Divergent Synthesis of 5- and 4-(2,1-Azaborine) Substituted Isoxazoles via Regioselective [3+2] Cycloadditions of Nitrile Oxides and B-Ethynyl-1,2-Azaborines

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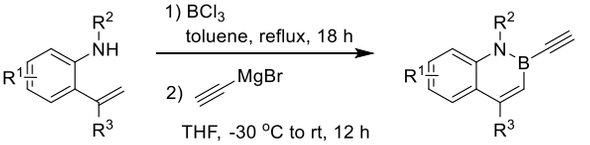
1. General Information

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker 400M and JEOL 500M spectrometers, chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) and DMSO-d_6 (δ = 2.50 ppm) as internal standards. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.0 ppm) and DMSO-d_6 (δ = 39.5 ppm). Data for ^{1}H NMR are recorded as following abbreviations: multiplicity (s = singlet, d = doublet, t = triplet, q = quarter, m = multiplet), coupling constant (*J*, Hz). High resolution mass spectroscopy (HRMS) analysis was performed at an Exactive Plus (Thermo Scientific) or Agilent 8890-7250.

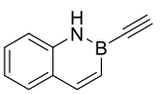
2. Synthesis of B-ethynyl-2,1-borazaronaphthalene



1a-1n

By analogy to a modified literature procedure[1], substituted vinylaniline (5 mmol, 1.0 equiv) was dissolved in 10 mL anhydrous toluene in a Schlenk flask. Borontrichloride solution (1.0 M in toluene; 10 mL, 10 mmol, 2.0 equiv) was added dropwise via syringe to the vigorously stirring solution of amine in toluene. At the conclusion of the addition, the reaction mixture was heated at reflux for 18 h. At the end of the reaction, volatiles were removed under reduced pressure to afford the corresponding B−Cl intermediate 2-chloro-1-aza-2-boranaphthalene as an air- and moisture-sensitive oil, which could be used as is in the next step without further purification. To the Schlenk flask containing the 2-chloro-2,1-borazaronaphthalene was added 10 mL anhydrous THF and the resulting solution was cooled to -30 °C. The ethynylmagnesium bromide solution (0.5 M in THF; 30 mL, 15 mmol, 3.0 equiv) was added dropwise using a syringe, and then the reaction mixture was allowed to warm to room temperature and stirred for 12 h. At the end of the reaction, the mixture was concentrated under reduced pressure, and the remaining residue was purified by flash column chromatography (petroleum ether and ethyl acetate) to afford the corresponding B-ethynyl-2,1-borazaronaphthalene **1a-1n**.

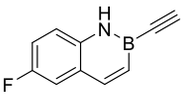
2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1a)



The general procedure was followed by using 2-vinylaniline (5 mmol) to afford the desired product **1a** (85%) as a white solid (mp: 66-68 °C). R_f = 0.6 (silica gel, PE:EtOAc = 20:1).

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.11 (d, *J* = 11.4 Hz, 1H), 7.67 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.53 – 7.42 (m, 1H), 7.30 – 7.22 (m, 2H), 6.97 (dd, *J* = 11.4, 1.8 Hz, 1H), 2.96 (s, H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.6, 139.3, 129.4, 128.6, 125.3, 121.6, 118.0, 93.1. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 25.1 (s).
HRMS (EI) calcd for $C_{10}H_8BN$: 153.0750, found: 153.0743

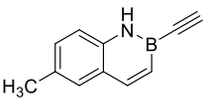
2-ethynyl-6-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1b)



The general procedure was followed by using 4-fluoro-2-vinylaniline (5 mmol) to afford the desired product **1b** (71%) as a white solid (mp: 66-68 ºC). R_f = 0.5 (silica gel, PE:EtOAc = 20:1).

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.99 (d, *J* = 11.5 Hz, 1H), 7.30 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.03 – 6.90 (m, 1H), 2.92 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.4 (d, *J* = 240.2 Hz), 144.7 (d, *J* = 3.3 Hz), 135.8, 131.2, 125.8 (d, *J* = 8.3 Hz), 119.2 (d, *J* = 8.5 Hz), 116.8 (d, *J* = 24.7 Hz), 113.8 (d, *J* = 21.7 Hz), 93.3. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 24.9 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -121.23 (s). **HRMS (EI)** calcd for $C_{10}H_7BFN$: 171.0656, found: 171.0657

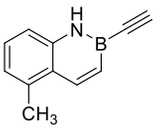
2-ethynyl-6-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1c)



The general procedure was followed by using 4-methyl-2-vinylaniline (5 mmol) to afford the desired product **1c** (45%) as a white solid (mp: 66-68 ºC). R_f = 0.5 (silica gel, PE:EtOAc = 20:1).

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.02 (d, *J* = 11.5 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.27 (dd, *J* = 8.0, 2.2 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.92 (dd, *J* = 11.4, 1.9 Hz, 1H), 2.92 (s, 1H), 2.44 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.3, 137.4, 130.9, 130.0, 129.1, 125.3, 117.8, 92.8, 20.8. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 24.9 (s). **HRMS (EI)** calcd for $C_{11}H_{10}BN$: 167.0906, found: 167.0903

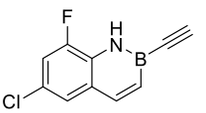
2-ethynyl-5-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1d)



The general procedure was followed by using 3-methyl-2-vinylaniline (5 mmol) to afford the desired product **1d** (60%) as a colorless oil. R_f = 0.5 (silica gel, PE:EtOAc = 20:1).

^{1}H NMR NMR (500 MHz, $CDCl_3$)δ 8.35 (d, *J* = 11.7 Hz, 1H), 8.208.14 (s, 1H), 7.33 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.98 (dd, *J* = 11.7, 2.0 Hz, 1H), 2.948.14 (s, 1H), 2.628.14 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.8, 139.8, 136.5, 128.4, 124.1, 123.4, 116.8, 93.2, 19.6. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 22.6 (s). **HRMS (EI)** calcd for $C_{11}H_{10}BN$: 167.0906, found: 167.0906

6-chloro-2-ethynyl-8-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1e)

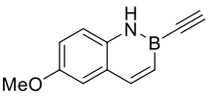


The general procedure was followed by using 4-chloro-2-fluoro-6-vinylaniline (5 mmol) to afford the desired product **1e** (74%) as a white solid (mp: 106-108 ºC). R_f = 0.4 (silica gel, PE:EtOAc = 20:1).

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.95 (dd, *J* = 11.7, 1.8 Hz, 1H), 7.40 (d, *J* = 1.7 Hz, 1H), 7.23 (dd, *J* = 10.3, 2.1 Hz, 1H), 7.03 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.96 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ

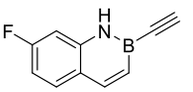
151.0 (d, *J* = 247.5 Hz), 143.6 (d, *J* = 3.0 Hz), 127.2 (d, *J* = 3.8 Hz), 127.1 (d, *J* = 12.6 Hz), 125.5 (d, *J* = 10.3 Hz), 123.9 (d, *J* = 3.6 Hz), 114.1 (d, *J* = 21.2 Hz), 94.0. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 25.2 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -133.52 (s). **HRMS (EI)** calcd for $C_{10}H_6BClFN$: 205.0266, found: 205.0273

2-ethynyl-6-methoxy-1,2-dihydrobenzo[e][1,2]azaborinine (1f)



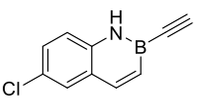
The general procedure was followed by using 4-methoxy-2-vinylaniline (5 mmol) to afford the desired product **1f** (44%) as a white solid (mp: 105-107 °C). R_f = 0.3 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.01 (d, *J* = 11.4 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.94 (dd, *J* = 11.5, 1.9 Hz, 1H), 3.86 (s, 3H), 2.90 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.1, 145.0, 134.1, 130.4, 125.8, 119.0, 118.1, 110.3, 92.8, 55.5. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 22.2 (s). **HRMS (EI)** calcd for $C_{11}H_{10}BNO$: 183.0855, found: 183.0859

2-ethynyl-7-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1g)



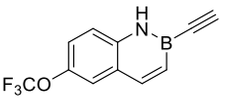
The general procedure was followed by using 5-fluoro-2-vinylaniline (5 mmol) to afford the desired product **1g** (54%) as a white solid (mp: 51-52 °C). R_f = 0.5 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$)δ 8.15 (s, 1H), 8.03 (d, *J* = 11.4 Hz, 1H), 7.59 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.04 – 6.91 (m, 2H), 6.87 (dd, *J* = 11.4, 2.0 Hz, 1H), 2.94 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.6 (d, *J* = 247.7 Hz), 145.1, 140.5 (d, *J* = 10.9 Hz), 131.2 (d, *J* = 10.2 Hz), 122.1, 110.1 (d, *J* = 23.0 Hz), 103.8 (d, *J* = 23.7 Hz), 93.7. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 25.5 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -111.05 (s).
HRMS (EI) calcd for $C_{10}H_7BFN$: 171.0656, found: 171.0663

6-chloro-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1h)



The general procedure was followed by using 4-chloro -2-vinylaniline (5 mmol) to afford the desired product **1h** (65%) as a white solid (mp: 113-115 °C). R_f = 0.4 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.96 (d, *J* = 11.4 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.97 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.94 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.4, 137.7, 128.7, 128.4, 126.6, 126.1, 119.2, 93.7. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 25.2 (s). **HRMS (EI)** calcd for C10H7BClN: 187.0360, found: 187.0362

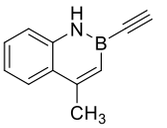
2-ethynyl-6-(trifluoromethoxy)-1,2-dihydrobenzo[e][1,2]azaborinine (1i)



The general procedure was followed by using 4-trifluoromethoxy-2-vinylaniline (5 mmol) to afford the desired product **1i** (54%) as a white solid (mp: 38-39 °C). R_f = 0.3 (silica gel, PE:EtOAc = 20:1).

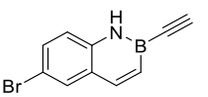
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.02 (d, *J* = 11.5 Hz, 1H), 7.49 (d, *J* = 2.5 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.26 (d, *J* = 8.9 Hz, 1H), 7.00 (dd, *J* = 11.5, 1.8 Hz, 1H), 2.94 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.8, 143.2, 137.8, 125.6, 122.1, 121.1, 120.6 (q, *J*=257.0 Hz), 119.2, 93.7. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 25.3 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -58.04 (s). **HRMS (EI)** calcd for $C_{11}H_7BF_3NO$: 237.0573, found: 237.0570

2-ethynyl-4-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1j)



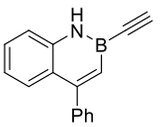
The general procedure was followed by using 2-isopropenylaniline (5 mmol) to afford the desired product **1j** (65%) as a white solid (mp: 66-68 ºC). R_f = 0.6 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83 (dt, *J* = 8.6, 1.1 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.28 – 7.22 (m, 2H), 6.78 (t, *J* = 1.6 Hz, 1H), 2.91 (s, 1H), 2.61 (d, *J* = 1.2 Hz, 3H)). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.2, 139.7, 128.3, 125.7, 125.5, 121.5, 118.6, 92.6, 22.7. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 22.6 (s). **HRMS (EI)** calcd for $C_{10}H_8BN$: 167.0906, found: 167.0911

6-bromo-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1k)



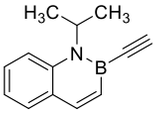
The general procedure was followed by using 4-bromo-2-vinylaniline (5 mmol) to afford the desired product **1k** (37%) as a white solid (mp: 122-123 ºC). R_f = 0.5 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.95 (d, *J* = 11.5 Hz, 1H), 7.76 (d, *J* = 2.3 Hz, 1H), 7.50 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.96 (dd, *J* = 11.5, 2.0 Hz, 1H), 2.94 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 138.0, 131.5, 131.3, 126.7, 119.5, 114.0, 93.6. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 23.0 (s). **HRMS (EI)** calcd for $C_{10}H_7BBrN$: 230.9855, found: 230.9846

2-ethynyl-4-phenyl-1,2-dihydrobenzo[e][1,2]azaborinine (1l)



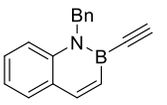
The general procedure was followed by using 2-(1-phenylvinyl)aniline (5 mmol) to afford the desired product **1l** (53%) as a white solid (mp: 90-92 ºC). R_f = 0.4 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.65 – 7.61 (m, 1H), 7.50 – 7.40 (m, 6H), 7.32 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.87 (d, *J* = 1.9 Hz, 1H), 2.93 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)**156.9, 141.9, 140.0, 128.9, 128.5, 128.2, 128.1, 127.5, 124.5, 121.5, 118.5, 93.0. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 22.8 (s)**. HRMS (EI)** calcd for $C_{16}H_{12}BN$: 229.1063, found: 229.1058

2-ethynyl-1-isopropyl-1,2-dihydrobenzo[e][1,2]azaborinine (1m)



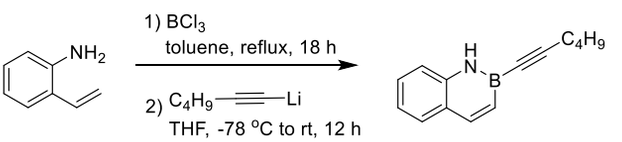
The general procedure was followed by using N-isopropyl-2-vinylaniline (5 mmol) to afford the desired product **1m** (65%) as a colorless oil**.** R_f = 0.5 (silica gel, PE:EtOAc = 20:1). **^{1}H NMR NMR (500 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 11.3 Hz, 1H), 7.94 – 7.73 (m, 1H), 7.69 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 11.3 Hz, 1H), 5.36 (d, *J* = 362.2 Hz, 1H), 3.24 (s, 1H), 1.78 (d, *J* = 7.3 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.9, 130.9, 127.6, 120.7, 118.4, 114.2, 99.0, 96.1, 53.8, 49.6, 23.0, 21.6. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 22.5 (s). **HRMS (EI)** calcd for $C_{13}H_{14}BN$: 195.1219, found: 195.1213

1-benzyl-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1n)



The general procedure was followed by using N-benzyl-2-vinylaniline (5 mmol) to afford the desired product **1n** (65%) as a white solid (mp: 75- 76 ºC). R_f = 0.5 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 11.4 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.31 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.27 – 7.17 (m, 4H), 7.07 (d, *J* = 11.4 Hz, 1H), 5.68(s, 2H), 3.07(s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 140.8, 138.2, 130.3, 128.7, 128.6, 127.1, 127.0, 126.0, 121.3, 116.4, 96.0, 53.56. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 24.9 (s). **HRMS (EI)** calcd for $C_{17}H_{14}BN$: 243.1219, found: 243.1228

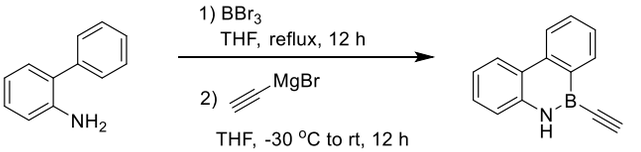
2-(hex-1-yn-1-yl)-1,2-dihydrobenzo[e][1,2]azaborinine (1o)



By analogy to a modified literature procedure[1], o-vinylaniline (5 mmol, 1.0 equiv) was dissolved in 10 mL anhydrous toluene in a Schlenk flask. Borontrichloride solution (1.0 M in toluene; 10 mL, 10 mmol, 2.0 equiv) was added dropwise via syringe to the vigorously stirring solution of amine in toluene. At the conclusion of the addition, the reaction mixture was heated at reflux for 18 h. At the end of the reaction, volatiles were removed under reduced pressure to afford the corresponding B−Cl intermediate 2-chloro-1-aza-2-boranaphthalene as an air- and moisture-sensitive oil, which could be used as is in the next step without further purification. To the Schlenk flask containing the 2-chloro-2,1-borazaronaphthalene was added 10 mL anhydrous THF and the resulting solution was cooled to -78 ºC. The hexynyllithium (6.5 mmol, 1.3 equiv), prepared from hexyne and *n*-butyllithium, was added dropwise using a syringe, and then the reaction mixture was allowed to warm to room temperature and stirred for 12 h. At the end of the reaction, the mixture was concentrated under reduced pressure, and the remaining residue was purified by flash column chromatography (petroleum ether and ethyl acetate) to afford the desired product **1o** (50%) as a colorless oil. R_f = 0.5 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 11.4 Hz, 2H), 7.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.24 – 7.13 (m, 2H), 6.92 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.44 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.58 –

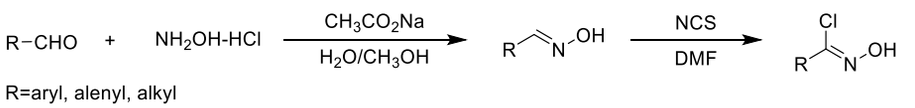
1.49 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.0, 139.7, 129.3, 128.3, 125.2, 121.1, 117.8, 107.9, 30.8, 22.0, 19.7, 13.6. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 25.4 (s). **HRMS (EI)** calcd for $C_{14}H_{16}BN$: 209.1376, found: 209.1373

6-ethynyl-5,6-dihydrodibenzo[c,e][1,2]azaborinine (5)



By analogy to a modified literature procedure, [1,2] to the stirring solution of 2-aminodiphenyl (5 mmol, 1 equiv) in 10 mL dry CH_2Cl_2 at 0 °C was added BBr_3 (1.0M in CH_2Cl_2, 3 equiv) drop-wise under argon atmosphere. Then the solution was warmed to room temperature and then stirred at 45 °C for 12 h. At the conclusion of the reaction, volatiles were removed under reduced pressure to afford the corresponding B−Br intermediate as an air- and moisture-sensitive oil, which could be used as is in the next step without further purification.the mixture was concentrated under reduced pressure and reused argon protection. To the Schlenk flask containing the B−Br intermediate was added 10 mL anhydrous THF and the resulting solution was cooled to -30 °C. The ethynylmagnesium bromide solution (0.5 M in THF; 30 mL, 15 mmol, 3.0 equiv) was added dropwise using a syringe, and then the reaction mixture was allowed to warm to room temperature and stirred for 12 h. At the end of the reaction, the mixture was concentrated under reduced pressure, and the remaining residue was purified by flash column chromatography (petroleum ether and ethyl acetate) to afford the desired product **5** (30%) as a white solid (mp: 92- 94 °C). R_f = 0.4 (silica gel, PE:EtOAc = 20:1).
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.51 – 8.34 (m, 3H), 7.93 (s, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 3.12 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.3, 138.0, 135.8, 131.5, 128.0, 126.2, 123.9, 123.4, 122.1, 121.9, 119.0, 95.0. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 25.2 (s). **HRMS (EI)** calcd for $C_{14}H_{10}BN$: 203.0906, found: 203.0915

3. Synthesis of oxime chlorides

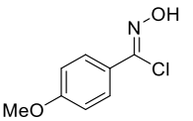


The oxime chloride **2a-2r** were prepared according to the reference.[3,4]

A 100 mL round-bottomed flask was charged with aldehyde (5 mmol, 1 equiv), hydroxylamine hydrochloride (10 mmol, 2 equiv), 2.5 mL H_2O and 22.5 mL methanol. Then, CH_3CO_2Na (10 mmol, 2 equiv) was added to the solution. The reaction was stirred at room temperature for 2 h. Upon completion, methanol was removed, aqueous layers was extracted with ethyl acetate thrice. The combine organic layers were dried over anhydrous Na_2SO_4. After removal of the solvent, the crude aldoxime was used in the next step.

A 100 mL round-bottomed flask was charged with the crude aldoxime of the first step and 15 mL DMF. Then, N-chlorosuccinimide (5.5 mmol, 1.1 equiv) in 15 mL DMF was added dropwise over a period of 20 minutes to the solution. The reaction was stirred for 2 hours at room temperature. Upon completion, the reaction mixture was diluted with 5% LiCl (aq), extracted with ethyl acetate thrice, the combine organic layers were washed with 5% LiCl (aq) and brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue purified on silica gel (petroleum ether: ethyl acetate = 30:1-5:1) to afford desired oxime chloride.

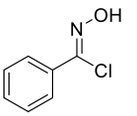
N-hydroxy-4-methoxybenzimidoyl chloride (2a)



The general procedure was followed by using 4-methoxybenzaldehyde (4 mmol) to afford the desired product **2a** (85%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.89 – 7.66 (m, 2H), 6.95 – 6.89 (m, 2H), 3.85 (s, 3H).

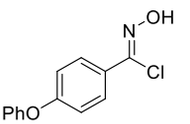
N-hydroxybenzimidoyl chloride (2b)



The general procedure was followed by using benzaldehyde (4 mmol) to afford the desired product **2b** (71%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.91 – 7.79 (m, 2H), 7.49 – 7.37 (m, 3H).

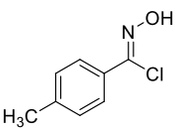
N-hydroxy-4-phenoxybenzimidoyl chloride (2c)



The general procedure was followed by using 4-phenoxy benzaldehyde (4 mmol) to afford the desired product **2c** (95%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.83 – 7.76 (m, 2H), 7.38 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.10 – 7.04 (m, 2H), 7.03 – 6.99 (m, 2H).

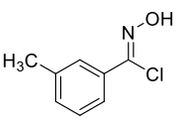
N-hydroxy-4-methylbenzimidoyl chloride (2d)



The general procedure was followed by using 4-methylbenzaldehyde (4 mmol) to afford the desired product **2d** (80%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.39.

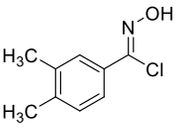
N-hydroxy-3-methylbenzimidoyl chloride (2e)



The general procedure was followed by using 3-methylbenzaldehyde (4 mmol) to afford the desired product **2e** (85%) as a colorless oil. Known compound.[4]

^{1}H NMR NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.24 (m, 2H), 2.40 (s, 3H).

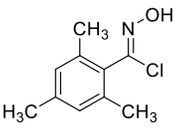
N-hydroxy-3,4-dimethylbenzimidoyl chloride (2f)



The general procedure was followed by using 3,4-dimethylbenzaldehyde (4 mmol) to afford the desired product **2f** (80%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.56 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 6H).

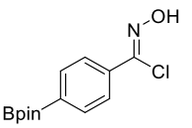
N-hydroxy-2,4,6-trimethylbenzimidoyl chloride (2g)



The general procedure was followed by using 2,4,6-trimethylbenzaldehyde (4 mmol) to afford the desired product **2g** (75%) as a colorless oil. Known compound.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 2.41 (s, 6H), 2.30 (s, 3H).

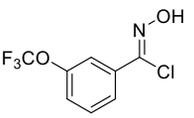
N-hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzimidoyl chloride (2h)



The general procedure was followed by using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (4 mmol) to afford the desired product **2h** (55%) as a colorless oil. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.88 – 7.79 (m, 4H), 1.37 (s, 12H).

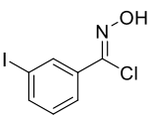
N-hydroxy-3-(trifluoromethoxy)benzimidoyl chloride (2i)



The general procedure was followed by using 3-(trifluoromethoxy)benzaldehyde (4 mmol) to afford the desired product **2i** (55%) as a colorless oil. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.81 – 7.76 (m, 1H), 7.71 (s, 1H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.33 – 7.27 (m, 1H).

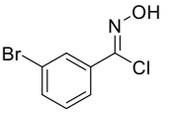
N-hydroxy-3-iodobenzimidoyl chloride (2j)



The general procedure was followed by using 3-iodobenzaldehyde (4 mmol) to afford the desired product **2j** (65%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.19 (s, 1H), 7.82 – 7.74 (m, 2H), 7.14 (t, *J* = 7.9 Hz, 1H).

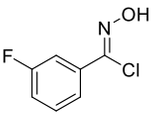
3-bromo-N-hydroxybenzimidoyl chloride (2k)



The general procedure was followed by using 3-bromobenzaldehyde (4 mmol) to afford the desired product **2k** (75%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.00 (t, *J* = 1.9 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.60 – 7.55 (m, 1H), 7.28 (t, *J* = 8.0 Hz, 1H).

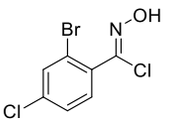
3-fluoro-N-hydroxybenzimidoyl chloride (2l)



The general procedure was followed by using 3-fluorobenzaldehyde (4 mmol) to afford the desired product **2l** (73%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.69 – 7.62 (m, 1H), 7.60 – 7.52 (m, 1H), 7.41 – 7.35 (m, 1H), 7.19 – 7.10 (m, 1H).

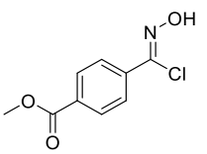
2-bromo-4-chloro-N-hydroxybenzimidoyl chloride (2m)



The general procedure was followed by using 2-bromo-4-chlorobenzaldehyde (4 mmol) to afford the desired product **2m** (80%) as a white solid (mp: 94-96 ºC). R_f = 0.5 (silica gel, PE:EtOAc = 20:1).

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.34 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.4, 137.0, 133.2, 132.9, 131.8, 127.8, 122.7. **HRMS (ESI)** calcd for $C_7H_5BrCl_2NO$ $[M+H]^+$: 267.8932, found: 267.8931.

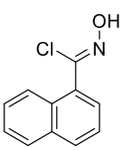
methyl 4-(chloro(hydroxyimino)methyl)benzoate (2n)



The general procedure was followed by using methyl 4-formylbenzoate (4 mmol) to afford the desired product **2n** (81%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.06 (d, *J* = 8.6 Hz), 7.91 (d, *J* = 8.4 Hz), 3.95 (s, 3H).

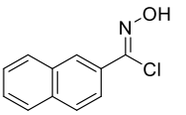
N-hydroxy-1-naphthimidoyl chloride (2o)



The general procedure was followed by using 1-naphthaldehyde (4 mmol) to afford the desired product **2o** (65%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$)δ 8.63 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.72 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.61 – 7.48 (m, 3H).

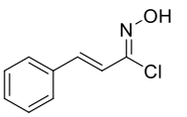
N-hydroxy-2-naphthimidoyl chloride (2p)



The general procedure was followed by using 2-naphthaldehyde (4 mmol) to afford the desired product **2p** (60%) as a white solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.34 (s, 1H), 7.96 – 7.81 (m, 4H), 7.60 – 7.48 (m, 2H).

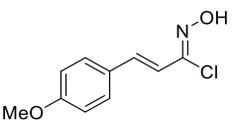
N-hydroxycinnamimidoyl chloride (2q)



The general procedure was followed by using cinnamaldehyde (4 mmol) to afford the desired product **2q** (61%) as a colorless oil. Known compound.[4]

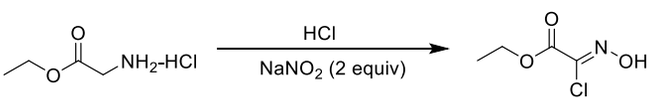
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.52 – 7.47 (m, 2H), 7.41 – 7.30 (m, 4H), 6.88 (d, *J* = 15.7 Hz, 1H).

N-hydroxy-3-(4-methoxyphenyl)acrylimidoyl chloride (2r)



The general procedure was followed by using 3-(4-methoxyphenyl)acrylaldehyde (4 mmol) to afford the desired product **2r** (65%) as a brown solid. Known compound.[4]

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 15.7 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 15.6 Hz, 1H), 3.83 (s, 3H).

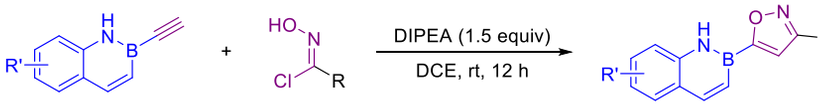


The oxime chloride **2u** were prepared according to the reference.[5]

To a solution of glycine ester hydrochloride (2 g, 14 mmol) in 3 mL water was added conc.HCl (1.2 mL). Upon completion of addition, the resulting solution was cooled to -5 ºC and then a solution of sodium nitrite (1 g, 14 mmol) in water (1.4 mL) was added. The resulting mixture was stirred at 0 ºC for 10 min and then another a sodium nitrite (1 g, 14 mmol) in water (1.4 mL) was added. The resulting mixture was stirred at 0 ºC for 45 min. Upon completion, a brine solution was added. The reaction mixture was extracted with ether thrice, dried over anhydrous Na_2SO_4, evaporated under reduced pressure to yield oxime chloride **2u**, was taken to the next step immediately without further purification.

4. General procedure for the regioselective [3+2] cycloaddition reaction

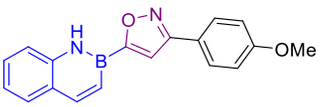
A. Synthesis of 5-(2,1-azaborine) substituted isoxazoles



1 or 5 **2** **3 or 6**

In air, a 25 mL schlenk tube was charged with **1** or **5** (0.2 mmol, 2 equiv) and **2** (0.3 mmol, 1.5 equiv). The tube was evacuated and filled with argon for three cycles. Then, DCE (2 mL) and DIPEA (0.3 mmol, 1.5 equiv) were added under argon. The reaction was allowed to stir at room temperature for 12 hours. Upon completion, proper amount of silica gel was added to the reaction mixture. After removal of the solvent, the crude reaction mixture was purified on silica gel (petroleum ether and ethyl acetate) to afford the desired products **3** or **6**.

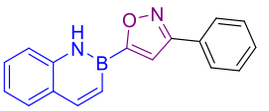
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3a)



White solid, mp: 185-186 ºC. Yield: 85%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 11.08 (s, 1H), 8.28 (d, *J* = 11.4 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.78 (dd, *J* = 14.0, 8.0 Hz, 2H), 7.67 (s, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.83 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.8, 160.6, 146.6, 140.2, 129.4, 128.9, 128.18, 125.5, 121.5, 121.2, 119.0, 114.6, 110.8, 55.3. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.1 (s). **HRMS (EI)** calcd for $C_{18}H_{15}BN_2O_2$: 302.1227, found: 302.1232

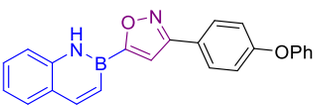
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenylisoxazole (3b)



White solid, mp: 166-168 ºC. Yield: 87%. R_f = 0.6 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.11 (s, 1H), 8.29 (d, *J* = 11.5 Hz, 1H), 8.00 – 7.92 (m, 2H), 7.82 – 7.76 (m, 2H), 7.74 (s, 1H), 7.60 – 7.48 (m, 4H), 7.30 – 7.22 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.2, 146.6, 140.2, 130.0, 129.4, 129.2, 129.2, 128.9, 126.7, 125.5, 121.6, 119. 21, found: 272.11120, 111.0. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.3(s). **HRMS (EI)** calcd for $C_{17}H_{13}BN_2O$: 272.11

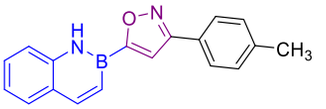
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-phenoxyphenyl)isoxazole (3c)



White solid, mp: 100-102 ºC. Yield: 90%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.10 (s, 1H), 8.28 (d, *J* = 11.5 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.78 (dd, *J* = 11.5, 8.1 Hz, 2H), 7.70 (s, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.18 (m, 3H), 7.13 (dd, *J* = 13.4, 8.2 Hz, 4H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.6, 158.4, 155.83, 146.6, 140.2, 130.2, 129.4, 128.9, 128.6, 125.5, 124.2, 123.7, 121.5, 119.4, 119.0, 118.6, 110.9. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 28.3 (s). **HRMS (EI)** calcd for $C_{23}H_{17}BN_2O_2$: 364.1383, found: 364.1385

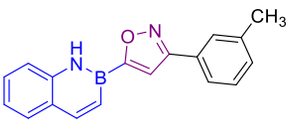
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3d)



White solid, mp: 169-171 ºC. Yield: 91%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.09 (s, 1H), 8.28 (d, *J* = 11.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.78 (dd, *J* = 13.0, 8.0 Hz, 2H), 7.70 (s, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.30 – 7.21 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.1, 146.6, 140.2, 139.6, 129.7, 129.4, 128.9, 126.6, 126.0, 125.5, 121.5, 119.0, 110.9, 20.9. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.3 (s). **HRMS (EI)** calcd for $C_{18}H_{15}BN_2O$: 286.1277, found: 286.1276

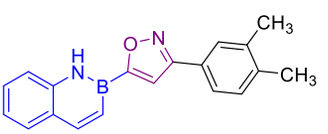
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3e)



White solid, mp: 233-234 ºC. Yield: 92%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.09 (s, 1H), 8.29 (d, *J* = 11.4 Hz, 1H), 7.82 – 7.71 (m, 5H), 7.60 – 7.49 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.21 (m, 2H), 2.40 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.2, 146.6, 140.2, 138.5, 130.6, 129.4, 129.1, 128.9, 128.7, 127.21, 125.5, 123.9, 121.5, 119.0, 111.1, 20.9. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 26.9. **HRMS (EI)** calcd for $C_{18}H_{15}BN_2O$: 286.1277, found: 286.1273

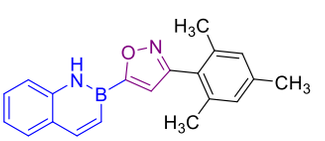
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3,4-dimethylphenyl)isoxazole (3f)



White solid, mp: 157-159 ºC. Yield: 91%. R_f = 0.6 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.08 (s, 1H), 8.28 (d, *J* = 11.4 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.73 (d, *J* = 1.7 Hz, 1H), 7.69 (s, 1H), 7.65 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.22 (m, 2H), 2.31 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.1, 146.6, 140.2, 138.4, 137.1, 130.2, 129.4, 128.9, 127.6, 126.3, 125.5, 124.2, 121.5, 119.0, 111.0, 19.4, 19.3. **^{11}B NMR (160 MHz, DMSO- *d*$_6$)** δ 27.0 (s). **HRMS (EI)** calcd for $C_{19}H_{17}BN_2O$: 300.1434, found: 300.1431

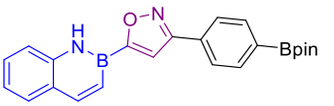
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-mesitylisoxazole (3g)



White solid, mp: 210-212 ºC. Yield: 48%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.02 (s, 1H), 8.24 (d, *J* = 11.4 Hz, 1H), 7.86 – 7.62 (m, 2H), 7.60 – 7.40 (m, 1H), 7.26 – 7.16 (m, 3H), 6.96 (s, 2H), 2.25 (s, 3H), 2.06 (s, 6H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.6, 146.6, 140.2, 138.1, 136.5, 129.4, 129.0, 128.3, 126.3, 125.5, 121.6, 119.0, 114.2, 20.7, 20.0. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.5 (s). **HRMS (EI)** calcd for $C_{20}H_{19}BN_2O$: 314.1590, found: 314.1586

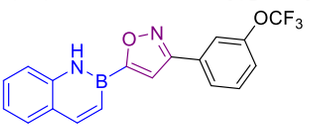
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)isoxazole (3h)



White solid, mp: 200-201 ºC. Yield: 93%. R_f = 0.2 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.11 (s, 1H), 8.29 (d, *J* = 11.4 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.82 – 7.73 (m, 3H), 7.64 – 7.44 (m, 1H), 7.38 – 7.09 (m, 2H), 1.31 (s, 12H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.0, 146.7, 140.2, 135.2, 131.5, 129.4, 129.0, 126.1, 125.5, 121.6, 119.0, 111.1, 83.9, 24.7. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.3 (s). **HRMS (ESI)** calcd for $C_{23}H_{25}B_2N_2O_3$ $[M+H]^+$: 399.2051, found: 399.2042

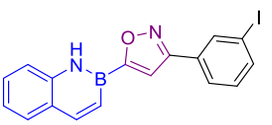
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-(trifluoromethoxy)phenyl)isoxazole (3i)



White solid, mp: 109-110 ºC. Yield: 92%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.13 (s, 1H), 8.29 (d, *J* = 11.4 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.91 (s, 1H), 7.84 (s, 1H), 7.78 (dd, *J* = 11.0, 8.0 Hz, 2H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.18 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.09, 148.91, 146.69, 140.16, 131.42, 131.07, 129.38, 128.97, 125.85, 125.55, 122.50, 121.59, 120.1 (q, *J* = 257.04 Hz), 119.13, 119.03, 111.23. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 26.2 (s). **^{19}F NMR (471 MHz, DMSO-*d*$_6$)** δ -56.69 (s). **HRMS (EI)** calcd for $C_{18}H_{12}BF_3N_2O_2$: 356.0944, found: 356.0942

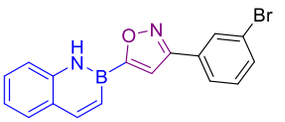
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-iodophenyl)isoxazole (3j)



White solid, mp: 163-164 ºC. Yield: 93%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.10 (s, 1H), 8.33 – 8.24 (m, 2H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.20 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.0, 146.7, 140.2, 138.6, 135.0, 131.3, 131.0, 129.4, 129.0, 126.1, 125.6, 121.7, 119.1, 111.2, 95.5. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.2 (s). **HRMS (EI)** calcd for $C_{17}H_{12}BIN_2O$: 398.0087, found: 398.0078

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-bromophenyl)isoxazole (3k)

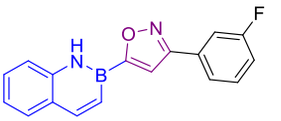


White solid, mp: 163-165 ºC. Yield: 86%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.11 (s, 1H), 8.29 (d, *J* = 11.5 Hz, 1H), 8.13 (t, *J* = 1.9 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.82 (s, 1H), 7.81 – 7.74 (m, 2H), 7.72 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.29 – 7.20 (m,2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.0, 146.7, 140.2, 132.8, 131.4, 131.1, 129.4, 129.2, 129.0, 125.7, 125.5, 122.4, 121.6, 119.0, 111.2. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.2 (s). **HRMS (EI)**

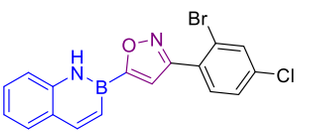
calcd for $C_{17}H_{12}BBrN_2O$: 350.0226, found: 350.0220

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole(3l)



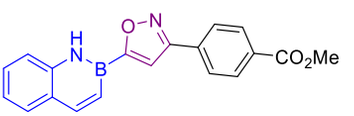
White solid, mp: 167-168 ºC. Yield: 94%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$)δ 11.12 (s, 1H), 8.29 (d, *J* = 11.4 Hz, 1H), 7.85 – 7.74 (m, 5H), 7.65 – 7.57 (m, 1H), 7.57 – 7.51 (m, 1H), 7.41 – 7.33 (m, 1H), 7.30 – 7.20 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 162.5 (d, *J* = 243.2 Hz), 160.3 (d, *J* = 2.9 Hz), 146.7, 140.2, 131.4 (d, *J* = 8.4 Hz), 131.1 (d, *J* = 8.4 Hz), 129.4, 128.9, 125.5, 122.9 (d, *J* = 2.9 Hz), 121.6, 119.0, 116.8 (d, *J* = 21.1 Hz), 113.5 (d, *J* = 23.0 Hz), 111.2. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.6 (s). **^{19}F NMR (471 MHz, DMSO-*d*$_6$)** δ -111.99 (s). **HRMS (EI)** calcd for $C_{17}H_{12}BFN_2O$: 290.1027, found: 290.1021

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(2-bromo-4-chlorophenyl)isoxazole (3m)



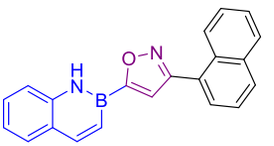
White solid, mp: 181-182 ºC. Yield: 85%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.14 (s, 1H), 8.29 (d, *J* = 11.5 Hz, 1H), 7.99 (d, *J* = 2.1 Hz, 1H), 7.77 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.59 – 7.50 (m, 1H), 7.32 – 7.19 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.5, 146.7, 140.2, 132.8, 132.6, 129.4, 129.4, 129.0, 128.3, 125.5, 122.4, 121.6, 119.0, 113.6, 113.6. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.3 (s). **HRMS (EI)** calcd for $C_{17}H_{11}BBrClN_2O$: 383.9836, found: 383.9834

methyl 3-(5-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazol-3-yl)benzoate (3n)



White solid, mp: 225-226 ºC. Yield: 80%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.12 (s, 1H), 8.29 (d, *J* = 11.5 Hz, 1H), 8.10 (q, *J* = 8.1 Hz, 4H), 7.78 (dd, *J* = 18.0, 8.9 Hz, 3H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 8.2 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 165.7, 160.4, 146.7, 140.2, 133.1, 130.7, 130.0, 129.4, 129.0, 127.0, 125.6, 121.6, 119.0, 111.2, 52.3. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 26.3 (s). **HRMS (EI)** calcd for $C_{19}H_{15}BN_2O_3$: 330.1176 found: 330.1175

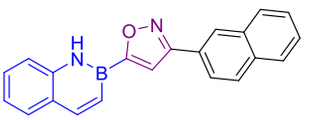
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphth654-alen-1-yl)isoxazole (3o)



White solid, mp: 141-143 ºC. Yield: 88%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.16 (s, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 11.5 Hz, 1H),

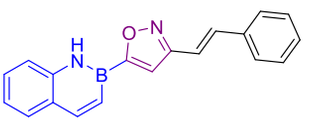
8.17 – 8.00 (m, 2H), 7.88 (d, *J* = 6.9 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 2H), 7.74 – 7.60 (m, 4H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.22 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)**δ 161.3, 146.7, 140.2, 133.5, 130.36, 130.1, 129.4, 129.0, 128.6, 128.0, 127.3, 126.6, 126.4, 125.6, 125.6, 125.4, 121.6, 119.0, 114.1. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.3 (s). **HRMS (ESI)** calcd for $C_{21}H_{16}BN_2O$ $[M+H]^+$: 323.1356, found: 323.1357

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphthalen-2-yl)isoxazole (3p)



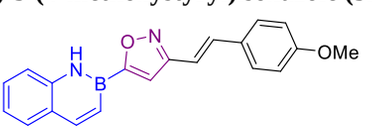
White solid, mp: 204-206 ºC. Yield: 84%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.15 (s, 1H), 8.54 (s, 1H), 8.31 (d, *J* = 11.4 Hz, 1H), 8.08 (dd, *J* = 8.6, 3.8 Hz, 3H), 8.04 – 7.96 (m, 1H), 7.90 (s, 1H), 7.80 (dd, *J* = 19.3, 8.0 Hz, 2H), 7.65 – 7.53 (m, 3H), 7.36 – 7.21 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.2, 146.6, 140.2, 133.5, 132.9, 129.4, 129.0, 128.8, 128.4, 127.8, 127.1, 126.9, 126.4, 126.3, 125.5, 124.0, 121.5, 119.0, 111.3. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.2 (s). **HRMS (EI)** calcd for $C_{21}H_{15}BN_2O$: 322.1277, found: 322.1275

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-styrylisoxazole (3q)



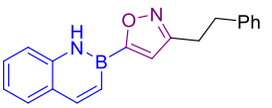
White solid, mp: 184-186 ºC. Yield: 90%. R_f = 0.2 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.08 (s, 1H), 8.28 (d, *J* = 11.5 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.74 – 7.67 (m, 2H), 7.64 (s, 1H), 7.57 – 7.32 (m,6H), 7.29 – 7.19 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.8, 146.6, 140.2, 135.8, 135.8, 129.3, 128.9, 128.9, 128.9, 127.1, 125.5, 121.5, 119.0, 115.9, 110.3. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.4 (s). **HRMS (EI)** calcd for $C_{19}H_{15}BN_2O$: 298.1277, found: 298.1278

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxystyryl)isoxazole (3r)



White solid, mp: 189-190 ºC. Yield: 93%. R_f = 0.1 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$)δ 11.06 (s, 1H), 8.28 (d, *J* = 11.5 Hz,1H), 7.82 – 7.73 (m,2H), 7.68 – 7.62 (m, 2H), 7.60 (s, 1H), 7.56 – 7.50 (m, 1H), 7.41 (d, *J* = 16.5 Hz, 1H), 7.29 – 7.17 (m,3H), 7.02 – 6.95 (m, 2H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, DMSO *d*$_6$)** δ 171.0, 159.9, 146.6, 140.2, 135.5, 129.3, 128.9, 128.6, 128.4, 125.5, 121.5, 119.0, 114.3, 113.4, 110.2, 55.2. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 26.9 (s). **HRMS (EI)** calcd for $C_{20}H_{17}BN_2O_2$: 328.1383, found: 328.1382

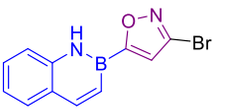
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenethylisoxazole (3s)



White solid, mp: 159-161 ºC. Yield: 75%. R_f = 0.6 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.20 (d, *J* = 11.5 Hz, 1H), 7.69 (d, *J* = 7.9 Hz,1H), 7.50 (t, *J* = 7.7 Hz,1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.20 (m, 6H), 7.13 (d, *J* = 11.4 Hz, 1H), 6.72 (s, 1H), 3.32 –

2.86 (m, *J* = 4.3 Hz, 4H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 162.5, 146.8, 140.7, 139.4, 129.6, 129.0, 128.5, 128.4, 126.3, 125.9, 121.8, 118.6, 112.6, 34.7, 27.6. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 27.0 (s). **HRMS (EI)** calcd for $C_{19}H_{17}BN_2O$: 300.1434, found: 300.1426

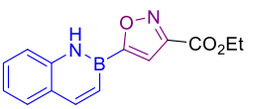
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-bromoisoxazole (3t)



White solid, mp: 186-188 ºC. Yield: 26%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$)δ δ 11.12 (s, 1H), 8.29 (d, *J* = 11.4 Hz, 1H), 7.82 – 7.70 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 (s, 1H), 7.31 – 7.24 (m, 1H), 7.19 (dd, *J* = 11.4, 1.8 Hz,1H). **^{13}C NMR (126 MHz, DMSO -*d*$_6$)** δ 146.9, 140.0, 139.8, 129.4, 129.1, 125.6, 121.8, 119.0, 115.8. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 26.82 (s). **HRMS (EI)** calcd for $C_{11}H_8BBrN_2O$: 273.9913, found: 273.9908

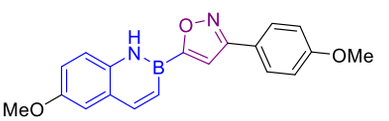
ethyl 5-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole-3-carboxylate (3u)



White solid, mp: 114-115 ºC. Yield: 28%. R_f = 0.2 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.67 (s, 1H), 8.24 (d, *J* = 11.6 Hz, 1H), 7.71 (d, *J* = 8.2 Hz,1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.2 Hz,1H), 7.34 – 7.23 (m, 2H), 7.17 (d, *J* = 11.7 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 171.8, 160.3, 156.0, 147.3, 139.2, 129.7, 129.2, 126.0, 122.2, 118.7, 113.0, 62.2, 14.2. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 24.6 (s). **HRMS (EI)** calcd for $C_{14}H_{13}BN_2O_3$: 268.1019, found: 268.1014

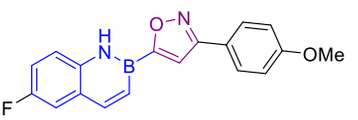
5-(6-methoxybenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3v)



White solid, mp: 204-205 ºC. Yield: 86%. R_f = 0.2 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 10.99 (s, 1H), 8.24 (d, *J* = 11.4 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.6 (s, 1H), 7.28 (d, *J* = 3.0 Hz, 1H), 7.26 – 7.16 (m, 2H), 7.09 (d, *J* = 8.4 Hz,2H), 3.83 (s, 6H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.7, 160.5, 153.9, 146.0, 134.9, 128.2, 126.1, 121.3, 120.1, 118.6, 114.6, 110.4, 110.1, 55.3, 55.3. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 24.4 (s). **HRMS (EI)** calcd for $C_{19}H_{17}BN_2O_3$: 332.1332, found: 332.1328

5-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3w)

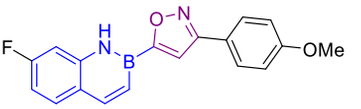


White solid, mp: 215-216 ºC. Yield: 91%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.15 (s, 1H), 8.26 (d, *J* = 11.5 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.81 (dd, *J* = 9.1, 5.1 Hz, 1H), 7.66 (s, 1H), 7.61 (dd, *J* = 9.6, 3.0 Hz, 1H), 7.50 – 7.38 (m, 1H), 7.30 (dd, *J* = 11.5, 1.7 Hz, 1H), 7.17 – 7.01 (m, 2H), 3.82 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.7 (d, *J* = 26.7 Hz),

157.8, 155.9, 145.8, 136.9, 128.2, 126.01 (d, *J* = 8.6 Hz), 121.2, 120.7 (d, *J* = 8.4 Hz), 117.2 (d, *J* = 24.2 Hz), 114.6, 113.5 (d, *J* = 21.5 Hz), 111.0. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.4 (s). **^{19}F NMR (471 MHz, DMSO-*d*$_6$)** δ -121.41 (s). **HRMS (EI)** calcd for $C_{18}H_{14}BFN_2O_2$: 320.1132, found: 320.1129

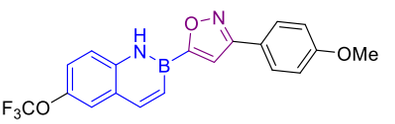
5-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3x)



White solid, mp: 213-214 °C. Yield: 83%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.16 (s, 1H), 8.28 (d, *J* = 11.5 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.83 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.67 (s, 1H), 7.55 (dd, *J* = 10.7, 2.6 Hz, 1H), 7.19 (dd, *J* = 11.4, 1.7 Hz, 1H), 7.16 – 7.07 (m, 3H), 3.82 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 163.1, 161.1, 160.7 (d, *J* = 30.9 Hz), 146.2, 141.4 (d, *J* = 12.0 Hz), 131.6 (d, *J* = 10.2 Hz), 128.2, 122.6, 121.1, 114.6, 111.2, 110.0 (d, *J* = 23.2 Hz), 104.4 (d, *J* = 24.1 Hz), 55.3. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 25.6 (s). **^{19}F NMR (471 MHz, DMSO-*d*$_6$)** δ -110.98 (s). **HRMS (EI)** calcd for $C_{18}H_{14}BFN_2O_2$: 320.1132, found: 320.1140

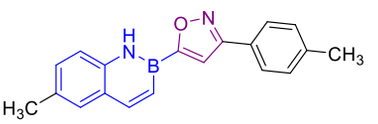
3-(4-methoxyphenyl)-5-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (3y)



White solid, mp: 186-187 °C. Yield: 85%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.27 (s, 1H), 8.33 (d, *J* = 11.4 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 3H), 7.83 (d, *J* = 2.7 Hz, 1H), 7.69 (s, 1H), 7.55 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.33 (dd, *J* = 11.3, 1.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 160.8, 160.6, 146.0, 142.3, 139.0, 128.2, 125.8, 122.3, 121.1, 120.3 (q, *J* = 256.4 Hz), 120.9, 120.7, 114.6, 111.3, 55.3. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.4 (s). **^{19}F NMR (471 MHz, DMSO-*d*$_6$)** δ -57.58 (s). **HRMS (EI)** calcd for $C_{19}H_{14}BF_3N_2O_3$: 386.1050, found: 386.1058

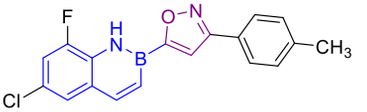
5-(6-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3z)



White solid, mp: 208-210 °C. Yield: 95%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.00(s, 1H), 8.20 (d, *J* = 11.4 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 10.7 Hz, 2H), 7.53(s, 1H), 7.35 (t, *J* = 6.6 Hz. 3H), 7.21 (d, *J* = 11.4 Hz, 1H), 2.39(s, 3H), 2.37(s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.0, 146.3, 139.7, 138.3, 130.4, 130.3, 129.7, 128.8, 126.6, 126.1, 125.5, 118.9, 110.7, 21.0, 20.5. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 25.5 (s). **HRMS (EI)** calcd for $C_{19}H_{17}BN_2O$: 300.1434, found: 300.1439.

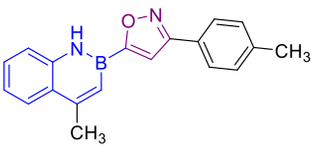
5-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3aa)



White solid, mp: 197-199 ºC. Yield: 94%. R_f = 04 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 10.67 (s, 1H), 8.26 (d, *J* = 11.5 Hz, 1H), 7.91 (s, 1H), 7.82 – 7.71 (m, 3H), 7.63 (d, *J* = 10.7 Hz, 1H), 7.36 (dd, *J* = 22.9, 9.6 Hz, 3H), 2.36 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.0, 152.6, 150.7, 145.1, 139.6, 129.7, 129.6, 127.9, 127.4 (d, *J* = 13.6 Hz), 126.5, 126.0, 124.5 (d, *J* = 9.4 Hz), 124.3, 114.6 (d, *J* = 22.5 Hz), 111.5, 21.0. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 26.2 (s). **^{19}F NMR (471 MHz, DMSO-*d*$_6$)** δ -129.14 (s). **HRMS (EI)** calcd for $C_{18}H_{13}BClFN_2O$: 338.0793, found: 338.0801

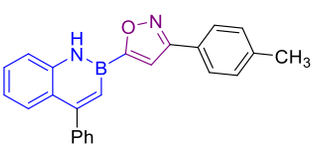
5-(4-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3ab)



White solid, mp: 156-158 ºC. Yield: 90%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 10.87 (s, 1H), 7.88 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.81 – 7.76 (m, 1H), 7.66 (s, 1H), 7.57 – 7.50 (m, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.07 (s, 1H), 2.63 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.0, 152.9, 140.5, 139.6, 129.7, 128.6, 126.6, 126.1, 125.6, 125.3, 121.4, 119.5, 110.7, 22.8, 21.0. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 25.1 (s). **HRMS (EI)** calcd for $C_{19}H_{17}BN_2O$: 300.1434, found: 300.1430

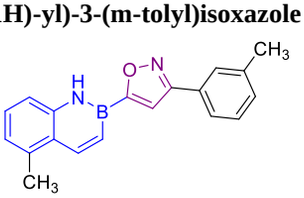
5-(4-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3ac)



White solid, mp: 224-225 ºC. Yield: 92%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.15 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.59 – 7.51 (m, 4H), 7.51 – 7.43 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.12 (d, *J* = 1.9 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.1, 157.3, 141.8, 141.0, 139.6, 129.7, 128.9, 128.7, 128.4, 127.8, 127.4, 126.6, 126.0, 124.2, 121.5, 119.7, 111.2, 20.9. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 25.3 (s). **HRMS (EI)** calcd for $C_{24}H_{19}BN_2O$: 362.1590, found: 362.1591

5-(5-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3ad)

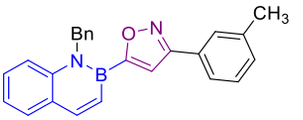


White solid, mp: 130-131 ºC. Yield: 89%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 11.05 (s, 1H), 8.48 (d, *J* = 11.7 Hz, 1H), 7.78 (s, 1H), 7.76 – 7.71 (m, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.42 (dt, *J* = 10.0, 7.6 Hz, 2H), 7.36 – 7.25 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 1H), 2.60 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.2, 142.7, 140.4, 138.5, 135.7, 130.6, 129.1,

128.8, 128.5, 127.2, 127.2, 123.9, 122.9, 117.5, 111.0, 21.0, 19.1. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 27.1 (s). **HRMS (EI)** calcd for $C_{19}H_{17}BN_2O$: 300.1434, found: 300.1432

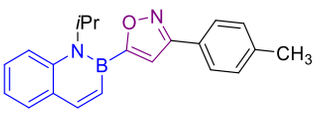
5-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3ae)



White solid, mp: 138-140 ºC. Yield: 88%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 8.33 (d, *J* = 11.5 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.74 (s, 1H), 7.72 – 7.66 (m, 2H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 8.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 4H), 7.25 – 7.16 (m, 3H), 5.79 (s, 2H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 161.1, 146.8, 140.5, 138.4, 138.3, 130.7, 130.5, 129.4, 129.0, 128.7, 128.4, 127.3, 127.2, 127.0, 125.8, 123.9, 122.0, 116.9, 113.0, 51.9, 21.0. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 30.3 (s). **HRMS (EI)** calcd for $C_{25}H_{21}BN_2O$: 376.1747, found: 376.1744

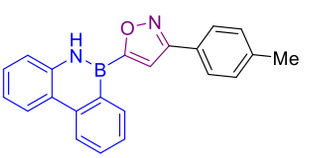
5-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole(3af)



White solid, mp: 96-98 ºC. Yield: 55%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 8.18 (d, *J* = 11.3 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.83 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.55 (s, 1H), 7.32 (dd, *J* = 16.4, 7.8 Hz, 3H), 7.11 (d, *J* = 11.2 Hz, 1H), 5.25 (m, 1H), 2.37 (s, 3H), 1.68 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 160.9, 146.3, 139.6, 131.0, 129.6, 128.2, 127.9, 126.8, 125.9, 121.5, 118.6, 114.1, 111.2, 52.1, 21.9, 21.0, 20.94. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 29.3 (s). **HRMS (EI)** calcd for $C_{21}H_{21}BN_2O$: 328.1747, found: 328.1741

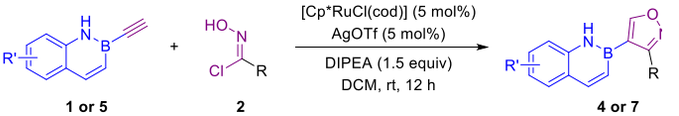
5-(dibenzo[c,e][1,2]azaborinin-6(5H)-yl)-3-(p-tolyl)isoxazole (6)



White solid, mp: 164-165 ºC. Yield: 50%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 10.71 (s, 1H), 8.68 (t, *J* = 7.4 Hz, 2H), 8.59 (d, *J* = 8.2 Hz,1H), 7.95 – 7.84 (m, 4H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.30 (m, 3H), 2.39 (s, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 161.0, 139.8, 139.0, 138.7, 135.0, 131.8, 129.8, 128.4, 126.8, 126.5, 126.0, 124.0, 123.0, 122.7, 122.3, 119.9, 111.6, 21.00. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 29.5 (s). **HRMS (EI)** calcd for $C_{22}H_{17}BN_2O$: 336.1434, found: 336.1445

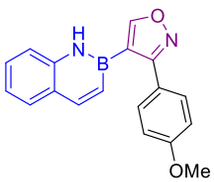
B. Synthesis of 4-(2,1-azaborine) substituted isoxazoles



1 or 5 2 4 or 7

In air, a 25 mL schlenk tube was charged with **1** (0.2 mmol, 2 equiv), **2** (0.24 mmol, 1.2 equiv), AgOTf (5 mol%), [Cp*RuCl(cod)] (5 mol%). The tube was evacuated and filled with argon for three cycles. Then, DCM (2 mL) and DIPEA (0.24mmol, 1.2 equiv) were added under argon. The reaction was allowed to stir at room temperature for 12 hours. Upon completion, proper amount of silica gel was added to the reaction mixture. After removal of the solvent, the crude reaction mixture was purified on silica gel (petroleum ether and ethyl acetate) to afford the desired products.

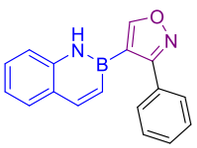
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4a)



White solid, mp: 120-122 °C. Yield: 72%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, DMSO-*d*$_6$) δ 10.52 (s, 1H), 9.07 (s, 1H), 8.02 (d, *J* = 11.5 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 3H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.56 (d, *J* = 11.4 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 164.0, 163.6, 160.3, 144.9, 140.6, 129.8, 129.2, 128.5, 124.9, 122.2, 121.0, 118.5, 114.1, 55.2. **^{11}B NMR (160 MHz, DMSO-*d*$_6$)** δ 30.8 (s). **HRMS (EI)** calcd for $C_{18}H_{15}BN_2O_2$: 302.1227, found: 302.1227

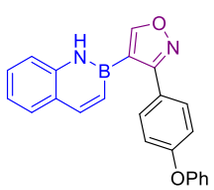
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenylisoxazole (4b)



White solid, mp: 104-106 °C. Yield: 81%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.75 (s, 1H), 8.07 (d, *J* = 11.6 Hz, 1H), 7.78 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 11.7, 6.9 Hz, 3H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 9.1 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.5, 164.0, 145.6, 139.5, 130.3, 129.9, 129.5, 128.9, 128.5, 125.3, 121.4, 118.1. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 28.52 (s). **HRMS (EI)** calcd for $C_{17}H_{13}BN_2O$: 272.1121, found: 272.1123

4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-phenoxyphenyl)isoxazole(4c)

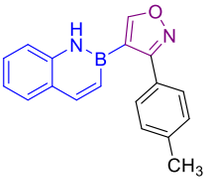


White solid, mp: 200-201 °C. Yield: 65%. R_f = 0.2 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.75 – 8.68 (m, 1H), 8.08 (d, *J* = 11.6 Hz, 1H), 7.85 (s, 1H), 7.71 – 7.66

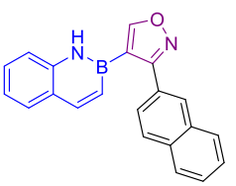
(m, 2H), 7.64 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.24 – 7.14 (m, 2H), 7.14 – 7.09 (m, 3H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.96 (dd, *J* = 11.4, 1.8 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.9, 163.8, 159.0, 156.3, 145.7, 139.5, 130.4, 129.9, 129.5, 128.6, 125.3, 124.8, 124.0, 121.5, 119.5, 118.6, 118.1. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 28.58 (s). **HRMS (EI)** calcd for $C_{23}H_{17}BN_2O_2$: 364.1383, found: 364.1384

4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4d)



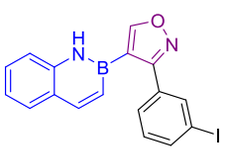
White solid, mp: 215-216 °C. Yield: 70%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.7 (s, 1H), 8.07 (d, *J* = 11.5 Hz, 1H), 7.82 (s, 1H), 7.62 (dd, *J* = 12.6, 7.7 Hz, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.99 (dd, *J* = 18.9, 9.8 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.4, 164.0, 145.5, 139.9, 139.5, 129.6, 129.5, 128.7, 128.5, 127.3, 125.3, 121.4, 118.1, 21.4. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 28.4 (s). **HRMS (EI)** calcd for $C_{18}H_{15}BN_2O$: 286.1277, found: 286.1280

4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphthalen-2-yl)isoxazole (4e)



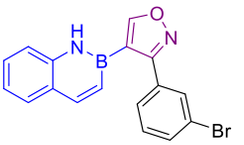
White solid, mp: 92-94 °C. Yield: 79%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.25 (d, *J* = 1.5 Hz, 1H), 8.07 (d, *J* = 11.5 Hz, 1H), 7.95 (dd, *J* = 17.3, 8.2 Hz, 2H), 7.90 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.81 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.37 – 7.29 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.07 – 6.87 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.4, 164.1, 145.6, 139.5, 133.8, 133.1, 129.4, 128.6, 128.5, 128.5, 128.4, 127.8, 127.6, 1271, 126.8, 125.9, 125.3, 121.4, 118.1. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 27.6 (s). **HRMS (EI)** calcd for $C_{21}H_{15}BN_2O$: 322.1277, found: 322.1277

4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-iodophenyl)isoxazole (4f)



White solid, mp: 116-117 °C. Yield: 68%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.14 (d, *J* = 2.2 Hz, 1H), 8.08 (d, *J* = 11.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.83 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.92 (dd, *J* = 11.5, 2.1 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.8, 162.8, 145.5, 139.2, 138.5, 137.2, 132.0, 130.1, 129.3, 128.4, 127.8, 125.1, 121.3, 117.9, 94.2. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 30.5 (s). **HRMS (EI)** calcd for $C_{17}H_{12}BIN_2O$: 398.0087, found: 398.0078

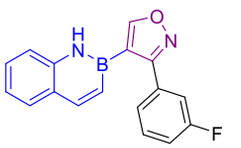
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-bromophenyl)isoxazole (4g)



White solid, mp: 97-98 ºC. Yield: 80%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.08 (d, *J* = 11.5 Hz, 1H), 7.93 (s, 1H), 7.84 (s, 1H), 7.72 – 7.56 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 11.5 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.95, 163.19, 145.8, 139.5, 132.8, 132.3, 131.7, 130.3, 129.5, 128.7, 127.4, 125.4, 122.9, 121.6, 118.2. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 30.1 (s). **HRMS (EI)** calcd for $C_{17}H_{12}BBrN_2O$: 350.0226, found: 350.0229

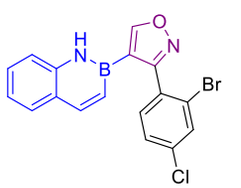
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole (4h)



White solid, mp: 83-84 ºC. Yield: 79%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.08 (d, *J* = 11.5 H, 1Hz), 7.83 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.35 (m, 4H), 7.22 (q, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 11.5 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.8, 163.4, 161.8, 145.8, 139.5, 132.3 (d, *J* = 8.4 Hz), 130.5 (d, *J* = 8.2 Hz), 129.5, 128.7, 125.4, 124.6, 121.6, 118.2, 116.8 (d, *J* = 21.4 Hz), 115.9 (d, *J* = 22.9 Hz). **^{11}B NMR (160 MHz, $CDCl_3$)** δ 30.4 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -111.51 (s). **HRMS (EI)** calcd for $C_{17}H_{12}BFN_2O$: 290.1027, found: 290.1028

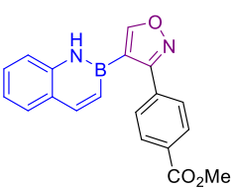
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(2-bromo-4-chlorophenyl)isoxazole (4i)



White solid, mp: 136-138 ºC. Yield: 75%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.01 (d, *J* = 11.5 Hz, 1H), 7.78 (d, *J* = 1.3 H, 1Hz), 7.68 – 7.54 (m, 2H), 7.48 (d, *J* = 1.5 Hz, 2H), 7.43 – 7.35 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.76 (dd, *J* = 11.5, 2.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.4, 163.2, 145.8, 139.4, 136.5, 133.0, 132.3, 130.5, 129.5, 128.6, 128.0, 125.3, 123.9, 121.5, 118.1. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 27.6 (s). **HRMS (EI)** calcd for $C_{17}H_{11}BBrClN_2O$: 383.9836, found: 383.9836

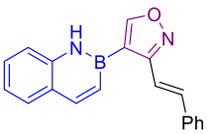
methyl 4-(4-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazol-3-yl)benzoate (4j)



White solid, mp: 151-153 °C. Yield: 80%. R_f = 0.2 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.72 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 11.5 Hz, 1H), 7.88 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.94 – 6.84 (m, 1H), 3.96 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 166.5, 163.7, 163.6, 145.8, 139.5, 134.6, 131.2, 130.0, 129.5, 128.8, 128.6, 125.3, 121.6, 118.2, 52.3. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 28.4 (s). **HRMS (EI)** calcd for $C_{19}H_{15}BN_2O_3$: 330.1176, found: 330.1181

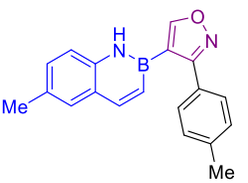
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-styrylisoxazole (4k)



White solid, mp: 96-97 °C. Yield: 75%. R_f = 0.2 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.58 (s, 1H), 8.18 (d, *J* = 11.0 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.50 (dd, *J* = 15.5, 8.4 Hz, 3H), 7.46 – 7.30 (m, 5H), 7.30 – 7.22 (m, 2H), 7.11 (d, *J* = 11.4 Hz, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 162.3, 162.1, 145.9, 139.7, 136.6, 136.0, 129.6, 128.8, 128.8, 128.8, 127.0, 125.5, 121.6, 118.2, 116.2, 77.3, 77.0, 76.8. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 28.6 (s). **HRMS (EI)** calcd for $C_{19}H_{15}BN_2O$: 298.1277, found: 298.1279

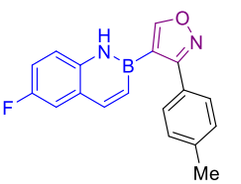
4-(6-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4l)



White solid, mp: 94-95 °C. Yield: 95%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.70 (s, 1H), 8.00 (d, *J* = 11.5 Hz, 1H), 7.78 (s, 1H), 7.64 – 7.56 (m, 2H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.21 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.97 – 6.89 (m, 2H), 2.46 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.4, 163.8, 145.3, 139.9, 137.6, 130.7, 129.8, 129.5, 129.1, 128.7, 127.3, 125.3, 117.9, 21.4, 20.8. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 28.0 (s). **HRMS (EI)** calcd for $C_{19}H_{17}BN_2O$: 300.1434, found: 300.1438

4-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4m)

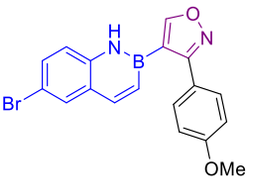


White solid, mp: 105-106 °C. Yield: 83%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.71 (s, 1H), 7.98 (d, *J* = 11.5 Hz, 1H), 7.87 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.26 (m, 3H), 7.15 – 7.09 (m, 1H), 7.04 – 6.94 (m, 2H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$** δ 164.4, 163.9, 157.3 (d, *J* = 239.9 Hz), 144.6 (d, *J* = 3.3 Hz), 140.0, 136.0, 129.6, 128.6, 127.2, 125.7 (d, *J* = 8.1 Hz), 119.3 (d, *J* = 8.2 Hz), 116.5 (d, *J* = 24.6 Hz), 113.8 (d, *J* = 21.5 Hz), 21.4. **^{11}B NMR (160 MHz,**

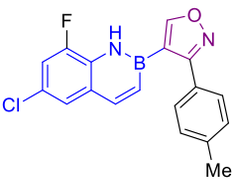
$CDCl_3$) δ 28.2 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -123.91 (s). **HRMS (EI)** calcd for $C_{18}H_{14}BFN_2O$: 304.1183, found: 304.1186

4-(6-bromobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4n)



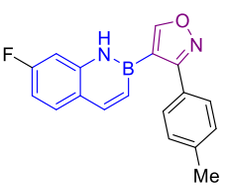
White solid, mp: 114-115 °C. Yield: 76%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.94 (d, *J* = 11.6 Hz, 1H), 7.84 (s, 1H), 7.75 (d, *J* = 2.3 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.44 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.06 – 6.96 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.0, 160.9, 144.3, 138.3, 131.5, 131.3, 130.1, 126.7, 122.2, 119.7, 114.3, 113.8, 55.4. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 28.5 (s). **HRMS (EI)** calcd for $C_{18}H_{14}BBrN_2O_2$: 380.0332, found: 380.0332

4-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4o)



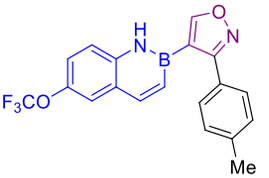
White solid, mp: 118-120 °C. Yield: 84%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.06 (s, 1H), 7.93 (dd, *J* = 11.8, 1.7 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.39 (s, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.16 (dd, *J* = 10.3, 2.2 Hz, 1H), 7.08 (dd, *J* = 11.7, 2.0 Hz, 1H), 2.46 (s, 3H). **^{113}C NMR (126 MHz, $CDCl_3$)** δ 164.5, 152.3, 150.4, 143.6 (d, *J* = 3.3 Hz), 140.1, 129.8, 128.6, 127.0, 127.2 (d, *J* = 3.8 Hz), 127.3 (d, *J* = 13.9 Hz), 125.2 (d, *J* = 9.8 Hz), 123.9 (d, *J* = 3.6 Hz), 114.0 (d, *J* = 21.6 Hz), 21.4. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 28.3 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -134.41 (s). **HRMS (EI)** calcd for $C_{18}H_{13}BClFN_2O$: 1 338.0793, found: 338.0797

4-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4p)



White solid, mp: 106-107 °C. Yield: 90%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1)
^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.01 (d, *J* = 11.6 Hz, 1H), 7.83 (s, 1H), 7.57 (dd, *J* = 8.1, 5.4 Hz, 3H), 7.31 (d, *J* = 7.8 Hz, 2H), 6.99 – 6.82 (m, 2H), 6.69 (dd, *J* = 9.9, 2.5 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.3 (d, *J* = 21.5 Hz), 163.8, 161.3, 145.0, 140.7 (d, *J* = 11.1 Hz), 140.1, 131.1 (d, *J* = 10.0 Hz), 129.6, 128.7, 127.1, 122.0, 109.8 (d, *J* = 23.2 Hz), 104.0 (d, *J* = 24.1 Hz), 21.4. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 28.8 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ -111.45 (s). **HRMS (EI)** calcd for $C_{18}H_{14}BFN_2O$: 304.1183, found: 304.1185

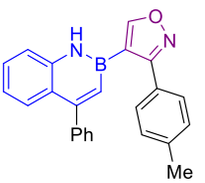
3-(p-tolyl)-4-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4q)



White solid, mp: 86-87 °C. Yield: 82%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.73 (s, 1H), 8.01 (d, *J* = 11.6 Hz, 1H), 7.91 (s, 1H), 7.61 – 7.55 (m, 2H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.28 – 7.21 (m, 1H), 7.07 – 6.98 (m, 2H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.4, 164.2, 144.7, 143.1, 140.1, 138.0, 129.6, 128.7, 127.1, 125.5, 122.0, 121.1, 119.3, 21.41. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 28.6 (s). **^{19}F NMR (471 MHz, CDCl$_3$)** δ -60.14 (s). **HRMS (EI)** calcd for $C_{19}H_{14}BF_3N_2O_2$: 370.1100, found: 370.1105

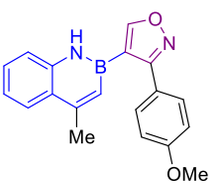
4-(4-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4r)



White solid, mp: 157-159 °C. Yield: 90%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.74 (s, 1H), 7.86 (s, 1H), 7.71 – 7.63 (m, 2H), 7.63 – 7.59 (m, 1H), 7.52 – 7.46 (m, 2H), 7.46 – 7.42 (m, 3H), 7.41 – 7.36 (m, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.15 – 7.08 (m, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.4, 164.2, 156.9, 142.12, 140.1, 140.0, 129.6, 128.9, 128.7, 128.45, 128.2, 127.5, 127.3, 124.4, 121.2, 118.6, 21.4. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 27.8 (s). **HRMS (EI)** calcd for $C_{24}H_{19}BN_2O$: 362.1590, found: 362.1592

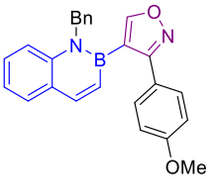
3-(4-methoxyphenyl)-4-(4-methylbenzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4s)



White solid, mp: 115-116 °C. Yield: 95%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.68 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.70 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.02 (dd, *J* = 8.3, 4.6 Hz, 3H), 6.81 (s, 1H), 3.89 (s, 3H), 2.61 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.0, 163.7, 160.7, 152.0, 139.8, 130.1, 128.2, 125.7, 125.3, 122.5, 121.3, 118.7, 114.2, 55.3, 22.9. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 28.2 (s). **HRMS (EI)** calcd for $C_{19}H_{17}BN_2O_2$: 316.1383, found: 316.1385

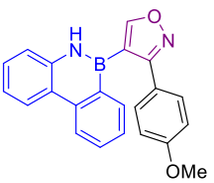
4-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4t)



White solid, mp: 133-135 ºC. Yield: 92%. R_f = 0.2 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.15 (s, 1H), 8.07 (d, *J* = 11.4 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 4.0 Hz, 2H), 7.35 – 7.21 (m, 4H), 7.04 (d, *J* = 7.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 11.5 Hz, 1H), 5.40 (s, 2H), 3.83 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 163.8, 160.5, 160.1, 145.3, 141.2, 138.2, 130.4, 129.6, 128.8, 128.8, 127.3, 127.1, 125.4, 122.4, 121.5, 116.8, 114.0, 55.2, 52.5. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 32.2 (s). **HRMS (EI)** calcd for $C_{25}H_{21}BN_2O_2$: 392.1696, found: 392.1702

4-(dibenzo[c,e][1,2]azaborinin-6(5H)-yl)-3-(4-methoxyphenyl)isoxazole (7)

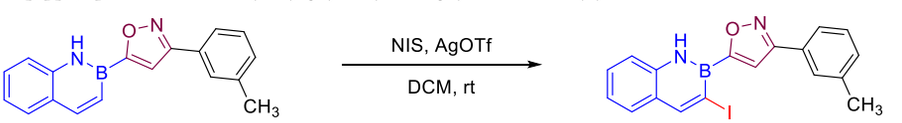


White solid, mp: 167-169 ºC. Yield: 80%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1)

^{1}H NMR NMR (500 MHz, CDCl$_3$) δ 8.59 (s, 1H), 8.49 (dd, *J* = 22.9, 8.2 Hz, 2H), 8.00 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.66 (s, 1H), 7.64 – 7.59 (m, 2H), 7.50 – 7.40 (m, 2H), 7.36 – 7.29 (m, 1H), 7.13 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.88 – 6.79 (m, 2H), 3.77 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.0, 162.3, 160.6, 138.8, 138.2, 135.7, 131.5, 129.8, 128.2, 126.4, 123.9, 123.4, 122.3, 122.1, 122.0 119.2, 114.1, 55.2. **^{11}B NMR (160 MHz, CDCl$_3$)** δ 32.1 (s). **HRMS (EI)** calcd for $C_{18}H_{14}BBrN_2O_2$: 380.0332, found: 380.0332

5. Synthetic transformations

5-(3-iodobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (8)



3e **8**

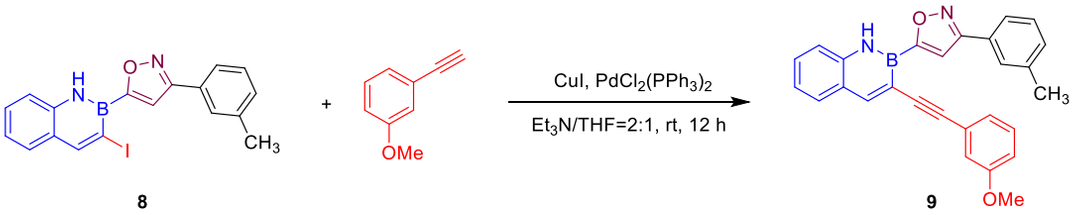
In air, a 100 mL schlenk flask was charged with **3e** (1.5 mmol, 1 equiv), NIS (1.8 mmol, 1.2 equiv) and AgOTf (10 mol%). The flask was evacuated and filled with argon for three cycles. 15 mL of dry DCM was added under argon. The reaction was allowed to stir at room temperature for 12 h. Upon completion, after removal of the solvent, the crude reaction mixture was purified on column chromatography (petroleum ether and ethyl acetate) to afford the desired product **8**.

White solid, mp: 178 – 180 ºC. Yield: 82%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.85 (s, 1H), 8.78 (s, 1H), 7.84 (s, 1H), 7.76 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.45 – 7.36 (m, 2H), 7.31 – 7.25 (m, 2H), 2.46 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 161.9, 155.1, 138.7, 138.6, 130.6, 129.6, 128.8, 128.7, 128.6, 127.6, 126.3, 124.2,

122.4, 118.6, 112.4, 21.4. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 26.9 (s). **HRMS (EI)** calcd for $C_{18}H_{14}BIN_2O$: 412.0244, found: 412.0239

5-(3-((3-methoxyphenyl)ethynyl)benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (9)

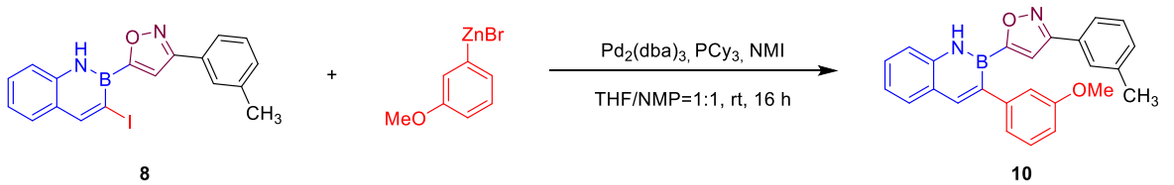


In air, a 25 mL schlenk tude was charged with **8** (0.2 mmol, 1 equiv), CuI (5 mol%) and $PdCl_2(PPh_3)_2$ (5 mol%). The flask was evacuated and filled with argon for three cycles. 1.35 mL Et_3N , 0.65 mL THF and 3-ethynylanisole (0.6 mmol, 3 equiv) was added under argon. The reaction was allowed to stir at room temperature for 12 h. Upon completion, after removal of the solvent, the crude reaction mixture was purified on column chromatography (petroleum ether and ethyl acetate) to afford the desired product **9**.

White solid, mp: 169 – 170 ºC. Yield: 81%. R_f = 0.3 (silica gel, PE:EtOAc = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.39 (s, 1H), 7.81(s, 1H), 7.72 (s, 1H), 7.68 (dd, J = 13.1, 7.7 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.27 (d, J = 6.9 Hz, 2H), 7.22 (d, J = 7.5 Hz, 1H), 7.15 (s, 1H), 6.99 – 6.90 (m, 1H), 3.83 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.1, 159.5, 149.6, 138.8, 138.6, 130.6, 129.9, 129.7, 129.6, 129.1, 128.8, 127.6, 125.0, 124.9, 124.1, 123.9, 122.5, 118.5, 116.1, 114.8, 112.9, 94.6, 91.8, 55.2, 21.3. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 26.1 (s). **HRMS (ESI)** calcd for $C_{27}H_{22}BN_2O_2$ $[M+H]^+$: 417.1774, found: 417.1777

5-(3-(3-methoxyphenyl)benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (10)

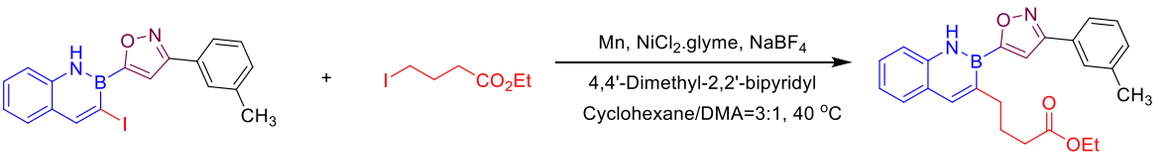


In glove box, a 25 mL schlenk tude was charged with $ZnCl_2$ (0.32 mmol, 1.6 equiv), 3-Methoxymagnesium bromide (1.0M in THF; 0.32 mL, 0.32 mmol, 1.6 equiv) and 1 mL THF. The reaction was allowed to stir at room temperature for 20 min. Then, **8** (0.2 mmol, 1 equiv), NMI (1.2 equiv), $Pd_2(dba)_3$ (2 mol%), PCy_3 (8 mol%) and 1 mL NMP were added to the tube. The reaction was allowed to stir at room temperature for 16 h. Upon completion, after removal of the solvent, the crude reaction mixture was purified on column chromatography (petroleum ether and ethyl acetate) to afford the desired product **10.**

White solid, mp: 99 – 101 ºC. Yield: 80%. R_f = 0.5 (silica gel, PE:EtOAc = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.08 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.61 (s, 1H), 7.57 – 7.44 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 2.1 Hz, 1H), 6.97 (dd, *J* = 8.1, 2.6 Hz, 1H), 6.61 (s, 1H), 3.86 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.9, 159.5, 145.2, 144.7, 138.8, 138.5, 130.5, 129.7, 129.0, 129.1, 128.9, 128.7, 127.5, 125.3, 124.1, 122.3, 121.1, 118.3, 113.8, 112.5, 112.1, 55.3, 21.3. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 27.0 (s). **HRMS (ESI)** calcd for $C_{25}H_{22}BN_2O_2$ $[M+H]^+$: 393.1774, found: 393.1777

ethyl 4-(2-(3-(m-tolyl)isoxazol-5-yl)-1,2-dihydrobenzo[e][1,2]azaborinin-3-yl)butanoate (11)



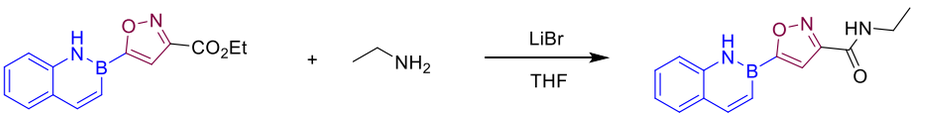
8 **11**

In air, a 25 mL schlenk tude was charged with **8** (0.2 mmol, 1 equiv), Mn (0.4 mmol, 2 equiv), $NaBF_4$ (0.1 mmol, 0.5 equiv), $NiCl_2$.glyme (10 mol%), 4,4'-Dimethyl-2,2'-bipyridyl (10 mol%). The tube was evacuated and filled with argon for three cycles. 1.5 mL Cyclohexane, 0.5 mL DMA and ethyl 4-Iodobutyrate (0.24 mmol, 1.2 equiv) was added under argon. The reaction was allowed to stir at 40 °C for 16 h. Upon completion, after removal of the solvent, the crude reaction mixture was purified on column chromatography (petroleum ether and ethyl acetate) to afford the desired product **11**.

White solid, mp: 70 – 72 °C. Yield: 85%. R_f = 0.4 (silica gel, PE:EtOAc = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.92 (s, 1H), 7.81 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.32 – 7.19 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.92 (t, *J* = 7.9 Hz, 2H), 2.56 – 2.32 (m, 5H), 2.11 – 1.89 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.7, 162.2, 144.1, 138.6, 138.4, 130.5, 129.1, 128.9, 128.8, 128.2, 127.7, 125.5, 124.1, 121.9, 118.1, 111.2, 60.3, 34.9, 33.8, 26.2, 21.4, 14.2. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 27.6 (s). **HRMS (EI)** calcd for $C_{24}H_{25}BN_2O_3$: 400.1958, found: 400.1965

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-N-ethylisoxazole-3-carboxamide (12)



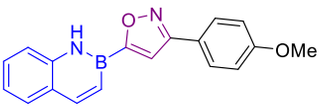
3u **12**

In air, a 25 mL schlenk tude was charged with 3t (0.1 mmol, 1 equiv) and LiBr (10 mol%). The tube was evacuated and filled with argon for three cycles. Ethylamine (2.0 M in THF; 0.5 mL, 1 mmol, 10 equiv) and 1 mLTHF was added under argon. The reaction was allowed to stir at room temperature for 12 h. Upon completion, after removal of the solvent, the crude reaction mixture was purified on column chromatography (petroleum ether and ethyl acetate) to afford the desired product **12.**

White solid, mp: 204 - 206 °C. Yield: 90%. R_f = 0.3 (silica gel, PE:EtOAc = 5:1).

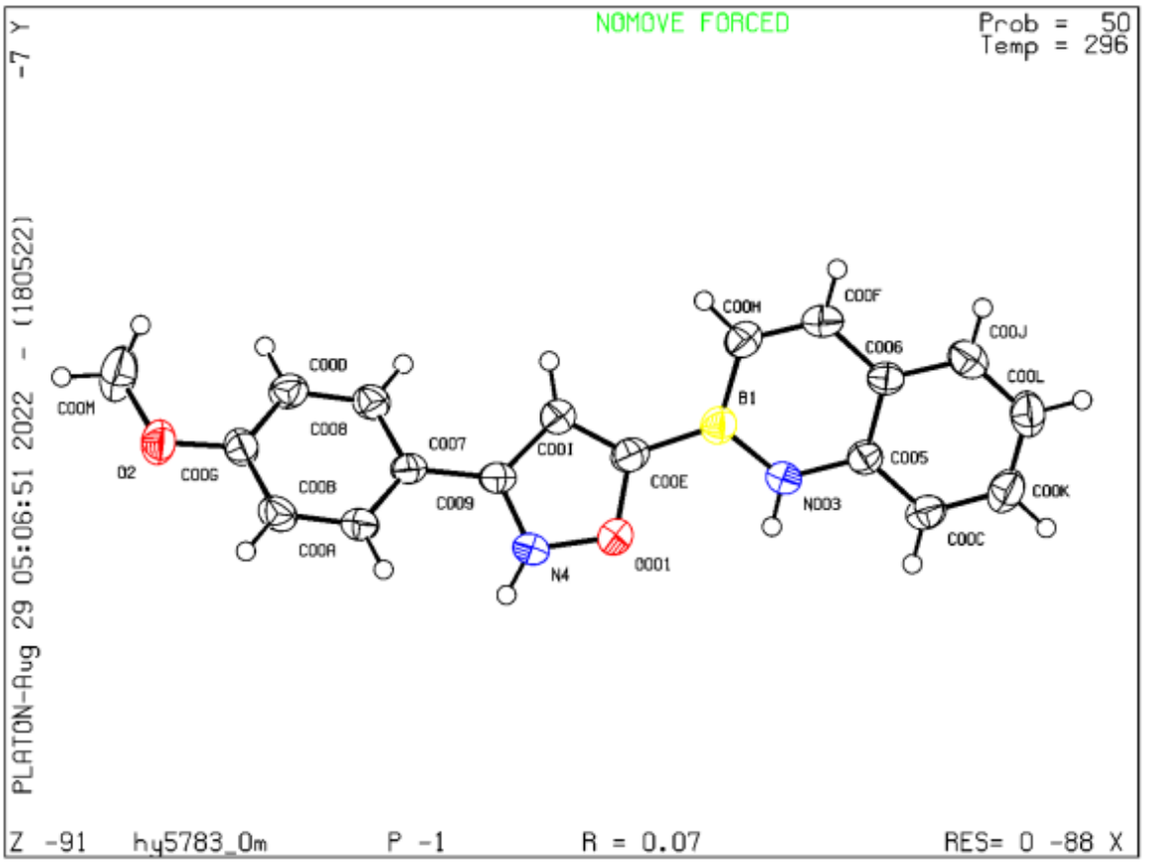
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.22 (d, *J* = 11.5 Hz, 1H), 7.70 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35, 7.30 – 7.24 (m, 1H), 7.18 (dd, *J* = 11.4, 1.9 Hz, 1H), 6.92 (s, 1H), 3.61 – 3.39 (m, 2H), 1.27 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.1, 158.2, 147.2, 139.2, 129.8, 129.1, 126.1, 122.1, 118.6, 112.1, 34.5, 14.7. **^{11}B NMR (160 MHz, $CDCl_3$)** δ 27.1 (s). **HRMS (ESI)** calcd for $C_{14}H_{15}BN_3O_2$ $[M+H]^+$: 268.1257, found: 268.1260

6. Crystal structure of compound 3a and 4i



3a

(CCDC 2202557)



Bond precision: C-C = 0.0049 A Wavelength=0.71073

Cell: a=5.822(4) b=9.698(8) c=17.608(14)
alpha=84.39(4) beta=83.54(4) gamma=49.04(3)

Temperature: 296 K

	Calculated	Reported
Volume	745.6(11)	745.7(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C18 H16 B N2 O2	C18 H16 B N2 O2
Sum formula	C18 H16 B N2 O2	C18 H16 B N2 O2
Mr	303.14	303.14
Dx,g cm-3	1.350	1.350

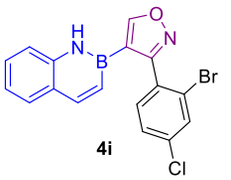
Z	2	2
Mu (mm-1)	0.088	0.088
F000	318.0	318.0
F000'	318.13	
h,k,lmax	6,11,20	6,11,20
Nref	2626	2614
Tmin,Tmax	0.987,0.989	0.623,0.747
Tmin'	0.987	

Correction method= # Reported T Limits: Tmin=0.623 Tmax=0.747 AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 25.022

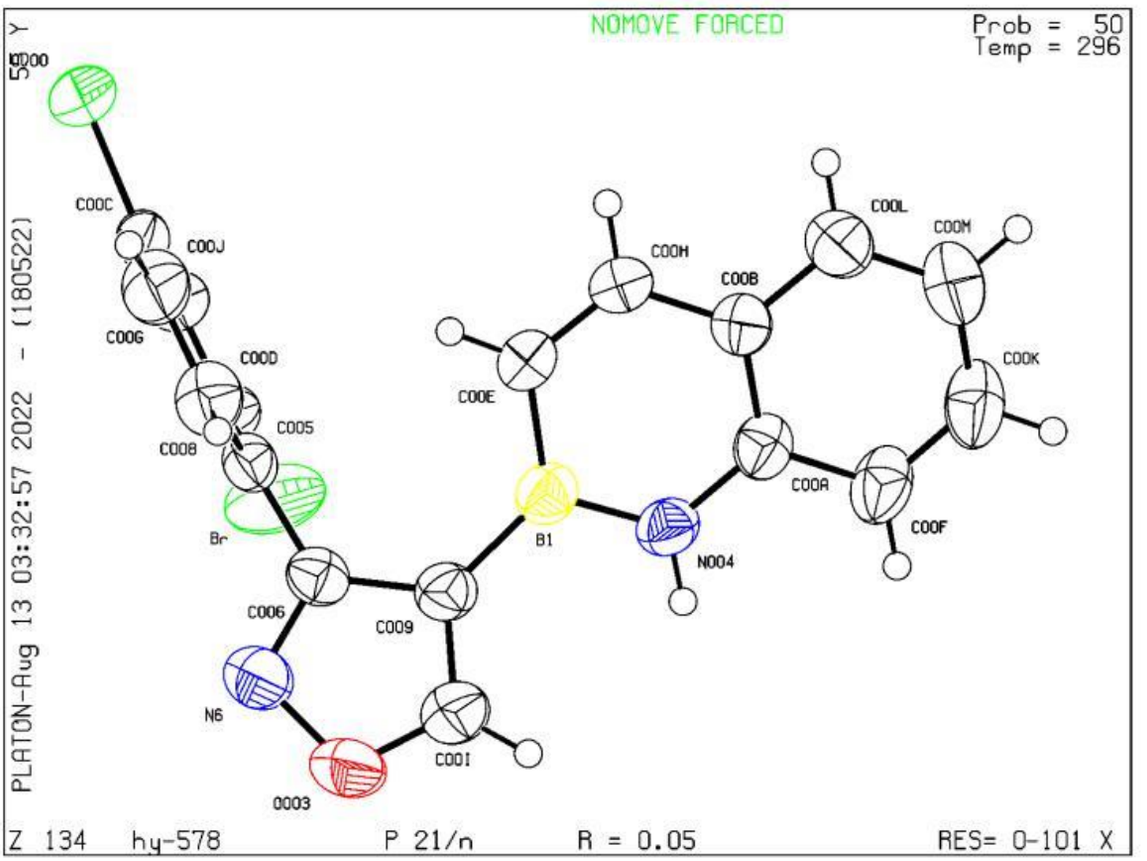
R(reflections)= 0.0658(1564) wR2(reflections)= 0.1873(2614)

S = 1.028 Npar= 209



4i

(CCDC 2202558)



Bond precision: C-C = 0.0061 A Wavelength=0.71073

Cell: a=9.0910(6) b=17.1679(11) c=10.8642(7)

alpha=90 beta=105.897(2) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1630.77(18)	1630.76(18)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C17 H11 B Br Cl N2 O	?
Sum formula	C17 H11 B Br Cl N2 O	C17 H11 B Br Cl N2 O
Mr	385.44	385.45
Dx,g cm-3	1.570	1.570
Z	4	4
Mu (mm-1)	2.688	2.688
F000	768.0	768.0

F000'	767.69	
h,k,lmax	10,20,12	10,20,12
Nref	2861	2860
Tmin,Tmax		
Tmin'		

Correction method= Not given

Data completeness= 1.000 Theta(max)= 24.999

R(reflections)= 0.0519(2353) wR2(reflections)= 0.1345(2860)

S = 1.091 Npar= 209

7. References

(1) I. Valencia, P. García-García, D. Sucunza, F. Mendicuti and J. J. Vaquero, 1,10a-Dihydro-1-aza-10a-boraphenanthrene and 6a,7-Dihydro-7-aza-6a-boratetraphene: Two New Fluorescent BN-PAHs, *J. Org. Chem.*, 2021, **86**, 16259-16267.

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(3) R. J. B. Schäfer, M. R. Monaco, M. Li, A. Tirla, P. Rivera-Fuentes and H. Wennemers, The Bioorthogonal Isonitrile–Chlorooxime Ligation, *J. Am. Chem. Soc.*, 2019, **141**, 18644-18648.

(4) K. Yang, F. Zhang, T. Fang, G. Zhang and Q. Song, Stereospecific 1,4-metallate shift enables stereoconvergent synthesis of ketoximes. *Angew. Chem., Int. Ed*., 2019, **58**, 13421–13426.

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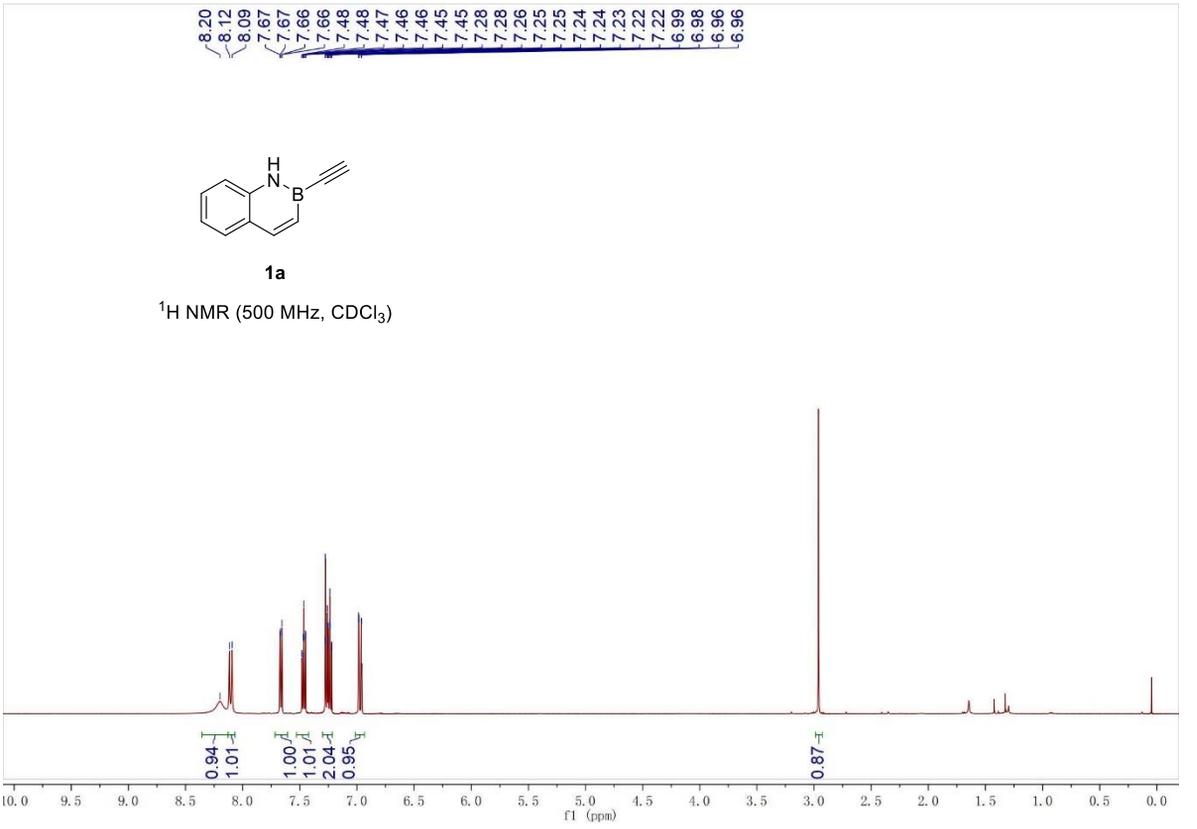
8. NMR Spectra

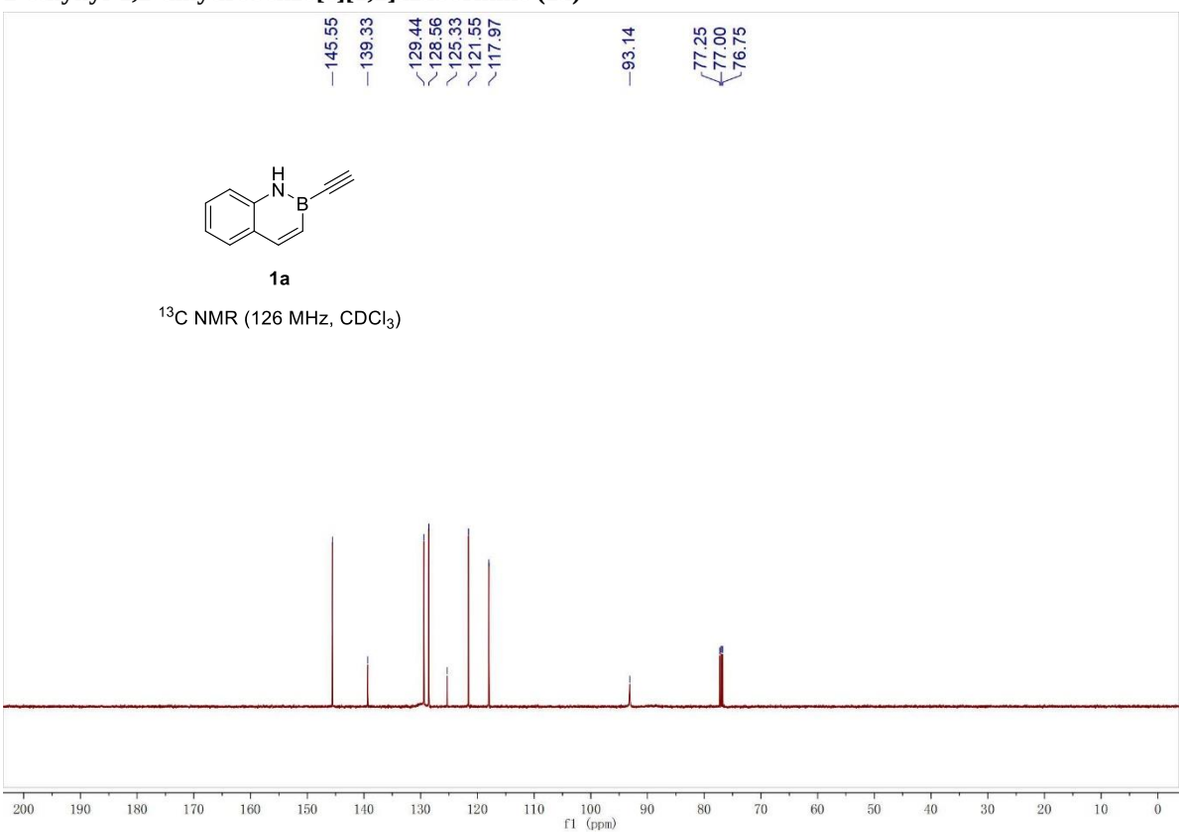
2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1a)



1a

^{1}H NMR (500 MHz, $CDCl_3$)

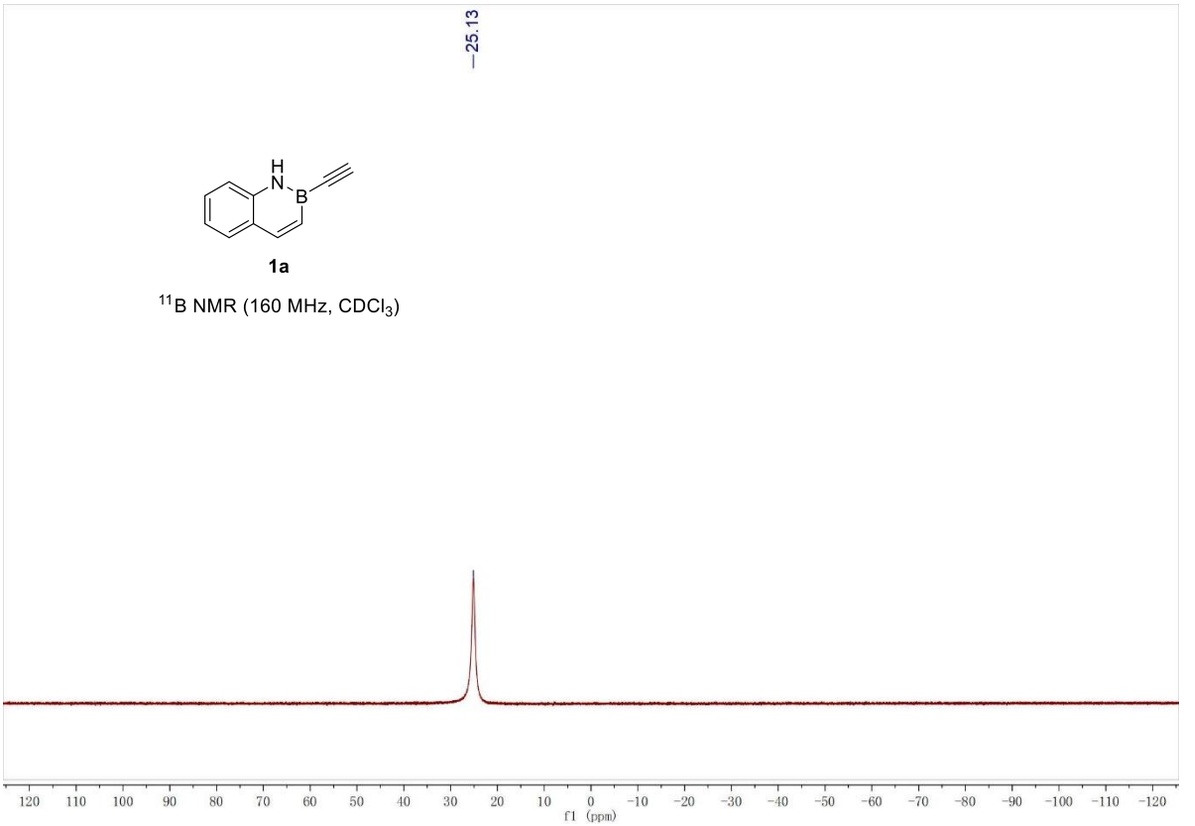
2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1a)



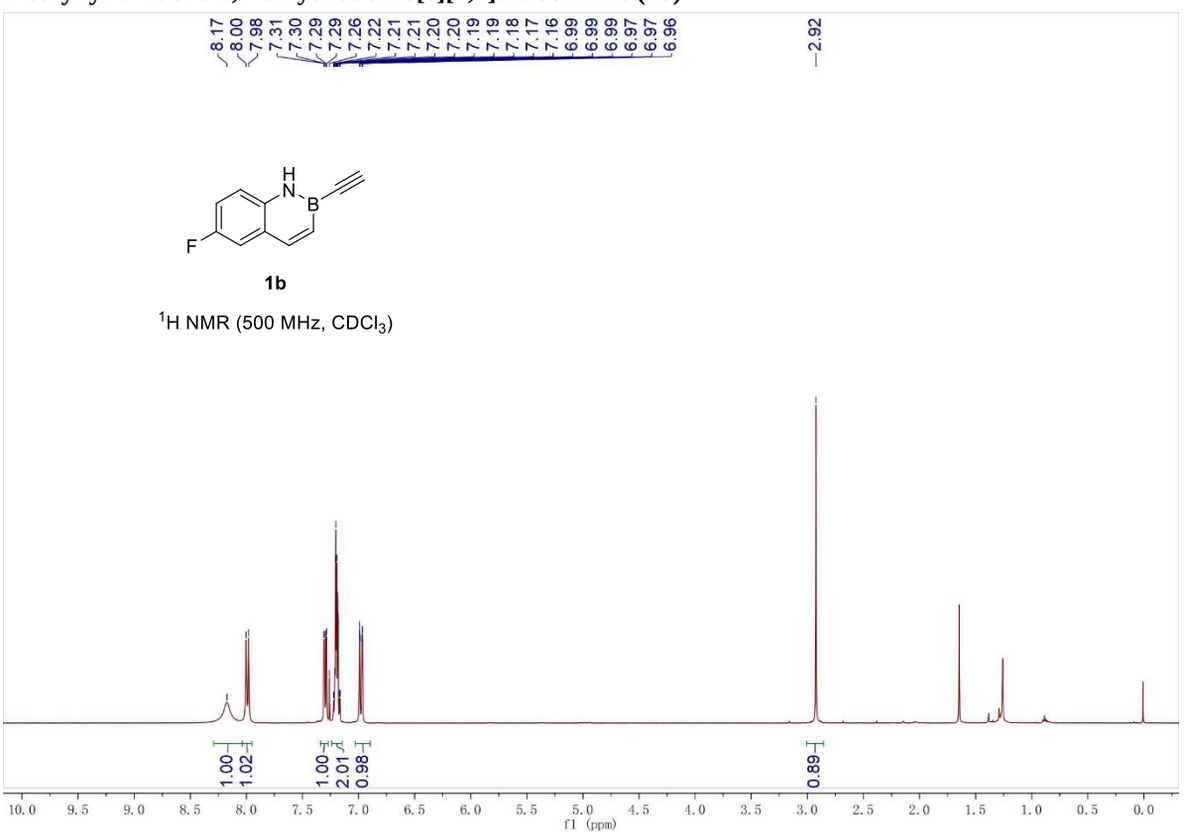
1a

^{13}C NMR (126 MHz, $CDCl_3$)

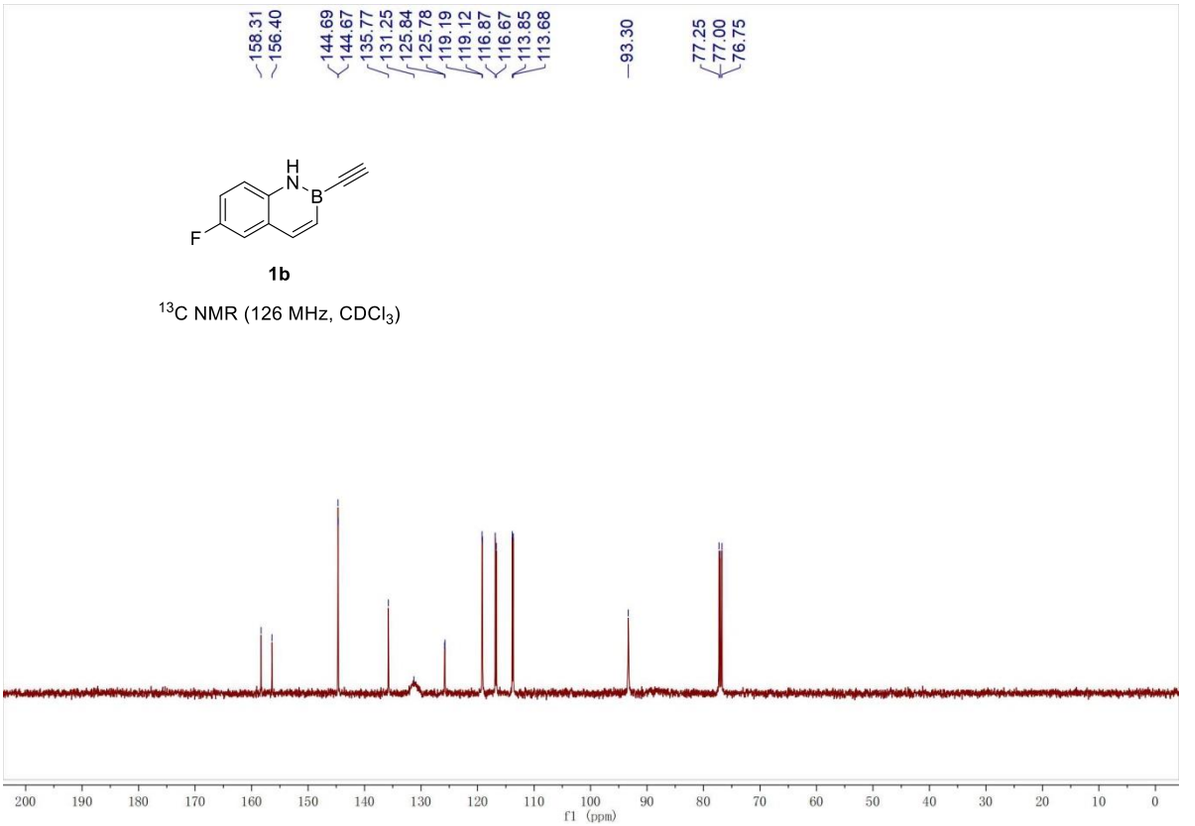
2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1a)



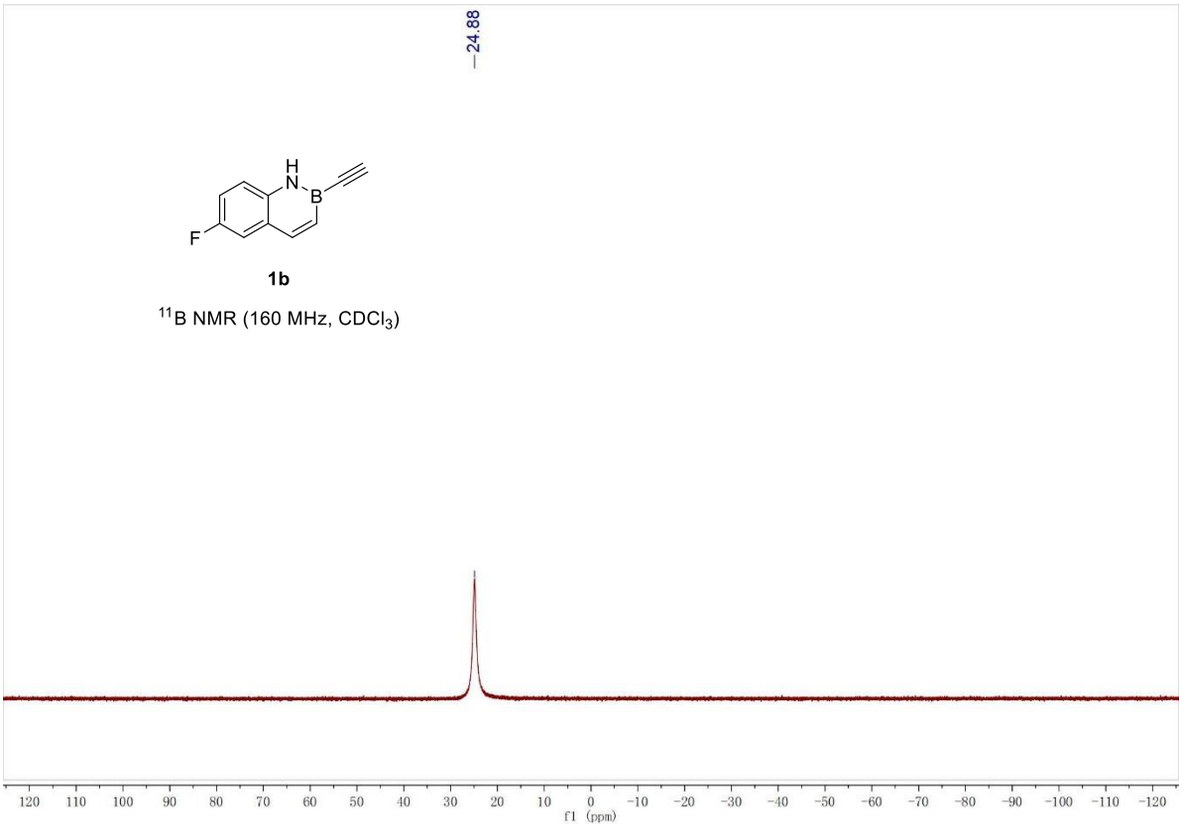
2-ethynyl-6-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1b)



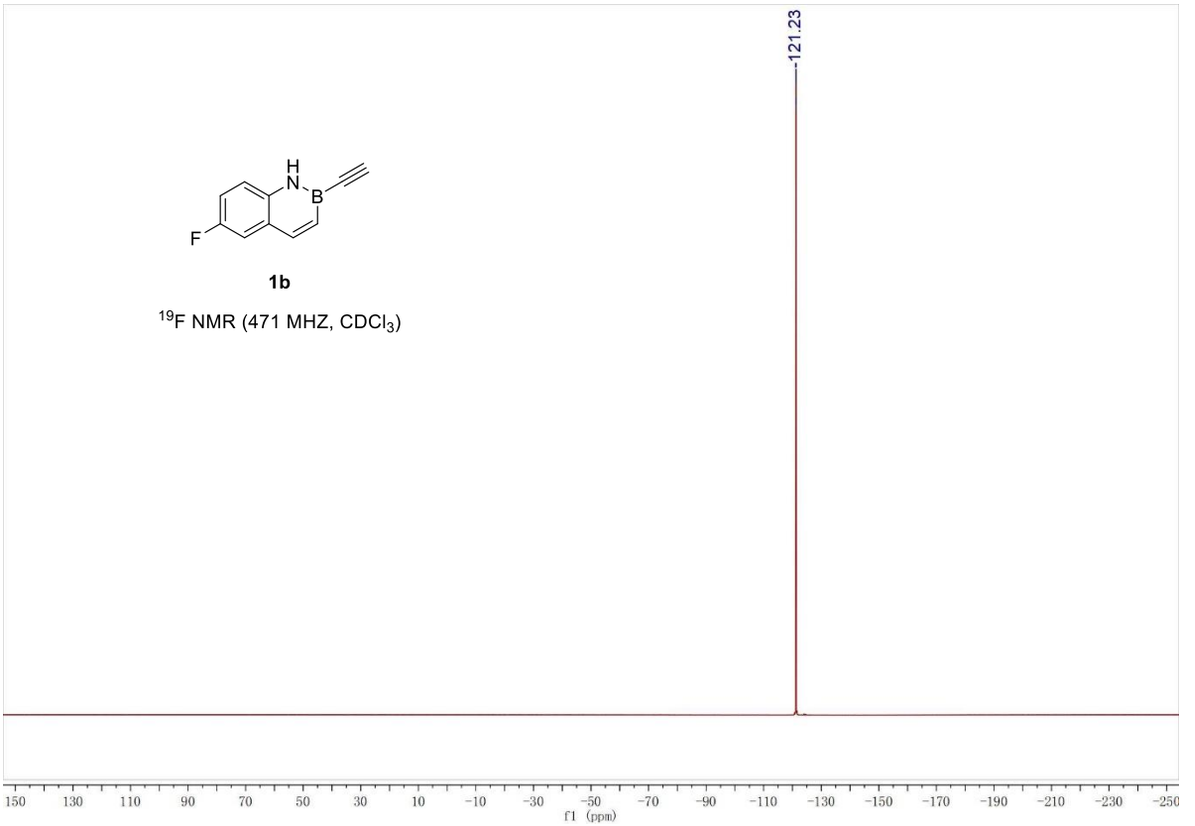
2-ethynyl-6-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1b)



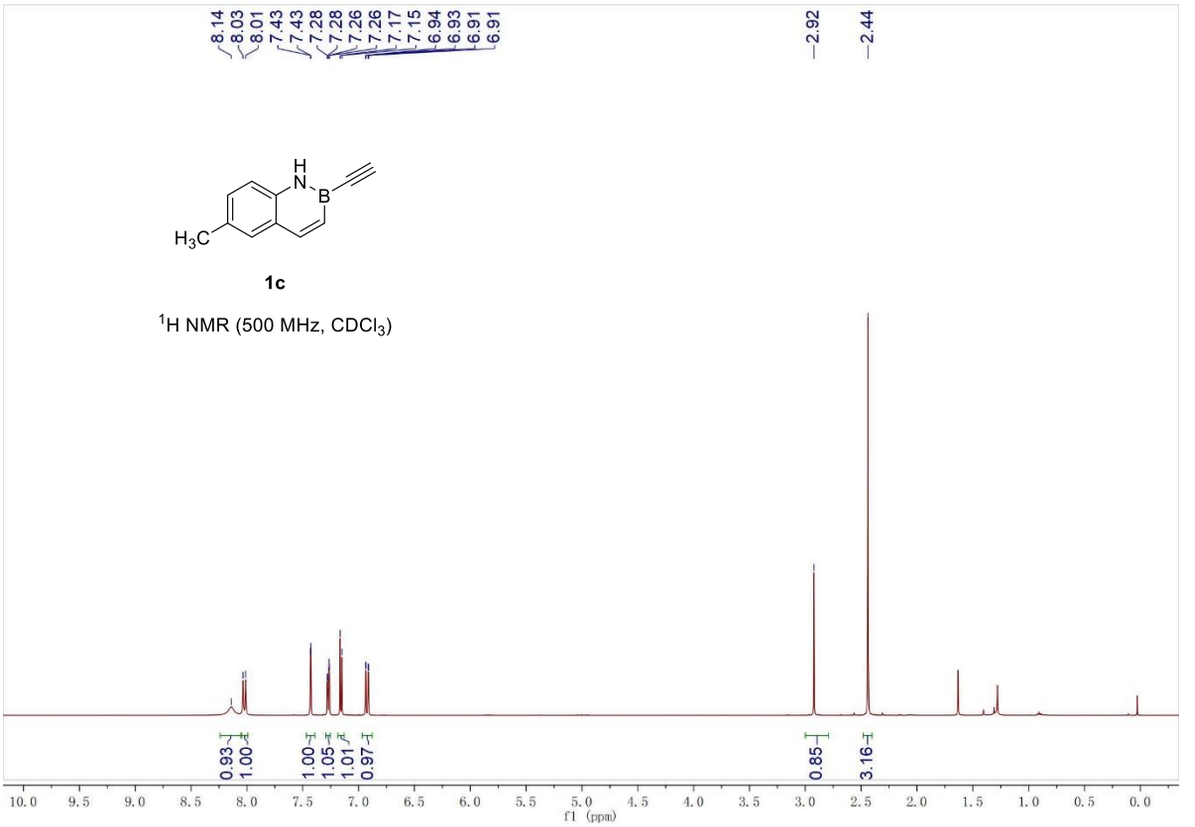
2-ethynyl-6-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1b)



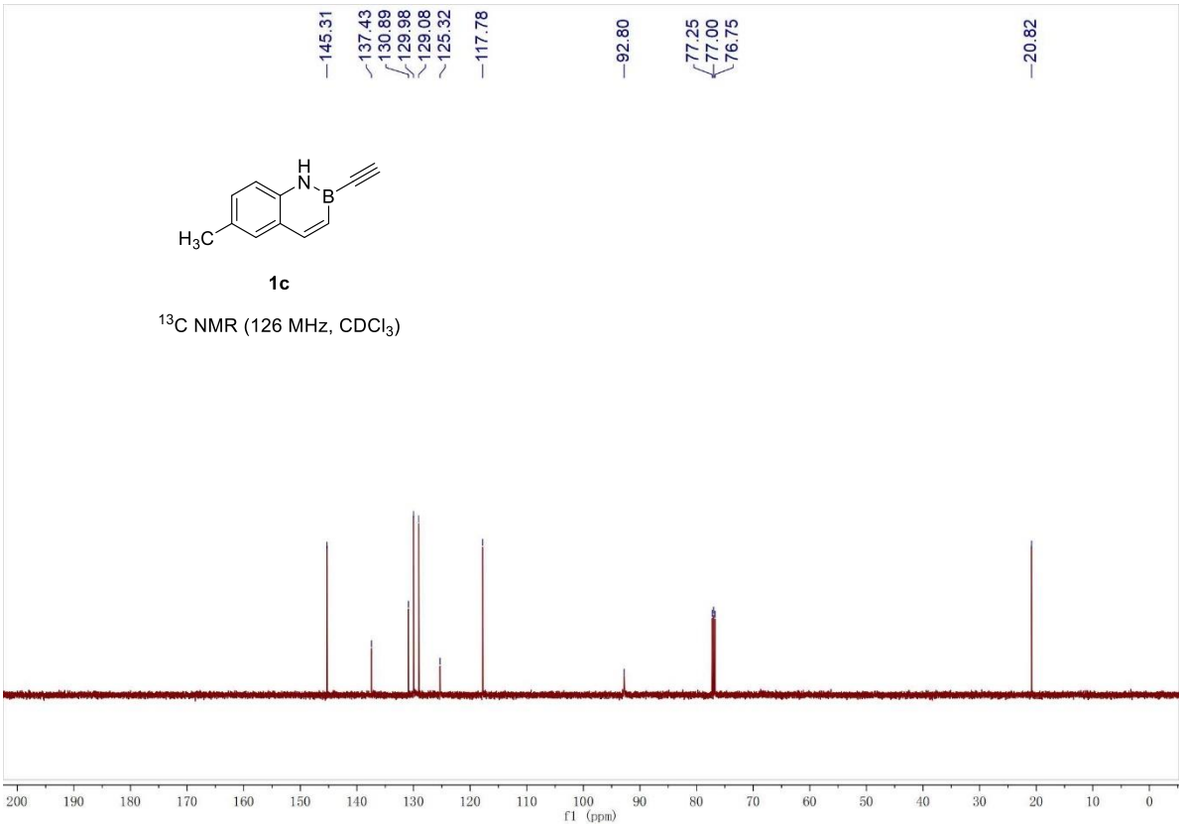
2-ethynyl-6-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1b)



2-ethynyl-6-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1c)



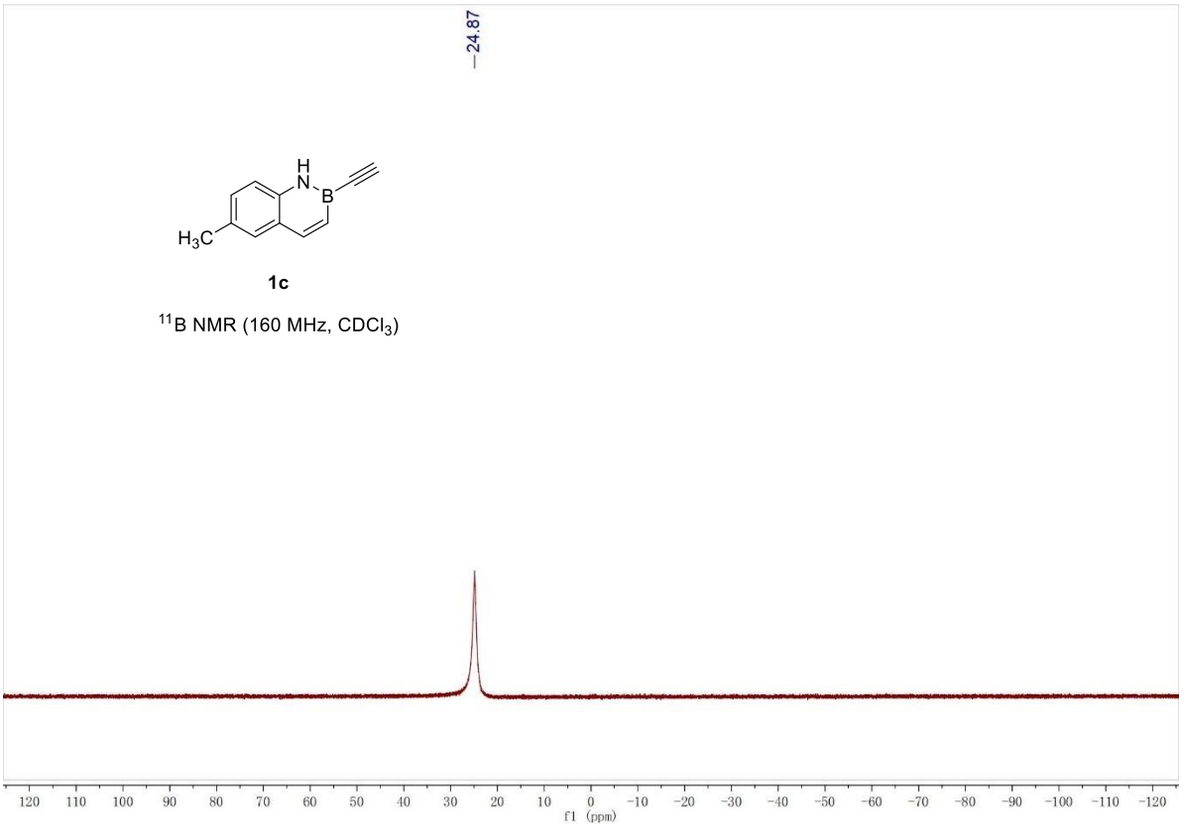
2-ethynyl-6-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1c)



1c

^{13}C NMR (126 MHz, $CDCl_3$)

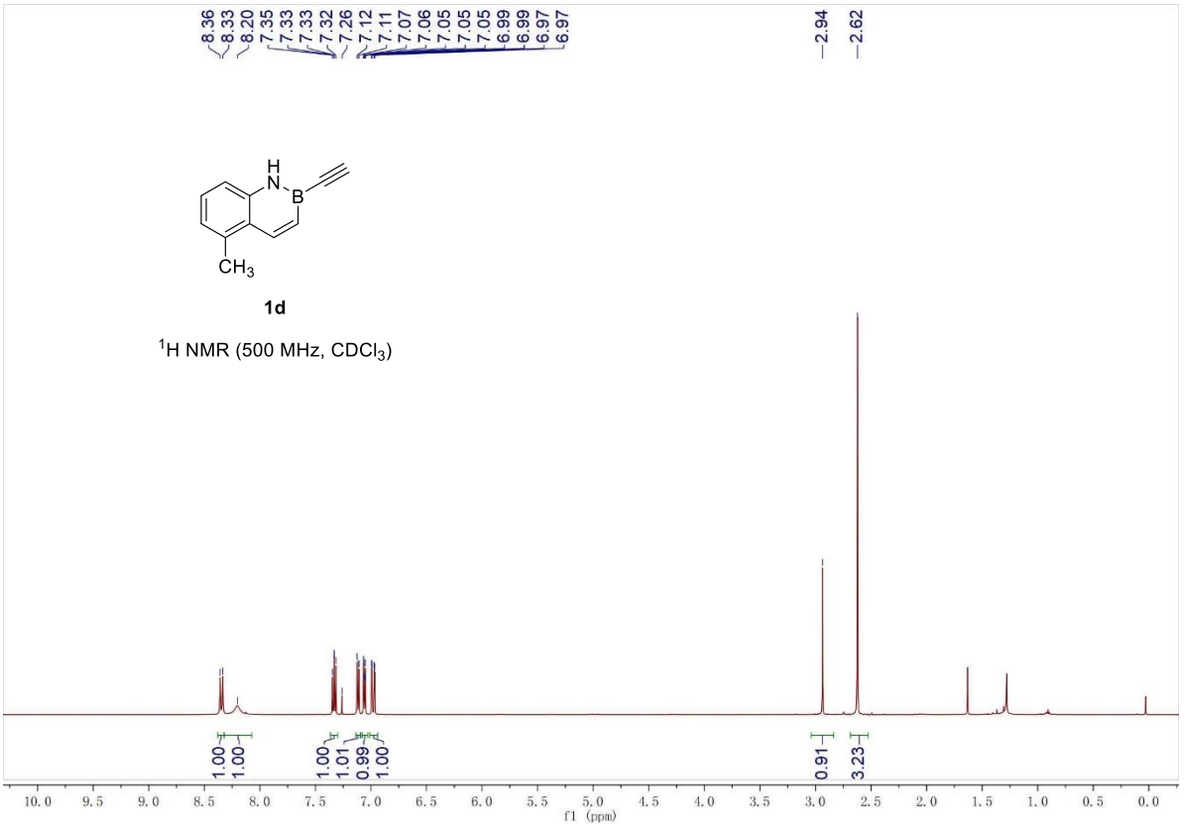
2-ethynyl-6-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1c)



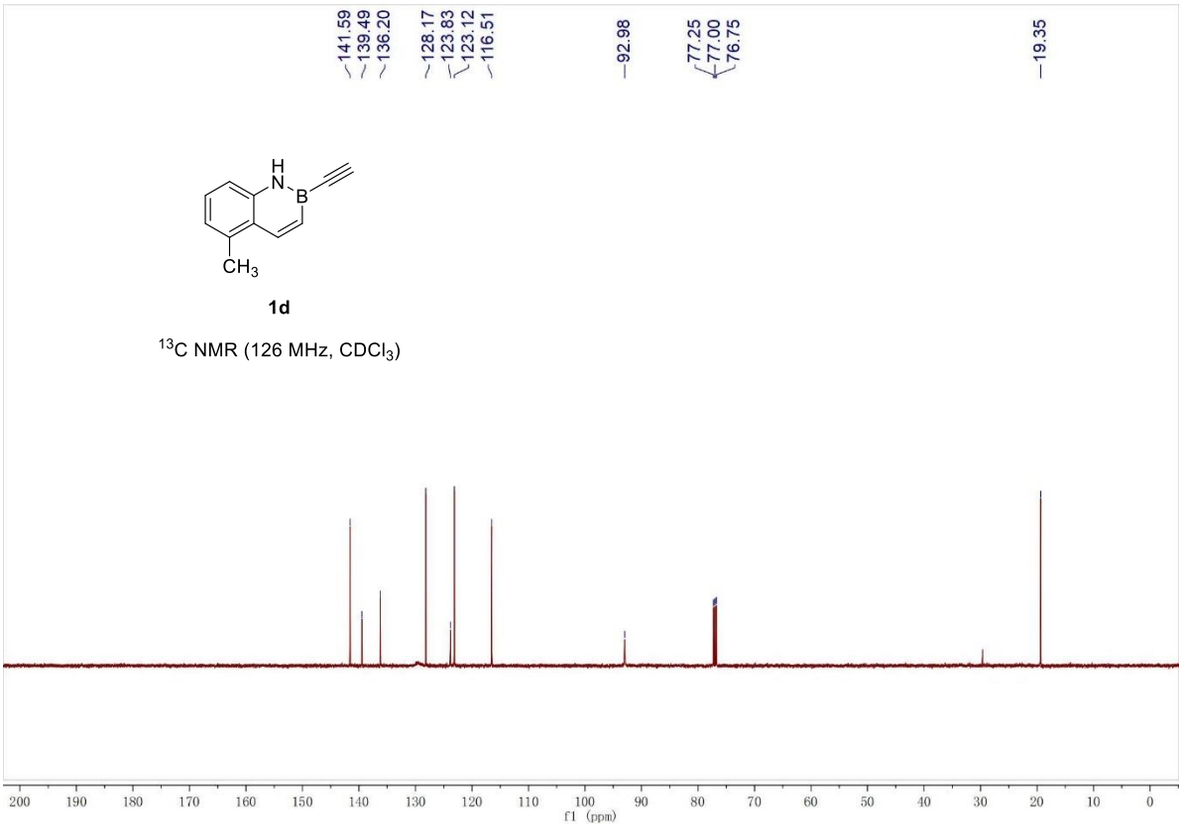
1c

^{11}B NMR (160 MHz, $CDCl_3$)

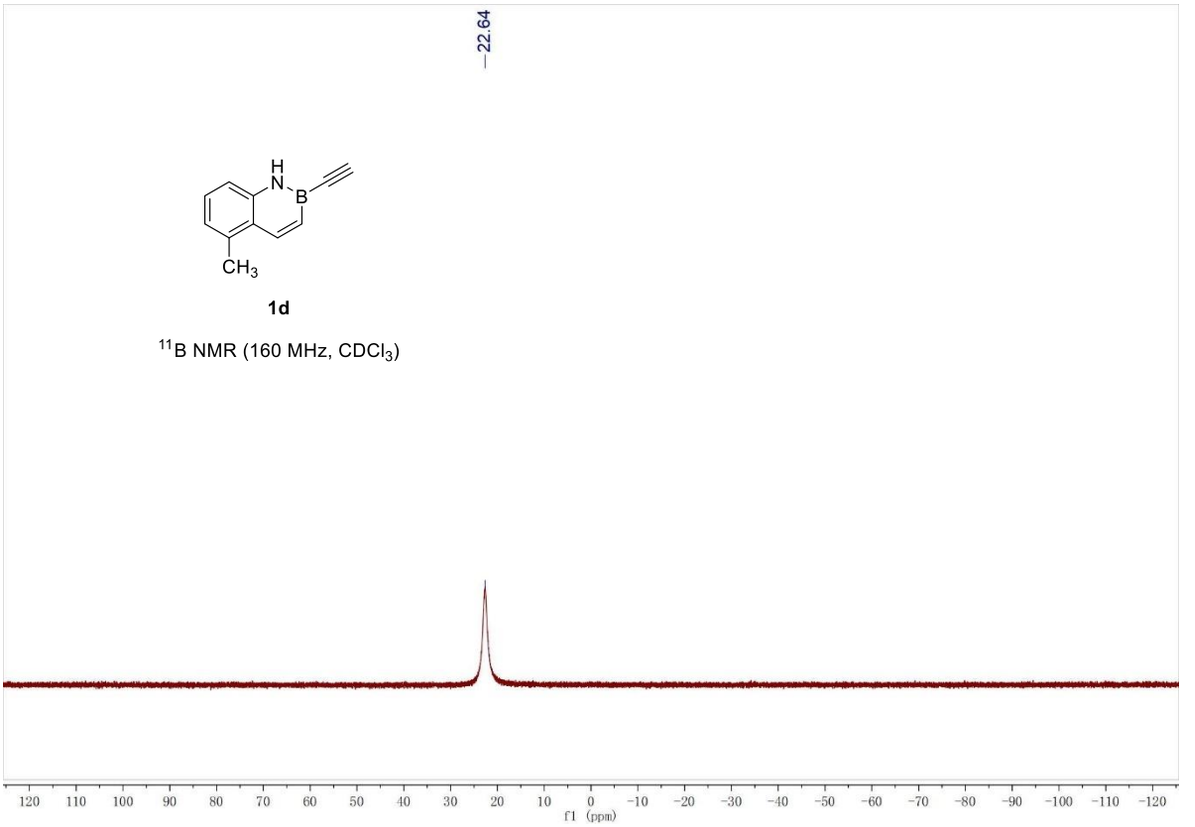
2-ethynyl-5-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1d)



2-ethynyl-5-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1d)



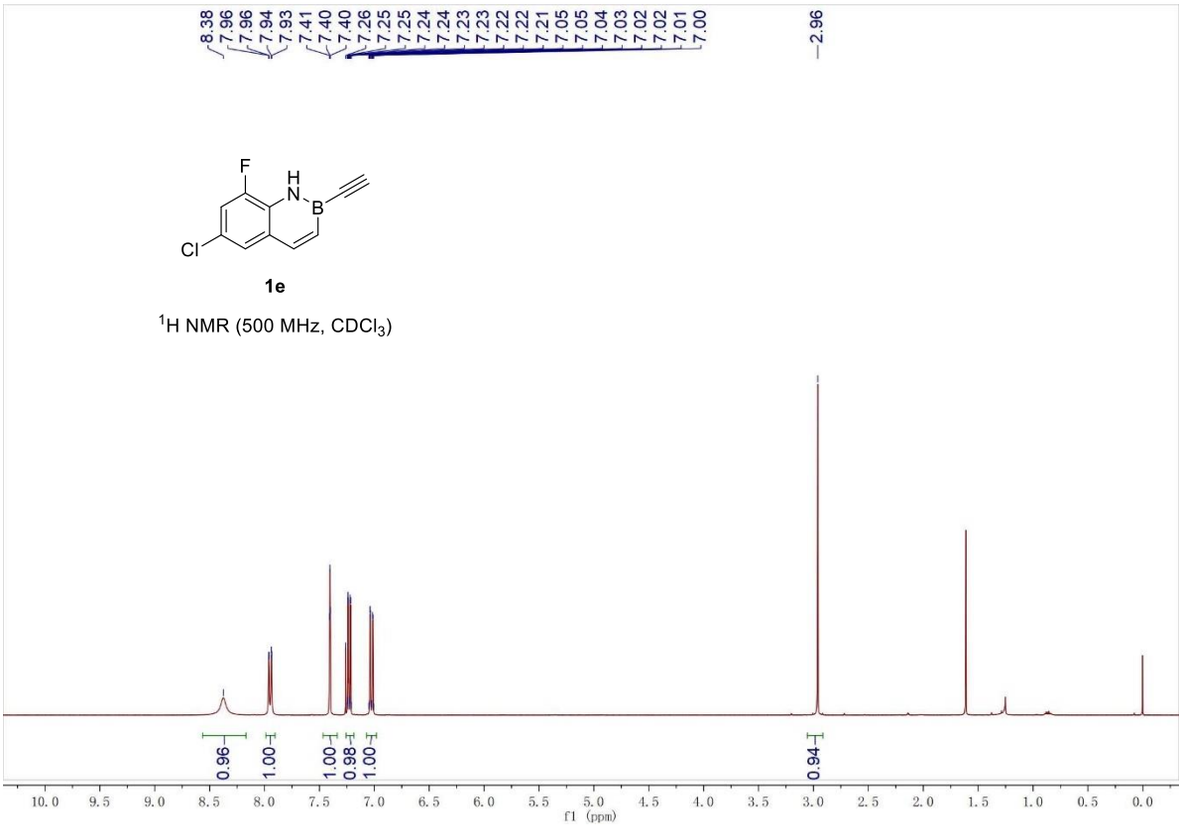
2-ethynyl-5-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1d)



1d

^{11}B NMR (160 MHz, $CDCl_3$)

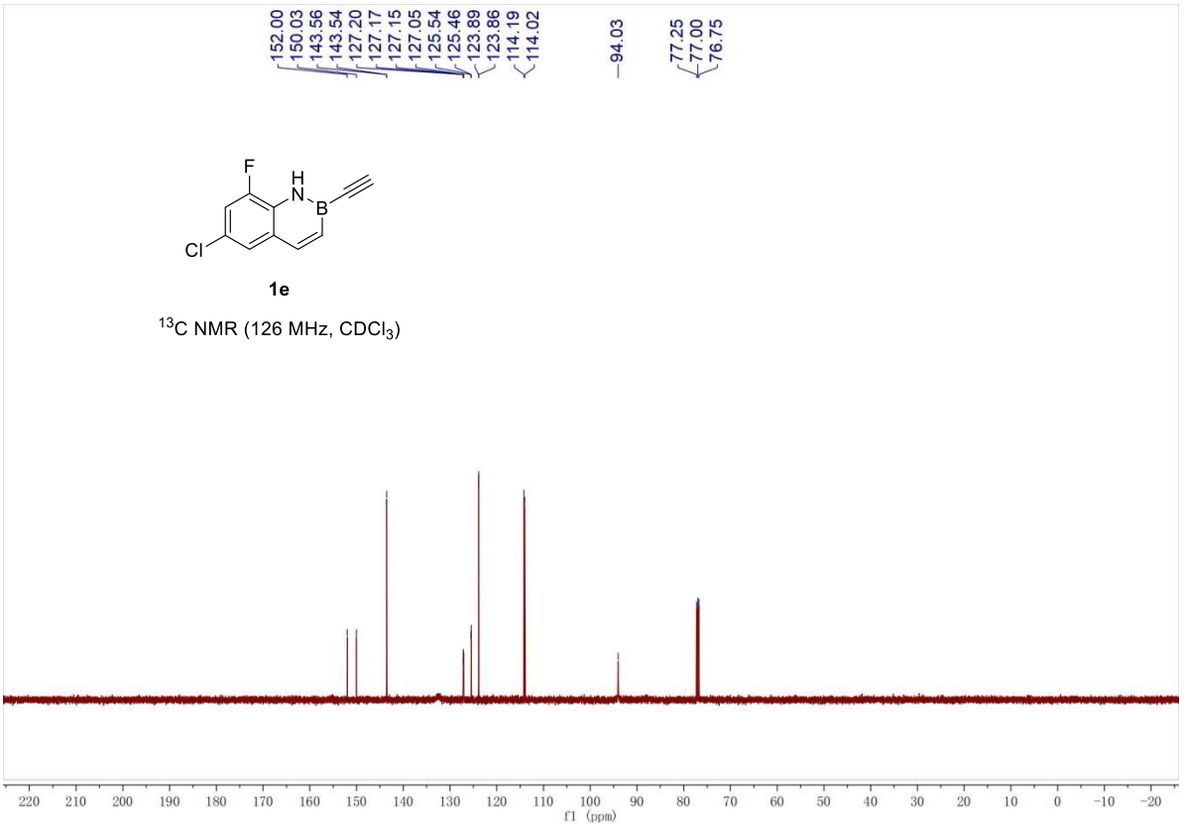
6-chloro-2-ethynyl-8-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1e)



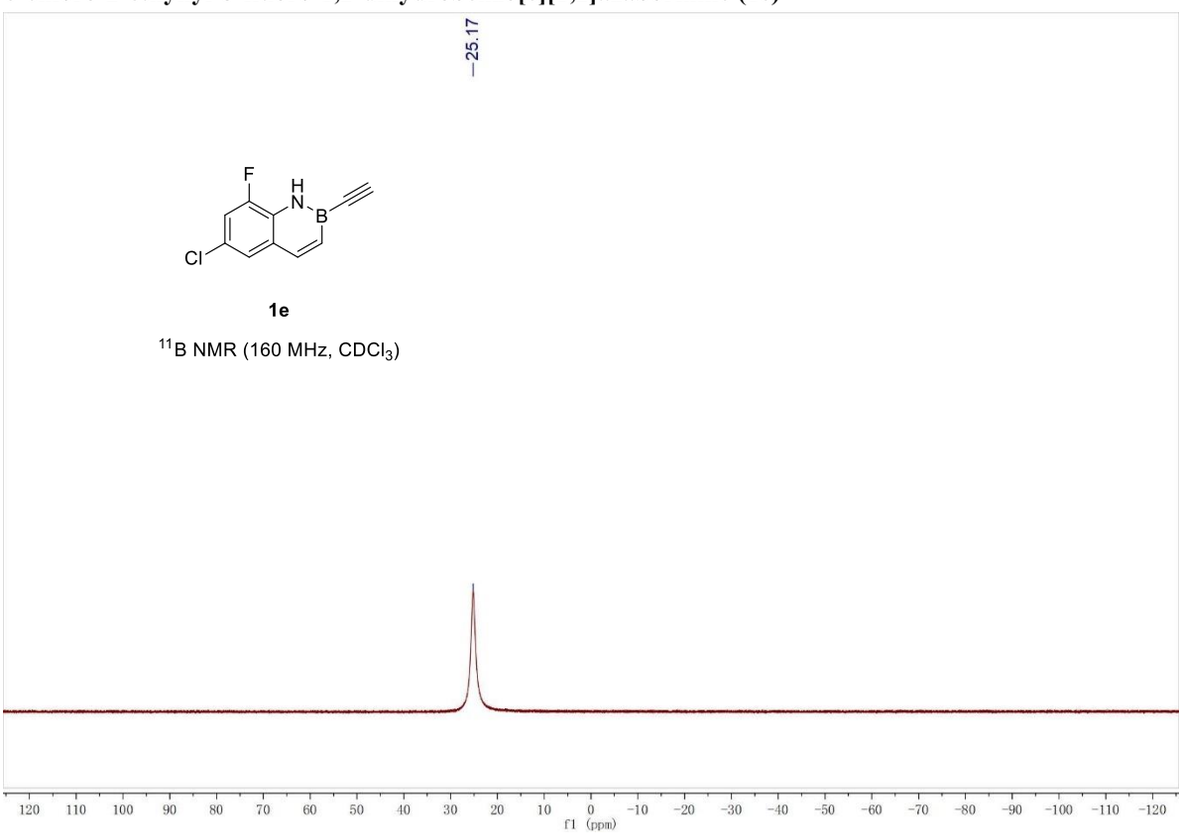
1e

^{1}H NMR (500 MHz, $CDCl_3$)

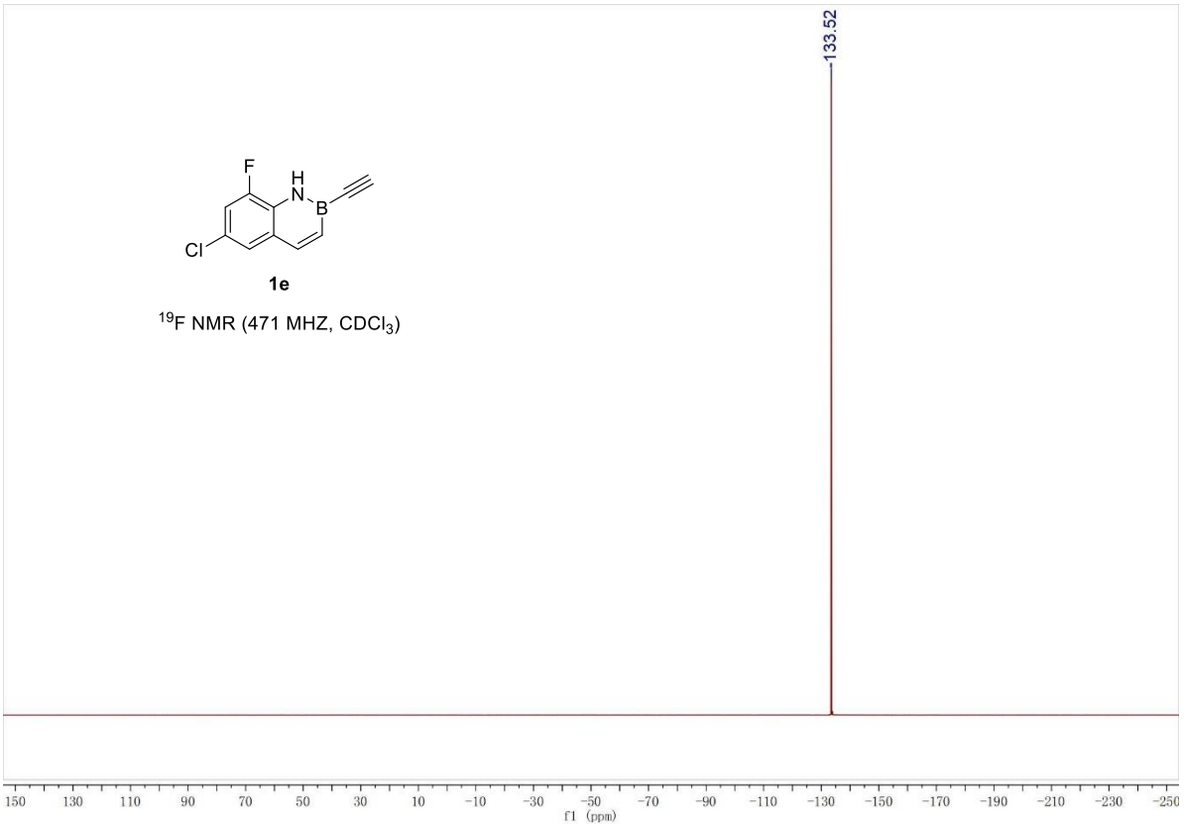
6-chloro-2-ethynyl-8-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1e)



6-chloro-2-ethynyl-8-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1e)



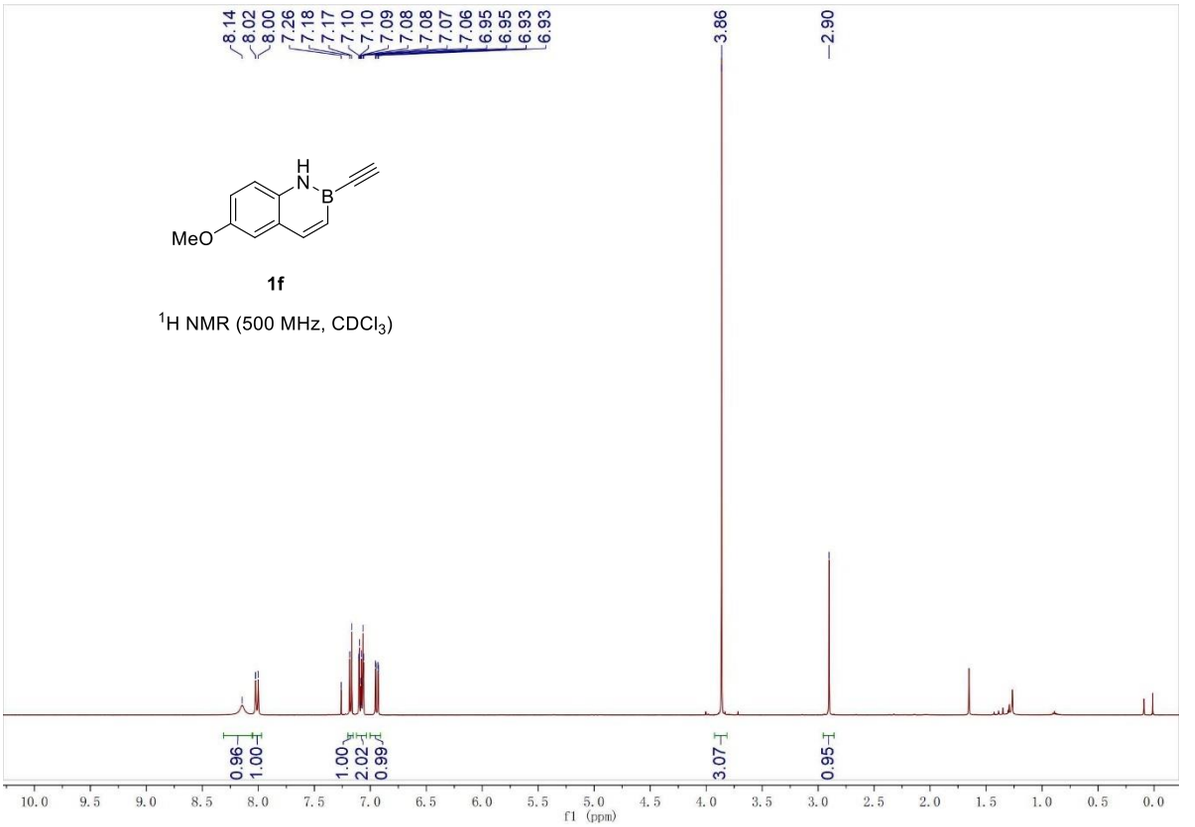
6-chloro-2-ethynyl-8-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1e)



1e

^{19}F NMR (471 MHZ, $CDCl_3$)

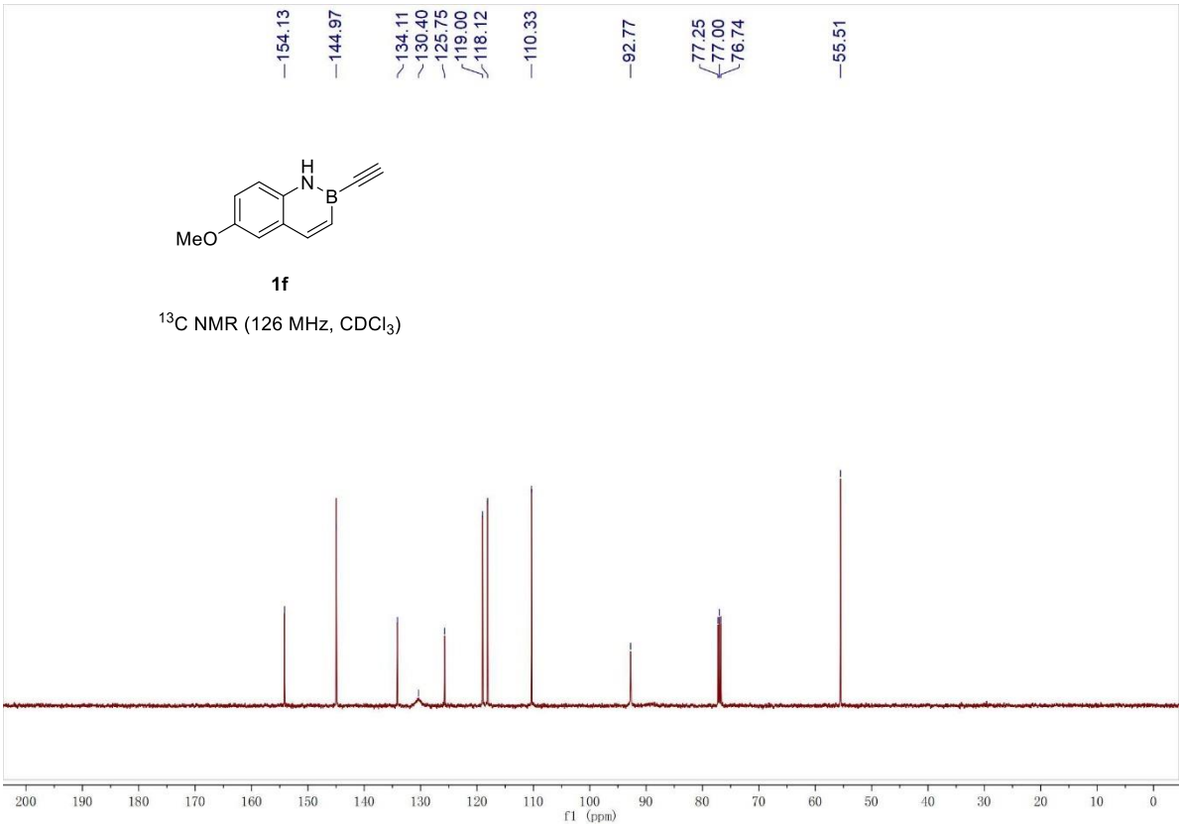
2-ethynyl-6-methoxy-1,2-dihydrobenzo[e][1,2]azaborinine (1f)



1f

^{1}H NMR (500 MHz, $CDCl_3$)

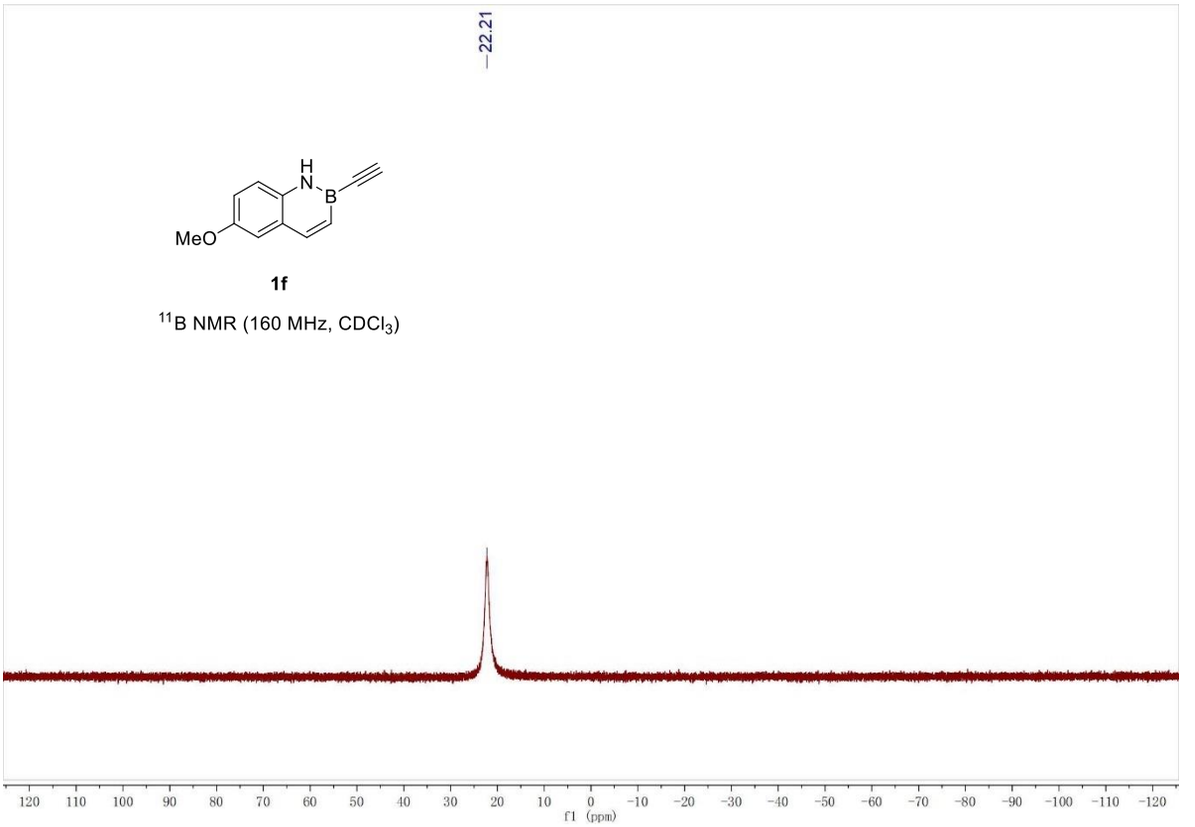
2-ethynyl-6-methoxy-1,2-dihydrobenzo[e][1,2]azaborinine (1f)



1f

^{13}C NMR (126 MHz, $CDCl_3$)

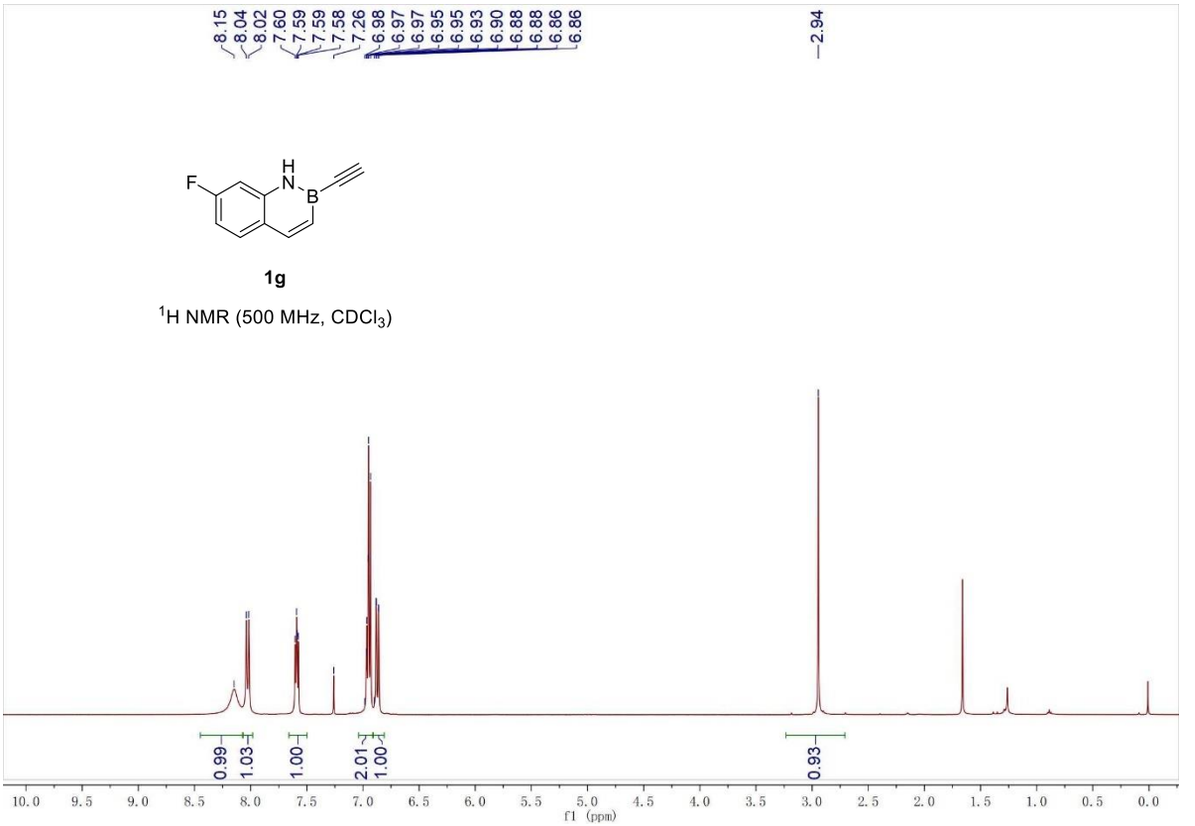
2-ethynyl-6-methoxy-1,2-dihydrobenzo[e][1,2]azaborinine (1f)



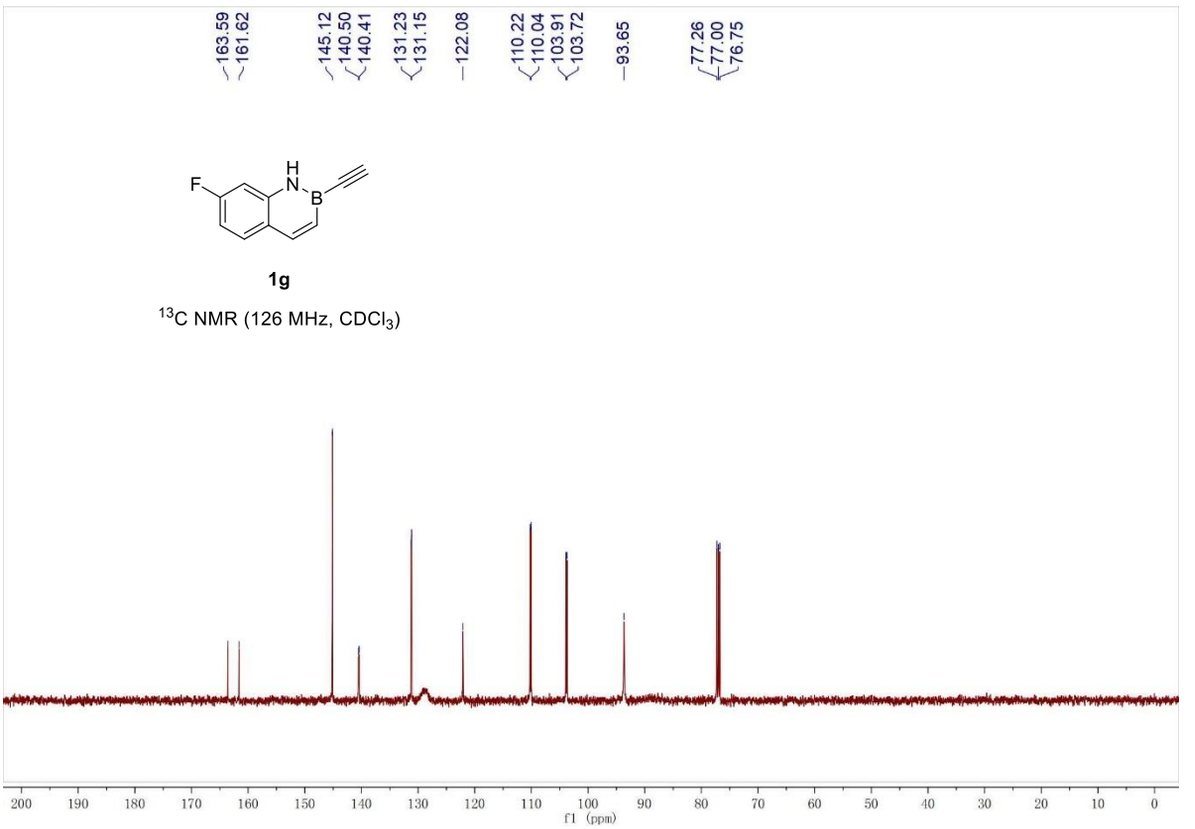
1f

^{11}B NMR (160 MHz, $CDCl_3$)

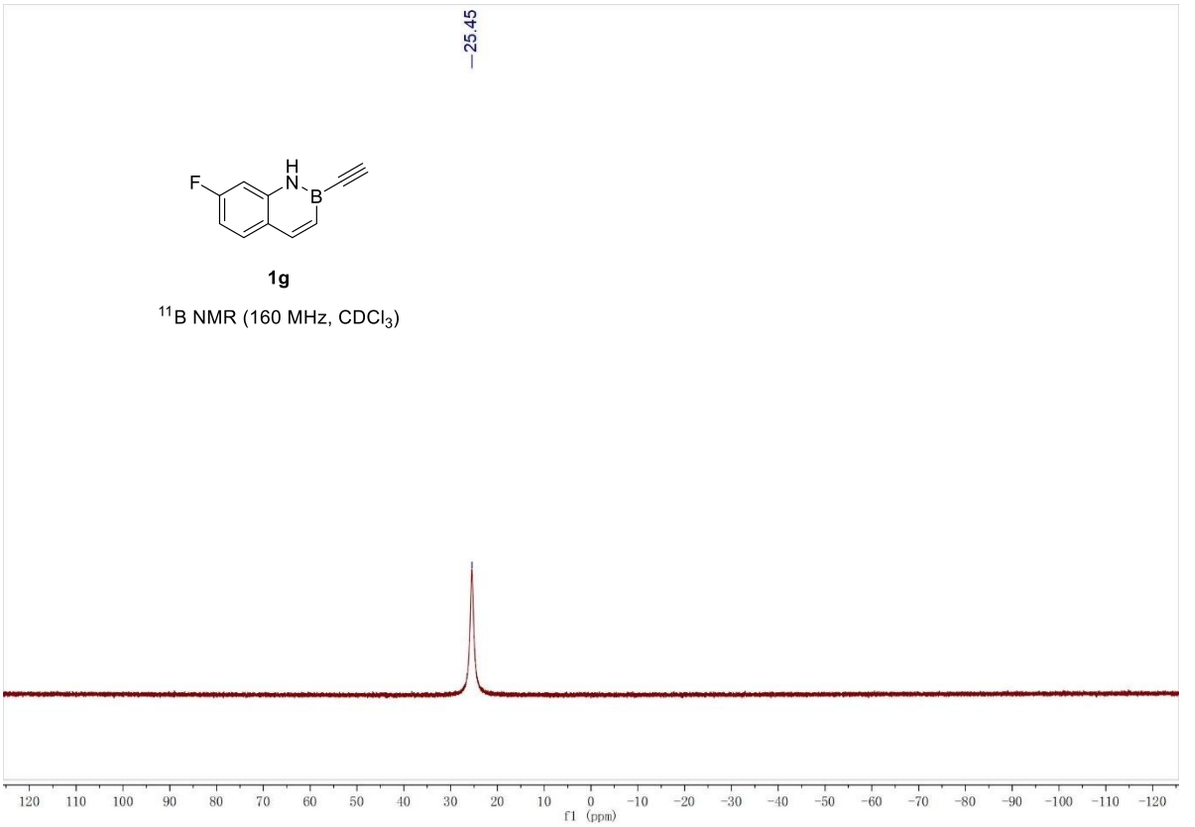
2-ethynyl-7-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1g)



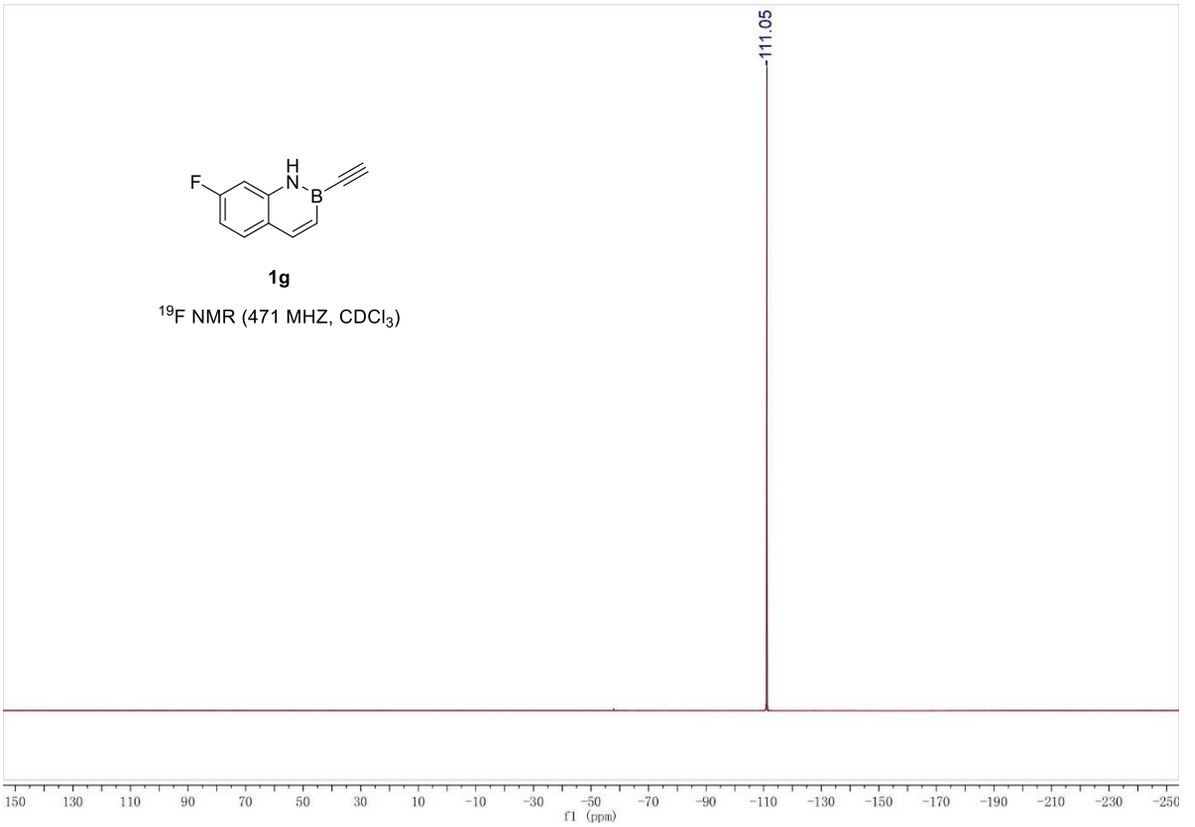
2-ethynyl-7-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1g)



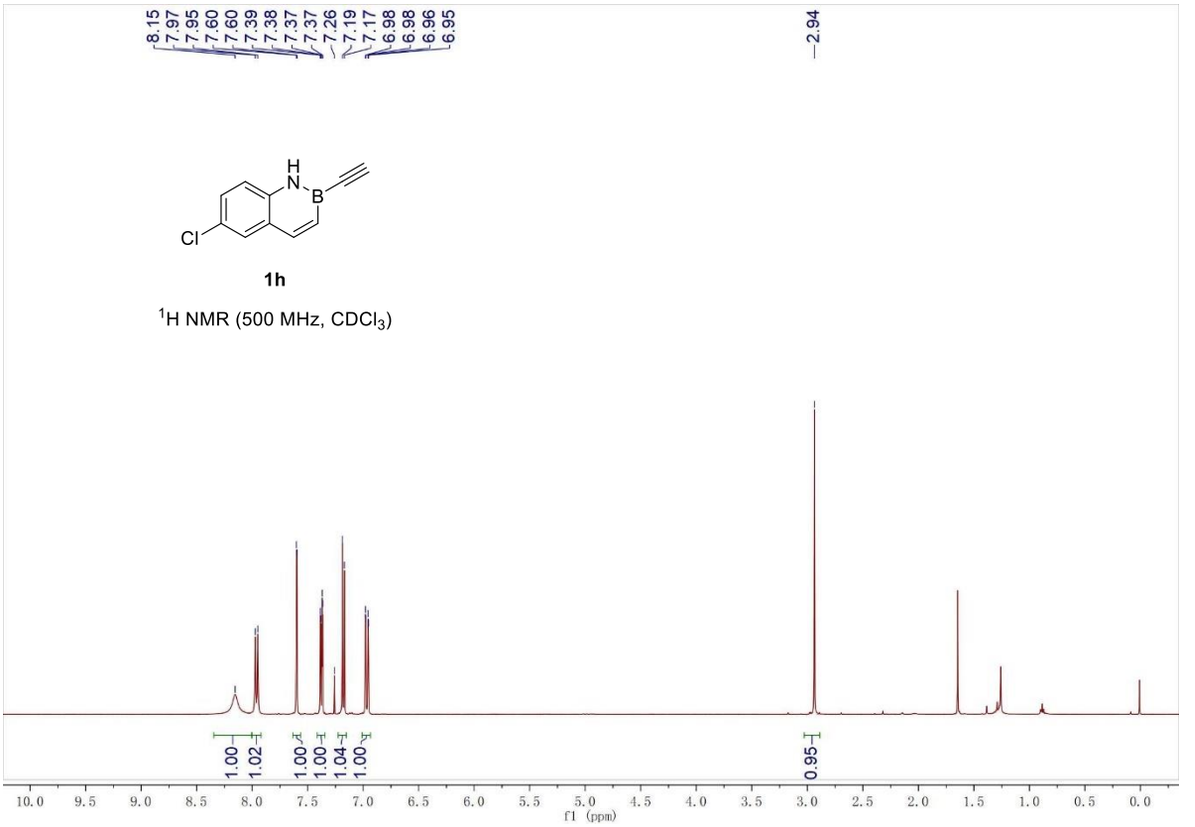
2-ethynyl-7-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1g)



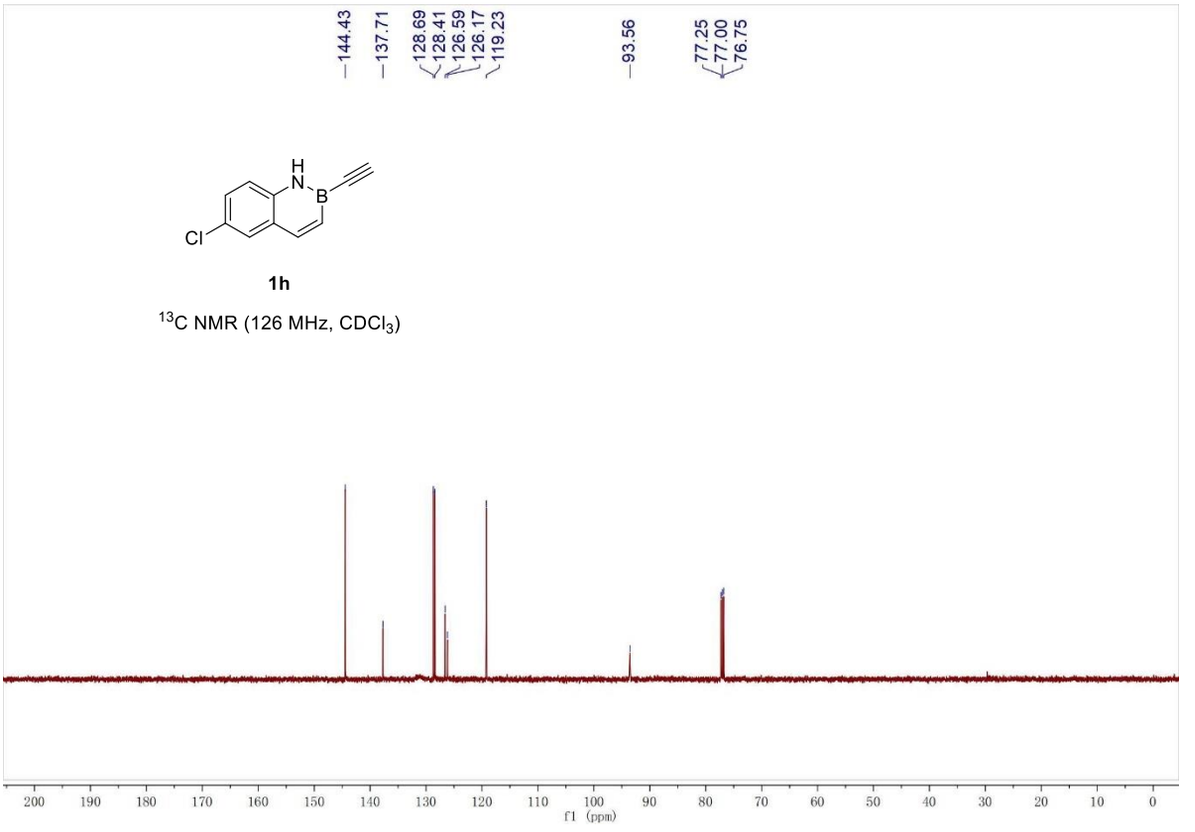
2-ethynyl-7-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (1g)



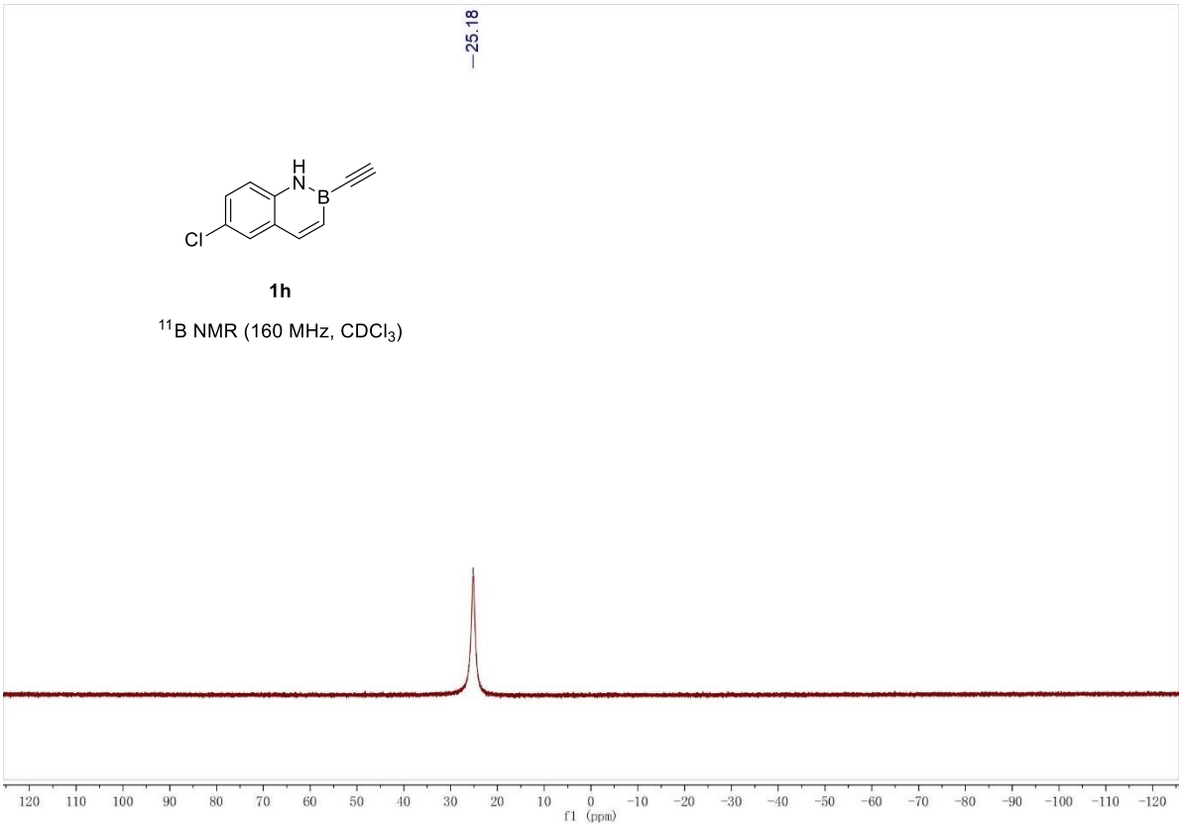
6-chloro-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1h)



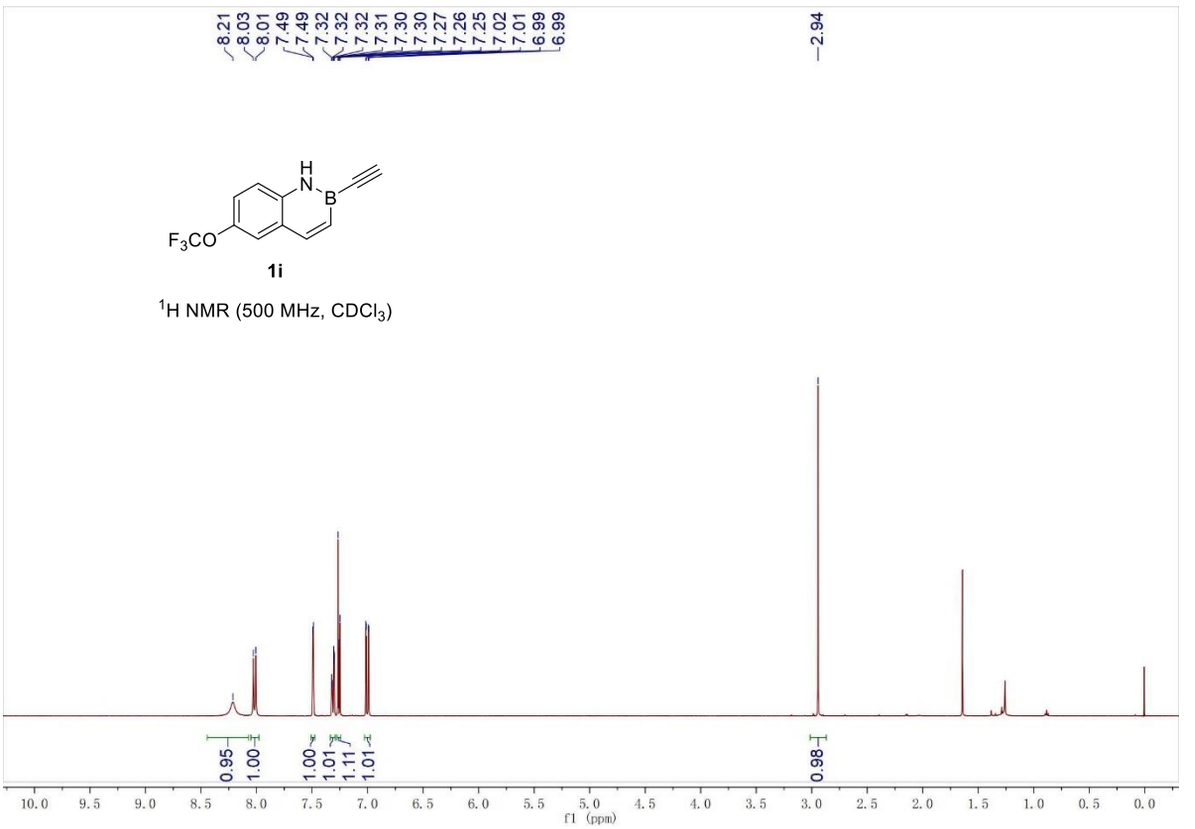
6-chloro-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1h)



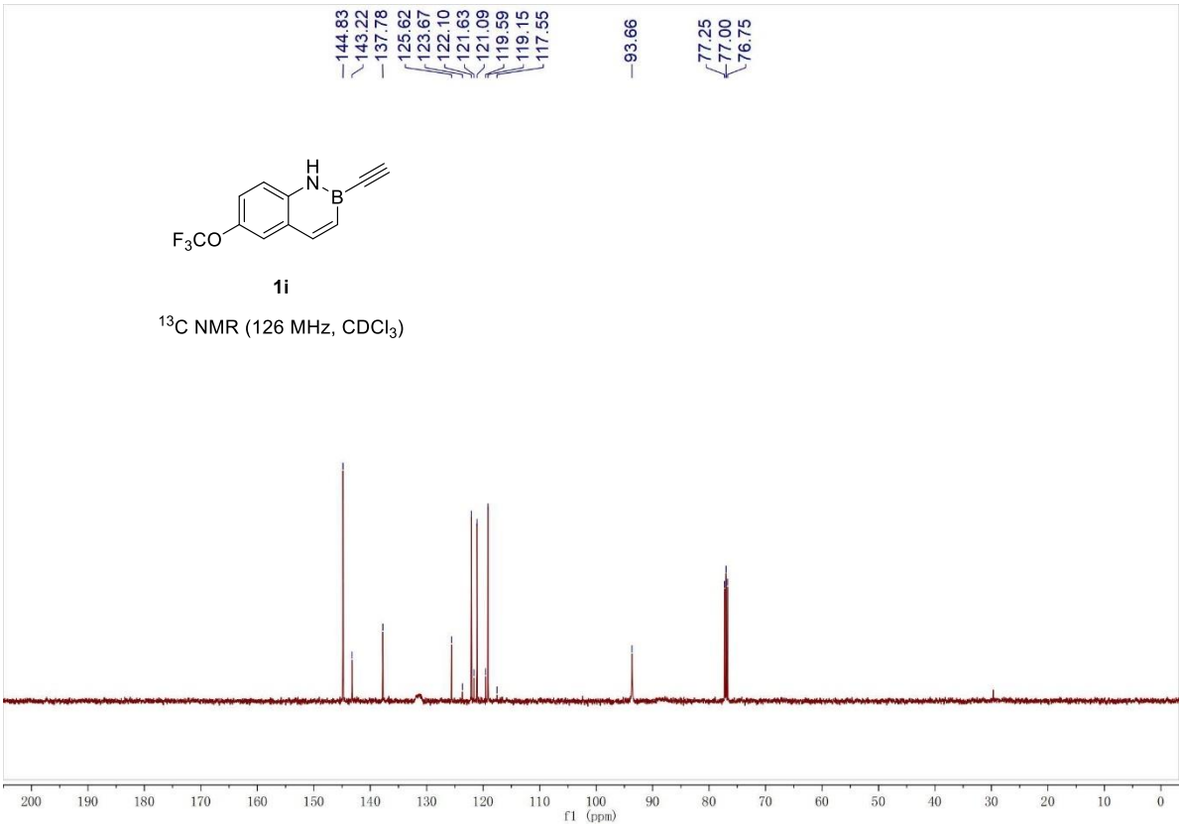
6-chloro-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1h)



2-ethynyl-6-(trifluoromethoxy)-1,2-dihydrobenzo[e][1,2]azaborinine (1i)



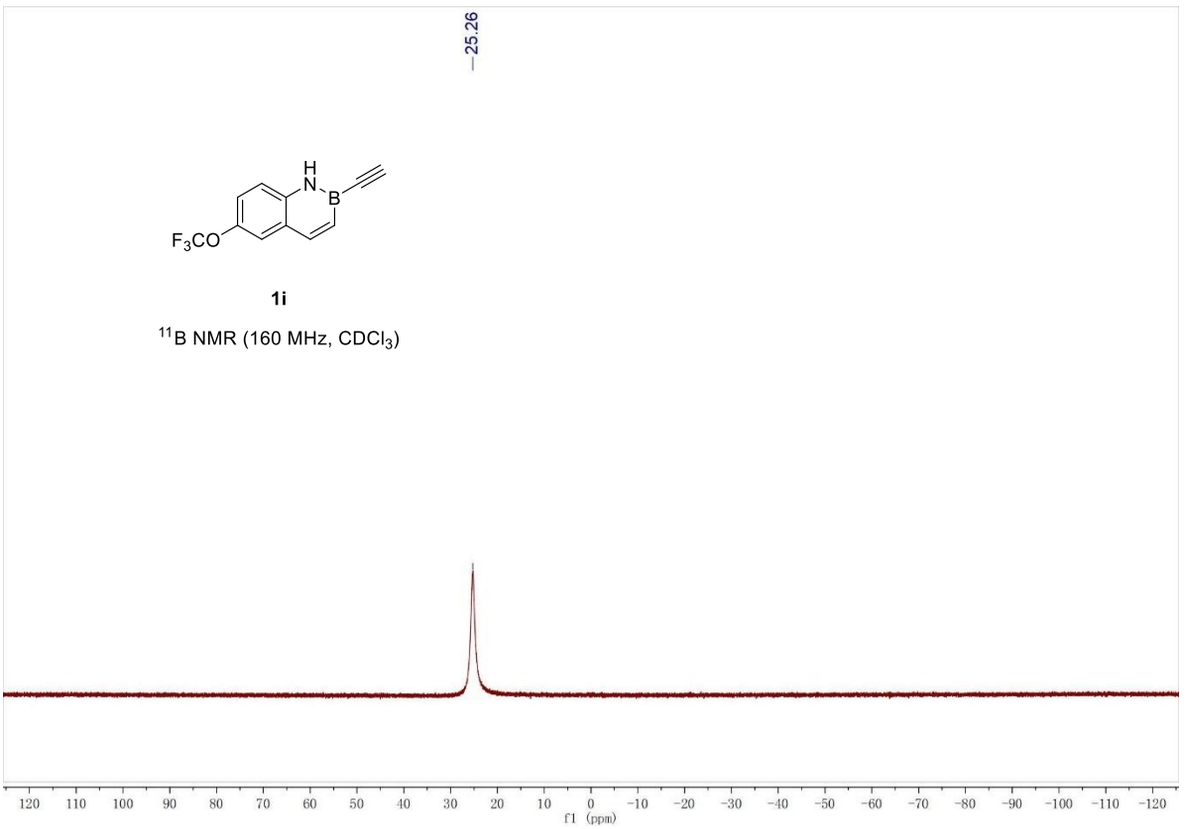
2-ethynyl-6-(trifluoromethoxy)-1,2-dihydrobenzo[e][1,2]azaborinine (1i)



1i

^{13}C NMR (126 MHz, $CDCl_3$)

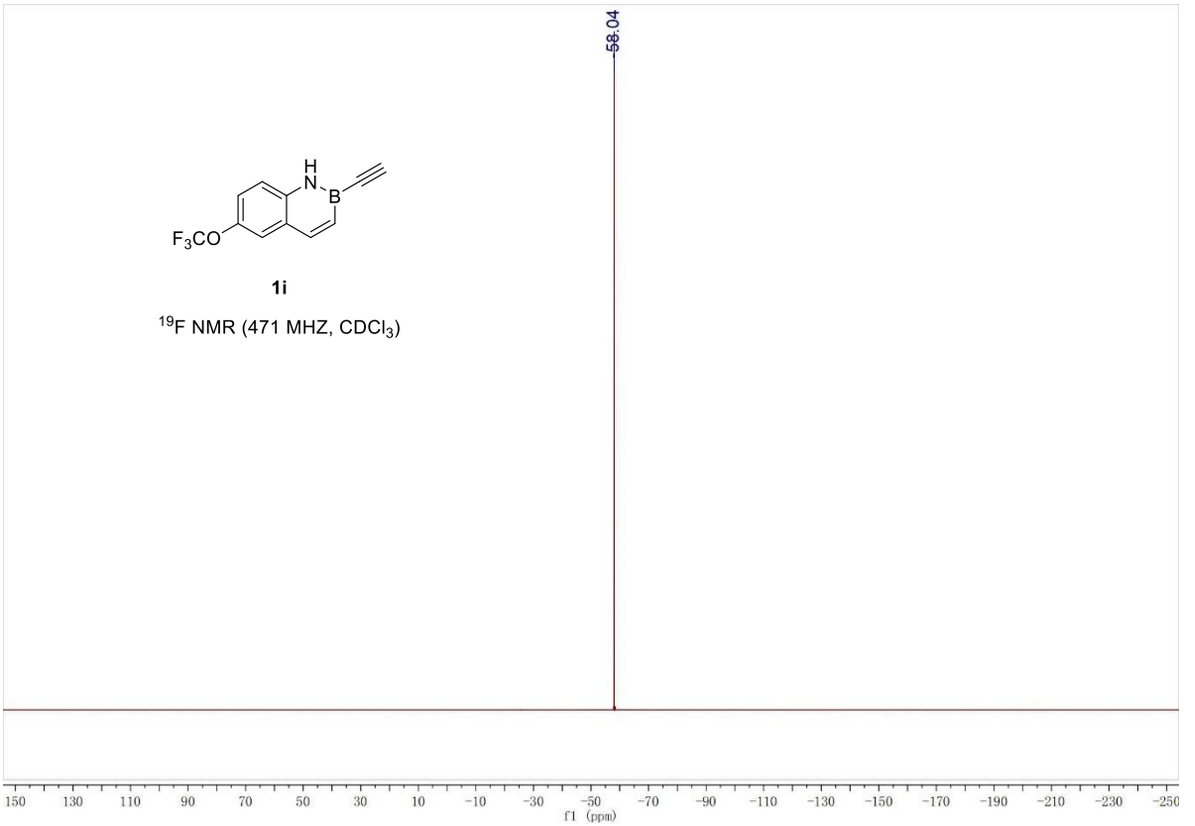
2-ethynyl-6-(trifluoromethoxy)-1,2-dihydrobenzo[e][1,2]azaborinine (1i)



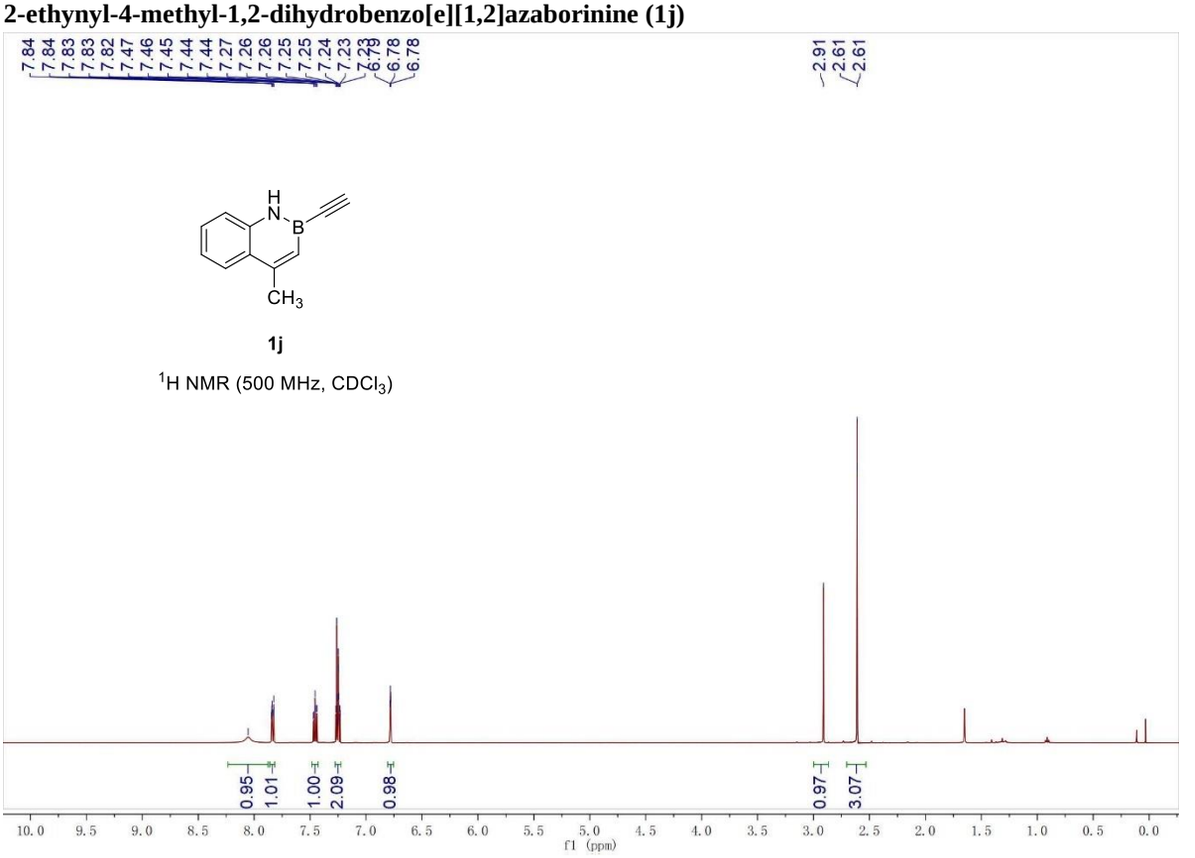
1i

^{11}B NMR (160 MHz, $CDCl_3$)

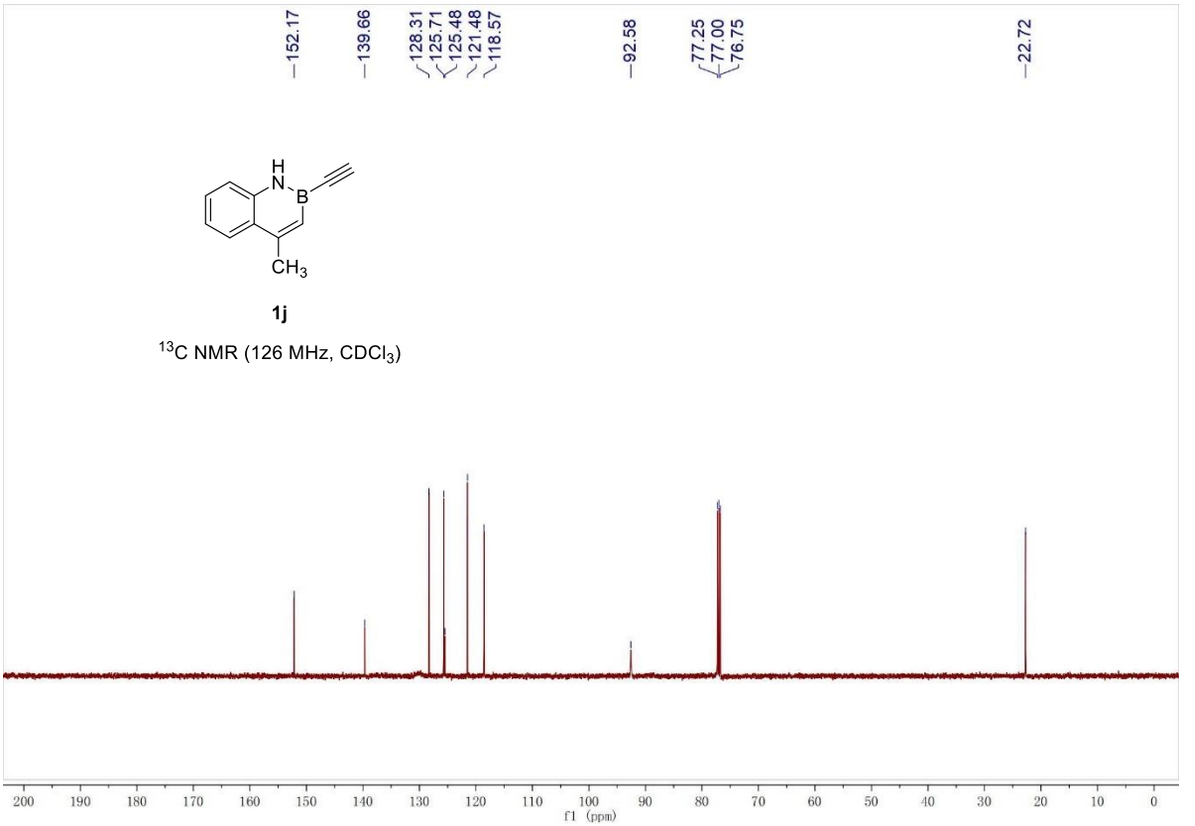
2-ethynyl-6-(trifluoromethoxy)-1,2-dihydrobenzo[e][1,2]azaborinine (1i)



2-ethynyl-4-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1j)



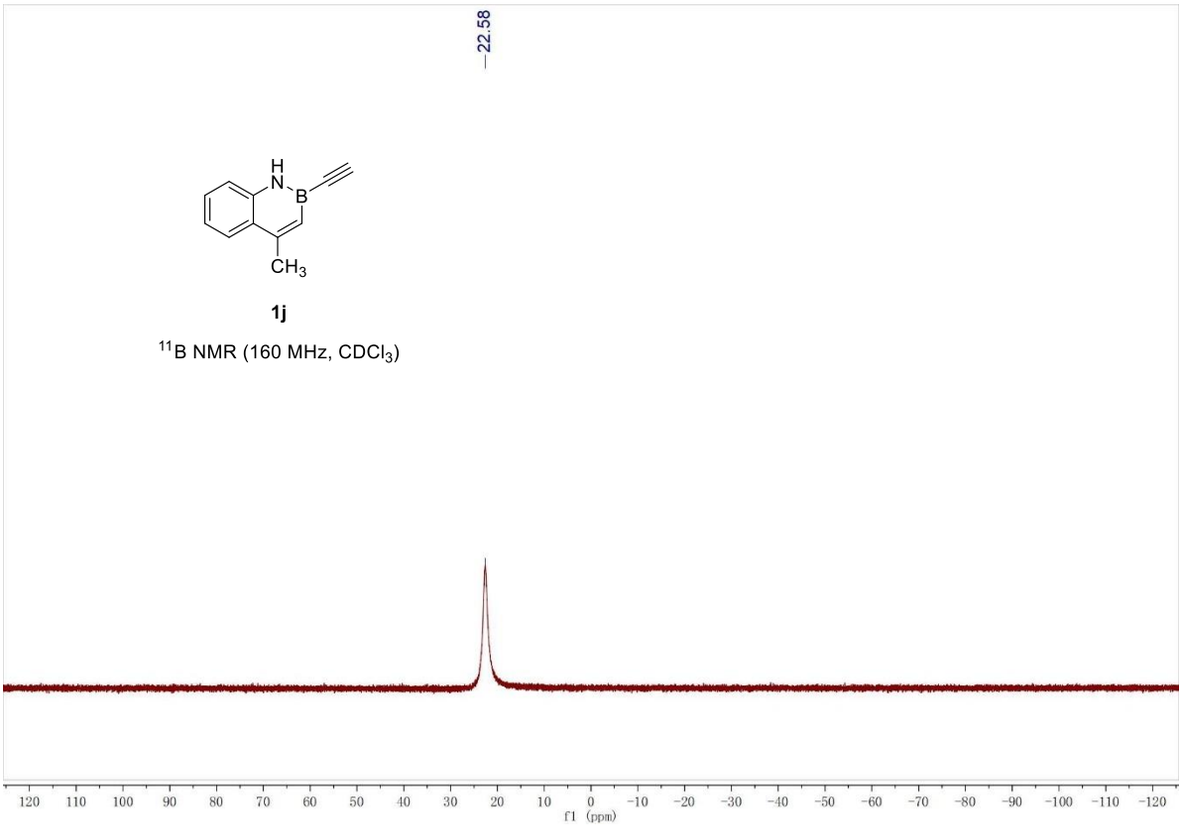
2-ethynyl-4-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1j)



1j

^{13}C NMR (126 MHz, $CDCl_3$)

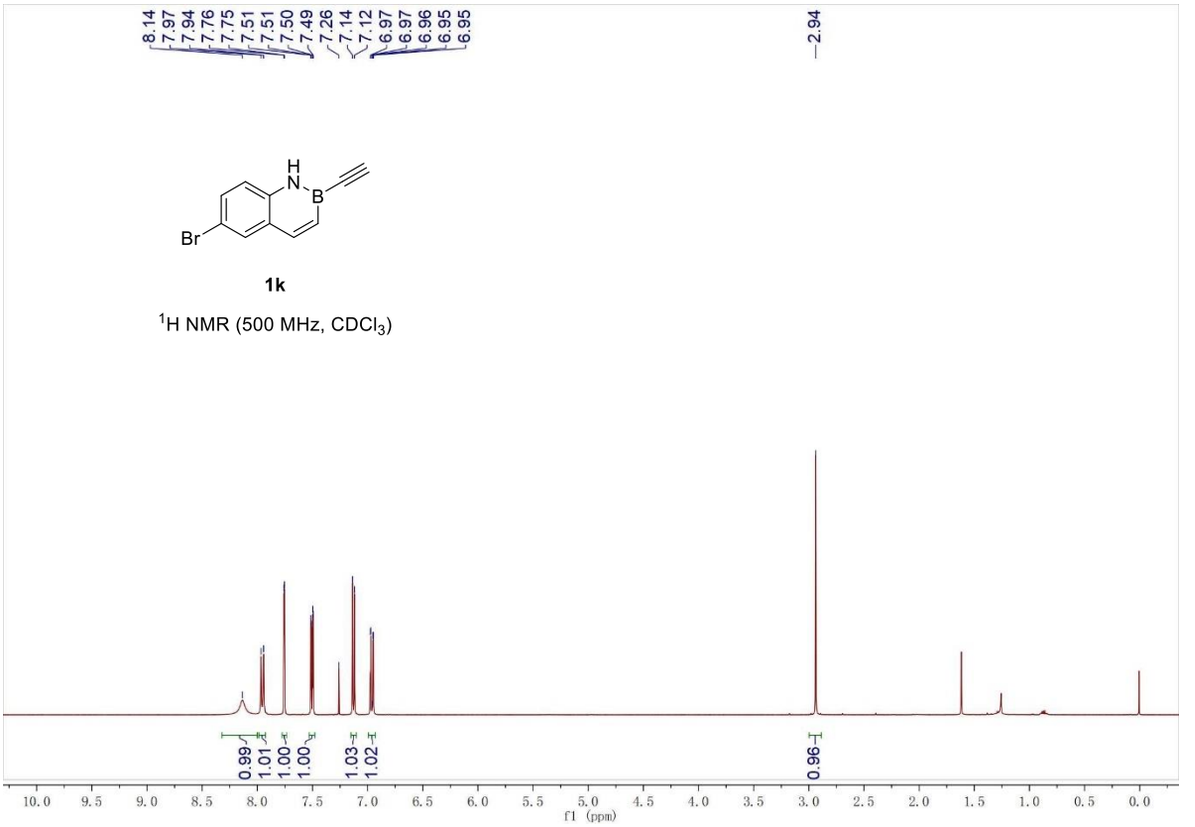
2-ethynyl-4-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (1j)



1j

^{11}B NMR (160 MHz, $CDCl_3$)

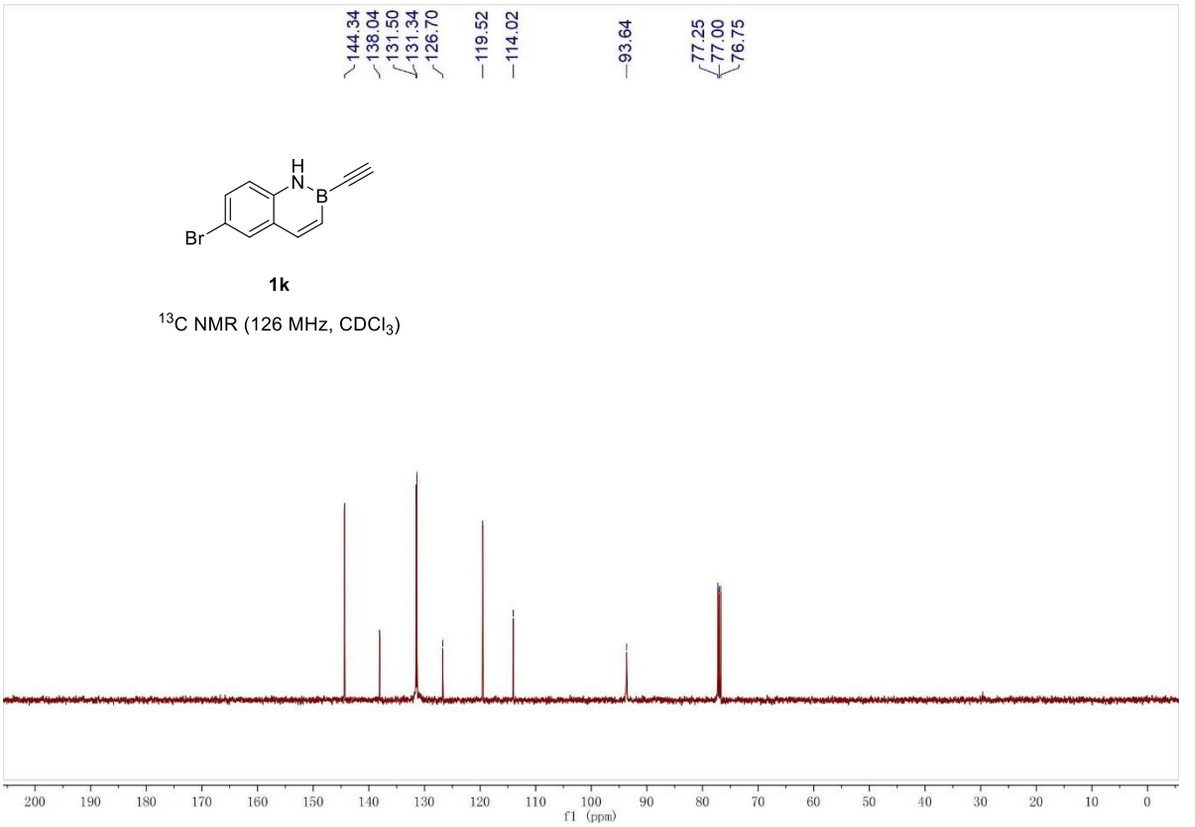
6-bromo-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1k)



1k

^{1}H NMR (500 MHz, $CDCl_3$)

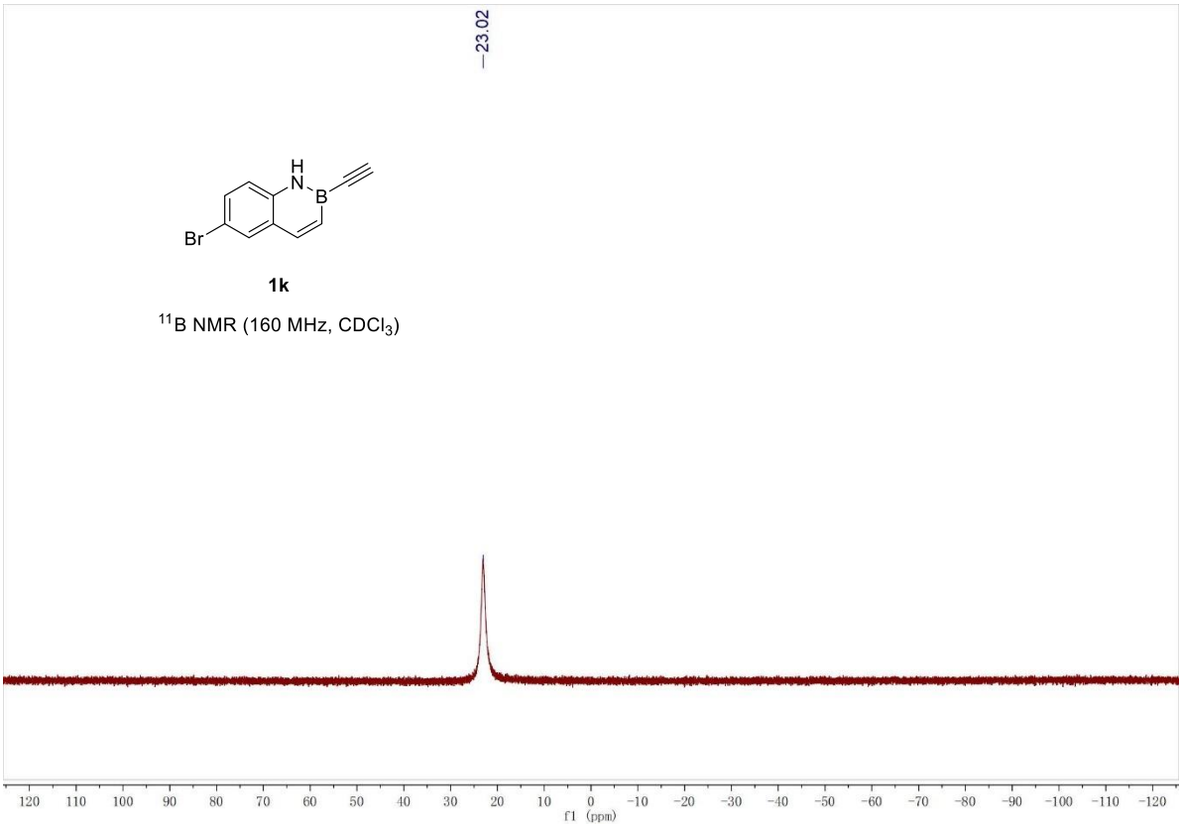
6-bromo-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1k)



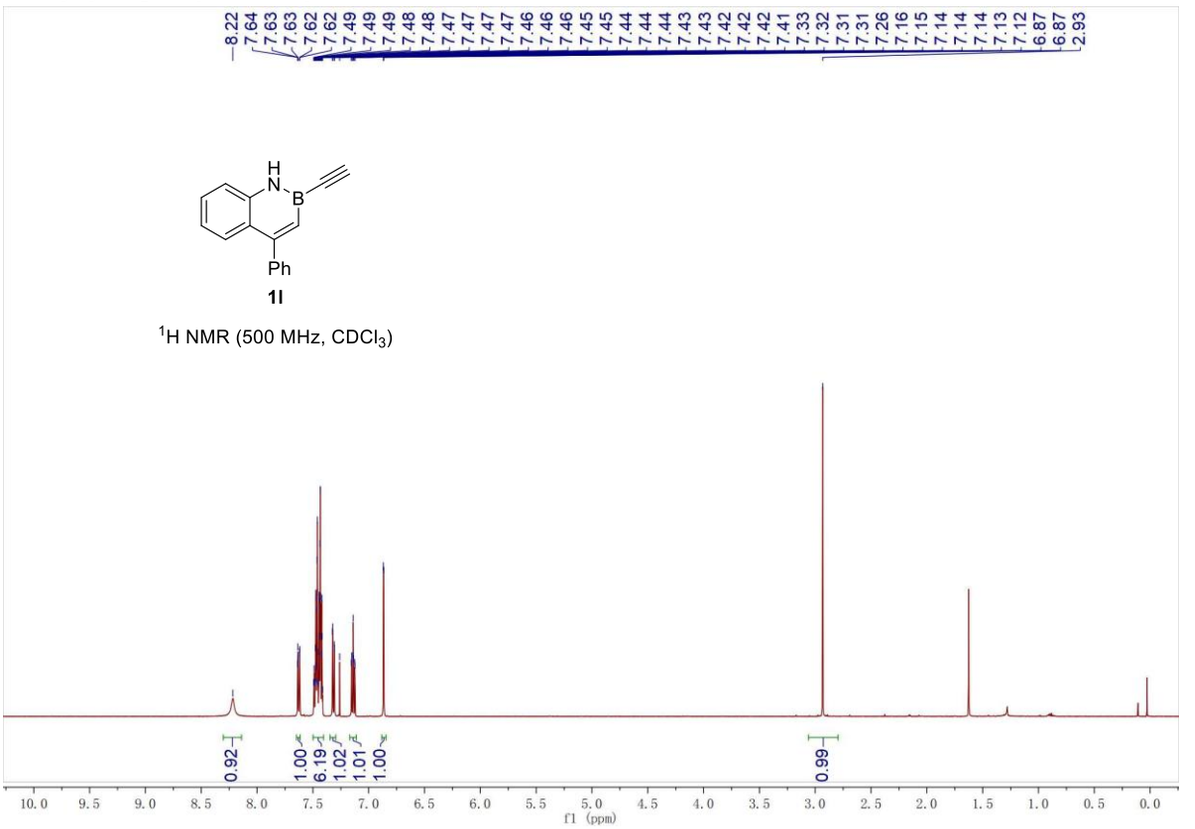
1k

^{13}C NMR (126 MHz, $CDCl_3$)

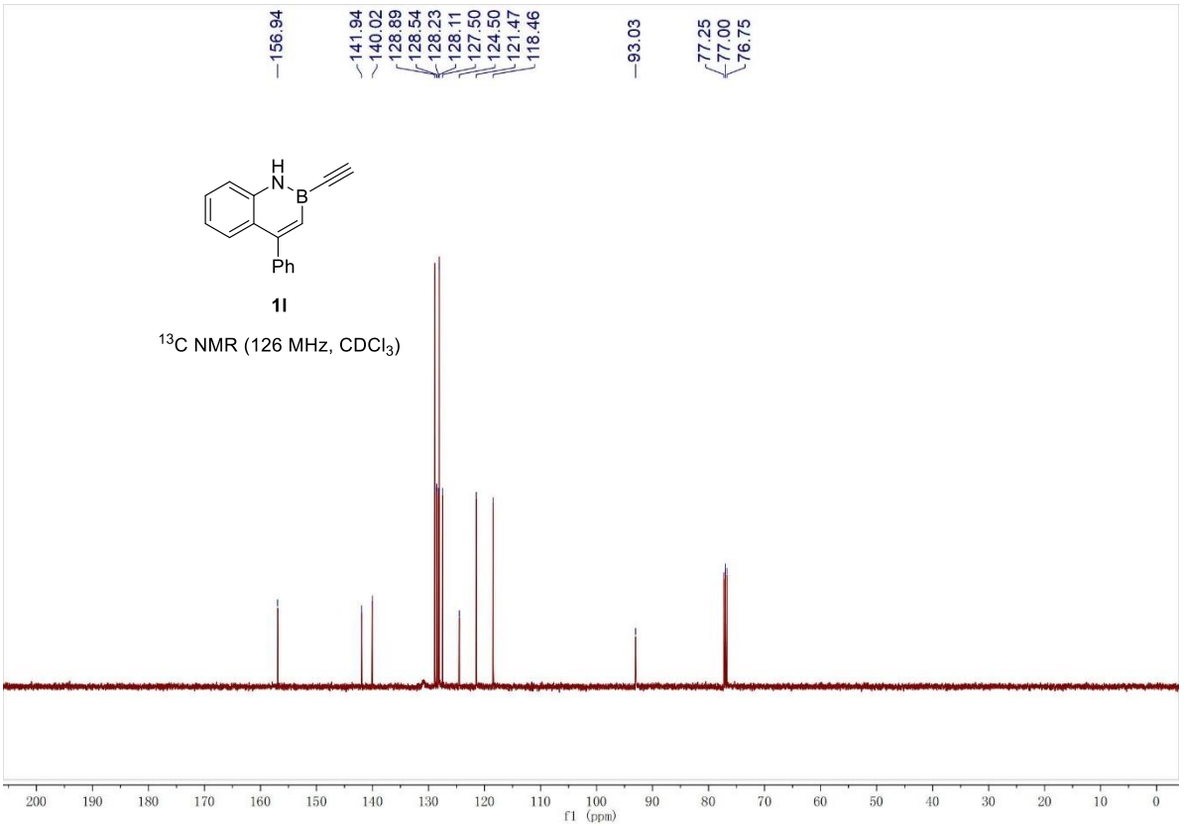
6-bromo-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1k)



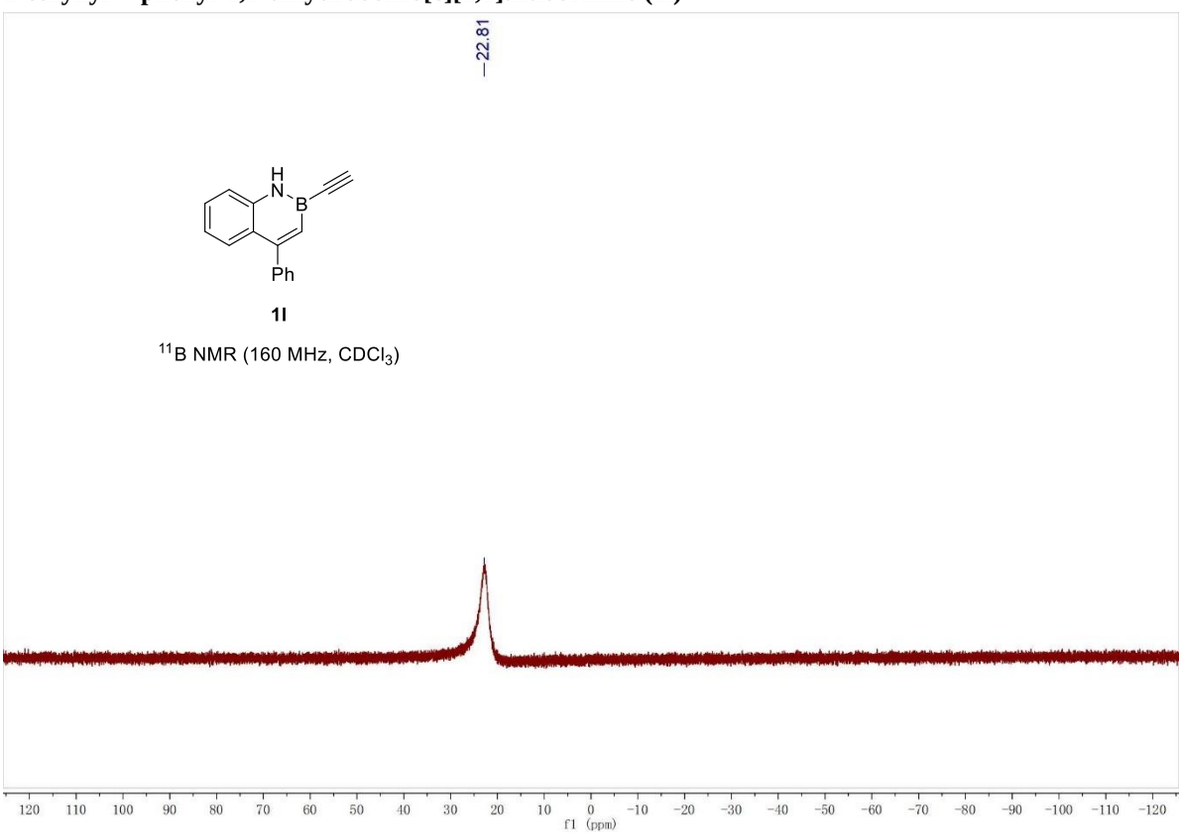
2-ethynyl-4-phenyl-1,2-dihydrobenzo[e][1,2]azaborinine (1l)



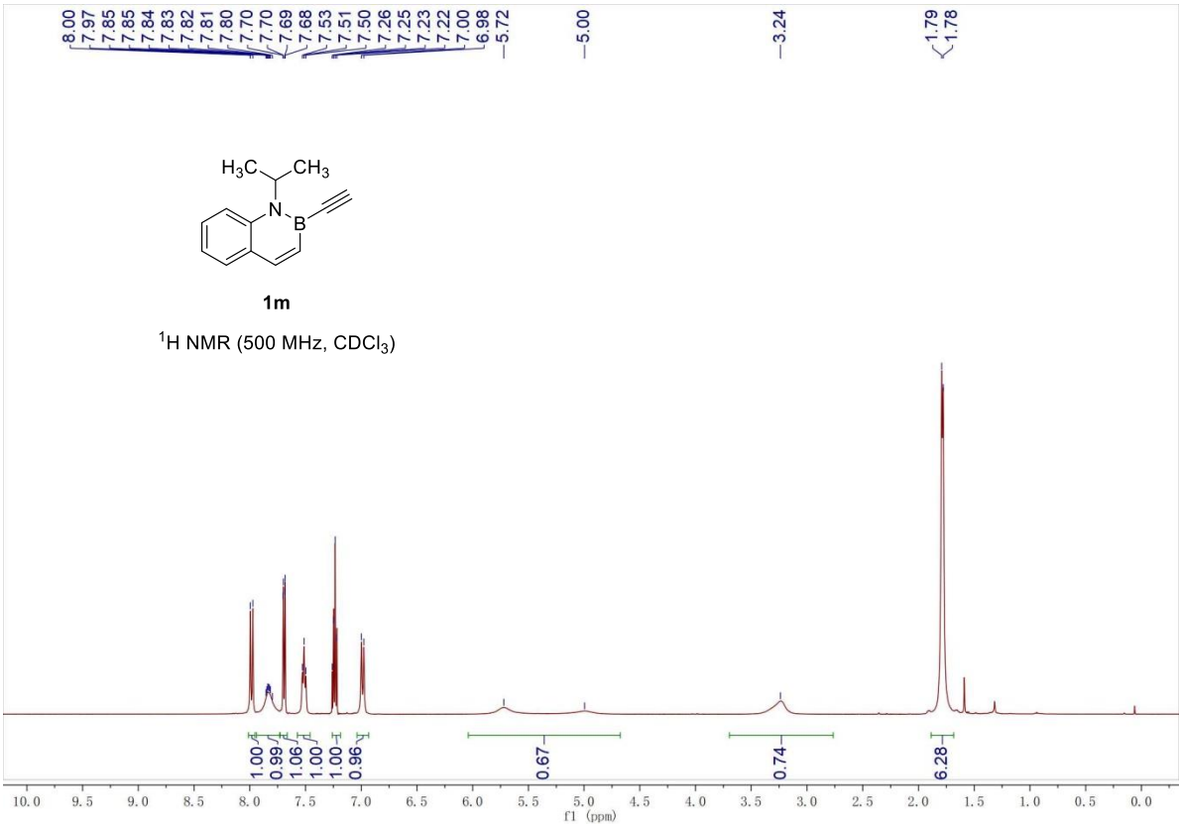
2-ethynyl-4-phenyl-1,2-dihydrobenzo[e][1,2]azaborinine (1l)



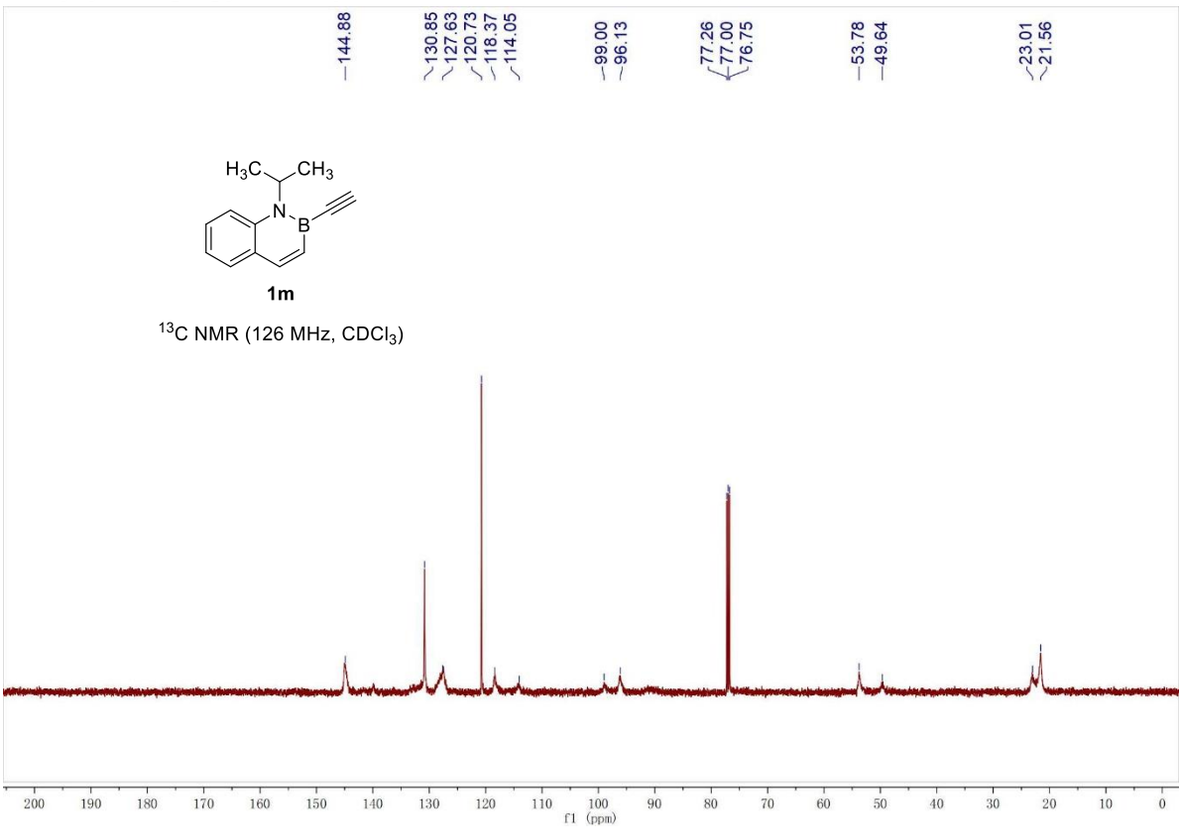
2-ethynyl-4-phenyl-1,2-dihydrobenzo[e][1,2]azaborinine (1l)



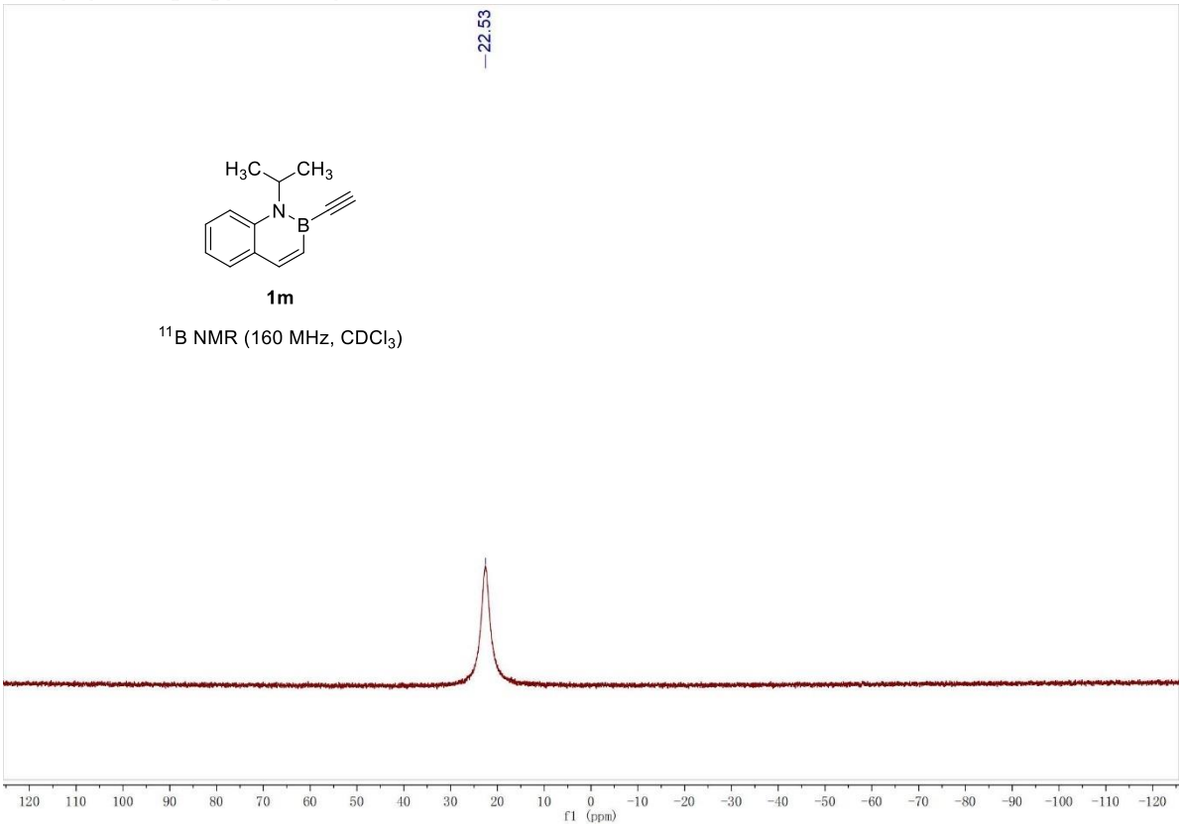
2-ethynyl-1-isopropyl-1,2-dihydrobenzo[e][1,2]azaborinine (1m)



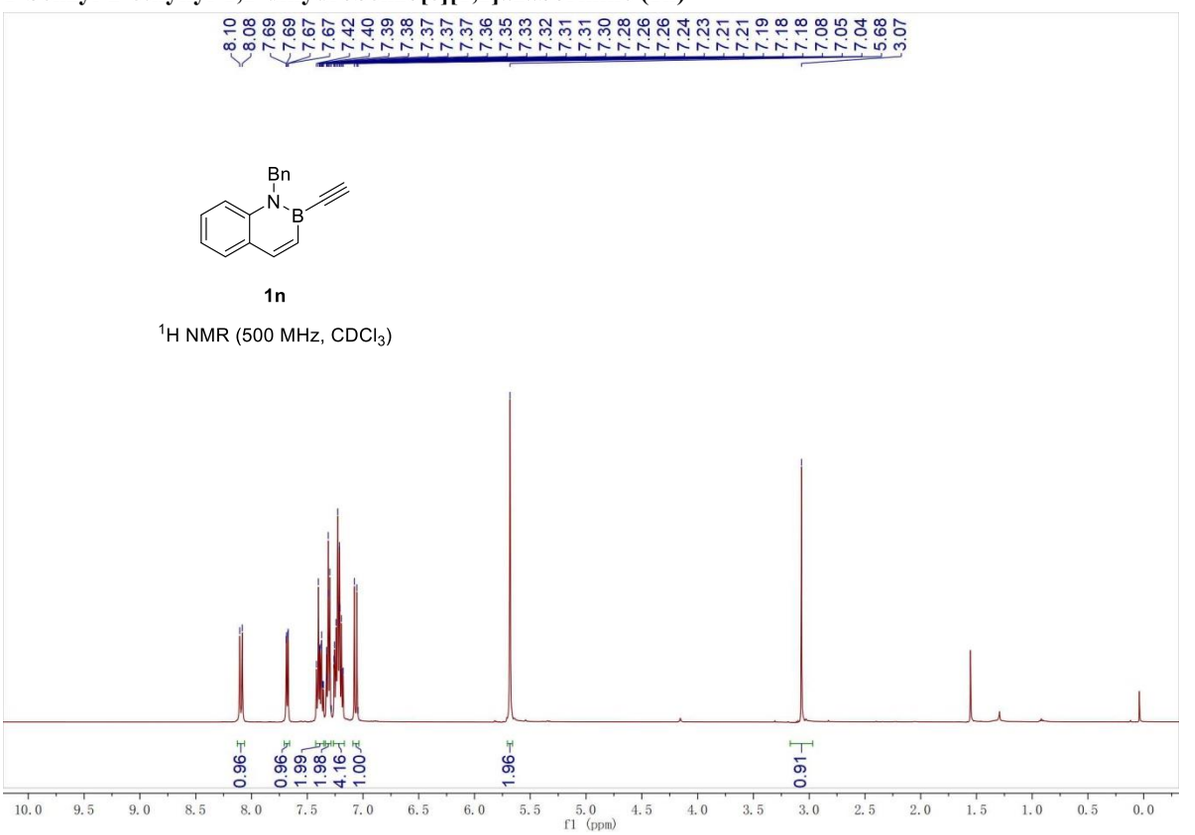
2-ethynyl-1-isopropyl-1,2-dihydrobenzo[e][1,2]azaborinine (1m)



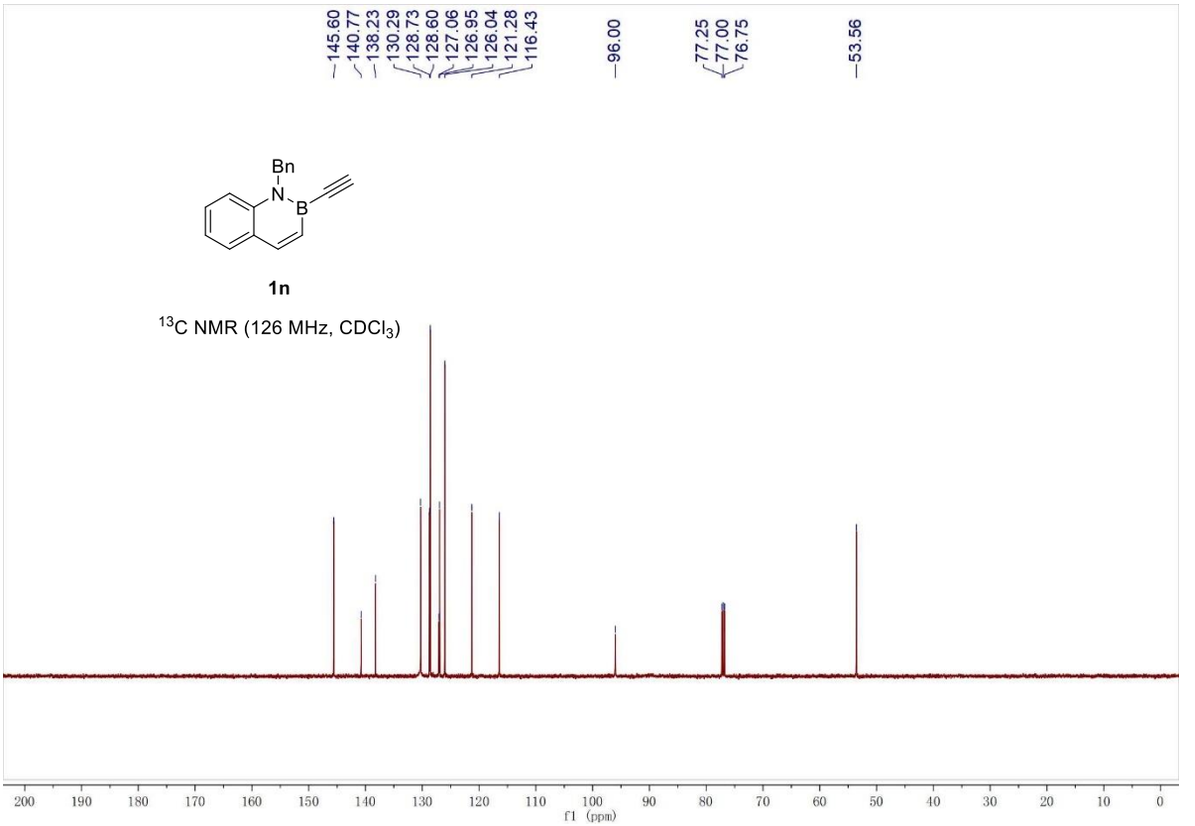
2-ethynyl-1-isopropyl-1,2-dihydrobenzo[e][1,2]azaborinine (1m)



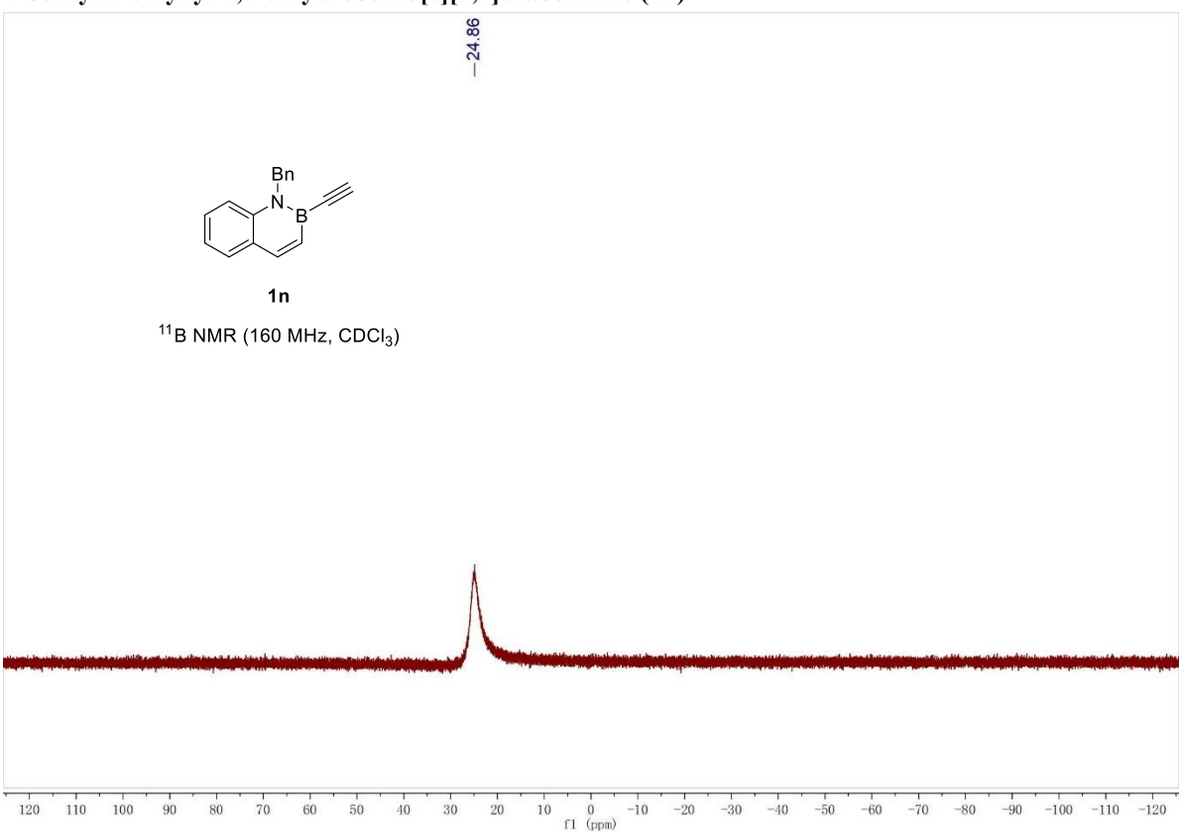
1-benzyl-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1n)



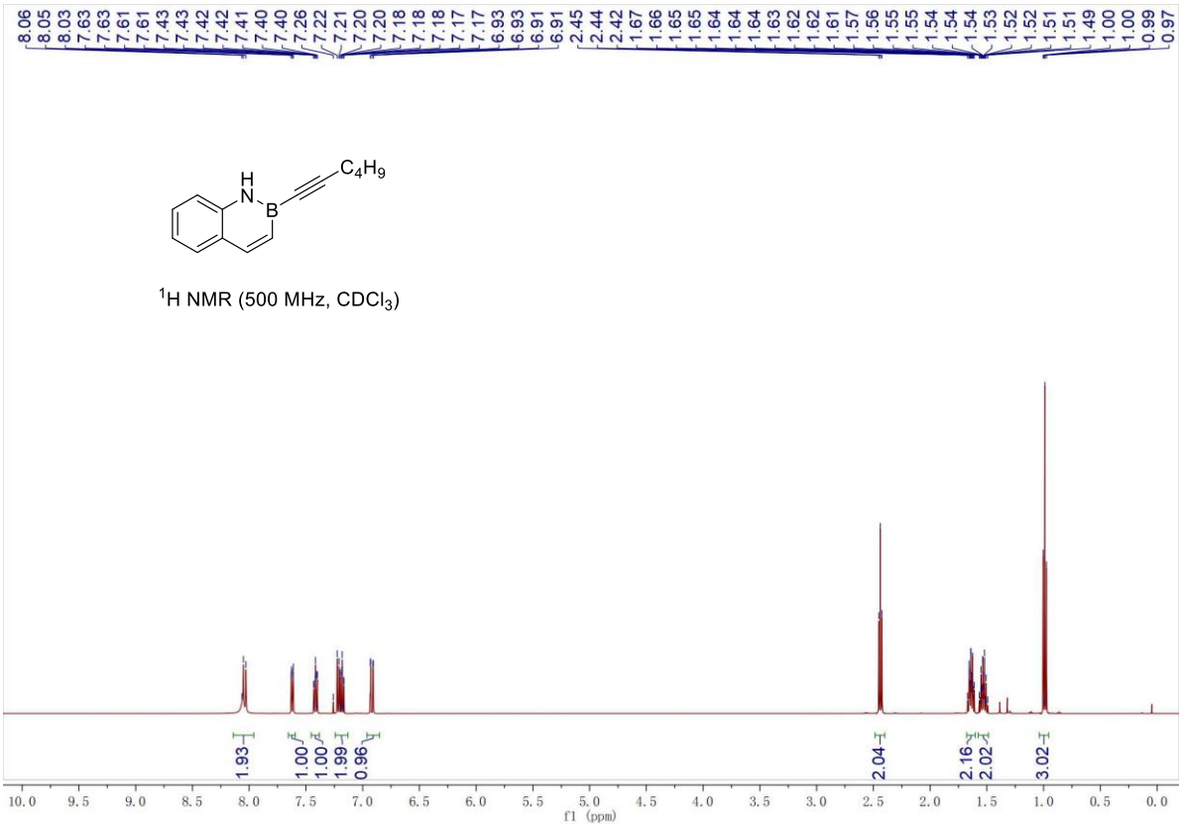
1-benzyl-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1n)



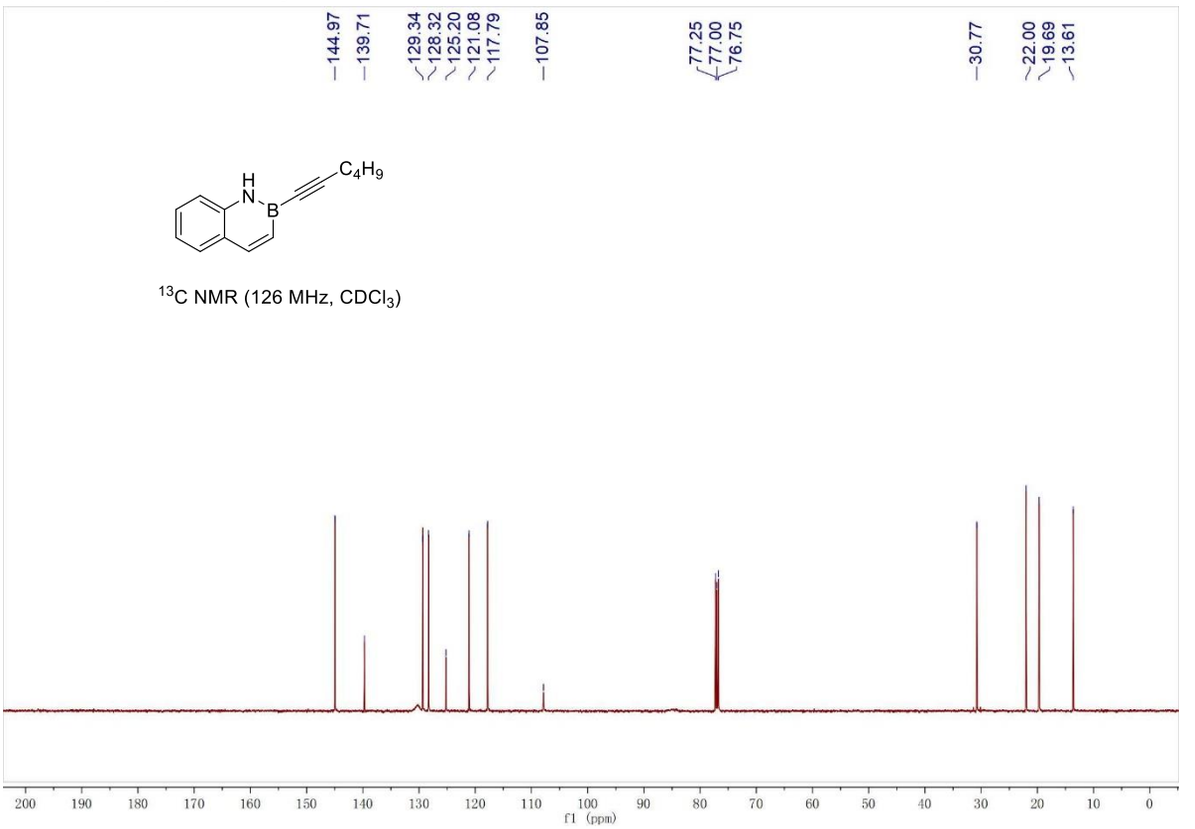
1-benzyl-2-ethynyl-1,2-dihydrobenzo[e][1,2]azaborinine (1n)



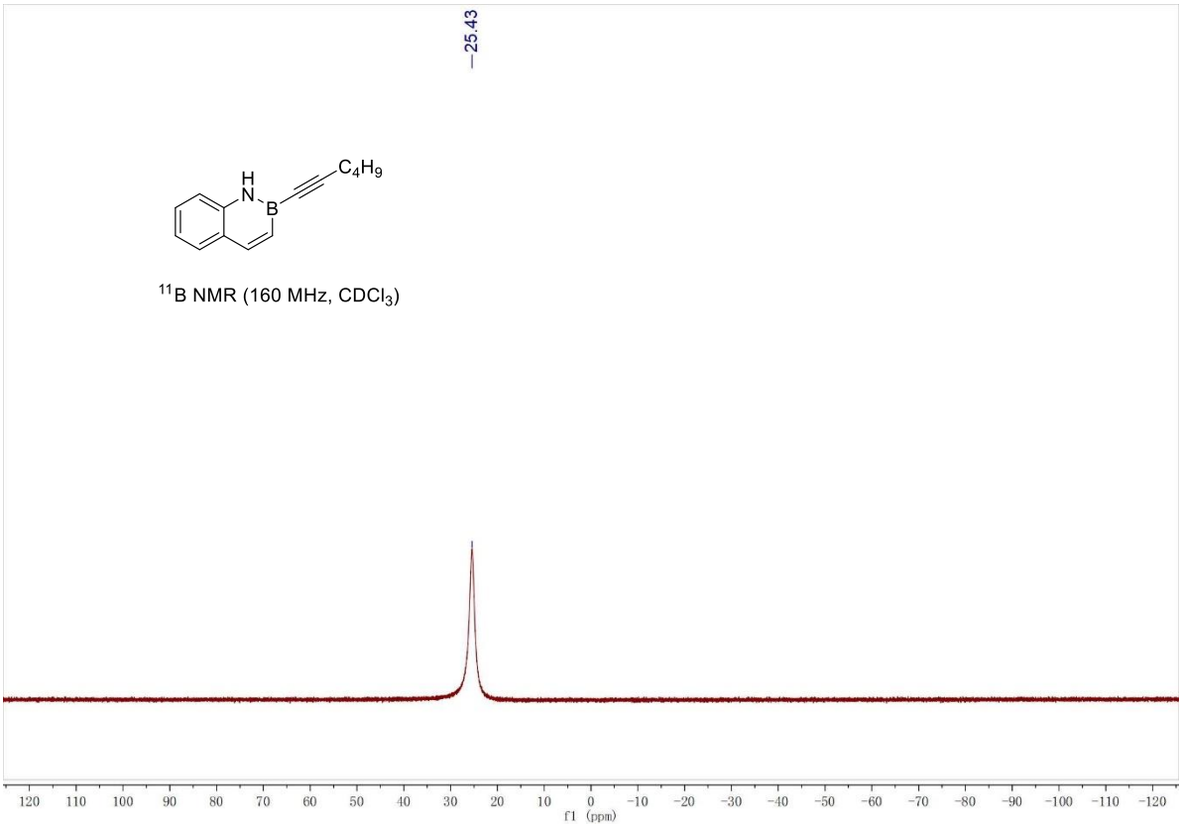
2-(hex-1-yn-1-yl)-1,2-dihydrobenzo[e][1,2]azaborinine (1o)



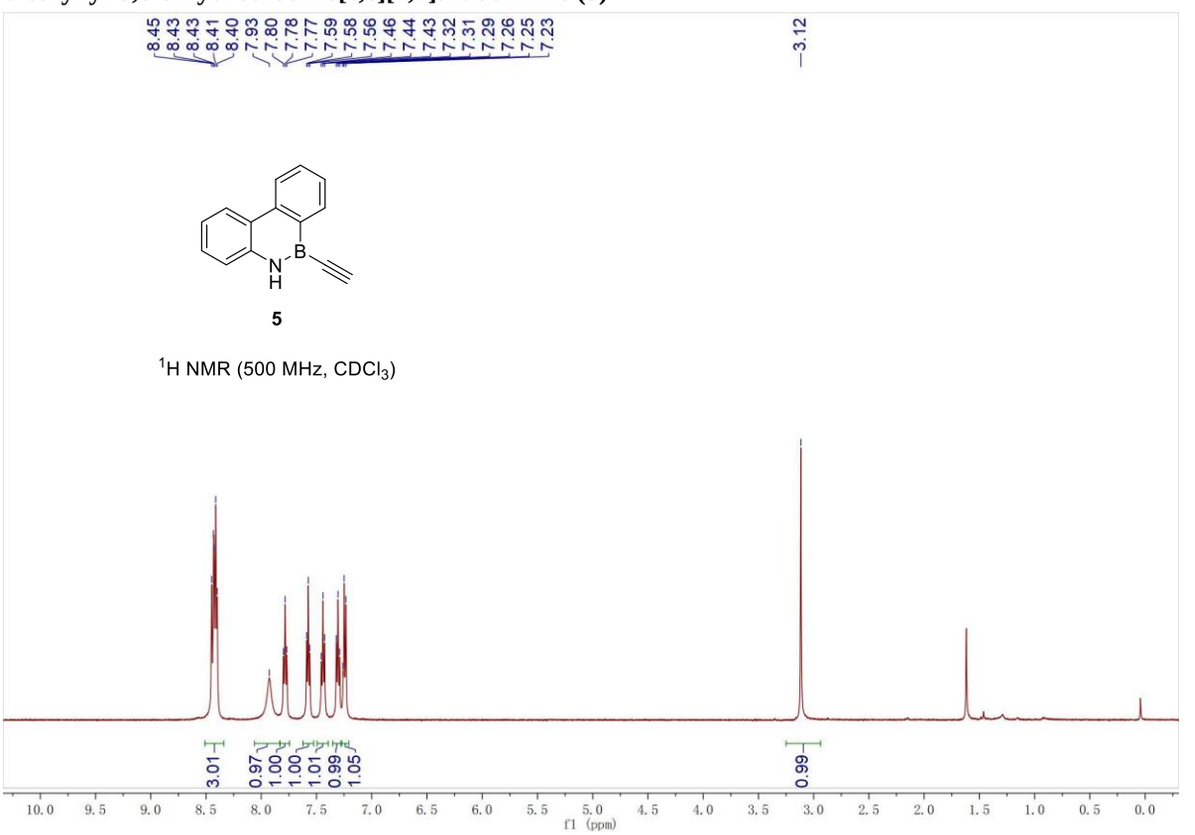
2-(hex-1-yn-1-yl)-1,2-dihydrobenzo[e][1,2]azaborinine (1o)



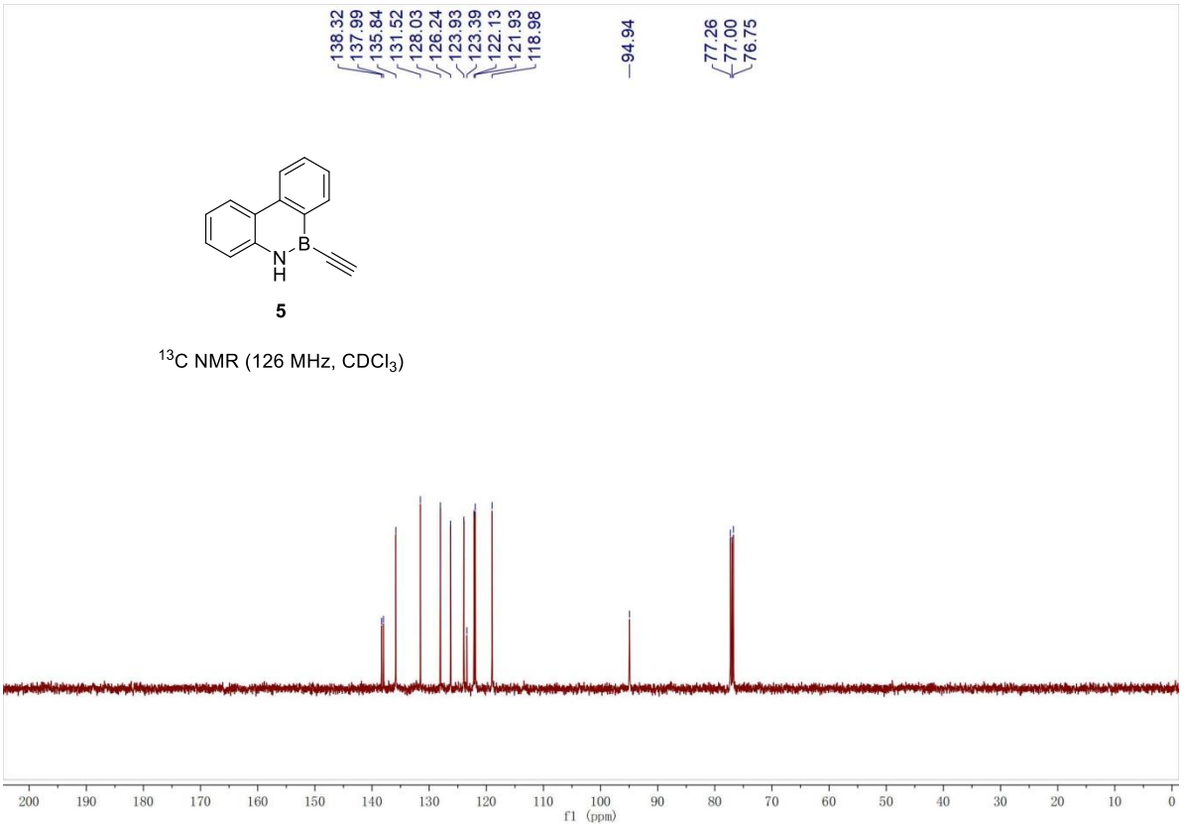
2-(hex-1-yn-1-yl)-1,2-dihydrobenzo[e][1,2]azaborinine (1o)



6-ethynyl-5,6-dihydrodibenzo[c,e][1,2]azaborinine (5)



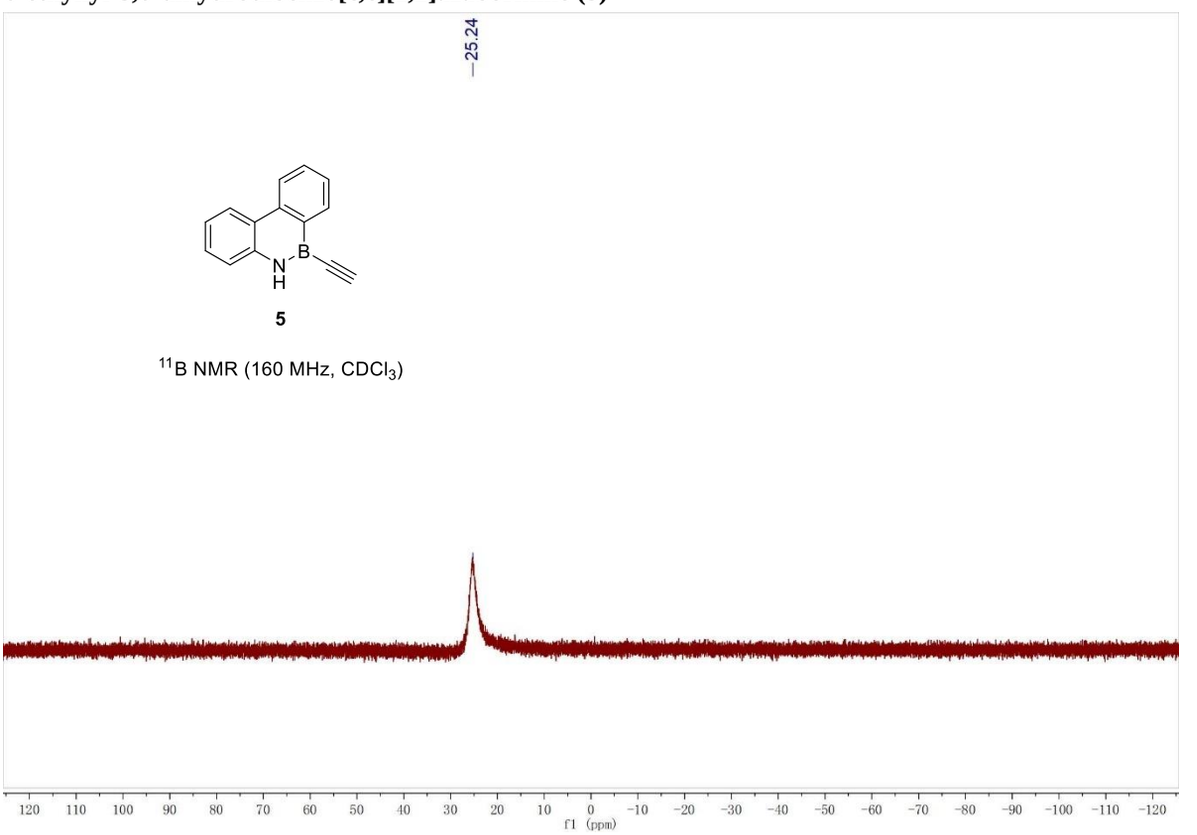
6-ethynyl-5,6-dihydrodibenzo[c,e][1,2]azaborinine (5)



5

^{13}C NMR (126 MHz, $CDCl_3$)

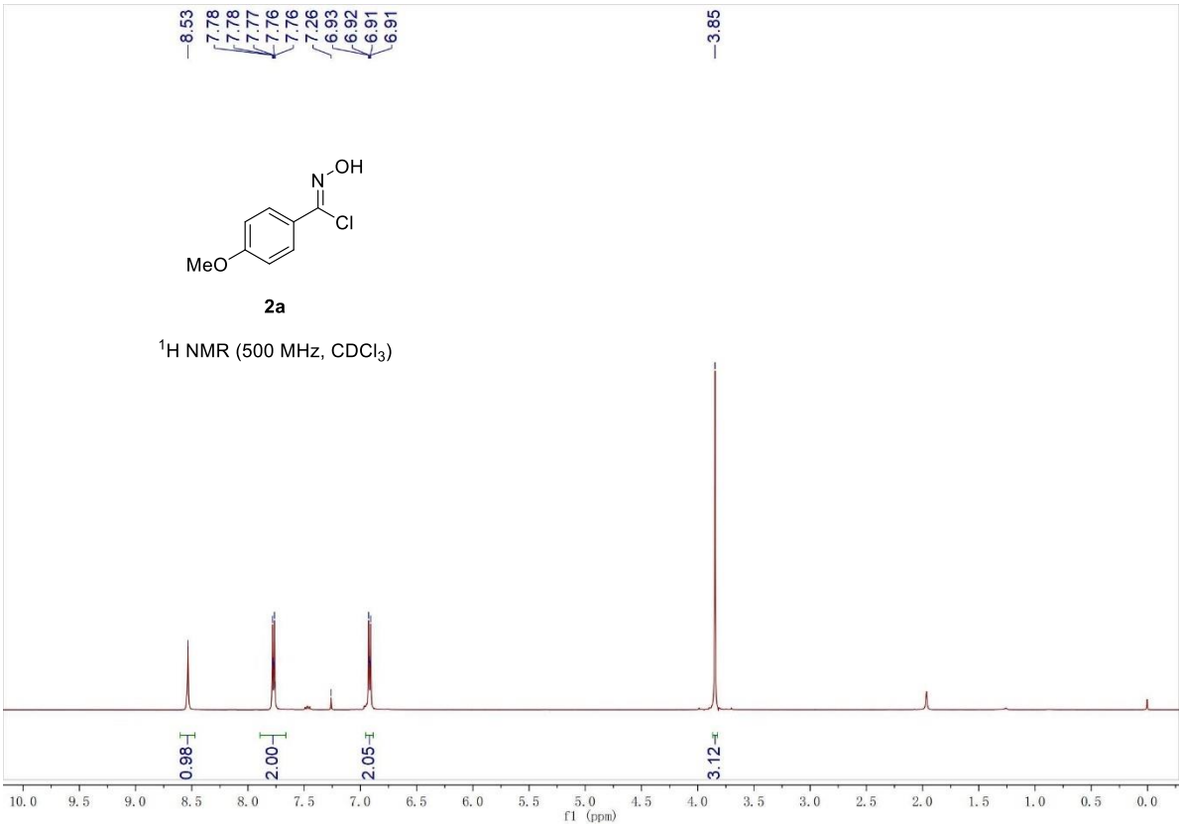
6-ethynyl-5,6-dihydrodibenzo[c,e][1,2]azaborinine (5)



5

^{11}B NMR (160 MHz, $CDCl_3$)

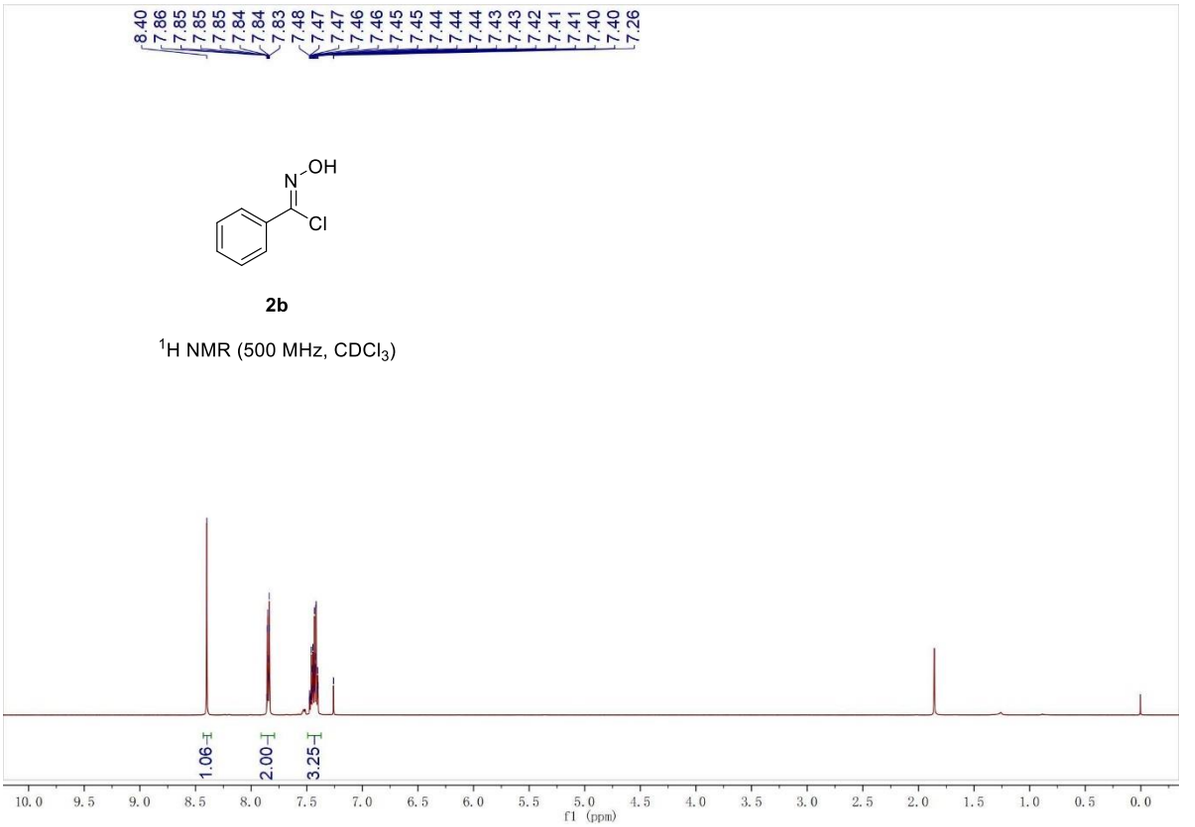
N-hydroxy-4-methoxybenzimidoyl chloride (2a)



2a

^{1}H NMR (500 MHz, $CDCl_3$)

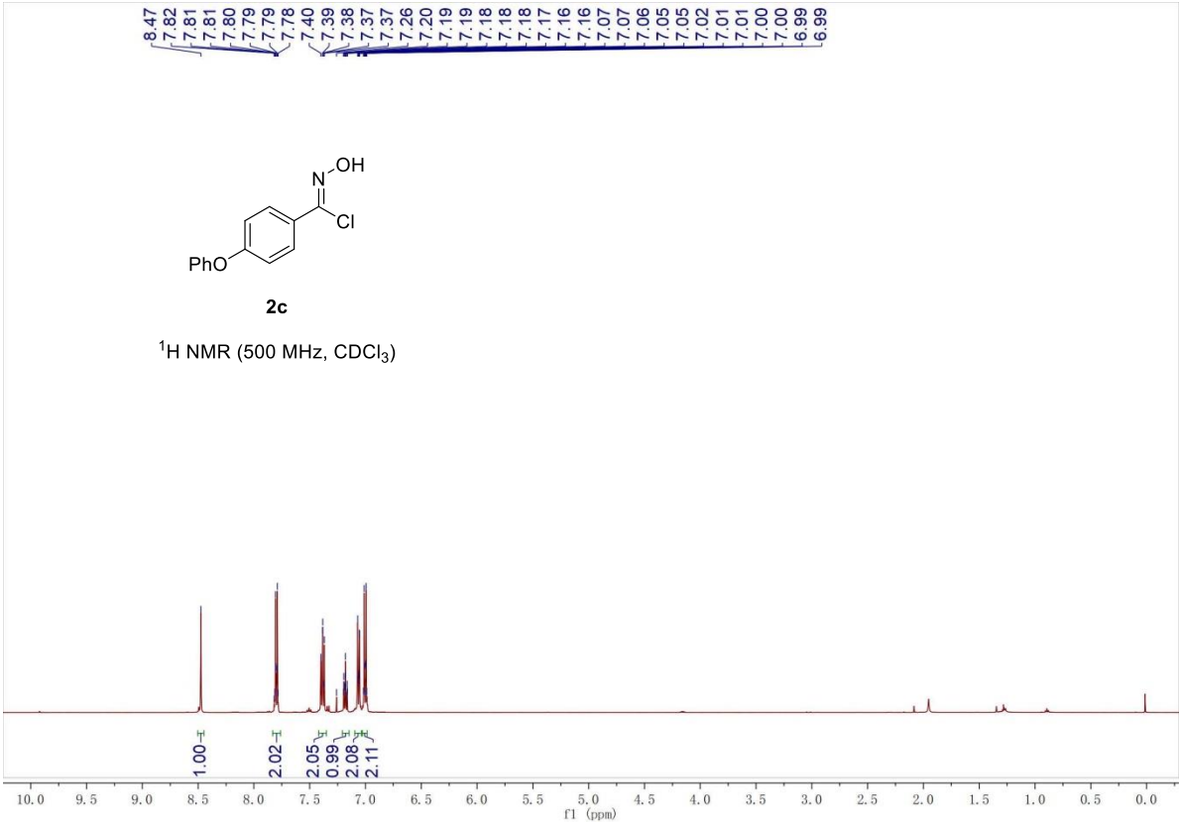
N-hydroxybenzimidoyl chloride (2b)



2b

^{1}H NMR (500 MHz, $CDCl_3$)

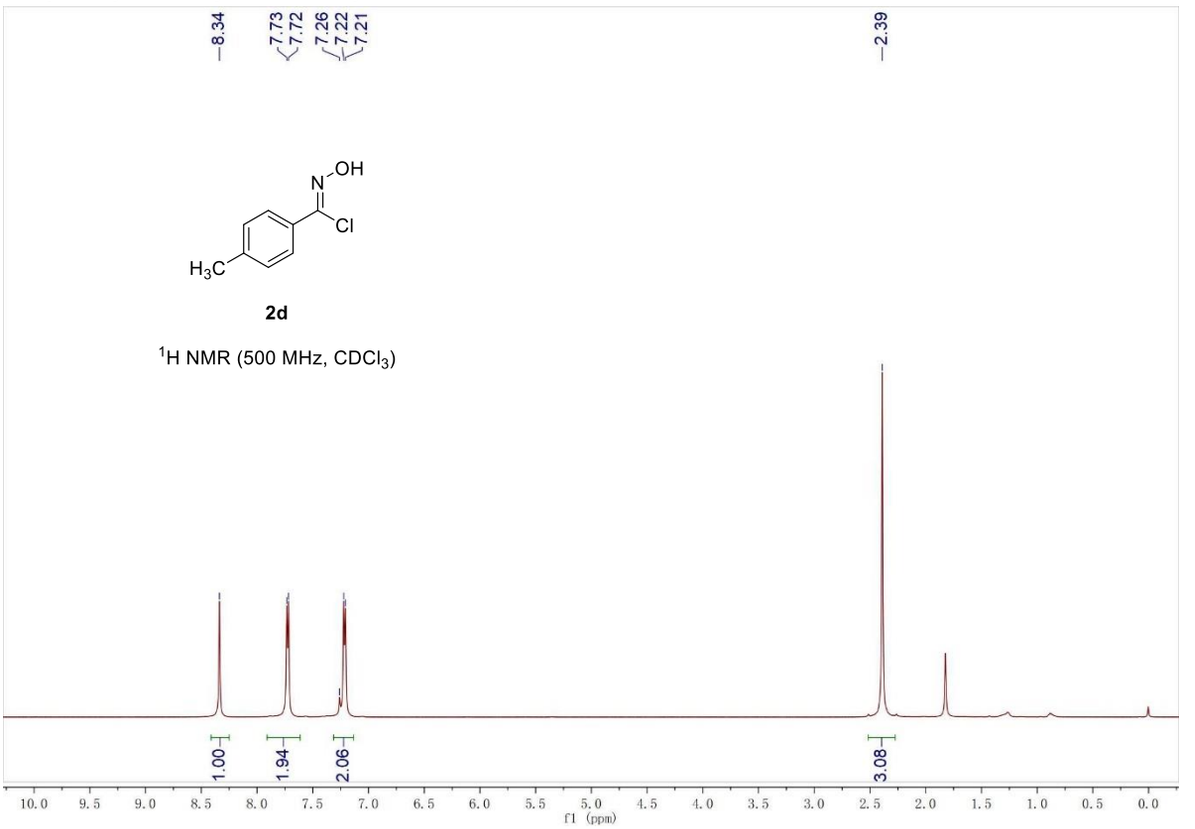
N-hydroxy-4-phenoxybenzimidoyl chloride (2c)



2c

^{1}H NMR (500 MHz, $CDCl_3$)

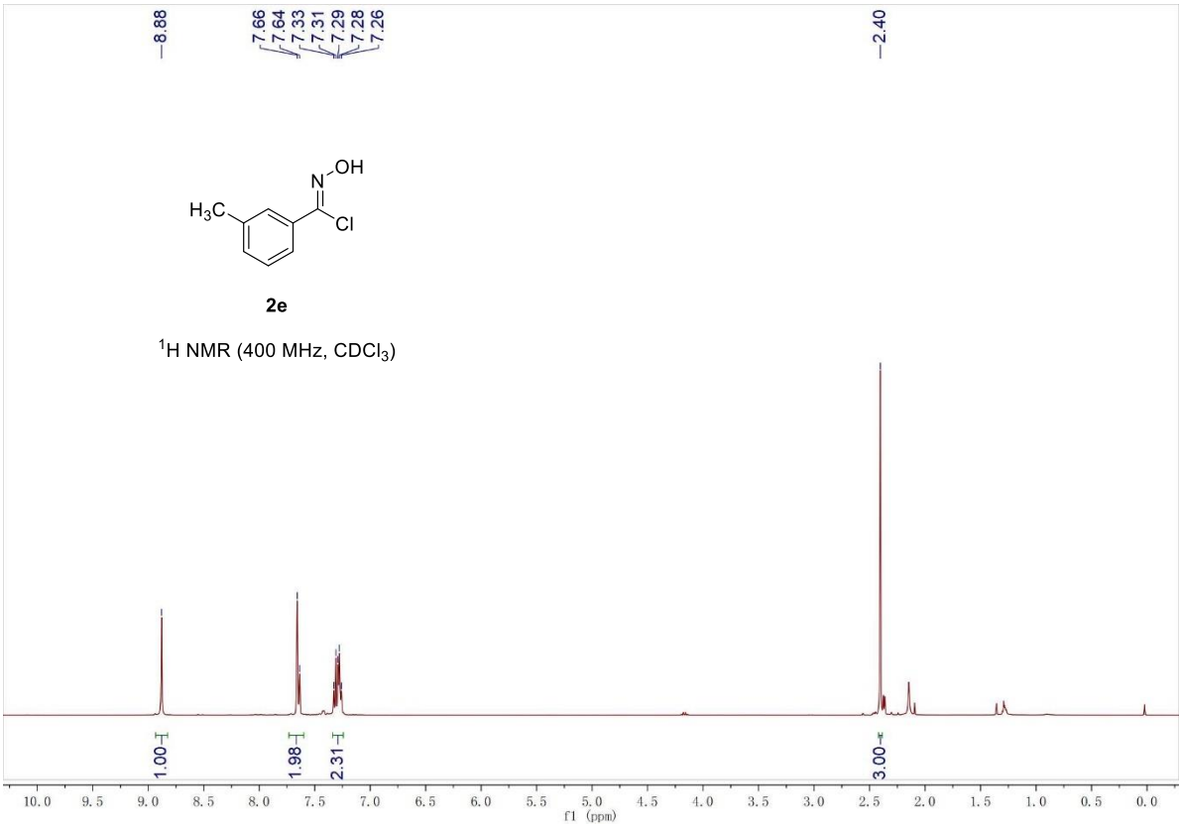
N-hydroxy-4-methylbenzimidoyl chloride (2d)



2d

^{1}H NMR (500 MHz, $CDCl_3$)

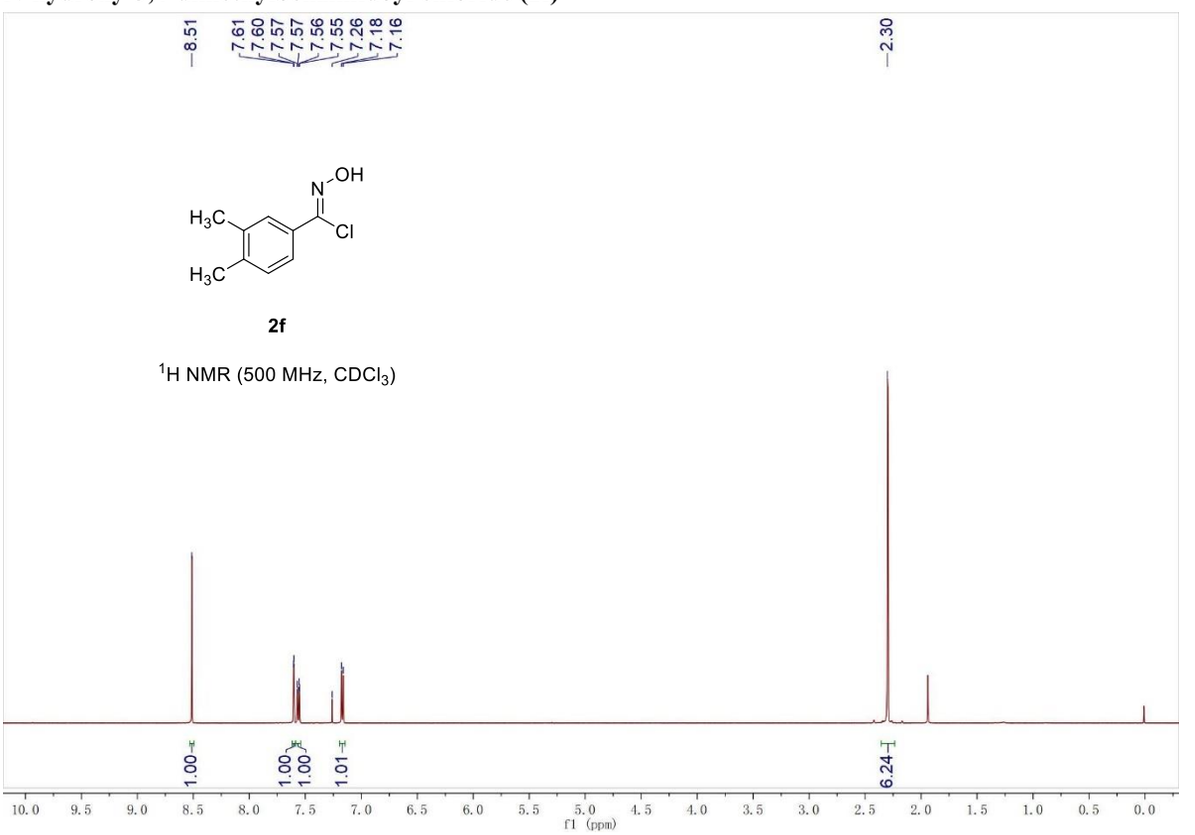
N-hydroxy-3-methylbenzimidoyl chloride (2e)



2e

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

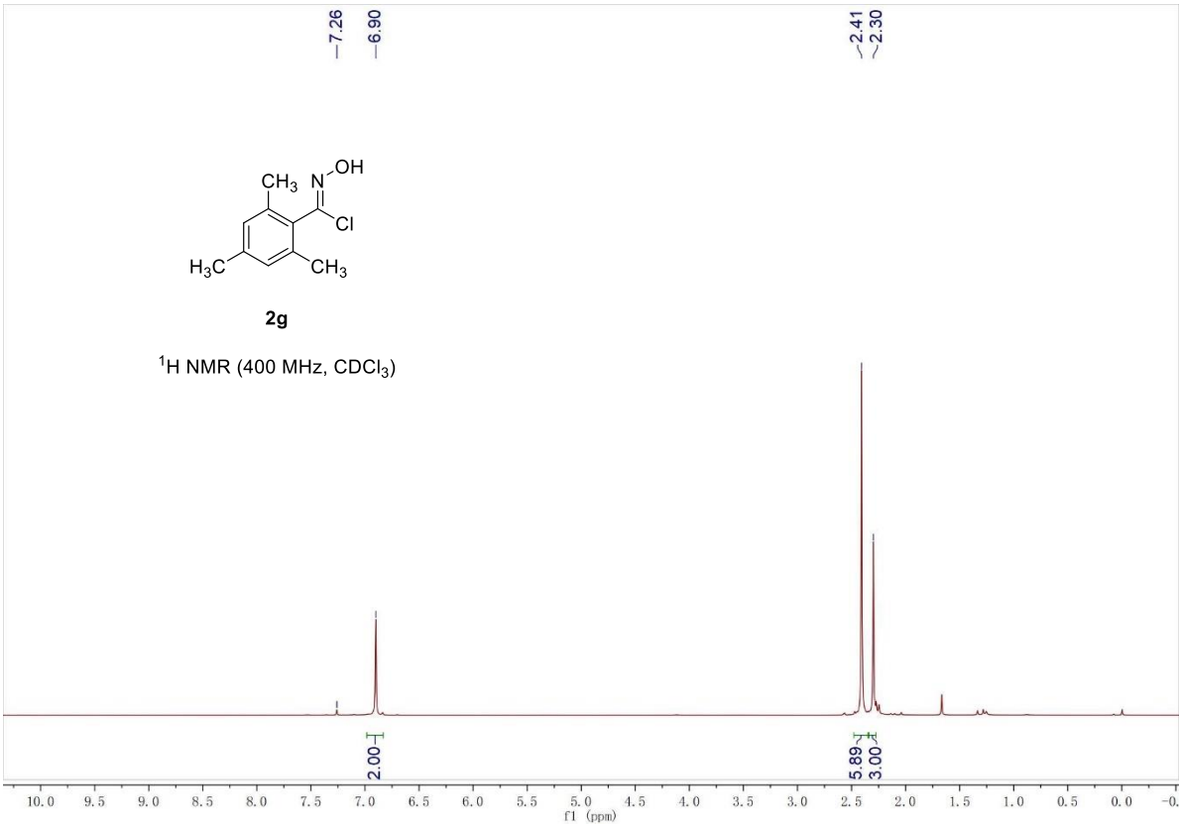
N-hydroxy-3,4-dimethylbenzimidoyl chloride (2f)



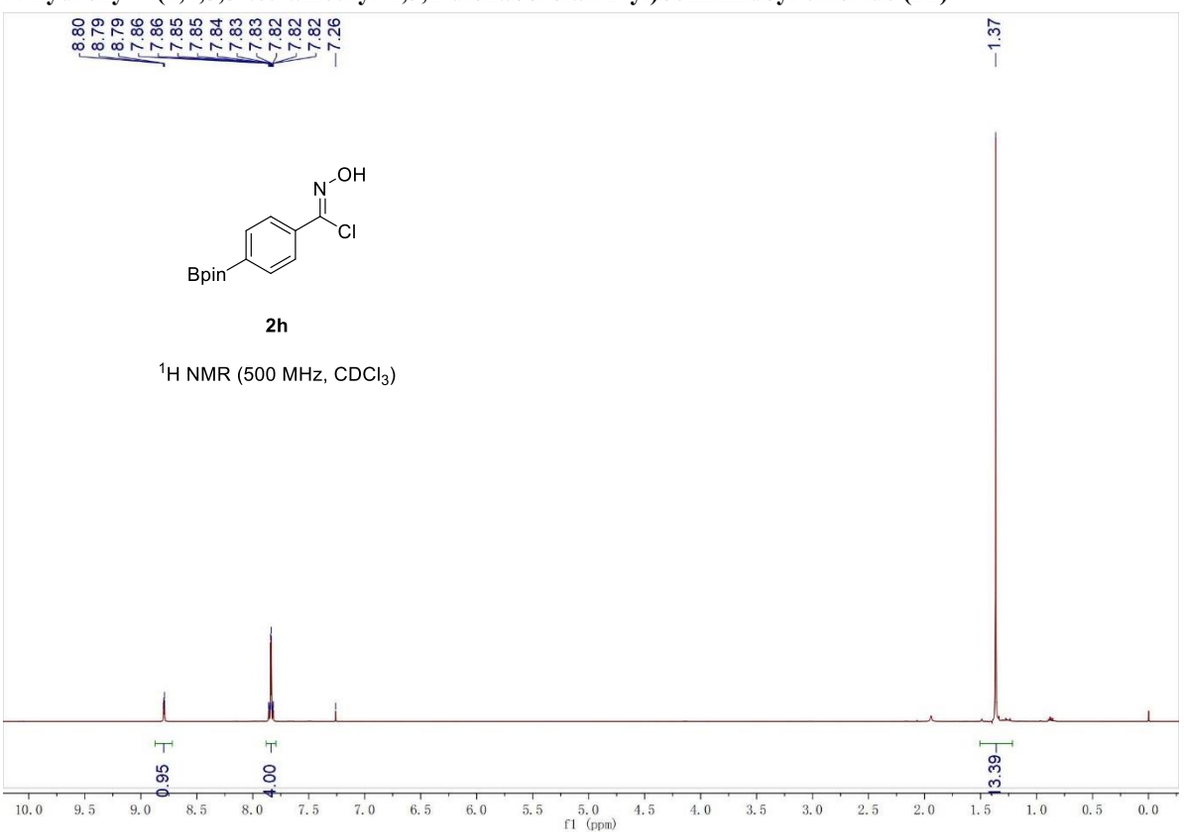
2f

^{1}H NMR (500 MHz, $CDCl_3$)

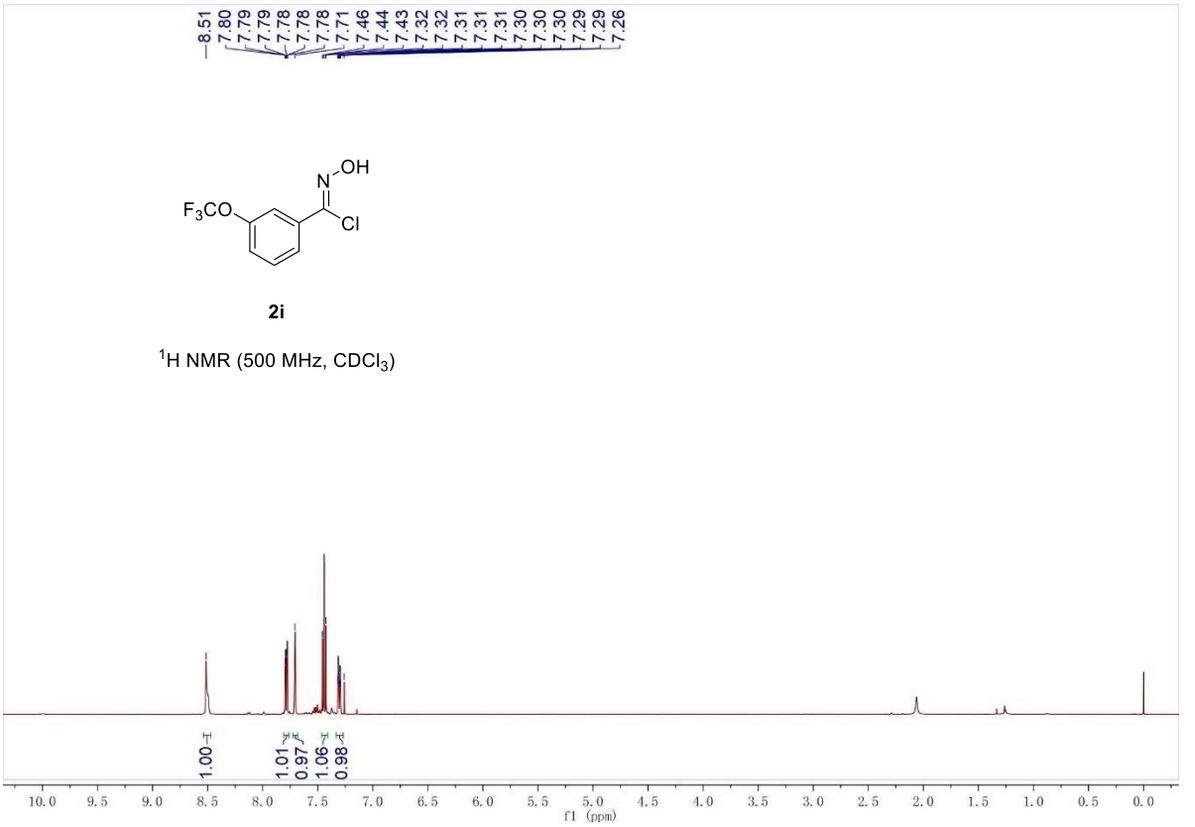
N-hydroxy-2,4,6-trimethylbenzimidoyl chloride (2g)



N-hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzimidoyl chloride (2h)



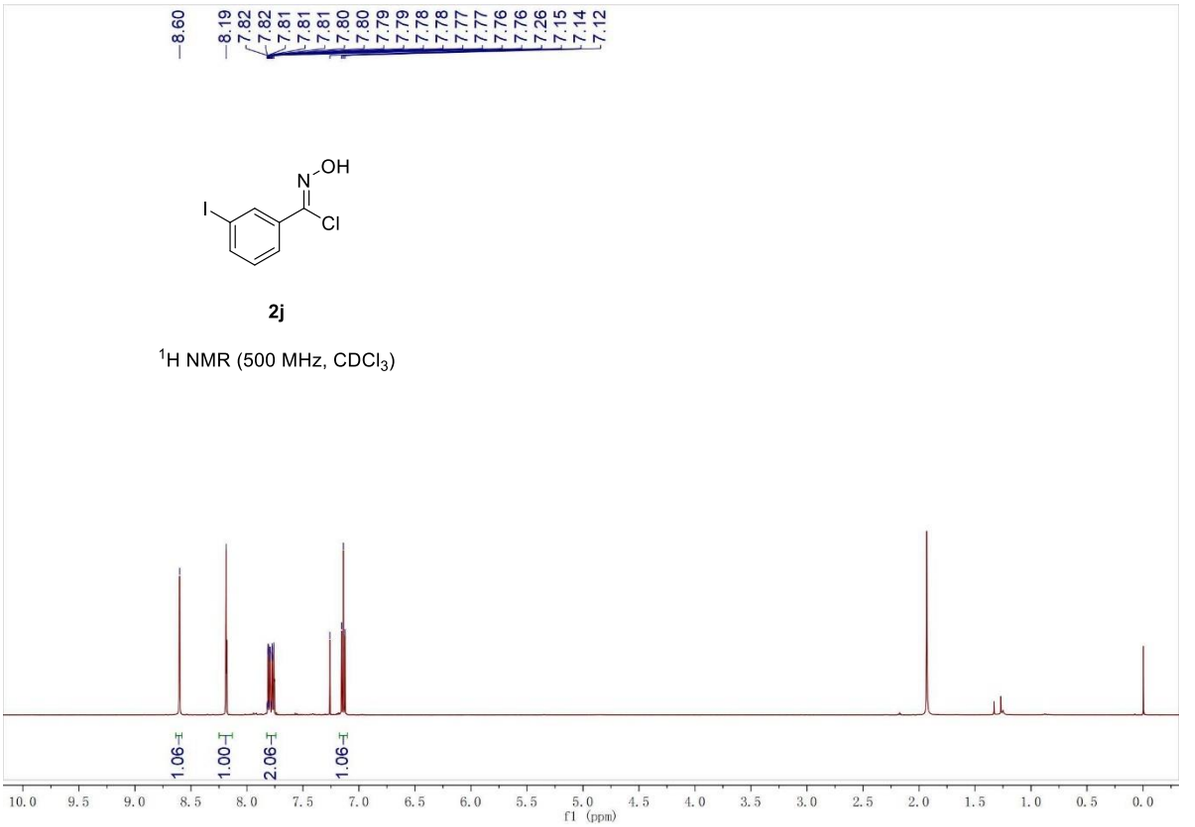
N-hydroxy-3-(trifluoromethoxy)benzimidoyl chloride (2i)



2i

^{1}H NMR (500 MHz, $CDCl_3$)

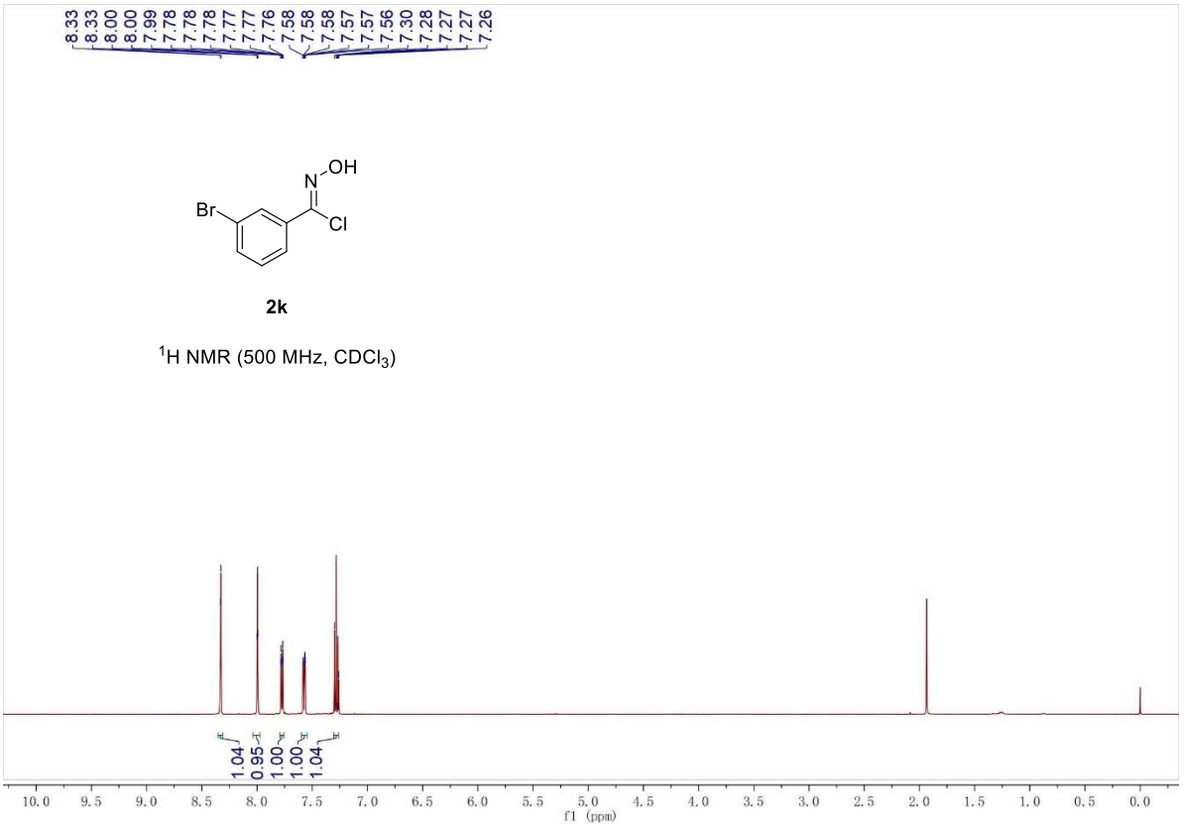
N-hydroxy-3-iodobenzimidoyl chloride (2j)



2j

^{1}H NMR (500 MHz, $CDCl_3$)

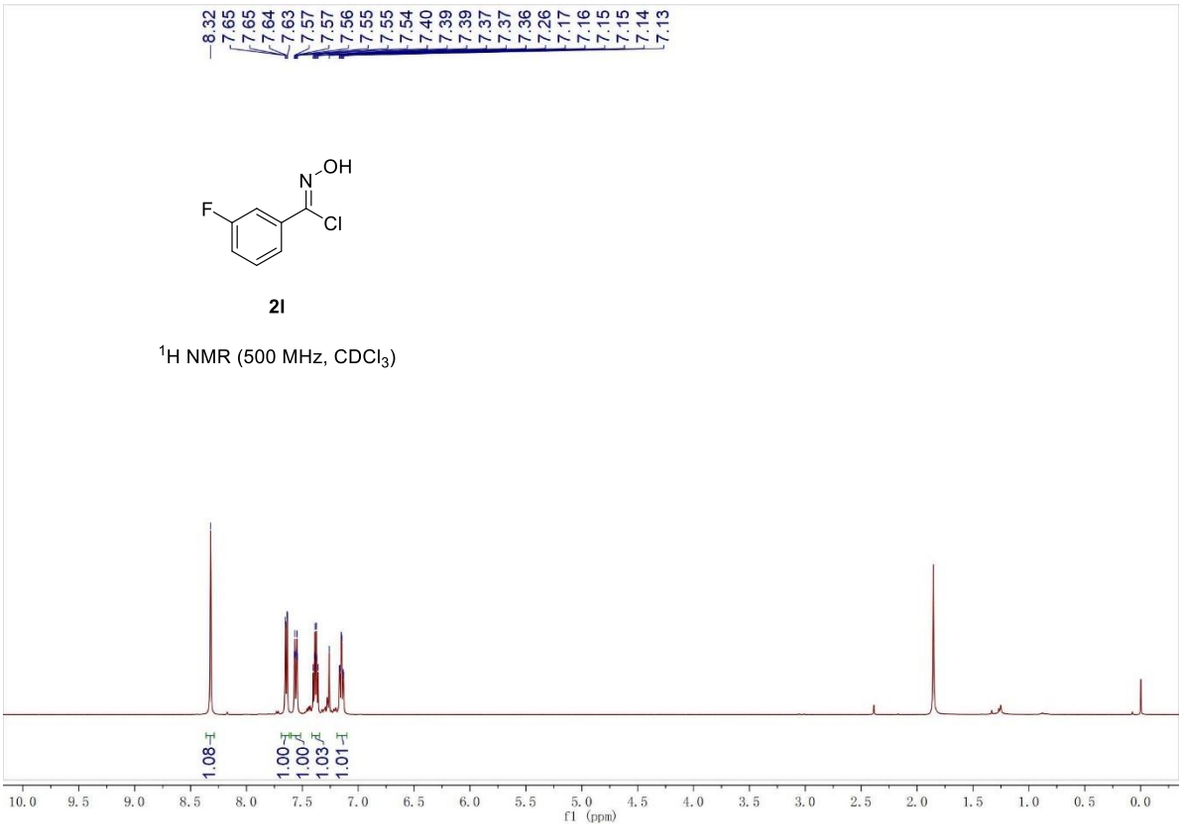
3-bromo-N-hydroxybenzimidoyl chloride (2k)



2k

^{1}H NMR (500 MHz, $CDCl_3$)

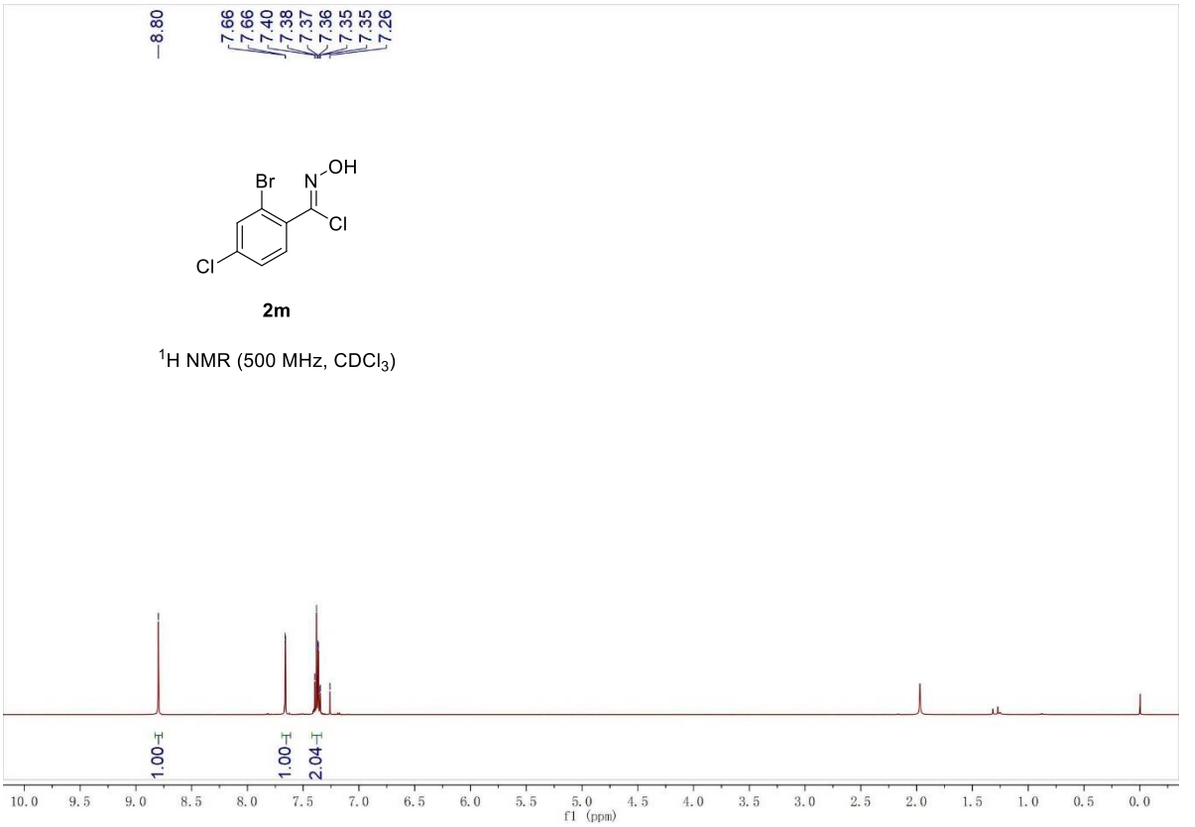
3-fluoro-N-hydroxybenzimidoyl chloride (2l)



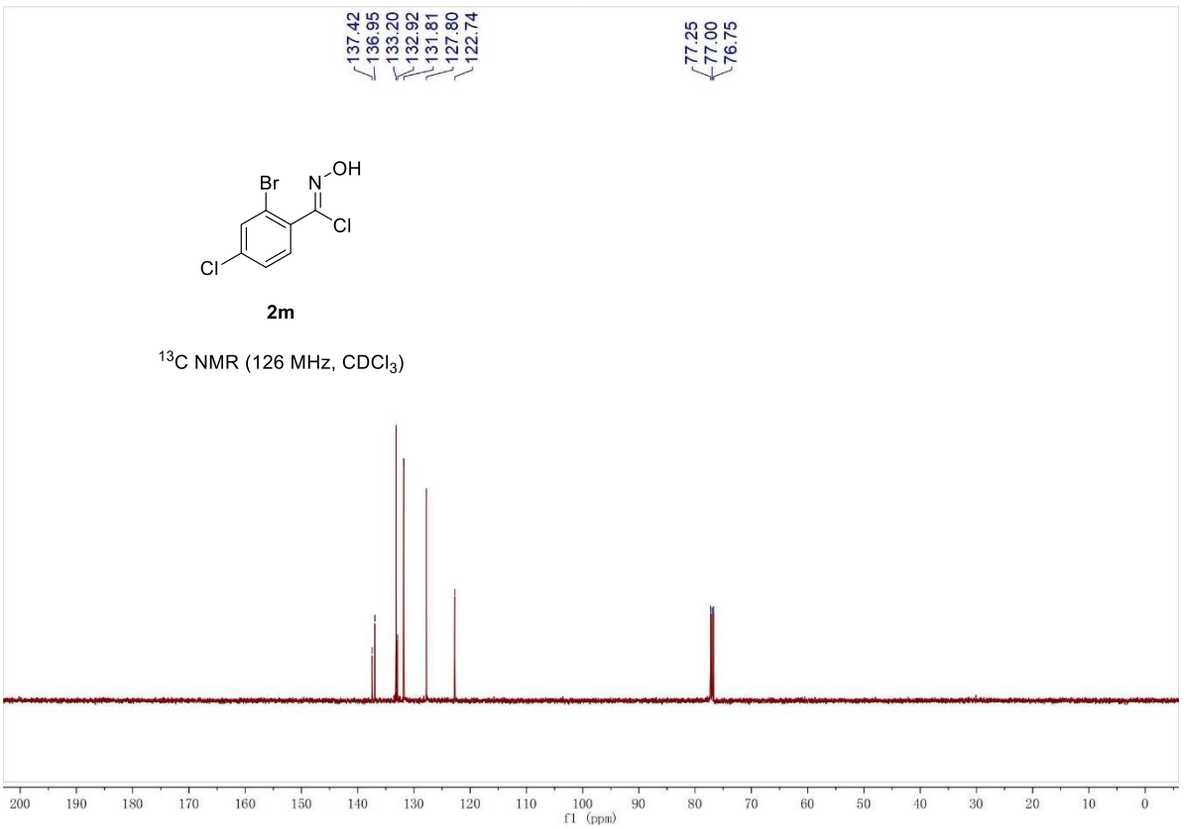
2l

^{1}H NMR (500 MHz, $CDCl_3$)

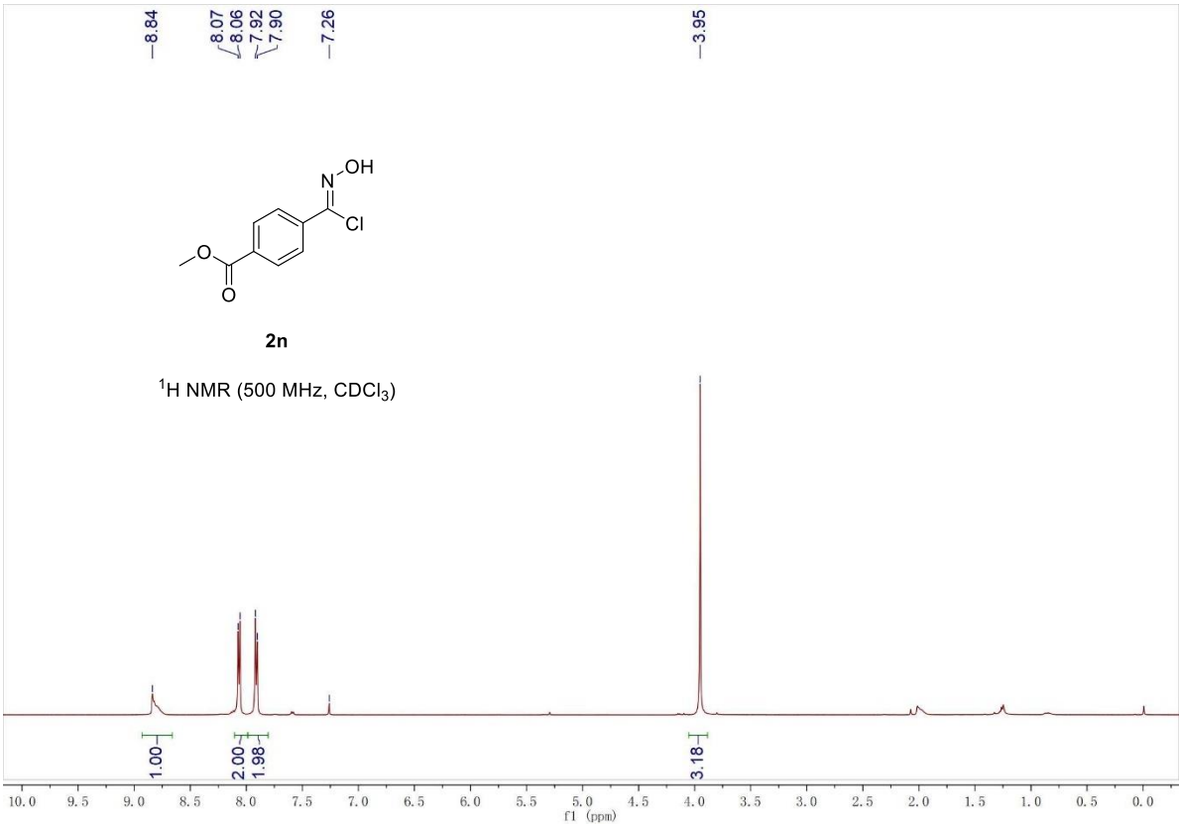
2-bromo-4-chloro-N-hydroxybenzimidoyl chloride (2m)



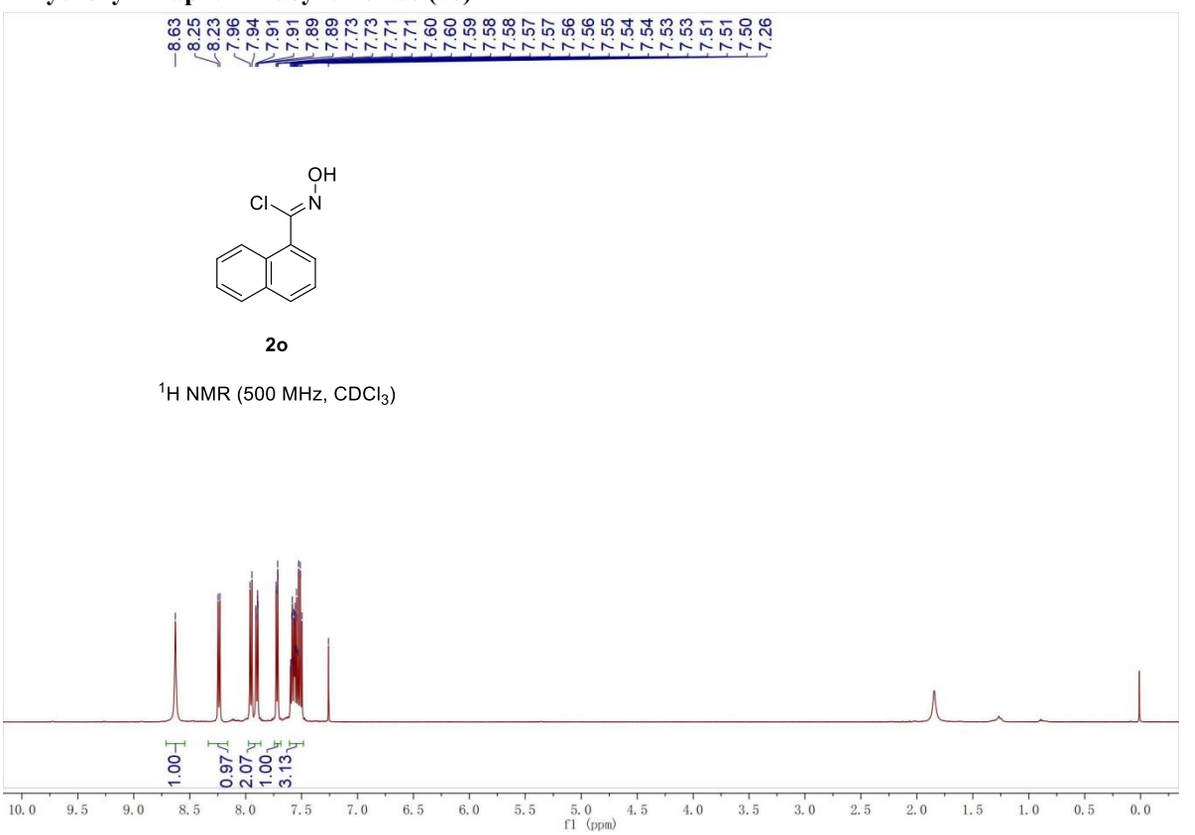
2-bromo-4-chloro-N-hydroxybenzimidoyl chloride (2m)



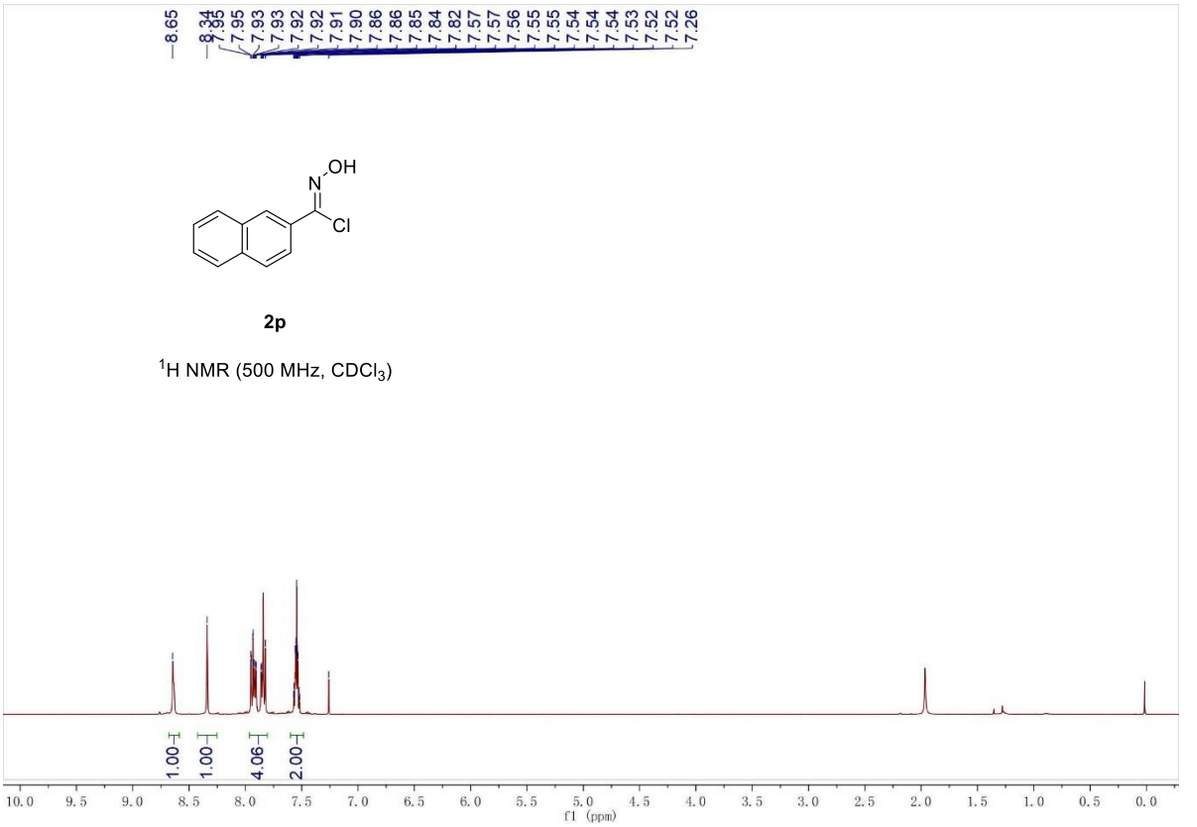
methyl 4-(chloro(hydroxyimino)methyl)benzoate (2n)



N-hydroxy-1-naphthimidoyl chloride (2o)



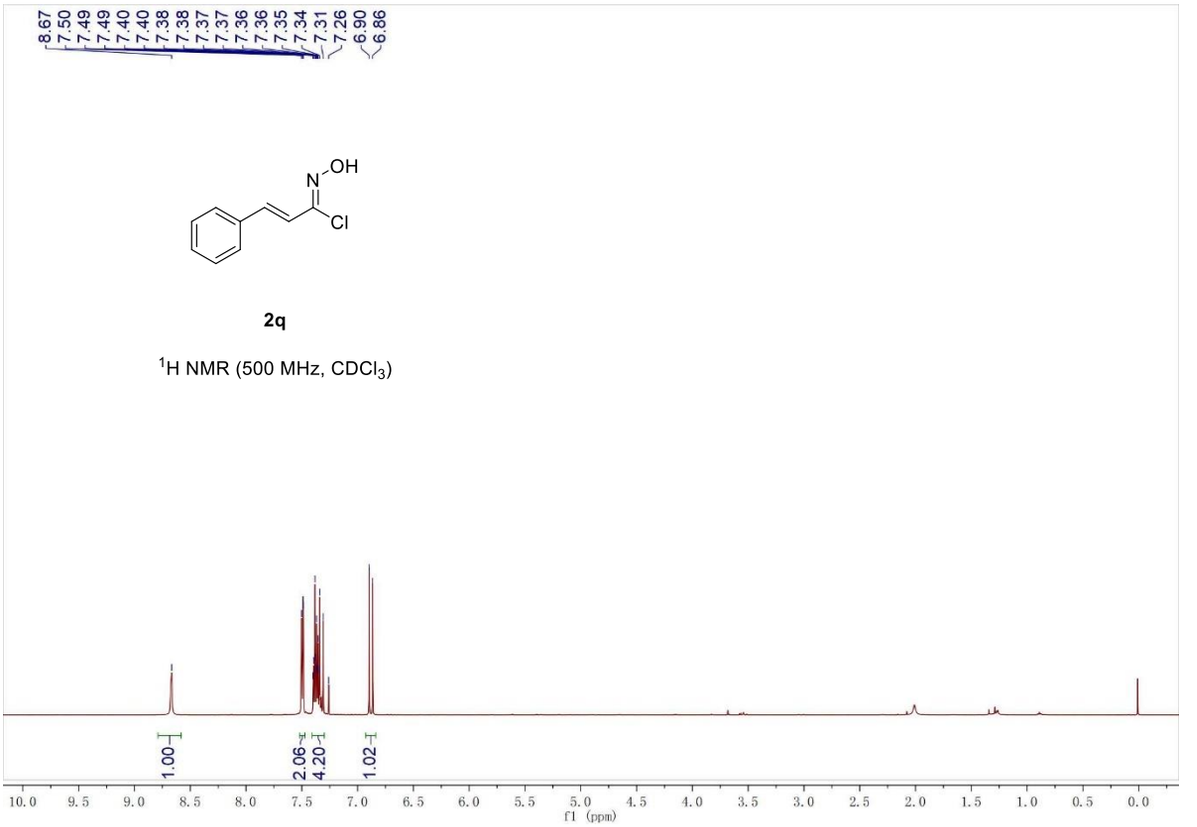
N-hydroxy-2-naphthimidoyl chloride (2p)



2p

^{1}H NMR (500 MHz, $CDCl_3$)

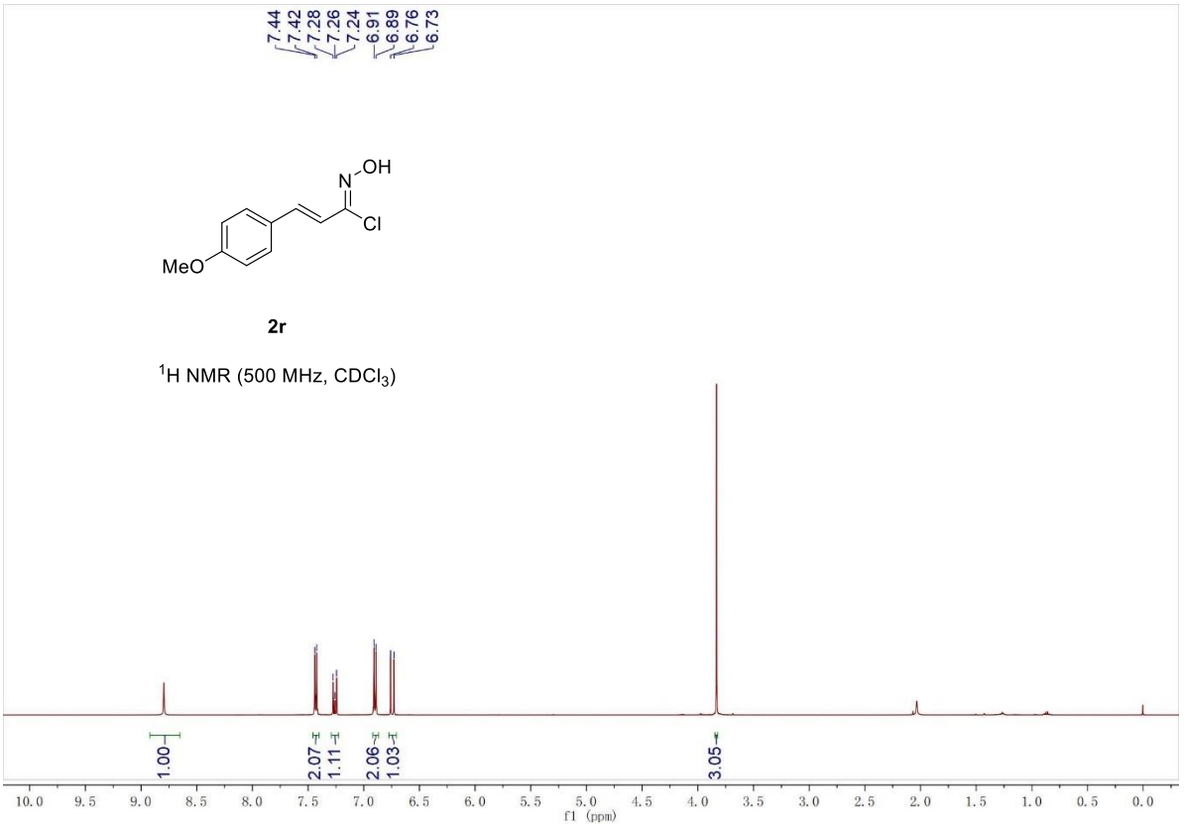
N-hydroxycinnamimidoyl chloride (2q)



2q

^{1}H NMR (500 MHz, $CDCl_3$)

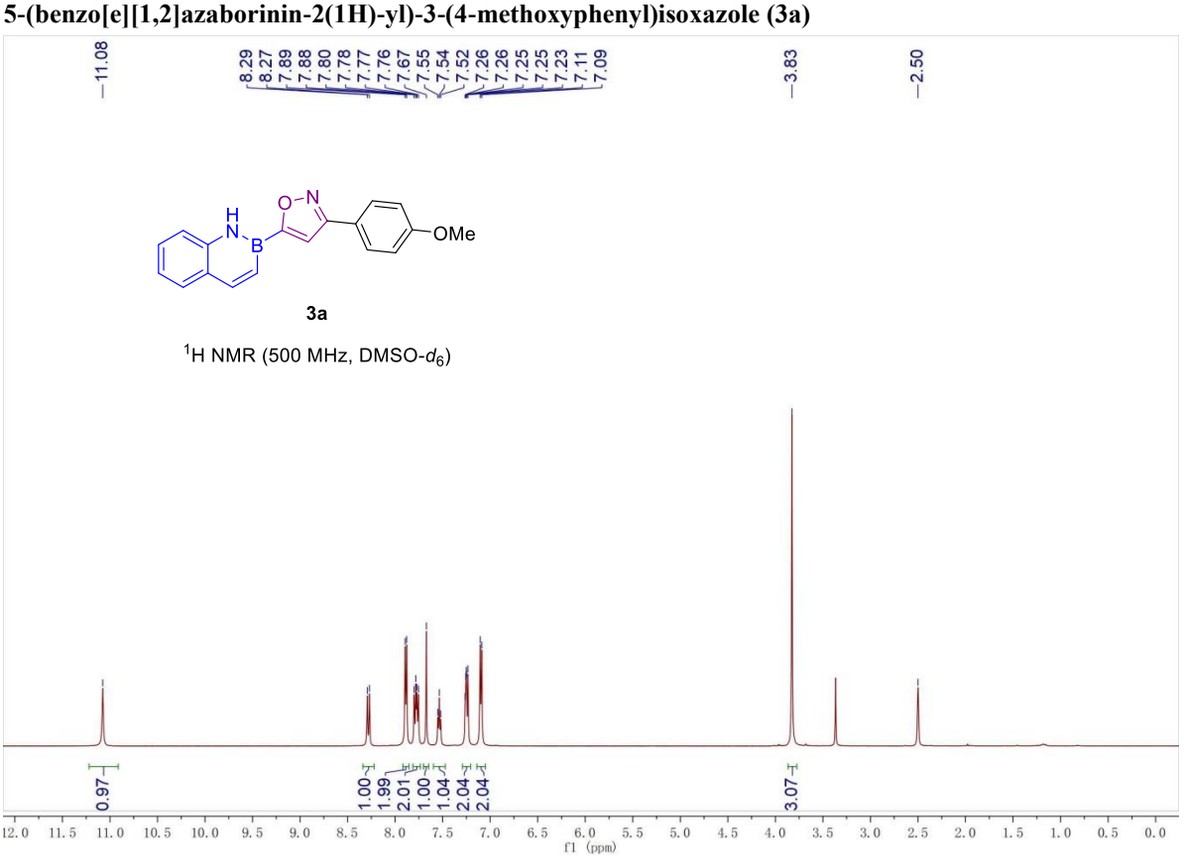
N-hydroxy-3-(4-methoxyphenyl)acrylimidoyl chloride (2r)



2r

^{1}H NMR (500 MHz, $CDCl_3$)

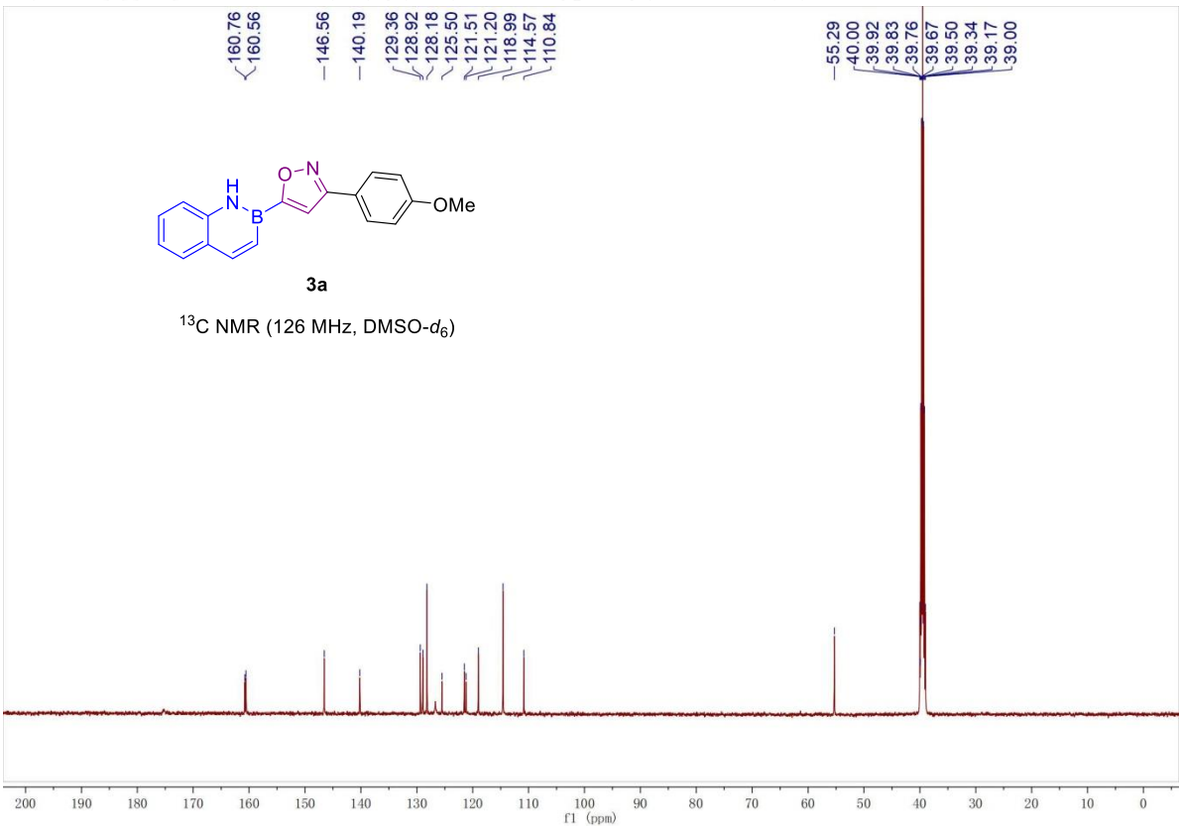
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3a)



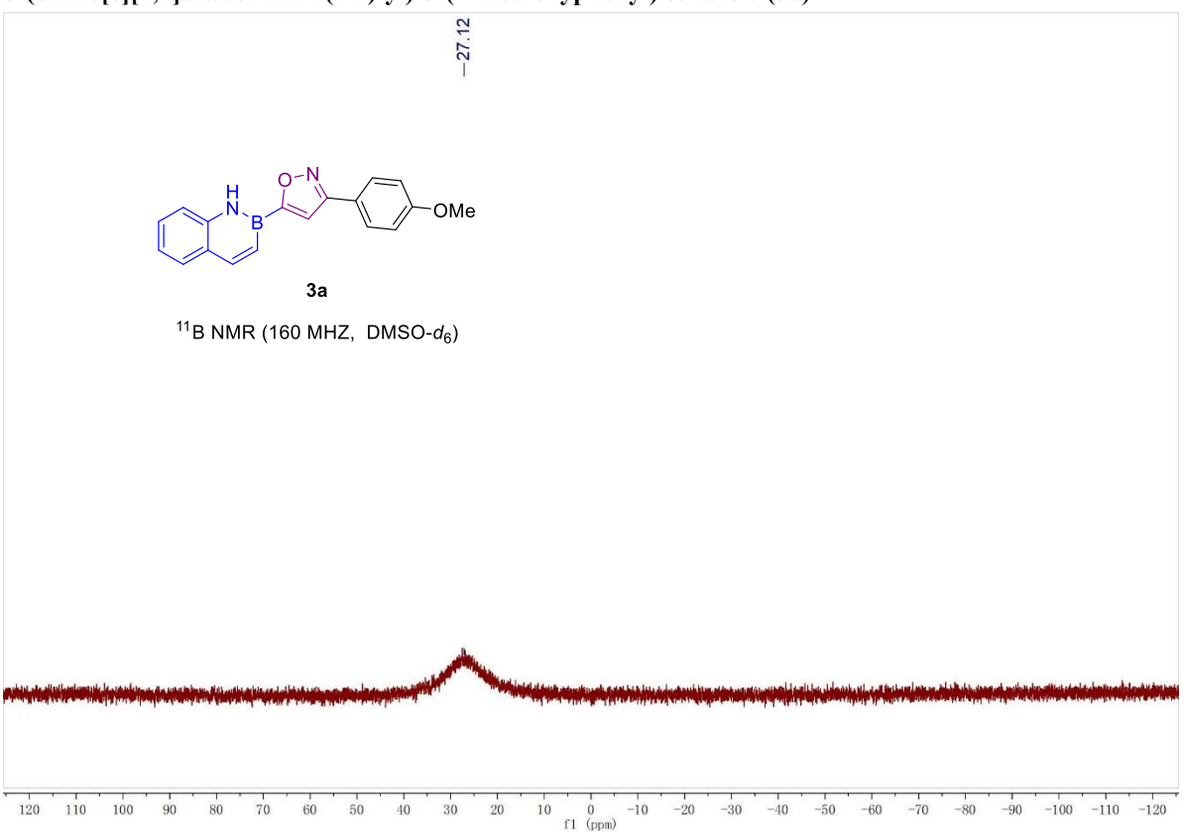
3a

^{1}H NMR (500 MHz, DMSO-d_6)

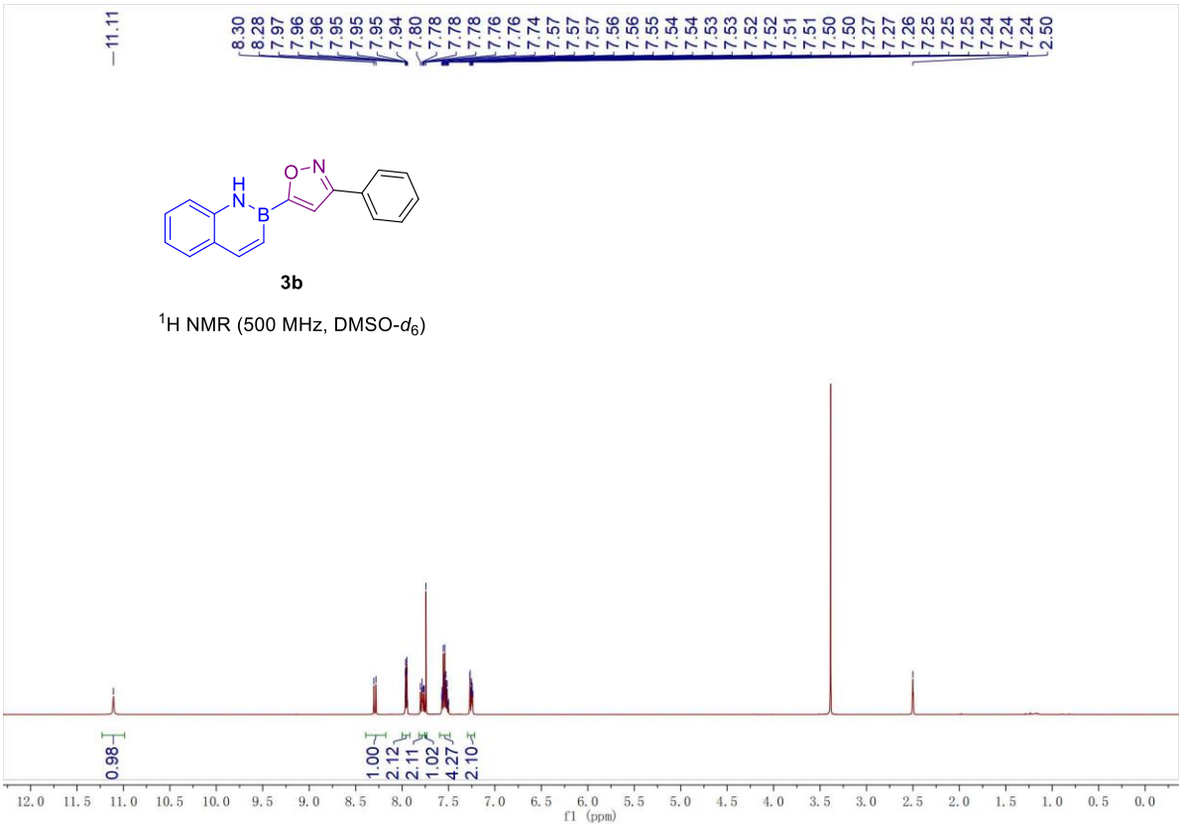
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3a)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3a)



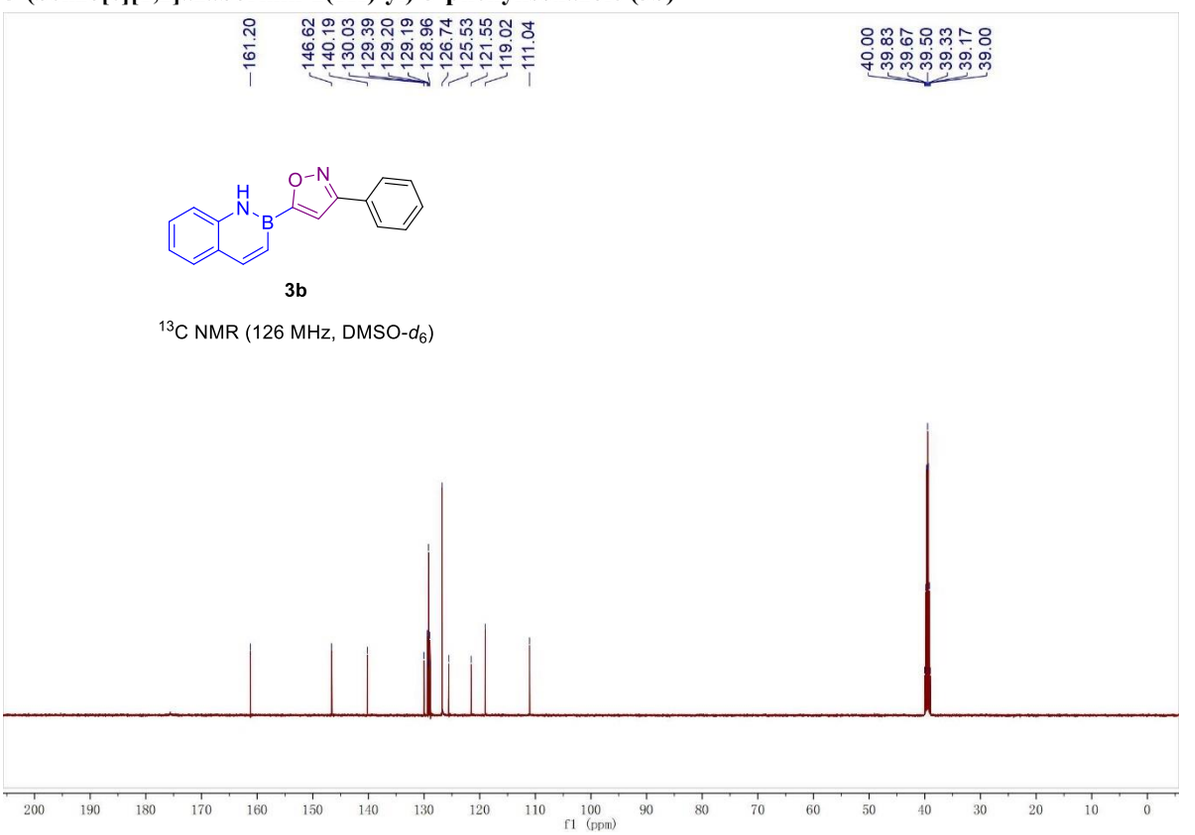
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenylisoxazole (3b)



3b

^{1}H NMR (500 MHz, DMSO-d_6)

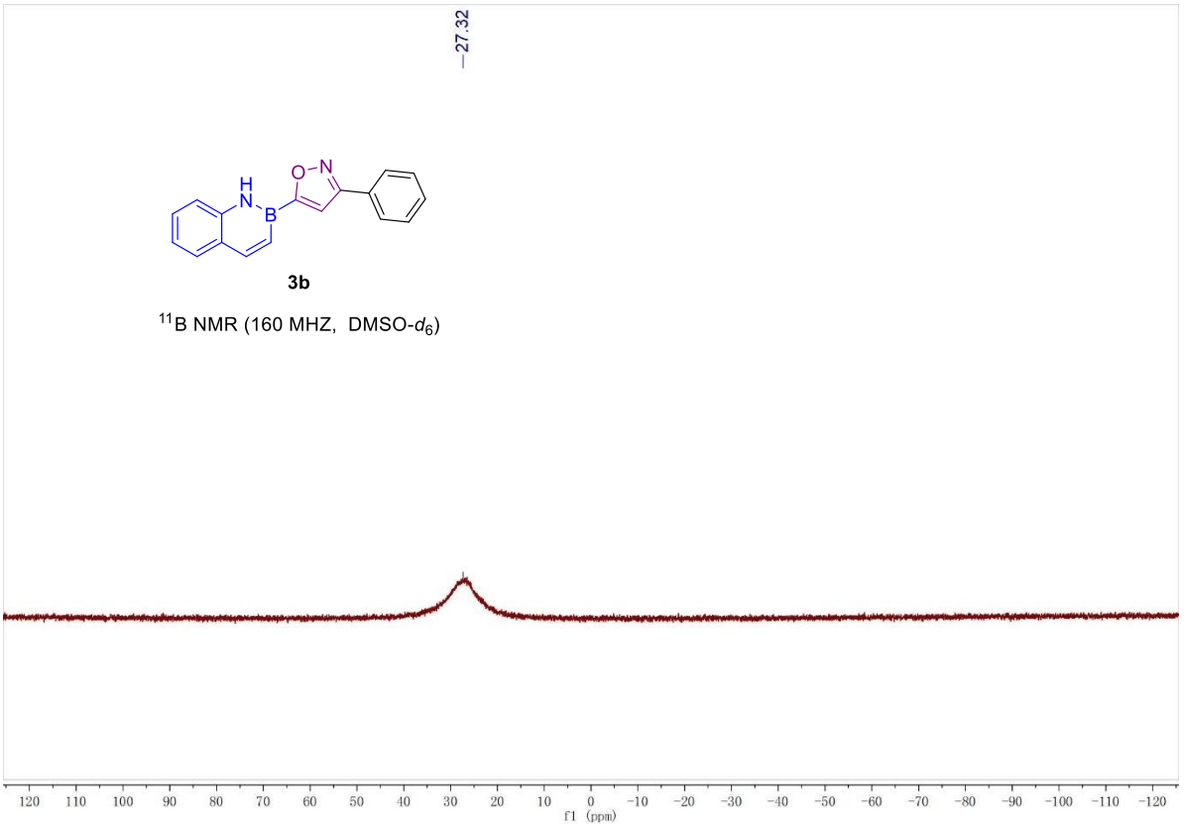
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenylisoxazole (3b)



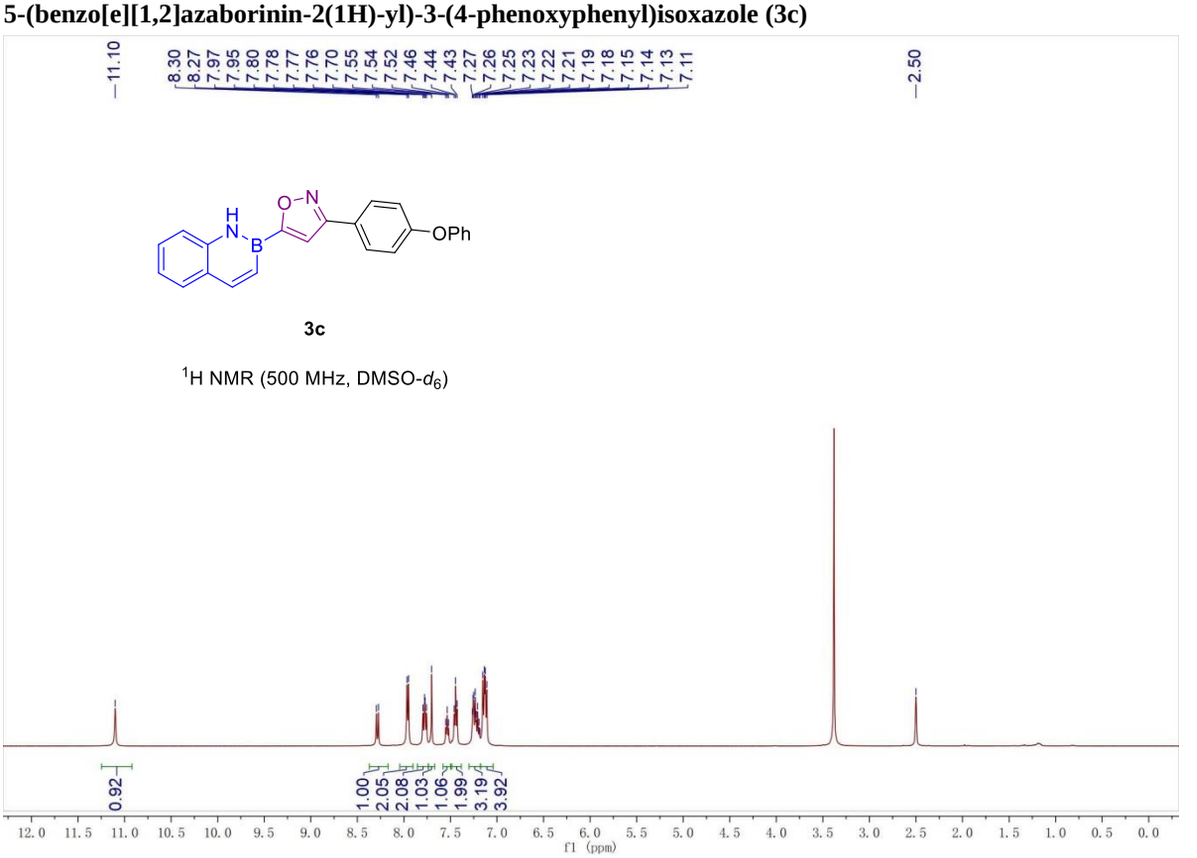
3b

^{13}C NMR (126 MHz, DMSO-d_6)

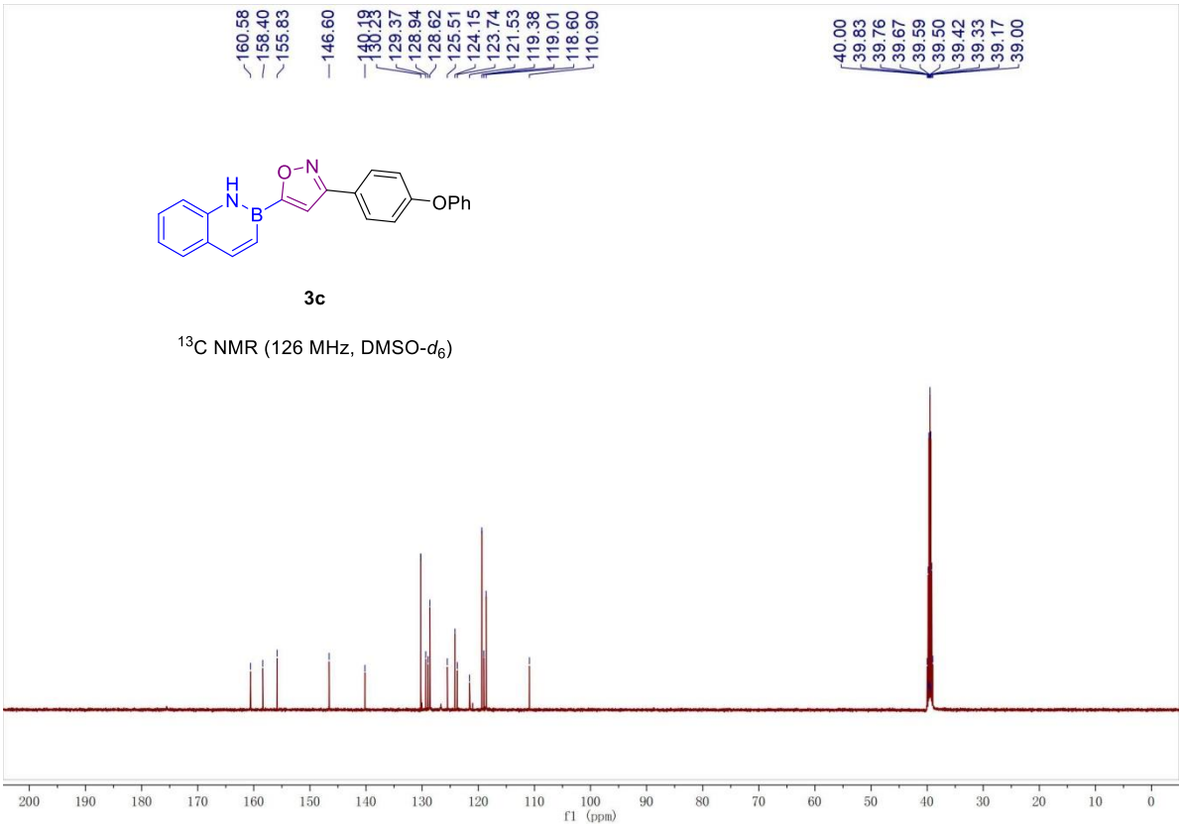
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenylisoxazole (3b)



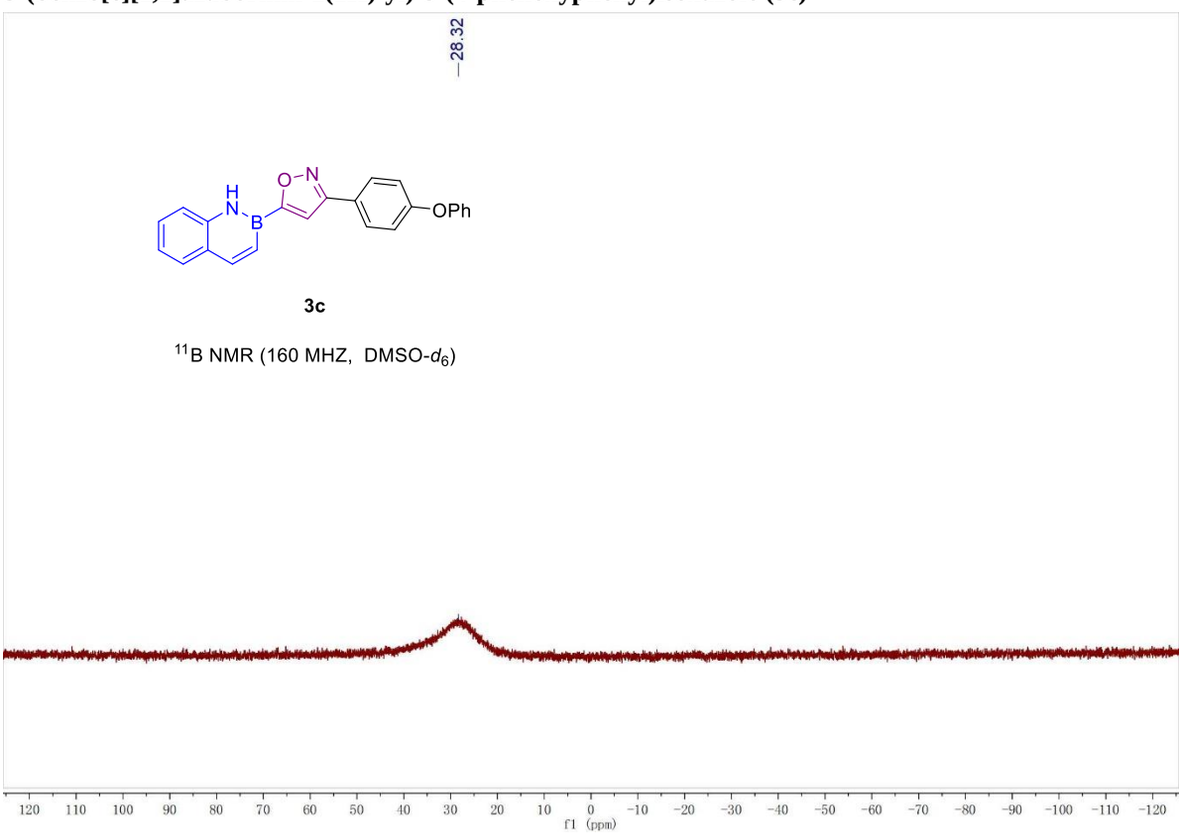
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-phenoxyphenyl)isoxazole (3c)



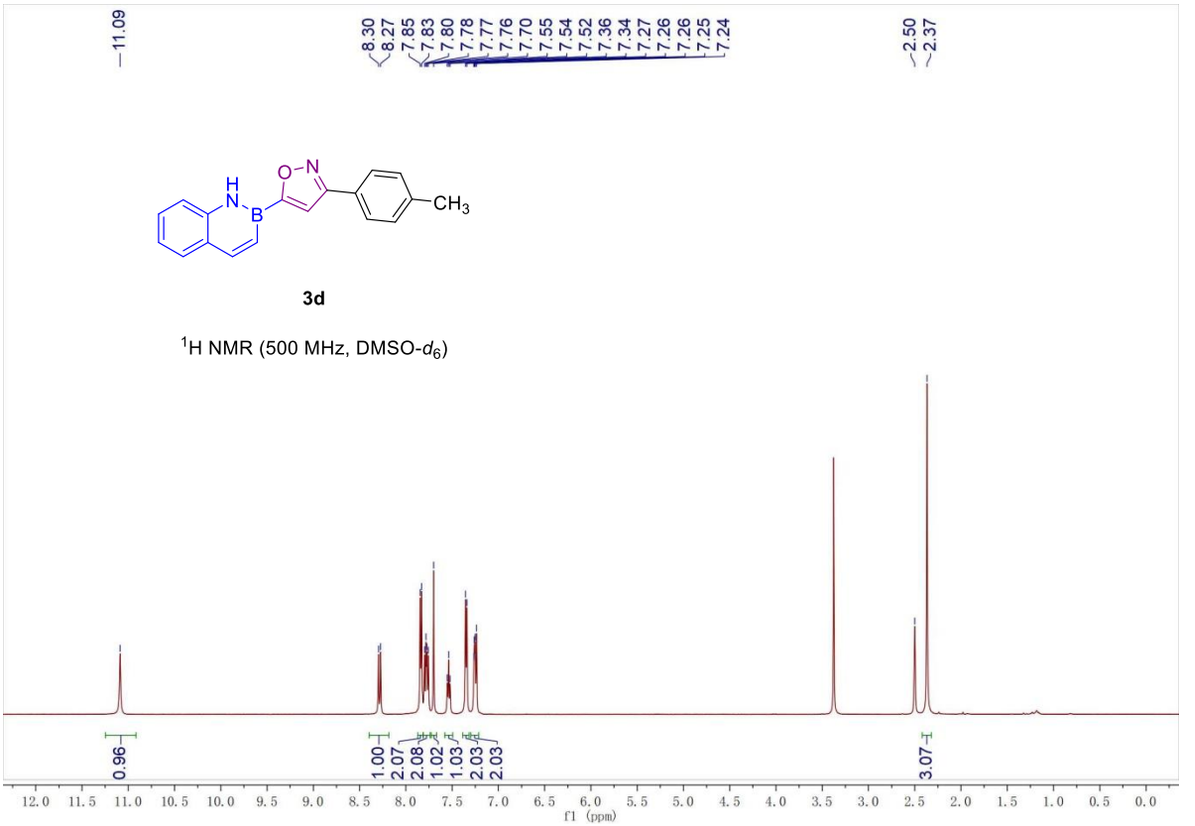
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-phenoxyphenyl)isoxazole (3c)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-phenoxyphenyl)isoxazole (3c)



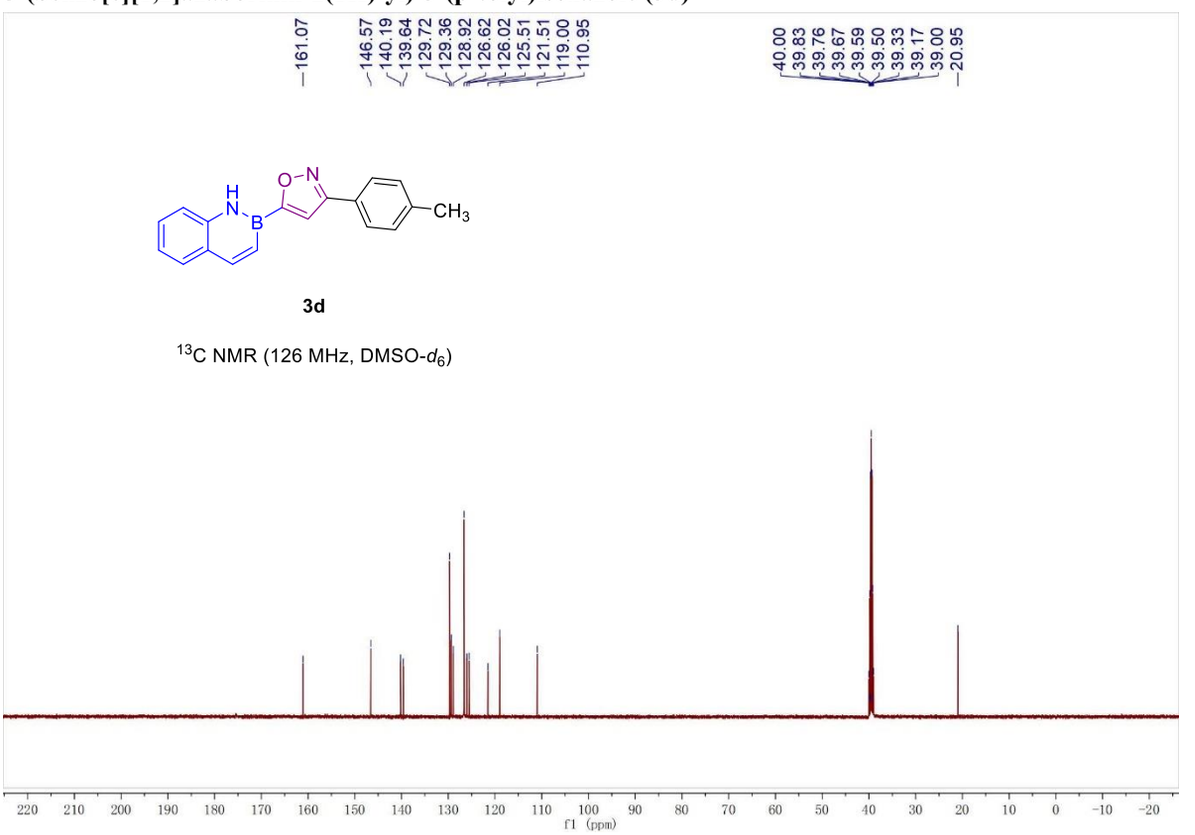
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3d)



3d

^{1}H NMR (500 MHz, DMSO-d_6)

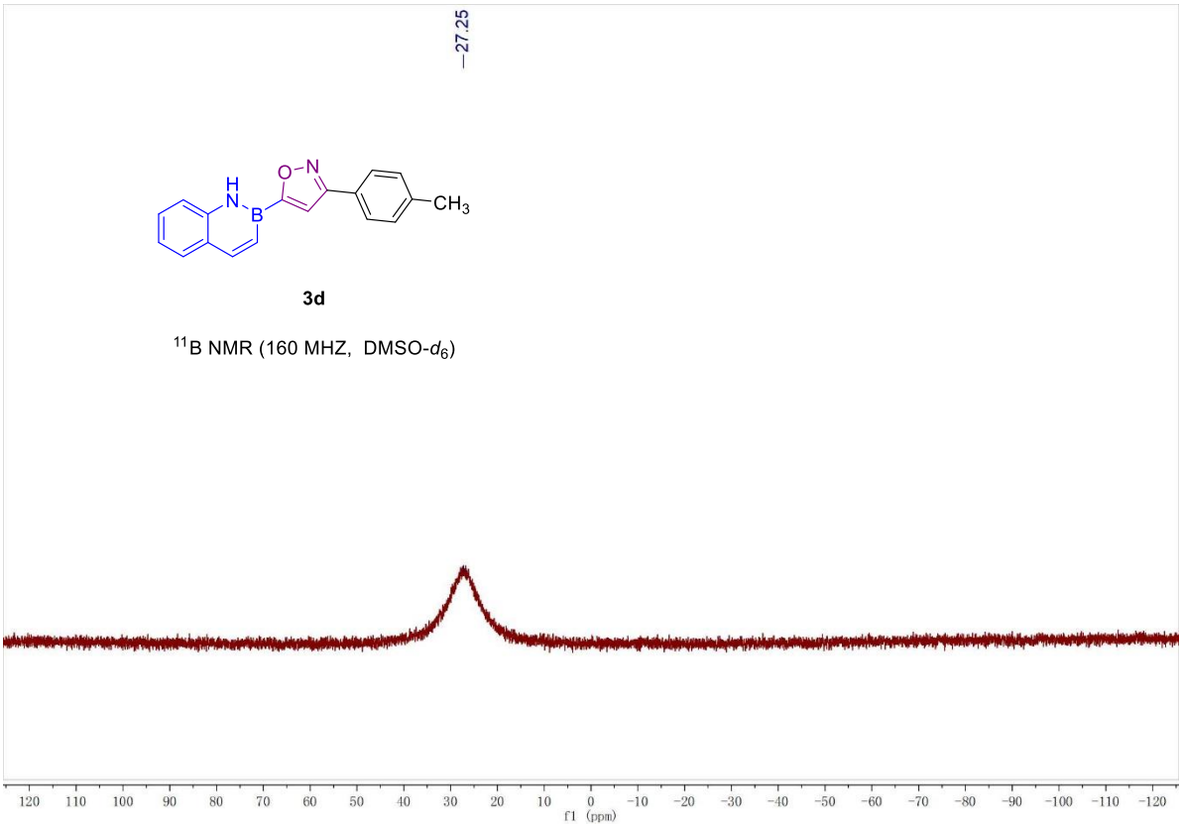
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3d)



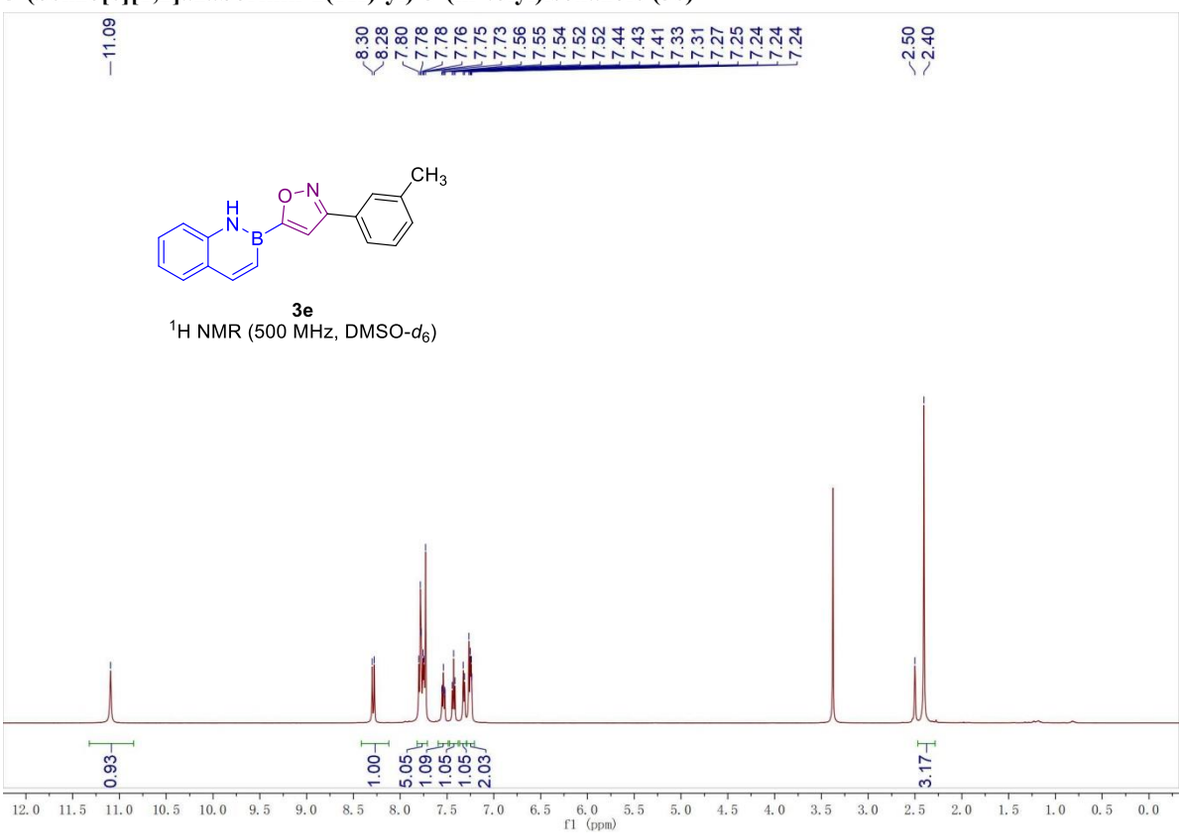
3d

^{13}C NMR (126 MHz, DMSO-d_6)

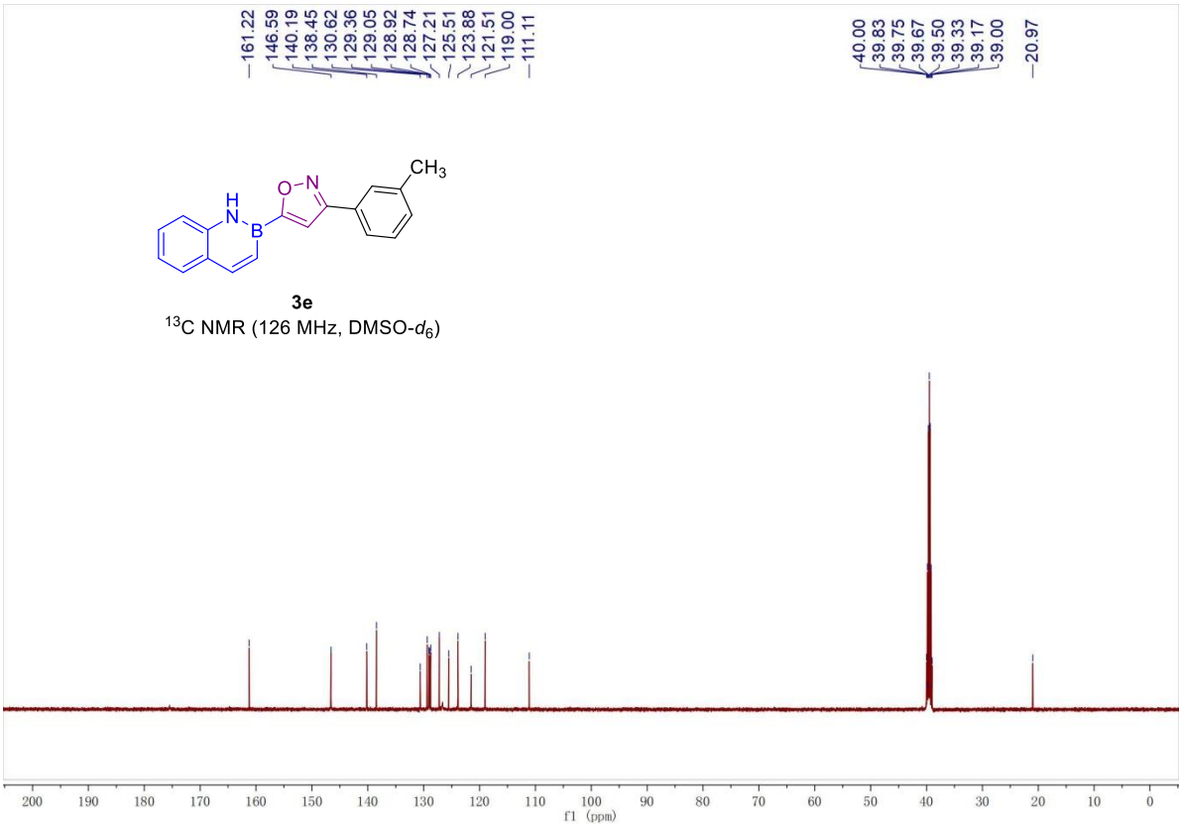
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3d)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3e)



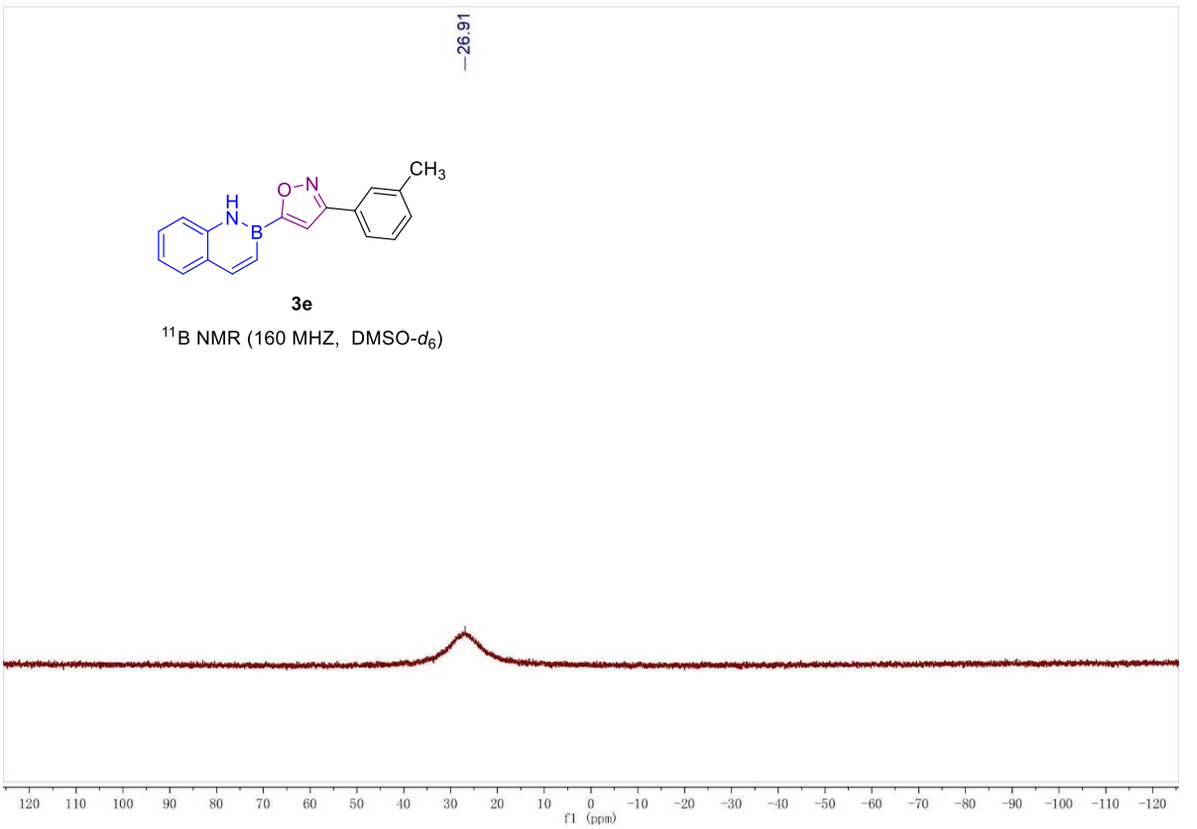
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3e)



3e

^{13}C NMR (126 MHz, DMSO-d_6)

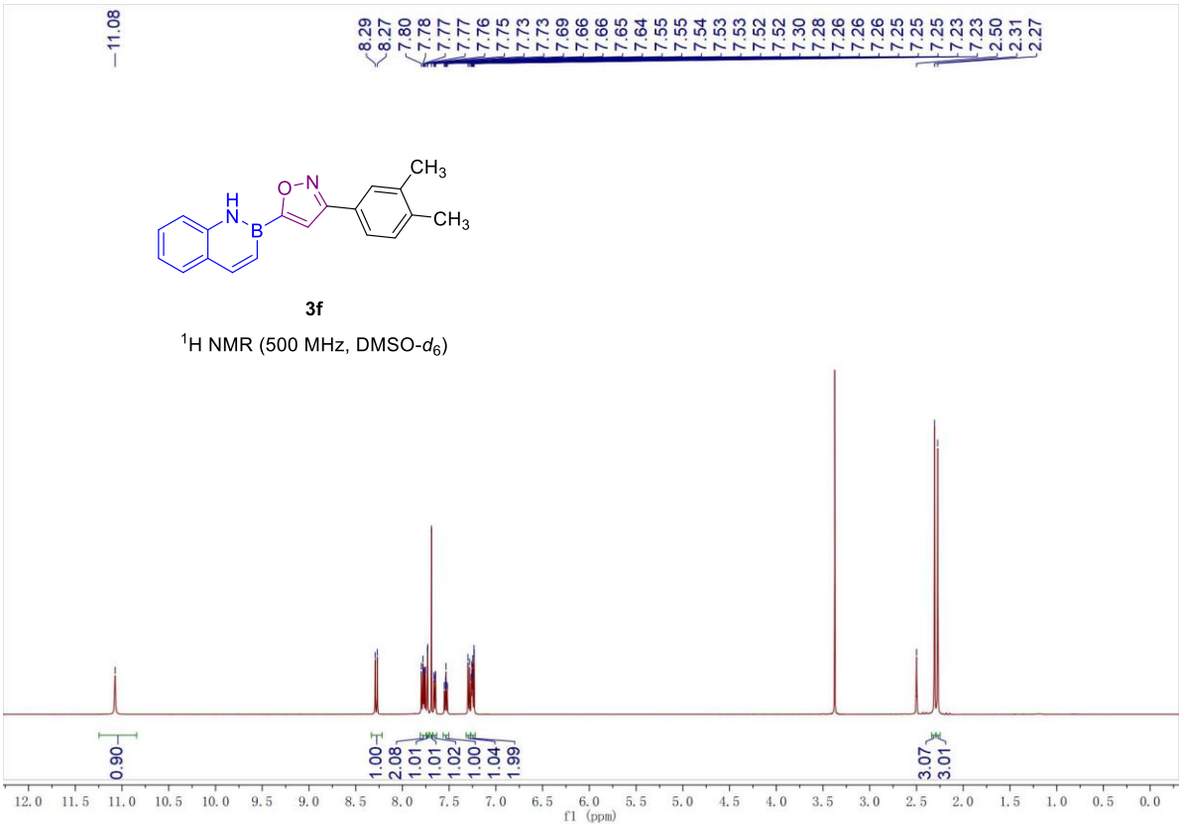
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3e)



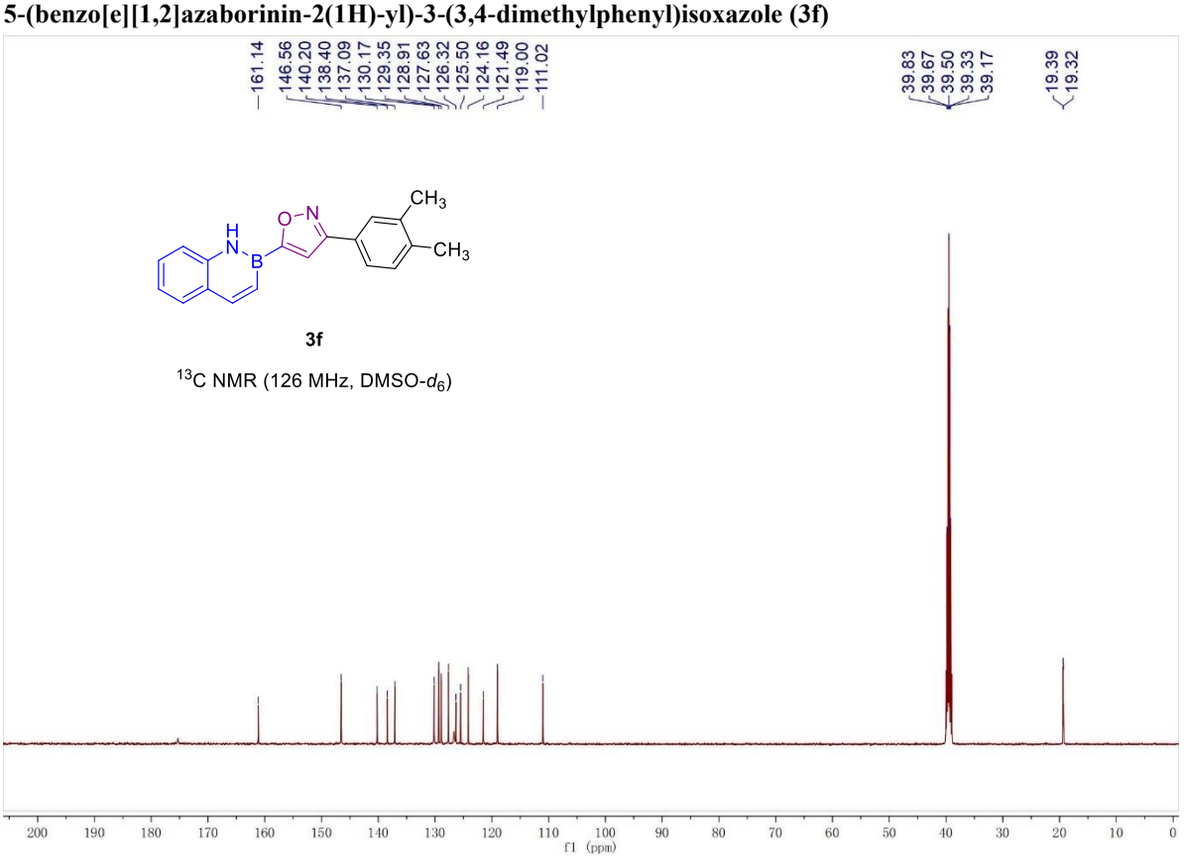
3e

^{11}B NMR (160 MHZ, DMSO-d_6)

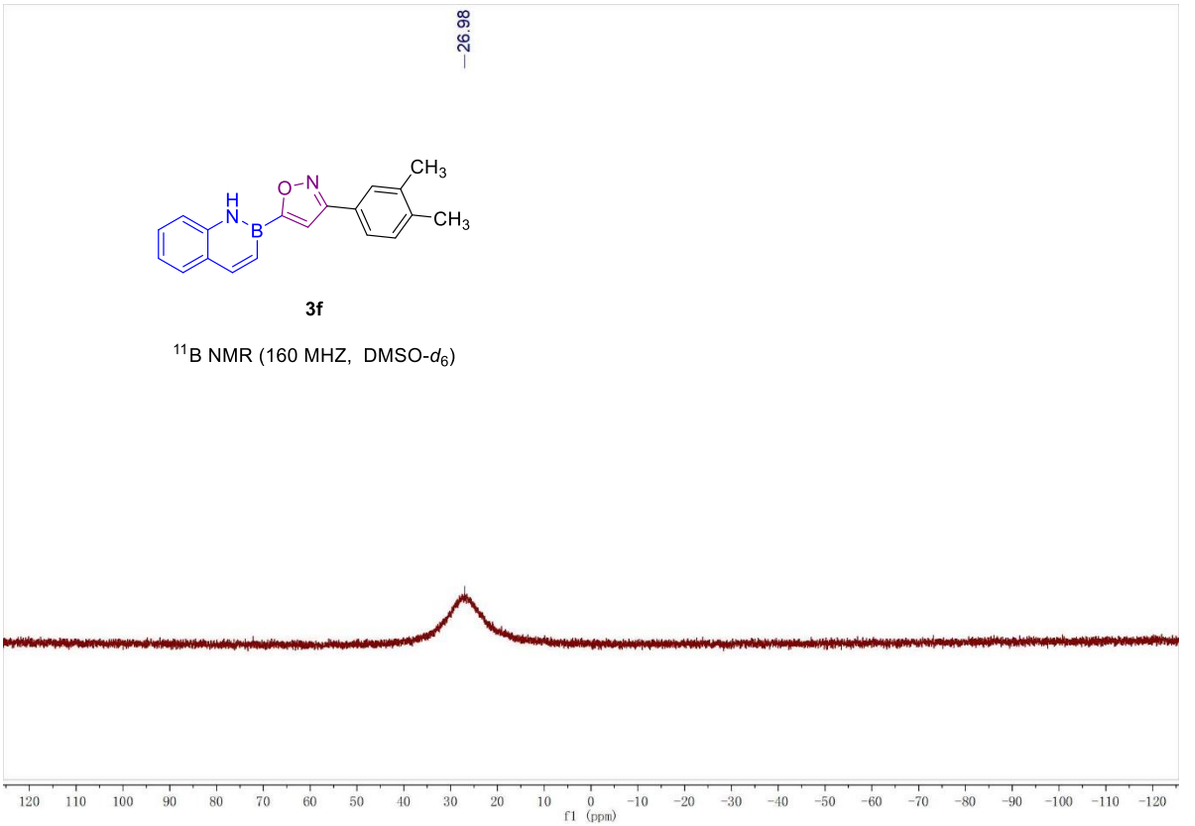
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3,4-dimethylphenyl)isoxazole (3f)



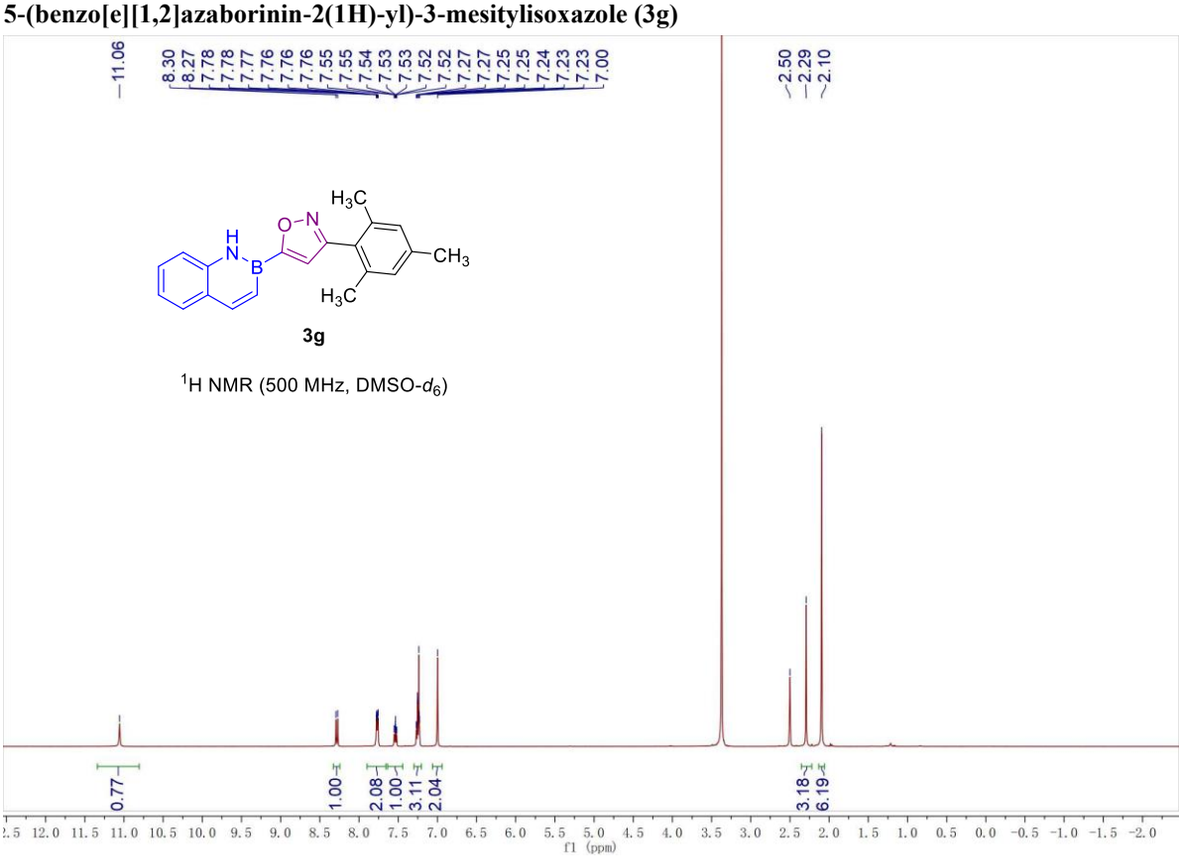
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3,4-dimethylphenyl)isoxazole (3f)



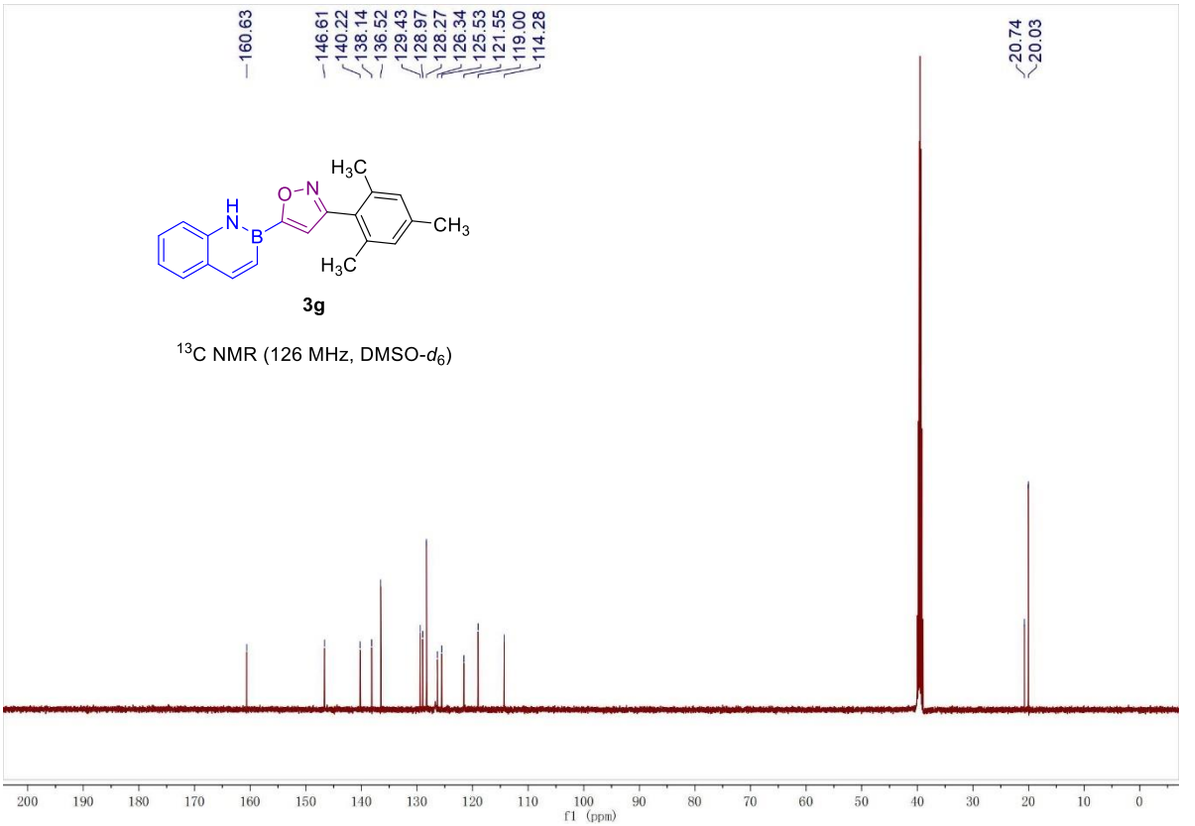
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3,4-dimethylphenyl)isoxazole (3f)



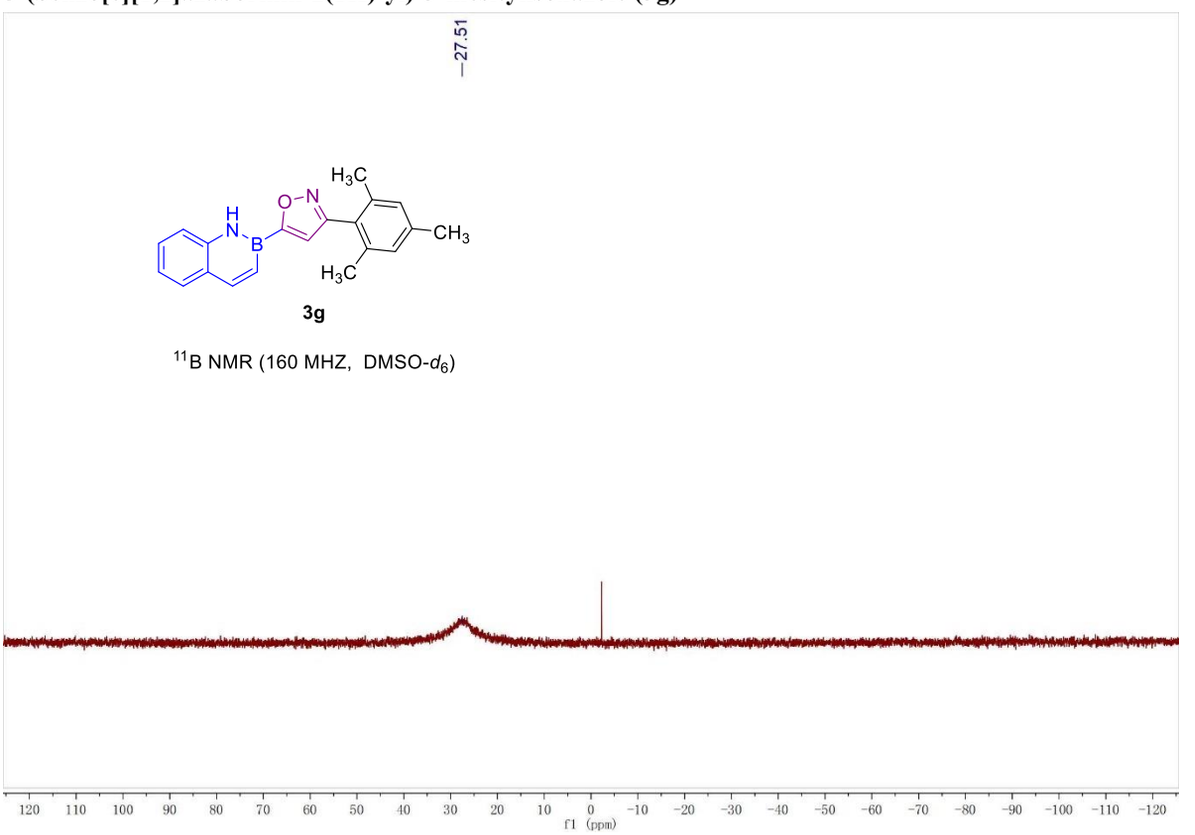
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-mesitylisoxazole (3g)



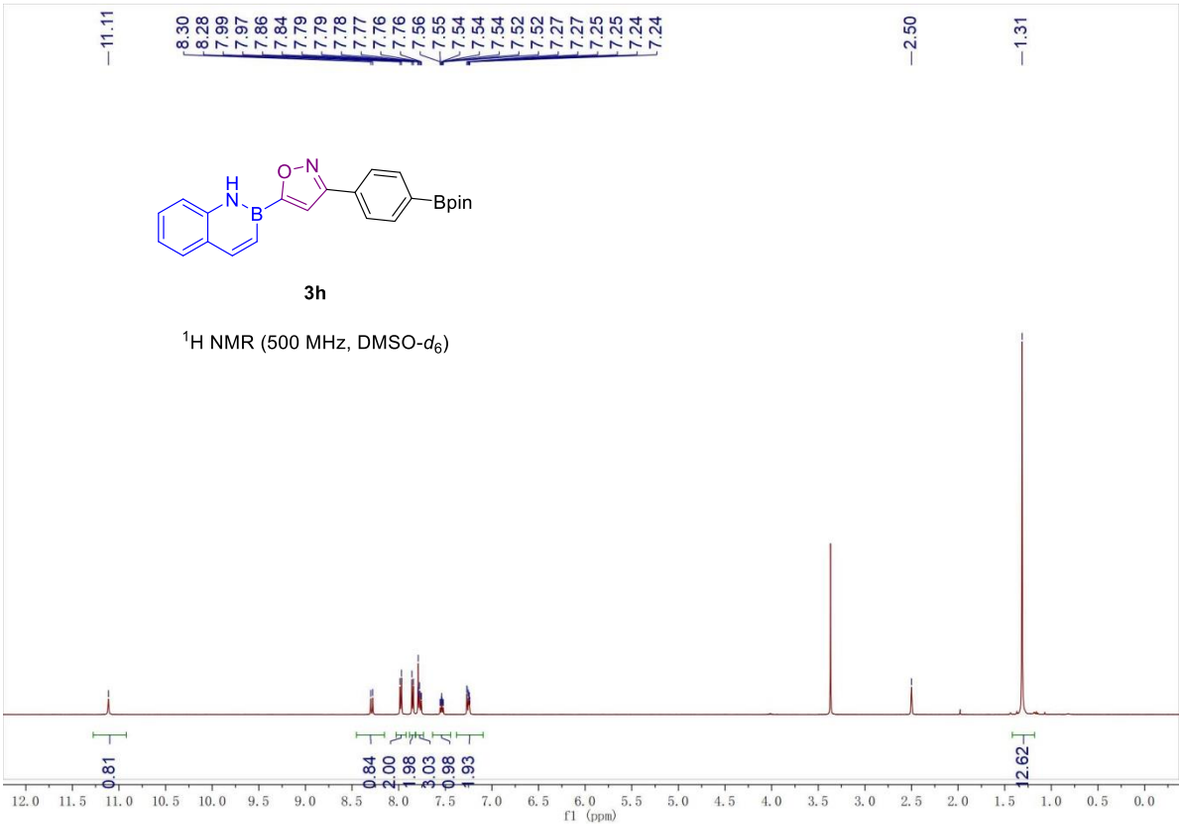
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-mesitylisoxazole (3g)



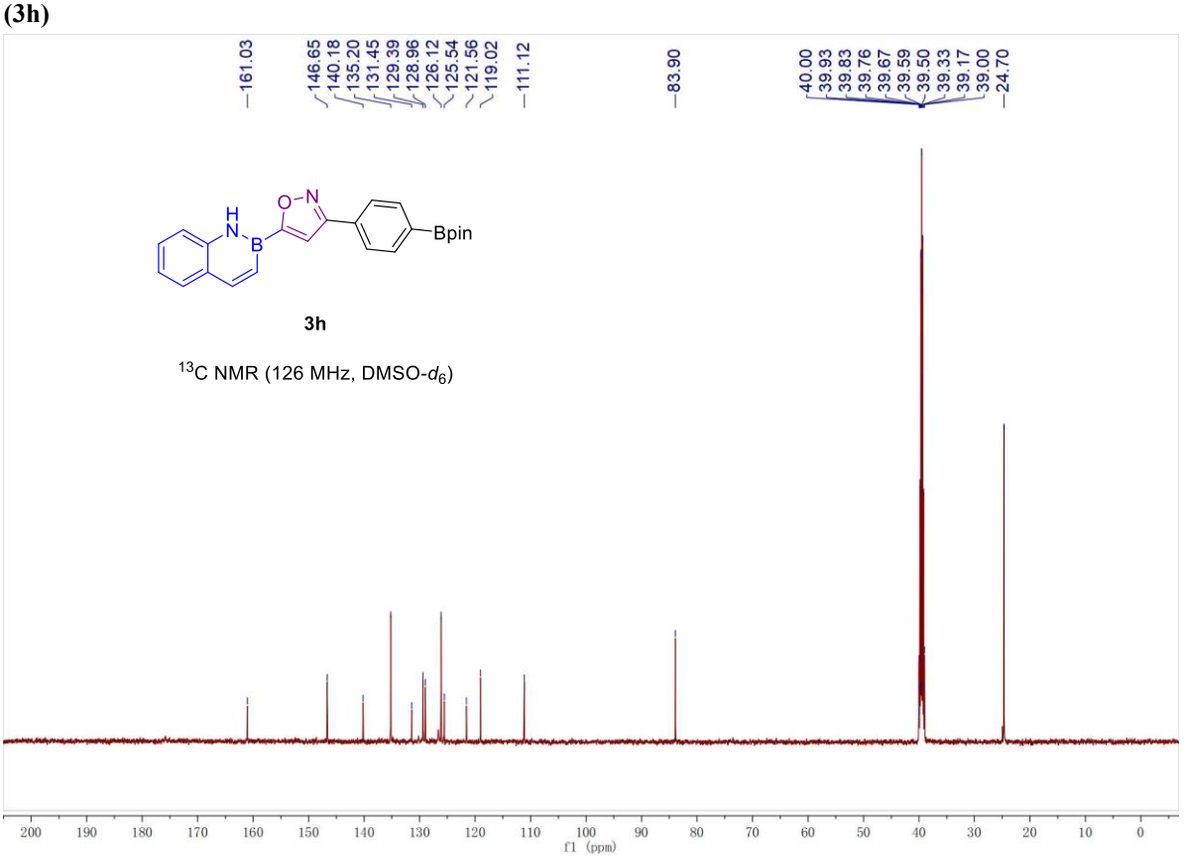
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-mesitylisoxazole (3g)



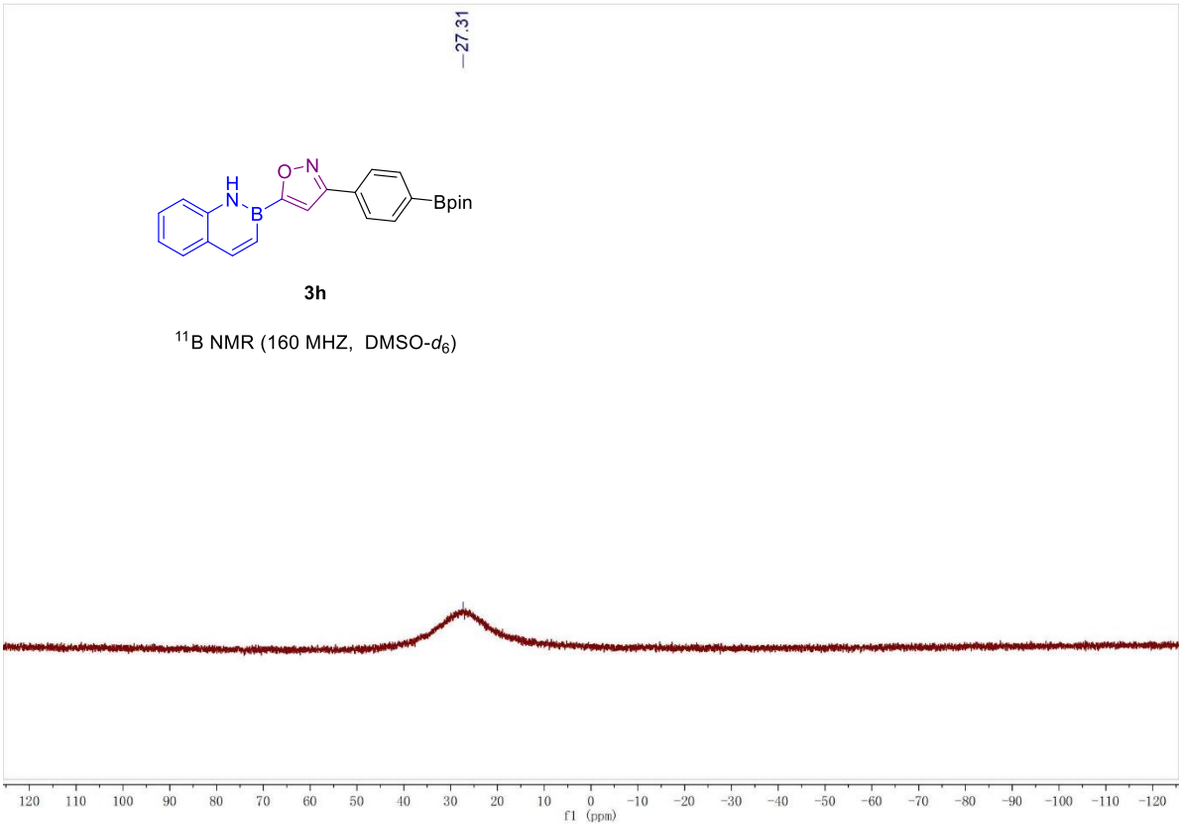
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)isoxazole (3h)



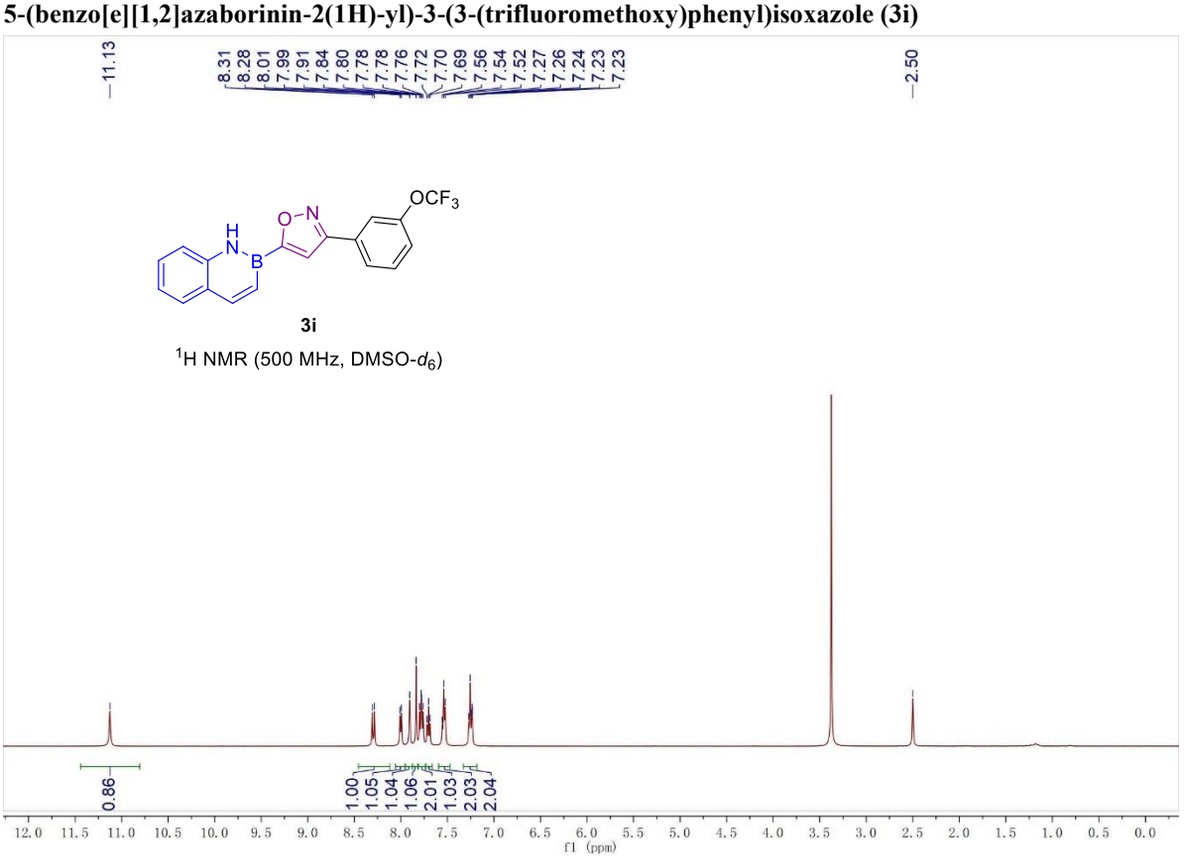
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)isoxazole (3h)



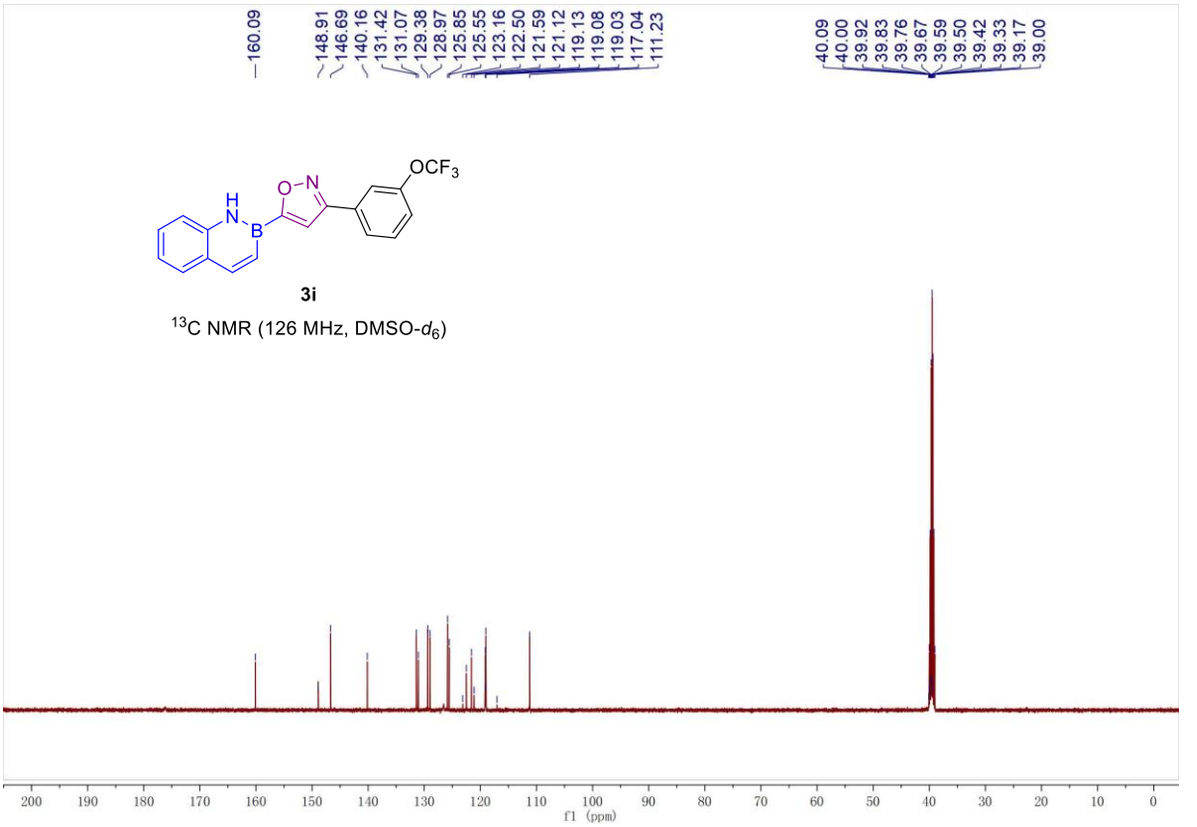
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)isoxazole (3h)



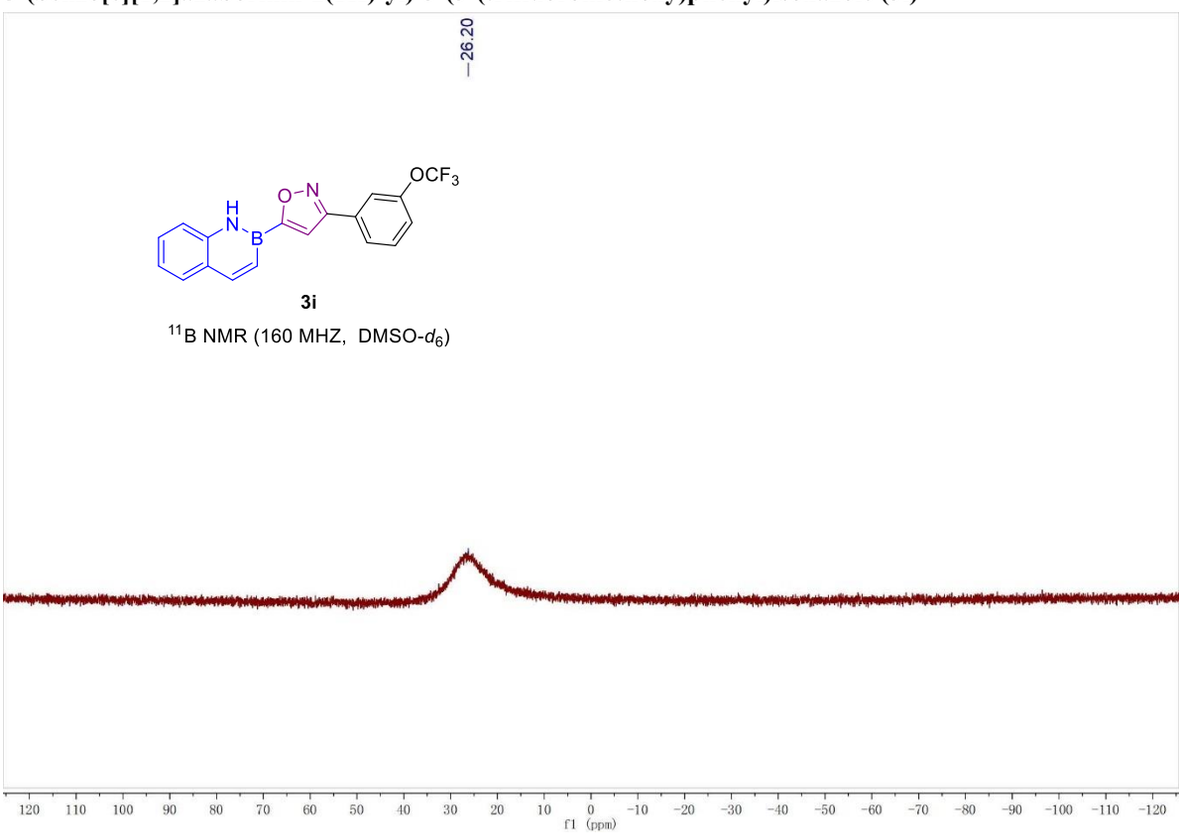
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-(trifluoromethoxy)phenyl)isoxazole (3i)



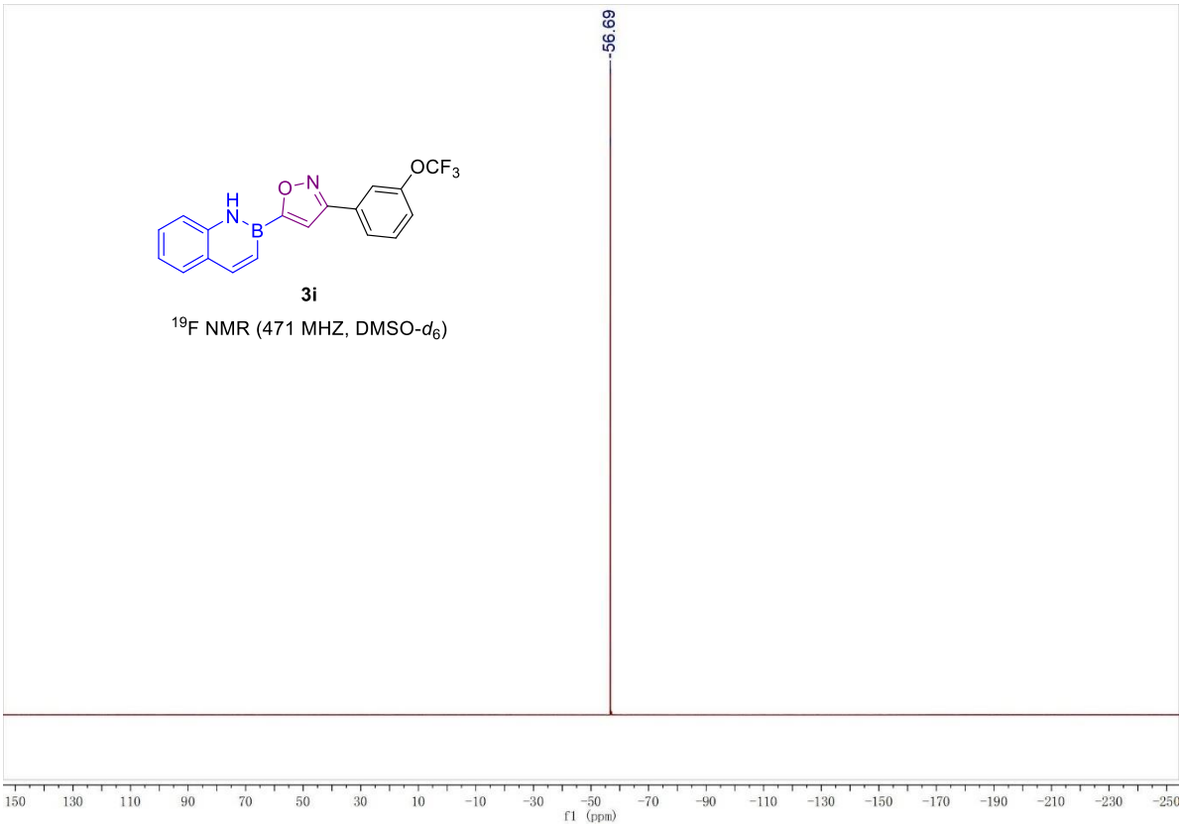
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-(trifluoromethoxy)phenyl)isoxazole (3i)



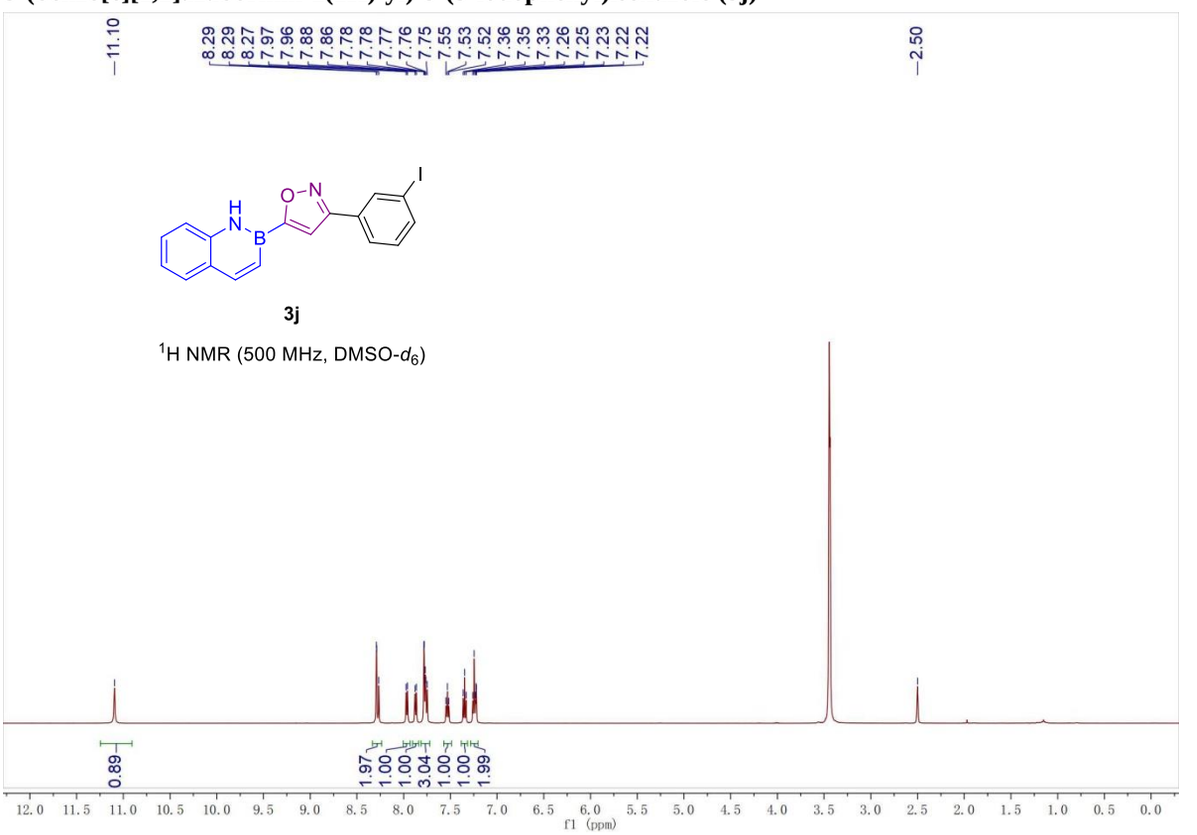
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-(trifluoromethoxy)phenyl)isoxazole (3i)



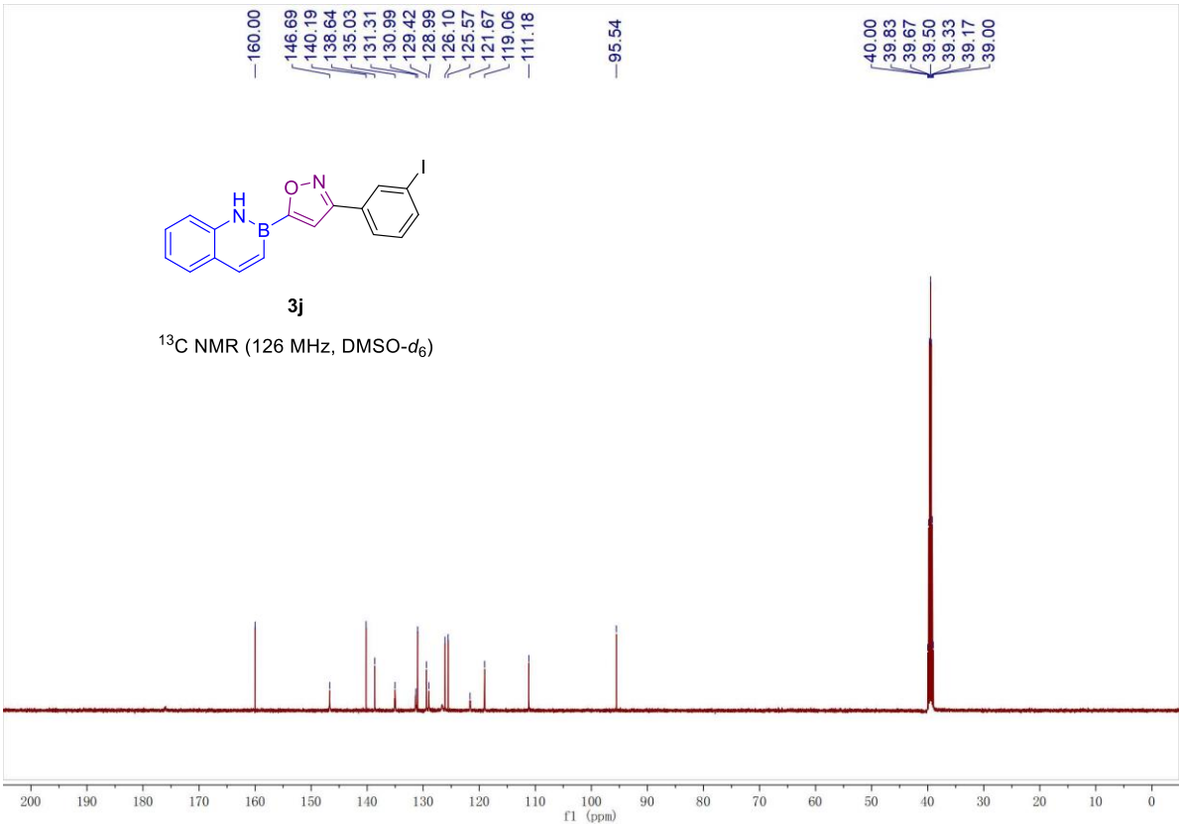
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-(trifluoromethoxy)phenyl)isoxazole (3i)



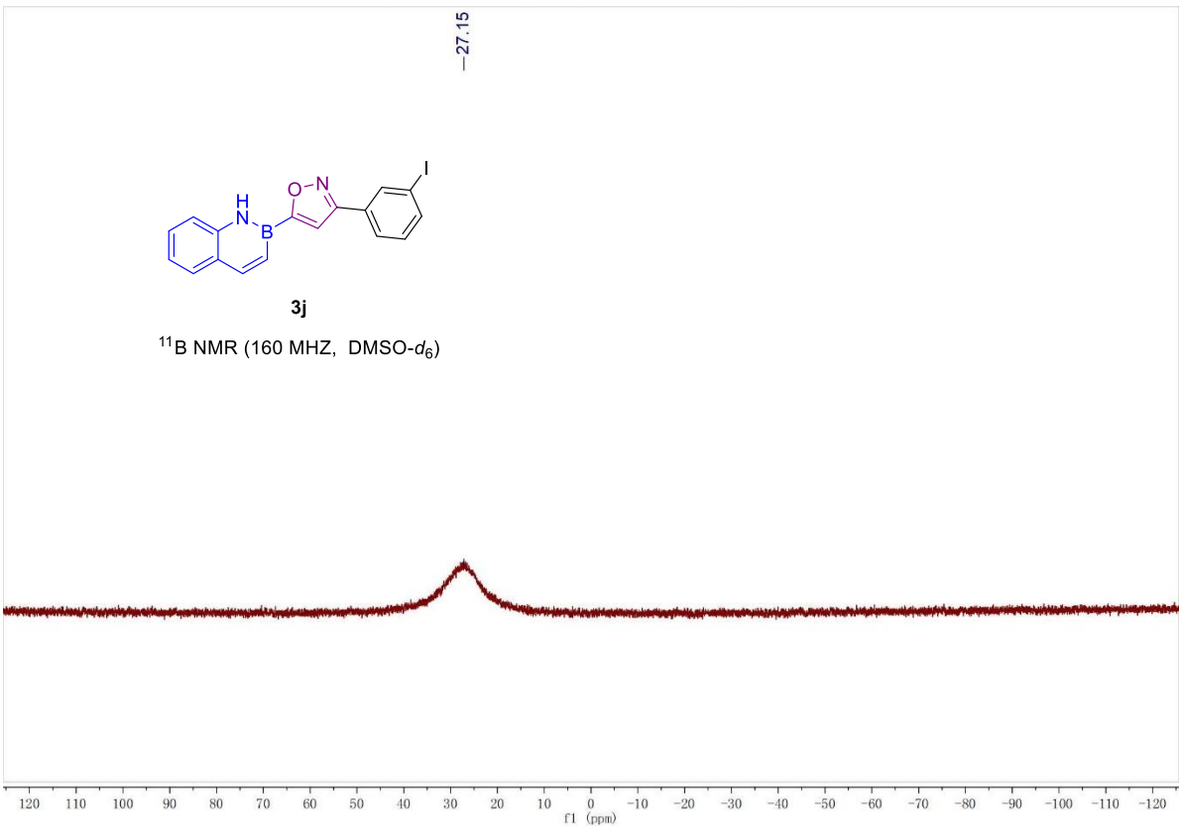
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-iodophenyl)isoxazole (3j)



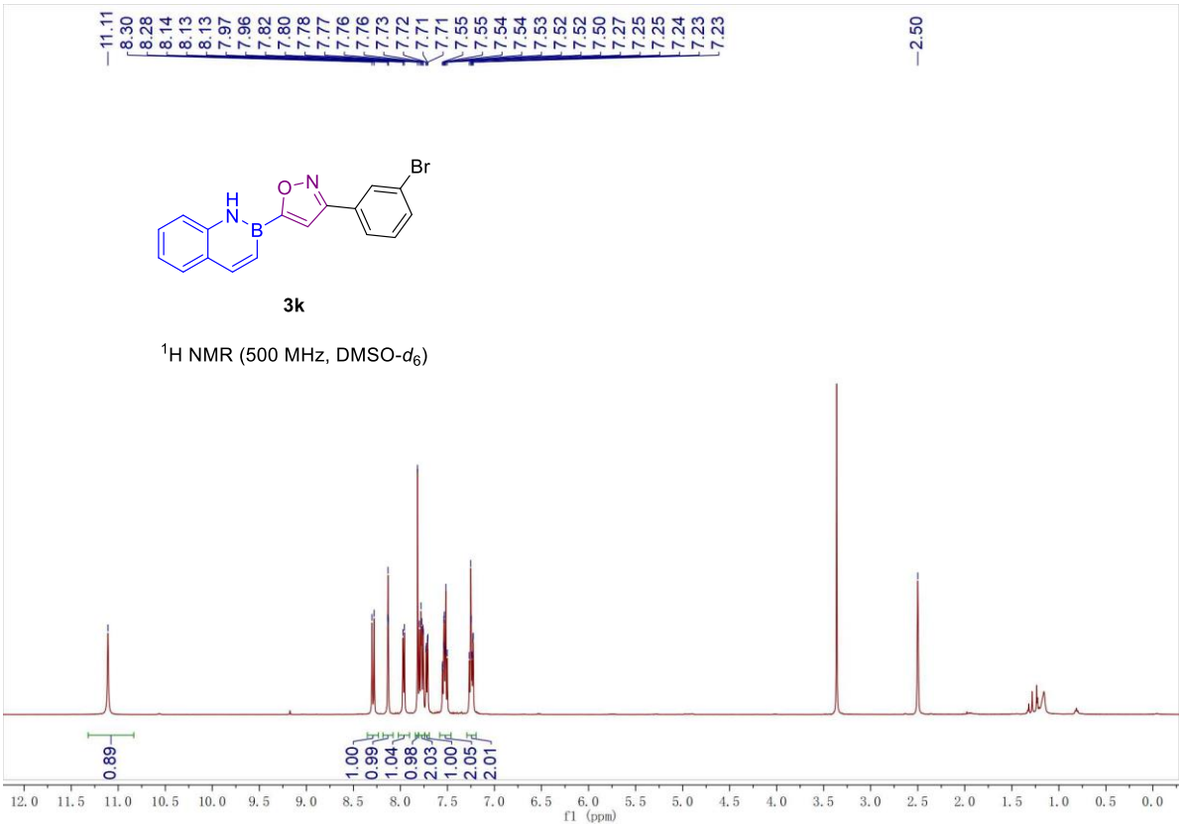
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-iodophenyl)isoxazole (3j)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-iodophenyl)isoxazole (3j)

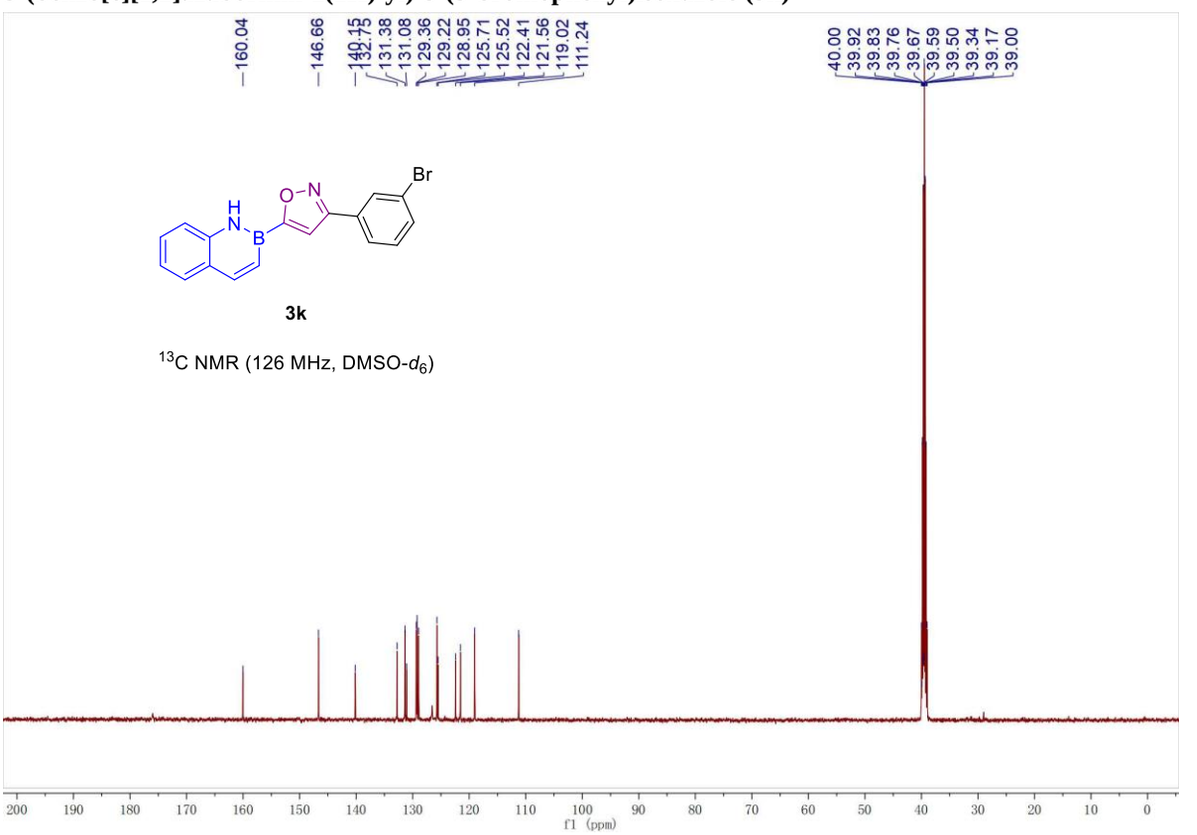


5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-bromophenyl)isoxazole (3k)



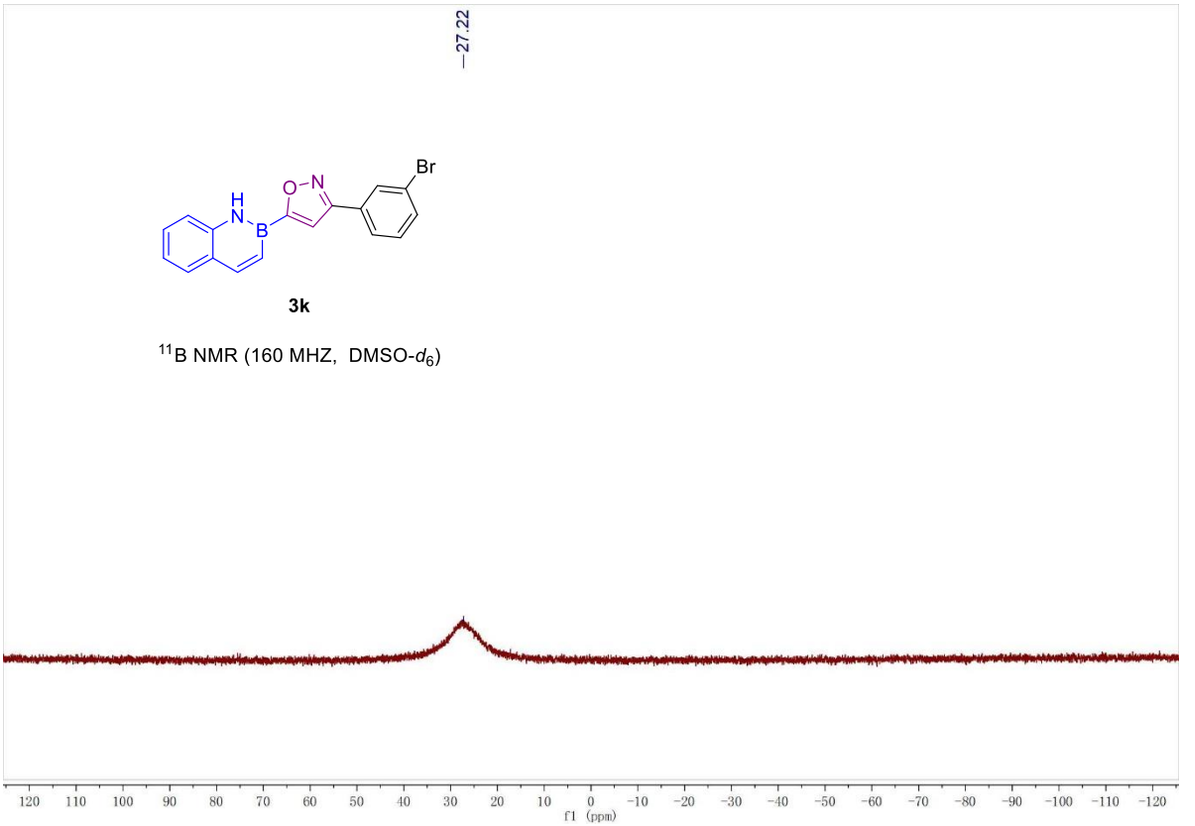
^{1}H NMR (500 MHz, DMSO-d_6)

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-bromophenyl)isoxazole (3k)

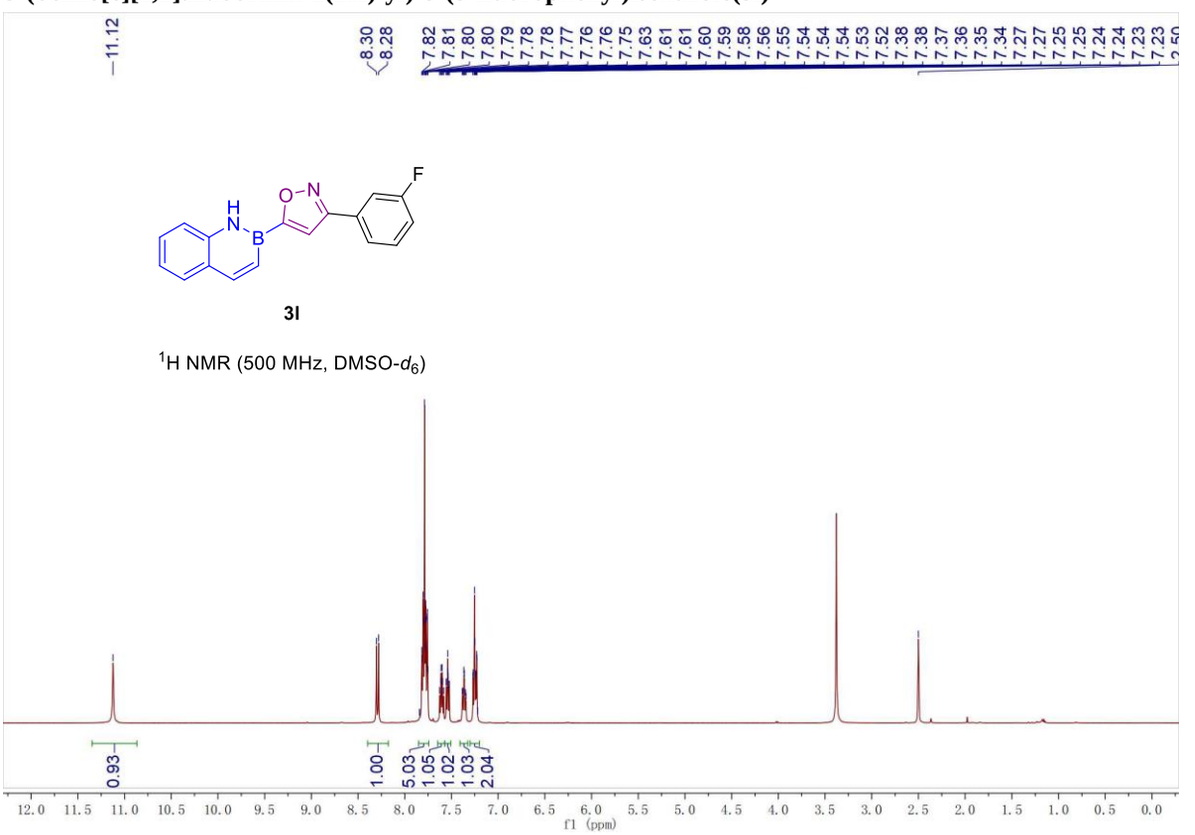


^{13}C NMR (126 MHz, DMSO-d_6)

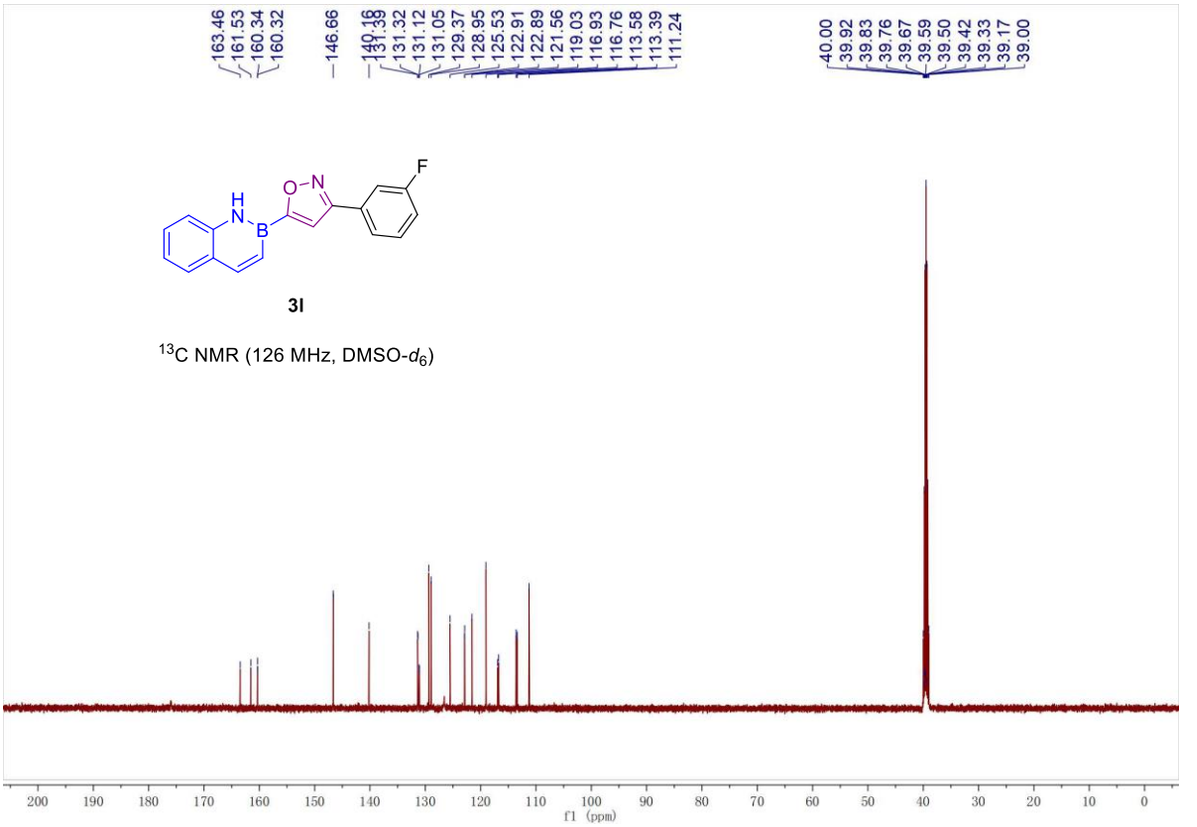
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-bromophenyl)isoxazole (3k)



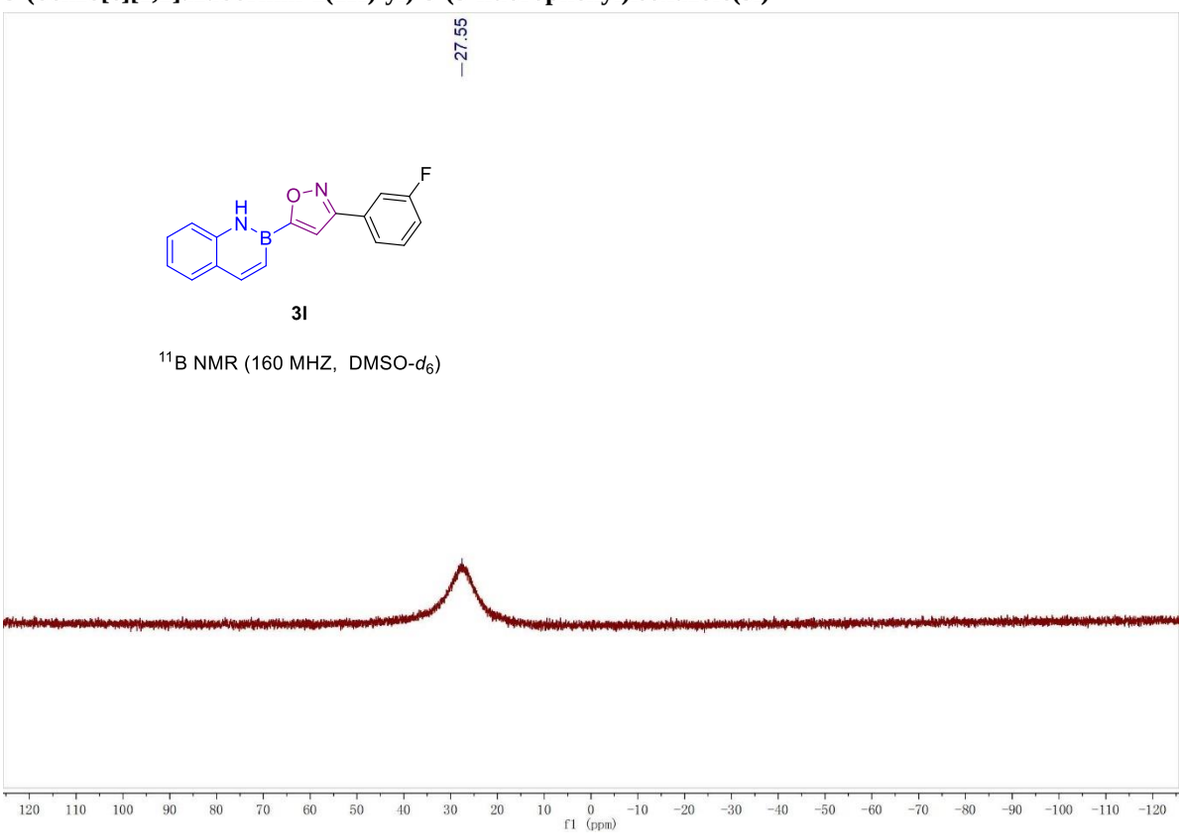
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole(3l)



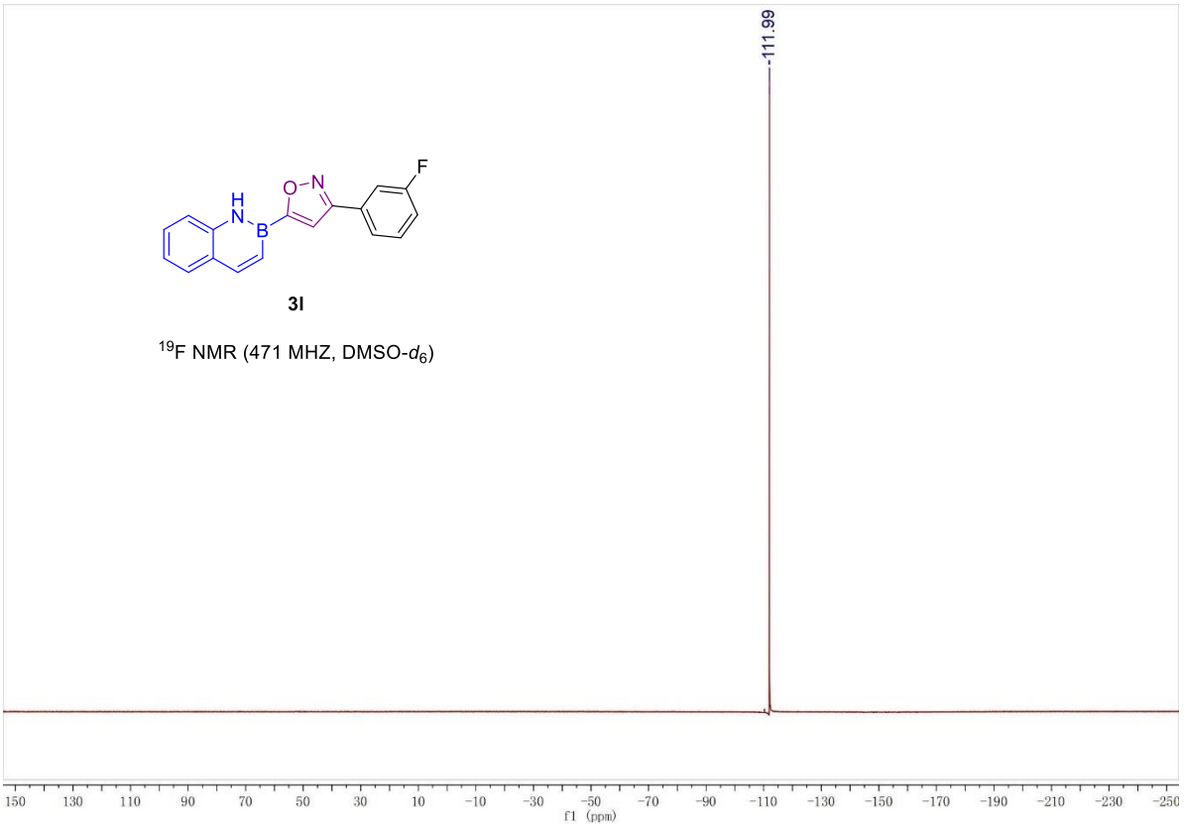
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole(3l)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole(3l)



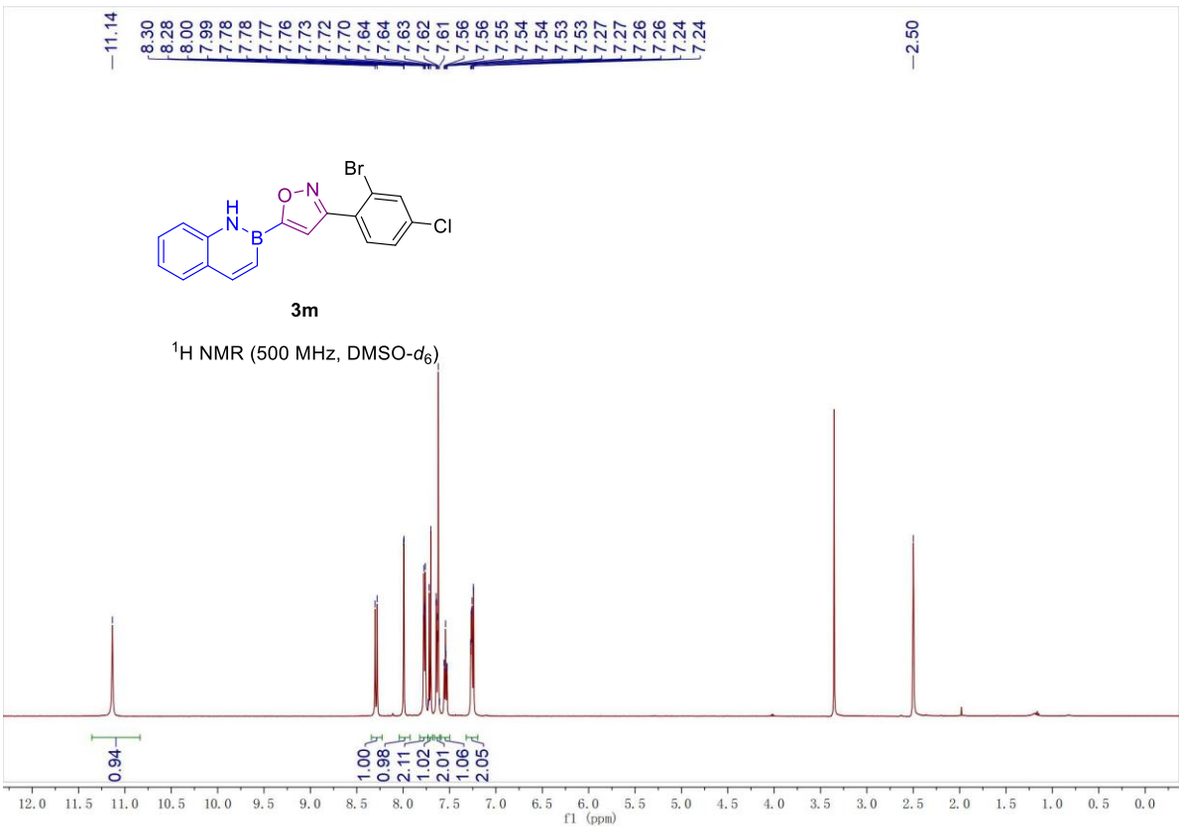
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole(3l)



3l

^{19}F NMR (471 MHZ, DMSO-d_6)

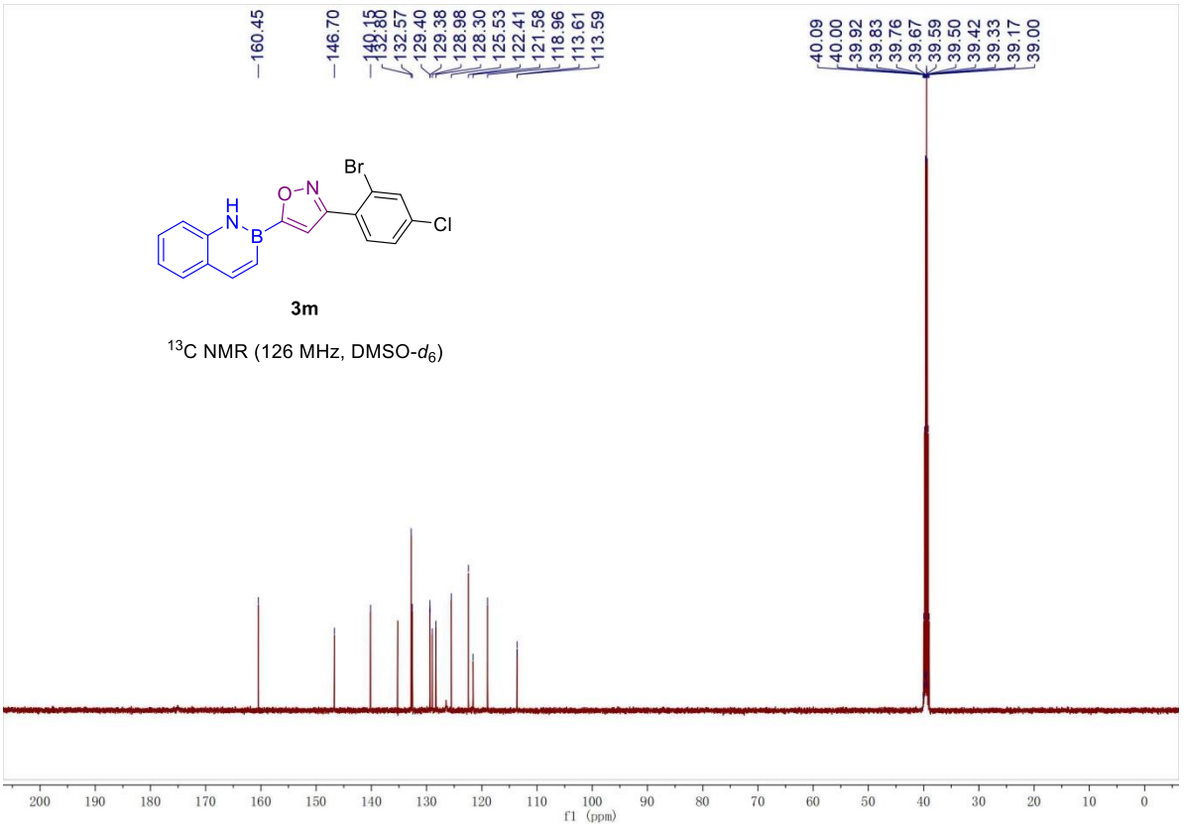
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(2-bromo-4-chlorophenyl)isoxazole (3m)



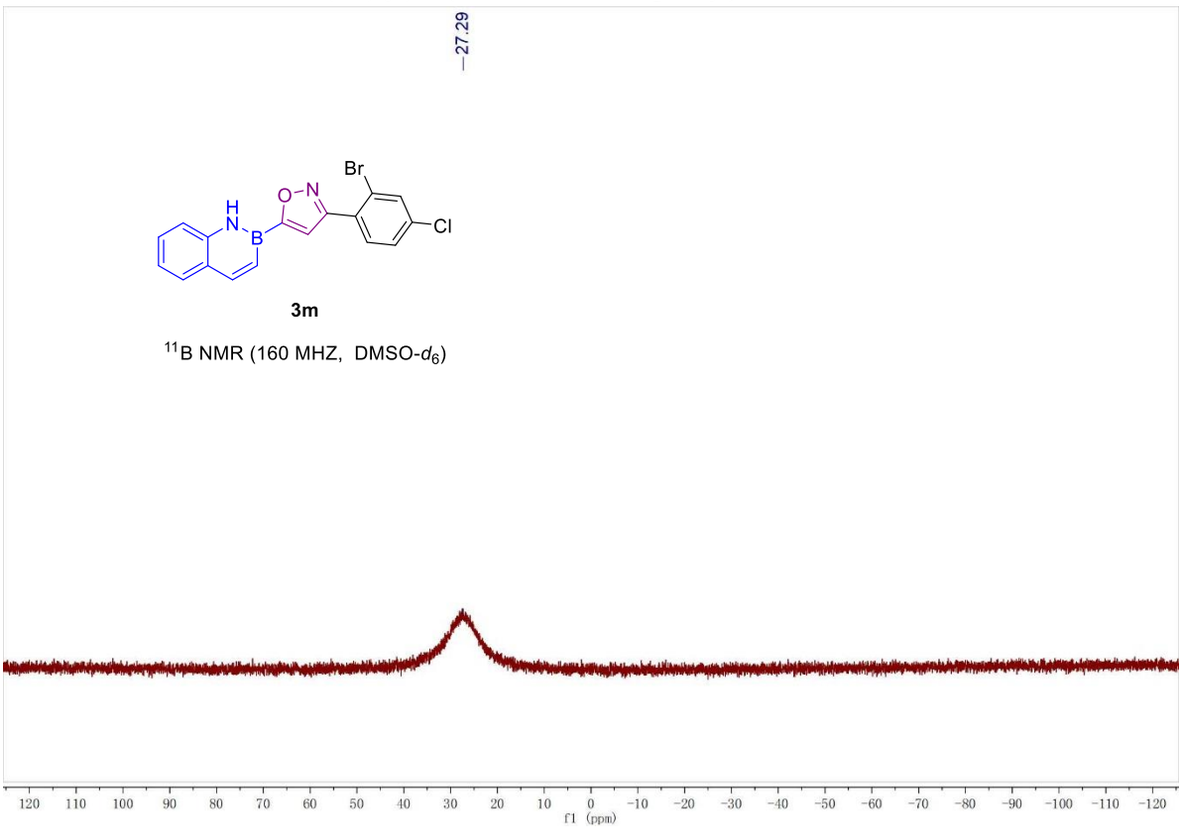
3m

^{1}H NMR (500 MHz, DMSO-d_6)

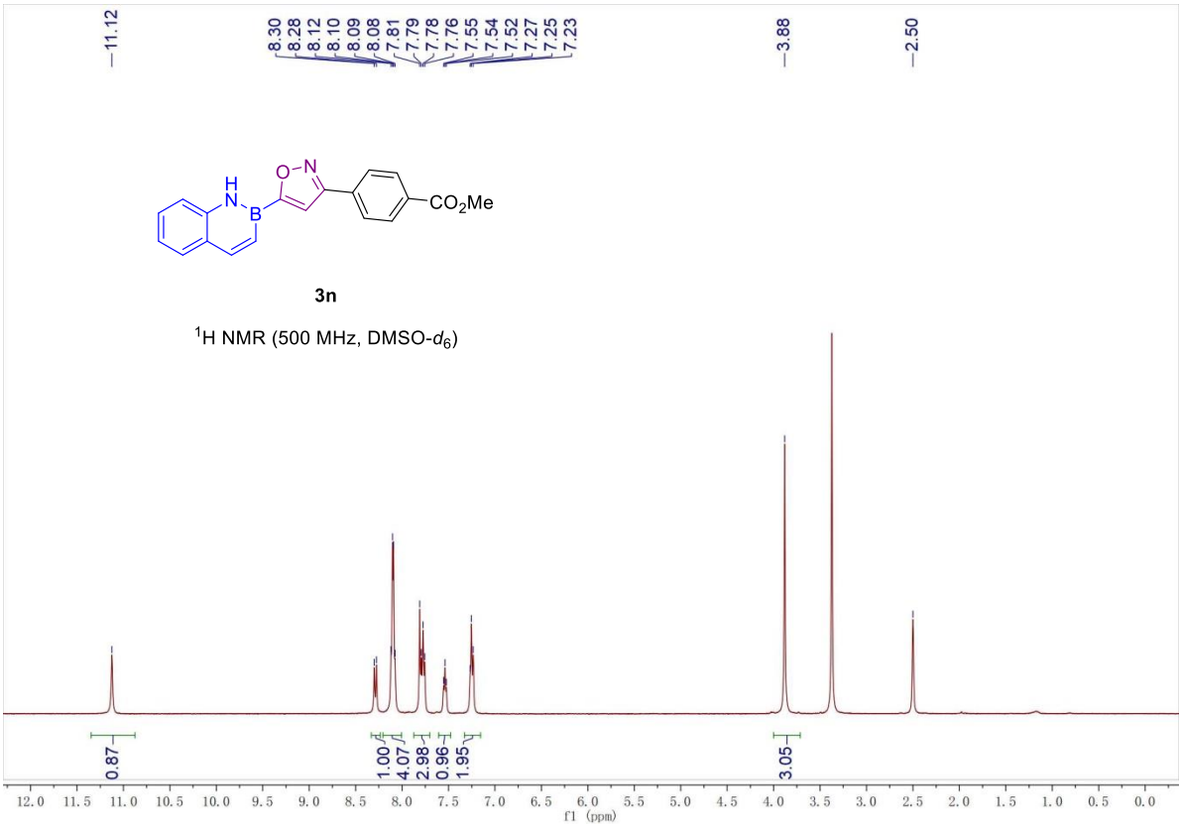
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(2-bromo-4-chlorophenyl)isoxazole (3m)



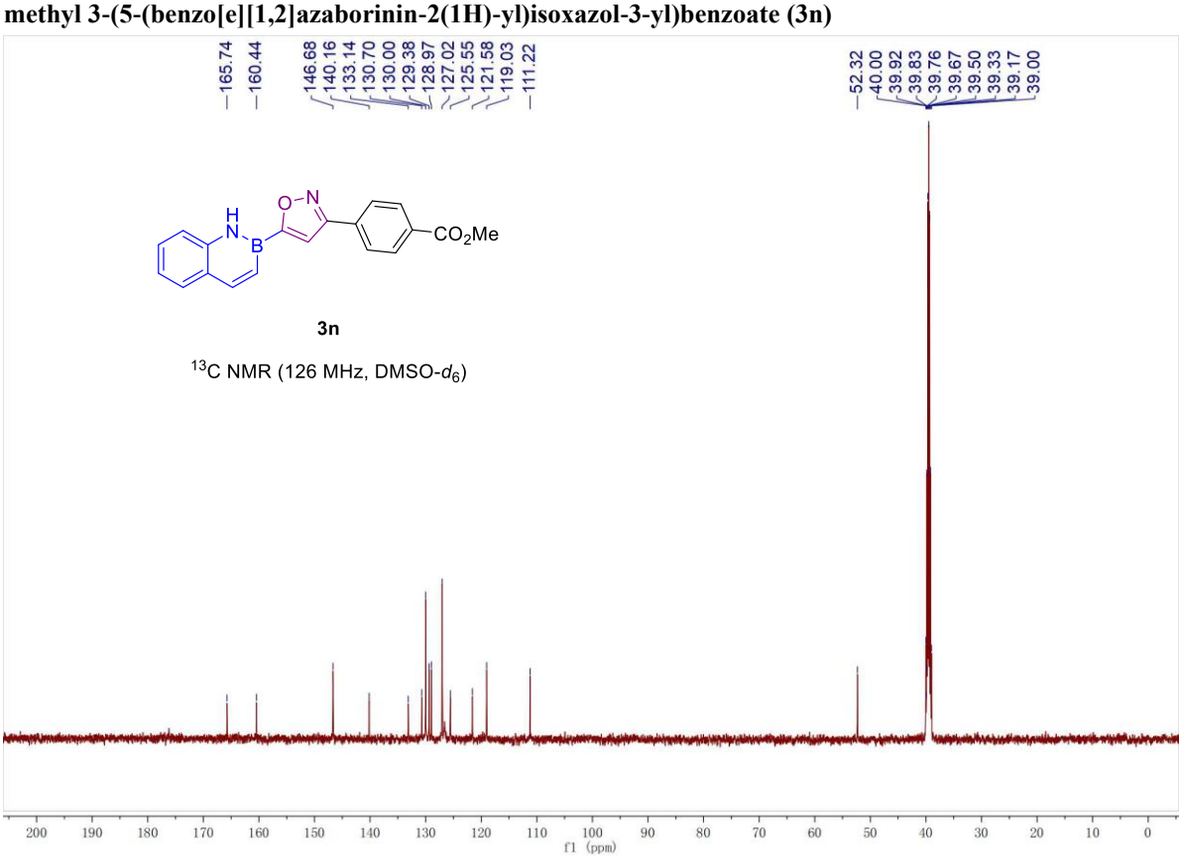
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(2-bromo-4-chlorophenyl)isoxazole (3m)



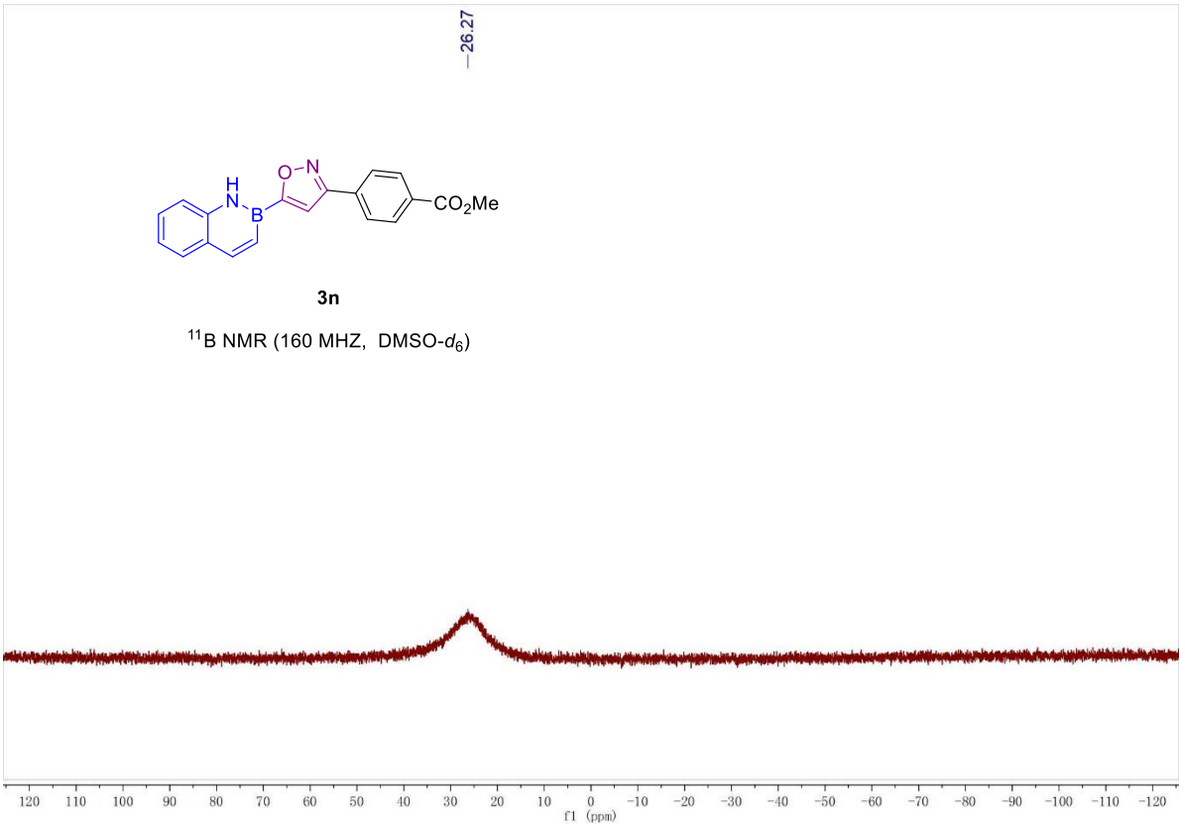
methyl 3-(5-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazol-3-yl)benzoate (3n)



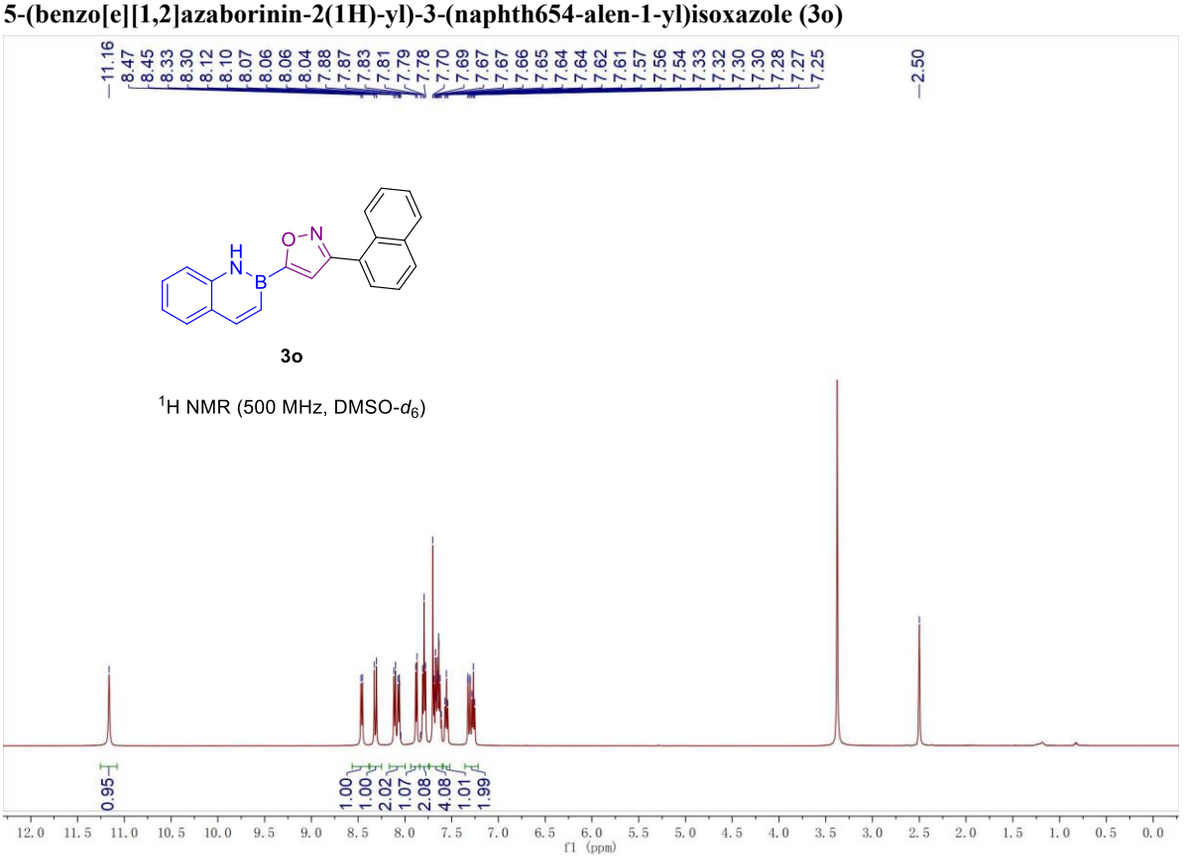
methyl 3-(5-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazol-3-yl)benzoate (3n)



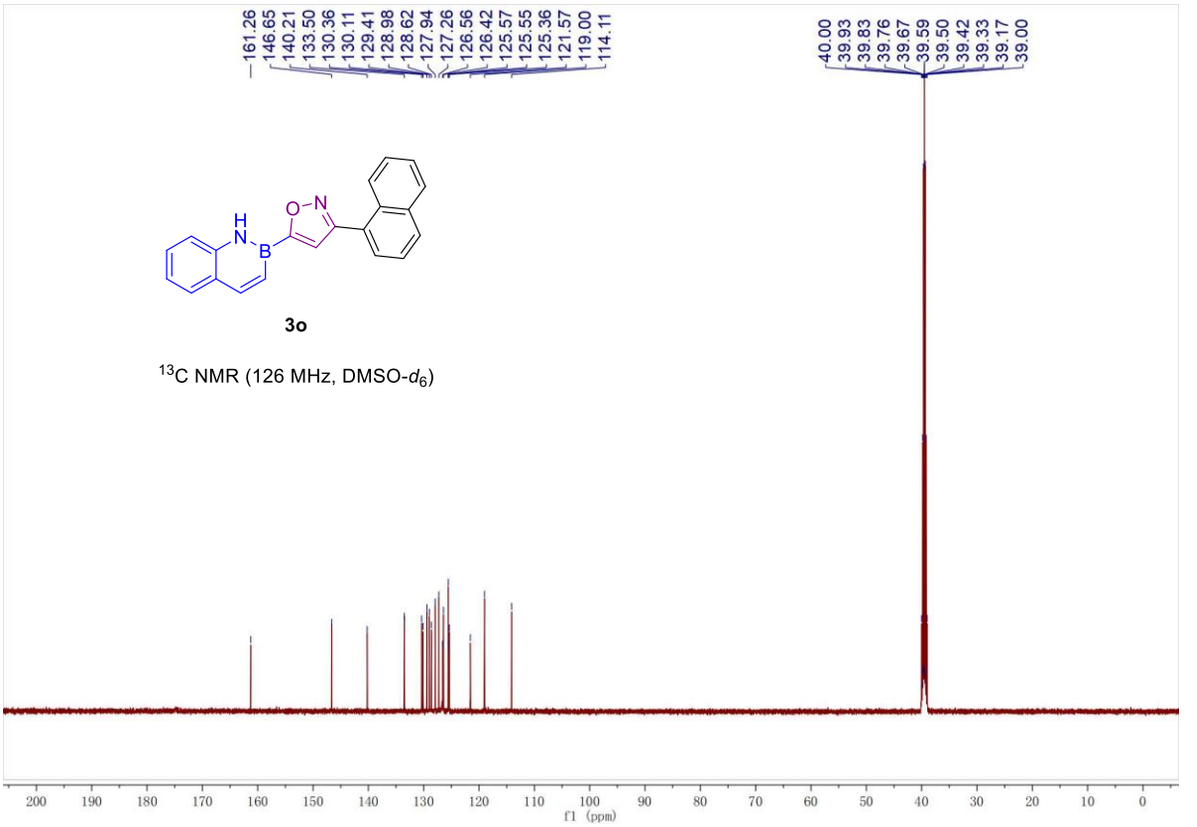
methyl 3-(5-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazol-3-yl)benzoate (3n)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphth654-alen-1-yl)isoxazole (3o)

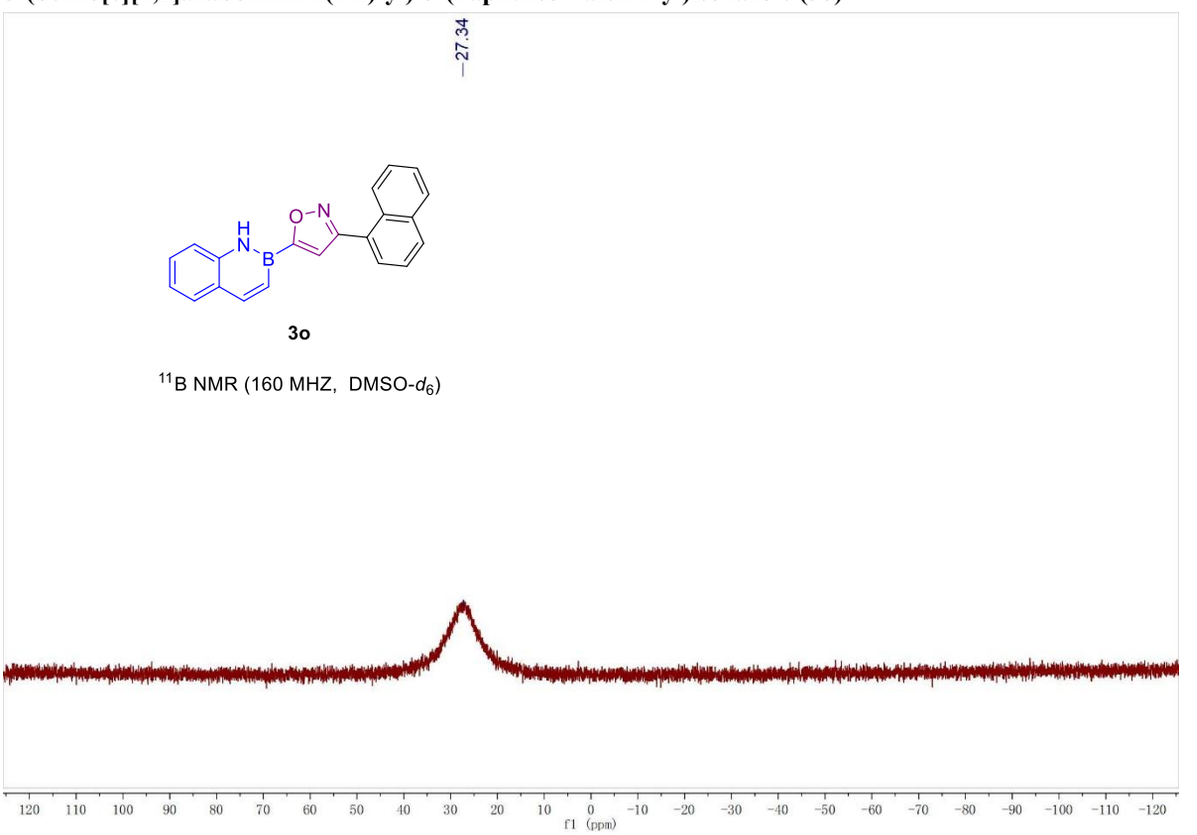


5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphth654-alen-1-yl)isoxazole (3o)



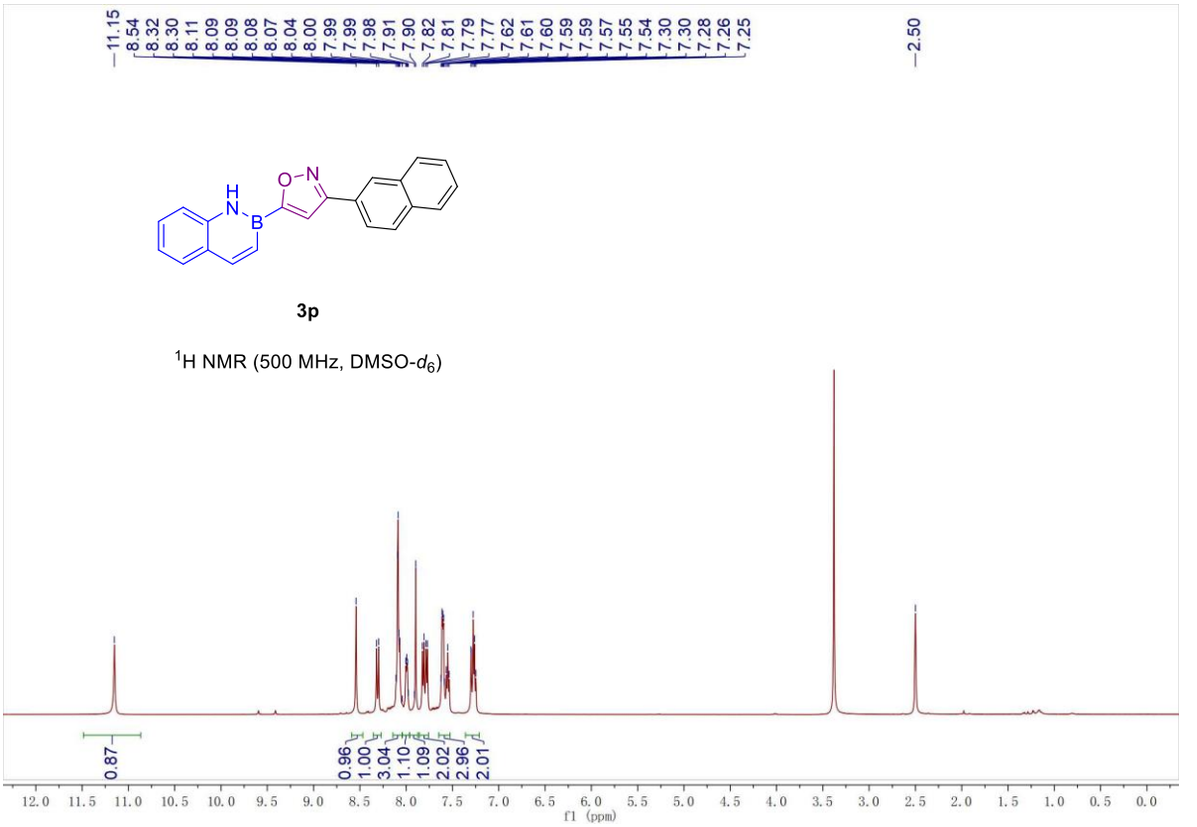
^{13}C NMR (126 MHz, DMSO-d_6)

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphth654-alen-1-yl)isoxazole (3o)

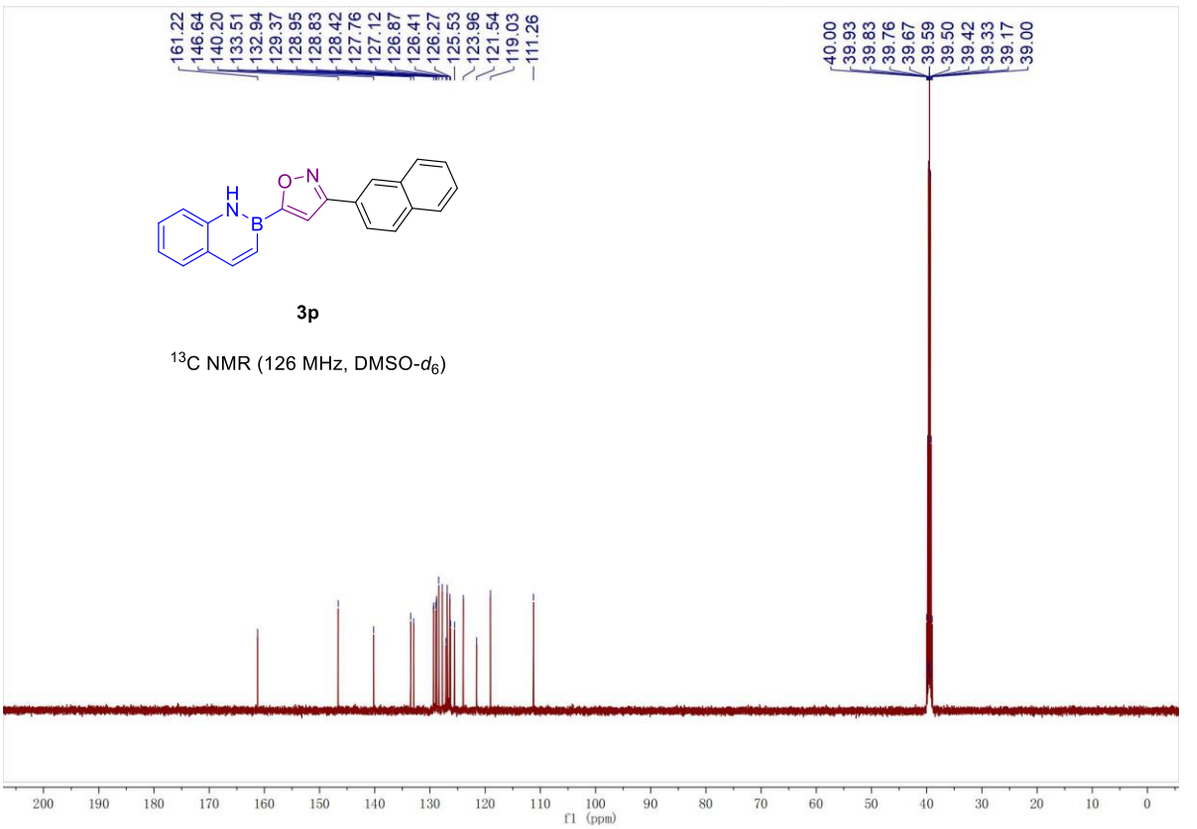


^{11}B NMR (160 MHZ, DMSO-d_6)

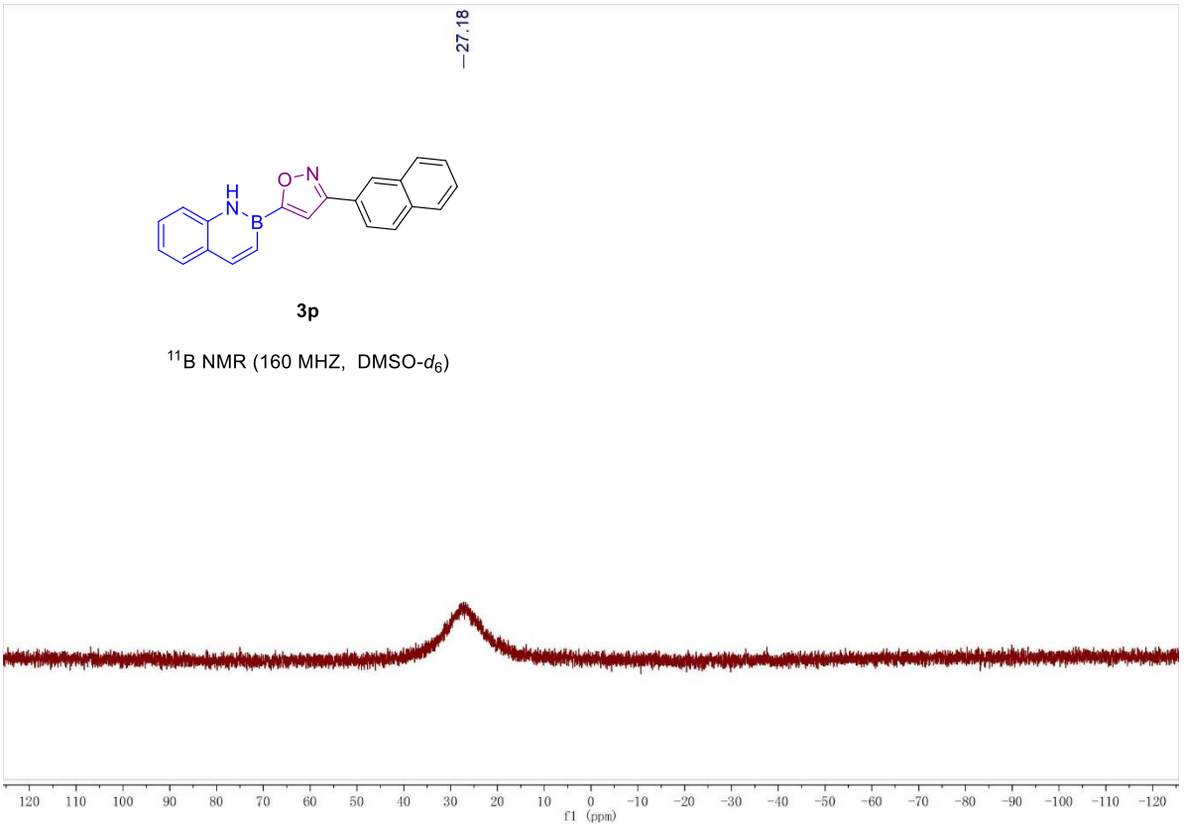
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphthalen-2-yl)isoxazole (3p)



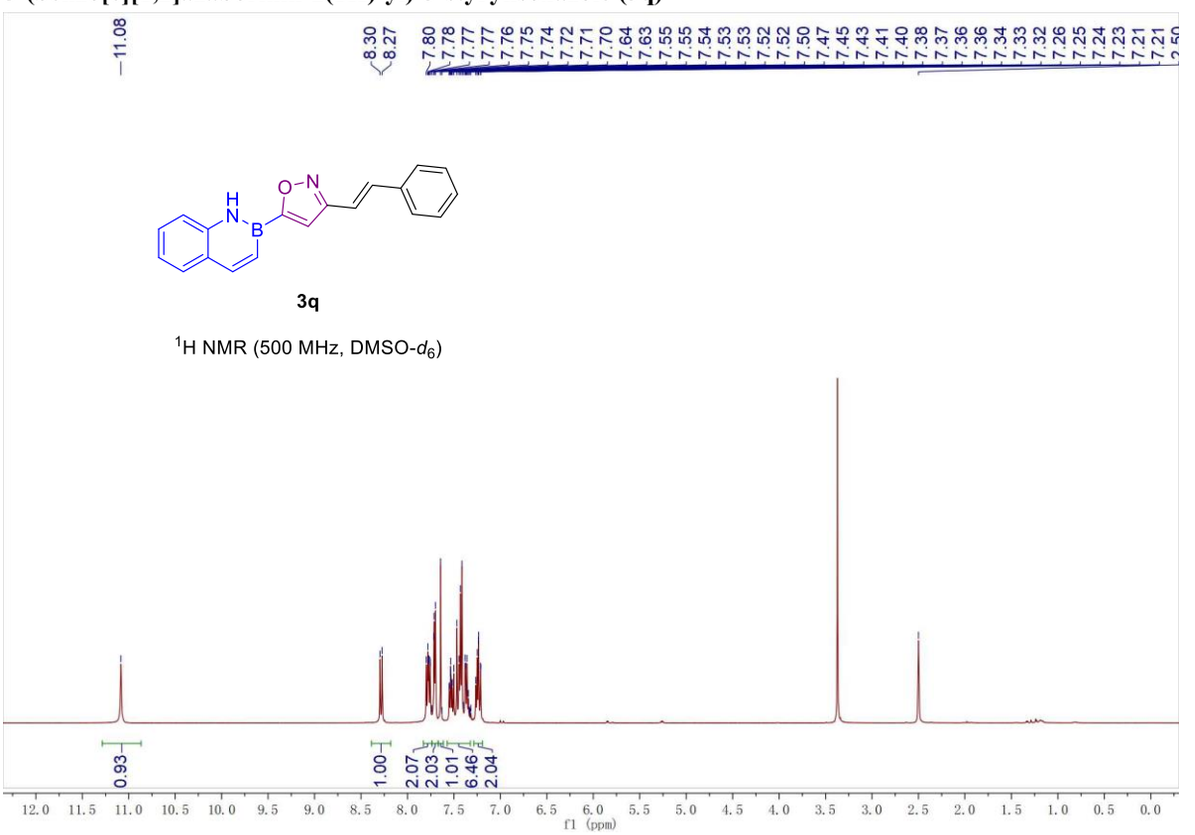
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphthalen-2-yl)isoxazole (3p)



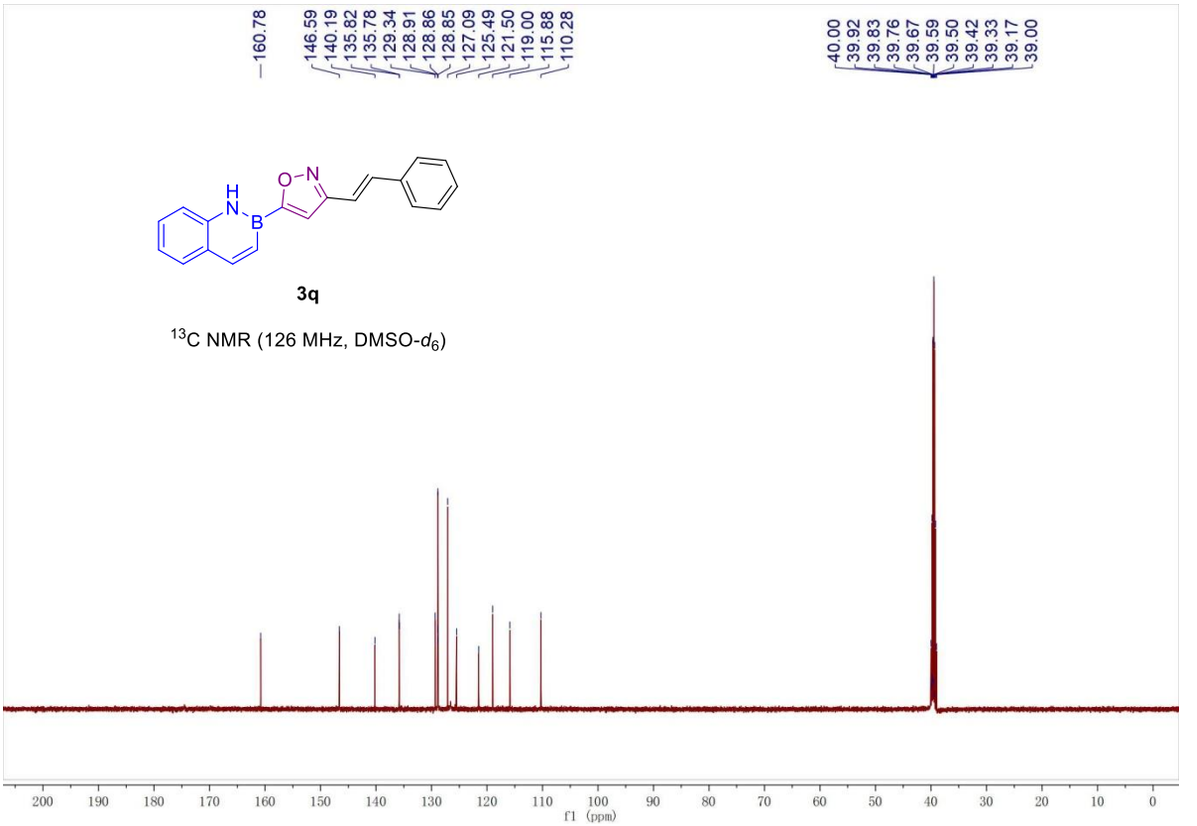
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphthalen-2-yl)isoxazole (3p)



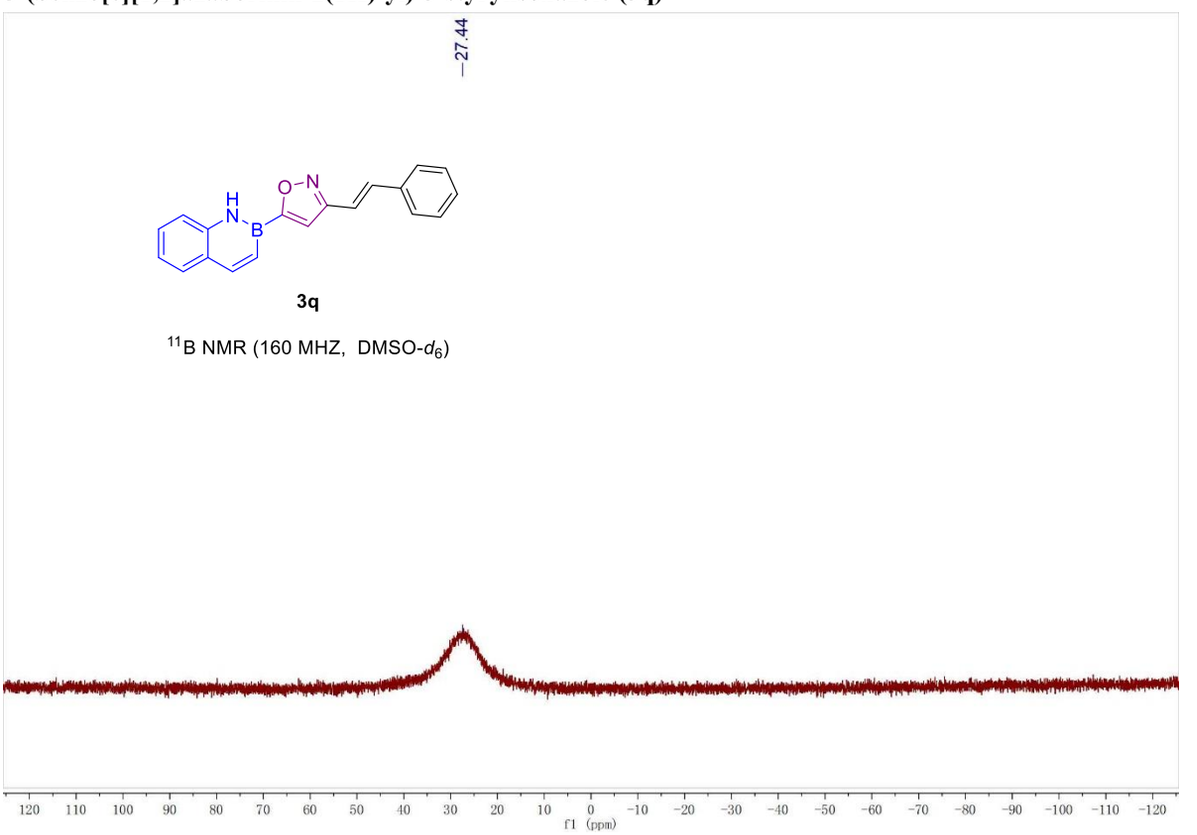
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-styrylisoxazole (3q)



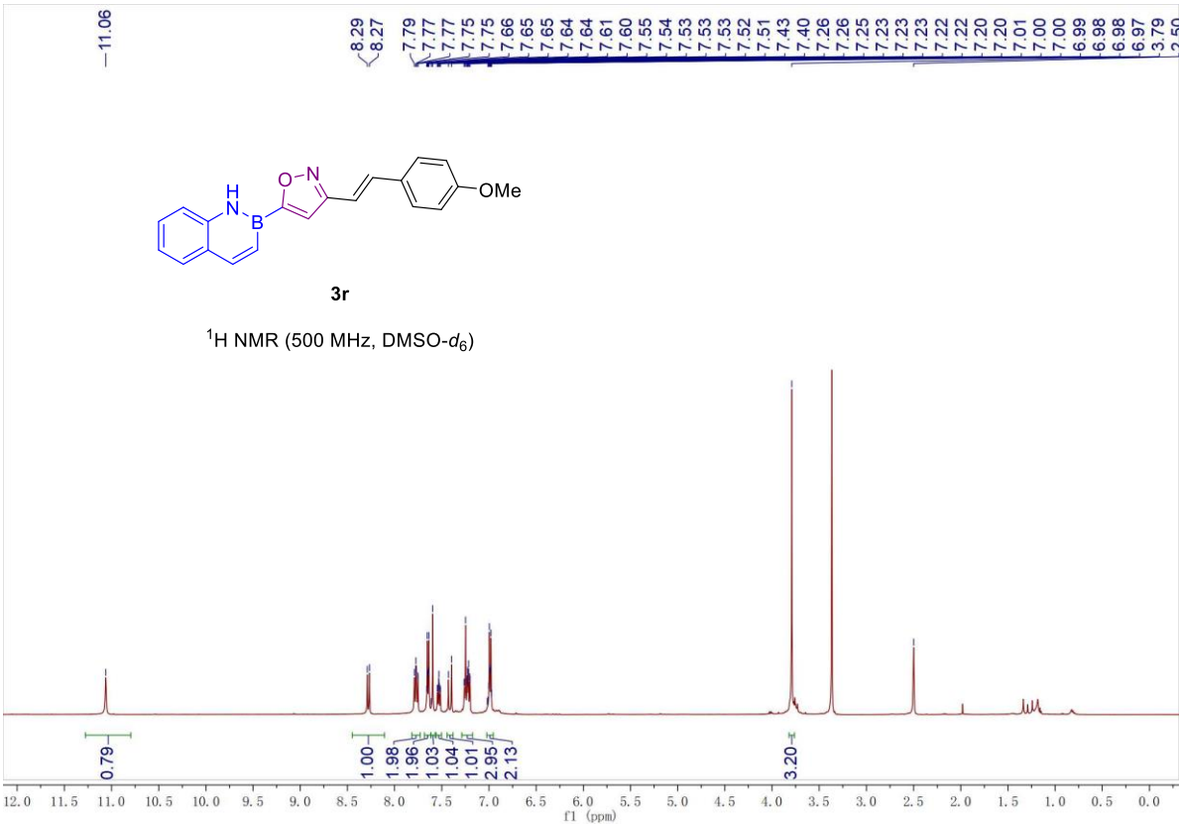
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-styrylisoxazole (3q)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-styrylisoxazole (3q)



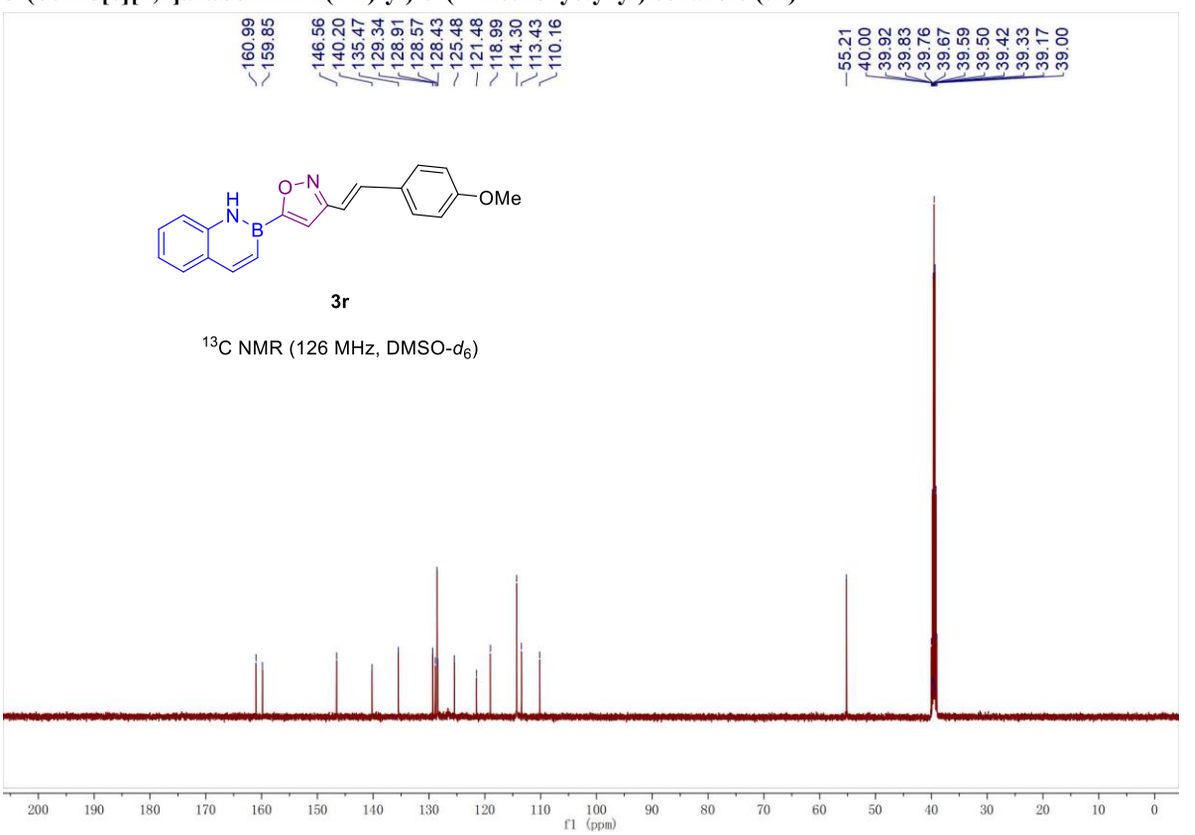
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxystyryl)isoxazole (3r)



3r

^{1}H NMR (500 MHz, DMSO-d_6)

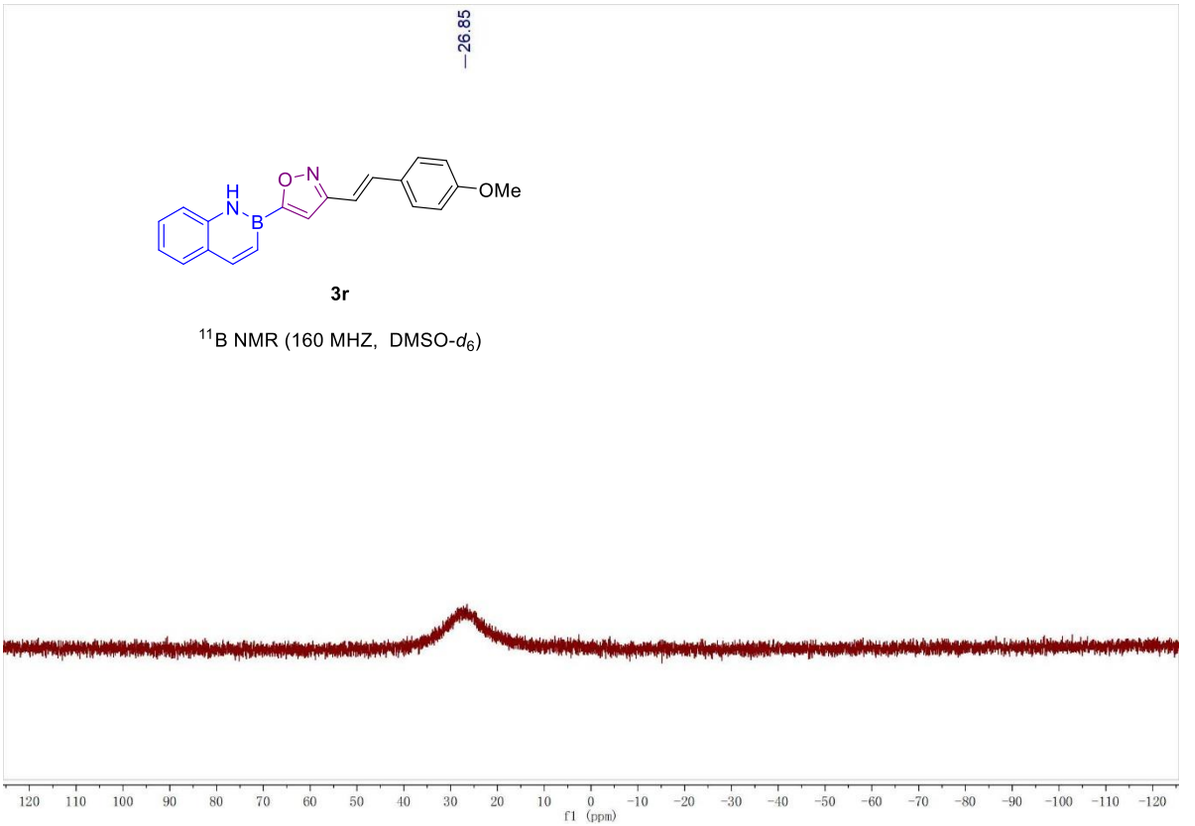
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxystyryl)isoxazole (3r)



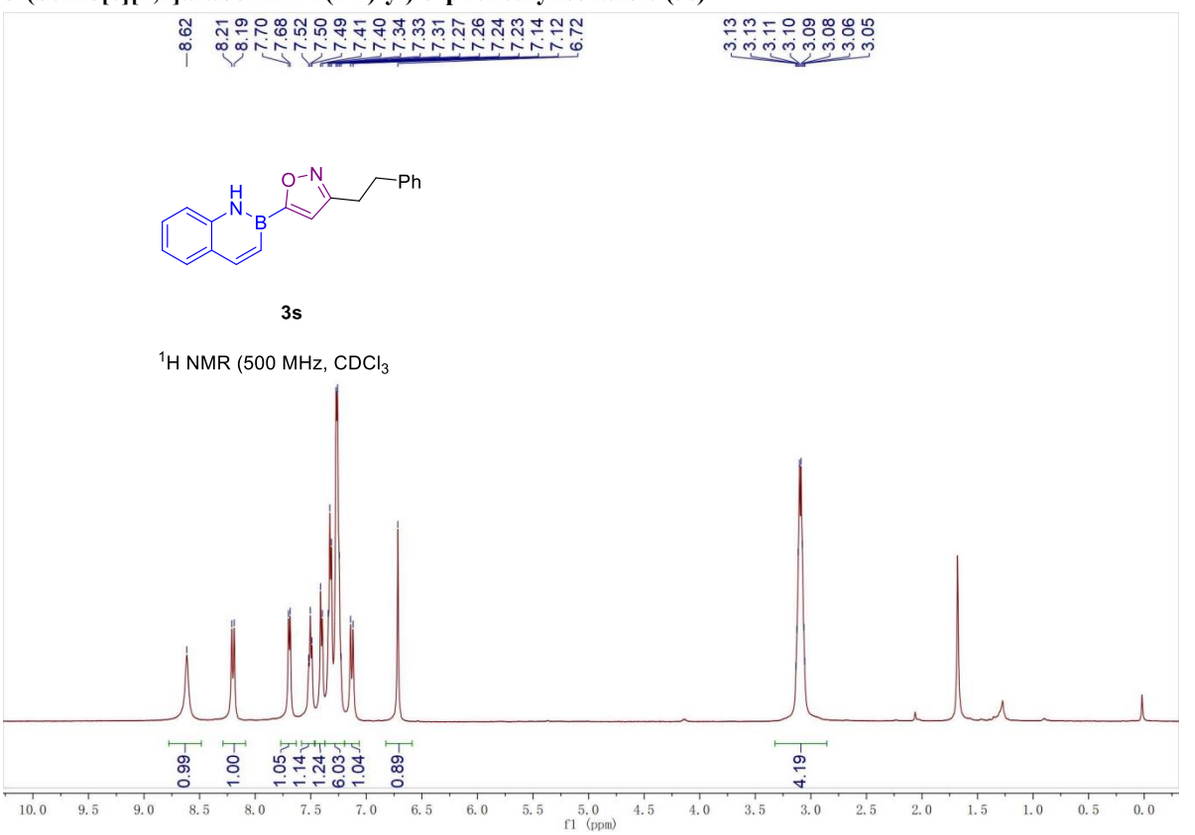
3r

^{13}C NMR (126 MHz, DMSO-d_6)

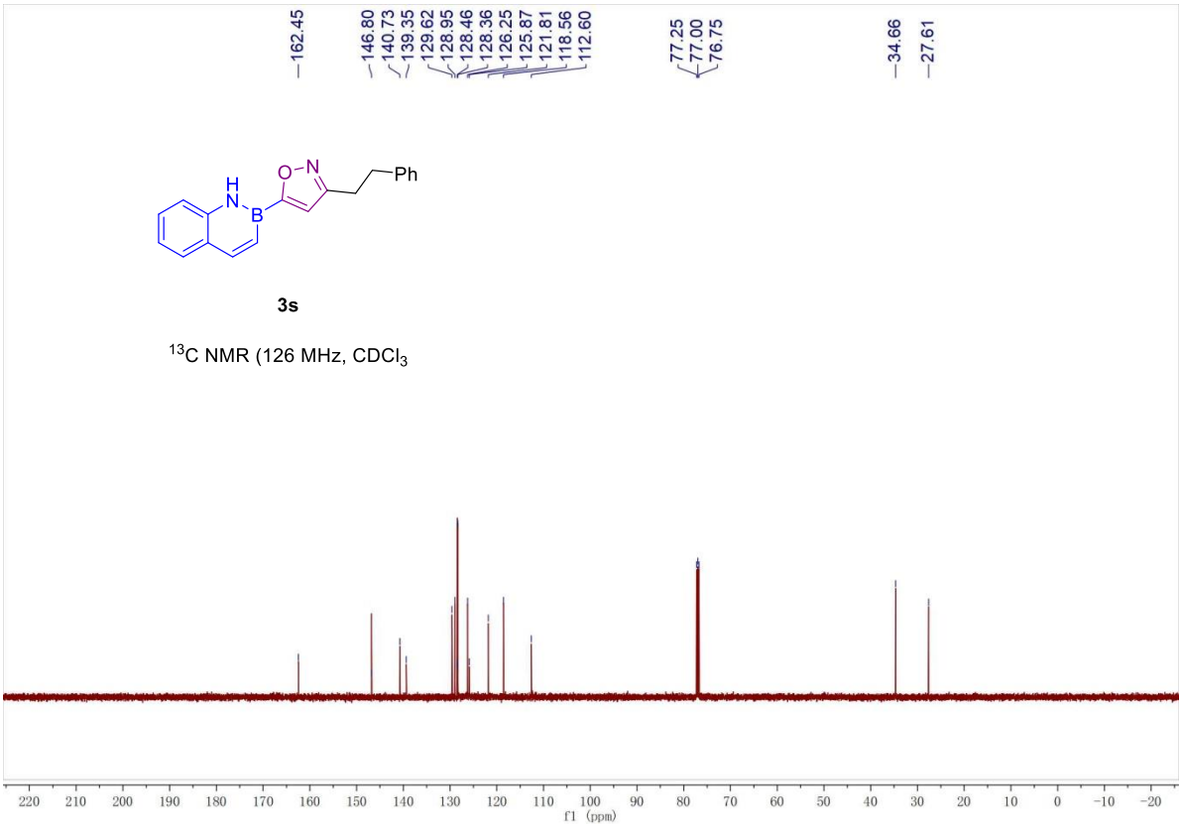
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxystyryl)isoxazole (3r)



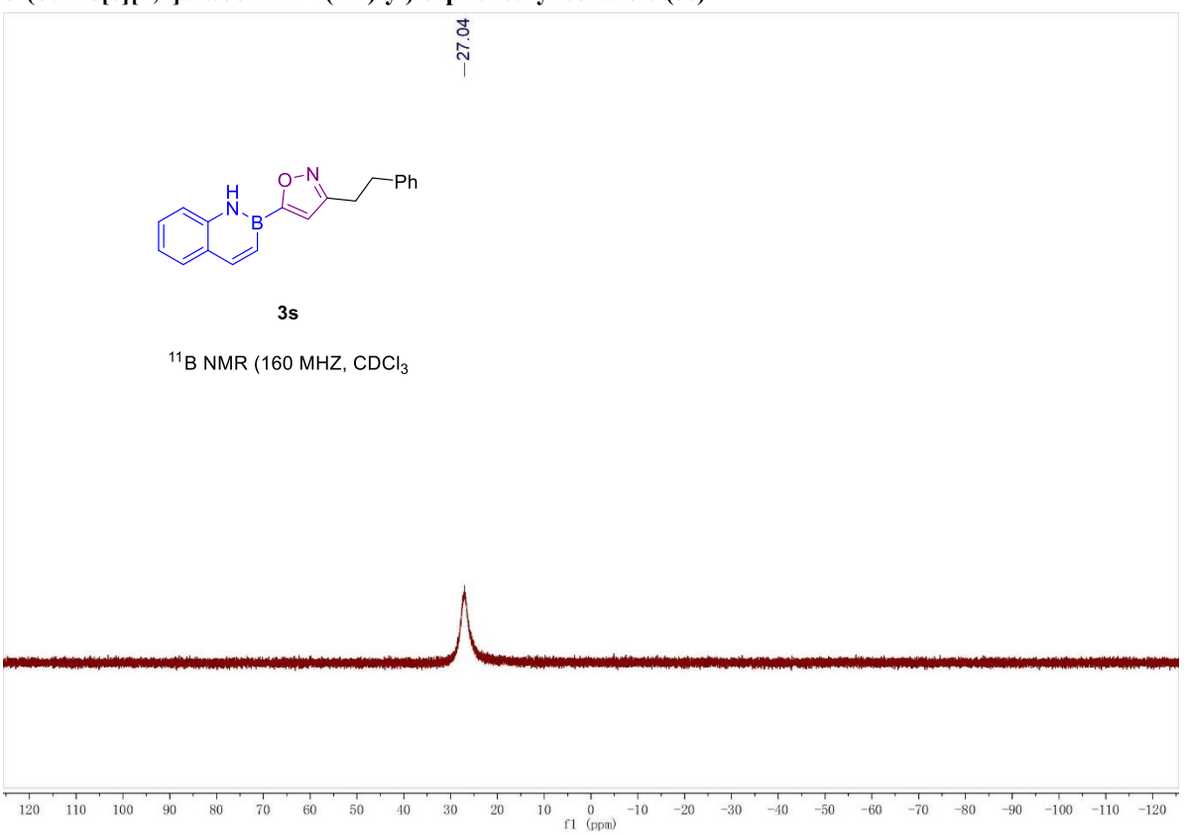
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenethylisoxazole (3s)



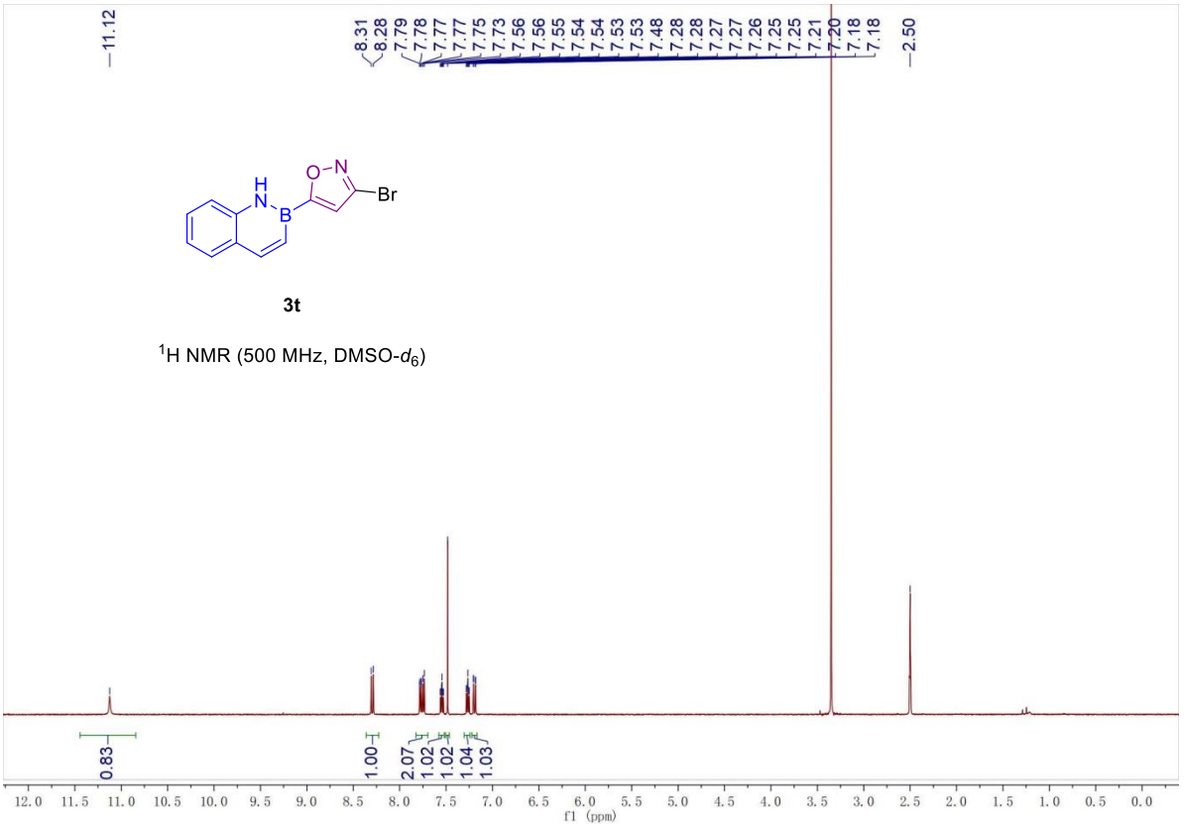
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenethylisoxazole (3s)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenethylisoxazole (3s)



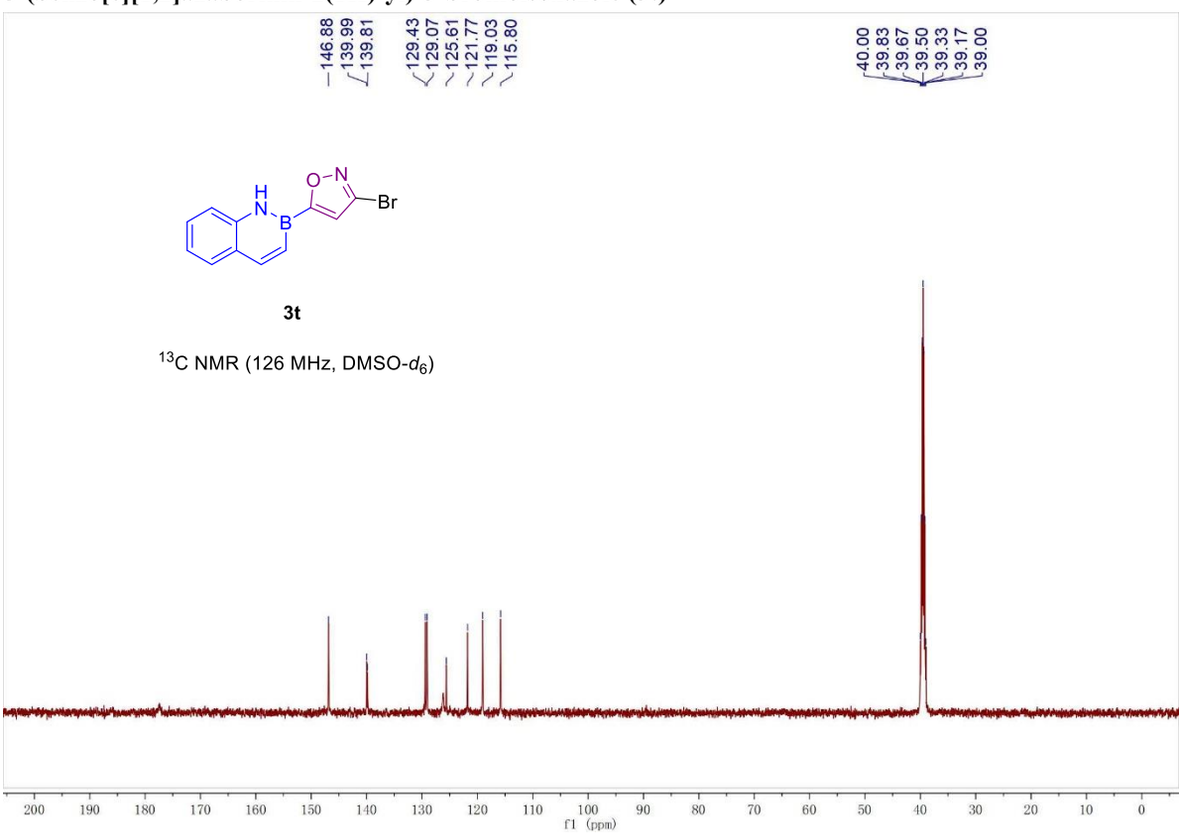
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-bromoisoxazole (3t)



3t

^{1}H NMR (500 MHz, DMSO-d_6)

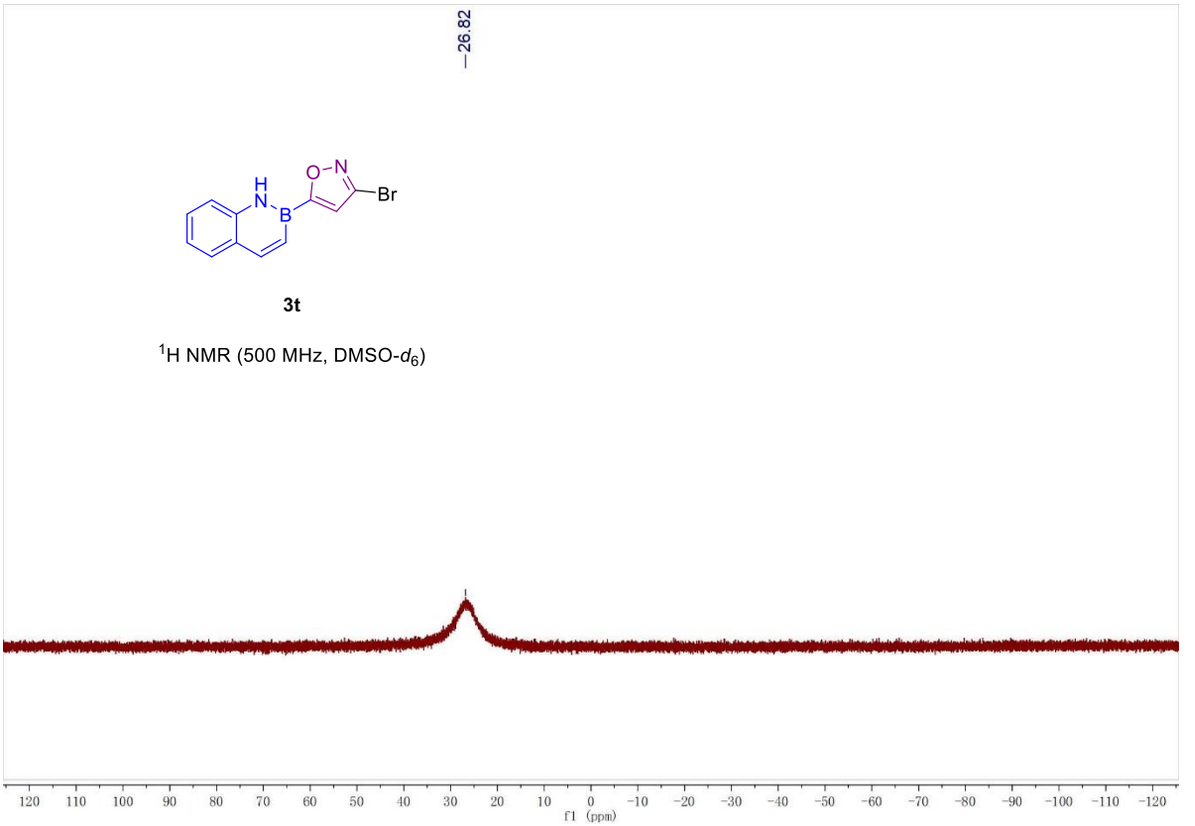
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-bromoisoxazole (3t)



3t

^{13}C NMR (126 MHz, DMSO-d_6)

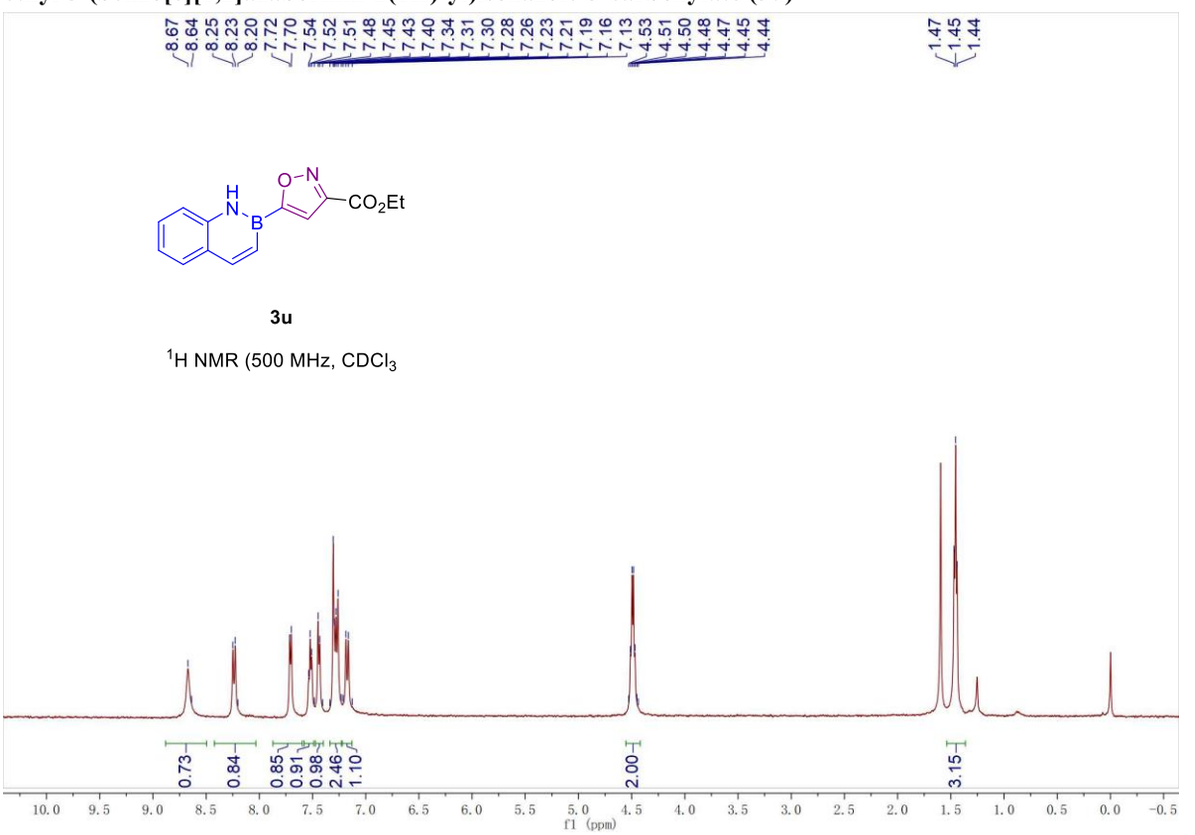
5-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-bromoisoxazole (3t)



3t

^{1}H NMR (500 MHz, DMSO-d_6)

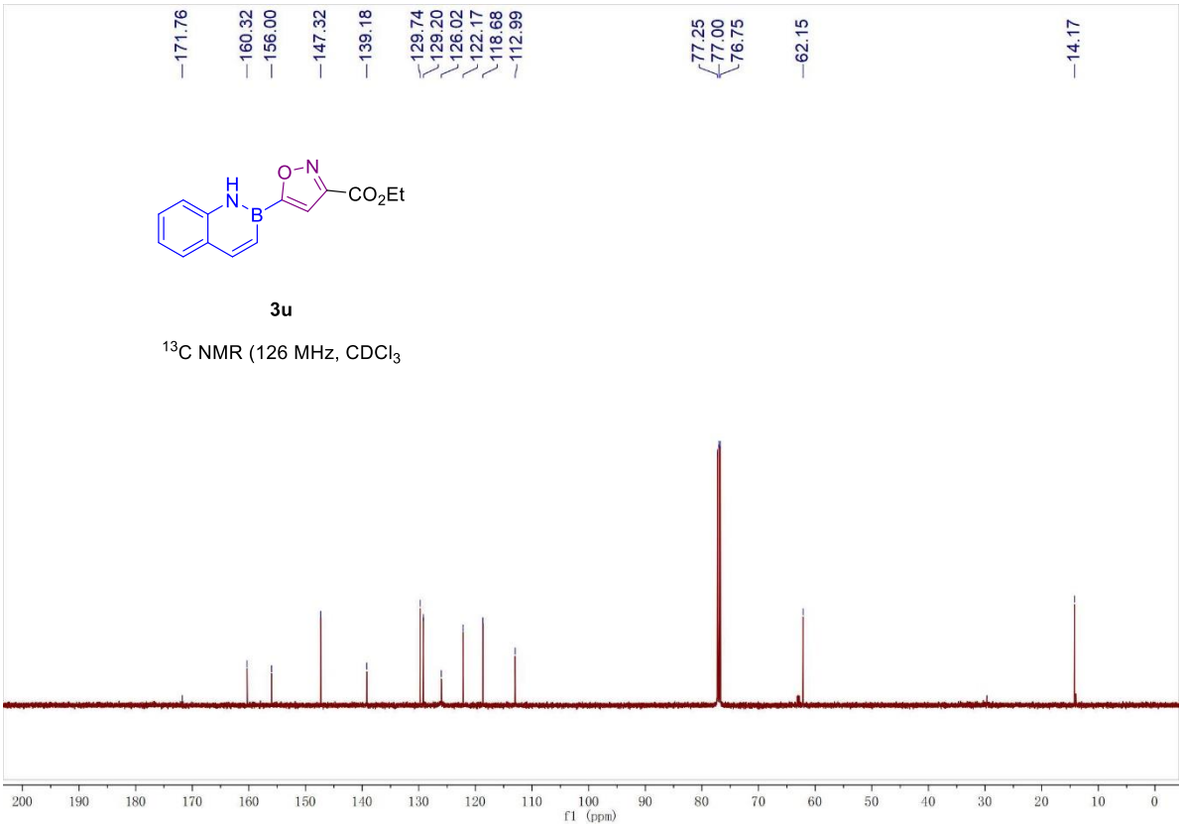
ethyl 5-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole-3-carboxylate (3u)



3u

^{1}H NMR (500 MHz, $CDCl_3$

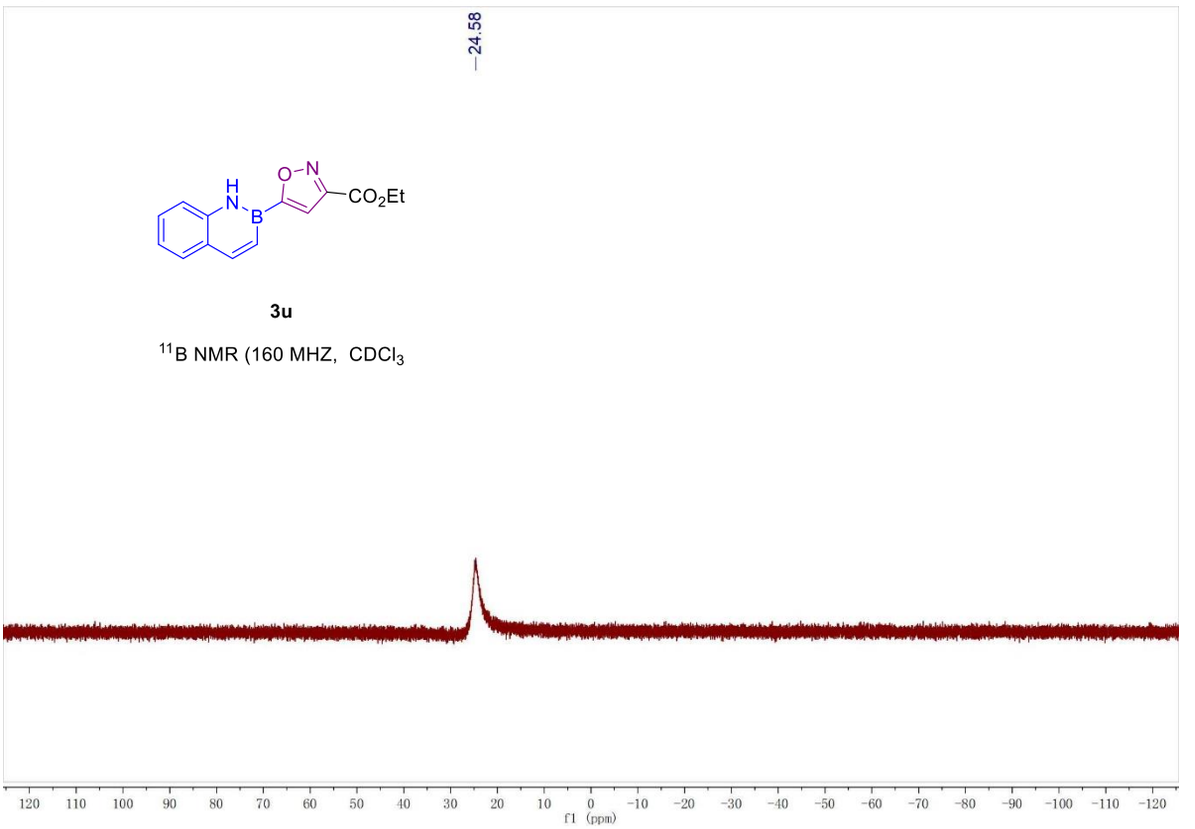
ethyl 5-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole-3-carboxylate (3u)



3u

^{13}C NMR (126 MHz, $CDCl_3$

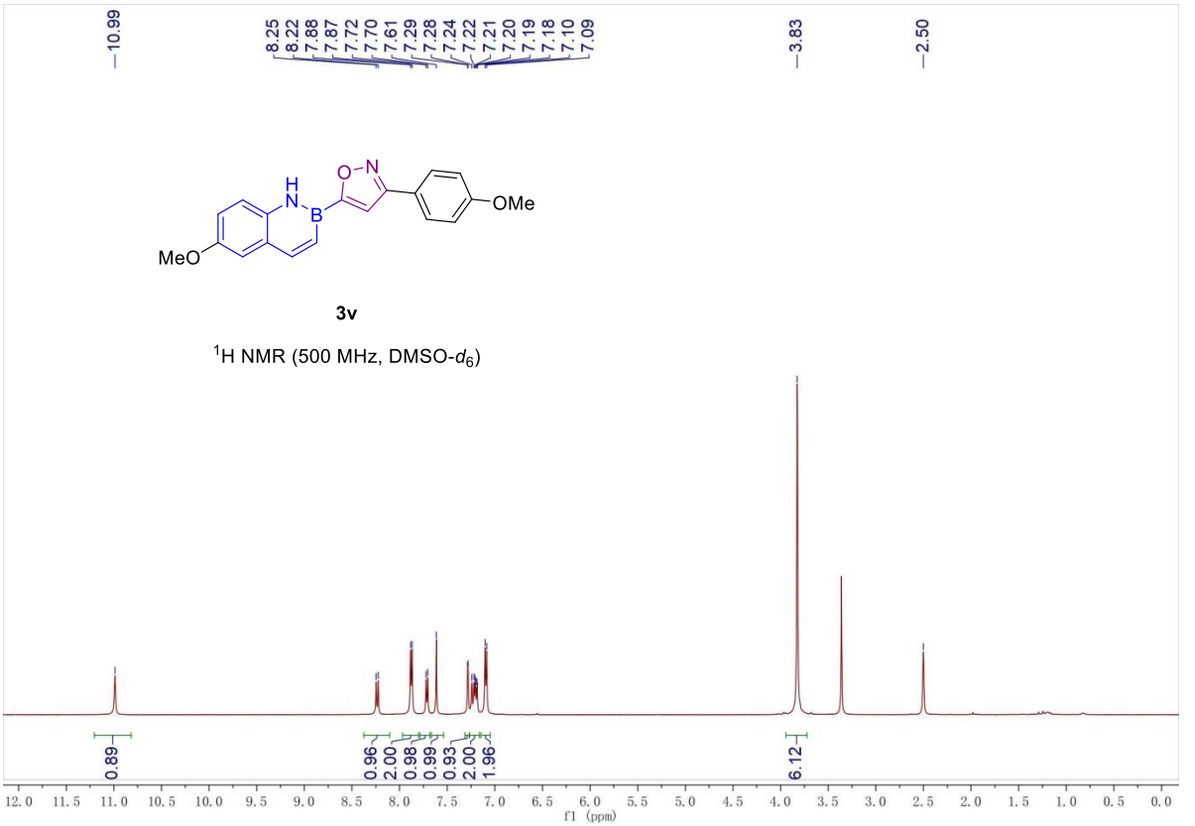
ethyl 5-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole-3-carboxylate (3u)



3u

^{11}B NMR (160 MHZ, $CDCl_3$

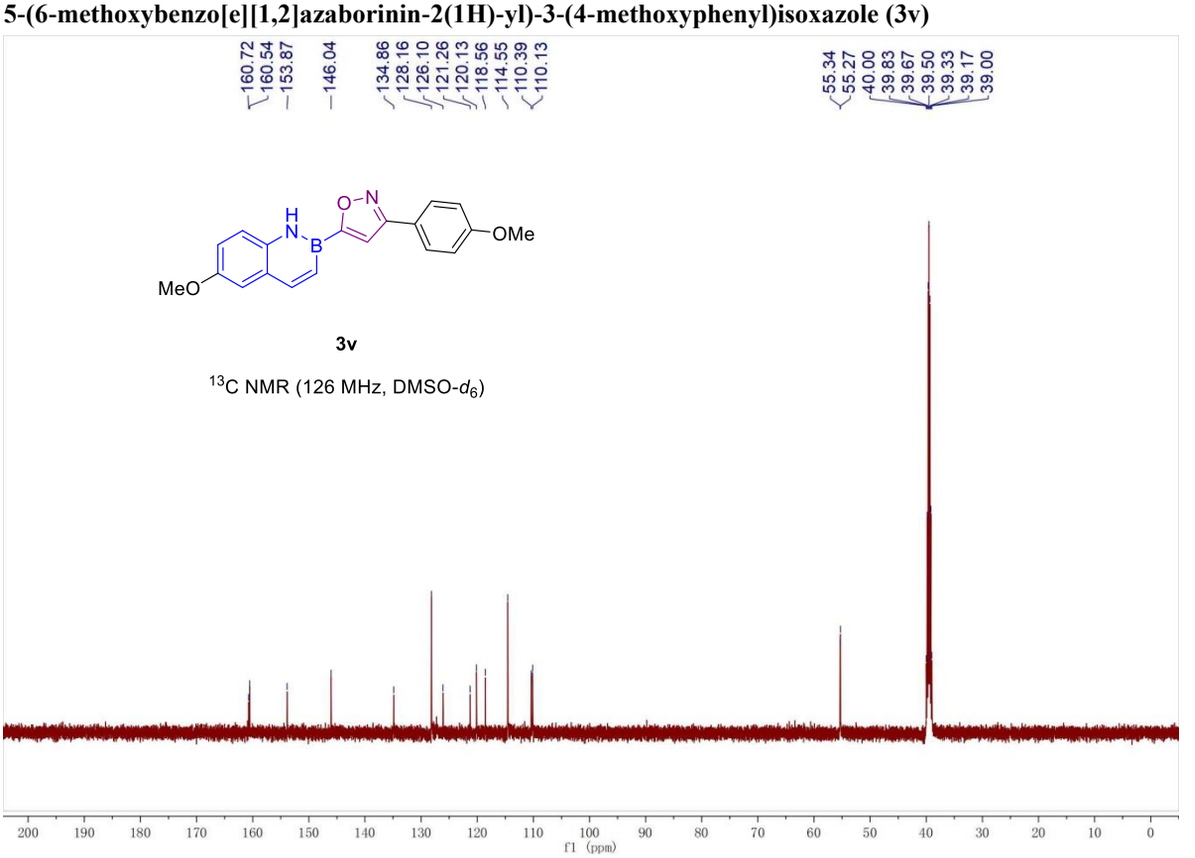
5-(6-methoxybenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3v)



3v

^{1}H NMR (500 MHz, DMSO-d_6)

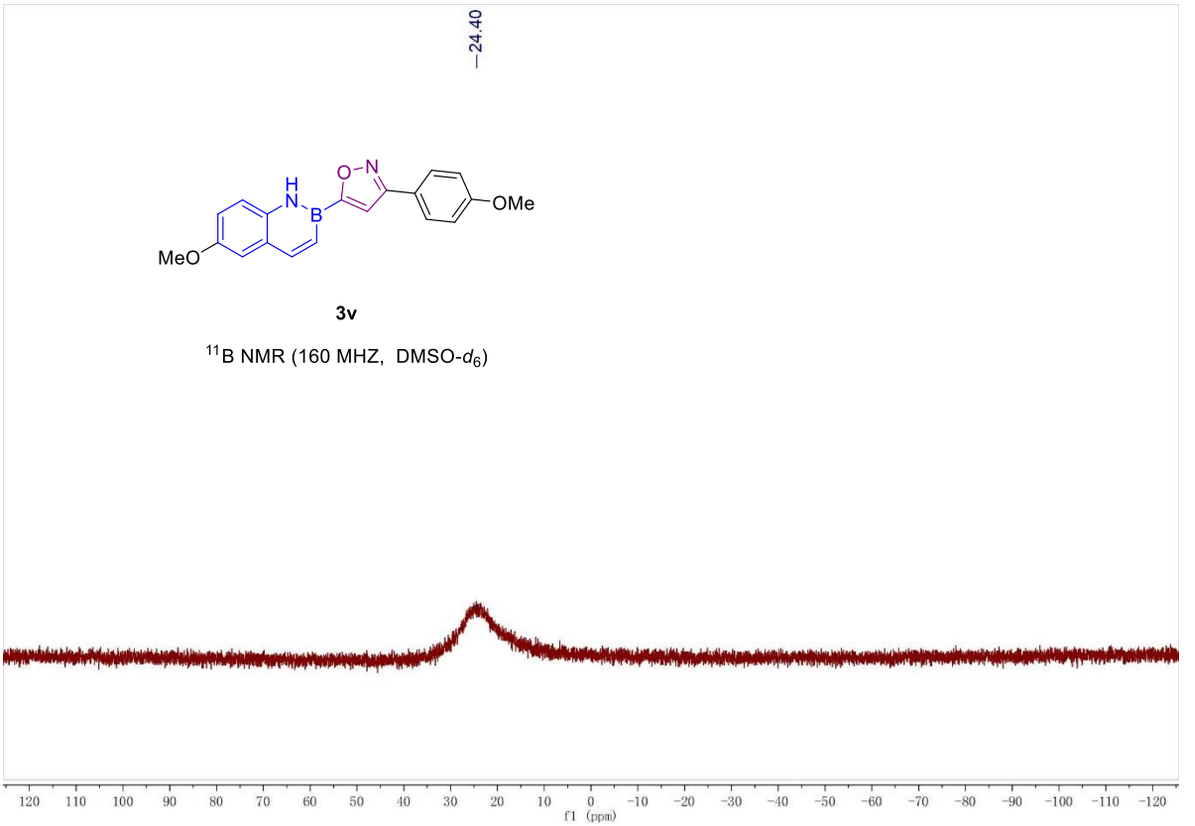
5-(6-methoxybenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3v)



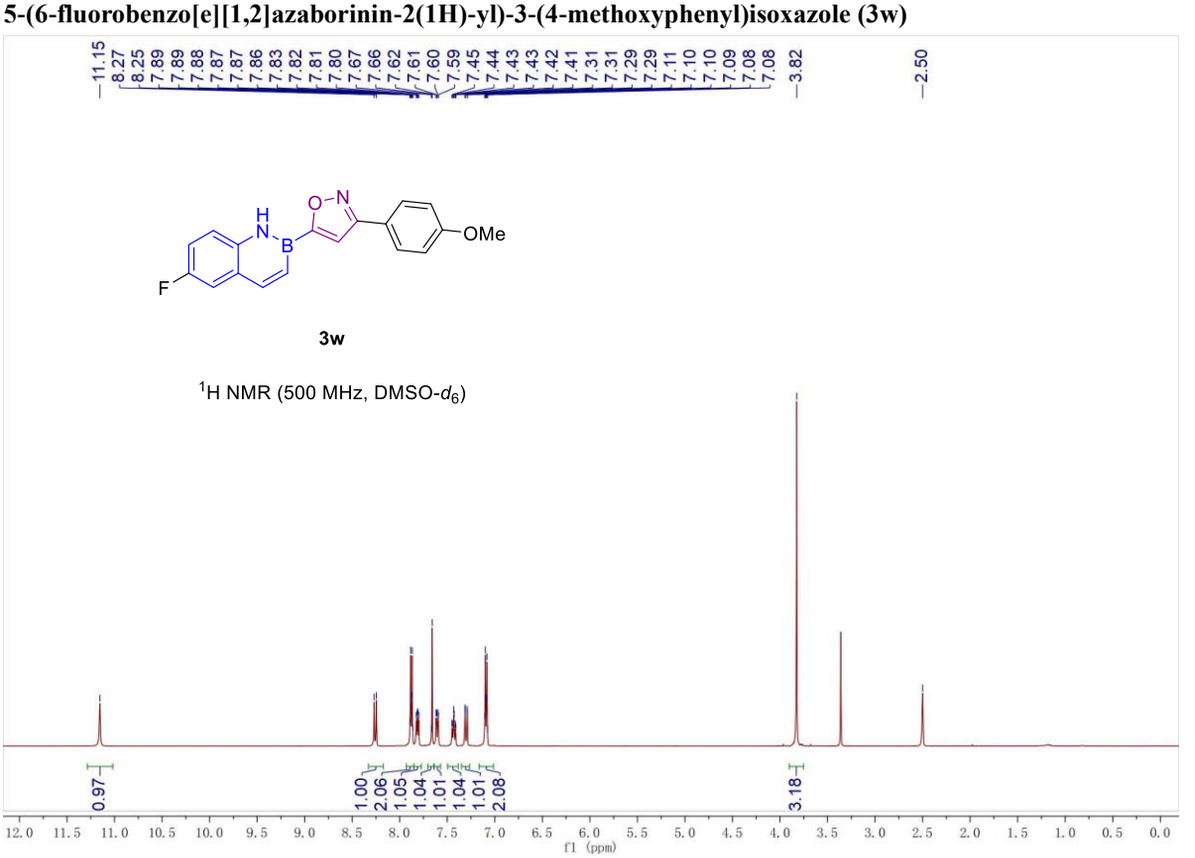
3v

^{13}C NMR (126 MHz, DMSO-d_6)

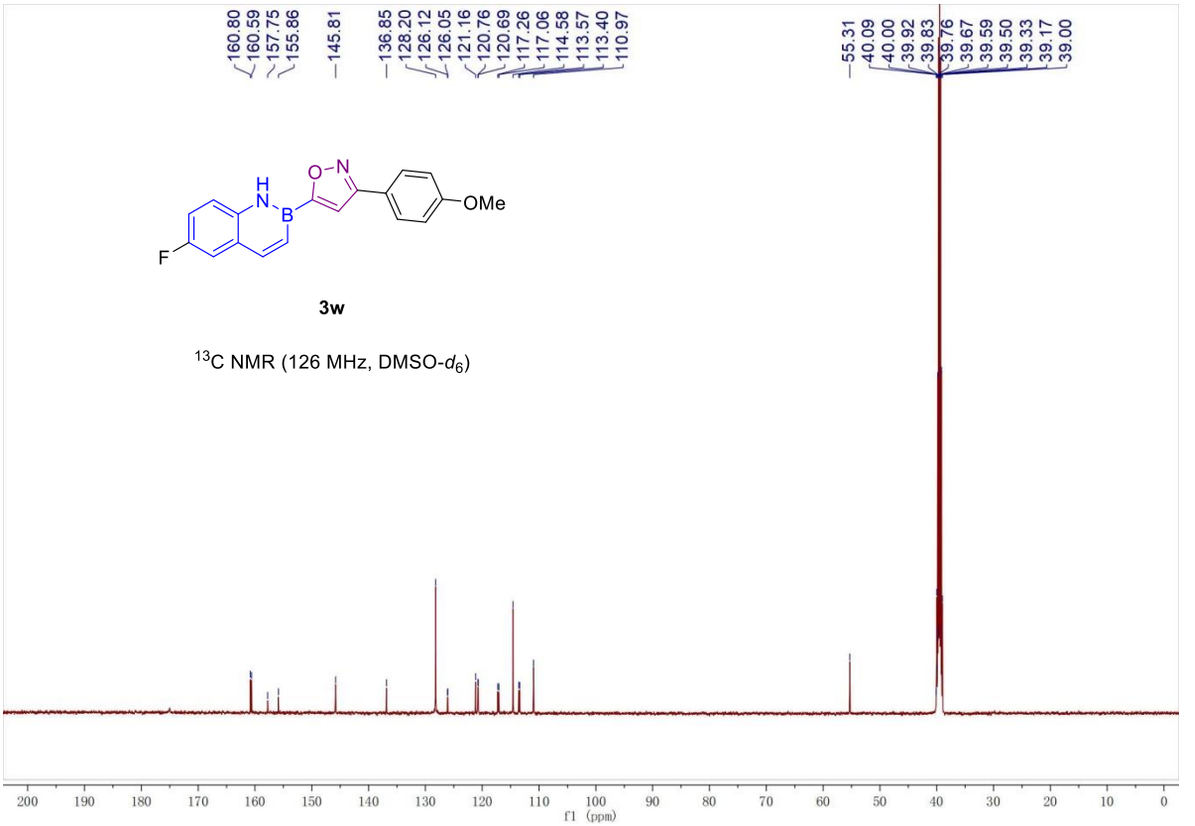
5-(6-methoxybenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3v)



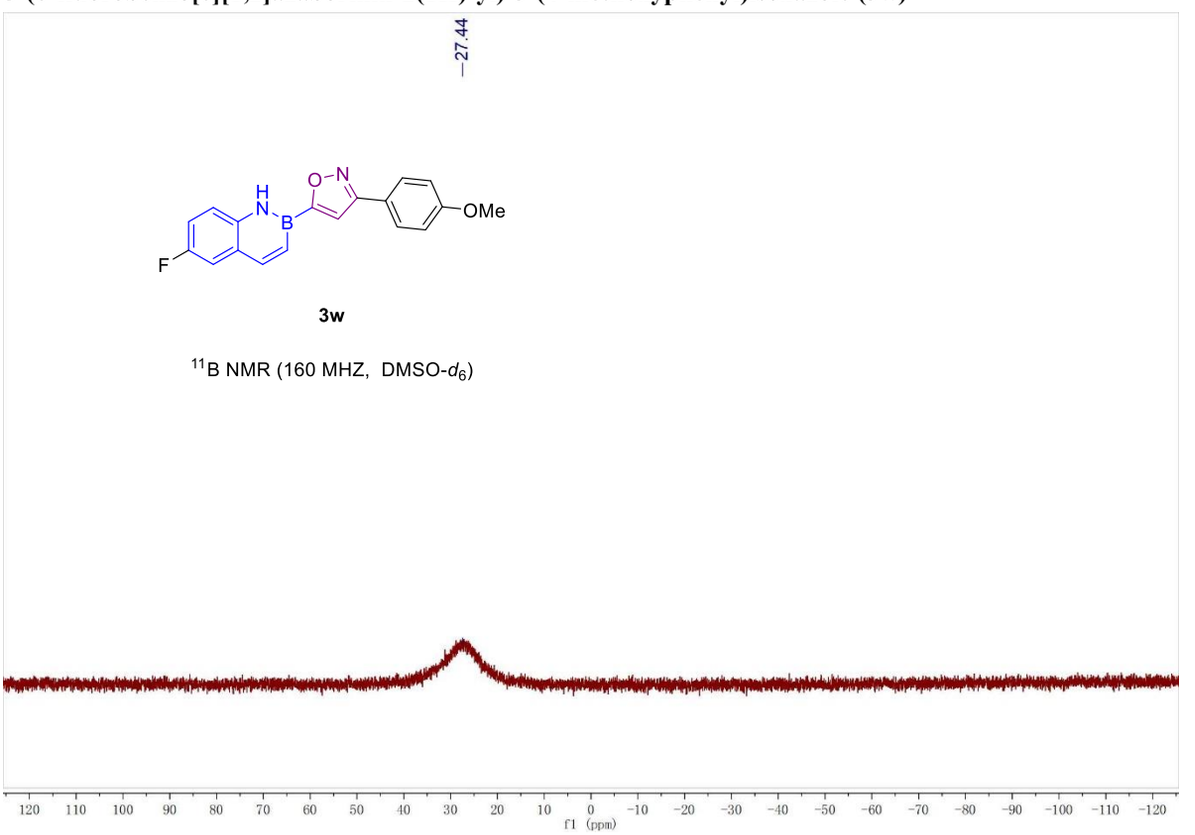
5-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3w)



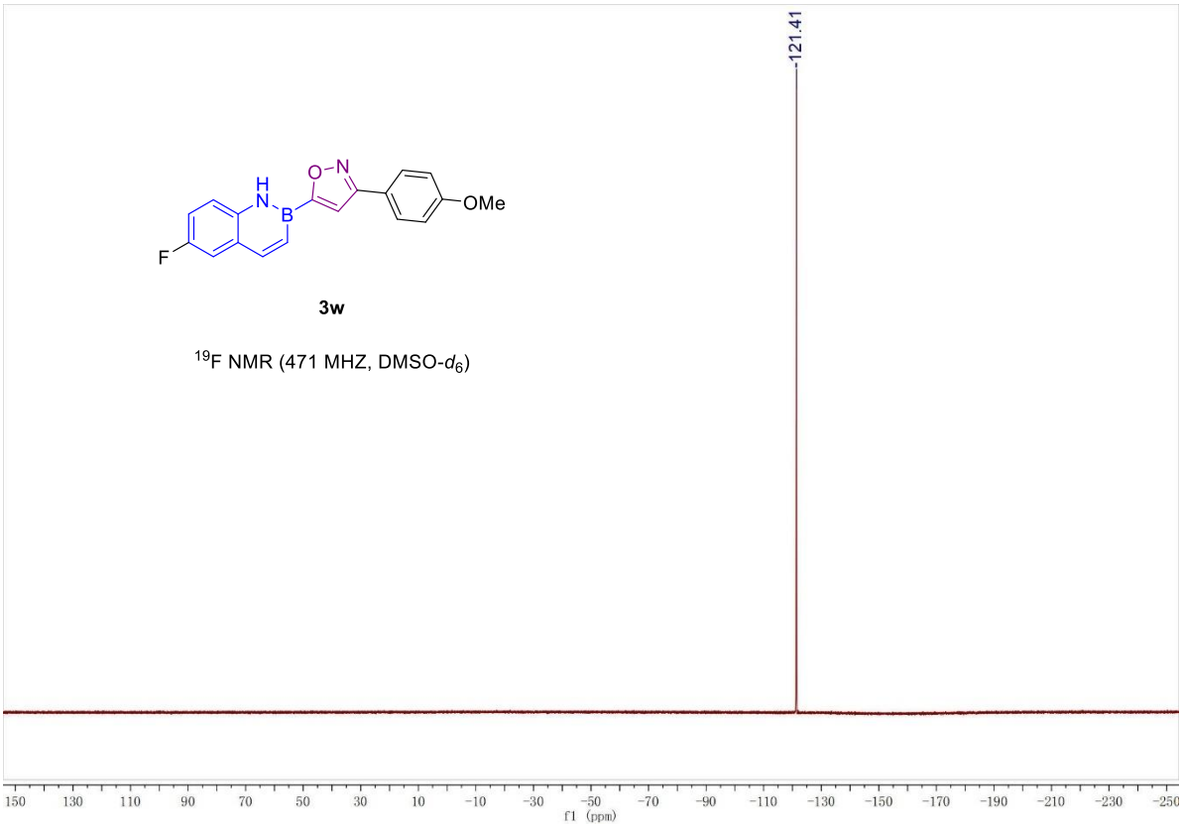
5-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3w)



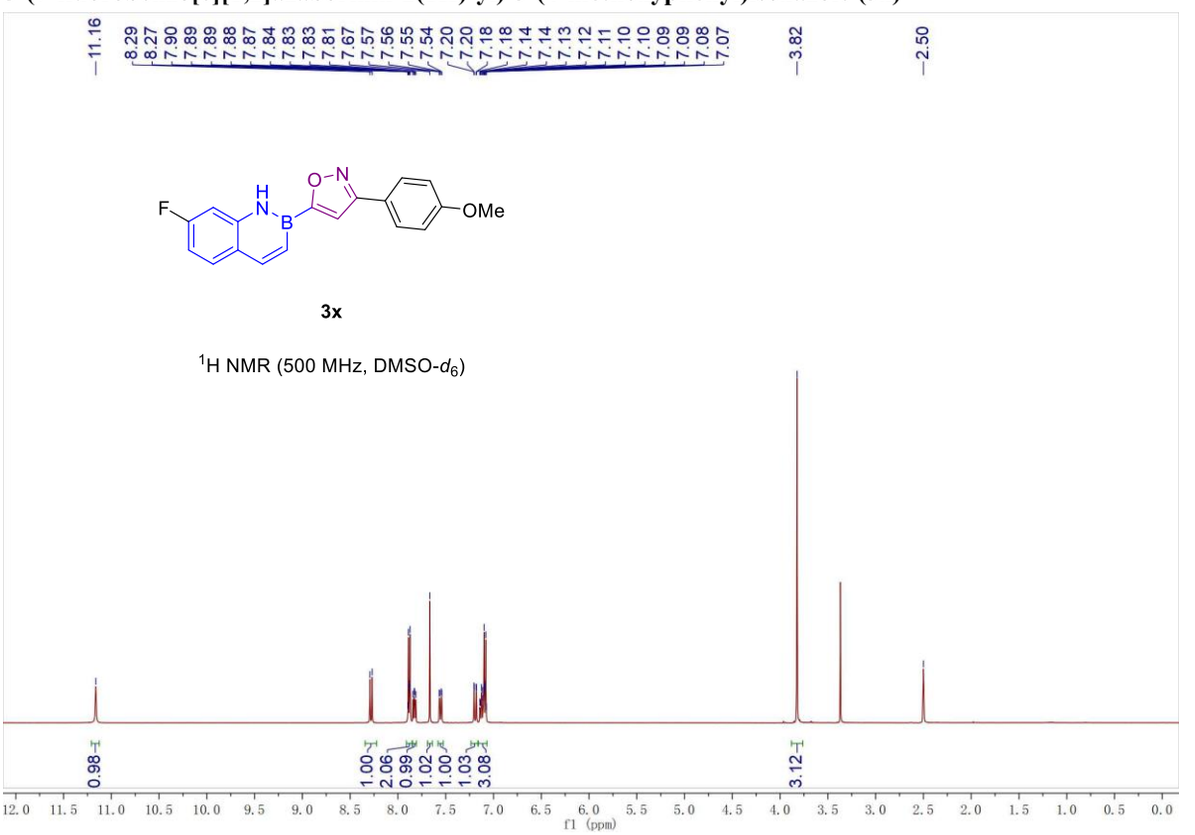
5-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3w)



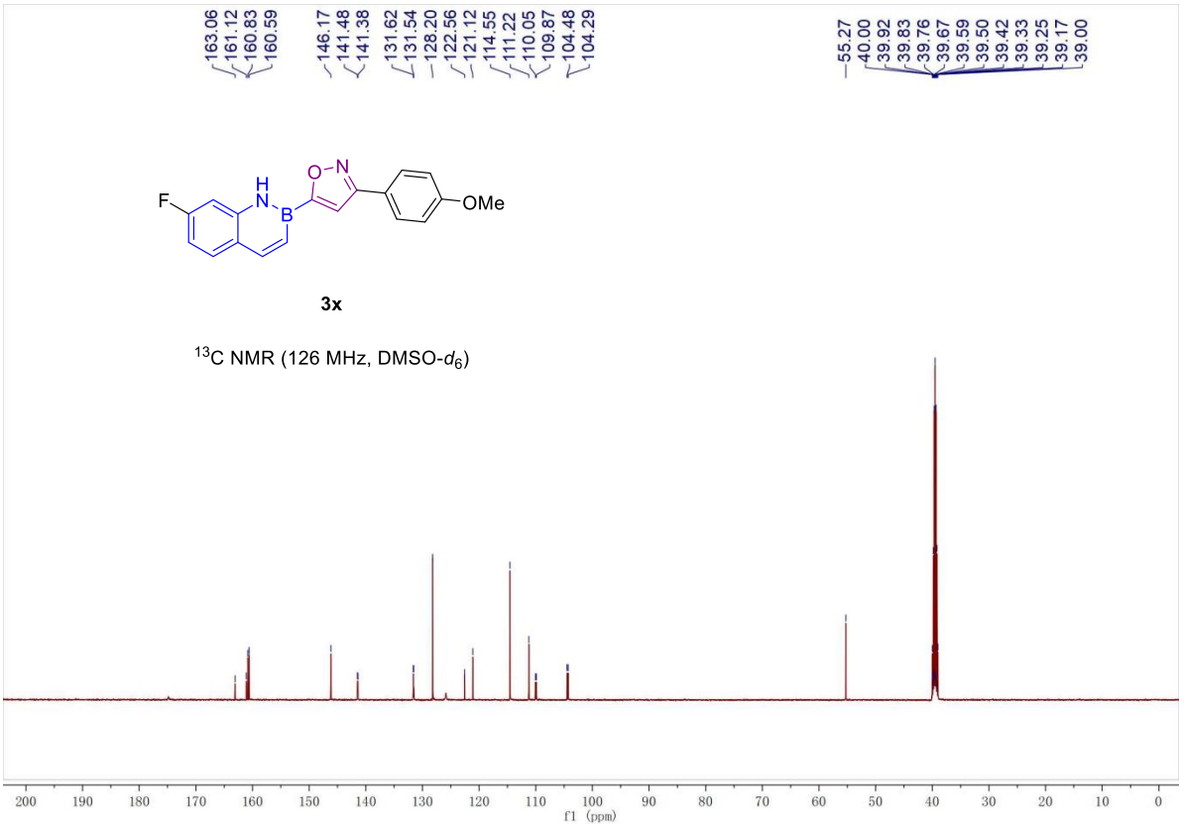
5-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3w)



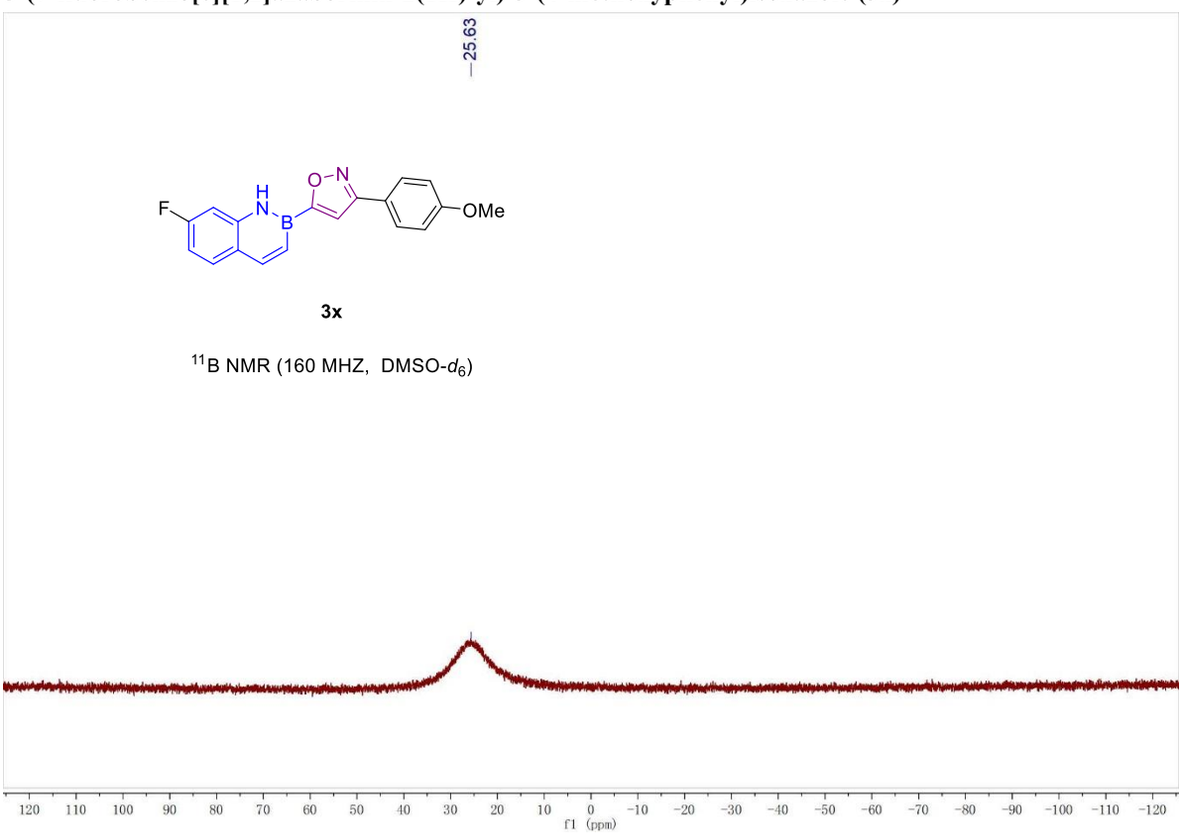
5-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3x)



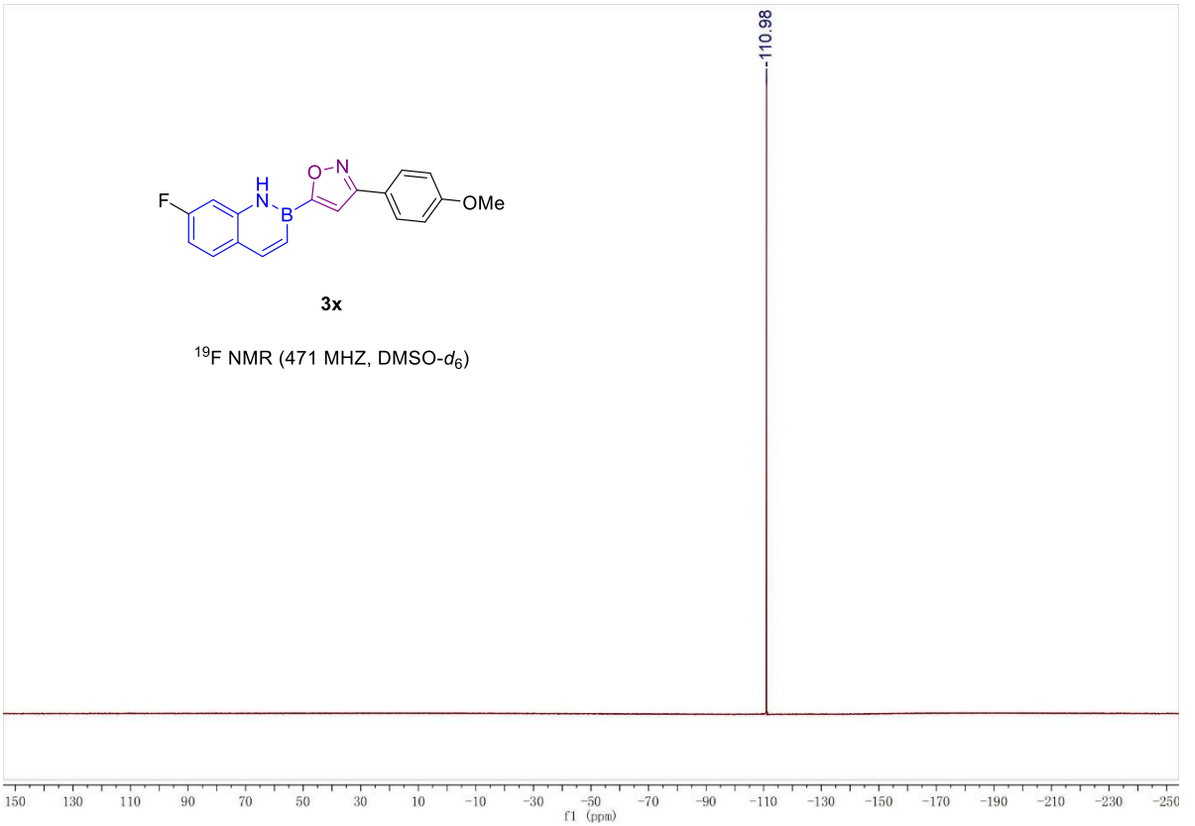
5-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3x)



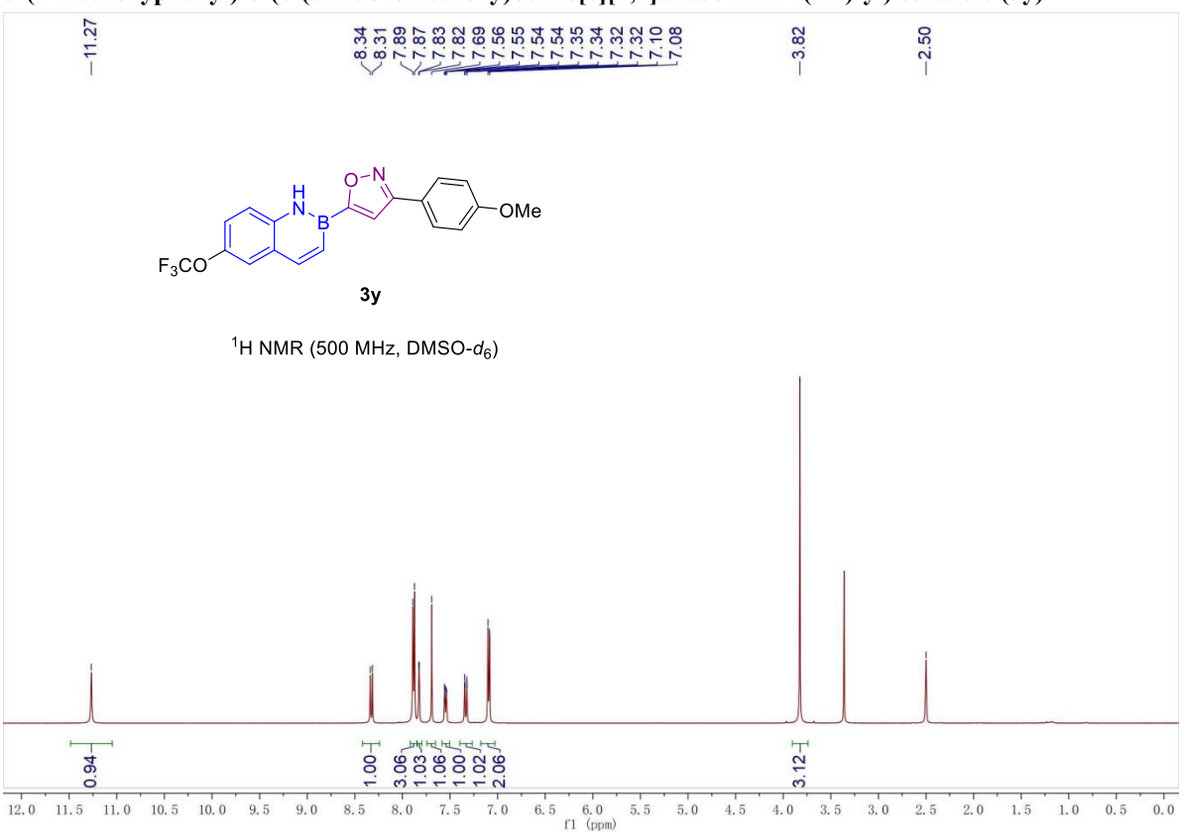
5-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3x)



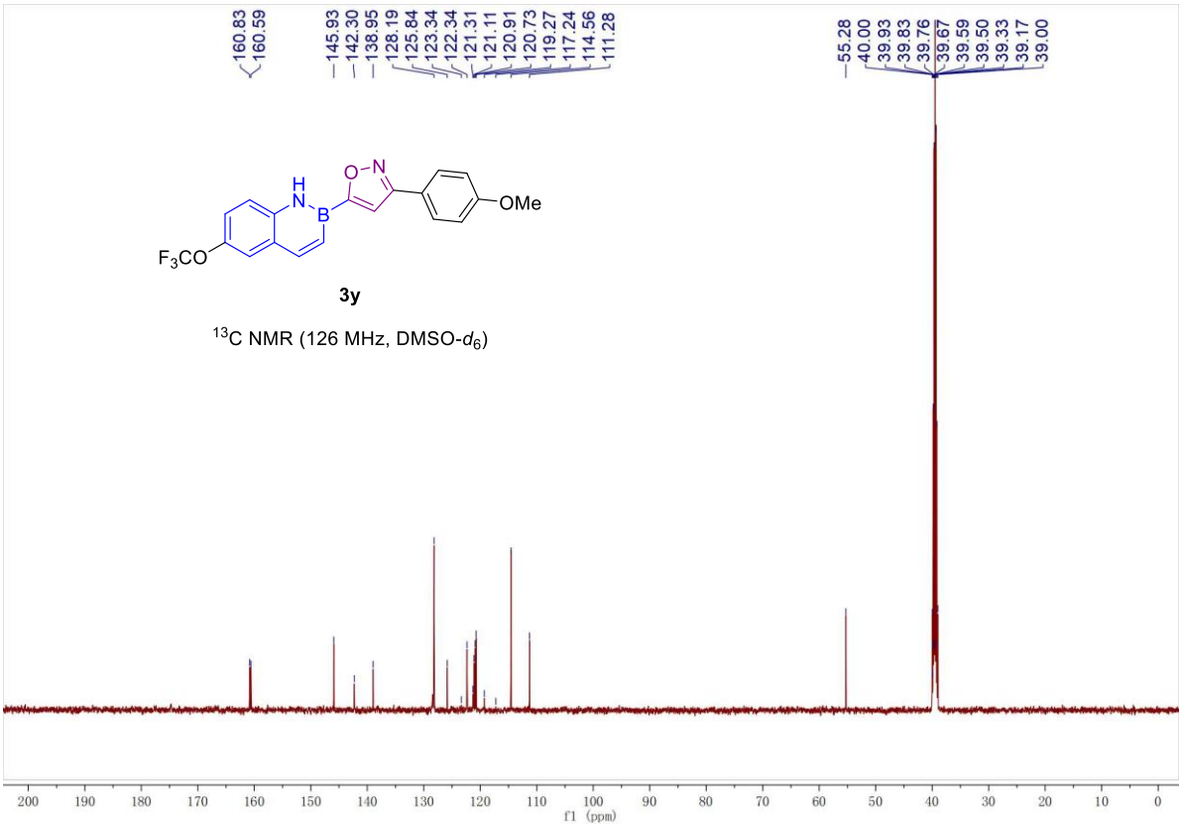
5-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (3x)



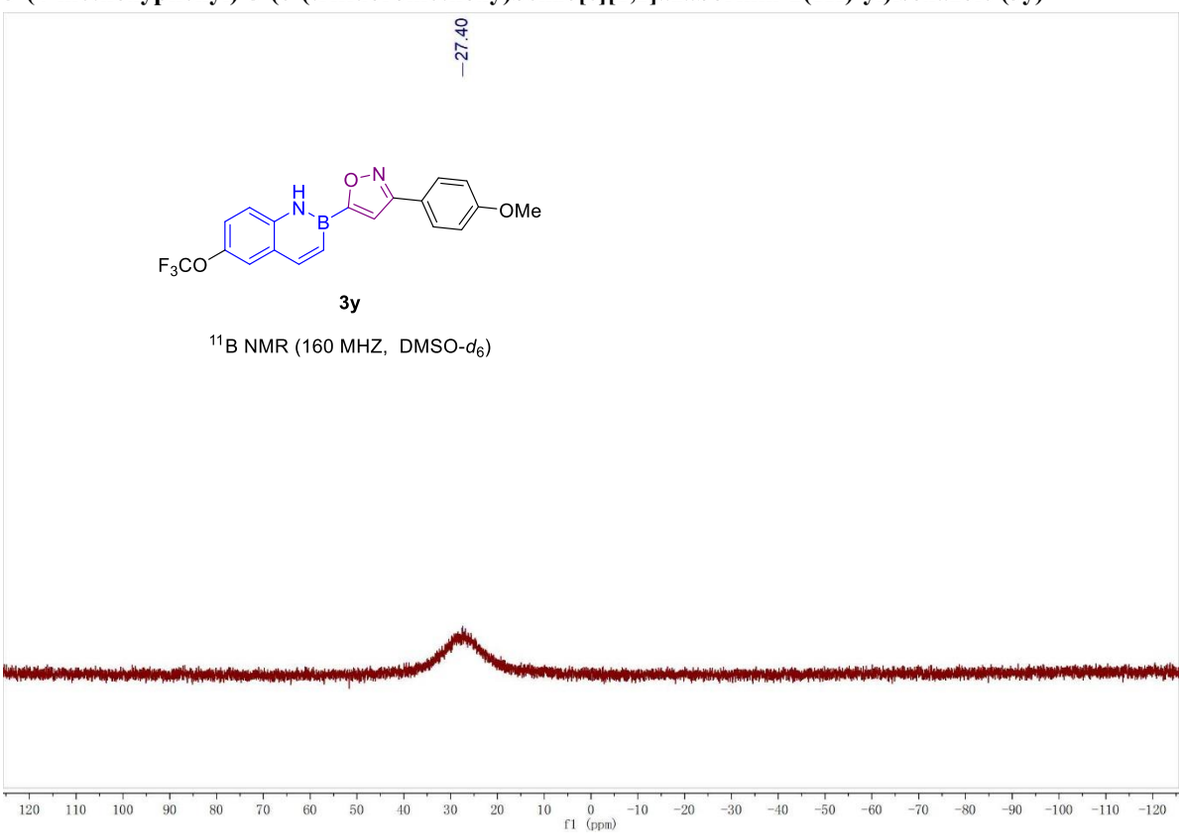
3-(4-methoxyphenyl)-5-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (3y)



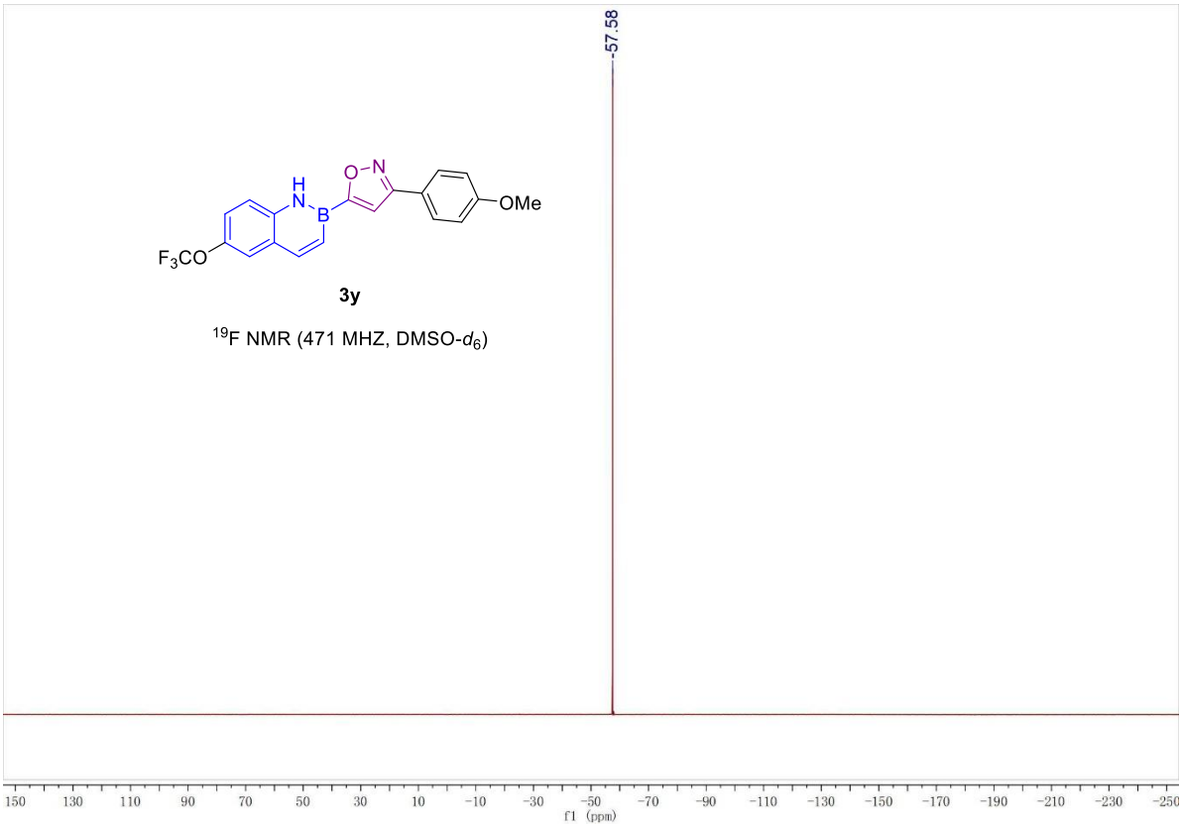
3-(4-methoxyphenyl)-5-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (3y)



3-(4-methoxyphenyl)-5-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (3y)



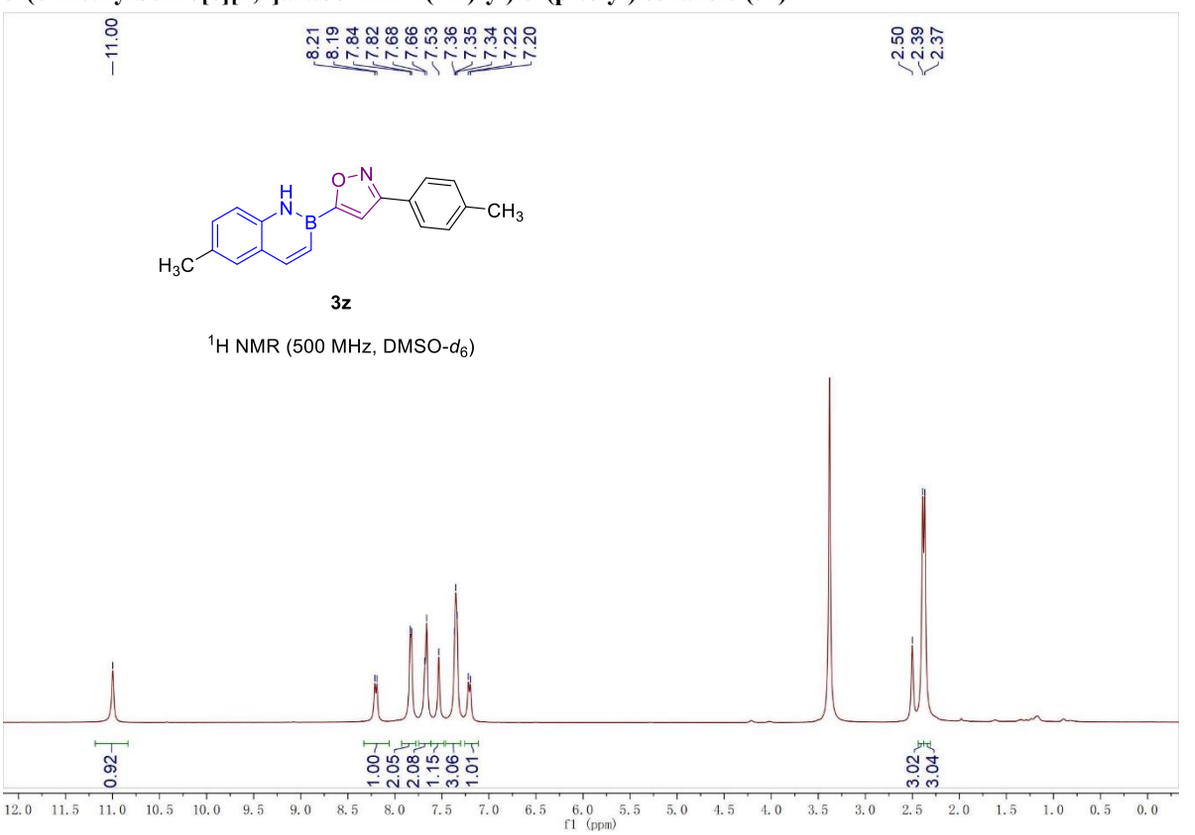
3-(4-methoxyphenyl)-5-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (3y)



3y

^{19}F NMR (471 MHZ, DMSO-d_6)

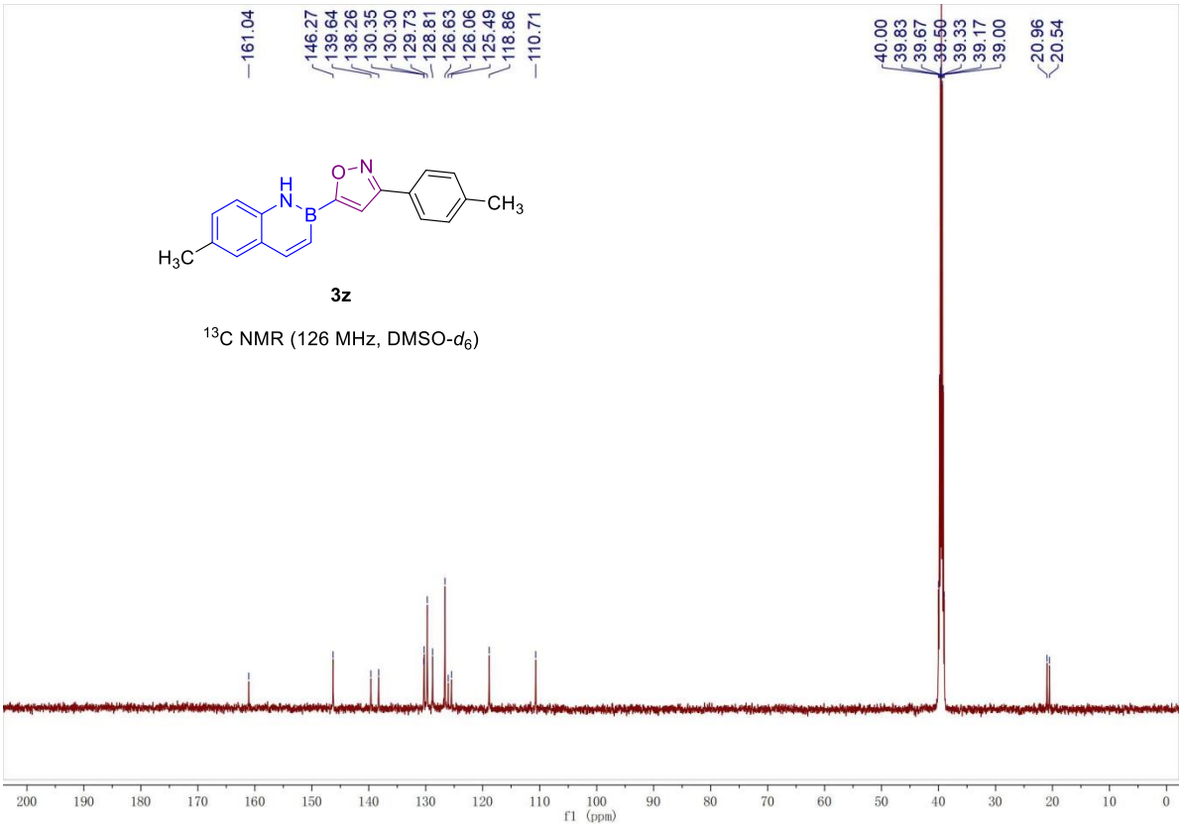
5-(6-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3z)



3z

^{1}H NMR (500 MHz, DMSO-d_6)

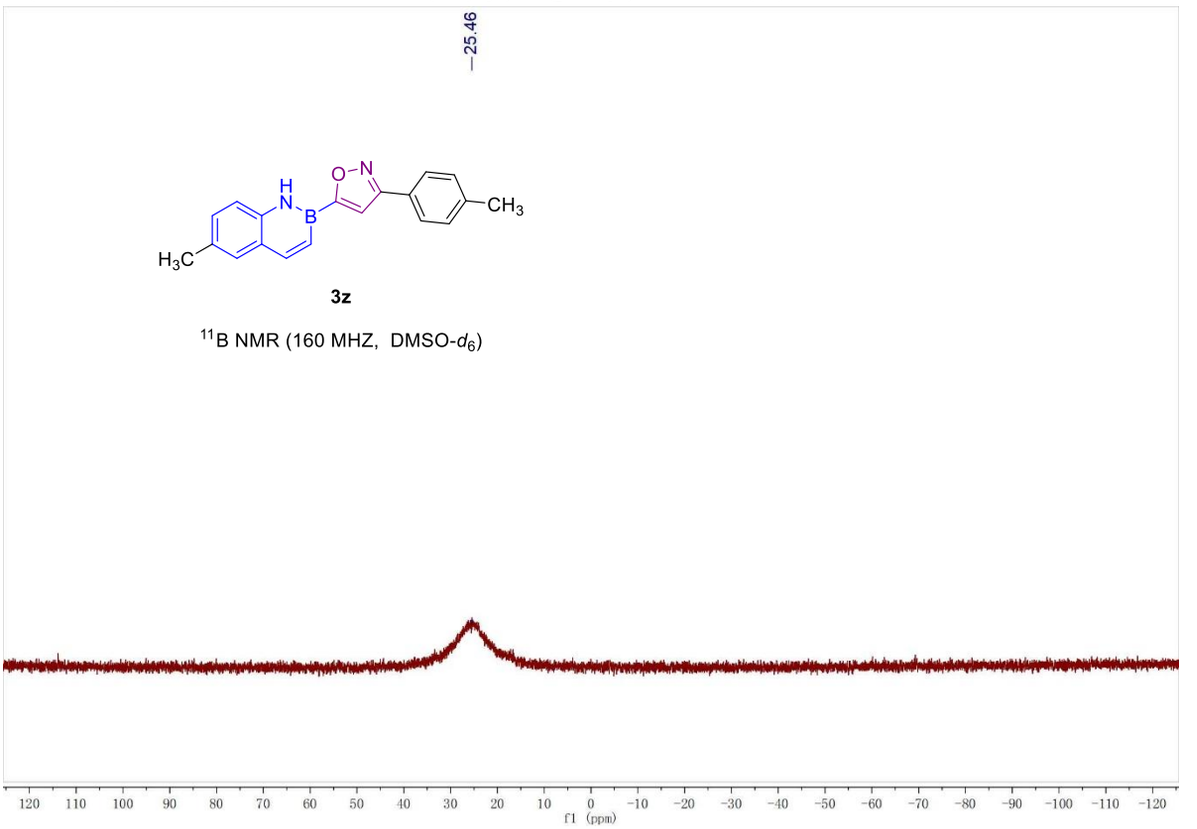
5-(6-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3z)



3z

^{13}C NMR (126 MHz, DMSO-d_6)

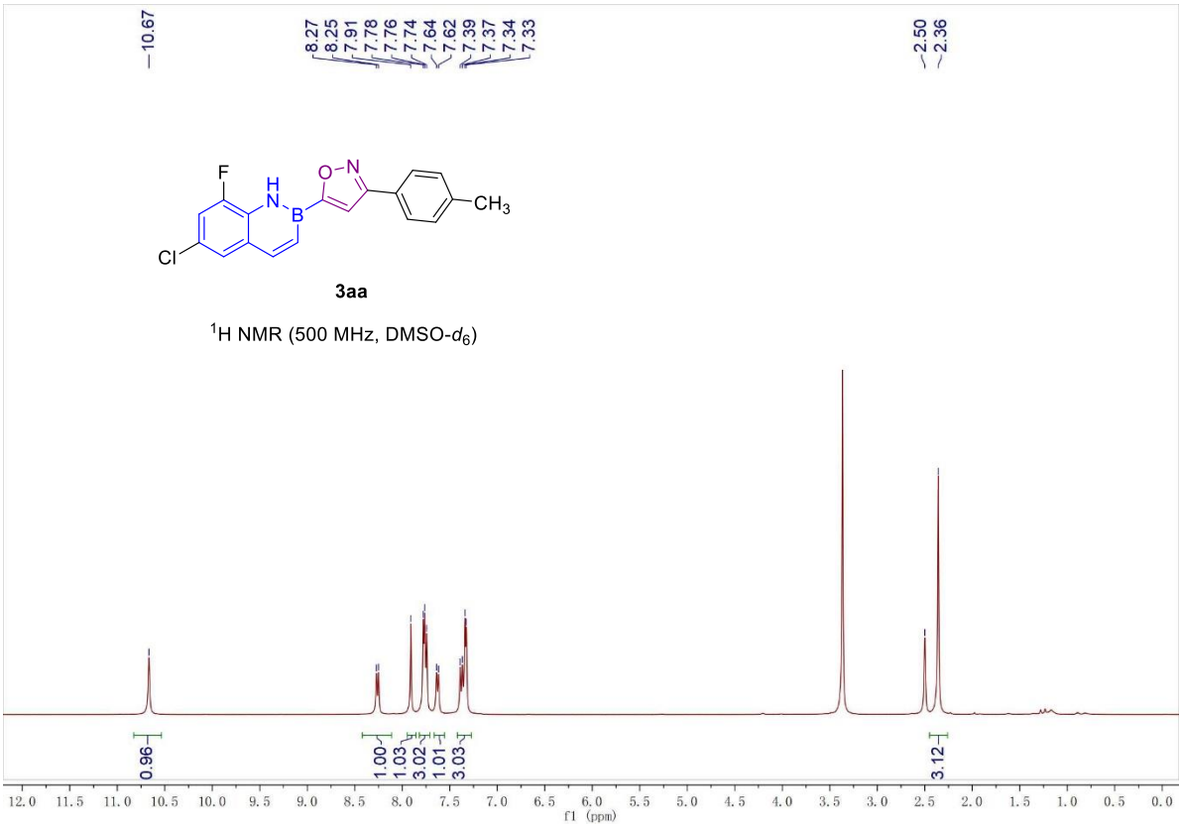
5-(6-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3z)



3z

^{11}B NMR (160 MHZ, DMSO-d_6)

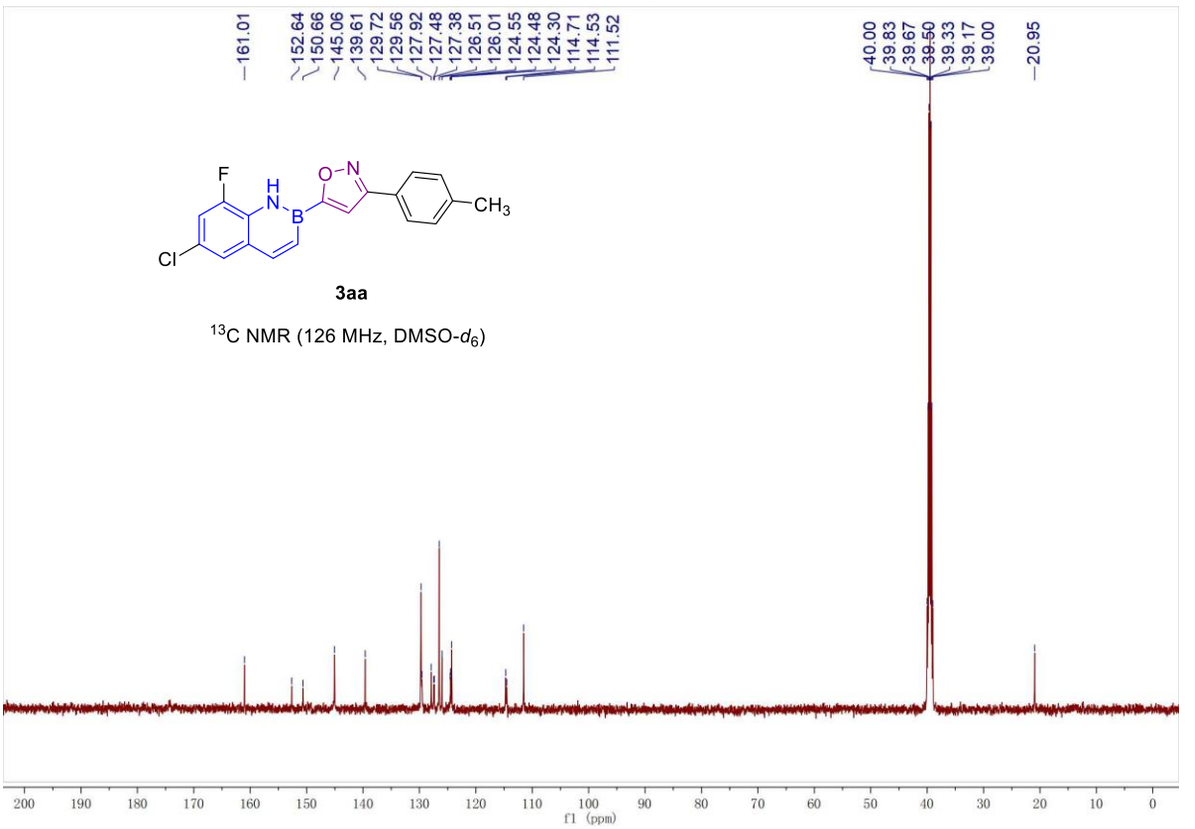
5-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3aa)



3aa

^{1}H NMR (500 MHz, DMSO-d_6)

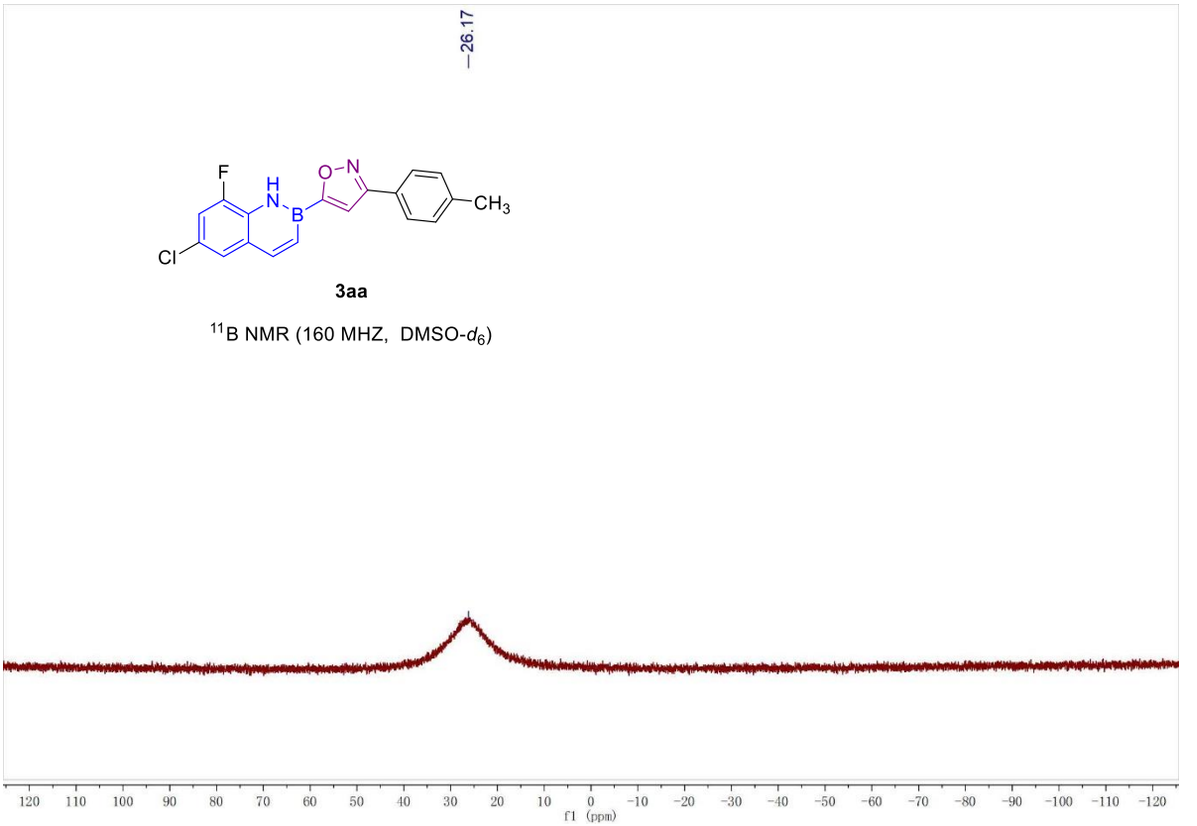
5-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3aa)



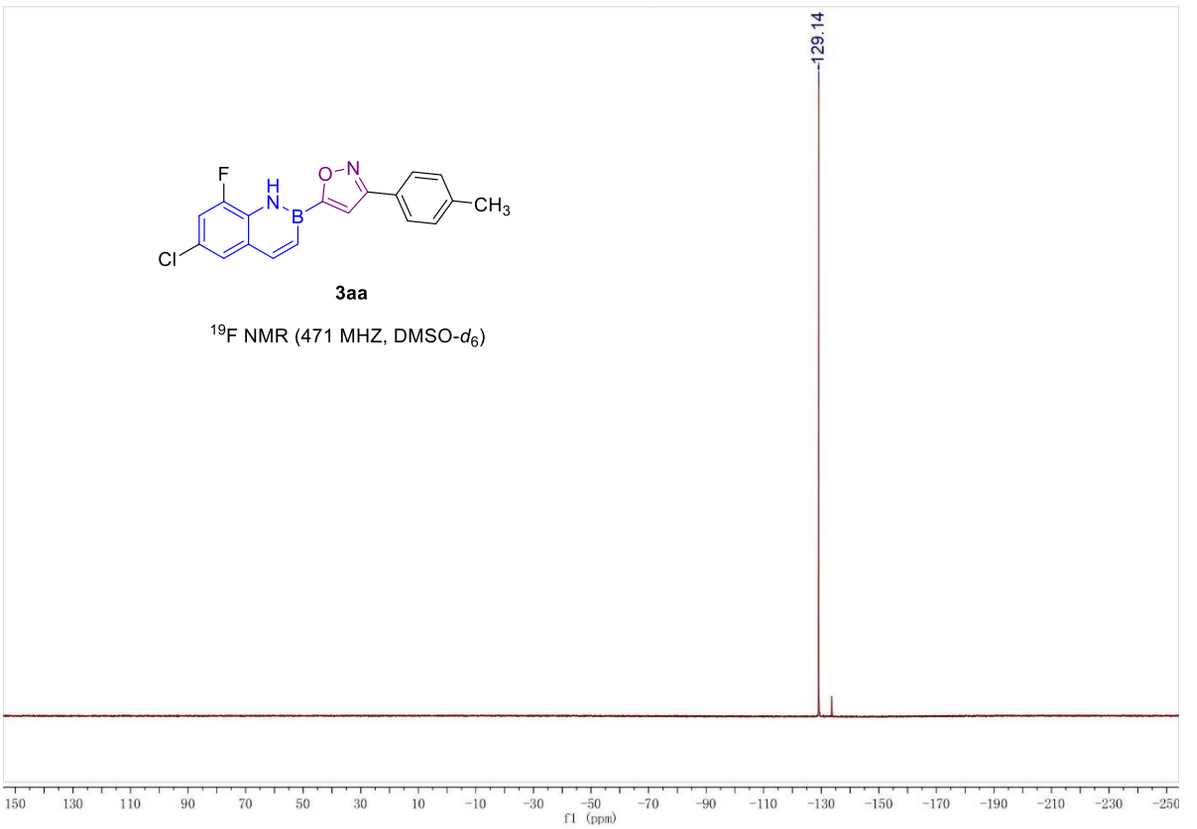
3aa

^{13}C NMR (126 MHz, DMSO-d_6)

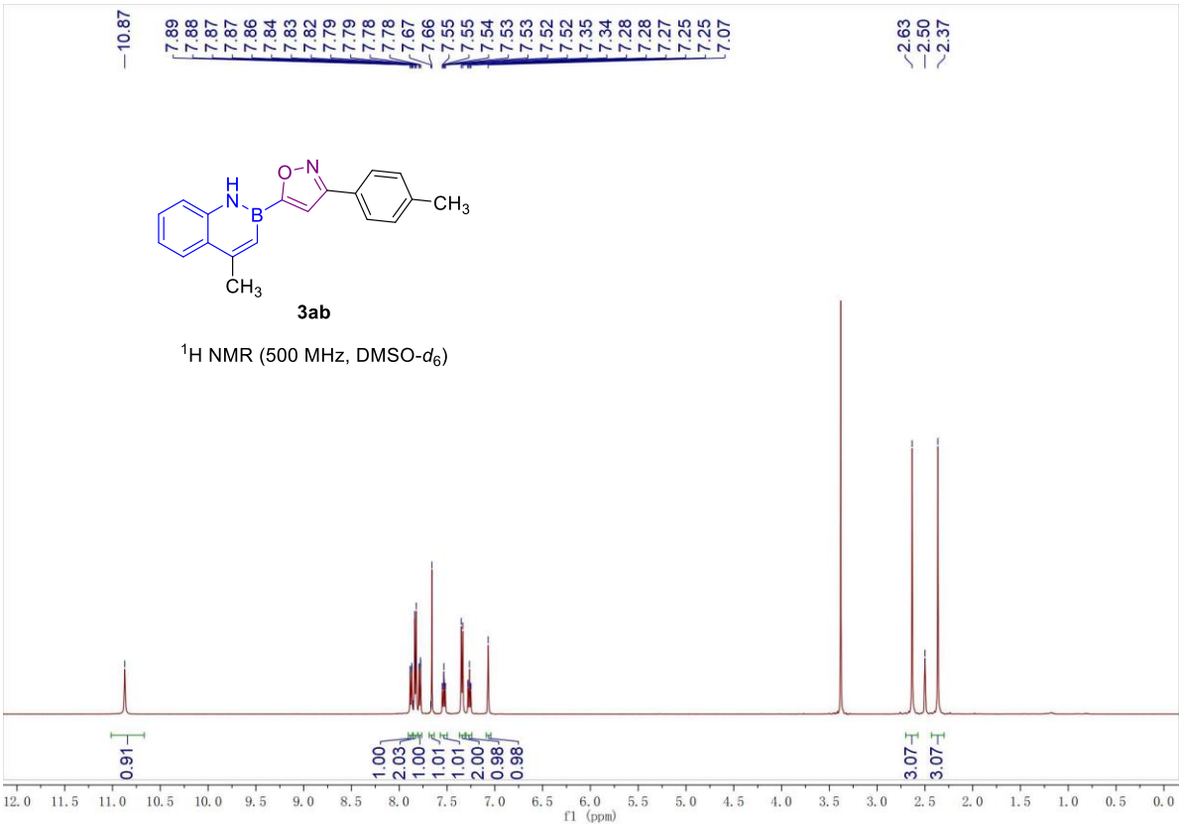
5-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3aa)



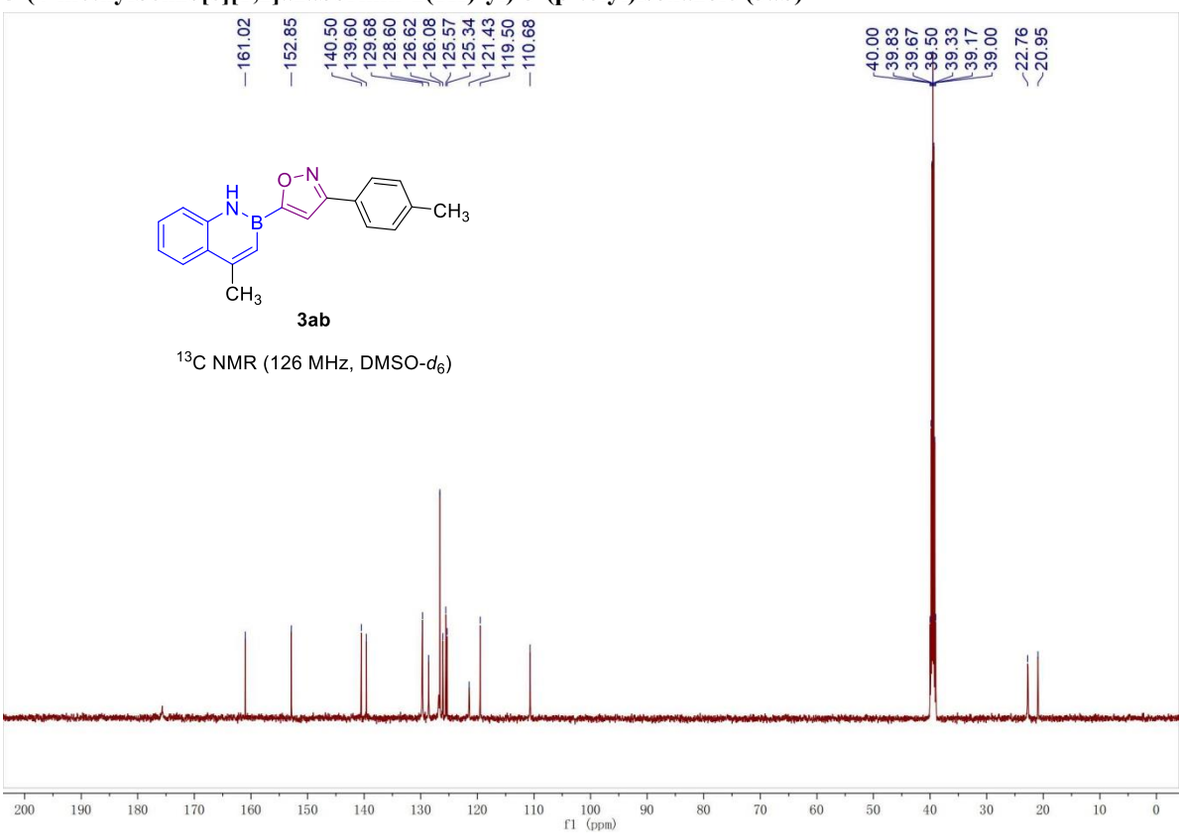
5-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3aa)



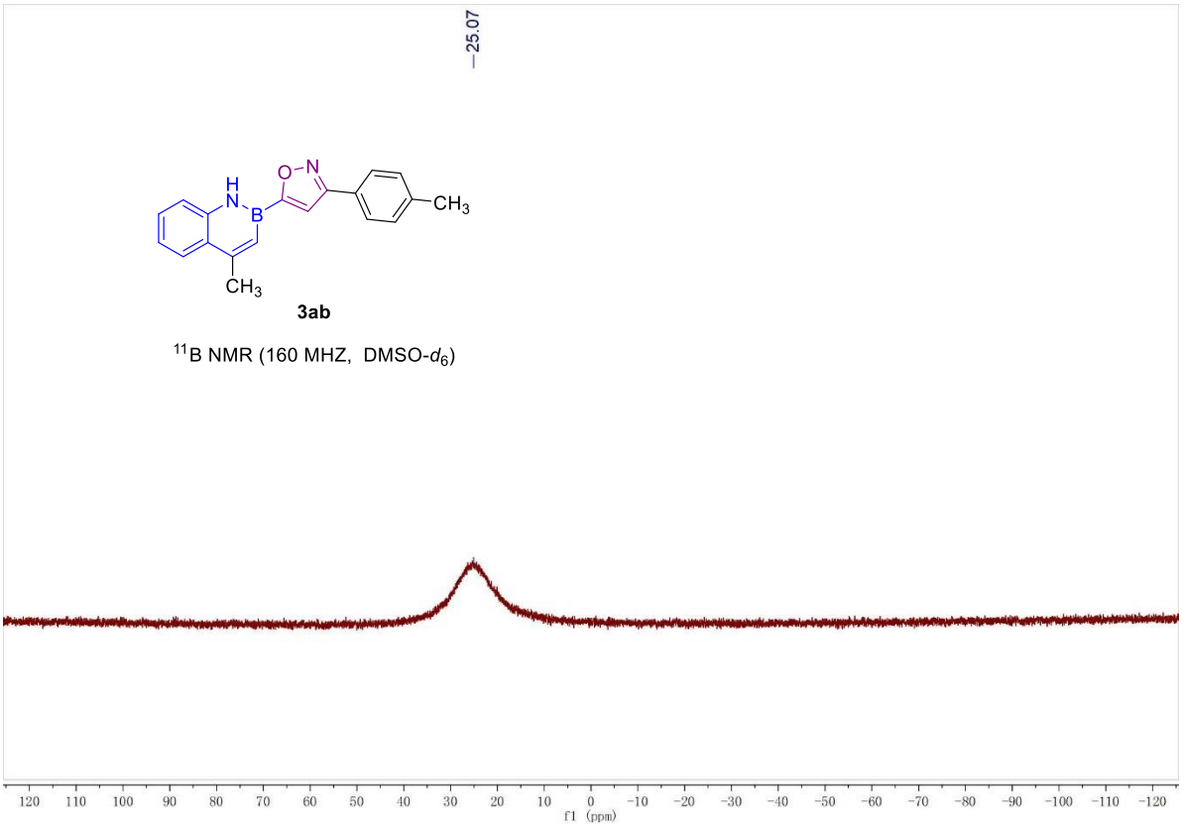
5-(4-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3ab)



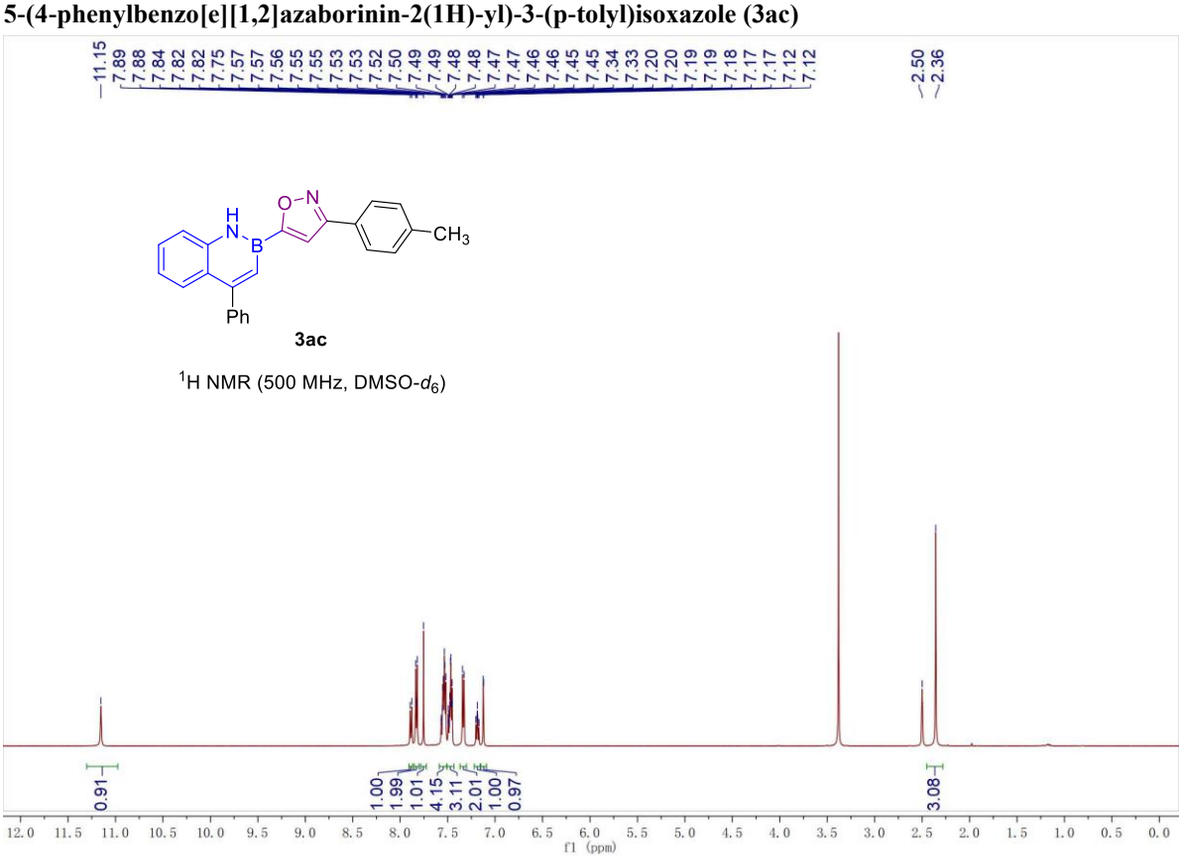
5-(4-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3ab)



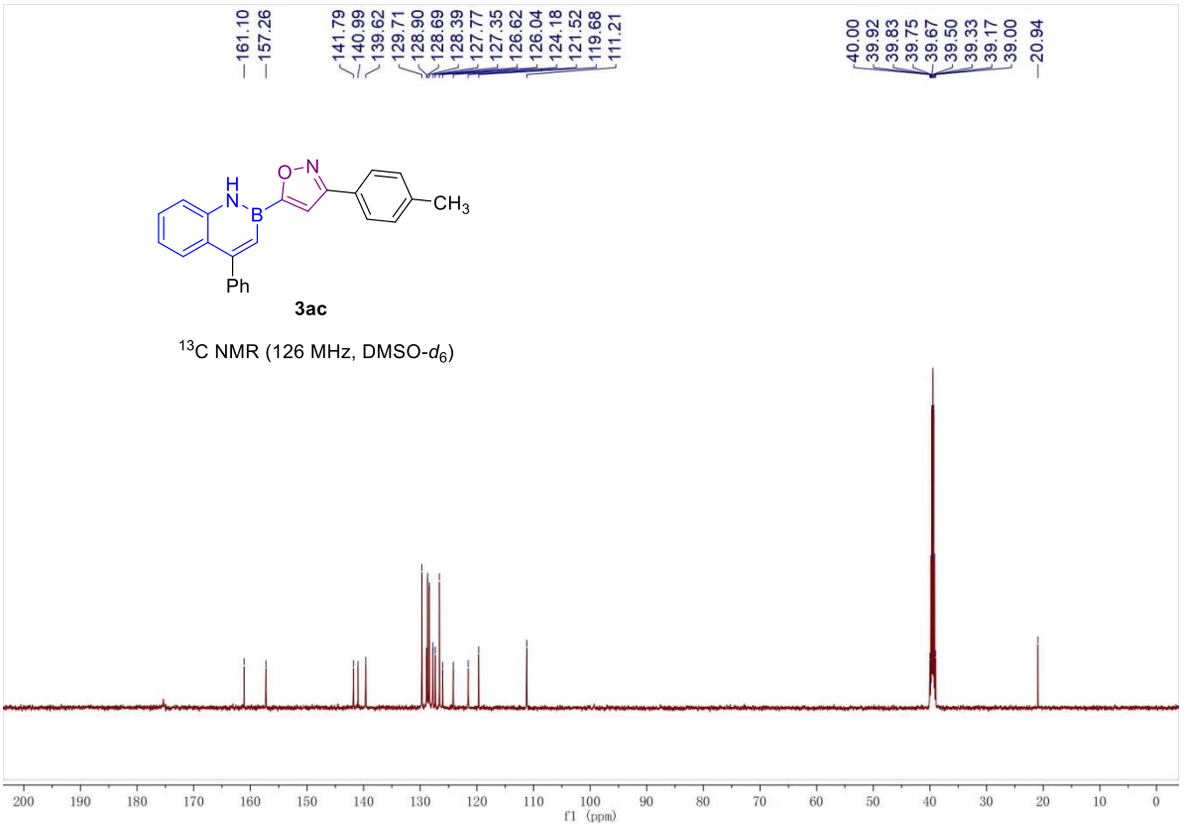
5-(4-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3ab)



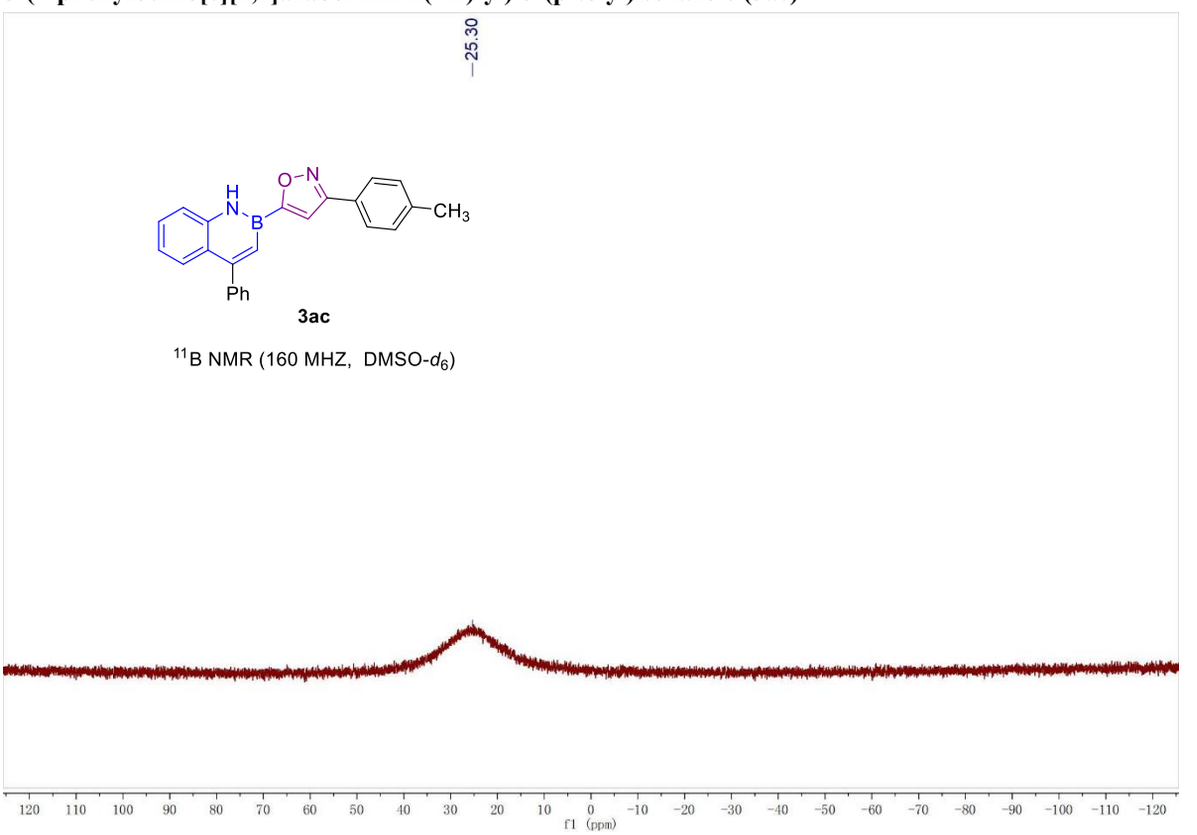
5-(4-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3ac)



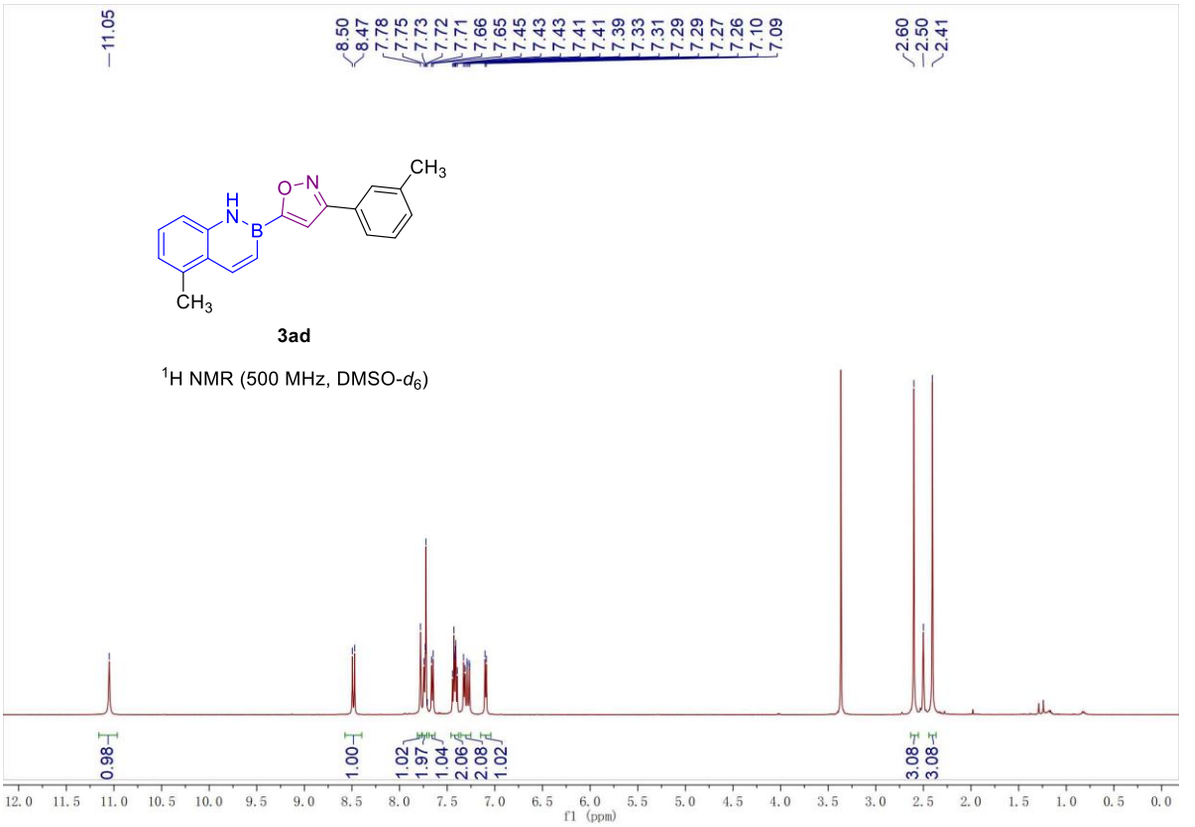
5-(4-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3ac)



5-(4-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (3ac)



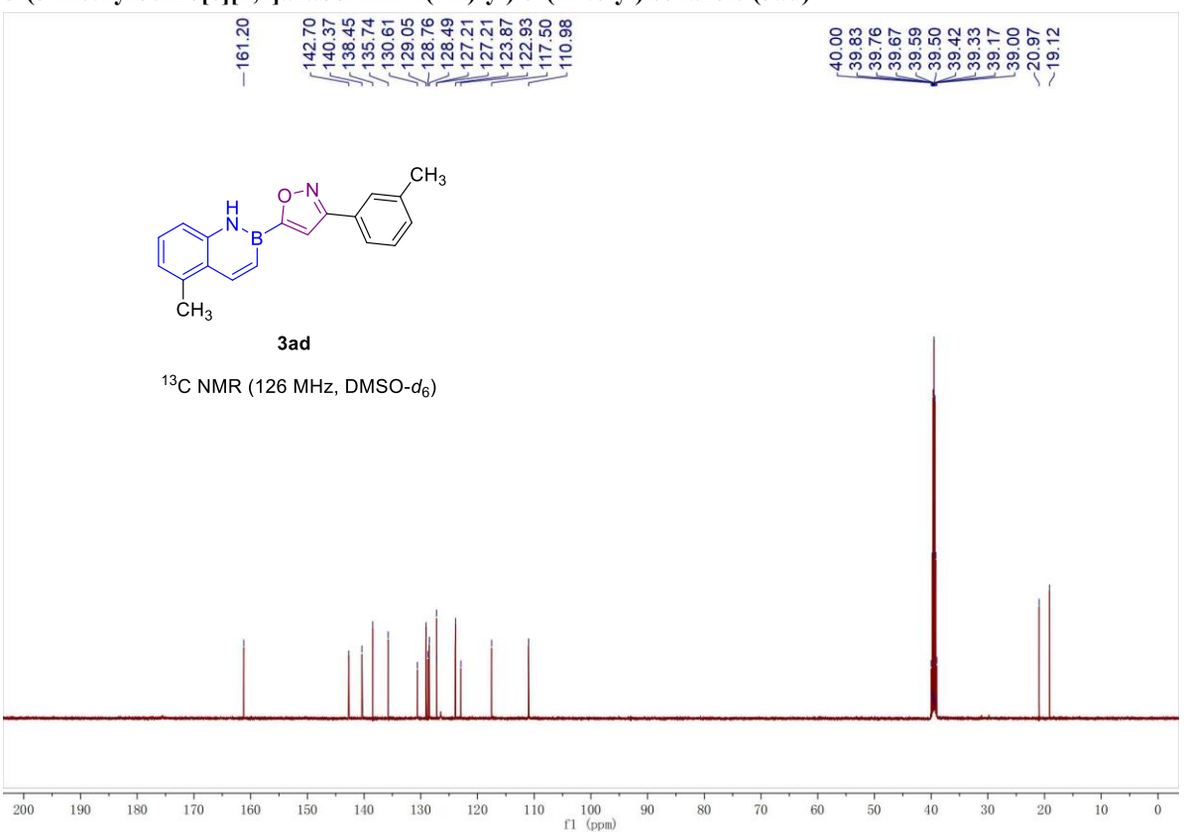
5-(5-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3ad)



3ad

^{1}H NMR (500 MHz, DMSO-d_6)

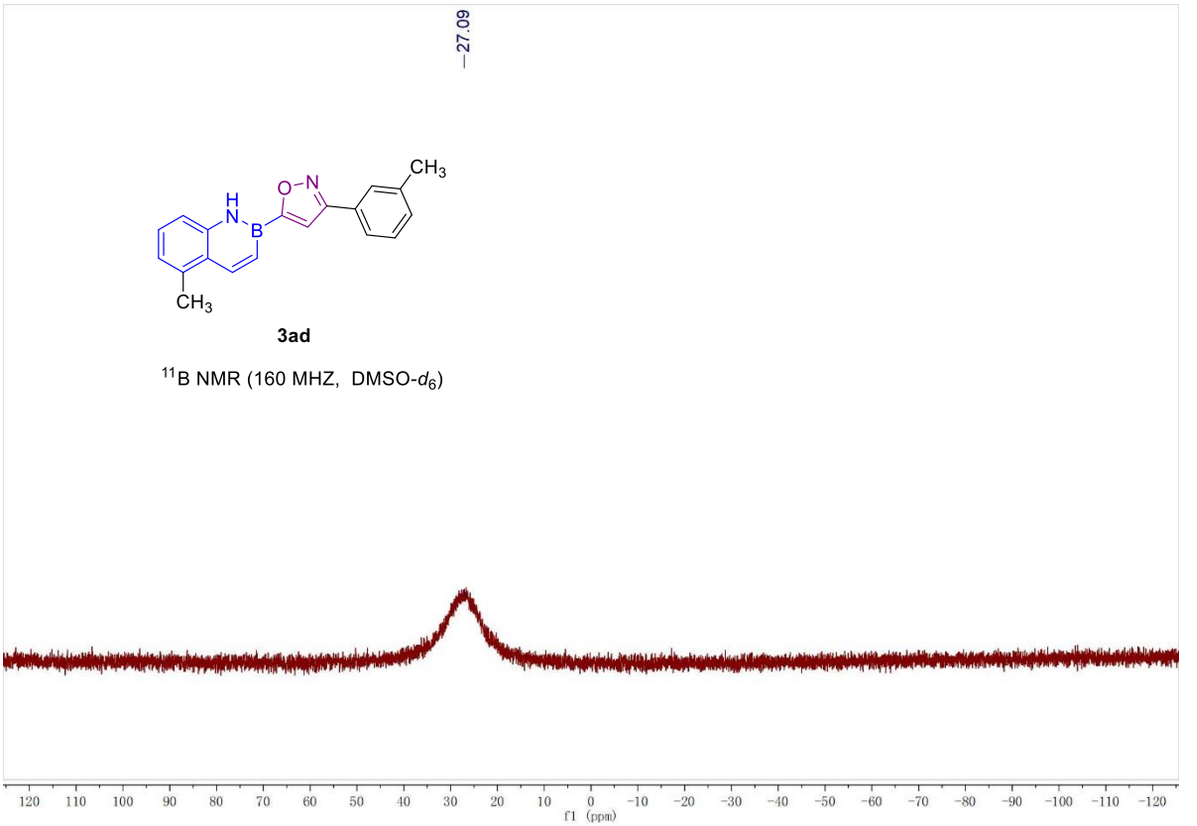
5-(5-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3ad)



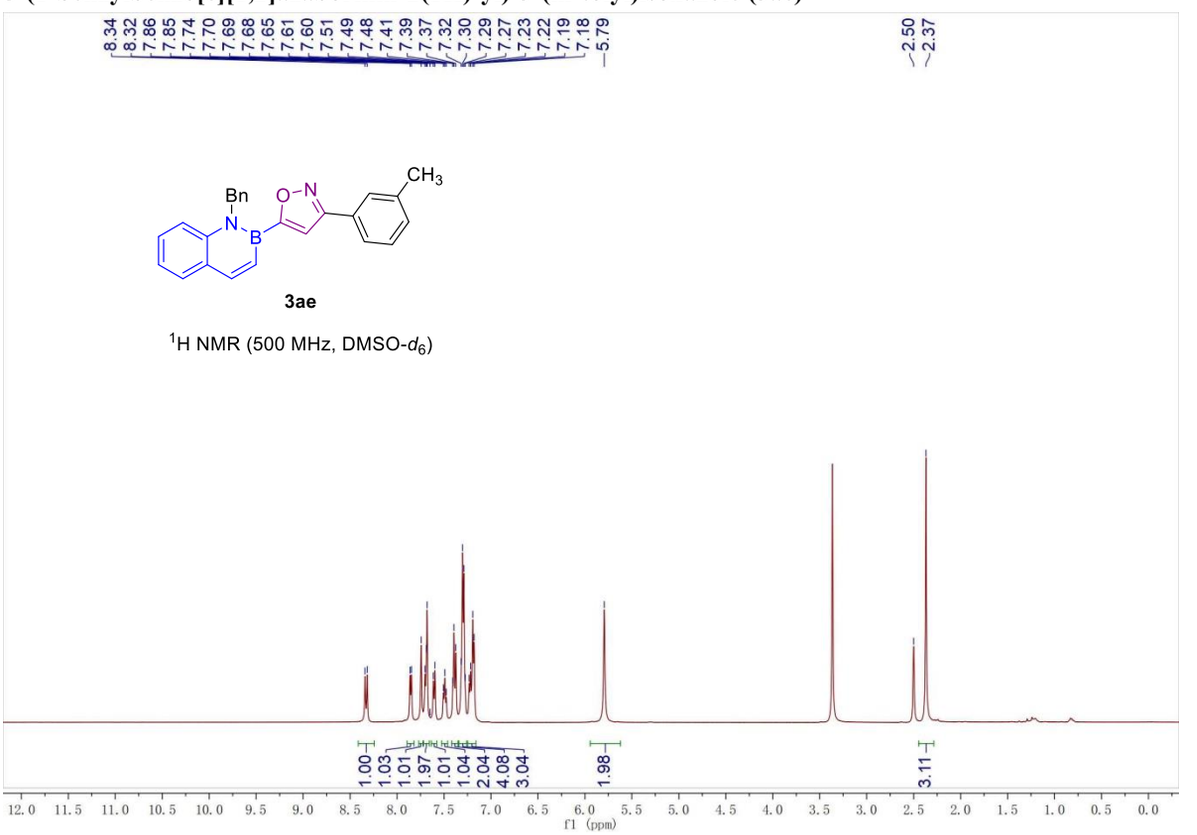
3ad

^{13}C NMR (126 MHz, DMSO-d_6)

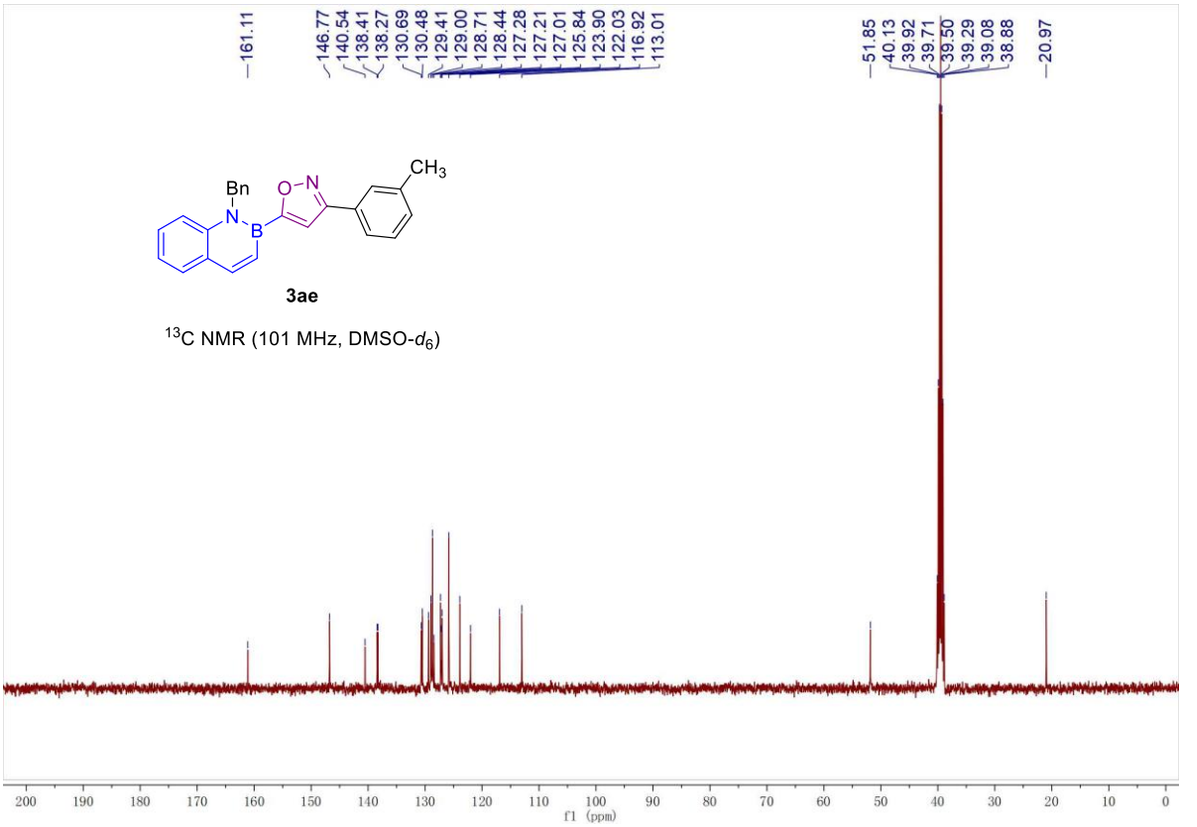
5-(5-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3ad)



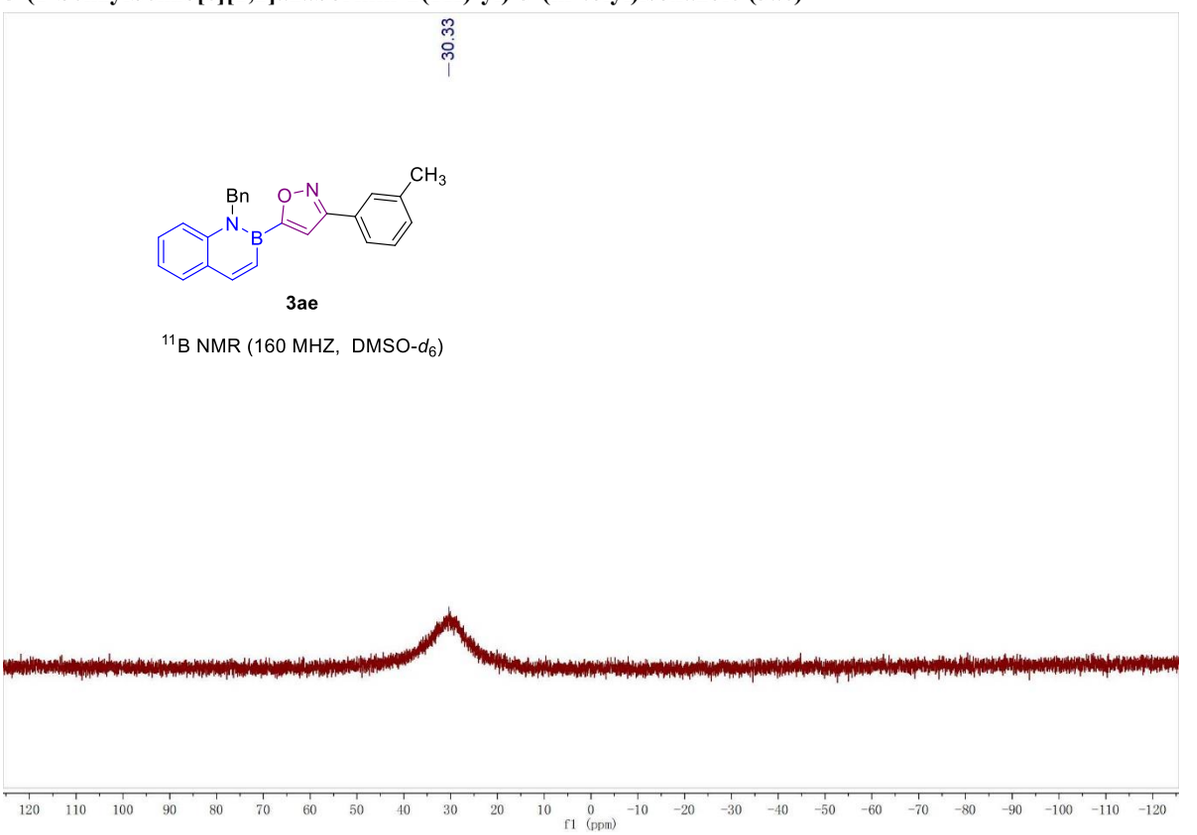
5-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3ae)



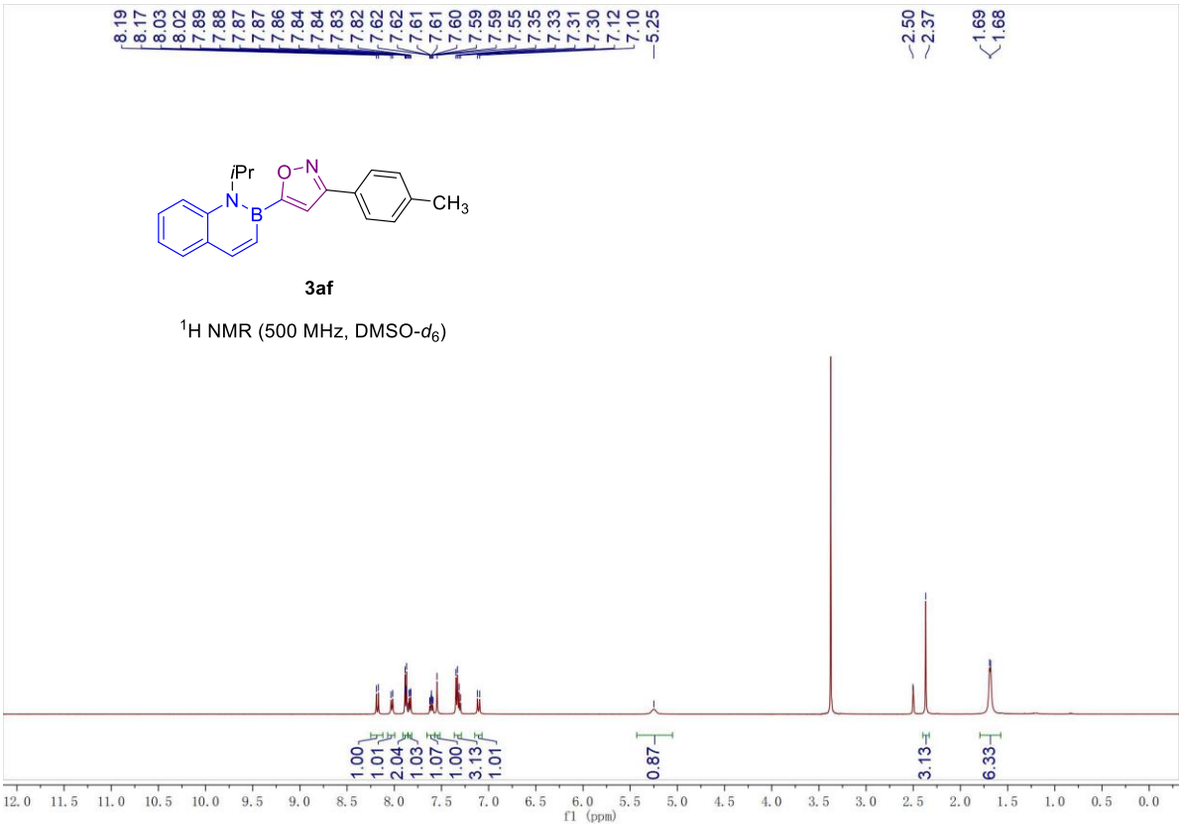
5-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3ae)



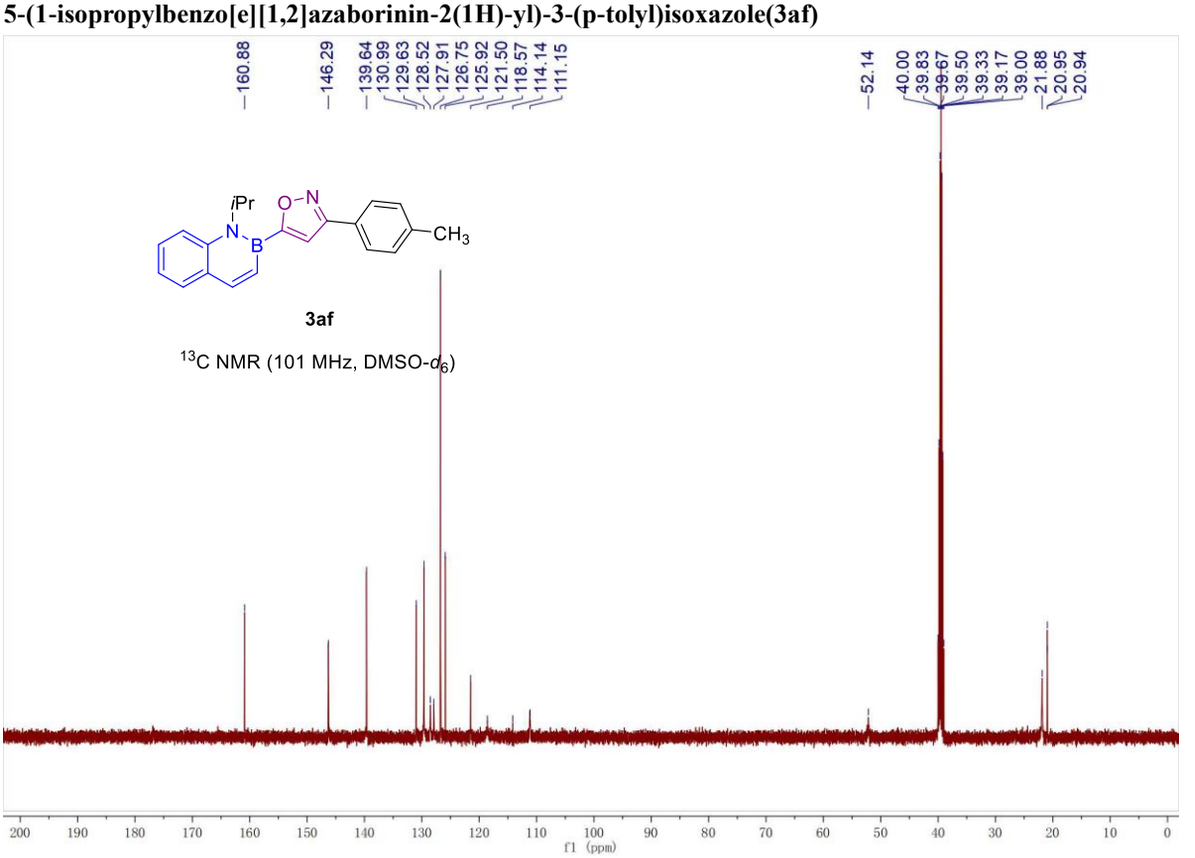
5-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (3ae)



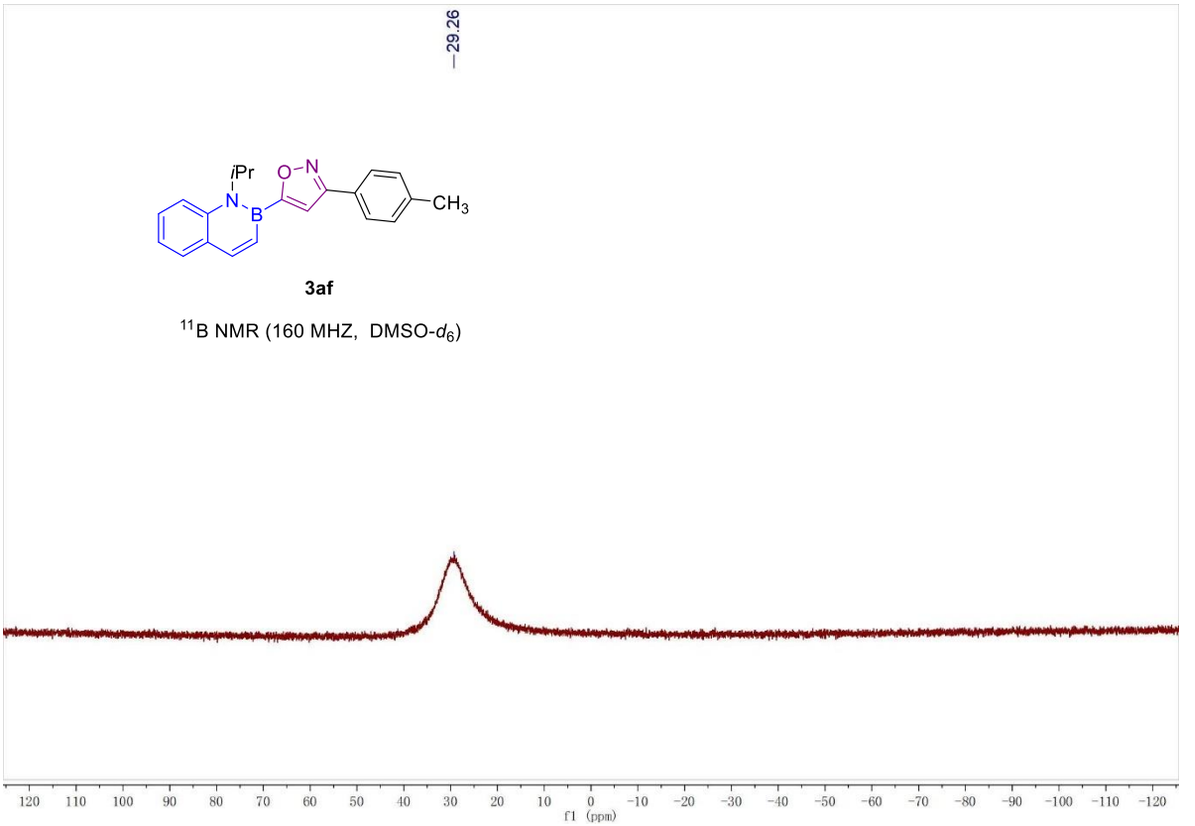
5-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole(3af)



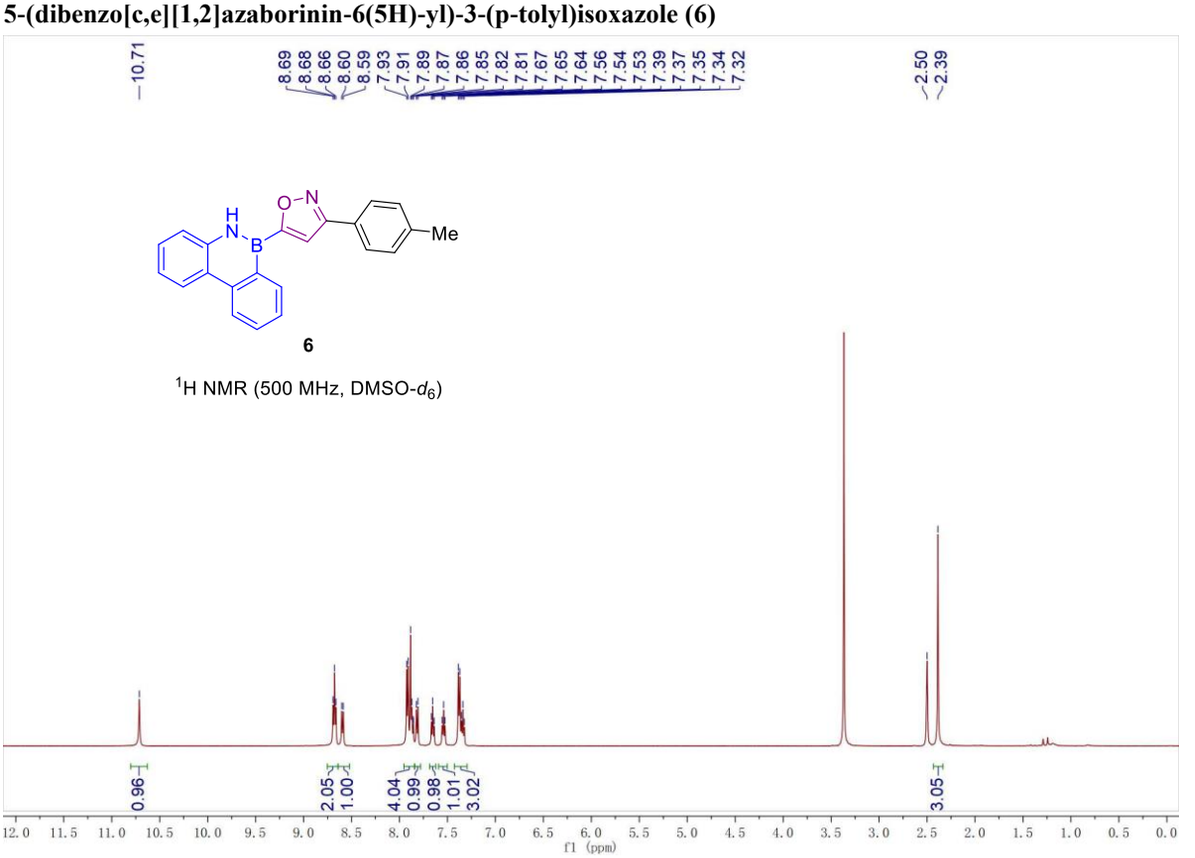
5-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole(3af)



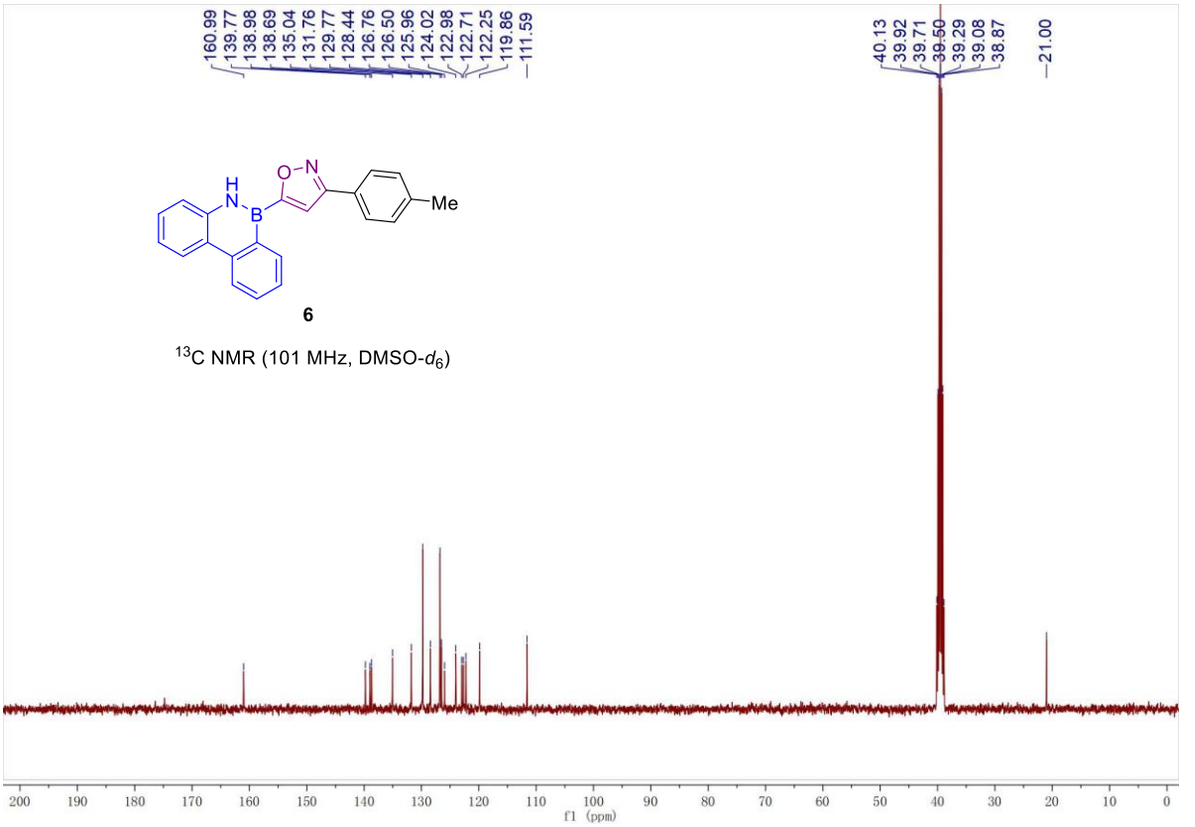
5-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole(3af)



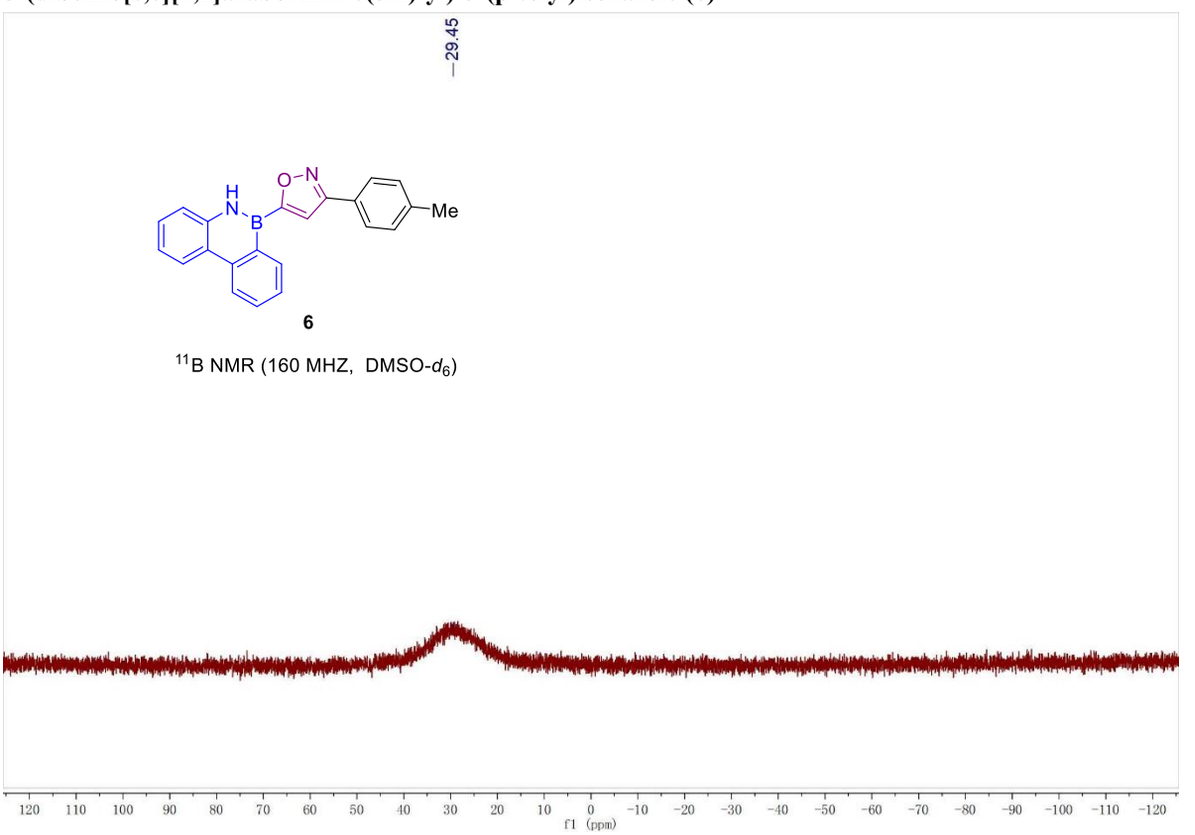
5-(dibenzo[c,e][1,2]azaborinin-6(5H)-yl)-3-(p-tolyl)isoxazole (6)



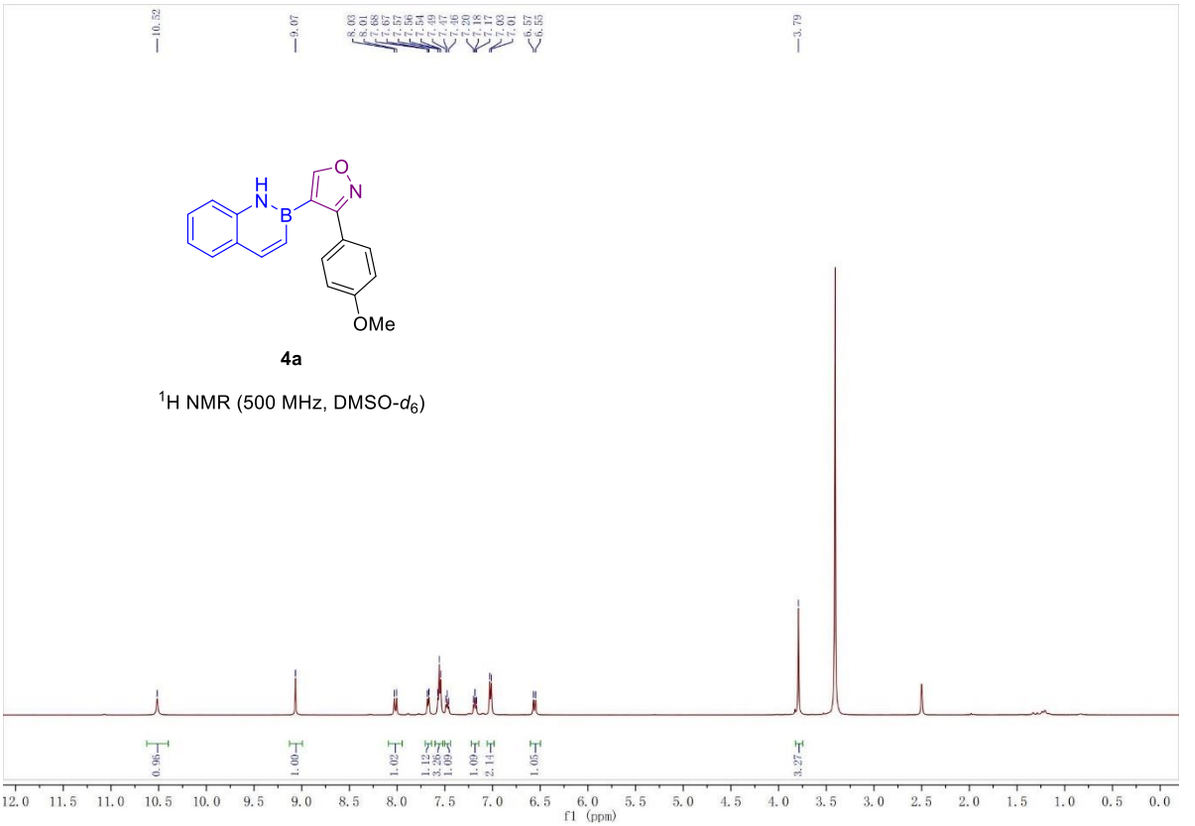
5-(dibenzo[c,e][1,2]azaborinin-6(5H)-yl)-3-(p-tolyl)isoxazole (6)



5-(dibenzo[c,e][1,2]azaborinin-6(5H)-yl)-3-(p-tolyl)isoxazole (6)



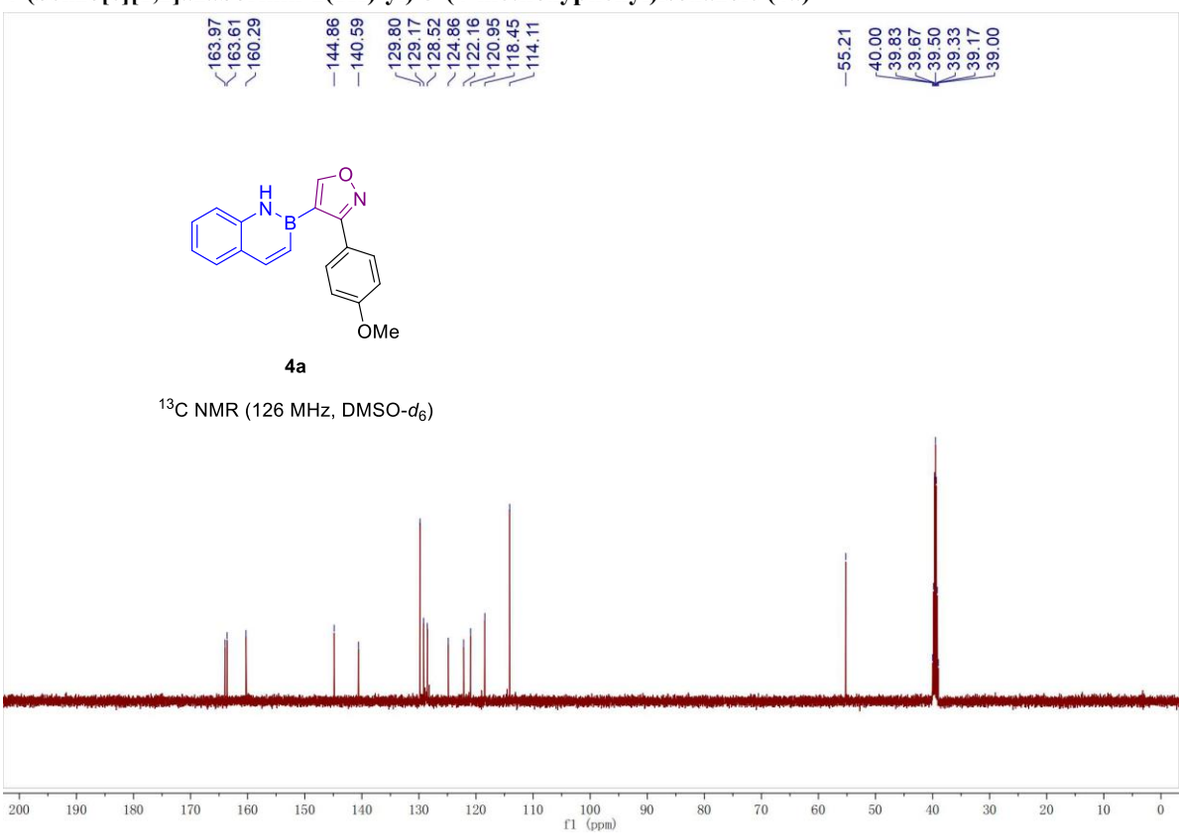
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4a)



4a

^{1}H NMR (500 MHz, DMSO-d_6)

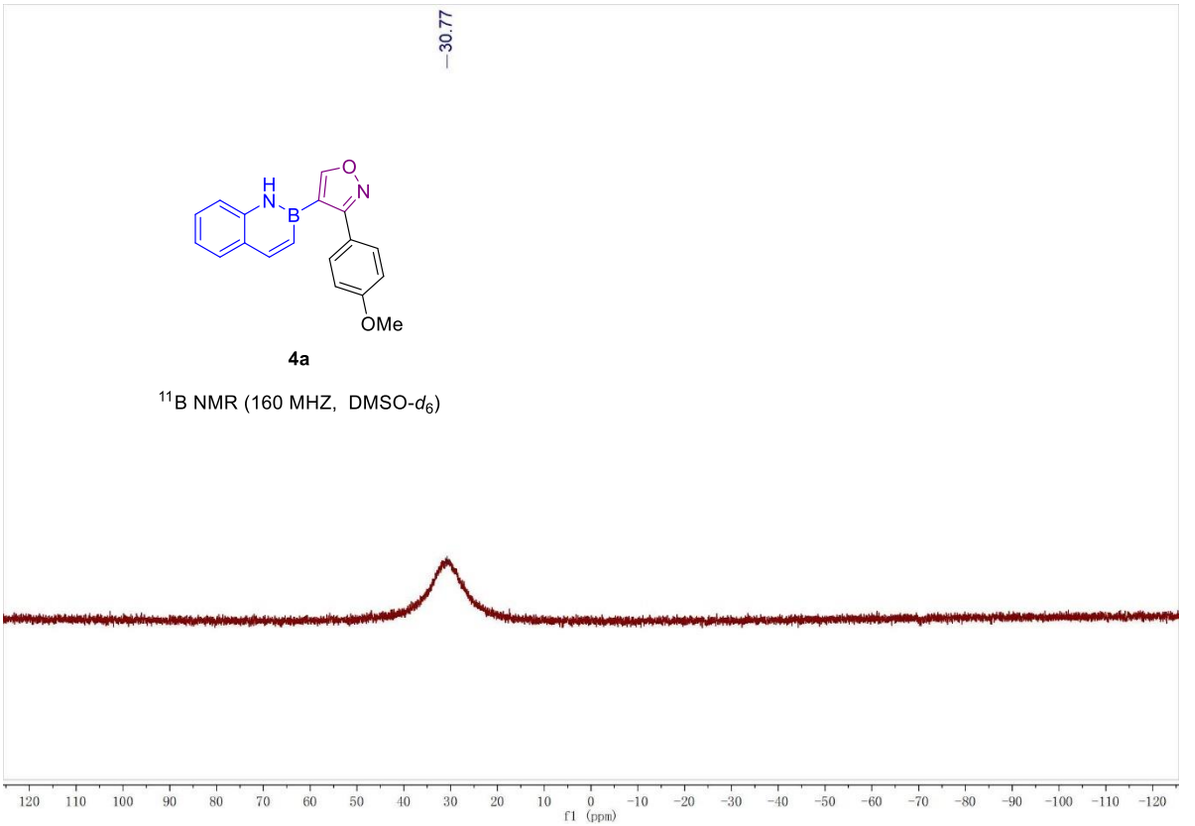
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4a)



4a

^{13}C NMR (126 MHz, DMSO-d_6)

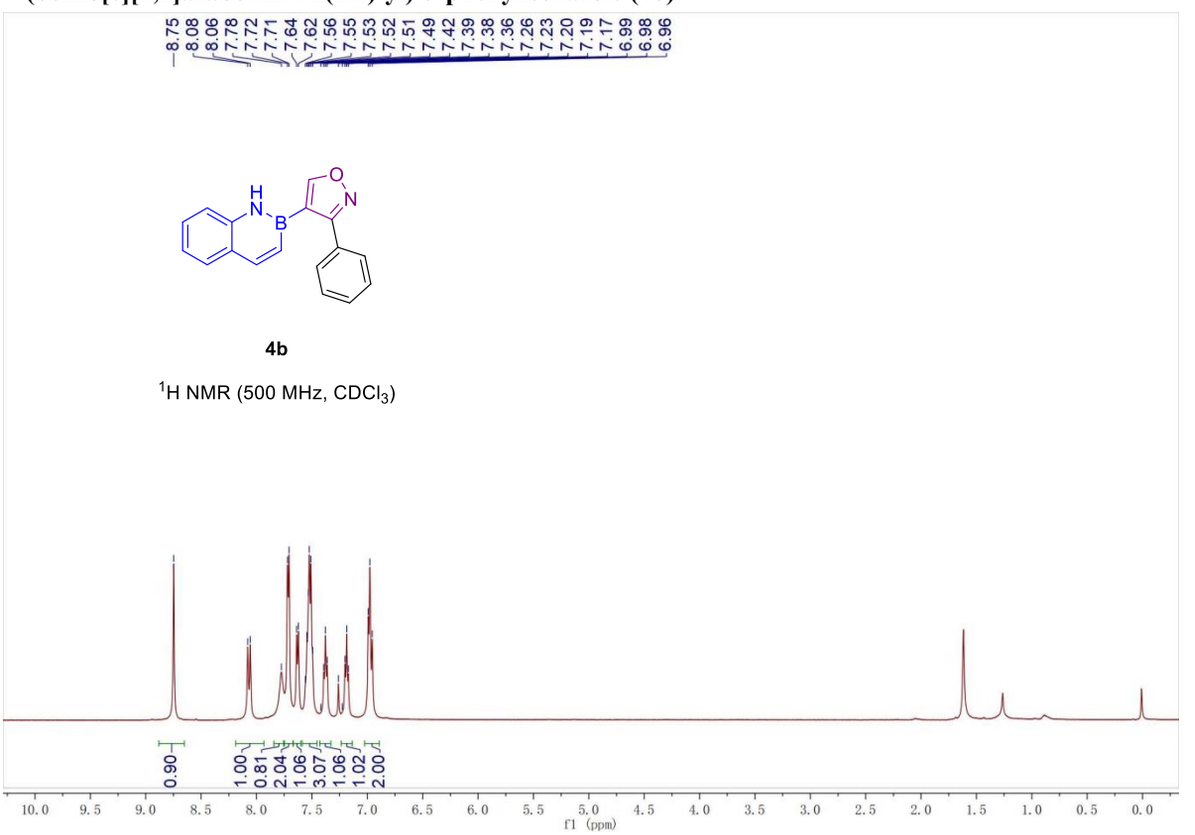
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4a)



4a

^{11}B NMR (160 MHZ, DMSO-d_6)

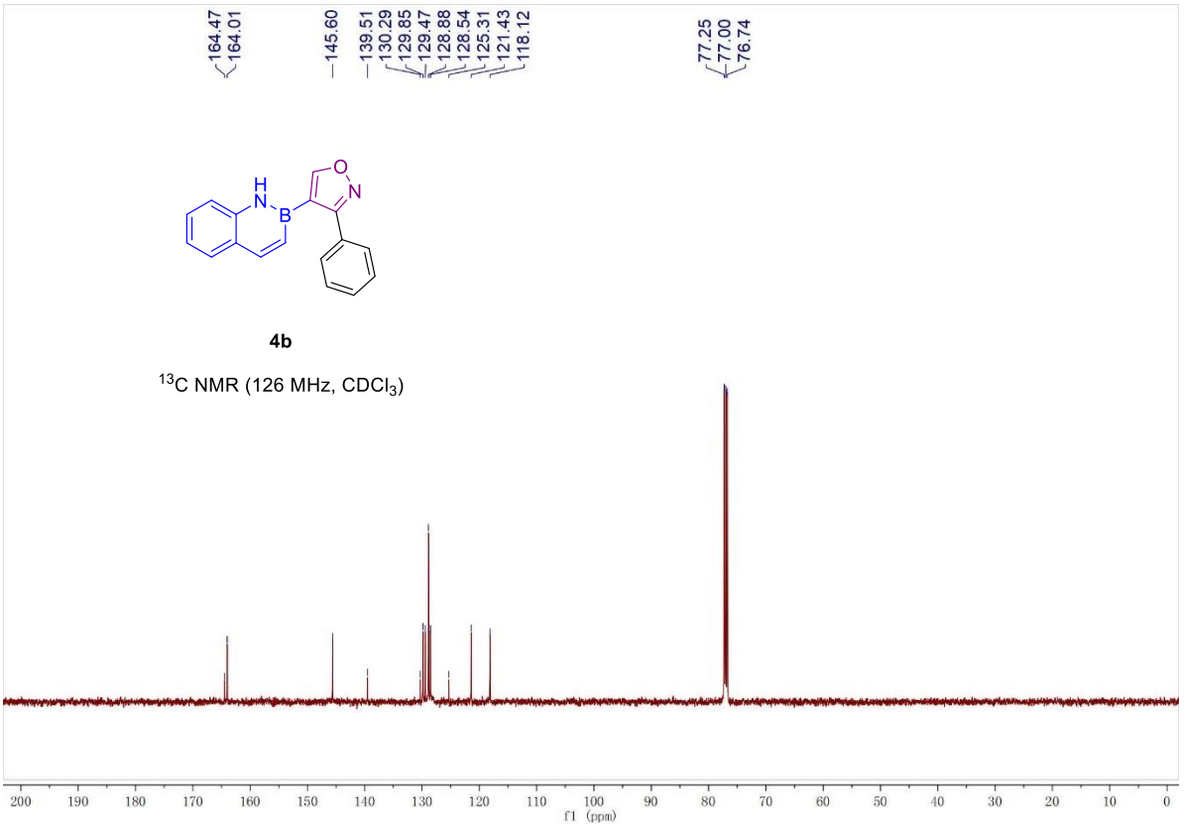
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenylisoxazole (4b)



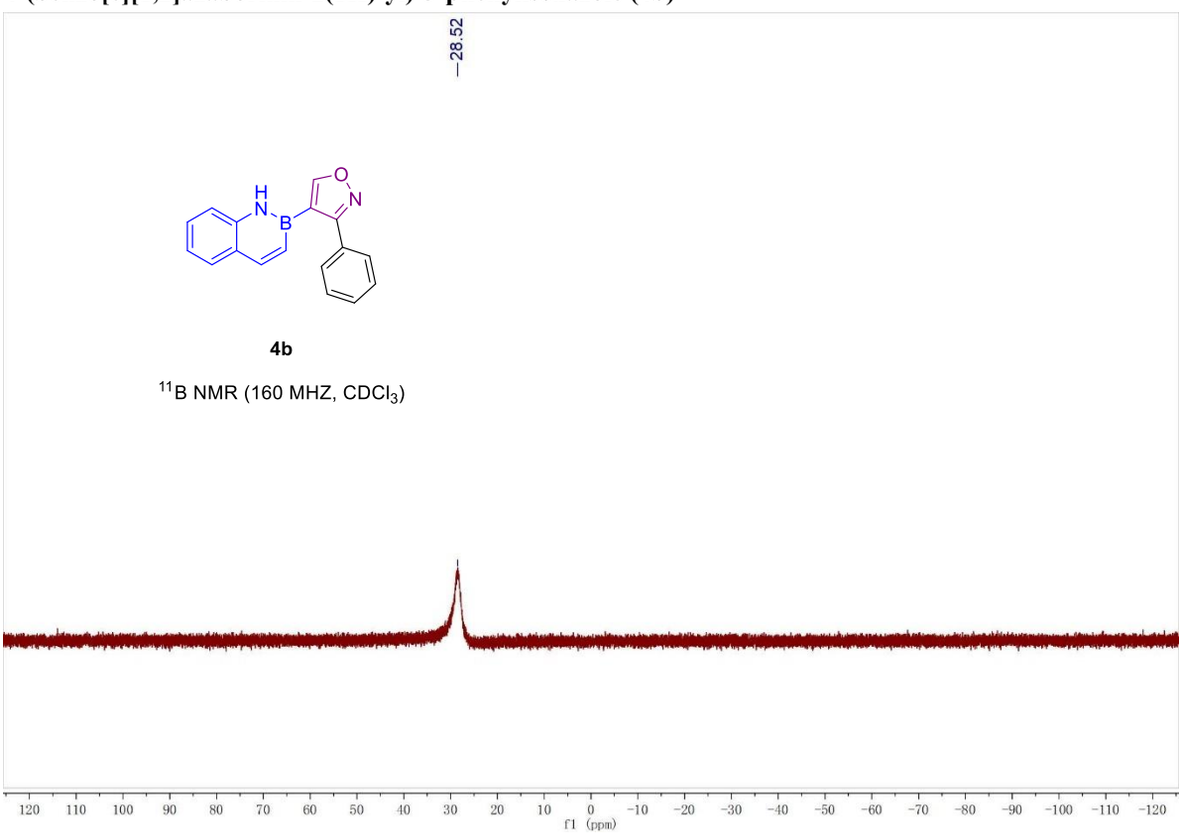
4b

^{1}H NMR (500 MHz, $CDCl_3$)

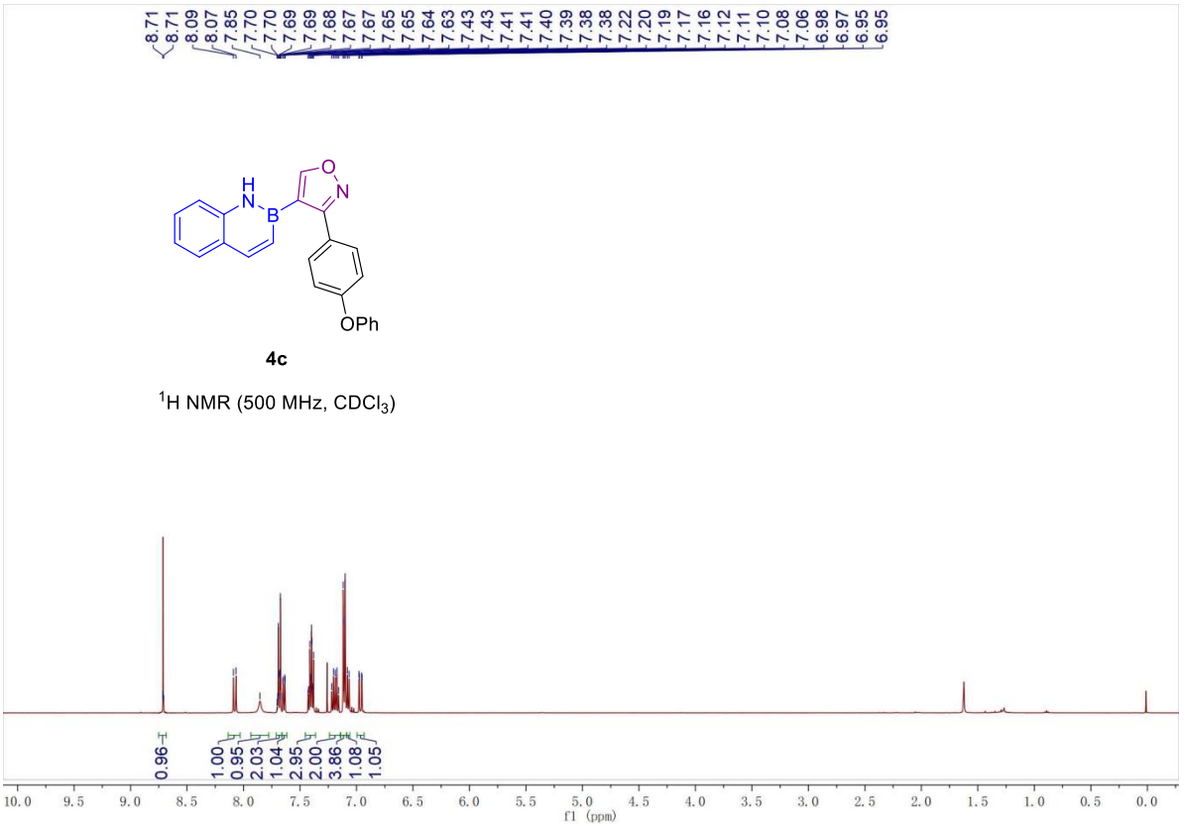
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenylisoxazole (4b)



4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-phenylisoxazole (4b)



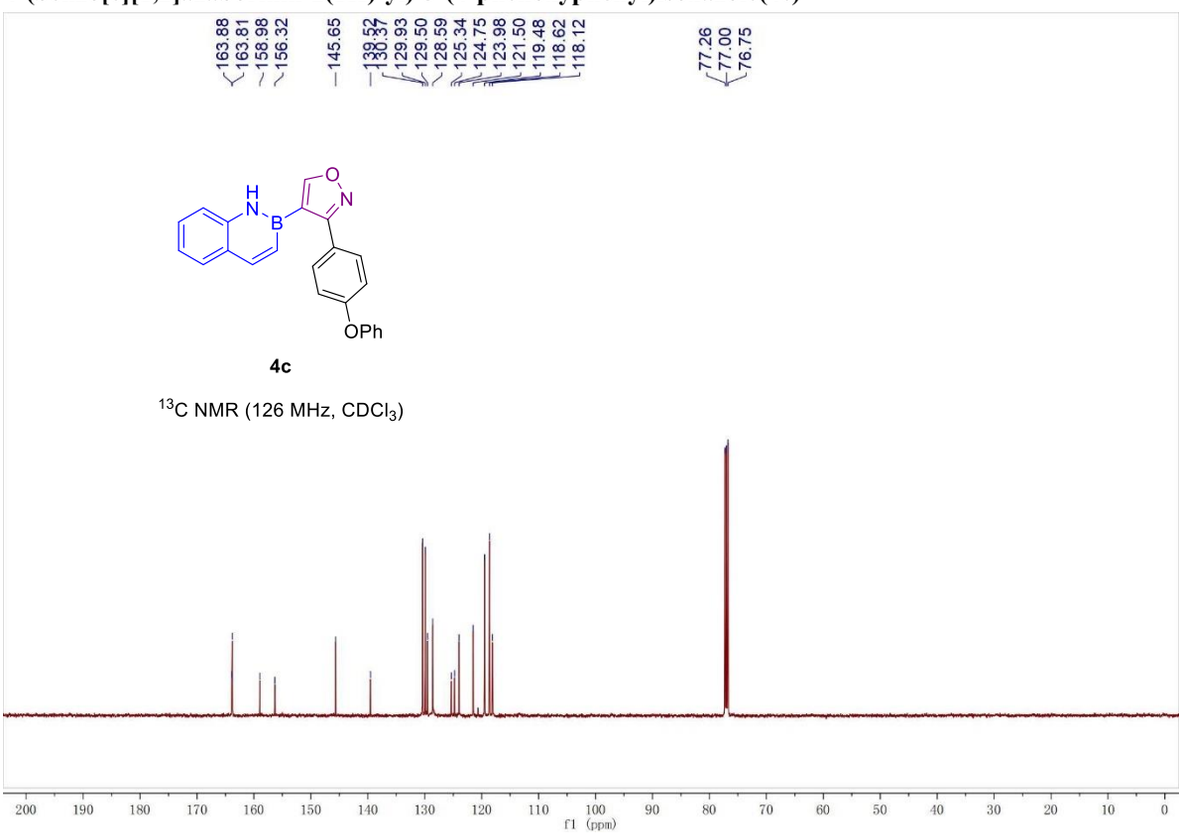
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-phenoxyphenyl)isoxazole(4c)



4c

^{1}H NMR (500 MHz, $CDCl_3$)

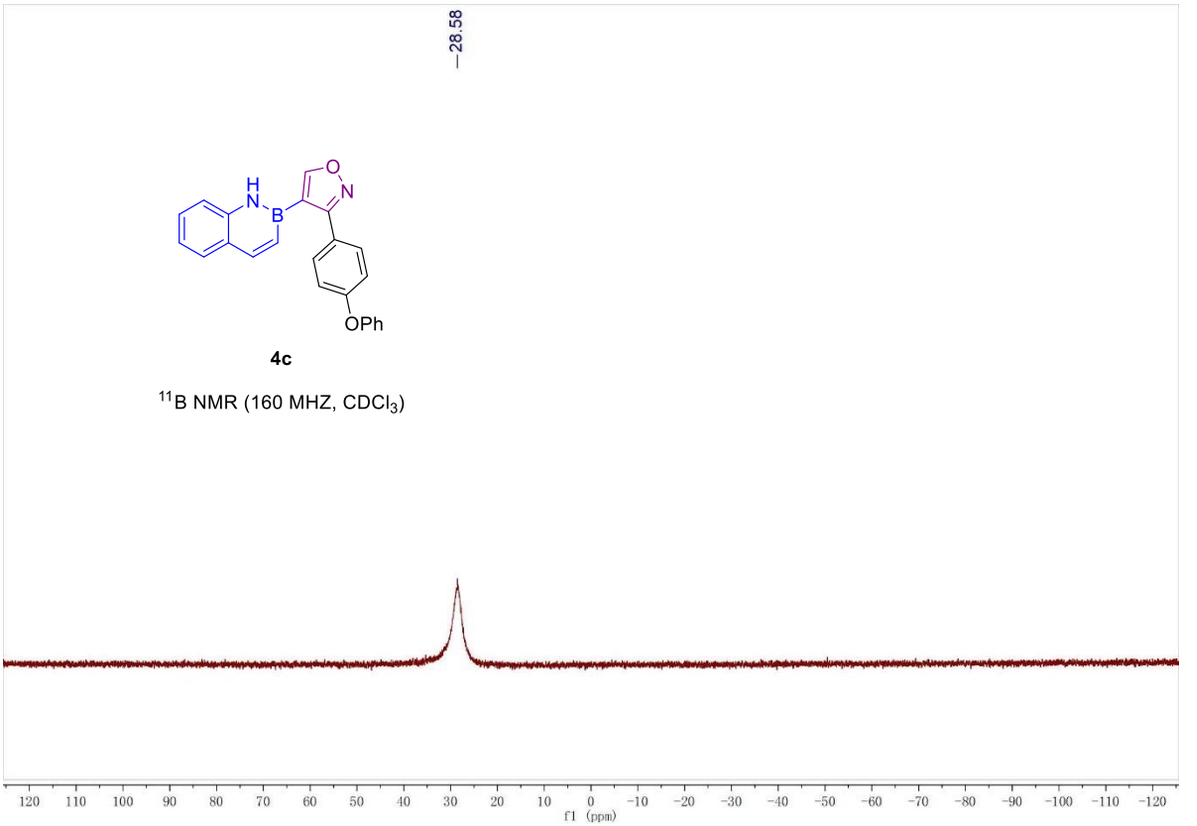
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-phenoxyphenyl)isoxazole(4c)



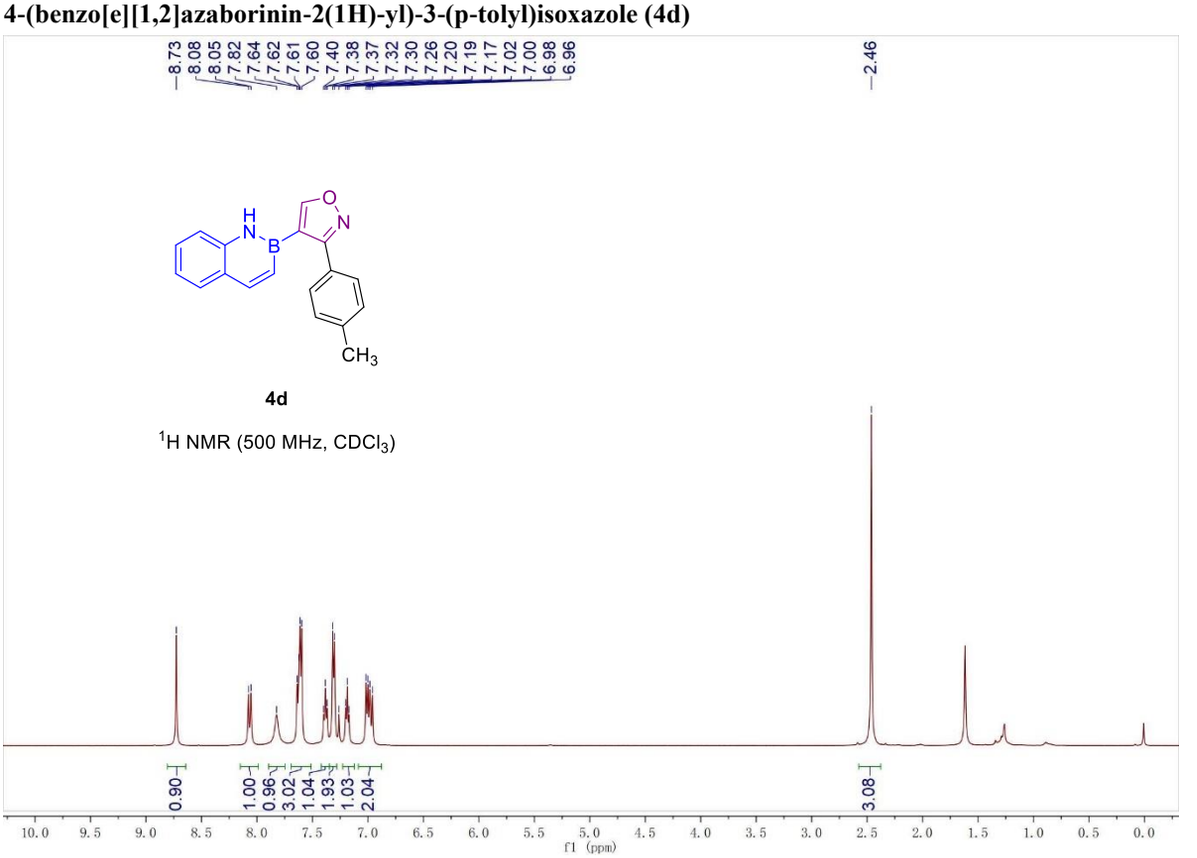
4c

^{13}C NMR (126 MHz, $CDCl_3$)

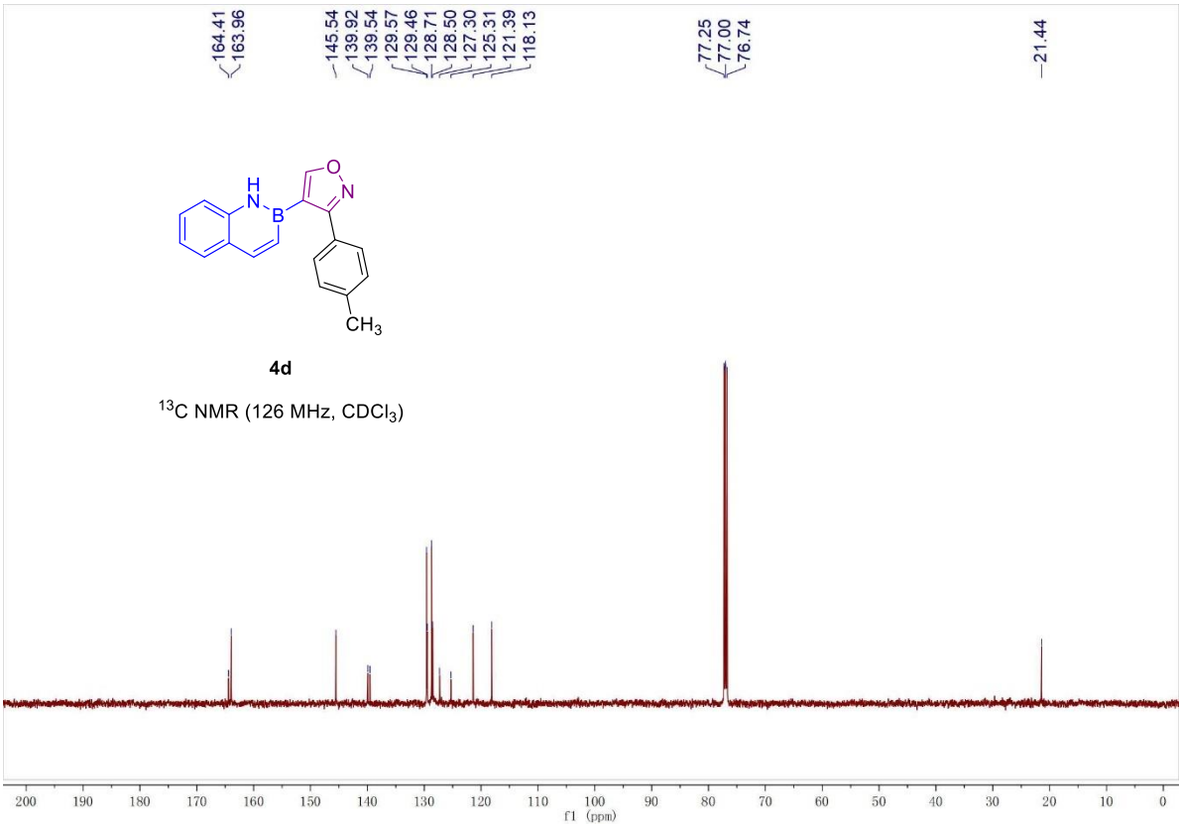
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-phenoxyphenyl)isoxazole (4c)



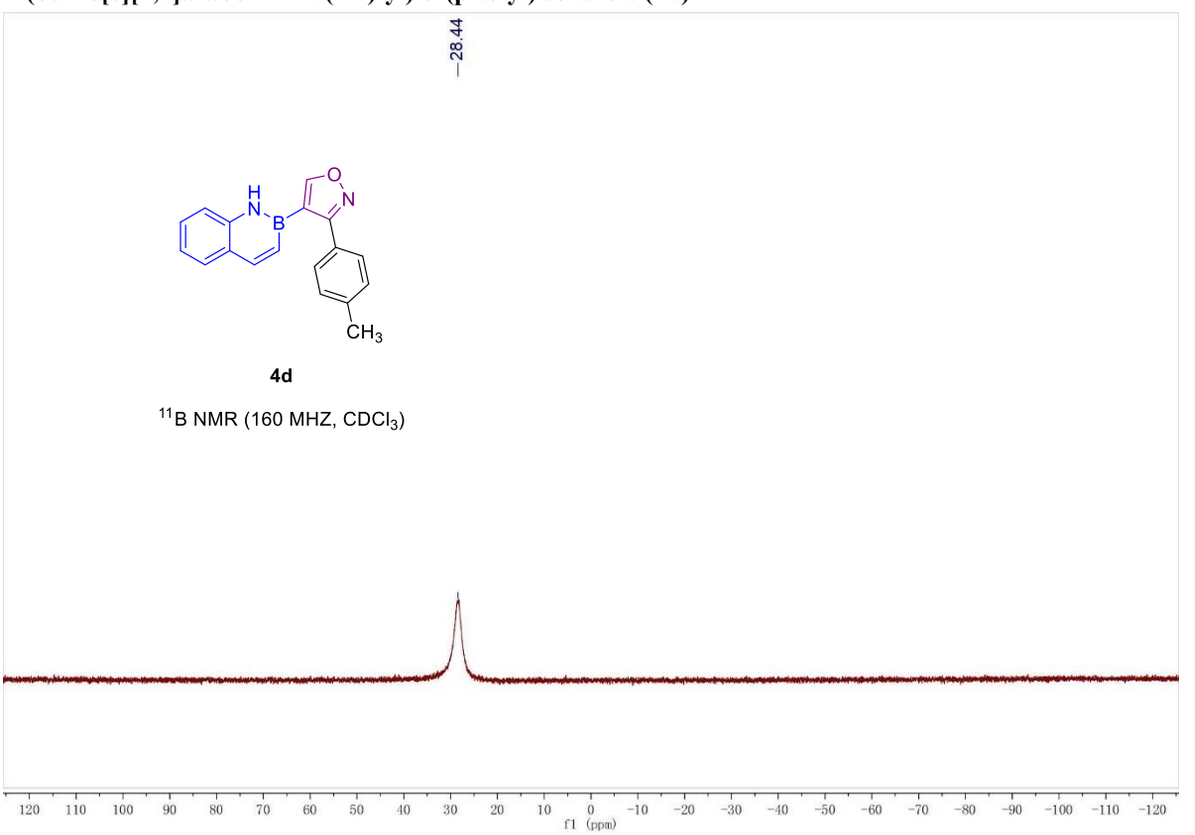
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4d)



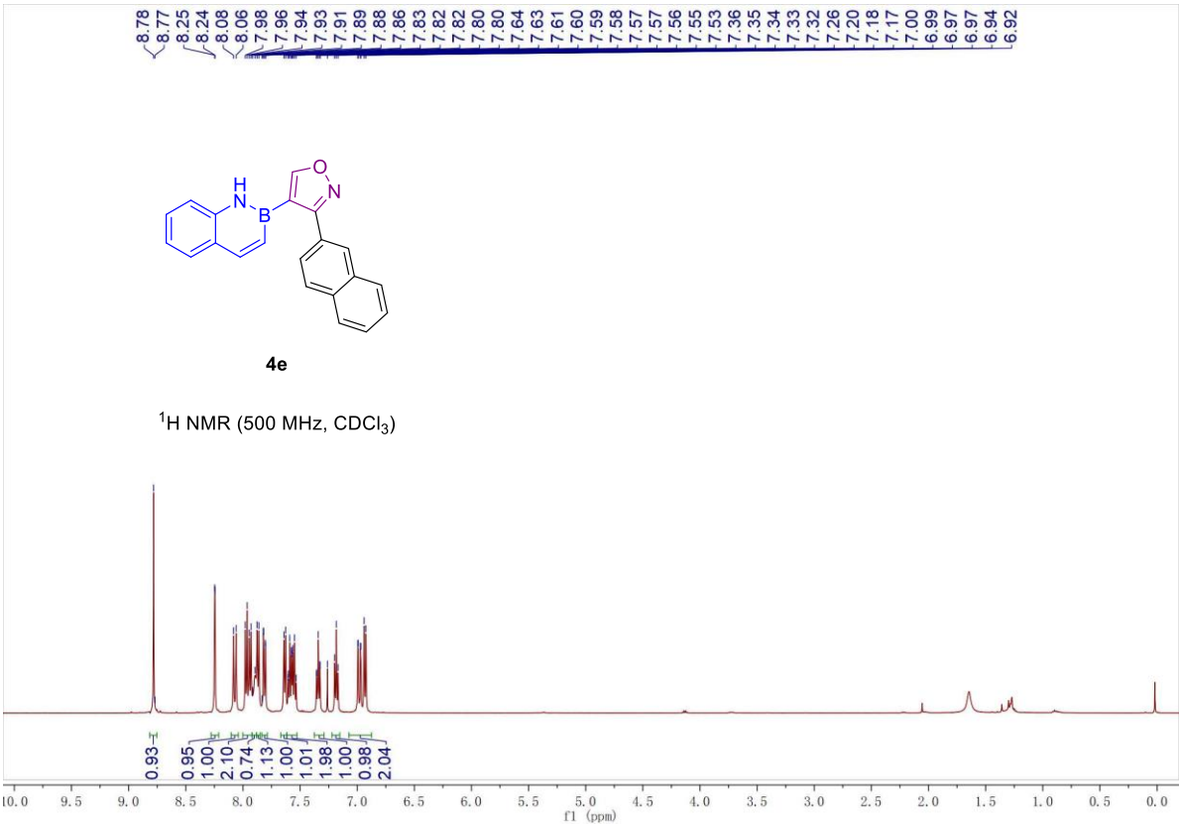
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4d)



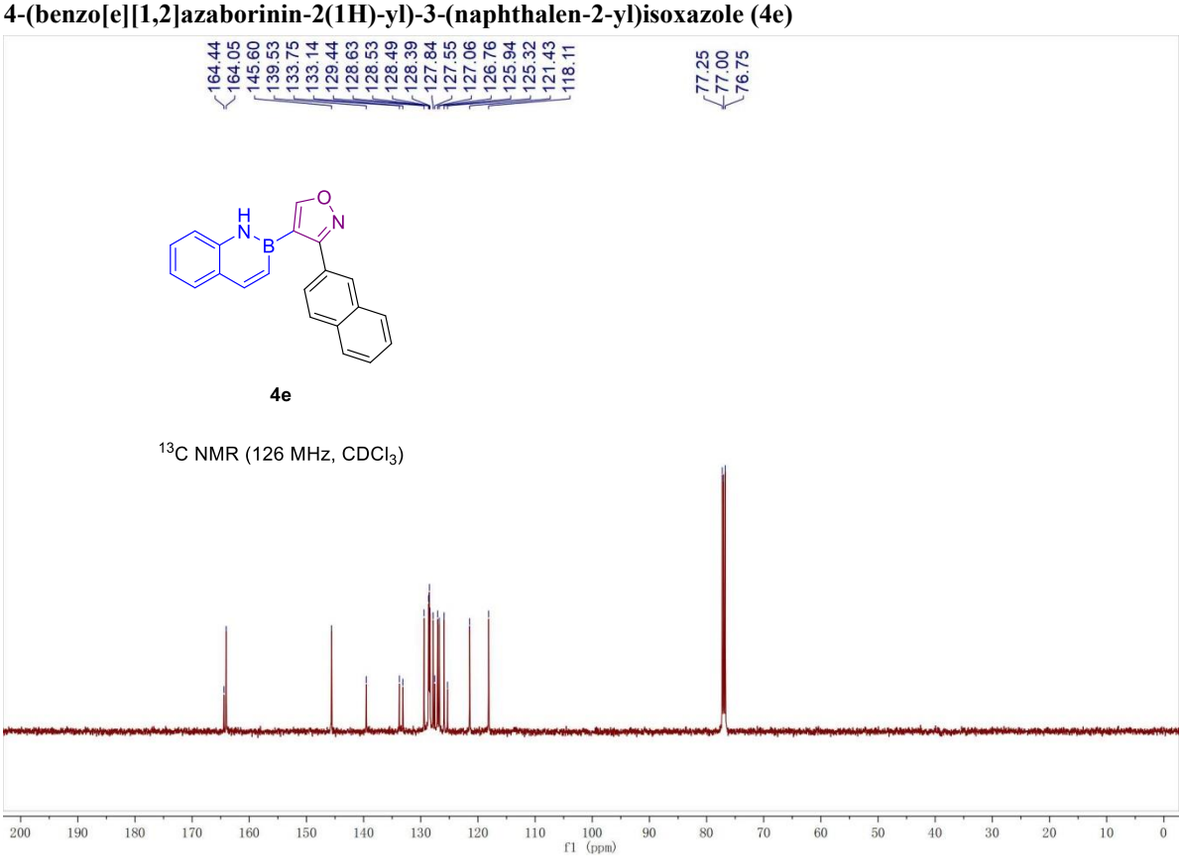
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4d)



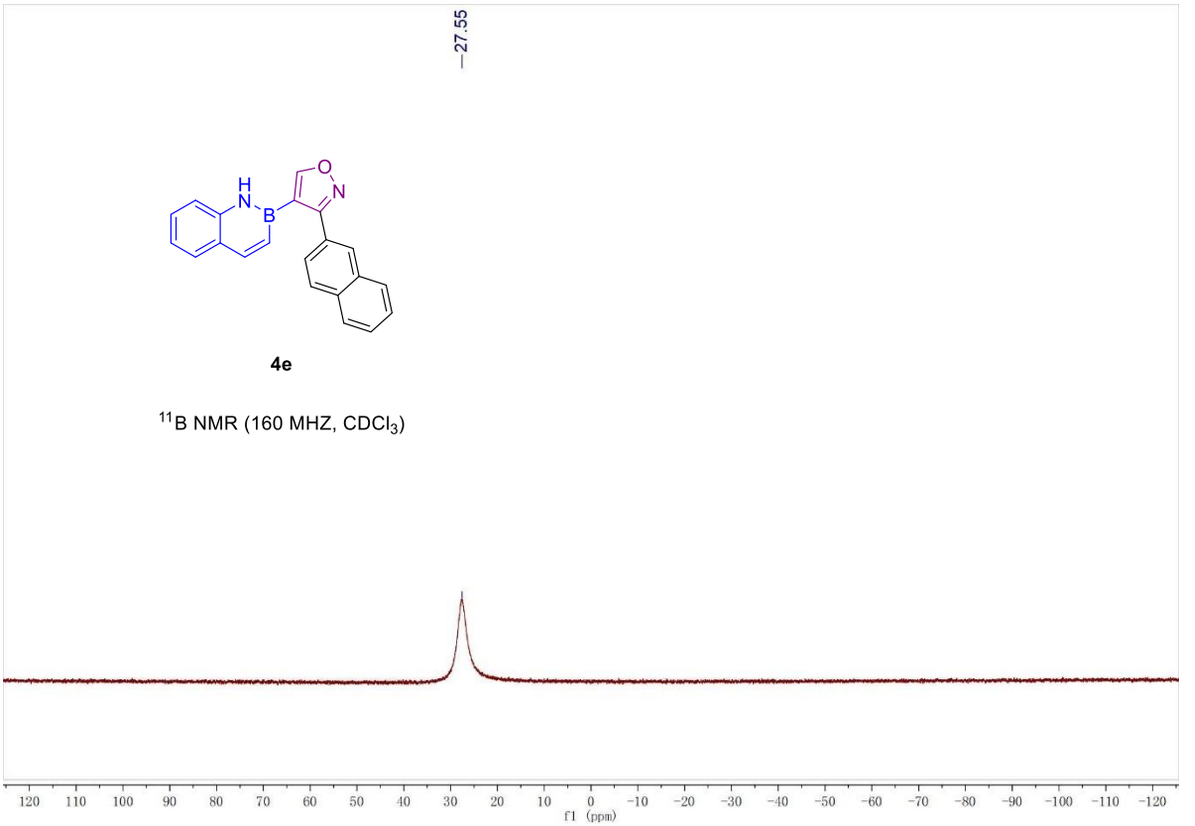
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphthalen-2-yl)isoxazole (4e)



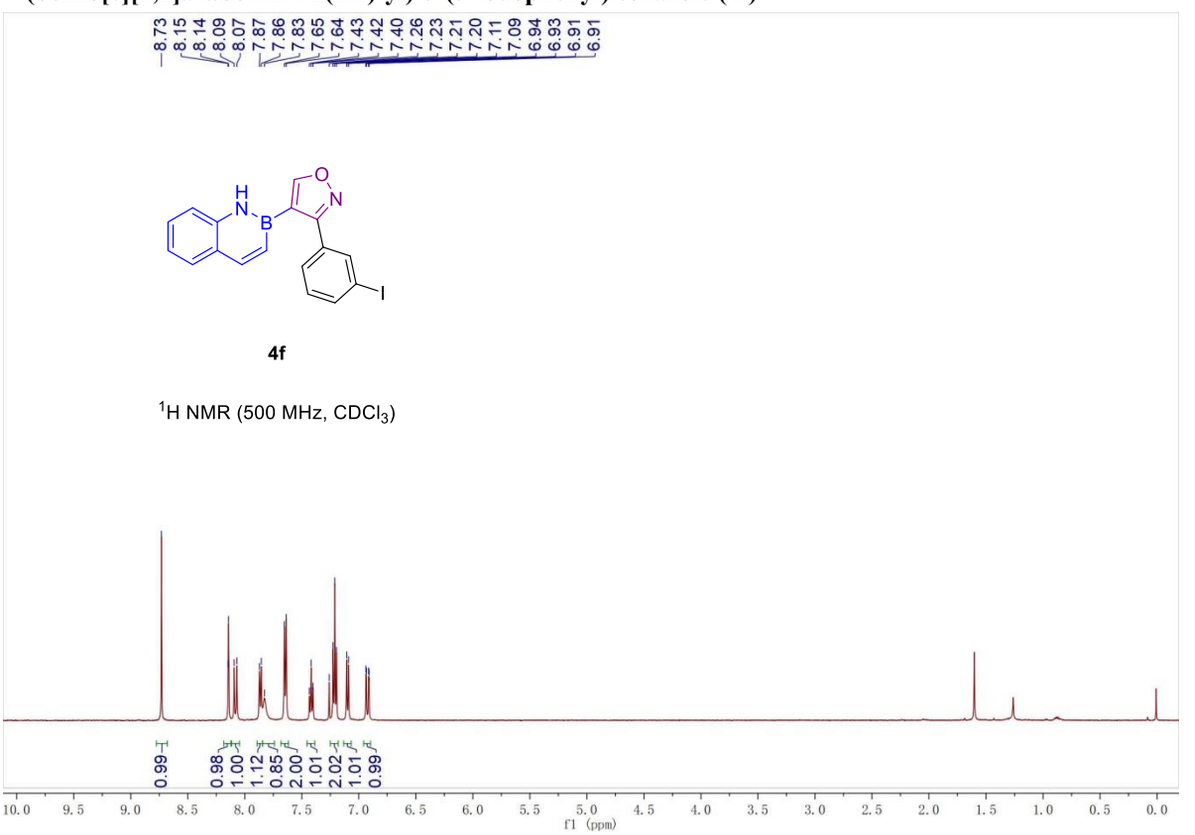
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphthalen-2-yl)isoxazole (4e)



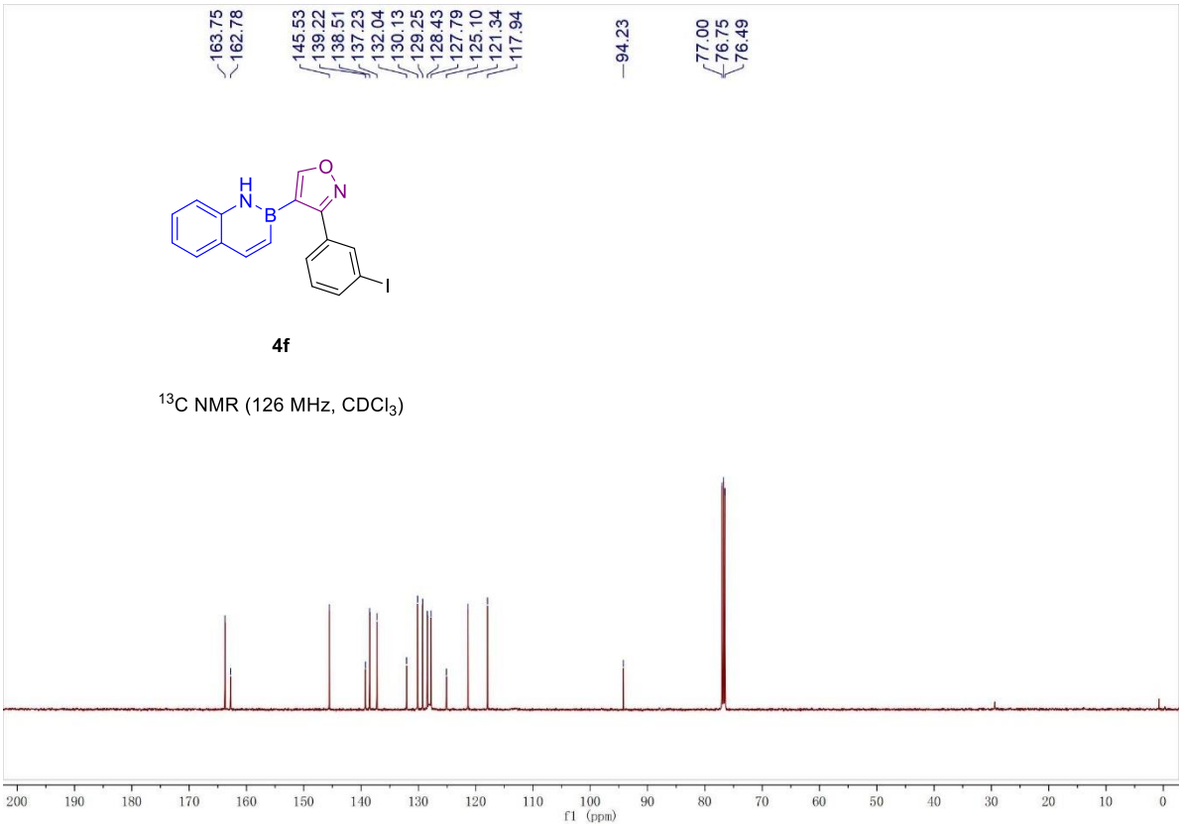
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(naphthalen-2-yl)isoxazole (4e)



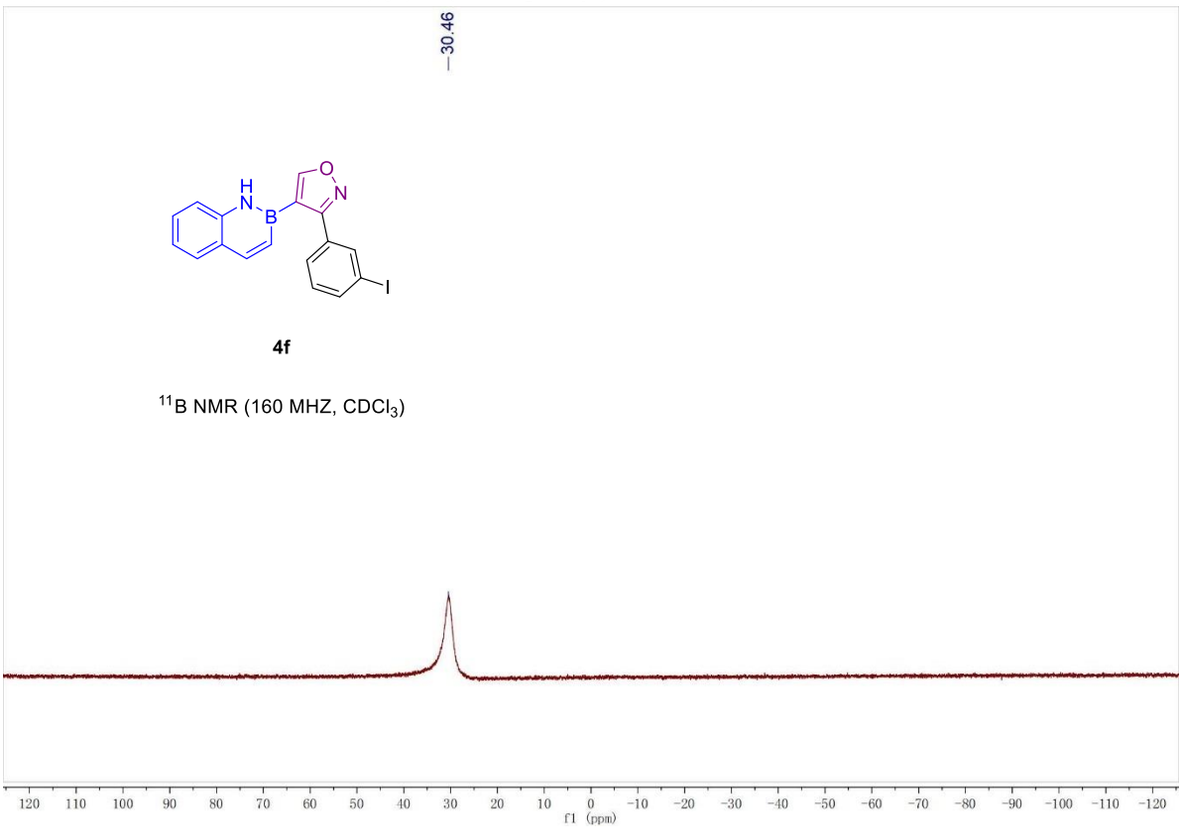
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-iodophenyl)isoxazole (4f)



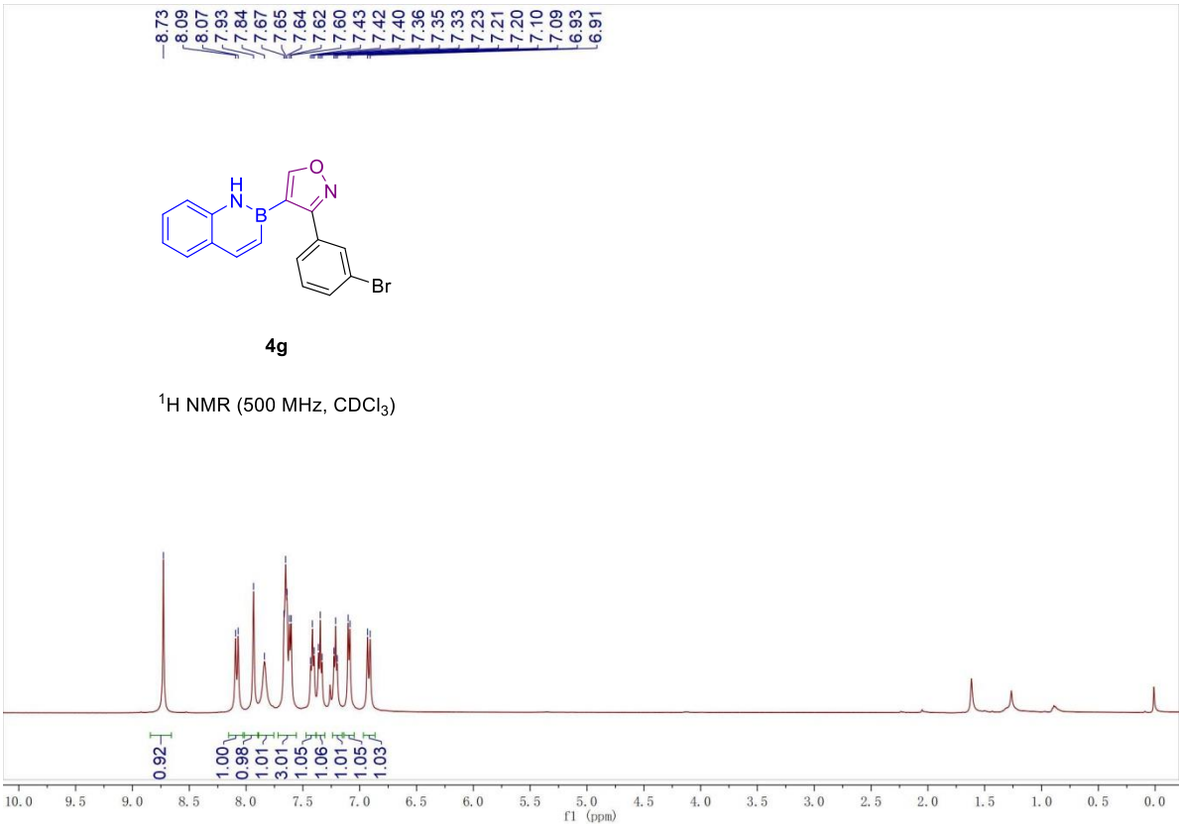
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-iodophenyl)isoxazole (4f)



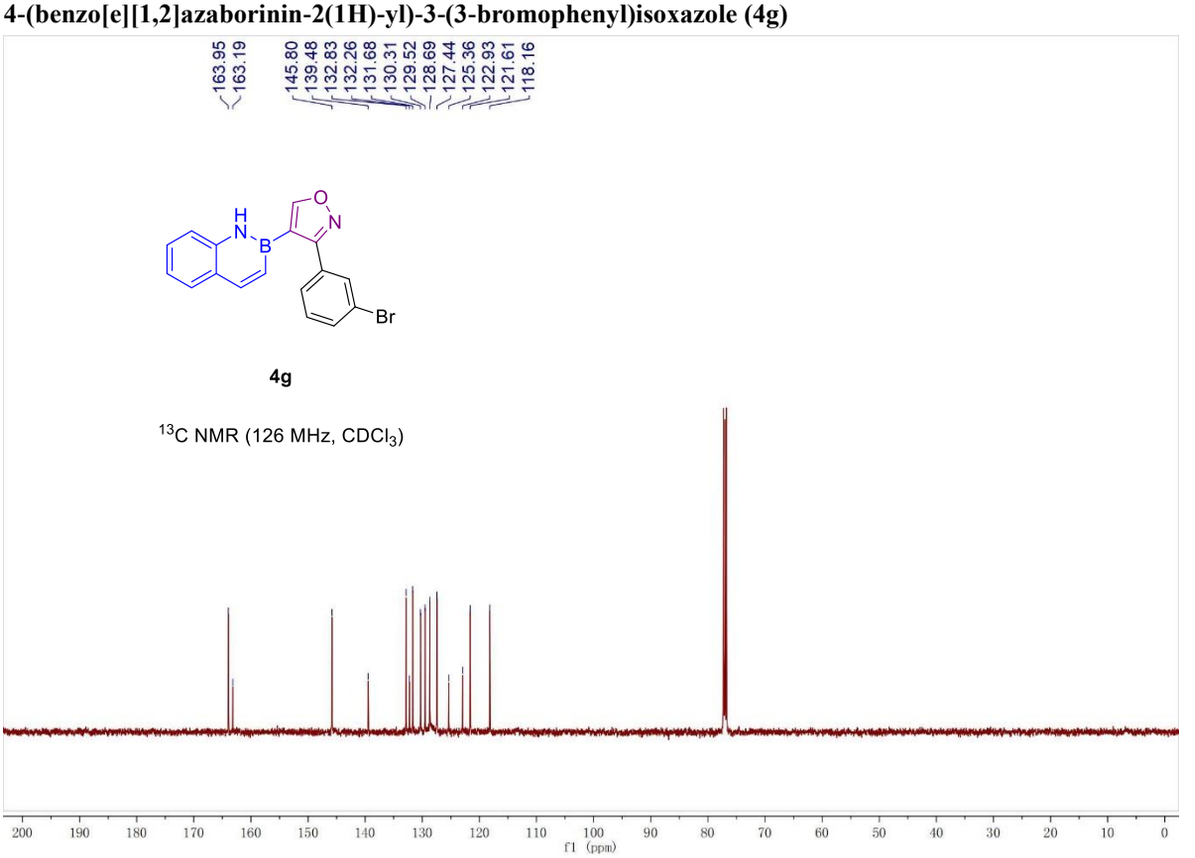
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-iodophenyl)isoxazole (4f)



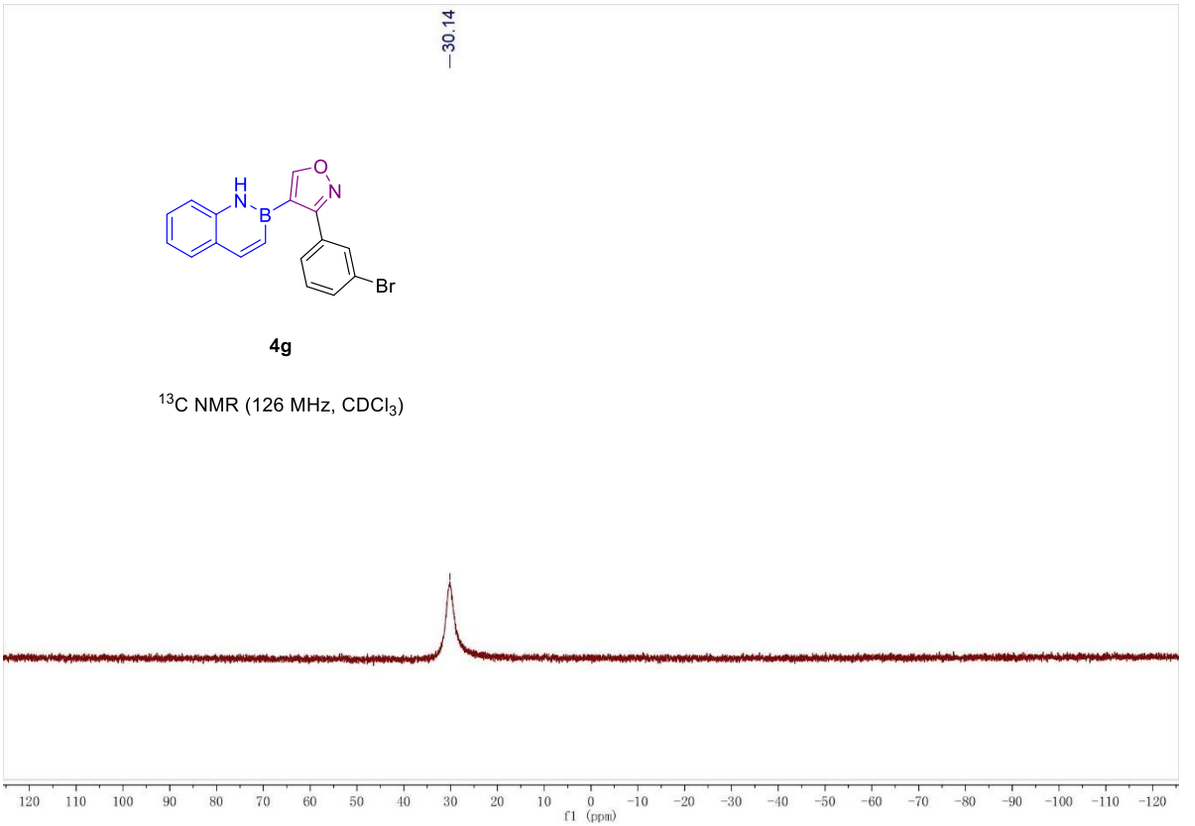
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-bromophenyl)isoxazole (4g)



4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-bromophenyl)isoxazole (4g)



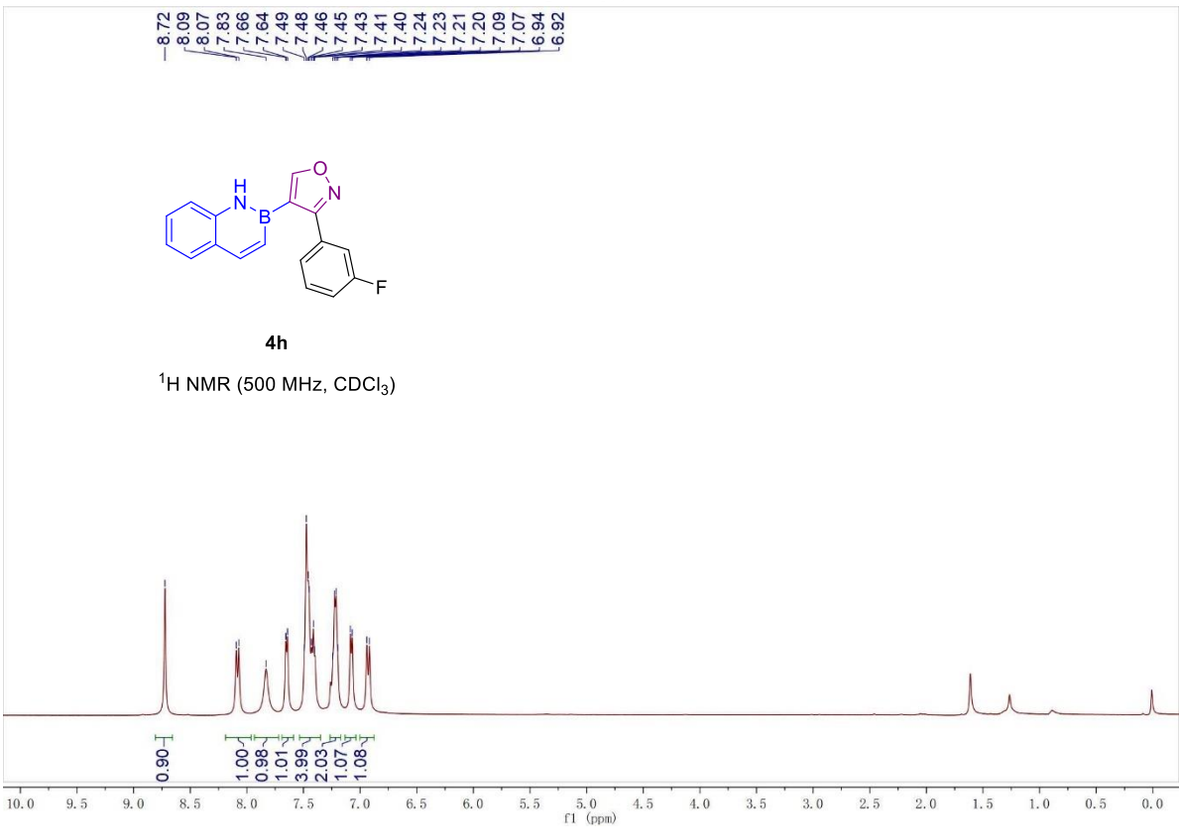
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-bromophenyl)isoxazole (4g)



4g

^{13}C NMR (126 MHz, $CDCl_3$)

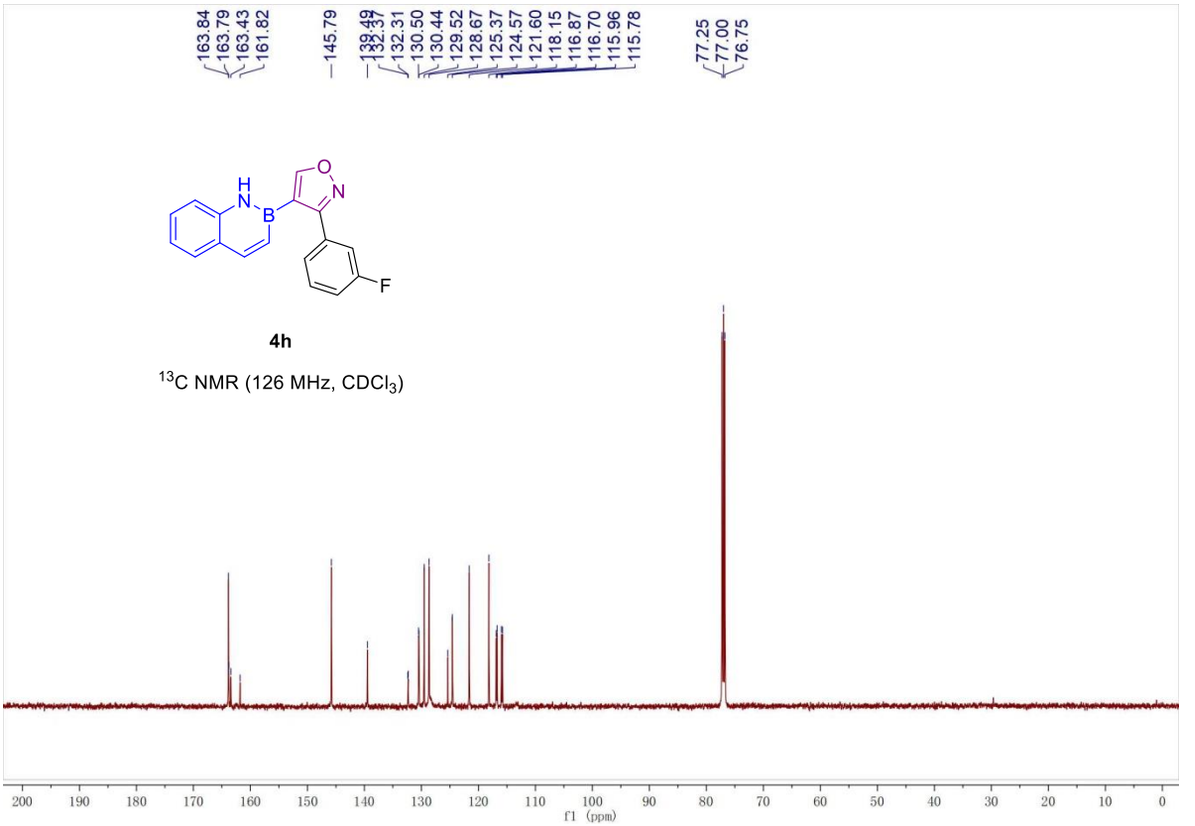
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole (4h)



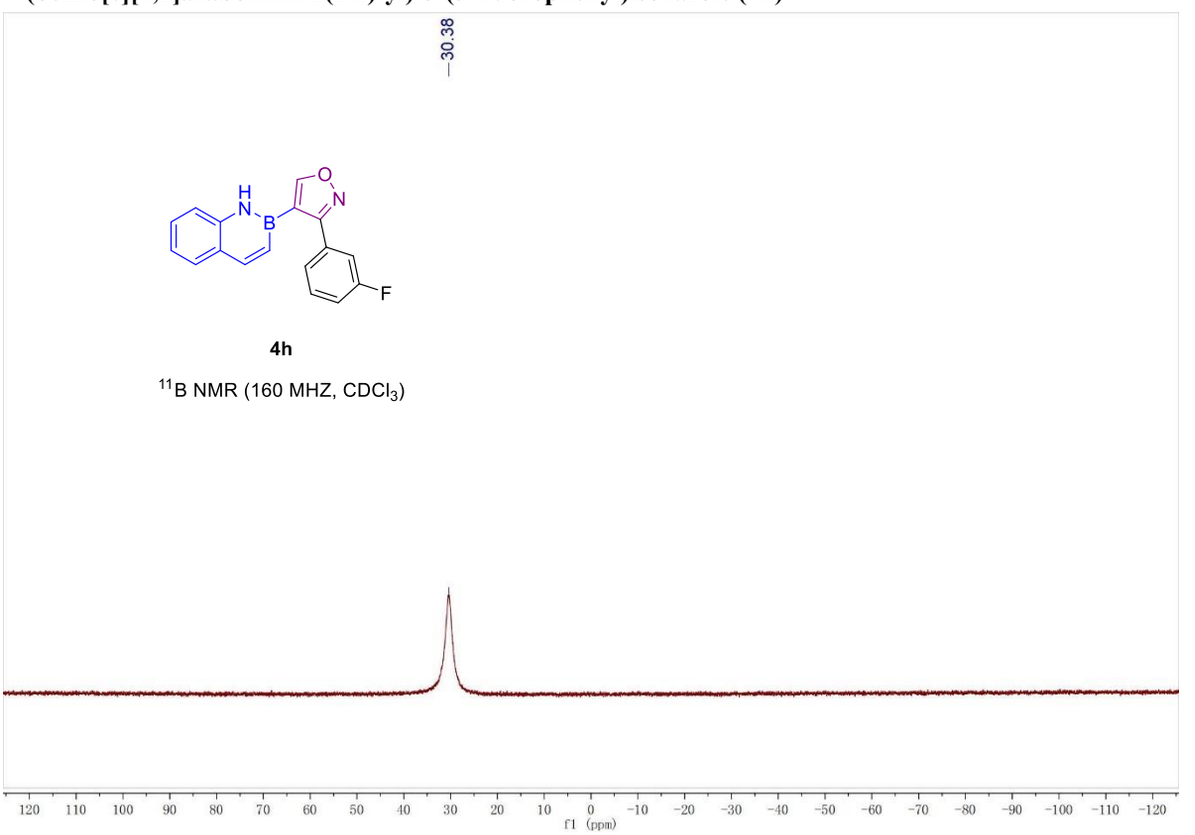
4h

^{1}H NMR (500 MHz, $CDCl_3$)

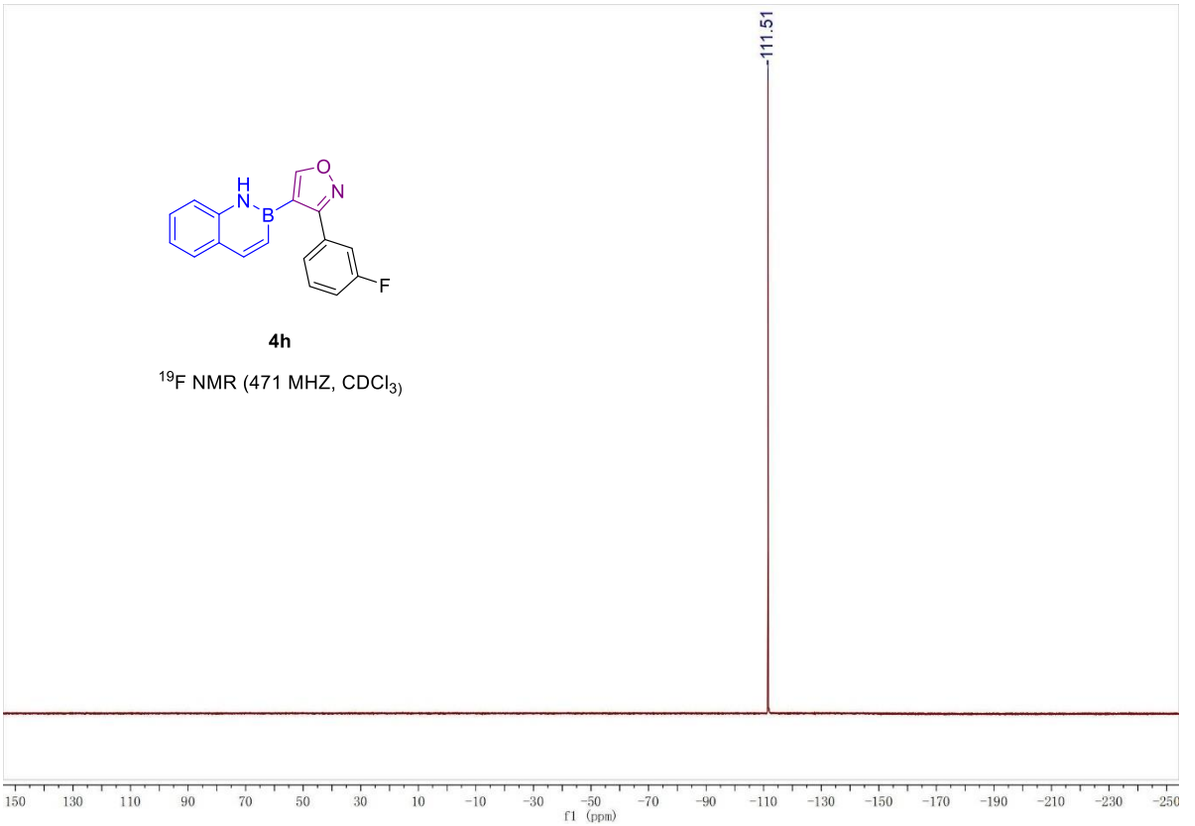
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole (4h)



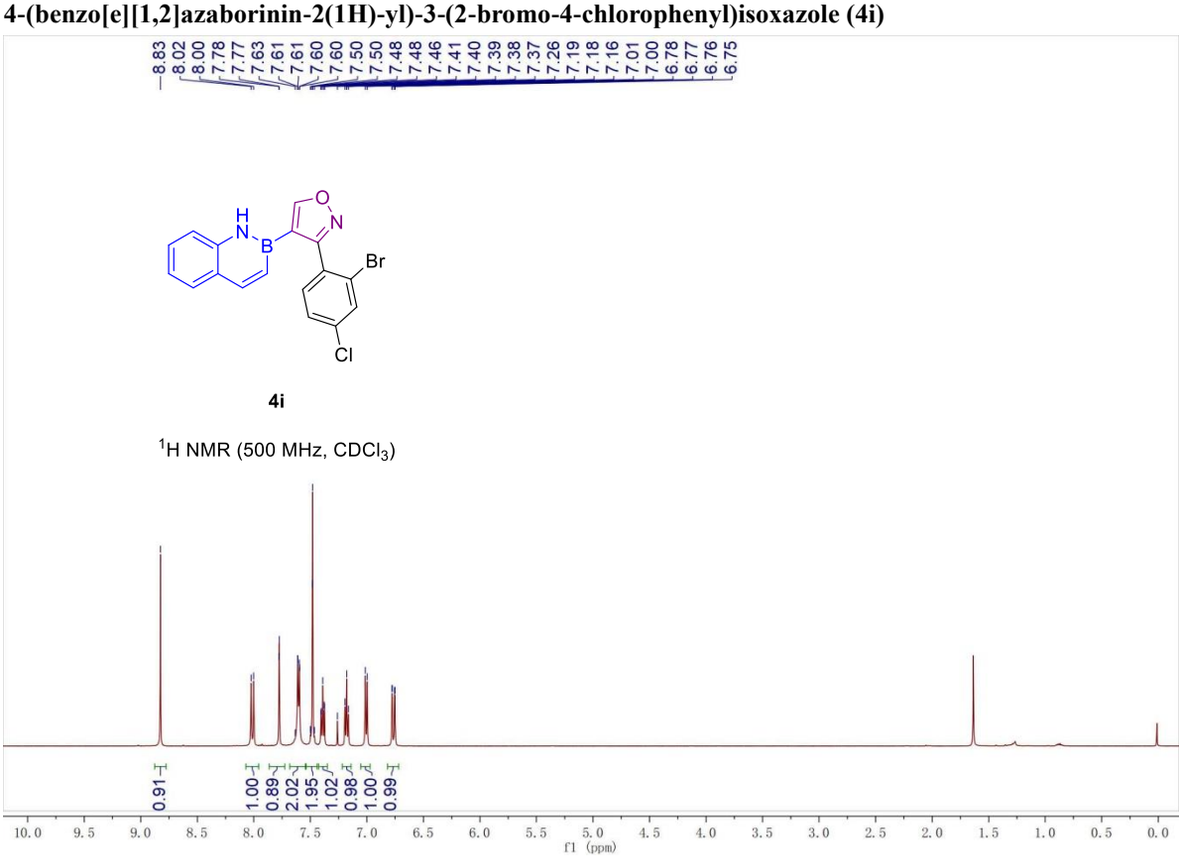
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole (4h)



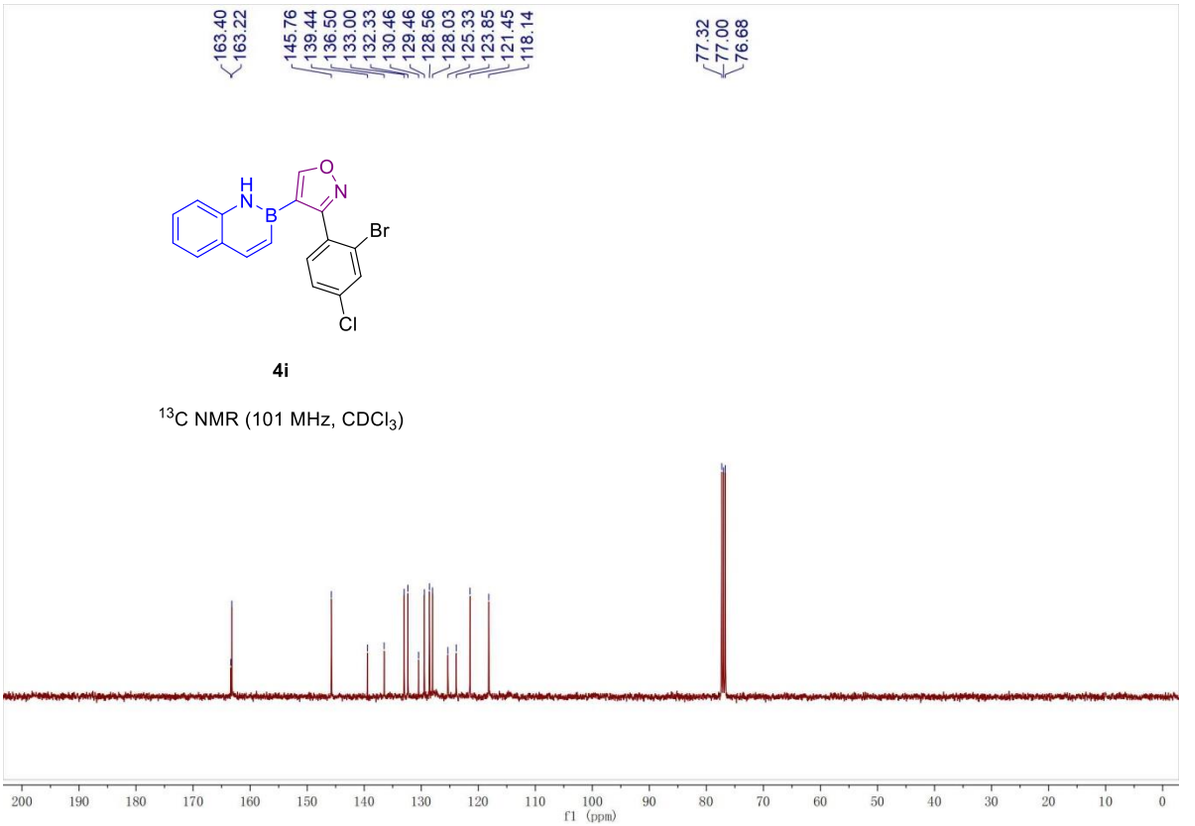
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(3-fluorophenyl)isoxazole (4h)



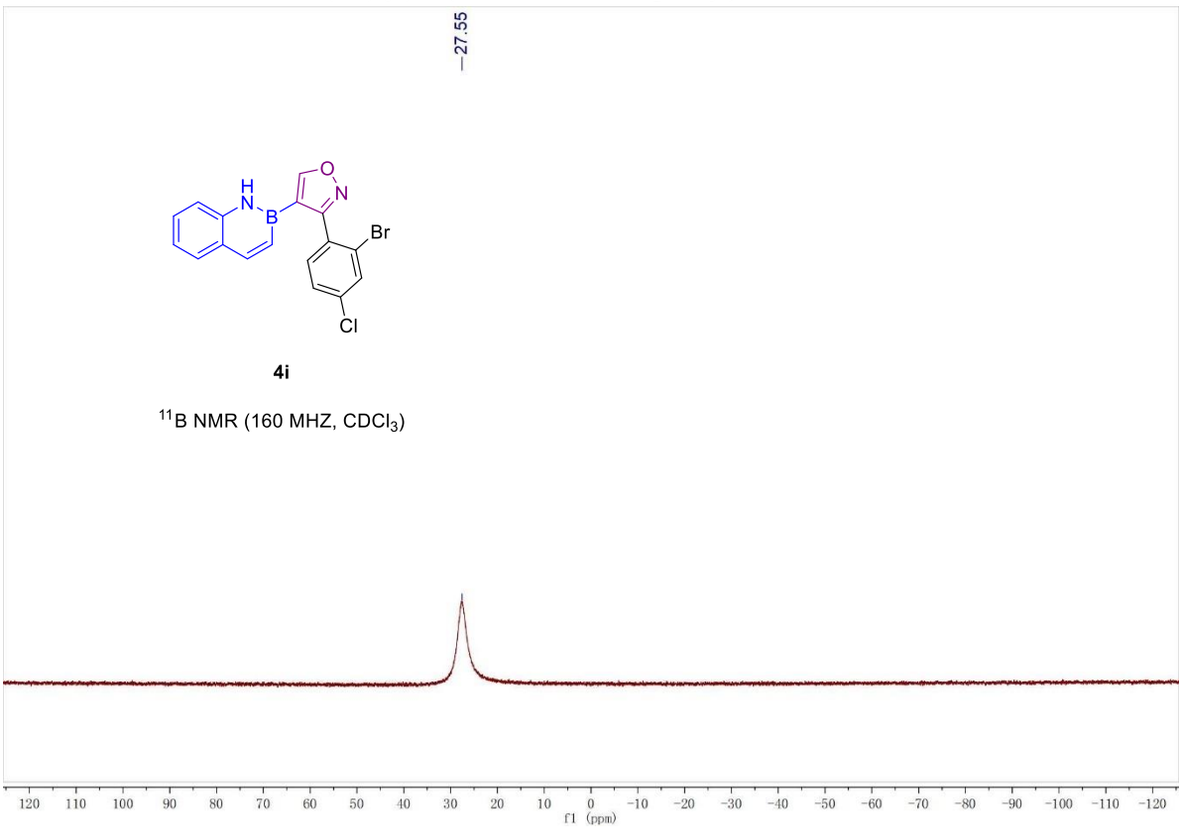
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(2-bromo-4-chlorophenyl)isoxazole (4i)



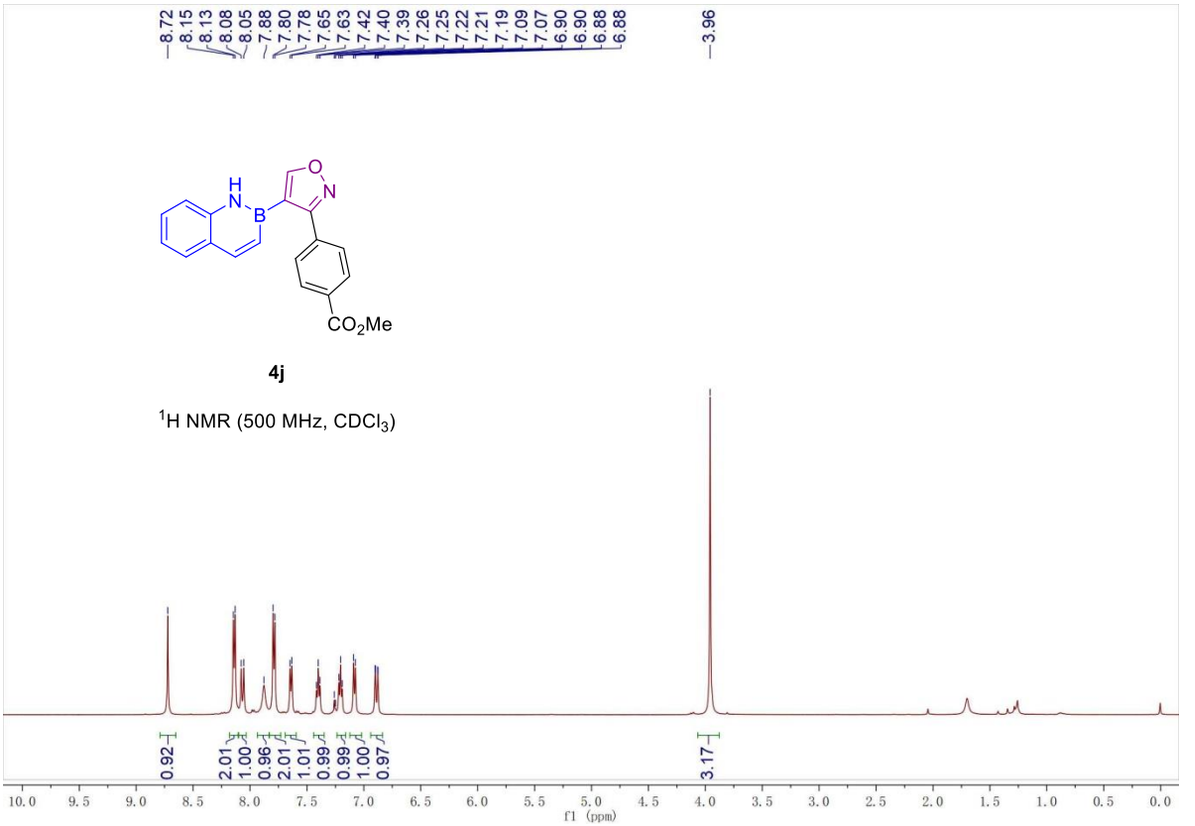
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(2-bromo-4-chlorophenyl)isoxazole (4i)



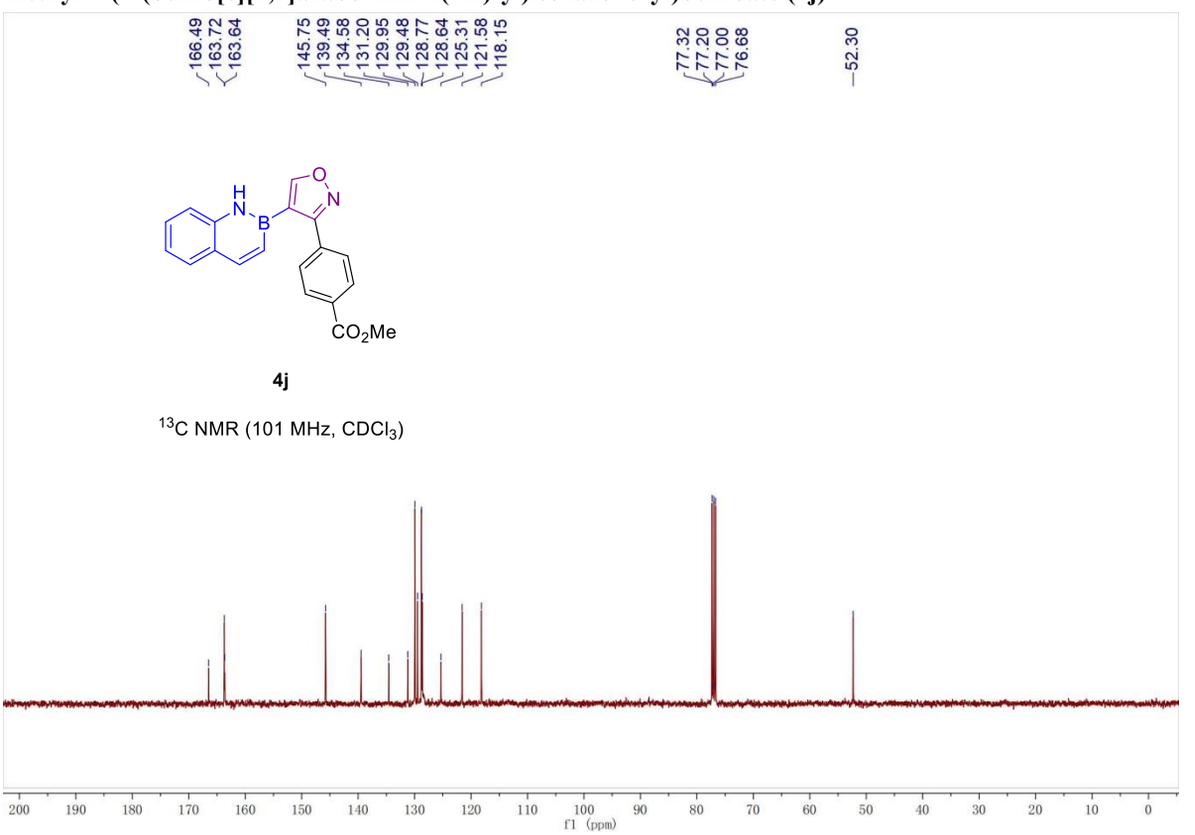
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-(2-bromo-4-chlorophenyl)isoxazole (4i)



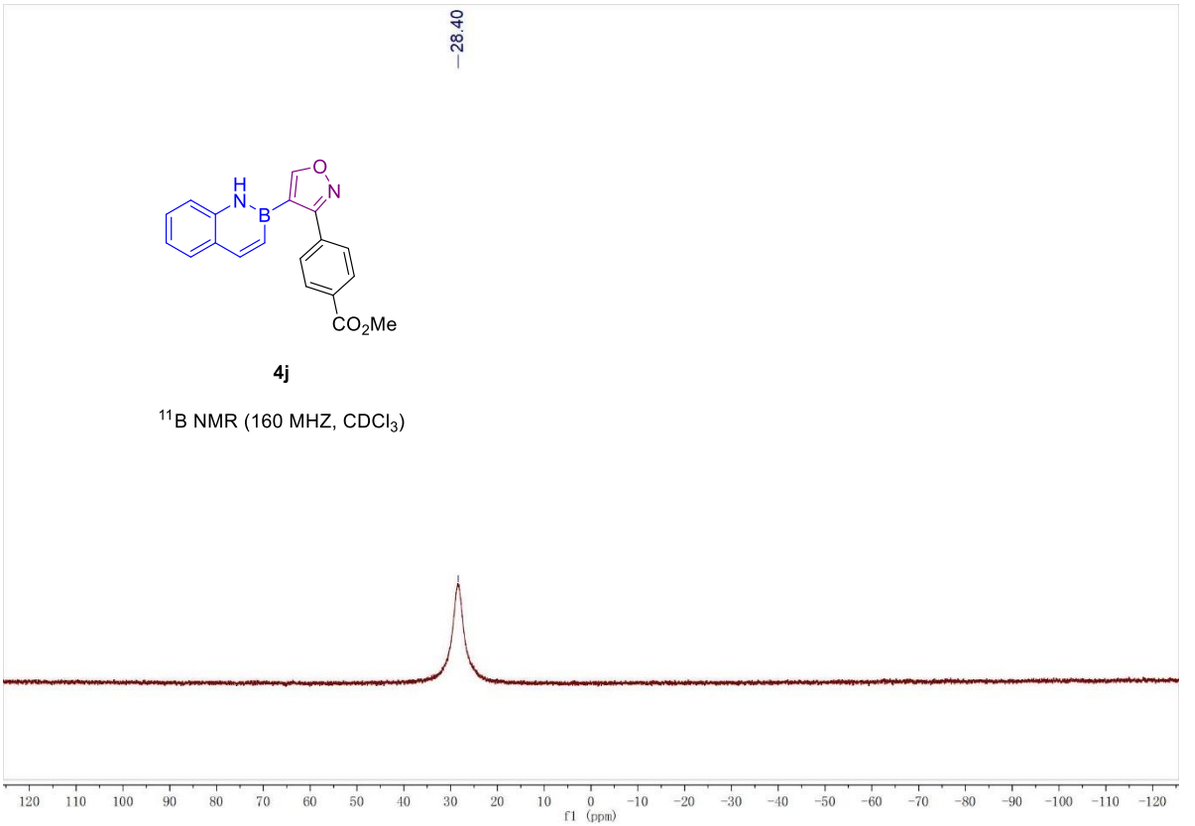
methyl 4-(4-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazol-3-yl)benzoate (4j)



methyl 4-(4-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazol-3-yl)benzoate (4j)



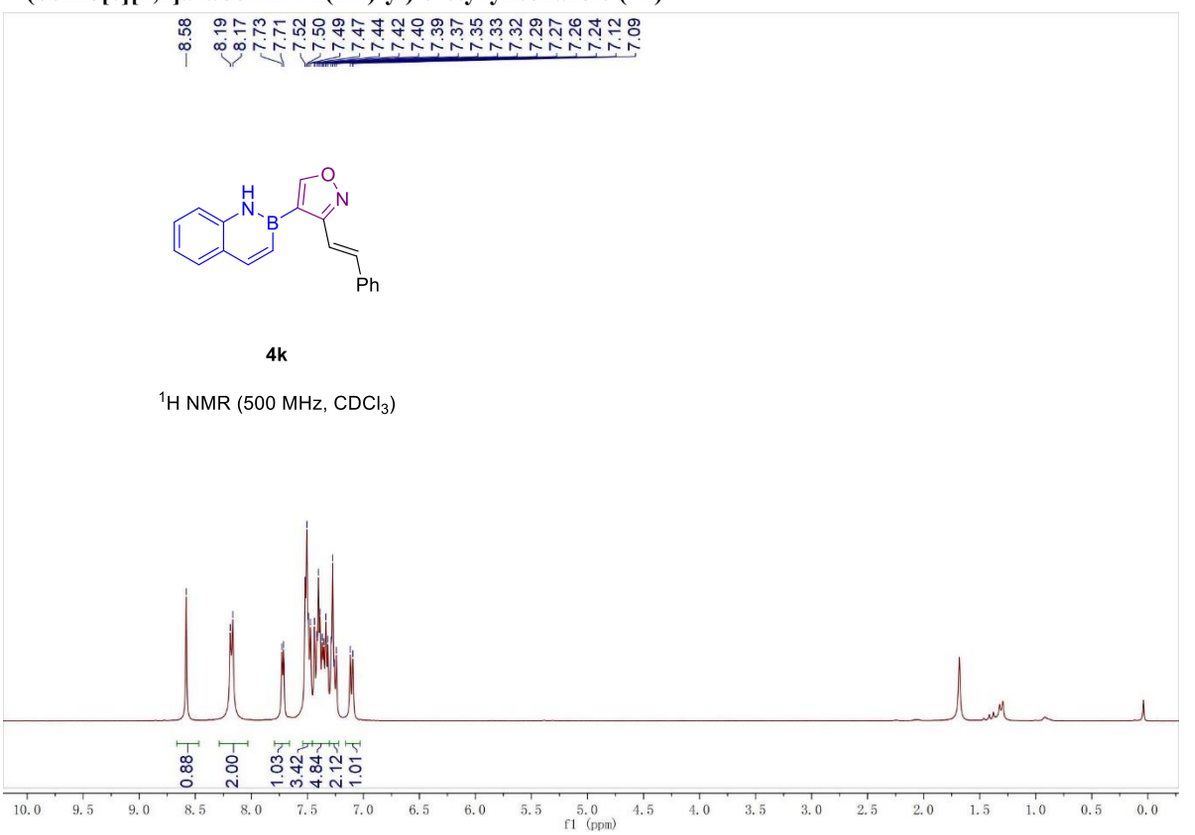
methyl 4-(4-(benzo[e][1,2]azaborinin-2(1H)-yl)isoxazol-3-yl)benzoate (4j)



4j

^{11}B NMR (160 MHZ, $CDCl_3$)

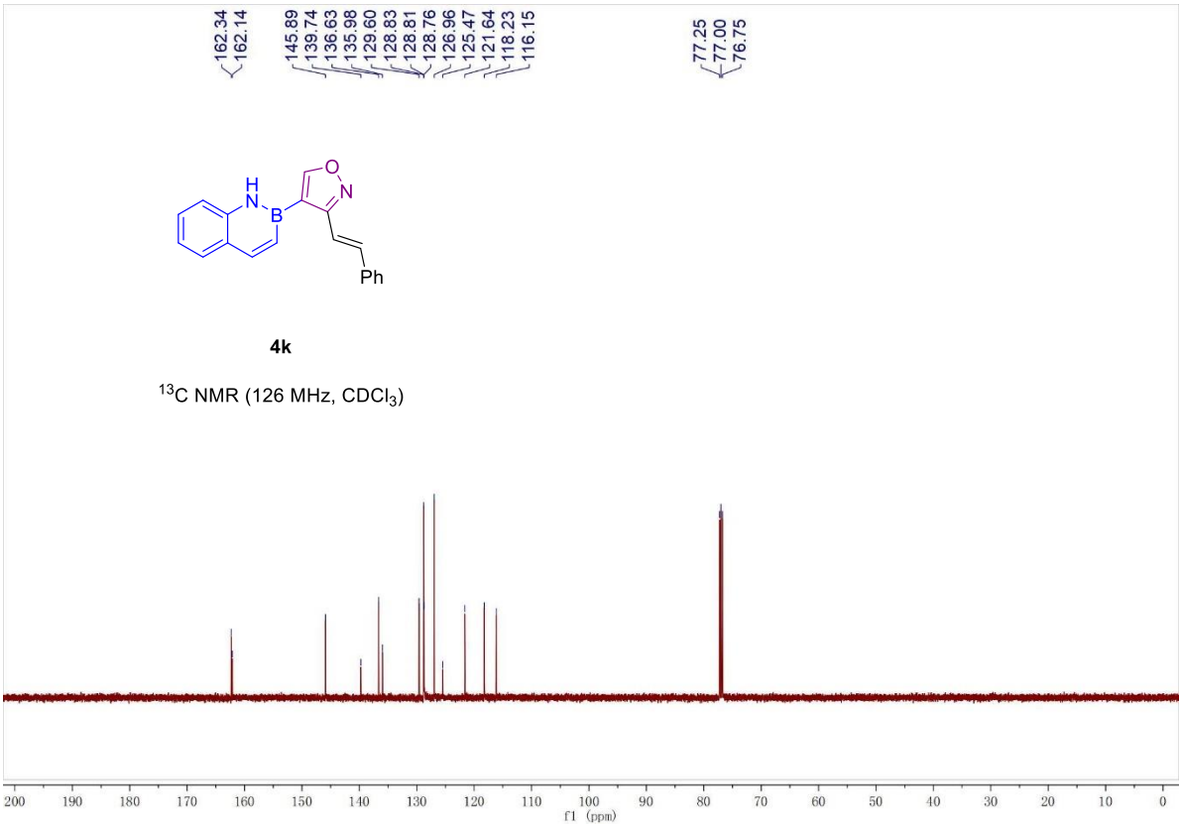
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-styrylisoxazole (4k)



4k

^{1}H NMR (500 MHz, $CDCl_3$)

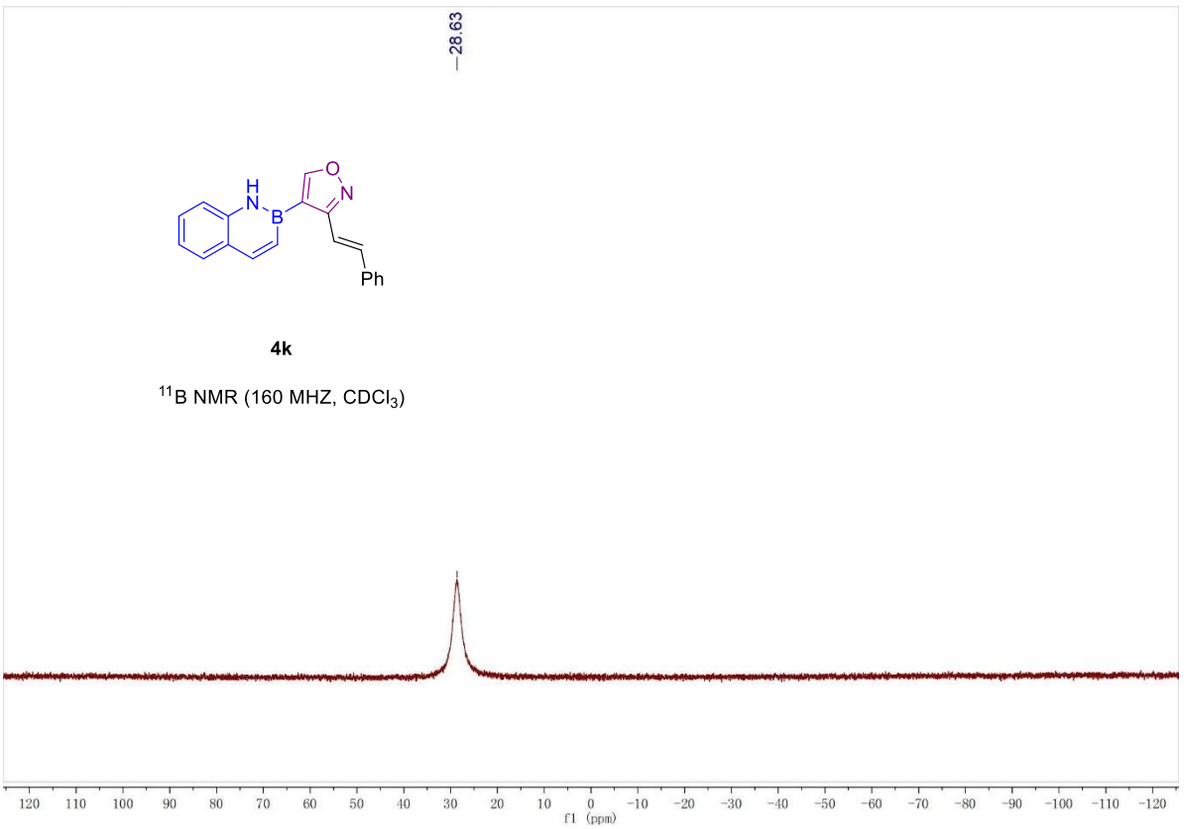
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-styrylisoxazole (4k)



4k

^{13}C NMR (126 MHz, $CDCl_3$)

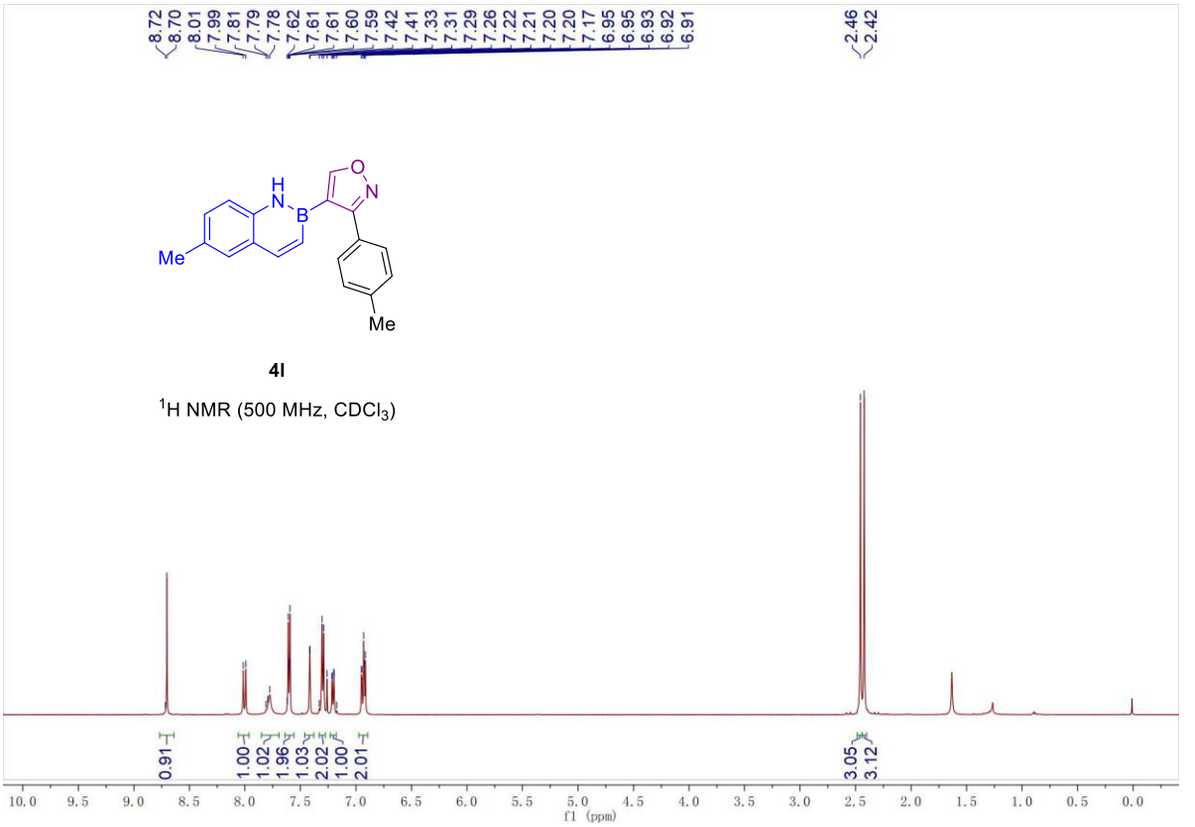
4-(benzo[e][1,2]azaborinin-2(1H)-yl)-3-styrylisoxazole (4k)



4k

^{11}B NMR (160 MHZ, $CDCl_3$)

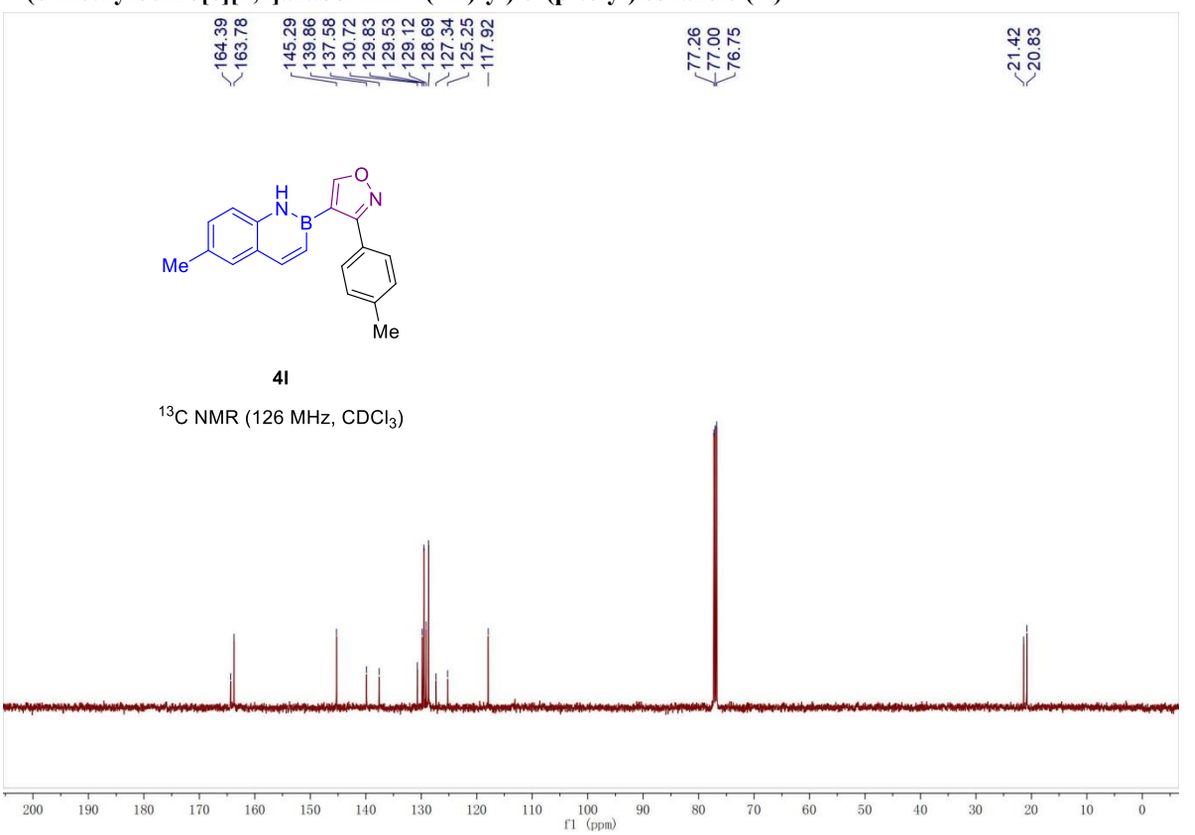
4-(6-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4l)



4l

^{1}H NMR (500 MHz, $CDCl_3$)

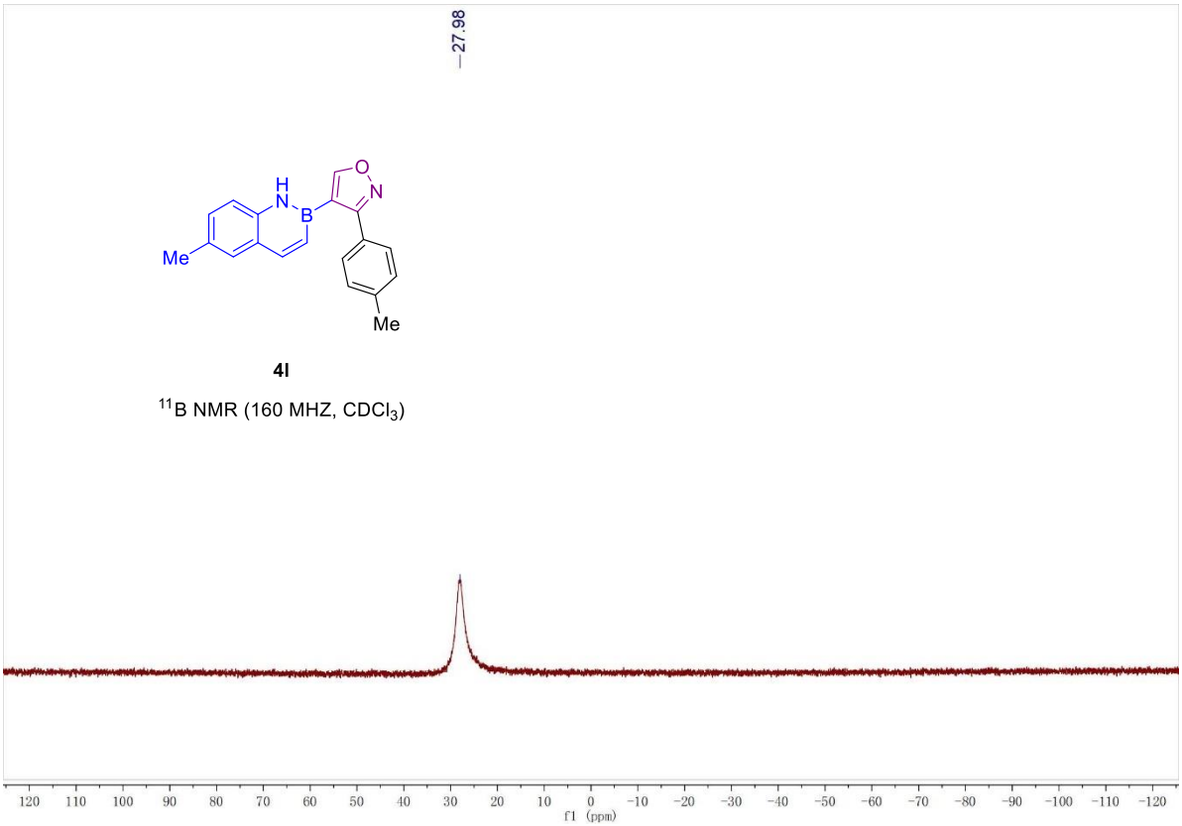
4-(6-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4l)



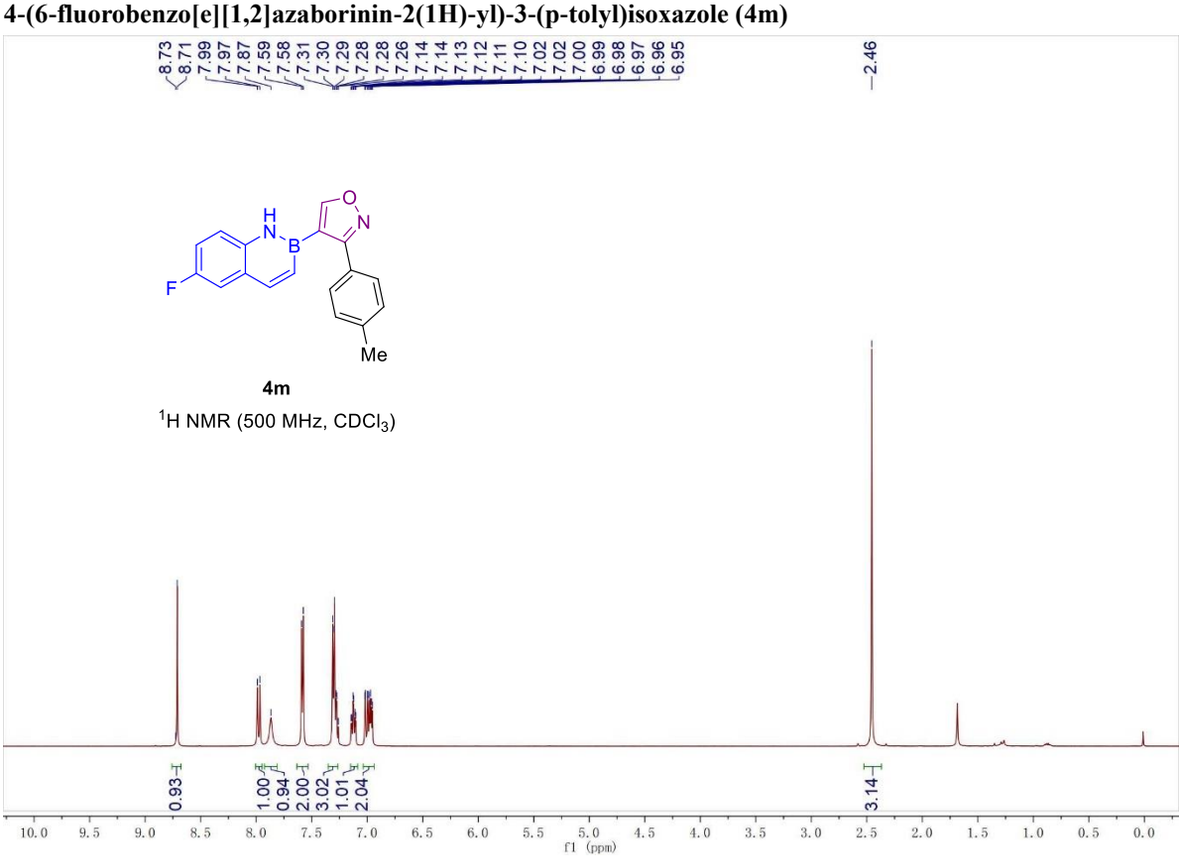
4l

^{13}C NMR (126 MHz, $CDCl_3$)

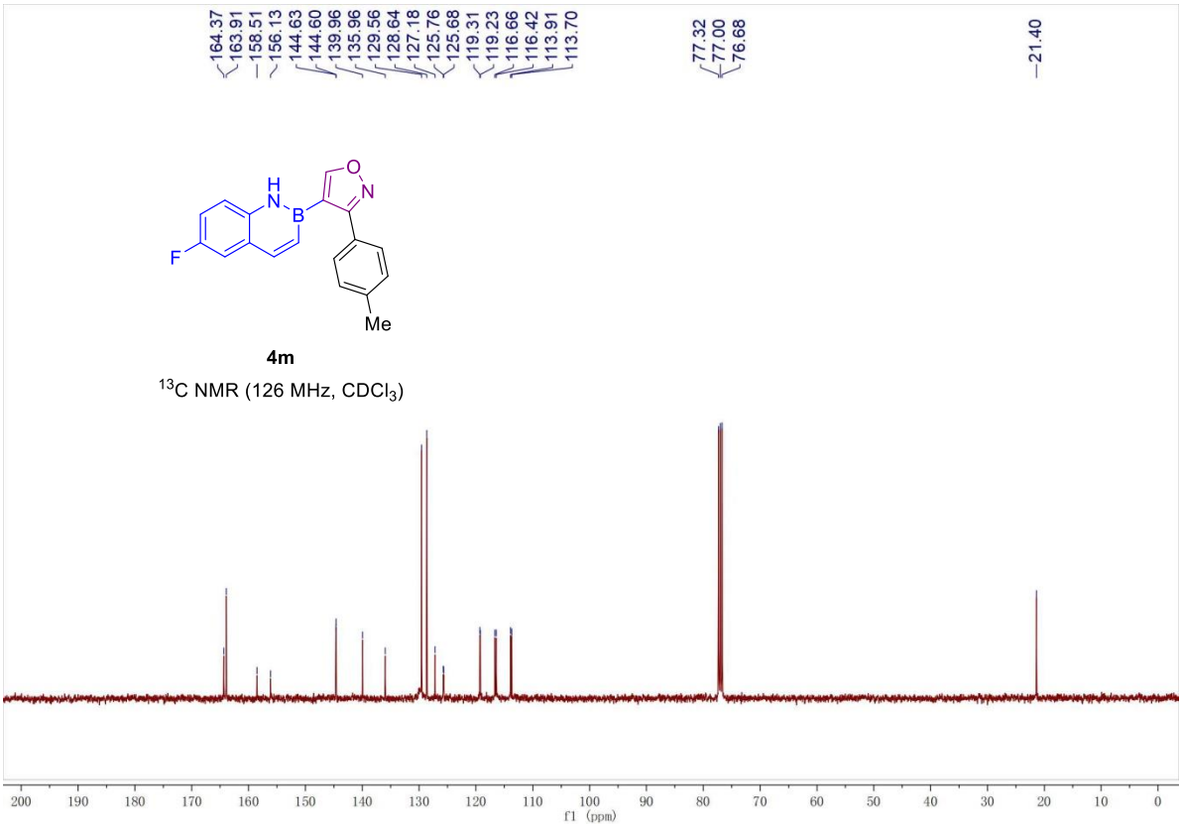
4-(6-methylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4l)



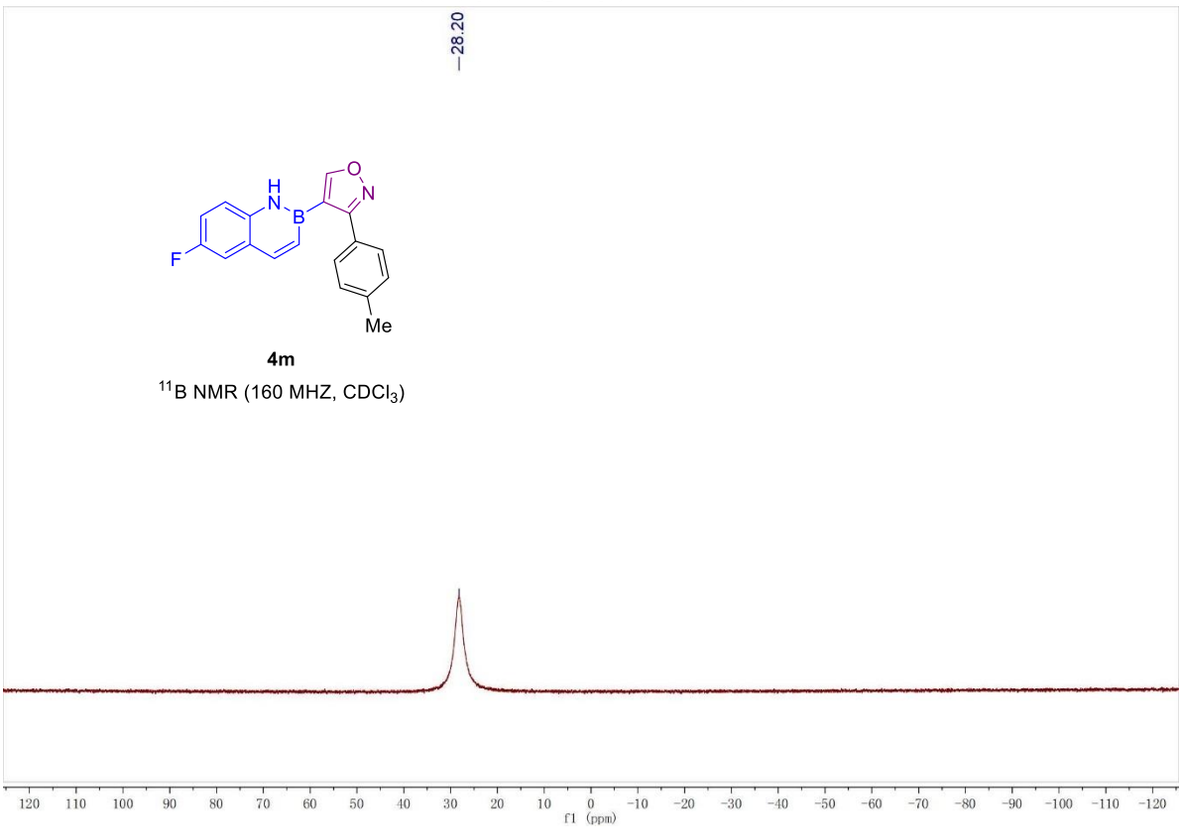
4-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4m)



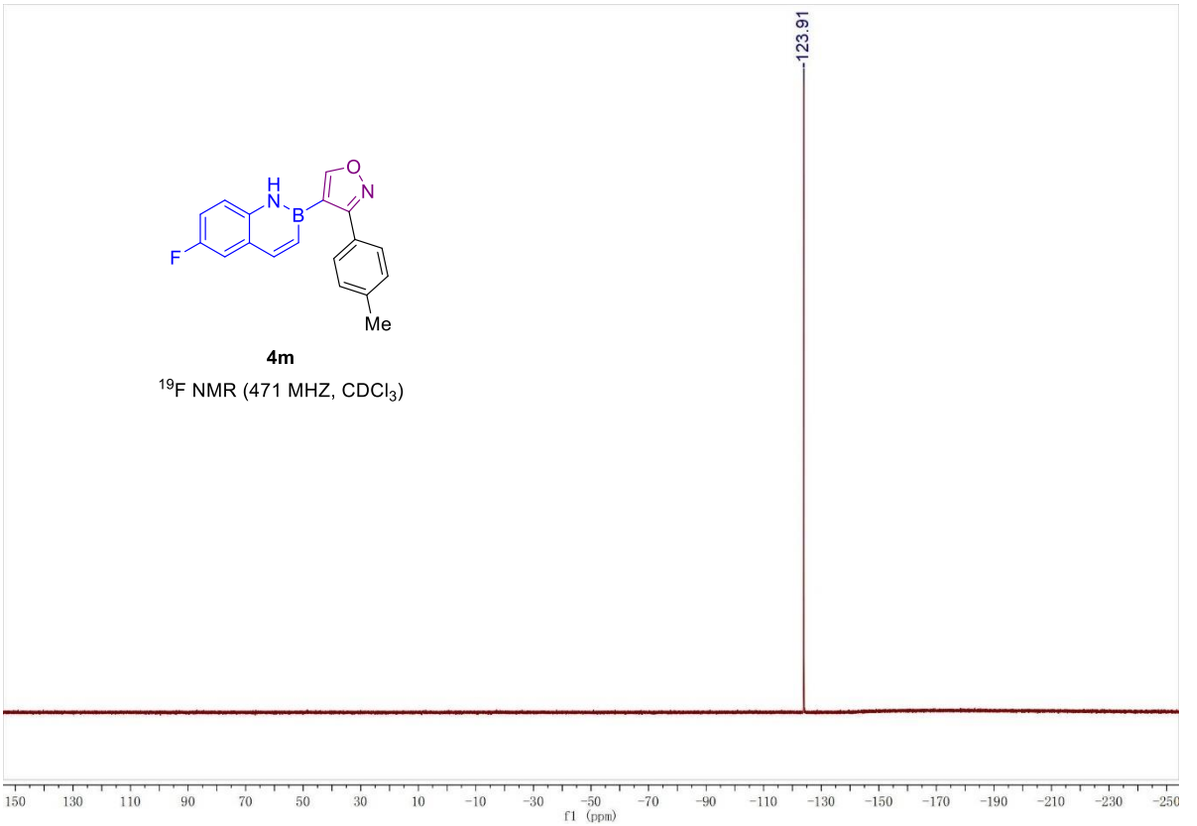
4-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4m)



4-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4m)



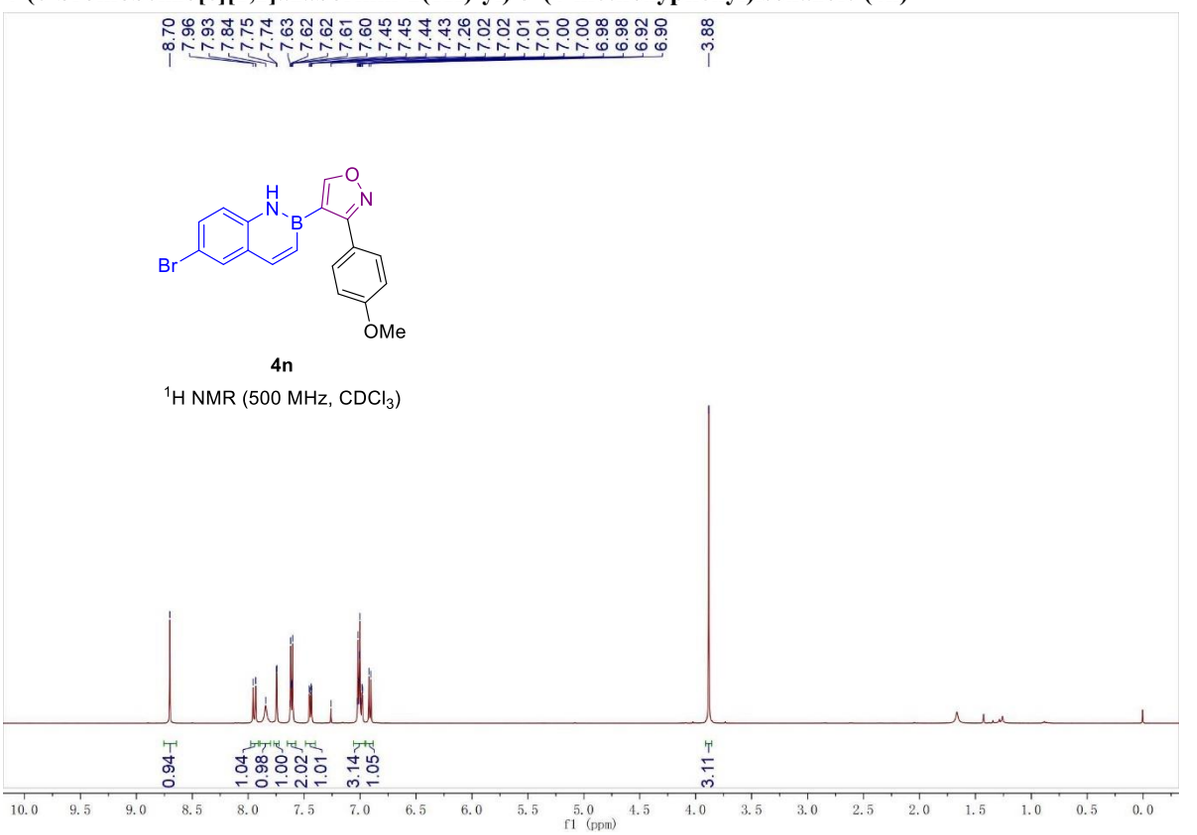
4-(6-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4m)



4m

^{19}F NMR (471 MHZ, $CDCl_3$)

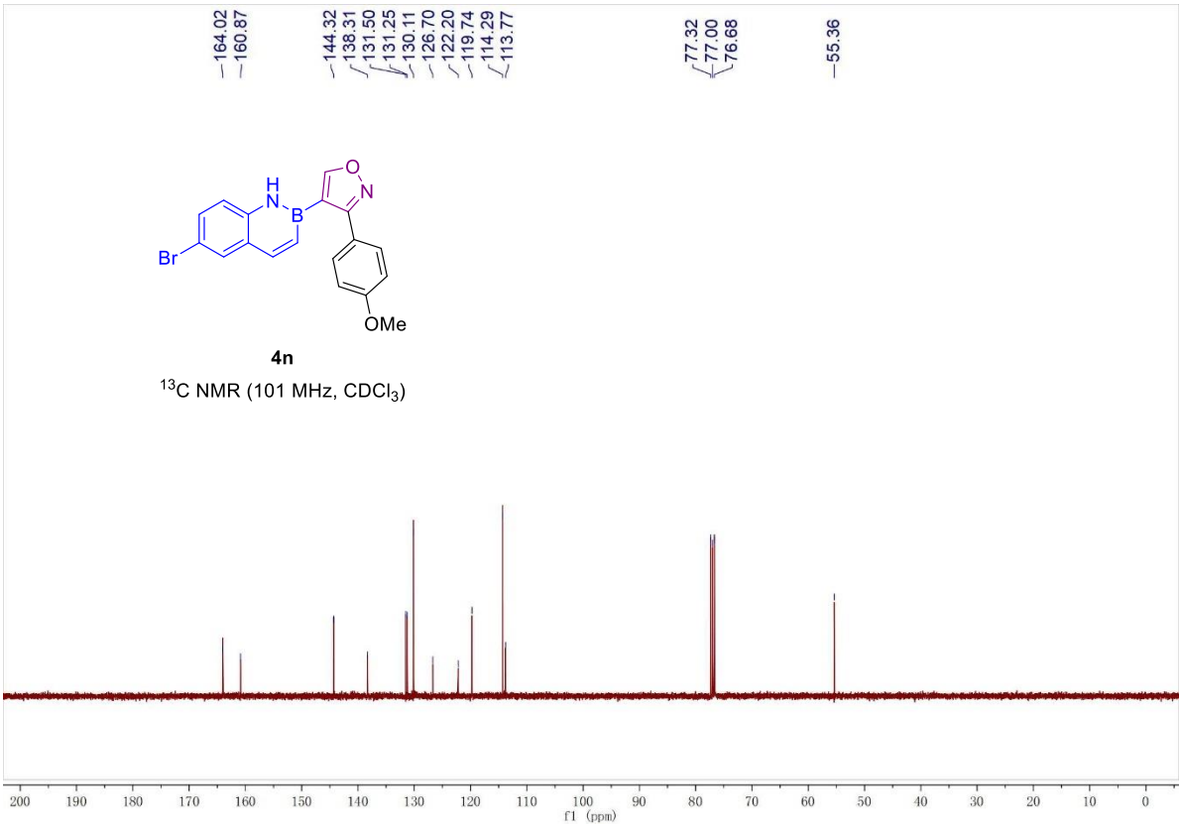
4-(6-bromobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4n)



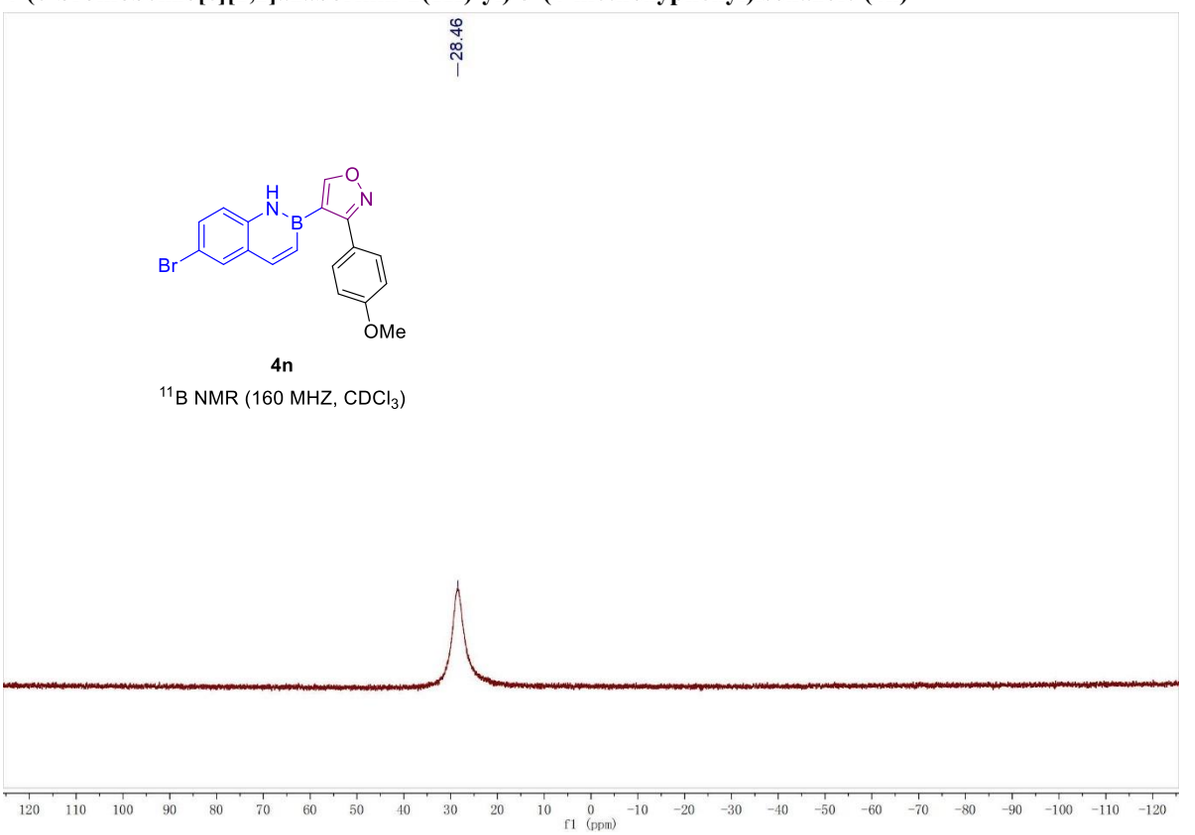
4n

^{1}H NMR (500 MHz, $CDCl_3$)

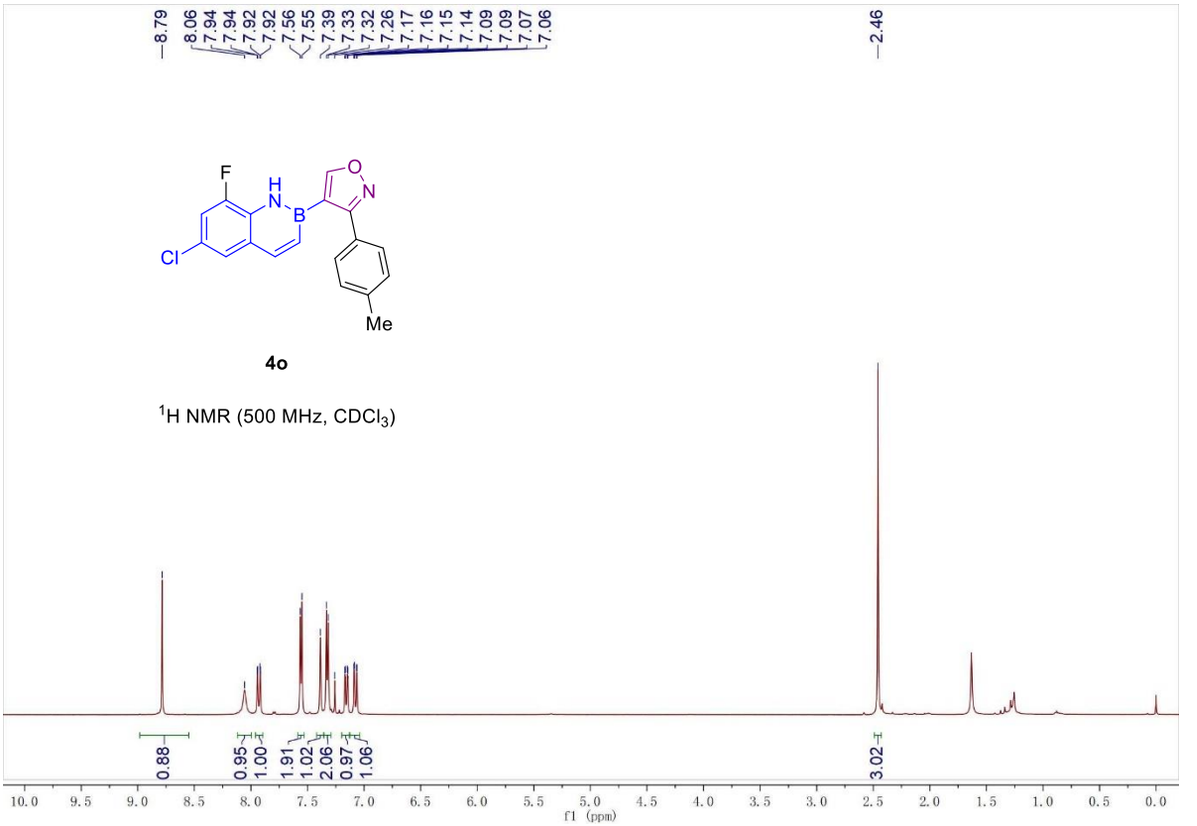
4-(6-bromobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4n)



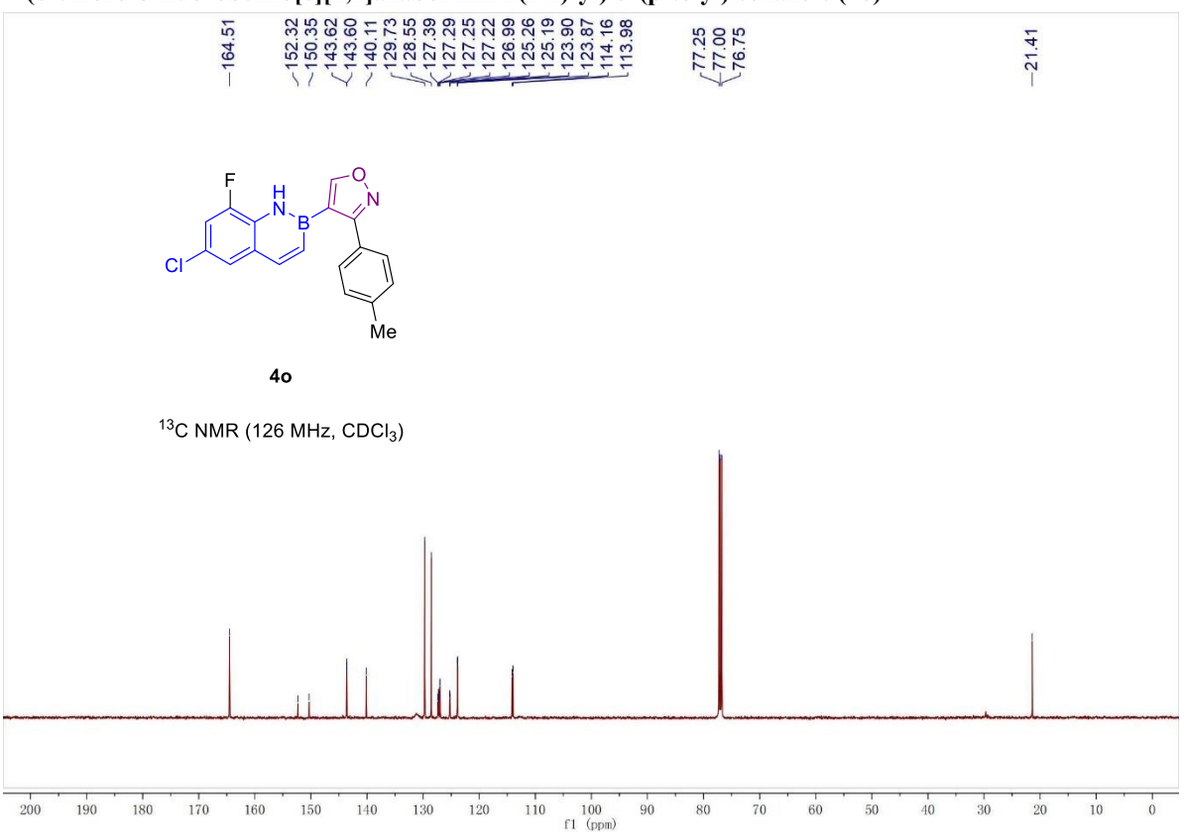
4-(6-bromobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4n)



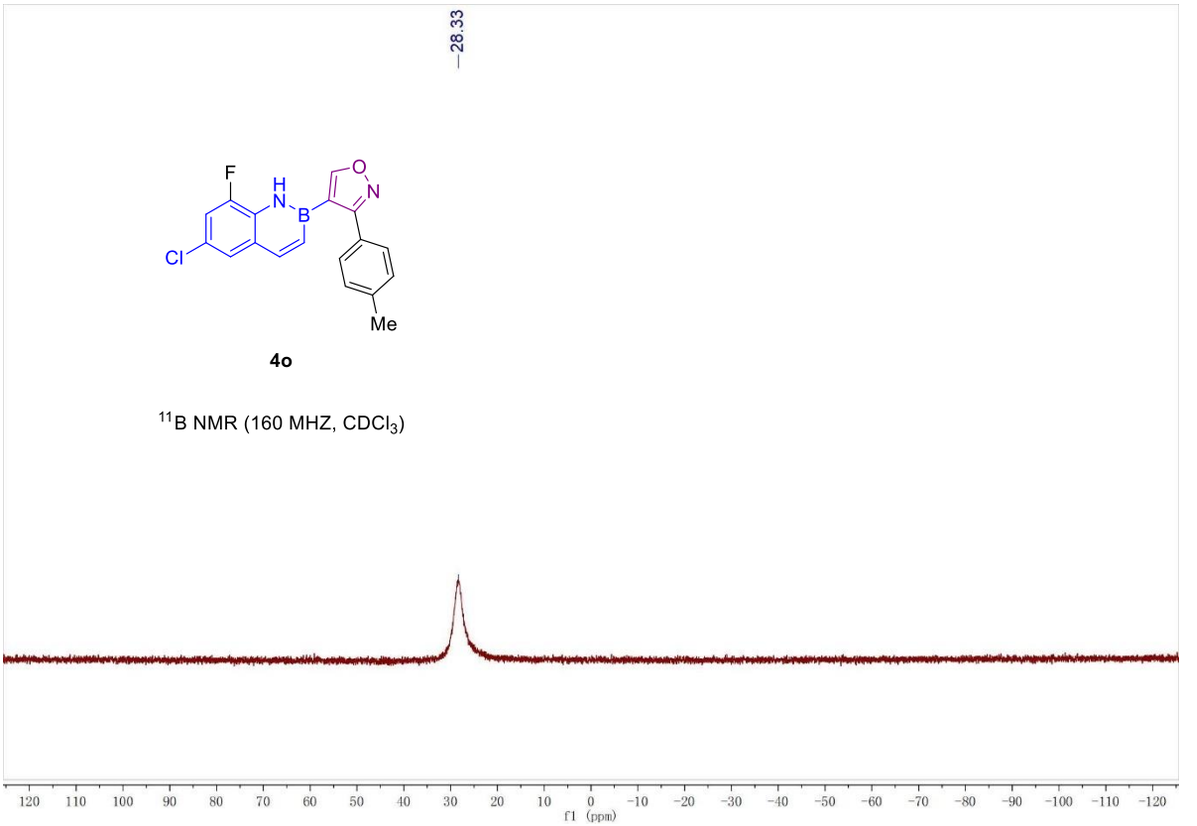
4-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4o)



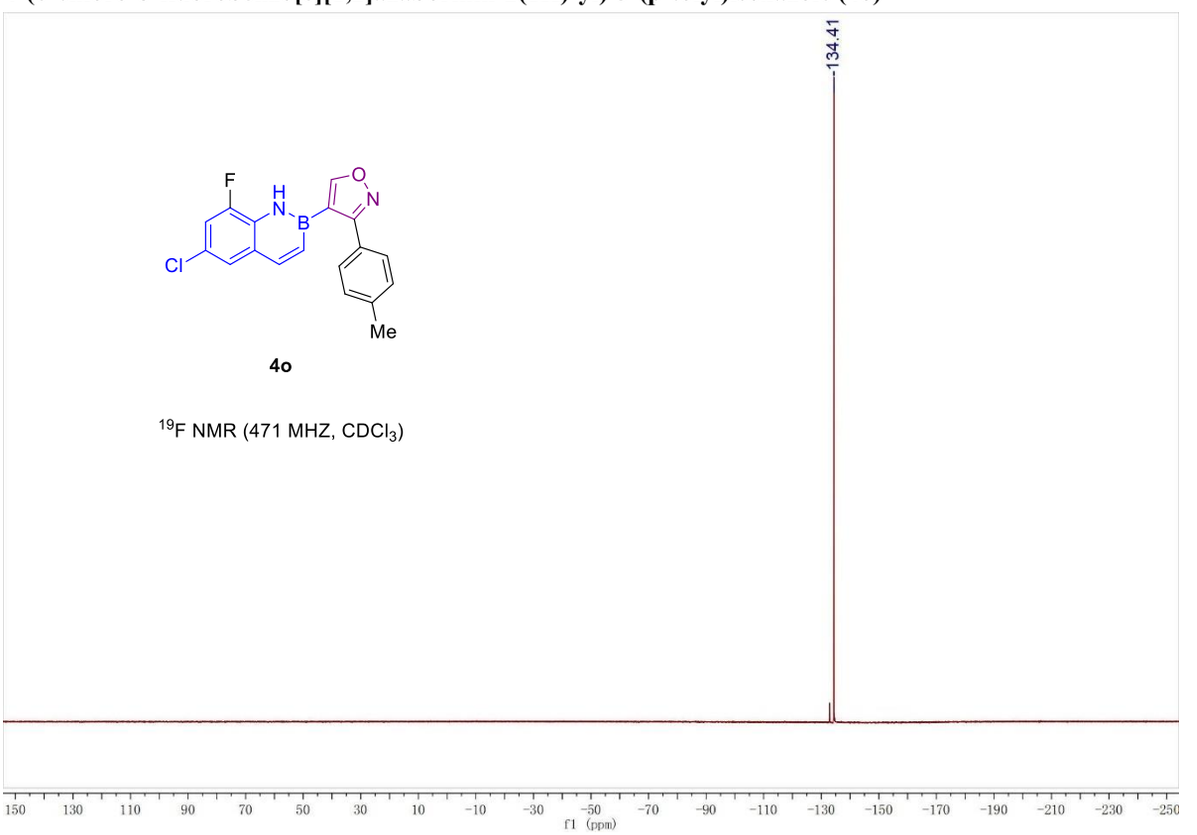
4-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4o)



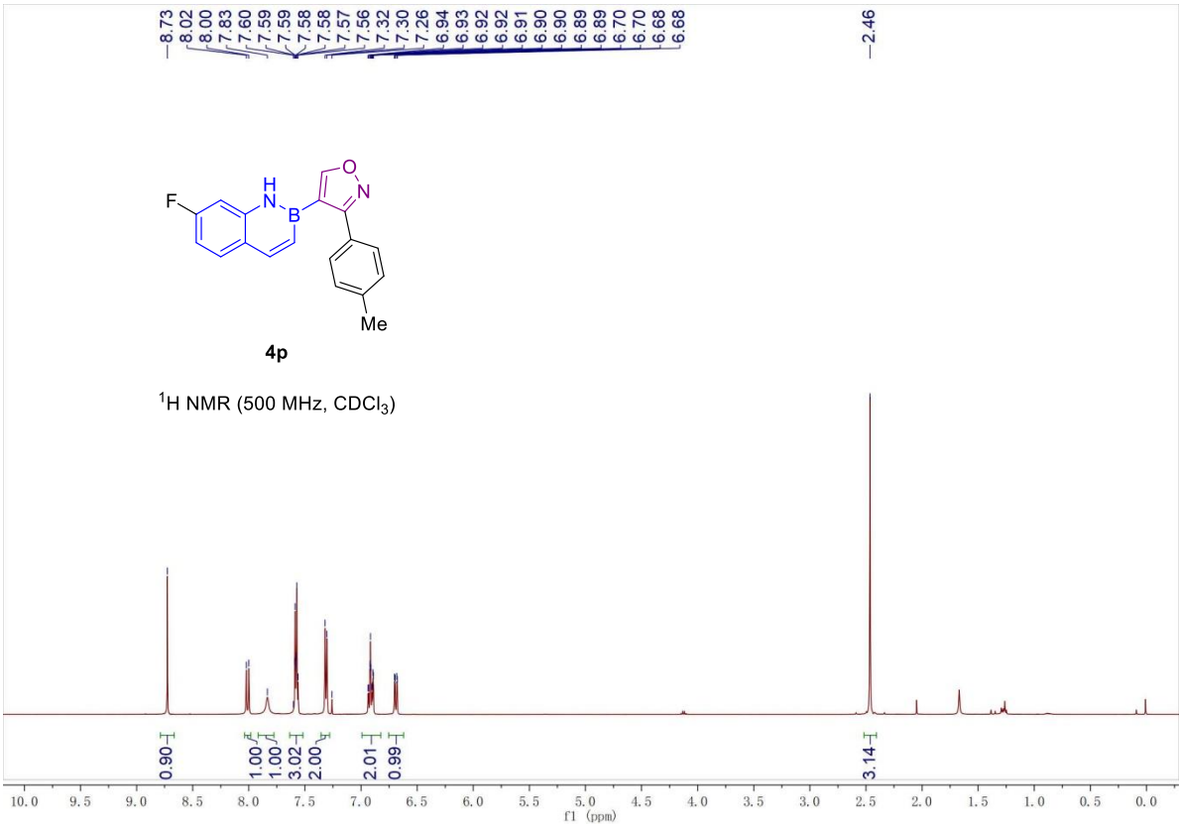
4-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4o)



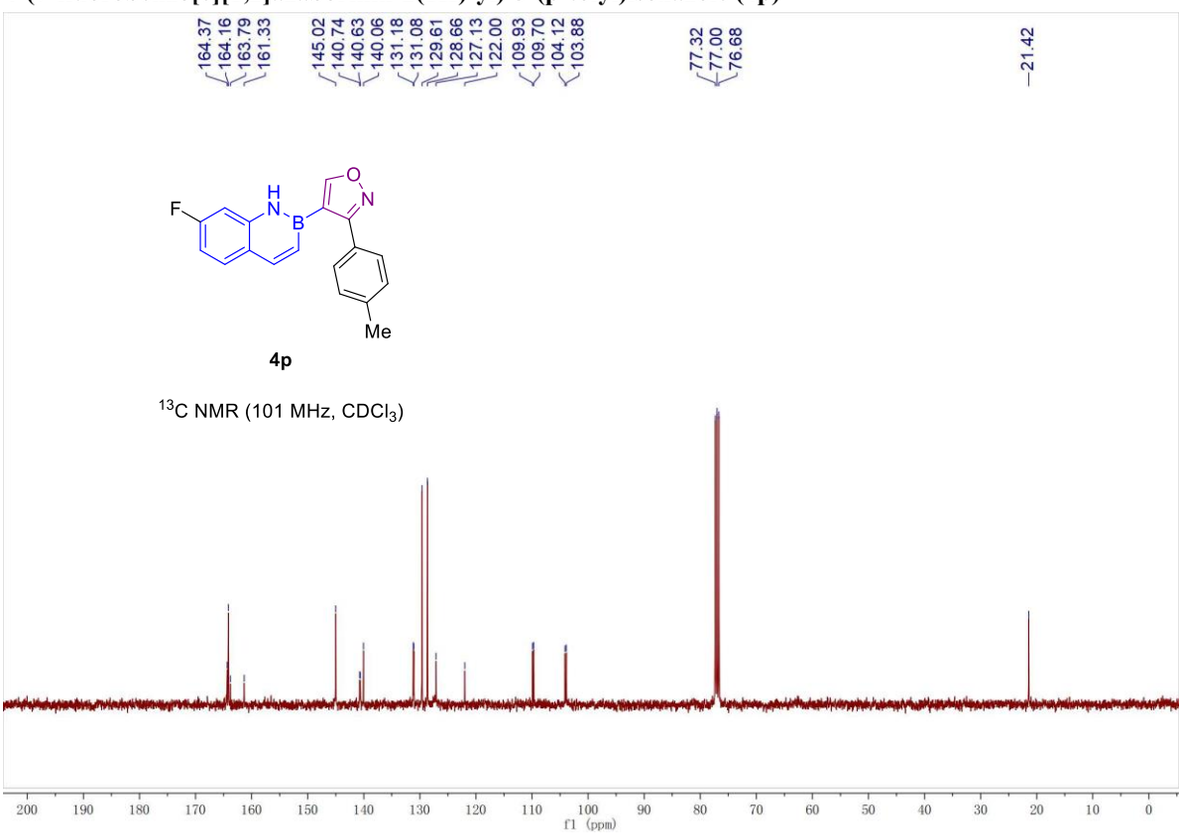
4-(6-chloro-8-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4o)



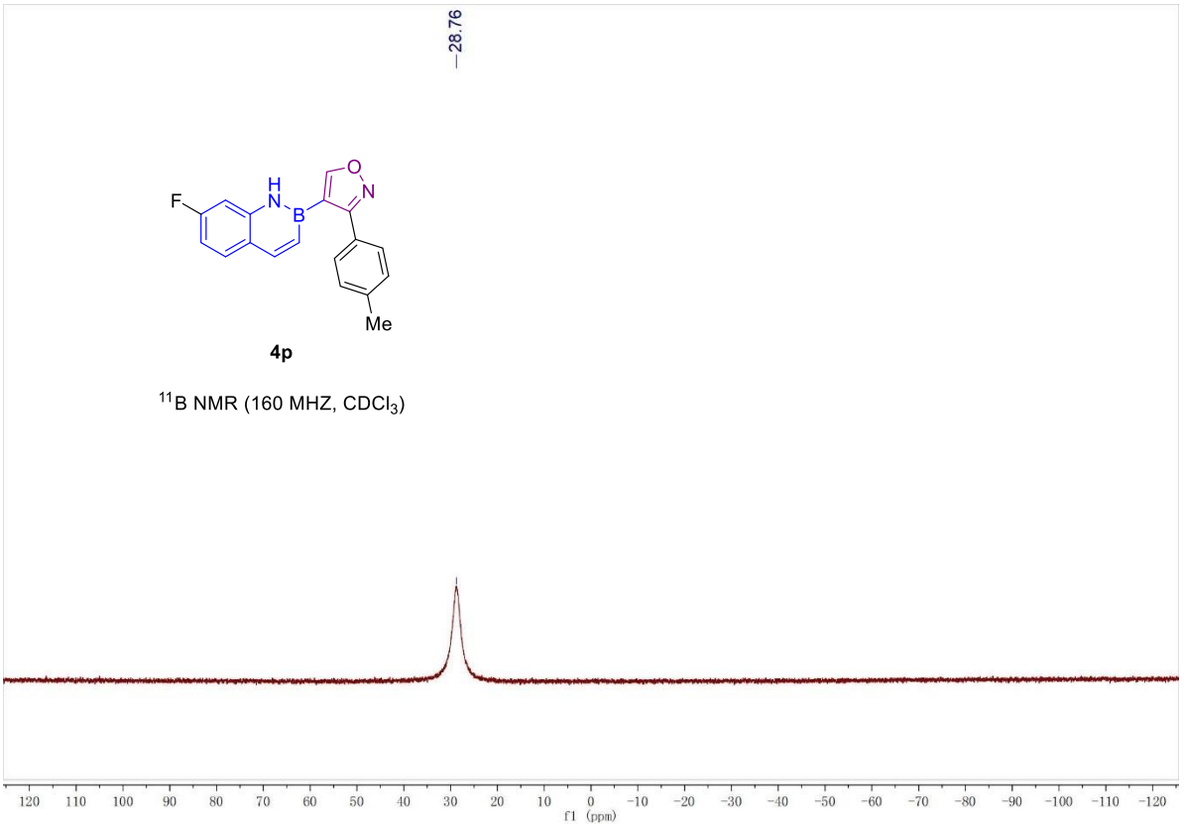
4-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4p)



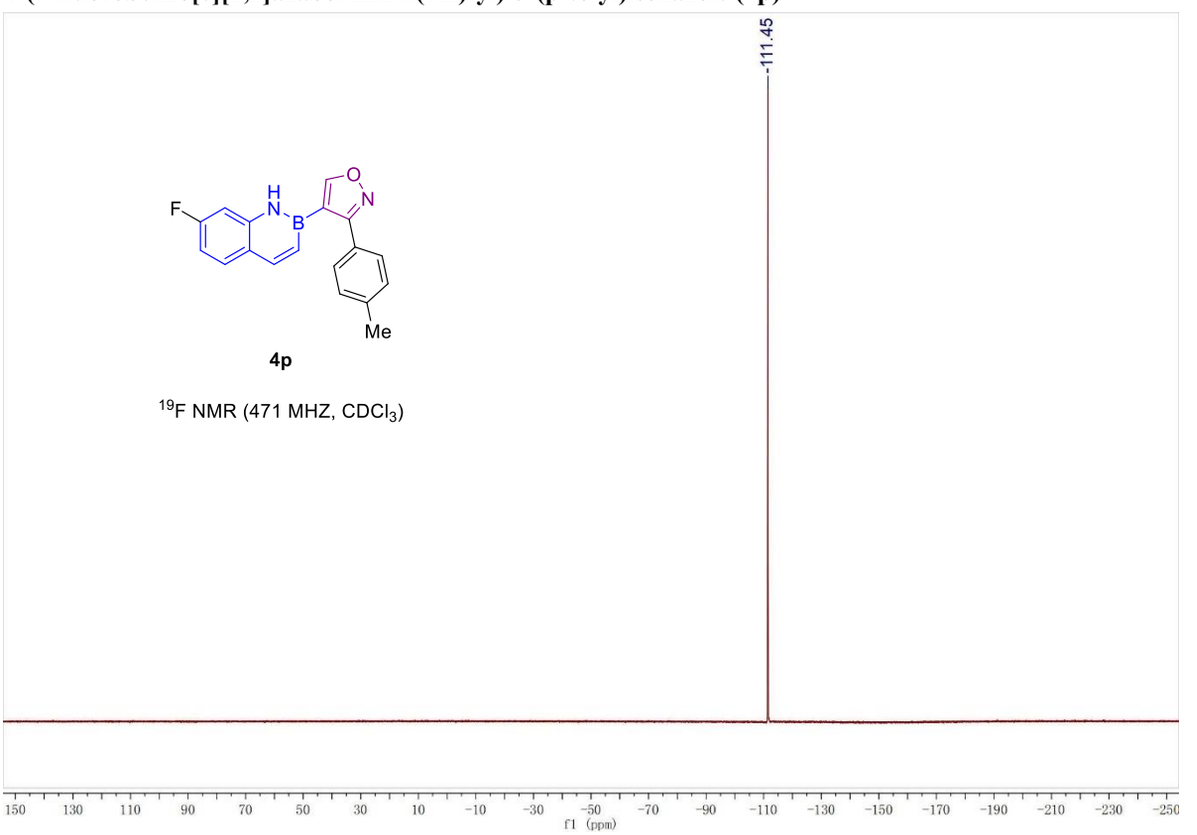
4-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4p)



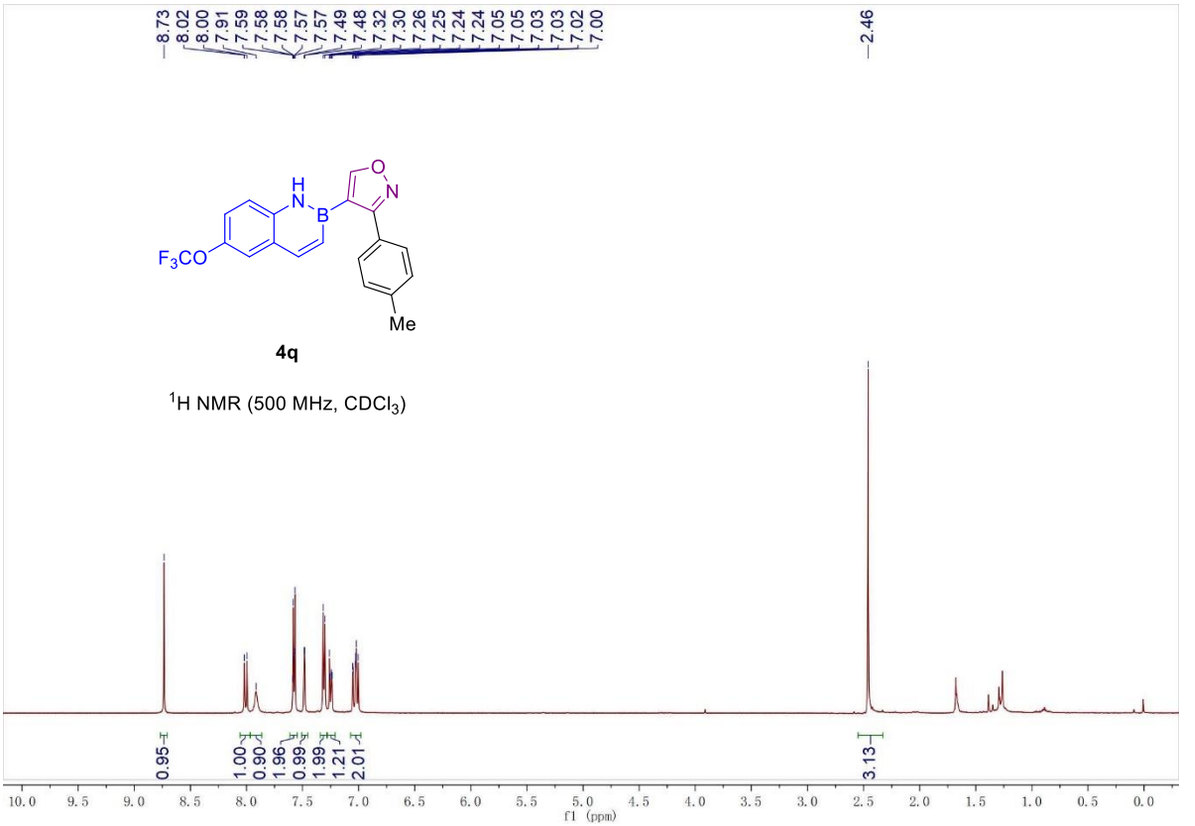
4-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4p)



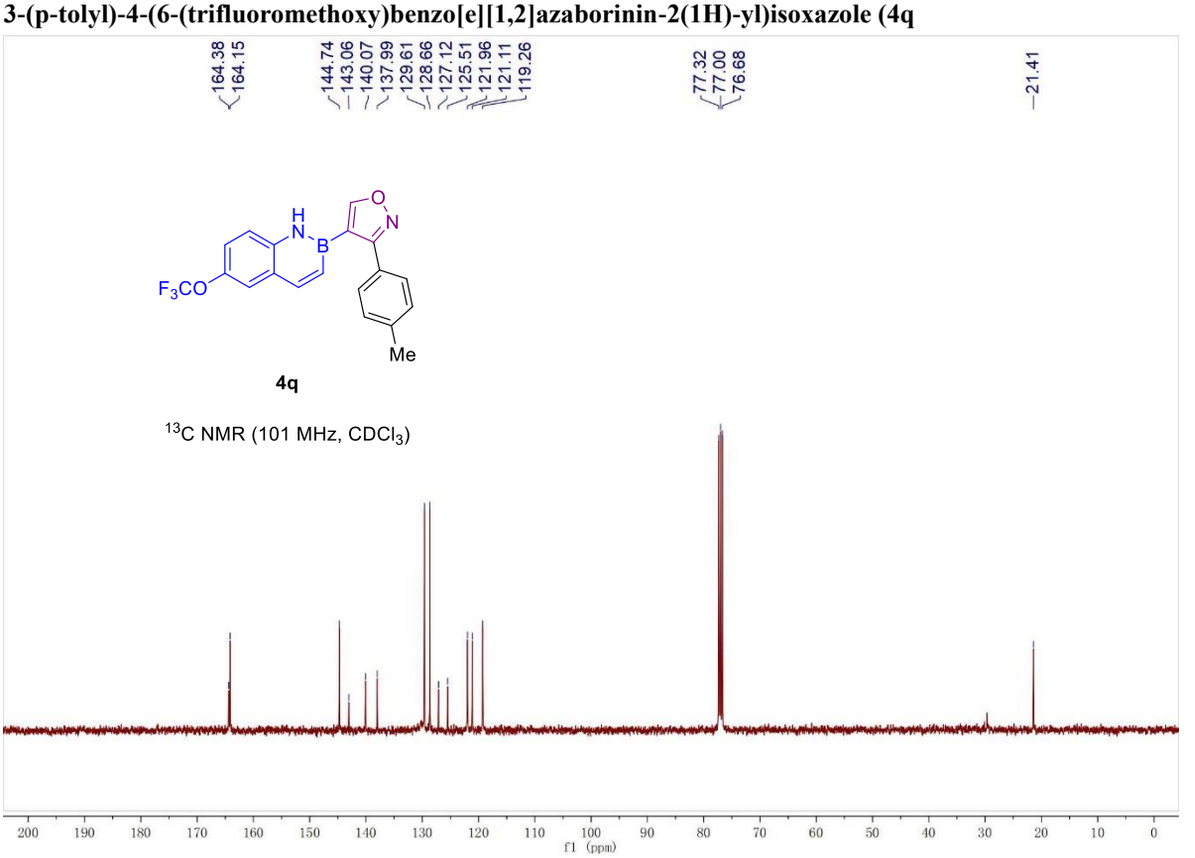
4-(7-fluorobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4p)



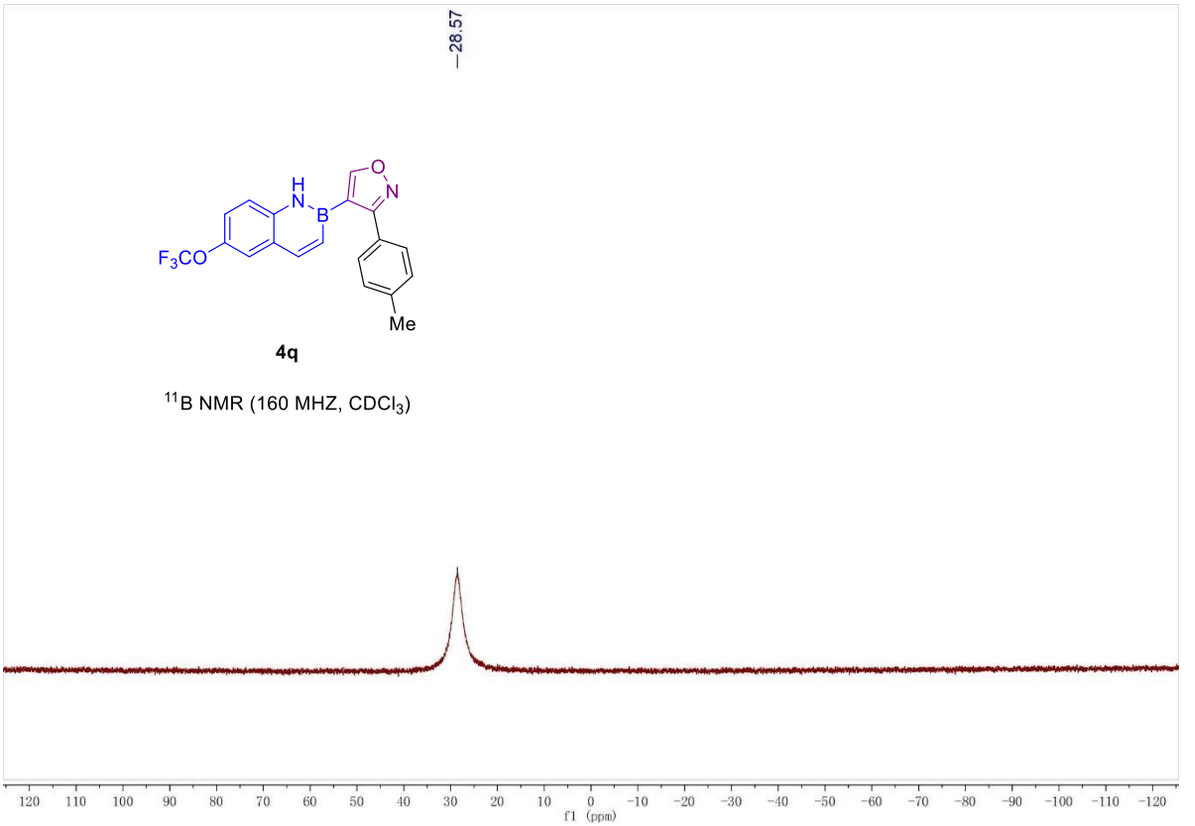
3-(p-tolyl)-4-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4q)



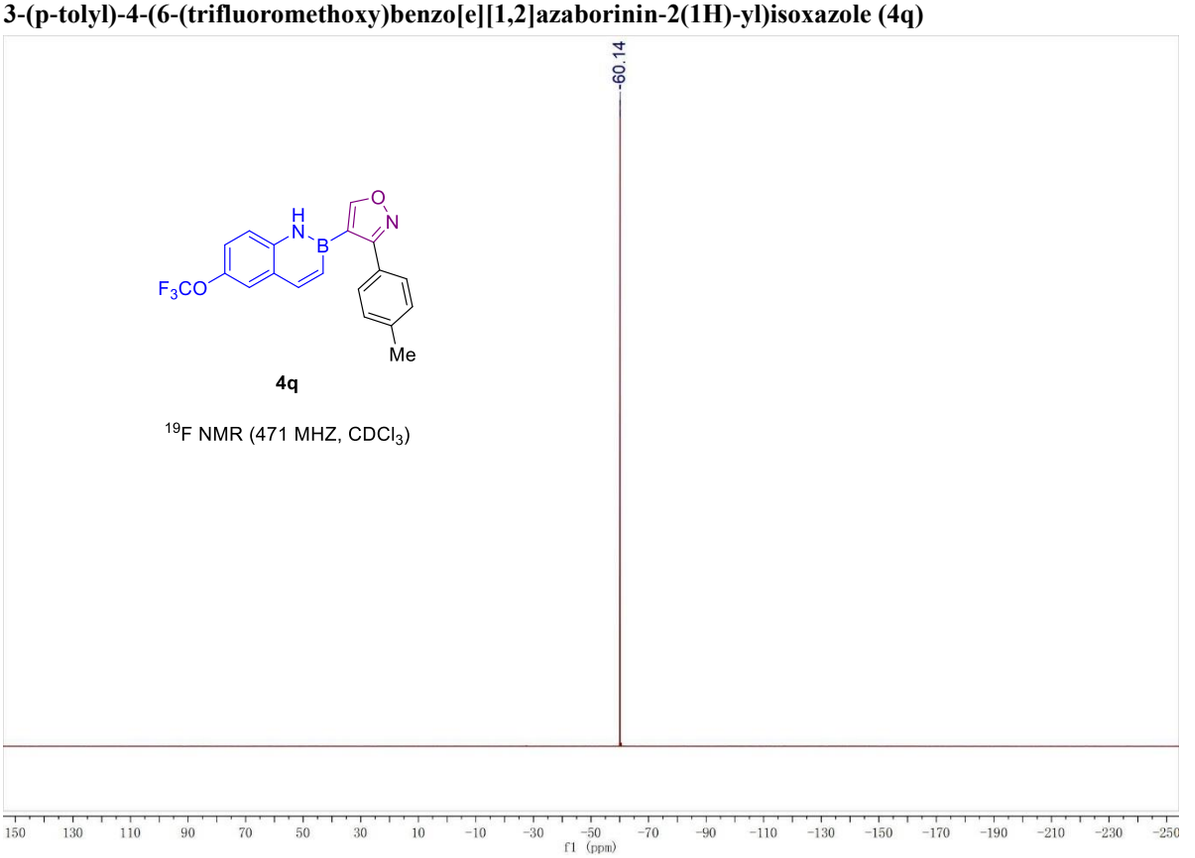
3-(p-tolyl)-4-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4q



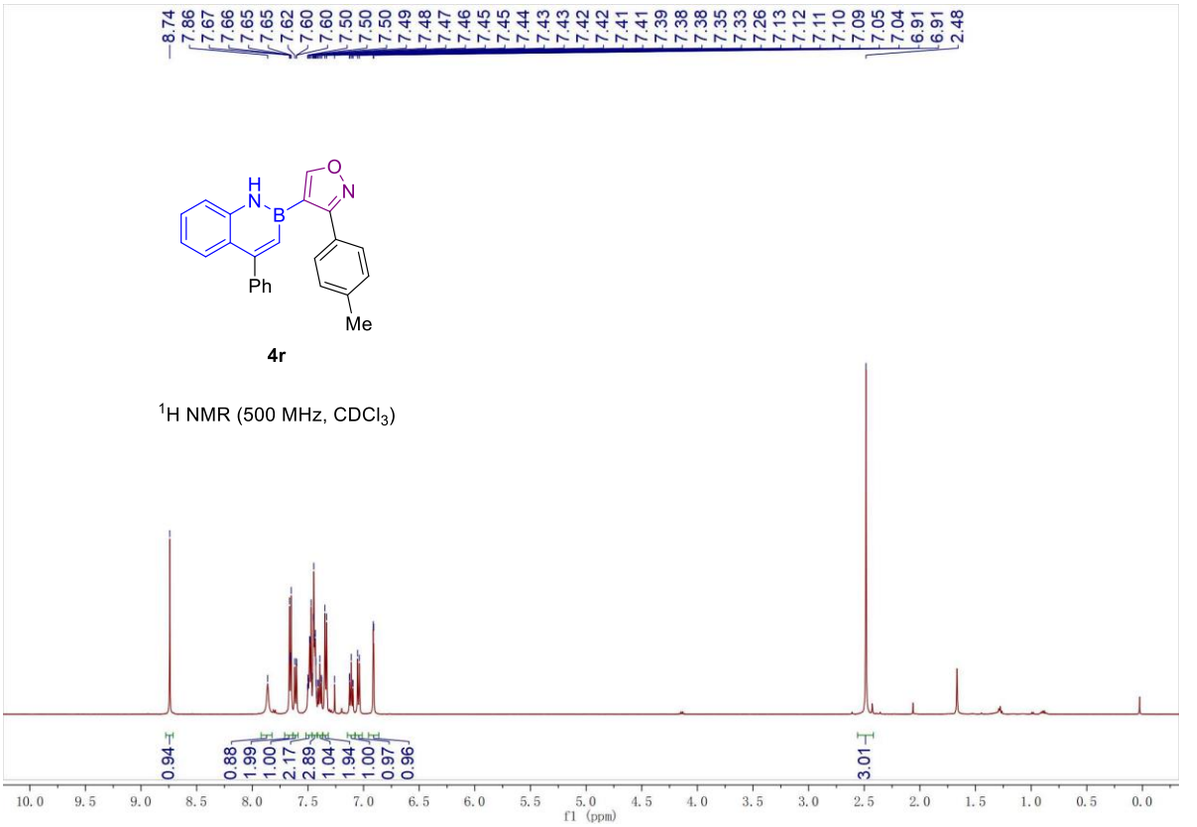
3-(p-tolyl)-4-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4q)



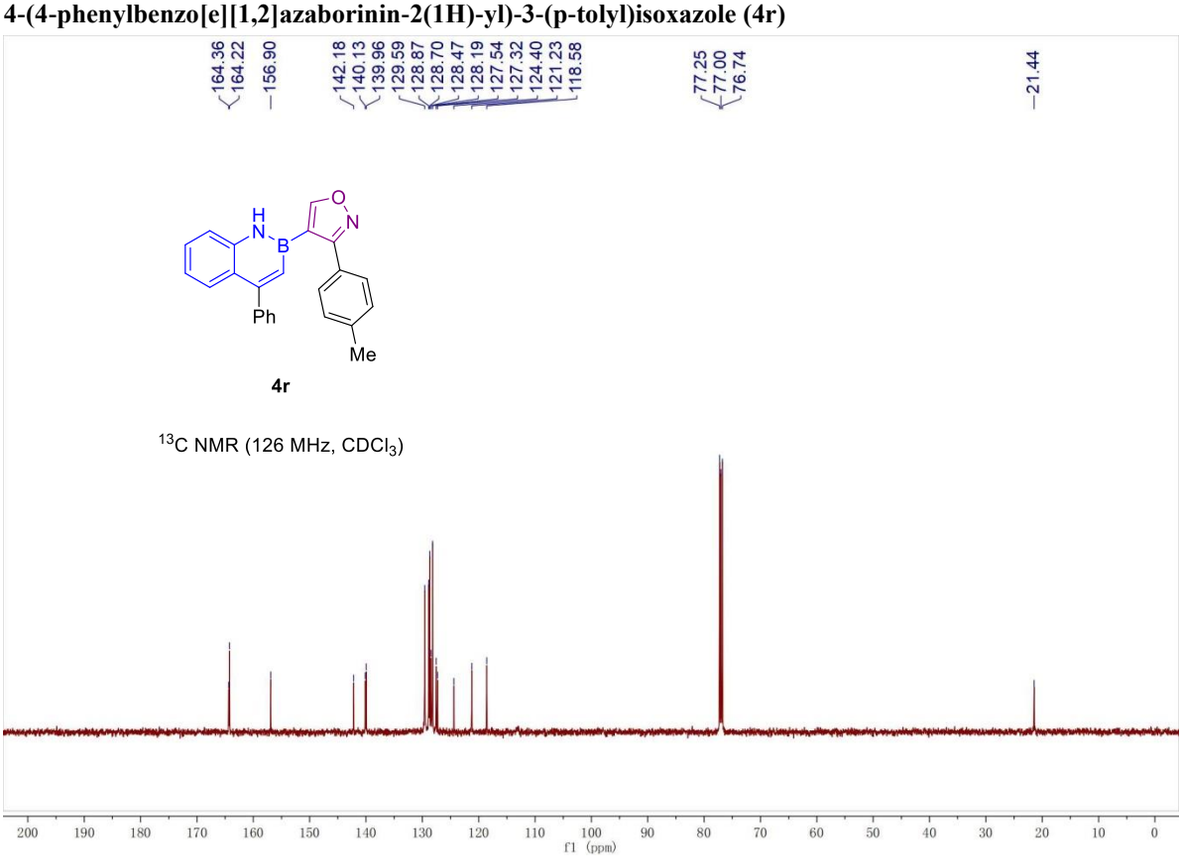
3-(p-tolyl)-4-(6-(trifluoromethoxy)benzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4q)



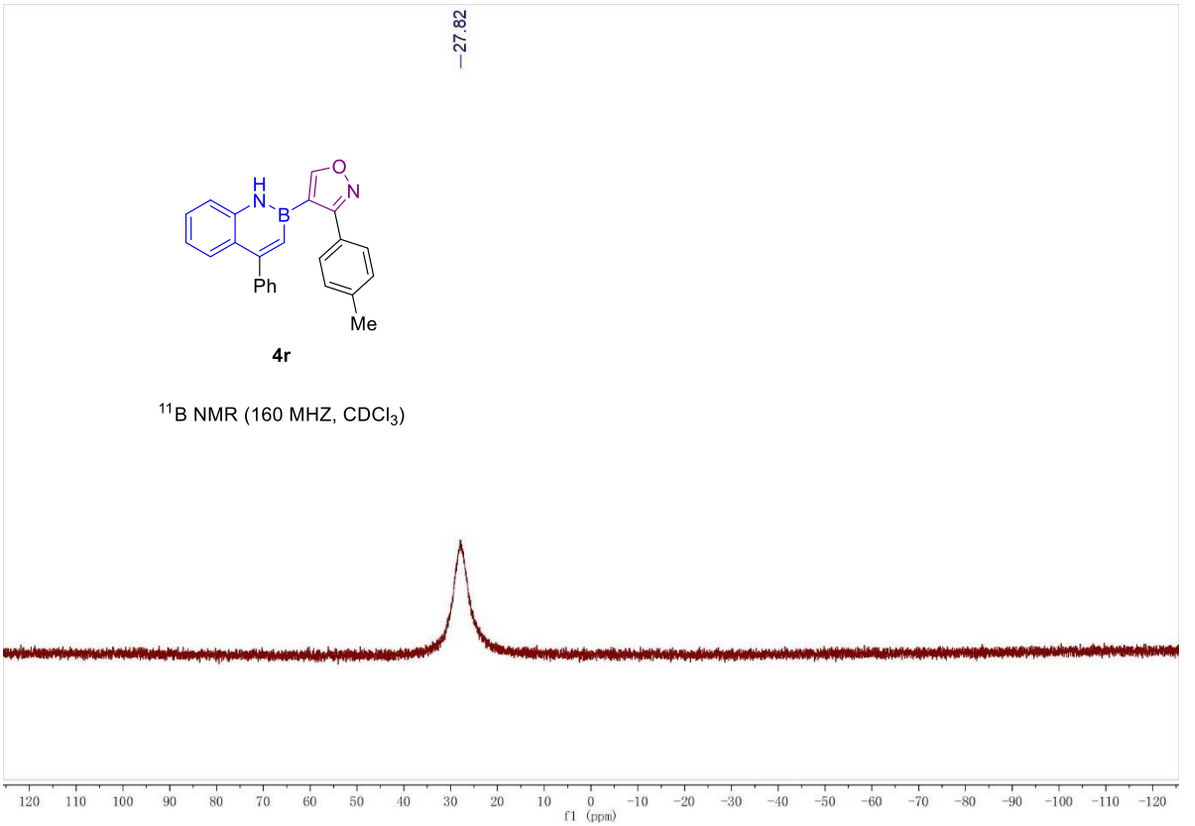
4-(4-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4r)



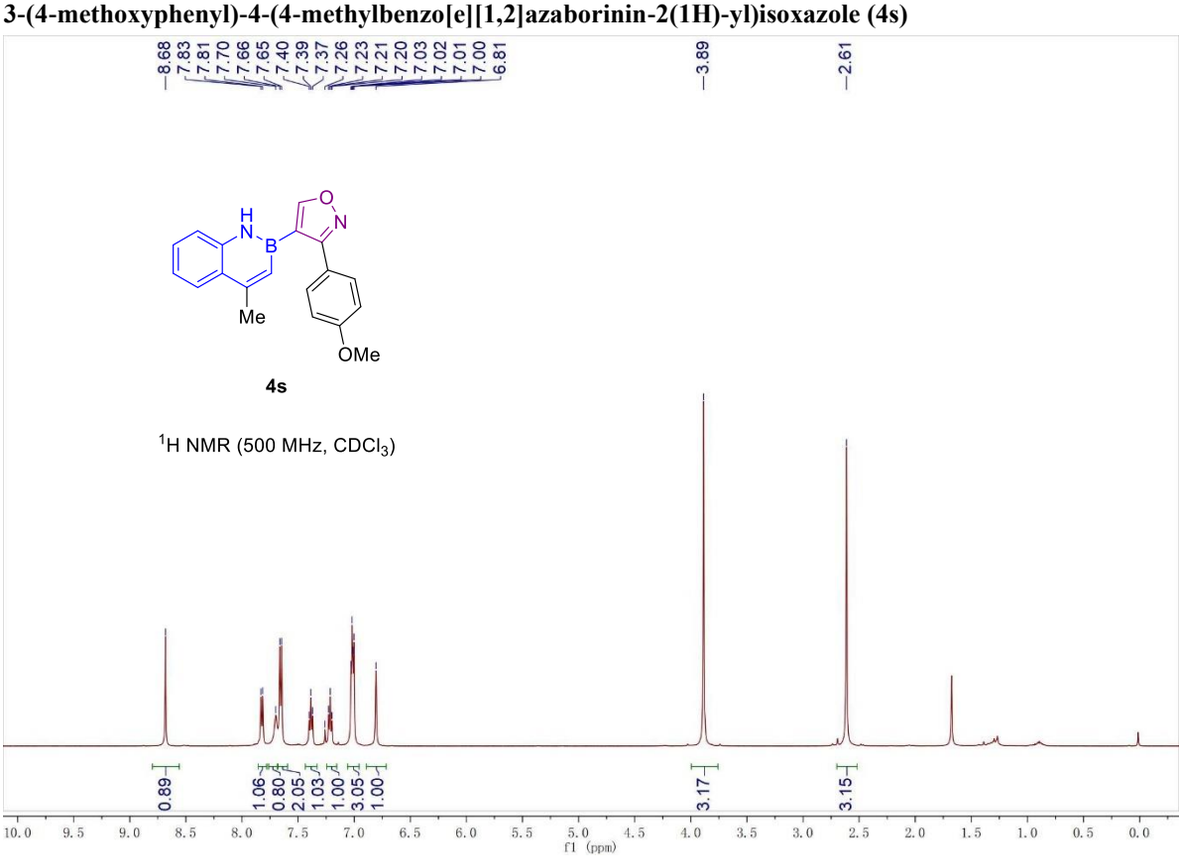
4-(4-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4r)



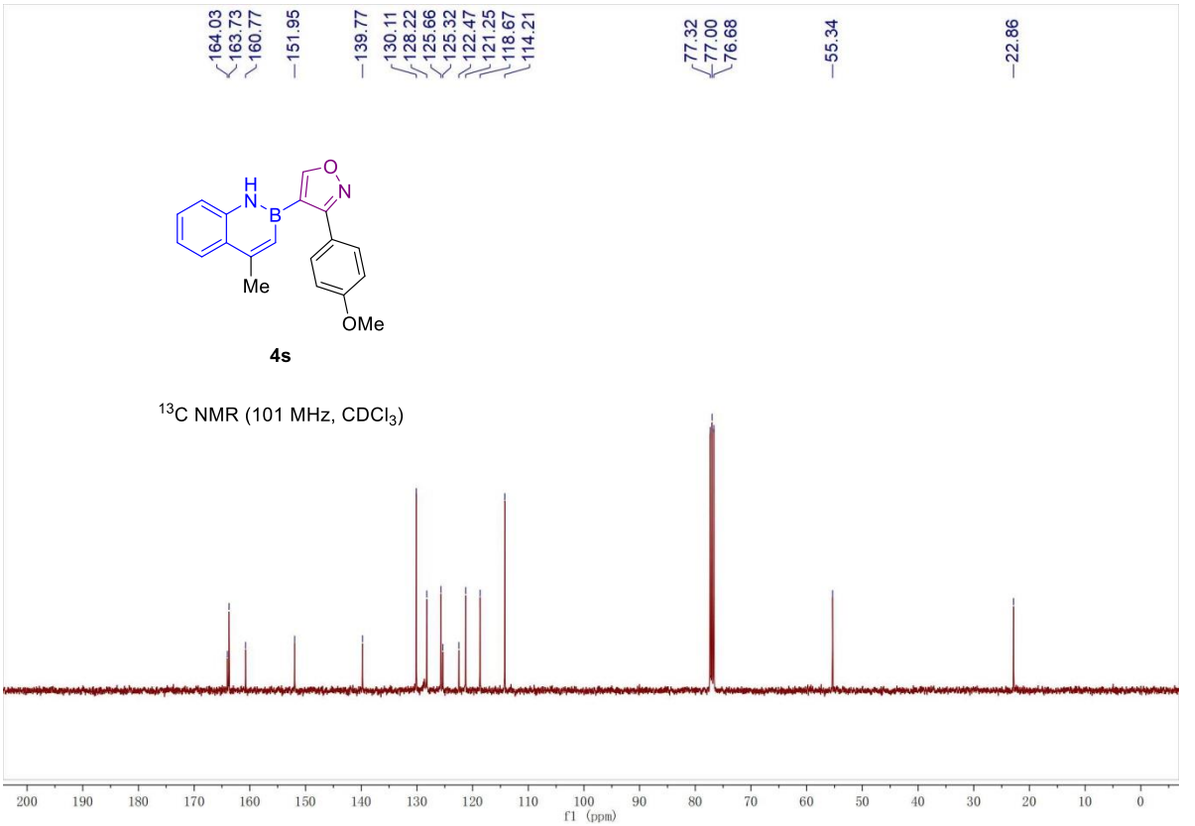
4-(4-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(p-tolyl)isoxazole (4r)



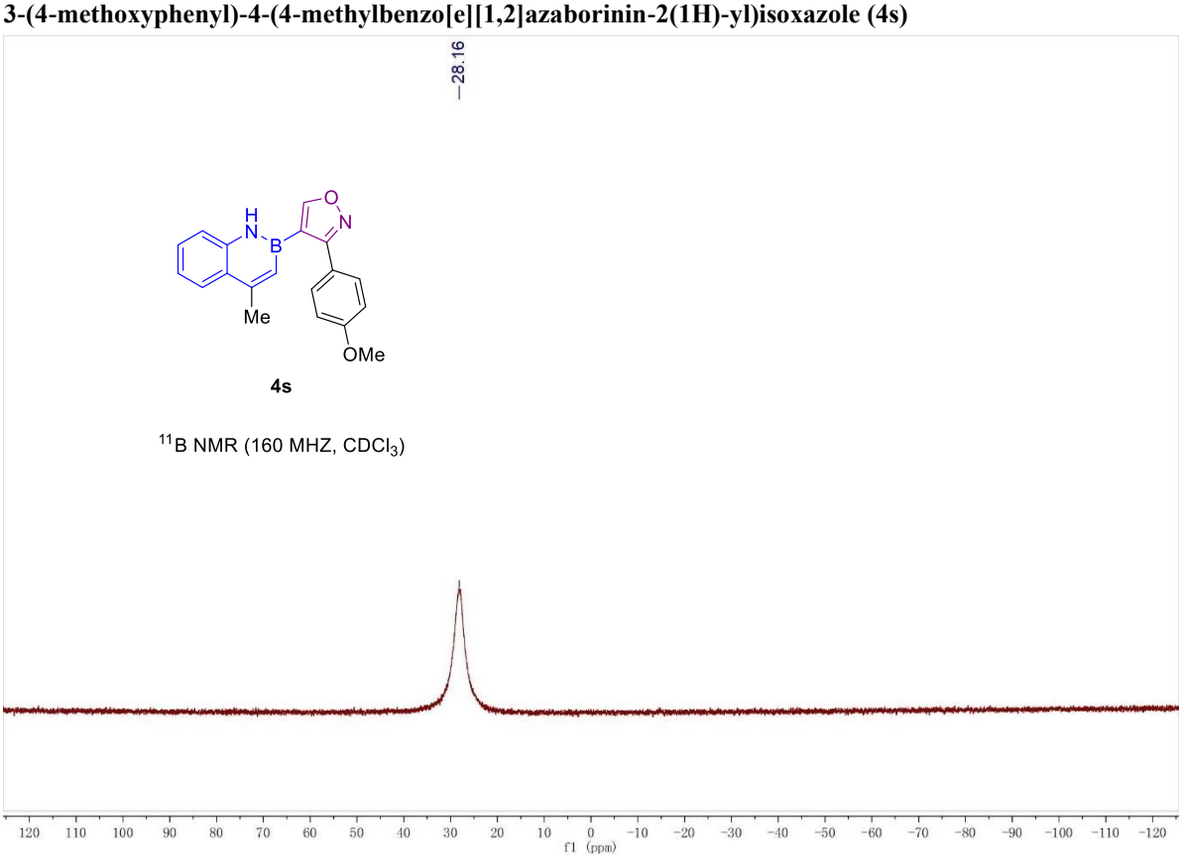
3-(4-methoxyphenyl)-4-(4-methylbenzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4s)



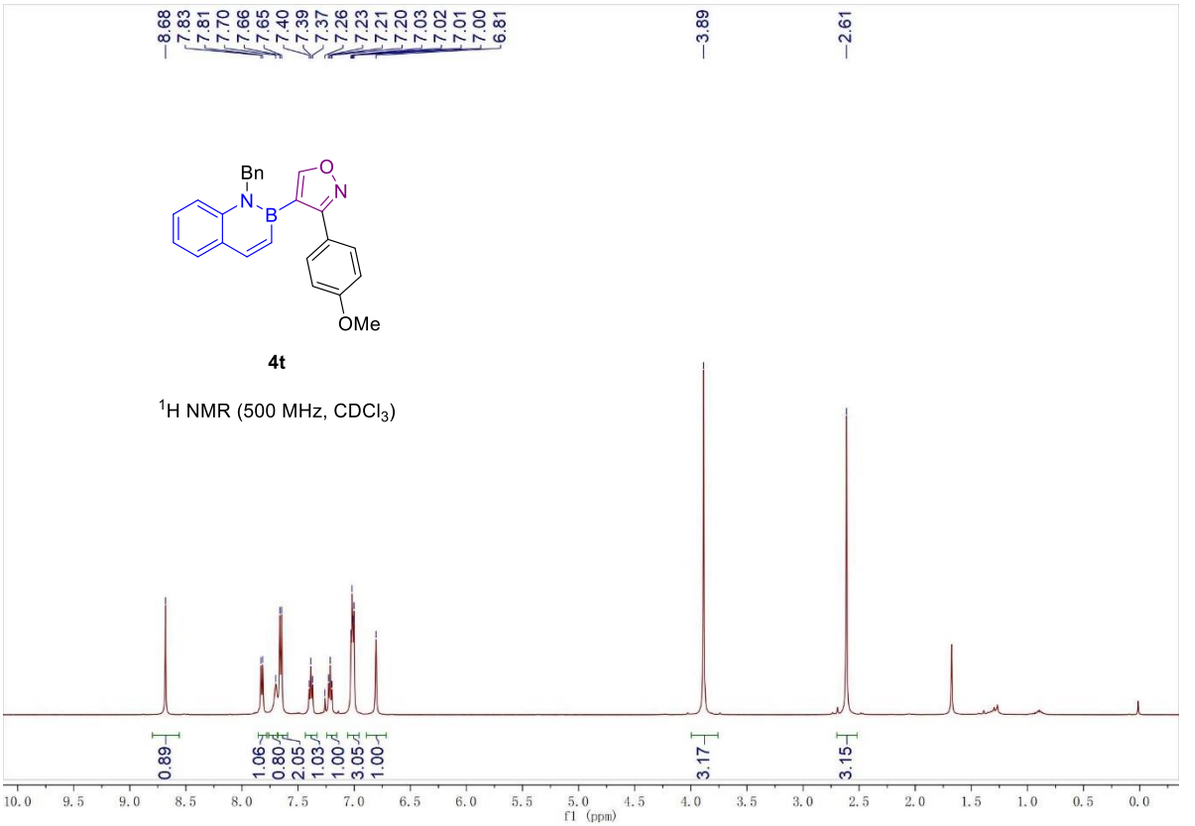
3-(4-methoxyphenyl)-4-(4-methylbenzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4s)



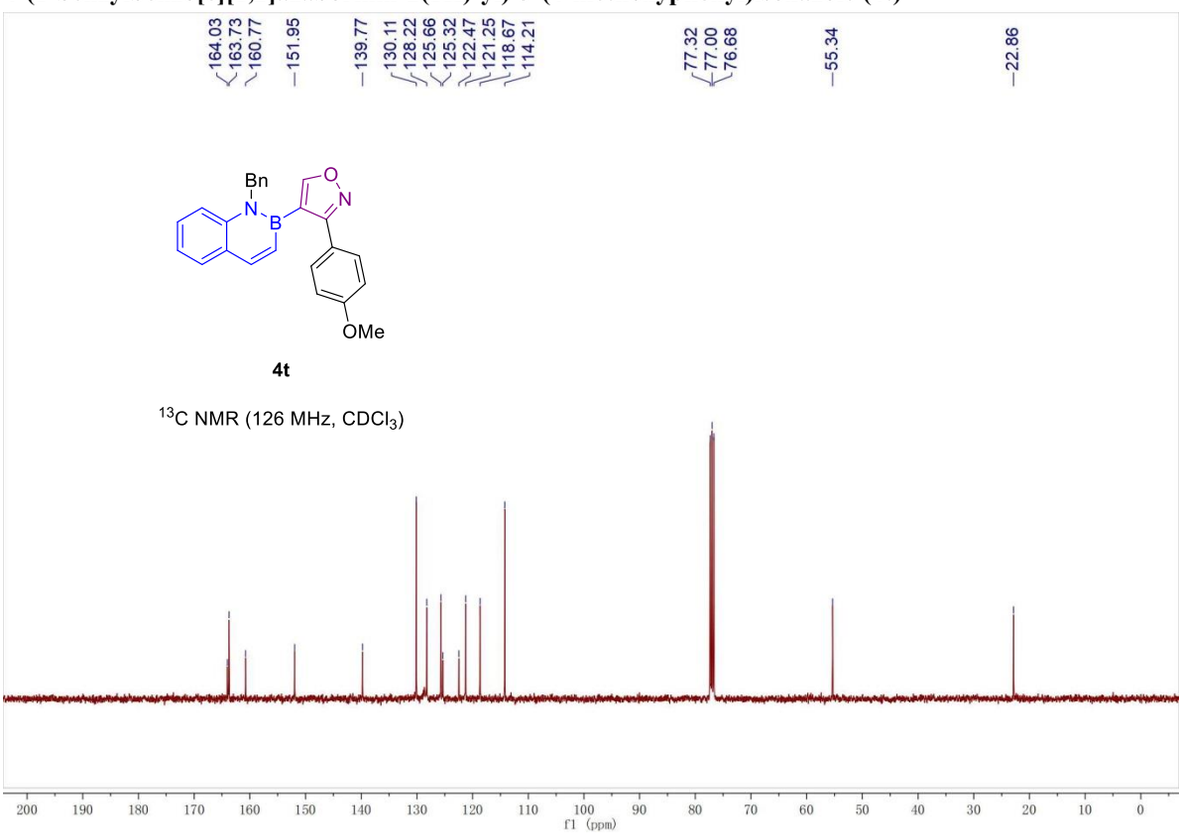
3-(4-methoxyphenyl)-4-(4-methylbenzo[e][1,2]azaborinin-2(1H)-yl)isoxazole (4s)



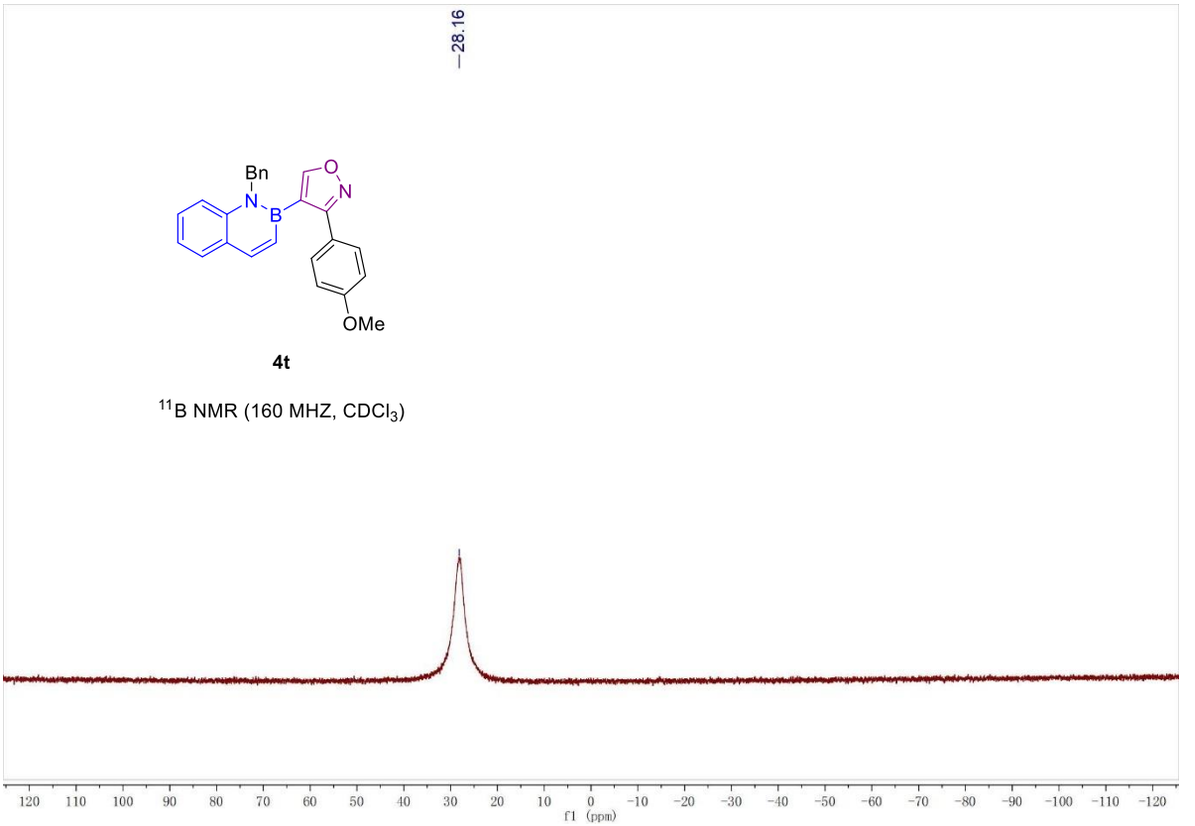
4-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4t)



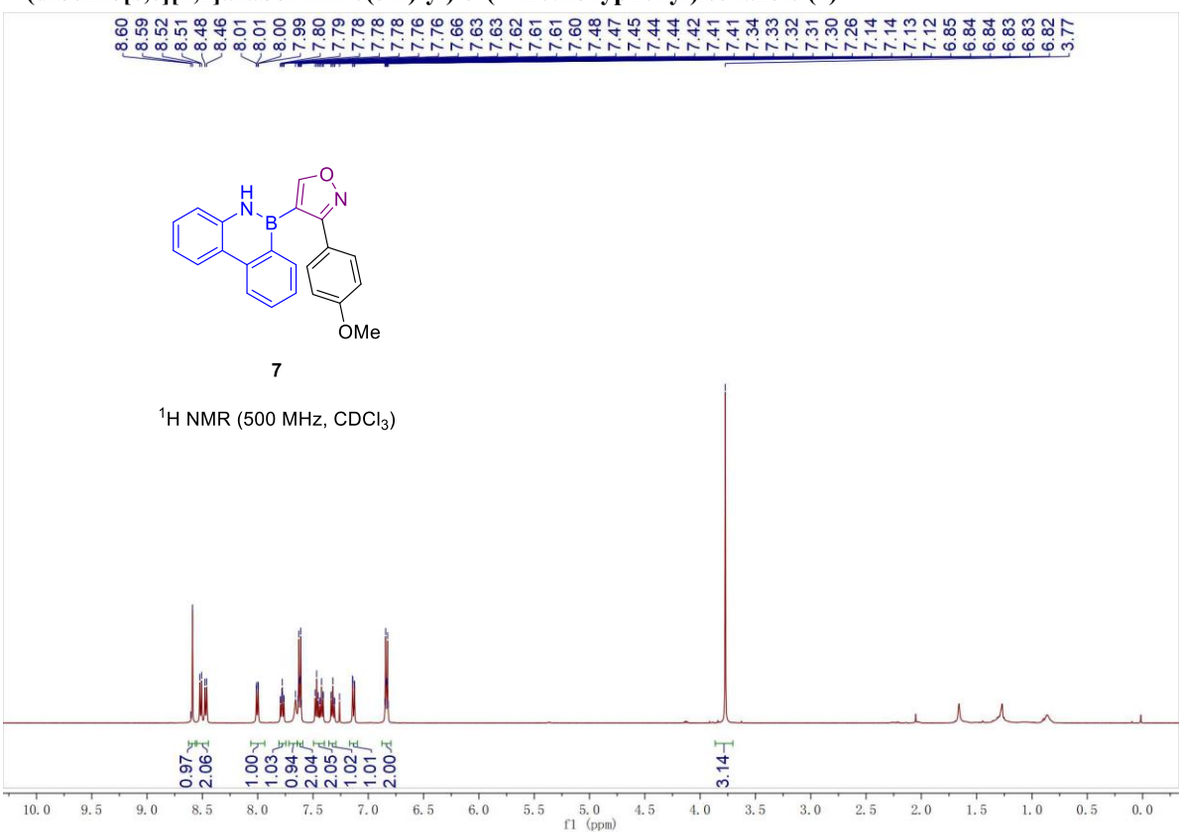
4-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4t)



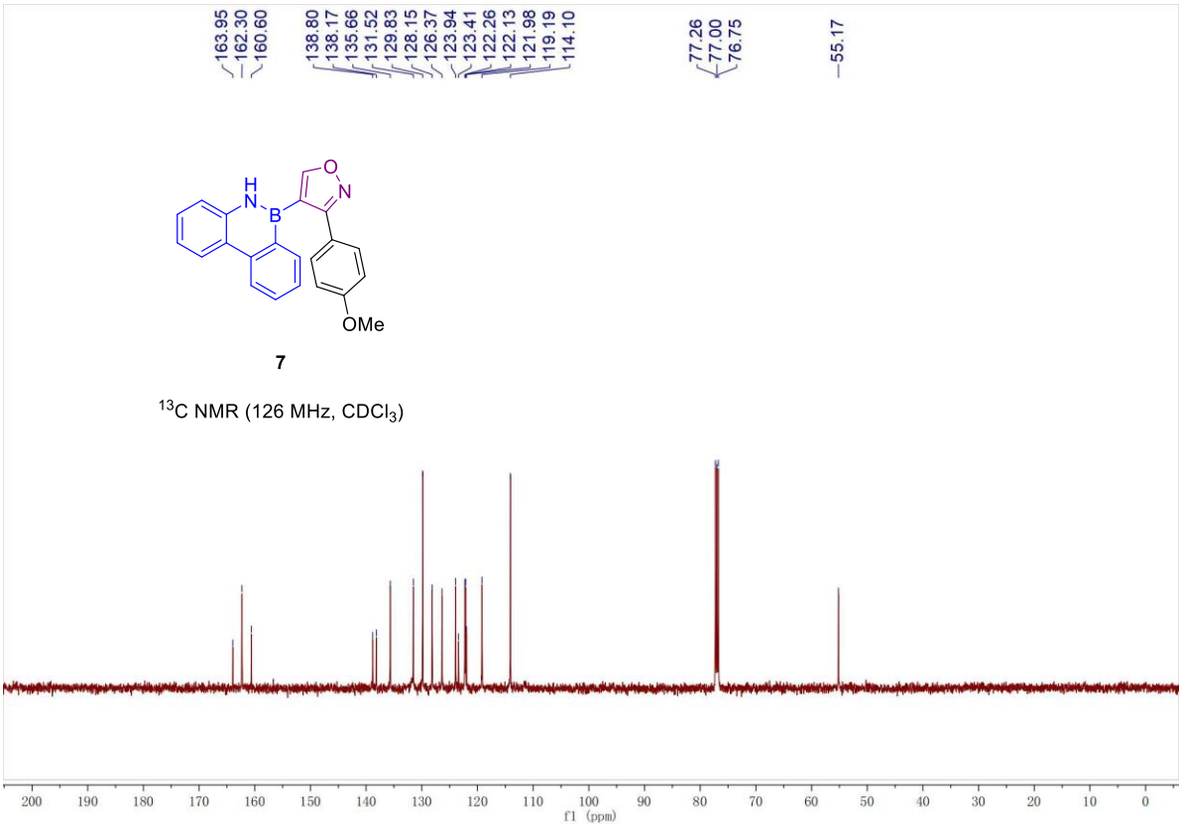
4-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-3-(4-methoxyphenyl)isoxazole (4t)



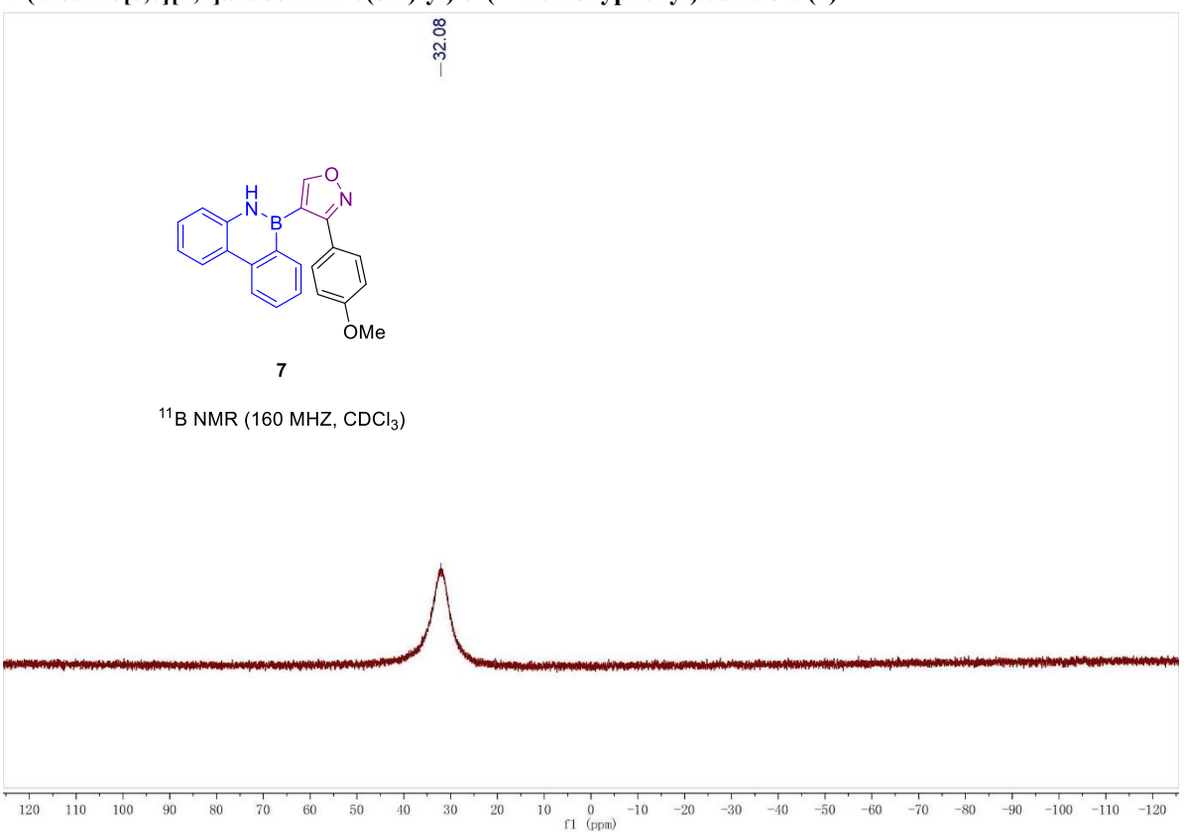
4-(dibenzo[c,e][1,2]azaborinin-6(5H)-yl)-3-(4-methoxyphenyl)isoxazole (7)



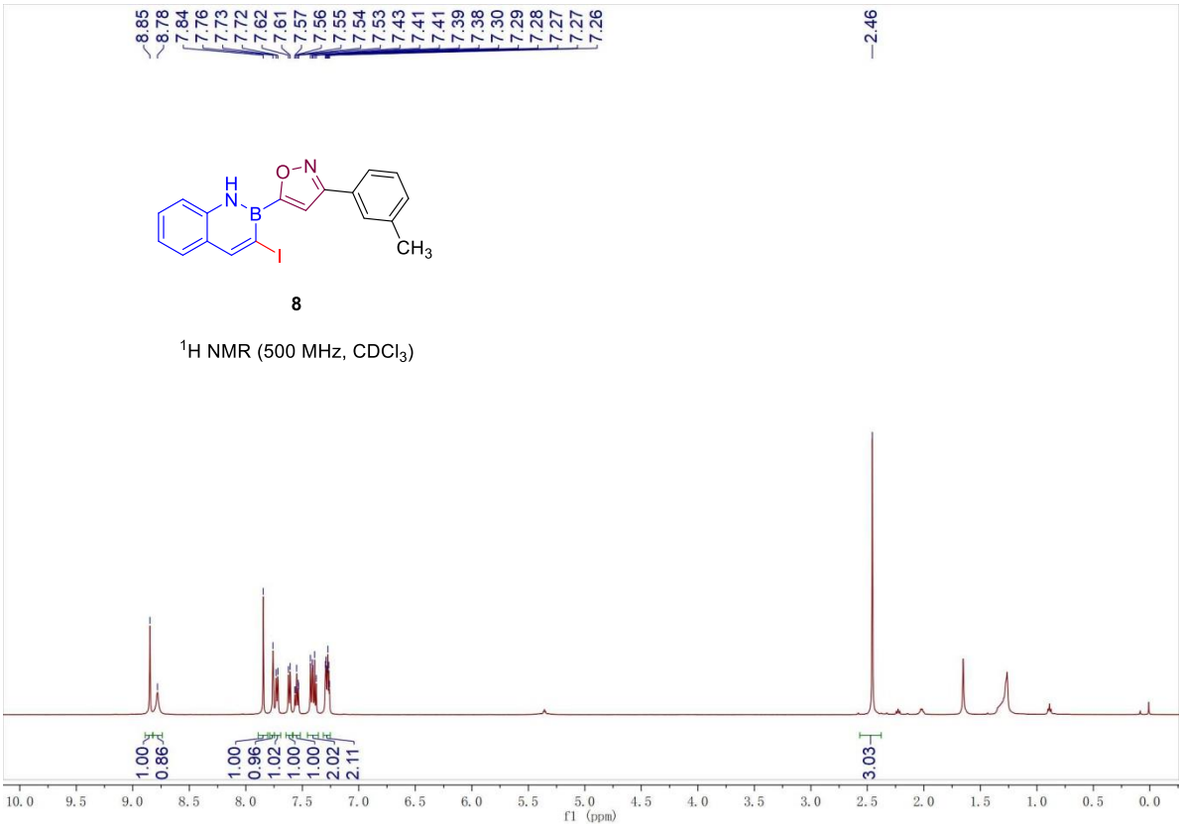
4-(dibenzo[c,e][1,2]azaborinin-6(5H)-yl)-3-(4-methoxyphenyl)isoxazole (7)



4-(dibenzo[c,e][1,2]azaborinin-6(5H)-yl)-3-(4-methoxyphenyl)isoxazole (7)



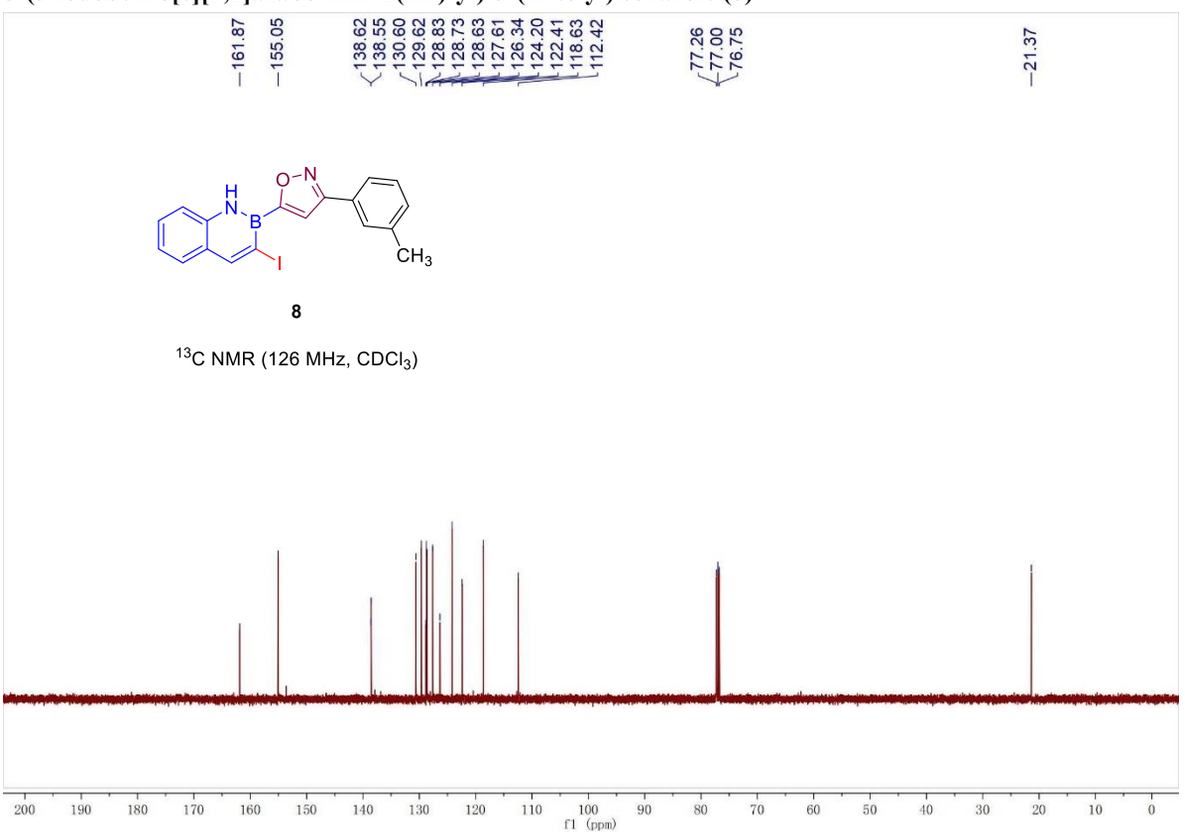
5-(3-iodobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (8)



8

^{1}H NMR (500 MHz, $CDCl_3$)

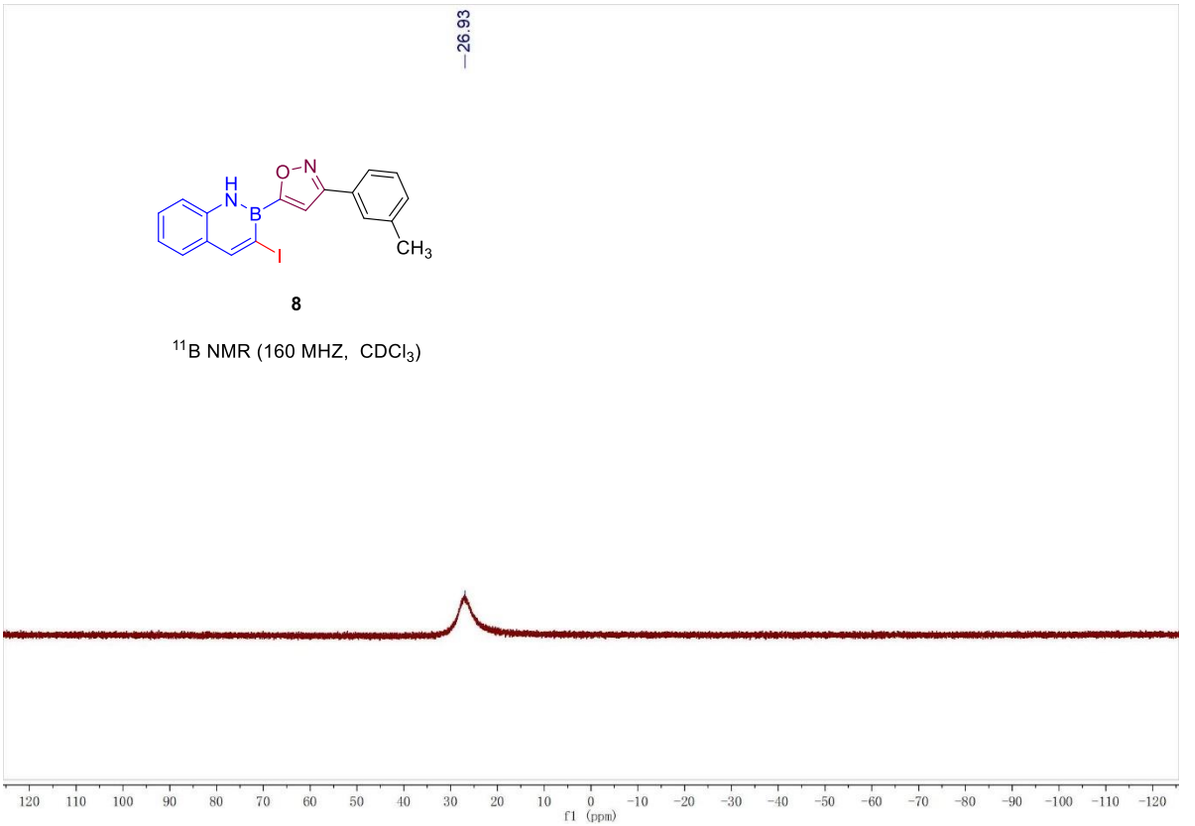
5-(3-iodobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (8)



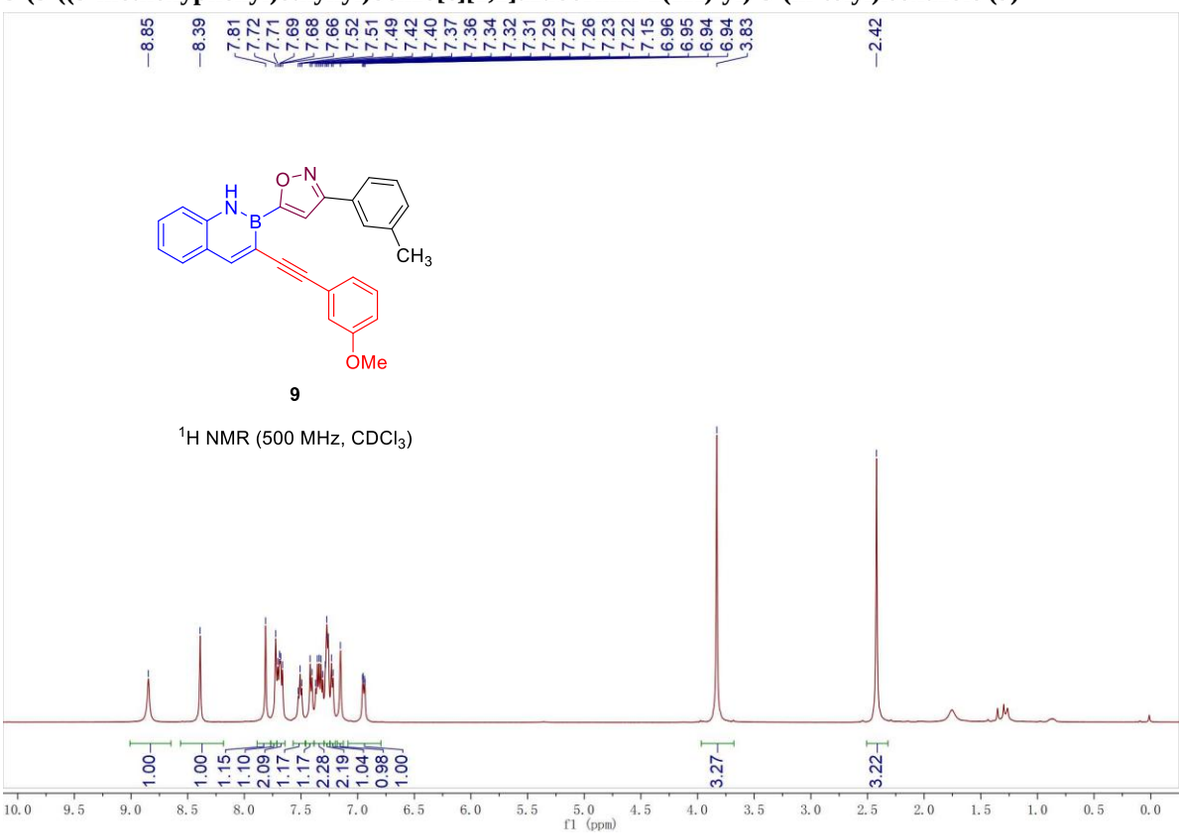
8

^{13}C NMR (126 MHz, $CDCl_3$)

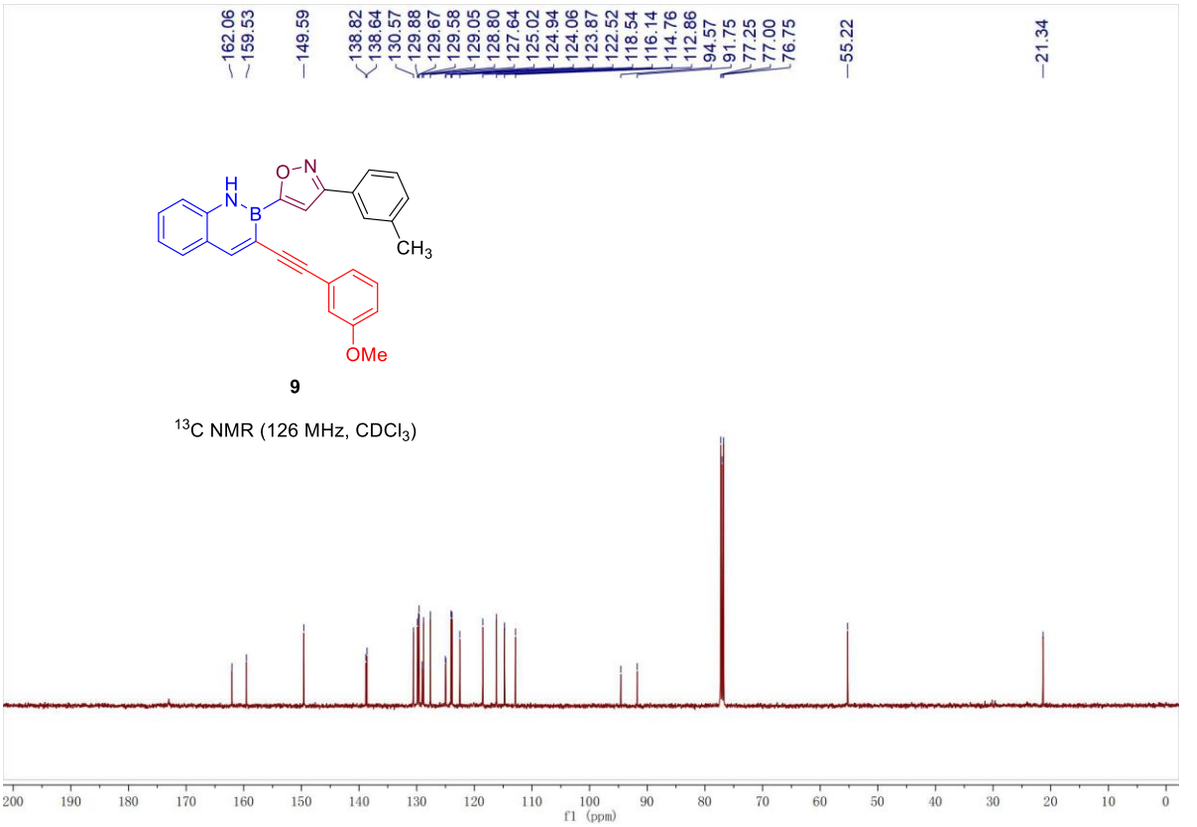
5-(3-iodobenzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (8)



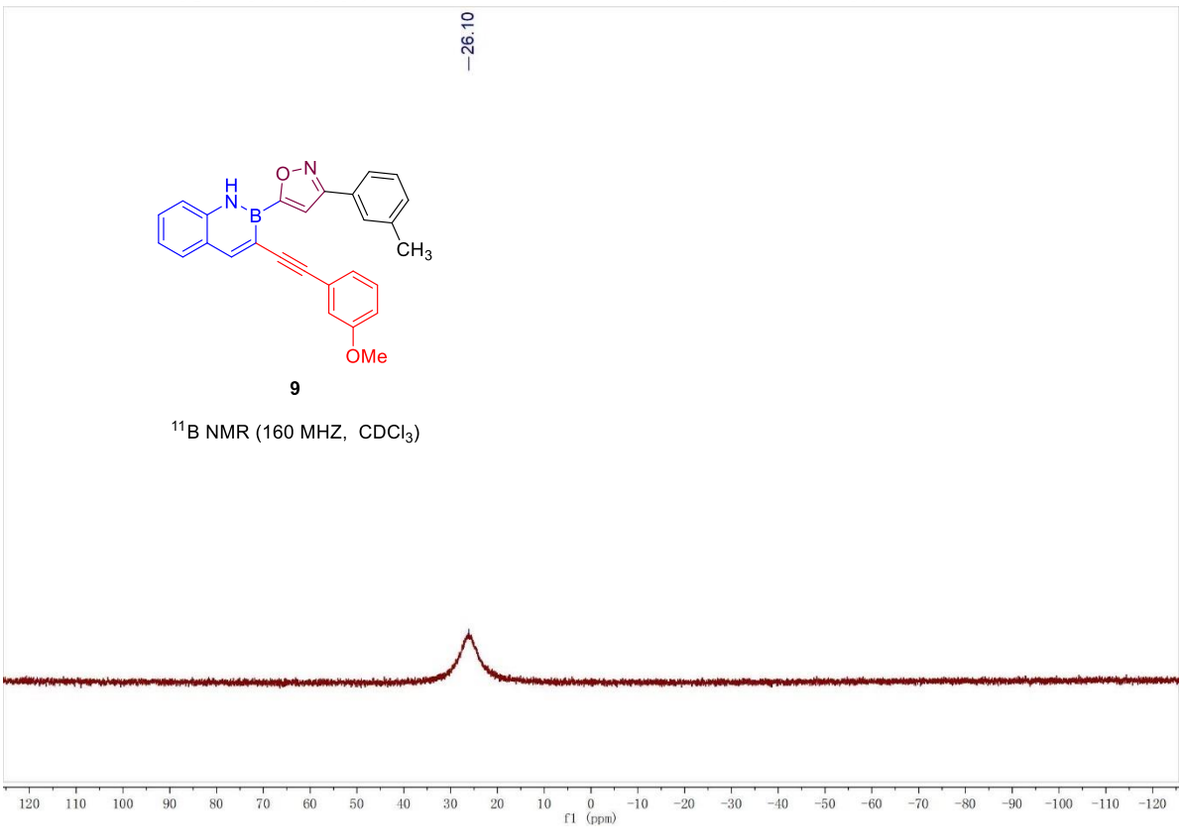
5-(3-((3-methoxyphenyl)ethynyl)benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (9)



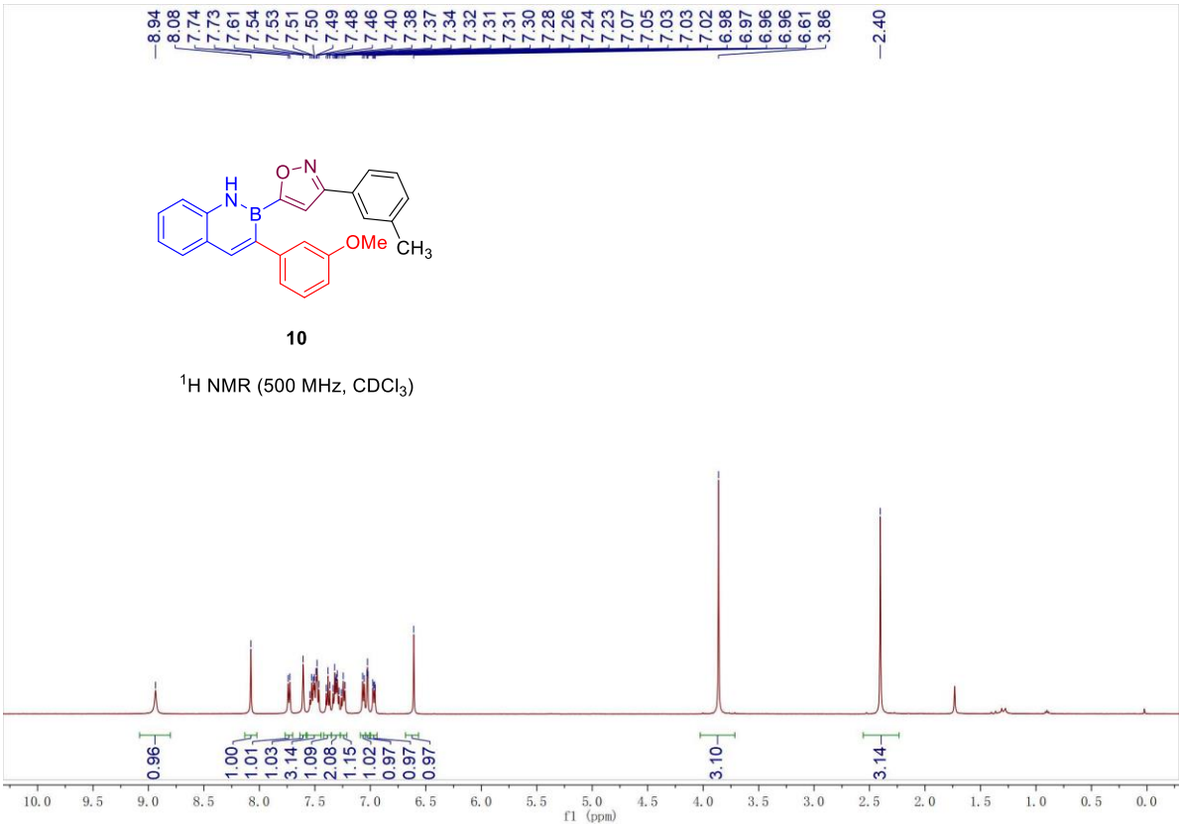
5-(3-((3-methoxyphenyl)ethynyl)benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (9)



5-(3-((3-methoxyphenyl)ethynyl)benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (9)



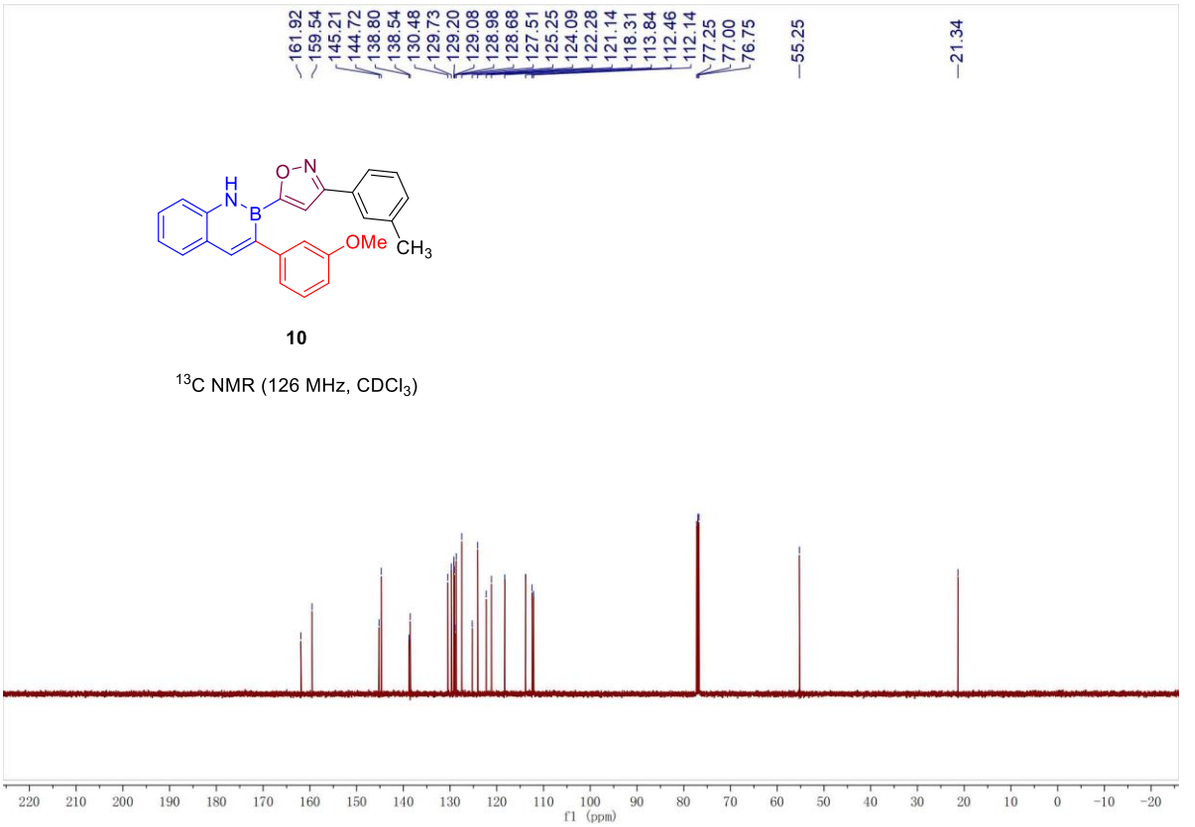
5-(3-(3-methoxyphenyl)benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (10)



10

^{1}H NMR (500 MHz, $CDCl_3$)

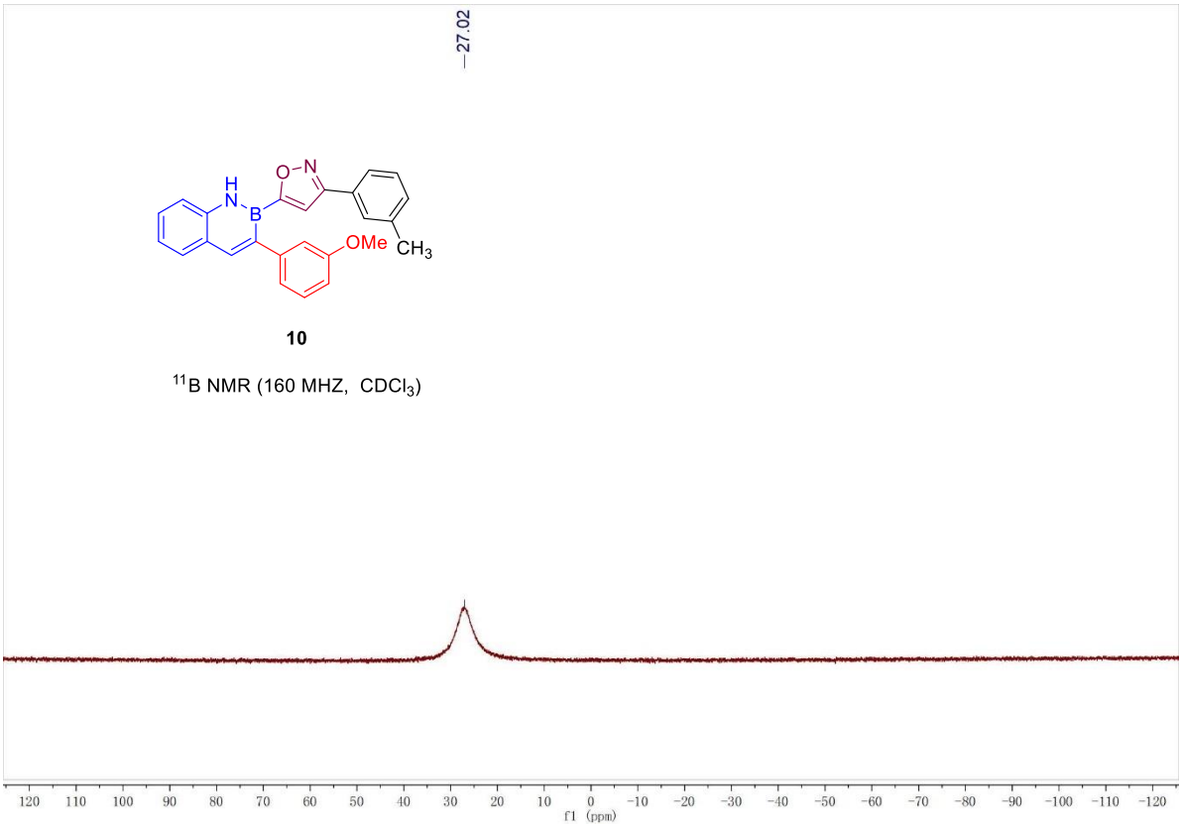
5-(3-(3-methoxyphenyl)benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (10)



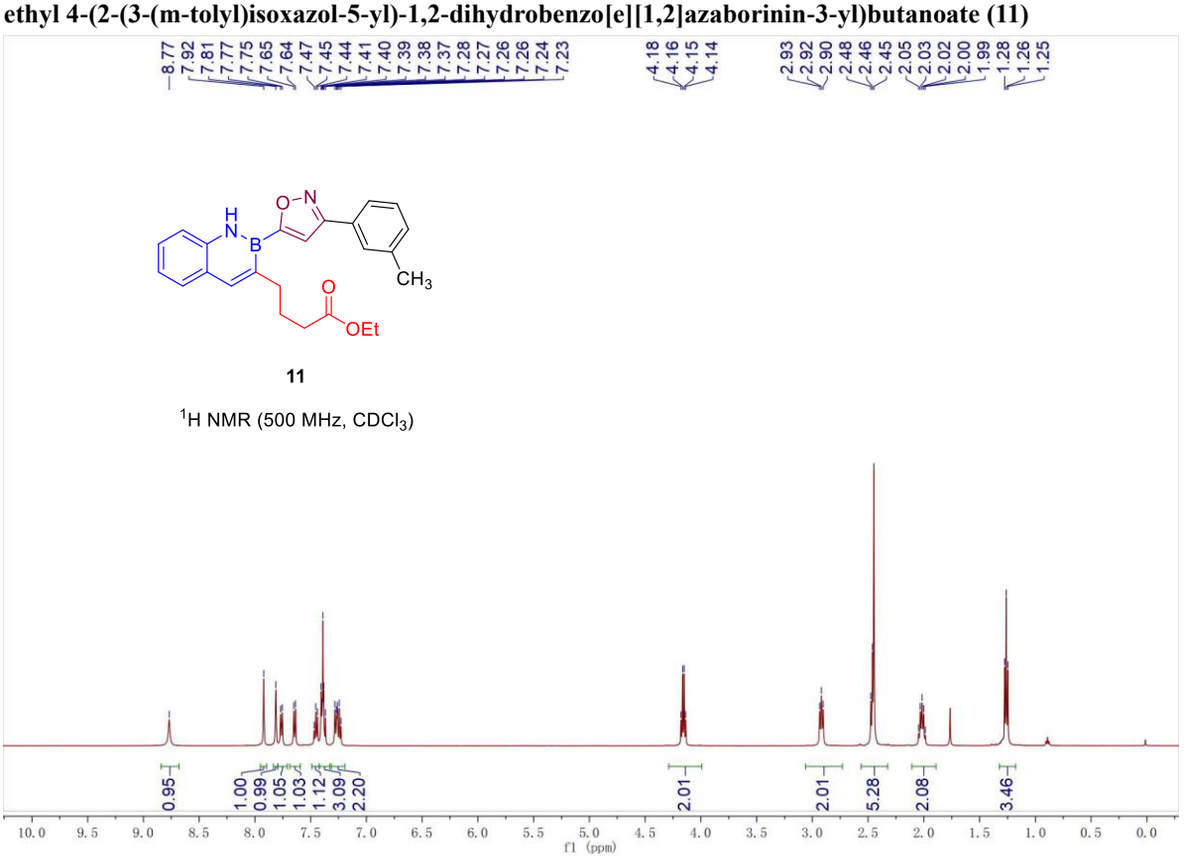
10

^{13}C NMR (126 MHz, $CDCl_3$)

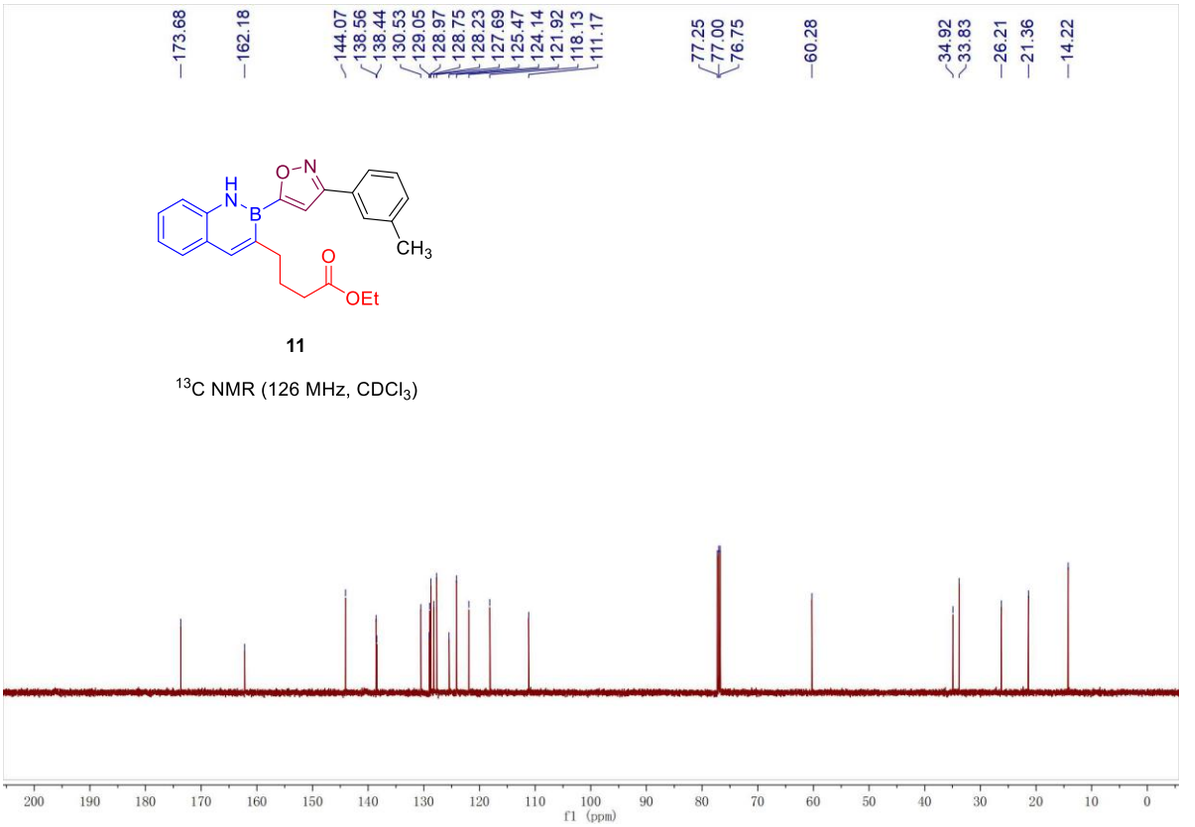
5-(3-(3-methoxyphenyl)benzo[e][1,2]azaborinin-2(1H)-yl)-3-(m-tolyl)isoxazole (10)



ethyl 4-(2-(3-(m-tolyl)isoxazol-5-yl)-1,2-dihydrobenzo[e][1,2]azaborinin-3-yl)butanoate (11)



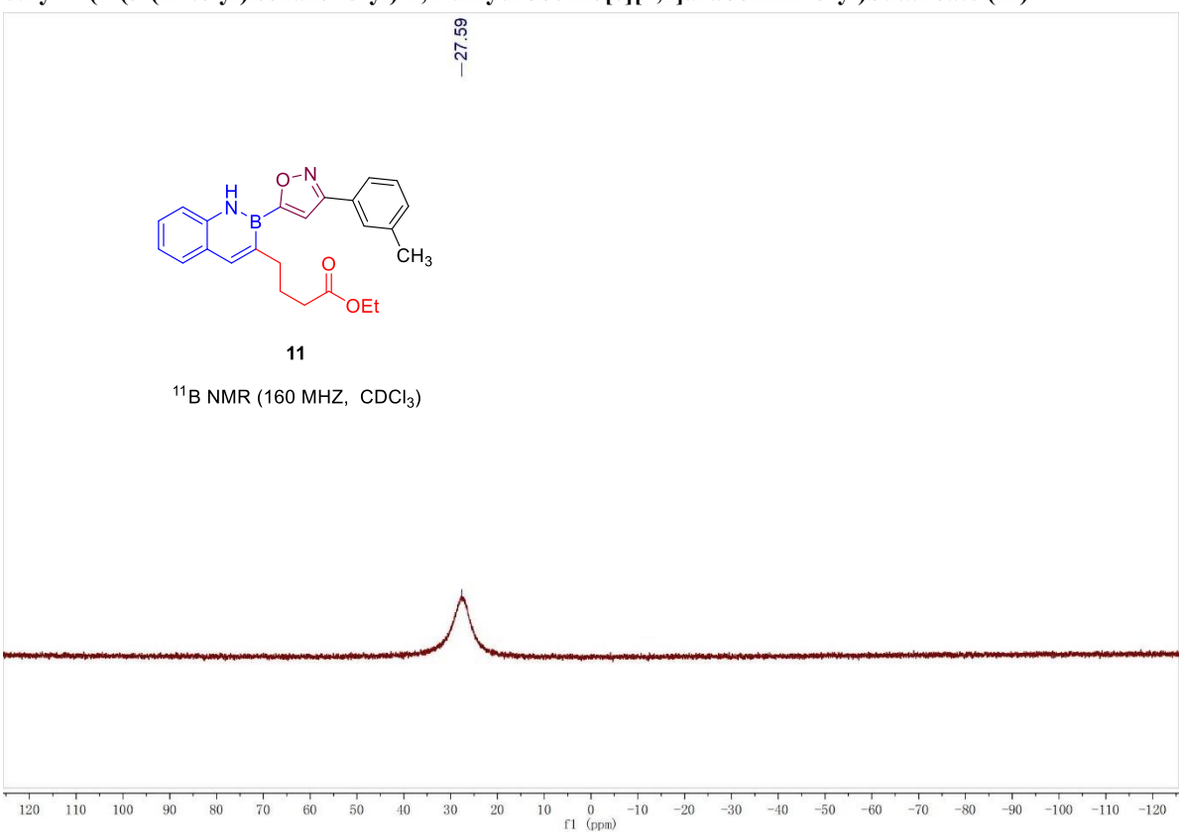
ethyl 4-(2-(3-(m-tolyl)isoxazol-5-yl)-1,2-dihydrobenzo[e][1,2]azaborinin-3-yl)butanoate (11)



11

^{13}C NMR (126 MHz, $CDCl_3$)

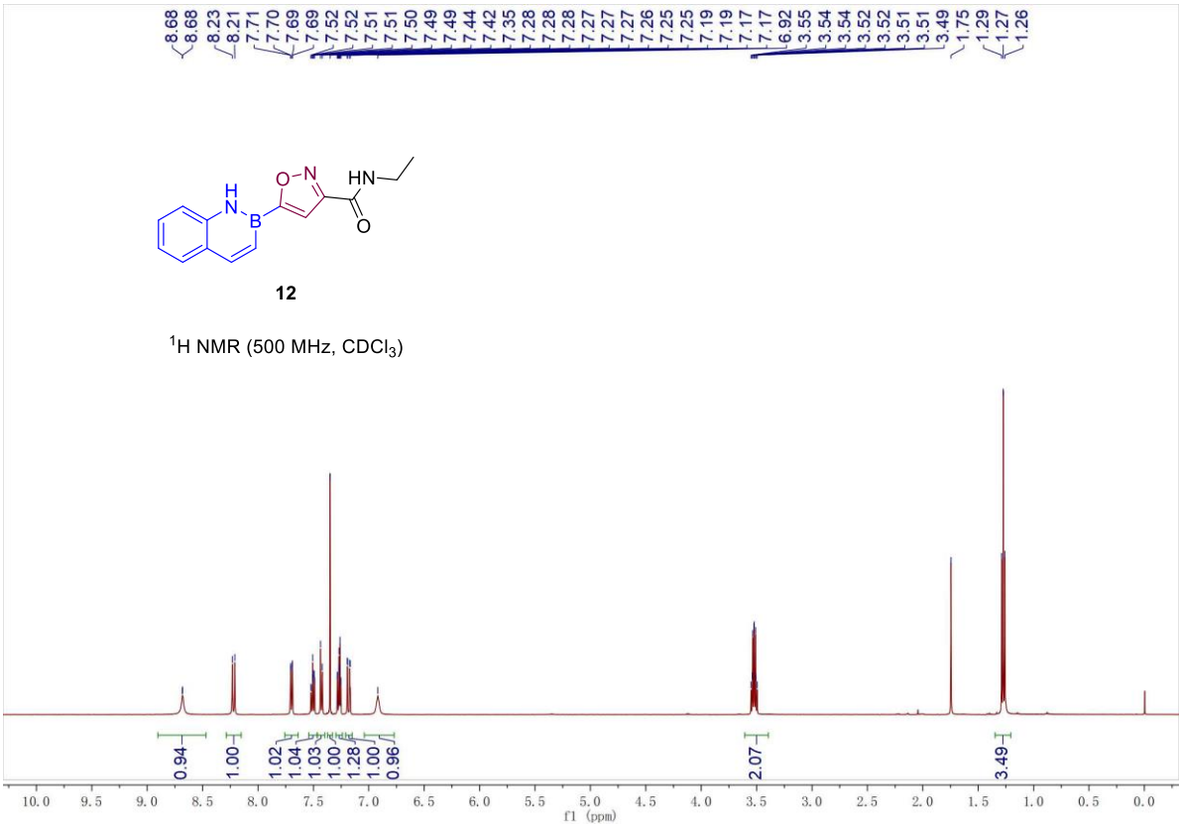
ethyl 4-(2-(3-(m-tolyl)isoxazol-5-yl)-1,2-dihydrobenzo[e][1,2]azaborinin-3-yl)butanoate (11)



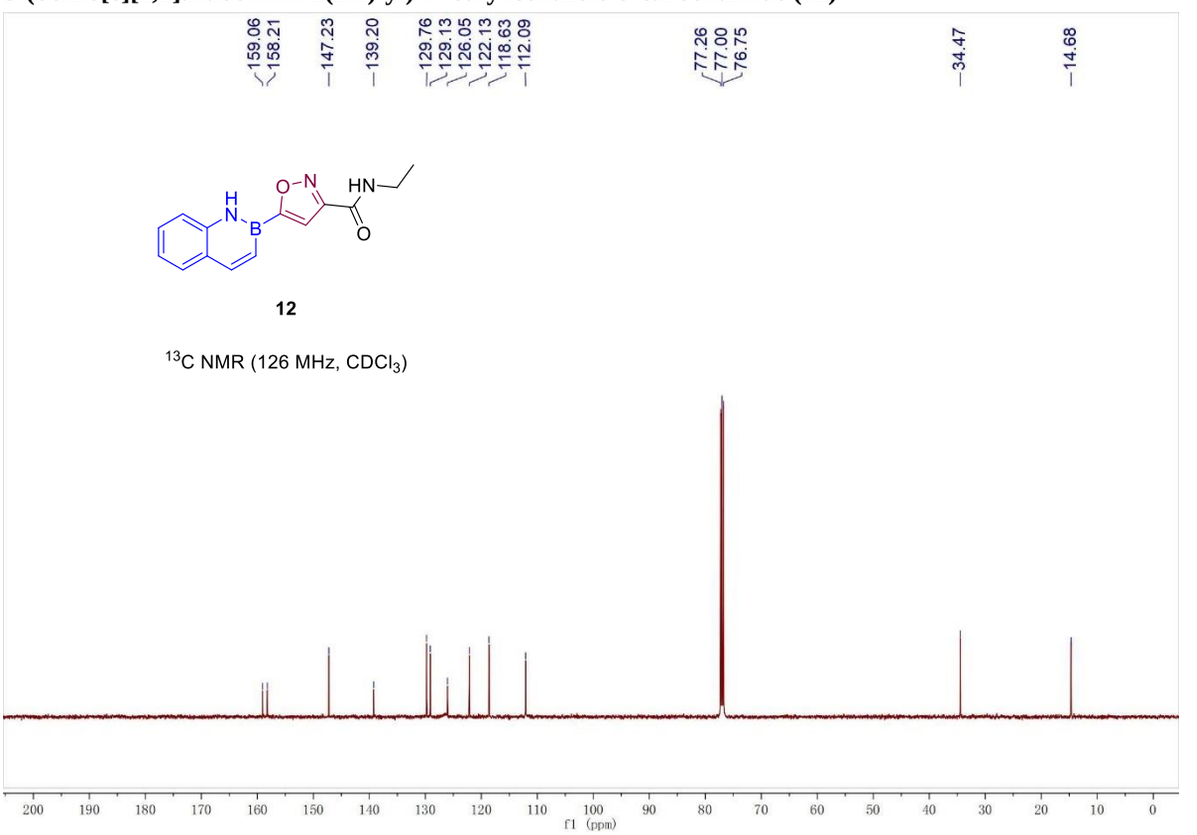
11

^{11}B NMR (160 MHZ, $CDCl_3$)

5-(benzo[e][1,2]azaborinin-2(1H)-yl)-N-ethylisoxazole-3-carboxamide (12)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-N-ethylisoxazole-3-carboxamide (12)



5-(benzo[e][1,2]azaborinin-2(1H)-yl)-N-ethylisoxazole-3-carboxamide (12)