

## Supporting Information

for

### Photoredox-catalyzed cascade annulation of *N*-propargylindoles with sulfonyl chlorides: access to 2-sulfonated 9*H*-pyrrolo[1,2-*a*]indoles

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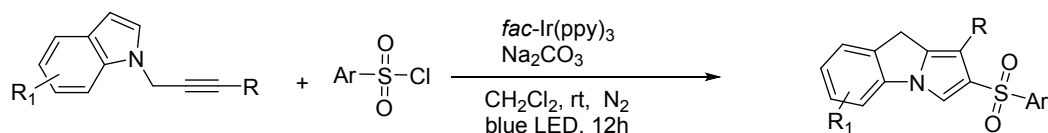
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### General:

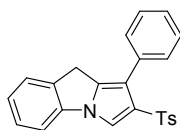
Unless otherwise stated, all reactions were carried out under Ar. CH<sub>2</sub>Cl<sub>2</sub> was freshly purified. <sup>1</sup>H NMR (600MHz) and <sup>13</sup>C NMR (151 MHz) spectra were measured on Bruker AVIII 600M spectrometers with CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the <sup>1</sup>H spectrum as 0.00 ppm and CDCl<sub>3</sub> resonance in the <sup>13</sup>C spectrum as 77.23 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Chemical shifts of common trace <sup>1</sup>H NMR impurities (ppm): H<sub>2</sub>O: 1.56, CHCl<sub>3</sub>: 7.26. Column chromatography was performed on silica gel 300-400 mesh. Mass spectra were obtained on an ion trap mass spectrometry equipped with an ESI source. The unknown products were further characterized by HRMS-ESI. The CAS number of the known compound was listed.

### Experimental procedures



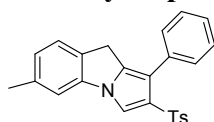
To a flame dried transparent Schlenk tube equipped with a stirring bar was added *N*-propargylindoles (0.2 mmol), *fac*-Ir(bpy)<sub>3</sub> (3 mol %), benzenesulfonyl chloride (0.4 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.4 mmol). Then dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added under Ar. The reaction mixture was stirred under the irradiation of a 24 W blue LEDs at room temperature for 12 h. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt as the eluent to give the corresponding products.

**1-Phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (3a) (CAS: 2095737-49-6)**



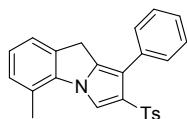
Yield: 54 mg, 71%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (s, 1H), 7.48 (d,  $J = 8.3$  Hz, 2H), 7.46 – 7.39 (m, 5H), 7.39 – 7.30 (m, 3H), 7.26-7.22 (m, 1H), 7.09 (d,  $J = 8.1$  Hz, 2H), 3.88 (s, 2H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 151 MHz):  $\delta$  143.3, 139.9, 139.8, 135.5, 134.2, 132.7, 129.9, 129.3, 128.3, 128.2, 127.5, 127.4, 127.3, 126.4, 125.4, 117.7, 115.7, 111.4, 29.4, 21.7. MS-ESI:  $m/z$  407.94,  $[\text{M} + \text{Na}]^+$ .

**6-Methyl-1-phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (3b) (CAS: 2095737-63-4)**



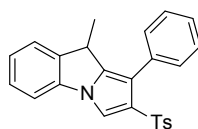
Yield: 64 mg, 80%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (s, 1H), 7.46 (d,  $J = 8.2$  Hz, 2H), 7.41 (d,  $J = 6.6$  Hz, 2H), 7.35 – 7.18 (m, 5H), 7.05 (d,  $J = 8.1$  Hz, 2H), 6.99 (d,  $J = 7.6$  Hz, 1H), 3.79 (s, 2H), 2.44 (s, 3H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 151 MHz):  $\delta$  143.2, 140.1, 139.8, 138.4, 135.9, 132.74, 131.2, 129.9, 129.3, 128.2, 127.4, 127.3, 127.1, 126.1, 125.9, 117.6, 115.5, 111.7, 28.9, 21.7, 21.6. MS-ESI:  $m/z$  421.95,  $[\text{M} + \text{Na}]^+$ .

**5-Methyl-1-phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (3c) (CAS: 2095737-64-5)**



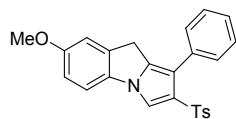
Yield: 52 mg, 65%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (s, 1H), 7.45 (d,  $J = 8.3$  Hz, 2H), 7.42-7.36 (m, 2H), 7.36-7.28 (m, 3H), 7.26-7.23 (m, 1H), 7.18-7.09 (m, 2H), 7.05 (d,  $J = 8.0$  Hz, 2H), 3.84 (s, 3H), 2.67 (s, 3H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.2, 140.1, 138.7, 136.0, 134.4, 132.7, 130.4, 130.0, 129.3, 128.3, 127.4, 127.4, 127.0, 125.3, 123.9, 123.1, 118.4, 117.3, 29.2, 21.7, 18.7. MS-ESI:  $m/z$  421.98,  $[\text{M} + \text{Na}]^+$ .

**9-Methyl-1-phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (3d) (CAS: 2095737-70-3)**



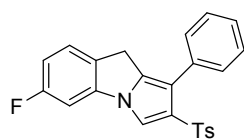
Yield: 64 mg, 81%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (s, 1H), 7.47 – 7.27 (m, 10H), 7.24 – 7.17 (m, 1H), 7.05 (d,  $J = 8.1$  Hz, 2H), 4.12 (q,  $J = 7.2$  Hz, 1H), 2.34 (s, 3H), 1.24 (d,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.2, 140.5, 140.4, 139.9, 138.8, 132.2, 130.5, 129.3, 128.2, 128.1, 127.6, 127.5, 125.5, 125.2, 117.9, 114.8, 110.9, 36.3, 21.7, 17.6. MS-ESI:  $m/z$  421.96,  $[\text{M} + \text{Na}]^+$ .

**7-Methoxy-1-phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (3e) (CAS: 2095737-65-6)**



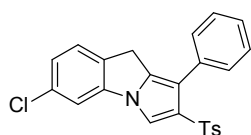
Yield: 57 mg, 69%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84 (s, 1H), 7.46 (d,  $J = 8.3$  Hz, 2H), 7.44 – 7.38 (m, 2H), 7.36 – 7.27 (m, 4H), 7.05 (d,  $J = 8.1$  Hz, 2H), 6.96 (d,  $J = 2.1$  Hz, 1H), 6.88 (dd,  $J = 8.6, 2.4$  Hz, 1H), 3.82 (s, 3H), 3.81 (s, 2H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.9, 143.1, 140.2, 135.8, 135.3, 133.6, 132.7, 129.9, 129.3, 128.3, 127.4, 126.5, 117.7, 115.4, 112.9, 112.8, 111.4, 56.0, 29.6, 21.7. MS-ESI:  $m/z$  438.00,  $[\text{M} + \text{Na}]^+$ .

**6-Fluoro-1-phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (3f) (CAS: 2095737-66-7)**



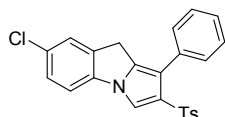
Yield: 57 mg, 71%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (s, 1H), 7.44 (d,  $J = 8.2$  Hz, 2H), 7.40 (d,  $J = 6.7$  Hz, 2H), 7.37 – 7.28 (m, 4H), 7.12 (dd,  $J = 8.1, 2.2$  Hz, 1H), 7.06 (d,  $J = 8.1$  Hz, 2H), 6.94 – 6.88 (m, 1H), 3.82 (s, 2H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.9 (d,  $J_{\text{C-F}} = 246.3$  Hz), 143.4, 140.8 (d,  $J_{\text{C-F}} = 11.3$  Hz), 139.8, 136.4, 132.4, 129.9, 129.6 (d,  $J_{\text{C-F}} = 2.7$  Hz), 129.3, 128.3, 128.2, 127.6, 127.5, 127.2 (d,  $J_{\text{C-F}} = 9.7$  Hz), 118.0, 115.6, 112.1 (d,  $J_{\text{C-F}} = 22.7$  Hz), 99.6 (d,  $J_{\text{C-F}} = 27.3$  Hz), 28.8, 21.7. MS-ESI:  $m/z$  425.98,  $[\text{M} + \text{Na}]^+$ .

**6-Chloro-1-phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (3g) (CAS: 2095737-67-8)**



Yield: 66 mg, 79%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (s, 1H), 7.49 – 7.38 (m, 5H), 7.37 – 7.29 (m, 4H), 7.19 (dd,  $J = 8.0, 1.8$  Hz, 1H), 7.06 (d,  $J = 8.0$  Hz, 2H), 3.83 (s, 2H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.4, 140.8, 139.7, 135.8, 134.1, 132.7, 132.3, 129.9, 129.4, 128.3, 128.3, 127.6, 127.5, 127.2, 125.4, 118.0, 115.6, 111.8, 29.0, 21.7. MS-ESI:  $m/z$  419.97,  $[\text{M} + \text{H}]^+$ .

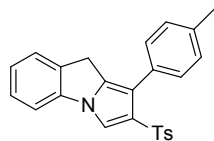
**7-Chloro-1-phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (3h) (CAS: 2095737-68-9)**



Yield: 60 mg, 72%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (s, 1H), 7.50-7.45 (m, 2H), 7.44 – 7.27 (m, 8H), 7.09 (d,  $J = 8.1$  Hz, 2H), 3.86 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.4, 139.8, 138.4, 136.0, 135.2, 132.3, 130.9,

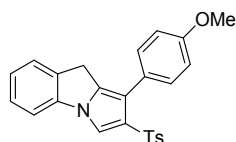
129.9, 129.3, 128.3, 127.9, 127.6, 127.5, 126.7, 118.0, 115.7, 111.9, 29.3, 21.7. MS-ESI:  $m/z$  419.92,  $[M + H]^+$ .

**1-(*p*-Tolyl)-2-tosyl-9*H*-pyrrolo[1,2-*a*]indole (3i) (CAS: 2095737-50-9)**



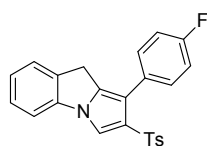
Yield: 53 mg, 66%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (s, 1H), 7.52 (d,  $J = 8.2$  Hz, 3H), 7.41 (dd,  $J = 12.8, 6.9$  Hz, 4H), 7.34 (d,  $J = 7.9$  Hz, 3H), 7.27 – 7.15 (m, 4H), 7.11 (d,  $J = 8.0$  Hz, 2H), 3.86 (s, 3H), 2.42 (s, 4H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.2, 140.2, 139.8, 137.1, 135.3, 134.3, 129.7, 129.7, 129.3, 129.0, 128.2, 127.4, 127.2, 126.4, 125.3, 117.7, 115.6, 111.0, 29.3, 21.7, 21.5. MS-ESI:  $m/z$  422.01,  $[M + \text{Na}]^+$ .

**1-(4-Methoxyphenyl)-2-tosyl-9*H*-pyrrolo[1,2-*a*]indole (3j) (CAS: 2095737-51-0)**



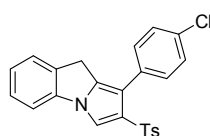
Yield: 38 mg, 46%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (s, 1H), 7.47 (d,  $J = 8.3$  Hz, 2H), 7.43 – 7.31 (m, 5H), 7.22-7.18 (m, 1H), 7.08 (d,  $J = 8.4$  Hz, 2H), 6.91-6.87 (m, 2H), 3.86 (s, 2H), 3.84 (s, 2H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.8, 143.0, 139.9, 139.6, 135.0, 134.1, 130.9, 129.1, 128.0, 127.2, 127.1, 126.2, 125.1, 124.8, 117.2, 115.3, 113.5, 110.8, 55.3, 29.1, 21.5. MS-ESI:  $m/z$  438.01,  $[M + \text{Na}]^+$ .

**1-(4-Fluorophenyl)-2-tosyl-9*H*-pyrrolo[1,2-*a*]indole (3k) (CAS: 2095737-54-3)**



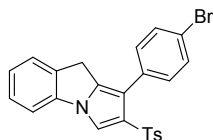
Yield: 62 mg, 77%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (s, 1H), 7.51 – 7.34 (m, 7H), 7.22 (t,  $J = 7.0$  Hz, 1H), 7.12 – 6.97 (m, 4H), 3.83 (s, 3H), 2.33 (s, 4H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.3 (d,  $J = 246.6$  Hz), 143.4, 139.8 (d,  $J = 27.0$  Hz), 135.5, 134.1, 131.7 (d,  $J = 8.1$  Hz), 129.4, 128.6 (d,  $J = 3.4$  Hz), 128.3, 127.4, 127.3, 126.4, 125.5, 116.6, 115.6, 115.3, 115.1, 111.1, 29.2, 21.7. MS-ESI:  $m/z$  425.96,  $[M + \text{Na}]^+$ .

**1-(4-Chlorophenyl)-2-tosyl-9*H*-pyrrolo[1,2-*a*]indole (3l) (CAS:2095737-55-4)**



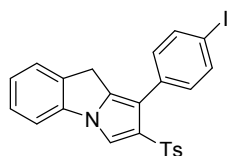
Yield: 58 mg, 70%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (s, 1H), 7.48 (d,  $J = 8.3$  Hz, 2H), 7.43-7.35 (m, 5H), 7.32-7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.10 (d,  $J = 8.1$  Hz, 2H), 3.84 (s, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.5, 139.9, 139.6, 135.7, 134.0, 133.3, 131.2 (2C, overlap), 129.4, 128.5, 128.3, 127.4, 127.2, 126.4, 125.6, 116.4, 115.9, 111.1, 29.4, 21.7. MS-ESI:  $m/z$  441.92,  $[\text{M} + \text{Na}]^+$ .

**1-(4-Bromophenyl)-2-tosyl-9H-pyrrolo[1,2-a]indole (3m) (CAS: 2095737-56-5)**



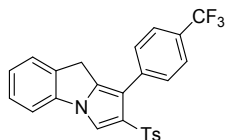
Yield: 69 mg, 75%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (s, 1H), 7.50-7.46 (m, 4H), 7.42-7.38 (m, 3 H), 7.31 (d,  $J = 8.4$  Hz, 2H), 7.25-7.19 (m, 1H), 7.11 (d,  $J = 8.1$  Hz, 2H), 3.83 (s, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.5, 139.9, 139.6, 135.6, 134.0, 131.7, 131.5, 131.4, 129.4, 128.3, 127.4, 127.1, 126.4, 125.6, 121.5, 116.4, 115.9, 111.1, 29.3, 21.7. MS-ESI:  $m/z$  485.92,  $[\text{M} + \text{Na}]^+$ .

**1-(4-Iodophenyl)-2-tosyl-9H-pyrrolo[1,2-a]indole (3n) (CAS: 2095737-57-6)**



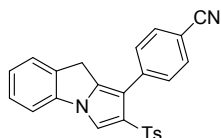
Yield: 76 mg, 74%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (s, 1H), 7.66 (d,  $J = 8.3$  Hz, 2H), 7.48 (t,  $J = 10.0$  Hz, 2H), 7.43 – 7.33 (m, 3H), 7.24 – 7.12 (m, 3H), 7.11 (d,  $J = 8.1$  Hz, 2H), 3.84 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.5, 139.9, 139.6, 137.4, 135.6, 134.0, 132.3, 131.7, 129.5, 128.3, 127.4, 127.1, 126.4, 125.6, 116.5, 116.0, 111.1, 93.1, 29.4, 21.7. MS-ESI:  $m/z$  533.93,  $[\text{M} + \text{Na}]^+$ .

**2-Tosyl-1-(4-(trifluoromethyl)phenyl)-9H-pyrrolo[1,2-a]indole (3o) (CAS: 2095737-59-8)**



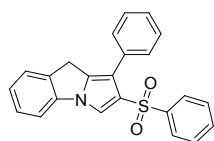
Yield: 64 mg, 71%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (s, 1H), 7.57 (dd,  $J = 24.6, 8.2$  Hz, 4H), 7.50 – 7.37 (m, 5H), 7.26 – 7.22 (m, 1H), 7.09 (d,  $J = 8.1$  Hz, 2H), 3.87 (s, 2H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.6, 139.8, 139.6, 136.6, 136.1, 133.9, 130.1, 129.5, 129.4 (q,  $J_{\text{C-F}} = 32.3$  Hz), 128.4, 127.4, 127.4, 126.7 (q,  $J_{\text{C-F}} = 270.2$  Hz), 126.5, 125.7, 125.2 (q,  $J_{\text{C-F}} = 3.6$  Hz), 116.3, 116.2, 111.2, 29.4, 21.7. MS-ESI:  $m/z$  441.92,  $[\text{M} + \text{Na}]^+$ . MS-ESI:  $m/z$  475.99,  $[\text{M} + \text{Na}]^+$ .

**4-(2-Tosyl-9H-pyrrolo[1,2-a]indol-1-yl)benzotrile (3p) (CAS: 2095737-58-7)**



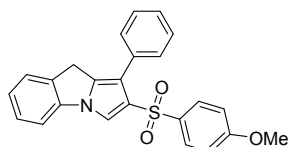
Yield: 62 mg, 76%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (s, 1H), 7.64-7.58 (m, 4H), 7.50 (d,  $J = 8.2$  Hz, 2H), 7.45-7.38 (m, 3H), 7.27-7.23 (m, 1H), 7.12 (d,  $J = 8.1$  Hz, 2H), 3.89 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.8, 139.6, 139.4, 137.8, 136.4, 133.7, 132.1, 130.3, 129.5, 128.4, 127.3, 127.2, 126.4, 125.8, 119.2, 116.7, 115.8, 111.2, 110.8, 29.6, 21.7. MS-ESI:  $m/z$  432.97,  $[\text{M} + \text{Na}]^+$ .

**1-Phenyl-2-(phenylsulfonyl)-9H-pyrrolo[1,2-a]indole (3q) (CAS: 2095737-73-6)**



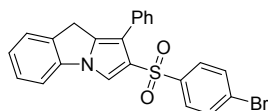
Yield: 56 mg, 75%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (s, 1H), 7.58-7.56 (m, 2H), 7.42-7.38 (m, 6H), 7.34-7.31 (m, 3H), 7.26-7.23 (m, 2H), 7.21 (t,  $J = 7.3$  Hz, 1H), 3.85 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.8, 139.7, 135.5, 134.2, 132.6, 132.5, 129.9, 128.7, 128.3, 128.2, 127.5, 127.4, 126.9, 126.4, 125.5, 117.8, 115.9, 111.1, 29.3. HRMS:  $m/z$  394.0865,  $[\text{M} + \text{Na}]^+$ .

**2-((4-Methoxyphenyl)sulfonyl)-1-phenyl-9H-pyrrolo[1,2-a]indole (3r) (CAS: 2095737-74-7)**



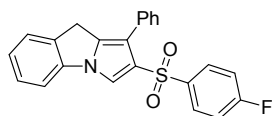
Yield: 43 mg, 53%; Pale yellow solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (s, 1H), 7.49 (d,  $J = 8.9$  Hz, 2H), 7.45 – 7.28 (m, 8H), 7.20 (td,  $J = 7.3, 1.7$  Hz, 1H), 6.72 (d,  $J = 8.9$  Hz, 2H), 3.84 (s, 2H), 3.76 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.8, 139.7, 135.4, 134.5, 134.2, 132.7, 129.9, 129.6, 128.3, 128.2, 127.7, 127.4, 126.4, 125.3, 117.5, 115.3, 113.8, 111.0, 55.7, 29.3. HRMS:  $m/z$  424.0973,  $[\text{M} + \text{Na}]^+$ .

**2-((4-Bromophenyl)sulfonyl)-1-phenyl-9H-pyrrolo[1,2-a]indole (3s) (CAS: 2095737-76-9)**



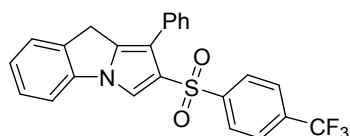
Yield: 58 mg, 65%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (s, 1H), 7.42-7.34 (m, 12 H), 7.22 (t,  $J = 8.6$  Hz, 1H), 3.84 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.8, 139.6, 135.7, 134.2, 132.4, 131.9, 130.0, 129.0, 128.4, 128.2, 127.7, 127.5, 126.4, 126.4, 125.6, 117.7, 115.8, 111.1, 29.2. MS-ESI:  $m/z$  471.91,  $[\text{M} + \text{Na}]^+$ .

**2-((4-Fluorophenyl)sulfonyl)-1-phenyl-9H-pyrrolo[1,2-*a*]indole (3t) (CAS: 2095737-75-8)**



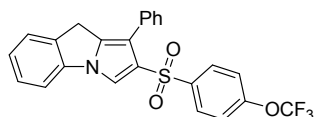
Yield: 50 mg, 64%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.97 (s, 1H), 7.50-7.44 (m, 2H), 7.38 – 7.22 (m, 8H), 7.16-7.12 (m, 1H), 6.83 (t,  $J = 8.6$  Hz, 2H), 3.87 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.2 (d,  $J_{\text{C-F}} = 259.2$  Hz), 139.7, 138.8 (d,  $J_{\text{C-F}} = 3.1$ Hz), 135.6, 134.2, 132.4, 130.2 (d,  $J_{\text{C-F}} = 9.3$  Hz), 130.2, 128.4, 128.2, 127.6, 126.8, 126.4, 125.5, 117.7, 115.9 (d,  $J_{\text{C-F}} = 32.9$  Hz), 115.7, 111.1, 29.2. MS-ESI:  $m/z$  411.97,  $[\text{M} + \text{Na}]^+$ .

**1-Phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)-9H-pyrrolo[1,2-*a*]indole (3u) (CAS: 2095737-78-1)**



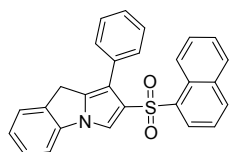
Yield: 51 mg, 58%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (s, 1H), 7.64 (d,  $J = 8.2$  Hz, 2H), 7.50 (d,  $J = 8.4$  Hz, 2H), 7.43-7.40 (m, 3H), 7.39 – 7.30 (m, 5H), 7.25-7.20 (m, 1H), 3.86 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.3, 139.6, 135.8, 134.2, 134.0 (q,  $J_{\text{C-F}} = 34.0$  Hz), 132.3, 130.0, 128.4, 128.3, 127.9, 127.8, 126.5, 125.9, 125.8 (d,  $J_{\text{C-F}} = 3.7$  Hz), 125.7, 125.5 (q,  $J_{\text{C-F}} = 272.0$  Hz), 117.9, 116.1, 111.2, 29.3. MS-ESI:  $m/z$  461.94,  $[\text{M} + \text{Na}]^+$ .

**1-Phenyl-2-((4-(trifluoromethoxy)phenyl)sulfonyl)-9H-pyrrolo[1,2-*a*]indole (3v) (CAS: 2095737-77-0)**



Yield: 54 mg, 60%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 1H), 7.60 – 7.53 (m, 2H), 7.45 – 7.29 (m, 8H), 7.23 (t,  $J = 7.2$  Hz, 1H), 7.05 (d,  $J = 8.2$  Hz, 2H), 3.85 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.0, 141.0, 139.6, 135.7, 134.2, 132.3, 130.0, 129.6, 128.4, 128.3, 127.7, 126.5, 126.5, 125.6, 120.6, 120.5 (q,  $J_{\text{C-F}} = 259.0$  Hz), 117.7, 115.7, 111.1, 29.2. MS-ESI:  $m/z$  477.96,  $[\text{M} + \text{Na}]^+$ .

**2-(Naphthalen-2-ylsulfonyl)-1-phenyl-9H-pyrrolo[1,2-*a*]indole (3w) (CAS: 2095737-80-5)**

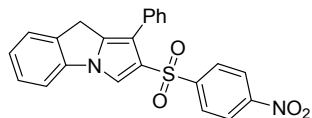


Yield: 26 mg, 31%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (s, 1H), 8.02 (s, 1H), 7.81 – 7.71 (m, 2H), 7.70 – 7.60 (m, 2H), 7.56 – 7.46 (m, 2H), 7.40-7.34



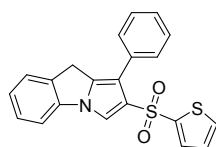
(m, 5H), 7.33 – 7.28 (m, 3H), 7.19 (t,  $J = 7.2$  Hz, 1H), 3.83 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.7, 139.6, 135.5, 134.8, 134.1, 132.5, 132.1, 130.0, 129.4, 128.9, 128.8, 128.7, 128.2, 128.1, 127.8, 127.5, 127.2, 126.9, 126.3, 125.4, 122.7, 117.7, 115.7, 111.0, 29.2. MS-ESI:  $m/z$  443.98,  $[\text{M} + \text{Na}]^+$ .

**2-((4-Nitrophenyl)sulfonyl)-1-phenyl-9H-pyrrolo[1,2-*a*]indole (3x) (CAS: 2095737-79-2)**

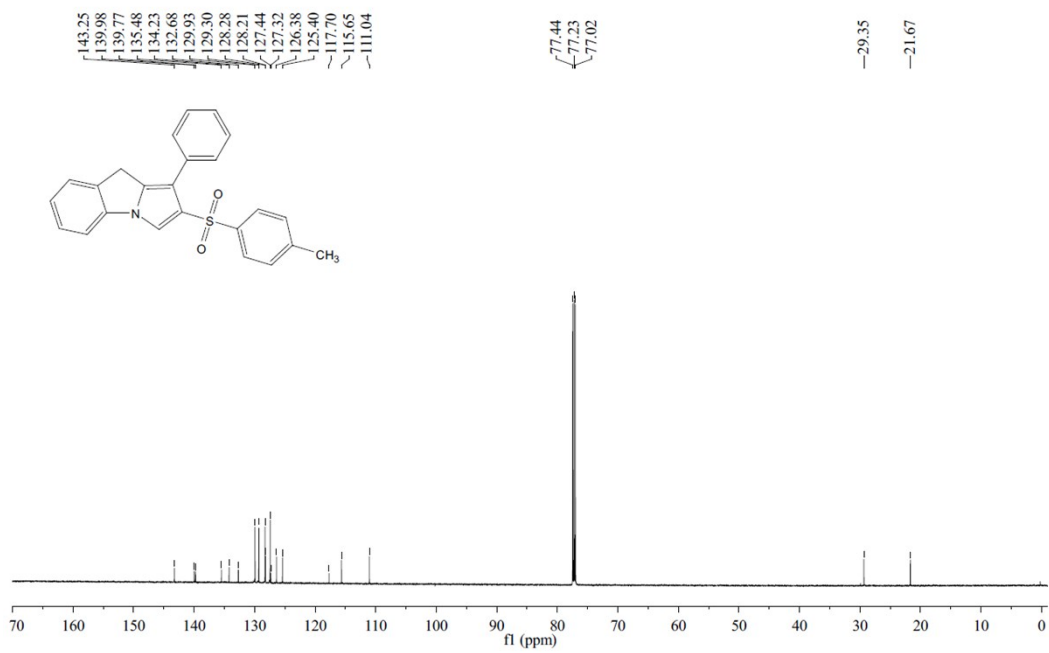
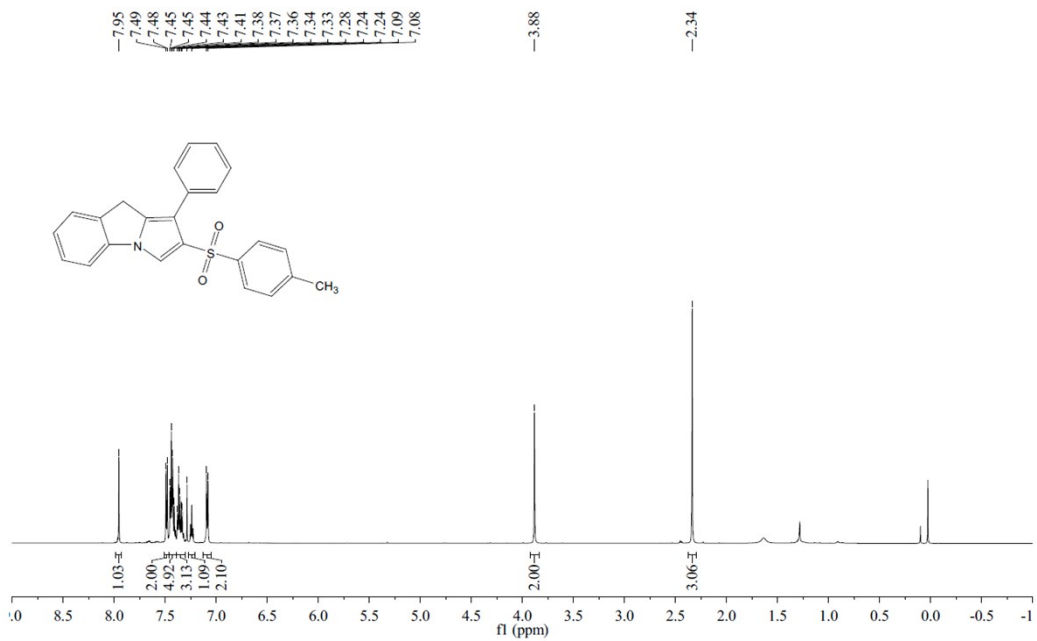


Yield: 37 mg, 45%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.07 (d,  $J = 8.7$  Hz, 2H), 8.00 (s, 1H), 7.68 (d,  $J = 8.3$  Hz, 2H), 7.46-7.43 (m, 4H), 7.43-7.35 (m, 4H), 7.26 – 7.22 (m, 1H), 3.87 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.9, 148.4, 139.5, 136.0, 134.2, 132.1, 130.2, 128.9, 128.7, 128.5, 128.4, 126.5, 125.9, 125.4, 123.9, 117.9, 116.3, 111.3, 29.2. MS-ESI:  $m/z$  438.96,  $[\text{M} + \text{Na}]^+$ .

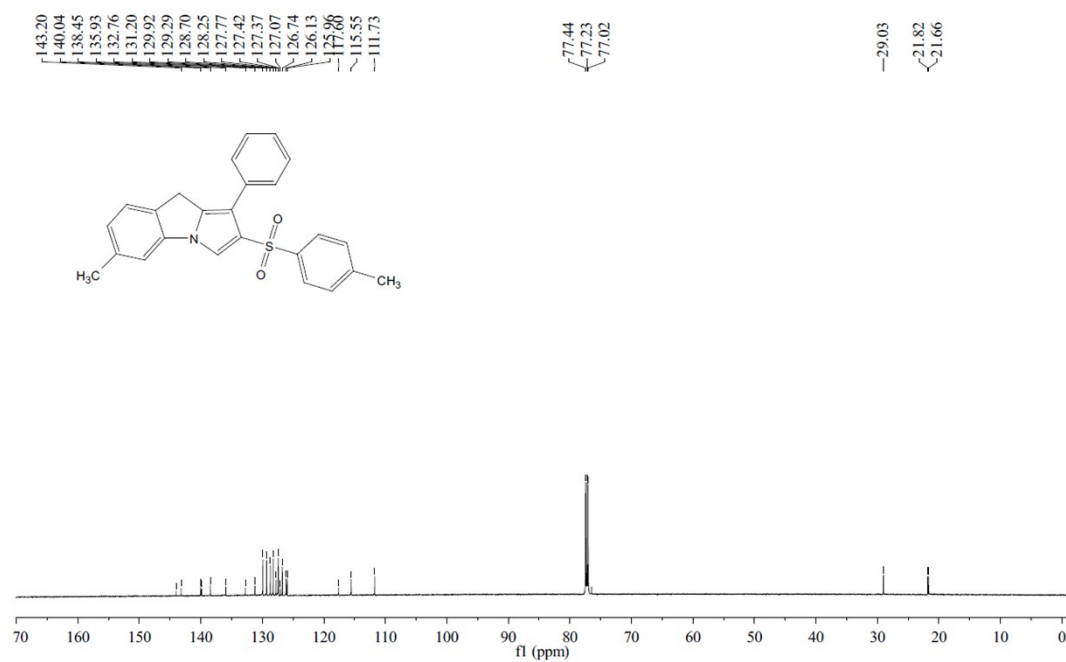
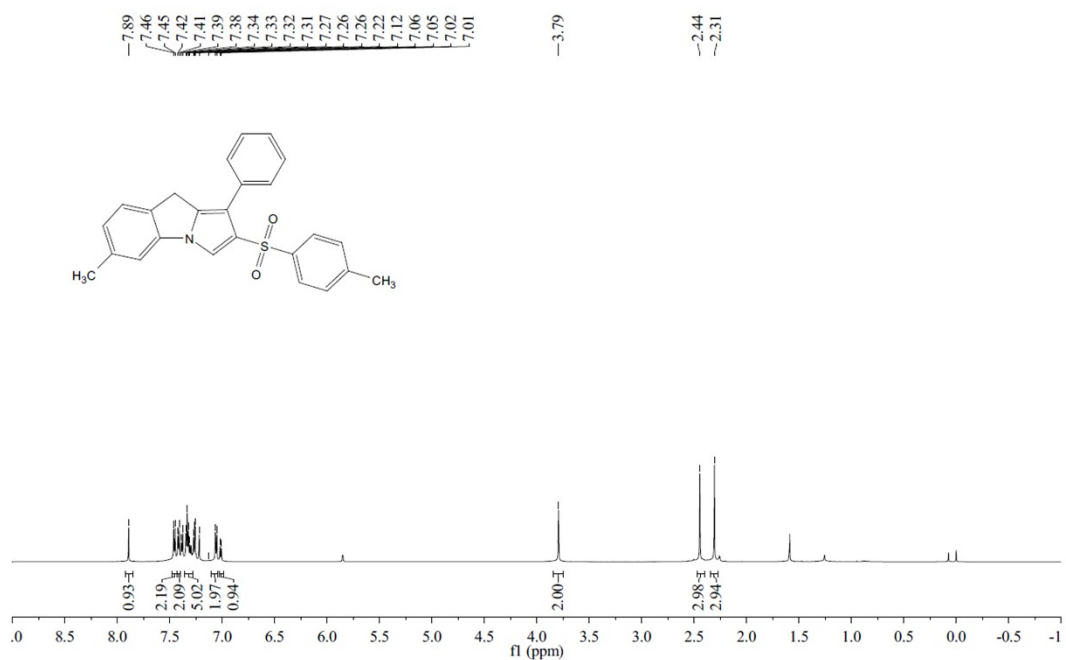
**1-Phenyl-2-(thiophen-2-ylsulfonyl)-9H-pyrrolo[1,2-*a*]indole (3y) (New compound)**



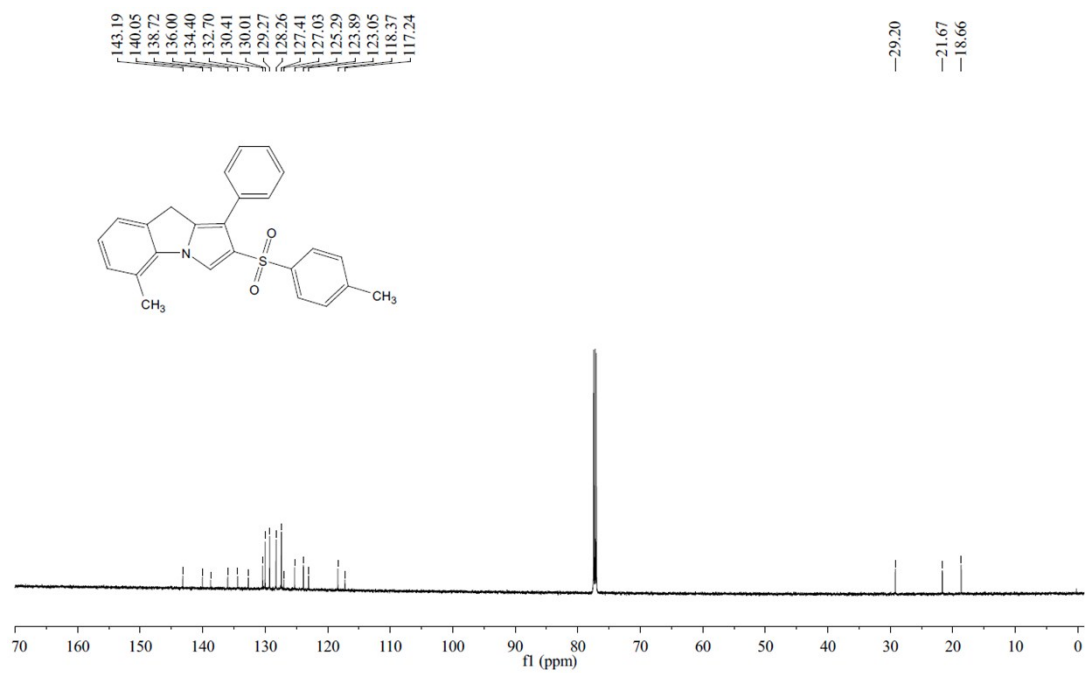
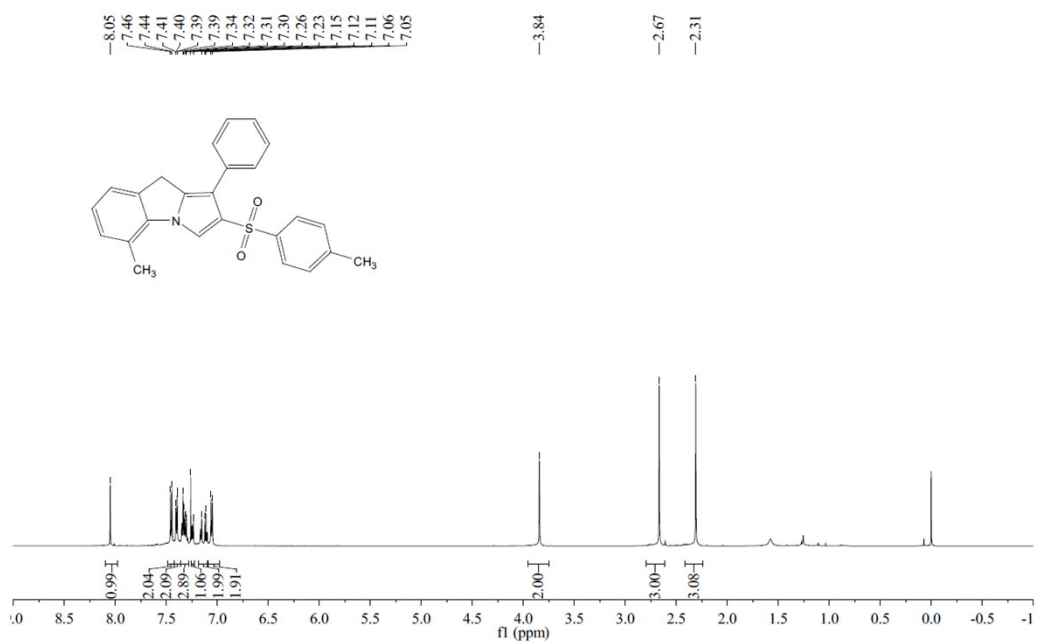
Yield: 46 mg, 61%; Pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (s, 1H), 7.49 (d,  $J = 7.6$  Hz, 2H), 7.44 – 7.30 (m, 7H), 7.22 (t,  $J = 7.3$  Hz, 1H), 7.18 (d,  $J = 3.6$  Hz, 1H), 6.82 (t,  $J = 4.3$  Hz, 1H), 3.88 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 139.7, 135.5, 134.2, 132.6, 132.5, 129.9, 128.7, 128.3, 128.2, 127.5, 127.4, 126.9, 126.4, 125.5, 117.8, 115.8, 111.1, 29.3. HRMS:  $[\text{M} + \text{Na}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{15}\text{NNaO}_2\text{S}_2^+$ : 400.0436, found: 400.0426



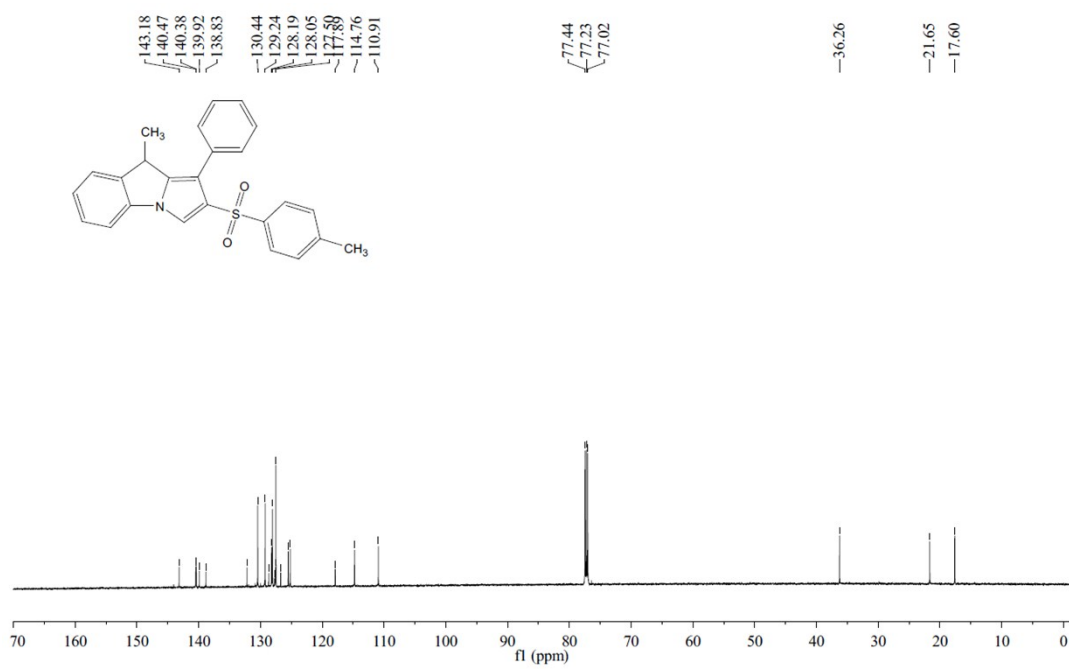
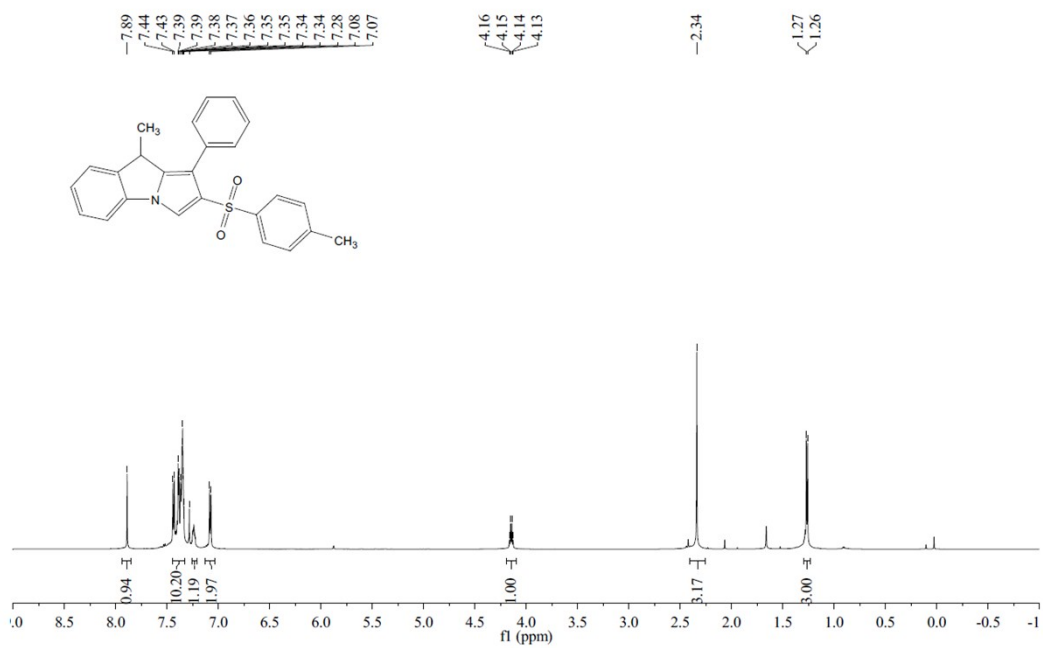
3b



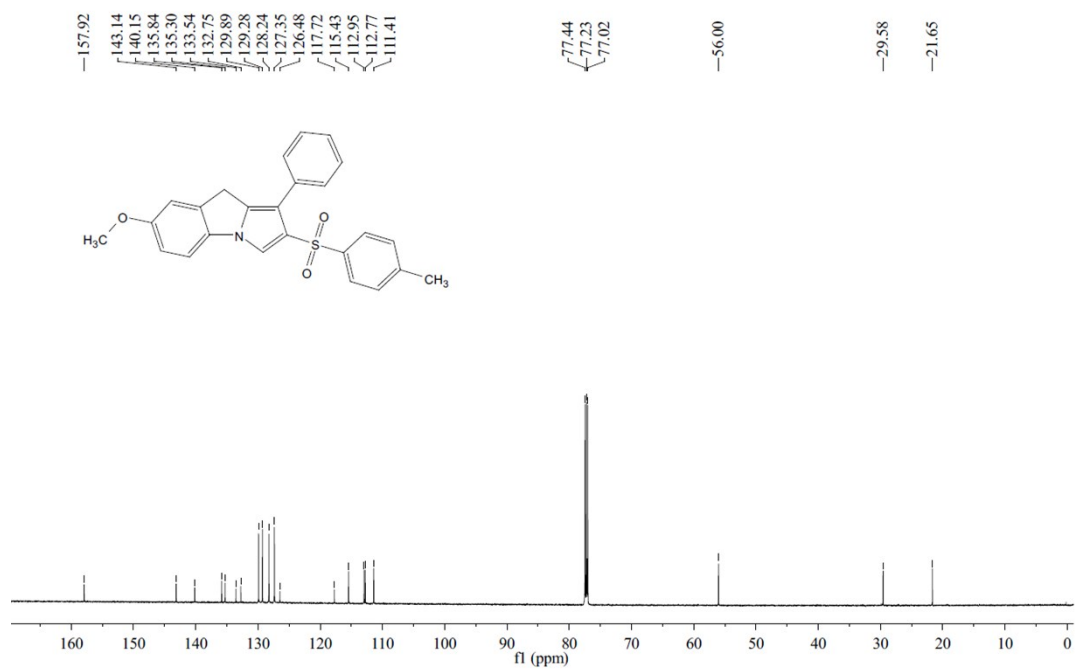
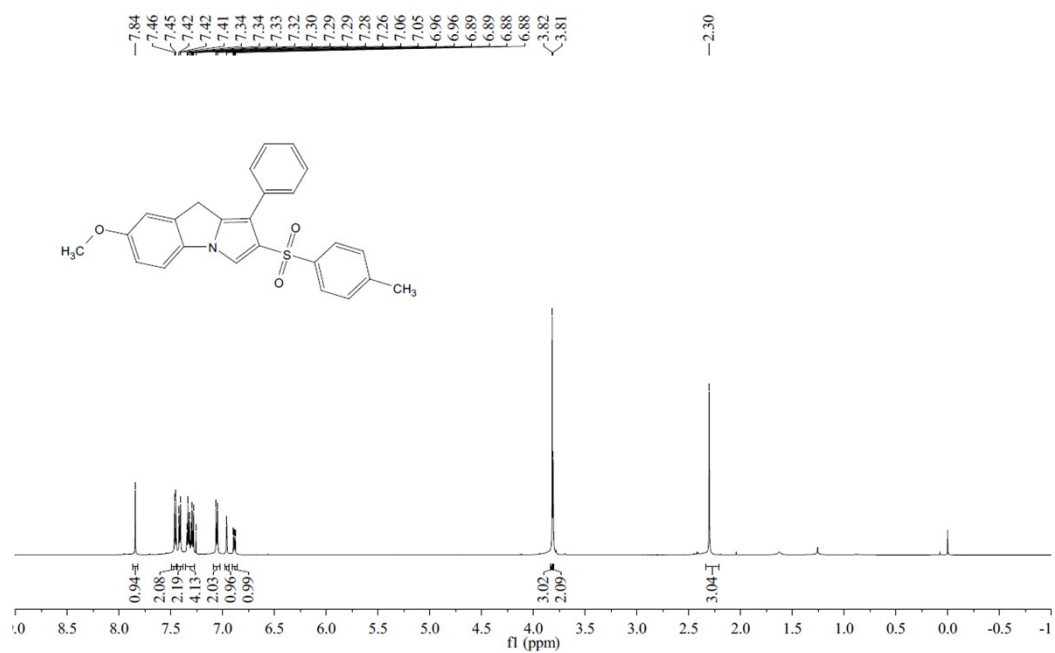
3c



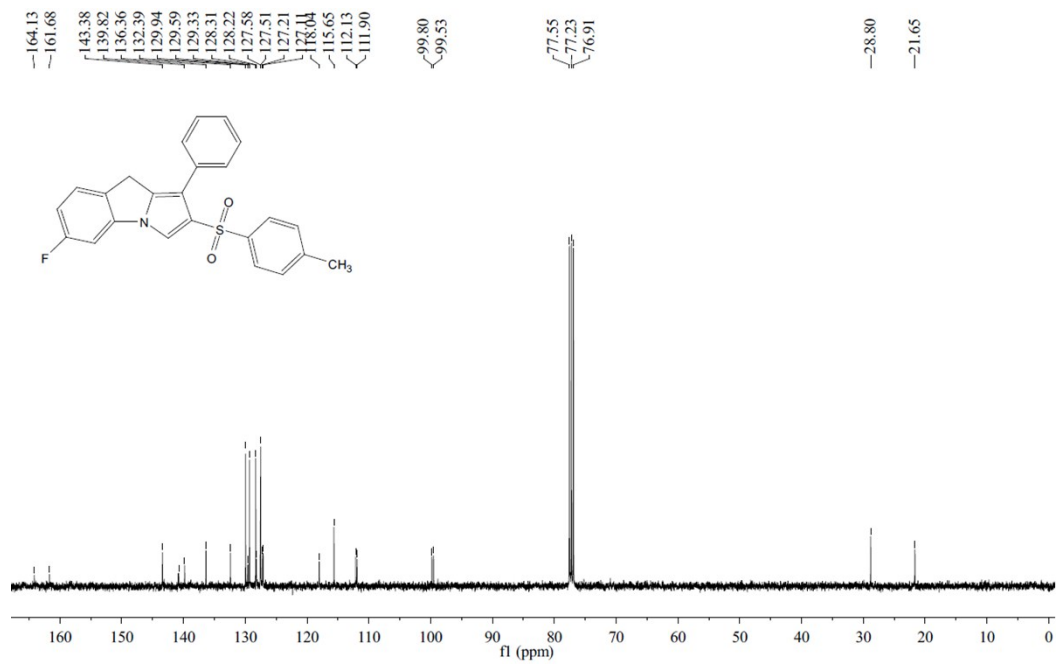
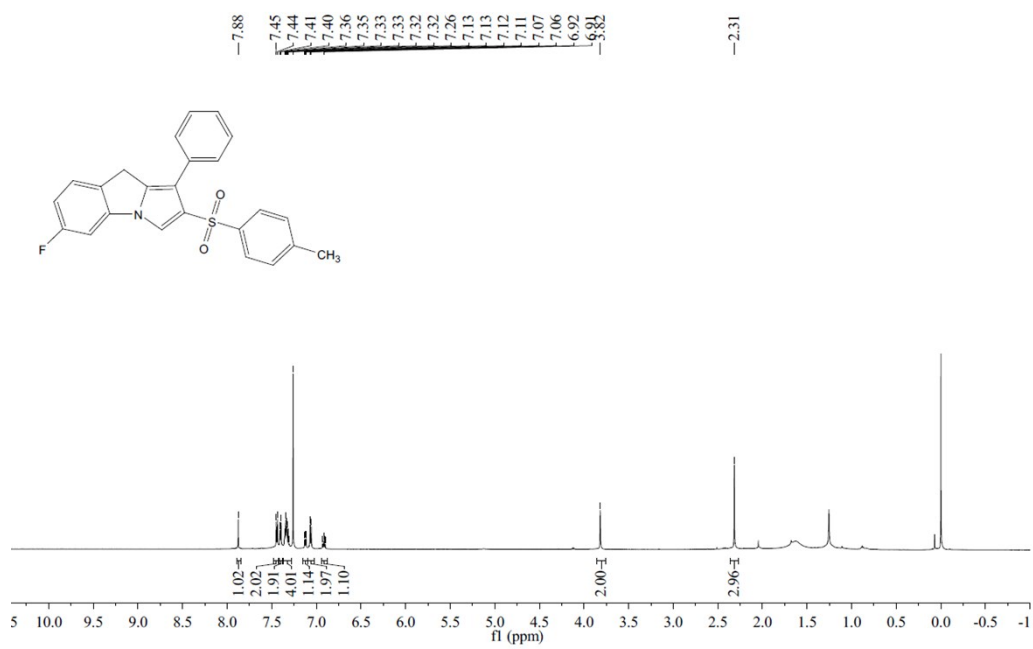
3d



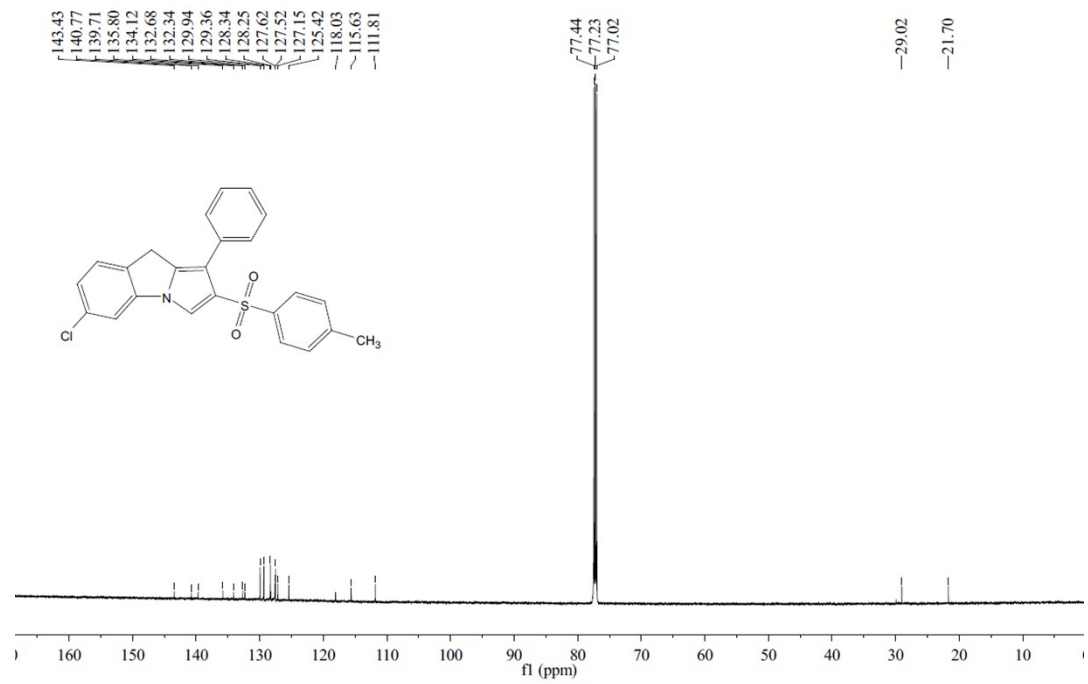
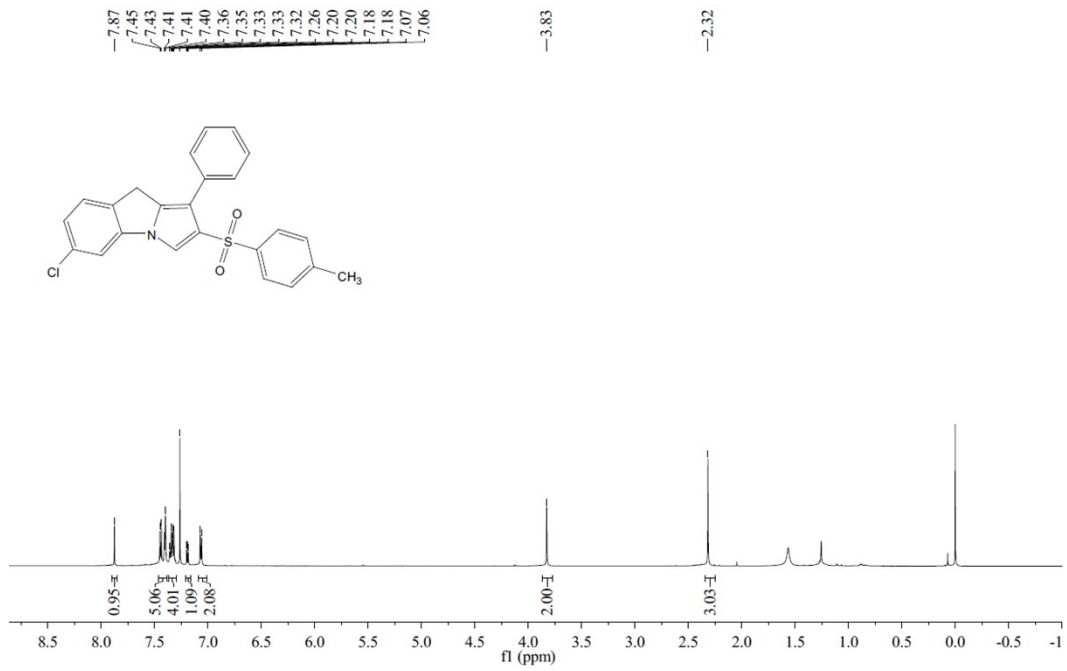
3e



3f

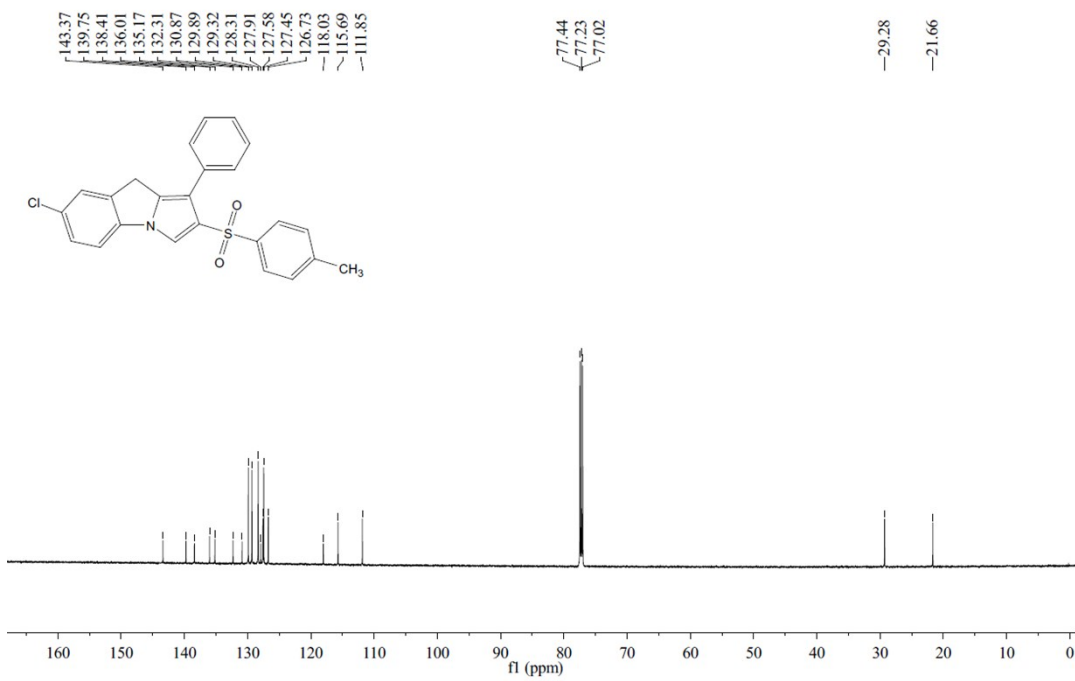
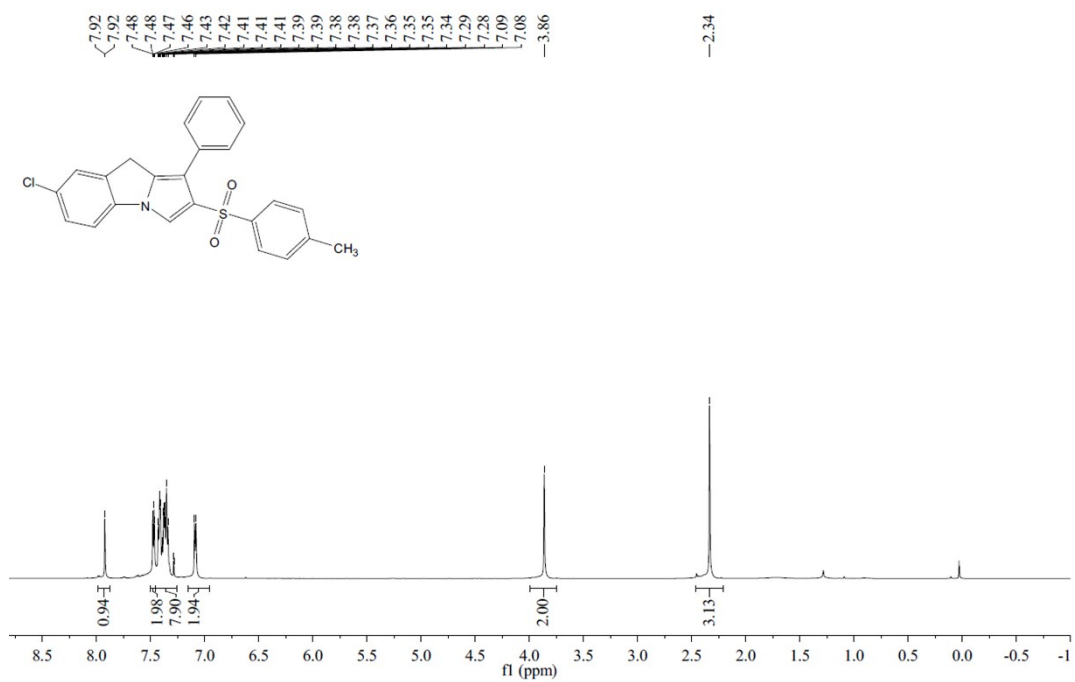


3g

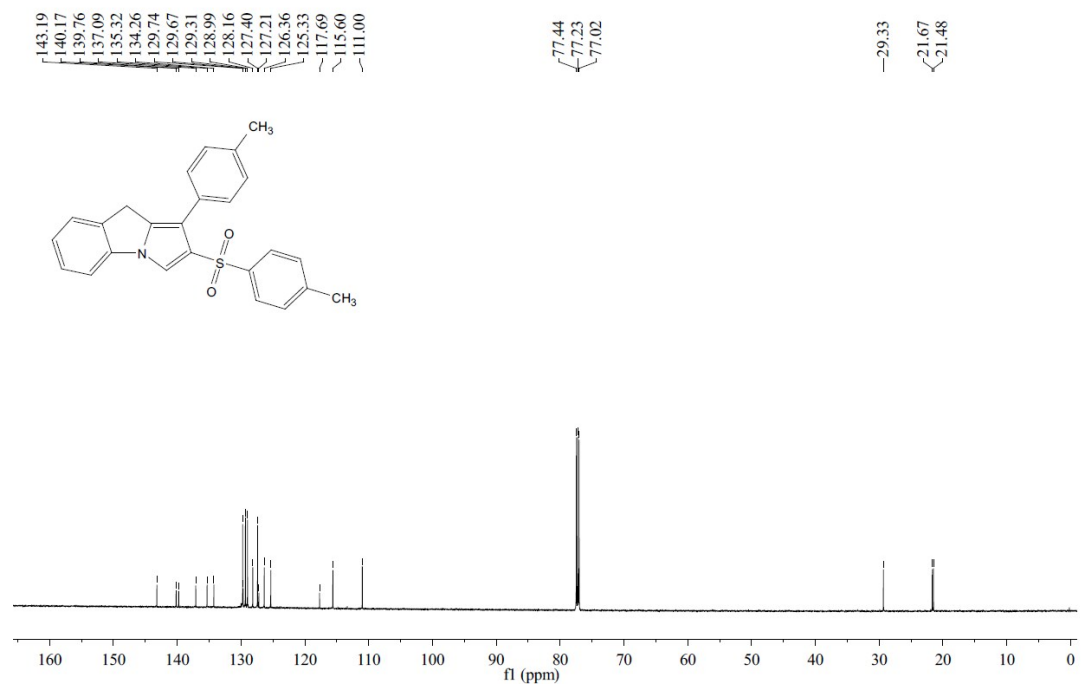
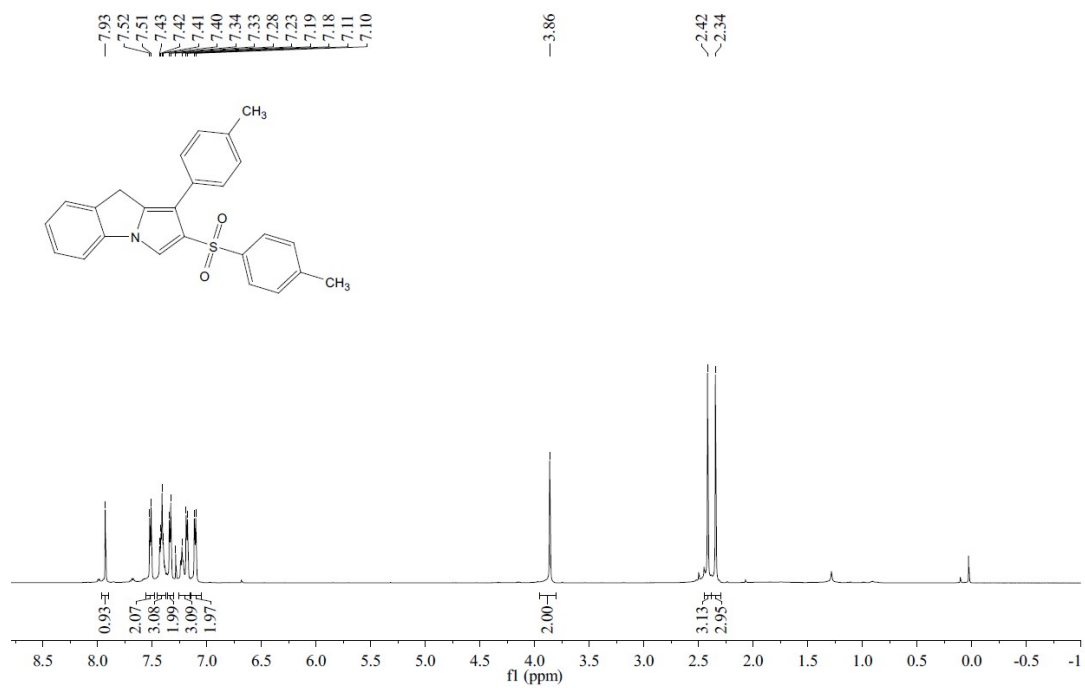


**3h**

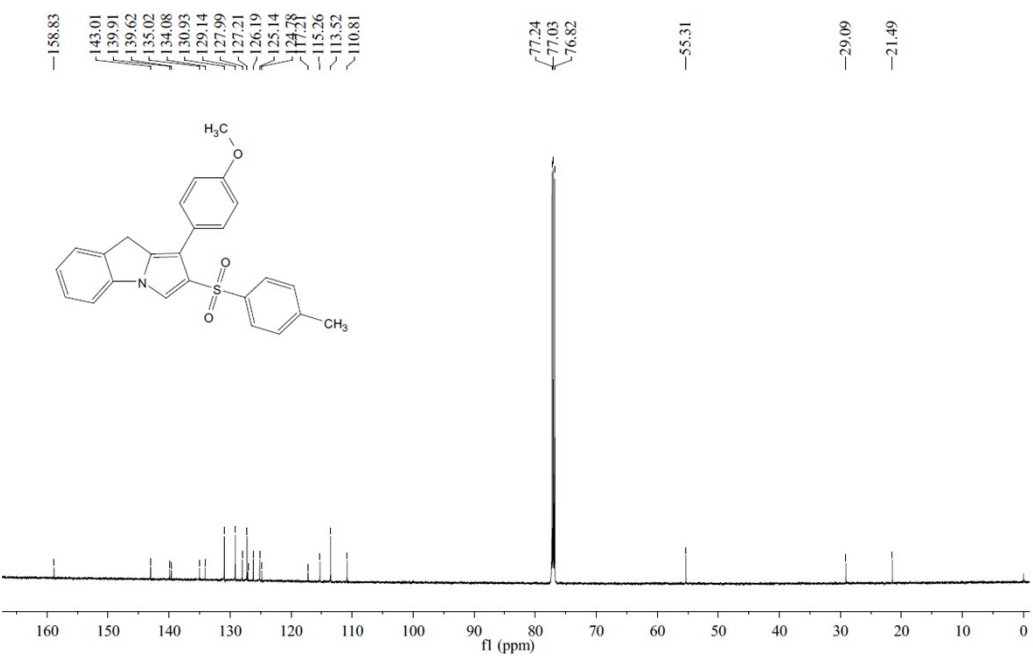
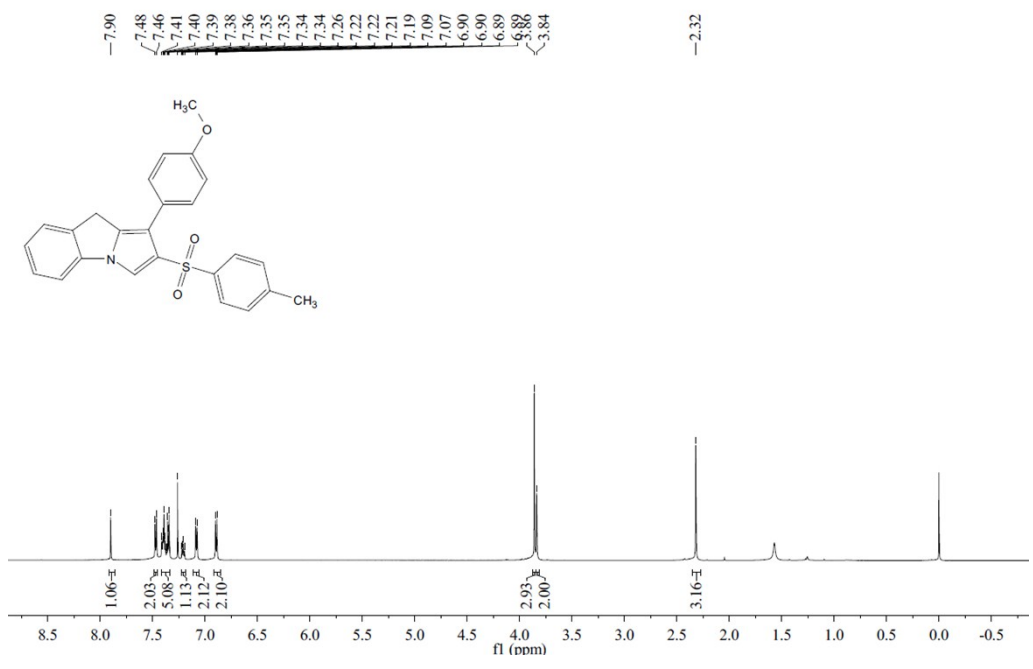




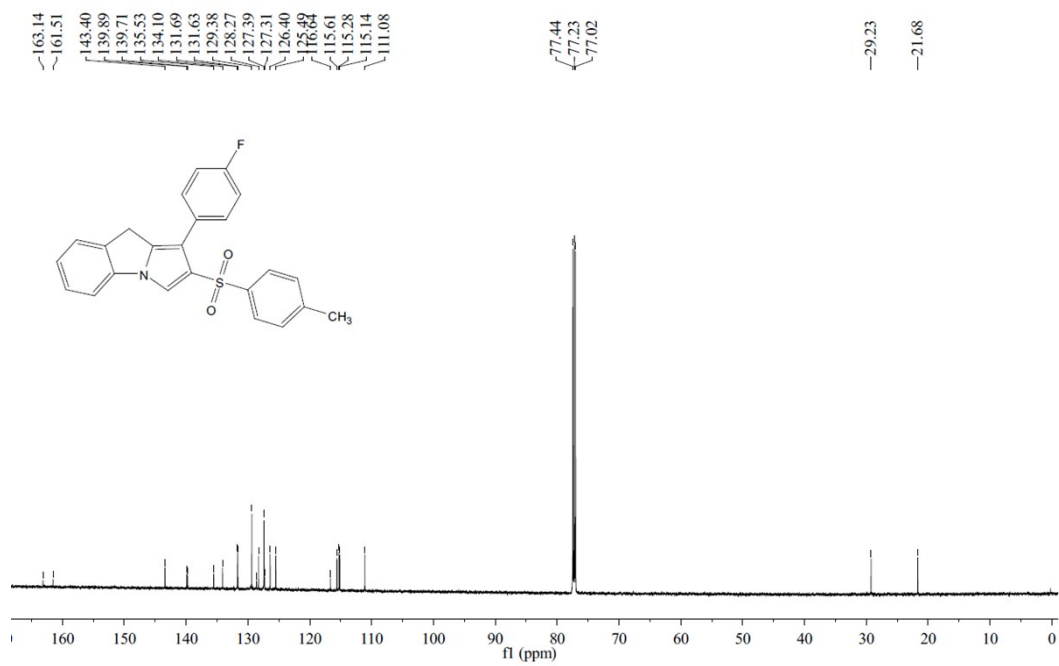
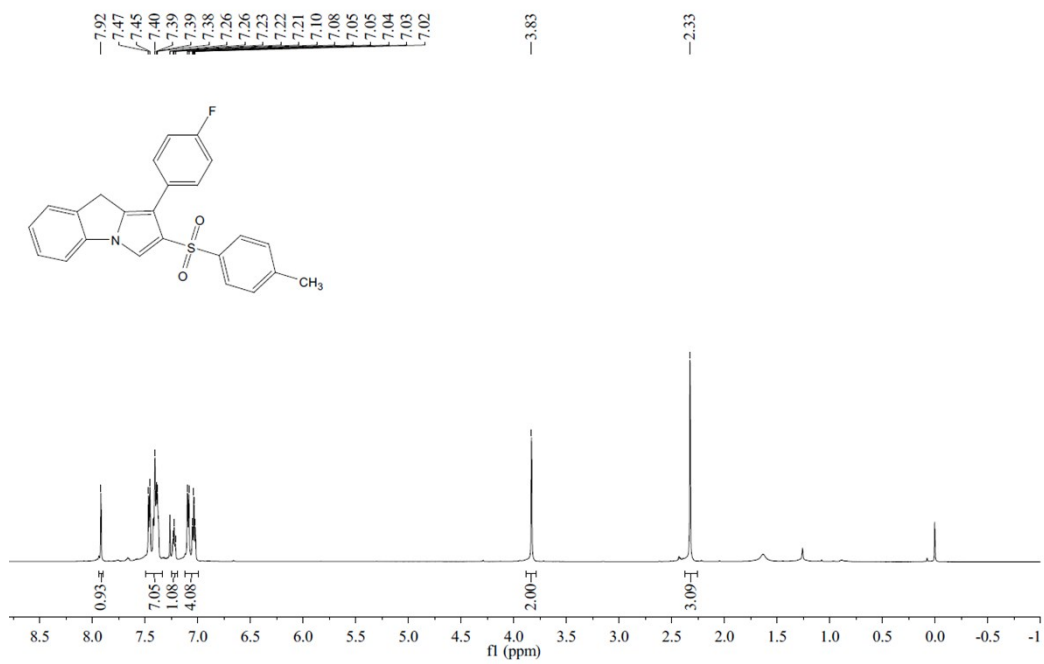
3i

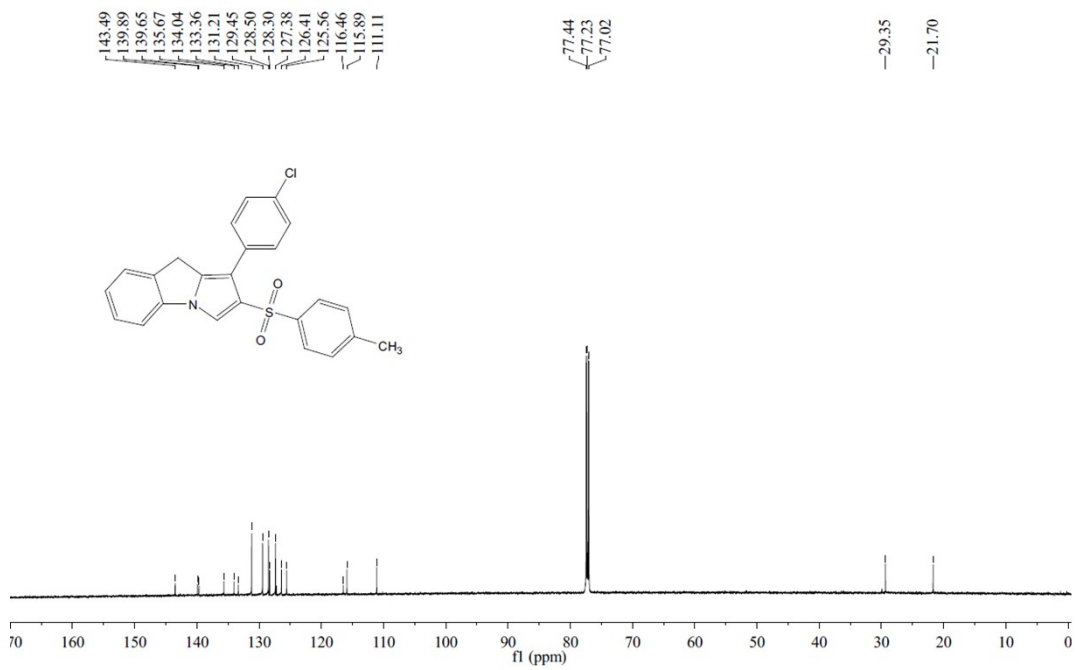
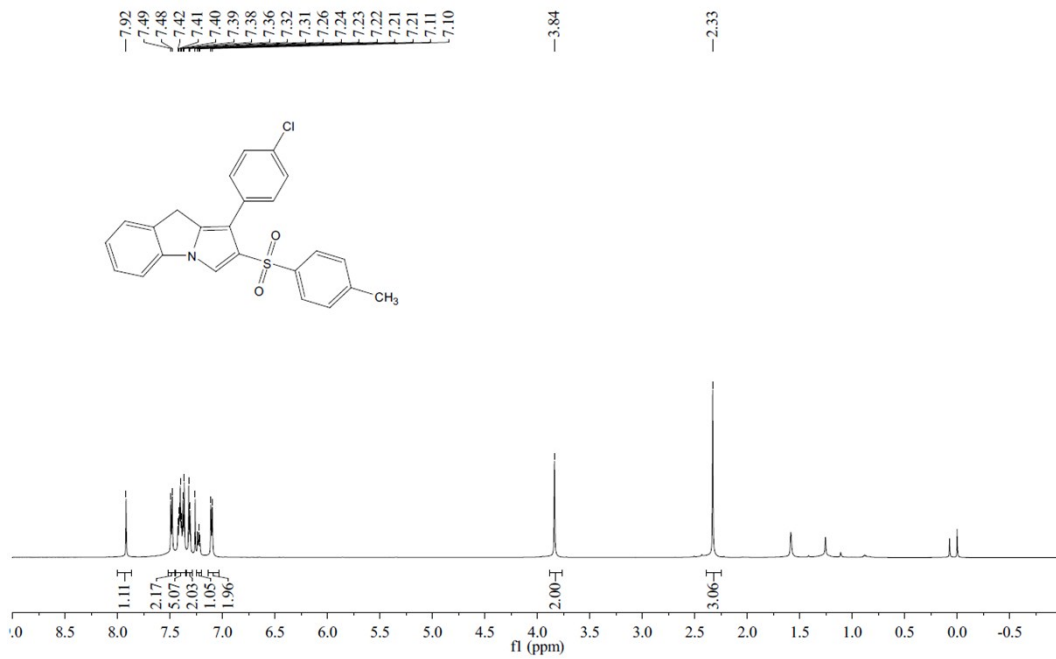


3j

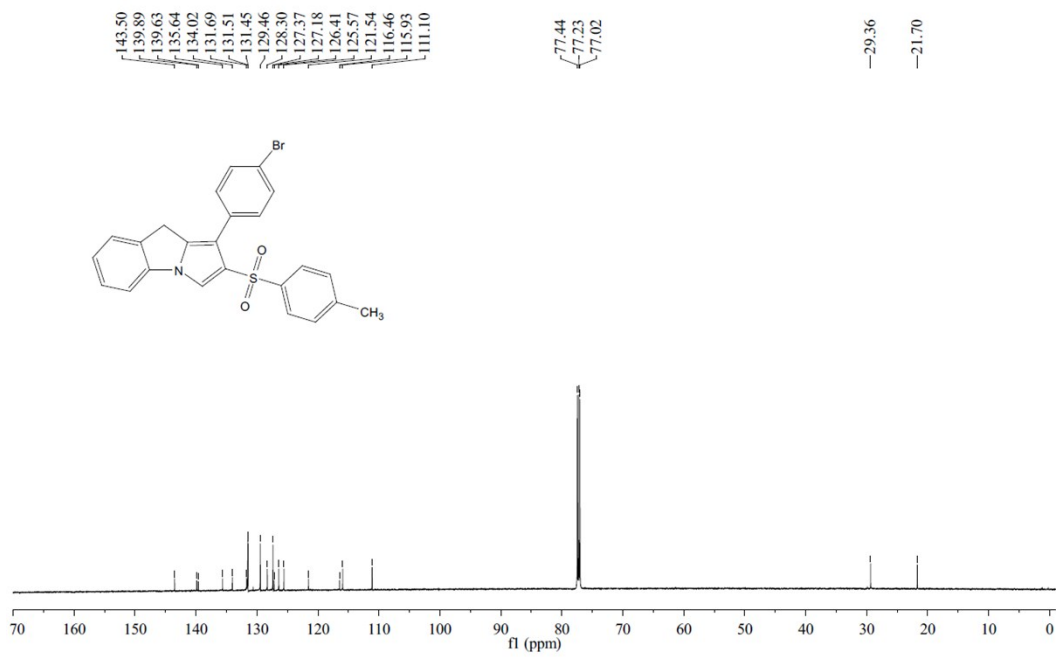
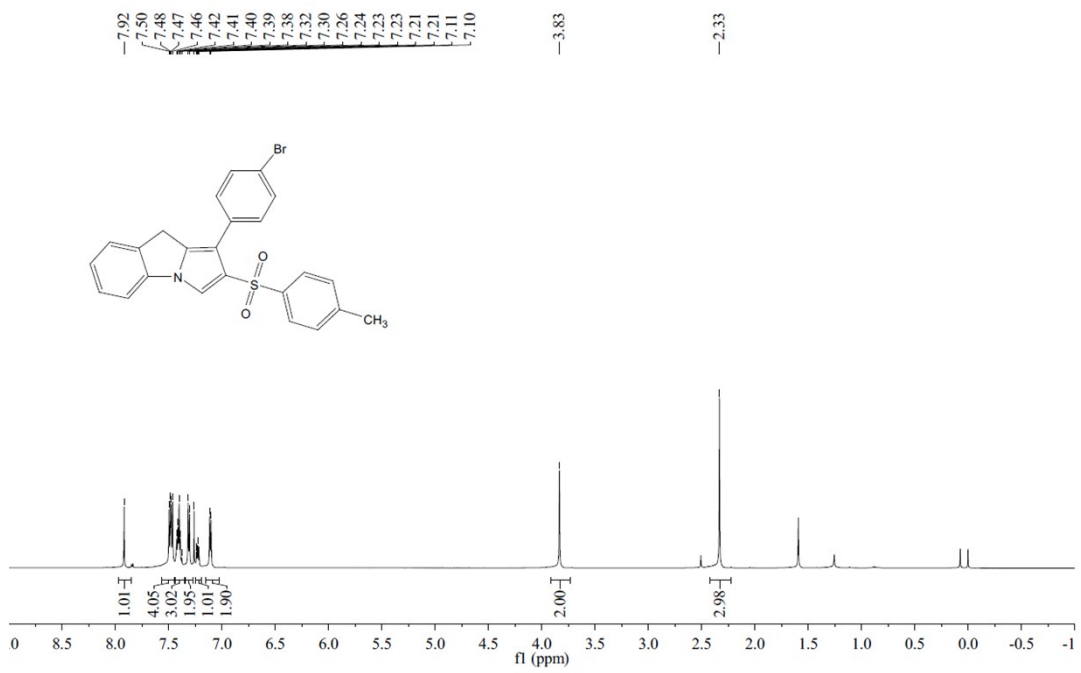


3k

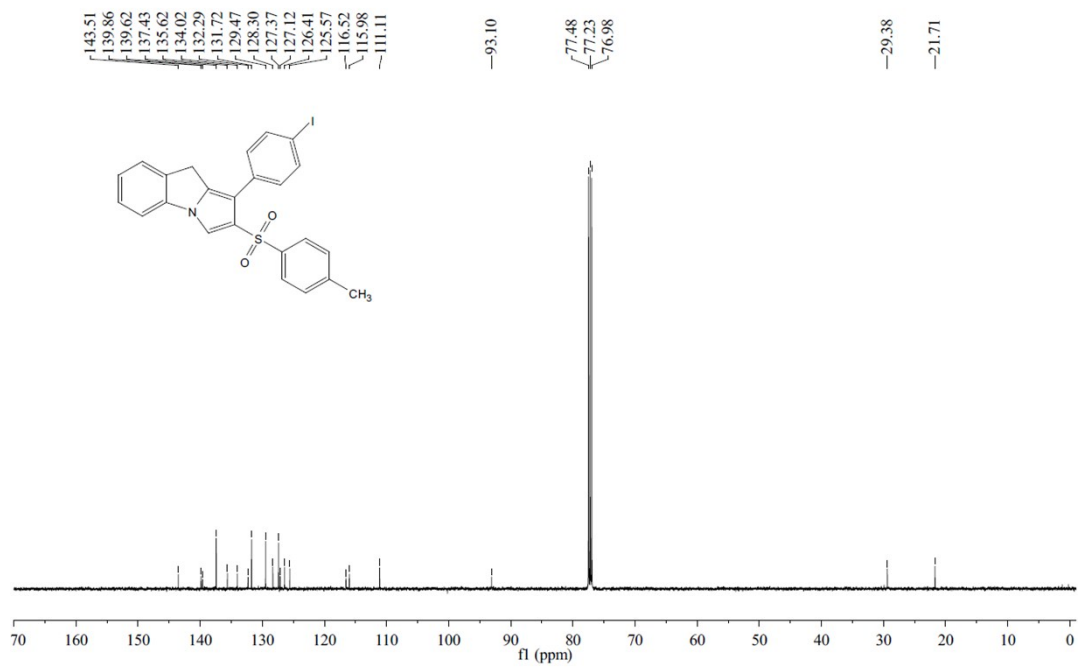
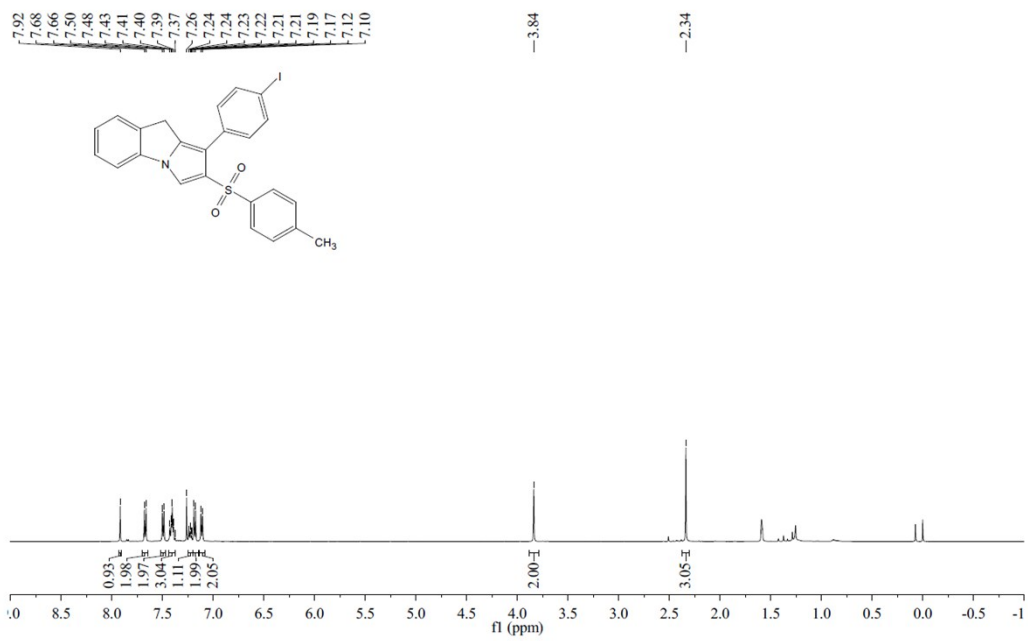


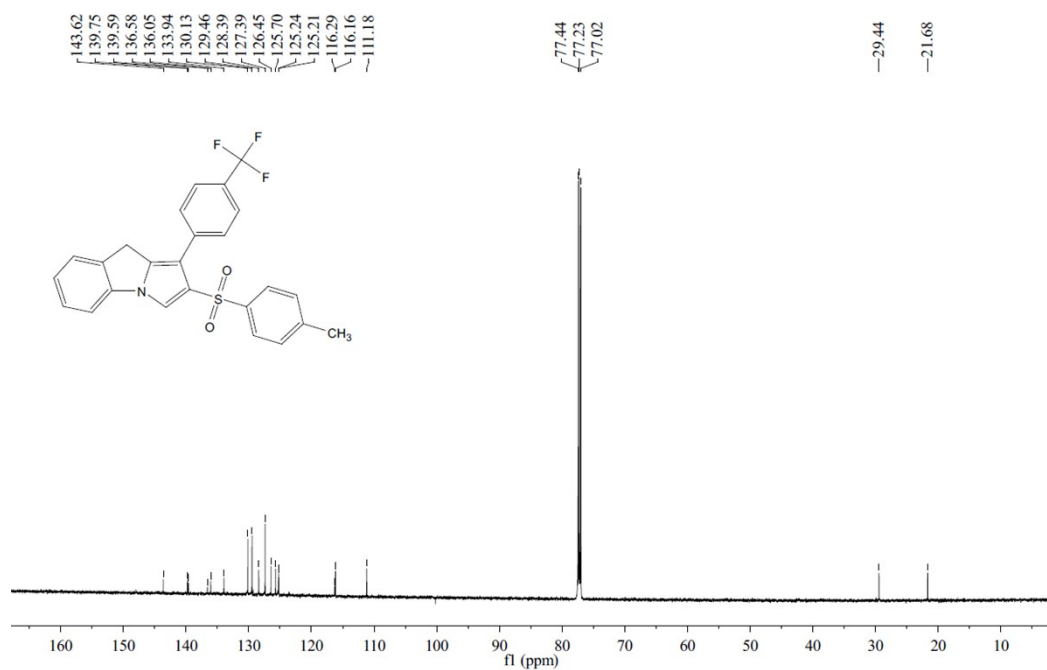
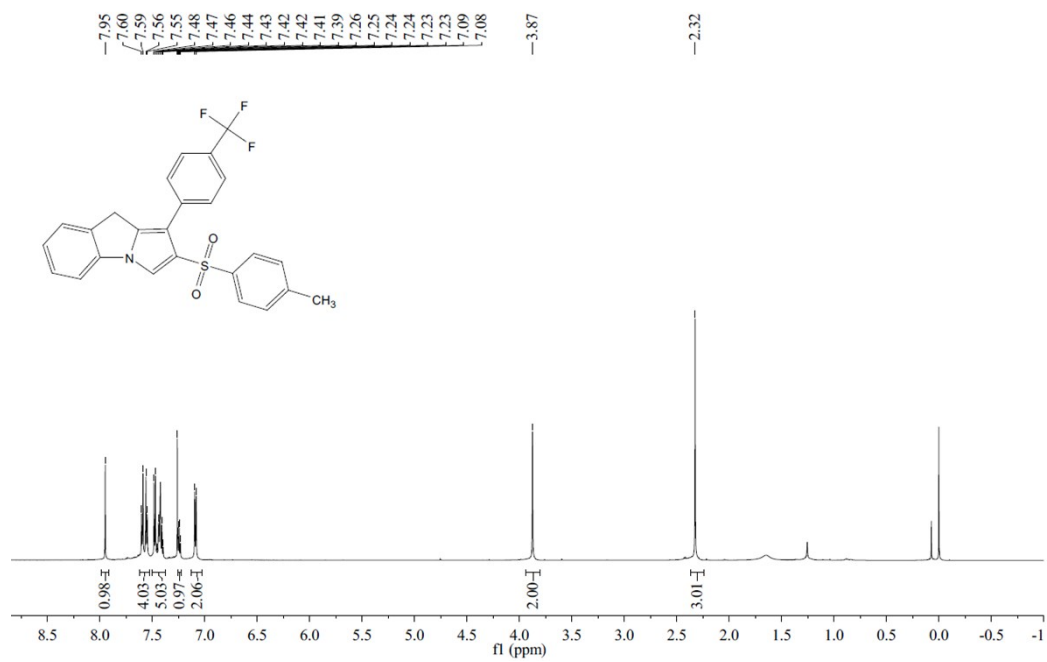


**3m**



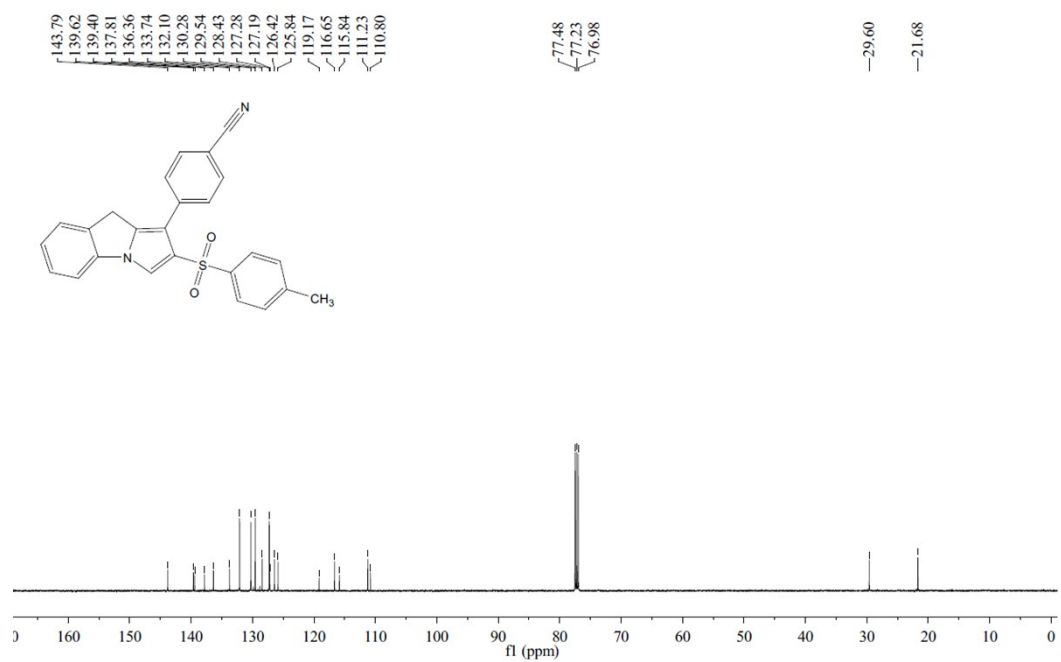
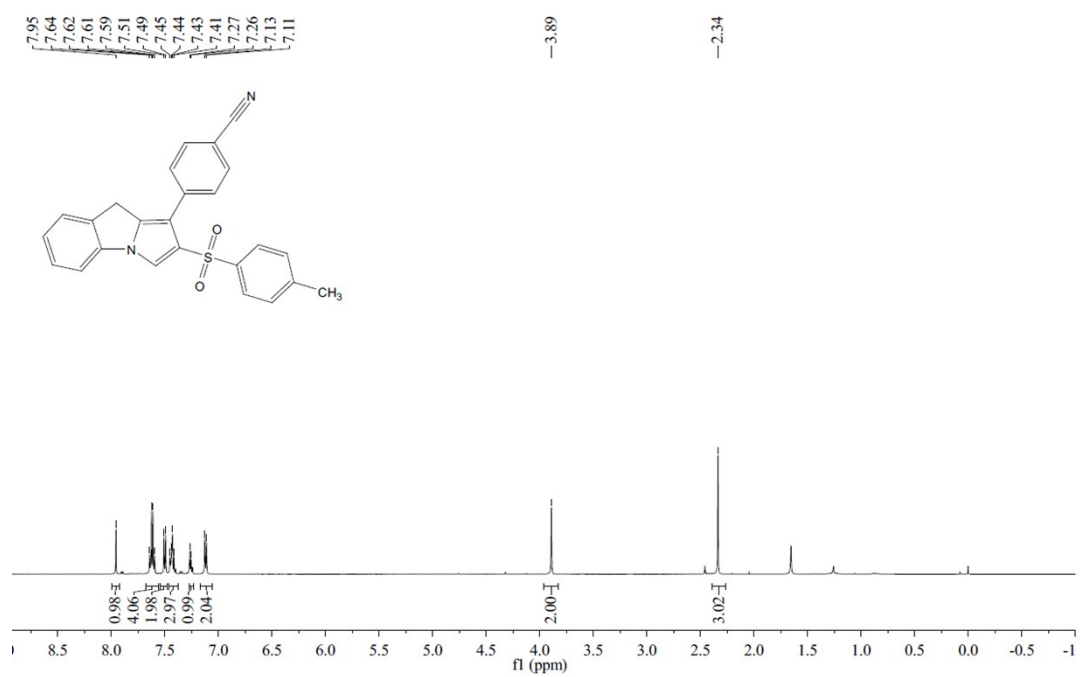
**3n**



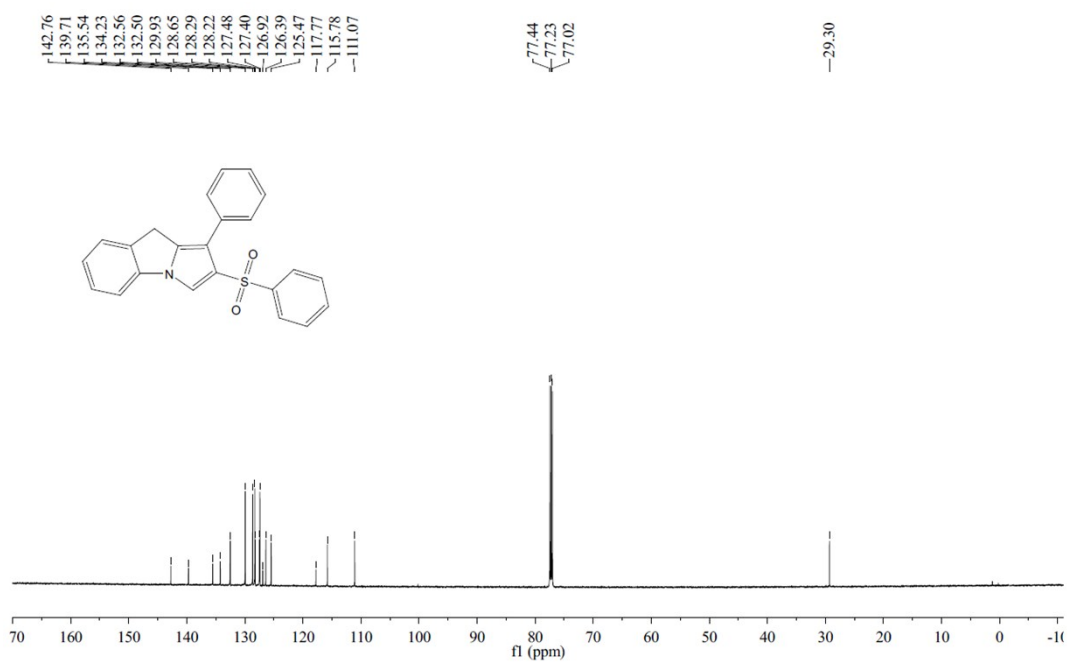
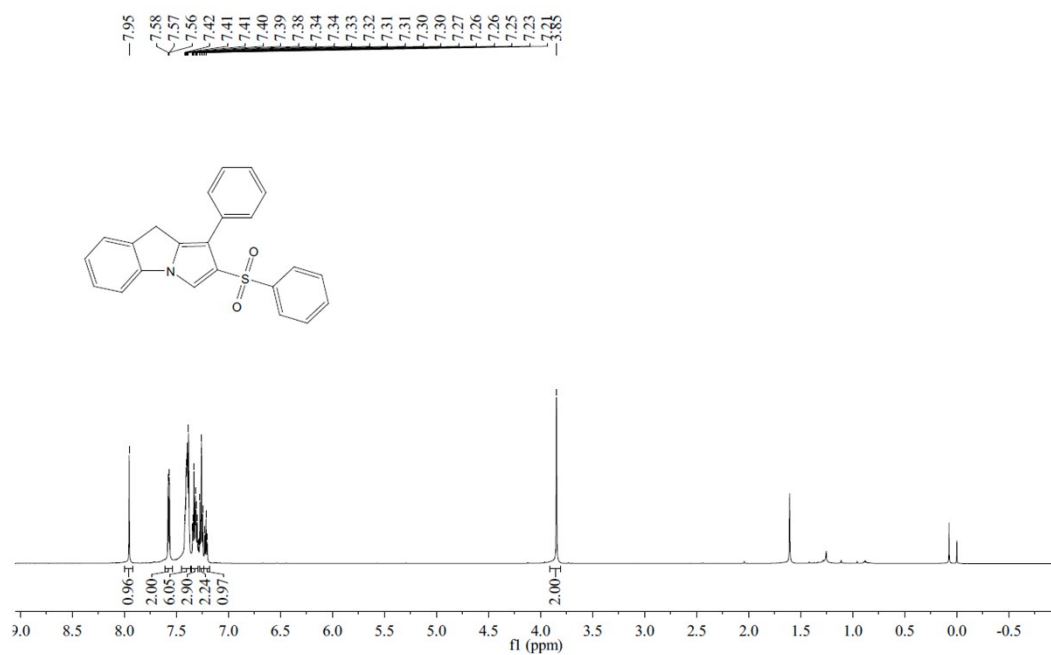


3p

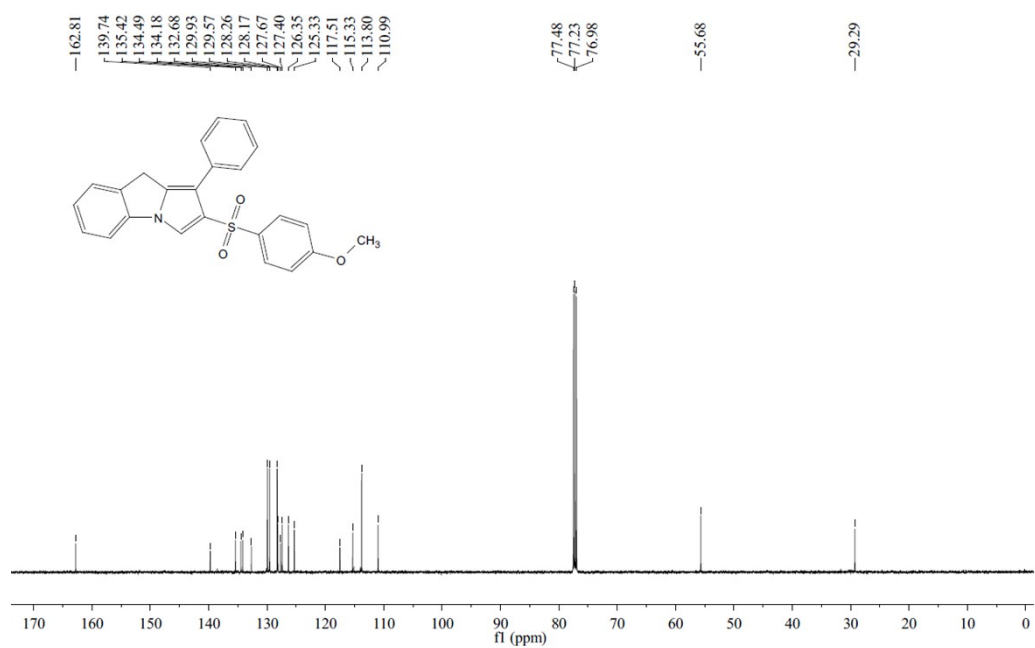
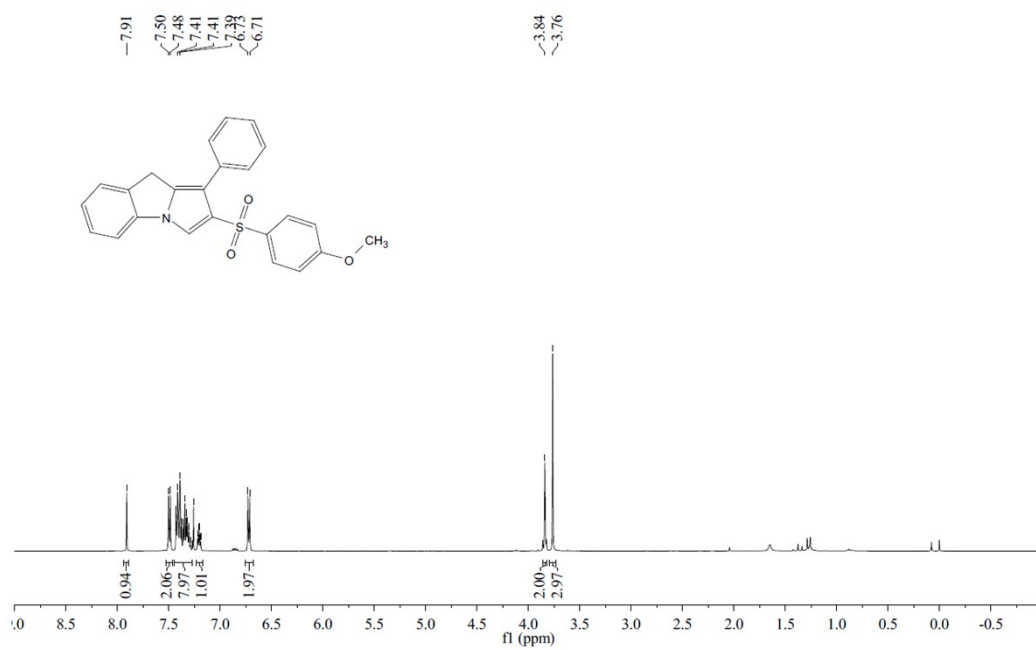




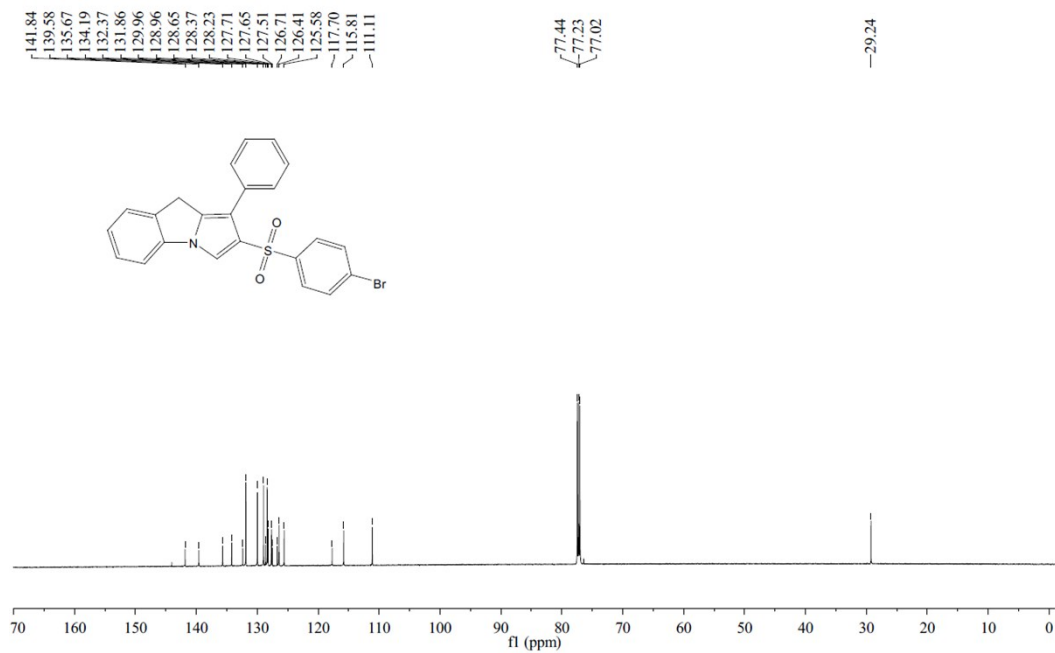
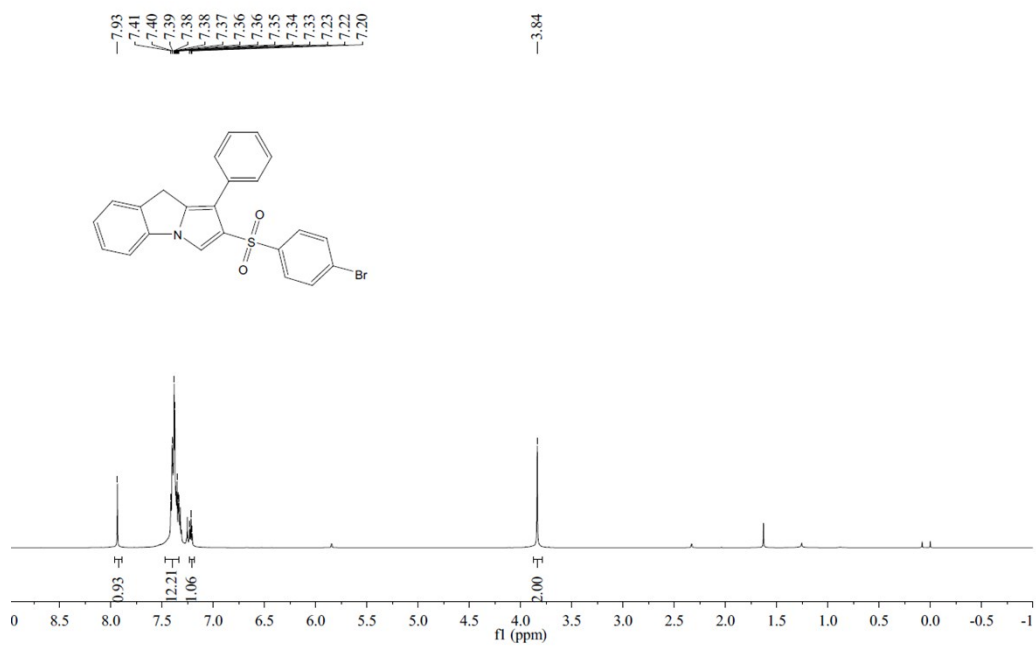
3q



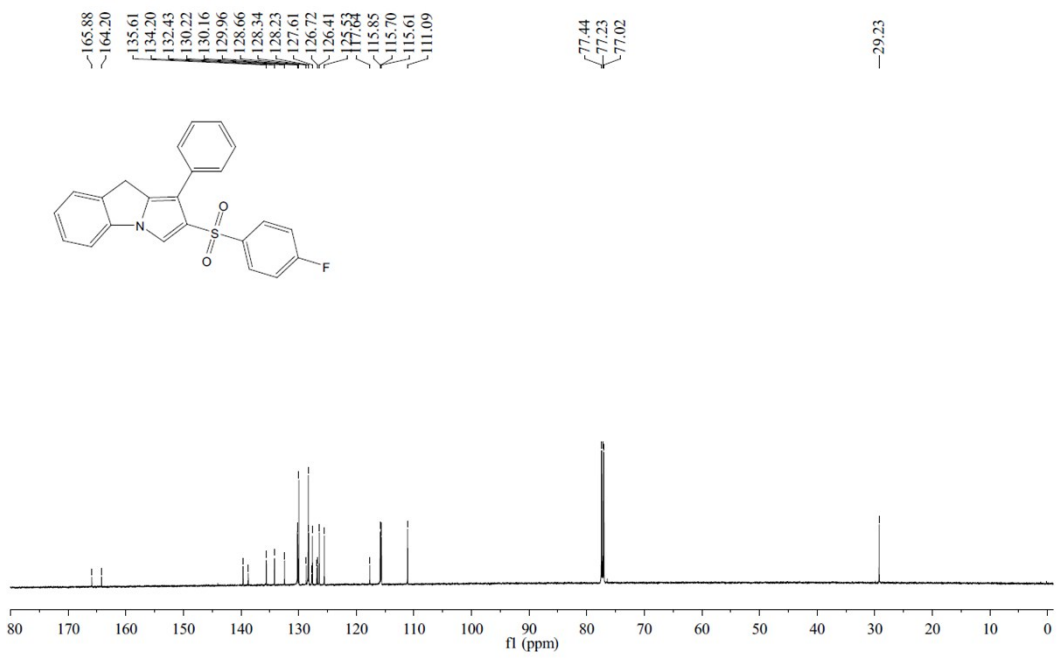
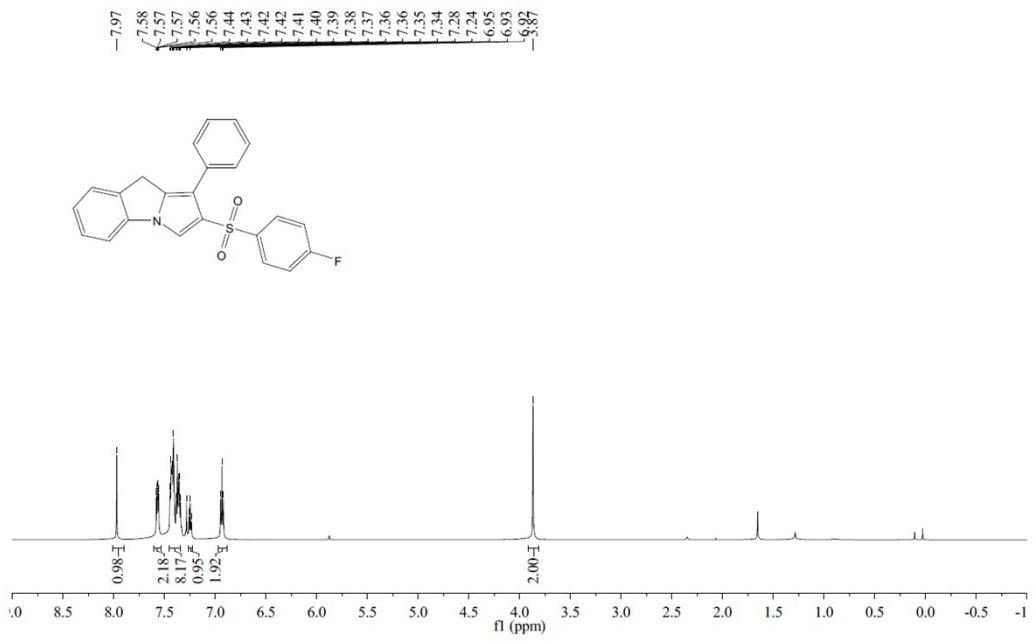
**3r**



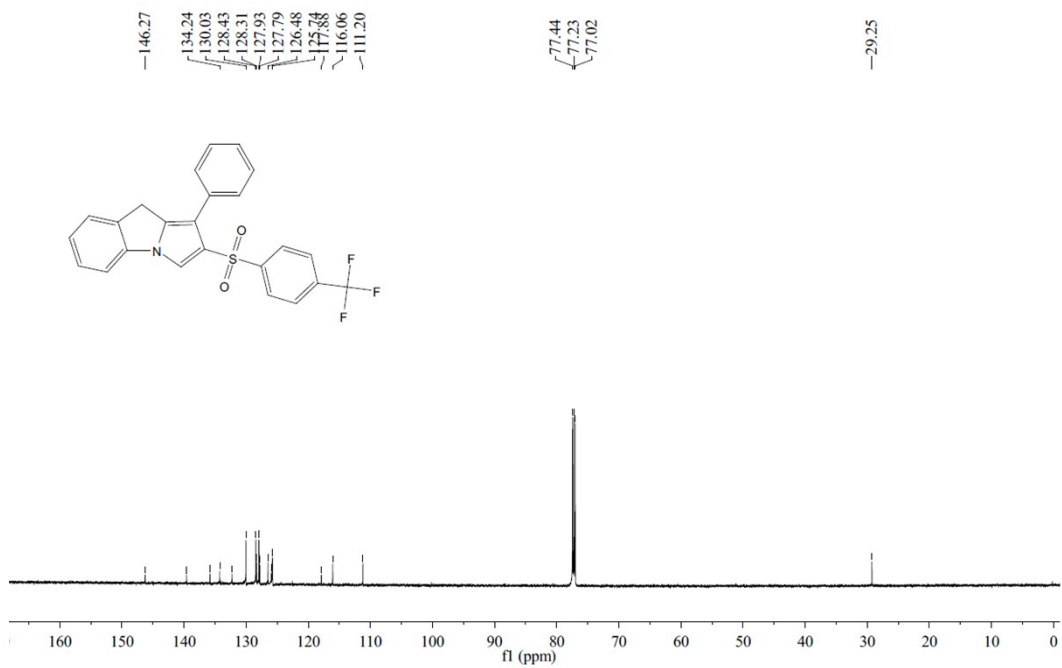
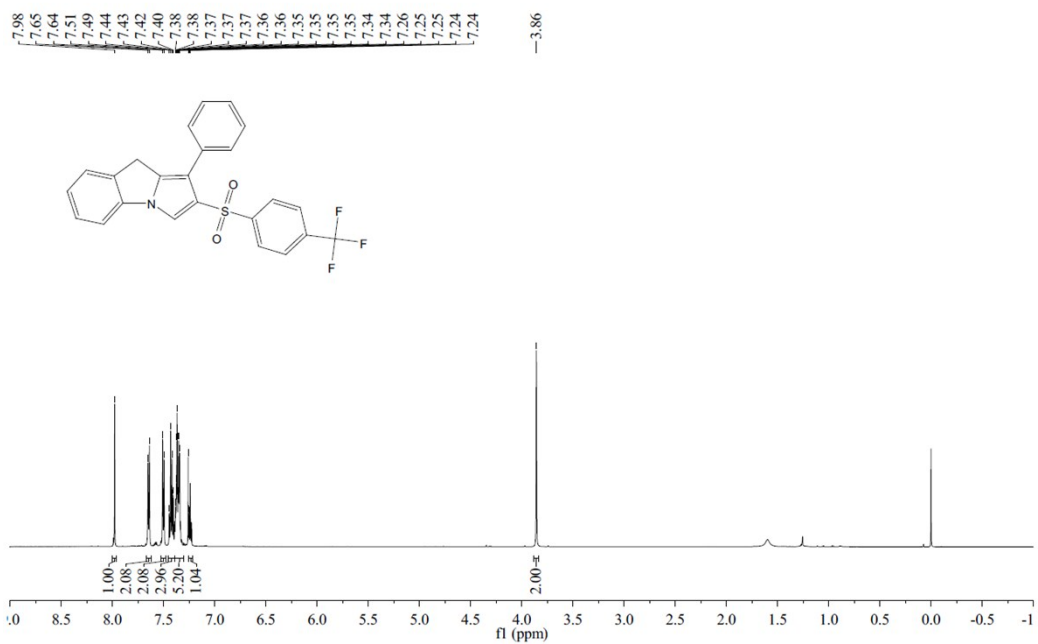
3s



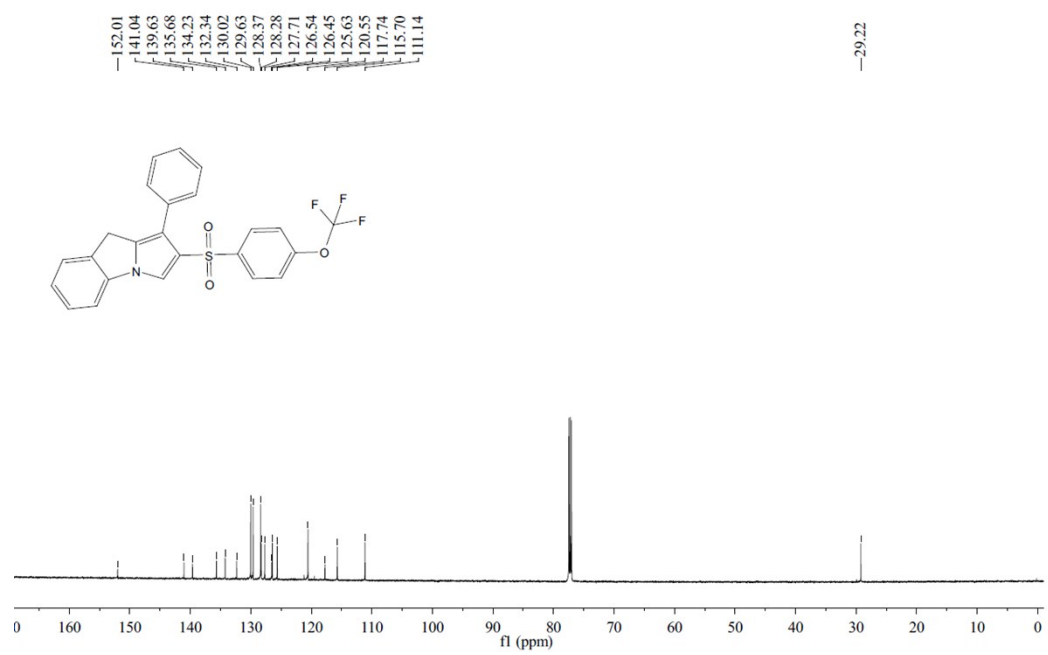
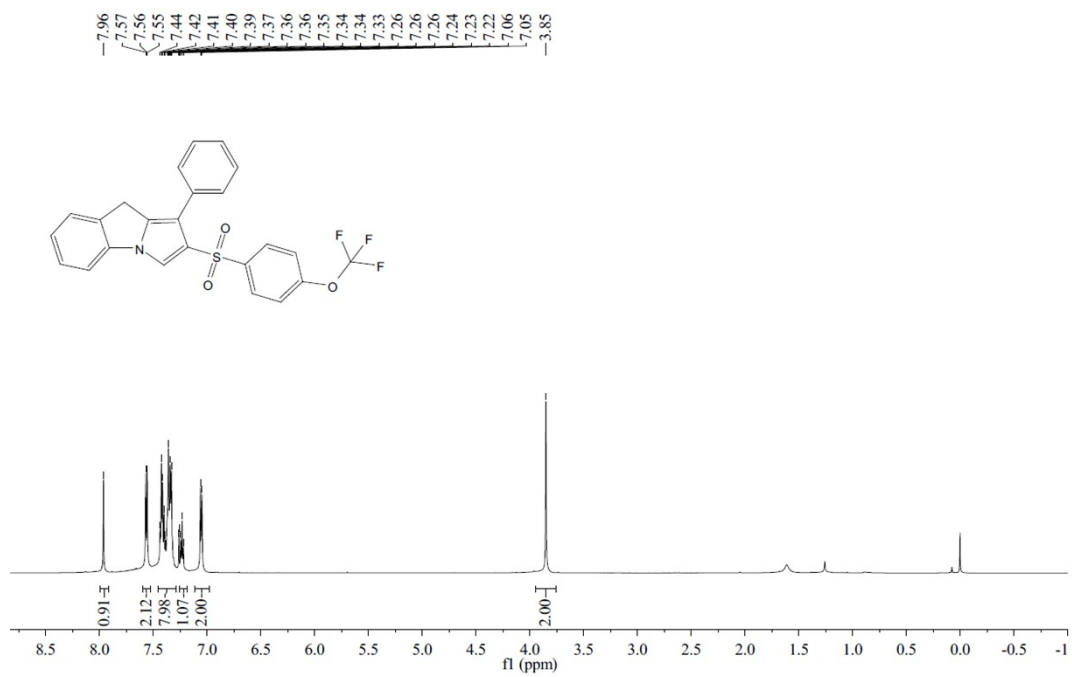
**3t**



**3u**



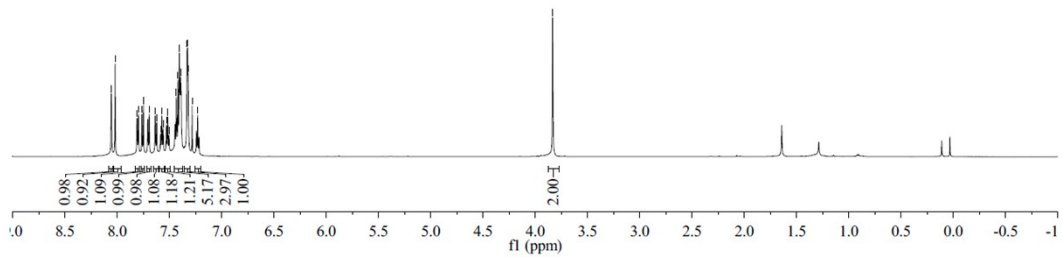
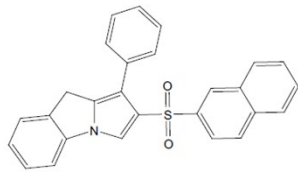
3v



3w

8.06  
8.02  
7.81  
7.80  
7.76  
7.75  
7.69  
7.63  
7.62  
7.62  
7.58  
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7.56  
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7.33  
7.33  
7.32  
7.28  
7.23

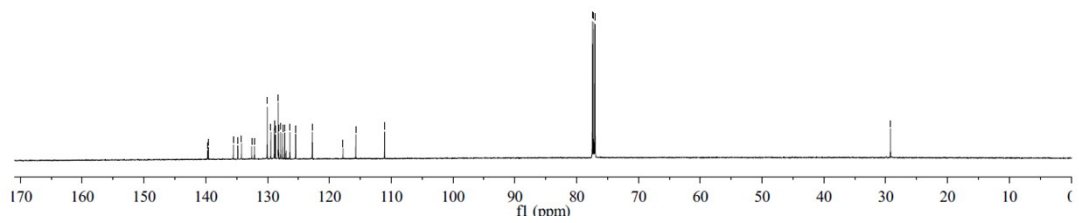
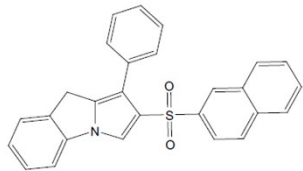
-3.83



139.70  
139.58  
135.53  
134.81  
134.21  
132.57  
132.13  
130.04  
129.47  
128.90  
128.87  
128.72  
128.26  
128.20  
127.86  
127.55  
127.21  
126.37  
125.45  
122.77  
117.79  
115.73  
111.07

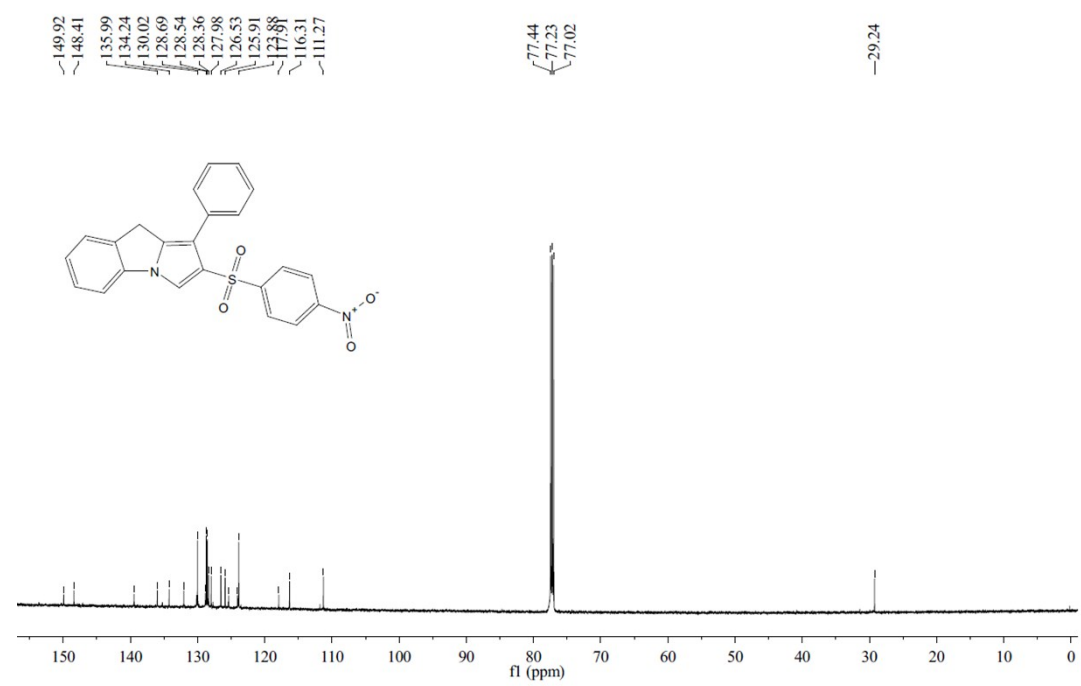
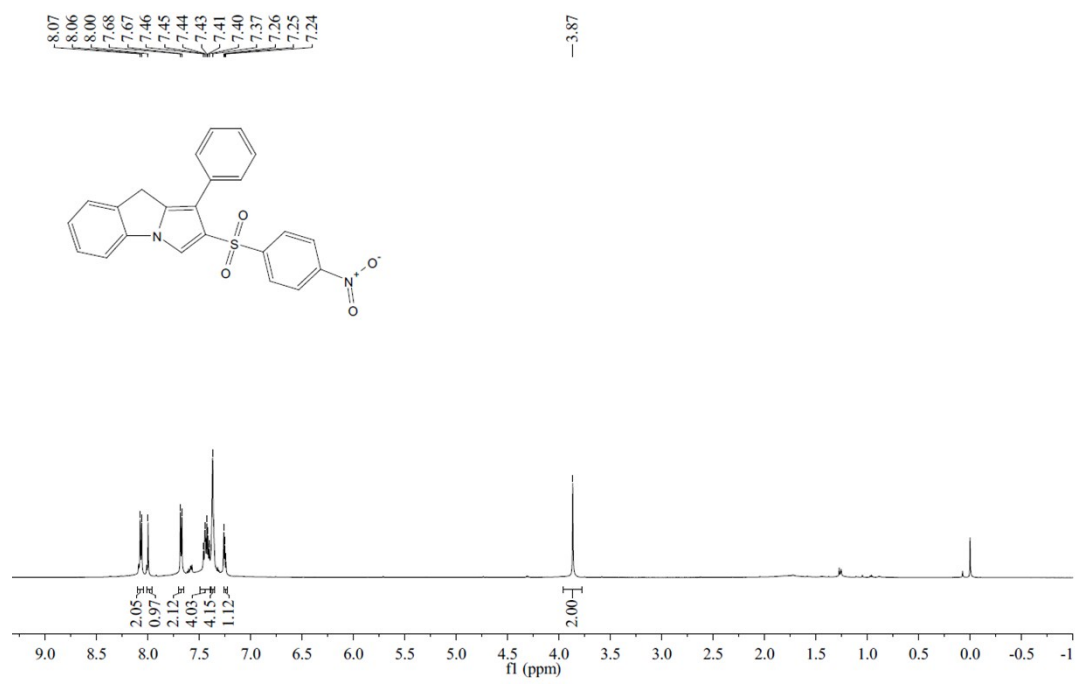
77.44  
77.23  
77.02

-29.21



3x





3y

