α-Diazo N-heteroarenium salts: synthesis and reactivity of a novel class of 'Onium' diazo compounds

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Supporting Information

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I. General information and materials

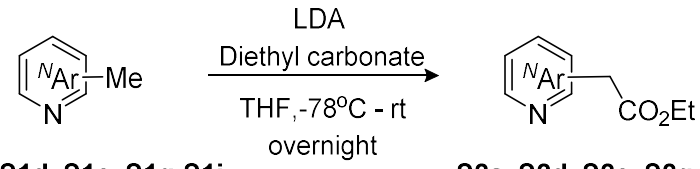
NMR spectra were recorded using Bruker AV - 300 / AV- 400 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired by the Shanghai Institute of Organic Chemistry National Center for Organic Mass Spectrometry in China on a Thermo Fisher Scientific LTQ FT Ulta. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 60Å (40 – 60 μm) mesh silica gel (SiO_2). All reactions were carried out under nitrogen or argon with anhydrous solvents in oven-dried glassware, unless otherwise noted. All reagents were commercially obtained and, where appropriate, purified prior to use.

II. Preparation and characterization of substrates

S1a-S1d, S1h-S1i are commercially available.

S1e-S1g were obtained following literature protocols. [1]

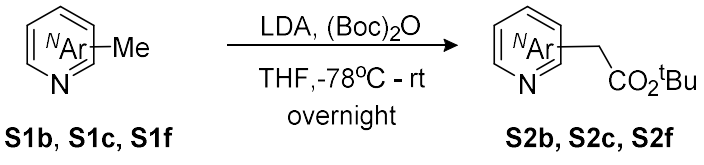
A. General procedure for the preparation of ethyl N-heteroaryleacetate S2



S1a, **S1d**, **S1e**, **S1g-S1i** **S2a**, **S2d**, **S2e**, **S2g-S2i**

S2a, **S2d**, **S2e**, **S2g-S2i** were obtained following the method reported by Richard Frenette and co-workers.[2] To a 100 mL Schlenk flask, diisopropylamine (5.6 mL, 40.0 mmol) and THF (30 mL) were added and cooled to −78° C. Butyllithium (14.4 mL, 36.0 mmol) (2.5M in hexane) was then added dropwise and the mixture was stirred for 30 minutes. The solution of methyl-substituted N-heterocyclic compound (20.0 mmol) in 10 mL THF was added, and the mixture was stirred for 1 h. Diethyl carbonate (4.8 mL, 40.0 mmol) was added, and the mixture was stirred at −78° C overnight when temperature was slowly raised to ambient temperature. The reaction was quenched with the aq. NH_4Cl and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude oil was purified by flash column chromatography on silica gel using petroleum ether/ethylacetate (PE: EA = 5:1) as an eluent to afford **S2a**, **S2d**, **S2e**, **S2g-S2i** in 46~86% yields.

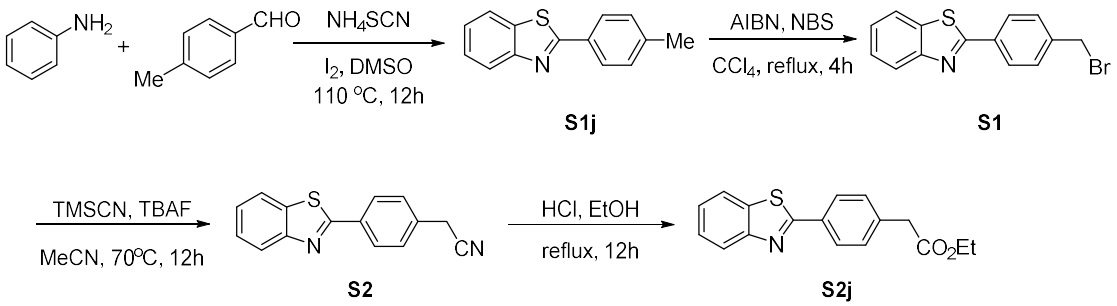
B. General procedure for preparation of t-butyl N-heteroaryleacetate S2



S1b, **S1c**, **S1f** **S2b**, **S2c**, **S2f**

S2b, **S2c**, **S2f** were obtained following the method reported by Richard Frenette and co-workers.[2]To a 100 mL Schlenk flask, diisopropylamine (5.6 mL, 40.0 mmol) and THF (30 mL) were added and cooled to −78° C. Butyllithium (14.4 mL, 36.0 mmol) (2.5M in hexane) was added dropwise and the mixture was stirred for 30 minutes. The solution of methyl-substituted N-heterocyclic compound (20.0 mmol) in 10 mL THF was added, and the mixture was stirred for 1 h. Di-tert-butyl decarbonate (9.2 mL, 40.0 mmol) was added, and the mixture was stirred at −78° C overnight when temperature was slowly raised to ambient temperature. The reaction was quenched with the aq. NH_4Cl and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude oil was purified by flash column chromatography on silica gel using petroleum ether/ethylacetate (PE: EA = 5:1) as an eluent to afford **S2b**, **S2c**, **S2f** in 63~80% yields.

C. Preparation of ethyl N-heteroaryleacetate S2j



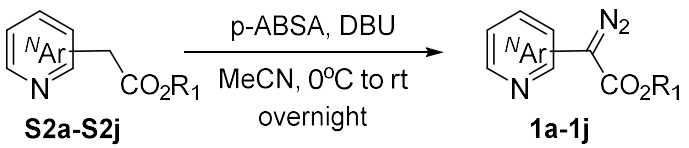
S1j was obtained following the method reported by Alakananda Hajra and co-workers.[3] An oven-dried reaction vessel was charged with aniline (913.20 mg, 10.0 mmol), p-tolualdehyde (1.22 g, 10.0 mmol), NH_4SCN (1.52g, 2.0 equiv), I_2 (2.58 g, 1.0 equiv) and DMSO (40.0 mL). The reaction mixture was stirred at 110 °C for 12 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was allowed to cool to room temperature and quenched with saturated $Na_2S_2O_3$ solution. Then the reaction mixture was extracted with ethyl acetate and the organic phase was dried over anhydrous Na_2SO_4. Concentration in vacuo and purification by column chromatography on silica gel using petroleum ether/ethylacetate (PE: EA = 9:1) as an eluent afforded the pure product **S1j** (2.04 g, 90%).

S1j (1.81 g, 8 mmol) was added to a stirring solution of N-bromosuccinimide (NBS) (1.43 g, 8 mmol) and 2,2'-Azobis(2-methylpropionitrile) (AIBN) (65.68mg, 0.4 mmol) in 40 mL of CCl_4. The solution was refluxed for 4 h. The progress of the reaction was monitored by TLC. The precipitated succinaimide was filtered and the filtrate was concentrated in vacuo to yield a gray oil. **S1** (2.27 g, 94%) was obtained by recrystallization from ethanol.

S2 was obtained following the method reported by Philip DeShong and co-workers.[4] Trimethyl-silyl cyanide (0.8 mL, 6.0 mmol) and TBAF (6.0 mL, 6.0 mmol) were added to a stirring solution of **S1** (1.22g, 4.00 mmol) in 40 mL of acetonitrile under an atmosphere of nitrogen at 70 °C. The reaction was completed for 12 h. The yellow reaction mixture was concentrated in vacuo, and the resulting crude product was purified by flash chromatography on silica gel (PE: DCM = 9:1) to afford **S2** (0.96 g, 95%) as a white soild.

S2 (1.50 g, 6.0 mmol) was dissolved in anhydrous ethanol (30 mL), HCl (36%, 6 mL) was added. The resulting slurry was refluxed for 12 h. After concentration in vacuo, the resulting residue was dissolved in EtOAc (12 mL) and quenched by aq. $NaHCO_3$ slowly to achieve pH 8.0 in the aqueous layer. Organic layer was separated and dried over anhydrous Na_2SO_4. Filtration and concentration yielded **S2j** (1.77 g, 99%).

D. General procedure for preparation of α-N-heteroaryldiazoalkanes 1

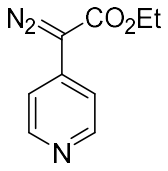


S2a-S2j **1a-1j**

R_1 = Et or ^{t}Bu

p-ABSA (10.1 mmol, 1.01 equiv) was added to a solution of **S2** (10 mmol, 1.0 equiv) and DBU (15 mmol, 1.5 equiv) in CH_3CN (50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then it was concentrated in vacuo and diluted with EtOAc and H_2O. The aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using petroleum ether/ethylacetate as an eluent to afford α-N-heteroaryldiazoalkanes **1a-1j** in 67~99% yields.

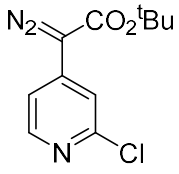
Ethyl 2-diazo-2-(pyridin-4-yl) acetate (1a) [5]



1a

1a: Light yellow solid (1.64 g, 86%), mp 55-56 °C; R_f 0.3 (PE: EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 6.0 Hz, 2H), 7.40 (d, J = 6.2 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 149.8, 136.1, 117.2, 82.9, 64.6, 28.3.

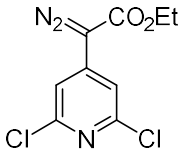
Tert-butyl 2-(2-chloropyridin-4-yl)-2-diazoacetate (1c)



1c

1c: Yellow solid (2.34 g, 92%), mp 93-94 °C; R_f 0.3 (PE: EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 5.5 Hz, 1H), 7.50 (s, 1H), 7.23 (dd, J = 5.5, 1.8 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 152.1, 149.4, 139.5, 117.1, 115.6, 83.4, 64.9, 28.3; HRMS-ESI (m/z) calculated for $C_{11}H_{13}ClN_3O_2^+$ $[M+H]^+$ 254.0691, found 254.0692; IR (KBr): 3449, 2983, 2098, 1700, 1590, 1541, 1470, 1149, 1044, 846, 769 cm^{-1}.

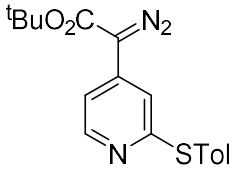
Ethyl 2-diazo-2-(2,6-dichloropyridin-4-yl) acetate (1d)



1d

1d: Yellow solid (2.31 g, 89%), mp 109-110 °C; R_f 0.55 (PE: EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 4.34 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 151.0, 141.6, 115.4, 64.3, 62.0, 14.4; HRMS-ESI (m/z) calculated for $C_9H_8Cl_2N_3O_2$ $^+$[M+H]$^+$ 259.9988, found 259.9992.

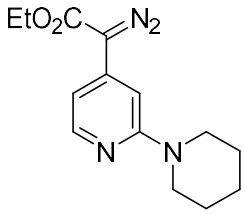
Tert-butyl 2-diazo-2-(2-(p-tolylthio)pyridin-4-yl)acetate (1f)



1f

1f: Orange solid (2.49 g, 73%), mp 45-47 °C; R_f 0.4 (PE: EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 5.5 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.14 (dd, J = 5.5, 1.8 Hz, 1H), 6.94 (s, 1H), 2.37 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 162.0, 149.5, 139.4, 136.9, 135.0, 130.4, 127.2, 114.3, 114.0, 83.0, 64.6, 28.3, 21.3; HRMS-ESI (m/z) calculated for $C_{18}H_{20}N_3O_2S^+$ [M+H]$^+$ 342.1271, found 342.1274; IR (KBr): 3452, 2981, 2923, 2098, 1700, 1575, 1532, 1149, 812 cm^{-1}.

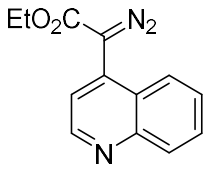
Ethyl 2-diazo-2-(2-(piperidin-1-yl)pyridin-4-yl)acetate (1g)



1g

1g: Yellow solid (1.89 g, 69%), mp 49-50 °C; R_f 0.4 (PE: EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 5.4 Hz, 1H), 7.03 (d, J = 1.6 Hz, 1H), 6.42 (dd, J = 5.5, 1.6 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.51 (s, 4H), 1.61 (s, 6H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 160.0, 148.1, 136.2, 106.1, 100.9, 63.9, 61.1, 46.3, 25.6, 24.7, 14.5; HRMS-ESI (m/z) calculated for $C_{14}H_{19}N_4O_2^+$ [M+H]$^+$ 275.1503, found 275.1507.

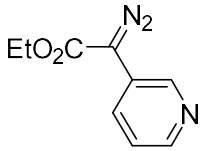
ethyl 2-diazo-2-(quinolin-4-yl) acetate (1h)



1h

1h: Yellow solid (1.89 g, 71%), mp 69-71 °C; R_f 0.4 (PE: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 4.6 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.77-7.72 (m, 1H), 7.70-7.56 (m, 1H), 7.22 (dd, J = 8.4, 2.4 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.96, 149.7, 148.8, 131.9, 130.6, 129.7, 127.0, 126.4, 125.3, 123.8, 121.97, 61.8, 60.5, 14.5; HRMS-ESI (m/z) calculated for $C_{13}H_{12}N_3O_2^+$ $[M+H]^+$ 242.0924, found 242.0928; IR (KBr): 3439, 3134, 2916, 2098, 1698, 1647, 1577, 1249 cm^{-1}.

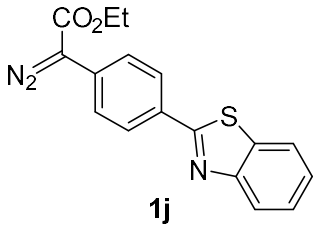
ethyl 2-diazo-2-(pyridin-3-yl)acetate (1i) [6]



1i

1i: Yellow solid (1.89 g, 99%), mp 39-40 °C; R_f 0.3 (PE : EA = 5:1); IR (KBr): 3422, 3127, 2983, 2091, 1702, 1560, 1484, 1420, 1399, 1385, 1342, 1257, 1192, 1172, 1061, 1033, 802, 739, 706, 619 cm^{-1}.

Ethyl 2-(4-(benzo[d]thiazol-2-yl)phenyl)-2-diazoacetate (1j)

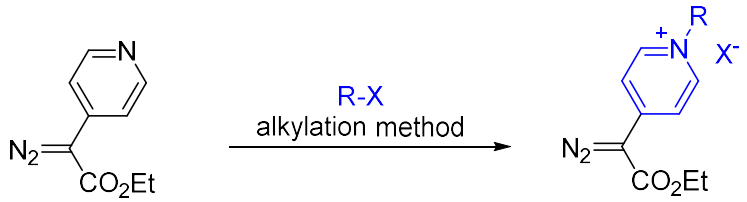


1j

1j: Yellow solid (2.71 g, 84%), mp 126-127 °C; R_f 0.4 (PE : EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.6 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.6 Hz, 2H), 7.51-7.47 (m, 1H), 7.40-7.36 (m, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 164.6, 154.1, 134.9, 130.7, 128.8, 128.0, 126.4, 125.2, 123.7, 123.1, 121.6, 64.2, 61.3, 14.5; HRMS-ESI (m/z) calculated for $C_{17}H_{13}N_3O_2SNa^+$ $[M+Na]^+$ 346.0621, found 346.0626; IR (KBr): 3422, 3134, 2961, 2923, 2852, 2088, 1706, 1647, 1654, 1636, 1559, 1541, 1522, 1507, 1458, 1399, 1385, 1270, 1163, 1084, 1028, 756, 726,619 cm^{-1}.

III. N-alkylation of substrates 1

Methods for *N*-alkylation taking 1a for example



1a **2**

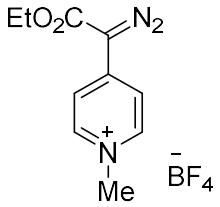
Method a: To a 10 mL pressure tube, methyl iodide CH_3I (0.2 mL, 3 mmol) was added to a solution of α-4-pyridyldiazoester **1a** (191.2 mg, 1 mmol) in CH_2Cl_2 (1 mL). The tube was sealed and the reaction mixture was stirred at room temperature for 6 h. The crude product was purified by recrystallization with acetone and diethyl ether. **2a-I** (319.8 mg, 96%) was obtained as a khaki solid.

Method b: Follow the method reported by Radek Cibulka and co-workers.[7] Methyl triflate MeOTf (0.12 mL, 1.0 mmol) was added dropwise to the solution of α-4-pyridyldiazoester **1a** (191.2 mg, 1 mmol, 1 equiv) in dry CH_2Cl_2 (1 mL) at 0 °C under argon. The progress of the reaction was monitored by TLC. Solid was precipitated and collected by filtration. Or the reaction mixture was concentrated and the crude product was purified by recrystallization with acetone and diethyl ether. **2a-OTf** (305.5 mg, 86% yield) was obtained as a yellow semicrystalline solid.

Method c: In glovebox, $Et_3O^+BF_4^-$ (1.0 mmol, 147.9 mg) was added to a solution of α-4-pyridyldiazoester **1a** (191.2 mg, 1 mmol, 1 equiv) in CH_2Cl_2 (1 mL). The reaction was stirred at rt for 1 h. The reaction mixture was concentrated and the crude product was purified by recrystallization with acetone and diethyl ether. **2a-BF$_4$** (278.4 mg, 95%) was obtained as a khaki solid.

Method d: Benzyl bromide (1.1 mmol, 1.1 equiv) was added to a solution of α-4-pyridyldiazoester **1a** (1 mmol, 1.0 equiv.) in MeCN (5 mL). The mixture was heated with stirring for 8 h in an oil bath (80°C). Solid was precipitated and purified by recrystallization with acetone and diethyl ether. **2a'-Br** (318.8 mg, 88%) was obtained as a khaki solid.

4-(1-diazo-2-ethoxy-2-oxoethyl)-1-methylpyridin-1-ium (2a-BF$_4$)

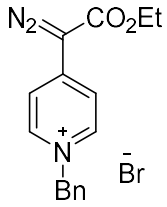


2a-BF$_4$

2a-BF$_4$: Yellow solid (278.4 mg, 95%), mp 86-88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (d, J = 7.3 Hz, 2H), 8.23 – 8.06 (m, 2H), 4.50 (s, 3H), 4.38 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 146.1, 144.0, 118.8, 77.0, 68.1, 62.4, 47.8, 14.1. HRMS-ESI (m/z) calculated for $C_{10}H_{12}N_3O_2^+$ $[M\text{-}BF_4^-]^+$ 206.0924, found 206.0933; IR (KBr): 3432, 3134, 2961, 2922, 2120, 1701, 1685, 1653,

1636, 1559, 1458, 1340, 1384, 1244, 1084, 1039, 619 cm^{-1}.

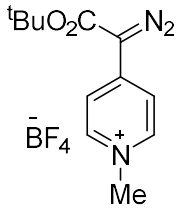
1-benzyl-4-(1-diazo-2-ethoxy-2-oxoethyl) pyridin-1-ium bromide (2a'-Br)



2a'-Br

2a'-Br: Khaki solid (318.8 mg, 88%), mp: 121-123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.22 (d, *J* = 7.1 Hz, 2H), 8.06 (d, *J* = 7.2 Hz, 2H), 7.70 – 7.49 (m, 2H), 7.36 – 7.27 (m, 3H), 6.03 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 146.5, 143.6, 133.4, 129.7, 129.5, 129.5, 119.1, 68.3, 62.6, 62.6, 14.3; IR (KBr): 3422, 3133, 2963, 2921, 2120, 1773, 1735, 1701, 1685, 1654, 1647, 1636, 1570, 1534, 1458, 1400, 1384, 1244, 1083, 1040, 620 cm^{-1}.

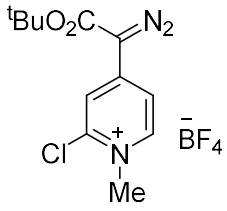
4-(2-(tert-butoxy)-1-diazo-2-oxoethyl)-1-methylpyridin-1-ium tetrafluoroborate (2b-BF_4)



2b-BF_4

2b-BF_4: Khaki solid (295.4 mg, 92%), mp 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.38 (d, *J* = 6.8 Hz, 2H), 7.92 (d, *J* = 6.6 Hz, 2H), 4.16 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 160.5, 146.9, 143.8, 118.9, 84.8, 68.6, 47.0, 28.2; HRMS-ESI (m/z) calculated for $C_{12}H_{16}N_3O_2^+$ $[M\text{-}BF_4^-]^+$ 234.1237, found 234.1241.

4-(2-(tert-butoxy)-1-diazo-2-oxoethyl)-2-chloro-1-methylpyridin-1-ium tetrafluoroborate (2c-BF_4)

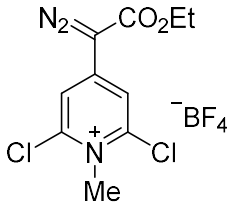


2c-BF_4

2c-BF_4 : Light yellow solid (298.6 mg, 84%), mp 133-134 °C; ^{1}H NMR (400 MHz, d_6-DMSO) *δ* 8.77 (d, *J* = 7.0 Hz, 1H), 8.19 (s, 1H), 8.03 (dd, J = 7.0, 2.4 Hz, 1H), 4.12 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, d_6-DMSO) *δ* 159.8, 148.8, 147.0, 145.6, 119.8, 117.3, 85.5, 69.2, 47.1, 28.2; HRMS-ESI (m/z) calculated for $C_{12}H_{15}ClN_3O_2^+$ $[M\text{-}BF_4^-]^+$ 268.0847, found 268.0851; IR (KBr): 3423, 3134, 2961, 2921, 2851, 1697, 1654, 1637, 1560, 1542, 1523, 1458, 1399, 1384, 1270, 1215, 1157, 1083, 1069, 788, 762,

679, 620, 562 cm^{-1}.

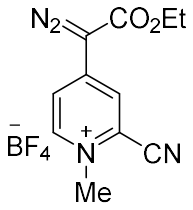
2,6-dichloro-4-(1-diazo-2-ethoxy-2-oxoethyl)-1-methylpyridin-1-ium tetrafluoroborate



2d-BF_4

2d-BF_4: Light yellow solid (298.6 mg, 84%), mp 140-141 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 2H), 4.36 (q, J = 7.5 Hz, 2H), 4.29 (s, 3H), 1.35(t, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.80, 148.65, 147.32, 118.50, 69.12, 62.89, 43.24, 14.26; HRMS-ESI (m/z) calculated for $C_{10}H_{10}Cl_2N_3O_2^+$ [M-BF_4^-]$^+$ 274.0145, found 274.0147.

2-cyano-4-(1-diazo-2-ethoxy-2-oxoethyl)-1-methylpyridin-1-ium tetrafluoroborate (2e-BF_4)

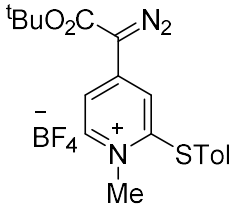


2e-BF_4

2e-BF_4: Light yellow solid (279.9 mg, 84%), mp 131-133 ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.94 (d, J = 7.0 Hz, 1H), 8.70 (d, J = 2.5 Hz, 1H), 8.36 (dd, J = 6.9, 2.5 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 4.32 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 161.2, 146.9, 146.7, 126.2, 124.3, 120.1, 111.2, 70.3, 62.3, 46.4, 14.0; IR (KBr): 3435, 2955, 2926, 2109, 1700, 1626, 1558, 1260, 1042, 519 cm^{-1}.

4-(2-(tert-butoxy)-1-diazo-2-oxoethyl)-1-methyl-2-(p-tolylthio)

pyridin-1-ium tetrafluoroborate (2f-BF_4)

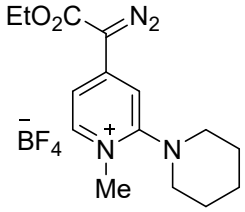


2f-BF_4

2f-BF_4: Light yellow solid (385.6 mg, 87%), decomposed at 142 ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.70 (d, J = 7.0 Hz, 1H), 7.69 – 7.53 (m, 3H), 7.47 (d, J = 7.9 Hz, 2H), 7.37 (s, 1H), 4.15 (s, 3H), 2.41 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, d_6-

DMSO) δ 160.6, 158.2, 145.2, 144.5, 142.1, 135.5, 131.7, 121.6, 115.7, 114.8, 83.8, 68.7, 44.5, 27.5, 20.9; HRMS-ESI (m/z) calculated for $C_{19}H_{22}N_3O_2S^+[M\text{-}BF_4^-]^+$ 356.1427, found 356.1428; IR (KBr): 3438, 2986, 2129, 1703, 1620, 1532, 1504, 1453, 1147, 1041 cm^{-1}.

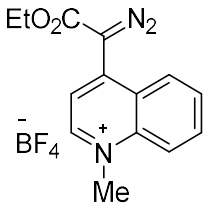
4-(1-diazo-2-ethoxy-2-oxoethyl)-1-methyl-2-(piperidin-1-yl)pyridin-1-ium tetrafluoroborate (2g-BF_4)



2g-BF_4

2g-BF_4 : Khaki solid (293.4 mg, 78%), mp 171-172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 5.4 Hz, 1H), 7.89 (s, 1H), 7.75 (dd, J = 5.4, 1.4 Hz, 1H), 4.57 (d, J = 13.1 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.82 (td, J = 12.4, 2.9 Hz, 2H), 3.42 (s, 3H), 2.00 – 1.90 (m, 2H), 1.77 – 1.56 (m, 4H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 154.4, 149.2, 142.5, 118.8, 108.8, 65.5, 61.9, 61.5, 57.4, 21.4, 20.7, 14.4; HRMS-ESI (m/z) calculated for $C_{15}H_{21}N_4O_2$ $[M\text{-}BF_4^-]^+$ 289.1659, found 289.1659.

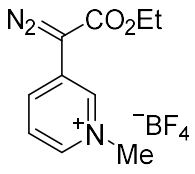
4-(1-diazo-2-ethoxy-2-oxoethyl)-1-methylquinolin-1-ium tetrafluoroborate (2h-BF_4)



2h-BF_4

2h-BF_4: Light yellow solid (305.4 mg, 89%), mp 151-153 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, J = 6.5 Hz, 1H), 8.46 (d, J = 8.9 Hz, 1H), 8.20 (d, J = 6.2 Hz, 1H), 8.17 (d, J = 8.2 Hz, 1H), 8.10 (d, J = 8.6 Hz, 1H), 7.93 (t, J = 7.8 Hz, 1H), 4.73 (s, 3H), 4.33 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 147.8, 144.9, 138.8, 136.2, 130.0, 126.1, 124.6, 120.2, 119.6, 65.5, 62.9, 46.6, 14.4; IR (KBr): 3441, 2918,2109, 1714, 1609, 1368, 1255, 1167, 1101, 1016, 772 cm^{-1}.

3-(1-diazo-2-ethoxy-2-oxoethyl)-1-methylpyridin-1-ium tetrafluoroborate (2i-BF_4)

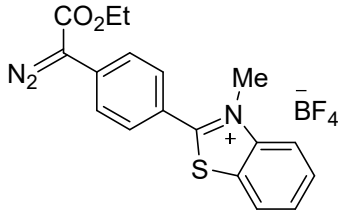


2i-BF_4

2i-BF_4 : Orange solid (240.3 mg, 82%), mp 62.4-63.4 ºC; ^{1}H NMR (400 MHz, d_6-

DMSO) δ 9.11 (s, 1H), 8.72 (d, J = 6.0 Hz, 1H), 8.57 (d, J = 8.5 Hz, 1H), 8.09 (t, J = 7.3 Hz, 1H), 4.36 (s, 3H), 4.34-4.31 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 163.1, 141.4, 139.2, 137.8, 128.8, 127.1, 62.7, 61.7, 48.3 14.1; HRMS-ESI (m/z) calculated for $C_{10}H_{12}N_3O_2^+[M\text{-}BF_4^-]^+$ 206.0924, found 206.0927; IR (KBr): 3448, 3147, 2923, 2095, 1685, 1654, 1648, 1508, 1458, 1399, 1384, 1260, 1163, 1084, 1057, 1037, 816, 674 cm.

2-(4-(1-diazo-2-ethoxy-2-oxoethyl)phenyl)-3-methylbenzo[d]thiazol-3-ium tetrafluoroborate (2j-BF$_4$)



2j-BF$_4$

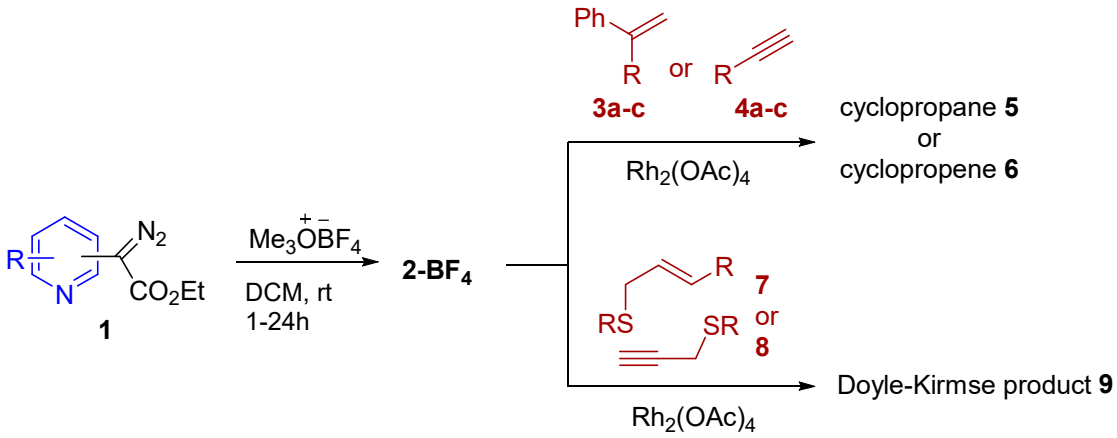
2j-BF$_4$: Light yellow solid (391.3 mg, 92%), decomposed at 109 ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.51 (d, J = 8.3 Hz, 1H), 8.39 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 8.3 Hz, 3H), 7.89 (d, J = 8.1 Hz, 3H), 4.32 (q, J = 7.1 Hz, 2H), 4.26 (s, 3H), 1.30 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 173.6, 163.6, 142.5, 132.7, 131.0, 129.8, 128.6, 124.4, 123.8, 123.7, 121.6, 117.6, 64.8, 61.3, 38.0, 14.2; HRMS-ESI (m/z) calculated for $C_{18}H_{16}N_3O_2S^+[M\text{-}BF_4^-]^+$ 338.0958, found 338.0958; IR (KBr): 3422, 3134, 2961, 2921, 2851, 2096, 1869, 1845, 1773, 1735, 1685, 1654, 1647, 1636, 1636, 1559, 1540, 1522, 1507, 1400, 1385, 1270, 1084, 1037, 669, 619 cm^{-1}.

IV. Transformations of α-N-heteroaryldiazoalkane tetrafluoroborates enabled by Rhodium catalysis

General Procedure for cyclopropenation of 2-BF$_4$

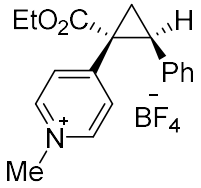
A solution of α-N-heteroaryldiazoalkane tetrafluoroborates **2-BF$_4$** (0.3 mmol, 1 equiv) in DCM (0.3 M) was added dropwise to a stirred solution of alkene (0.9 mmol, 3 equiv) in DCM at room temperature. The progress of the reaction was monitored by TLC. After completion (0.5-12 h), the reaction mixture was concentrated in vacuo and the residue was purified by silica gel chromatography.

One-pot procedure



In the glovebox, $Et_3O^+BF_4^-$ (0.33 mmol, 47 mg, 1.1 equiv) was added to a solution of α-N-heteroaryldiazoalkanes **1** (0.30 mmol, 1 equiv) in CH_2Cl_2 (1 mL) containing 4 Å molecular sieves (0.1 g) at room temperature. The progress of the reaction was monitored by TLC. After completion (1 h to 24 h), 3 equiv of terminal alkenes **3a-c**, terminal alkynes **4a-c**, allyl thioethers **7,** or propargyl thioether **8** was added, followed by the addition of $Rh_2(OAc)_4$ (3.4 mg, 2 mol%). The resulting reaction solution was stirred at room temperature for 2-12 h, monitored by TLC. Then the reaction mixture was concentrated in vacuo and the residue was purified by silica gel chromatography (30:1 DCM/MeOH) to give the products **5**, **6**, **9**.

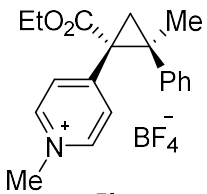
4-(1-(ethoxycarbonyl)-2-(naphthalen-2-yl)cycloprop-2-en-1-yl)-1-methylpyridin-1-ium tetrafluoroborate (5a)



5a

5a: Followed **One-pot procedure**. White solid (94.5 mg, 86%), mp 67-69 °C; R_f 0.1 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 6.2 Hz, 2H), 7.64 (d, J = 6.1 Hz, 2H), 7.27 – 6.68 (m, 5H), 4.22 (s, 3H), 4.16-4.12 (m, 2H), 3.33 (s, 1H), 2.24 (d, J = 8.5 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.93, 155.56, 144.09, 133.30, 130.89, 128.79, 128.12, 127.74, 62.53, 47.97, 36.78, 35.21, 18.82, 14.00; HRMS-ESI (m/z) calculated for $C_{18}H_{20}NO_2^+$ $[M\text{-}BF_4^-]^+$ 282.1489, found 282.1489.

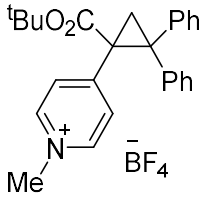
4-(1-(ethoxycarbonyl)-2-methyl-2-phenylcyclopropyl)-1-methylpyridin-1-ium tetrafluoroborate (5b)



5b

5b : Followed **One-pot procedure**. White solid (98.9 mg, 86%), mp 75-76 ºC; R_f 0.1 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 6.3 Hz, 2H), 7.75 (d, J = 6.5 Hz, 2H), 7.20 – 6.94 (m, 5H), 4.28 – 4.19 (m, 2H), 4.17 (s, 3H), 2.41 (d, J = 6.6 Hz, 1H), 2.26 (d, J = 6.5 Hz, 1H), 1.71 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.10, 157.16, 143.54, 138.67, 129.61, 128.92, 127.95, 127.68, 62.53, 47.71, 40.97, 40.05, 23.30, 22.51, 14.17; HRMS-ESI (m/z) calculated for $C_{19}H_{22}NO_2^+$ $[M\text{-}BF_4^-]^+$ 296.1645, found.296.1653.

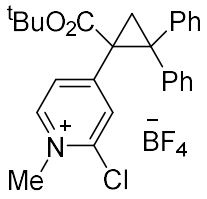
4-(1-(tert-butoxycarbonyl)-2,2-diphenylcyclopropyl)-1-methylpyridin-1-ium tetrafluoroborate (5c)



5c

5c: Followed **General procedure for cyclopropenation of 2-BF$_4$**. White solid (100.8 mg, 71%), mp 81-82 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.72 (d, J = 6.5 Hz, 2H), 8.27 (d, J = 6.7 Hz, 2H), 7.70 – 7.62 (m, 2H), 7.36 – 7.25 (m, 4H), 7.21 (t, J = 7.1 Hz, 1H), 7.03 (t, J = 7.5 Hz, 2H), 6.99 – 6.93 (m, 2H), 4.15 (s, 3H), 2.86 (d, J = 6.4 Hz, 1H), 2.61 (d, J = 6.3 Hz, 1H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 176.1, 166.4, 155.1, 143.9, 141.3, 139.1, 130.0, 129.5, 129.1, 128.33, 128.28, 127.1, 82.0, 47.9, 47.1, 41.6, 26.9, 22.0; HRMS-ESI (m/z) calculated for $C_{26}H_{28}NO_2^+$ $[M\text{-}BF_4^-]^+$ 386.2115, found 386.2115.

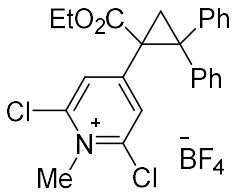
4-(1-(tert-butoxycarbonyl)-2,2-diphenylcyclopropyl)-2-chloro-1-methylpyridin-1-ium (5d)



5d

5d : Followed **General procedure for cyclopropenation of 2-BF$_4$**. Light yellow solid (117.3 mg, 77%), mp 100-102 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 6.5 Hz, 1H), 8.08 (d, J = 2.0 Hz, 1H), 7.89 (dd, J = 6.5, 2.1 Hz, 1H), 7.52 (d, J = 7.1 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.26-7.24 (m, 1H), 7.18-7.12 (m, 4H), 7.04 (t, J = 7.1 Hz, 1H), 4.27 (s, 3H), 2.91 (d, J = 6.5 Hz, 1H), 2.71 (d, J = 6.6 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.4, 147.2, 145.0, 140.0, 137.8, 130.9, 129.4, 129.0, 128.8, 128.7, 127.9, 127.73, 127.70, 83.7, 49.6, 47.1, 42.3, 27.3, 23.3; HRMS-ESI (m/z) calculated for $C_{26}H_{27}ClNO_2^+$ $[M\text{-}BF_4^-]^+$ 420.1725, found 420.1726.

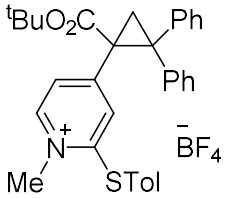
2,6-dichloro-4-(1-(ethoxycarbonyl)-2,2-diphenylcyclopropyl)-1-methylpyridin-1-ium tetrafluoroborate (5e)



5e

5e: Followed **One-pot procedure**. Yellow solid (121.8 mg, 79%), mp 82-83 ºC; R_f 0.3 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 14.3 Hz, 1H), 7.58 – 7.28 (m, 11H), 4.74 (q, J = 7.1 Hz, 2H), 4.14 (s, 3H), 3.81 (s, 2H), 1.56 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 150.7, 142.3, 128.9, 128.63, 125.6, 117.9, 94.97, 84.3, 77.3, 69.6, 41.8, 15.1; HRMS-ESI (m/z) calculated for $C_{24}H_{22}Cl_2NO_2^+$ [M-BF_4^-]$^+$ 426.1022, found 426.1026.

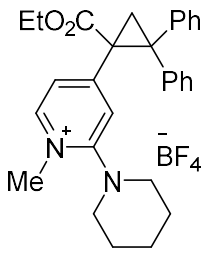
4-(1-(tert-butoxycarbonyl)-2,2-diphenylcyclopropyl)-1-methyl-2-(p-tolylthio)pyridin-1-ium tetrafluoroborate (5f)



5f

5f: Followed **General procedure for cyclopropenation of 2-BF4**. Light yellow solid (126.2 mg, 89%), mp 139-140 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.76 (d, J = 6.6 Hz, 1H), 7.83 (dd, J = 6.6, 2.0 Hz, 1H), 7.59 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 2H), 7.24 – 7.20 (m, 1H), 7.17-7.13 (m, 2H), 7.08 (d, J = 7.3 Hz, 1H), 7.02 – 6.95 (m, 3H), 4.11 (s, 3H), 2.54 – 2.48 (m, 2H), 2.50 (s, 3H), 0.99 (s, 9H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 157.9, 153.3, 145.7, 142.5, 140.6, 138.5, 135.7, 131.8, 129.3, 128.8, 128.4, 128.3, 127.7, 127.2(4), 127.2(0), 124.8, 121.5, 82.1, 47.4, 45.3, 41.8, 26.9, 22.1, 21.0; HRMS-ESI (m/z) calculated for $C_{33}H_{34}NO_2S^+$ [M-BF_4^-]$^+$ 508.2305, found 508.2309.

4-(1-(ethoxycarbonyl)-2,2-diphenylcyclopropyl)-1-methyl-2-(piperidin-1-yl)pyridin-1-ium tetrafluoroborate (5g)

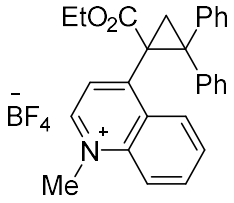


5g

5g: Followed **General procedure for cyclopropenation of 2-BF4**. Light yellow solid (118.8 mg, 75%), mp 108-110 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, d6-DMSO) δ 8.44 (d, J = 5.0 Hz, 1H), 8.10 (d, J = 2.8 Hz, 1H), 7.75 (d, J = 5.1 Hz,

1H), 7.68 (d, J = 7.5 Hz, 2H), 7.38 – 7.31 (m, 4H), 7.27 (t, J = 7.3 Hz, 1H), 7.05 (t, J = 7.6 Hz, 2H), 6.96 (t, J = 7.3 Hz, 1H), 4.51 (d, J = 13.2 Hz, 1H), 4.44 (d, J = 12.7 Hz, 1H), 3.87 – 3.80 (m, 1H), 3.73 – 3.68 (m, 2H), 3.68-3.65 (m, 1H), 3.24 (s, 3H), 2.98 (d, J = 6.4 Hz, 1H), 2.61 (d, J = 6.3 Hz, 1H), 1.92 – 1.71 (m, 2H), 1.55-1.48 (m, 2H), 1.40 – 1.24 (m, 1H), 1.18 – 1.03 (m, 1H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d6-DMSO) δ 168.4, 153.2, 150.5, 148.1, 141.6, 139.1, 129.4, 129.1, 128.2, 127.96, 127.0, 126.7, 119.9, 61.1, 61.1, 60.7, 46.9, 40.8, 21.5, 20.7, 20.5, 13.3; HRMS-ESI (m/z) calculated for $C_{29}H_{33}N_2O_2^+$ $[M\text{-}BF_4^-]^+$ 441.2537, found 441.2538.

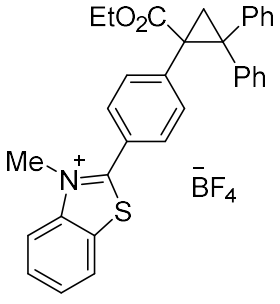
4-(1-(ethoxycarbonyl)-2,2-diphenylcyclopropyl)-1-methylquinolin-1-ium tetrafluoroborate (5h)



5h

5h: Followed **General procedure for cyclopropenation of 2-BF$_4$**. White solid (111.4 mg, 75%), mp 109-110 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.60 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.9 Hz, 1H), 8.12 (t, J = 7.5 Hz, 1H), 7.96 – 7.71 (m, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.03 – 6.77 (m, 5H), 4.62 (s, 3H), 3.96-3.91 (m, 1H), 3.82 – 3.63 (m, 1H), 3.11 (d, J = 5.9 Hz, 1H), 2.79 (s, 1H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 140.0, 138.7, 138.6, 137.2, 135.1, 130.2, 130.1, 128.8, 128.4, 127.97, 127.9, 127.5, 126.9, 62.5, 45.9, 41.4, 29.7, 25.7, 13.5; HRMS-ESI (m/z) calculated for $C_{28}H_{26}NO_2^+$ $[M\text{-}BF_4^-]^+$ 408.1958, found 408.1957.

2-(4-(1-(ethoxycarbonyl)-2,2-diphenylcyclopropyl)phenyl)-3-methylbenzo[d]thiazol-3-ium tetrafluoroborate (5i)

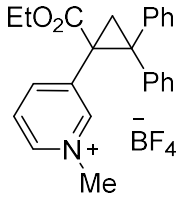


5i

5i: Followed **General procedure for cyclopropenation of 2-BF$_4$**. White solid (83.6 mg, 48%), mp 136-137 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.49 (d, J = 8.2 Hz, 1H), 8.36 (d, J = 8.5 Hz, 1H), 7.98 (t, J = 7.9 Hz, 1H), 7.87 (d, J = 8.5 Hz, 3H), 7.74 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.6 Hz, 3H), 7.06 (t, J = 7.5 Hz, 2H), 6.98 (d, J = 7.3 Hz, 1H), 4.09 (s, 3H), 3.86-3.78 (m, 1H), 3.69-3.61 (m, 1H), 2.80 (d, J = 6.1 Hz, 1H), 2.65 (d, J = 6.0 Hz, 1H), 0.79 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 173.8, 169.3, 142.3,

142.0, 139.5, 133.1, 129.9, 129.5, 129.2, 129.1, 128.6, 128.3, 127.8, 126.9, 126.4, 124.4, 123.6, 117.6, 60.9, 45.7, 41.7, 37.8, 21.8, 13.3; HRMS-ESI (m/z) calculated for $C_{32}H_{28}NO_2S^+$ $[M\text{-}BF_4^-]^+$ 490.1835, found 490.1834.

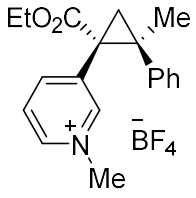
3-(1-(ethoxycarbonyl)-2,2-diphenylcyclopropyl)-1-methylpyridin-1-ium tetrafluoroborate (5j)



5j

5j : Followed **One-pot procedure**. White solid (119.2 mg, 89%), mp 70-72 ºC; R_f 0.3 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.25 (s, 1H), 8.74-8.69 (m, 2H), 7.93-7.90 (m, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.38-7.34 (m, 4H), 7.27 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 7.6 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 4.27 (s, 3H), 3.84-3.80 (m, 1H), 3.67-3.63 (m, 1H), 2.94 (d, J = 6.4 Hz, 1H), 2.67 (d, J = 6.4 Hz, 1H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 168.4, 148.0, 147.8, 143.8, 141.4, 138.8, 136.7, 129.4, 129.0, 128.3, 127.1, 127.0, 126.1, 61.3, 47.6, 46.4, 38.7, 21.4, 13.2; HRMS-ESI (m/z) calculated for $C_{24}H_{24}NO_2^+$ $[M\text{-}BF_4^-]^+$ 358.1802, found 358.1803.

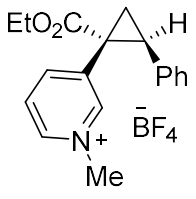
3-(1-(ethoxycarbonyl)-2-methyl-2-phenylcyclopropyl)-1-methylpyridin-1-ium (5k)



5k

5k: Followed **One-pot procedure**. White solid (94.3 mg, 82%), mp 76-78 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.89 (s, 1H), 8.61 (d, J = 6.0 Hz, 1H), 8.34 (d, J = 8.2 Hz, 1H), 7.78 (t, J = 7.1 Hz, 1H), 7.22-7.04 (m, 5H), 4.19 (s, 3H), 4.17-4.11 (m, 2H), 2.65 (d, J = 6.5 Hz, 1H), 2.06 (d, J = 6.3 Hz, 1H), 1.72 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 168.8, 147.9, 146.9, 143.6, 139.6, 137.5, 128.3, 127.9, 127.0, 125.9, 61.7, 47.5, 37.9, 36.6, 21.8, 21.0, 13.9; HRMS-ESI (m/z) calculated for $C_{19}H_{22}NO_2^+$ $[M\text{-}BF_4^-]^+$ 296.1645, found 296.1644.

3-(1-(ethoxycarbonyl)-2-phenylcyclopropyl)-1-methylpyridin-1-ium tetrafluoroborate (5l)

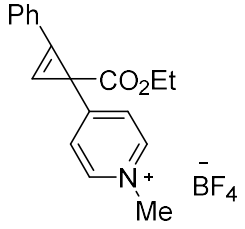


5l

5l: Followed **One-pot procedure**. White solid (105.2 mg, 95%), mp 72-73 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.58 (d, J = 6.0 Hz,

1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 6.8 Hz, 1H), 7.20 – 7.02 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 2H), 4.31 (s, 3H), 4.19-4.11 (m, 2H), 3.28 (t, *J* = 8.4 Hz, 1H), 2.39 (t, *J* = 6.9 Hz, 1H), 2.28-2.24 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 148.4, 147.2, 143.7, 137.7, 133.8, 128.7, 128.3, 127.5, 126.9, 62.3, 48.3, 34.3, 33.6, 18.4, 13.96; HRMS-ESI (m/z) calculated for $C_{18}H_{20}NO_2^+$ $[M\text{-}BF_4^-]^+$ 282.1489, found 282.1489.

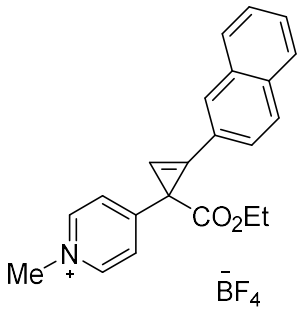
4-(1-(ethoxycarbonyl)-2-phenylcycloprop-2-en-1-yl)-1-methylpyridin-1-ium tetrafluoroborate (6a)



6a

6a: Followed **One-pot procedure**. White solid (83.7 mg, 76%), mp 86-88 ºC; R_f 0.3 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 6.4 Hz, 2H), 8.05 (d, *J* = 6.5 Hz, 2H), 7.58 – 7.32 (m, 5H), 7.18 (s, 1H), 4.29 (s, 3H), 4.21-4.16 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 161.4, 144.1, 131.3, 130.3, 129.4, 127.0, 122.8, 113.2, 96.6, 61.8, 47.6, 33.1, 14.1; HRMS-ESI (m/z) calculated for $C_{18}H_{18}NO_2^+$ $[M\text{-}BF_4^-]^+$ 280.1332, found 280.1339.

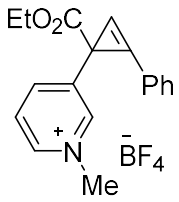
4-(1-(ethoxycarbonyl)-2-(naphthalen-2-yl)cycloprop-2-en-1-yl)-1-methylpyridin-1-ium tetrafluoroborate (6b)



6b

6b : Followed **One-pot procedure**. Yellow solid (41.9 mg, 32%), mp 134-136 ºC; R_f 0.3 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.74 (d, *J* = 6.5 Hz, 2H), 8.15 (s, 1H), 8.07 (d, *J* = 6.5 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.97-7.92 (m, 2H), 7.87 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.55 (p, *J* = 7.1 Hz, 2H), 4.83 (q, *J* = 7.0 Hz, 2H), 4.20 (s, 3H), 1.57 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 160.99, 147.5, 145.3, 144.96, 133.5, 132.6, 129.2, 128.4, 128.2, 127.5, 126.8, 126.7, 126.2, 121.6, 121.1, 121.1, 106.1, 96.9, 69.5, 55.4, 46.9, 15.3; HRMS-ESI (m/z) calculated for $C_{22}H_{20}NO_2^+$ $[M\text{-}BF_4^-]^+$ 330.1489, found 330.1489.

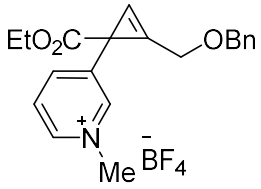
3-(1-(ethoxycarbonyl)-2-phenylcycloprop-2-en-1-yl)-1-methylpyridin-1-ium tetrafluoroborate (6c)



6c

6c : Followed **One-pot procedure**. White solid (94.2 mg, 85%), mp 74-76 ºC; R_f 0.2 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.51 (d, J = 5.9 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H), 7.77 (t, J = 7.2 Hz, 1H), 7.48 (d, J = 7.2 Hz, 2H), 7.40 – 7.24 (m, 4H), 4.26 (s, 3H), 4.07 (d, J = 7.1 Hz, 2H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 145.2, 144.40 143.1, 142.9, 131.1, 130.1, 129.3, 127.4, 123.3, 115.2, 97.1, 61.9, 48.6, 30.8, 14.1; HRMS-ESI (m/z) calculated for $C_{18}H_{18}NO_2^+$ $[M\text{-}BF_4^-]^+$ 280.1332, found 280.1332.

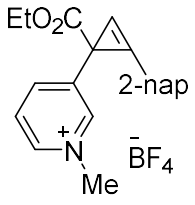
3-(2-((benzyloxy)methyl)-1-(ethoxycarbonyl)cycloprop-2-en-1-yl)-1-methylpyridin-1-ium tetrafluoroborate (6d)



6d

6d : Followed **One-pot procedure**. White solid (55.5 mg, 45%), mp 81-83 ºC; R_f 0.3 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.57 (d, J = 6.1 Hz, 1H), 8.38-8.35 (m, 1H), 7.82 (dd, J = 8.1, 6.1 Hz, 1H), 7.35 - 7.24 (m, 5H), 7.13 (s, 1H), 4.69-4.57 (m, 2H), 4.56-4.52 (m, 2H),, 4.27 (s, 3H), 4.17-4.11 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 145.6, 145.2, 143.0, 142.8, 137.2, 128.6, 128.2, 128.0, 127.3, 115.0, 99.3, 73.1, 62.4, 61.9, 48.5, 31.1, 14.2; HRMS-ESI (m/z) calculated for $C_{20}H_{22}NO_3^+$ $[M\text{-}BF_4^-]^+$ 324.1594, found 324.1593.

4-(1-(ethoxycarbonyl)-2-(naphthalen-2-yl)cycloprop-2-en-1-yl)-1-methylpyridin-1-ium tetrafluoroborate (6e)

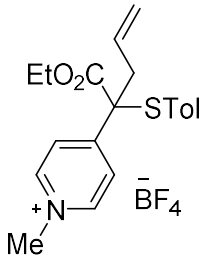


6e

6e : Followed **One-pot procedure**. White solid (67.2 mg, 76%), mp 101-103 ºC; R_f 0.3 (DCM/MeOH= 30/1); ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.16 (s, 1H), 8.79-8.71 (m, 2H), 8.17-8.13 (m, 2H), 8.08 – 7.89 (m, 3H), 7.81 (d, J = 8.6 Hz, 1H), 7.75 (s, 1H), 7.63 – 7.43 (m, 2H), 4.73 (q, J = 7.1 Hz, 2H), 4.40 (s, 3H), 1.54 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 172.0, 145.3, 144.6, 143.6, 141.3, 133.6, 132.7, 130.0, 129.1, 128.5, 128.0, 127.8, 127.1, 127.0, 126.2, 121.0, 116.1, 98.5, 61.2, 48.0, 30.6,

14.0; HRMS-ESI (m/z) calculated for $C_{22}H_{20}NO_2^+$ [M-BF_4^-]$^+$ 330.1489, found 330.1489.

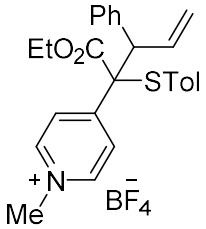
4-(1-ethoxy-1-oxo-2-(p-tolylthio)pent-4-en-2-yl)-1-methylpyridin-1-ium tetrafluoroborate (9a)



9a

9a: Followed **One-pot procedure**. Reddish brown solid (60.2 mg, 64%), mp 98-100 ^oC; R_f 0.4 (DCM/MeOH= 30/1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 6.5 Hz, 2H), 7.83 (d, J = 6.5 Hz, 2H), 7.06 (s, 4H), 5.73-5.65 (m, 1H), 5.14-5.05 (m, 2H), 4.42 (s, 3H), 4.27 – 4.10 (m, 2H), 3.00-2.95 (m, 1H), 2.86-2.80 (m, 1H), 2.29 (s, 3H), 1.21 (t, J = 7.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 159.0, 144.6, 141.3, 136.8, 130.4, 130.3, 127.4, 124.7, 121.3, 63.0, 62.9, 48.2, 40.7, 21.3, 13.9; HRMS-ESI (m/z) calculated for $C_{20}H_{24}NO_2S$ [M-BF_4^-]$^+$ 342.1522, found 342.1523.

4-(1-ethoxy-1-oxo-3-phenyl-2-(p-tolylthio)pent-4-en-2-yl)-1-methylpyridin-1-ium tetrafluoroborate (9b)

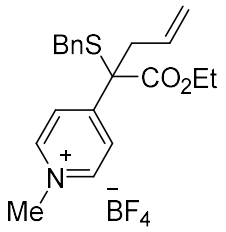


9b

9b : Followed **One-pot procedure**. Reddish brown solid (62.1 mg, 70%), mp 110-112 ^oC; R_f 0.45 (DCM/MeOH= 30/1). **9b** was an inseparable mixture of two isomers. The area of pyridine-H peak in major isomer was compared with that in minor isomer to derive a ^1H NMR ratio of dr = 10: 3. The major isomer :^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 6.5 Hz, 2H), 7.84 (d, J = 6.5 Hz, 2H), 7.25 – 7.16 (m, 3H), 7.09 (d, J = 8.2 Hz, 2H), 7.06 – 6.95 (m, 2H), 6.89 – 6.83 (m, 2H), 6.02 – 5.75 (m, 1H), 5.46 – 5.37 (m, 1H), 5.33 (dd, J = 10.0, 1.5 Hz, 1H), 4.74 (d, J = 10.2 Hz, 1H), 4.45 (s, 3H), 4.06 – 3.99 (m, 1H), 3.91 – 3.83 (m, 1H), 2.22 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 156.1, 143.2, 140.7, 137.5, 135.6, 132.5, 130.5, 130.1, 129.5, 128.6, 126.2, 121.6, 69.2, 62.6, 56.5, 48.2, 21.2, 13.7; The minor isomer :^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 6.5 Hz, 2H), 8.04 (d, J = 6.6 Hz, 2H), 7.25 – 7.22 (m, 3H), 7.09 (d, J = 8.1 Hz, 2H), 7.05 – 6.96 (m, 2H), 6.89 – 6.83 (m, 2H), 6.01 – 5.90 (m, 1H), 5.29 – 5.22 (m, 1H), 4.67 (d, J = 9.5 Hz, 1H), 4.13 – 4.06 (m, 1H), 3.97 – 3.91 (m, 1H), 2.20 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 156.1, 143.4, 140.7, 137.52, 135.5, 134.7, 132.5, 130.8, 129.5, 128.4, 126.1, 121.6, 69.6, 62.6,

57.3, 48.2, 21.2, 13.7; HRMS-ESI (m/z) calculated for $C_{26}H_{28}NO_2S^+$ $[M\text{-}BF_4^-]^+$ 418.1835, found 418.1841.

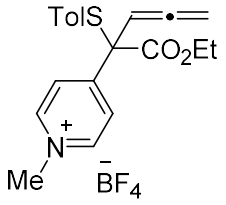
4-(2-(benzylthio)-1-ethoxy-1-oxopent-4-en-2-yl)-1-methylpyridin-1-ium tetrafluoroborate (9c)



9c

9c : Followed **One-pot procedure**. Reddish brown solid (90.2 mg, 70%), mp 100-102 ^oC; R_f 0.45 (DCM/MeOH= 30/1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 6.5 Hz, 2H), 7.96 (d, J = 6.4 Hz, 2H), 7.23 – 7.06 (m, 5H), 5.60-5.5 (m, 1H), 5.04 (d, J = 10.1 Hz, 1H), 4.92 (d, J = 16.9 Hz, 1H), 4.35 (s, 3H), 4.30-4.25 (m, 2H), 3.68 (s, 2H), 3.08-3.03 (m, 1H), 2.78-2.73 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 158.3, 144.4, 135.7, 130.1, 129.4, 128.6, 128.0, 127.5, 121.6, 63.0, 60.1, 48.0, 42.4, 35.6, 14.0; HRMS-ESI (m/z) calculated for $C_{20}H_{24}NO_2S^+$ $[M\text{-}BF_4^-]^+$ 342.1522, found.342.1523.

4-(1-ethoxy-1-oxo-2-(p-tolylthio)penta-3,4-dien-2-yl)-1-methylpyridin-1-ium tetrafluoroborate (9d)



9d

9d : Followed **One-pot procedure**. Reddish brown solid (71.2 mg, 78%), mp 96-98 ^oC; R_f 0.45 (DCM/MeOH= 30/1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 6.2 Hz, 2H), 8.01 (d, J = 6.1 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 7.7 Hz, 2H), 5.73 (t, J = 6.6 Hz, 1H), 4.89-4.77 (m, 2H), 4.41 (s, 3H), 4.24 – 3.99 (m, 2H), 2.28 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 167.7, 158.1, 144.7, 141.3, 136.9, 130.1, 128.1, 125.4, 91.8, 63.4, 62.9, 48.2, 21.3, 13.8; HRMS-ESI (m/z) calculated for $C_{20}H_{22}NO_2S^+$ $[M\text{-}BF_4^-]^+$ 340.1366, found 340.1368.

V. Reduction reaction of product 5, 6 or 9

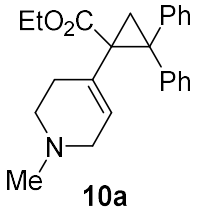
General Procedure[8]

To a solution of pyridinium salt **5**, **6** or **9** (1 equiv.) in MeOH : H_2O (9:1, 2.5 mL/mmol of pyridinium salt) was added $NaBH_4$ (3 equiv.) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, then allowed to warm to room temperature over 1 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. DCM (5 mL) was added and the

aqueous phase was extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine, dried over anhydrous $NaSO_4$ and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (PE:EA:TEA) to afford the corresponding tetrahydropyridines **10a-f**.

ethyl 1-(1-methyl-1,2,3,6-tetrahydropyridin-4-yl)-2,2-diphenylcyclopropane

-1-carboxylate (10a)

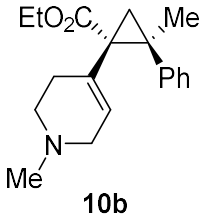


10a

10a: colorless oil, yield 67%; R_f = 0.60 (PE:EA:TEA = 5:1:0.02); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.29 (s, 2H), 7.25 – 7.20 (m, 1H), 7.20 – 7.09 (m, 5H), 5.72 – 5.59 (m, 1H), 3.96 – 3.82 (m, 1H), 3.82 – 3.65 (m, 1H), 3.15-3.10 (m, 1H), 2.84 – 2.61 (m, 2H), 2.51-2.46 (m, 1H), 2.37 (d, *J* = 5.5 Hz, 1H), 2.24 (d, *J* = 5.5 Hz, 1H), 2.21 (s, 3H), 1.72 – 1.54 (m, 2H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 141.8, 139.2, 132.0, 130.3, 128.7, 128.2, 127.6, 126.9, 126.4, 126.3, 60.8, 54.4, 51.8, 45.2, 43.8, 43.3, 29.4, 22.4, 13.8; HRMS-ESI (m/z) calculated for $C_{24}H_{28}NO_2^+$ $[M+H]^+$ 362.2115, found 362.2123.

ethyl 2-methyl-1-(1-methyl-1,2,3,6-tetrahydropyridin-4-yl)

-2-phenylcyclopropane-1-carboxylate (10b)

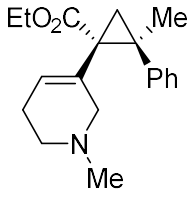


10b

10b: colorless oil, yield 68%; R_f = 0.40 (PE:EA:TEA = 5:1:0.02); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.30 – 7.16 (m, 5H), 5.70 – 5.67 (m, 1H), 4.26 – 4.12 (m, 2H), 3.28 – 3.18 (m, 1H), 2.41 – 2.35 (m, 1H), 2.17 – 2.05 (m, 2H), 2.02 (s, 1H), 2.01 – 1.94 (m, 1H), 1.87 (d, *J* = 5.7 Hz, 1H), 1.62 (d, *J* = 5.7 Hz, 1H), 1.57 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 171.2, 140.8, 131.6, 127.97, 127.7, 126.51, 126.50, 61.0, 55.8, 50.6, 44.4, 41.7, 32.1, 25.0, 22.0, 21.8, 14.3. HRMS-ESI (m/z) calculated for $C_{19}H_{26}NO_2^+$ $[M+H]^+$ 300.1958, found 300.1960.

ethyl 2-methyl-1-(1-methyl-1,4,5,6-tetrahydropyridin-3-yl)

-2-phenylcyclopropane-1-carboxylate (10c)

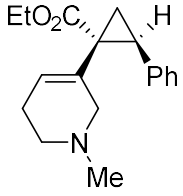


10c

10c: colorless oil, yield 61%; R_f = 0.50 (PE:EA:TEA = 5:1:0.02); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.14 (m, 5H), 5.52 – 5.50 (m, 1H), 4.24 – 4.11 (m, 2H), 3.09 – 3.03 (m, 1H), 2.62 – 2.57 (m, 1H), 2.49 – 2.35 (m, 2H), 2.15 (s, 3H), 1.89 (d, *J* = 5.7 Hz, 1H), 1.62 (d, *J* = 5.7 Hz, 1H), 1.58 (s, 3H), 1.56 – 1.48 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.37, 140.68, 132.04, 127.98, 127.55, 126.31, 125.57, 60.85, 54.35, 51.75, 45.20, 42.90, 32.46, 28.97, 21.85, 21.82, 14.34. HRMS-ESI (m/z) calculated for $C_{19}H_{26}NO_2^+$ $[M+H]^+$ 300.1953, found 300.1958.

ethyl 1-(1-methyl-1,2,3,6-tetrahydropyridin-4-yl)-2-phenylcyclopropane

-1-carboxylate (10d)

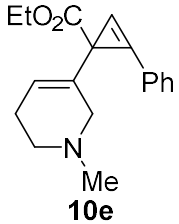


10d

10d: colorless oil, yield 76%; R_f = 0.50 (PE:EA:TEA = 5:1:0.02); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.22 – 7.08 (m, 3H), 7.04 – 6.89 (m, 2H), 4.25 – 3.97 (m, 2H), 2.96 (d, *J* = 15.7 Hz, 1H), 2.86 (t, *J* = 8.2 Hz, 1H), 2.44 – 2.32 (m, 1H), 2.21 – 2.08 (m, 1H), 1.98 (s, 2H), 1.98 (s, 3H), 1.96 – 1.91 (m, 1H) 1.86-1.81 (m, 1H), 1.75 – 1.56 (m, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 173.5, 136.3, 130.8, 128.0, 127.8, 126.9, 126.6, 61.2, 56.3, 50.96, 45.1, 36.6, 31.5, 25.5, 19.3, 14.3; HRMS-ESI (m/z) calculated for $C_{18}H_{24}NO_2^+$ $[M+H]^+$ 286.1802, found 286.1804.

ethyl 1-(1-methyl-1,2,5,6-tetrahydropyridin-3-yl)-2-phenylcycloprop-2-ene

-1-carboxylate (10e)

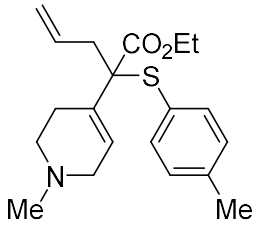


10e

10e: colorless oil, yield 65%; R_f = 0.60 (PE:EA:TEA = 5:1:0.02); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.55 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.31 (m, 3H), 7.08 (d, *J* = 2.1 Hz, 1H), 5.70 (t, *J* = 3.4 Hz, 1H), 4.13 (q, *J* = 6.8 Hz, 2H), 3.20 – 2.93 (m, 2H), 2.54 – 2.27 (m, 4H), 2.36 (s, 3H), 1.22-1.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.42, 136.64, 129.76, 128.79, 125.99, 122.04, 117.75, 116.67, 100.98, 60.74, 56.37, 51.46, 45.65, 29.71, 25.72, 14.32; HRMS-ESI (m/z) calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found

284.1647.

ethyl 2-(1-methyl-1,2,3,6-tetrahydropyridin-4-yl)-2-(p-tolylthio)pent-4-enoate (10f)



10f

10f: colorless oil, yield 60%; R_f = 0.60 (PE:EA:TEA = 5:1:0.02); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.04 (d, J = 7.7 Hz, 2H), 6.00-5.90 (m, 1H), 5.17 (t, J = 3.6 Hz, 1H), 5.09 – 5.01 (m, 2H), 4.22 – 3.99 (m, 2H), 3.02 – 2.93 (m, 1H), 2.78 – 2.70 (m, 1H), 2.61-2.57 (m, 1H), 2.47-2.35 (m, 3H), 2.27 (s, 6H), 2.12-2.05 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.58, 139.81, 137.95, 133.85, 132.99, 129.47, 127.60, 123.19, 118.66, 65.80, 62.01, 54.82, 52.28, 46.04, 38.11, 26.82, 21.63, 14.51; HRMS-ESI (m/z) calculated for $C_{20}H_{28}NO_2S$ $[M+H]^+$ 346.1835, found 346.1833.

VI. References

(1) (a) Schareina, T.; Zapf, A.; Cotte A. *Synthesis.* **2008**, 3351-3355; (b) Sreedhar, B.; Reddy, P. S.; Reddy, M. A. *Synthesis.* **2009**, *2009(10)*, 1732-1738; (c) Nandi, D.; Islam, R. U.; Devi, N. *New J. Chem.* **2018**, *42(2)*, 812-816.
(2) Frenette, R.; Blouin, M.; Brideau, C. *Bioorg. Med. Chem. Lett.* **2002**, *12(20)*, 3009-3013.
(3) Dey, A.; Hajra, A. *Org. Lett.* **2019**, *21(6)*, 1686-1689.
(4) Soli, E. D.; Manoso, A. S.; Patterson, M. C. *J. Org. Chem.* **1999**, *64(9)*, 3171-3177.
(5) Green, S. P.; Wheelhouse, K. M.; Payne, A. D.; Hallett, J. P.; Miller, P. W.; Bull, J. A. *Org. Proc. Res. Dev*. **2019**, *24*(1), 67-84.
(6) Pitters, J. L. *Can. J. Chem*. **2011**, *89*, 117–121.
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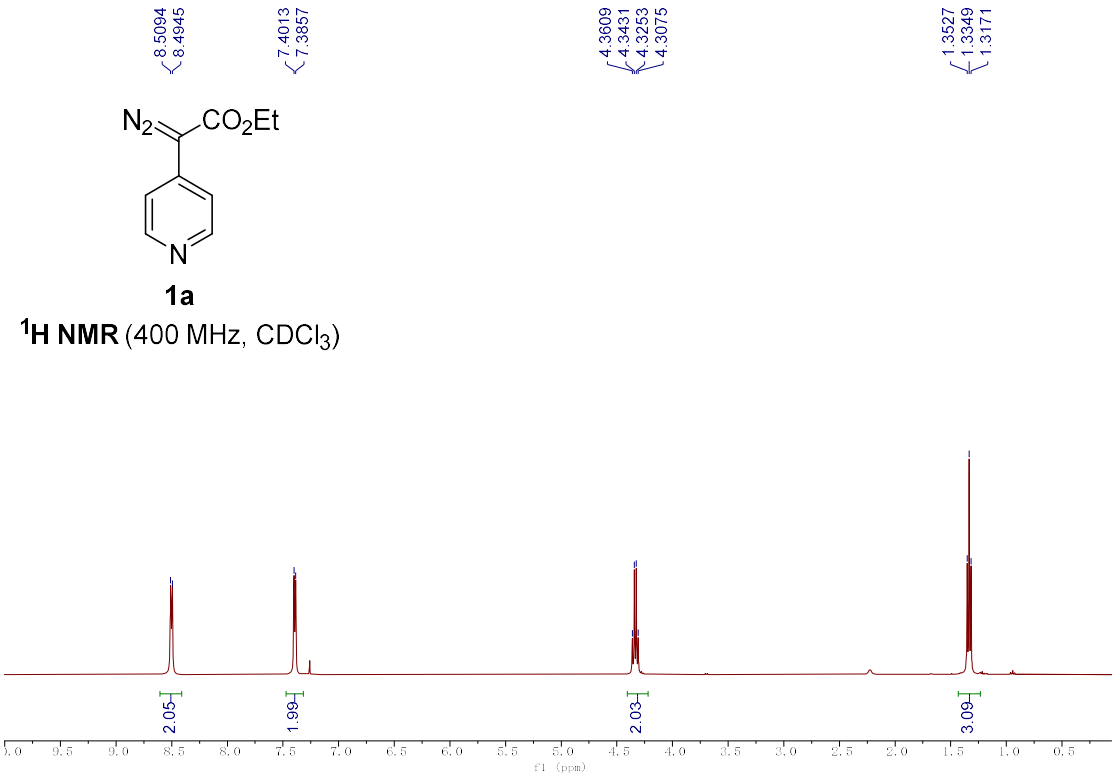
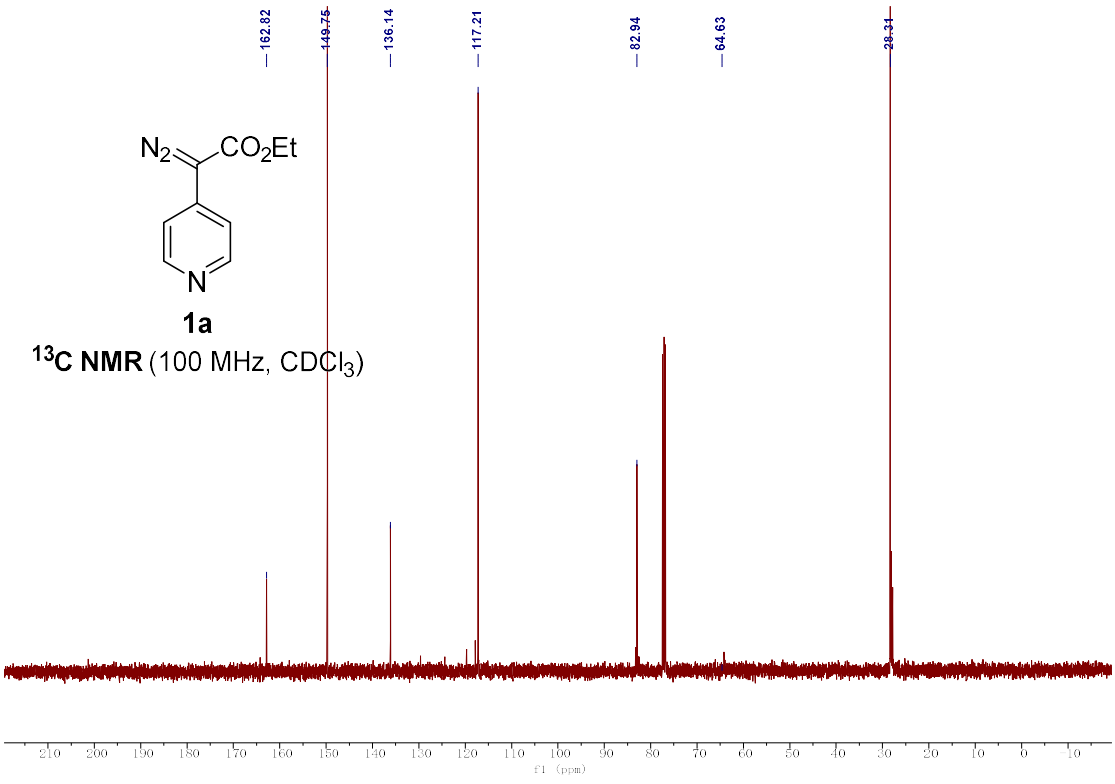
(8) Harawa, V.; Thorpe, T. W. *J. Am. Chem. Soc.* **2022**, *144(46)*, 21088-21095.

VII. ^{1}H and ^{13}C NMR spectra of compounds



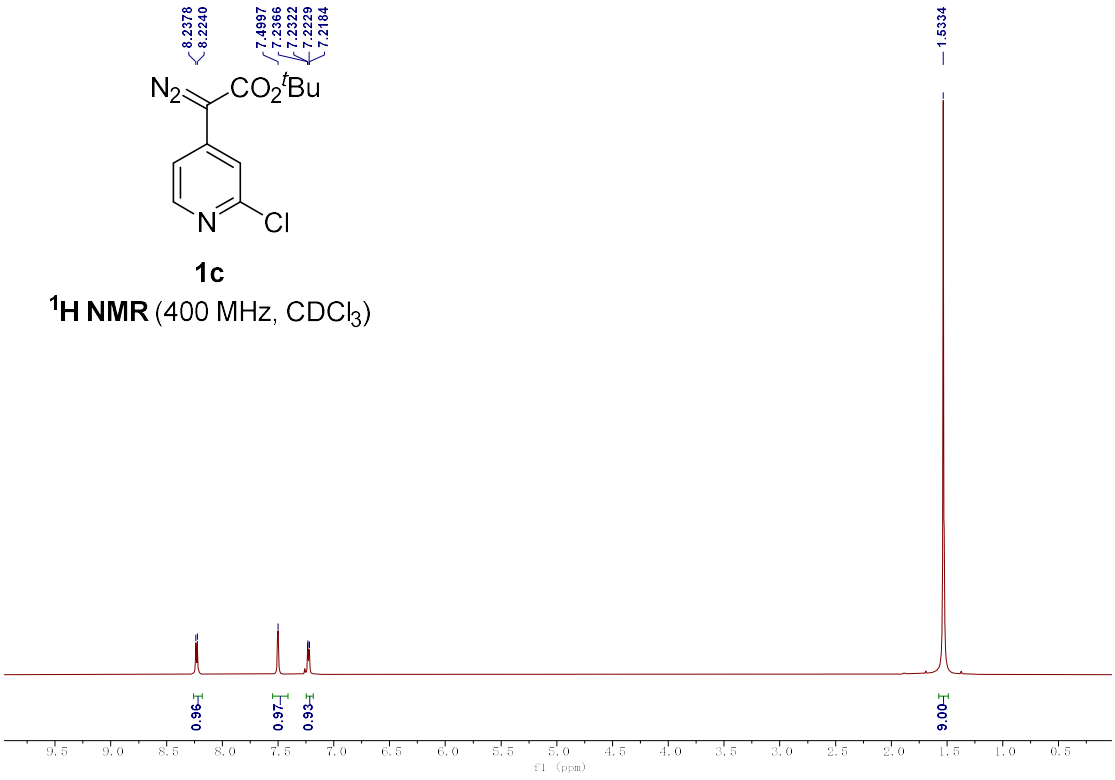
1a

^{1}H NMR (400 MHz, $CDCl_3$)



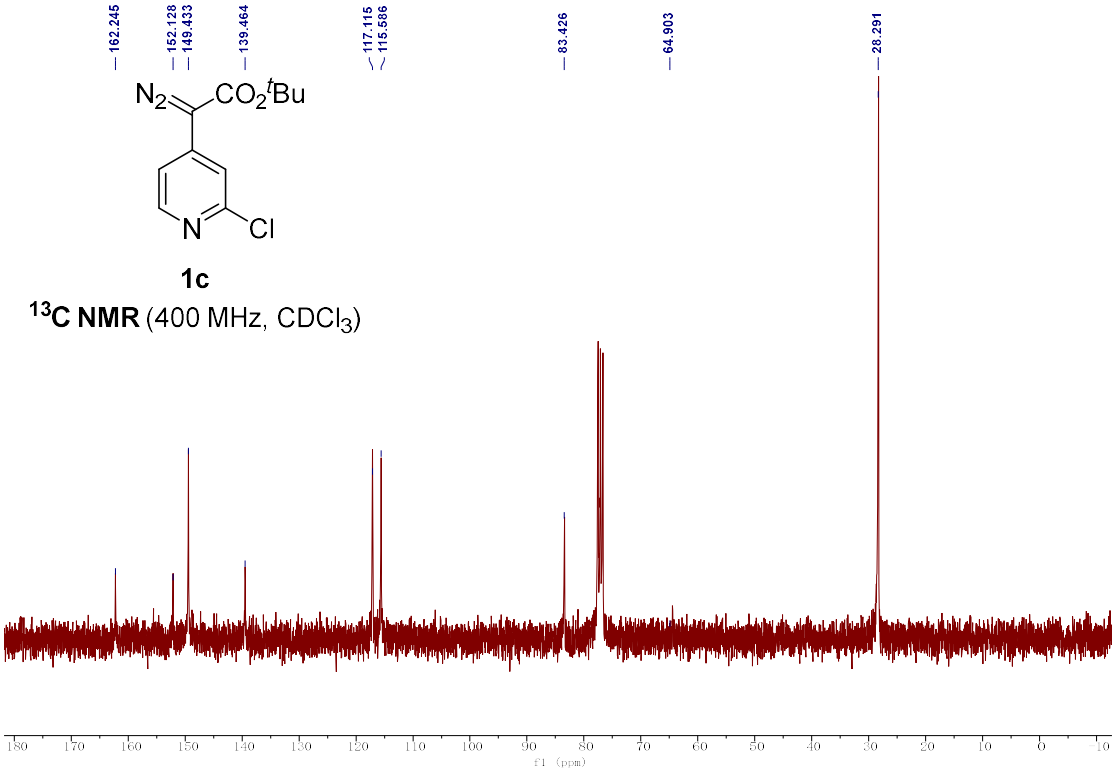
1a

^{13}C NMR (100 MHz, $CDCl_3$)



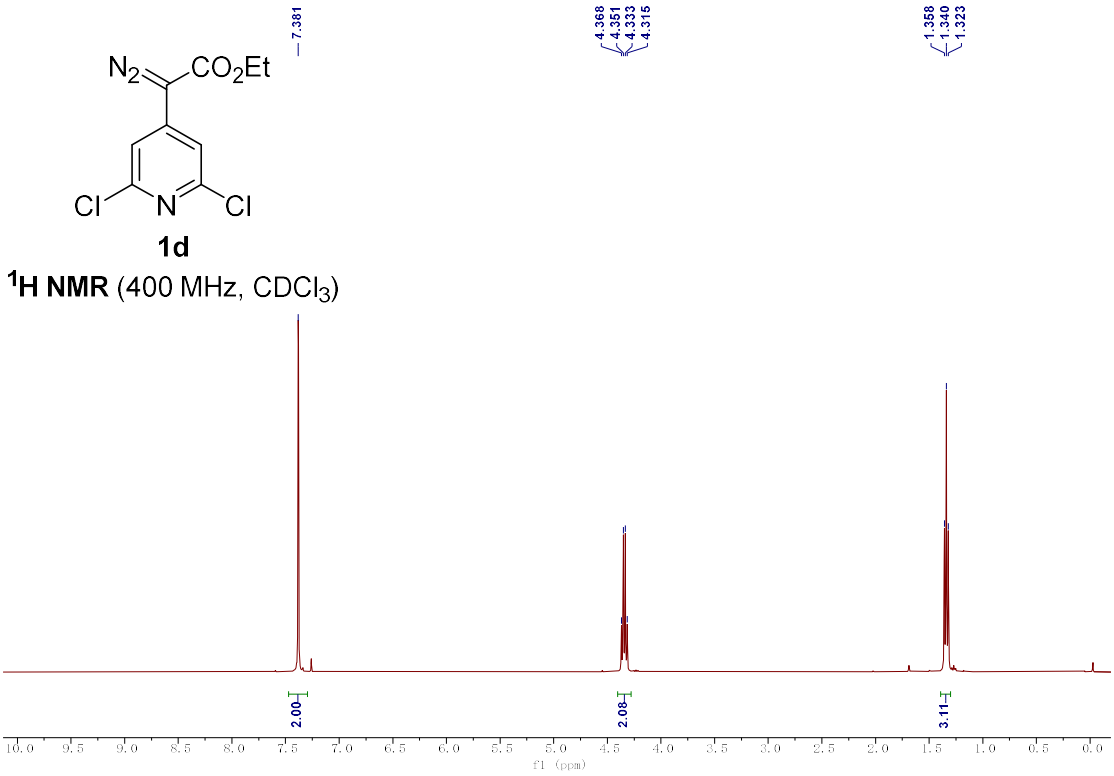
1c

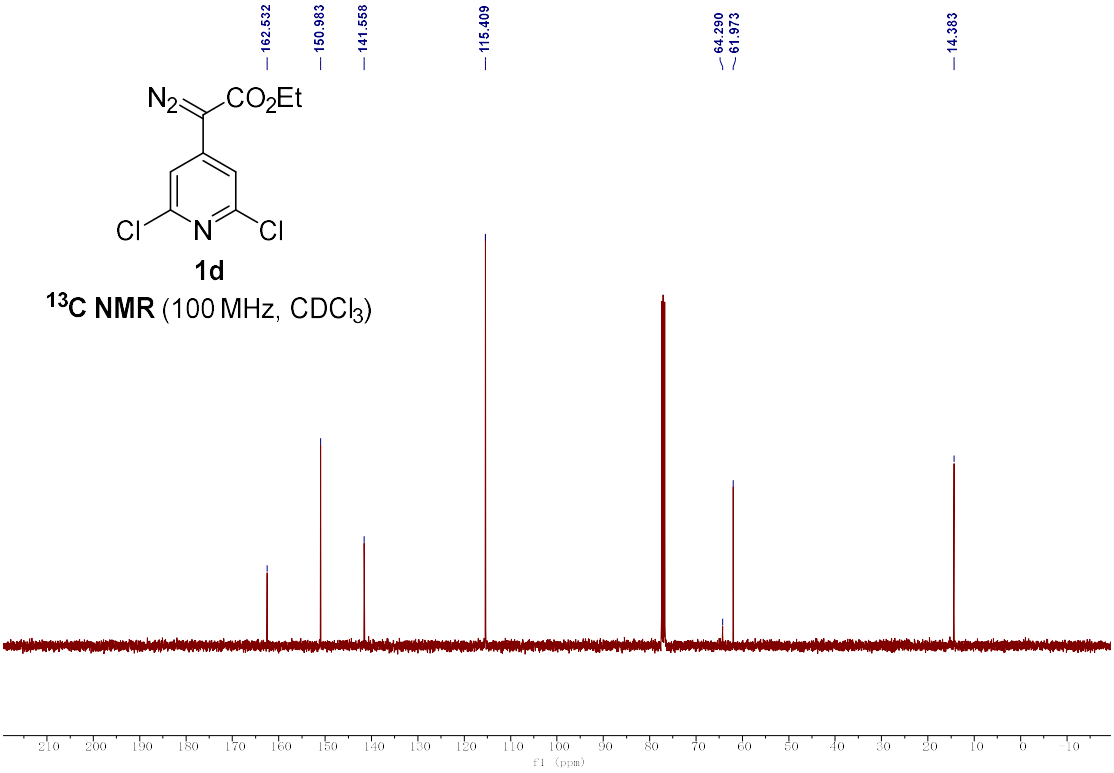
^{1}H NMR (400 MHz, $CDCl_3$)

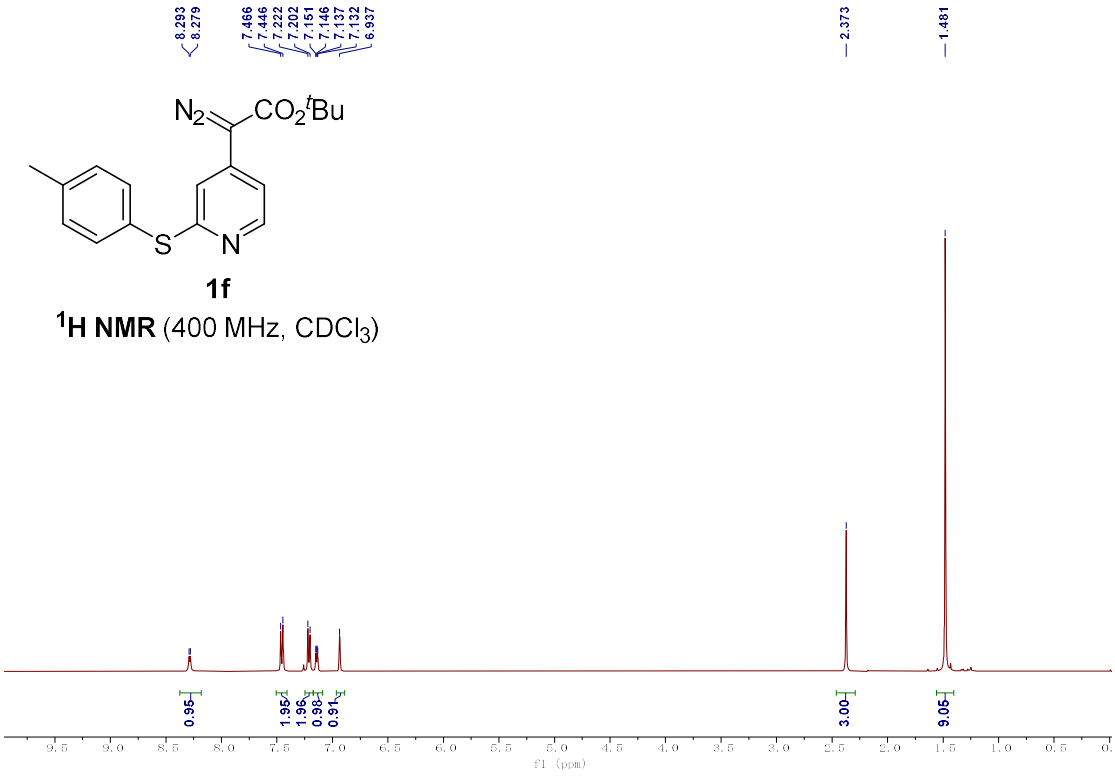


1c

^{13}C NMR (400 MHz, $CDCl_3$)

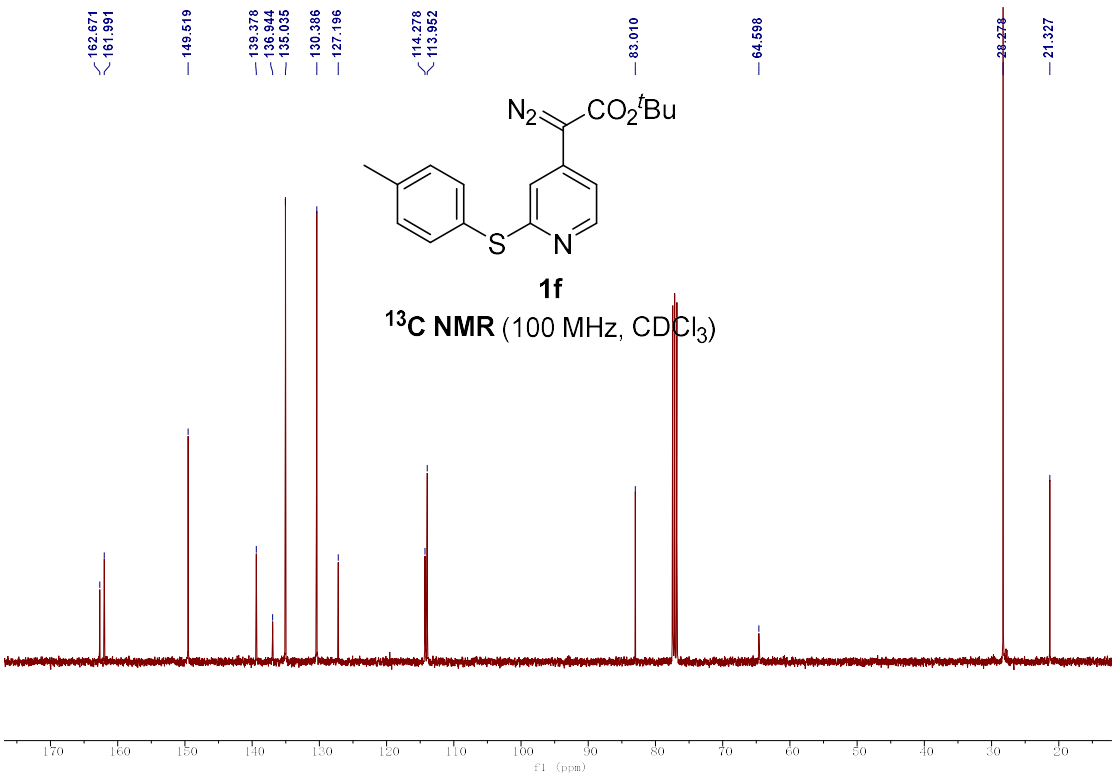

N2
CO2Et
Cl
N
Cl
1d
1H NMR (400 MHz, CDCl3)
7.381
4.368
4.351
4.333
4.315
1.358
1.340
1.323
2.00
2.08
3.11
f1 (ppm)


N2
CO2Et
Cl
N
Cl
1d
13C NMR (100 MHz, CDCl3)
162.532
150.983
141.558
115.409
64.290
61.973
14.383
f1 (ppm)



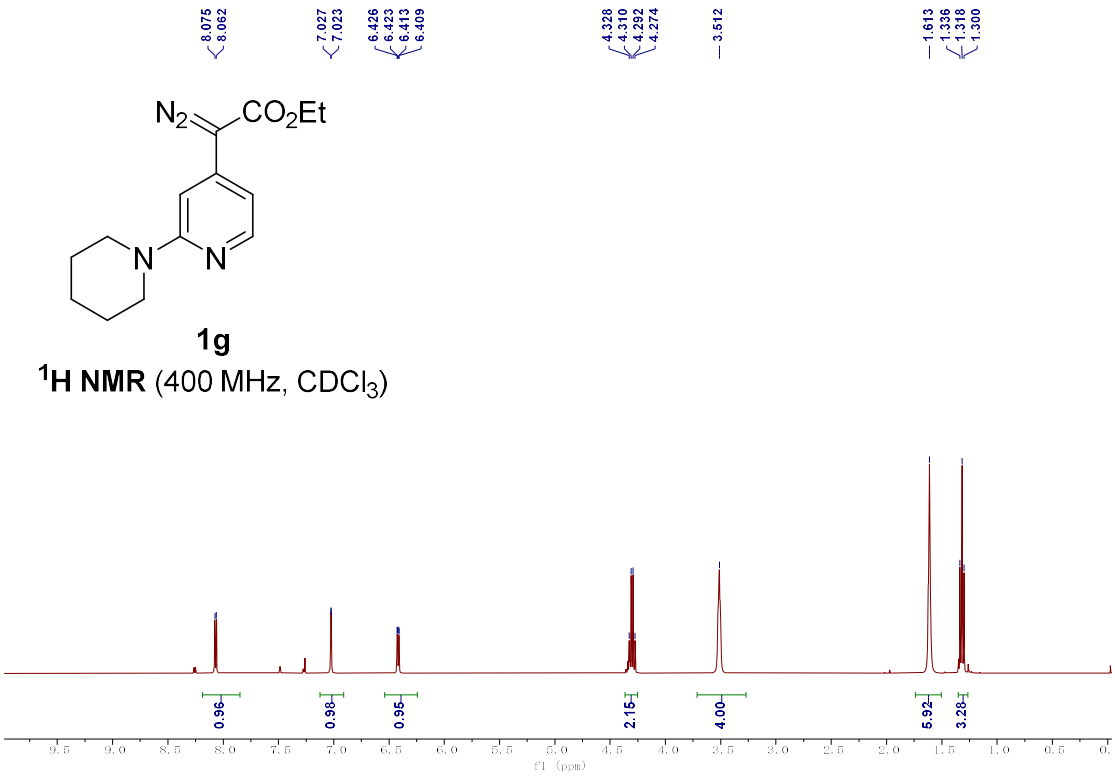
1f

^{1}H NMR (400 MHz, $CDCl_3$)



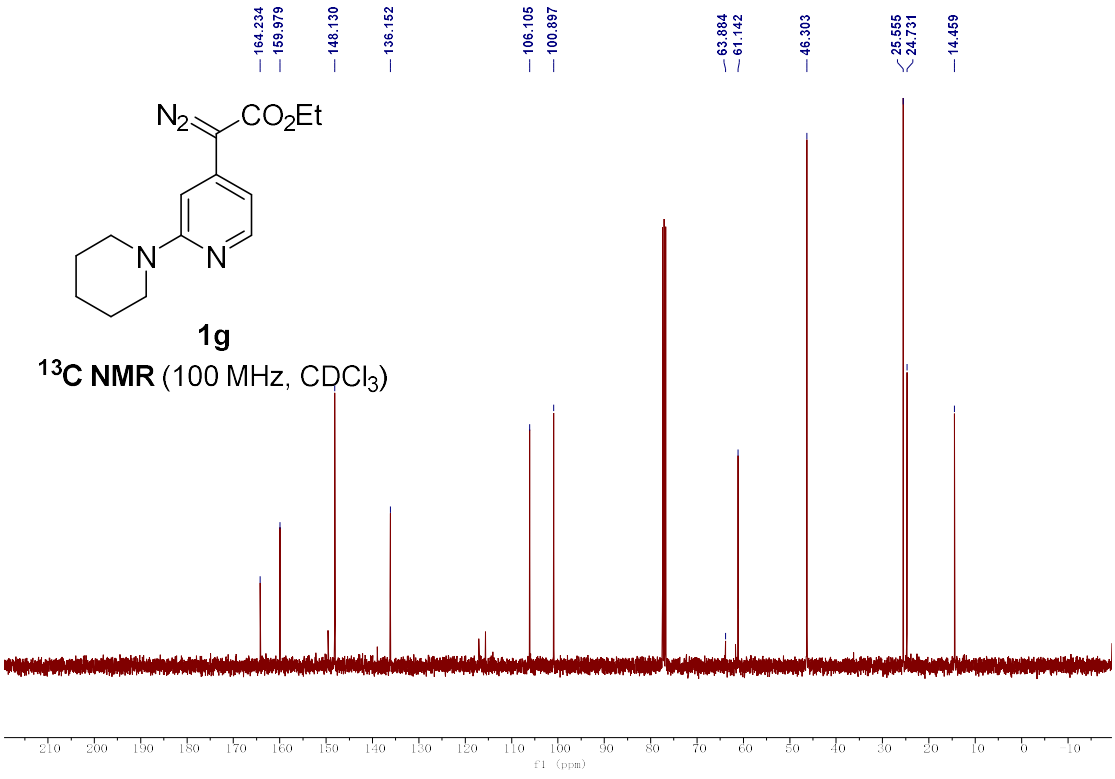
1f

^{13}C NMR (100 MHz, $CDCl_3$)



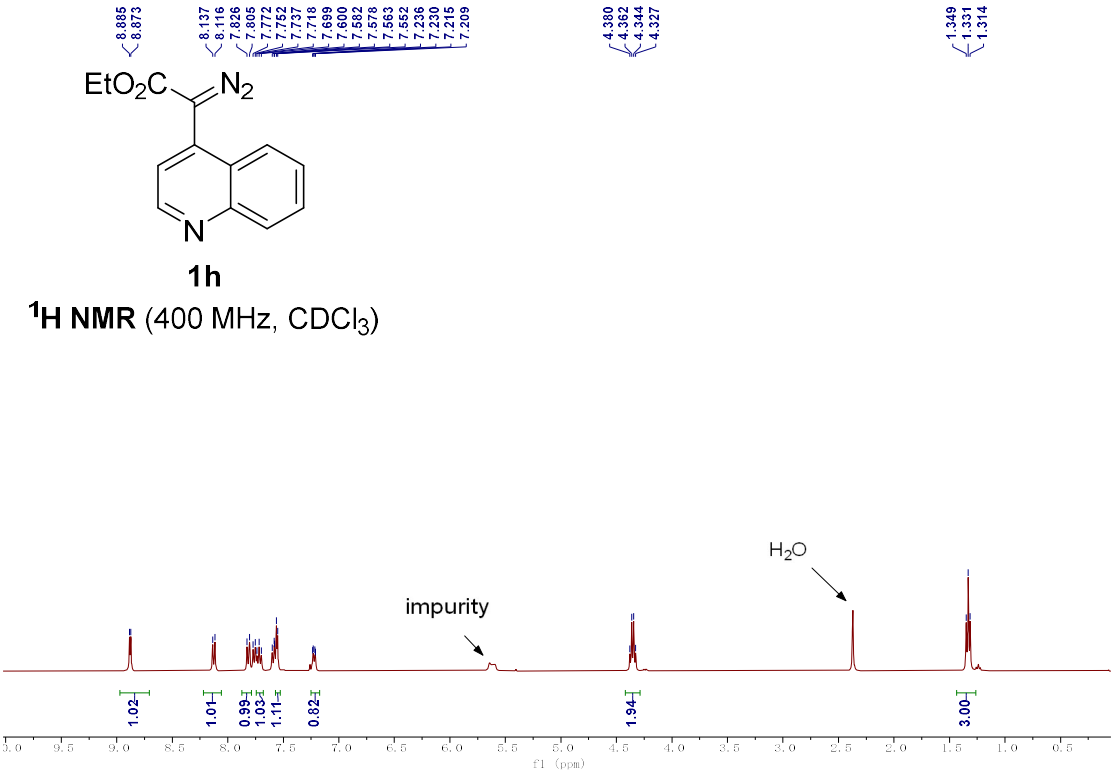
1g

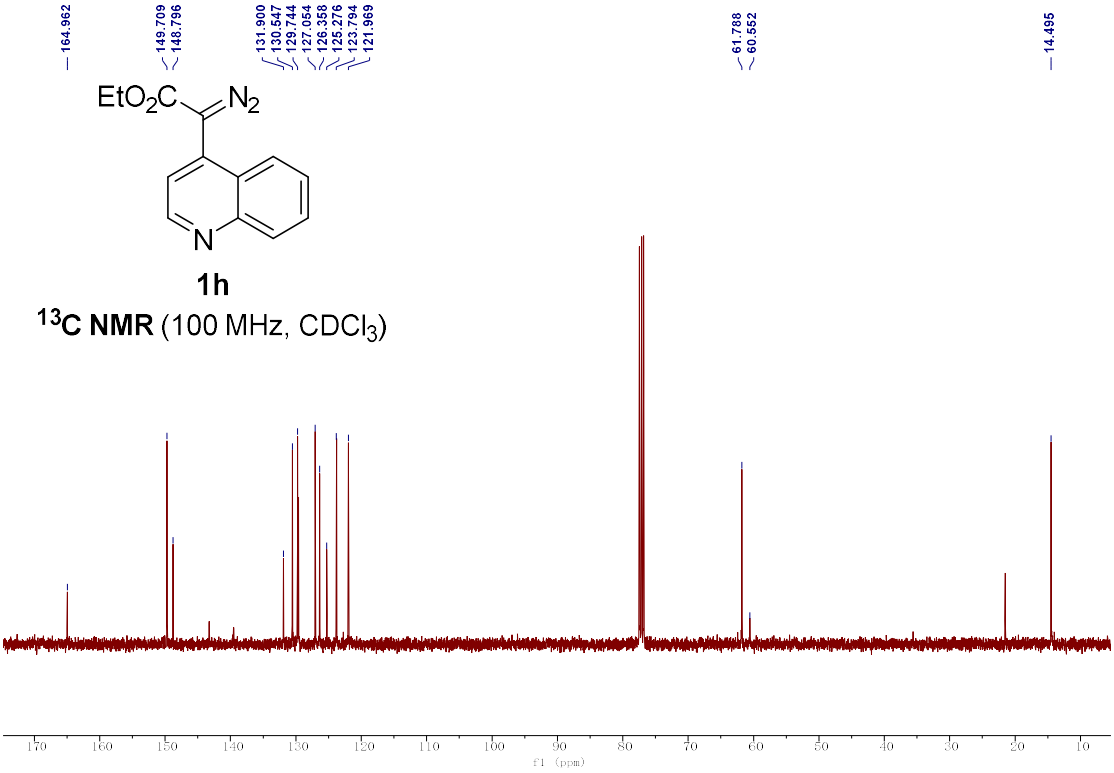
^{1}H NMR (400 MHz, $CDCl_3$)

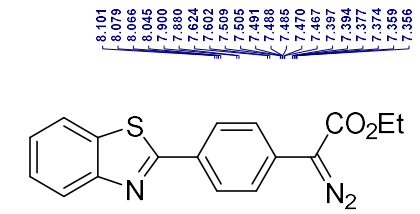


1g

^{13}C NMR (100 MHz, $CDCl_3$)

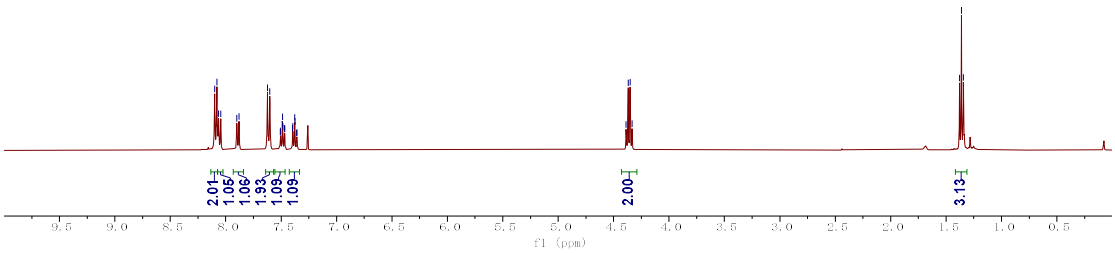

8.885
8.873
8.137
8.116
7.826
7.805
7.772
7.752
7.737
7.718
7.699
7.600
7.582
7.578
7.563
7.552
7.236
7.230
7.215
7.209
4.380
4.362
4.344
4.327
1.349
1.331
1.314
EtO2C
N2
N
1h
1H NMR (400 MHz, CDCl3)
H2O
impurity
1.02
1.01
0.99
1.03
1.11
0.82
1.94
3.00
f1 (ppm)

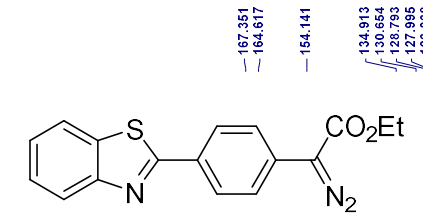

164.962
149.709
148.796
131.900
130.547
129.744
127.054
126.358
125.276
123.794
121.969
61.788
60.552
14.495
EtO2C
N2
N
1h
13C NMR (100 MHz, CDCl3)
f1 (ppm)



1j

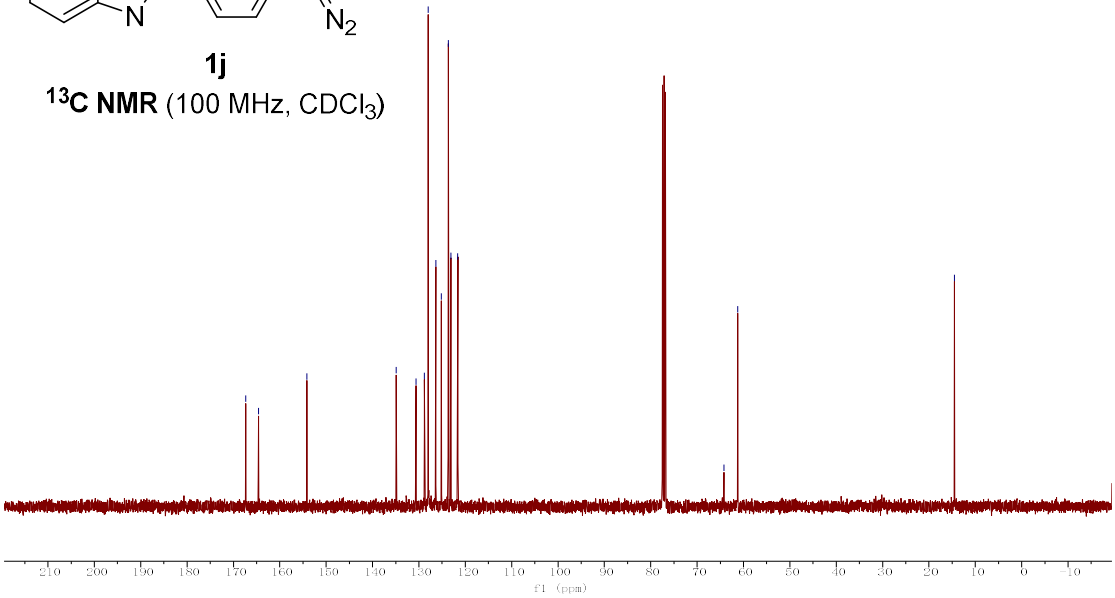
^{1}H NMR (400 MHz, $CDCl_3$)

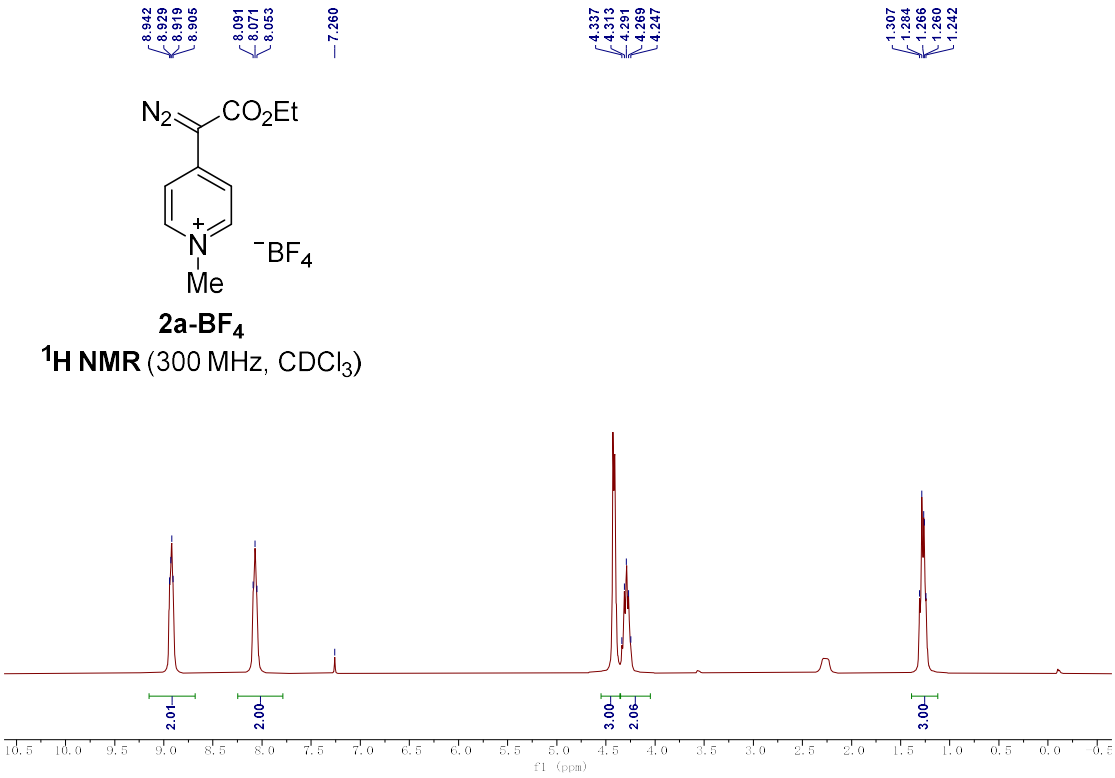




1j

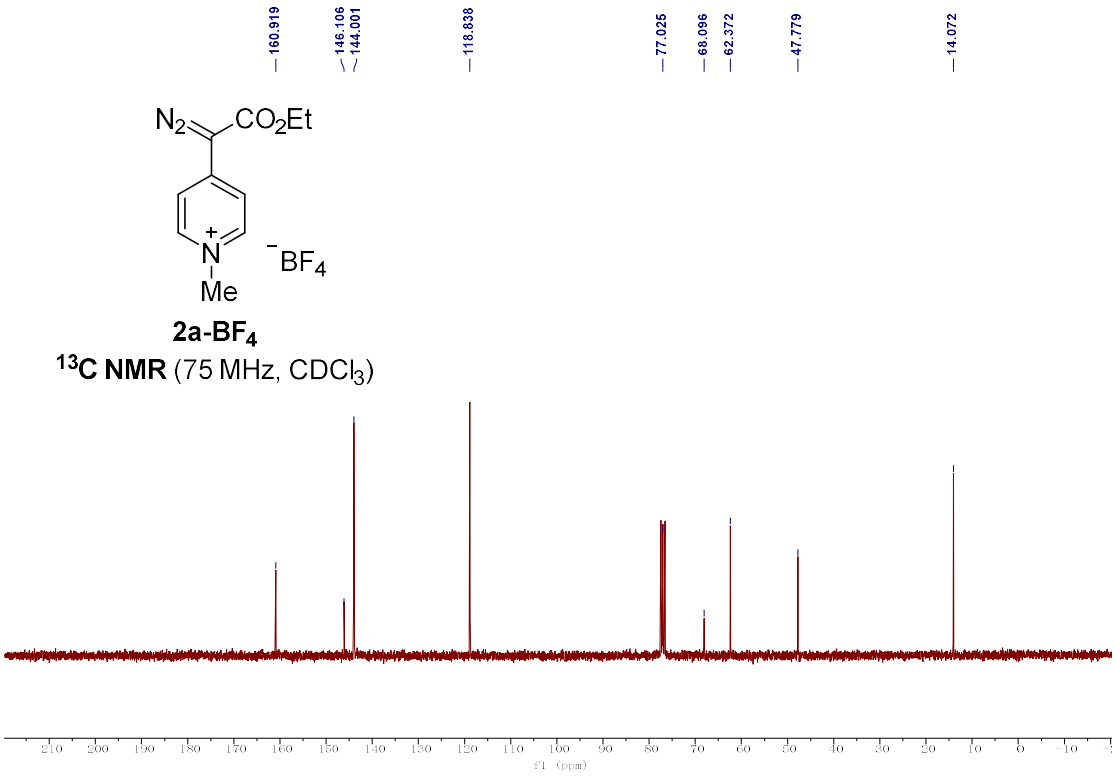
^{13}C NMR (100 MHz, $CDCl_3$)





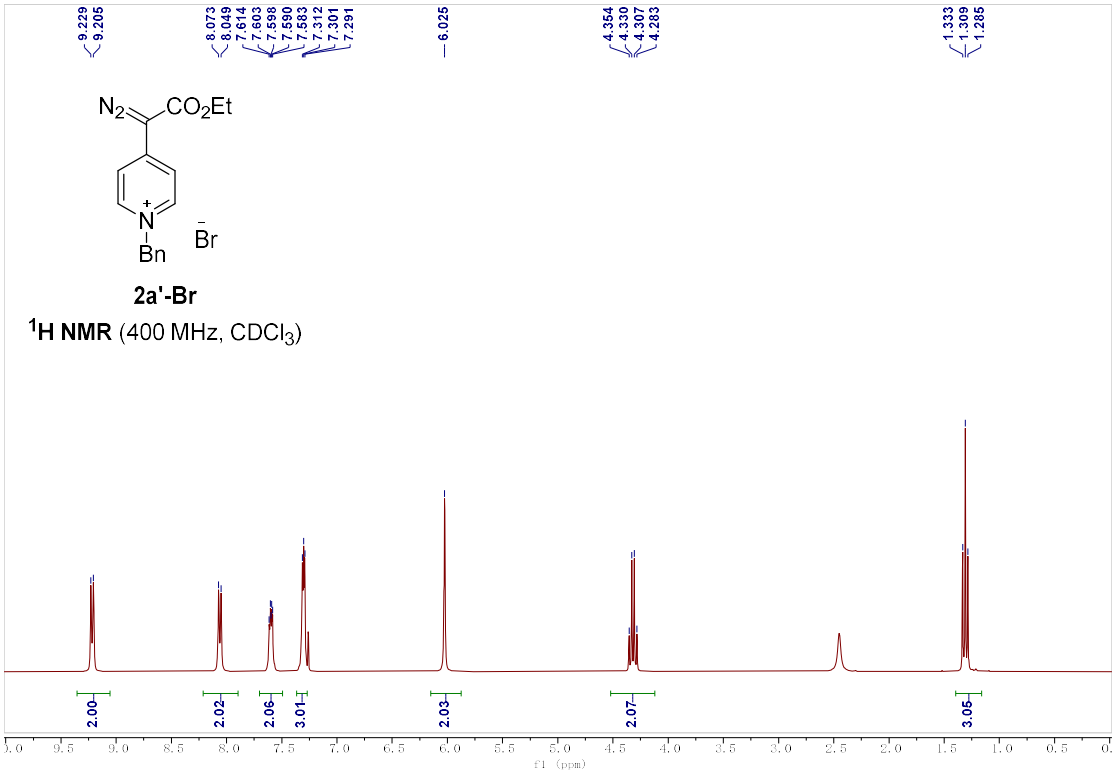
2a-BF_4

^{1}H NMR (300 MHz, $CDCl_3$)



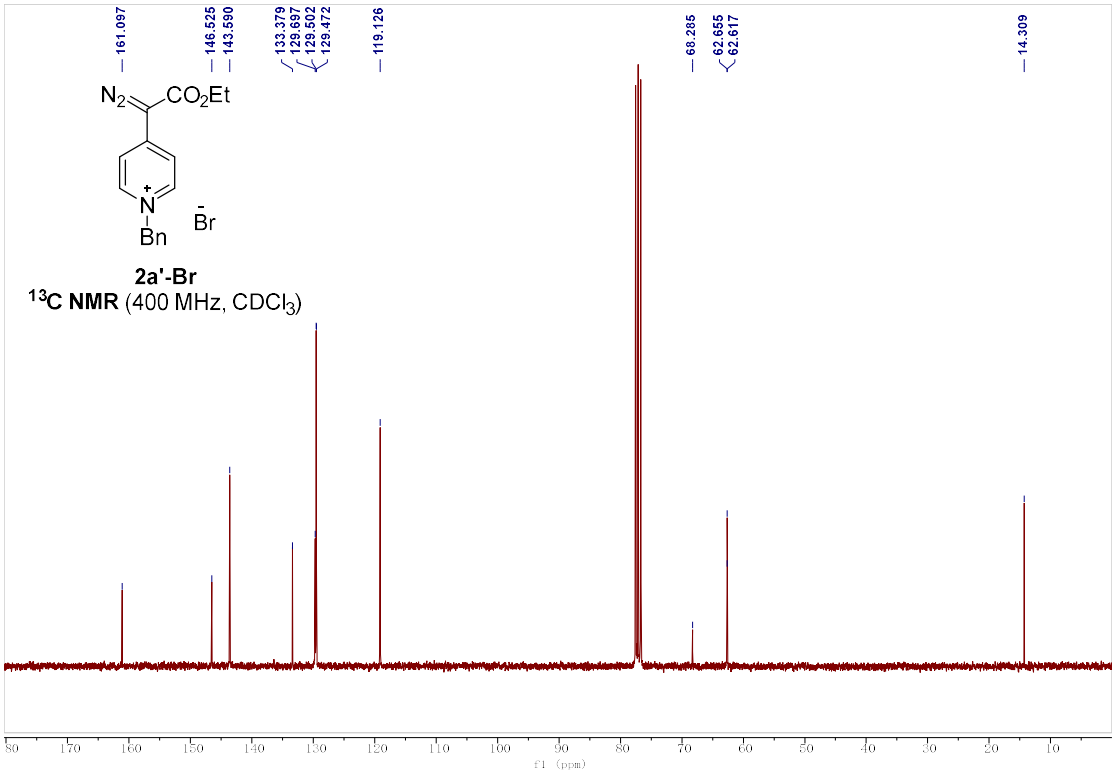
2a-BF_4

^{13}C NMR (75 MHz, $CDCl_3$)



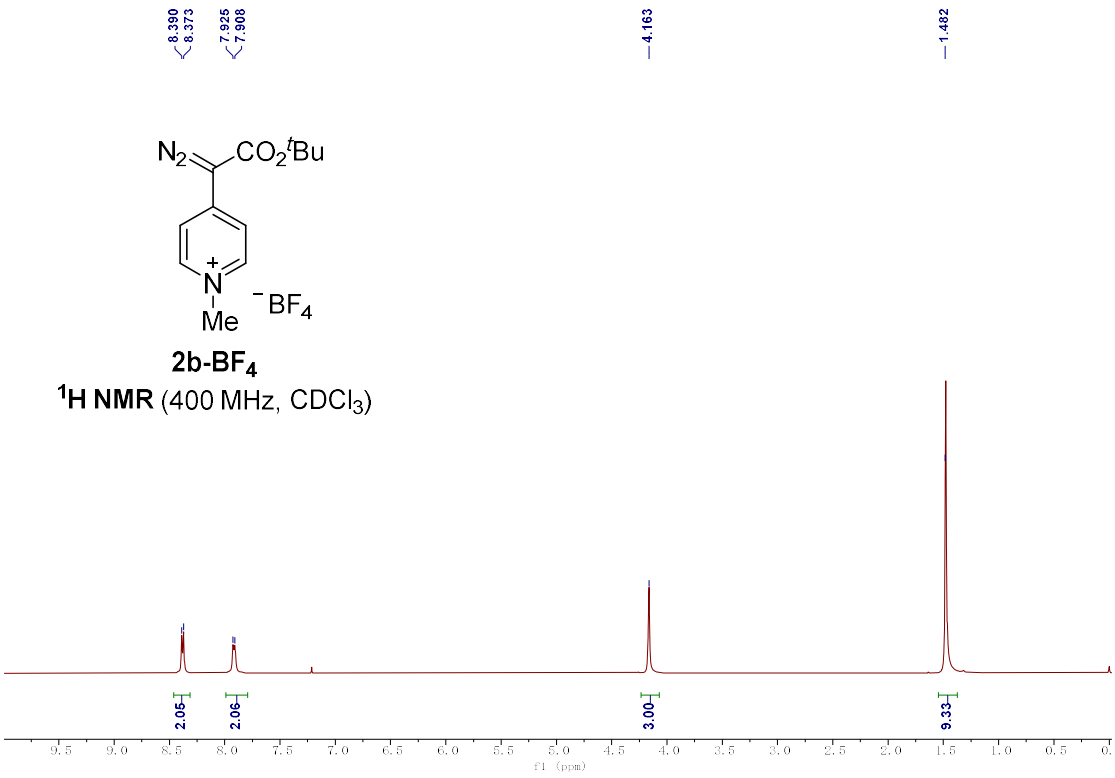
2a'-Br

^{1}H NMR (400 MHz, $CDCl_3$)



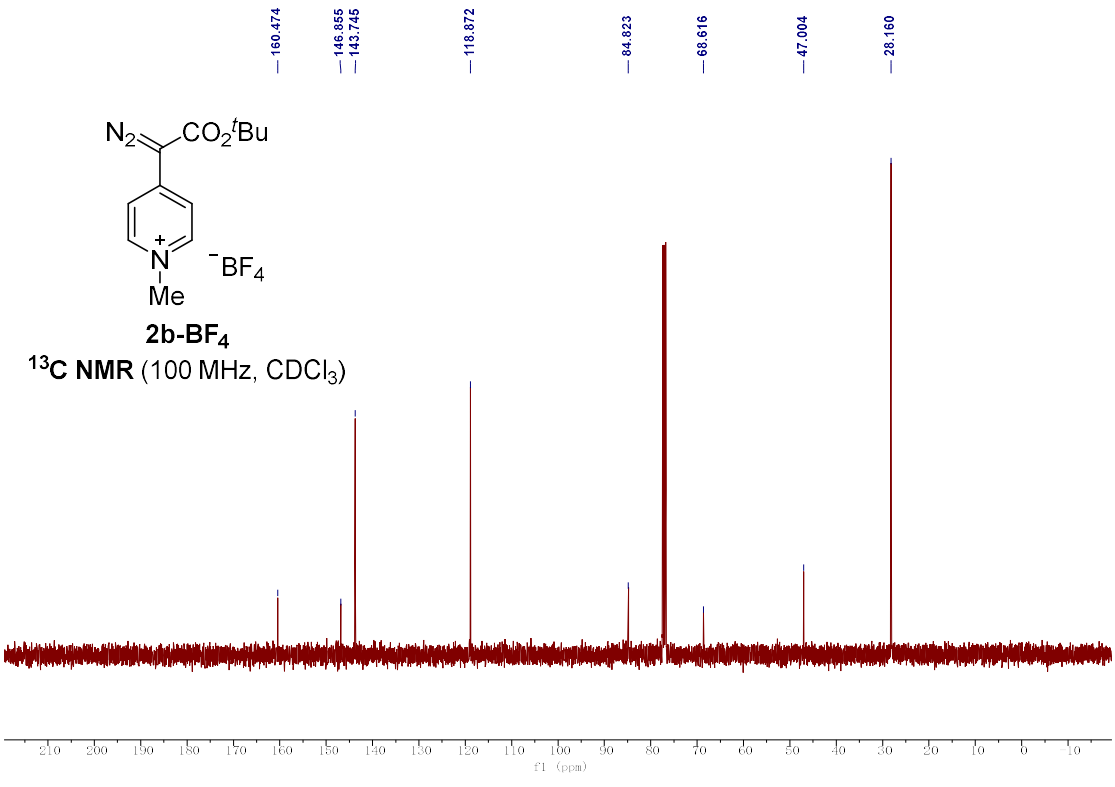
2a'-Br

^{13}C NMR (400 MHz, $CDCl_3$)



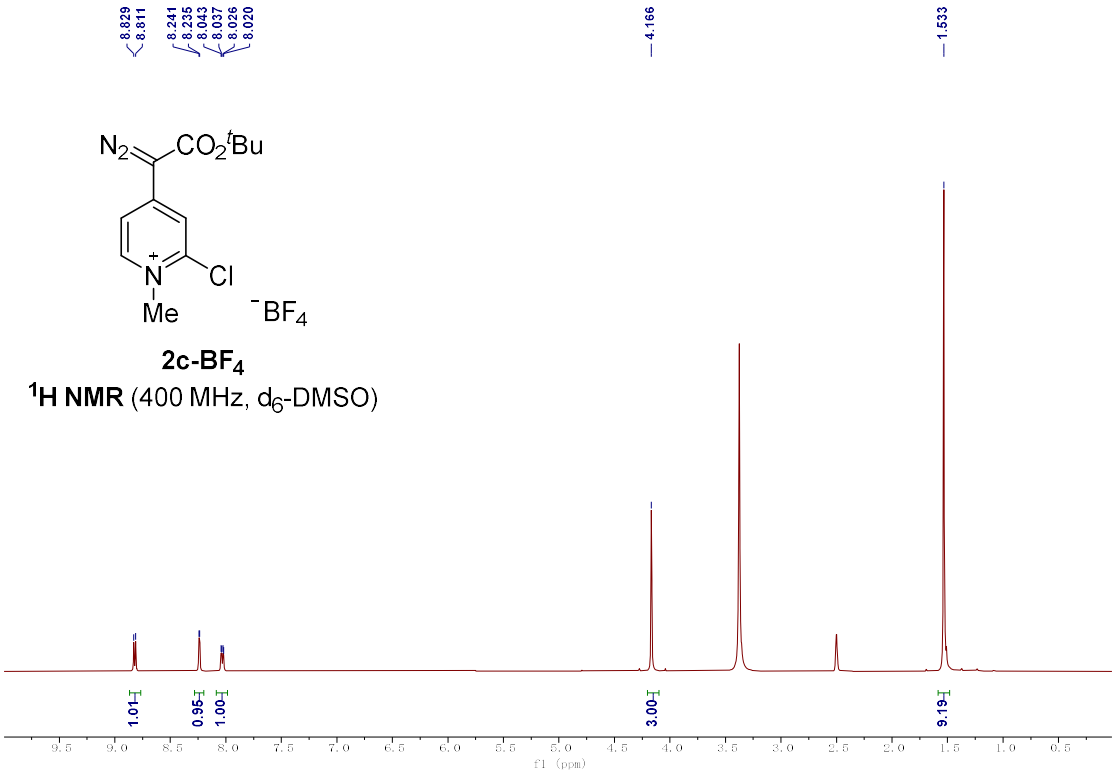
2b-BF_4

^{1}H NMR (400 MHz, $CDCl_3$)



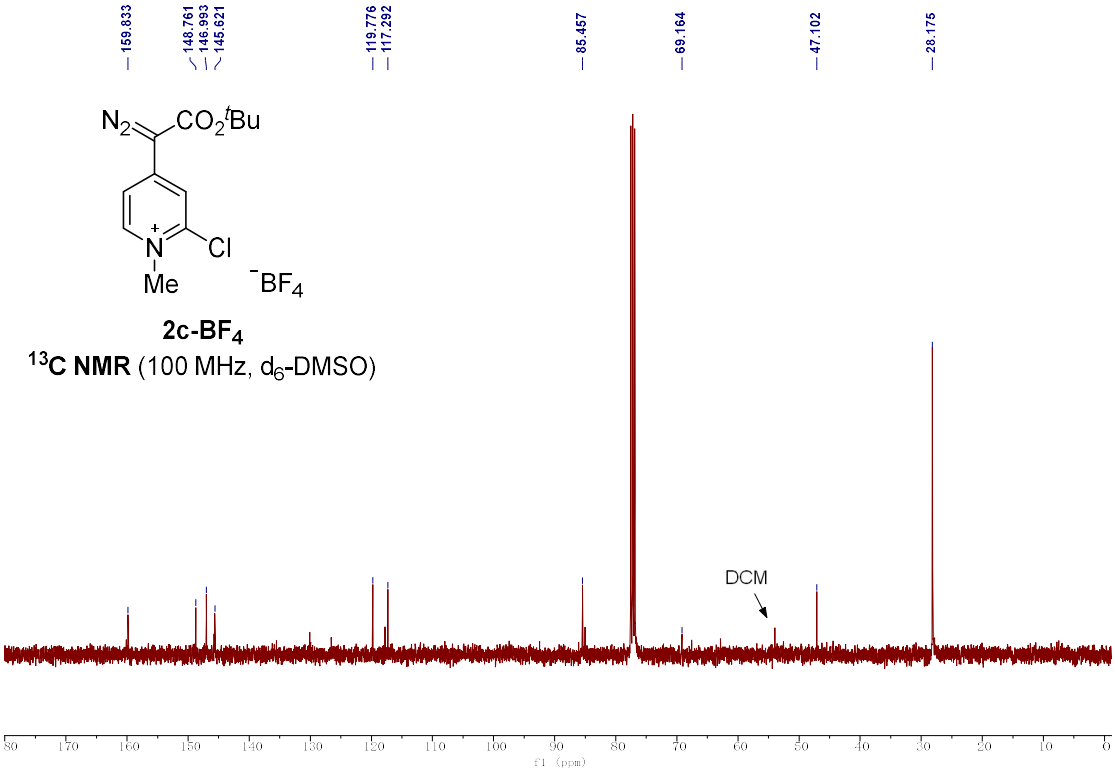
2b-BF_4

^{13}C NMR (100 MHz, $CDCl_3$)



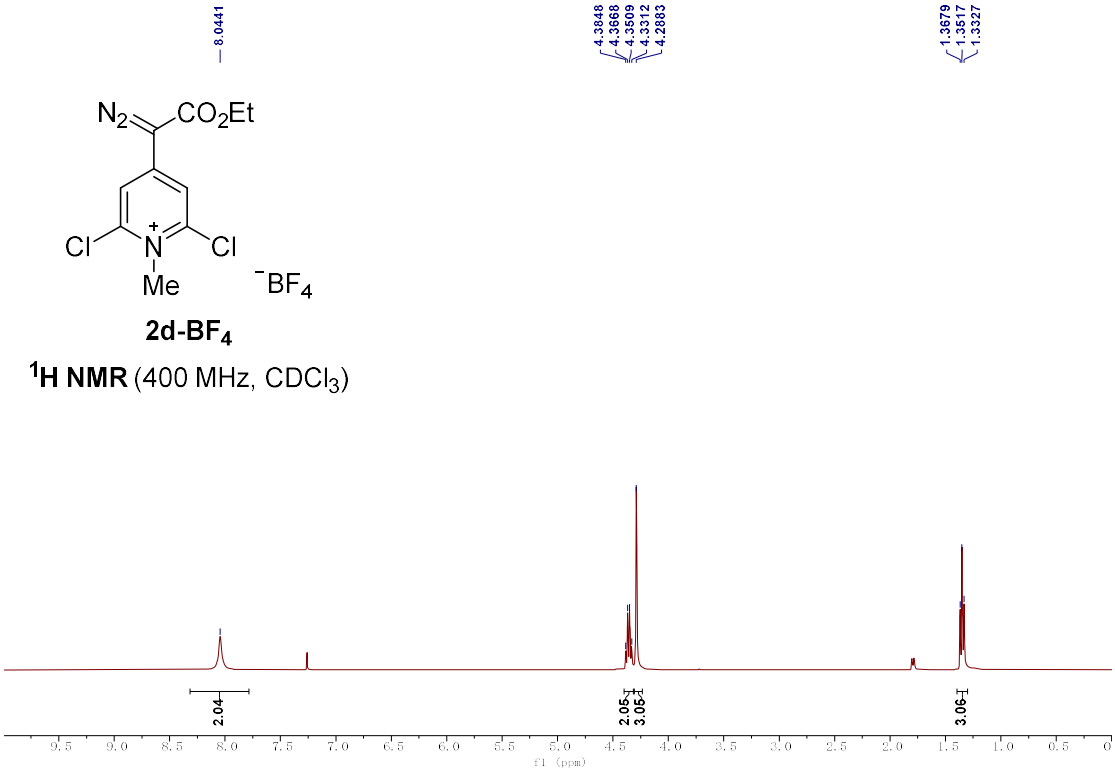
2c-BF_4

^{1}H NMR (400 MHz, d_6-DMSO)



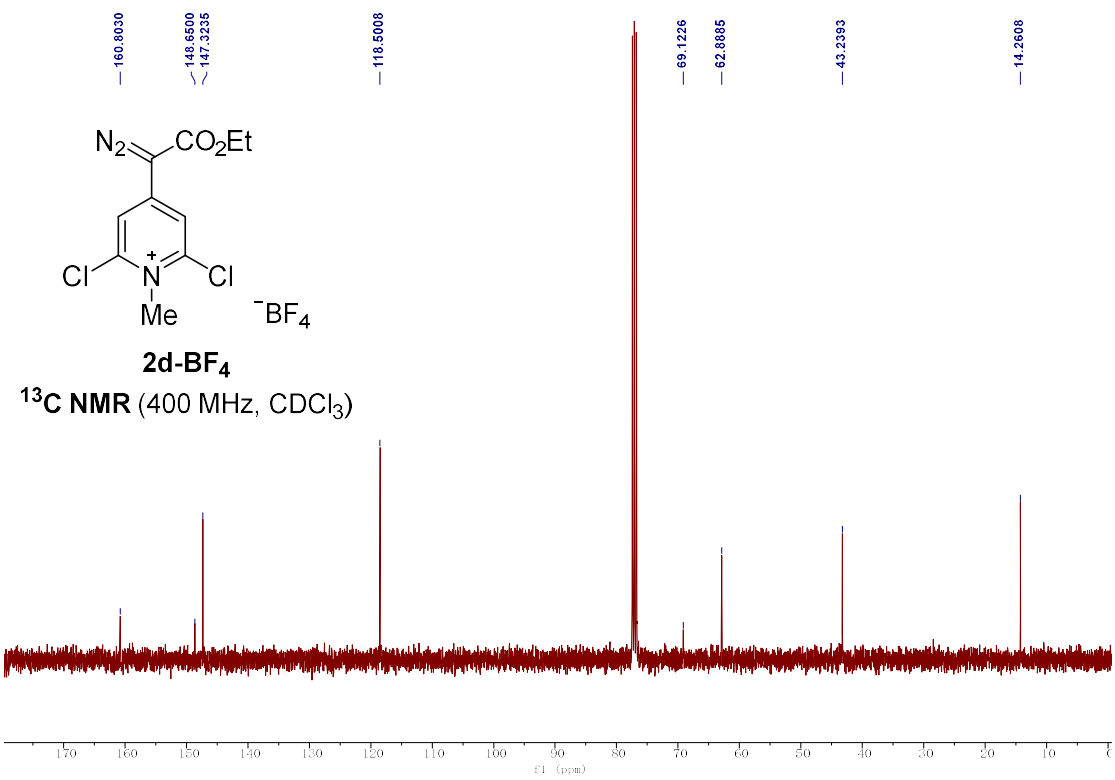
2c-BF_4

^{13}C NMR (100 MHz, d_6-DMSO)



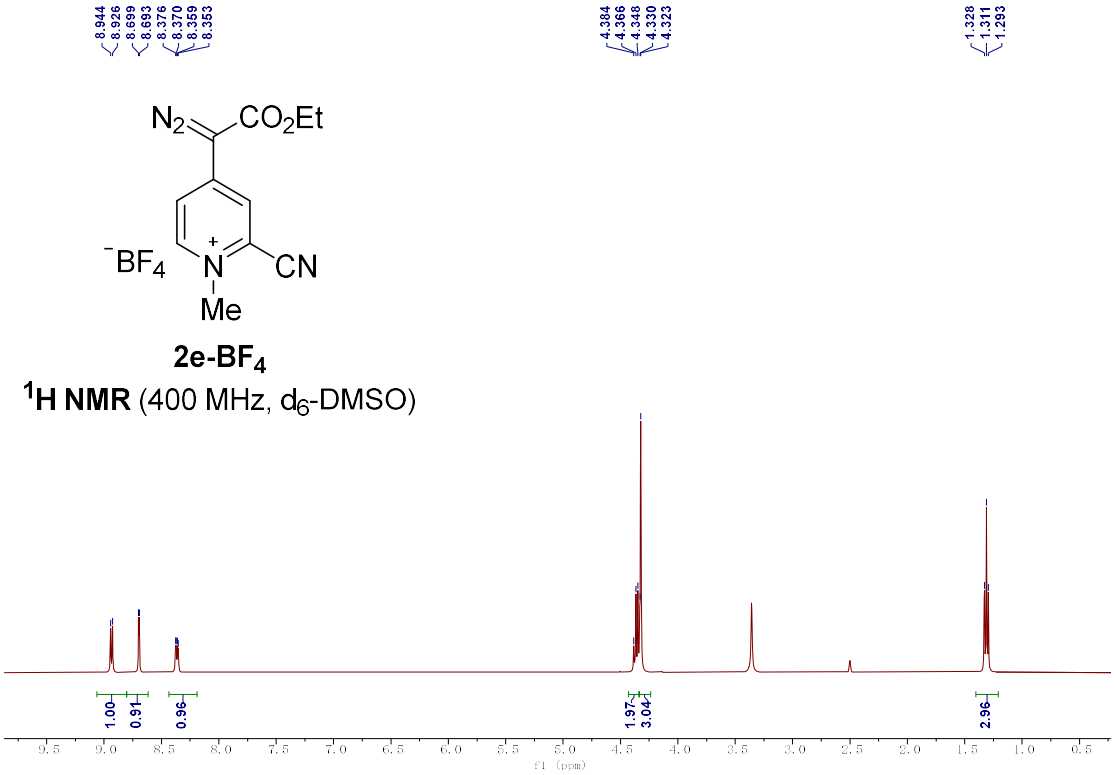
2d-BF_4

^{1}H NMR (400 MHz, $CDCl_3$)



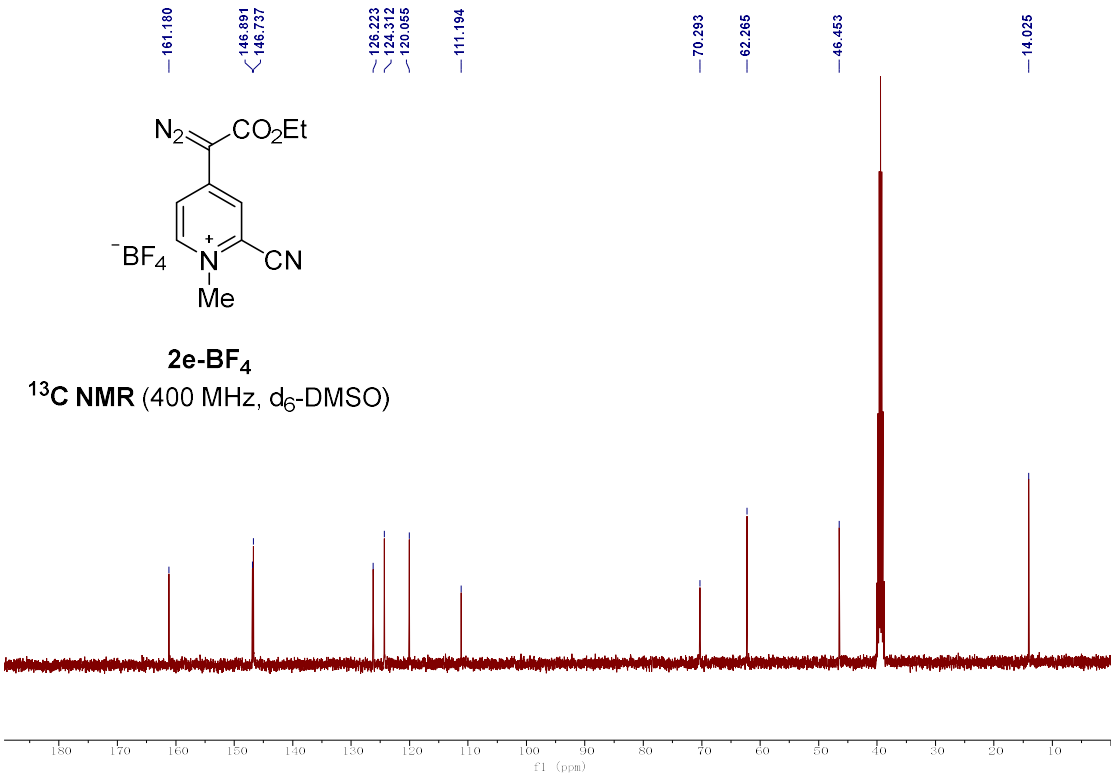
2d-BF_4

^{13}C NMR (400 MHz, $CDCl_3$)



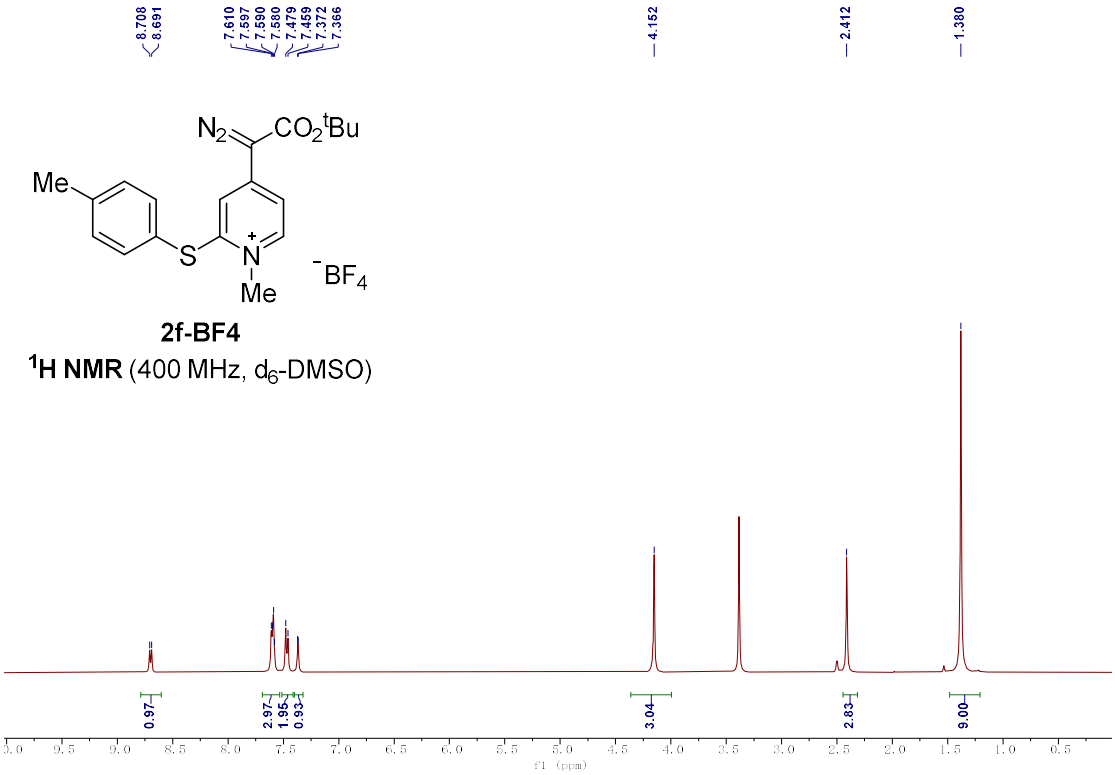
2e-BF_4

^{1}H NMR (400 MHz, d_6-DMSO)



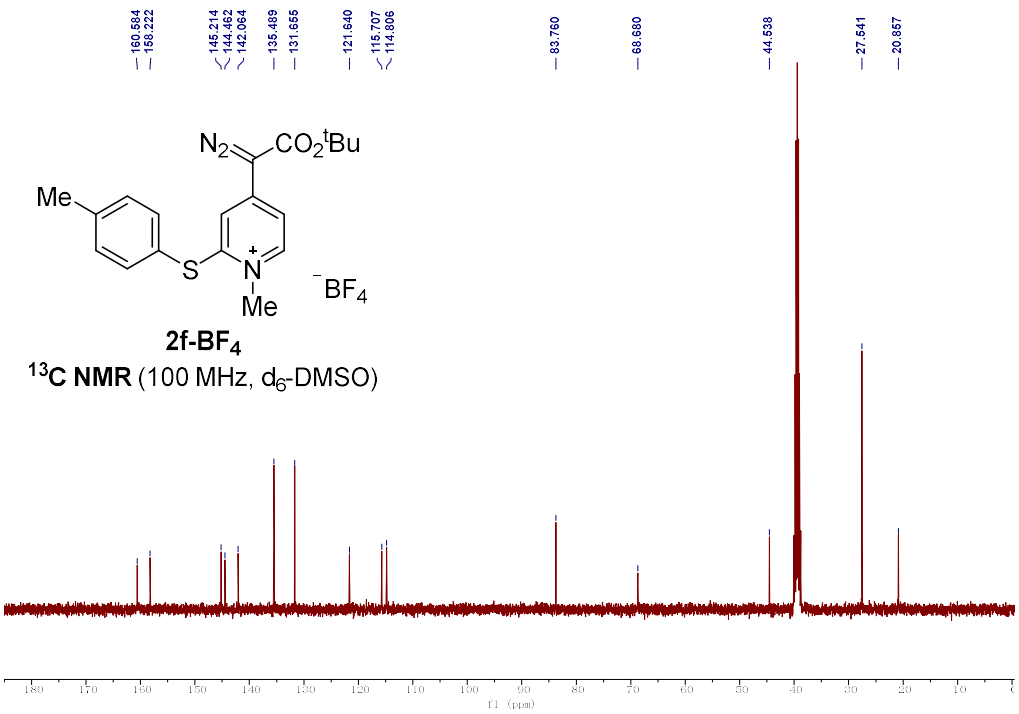
2e-BF_4

^{13}C NMR (400 MHz, d_6-DMSO)



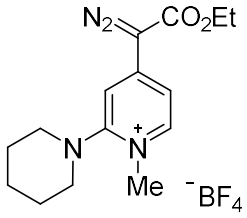
2f-BF4

^{1}H NMR (400 MHz, d_6-DMSO)



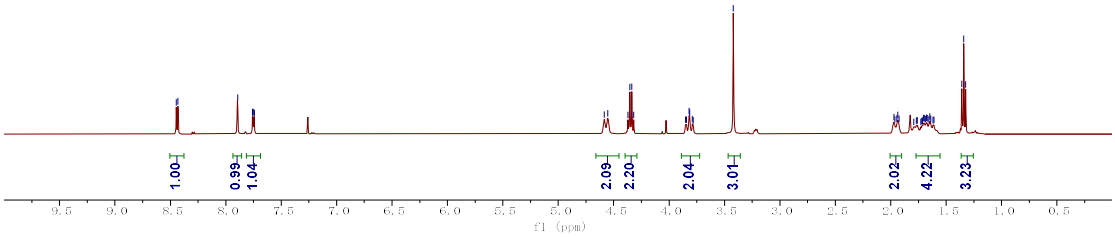
2f-BF$_4$

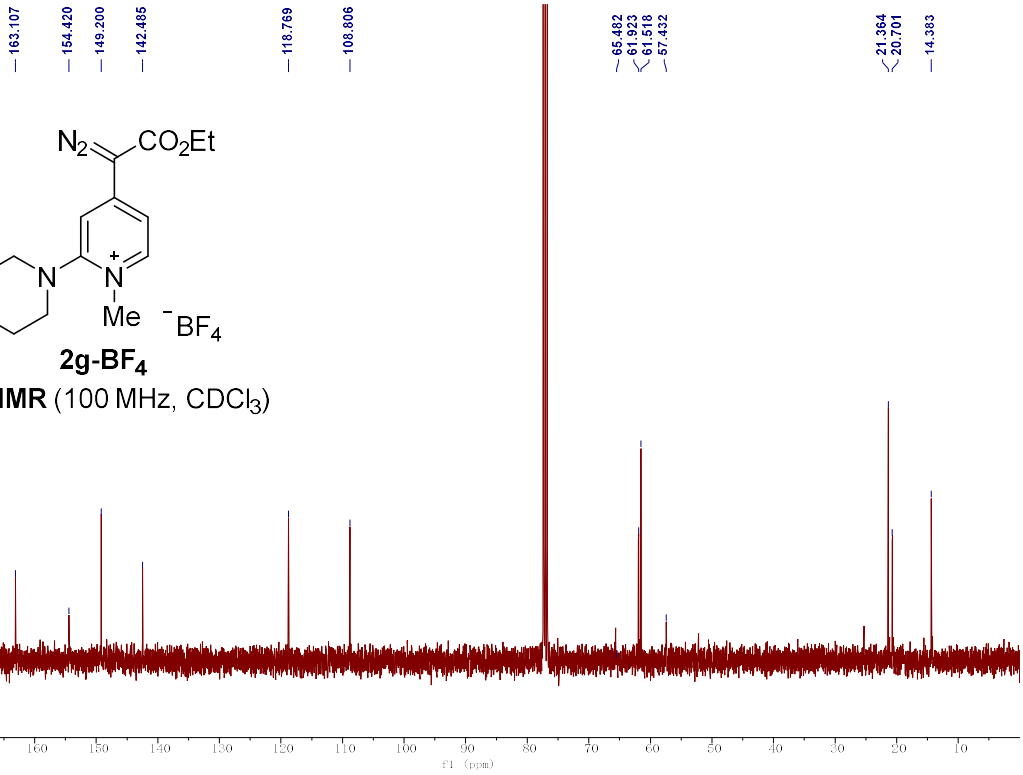
^{13}C NMR (100 MHz, d_6-DMSO)



2g-BF_4

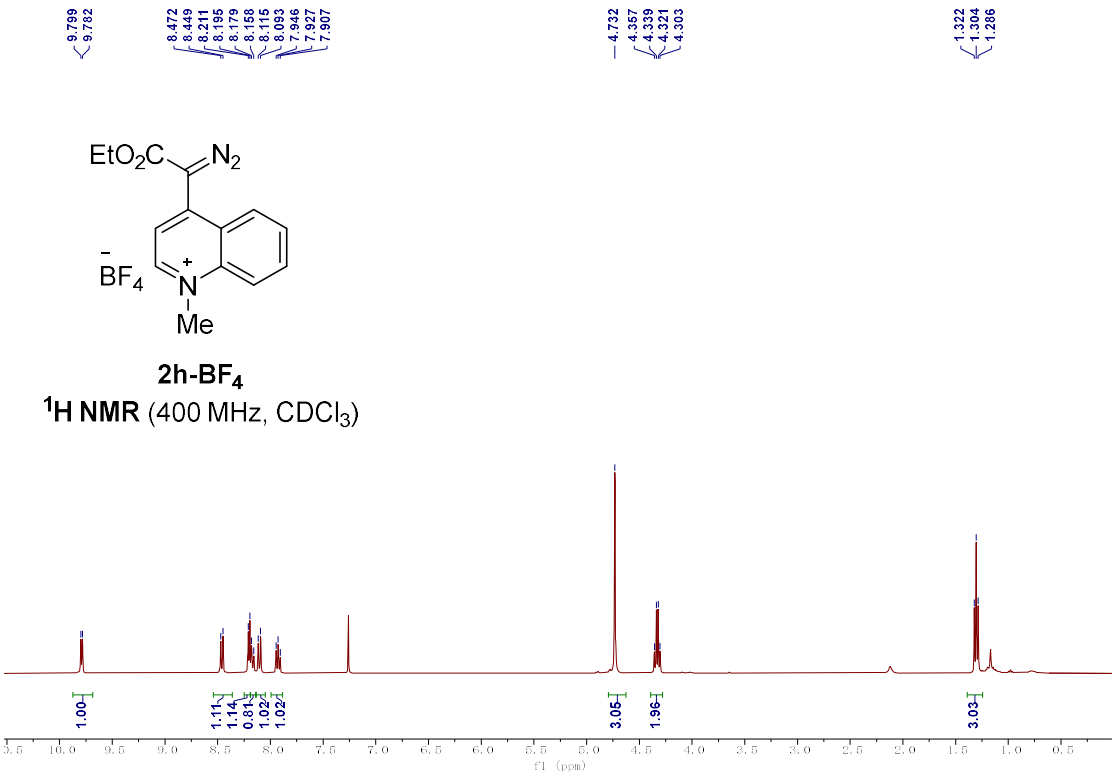
^{1}H NMR (400 MHz, $CDCl_3$)





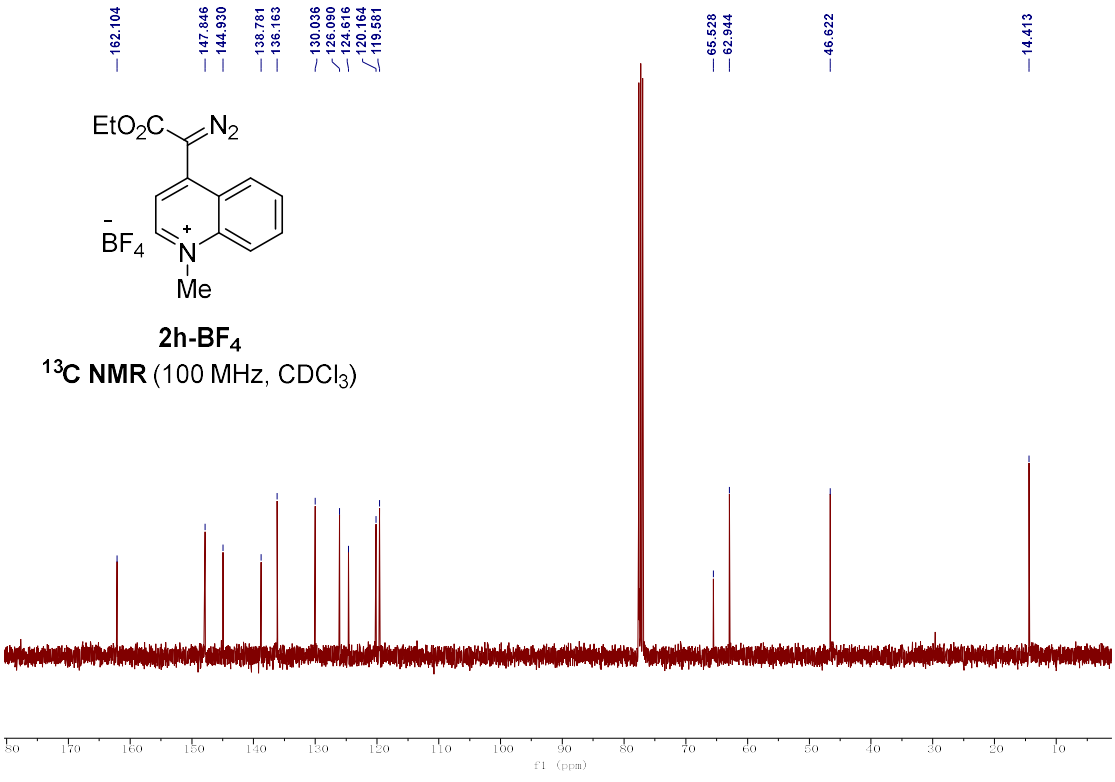
2g-BF_4

^{13}C NMR (100 MHz, $CDCl_3$)



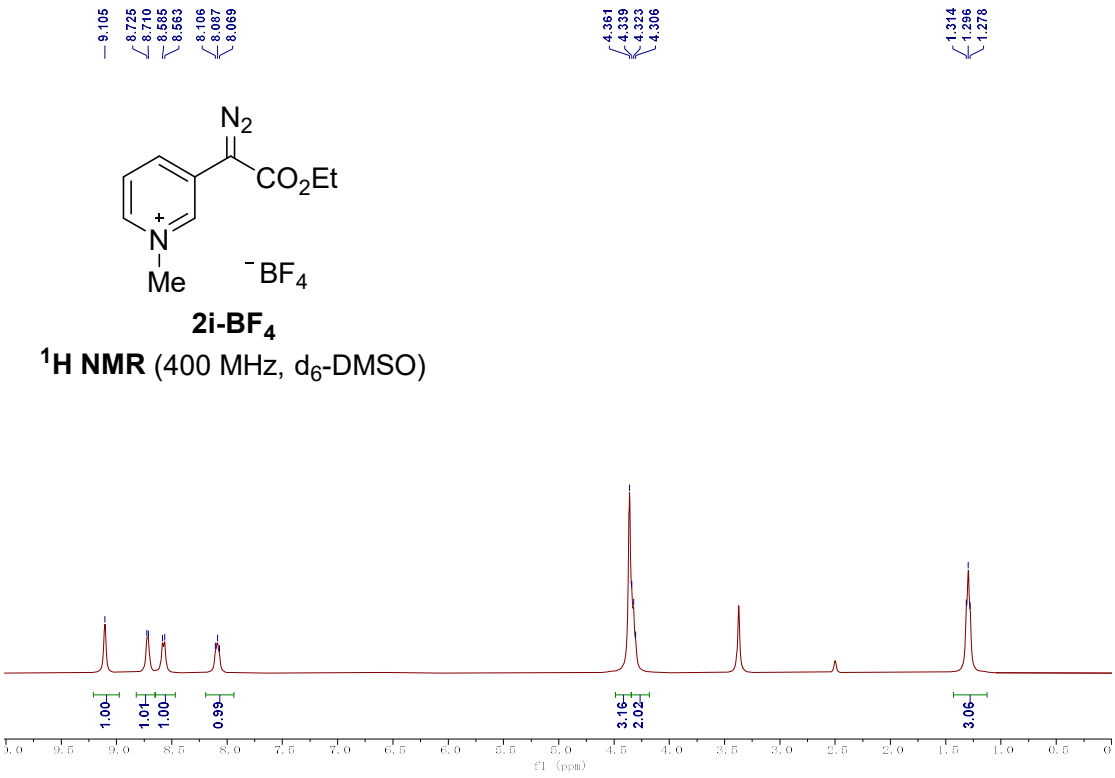
2h-BF_4

^{1}H NMR (400 MHz, $CDCl_3$)



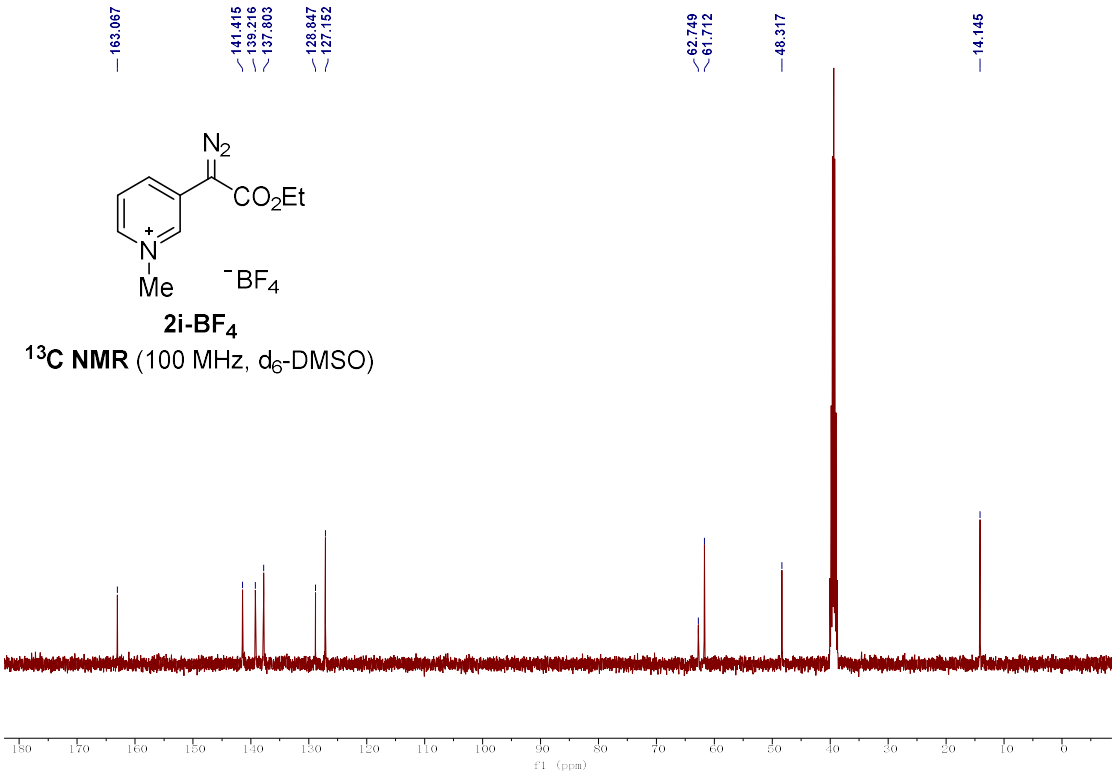
2h-BF_4

^{13}C NMR (100 MHz, $CDCl_3$)



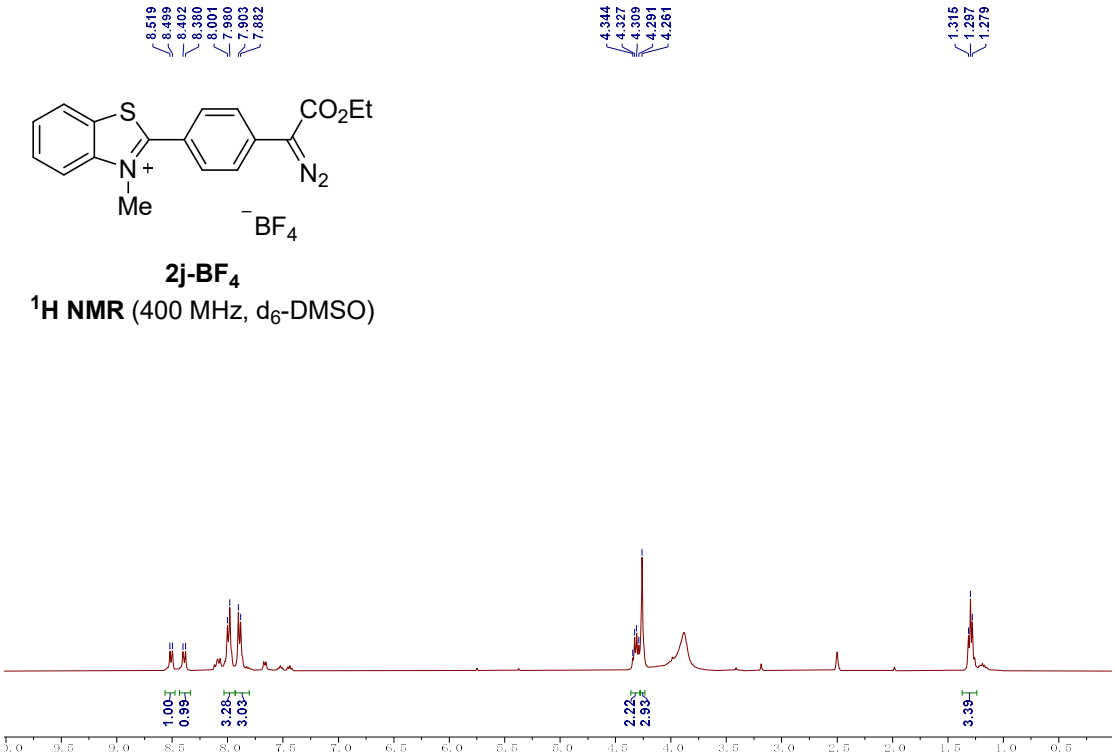
2i-BF_4

^{1}H NMR (400 MHz, d_6-DMSO)



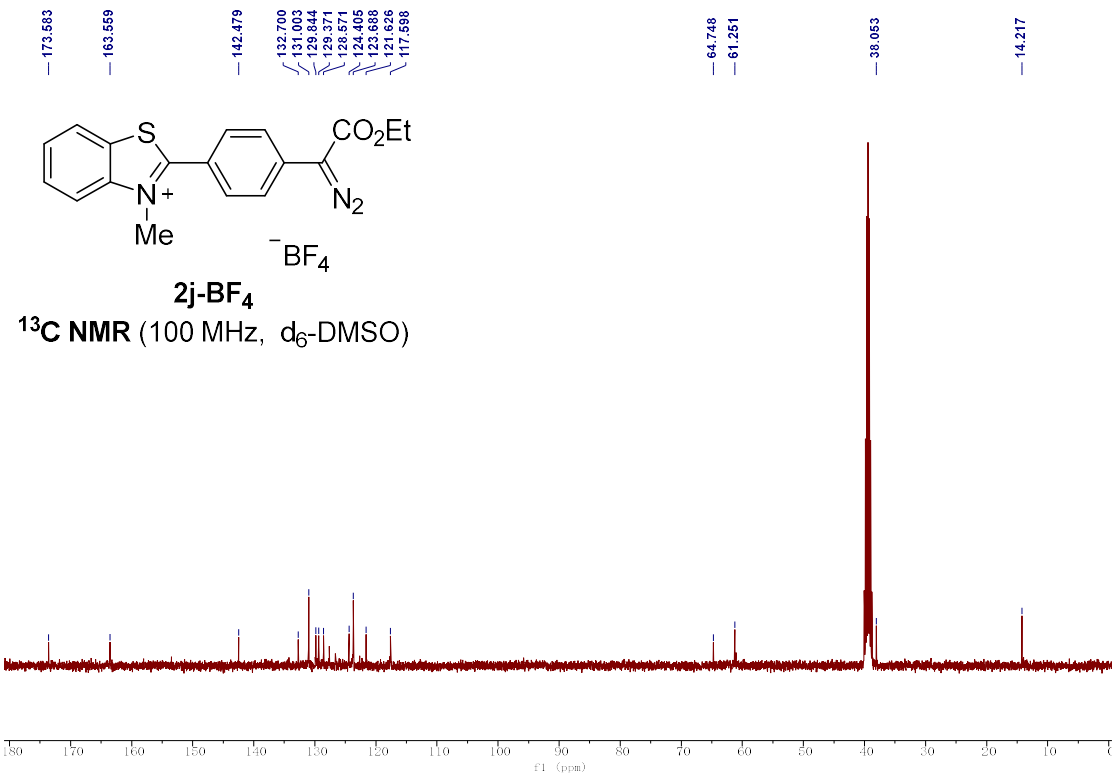
2i-BF_4

^{13}C NMR (100 MHz, d_6-DMSO)



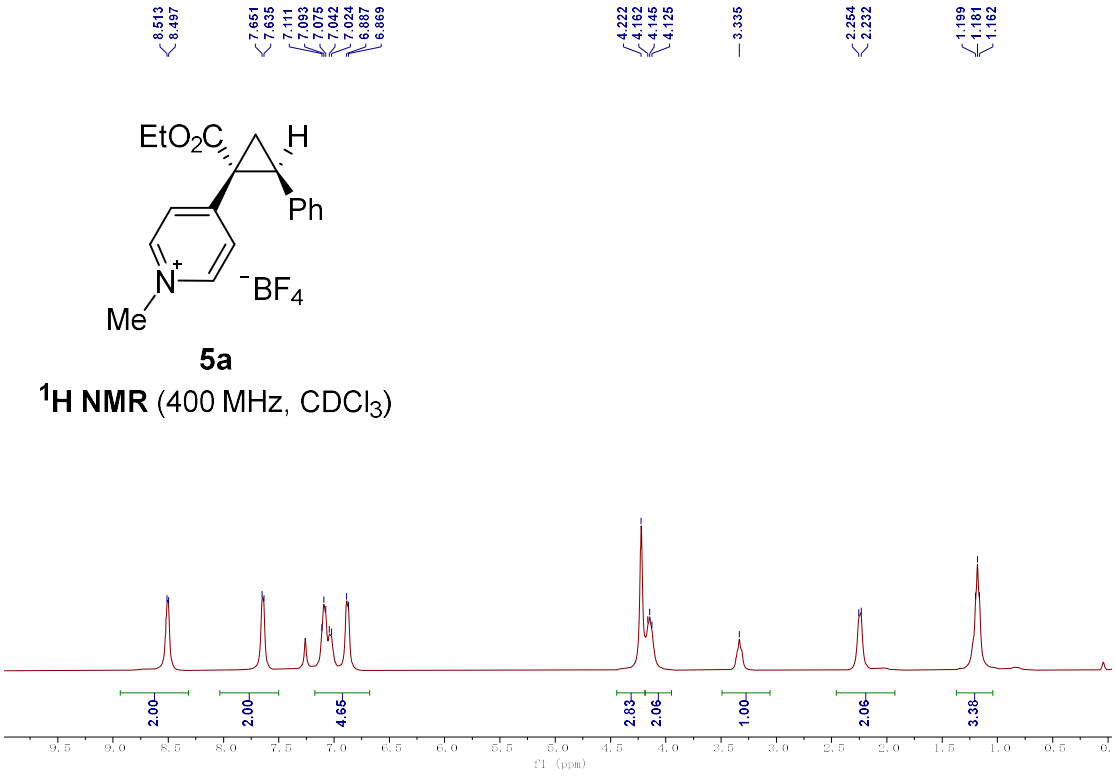
2j-BF_4

^{1}H NMR (400 MHz, d_6-DMSO)



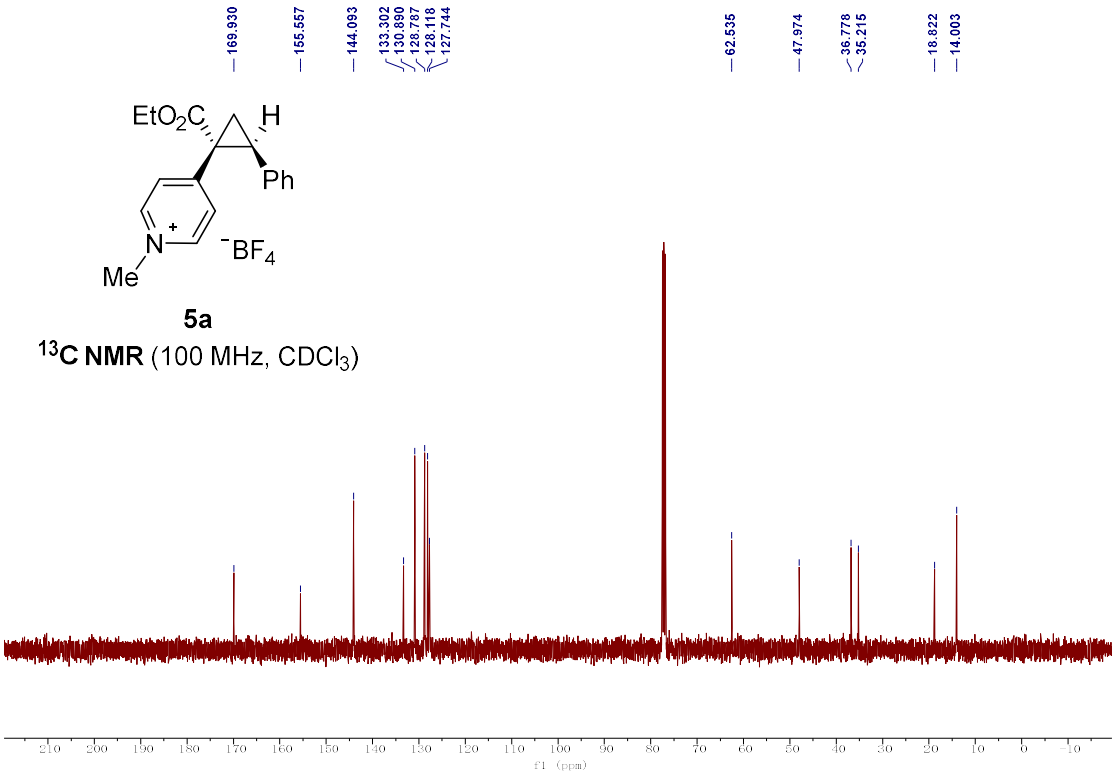
2j-BF_4

^{13}C NMR (100 MHz, d_6-DMSO)



5a

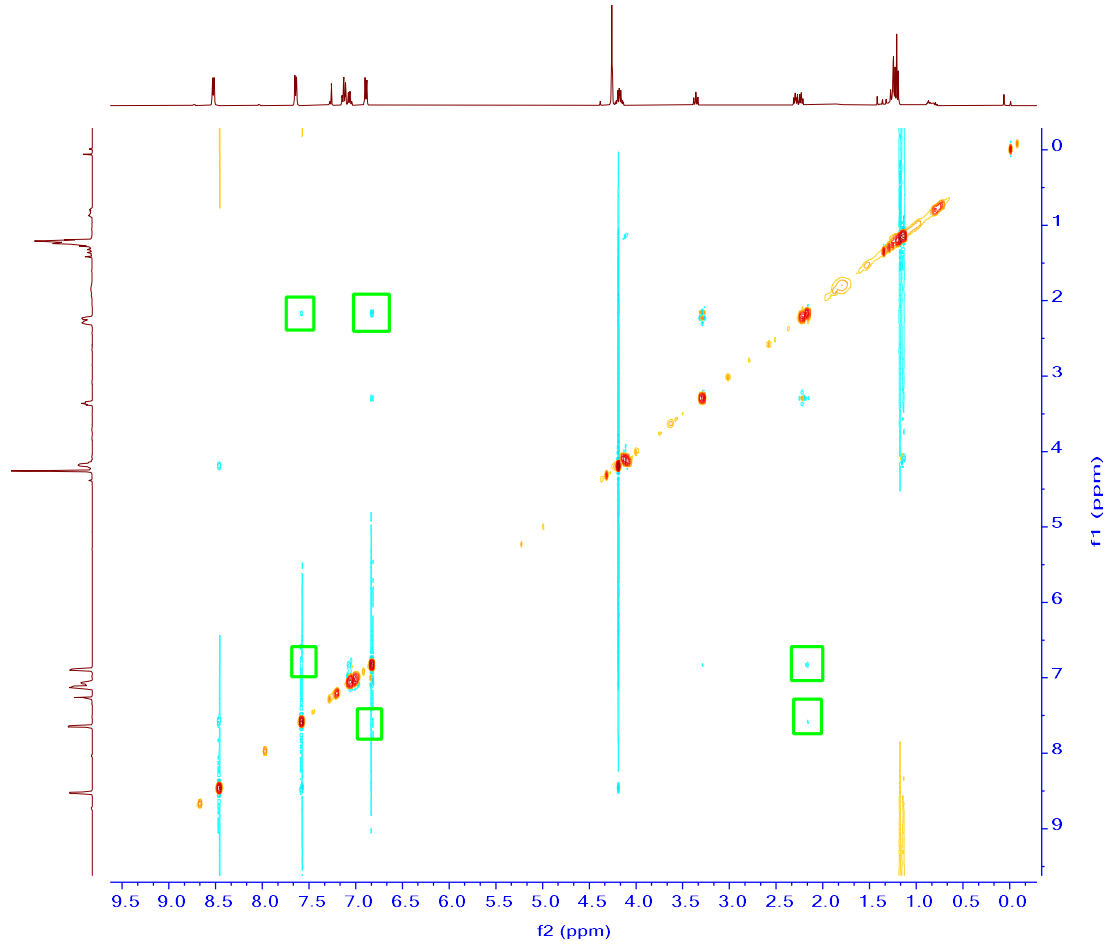
^{1}H NMR (400 MHz, $CDCl_3$)

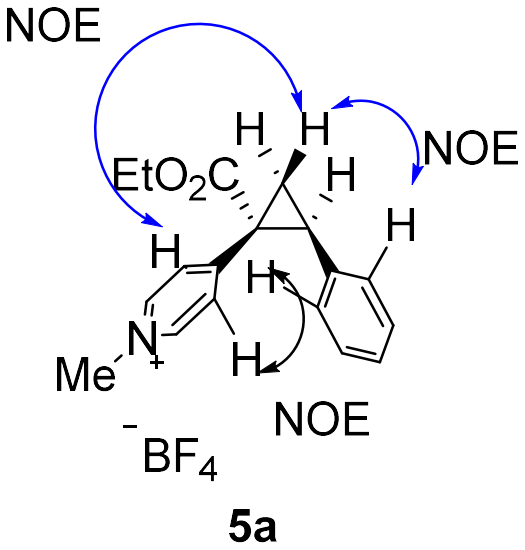


5a

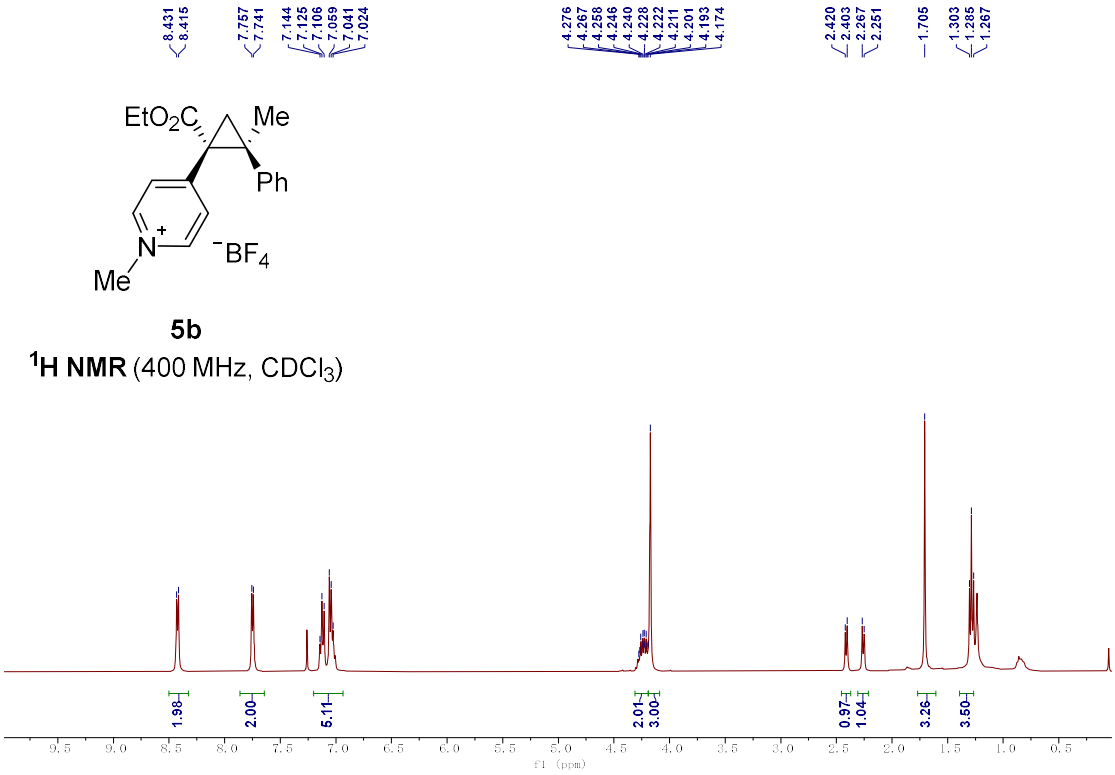
^{13}C NMR (100 MHz, $CDCl_3$)

^{1}H-^{1}H NOESY of 5a



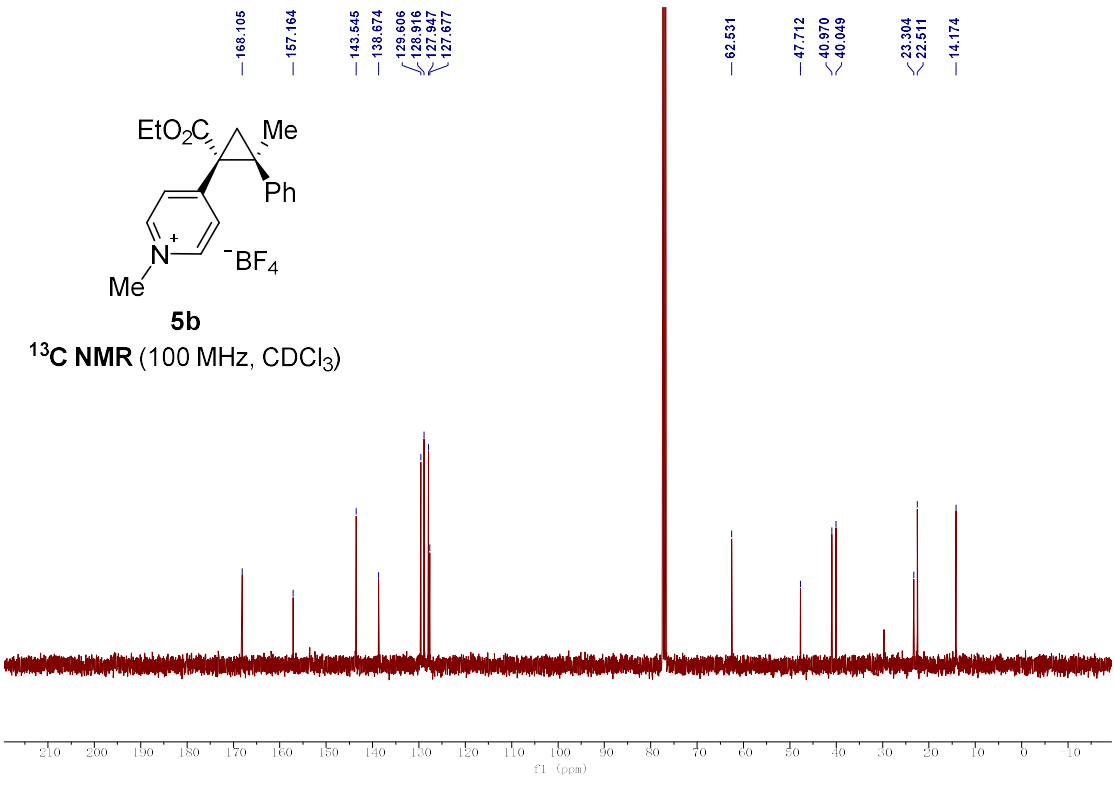


5a



5b

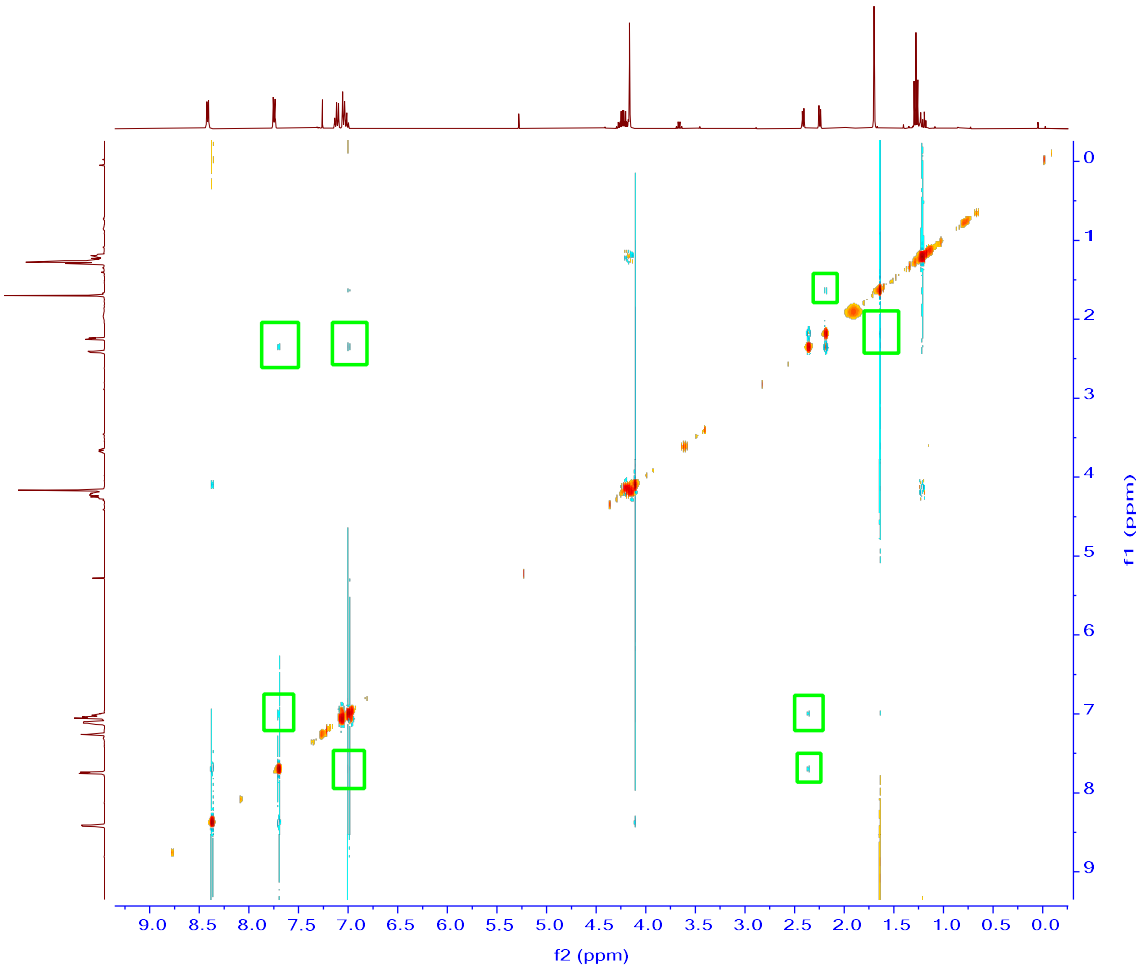
^{1}H NMR (400 MHz, $CDCl_3$)

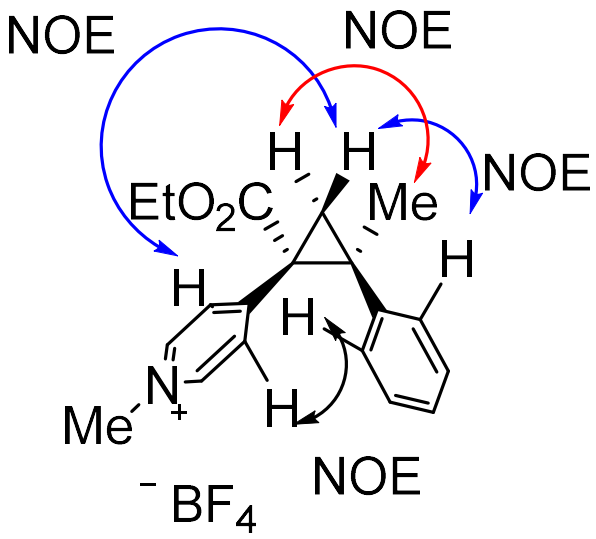


5b

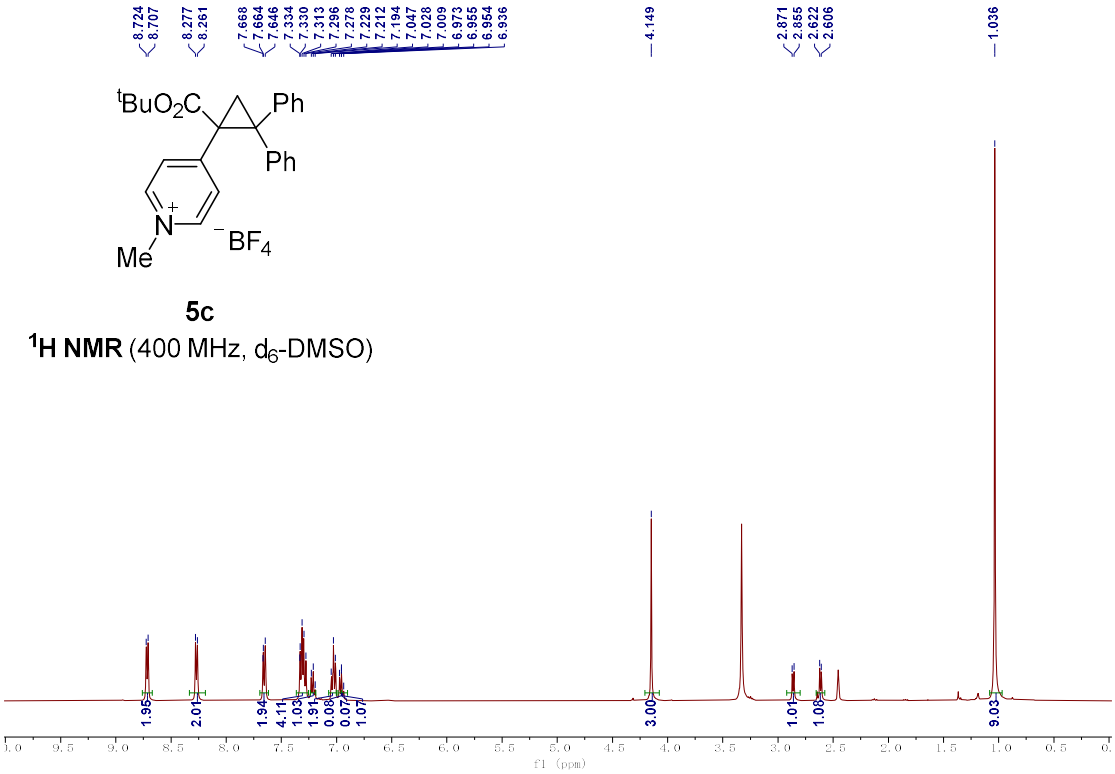
^{13}C NMR (100 MHz, $CDCl_3$)

^{1}H-^{1}H NOESY of 5b



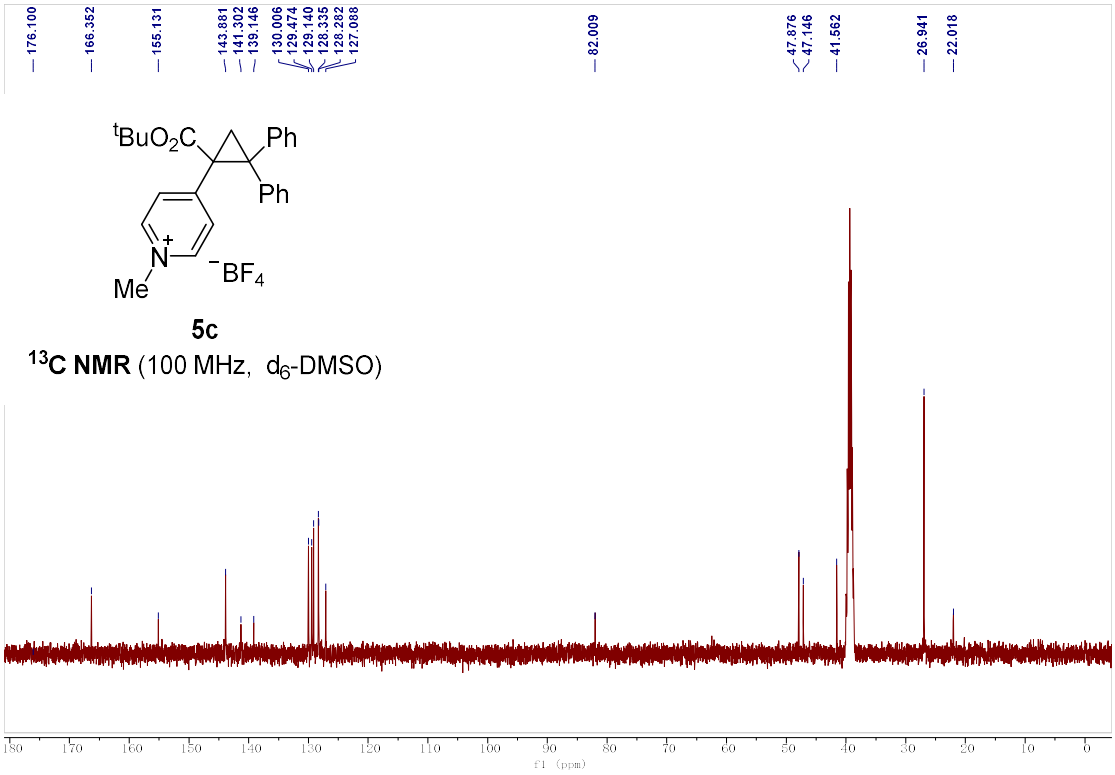


5b



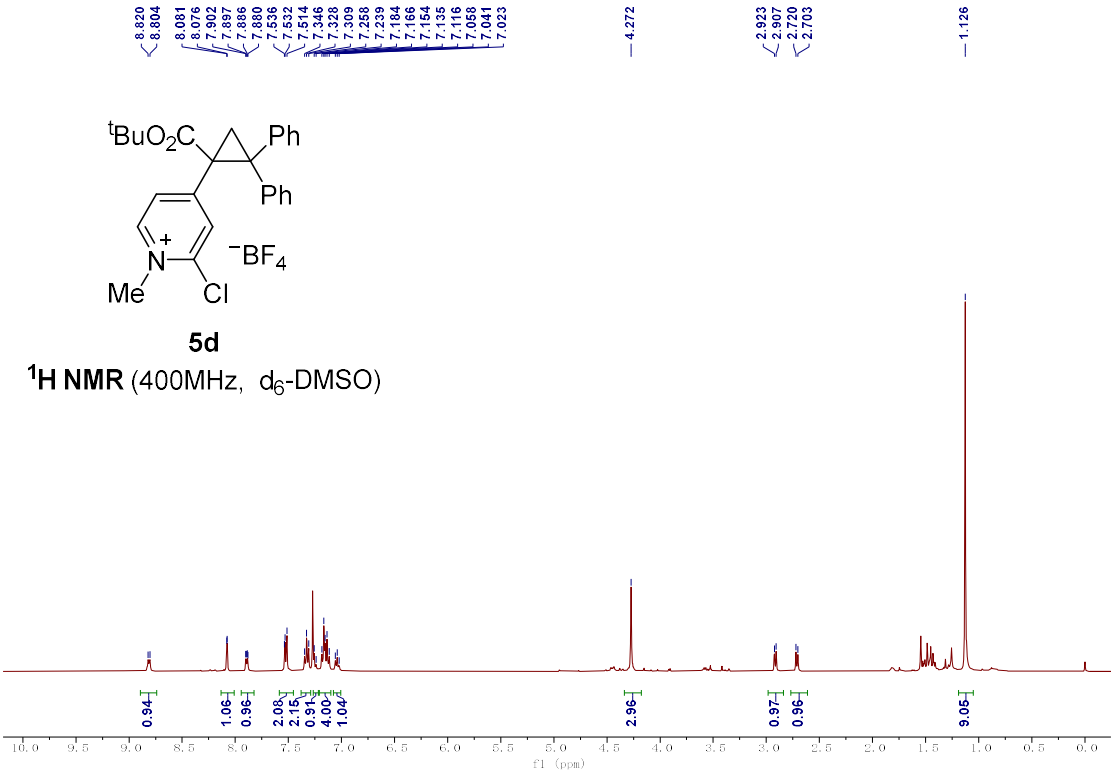
5c

^{1}H NMR (400 MHz, d_6-DMSO)



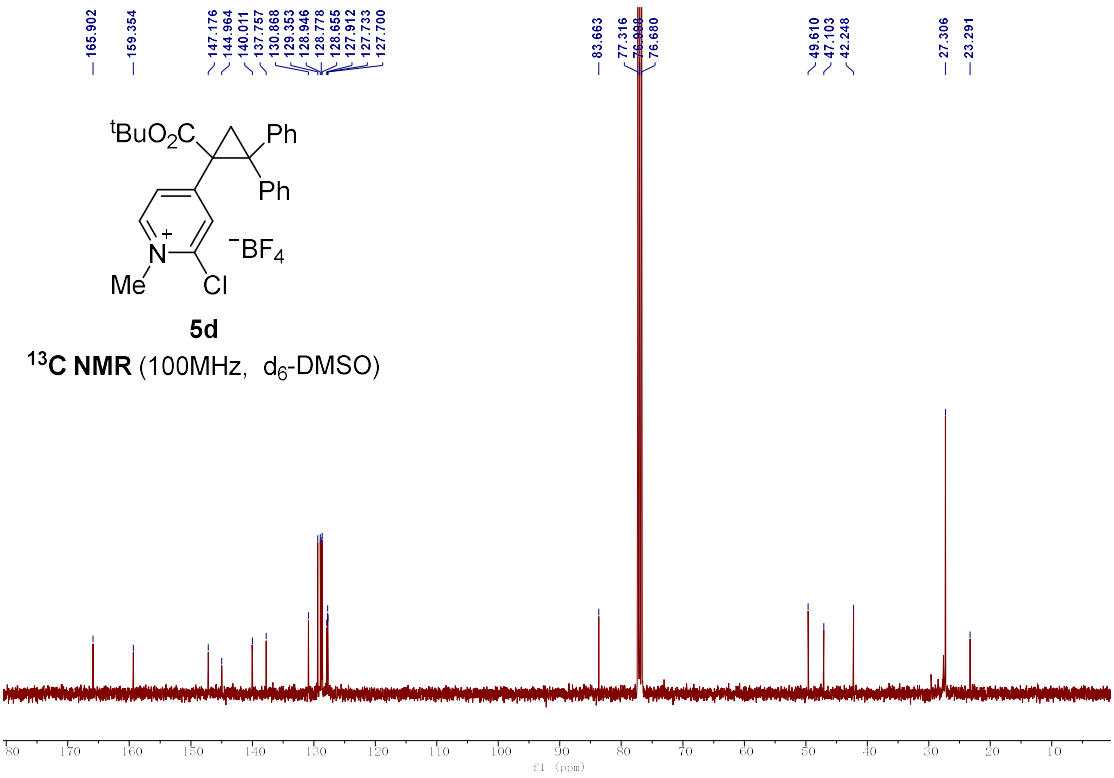
5c

^{13}C NMR (100 MHz, d_6-DMSO)



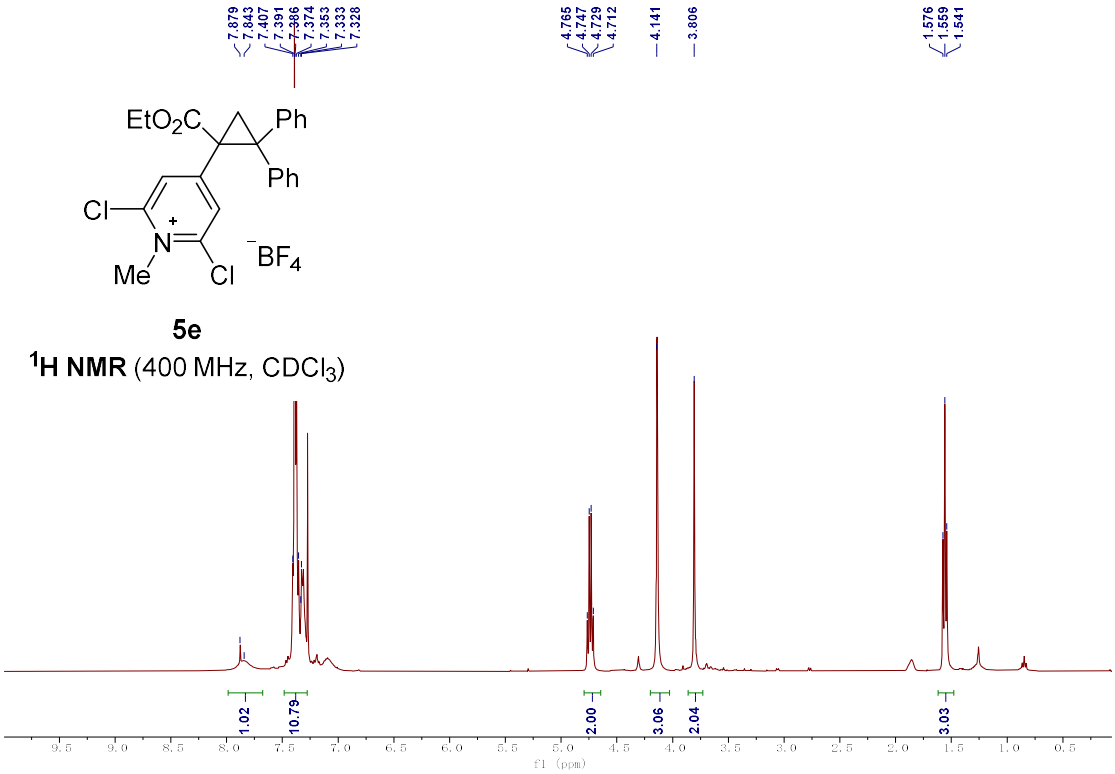
5d

^{1}H NMR (400MHz, d_6-DMSO)



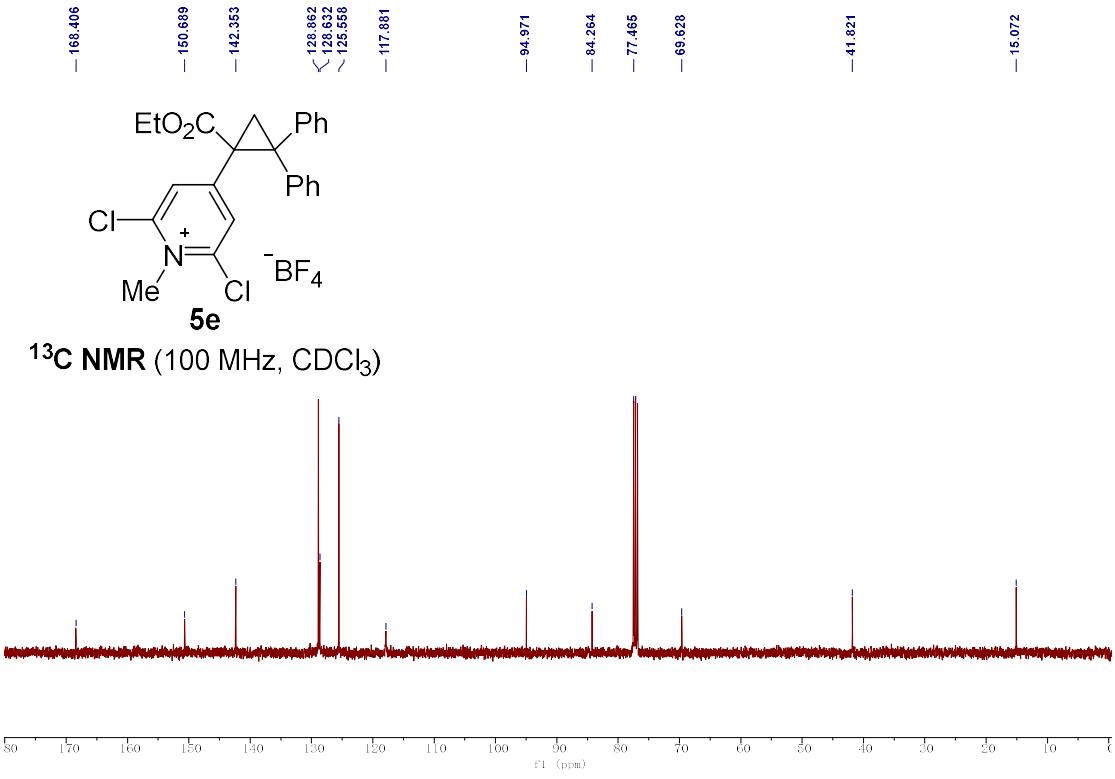
5d

^{13}C NMR (100MHz, d_6-DMSO)



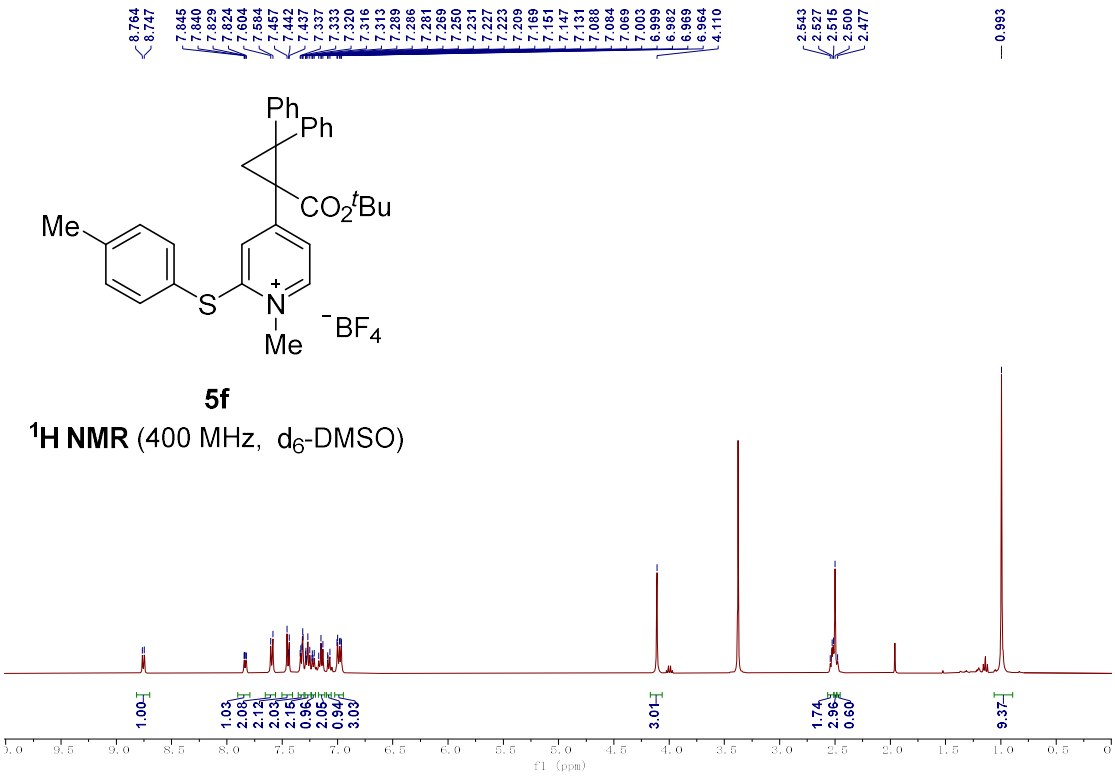
5e

^{1}H NMR (400 MHz, $CDCl_3$)



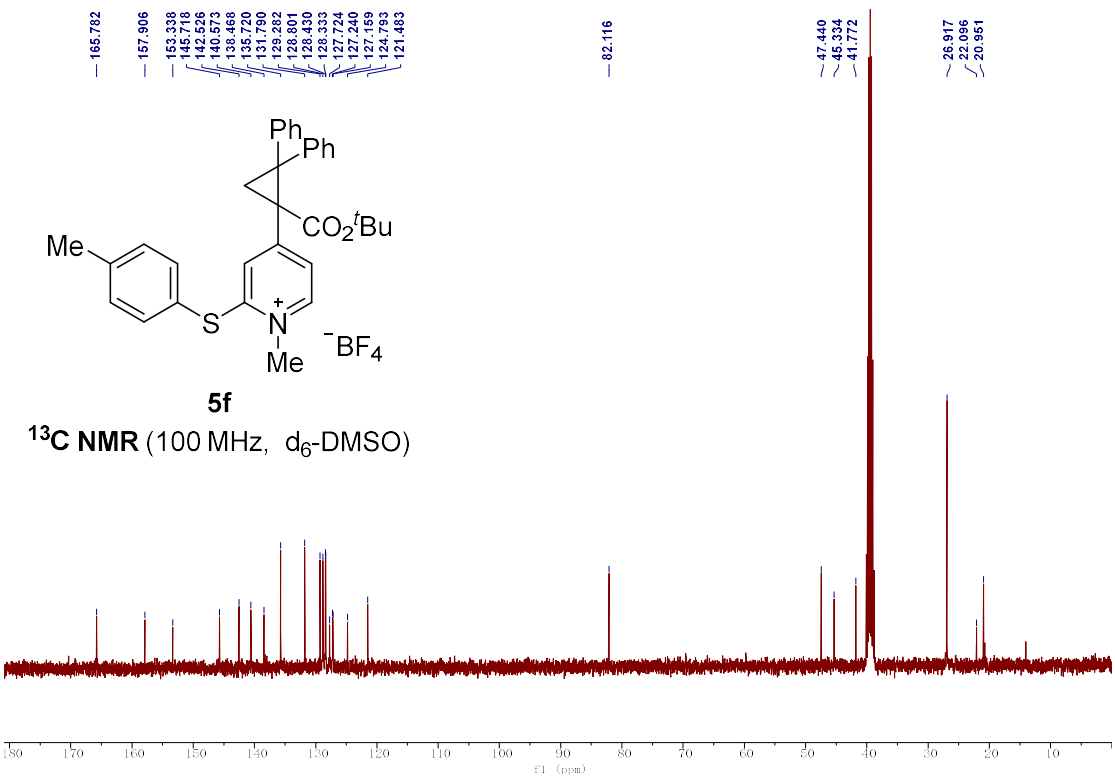
5e

^{13}C NMR (100 MHz, $CDCl_3$)



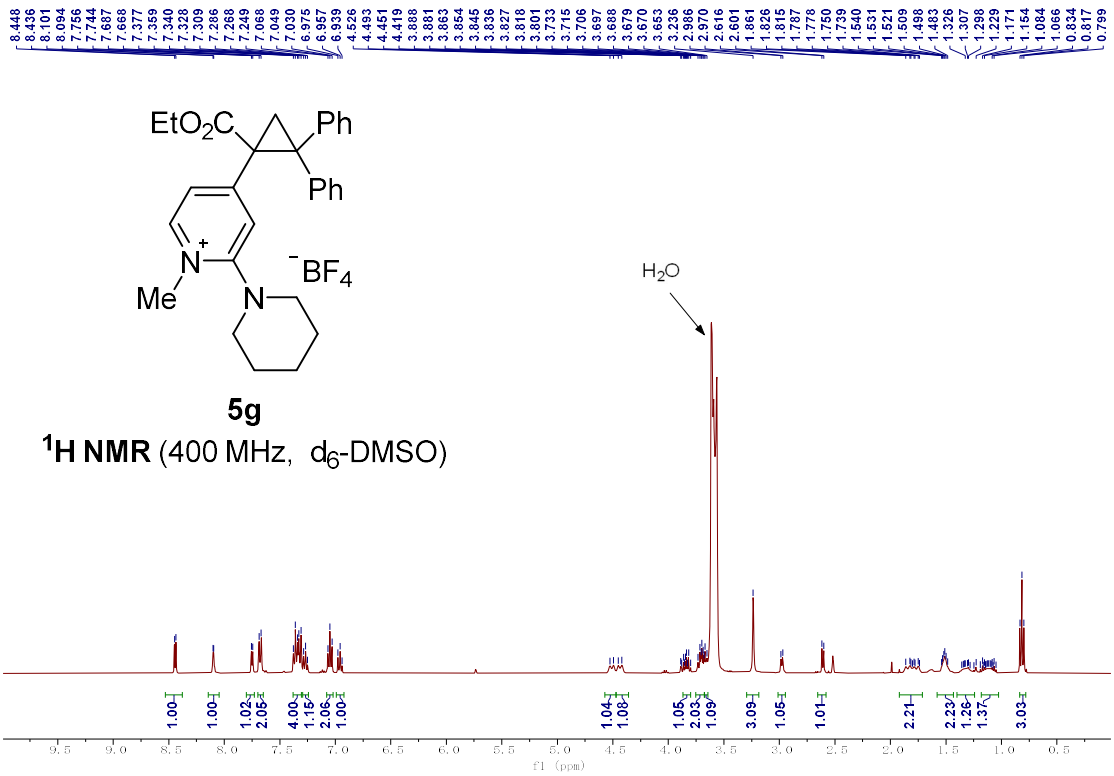
5f

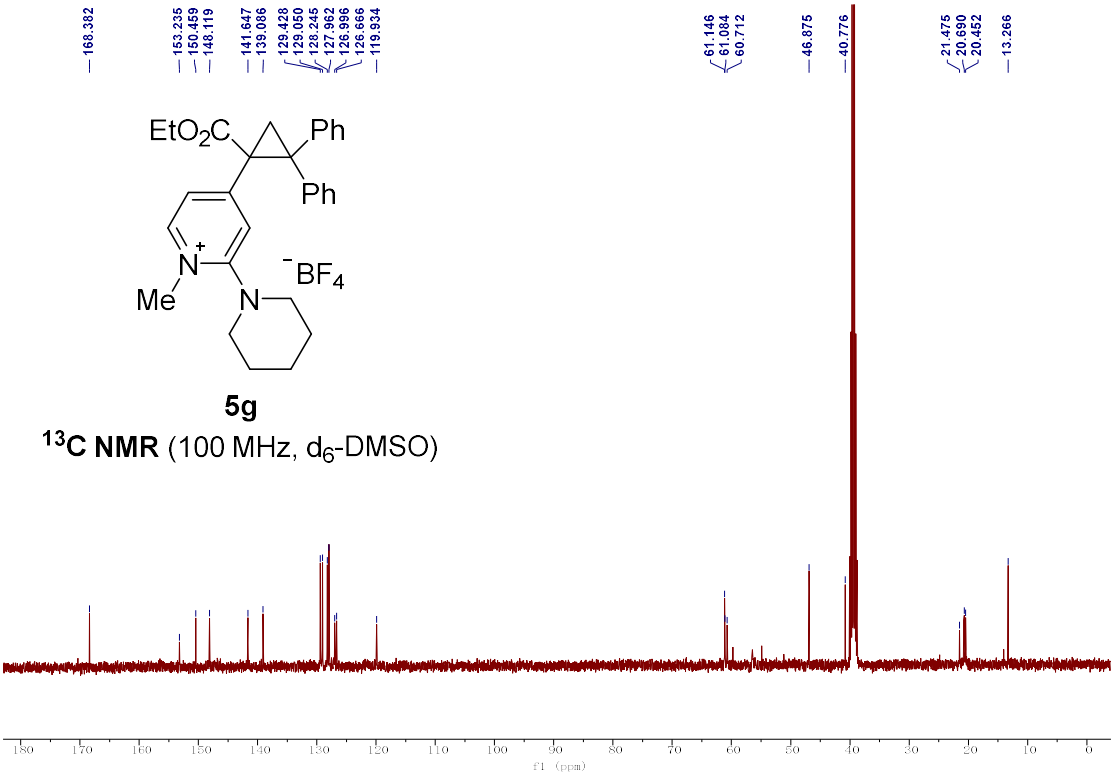
^{1}H NMR (400 MHz, d_6-DMSO)

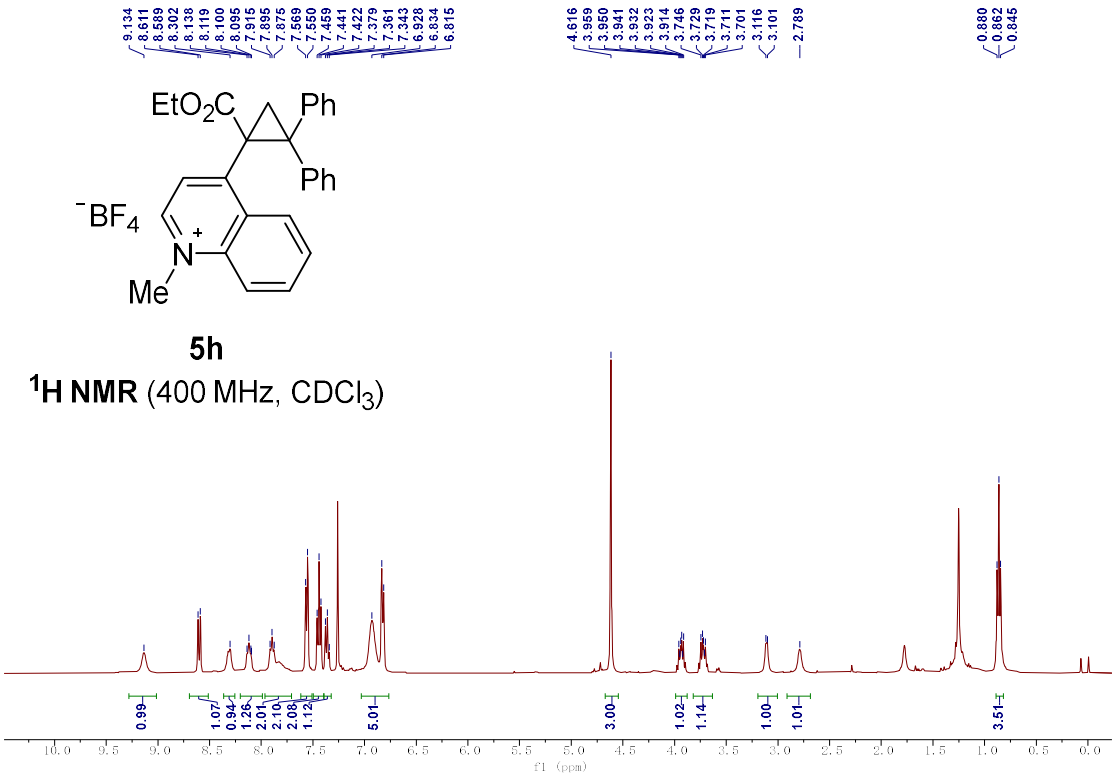


5f

^{13}C NMR (100 MHz, d_6-DMSO)

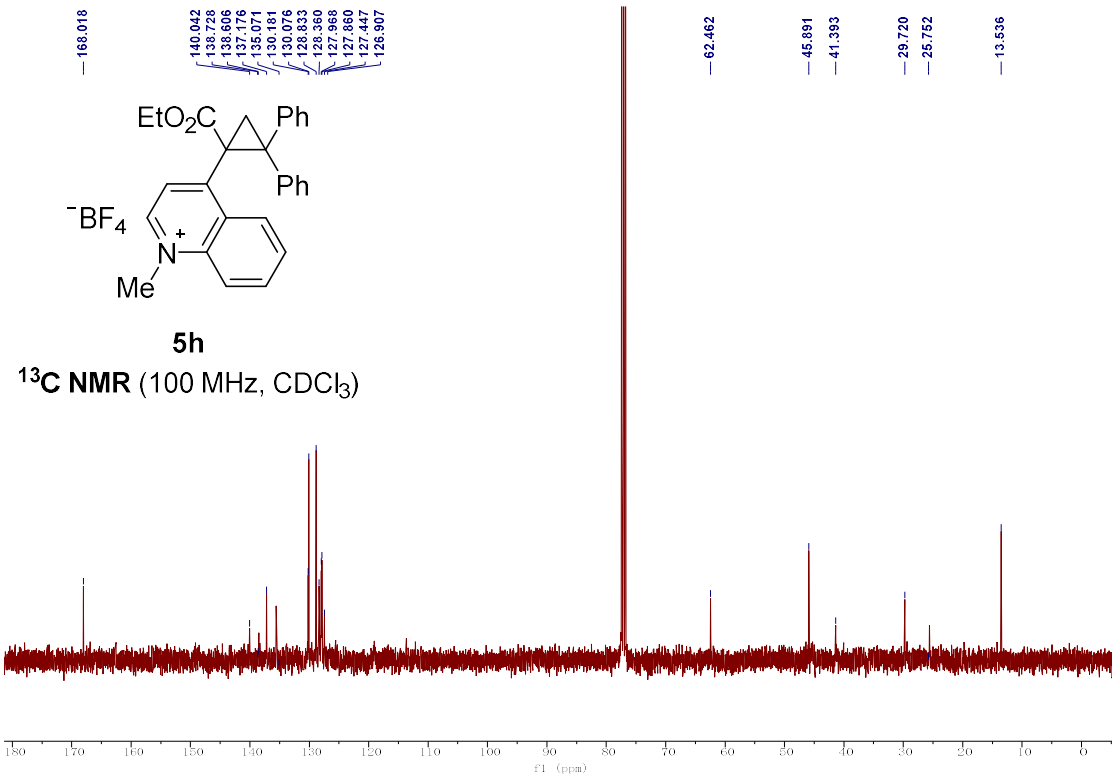

EtO2C
Ph
Ph
N+
Me
N
-BF4
H2O
5g
1H NMR (400 MHz, d6-DMSO)


EtO2C
Ph
Ph
N+
Me
N
-BF4
5g
13C NMR (100 MHz, d6-DMSO)



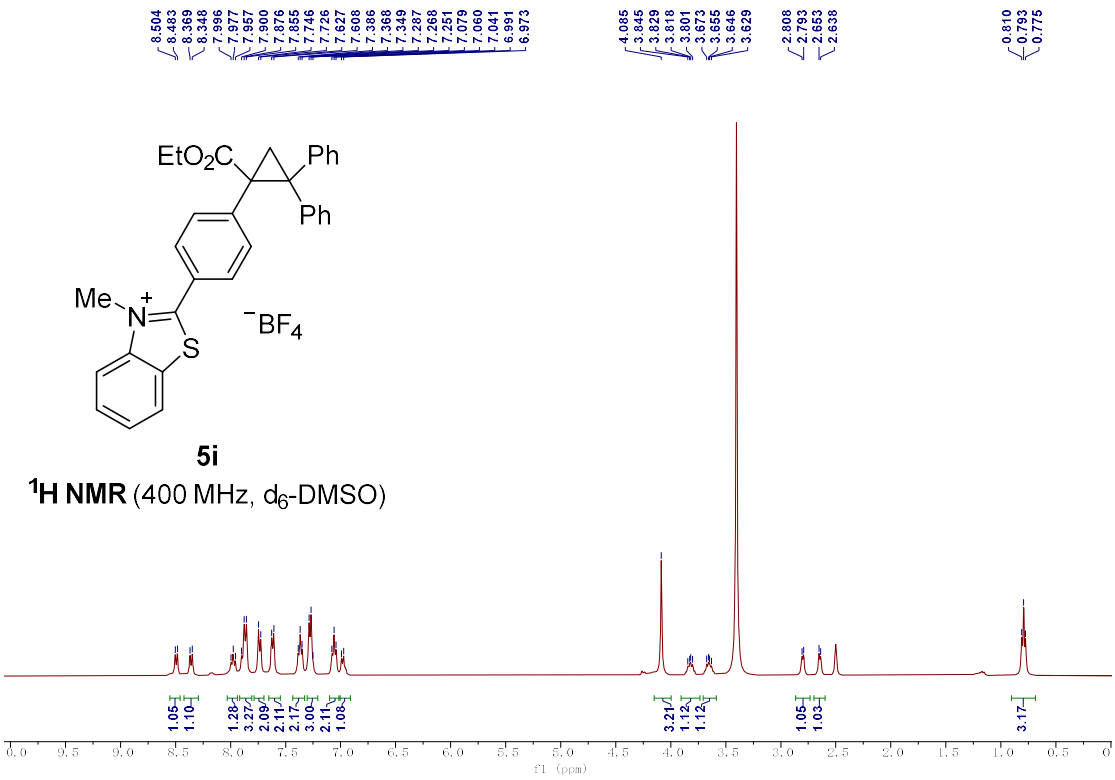
5h

^{1}H NMR (400 MHz, $CDCl_3$)



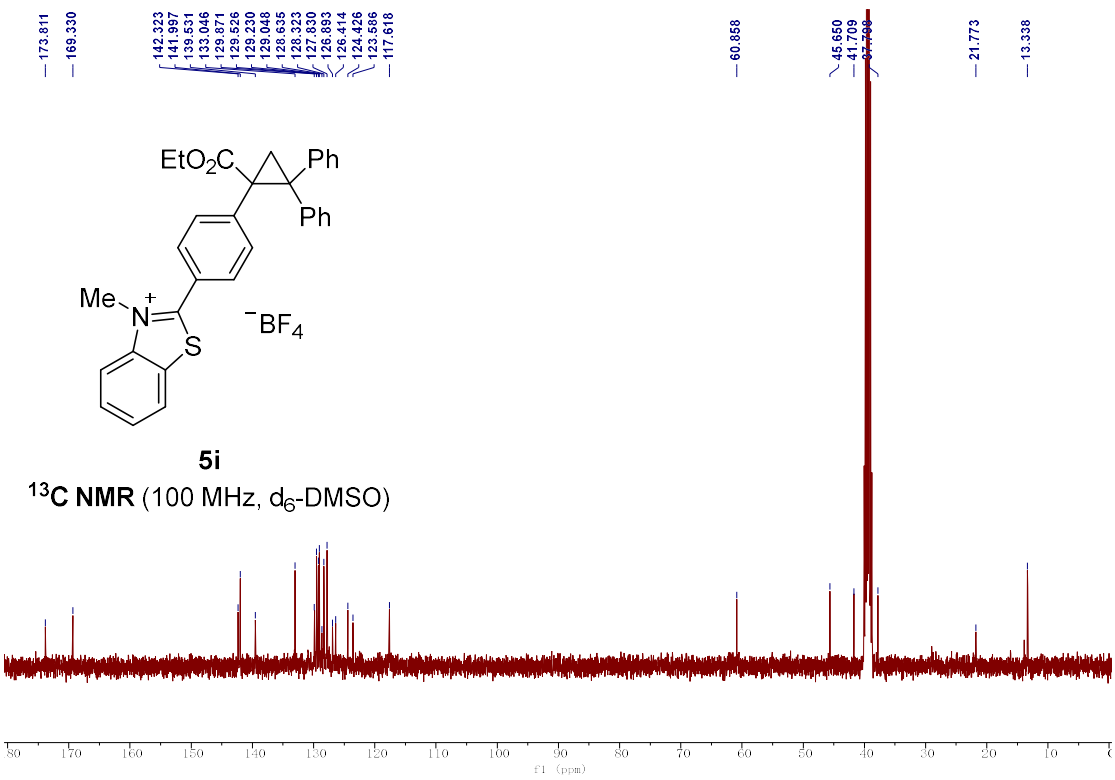
5h

^{13}C NMR (100 MHz, $CDCl_3$)



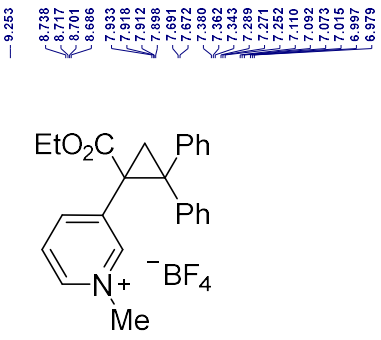
5i

^{1}H NMR (400 MHz, d_6-DMSO)



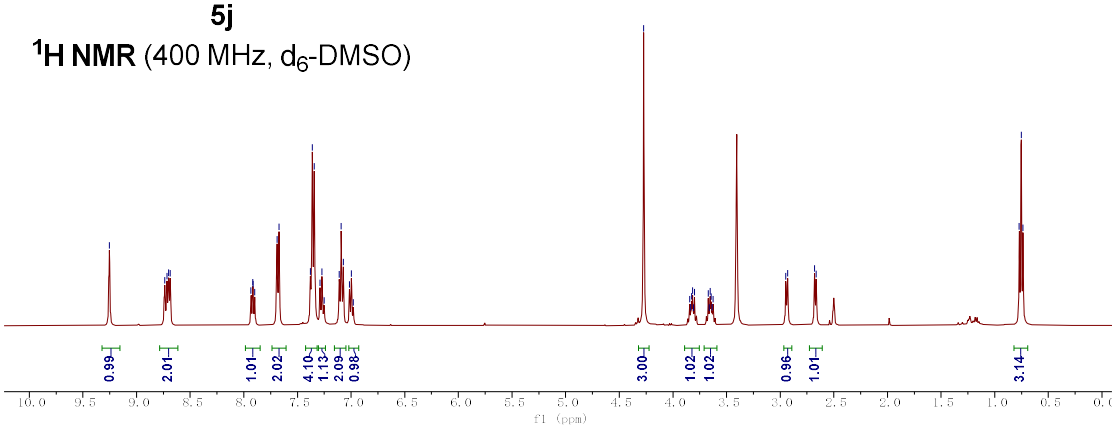
5i

^{13}C NMR (100 MHz, d_6-DMSO)

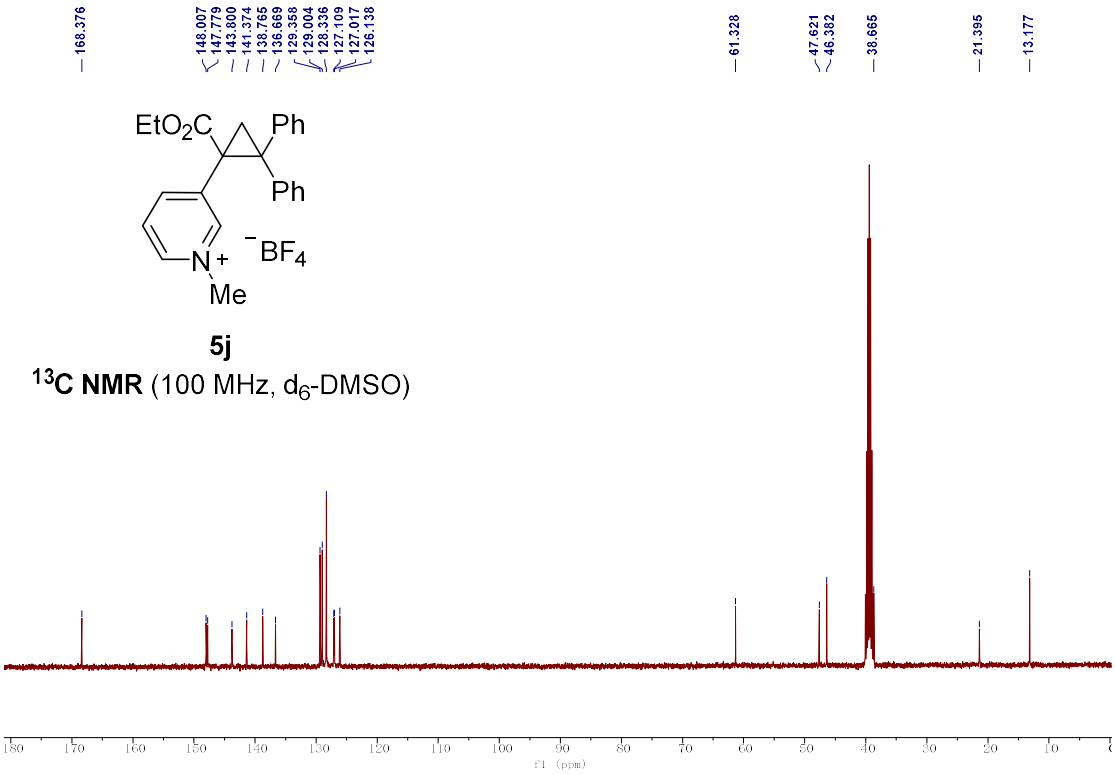


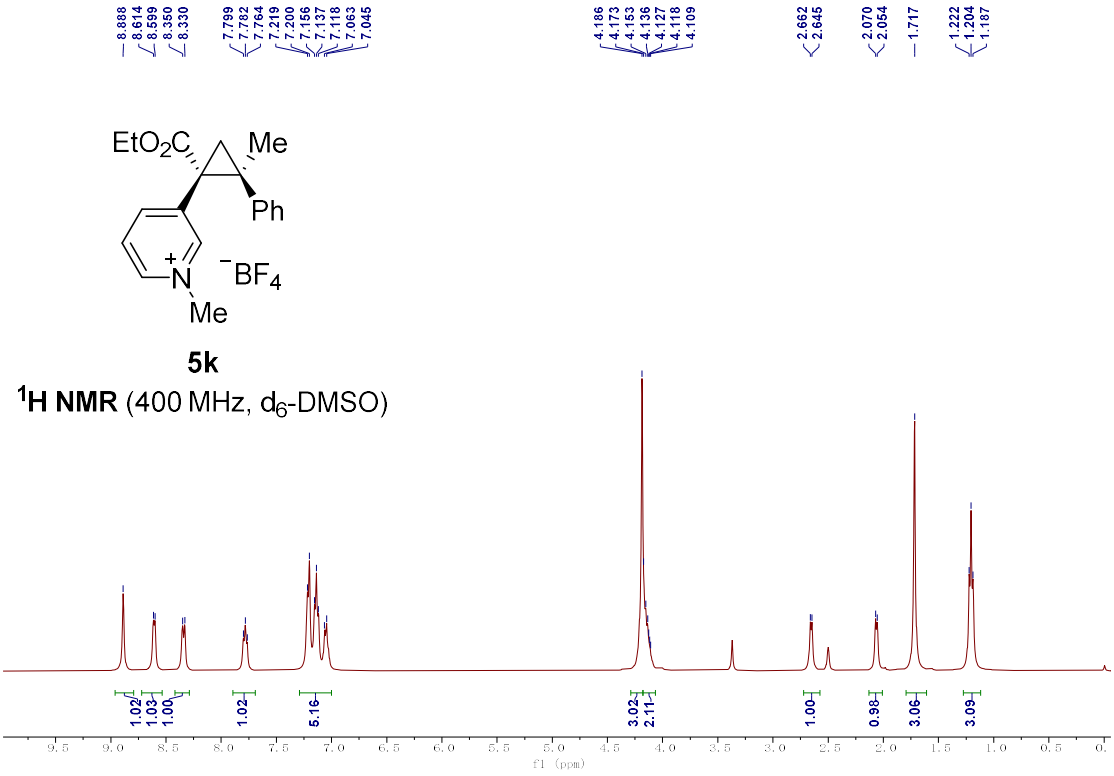
5j

^{1}H NMR (400 MHz, d_6-DMSO)



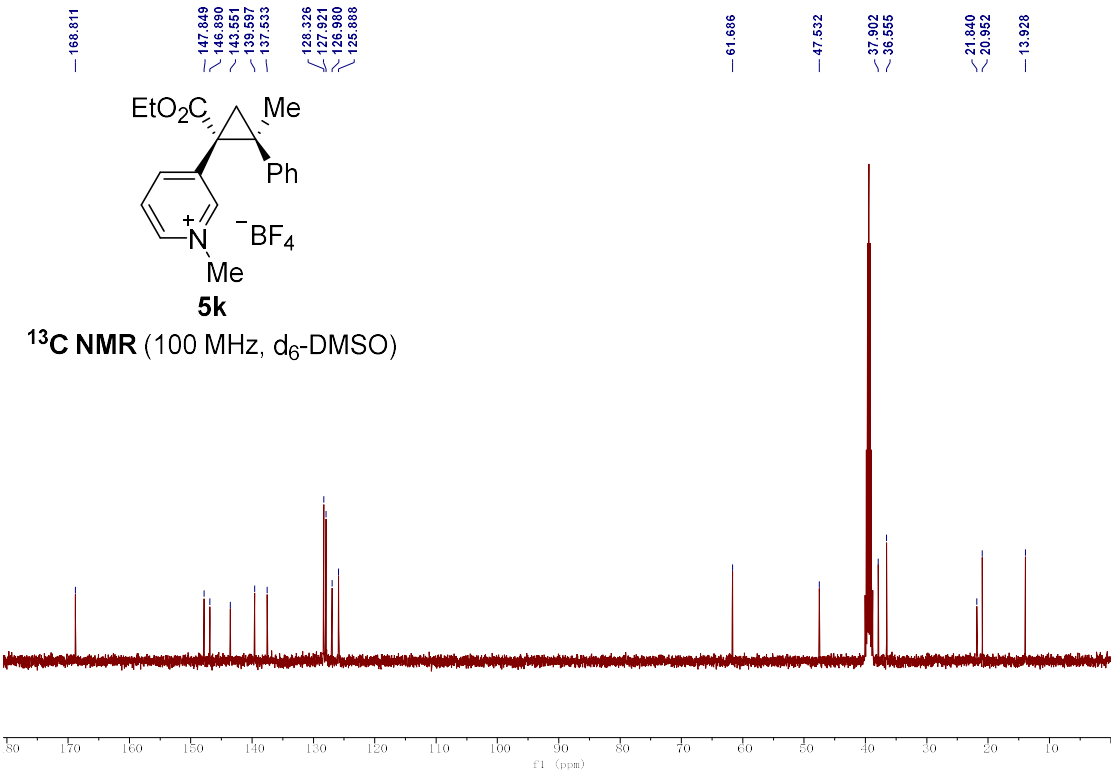
^{13}C NMR (100 MHz, d_6-DMSO)





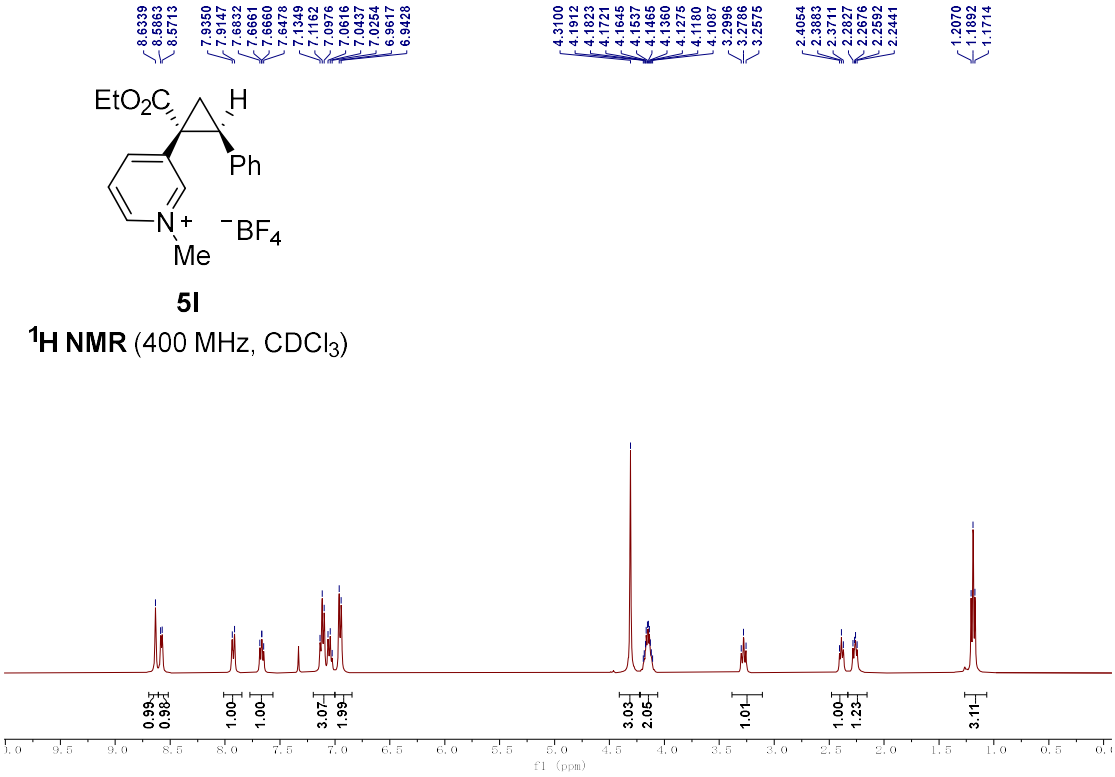
5k

^{1}H NMR (400 MHz, d_6-DMSO)



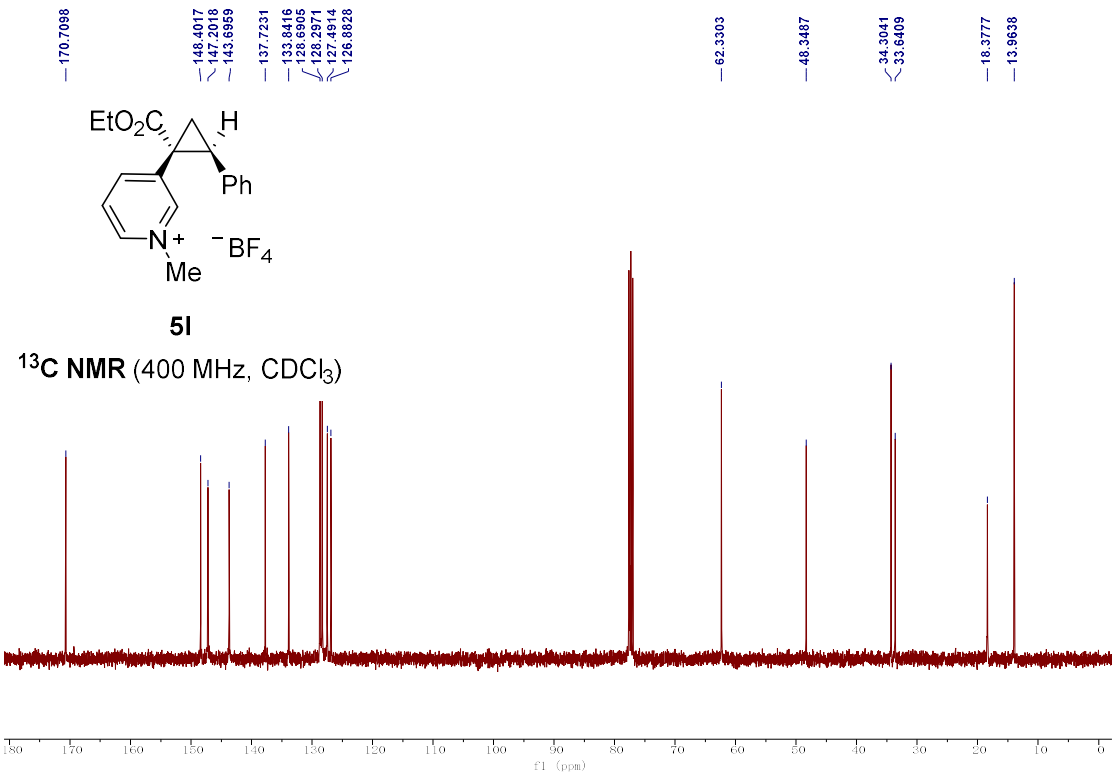
5k

^{13}C NMR (100 MHz, d_6-DMSO)



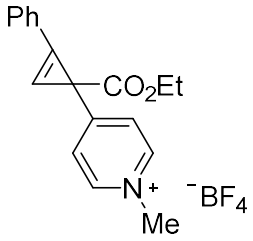
5l

^{1}H NMR (400 MHz, $CDCl_3$)



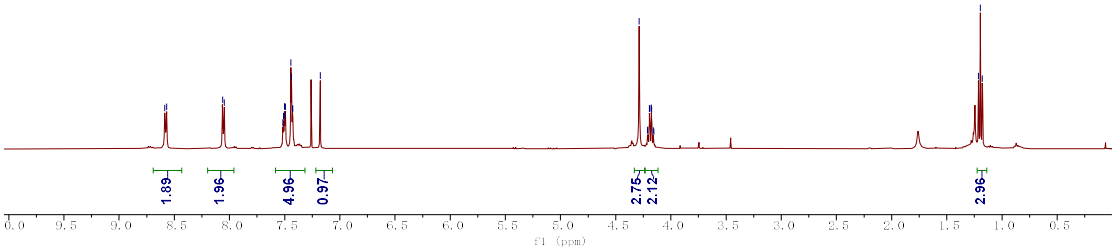
5l

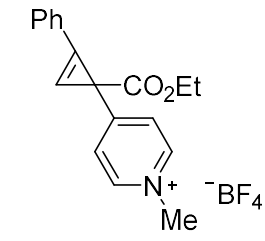
^{13}C NMR (400 MHz, $CDCl_3$)



6a

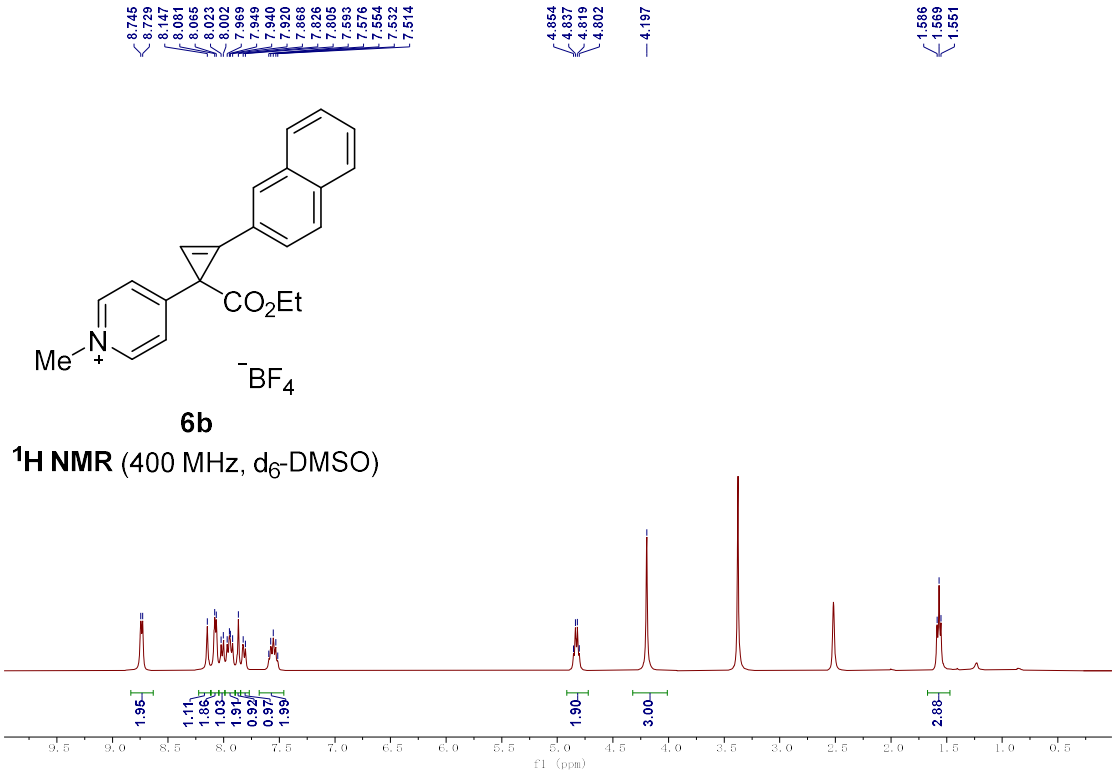
^{1}H NMR (400 MHz, $CDCl_3$)





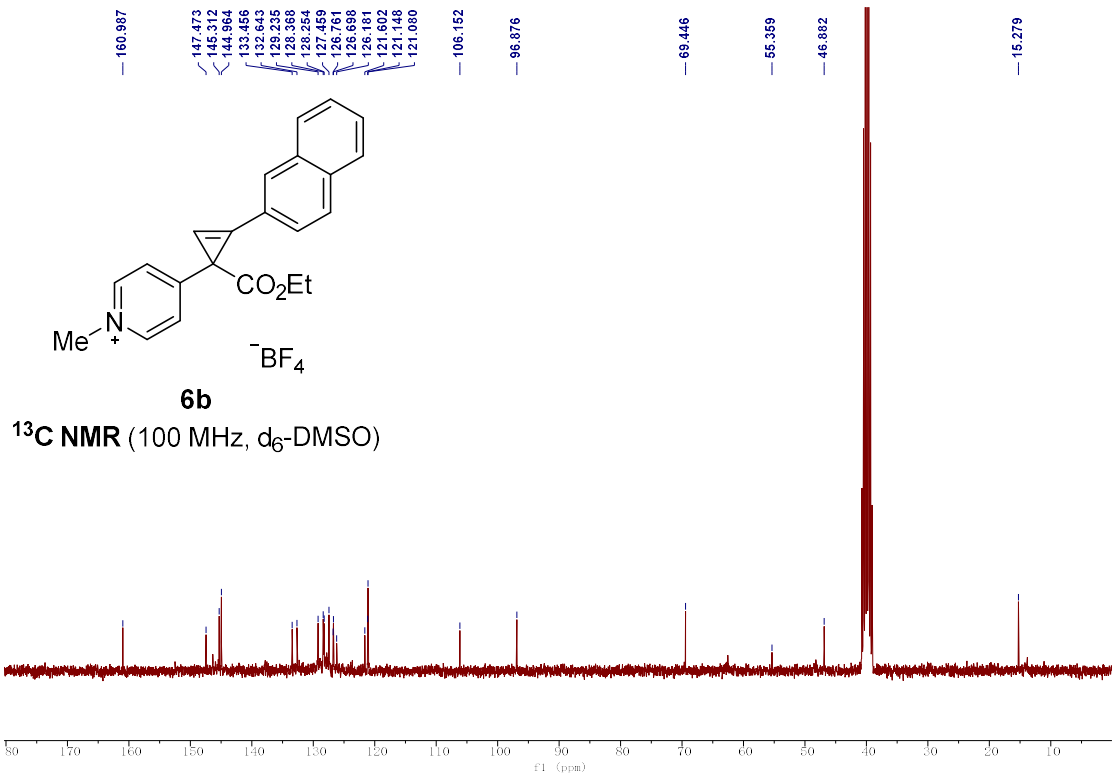
6a

^{13}C NMR (100 MHz, $CDCl_3$)



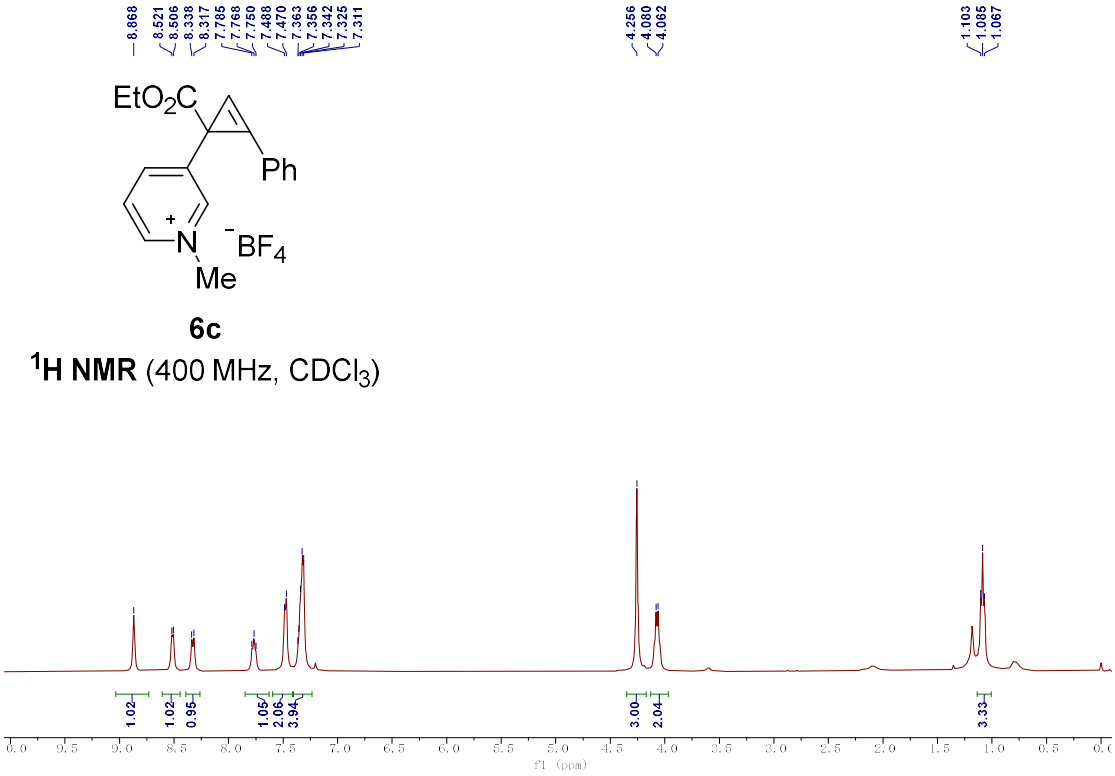
6b

^{1}H NMR (400 MHz, d_6-DMSO)



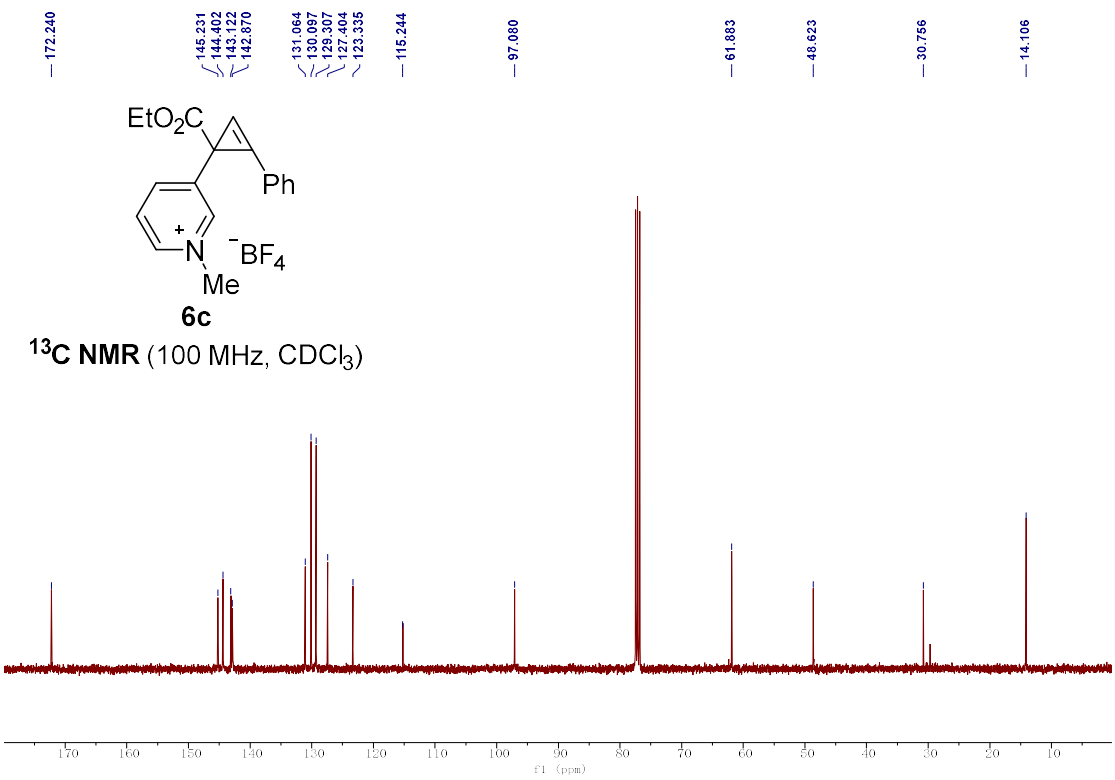
6b

^{13}C NMR (100 MHz, d_6-DMSO)



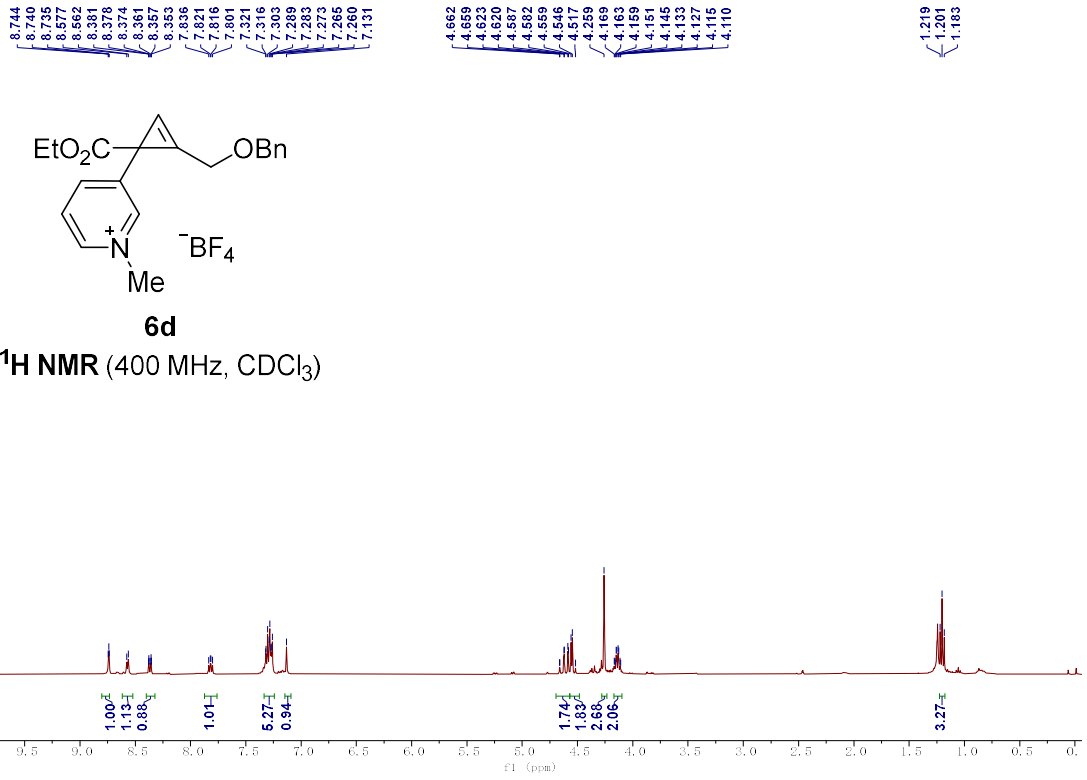
6c

^{1}H NMR (400 MHz, $CDCl_3$)



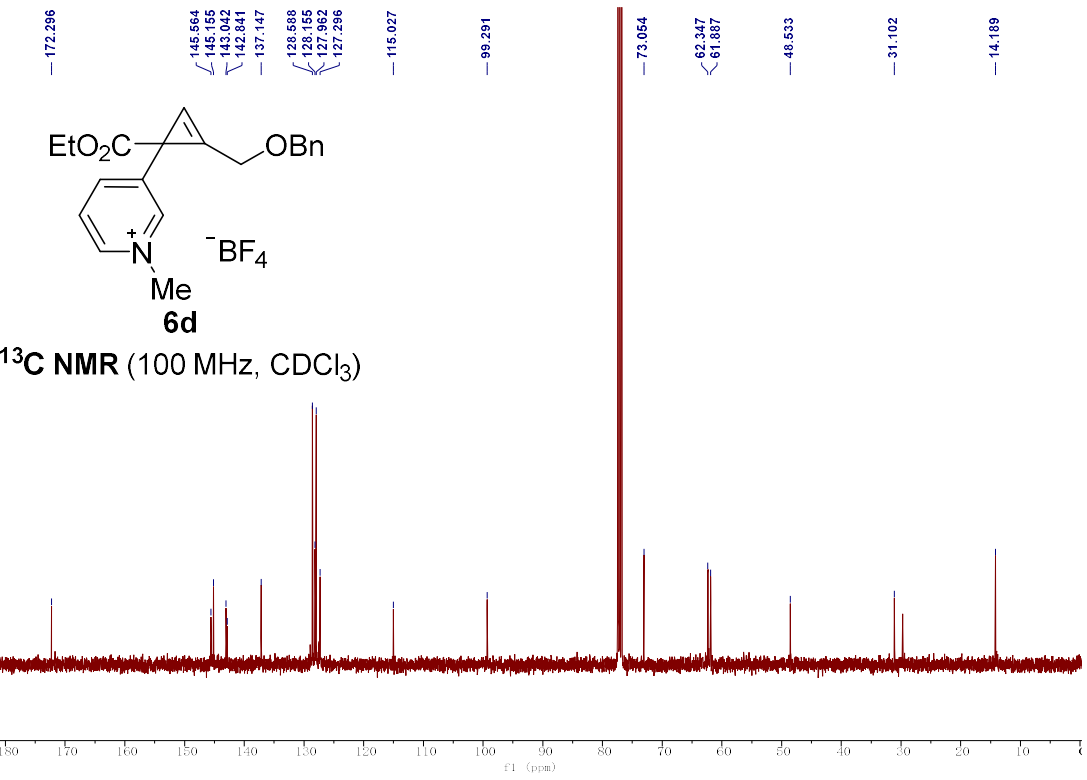
6c

^{13}C NMR (100 MHz, $CDCl_3$)



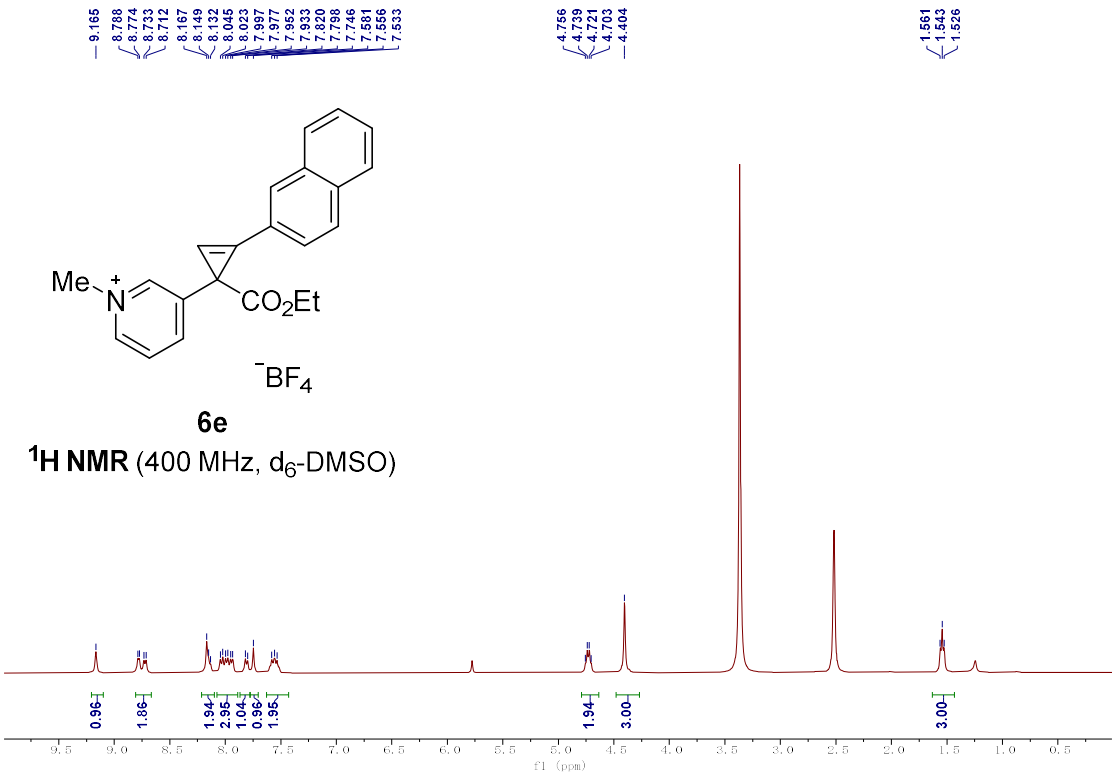
6d

^{1}H NMR (400 MHz, $CDCl_3$)



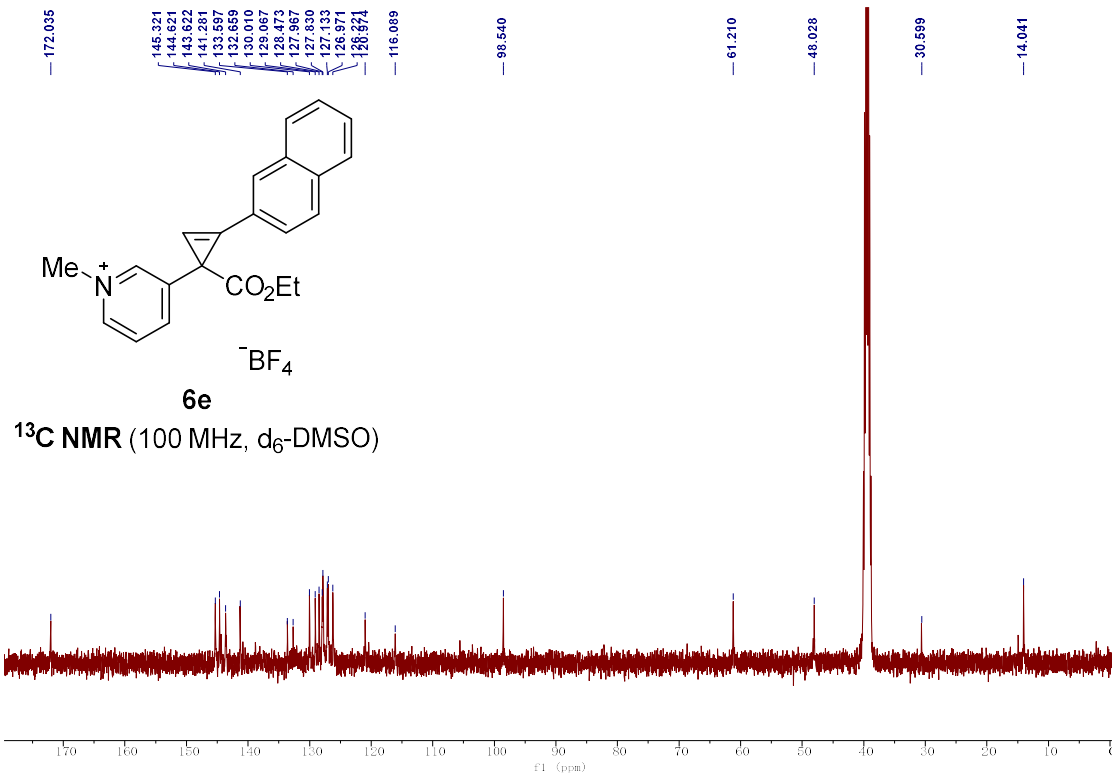
6d

^{13}C NMR (100 MHz, $CDCl_3$)



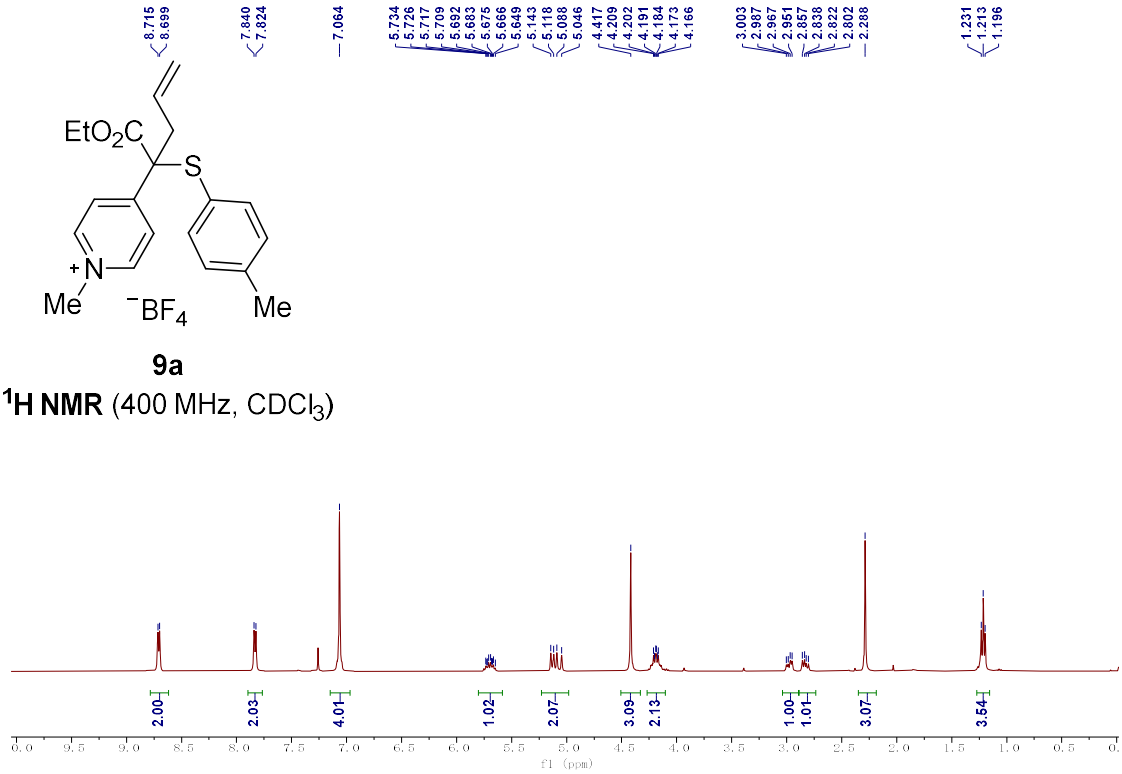
6e

^{1}H NMR (400 MHz, d_6-DMSO)



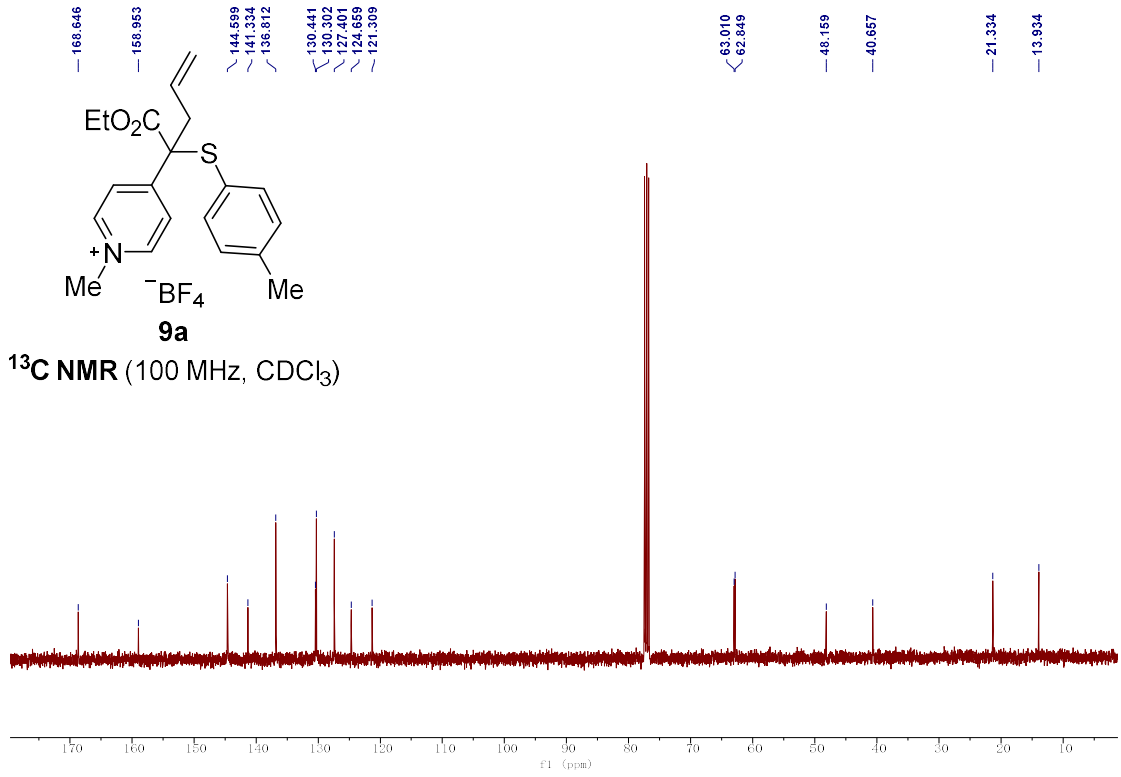
6e

^{13}C NMR (100 MHz, d_6-DMSO)



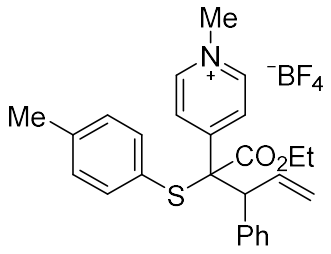
9a

^{1}H NMR (400 MHz, $CDCl_3$)



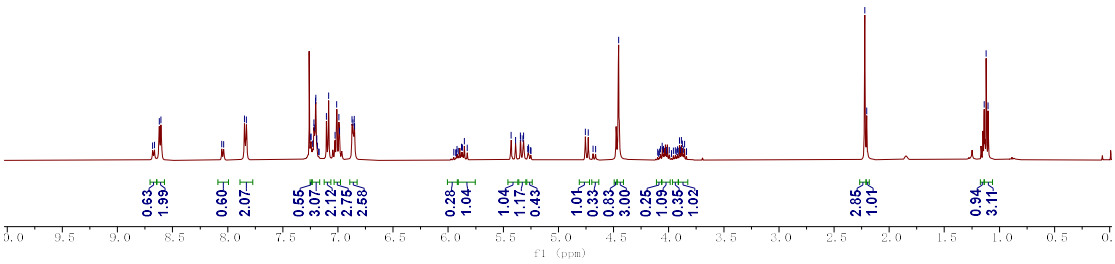
9a

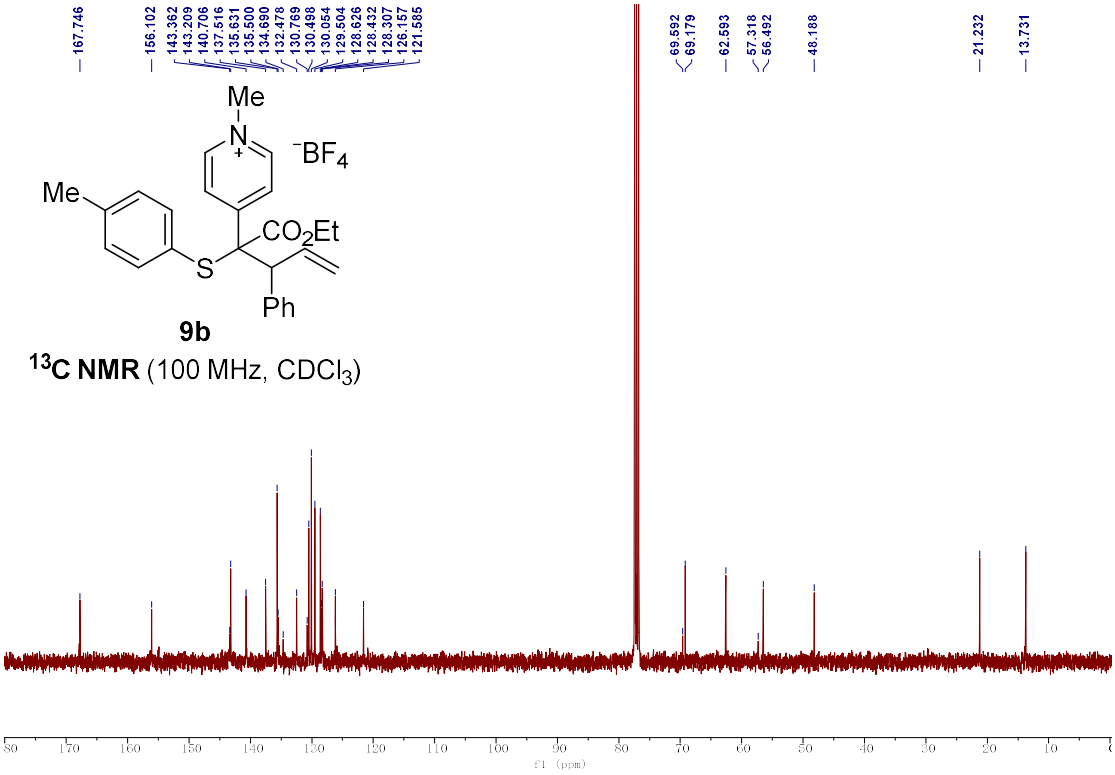
^{13}C NMR (100 MHz, $CDCl_3$)



9b

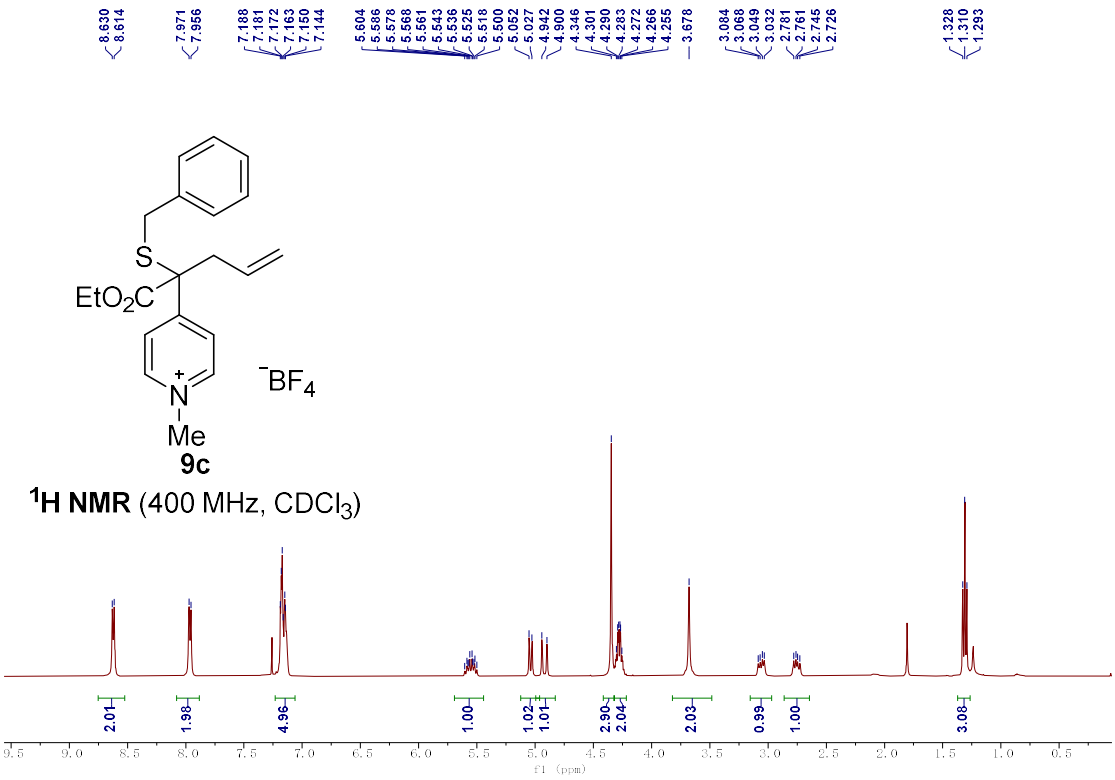
^{1}H NMR (400 MHz, $CDCl_3$)

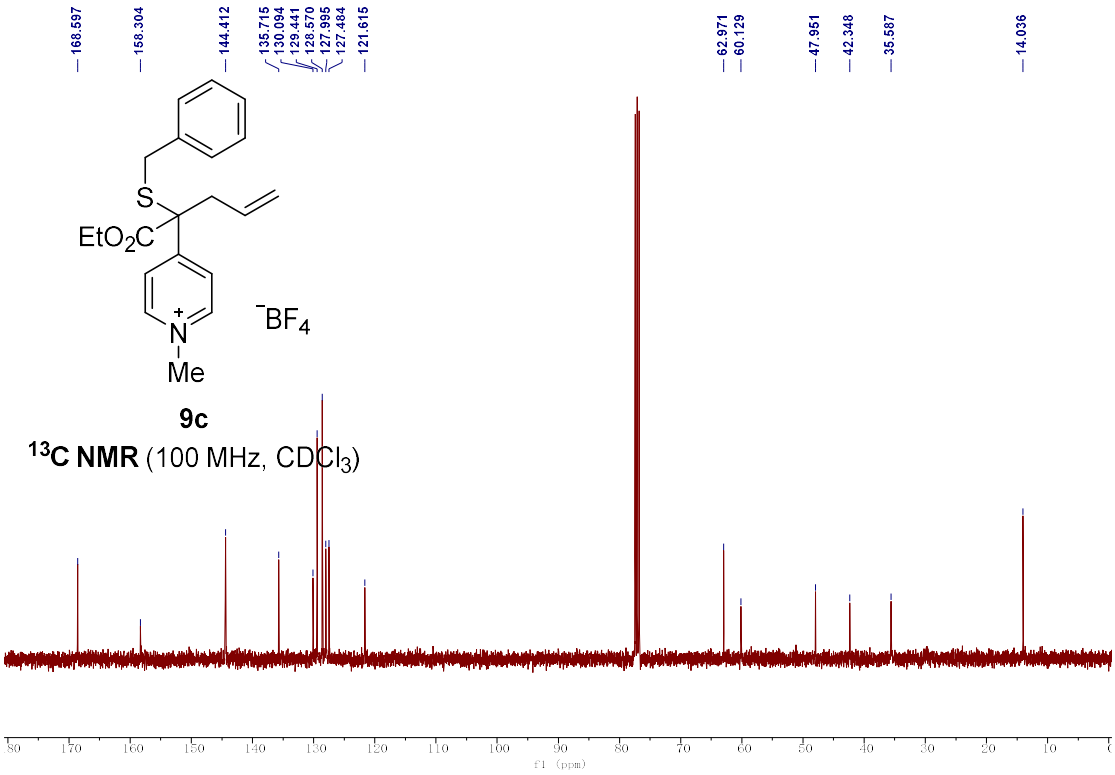


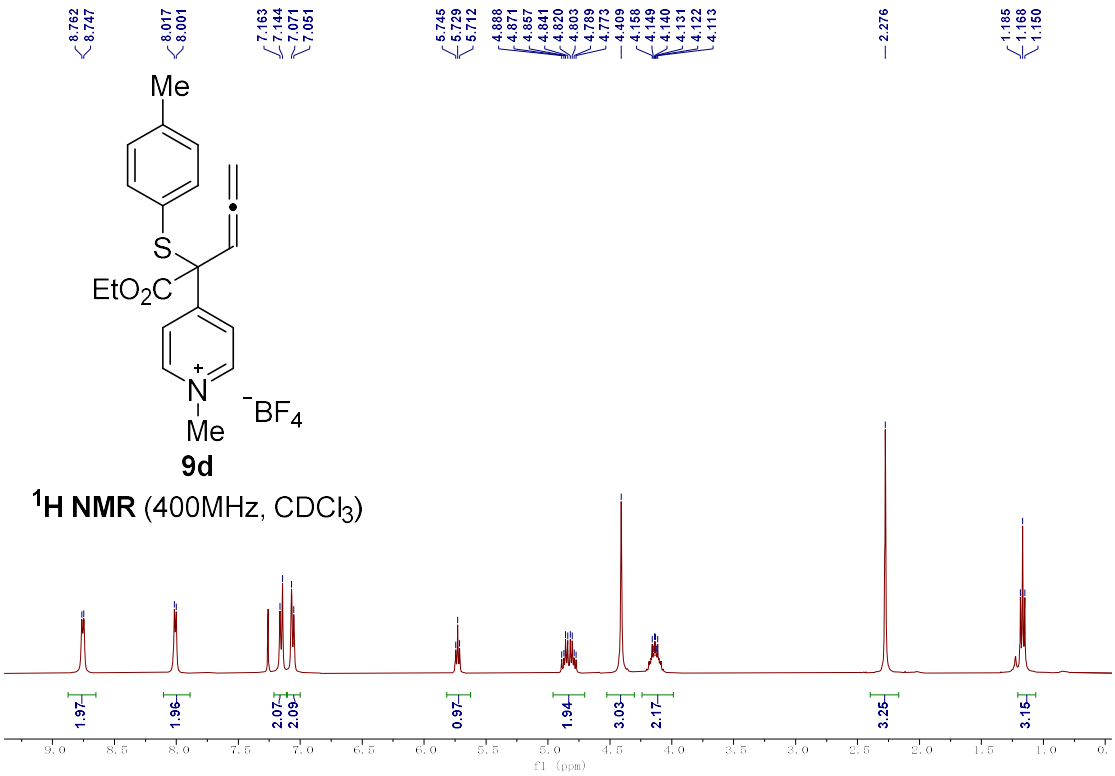


9b

^{13}C NMR (100 MHz, $CDCl_3$)

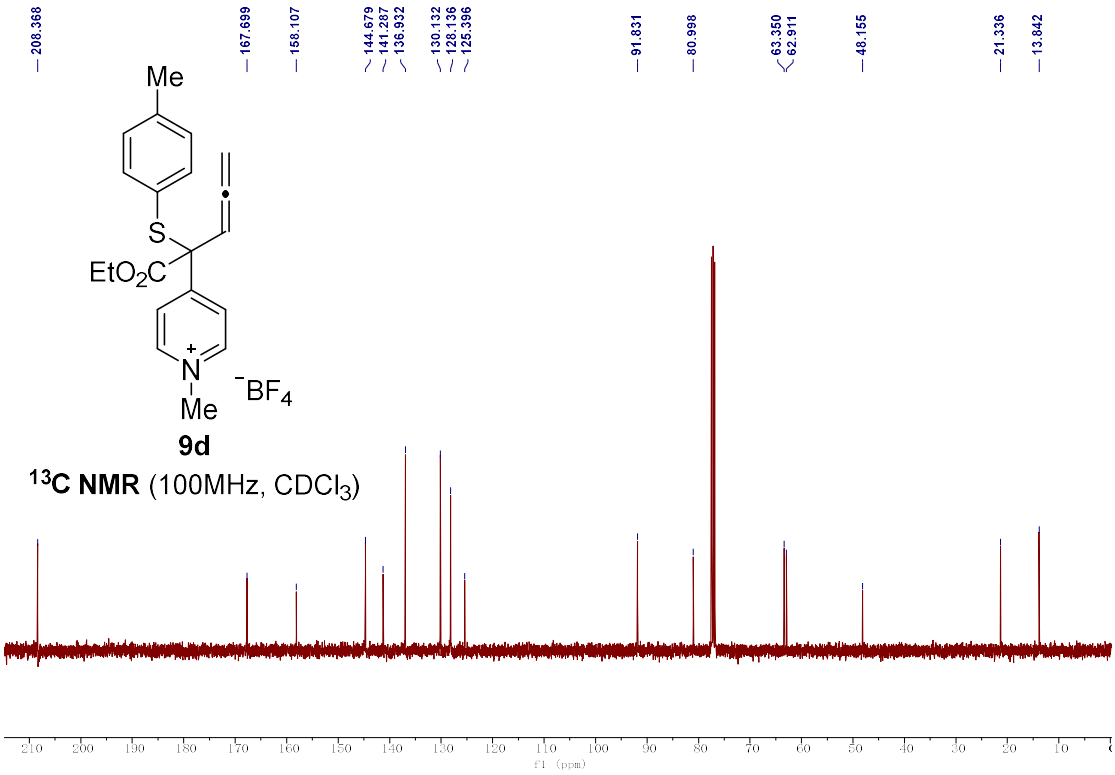

8.630
8.614
7.971
7.956
7.188
7.181
7.172
7.163
7.150
7.144
5.604
5.586
5.578
5.568
5.561
5.543
5.536
5.525
5.518
5.500
5.052
5.027
4.942
4.900
4.346
4.301
4.290
4.283
4.272
4.266
4.255
3.678
3.084
3.068
3.049
3.032
2.781
2.761
2.745
2.726
1.328
1.310
1.293
S
EtO2C
N
Me
BF4
9c
1H NMR (400 MHz, CDCl3)
2.01
1.98
4.96
1.00
1.02
1.01
2.90
2.04
2.03
0.99
1.00
3.08
f1 (ppm)


168.597
158.304
144.412
135.715
130.094
129.441
128.570
127.995
127.484
121.615
62.971
60.129
47.951
42.348
35.587
14.036
S
EtO2C
N
Me
BF4
9c
13C NMR (100 MHz, CDCl3)
f1 (ppm)



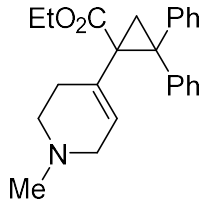
9d

^{1}H NMR (400MHz, $CDCl_3$)



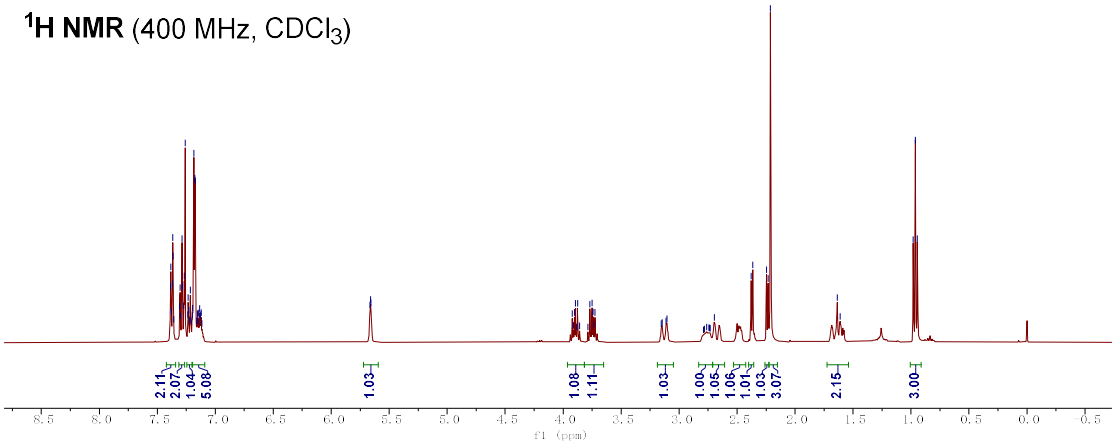
9d

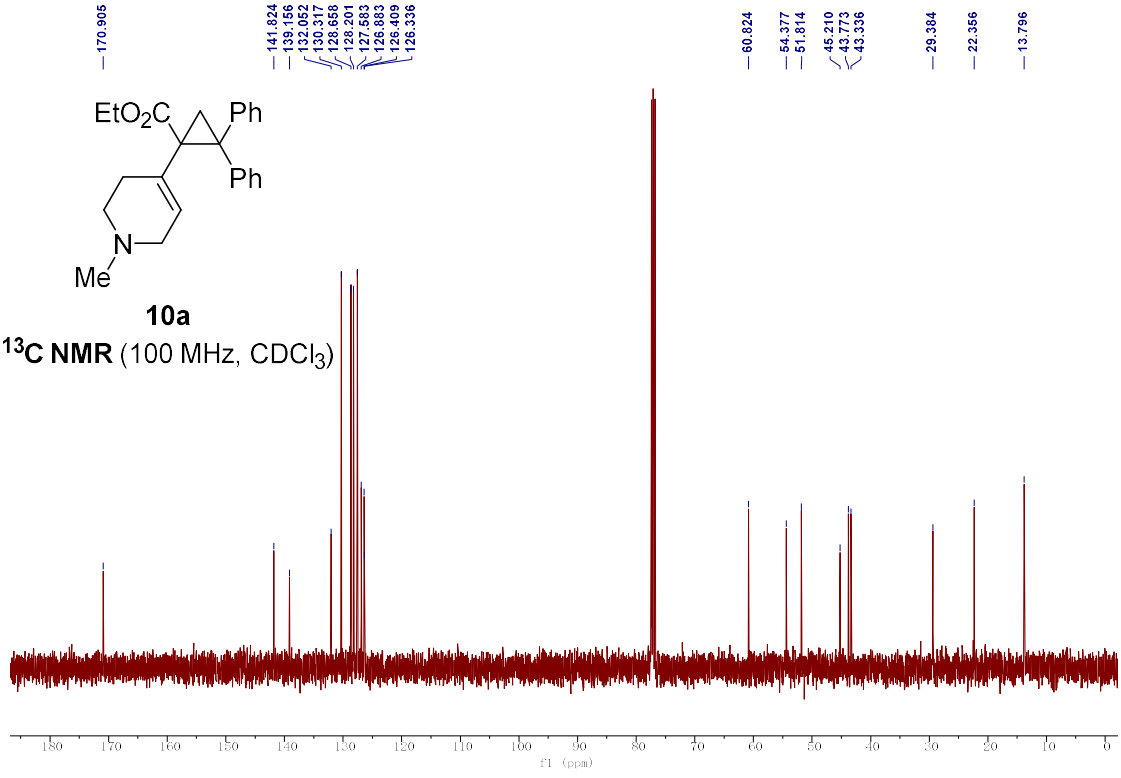
^{13}C NMR (100MHz, $CDCl_3$)



10a

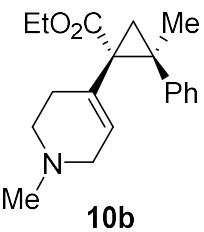
^{1}H NMR (400 MHz, $CDCl_3$)





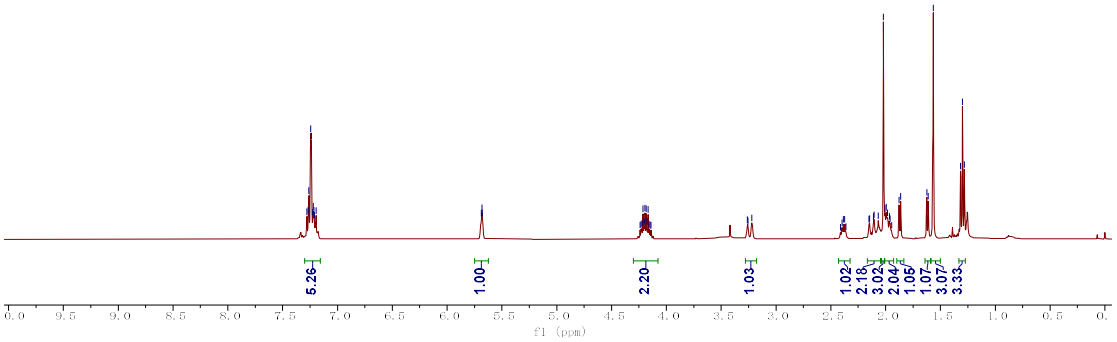
10a

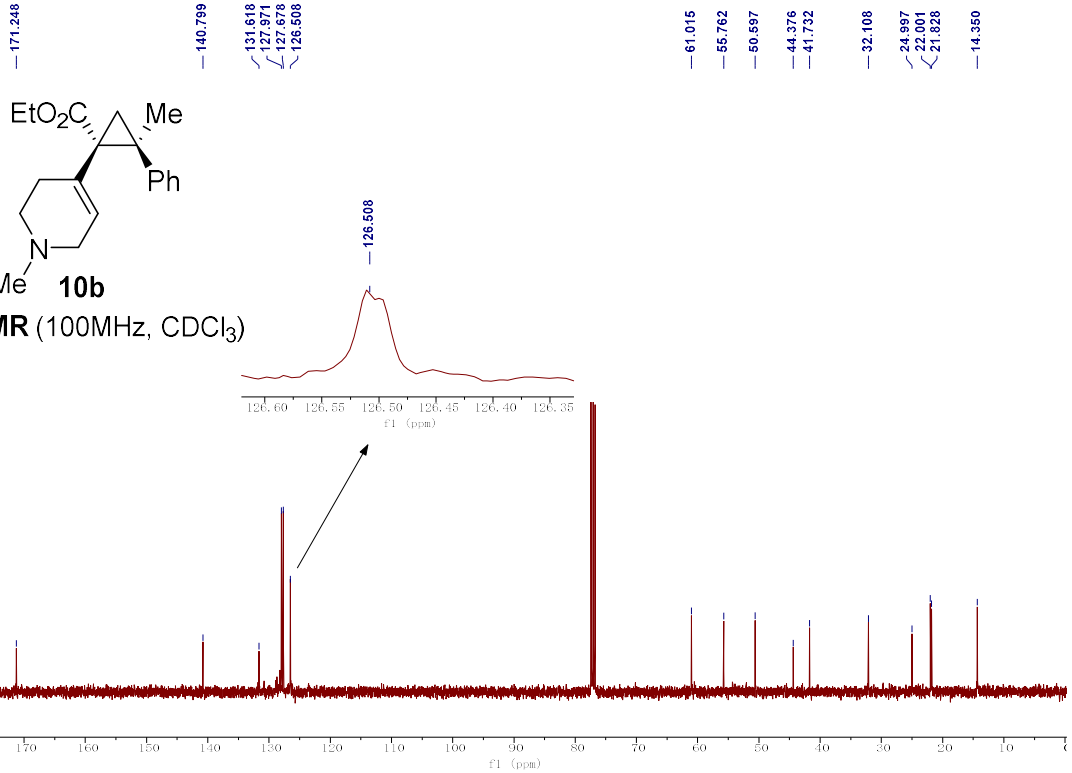
^{13}C NMR (100 MHz, $CDCl_3$)



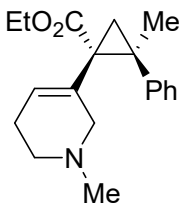
10b

^{1}H NMR (400MHz, $CDCl_3$)



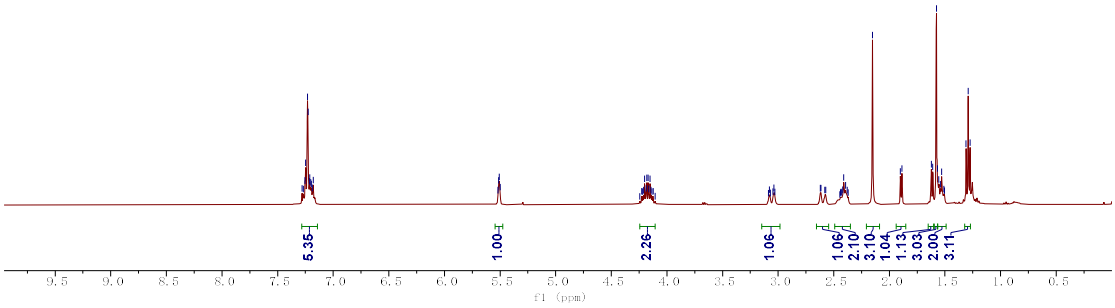


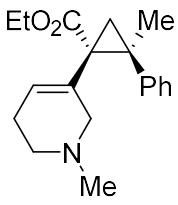
^{13}C NMR (100MHz, $CDCl_3$)



10c

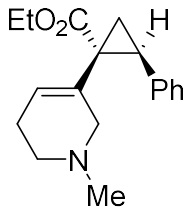
^{1}H NMR (400 MHz, $CDCl_3$)





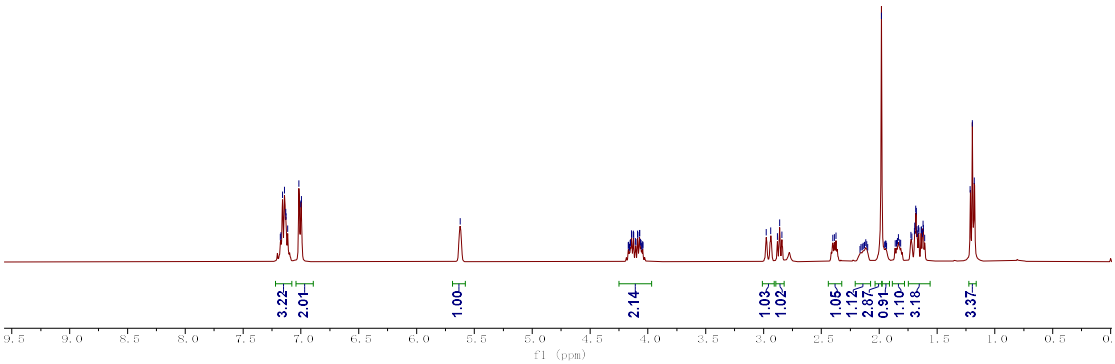
10c

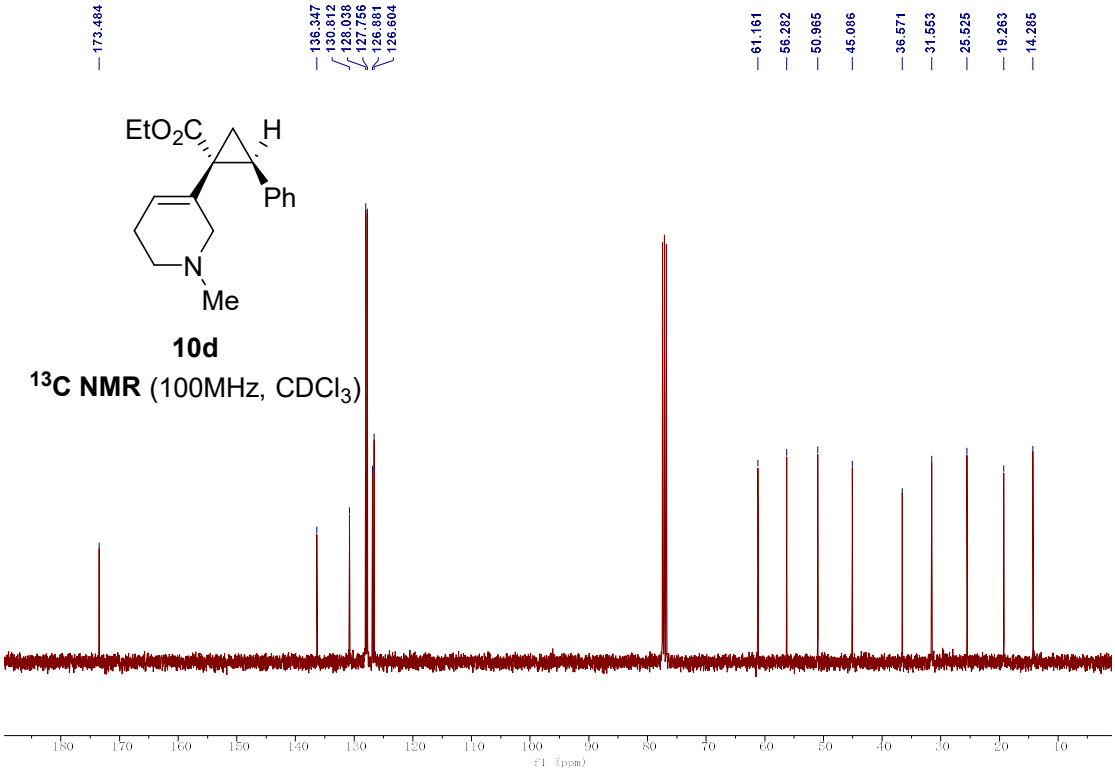
^{13}C NMR (100 MHz, $CDCl_3$)



10d

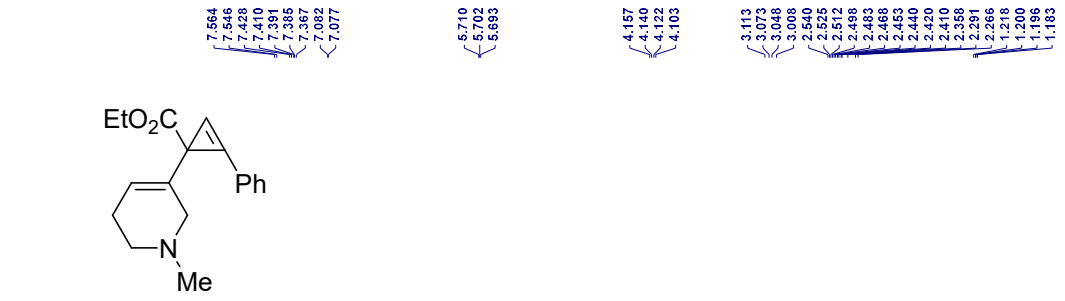
^{1}H NMR (400MHz, $CDCl_3$)





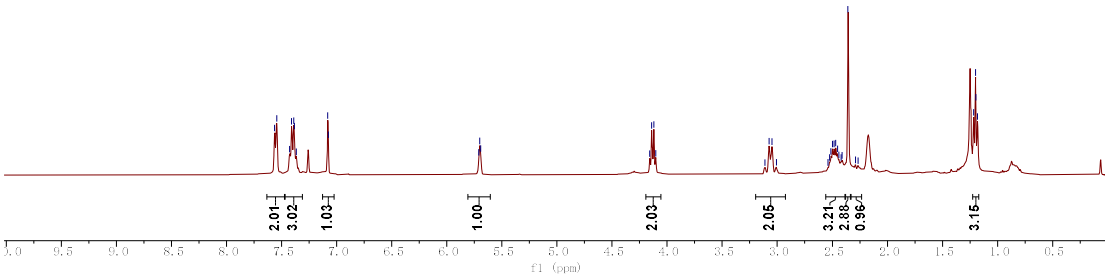
10d

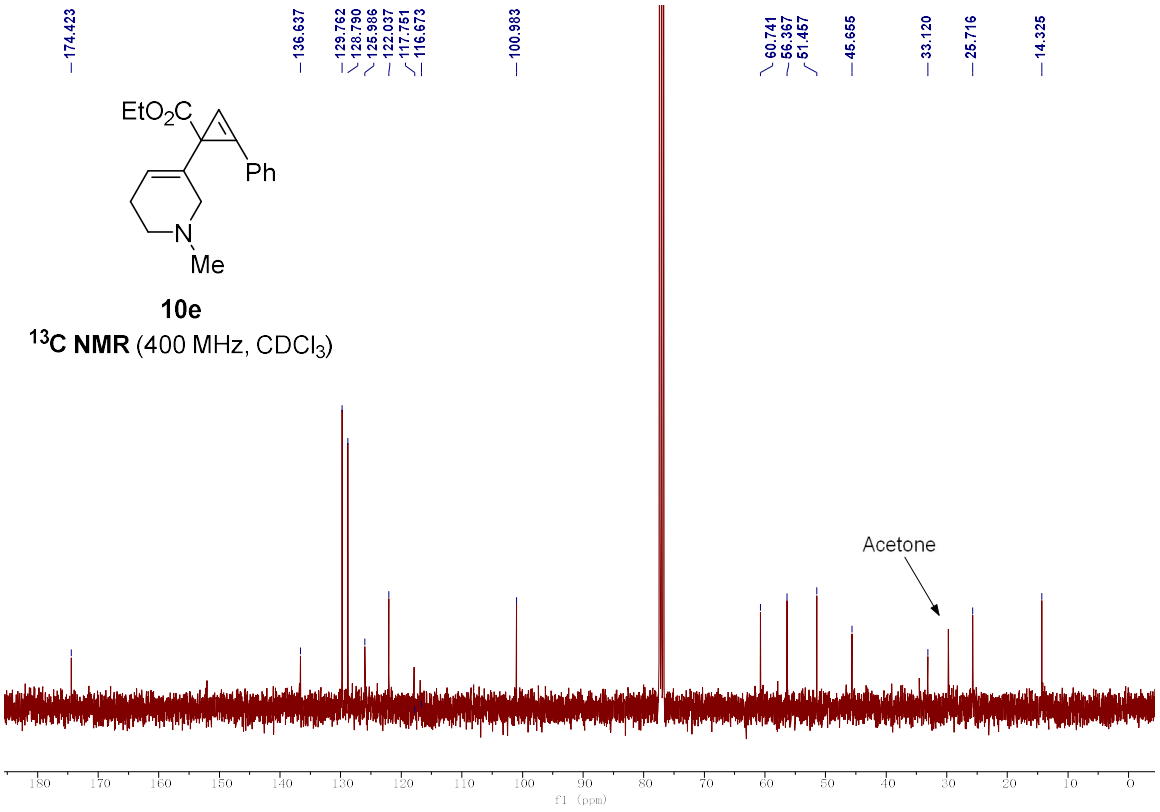
^{13}C NMR (100MHz, $CDCl_3$)



10e

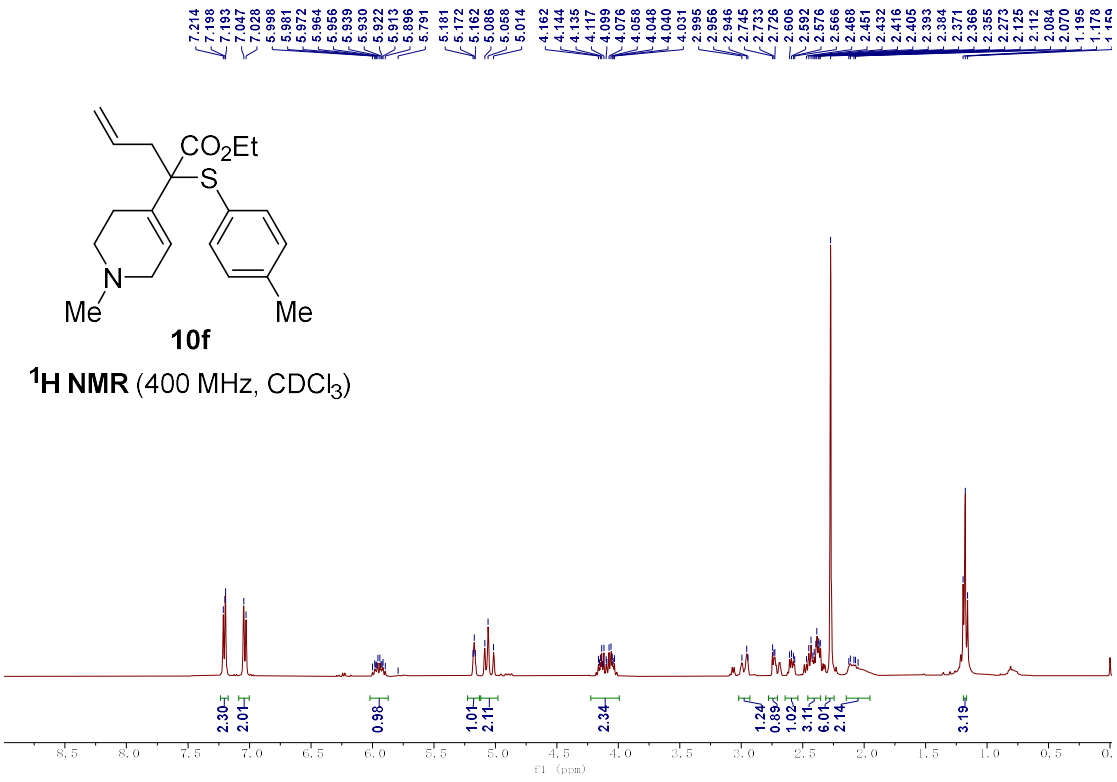
^{1}H NMR (400 MHz, $CDCl_3$)





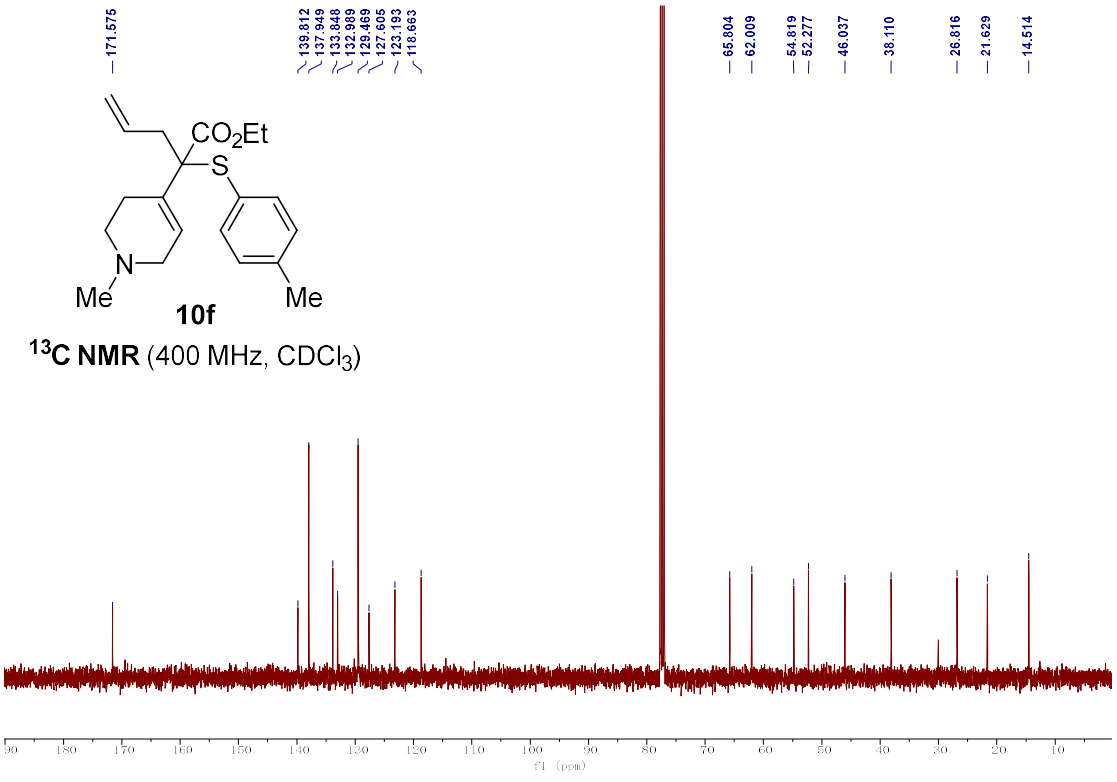
10e

^{13}C NMR (400 MHz, $CDCl_3$)



10f

^{1}H NMR (400 MHz, $CDCl_3$)



10f

^{13}C NMR (400 MHz, $CDCl_3$)