Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Facile One-Pot Synthesis of Indolizinium Derivatives by Rhodium(III)-Catalyzed Intramolecular Oxidative Annulation via C–H Activation: Application to Ficuseptine Synthesis

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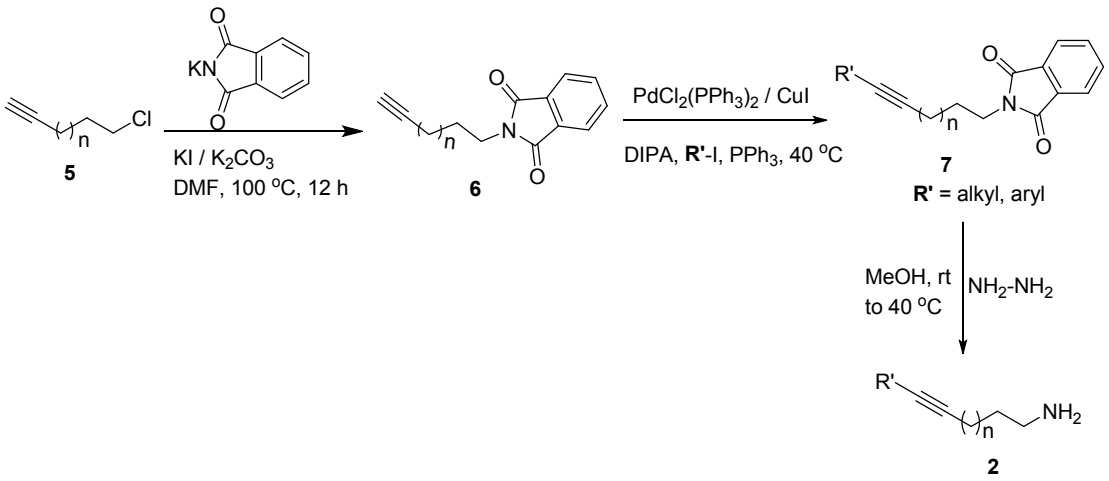
General. All reactions were conducted under a nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. All solvents were dried according to known methods and distilled prior to use.[1] $[Cp^*RhCl_2]_2$, $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ and $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ were prepared from $RhCl_3 \cdot xH_2O$ following a literature procedure.[2] Other reagents were commercially available and used as purchased.

General procedure for the synthesis of alkyne-amine[3,4]

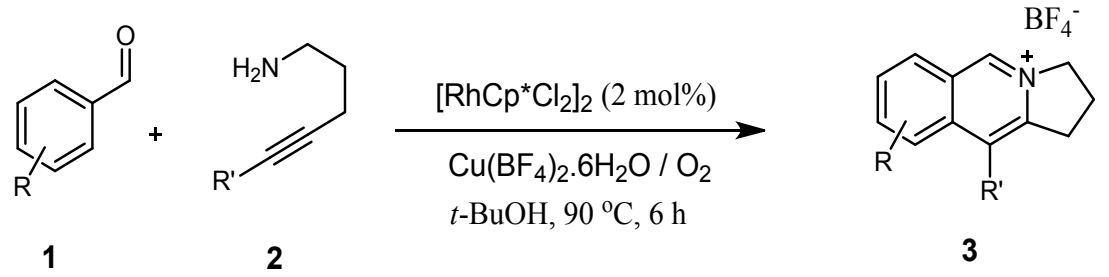
To a single-neck round bottom flask (100 mL) containing 5-chloropent-1-yne (5.0 g, 49.0 mmol, 1.0 equiv), potassium pthalimide (8.6 g, 59.0 mmol, 1.2 equiv), K_2CO_3 (5.0 g, 59.0 mmol, 1.2 equiv) and KI (0.88 g, 4.93 mmol, 0.12 equiv) in 50 mL anhydrous DMF under argon atmosphere was added. The resulting reaction mixture was stirred at 100 ^oC for 12 h and after cooling, the solution was poured into 250 mL ice water, washed and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure to afford intermediate **6** in quantitative yield. The crude product was pure enough for the next step.

Intermediate **6** (2.6 g 12.0 mmol, 1.0 equiv), aryl iodide (2.6 g 13.0 mmol, 1.1 equiv), $Pd(PPh_3)_2Cl_2$ (171 mg, 0.24 mmol, 0.02 equiv), CuI (91 mg, 0.48 mmol, 0.04 equiv), PPh_3 (126 mg, 0.48 mmol, 0.04 equiv), and $^iPr_2NH$ (15 mL) were placed in a round-bottomed flask. After stirring the resulting reaction mixture at 25 to 40 °C for overnight, saturated aqueous NH_4Cl solution was added. Then, the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. After purifying by flash chromatography (EtOAc/hexane, 20:80), compound **7** in 90% overall yield was isolated as a brown solid.



Compound **7** (1.0 equiv) were placed in a round-bottomed flask containing methanol and hydrazine hydrate (1.5 equiv) were added drop wise then the reaction mixture was stirred for 4 h at 40 °C and was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum to give the desired alkyne-amine **2** in 80% yield. No further purification was required and **2** was stored at 5-10 °C.

General procedure for the synthesis of isoquinolinium salts (3)



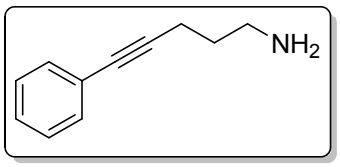
A sealed tube containing $[RhCp^*Cl_2]_2$ (2.0 mol %), $Cu(BF_4)_2{\cdot}6H_2O$ (0.45 mmol) and aryl aldehyde **1** (0.48 mmol), amine alkyne-amine **2** (0.40 mmol) was evacuated and filled with oxygen (O_2, 1 atm), then *t*-butyl alcohol (2.5 mL) was added to the system via syringe and the reaction mixture was allowed to stir at 90 °C for 6 h. When the reaction was complete, the mixture was cooled and diluted with CH_2Cl_2 (10 mL).

The mixture was filtered through a Celite pad which was further washed with CH_2Cl_2 (30 mL) and MeOH (20 mL). The combined filtrate was concentrated in vacuo and the residue was purified on a silica gel column using DCM/MeOH (95:5) as eluent to afford the desired pure product **3**.

All products **3** were made according to the above procedure. The spectral data and a copy of ^{1}H and ^{13}C NMR spectra of all compounds **3** are listed below (p. S21).

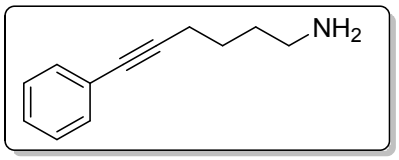
Spectral data of starting material

5-Phenylpent-4-yn-1-amine (2a)



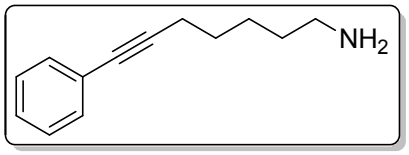
Brown liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 2 H), 7.35-7.23 (m, 3 H), 2.91 (s, NH_2), 3.07 (t, *J* = 7.6 Hz, 2 H), 2.49 (t, *J* = 7.6 Hz, 2 H), 1.97-1.93 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 131.5 (2 CH), 128.2 (2 CH), 127.5 (CH), 123.8 (C), 89.6 (C), 80.8 (C), 41.2 (CH_2), 32.36 (CH_2), 16.80 (CH_2).

6-Phenylhex-5-yn-1-amine (2b)



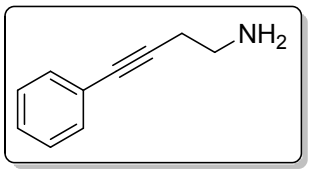
Brown liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 2 H), 7.27-7.22 (m, 3 H), 2.72 (t, *J* = 7.6 Hz, 2 H), 2.40 (t, *J* = 7.6 Hz, 2 H), 1.65-1.59 (m, 4 H), 1.58 (bs, NH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 131.2 (2 CH), 127.9 (2 CH), 127.2 (CH), 123.6 (C), 89.7 (C), 80.5 (C), 41.4 (CH_2), 32.7 (CH_2), 25.8 (CH_2), 19.0 (CH_2).

7-Phenylhept-6-yn-1-amine (2d)



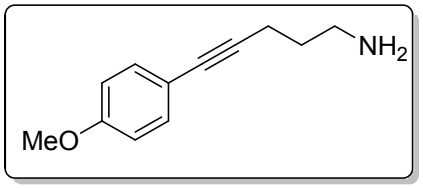
Brown liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.37 (m, 2 H), 7.27-7.24 (m, 3 H), 2.73 (t, *J* = 7.6 Hz, 2 H), 2.39 (t, *J* = 7.6 Hz, 2 H), 2.38 (bs, 2 H), 1.62-1.58 (m, 2 H), 1.49-1.47 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 131.5 (2 CH), 128.1 (2 CH), 127.4 (CH), 123.9 (C), 90.0 (C), 80.7 (C), 41.8 (CH_2), 32.7 (CH_2), 28.5 (CH_2), 26.1 (CH_2), 19.3 (CH_2).

4-Phenylbut-3-yn-1-amine (2e)



Brown liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 2 H), 7.28-7.24 (m, 3 H), 2.91 (t, *J* = 7.6 Hz, 2 H), 2.55 (t, *J* = 7.6 Hz, 2 H), 2.30 (s, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 131.5 (2 CH), 128.2 (2 CH), 127.7 (CH), 123.5 (C), 87.4 (C), 82.1 (C), 40.8 (CH_2), 24.0 (CH_2).

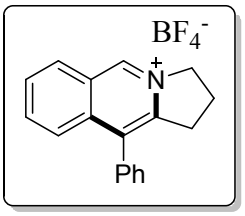
5-(4-Methoxyphenyl)pent-4-yn-1-amine (2g)



Brown liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 2 H), 6.79-6.74 (m, 2 H), 3.76 (s, 2 H), 3.06 (t, *J* = 7.6 Hz, 2 H), 2.46 (s, 2 H), 1.90 (s, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5 (C), 132.3 (2 CH), 129.3 (C), 115.0 (C), 113.2 (2 CH), 85.8 (C), 80.9 (C), 54.6 (CH_3), 38.6 (CH_2), 26.0 (CH_2), 16.3 (CH_2).

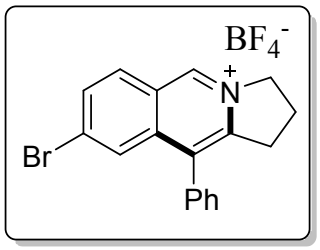
Spectral data of product 3

10-Phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3aa)



Brown solid; m.p. 196-198 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.95 (s, 1 H), 8.45 (d, *J* = 8.0 Hz, 2 H), 7.95-7.93 (m, 1 H), 7.91-7.85 (m, 1 H), 7.83-7.81 (m, 1 H), 7.74-7.72 (m, 3 H), 7.59-7.37 (m, 2 H), 5.20 (t, *J* = 7.6 Hz, 2 H), 3.31 (t, *J* = 7.6 Hz, 2 H), 2.54-2.51 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.4 (C), 145.9 (CH), 137.9 (C), 136.5 (CH), 134.7 (C), 133.0 (C), 131.2 (CH), 130.3 (CH), 129.8 (CH), 129.6 (2 CH), 129.5 (2 CH), 127.8 (C), 125.5 (CH), 59.6 (CH_2), 31.3 (CH_2), 22.7 (CH_2); **^{11}B NMR** (160 MHz, $CDCl_3$): δ -3.48; **^{19}F NMR** (470 MHz, $CDCl_3$): δ -151.152, -151.205 and secondary isotopic shift (^{10}B, ^{11}B) of 0.054 ppm; **HRMS** (FAB^+) calcd for $C_{22}H_{18}N^+$ 246.1277, found 246.1278; IR (KBr): 3070, 1619, 1473, 1056 (ν_{B-F}), 771 and 547cm^{-1}

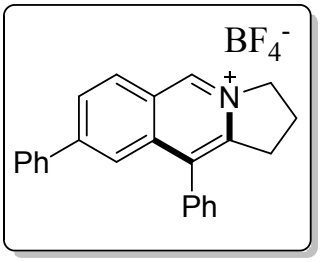
8-Bromo-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ba)



Brown solid; m.p. 135-137 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1 H), 8.25 (d, *J* = 9.6 Hz, 1 H), 7.83-7.80 (m, 2 H), 7.58-7.55 (m, 2 H), 7.40-7.37 (m, 2 H), 5.11 (t, *J* = 7.6 Hz, 2 H), 3.29 (t, *J* = 7.6 Hz, 2 H), 2.51-2.47 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.7 (*C*), 145.5 (CH), 138.3 (C), 133.5 (CH),

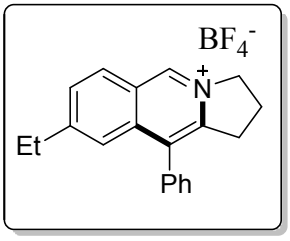
133.2 (*C*), 132.4 (CH), 132.2 (*C*), 132.0 (C), 129.6 (*C*H), 129.4 (*C*H), 129.3 (2 *C*H), 127.5 (CH), 126.0 (*C*), 59.4 (CH_2), 31.1 (CH_2), 22.2 (CH_2); **HRMS** (FAB^+) calcd for $C_{18}H_{15}BrN^+$ 324.0382, found 324.0380; IR (KBr): 3085, 1635, 1581, 1056 (ν_{B-F}), 771 and 501 cm^{-1}

8,10-Diphenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ca)



Brown solid; m.p. 196-198 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.87 (s, 1 H), 8.44 (d, *J* = 8.0 Hz, 1 H), 7.98-7.96 (m, 1 H), 7.81 (s, 1 H), 7.60-7.54 (m, 3 H), 7.51-7.48 (m, 2 H), 7.44-7.40 (m, 4 H), 5.17 (t, *J* = 7.6 Hz, 2 H), 3.30 (t, *J* = 7.6 Hz, 2 H), 2.53-2.49 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.7 (*C*), 146.6 (C), 145.0 (CH), 138.5 (C), 138.0 (*C*), 134.1 (C), 132.8 (*C*), 131.3 (CH), 129.6 (*C*H), 129.5 (*C*H), 129.4 (2 *C*H), 129.3 (2 CH), 129.2 (3 *CH*), 127.7 (2 *CH*), 126.5 (*C*), 122.3 (*CH*), 59.1 (CH_2), 31.0 (CH_2), 22.4 (CH_2); **HRMS** (FAB^+) calcd for $C_{24}H_{20}N^+$ 322.1590, found 322.1590; IR (KBr): 3062, 1635, 1465, 1056 (ν_{B-F}), 725 and 586 cm^{-1}

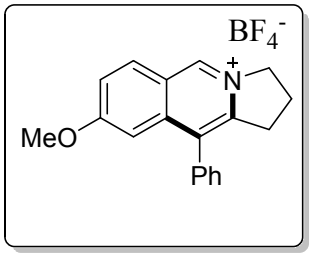
8-Ethyl-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3da)



Brown solid; m.p. 172-174°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1 H), 8.33 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.0 Hz,

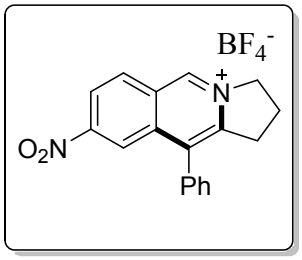
1 H), 7.59-7.53 (m, 3 H), 7.44 (s, 1 H), 7.37-7.36 (m, 2 H), 5.12 (t, *J* = 7.6 Hz, 2 H), 3.25 (t, *J* = 7.6 Hz, 2 H), 2.81-2.75 (m, 2 H), 2.48 (t, *J* = 7.6 Hz, 2 H)), 1.21 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.2 (C), 146.1 (C), 144.7 (CH), 138.0 (C), 133.6 (C), 132.9 (C), 131.2 (CH), 130.7 (CH), 129.3 (3 CH), 129.2 (2 CH), 126.1 (C), 122.8 (CH), 59.0 (CH_2), 30.9 (CH_2), 29.8 (CH_2), 22.4 (CH_2), 14.6 (CH_3); **HRMS** (FAB^+) calcd for $C_{20}H_{20}N^+$ 274.1590, found 274.1588; IR (KBr): 3494, 2992, 2275, 817, 1056 (ν_{B-F}), 740 and 509 cm^{-1}

8-Methoxy-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ea)



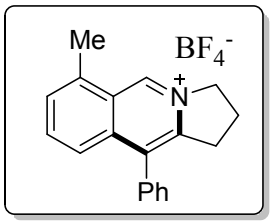
Yellow solid; m.p. 220-222 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.63 (s, 1 H), 8.27 (d, *J* = 9.2 Hz, 1 H), 7.58-7.52 (m, 3 H), 7.39-7.34 (m, 3 H), 6.86-6.85 (m, 1 H), 5.04 (t, *J* = 7.6 Hz, 2 H), 3.78 (s, 3 H), 3.22 (t, *J* = 7.6 Hz, 2 H), 2.48-2.44 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.7 (C), 146.3 (C), 143.5 (CH), 140.5 (C), 133.0 (C), 132.5 (C), 132.1 (C), 129.3 (CH), 129.3 (2 CH), 129.1 (2 CH), 123.0 (C), 122.8 (CH), 103.4 (CH), 58.4 (CH_3), 55.9 (CH_2), 30.9 (CH_2), 22.3 (CH_2); **HRMS** (FAB^+) calcd for $C_{19}H_{18}NO^+$ 276.1383, found 276.1382; IR (KBr): 3779, 3070, 1619, 1473, 1056 (ν_{B-F}), 771 and 547 cm^{-1}

8-Nitro-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3fa)



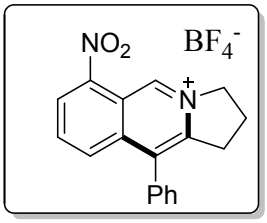
Orange solid; m.p. 175-177 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.06 (s, 1 H), 8.65 (d, *J* = 8.4 Hz, 1 H), 8.52 (s, 1 H), 8.43 (d, *J* = 8.4 Hz, 1 H), 7.60-7.43 (m, 5 H), 5.21 (t, *J* = 7.6 Hz, 2 H), 3.36 (t, *J* = 7.6 Hz, 2 H), 2.54 (t, *J* = 7.6 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.4 (C), 148.9 (C), 146.1 (C), 137.6 (C), 136.5 (C), 133.4 (CH), 131.7 (C), 130.1 (CH), 129.5 (3 CH), 129.4 (2 CH), 122.9 (CH), 121.1 (CH), 60.1 (CH_2), 31.3 (CH_2), 22.2 (CH_2); **HRMS** (FAB^+) calcd for $C_{18}H_{15}O_2N_2^+$ 291.1128, found 291.1130; IR (KBr): 3070, 1727, 1601,1532, 1056 (ν_{B-F}), 755 and 546 cm^{-1}

6-Methyl-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ga)



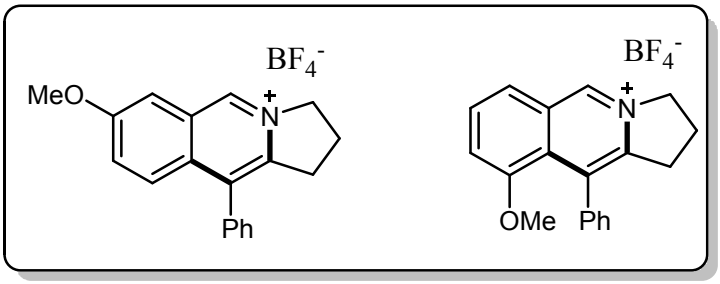
Yellow solid; m.p. 114-116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.91 (s, 1 H), 7.78-7.74 (m, 1 H), 7.59-7.51 (m, 5 H), 7.36-7.34 (m, 2 H), 5.21 (t, *J* = 7.6 Hz, 2 H), 3.26 (t, *J* = 7.6 Hz, 2 H), 2.88 (s, 3 H), 2.53-2.47 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.8 (C), 142.6 (CH), 139.6 (C), 138.3 (C), 135.9 (CH), 134.5 (C), 133.0 (C), 130.5 (CH), 129.3 (3 CH), 129.1 (2 CH), 127.1 (C), 123.3 (CH), 59.5 (CH_2), 31.0 (CH_2), 22.3 (CH_2), 18.5 (CH_3); **HRMS** (FAB^+) calcd for $C_{19}H_{18}N^+$ 260.1434, found 260.1436; IR (KBr): 3694, 2946, 1712, 1504, 1056 (ν_{B-F}), 771 and 593 cm^{-1}

6-Nitro-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ha)



Brown solid; m.p. 186-188 °C; **^{1}H NMR** (400 MHz, C_2D_6CO): δ 9.85 (s, 1 H), 8.71 (d, *J* = 5.6 Hz, 1 H), 7.68-7.60 (m, 6 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 5.20 (t, *J* = 7.6 Hz, 2 H), 3.53 (t, *J* = 7.6 Hz, 2 H), 2.69-2.61 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.4 (C), 142.0 (C), 138.8 (C), 135.8 (C), 133.9 (CH), 132.4 (CH), 132.1 (C), 131.3 (CH), 130.0 (CH), 129.5 (2 CH), 129.5 (2 CH), 128.2 (CH), 125.1 (C), 61.2 (CH_2), 31.6 (CH_2), 22.0 (CH_2); **HRMS** (FAB^+) calcd for $C_{18}H_{15}N_2O_2^+$ 291.1128 found 291.1130; IR (KBr): 3040, 1727, 1571, 1056 (ν_{B-F}), 701 and 556 cm^{-1}

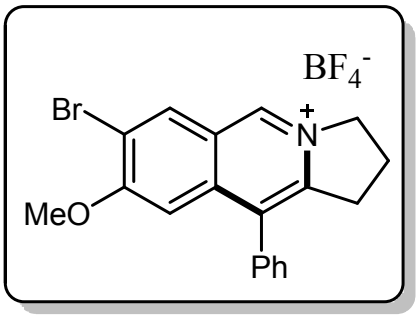
9-Methoxy-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ia) and 7-methoxy-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ia')



Brown solid; m.p. 180-182 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (s, 1 H), 9.74 (s, 1 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 7.72-7.68 (m, 2 H), 7.61-7.47 (m, 5 H), 7.44-7.41 (m, 4 H), 7.38-7.36 (m, 2 H), 7.25-7.19 (m, 4 H), 5.12 (q, *J* = 7.6 Hz, 4 H), 3.93 (s, 3 H), 3.46 (s, 3 H), 3.27 (t, *J* = 7.6 Hz, 2 H), 3.13 (t, *J* = 7.6 Hz, 2 H), 2.51-2.42 (m, 2 H);

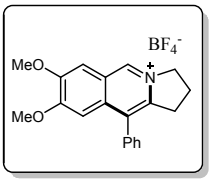
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (C), 155.6 (C), 146.9 (C), 145.0 (C), 144.2 (C), 143.1 (CH), 137.3 (C), 134.3 (C), 133.6 (C), 133.4 (C), 132.9 (C), 130.9 (CH), 129.9 (CH), 129.6 (C), 129.4 (CH), 129.3 (3 CH), 129.2 (C), 128.8 (C), 127.9 (3 CH), 127.7 (2 CH), 126.5 (CH), 122.6 (2 CH), 115.1 (CH), 106.9 (CH), 59.4 (OCH_3), 59.3 (OCH_3), 56.2 (CH_2), 55.7 (CH_2), 31.4 (CH_2), 30.8 (CH_2), 22.4 (CH_2), 22.1 (CH_2); **HRMS** (FAB^+) calcd for $C_{19}H_{18}ON^+$ 276.1383, found 276.1382; IR (KBr): 3070, 1617, 1481, 1241, 1056 (ν_{B-F}), 771 and 547 cm^{-1}

7-Bromo-8-methoxy-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ja)



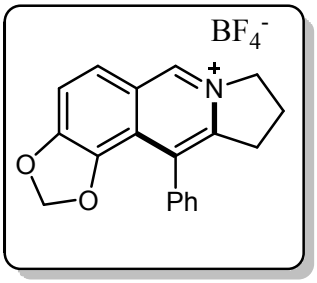
Brown solid; m.p. 130-132 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.70 (s, 1 H), 8.54 (s, 1 H), 7.61-7.55 (m, 3 H), 7.41-7.38 (m, 2 H), 6.86 (s, 1 H), 5.11 (t, *J* = 7.6 Hz, 2 H), 3.84 (s, 3 H), 3.24 (t, *J* = 7.6 Hz, 2 H), 2.51-2.47 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.7 (C), 146.8 (C), 143.2 (CH), 139.4 (C), 134.7 (CH), 132.8 (C), 132.5 (C), 129.7 (CH), 129.6 (2 CH), 129.1 (2 CH), 123.5 (C), 118.9 (C), 103.4 (CH), 58.4 (OCH_3), 56.8 (CH_2), 31.1 (CH_2), 22.4 (CH_2); **HRMS** (FAB^+) calcd for $C_{19}H_{17}BrNO^+$ 354.0488, found 354.0497; IR (KBr): 3062, 1635, 1419, 1056 (ν_{B-F}), 740 and 632 cm^{-1}

7,8-Dimethoxy-10-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ka)



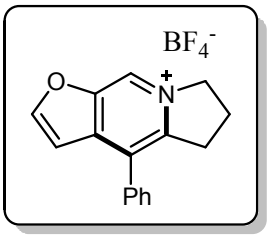
Brown solid; m.p. 229-230 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.59 (s, 1 H), 7.71 (s, 1 H), 7.68-7.64 (m, 3 H), 7.57-7.56 (m, 2 H), 6.84 (S, 1 H), 5.04 (t, *J* = 7.6 Hz, 2 H), 4.02 (t, *J* = 7.6 Hz, 3 H), 3.82 (t, *J* = 7.6 Hz, 3 H), 3.24-3.20 (m, 2 H), 2.49-2.45 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.8 (C), 152.3 (C), 144.5 (CH), 141.3 (C), 135.6 (C), 133.3 (C), 131.9 (C), 129.4 (2 CH), 129.1 (2 CH), 128.1 (CH), 124.4 (C), 107.6 (CH), 102.9(CH), 58.7 (CH_2), 56.7 (OCH_3), 56.4 (OCH_3), 31.0 (CH_2), 22.4 (CH_2); **HRMS** (FAB^+) calcd for $C_{20}H_{20}NO_2^+$ 306.1489, found 306.1486; IR (KBr): 3072, 1465, 1056 ($\nu_{B\text{-}F}$), 1041, 724 and 571 cm^{-1}

11-Phenyl-9,10-dihydro-8*H*-[1,3]dioxolo[4,5-f]pyrrolo[1,2-b]isoquinolin-7-ium tetrafluoroborate (3la)



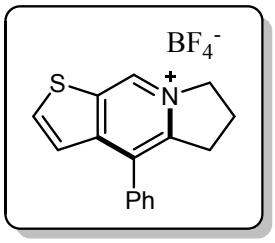
Orange solid; m.p. 209-211 °C; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 9.65 (s, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 7.57 (d, *J* = 8.4 Hz, 1 H), 7.82-7.49 (m, 3 H), 7.38-7.36 (m, 2 H), 6.06 (s, 2 H), 5.00 (t, *J* = 7.6 Hz, 2 H), 3.18 (t, *J* = 7.6 Hz, 2 H), 2.51-2.45 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.4 (C), 146.0 (CH), 145.8 (C), 141.2 (C), 134.0 (C), 129.1 (2 CH), 129.0 (C), 128.9 (CH), 128.8 (CH), 128.2 (2 CH), 123.5 (C), 122.2 (C), 114.7(CH), 103.1 (CH_2), 58.6 (CH_2), 30.6 (CH_2), 22.3 (CH_2); **HRMS** (FAB^+) for $C_{19}H_{16}NO_2^+$ 290.1176, found 290.1178; IR (KBr): 3062, 1465, 1303, 1056 ($\nu_{B\text{-}F}$), 1041, 763 and 593 cm^{-1}

4-Phenyl-6,7-dihydro-5*H*-furo[2,3-f]indolizin-8-ium tetrafluoroborate (3ma)



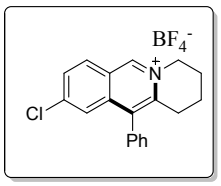
Brown solid; m.p. 192-194 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.28 (s, 1 H), 8.20-8.19 (m, 1 H), 7.59-7.53 (m, 3 H), 7.49-7.46 (m, 2 H), 6.94-6.93 (m, 1 H), 5.14 (t, *J* = 7.6 Hz, 2 H), 3.44 (t, *J* = 7.6 Hz, 2 H), 2.60-2.52 (m, 2 H); **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 157.1 (CH), 151.1 (C), 149.5 (C), 141.8 (C), 132.7 (C), 130.6 (C), 130.3 (C), 129.8 (2 CH), 129.1 (2 CH), 125.9 (CH), 107.4 (CH), 60.2 (CH_2), 31.6 (CH_2), 23.3 (CH_2); **HRMS** (FAB^+) calcd for $C_{16}H_{14}NO^+$ 236.1070 ,found 236.1072; IR (KBr): 3112, 1617, 1441, 1056 (ν_{B-F}), 717 and 476 cm^{-1}

4-Phenyl-6,7-dihydro-5*H*-thieno[2,3-f]indolizin-8-ium tetrafluoroborate (3na)



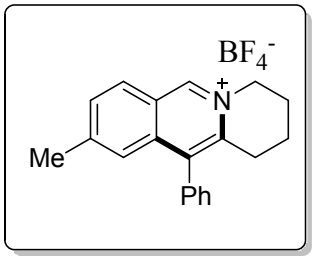
Brown solid; m.p. 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (s, 1 H), 8.23 (d, *J* = 5.6 Hz, 1 H), 7.57-7.53 (m, 3 H), 7.45-7.42 (m, 2 H), 7.34 (d, *J* = 5.6 Hz, 1 H), 5.13 (t, *J* = 7.6 Hz, 2 H), 3.36 (t, *J* = 7.6 Hz, 2 H), 2.57-2.50 (m, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 149.7 (C), 148.3 (C), 143.1 (CH), 136.6 (C), 136.5 (C), 133.1 (C), 131.9 (CH), 129.8 (CH), 129.3 (2 CH), 128.8 (2 CH), 123.0 (CH), 59.3 (CH_2), 31.0 (CH_2), 22.9 (CH_2); HRMS (FAB^+) calcd for $C_{16}H_{14}NS^+$ Exact Mass: 252.0841, found 252.0841; IR (KBr): 3694, 1619, 1442, 1056 (ν_{B-F}), 779 and 593 cm^{-1}

9-Chloro-11-phenyl-1,2,3,4-tetrahydropyrido[1,2-b]isoquinolin-5-ium tetrafluoroborate (3ob)



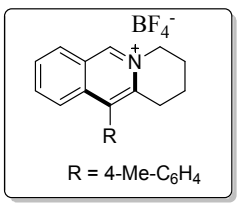
Brown solid; m.p. 127-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1 H), 8.37 (d, *J* = 8.8 Hz, 1 H), 7.65 (d, *J* = 8.8 Hz, 1 H), 7.57-7.56 (m, 3 H), 7.41 (s, 1 H), 7.31-7.29 (m, 2 H) 4.84 (t, *J* = 7.6 Hz, 2 H), 2.91 (t, *J* = 7.6 Hz, 2 H), 2.19-2.16 (m, 2 H), 1.91-1.83 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.2 (CH), 144.8 (C), 143.4 (C), 138.5 (C), 136.0 (C), 132.5 (C), 132.4 (CH), 131.2 (CH), 129.5 (5 CH), 124.7 (C), 124.4 (CH), 56.4 (CH_2), 25.9 (CH_2), 20.6 (CH_2), 17.8 (CH_2); **HRMS** (FAB^+) calcd for $C_{19}H_{17}ClN^+$ 294.1044, found 294.1043; IR (KBr): 3085, 1635, 1465, 1056 ($\nu_{B\text{-}F}$), 779 and 593 cm^{-1}

9-Methyl-11-phenyl-1,2,3,4-tetrahydropyrido[1,2-b]isoquinolin-5-ium tetrafluoroborate (3pb)



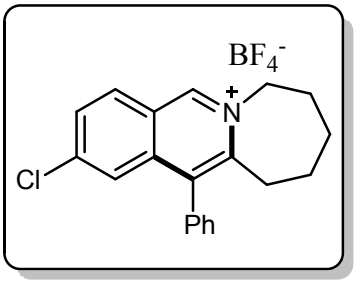
Brown solid; m.p. 215-217 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.70 (s, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H), 7.60-7.55 (m, 3 H), 7.28-7.20 (m, 3 H), 4.82 (t, *J* = 7.6 Hz, 2 H), 2.90-2.86 (m, 2 H), 2.45 (s, 3 H), 2.18-2.15 (m, 2 H), 1.91-1.82 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.7 (C), 148.6 (CH), 143.6 (C), 138.3 (C), 136.3 (CH), 133.4 (C), 132.6 (C), 130.6 (CH), 129.8 (2 CH), 129.6 (2 CH), 129.5 (CH), 125.1 (C), 124.5 (CH), 56.3 (CH_2), 26.0 (CH_2), 23.2 (CH_2), 21.0 (CH_2), 18.2 (CH_3); **HRMS** (FAB^+) calcd for $C_{20}H_{20}N^+$ 274.1590, found 274.1590; IR (KBr): 3494, 1712, 1504, 1056 ($\nu_{B\text{-}F}$), 771 and 593 cm^{-1}

11-(*p*-Tolyl)-1,2,3,4-tetrahydropyrido[1,2-b]isoquinolin-5-ium tetrafluoroborate (3ac)



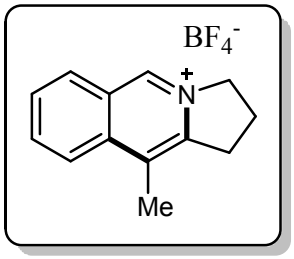
Brown sticky solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.86 (s, 1 H), 8.45 (d, 1 H), 7.88-7.84 (m, 1 H), 7.80-7.76 (m, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 7.38-7.36 (m, 2 H) 7.18-7.16 (m, 2 H), 4.89 (t, *J* = 7.6 Hz, 2 H), 2.94 (t, *J* = 7.6 Hz, 2 H), 2.46 (s, 3 H), 2.21-2.16 (m, 2 H), 1.93-1.83 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.7 (C), 143.5 (C), 139.2 (C), 137.9 (C), 137.0 (C), 136.1 (CH), 130.4 (CH), 129.9 (4 CH), 129.3 (2 CH), 126.3 (C), 125.4 (CH), 55.2 (CH_2), 25.6 (CH_2), 21.2 (CH_2), 20.6 (CH_2), 17.8 (CH_3); **HRMS** (FAB^+) calcd for $C_{20}H_{10}N^+$ 274.1590, found 274.1589; IR (KBr): 3077, 1612, 1511, 1058 ($\nu_{B\text{-}F}$), 760 and 546 cm^{-1}

2-Chloro-12-phenyl-8,9,10,11-tetrahydro-7*H*-azepino[1,2-b]isoquinolin-6-ium tetrafluoroborate (3od)



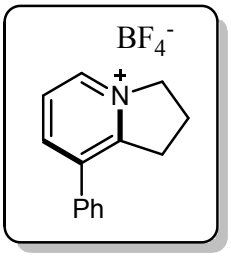
Yellow solid; m.p. 201-203 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.05 (s, 1 H), 8.50 (d, *J* = 8.8 Hz, 1 H), 7.74-7.72 (m, 1 H), 7.61-7.58 (m, 3 H), 7.36 (s, 1 H), 7.27-7.25 (m, 2 H), 5.05 (t, *J* = 7.6 Hz, 2 H), 3.05 (t, *J* = 7.6 Hz, 2 H), 2.14-2.12 (m, 2 H), 1.80-1.86 (m, 2 H), 1.76-1.71 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.6 (C), 148.2 (C), 144.1 (C), 138.8 (C), 136.6 (C), 133.4 (C), 132.9 (CH), 131.4 (CH), 129.5 (3 CH), 129.3 (2 CH), 125.0 (CH), 62.4 (CH_2), 30.3 (CH_2), 28.2 (CH_2), 27.9 (CH_2), 25.9 (CH_2); **HRMS** (FAB^+) calcd for $C_{20}H_{19}ClN^+$ 308.1201, found 308.1200; IR (KBr): 3200, 1672, 1590, 1056 ($\nu_{B\text{-}F}$), 775 and 601 cm^{-1}

10-Methyl-2,3-dihydro-1*H*-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3af)



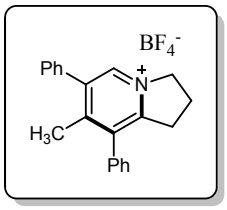
Brown solid; m.p. 131-132 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.63 (s, 1 H), 8.38-8.35 (m, 1 H), 8.20-8.18 (m, 1 H), 8.15-8.10 (m, 1 H), 7.92-7.88 (m, 1 H), 5.05 (t, *J* = 7.6 Hz, 2 H), 3.54 (t, *J* = 7.6 Hz, 2 H), 2.27 (s, 3 H), 2.63-2.57 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.0 (C), 144.3 (CH), 138.3 (C), 136.7 (CH), 131.2 (CH), 130.6 (C), 130.6 (CH), 127.3 (C), 123.9 (CH), 59.6 (CH_2), 30.7 (CH_2), 22.4 (CH_2), 15.0 (CH_3); **HRMS** (FAB^+) calcd for $C_{13}H_{14}N^+$ 184.1121, found 184.1120; IR (KBr): 3070, 1427, 1581, 1056 (ν_{B-F}), 755 and 486 cm^{-1}

8-Phenyl-2,3-dihydro-1*H*-indolizin-4-ium tetrafluoroborate (3qa)



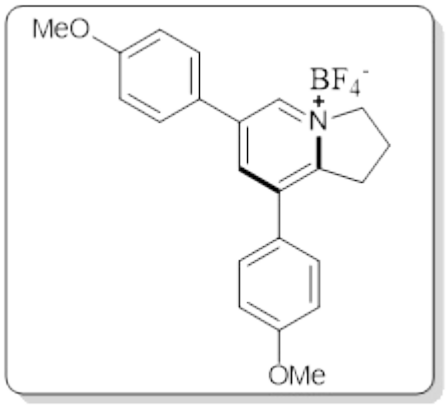
Brown solid; m.p. 150-151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.0 Hz, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 7.89-7.85 (m, 1 H), 7.50-7.42 (m, 5 H), 5.01 (t, *J* = 7.6 Hz, 2 H), 3.51 (t, *J* = 7.6 Hz, 2 H), 2.50-2.47 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.8 (C), 144.1 (CH), 140.0 (CH), 138.9 (C), 134.2 (C), 129.7 (CH), 129.2 (2 CH), 128.4 (2 CH), 126.0 (CH), 59.8 (CH_2), 32.4 (CH_2), 21.6 (CH_2); **HRMS** (FAB^+) calcd for $C_{14}H_{14}N^+$ 196.1121, found 196.1120; IR (KBr): 3060, 1627, 1256, 1058 (ν_{B-F}), 755 and 590 cm^{-1}

7-Methyl-6,8-diphenyl-2,3-dihydro-1*H*-indolizin-4-ium tetrafluoroborate (3ra)



Brown solid; m.p. 161-163 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (s, 1 H), 7.23-7.19 (m, 6 H), 7.06-7.04 (m, 2 H), 6.99-6.97 (m, 2 H), 5.03 (t, *J* = 7.6 Hz, 2 H), 3.24 (t, *J* = 7.6 Hz, 2 H), 2.50-2.43 (m, 2 H), 2.25 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.4 (C), 154.8 (C), 139.6 (CH), 137.6 (C), 136.1 (C), 134.1 (C), 133.7 (C), 129.1 (2 CH), 128.5 (2 CH), 128.4 (3 CH), 128.3 (2 CH), 128.2 (2 CH), 59.4 (CH_2), 32.5 (CH_2), 21.3 (CH_2), 18.0 (CH_3); **HRMS** (FAB^+) calcd for $C_{21}H_{20}N^+$ 286.1590, found 286.1591; IR (KBr): 3062, 1673, 1442, 1058 ($\nu_{B\text{-}F}$), 755 and 593 cm^{-1}

6,8-Bis(4-methoxyphenyl)-2,3-dihydro-1*H*-indolizin-4-ium tetrafluoroborate (4) or (ficuseptine)



Yellow solid; m.p. 201-203 °C (ref. m.p 186-187 °C);[5] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.02 (s, 1 H), 8.16 (s, 1 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.02 (d, *J* = 6.0 Hz, 2 H), 6.93 (d, *J* = 6.0 Hz, 2 H), 5.06 (t, *J* = 7.6 Hz, 2 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 3.48 (t, *J* = 7.6 Hz, 2 H), 2.48-2.43 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.1 (C), 160.8 (C), 153.5 (C), 140.6 (CH), 139.2 (C), 138.4 (C), 136.7 (CH), 129.8 (2 CH), 128.7 (2 CH), 126.5 (C), 125.2

(C), 115.0 (2 CH), 114.7 (2 CH), 60.0(CH_2), 55.4 (CH_3), 55.4 (CH_3), 32.2 (CH_2), 21.9 (CH_2); **HRMS** (FAB^+) calcd for $C_{22}H_{22}N^+O_2$ 332.1651, found 332.1652; IR (KBr): 3077, 1612, 1180, 1056 ($\nu_{B\text{-}F}$), 717 and 601 cm^{-1}

References:

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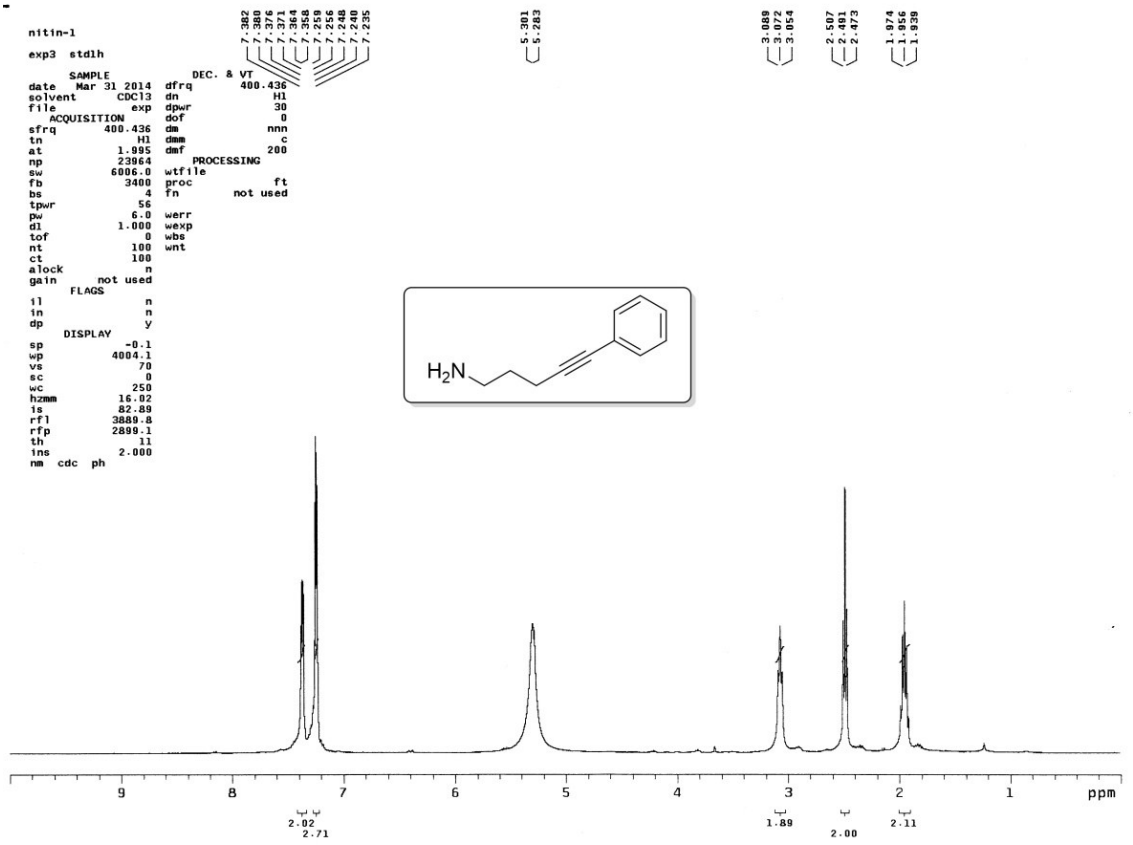
^{1}H and ^{13}C NMR spectra of compound **2a**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SAMPLE
date Mar 31 2014
solvent CDCl3
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at 1.995
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fb 3400
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tpwr 56
pw 6.0
dl 1.000
tof 0
nt 100
ct 100
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
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sc 0
wc 250
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rfl 3889.8
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th 11
ins 2.000
nm cdc ph
DEC. & VT
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dpwr 30
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dmm c
dmf 200
PROCESSING
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proc ft
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wexp
wbs
wnt
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7.380
7.376
7.371
7.364
7.358
7.259
7.256
7.248
7.240
7.235
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3.072
3.054
2.507
2.491
2.473
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1.956
1.939
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7
6
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3
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ppm
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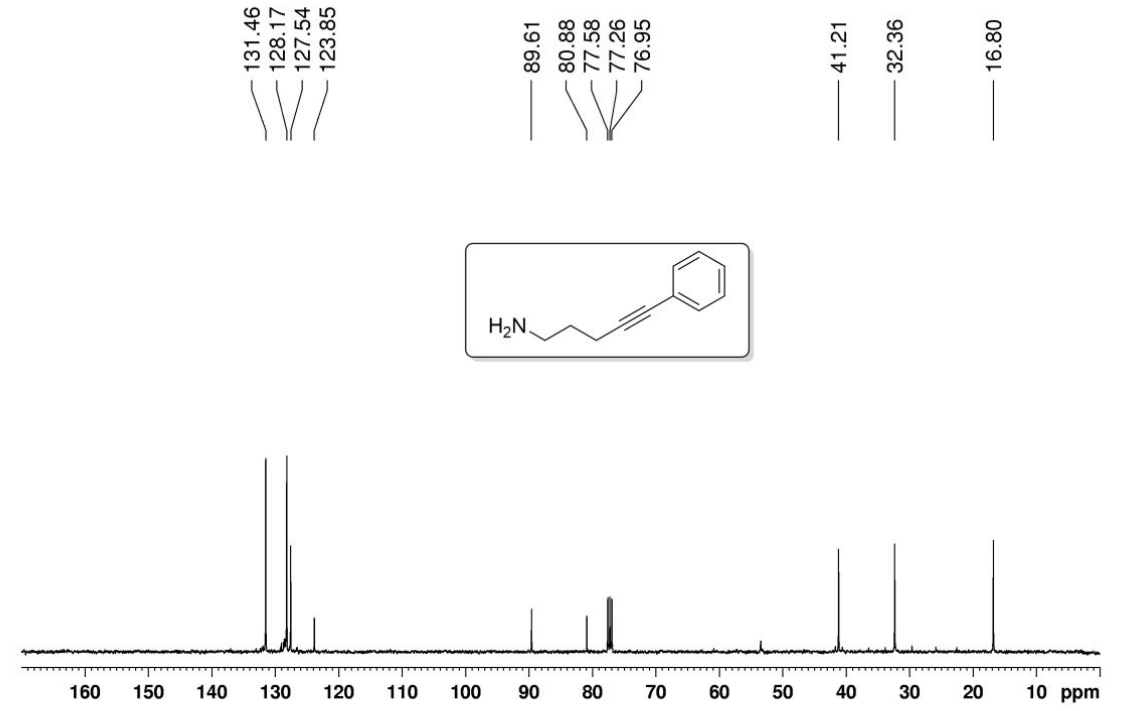
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H2N
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150
140
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50
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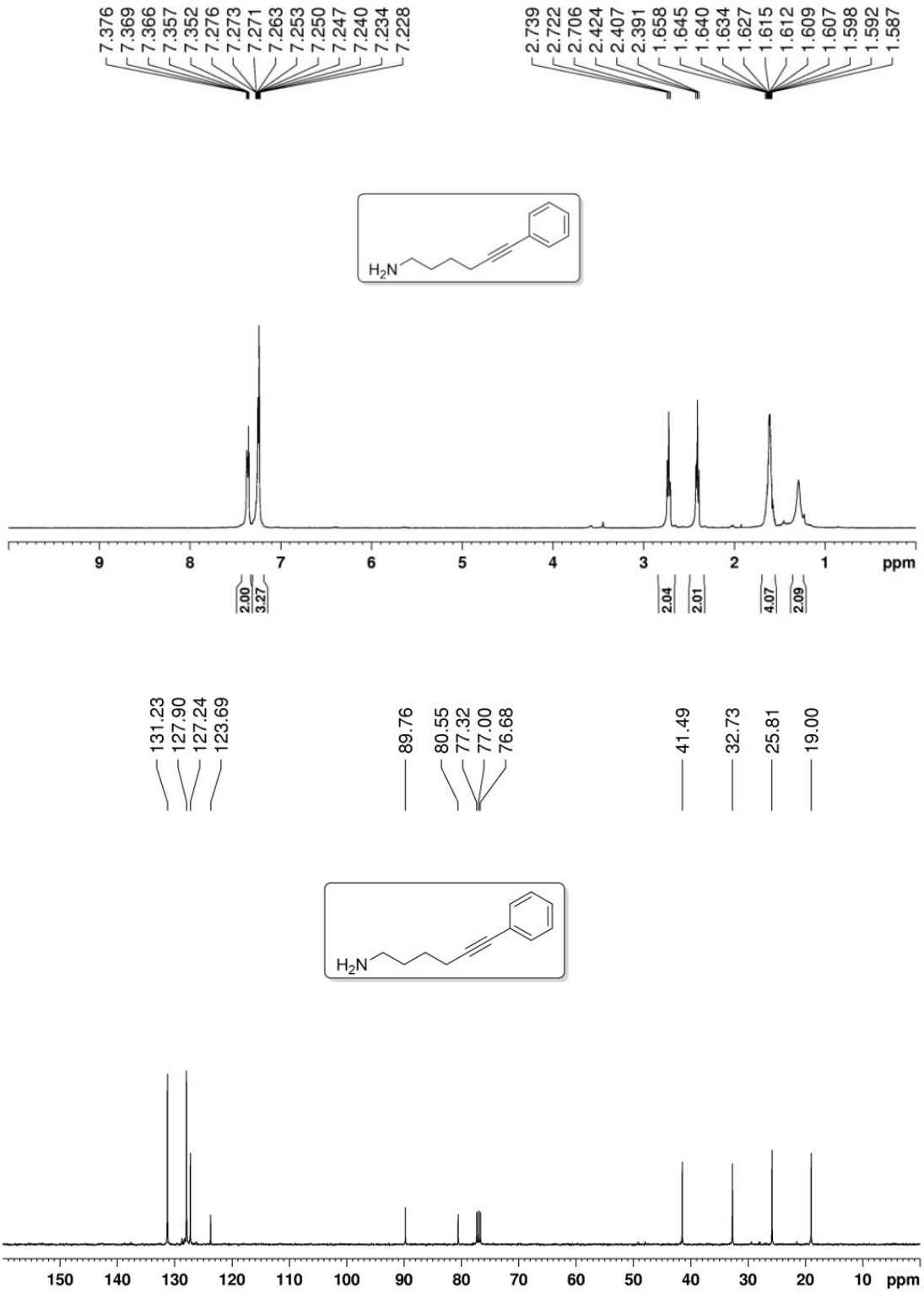
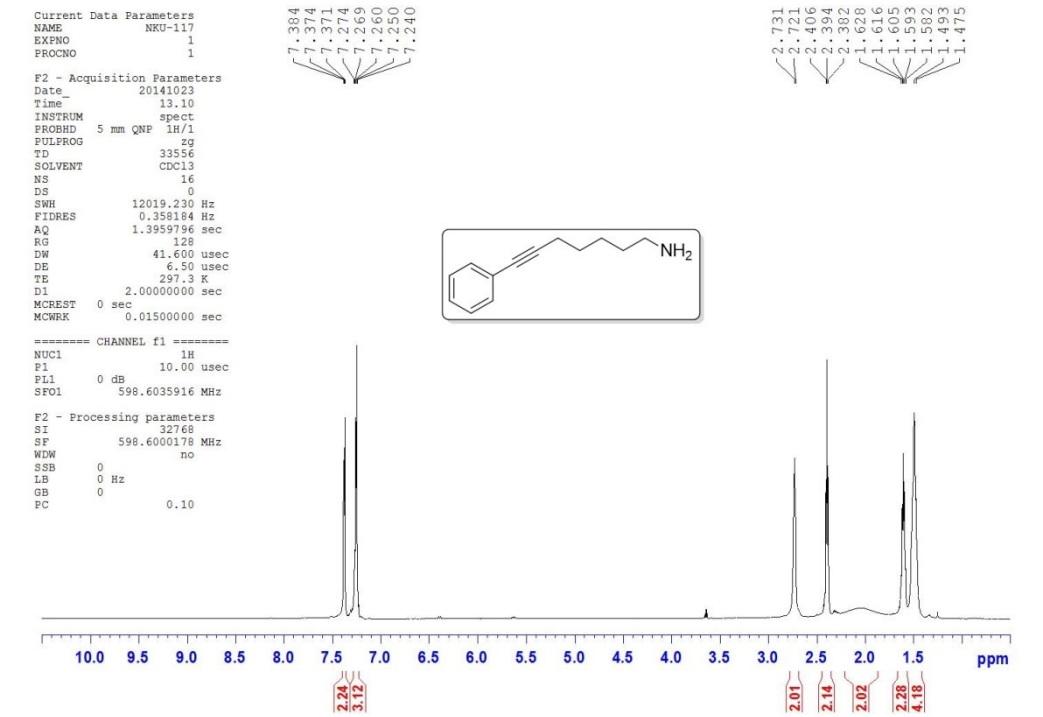
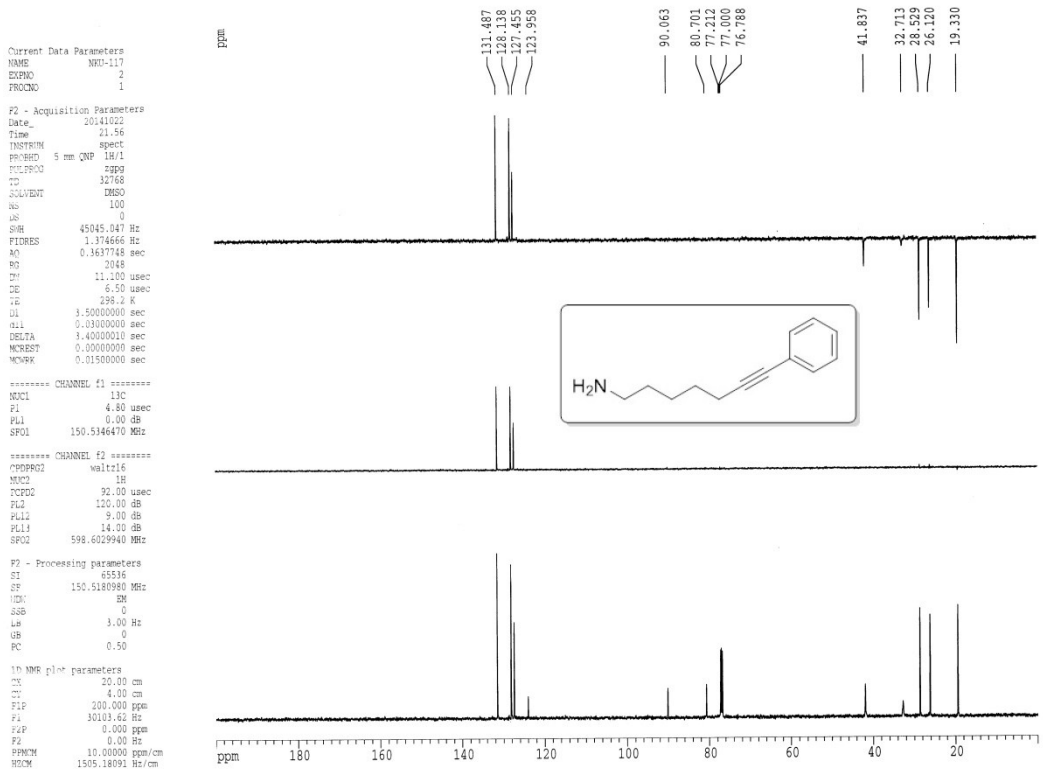
10
ppm

^{1}H and ^{13}C NMR spectra of compound **2b**

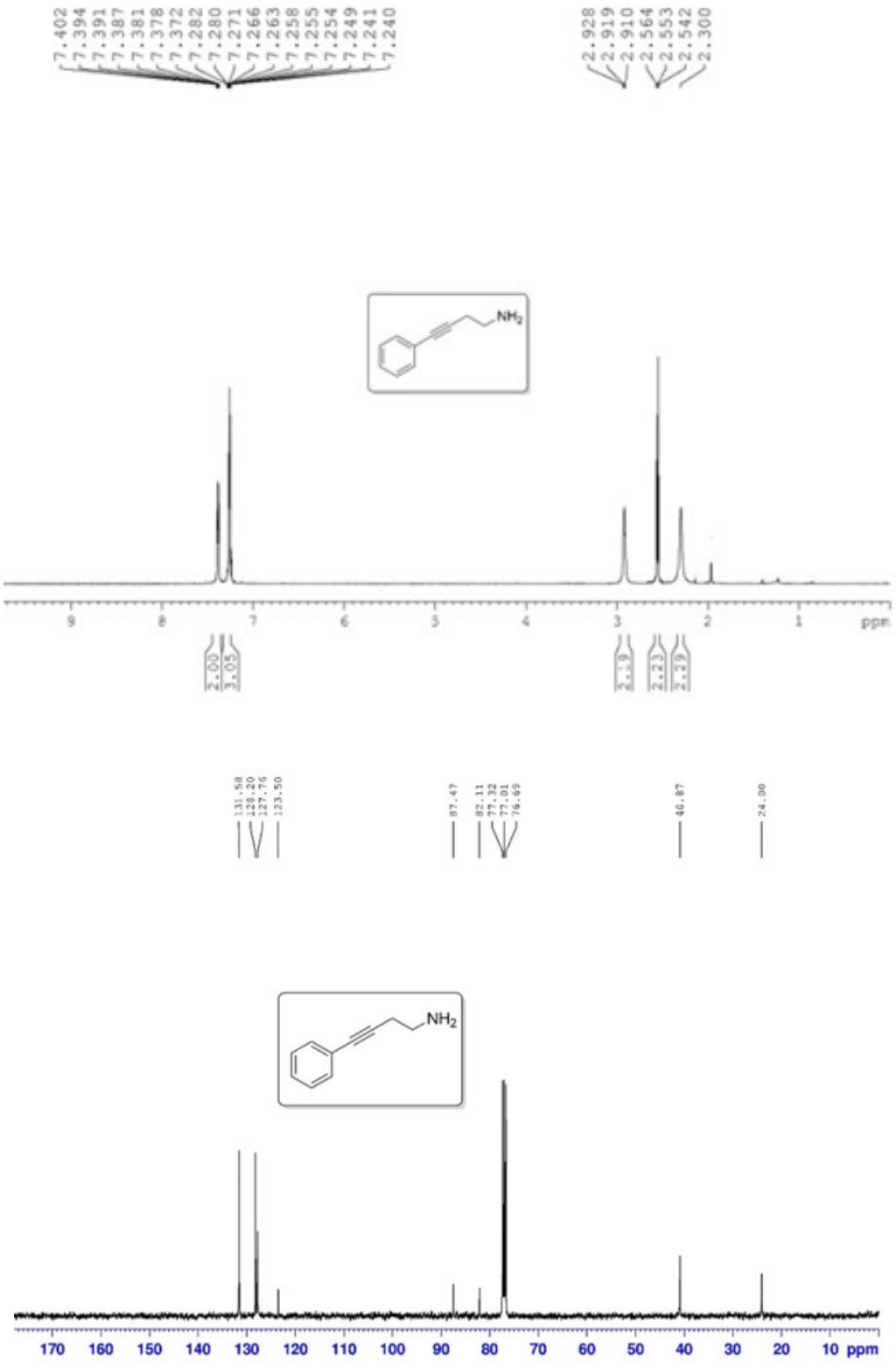


^{1}H and ^{13}C NMR spectra of compound **2d**

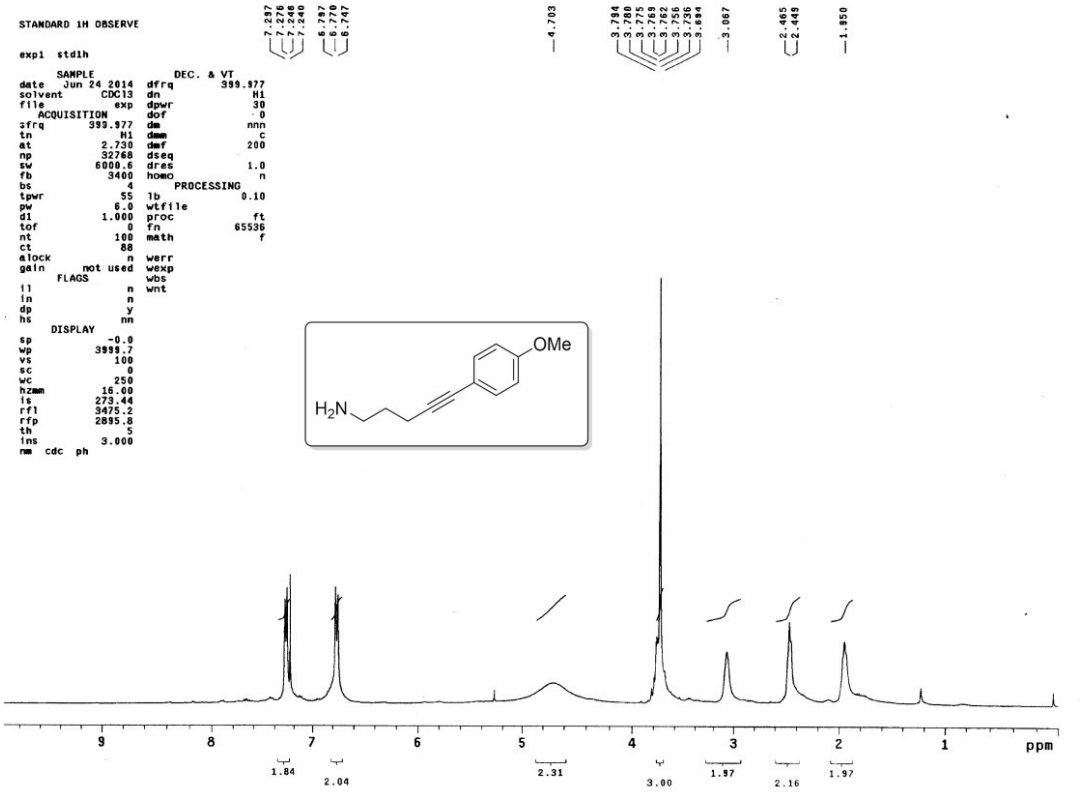


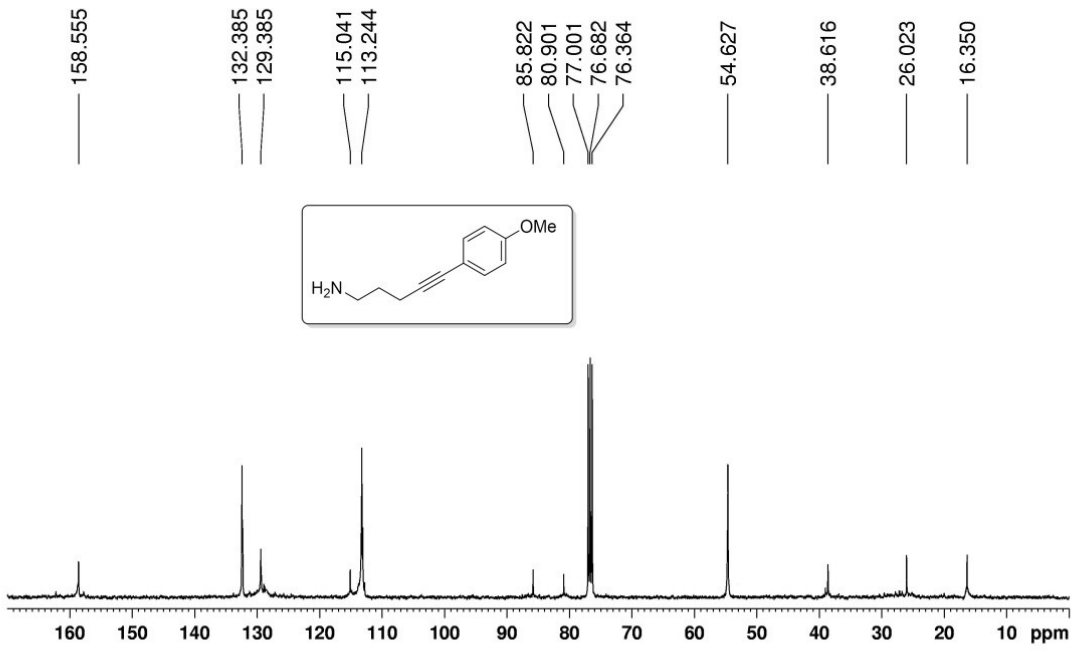


^{1}H and ^{13}C NMR spectra of compound **2e**

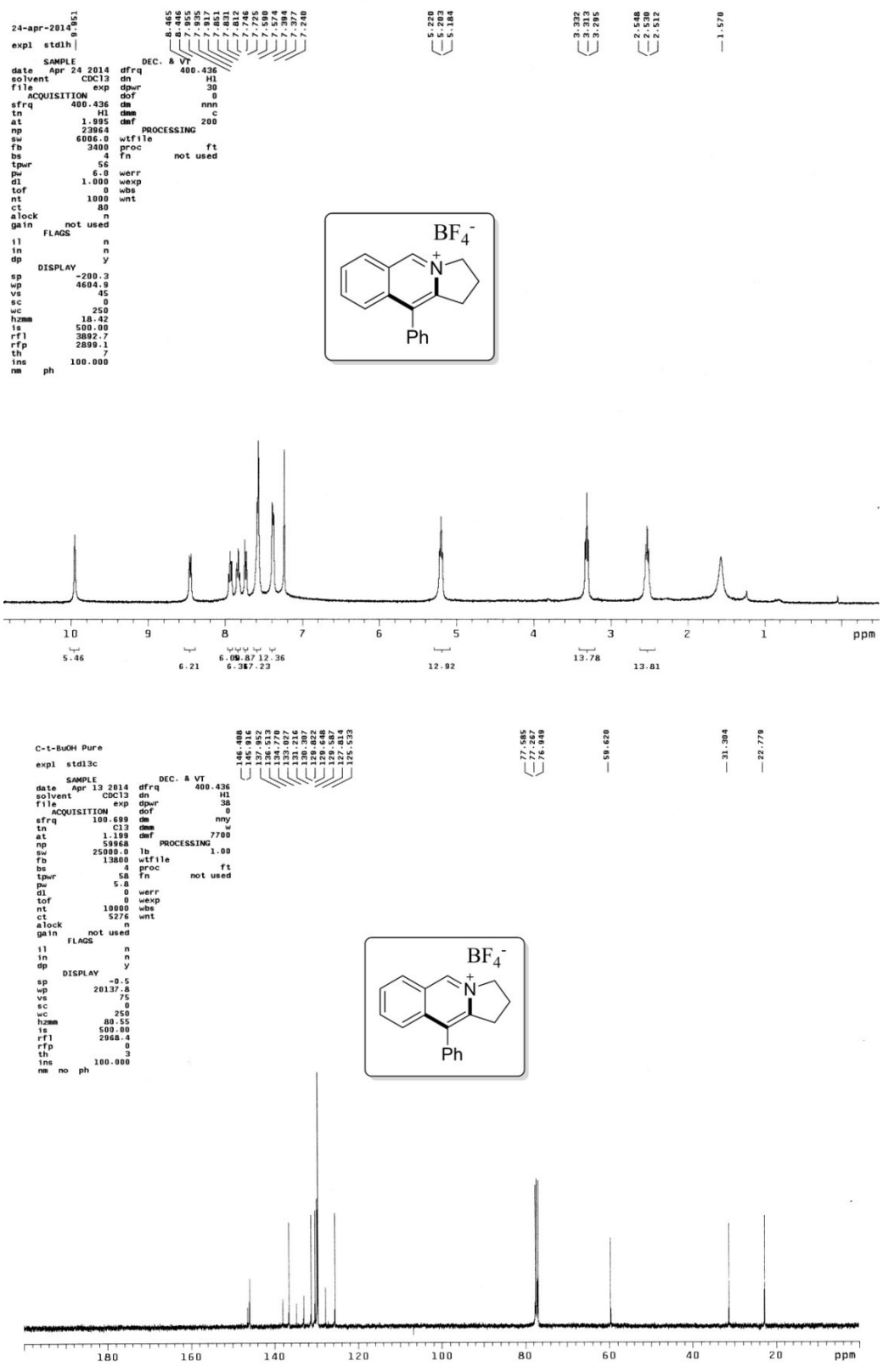


^{1}H and ^{13}C NMR spectra of compound **2g**

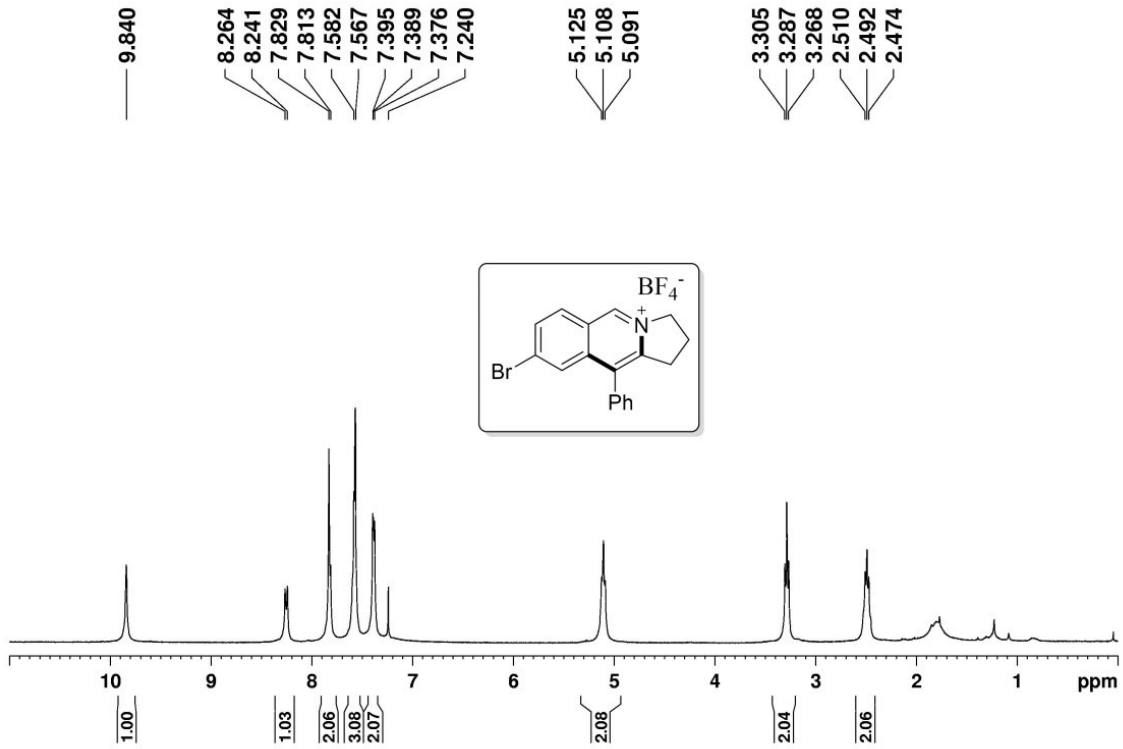


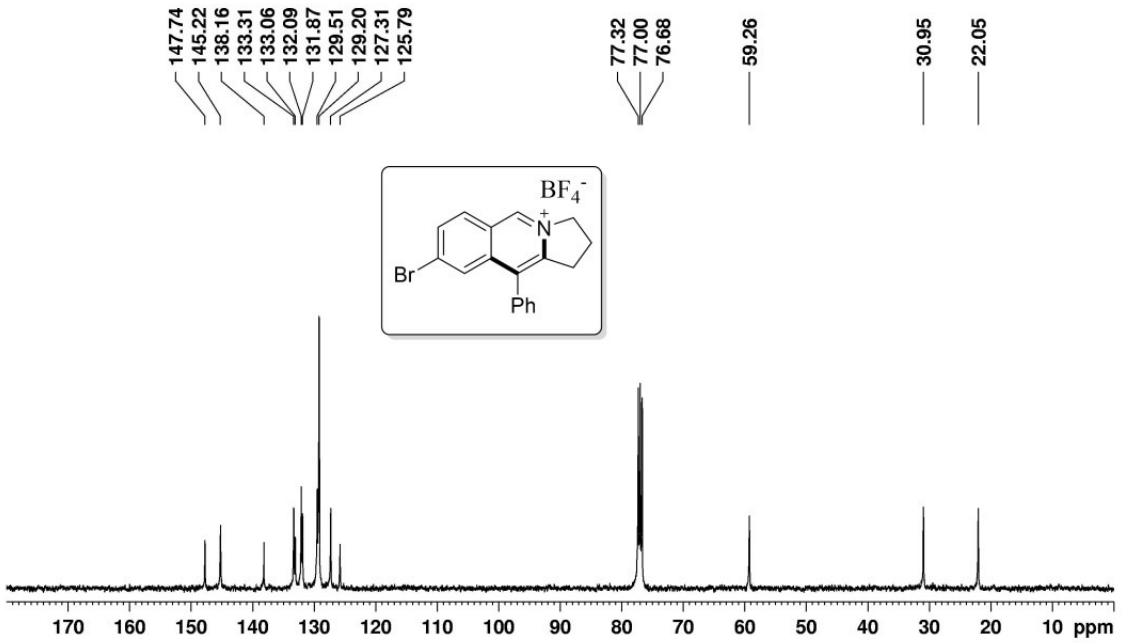


^{1}H and ^{13}C NMR spectra of compound **3aa.**

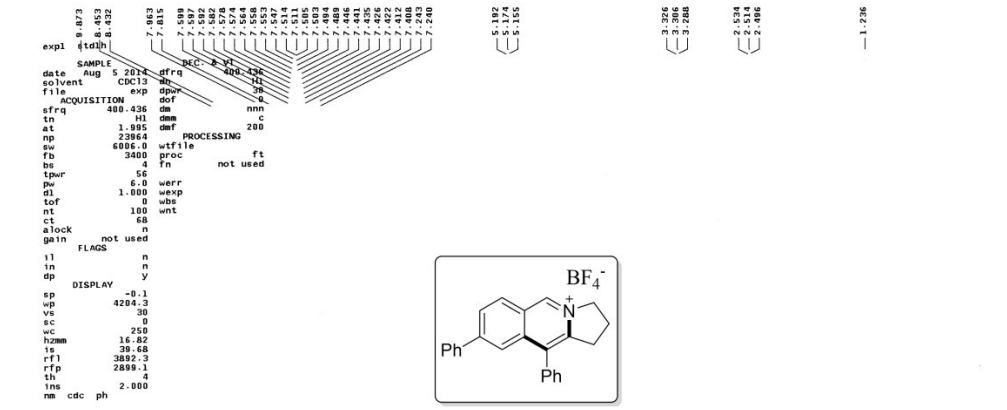


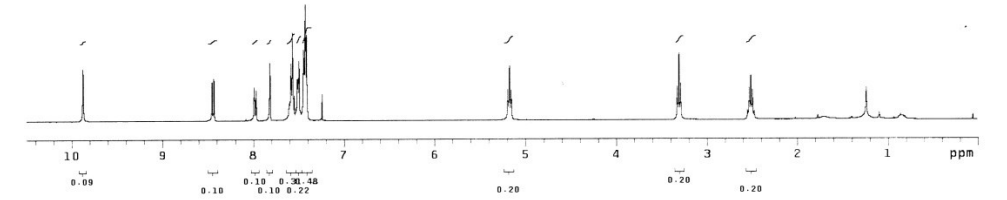
^{1}H and ^{13}C NMR spectra of compound **3ba.**

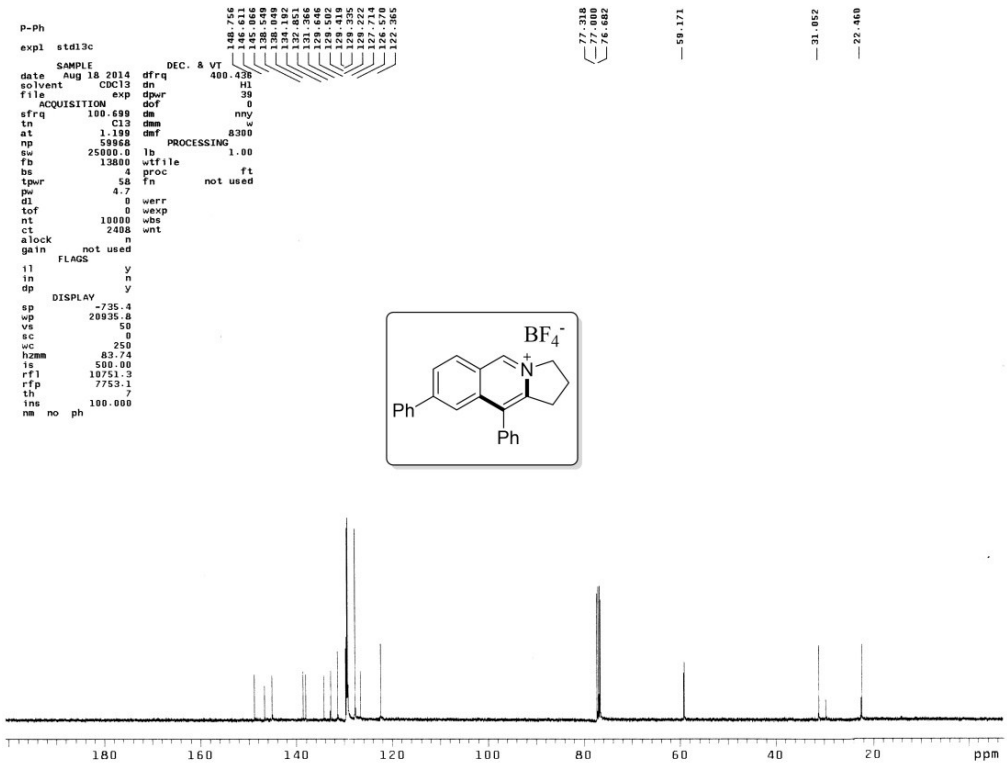




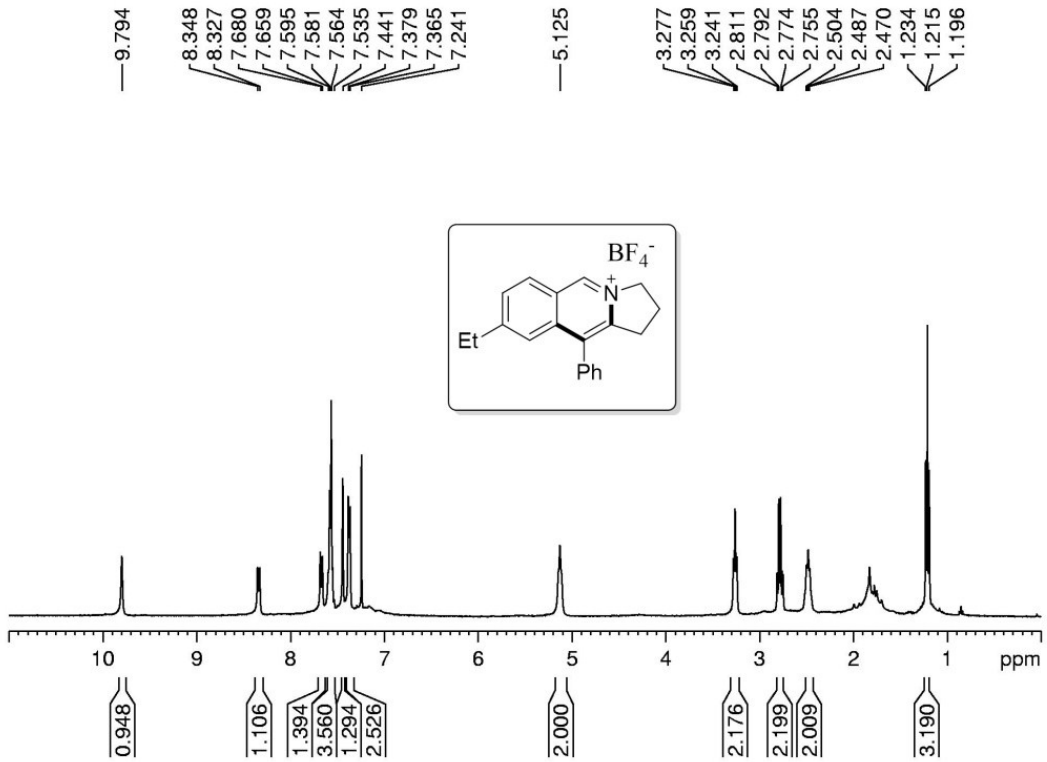
^{1}H and ^{13}C NMR spectra of compound **3ca.**

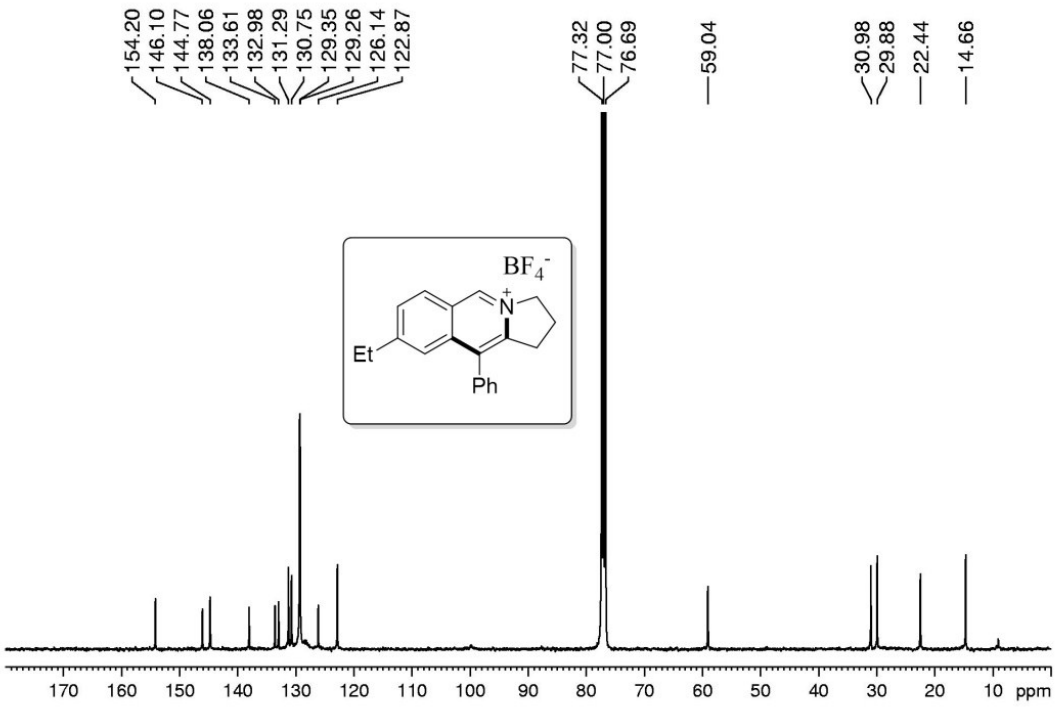




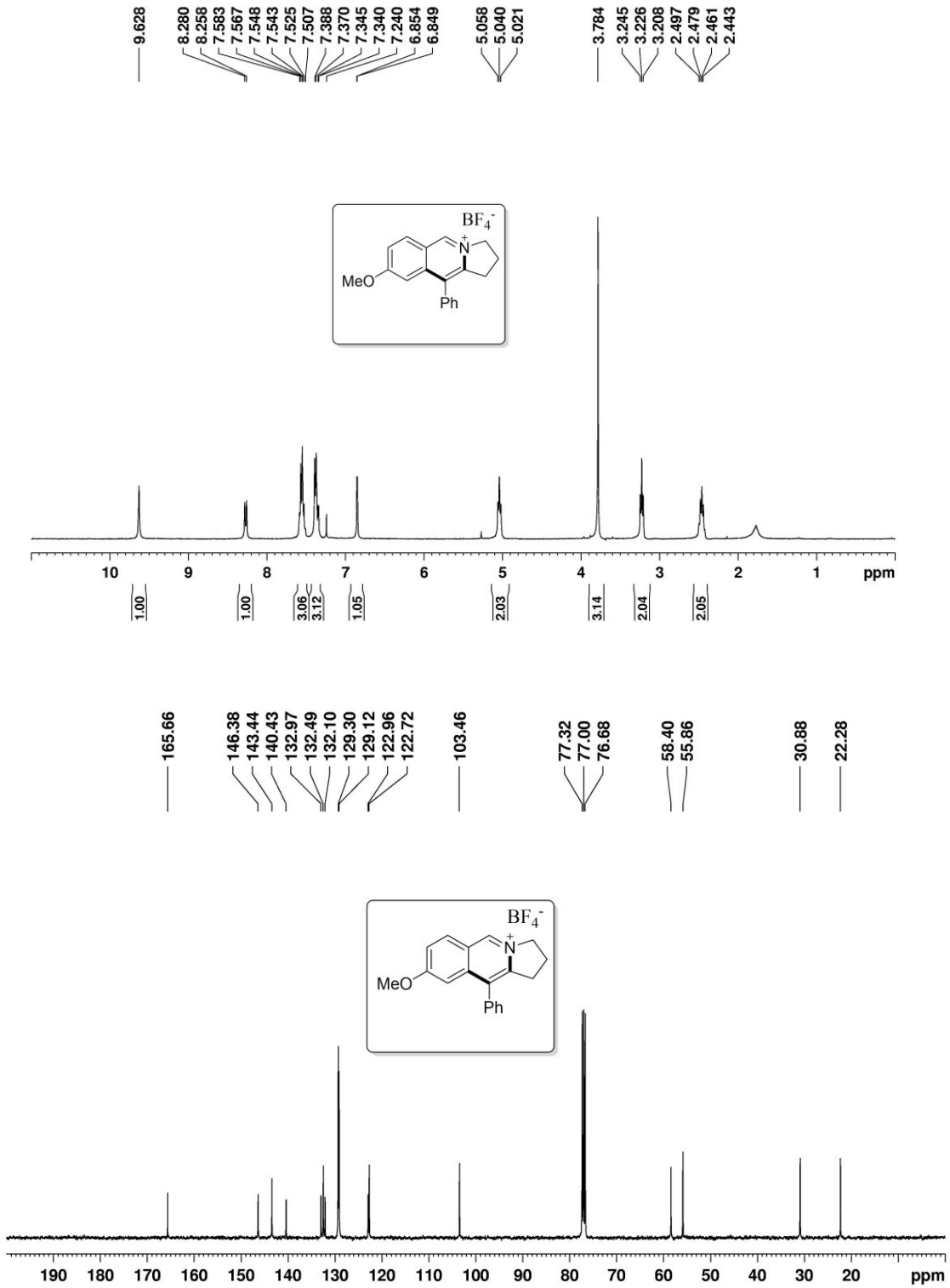


^{1}H and ^{13}C NMR spectra of compound **3da.**

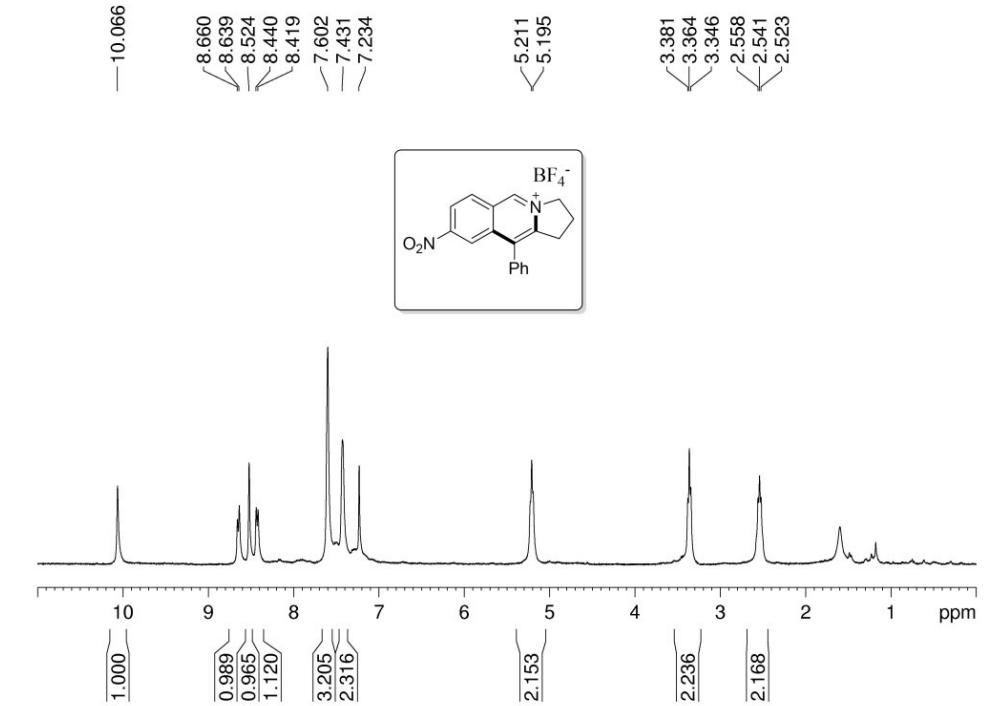


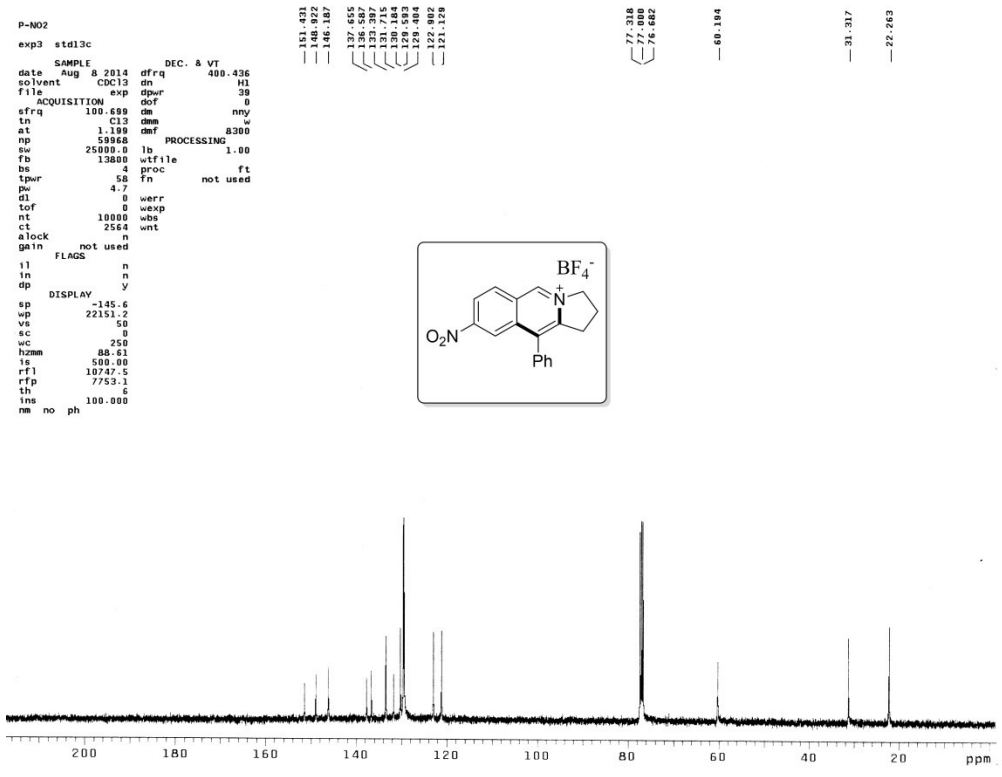


^{1}H and ^{13}C NMR spectra of compound **3ea.**

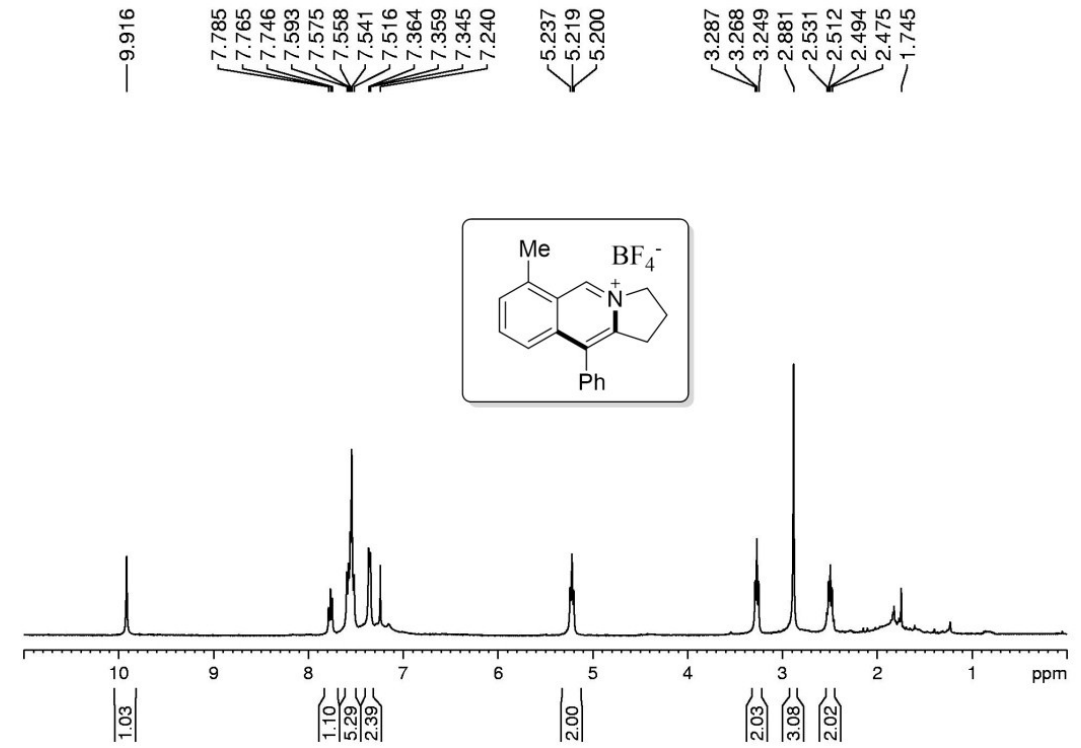


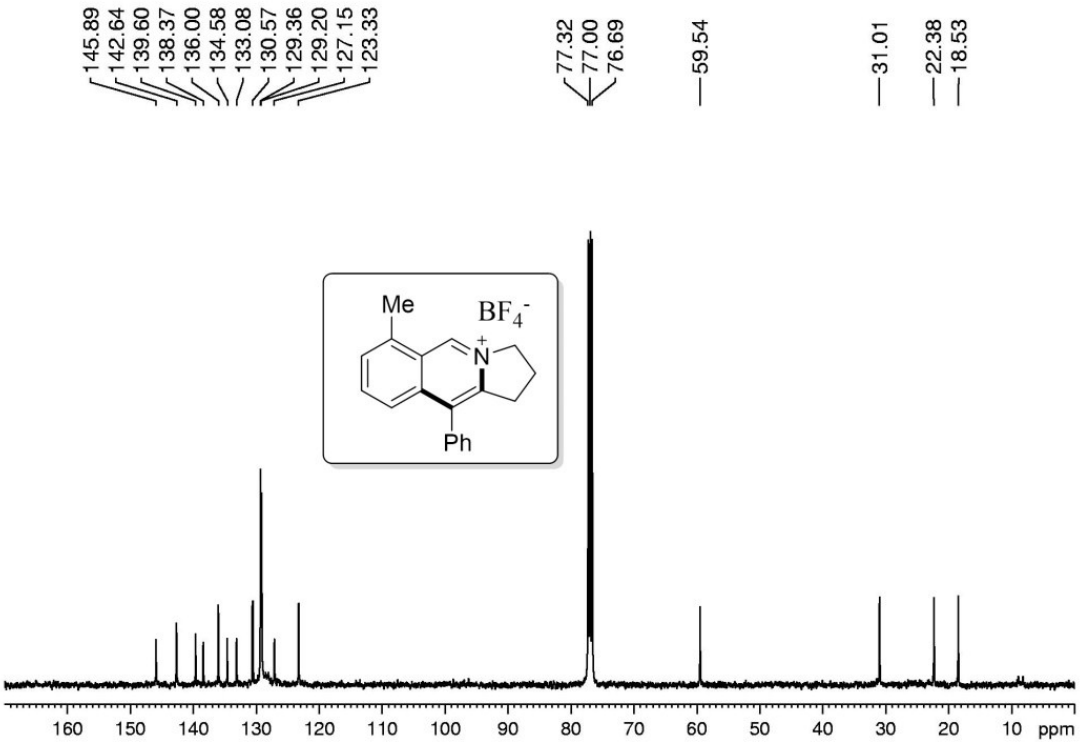
^{1}H and ^{13}C NMR spectra of compound **3fa.**



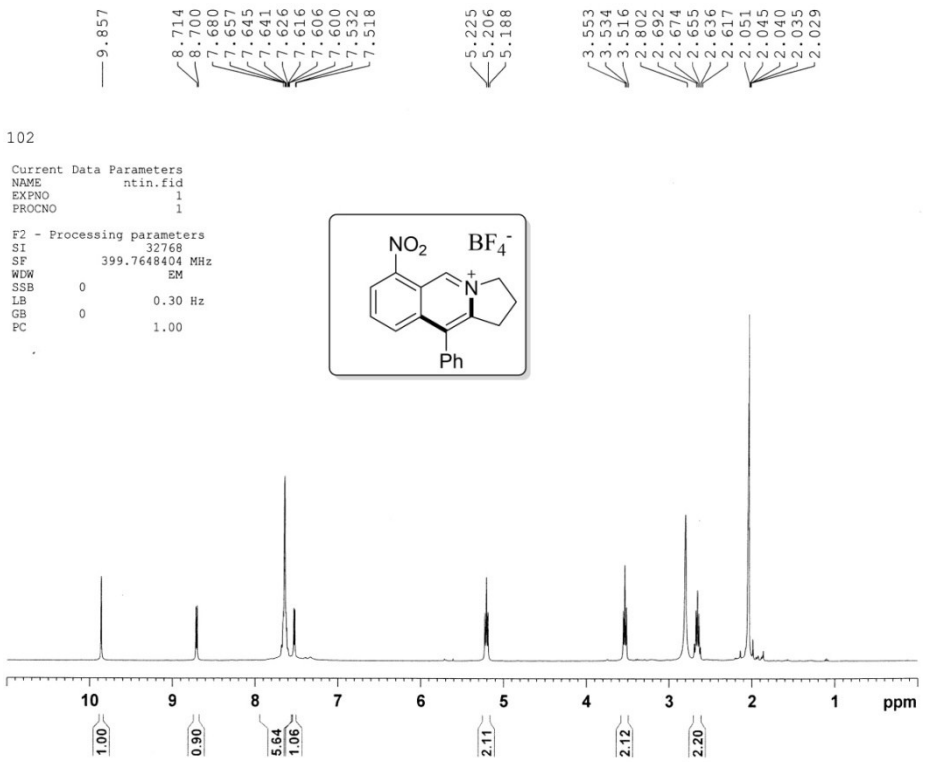


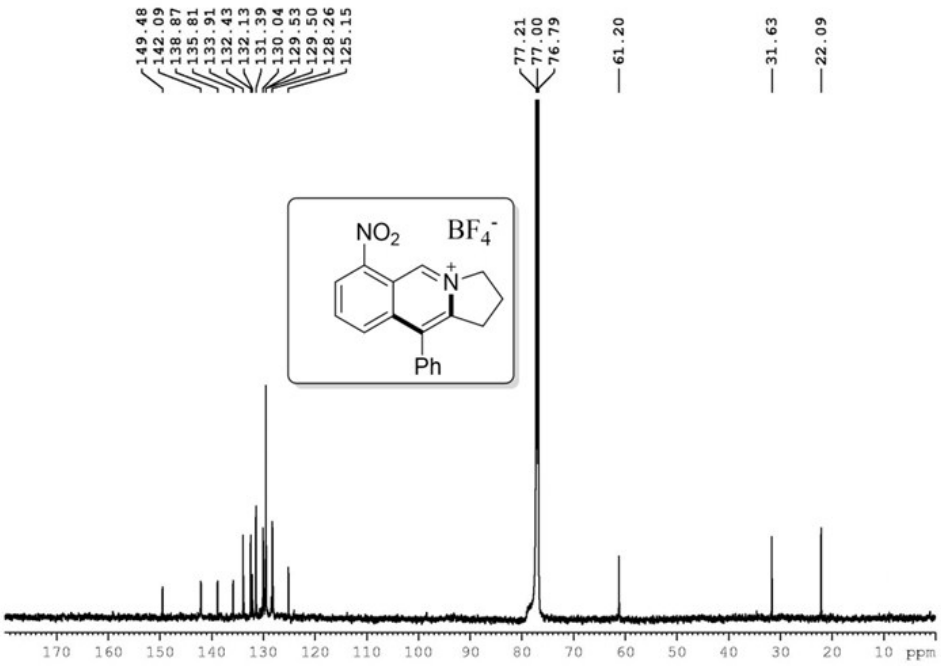
^{1}H and ^{13}C NMR spectra of compound **3ga.**



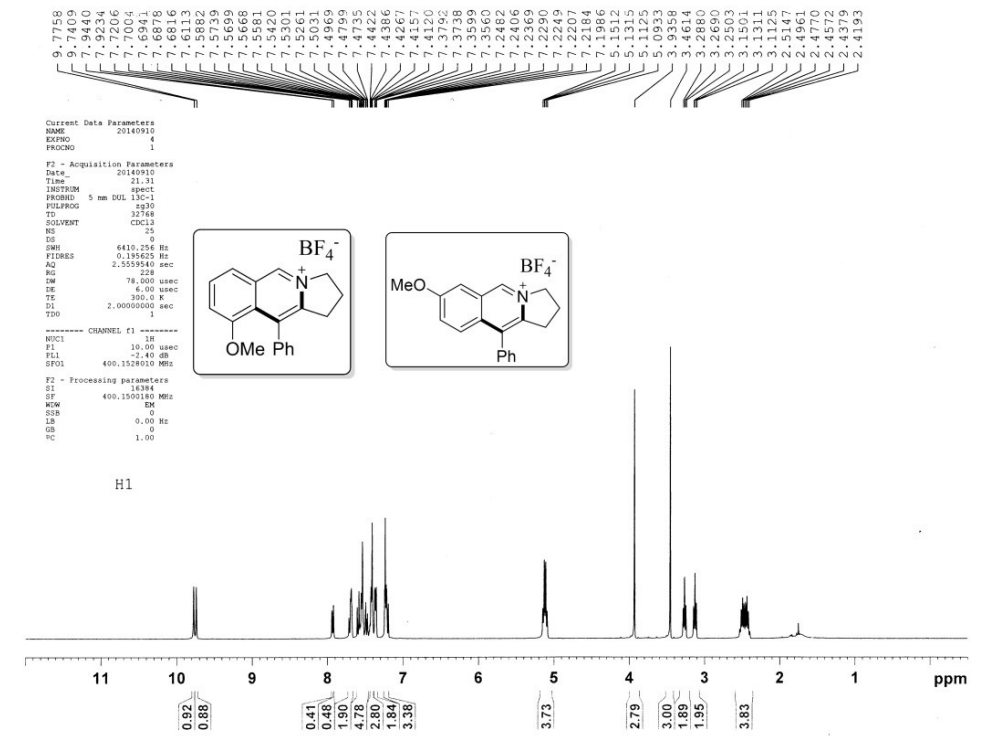


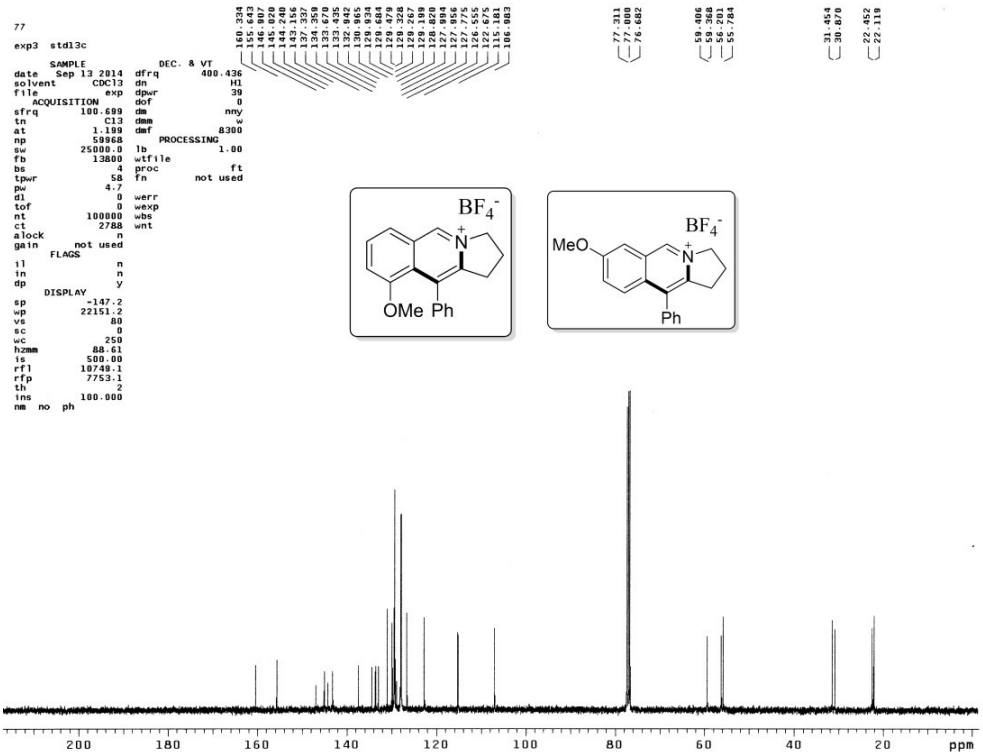
^{1}H and ^{13}C NMR spectra of compound **3ha.**



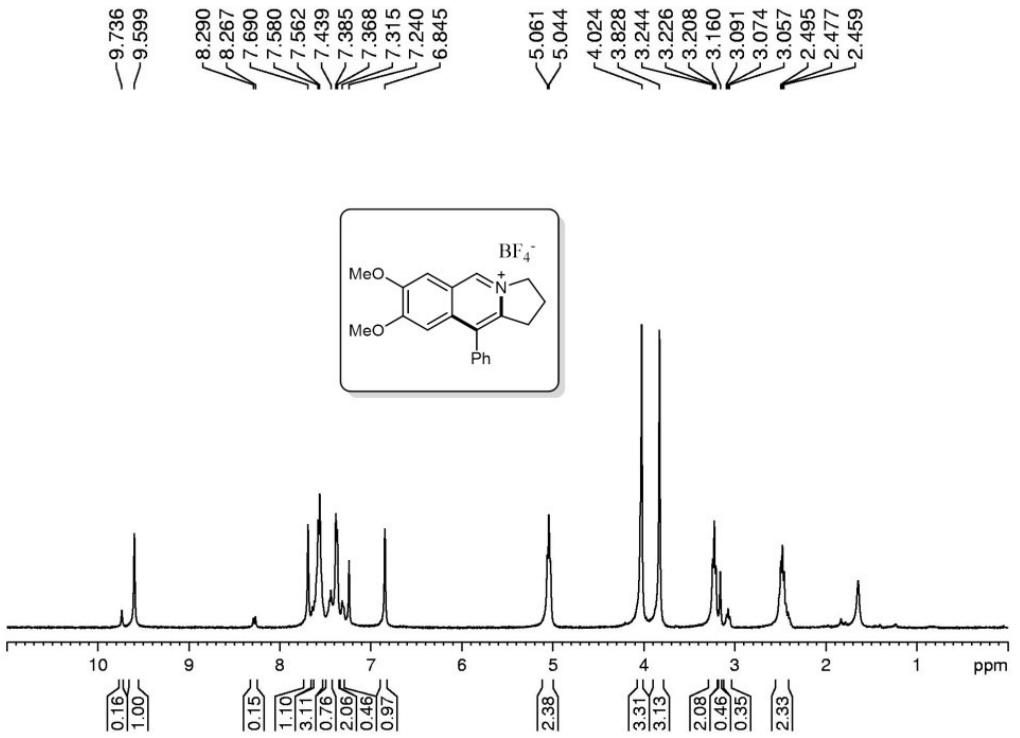


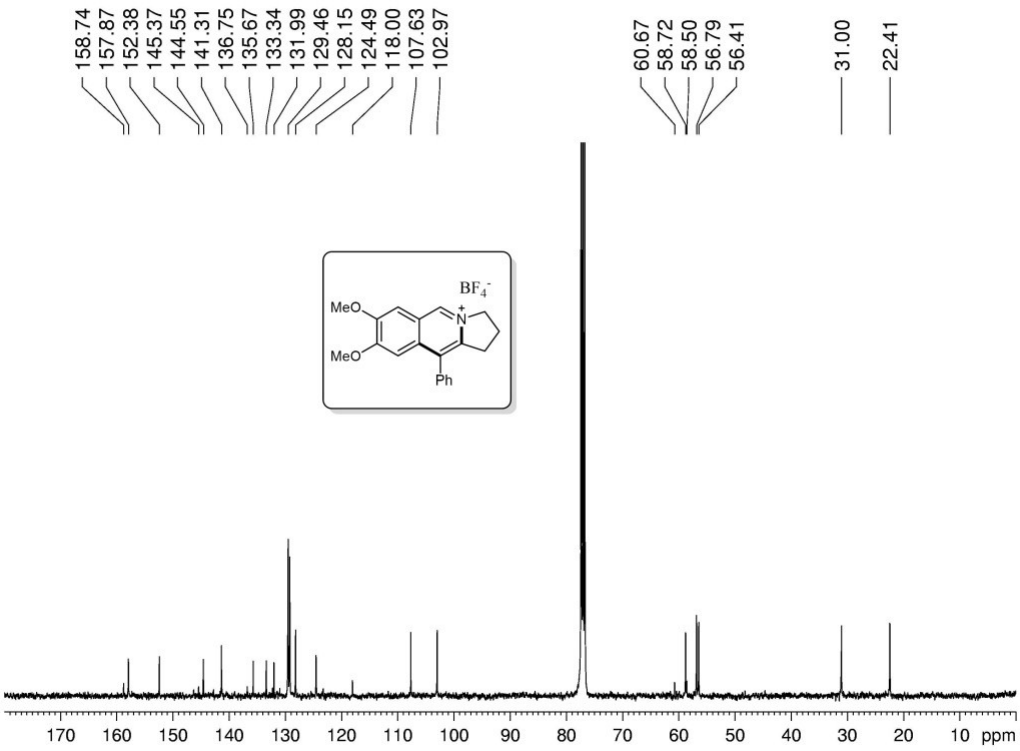
^{1}H and ^{13}C NMR spectra of compound **3ia.**



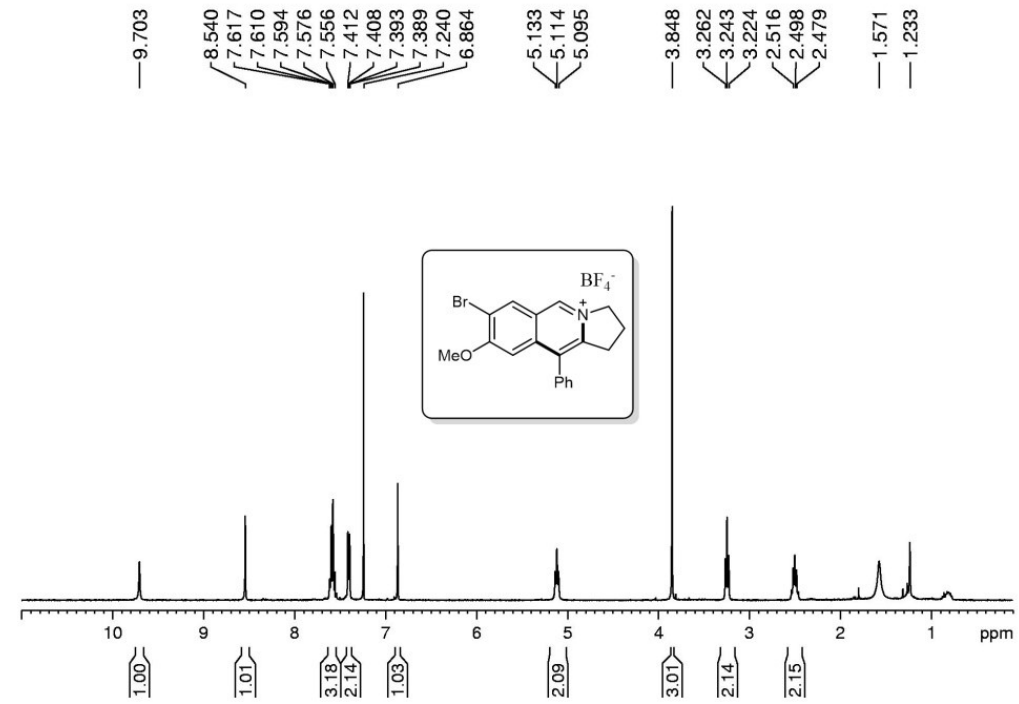


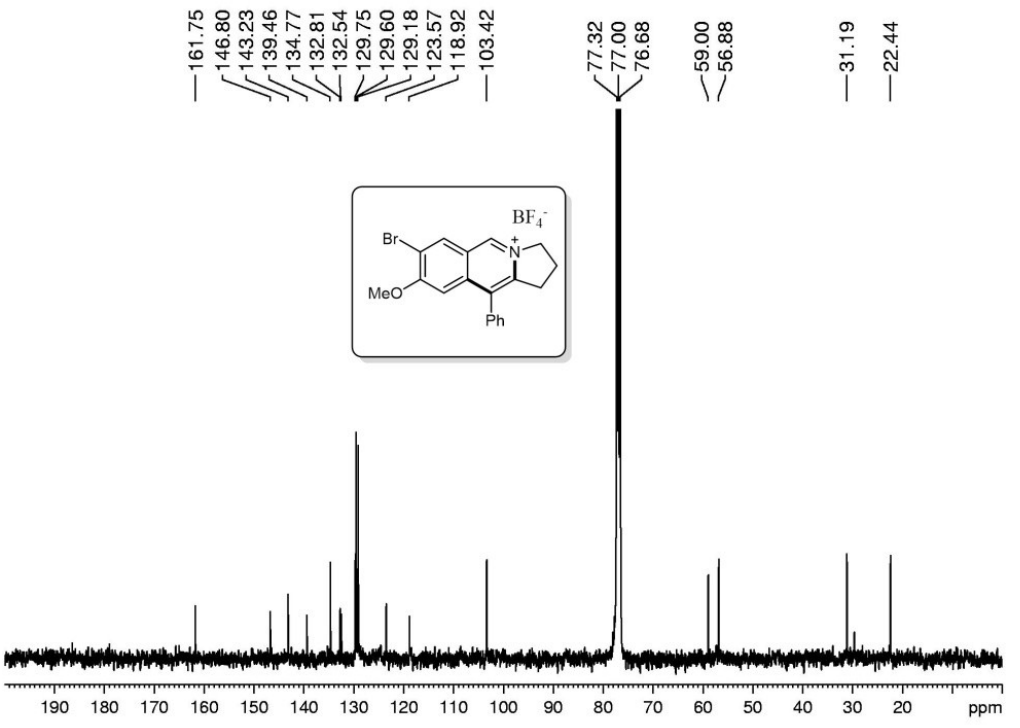
^{1}H and ^{13}C NMR spectra of compound **3ka.**



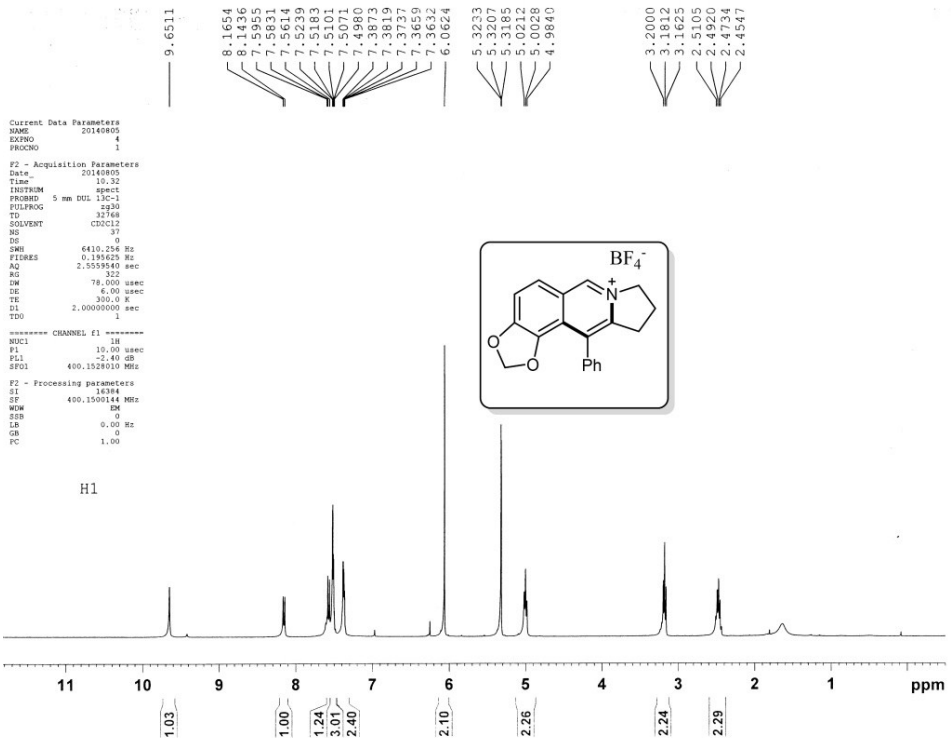


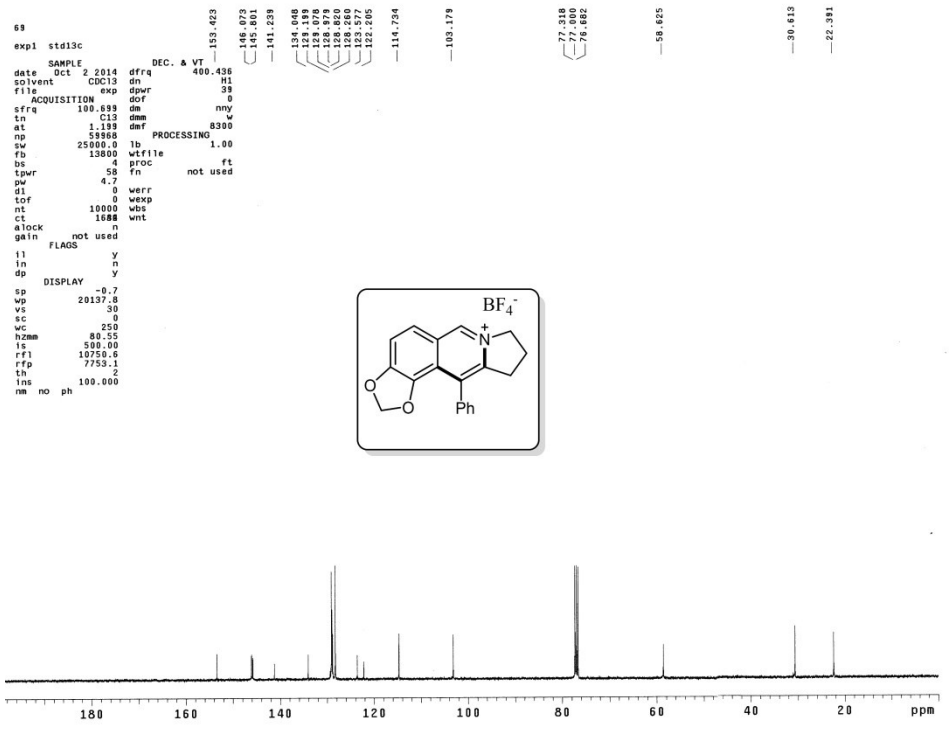
^{1}H and ^{13}C NMR spectra of compound **3ja.**



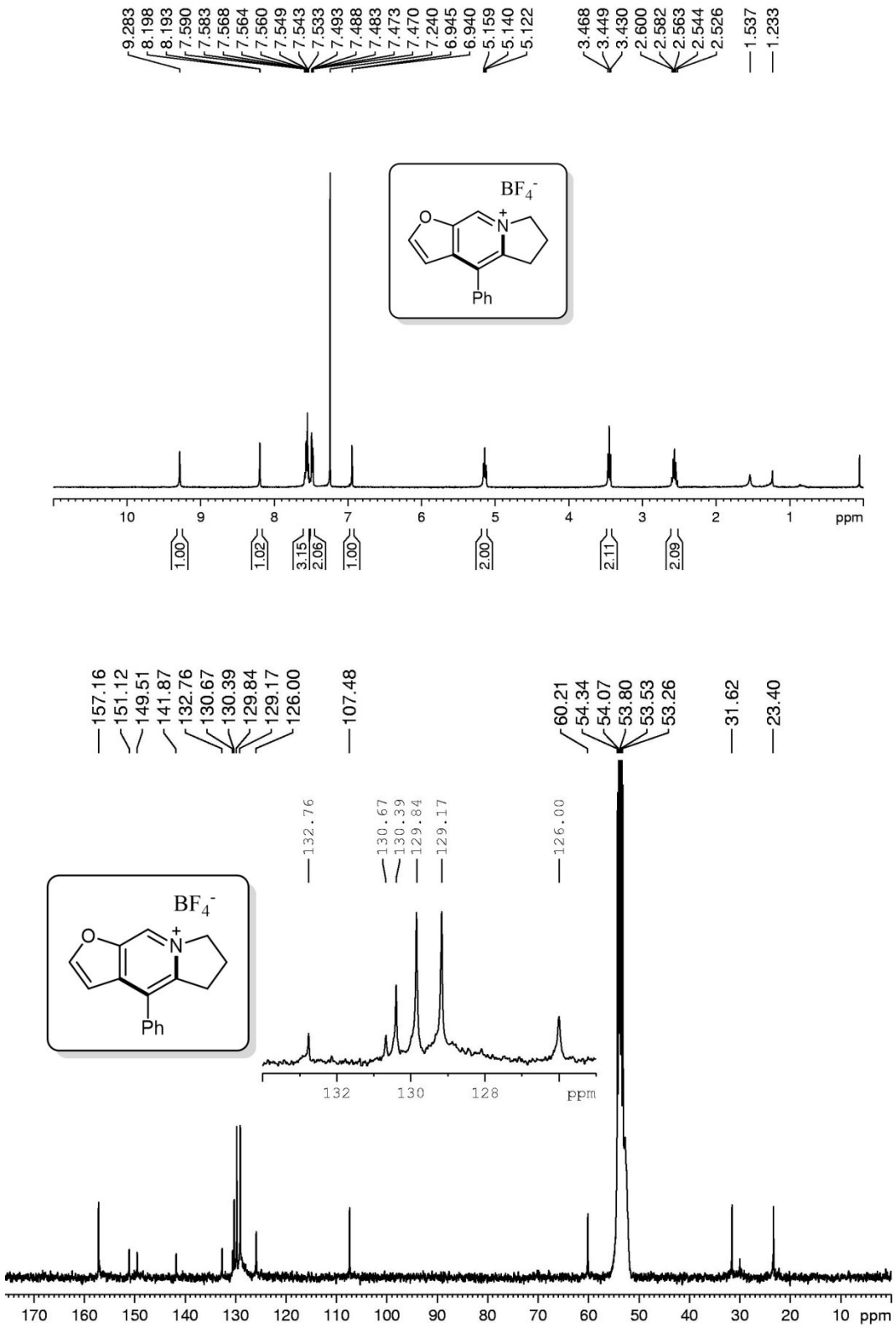


^{1}H and ^{13}C NMR spectra of compound **3la.**

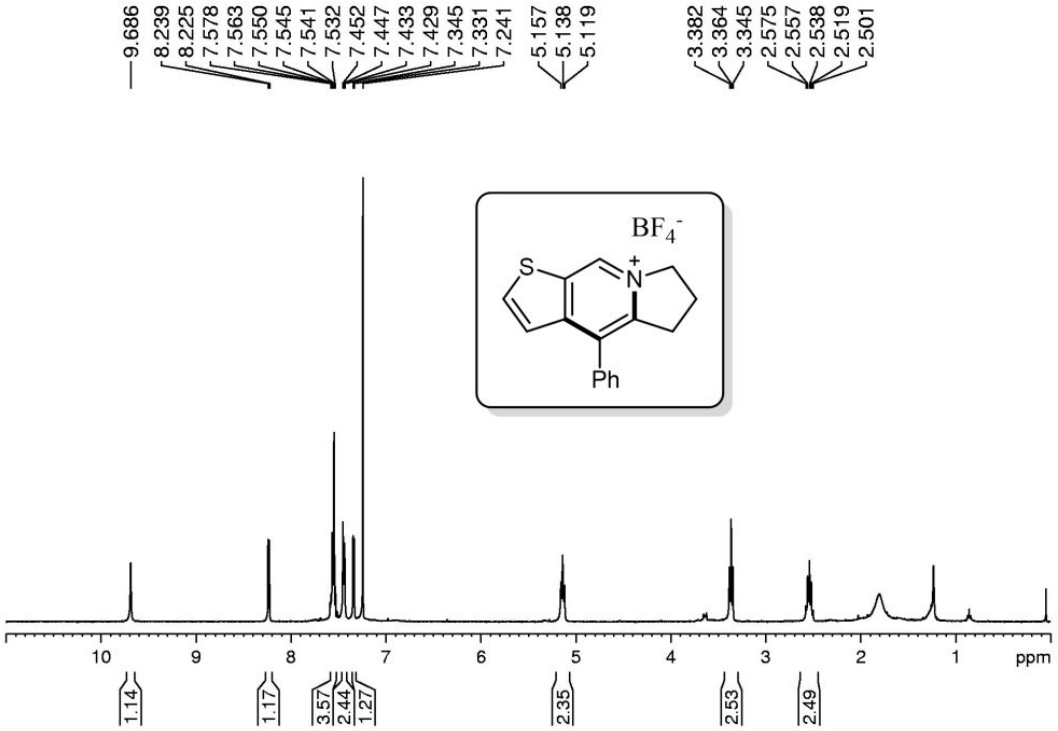


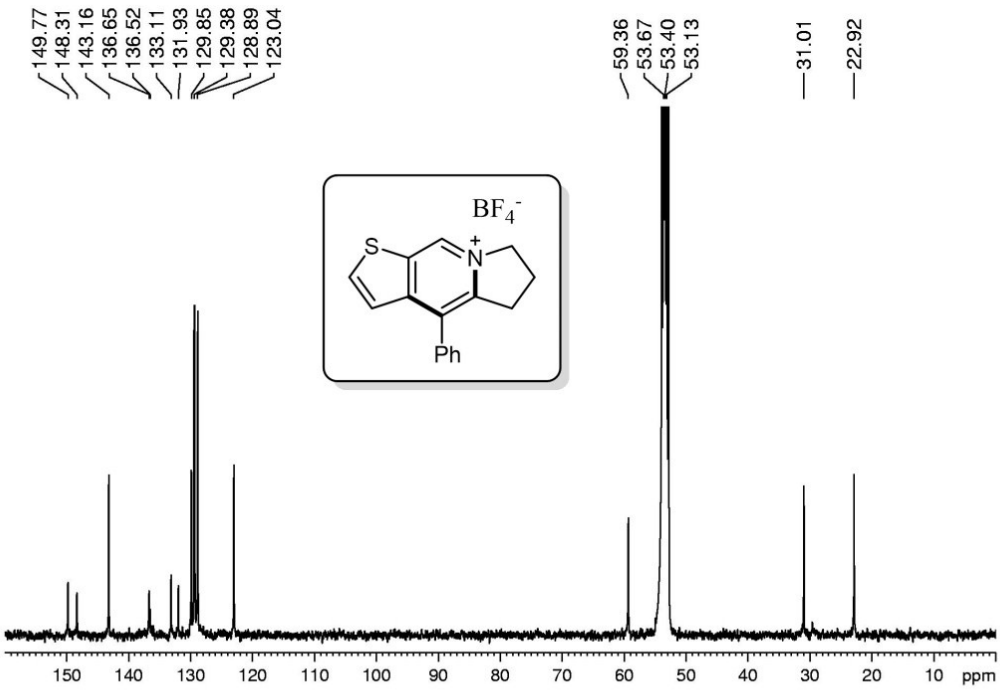


^{1}H and ^{13}C NMR spectra of compound **3ma.**

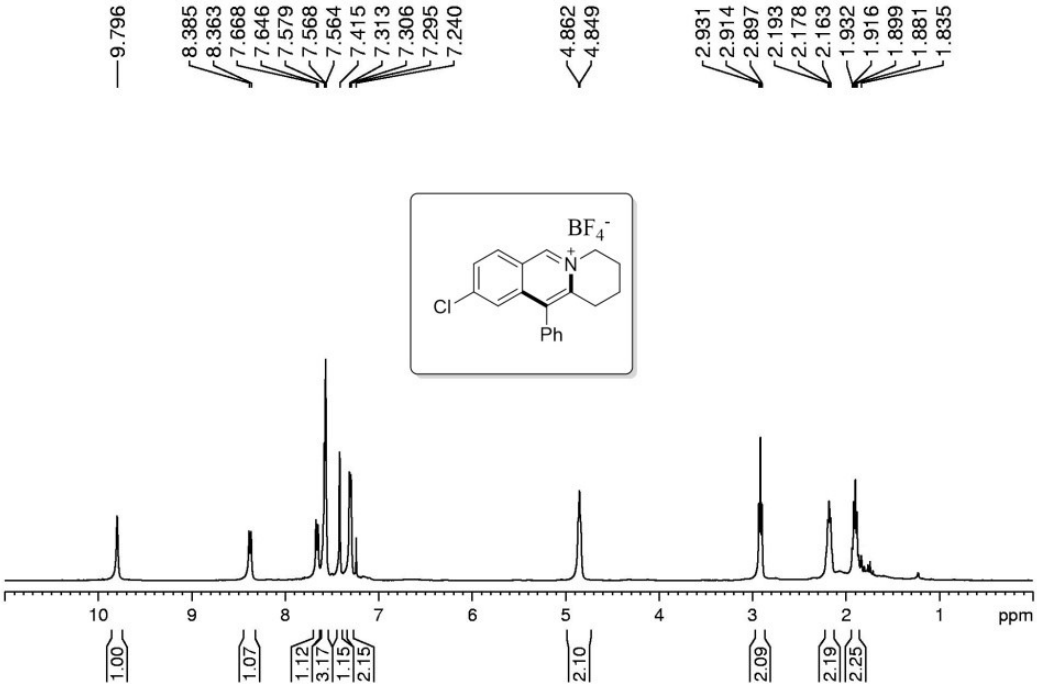


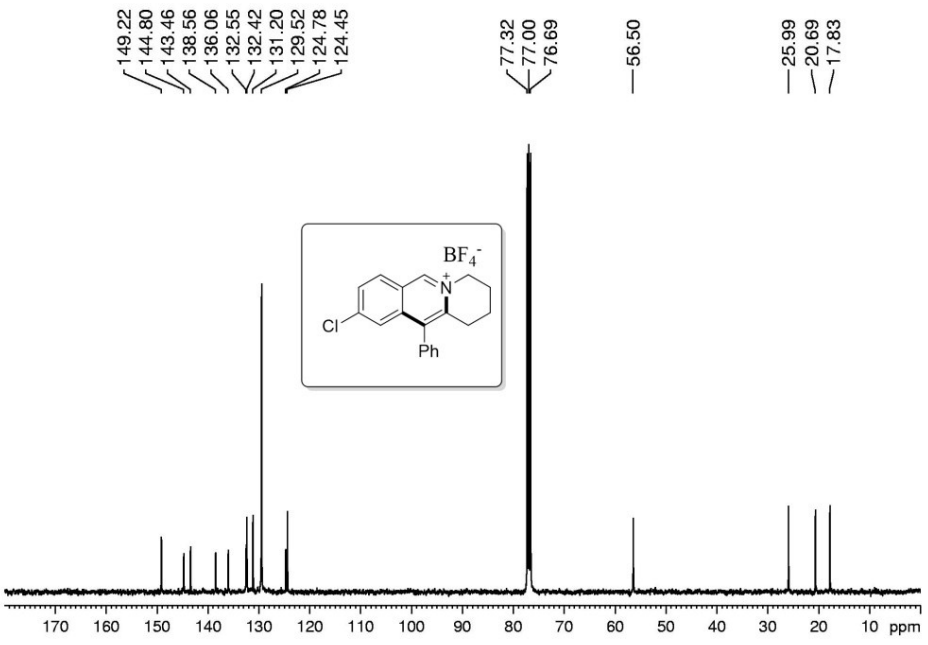
^{1}H and ^{13}C NMR spectra of compound **3na.**



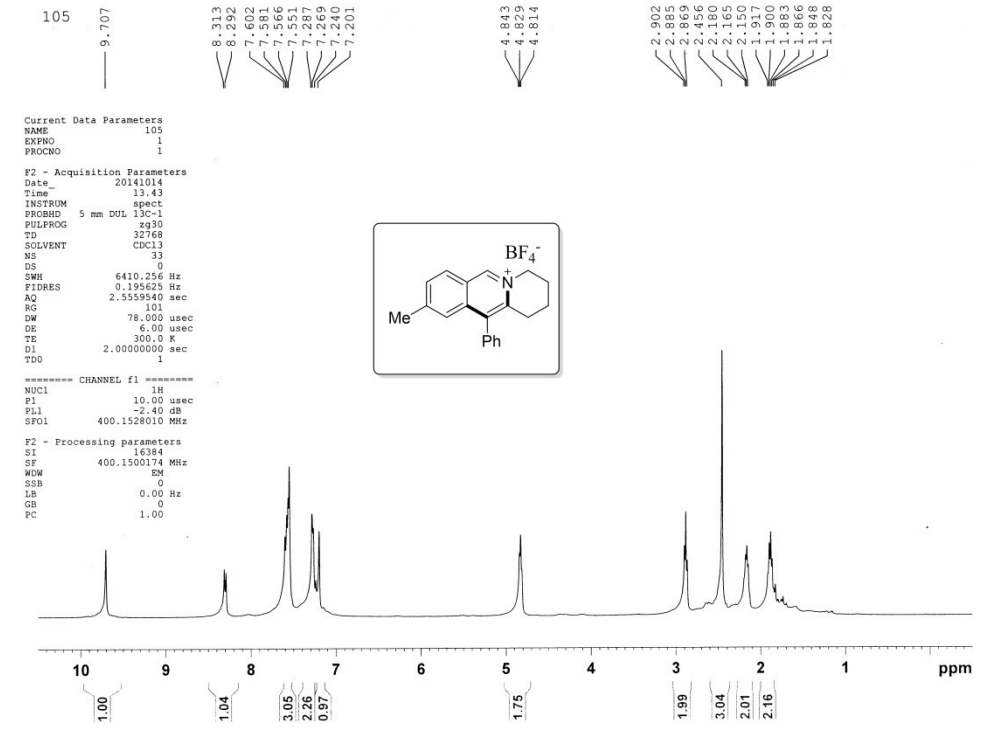


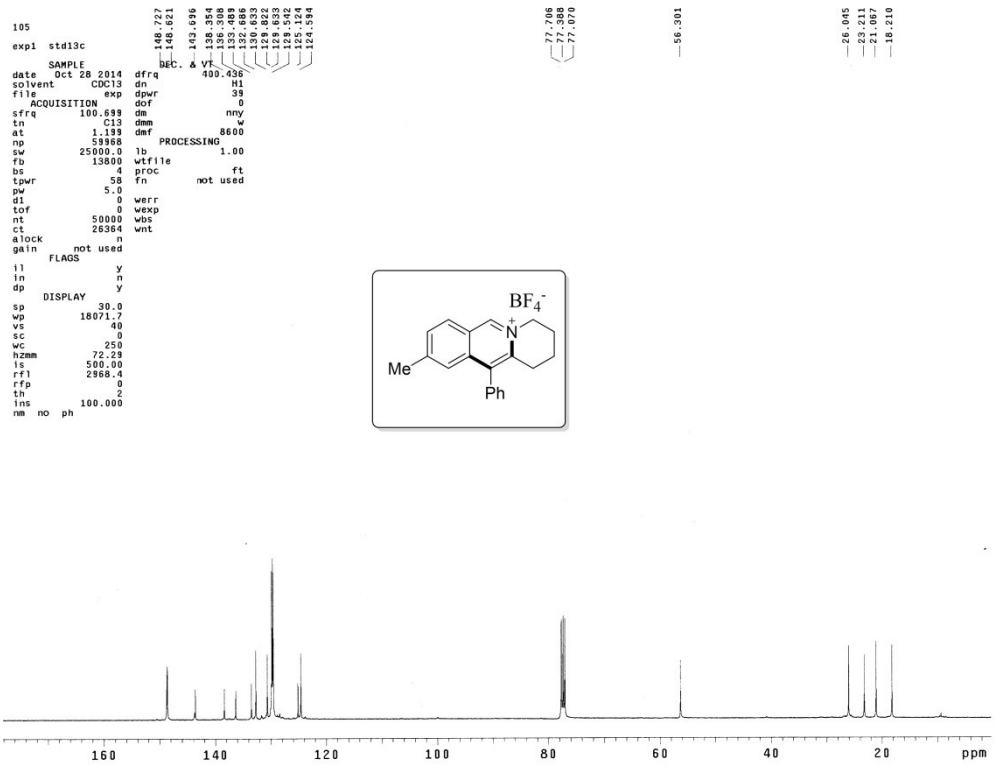
^{1}H and ^{13}C NMR spectra of compound **3ob.**



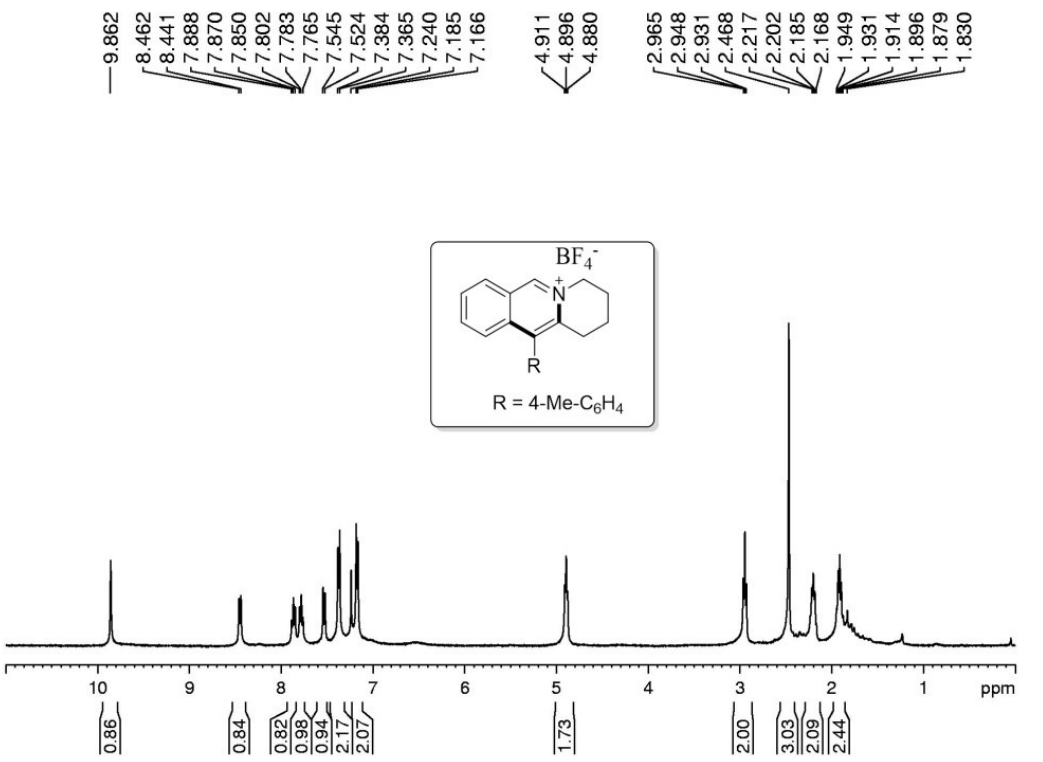


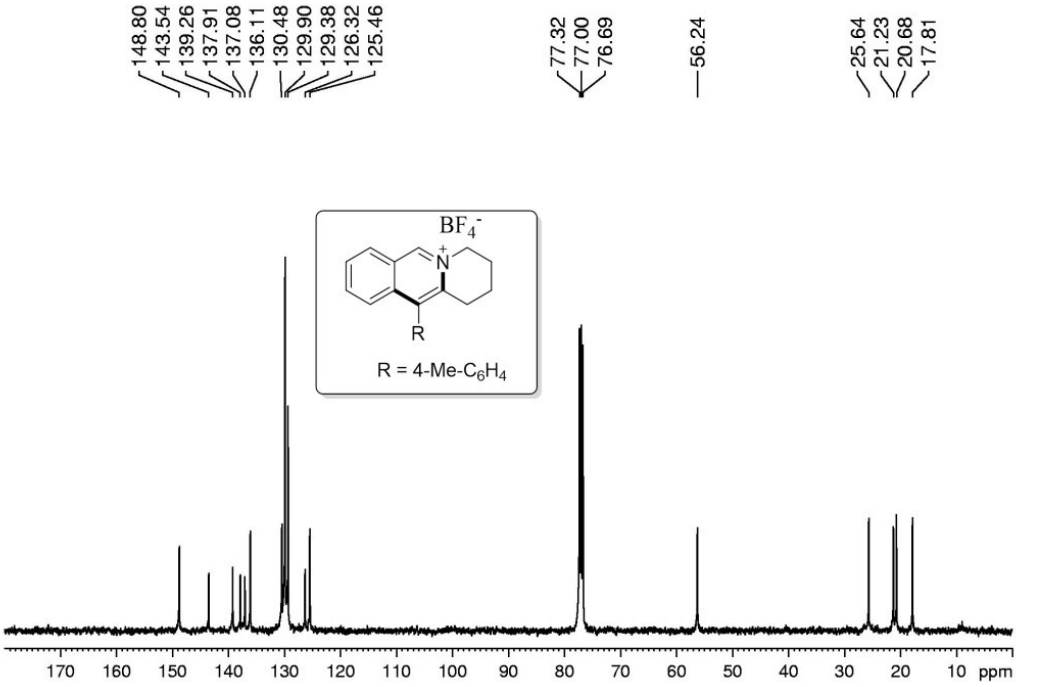
^{1}H and ^{13}C NMR spectra of compound **3pb.**



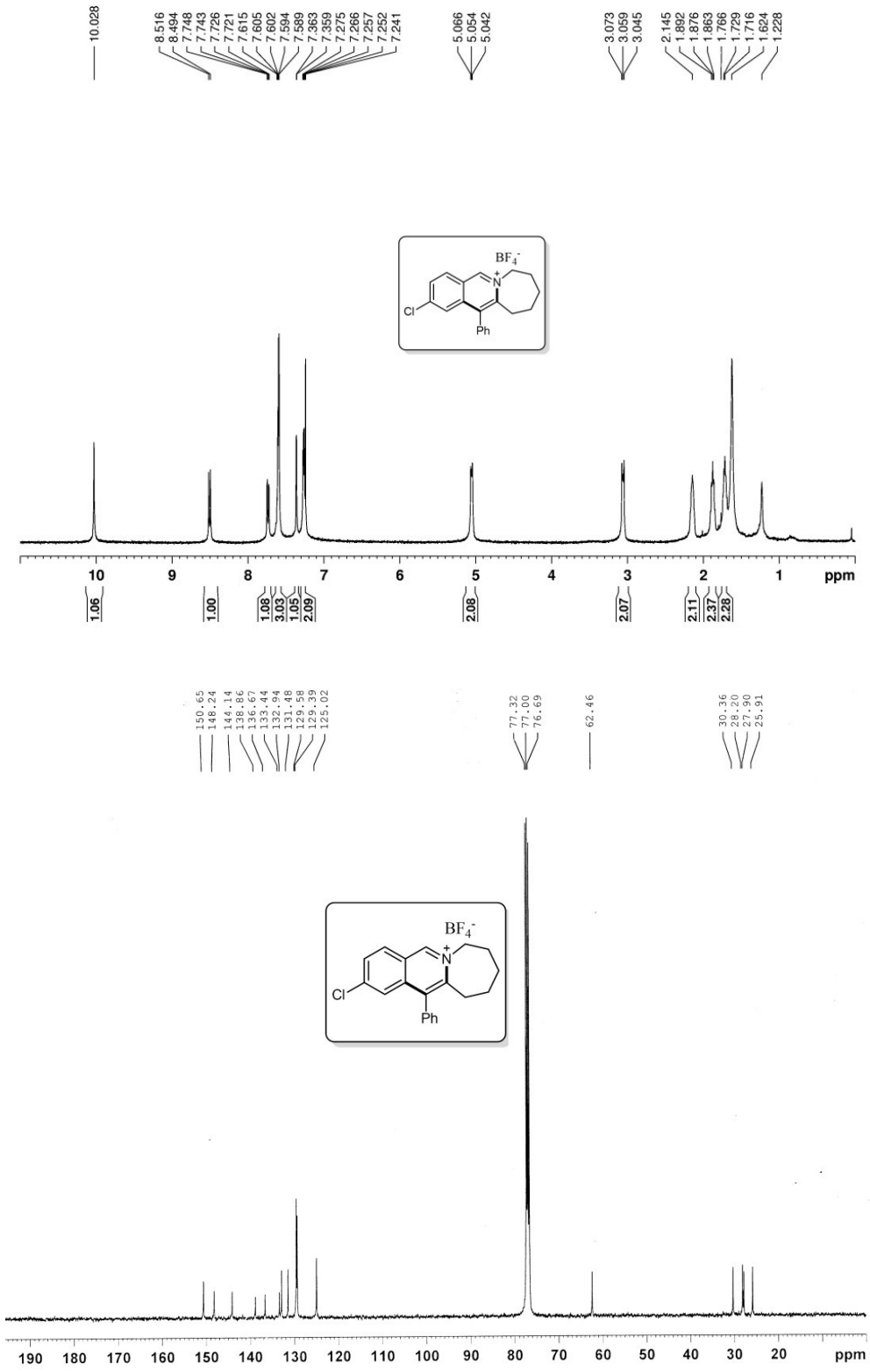


^{1}H and ^{13}C NMR spectra of compound **3ac**

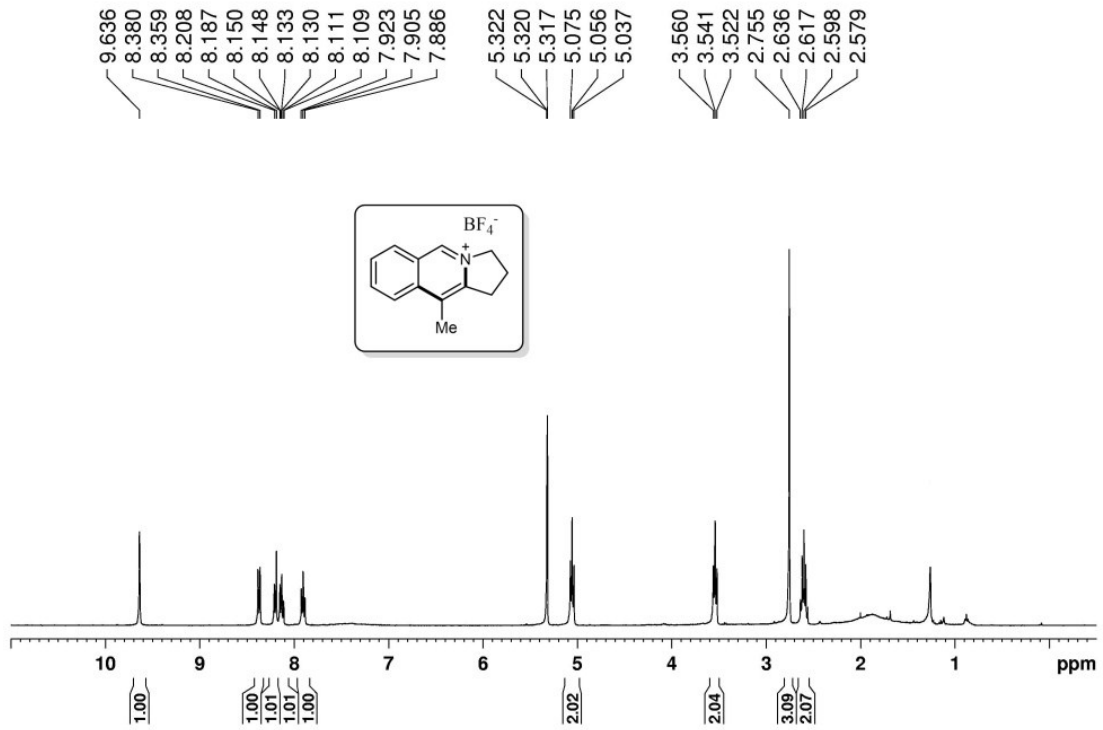


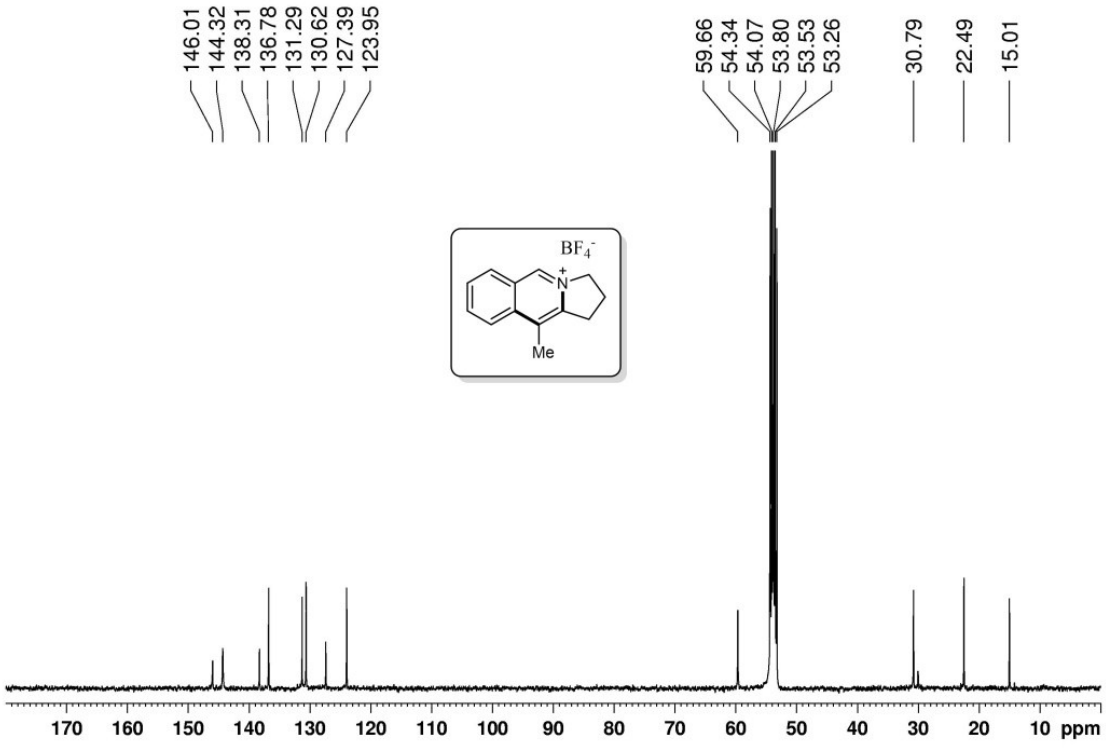


^{1}H and ^{13}C NMR spectra of compound **3od**

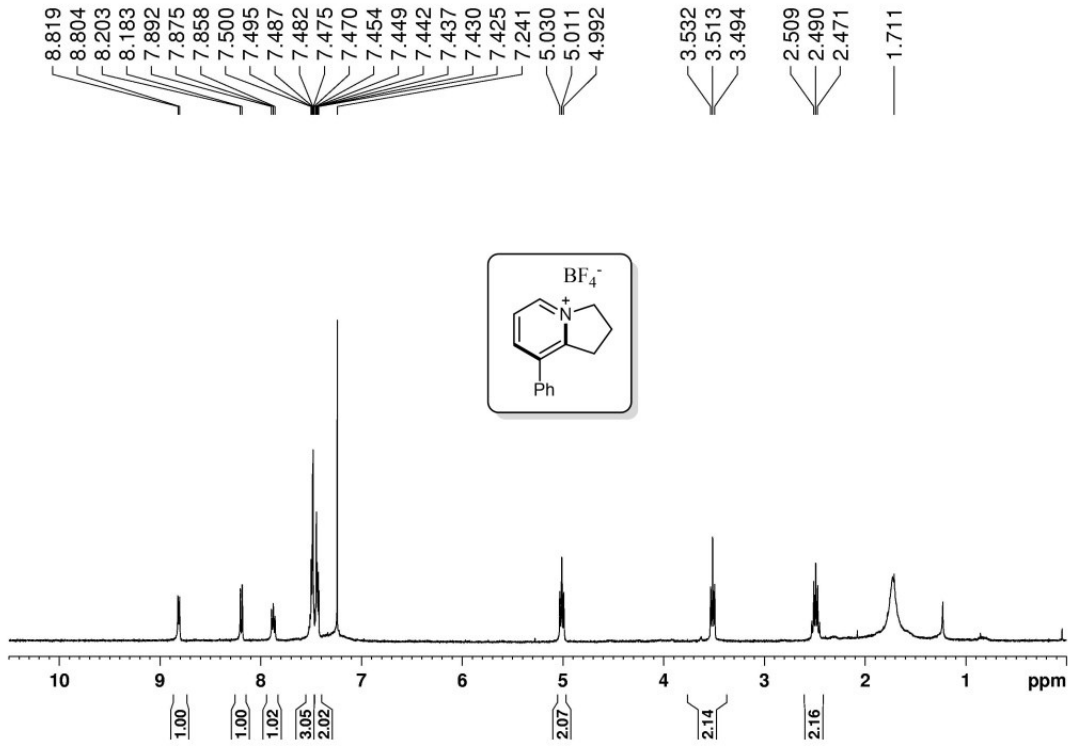


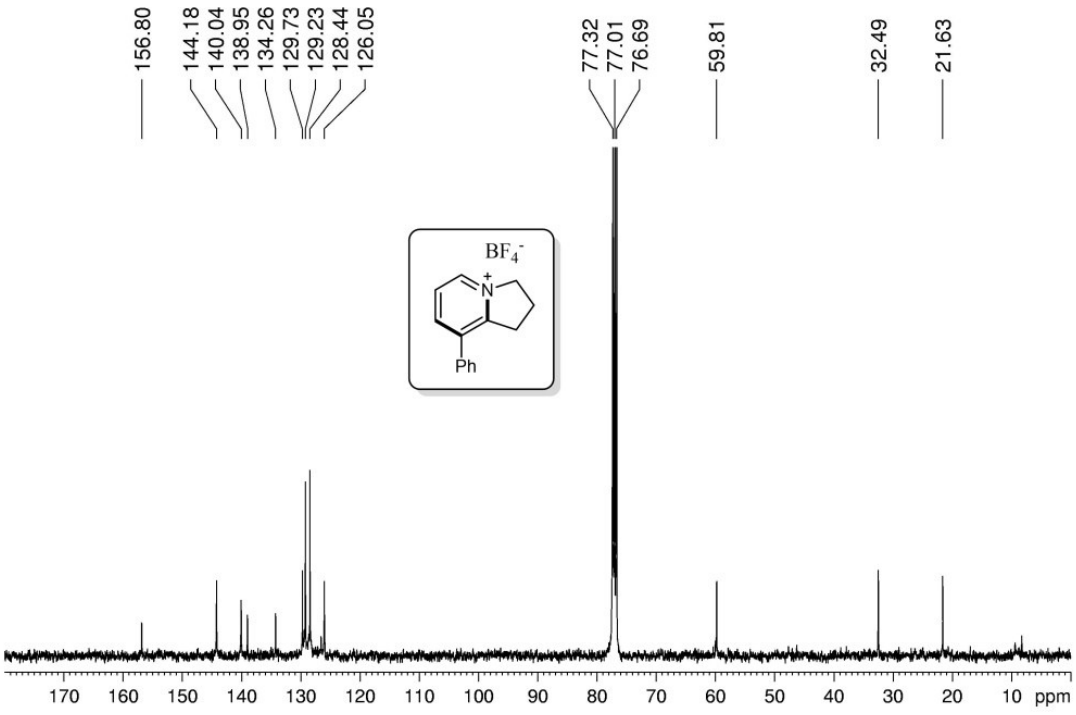
^{1}H and ^{13}C NMR spectra of compound **3af**



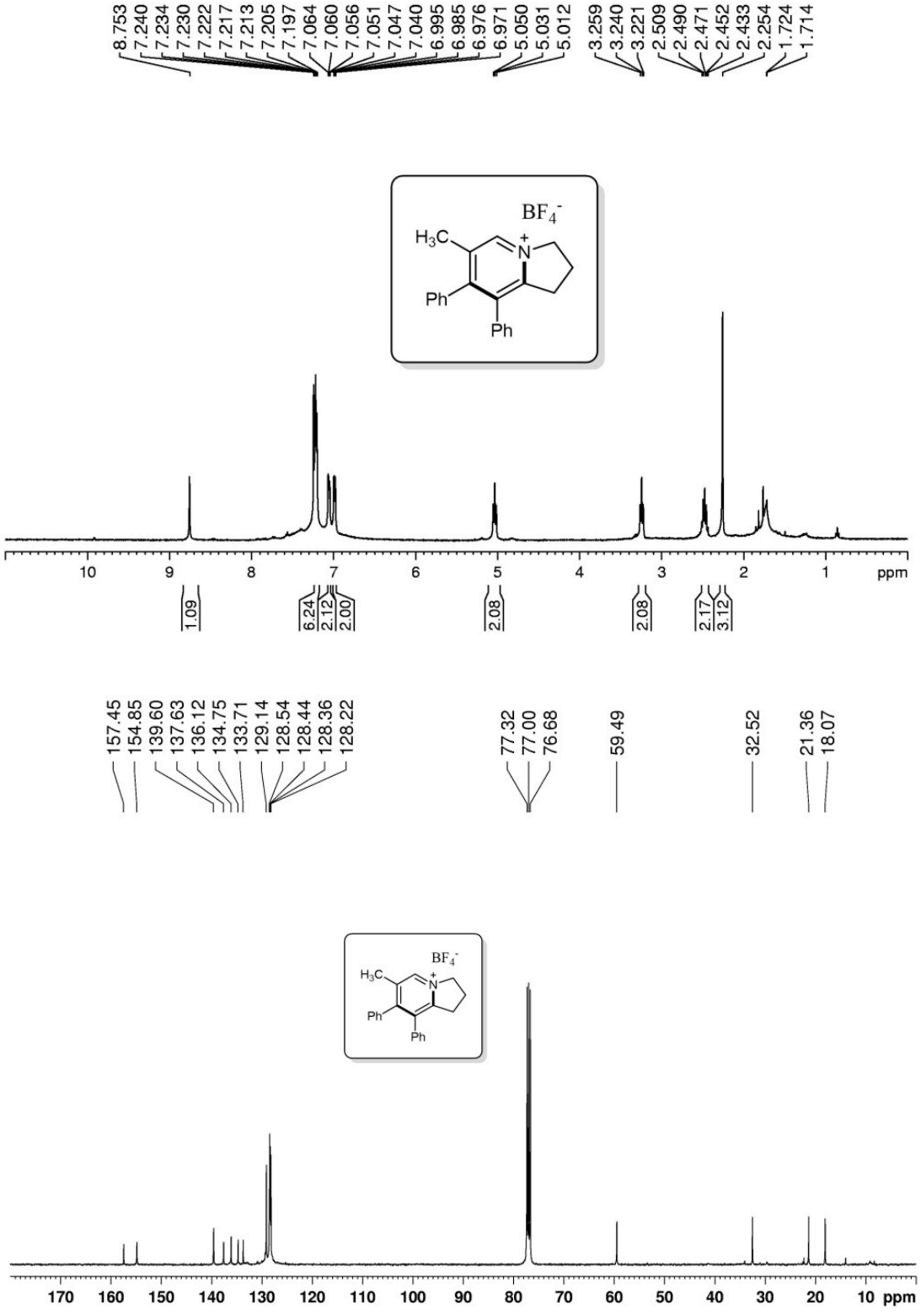


^{1}H and ^{13}C NMR spectra of compound **3qa**

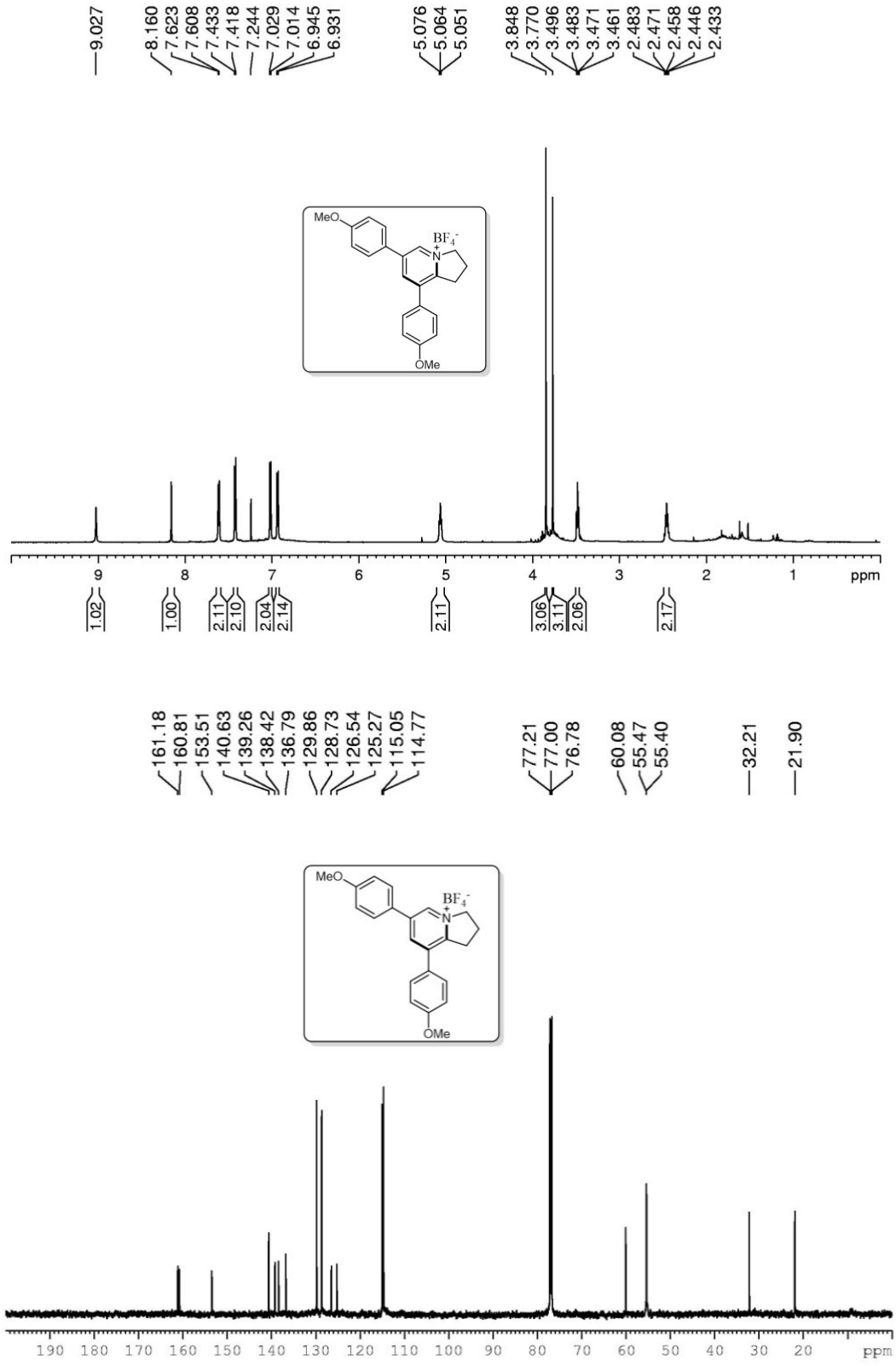




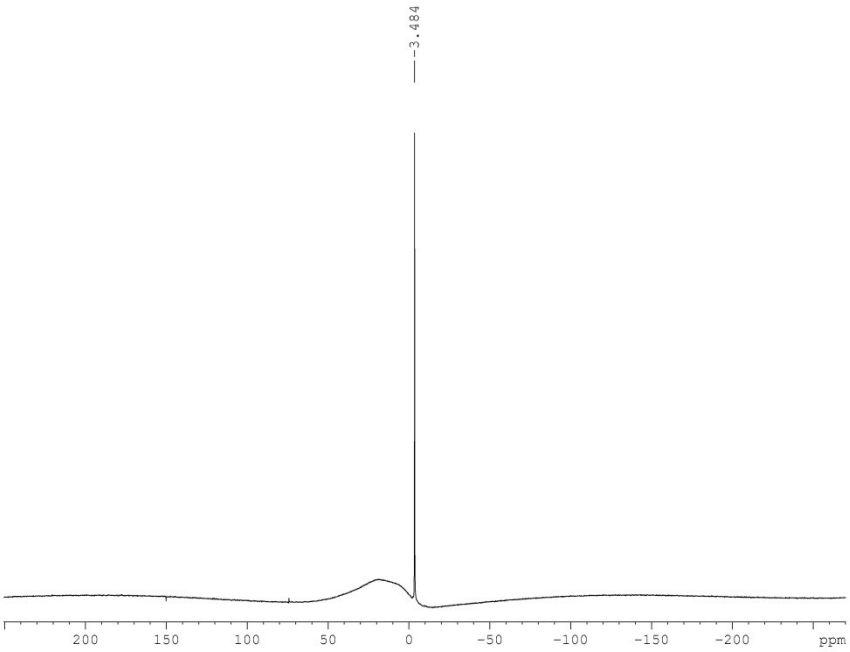
^{1}H and ^{13}C NMR spectra of compound **3ra**

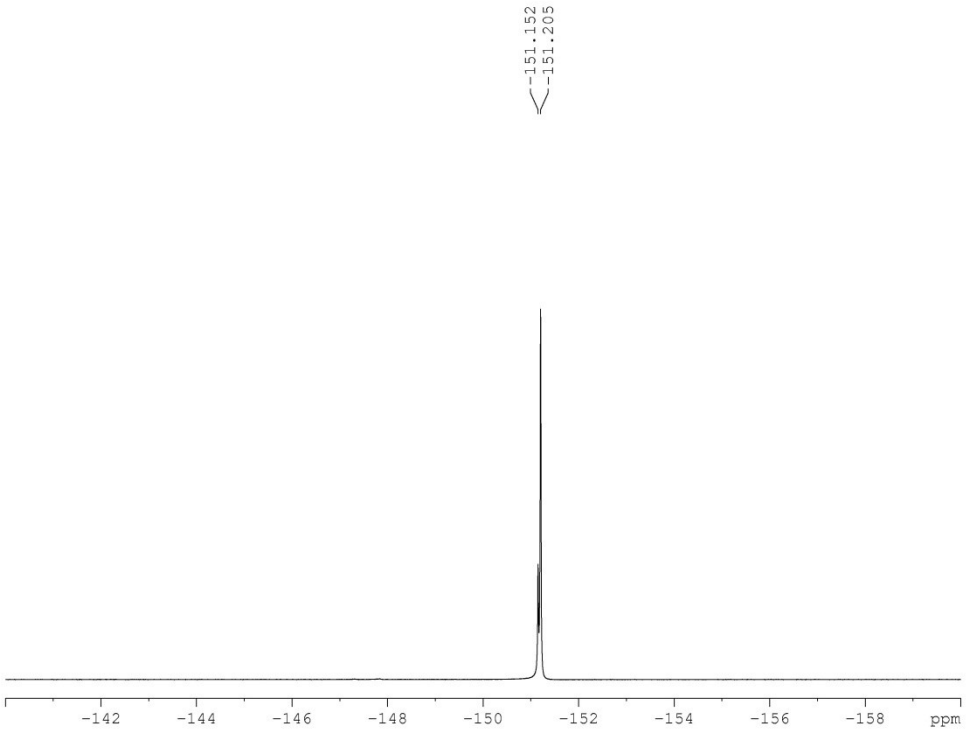


^{1}H and ^{13}C NMR spectra of compound **(ficuseptine) 4**



^{11}B & ^{19}F NMR spectra of compound **3aa**





ORTEP diagram of compound **3aa**

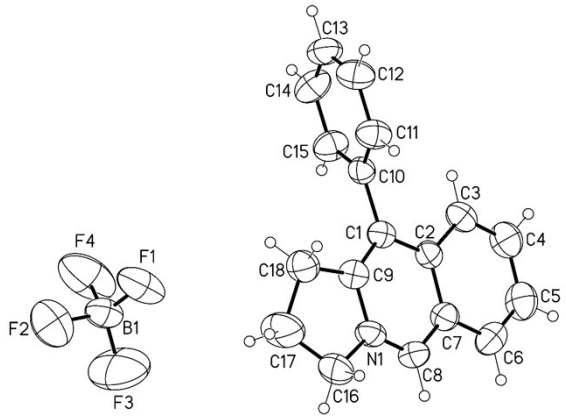


Table 1. Crystal data and structure refinement for **3aa** (140501LT_a).

Identification code	140501LT_a
Empirical formula	C18 H16 B F4 N
Formula weight	333.13
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P n a 21
Unit cell dimensions	a = 20.2206(11) Å □= 90°.

	b = 9.2842(5) Å □= 90°.
	c = 8.5994(5) Å □ = 90°.
Volume	1614.38(16) Å^3
Z	4
Density (calculated)	1.371 Mg/m^3
Absorption coefficient	0.111 mm^{-1}
F(000)	688
Crystal size	0.20 x 0.15 x 0.15 mm^3
Theta range for data collection	2.014 to 26.436°.
Index ranges	-25<=h<=24, -11<=k<=11, -10<=l<=10
Reflections collected	12010
Independent reflections	3276 [R(int) = 0.0317]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9485 and 0.8438
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3276 / 187 / 264
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1324
R indices (all data)	R1 = 0.0769, wR2 = 0.1486
Absolute structure parameter	0.0(19)
Extinction coefficient	n/a
Largest diff. peak and hole	0.265 and -0.236 e.Å^{-3}