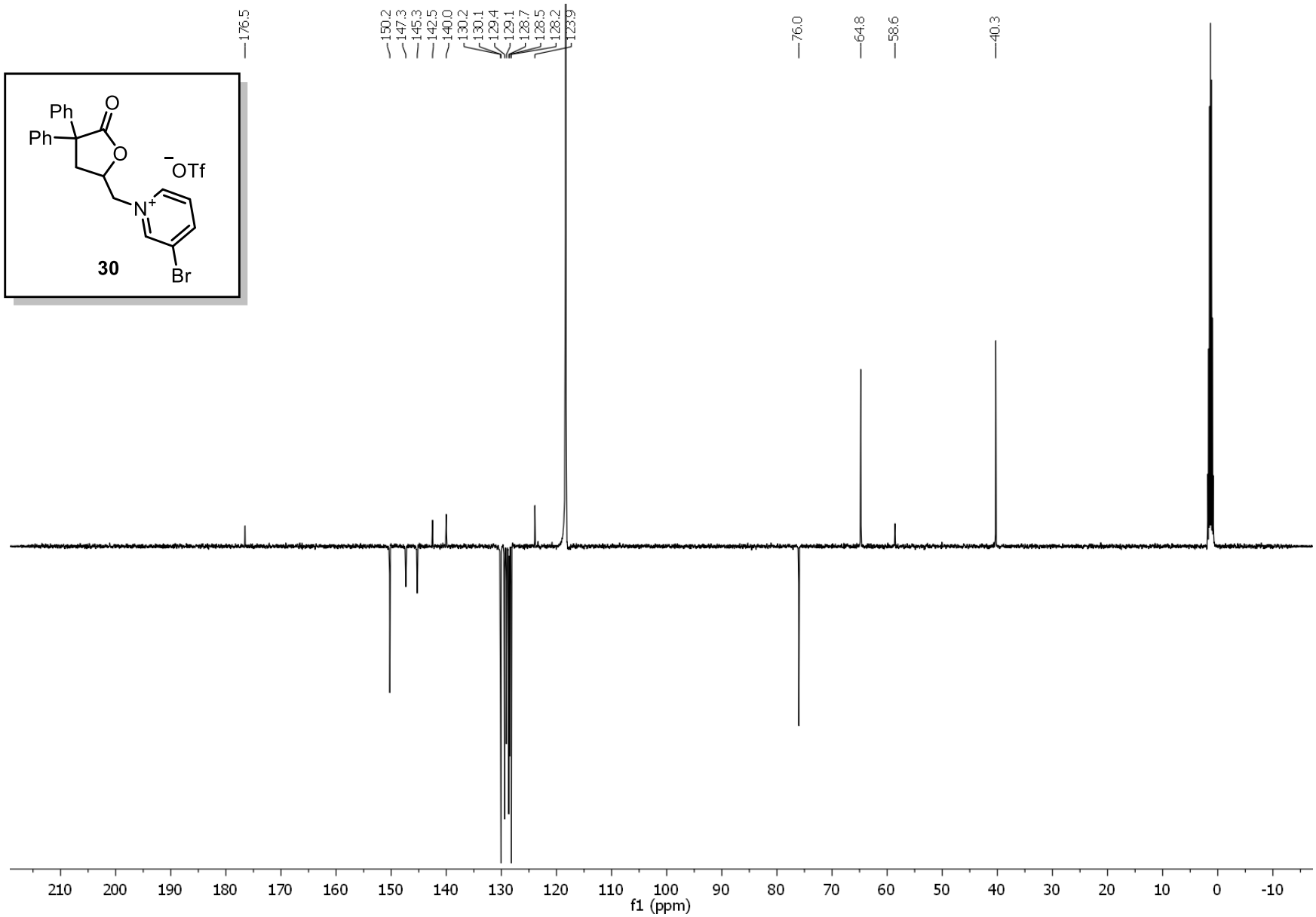

194.2
176.5
148.7
146.6
146.2
142.6
139.9
137.2
130.0
129.8
129.4
129.1
128.7
128.4
128.2
76.2
71.5
64.9
58.6
40.3
27.4
Ph
Ph
O
O
OTf
N+
Ac
29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

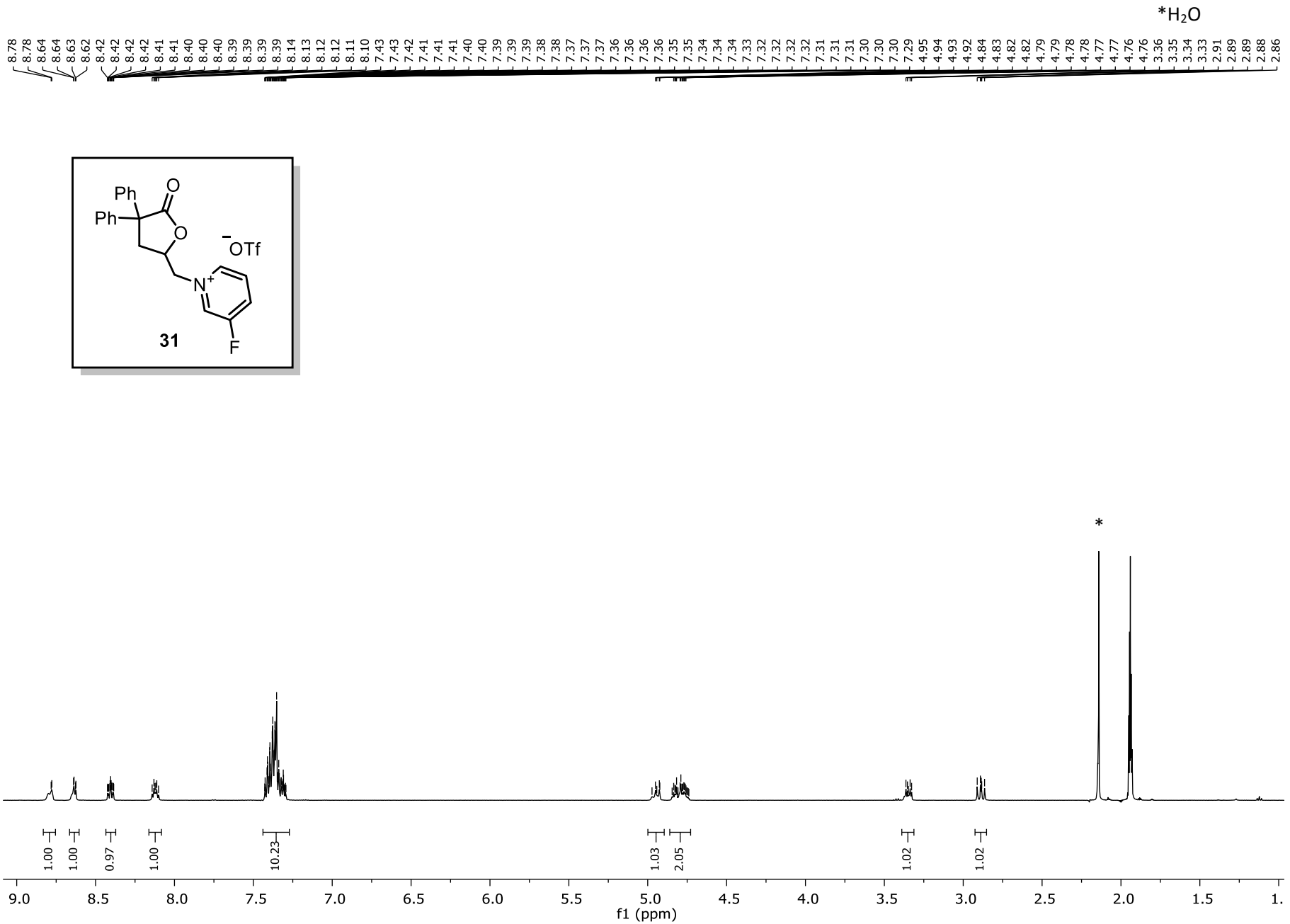

8.97 8.97 8.96 8.96 8.76 8.76 8.75 8.75 8.74 8.74 8.74 8.71 8.71 8.70 8.70 8.69 8.69 8.69 8.68 7.99 7.98 7.98 7.96 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.31 7.31 7.31 7.30 4.96 4.95 4.94 4.93 4.93 4.92 4.82 4.81 4.80 4.79 4.79 4.78 4.78 4.77 4.77 4.77 3.38 3.38 3.37 3.37 3.37 3.35 3.34 3.34 2.90 2.89 2.88 2.87 2.87 2.86 2.85

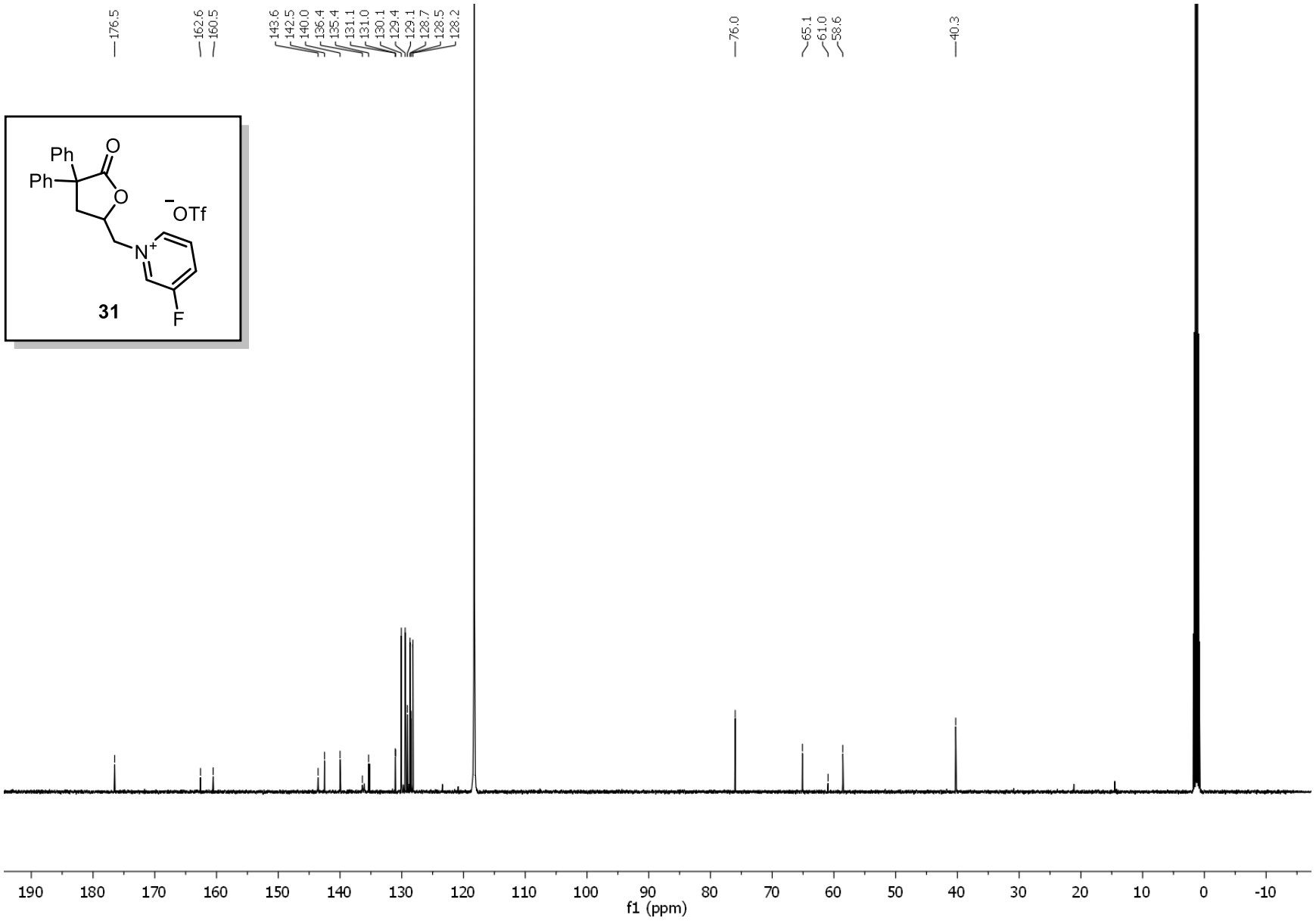

Ph
Ph
O
O
OTf
N+
Br

30


*
1.05
1.03
1.00
0.99
10.49
1.10
2.19
1.04
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


176.5
150.2
147.3
145.3
142.5
140.0
130.2
130.1
129.4
129.1
128.7
128.5
128.2
123.9
76.0
64.8
58.6
40.3
Ph
Ph
O
O
OTf
N+
Br
30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


*H2O
8.78 8.78 8.64 8.64 8.63 8.62 8.42 8.42 8.42 8.42 8.41 8.41 8.40 8.40 8.40 8.39 8.39 8.39 8.39 8.14 8.13 8.12 8.12 8.11 8.10 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 4.95 4.94 4.93 4.92 4.84 4.83 4.82 4.82 4.79 4.79 4.78 4.78 4.77 4.76 4.76 3.36 3.35 3.34 3.33 2.91 2.89 2.89 2.88 2.86
Ph
Ph
O
O
OTf
N+
F
31
*
1.00
1.00
0.97
1.00
10.23
1.03
2.05
1.02
1.02
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
f1 (ppm)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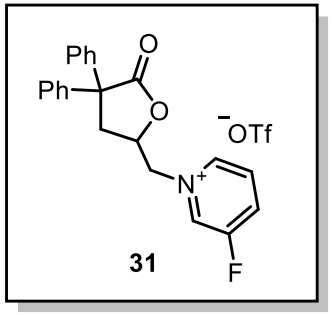
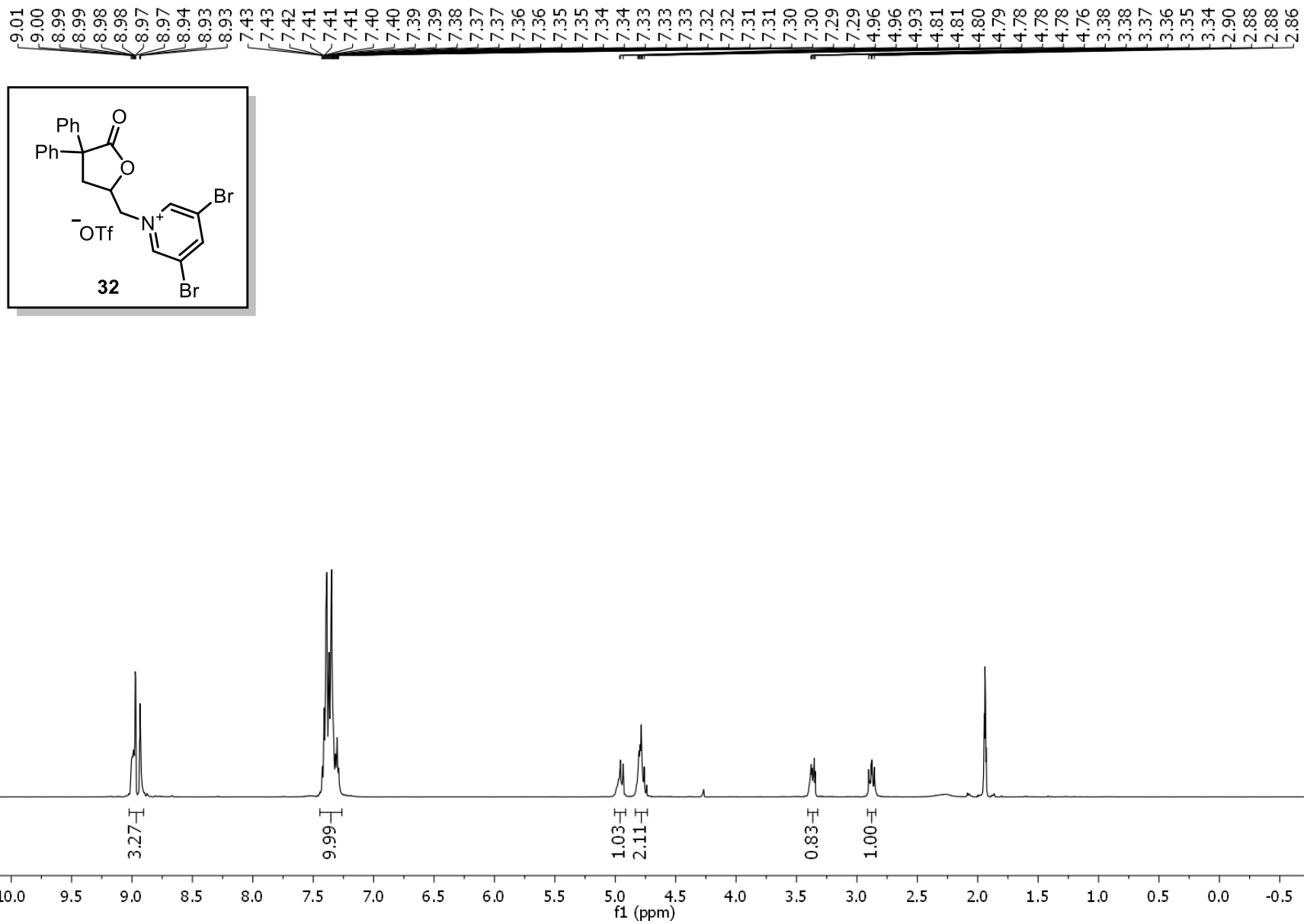
162.6
160.5
143.6
142.5
140.0
136.4
135.4
131.1
131.0
130.1
129.4
129.1
128.7
128.5
128.2
76.0
65.1
61.0
58.6
40.3
Ph
Ph
O
O
OTf
N+
F
31
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
Ph
O
O
OTf
N+
F

31

-79.34
-116.08
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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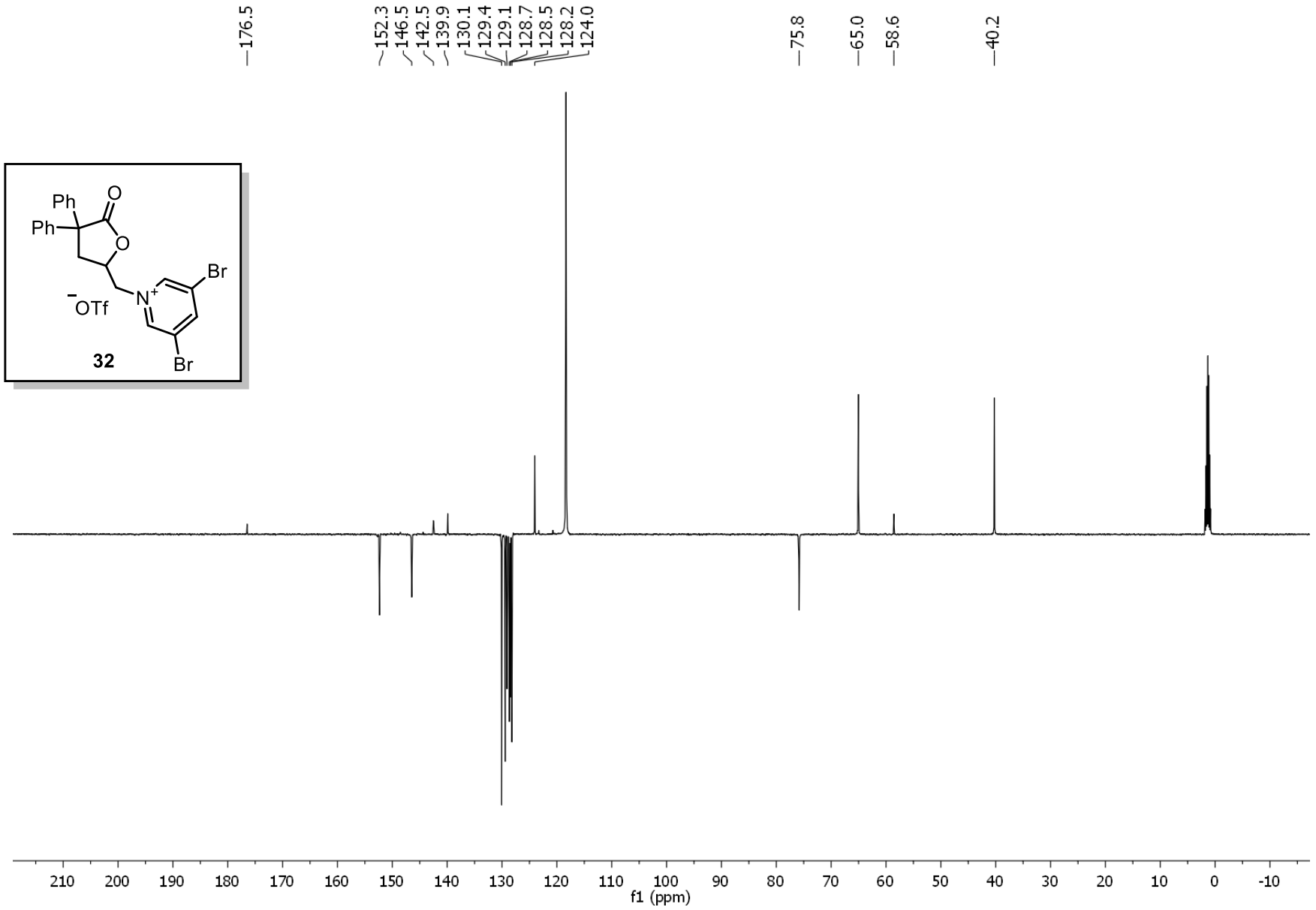
7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29
4.96 4.96 4.93 4.81 4.81 4.80 4.79 4.78 4.78 4.78 4.76
3.38 3.38 3.37 3.36 3.35 3.34 2.90 2.88 2.88 2.86
Ph
Ph
O
O
Br
N+
−OTf
Br
32
3.27
9.99
1.03
2.11
0.83
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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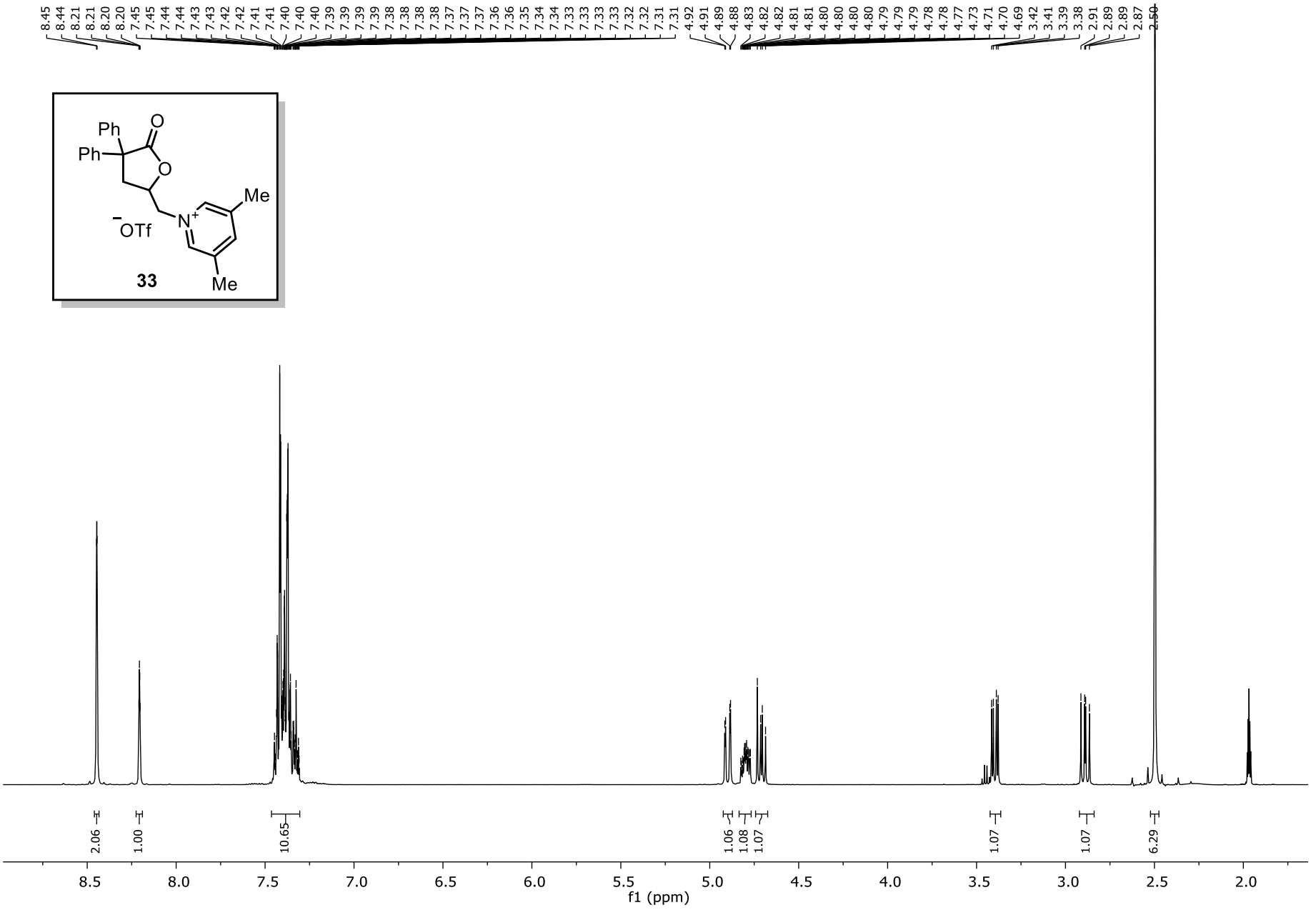
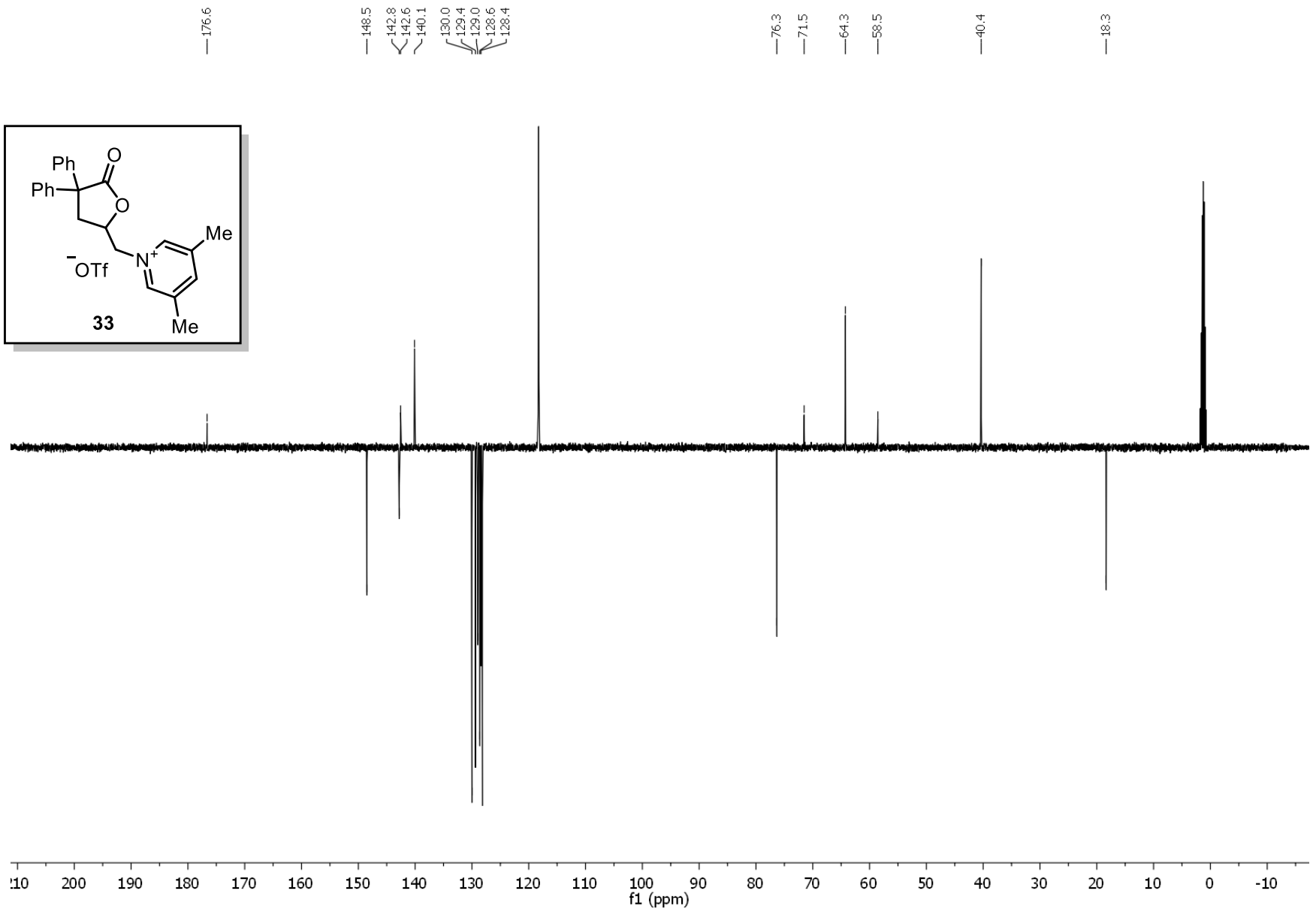
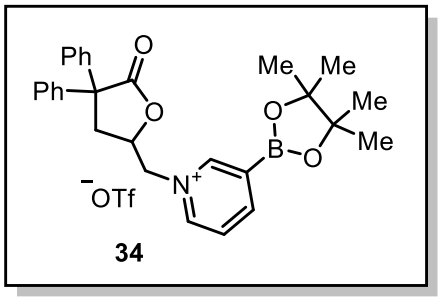
152.3
146.5
142.5
139.9
130.1
129.4
129.1
128.7
128.5
128.2
124.0
75.8
65.0
58.6
40.2
Ph
Ph
O
O
Br
N+
OTf
Br
32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.45 8.44 8.21 8.21 8.20 8.20 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.40 7.39 7.39 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 4.92 4.91 4.89 4.88 4.83 4.82 4.82 4.81 4.81 4.80 4.80 4.80 4.80 4.79 4.79 4.79 4.78 4.78 4.77 4.73 4.71 4.70 4.69 3.42 3.41 3.39 3.38 2.91 2.89 2.89 2.87 2.50
Ph
Ph
O
O
Me
N+
−OTf
33
Me
2.06
1.00
10.65
1.06
1.08
1.07
1.07
1.07
6.29
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
f1 (ppm)

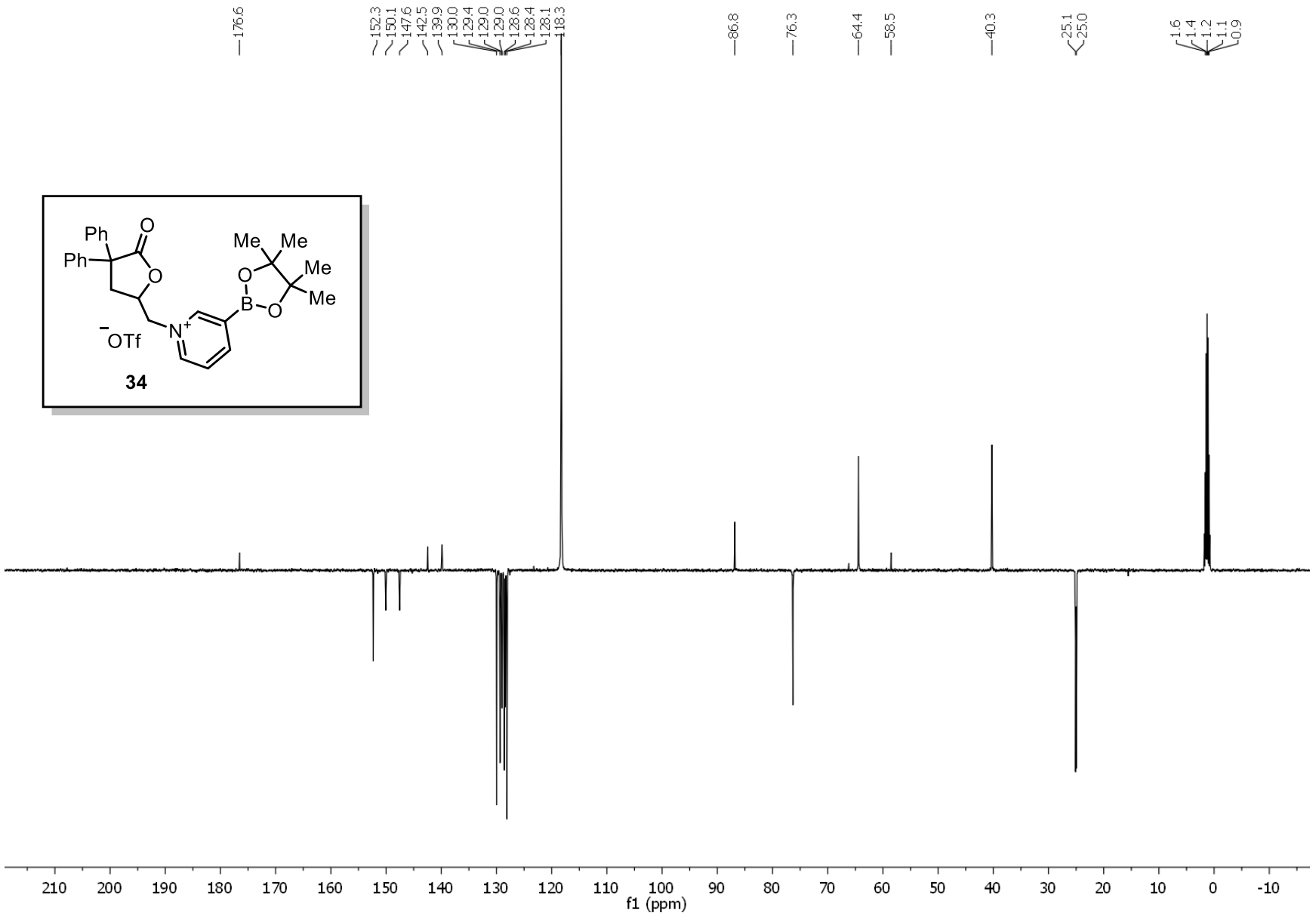

176.6
148.5
142.8
142.6
140.1
130.0
129.4
129.0
128.6
128.4
76.3
71.5
64.3
58.5
40.4
18.3
Ph
Ph
O
O
Me
N+
OTf
33
Me
f1 (ppm)

*Et_2O


Ph
Ph
O
O
Me
Me
Me
Me
O
B
O
N+
−OTf

34

*
*
0.93
1.04
1.01
0.93
10.87
1.00
2.13
1.04
1.02
11.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


176.6
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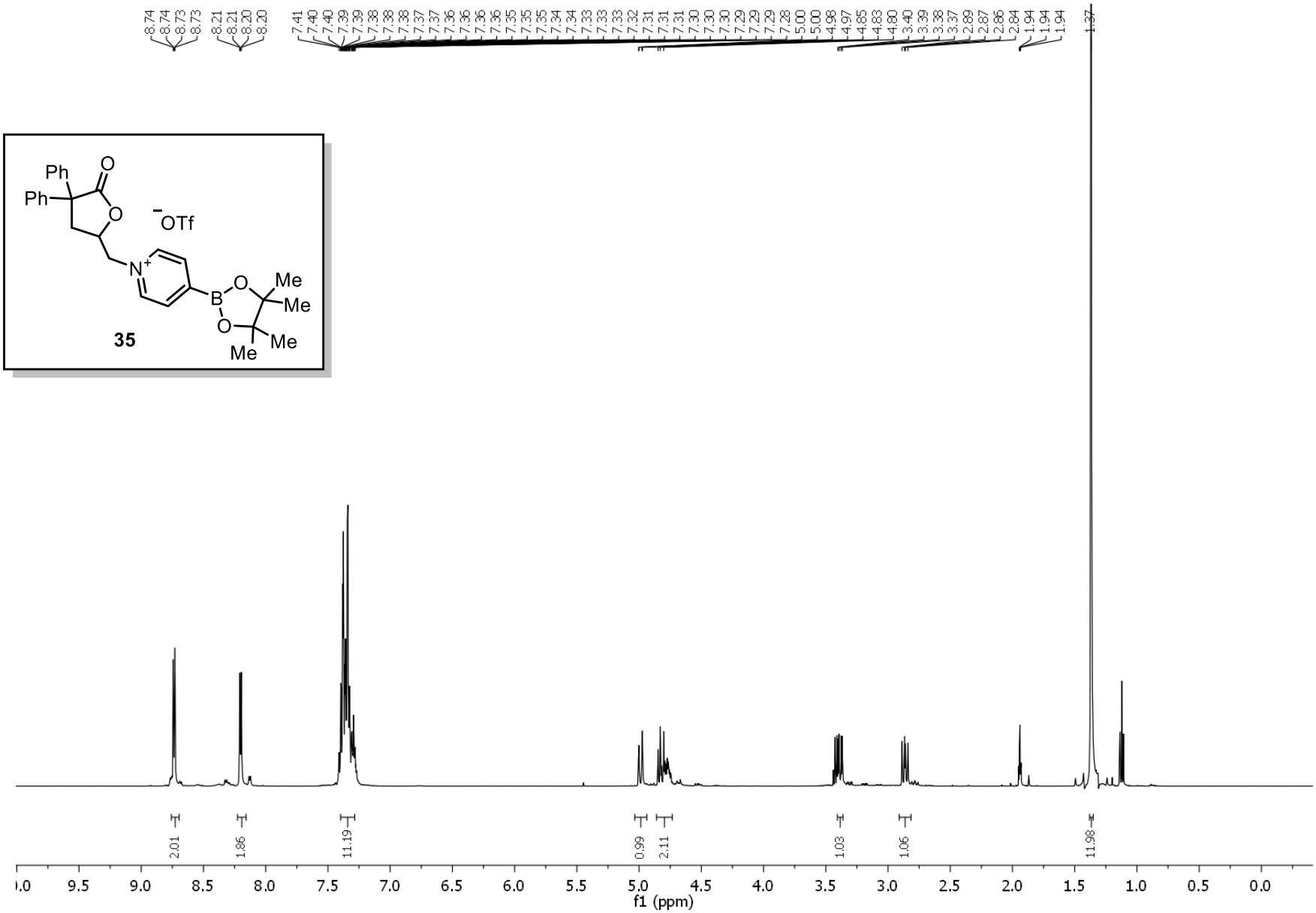
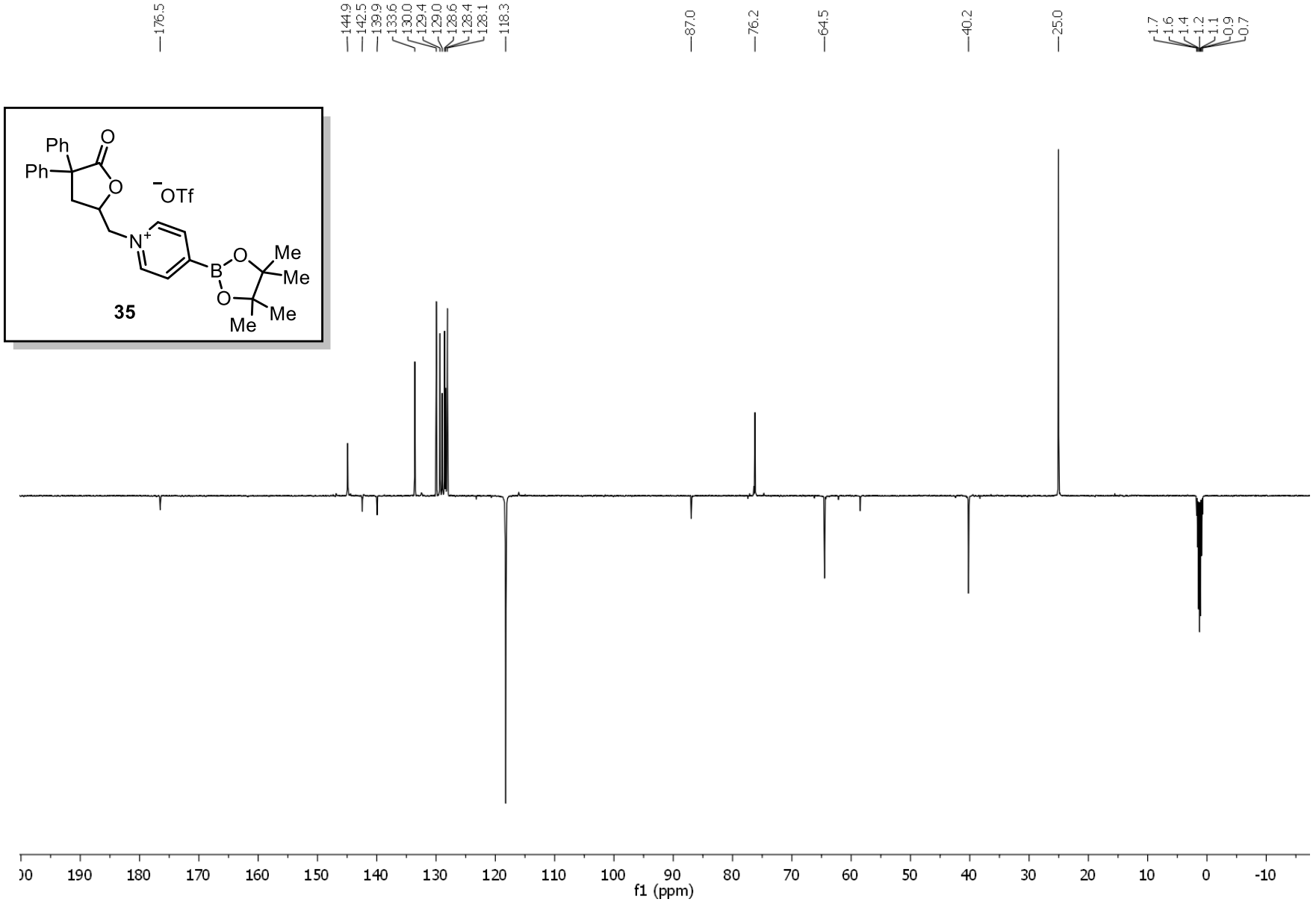
150.1
147.6
142.5
139.9
130.0
129.4
129.0
129.0
128.6
128.4
128.1
118.3
86.8
76.3
64.4
58.5
40.3
25.1
25.0
1.6
1.4
1.2
1.1
0.9
Ph
Ph
O
O
Me
Me
Me
Me
O
B
O
N+
OTf
34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.74 8.74 8.73 8.73 8.21 8.21 8.20 8.20 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 5.00 5.00 4.98 4.97 4.85 4.83 4.80 3.40 3.39 3.38 3.37 2.89 2.87 2.86 2.84 1.94 1.94 1.94 1.37
Ph
Ph
O
O
OTf
N+
B
O
O
Me
Me
Me
Me
35
2.01
1.86
11.19
0.99
2.11
1.03
1.06
11.98
f1 (ppm)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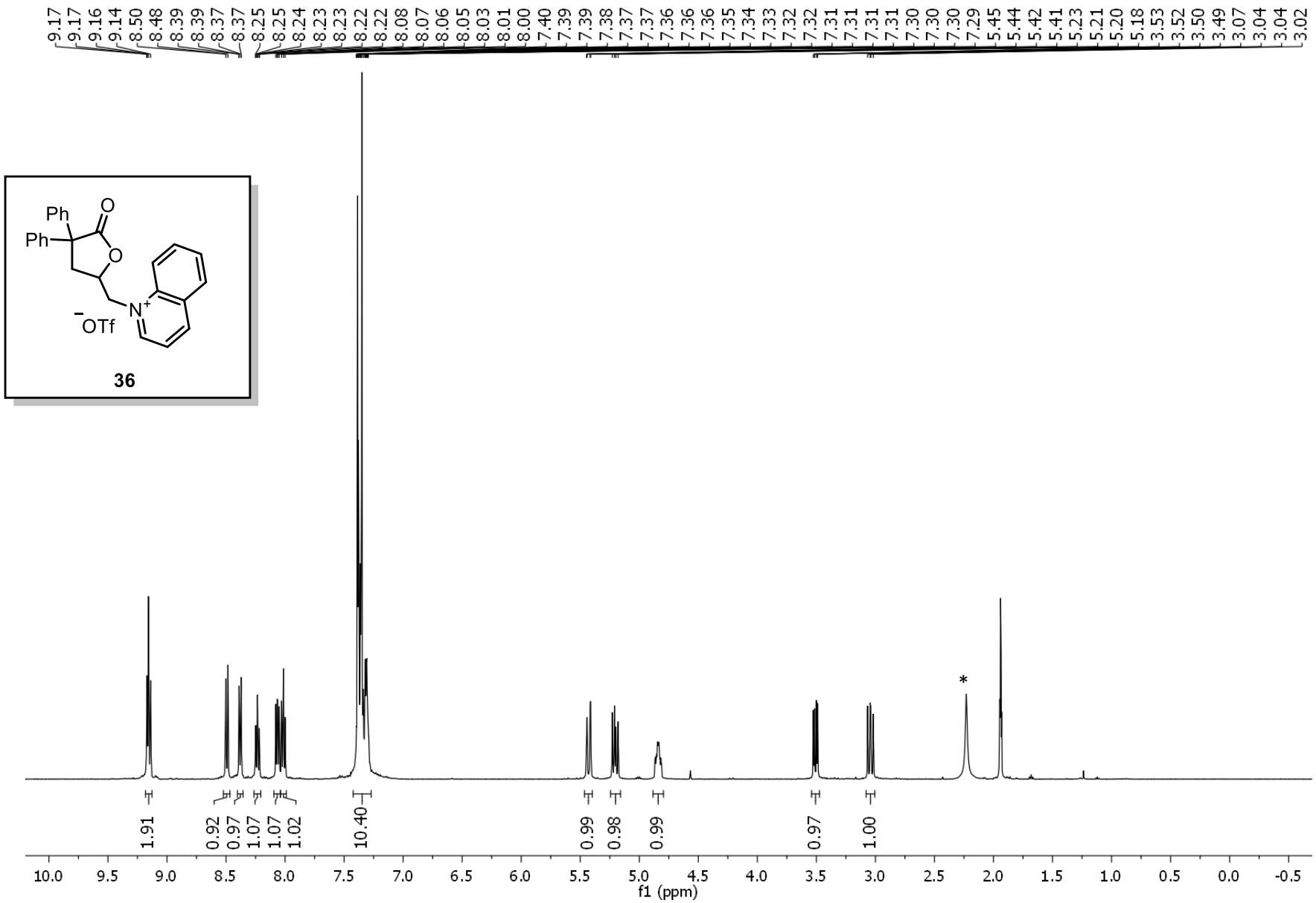
144.9
142.5
139.9
133.6
130.0
129.4
129.0
128.6
128.4
128.1
118.3
87.0
76.2
64.5
40.2
25.0
1.7
1.6
1.4
1.2
1.1
0.9
0.7
Ph
Ph
O
O
OTf
N+
B
O
O
Me
Me
Me
Me
35
f1 (ppm)

*H_2O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9.17
9.16
9.14
8.50
8.48
8.39
8.39
8.37
8.37
8.25
8.25
8.24
8.23
8.23
8.22
8.22
8.08
8.07
8.06
8.05
8.03
8.01
8.00
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.30
7.29
5.45
5.44
5.42
5.41
5.23
5.21
5.20
5.18
3.53
3.52
3.50
3.49
3.07
3.04
3.04
3.02
Ph
Ph
O
O
N+
OTf
36
1.91
0.92
0.97
1.07
1.07
1.02
10.40
0.99
0.98
0.99
0.97
1.00
*
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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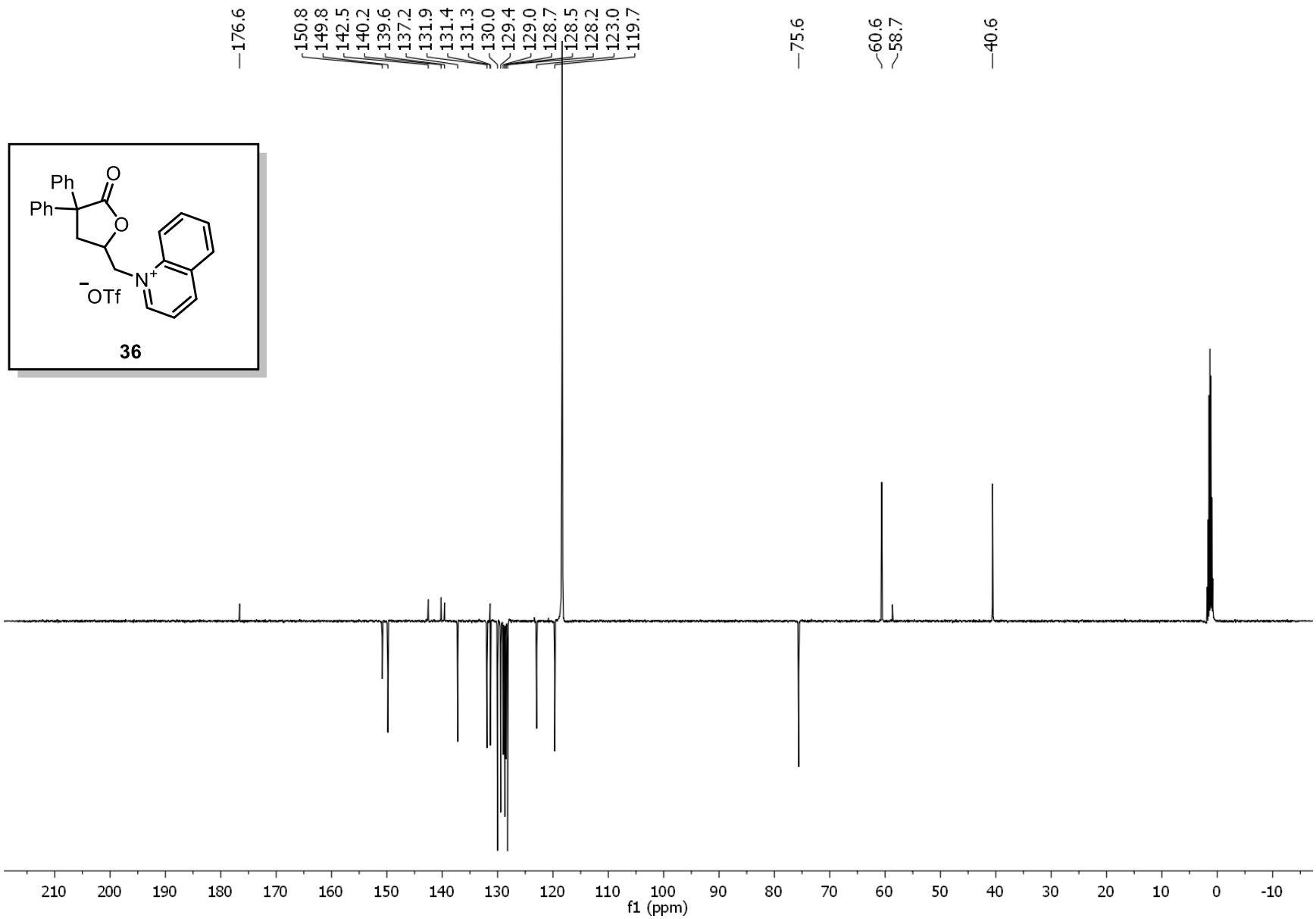
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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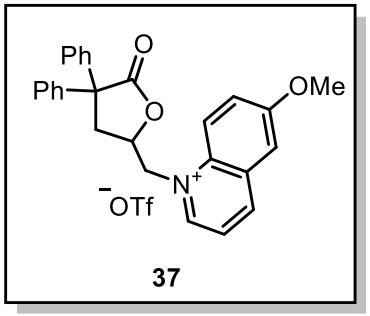
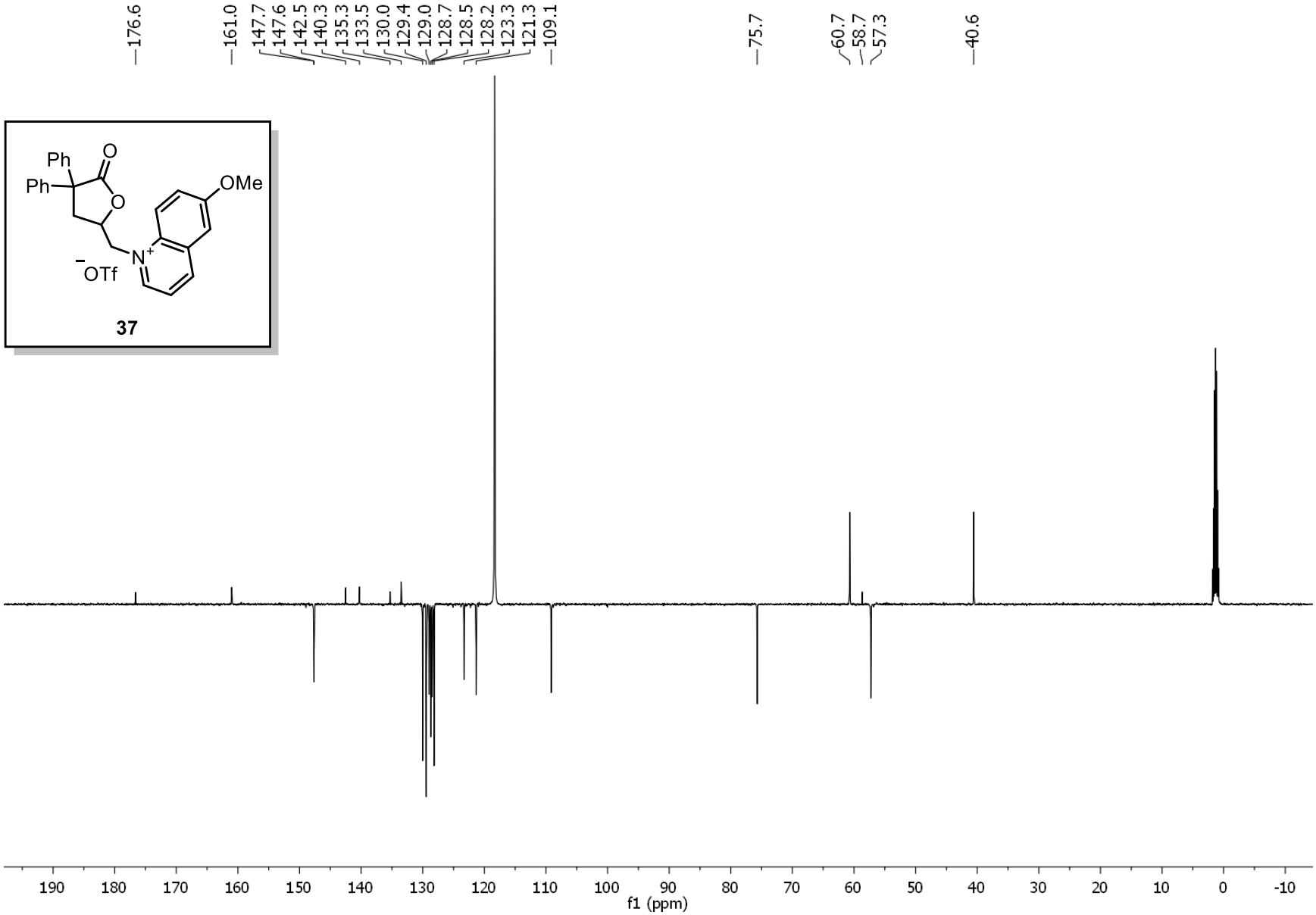
150.8
149.8
142.5
140.2
139.6
137.2
131.9
131.4
131.3
130.0
129.4
129.0
128.7
128.5
128.2
123.0
119.7
75.6
60.6
58.7
40.6
Ph
Ph
O
O
N+
OTf
36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
Ph
O
O
OMe
N+
−OTf

37

8.98 8.98 8.98 8.96 8.96 8.96 8.96 8.95 8.94 8.40 8.38 7.99 7.98 7.98 7.96 7.83 7.83 7.81 7.81 7.70 7.70 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 5.36 5.36 5.33 5.33 5.17 5.15 5.14 5.12 4.01 3.50 3.49 3.47 3.46 3.04 3.02 3.02 3.00
2.13 0.88 0.97 1.02 1.01 9.74 1.01 1.00 0.95 3.20 0.93 1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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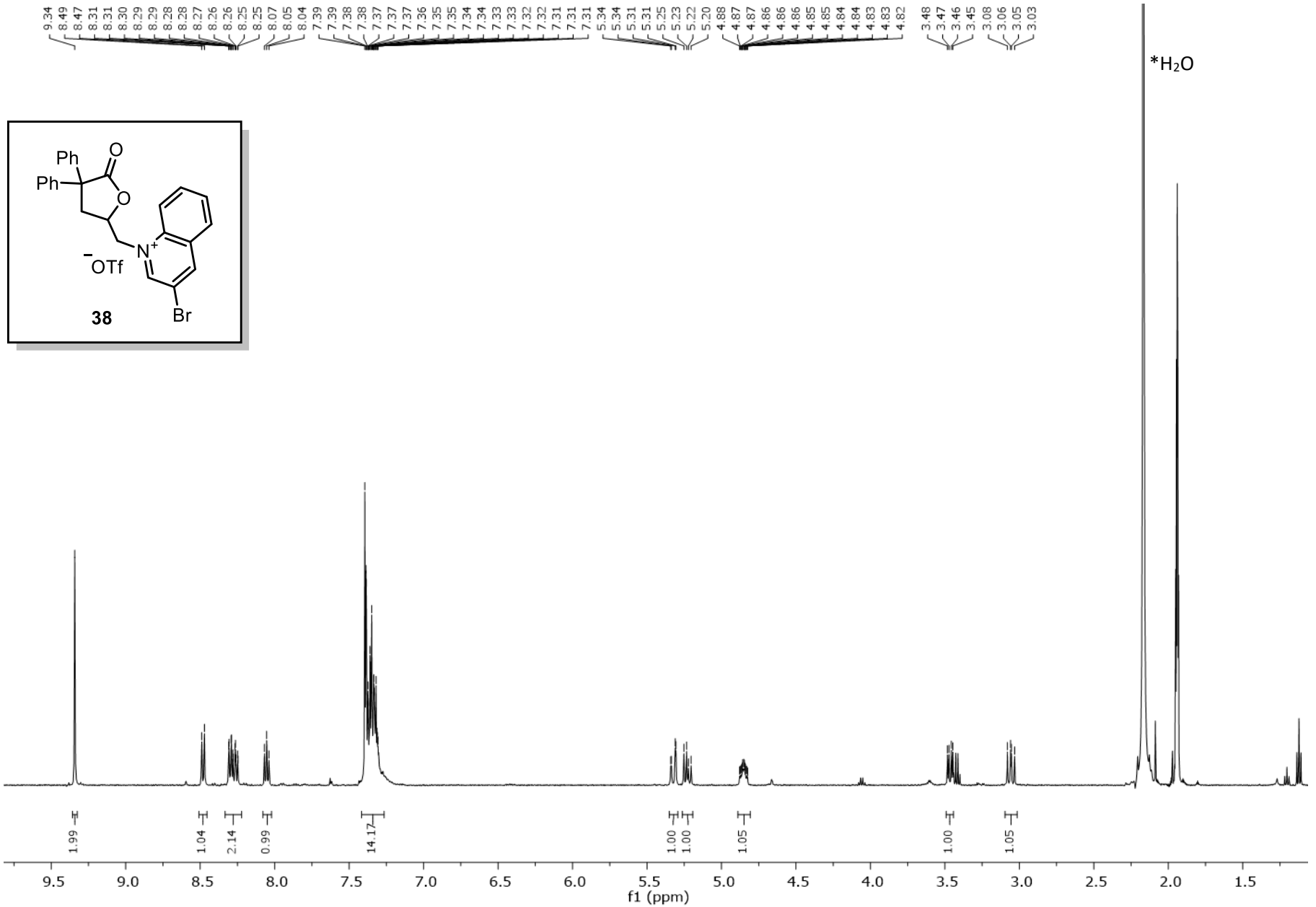
147.6
142.5
140.3
135.3
133.5
130.0
129.4
129.0
128.7
128.5
128.2
123.3
121.3
109.1
75.7
60.7
58.7
57.3
40.6
Ph
Ph
O
O
OMe
N+
−OTf
37
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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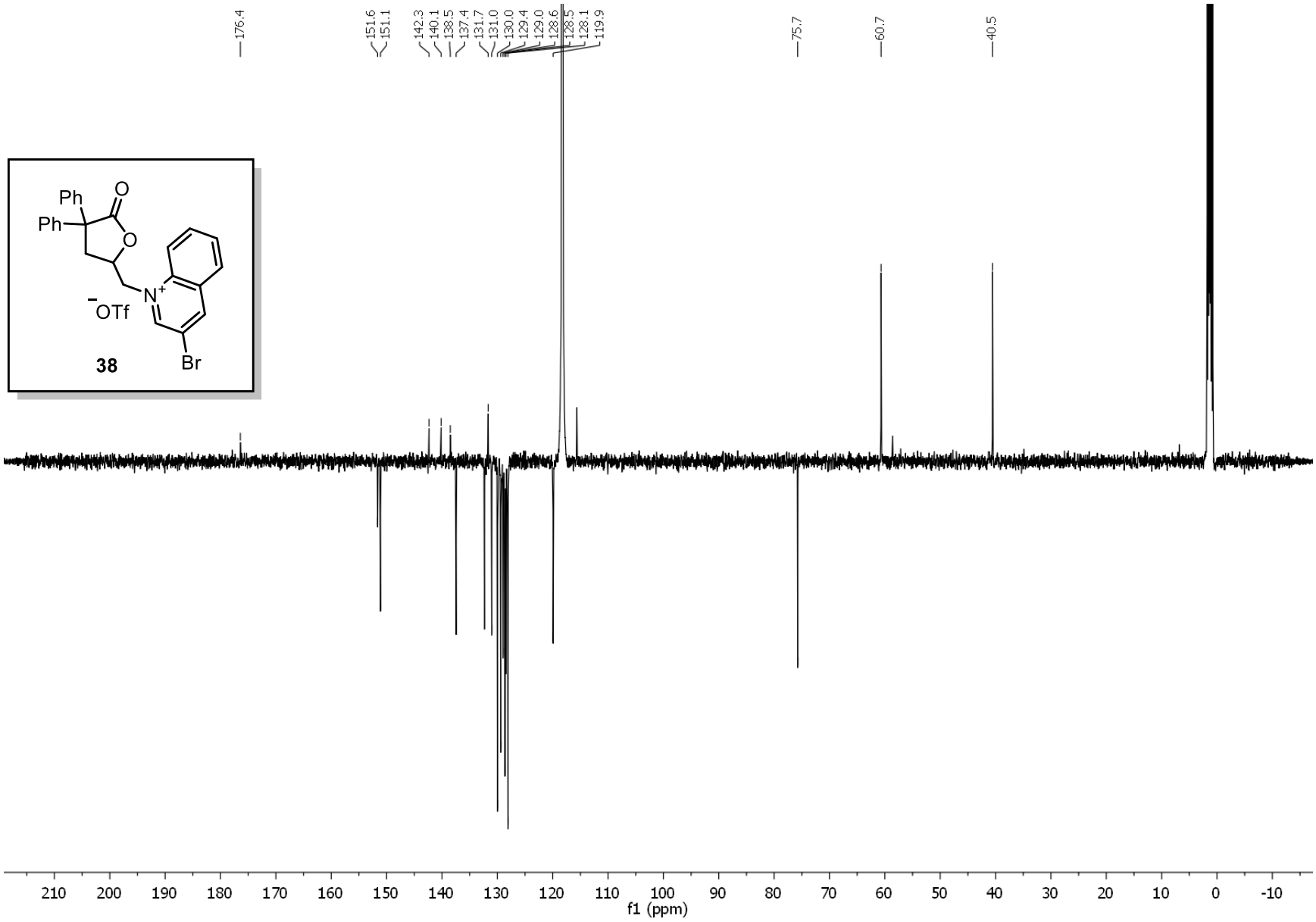
8.49
8.47
8.31
8.31
8.30
8.29
8.29
8.28
8.28
8.27
8.26
8.26
8.25
8.25
8.07
8.05
8.04
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.31
5.34
5.34
5.31
5.31
5.25
5.23
5.22
5.20
4.88
4.87
4.87
4.86
4.86
4.86
4.85
4.85
4.84
4.84
4.83
4.83
4.82
3.48
3.47
3.46
3.45
3.08
3.06
3.05
3.03
*H2O
Ph
Ph
O
O
N+
OTf
Br
38
1.99
1.04
2.14
0.99
14.17
1.00
1.00
1.05
1.00
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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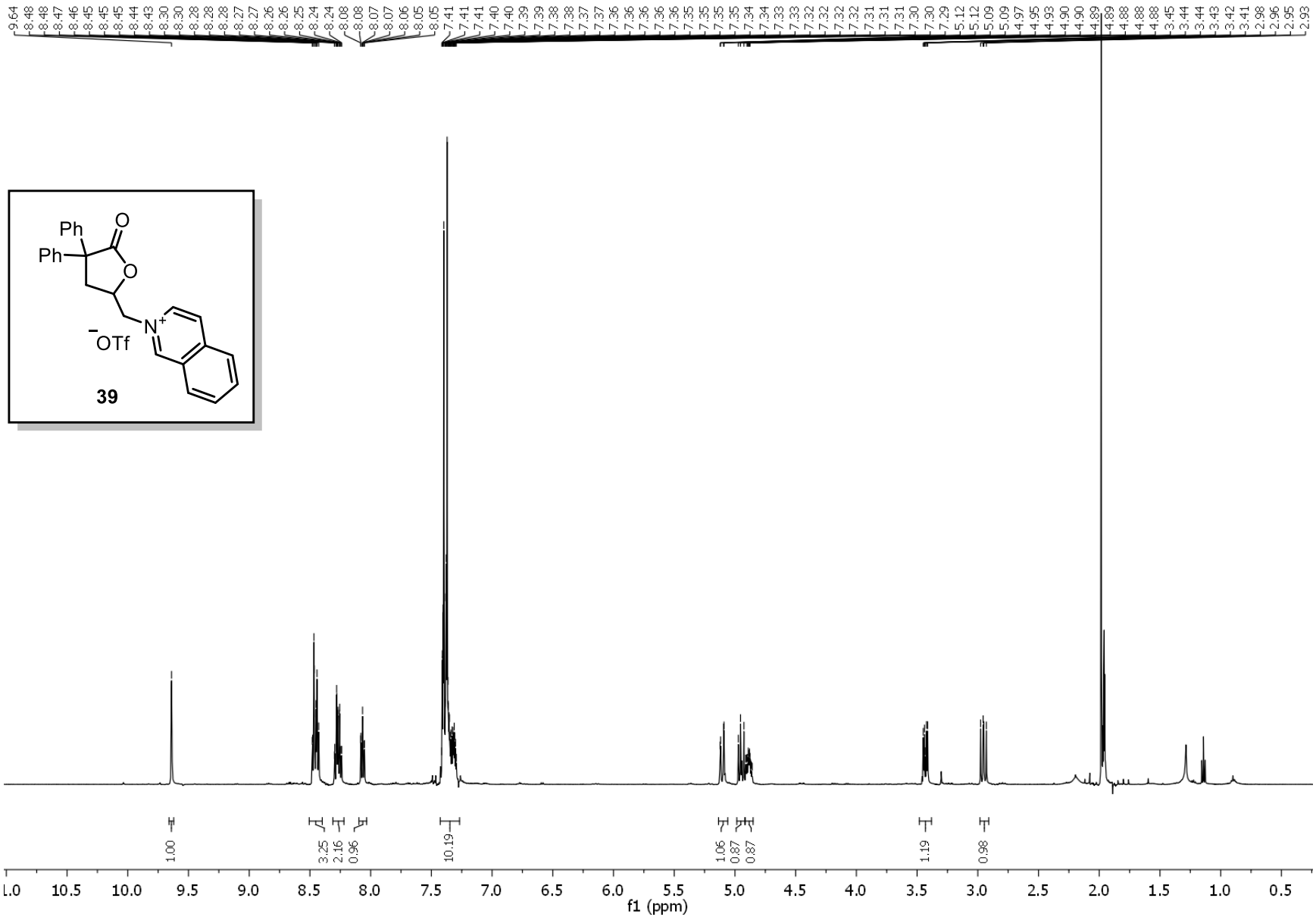
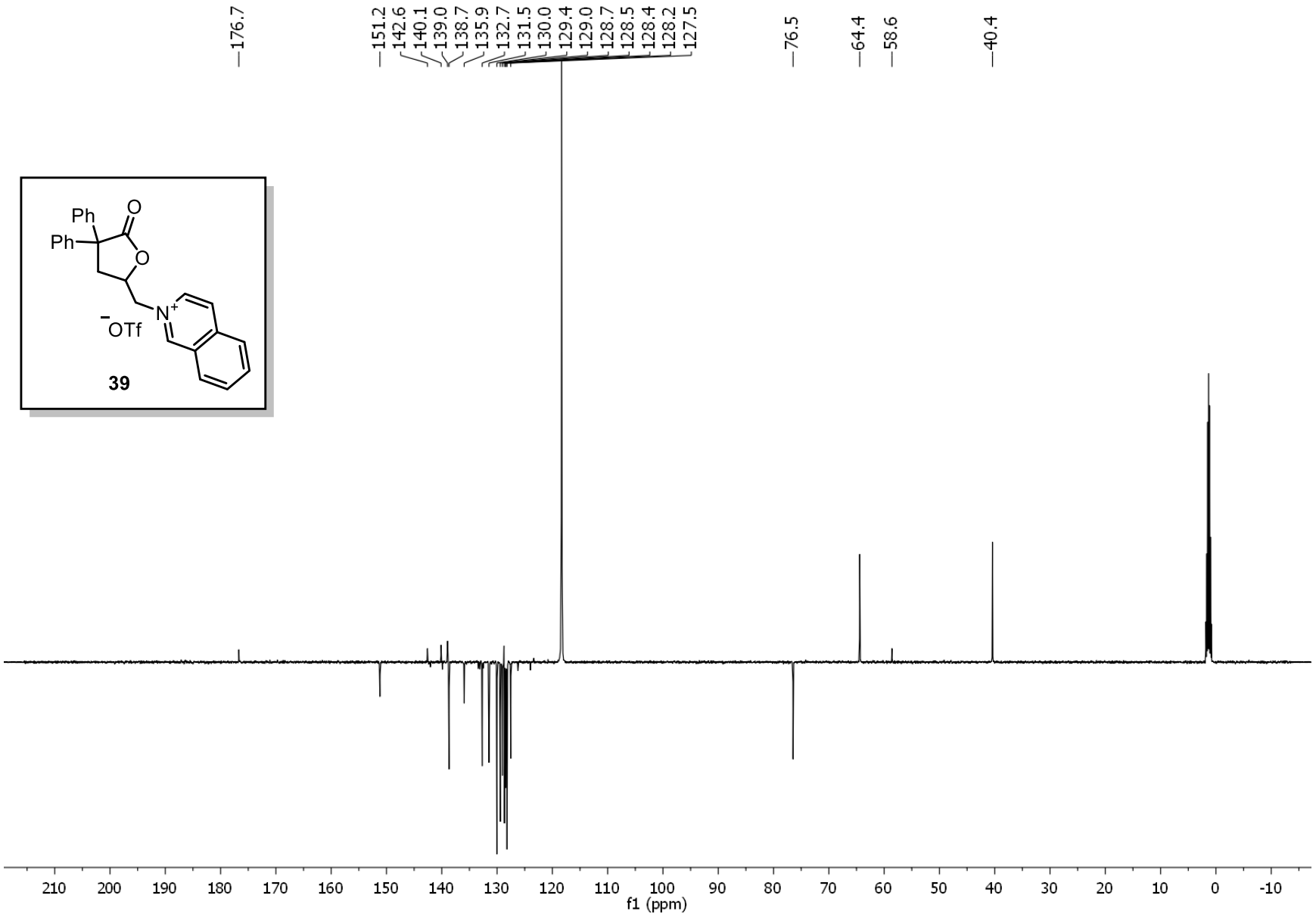
151.1
142.3
140.1
138.5
137.4
131.7
131.0
130.0
129.4
129.0
128.6
128.5
128.1
119.9
75.7
60.7
40.5
Ph
Ph
O
O
N+
−OTf
Br
38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
Ph
O
O
N+
−OTf
39
f1 (ppm)


176.7
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142.6
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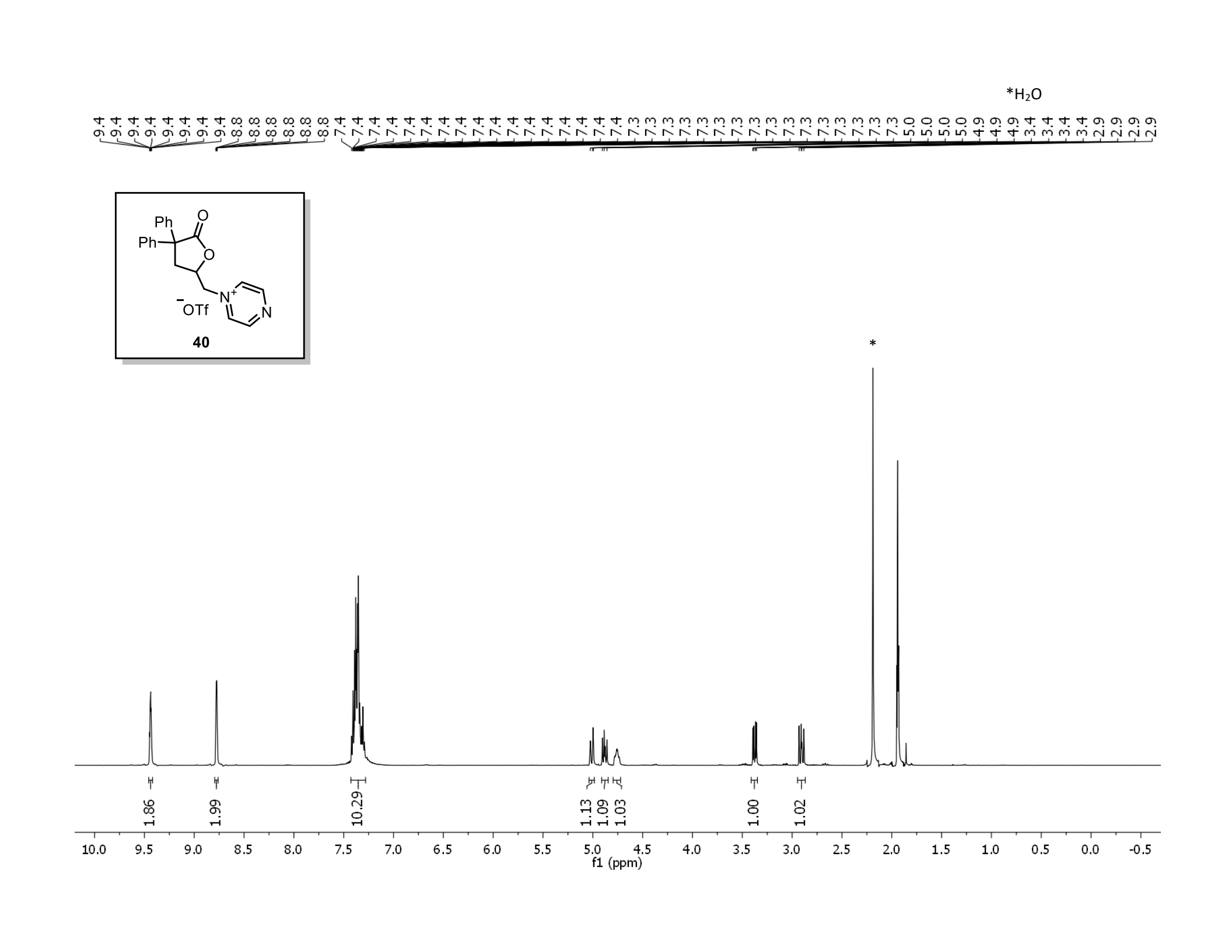
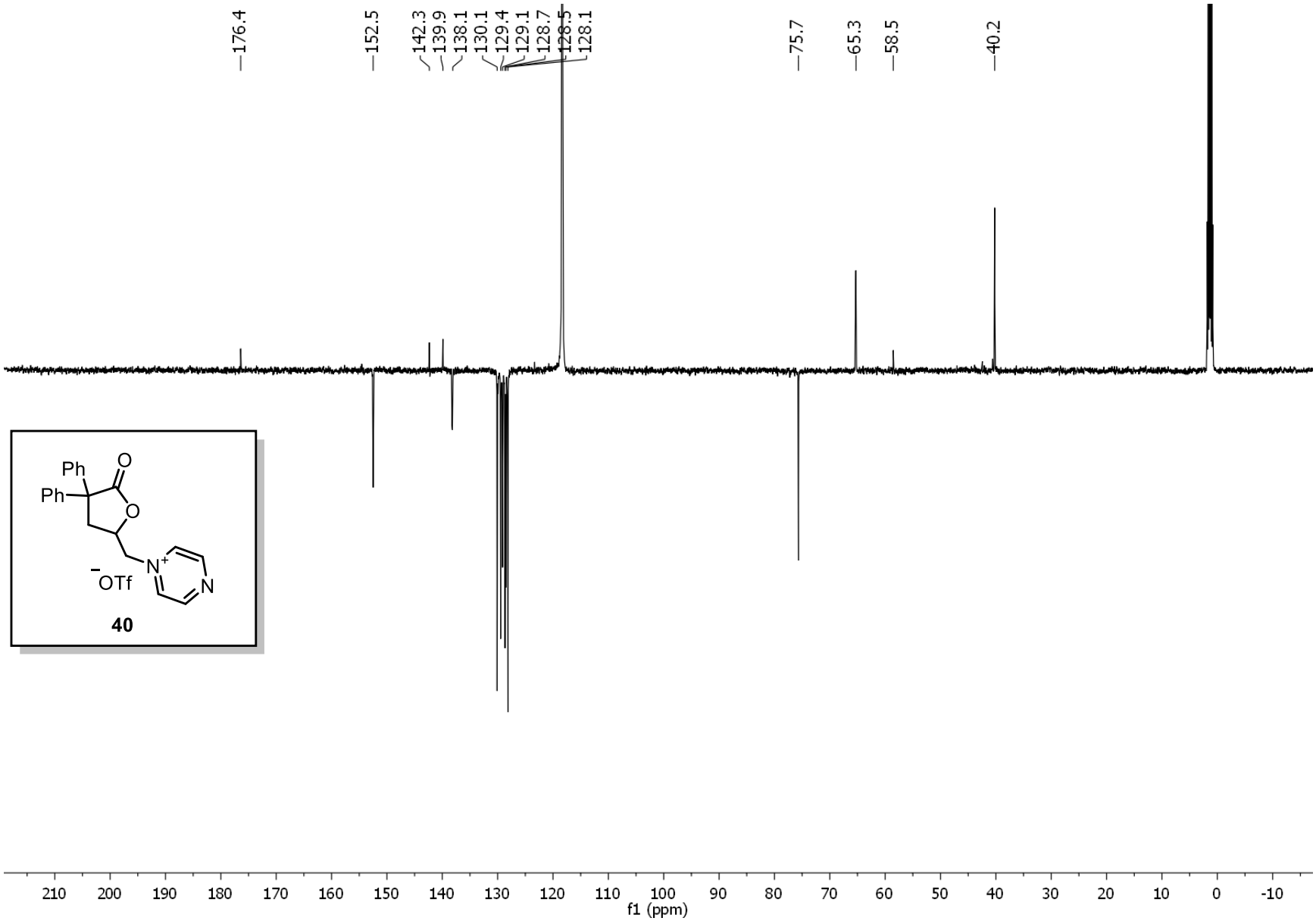
138.7
135.9
132.7
131.5
130.0
129.4
129.0
128.7
128.5
128.4
128.2
127.5
76.5
64.4
58.6
40.4
Ph
Ph
O
O
N+
OTf
39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


*H2O
Ph
Ph
O
O
N+
N
OTf
40
*
1.86
1.99
10.29
1.13
1.09
1.03
1.00
1.02
f1 (ppm)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152.5
142.3
139.9
138.1
130.1
129.4
129.1
128.7
128.5
128.1
75.7
65.3
58.5
40.2
Ph
Ph
O
O
N+
N
−OTf
40
210
200
190
180
170
160
150
140
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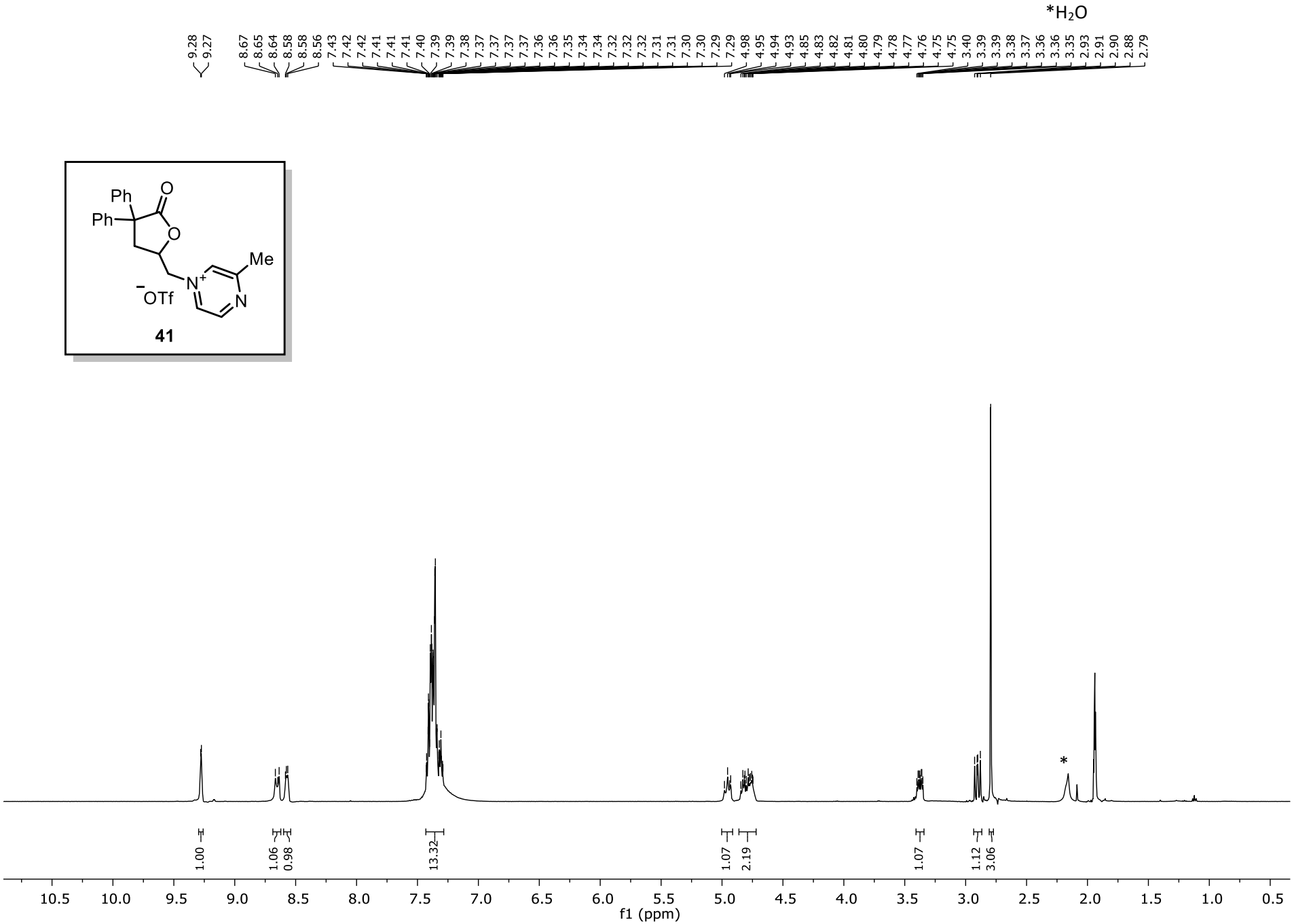
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


*H2O
9.28
9.27
8.67
8.65
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8.58
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7.43
7.42
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7.41
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7.37
7.37
7.37
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7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
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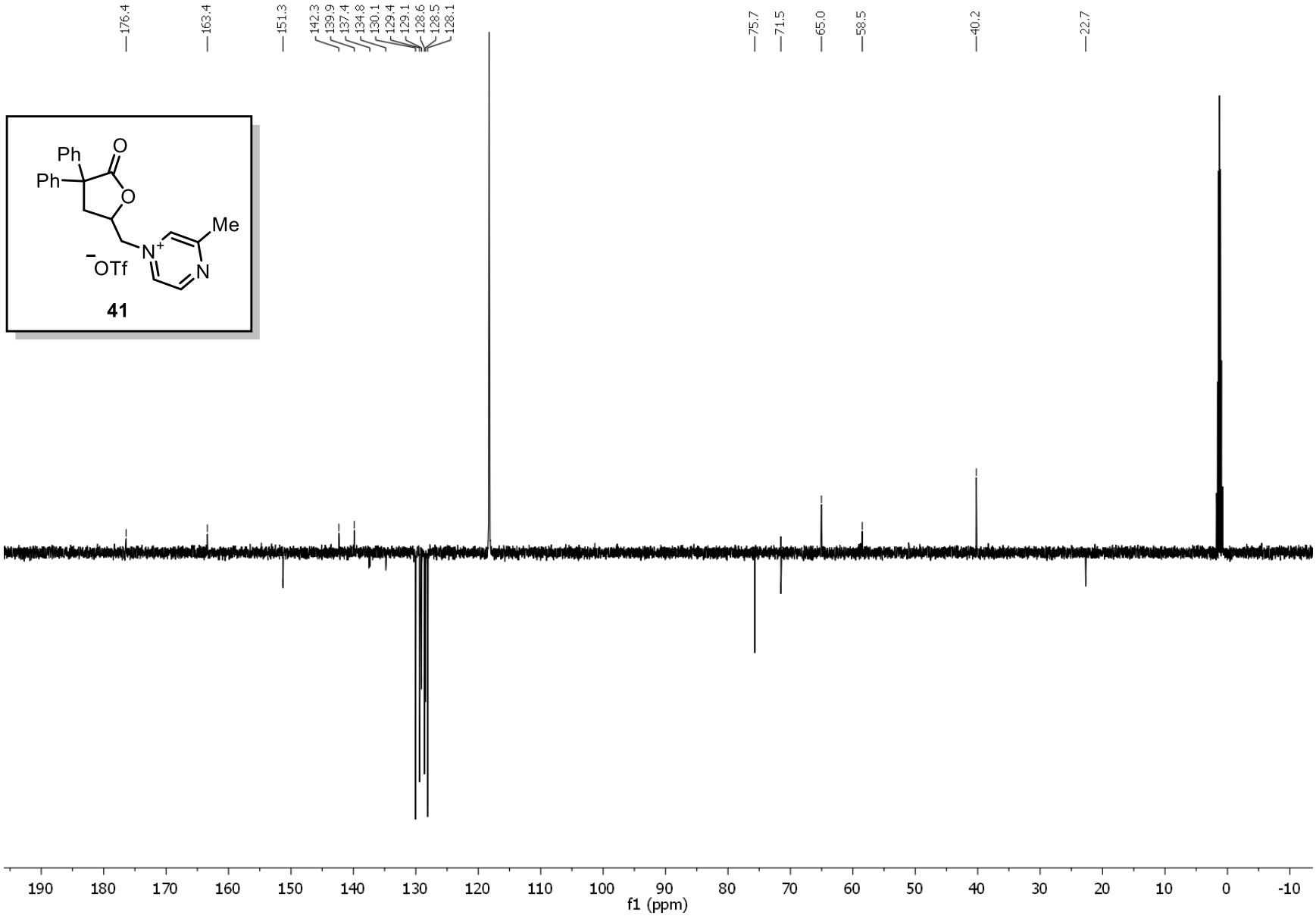
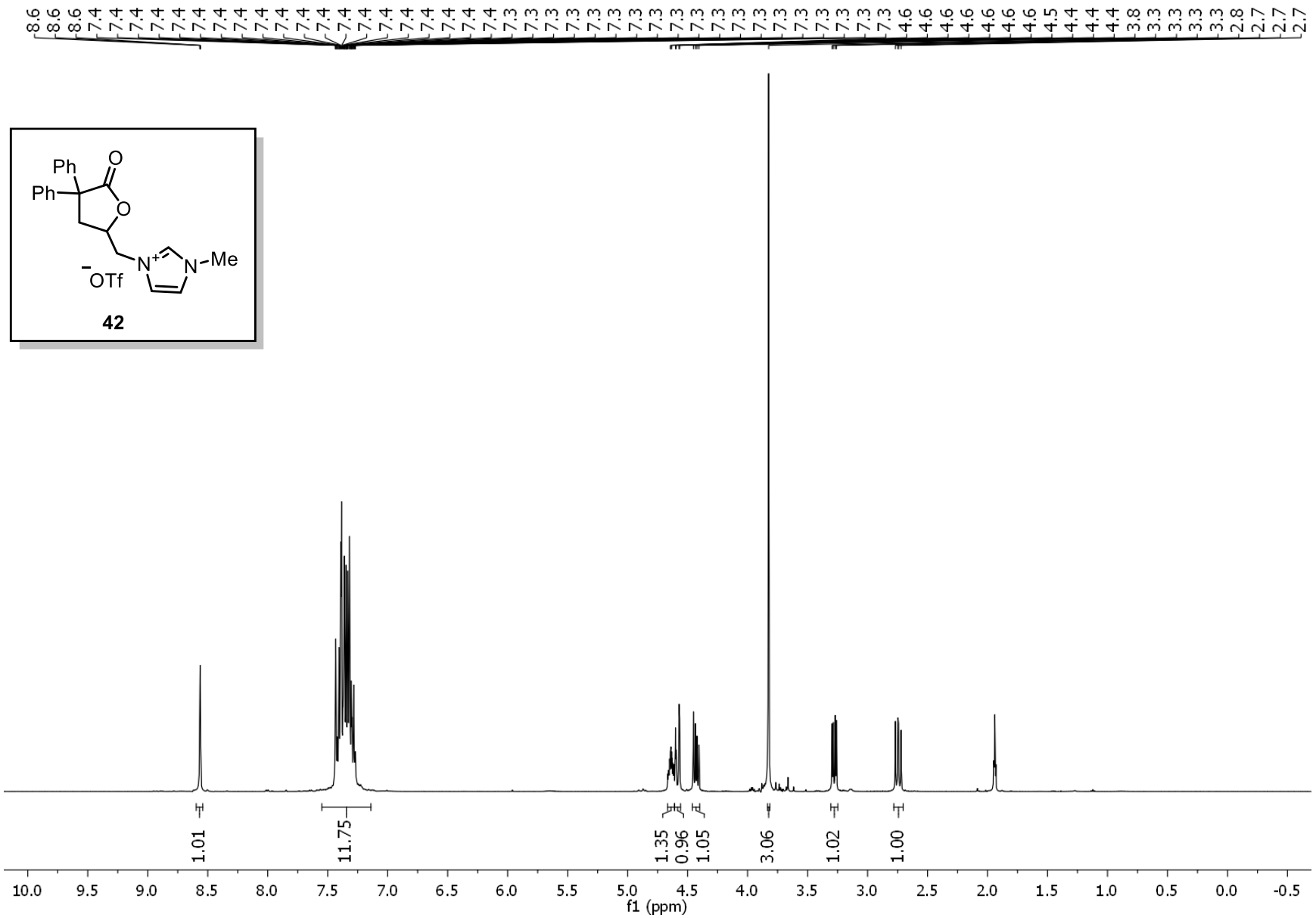
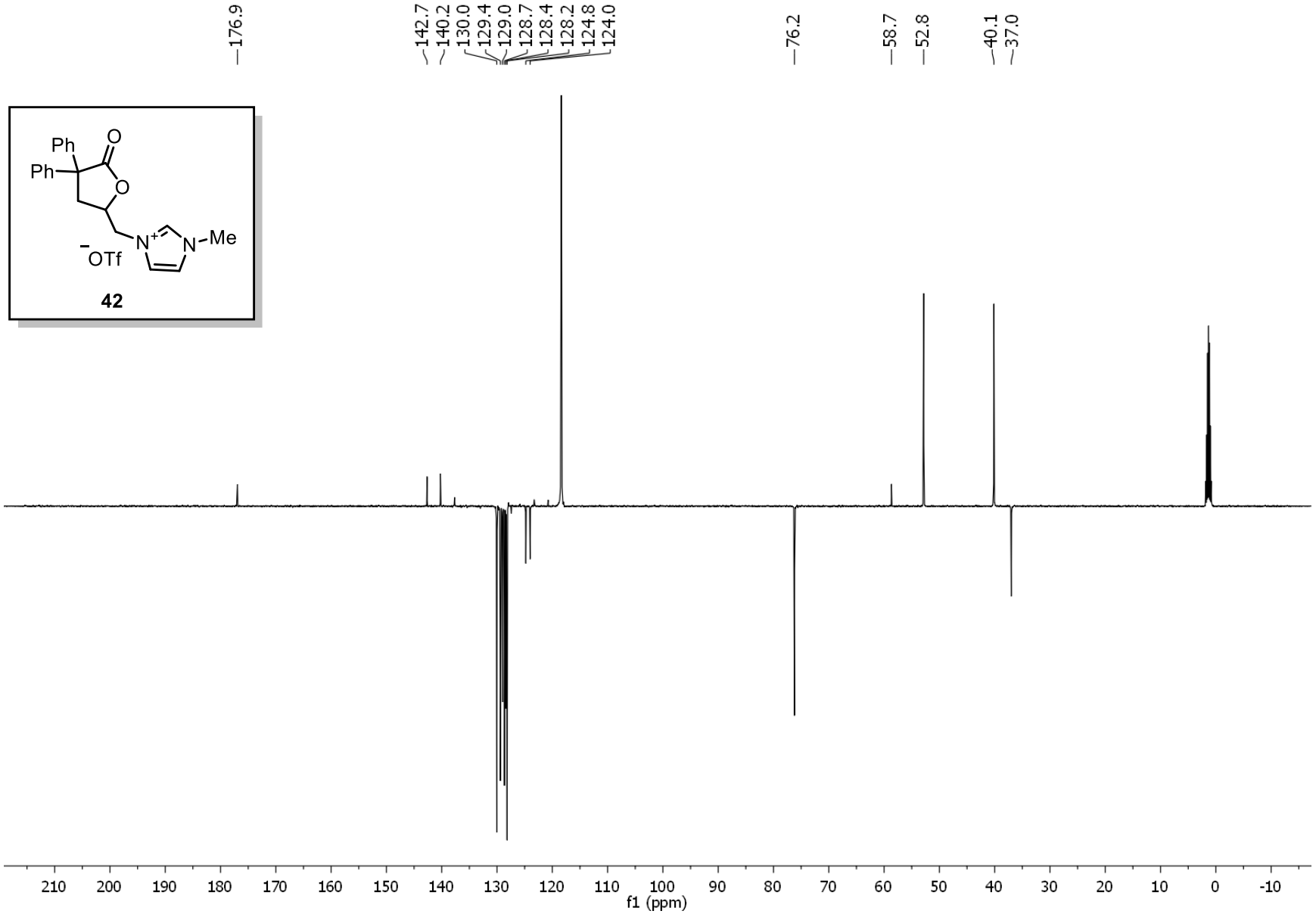
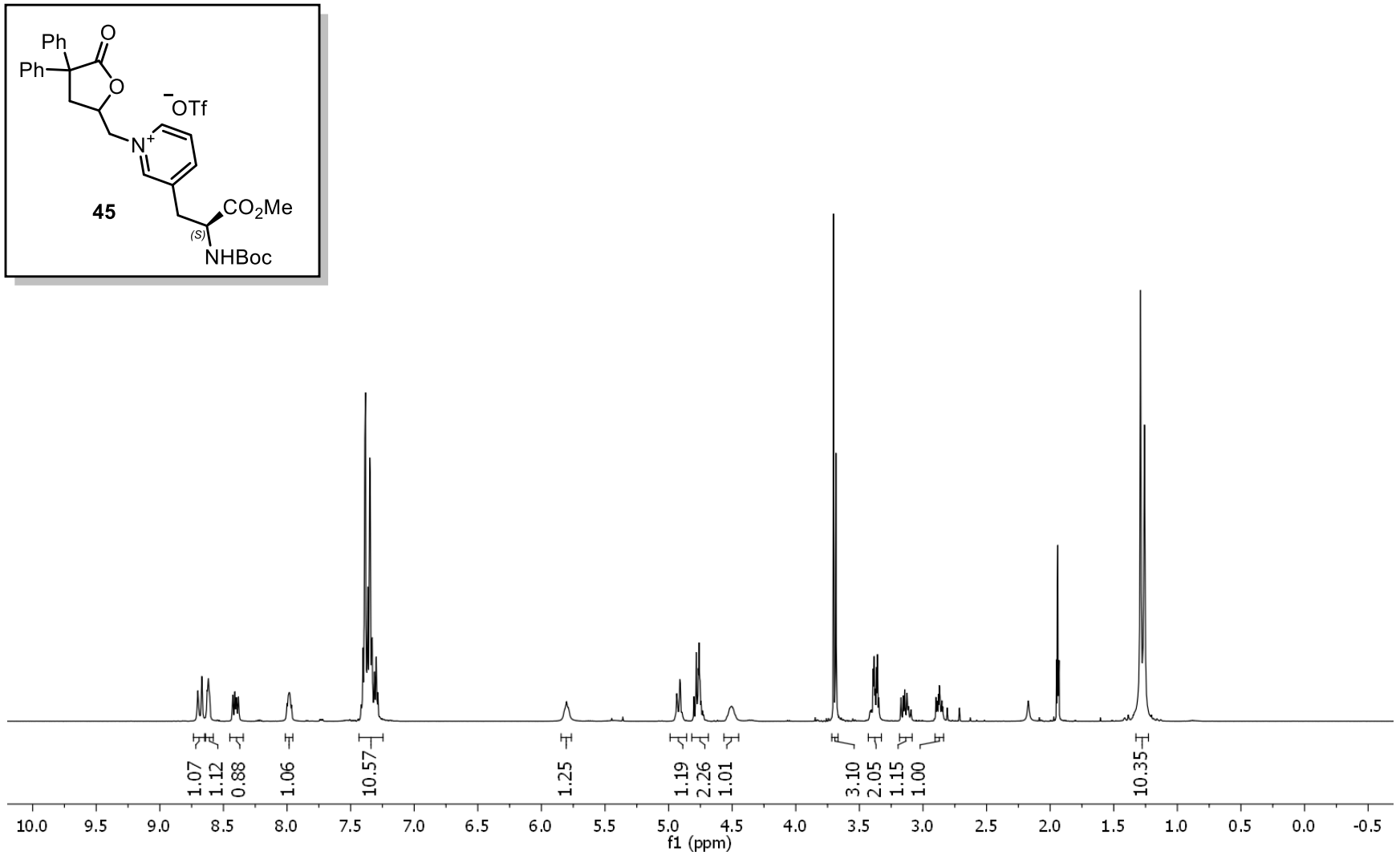
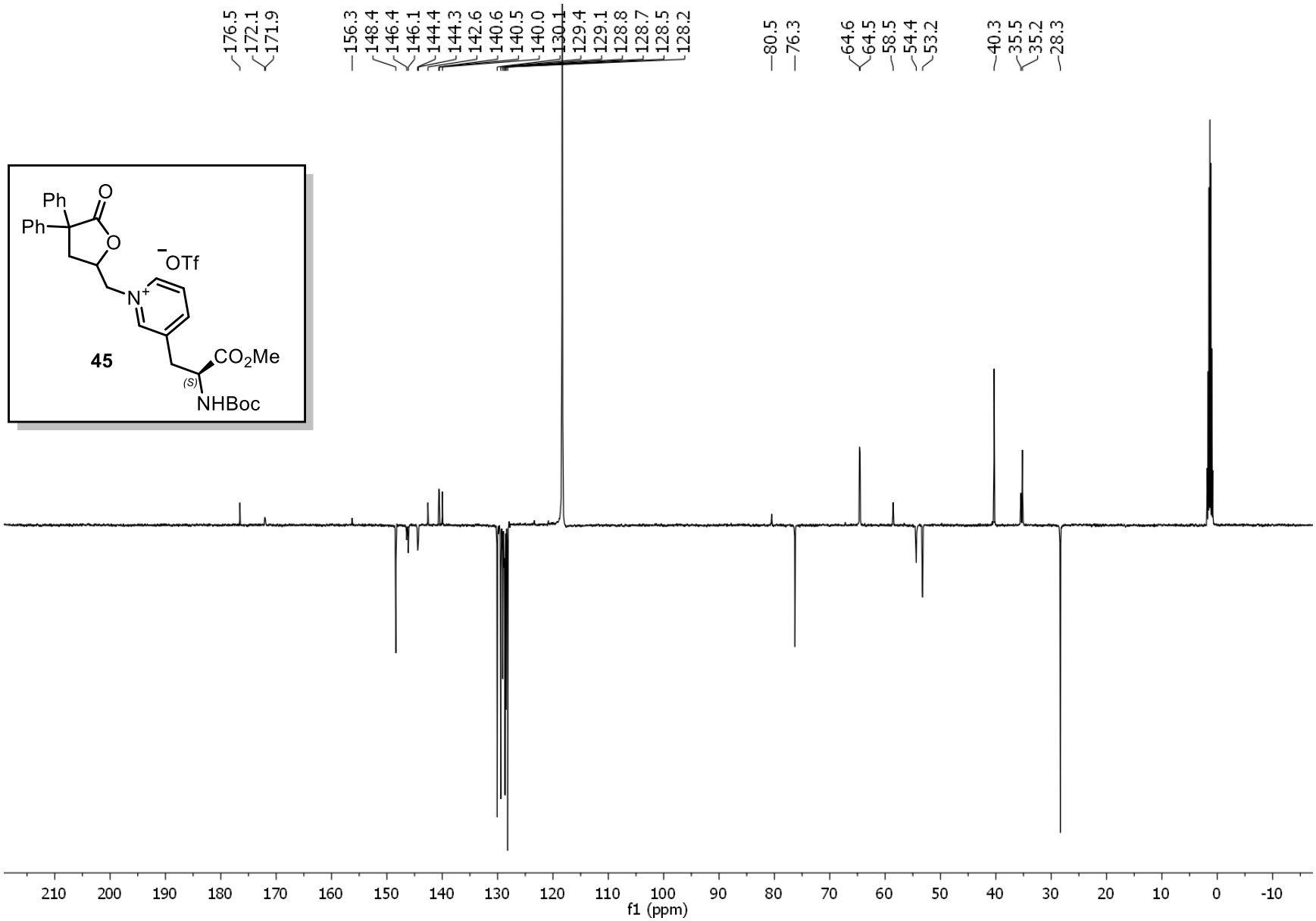
4.95
4.94
4.93
4.85
4.83
4.82
4.81
4.80
4.79
4.78
4.77
4.76
4.75
4.75
3.40
3.39
3.39
3.38
3.37
3.36
3.35
2.93
2.91
2.90
2.88
2.79
Ph
Ph
O
O
Me
N+
N
OTf
41
*
1.00
1.06
0.98
13.32
1.07
2.19
1.07
1.12
3.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

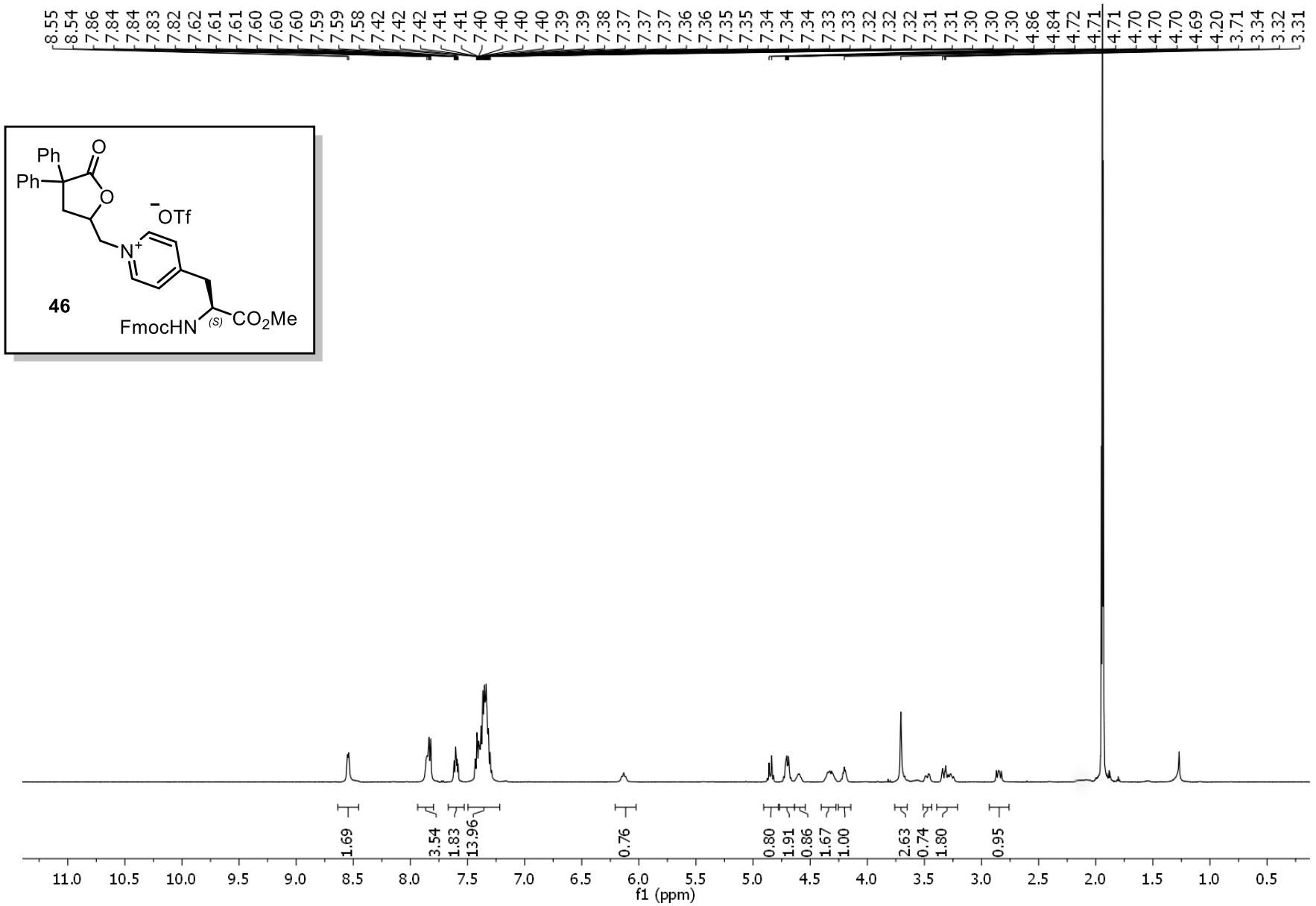

176.4
163.4
151.3
142.3
139.9
137.4
134.8
130.1
129.4
129.1
128.6
128.5
128.1
75.7
71.5
65.0
58.5
40.2
22.7
Ph
Ph
O
O
Me
N+
N
OTf
41
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

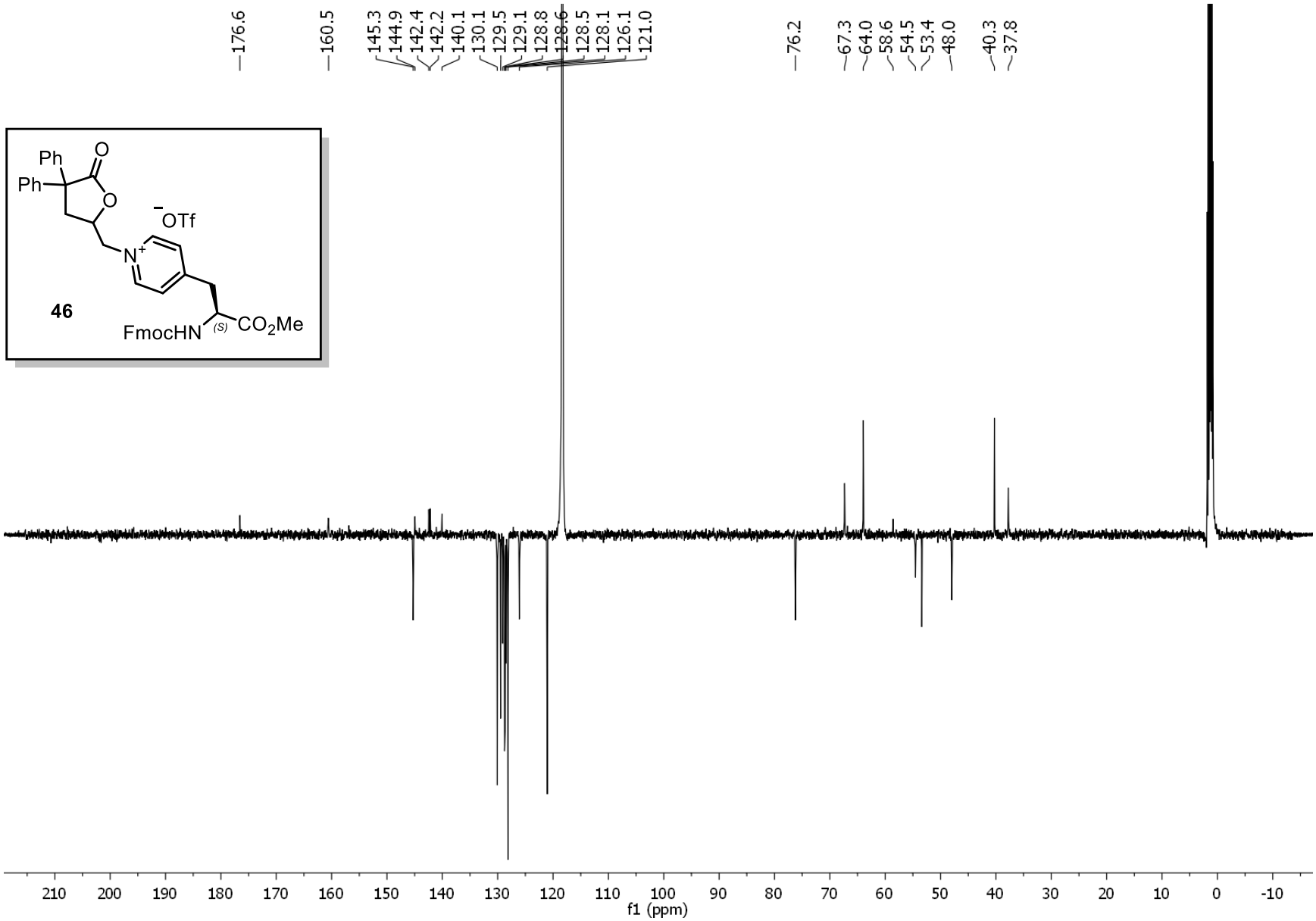

Ph
Ph
O
O
N+
N
Me
OTf
42
1.01
11.75
1.35
0.96
1.05
3.06
1.02
1.00
f1 (ppm)

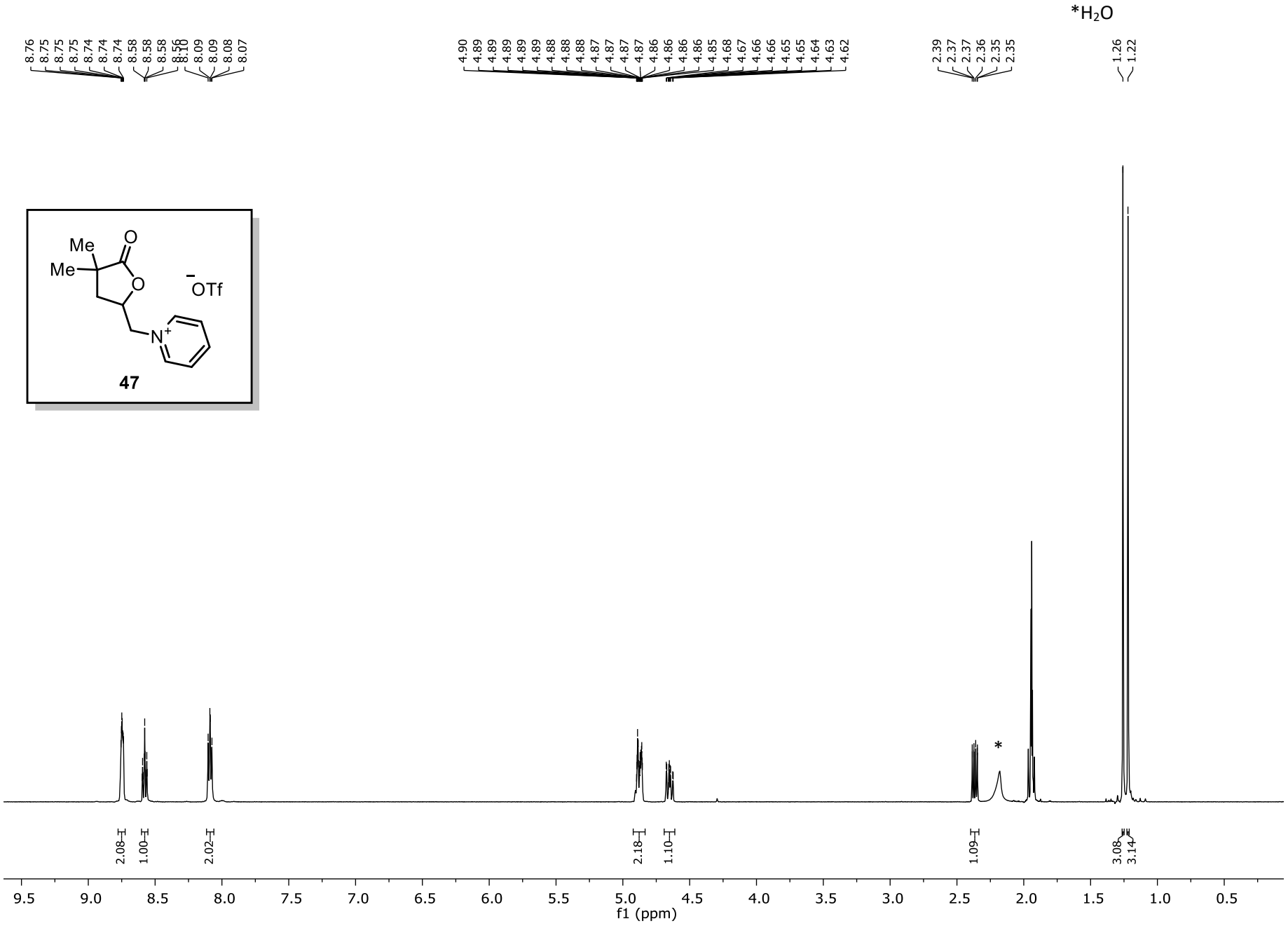

176.9
142.7
140.2
130.0
129.4
129.0
128.7
128.4
128.2
124.8
124.0
76.2
58.7
52.8
40.1
37.0
Ph
Ph
O
O
N+
N
Me
OTf
42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

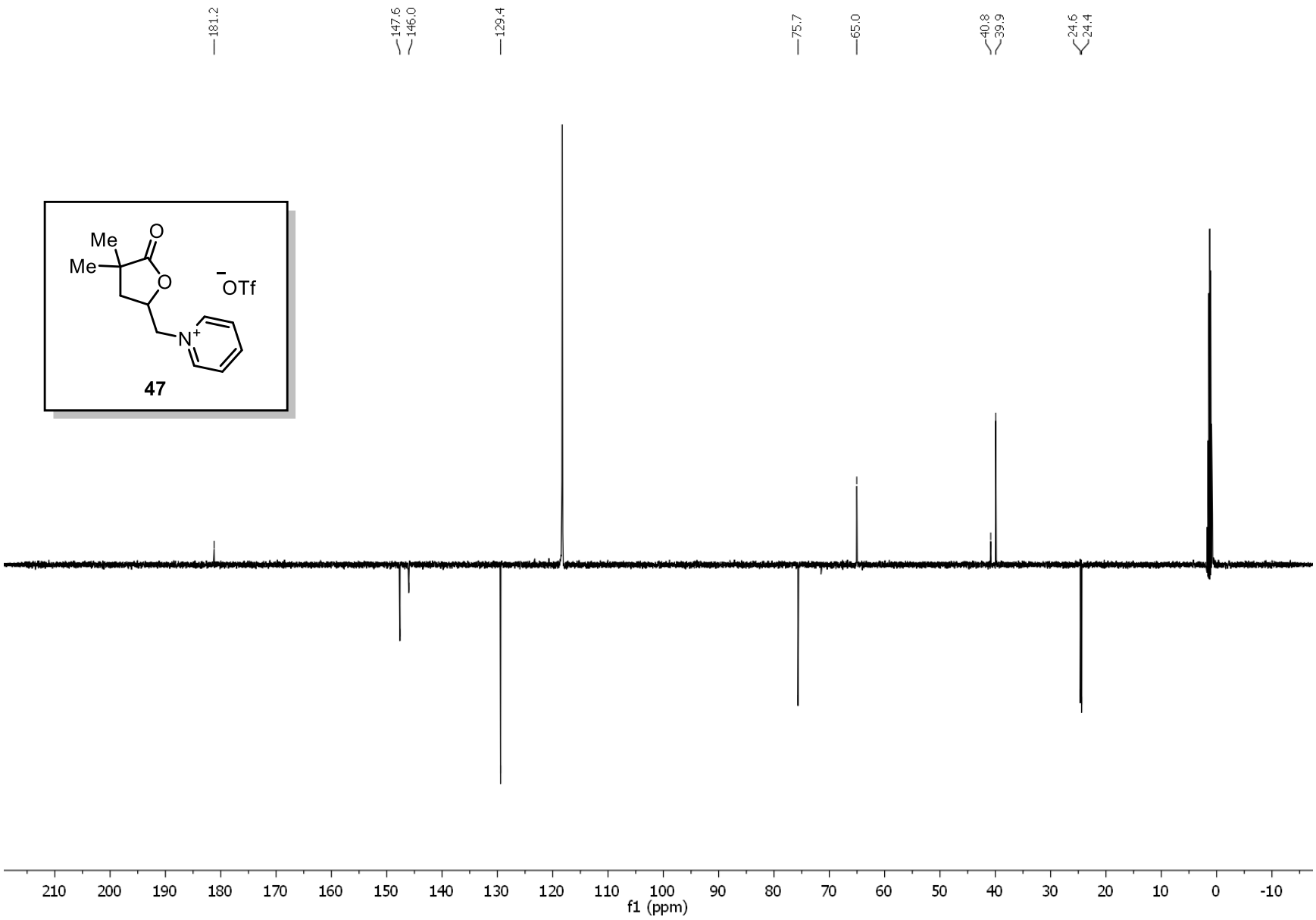

8.70 8.67 8.63 8.62 8.61 8.41 7.99 7.99 7.98 7.98 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.30 7.29 4.94 4.91 4.91 4.78 4.78 4.77 4.77 4.77 4.76 4.76 4.75 3.70 3.68 3.39 3.39 3.38 3.38 3.37 3.36 3.14 3.13 2.87 1.29 1.26
Ph
Ph
O
O
OTf
N+
CO2Me
(S)
NHBoc
45
1.07 1.12 0.88 1.06 10.57 1.25 1.19 2.26 1.01 3.10 2.05 1.15 1.00 10.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

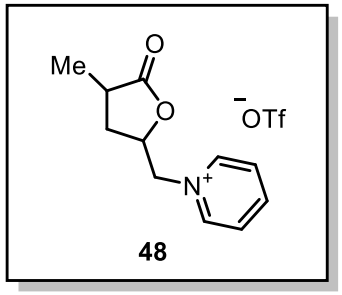

176.5
172.1
171.9
156.3
148.4
146.4
146.1
144.4
144.3
142.6
140.6
140.5
140.0
130.1
129.4
129.1
128.8
128.7
128.5
128.2
80.5
76.3
64.6
64.5
58.5
54.4
53.2
40.3
35.5
35.2
28.3
Ph
Ph
O
O
OTf
N+
CO2Me
(S)
NHBoc
45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.55 8.54 7.86 7.84 7.84 7.83 7.82 7.62 7.61 7.61 7.60 7.60 7.60 7.59 7.59 7.58 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.30 4.86 4.84 4.72 4.71 4.71 4.70 4.70 4.70 4.69 4.20 3.71 3.34 3.32 3.31
Ph
Ph
O
O
OTf
N+
46
FmocHN
(S)
CO2Me
1.69
3.54
1.83
13.96
0.76
0.80
1.91
0.86
1.67
1.00
2.63
0.74
1.80
0.95
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

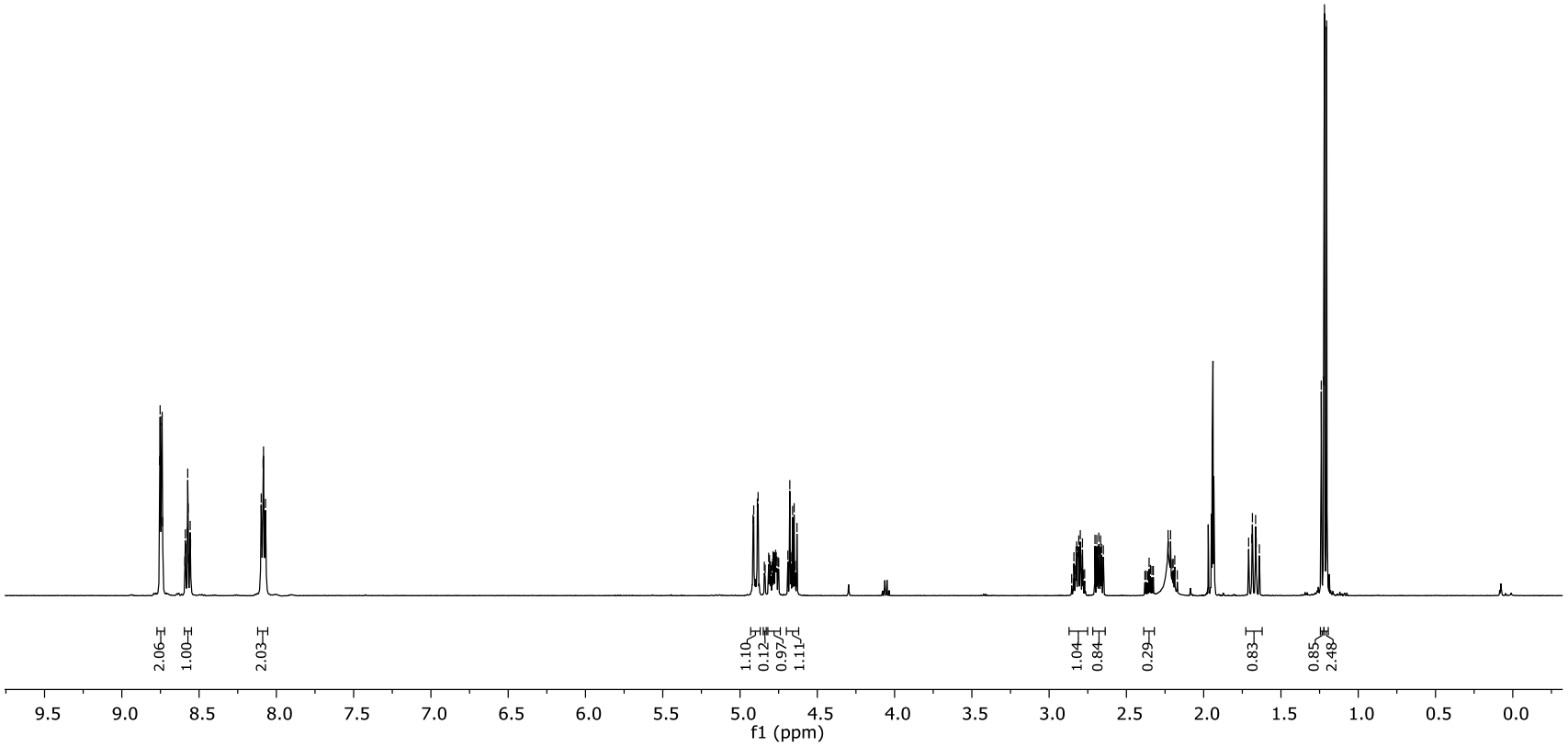

176.6
160.5
145.3
144.9
142.4
142.2
140.1
130.1
129.5
129.1
128.8
128.6
128.5
128.1
126.1
121.0
76.2
67.3
64.0
58.6
54.5
53.4
48.0
40.3
37.8
Ph
Ph
O
O
OTf
N+
46
FmocHN
(S)
CO2Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

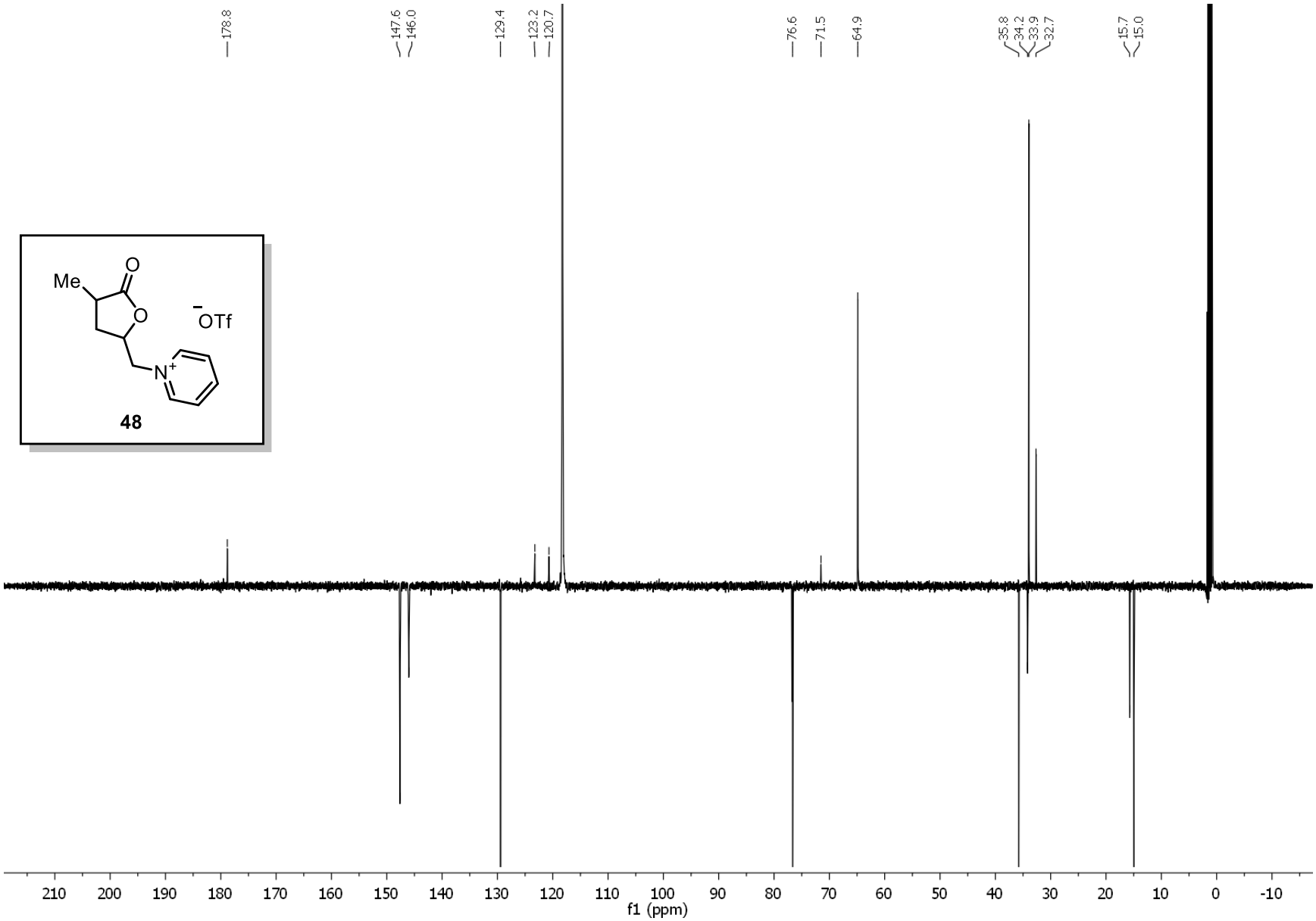

*H2O
8.76 8.75 8.75 8.75 8.74 8.74 8.74 8.58 8.58 8.58 8.56 8.10 8.09 8.09 8.08 8.07
4.90 4.89 4.89 4.89 4.89 4.89 4.88 4.88 4.88 4.87 4.87 4.87 4.87 4.86 4.86 4.86 4.86 4.85 4.68 4.67 4.66 4.66 4.65 4.65 4.64 4.63 4.62
2.39 2.37 2.37 2.36 2.35 2.35
1.26 1.22
Me
Me
O
O
OTf
N+
47
*
2.08 1.00 2.02 2.18 1.10 1.09 3.08 3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

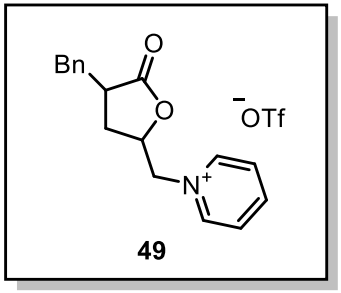

181.2
147.6
146.0
129.4
75.7
65.0
40.8
39.9
24.6
24.4
Me
Me
O
O
OTf
N+
47
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
O
O
OTf
N+

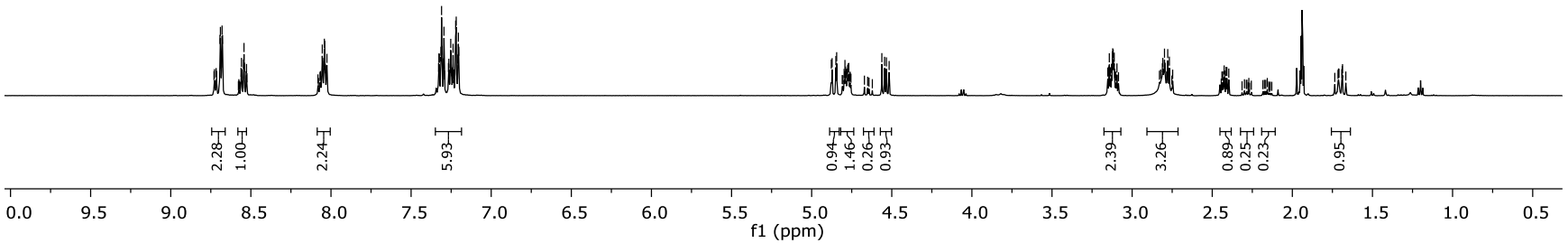
48

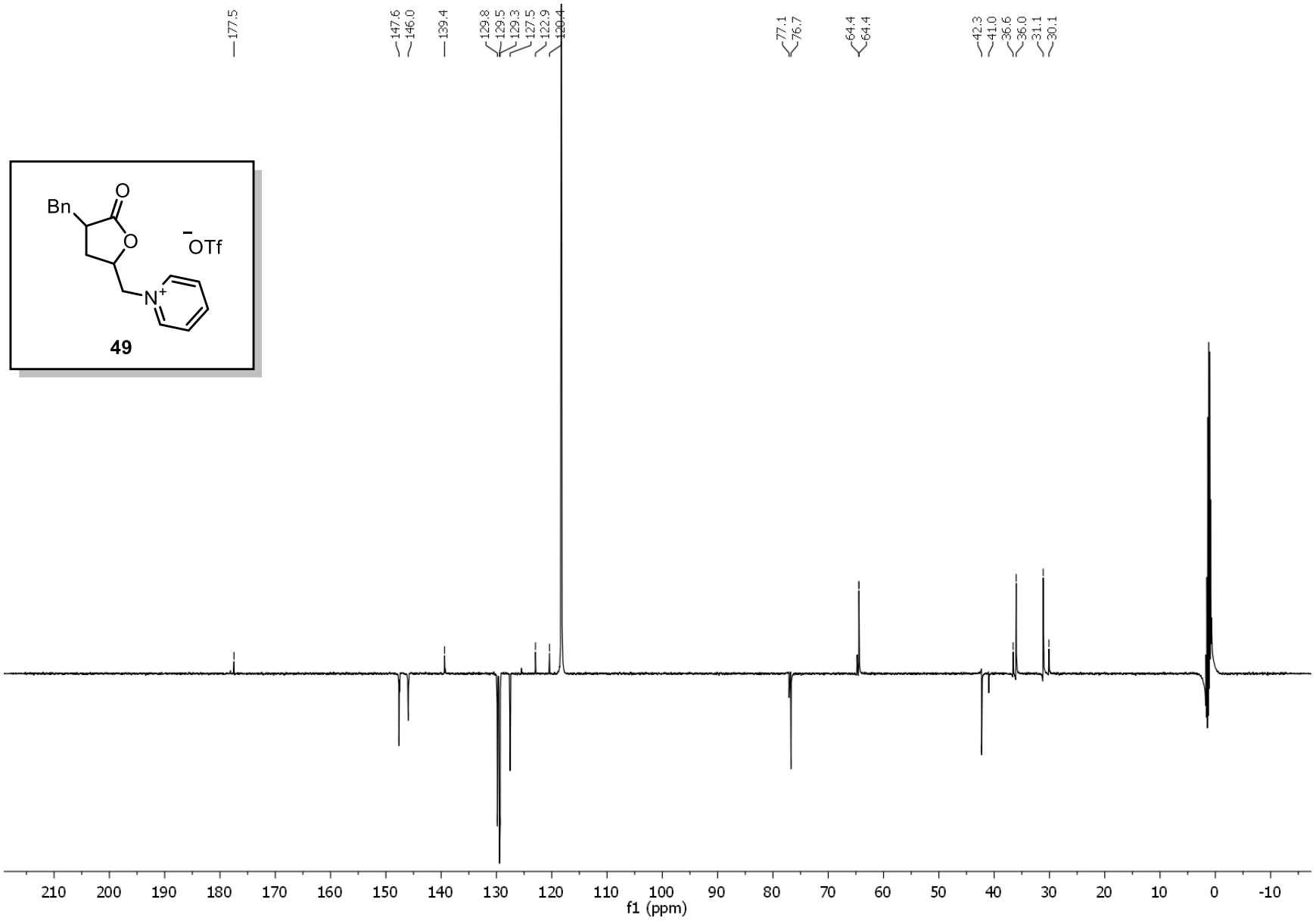

2.06
1.00
2.03
1.10
0.12
0.97
1.11
1.04
0.84
0.29
0.83
0.85
2.48
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

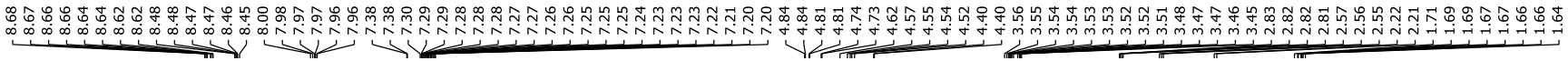

178.8
147.6
146.0
129.4
123.2
120.7
76.6
71.5
64.9
35.8
34.2
33.9
32.7
15.7
15.0
Me
O
O
N+
OTf
48
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

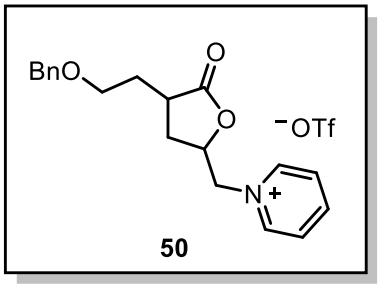

Bn
O
O
OTf
N+

49

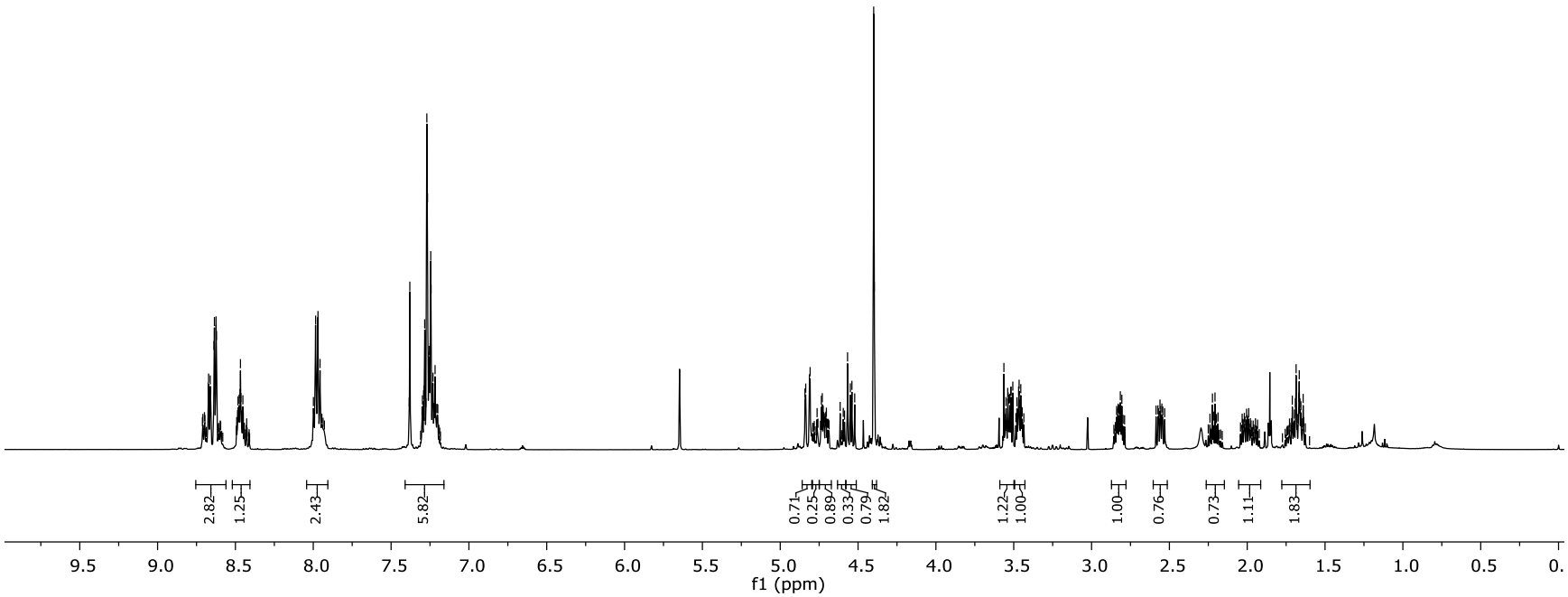

2.28
1.00
2.24
5.93
0.94
1.46
0.26
0.93
2.39
3.26
0.89
0.25
0.23
0.95
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

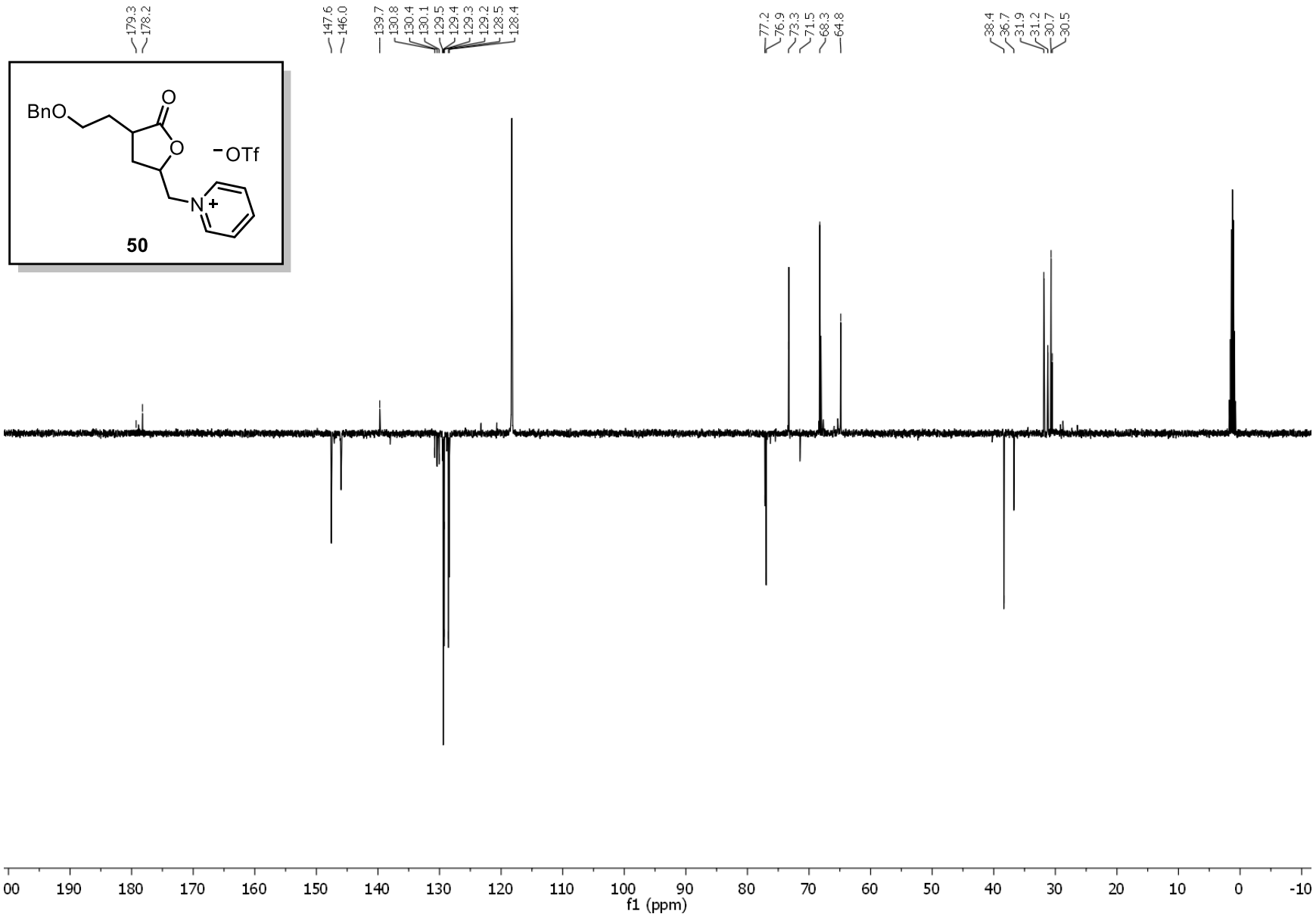

177.5
147.6
146.0
139.4
129.8
129.5
129.3
127.5
122.9
120.4
77.1
76.7
64.4
64.4
42.3
41.0
36.6
36.0
31.1
30.1
Bn
O
O
OTf
N+
49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

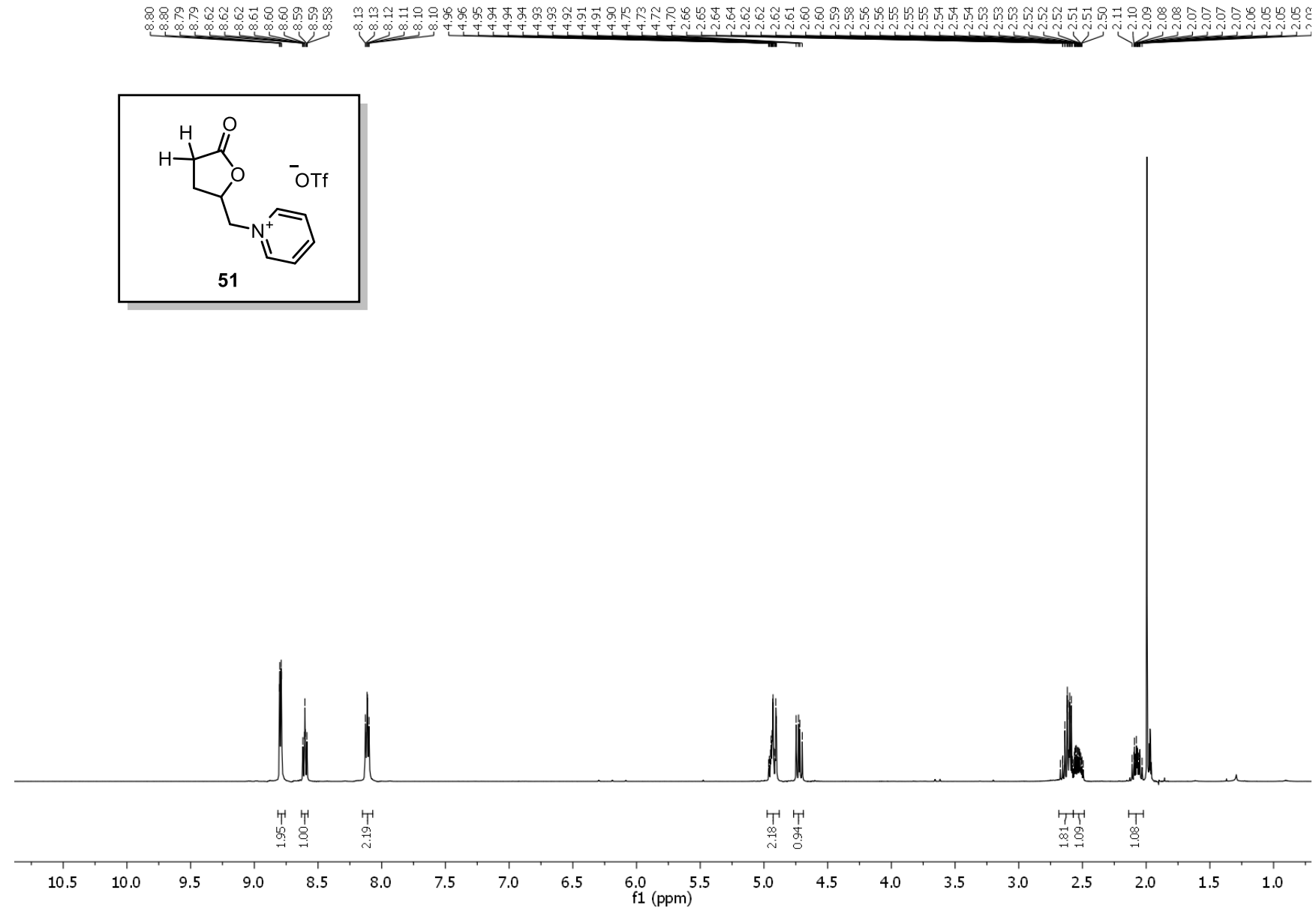

8.68 8.67 8.66 8.66 8.64 8.64 8.62 8.62 8.48 8.48 8.47 8.47 8.46 8.45 8.00 7.98 7.97 7.97 7.96 7.96 7.38 7.38 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.21 7.20 7.20 4.84 4.84 4.81 4.81 4.74 4.73 4.62 4.57 4.55 4.54 4.52 4.40 4.40 3.56 3.55 3.54 3.53 3.53 3.52 3.52 3.51 3.48 3.47 3.47 3.46 3.45 2.83 2.82 2.82 2.81 2.57 2.56 2.55 2.22 2.21 1.71 1.69 1.69 1.67 1.67 1.66 1.66 1.64

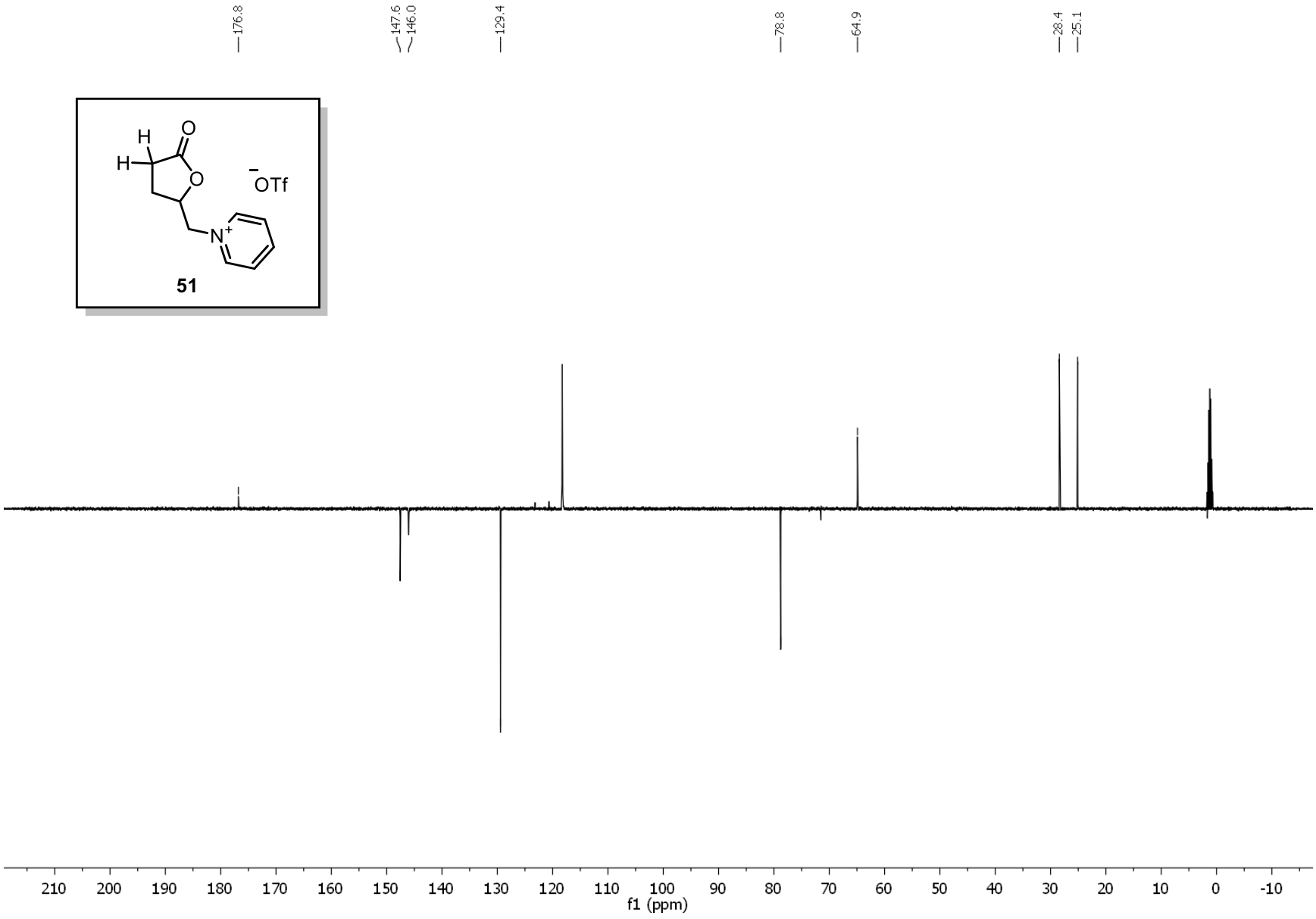

BnO
O
O
⁻OTf
N+

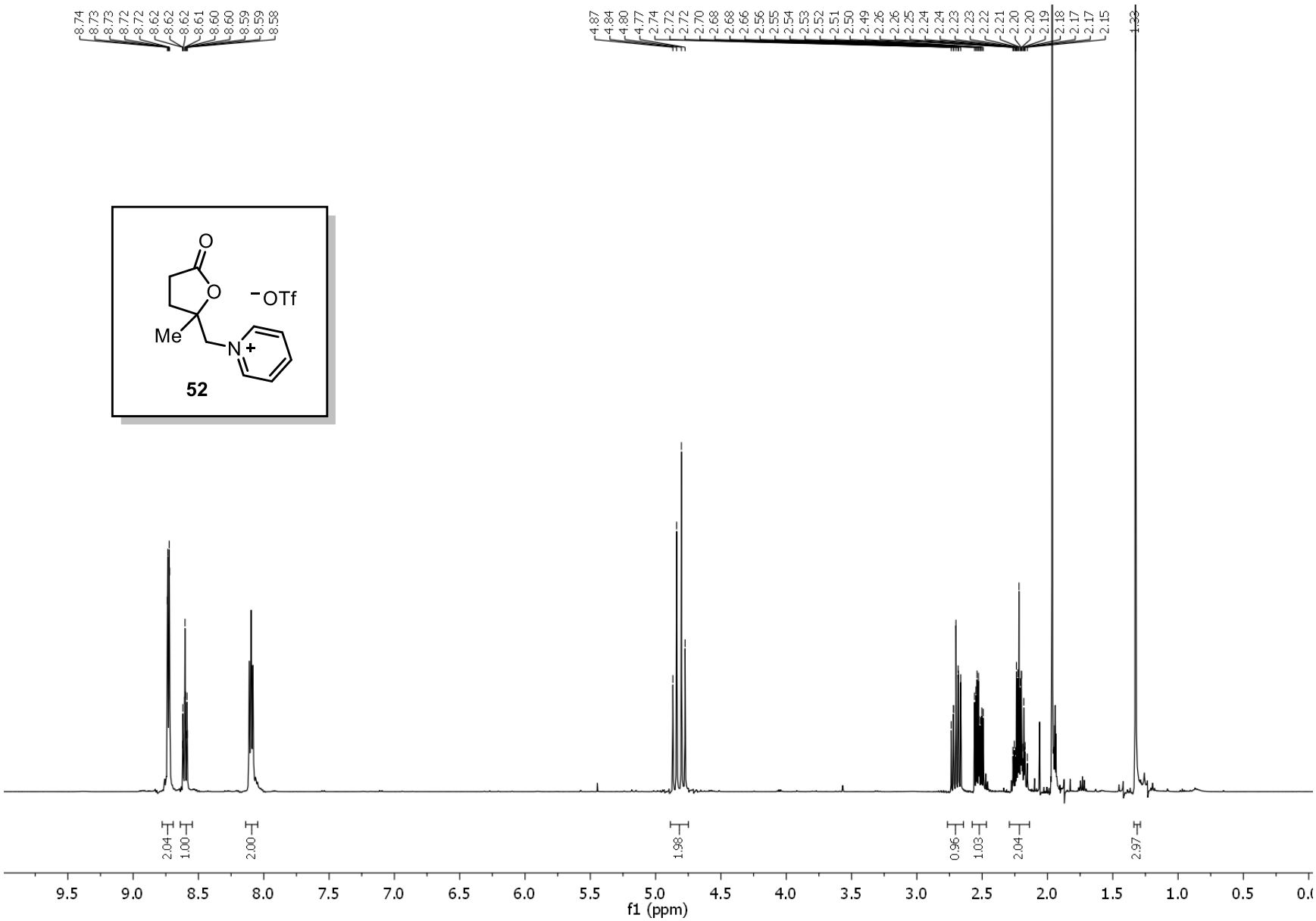
50

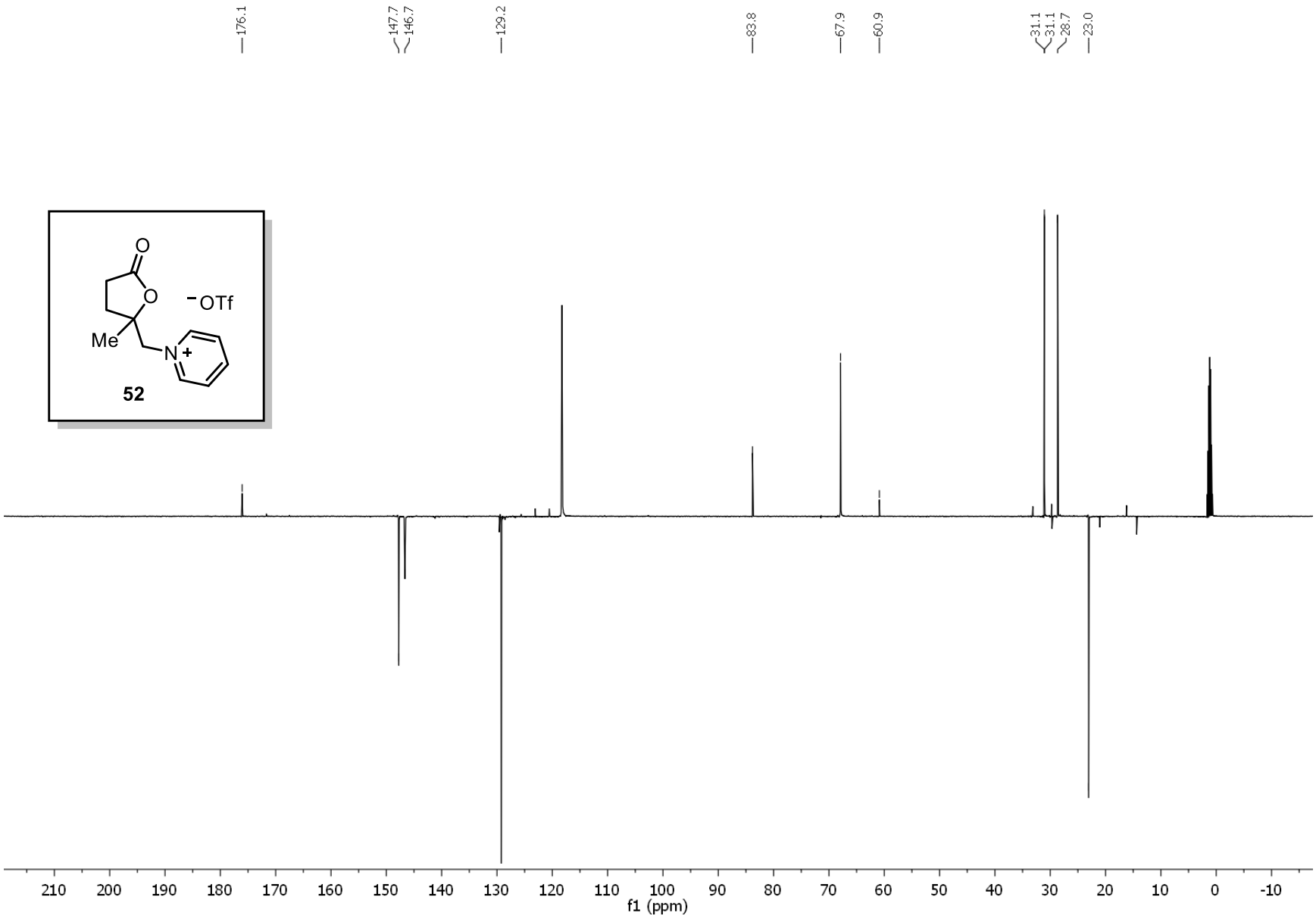

2.82
1.25
2.43
5.82
0.71
0.25
0.89
0.33
0.79
1.82
1.22
1.00
1.00
0.76
0.73
1.11
1.83
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

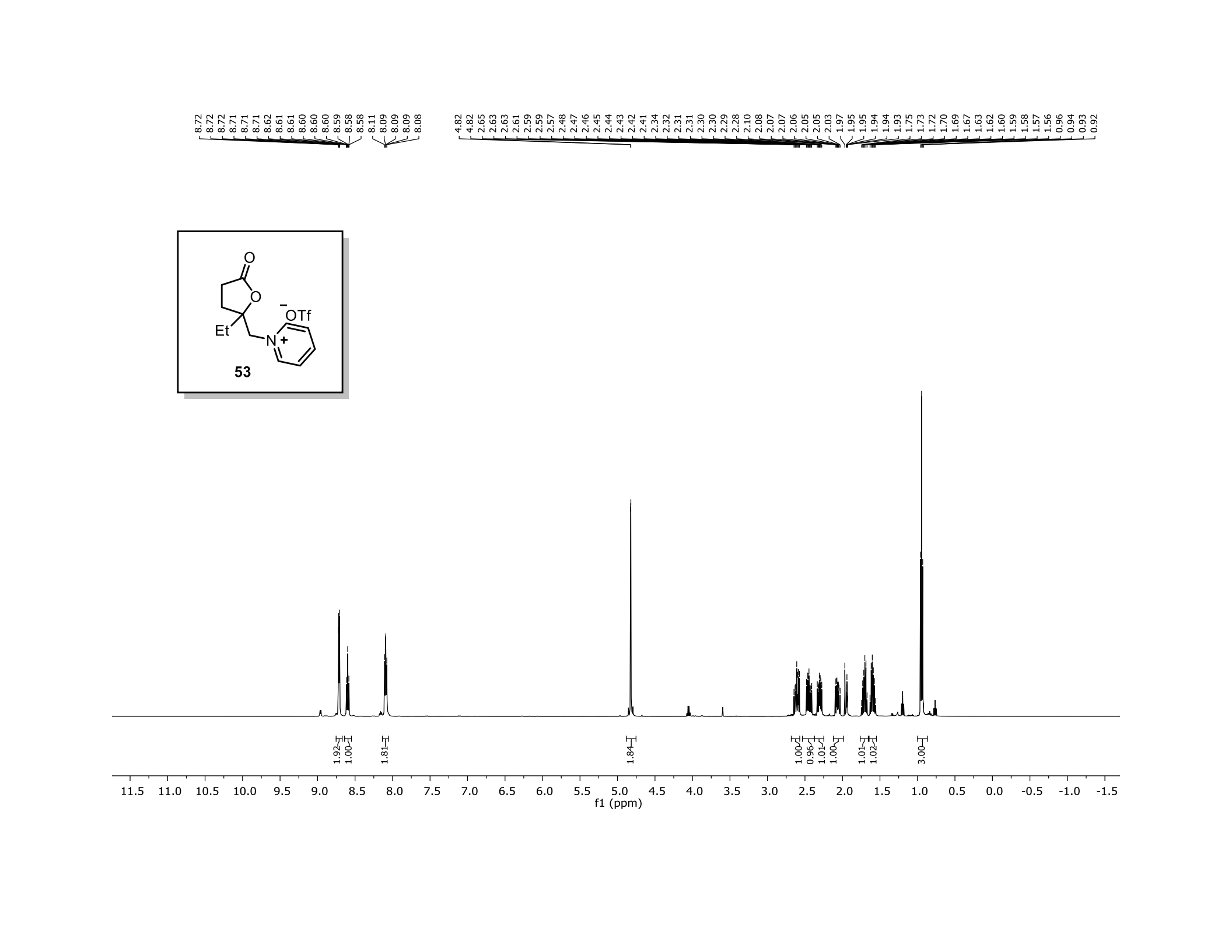

179.3
178.2
147.6
146.0
139.7
130.8
130.4
130.1
129.5
129.4
129.3
129.2
128.5
128.4
77.2
76.9
73.3
71.5
68.3
64.8
38.4
36.7
31.9
31.2
30.7
30.5
BnO
O
O
−OTf
N+
50
f1 (ppm)

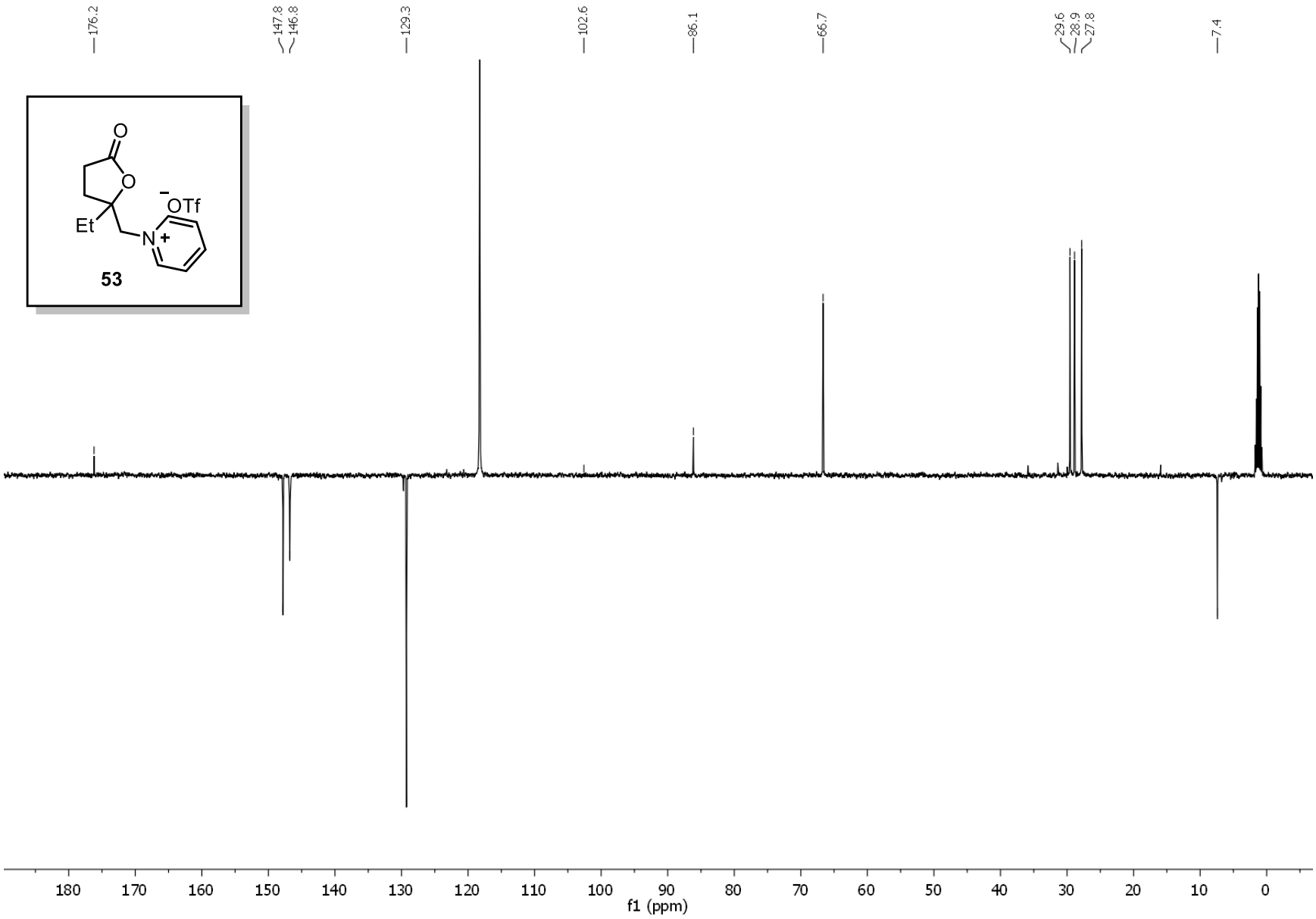

H
H
O
O
OTf
N+
51
1.95
1.00
2.19
2.18
0.94
1.81
1.09
1.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

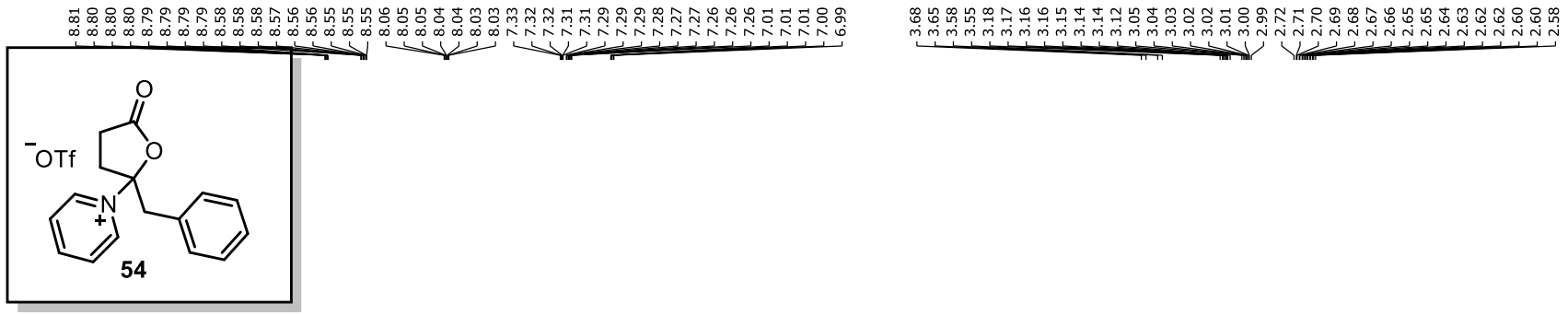

176.8
147.6
146.0
129.4
78.8
64.9
28.4
25.1
H
H
O
O
OTf
N+
51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

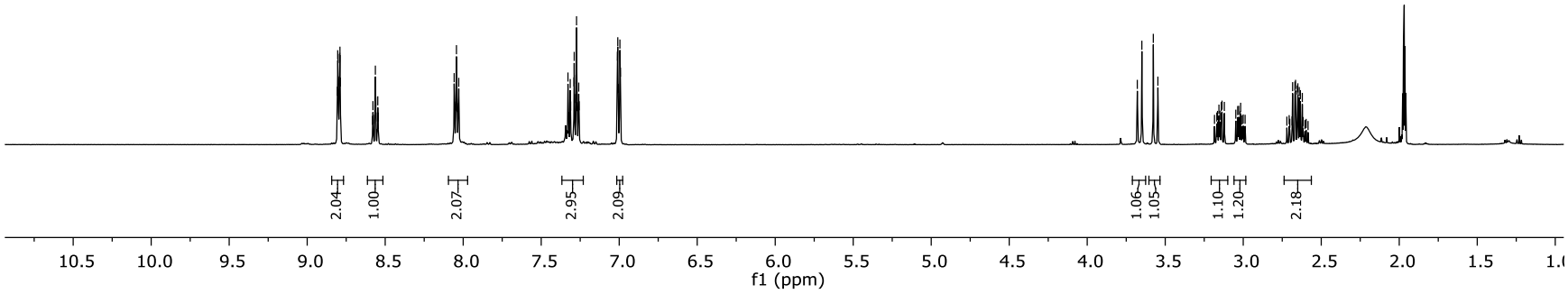

8.74
8.73
8.73
8.72
8.72
8.62
8.62
8.62
8.61
8.60
8.60
8.59
8.59
8.58
4.87
4.84
4.80
4.77
2.74
2.72
2.72
2.70
2.68
2.68
2.66
2.56
2.55
2.54
2.53
2.52
2.51
2.50
2.49
2.26
2.26
2.25
2.24
2.24
2.23
2.23
2.22
2.21
2.20
2.20
2.19
2.18
2.17
2.17
2.15
1.33
O
O
OTf
Me
N+
52
2.04
1.00
2.00
1.98
0.96
1.03
2.04
2.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

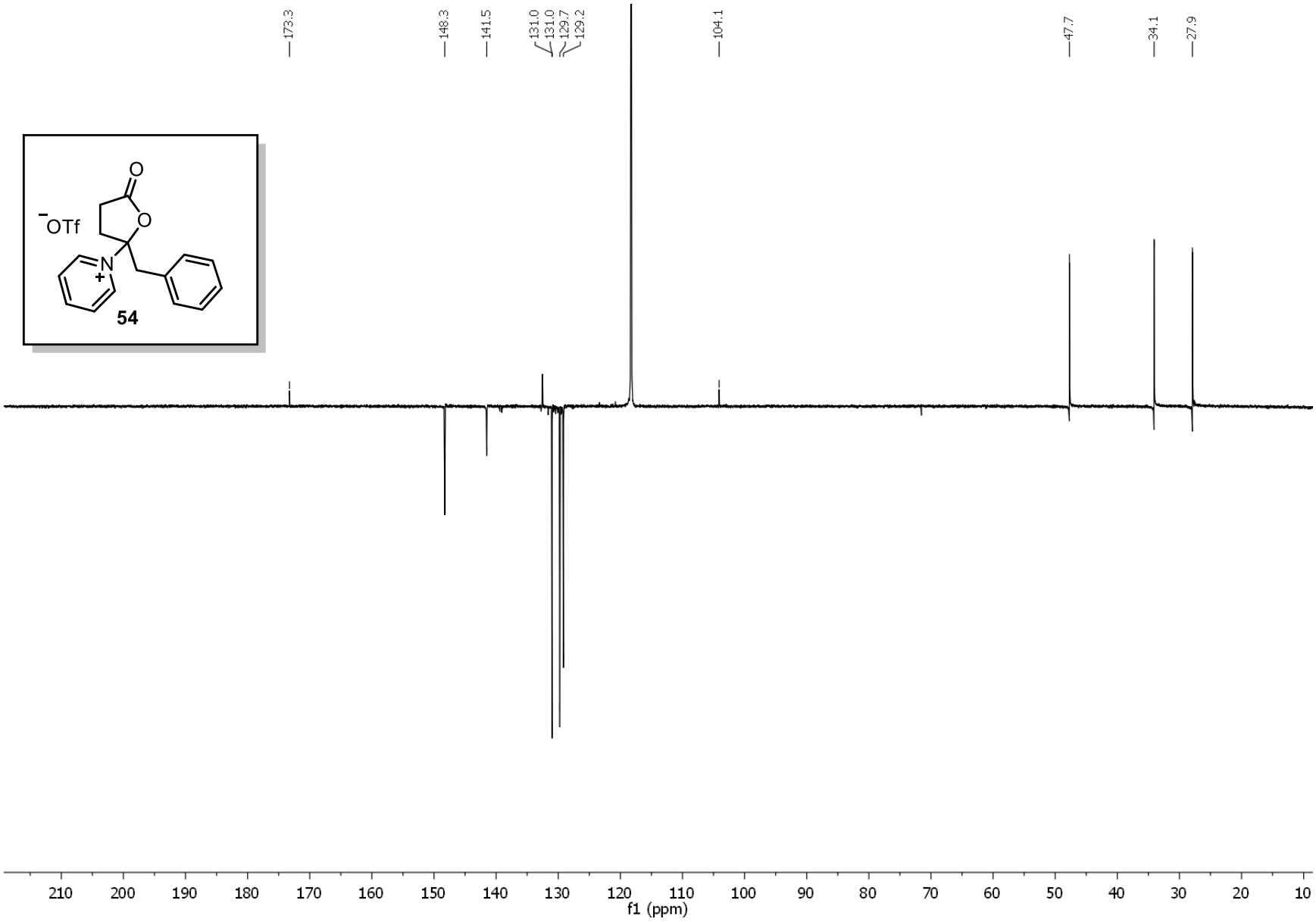

176.1
147.7
146.7
129.2
83.8
67.9
60.9
31.1
31.1
28.7
23.0
O
O
⁻OTf
Me
N+
52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

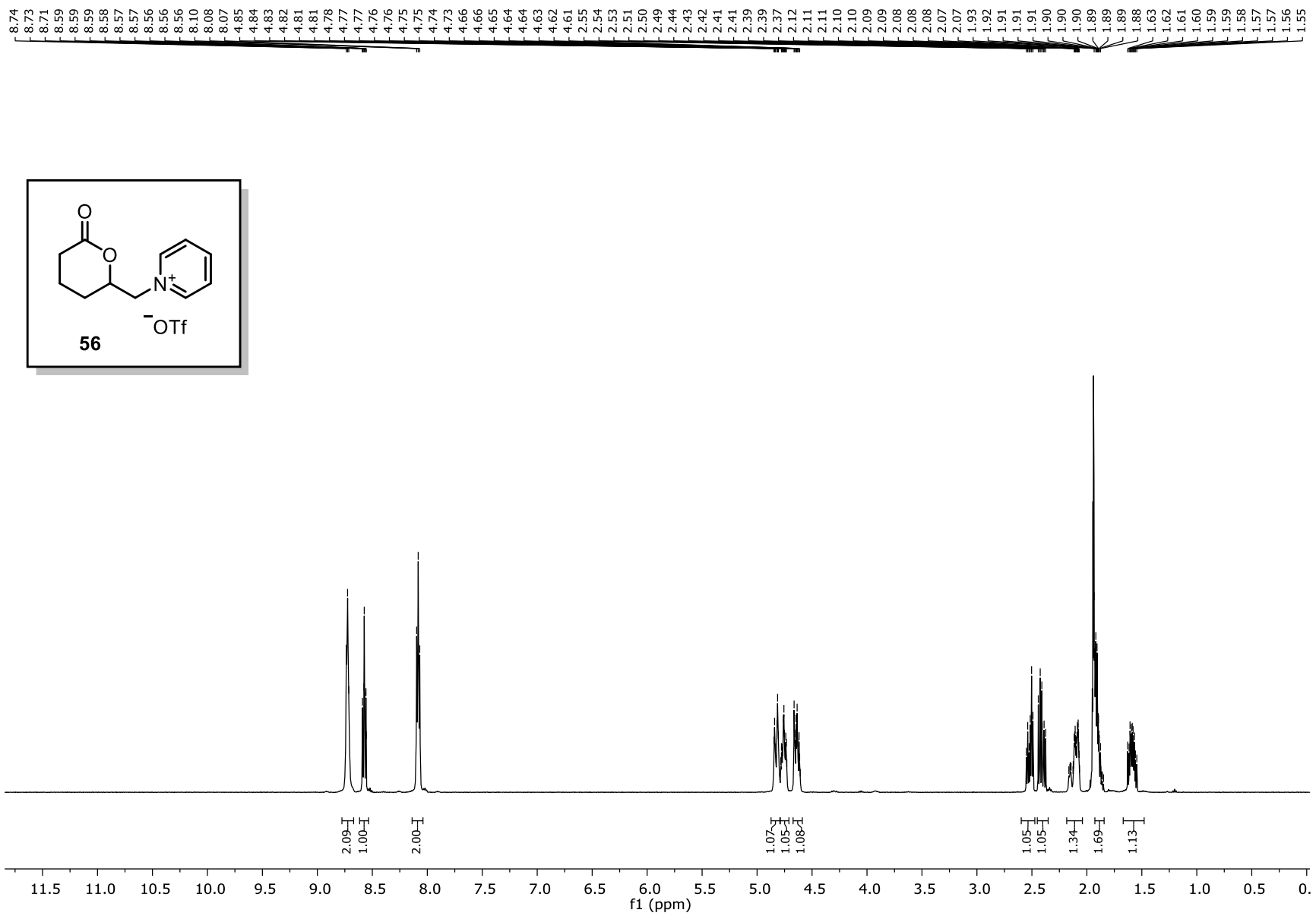

8.72 8.72 8.72 8.71 8.71 8.71 8.62 8.61 8.61 8.60 8.60 8.60 8.59 8.58 8.58 8.11 8.09 8.09 8.09 8.08
4.82 4.82 2.65 2.63 2.63 2.61 2.59 2.59 2.57 2.48 2.47 2.46 2.45 2.44 2.43 2.42 2.41 2.34 2.32 2.31 2.31 2.30 2.30 2.29 2.28 2.10 2.08 2.07 2.07 2.06 2.05 2.05 2.03 1.97 1.95 1.95 1.94 1.94 1.93 1.75 1.73 1.72 1.70 1.69 1.67 1.63 1.62 1.60 1.59 1.58 1.57 1.56 0.96 0.94 0.93 0.92
O
O
Et
N+
OTf
53
1.92
1.00
1.81
1.84
1.00
0.96
1.01
1.00
1.01
1.02
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

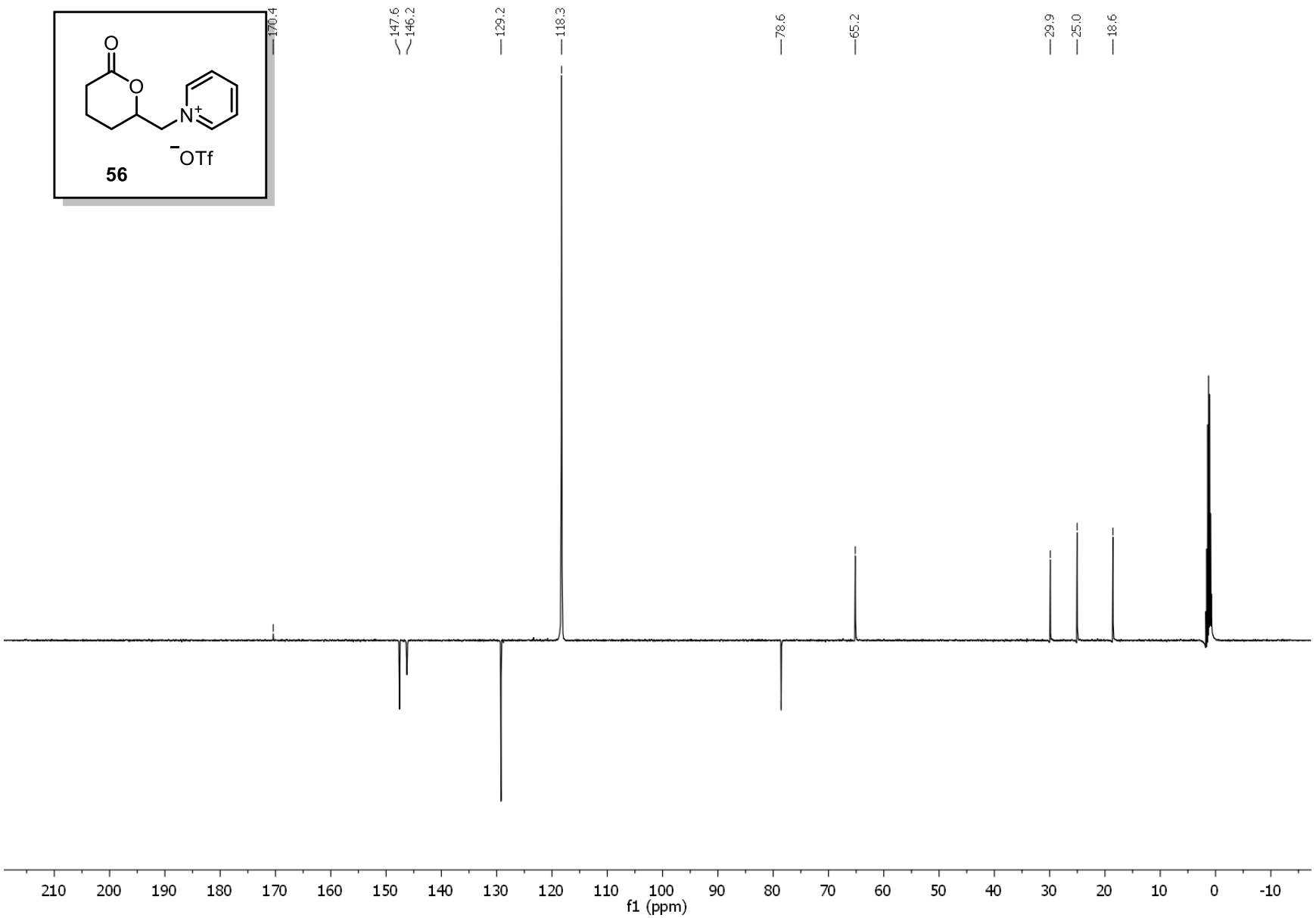

176.2
147.8
146.8
129.3
102.6
86.1
66.7
29.6
28.9
27.8
7.4
O
O
Et
N+
OTf
53
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

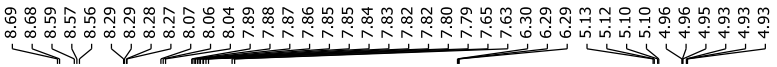

8.81 8.80 8.80 8.80 8.79 8.79 8.79 8.79 8.58 8.58 8.58 8.57 8.56 8.56 8.55 8.55 8.55 8.06 8.05 8.05 8.04 8.04 8.03 8.03 7.33 7.32 7.32 7.31 7.31 7.29 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.26 7.01 7.01 7.01 7.00 6.99
3.68 3.65 3.58 3.55 3.18 3.17 3.16 3.16 3.15 3.14 3.14 3.12 3.05 3.04 3.03 3.02 3.02 3.01 3.00 2.99 2.72 2.71 2.70 2.69 2.68 2.67 2.66 2.65 2.65 2.64 2.63 2.62 2.62 2.60 2.60 2.58
OTf
O
O
N
+
54

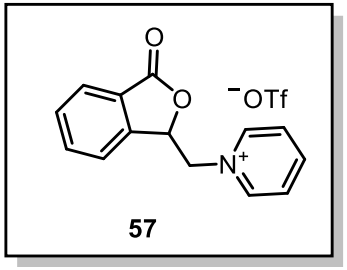

2.04
1.00
2.07
2.95
2.09
1.06
1.05
1.10
1.20
2.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)


173.3
148.3
141.5
131.0
131.0
129.7
129.2
104.1
47.7
34.1
27.9
OTf
O
O
N
54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

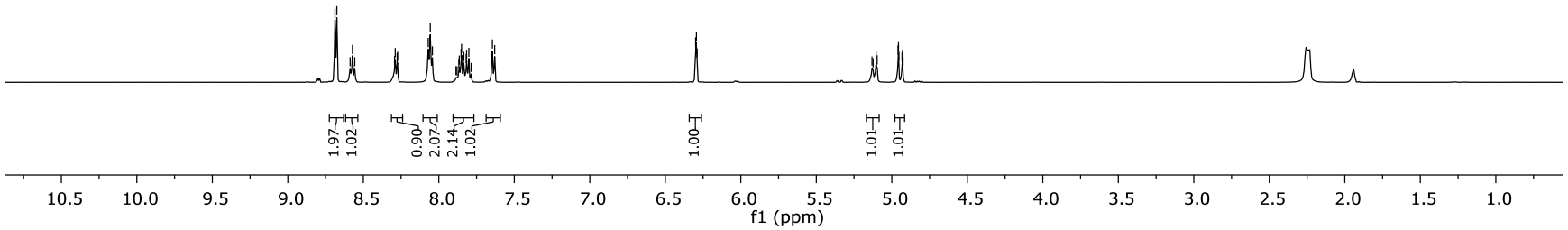

8.74 8.73 8.71 8.59 8.59 8.59 8.58 8.57 8.57 8.56 8.56 8.56 8.10 8.08 8.07 4.85 4.84 4.83 4.82 4.81 4.81 4.78 4.77 4.77 4.76 4.76 4.75 4.75 4.74 4.73 4.66 4.66 4.65 4.64 4.64 4.63 4.62 4.61 2.55 2.54 2.53 2.51 2.50 2.49 2.44 2.43 2.42 2.41 2.41 2.39 2.39 2.37 2.12 2.11 2.11 2.10 2.09 2.09 2.08 2.08 2.08 2.07 2.07 1.93 1.92 1.91 1.91 1.91 1.90 1.90 1.90 1.89 1.89 1.89 1.88 1.63 1.62 1.61 1.60 1.59 1.59 1.58 1.57 1.57 1.56 1.55
O
O
N+
−OTf
56
2.09
1.00
2.00
1.07
1.05
1.08
1.05
1.05
1.34
1.69
1.13
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

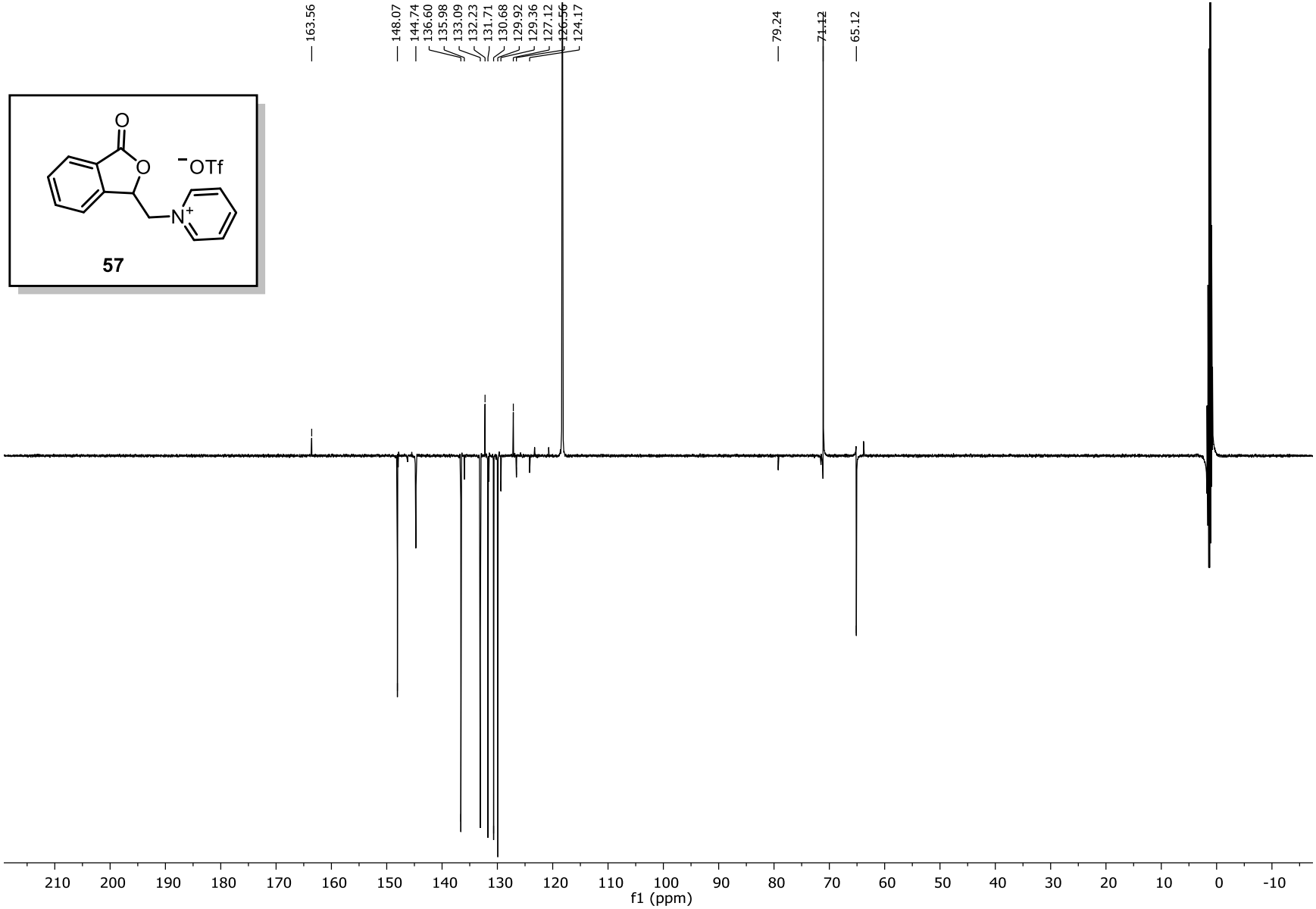

O
O
N+
−OTf
56
170.4
147.6
146.2
129.2
118.3
78.6
65.2
29.9
25.0
18.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.69
8.68
8.59
8.57
8.56
8.29
8.29
8.28
8.27
8.07
8.06
8.04
7.89
7.88
7.87
7.86
7.85
7.85
7.84
7.83
7.82
7.82
7.80
7.79
7.65
7.63
6.30
6.29
5.13
5.12
5.10
5.10
4.96
4.96
4.95
4.93
4.93
4.93


O
O
−OTf
N+

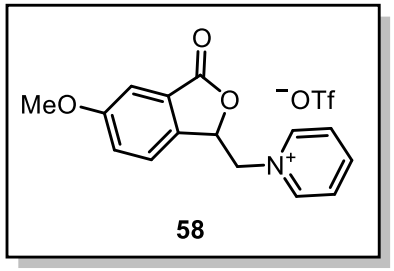
57


1.97
1.02
0.90
2.07
2.14
1.02
1.00
1.01
1.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

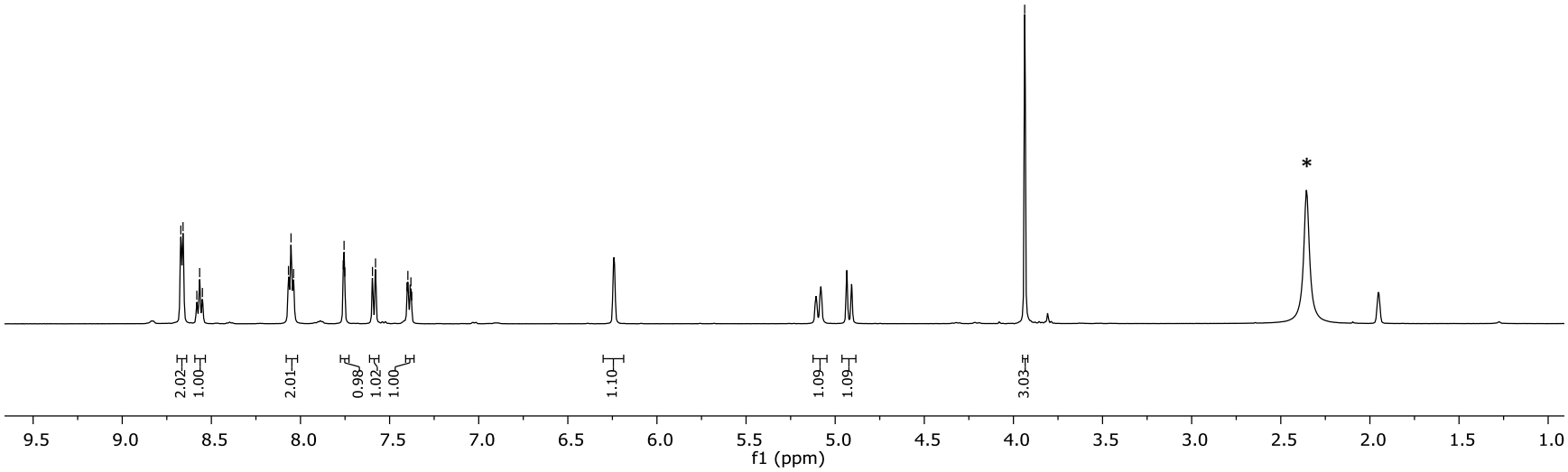

163.56
148.07
144.74
136.60
135.98
133.09
132.23
131.71
130.68
129.92
129.36
127.12
126.56
124.17
79.24
71.12
65.12
O
O
−OTf
N+
57
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

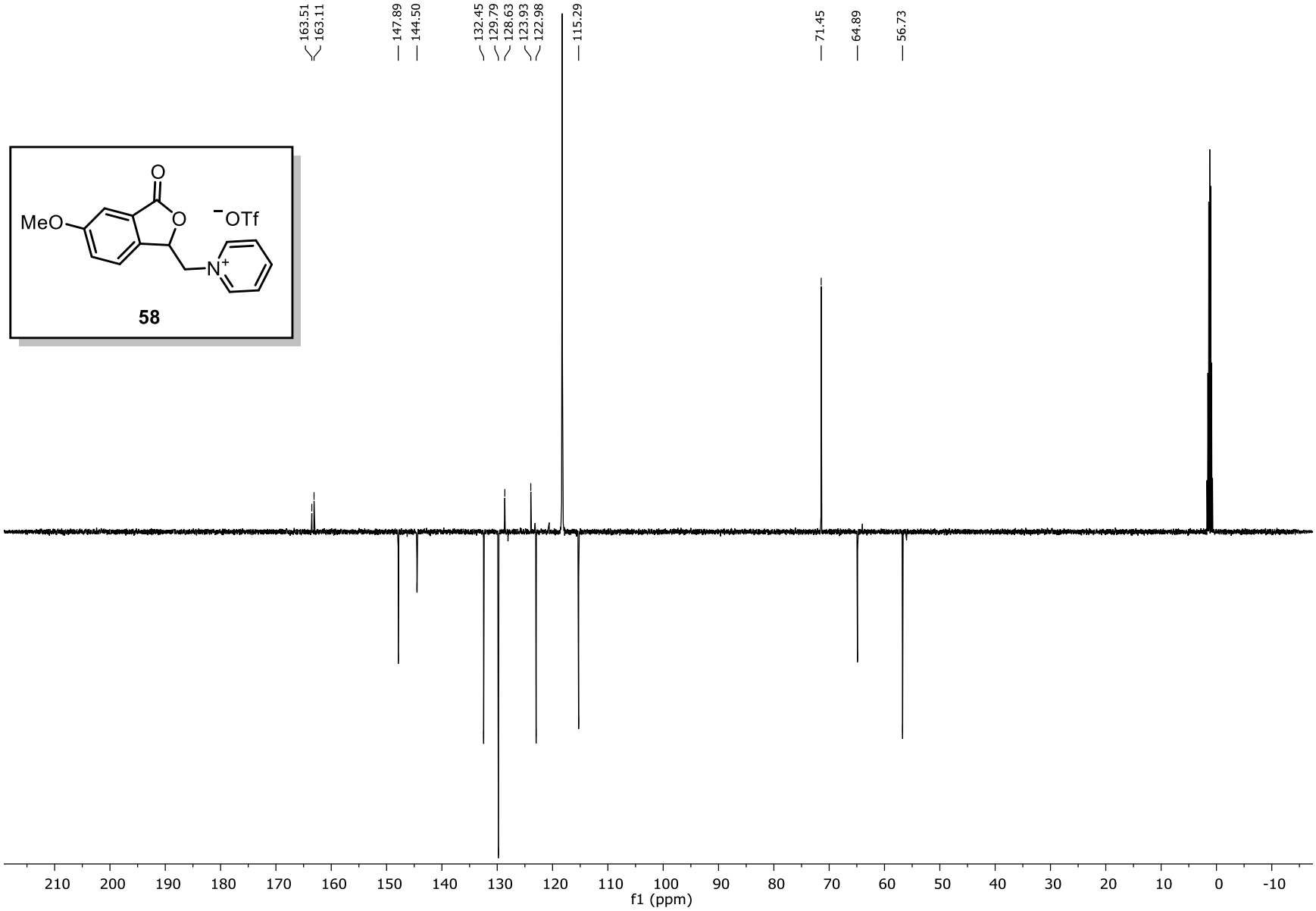
*H_2O

8.67 8.66 8.58 8.57 8.55 8.07 8.05 8.04 7.76 7.76 7.75 7.60 7.58 7.40 7.40 7.39 7.38 7.38 — 3.94



58

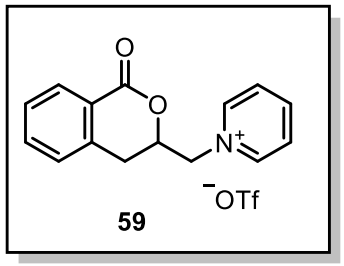



163.51
163.11
147.89
144.50
132.45
129.79
128.63
123.93
122.98
115.29
71.45
64.89
56.73
MeO
O
O
OTf
N+
58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

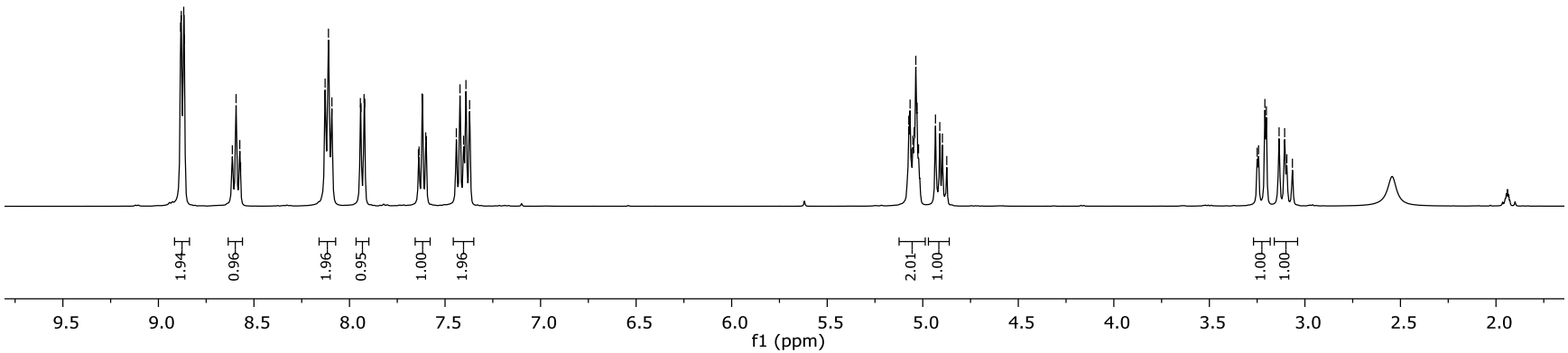
8.88
8.88
8.87
8.86
8.61
8.59
8.57
8.57
8.13
8.11
8.09
7.94
7.94
7.92
7.92
7.64
7.64
7.62
7.62
7.60
7.60
7.44
7.42
7.40
7.39
7.37

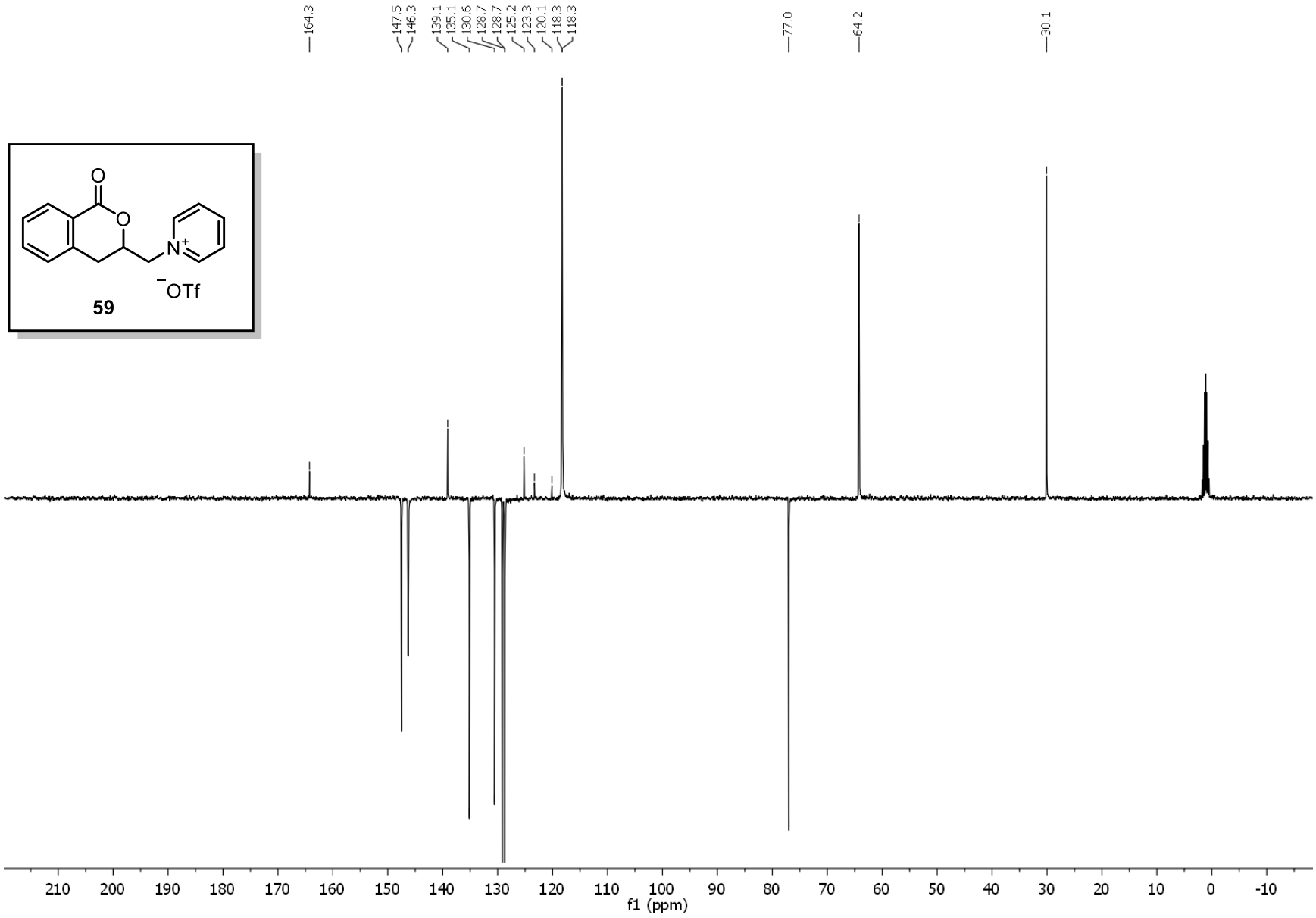
5.07
5.07
5.06
5.05
5.05
5.04
5.03
5.02
4.93
4.91
4.90
4.87

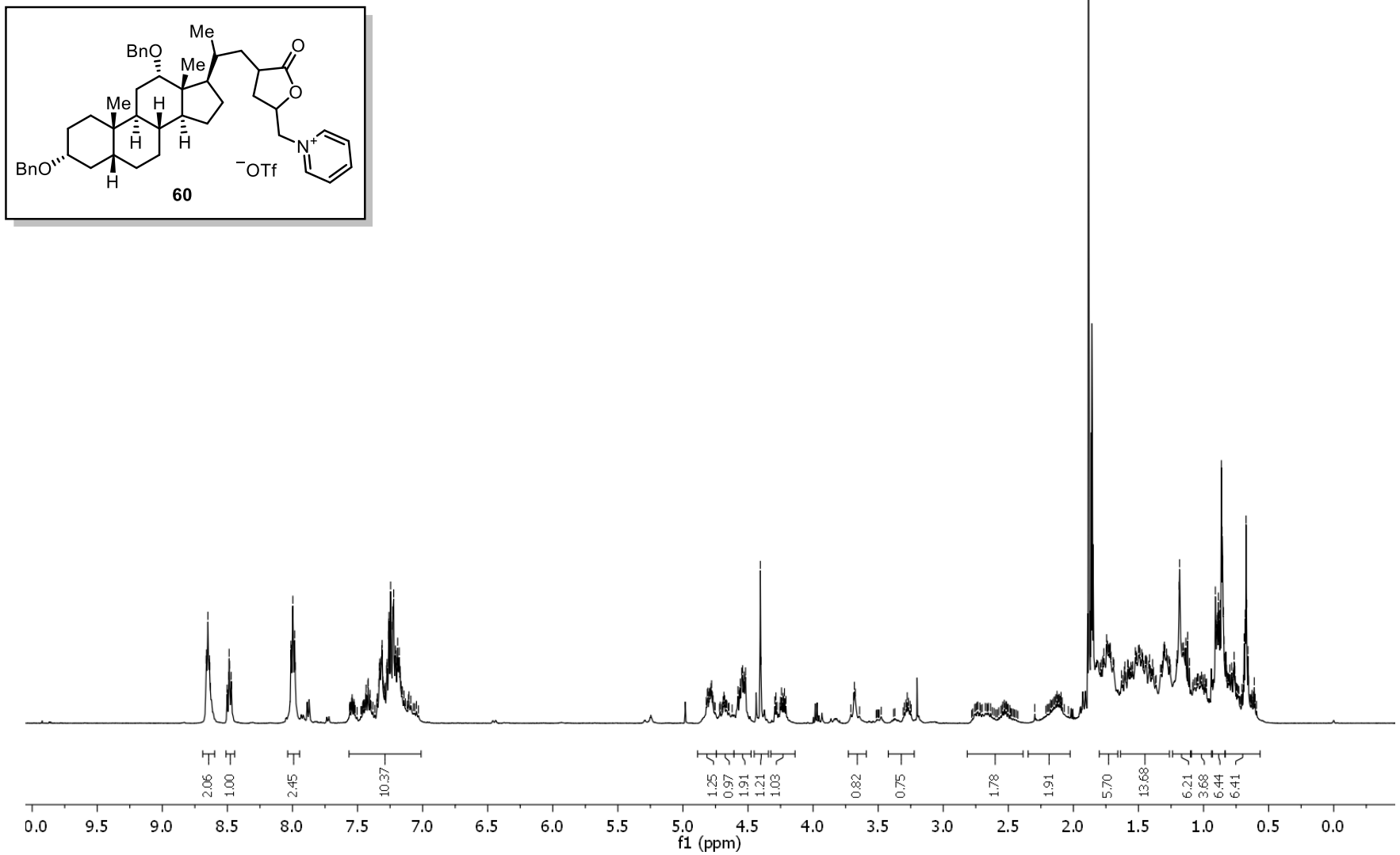
3.25
3.24
3.21
3.20
3.14
3.11
3.09
3.07

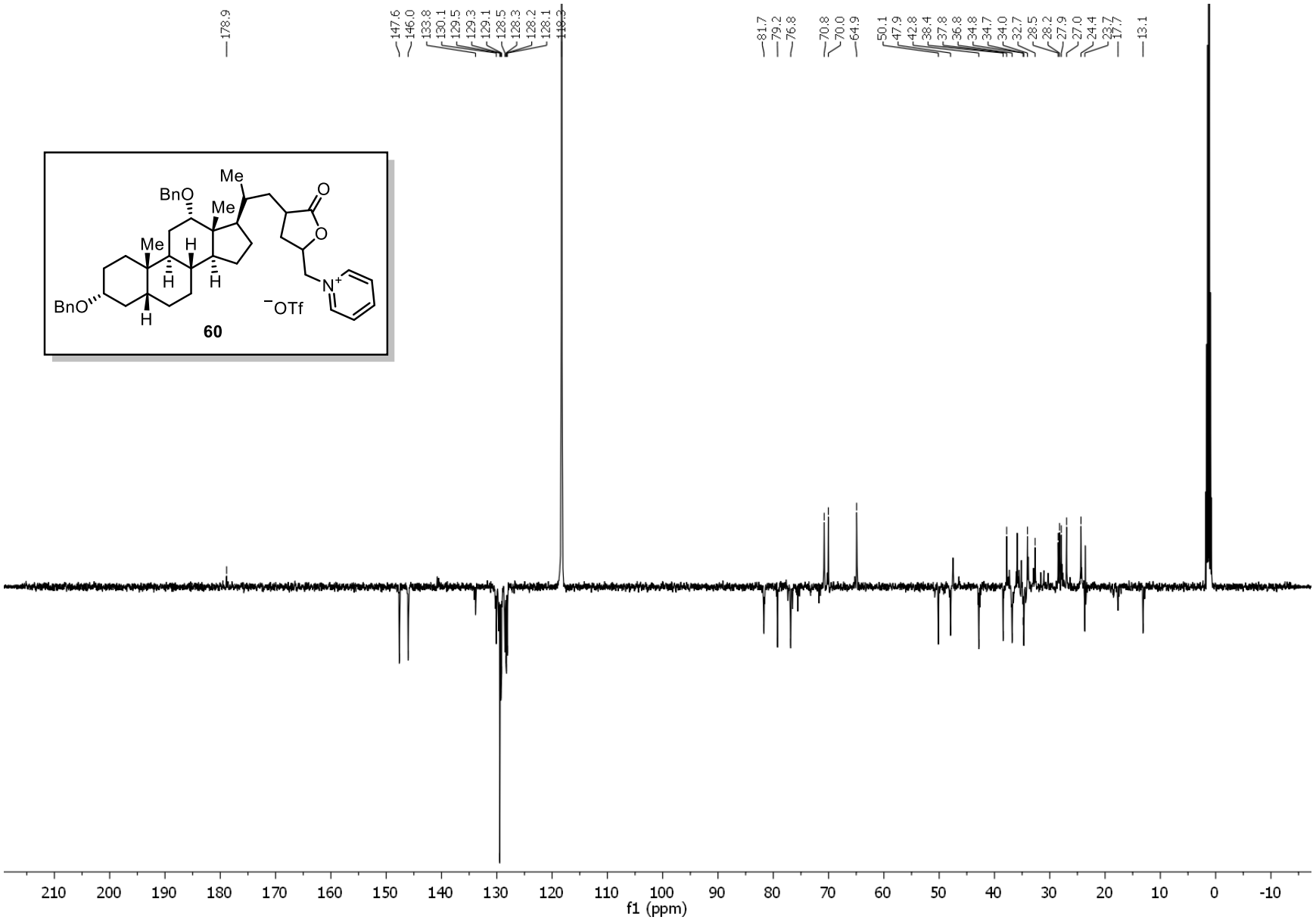


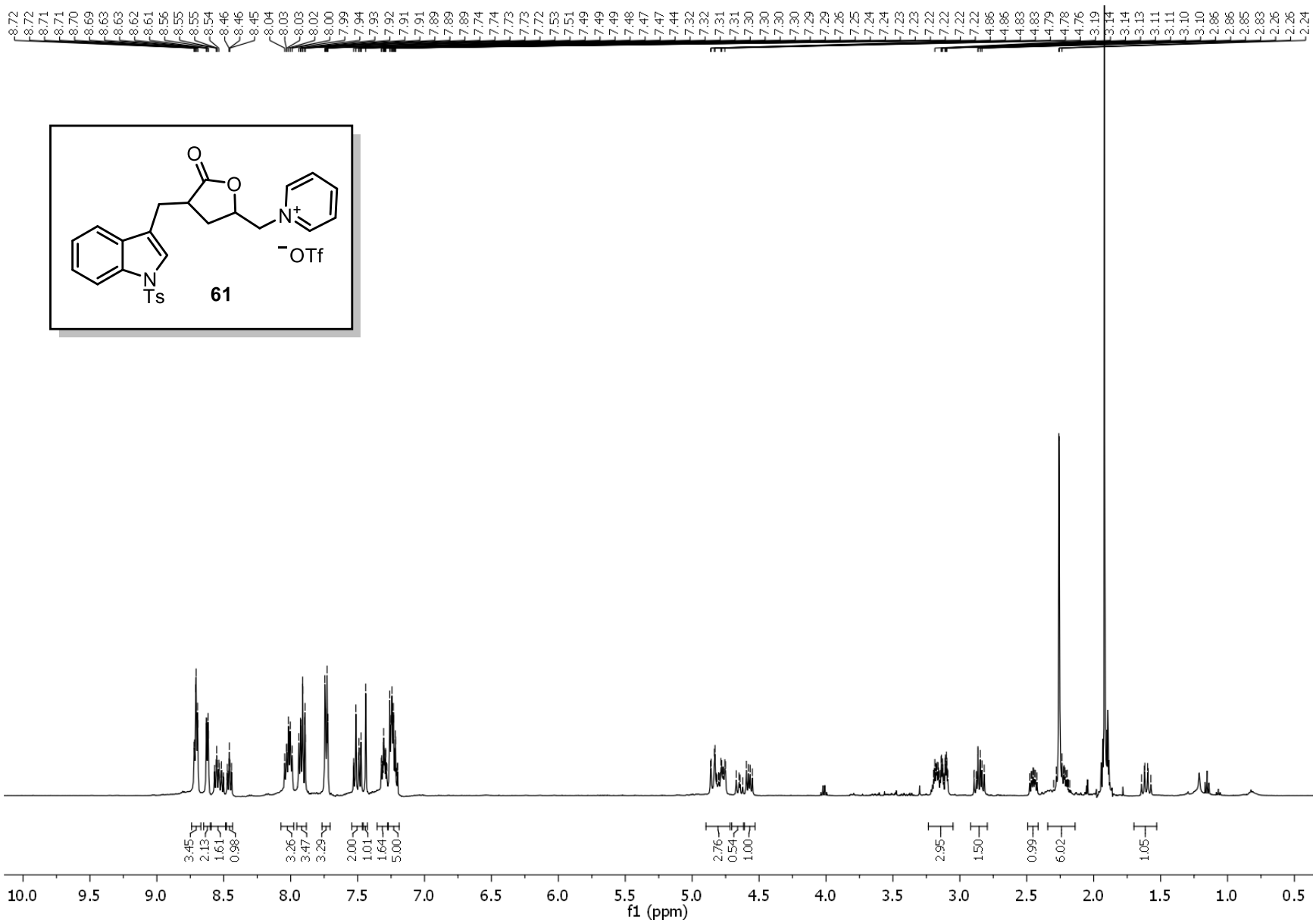
59

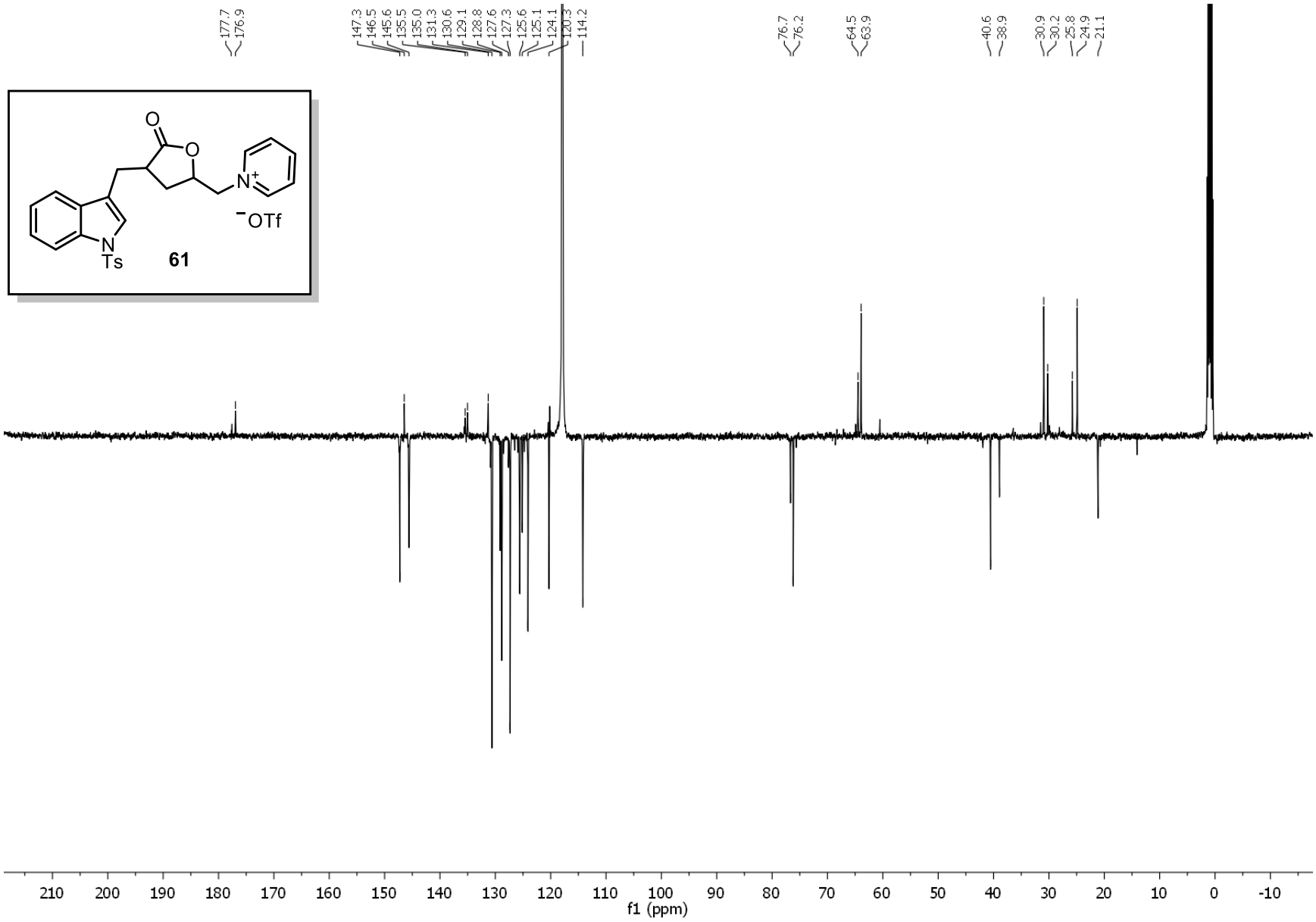


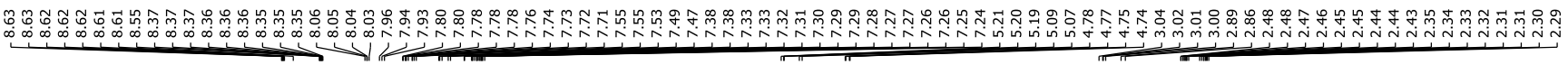

164.3
147.5
146.3
139.1
135.1
130.6
128.7
128.7
125.2
123.3
120.1
118.3
118.3
77.0
64.2
30.1
O
O
N+
−OTf
59
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

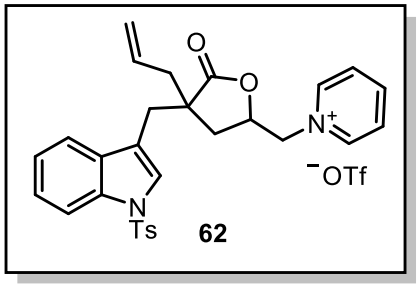

8.66 8.65 8.64 8.49 8.01 8.00 7.98 7.31 7.31 7.26 7.26 7.26 7.25 7.24 7.23 7.23 7.22 7.21 7.21 7.19 7.18
4.41 1.77 1.75 1.74 1.74 1.73 1.73 1.72 1.72 1.71 1.52 1.52 1.51 1.50 1.49 1.49 1.48 1.47 1.47 1.44 1.41 1.31 1.31 1.30 1.30 1.28 1.27 1.20 1.19 1.18 1.16 1.16 1.15 1.14 1.14 1.12 0.91 0.91 0.90 0.90 0.90 0.90 0.89 0.89 0.89 0.88 0.87 0.86 0.86 0.85 0.85 0.85 0.84 0.84 0.77 0.69 0.68 0.67 0.67 0.66
Me
BnO
Me
O
Me
H
O
H
H
N+
BnO
H
−OTf
60
2.06 1.00 2.45 10.37 1.25 0.97 1.91 1.21 1.03 0.82 0.75 1.78 1.91 5.70 13.68 6.21 3.68 6.44 6.41
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.9
147.6
146.0
133.8
130.1
129.5
129.3
129.1
128.5
128.3
128.2
128.1
118.3
81.7
79.2
76.8
70.8
70.0
64.9
50.1
47.9
42.8
38.4
37.8
36.8
34.8
34.7
34.0
32.7
28.5
28.2
27.9
27.0
24.4
23.7
17.7
13.1
Me
BnO
Me
Me
H
H
H
H
BnO
O
O
N+
−OTf
60
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

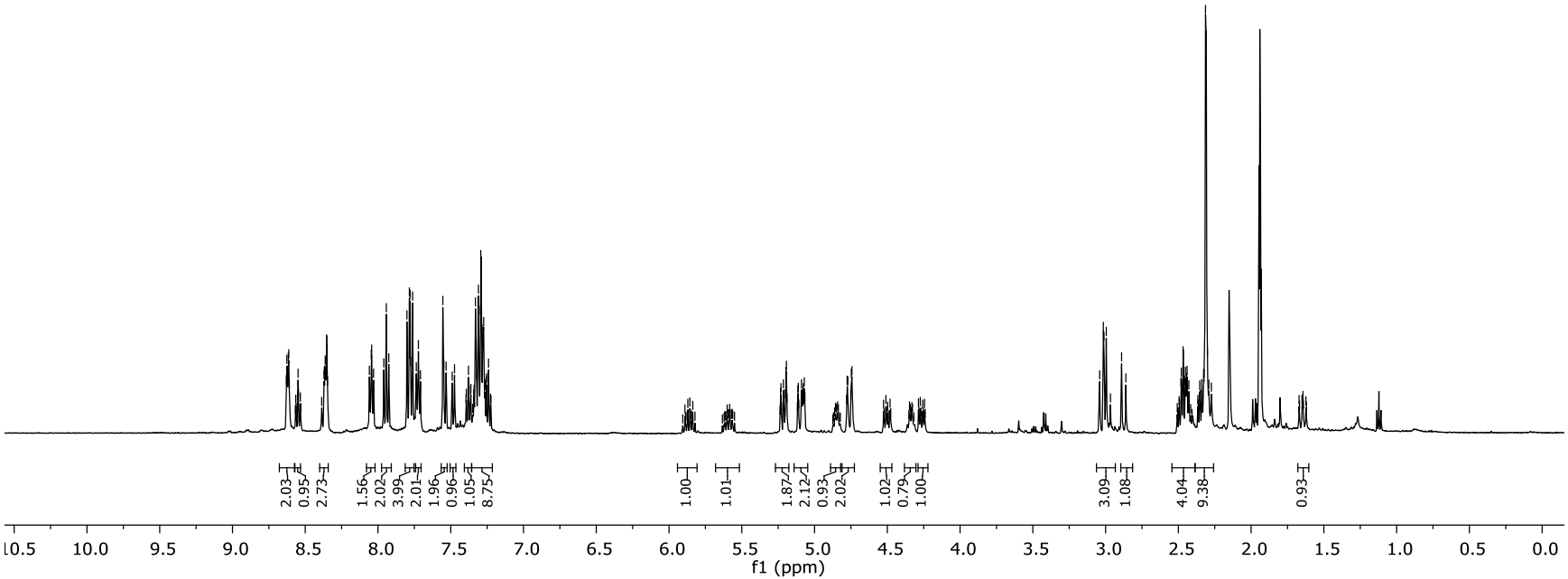

8.72 8.72 8.71 8.71 8.70 8.69 8.63 8.63 8.62 8.61 8.56 8.55 8.55 8.54 8.46 8.46 8.45 8.04 8.03 8.03 8.02 8.00 7.99 7.94 7.93 7.92 7.91 7.91 7.89 7.89 7.89 7.74 7.74 7.73 7.73 7.72 7.53 7.51 7.49 7.49 7.49 7.48 7.47 7.47 7.44 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.30 7.29 7.29 7.26 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.22 7.22 4.86 4.86 4.83 4.83 4.79 4.78 4.76 3.19 3.14 3.14 3.13 3.11 3.11 3.10 3.10 2.86 2.86 2.85 2.83 2.26 2.26 2.24
O
O
N+
−OTf
N
Ts
61
3.45
2.13
1.61
0.98
3.26
3.47
3.29
2.00
1.01
1.64
5.00
2.76
0.54
1.00
2.95
1.50
0.99
6.02
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

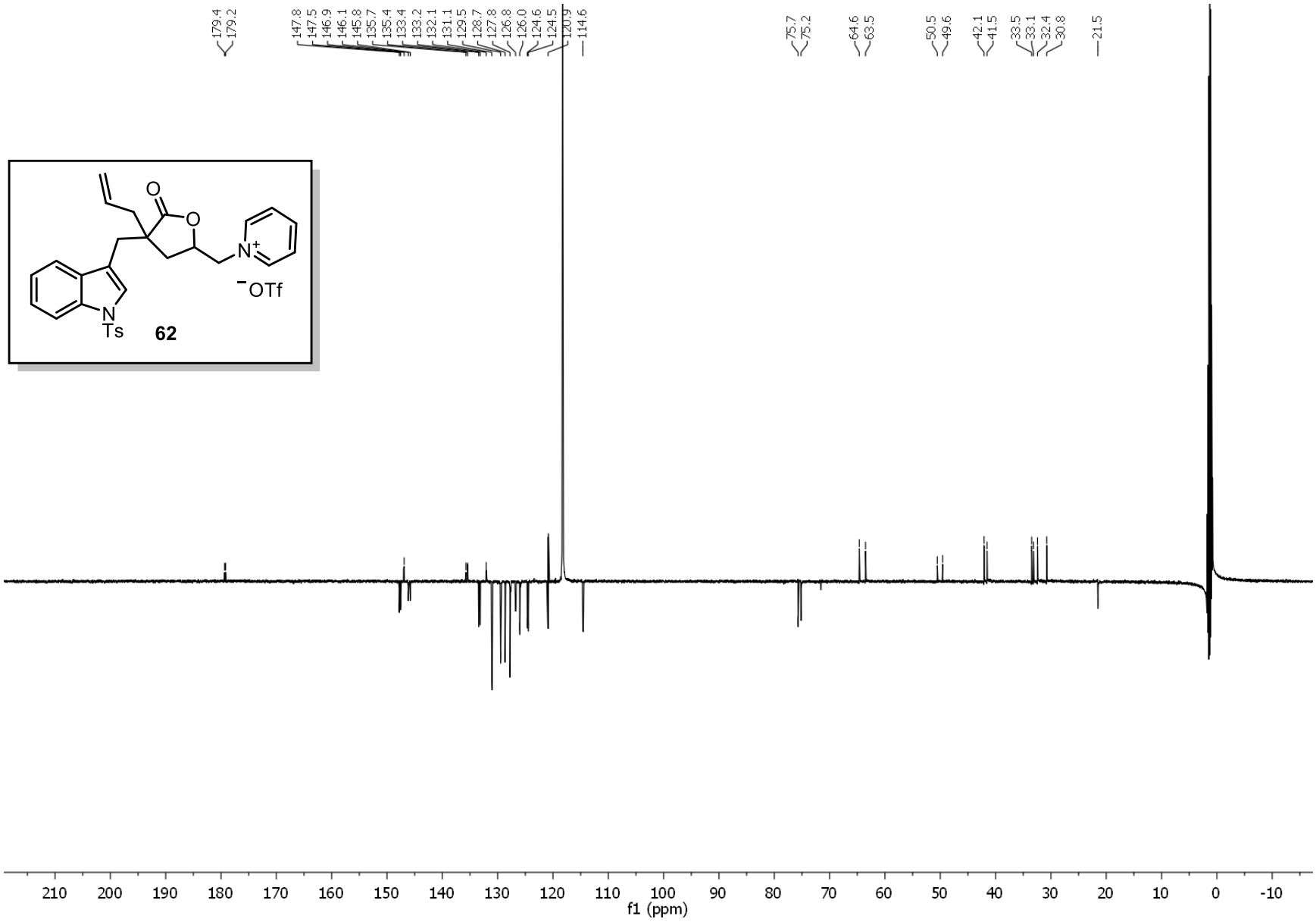

177.7
176.9
147.3
146.5
145.6
135.5
135.0
131.3
130.6
129.1
128.8
127.6
127.3
125.6
125.1
124.1
120.3
114.2
76.7
76.2
64.5
63.9
40.6
38.9
30.9
30.2
25.8
24.9
21.1
O
O
N+
−OTf
N
Ts
61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

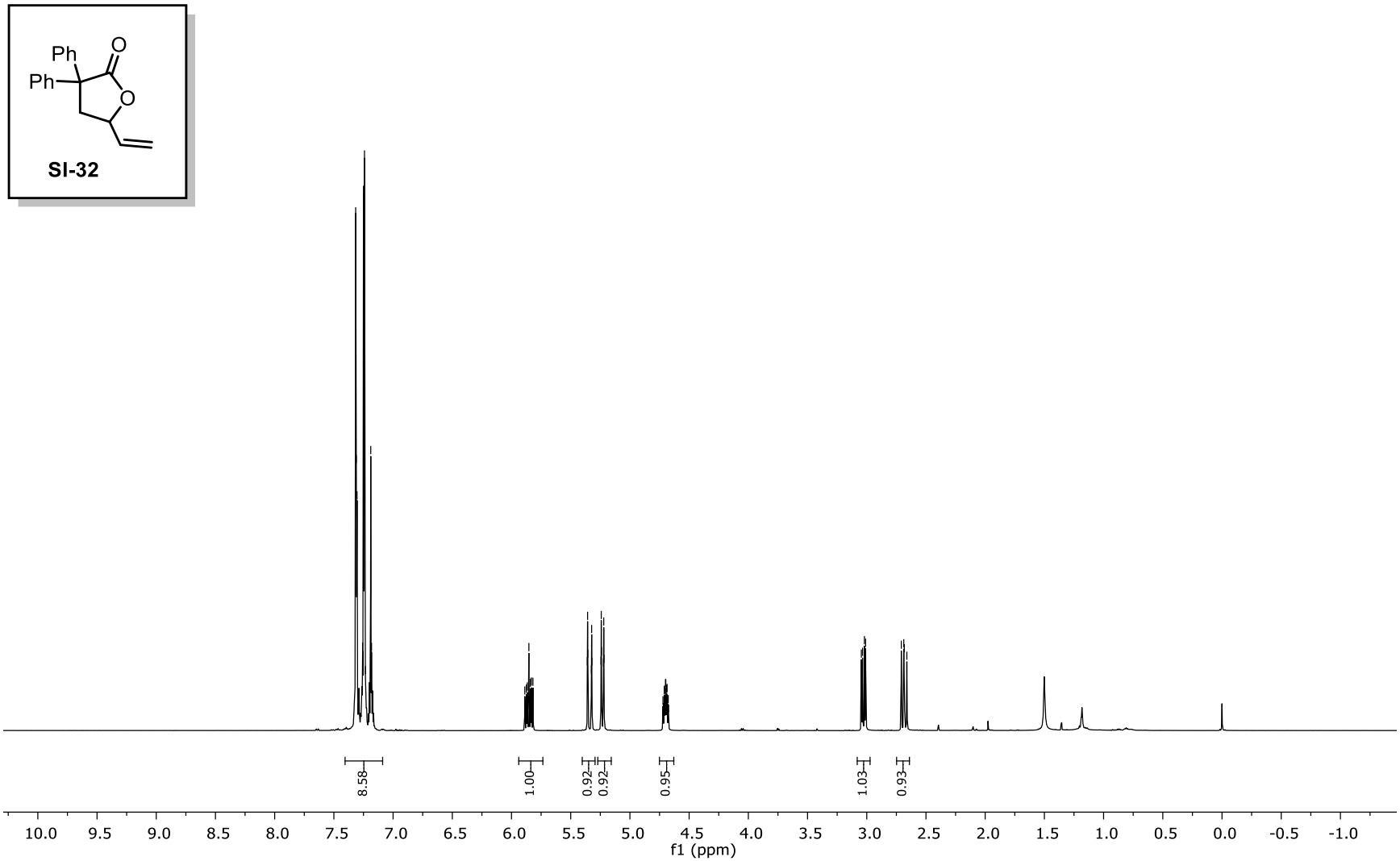

8.63 8.63 8.62 8.62 8.62 8.61 8.61 8.55 8.37 8.37 8.37 8.36 8.36 8.36 8.35 8.35 8.35 8.06 8.05 8.04 8.03 7.96 7.94 7.93 7.80 7.80 7.78 7.78 7.78 7.76 7.74 7.73 7.72 7.71 7.55 7.55 7.53 7.49 7.47 7.38 7.38 7.33 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.24 5.21 5.20 5.19 5.09 5.07 4.78 4.77 4.75 4.74 3.04 3.02 3.01 3.00 2.89 2.86 2.48 2.48 2.47 2.46 2.45 2.45 2.44 2.44 2.43 2.35 2.34 2.33 2.32 2.31 2.31 2.30 2.29

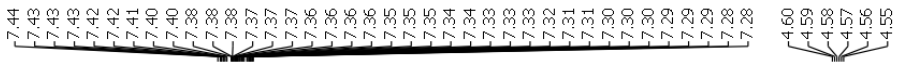

O
O
N+
−OTf
N
Ts

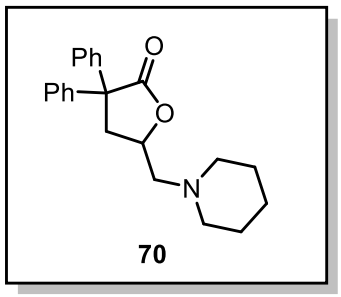
62


2.03 0.95 2.73 1.56 2.02 3.99 2.01 1.96 0.96 1.05 8.75 1.00 1.01 1.87 2.12 0.93 2.02 1.02 0.79 1.00 3.09 1.08 4.04 9.38 0.93
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

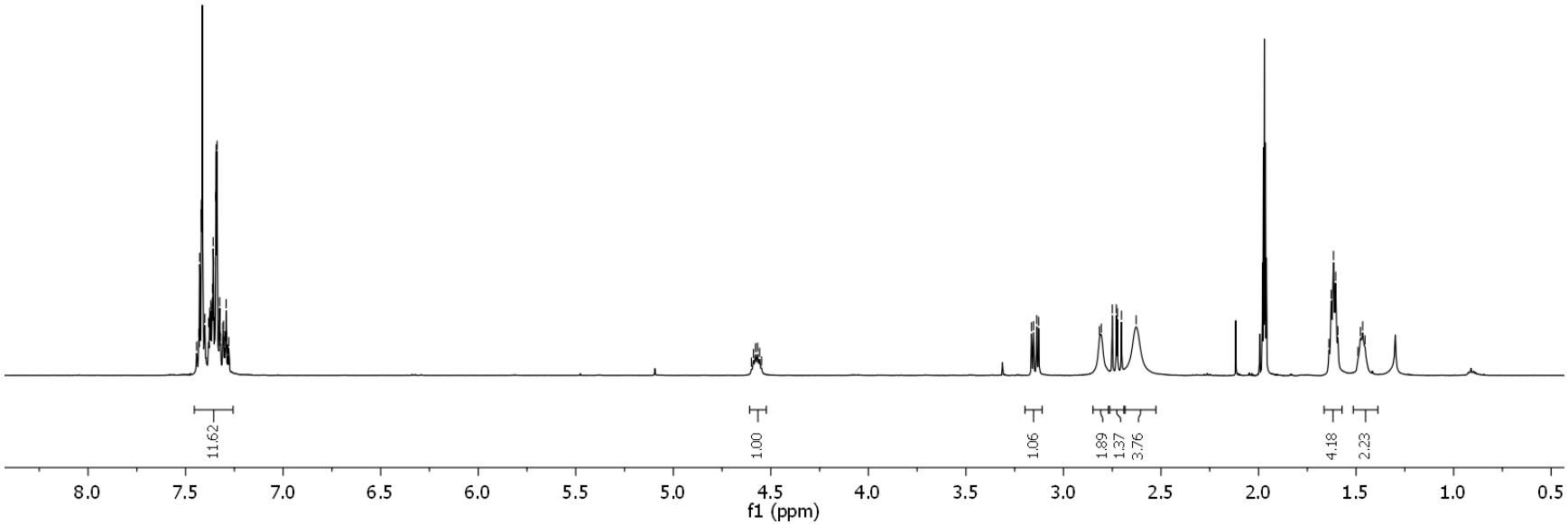

179.4
179.2
147.8
147.5
146.9
146.1
145.8
135.7
135.4
133.4
133.2
132.1
131.1
129.5
128.7
127.8
126.8
126.0
124.6
124.5
120.9
114.6
75.7
75.2
64.6
63.5
50.5
49.6
42.1
41.5
33.5
33.1
32.4
30.8
21.5
O
O
N+
−OTf
N
Ts
62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

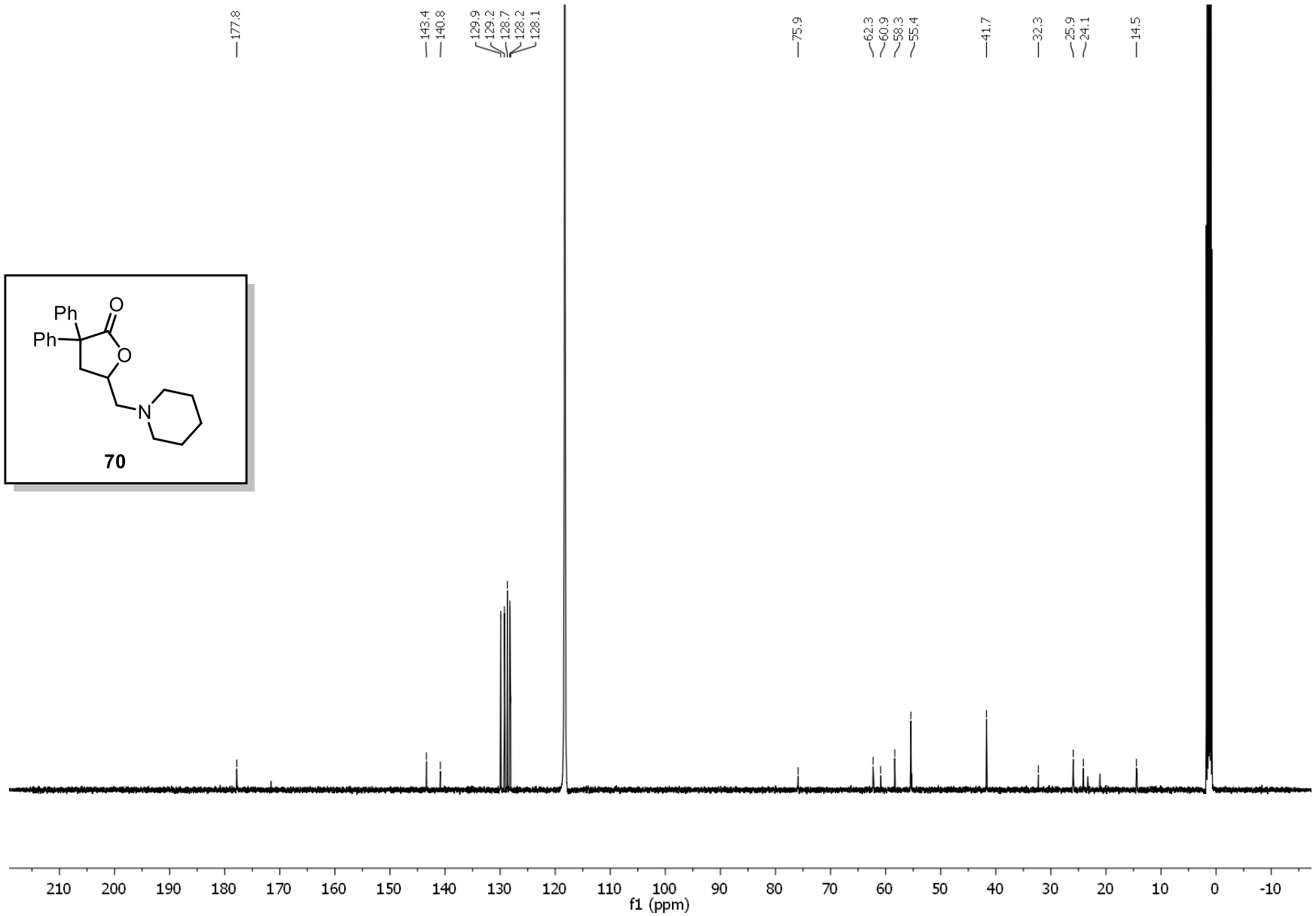

7.32
7.31
7.30
7.26
7.25
7.24
7.23
7.19
7.18
5.89
5.87
5.87
5.85
5.84
5.83
5.82
5.36
5.36
5.33
5.32
5.32
5.24
5.24
5.24
5.22
5.22
5.22
4.72
4.72
4.71
4.71
4.71
4.70
4.70
4.69
4.69
4.69
4.68
4.68
4.68
4.67
3.05
3.04
3.02
3.01
2.71
2.69
2.68
2.66
Ph
Ph
O
O
SI-32
8.58
1.00
0.92
0.92
0.95
1.03
0.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

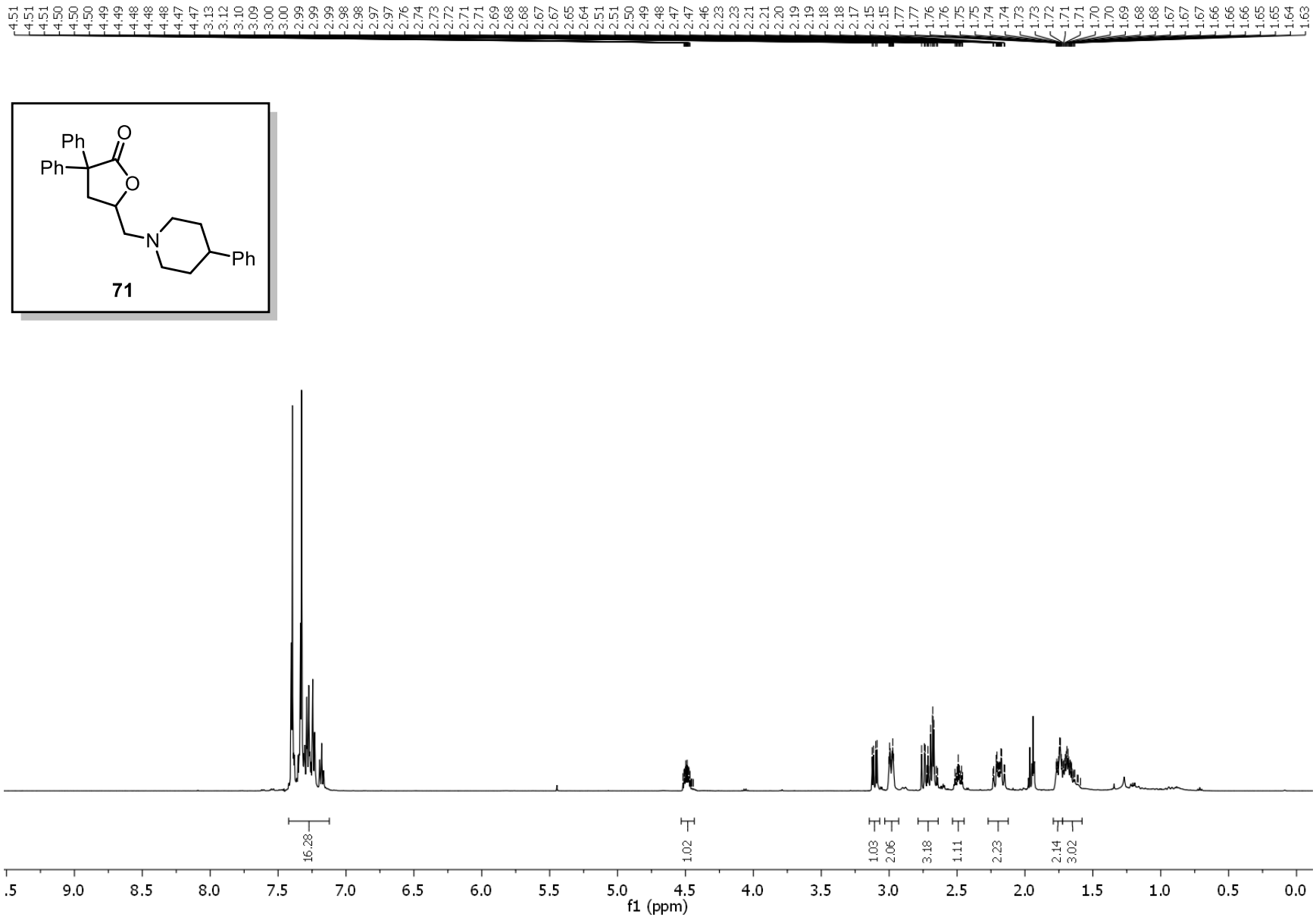

7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.28
4.60
4.59
4.58
4.57
4.56
4.55
3.16
3.15
3.14
3.13
2.82
2.81
2.75
2.73
2.72
2.70
2.63
1.64
1.63
1.62
1.60
1.59
1.49
1.48
1.47
1.45

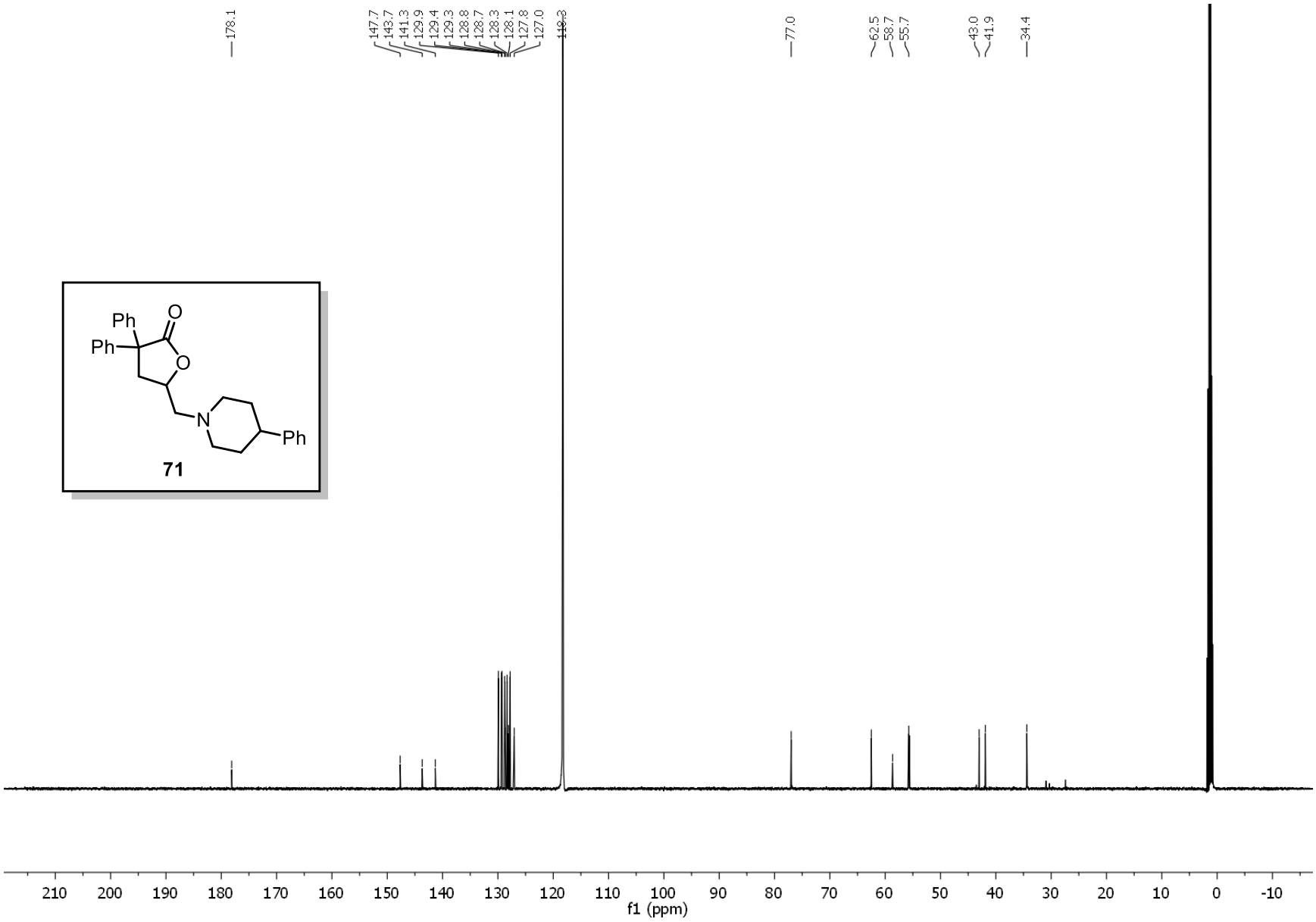

Ph
Ph
O
O
N

70

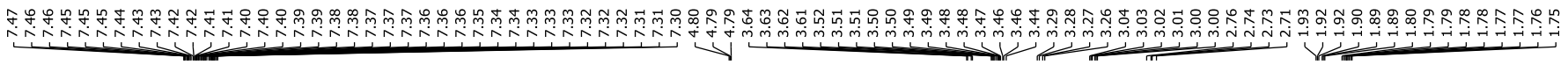

11.62
1.00
1.06
1.89
1.37
3.76
4.18
2.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

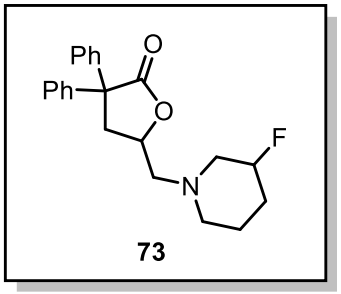

177.8
143.4
140.8
129.9
129.2
128.7
128.2
128.1
75.9
62.3
60.9
58.3
55.4
41.7
32.3
25.9
24.1
14.5
Ph
Ph
O
O
N
70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
Ph
O
O
N
Ph
71
16.28
1.02
1.03
2.06
3.18
1.11
2.23
2.14
3.02
f1 (ppm)

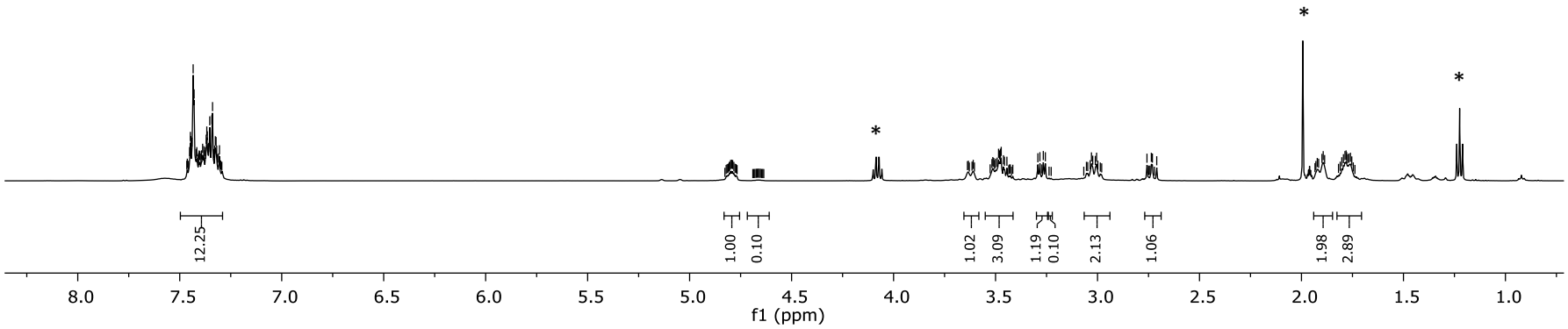

178.1
147.7
143.7
141.3
129.9
129.4
129.3
128.8
128.7
128.3
128.1
127.8
127.0
119.3
77.0
62.5
58.7
55.7
43.0
41.9
34.4
Ph
Ph
O
O
N
Ph
71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

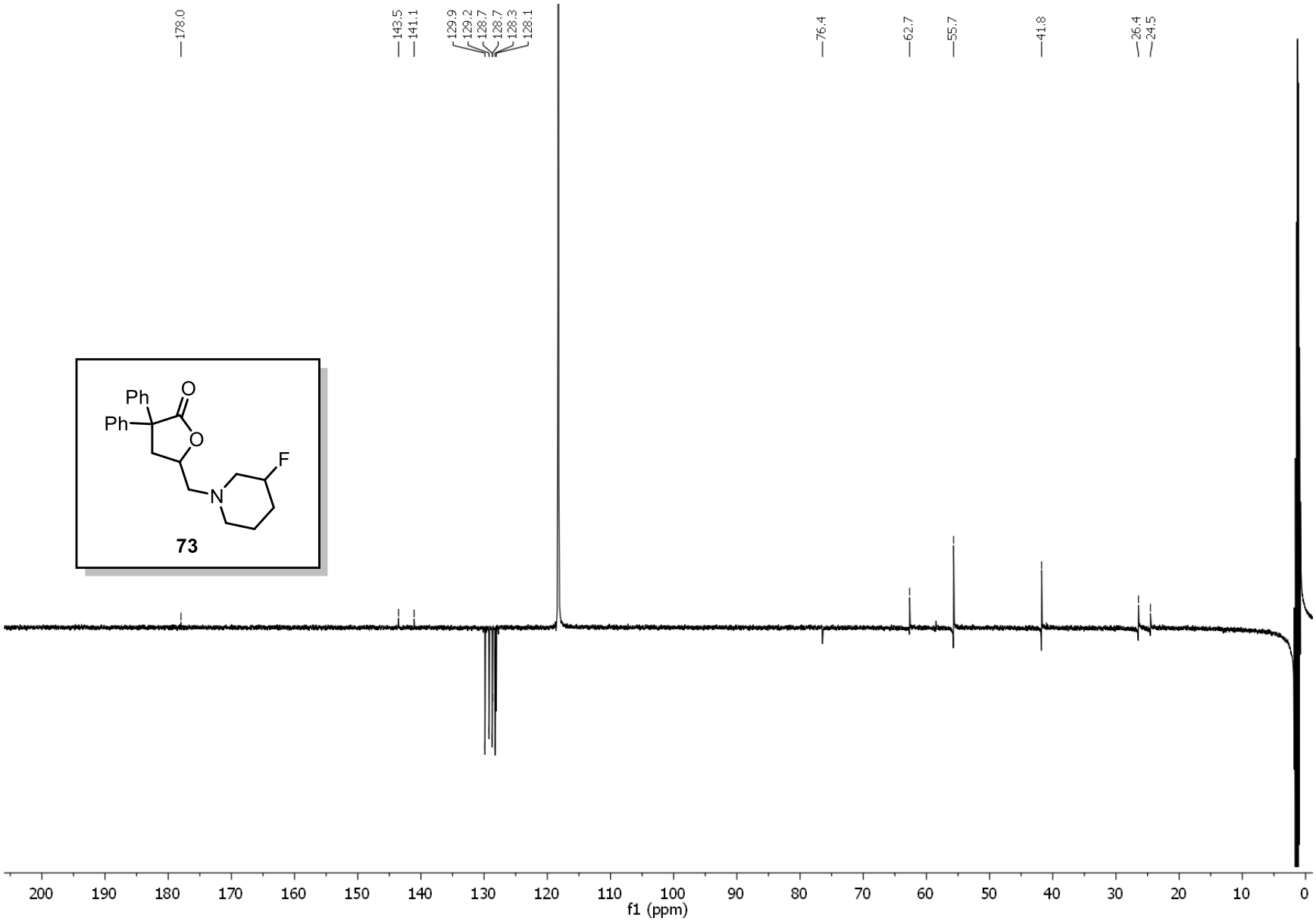
*EtOAc

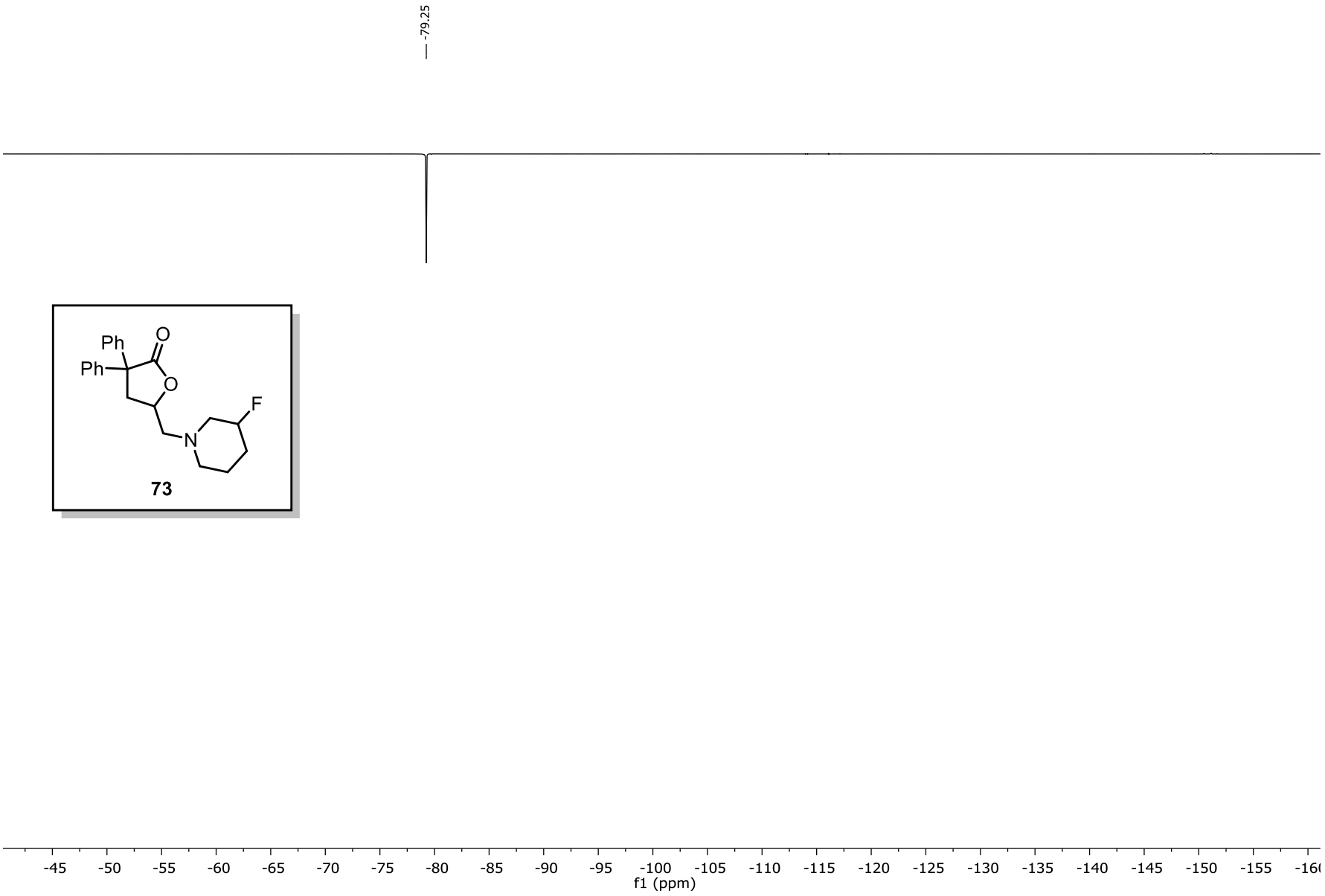

7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 4.80 4.79 4.79 3.64 3.63 3.62 3.61 3.52 3.51 3.51 3.50 3.50 3.49 3.49 3.48 3.48 3.47 3.46 3.46 3.44 3.29 3.28 3.27 3.26 3.04 3.03 3.02 3.01 3.00 3.00 2.76 2.74 2.73 2.71 1.93 1.92 1.92 1.90 1.89 1.89 1.80 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.75

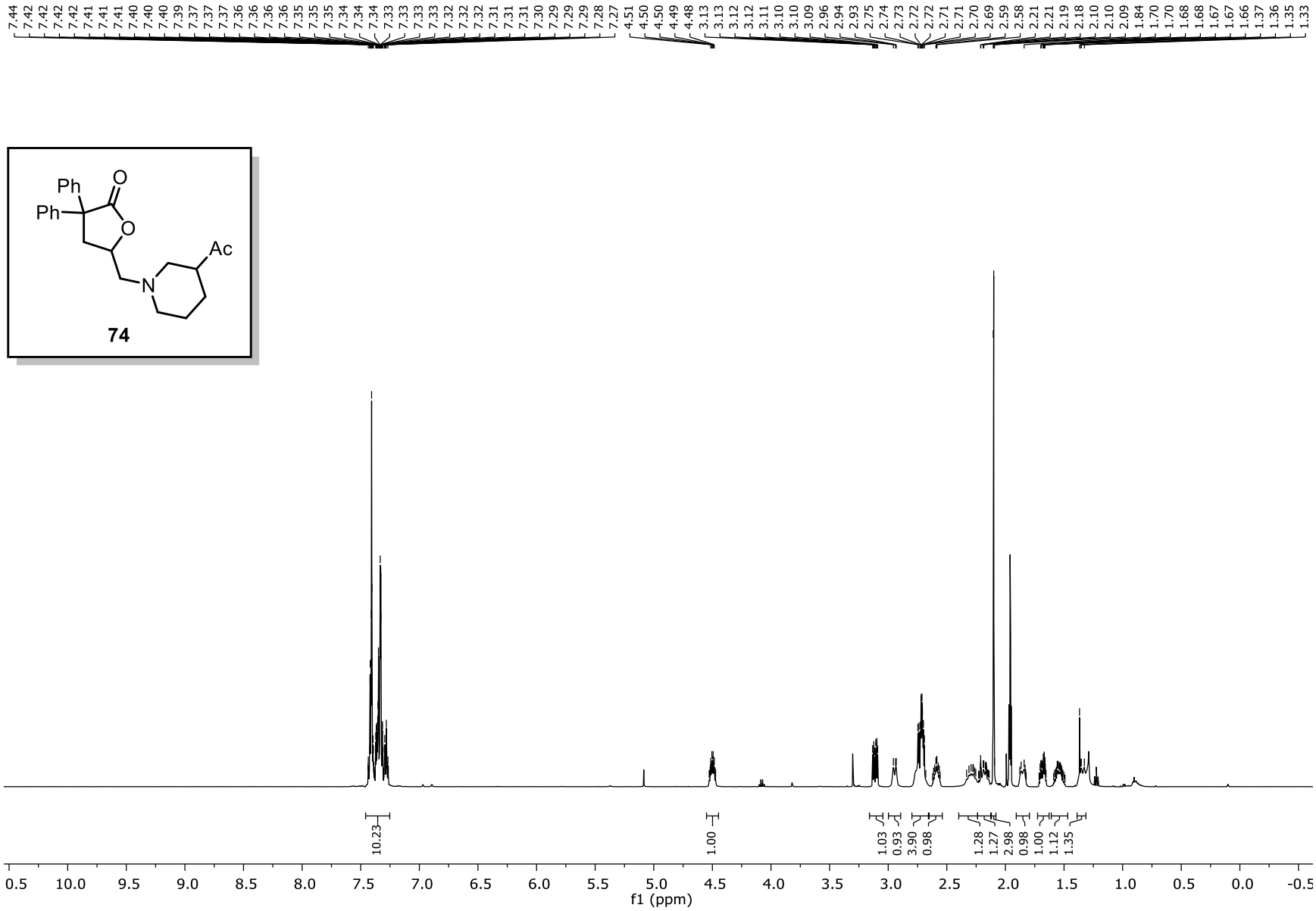

Ph
Ph
O
O
F
N

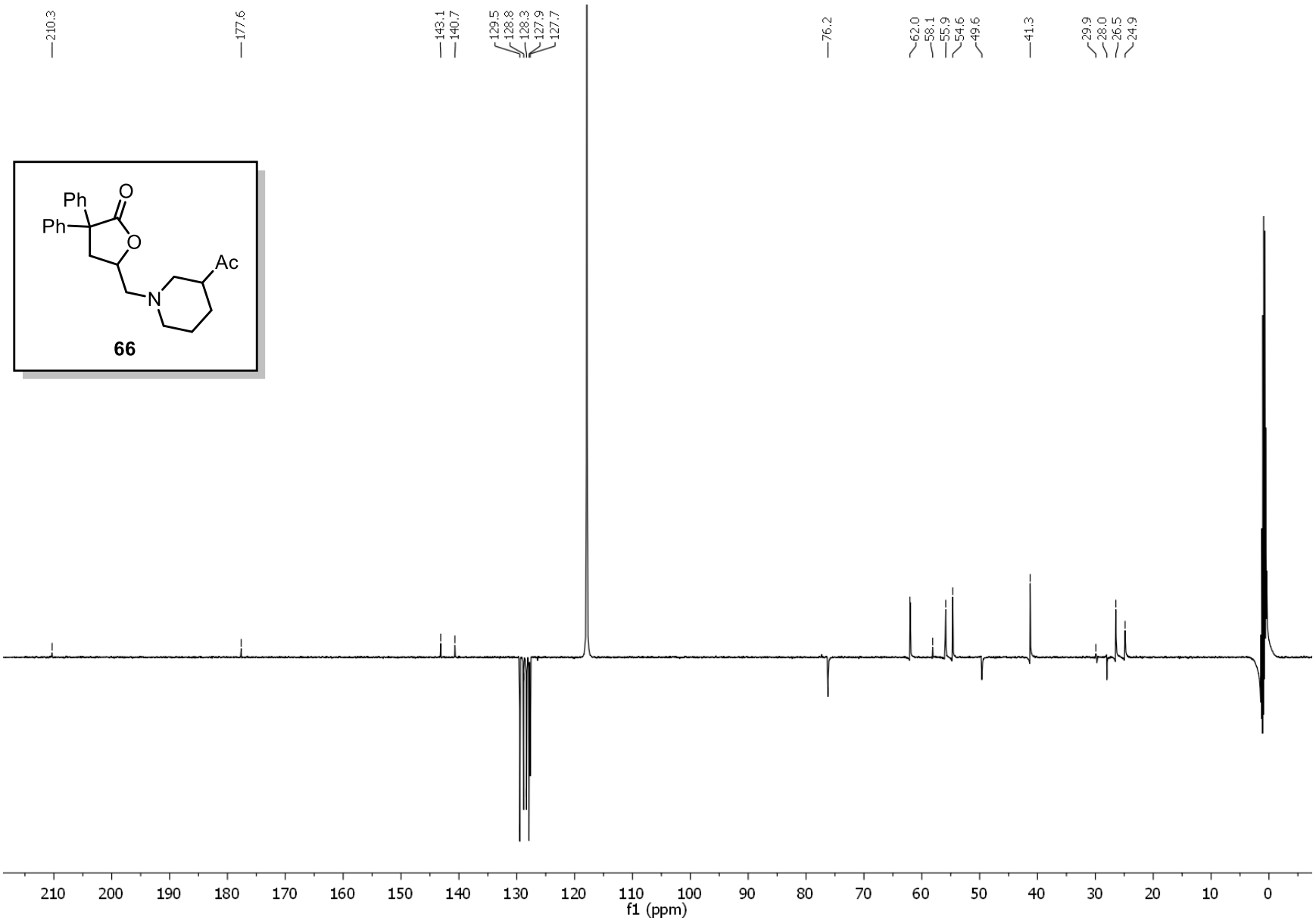
73


*
*
*
12.25
1.00
0.10
1.02
3.09
1.19
0.10
2.13
1.06
1.98
2.89
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
f1 (ppm)

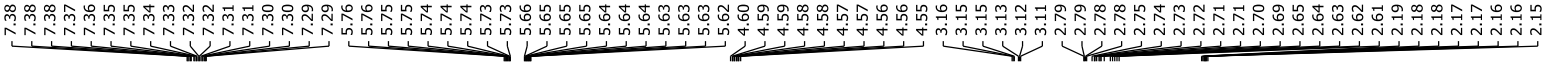

178.0
143.5
141.1
129.9
129.2
128.7
128.7
128.3
128.1
76.4
62.7
55.7
41.8
26.4
24.5
Ph
Ph
O
O
N
F
73
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

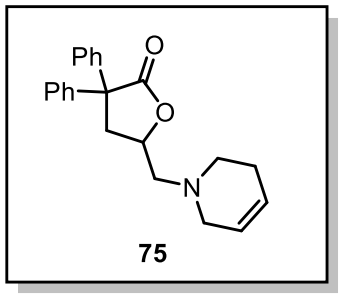

-79.25
Ph
Ph
O
O
N
F
73
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

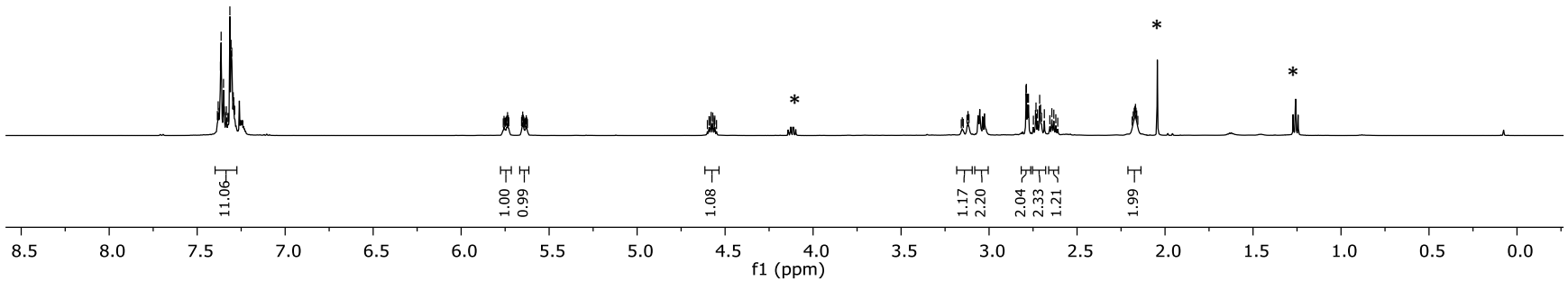

7.44 7.42 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.37 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.27
4.51 4.50 4.50 4.49 4.48 3.13 3.13 3.12 3.12 3.11 3.10 3.10 3.09 2.96 2.94 2.93 2.75 2.74 2.73 2.72 2.72 2.71 2.71 2.70 2.69 2.59 2.58 2.21 2.21 2.19 2.18 2.10 2.10 2.09 1.84 1.70 1.70 1.68 1.68 1.67 1.67 1.66 1.37 1.36 1.35 1.33
Ph
Ph
O
O
Ac
N
74
10.23
1.00
1.03
0.93
3.90
0.98
1.28
1.27
2.98
0.98
1.00
1.12
1.35
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

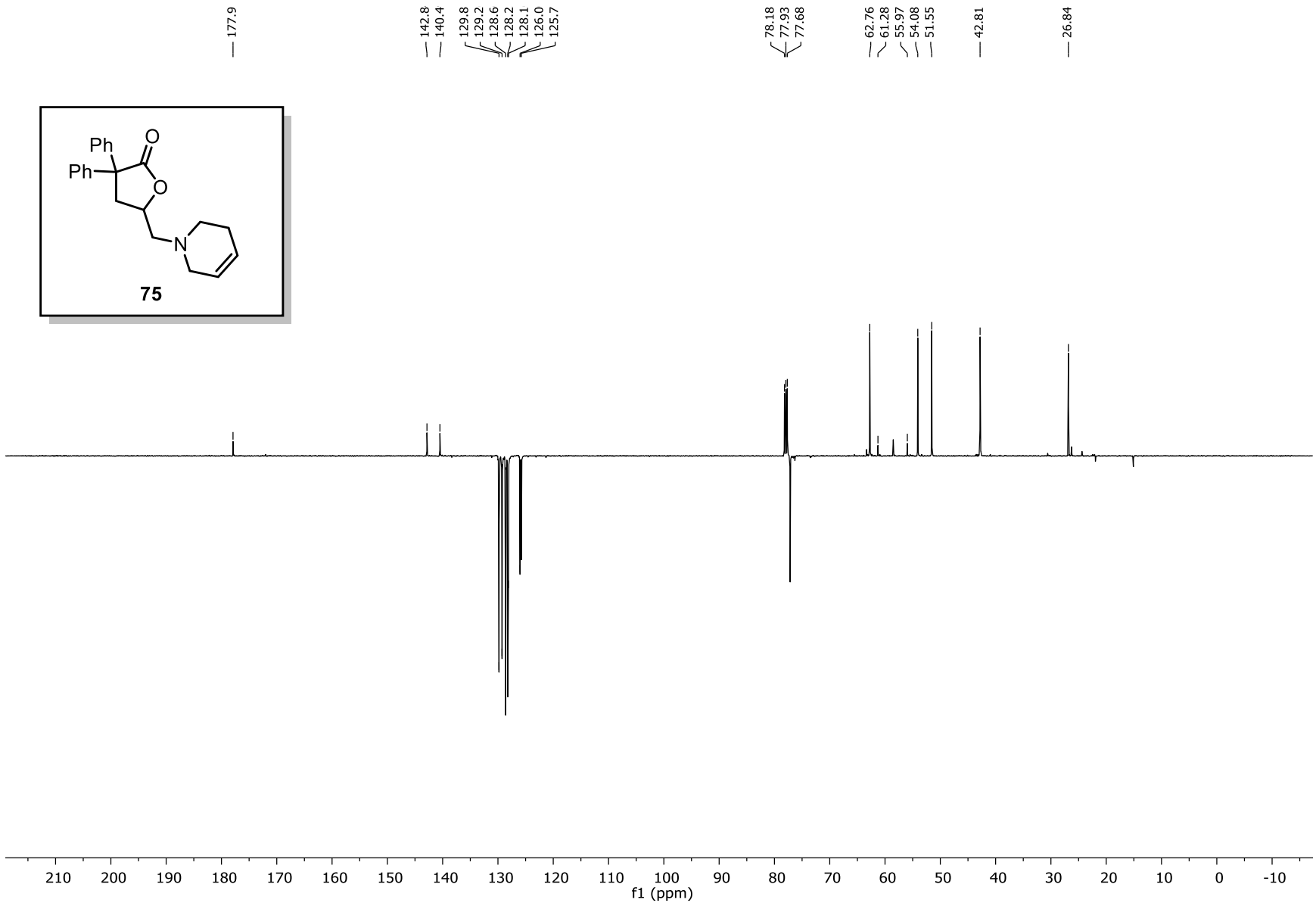

210.3
177.6
143.1
140.7
129.5
128.8
128.3
127.9
127.7
76.2
62.0
58.1
55.9
54.6
49.6
41.3
29.9
28.0
26.5
24.9
Ph
Ph
O
O
N
Ac
66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

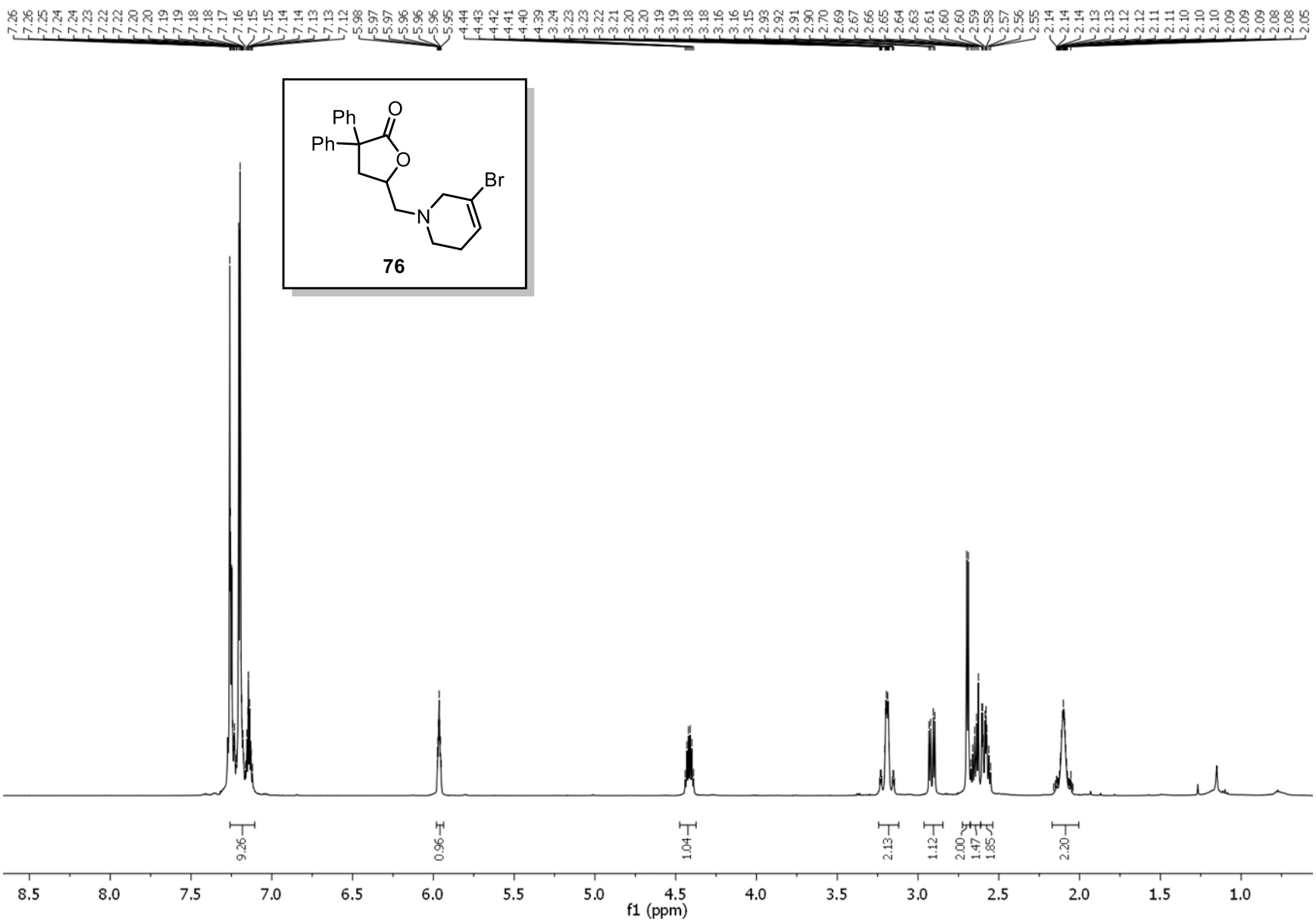
*EtOAc

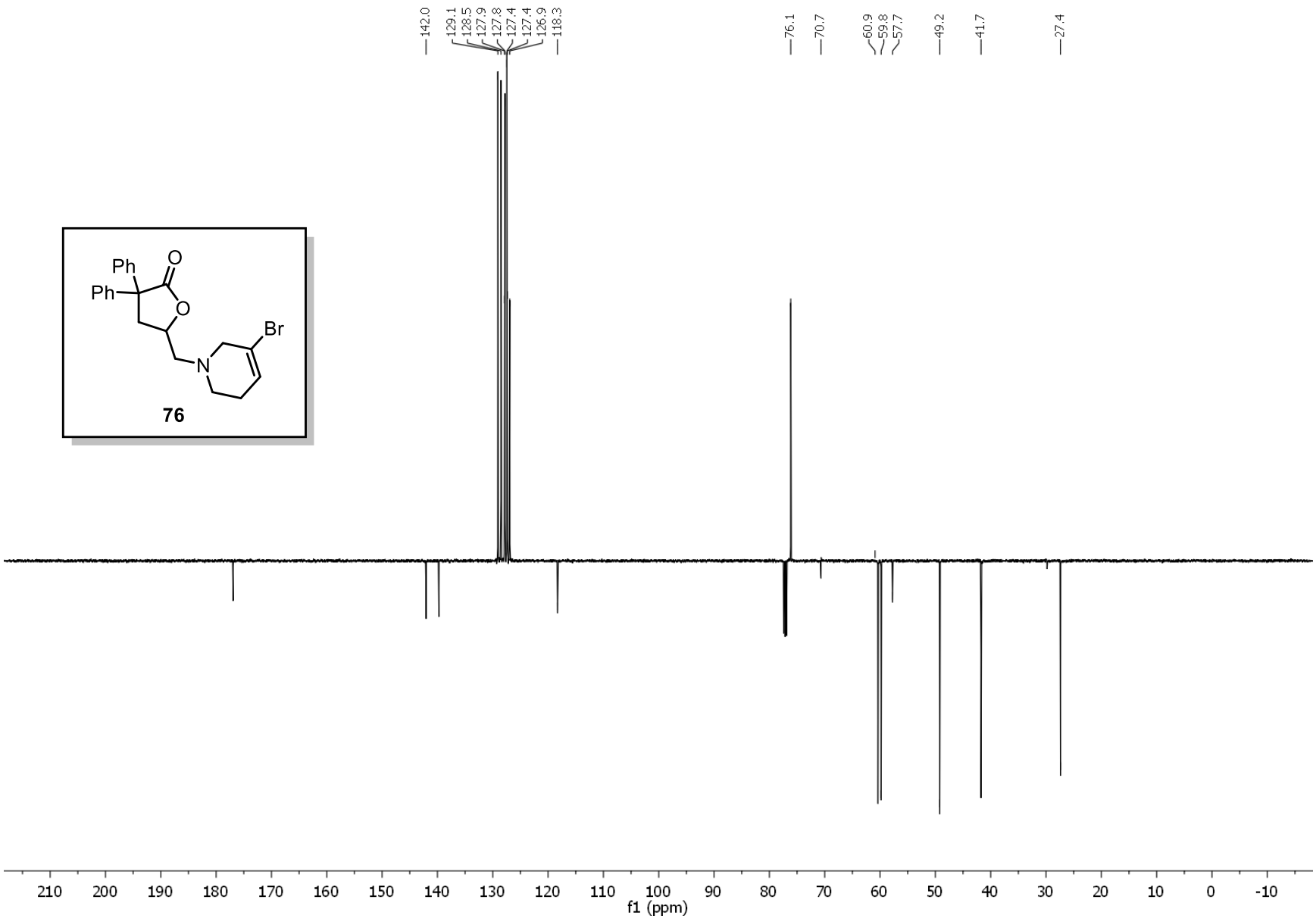

7.38 7.38 7.38 7.37 7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29
5.76 5.76 5.75 5.75 5.74 5.74 5.74 5.73 5.73 5.66 5.65 5.65 5.65 5.64 5.64 5.64 5.63 5.63 5.63 5.62
4.60 4.59 4.59 4.58 4.58 4.57 4.57 4.56 4.56 4.55
3.16 3.15 3.15 3.13 3.12 3.11
2.79 2.79 2.78 2.78 2.75 2.74 2.73 2.72 2.71 2.71 2.70 2.69 2.65 2.64 2.63 2.62 2.61 2.19 2.18 2.18 2.17 2.17 2.16 2.16 2.15

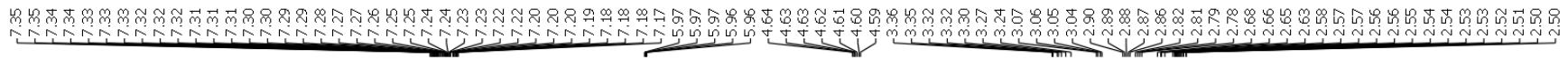

Ph
Ph
O
O
N
75

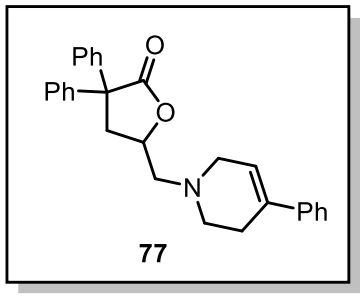

*
*
*
11.06
1.00
0.99
1.08
1.17
2.20
2.04
2.33
1.21
1.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


177.9
142.8
140.4
129.8
129.2
128.6
128.2
128.1
126.0
125.7
78.18
77.93
77.68
62.76
61.28
55.97
54.08
51.55
42.81
26.84
Ph
Ph
O
O
N
75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

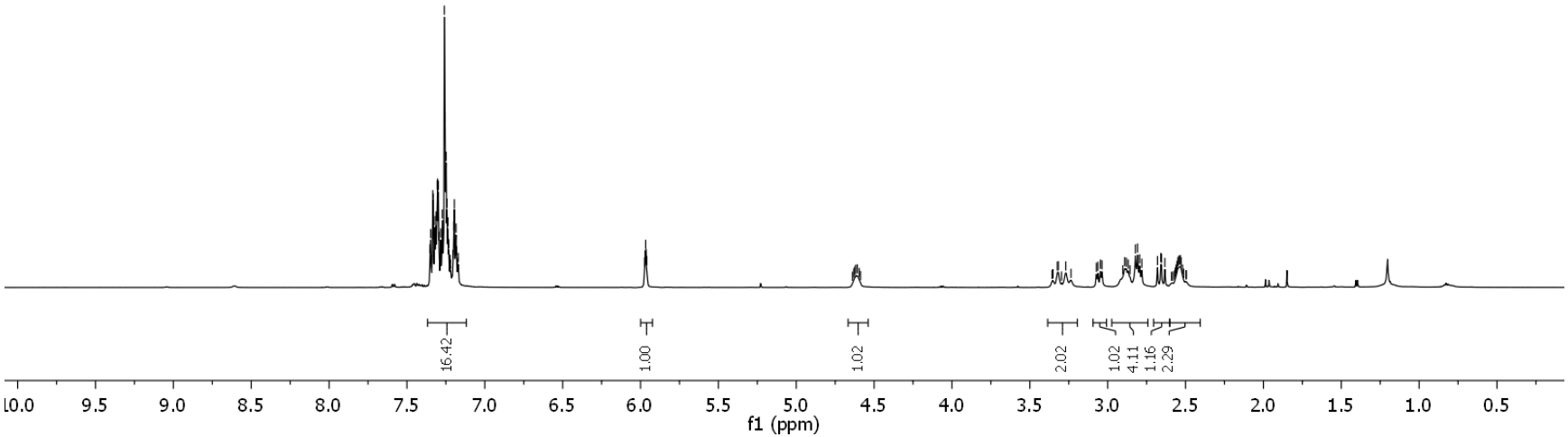

Ph
Ph
O
O
Br
N
76
9.26
0.96
1.04
2.13
1.12
2.00
1.47
1.85
2.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

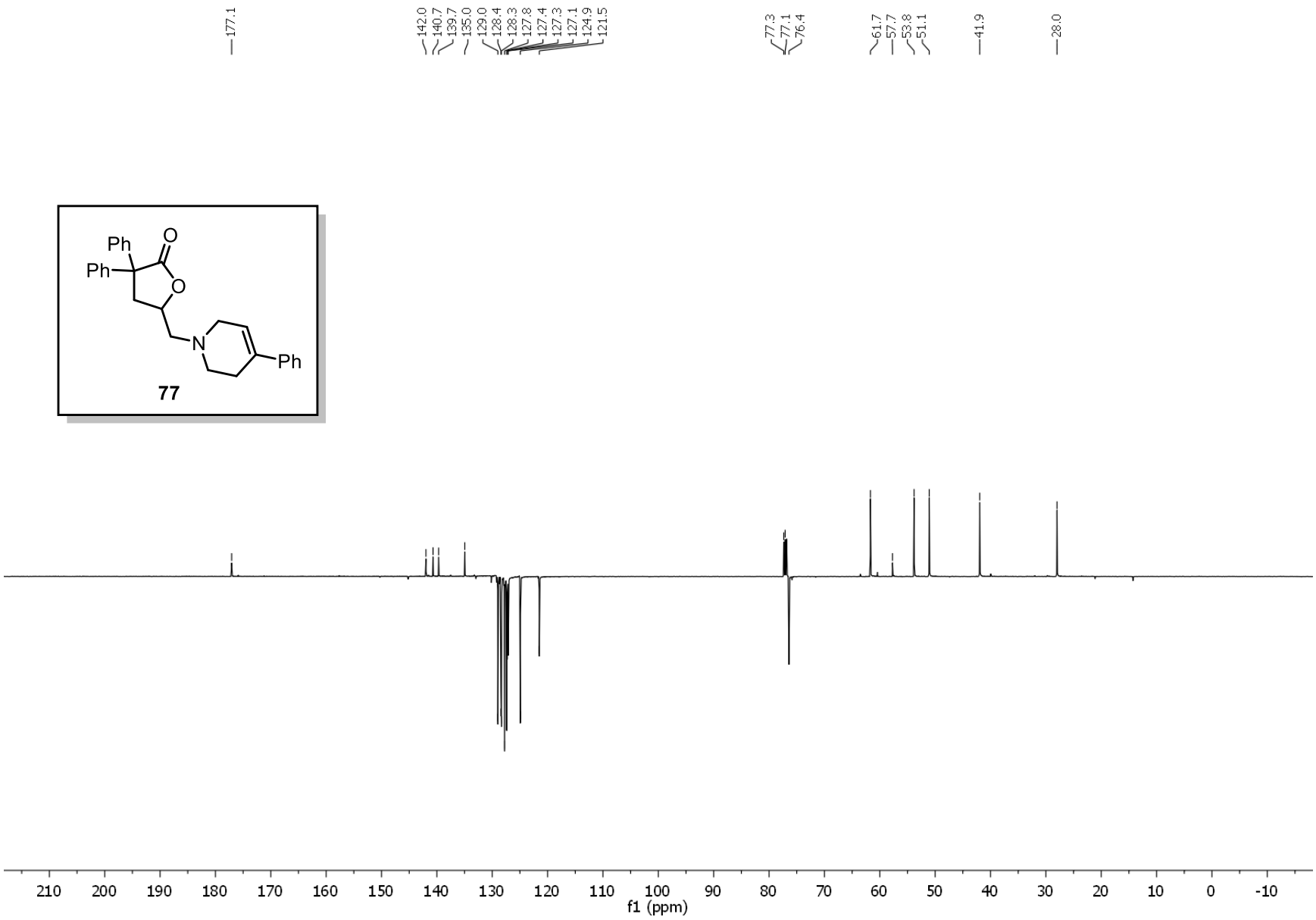

142.0
129.1
128.5
127.9
127.8
127.4
127.4
126.9
118.3
76.1
70.7
60.9
59.8
57.7
49.2
41.7
27.4
Ph
Ph
O
O
N
Br
76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

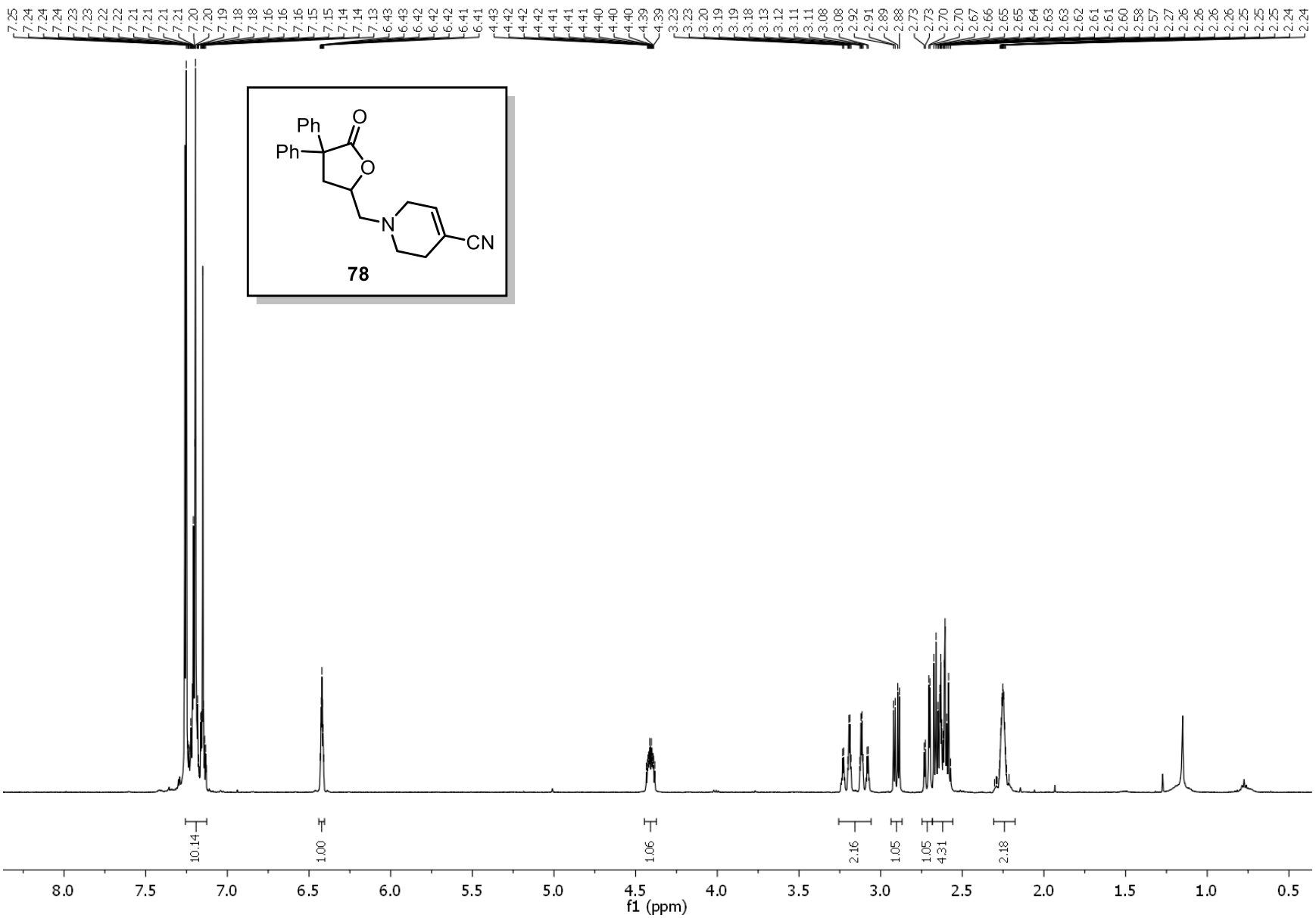

7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.20 7.20 7.20 7.19 7.18 7.18 7.18 7.17 5.97 5.97 5.97 5.96 5.96 4.64 4.63 4.63 4.62 4.61 4.60 4.59 3.36 3.35 3.32 3.32 3.30 3.27 3.24 3.07 3.06 3.05 3.04 2.90 2.89 2.88 2.87 2.86 2.82 2.81 2.79 2.78 2.68 2.66 2.65 2.63 2.58 2.57 2.57 2.56 2.56 2.55 2.54 2.54 2.53 2.53 2.52 2.51 2.50 2.50

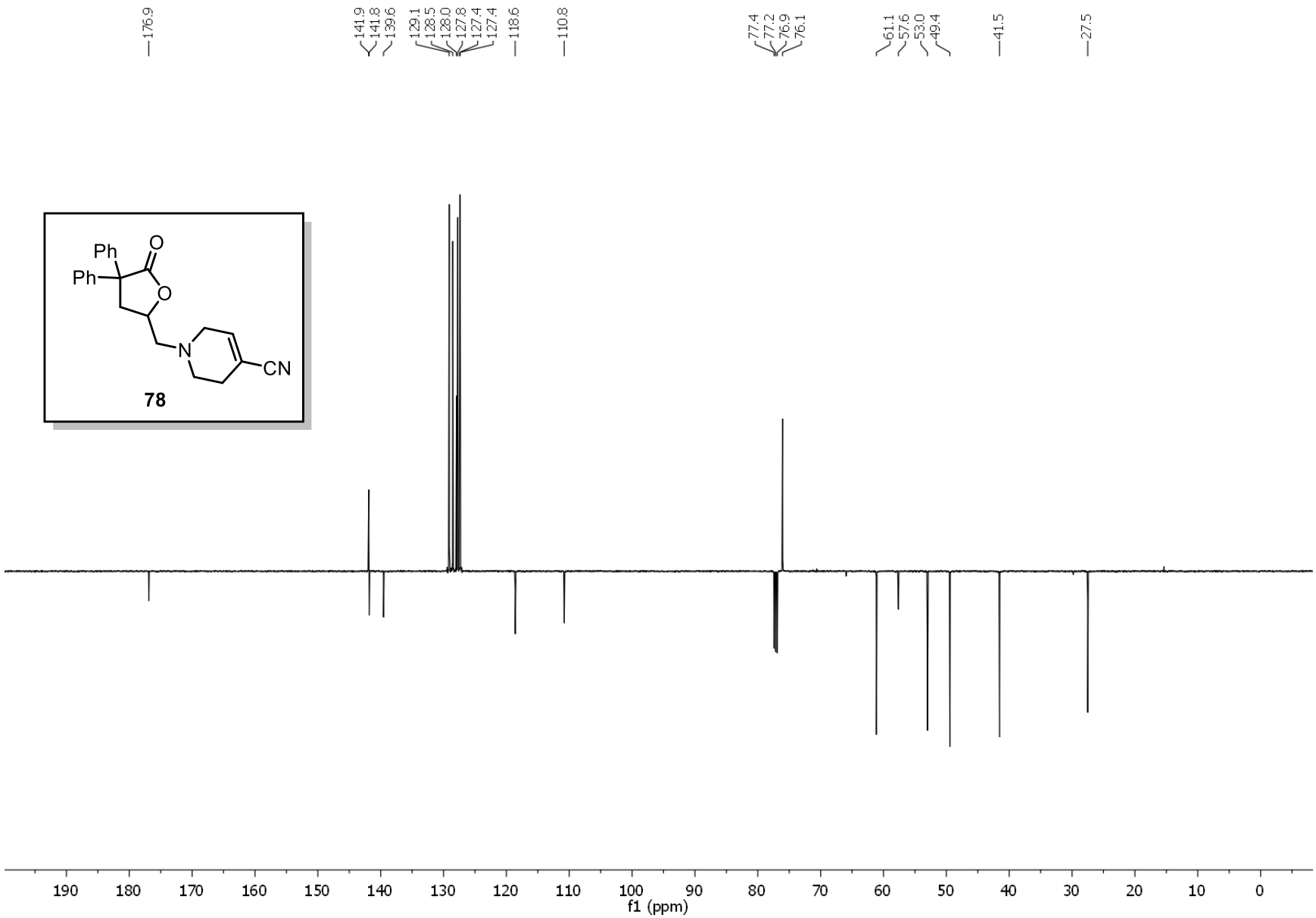

Ph
Ph
O
O
N
Ph

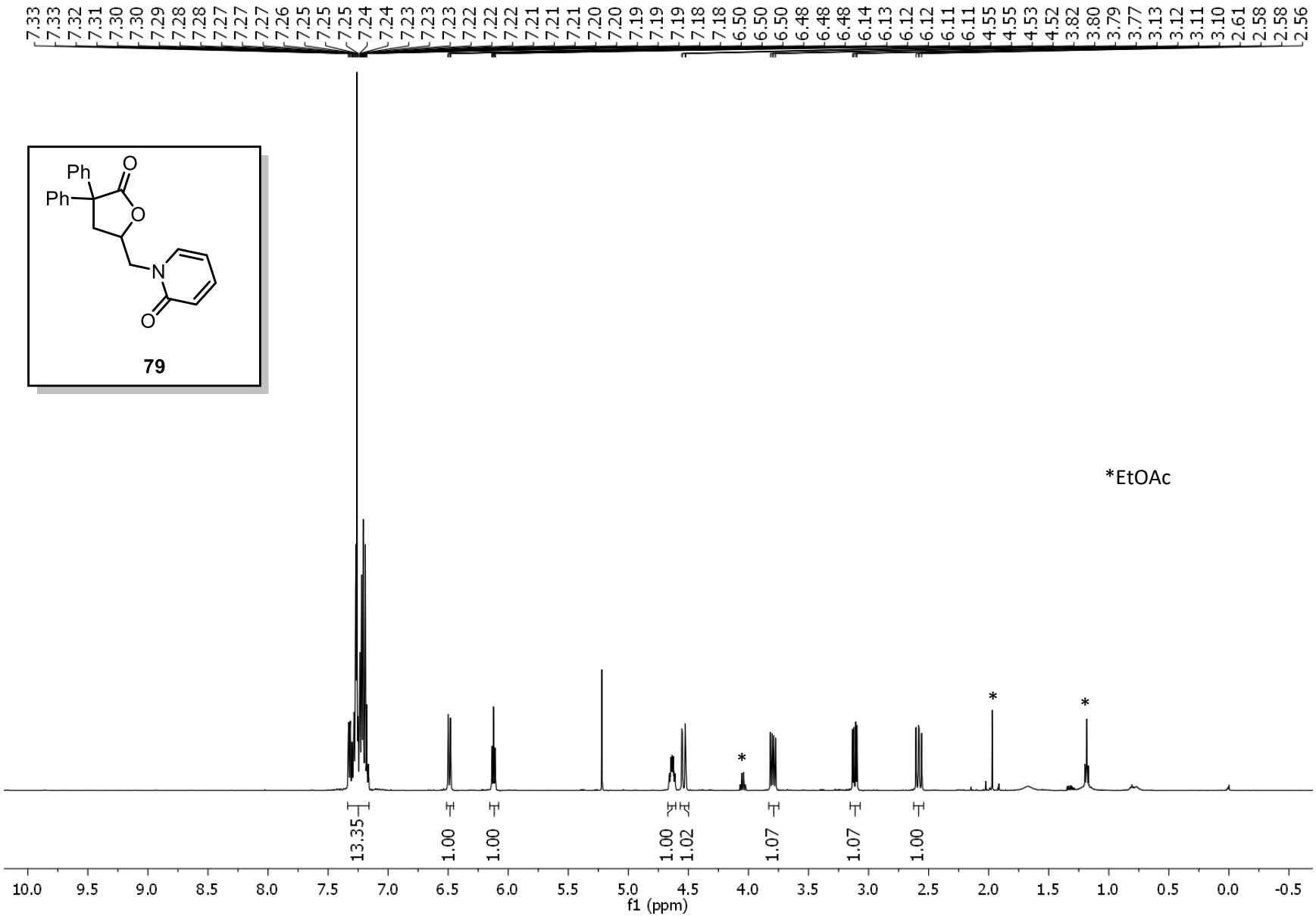
77

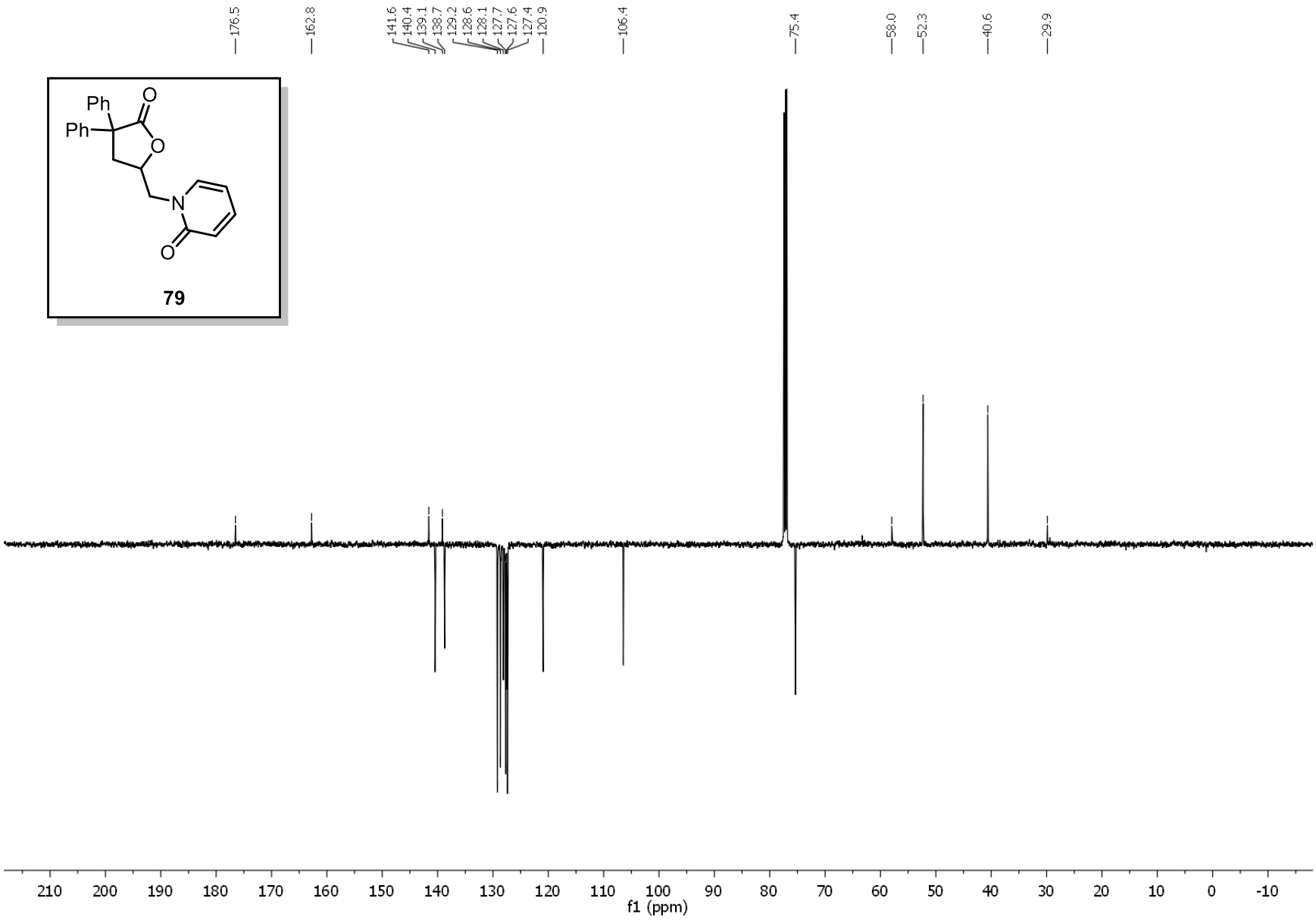

16.42
1.00
1.02
2.02
1.02
4.11
1.16
2.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

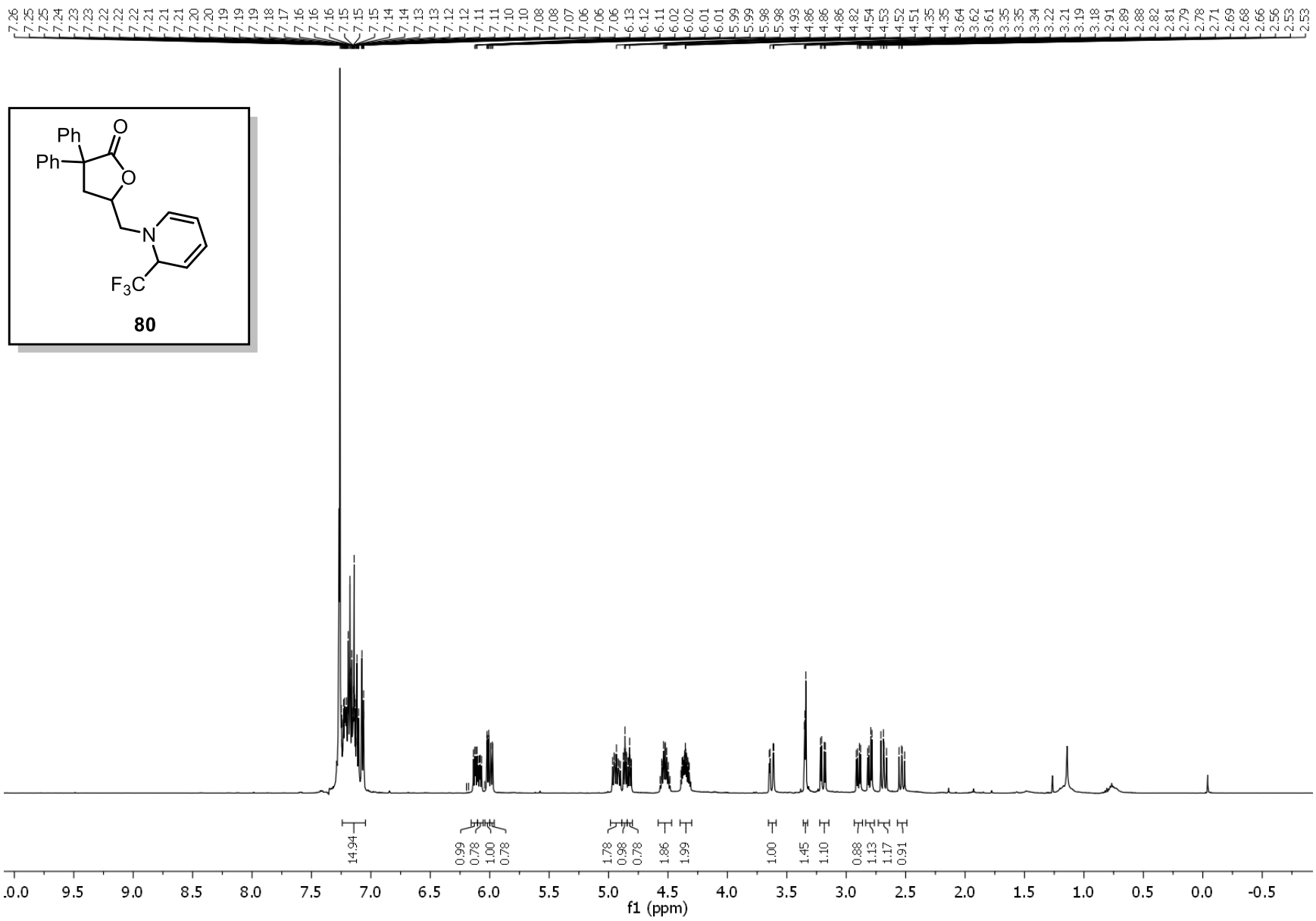

177.1
142.0
140.7
139.7
135.0
129.0
128.4
128.3
127.8
127.4
127.3
127.1
124.9
121.5
77.3
77.1
76.4
61.7
57.7
53.8
51.1
41.9
28.0
Ph
Ph
O
O
N
Ph
77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

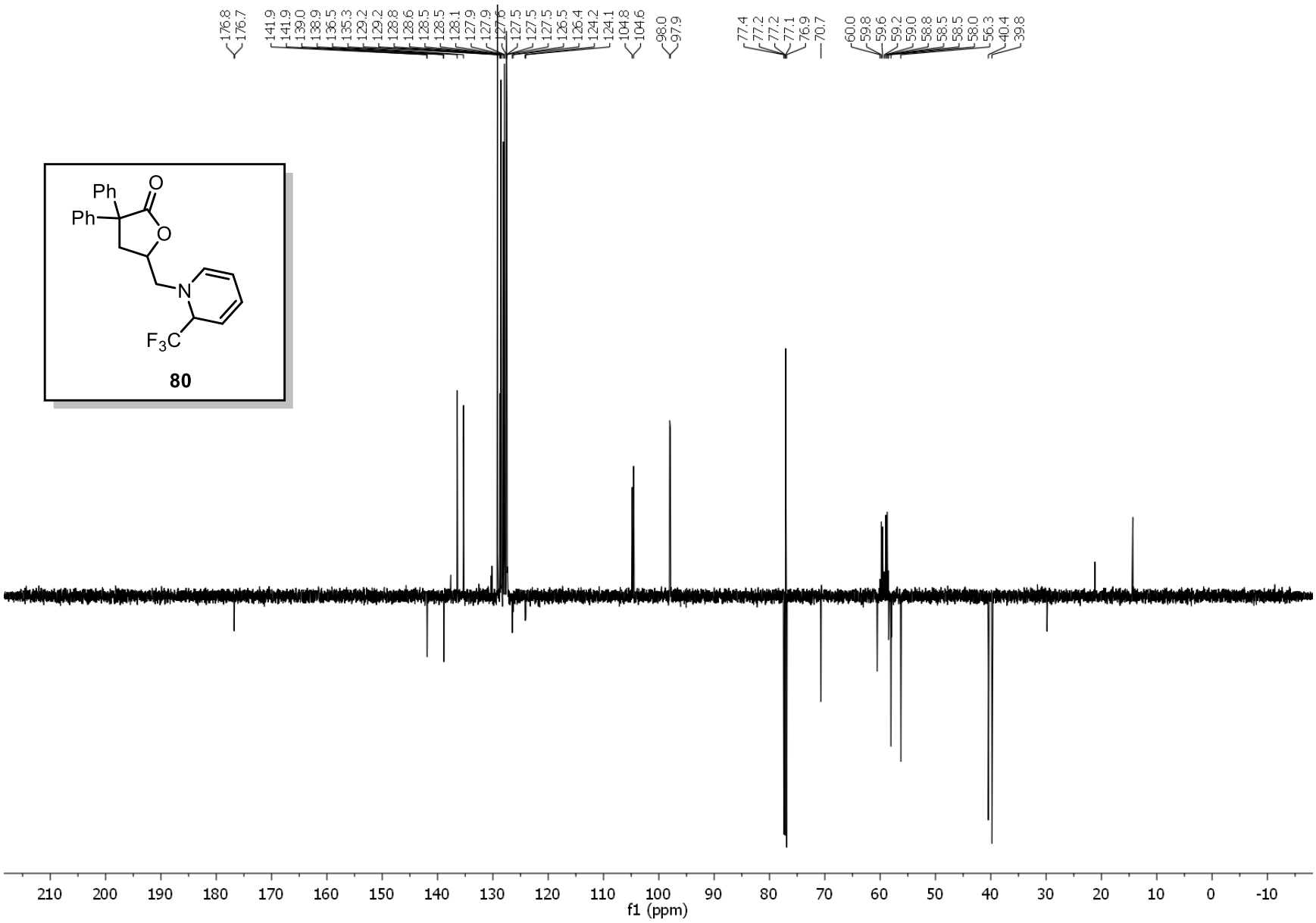

Ph
Ph
O
O
N
CN
78
10.14
1.00
1.06
2.16
1.05
1.05
4.31
2.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

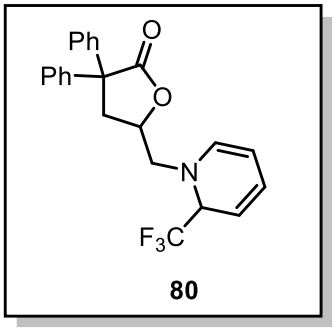

176.9
141.9
141.8
139.6
129.1
128.5
128.0
127.8
127.4
127.4
118.6
110.8
77.4
77.2
76.9
76.1
61.1
57.6
53.0
49.4
41.5
27.5
Ph
Ph
O
O
N
CN
78
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.21 7.20 7.20 7.19 7.19 7.19 7.18 7.18 6.50 6.50 6.50 6.48 6.48 6.48 6.14 6.13 6.12 6.12 6.11 6.11 4.55 4.55 4.53 4.52 3.82 3.80 3.79 3.77 3.13 3.12 3.11 3.10 2.61 2.58 2.58 2.56
Ph
Ph
O
O
N
O
79
*EtOAc
13.35
1.00
1.00
1.00
1.02
1.07
1.07
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


176.5
162.8
141.6
140.4
139.1
138.7
129.2
128.6
128.1
127.7
127.6
127.4
120.9
106.4
75.4
58.0
52.3
40.6
29.9
Ph
Ph
O
O
N
O
79
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

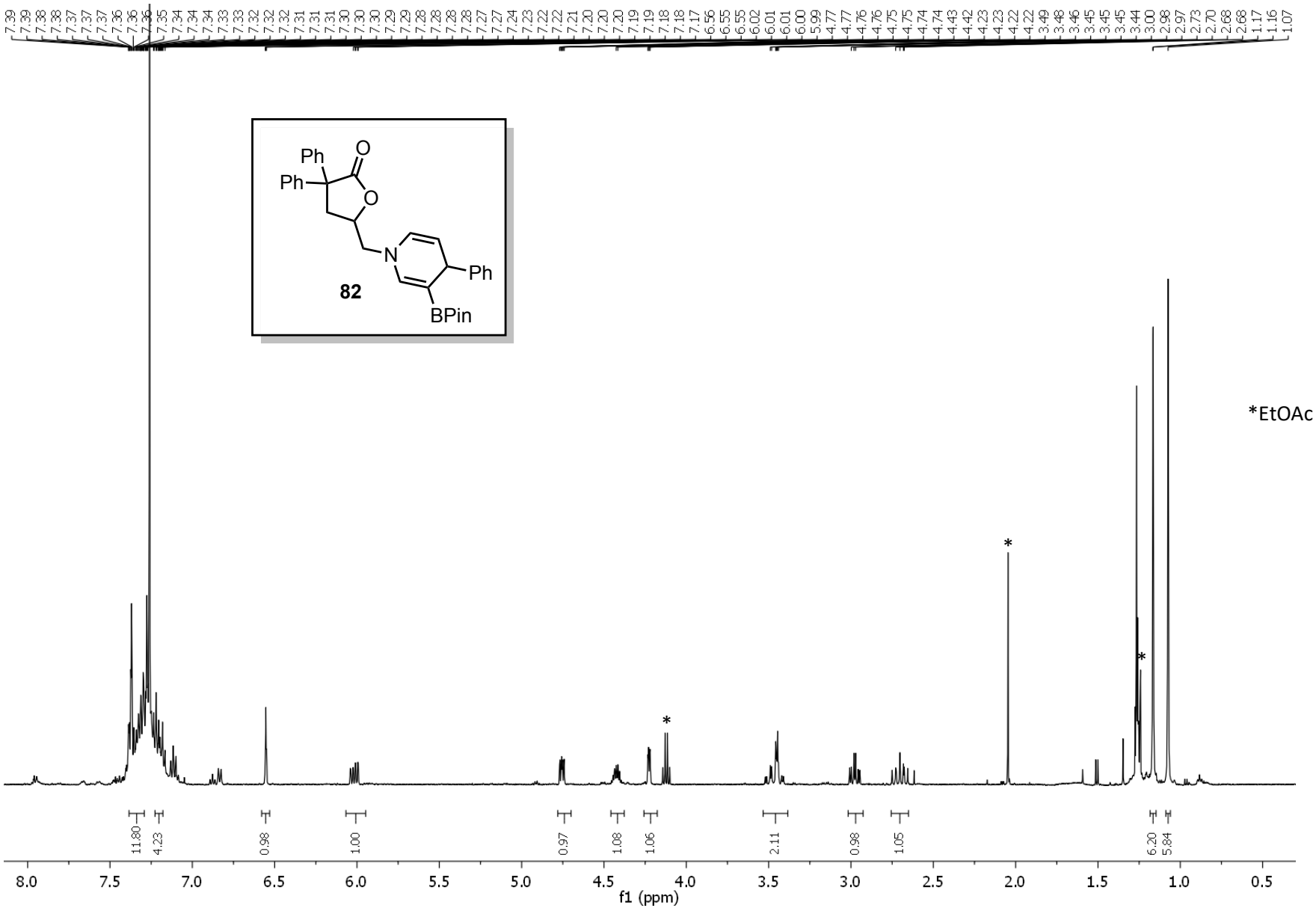

Ph
Ph
O
O
N
F3C
80
f1 (ppm)

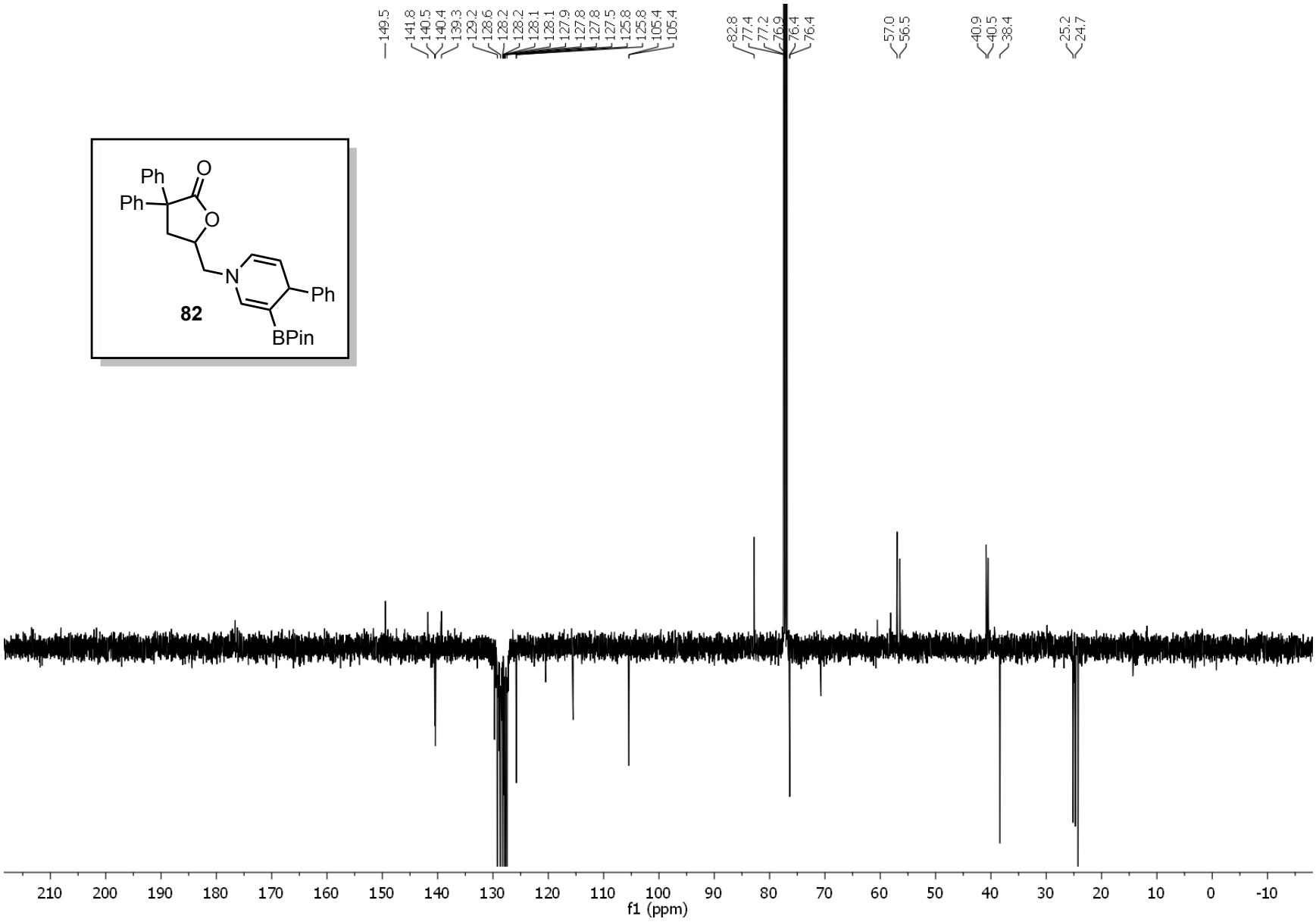

176.8
176.7
141.9
141.9
139.0
138.9
136.5
135.3
129.2
129.2
128.8
128.6
128.5
128.5
128.1
127.9
127.9
127.6
127.5
127.5
127.5
126.5
126.4
124.2
124.1
104.8
104.6
98.0
97.9
77.4
77.2
77.2
77.1
76.9
70.7
60.0
59.8
59.6
59.2
59.0
58.8
58.5
58.5
58.0
56.3
40.4
39.8
Ph
Ph
O
O
N
F3C
80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

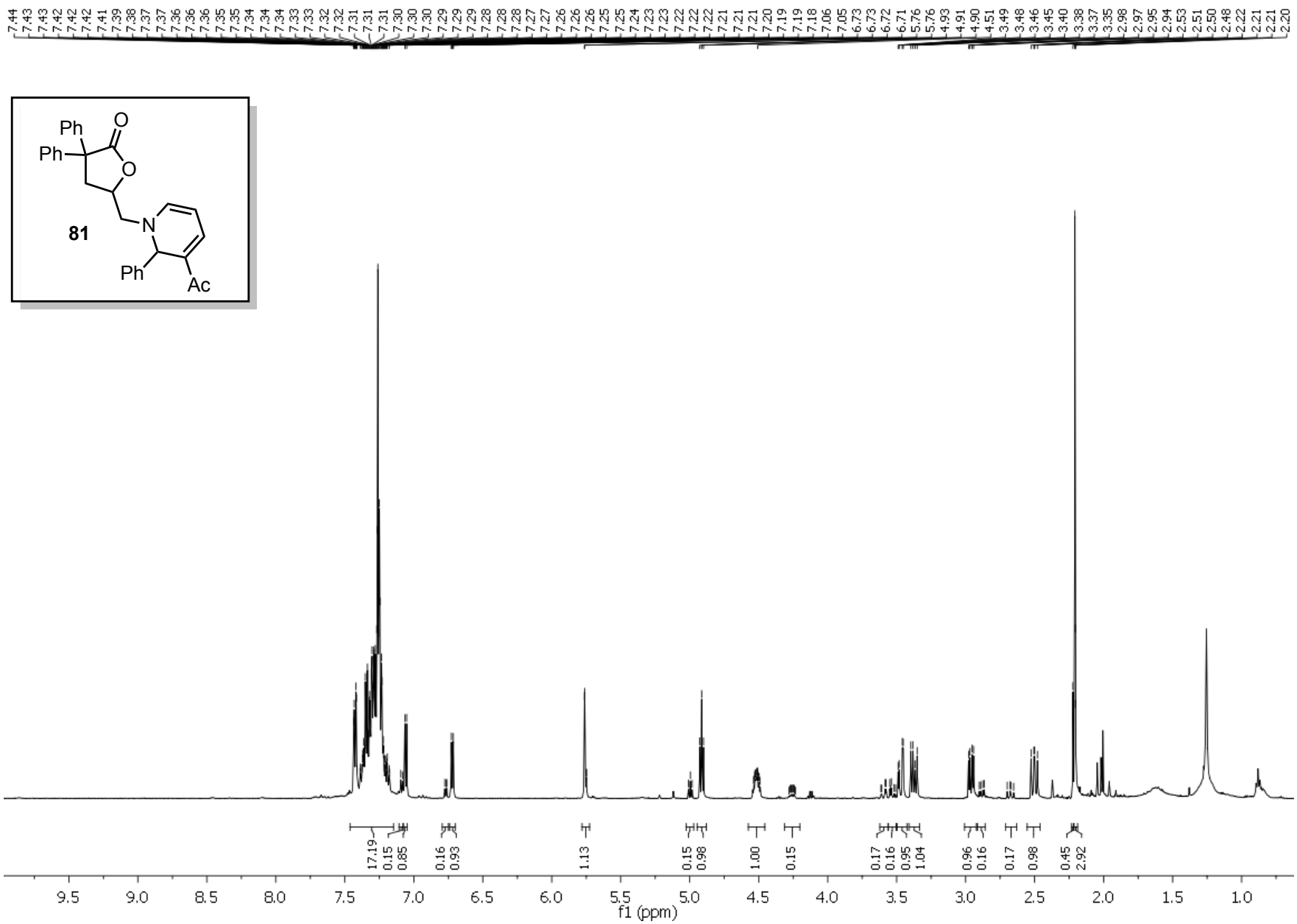

Ph
Ph
O
O
N
F3C

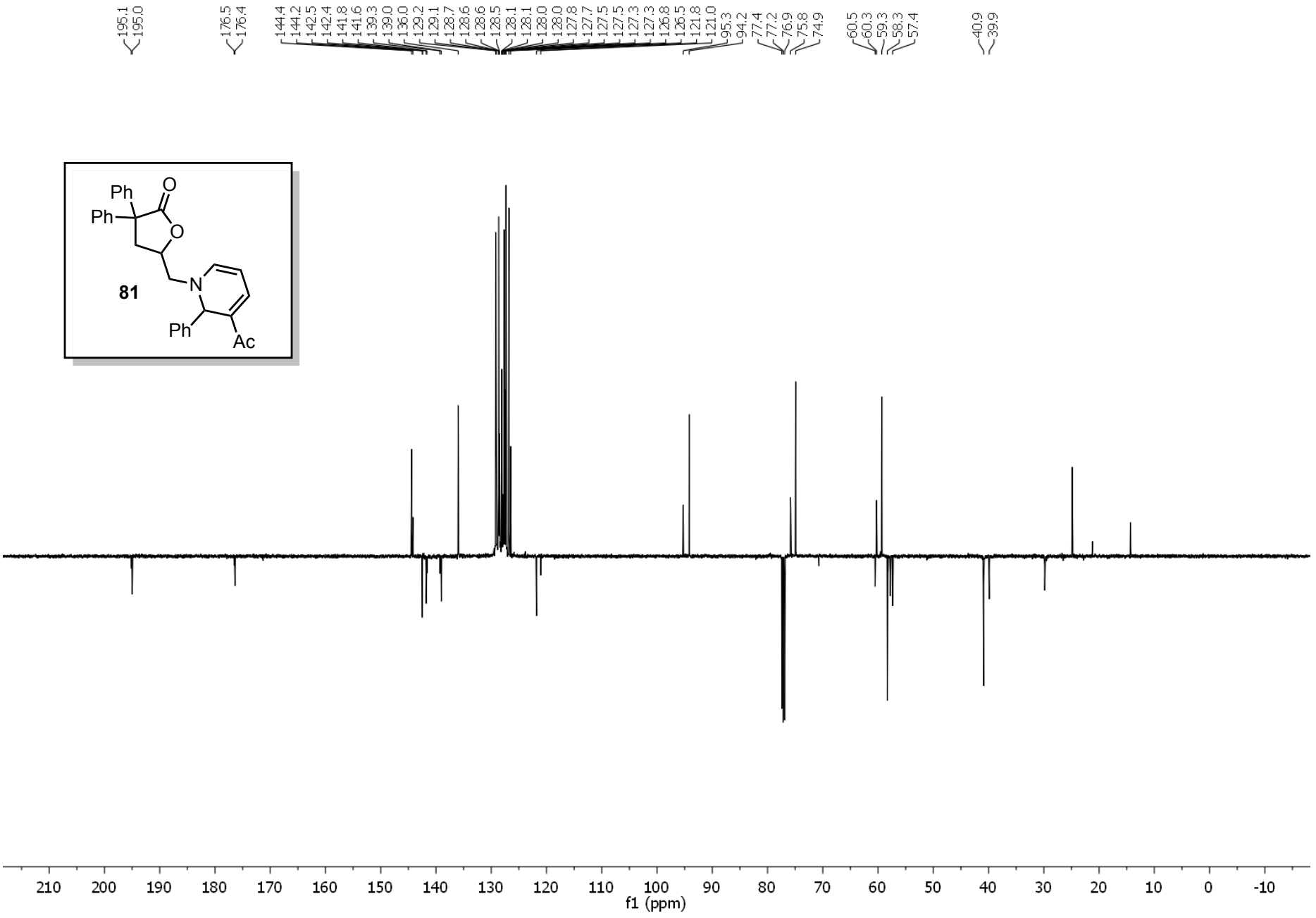
80

-79.901
-80.231
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
f1 (ppm)


Ph
Ph
O
O
N
Ph
BPin
82
*EtOAc
f1 (ppm)


149.5
141.8
140.5
140.4
139.3
129.2
128.6
128.2
128.2
128.1
128.1
127.9
127.8
127.8
127.5
125.8
125.8
105.4
105.4
82.8
77.4
77.2
76.9
76.4
76.4
57.0
56.5
40.9
40.5
38.4
25.2
24.7
Ph
Ph
O
O
N
Ph
BPin
82
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.39 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.21 7.20 7.19 7.19 7.18 7.06 7.05 6.73 6.73 6.72 6.71 5.76 5.76 4.93 4.91 4.90 4.51 3.49 3.48 3.46 3.45 3.40 3.38 3.37 3.35 2.98 2.97 2.95 2.94 2.53 2.51 2.50 2.48 2.22 2.21 2.21 2.20
Ph
Ph
O
O
N
81
Ph
Ac
17.19 0.15 0.85 0.16 0.93 1.13 0.15 0.98 1.00 0.15 0.17 0.16 0.95 1.04 0.96 0.16 0.17 0.98 0.45 2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


195.1
195.0
176.5
176.4
144.4
144.2
142.5
142.4
141.8
141.6
139.3
139.0
136.0
129.2
129.1
128.7
128.6
128.6
128.5
128.1
128.1
128.0
128.0
127.8
127.7
127.5
127.5
127.3
127.3
126.8
126.5
121.8
121.0
95.3
94.2
77.4
77.2
76.9
75.8
74.9
60.5
60.3
59.3
58.3
57.4
40.9
39.9
Ph
Ph
O
O
N
Ph
Ac
81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)