Supporting Information

N-Aminopyridinium Reagents as Traceless Activating Groups in the Synthesis of *N*-Aryl Aziridines

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A. General Considerations

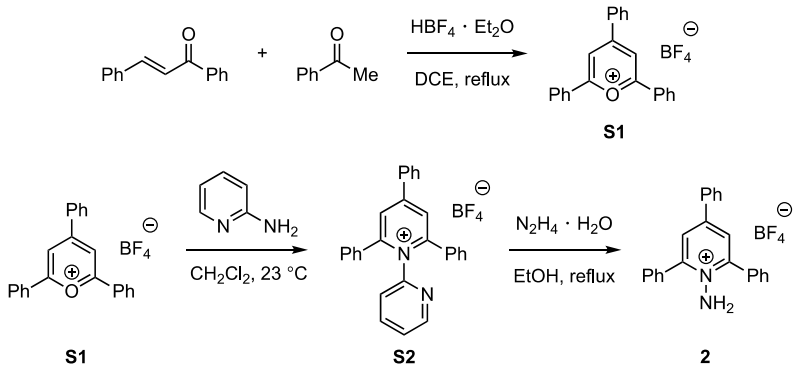
A.1 Materials All chemicals and solvents were obtained as ACS reagent grade and used as received. Styrene, tetrafluoroboric acid etherate, and 2,4,6-collidine were acquired from BeanTown Chemical (BTC). 4-Fluorostyrene, 4-acetoxystyrene, 2-bromostyrene, 4-tolueneboronic acid, 4-chlorophenylboronic acid, 4-fluorophenylboronic acid, 4-trifluoromethylphenylboronic acid 4-ethoxycarbonylphenylboronic acid, and 2-methylphenylboronic acid were purchased from Matrix Scientific. Isatin, 4-trifluoromethylstyrene, 3-bromostyrene, trifluoroboron etherate, *p*-thiocresol, hydrogen fluoride pyridine, 2-(4-isobutylphenyl)propanoic acid (Ibuprofen), 4-(dipropylsulfamoyl)benzoic acid (Probenecid) and *p*-biphenylboronic acid were acquired from Oakwood. Hexanes, ethyl acetate, dichloromethane, potassium phosphate, tetrabutylammonium iodide, anhydrous nickel(II) bromide, nickel(II) bromide dimethoxyethane complex, nickel(II) acetate tetrahydrate, 1,10-phenantroline, 4-methylstyrene, 4-bromophenylboronic acid, 3-(methylthio)phenylboronic acid, *p*-cresol, tetrabutylammonium bromide, tetrabutylammonium azide, carbazole, and chalcone were obtained from Sigma Aldrich. 4-Formylphenylboronic acid, 2-((3-chloro-2-methylphenyl)amino)benzoic acid (Tufnil), and loratadine were acquired from Ambeed. 4-Vinylaniline, 4-vinylbenzoic acid, 4-vinylbenzyl chloride, tetrabutylammonium chloride, and phenylboronic acid were acquired from TCI. 4-Methoxyphenylboronic acid and methyltriphenylphosphonium bromide were acquired from Chem Impex. 3-Nitrostyrene and *trans*-β-methylstyrene were acquired from Acros. Acetophenone, 2-aminopyridine, hydrazine monohydrate, aniline, *p*-methylbenzylamine, and benzyl mercaptan were acquired from Alfa Aesar. Anhydrous sodium sulfate and anhydrous potassium carbonate were obtained from VWR. Acetonitrile and methanol were obtained from Fischer Scientific. *cis*-β-Methylstyrene was acquired from ChemCruz Chemicals. Chloropyramine hydrochloride was acquired from Thermo Scientific. Dry dichloromethane and acetonitrile (purchased from Fisher scientific, HPLC grade) were obtained from a drying column and stored over activated 4 Å molecular sieves.[1] NMR solvents were purchased from Cambridge Isotope Laboratories and were used as received. All reactions were carried out under ambient atmosphere unless otherwise noted. *tert*-Butyl (4-vinylphenyl)carbamate (**1e**),[2] 1-(4-vinylphenyl)ethan-1-one (**1g**),[3] ethyl 4-vinylbenzoate (**1i**),[4] (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**1w**),[5] 4-vinylbenzyl 2-(4-isobutylphenyl)propanoate (**1x**),[6] methyl 2-(methyl(2-methyl-3-vinylphenyl)amino)benzoate (**1y**),[7] 4-vinylbenzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**1z**),[6] and (4-(6-methoxybenzo[d]thiazol-2-yl)phenyl)boronic acid[8] were prepared according to literature procedures.

A.2 Characterization Details ^{1}H and ^{13}C NMR spectral acquisitions were recorded on an Inova 500 FT NMR (Varian), a VNMRS 500 FT NMR (Varian), or an Acsend™ 400 NMR (Bruker) and were referenced against residual proteo solvent signals: $CDCl_3$ (7.26 ppm, ^{1}H; 77.16 ppm, ^{13}C) and acetonitrile-d_3 (1.94 ppm, ^{1}H). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), (multiplicity: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad), integration). ^{13}C NMR data are reported as follows: chemical shift (δ, ppm). Mass spectrometry data were recorded on either Orbitrap Fusion™ Tribrid™ Mass Spectrometer

or Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™ Mass Spectrometer from ThermoFisher Scientific. Preparative HPLC was carried out by Agilent 1260 Infinity II Preparative LC System, Agilent 1290 II Preparative Open-Bed Fraction Collector, using an Agilent Prep-C18 column (50 × 50 mm, 5 μm pore, part# 446905-502). HPLC grade acetonitrile was purchased from Sigma Aldrich and was used as the eluent.

B. Synthesis and Characterization

B.1 Synthesis of 1-amino-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2).



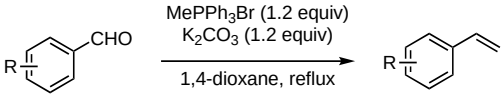
2,4,6-Triphenylpyrylium tetrafluoroborate (**2**) was synthesized according to the following literature procedure.[9] A 2-L round bottom flask was charged with chalcone (68.8 g, 33.2 mmol, 2.00 equiv), acetophenone (20.0 g, 16.6 mmol, 1.00 equiv), and dichloroethane (DCE, 120 mL). Tetrafluoroboric acid etherate (46 mL, 33.2 mmol, 2.00 equiv) was added dropwise using an addition funnel. The reaction mixture was heated to reflux for 4 h. The reaction mixture was cooled to 23 °C before diethyl ether was added and the crude mixture was filtered. The obtained yellow solid was washed with diethyl ether (50 × 5 mL) and dried under vacuum to yield 45.0 g of compound **S1** (68% yield). ^{1}H NMR (499 MHz, CD_3CN) δ 8.72 (s, 2H), 8.46–8.40 (m, 4H), 8.33–8.28 (m, 2H), 7.90–7.84 (m, 3H), 7.81–7.75 (m, 6H).

1-Amino-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**2**) was according to the following literature procedure.[10] To a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate (10.0 g, 25.3 mmol, 1.00 equiv) in dichloromethane (253 mL, 0.100 M) was added 2-aminopyridine (3.57 g, 38.0 mmol, 1.50 equiv). The reaction was stirred at 23 °C for 12 h before solvent was removed under reduced pressure. Addition of Et_2O to the residue resulted in crystallization of 11.6 g of **S2** (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 1H), 8.11 (s, 2H), 7.96–7.87 (m, 2H), 7.80–7.73 (m, 1H), 7.65–7.47 (m, 8H), 7.38–7.24 (m, 6H), 7.12 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1H).

To a suspension of **S2** (9.99 g, 21.2 mmol, 1.00 equiv) in ethanol (70 mL) was added hydrazine monohydrate (5.36 g, 106 mmol, 5.00 equiv). The reaction is heated under reflux for 4 h. The reaction mixture was cooled to 23 °C before a small amount of diethyl ether (1.0 mL) was added. The reaction mixture was cooled to –20 °C at which the target product crystallized. The obtained solid was recrystallized from CH_2Cl_2 and Et_2O and then dried under vacuum at 70 °C to afford 5.81 g of the title compound (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.86–7.76 (m, 4H), 7.77–7.70 (m, 2H), 7.66–7.57 (m, 6H), 7.60–7.50 (m, 3H), 6.20 (s, 2H).

B.2 Preparation of Vinyl Arenes

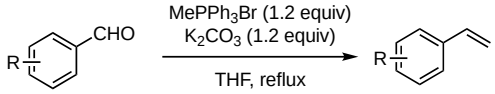
General Procedure A[11]



4-Vinylbenzonitrile (**1j**), 3-methylstyrene (**1l**), and 2-methylstyrene (**1q**) were synthesized according to the following procedure. Characterization data were well-matched to those reported in literature.

A 50-mL round bottom flask was charged with methyltriphenylphosphonium bromide (3.57 g, 10.0 mmol, 1.20 equiv), potassium carbonate (1.80 g, 13.0 mmol, 1.57 equiv), the appropriate benzaldehyde (8.30 mmol, 1.00 equiv), and 1,4-dioxane (10 mL). The reaction mixture was heated to reflux for 24 h. The reaction mixture was cooled to 23 °C, filtered, and the filtrate was concentrated under reduced pressure. The residue purified by silica gel column chromatography using 100% hexanes as the eluent to afford the corresponding styrene.

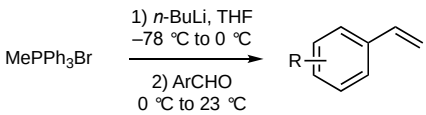
General Procedure B[12]



4-Vinylanisole (**1d**) and 2-vinylnaphthalene (**1p**) were synthesized according to the following procedure. Characterization data were well-matched to those reported in literature.

A 50-mL Schlenk flask was charged with methyltriphenylphosphonium bromide (2.70 g, 7.69 mmol, 1.20 equiv), potassium carbonate (1.30 g, 9.60 mmol, 1.50 equiv) and the corresponding benzaldehyde (6.40 mmol, 1.00 equiv) under N_2. Anhydrous tetrahydrofuran (15 mL) was added and the reaction mixture was heated at reflux for 48 h. The reaction was cooled to 23 °C, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using 100% hexanes as the eluent to give the corresponding styrene.

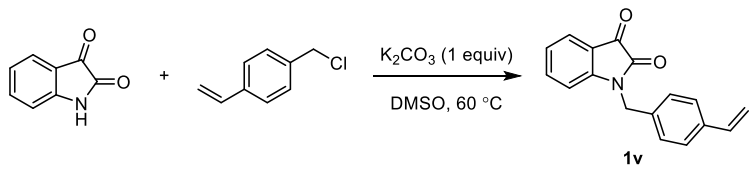
Gerenal Procedure C[13]



4-Vinyl-1,1'-biphenyl (**1c**), 3-chlorostyrene (**1n**), 2-vinylanisole (**1r**), and 2-vinylbenzo[b]thiophene (**1t**) were synthesized according to the following procedure. Characterization data were well-matched to those reported in literature.

A 50-mL Schlenk flask was charged with methyltriphenylphosphonium bromide (1.70 g, 4.75 mmol, 1.20 equiv) and tetrahydrofuran (35 mL). *n*-Butyl lithium (2.5 M, 4.40 mmol, 1.8 mL, 1.10 equiv) was added dropwise at −78 °C under N_2. The reaction mixture was warmed to 0 °C at which temperature it was stirred for 2h. The appropriate benzaldehyde was then added dropwise at 0 °C.[1] The reaction was allowed to stir at 23 °C overnight. Saturated aqueous NH_4Cl (35 mL) was added. The mixture was extracted with ethyl acetate (20 × 3 mL), washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using 100% hexanes or 5% ethyl acetate in hexanes as the eluent to give the corresponding styrene.

Synthesis of 1-(4-vinylbenzyl)indoline-2,3-dione (1v)

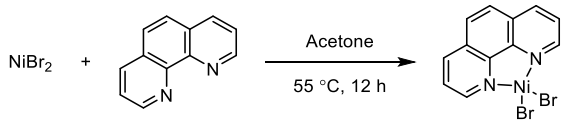


1v

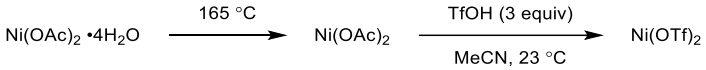
A 50-mL round bottom flask was charged with indoline-2,3-dione (13.6 mmol, 2.00 g, 1.00 equiv), potassium carbonate (13.6 mmol, 1.88 g, 1.00 equiv), and DMSO (45 mL). 1-(Chloromethyl)-4-vinylbenzene (4.20 g, 27.5 mmol, 2.02 equiv) was added and the reaction mixture was heated at 60 °C for 24 h. The reaction was cooled to 23 °C before water (40 mL) and EtOAc (40 mL) were added. The organic layer was washed with distilled water (30 mL × 5) and then brine (30 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using 10% EtOAc in hexanes as the eluent to yield a red solid (2.69 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.47 (td, *J* = 7.8, 1.4 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.25 (d, *J* = 10.8 Hz, 1H), 4.91 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3, 158.4, 150.8, 138.4, 137.7, 136.2, 134.0, 127.8, 127.0, 125.5, 124.0, 117.8, 114.7, 111.1, 43.9. HRMS-ESI$^+$: calculated for [M+1] = 264.1019, observed [M+1] = 264.1019.

[1] If the benzaldehyde is a solid, it was added to the reaction mixture as a solution in tetrahydrofuran.

B.3 Preparation of Nickel(II) Catalysts



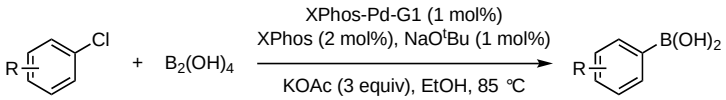
Ni(Phen)Br_2 was prepared according to the following modification of literature methods.[14] A 20-mL scintillation vial was charged with anhydrous nickel(II) bromide (218 mg, 1.00 mmol, 1.00 equiv) and acetone (2 mL). 1,10-Phenanthroline (180 mg, 1.00 mmol, 1.00 equiv) was dissolved in acetone (4 mL) and added to the reaction mixture. The reaction mixture was heated at 55 °C for 12 h. The reaction was cooled to 23 °C before the resulting green suspension was concentrated under reduced pressure. The residue was dried under vacuum at 65 °C to yield a blue-green powder (392 mg, 98% yield). ^{1}H NMR (400 MHz, DMSO) δ 49.6 (s, 2H), 45.7 (s, 2H), 25.2 (s, 2H), 23.5 (s, 2H), 18.9–19.2, (m, 4H). These spectral data are well-matched to those reported in the literature.[15]



Ni$(OTf)_2$ was prepared according to the following modification of literature methods.[16] Nickel(II) acetate tetrahydrate was first heated under air at 165 °C for overnight to afford anhydrous nickel(II) acetate. A 100-mL Schlenk flask was charged with anhydrous nickel(II) acetate (354 mg, 2.00 mmol, 1.00 equiv) and acetonitrile (25 mL) under N_2. Trifluoromethanesulfonic acid (900 mg, 6.00 mmol, 3.00 equiv) was added via syringe dropwise. The reaction was stirred at 23 °C for 2 h to give a blue solution. The reaction was concentrated to ~6 mL under reduced pressure. Diethyl ether (20 mL) was added and blue solid precipitated. The liquid was decanted and the solid was washed with diethyl ether and hexanes. The solid was dried under vacuum at 70 °C to yield a light green powder (454 mg, 64% yield).

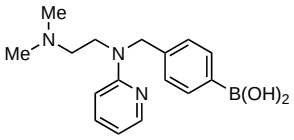
B.4 Preparation of Aryl boronic acids[2]

General Procedure[17]



Boronic acids **4a** (derivatized from indomethacin methyl ester)[17] and **4b** (derived from loratadine)[17] were synthesized according to the procedure above and characterization data matched those reported in literature.

A 50-mL sealed tube was charged with the appropriate aryl chloride (2.75 mmol, 1.00 equiv), hypodiboric acid (370 mg, 4.13 mmol, 1.50 equiv), XPhos-Pd-G1 (20.3 mg, 0.00275 mmol, 1 mol%), XPhos (26.2 mg, 0.0550 mmol, 2 mol%), sodium *tert*-butoxide (2.6 mg, 0.0550 mmol, 2 mol%), and potassium acetate (810 mg, 8.25 mmol, 3.00 equiv). Ethanol (15 mL) was added under N_2. The reaction was heated at 85 °C for 3 h. After cooling to 23 °C, the reaction mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The residue was dissolved in 5 mL of CH_2Cl_2 and the solution was added dropwise to a 250-mL beaker containing 100 mL of hexane. The resulting precipitate was isolated by filtraton and dried under vacuum to yield the respective boronic acids.

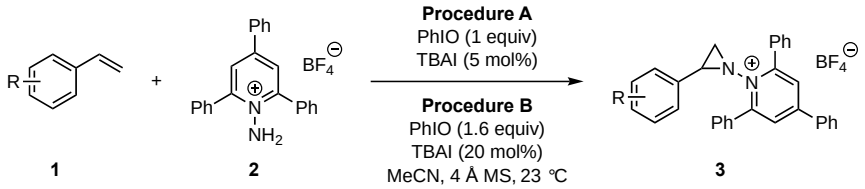


4c

(4-(((2-(dimethylamino)ethyl)(pyridin-2-yl)amino)methyl)phenyl)boronic acid (**4c**). Obtained from chloropyramine (840 mg, 2.90 mmol) according to the general procedure and obtained as a white solid (367 mg, 42% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11–8.05 (m, 1H), 7.96 (s, 2H), 7.75–7.68 (m, 2H), 7.43 (ddd, J = 8.9, 7.1, 2.0 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 6.57–6.49 (m, 2H), 4.74 (s, 2H), 3.62 (t, J = 7.1 Hz, 2H), 2.45 (t, J = 7.0 Hz, 2H), 2.19 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 157.7, 147.6, 141.0, 137.3, 134.3, 125.8, 111.6, 105.7, 56.5, 51.2, 45.9, 45.4. HRMS-ESI$^+$: calculated for [M+1] = 300.1878, observed [M+1] = 300.1878.

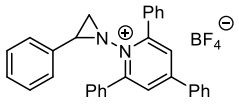
[2] Simple boronic acids acquired from commercial sources contains varied amount of the corresponding acid anhydrides. 4-Toluene boronic acid acquired from Matrix, contained ~90% of *p*-tolylboroxine indicated by ^{1}H NMR spectroscopy. Heating a sample at 120 °C under air for 48 h resulted in a sample of the boroxine containing less than 5% boronic acid. Other boronic acids were used as received.

B.5 Vinyl Arene Aziridination



Procedure A In an N_2 filled dry box, a 20-mL scintillation vial was charged with 1-amino-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**2**, 82.0 mg, 0.200 mmol, 1.00 equiv), tetrabutylammonium iodide (3.7 mg, 0.010 mmol, 5 mol%), 4 Å molecular sieves, vinyl arene (**1**, 0.200 mmol, 1.00 equiv),[3] and iodosylbenzene (44.0 mg, 0.200 mmol, 1.00 equiv). Acetonitrile (1.0 mL) was added, the vial was removed from the dry box, and the reaction mixture was stirred for 18 h. The reaction mixture was filtered through a pad of Celite and concentrated in vacuo. The residue was purified by silica gel flash chromatography (2:1 ethyl acetate:hexanes) to afford the title compound.

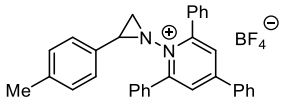
Procedure B In an N_2 filled dry box, a 20-mL scintillation vial was charged with 1-amino-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**2**, 131 mg, 0.320 mmol, 1.60 equiv), tetrabutylammonium iodide (14.8 mg, 0.0400 mmol, 20 mol%), 4 Å molecular sieves, vinyl arene (**1**, 0.200 mmol, 1.00 equiv, if is a solid), and iodosylbenzene (70.4 mg, 0.320 mmol, 1.60 equiv).[3] Acetonitrile (1.0 mL) was added, the vial was removed from the dry box, and the reaction mixture was stirred for 18 h. The reaction mixture was filtered through a pad of Celite and concentrated in vacuo. The residue was purified by silica gel flash chromatography (2:1 ethyl acetate:hexanes) to afford the title compound.



3a

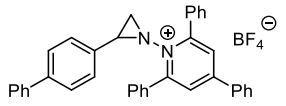
*2,4,6-triphenyl-1-(2-phenylaziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3a**)*. Prepared via Procedure A from styrene (**1a**) and obtained as a pale-yellow powder (72.8 mg, 71% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.14 (s, 2H), 8.04–7.92 (m, 5H), 7.68–7.25 (m, 9H), 7.23–7.17 (m, 1H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.72–6.57 (m, 2H), 3.52 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.69 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.36 (dd, *J* = 5.7, 3.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 154.0, 134.9, 134.8, 132.8, 132.6, 132.4, 130.8, 130.6, 130.0, 129.1, 128.8, 127.1, 126.4, 54.5, 49.0. ^{19}F NMR (376 MHz, CD_3CN) δ –151.92, –151.97. HRMS-ESI$^+$: calculated for [M$^+$] = 425.2012, observed [M$^+$] = 425.2007.

[3] If the vinyl arene is a solid, it is added to the reaction mixture neat. If the vinyl arene is a liquid, it is added to the reaction mixture as a solution in CH_3CN.



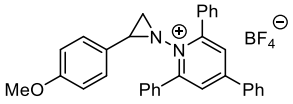
3b

*2,4,6-triphenyl-1-(2-(p-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3b**)*. Prepared via Procedure A from 4-methylstyrene (**1b**) and obtained as a yellow powder (75.8 mg, 72% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.14 (s, 2H), 8.07–7.85 (m, 6H), 7.73–7.18 (m, 9H), 6.99–6.90 (m, 2H), 6.60–6.48 (m, 2H), 3.48 (dd, *J* = 8.4, 5.8 Hz, 1H), 2.65 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.34 (dd, *J* = 5.8, 3.1 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 153.9, 139.1, 134.9, 132.8, 132.6, 132.5, 131.7, 130.8, 130.6, 130.0, 129.4, 129.1, 127.1, 126.4, 54.5, 48.9, 21.1. ^{19}F NMR (377 MHz, CD_3CN) δ –151.98, –152.03. HRMS-ESI$^+$: calculated for [M$^+$] = 439.2169, observed [M$^+$] = 439.2166.



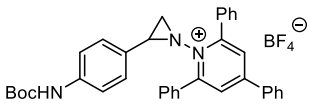
3c

*1-(2-([1,1'-biphenyl]-4-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3c**)*. Prepared via Procedure A from 4-vinyl-1,1'-biphenyl (**1c**) and obtained as a yellow powder (83.6 mg, 71% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.15 (s, 2H), 8.07–7.95 (m, 6H), 7.72–7.32 (m, 16H), 6.73 (d, *J* = 8.3 Hz, 2H), 3.55 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.71 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.43 (dd, *J* = 5.8, 3.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 154.0, 141.7, 141.2, 134.9, 134.0, 132.9, 132.6, 132.5, 130.8, 130.6, 130.1, 129.8, 129.1, 128.5, 127.8, 127.3, 127.1, 127.0, 54.4, 48.9. ^{19}F NMR (377 MHz, CD_3CN) δ –151.94, –152.00. HRMS-ESI$^+$: calculated for [M$^+$] = 501.2325, observed [M$^+$] = 501.2319.



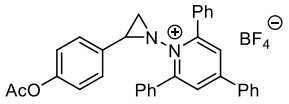
3d

*1-(2-(4-methoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3d**)*. Prepared via Procedure A from 4-vinylanisole (**1d**) and obtained as a yellow powder (61.8 mg, 57% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.14 (s, 2H), 8.04–7.88 (m, 6H), 7.72–7.35 (m, 9H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 3.74 (s, 3H), 3.48 (dd, *J* = 8.4, 5.8 Hz, 1H), 2.64 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.35 (dd, *J* = 5.9, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 160.7, 154.2, 153.9, 134.9, 132.9, 132.7, 132.5, 130.8, 130.6, 130.0, 129.1, 127.8, 127.1, 126.6, 114.2, 55.9, 54.5, 48.6. ^{19}F NMR (377 MHz, CD_3CN) δ –152.15, -152.21. HRMS-ESI$^+$: calculated for [M$^+$] = 455.2118, observed [M$^+$] = 455.2113.



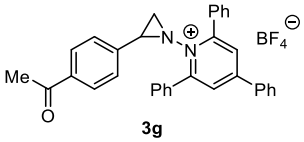
3e

*1-(2-(4-((tert-butoxycarbonyl)amino)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3e**)*. Prepared via Procedure A from tert-butyl (4-vinylphenyl)carbamate (**1e**) and obtained as a yellow powder (64.0 mg, 51% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.14 (s, 2H), 7.98 (ddd, *J* = 19.0, 7.6, 2.3 Hz, 6H), 7.69–7.35 (m, 9H), 7.19–7.12 (m, 2H), 6.58–6.51 (m, 2H), 3.46 (dd, *J* = 8.4, 5.8 Hz, 1H), 2.63 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.33 (dd, *J* = 5.8, 3.1 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 153.9, 153.7, 140.3, 134.9, 132.9, 132.6, 132.5, 130.8, 130.6, 130.2, 130.0, 129.1, 128.6, 127.1, 127.1, 80.6, 54.5, 48.7, 28.4. ^{19}F NMR (376 MHz, CD_3CN) δ –152.30, –152.35. HRMS-ESI$^+$: calculated for [M$^+$] = 540.2646, observed [M$^+$] = 540.2646.



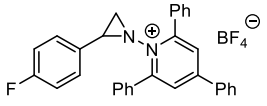
3f

*1-(2-(4-acetoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3f**)*. Prepared via Procedure A from 4-vinylphenyl acetate (**1f**) and obtained as a yellow powder (67.5 mg, 59% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.16 (s, 2H), 8.05–7.82 (m, 6H), 7.71–7.31 (m, 9H), 6.89–6.81 (m, 2H), 6.73–6.65 (m, 2H), 3.50 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.68 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.40 (dd, *J* = 5.7, 3.1 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 170.4, 154.2, 154.1, 151.8, 134.9, 132.9, 132.6, 132.5, 132.4, 130.8, 130.6, 130.1, 129.1, 127.6, 127.1, 122.3, 54.0, 49.0, 21.2. ^{19}F NMR (376 MHz, CD_3CN) δ –152.00, –152.06. HRMS-ESI$^+$: calculated for [M$^+$] = 483.2067, observed [M$^+$] = 483.2069.



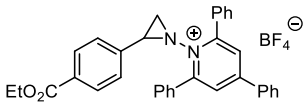
3g

*1-(2-(4-acetylphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3g**)*. Prepared via Procedure A from 1-(4-vinylphenyl)ethan-1-one (**1g**) and obtained as a yellow powder (72.1 mg, 65% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.15 (s, 2H), 7.99 (m, 6H), 7.77–6.99 (m, 11H), 6.83–6.77 (m, 2H), 3.57 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.75 (dd, *J* = 8.4, 3.0 Hz, 1H), 2.53 (s, 3H), 2.42 (dd, *J* = 5.7, 3.0 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 198.5, 154.1, 154.1, 140.0, 137.7, 134.8, 132.8, 132.5, 132.4, 130.7, 130.6, 130.0, 129.1, 128.6, 127.1, 126.6, 53.9, 49.3, 26.9. ^{19}F NMR (377 MHz, CD_3CN) δ –152.30, –152.35. HRMS-ESI$^+$: calculated for [M$^+$] = 467.2118, observed [M$^+$] = 467.2110.



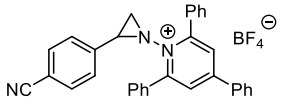
3h

*1-(2-(4-fluorophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3h**)*. Prepared via Procedure B from 4-fluorostyrene (**1h**) and obtained as a brown powder (88.0 mg, 83% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.14 (s, 2H), 8.04–7.88 (m, 6H), 7.67–7.22 (m, 9H), 6.92–6.81 (m, 2H), 6.73–6.61 (m, 2H), 3.53 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.69 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.35 (dd, *J* = 5.7, 3.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 164.7, 162.2, 154.2, 154.1, 134.9, 132.9, 132.5, 132.5, 131.0, 131.0, 130.8, 130.6, 130.0, 129.1, 128.5, 128.4, 127.1, 115.7, 115.5, 53.8, 48.9. ^{19}F NMR (377 MHz, CD_3CN) δ –115.20, –152.37, –152.42. HRMS-ESI$^+$: calculated for [M$^+$] = 443.1918, observed [M$^+$] = 443.1912.



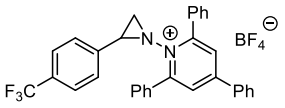
3i

*1-(2-(4-(ethoxycarbonyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3i**)*. Prepared via Procedure B from ethyl 4-vinylbenzoate (**1i**) and obtained as a brown powder (94.7 mg, 81% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.16 (s, 2H), 8.05–7.88 (m, 6H), 7.78–7.70 (m, 2H), 7.68–7.27 (m, 9H), 6.83–6.76 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.57 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.74 (dd, *J* = 8.4, 3.0 Hz, 1H), 2.40 (dd, *J* = 5.7, 3.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 166.4, 153.9, 153.8, 139.7, 134.5, 132.6, 132.2, 132.1, 130.9, 130.5, 130.3, 129.7, 129.3, 128.8, 126.8, 126.3, 61.5, 53.6, 49.1, 14.2. ^{19}F NMR (377 MHz, CD_3CN) δ –152.46, –152.52. HRMS-ESI$^+$: calculated for [M$^+$] = 497.2224, observed [M$^+$] = 497.2223.



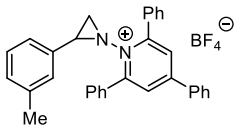
3j

*1-(2-(4-cyanophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3j**)*. Prepared via Procedure B from 4-vinylbenzonitrile (**1j**) and obtained as a brown powder (96.7 mg, 90% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.17 (s, 2H), 8.06–7.79 (m, 6H), 7.67–7.37 (m, 11H), 6.89–6.82 (m, 2H), 3.54 (dd, *J* = 8.1, 5.9 Hz, 1H), 2.75 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.43 (dd, *J* = 5.7, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.3, 154.2, 140.4, 134.8, 133.0, 132.6, 132.6, 132.4, 130.8, 130.6, 130.1, 129.1, 127.4, 127.2, 119.4, 112.4, 53.6, 49.4. ^{19}F NMR (377 MHz, CD_3CN) δ –151.98, –152.03. HRMS-ESI$^+$: calculated for [M$^+$] = 450.1965, observed [M$^+$] = 450.1955.



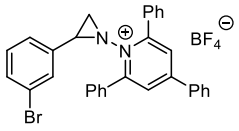
3k

*2,4,6-triphenyl-1-(2-(4-(trifluoromethyl)phenyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3k**)*. Prepared via Procedure B from 4-(trifluoromethyl)styrene (**1k**) and obtained as a brown powder (24.4 mg, 21% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.17 (s, 2H), 8.05–7.85 (m, 6H), 7.76–7.05 (m, 11H), 6.91–6.85 (m, 2H), 3.57 (dd, *J* = 8.4, 5.6 Hz, 1H), 2.75 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.44 (dd, *J* = 5.7, 3.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.3, 154.2, 139.5, 134.86, 133.0, 132.5, 132.4, 130.8, 130.6, 130.3, 130.1, 129.1, 127.2, 127.2, 126.5, 125.6, 125.6, 123.8, 53.7, 49.3. ^{19}F NMR (376 MHz, CD_3CN) δ –63.14, –152.02, –152.07. HRMS-ESI$^+$: calculated for [M$^+$] = 493.1886, observed [M$^+$] = 493.1874.



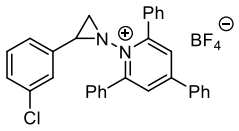
3l

*2,4,6-triphenyl-1-(2-(m-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3l**)*. Prepared via Procedure B from 3-methylstyrene (**1l**) and obtained as a brown powder (78.9 mg, 75% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.13 (s, 2H), 8.07–7.91 (m, 6H), 7.70–7.21 (m, 9H), 7.04–6.98 (m, 2H), 6.50–6.44 (m, 1H), 6.39 (s, 1H), 3.47 (dd, *J* = 8.4, 5.8 Hz, 1H), 2.67 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.37 (dd, *J* = 5.8, 3.1 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 154.0, 138.4, 134.9, 134.6, 132.8, 132.6, 132.4, 130.8, 130.6, 130.0, 129.8, 129.1, 128.7, 127.7, 127.1, 123.0, 54.6, 48.6, 21.0. ^{19}F NMR (376 MHz, CD_3CN) δ –151.75, –151.81. HRMS-ESI$^+$: calculated for [M$^+$] = 439.2169, observed [M$^+$] = 439.2161.



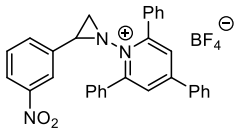
3m

*1-(2-(3-bromophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3m**)*. Prepared via Procedure B from 3-bromostyrene (**1m**) and obtained as a brown powder (76.8 mg, 65% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.16 (s, 2H), 8.05–7.89 (m, 6H), 7.69–7.40 (m, 9H), 7.36 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.80 (t, *J* = 1.9 Hz, 1H), 6.71–6.64 (m, 1H), 3.46 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.69 (dd, *J* = 8.4, 3.2 Hz, 1H), 2.42 (dd, *J* = 5.7, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 137.3, 134.8, 132.9, 132.6, 132.4, 132.1, 130.8, 130.7, 130.6, 130.0, 129.7, 129.1, 127.1, 125.2, 122.3, 53.7, 48.8. ^{19}F NMR (377 MHz, CD_3CN) δ –152.27, –152.33. HRMS-ESI$^+$: calculated for [M$^+$] = 503.1117, observed [M$^+$] = 503.1109.



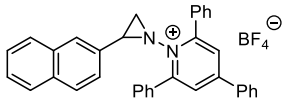
3n

*1-(2-(3-chlorophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3n**)*. Prepared via Procedure A from 3-chlorostyrene (**1n**) and obtained as a yellow powder (53.6 mg, 49% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.15 (s, 2H), 7.98 (m, 6H), 7.71–7.28 (m, 9H), 7.21 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.68–6.59 (m, 2H), 3.49 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.70 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.41 (dd, *J* = 5.7, 3.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 154.1, 137.2, 134.8, 134.2, 132.9, 132.5, 132.4, 130.8, 130.6, 130.4, 130.0, 129.1, 129.1, 127.1, 126.7, 124.8, 53.7, 48.8. ^{19}F NMR (377 MHz, CD_3CN) δ –152.33, –152.38. HRMS-ESI$^+$: calculated for [M$^+$] = 459.1623, observed [M$^+$] = 459.1614.



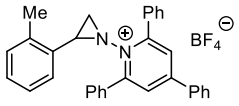
3o

*1-(2-(3-nitrophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3o**)*. Prepared via Procedure B from 3-nitrostyrene (**1o**) and obtained as a light-brown powder (83.5 mg, 75% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 7.91 (s, 2H), 7.81–7.55 (m, 7H), 7.46–7.01 (m, 11H), 6.87 (d, *J* = 7.7 Hz, 1H), 3.39 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.52 (dd, *J* = 8.4, 3.2 Hz, 1H), 2.25 (dd, *J* = 5.7, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.3, 154.1, 148.6, 137.1, 134.8, 132.9, 132.6, 132.5, 132.4, 130.8, 130.6, 130.2, 130.1, 129.1, 127.2, 124.0, 121.7, 53.4, 49.0. ^{19}F NMR (377 MHz, CD_3CN) δ –151.98, –152.03. HRMS-ESI$^+$: calculated for [M$^+$] = 470.1863, observed [M$^+$] = 470.1852.



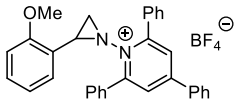
3p

*1-(2-(naphthalen-2-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3p**)*. Prepared via Procedure A from 2-vinylnaphthalene (**1p**) and obtained as a yellow powder (89.0 mg, 79% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.14 (s, 2H), 8.08–7.96 (m, 6H), 7.85–7.77 (m, 1H), 7.72–7.16 (m, 13H), 7.08 (d, *J* = 1.8 Hz, 1H), 6.82 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.68 (dd, *J* = 8.4, 5.8 Hz, 1H), 2.73 (dd, *J* = 8.4, 3.2 Hz, 1H), 2.47 (dd, *J* = 5.8, 3.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 154.0, 134.9, 134.0, 133.4, 132.8, 132.6, 132.4, 132.1, 130.8, 130.6, 130.0, 129.1, 128.6, 128.5, 128.4, 127.3, 127.2, 127.1, 126.8, 123.1, 54.8, 48.6. ^{19}F NMR (376 MHz, CD_3CN) δ –151.94, –152.00. HRMS-ESI$^+$: calculated for [M$^+$] = 475.2169, observed [M$^+$] = 475.2159.



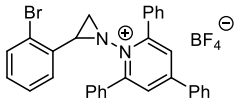
3q

*2,4,6-triphenyl-1-(2-(o-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3q**)*. Prepared via Procedure B from 2-methylstyrene (**1q**) and obtained as a brown powder (88.4 mg, 84% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.15 (s, 2H), 8.06–7.91 (m, 6H), 7.69–7.28 (m, 9H), 7.07 (m, 2H), 6.96–6.85 (m, 2H), 3.77 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.72 (dd, *J* = 8.4, 2.7 Hz, 1H), 2.15 (dd, *J* = 5.7, 2.7 Hz, 1H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.2, 153.9, 136.4, 134.9, 133.4, 132.8, 132.5, 132.2, 130.7, 130.6, 130.4, 129.9, 129.1, 128.5, 127.1, 126.7, 124.4, 51.4, 50.1, 18.6. ^{19}F NMR (377 MHz, CD_3CN) δ –151.93, –151.98. HRMS-ESI$^+$: calculated for [M$^+$] = 439.2169, observed [M$^+$] = 439.2164.



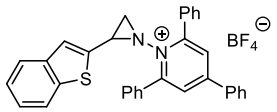
3r

*1-(2-(2-methoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3r**)*. Prepared via Procedure A from 2-vinylanisole (**1r**) and obtained as a yellow powder (66.2 mg, 61% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.13 (s, 2H), 8.04–7.85 (m, 6H), 7.70–7.23 (m, 9H), 7.15 (ddd, *J* = 8.3, 6.9, 2.2 Hz, 1H), 6.89–6.77 (m, 2H), 6.65 (d, *J* = 8.3 Hz, 1H), 3.96 (dd, *J* = 8.5, 5.9 Hz, 1H), 3.54 (s, 3H), 2.69 (dd, *J* = 8.5, 2.8 Hz, 1H), 2.28–2.23 (m, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 158.0, 154.2, 153.9, 134.9, 132.8, 132.4, 132.2, 130.7, 130.6, 130.0, 129.7, 129.1, 127.1, 125.5, 122.8, 121.0, 110.9, 55.7, 49.3, 48.8. ^{19}F NMR (376 MHz, CD_3CN) δ –152.37, –152.42. HRMS-ESI$^+$: calculated for [M$^+$] = 455.2118, observed [M$^+$] =455.2110.



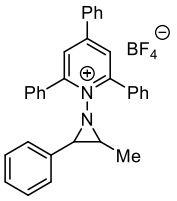
3s

*1-(2-(2-bromophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3s**)*. Prepared via Procedure B from 2-bromostyrene (**1s**) and obtained as a brown powder (89.9 mg, 76% yield). ^{1}H NMR (400 MHz,CD_3CN) δ 8.17 (s, 2H), 8.05–7.90 (m, 6H), 7.71–7.36 (m, 9H), 7.32–7.23 (m, 2H), 7.14–7.07 (m, 1H), 7.01 (dd, *J* = 7.7, 1.7 Hz, 1H), 3.98 (dd, *J* = 8.4, 5.6 Hz, 1H), 2.75 (dd, *J* = 8.4, 2.8 Hz, 1H), 2.22 (dd, *J* = 5.6, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.3, 154.2, 134.8, 134.4, 132.9, 132.9, 132.3, 132.3, 130.7, 130.6, 130.6, 130.1, 129.1, 128.4, 127.2, 126.8, 123.0, 53.6, 49.9. ^{19}F NMR (377 MHz, CD_3CN) δ –152.14, –152.19. HRMS-ESI$^+$: calculated for [M$^+$] = 503.1117, observed [M$^+$] = 503.1116.



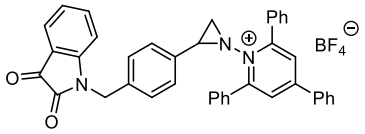
3t

*1-(2-(benzo[b]thiophen-2-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3t**)*. Prepared via Procedure A from 2-vinylbenzo[b]thiophene (**1t**) and obtained as a yellow powder (68.2 mg, 60% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 7.86 (s, 2H), 7.76–7.67 (m, 6H), 7.58–7.46 (m, 1H), 7.42–7.08 (m, 10H), 7.08–6.99 (m, 2H), 6.26 (s, 1H), 3.69 (dd, *J* = 8.3, 5.7 Hz, 1H), 2.51 (dd, *J* = 8.3, 3.3 Hz, 1H), 2.12 (dd, *J* = 5.7, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.3, 154.1, 139.8, 139.5, 138.6, 134.8, 132.9, 132.6, 132.5, 130.8, 130.6, 130.1, 129.1, 127.2, 125.7, 125.5, 124.9, 124.3, 123.1, 52.0, 49.7. ^{19}F NMR (376 MHz, CD_3CN) δ –152.04, –152.09. HRMS-ESI^{+}: calculated for [M^{+}] = 481.1773, observed [M^{+}] = 481.1727.



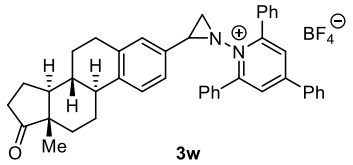
cis-**3u**

*1-(2-methyl-3-phenylaziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (cis-**3u**)*. Prepared via Procedure A from *trans*-β-methylstyrene. Only the *cis*-isomer was isolated in analytical purity and obtained as a yellow solid (21.2 mg, 20% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.12 (s, 2H), 8.04–7.85 (m, 6H), 7.68–7.35 (m, 9H), 7.22–7.09 (m, 3H), 6.88–6.81 (m, 2H), 3.66 (d, *J* = 8.7 Hz, 1H), 2.96 (dq, *J* = 8.7, 5.9 Hz, 1H), 0.18 (d, *J* = 6.0 Hz, 3H).



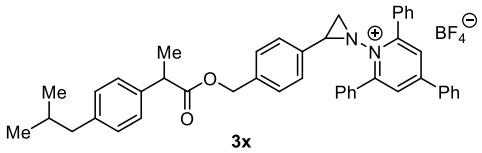
3v

*1-(2-(4-((2,3-dioxoindolin-1-yl)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3v**)*. Prepared via Procedure A from 1-(4-vinylbenzyl)indoline-2,3-dione (**1v**)and obtained as a red powder (90.0 mg, 67% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.12 (s, 2H), 8.05–7.83 (m, 6H), 7.72–7.20 (m, 11H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 4.90–4.74 (m, 2H), 3.48 (dd, *J* = 8.4, 5.8 Hz, 1H), 2.69 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.37 (dd, *J* = 5.8, 3.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 184.6, 159.3, 154.0, 151.6, 139.1, 136.4, 134.8, 134.5, 132.8, 132.5, 132.4, 130.7, 130.6, 130.5, 130.0, 129.1, 127.8, 127.0, 126.9, 125.5, 124.7, 118.7, 112.2, 54.2, 48.9, 43.9. ^{19}F NMR (376 MHz, CD_3CN) δ –151.56, –151.61. HRMS-ESI^{+}: calculated for [M^{+}] = 584.2333, observed [M^{+}] = 584.2335.



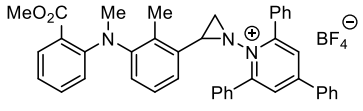
3w

*1-(2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3w**)*. Prepared via Procedure A from (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**1w**, 1.05 mmol) on 1.05 mmol scale and obtained as a yellow powder (453.3 mg, 63% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.15 (s, 2H), 8.08–7.78 (m, 6H), 7.75–7.14 (m, 9H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 6.23 (s, 1H), 3.48–3.33 (m, 1H), 2.71 (m, 2H), 2.62 (dd, *J* = 8.4, 3.2 Hz, 1H), 2.52–2.30 (m, 3H), 2.23 (d, *J* = 9.5 Hz, 1H), 2.12–1.97 (m, 4H), 1.86 (dt, *J* = 9.2, 2.8 Hz, 1H), 1.71–1.30 (m, 6H), 0.90 (d, *J* = 13.1 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 220.9, 154.2, 153.9, 141.2, 137.0, 134.9, 132.8, 132.6, 132.5, 131.6, 130.8, 130.6, 130.0, 129.1, 128.0, 127.1, 125.8, 122.9, 54.7, 51.1, 48.6, 48.3, 45.0, 38.9, 36.2, 32.4, 29.7, 27.0, 26.5, 22.1, 14.2.^{19}F NMR (377 MHz, CD_3CN) δ –151.89, –151.95. HRMS-ESI^{+}: calculated for [M^{+}] = 601.3213, observed [M^{+}] = 601.3220.



3x

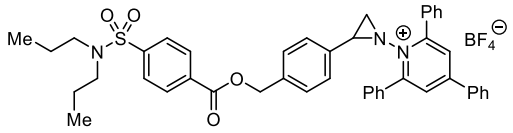
*1-(2-(4-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3x**)*. Prepared via Procedure A from 4-vinylbenzyl 2-(4-isobutylphenyl)propanoate (**1x**, 1.90 mmol) on 1.9 mmol scale and obtained as an orange powder (785.7 mg, 57% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.15 (s, 2H), 8.07–7.79 (m, 6H), 7.71–7.27 (m, 9H), 7.21–7.24 (m, 2H), 7.18–7.10 (m, 2H), 6.95 (dd, *J* = 8.3, 1.7 Hz, 2H), 6.58 (dd, *J* = 8.3, 2.2 Hz, 2H), 5.16–4.86 (m, 2H), 3.79 (q, *J* = 7.1 Hz, 1H), 3.44 (dd, *J* = 8.4, 5.8 Hz, 1H), 2.66 (dd, *J* = 8.4, 3.1 Hz, 1H), 2.47 (dd, *J* = 7.2, 2.8 Hz, 1H), 2.36 (ddd, *J* = 5.8, 3.1, 1.3 Hz, 1H), 1.85 (dtd, *J* = 13.6, 6.8, 2.2 Hz, 1H), 1.46 (d, *J* = 7.2 Hz, 3H), 0.89 (dd, *J* = 6.6, 2.0 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 175.0, 154.2, 154.1, 141.6, 139.1, 137.7, 134.9, 134.5, 132.9, 132.5, 132.5, 130.8, 130.6, 130.3, 130.0, 129.1, 128.2, 128.1, 128.0, 127.1, 126.5, 66.38, 66.36, 54.3, 49.0, 45.8, 45.7, 45.4, 31.0, 22.5, 18.8, 18.7. ^{19}F NMR (376 MHz, CD_3CN) δ –151.85, –151.91. HRMS-ESI^{+}: calculated for [M^{+}] = 643.3391, observed [M^{+}] = 643.3318.



3y

*1-(2-(3-((2-(methoxycarbonyl)phenyl)(methyl)amino)-2-methylphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3y**)*. Prepared via Procedure A from methyl 2-(methyl(2-methyl-3-vinylphenyl)amino)benzoate (**1y**, 0.30 mmol) on 0.3 mmol scale and obtained as a brown powder (154.2 mg, 82% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.17 (s, 2H), 8.03–7.90 (m, 6H), 7.70–7.36 (m, 11H), 7.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.02 (t, *J* = 7.9 Hz,

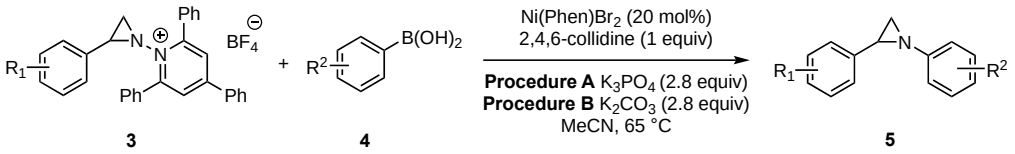
1H), 6.94–6.84 (m, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 3.76 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.19 (s, 3H), 3.00 (s, 3H), 2.72 (dd, *J* = 8.3, 2.5 Hz, 1H), 2.20 (dd, *J* = 5.7, 2.7 Hz, 1H), 1.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 154.2, 152.9, 149.1, 148.9, 134.9, 134.9, 133.7, 132.1, 131.8, 131.6, 131.2, 129.8, 129.7, 129.2, 128.2, 127.7, 127.5, 127.4, 126.3, 124.7, 122.9, 120.0, 119.7, 118.1, 51.5, 51.1, 49.8, 41.6, 13.6. ^{19}F NMR (377 MHz, CD_3CN) δ –151.95, –152.00. HRMS-ESI$^+$: calculated for [M$^+$] = 602.2802, observed [M$^+$] = 602.2804.



3z

*1-(2-(4-(((4-(N,N-dipropylsulfamoyl)benzoyl)oxy)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3z**)*. Prepared via Procedure A from 4-vinylbenzyl 4-(N,N-dipropylsulfamoyl)benzoate (**1z**, 1.6 mmol) on 1.6 mmol scale and obtained as a yellow powder (547.9 mg, 42% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 8.21–8.13 (m, 4H), 8.05–7.83 (m, 8H), 7.71–7.28 (m, 9H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 5.30 (s, 2H), 3.50 (dtd, *J* = 8.3, 4.0, 1.9 Hz, 1H), 3.17–3.02 (m, 4H), 2.69 (dt, *J* = 8.4, 3.2 Hz, 1H), 2.41 (ddd, *J* = 6.1, 3.2, 1.5 Hz, 1H), 1.51 (h, *J* = 7.4 Hz, 4H), 0.83 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ 165.8, 154.2, 154.1, 145.3, 137.2, 135.0, 134.9, 134.5, 132.9, 132.5, 131.1, 130.8, 130.6, 130.0, 129.1, 128.8, 128.2, 127.1, 126.7, 67.6, 54.3, 50.7, 49.0, 22.6, 11.3. ^{19}F NMR (377 MHz, CD_3CN) δ –151.93, –151.99. HRMS-ESI$^+$: calculated for [M$^+$] = 722.3047, observed [M$^+$] = 722.3045.

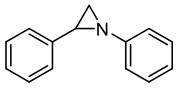
B.6 Cross-Coupling of Pyridinium Aziridines



3 **4** **5**

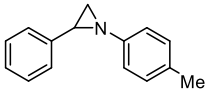
Procedure A A 20-mL scintillation vial was charged with Ni(Phen)Br_2 (20 mol%), potassium phosphate (2.8 equiv), aryl boronic acid (**4**, 2.4 equiv), pyridinium aziridine (**3**, 1 equiv) and a magnetic stir bar[4]. In an N_2 filled dry box, a solution of 2,4,6-collidine in acetonitrile (0.08 M, 1.0 equiv) was added to the scintillation vial with the rest of the reaction components. The reaction vial was heated at 65 °C for 36 h. After cooling to 23 °C, the reaction mixture was transferred to a centrifuge tube and centrifuged at 6000 rpm for 10 min. The supernatent was decanted. The residue was washed with CH_2Cl_2 and the combined supernatents were concentrated under reduced pressure and the crude mixture was purified as indicated below to afford the title compound.

Procedure B A 20-mL scintillation vial was charged with Ni(Phen)Br_2 (20 mol%), potassium carbonate (2.8 equiv), aryl boronic acid (**4**, 2.4 equiv), pyridinium aziridine (**3**, 1 equiv) and a magnetic stir bar. In an N_2 fill dry box, a solution of 2,4,6-collidine in acetonitrile (0.08 M, 1.0 equiv) was added to the reaction. The reaction was heated at 65 °C for 36 h. After colling to 23 °C, the reaction mixture was transferred to a centrifuge tube and centrifuged at 6000 rpm for 10 minutes. The supernatent was decanted. The residue was washed with CH_2Cl_2 and the combined supernatents were concentrated under reduced pressure and the crude mixture was purified as indicated below to afford the title compound.



5a

*1,2-diphenylaziridine (**5a**)*. Prepared via Procedure A from **3a** on 0.16 mmol scale (based on **3a**) and obtained as a colorless oil (17.8 mg, 57% yield). Purified by alumina flash column chromatography (0.1% to 1% diethyl ether in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.20 (m, 4H), 7.20–7.09 (m, 3H), 6.96–6.92 (m, 2H), 6.87 (m, 1H), 2.99 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.35 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.29 (dd, *J* = 3.4, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 139.6, 129.2, 128.6, 127.5, 126.3, 122.7, 120.7, 41.7, 37.7. These spectral data are well-matched to those reported in the literature.[18]

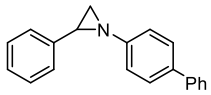


5b

*2-phenyl-1-(p-tolyl)aziridine (**5b**)*. Prepared via Procedure A from **3a** on 0.08 mmol scale (based on **3a**) and obtained as a yellow oil (12.6 mg, 67% yield). Purified by alumina flash column chromatography (0.1% to 1% diethyl ether in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.33 (m, 4H), 7.31–7.27 (m, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 3.05

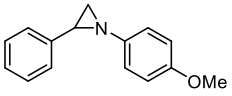
[4] All reaction components were weighed out under air and carried into an N_2 filled dry box.

(dd, *J* = 6.4, 3.3 Hz, 1H), 2.43 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.38 (dd, *J* = 3.3, 1.2 Hz, 1H). These spectral data are well-matched to those reported in the literature.[18]



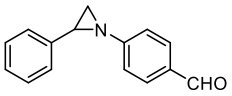
5c

*1-([1,1'-biphenyl]-4-yl)-2-phenylaziridine (**5c**)*.Prepared via Procedure A from **3a** on 0.16 mmol scale (based on **3a**) and obtained as a white solid (17.4 mg, 40% yield). Purified by C_{18} HPLC using 100% acetonitrile at 40 mL/min flow rate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.56 (m, 2H), 7.54–7.49 (m, 2H), 7.47–7.37 (m, 6H), 7.36–7.30 (m, 2H), 7.18–7.11 (m, 2H), 3.17 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.52 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.46 (dd, *J* = 3.3, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 141.0, 139.5, 135.7, 128.9, 128.8, 128.6, 127.9, 127.5, 126.9, 126.4, 121.1, 41.9, 37.9. HRMS-APCI: calculated for [M+1] = 272.1434, observed [M+1] = 272.1431.



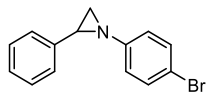
5d

*1-(4-methoxyphenyl)-2-phenylaziridine (**5d**)*. Prepared via Procedure B from **3a** on 0.08 mmol scale (based on **3a**) and obtained as a colorless oil (10.8 mg, 60% yield). Purified by alumina flash column chromatography (1% to 2% diethyl ether in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (m, 4H), 7.31–7.27 (m, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 3.77 (s, 3H), 3.03 (dd, *J* = 6.5, 3.4 Hz, 1H), 2.41 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.37 (dd, *J* = 3.5, 1.2 Hz, 1H). These spectral data are well-matched to those reported in the literature.[18]



5e

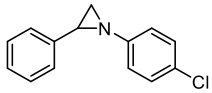
*4-(2-phenylaziridin-1-yl)benzaldehyde (**5e**)*. Prepared via Procedure B from **3a** on 0.08 mmol scale (based on **3a**) and obtained as a white solid (17.9 mg, >99% yield). Purified by alumina flash column chromatography (1% to 5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, CD_3CN) δ 9.86 (s, 1H), 7.86–7.72 (m, 2H), 7.44–7.33 (m, 4H), 7.32–7.29 (ddt, *J* = 6.4, 5.2, 2.6 Hz, 1H), 7.23–7.11 (m, 2H), 3.30 (dd, *J* = 6.4, 3.4 Hz, 1H), 2.58 (d, *J* = 6.4 Hz, 1H), 2.51 (dd, *J* = 3.4 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 192.0, 161.4, 139.9, 132.4, 131.9, 129.5, 128.5, 127.2, 121.8, 42.3, 38.2. HRMS-APCI: calculated for [M+1] = 224.1070, observed [M+1] = 224.1066.



5f

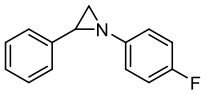
*1-(4-bromophenyl)-2-phenylaziridine (**5f**)*. Prepared via Procedure B from **3a** on 0.08 mmol scale (based on **3a**) and obtained as a white solid (18.9 mg, 86% yield). Purified by alumina flash column chromatography (0.1% to 1% diethyl ether in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.32 (m, 6H), 7.32–7.27 (m, 1H), 6.96–6.79 (m, 2H), 3.08 (dd, *J* = 6.4, 3.4 Hz,

1H), 2.52–2.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 139.0, 132.0, 128.7, 127.6, 126.3, 122.5, 115.1, 41.9, 37.8. HRMS-ESI$^+$: calculated for [M+1] = 306.0448, 308.0468, observed [M+1] = 306.0485, 308.0464. These spectral data are well-matched to those reported in the literature.[18]



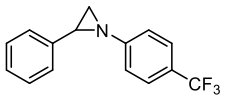
5g

*1-(4-chlorophenyl)-2-phenylaziridine (**5g**)*. Prepared via Procedure A from **3a** on 0.16 mmol scale (based on **3a**) and obtained as a colorless oil (16.4 mg, 45% yield). Purified by alumina flash column chromatography (0.1% to 1% diethyl ether in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 4.3 Hz, 4H), 7.36–7.27 (m, 1H), 7.23–7.17 (m, 2H), 7.01–6.94 (m, 2H), 3.08 (dd, *J* = 6.5, 3.4 Hz, 1H), 2.49–2.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 138.9, 129.0, 128.5, 127.5, 127.4, 126.2, 121.8, 41.8, 37.7. These spectral data are well-matched to those reported in the literature.[18]



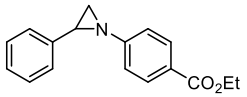
5h

*1-(4-fluorophenyl)-2-phenylaziridine (**5h**)*. Prepared via Procedure A from **3a** on 0.08 mmol scale (based on **3a**) and obtained as a colorless oil (11.7 mg, 69% yield). Purified by alumina flash column chromatography (0.1% to 1% diethyl ether in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.33 (m, 4H), 7.33–7.27 (m, 1H), 7.04–6.89 (m, 4H), 3.06 (dd, *J* = 6.5, 3.4 Hz, 1H), 2.43 (dd, *J* = 6.5, 1.1 Hz, 1H), 2.40 (dd, *J* = 3.3, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (d, *J* = 240.5 Hz), 150.5 (d, *J* = 2.6 Hz), 139.1, 128.5, 127.4, 126.2, 121.6 (d, *J* = 8.0 Hz), 115.6 (d, *J* = 22.5 Hz), 41.9, 37.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –121.37. These spectral data are well-matched to those reported in the literature.[18]



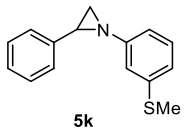
5i

*2-phenyl-1-(4-(trifluoromethyl)phenyl)aziridine (**5i**)*. Prepared via Procedure B from **3a** on 0.08 mmol scale (based on **3a**) and obtained as a colorless oil (13.6 mg, 65% yield). Purified by alumina flash column chromatography (0.1% to 1% diethyl ether in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.47 (m, 2H), 7.42–7.29 (m, 5H), 7.15–7.03 (m, 2H), 3.16 (dd, *J* = 6.4, 3.4 Hz, 1H), 2.50 (dd, *J* = 6.4, 1.1 Hz, 1H), 2.48 (dd, *J* = 3.4, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 138.7, 128.7, 127.8, 126.5, 126.5, 126.4, 126.4, 126.3, 125.9, 124.9, 124.5, 123.2, 120.8, 41.8, 37.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ –61.74. HRMS-APCI: calculated for [M+1] = 264.0995, observed [M+1] = 264.0990. These spectral data are well-matched to those reported in the literature.[18]



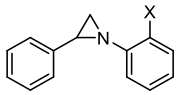
5j

*ethyl 4-(2-phenylaziridin-1-yl)benzoate (**5j**)*. Prepared via Procedure A from **3a** on 0.16 mmol scale (based on **3a**). Purified by alumina flash column chromatography and obtained as a colorless oil (22.2 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.93 (m, 2H), 7.39–7.28 (m, 5H), 7.10–7.01 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.17 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.51 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.48 (dd, *J* = 3.3, 1.2 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H). These spectral data are well-matched to those reported in the literature.[18]



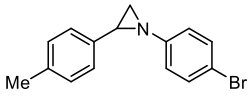
5k

*1-(3-(methylthio)phenyl)-2-phenylaziridine (**5k**)*. Prepared via Procedure A from **3a** on 0.16 mmol scale (based on **3a**) and obtained as a colorless oil (28.6 mg, 74% yield). Purified by C_{18} HPLC using 100% acetonitrile at 40 mL/min flow rate. ^{1}H NMR (400 MHz, CD_3CN) δ 7.41–7.34 (m, 4H), 7.33–7.26 (m, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.92 (t, *J* = 2.0 Hz, 1H), 6.87 (ddd, *J* = 7.8, 1.9, 1.0 Hz, 1H), 6.80 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 3.16 (dd, *J* = 6.5, 3.4 Hz, 1H), 2.47 (dd, *J* = 6.5, 0.9 Hz, 1H), 2.45 (s, 3H), 2.38 (dd, *J* = 3.4, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 156.4, 140.6, 140.4, 130.4, 129.4, 128.2, 127.2, 121.0, 118.7, 118.2, 42.1, 38.1, 15.4. HRMS-APCI: calculated for [M+1] = 242.0998, observed [M+1] = 242.0999.



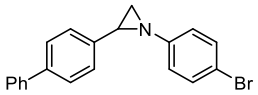
5l

Synthesis of aziridine **5l** was attempted by reacting pyridinium aziridine **3a** with o-tolylboronic acid as well as (2,4-dimethylphenyl)boronic acid via both Procedure A and Procedure B. None of the combinations gave the desired aziridine product **5l** detectable by the ^{1}H NMR spectrum of the crude mixture.



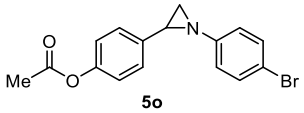
5m

*1-(4-bromophenyl)-2-(p-tolyl)aziridine (**5m**)*. Prepared via Procedure B from **3b** on 0.16 mmol scale (based on **3b**) and obtained as a white solid (30.9 mg, 67% yield). Purified by alumina flash column chromatography (0.1% to 1% diethyl ether in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 2H), 7.28–7.24 (m, 2H), 7.20–7.12 (m, 2H), 6.97–6.85 (m, 2H), 3.04 (dd, *J* = 6.4, 3.4 Hz, 1H), 2.43–2.36 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 137.4, 136.0, 132.0, 129.3, 126.2, 122.4, 115.0, 41.8, 37.7, 21.3. HRMS-APCI: calculated for [M+1] = 320.0645, 322.0624, observed [M+1] = 320.0646, 322.0625.



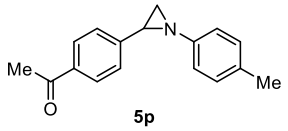
5n

*2-([1,1'-biphenyl]-4-yl)-1-(4-bromophenyl)aziridine (**5n**)*. Prepared via Procedure B from **3c** on 0.16 mmol scale (based on **3c**). The title compound was purified by C_{18} HPLC using 100% acetonitrile at 40 mL/min flow rate, which did not give a baseline separation and obtained as a mixture containing 23% of 2,4,6-triphenylpyridine. Spectroscopic data were extracted by comparing the spectra of the mixture with those of 2,4,6-triphenylpyridine, and the yield was determined to be 50% by integration of the ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.58 (m, 4H), 7.46–7.43 (m, 4H), 7.39–7.34 (m, 3H), 6.98–6.92 (m, 2H), 3.12 (dd, *J* = 6.4, 3.4 Hz, 1H), 2.48–2.45 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 140.9, 140.6, 138.1, 132.1, 128.9, 127.5, 127.4, 127.2, 126.7, 122.5, 115.2, 41.7, 37.9. HRMS-APCI: calculated for [M+1] = 350.0539, 352.0518, observed [M+1] = 350.0530, 352.0508.



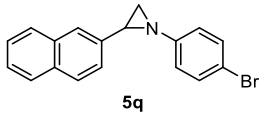
5o

*4-(1-(4-bromophenyl)aziridin-2-yl)phenyl acetate (**5o**)*. Prepared via Procedure B from **3f** on 0.16 mmol scale (based on **3f**) and obtained as a colorless oil (21.5 mg, 42% yield). Purified by alumina flash column chromatography (1% to 5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.31 (m, 4H), 7.14–7.05 (m, 2H), 6.98–6.83 (m, 2H), 3.06 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.42 (dd, *J* = 6.4, 1.1 Hz, 1H), 2.38 (dd, *J* = 3.3, 1.1 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 153.6, 150.2, 136.7, 132.1, 127.3, 122.4, 121.8, 115.2, 41.4, 37.9, 21.3. HRMS-APCI: calculated for [M+1] = 332.0281, 334.0260, observed [M+1] = 332.0279, 334.0256.



5p

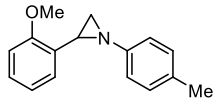
*1-(4-(1-(p-tolyl)aziridin-2-yl)phenyl)ethan-1-one (**5p**)*. Prepared via Procedure A from **3g** on 0.16 mmol scale (based on **3g**) and obtained as a white solid (31.9 mg, 79% yield). Purified by alumina flash column chromatography (1% to 5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.89 (m, 2H), 7.57–7.42 (m, 2H), 7.11–7.00 (m, 2H), 7.00–6.90 (m, 2H), 3.09 (dd, *J* = 6.4, 3.2 Hz, 1H), 2.61 (s, 3H), 2.49 (dd, *J* = 6.5, 1.3 Hz, 1H), 2.38 (dd, *J* = 3.3, 1.3 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 151.7, 145.4, 136.3, 132.3, 129.7, 128.7, 126.4, 120.4, 41.4, 38.3, 26.7, 20.8. HRMS-APCI: calculated for [M+1] = 252.1383, observed [M+1] = 252.1382.



5q

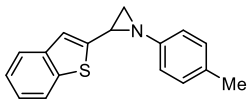
*1-(4-bromophenyl)-2-(naphthalen-2-yl)aziridine (**5q**)*. Prepared via Procedure B from **3p** on 0.16 mmol scale (based on **3p**) and obtained as a colorless oil (32.0 mg, 62% yield). Purified

by C_{18} HPLC using 100% acetonitrile at 40 mL/min flow rate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.74 (m, 4H), 7.52–7.42 (m, 3H), 7.39–7.34 (m, 2H), 6.99–6.94 (m, 2H), 3.24 (dd, *J* = 6.1, 3.7 Hz, 1H), 2.56–2.45 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 136.5, 133.5, 133.1, 132.1, 128.5, 127.9, 127.8, 126.5, 126.0, 125.3, 124.1, 122.5, 115.2, 42.2, 38.0. HRMS-APCI: calculated for [M+1] = 324.0382, 326.0362, observed [M+1] = 324.0381, 326.0359.



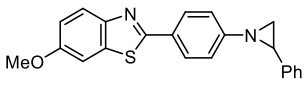
5r

*2-(2-methoxyphenyl)-1-(p-tolyl)aziridine (**5r**)*. Prepared via Procedure B from **3r** on 0.16 mmol scale (based on **3r**) and obtained as a yellow oil (16.3 mg, 43% yield). Purified by C_{18} HPLC using 100% acetonitrile at 40 mL/min flow rate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.26 (dd, *J* = 15.6, 1.8 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 7.03–6.99 (m, 2H), 6.96 (td, *J* = 7.4, 1.0 Hz, 1H), 6.90 (dd, *J* = 8.2, 1.1 Hz, 1H), 3.90 (s, 3H), 3.40 (dd, *J* = 6.5, 3.5 Hz, 1H), 2.40 (dd, *J* = 6.5, 1.3 Hz, 1H), 2.37 (dd, *J* = 3.5, 1.3 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 152.7, 131.8, 129.6, 128.3, 127.9, 126.9, 120.8, 120.7, 110.2, 55.6, 37.1, 36.7, 20.9. HRMS-APCI: calculated for [M+1] = 240.1383, observed [M+1] = 240.1385.



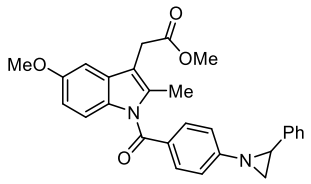
5s

*2-(benzo[b]thiophen-2-yl)-1-(p-tolyl)aziridine (**5s**)*. Prepared via Procedure A on 0.16 mmol scale (based on **3t**) and obtained as a yellow oil (15.3 mg, 36% yield). Purified by C_{18} HPLC using 100% acetonitrile at 40 mL/min flow rate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.77 (m, 1H), 7.75–7.67 (m, 1H), 7.38–7.25 (m, 3H), 7.11–7.05 (m, 2H), 7.01–6.96 (m, 2H), 3.36 (dd, *J* = 6.2, 3.2 Hz, 1H), 2.56 (dd, *J* = 3.2, 1.1 Hz, 1H), 2.52 (dd, *J* = 6.3, 1.1 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 145.3, 140.1, 139.3, 132.5, 129.8, 124.4, 124.1, 123.2, 122.5, 121.0, 120.5, 38.7, 38.5, 20.9. HRMS-APCI: calculated for [M+1] = 266.0998, observed [M+1] = 266.0998.



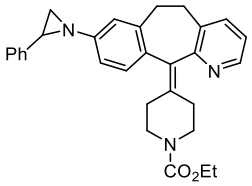
5t

*6-methoxy-2-(4-(2-phenylaziridin-1-yl)phenyl)benzo[d]thiazole (**5t**)*. Prepared via Procedure A from **3a** on 0.08 mmol scale (based on **3a**) and obtained as a pale-yellow oil (37.2 mg, 65% yield). Purified by alumina flash column chromatography (5% to 20% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.86 (m, 3H), 7.43–7.35 (m, 4H), 7.35–7.29 (m, 2H), 7.16– 7.10 (m, 2H), 7.07 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.18 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.53 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.48 (dd, *J* = 3.3, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 157.7, 156.9, 148.9, 139.0, 136.3, 128.7, 128.4, 128.3, 127.7, 126.3, 123.5, 121.1, 115.5, 104.4, 55.9, 41.9, 37.9. HRMS-APCI: calculated for [M+1] = 359.1213, observed [M+1] = 359.1211.



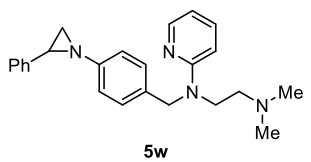
5u

*methyl 2-(5-methoxy-2-methyl-1-(4-(2-phenylaziridin-1-yl)benzoyl)-1H-indol-3-yl)acetate (**5u**)*. Prepared via Procedure A from **3a** and **4a** on 0.16 mmol scale (based on **3a**) and obtained as a white solid (52.5 mg, 72% yield). Purified by alumina flash column chromatography (3% to 10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.60 (m, 2H), 7.42–7.29 (m, 5H), 7.14–7.08 (m, 2H), 6.96 (d, *J* = 2.6 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.68 (s, 2H), 3.24 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.57 (dd, *J* = 6.4, 1.1 Hz, 1H), 2.53 (dd, *J* = 3.4, 1.1 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 169.0, 159.2, 155.9, 138.5, 136.3, 131.7, 131.2, 130.5, 129.3, 128.7, 127.8, 126.3, 120.7, 115.0, 111.8, 111.6, 101.1, 55.9, 52.2, 41.9, 37.9, 30.4, 13.2. HRMS-APCI: calculated for [M+1] = 455.1965, observed [M+1] = 455.1962.



5v

*ethyl 4-(8-(2-phenylaziridin-1-yl)-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (**5v**)*. Prepared via Procedure A from **3a** and **4b** on 0.11 mmol scale (based on **3a**) and obtained as a yellow oil (32.1 mg, 63% yield). Purified by alumina flash column chromatography (3% to 10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, CD_3CN) δ 7.93 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.15–7.07 (m, 1H), 7.02–6.85 (m, 5H), 6.72 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 6.59 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 6.42 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.68 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.36–3.18 (m, 2H), 3.03–2.90 (m, 2H), 2.69 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.49–2.31 (m, 2H), 2.06–1.86 (m, 5H), 1.83–1.75 (m, 1H), 0.82 (td, *J* = 7.1, 1.0 Hz, 3H).[5] ^{13}C NMR (101 MHz, CD_3CN) δ 159.5, 159.4, 156.1, 155.0, 147.3, 140.7, 139.69, 139.67, 137.92, 137.90, 136.72, 136.70, 135.8, 134.8, 134.2, 134.1, 130.9, 129.4, 128.2, 127.1, 123.1, 122.3, 122.2, 118.9, 118.8, 61.8, 45.7, 45.6, 42.14, 42.08, 38.1, 38.0, 32.6, 31.9, 31.8, 31.4, 31.3, 15.0.[5] HRMS-APCI: calculated for [M+1] = 466.2489, observed [M+1] = 466.2485.

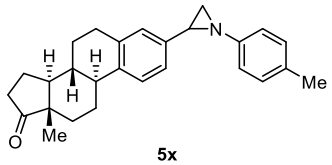


5w

*N^1,N^1-dimethyl-N^2-(4-(2-phenylaziridin-1-yl)benzyl)-N^2-(pyridin-2-yl)ethane-1,2-diamine (**5w**)*. Prepared via Procedure A from **3a** and **4c** on 0.14 mmol scale (based on **3a**) and obtained as a colorless oil (12.6 mg, 24% yield). Purified by alumina column chromatography

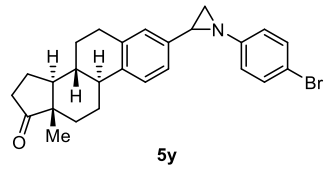
[5] The complexity of the spectra data is due to the presence of interconverting rotamers of the carbamate in **5v**.

(1% to 10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.41–7.33 (m, 5H), 7.31–7.27 (m, 1H), 7.15–7.10 (m, 2H), 7.00–6.95 (m, 2H), 6.53 (ddd, *J* = 7.1, 4.9, 0.8 Hz, 1H), 6.45 (d, *J* = 8.7 Hz, 1H), 4.71 (s, 2H), 3.66–3.59 (m, 2H), 3.07 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.52–2.46 (m, 2H), 2.43 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.38 (dd, *J* = 3.3, 1.2 Hz, 1H), 2.26 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 153.6, 148.2, 139.6, 137.3, 133.0, 128.6, 127.9, 127.4, 126.3, 120.8, 111.9, 105.9, 56.9, 51.5, 46.7, 46.0, 41.8, 37.8. HRMS-APCI: calculated for [M+1] = 373.2387, observed [M+1] = 373.2384.



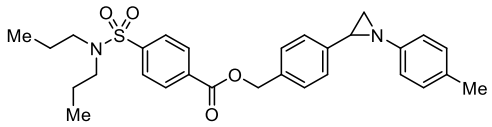
5x

*(8R,9S,13S,14S)-13-methyl-3-(1-(p-tolyl)aziridin-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**5x**)*. Prepared via Procedure A from **3v** on 0.16 mmol scale (based on **3w**) and obtained as a white solid (18.7 mg, 30% yield). Purified by alumina flash column chromatography (3% to 10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.13 (s, 1H), 7.08–7.02 (m, 2H), 6.97–6.90 (m, 2H), 3.00 (ddd, *J* = 6.5, 3.4, 1.5 Hz, 1H), 2.94 (dd, *J* = 9.1, 4.2 Hz, 2H), 2.57–2.46 (m, 1H), 2.49–2.40 (m, 1H), 2.40 (dt, *J* = 6.5, 1.2 Hz, 1H), 2.39–2.30 (m, 2H), 2.29 (s, 3H), 2.20–1.93 (m, 4H), 1.71–1.40 (m, 6H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 152.3, 139.0, 137.2, 136.9, 132.0, 129.7, 126.7, 125.6, 123.9, 120.5, 50.7, 48.1, 44.5, 41.5, 38.3, 37.7, 36.0, 31.7, 29.5, 26.6, 25.9, 21.7, 20.8, 14.0. HRMS-APCI: calculated for [M+1] = 386.2478, observed [M+1] = 386.2482.



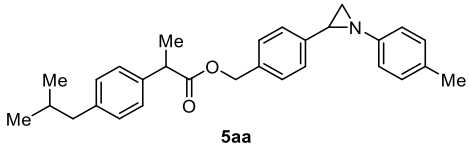
5y

*(8R,9S,13S,14S)-3-(1-(4-bromophenyl)aziridin-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**5y**)*. Prepared via Procedure B from **3v** on 0.16 mmol scale (based on **3w**) and obtained as a pale-yellow solid (23.4 mg, 32% yield). Purified by alumina flash column chromatography (3% to 10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.10 (s, 1H), 6.95–6.89 (m, 2H), 3.06–2.99 (m, 1H), 2.93 (dd, *J* = 9.2, 4.3 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.46–2.38 (m, 3H), 2.37–2.27 (m, 1H), 2.19–1.94 (m, 4H), 1.68–1.40 (m, 6H), 0.92 (s, 3H). ^{13}C NMR (126 MHz, $cdcl_3$) δ 220.9, 153.9, 139.3, 137.0, 136.5, 132.0, 126.7, 125.7, 123.9, 122.4, 115.1, 50.7, 48.1, 47.6, 44.5, 41.7, 38.3, 37.8, 36.0, 31.7, 26.6, 25.9, 21.7, 14.0. HRMS-APCI: calculated for [M+1] = 482.1689, 484.1669, observed [M+1] = 482.1690, 484.1666.



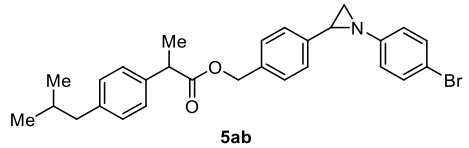
5z

*4-(1-(p-tolyl)aziridin-2-yl)benzyl 4-(N,N-dipropylsulfamoyl)benzoate (**5z**)*. Prepared via Procedure A from **3z** on 0.1 mmol scale (based on **3z**) and obtained as a yellow oil (29.5 mg, 58% yield). Purified by alumina flash column chromatography (5% to 20% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.15 (m, 2H), 7.93–7.83 (m, 2H), 7.52–7.37 (m, 4H), 7.10–7.02 (m, 2H), 6.97–6.90 (m, 2H), 5.39 (s, 2H), 3.19–2.97 (m, 5H), 2.44 (dd, *J* = 6.4, 1.3 Hz, 1H), 2.37 (dd, *J* = 3.3, 1.2 Hz, 1H), 2.29 (s, 3H), 1.60–1.47 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 152.0, 144.5, 140.3, 134.6, 133.6, 132.2, 130.5, 129.7, 128.8, 127.2, 126.7, 120.5, 67.3, 50.0, 41.5, 37.9, 22.1, 20.8, 11.3.HRMS-APCI: calculated for [M+1] = 507.2312, observed [M+1] = 507.2318.



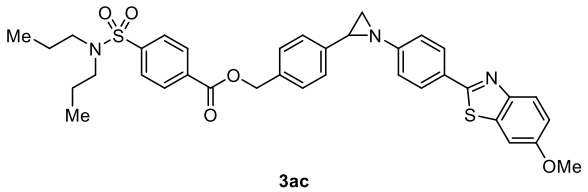
5aa

*4-(1-(p-tolyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**5aa**)*. Prepared via Procedure A from **3x** on 0.12 mmol scale (based on **3x**) and obtained as a yellow oil (32.4 mg, 63% yield). Purified by alumina flash column chromatography (1% to 5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.20–7.15 (m, 4H), 7.09–6.99 (m, 4H), 6.93–6.86 (m, 2H), 5.23–4.87 (m, 2H), 3.71 (q, *J* = 7.2 Hz, 1H), 2.98 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.41 (d, *J* = 7.2 Hz, 2H), 2.37 (dd, *J* = 6.5, 1.2 Hz, 1H), 2.30 (dd, *J* = 3.3, 1.2 Hz, 1H), 2.25 (s, 2H), 1.81 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 152.1, 140.7, 139.6, 137.7, 135.2, 132.1, 129.7, 129.5, 128.1, 127.4, 126.4, 120.5, 66.3, 45.3, 45.2, 41.5, 37.8, 30.3, 22.5, 20.8, 18.6, 14.6. HRMS-APCI: calculated for [M+1] = 428.2584, observed [M+1] = 428.2584.



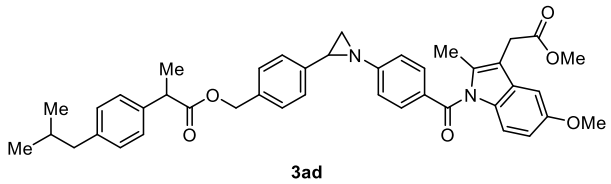
5ab

*4-(1-(4-bromophenyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**5ab**)*. Prepared via Procedure B from **3x** on 0.12 mmol scale (based on **3x**) and obtained as a colorless oil (38.7 mg, 65% yield). Purified by alumina column chromatography (1% to 3% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.33 (m, 2H), 7.32–7.29 (m, 2H), 7.25–7.19 (m, 4H), 7.13–7.06 (m, 2H), 6.94–6.88 (m, 2H), 5.17–5.04 (m, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 3.06 (dd, *J* = 6.5, 3.3 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.43 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.39 (dd, *J* = 3.4, 1.1 Hz, 1H), 1.86 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 153.6, 140.7, 138.9, 137.7, 135.5, 132.0, 129.4, 128.2, 127.4, 126.4, 122.4, 115.2, 66.2, 45.3, 45.2, 41.6, 37.8, 30.3, 22.5, 18.5. HRMS-APCI: calculated for [M+1] = 492.1553, 494.1512, observed [M+1] = 492.1533, 494.1509.



3ac

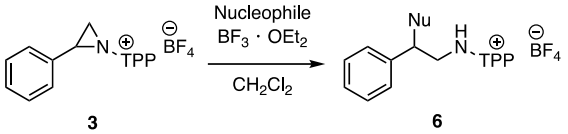
*4-(1-(4-(6-methoxybenzo[d]thiazol-2-yl)phenyl)aziridin-2-yl)benzyl 4-(N,N-dipropylsulfamoyl)benzoate (**3ac**)*. Prepared via Procedure A from **3z** on 0.12 mmol scale (based on **3z**) and obtained as a yellow solid (32.3 mg, 41% yield). Purified by alumina column chromatography (5% to 20% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.15 (m, 2H), 7.97–7.83 (m, 5H), 7.51–7.39 (m, 4H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.14–7.10 (m, 2H), 7.07 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.40 (s, 2H), 3.89 (s, 3H), 3.19 (dd, *J* = 6.4, 3.3 Hz, 1H), 3.14–3.05 (m, 4H), 2.55 (dd, *J* = 6.3, 1.2 Hz, 1H), 2.47 (dd, *J* = 3.3, 1.2 Hz, 1H), 1.61–1.47 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.2, 157.7, 156.7, 148.9, 144.6, 139.6, 136.3, 135.0, 133.5, 130.5, 128.9, 128.5, 128.4, 127.2, 126.7, 123.5, 121.1, 115.6, 104.4, 67.3, 56.0, 50.0, 41.6, 38.0, 22.1, 11.3. HRMS-APCI: calculated for [M+1] = 656.2247, observed [M+1] = 656.2253.



3ad

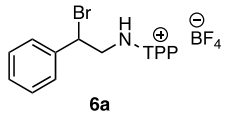
*4-(1-(4-(5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1H-indole-1-carbonyl)phenyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**3ad**)*. Prepared via Procedure A from **3x** and **4a** on 0.12 mmol scale (based on **3x**) and obtained as a yellow solid (53.9, 67% yield). Purified by alumina column chromatography (5% to 20% ethyl acetate in hexane). ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.70–7.61 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.27–7.19 (m, 4H), 7.11–7.07 (m, 4H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.18–5.06 (m, 2H), 3.84 (s, 3H), 3.76 (q, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 2H), 3.21 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.56 (d, *J* = 6.4 Hz, 1H), 2.49 (d, *J* = 3.4 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.86 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 171.6, 169.0, 159.0, 155.9, 140.7, 138.4, 137.7, 136.3, 135.8, 131.8, 131.2, 130.5, 129.5, 129.4, 128.2, 127.4, 126.4, 120.7, 115.0, 111.8, 111.6, 101.1, 66.1, 55.9, 52.2, 45.3, 45.2, 41.6, 37.9, 30.3, 22.5, 18.5, 13.2. HRMS-APCI: calculated for [M+1] = 673.3272, observed [M+1] = 673.3274.

B.7 Nucleophilic Opening of Pyridinium Aziridines

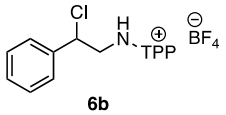


Procedure A The following procedure was carried out in an N_2-filled dry box. A 20-mL scintillation vial was charged with 2,4,6-triphenyl-1-(2-phenylaziridin-1-yl)pyridinium tetrafluoroborate (**3**, 300 mg, 0.586 mmol, 1.00 equiv), $BF_3{\cdot}OEt_2$ (0.075 mL, 0.59 mmol, 1.0 equiv), and CH_2Cl_2 (5 mL). A 25-mL Schlenk tube is charged with the appropriate nucleophile (0.703 mmol, 1.20 equiv). The CH_2Cl_2 solution of **3** and $BF_3{\cdot}OEt_2$ was added to the Schlenk flask that contained the nucleophile. The resulting reaction mixture was allowed to stir at 23 °C for 16 h. Solvent was removed under reduced pressure and the residue was purified by SiO_2 gel chromatography (eluent 2:1 ethyl acetate:hexane) to afford the title compound.

Procedure B The following procedure was carried out in an N_2-filled dry box. A 20-mL scintillation vial was charged with 2,4,6-triphenyl-1-(2-phenylaziridin-1-yl)pyridinium tetrafluoroborate (**3**, 300 mg, 0.586 mmol, 1.00 equiv), $BF_3{\cdot}OEt_2$ (0.075 mL, 0.586 mmol, 1.00 equiv), and CH_2Cl_2 (5 mL). A 25-mL Schlenk tube is charged with the appropriate nucleophile (0.703 mmol, 1.20 equiv). The CH_2Cl_2 solution of **3** and $BF_3{\cdot}OEt_2$ was added to the Schlenk flask that contained the nucleophile. The resulting reaction mixture was allowed to stir at 41 °C for 48 h. Solvent was removed under reduced pressure and the residue was purified by SiO_2 gel chromatography (eluent 2:1 ethyl acetate:hexane) to afford the title compound.

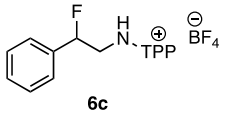


*1-((2-bromo-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6a**).* Prepared via Procedure B from tetrabutylammonium bromide as nucleophile and obtained in 98% NMR yield. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.88 (s, 2H), 7.85–7.83 (m, 4H), 7.77–7.75 (m, 2H), 7.60–7.51 (m, 9H), 7.14 (dt, J = 12.8, 6.6 Hz, 3H), 6.87 (d, J = 7.0 Hz, 2H), 6.42 (t, J = 7.2 Hz, 1H)4.34 (dd, J = 8.0, 4.8 Hz, 1H), 3.37–3.25 (m, 2H). ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): –78.3. HRMS-APCI: calculated for [M^+] = 505.1274, 507.1253, observed [M^+] = 505.1256, 507.1235. Attempts to isolate **6a** by column chromatography led to recovery of 2,4,6-triphenyl-1-(2-phenylaziridin-1-yl)pyridinium tetrafluoroborate **3a**.



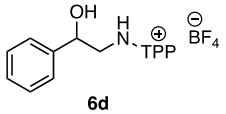
6b

*1-((2-chloro-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6b**).* Prepared via Procedure B from tetrabutylammonium chloride as nucleophile and obtained in 98% NMR yield. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.94 (s, 2H), 7.89–7.86 (m, 4H), 7.81–7.79 (m, 2H), 7.56 (dd, *J* = 22.6, 6.9 Hz, 9H), 7.21–7.14 (m, 3H), 6.90–6.88 (m, 2H), 6.56 (t, *J* = 6.0 Hz, 1H), 4.37–4.33 (m, 1H), 3.24–3.20 (m, 2H). ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): –78.3. HRMS-APCI: calculated for [M$^+$] = 461.1779, observed [M$^+$] = 461.1762. Attempts to isolate **6b** by column chromatography led to recovery of 2,4,6-triphenyl-1-(2-phenylaziridin-1-yl)pyridinium tetrafluoroborate **3a**.



6c

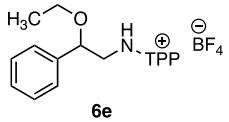
*1-((2-fluoro-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6c**).* A 25-ml Schlenk tube was charged with 2,4,6-triphenyl-1-(2-phenylaziridin-1-yl)pyridinium tetrafluoroborate (**3**, 300 mg, 0.586 mmol, 1.00 equiv) and CH_2Cl_2 (5 mL) under N_2. HF-pyridine was added to the CH_2CL_2 solution of **3a** dropwise at 0 °C and the reaction mixture was allowed to stir at 23 °C for 16 h. Solvent was removed under reduced pressure and the residue was purified by SiO_2 gel chromatography to obtain the product as white solid (281 mg, 90% yield). ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.87–7.90 (m, 4H), 7.89 (s, 2H), 7.76 (dq, *J* = 6.3, 1.9 Hz, 2H), 7.62–7.48 (m, 9H), 7.24–7.16 (m, 3H), 6.85–6.83 (m, 2H), 6.55 (t, *J* = 6.2 Hz, 1H), 4.92 (ddd, *J* = 48.1, 6.2, 4.5 Hz, 1H), 3.11–3.08 (m, 1H), 3.06–3.02 (m, 1H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 156.0, 155.9, 135.8, 135.6, 134.4, 132.1, 131.6, 130.9, 129.8, 129.6, 129.5, 128.9, 128.7, 128.3, 127.0, 125.2, 125.1, 92.5, 90.8, 55.9, 55.6 ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): –152.8 (d, *J* = 20.6 Hz), –184.1 (dt, *J* = 47.2, 24.2 Hz). HRMS-ESI: calculated for [M$^+$] = 445.2075, observed [M$^+$] = 445.2072.



6d

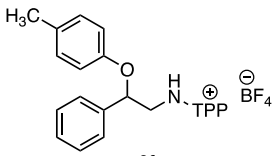
*1-((2-hydroxy-2-phenylethyl)amino)-2,4,6-triphenylpyridinium tetrafluoroborate (**6d**).* Prepared via Procedure A from water as nucleophile and obtained as an off-white solid (171 mg, 55% yield). ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.88 (s, 2H), 7.87–7.84 (m, 4H), 7.76 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.62–7.49 (m, 9H), 7.13–7.11 (m, 3H), 6.84–6.81 (m, 2H), 6.68 (t, *J* = 6.7 Hz, 1H), 4.27 (dd, *J* = 7.4, 3.4 Hz, 1H), 2.92–2.77 (m, 2H), 2.27 (s, 1H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 155.5, 155.4, 140.1, 134.3, 132.1, 131.6, 130.8, 129.8, 129.6, 129.5, 128.5, 128.2,

127.8, 126.8, 125.5, 70.4, 58.2. ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): –152.46, –152.51. HRMS-ESI: calculated for [M+] = 443.2118, observed [M+] = 443.2115.



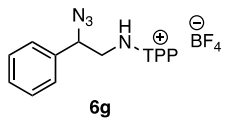
6e

*1-((2-ethoxy-2-phenylethyl)amino)-2,4,6-triphenylpyridinium tetrafluoroborate (**6e**)*. Prepared via Procedure A from ethanol as nucleophile and obtained as a yellow solid (320 mg, 98% yield). ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 8.78 (d, J = 6.2 Hz, 2H), 8.46 (bs, 1H), 8.26 (t, J = 7.7 Hz, 1H), 7.84 (t, J = 7.0 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 4.58 (q, J = 6.3 Hz, 1H), 1.63 (d, J = 6.6 Hz, 3H). ^{13}C NMR (δ, 23 °C, 101 MHz, $CDCl_3$): 155.3, 155.2, 138.3, 134.4, 132.0, 131.5, 130.9, 129.8, 129.6, 129.4, 128.6, 128.3, 128.1, 127.0, 126.3, 78.4, 64.1, 57.0, 15.2. ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): –153.21, –153.26. HRMS-APCI: calculated for [M$^+$] = 471.2431, observed [M$^+$] = 471.2424.



6f

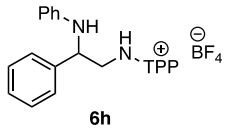
*2,4,6-triphenyl-1-((2-phenyl-2-(p-tolyloxy)ethyl)amino) pyridinium tetrafluoroborate (**6f**)*. Prepared via Procedure A from *p*-cresol as nucleophile and obtained as a light-yellow solid (75 mg, 31% yield). ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.92 (s, 2H), 7.85 (dd, J = 7.8, 1.6 Hz, 4H), 7.81 (dd, J = 7.8, 1.7 Hz, 2H), 7.59–7.53 (m, 9H), 7.17 (t, J = 3.3 Hz, 3H), 6.91–6.83 (m, 5H), 6.22 (d, J = 8.6 Hz, 2H), 4.71–4.68 (m, 1H), 3.14–3.03 (m, 2H), 2.22 (s, 3H).^{13}C NMR (δ, 23 °C, 101 MHz, $CDCl_3$): 155.6, 155.4, 154.5, 137.3, 134.6, 132.0, 131.5, 130.9, 130.6, 129.8, 129.7, 129.6, 129.4, 128.8, 128.3, 128.2, 127.1, 125.8, 115.3, 56.8, 20.5. ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): –152.85, –152.90. HRMS-APCI: calculated for [M$^+$] = 533.2587. observed [M$^+$] = 533.2583.



6g

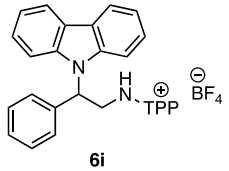
*1-((2-azido-2-phenylethyl)amino)-2,4,6-triphenylpyridinium tetrafluoroborate (**6g**).* Prepared via Procedure A from tetrabutylammonium azide as nucleophile and obtained as an off-white solid (254 mg, 78% yield). ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.89–7.87 (m, 6H), 7.77–7.75 (m, 2H), 7.64–7.48 (m, 9H), 7.24–7.19 (m, 3H), 6.87 (dd, J = 7.7, 1.6 Hz, 2H), 6.42 (dd, J = 7.6, 6.0 Hz, 1H), 4.03 (dd, J = 8.0, 4.5 Hz, 1H), 2.99–2.85 (m, 2H). ^{13}C NMR (δ,

23 °C, 100 MHz, $CDCl_3$): 155.9, 155.5, 135.4, 134.4, 132.0, 131.5, 130.8, 129.7, 129.6, 129.5, 129.0, 128.9, 128.3, 127.1, 126.7, 63.3, 55.4. ^{19}F NMR (δ, 23 °C, 377 MHz, $CDCl_3$): –152.66, –152.71. HRMS-APCI: calculated for [M^+] = 468.2183, observed [M^+] = 468.2192.



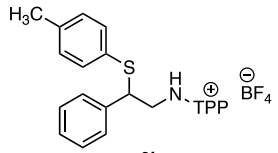
6h

*2,4,6-triphenyl-1-((2-phenyl-2-(phenylamino)ethyl)amino) pyridinium tetrafluoroborate (**6h**)*. Prepared via Procedure B from aniline as nucleophile and obtained as a yellow solid (251 mg, 71% yield). ^1H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.86 (s, 2H), 7.82–7.80 (m, 4H), 7.74 (dd, J = 8.2, 1.4 Hz, 2H), 7.61–7.47 (m, 9H), 7.15–7.08 (m, 3H), 6.95 (td, J = 8.0, 1.5 Hz, 2H), 6.85–6.82 (m, 2H), 6.58 (t, J = 7.3 Hz, 1H), 6.24 (t, J = 7.4 Hz, 1H), 6.06 (d, J = 7.7 Hz, 2H), 4.01–3.99 (m, 1H), 3.54 (s, 1H), 3.05 (dd, J = 7.2, 5.2 Hz, 2H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 155.9, 155.6, 146.2, 138.5, 134.3, 132.1, 131.6, 130.7, 129.8, 129.5, 129.4, 129.1, 129.0, 128.3, 127.7, 127.0, 126.0, 117.7, 113.4, 56.5, 55.1. ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): –152.61, –152.66. HRMS-APCI: calculated for [M^+] = 518.2591, observed [M^+] = 518.2584.



6i

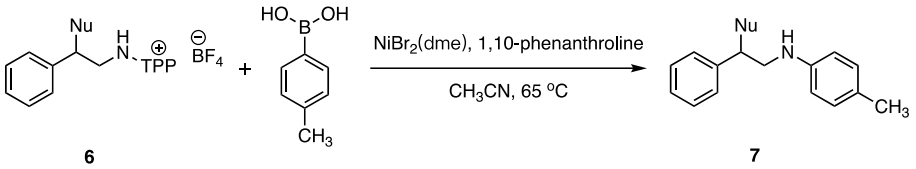
*1-((2-(9H-carbazol-9-yl)-2-phenylethyl)amino)-2,4,6-triphenylp pyridinium tetrafluoroborate (**6i**).* Prepared via Procedure B from carbazole as nucleophile and obtained as light-yellow solid (378 mg, 95% yield). ^1H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 8.03–8.01 (m, 2H), 7.84 (s, 2H), 7.75–7.73 (m, 2H), 7.64–7.62 (m, 4H), 7.53–7.46 (m, 3H), 7.38–7.34 (m, 2H), 7.29 (d, J = 7.7 Hz, 4H), 7.24–7.18 (m, 4H), 7.11 (dq, J = 8.3, 2.4 Hz, 3H), 6.79–6.73 (m, 4H), 5.70 (t, J = 7.7 Hz, 1H), 5.36 (t, J = 7.1 Hz, 1H), 3.97 (t, J = 7.5 Hz, 2H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 156.0, 154.7, 139.3, 135.5, 134.4, 131.8, 131.3, 130.0, 129.6, 129.0, 128.8, 128.7, 128.2, 127.8, 127.3, 126.1, 125.9, 123.3, 120.1, 119.5, 110.0, 55.0, 51.9. ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): –152.36, –152.44. HRMS-APCI: calculated for [M^+] = 592.2747, observed [M^+] = 592.2746.



6j

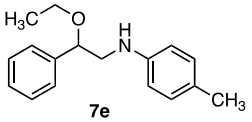
*2,4,6-triphenyl-1-((2-phenyl-2-(p-tolylthio)ethyl)amino)pyridinium tetrafluoroborate (**6j**)*. Prepared via Procedure B from *p*-thiocresol as nucleophile and obtained as light-yellow solid (268 mg, 72% yield). ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.86 (s, 2H), 7.78–7.73 (m, 6H), 7.59–7.48 (m, 9H), 7.14–7.13 (m, 1H), 7.10–7.06 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.88–6.86 (m, 2H), 6.69–6.67 (m, 2H), 6.13–6.09 (m, 1H), 3.46 (dd, *J* = 8.2, 6.0 Hz, 1H), 3.19–3.12 (m, 1H), 3.08–3.01 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 156.0, 155.4, 138.1, 137.2, 134.4, 133.1, 132.1, 131.4, 130.7, 130.0, 129.8, 129.5, 129.4, 129.0, 128.3, 128.0, 127.2, 127.1, 55.5, 51.0, 21.3. ^{19}F NMR (δ, 23 °C, 376 MHz, $CDCl_3$): −152.72, −152.77. HRMS-APCI: calculated for $[M^+]$ = 549.2359, observed $[M^+]$ = 549.2350.

B.8 Cross-Coupling of *N*-Pyridinium Amines



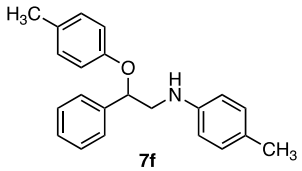
6 **7**

The following procedure was carried out in an N_2-filled dry box. A 20-mL scintillation vial was charged with compound **6** (0.100 mmol, 1.00 equiv) and CH_3CN (1 mL). A separate 20-mL was charged with $NiBr_2$(dme) (3.1 mg, 0.010 mmol, 10 mol%), 1,10-phenanthroline (2.4 mg, 0.014 mmol, 0.14 equiv), K_3PO_4 (53.1 mg, 0.250 mmol, 2.50 equiv), *p*-toluyl boronic acid (20.4 mg, 0.150 mmol, 1.50 equiv). The CH_3CN solution of **6** was added to the vial containing $NiBr_2$·DME. The reaction mixture was stirred at 65 °C for 18 h. The reaction mixture was cooled to 23 °C. The reaction mixture was centrifuged for 10 min and the supernatant was decanted. Solvent was removed under reduced pressure and the residue was purified by alumina gel column chromatography to obtain the title compound.



7e

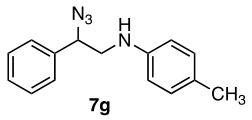
*N-(2-ethoxy-2-phenylethyl)-4-methylaniline (**7e**).* Prepared from 1-((2-ethoxy-2-phenylethyl)amino)-2,4,6-triphenylpyridinium tetrafluoroborate (**6e**) and obtained as a pale-yellow liquid (8.9 mg, 39% yield). The purification was done by alumina gel column chromatography using 95:5 hexanes:ethyl acetate as eluent. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.40–7.29 (m, 5H), 7.00 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 4.50 (dd, J = 8.4, 4.5 Hz, 1H), 3.49–3.25 (m, 4H), 2.25 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (δ, 23 °C, 126 MHz, $CDCl_3$): 145.6, 140.8, 129.9, 128.7, 128.1, 127.4, 126.8, 114.1, 80.3, 64.6, 51.6, 20.6, 15.5. HRMS-APCI: calculated for [M+1] = 256.1696, observed [M+1] = 256.1693



7f

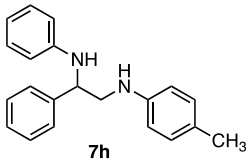
*4-methyl-N-(2-phenyl-2-(p-tolyloxy)ethyl)aniline (**7f**).* Prepared from 2,4,6-triphenyl-1-((2-phenyl-2-(p-tolyloxy)ethyl)amino) pyridinium tetrafluoroborate (**6f**) and obtained as an orange solid (30 mg, 93% yield). The purification was done by alumina gel column chromatography using 95:5 hexanes:ethyl acetate as eluent. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.40–7.26 (m, 5H), 7.01–6.96 (m, 4H), 6.76–6.73 (m, 2H), 6.61–6.58 (m, 2H), 5.29 (dd, J = 7.4, 5.1 Hz, 1H), 4.06 (s, 1H), 3.55–3.46 (m, 2H), 2.25 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (δ,

23 °C, 100 MHz, $CDCl_3$): 155.9, 145.5, 139.9, 130.5, 130.0, 129.9, 128.9, 128.1, 127.3, 126.3, 116.0, 113.8, 78.8, 51.6, 20.6, 20.5. HRMS-APCI: calculated for [M+1] = 318.1852, observed [M+1] = 318.1855.



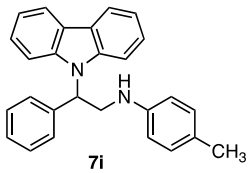
7g

*N-(2-azido-2-phenylethyl)-4-methylaniline (**7g**).* Prepared from 1-((2-azido-2-phenylethyl)amino)-2,4,6-triphenylpyridinium tetrafluoroborate (**6g**) and obtained as a pale-yellow liquid (25 mg, 98% yield). The purification was done by alumina gel column chromatography using 95:5 hexanes:ethyl acetate as eluent. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.45–7.34 (m, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 4.77 (dd, J = 8.5, 5.2 Hz, 1H), 3.38 (qd, J = 13.4, 6.9 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 144.7, 137.7, 130.1, 129.2, 128.8, 127.9, 127.2, 113.8, 65.0, 50.2, 20.6. HRMS-APCI: calculated for [M+1] = 253.1448, observed [M+1] = 253.1444.



7h

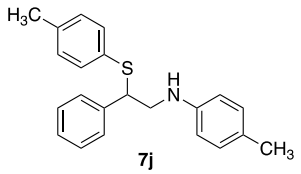
*N^1,1-diphenyl-N^2-(p-tolyl)ethane-1,2-diamine (**7h**).* Prepared from 2,4,6-triphenyl-1-((2-phenyl-2-(phenylamino)ethyl)amino) pyridinium tetrafluoroborate (**6h**) and obtained as an colorless solid (17 mg, 56% yield). The purification was done by alumina gel column chromatography using 95:5 hexanes:ethyl acetate as eluent. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.41–7.33 (m, 4H), 7.28 (dt, J = 7.1, 2.0 Hz, 1H), 7.09 (dd, J = 8.6, 7.4 Hz, 2H), 7.03–7.00 (m, 2H), 6.69–6.62 (m, 3H), 6.57–6.54 (m, 2H), 4.62 (dd, J = 8.1, 4.8 Hz, 1H), 3.51–3.38 (m, 2H), 2.25 (s, 3H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 147.3, 145.7, 141.6, 130.0, 129.3, 129.0, 127.7, 127.6, 126.6, 117.9, 113.8, 113.6, 57.6, 51.5, 20.5. HRMS-APCI: calculated for [M+1] = 303.1856, observed [M+1] = 303.1853.



7i

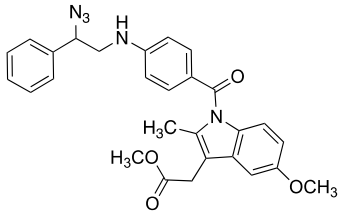
*N-(2-(9H-carbazol-9-yl)-2-phenylethyl)-4-methylaniline (**7i**).* Prepared from 1-((2-(9H-carbazol-9-yl)-2-phenylethyl)amino)-2,4,6-triphenylpyridinium tetrafluoroborate (**6i**) and obtained as a colorless solid (37 mg, 98% yield). The purification was done by alumina gel

column chromatography using 95:5 hexanes:ethyl acetate as eluent. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.45–7.34 (m, 5H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.77 (dd, *J* = 8.5, 5.2 Hz, 1H), 3.38 (qd, *J* = 13.4, 6.9 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 144.7, 140.3, 138.2, 129.9, 129.0, 127.9, 127.7, 126.8, 125.8, 123.6, 120.4, 119.5, 113.8, 110.5, 56.3, 45.5, 20.5. HRMS-APCI: calculated for [M+1] = 377.2012, observed [M+1] = 377.2014.



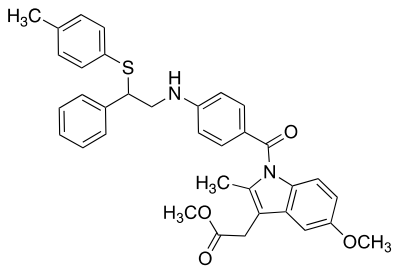
7j

*4-methyl-N-(2-phenyl-2-(p-tolylthio)ethyl)aniline (**7j**).* Prepared from 2,4,6-triphenyl-1-((2-phenyl-2-(p-tolylthio)ethyl)amino)pyridinium tetrafluoroborate (**6j**) and obtained as a pale-yellow liquid (28 mg, 85% yield). The purification was done by alumina gel column chromatography using 95:5 hexanes:ethyl acetate as eluent. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.33–7.26 (m, 5H), 7.24–7.22 (d, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 7.2 Hz, 1H), 3.63–3.49 (m, 2H), 2.32 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 145.0, 140.2, 138.0, 133.5, 130.2, 129.9, 129.8, 128.8, 128.1, 127.7, 127.4, 113.7, 52.8, 49.1, 21.3, 20.5. HRMS-APCI: calculated for [M+1] = 334.1624, observed [M+1] = 334.1618.



7k

*Methyl 2-(1-(4-((2-azido-2-phenylethyl)amino)benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**7k**).* Prepared from 1-((2-azido-2-phenylethyl)amino)-2,4,6-triphenylpyridinium tetrafluoroborate (**6g**) and obtained as a yellow liquid (26 mg, 53% yield). The purification was done by alumina gel column chromatography using 5:1 hexanes: ethyl acetate as eluent. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.64–7.60 (m, 2H), 7.46–7.35 (m, 5H), 6.97–6.94 (m, 2H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.63–6.59 (m, 2H), 4.78 (dd, *J* = 8.3, 5.2 Hz, 1H), 4.56 (t, *J* = 5.3 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.69 (s, 2H), 3.54–3.42 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 171.8, 168.9, 155.6, 151.6, 137.0, 136.3, 133.1, 131.4, 130.2, 129.3, 129.2, 127.1, 123.8, 114.8, 112.1, 111.4, 110.9, 101.0, 65.0, 55.9, 52.2, 48.7, 30.4, 13.0. HRMS-APCI: calculated for [M+1] = 498.2136, observed [M+1] = 498.2133.



7l

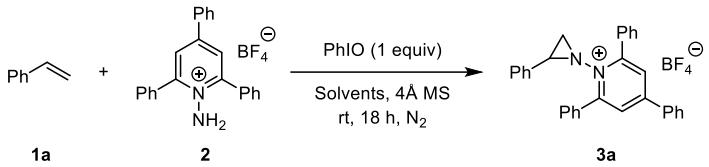
*Methyl 2-(5-methoxy-2-methyl-1-(4-((2-phenyl-2-(p-tolylthio)ethyl)amino)benzoyl)-1H-indol-3-yl)acetate (**7l**).* Prepared from 2,4,6-triphenyl-1-((2-phenyl-2-(p-tolylthio)ethyl)amino)pyridinium tetrafluoroborate (**6j**) and obtained as a yellow liquid (50 mg, 86% yield). The purification was done by alumina gel column chromatography using 5:1 hexanes:ethyl acetate as eluent. ^{1}H NMR (δ, 23 °C, 400 MHz, $CDCl_3$): 7.56 (d, J = 8.7 Hz, 2H), 7.36–7.23 (m, 7H), 7.08 (d, J = 7.9 Hz, 2H), 6.97–6.93 (m, 2H), 6.66 (dd, J = 9.0, 2.5 Hz, 1H), 6.47–6.44 (m, 2H), 4.51 (t, J = 6.0 Hz, 1H), 4.31 (t, J = 7.2 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.68 (s, 2H), 3.71–3.57 (m, 2H), 2.42 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (δ, 23 °C, 100 MHz, $CDCl_3$): 171.8, 169.0, 155.6, 151.7, 139.5, 138.5, 136.3, 133.7, 133.1, 131.4, 130.2, 130.00, 129.8, 129.0, 128.1, 128.0, 123.4, 114.7, 112.1, 111.4, 110.8, 100.9, 55.9, 53.0, 52.2, 47.9, 30.4, 21.3, 12.9. HRMS-APCI: calculated for [M+1] = 579.2312, observed [M+1] = 579.2310.

C. Additional Data

C.1. Optimization of Vinyl Arene Aziridination

Optimization tables for Procedure A

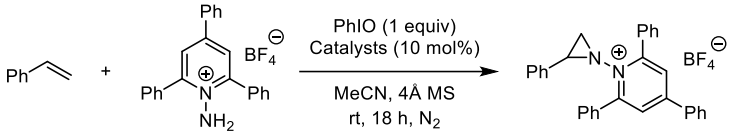
Table S1 *Examination of the Impact of Solvent on Aziridination Efficiency.*



1a 2 3a

Entry	Solvents	NMR yield
1	**MeCN**	**42%**
2	^{t}BuCN	19%
3	^{i}PrOAc	7%
4	PhMe	0
5	PhH	0
6	Propylene carbonate	26%
7	Propylene carbonate (10% in MeCN)	34%

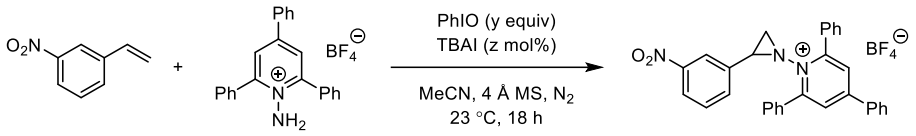
Table S2 *Catalyst Screen for Styrene Aziridination Reaction.* Reactions were carried out using 0.2 mmol of styrene, 0.2 mmol of *N*-aminotriphenylpyridinium tetrafluoroborate, and 0.2 mmol of iodosylbenzene with 1 mL of acetonitrile in an N_2 filled dry box. NMR yields were determined by adding 5~10 mg of 1,3,5-trimethoxybenzene as the internal standard to the crude mixture after reaction workup.



1a 2 3a

Entry	Catalysts	NMR yield
1	None, under air	42%
2	CuI	53%
3	CuI (30 mol%)	53%
4	$Cu(MeCN)_4PF_6$	16%
5	$Cu(OTf)_2$	20%
6	$Fe(OTf)_2$	0
7	MnTPPCl	4%
8	FeTPPCl	8%
9	$Rh_2(esp)_2$	35%
10	$Rh_2(tfacam)_4$	22%
11	AgOTf	25%
12	TBAI 5 mol%, I_2 10 mol% (under air)	21%
13	CuCl or CuBr	18%
14	CuI, BPhen	64%
15	$Cu(MeCN)_4(PF_6)_2$, TBAI	19%
16	**TBAI (5 mol%)**	**73%**
17	KI (5 mol%)	18%
18	CsI (5 mol%)	27%
19	TEAI (5 mol%)	71%
20	Ph_4PI (5 mol%)	36%

Table S3. *Screen of Catalyst and Reagent Loading for Aziridination with 3-Nitrostyrene.* Reactions were carried out using 0.2 mmol of 3-nitrostyrene with 1 mL of acetonitrile in an N_2 filled dry box. NMR yields were determined by comparing the product peak against the methylene peak from tetrabutylammonium iodide.

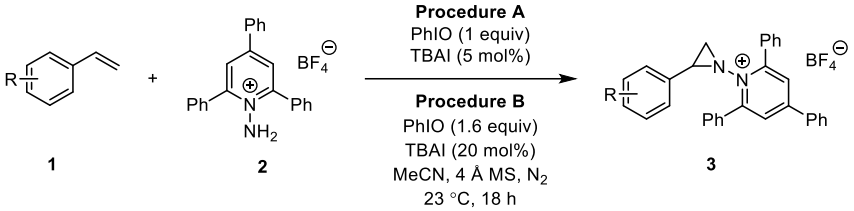


1o 2, x equiv 3o

Entry	Py*–NH_2 equiv	PhIO equiv	TBAI loading	Time	NMR yield
0	1	1	5 mol%	18 h	40%
1	1	1.4	5 mol%	48 h	40%
2	1	1	15 mol%	18 h	49%
3	1.4	1.4	15 mol%	18 h	52%
4	**1.4**	**1.4**	**21 mol%**	**18 h**	**58%**

Reagent (eq) \ TBAI (mol%)	15	20	24	27	30	50
1.4	52%	58%	45%	45%	58%	48%
1.6	61%	**67%**	58%	51%	41%	
1.8	38%	61%	45%			
2.0	42%	39%				

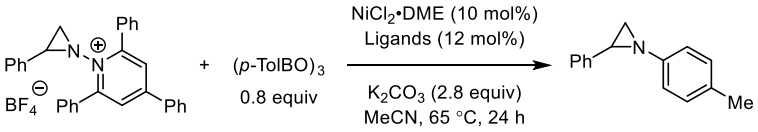
Table S4. *Head-to-Head NMR Yield Comparison of Procedure A with Procedure B for Styrene Aziridination.*



R	Procedure A	Procedure B
H	73%	77%
2-Me	69%	99%
2-Br	61%	82%
2-OMe	74%	70%
3-Me	69%	84%
3-Br	40%	71%
3-Cl	51%	58%
3-NO_2	40%	82%
4-Me	87%	95%
4-F	79%	83%
4-CF_3	32%	72%
4-AcO	62%	97%
4-CO_2Et	58%	87%
4-NHBoc	55%	56%
4-Ph	82%	70%
4-CN	46%	94%
4-OMe	59%	45%
4-Ac	75%	--
Isatin	77%	90%
Benzothiophene	62%	60%
2-Naph	85%	70%

C.2 Optimization of Pyridinium Aziridine Cross-Couplings

Table S5 *Screen of Catalyst and Ligand Loading.*



3a **5b**

Entry	Catalyst loading	Ligands	NMR yield
1	10 mol%	4,4'-dmbpy, 12 mol%	0
2	10 mol%	1,10-Phen, 12 mol%	5%
3	10 mol%	1,10-Phen, 20 mol%	0
4	20 mol%	1,10-Phen, 20 mol%	36%
5	**30 mol%**	**1,10-Phen, 30 mol%**	**67%**
6	30 mol%	BPhen, 32 mol%	0
7	30 mol%	3,4,7,8-Me_4-1,10-Phen, 32 mol%	22%
8	30 mol%	2,9-Me_2-1,10-Phen, 32 mol%	43%
9	30 mol%	terpy, 32 mol%	44%
10	30 mol%	dppf, 32 mol%	29%
11	30 mol%	PCy_3, 32 or 62 mol%	0
12	30 mol%	XPhos, 32 mol%	0

Table S6. *Investigation of Nucleophiles in Transmetalation.*

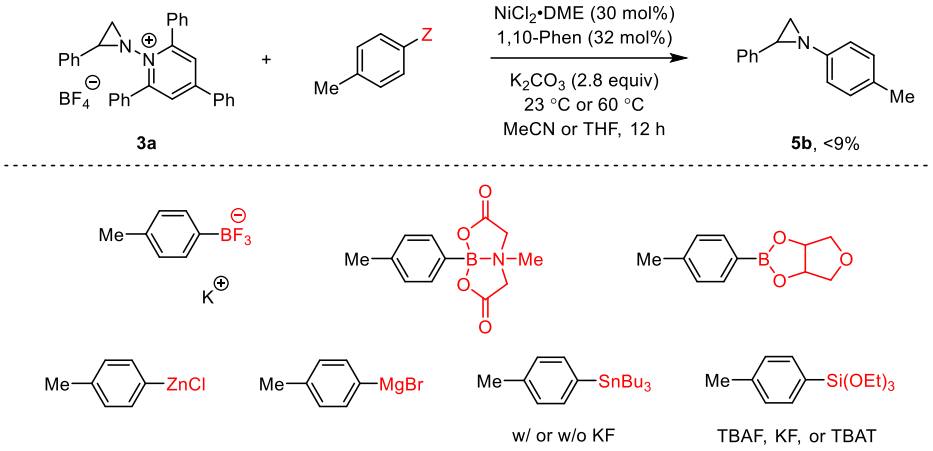
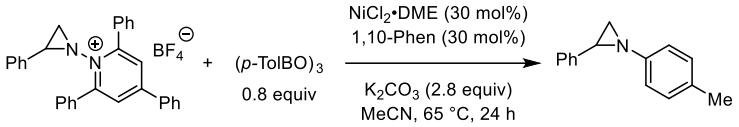


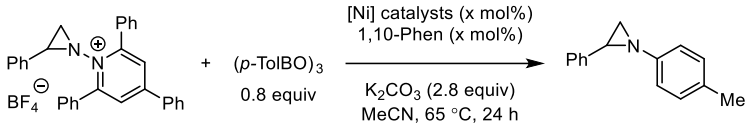
Table S7. *Variations with Solvent and Bases.*



3a 5b

Entry	Variations	NMR yield
1	1,4-dioxane	Trace
2	THF	0
3	K_3PO_4	57%
4	Cs_2CO_3	0
5	KO^tBu	0
6	KF (2.8 equiv as base)	53%
7	KF (1 equiv as additive)	49%

Table S8. *Investigation of Precatalyst.*

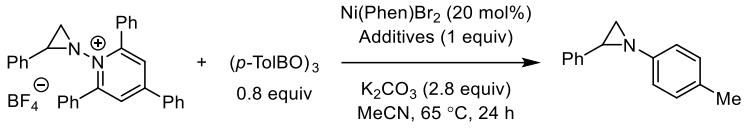


3a **5b**

Entry	Catalysts	NMR yield
1	**$NiBr_2$·DME (20 mol%)**	**60%**
2	$Ni(OAc)_2$ (30 mol%)	0
3	$Ni(OAc)_2·4H_2O$ (30 mol%)	13%
4	$Ni(acac)_2$ (30 mol%)	0
5	$Ni(cod)_2$ (30 mol%)	--
6	$Ni(Cp)_2$ (20 mol%)	27%
7	$NiSO_4·6H_2O$ (20 mol%)	0
8	$NiCl_2$ (20 mol%)	0
9	NiF_2 (20 mol%)	0
10	NiI_2 (20 mol%)	17%
11	**Ni(Phen)Br_2 (20 mol%)[6]**	**60%**
12	$Ni(Phen)_3Br_2$ (20 mol%)[6]	0

[6] 1,10-Phenanthroline was not added.

Table S9. *Screen of* N-*Containing Additives.* Reactions were carried out using 0.08 mmol of pyridinium aziridine with 1 mL of acetonitrile in an N_2 filled dry box. NMR yields were determined by adding 5~10 mg of 1,3,5-trimethoxybenzene as the internal standard to the crude mixture after reaction workup.



3a **5b**

Entry	Additives	NMR yield
1	2,4,6-Triphenylpyridine	70%
2	**2,4,6-Collidine**	**79%**
3	DABCO	Trace
4	DBU	40%
5	Et_3N	13%
6	Imidazole	4%
7	2,6-Lutidine	0
8	DIPEA	17%

C.3. Stereochemistry of Aziridination with *trans*- and *cis*-β-Methylstyrene

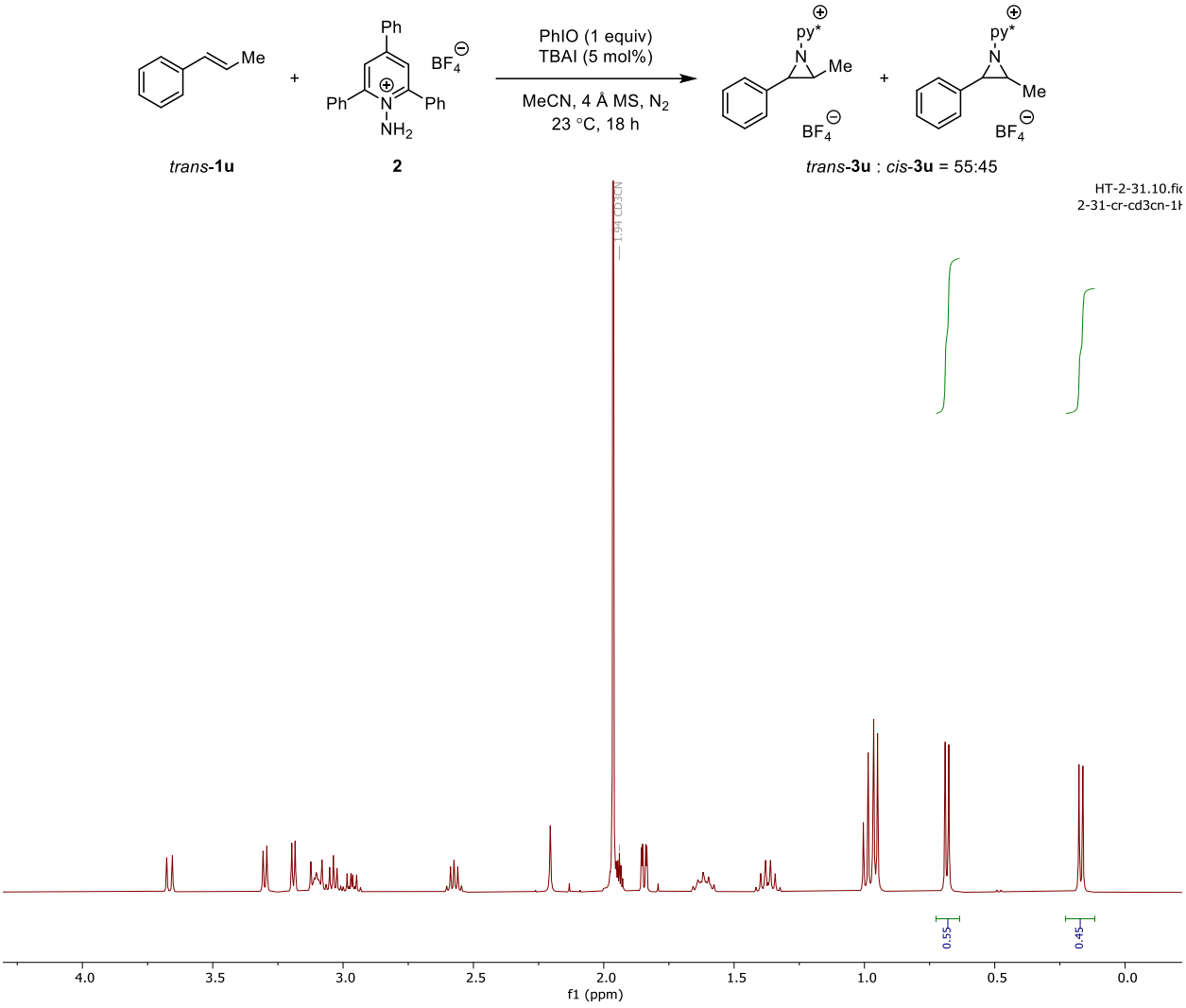


Figure S1. ^{1}H NMR spectrum of the crude mixture of the aziridination of *trans*-**1u** in CD_3CN. The reaction was carried out on 0.2 mmol scale (based on *trans*-**1u**) according to the general procedure A indicated in section **B.5**. The doublets at δ 0.68 and δ 0.17 were assigned as the methyl peaks in *trans*-**1u** and *cis*-**1u** respectively, the integration of which indicated the ratio of *trans*-**1u** to *cis*-**1u**. The chemical shifts and the coupling constants used to assign the formed products were similar as their analogs, 2-methyl-3-phenyl-1-tosylaziridine (*cis*- and *trans*) that were reported in literature.[19, 20] .

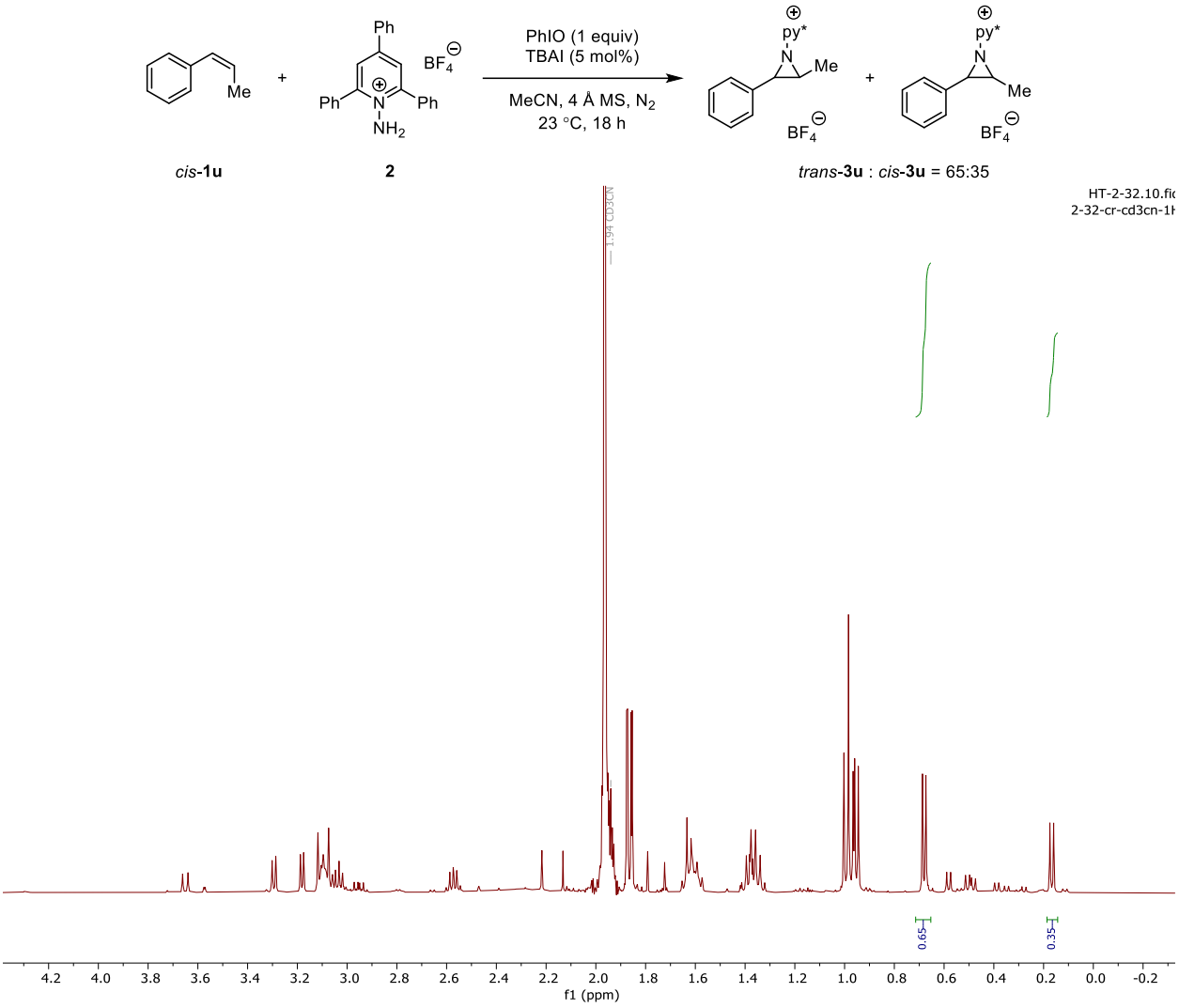


Figure S2. ^{1}H NMR spectrum of the crude mixture of the aziridination of *cis*-**1u** in CD_3CN. The reaction was carried out on 0.2 mmol scale (based on *cis*-**1u**) according to the general procedure A indicated in section **B.5**. The doublets at δ 0.68 and δ 0.17 were assigned as the methyl peaks in *trans*-**3u** and *cis*-**3u** respectively, the integration of which indicated the ratio of *trans*-**3u** to *cis*-**3u**. The chemical shifts and the coupling constants used to assign the formed products were similar as their analogs, 2-methyl-3-phenyl-1-tosylaziridine (*cis*- and *trans*) that were reported in literature.[19, 20]

C.4. Observation of Pyridinium Aziridine Ring-Opening under Cross-Coupling Conditions.

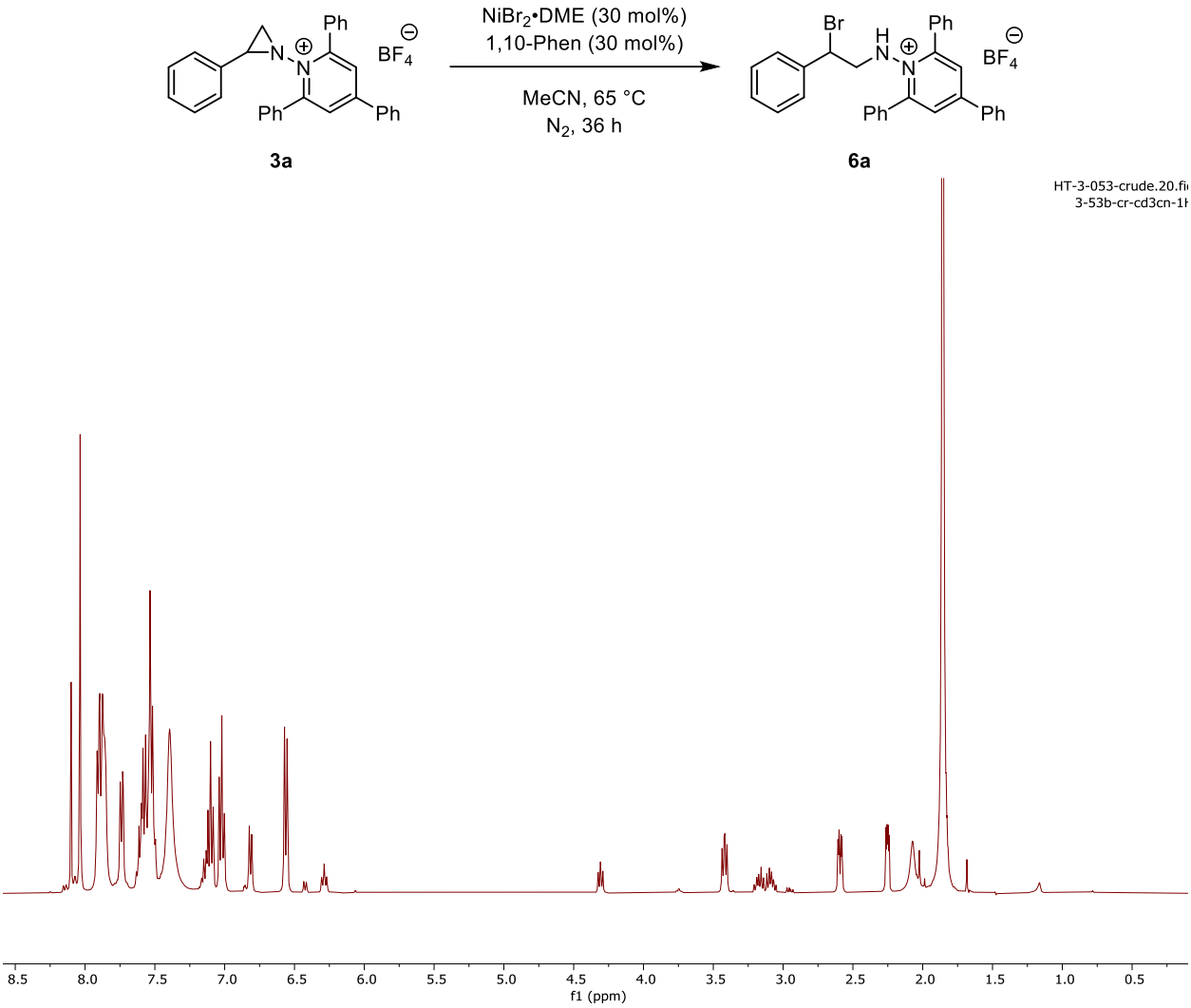
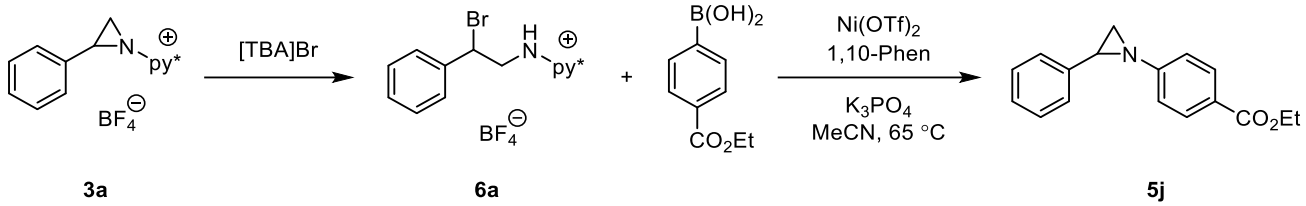


Figure S3. ^{1}H NMR spectrum of the crude mixture of **3a**, $NiBr_2$(dme), and 1,10-phenanthroline in CD_3CN. The reaction was carried out on 0.1 mmol scale (based on **3a**). The doublet of doublet peak at δ 3.53 was assigned to unreacted **3a**. Formation of **6a** was indicated by observation of a doublet of doublet peak at δ 4.42.

C.5 Ring-Closing and Cross-Coupling with NiX_2.



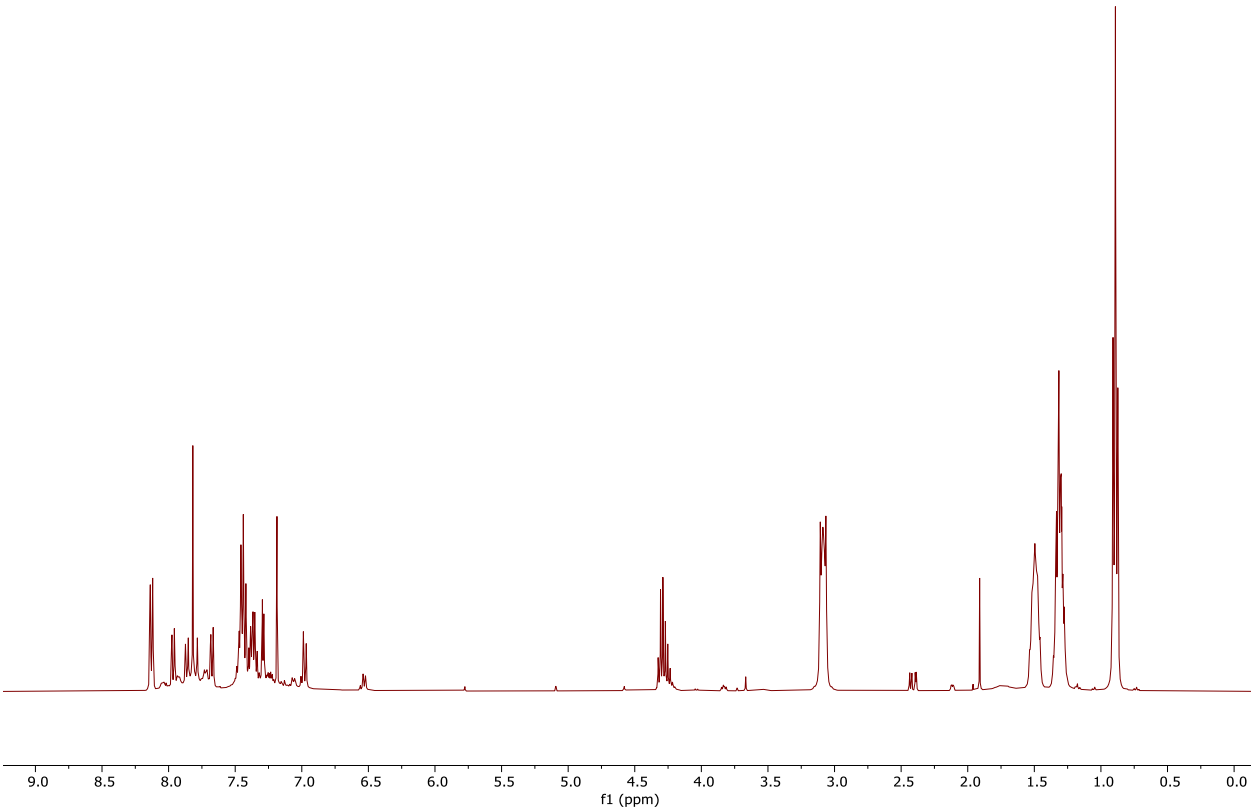


Figure S4. ^{1}H NMR spectrum of the crude mixture following cross-coupling in $CDCl_3$. **6a** was formed by reacting **3a** with [TBA]Br according to the general procedure in section **B.7** on 0.1 mmol scale (based on **6a**). The reaction mixture was concentrated under reduced pressure and then dissolved in dry acetonitrile without further purification. The crude solution was subjected to cross-coupling condition as indicated in section **B.8**. Formation of aziridine product **5j** was indicated by the observation of the doublet of doublet peaks at δ 2.50 and δ 2.46.

D. NMR Spectra for New Compounds

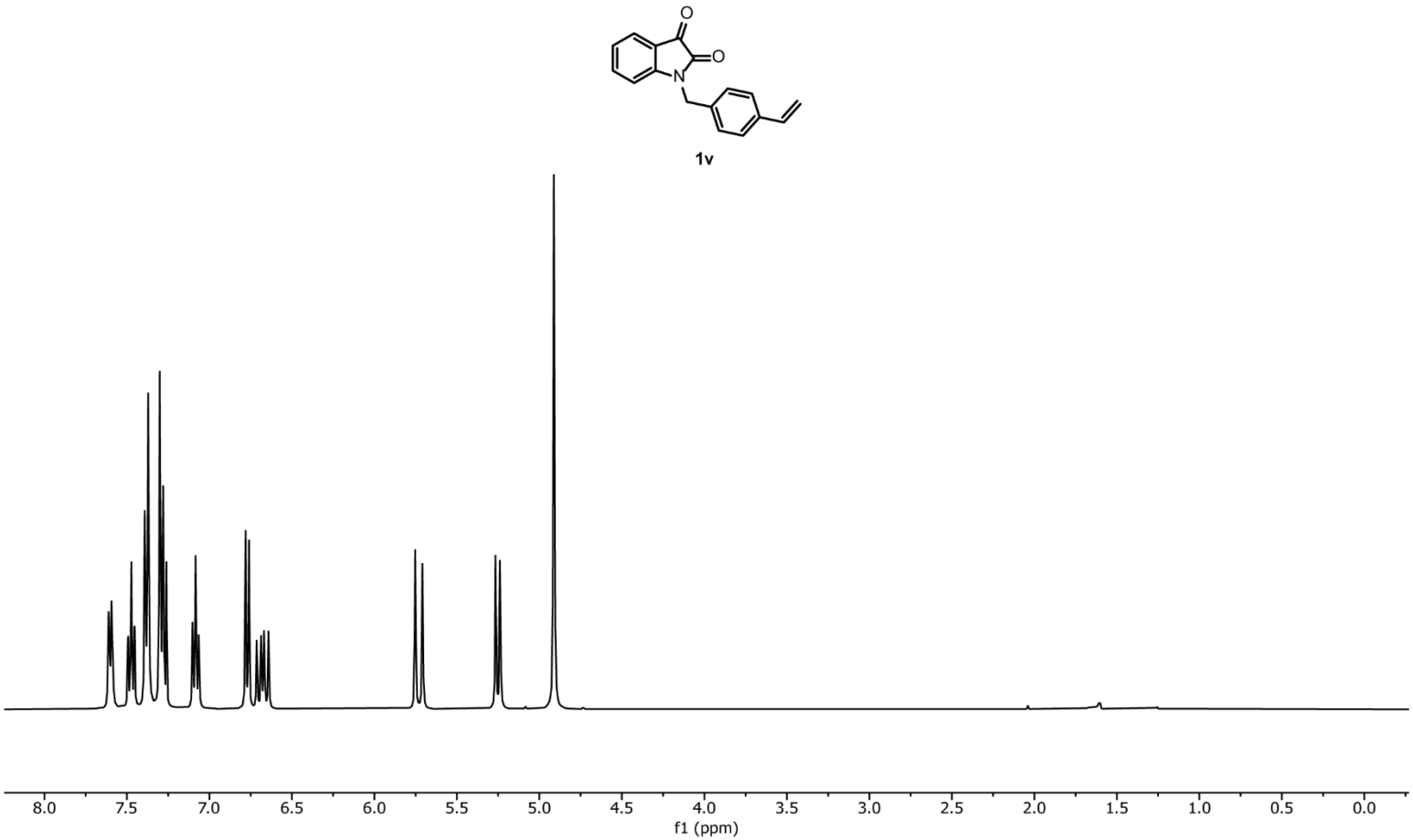


Figure S5. ^{1}H NMR spectrum of 1-(4-vinylbenzyl)indoline-2,3-dione (**1v**) in $CDCl_3$ (400 MHz) at 23 °C.

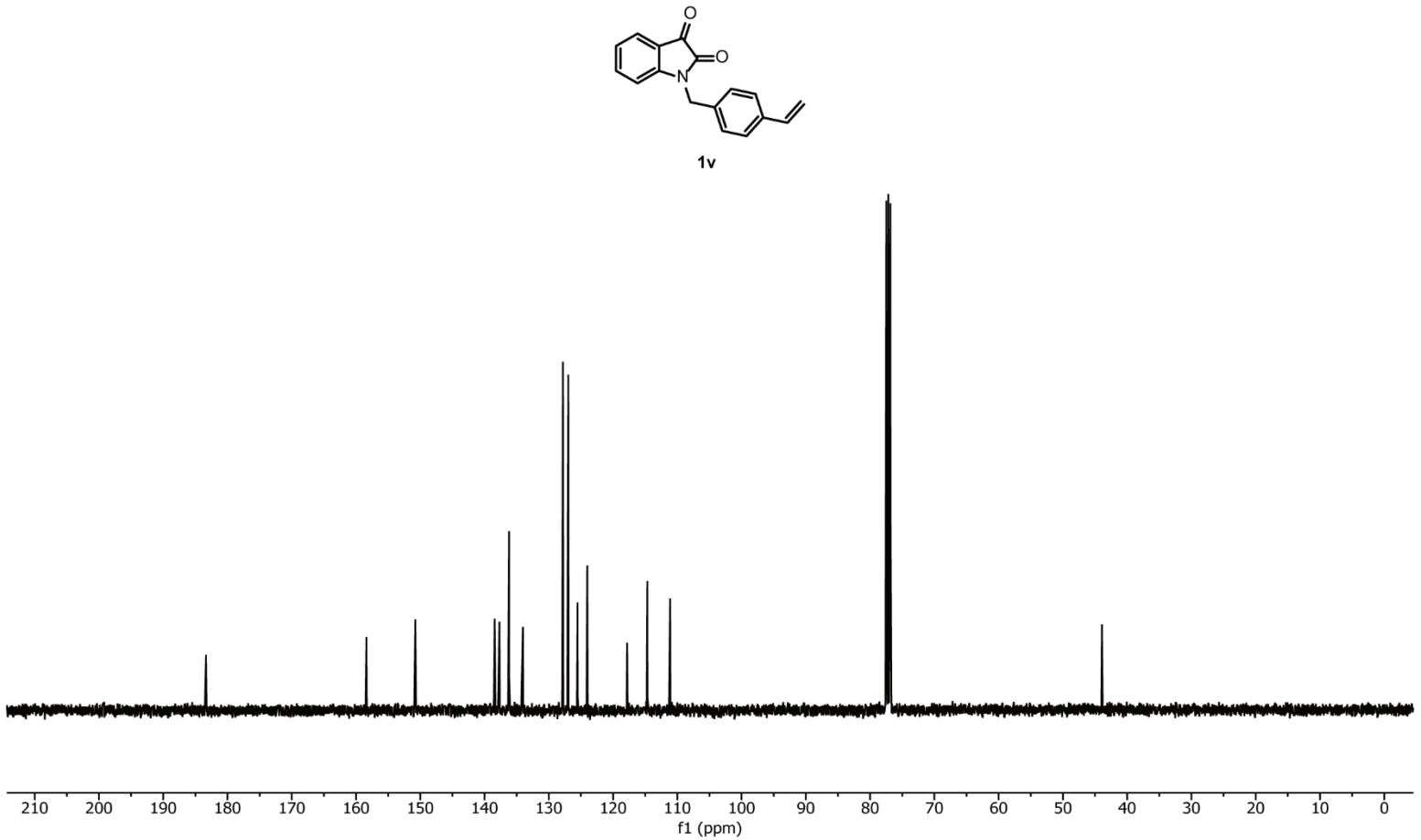


Figure S6. ^{13}C NMR spectrum of 1-(4-vinylbenzyl)indoline-2,3-dione (**1v**) in $CDCl_3$ (101 MHz) at 23 °C.

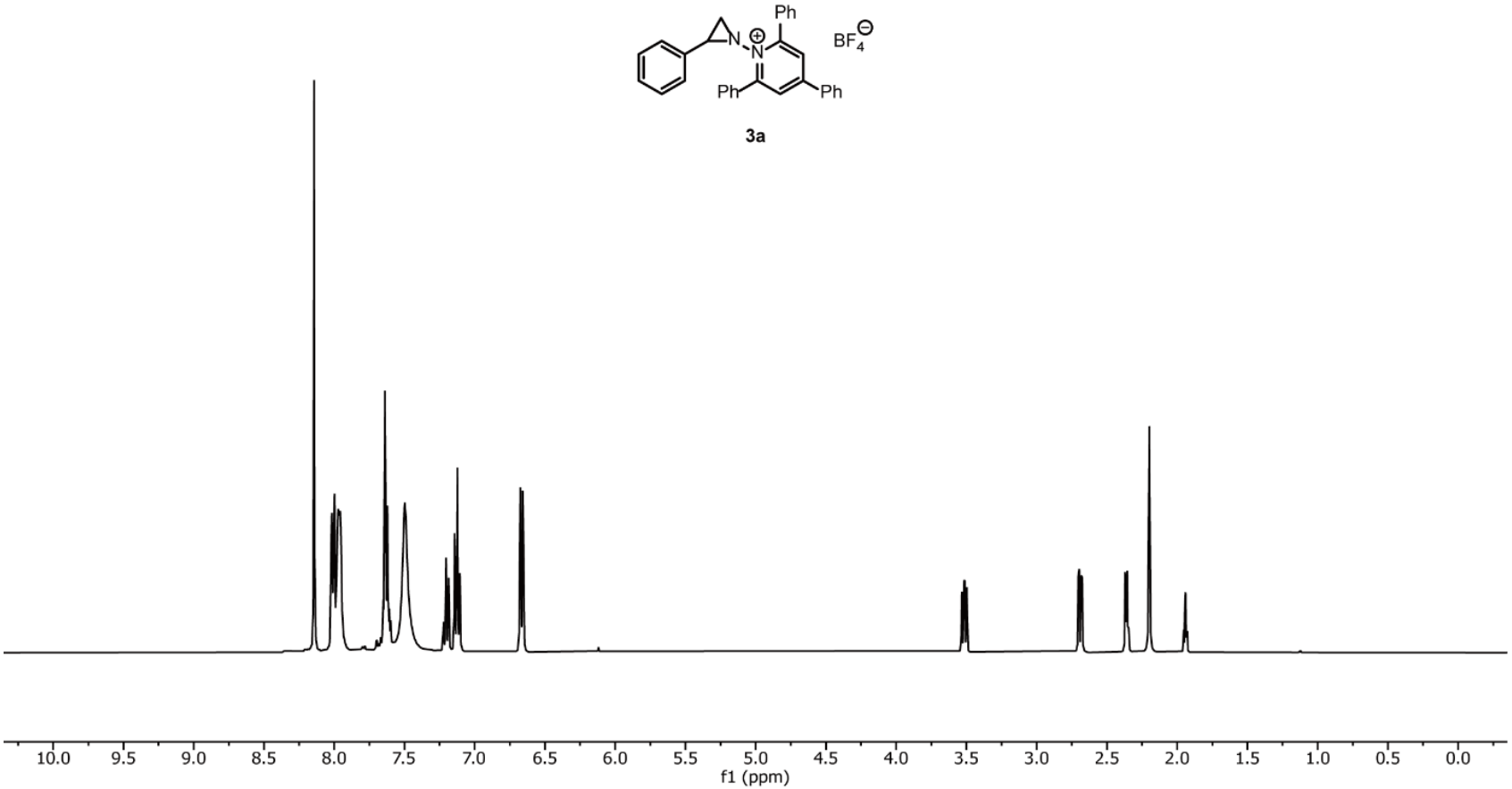


Figure S7. ^{1}H NMR spectrum of 2,4,6-triphenyl-1-(2-phenylaziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3a**) in CD_3CN (400 MHz) at 23 °C.

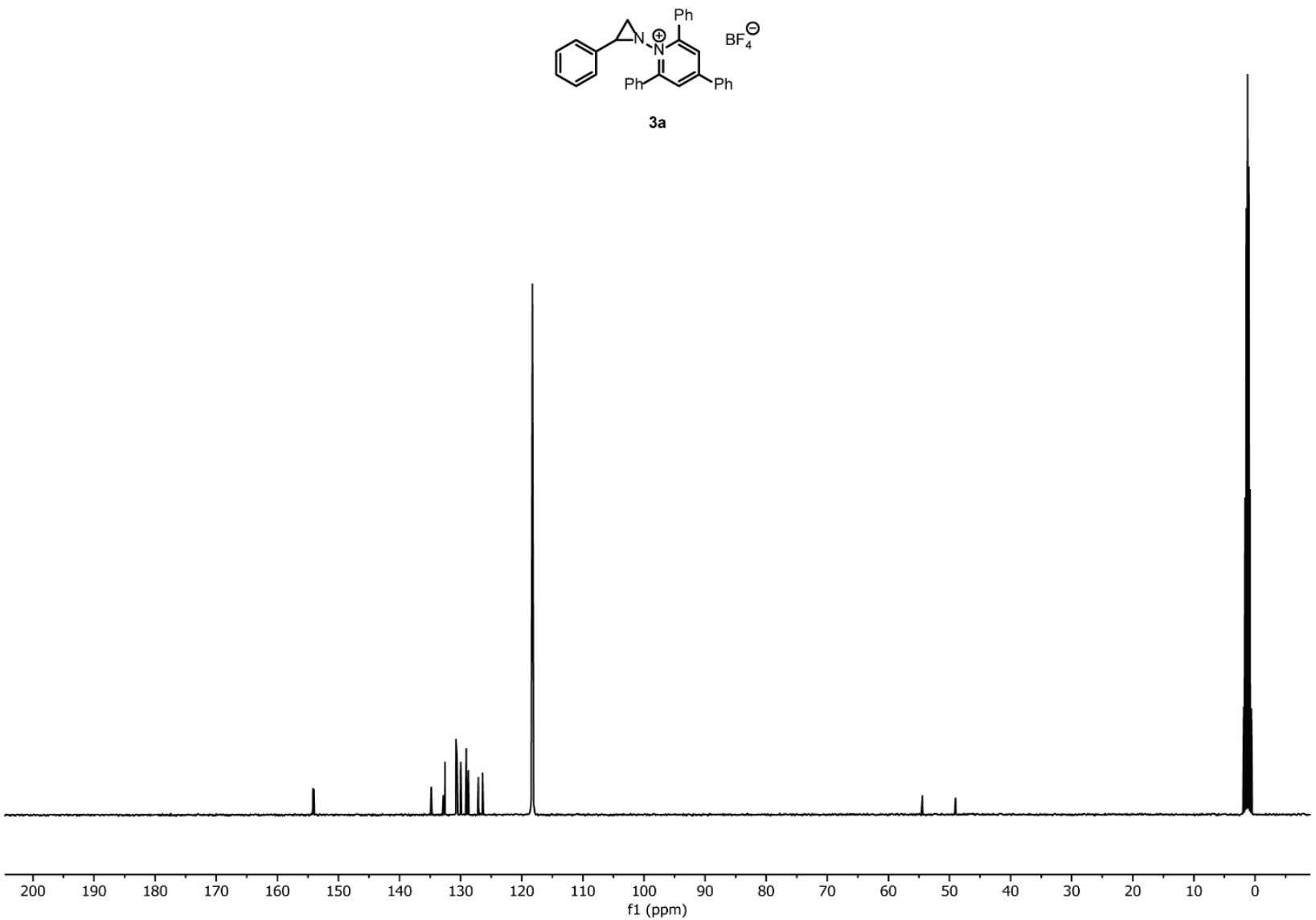


Figure S8. ^{13}C NMR spectrum of 2,4,6-triphenyl-1-(2-phenylaziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3a**) in CD_3CN (101 MHz) at 23 °C.

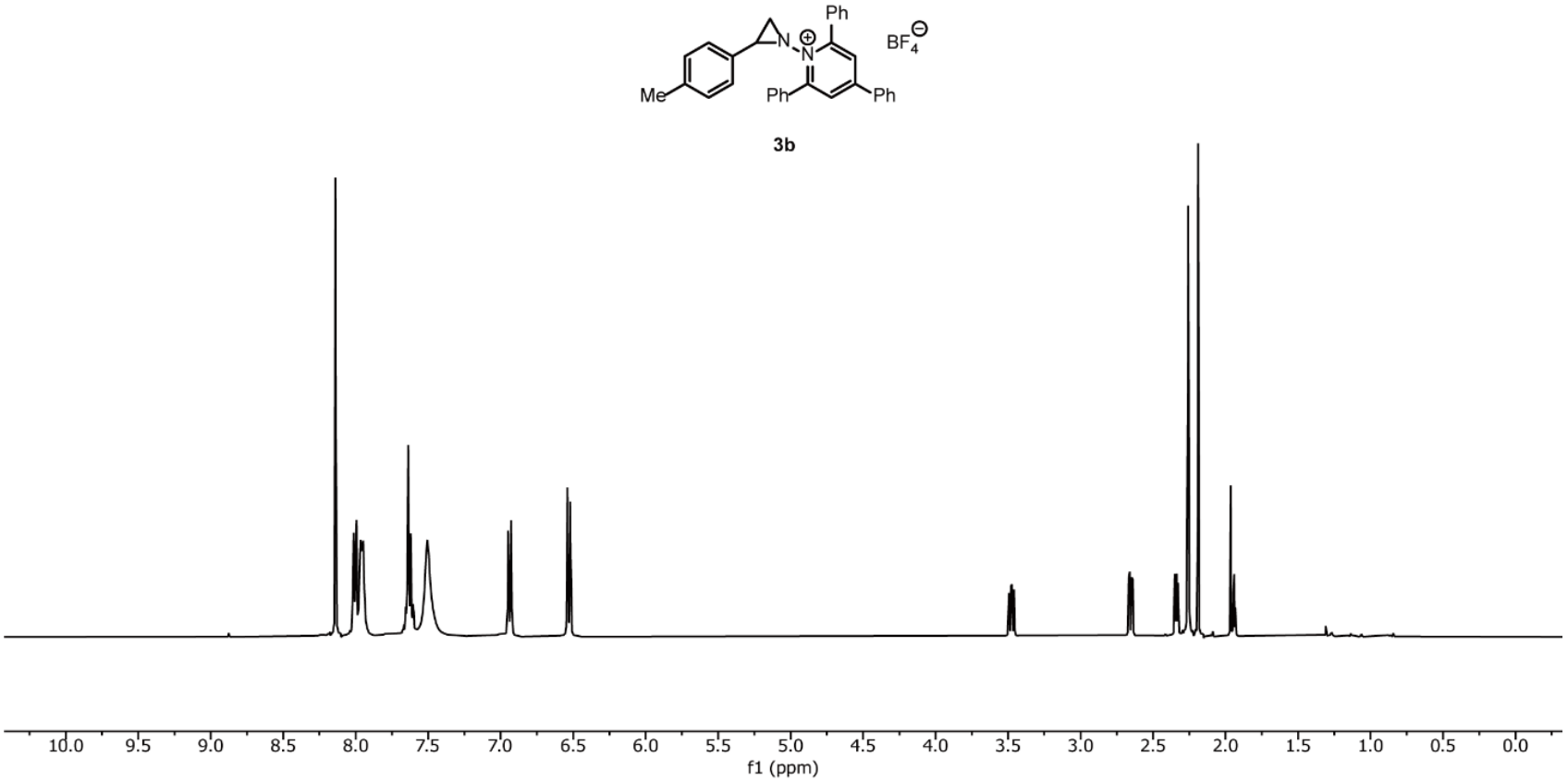


Figure S9. ^{1}H NMR spectrum of 2,4,6-triphenyl-1-(2-(*p*-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3b**) in CD_3CN (400 MHz) at 23 °C.

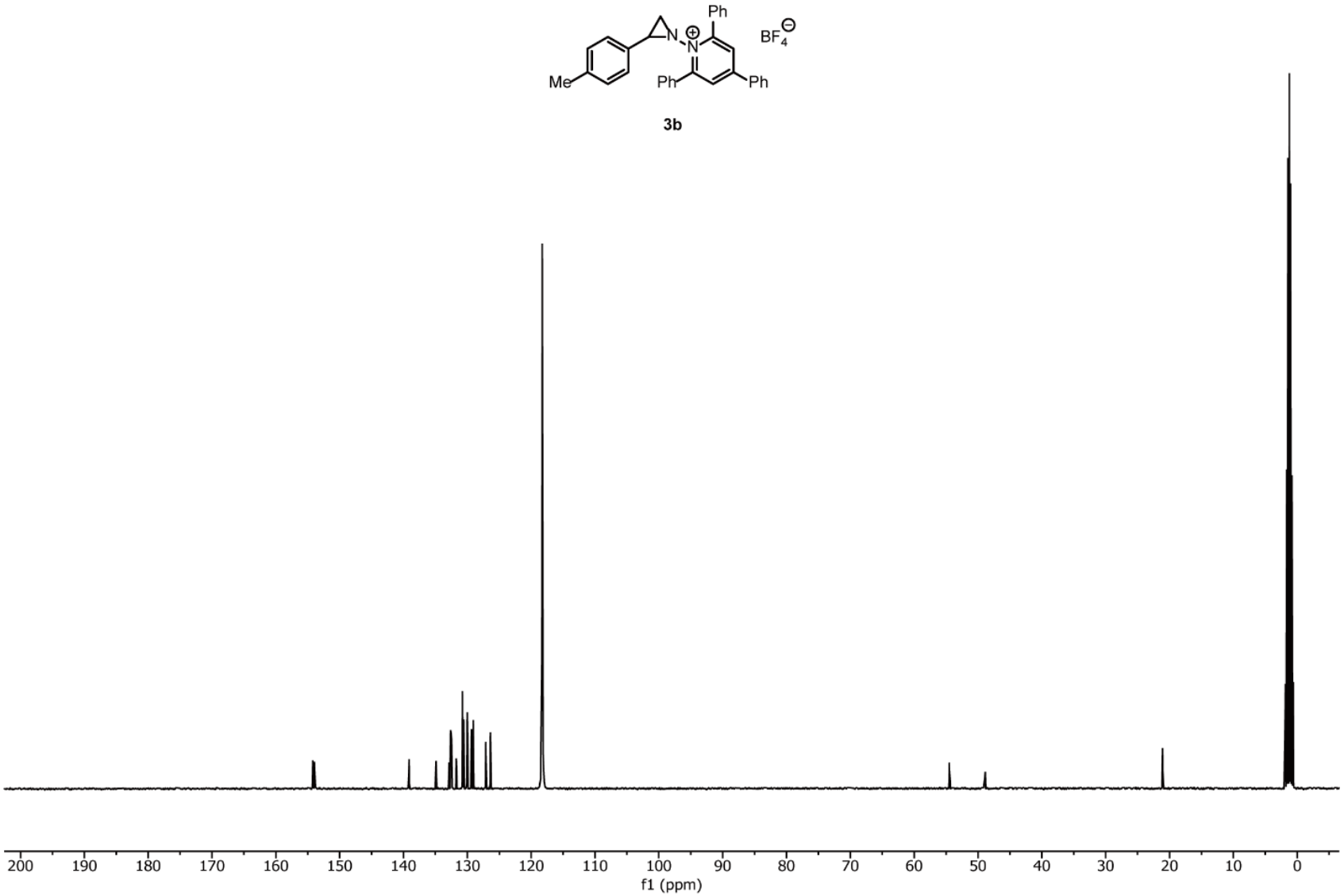


Figure S10. ^{13}C NMR spectrum of 2,4,6-triphenyl-1-(2-(*p*-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3b**) in CD_3CN (101 MHz) at 23 °C.

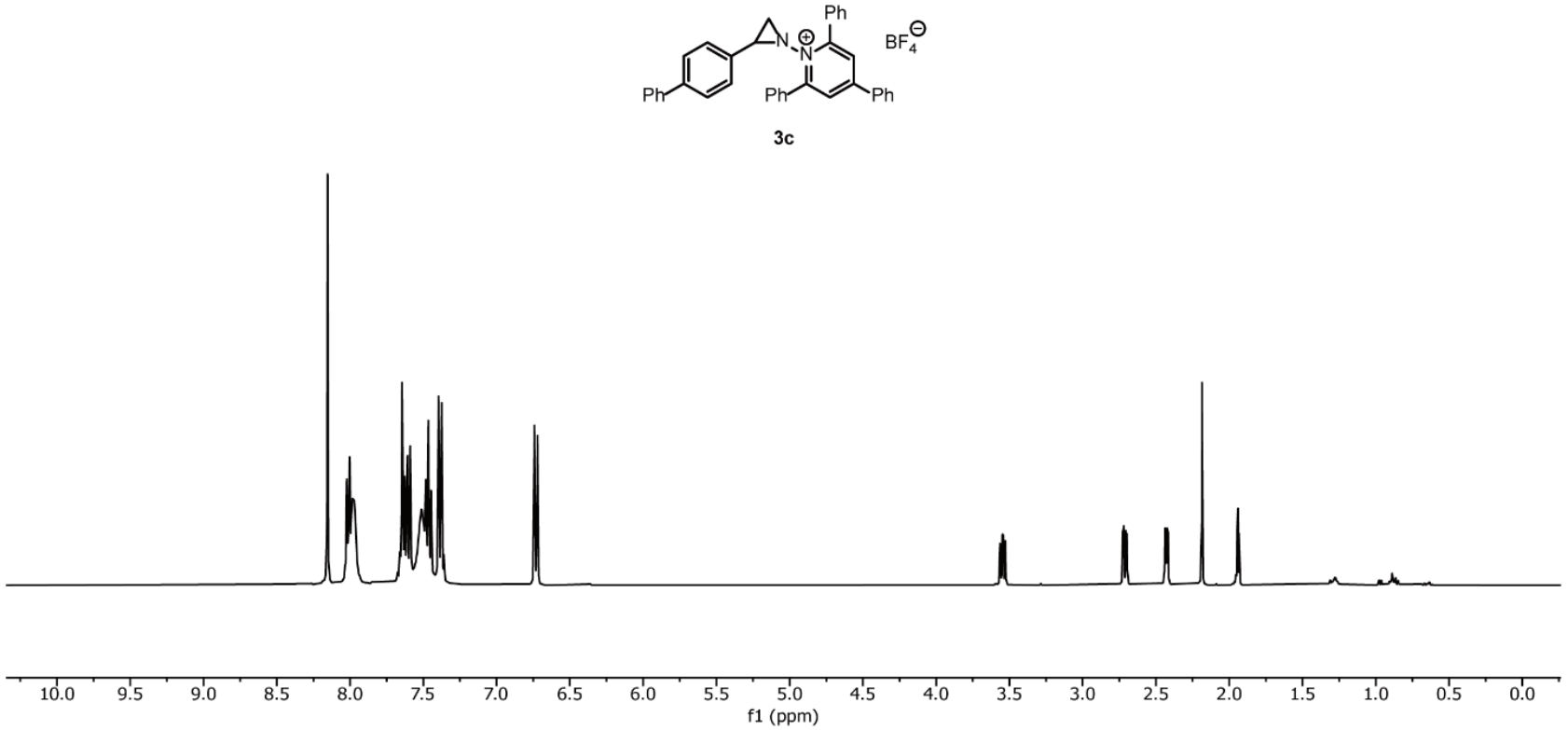


Figure S11. ^{1}H NMR spectrum of 1-(2-([1,1'-biphenyl]-4-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3c**) in CD_3CN (400 MHz) at 23 °C.

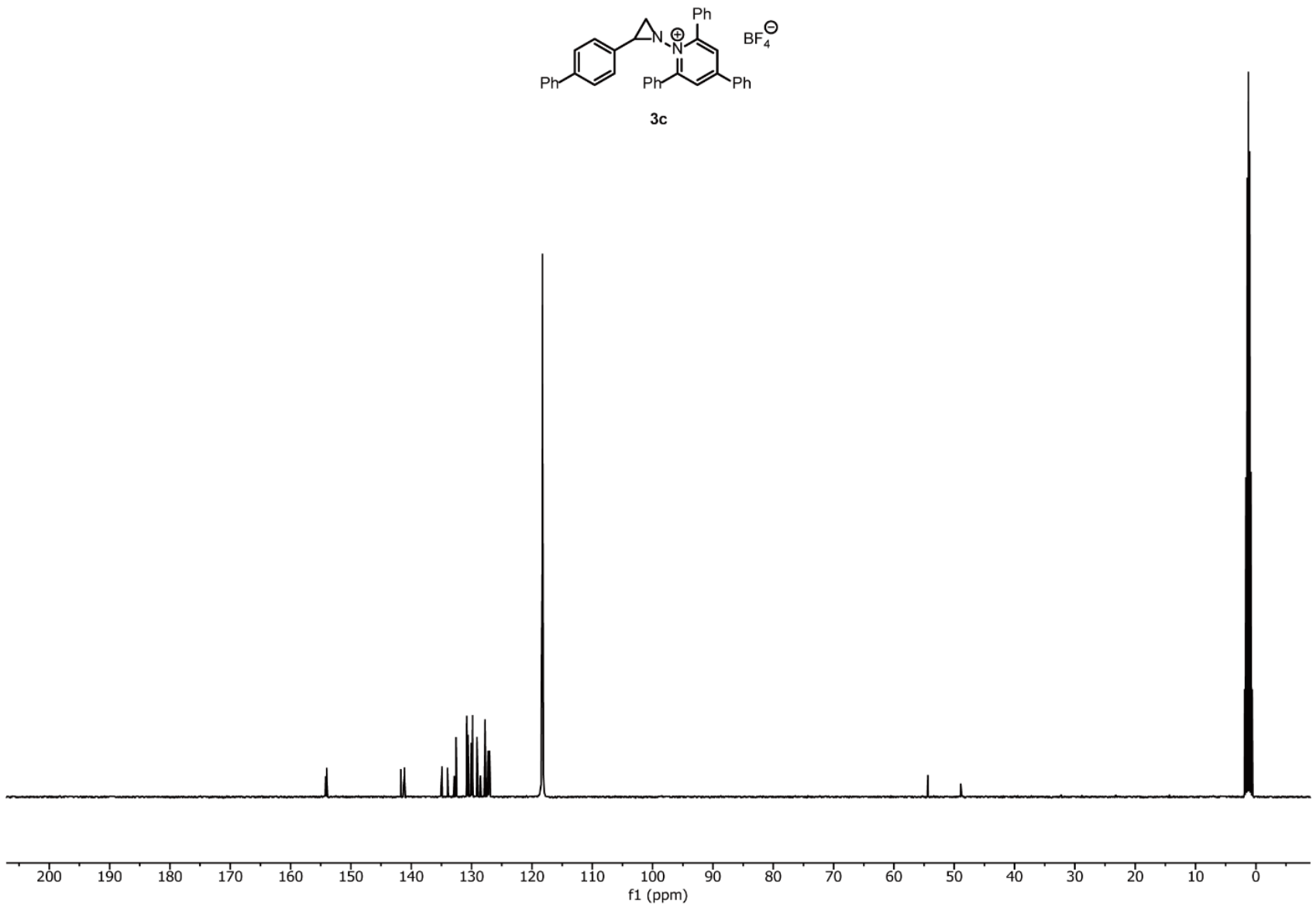


Figure S12. ^{13}C NMR spectrum of 1-(2-([1,1'-biphenyl]-4-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3c**) in CD_3CN (101 MHz) at 23 °C.

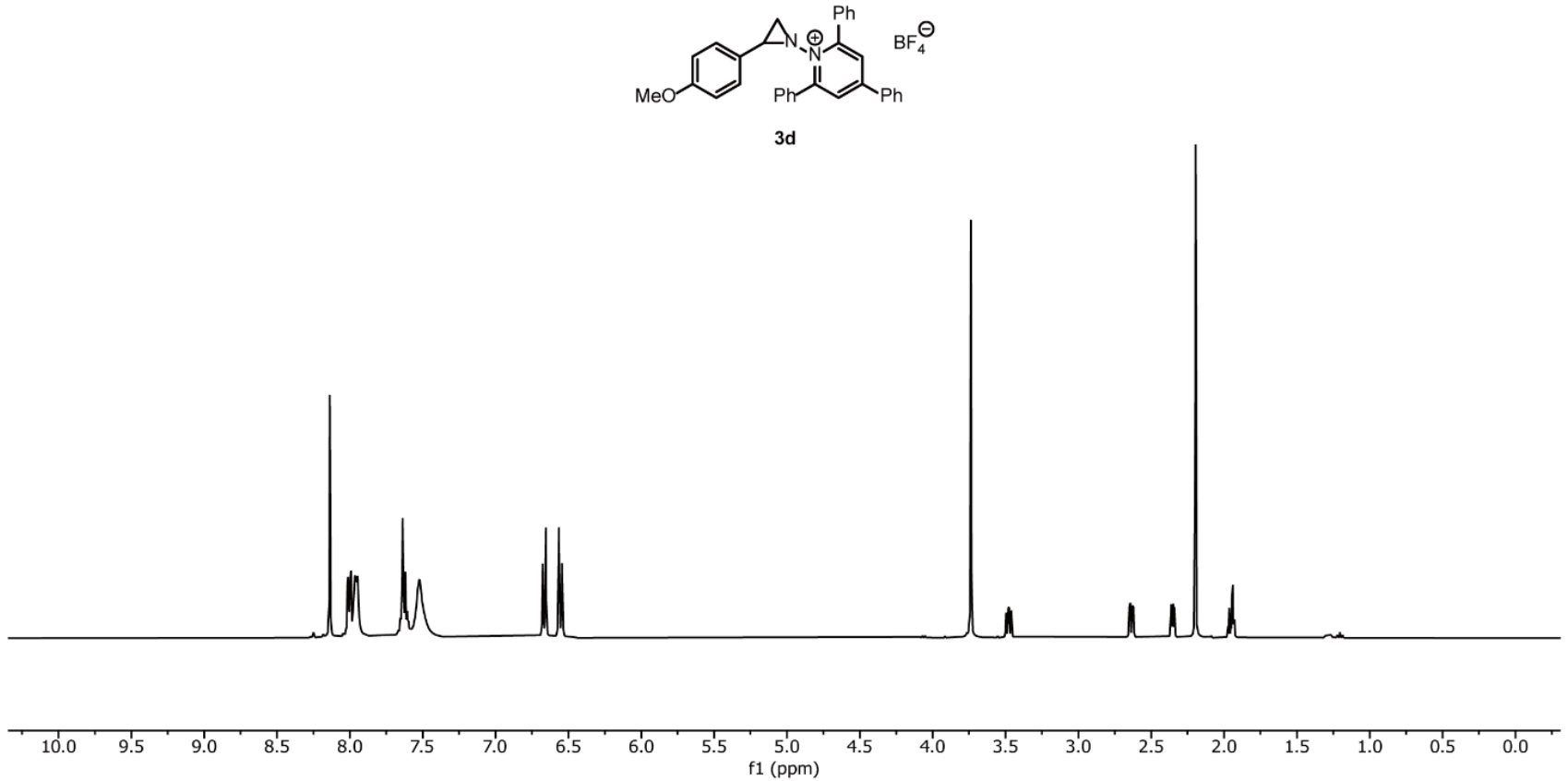


Figure S13. ^{1}H NMR spectrum of 1-(2-(4-methoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3d**) in CD_3CN (400 MHz) at 23 °C.

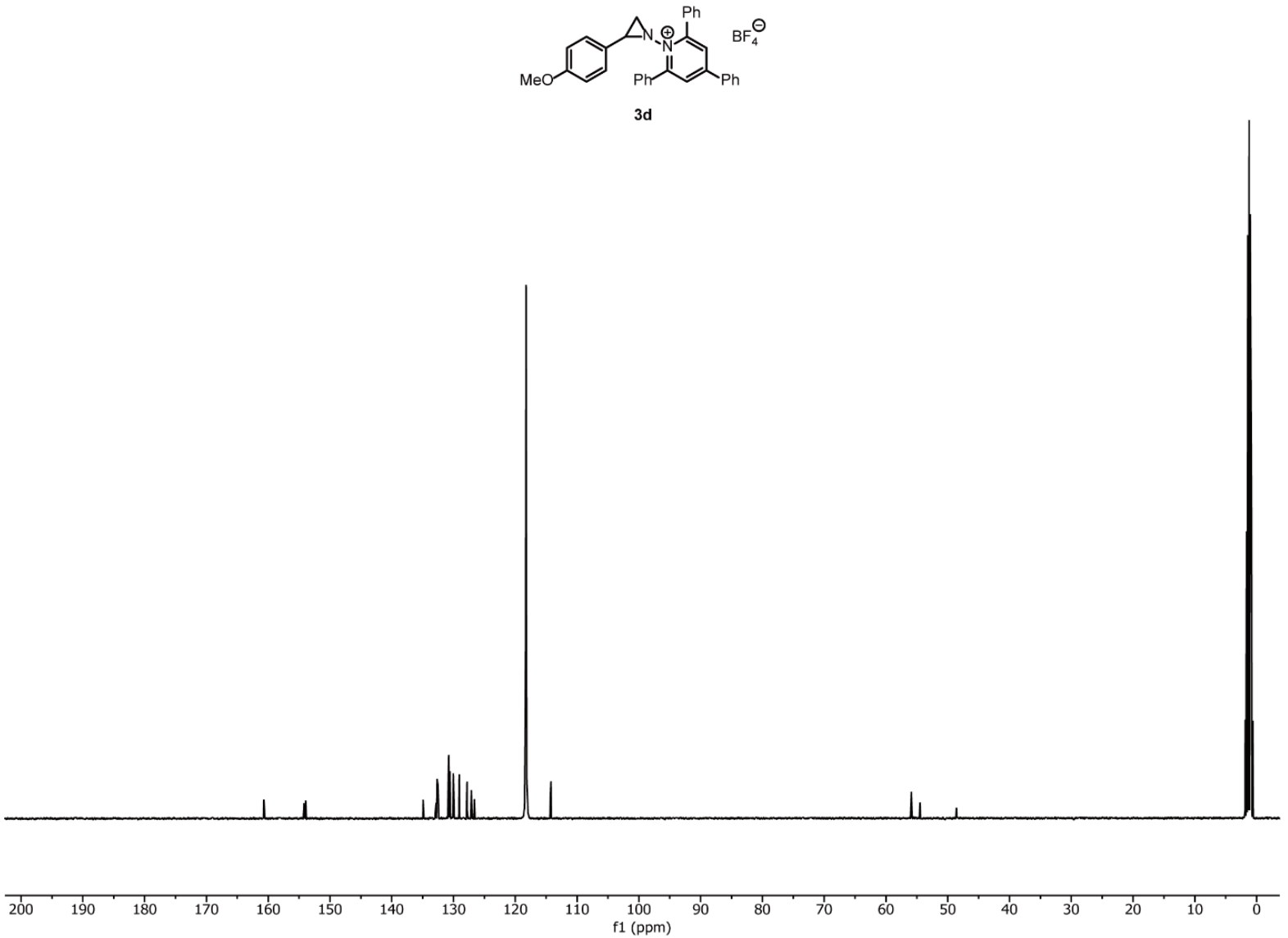


Figure S14. ^{13}C NMR spectrum of 1-(2-(4-methoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3d**) in CD_3CN (101 MHz) at 23 °C.

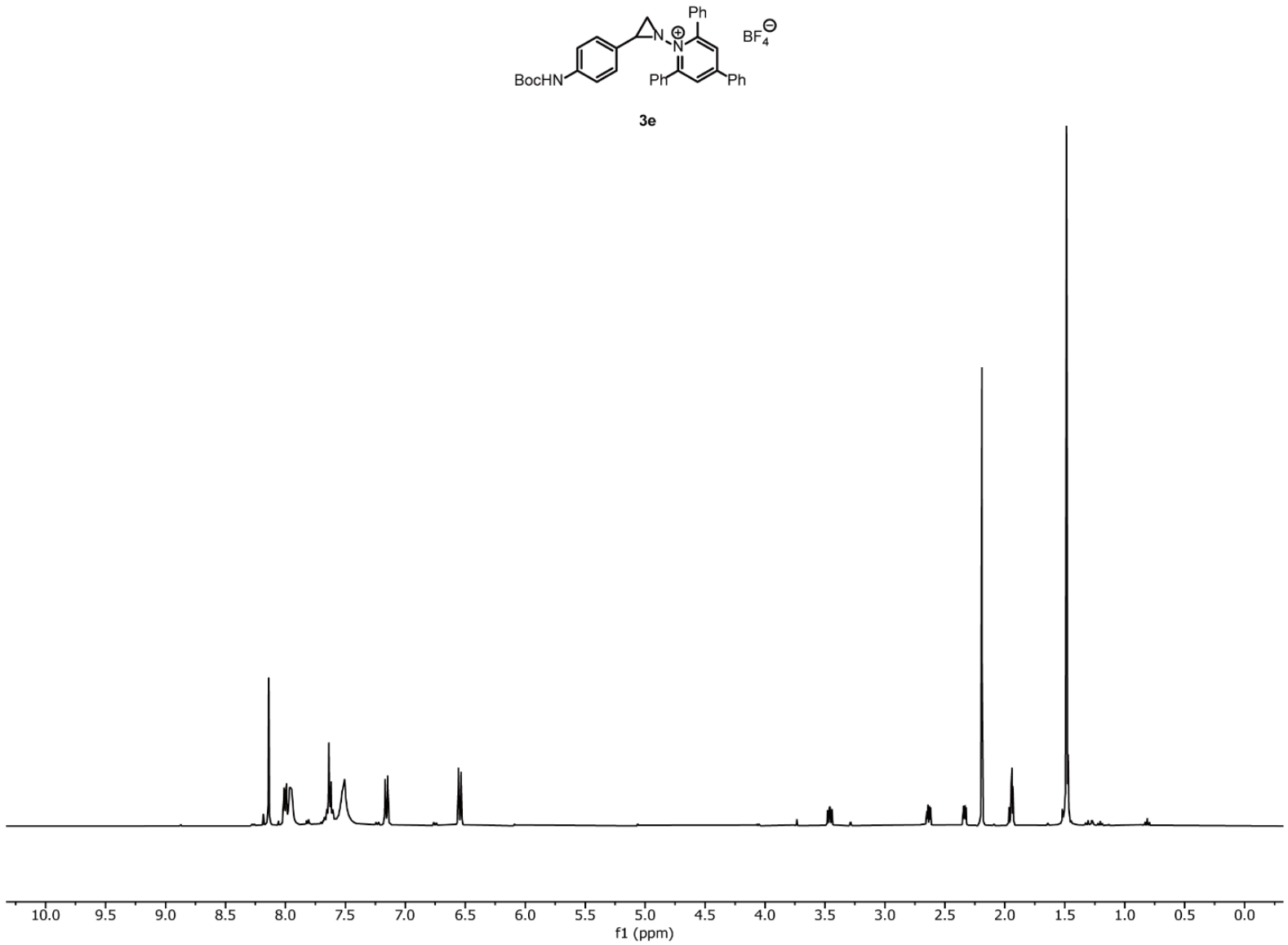


Figure S15. ^{1}H NMR spectrum of 1-(2-(4-((tert-butoxycarbonyl)amino)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3e**) in CD_3CN (400 MHz) at 23 °C.

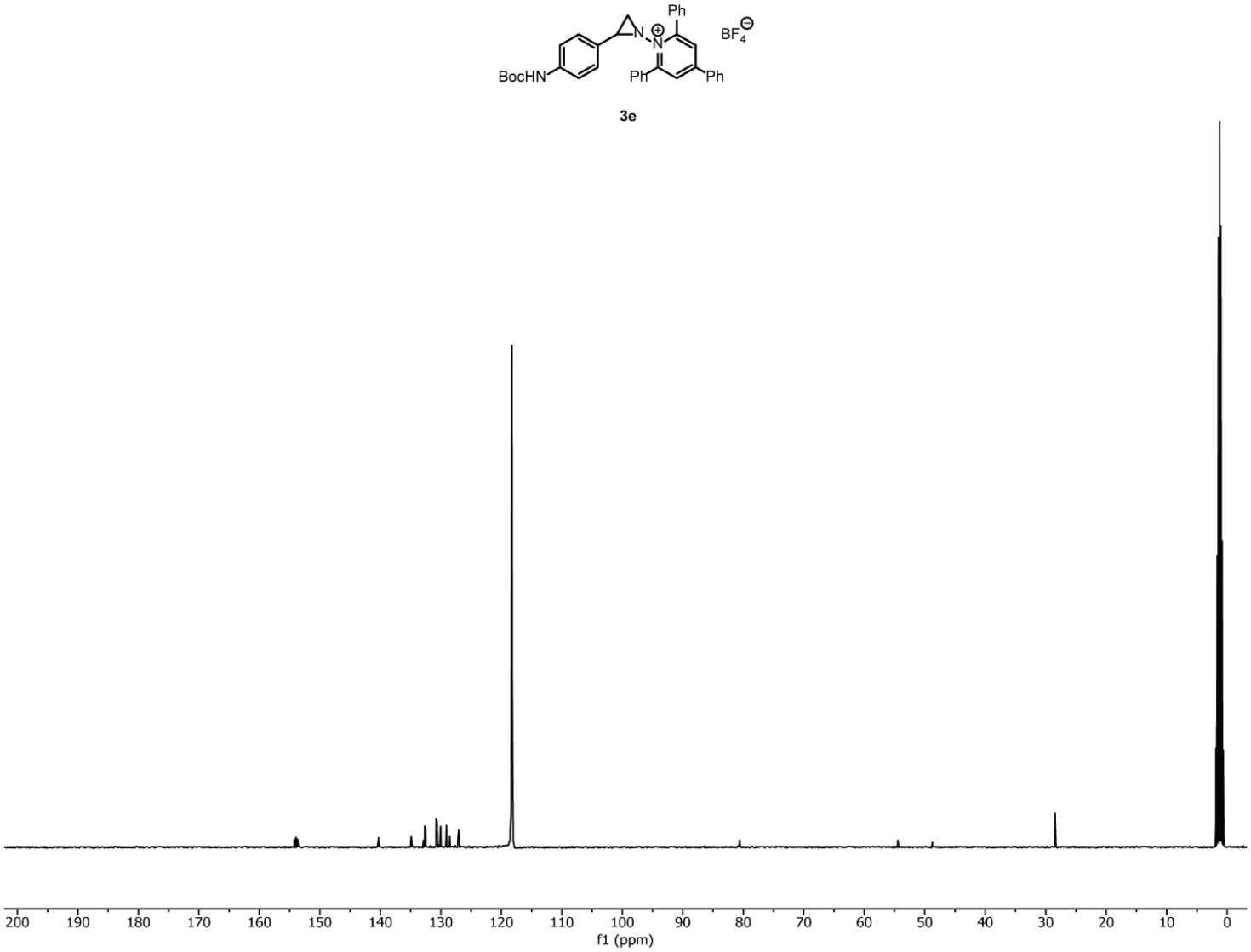


Figure S16. ^{13}C NMR spectrum of 1-(2-(4-((tert-butoxycarbonyl)amino)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3e**) in CD_3CN (101 MHz) at 23 °C.

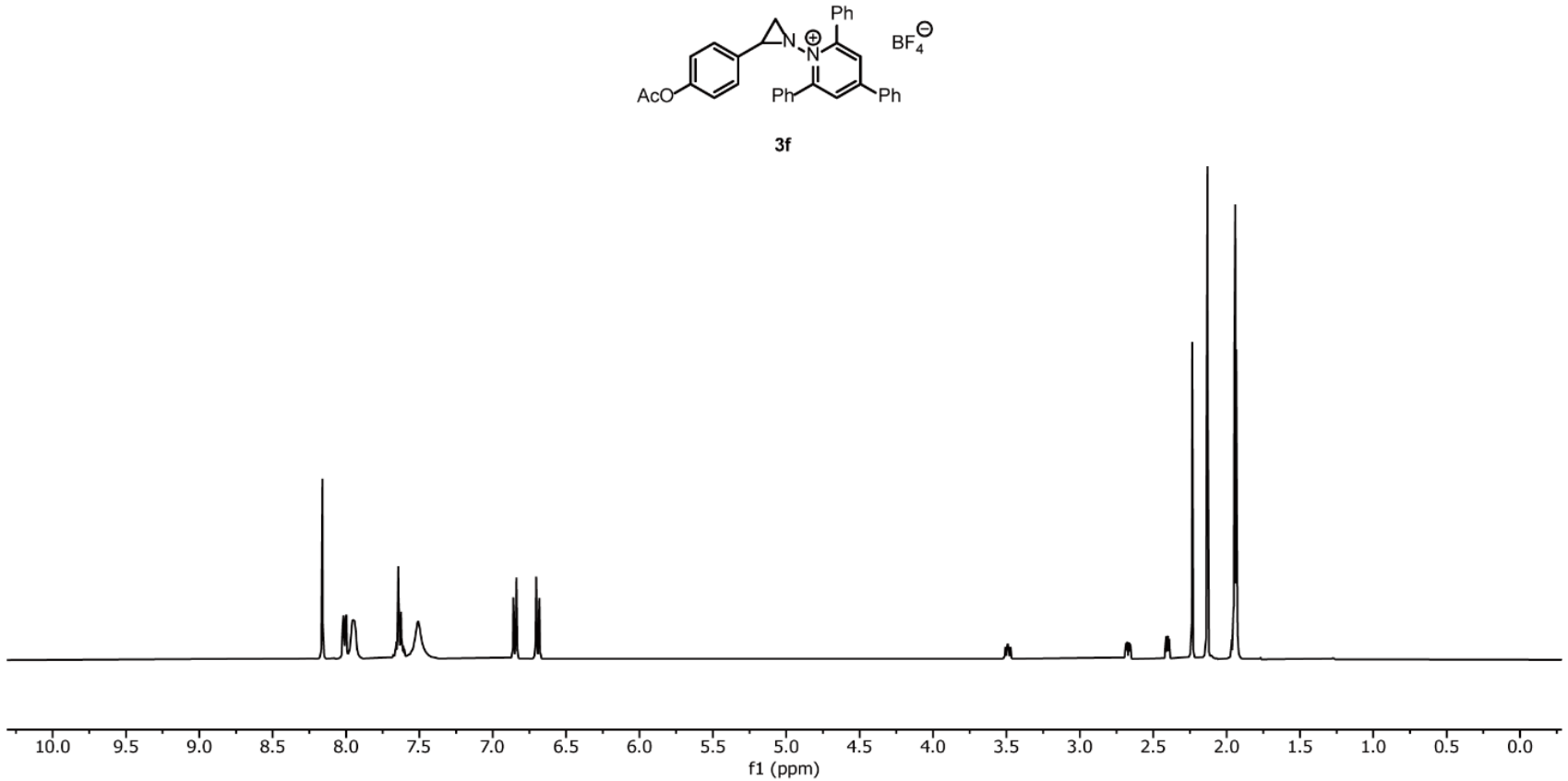


Figure S17. ^{1}H NMR spectrum of 1-(2-(4-acetoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3f**) in CD_3CN (400 MHz) at 23 °C.

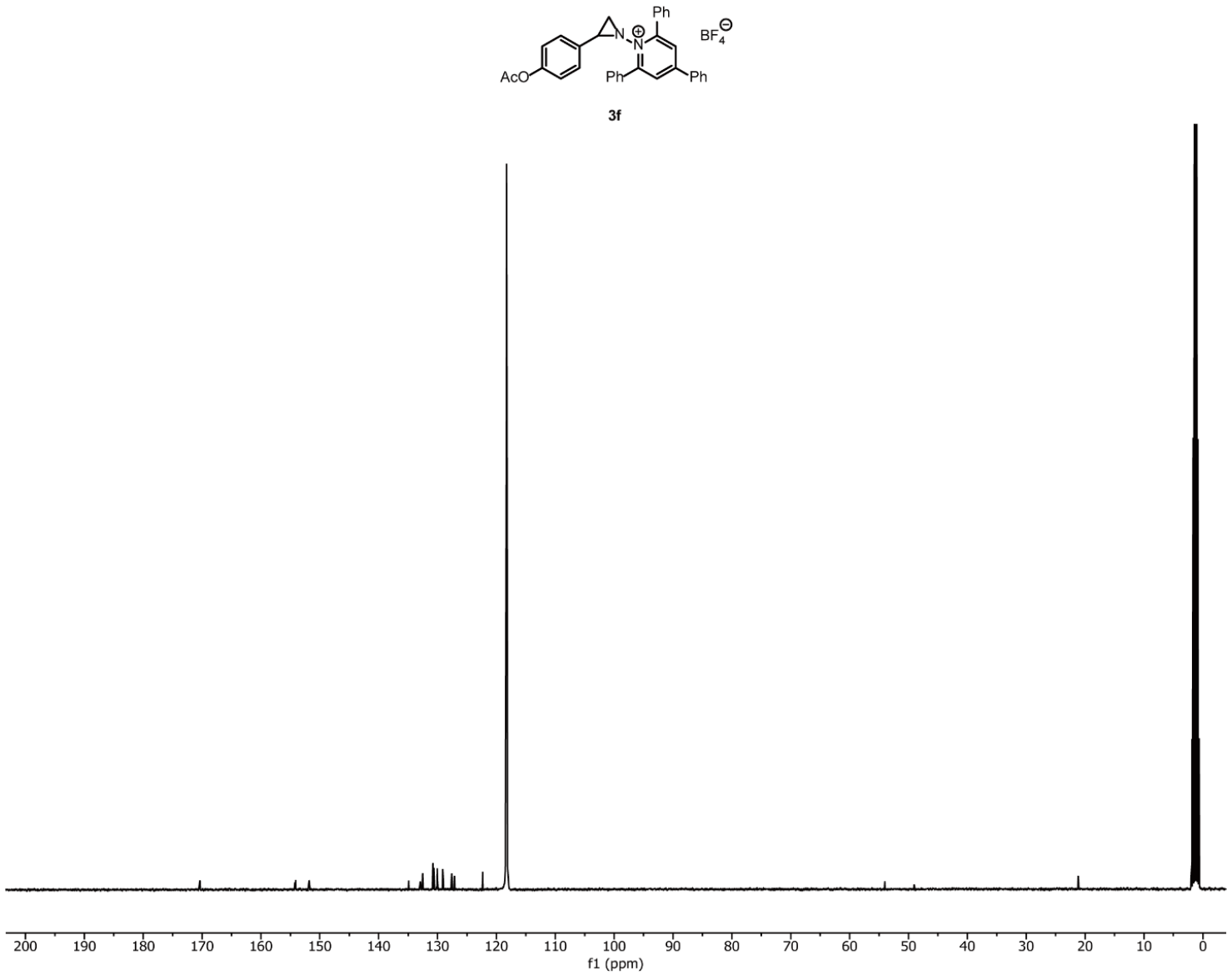


Figure S18. ^{13}C NMR spectrum of 1-(2-(4-acetoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3f**) in CD_3CN (101 MHz) at 23 °C.

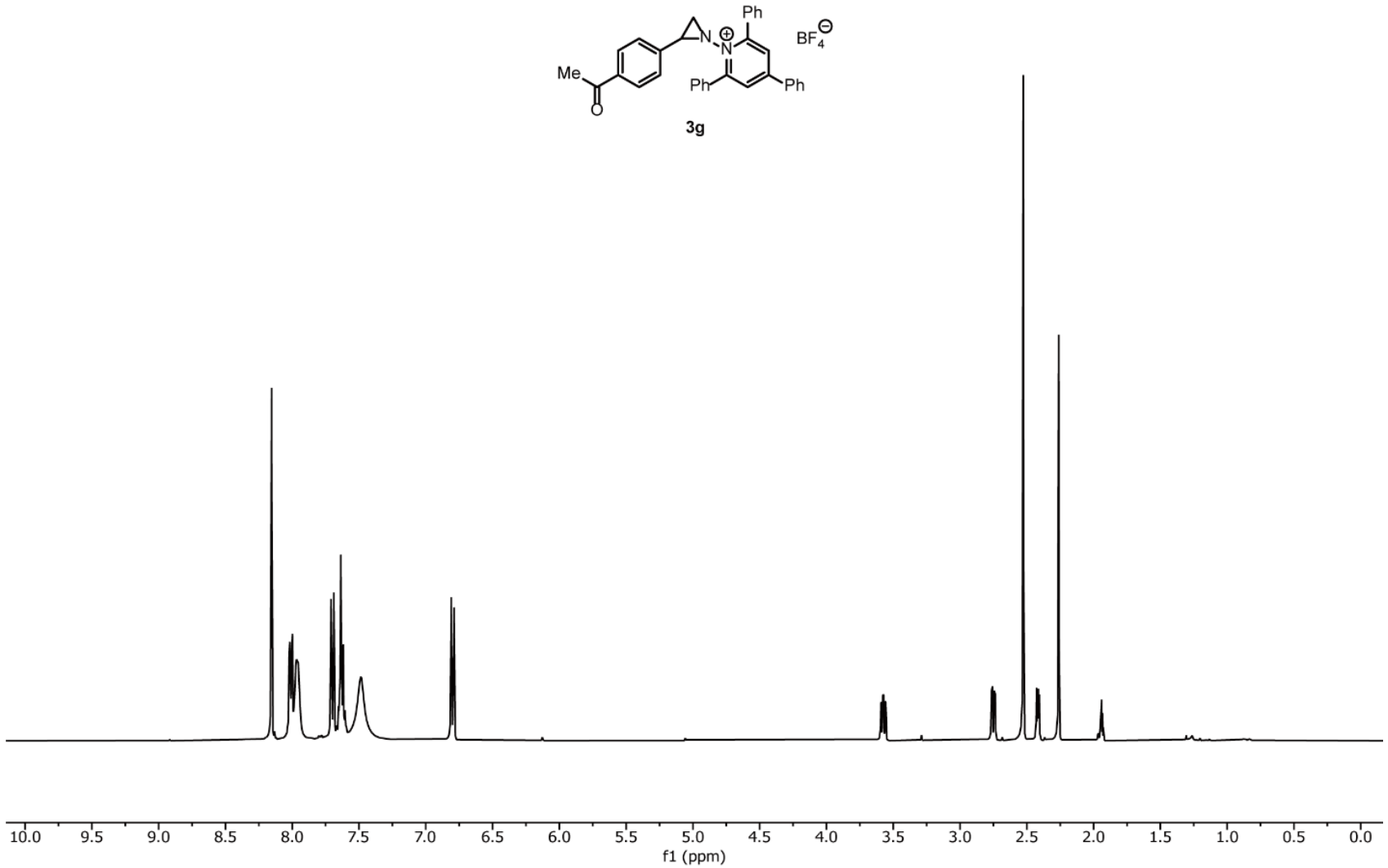


Figure S19. ^{1}H NMR spectrum of 1-(2-(4-acetylphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3g**) in CD_3CN (400 MHz) at 23 °C.

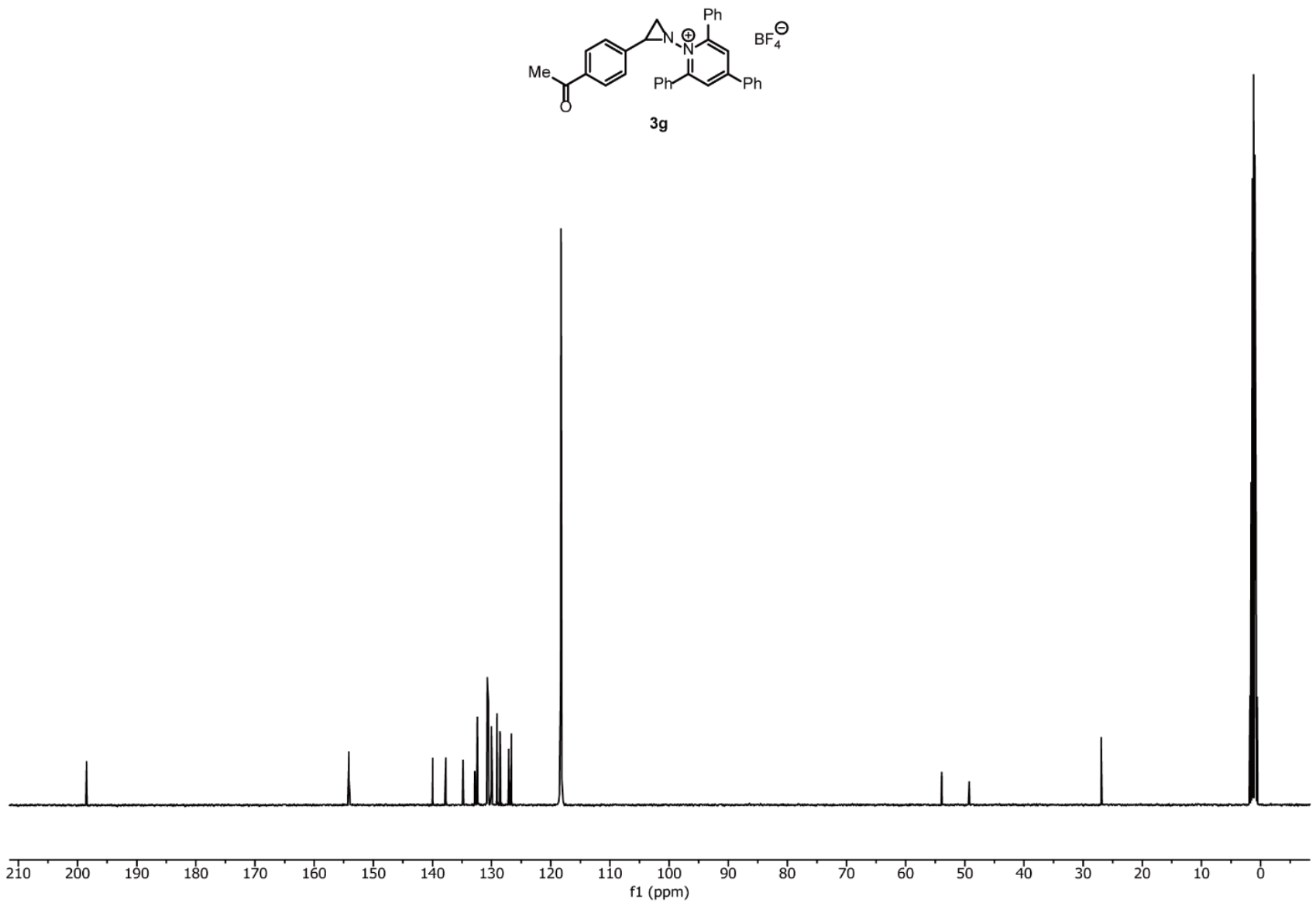


Figure S20. ^{13}C NMR spectrum of 1-(2-(4-acetylphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3g**) in CD_3CN (101 MHz) at 23 °C.

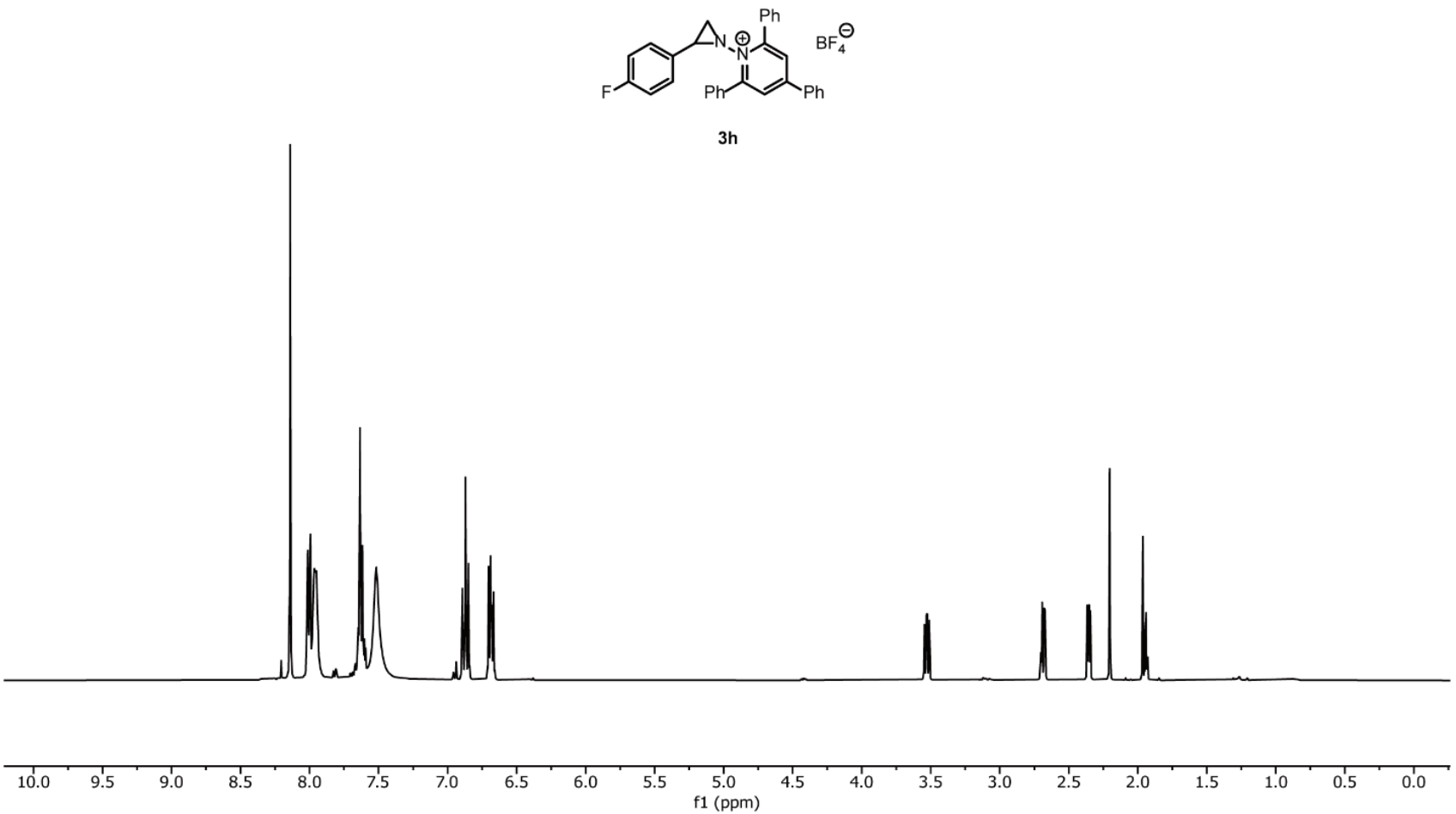


Figure S21. ^{1}H NMR spectrum of 1-(2-(4-fluorophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3h**) in CD_3CN (400 MHz) at 23 °C.

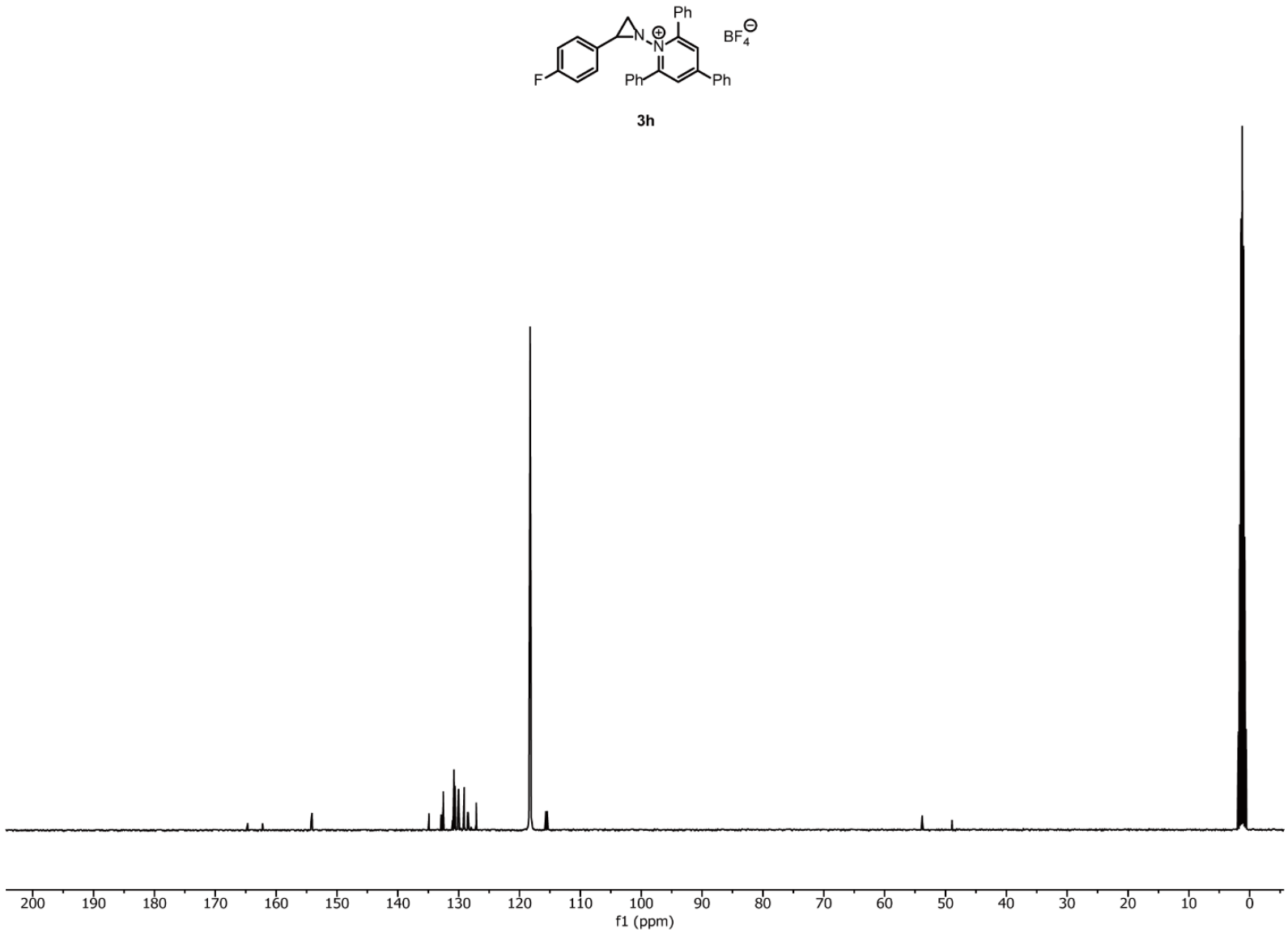


Figure S22. ^{13}C NMR spectrum of 1-(2-(4-fluorophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3h**) in CD_3CN (101 MHz) at 23 °C.

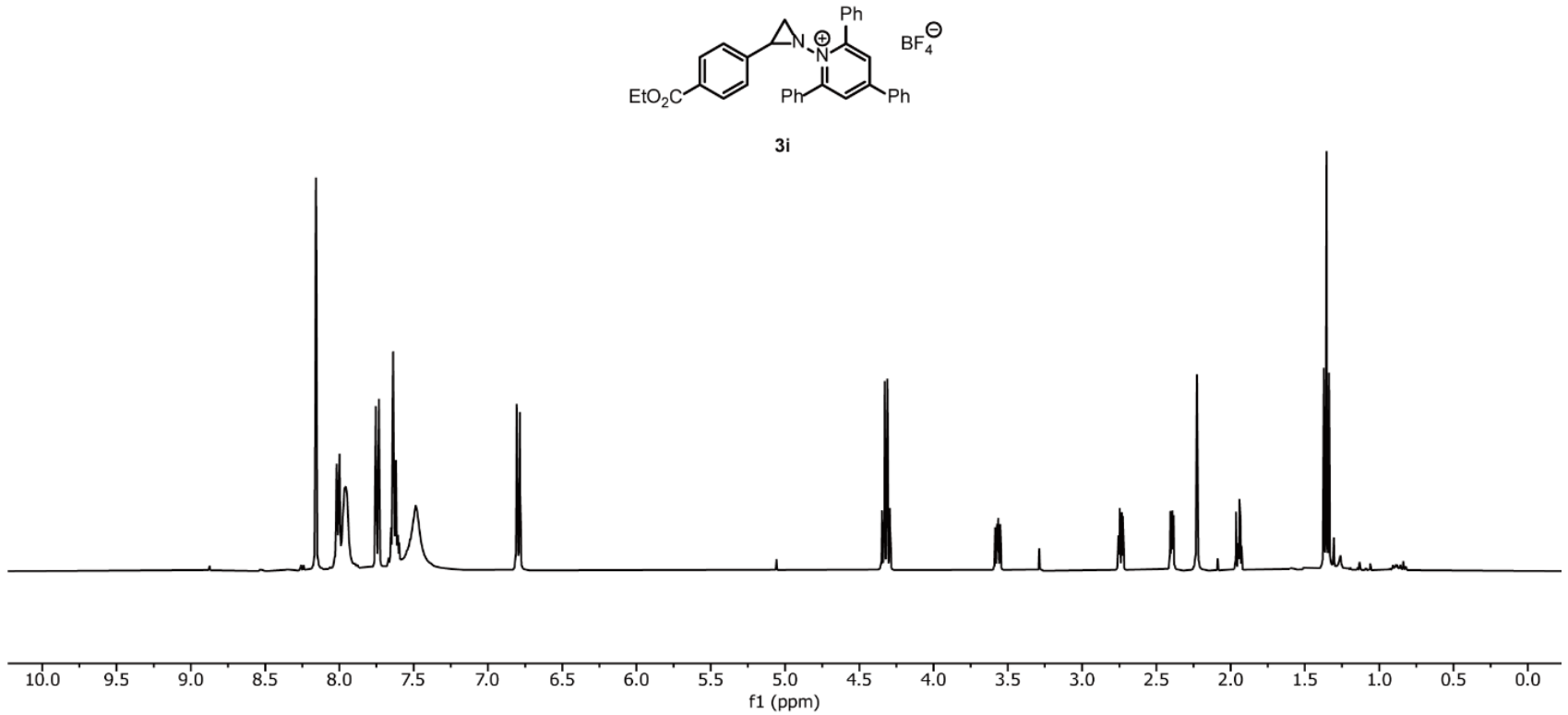


Figure S23. ^{1}H NMR spectrum of 1-(2-(4-(ethoxycarbonyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3i**) in CD_3CN (400 MHz) at 23 °C.

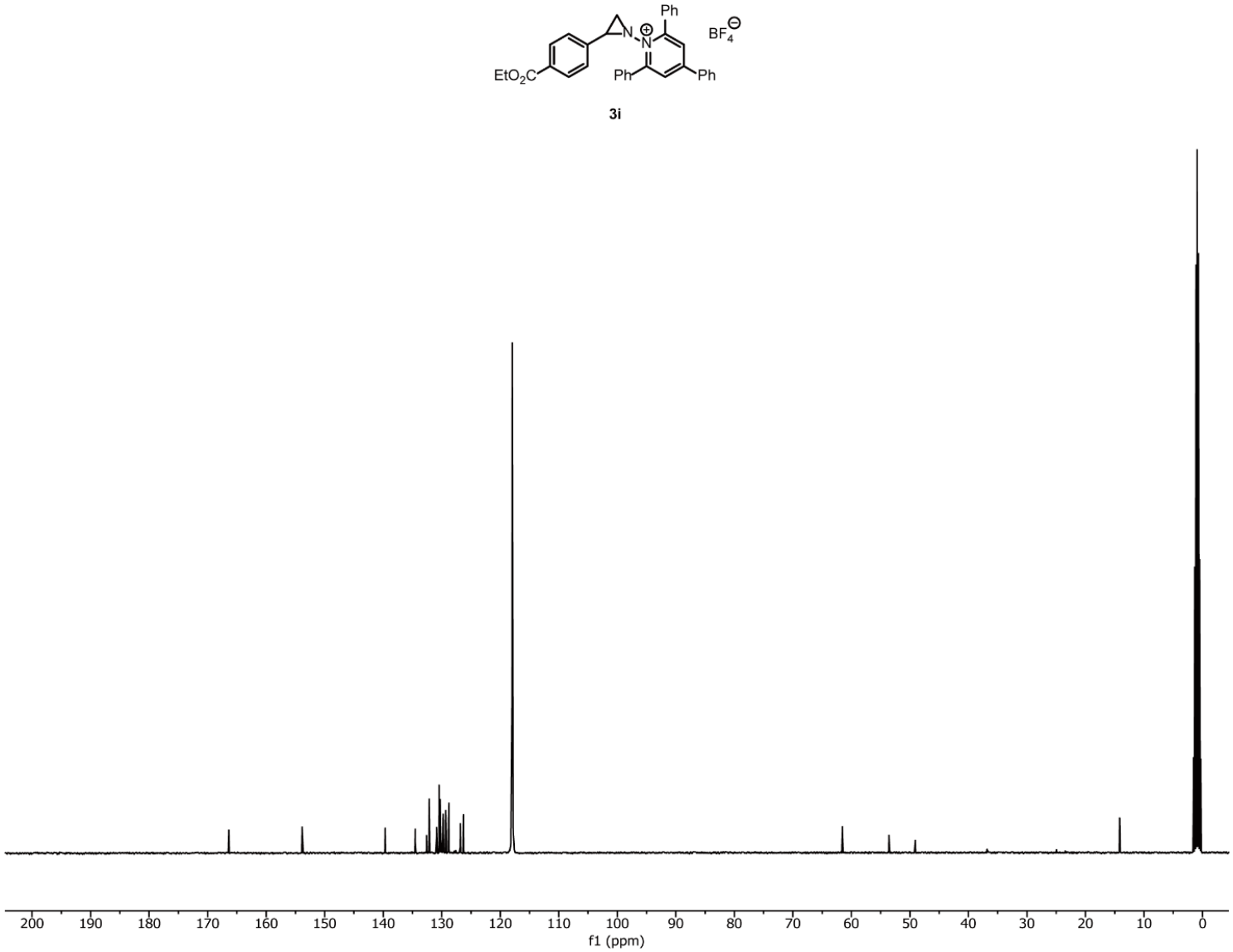


Figure S24. ^{13}C NMR spectrum of 1-(2-(4-(ethoxycarbonyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3i**) in CD_3CN (101 MHz) at 23 °C.

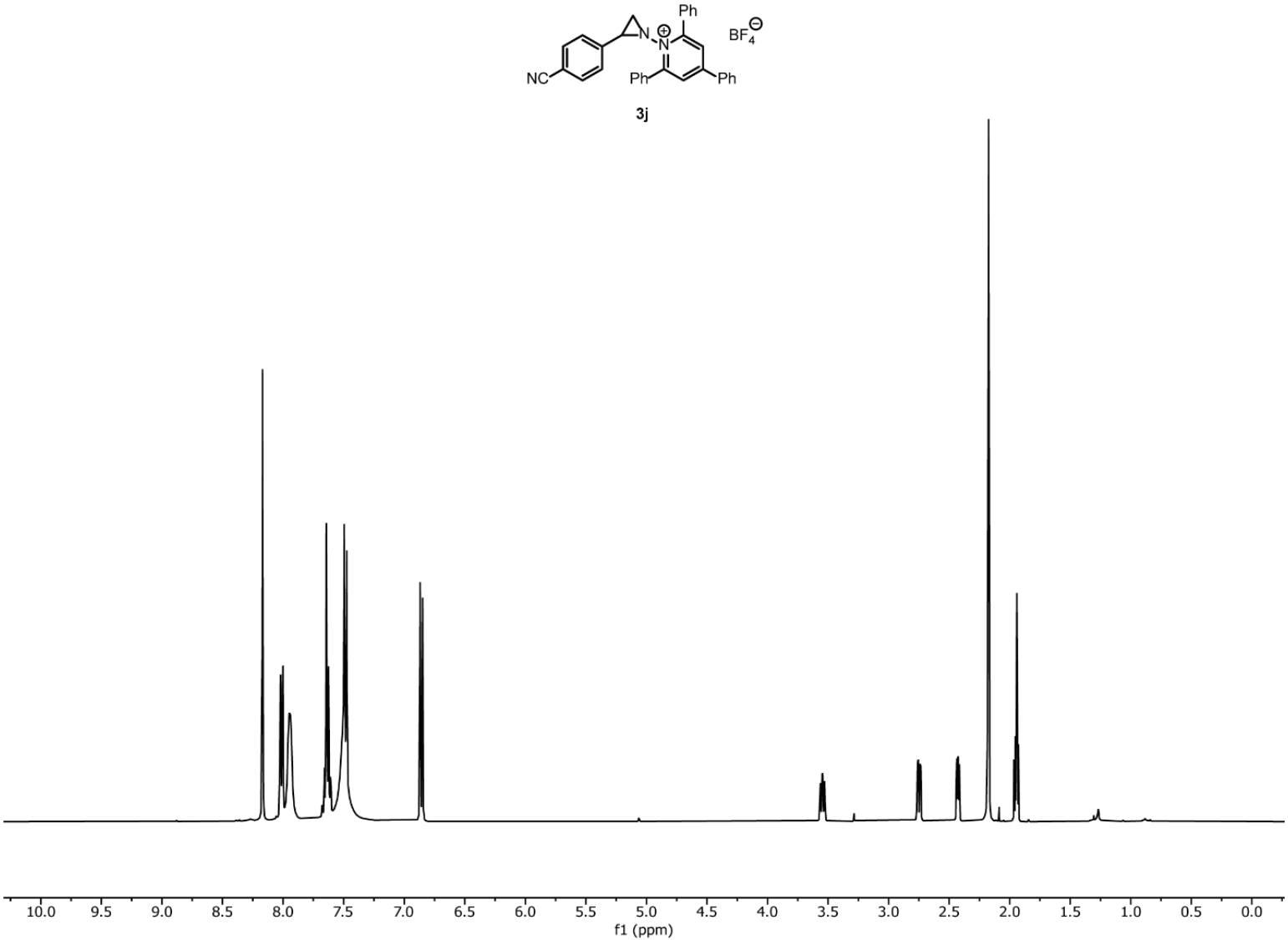


Figure S25. ^{1}H NMR spectrum of 1-(2-(4-cyanophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3j**) in CD_3CN (400 MHz) at 23 °C.

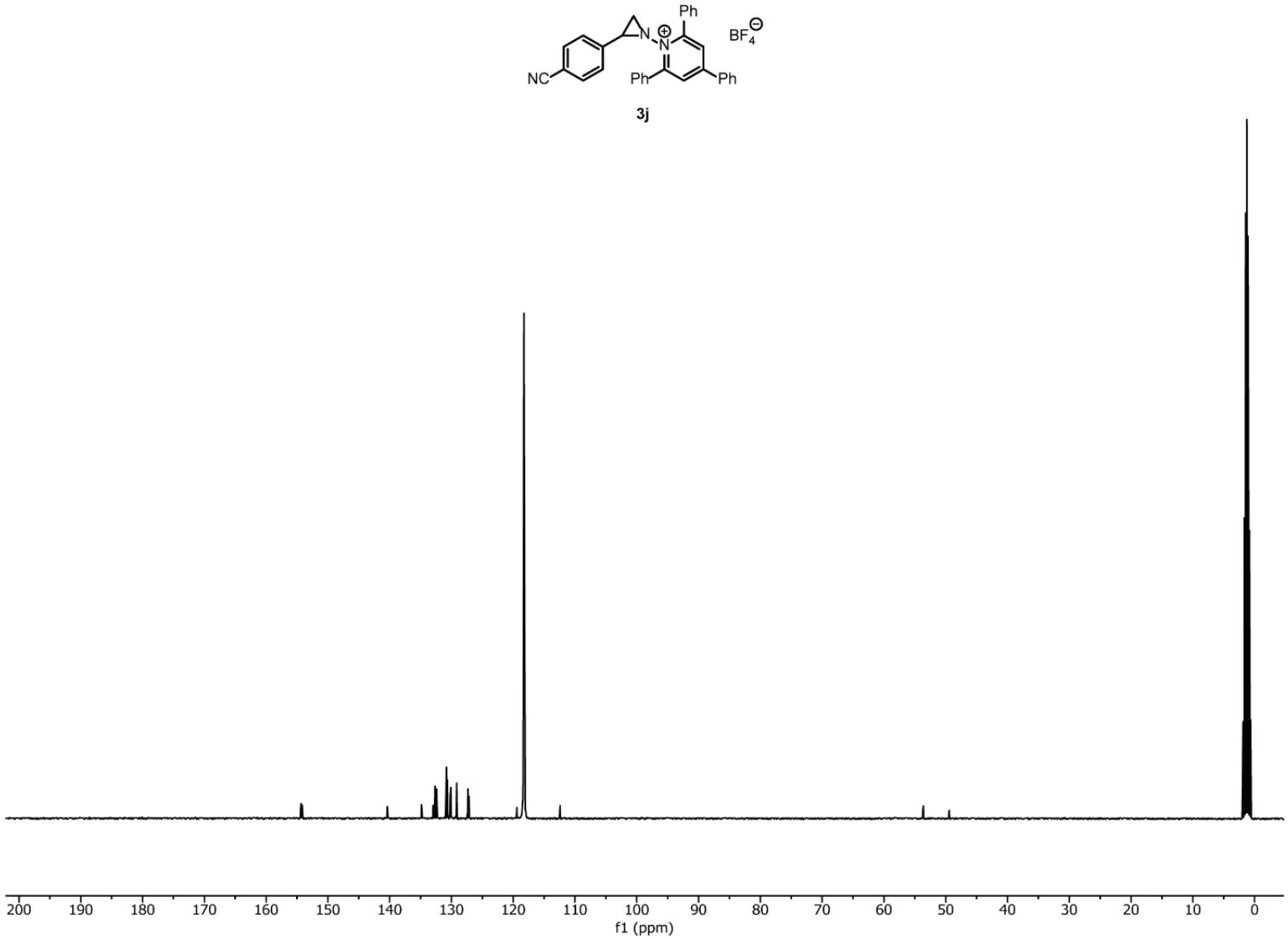


Figure S26. ^{13}C NMR spectrum of 1-(2-(4-cyanophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3j**) in CD_3CN (101 MHz) at 23 °C.

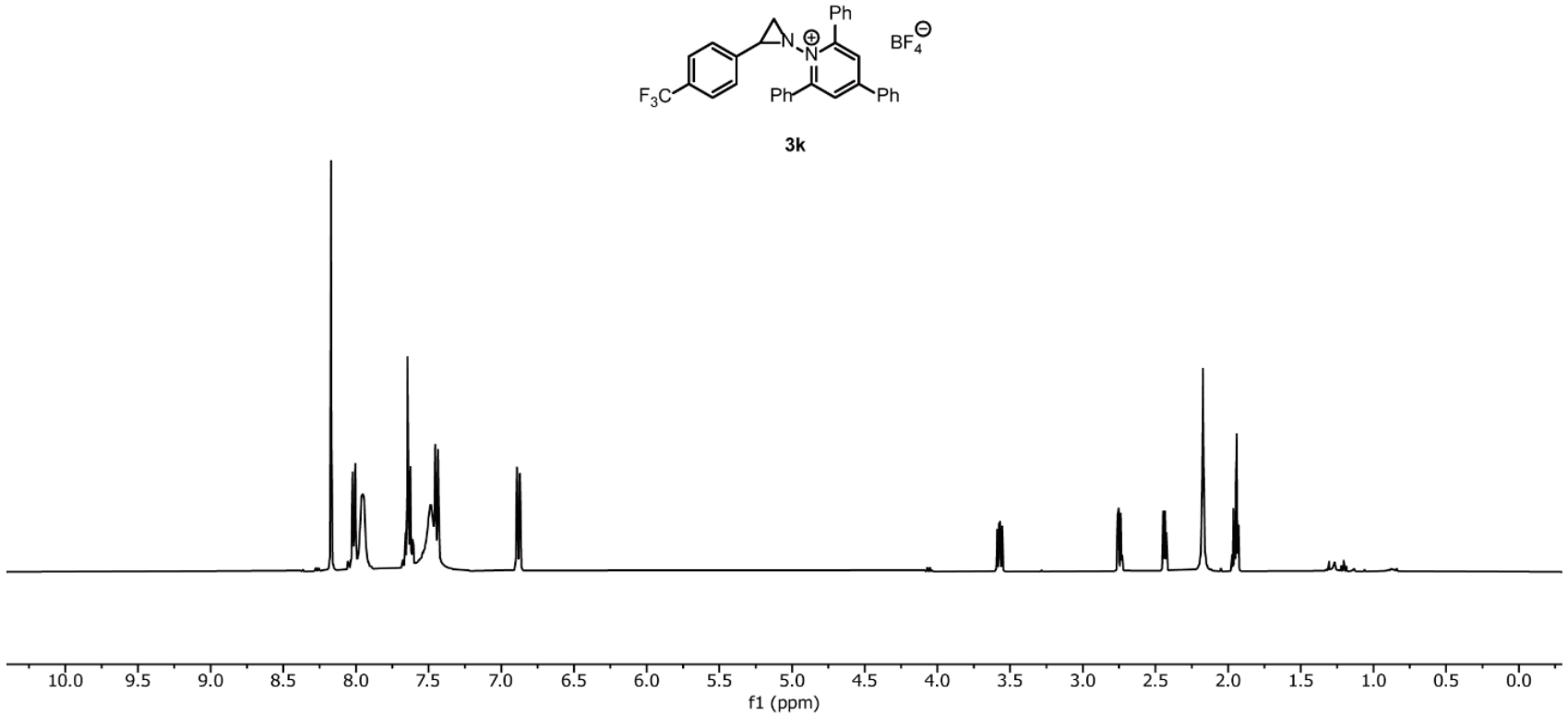


Figure S27. ^{1}H NMR spectrum of 2,4,6-triphenyl-1-(2-(4-(trifluoromethyl)phenyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3k**) in CD_3CN (400 MHz) at 23 °C.

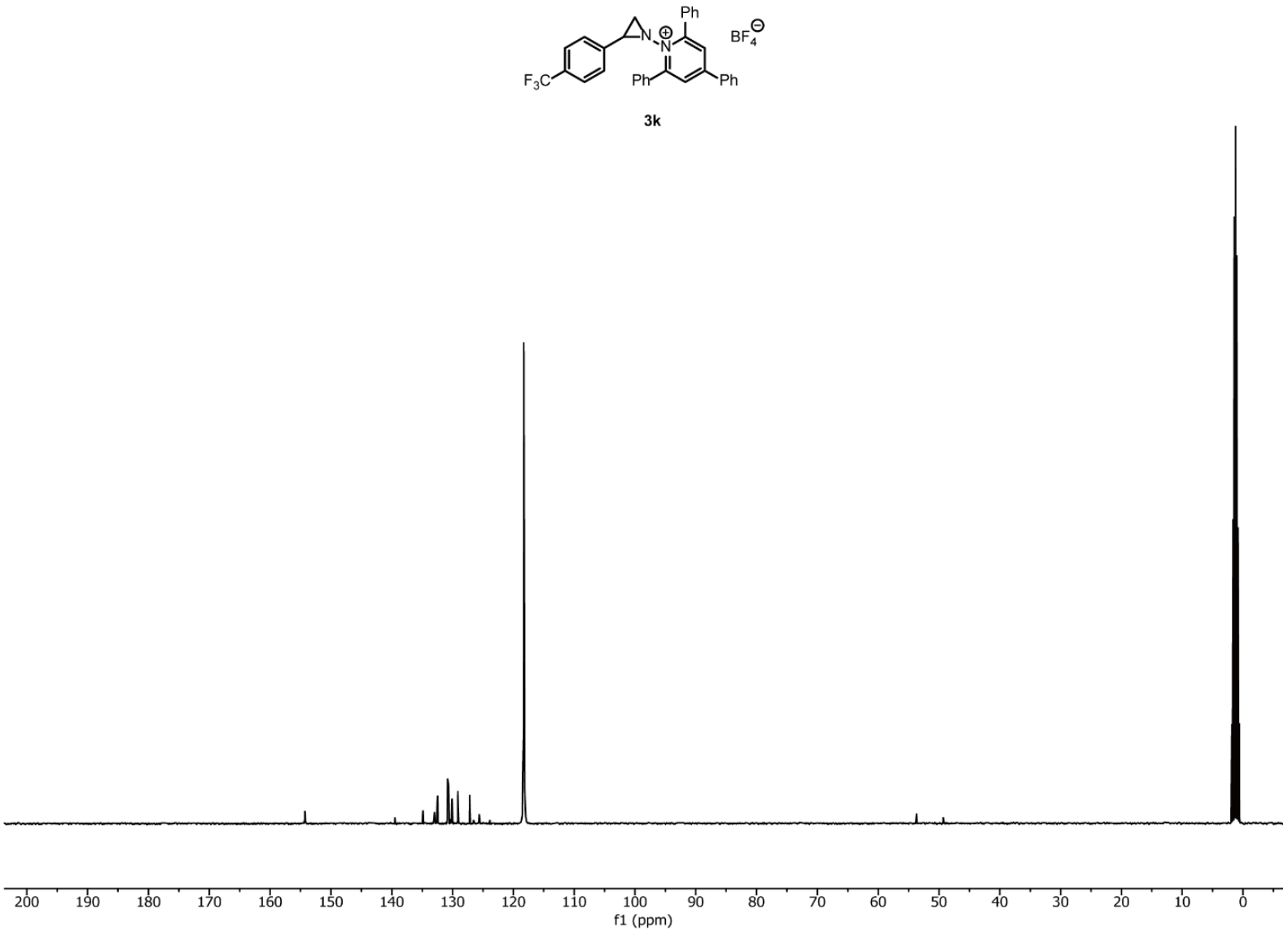


Figure S28. ^{13}C NMR spectrum of 2,4,6-triphenyl-1-(2-(4-(trifluoromethyl)phenyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3k**) in CD_3CN (101 MHz) at 23 °C.

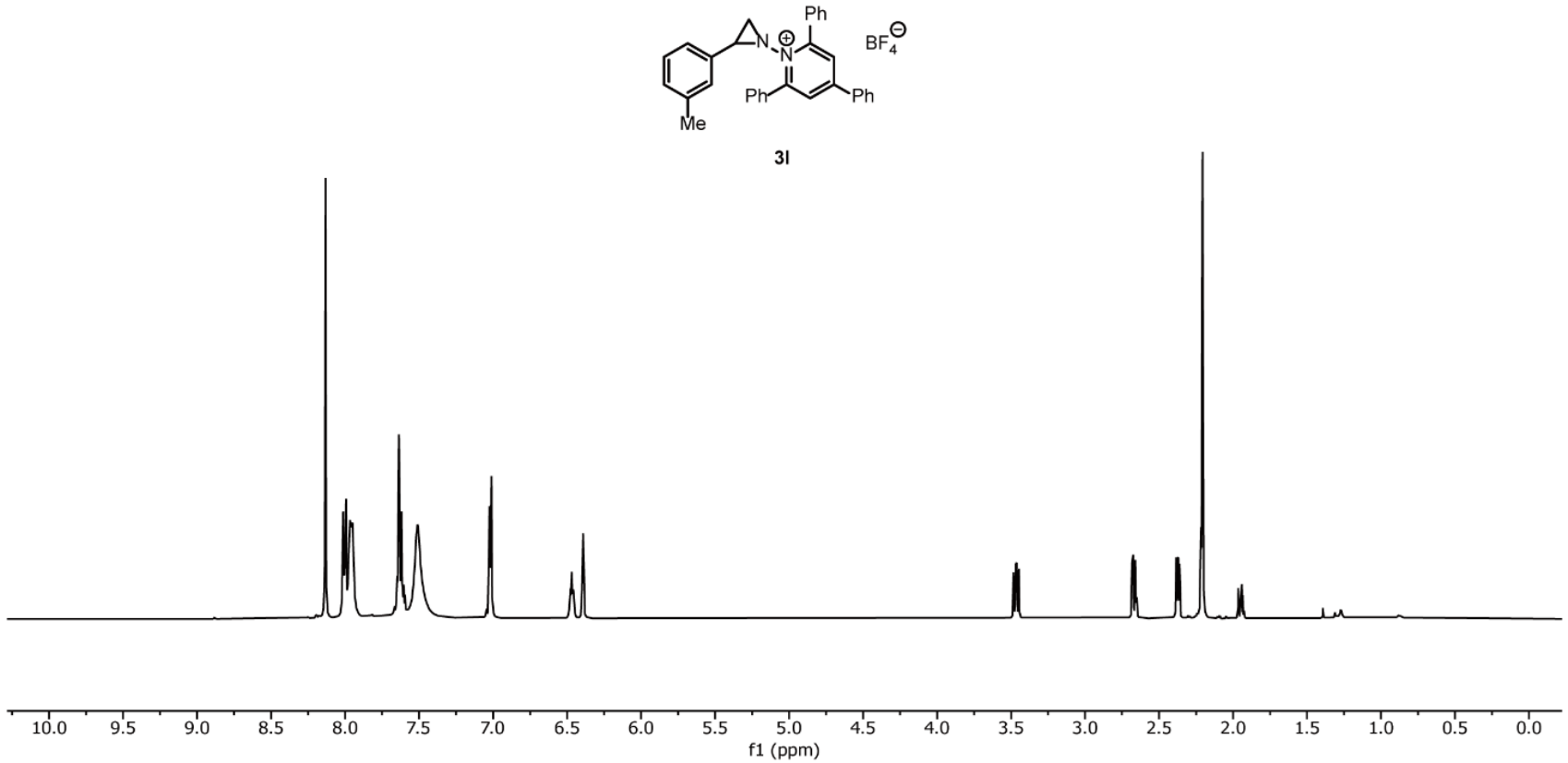


Figure S29. ^{1}H NMR spectrum of 2,4,6-triphenyl-1-(2-(*m*-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3l**) in CD_3CN (400 MHz) at 23 °C.

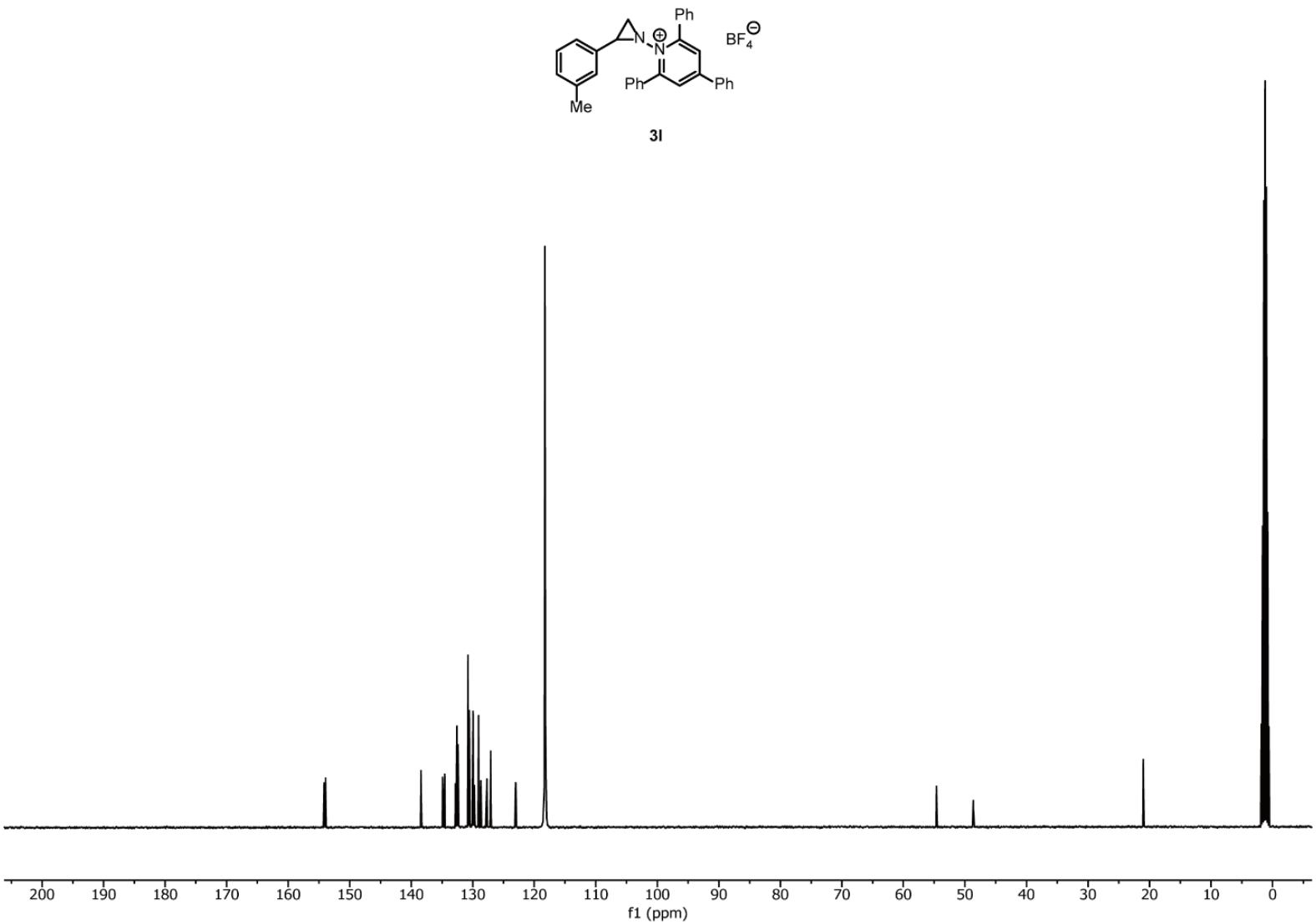


Figure S30. ^{13}C NMR spectrum of 2,4,6-triphenyl-1-(2-(*m*-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3l**) in CD_3CN (101 MHz) at 23 °C.

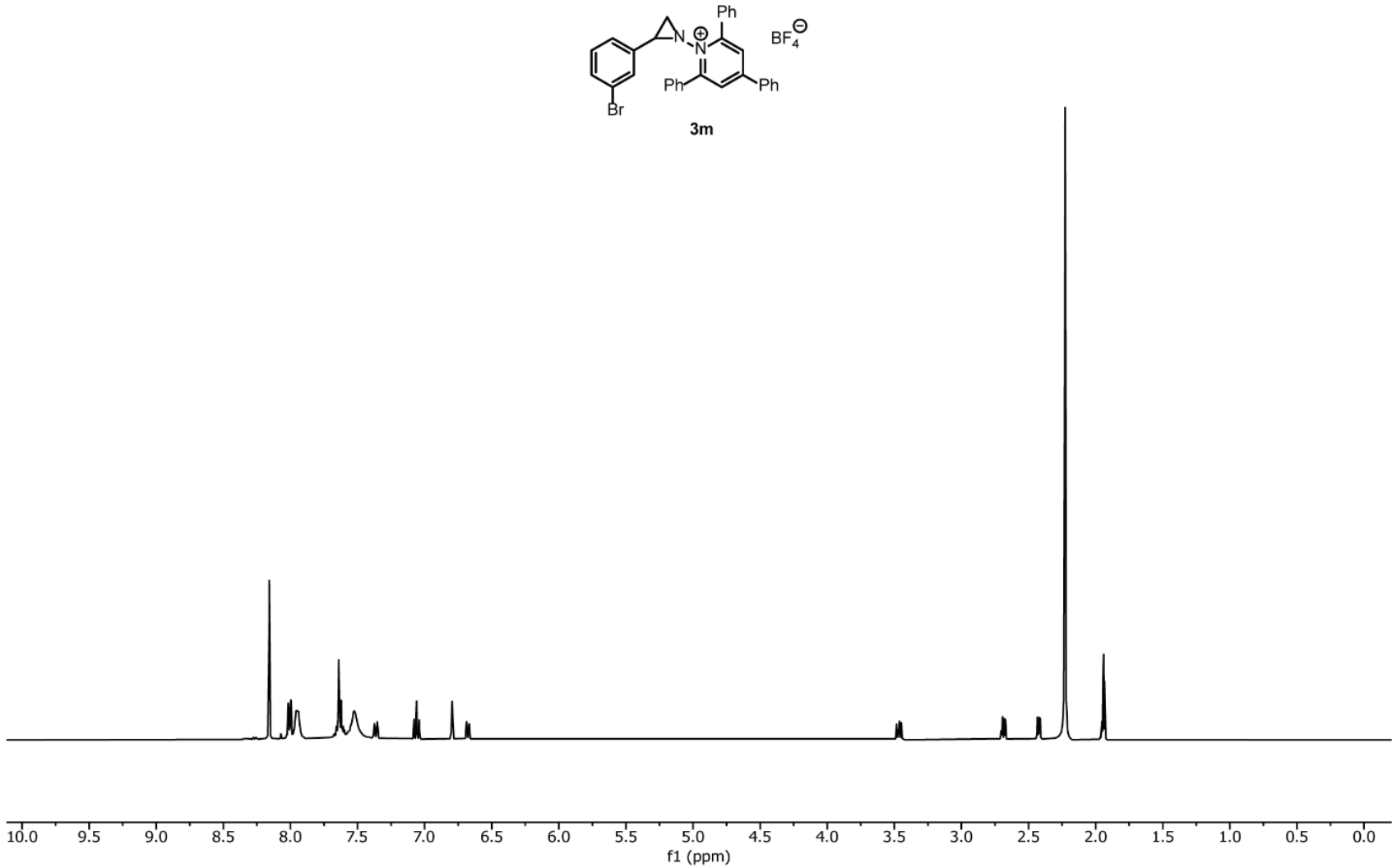


Figure S31. ^{1}H NMR spectrum of 1-(2-(3-bromophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3m**) in CD_3CN (400 MHz) at 23 °C.

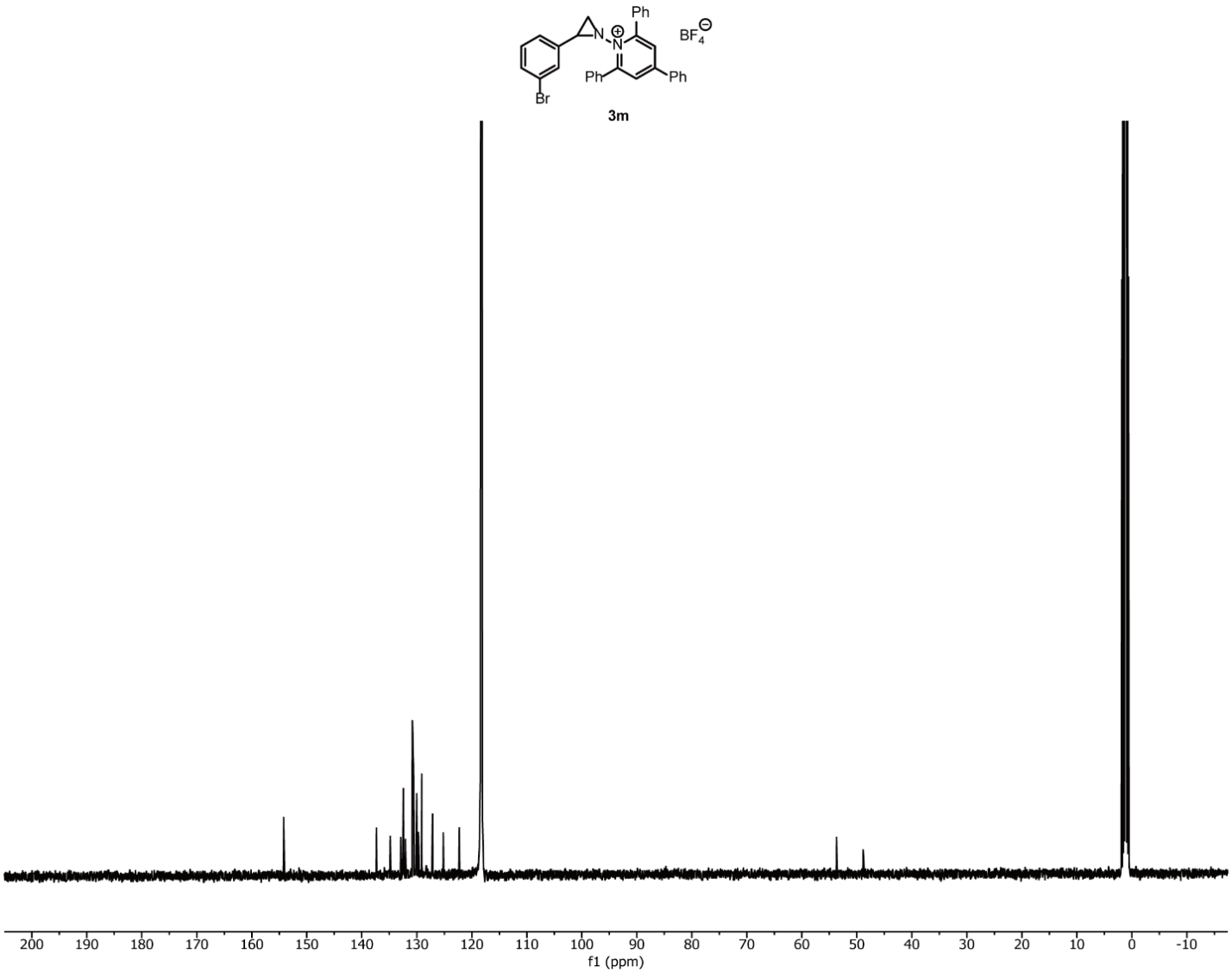


Figure S32. ^{13}C NMR spectrum of 1-(2-(3-bromophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3m**) in CD_3CN (101 MHz) at 23 °C.

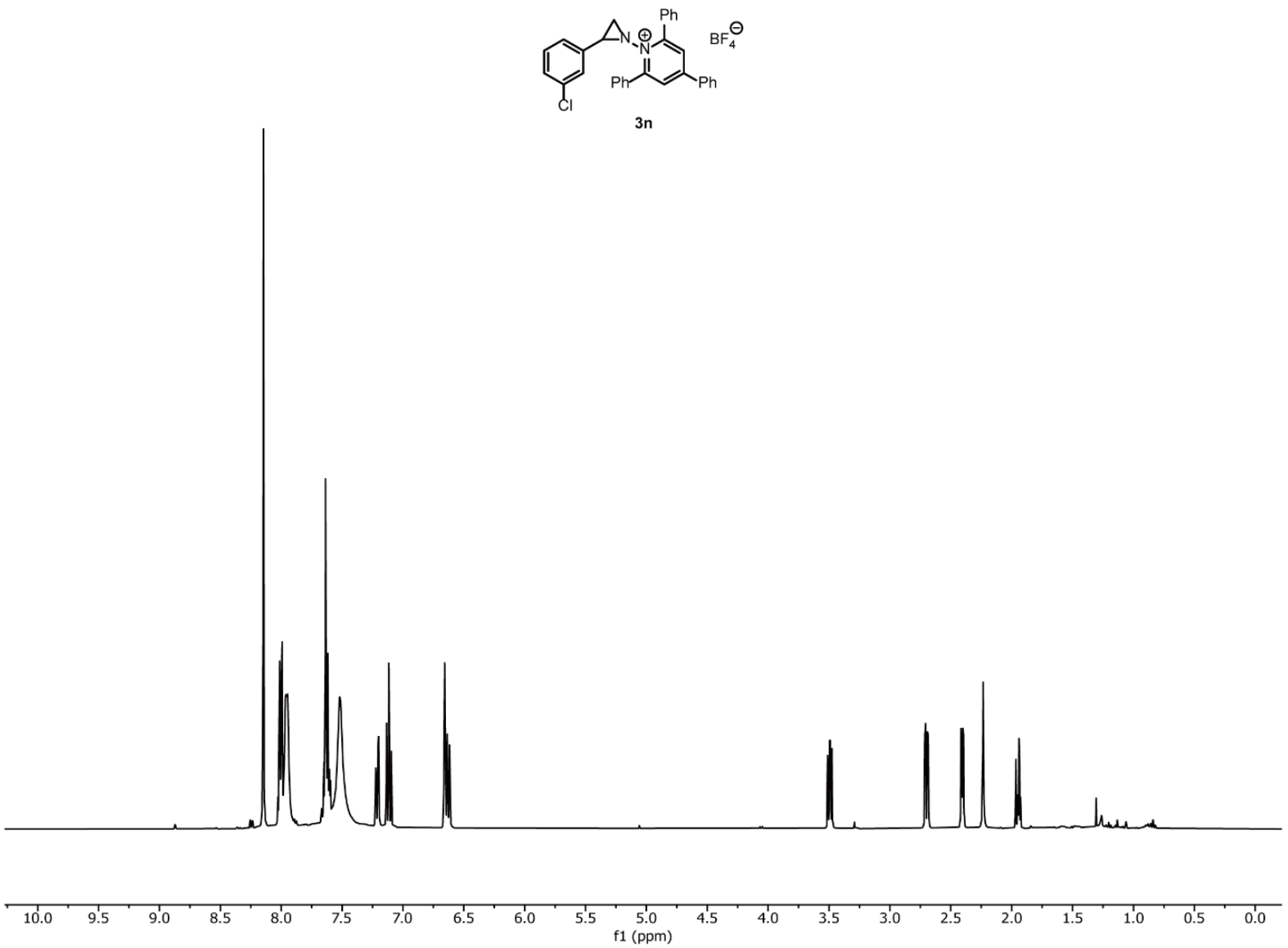


Figure S33. ^{1}H NMR spectrum of 1-(2-(3-chlorophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3n**) in CD_3CN (400 MHz) at 23 °C.

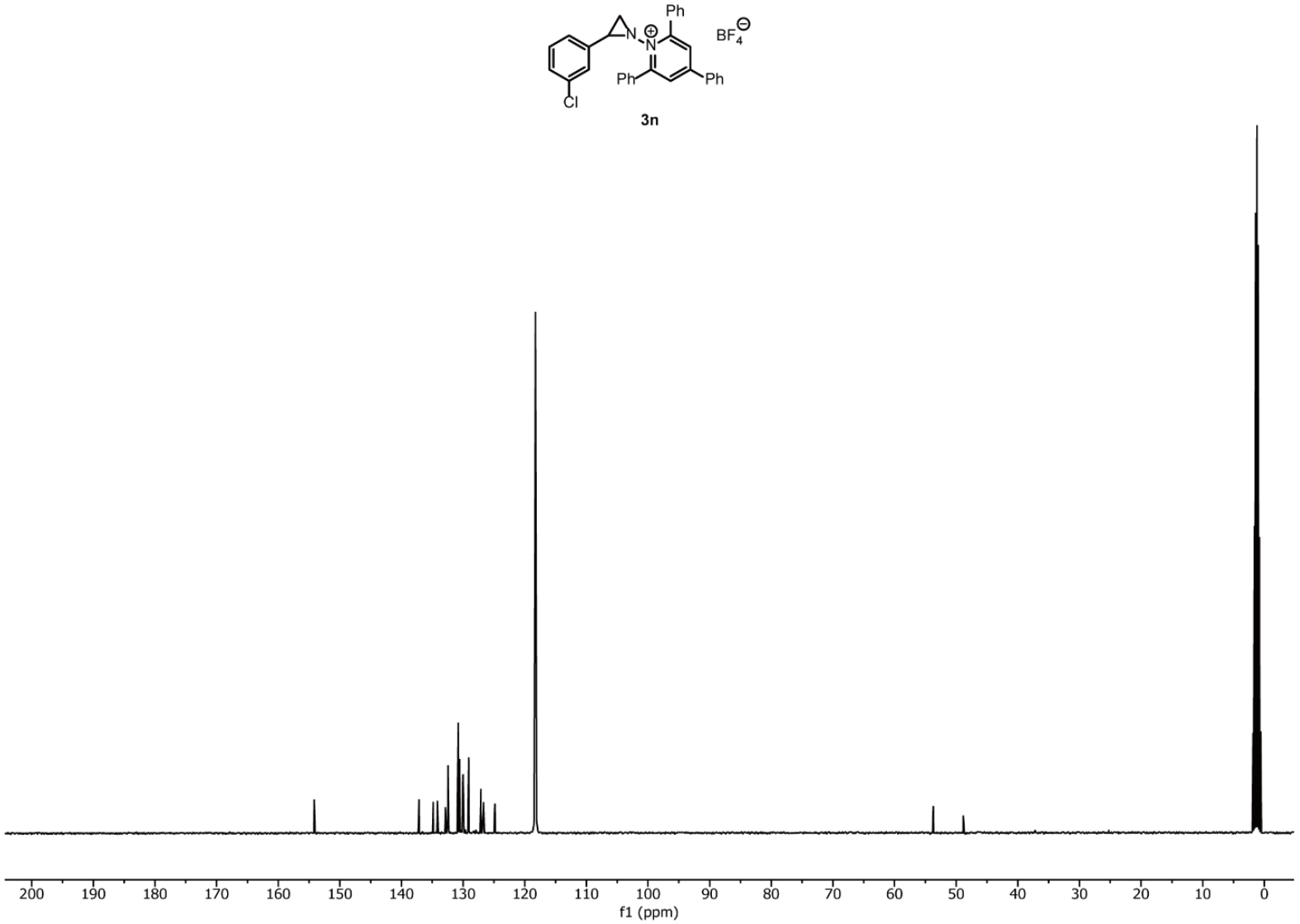


Figure S34. ^{13}C NMR spectrum of 1-(2-(3-chlorophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3n**) in CD_3CN (101 MHz) at 23 °C.

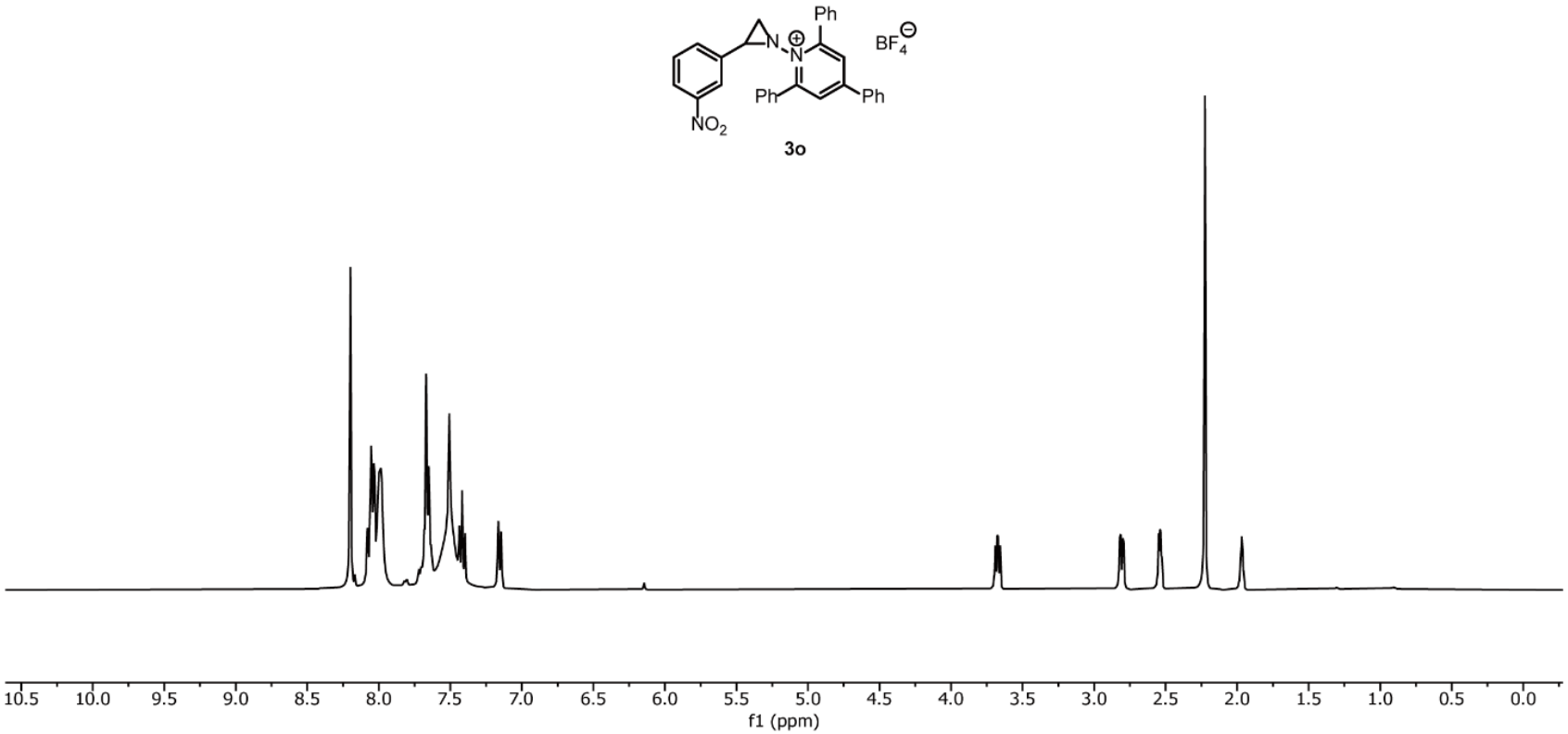


Figure S35. ^{1}H NMR spectrum of 1-(2-(3-nitrophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3o**) in CD_3CN (400 MHz) at 23 °C.

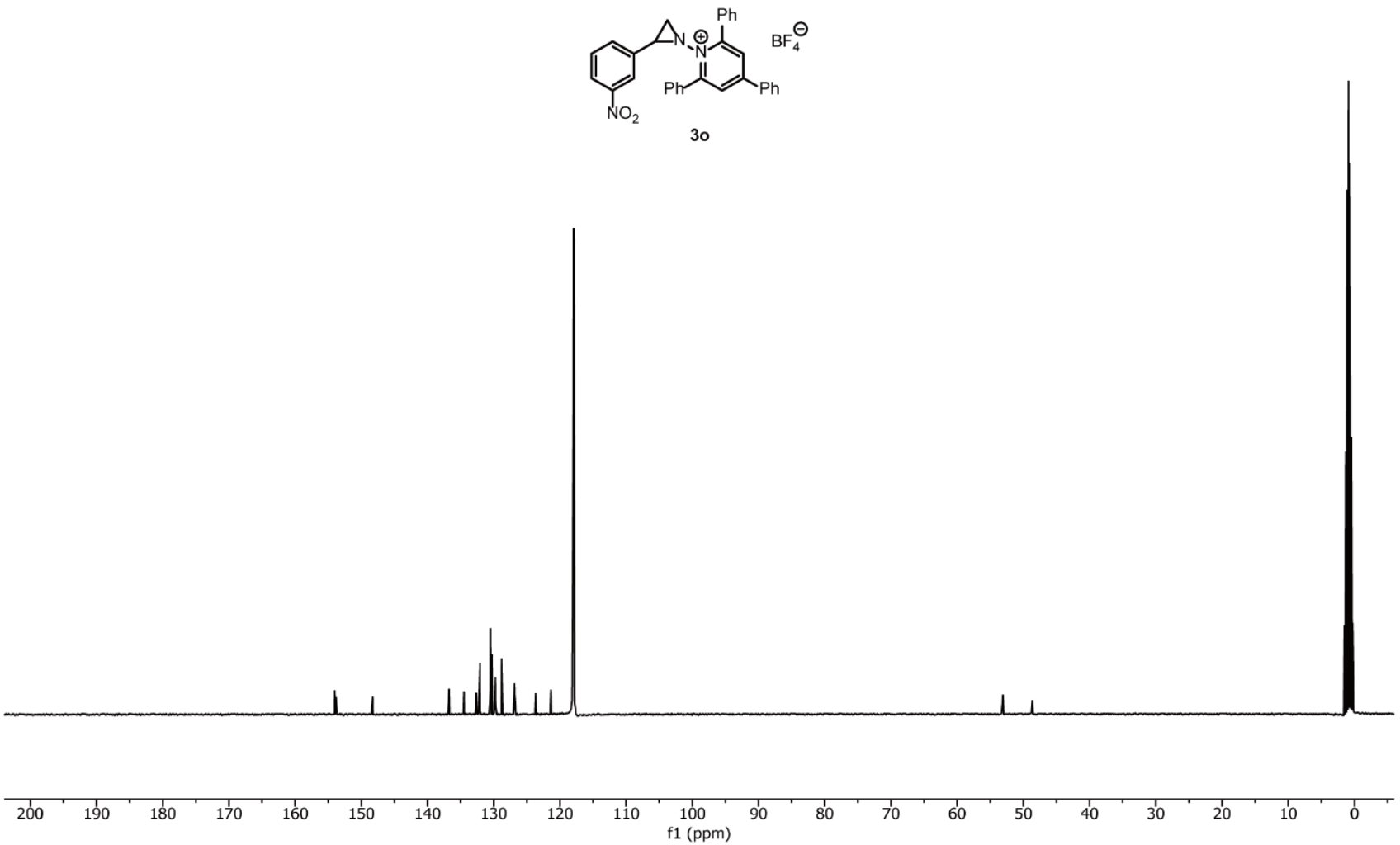


Figure S36. ^{13}C NMR spectrum of 1-(2-(3-nitrophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3o**) in CD_3CN (101 MHz) at 23 °C.

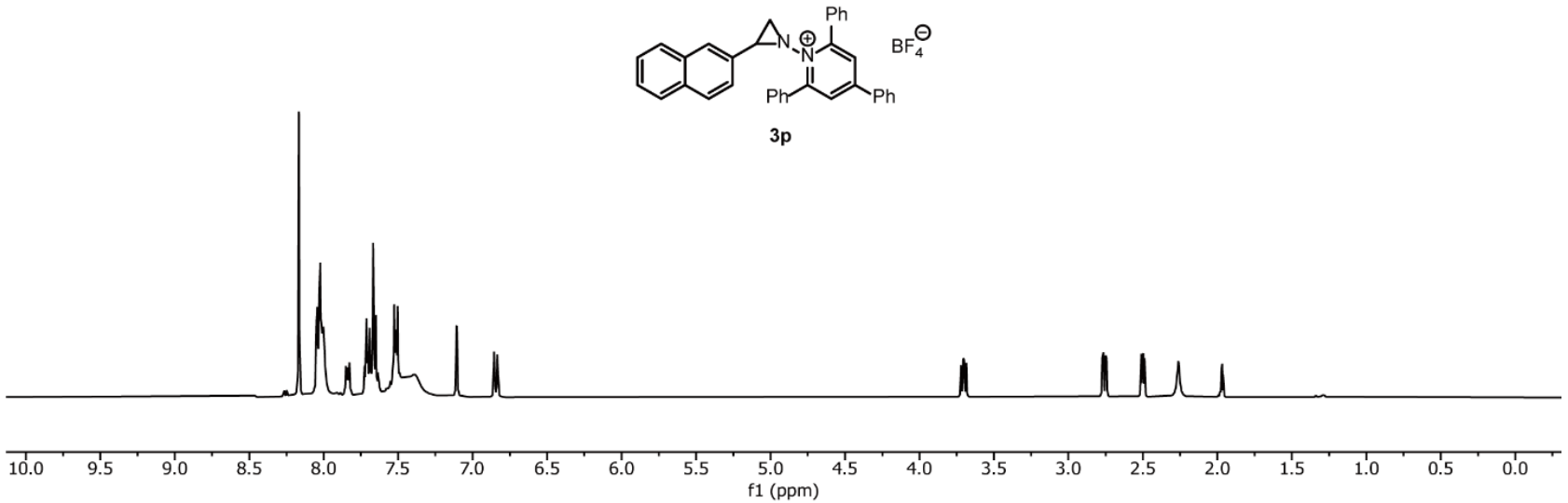


Figure S37. ^{1}H NMR spectrum of 1-(2-(naphthalen-2-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3p**) in CD_3CN (400 MHz) at 23 °C.

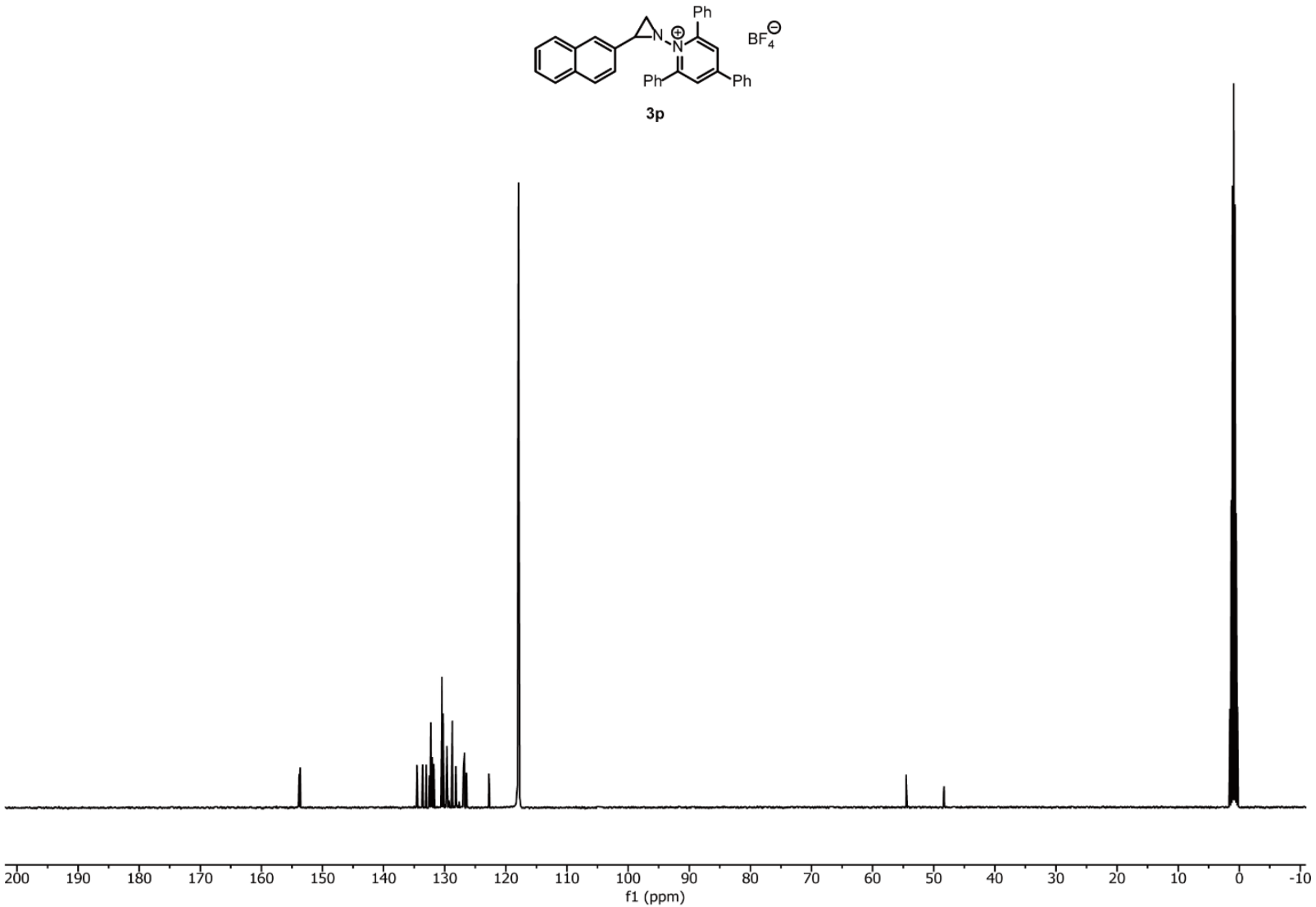


Figure S38. ^{13}C NMR spectrum of 1-(2-(naphthalen-2-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3p**) in CD_3CN (101 MHz) at 23 °C.

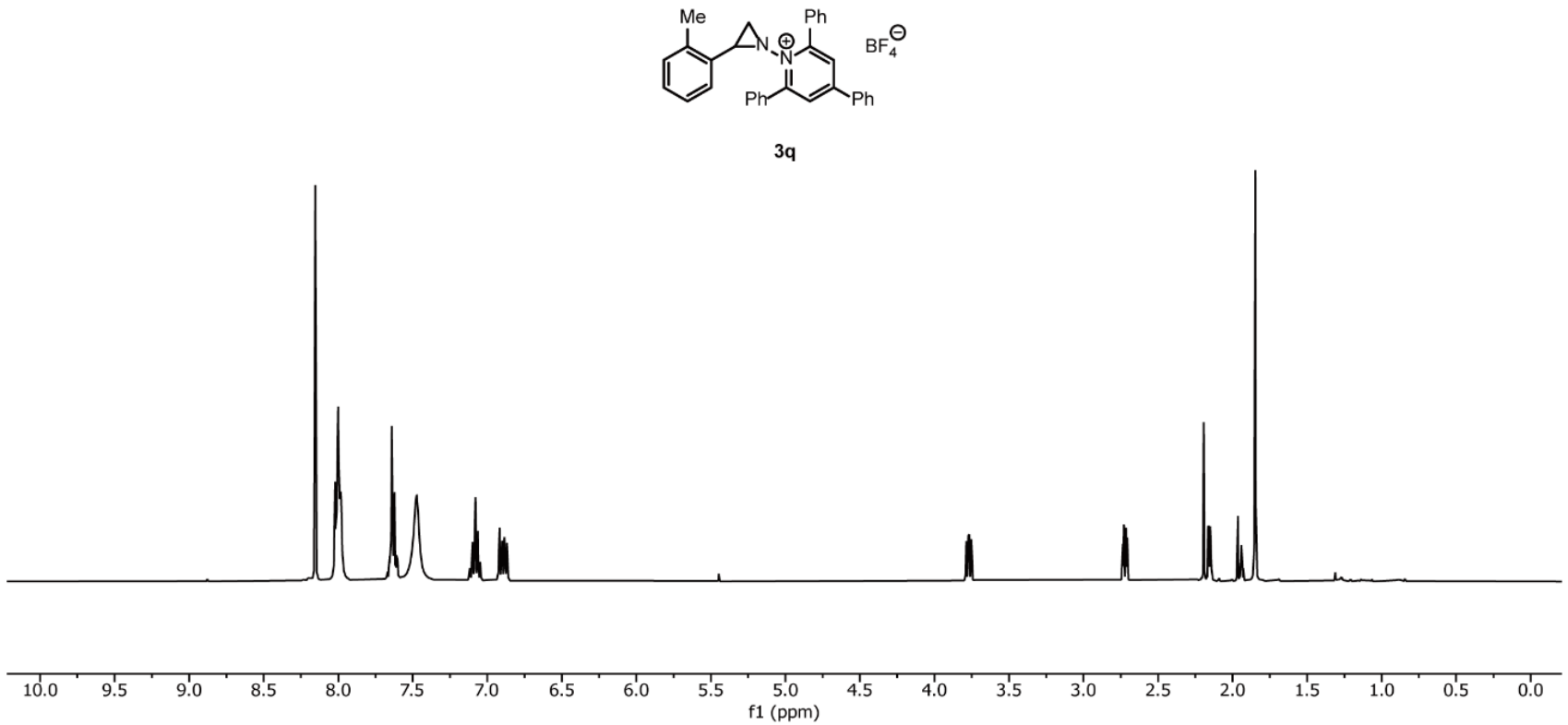


Figure S39. ^{1}H NMR spectrum of 2,4,6-triphenyl-1-(2-(*o*-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3q**) in CD_3CN (400 MHz) at 23 °C.

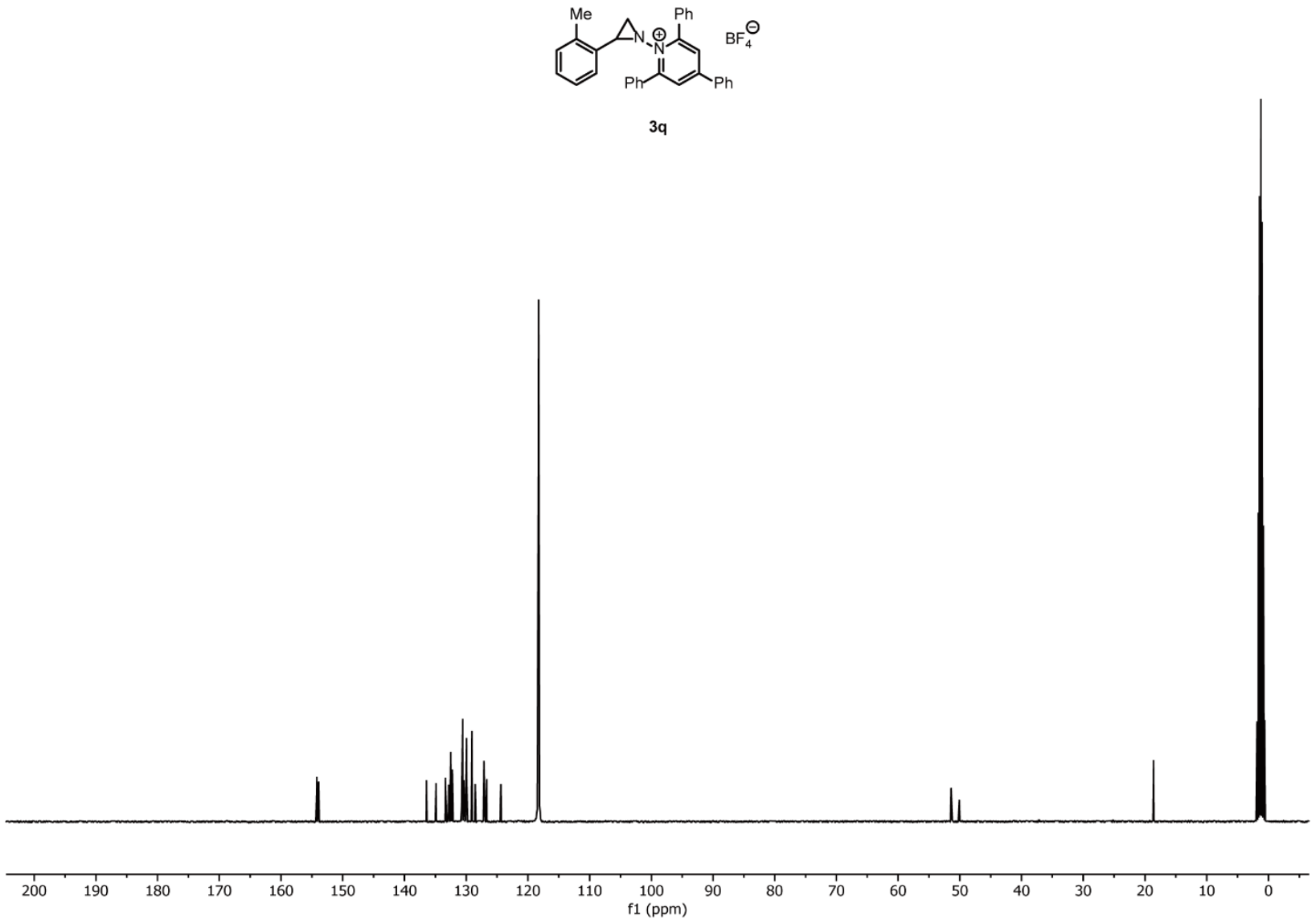


Figure S40. ^{13}C NMR spectrum of 2,4,6-triphenyl-1-(2-(*o*-tolyl)aziridin-1-yl)pyridin-1-ium tetrafluoroborate (**3q**) in CD_3CN (101 MHz) at 23 °C.

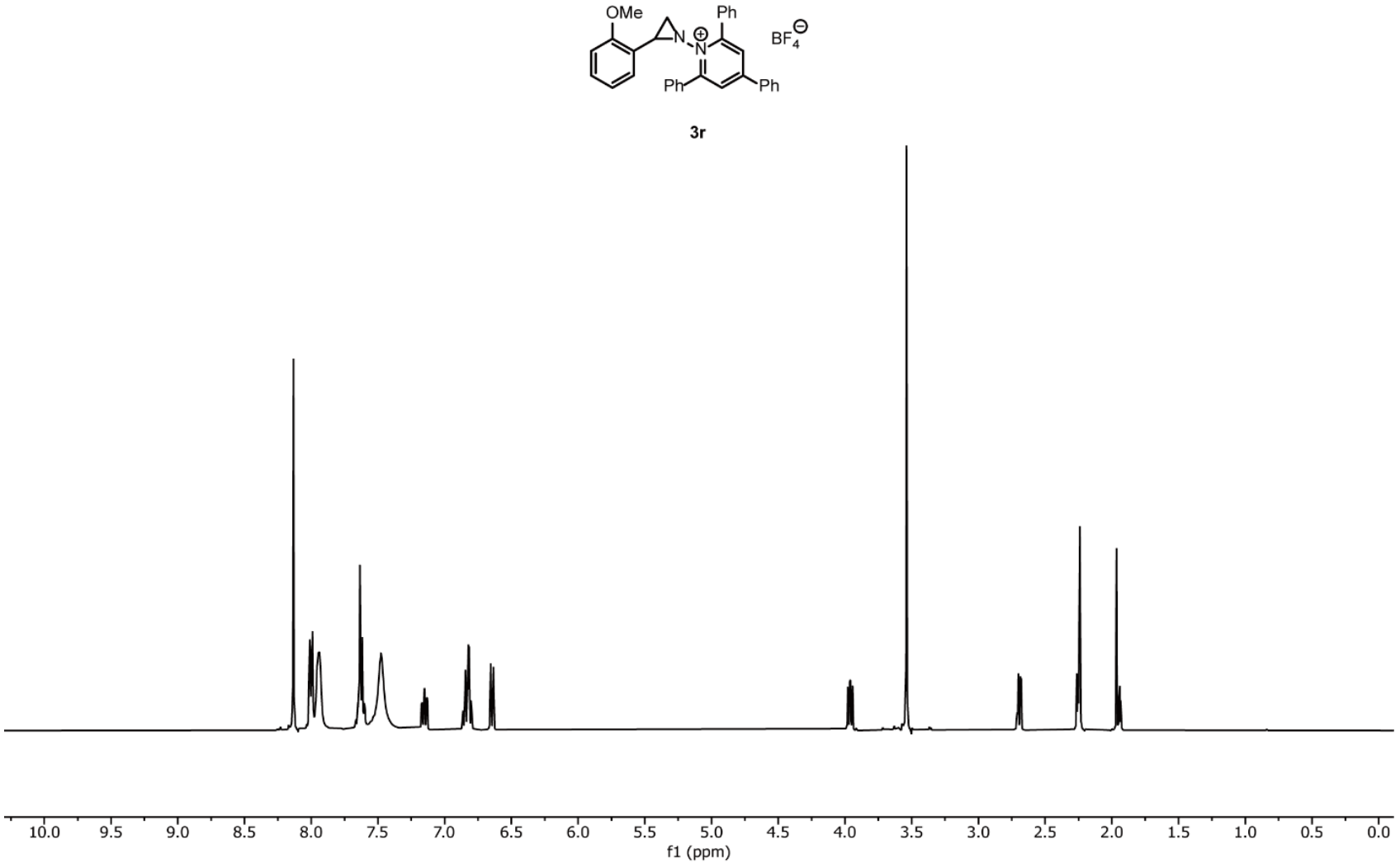


Figure S41. ^{1}H NMR spectrum of 1-(2-(2-methoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3r**) in CD_3CN (400 MHz) at 23 °C.

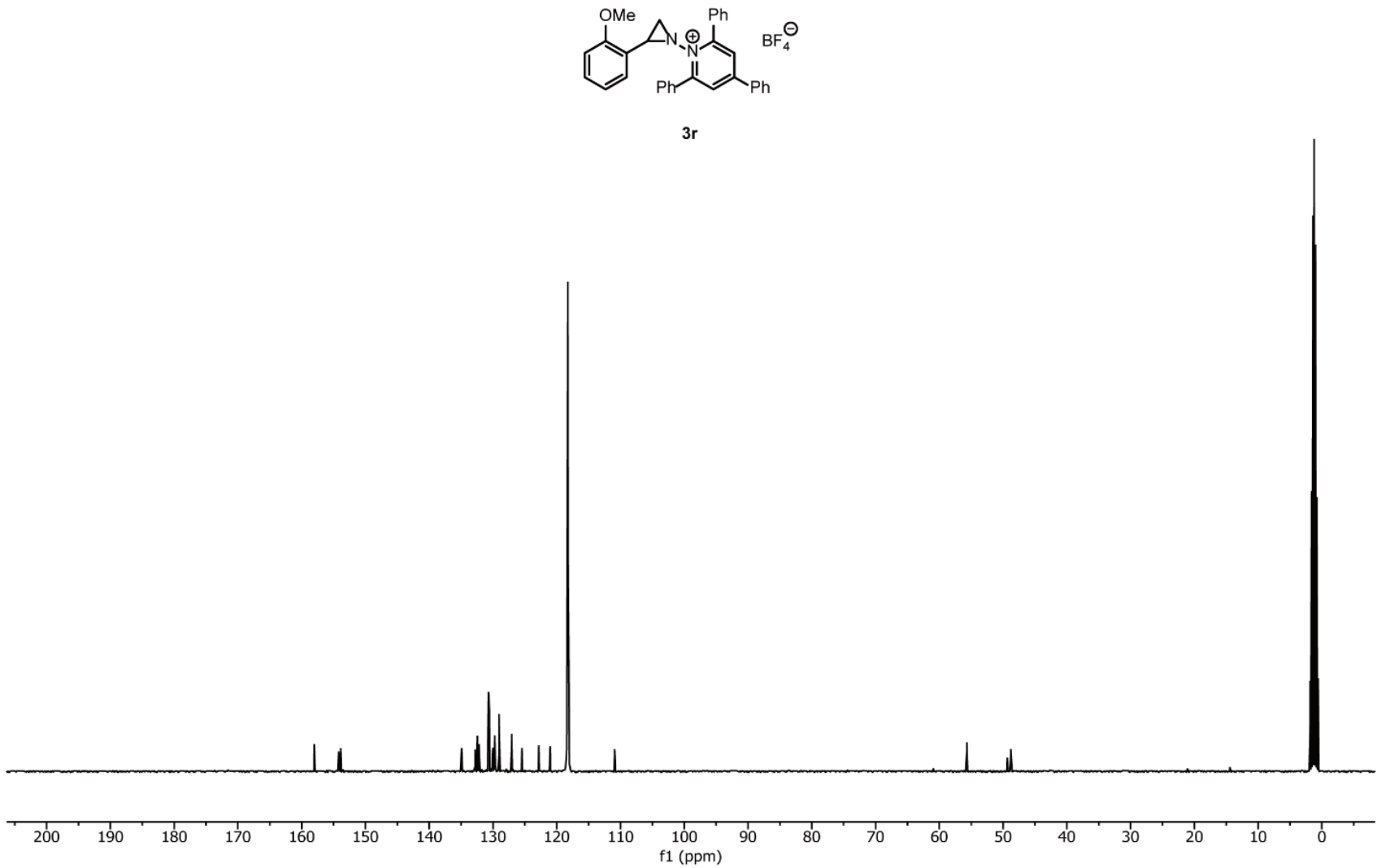


Figure S42. ^{13}C NMR spectrum of 1-(2-(2-methoxyphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3r**) in CD_3CN (101 MHz) at 23 °C.

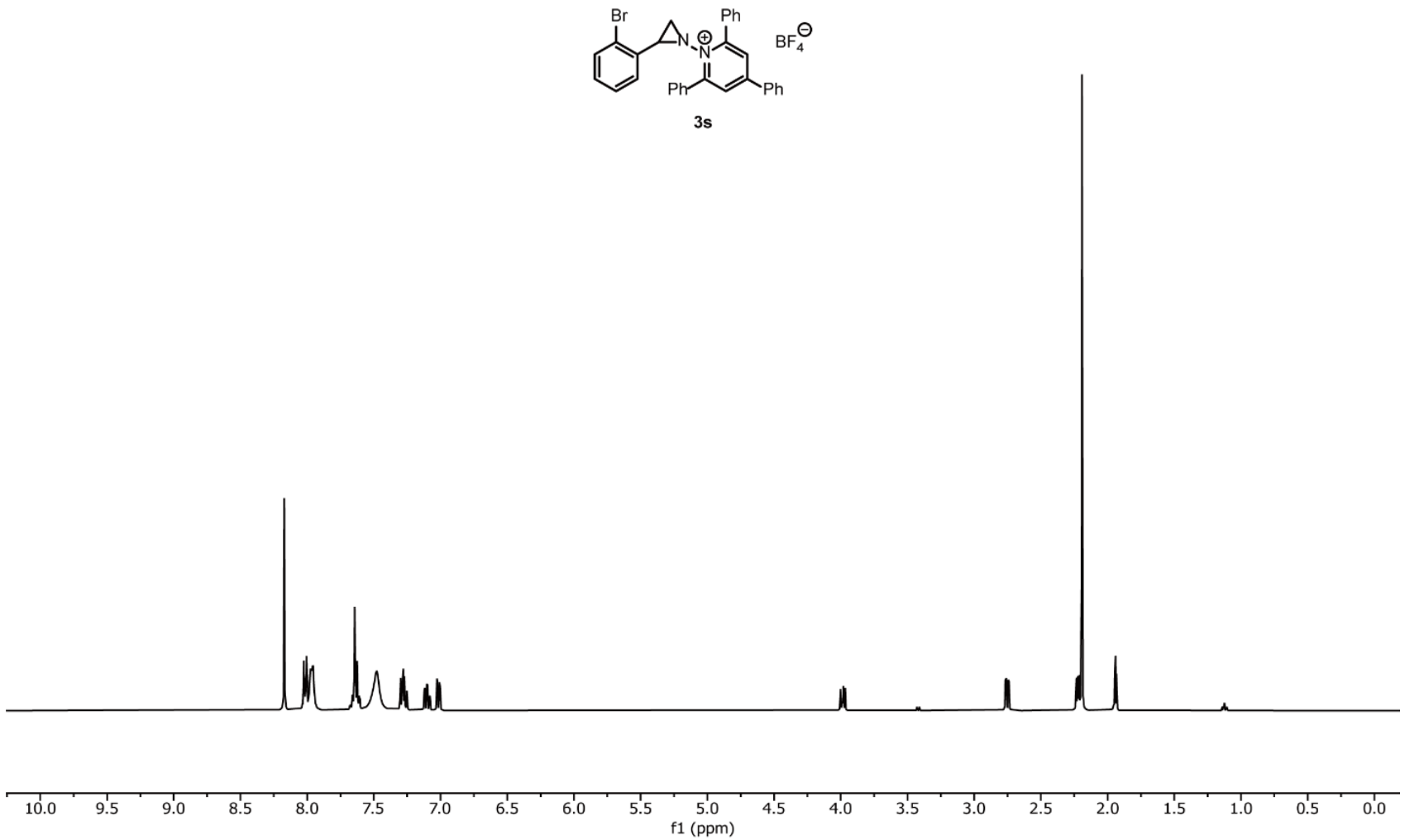


Figure S43. ^{1}H NMR spectrum of 1-(2-(2-bromophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3s**) in CD_3CN (400 MHz) at 23 °C.

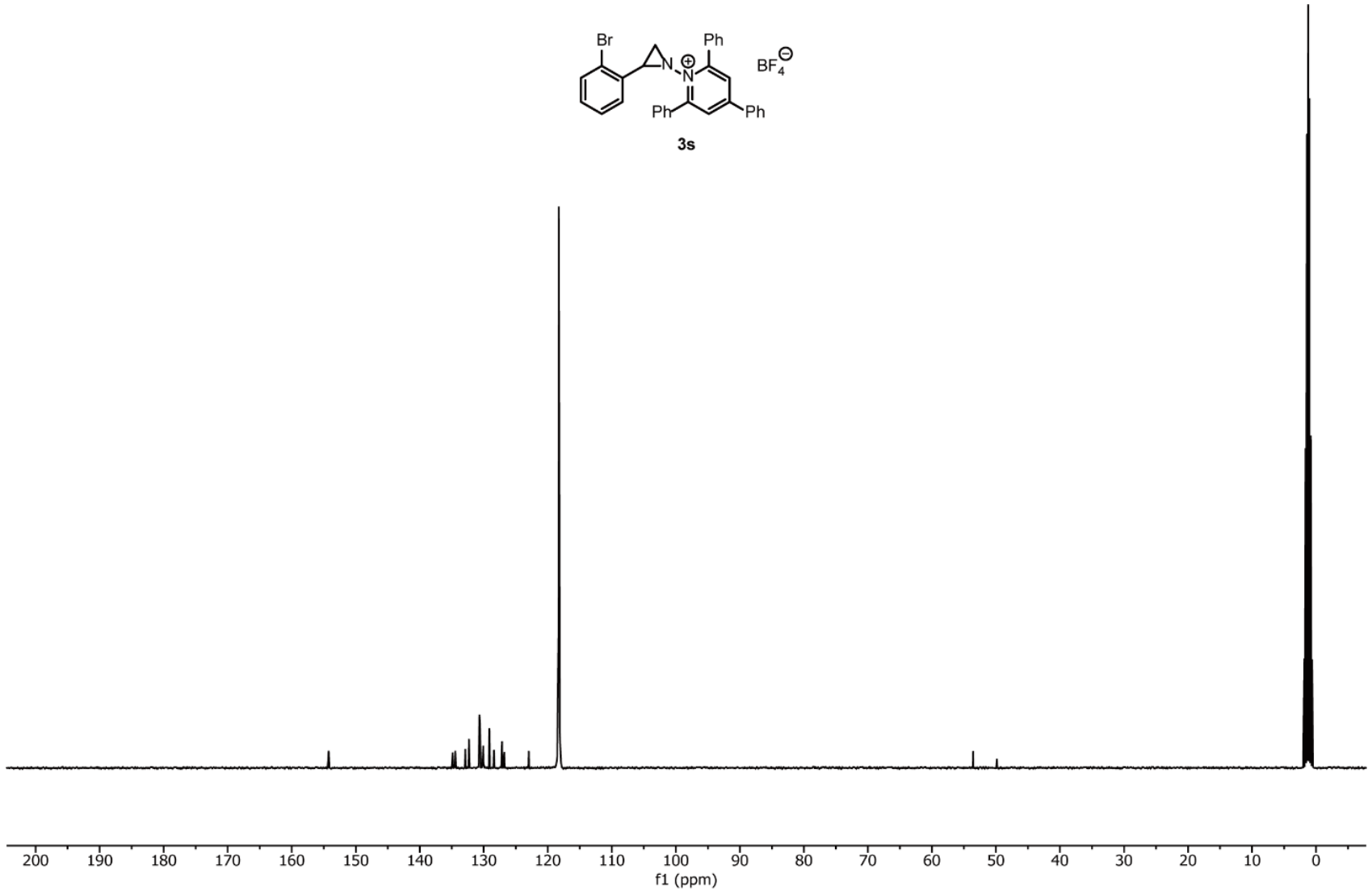


Figure S44. ^{13}C NMR spectrum of 1-(2-(2-bromophenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3s**) in CD_3CN (101 MHz) at 23 °C.

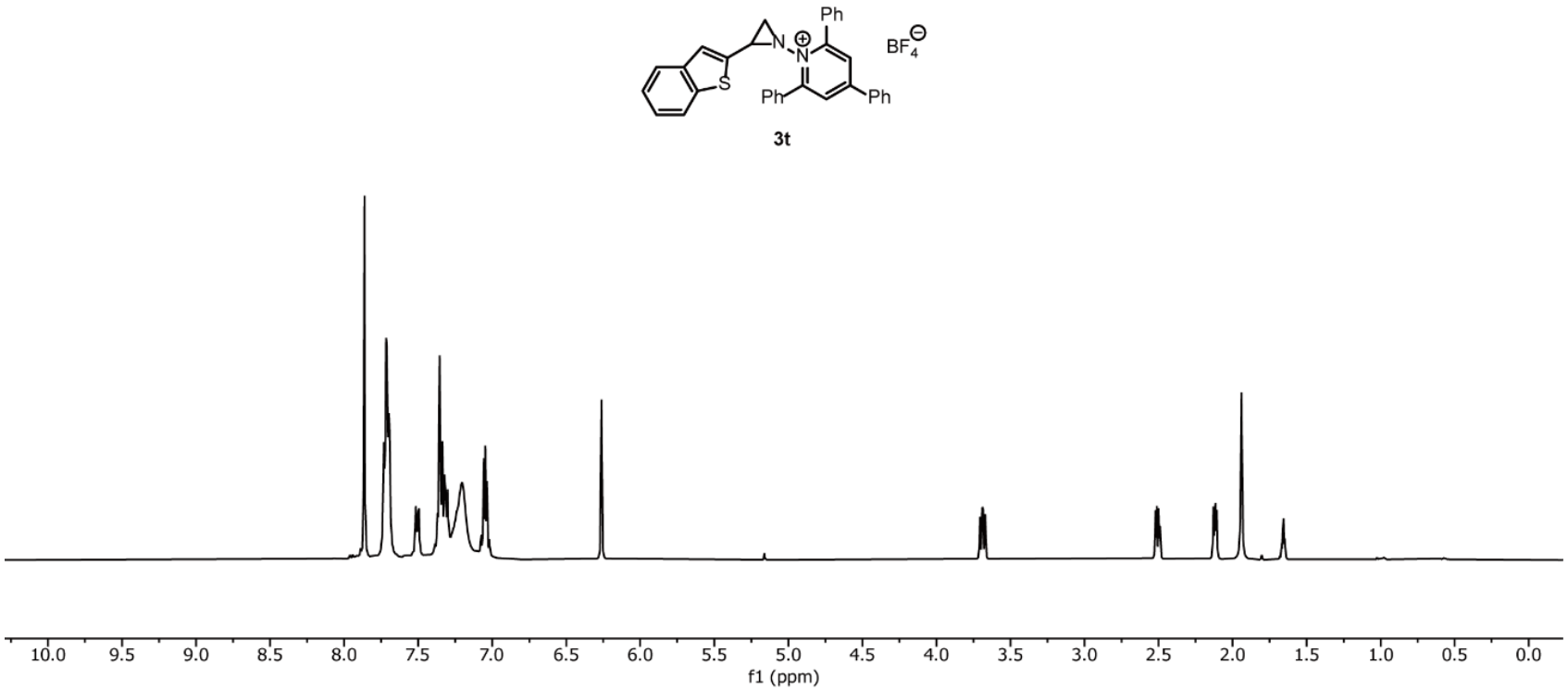


Figure S45. ^{1}H NMR spectrum of 1-(2-(benzo[*b*]thiophen-2-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3t**) in CD_3CN (400 MHz) at 23 °C.

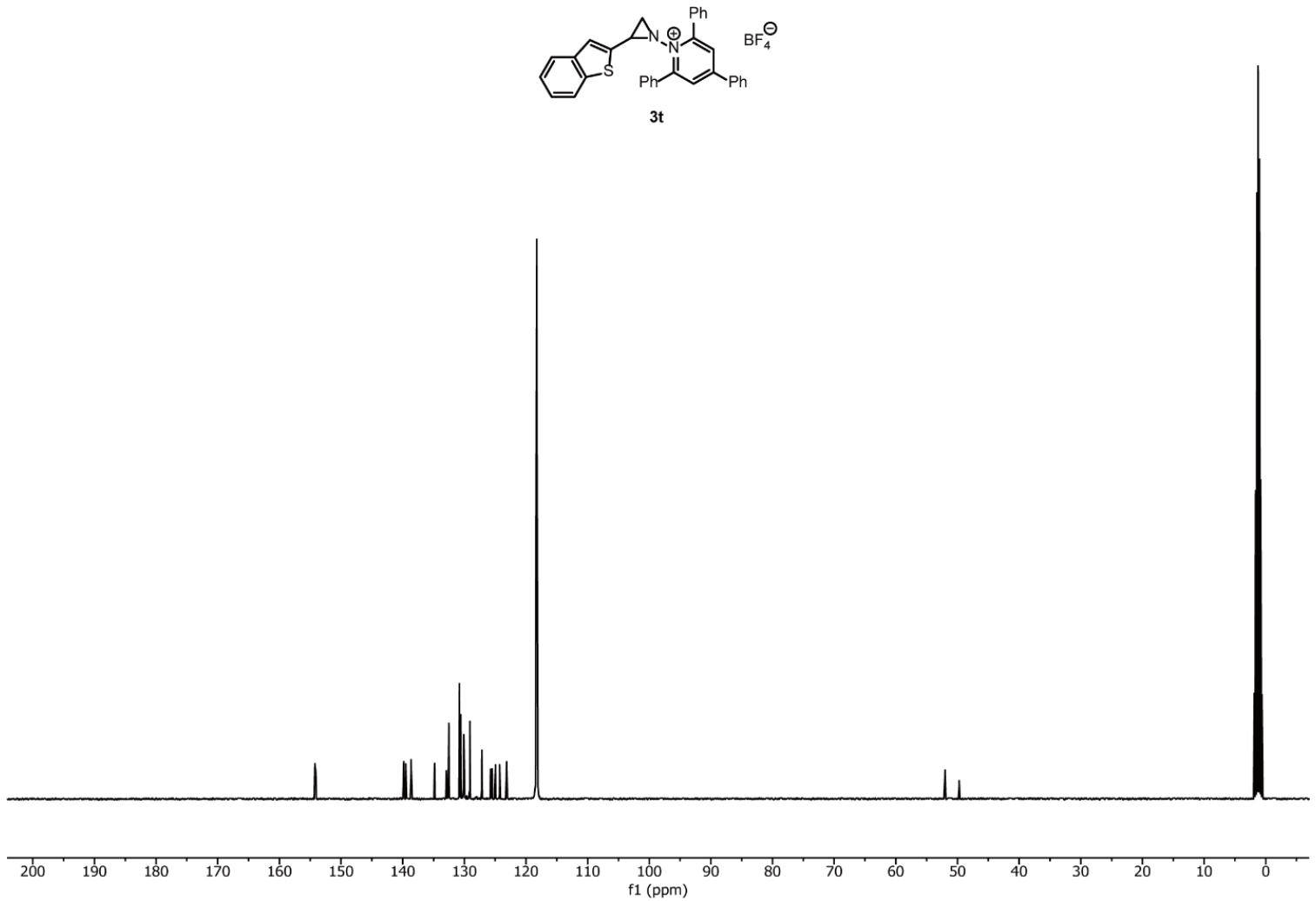


Figure S46. ^{13}C NMR spectrum of 1-(2-(benzo[*b*]thiophen-2-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3t**) in CD_3CN (101 MHz) at 23 °C.

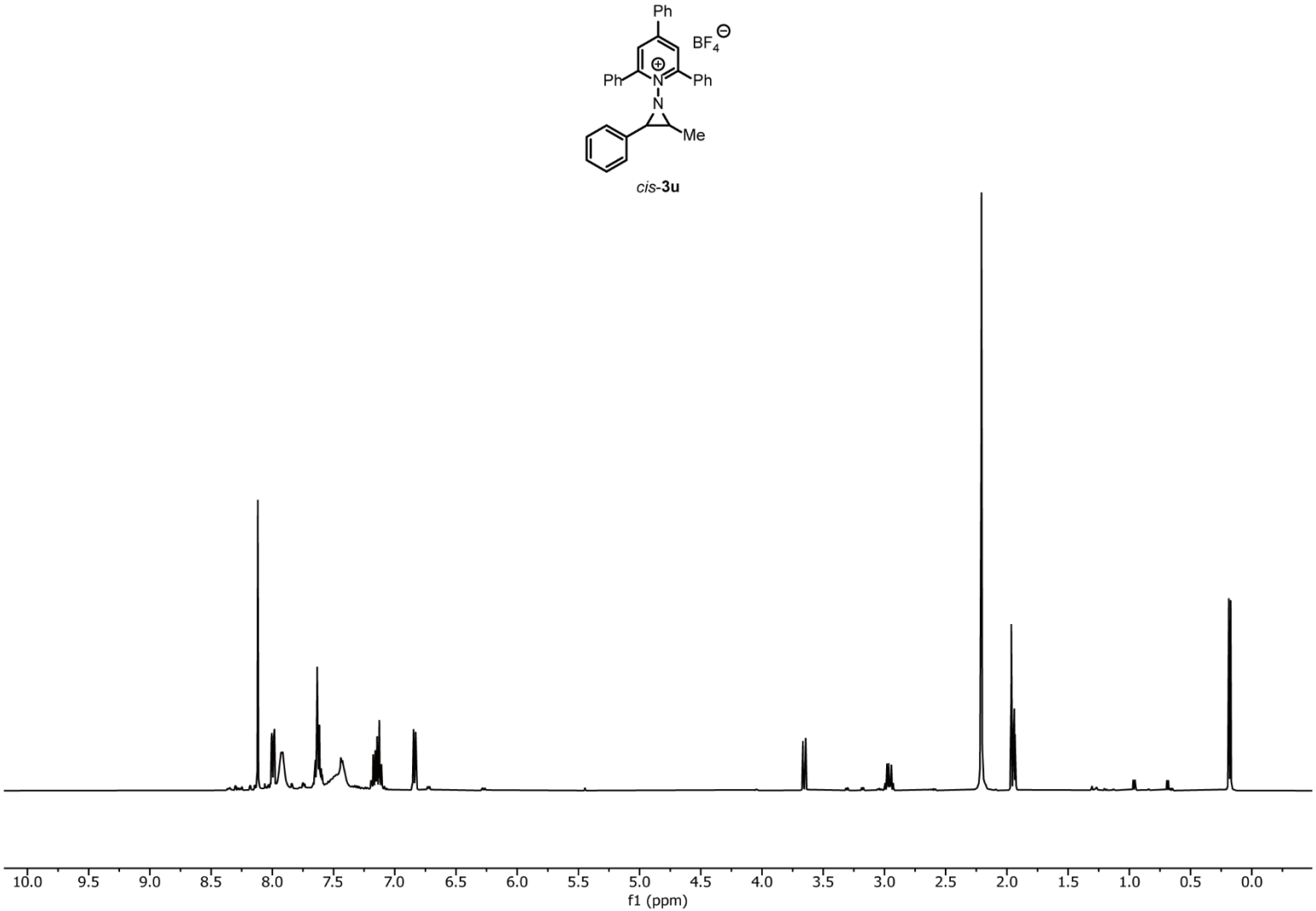


Figure S47. ^{1}H NMR spectrum of *cis*-1-(2-methyl-3-phenylaziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (*cis*-**3u**) in CD_3CN (400 MHz) at 23 °C

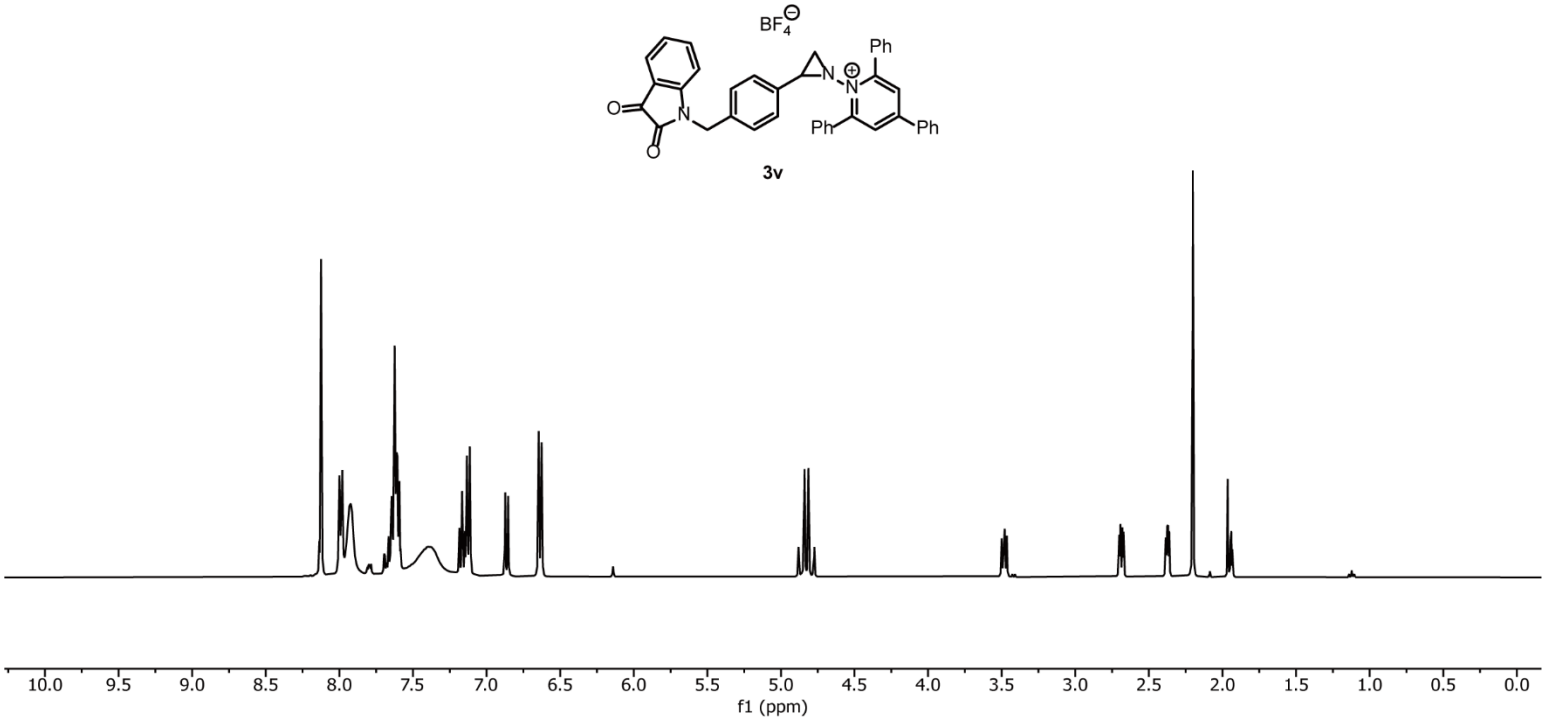


Figure S48. ^{1}H NMR spectrum of 1-(2-(4-((2,3-dioxoindolin-1-yl)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3v**) in CD_3CN (400 MHz) at 23 °C.

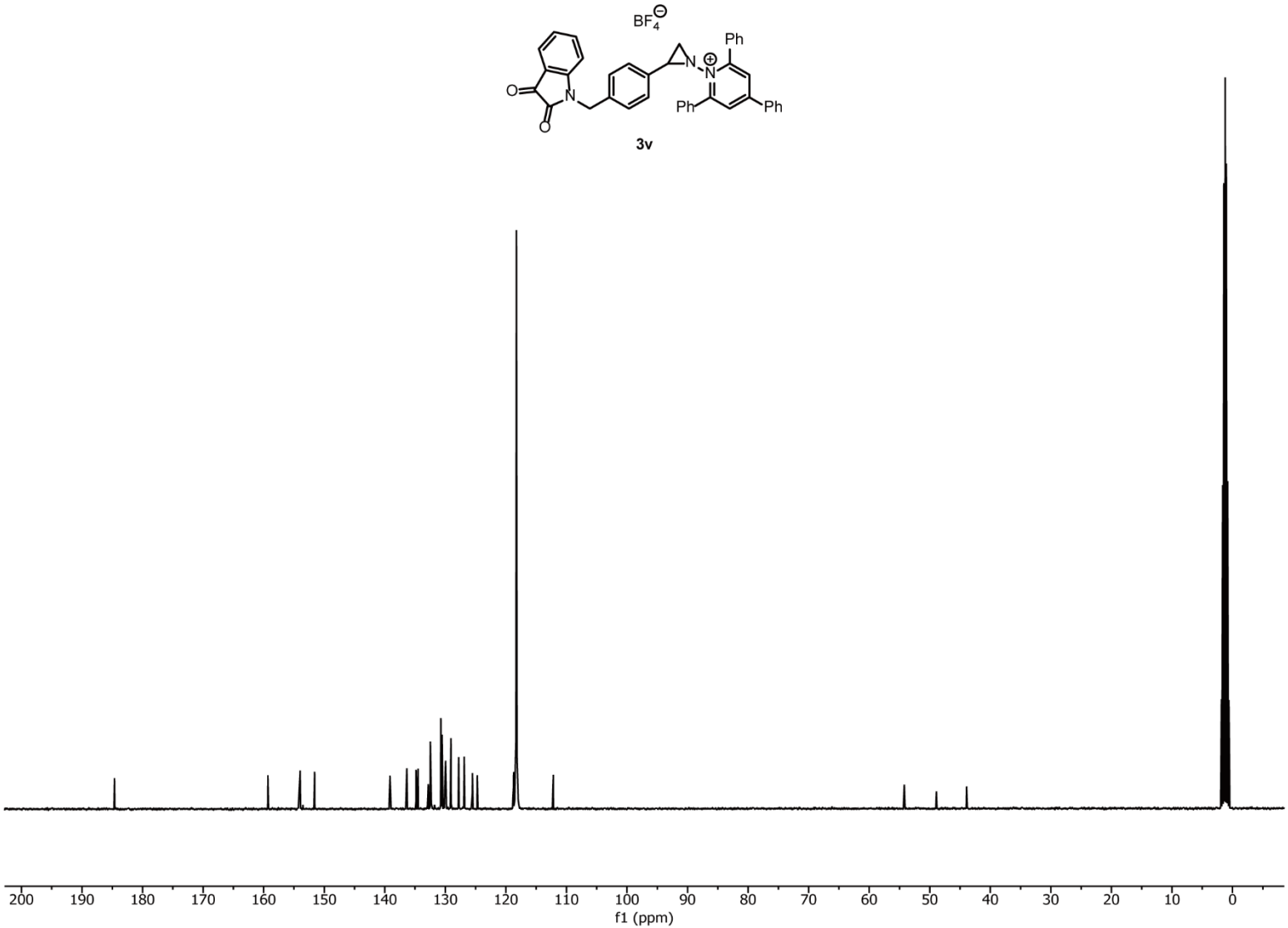


Figure S49. ^{13}C NMR spectrum of 1-(2-(4-((2,3-dioxoindolin-1-yl)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3v**) in CD_3CN (101 MHz) at 23 °C.

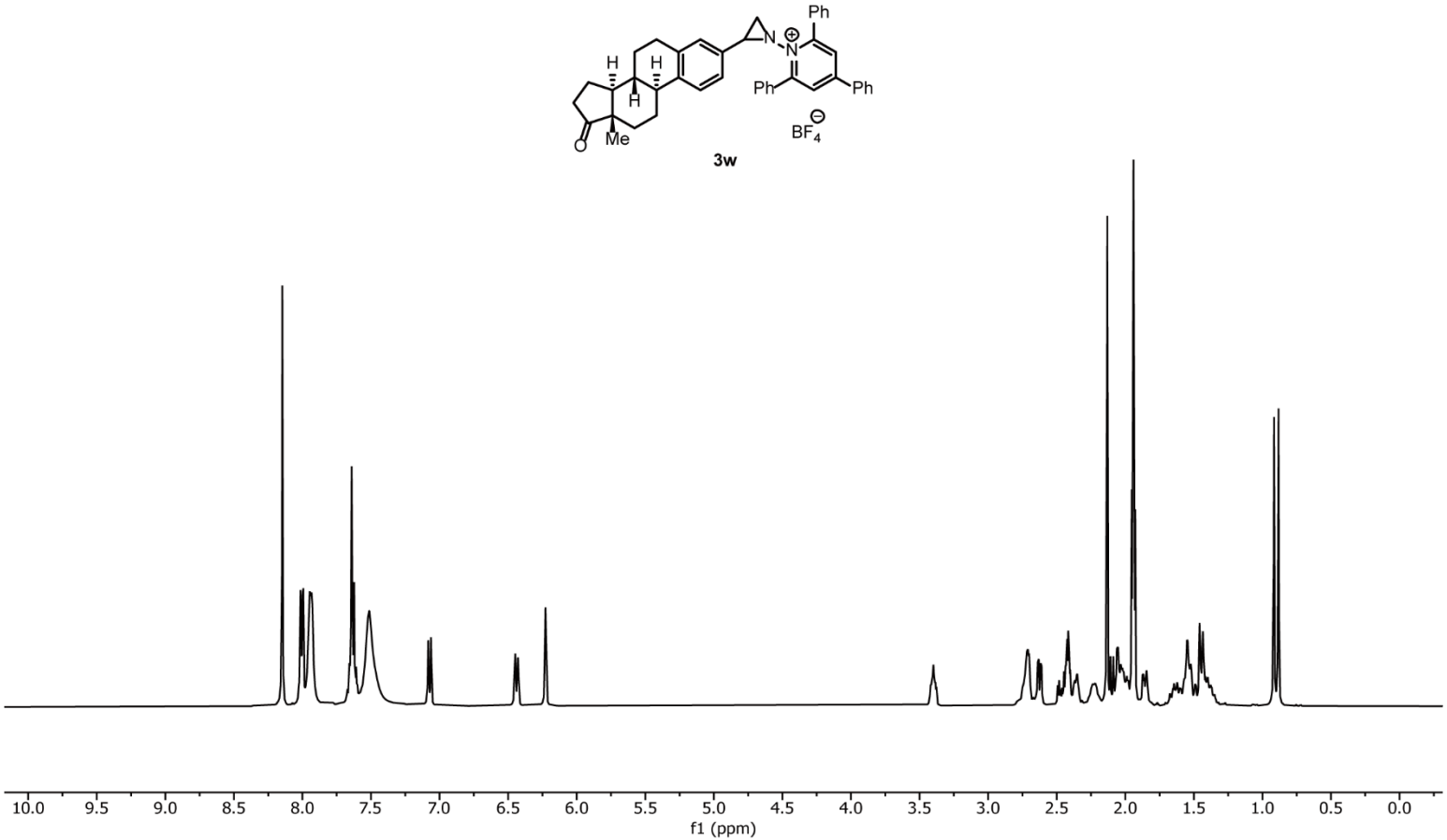


Figure S50. ^{1}H NMR spectrum of 1-(2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3w**) in CD_3CN (400 MHz) at 23 °C.

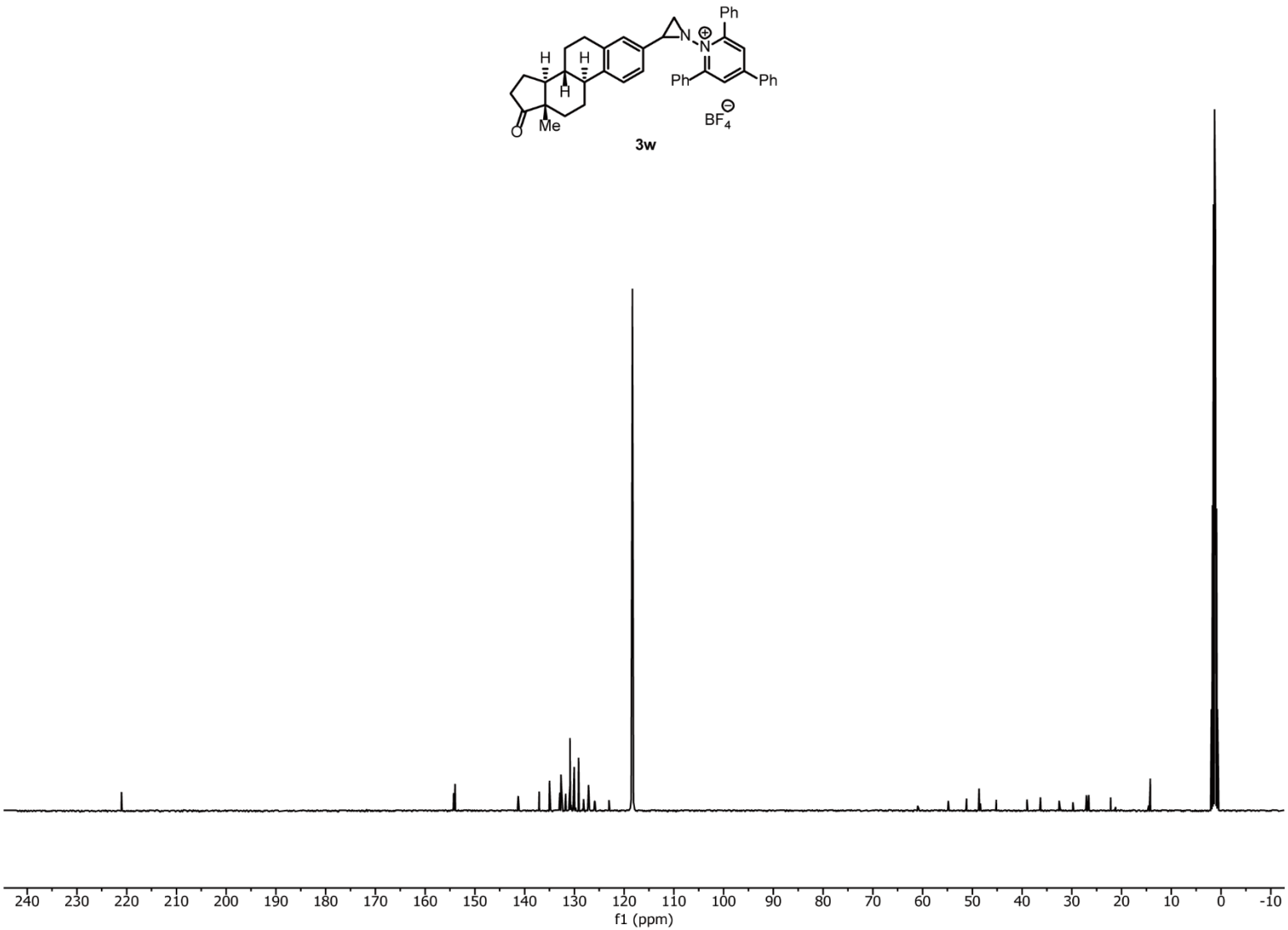


Figure S51. ^{13}C NMR spectrum of 1-(2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3w**) in CD_3CN (101 MHz) at 23 °C.

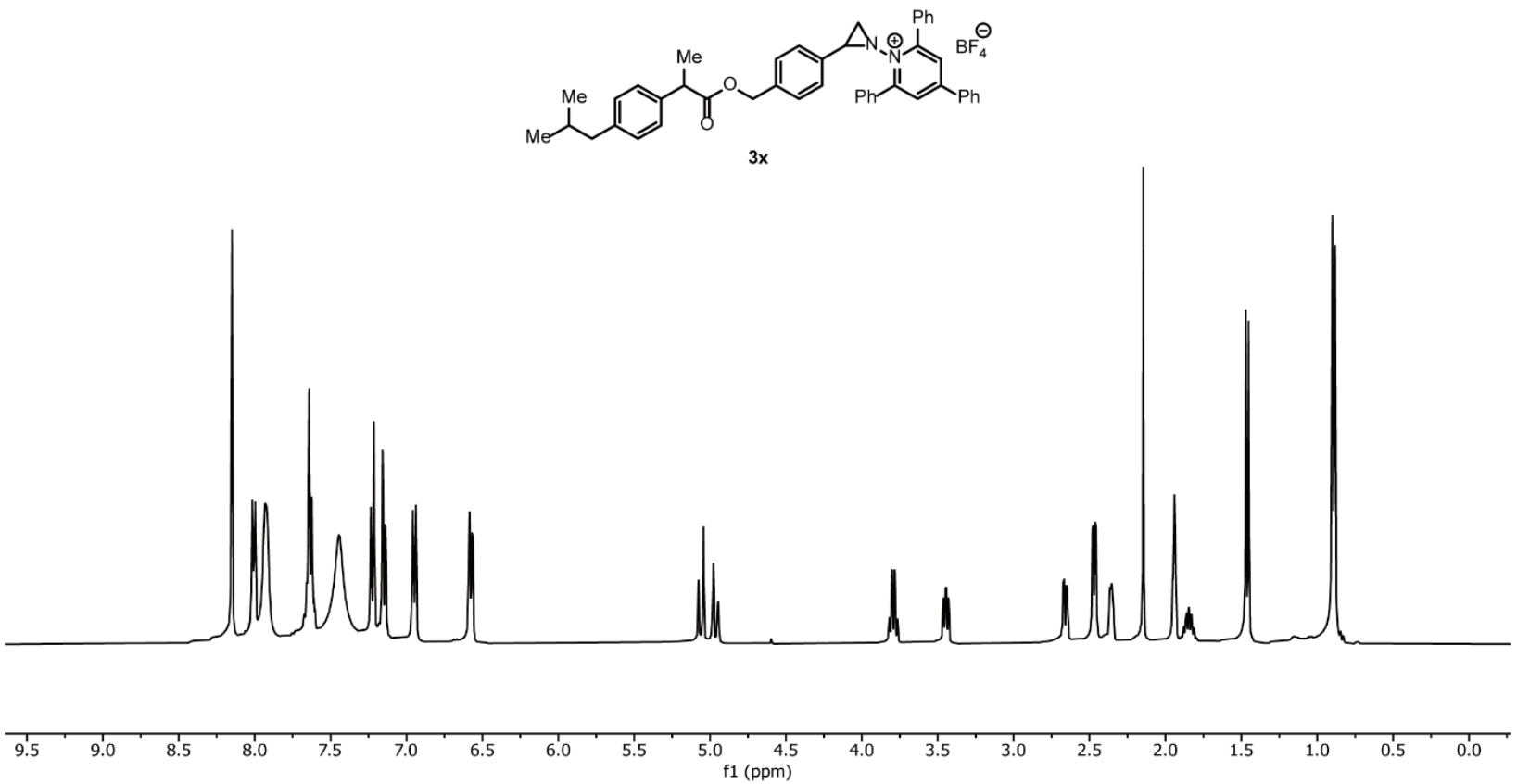


Figure S52. ^{1}H NMR spectrum of 1-(2-(4-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3x**) in CD_3CN (400 MHz) at 23 °C.

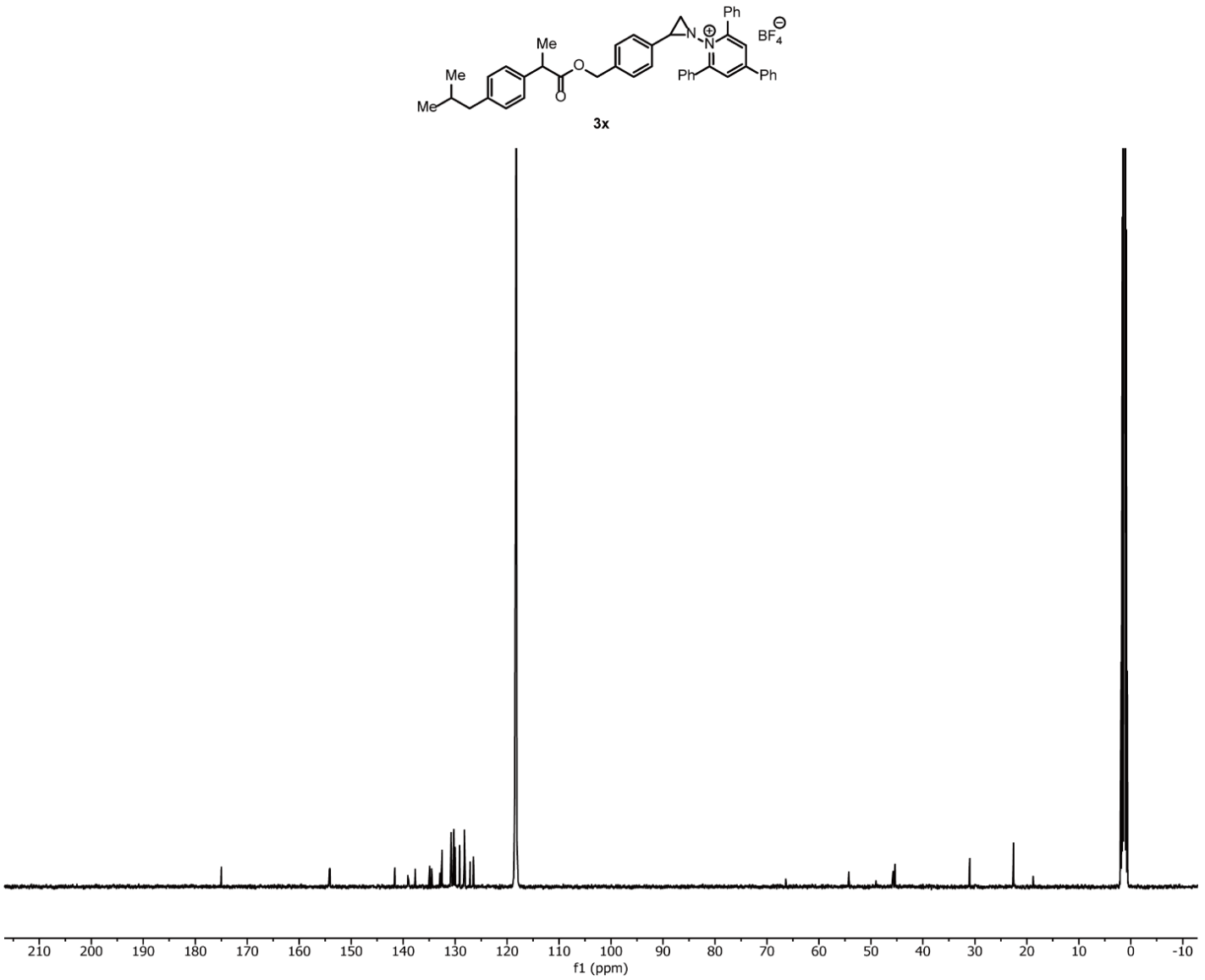


Figure S53. ^{13}C NMR spectrum of 1-(2-(4-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3x**) in CD_3CN (101 MHz) at 23 °C.

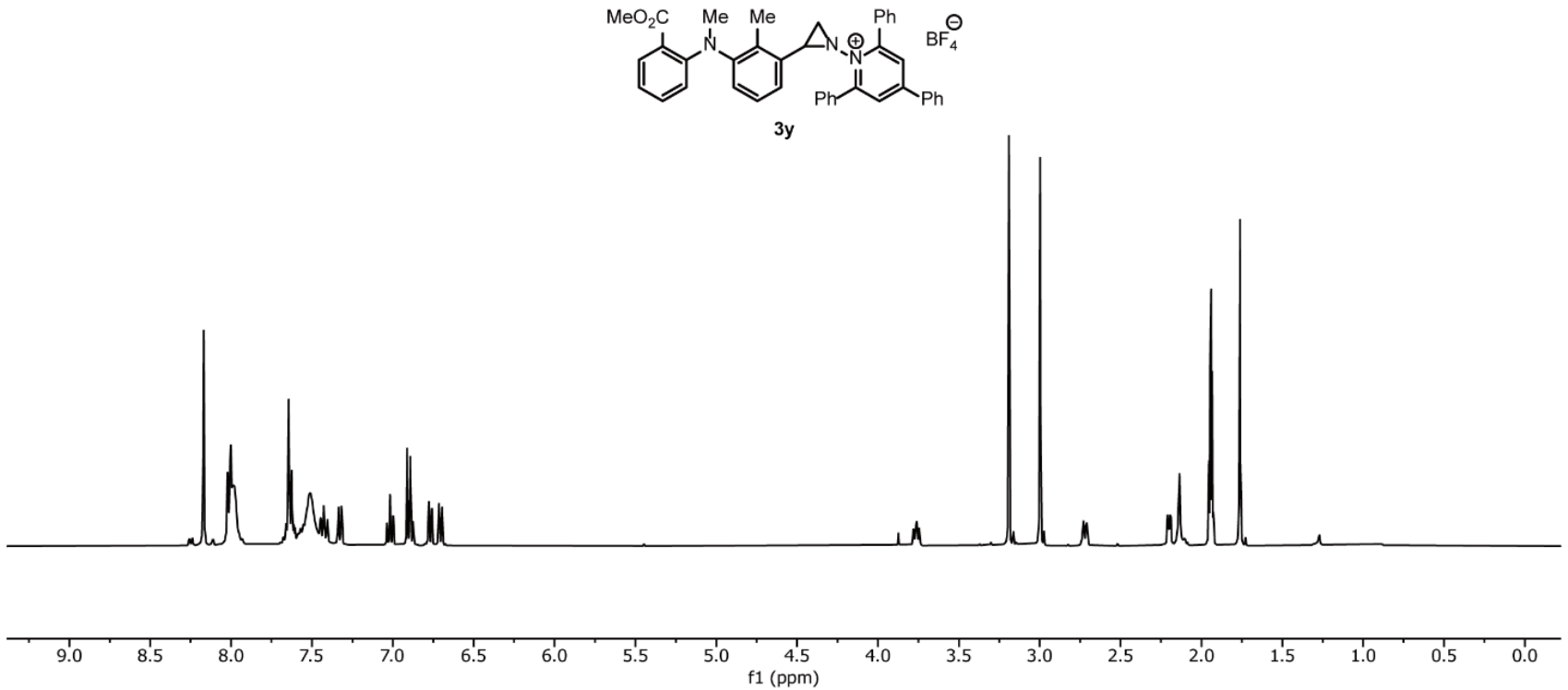


Figure S54. ^{1}H NMR spectrum of 1-(2-(3-((2-(methoxycarbonyl)phenyl)(methyl)amino)-2-methylphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3y**) in CD_3CN (400 MHz) at 23 °C.

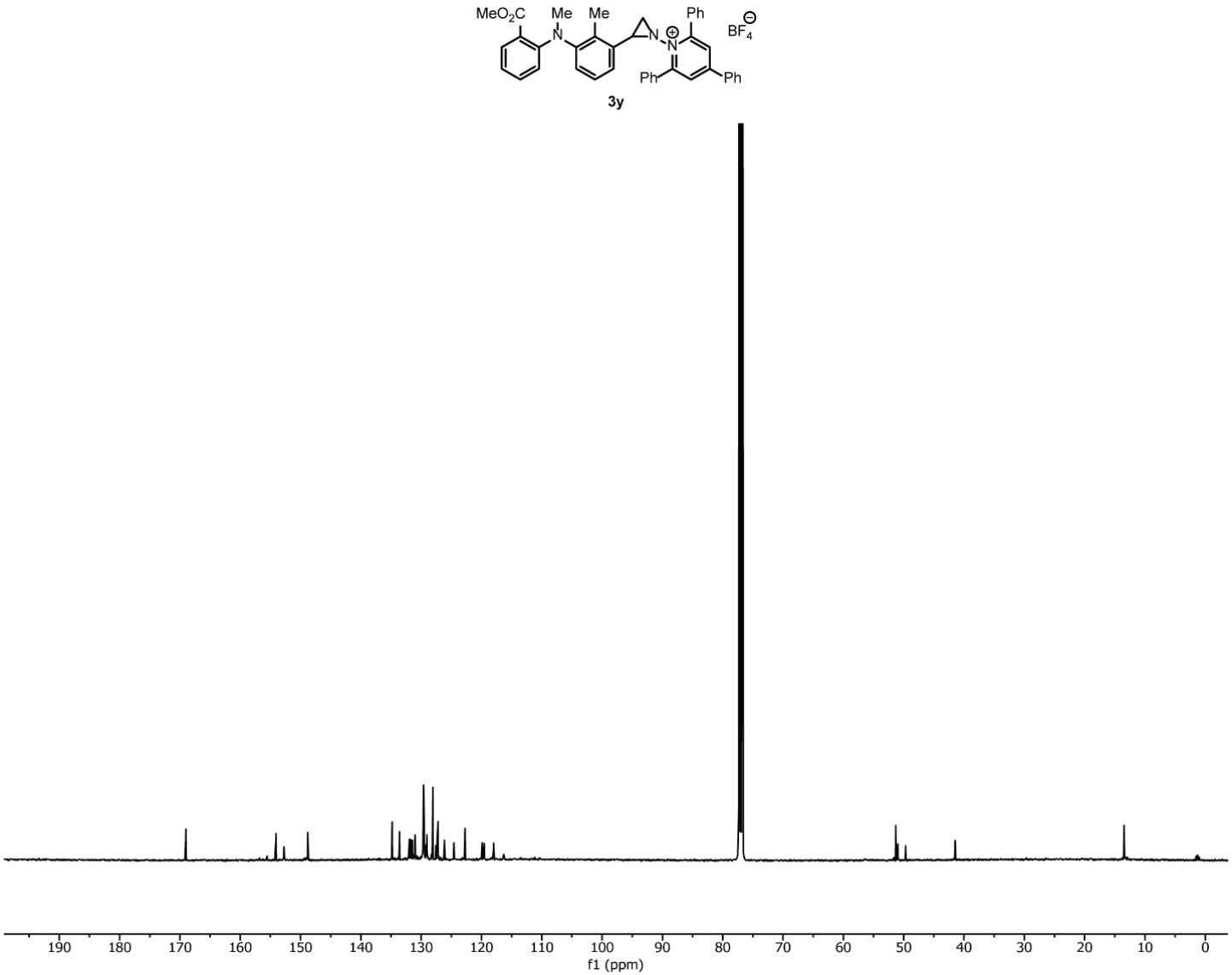


Figure S55. ^{13}C NMR spectrum of 1-(2-(3-((2-(methoxycarbonyl)phenyl)(methyl)amino)-2-methylphenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3y**) in $CDCl_3$ (101 MHz) at 23 °C.

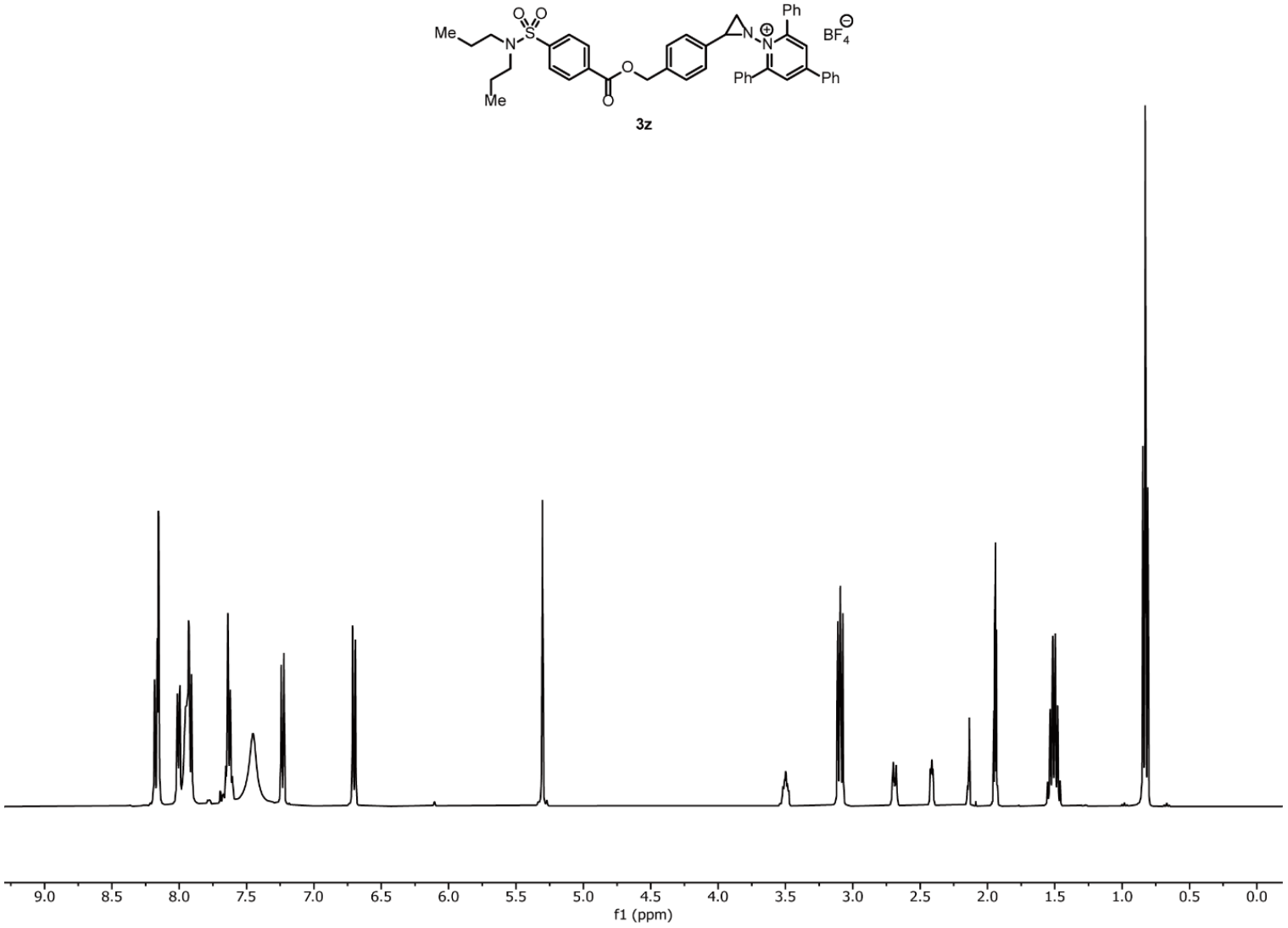


Figure S56. ^{1}H NMR spectrum of 1-(2-(4-(((4-(*N*,*N*-dipropylsulfamoyl)benzoyl)oxy)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3z**) in CD_3CN (400 MHz) at 23 °C.

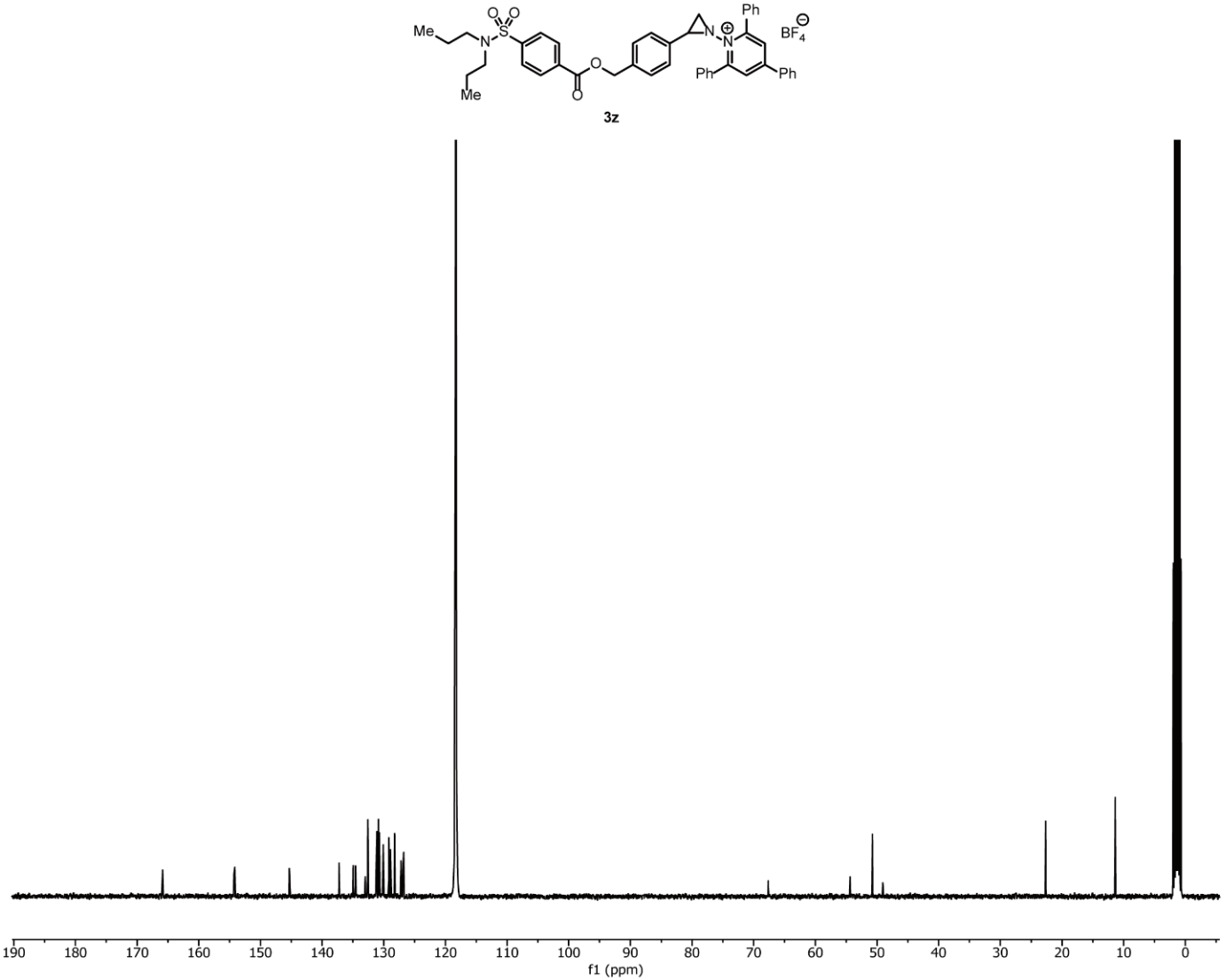


Figure S57. ^{13}C NMR spectrum of 1-(2-(4-(((4-(*N*,*N*-dipropylsulfamoyl)benzoyl)oxy)methyl)phenyl)aziridin-1-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**3z**) in CD_3CN (101 MHz) at 23 °C.

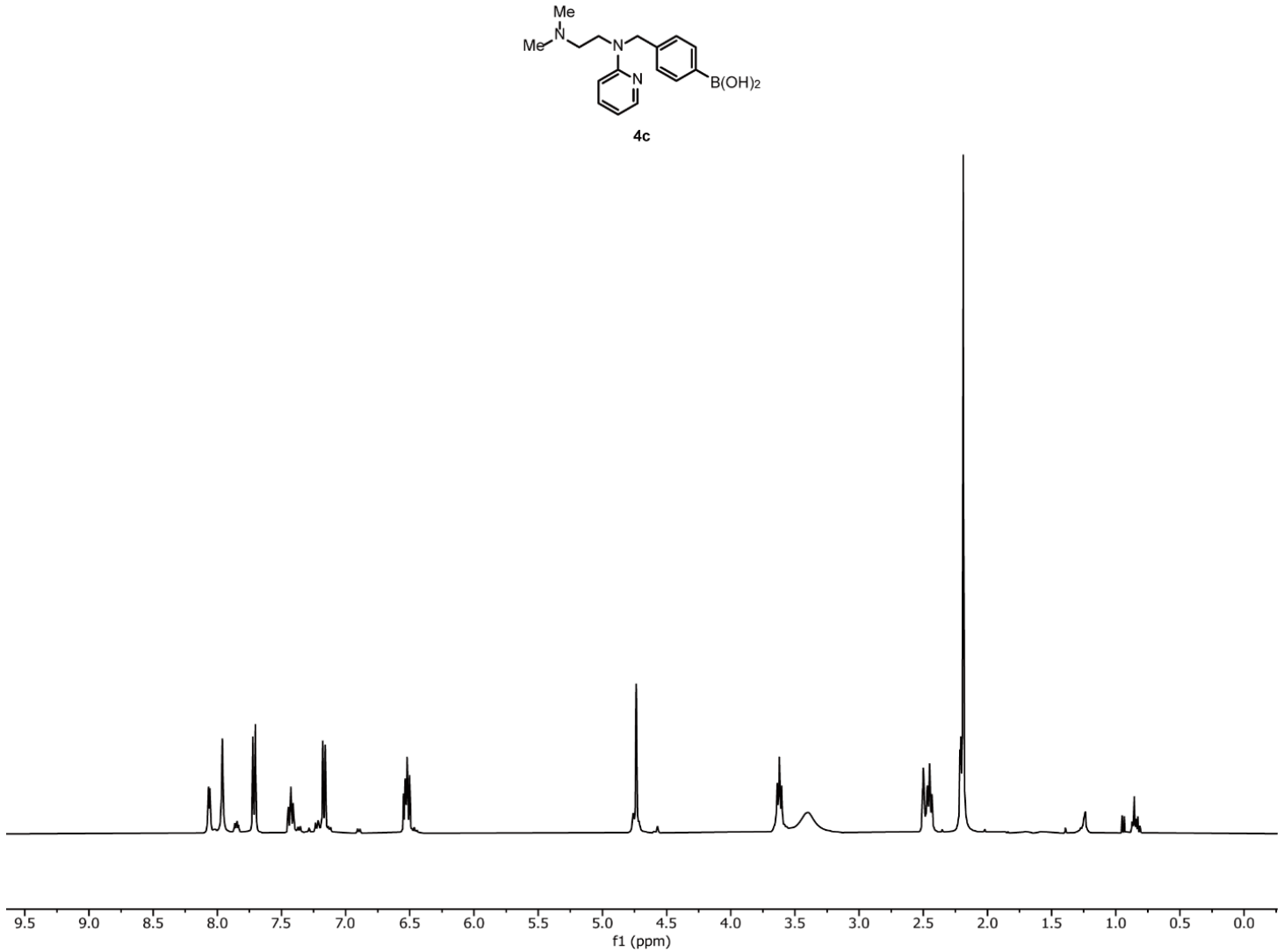


Figure S58. ^{1}H NMR spectrum of (4-(((2-(dimethylamino)ethyl)(pyridin-2-yl)amino)methyl)phenyl)boronic acid (**4c**) in DMSO-d_6 (400 MHz) at 23 °C.

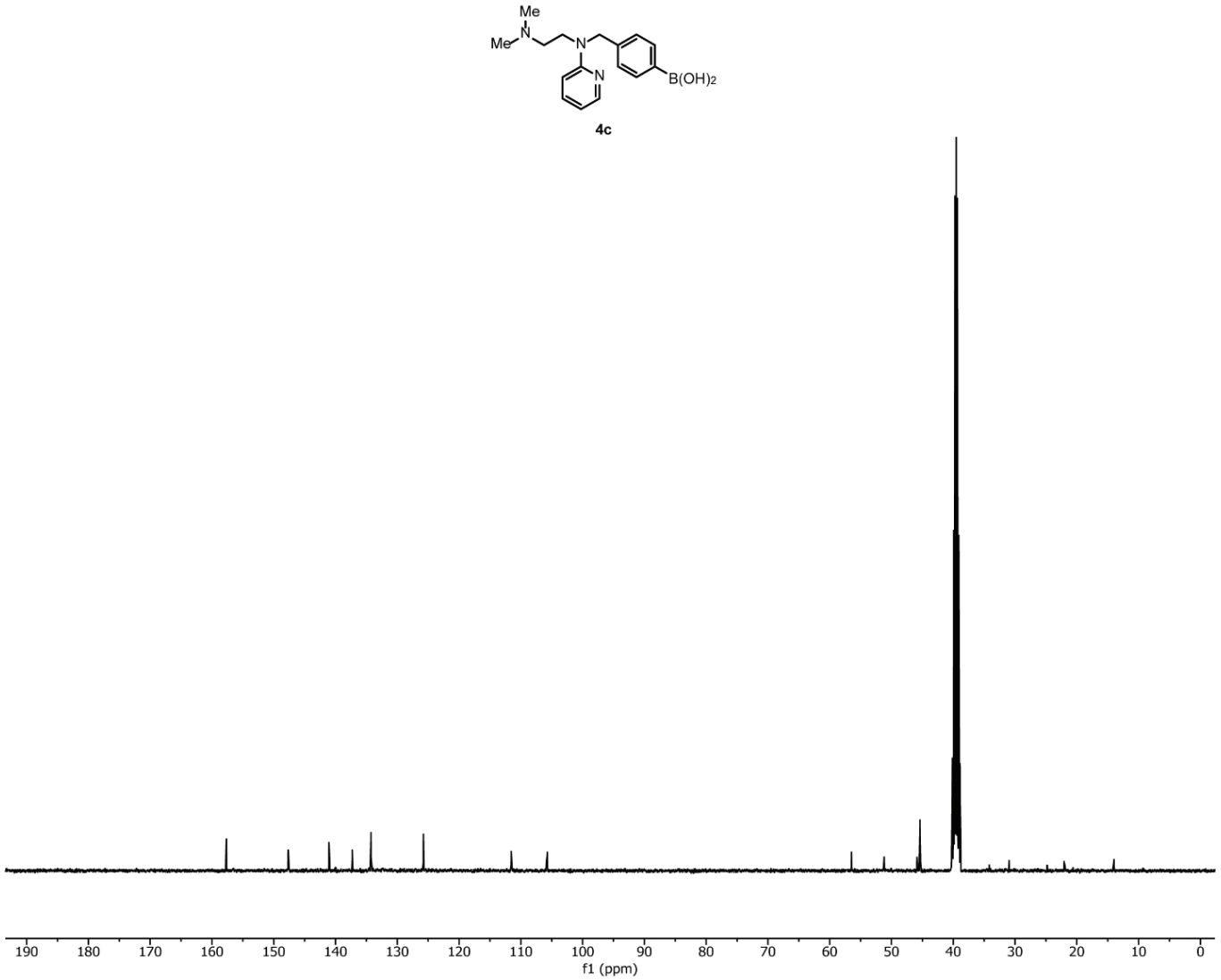


Figure S59. ^{13}C NMR spectrum of (4-(((2-(dimethylamino)ethyl)(pyridin-2-yl)amino)methyl)phenyl)boronic acid (**4c**) in DMSO-d_6 (101 MHz) at 23 °C.

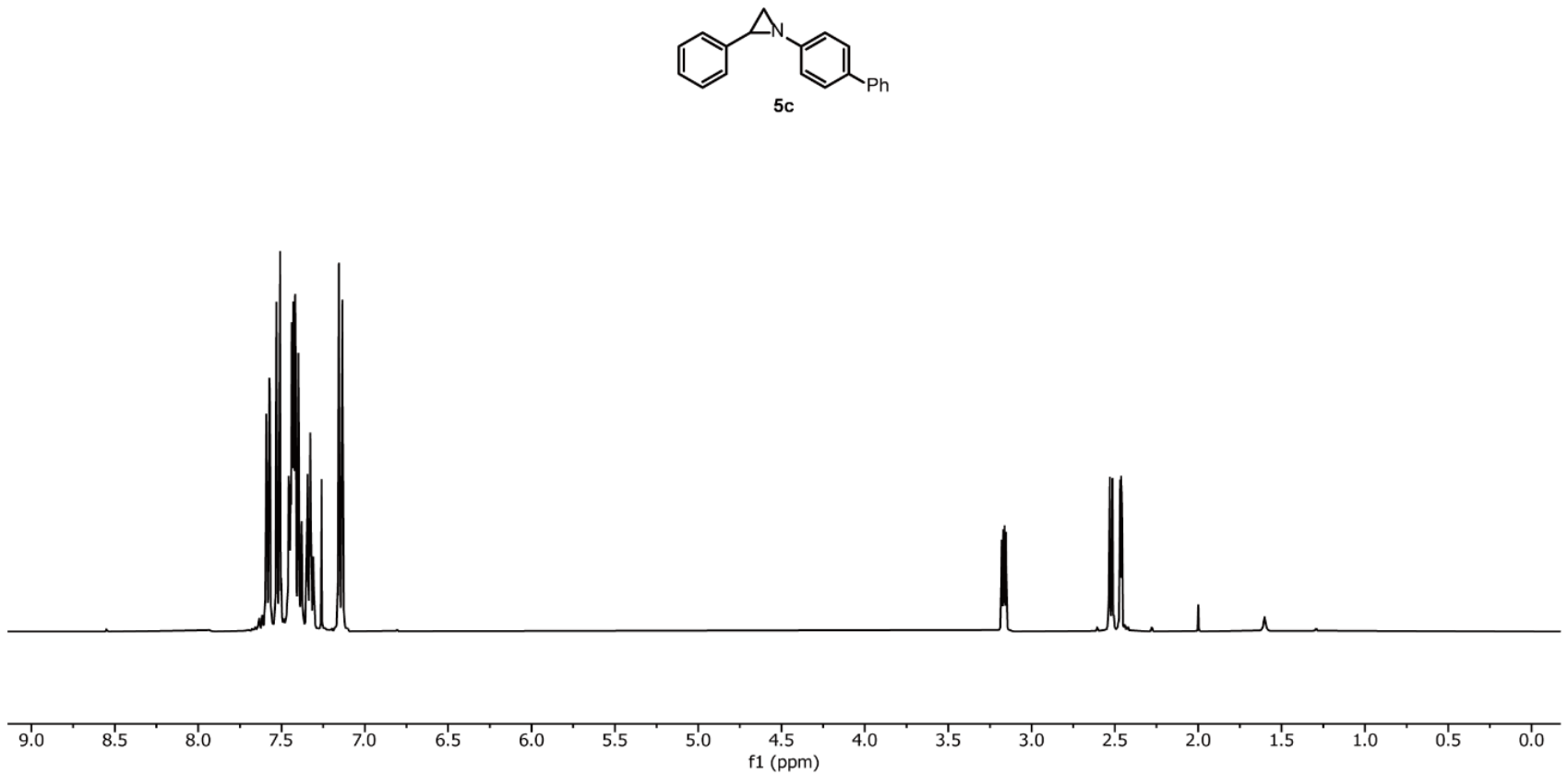


Figure S60. ^{1}H NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-2-phenylaziridine (**5c**) in $CDCl_3$ (400 MHz) at 23 °C.

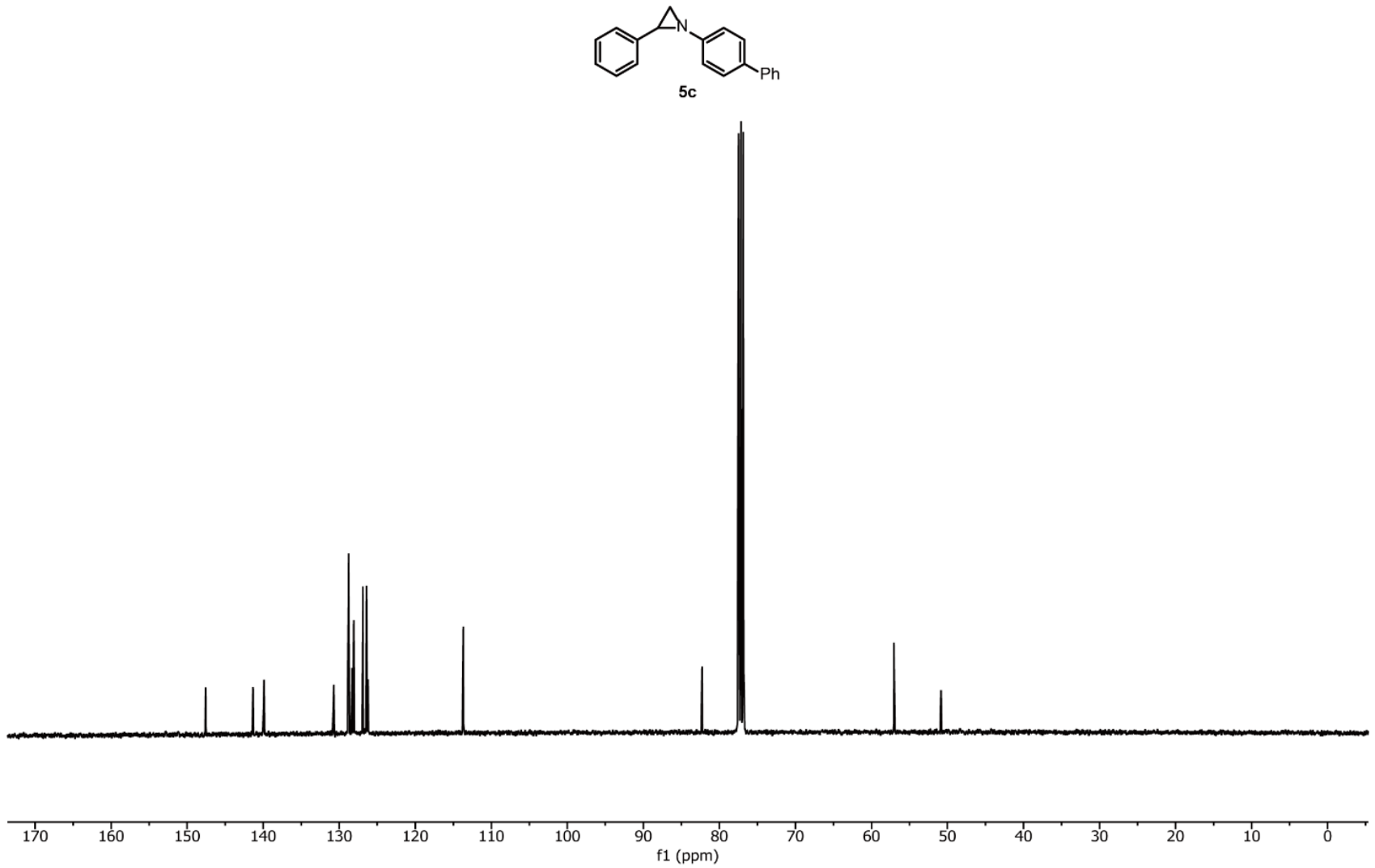


Figure S61. ^{13}C NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-2-phenylaziridine (**5c**) in $CDCl_3$ (101 MHz) at 23 °C.

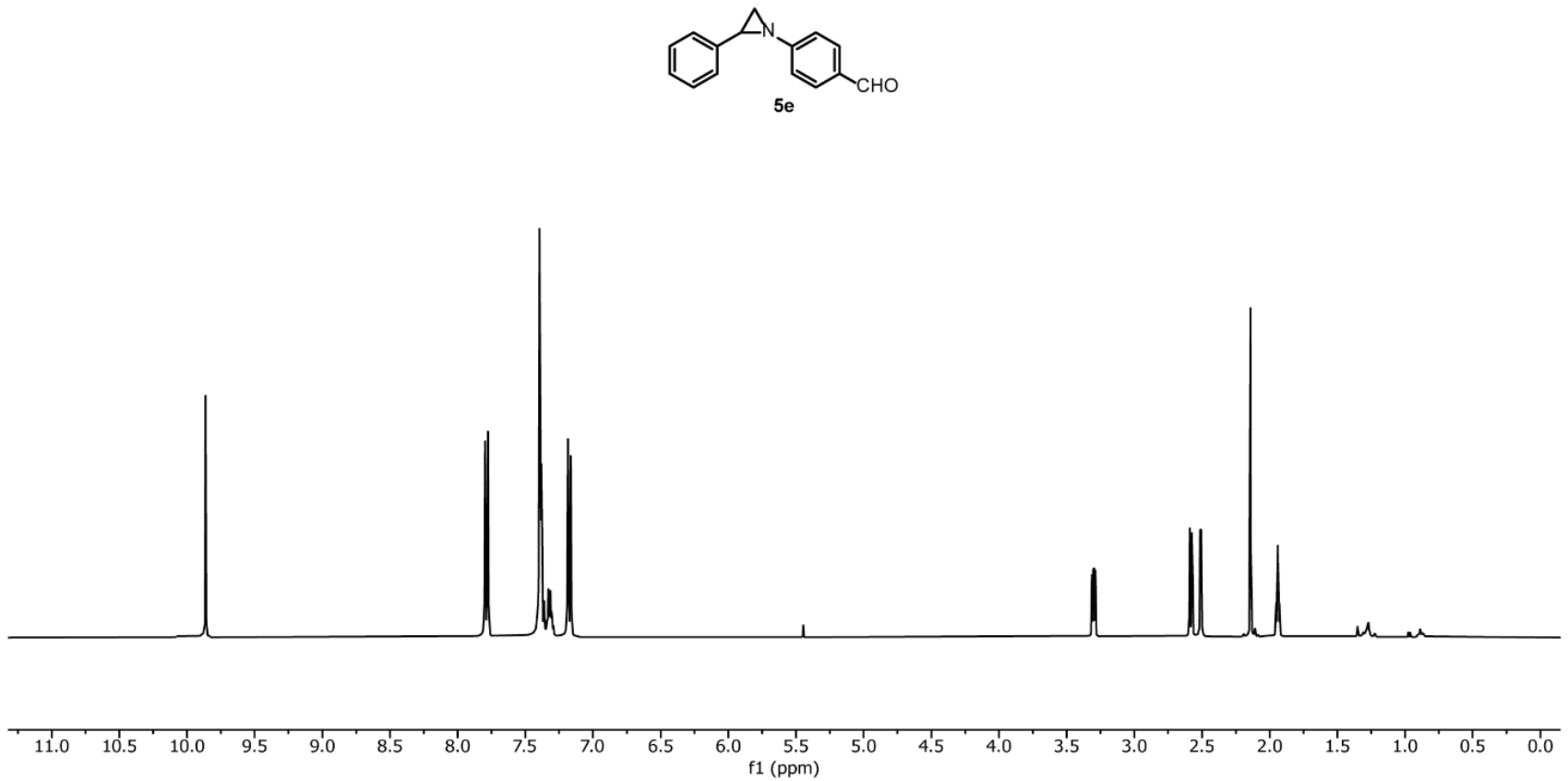


Figure S62. ^{1}H NMR spectrum of 4-(2-phenylaziridin-1-yl)benzaldehyde (**5e**) in CD_3CN (400 MHz) at 23 °C.

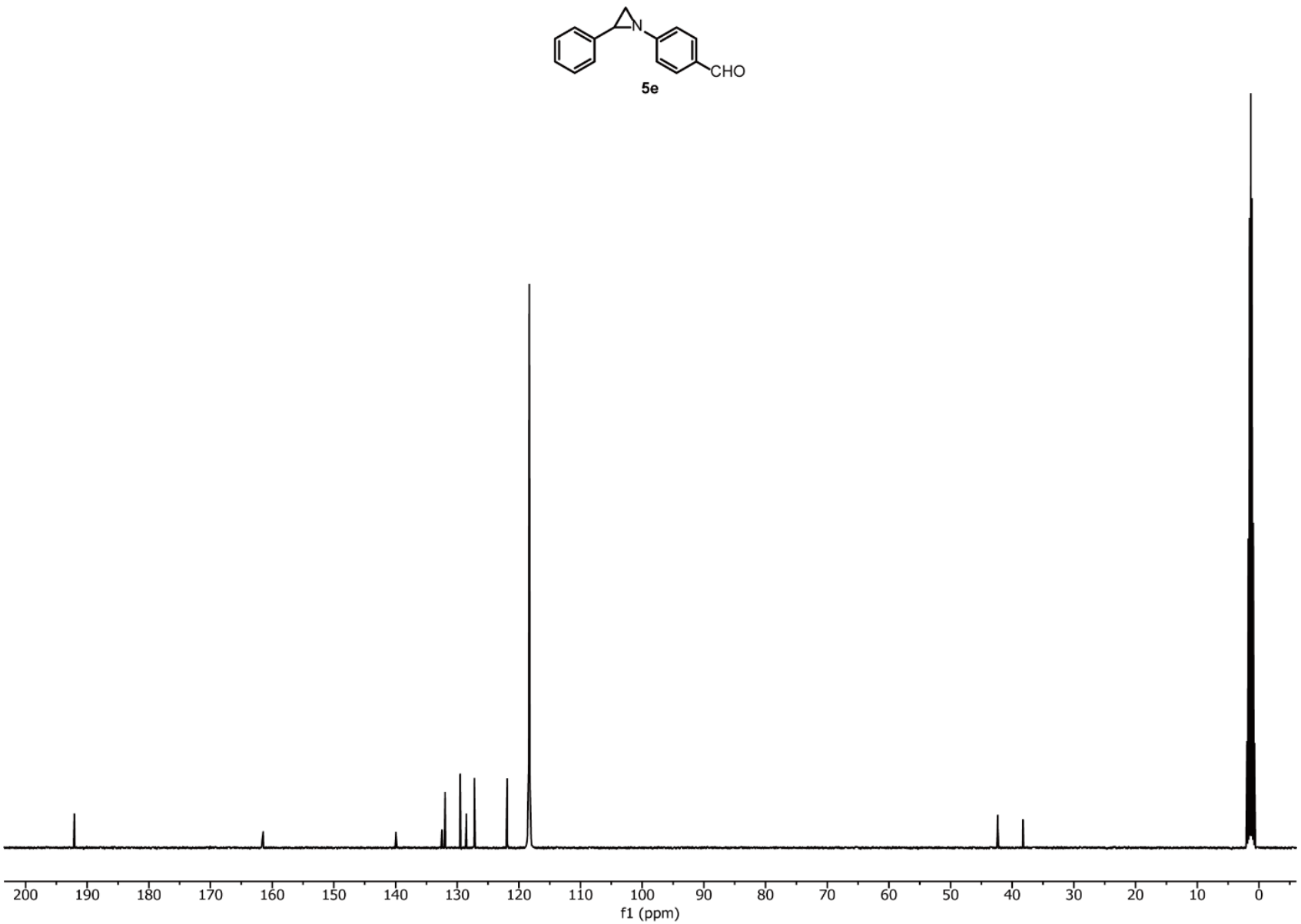


Figure S63. ^{13}C NMR spectrum of 4-(2-phenylaziridin-1-yl)benzaldehyde (**5e**) in CD_3CN (101 MHz) at 23 °C.

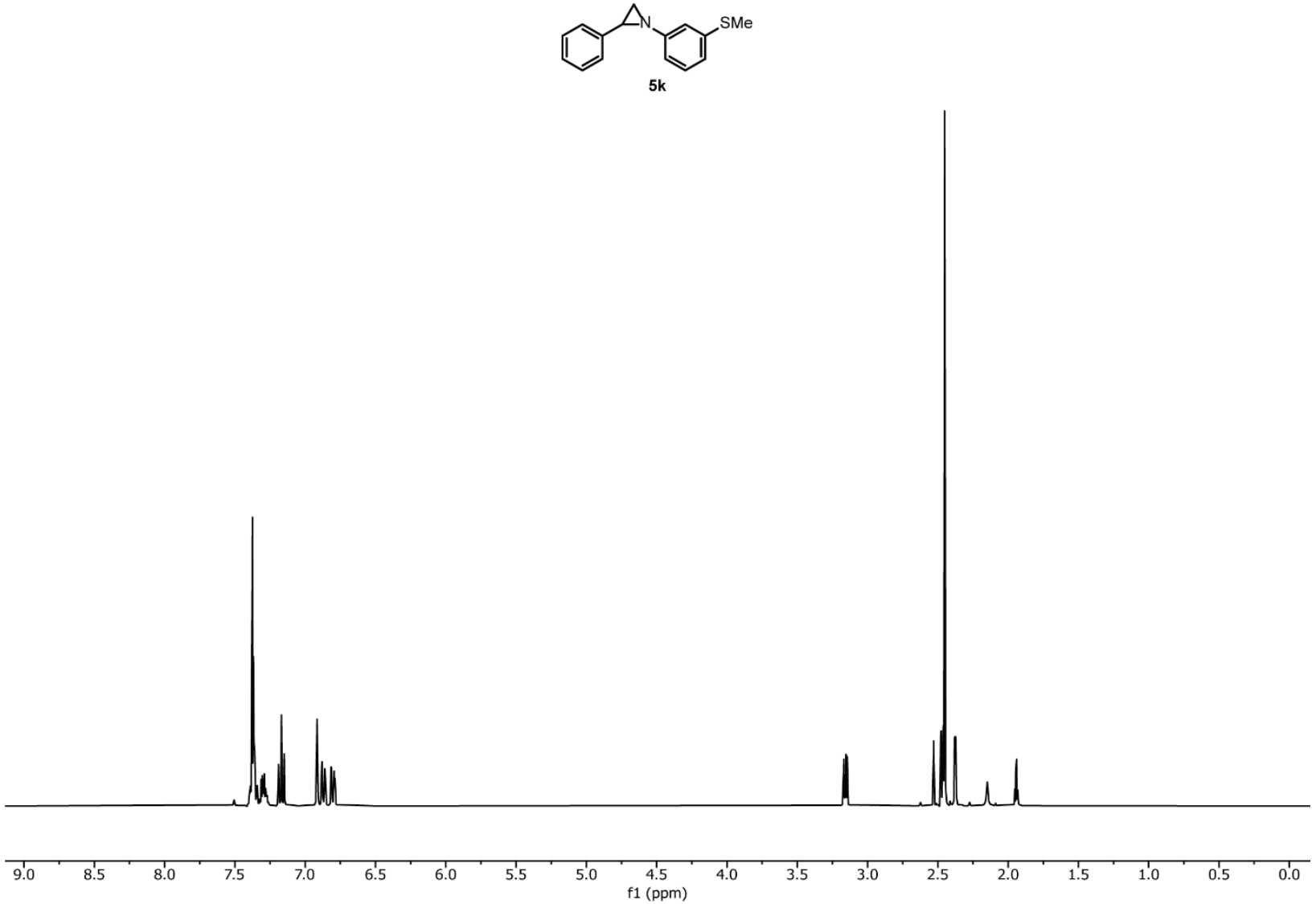


Figure S64. ^{1}H NMR spectrum of 1-(3-(methylthio)phenyl)-2-phenylaziridine (**5k**) in CD_3CN (400 MHz) at 23 °C.

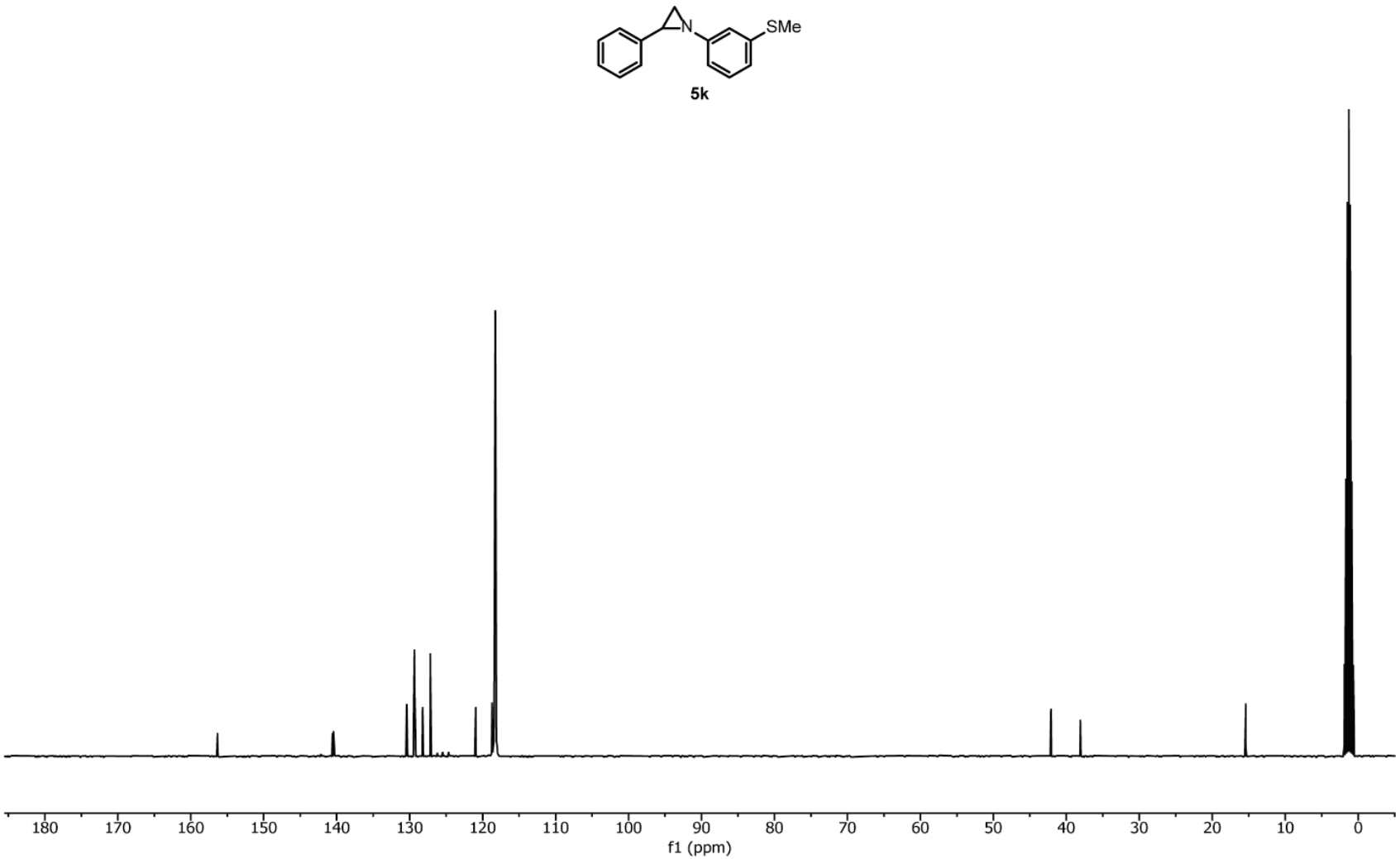


Figure S65. ^{13}C NMR spectrum of 1-(3-(methylthio)phenyl)-2-phenylaziridine (**5k**) in CD_3CN (101 MHz) at 23 °C.

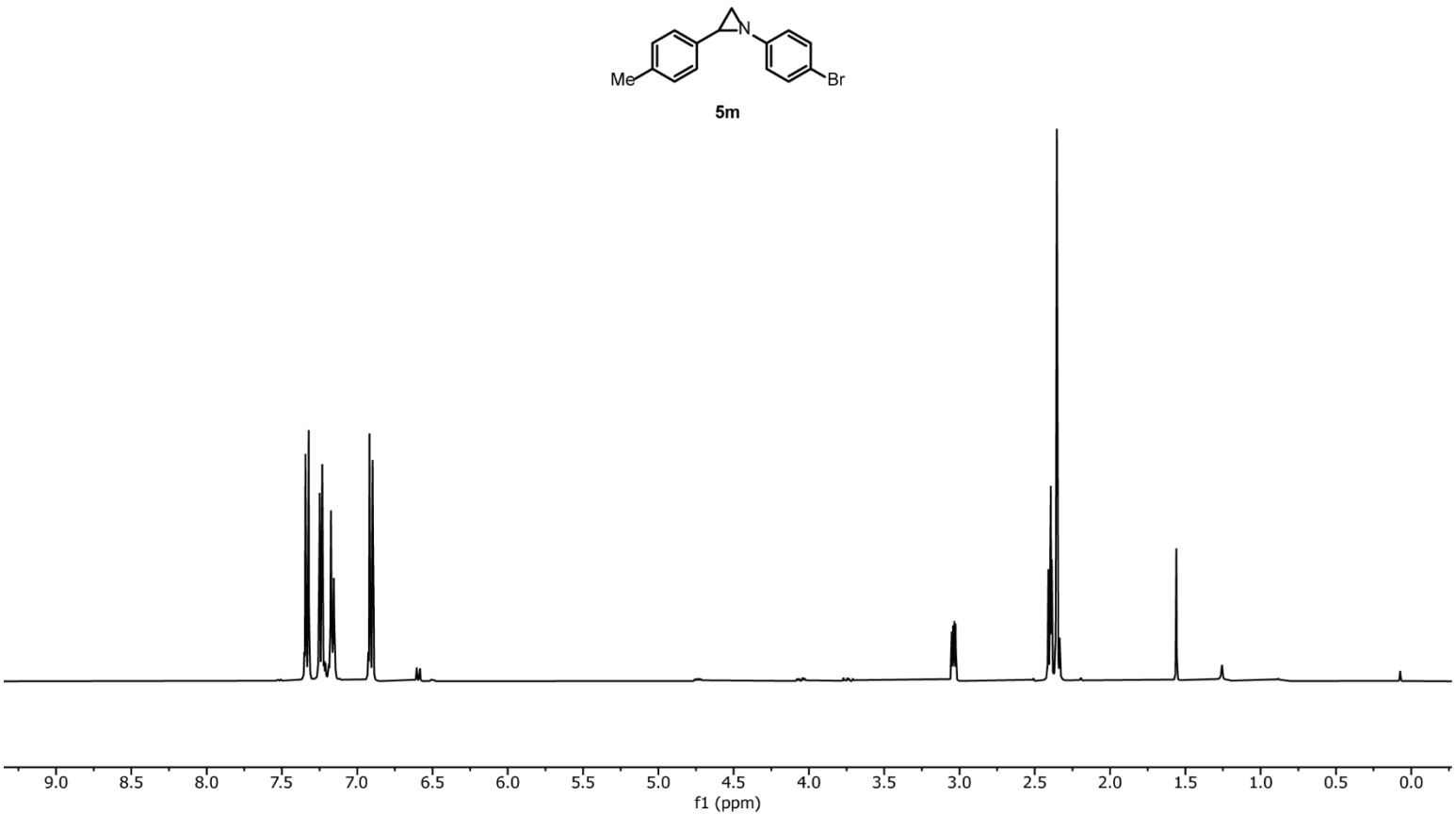


Figure S66. ^{1}H NMR spectrum of 1-(4-bromophenyl)-2-(*p*-tolyl)aziridine (**5m**) in $CDCl_3$ (400 MHz) at 23 °C.

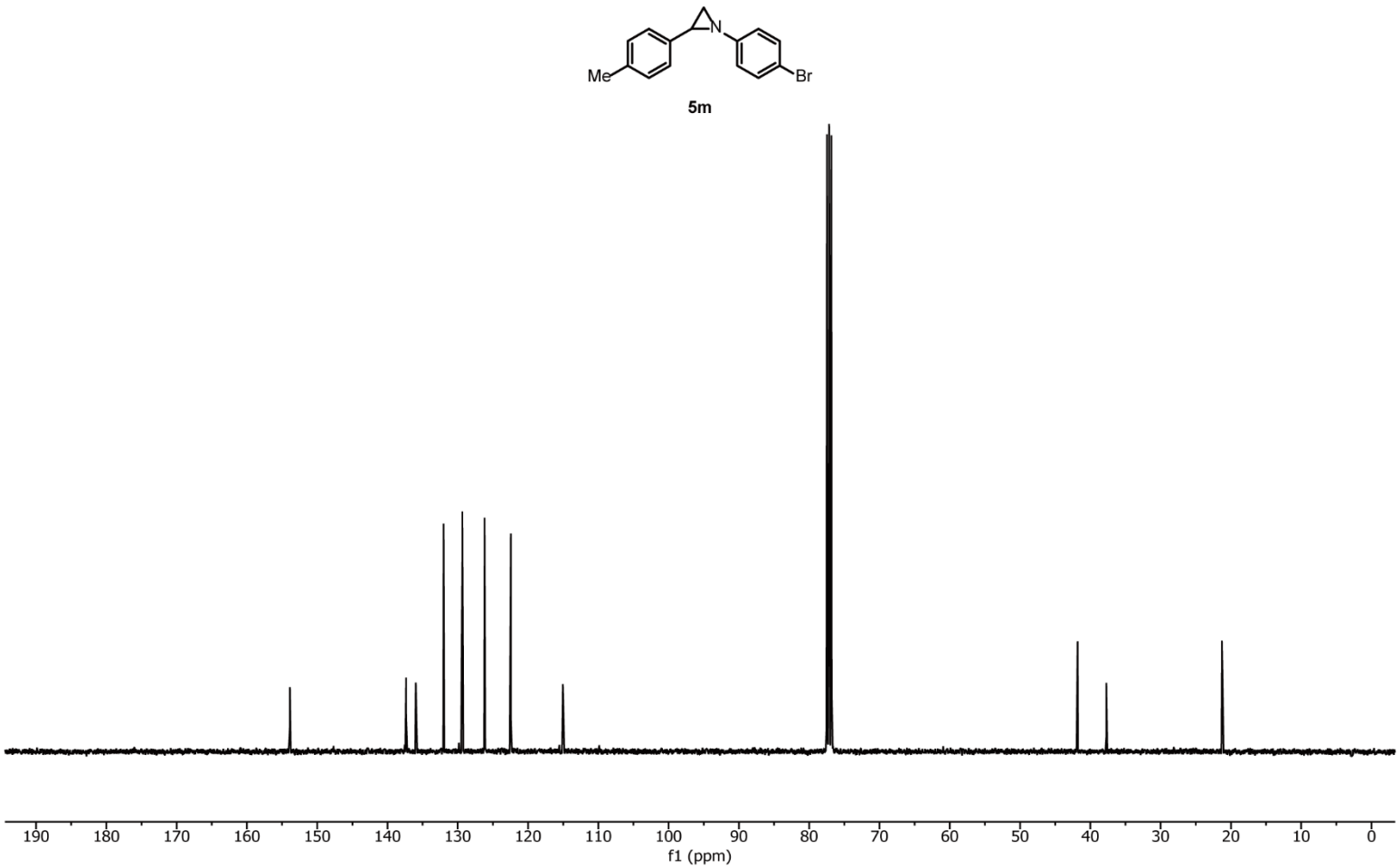


Figure S67. ^{13}C NMR spectrum of 1-(4-bromophenyl)-2-(*p*-tolyl)aziridine (**5m**) in $CDCl_3$ (101 MHz) at 23 °C.

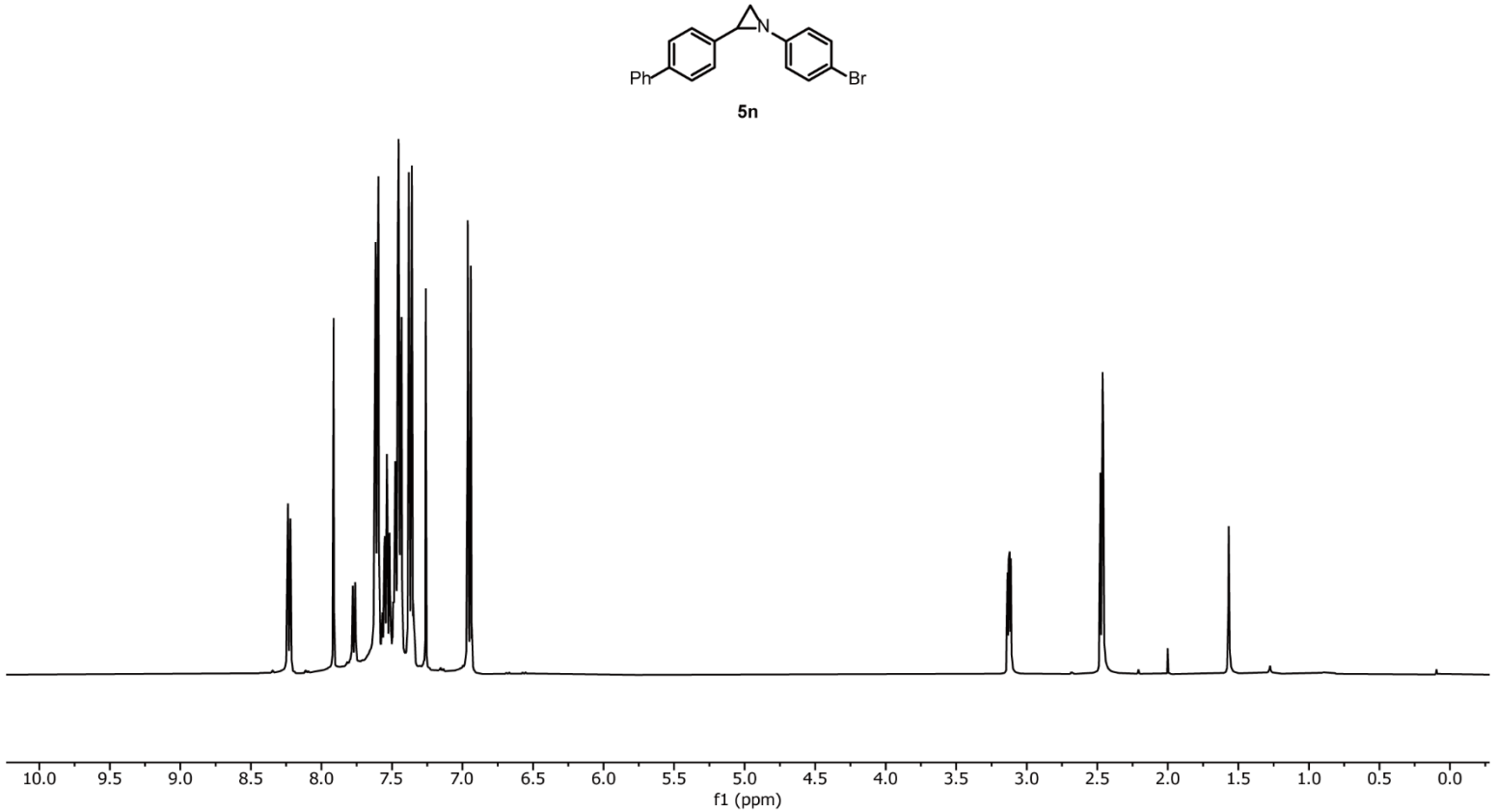


Figure S68. ^{1}H NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-1-(4-bromophenyl)aziridine (**5n**) containing 23% 2,4,6-triphenylpyridine in $CDCl_3$ (400 MHz) at 23 °C

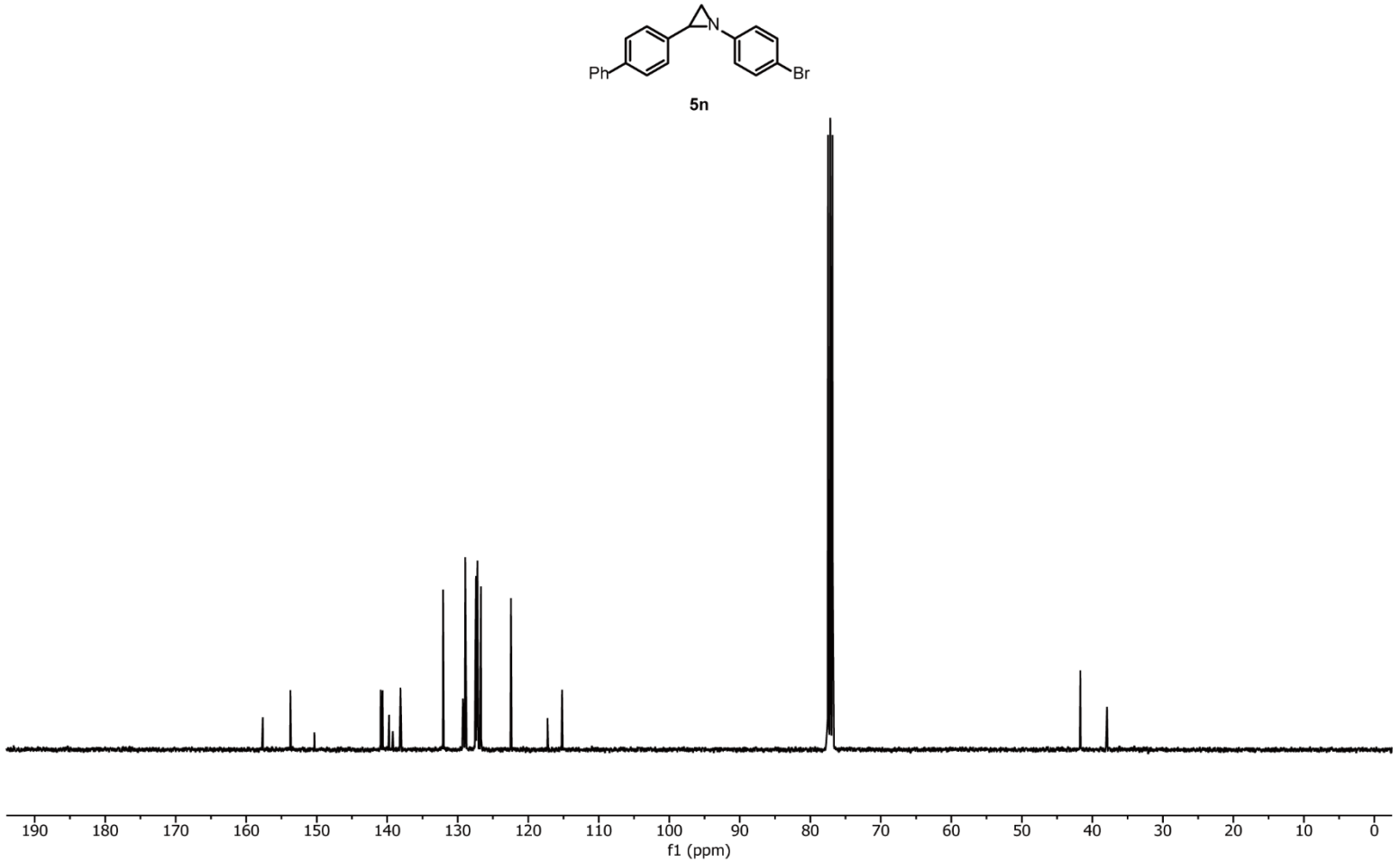


Figure S69. ^{13}C NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-1-(4-bromophenyl)aziridine (**5n**) containing 23% 2,4,6-triphenylpyridine in $CDCl_3$ (101 MHz) at 23 °C.

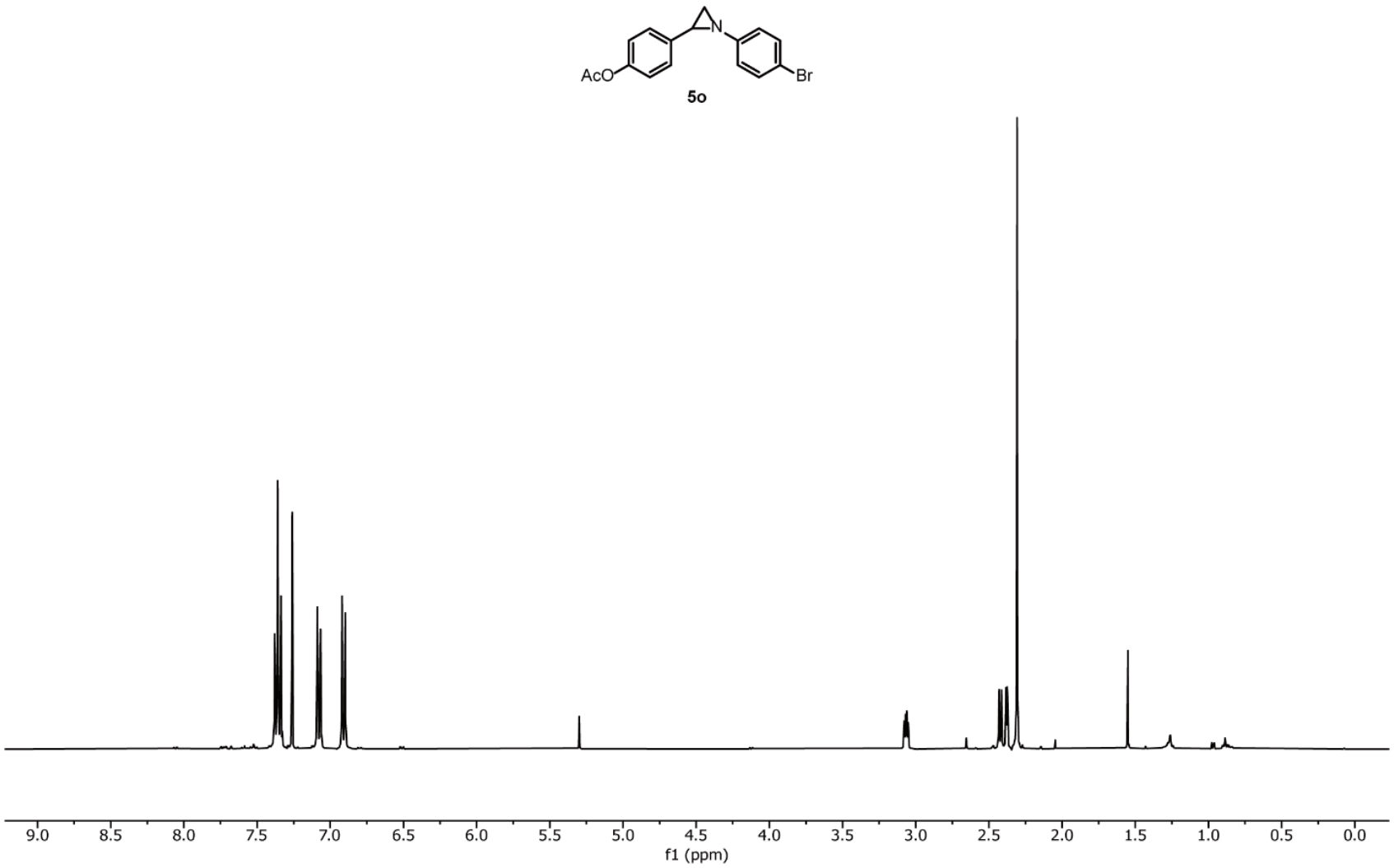


Figure S70. ^{1}H NMR spectrum of 4-(1-(4-bromophenyl)aziridin-2-yl)phenyl acetate (**5o**) in $CDCl_3$ (400 MHz) at 23 °C.

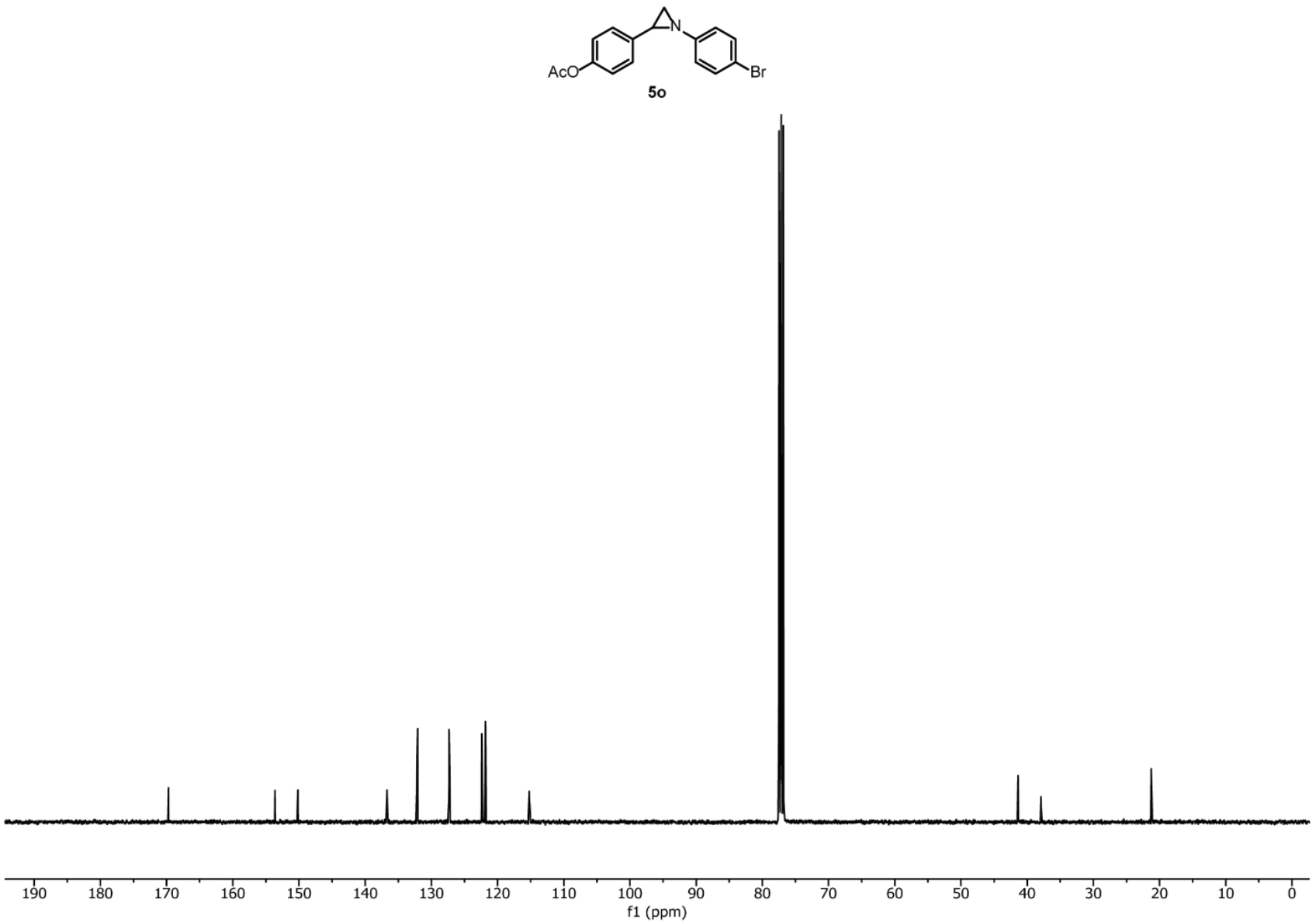


Figure S71. ^{13}C NMR spectrum of 4-(1-(4-bromophenyl)aziridin-2-yl)phenyl acetate (**5o**) in $CDCl_3$ (101 MHz) at 23 °C.

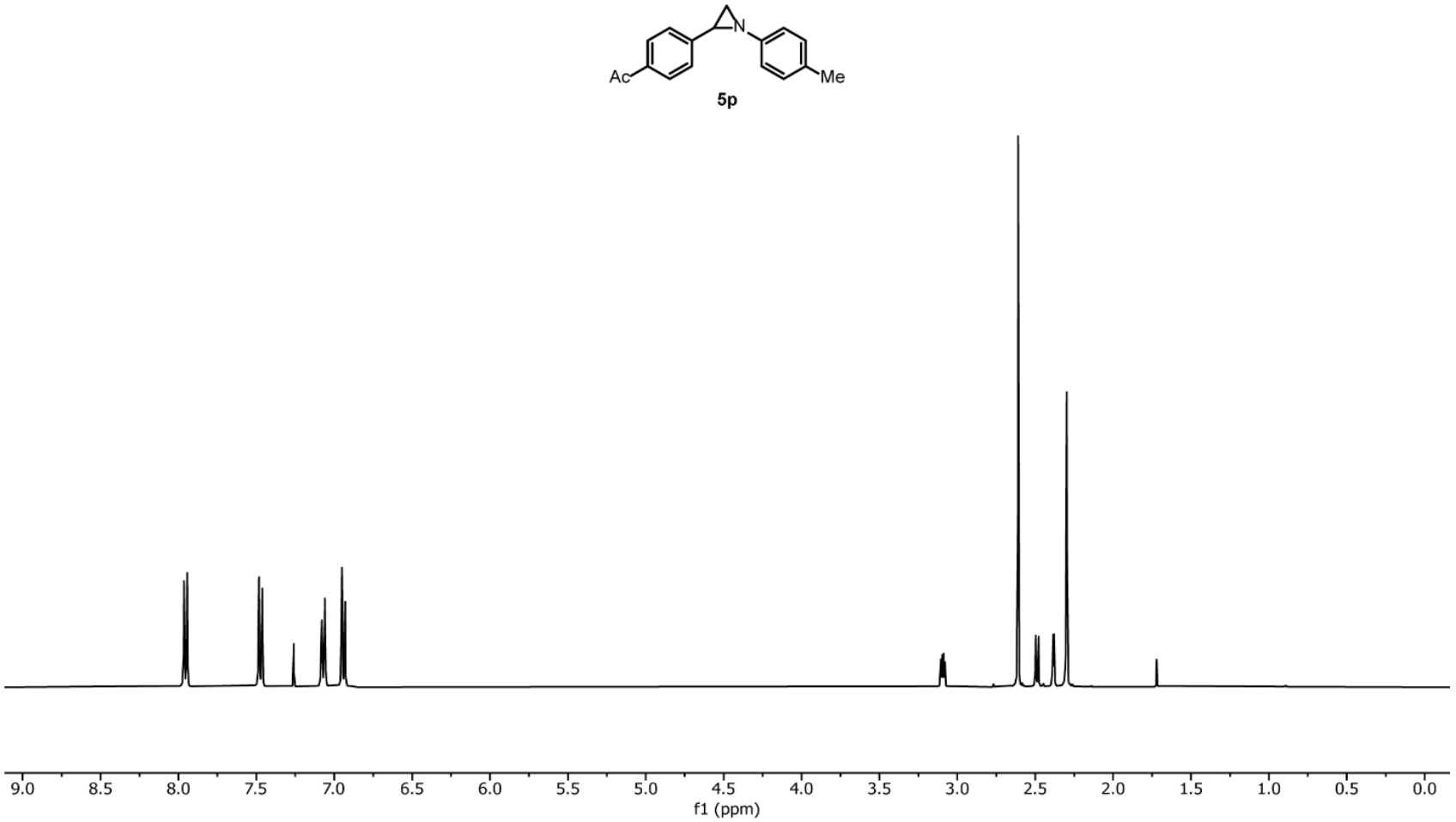


Figure S72. ^{1}H NMR spectrum of 1-(4-(1-(*p*-tolyl)aziridin-2-yl)phenyl)ethan-1-one (**5p**) in $CDCl_3$ (400 MHz) at 23 °C.

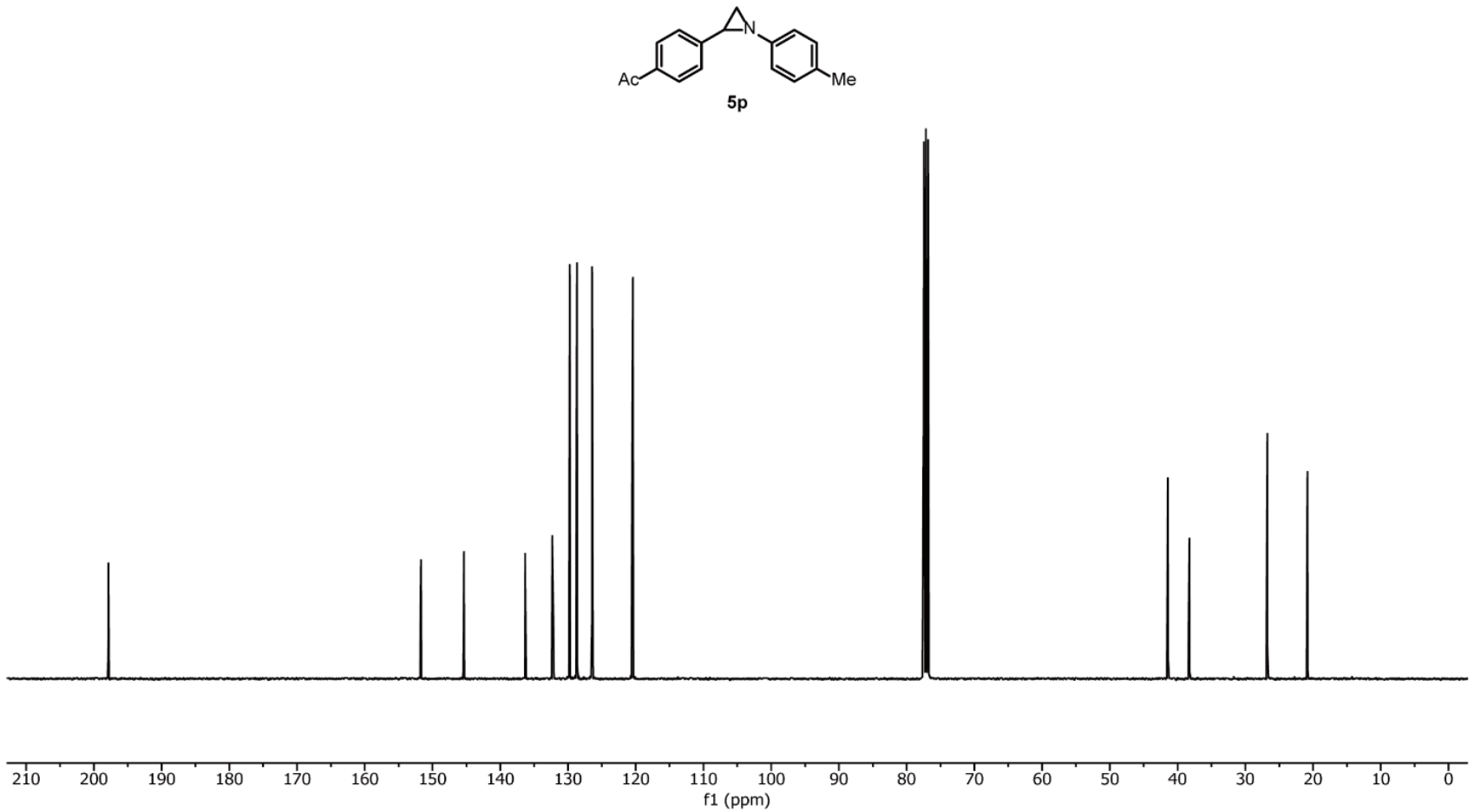


Figure S73. ^{13}C NMR spectrum of 1-(4-(1-(*p*-tolyl)aziridin-2-yl)phenyl)ethan-1-one (**5p**) in $CDCl_3$ (101 MHz) at 23 °C.

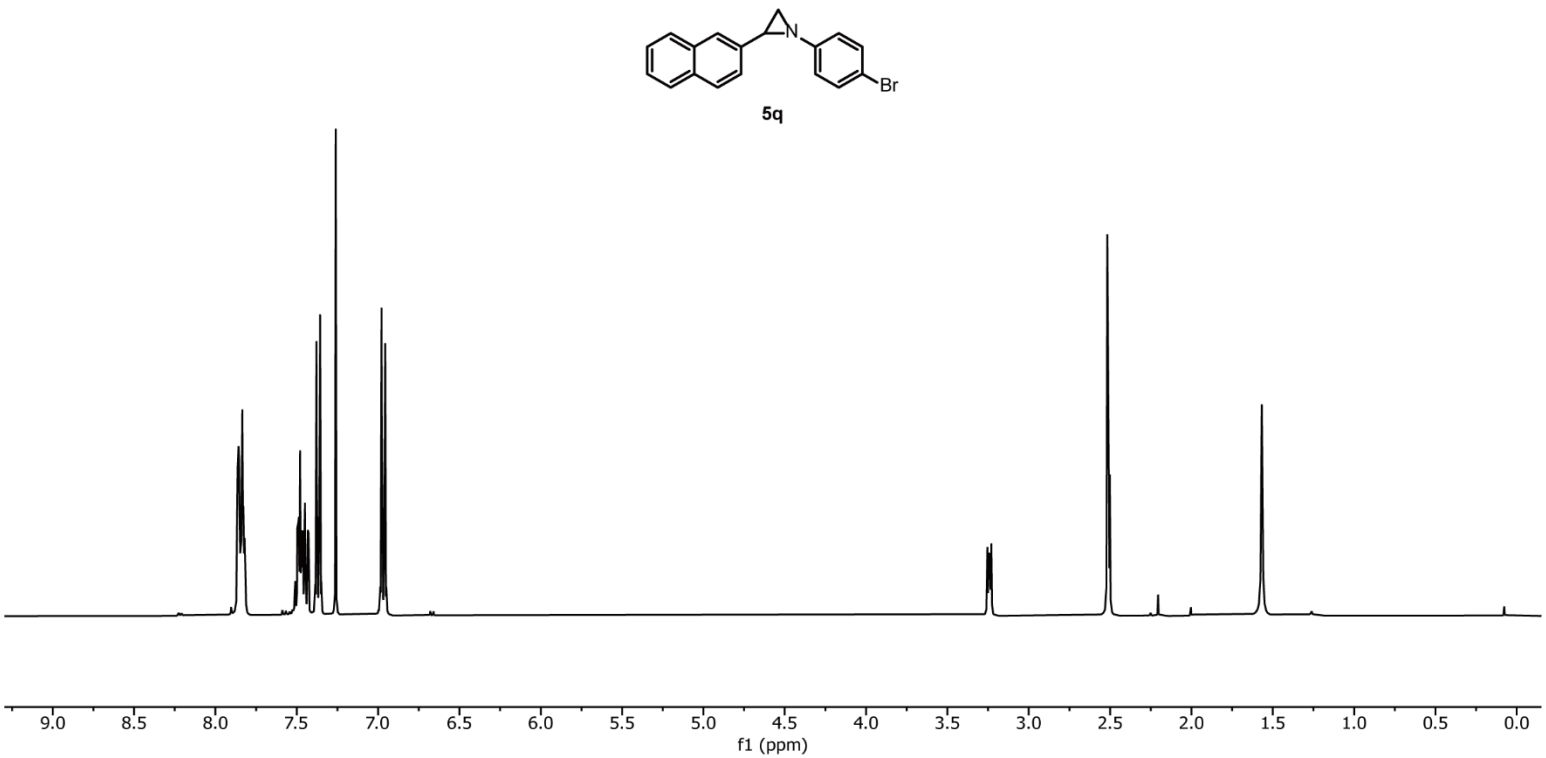


Figure S74. ^{1}H NMR spectrum of 1-(4-bromophenyl)-2-(naphthalen-2-yl)aziridine (**5q**) in $CDCl_3$ (400 MHz) at 23 °C.

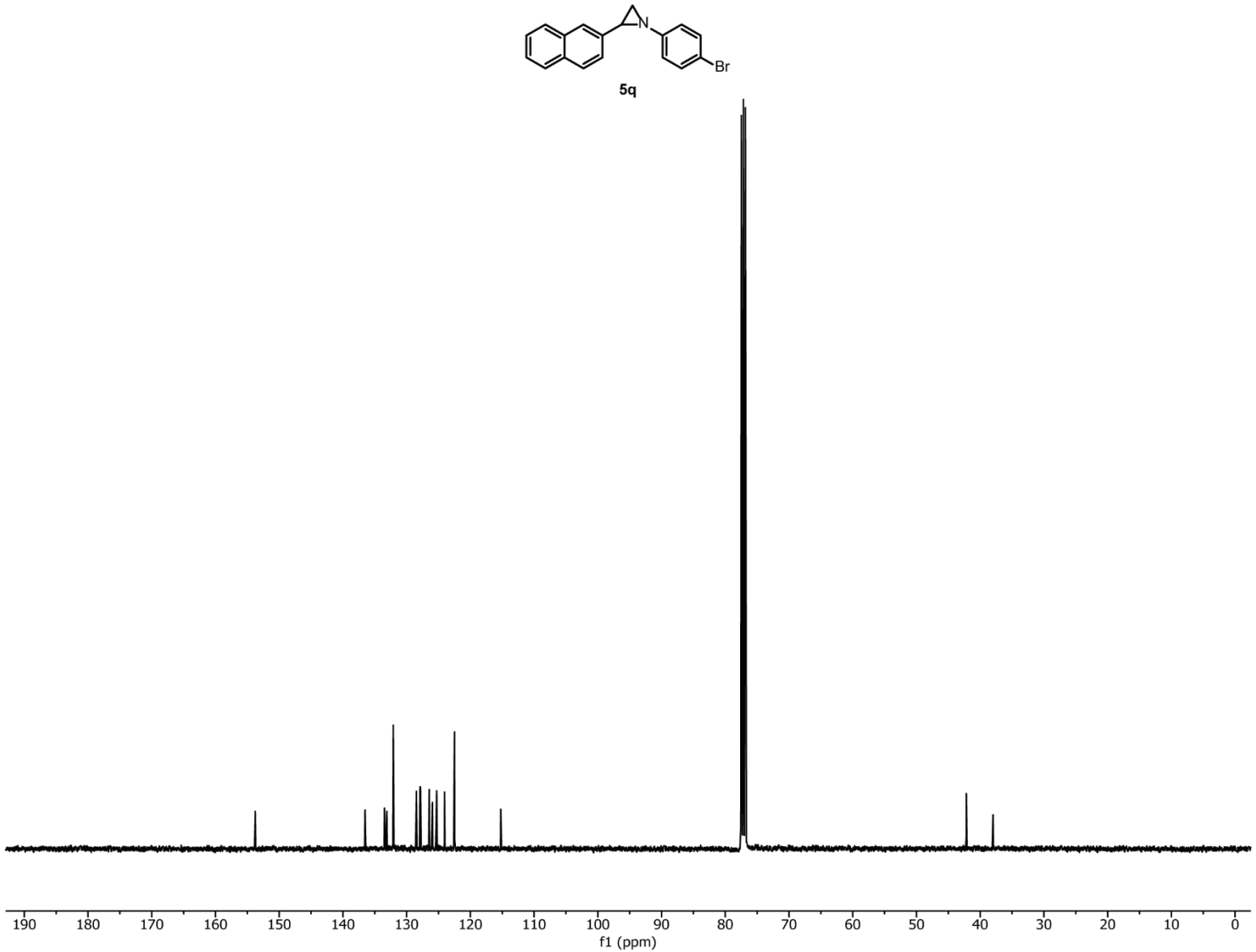


Figure S75. ^{13}C NMR spectrum of 1-(4-bromophenyl)-2-(naphthalen-2-yl)aziridine (**5q**) in $CDCl_3$ (101 MHz) at 23 °C.

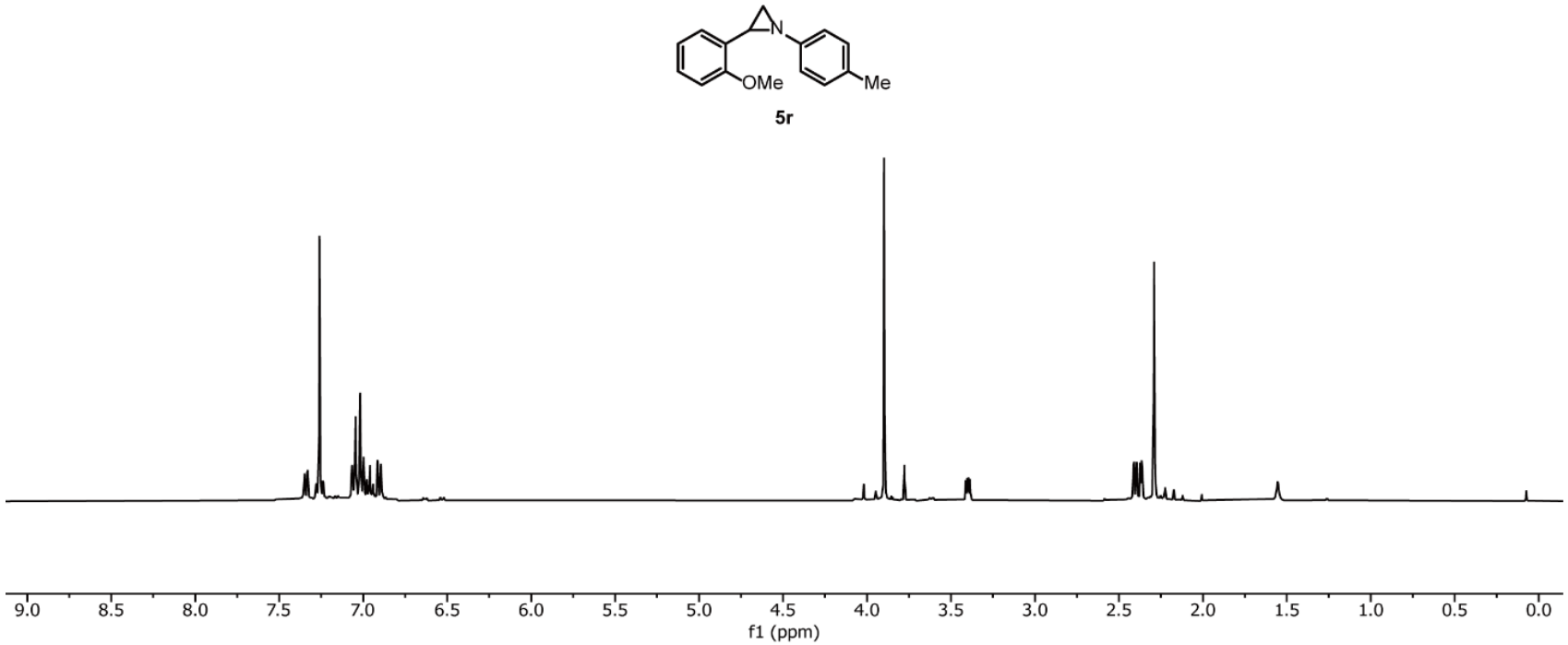


Figure S76. ^{1}H NMR spectrum of 2-(2-methoxyphenyl)-1-(*p*-tolyl)aziridine (**5r**) in $CDCl_3$ (400 MHz) at 23 °C.

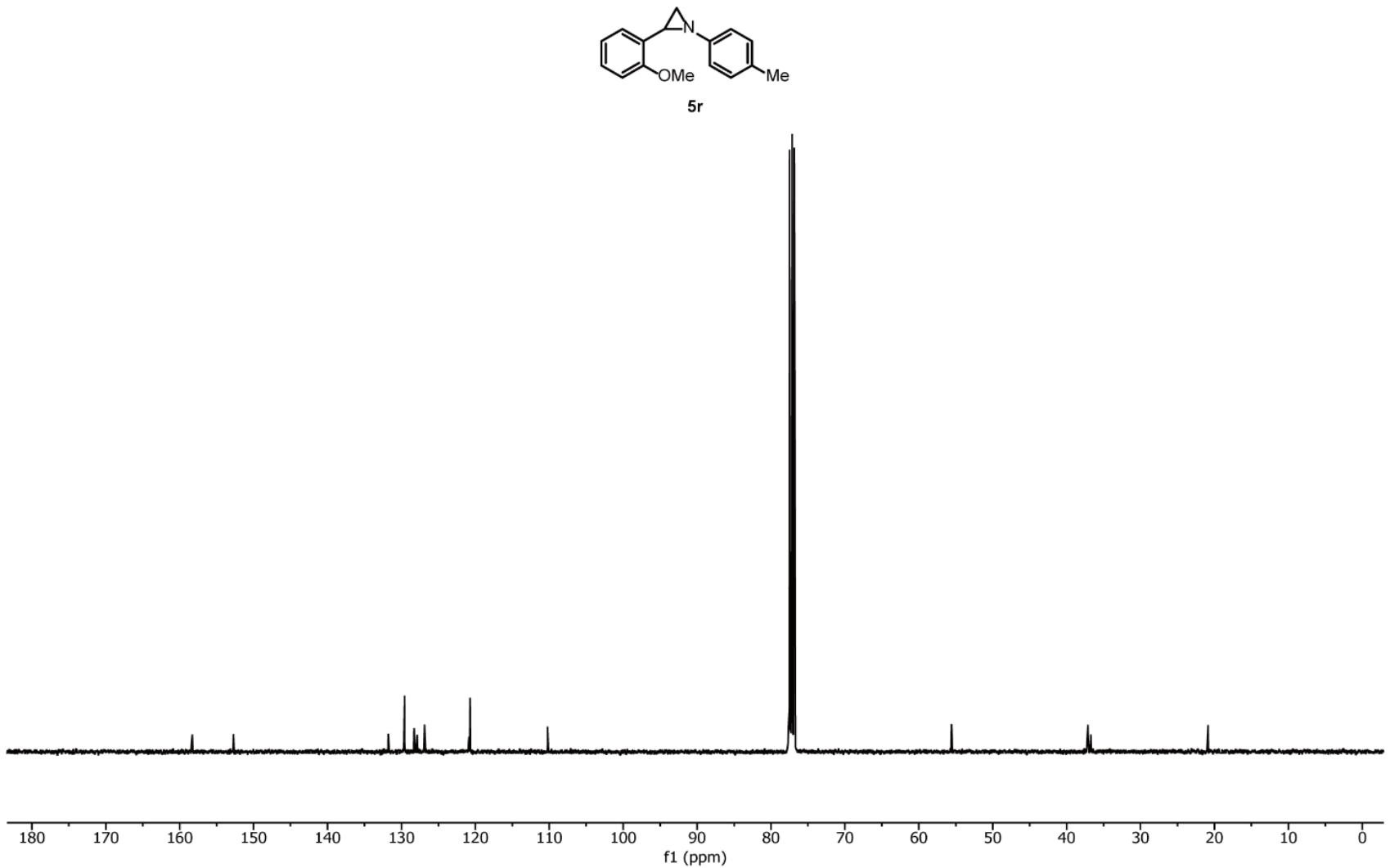


Figure S77. ^{13}C NMR spectrum of 2-(2-methoxyphenyl)-1-(*p*-tolyl)aziridine (**5r**) in $CDCl_3$ (101 MHz) at 23 °C.

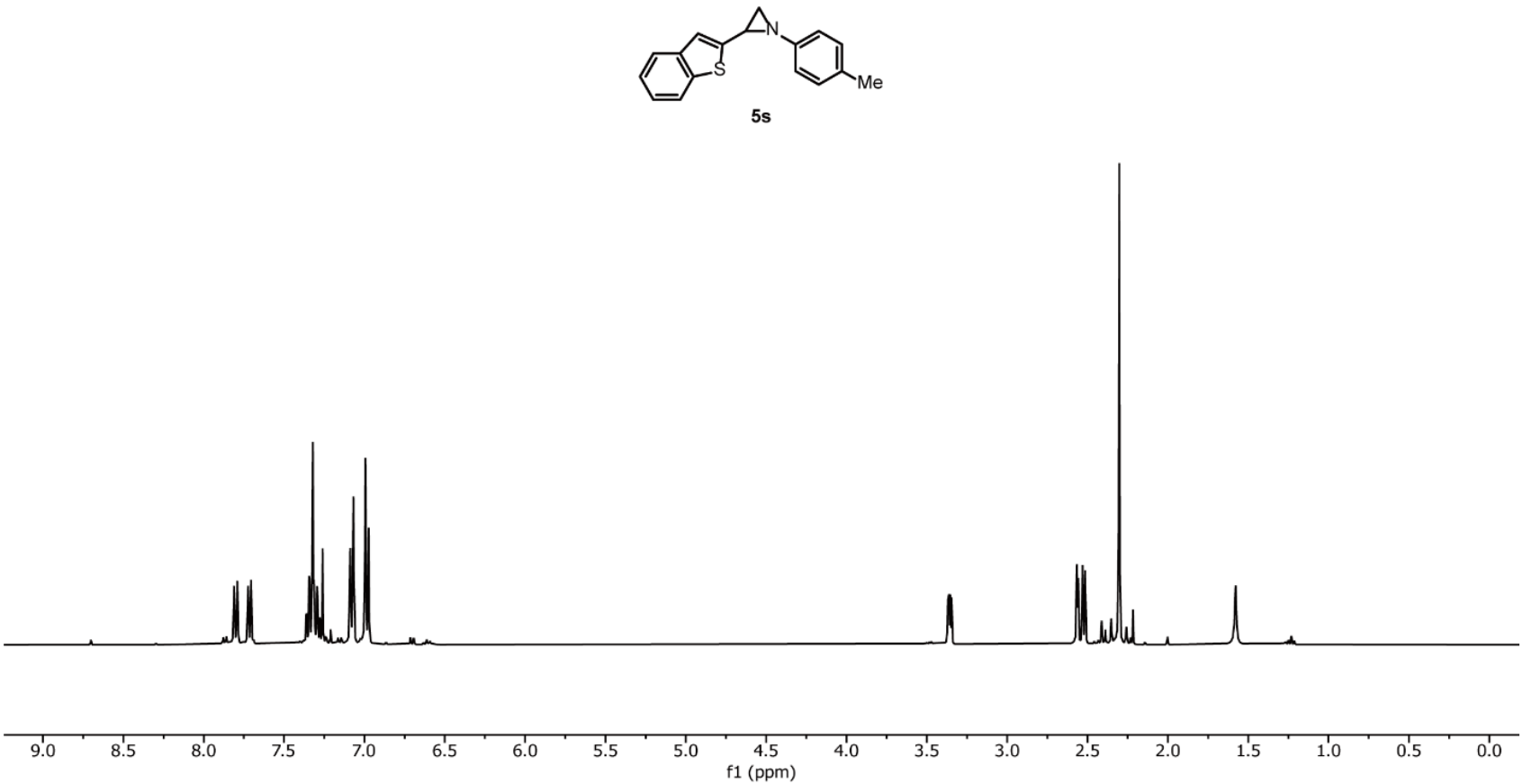


Figure S78. ^{1}H NMR spectrum of 2-(benzo[*b*]thiophen-2-yl)-1-(*p*-tolyl)aziridine (**5s**) in $CDCl_3$ (400 MHz) at 23 °C.

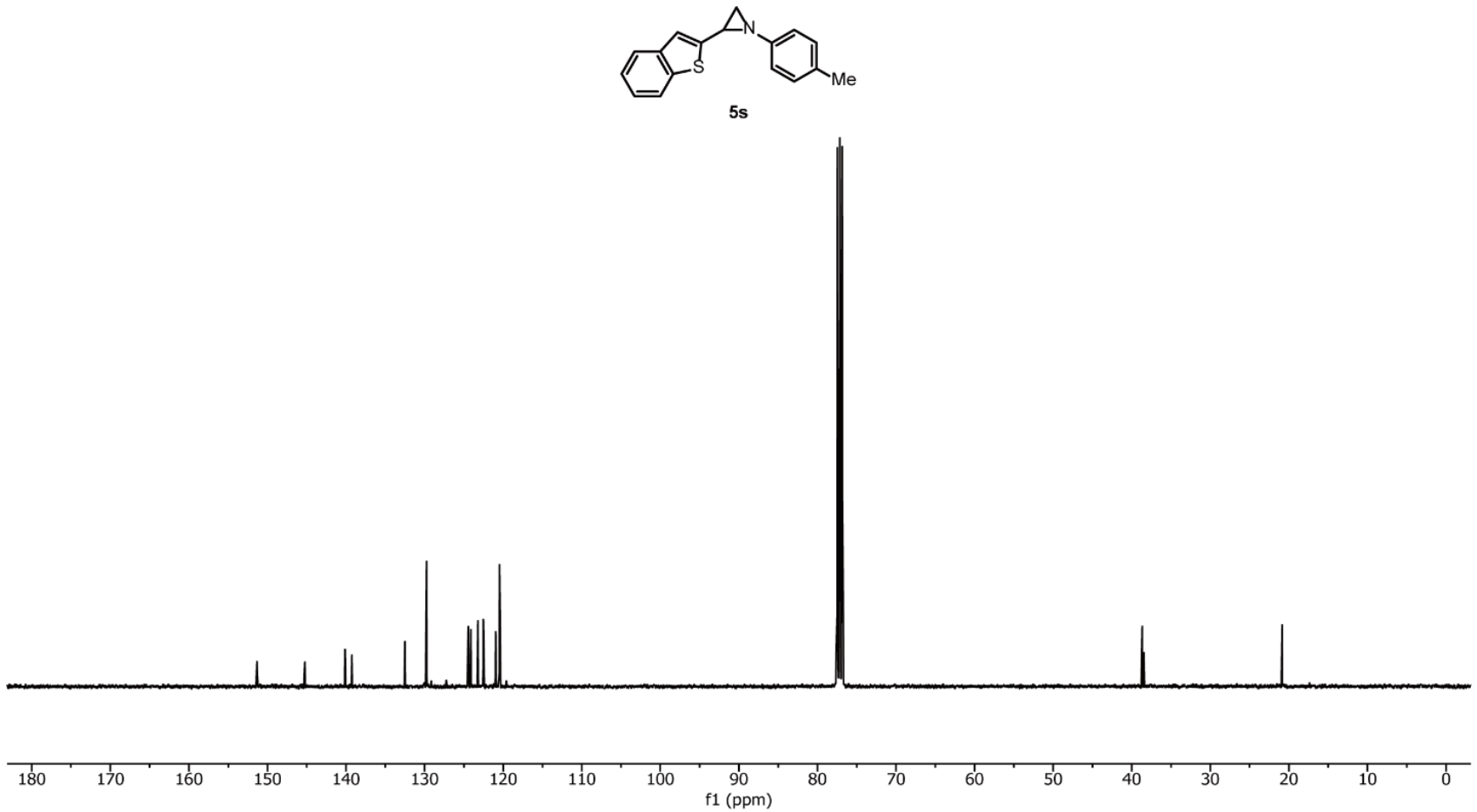


Figure S79. ^{13}C NMR spectrum of 2-(benzo[*b*]thiophen-2-yl)-1-(*p*-tolyl)aziridine (**5s**) in $CDCl_3$ (101 MHz) at 23 °C.

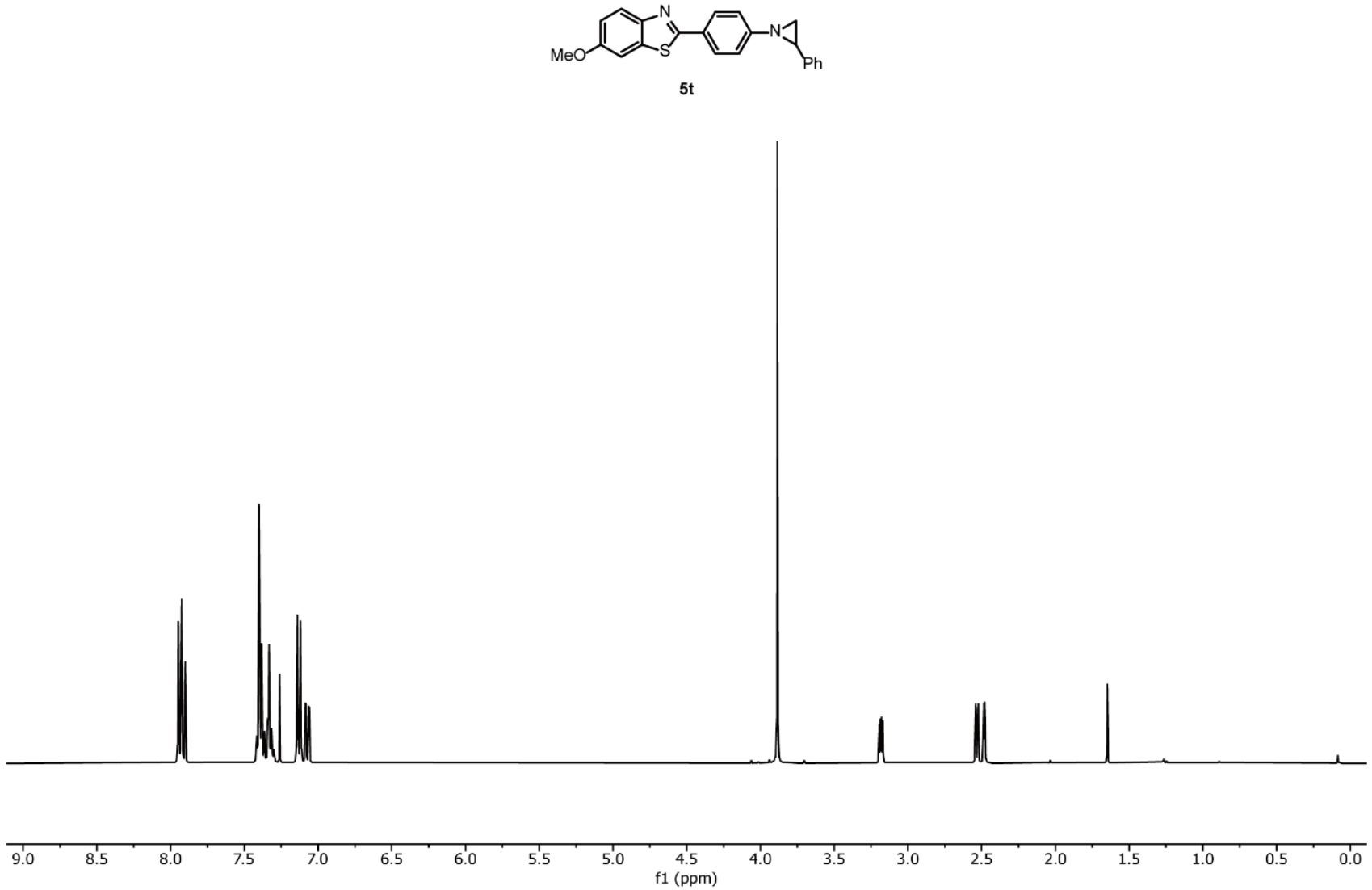


Figure S80. ^{1}H NMR spectrum of 6-methoxy-2-(4-(2-phenylaziridin-1-yl)phenyl)benzo[*d*]thiazole (**5t**) in $CDCl_3$ (400 MHz) at 23 °C.

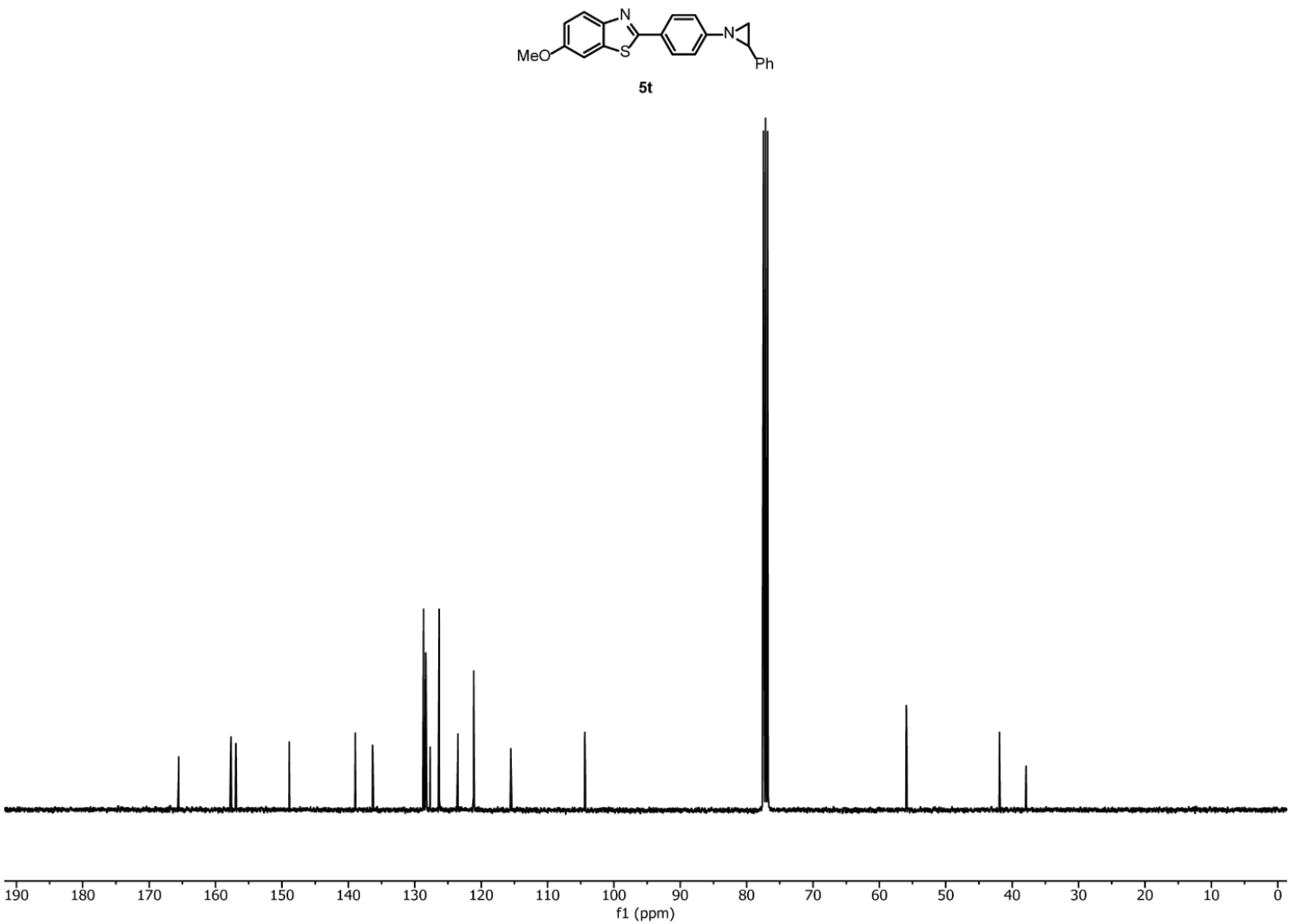


Figure S81. ^{13}C NMR spectrum of 6-methoxy-2-(4-(2-phenylaziridin-1-yl)phenyl)benzo[*d*]thiazole (**5t**) in $CDCl_3$ (101 MHz) at 23 °C.

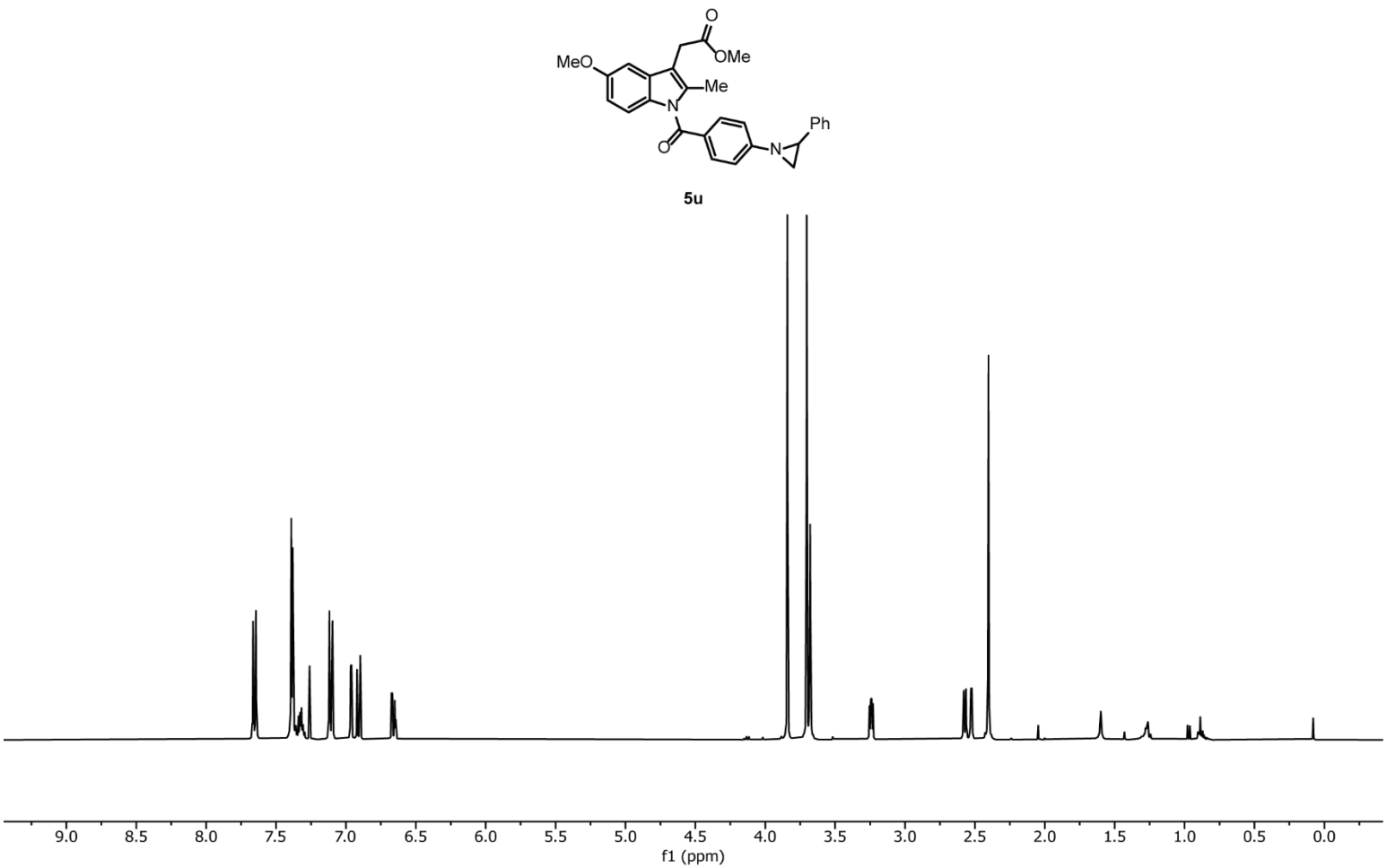


Figure S82. ^{1}H NMR spectrum of methyl 2-(5-methoxy-2-methyl-1-(4-(2-phenylaziridin-1-yl)benzoyl)-1*H*-indol-3-yl)acetate (**5u**) in $CDCl_3$ (400 MHz) at 23 °C.

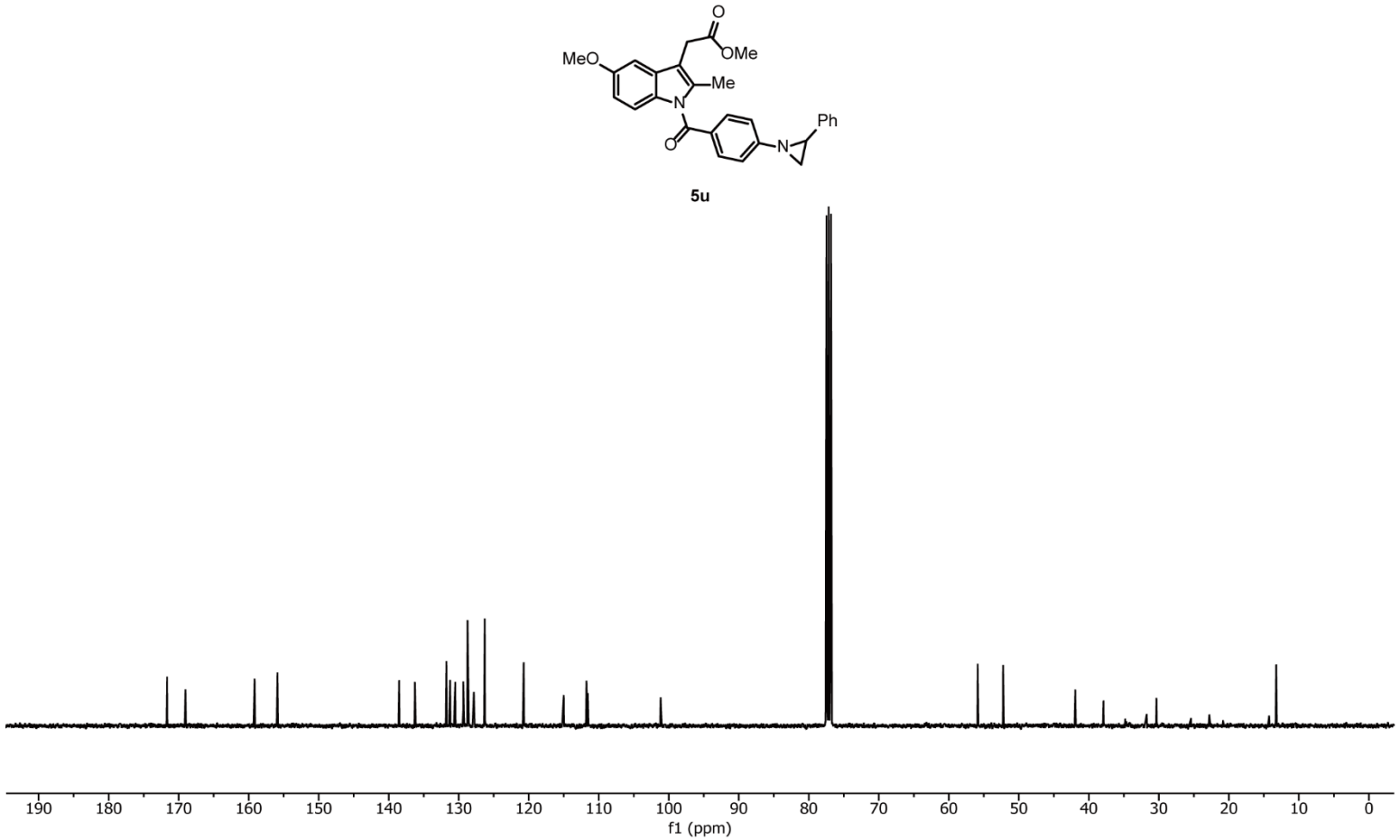


Figure S83. ^{13}C NMR spectrum of methyl 2-(5-methoxy-2-methyl-1-(4-(2-phenylaziridin-1-yl)benzoyl)-1*H*-indol-3-yl)acetate (**5u**) in $CDCl_3$ (101 MHz) at 23 °C.

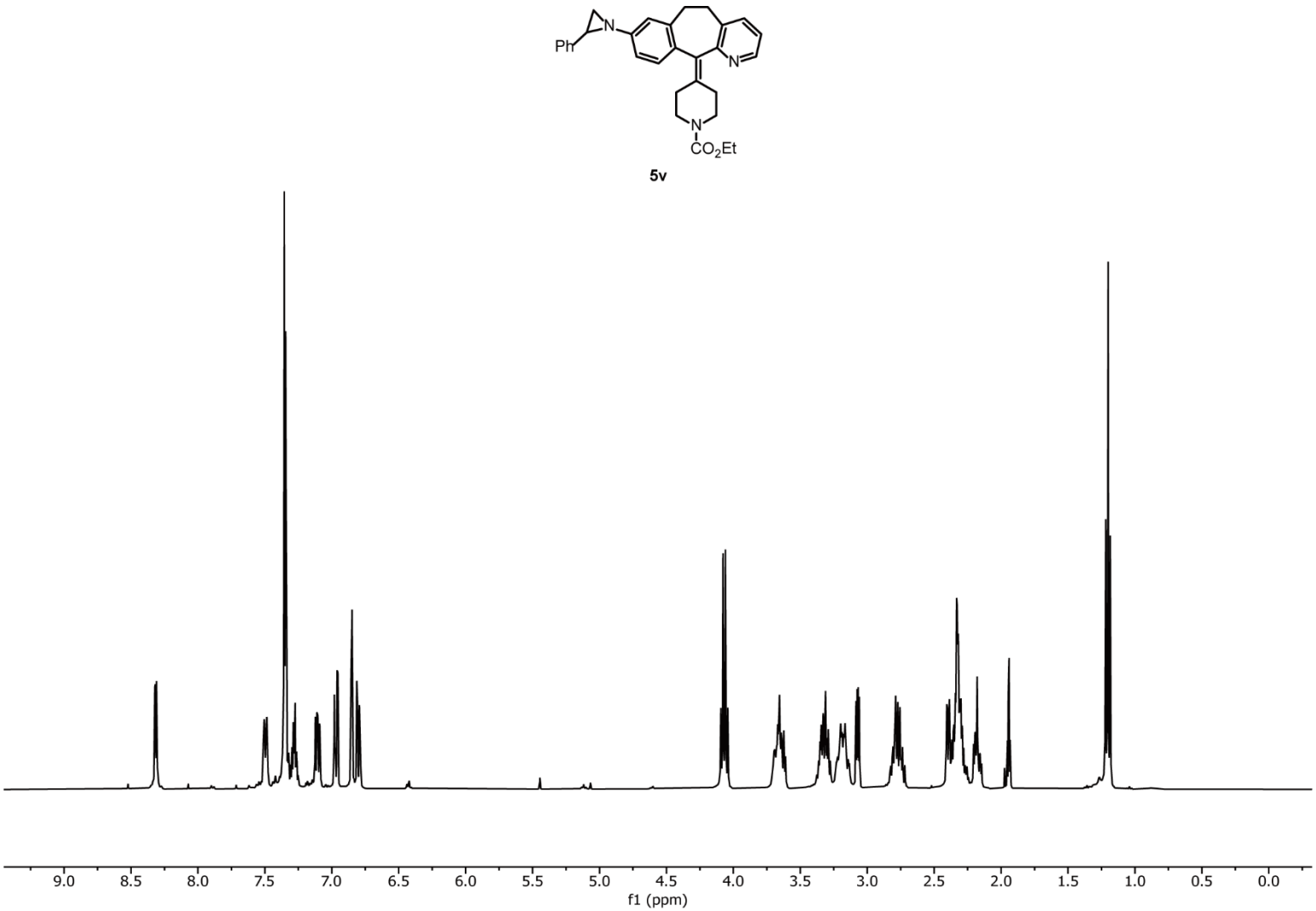


Figure S84. ^{1}H NMR spectrum of ethyl 4-(8-(2-phenylaziridin-1-yl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (**5v**) in $CDCl_3$ (400 MHz) at 23 °C.

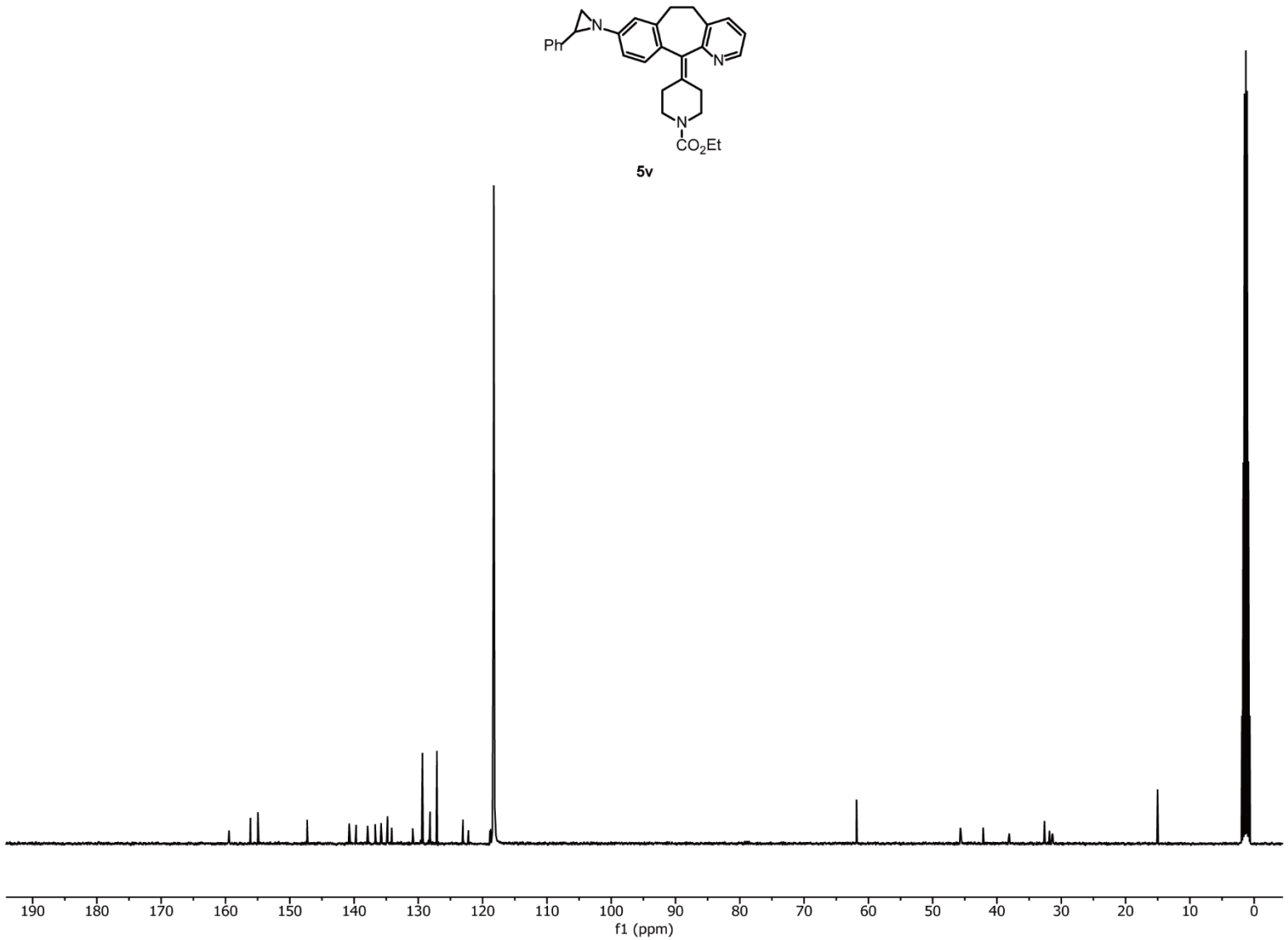


Figure S85. ^{13}C NMR spectrum of ethyl 4-(8-(2-phenylaziridin-1-yl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (**5v**) in $CDCl_3$ (101 MHz) at 23 °C.

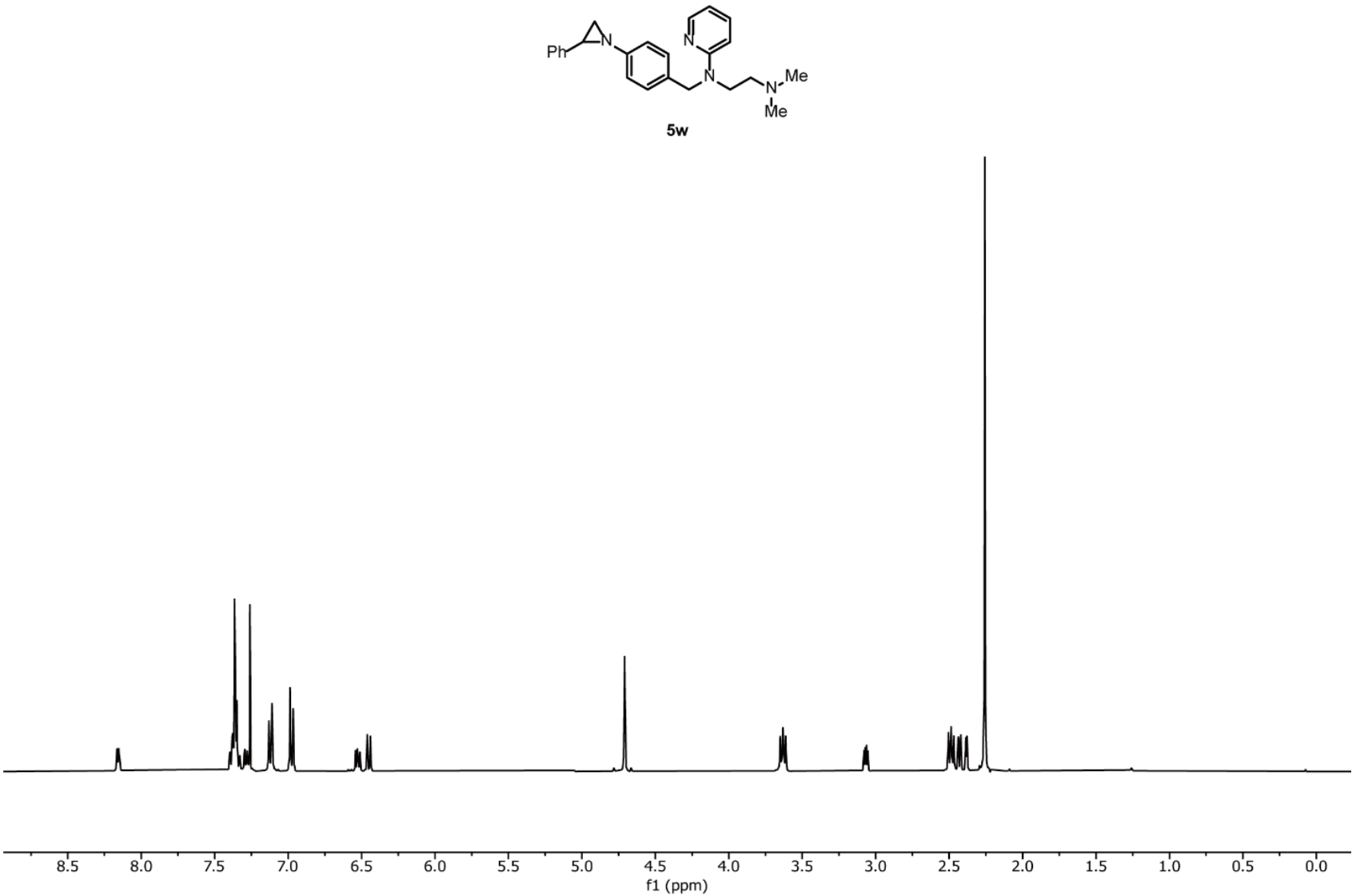


Figure S86. ^{1}H NMR spectrum of N^1,N^1-dimethyl-N^2-(4-(2-phenylaziridin-1-yl)benzyl)-N^2-(pyridin-2-yl)ethane-1,2-diamine (**5w**) in $CDCl_3$ (400 MHz) at 23 °C.

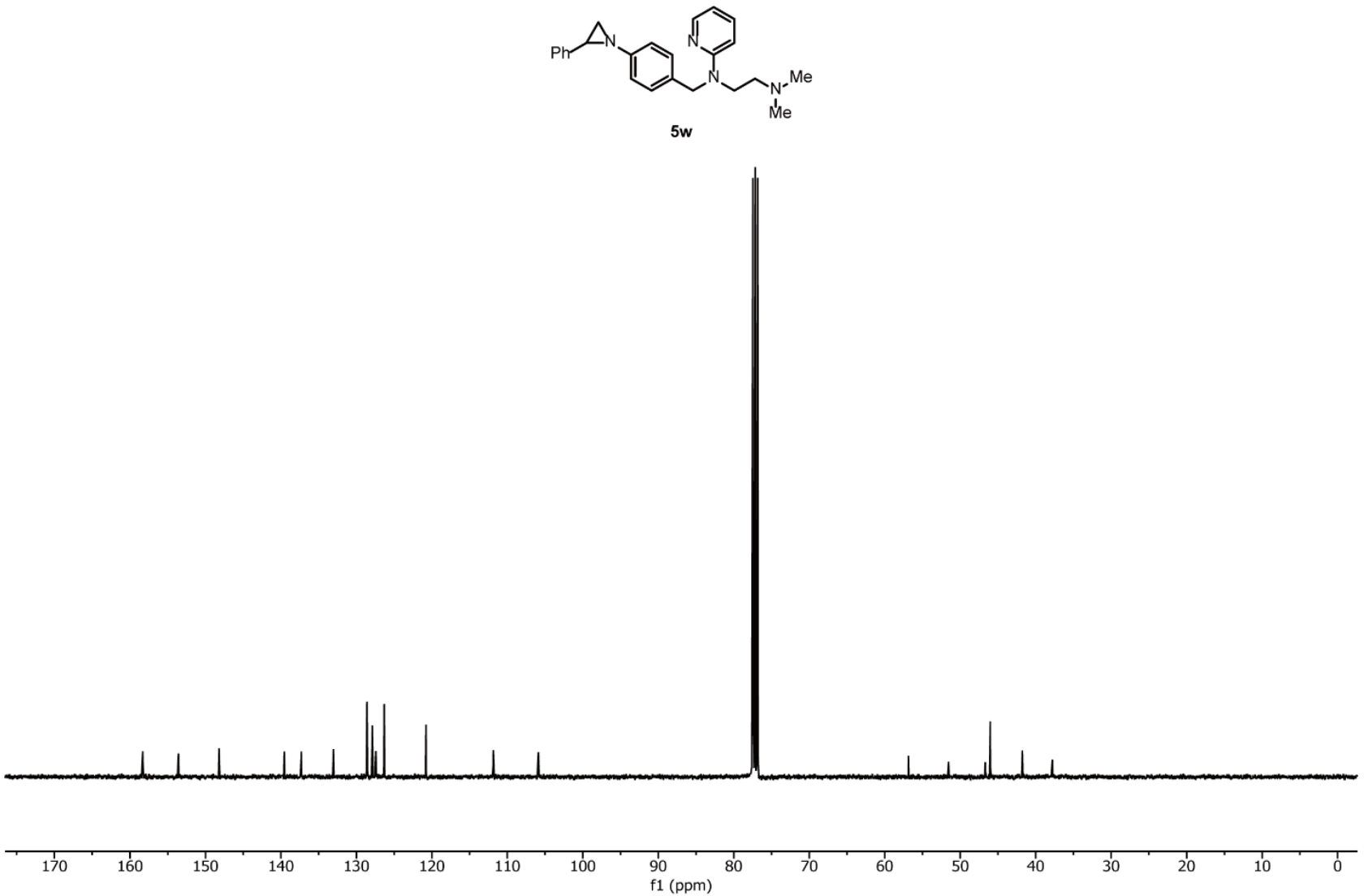


Figure S87. ^{13}C NMR spectrum of N^1,N^1-dimethyl-N^2-(4-(2-phenylaziridin-1-yl)benzyl)-N^2-(pyridin-2-yl)ethane-1,2-diamine (**5w**) in $CDCl_3$ (101 MHz) at 23 °C.

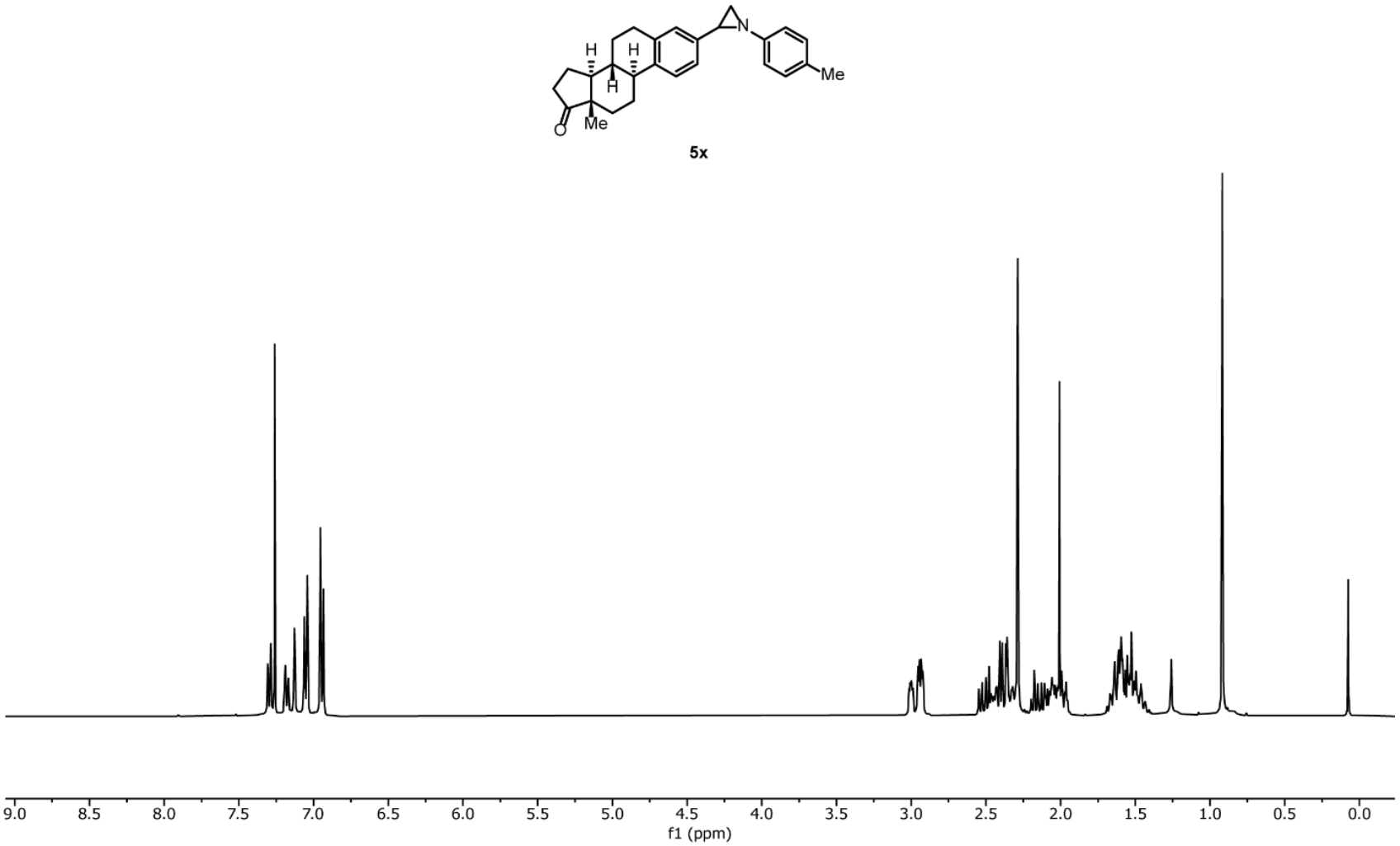


Figure S88. ^{1}H NMR spectrum of (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(1-(*p*-tolyl)aziridin-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**5x**) in $CDCl_3$ (400 MHz) at 23 °C.

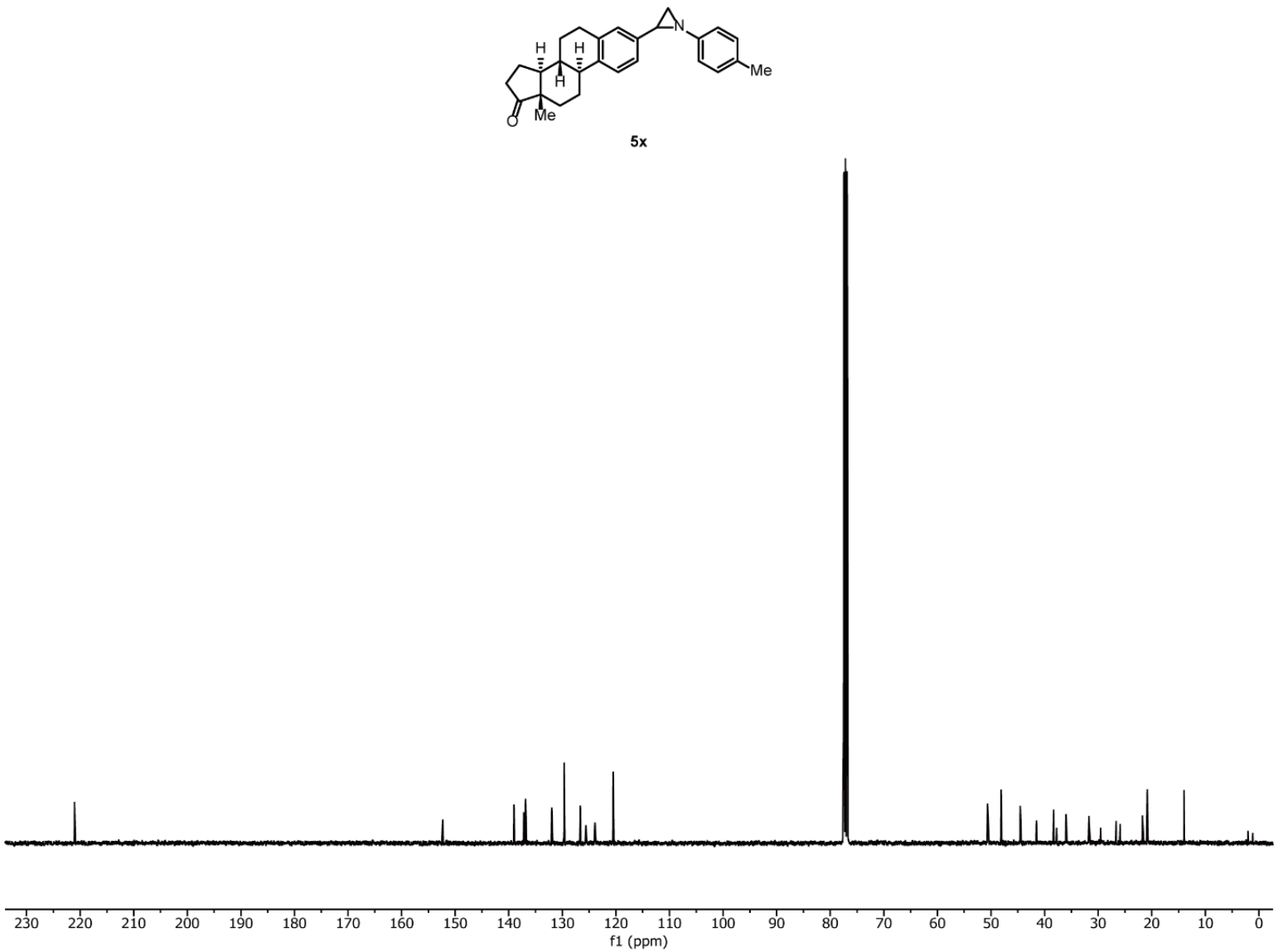


Figure S89. ^{13}C NMR spectrum of (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(1-(*p*-tolyl)aziridin-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**5x**) in $CDCl_3$ (101 MHz) at 23 °C.

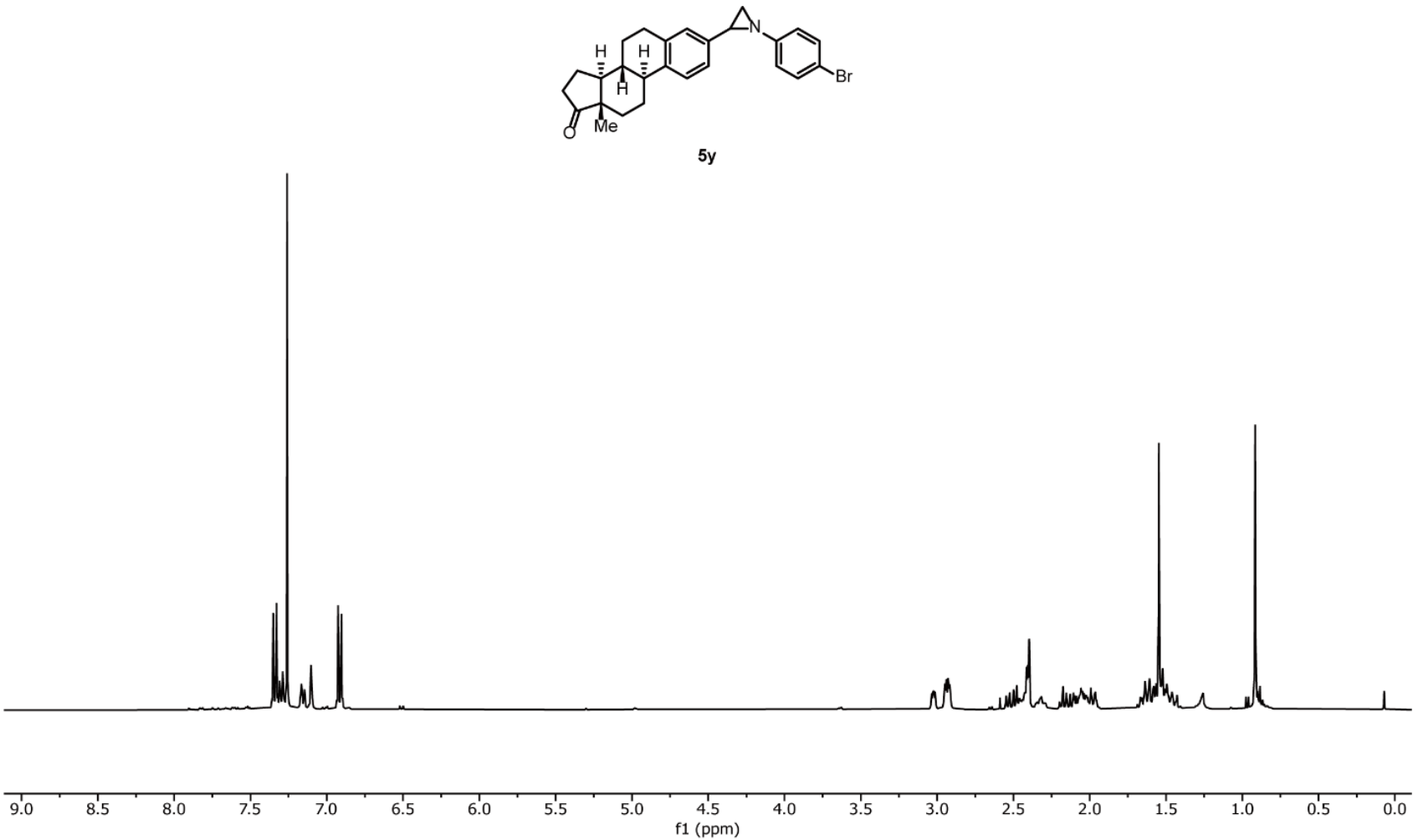


Figure S90. ^{1}H NMR spectrum of (8*R*,9*S*,13*S*,14*S*)-3-(1-(4-bromophenyl)aziridin-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**5y**) in $CDCl_3$ (400 MHz) at 23 °C.

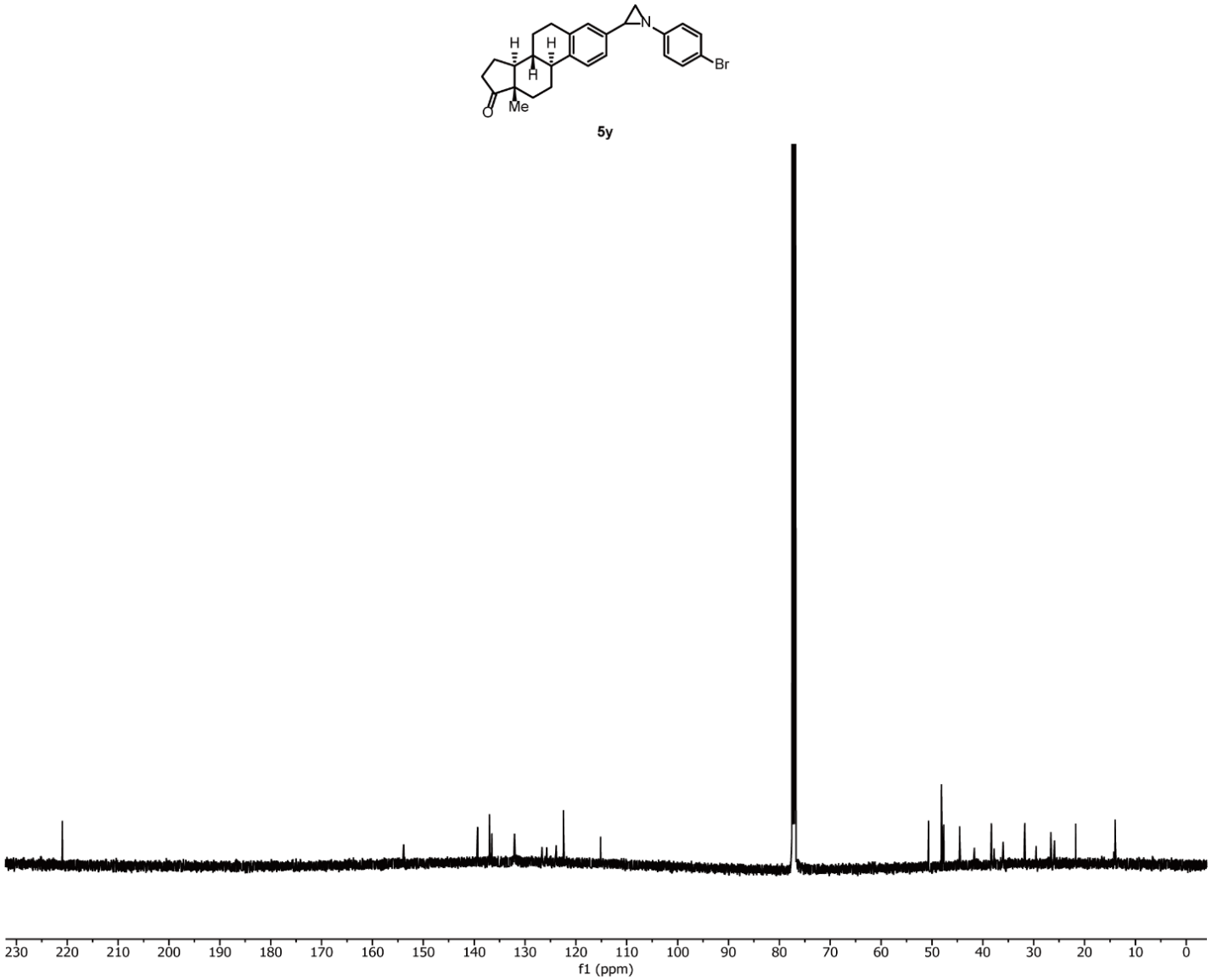


Figure S91. ^{13}C NMR spectrum of (8*R*,9*S*,13*S*,14*S*)-3-(1-(4-bromophenyl)aziridin-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**5y**) in $CDCl_3$ (101 MHz) at 23 °C.

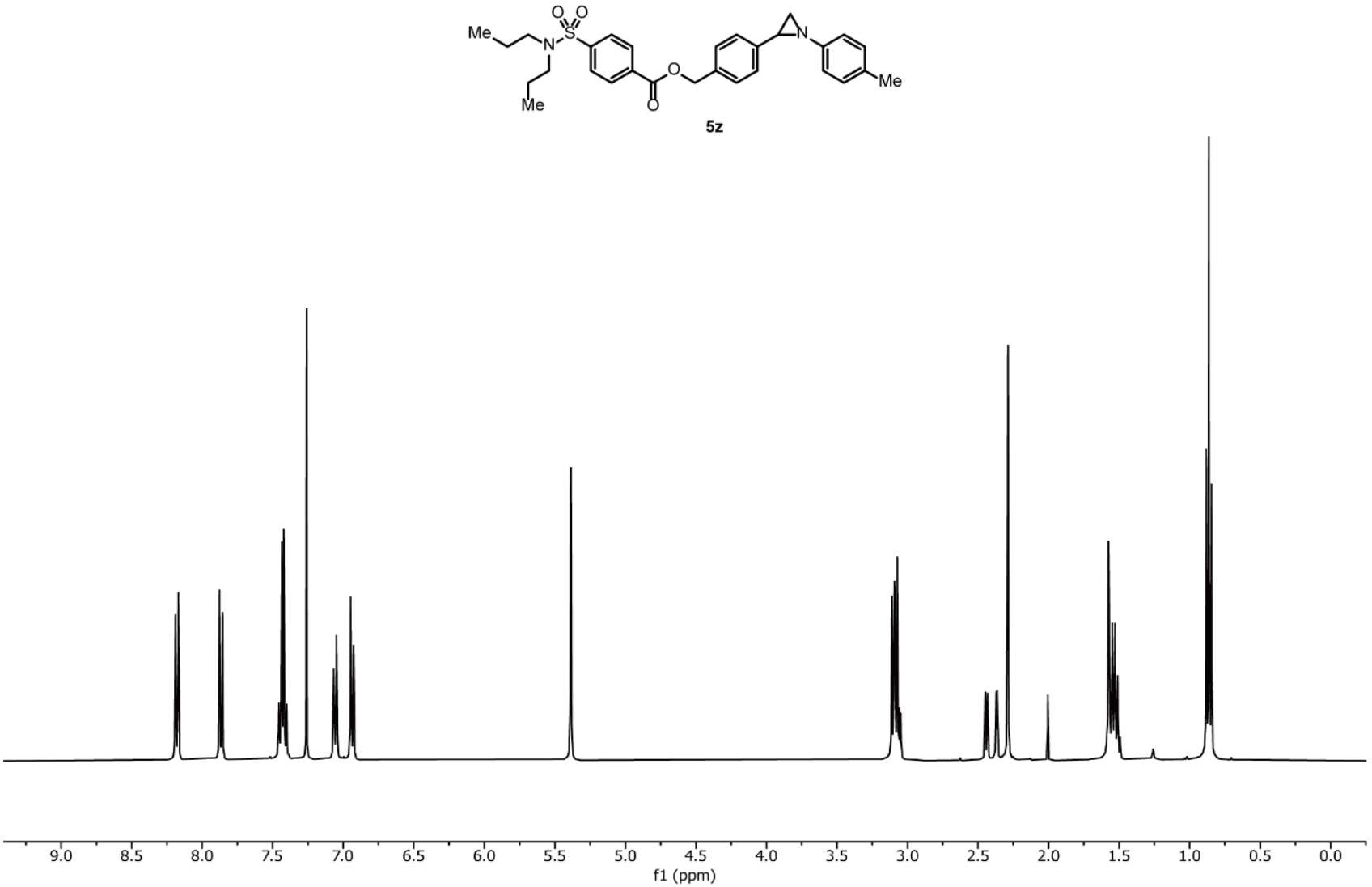


Figure S92. ^{1}H NMR spectrum of 4-(1-(*p*-tolyl)aziridin-2-yl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**5z**) in $CDCl_3$ (400 MHz) at 23 °C.

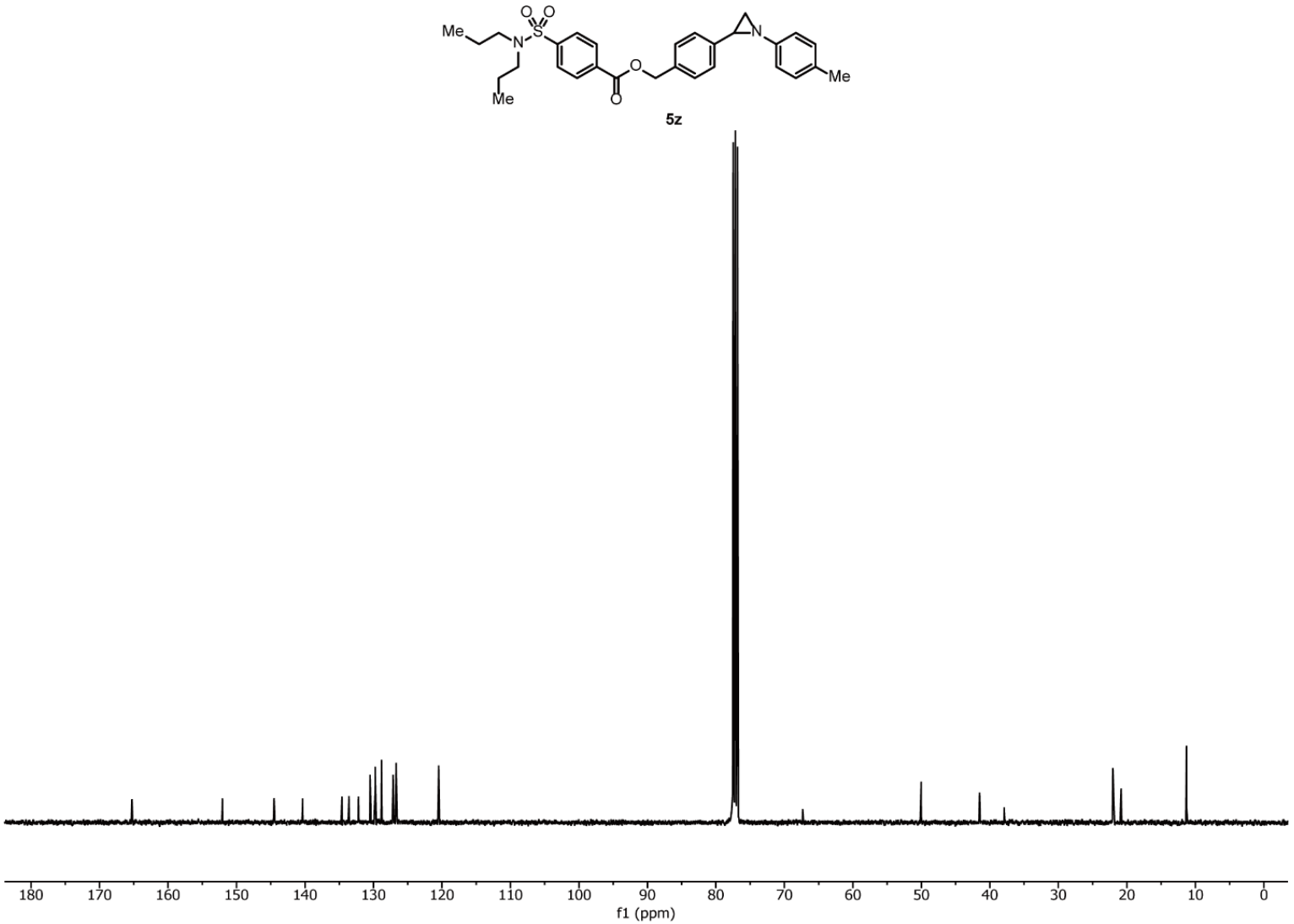


Figure S93. ^{13}C NMR spectrum of 4-(1-(*p*-tolyl)aziridin-2-yl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**5z**) in $CDCl_3$ (101 MHz) at 23 °C.

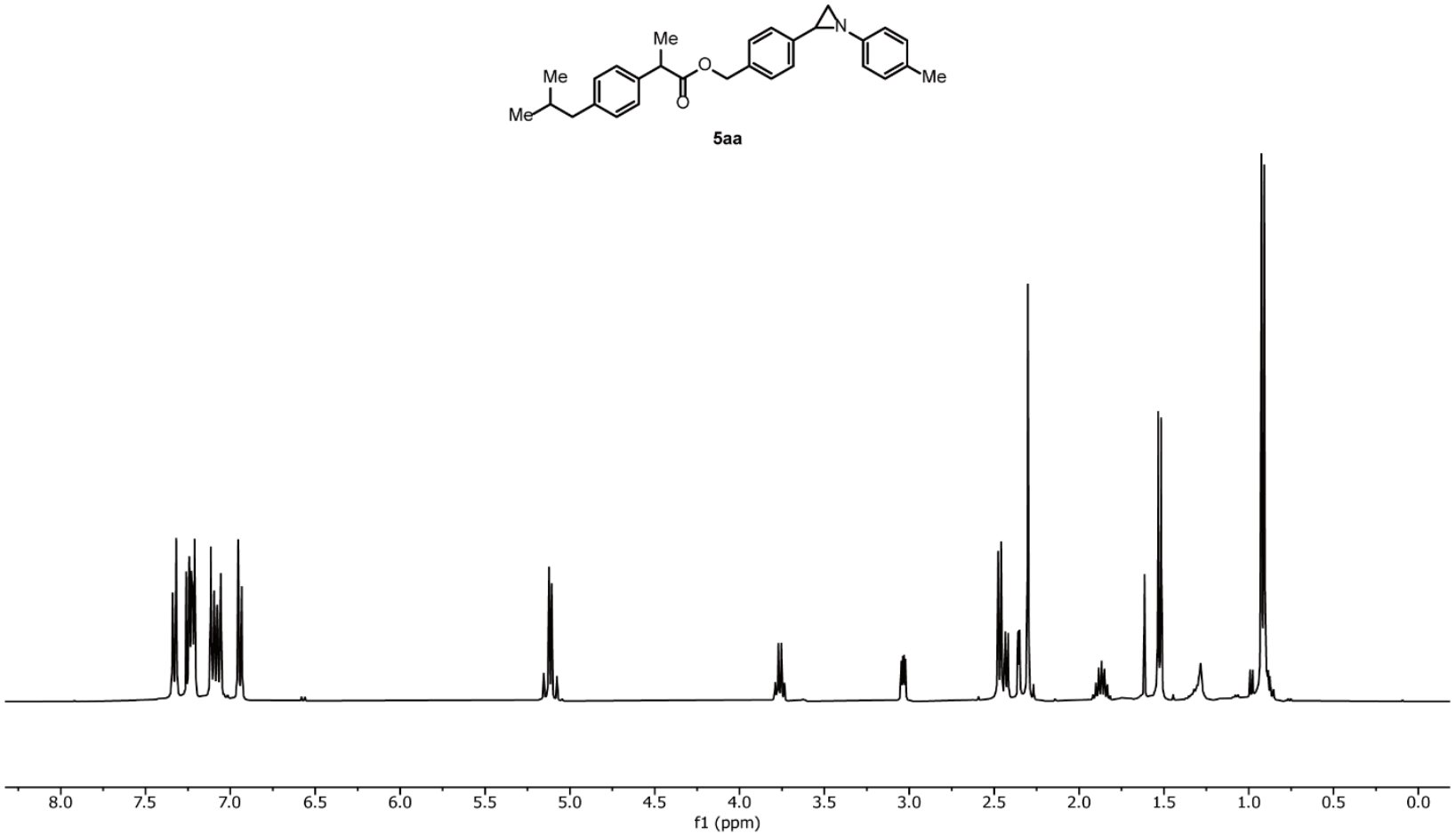


Figure S94. ^{1}H NMR spectrum of 4-(1-(*p*-tolyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**5aa**) in $CDCl_3$ (400 MHz) at 23 °C.

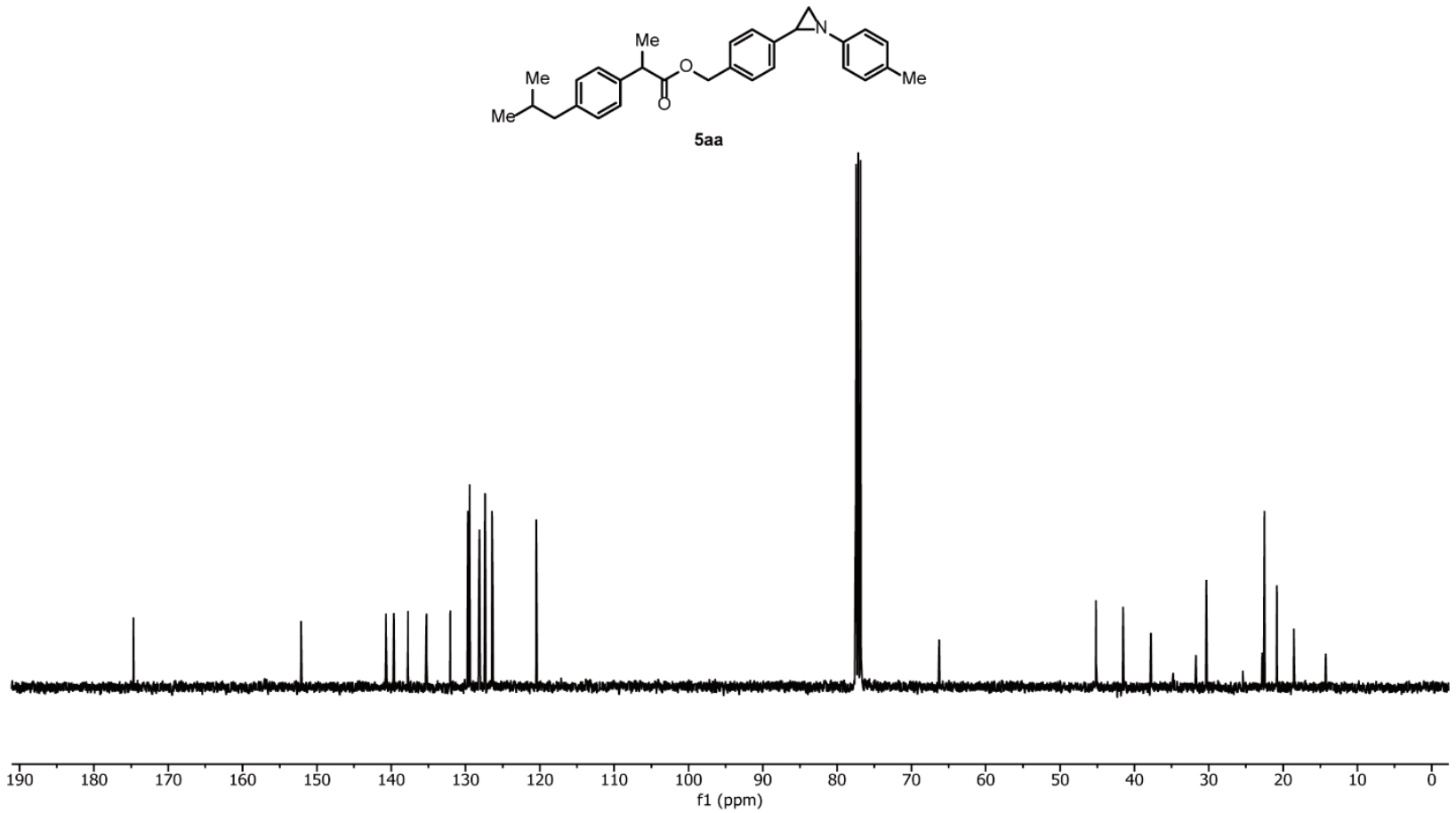


Figure S95. ^{13}C NMR spectrum of 4-(1-(*p*-tolyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**5aa**) in $CDCl_3$ (101 MHz) at 23 °C.

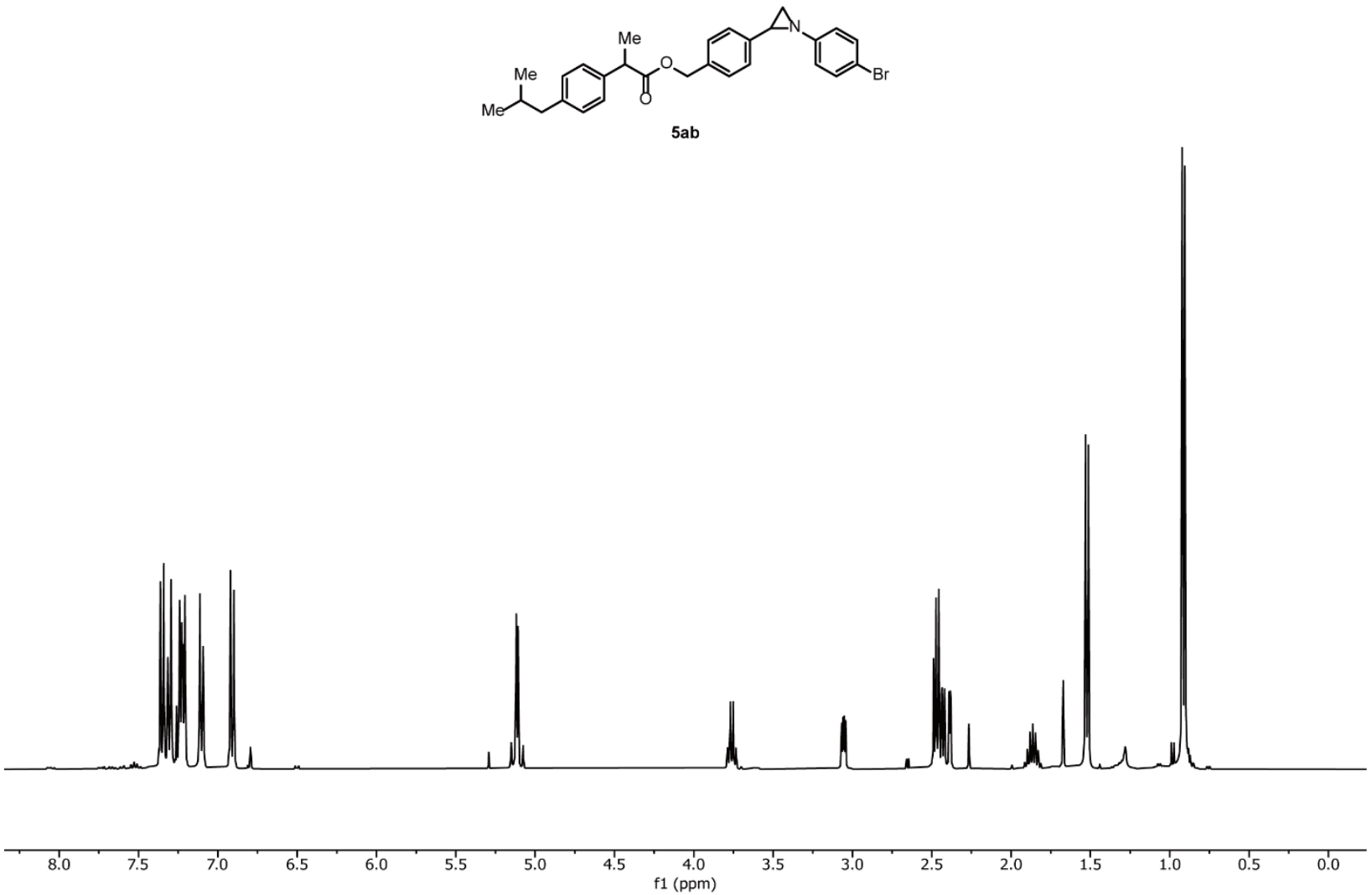


Figure S96. ^{1}H NMR spectrum of 4-(1-(4-bromophenyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**5ab**) in $CDCl_3$ (400 MHz) at 23 °C.

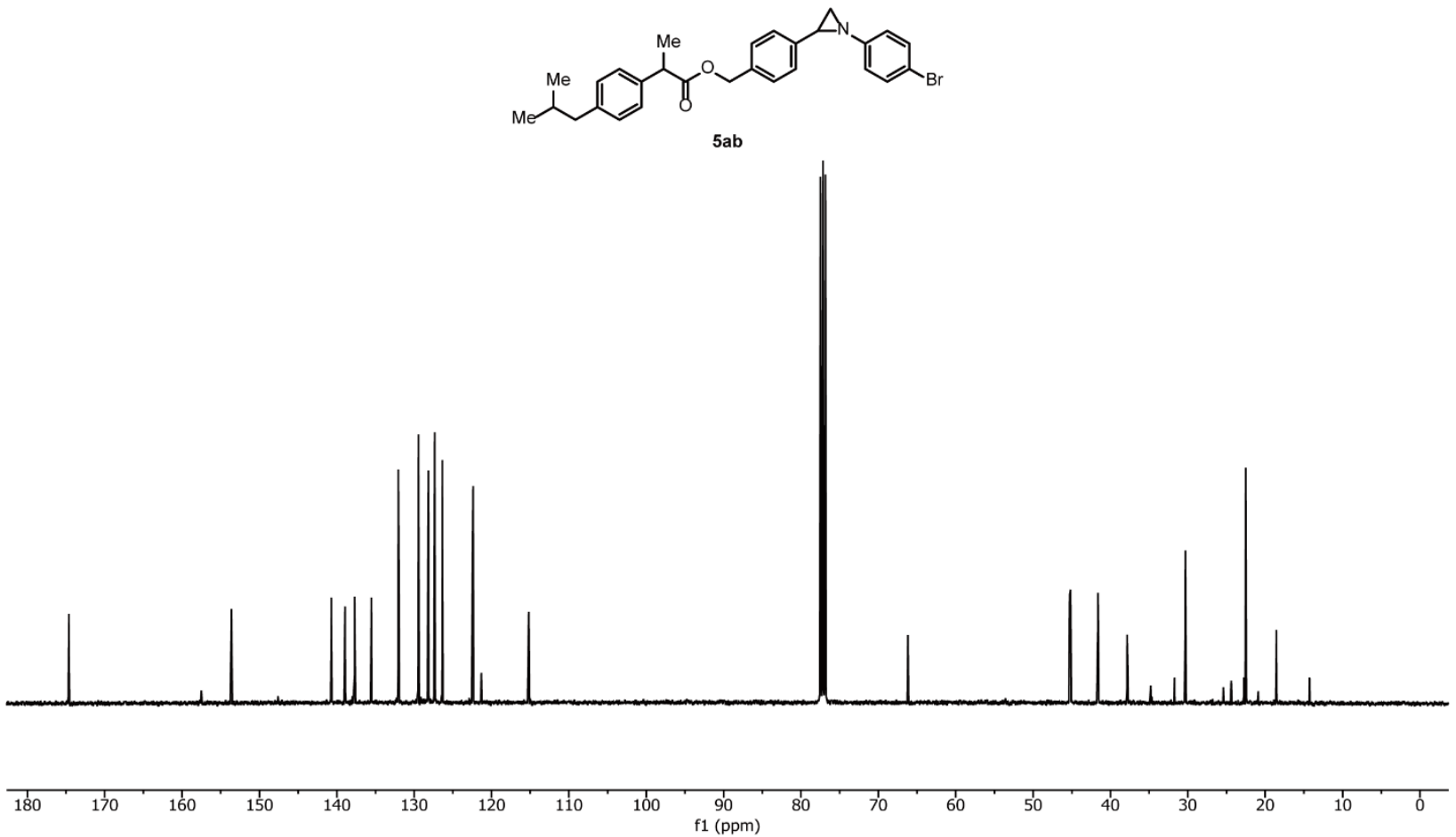


Figure S97. ^{13}C NMR spectrum of 4-(1-(4-bromophenyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**5ab**) in $CDCl_3$ (101 MHz) at 23 °C.

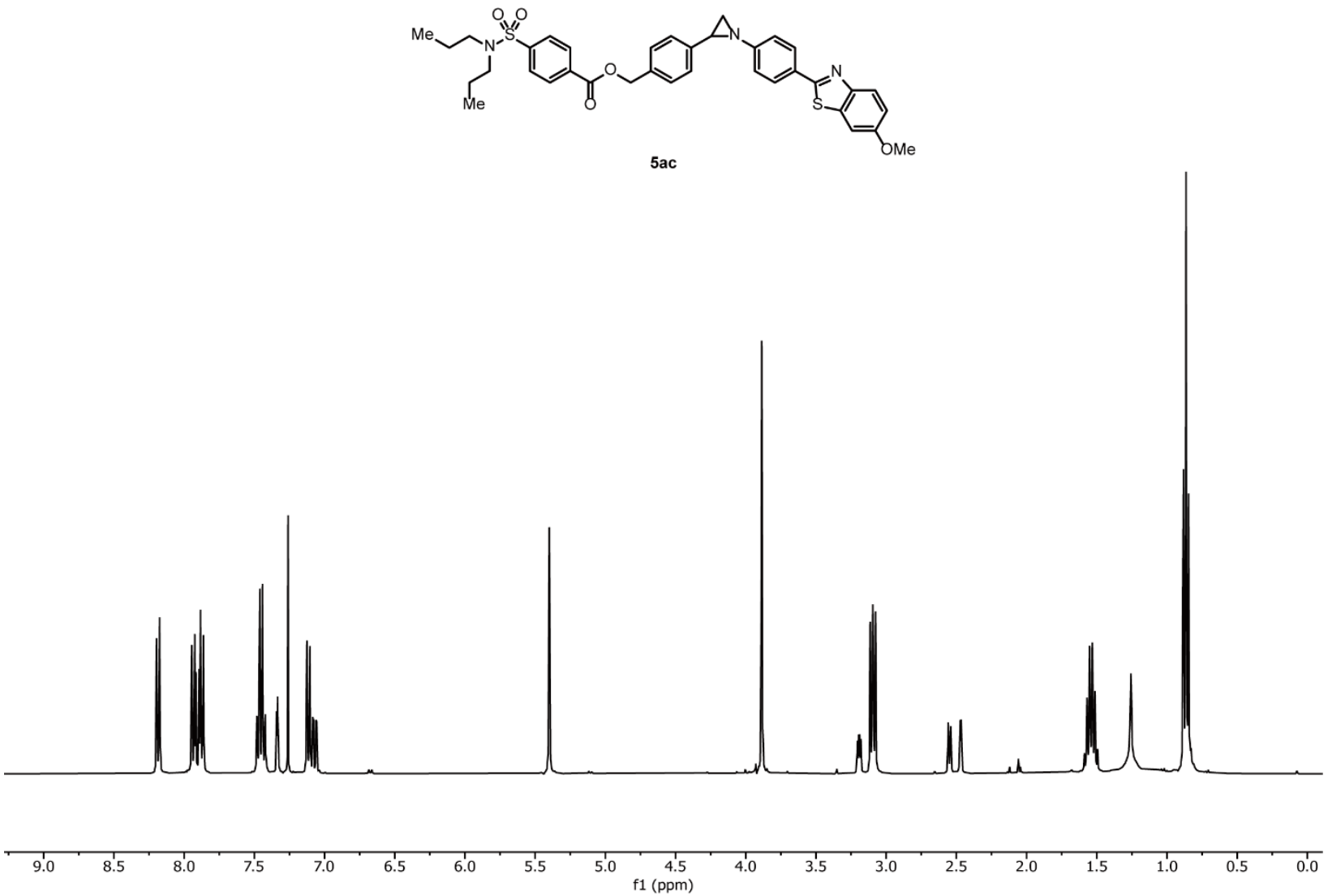


Figure S98. ^{1}H NMR spectrum of 4-(1-(4-(6-methoxybenzo[*d*]thiazol-2-yl)phenyl)aziridin-2-yl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**5ac**) in $CDCl_3$ (400 MHz) at 23 °C.

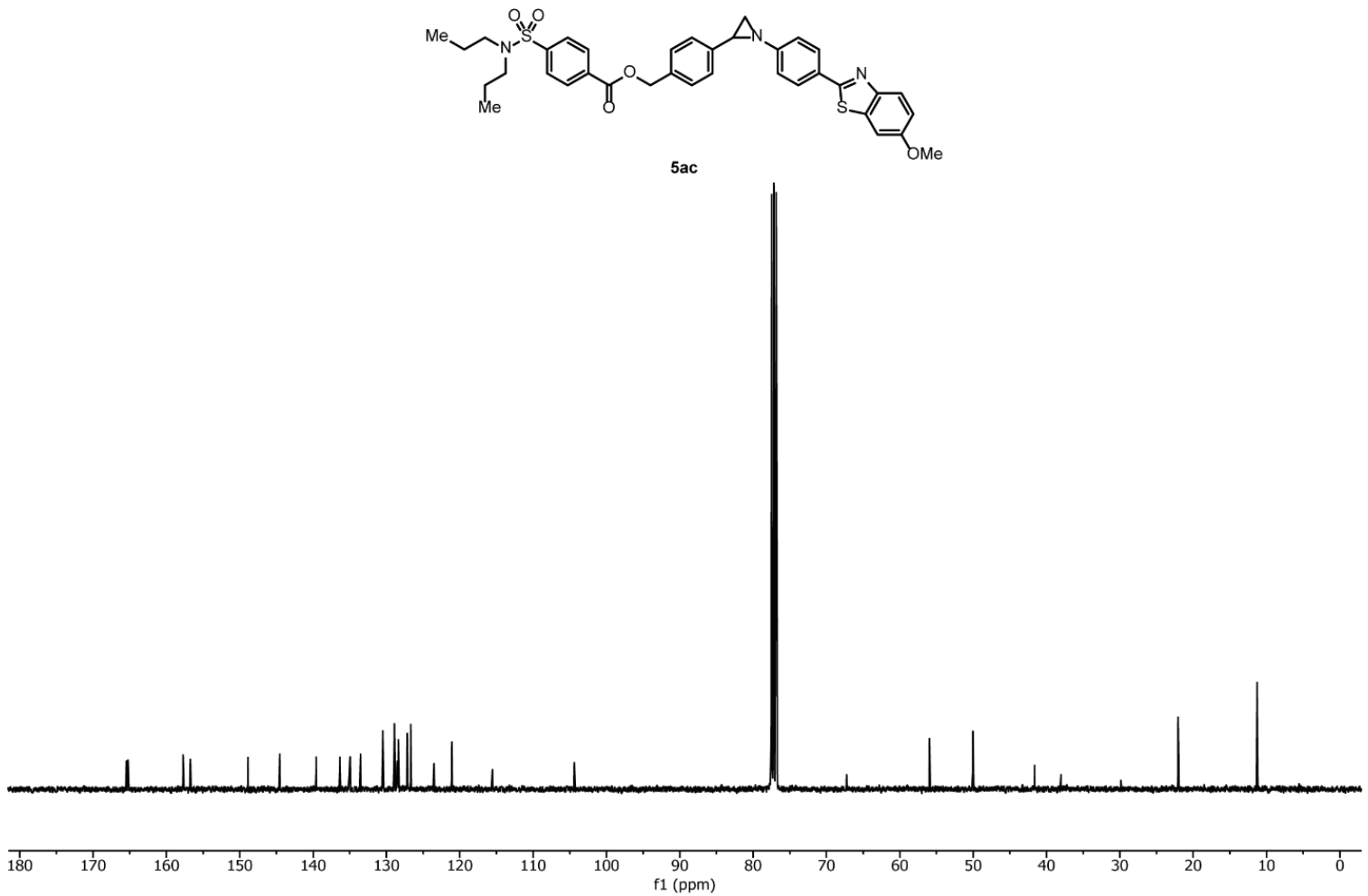


Figure S99. ^{13}C NMR spectrum of 4-(1-(4-(6-methoxybenzo[*d*]thiazol-2-yl)phenyl)aziridin-2-yl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**5ac**) in $CDCl_3$ (101 MHz) at 23 °C.

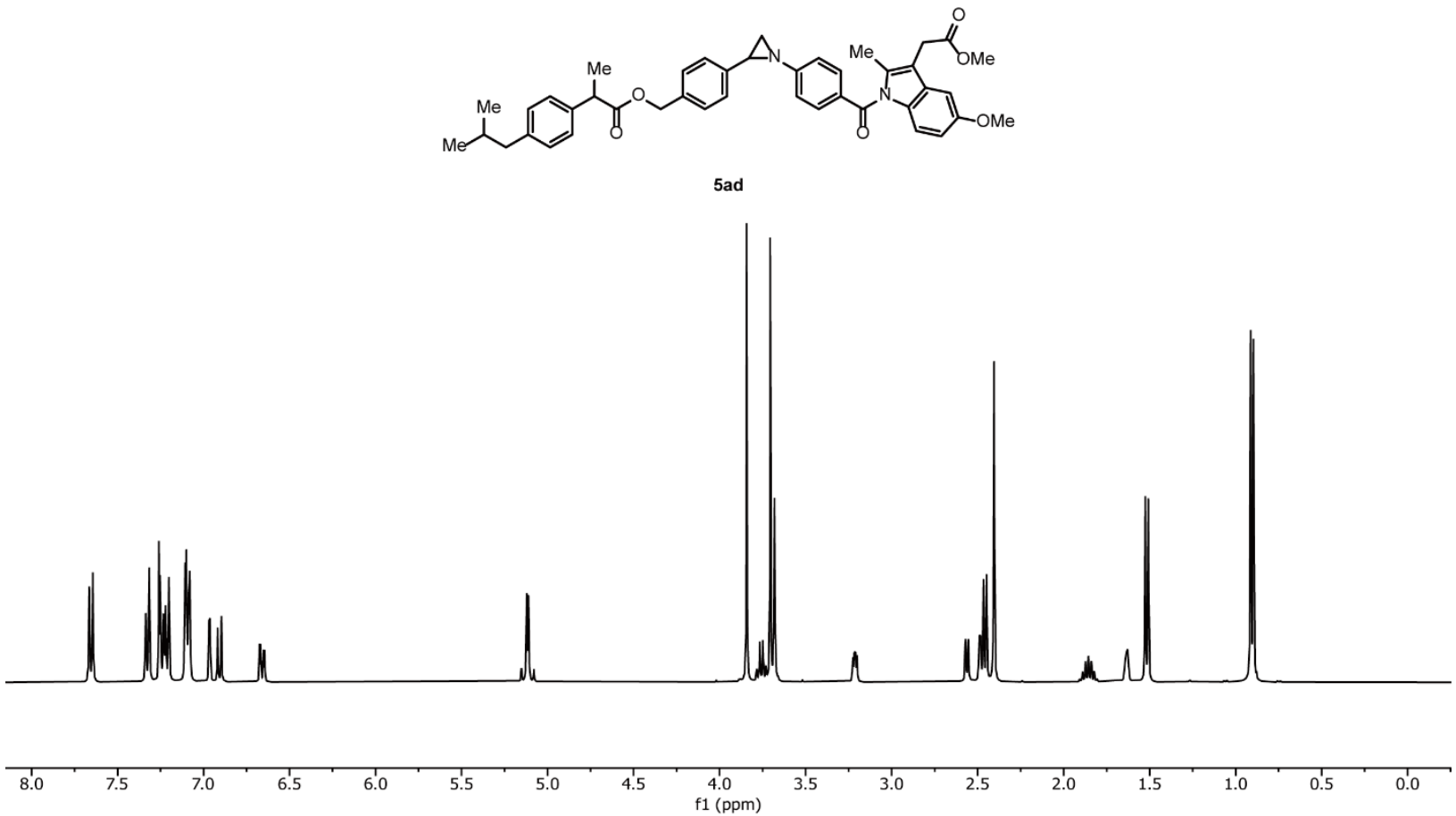


Figure S100. ^{1}H NMR spectrum of 4-(1-(4-(5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1*H*-indole-1-carbonyl)phenyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**5ad**) in $CDCl_3$ (400 MHz) at 23 °C.

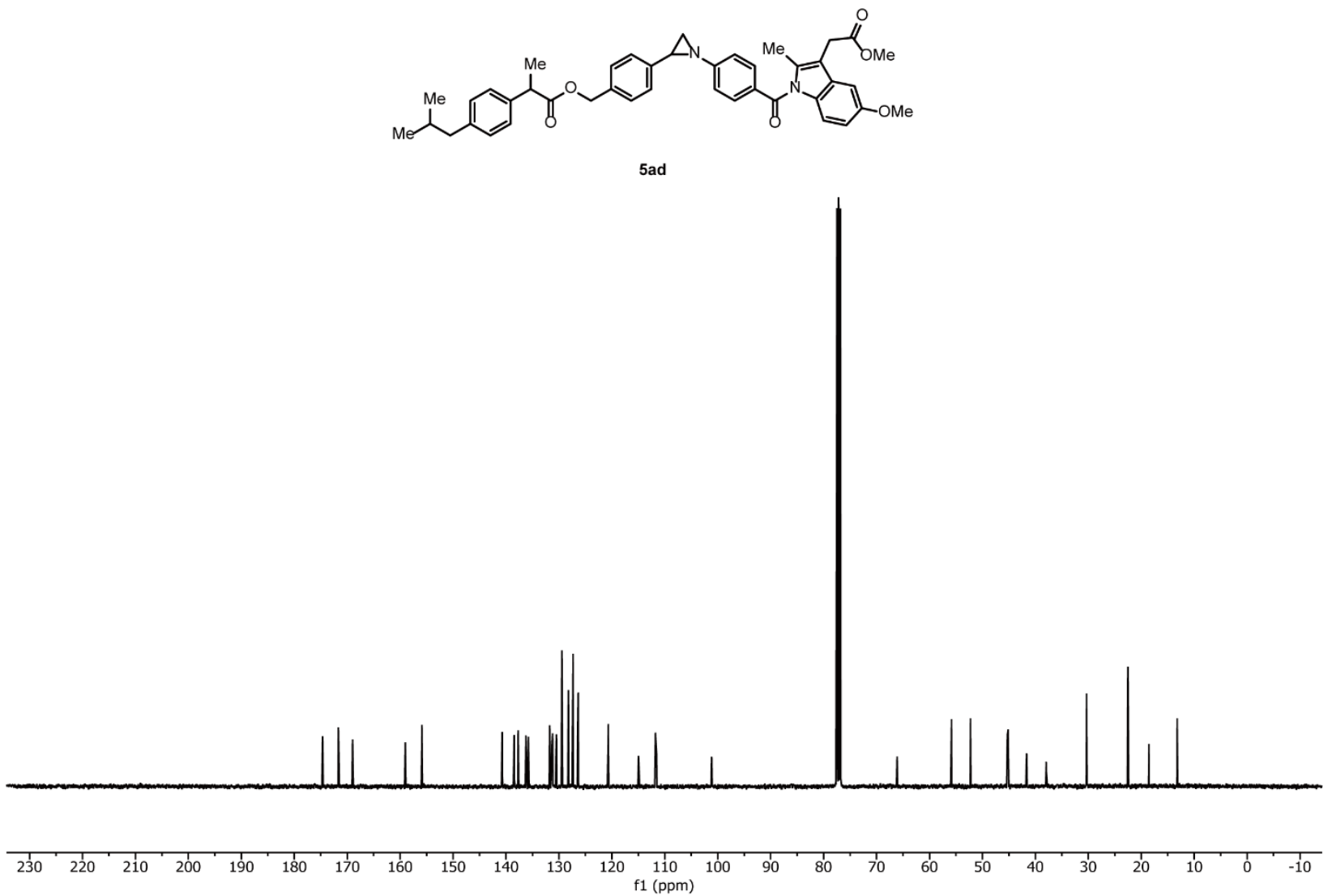


Figure S101. ^{13}C NMR spectrum of 4-(1-(4-(5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1*H*-indole-1-carbonyl)phenyl)aziridin-2-yl)benzyl 2-(4-isobutylphenyl)propanoate (**5ad**) in $CDCl_3$ (101 MHz) at 23 °C.

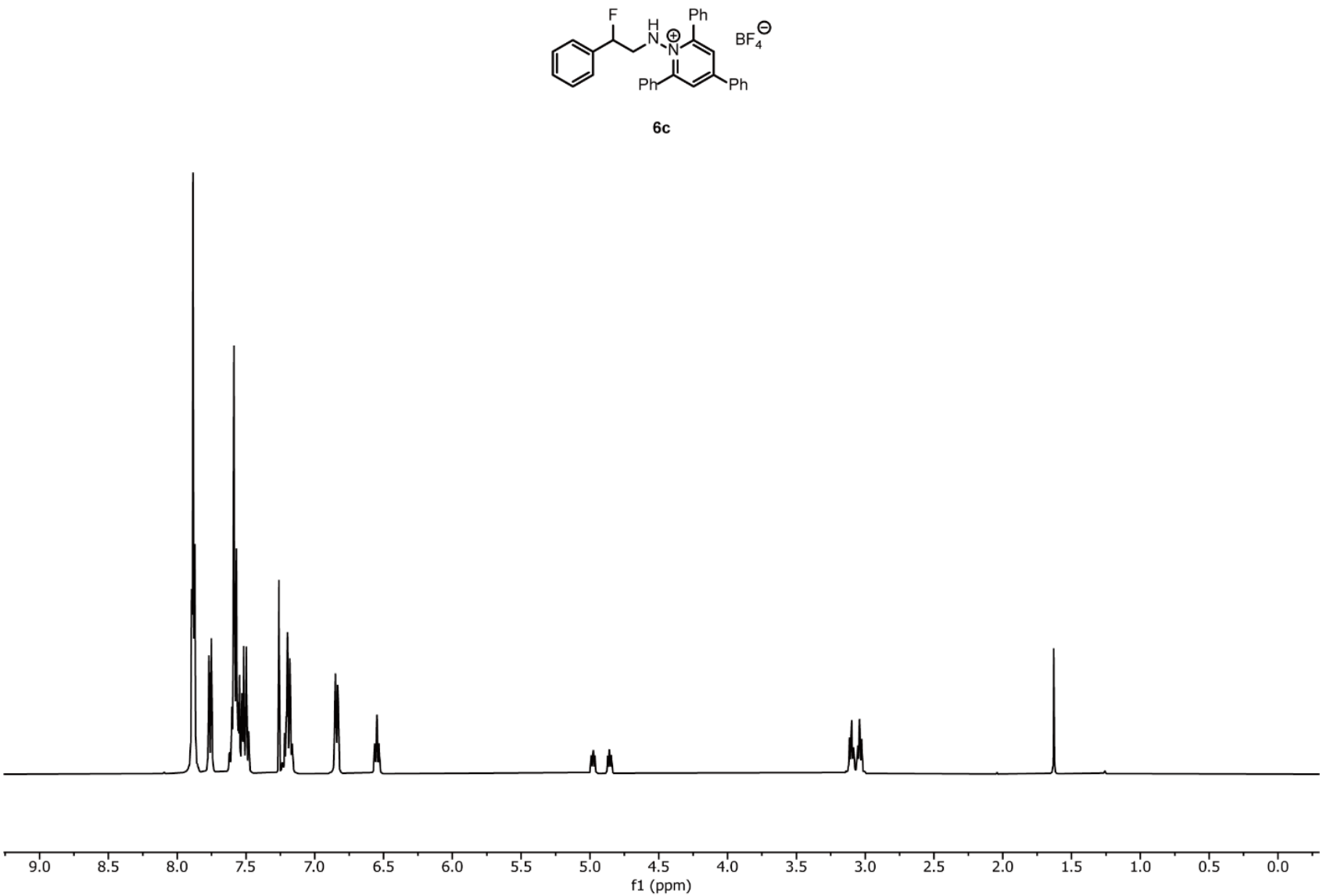


Figure S102. ^{1}H NMR spectrum of 1-((2-fluoro-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6c**) in $CDCl_3$ (400 MHz) at 23 °C.

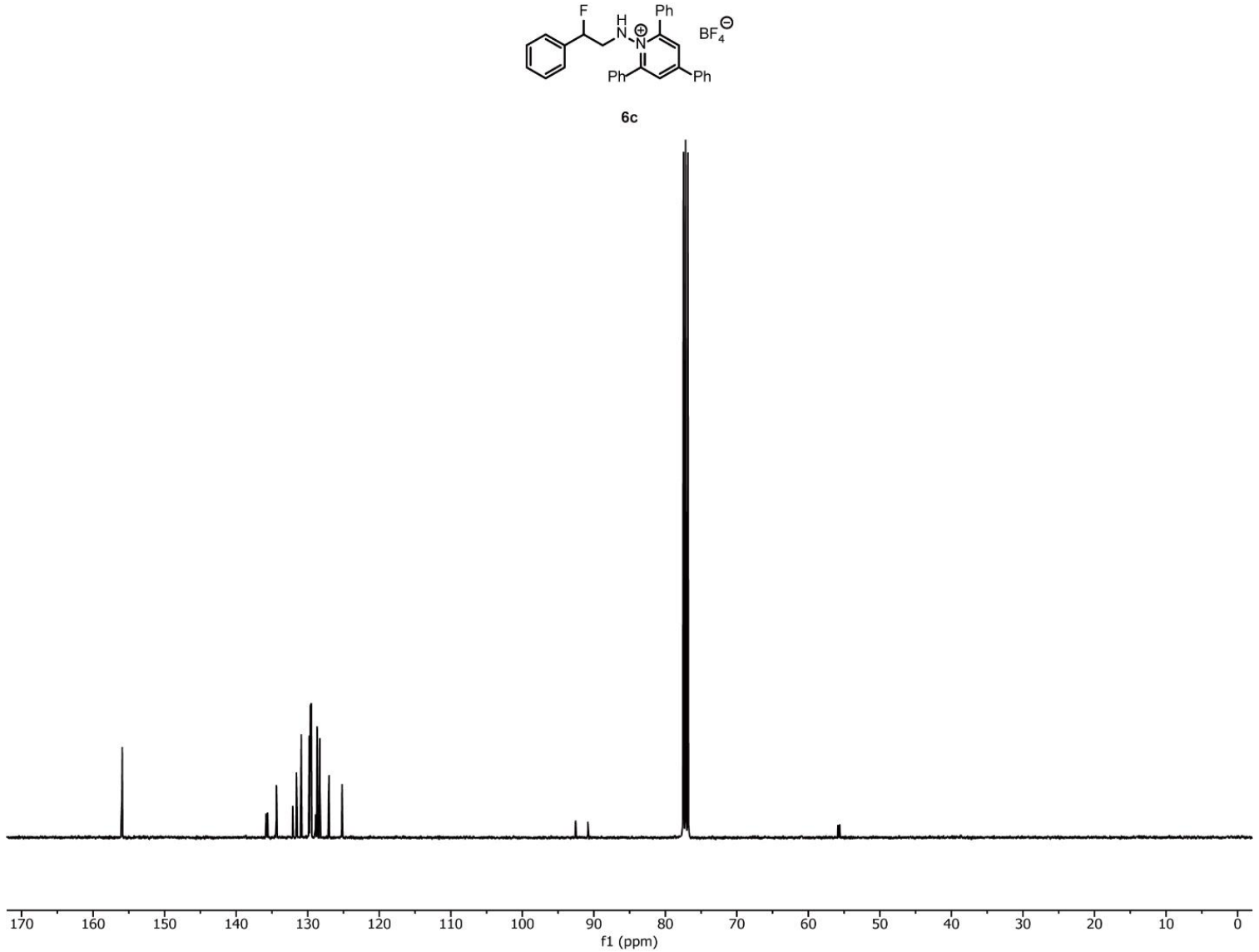


Figure S103. ^{13}C NMR spectrum of 1-((2-fluoro-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6c**) in $CDCl_3$ (101 MHz) at 23 °C.

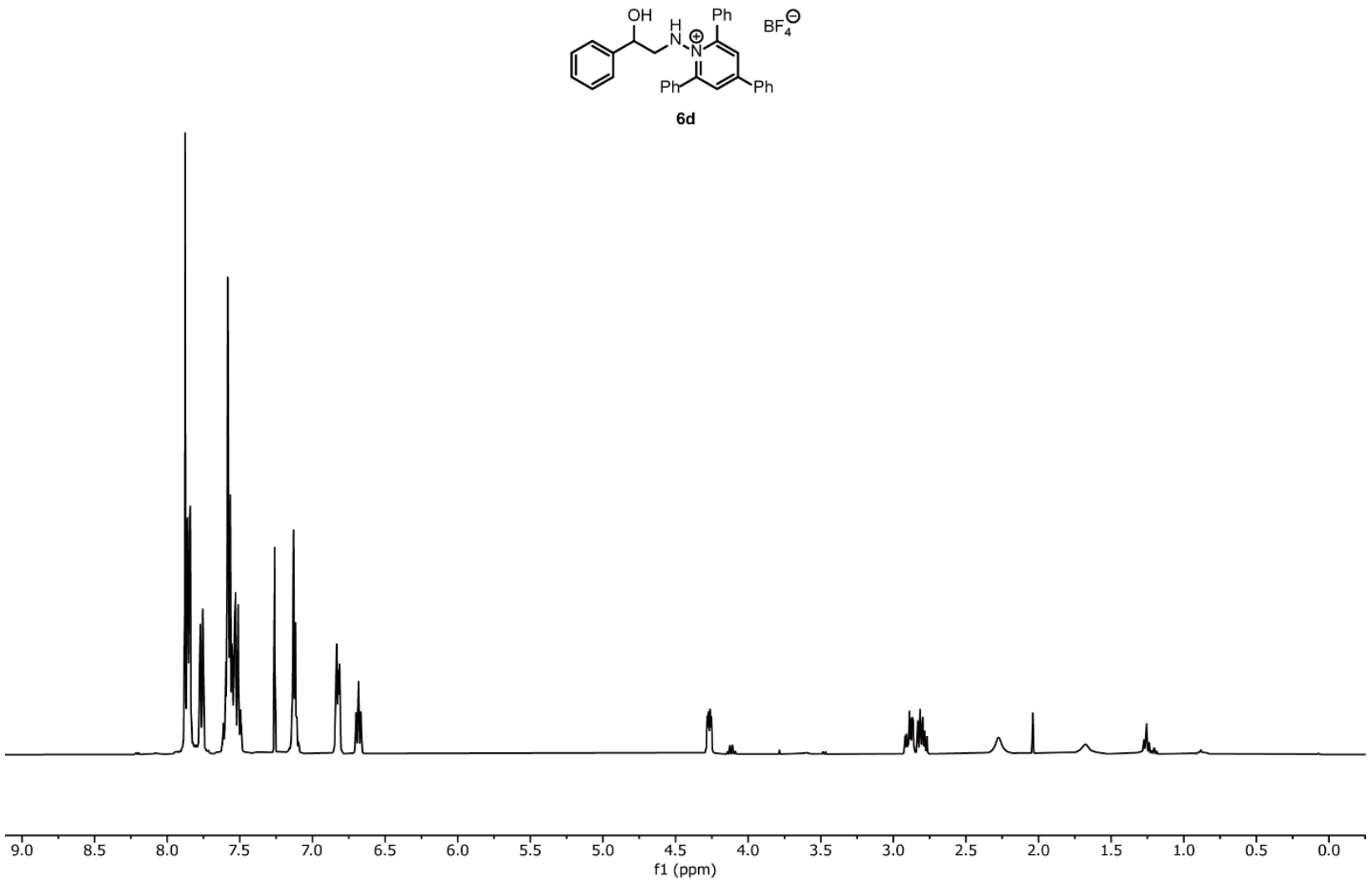


Figure S104. ^{1}H NMR spectrum of 1-((2-hydroxy-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6d**) in $CDCl_3$ (400 MHz) at 23 °C.

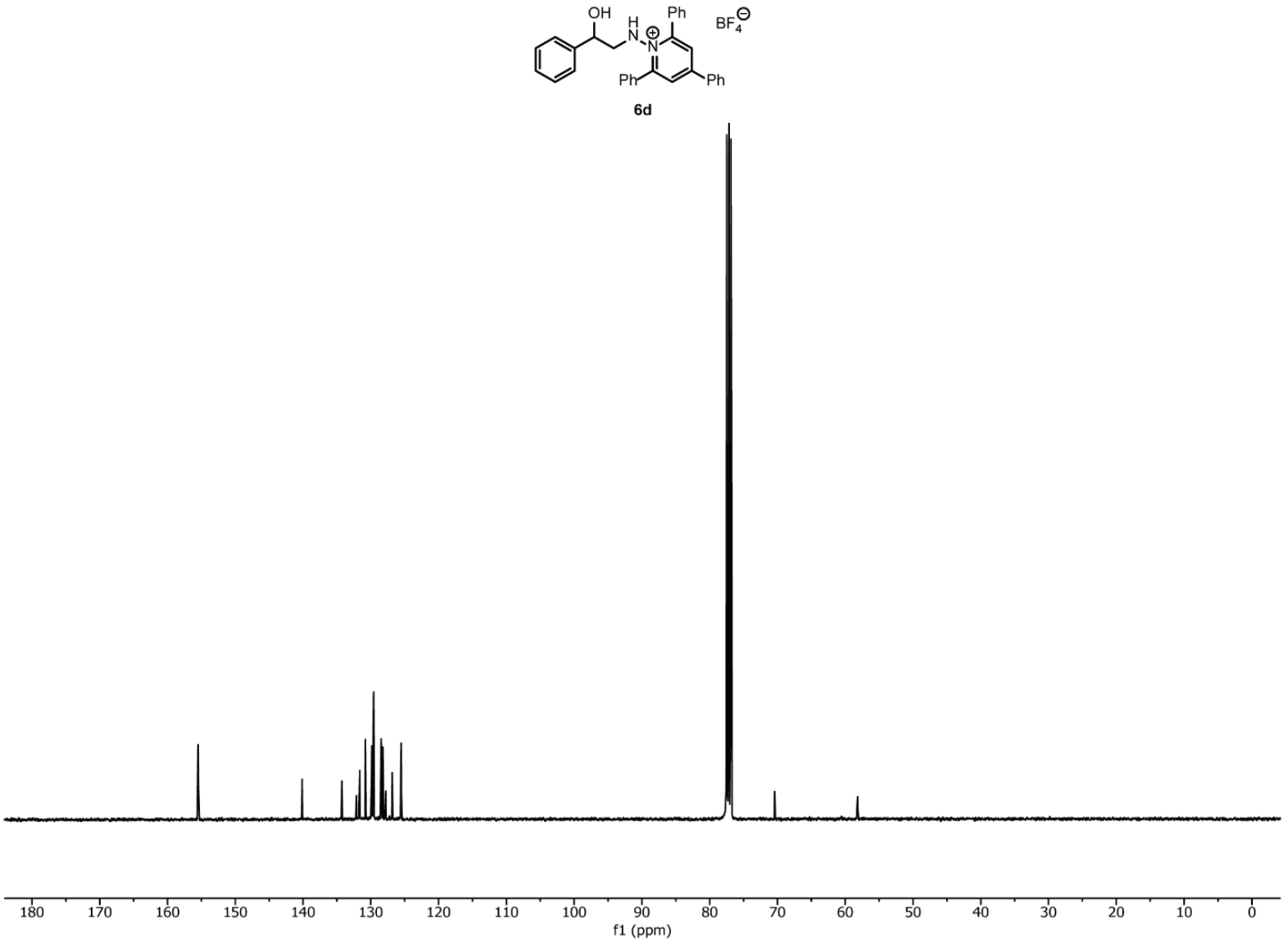


Figure S105. ^{13}C NMR spectrum of 1-((2-hydroxy-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6d**) in $CDCl_3$ (101 MHz) at 23 °C.

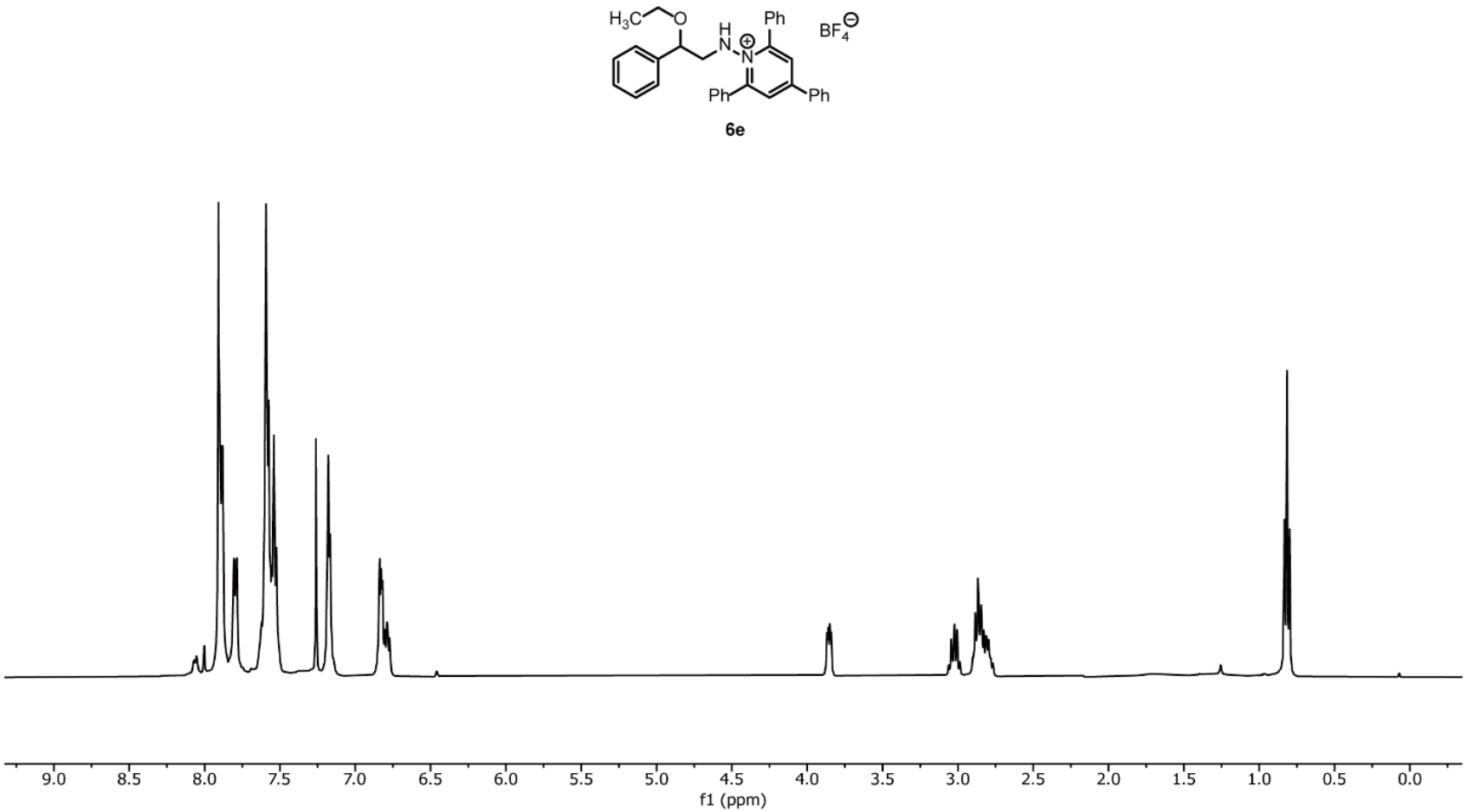


Figure S106. ^{1}H NMR spectrum of 1-((2-ethoxy-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6e**) in $CDCl_3$ (400 MHz) at 23 °C.

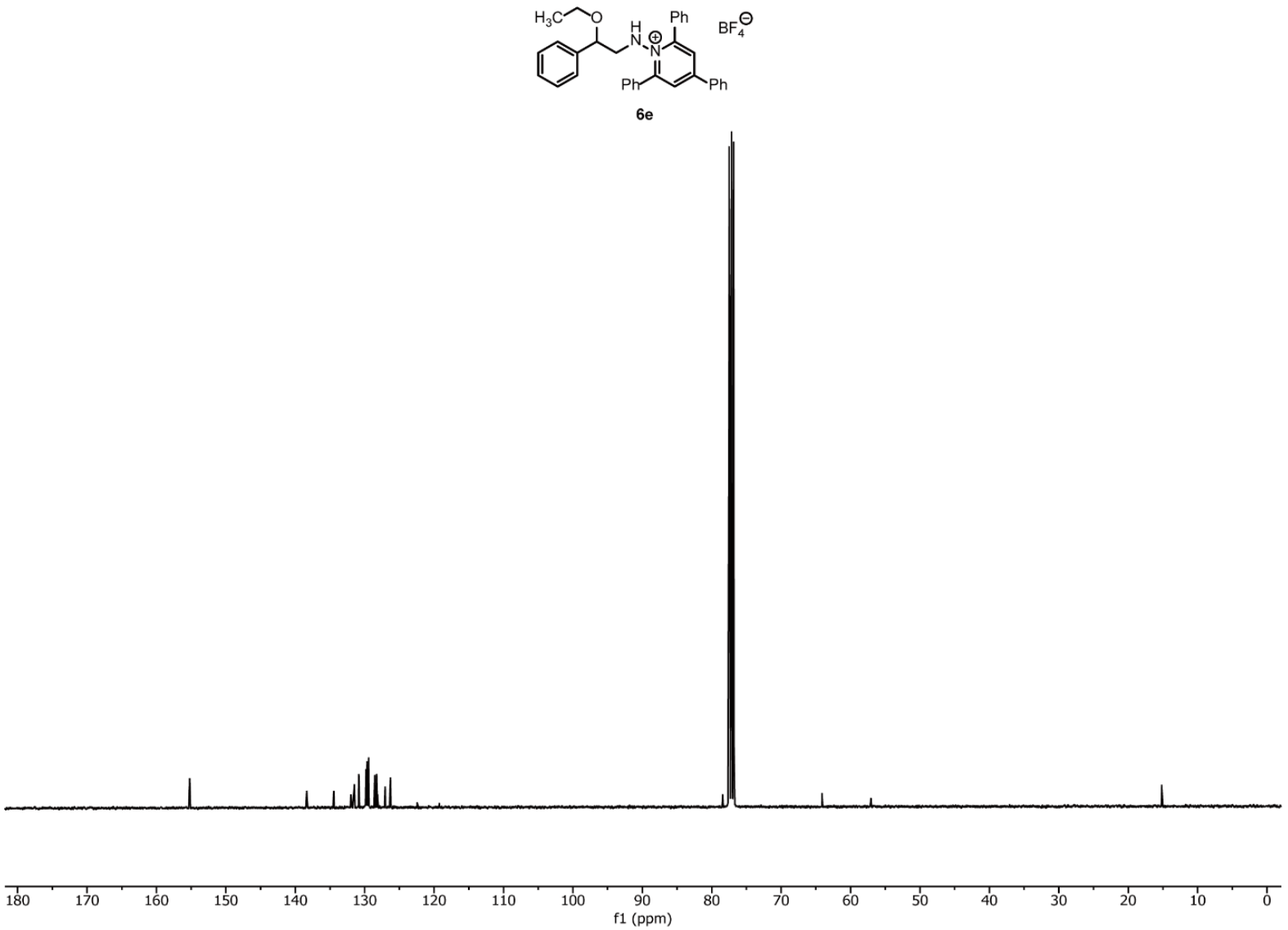


Figure S107. ^{13}C NMR spectrum of 1-((2-ethoxy-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6e**) in $CDCl_3$ (101 MHz) at 23 °C.

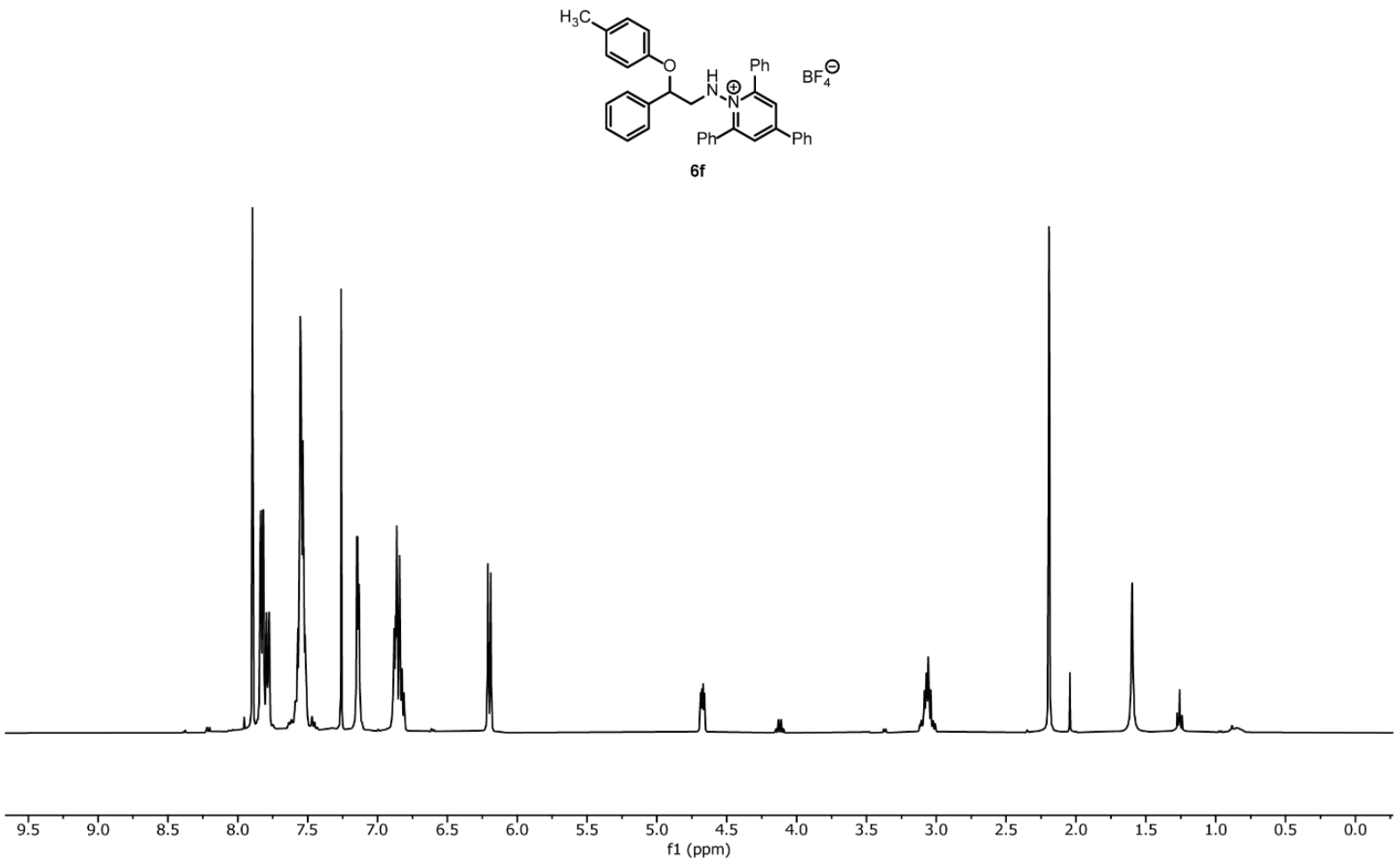


Figure S108. ^{1}H NMR spectrum of 2,4,6-triphenyl-1-((2-phenyl-2-(*p*-tolyloxy)ethyl)amino)pyridin-1-ium tetrafluoroborate (**6f**) in $CDCl_3$ (400 MHz) at 23 °C.

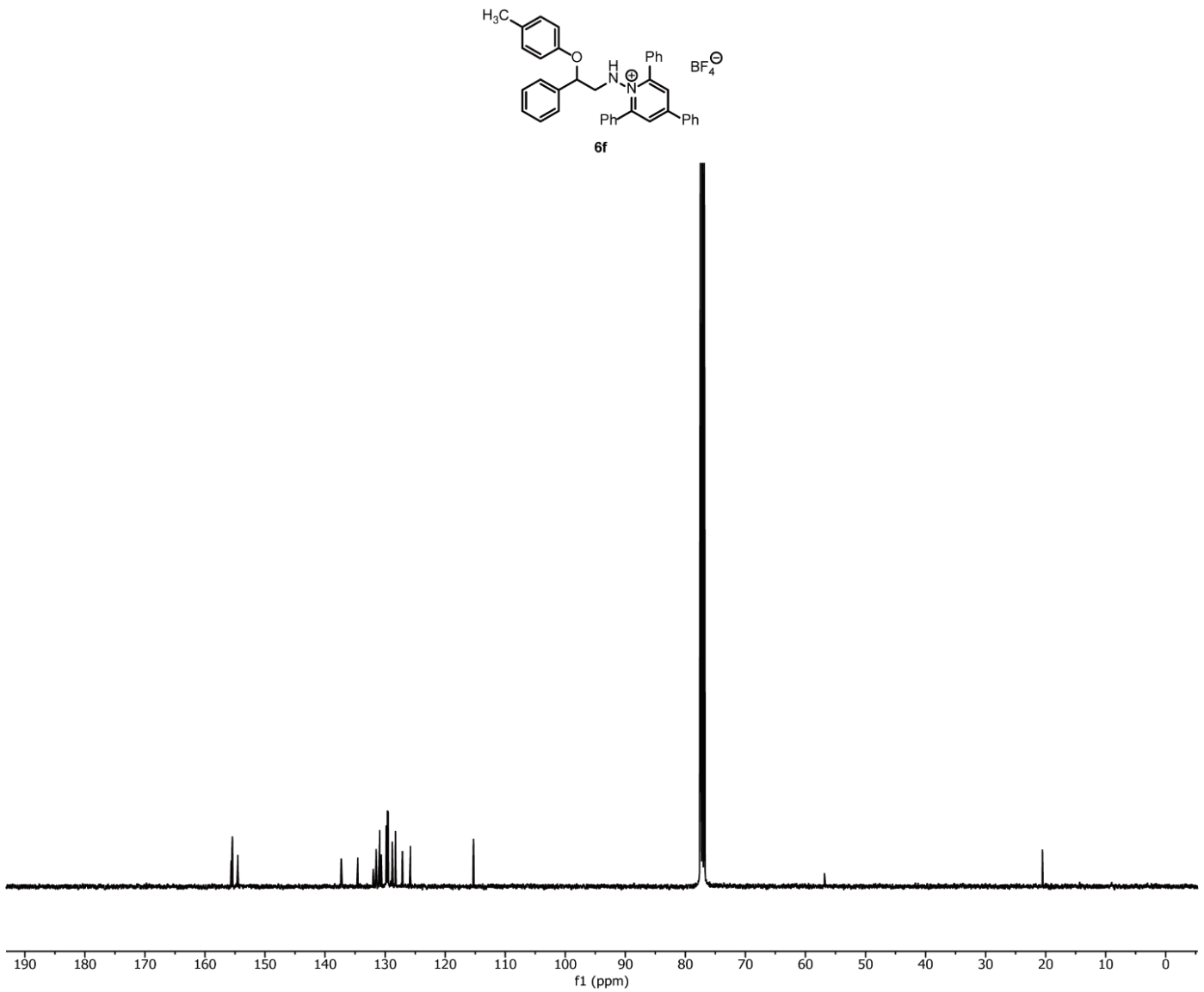


Figure S109. ^{13}C NMR spectrum of 2,4,6-triphenyl-1-((2-phenyl-2-(*p*-tolyloxy)ethyl)amino)pyridin-1-ium tetrafluoroborate (**6f**) in $CDCl_3$ (101 MHz) at 23 °C.

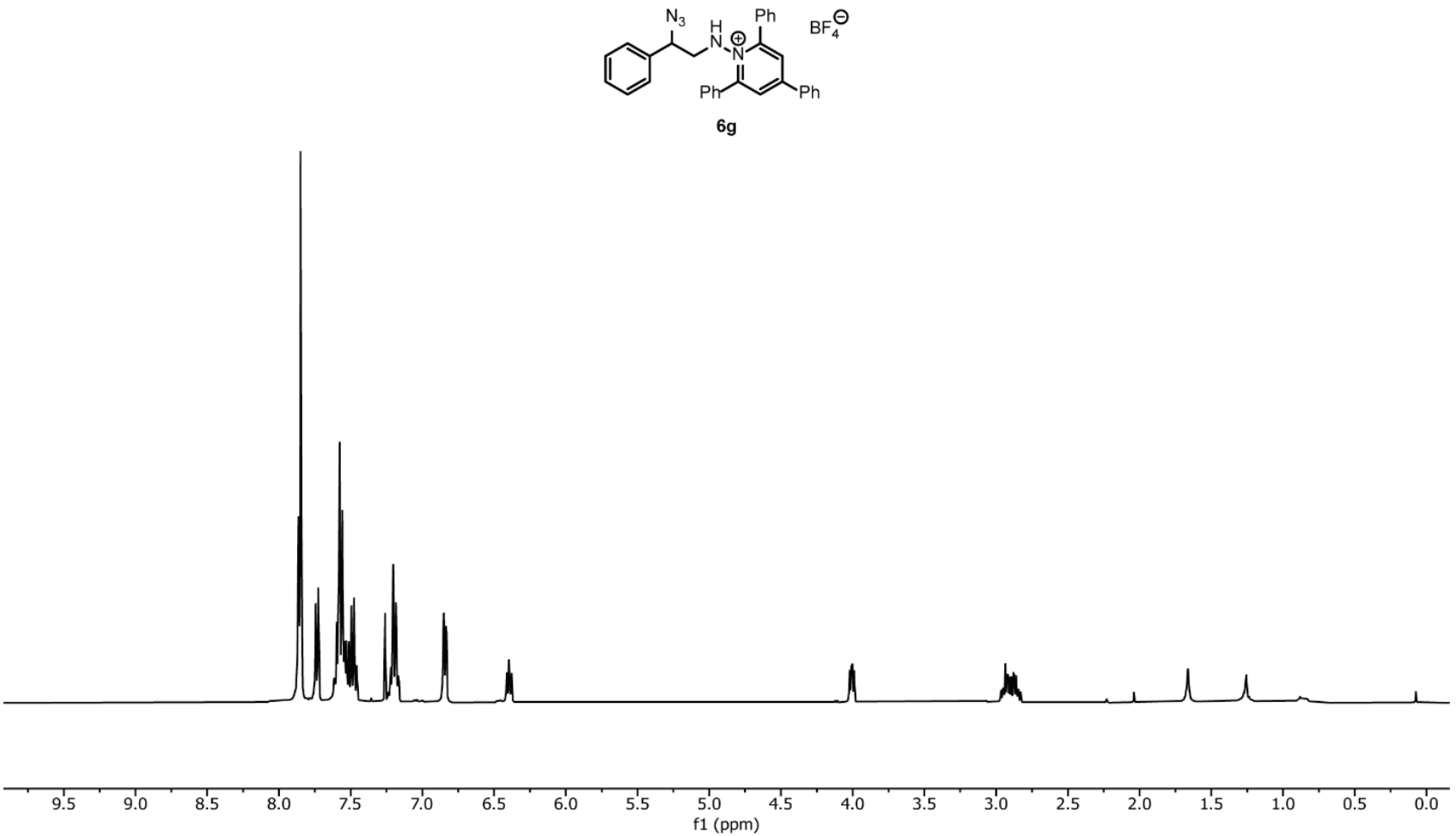


Figure S110. ^{1}H NMR spectrum of 1-((2-azido-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6g**) in $CDCl_3$ (400 MHz) at 23 °C.

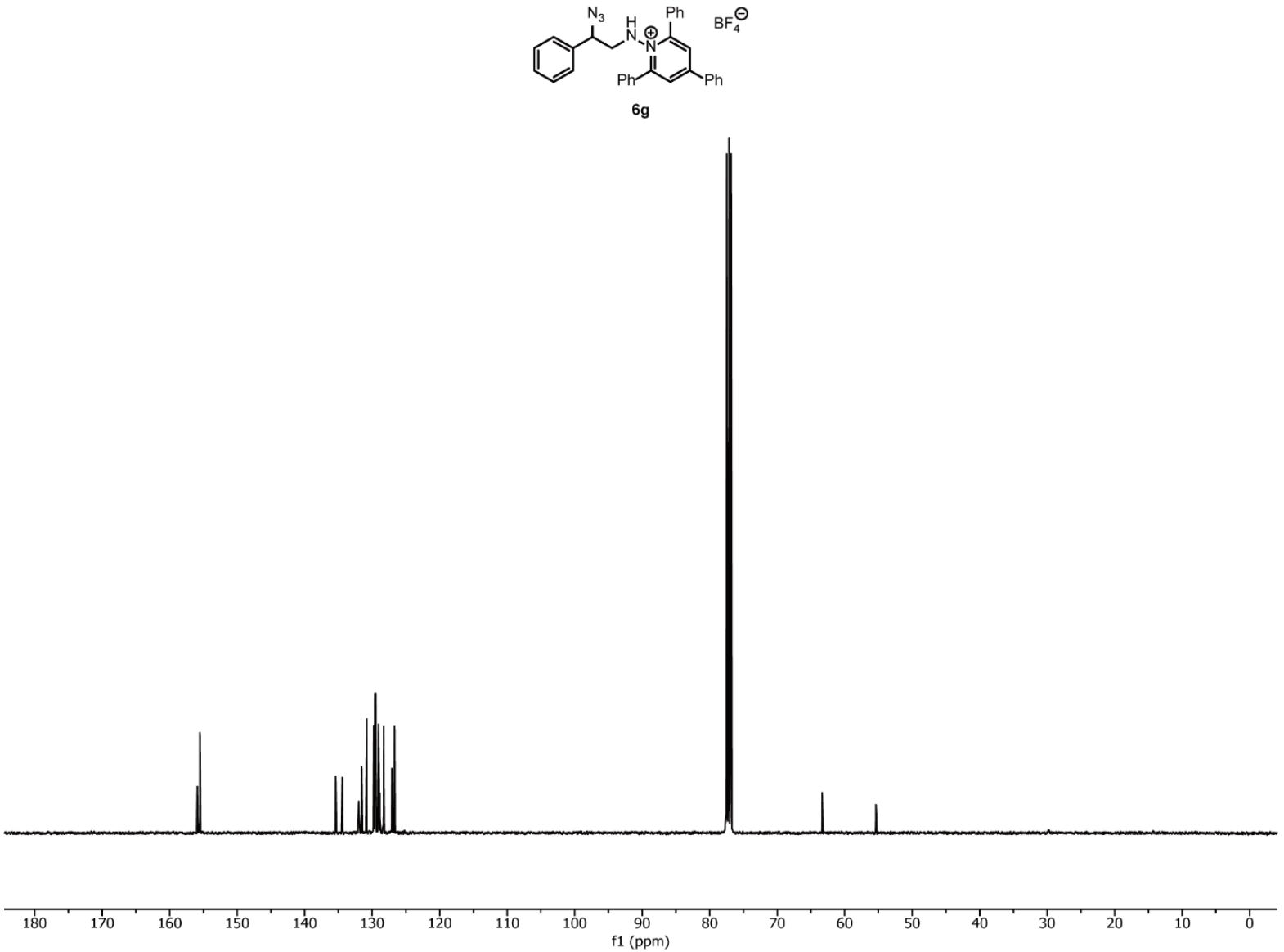


Figure S111. ^{13}C NMR spectrum of 1-((2-azido-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6g**) in $CDCl_3$ (101 MHz) at 23 °C.

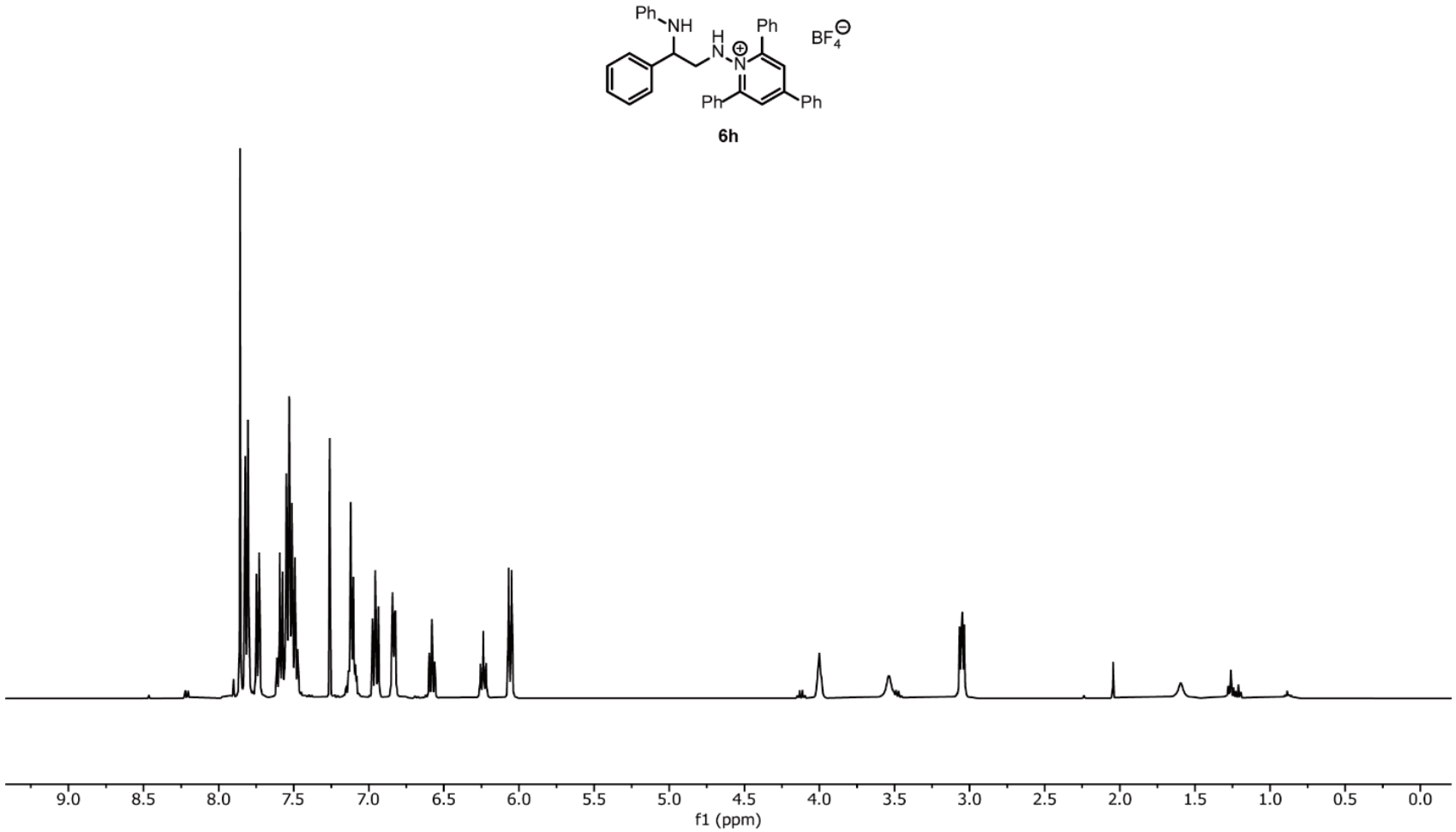


Figure S112. ^{1}H NMR spectrum of 2,4,6-triphenyl-1-((2-phenyl-2-(phenylamino)ethyl)amino)pyridin-1-ium tetrafluoroborate (**6h**) in $CDCl_3$ (400 MHz) at 23 °C.

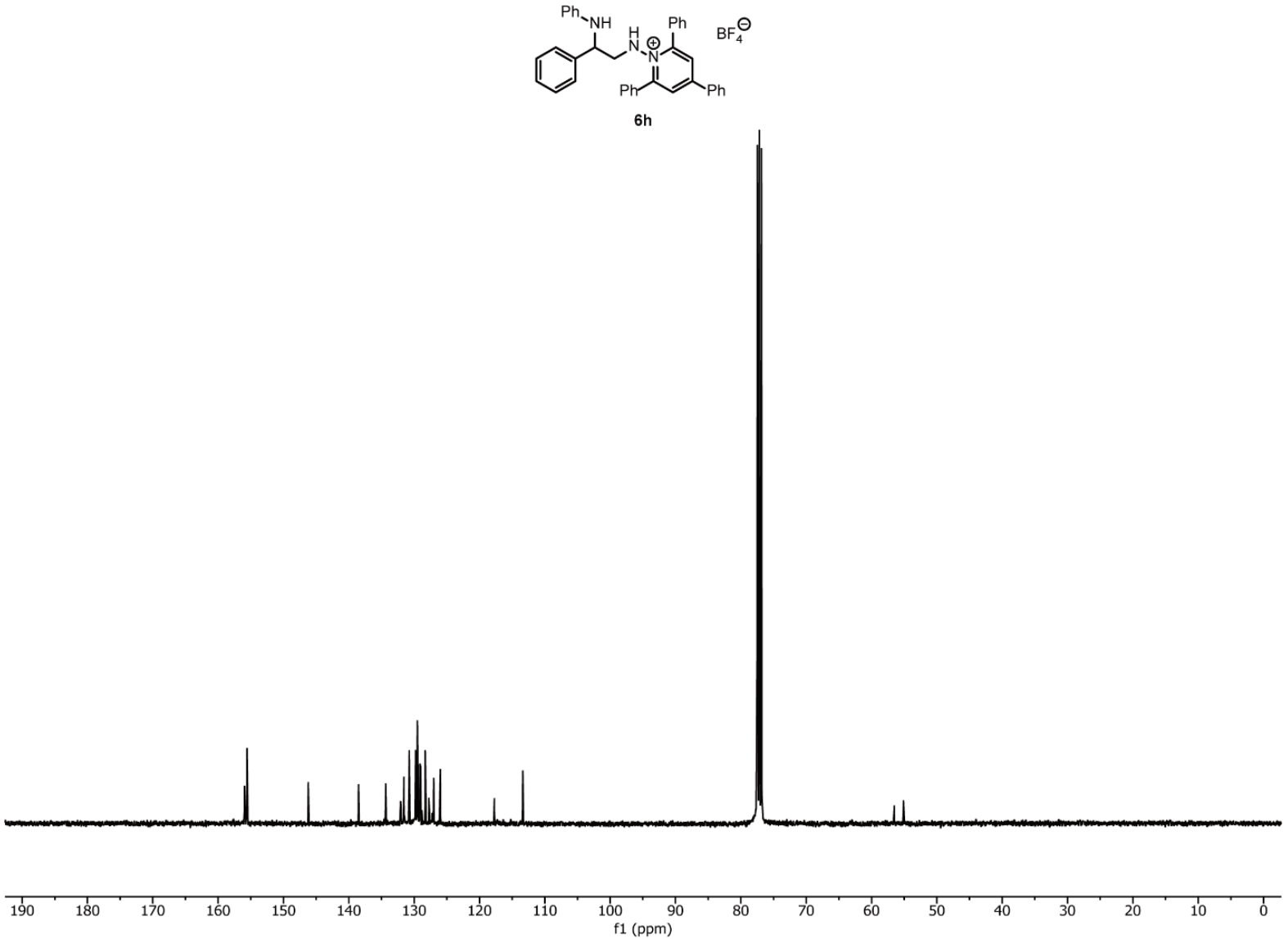


Figure S113. ^{13}C NMR spectrum of 2,4,6-triphenyl-1-((2-phenyl-2-(phenylamino)ethyl)amino)pyridin-1-ium tetrafluoroborate (**6h**) in $CDCl_3$ (101 MHz) at 23 °C.

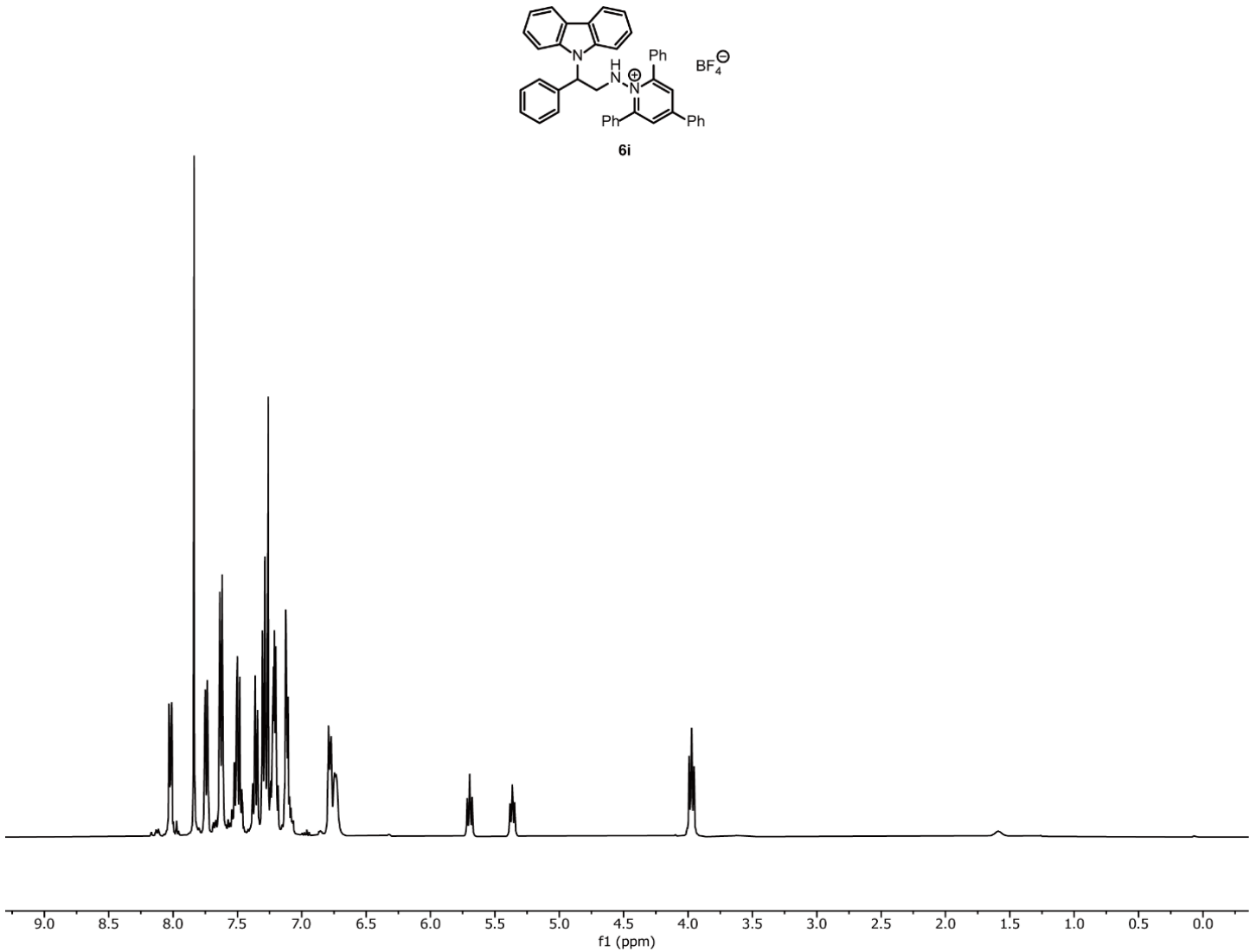


Figure S114. ^{1}H NMR spectrum of 1-((2-(9*H*-carbazol-9-yl)-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6i**) in $CDCl_3$ (400 MHz) at 23 °C.

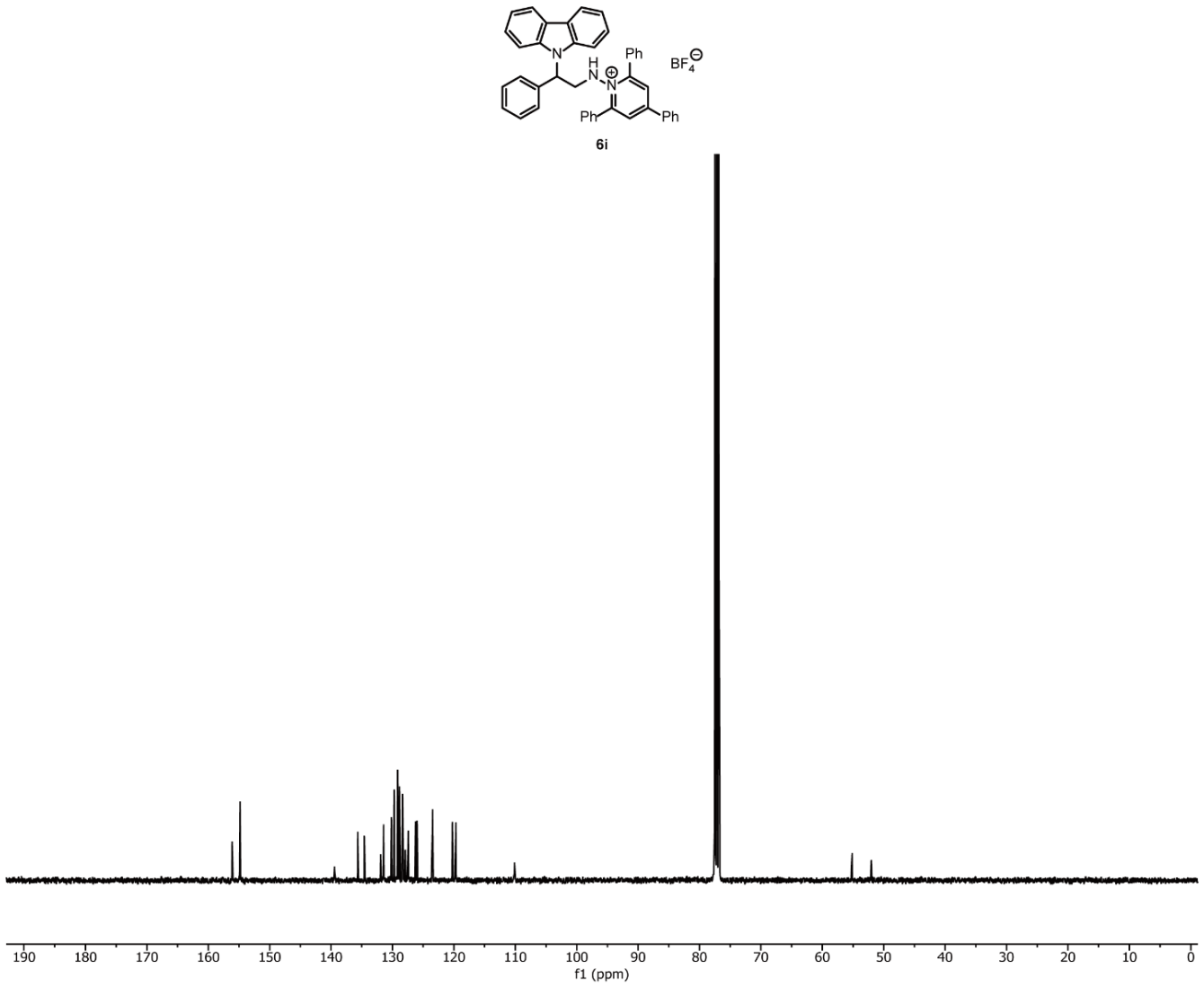


Figure S115. ^{13}C NMR spectrum of 1-((2-(9*H*-carbazol-9-yl)-2-phenylethyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**6i**) in $CDCl_3$ (101 MHz) at 23 °C.

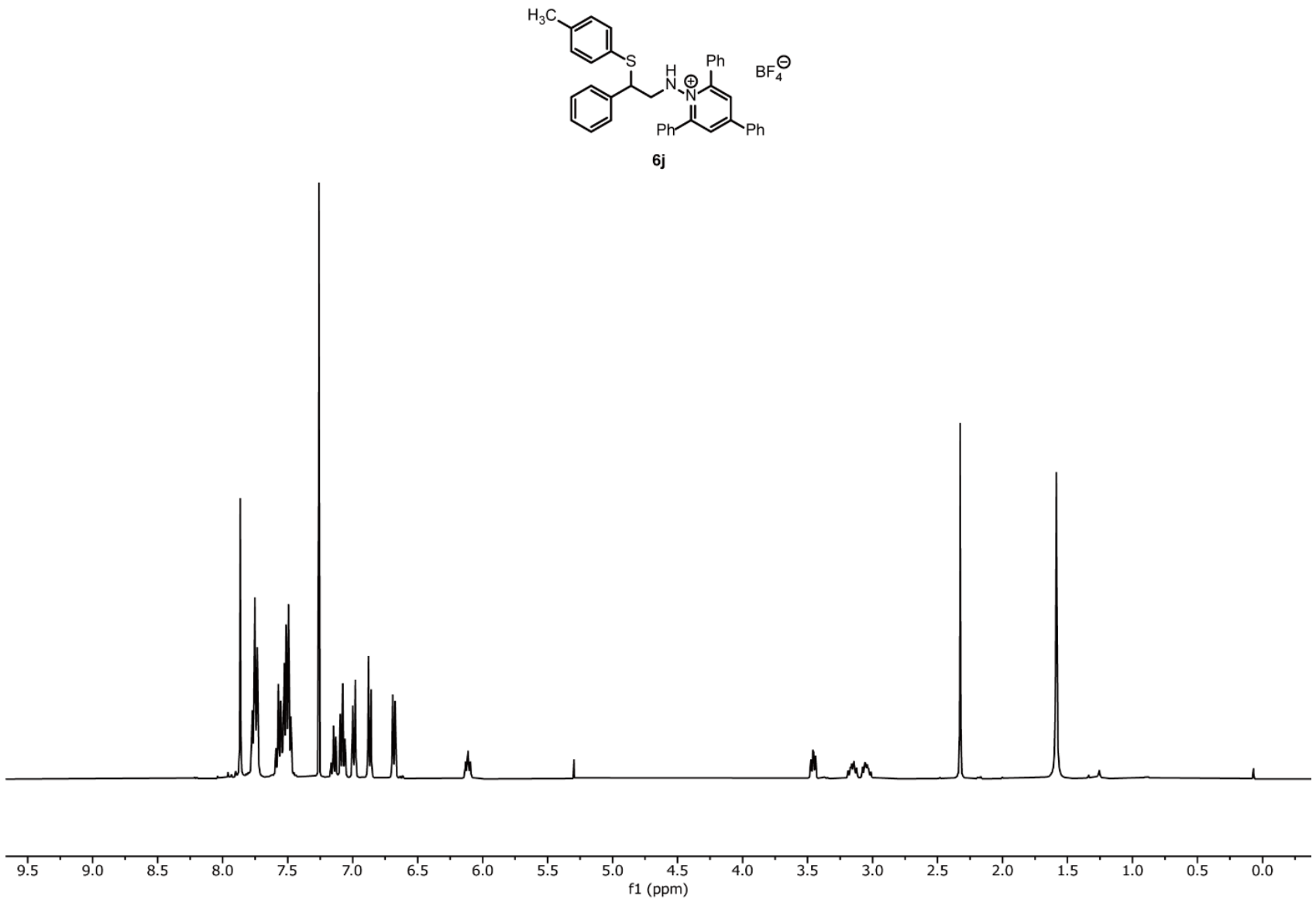


Figure S116. ^{1}H NMR spectrum of 2,4,6-triphenyl-1-((2-phenyl-2-(*p*-tolylthio)ethyl)amino)pyridin-1-ium tetrafluoroborate (**6j**) in $CDCl_3$ (400 MHz) at 23 °C.

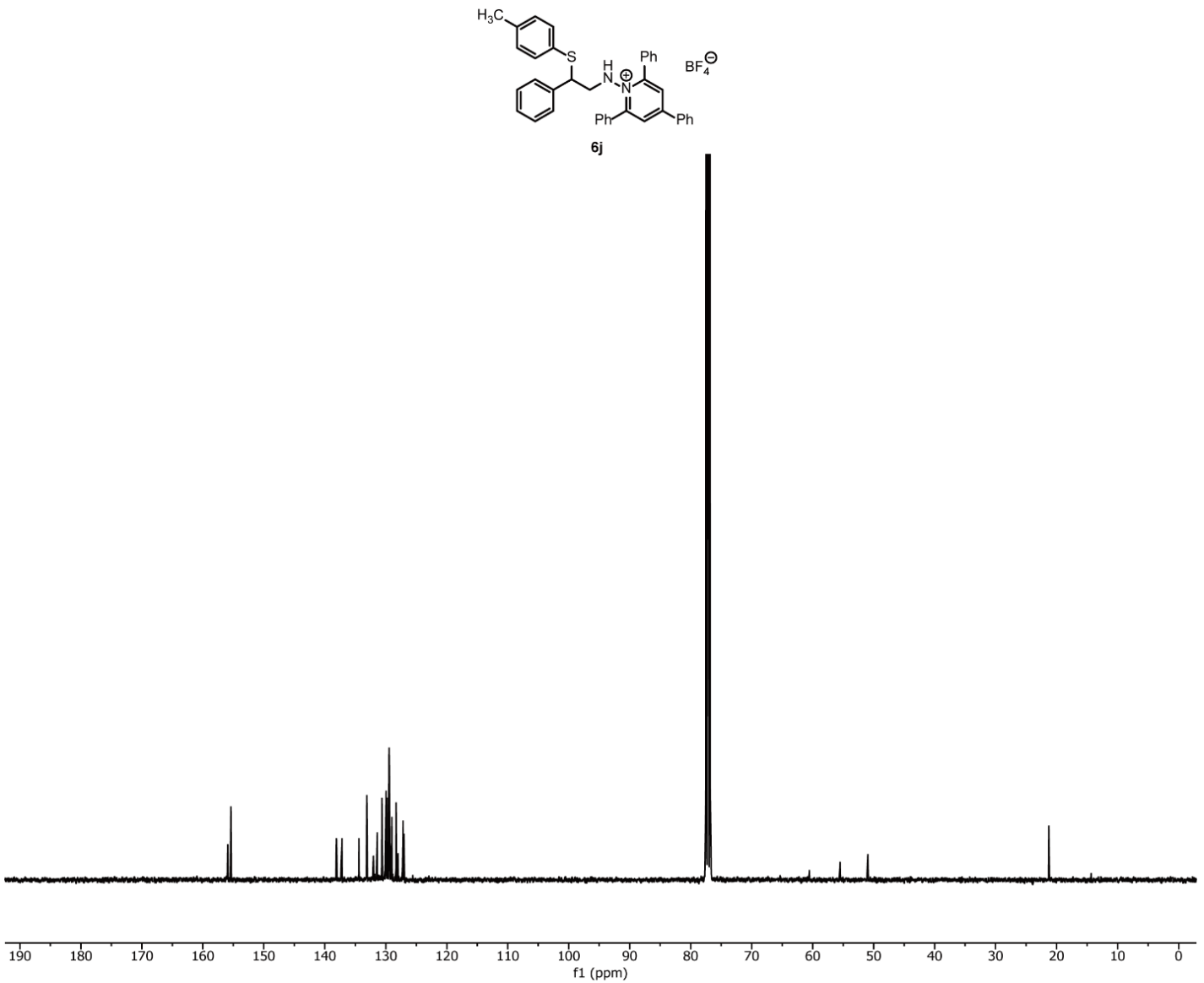


Figure S117. ^{13}C NMR spectrum of 2,4,6-triphenyl-1-((2-phenyl-2-(*p*-tolylthio)ethyl)amino)pyridin-1-ium tetrafluoroborate (**6j**) in $CDCl_3$ (101 MHz) at 23 °C.

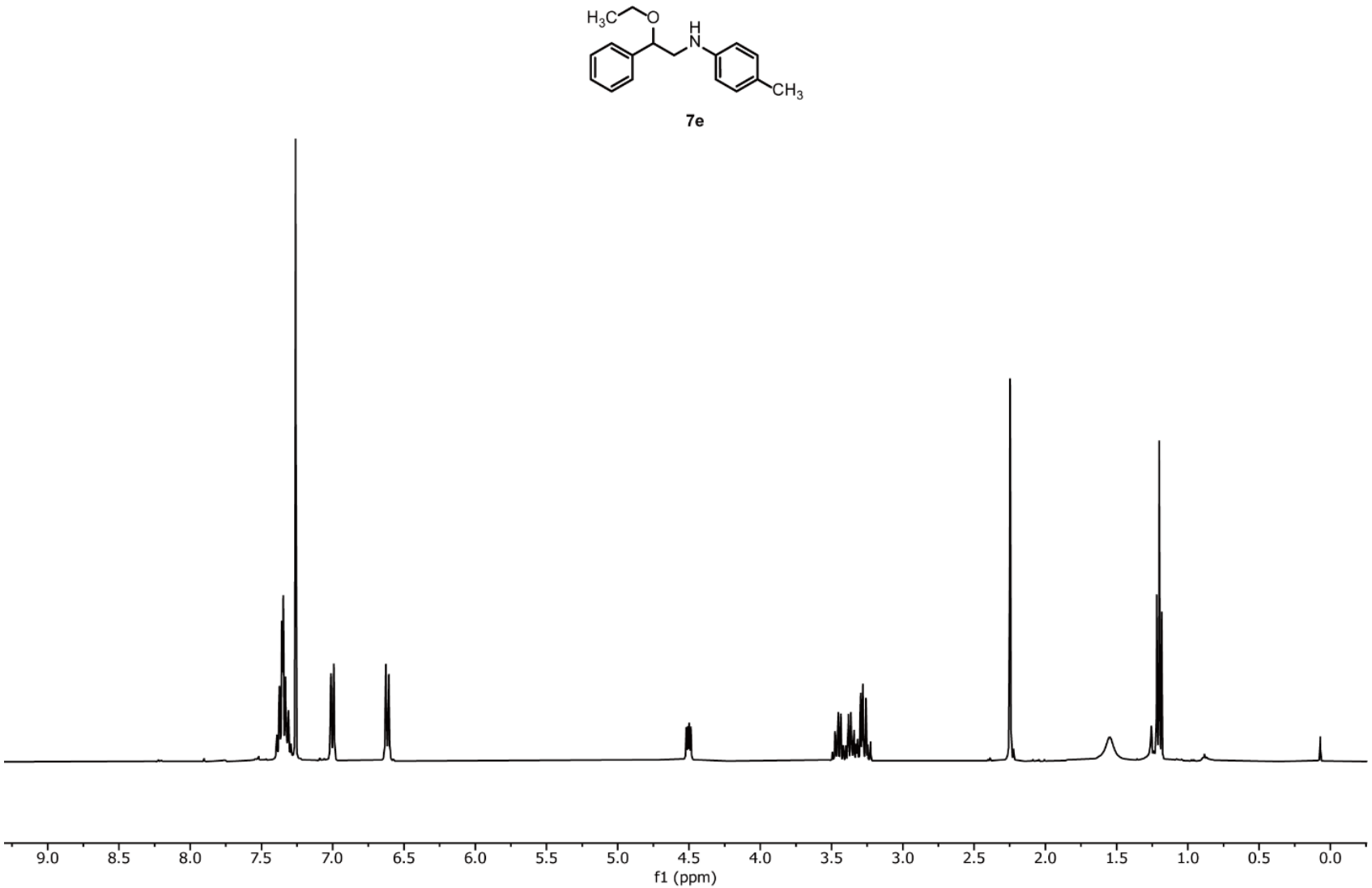


Figure S118. ^{1}H NMR spectrum of *N*-(2-ethoxy-2-phenylethyl)-4-methylaniline (**7e**) in $CDCl_3$ (400 MHz) at 23 °C.

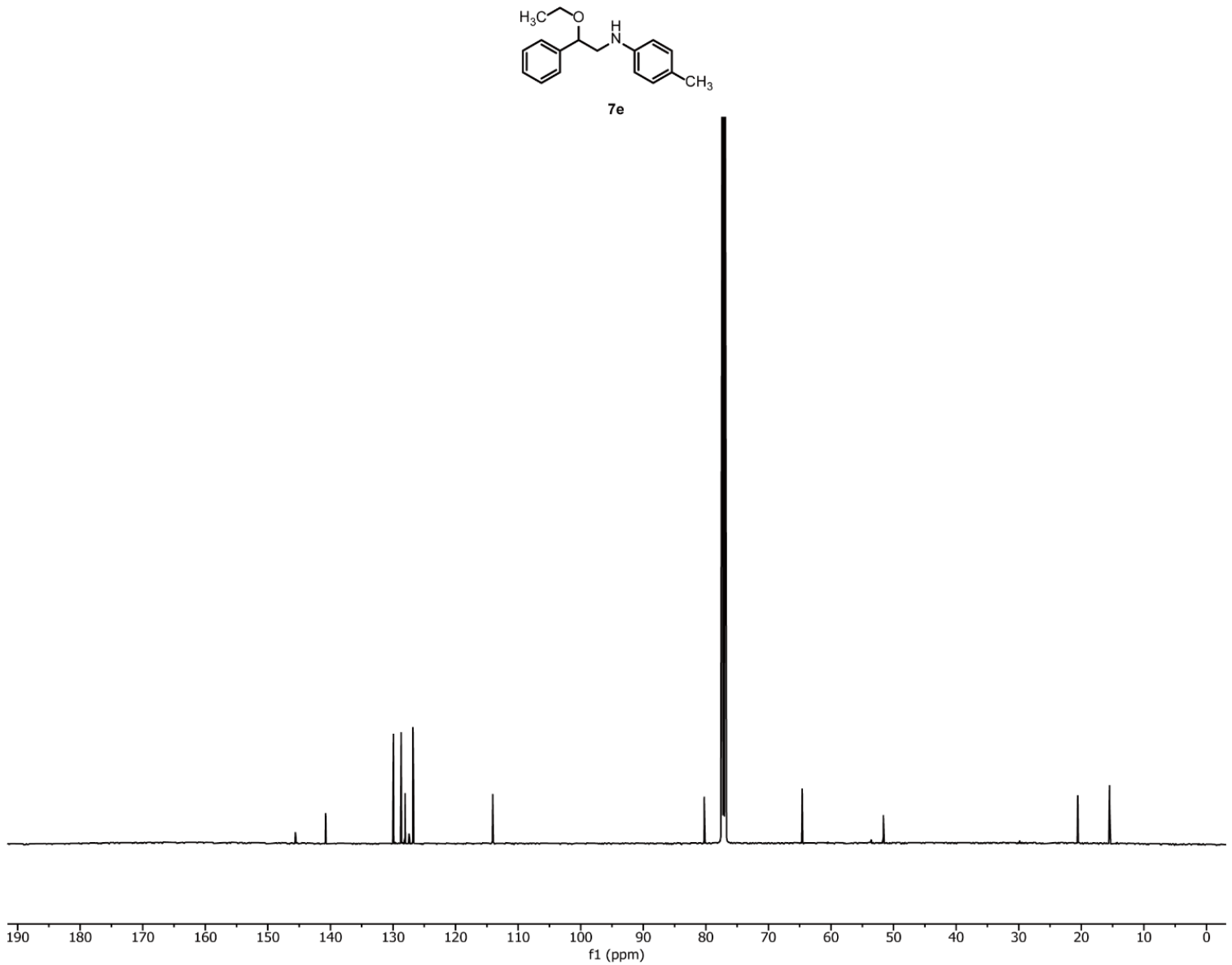


Figure S119. ^{13}C NMR spectrum of *N*-(2-ethoxy-2-phenylethyl)-4-methylaniline (**7e**) in $CDCl_3$ (101 MHz) at 23 °C.

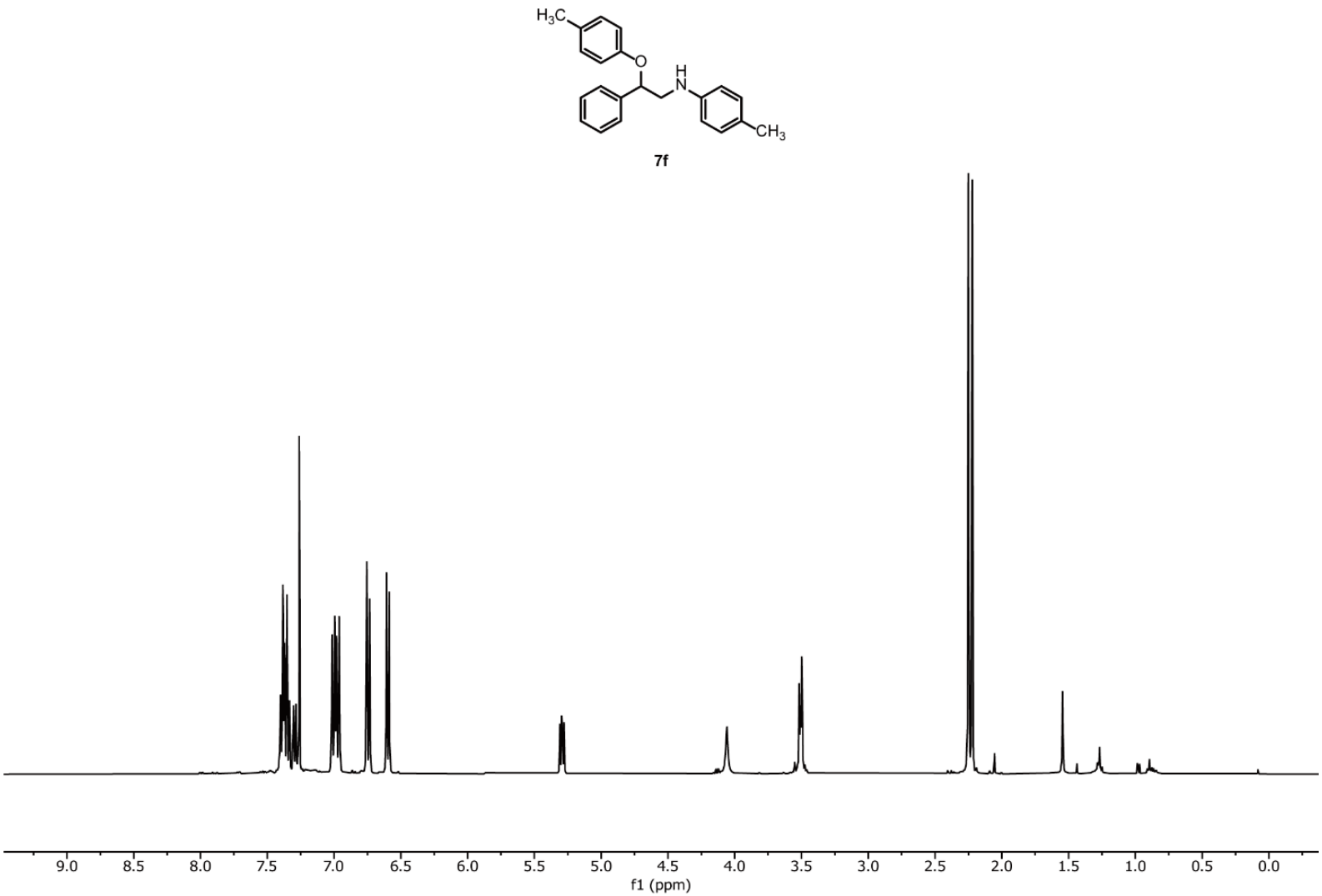


Figure S120. ^{1}H NMR spectrum of 4-methyl-*N*-(2-phenyl-2-(*p*-tolyloxy)ethyl)aniline (**7f**) in $CDCl_3$ (400 MHz) at 23 °C.

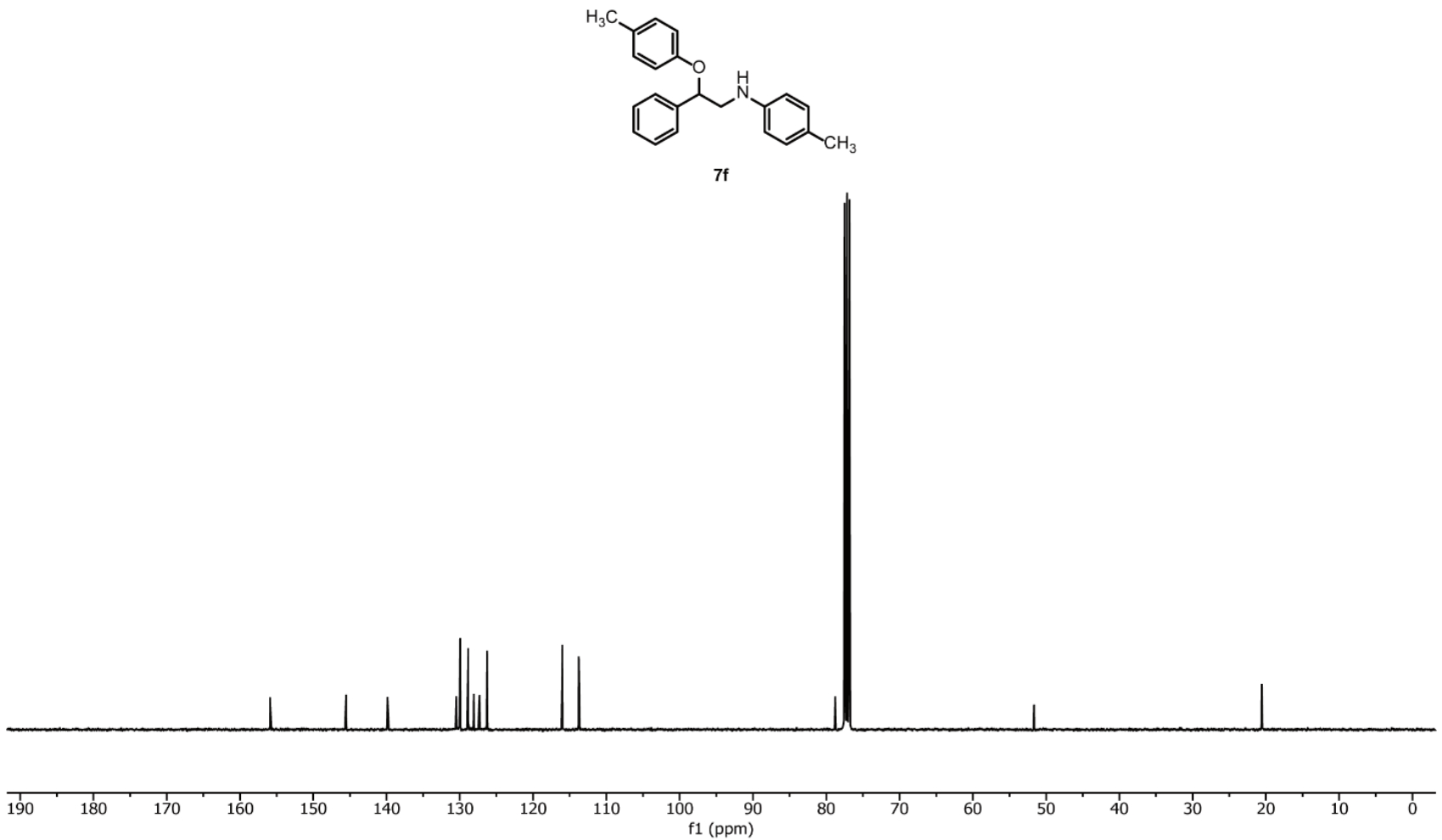


Figure S121. ^{13}C NMR spectrum of 4-methyl-*N*-(2-phenyl-2-(*p*-tolyloxy)ethyl)aniline (**7f**) in $CDCl_3$ (101 MHz) at 23 °C.

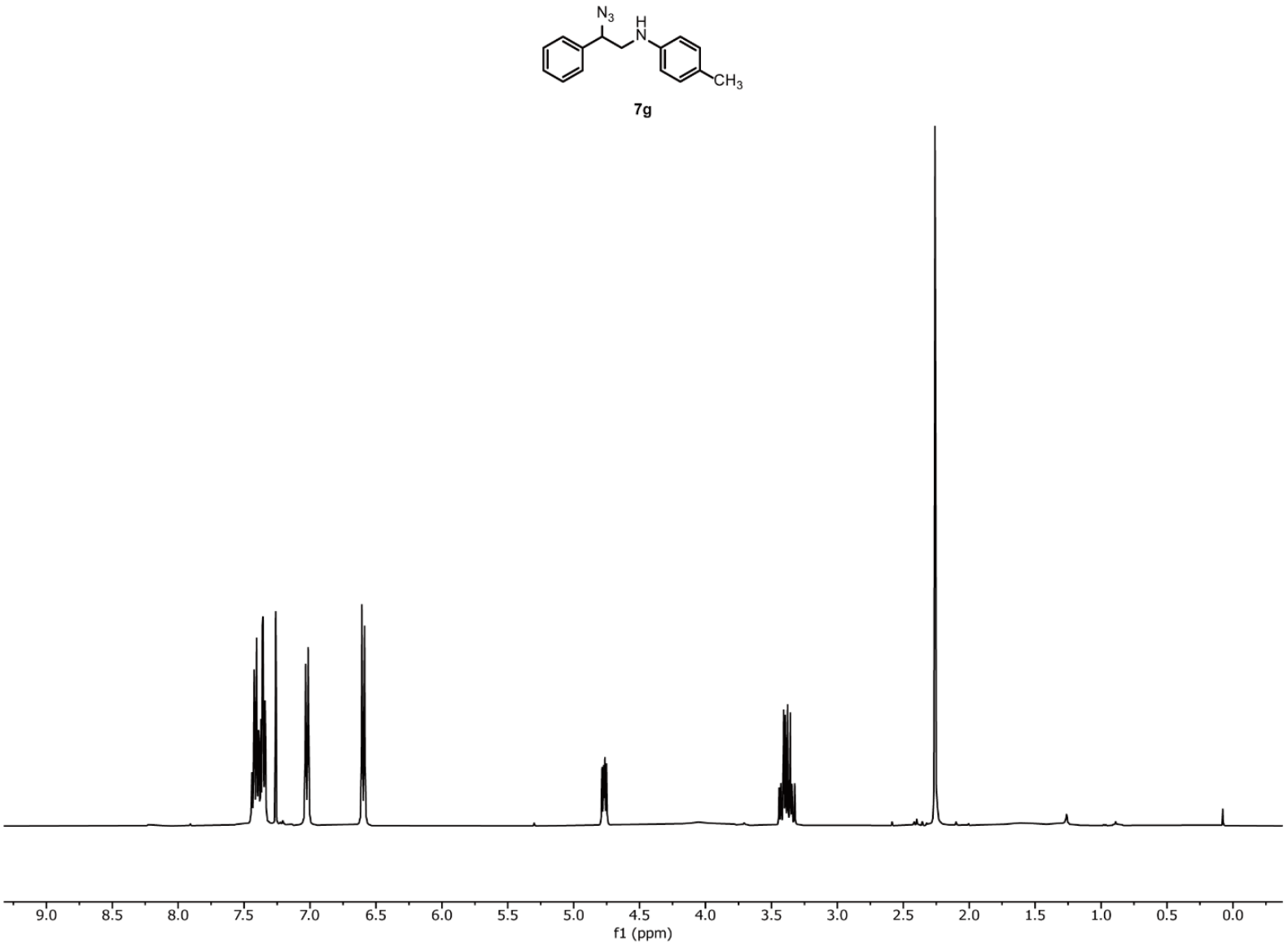


Figure S122. ^{1}H NMR spectrum of *N*-(2-azido-2-phenylethyl)-4-methylaniline (**7g**) in $CDCl_3$ (400 MHz) at 23 °C.

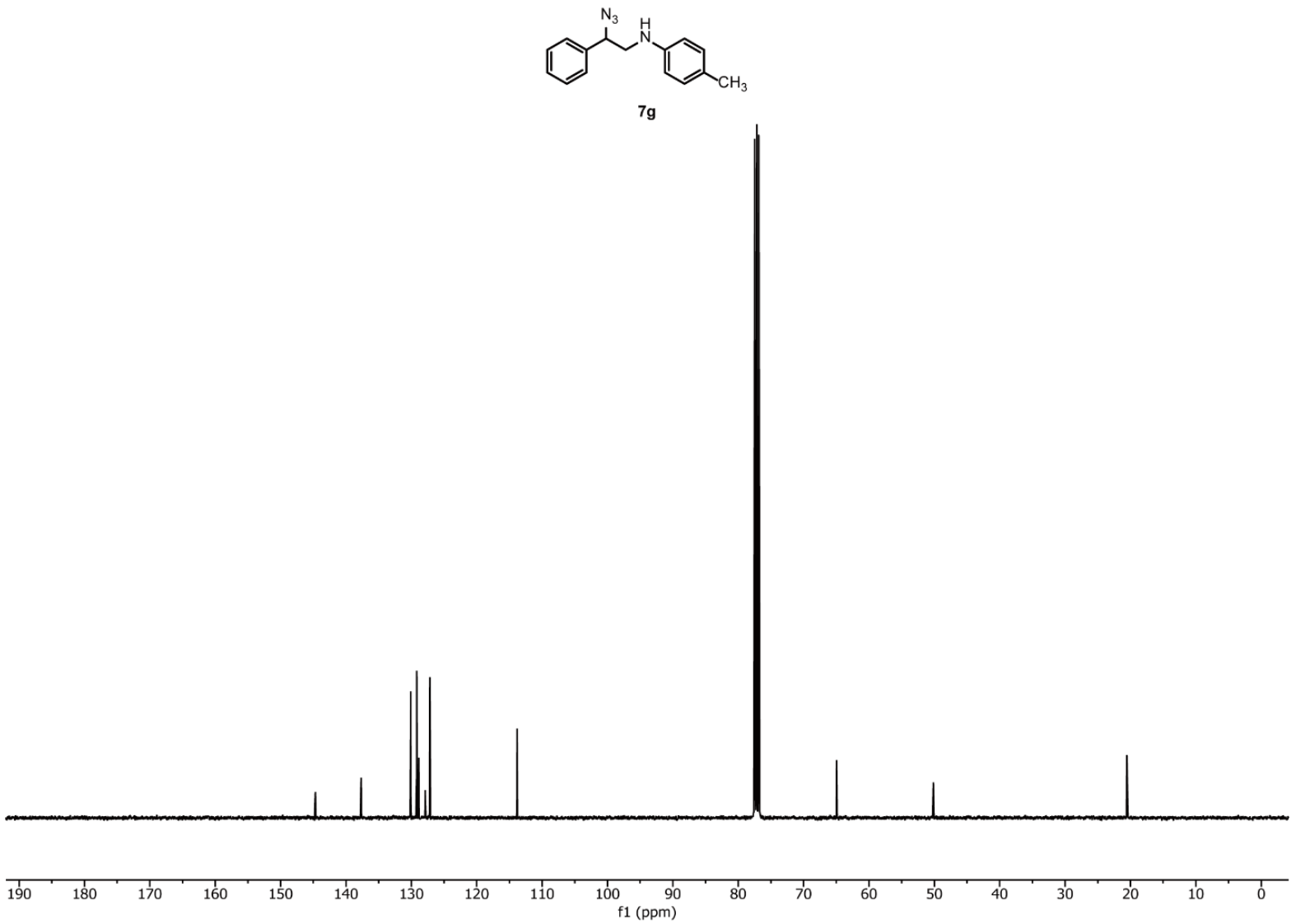


Figure S123. ^{13}C NMR spectrum of *N*-(2-azido-2-phenylethyl)-4-methylaniline (**7g**) in $CDCl_3$ (101 MHz) at 23 °C.

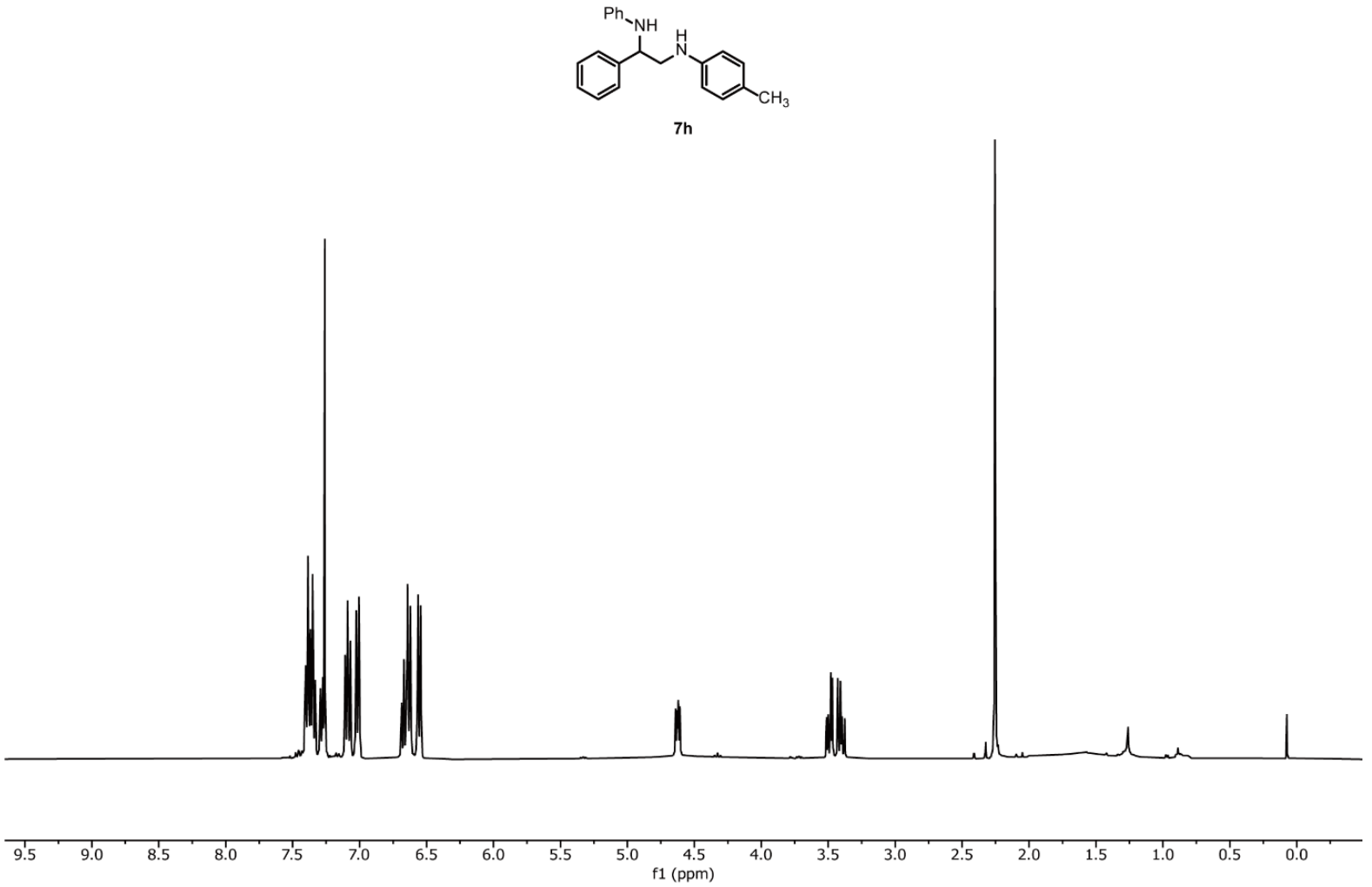


Figure S124. ^{1}H NMR spectrum of N^{1},^{1}-diphenyl-N^{2}-(*p*-tolyl)ethane-1,2-diamine (**7h**) in $CDCl_3$ (400 MHz) at 23 °C.

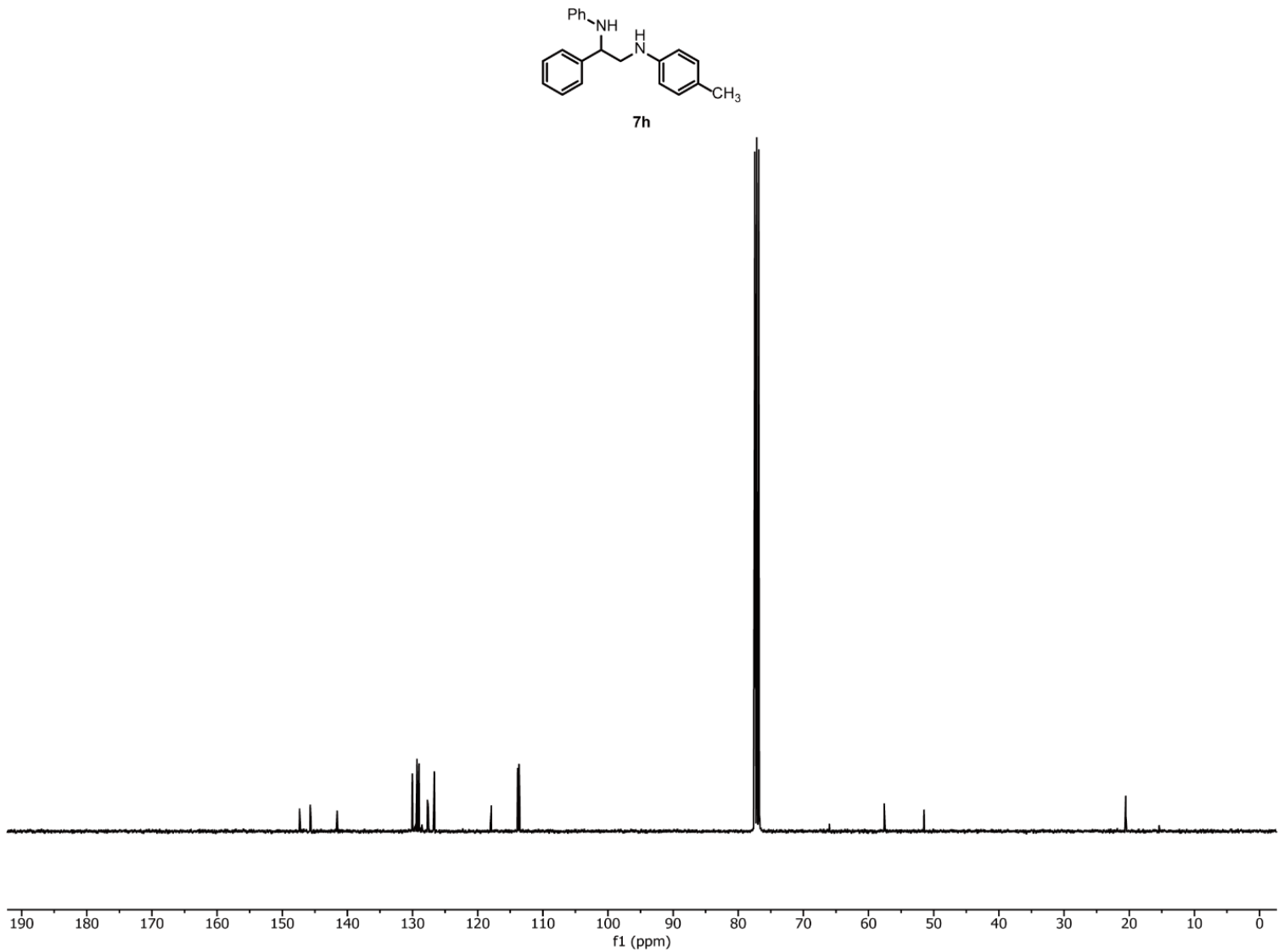


Figure S125. ^{13}C NMR spectrum of N^1,^{1}-diphenyl-N^2-(*p*-tolyl)ethane-1,2-diamine (**7h**) in $CDCl_3$ (101 MHz) at 23 °C.

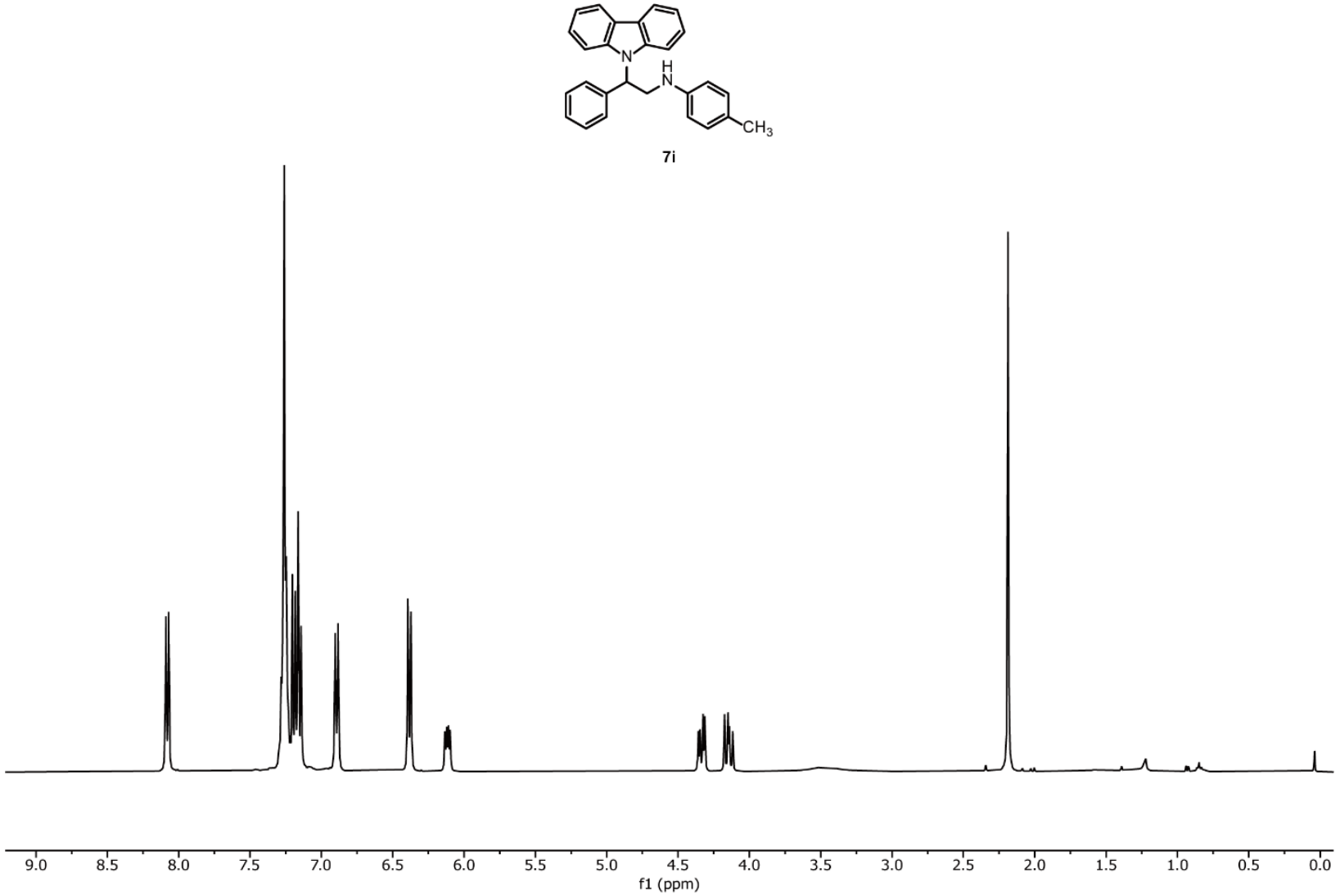


Figure S126. ^{1}H NMR spectrum of *N*-(2-(9*H*-carbazol-9-yl)-2-phenylethyl)-4-methylaniline (**7i**) in $CDCl_3$ (400 MHz) at 23 °C.

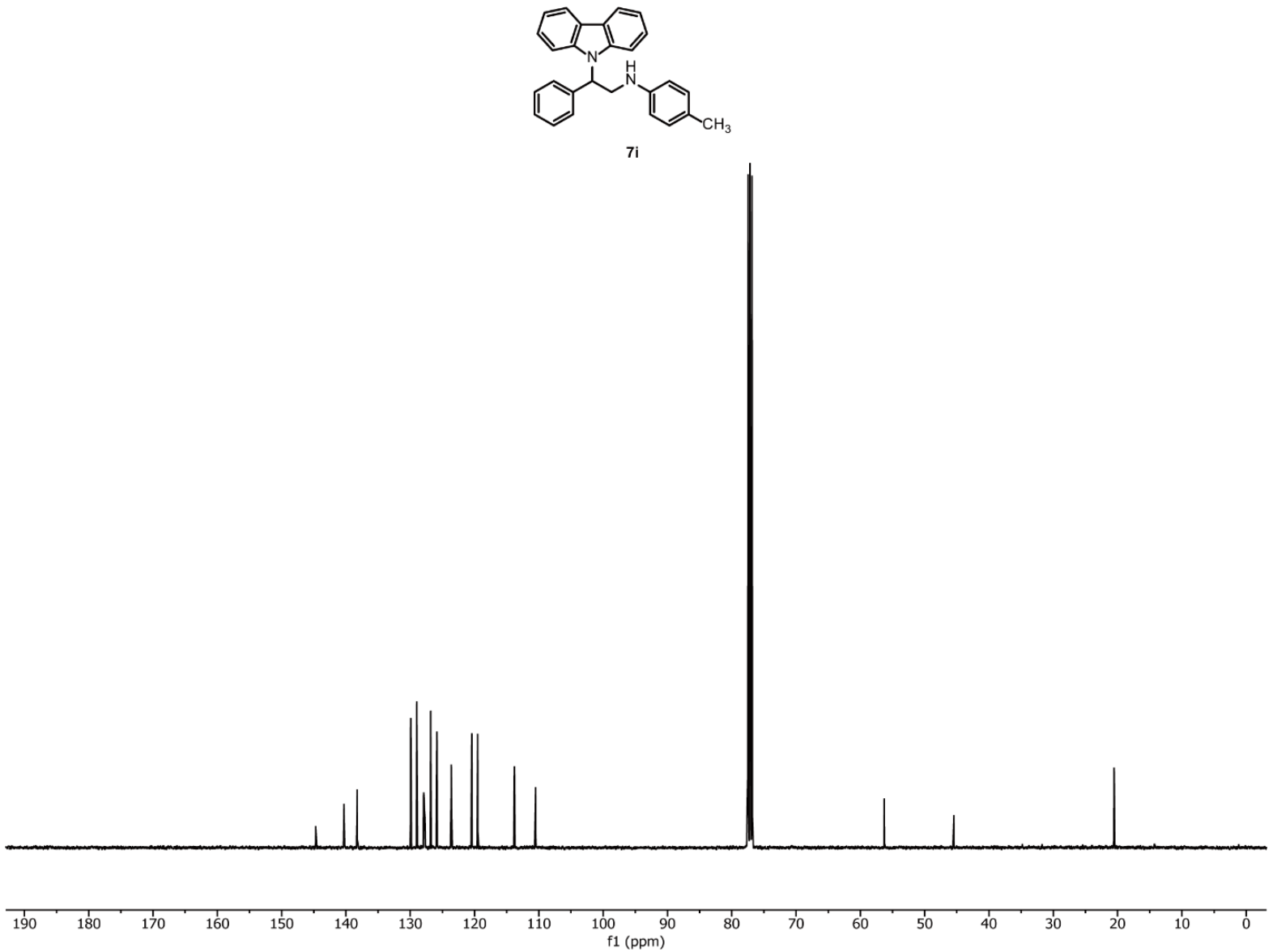


Figure S127. ^{13}C NMR spectrum of *N*-(2-(9*H*-carbazol-9-yl)-2-phenylethyl)-4-methylaniline (**7i**) in $CDCl_3$ (101 MHz) at 23 °C.

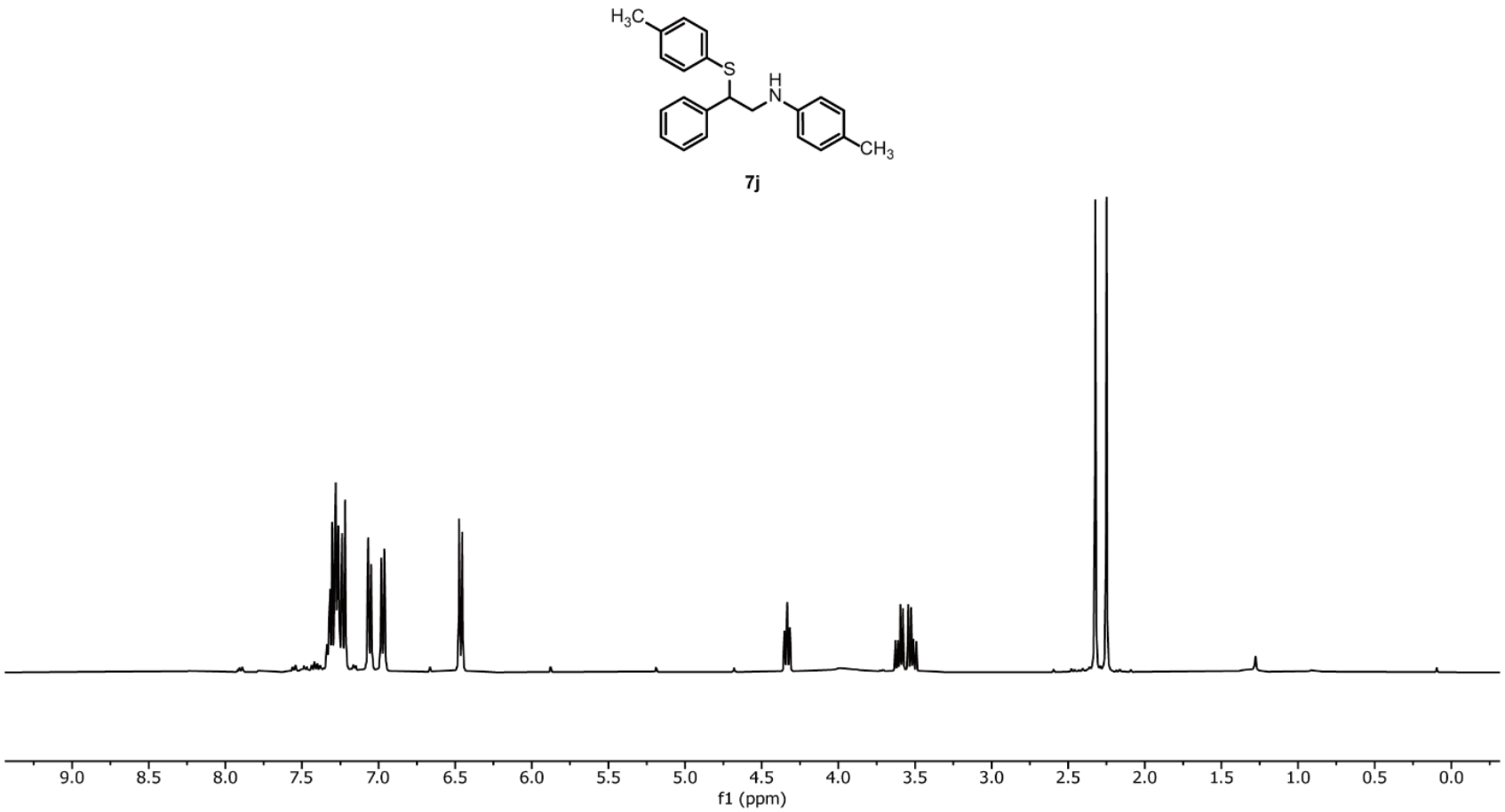


Figure S128. ^{1}H NMR spectrum of 4-methyl-*N*-(2-phenyl-2-(*p*-tolylthio)ethyl)aniline (**7j**) in $CDCl_3$ (400 MHz) at 23 °C.

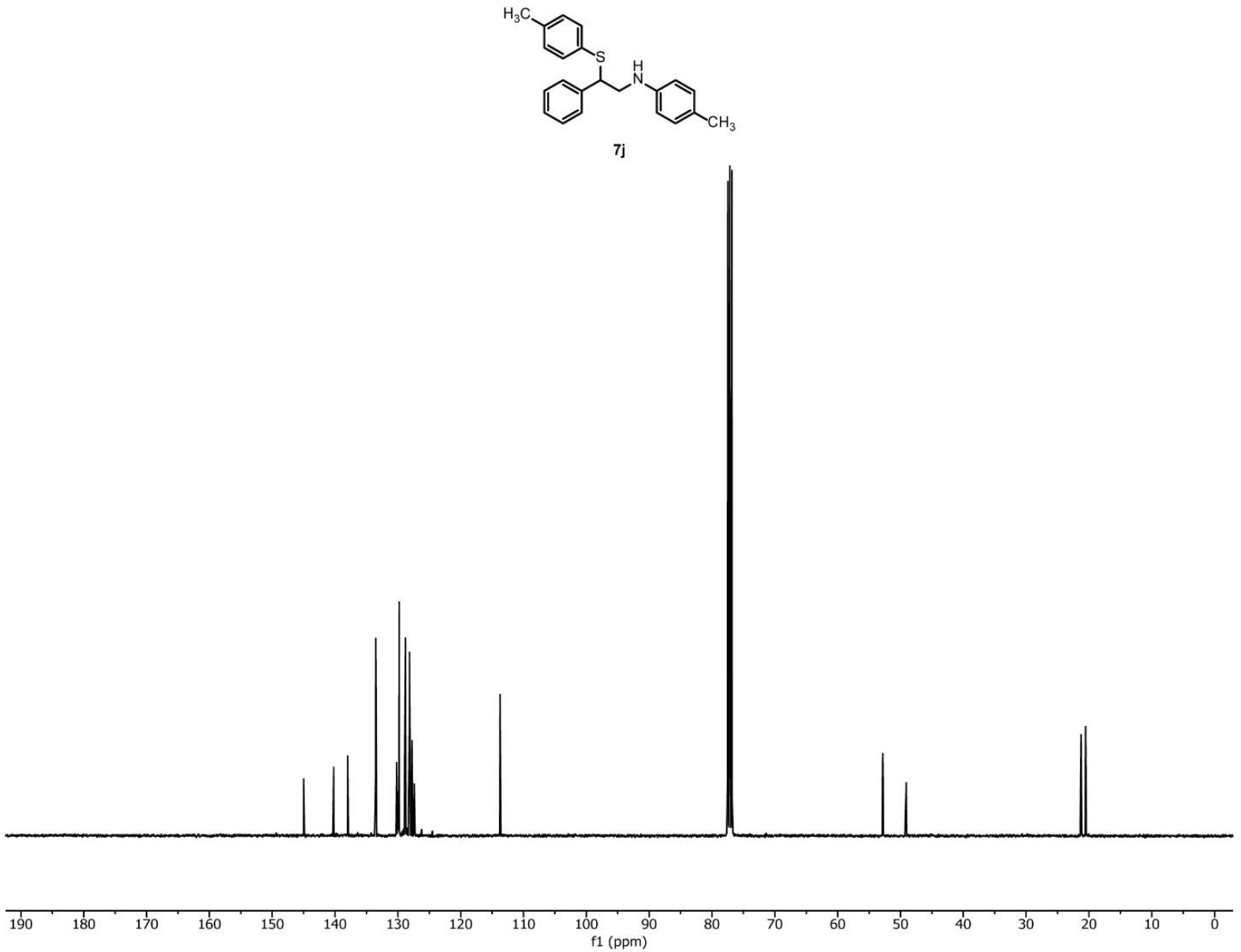


Figure S129. ^{13}C NMR spectrum of 4-methyl-*N*-(2-phenyl-2-(*p*-tolylthio)ethyl)aniline (**7j**) in $CDCl_3$ (101 MHz) at 23 °C.

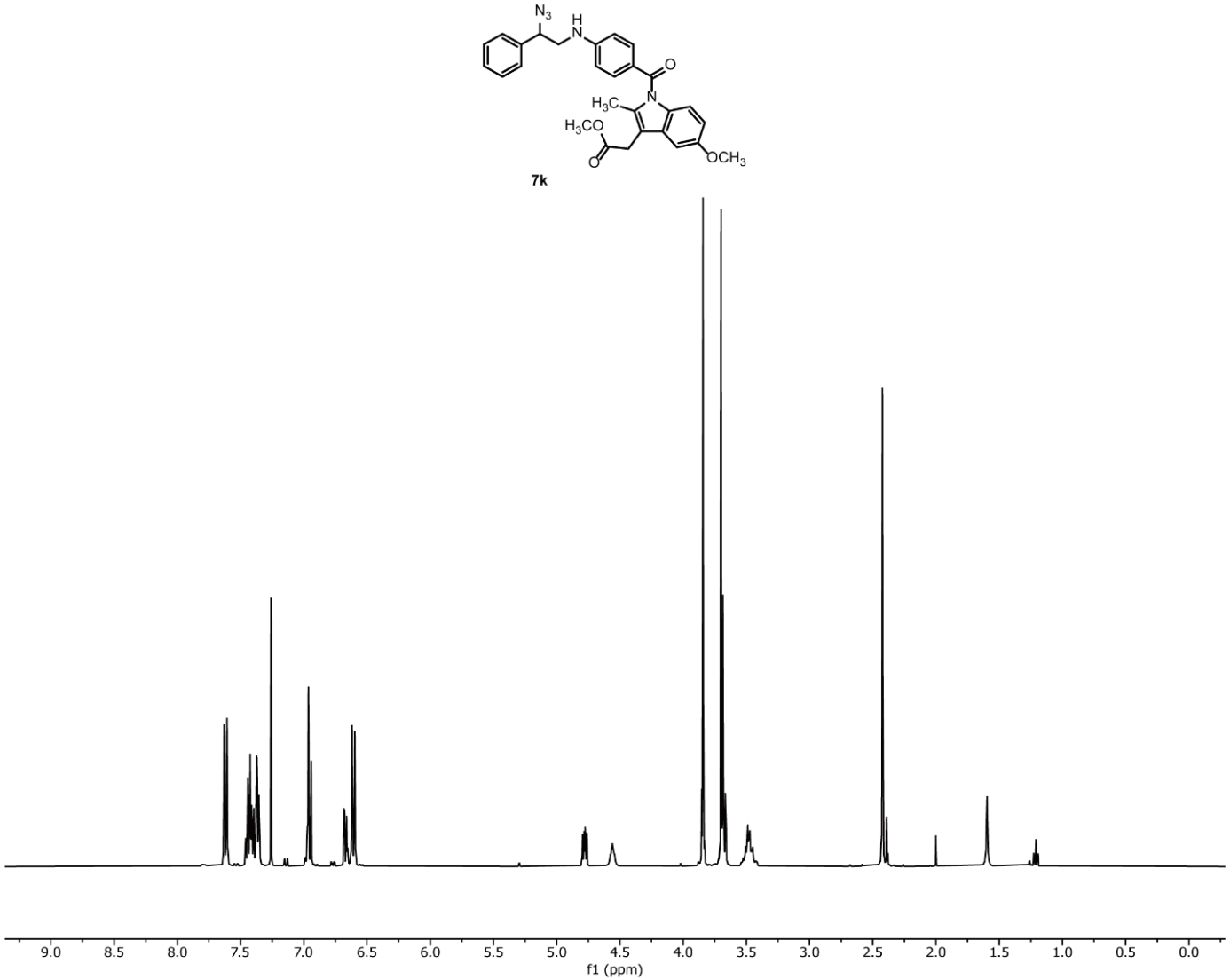


Figure S130. ^{1}H NMR spectrum of methyl 2-(1- (4-((2-azido-2-phenylethyl)amino)benzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (**7k**) in $CDCl_3$ (400 MHz) at 23 °C.

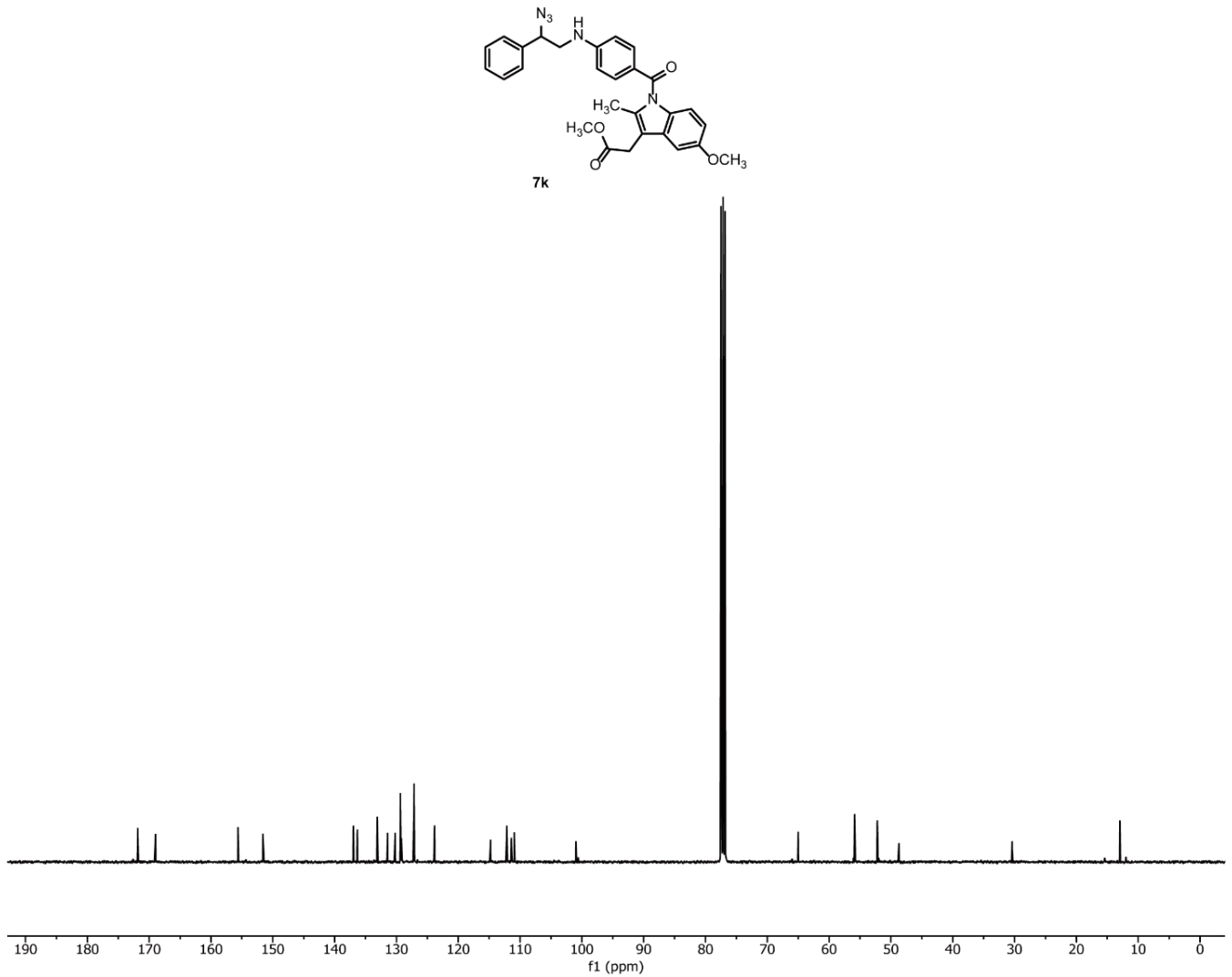


Figure S131. ^{13}C NMR spectrum of methyl 2-(1-(4-((2-azido-2-phenylethyl)amino)benzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (**7k**) in $CDCl_3$ (101 MHz) at 23 °C.

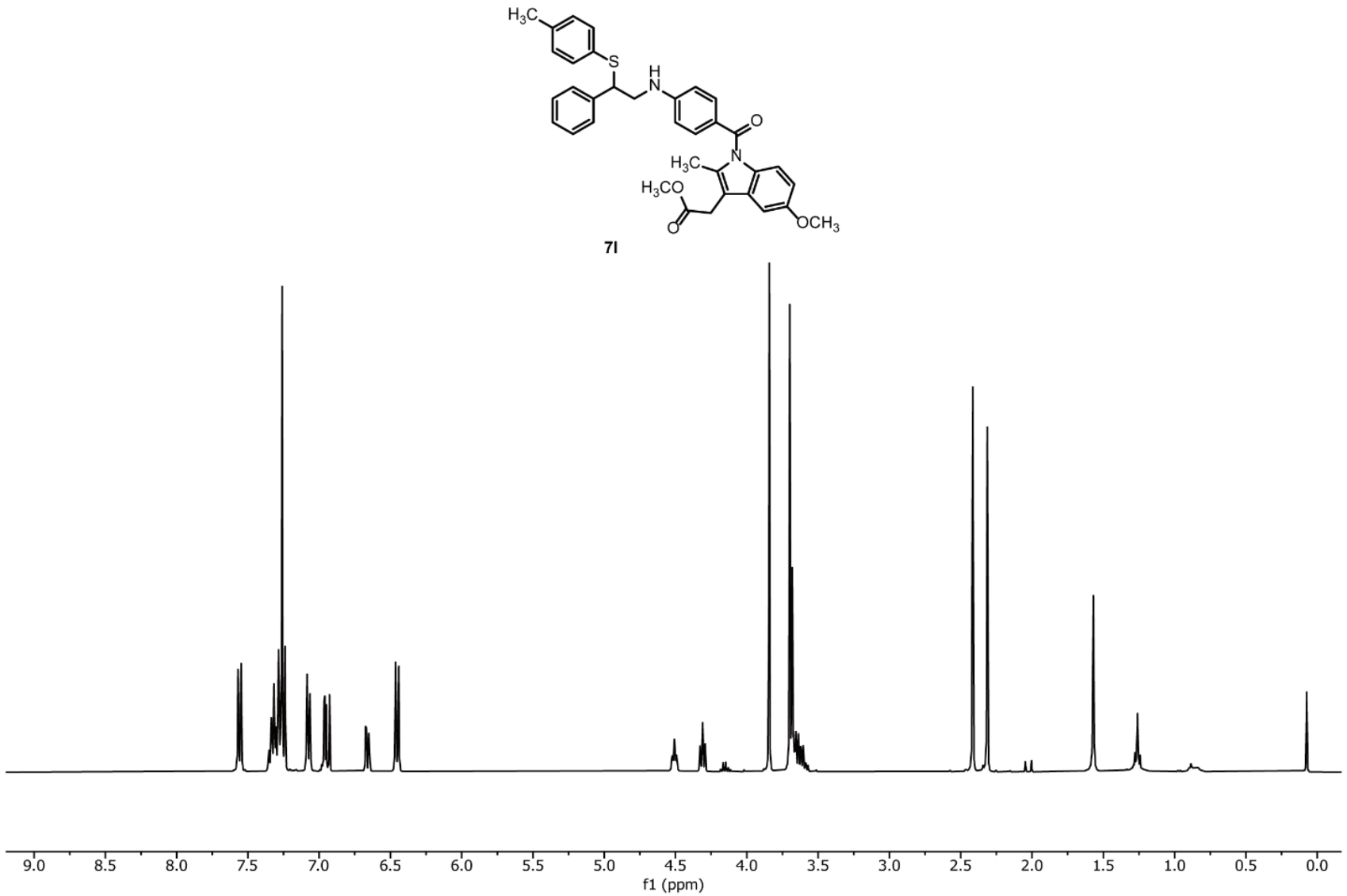


Figure S132. ^{1}H NMR spectrum of methyl 2-(5-methoxy-2-methyl-1-(4-((2-phenyl-2-(*p*-tolylthio)ethyl)amino)benzoyl)-1*H*-indol-3-yl)acetate (**7l**) in $CDCl_3$ (400 MHz) at 23 °C.

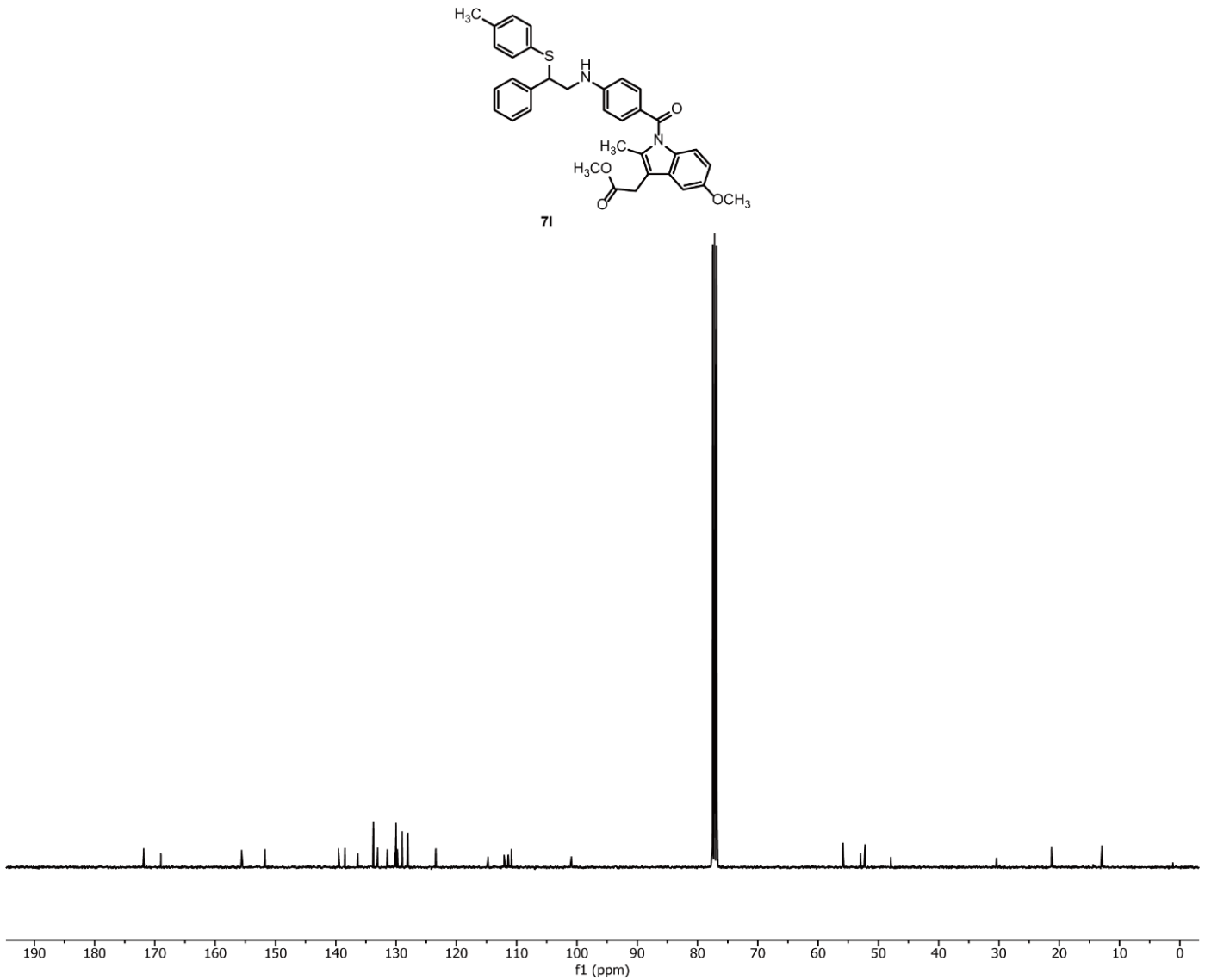


Figure S133. ^{13}C NMR spectrum of methyl 2-(1-(4-((2-azido-2-phenylethyl)amino)benzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (**7l**) in $CDCl_3$ (101 MHz) at 23 °C.

E. References

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.
2. Zha, Z.; Choi, S. R.; Ploessl, K.; Lieberman, B. P.; Qu, W.; Hefti, F.; Mintun, M.; Skovronsky, D.; Kung, H. F. Multidentate ^{18}F-Polypegylated Styrylpyridines As Imaging Agents for Aβ Plaques in Cerebral Amyloid Angiopathy (CAA). *J. Med. Chem.* **2011**, *54*, 8085–8098.
3. Gordillo, A.; Ortuño, M. A.; López-Mardomingo, C.; Lledós, A.; Ujaque, G.; de Jesús, E. Mechanistic Studies on the Pd-Catalyzed Vinylation of Aryl Halides with Vinylalkoxysilanes in Water: The Effect of the Solvent and NaOH Promoter. *J. Am. Chem. Soc.* **2013**, *135*, 13749–13763.
4. Gao, S.; Zhao, L.; Zhao, P.; Huang, Y.; Zhao, H. Synthesis, structure and characterization of a new highly porous zirconium-based metal-organic frameworks. *Inorg. Chim. Acta* **2018**, *480*, 173–176.
5. Rao, D. S.; Reddy, T. R.; Gurawa, A.; Kumar, M.; Kashyap, S. Photoswitchable Regiodivergent Azidation of Olefins with Sulfonium Iodate(I) Reagent. *Org. Lett.* **2019**, *21*, 9990–9994.
6. Chen, F.; Tang, Y.-T.; Li, X.-R.; Duan, Y.-Y.; Chen, C.-X.; Zheng, Y. Oxoammonium Salt-Mediated Vicinal Oxyazidation of Alkenes with NaN_3: Access to β-Aminooxy Azides. *Adv. Synth. Catal.* **2021**, *363*, 5079–5084.
7. Niu, D.; Buchwald, S. L. Design of Modified Amine Transfer Reagents Allows the Synthesis of α-Chiral Secondary Amines via CuH-Catalyzed Hydroamination. *J. Am. Chem. Soc.* **2015**, *137*, 9716–9721.
8. Li, G.; Qin, Z.; Radosevich, A. T. P(III)/P(V)-Catalyzed Methylamination of Arylboronic Acids and Esters: Reductive C–N Coupling with Nitromethane as a Methylamine Surrogate. *J. Am. Chem. Soc.* **2020**, *142*, 16205–16210.
9. Schönbauer, D.; Sambiago, C.; Noël, T.; Schnürch, M. Photocatalytic Deaminative Benzylation and Alkylation of Tetrahydroisoquinolines with *N*-Alkylpyrydinium Salts. *Beilstein J. Org. Chem.* **2020**, *16*, 809–817.
10. Beltrami, H.; Mallen, J. Reactions of 1-amino-2,4,6-triphenylpyridinium cations with α,β-unsaturated compounds synthesis of highly substituted pyrazolo [1,5-a]pyridine derivatives. *Tetrahedron* **1984**, *40*, 1683–1690.
11. Zhang, J.-Z.; Tang, Y. Iron-Catalyzed Regioselective Oxo- and Hydroxy-Phthalimidation of Styrenes: Access to α-Hydroxyphthalimide Ketones. *Adv. Synth. Catal.* **2016**, *358*, 752–764.
12. Song, C.-X.; Chen, P.; Tang, Y. Carboxylation of Styrenes with CBr_4 and DMSO via Cooperative Photoredox and Cobalt Catalysis. *RSC Advances* **2017**, *7*, 11233–11243.
13. Tang, M.; Han, S.; Huang, S.; Huang, S.; Xie, L.-G. Carbosulfenylation of Alkenes with Organozinc Reagents and Dimethyl(methylthio)sulfonium Trifluoromethanesulfonate. *Org. Lett.* **2020**, *22*, 9729–9734.
14. Bialek, M.; Cramail, H.; Deffieux, A.; Guillaume, S. M. Styrene Polymerization using Nickel(II) Complexes as Catalysts. *Eur. Polym. J.* **2005**, *41*, 2678–2684.
15. Lin, Q.; Diao, T. Mechanism of Ni-Catalyzed Reductive 1,2-Dicarbofunctionalization of Alkenes. *J. Am. Chem. Soc.* **2019**, *141*, 17937–17948.
16. Aihara, Y.; Chatani, N. Nickel-Catalyzed Direct Alkylation of C–H Bonds in Benzamides and Acrylamides with Functionalized Alkyl Halides via Bidentate-Chelation Assistance. *J. Am. Chem. Soc.* **2013**, *135*, 5308–5311.
17. Graham, T. J. A.; Doyle, A. G. Nickel-Catalyzed Cross-Coupling of Chromene Acetals and Boronic Acids. *Org. Lett.* **2012**, *14*, 1616–1619.
18. Sebest, F.; Casarrubios, L.; Rzepa, H. S.; White, A. J. P.; Díez-González, S. Thermal azide–alkene cycloaddition reactions: straightforward multi-gram access to Δ2-1,2,3-triazolines in deep eutectic solvents. *Green Chemistry* **2018**, *20*, 4023–4035.

19. Kiyokawa, K.; Kosaka, T.; Minakata, S. Metal-Free Aziridination of Styrene Derivatives with Iminoiodinane Catalyzed by a Combination of Iodine and Ammonium Iodide. *Org. Lett.* **2013**, *15*, 4858–4861.
20. Evans, D. A.; Bilodeau, M. T.; Faul, M. M. Development of the Copper-Catalyzed Olefin Aziridination Reaction. *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753.