Supporting Information

Pyridinium Salt Forming Rh(III)-Catalyzed Annulation Reaction of Secondary Allylamines with Internal Alkynes and Its Application to Surface Modification of a Mesoporous Material

Ye Ri Han, Su-Hyang Shim, Dong-Su Kim and Chul-Ho Jun*

*E-mail:junch@yonsei.ac.kr

Contents

1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column Chromatography were monitored using analytical thin-layer chromatography (TLC) carried out on 0.25 Merck silica gel plates (60 F-254) using UV light as a visualizing. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance II/DPX 400 (400 MHz ^{1}H, 100 MHz ^{13}C) spectrometer with chemical shifts reported relative to residual deuterated solvent peaks. Infrared spectra were obtained using a Nicolet Impact 400 spectrometer. ^{1}H NMR spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet). ^{13}C NMR spectra were referenced to the residual $CDCl_3$ (77.26 ppm), DMSO (39.5 ppm). Fluorescence data were recorded on a Hitachi F-4500 spectrometer. Transmission Electron Microscope datas were recorded by JEM-F200. Elemental analyses were recorded by 2400 Series II CHNS/O and High resolution mass spectra (HRMS) were acquired on 1290 Infinity LC/ 6530 Accurate-Mass Q-TOF (Agilent) at YCRF of Yonsei University facility.

2. Materials

Commercially available reagent grade chemicals were used as received without further purification unless otherwise stated. $[Cp^*RhCl_2]_2$[1] and functionalized internal alkynes[2] were prepared according to literature procedures.

3. Experimental

- General procedure for the preparation of pyridinium salt (3a, 3c-3n)

5-methyl-1-phenethyl-2,3-diphenylpyridin-1-ium tetrafluoroborate (**3a**): To a l mL pressure vial were added *N*-phenethyl-*N*-methallyl-amine (0.2 mmol), diphenylacetylene (0.4 mmol), copper acetate (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), tetrafluoroboric acid (48% in water, 0.3 mmol) and methanol. The resulting solution was stirred at 130 ^{o}C for 6 h, dried over

anhydrous $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo* giving a residue that was subjected to silica gel column chromatography (DCM:MeOH = 1:1) to yield 5-methyl-1-phenethyl-2,3-diphenylpyridin-1-ium tetrafluoroborate (**3a**) in 84% yield (white solid, 71 mg).

- Preparation of pyridinium salt 3i in 2 mmol scale

To a a 5 mL pressure vial were added *N*-phenethyl-*N*-methallyl-amine (2 mmol), 1,2-bis(4-fluorophenyl)ethyne (4 mmol), copper acetate (4 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), tetrafluoroboric acid (48% in water, 3 mmol) and methanol. The resulting solution was stirred at 130 ^oC for 6 h, dried over anhydrous $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo* giving a residue that was subjected to silica gel column chromatography (DCM:MeOH = 1:1) to yield 2,3-bis(4-fluorophenyl)-5-methyl-1-phenethylpyridin-1-ium tetrafluoroborate (**3i**) in 76% yield (white solid, 719 mg).

- Procedure for the preparation of 1,5-dimethyl-2,3-diphenylpyridin-1-ium tetrafluoroborate (3b)

To a l mL pressure vial were added *N*,2-dimethylprop-2-en-1-aminium chloride (0.2 mmol), $NaHCO_3$ (0.4 mmol), diphenylacetylene (0.4 mmol), copper acetate (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), tetrafluoroboric acid (48% in water, 0.3 mmol) and methanol. The resulting solution was stirred at 130 ^oC for 6 h, dried over anhydrous $MgSO_4$, filtered, and filtrate was concentrated *in vacuo* giving a residue that was subjected to silica gel column chromatography (DCM:MeOH = 1:1) to yield 1,5-dimethyl-2,3-diphenylpyridin-1-ium tetrafluoroborate (**3b**) in 65% yield (yellow solid, 45 mg).

- Procedure for the preparation of *N*-(2-methaylallyl)-11-((2-methylallyl)(3-methylbut-3-en-2-yl)silyl)undecan-1-amine (1h)

To a 5 mL pressure vial were added (11-chloroundecyl)(methyl)bis(2-methylallyl)silane (CAS No. 1027771-65-8, 3.67 mmol), methylallylamine (1.5 eq), TBAI (0.4 eq) and Et_3N (2 eq). The resulting solution was stirred at 100 ^oC for 12 h, filtered, and the filtrate was concentrated *in vacuo*. The residue was subjected to silica gel column chromatography (n-hexane:EA = 5:1) to give **1h** as a yellow liquid (24% yield, 333 mg).

- Preparation of secodary allylamine-impregnated SBA-15 (10a)

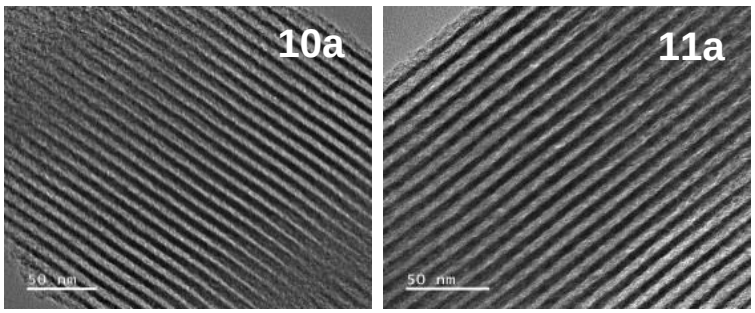
A solution of pluronic P123 (500 mg) in distilled water (4 mL) was stirred at 35 ^oC for 4 h. Then, 2 M HCl solution (15 mL) was added, and the mixture was stirred vigorously for 1 h at ambient temperature and 40 ^oC for additional 1 h. After adding 1.11 mL of TEOS (5 mmol) dropwise, the mixture was stirred for 3 h. Secondary allylamine-linked methallylsilane (**1h**, 0.05 mmol, 18.8 mg) was added slowly and the mixture was stirred vigorously for 21 h, transferred to a hydrothermal reactor, and let stand at 100 ^oC for 48 h. The mixture was washed with excess H_2O, ethanol, acetone and diethyl ether thoroughly to give solid powder, which was dispersed in ethanol, and the resulting slurry was stirred at 80 ^oC for 24 h. The mixture was filtered, and the filter cake was washed with ethanol and acetone thoroughly, and dried *in vacuo* to give **10a**.

- Preparation of pyridinium salt modified SBA-15, 11a by surface modification

To a l mL pressure vial were added **10a** (30 mg), diphenylacetylene (2 eq), copper acetate (5 eq), $[Cp^*RhCl_2]_2$ (5 mol%), tetrafluoroboric acid (48% in water, 1.5 eq) and methanol. The resulting slurry was stirred at 100 ^oC 2 h and filtered. The precipitate was washed thoroughly with methanol, H_2O, acetone and DCM and then dispersed in Et_2NCS_2Na solution (0.1 M). The resulting slurry was stirred at RT for 1 h and filtered, giving a precipitate that was washed

with methanol, a NaOAc solution (0.01 M, MeOH), acetone and DCM. The resulting precipitate was dried *in vacuo* to give **11a**.

- TEM images of 10a, 11a



- Fluorescent detection of nitrobenzene

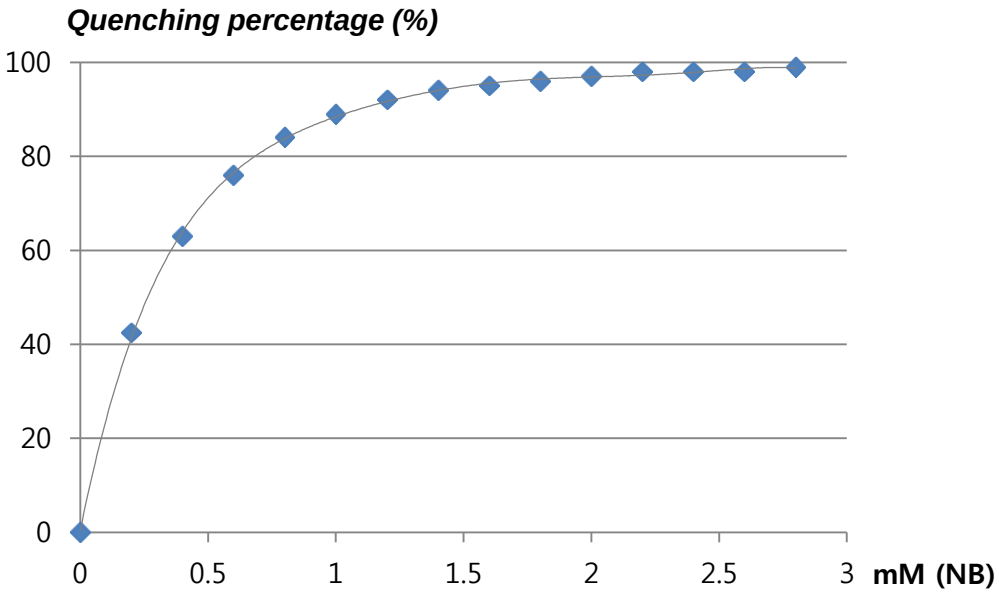
Before addition of nitrobenzene, the fluorescent spectra of **11a** (1.5 mg in 2mL DCM) was recorded (excitation at 300 nm). Then, 20 μL to 280 μL of a solution of nitrobenzene (0.02 M) in DCM was added and fluorescent spectra of the mixture was recorded (Figure 3). This procedure was repeated using 280 μL of the nitrobenzene solution. After use in the fluorescence quenching experiment, **11a** was subjected to centrifugation and washed thoroughly with DCM (1 mL for 5 times) and acetone (1 mL for 2 times) to give recovered **11a**, which was monitored by fluorometer. This procedure was repeated three times (Figure 4).

- Quenching efficiency of 11a with nitrobenzene

It is very hard to compare the quenching effect of **11a** (1.5 mg dispersed in CH_2Cl_2 2 mL) with nitrobenzene compared with others due to the different conditions. But this method shows following efficiency as 99% at 2.8 mM of nitrobenzene (NB).

$$\frac{I_0 - I}{I_0} \times 100 = \text{quenching rate (\%)}$$

I_0 : fluorescence intensity in the absence of the analyte
I : fluorescence intensity in the presence of the analyte



4. Compounds characterization data

5-methyl-1-phenethyl-2,3-diphenylpyridin-1-ium tetrafluoroborate (3a, CAS No. 2097667-91-7)[3] Obtained as a white solid (84% yield, 71.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.09 (s, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.19-7.12 (m, 8H), 7.05-7.04 (m, 2H), 6.81-6.79 (m, 2H), 4.62 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 8 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 146.8, 145.0, 142.6, 138.7, 135.5, 135.4, 130.8, 130.09, 130.04, 129.4, 129.2, 129.0, 128.8, 128.7, 128.6, 127.5, 60.7, 37.2, 18.4.

1,5-Dimethyl-2,3-diphenylpyridin-1-ium tetrafluoroborate (**3b**) Obtained as a yellow solid (65% yield, 45.1 mg); m.p. 158-160 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.12 (s, 1H), 7.39-7.31 (m, 3H), 7.29-7.26 (m, 2H), 7.21-7.13 (m, 3H), 7.06-7.04 (m, 2H), 4.07 (s,

3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 151.2, 146.5, 145.7, 141.9, 137.9, 135.2, 130.5, 130.2, 129.6, 129.3, 129.0, 128.5, 128.3, 48.1, 18.3; IR (neat): 3645, 3559, 3447, 3352, 3067, 2970, 2934, 1969, 1897, 1821, 1770,1700, 1620, 1578, 1513, 1484, 1445, 1398, 1328, 1290, 1259, 1039(ν_{B-F}), 888, 777, 732, 704, 606, 576 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{18}N^+$ 260.1434, found 260.1477.

1-Butyl-5-methyl-2,3-diphenylpyridin-1-ium tetrafluoroborate (**3c**) Obtained as a yellow liquid (56% yield, 43.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.16 (s, 1H), 7.42-7.37 (m, 3H), 7.31-7.28 (m, 2H), 7.22-7.17 (m, 3H), 7.09-7.06 (m, 2H), 4.45 (t, *J* = 8 Hz, 2H), 2.681 (s, 3H), 1.83-1.75 (m, 2H), 1.25-1.16 (m, 2H) 0.72 (t, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 151.1, 146.7, 144.7, 142.6, 138.7, 135.3, 130.7, 130.1, 129.8, 129.4, 129.1, 128.8, 128.5, 59.5, 33.3, 19.5, 18.4, 13.2; IR (neat): 3764, 3644, 3553, 3064, 2963, 2935, 2873, 1976, 1904, 1826, 1762, 1729, 1668, 1615, 1507, 1475, 1446, 1384, 1327, 1278, 1243, 1058(ν_{B-F}), 890, 772, 734, 704, 599, 576, 519 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}N^+$ 302.1903, found 302.1955.

5-Methyl-2,3-diphenyl-1-(3-phenylpropyl)pyridin-1-ium tetrafluoroborate (**3d**) Obtained as a yellow liquid (89% yield, 80.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.09 (s, 1H), 7.39-7.28 (m, 3H), 7.24-7.10 (m, 8H), 7.03-7.01 (m, 2H), 6.93-6.91 (m, 2H), 4.49 (t, *J* = 8 Hz, 2H), 2.65 (s, 3H), 2.57 (t, *J* = 8 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 151.0, 146.8, 145.1, 142.6, 139.6, 138.8, 135.3, 130.7, 129.9, 129.7, 129.4, 129.1, 128.8, 128.7, 128.6, 128.3, 126.4, 59.4, 32.5, 32.4, 18.4; IR (neat): 3765, 3660, 3552, 3062, 3029, 2924, 2855, 1964, 1894, 1817, 1719, 1668, 1608, 1579, 1475, 1446, 1382, 1326, 1281,

1241, 1058(ν_{B-F}), 763, 702, 631 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}N^+$ 364.2060, found 364.2088.

1-Cyclohexyl-5-methyl-2,3-diphenylpyridin-1-ium tetrafluoroborate (**3e**) Obtained as a yellow solid (72% yield, 59.8 mg); m.p. 91-93 ℃, ^1H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.12 (s, 1H), 7.42-7.35 (m, 3H), 7.25-7.23 (m, 2H), 7.20-7.15 (m, 3H), 7.09-7.06 (m, 2H), 4.36-4.29 (m, 1H), 2.71 (s, 3H), 2.12-2.06 (m, 4H), 1.88-1.85 (m, 2H), 1.58-1.55 (m, 1H), 1.41-1.31 (m, 1H), 1.08-0.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 151.1, 146.7, 142.6, 141.1, 139.3, 135.6, 130.8, 130.4, 129.4, 129.3, 128.7, 128.5, 68.5, 33.3, 25.7, 24.2, 18.6; IR (neat): 3651, 3556, 3063, 2938, 2861,1972, 1902, 1824, 1664, 1614, 1580, 1501, 1475, 1448, 1384, 1338, 1272, 1227, 1056(ν_{B-F}), 947, 887, 843, 774, 733, 703, 626 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}N^+$ 328.2060, found 328.2095.

5-Methyl-1,2,3-triphenylpyridin-1-ium tetrafluoroborate (**3f**) Obtained as a purple solid (72% yield, 58.9 mg); m.p. 116-118 ℃, ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.33 (s, 1H), 7.48-7.46 (m, 2H), 7.34-7.28 (m, 3H), 7.24-7.19 (m, 5H), 7.13-7.01 (m, 5H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.0, 148.7, 144.7, 142.6, 142.4, 138.2, 135.5, 130.9, 130.57, 130.54, 129.9, 129.75, 129.71, 128.8, 128.5, 128.3, 126.7, 18.6; IR (neat): 3765, 3661, 3552, 3379, 3063, 2965, 2925, 1970, 1902, 1816, 1760, 1730. 1682, 1592, 1494, 1468, 1445, 1331, 1286, 1247, 1178, 1056(ν_{B-F}), 771, 731, 700, 605 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{20}N^+$ 322.1590, found 322.1661.

1,2,3,5-Tetraphenylpyridin-1-ium tetrafluoroborate (**3g**) Obtained as a brown solid (82% yield, 77.3 mg); m.p. 148-150 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 2 Hz, 1H), 8.56 (d, *J* = 1.6 Hz, 1H), 7.74-7.71 (m, 2H), 7.59-7.57 (m, 2H), 7.49-7.48 (m, 3H), 7.37-7.35 (m, 3H), 7.30-7.27 (m, 3H), 7.23-7.05 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.2, 145.9, 143.2, 142.75, 142.73, 140.1, 135.7, 133.6, 131.0, 130.6, 130.5, 130.2, 129.9, 129.8, 129.7, 129.6, 128.8, 128.5, 128.25, 128.22, 126.8; IR (neat): 3764, 3661, 3552, 3062, 1968, 1900, 1817, 1731, 1594, 1491, 1463, 1445, 1391, 1344, 1244, 1182, 1056(ν_{B-F}), 924, 894, 762, 733, 699 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{22}N^{+}$ 384.1747, found 384.1783.

5-Methyl-1-phenethyl-2,3-dipropylpyridin-1-ium tetrafluoroborate (**3h**) Obtained as a yellow liquid (70% yield, 51.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.89 (s, 1H), 7.24-7.21 (m, 3H), 7.06-7.04 (m, 2H), 4.77 (t, *J* = 8 Hz, 2H), 3.26 (t, *J* = 8 Hz, 2H) 2.73-2.64 (m, 4H), 1.66-1.53 (m, 4H), 1.04 (t, *J* = 8 Hz, 3H), 0.99 (t, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.3, 146.5, 143.6, 141.7, 136.7, 135.5, 129.2, 129.0, 127.7, 59.3, 37.6, 34.1, 30.4, 23.6, 22.4, 17.9, 14.3, 13.9; IR (neat): 3765, 3655, 3552, 3067, 3030, 2964, 2932, 2874, 1958, 1816, 1668, 1628, 1598, 1496, 1460, 1383, 1351, 1286, 1220, 1058(ν_{B-F}), 886, 752, 704, 625 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}N^{+}$ 282.2216, found 282.2233.

2,3-bis(4-fluorophenyl)-5-methyl-1-phenethylpyridin-1-ium tetrafluoroborate (3i, CAS No. 2097667-94-0)[3] Obtained as a yellow solid (78% yield, 73.8 mg); ^{1}H NMR (400 MHz, DMSO) δ 9.18 (s, 1H), 8.56 (s, 1H), 7.45 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.32 (t, *J* = 8.8 Hz, 2H), 7.29-7.23 (m, 3H), 7.22-7.13 (m, 4H), 6.92 (d, *J* = 7.2 Hz, 2H), 4.50 (t, *J* = 7.6 Hz, 2H), 3.07 (t, *J* = 8 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 162.7 (d, J_{C-F} = 247.6 Hz), 161.7 (d, J_{C-F} = 245.1 Hz), 149.9, 146.8 (d, J_{C-F} = 5.1 Hz), 144.2, 140.5, 137.4, 135.8, 132.4

(d, J_{C-F} = 9.1 Hz), 131.7 (d, J_{C-F} = 3.2 Hz), 131.4 (d, J_{C-F} = 8.4 Hz), 128.6, 128.4, 127.0, 126.2 (d, J_{C-F} = 3.4 Hz), 115.8 (d, J_{C-F} = 22 Hz), 115.1 (d, J_{C-F} = 21.7 Hz), 59.4, 35.9, 17.4.

2,3-Bis(4-chlorophenyl)-5-methyl-1-phenethylpyridin-1-ium tetrafluoroborate (**3j**) Obtained as a yellow solid (60% yield, 60.7 mg); m.p. 128-130 ℃, ^{1}H NMR (400 MHz, DMSO) δ 9.16 (s, 1H), 8.56 (s, 1H), 7.56 (d, *J* = 8 Hz, 2H), 7.40 (dd, *J* = 8.8, 2.4 Hz, 4H), 7.28-7.23 (m, 3H), 7.17 (d, *J* = 8 Hz, 2H), 6.92 (d, *J* = 4 Hz, 2H), 4.49 (t, *J* = 8 Hz, 2H), 3.06 (t, *J* = 8 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, DMSO) 149.7, 146.9, 144.6, 140.3, 137.7, 135.9, 135.5, 134.2, 133.6, 131.8, 131.1, 128.9, 128.7, 128.69, 128.65, 128.3, 127.2, 59.6, 17.5; IR (neat): 3645, 3066, 2923, 1906, 1861, 1816, 1788, 1766, 1732, 1703, 1686, 1670, 1640, 1591, 1462, 1392, 1311, 1259, 1178, 1024(ν_{B-F}), 827, 755, 736, 705 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{22}Cl_2N^+$ 418.1124, found 418.1157.

5-Methyl-1-phenethyl-2,3-di-p-tolylpyridin-1-ium tetrafluoroborate (**3k**) Obtained as a yellow solid (61% yield, 56.8 mg); m.p. 191-193 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.16 (s, 1H), 7.24-7.22 (m, 5H), 7.045 (dd, *J* = 12, 8 Hz, 4H), 6.97-6.95 (m, 2H), 6.88 (t, *J* = 4 Hz, 2H), 4.64 (t, *J* = 8 Hz, 2H), 3.06 (t, *J* = 8 Hz, 2H), 2.60 (s, 3H), 2.39 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.0, 147.5, 144.5, 143.2, 141.8, 139.4, 138.8, 135.8, 132.8, 130.2, 130.0, 129.64, 129.60, 129.4, 129.3, 127.9, 127.3, 60.9, 37.5, 21.6, 21.3, 18.4; IR (neat): 3064, 3032, 2926, 2865, 1932, 1823, 1733, 1671, 1611, 1485, 1455, 1410, 1325, 1264, 1187, 1066(ν_{B-F}), 968, 895, 822, 739, 701 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{28}N^+$ 378.2216, found 378.2248.

2,3-Bis(4-methoxyphenyl)-5-methyl-1-phenethylpyridin-1-ium tetrafluoroborate (3l) Obtained as a yellow solid (80% yield, 79.6 mg); m.p. 91-93 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.04 (s, 1H), 7.15-7.13 (m, 3H), 7.03 (d, *J* = 8.8Hz, 2H), 6.94 (d, *J* = 4Hz, 2H), 6.86-6.84 (m, 4H), 6.69 (d, *J* = 8.4 Hz, 2H), 4.63 (t, *J* = 8 Hz, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 3.02 (t, *J* = 8 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 161.1, 159.8, 151.3, 146.7, 144.1, 142.5, 138.1, 135.6, 131.4, 130.7, 129.0, 128.9, 127.7, 127.4, 122.0, 114.6, 114.0, 60.4, 55.5, 55.3, 37.0, 18.2; IR (neat): 3765, 3658, 3553, 3070, 2962, 2937, 2841, 1896, 1720, 1609, 1578, 1515, 1482, 1296, 1253, 1181, 1059(ν_{B-F}), 836, 733, 703 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{28}N_1O_2^+$ 410.2115, found 410.2122.

2,3-bis(4-(dimethylamino)phenyl)-5-methyl-1-phenethylpyridin-1-ium tetrafluoroborate (3m, CAS No. 2097667-96-2)[3] Obtained as a brown solid (94% yield, 98.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.99 (s, 1H), 7.20-7.16 (m, 3H), 6.93-6.85 (m, 6H), 6.64 (d, *J* = 9.2 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.75 (t, *J* = 7.2 Hz, 2H), 3.07-3.03 (m, 2H), 3.01 (s, 6H), 2.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 151.3, 150.3, 146.1, 143.0, 137.4, 135.7, 130.9, 130.4, 129.1, 129.0, 127.4, 122.7, 116.6, 112.0, 111.9, 60.4, 40.3, 40.2, 37.1, 18.3.

5-Methyl-1-phenethyl-2,3-di(thiophen-2-yl)pyridin-1-ium tetrafluoroborate (3n) Obtained as a brown solid (63% yield, 56.6 mg); m.p. 91-93 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.30 (s, 1H), 7.70 (d, *J* = 5.2 Hz, 1H), 7.36 (d, *J* = 4.8 Hz, 1H), 7.27-7.26 (m, 1H), 7.23-7.20 (m, 4H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.99-6.95 (m, 3H), 4.71 (t, *J* = 8 Hz, 2H), 6H), 3.17 (t, *J* = 8 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 145.6, 143.1, 139.8, 137.7, 135.6, 135.4, 134.0, 131.7, 131.6, 130.3, 129.1, 128.6, 128.3, 127.8, 127.6, 61.0, 37.7,

18.4; IR (neat): 3765, 3661, 3553, 3416, 3064, 3034, 2896, 2861, 2810, 1735, 1662, 1609, 1528, 1486, 1448, 1363, 1272, 1229, 1199, 1170, 1057(ν_{B-F}), 945, 889, 820, 732, 702, 631 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{20}NS_2^+$ 362.1032, found 362.1055.

***N*-(2-Methaylallyl)-11-((2-methylallyl)(3-methylbut-3-en-2-yl)silyl)undecan-1-amine (1h)**

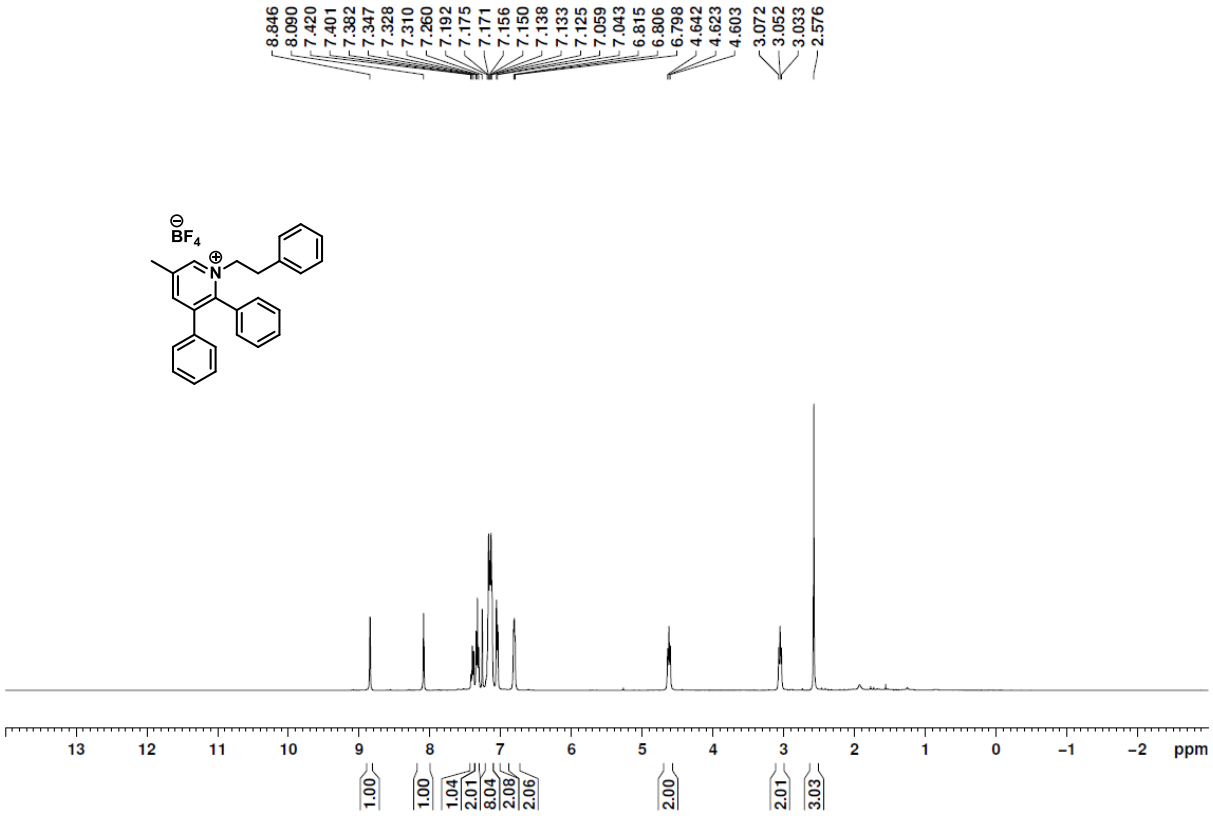
Obtained as a yellow liquid (24% yield, 333 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (s, 1H), 4.81 (s, 1H), 4.59 (s, 2H), 4.48 (s, 2H), 3.16 (s, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.73 (s, 3H), 1.71 (s, 6H), 1.56 (s, 4H), 1.48-1.46 (m, 2H), 1.27-1.25 (m, 16H), 0.57-0.54 (m, 2H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 144.36, 144.32, 143.8, 143.7, 110.6, 108.8, 56.0, 49.6, 33.9, 30.3, 29.8, 29.5, 27.6, 25.9, 25.6, 23.9, 21.0, 14.2, -4.2; IR (neat): 3073, 2967, 2920, 2851, 2815, 1732, 1637, 1450, 1372, 1278, 1250, 1161, 1121, 1030, 1000, 971, 893, 868, 839, 817, 720, 512 cm^{-1}; Anal. Calcd for $C_{24}H_{47}NSi$: C, 76.31; H, 12.54; N, 3.71; found: C, 74.78; H, 13.35; N, 3.59.

References

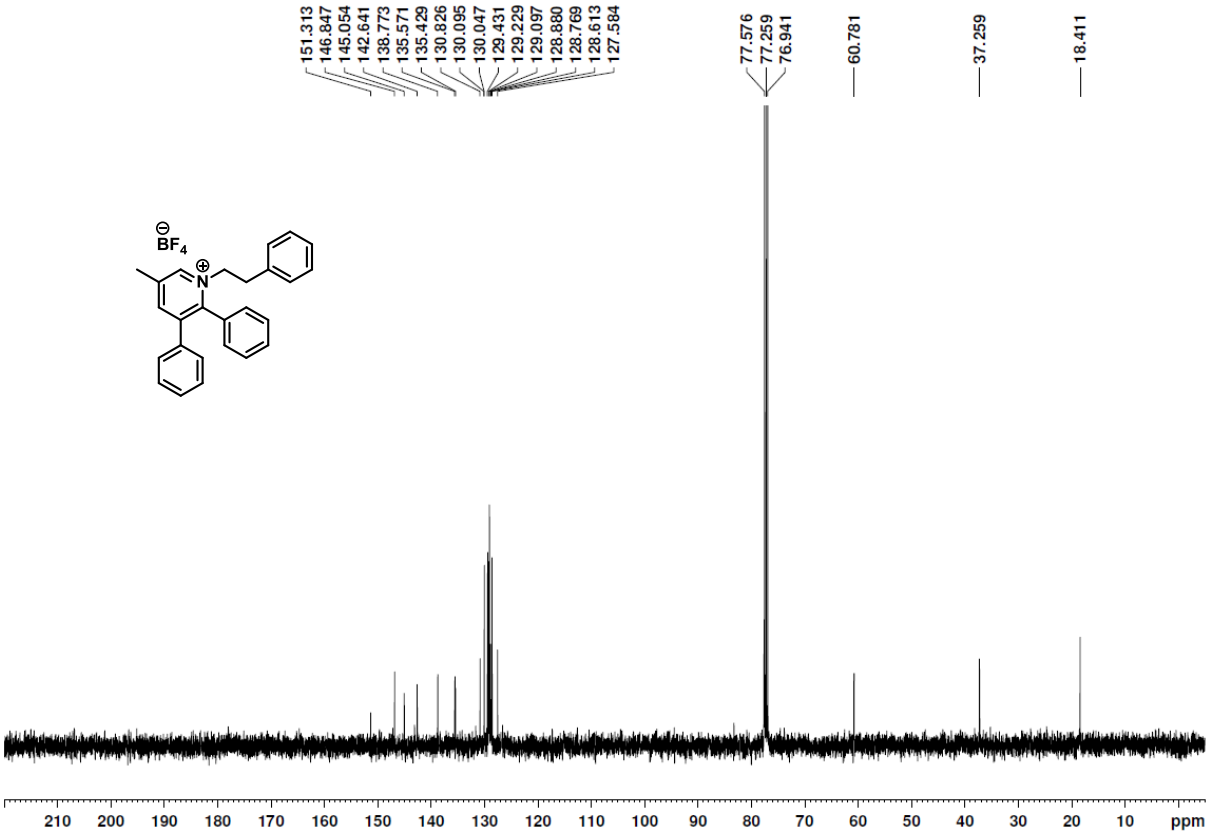
(1) Fujita, K.-I.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. *Org.Lett.* **2004**, *6*, 2785.
(2) Chen, Z.-W.; Zhu, Y.-Z.; Ou, J.-W.; Wang, Y.-P.; Zheng, J.-Y. *J. Org. Chem.* **2014**, *79*, 10988.
(3) Han, Y. R.; Shim, S.-H.; Kim, D.-S.; Jun, C.-H. *Org. Lett.* **2017**, *19*, 2941.

5. ^{1}H and ^{13}C NMR spectra for new compounds

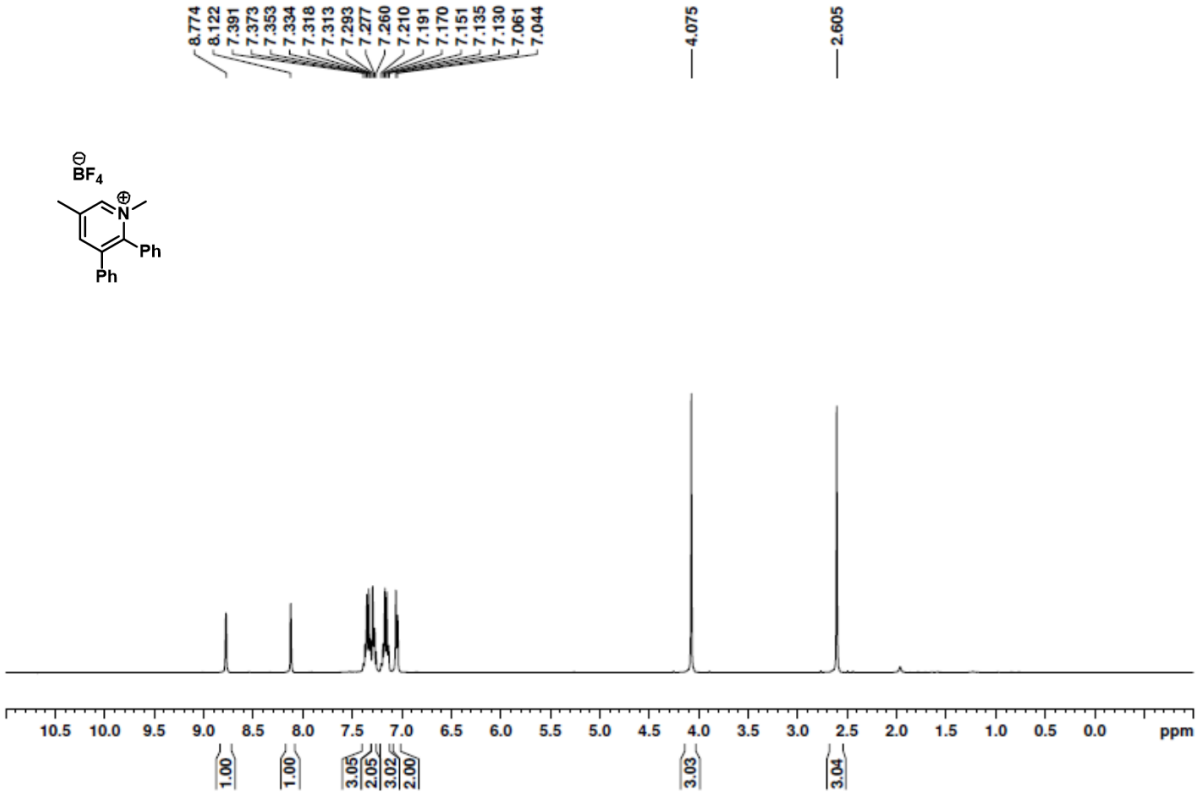
-^{1}H NMR of **3a**



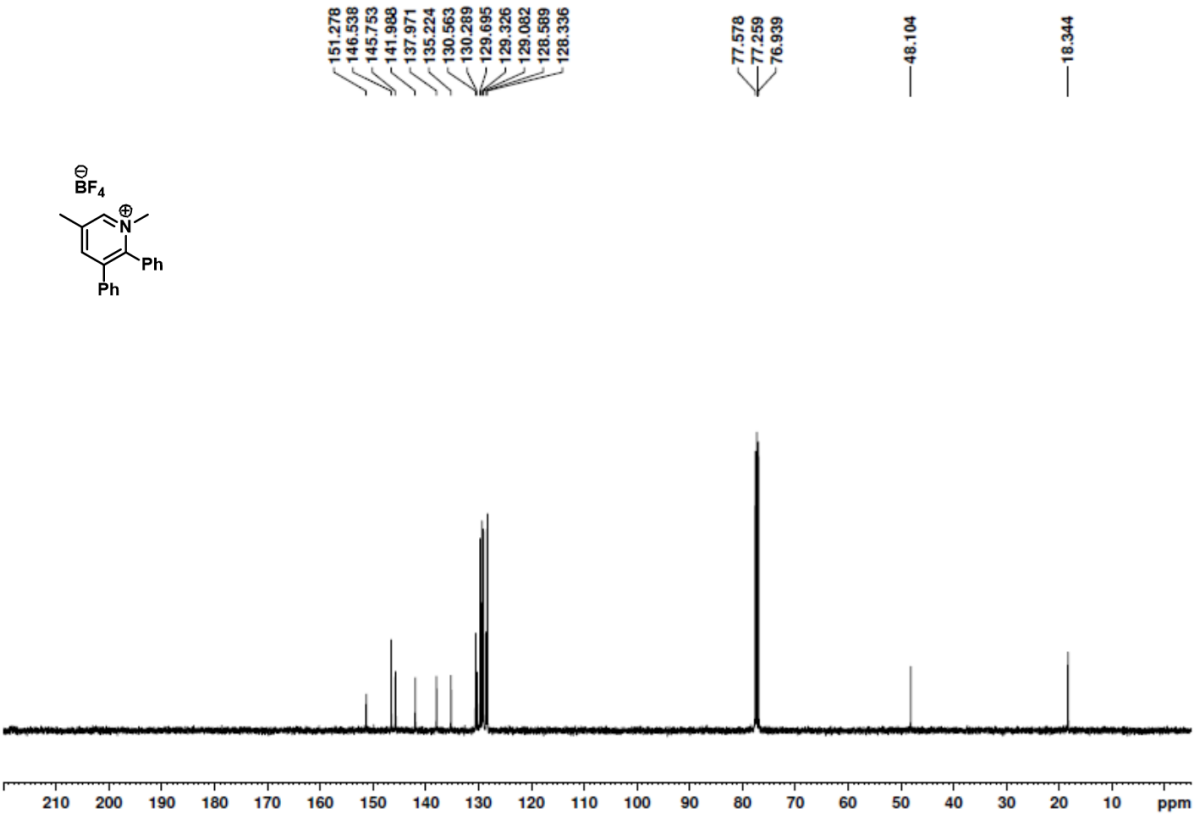
-^{13}C NMR of **3a**



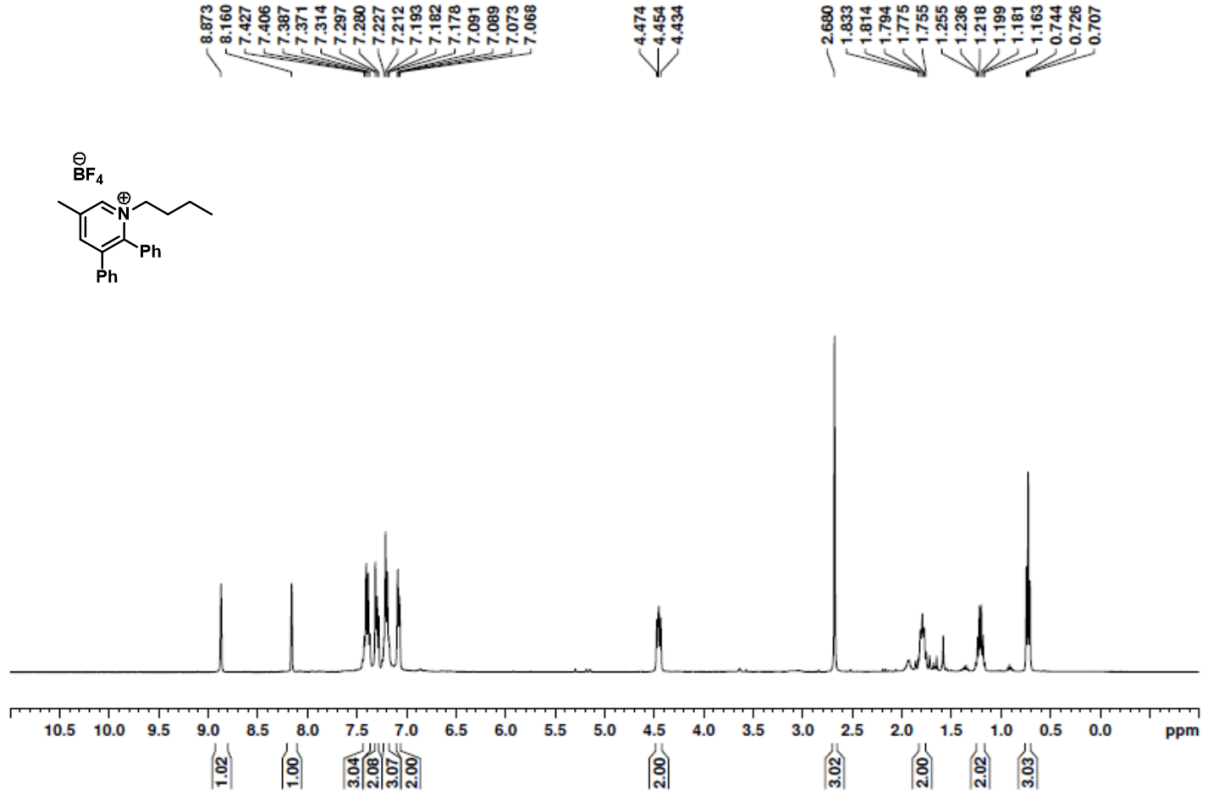
-^{1}H NMR of **3b**



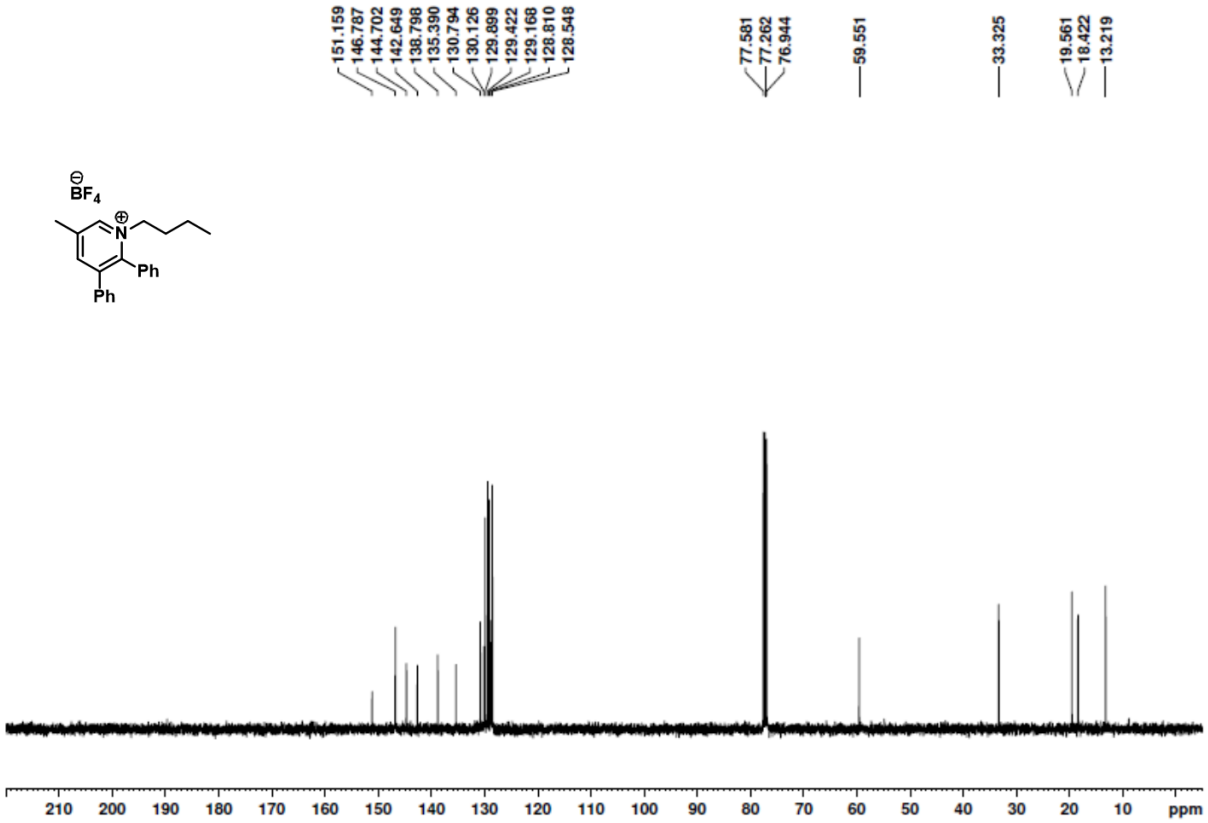
-^{13}C NMR of **3b**



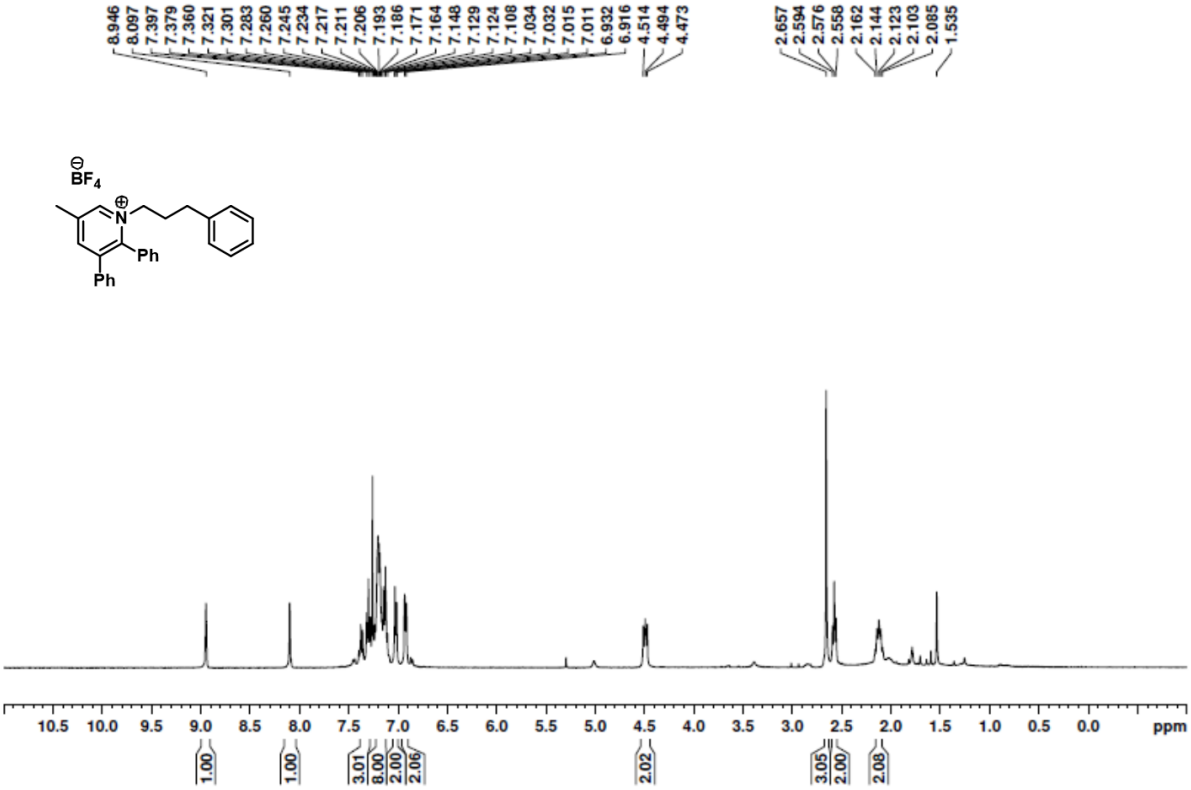
-^{1}H NMR of **3c**



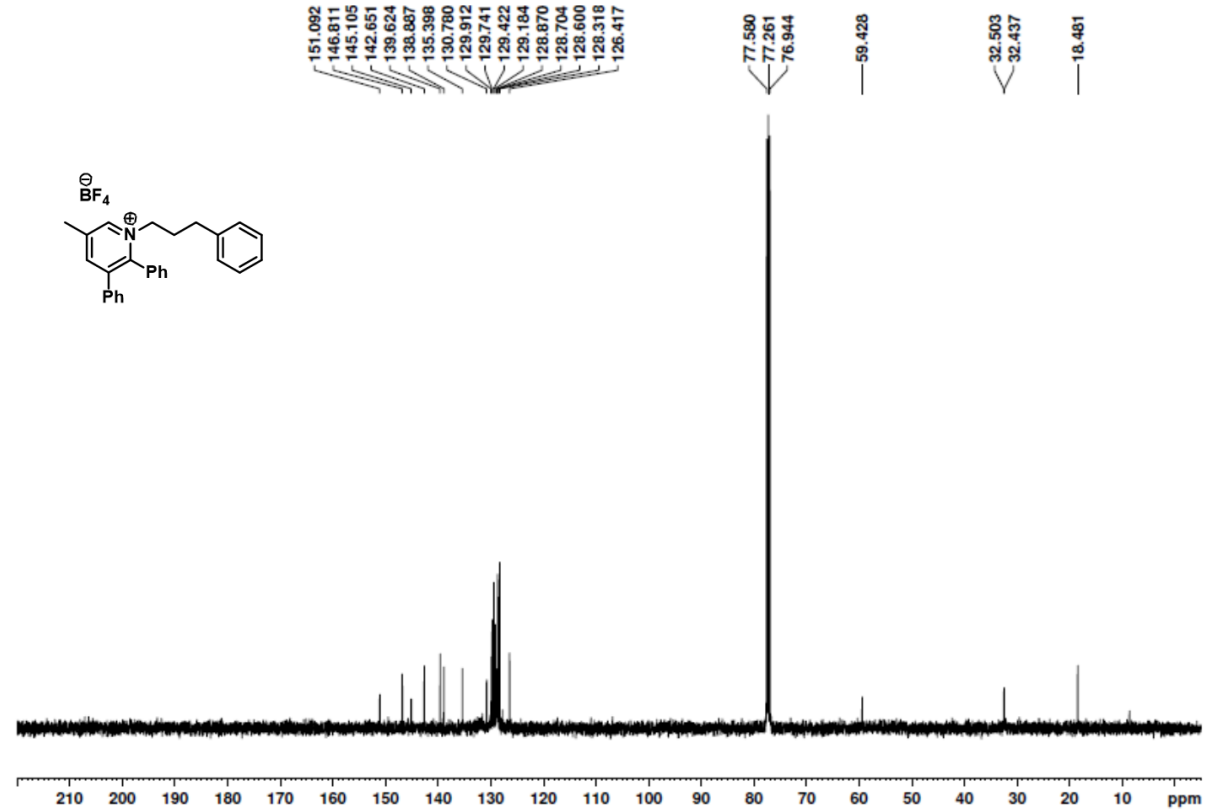
-^{13}C NMR of **3c**



-^{1}H NMR of **3d**



-^{13}C NMR of **3d**



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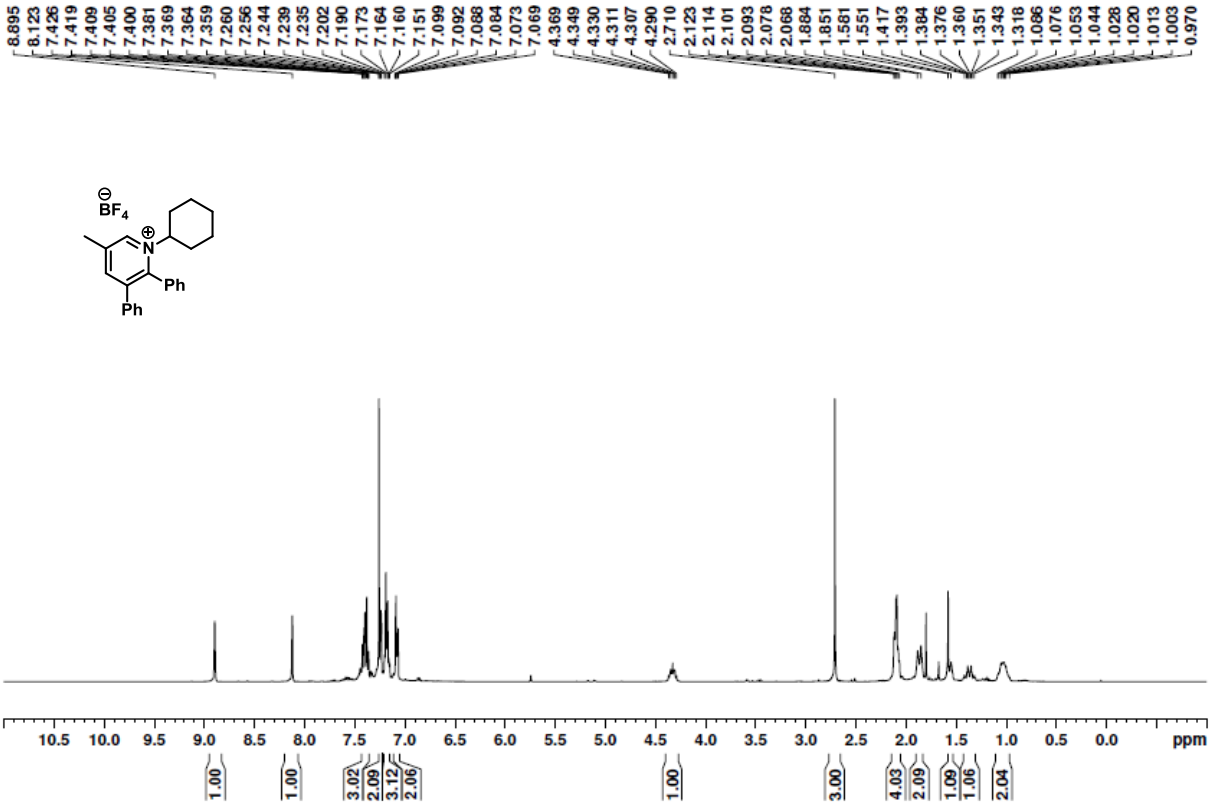

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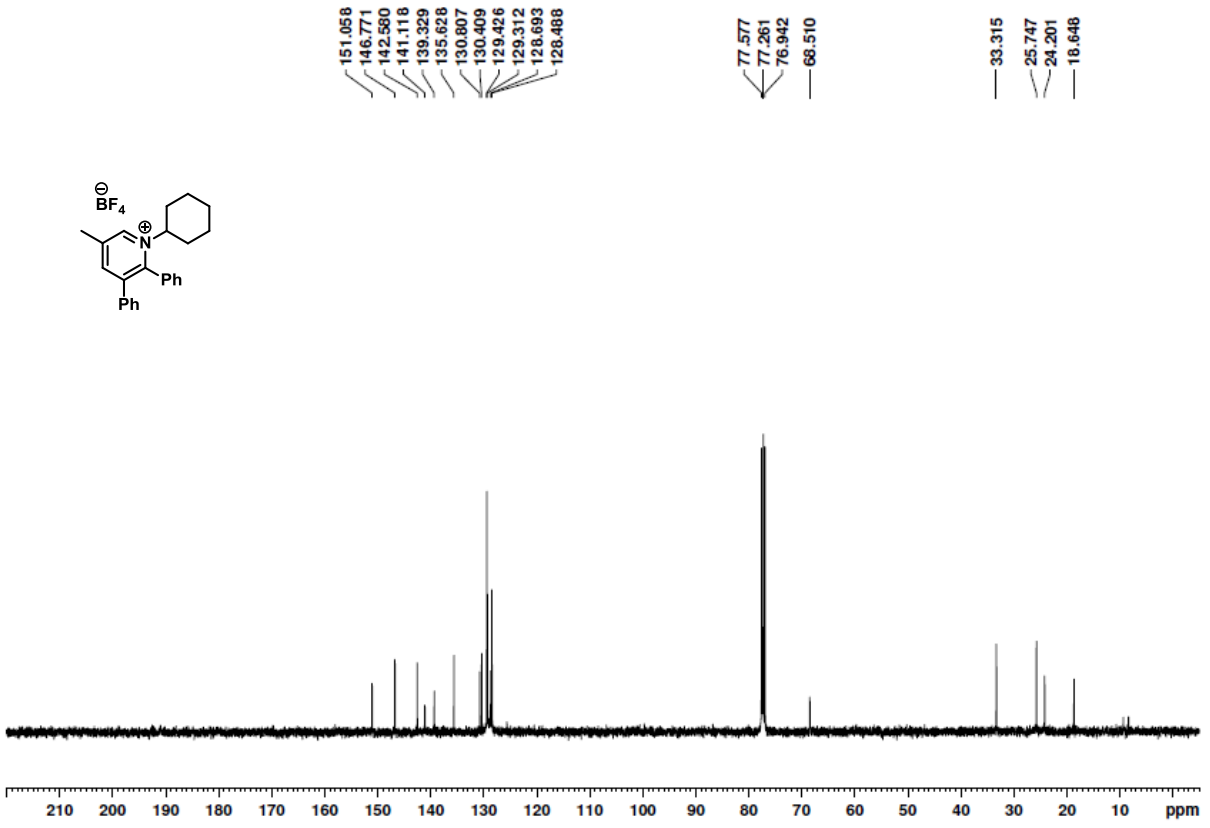
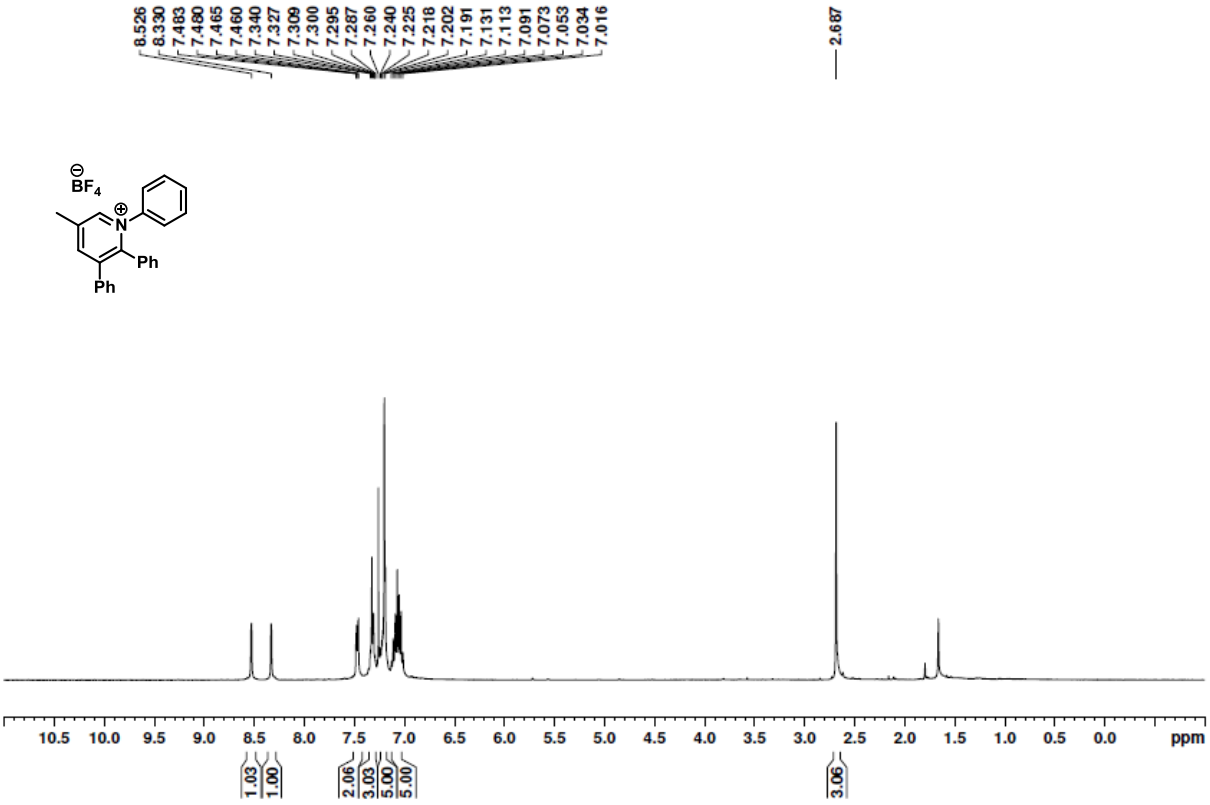
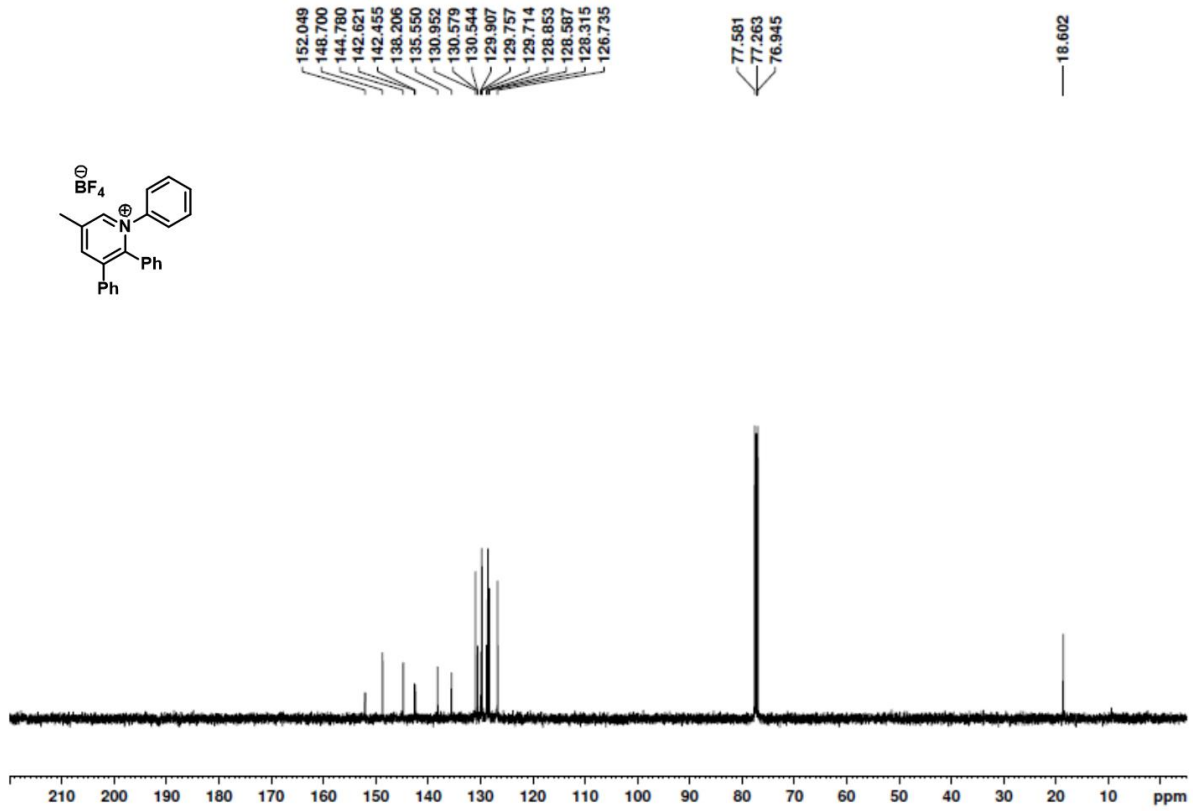


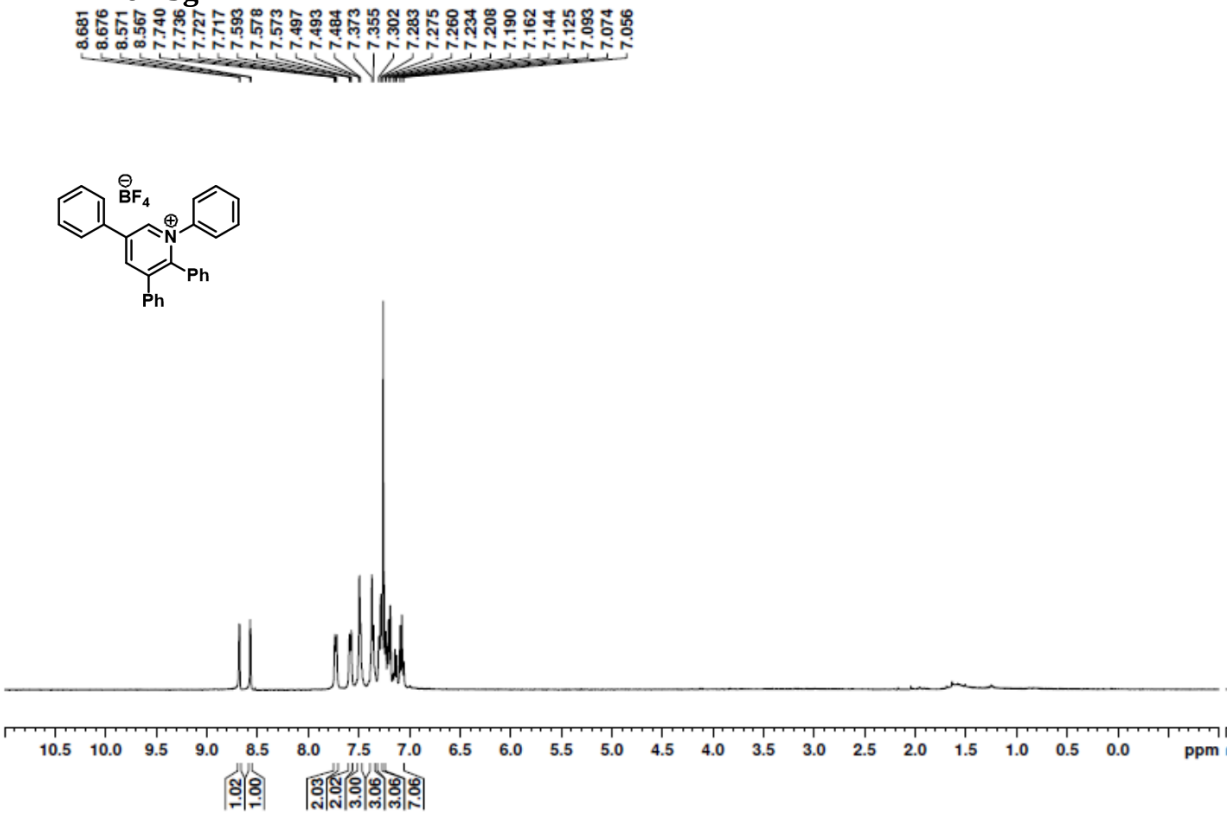
-^{1}H NMR of **3f**



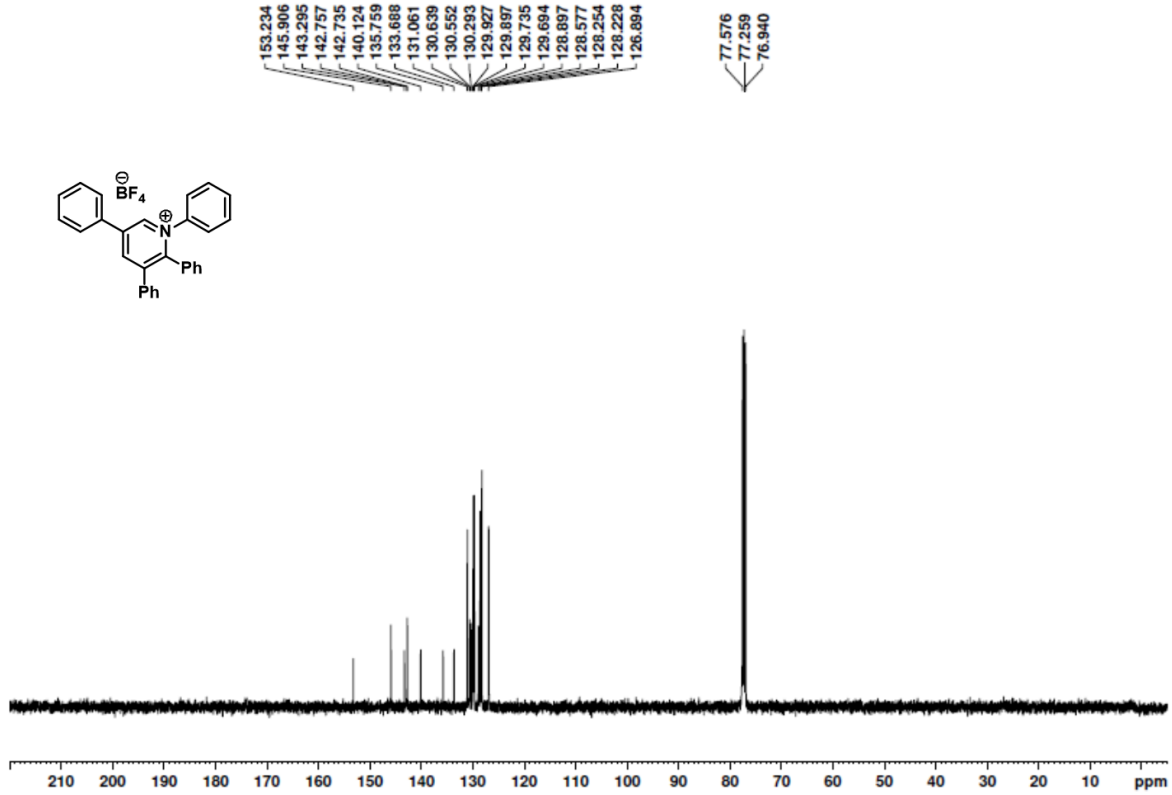
-^{13}C NMR of **3f**



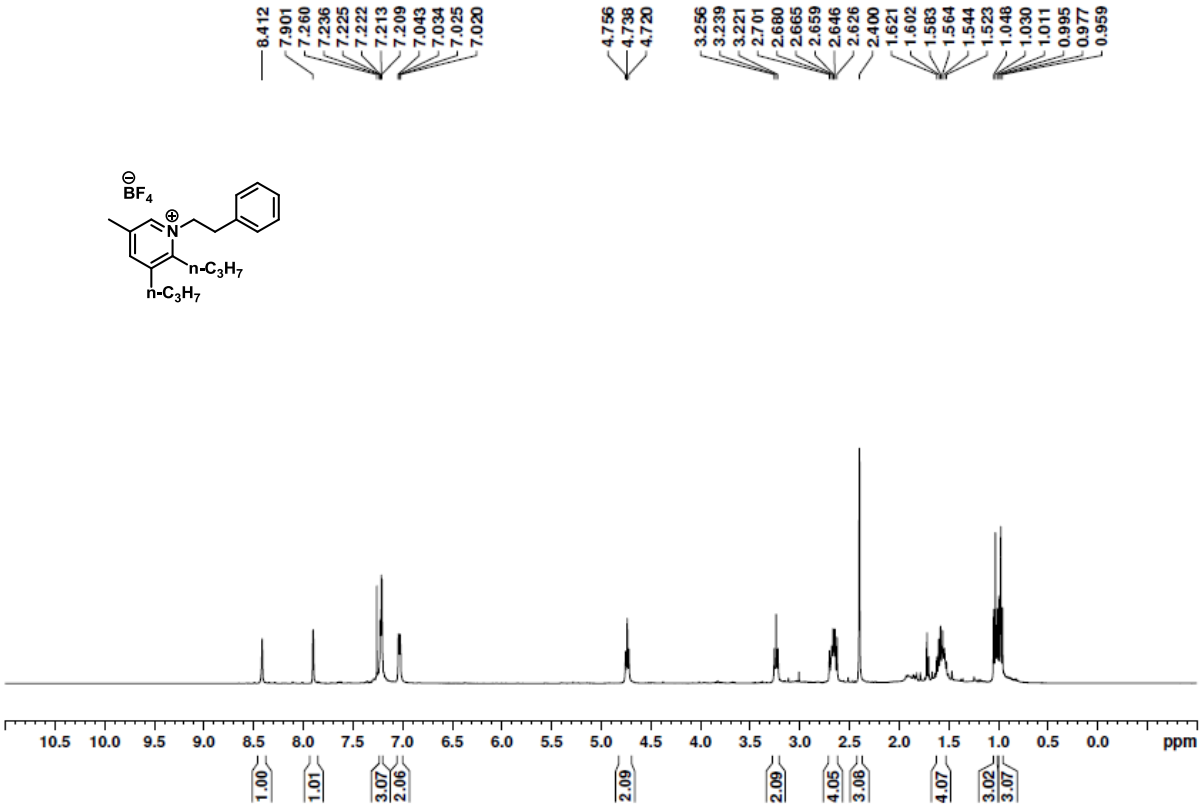
-^{1}H NMR of **3g**



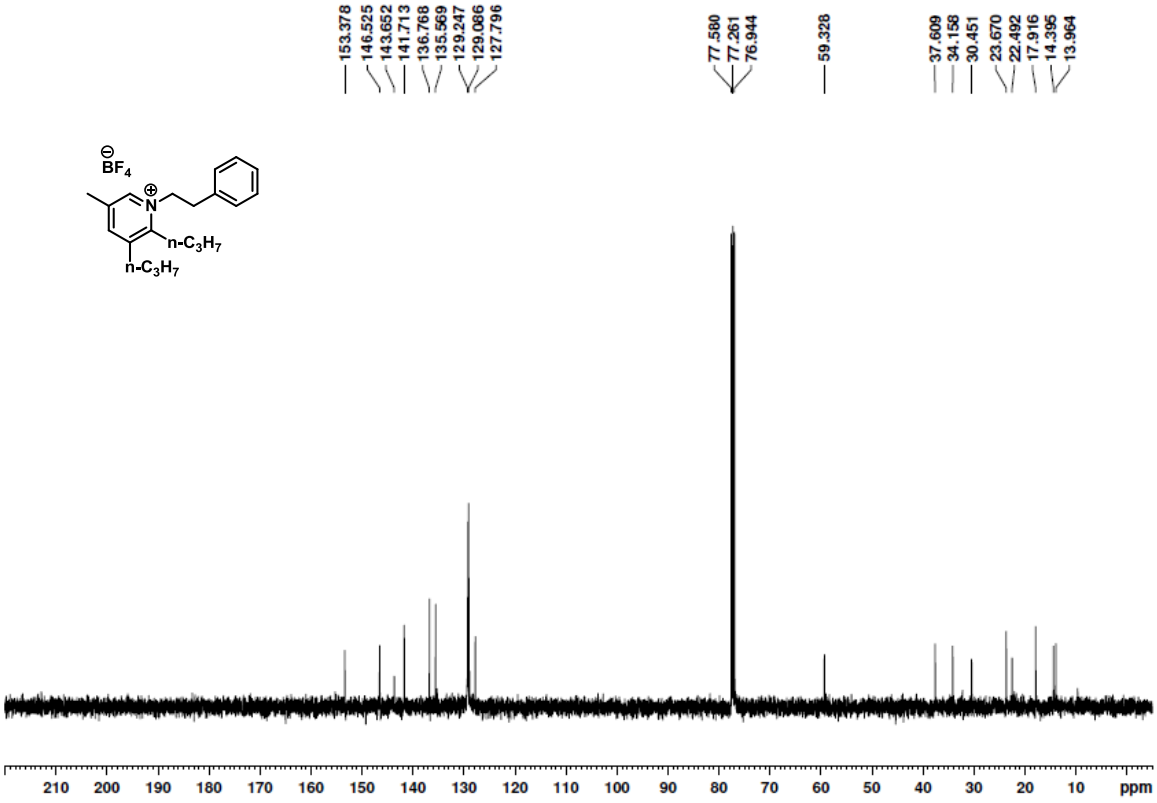
-^{13}C NMR of **3g**



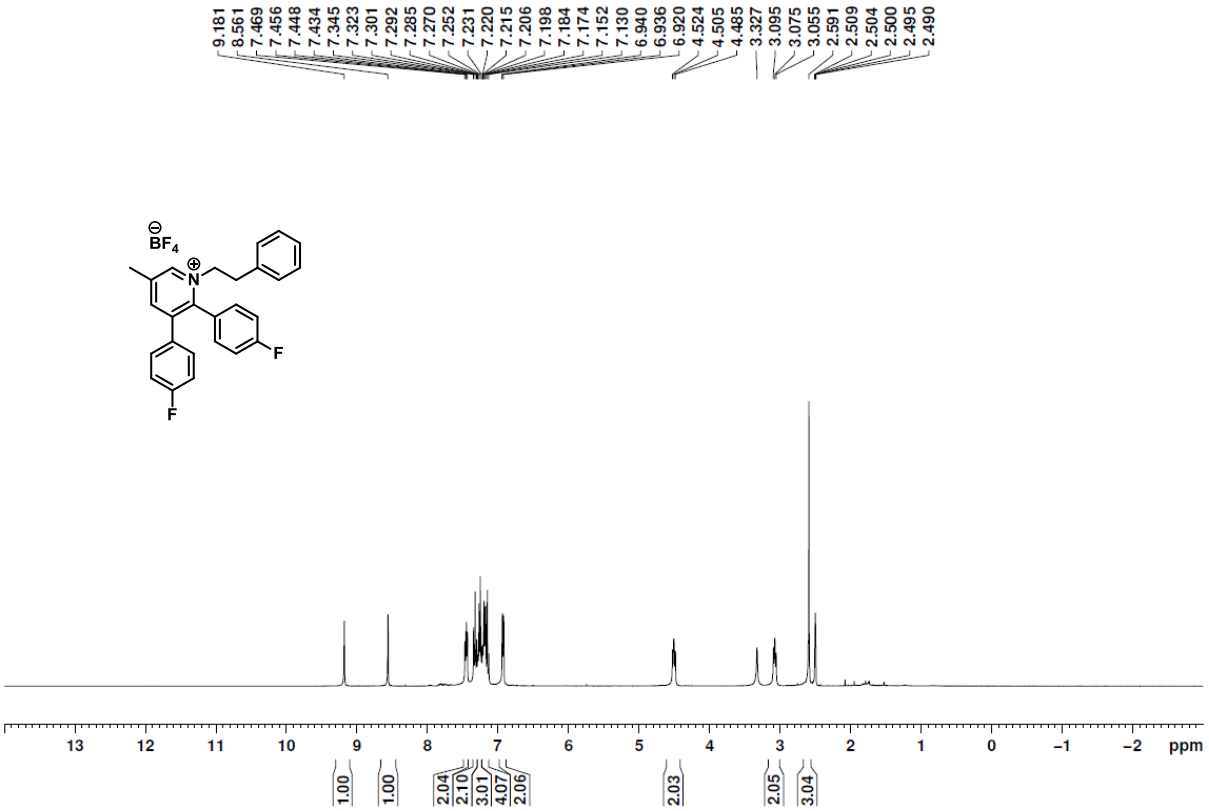
-^{1}H NMR of **3h**



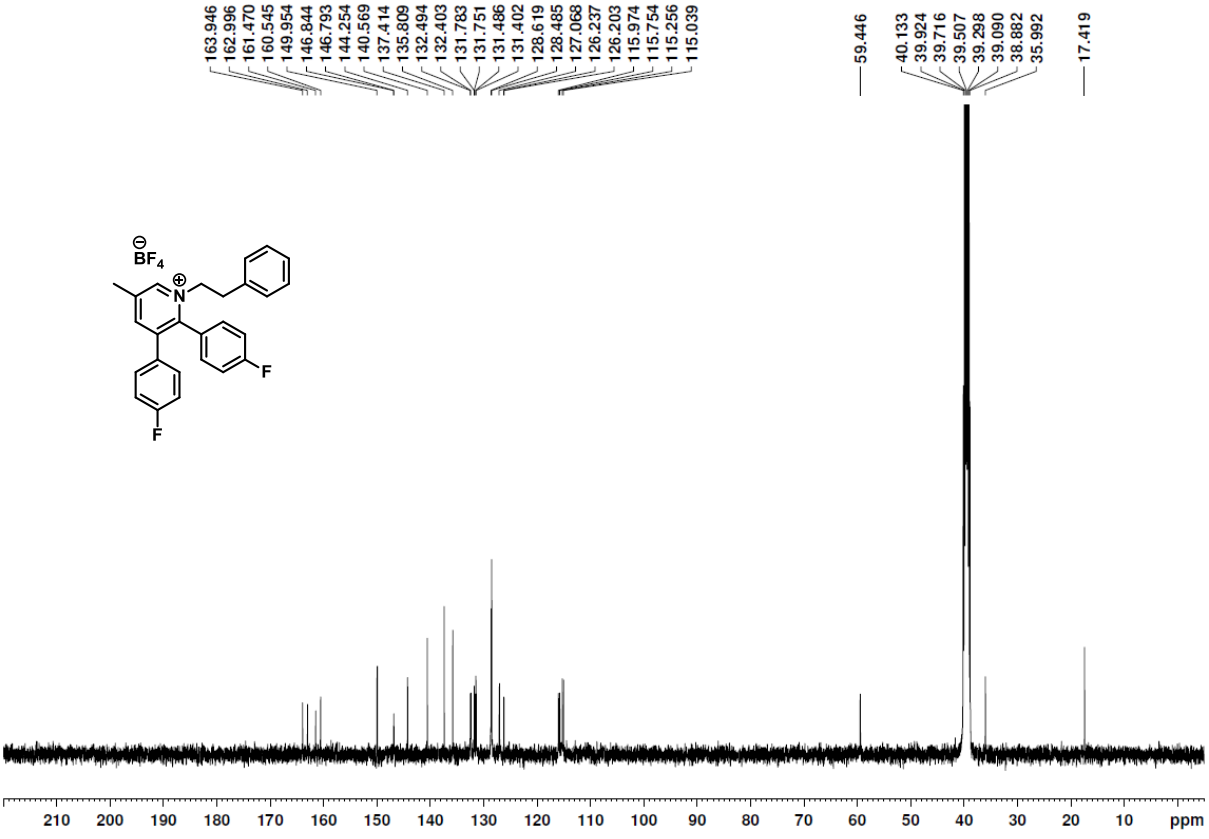
-^{13}C NMR of **3h**



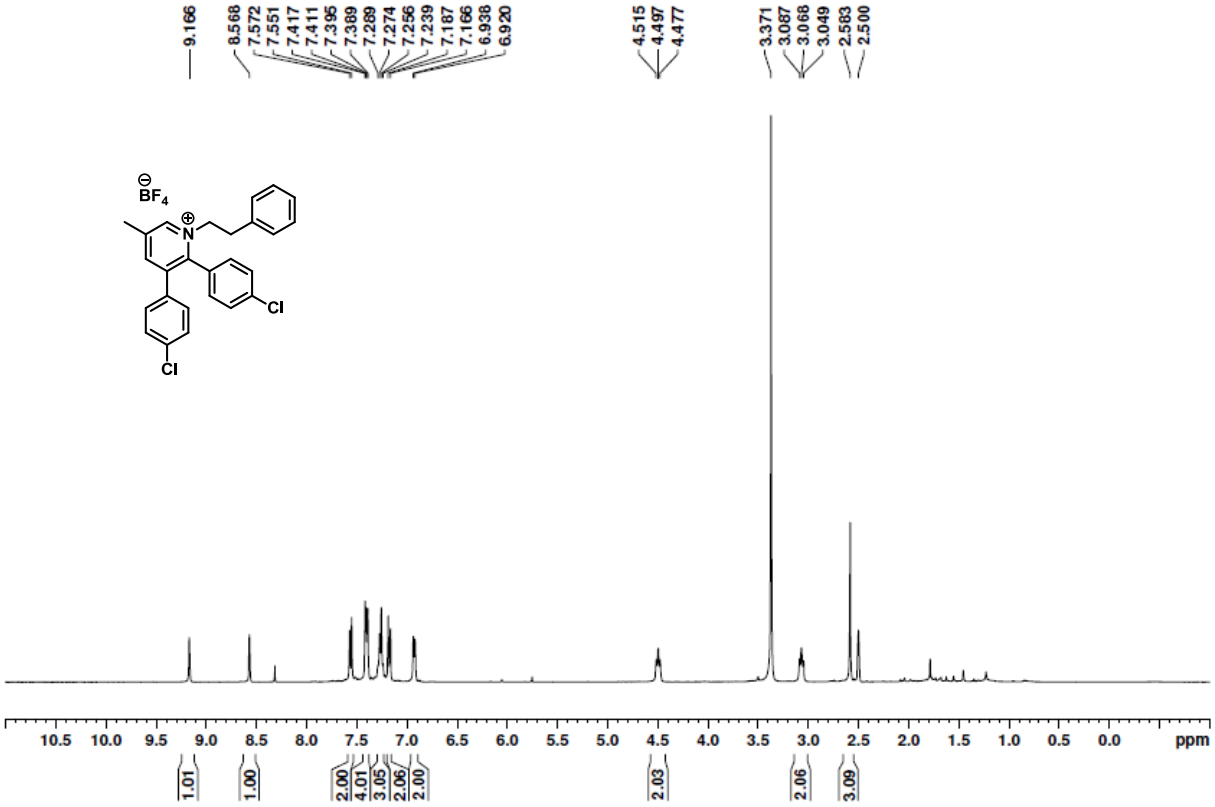
-^{1}H NMR of **3i**



-^{13}C NMR of **3i**



-^{1}H NMR of **3j**



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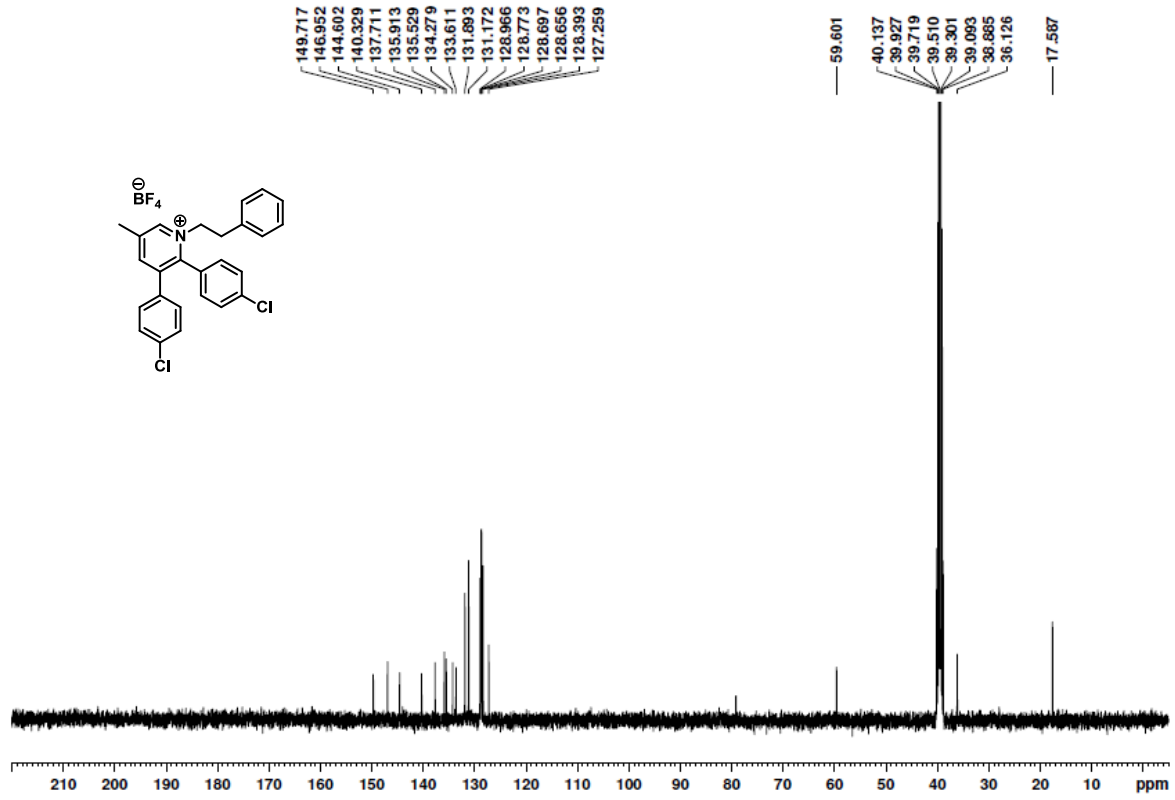
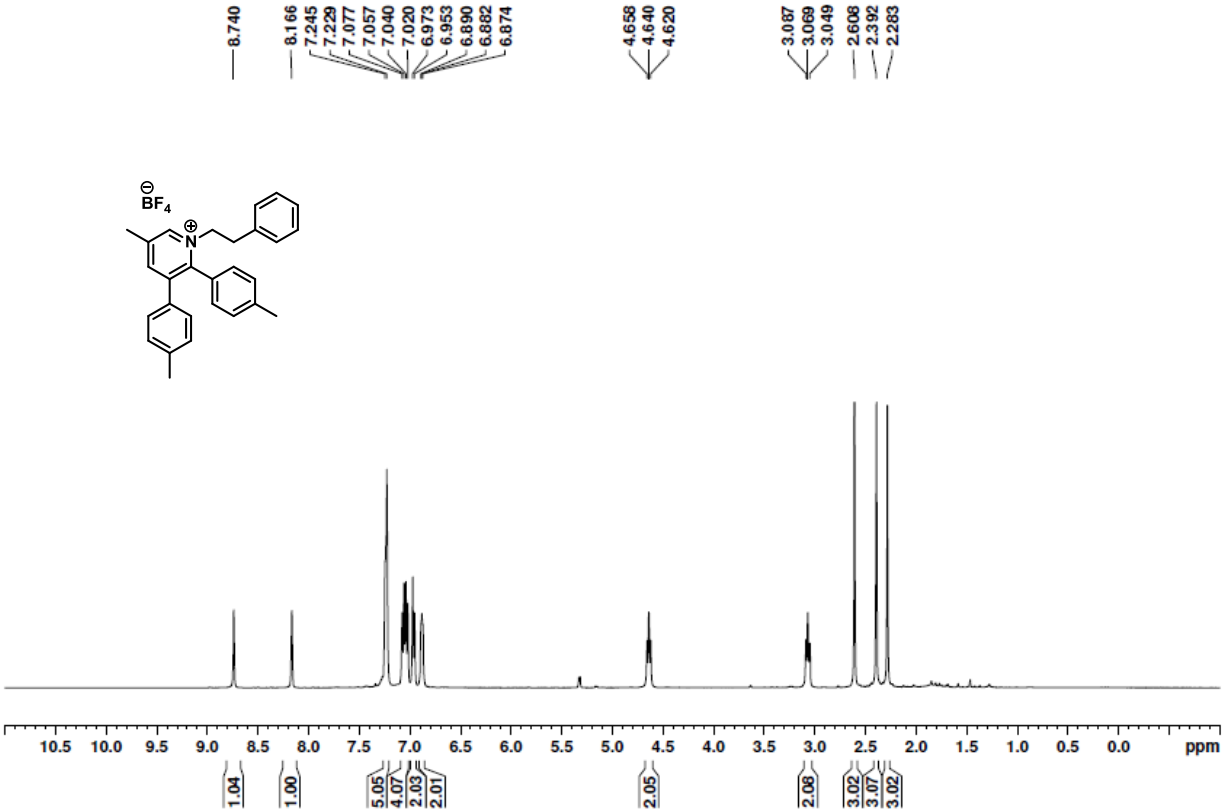


-^{1}H NMR of **3k**



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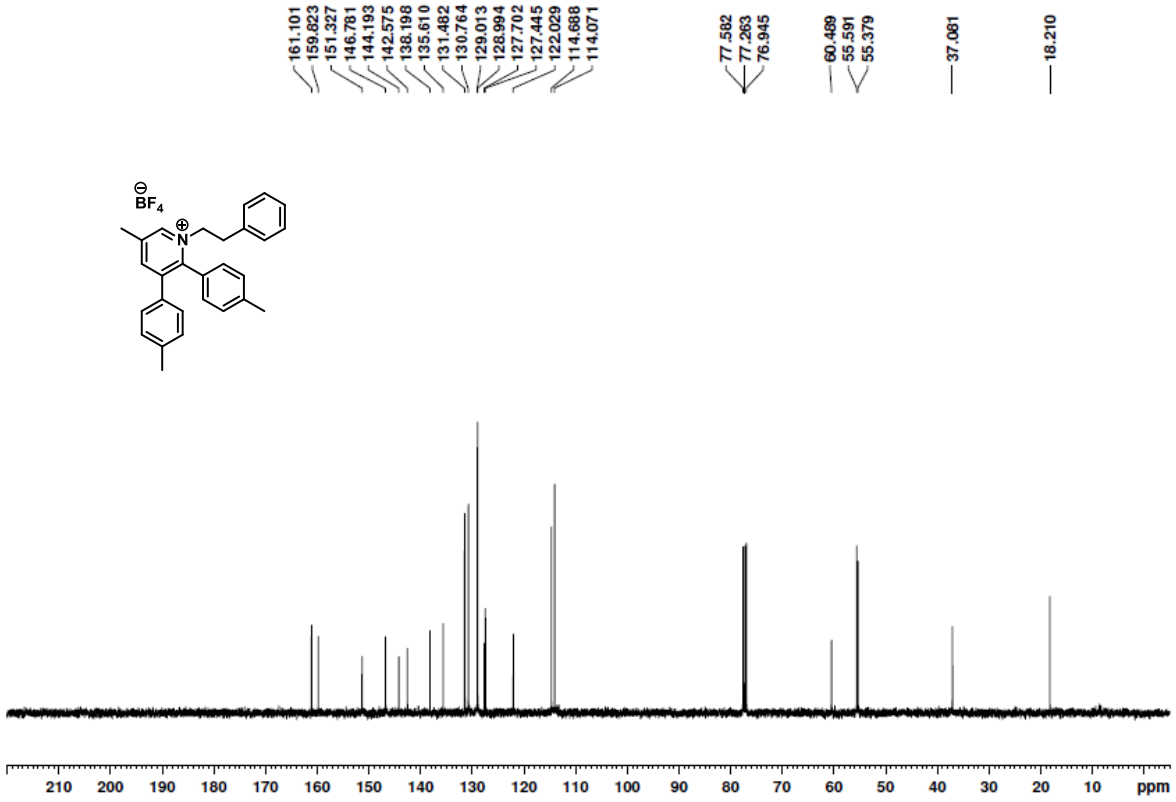
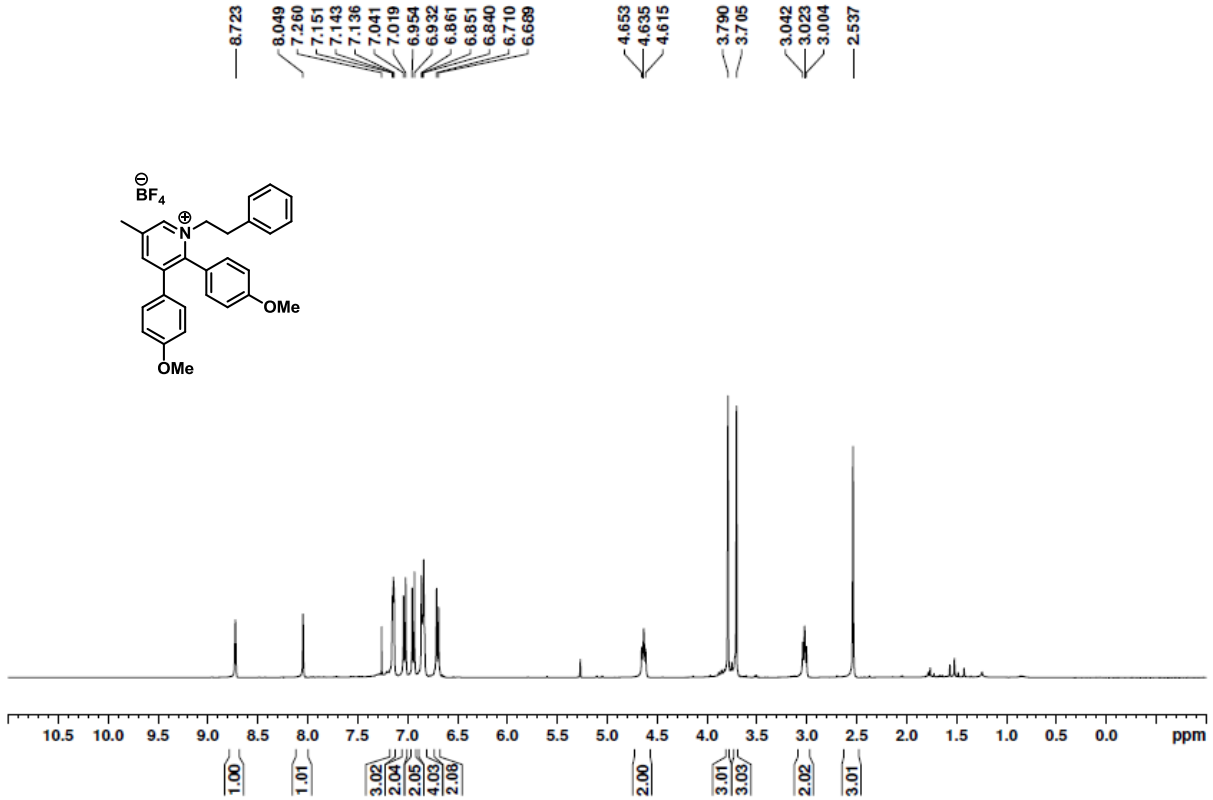


-^{1}H NMR of **3l**



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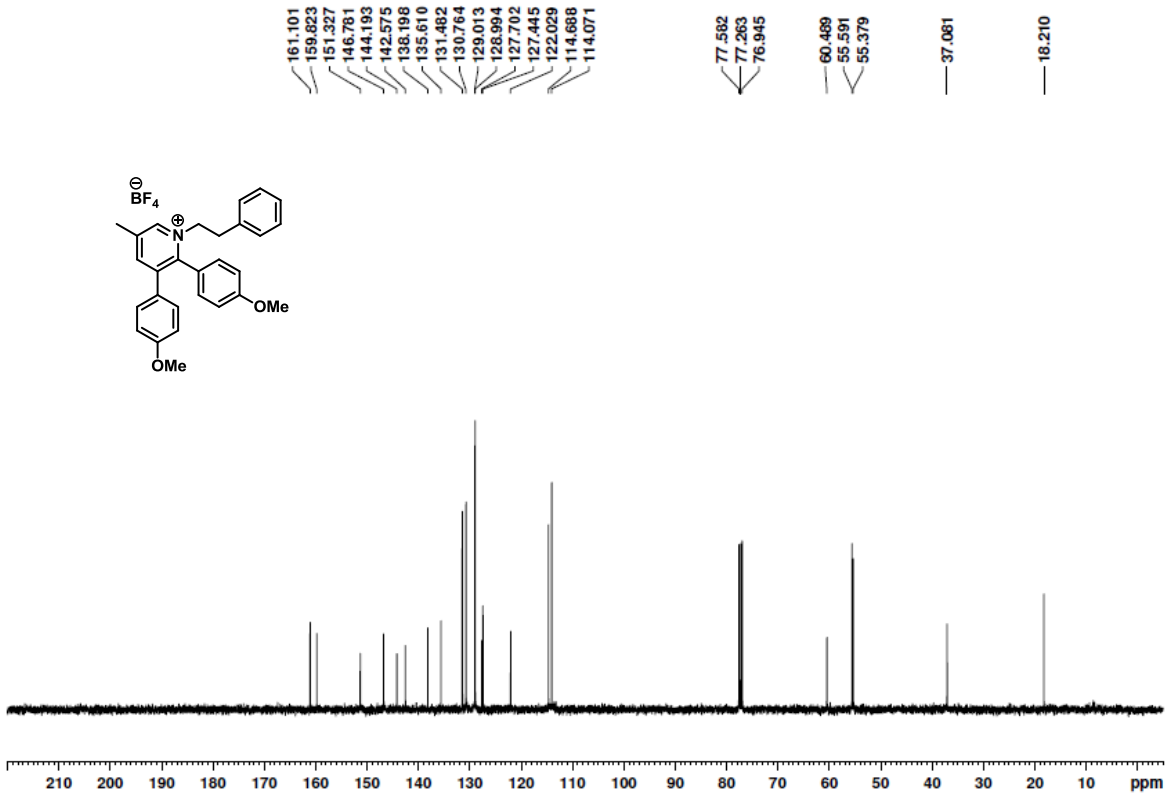
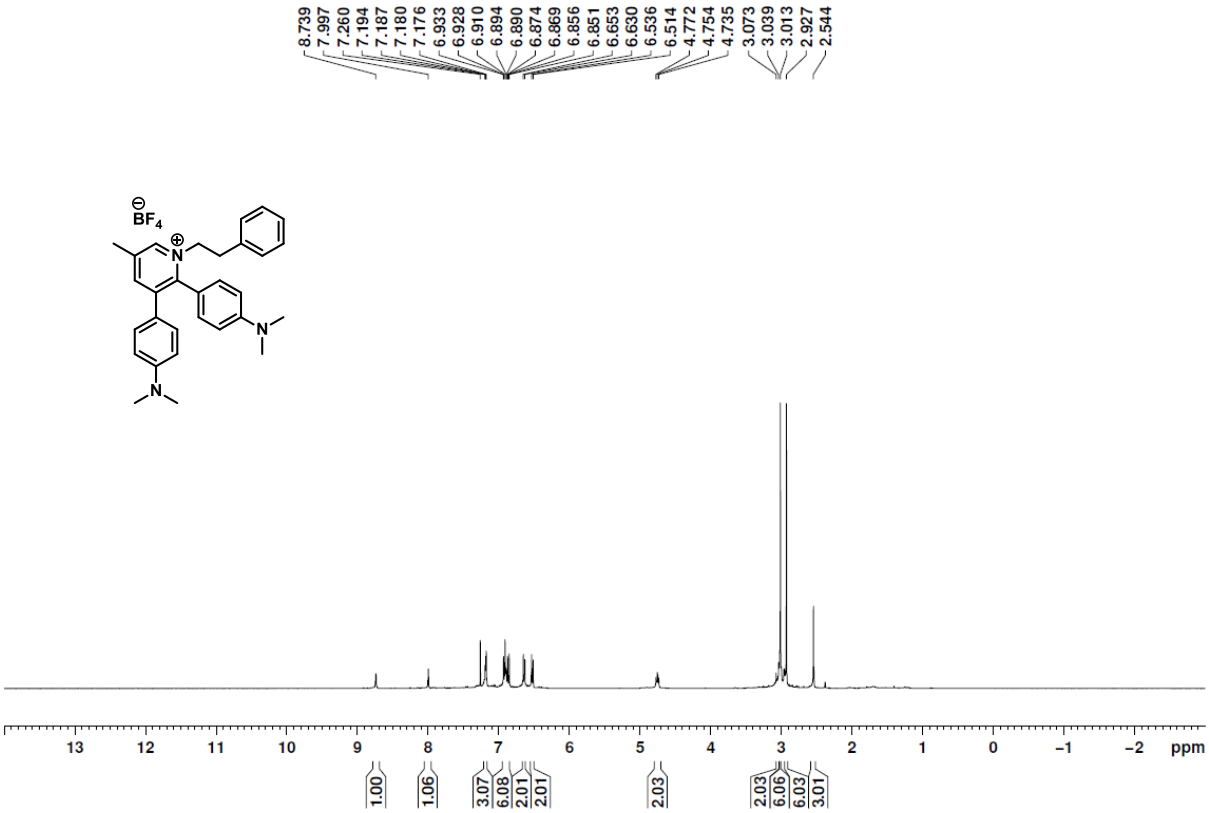
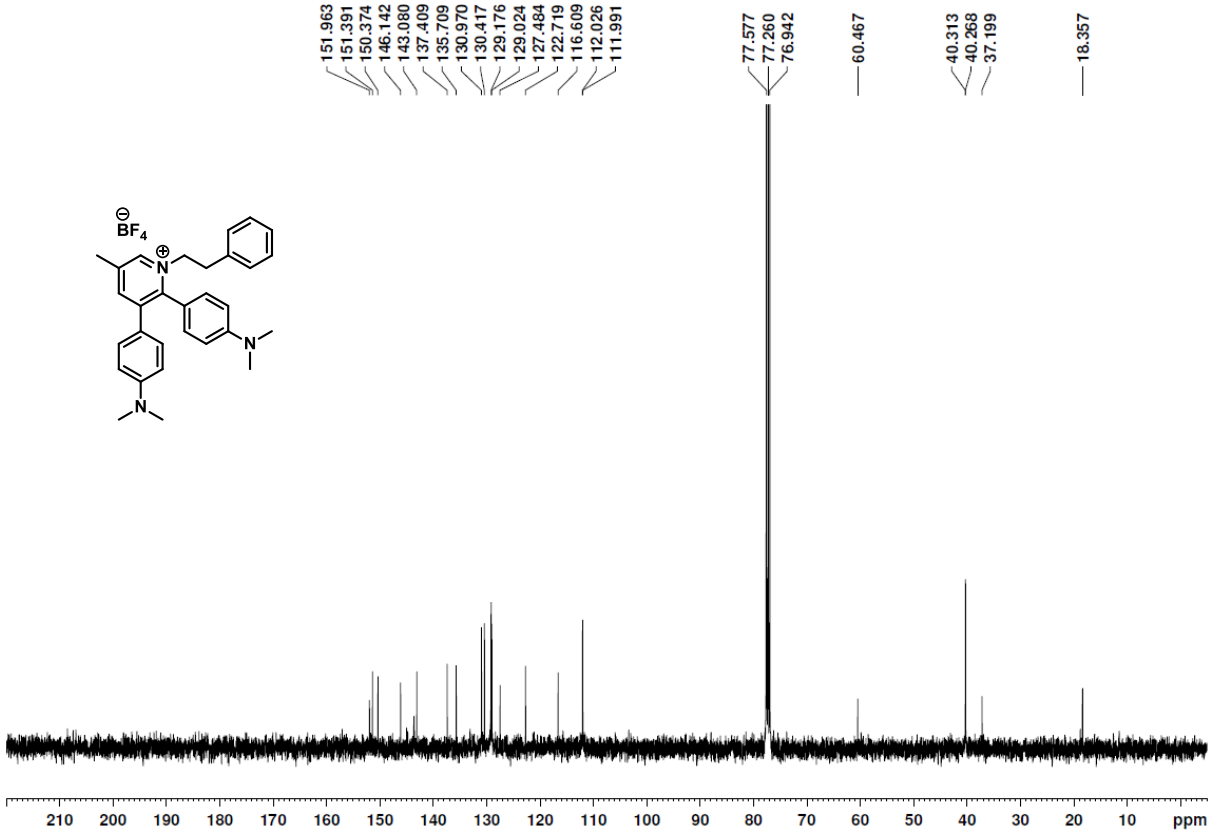


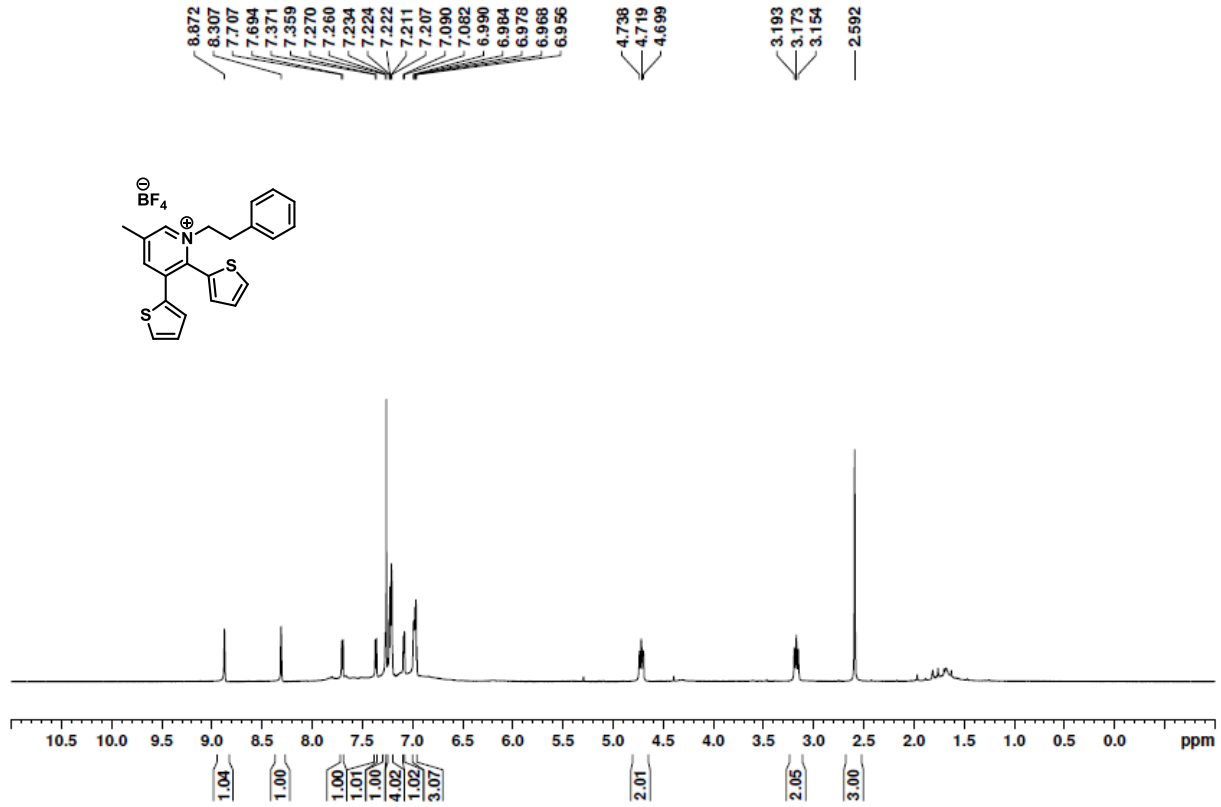
-^{1}H NMR of **3m**



-^{13}C NMR of **3m**



-^{1}H NMR of **3n**



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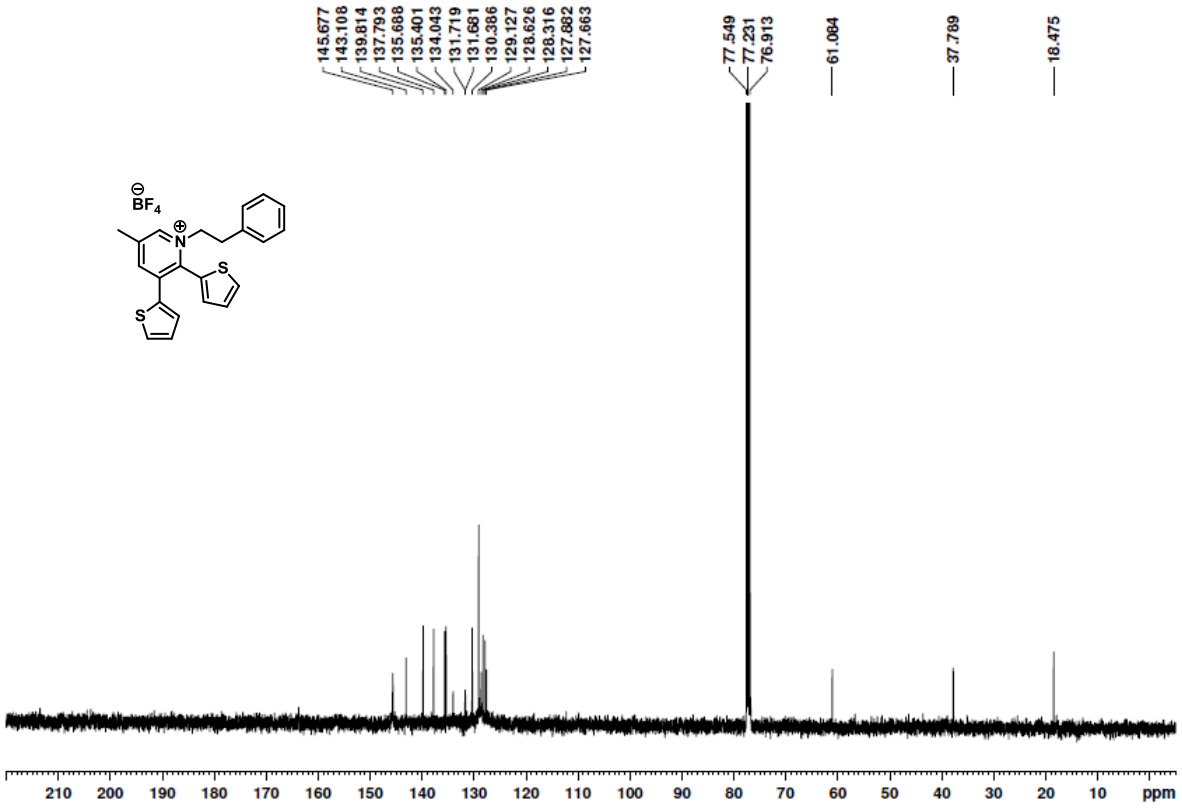
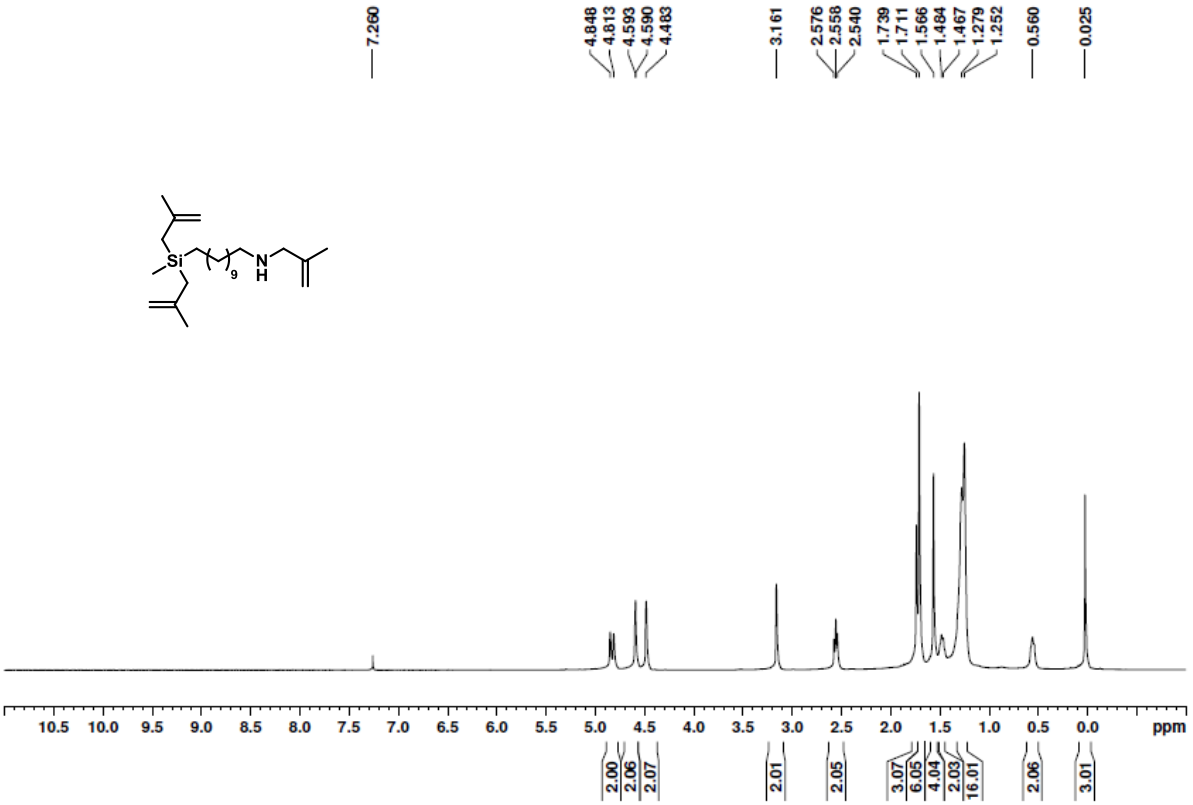


-^{1}H NMR of **1h**



-^{13}C NMR of **1h**