Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

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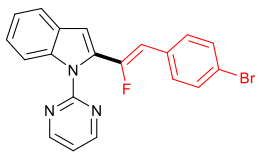
1. General Methods

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques in absolute TFE under N_2. The ^1H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^1H and ^{13}C NMR spectroscopy. High resolution mass spectra were obtained on an Agilent Q-TOF 6540 spectrometer. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA) /petroleum ether (PE). Substrates **2a** was obtained from commercial sources. Arenes **1a-1s**[1] and olefins **2b-2m**[2] were synthesized according to literature reports.

Experimental procedure and characterization

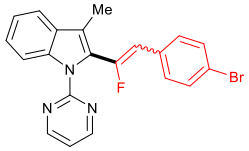
General procedure for the synthesis of fluoroalkenes

Indole (0.2 mmol), *gem*-difluoroalkene (0.32 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $Ca(OH)_2$ (2.0 equiv), and TFE (1 mL) were charged into a pressure tube. The reaction mixture was stirred under Ar at 100 ºC for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA to afford the product.



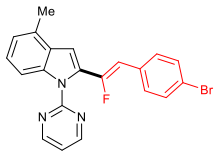
(*Z*)-2-(2-(4-bromophenyl)- 1 -fluorovinyl)- 1 -(pyrimidin-2-yl)-1H-indole (**3aa**)

3aa was obtained according to the general procedure in 94% yield (73.8 mg). white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.25 (dd, *J* = 10.0, 4.5 Hz, 1H), 7.15 (t, *J* = 4.8 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 6.21 (d, *J* = 35.7 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.11 (d, *J* = 35.6 Hz, 1F). The NMR data agree with those in a literature report.[3] HRMS: $[M + Na]^+$ calculated for $C_{20}H_{13}BrFN_3Na^+$: 416.0169, found: 416.0165.



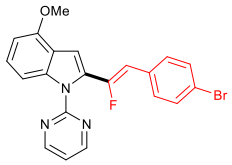
3ba (Z/E=8:1)

3ba was obtained according to the general procedure in 95% yield (77.3 mg). white solid; **Z isomer** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (s, 2H), 8.46 (d, *J* = 7.1 Hz, 1H), 7.62 (d, *J* = 5.3 Hz, 1H), 7.48 (s, 4H), 7.38 (s, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.05 (s, 1H), 5.97 (d, *J* = 36.0 Hz, 1H), 2.46 (s, 3H). The NMR data agree with those in a literature report.[4] **E isomer** (only clearly assignable signals are listed) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (s, 2H), 8.59 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 5.3 Hz, 1H), 7.48 (s, 4H), 7.38 (s, 1H), 7.22 (d, *J* = 7.0 Hz, 1H), 7.05 (s, 1H),6.50 (d, *J* = 17.1 Hz, 1H), 2.00 (s, 3H). HRMS: [M + Na]$^+$ calculated for $C_{21}H_{15}BrFN_3Na^+$: 430.0326, found: 430.0336.



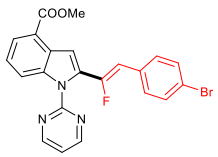
(Z)-2-(2-(4-bromophenyl)-1-fluorovinyl)-4-methyl-1-(pyrimidin-2-yl)-1H-indole (**3ca**)

3ca was obtained according to the general procedure in 95% yield (77.3 mg). white solid, mp 79.0-83.1°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (s, 2H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.46 (s, 4H), 7.27 – 7.24 (m, 1H), 7.15 (d, *J* = 2.6 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.23 (d, *J* = 35.6 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (d, *J* = 92.0 Hz), 157.7, 153.4, 151.8, 138.9, 132.9, 132.3 (d, *J* = 194.3 Hz), 130.4 (t, *J* = 15.5 Hz, 1H), 126.1, 121.0, 119.2, 117.7, 108.4 (d, *J* = 5.5 Hz), 107.6 (d, *J* = 10.3 Hz,), 107.1, 102.4, 55.5.^{19}F NMR (565 MHz, $CDCl_3$) -99.23 (d, *J* = 35.7 Hz, 1F). HRMS: [M + Na]$^+$ calculated for $C_{21}H_{15}BrFN_3Na^+$: 430.0326, found: 430.0329.



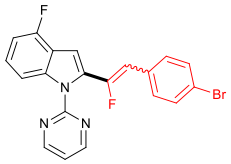
(Z)-2-(2-(4-bromophenyl)-1-fluorovinyl)-4-methoxy-1-(pyrimidin-2-yl)-1H-indole (**3da**)

3da was obtained according to the general procedure in 80% yield (67.7mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 – 8.68 (m, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.45 (dd, *J* = 15.7, 7.6 Hz, 4H),7.27(s,1H) 7.19 – 7.08 (m, 2H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.21 (d, *J* = 35.7 Hz, 1H), 3.97 (s, 3H). The NMR data agree with those in a literature report.[4] HRMS: [M + Na]$^+$ calculated for $C_{21}H_{15}BrFN_3ONa^+$: 446.0280, found: 446.0275.



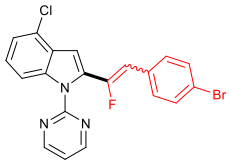
(Z)-methyl 2-(2-(4-bromophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate (**3ea)**

3ea was obtained according to the general procedure in 69% yield (62.2 mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.3 Hz, 2H), 8.57 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 1H), 7.70 (s, 1H), 7.52 – 7.45 (m, 4H), 7.40 (s, 1H), 7.24 (s, 2H), 6.35 (d, *J* = 35.9 Hz, 1H), 4.02 (s, 3H). The NMR data agree with those in a literature report.[4] HRMS: [M + Na]$^+$ calculated for $C_{22}H_{15}BrFN_3O_2Na^+$: 474.0224, found: 474.0221.



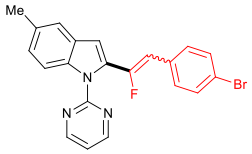
3fa (Z/E=7:1)

3fa was obtained according to the general procedure in 88% yield (72.3 mg). white solid, mp 93.1-95.0°C **Z isomer** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 3.4 Hz, 2H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, *J* = 16.6, 7.1 Hz, 4H), 7.30 – 7.24 (m, 2H), 7.22 (s, 1H), 7.08 (s, 1H), 6.94 (t, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 35.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 157.4 156.9, 155.3, 152.9, 151.1, 139.6(d, *J* = 9.3 Hz), 131.7, 130.4 (d, *J* = 7.8 Hz), 125.7 (d, *J* = 7.6 Hz), 121.3, 118.0, 117.7 (d, *J* = 22.6 Hz), 110.2 (d, *J* = 3.6 Hz), 108.5 (d, *J* = 9.9 Hz), 107.5 (d, *J* = 18.3 Hz), 106.5 (d, *J* = 5.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.88 (d, *J* = 35.7 Hz, 1F), -121.58 (dd, *J* = 9.4, 5.4 Hz, 1F). **E isomer** (only clearly assignable signals are listed) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 3.6 Hz, 2H), 8.27 (d, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 7.06 (s, 1H), 6.42 (d, *J* = 17.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 148.6,147.8, 132.6 (d, *J* = 4.0 Hz), 132.2 (d, *J* = 6.4 Hz), 132.0, 131.5, 130.0 (d, *J* = 2.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -91.27 (d, *J* = 17.4 Hz, 1F), -121.16 (d, *J* = 9.4 Hz,1F). HRMS: $[M + Na]^+$ calculated for $C_{20}H_{12}BrF_2N_3Na^+$: 434.0074, found: 434.0078.



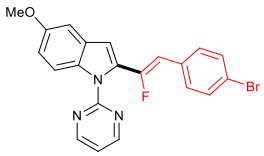
3ga (Z/E=3:1)

3ga was obtained according to the general procedure in 71% yield (60.6 mg). white solid; **Z isomer** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 2H), 8.26 (d, *J* = 5.1 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 4H), 7.26 (s, 2H), 7.20 (s, 1H), 7.11 (s, 1H), 7.04 (d, *J* = 7.7 Hz, 1H) , 6.27 (d, *J* = 35.7 Hz, 1H). The NMR data agree with those in a literature report.[4] **E isomer** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.38 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 4H), 7.26 (s, 2H), 7.15 (s, 1H), 6.93 (s, 1H), 6.42 (d, *J* = 18.1 Hz, 1H). HRMS: $[M + Na]^+$ calculated for $C_{20}H_{12}BrClFN_3Na^+$: 449.9779, found: 449.9777.



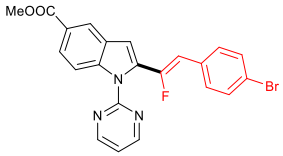
3ha (Z/E=14:1)

3ha was obtained according to the general procedure in 90% yield (73.3 mg). white solid; **Z isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.8 Hz, 2H), 8.19 (d, *J* = 8.6 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.34 (s, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 7.06 (t, *J* = 4.8 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.13 (d, *J* = 35.7 Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) -98.69 (d, *J* = 35.6 Hz, 1F). The NMR data agree with those in a literature report.[4] **E isomer** (only clearly assignable signals are listed) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.6 Hz, 1H), 7.48 – 7.42 (m, 4H), 7.30 (s, 1H), 7.03 – 6.94 (m, 2H), 6.64 (d, *J* = 3.5 Hz, 1H), 6.30 (d, *J* = 17.9 Hz, 1H), 2.36 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -90.04 (d, *J* = 17.8 Hz, 1F). HRMS: $[M + Na]^+$ calculated for $C_{21}H_{15}BrFN_3Na^+$: 430.0326, found: 430.0324.



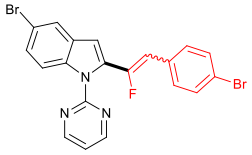
(Z)-2-(2-(4-bromophenyl)-1-fluorovinyl)-5-methoxy-1-(pyrimidin-2-yl)-1H-indole (**3ia**)

3ia was obtained according to the general procedure in 52% yield (43.9 mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 2.3 Hz, 2H), 8.32 (d, *J* = 9.0 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.14 (s, 1H), 7.07 (s, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.91 (s, 1H), 6.19 (d, *J* = 35.5 Hz, 1H), 3.88 (s, 3H). The NMR data agree with those in a literature report.[4] HRMS: $[M + Na]^+$ calculated for $C_{21}H_{15}BrFN_3ONa^+$: 446.0280, found: 446.0272.



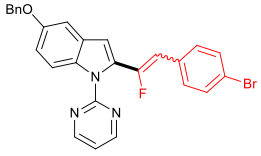
(Z)-methyl 2-(2-(4-bromophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole-5-carboxylate (**3ja**)

3ja was obtained according to the general procedure in 41% yield (37.0 mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (d, *J* = 3.0 Hz, 2H), 8.39 (d, *J* = 13.7 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.48 (dd, *J* = 18.3, 7.4 Hz, 4H), 7.26 (d, *J* = 16.3 Hz, 1H), 7.07 (s, 1H), 6.26 (d, *J* = 35.6 Hz, 1H), 3.97 (s, 3H). The NMR data agree with those in a literature report.[4] HRMS: $[M + Na]^+$ calculated for $C_{22}H_{15}BrFN_3O_2Na^+$: 474.0224, found: 474.0229.



3ka (Z/E=7:1)

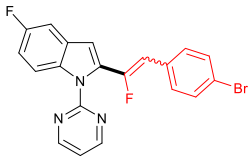
3ka was obtained according to the general procedure in 88% yield (82.9 mg). white solid; **Z isomer** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.7 Hz, 2H), 8.27 (d, *J* = 8.9 Hz, 1H), 7.77 (s, 1H), 7.46 (dt, *J* = 20.1, 9.9 Hz, 5H), 7.20 (s, 1H), 6.92 (s, 1H), 6.22 (d, *J* = 35.6 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) -99.64 (d, *J* = 35.7 Hz, 1F).The NMR data agree with those in a literature report.[4] **E isomer** (only clearly assignable signals are listed)^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.7 Hz, 2H), 8.41 (d, *J* = 8.9 Hz, 1H), 7.69 (s, 1H), 7.27 (s, 1H), 7.16 (t, *J* = 4.7 Hz, 1H), 6.42 (d, *J* = 17.9 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -91.38 (d, *J* = 18.0 Hz, 1H).HRMS: $[M + Na]^+$ calculated for $C_{20}H_{12}Br_2FN_3Na^+$: 495.9259, found: 495.9258.



3la (Z/E=11:1)

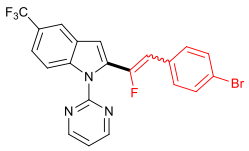
3la was obtained according to the general procedure in 49% yield (48.9 mg). white solid, mp 151.8-153.0 °C; **Z isomer** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 3.9 Hz, 2H), 8.32 (d, *J* = 8.9 Hz, 1H), 7.46 (dd, *J* = 13.2, 8.1 Hz, 6H), 7.39 (t, *J* = 6.7 Hz, 2H), 7.33 (d, *J* = 6.8 Hz, 1H), 7.13 (d, *J* = 13.4

Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 1H), 6.89 (s, 1H), 6.18 (d, *J* = 35.5 Hz, 1H), 5.12 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 157.5, 155.0, 153.5, 151.8, 137.3, 132.8, 132.8 (d, *J* = 5.3 Hz), 132.6, 132.4, 131.7, 130.4 (d, *J* = 7.8 Hz,), 130.4 (d, *J* = 7.8 Hz), 129.1, 128.6, 127.9, 127.6 121.1, 117.4, 115.7, 115.4 (d, *J* = 15.7 Hz), 111.2 (d, *J* = 5.2 Hz), 107.9 (d, *J* = 10.2 Hz,) , 104.4, 70.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.69 (d, *J* = 35.4 Hz, 1F). **E isomer** (only clearly assignable signals are listed) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.1 Hz, 2H), 8.46 (d, *J* = 8.8 Hz, 1H), 7.39 (t, *J* = 6.7 Hz, 2H), 6.69 (s, 1H), 6.38 (d, *J* = 17.6 Hz, 1H), 5.10(s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 157.3, 133.1, 131.5, 130.1 (d, *J* = 2.5 Hz), 116.2, 112.7 (d, *J* = 5.6 Hz), 110.24 (d, *J* = 31.5 Hz,), 60.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ -90.20 (d, *J* = 17.7 Hz, 1F). HRMS: $[M + Na]^+$ calculated for $C_{27}H_{19}BrFN_3ONa^+$: 522.0587, found: 522.0588.



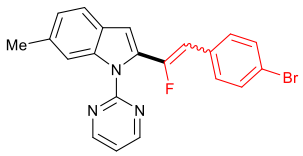
3ma (Z/E=11:1)

3ma was obtained according to the general procedure in 94% yield (77.3 mg). white solid; **Z isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 10.7, 4.8 Hz, 2H), 8.36 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.47 (q, *J* = 8.7 Hz, 4H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.18 (t, *J* = 4.7 Hz, 1H), 7.09 (t, *J* = 8.5 Hz, 1H), 6.93 (s, 1H), 6.21 (d, *J* = 35.6 Hz, 1H). **E isomer** (only clearly assignable signals are listed) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 8.6, 4.6 Hz, 1H), 6.41 (d, *J* = 17.9 Hz, 1H). The NMR data agree with those in a literature report.[4] HRMS: $[M + Na]^+$ calculated for $C_{20}H_{12}BrF_2N_3Na^+$: 434.0074, found: 434.0080.



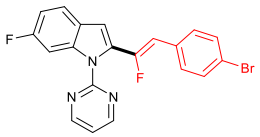
3na (Z/E=5:1)

3na was obtained according to the general procedure in 53% yield (48.9 mg). white solid, mp 118.5-122.1°C; **Z isomer** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 16.7 Hz, 2H), 8.45 (d, *J* = 8.7 Hz, 1H), 7.93 (s, 1H), 7.58 (d, *J* = 9.2 Hz, 1H), 7.47 (dd, *J* = 18.8, 8.0 Hz, 4H), 7.24 (s, 1H), 7.04 (s, 1H), 6.25 (d, *J* = 35.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 152.6, 150.9, 138.9, 133.9,133.7, 132.4, 131.8, 130.4 (d, *J* = 7.8 Hz), 127.9, 121.7(d, *J* = 3.0 Hz), 118.8 (d, *J* = 4.0 Hz), 118.6, 114.6, 110.9(d, *J* = 5.4 Hz), 108.9 (d, *J* = 9.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.98 (s, 3F), -100.06 (d, *J* = 35.7 Hz, 1F). **E isomer**(only clearly assignable signals are listed) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.59 (d, *J* = 8.9 Hz, 1H), 7.86 (s, 1H), 6.45 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 130.6 (d, *J* = 3.4 Hz), 128.0, 125.7, 125.0, 124.8 (d, *J* = 1.7 Hz), 123.9, 121.5 (d, *J* = 3.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -61.07 (s, 3F), -91.89 (d, *J* = 18.0 Hz, 1F). HRMS: $[M + Na]^+$ calculated for $C_{21}H_{12}BrF_4N_3Na^+$: 484.0043, found: 484.0043.



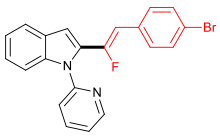
3oa (Z/E=13:1)

3oa was obtained according to the general procedure in 64% yield (52.1 mg). white solid; **Z isomer** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 2.2 Hz, 2H), 8.17 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.45 (q, *J* = 8.1 Hz, 4H), 7.16 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.95 (s, 1H), 6.19 (d, *J* = 35.7 Hz, 1H), 2.51 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$), -99.05 (d, *J* = 35.7 Hz, 1F). The NMR data agree, with those in a literature report.[4] **E isomer** (only clearly assignable signals are listed): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.6 Hz, 2H), 8.31 (s, 1H), 7.06 (d, *J* = 9.1 Hz, 1H), 6.75 (s, 1H), 6.36 (d, *J* = 18.0 Hz, 1H), 2.52 (s, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -90.20 (d, *J* = 17.9 Hz, 1F). HRMS: $[M + Na]^+$ calculated for $C_{21}H_{15}BrFN_3Na^+$: 430.0326, found: 430.0329.



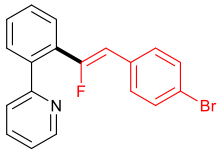
(Z)-2-(2-(4-bromophenyl)-1-fluorovinyl)-6-fluoro-1-(pyrimidin-2-yl)-1H-indole (**3pa**)

3pa was obtained according to the general procedure in 77% yield (63.3 mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 3.2 Hz, 2H), 8.15 (d, *J* = 10.6 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.44 (dd, *J* = 15.6, 7.9 Hz, 4H), 7.17 (t, *J* = 3.7 Hz, 1H), 7.00 (t, *J* = 8.8 Hz, 1H), 6.93 (s, 1H), 6.17 (d, *J* = 35.4 Hz, 1H). The NMR data agree with those in a literature report.[4] HRMS: $[M + Na]^+$ calculated for $C_{20}H_{12}BrF_2N_3Na^+$: 434.0074, found: 434.0079.



(Z)-2-(2-(4-bromophenyl)-1-fluorovinyl)-1-(pyridin-2-yl)-1H-indole (**3qa**)

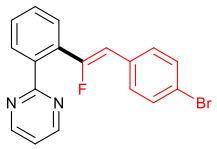
3qa was obtained according to the general procedure in 31% yield (24.3mg). white oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.4 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.41 – 7.31 (m, 3H), 7.29 – 7.25 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 5.95 (d, *J* = 37.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4, 151.6, 150.6, 149.6, 138.7, 138.5, 132.3 (d, *J* = 3.7 Hz), 131.9, 131.8, 131.7, 130.3 (d, *J* = 8.1 Hz), 127.7, 124.5, 122.5, 121.7, 121.4, 120.6, 111.2, 108.8 (d, *J* = 9.5 Hz), 107.7 (d, *J* = 4.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -105.02 (s, 1F). HRMS: $[M + H]^+$ calculated for $C_{24}H_{16}BrFN_3H^+$: 393.0397, found: 393.0407.



(Z)-2-(2-(2-(4-bromophenyl)-1-fluorovinyl)phenyl)pyridine(**3ra**)

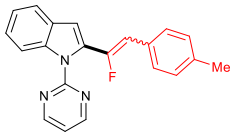
3ra was obtained according to the general procedure in 33% yield (23.3 mg). green oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.61 (dd, *J* = 12.0, 7.7 Hz, 2H), 7.51 (t, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.22 (m, 2H), 5.82 (d, *J* = 37.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 158.9, 157.7, 149.5, 139.5, 136.3, 132.7 (d, *J* = 3.5 Hz), 132.0, 131.9, 131.6, 130.6, 130.2 (d, *J* = 8.1 Hz), 129.80 (s, 1H), 129.2 (d, *J* = 4.7 Hz), 128.4, 123.4, 122.1, 121.0 (d, *J* = 3.4 Hz), 109.2 (d, *J* = 10.1 Hz). ^{19}F NMR (565

MHz, $CDCl_3$) δ -96.16 (s, 1F). HRMS: $[M + H]^+$ calculated for $C_{19}H_{13}BrFNH^+$: 354.0288, found: 354.0287.



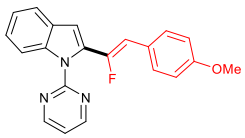
(Z)-2-(2-(2-(4-bromophenyl)-1-fluorovinyl)phenyl)pyrimidine(**3sa**)

3sa was obtained according to the general procedure in 42% yield (29.7 mg). white oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.9 Hz, 2H), 7.82 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.50 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 2H), 7.13 (t, *J* = 4.9 Hz, 1H), 5.90 (d, *J* = 37.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 160.6, 157.9, 157.1, 137.7, 132.9 (d, *J* = 3.5 Hz), 132.9, 132.6, 131.6, 130.9, 130.3 (d, *J* = 8.0 Hz), 129.8, 129.7 (d, *J* = 4.5 Hz), 129.6, 120.9 (d, *J* = 3.6 Hz), 119.1, 108.0 (d, *J* = 10.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.45 (d, *J* = 37.4 Hz,1F). HRMS: $[M + H]^+$ calculated for $C_{18}H_{12}BrFN_2H^+$: 355.0241, found: 355.0238.



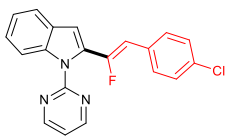
3ab (Z/E=16:1)

3ab was obtained according to the general procedure in 94% yield (61.9 mg). white solid; **Z isomer** ^1H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 3.5 Hz, 2H), 8.35 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 6.0 Hz, 1H), 7.19 – 7.13 (m, 3H), 6.97 (s, 1H), 6.25 (d, *J* = 36.5 Hz, 1H), 2.36 (s, 3H). **E isomer** (only clearly assignable signals are listed) ^1H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 3.5 Hz, 2H), 8.51 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 6.82 (s, 1H), 6.45 (d, *J* = 18.8 Hz, 1H), 2.24 (s, 1H). The NMR data agree with those in a literature report.[3] HRMS: $[M + Na]^+$ calculated for $C_{21}H_{16}FN_3Na^+$: 352.1220, found: 352.1227.



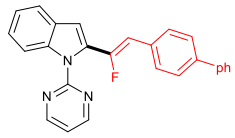
(Z)-2-(1-fluoro-2-(4-methoxyphenyl)vinyl)-1-(pyrimidin-2-yl)-1H-indole (**3ac**)

3ac was obtained according to the general procedure in 60% yield (41.4 mg). white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 4.8 Hz, 1H), 6.95 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.22 (d, *J* = 36.6 Hz, 1H), 3.82 (s, 3H). The NMR data agree with those in a literature report.[4] HRMS: $[M + Na]^+$ calculated for $C_{21}H_{16}FN_3ONa^+$: 368.1170, found: 368.1169.



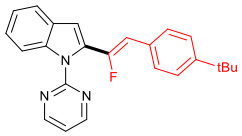
(Z)-2-(2-(4-chlorophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole (**3ad**)

3ad was obtained according to the general procedure in 88% yield (61.4 mg). white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 13.7, 8.1 Hz, 3H), 7.26 (t, *J* = 6.7 Hz, 1H), 7.15 (t, *J* = 4.8 Hz, 1H), 6.99 (s, 1H), 6.23 (d, *J* = 35.7 Hz, 1H). The NMR data agree with those in a literature report.[4] HRMS: $[M + Na]^+$ calculated for $C_{20}H_{13}ClFN_3Na^+$: 372.0674, found: 372.0679.



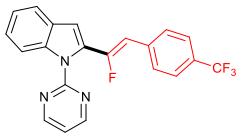
(Z)-2-(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole (**3ae**)

3ae was obtained according to the general procedure in 80% yield (62.6 mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 3.9 Hz, 2H), 8.37 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.58 (m, 7H), 7.44 (t, *J* = 7.0 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.25 (dd, *J* = 13.3, 5.6 Hz, 1H), 7.16 (s, 1H), 7.01 (s, 1H), 6.32 (d, *J* = 36.2 Hz, 1H). The NMR data agree with those in a literature report.[4] HRMS: $[M + Na]^+$ calculated for $C_{26}H_{18}FN_3Na^+$: 414.1377, found: 414.1379.



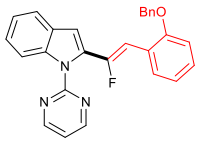
(Z)-2-(2-(4-(tert-butyl)phenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole (**3af**)

3af was obtained according to the general procedure in 66% yield (49.0 mg). white solid, mp 77.2-79.3°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.0 Hz, 2H), 8.35 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.13 (d, *J* = 3.2 Hz, 1H), 6.97 (s, 1H), 6.26 (d, *J* = 36.6 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 152.5, 150.8, 150.5, 137.6, 132.7, 132.6 (d, *J* = 25.7 Hz), 131.1 (d, *J* = 3.9 Hz), 128.6 (d, *J* = 7.5 Hz), 125.5,124.9, 122.5, 121.2, 117.6, 114.0, 110.8(d, *J* = 5.1 Hz), 108.90 (d, *J* = 10.3 Hz), 34.7, 31.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -101.53 (d, *J* = 36.6 Hz, 1F). HRMS: $[M + Na]^+$ calculated for $C_{24}H_{22}FN_3Na^+$:394.1690, found: 394.1697.



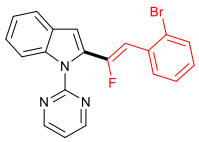
(Z)-2-(1-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)-1-(pyrimidin-2-yl)-1H-indole (**3ag**)

3ag was obtained according to the general procedure in 80% yield (62.6 mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 3.8 Hz, 2H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.66 (dd, *J* = 18.4, 7.8 Hz, 3H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.14 (s, 1H), 7.02 (s, 1H), 6.30 (d, *J* = 35.3 Hz, 1H). The NMR data agree with those in a literature report.[3] HRMS: $[M + Na]^+$ calculated for $C_{21}H_{13}F_4N_3Na^+$:406.0938, found: 406.0939.



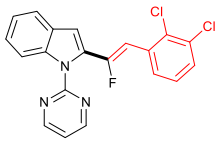
(Z)-2-(2-(2-(benzyloxy)phenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole(**3ah**)

3ah was obtained according to the general procedure in 87% yield (73.3 mg). white oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.1 Hz, 2H), 8.36 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.27 (d, *J* = 5.6 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.15 (dd, *J* = 26.9, 5.7 Hz, 2H), 6.98 (s, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.24 (d, *J* = 35.9 Hz, 1H), 5.07 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 158.3, 157.6, 153.2, 151.4, 137.7, 137.07, 135.2 (d, *J* = 4.0 Hz), 132.4, 132.3, 129.5, 128.6 (d, *J* = 13.7 Hz), 128.0, 127.6, 125.1, 122.6, 121.9 (d, *J* = 6.9 Hz), 121.3, 117.6, 115.2 (d, *J* = 8.5 Hz), 114.1 (d, *J* = 4.3 Hz), 111.1 (d, *J* = 5.2 Hz), 108.9 (d, *J* = 9.7 Hz), 70.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.52 (d, *J* = 35.9 Hz). HRMS: $[M + Na]^+$ calculated for $C_{27}H_{20}FN_3ONa^+$:444.1483, found: 444.1487.



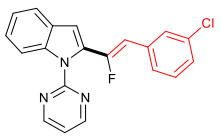
(Z)-2-(2-(2-bromophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole (**3ai**)

3ai was obtained according to the general procedure in 39% yield (30.7mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 2H), 8.38 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 7.1 Hz, 1H), 7.63 (dd, *J* = 36.6, 7.2 Hz, 2H), 7.36 (s, 1H), 7.27 (dd, *J* = 20.1, 13.3 Hz, 2H), 7.16 (s, 1H), 7.09 (d, *J* = 14.9 Hz, 2H), 6.61 (d, *J* = 35.4 Hz, 1H). The NMR data agree with those in a literature report.[4] HRMS: $[M + Na]^+$ calculated for $C_{20}H_{13}BrFN_3Na^+$:416.0169, found: 416.0167.



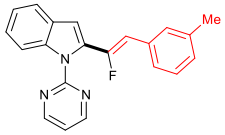
(Z)-2-(2-(2,3-dichlorophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole (**3aj**)

3aj was obtained according to the general procedure in 34% yield (26.0mg). white solid, mp 93.9-95.0°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.16 (dt, *J* = 7.8, 6.5 Hz, 2H), 7.06 (s, 1H), 6.62 (d, *J* = 34.7 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 157.6, 154.6, 152.9, 133.9, 131.8, 131.2, 128.5, 128.4, 125.4, 121.4, 114.3, 111.4 (d, *J* = 5.3 Hz), 104.9 (d, *J* = 8.5). ^{19}F NMR (565 MHz, $CDCl_3$) δ-98.93 (d, *J* = 34.8 Hz, 1F). HRMS: $[M + Na]^+$ calculated for $C_{20}H_{12}Cl_2FN_3Na^+$: 406.0284, found: 406.0276.



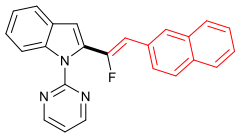
(Z)-2-(2-(3-chlorophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indole **(3ak)**

3akwas obtained according to the general procedure in 71% yield (49.6mg). white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.7 Hz, 2H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.29 (dd, *J* = 15.4, 7.7 Hz, 3H), 7.18 (d, *J* = 5.2 Hz, 1H), 7.01 (s, 1H), 6.24 (d, *J* = 35.4 Hz). The NMR data agree with those in a literature report.[3] HRMS: $[M + Na]^+$ calculated for $C_{20}H_{13}ClFN_3Na^+$: 372.0680, found: 372.0680.



(Z)-2-(1-fluoro-2-(m-tolyl)vinyl)-1-(pyrimidin-2-yl)-1H-indole (**3al**)

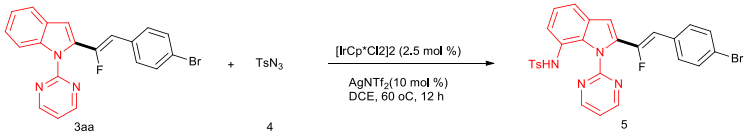
3al was obtained according to the general procedure in 64% yield (42.0mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.1 Hz, 2H), 8.32 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 10.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.13 – 7.02 (m, 2H), 6.95 (s, 1H), 6.21 (d, *J* = 36.4 Hz, 1H), 2.33 (s, 3H). The NMR data agree with those in a literature report.[3] HRMS: $[M + Na]^+$ calculated for $C_{21}H_{16}FN_3Na^+$: 352.1220, found: 352.1230.



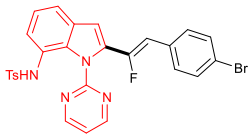
(Z)-2-(1-fluoro-2-(naphthalen-2-yl)vinyl)-1-(pyrimidin-2-yl)-1H-indole (**3am**)

3am was obtained according to the general procedure in 82% yield (59.9mg). white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.4 Hz, 2H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.02 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 3H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 4.4 Hz, 1H), 7.02 (s, 1H), 6.43 (d, *J* = 36.2 Hz, 1H). The NMR data agree with those in a literature report.[3] HRMS: $[M + Na]^+$ calculated for $C_{24}H_{16}FN_3Na^+$: 388.1220, found: 388.1220.

Further Functionalization of 3aa



In a Schlenk tube, substrate **3aa** (98.3mg, 0.25 mmol, 1.0 equiv), sulfonyl azide (98.6 mg, 0.50 mmol, 2.0 equiv), $[IrCp^*Cl_2]_2$ (5.0 mg, 2.5 mol %), $AgNTf_2$ (9.7 mg, 10.0 mol %) and DCE (2 mL) were added. Then the mixture was stirred at 60 °C (oil temperature) for 12 h under Ar atmosphere. After cooled to room temperature, the reaction mixture was diluted with EtOAc (20 mL) and the organic layer was washed by water (10 mL), dried over Na_2SO_4 and filtered through a plug of celite. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **5**.[5]



(Z)-N-(2-(2-(4-bromophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1H-indol-7-yl)-4-methylbenzenesulfonamide (**5**)

5 was obtained according to the general procedure in 70% yield (98.4mg). white solid, mp 155.2-157.3°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 8.80 (d, *J* = 4.9 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 4.9 Hz, 6H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 3H), 6.10 (d, *J* = 36.2 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.35, 156.98, 143.34, 138.93 – 136.64, 132.31 (d, *J* = 24.9 Hz), 131.98 (d, *J* = 73.1 Hz), 130.87, 130.24 (d, *J* = 7.8 Hz), 129.62, 129.28, 126.48, 124.28, 123.34, 121.02, 118.89, 118.25, 112.00, 108.22 (d, *J* = 10.2 Hz), 99.99, 21.45. ^{19}F NMR (565 MHz, $CDCl_3$) δ -101.31 (d, *J* = 36.2 Hz). HRMS: $[M + Na]^+$ calculated for $C_{27}H_{20}BrFN_4O_2S\ Na^+$: 585.0367, found: 585.0369.

2. References

(1) a) L. Ackermann and A. V. Lygin, *Org. Lett.* **2011**, *13*, 3332. (b) M. Nishino, K. Hirano, Satoh and M. Miura, *Angew. Chem.* **2012**, *124*, 7099.

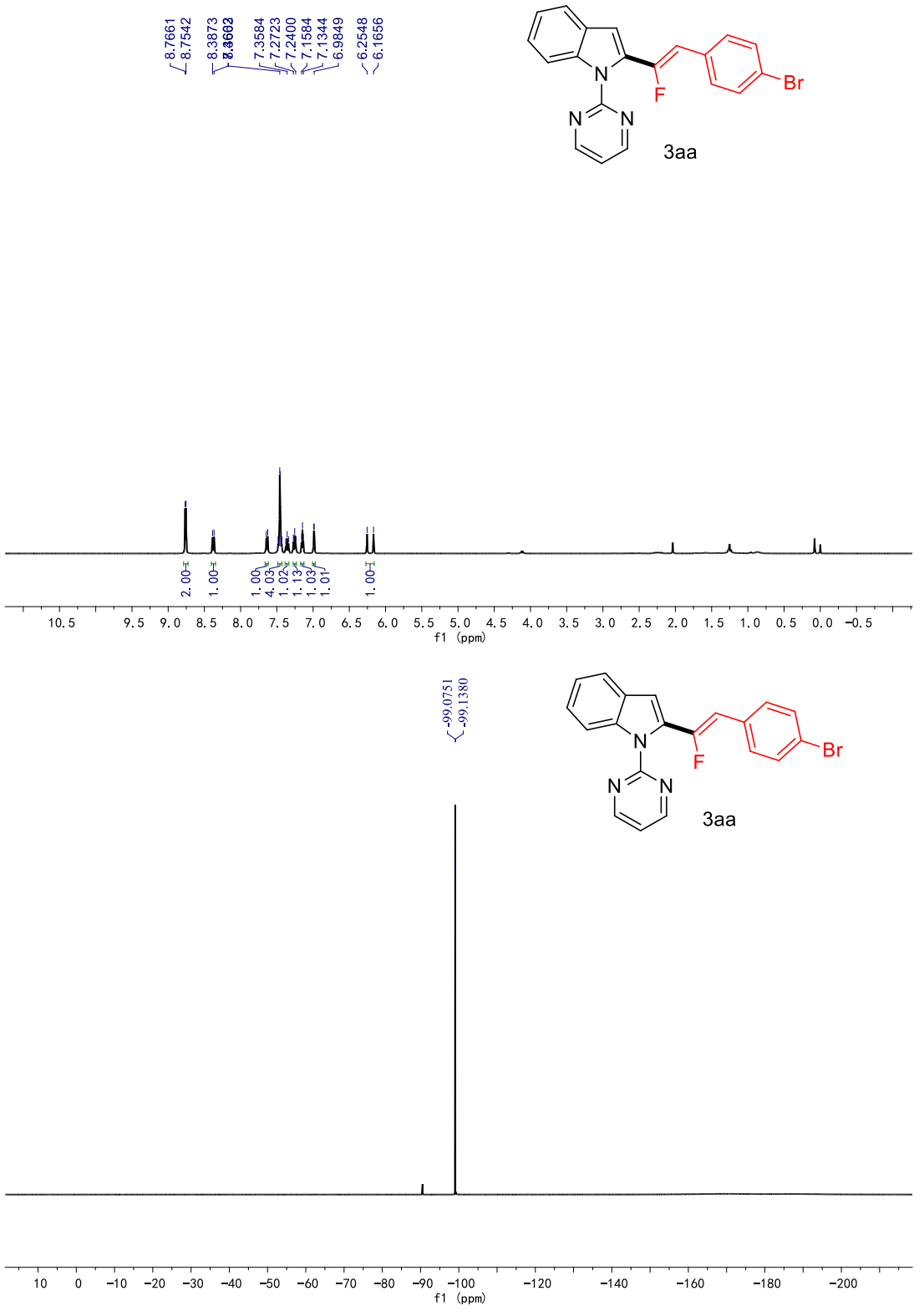
(2) C. S. Thomoson, H. Martinez, and W. R. Dolbier Jr. *J. Fluorine Chem.* **2013**, *150*, 53.

(3) P. Tian, C. Feng and T.-P. Loh, *Nat. Commun*. **2015**, *6*, 7472.

(4) L.H. Kong, X.K. Zhou and X.W. Li, *Org. Lett.* **2016**, *18*, 6320.

(5) T. Okada, K. Nobushige, T. Satoh and M. Miura, *Org. Lett.* **2016**, *18*, 1150.

4. NMR Spectra




8.6984
8.6984
8.4521
7.6210
7.4756
7.3816
7.2721
7.2604
7.2229
7.0523
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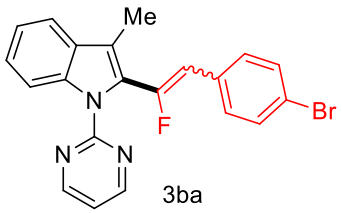
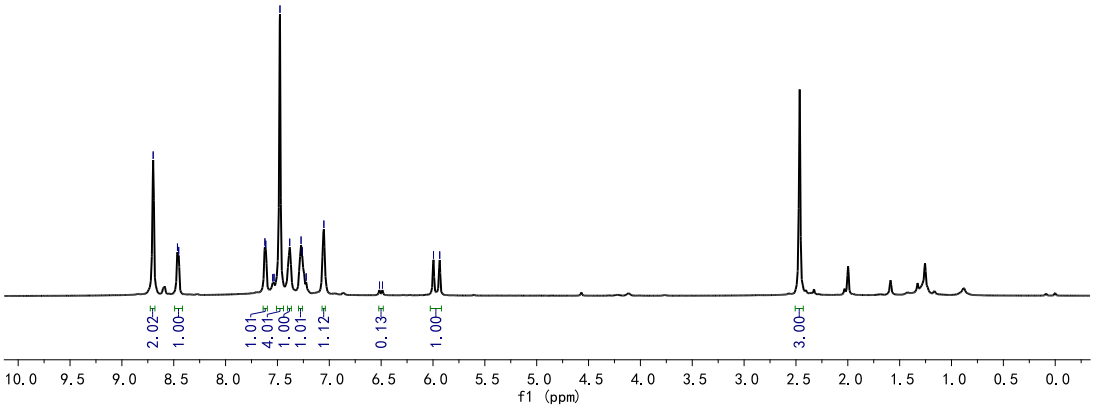
6.4872
5.9951
5.9951
5.9351
5.9351


Me
N
F
Br
N
N

3ba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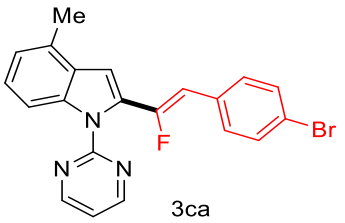
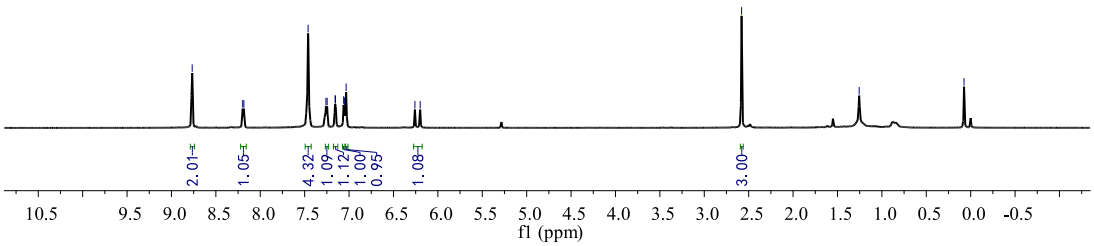
1.00
1.01
4.01
1.00
1.01
1.12
0.13
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.7665
8.1982
8.1846
7.4617
7.4612
7.0614
7.0502
7.0330
6.2584
6.1990


2.5798
1.2555
0.0748


Me
N
F
Br
N
N

3ca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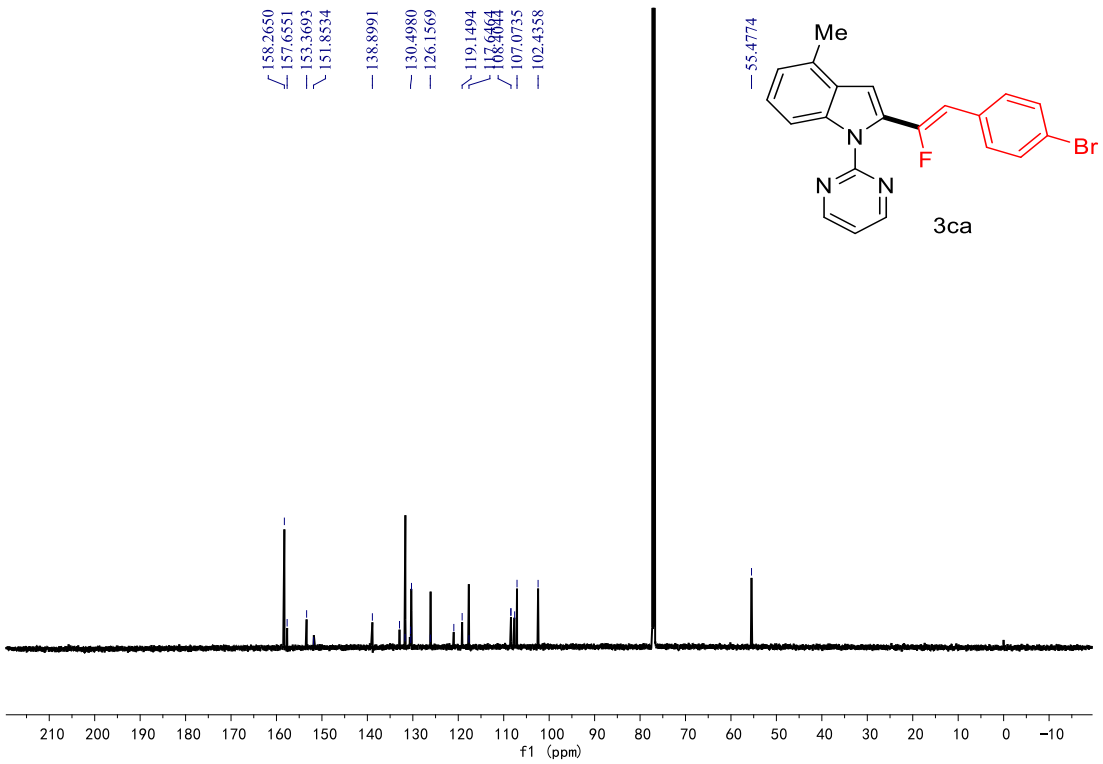
1.05
4.32
1.09
1.12
1.00
0.95
1.08
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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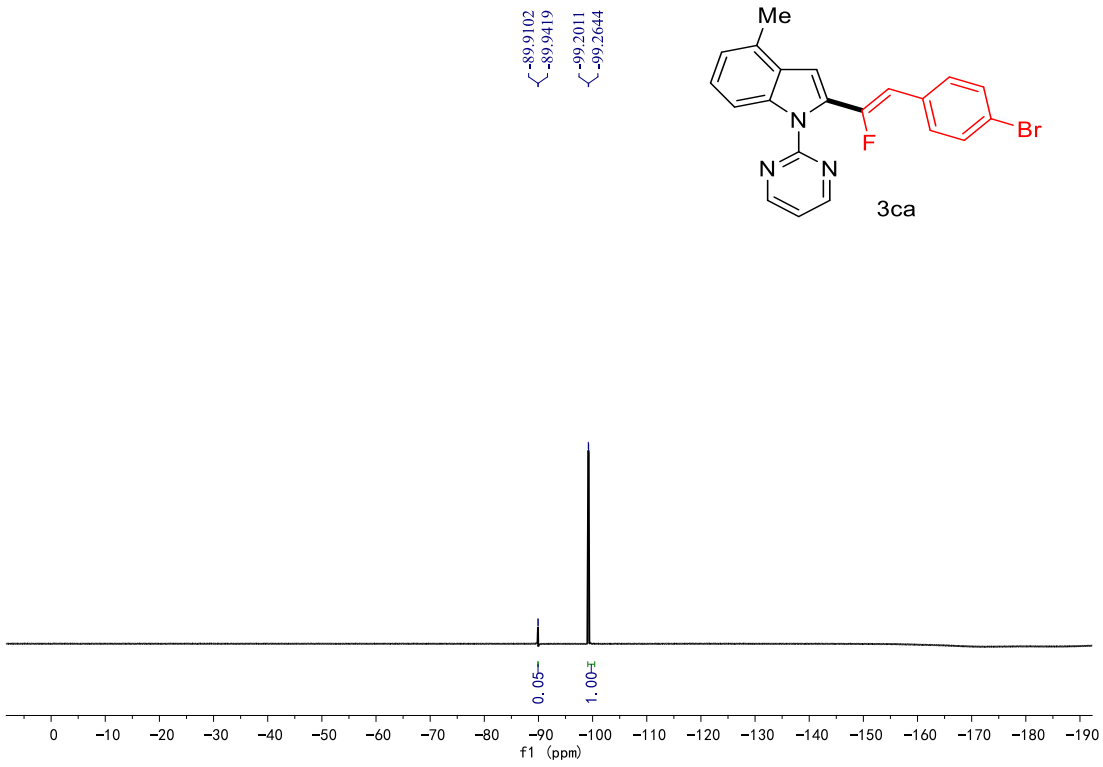
153.3693
151.8534
138.8991
130.4980
126.1569
119.1494
108.4044
107.0735
102.4358
55.4774
Me
N
F
Br
N
N
3ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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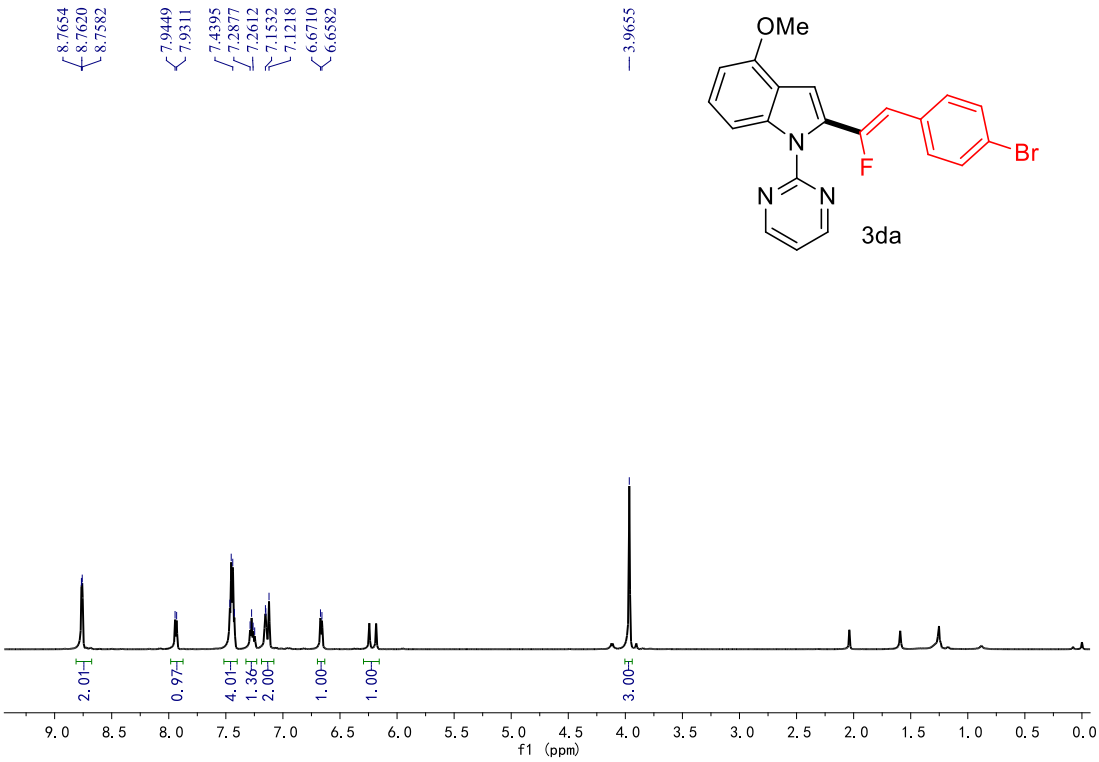
-89.9419
-99.2011
-99.2644
Me
N
F
Br
N
N
3ca
0.05
1.00
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)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7.2877
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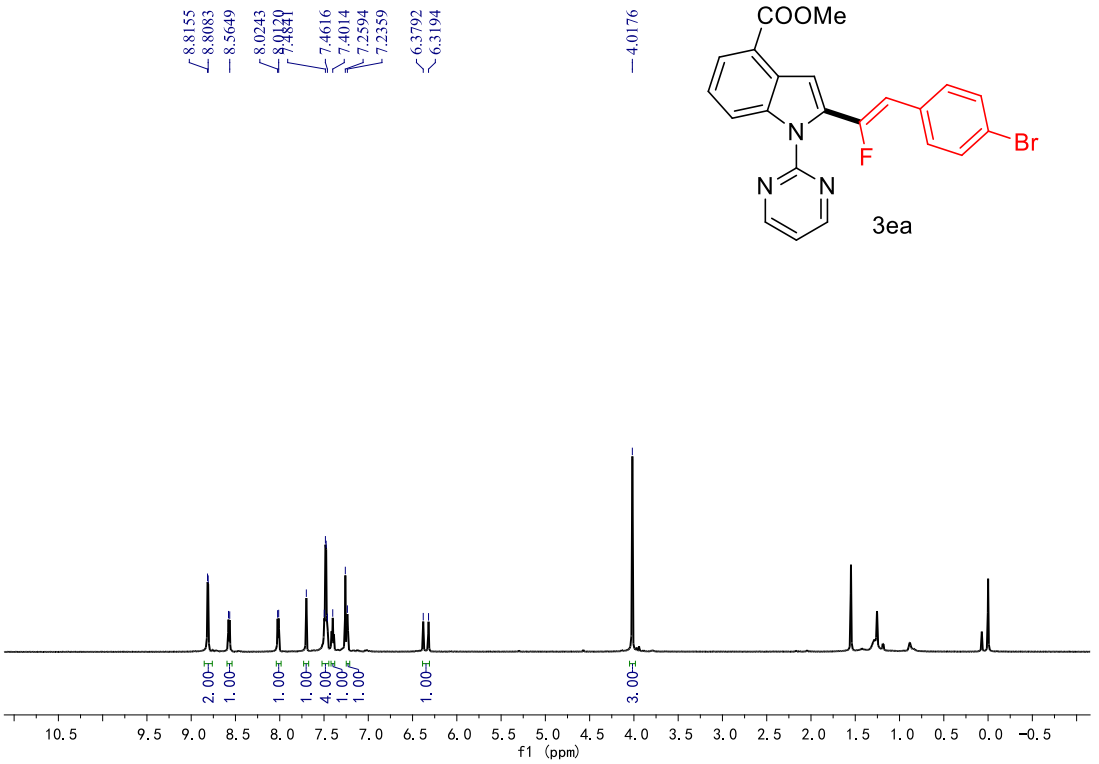
7.1532
7.1218
6.6710
6.6582
3.9655
OMe
N
F
Br
N
N
3da
2.01
0.97
4.01
1.36
2.00
1.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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8.0243
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7.4616
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6.3792
6.3194
4.0176
COOMe
N
F
Br
N
N
3ea
2.00
1.00
1.00
1.00
4.00
1.00
1.00
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


8.7973
8.7916
8.1425
8.1291
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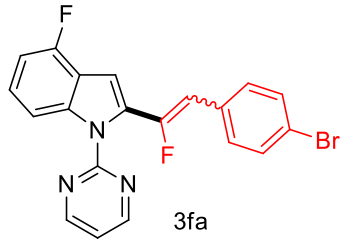
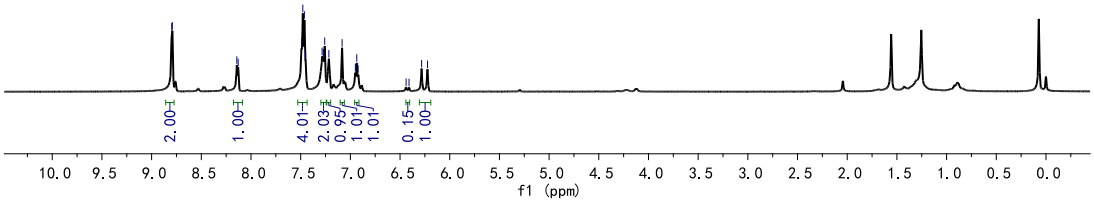
7.2715
7.2164
6.9497
6.9218
6.4390
6.4096
6.2831
6.2238


F
N
F
Br
N
N
3fa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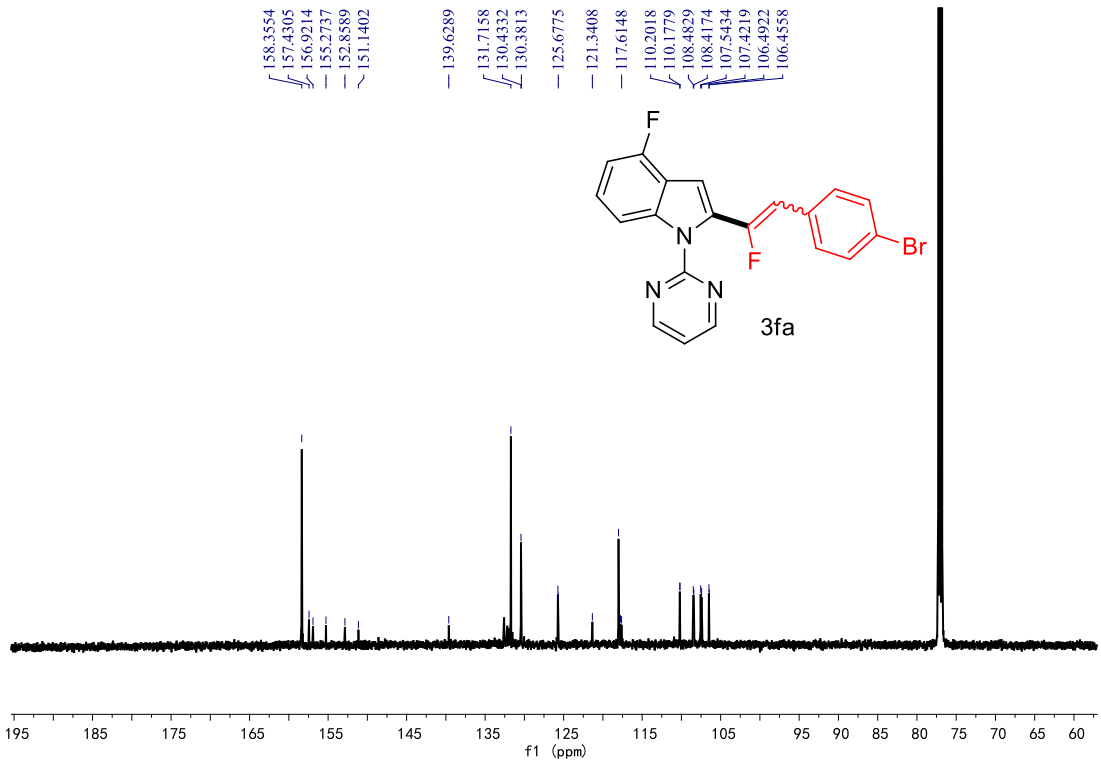
1.01
1.01
0.15
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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121.3408
117.6148
110.2018
110.1779
108.4829
108.4174
107.5434
107.4219
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F
N
F
Br
N
N
3fa
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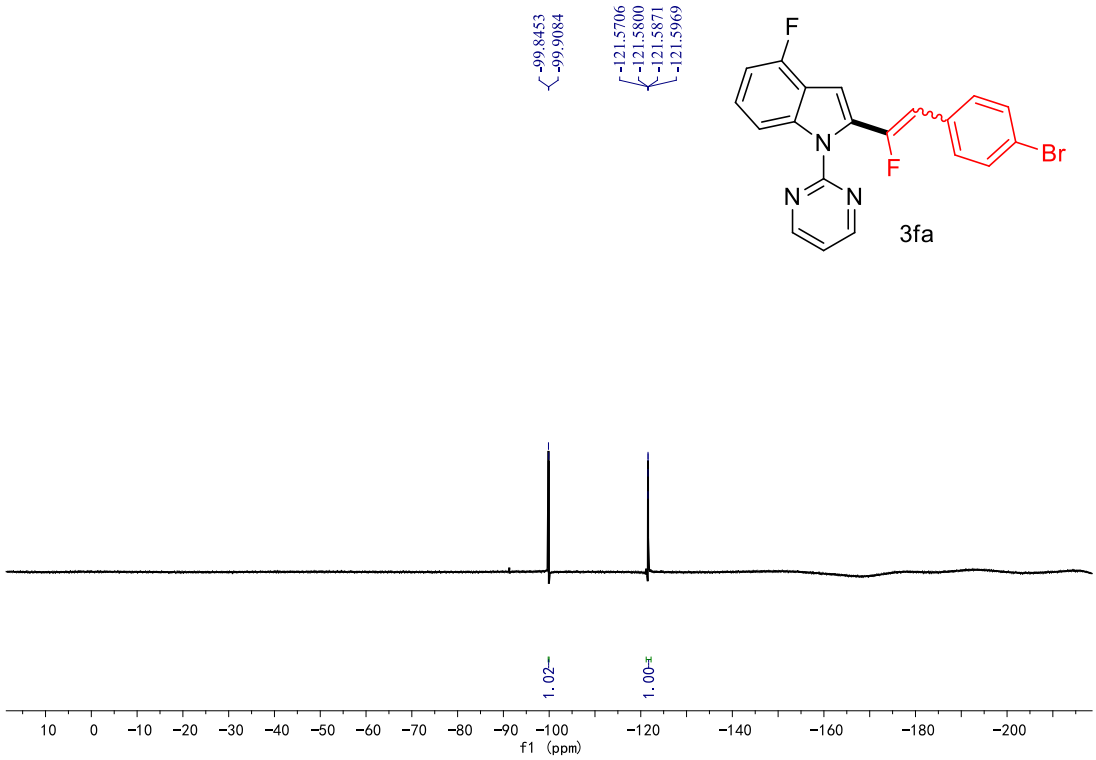
f1 (ppm)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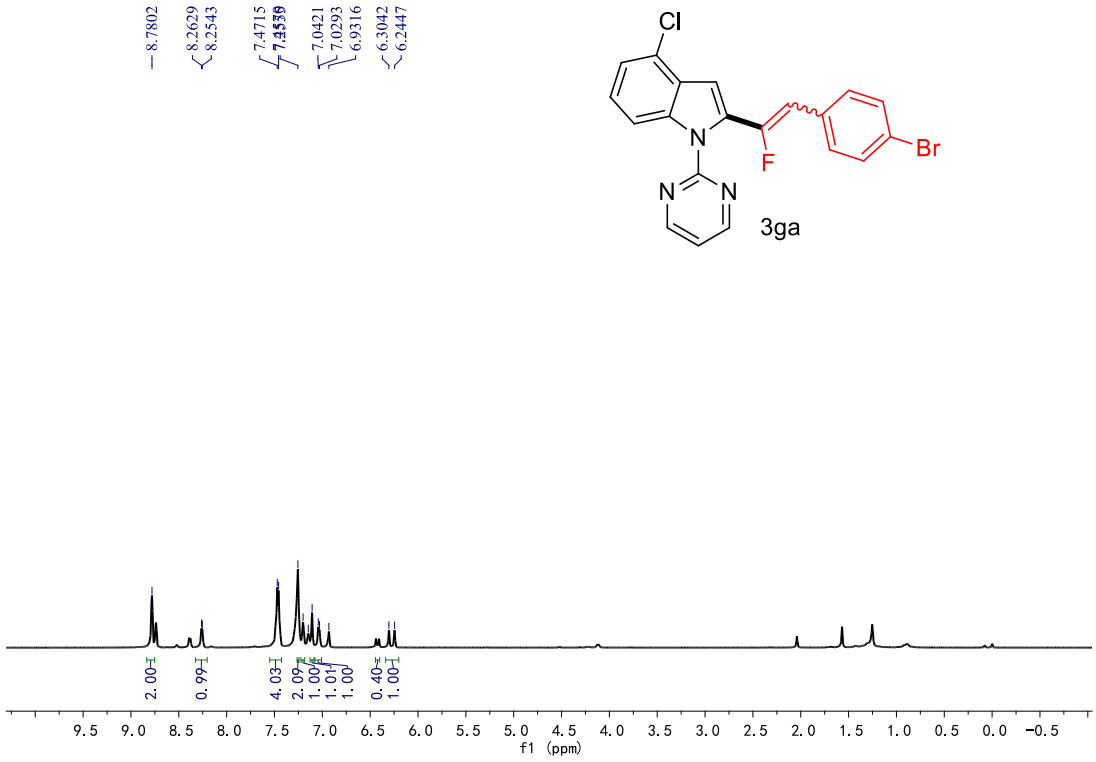
-121.5706
-121.5800
-121.5871
-121.5969
F
N
F
Br
N
N
3fa
1.02
1.00
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)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Cl
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F
Br
N
N
3ga
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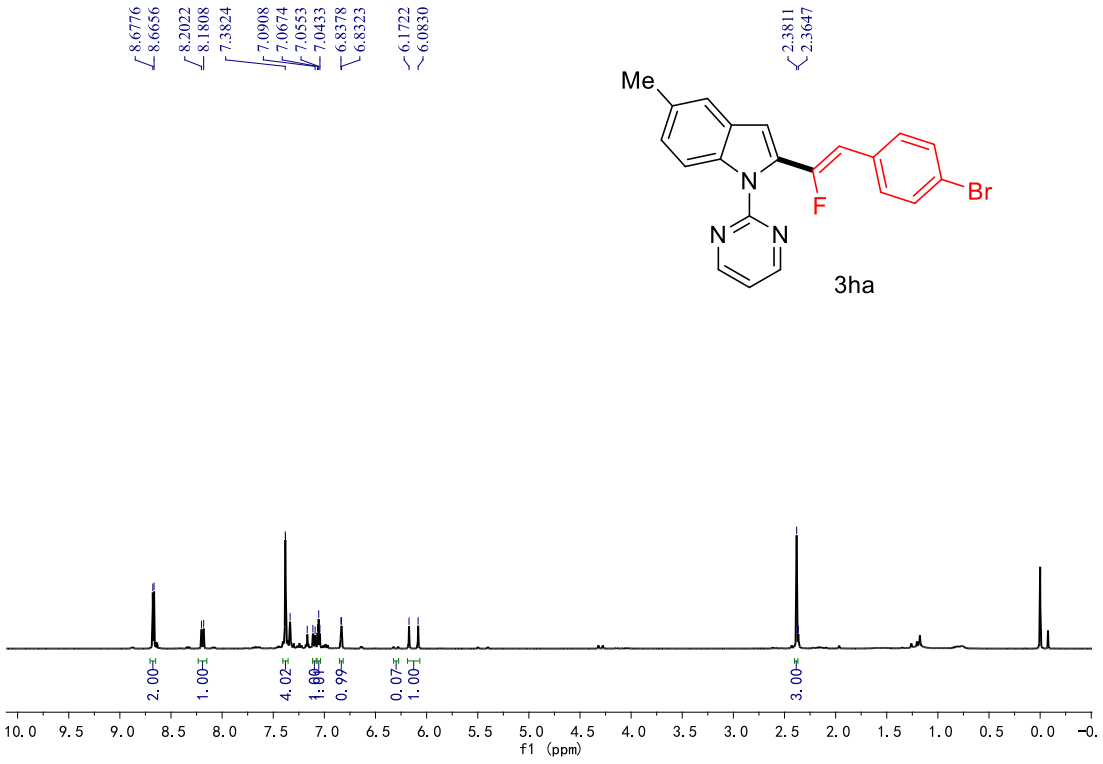
0.99
4.03
2.09
1.00
1.01
1.00
0.40
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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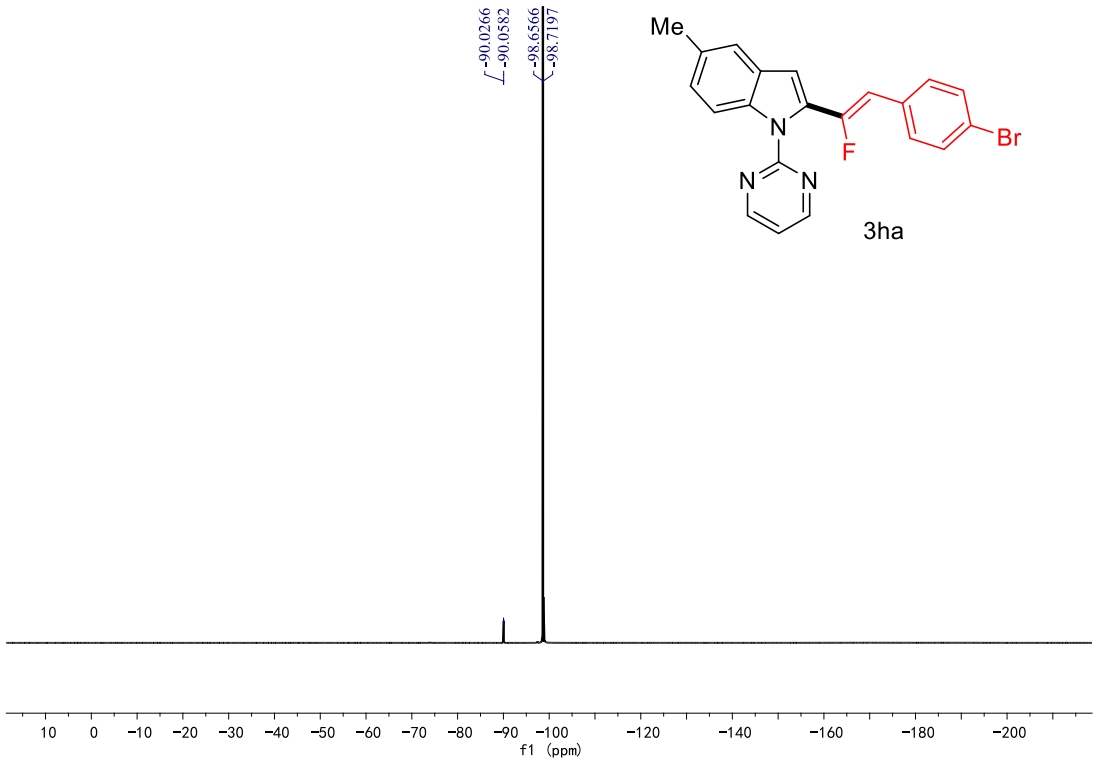
6.1722
6.0830
2.3811
2.3647
Me
N
F
Br
N
N
3ha
2.00
1.00
4.02
0.99
0.07
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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Br
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N
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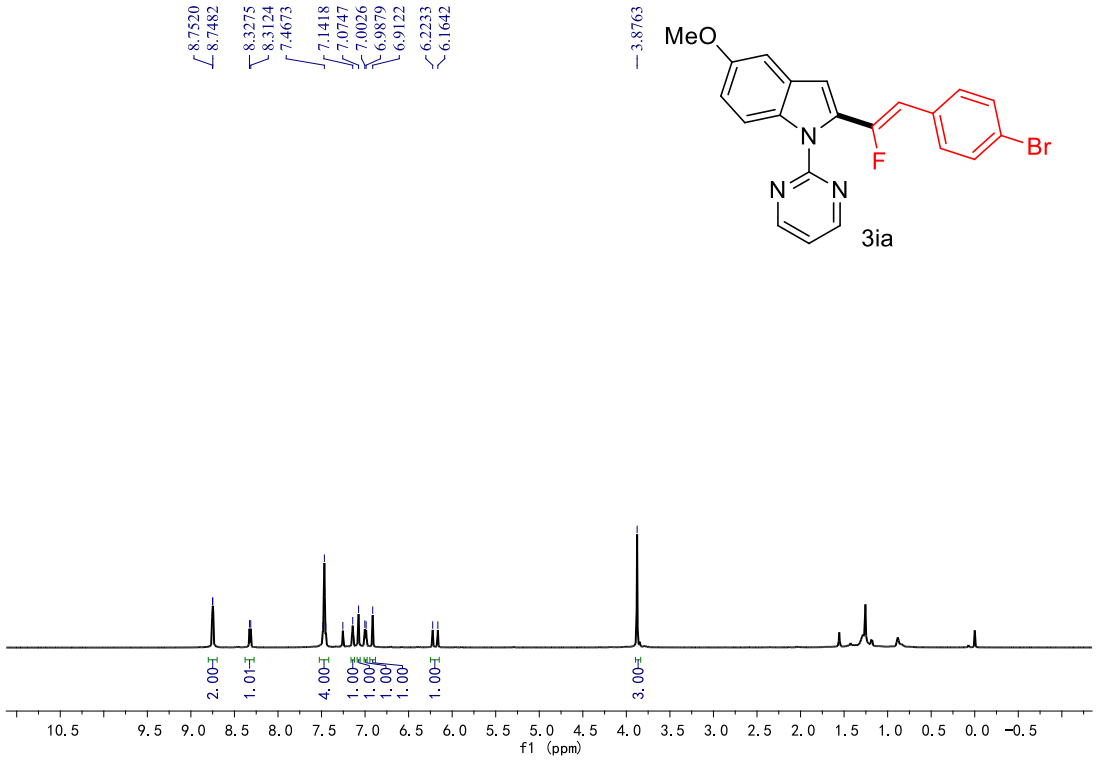
f1 (ppm)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6.2233
6.1642
3.8763
MeO
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F
Br
N
N
3ia
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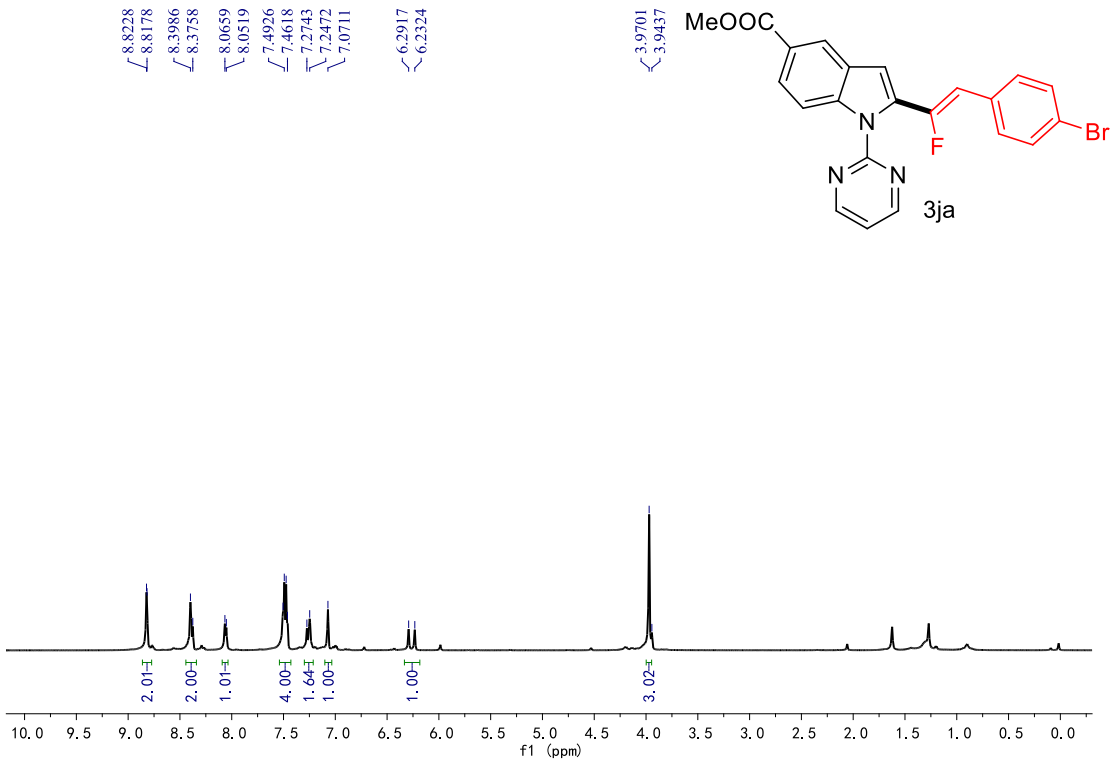
1.01
4.00
1.00
1.00
1.00
1.00
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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7.4926
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7.2743
7.2472
7.0711
6.2917
6.2324
3.9701
3.9437
MeOOC
N
F
Br
N
N
3ja
2.01
2.00
1.01
4.00
1.64
1.00
1.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.7813
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8.7539
8.7461
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7.1929
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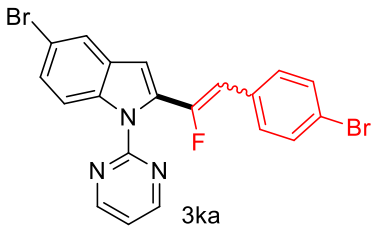
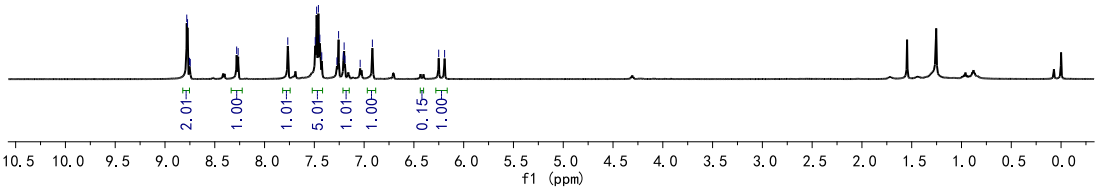
6.1915


Br
N
F
Br
N
N
3ka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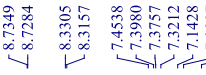
1.00
1.01
5.01
1.01
1.00
0.15
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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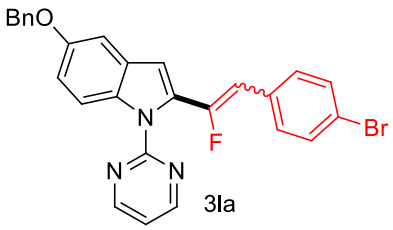
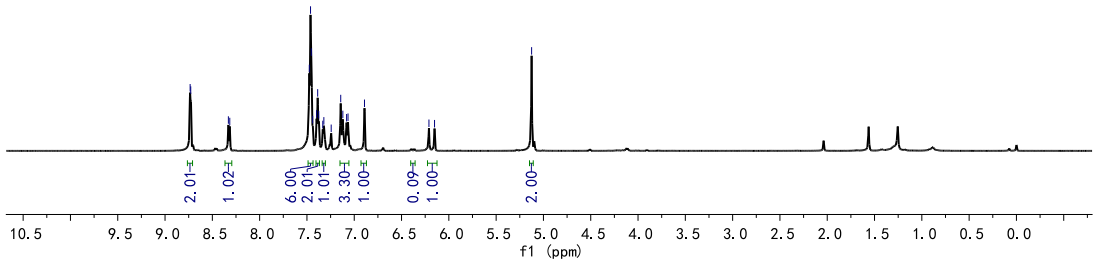
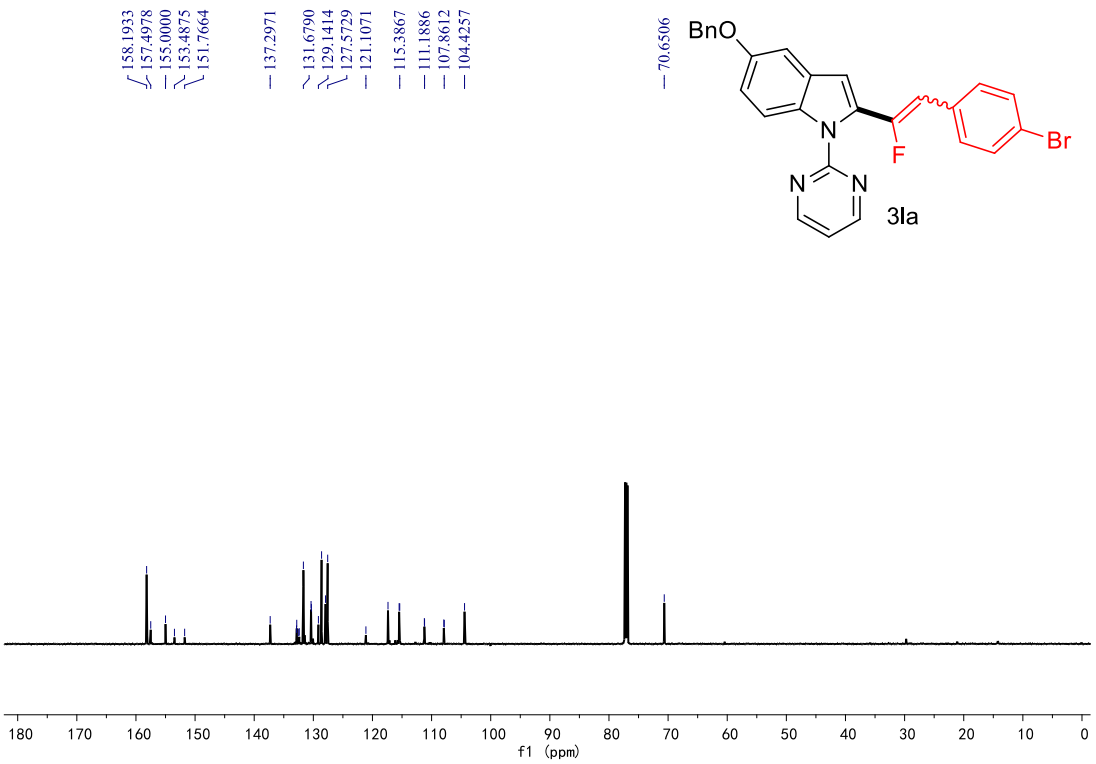
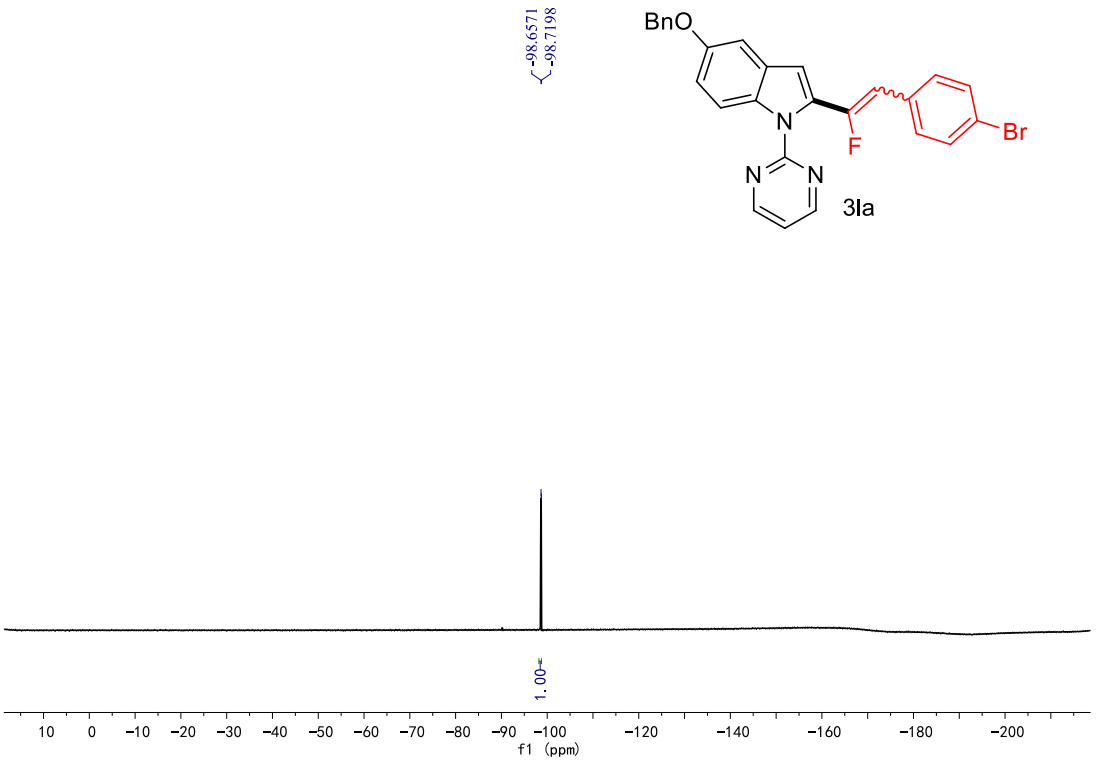
6.1512
5.1249

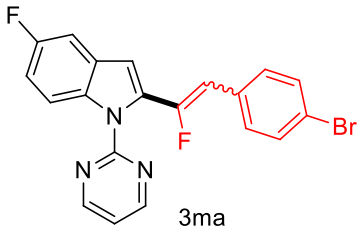

BnO
N
F
Br
N
N
3la


2.01
1.02
6.00
2.01
1.01
3.30
1.00
0.09
1.00
2.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

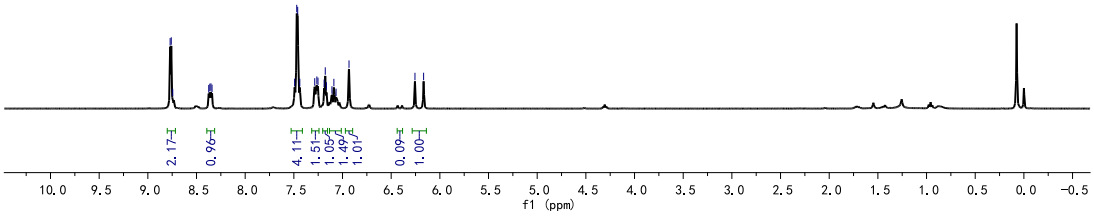

158.1933
157.4978
155.0000
153.4875
151.7664
137.2971
131.6790
129.1414
127.5729
121.1071
115.3867
111.1886
107.8612
104.4257
70.6506
BnO
N
F
Br
N
N
3la
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-98.6571
-98.7198
BnO
N
F
Br
N
N
3la
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

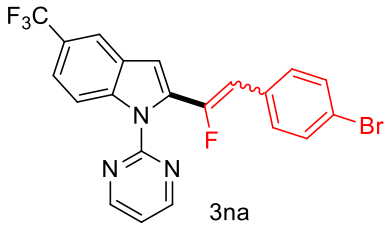
8.7710
8.7592
8.7445
8.3632
8.3518
8.3406
7.4705
7.4387
7.2638
7.1889
7.1655
7.0887
6.9332
6.2557
6.1668



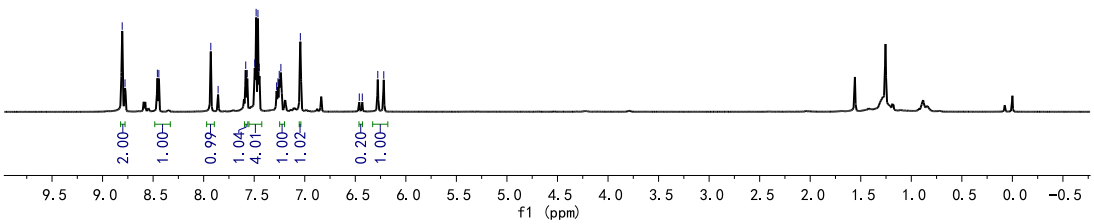
3ma

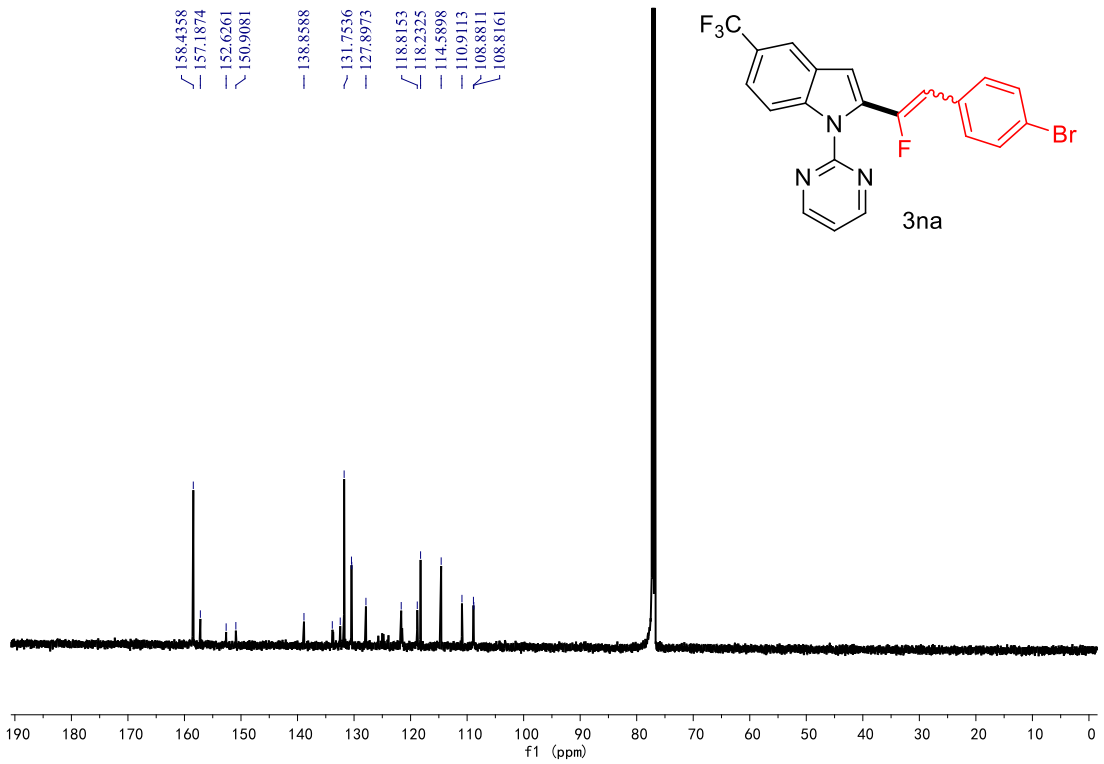


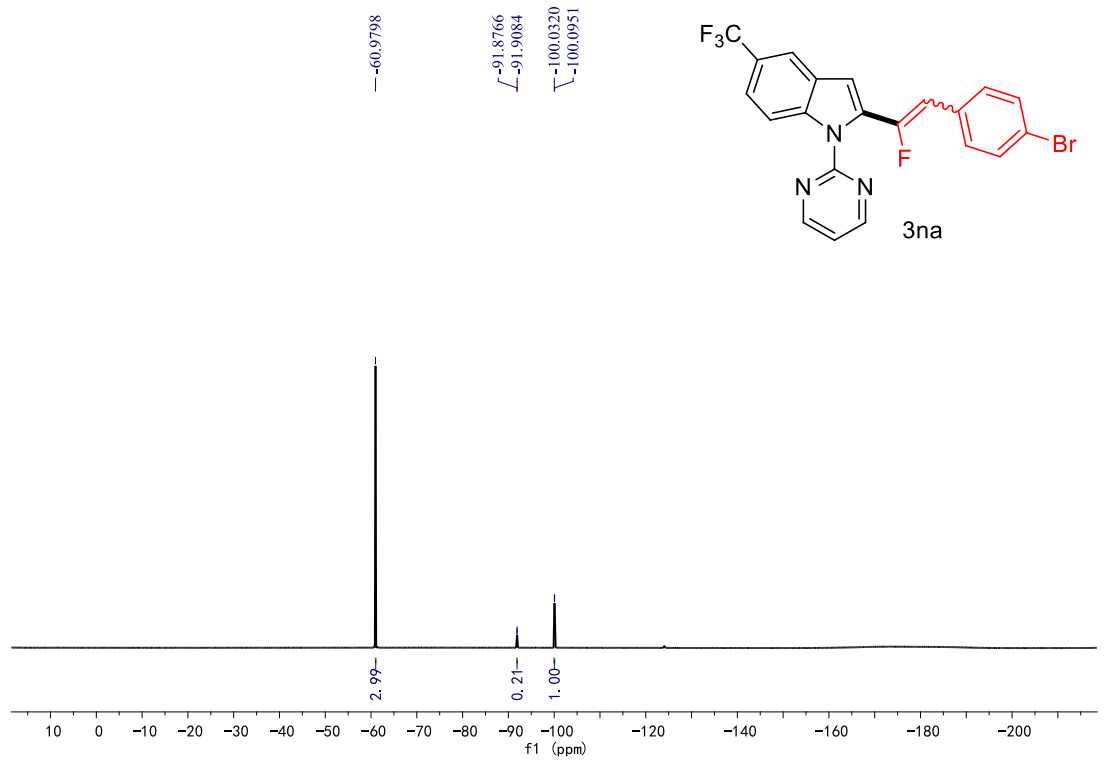
8.8058
8.7780
8.4578
8.4432
7.9292
7.8571
7.4630
7.2360
7.0435
6.4606
6.4307
6.2776
6.2183

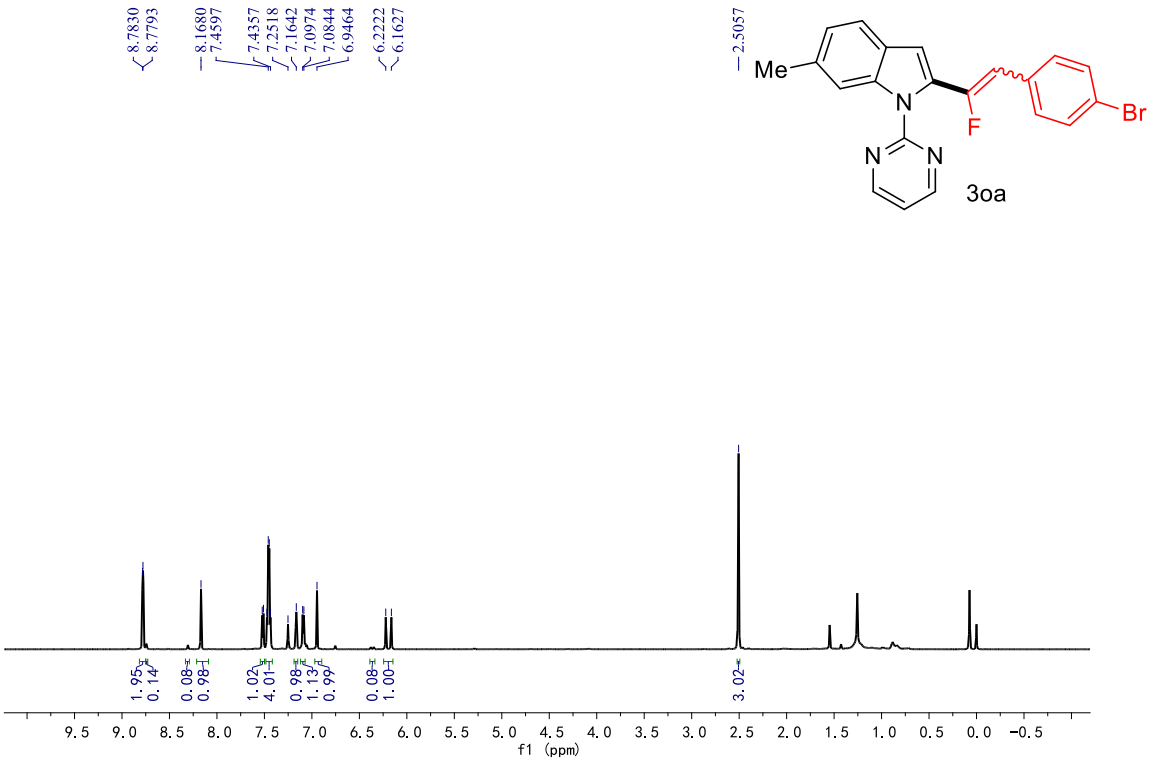


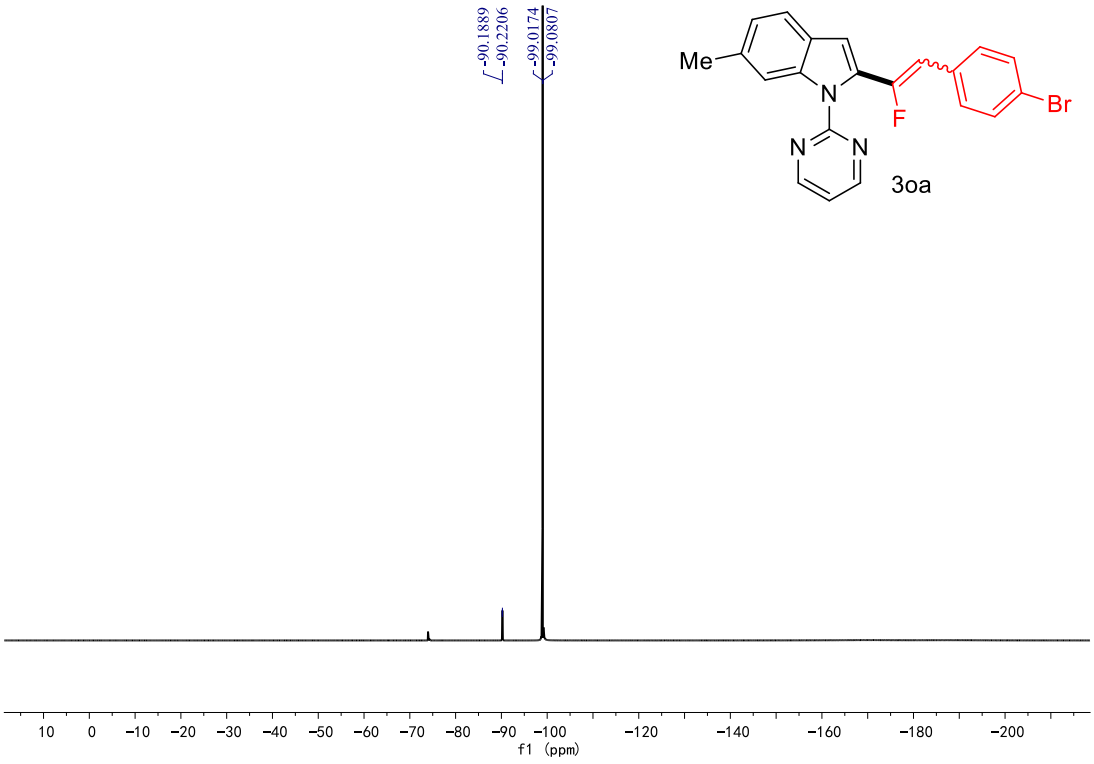
3na

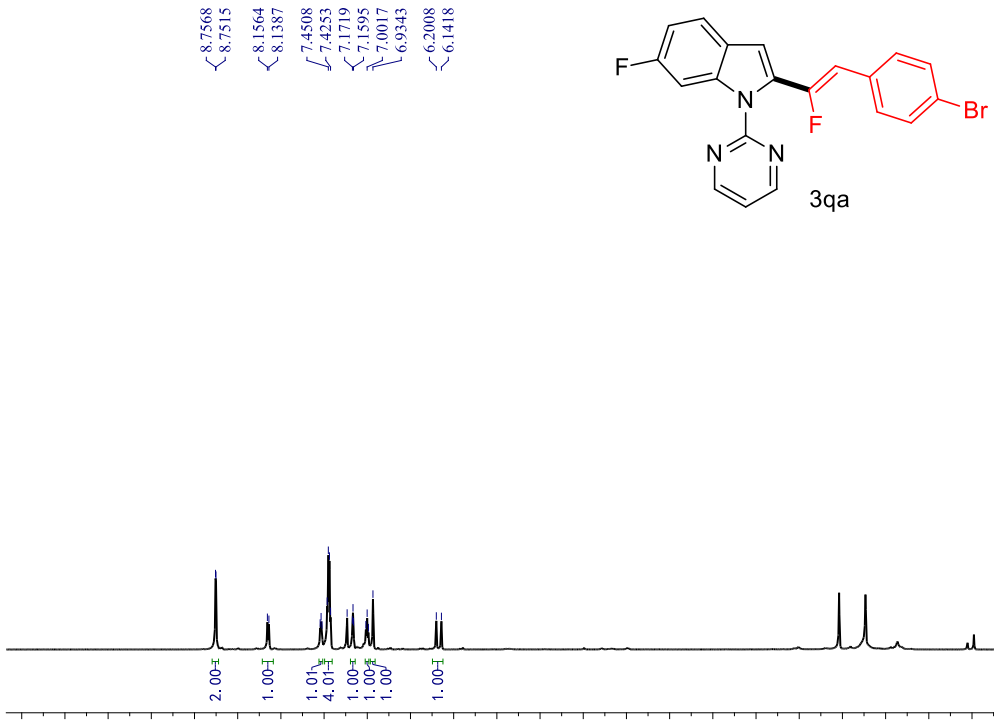


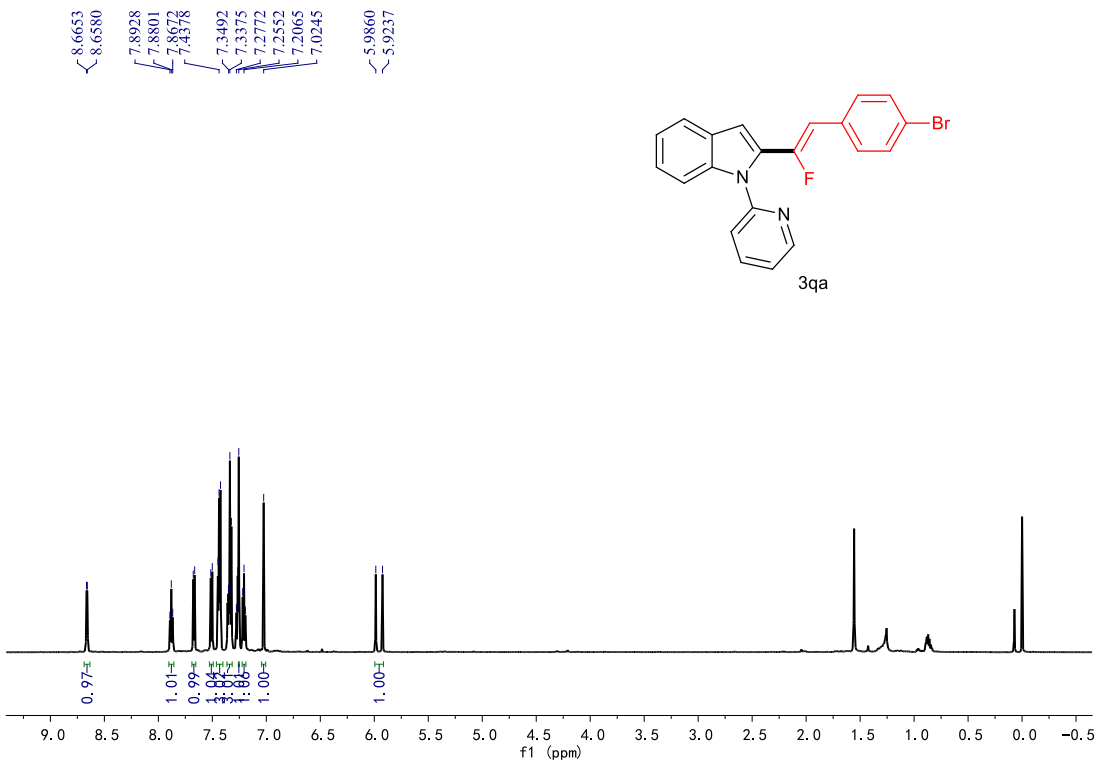

158.4358
157.1874
152.6261
150.9081
138.8588
131.7536
127.8973
118.8153
118.2325
114.5898
110.9113
108.8811
108.8161
F3C
N
N
N
F
Br
3na
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

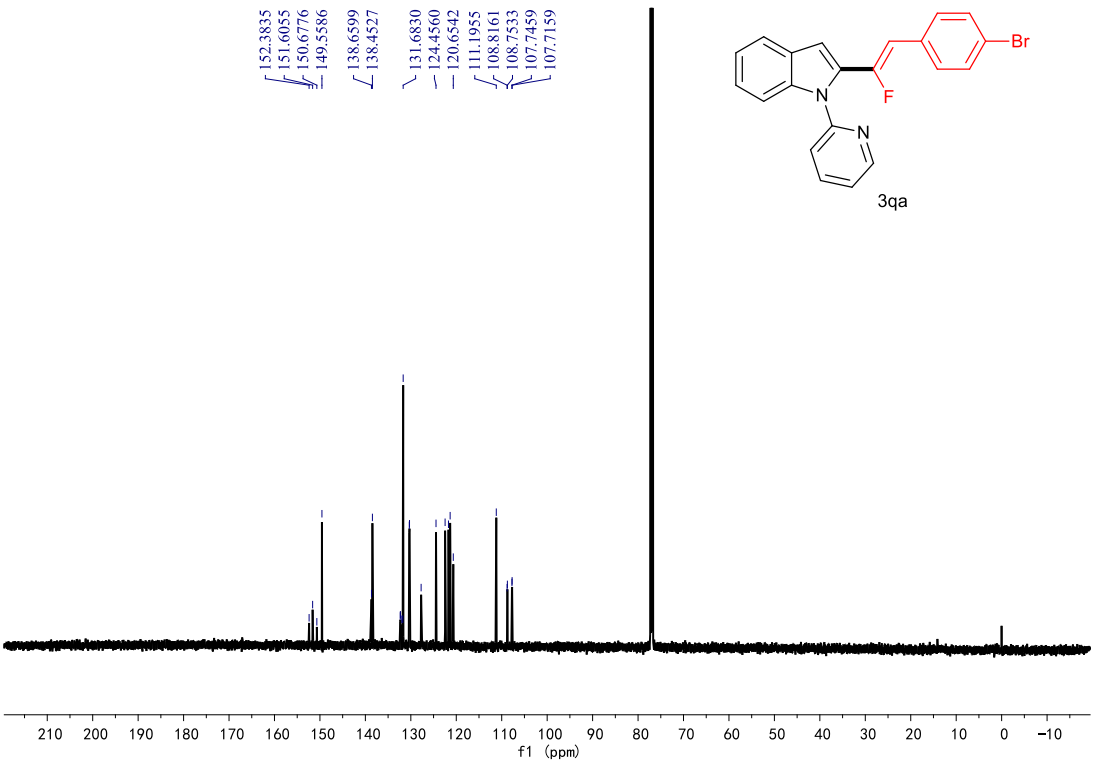

-60.9798
-91.8766
-91.9084
-100.0320
-100.0951
F3C
N
N
N
F
Br
3na
2.99
0.21
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

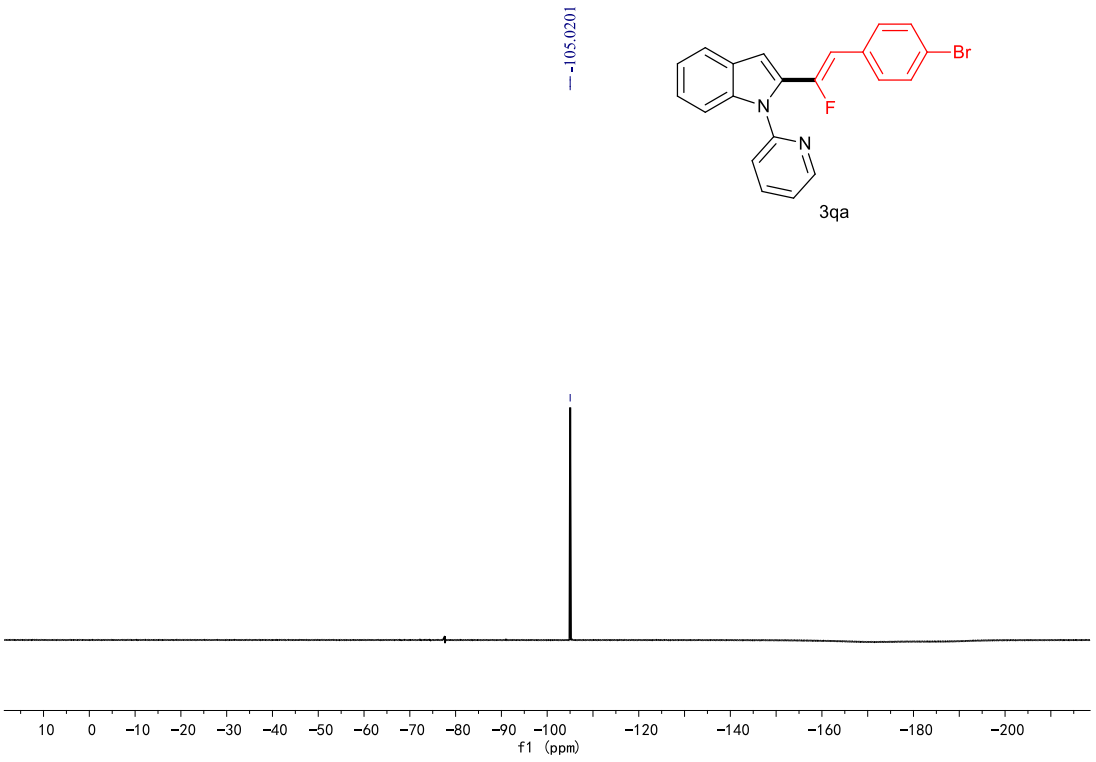

8.7830
8.7793
8.1680
7.4597
7.4357
7.2518
7.1642
7.0974
7.0844
6.9464
6.2222
6.1627
2.5057
Me
N
F
Br
N
N
3oa
1.95
0.14
0.08
0.98
1.02
4.01
0.98
1.13
0.99
0.08
1.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


-90.1889
-90.2206
-99.0174
-99.0807
Me
N
F
Br
N
N
3oa
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)

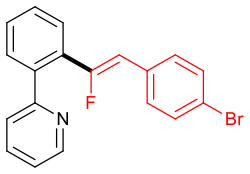

8.7568
8.7515
8.1564
8.1387
7.4508
7.4253
7.1719
7.1595
7.0017
6.9343
6.2008
6.1418
F
N
F
Br
N
N
3qa
2.00
1.00
1.01
4.01
1.00
1.00
1.00
f1 (ppm)


8.6653
8.6580
7.8928
7.8801
7.8672
7.4378
7.3492
7.3375
7.2772
7.2552
7.2065
7.0245
5.9860
5.9237
Br
F
N
N
3qa
0.97
1.01
0.99
1.00
1.00
f1 (ppm)

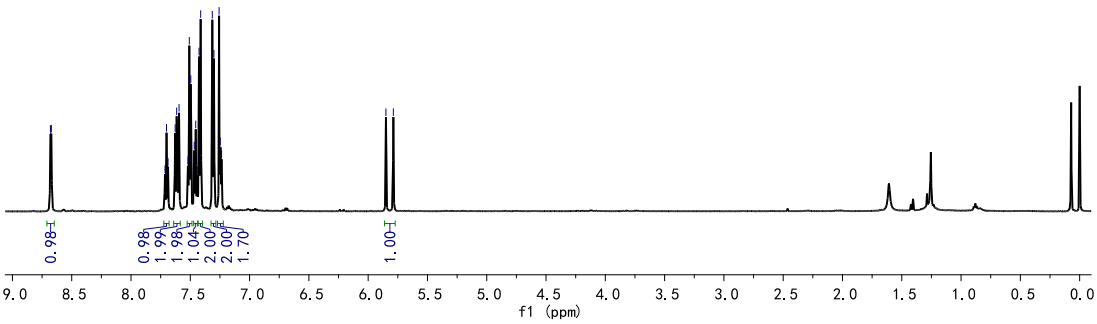

152.3835
151.6055
150.6776
149.5586
138.6599
138.4527
131.6830
124.4560
120.6542
111.1955
108.8161
108.7533
107.7459
107.7159
Br
F
N
N
3qa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-105.0201
Br
F
N
N
3qa
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)

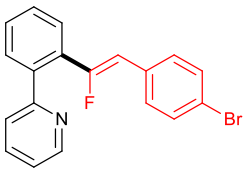

8.6795
8.6718
7.5083
7.4668
7.4542
7.4416
7.4263
7.4125
7.3144
7.3005
7.2572
7.2475
7.2360
5.8502
5.7875


F
N
Br

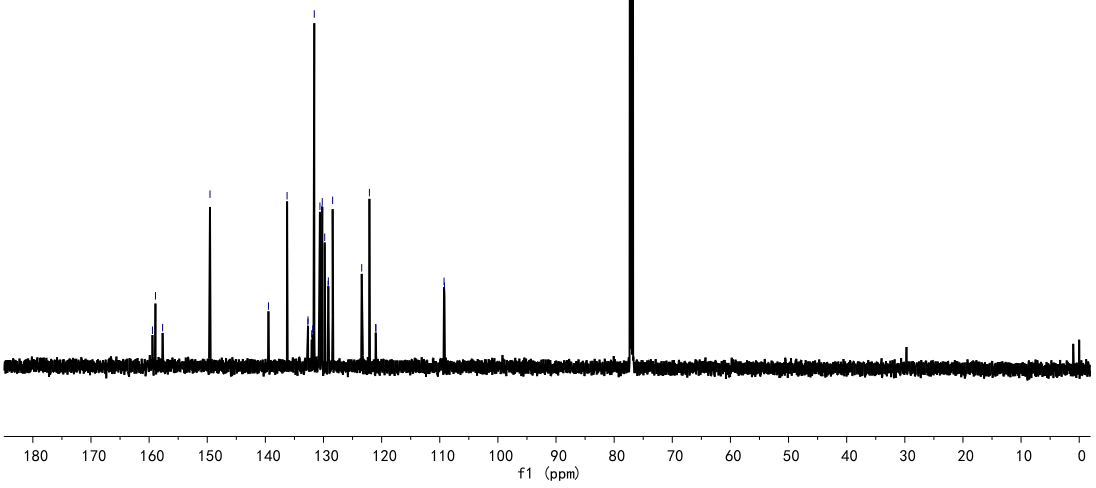
3ra

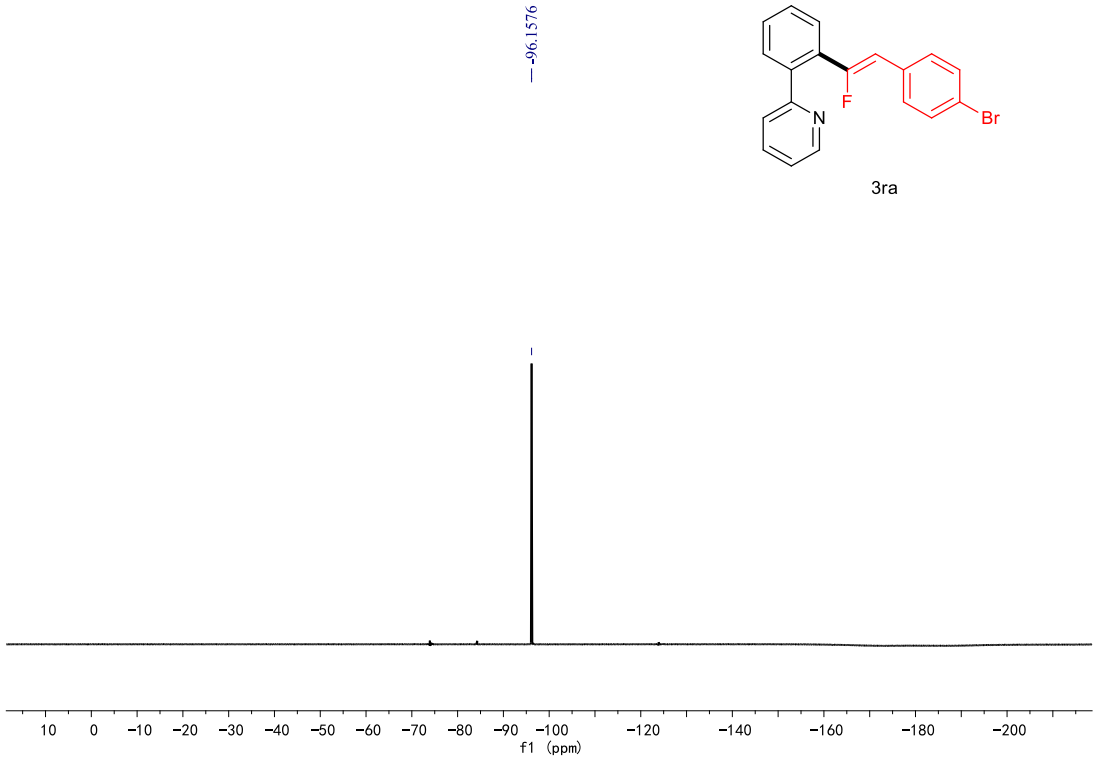

0.98
0.98
1.99
1.98
1.04
2.00
2.00
1.70
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.4256
158.9063
157.6767
149.5266
139.4693
136.2665
130.6149
128.4270
122.1039
121.0134
120.9908
109.2630
109.1964

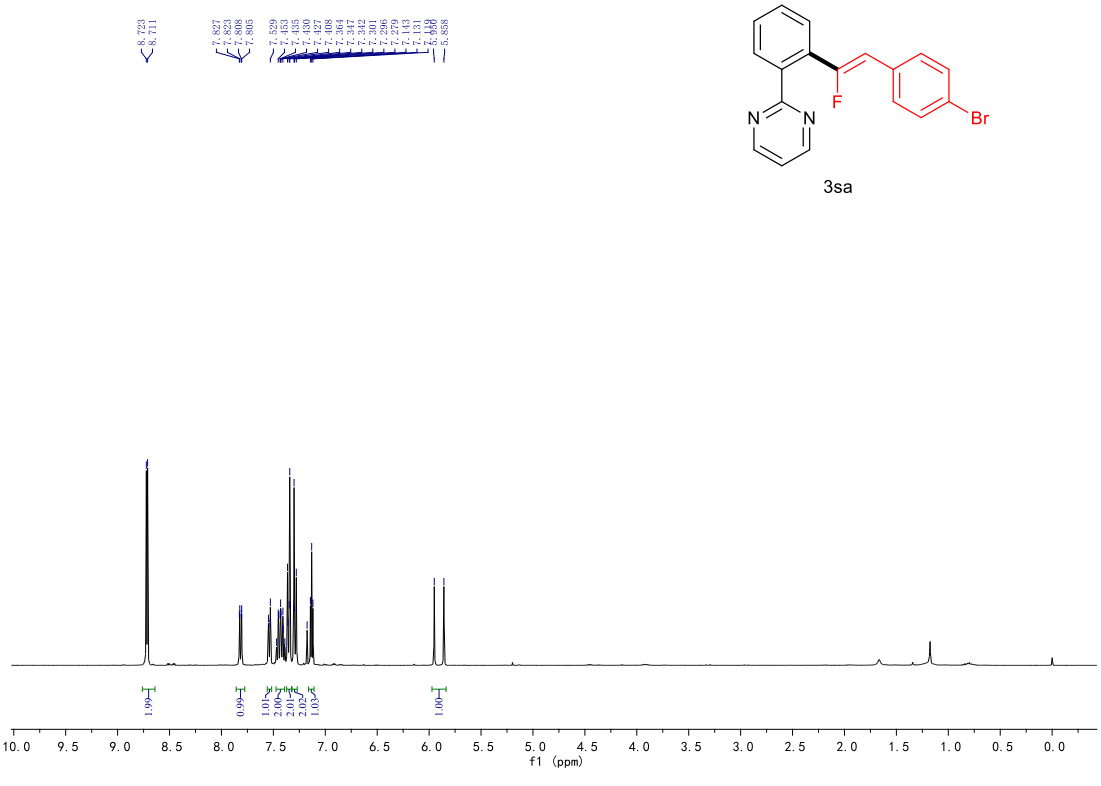

F
N
Br

3ra

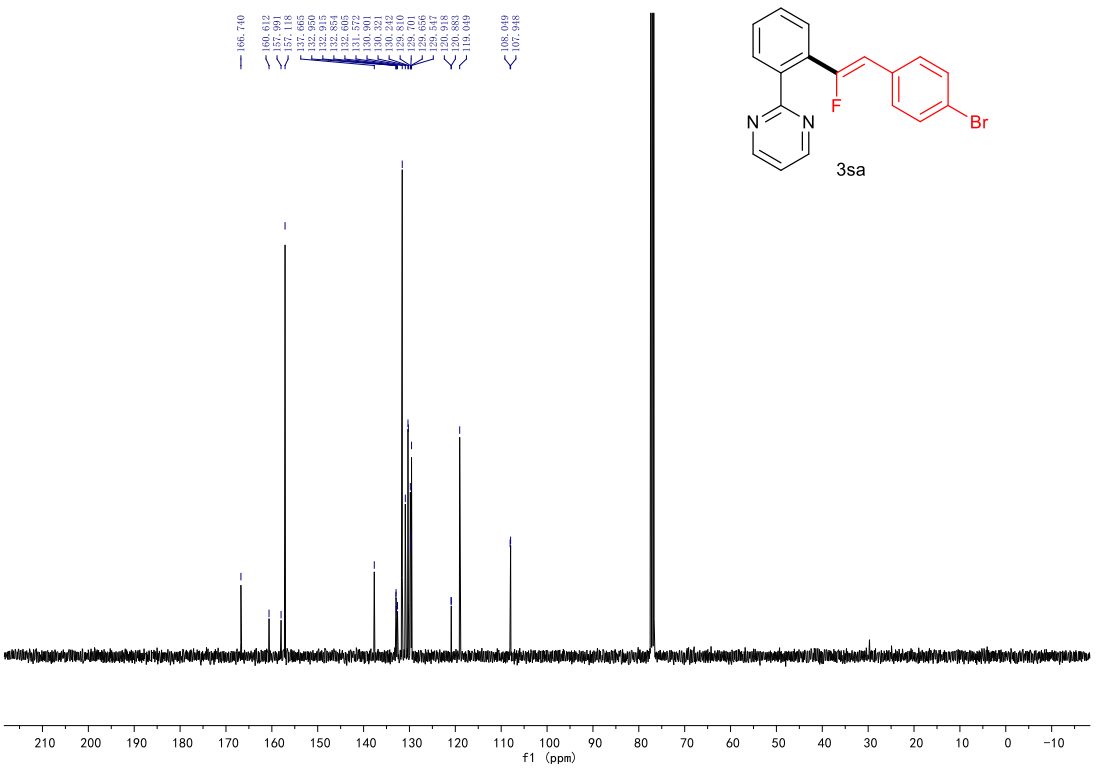

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

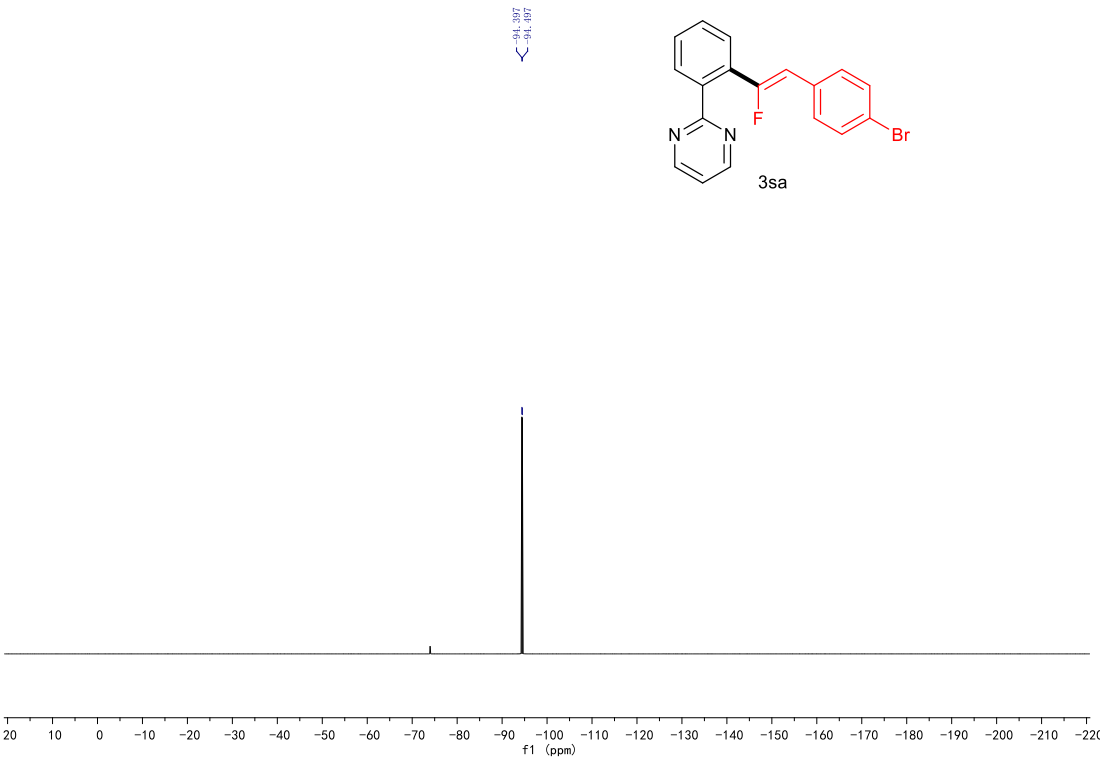

-96.1576
F
N
Br
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)

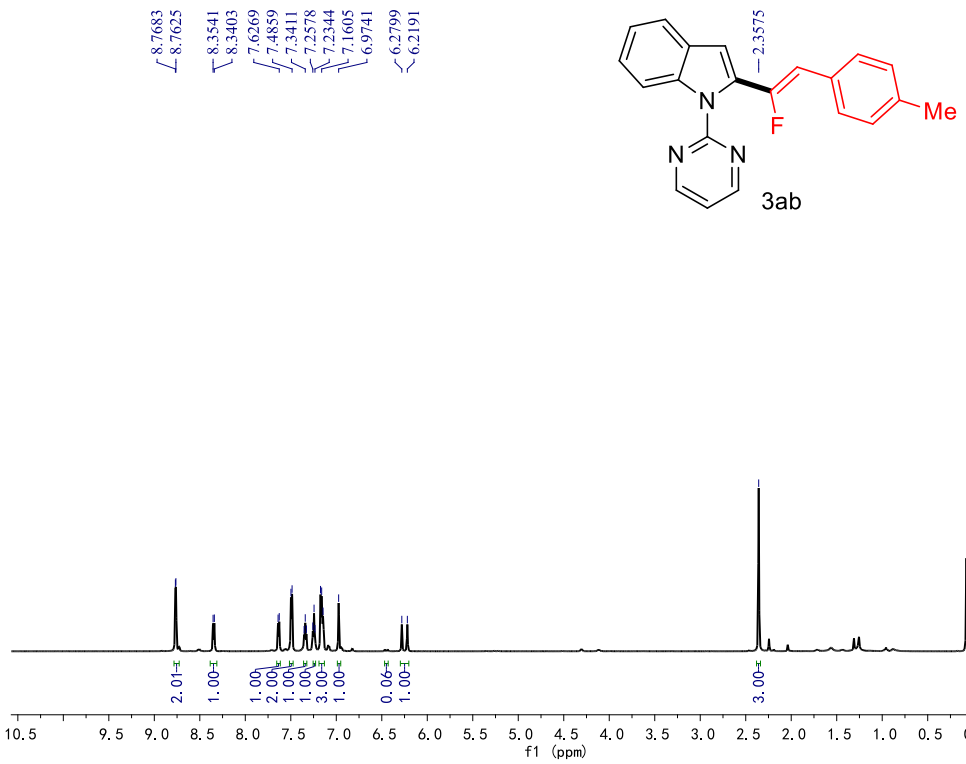
3ra

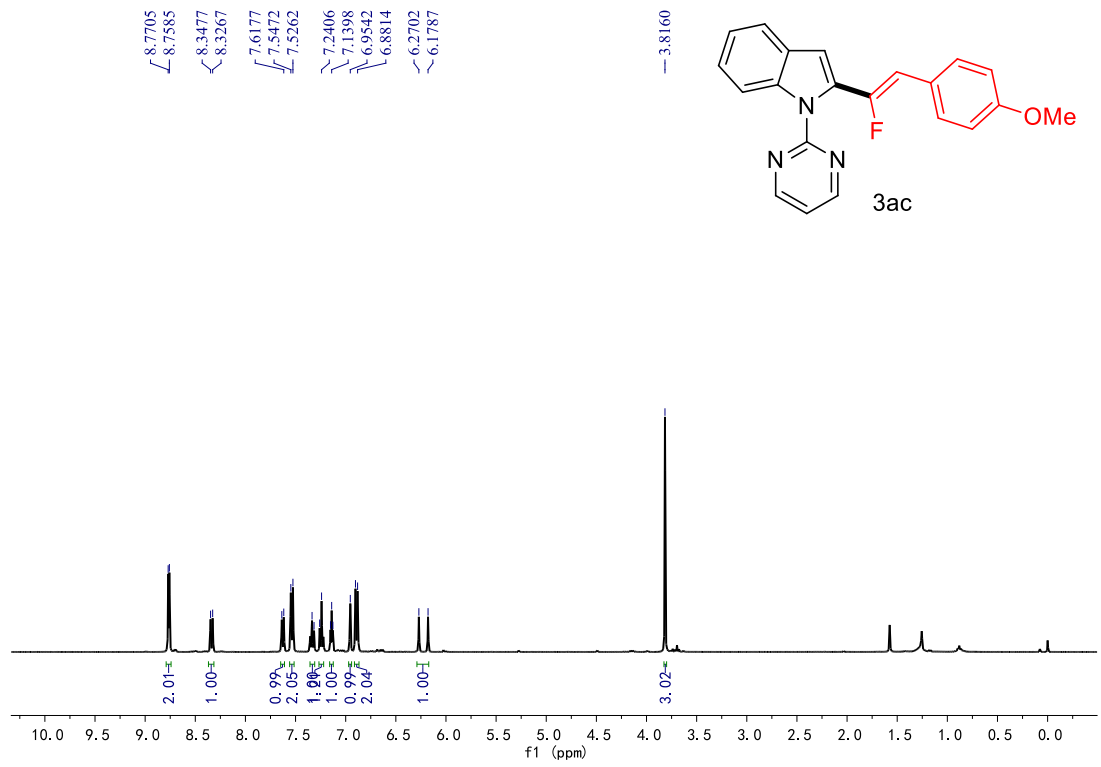

8.723
8.711
7.827
7.823
7.808
7.805
7.529
7.453
7.435
7.409
7.427
7.408
7.364
7.347
7.342
7.301
7.296
7.279
7.133
7.131
5.449
5.440
5.438
F
N
N
Br
1.99
0.99
1.01
2.06
2.01
2.05
1.03
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3sa

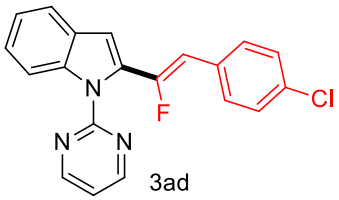

166.740
160.612
157.991
157.118
132.695
132.560
132.915
132.854
132.605
131.572
130.901
130.321
130.242
129.810
129.701
129.656
129.547
120.918
120.883
110.049
108.049
107.948
F
N
N
Br
3sa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-91.397
-91.497
F
N
N
Br
3sa
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

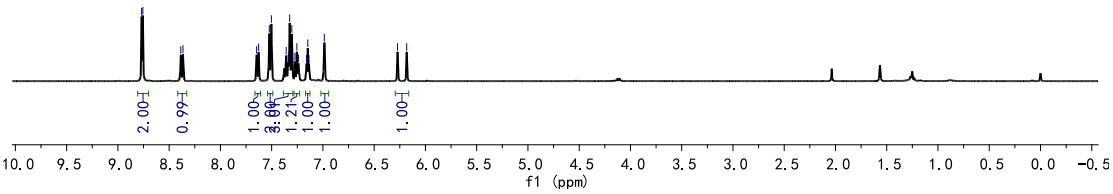

8.7683
8.7625
8.3541
8.3403
7.6269
7.4859
7.3411
7.2578
7.2344
7.1605
6.9741
6.2799
6.2191
2.3575
Me
F
N
N
3ab
2.01
1.00
1.00
2.00
1.00
1.00
3.00
1.00
0.06
1.00
3.00
f1 (ppm)


8.7705
8.7585
8.3477
8.3267
7.6177
7.5472
7.5262
7.2406
7.1398
6.9542
6.8814
6.2702
6.1787
3.8160
OMe
F
N
N
3ac
2.01
1.00
0.99
2.05
1.00
0.99
2.04
1.00
3.02
f1 (ppm)

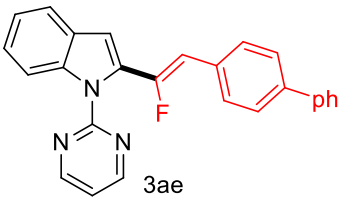

8.7683
8.7564
8.3859
8.3649
7.3241
7.2729
7.2541
7.2393
7.1594
7.1476
7.1357
6.9863
6.2719
6.1826


N
F
Cl
N
N

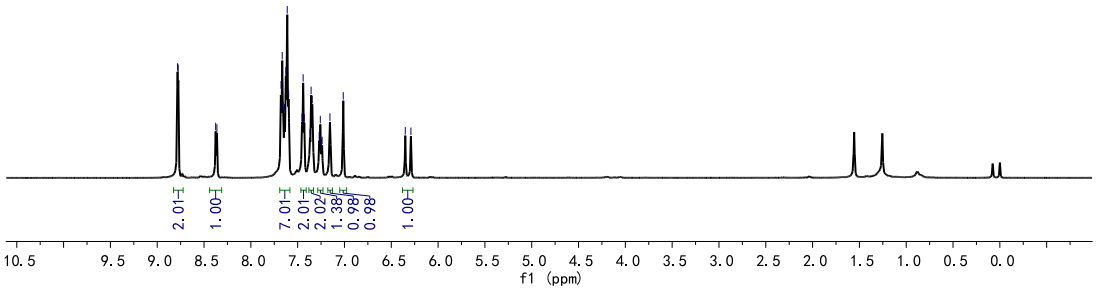
3ad

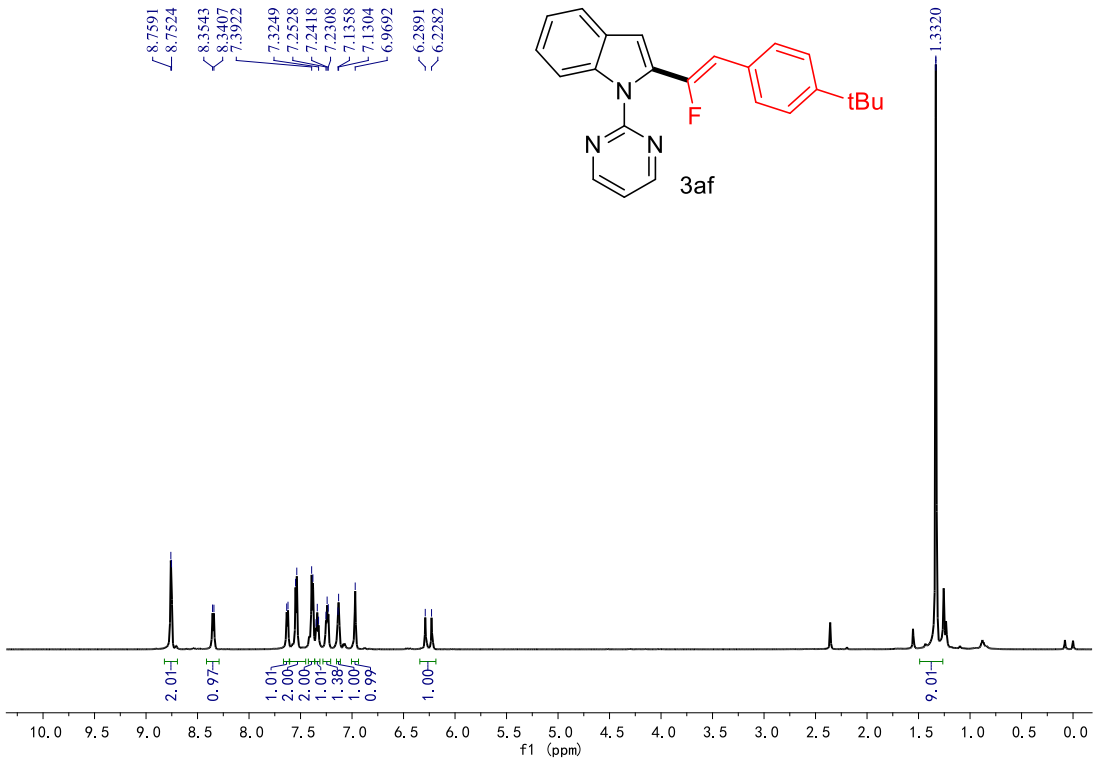

2.00
0.99
1.00
3.00
1.21
1.00
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

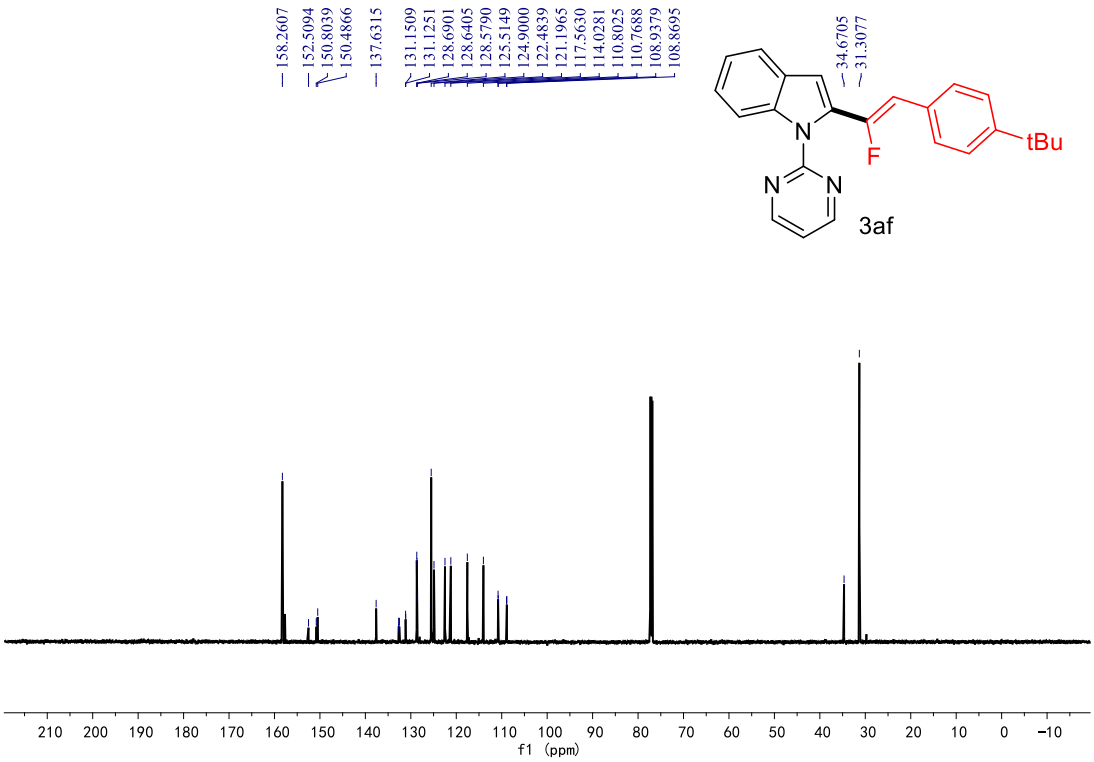

8.7826
8.7762
8.3760
7.4414
7.3683
7.3443
7.2581
7.2387
7.0129
6.3505
6.2901

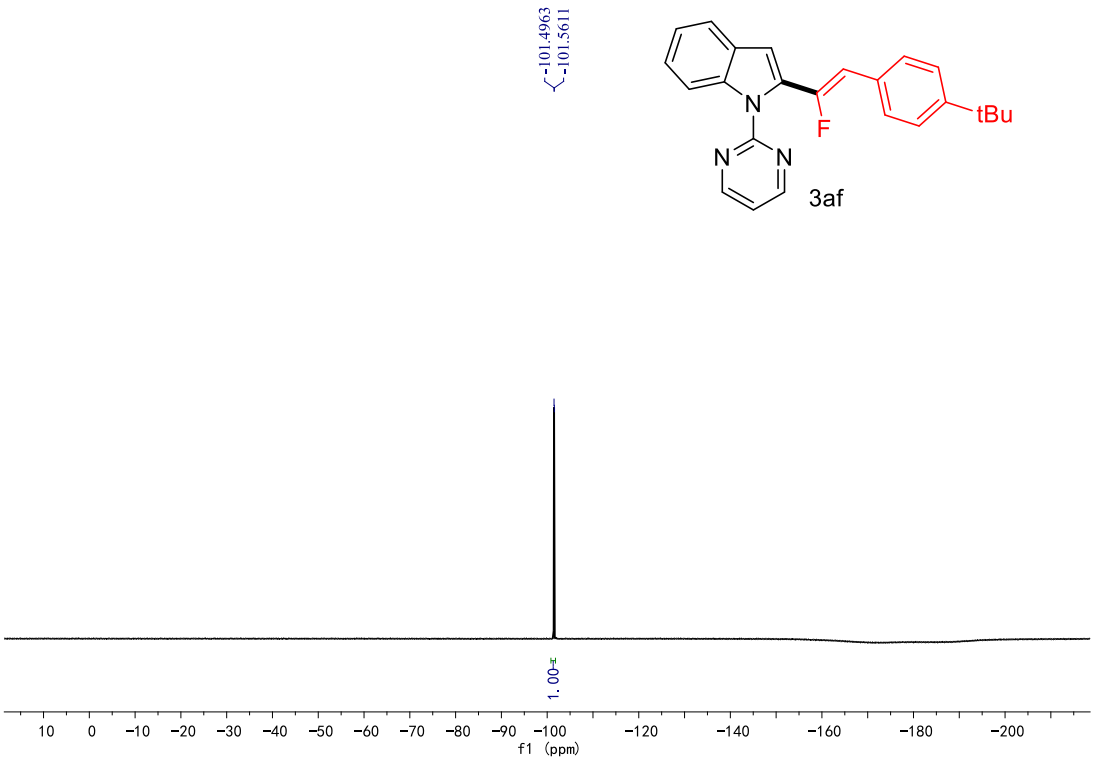

N
F
ph
N
N

3ae

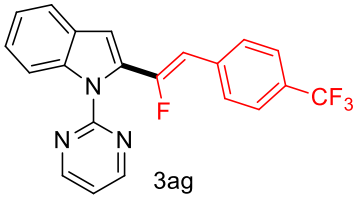

2.01
1.00
7.01
2.01
2.02
1.38
0.98
0.98
1.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.7591
8.7524
8.3543
8.3407
7.3922
7.3249
7.2528
7.2418
7.2308
7.1358
7.1304
6.9692
6.2891
6.2282
1.3320
N
N
N
F
tBu
3af
2.01
0.97
1.01
2.00
2.00
1.01
1.38
1.00
0.99
1.00
9.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

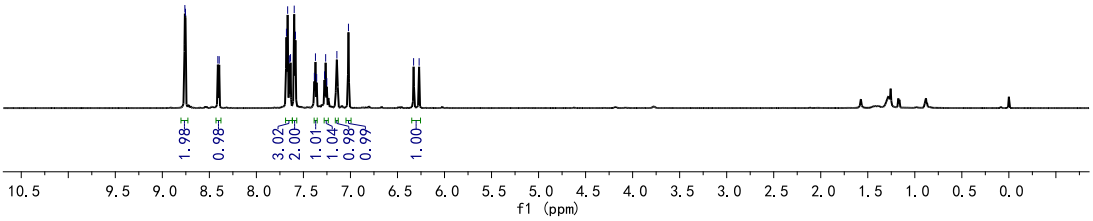

158.2607
152.5094
150.8039
150.4866
137.6315
131.1509
131.1251
128.6901
128.6405
128.5790
125.5149
124.9000
122.4839
121.1965
117.5630
114.0281
110.8025
110.7688
108.9379
108.8695
34.6705
31.3077
N
N
N
F
tBu
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-101.4963
-101.5611
N
N
N
F
tBu
3af
1.00
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)

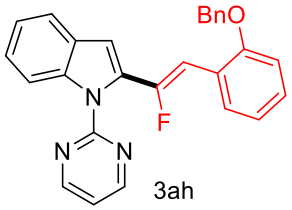

8.7604
8.7541
8.4097
8.3957
7.6676
7.6370
7.5847
7.3720
7.2759
7.2514
7.0212
6.3286
6.2697


N
F
CF3
N
N

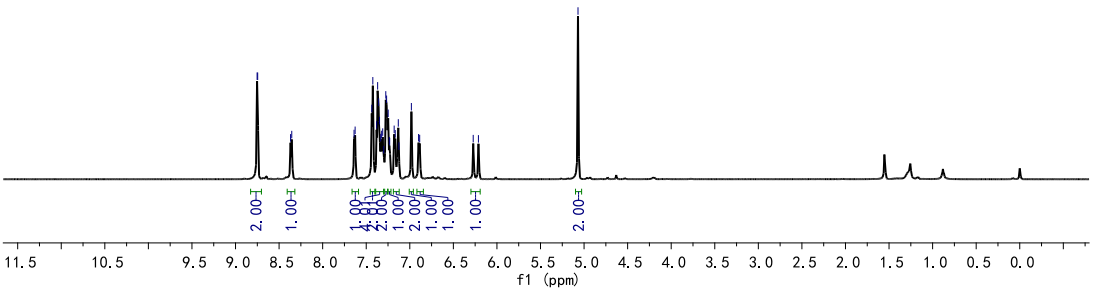
3ag

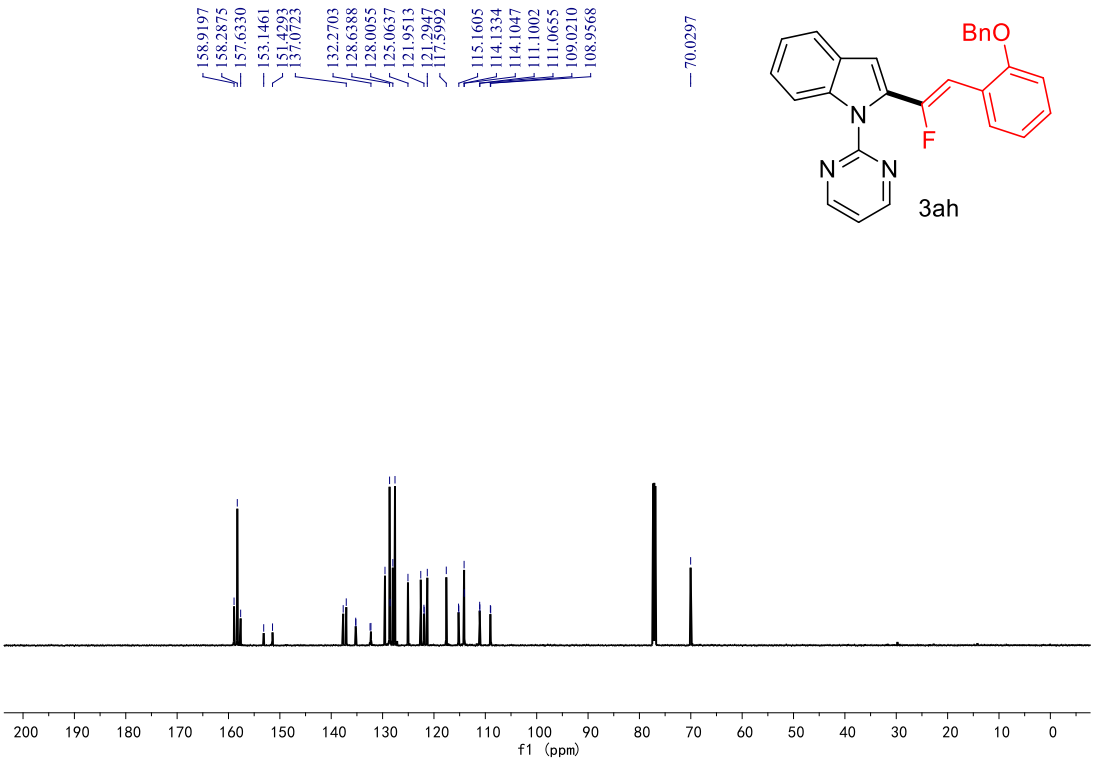

1.98
0.98
3.02
2.00
1.01
1.04
0.98
0.99
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

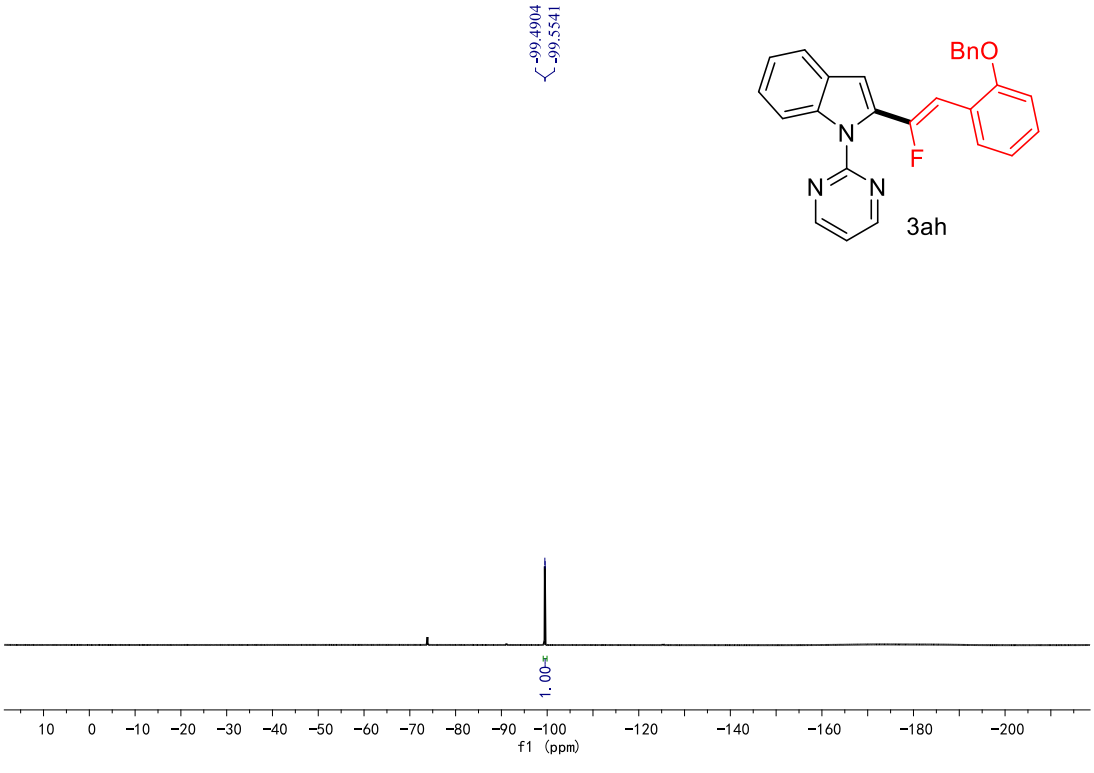

8.7525
8.7456
8.3683
8.3547
7.3689
7.3338
7.2995
7.2481
7.1793
7.1250
6.8864
6.2721
6.2123
5.0696

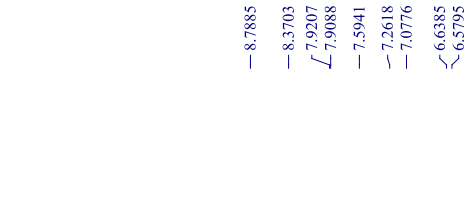

BnO
N
F
N
N

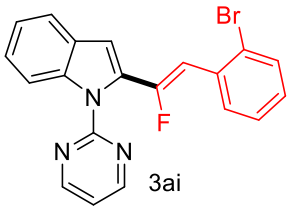
3ah


2.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

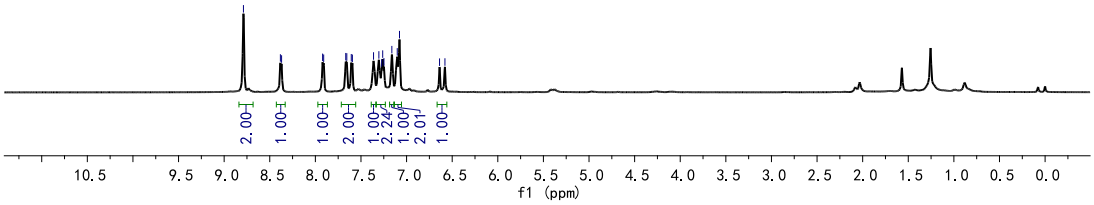

158.9197
158.2875
157.6330
153.1461
151.4293
137.0723
132.2703
128.6388
128.0055
125.0637
121.9513
121.2947
117.5992
115.1605
114.1334
114.1047
111.1002
111.0655
109.0210
108.9568
70.0297
BnO
F
N
N
N
3ah
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-99.4904
-99.5541
BnO
F
N
N
N
3ah
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

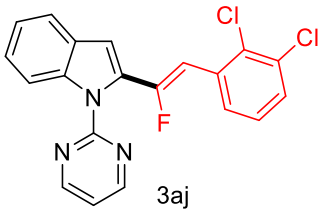

8.7885
8.3703
7.9207
7.9088
7.5941
7.2618
7.0776
6.6385
6.5795


Br
N
F
N
N

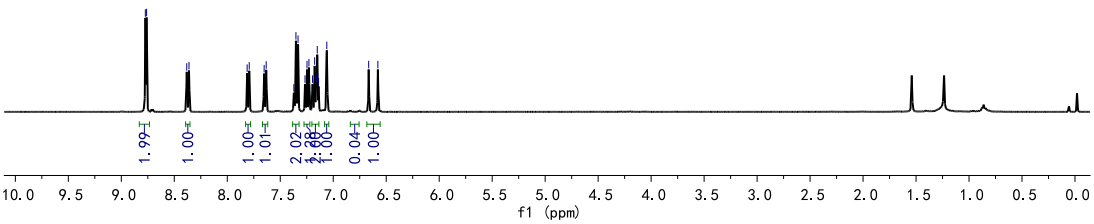
3ai

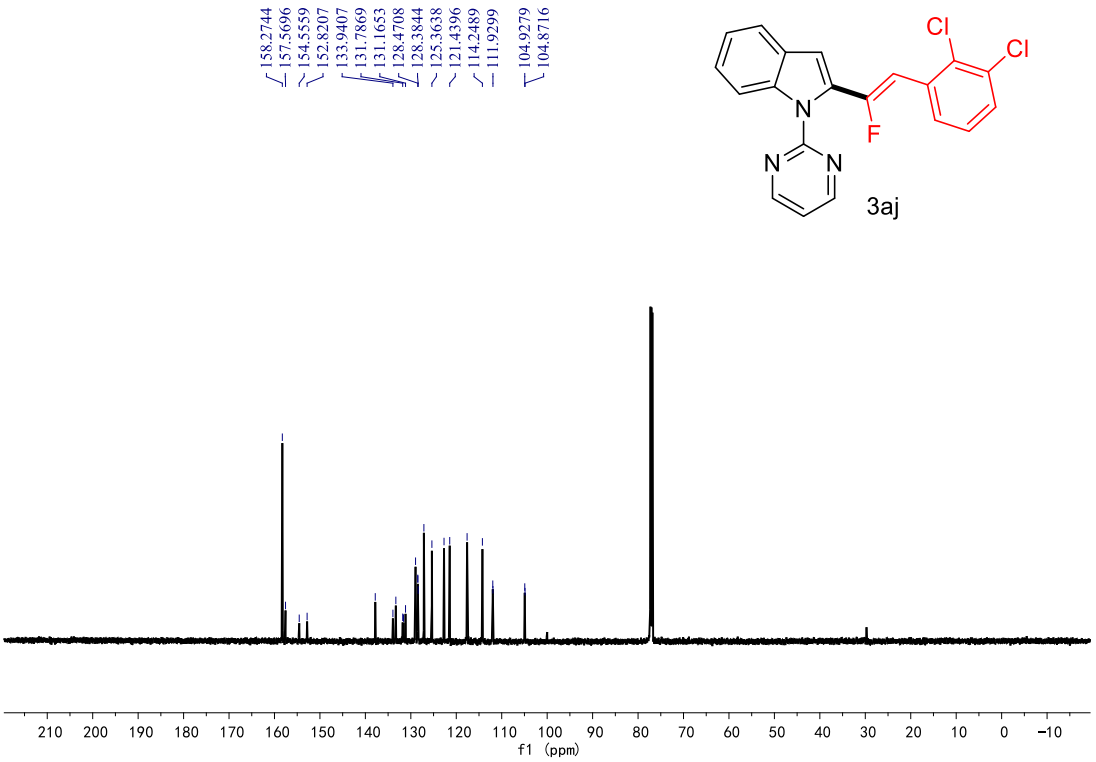

2.00
1.00
1.00
2.00
1.00
2.24
1.00
2.01
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

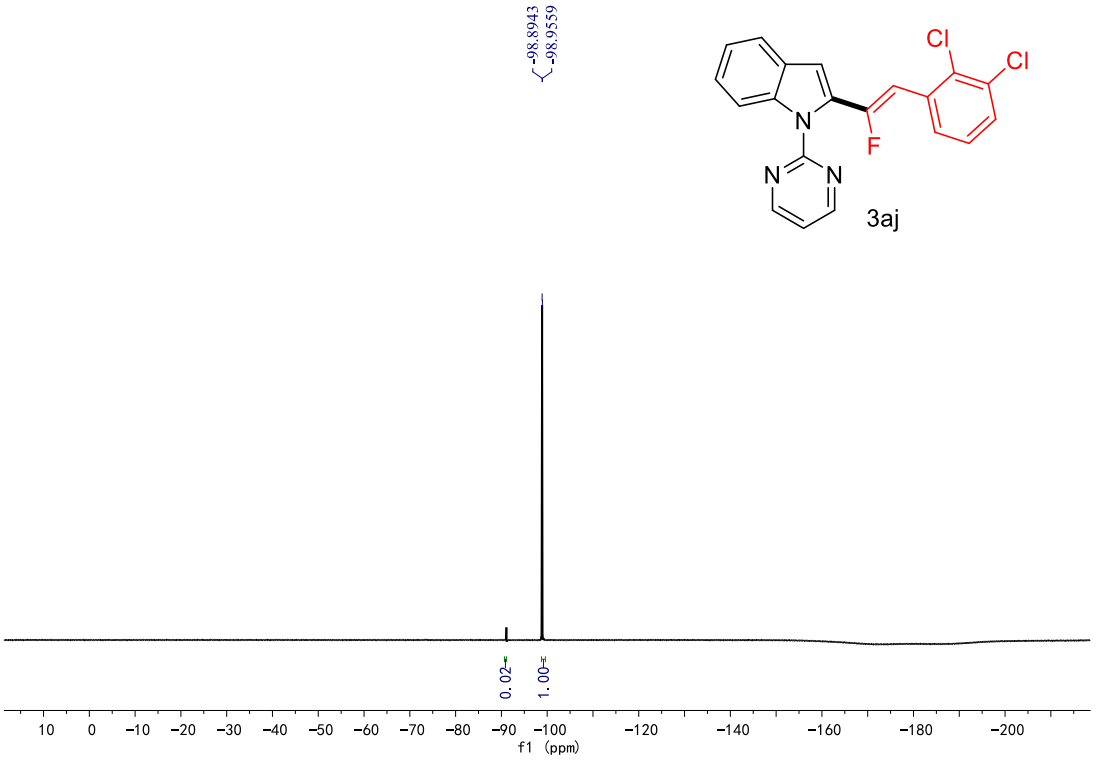

8.7733
8.7614
8.3824
8.3613
7.7927
7.6521
7.6326
7.1952
7.0607
6.6656
6.5788

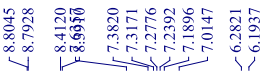

Cl
Cl
N
F
N
N

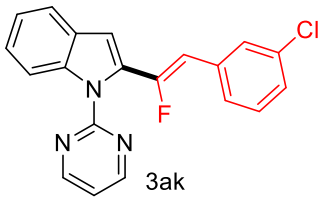
3aj


1.99
1.00
1.00
1.01
2.02
1.00
0.04
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

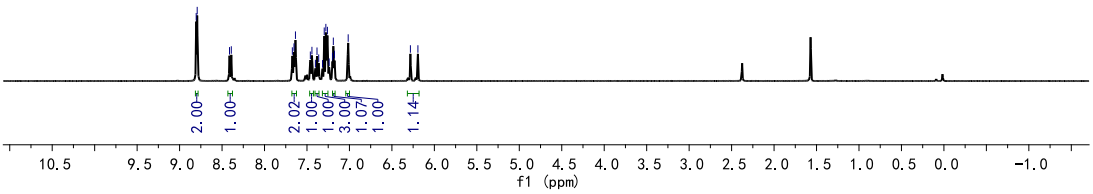

158.2744
157.5696
154.5559
152.8207
133.9407
131.7869
131.1653
128.4708
128.3844
125.3638
121.4396
114.2489
111.9299
104.9279
104.8716
Cl
Cl
F
N
N
N
3aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-98.8943
-98.9559
Cl
Cl
F
N
N
N
3aj
0.02
1.00
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)

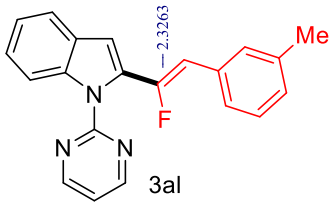

8.8045
8.7928
8.4120
7.3820
7.3171
7.2776
7.2392
7.1896
7.0147
6.2821
6.1937


Cl
F
N
N
N

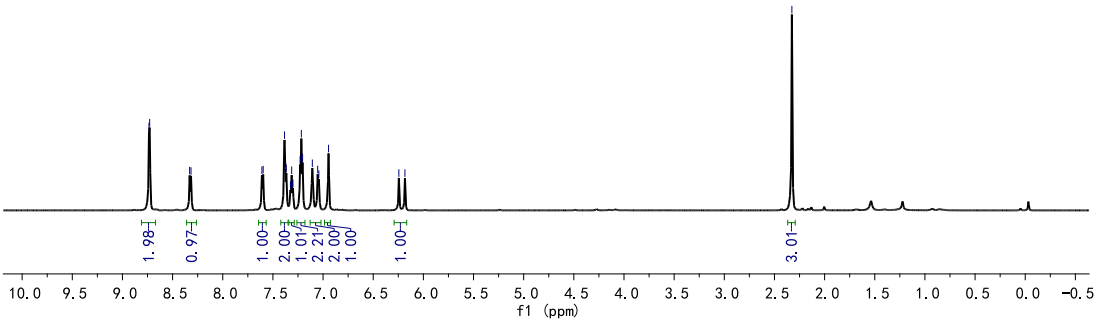
3ak

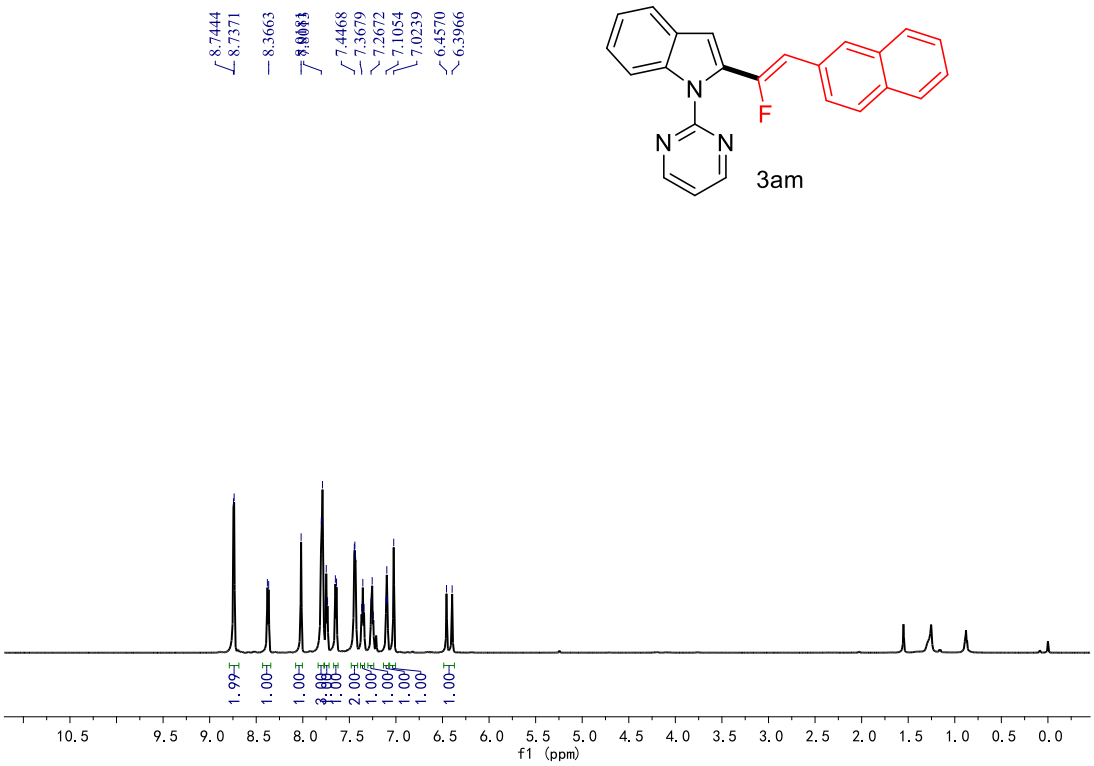

2.00
1.00
2.02
1.00
1.00
3.00
1.07
1.00
1.14
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

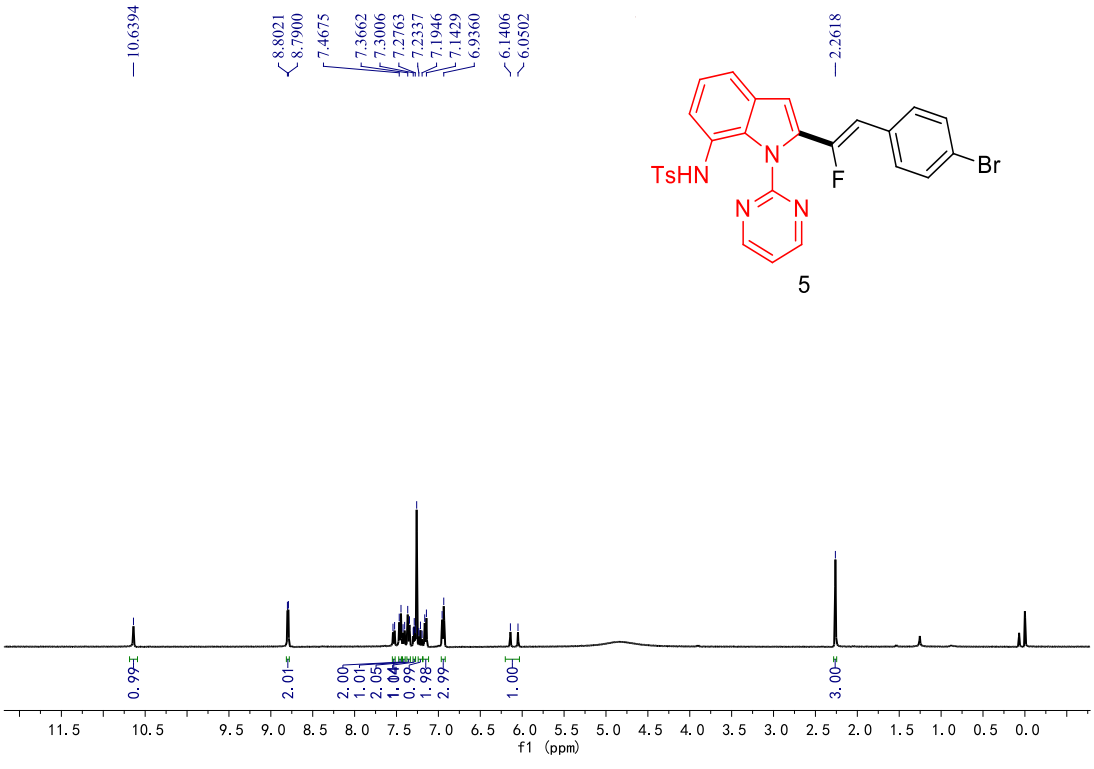

8.7355
8.7287
8.3302
8.3165
7.6097
7.2286
7.2042
7.0538
6.9455
6.2445
6.1838

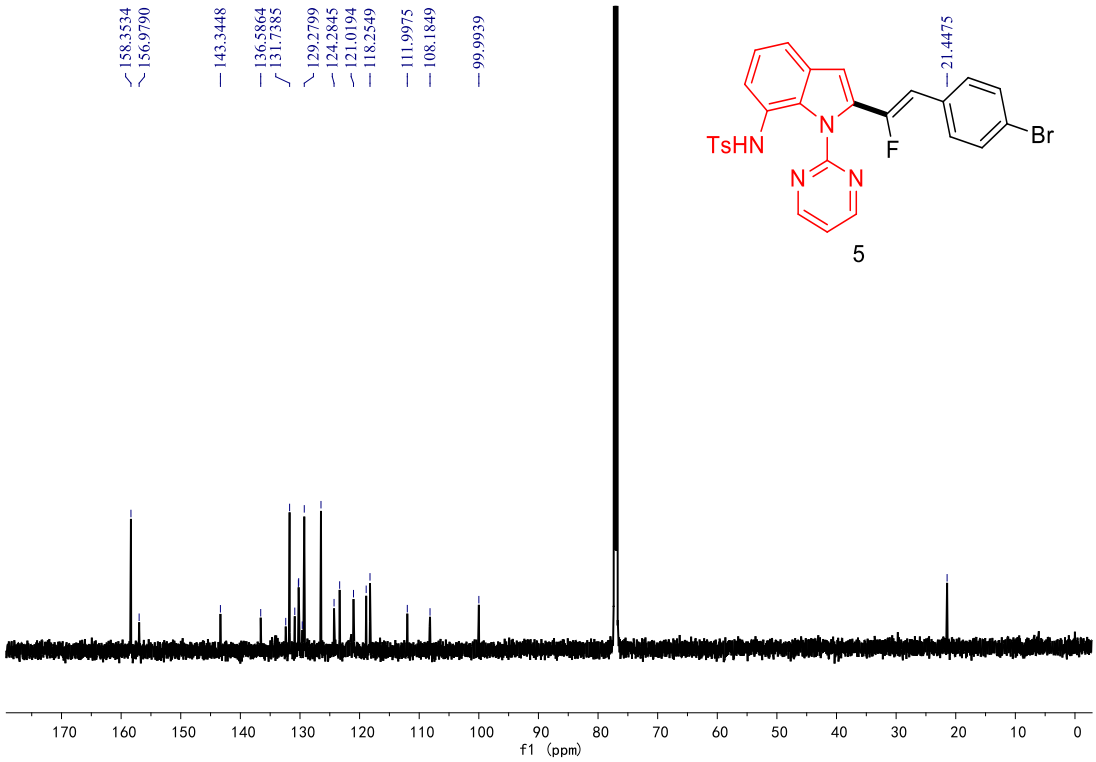

2.3263
Me
F
N
N
N

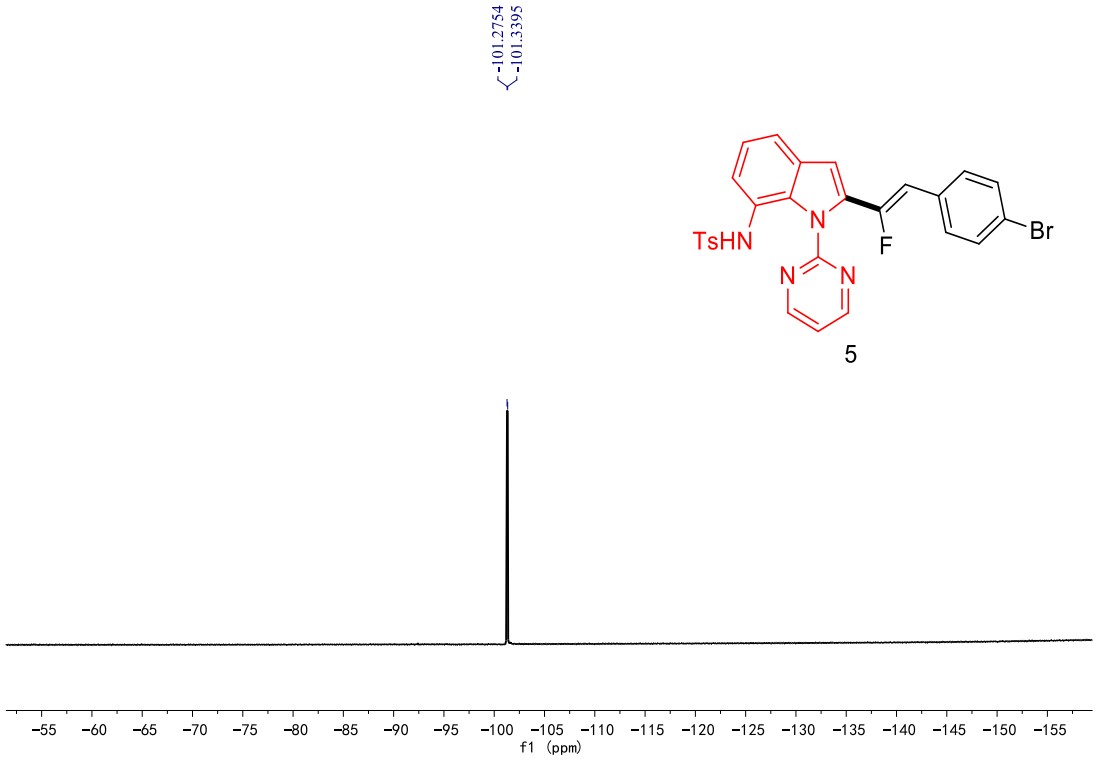
3al


1.98
0.97
1.00
2.00
1.01
2.21
2.00
1.00
1.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


8.7444
8.7371
8.3663
7.4468
7.3679
7.2672
7.1054
7.0239
6.4570
6.3966
N
N
N
F
3am
1.99
1.00
1.00
1.00
2.00
1.00
1.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


10.6394
8.8021
8.7900
7.4675
7.3662
7.3006
7.2763
7.2337
7.1946
7.1429
6.9360
6.1406
6.0502
2.2618
TsHN
N
N
N
F
Br
5
0.99
2.01
2.00
1.01
2.05
1.04
0.99
1.98
2.99
1.00
3.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.3534
156.9790
143.3448
136.5864
131.7385
129.2799
124.2845
121.0194
118.2549
111.9975
108.1849
99.9939
21.4475
TsHN
N
F
Br
N
N
5
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-101.2754
-101.3395
TsHN
N
F
Br
N
N
5
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)