Supporting information

Table of Contents

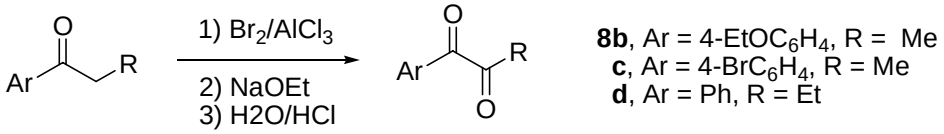
1. Experimental section — Page 1 ─ Page 6
2. Crystallography data of Compound **12** — Page 6 ─ Page 6
3. Copies of ^{1}H and ^{13}C NMR Spectra — Page 7 ─ Page 29
4. Copies of HRMS spectra — Page 30 ─ Page 39

1. Experimental section

1.1 General Methods

All reagents and solvents were commercial grade and purified prior to use when necessary. NMR spectra were acquired on a Varian 400 MHz instrumental. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.0 ($CDCl_3$), δ 2.50 and δ 39.52 (DMSO-d_6). HRMS was performed on a Varian QFT-ESI instrumental. Melting points were determined on a Taike X-4 melting point apparatus. All temperatures were uncorrected.

1.2 Preparation of 1-arylpropan-1,2-diones 8b-d [1,2]



8b, Ar = 4-$EtOC_6H_4$, R = Me
c, Ar = 4-BrC_6H_4, R = Me
d, Ar = Ph, R = Et

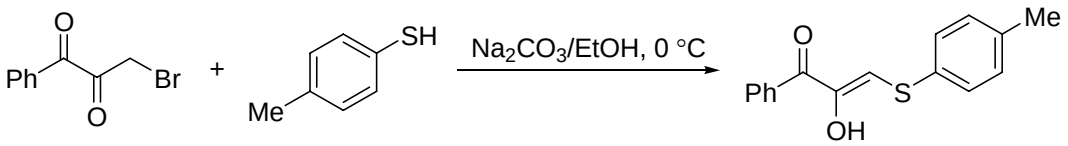
To a mixture of the corresponding ketone (30 mmol) and anhydrous aluminum chloride (0.15 g) in ether (45 mL) was added bromine (11.5 g, 72 mmol) at a rate to maintain a gentle reflux. When the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure to obtain an oil. The oil was slowly added to a solution of sodium ethoxide in ethanol (formed by 72 mmol of sodium and 45 mL of ethanol) and the resulting mixture was stirred at room temperature for 1 h. Then, concentrated hydrochloric acid (15 mL) was added and the mixture was stirred at room temperature for 3 h. The precipitate was filtered off and the filtrate was diluted with 30 mL of water, and extracted with methylene chloride (3×15 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (200–300 mesh, eluted with petroleum ether:ethyl acetate = 20:1) to afford the target compound **8**.

1-(4-Ethoxyphenyl)propane-1,2-dione (**8b**): Yellow liquid, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.4 Hz, 2 H), 6.95 (d, J = 8.4 Hz, 2 H), 4.11 (q, J = 6.8 Hz, 2 H), 2.48 (s, 3 H), 1.44 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 201.2, 190.0, 164.2, 132.8, 124.4, 114.6, 63.9, 26.4, 14.5.

1-(4-Bromophenyl)propane-1,2-dione (**8c**): Yellow liquid, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H), 2.48 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 199.6, 189.5, 132.0, 131.7, 130.5, 130.0, 26.1.

1-Phenylbutane-1,2-dione (**8d**): Pale yellow liquid, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 2 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.58 (t, J = 7.6 Hz, 2 H), 2.92 (q, J = 7.2 Hz, 2 H), 1.20 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 203.7, 192.4, 134.4, 131.9, 130.0, 128.7, 32.0, 6.7.

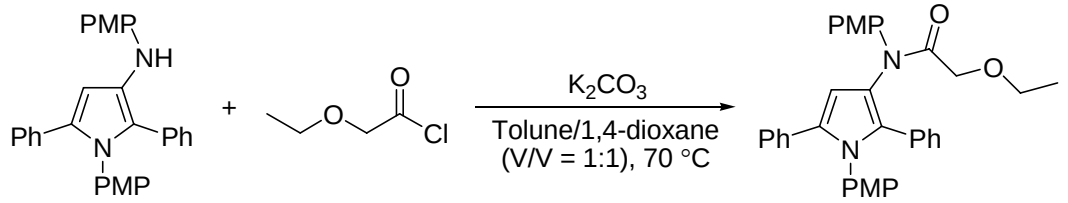
1.3 3-(p-Tolylthio)-1-(4-bromophenyl)-2-hydroxyprop-2-en-1-one (8e):



8e

To a solution of 4-methylbenzenethiol (5 mmol) in ethanol (20 mL) was added aqueous sodium carbonate (6 mmol of sodium carbonate in 15 mL of water). Then, to the resulting mixture was added dropwise a solution of 3-bromo-1-phenylpropane-1,2-dione (5 mmol) in ethanol (5 mL) at 0 °C. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with water (25 mL), and extracted with methylene chloride (3×20 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh, eluted with petroleum ether:ethyl acetate = 20:1) to afford compound **8e** as a pale yellow oil in 62% yield. NMR analysis indicates that this compound exists predominantly in its enol form. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.6 Hz, 2 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 6.96 (s, 1 H), 6.57 (s, 1 H), 2.34 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 187.8, 144.8, 138.3, 135.7, 132.1, 130.8, 130.2, 130.2, 128.8, 128.4, 123.2, 21.1.

1.4 Preparation of 2-ethoxy-*N*-(4-methoxyphenyl)-*N*-(1-(4-methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-yl)acetamide (12):



11a PMP = 4-Methoxyphenyl **12**

To a stirring mixture of ,1-bis(4-methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine **11a** (447 mg, 1 mmol), potassium carbonate (415 mg, 3 mmol) in toluene/1,4-dioxane (40 mL, V/V = 1:1) was added 2-ethoxyacetyl chloride (147 mg, 1.2 mmol) in one portion. The resulting mixture was stirred under a nitrogen atmosphere at 70 °C for 5 h. After cooling to room temperature, the reaction mixture was quenched with water (20 mL) and extracted with methylene choride (3×30 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh, eluted with petroleum ether/ethyl acetate = 6:1) to afford the corresponding amide **12** as a white solid. 383 mg, 72% yield, m.p. 95–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.26 (m, 10 H), 7.68–6.90 (m, 8 H), 6.47 (s, 1 H), 4.13 (s, 2 H), 3.75 (s, 3 H), 3.73 (s, 3 H), 3.50 (q, *J* = 6.8 Hz, 2 H), 1.93 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.3, 158.5, 157.0, 136.0, 134.1, 132.1, 131.4, 130.9, 130.5, 130.1, 129.8, 129.6, 128.4, 128.0, 127.4, 126.7, 126.2, 123.5, 114.4, 113.8, 113.7, 108.6, 107.6, 69.4, 66.8, 55.3, 55.2, 15.0. HRMS (ESI) *m/z* calc'd for $C_{37}H_{33}N_2O_2S$ $[M+H]^+$: 533.2435, found 533.2437.

1.5 General procedure for the synthesis of polysubstituted pyrroles 11

To a solution of 1,2-dione **8** (0.2 mmol), arylamine **9** (0.44 mmol), and aldehyde **10** (0.2 mmol) in acetonitrile (1 mL) was added 4-methylbenzenesulfonic acid monohydrate (20 mol%) at room temperature. The resulting mixture was stirred for the total consumption of 1,2-dione **8**

(Monitored by TLC). Work-up procedure A: After completion of the reaction, the product was precipitated by the addition of 1 mL of petroleum ether followed by cooling to 0 °C. The precipitate was filtered off, and washed with cold petroleum ether to afford the pure product (Table 2, entries 1, 5–9, 11 and 12). Work-up procedure B: After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel (200–300 mesh, eluted with petroleum ether:ethyl acetate = 20:1) to afford polysubstituted pyrrole **11** (Table 2, entries 3, 4, 9, and 12–17).

N,1-Bis(4-methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (**11a**): Yellow solid, m.p. 158–160 °C, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05–7.15 (m, 6 H), 6.96–7.05 (m, 4 H), 6.84 (d, *J* = 9.2 Hz, 2 H), 6.83 (d, *J* = 9.2 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 6.43 (s, 1 H), 5.02 (s, 1 H), 3.68 (s, 3 H), 3.67 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.2, 152.7, 140.9, 133.1, 132.9, 131.7, 131.4, 130.0, 129.8, 128.5, 128.1, 127.9, 126.3, 126.1, 126.1, 115.9, 114.7, 113.7, 105.3, 55.7, 55.3. HRMS (ESI) *m/z* calc'd for $C_{30}H_{27}N_2O_2$ $[M+H]^+$: 447.2067, found 447.2068.

N,1-Bis(3-methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (**11b**): Yellow solid, m.p. 123–125 °C, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05–7.22 (m, 12 H), 6.75 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.59 (d, *J* = 8.0 Hz, 1 H), 6.57 (s, 1 H), 6.50–6.54 (m, 3 H), 6.34 (dd, *J* = 8.4, 2.0 Hz, 1 H), 5.27 (s, 1 H), 3.77 (s, 3 H), 3.53 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 160.8, 159.5, 148.6, 139.6, 133.1, 132.8, 131.2, 130.0, 129.9, 129.2, 128.8, 128.5, 128.4, 128.1, 127.9, 127.1, 126.6, 126.4, 125.8, 124.8, 121.2, 114.2, 114.1, 113.3, 107.2, 106.6, 103.2, 100.1, 55.2, 55.1. HRMS (ESI) *m/z* calc'd for $C_{30}H_{27}N_2O_2$ $[M+H]^+$: 447.2067, found 447.2073.

N,1-Bis(2-methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (**11c**): Redish brown solid, m.p. 116–118 °C, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.25 (m, 12 H), 7.01 (dd, *J* = 7.6, 1.6 Hz, 1 H), 6.88 (dt, *J* = 8.0, 1.2 Hz, 1 H), 6.78–6.84 (m, 3 H), 6.72 (dt, *J* = 8.0, 1.2 Hz, 1 H), 6.61 (s, 1 H), 5.83 (s, 1 H), 3.83 (s, 3 H), 3.40 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.5, 146.9, 137.2, 133.6, 133.4, 131.7, 130.8, 129.4, 129.0, 128.1, 127.9, 127.8 (2 C), 127.7, 126.2, 126.1, 124.5, 121.1, 120.5, 117.0, 112.1, 112.1, 110.0, 106.0, 55.6, 55.3. HRMS (ESI) *m/z* calc'd for $C_{30}H_{27}N_2O_2$ $[M+H]^+$: 447.2067, found 447.2075.

2,5-Diphenyl-*N*,1-di(*p*-tolyl)-1*H*-pyrrol-3-amine (**11d**): Yellow solid, m.p. 154–156 °C, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.21 (m, 6 H), 7.04–7.11 (m, 4 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 6.89 (d, *J* = 8.0 Hz, 2 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.56 (s, 1 H), 5.19 (s, 1 H), 2.31 (s, 3 H), 2.28 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.7, 136.7, 136.1, 133.0 (2 C), 131.4, 130.1, 129.7, 129.2, 128.5, 128.0, 127.9, 127.4, 126.5, 126.4, 126.2, 126.0, 125.6, 114.4, 105.9, 21.1, 20.5. HRMS (ESI) *m/z* calc'd for $C_{30}H_{27}N_2$ $[M+H]^+$: 415.2169, found 415.2167.

N,1-Bis(4-butylphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (**11e**): Yellow solid, m.p. 96–98 °C, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.19 (m, 6 H), 7.04–7.10 (m, 4 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 6.58 (s, 1 H), 5.04 (br. s, 1 H), 2.57 (t, *J* = 7.6 Hz, 2 H), 2.54 (t, *J* = 7.6 Hz, 2 H), 1.52–1.62 (m, 4 H), 1.26–1.42 (m, 4 H), 0.93 (t, *J* = 7.6 Hz, 3 H), 0.92 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.8, 141.7, 136.3, 133.0, 132.7, 131.4, 130.1, 129.0, 128.6 (2 C), 128.5, 128.0, 127.9, 126.4, 126.3, 126.1, 125.9, 125.7, 114.4, 105.8, 35.1, 34.8, 34.0, 33.3, 22.4, 22.1, 14.0, 13.9. HRMS (ESI) *m/z* calc'd for $C_{36}H_{39}N_2$ $[M+H]^+$: 499.3108, found 499.3118.

N,1,2,5-Tetraphenyl-1*H*-pyrrol-3-amine (**11f**): Yellow solid, m.p. 147–148 °C, 84% yield. ^{1}H

NMR (400 MHz, $CDCl_3$): δ 7.17–7.24 (m, 11 H), 7.00–7.10 (m, 6 H), 6.96 (d, *J* = 8.0 Hz, 2 H), 6.79 (t, *J* = 7.2 Hz, 1 H), 6.60 (s, 1 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.1, 138.7, 133.1, 132.9, 131.2, 130.1, 129.2, 128.9, 128.6 (2 C), 128.0, 127.9, 127.0, 126.5, 126.3, 125.2, 118.2, 114.2, 106.4. HRMS (ESI) *m/z* calc'd for $C_{28}H_{23}N_2$ $[M+H]^+$: 387.1856, found 387.1857.

N,1-Bis(4-fluorophenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (**11g**): Yellow solid, m.p. 190–192 °C, 79% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.09–7.24 (m, 14 H), 6.90 (t, *J* = 8.4 Hz, 2 H), 6.74–6.77 (m, 2 H), 6.44 (s, 1 H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 160.8 (d, *J* = 244.8 Hz), 154.6 (d, *J* = 231.8 Hz), 144.8, 135.0 (d, *J* = 2.8 Hz), 133.3, 132.4, 131.1 (d, *J* = 8.8 Hz), 131.0, 129.9, 129.1, 128.2, 128.1, 127.8, 126.5, 125.5, 125.2, 115.7 (d, *J* = 22.7 Hz), 115.2 (d, *J* = 22.0 Hz), 113.8 (d, *J* = 7.2 Hz), 107.5. HRMS (ESI) *m/z* calc'd for $C_{28}H_{21}F_2N_2$ $[M+H]^+$: 423.1667, found 423.1673.

N,1-Bis(4-methoxyphenyl)-2-phenyl-5-(*p*-tolyl)-1*H*-pyrrol-3-amine (**11h**): Yellow solid, m.p. 178–180 °C, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.21 (m, 14 H), 7.03 (d, *J* = 7.2 Hz, 2 H), 6.99 (s, 4 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 6.47 (s, 1 H), 5.12 (s, 1 H), 3.68 (s, 6 H), 2.29 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.2, 152.7, 141.0, 135.9, 133.3, 131.8, 131.5, 130.1 (2 C), 129.8, 128.7, 128.4, 128.1, 126.3, 125.8, 116.0, 114.7, 113.7, 104.9, 55.8, 55.3, 21.1. HRMS (ESI) *m/z* calc'd for $C_{31}H_{29}N_2O_2$ $[M+H]^+$: 461.2224, found 461.2229.

N,1-Bis(4-methoxyphenyl)-2-phenyl-5-(*o*-tolyl)-1*H*-pyrrol-3-amine (**11i**): Yellow solid, m.p. 107–109 °C, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04–7.21 (m, 9 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.0 Hz, 2 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 6.59 (d, *J* = 8.8 Hz, 2 H), 6.32 (s, 1 H), 5.14 (s, 1 H), 3.77 (s, 3 H), 3.70 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.7, 152.7, 141.1, 137.9, 133.1, 132.6, 131.8, 131.7, 129.7 (2 C), 129.1, 128.1, 127.5, 126.1, 125.8, 125.0, 124.3, 115.8, 114.8, 113.4, 106.0, 55.8, 55.2, 20.5. HRMS (ESI) *m/z* calc'd for $C_{31}H_{29}N_2O_2$ $[M+H]^+$: 461.2224, found 461.2232.

5-(3-Chlorophenyl)-*N*,1-bis(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-3-amine (**11j**): Yellow solid, m.p. 134–136 °C, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07–7.20 (m, 8 H), 6.82–6.93 (m, 7 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 6.52 (s, 1 H), 5.24 (s, 1 H), 3.77 (s, 6 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.5, 152.9, 140.7, 134.7, 133.8, 131.6, 131.4, 131.2, 130.1, 129.7, 129.1, 128.3, 128.1, 126.7, 126.6 (2 C), 126.4, 126.1, 116.1, 114.8, 113.9, 105.7, 55.8, 55.3. HRMS (ESI) *m/z* calc'd for $C_{30}H_{26}ClN_2O_2$ $[M+H]^+$: 481.1677, found 481.1680.

N,1-Bis(4-methoxyphenyl)-5-(4-nitrophenyl)-2-phenyl-1*H*-pyrrol-3-amine (**11k**): Yellow solid, m.p. 122–124 °C, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2 H), 7.17–7.26 (m, 5 H), 7.08 (s, 2 H), 6.91–6.96 (m, 4 H), 6.78–6.83 (m, 4 H), 6.68 (s, 1 H), 5.12 (s, 1 H), 3.79 (s, 6 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.8, 153.2, 145.3, 140.2, 139.2, 131.1, 130.6 (2 C), 130.1, 129.7, 128.5, 128.3, 127.9, 127.5, 127.1, 123.5, 116.5, 114.8, 114.2, 107.0, 55.8, 55.4. HRMS (ESI) *m/z* calc'd for $C_{30}H_{26}N_3O_4$ $[M+H]^+$: 492.1918, found 492.1925.

5-(Furan-2-yl)-*N*,1-bis(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-3-amine (**11l**): Yellow solid, m.p. 100–102 °C, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 1.6 Hz, 1 H), 7.11–7.21 (m, 7 H), 6.92 (d, *J* = 9.2 Hz, 2 H), 6.84 (t, *J* = 8.4 Hz, 4 H), 6.70 (s, 1 H), 6.21 (dd, *J* = 3.2, 1.6 Hz, 1 H), 5.32 (d, *J* = 3.6 Hz, 1 H), 5.09 (s, 1 H), 3.82 (s, 3 H), 3.78 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.0, 152.8, 147.5, 140.8, 140.6, 131.7, 130.9, 130.2, 129.8, 128.1, 126.9, 126.5, 126.4, 125.1, 122.3, 116.0, 114.8, 113.9, 110.8, 105.1, 103.9, 55.8, 55.3. HRMS (ESI) *m/z* calc'd for $C_{28}H_{25}N_2O_3$ $[M+H]^+$: 437.1860, found 437.1866.

N,1-Bis(4-methoxyphenyl)-2-phenyl-5-styryl-1*H*-pyrrol-3-amine (**11m**): Redish-brown solid, m.p. 137–139 °C, 54% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.27 (d, *J* = 4.4 Hz, 4 H), 7.06–7.19 (m, 8 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 6.92 (d, *J* = 16.4 Hz, 1 H), 6.83 (s, 1 H), 6.77 (d, *J* = 8.8 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.70 (s, 1 H), 6.62 (d, *J* = 16.4 Hz, 1 H), 3.78 (s, 3 H), 3.65 (s, 3 H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 158.4, 151.3, 141.8, 137.4, 131.8, 131.1, 130.5, 130.0, 129.2, 128.7, 128.1, 127.8, 127.0, 126.9, 126.0, 125.6, 125.4, 117.4, 114.7, 114.5, 114.2, 103.6, 55.3. HRMS (ESI) *m/z* calc'd for $C_{32}H_{29}N_2O_2$ $[M+H]^+$: 473.2224, found 473.2222.

2-(4-Ethoxyphenyl)-*N*,1-bis(4-methoxyphenyl)-5-phenyl-1*H*-pyrrol-3-amine (**11n**): Yellow solid, m.p. 153–155 °C, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.21 (m, 5 H), 6.91–6.98 (m, 6 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 6.73 (d, *J* = 8.4 Hz, 4 H), 6.51 (s, 1 H), 3.97 (q, *J* = 6.8 Hz, 2 H), 3.77 (s, 6 H), 1.39 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.1, 157.5, 152.6, 141.2, 133.0, 132.6, 131.8, 131.4, 129.8, 128.4, 127.9, 126.4, 126.0, 125.8, 123.5, 115.7, 114.7, 114.0, 113.7, 105.3, 63.2, 55.7, 55.3, 14.8. HRMS (ESI) *m/z* calc'd for $C_{32}H_{31}N_2O_3$ $[M+H]^+$: 491.2329, found 491.2338.

2-(4-Bromophenyl)-*N*,1-bis(4-methoxyphenyl)-5-phenyl-1*H*-pyrrol-3-amine (**11o**): Yellow solid, m.p. 150–152 °C, 83% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.36 (d, *J* = 8.4 Hz, 2 H), 7.01–7.22 (m, 9 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.76 (d, *J* = 8.8 Hz, 2 H), 6.71(d, *J* = 8.8 Hz, 2 H), 6.39 (s, 1 H), 3.72 (s, 3 H), 3.64 (s, 3 H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 158.2, 151.3, 141.7, 133.6, 132.5, 131.6, 131.2, 130.7, 130.1, 128.1, 128.0, 126.9, 126.5, 126.3, 119.4, 114.5, 114.0, 106.6, 55.3, 55.2. HRMS (ESI) *m/z* calc'd for $C_{30}H_{26}BrN_2O_2$ $[M+H]^+$: 525.1172, found 525.1178.

N,1-Bis(4-methoxyphenyl)-4-methyl-2,5-diphenyl-1*H*-pyrrol-3-amine (**11p**): Yellow solid, m.p. 67–69 °C, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.24 (m, 8 H), 7.01 (d, *J* = 6.8 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 5.01 (s, 1 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 2.03 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.8, 152.1, 142.6, 132.7, 132.0, 131.5, 130.6, 129.8, 129.8, 128.7, 127.8, 127.7, 126.2, 124.4, 115.9, 114.7, 114.6, 113.5, 55.7, 55.2, 9.7. HRMS (ESI) *m/z* calc'd for $C_{31}H_{29}N_2O_2$ $[M+H]^+$: 461.2224, found 461.2230.

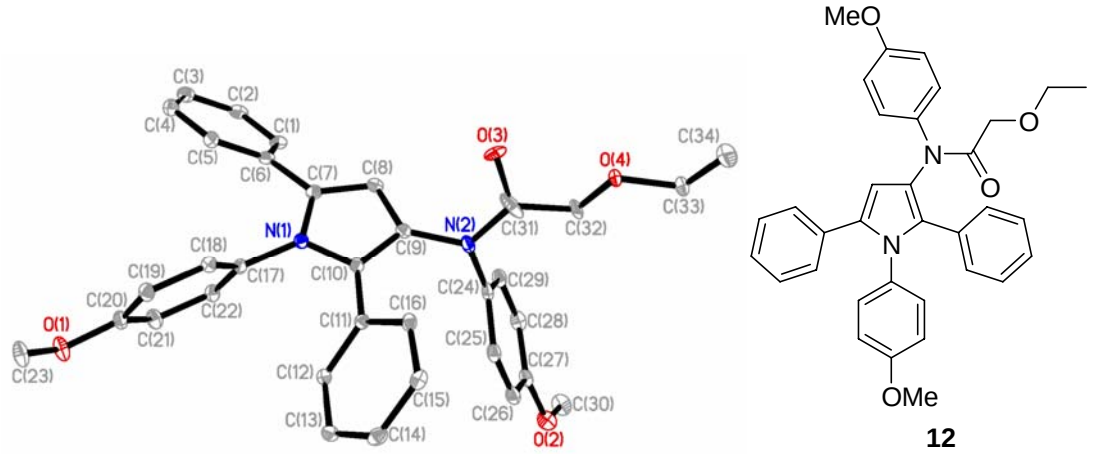
4-(*p*-Tolylthio)-*N*,1-bis(4-methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (**11q**): Yellow solid, m.p. 189–191 °C, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.19 (m, 3 H), 7.10–7.13 (m, 7 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 6.96 (d, *J* = 8.0 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 6.54 (d, *J* = 8.8 Hz, 2 H), 5.04 (s, 1 H), 3.74 (s, 3 H), 3.70 (s, 3 H), 2.26 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.3, 152.5, 141.4, 137.7, 135.8, 134.5, 131.5, 131.4, 131.2, 129.8, 129.7, 129.4, 128.7, 128.5, 128.1, 127.8, 127.5, 127.2, 126.5 (2 C), 121.5, 115.7, 114.4, 114.1, 113.7, 107.1, 55.6, 55.3, 20.9. HRMS (ESI) *m/z* calc'd for $C_{37}H_{33}N_2O_2S$ $[M+H]^+$: 569.2257, found 569.2264.

5-Cyclohexyl-*N*,1-bis(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-3-amine (**11r**): Yellow solid, m.p. 80–82 °C, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (t, *J* = 7.6 Hz, 2 H), 7.07 (d, J = 8.8 Hz, 2 H), 7.01–7.06 (m, 3 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 6.09 (s, 1 H), 5.08 (br. s, 1 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 2.36–2.43 (m, 1 H), 1.78–1.81 (m, 2 H), 1.68–1.71 (m, 2 H), 1.29–1.38 (m, 3 H), 1.11–1.20 (m, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.3, 152.5, 141.2, 140.2, 131.8, 131.7, 129.8, 129.4, 128.0, 125.6, 125.3, 123.7, 115.7, 114.7, 113.8, 100.3, 55.8, 55.3, 35.6, 33.9, 26.5, 26.0. HRMS (ESI) *m/z* calc'd for $C_{30}H_{33}N_2O_2$ $[M+H]^+$: 453.2537, found 453.2540.

Reference

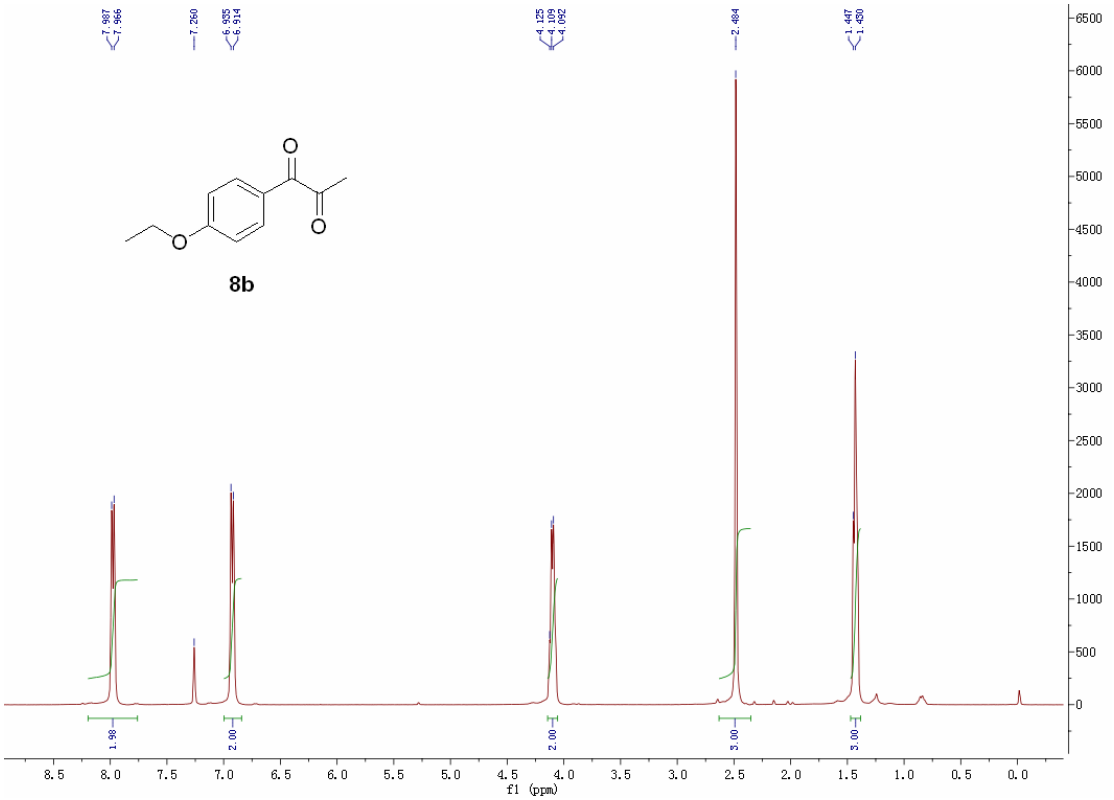
1. S. Ammermann, C. Hrib, P. G. Jones, W.-W. du Mont, W. Kowalsky, H.-H. Johannes, *Org. Lett.* **2012**, *14*, 5090.
2. W. R. Tully, *US 4,643,999*, **1984**.

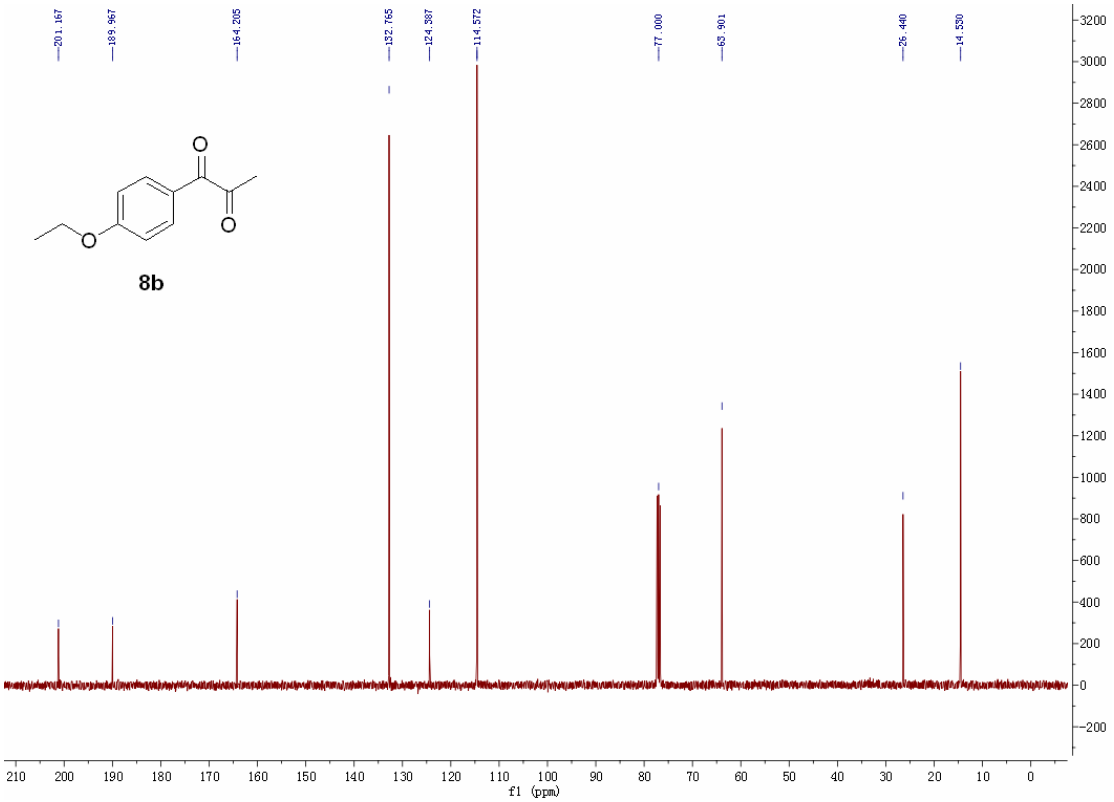
2. Crystallography data of Compound 12

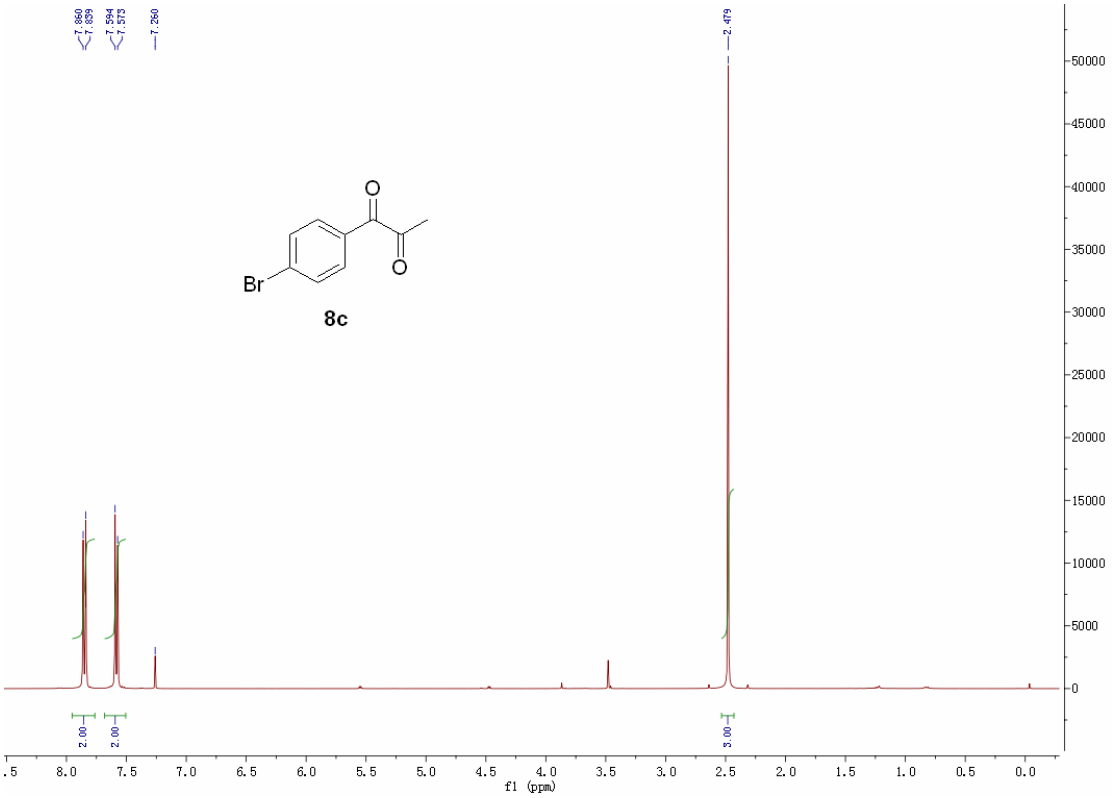


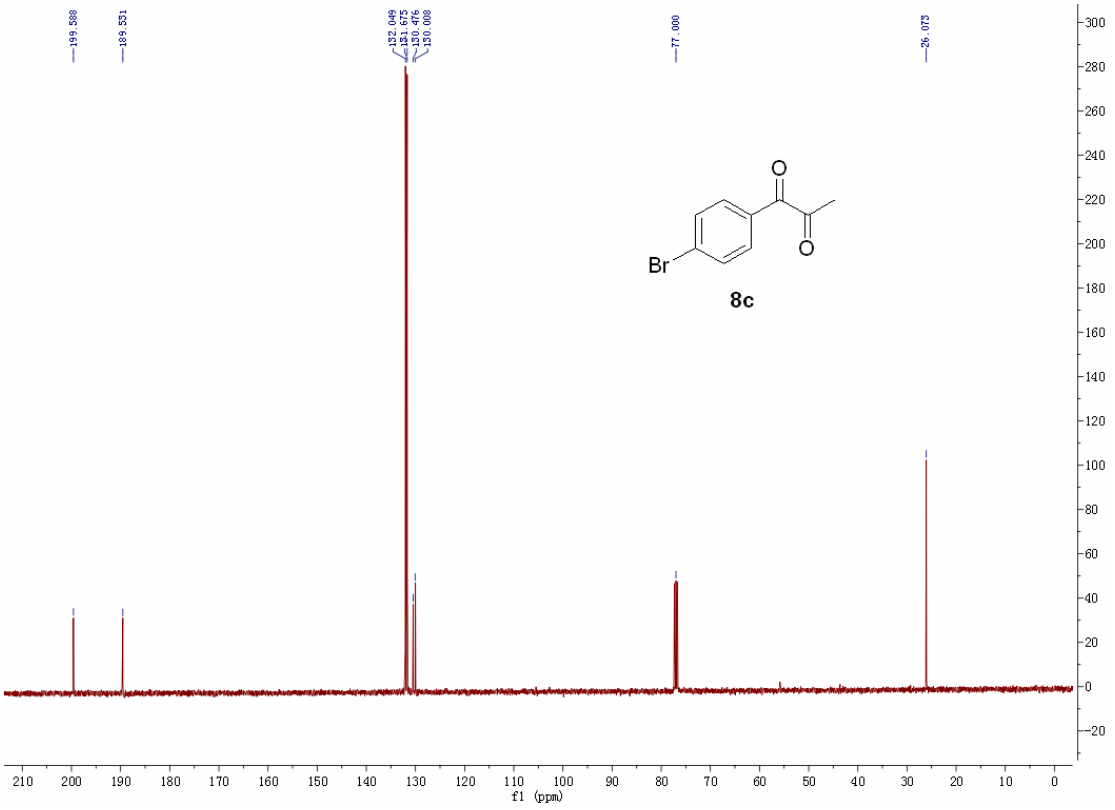
Identification code	shelxl
Empirical formula	C35 H34 Cl2 N2 O4
Formula weight	617.54
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 26.271(4) A alpha = 90 deg. b = 5.9202(8) A beta = 108.458(2) deg. c = 21.057(3) A gamma = 90 deg.
Volume	3106.5(8) A^3
Z, Calculated density	4, 1.320 Mg/m^3
Absorption coefficient	0.251 mm^-1
F(000)	1296
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	3.26 to 27.56 deg.
Limiting indices	-34<=h<=34, -7<=k<=7, -27<=l<=27
Reflections collected / unique	18964 / 6938 [R(int) = 0.0164]
Completeness to theta = 27.56	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9705 and 0.9515
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6938 / 110 / 463
Goodness-of-fit on F^2	0.997
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0813
R indices (all data)	R1 = 0.0314, wR2 = 0.0820
Largest diff. peak and hole	0.391 and -0.345 e.A^-3

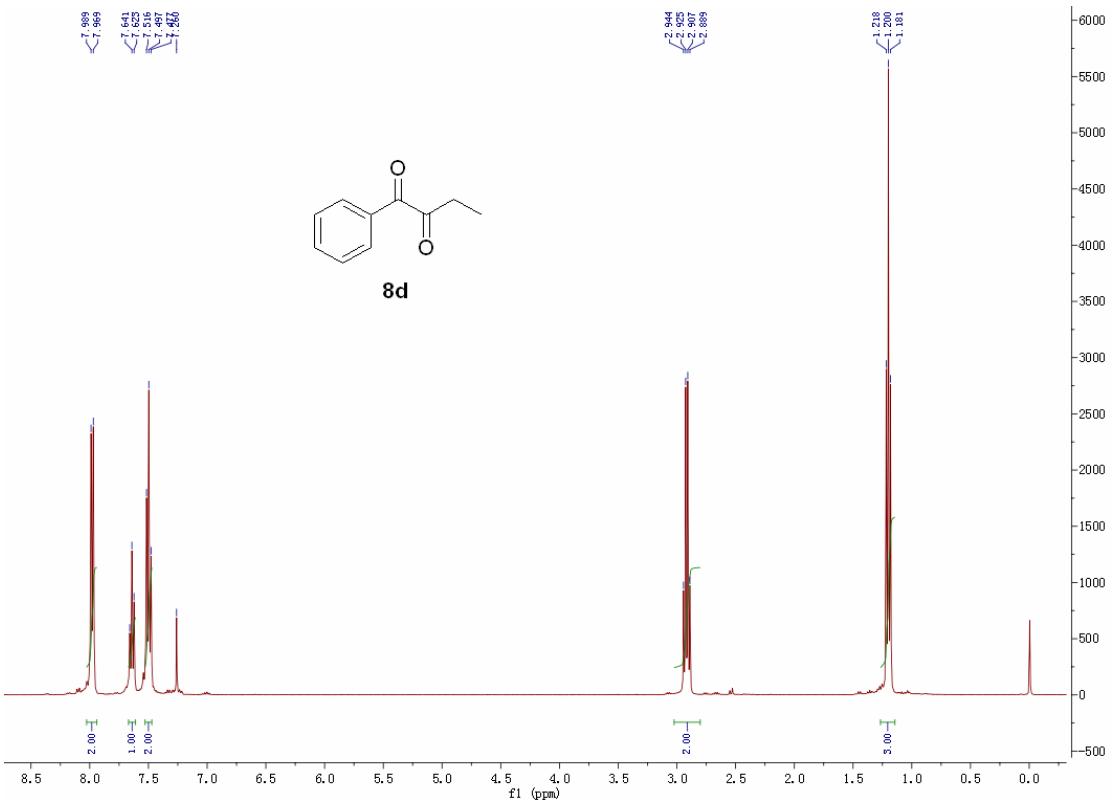
3. Copies of ^{1}H and ^{13}C NMR Spectra

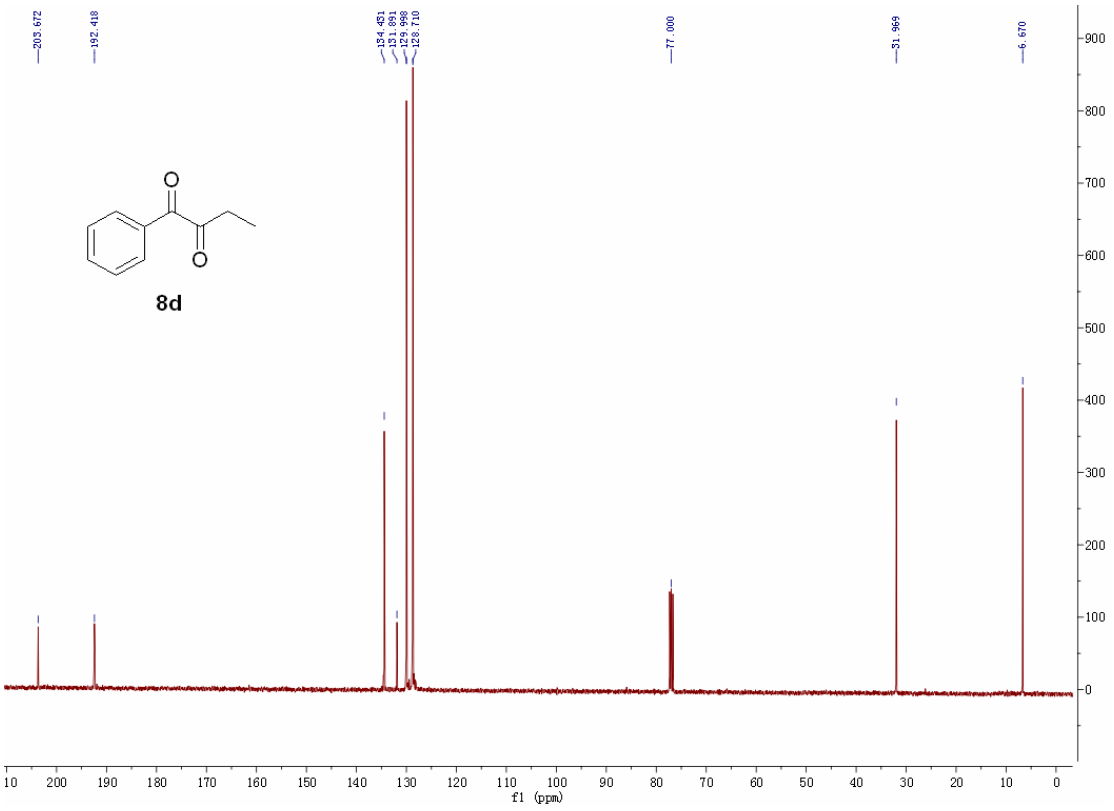


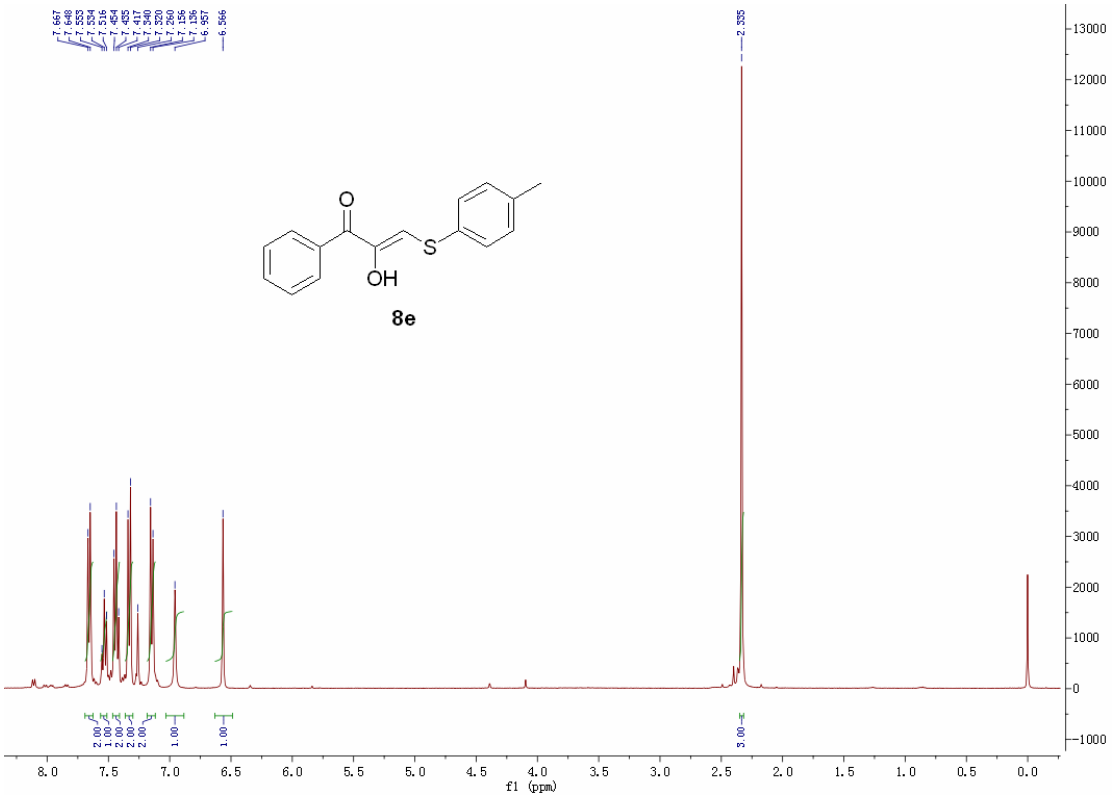


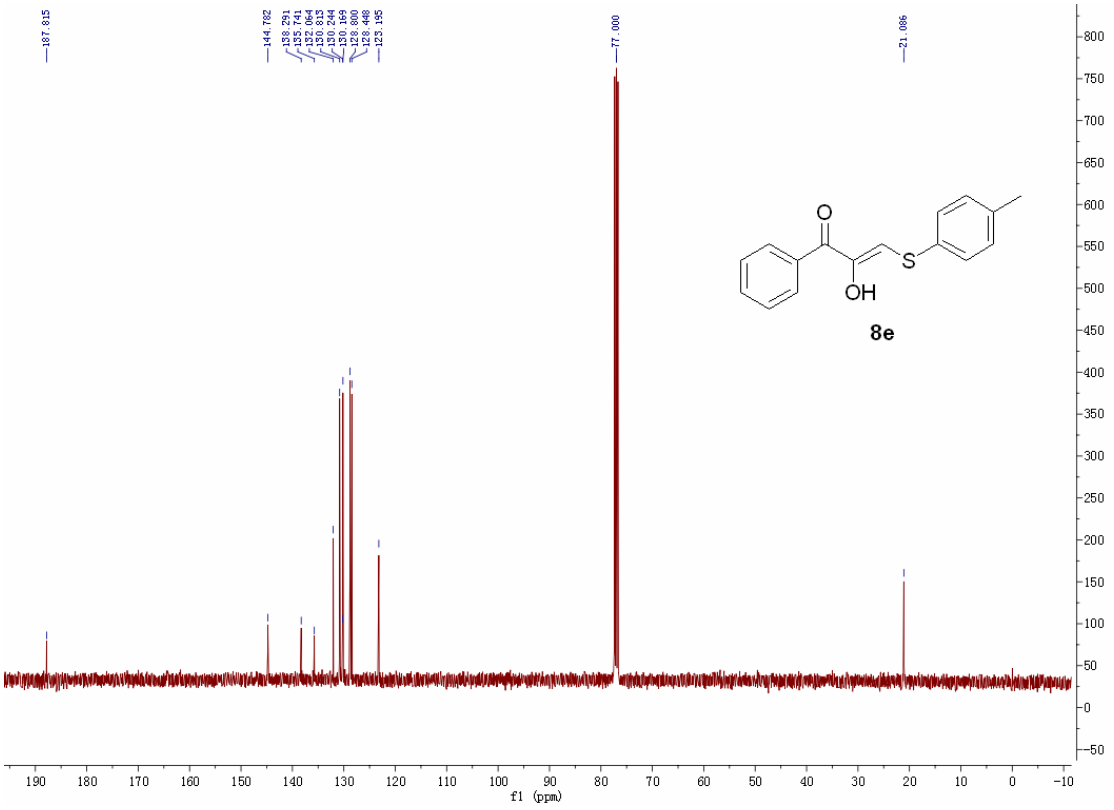

7.880
7.859
7.594
7.573
7.260
2.479
Br
O
O
8c
2.00
2.00
3.00
f1 (ppm)

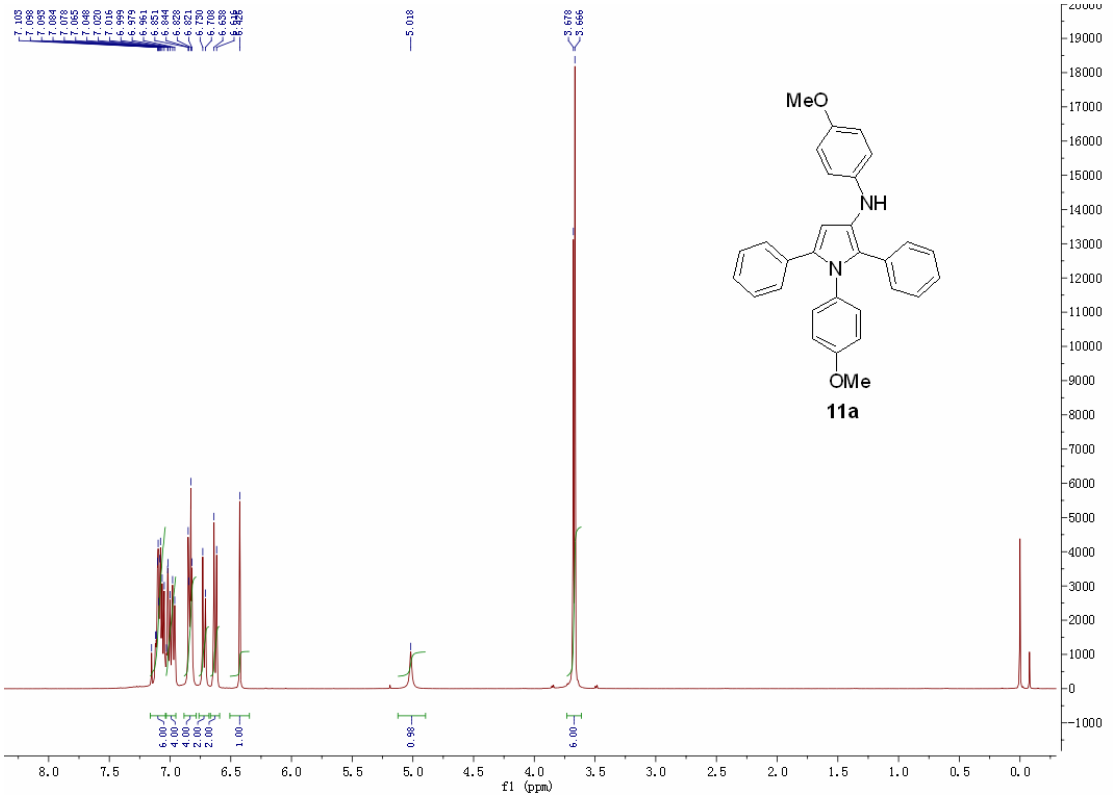

199.588
189.531
132.049
131.675
130.476
130.008
77.000
26.073
Br
O
O
8c
f1 (ppm)

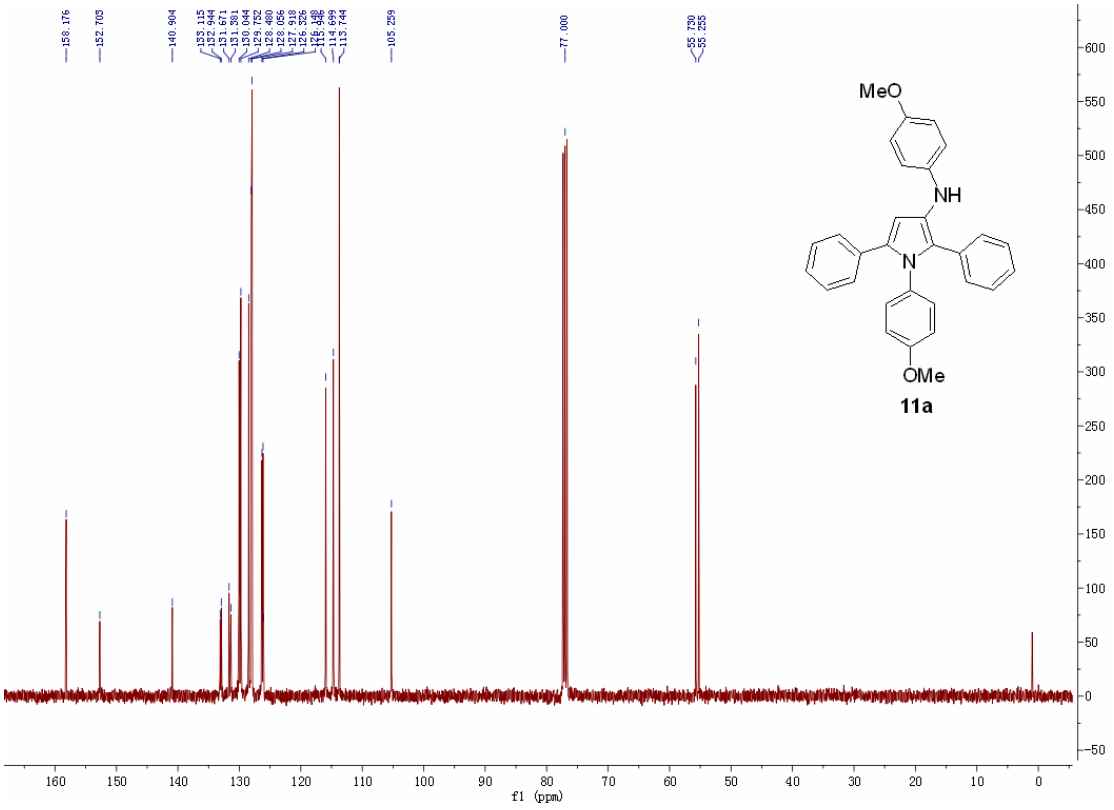

7.999
7.969
7.641
7.623
7.516
7.497
2.944
2.925
2.907
2.889
1.218
1.200
1.181
8d
2.00
1.00
2.00
2.00
3.00
f1 (ppm)

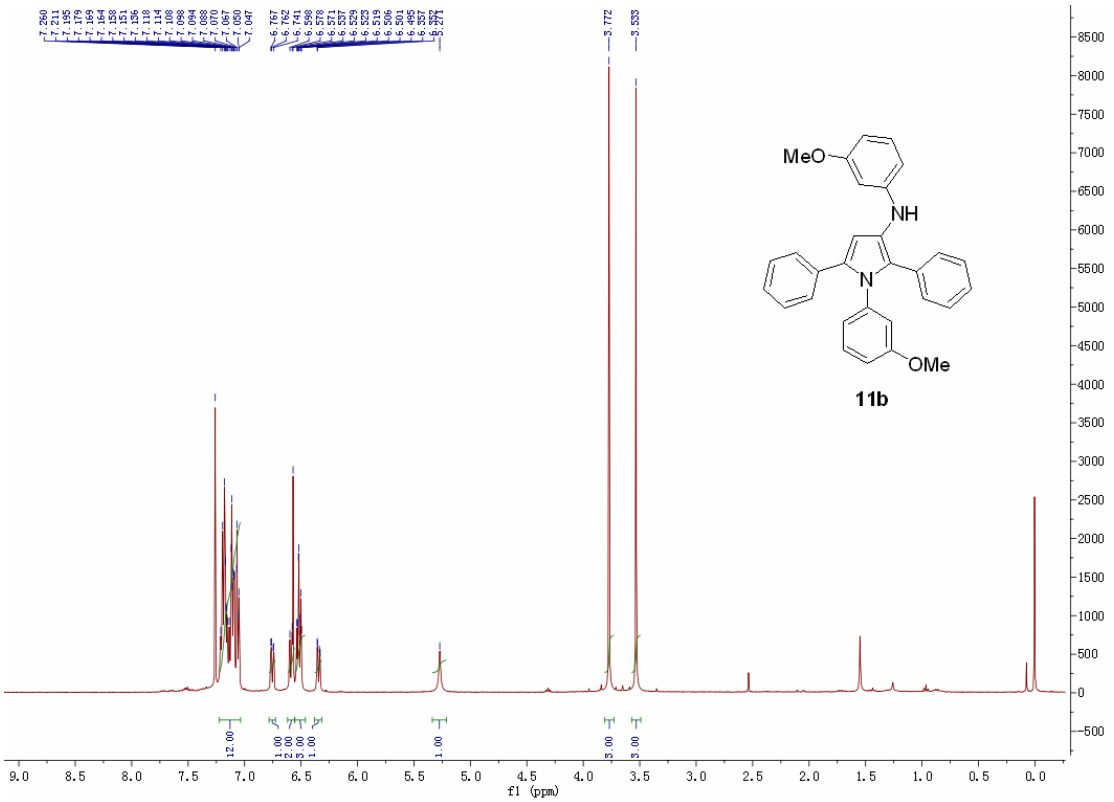

203.672
192.418
134.451
133.991
129.998
128.710
77.000
31.969
6.670
8d
f1 (ppm)

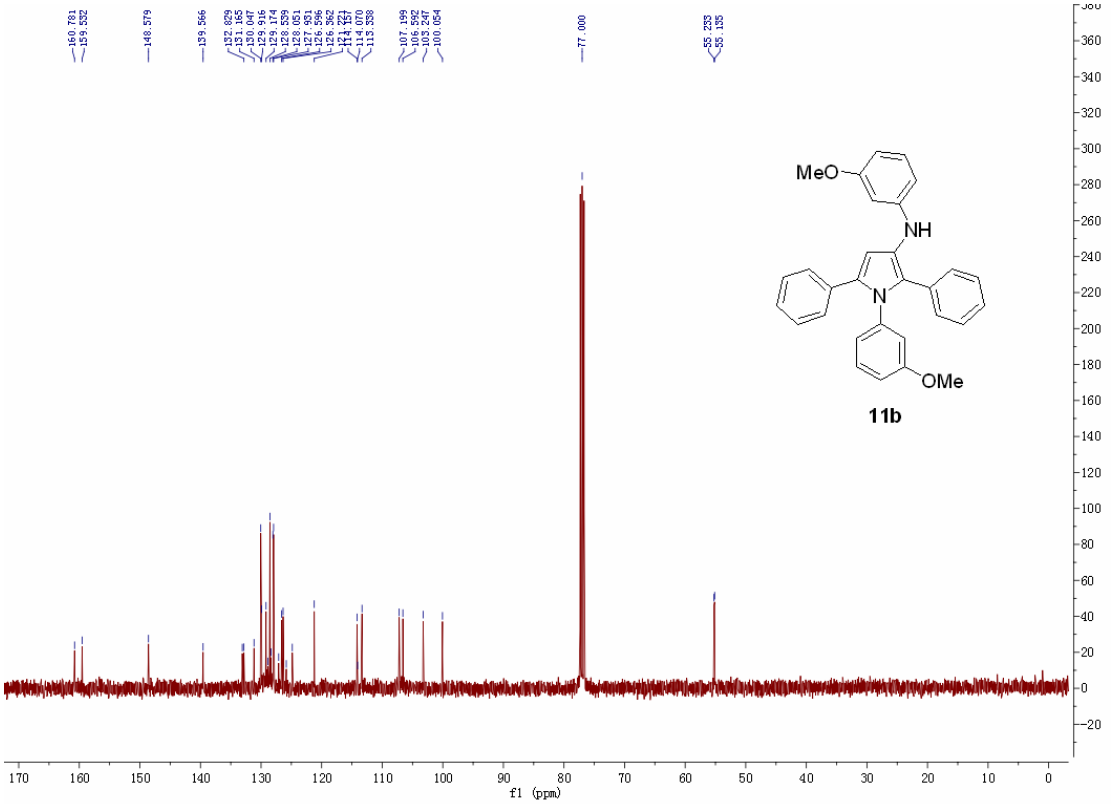

O
S
OH
8e
f1 (ppm)

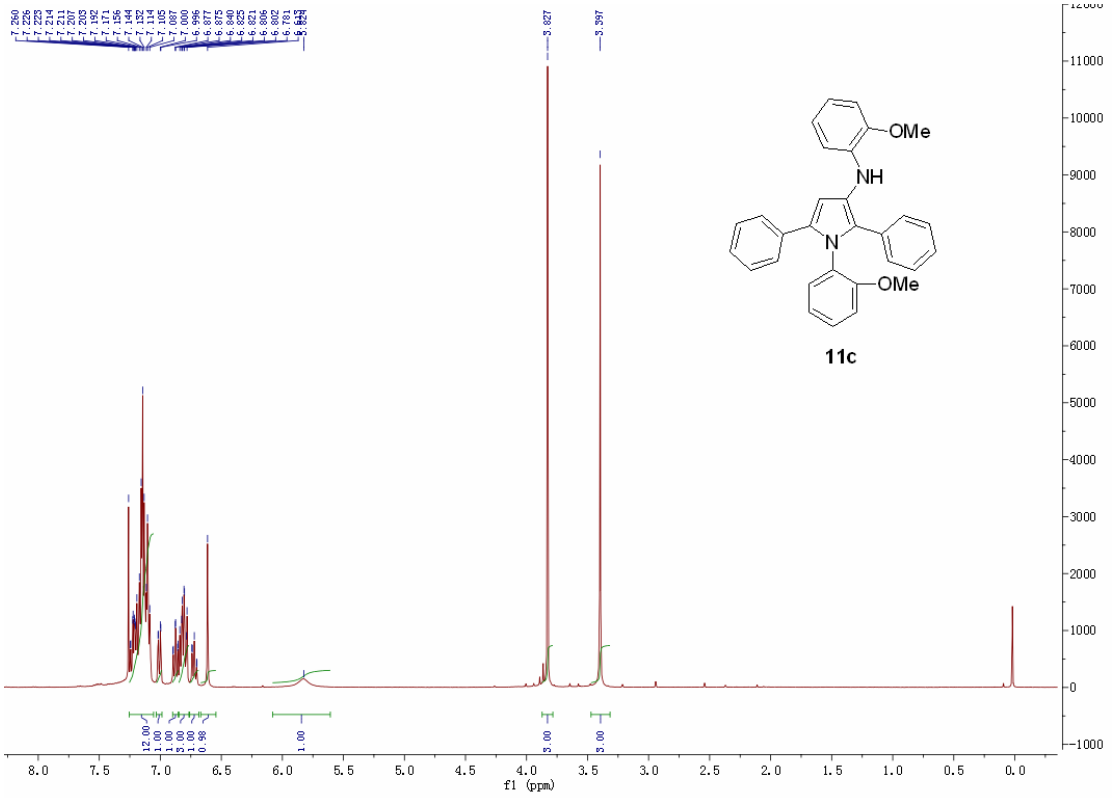

O
S
OH
8e
f1 (ppm)

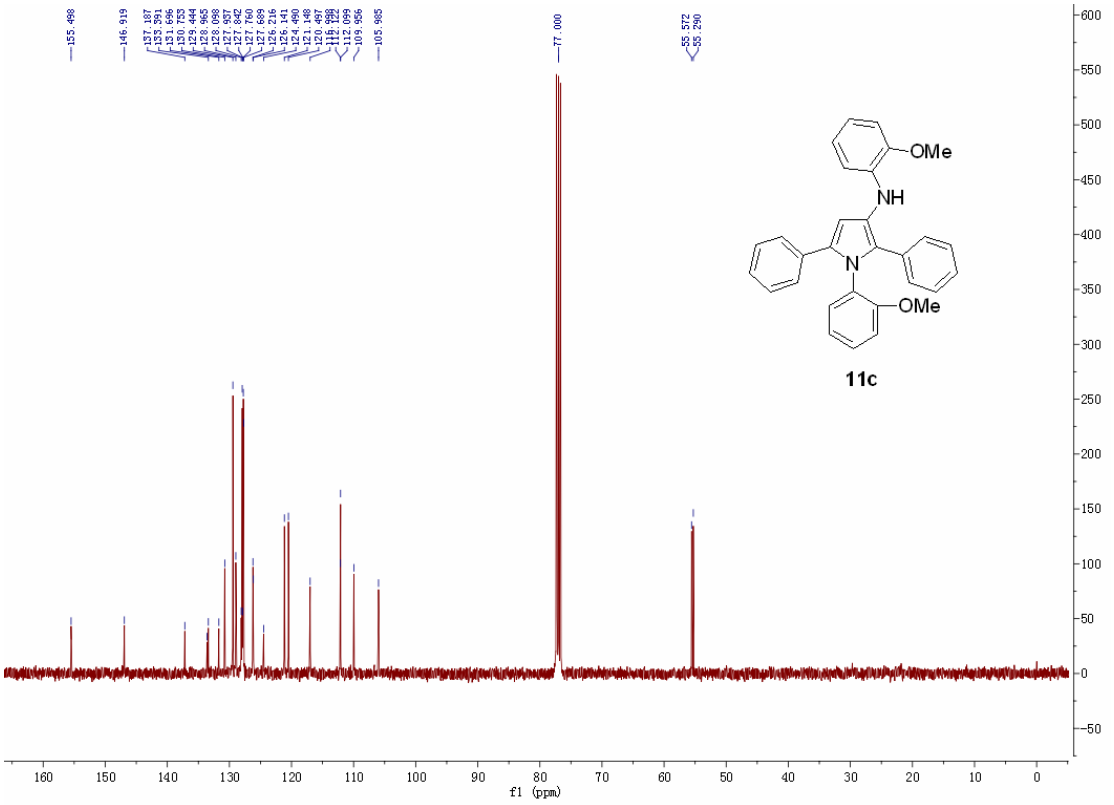

MeO
NH
N
OMe
11a
f1 (ppm)

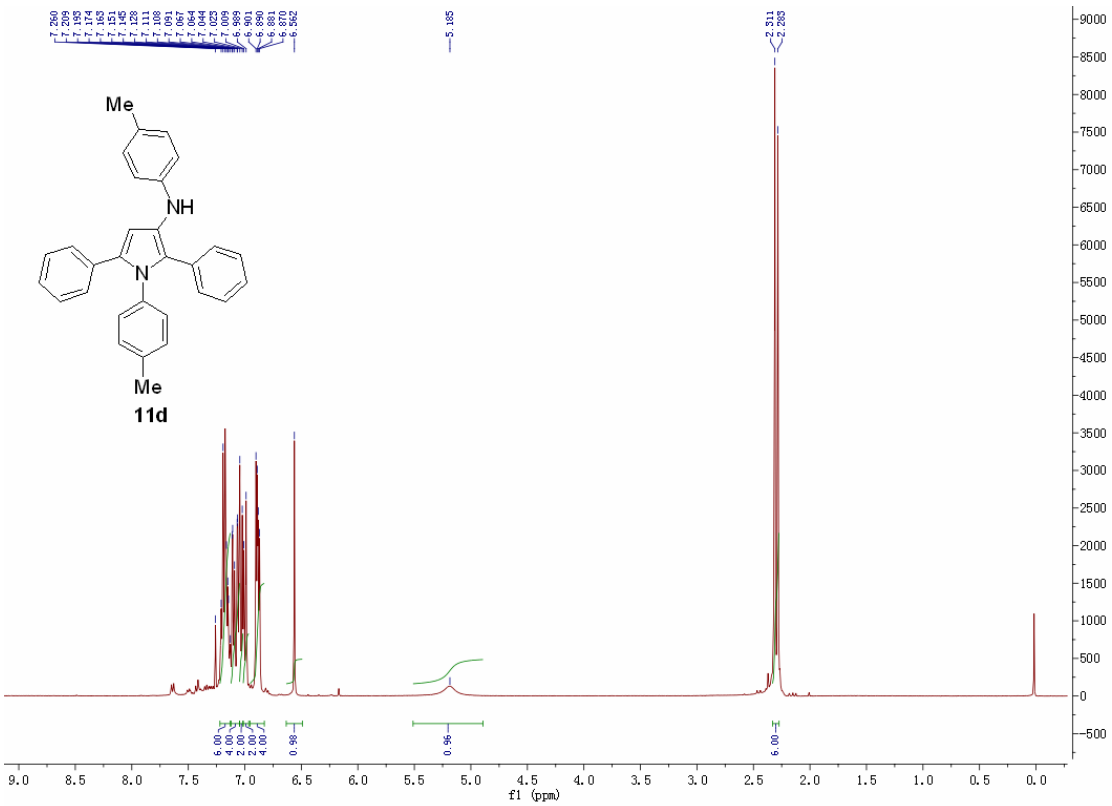

MeO
NH
N
OMe
11a
f1 (ppm)

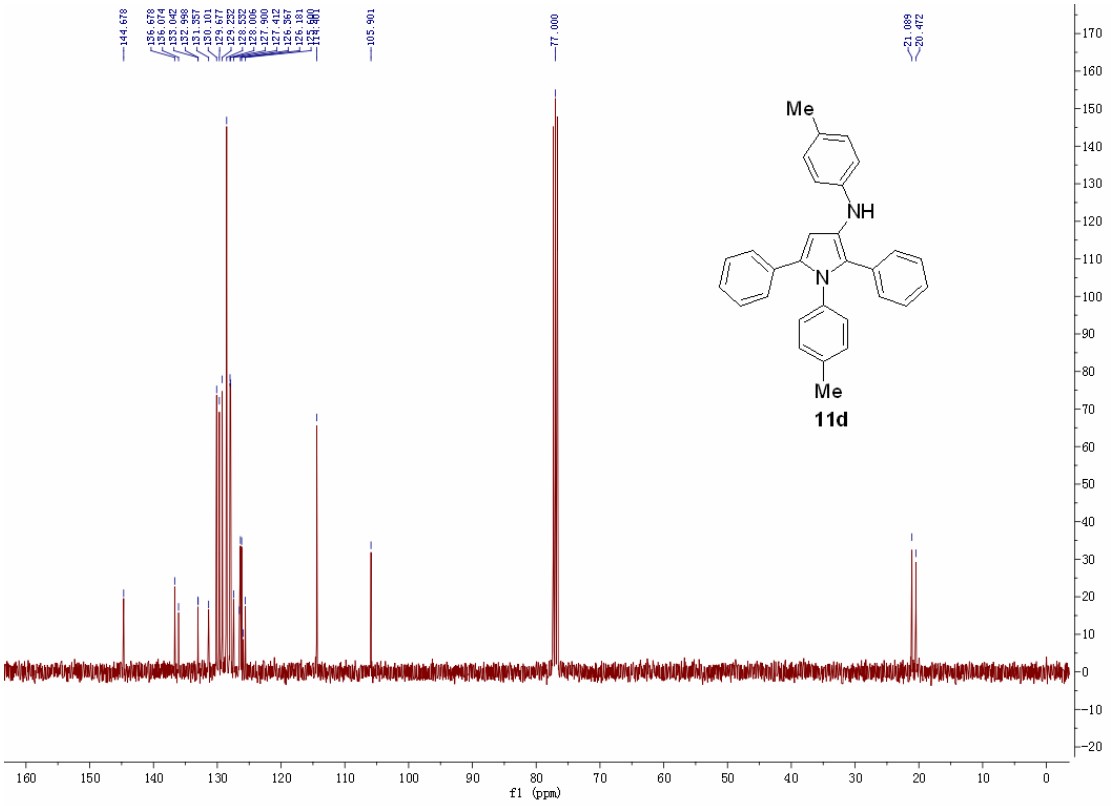

MeO
NH
N
OMe
11b
f1 (ppm)

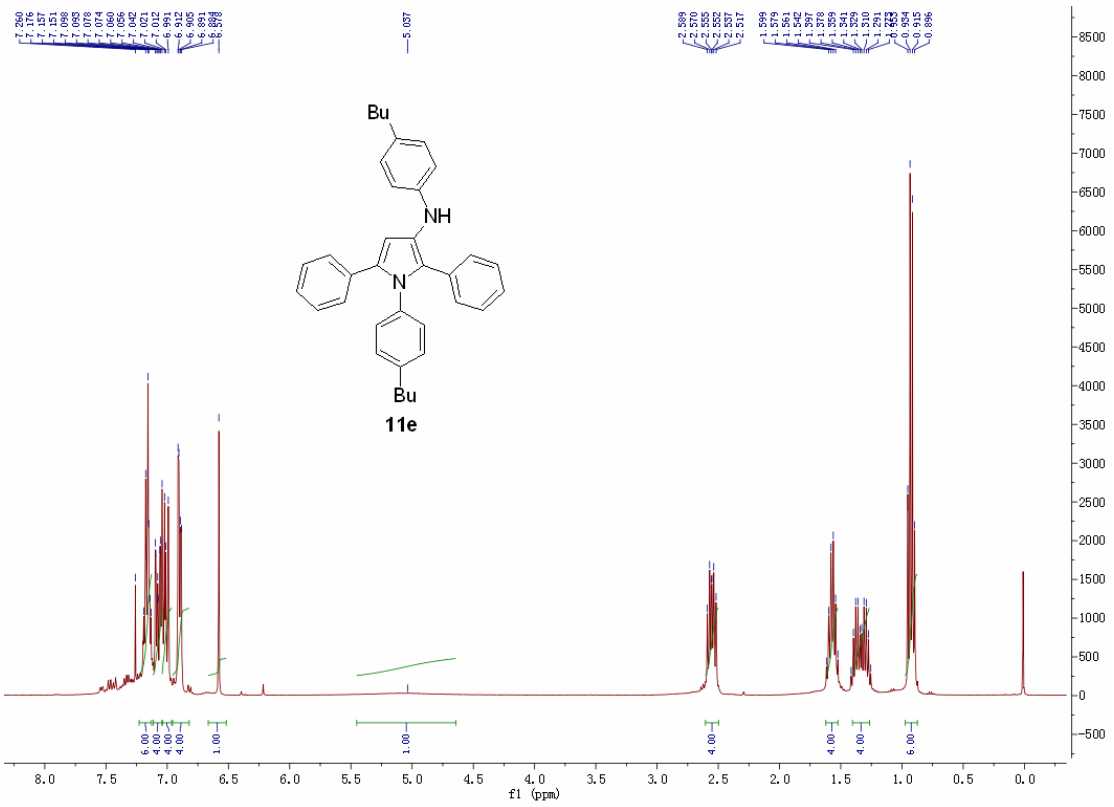

MeO
NH
N
OMe
11b
f1 (ppm)

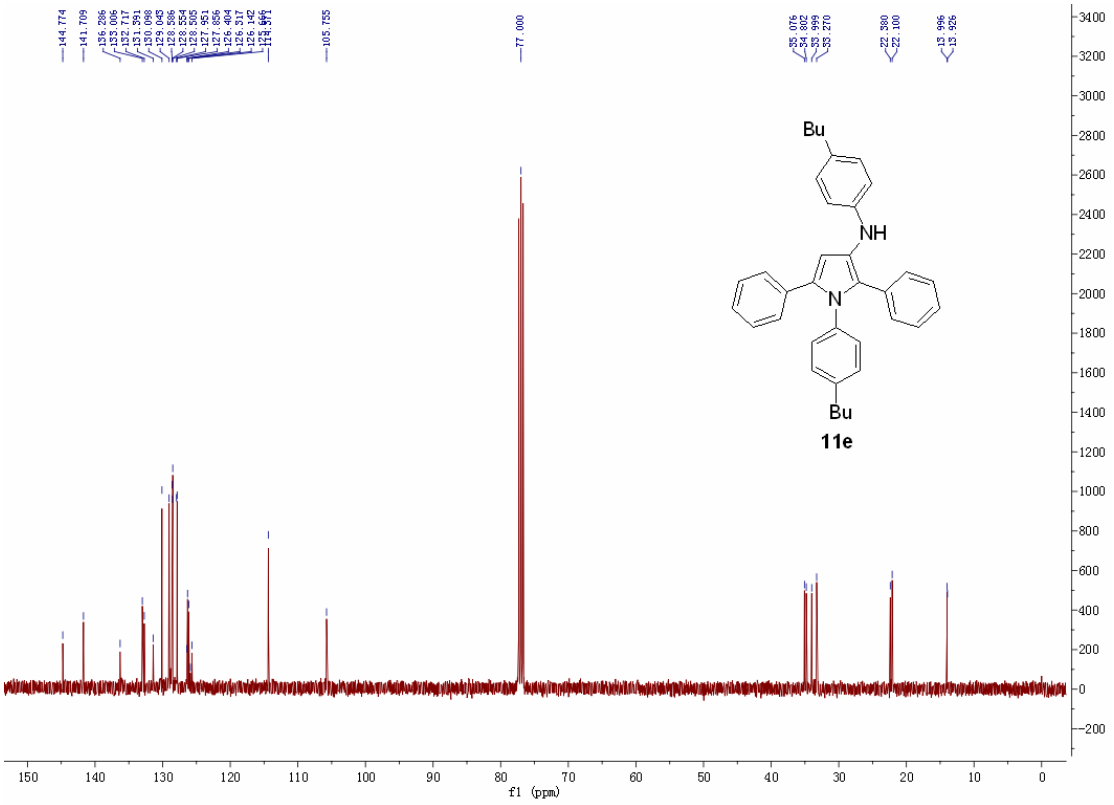

OMe
NH
N
OMe
11c
f1 (ppm)

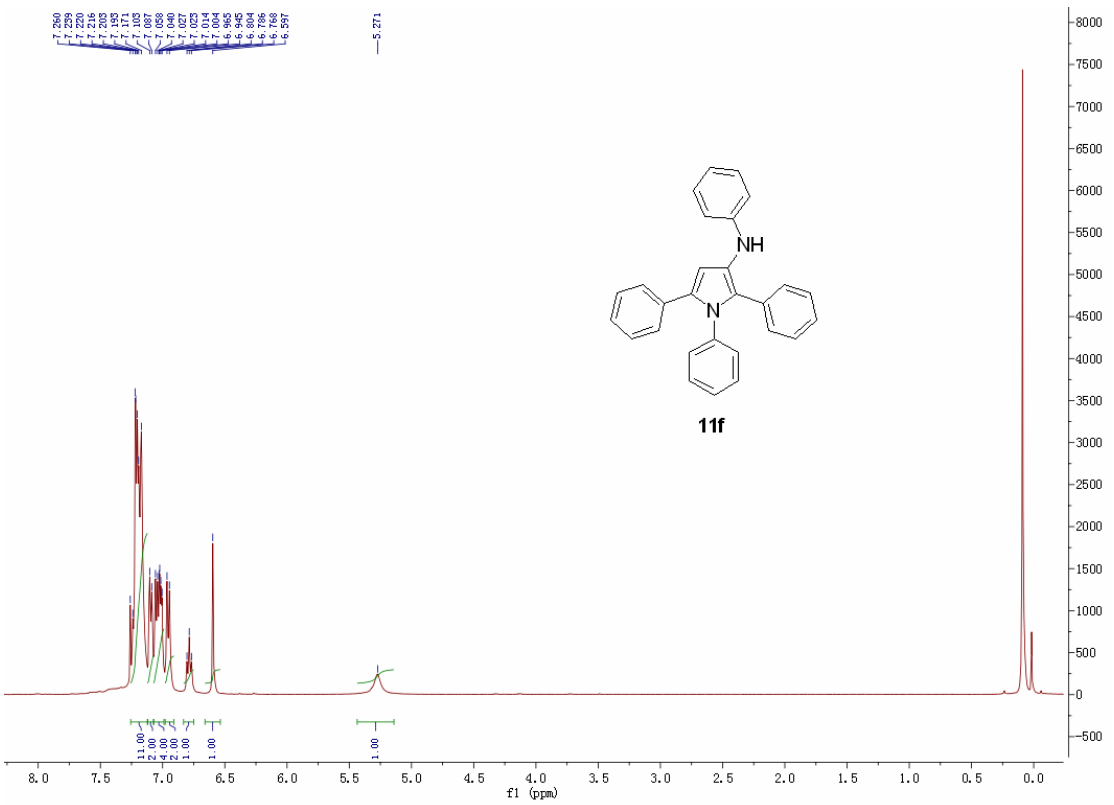

OMe
NH
N
OMe
11c
f1 (ppm)

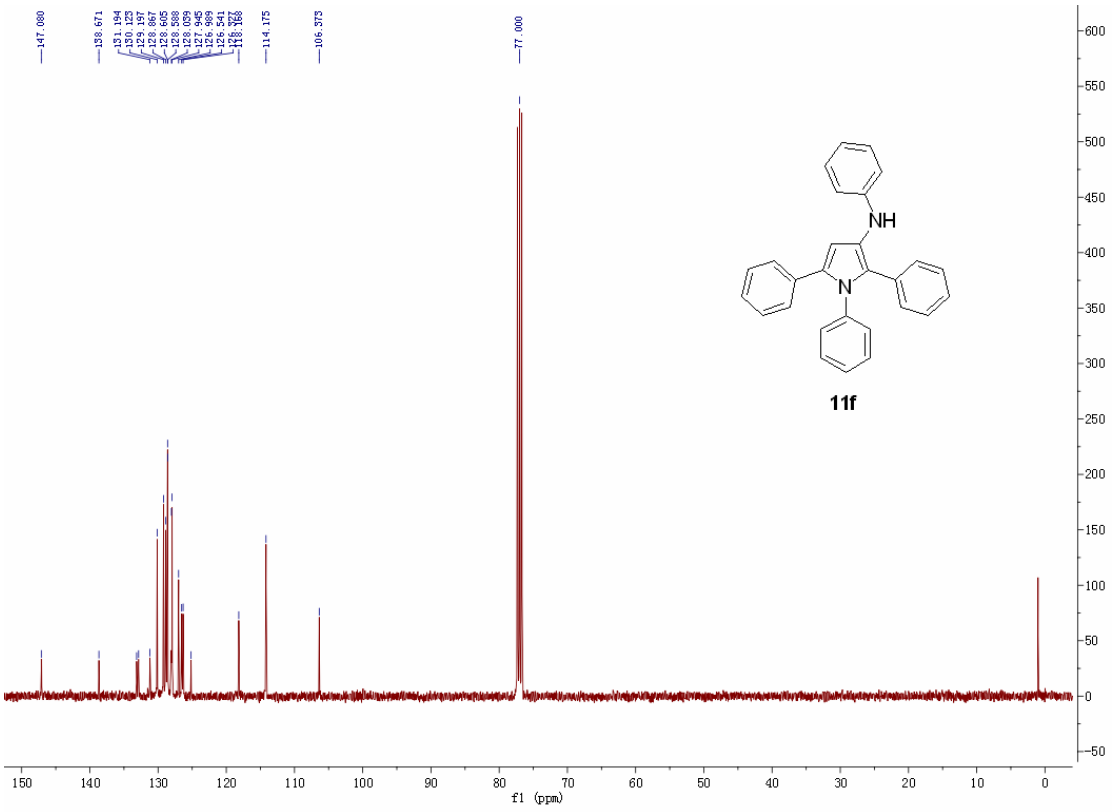

Me
NH
N
Me
11d
f1 (ppm)

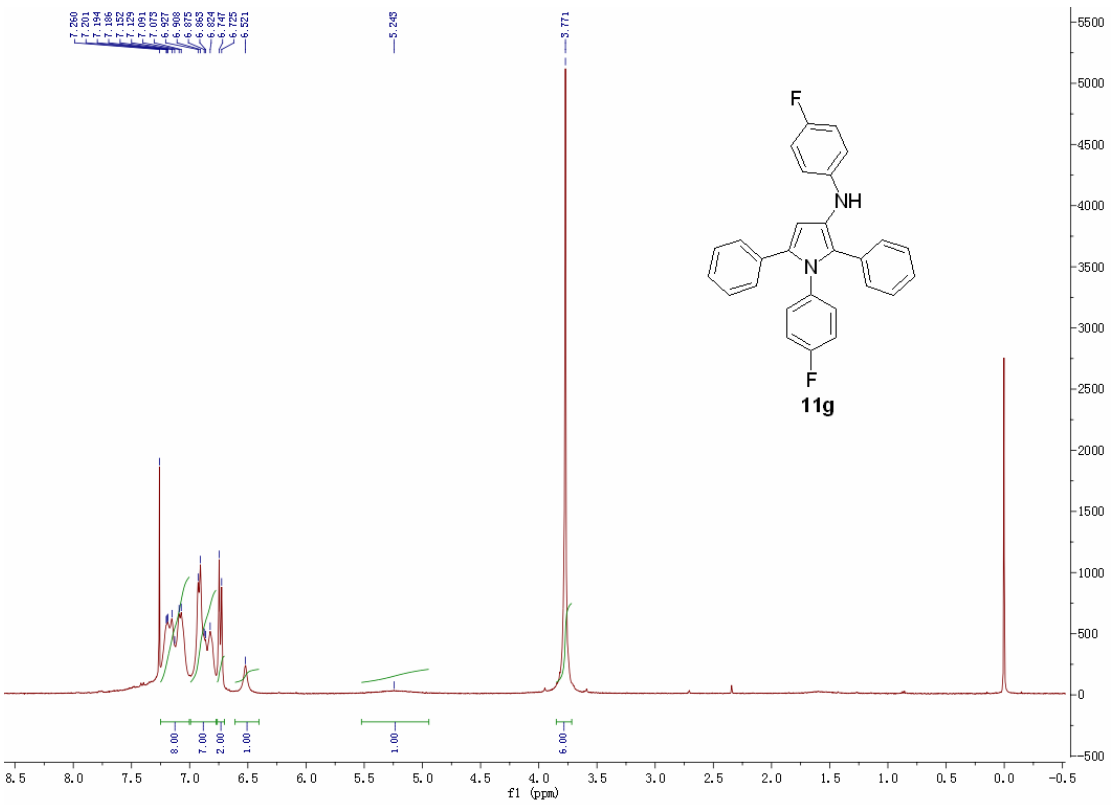

Me
NH
N
Me
11d
f1 (ppm)

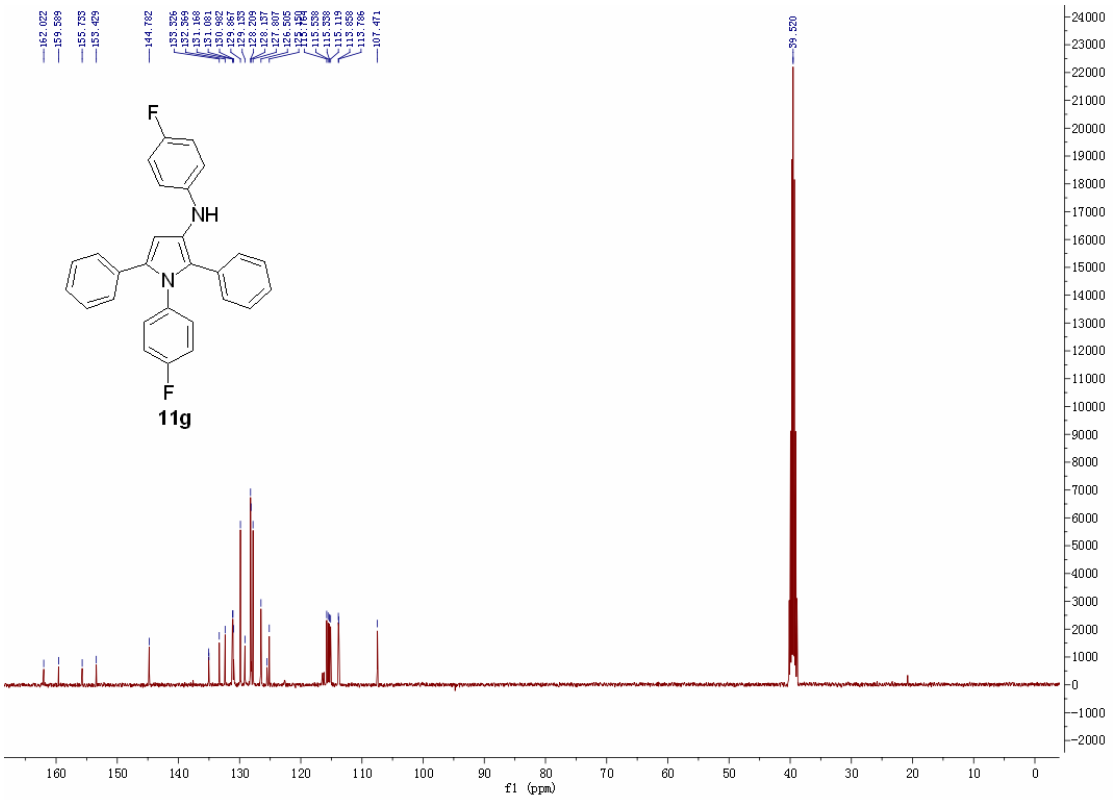

Bu
NH
N
Bu
11e
f1 (ppm)

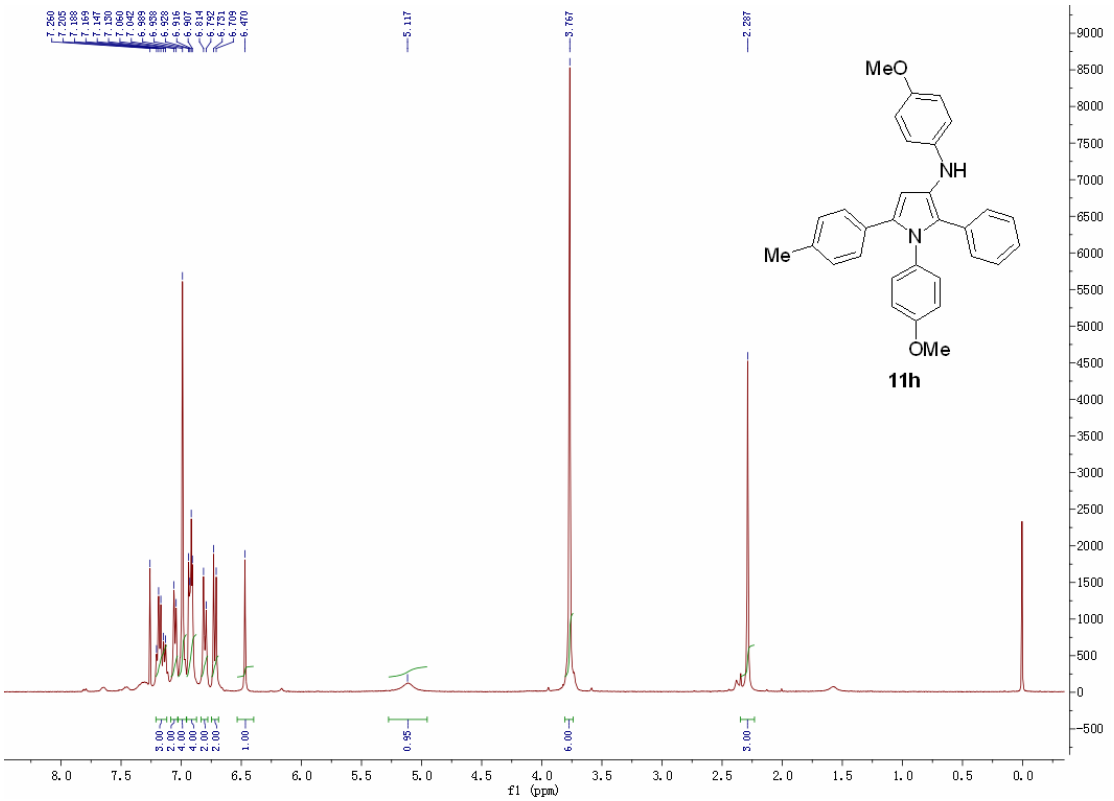

Bu
NH
N
Bu
11e
f1 (ppm)

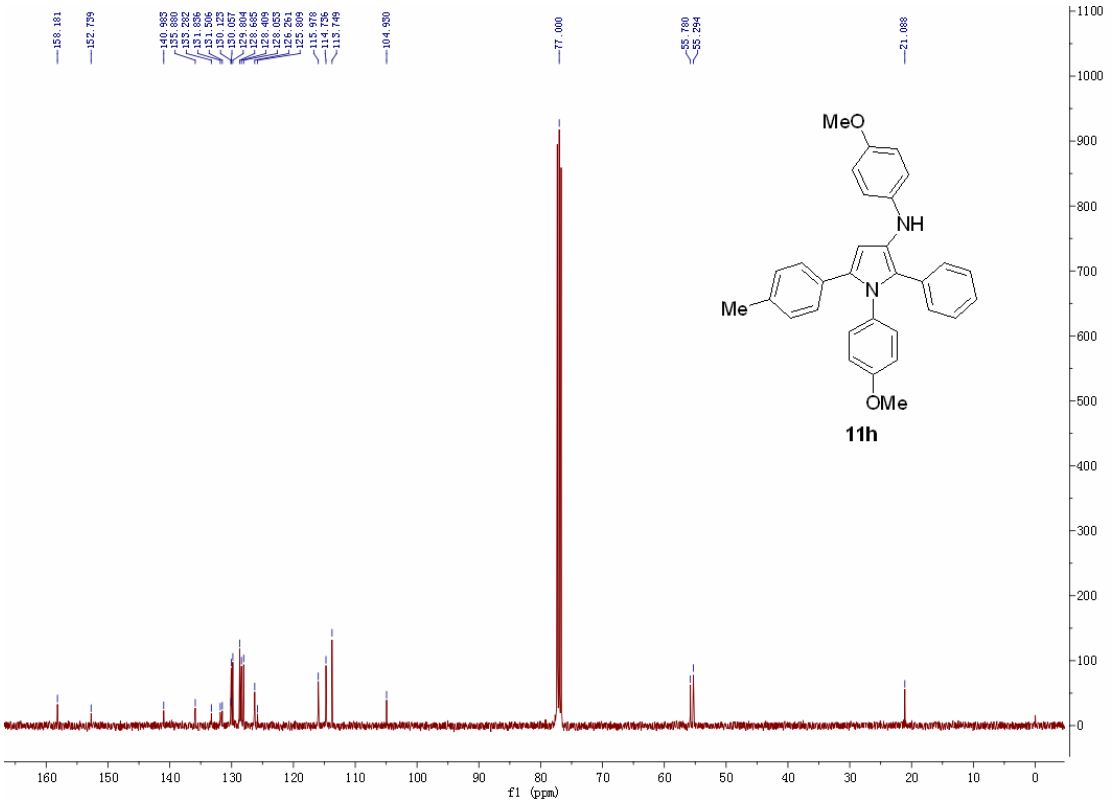

NH
N
11f
f1 (ppm)

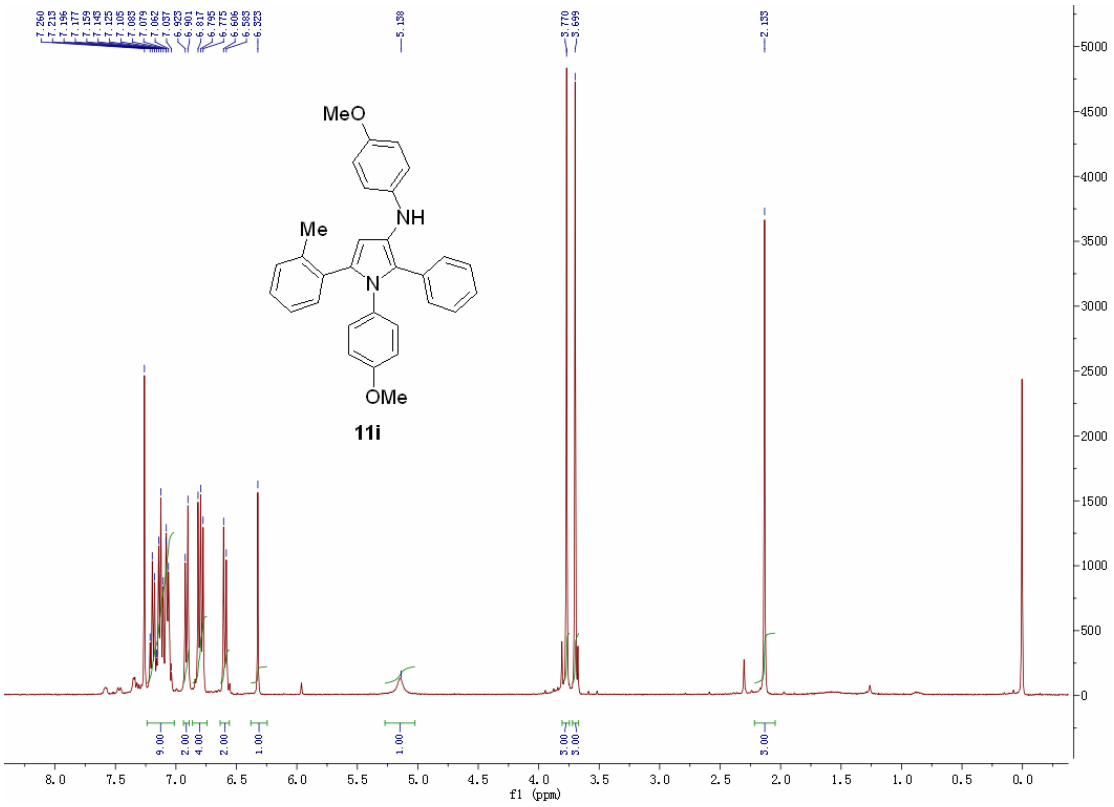

NH
N
11f
f1 (ppm)

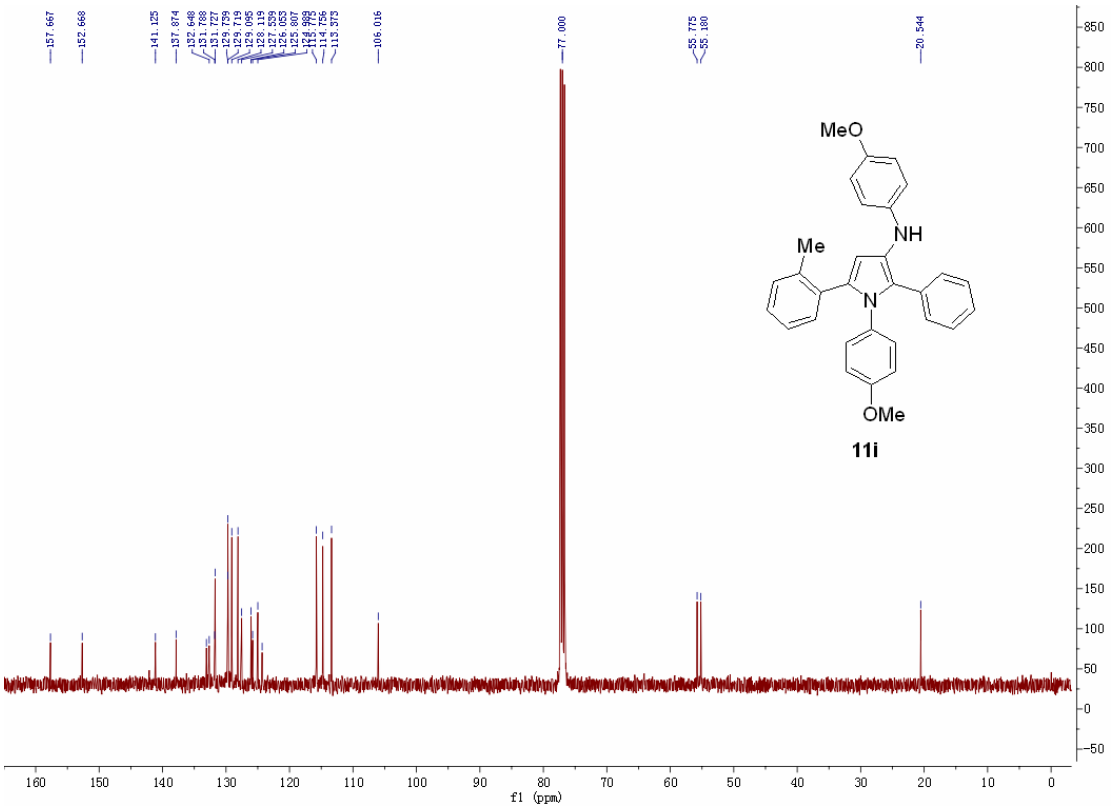

F
NH
N
F
11g
f1 (ppm)

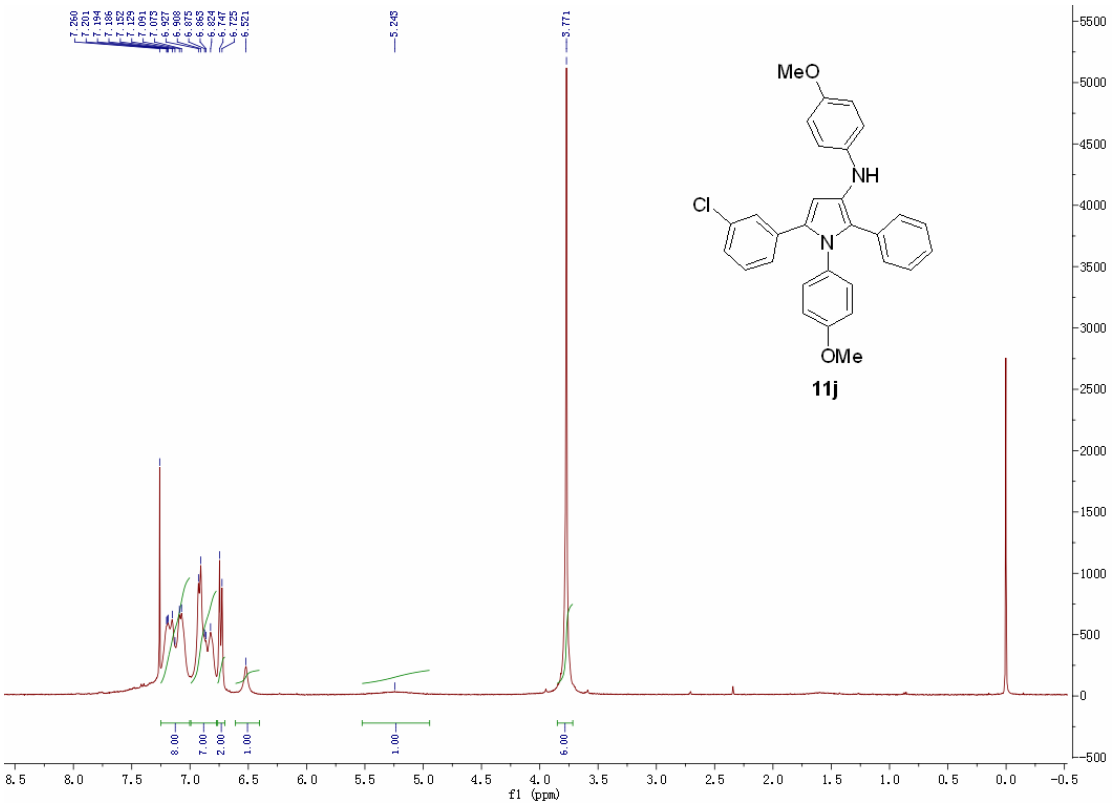

F
NH
N
F
11g
f1 (ppm)

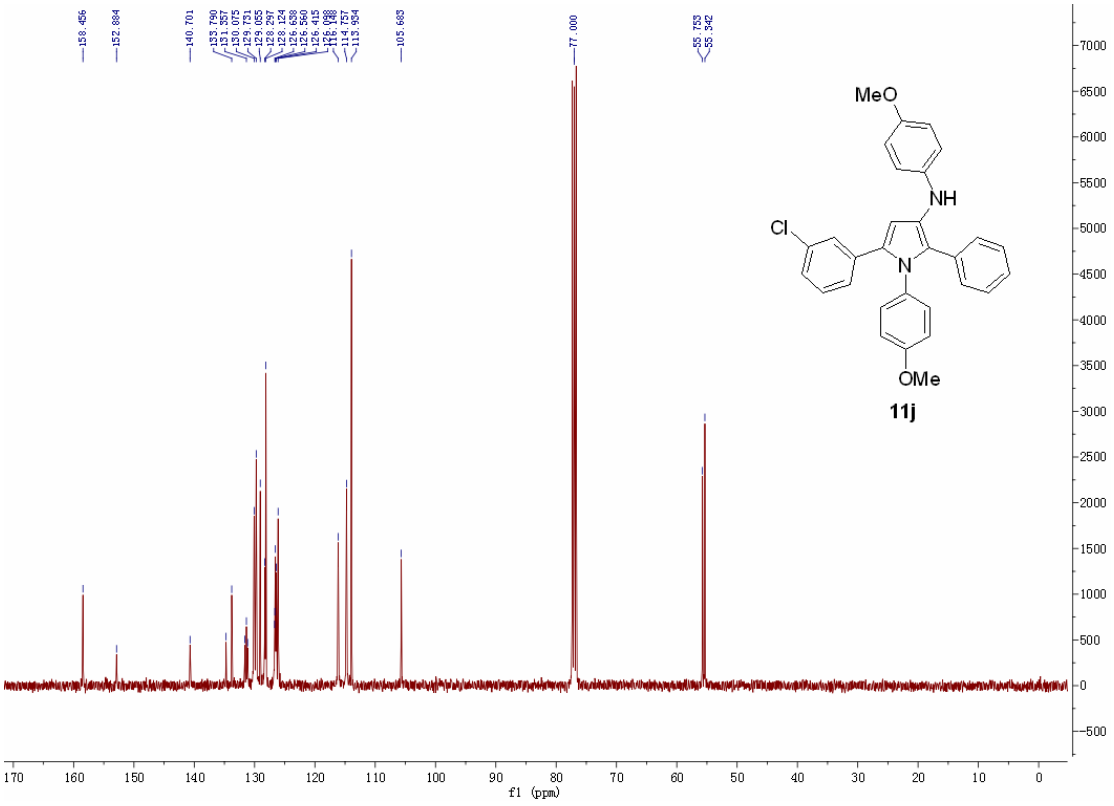

MeO
NH
N
Me
OMe
11h
f1 (ppm)

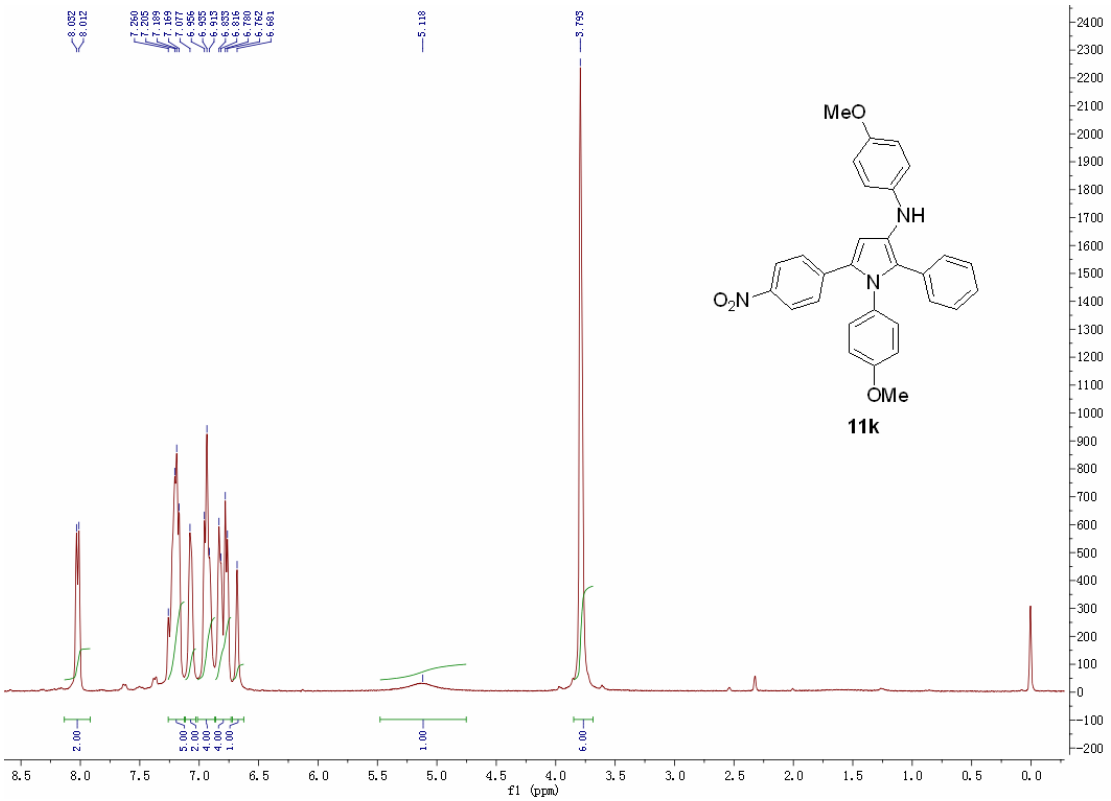

MeO
NH
N
Me
OMe
11h
f1 (ppm)

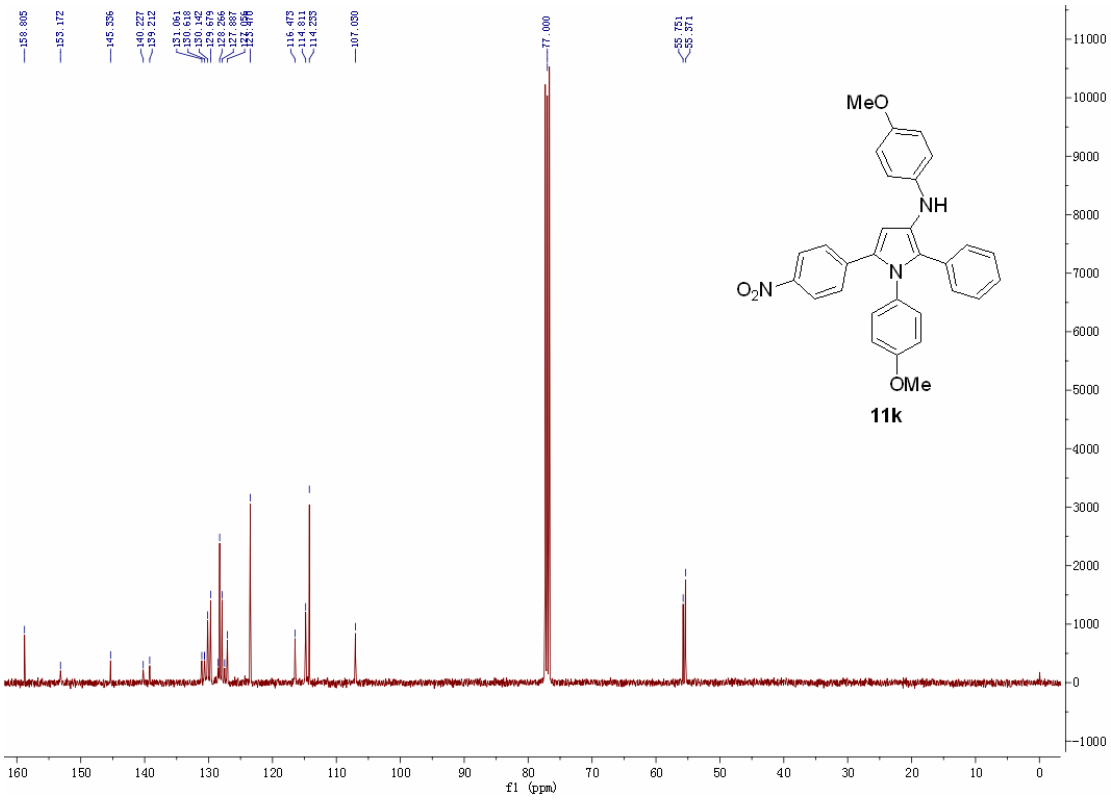

MeO
NH
Me
N
OMe
11i
f1 (ppm)

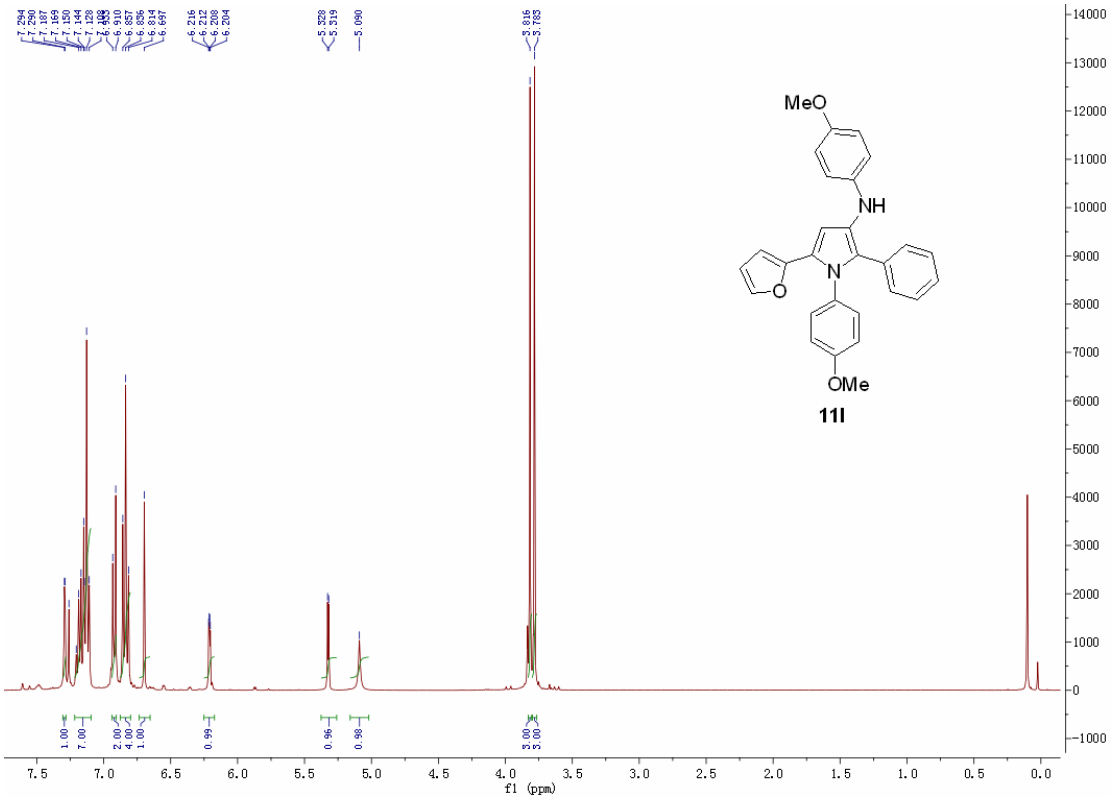

MeO
NH
Me
N
OMe
11i
f1 (ppm)

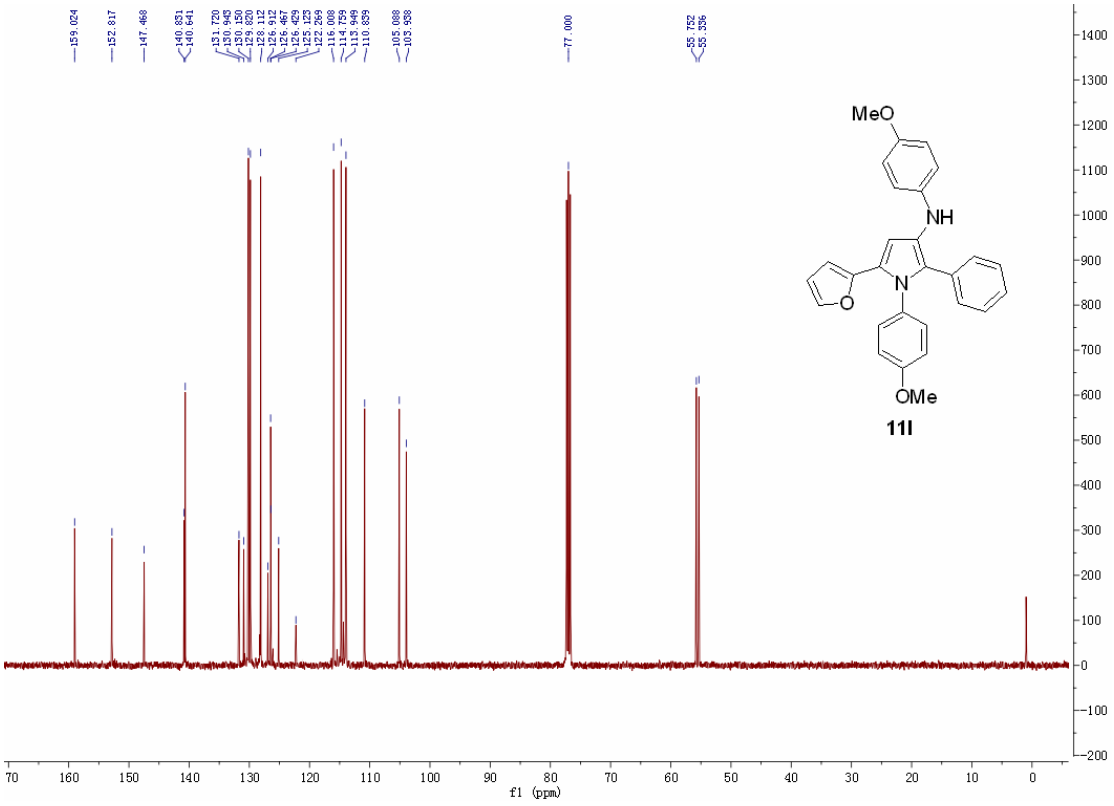

MeO
NH
Cl
N
OMe
11j
f1 (ppm)

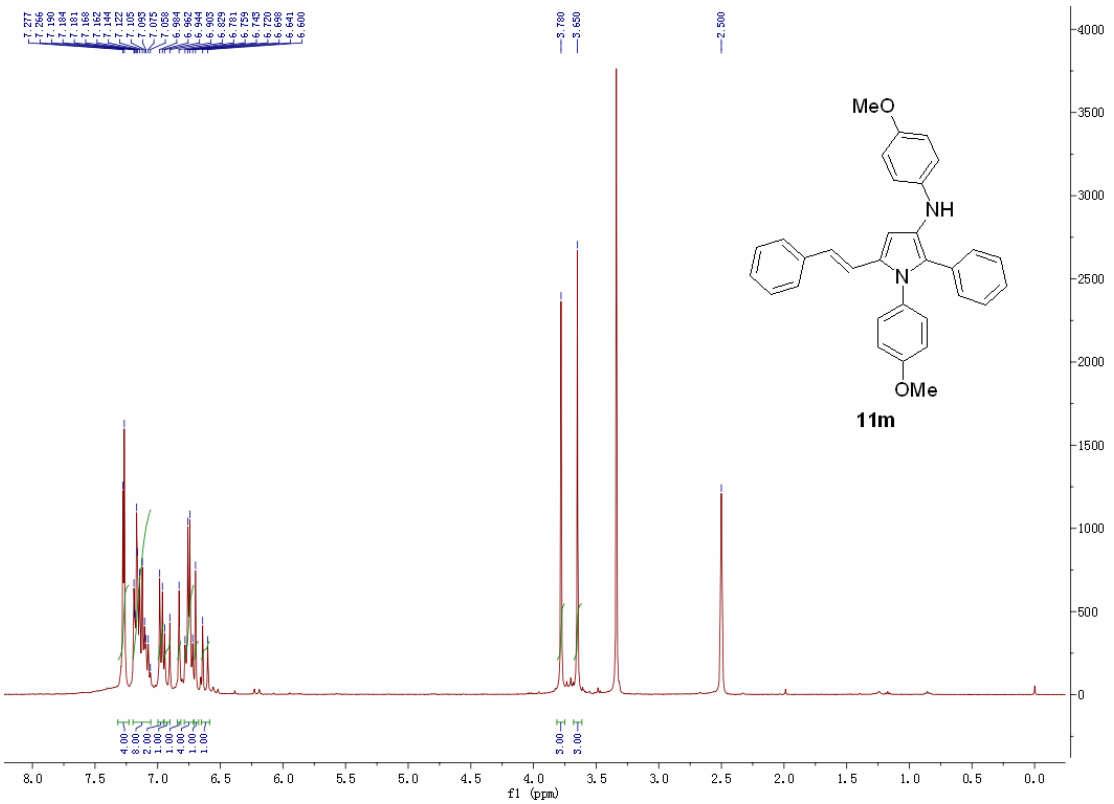

MeO
NH
Cl
N
OMe
11j
f1 (ppm)

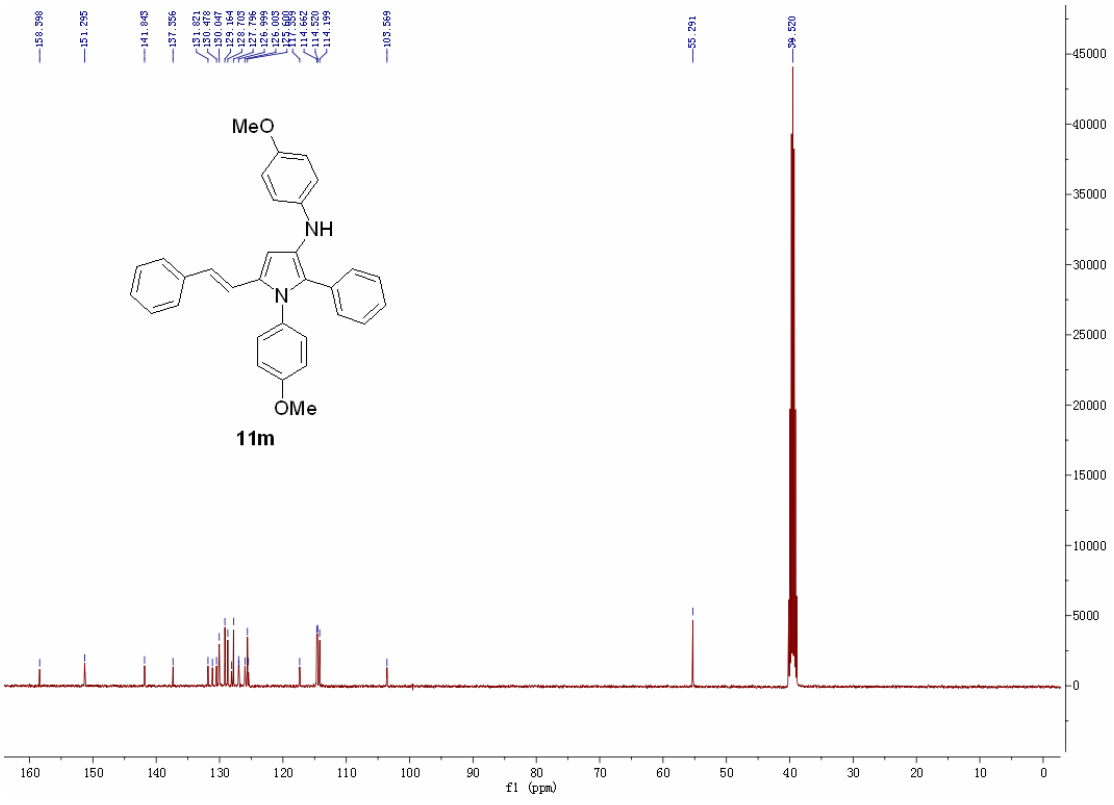

MeO
NH
O_2N
N
OMe
11k

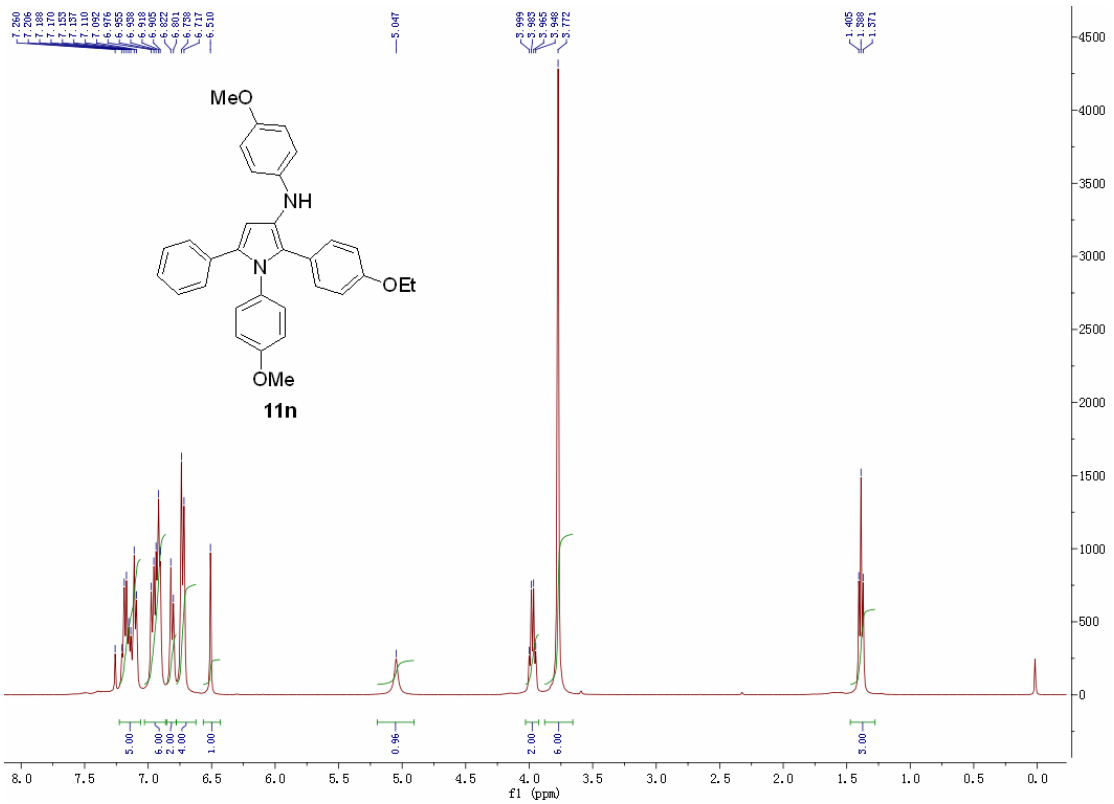

MeO
NH
O_2N
N
OMe
11k

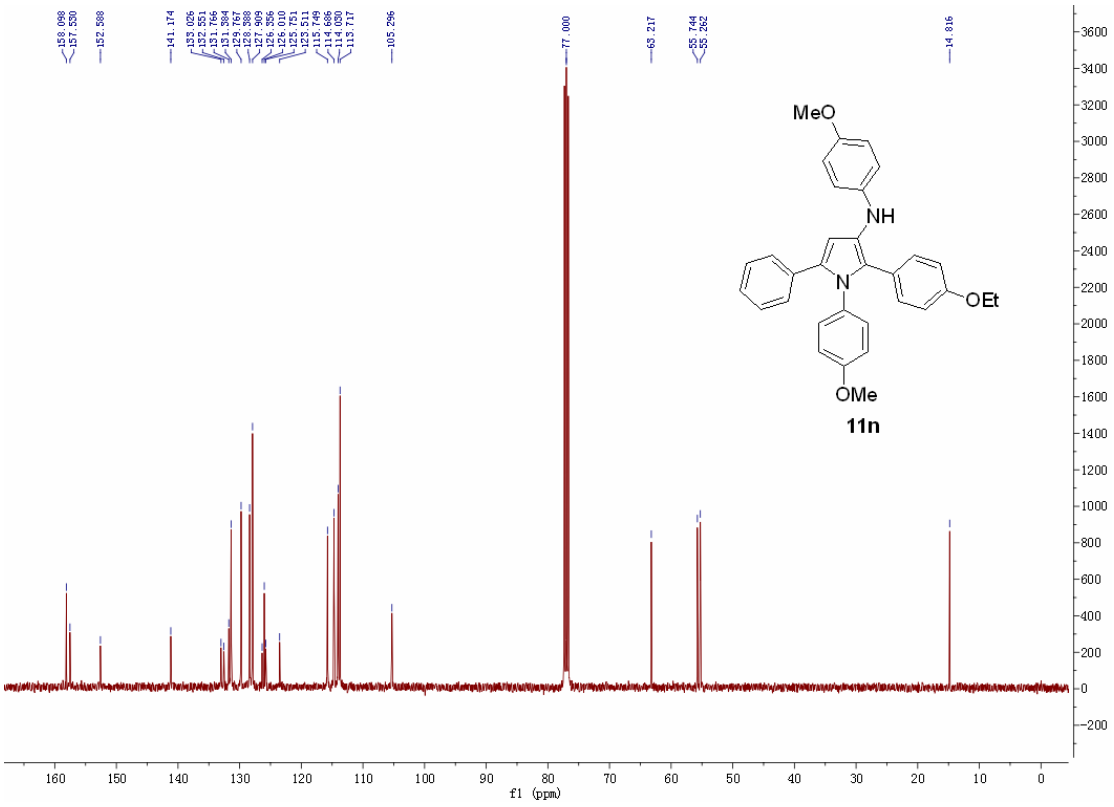

MeO
NH
N
O
OMe
11l

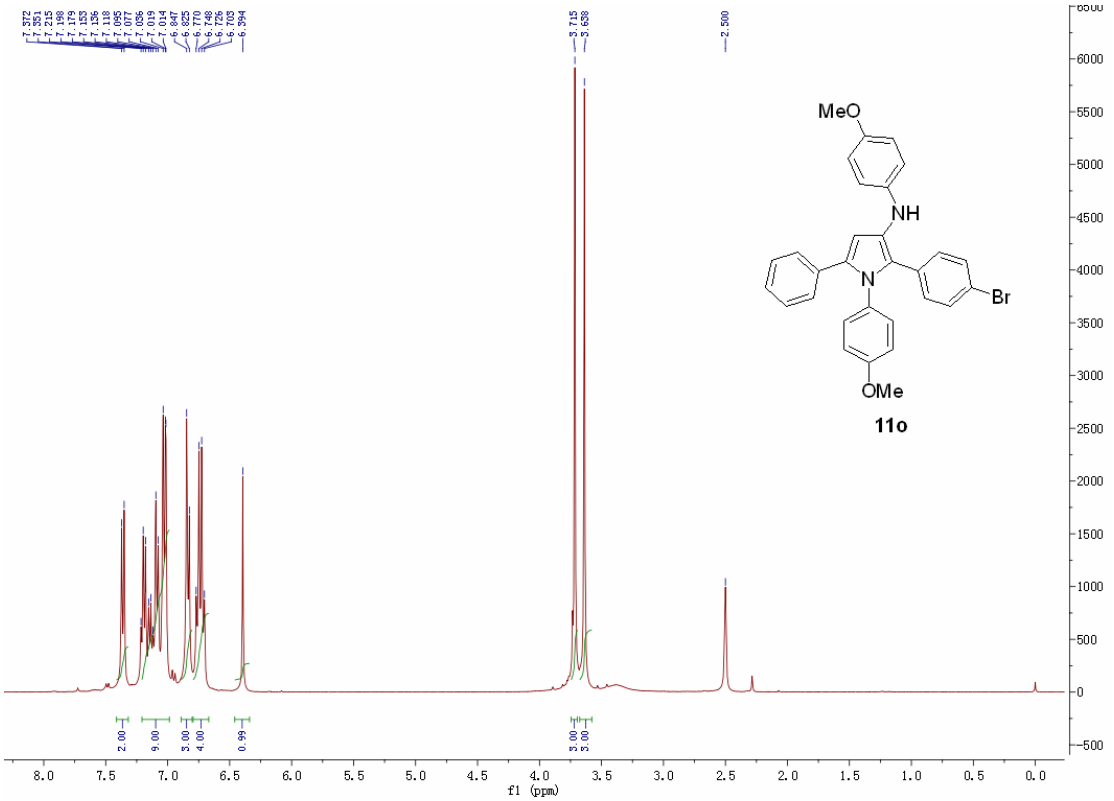

MeO
NH
N
O
OMe
11l

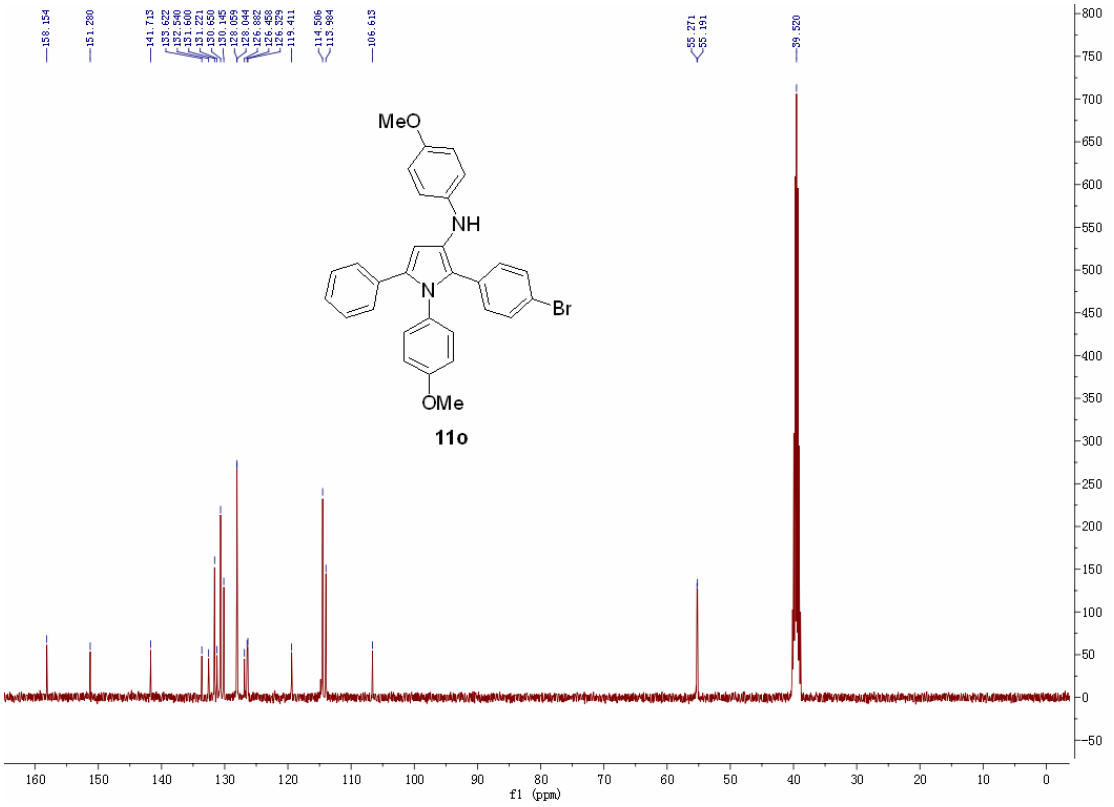

MeO
NH
N
OMe
11m
f1 (ppm)

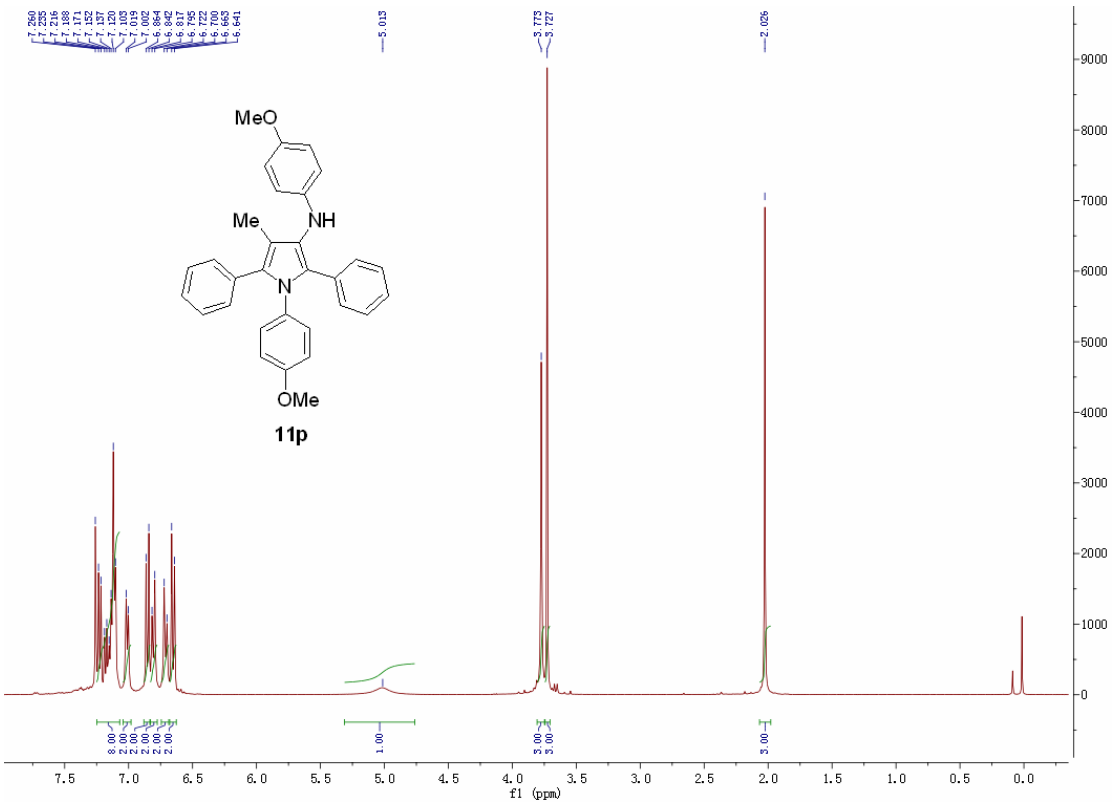

MeO
NH
N
OMe
11m
f1 (ppm)

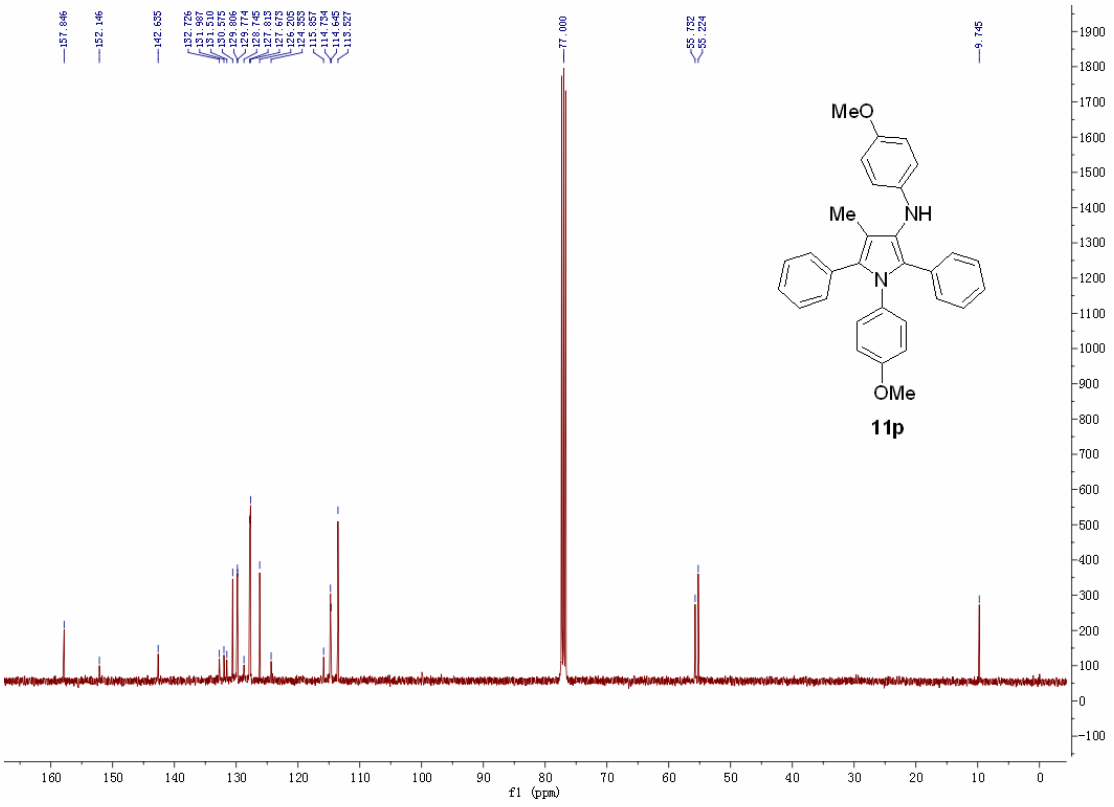

MeO
NH
N
OEt
OMe
11n
f1 (ppm)

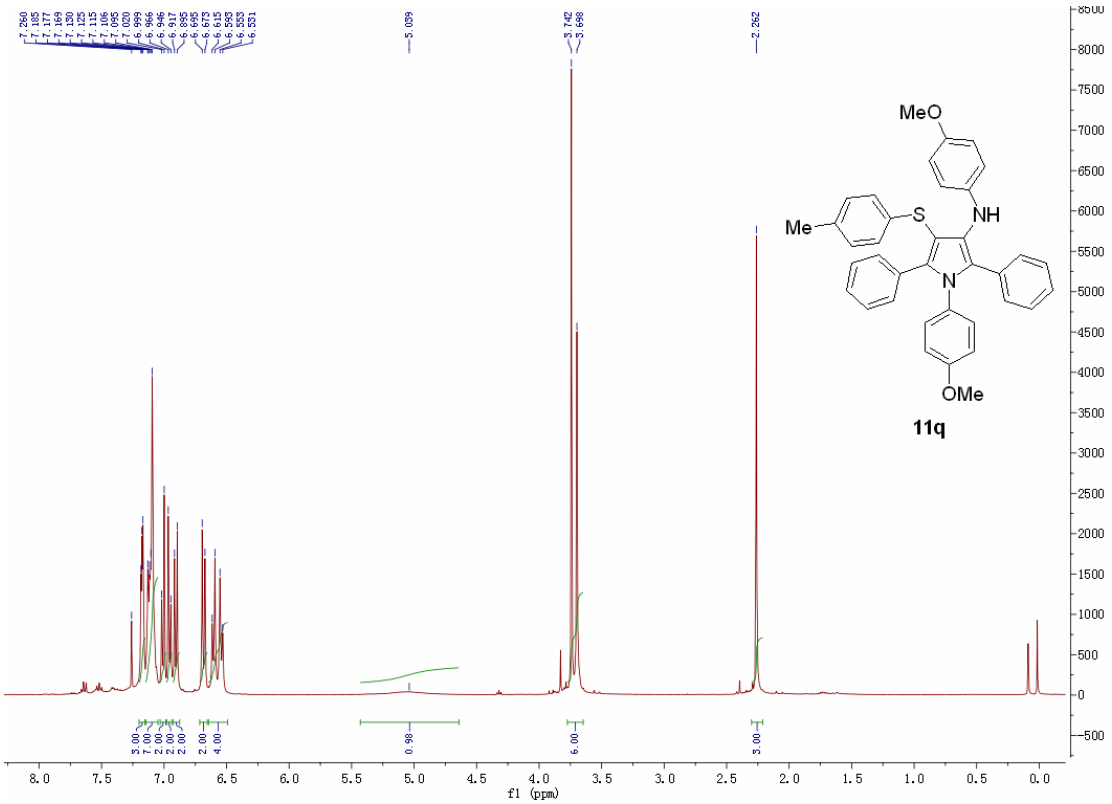

MeO
NH
N
OEt
OMe
11n
f1 (ppm)

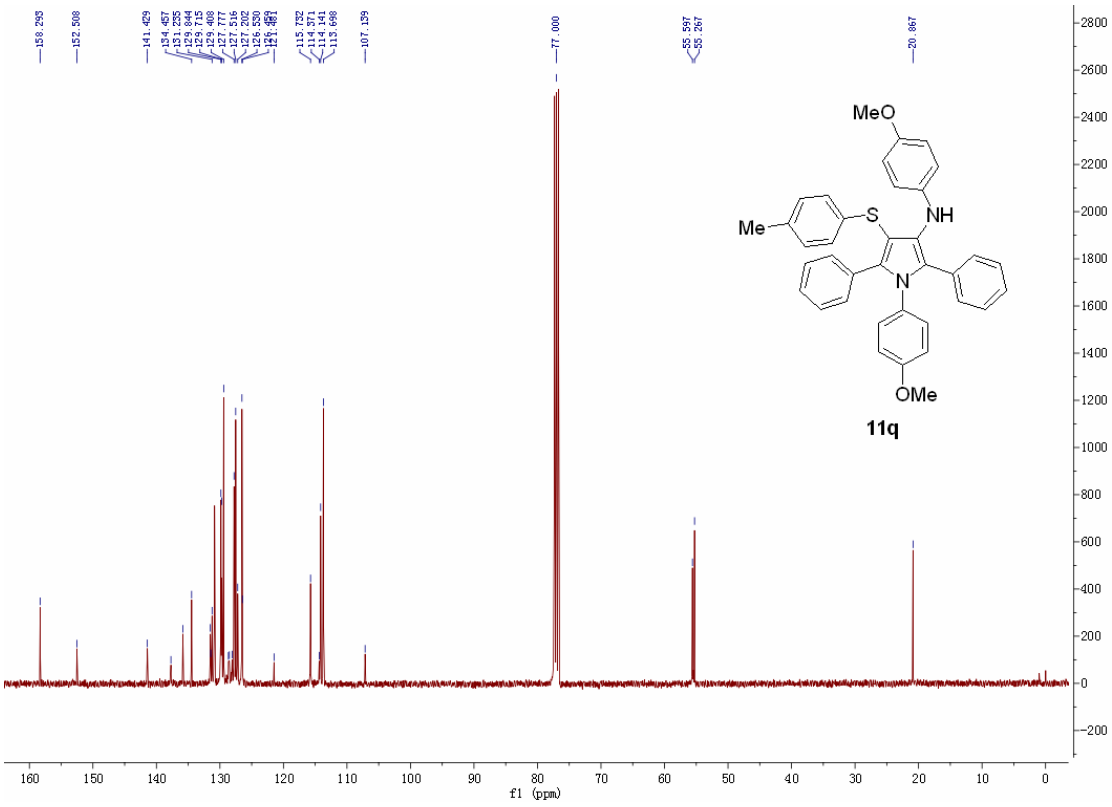

MeO
NH
N
Br
OMe
11o
f1 (ppm)

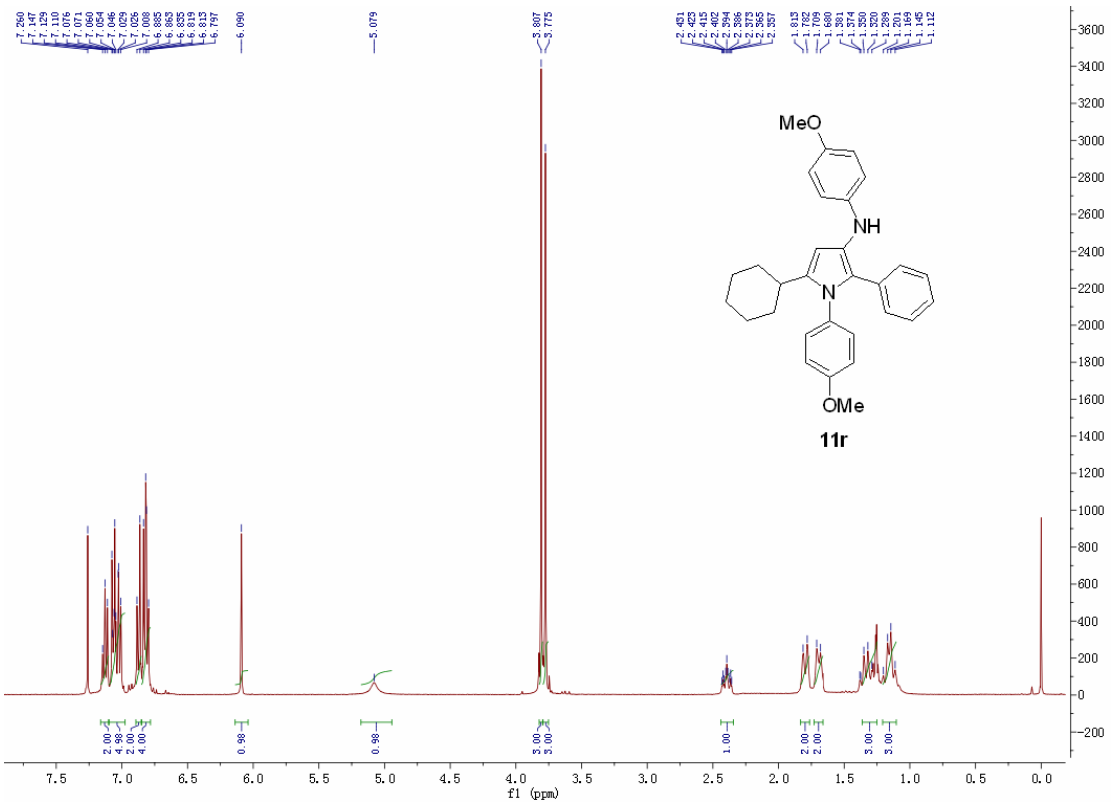

MeO
NH
N
Br
OMe
11o
f1 (ppm)

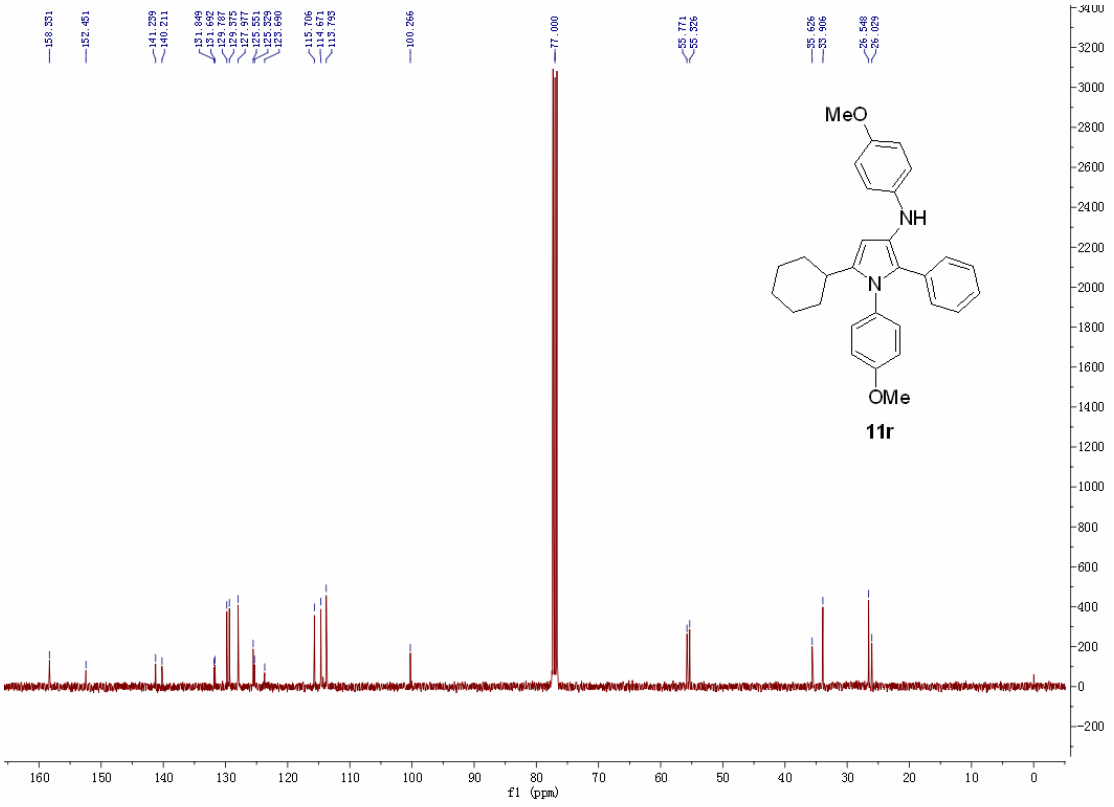

MeO
Me
NH
N
OMe
11p
f1 (ppm)

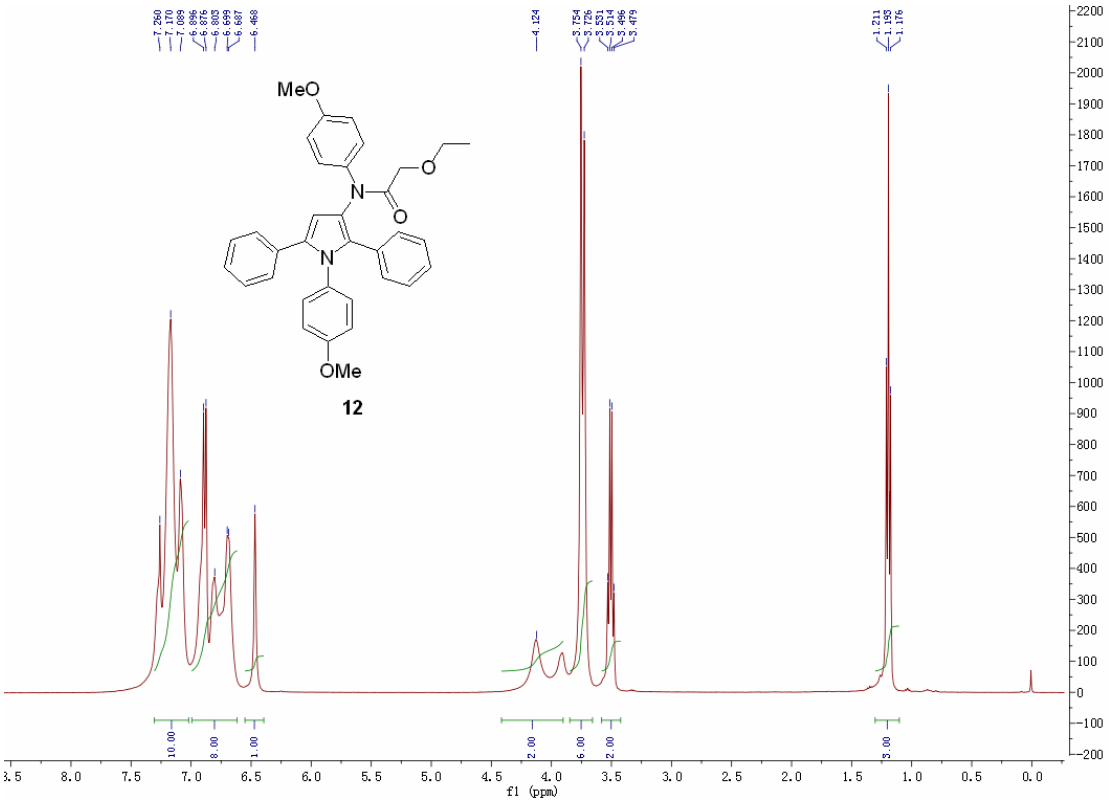

MeO
Me
NH
N
OMe
11p
f1 (ppm)

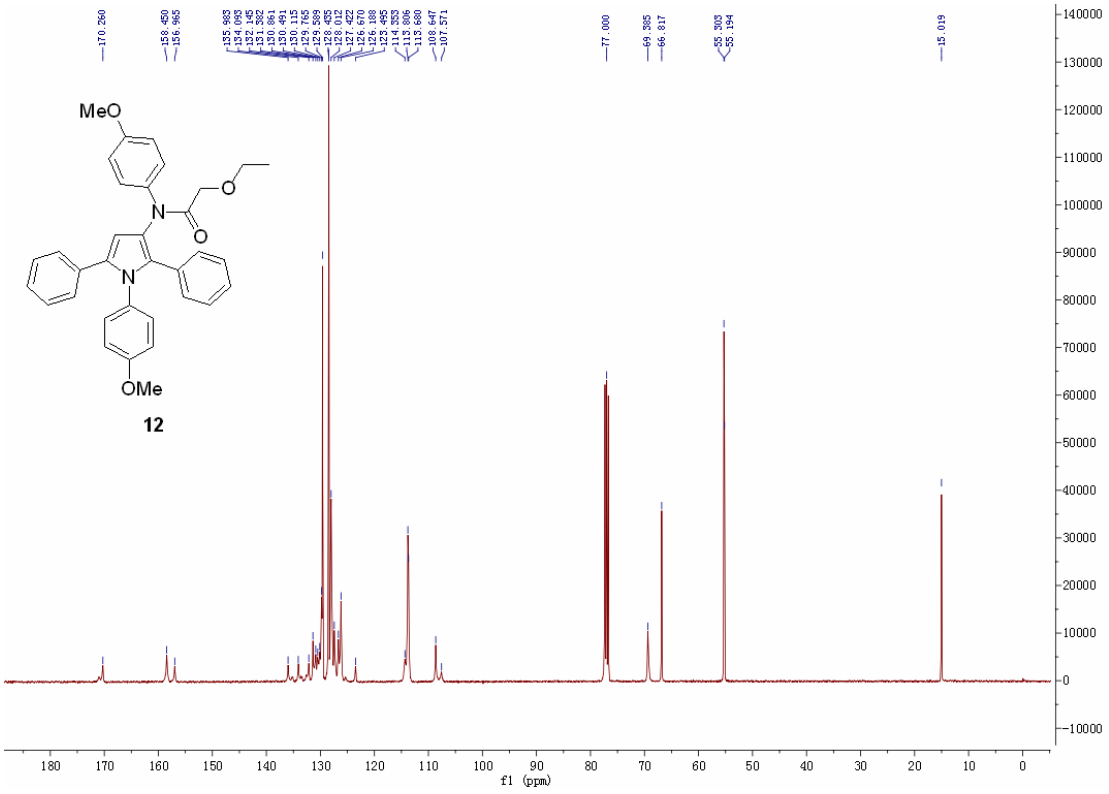

MeO
NH
S
Me
N
OMe
11q


MeO
NH
S
Me
N
OMe
11q

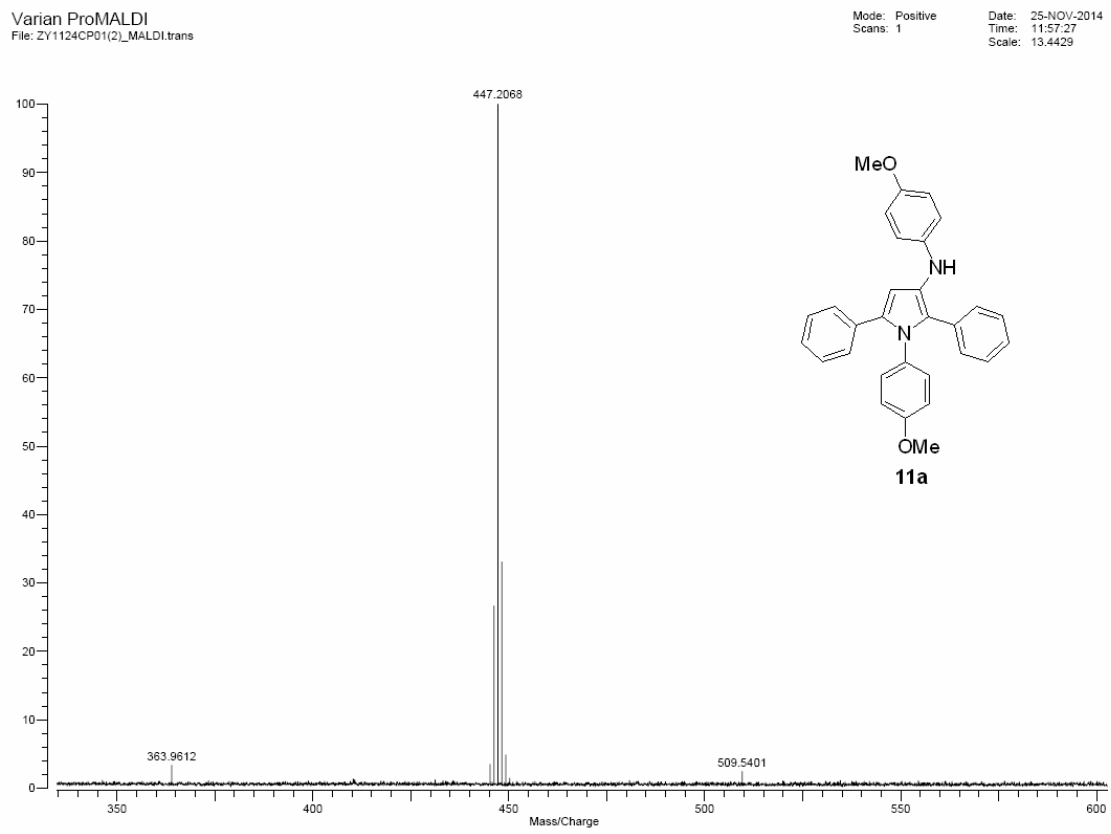

MeO
NH
N
OMe
11r
f1 (ppm)


MeO
NH
N
OMe
11r
f1 (ppm)

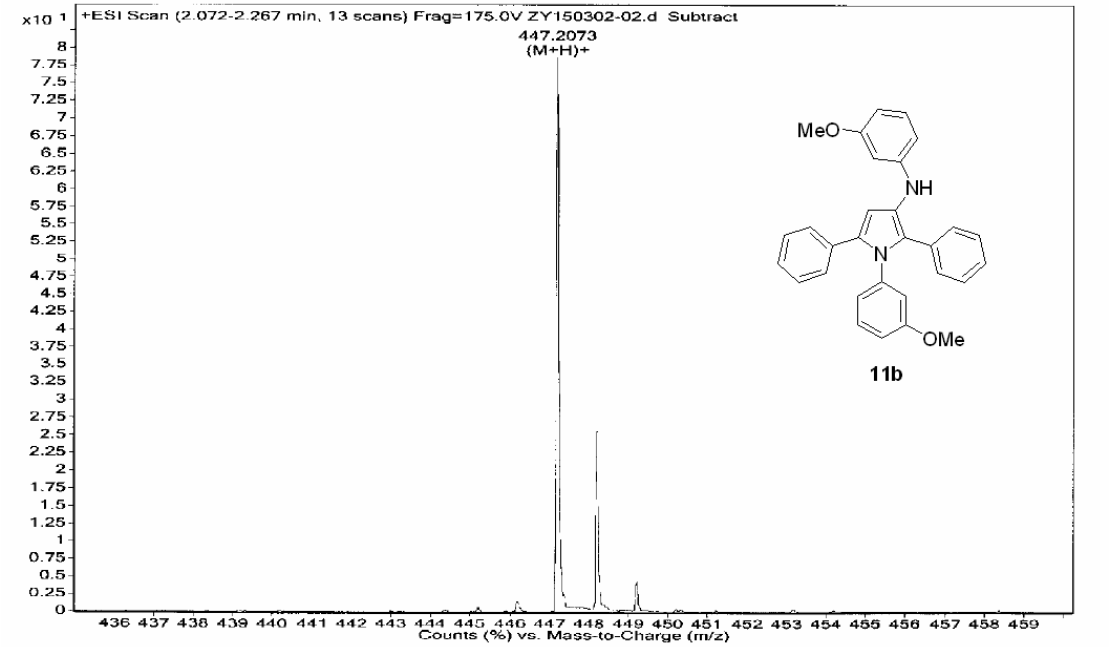

MeO
N
O
O
N
OMe
12
f1 (ppm)


MeO
N
O
O
N
OMe
12
f1 (ppm)

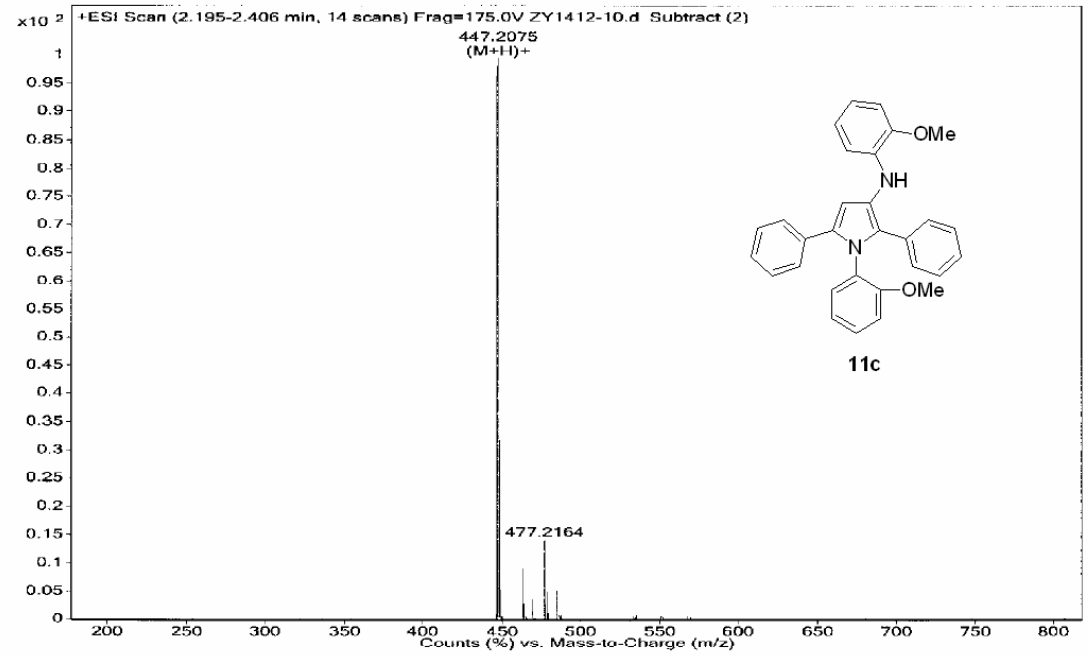
4. Copies of HRMS Spectra



Sample Name	A6	**Position**	P1-A6	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY150302-02.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:04:04 AM

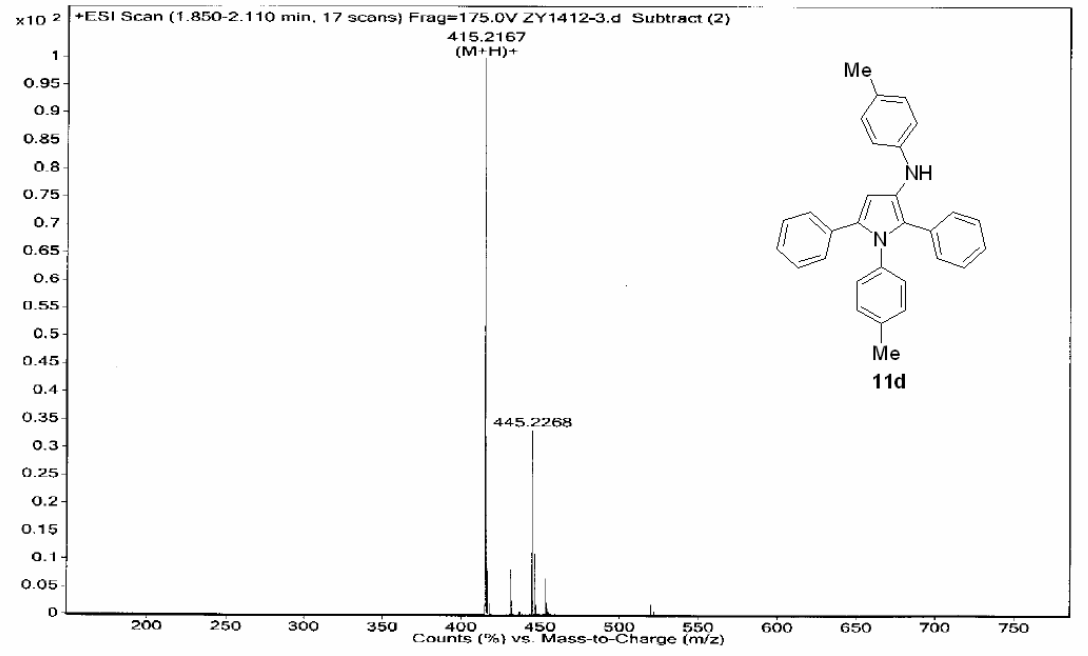


Sample Name	A5	**Position**	P1-A5	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY1412-10.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 9:59:19 A



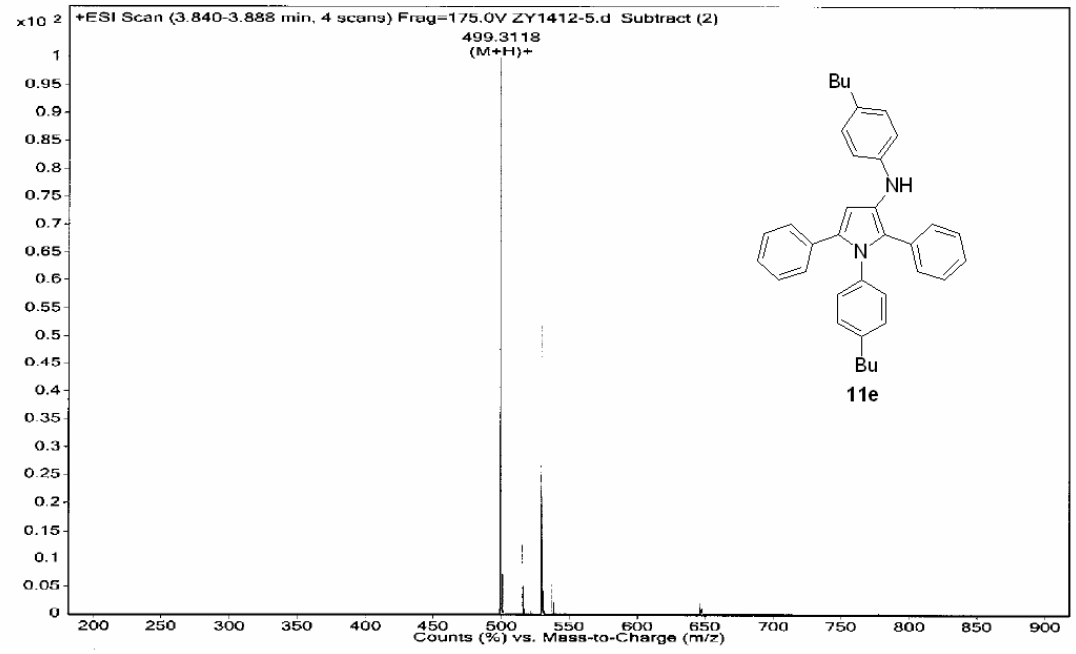
11c

Sample Name	A2	**Position**	P1-A2	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY1412-3.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 9:45:05 AM



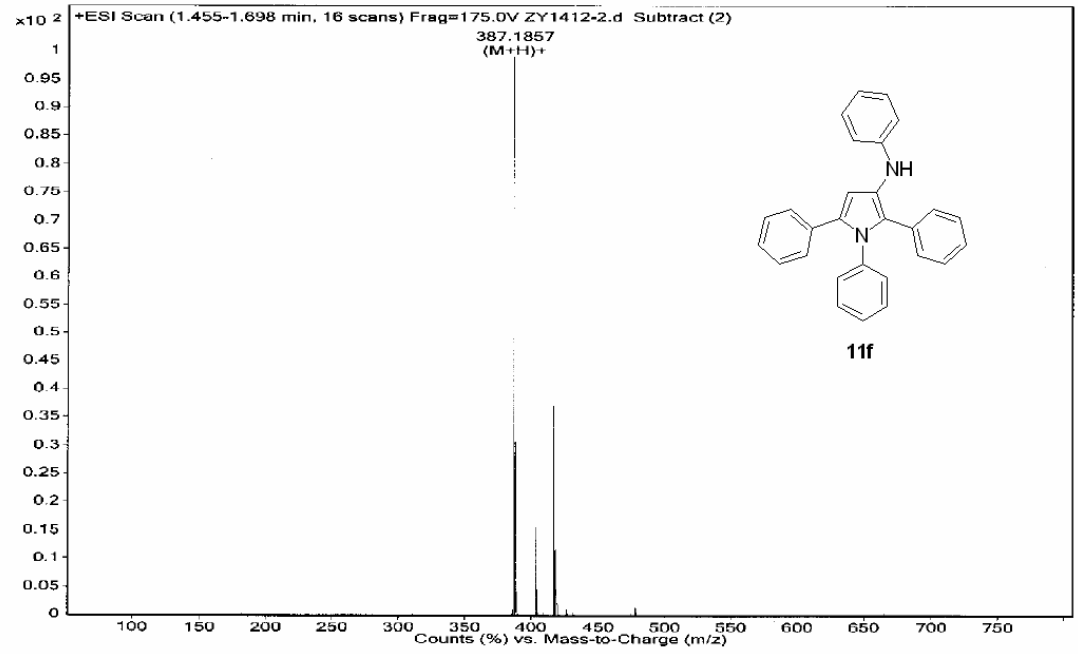
11d

Sample Name	A3	**Position**	P1-A3	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY1412-5.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 9:49:49 AM



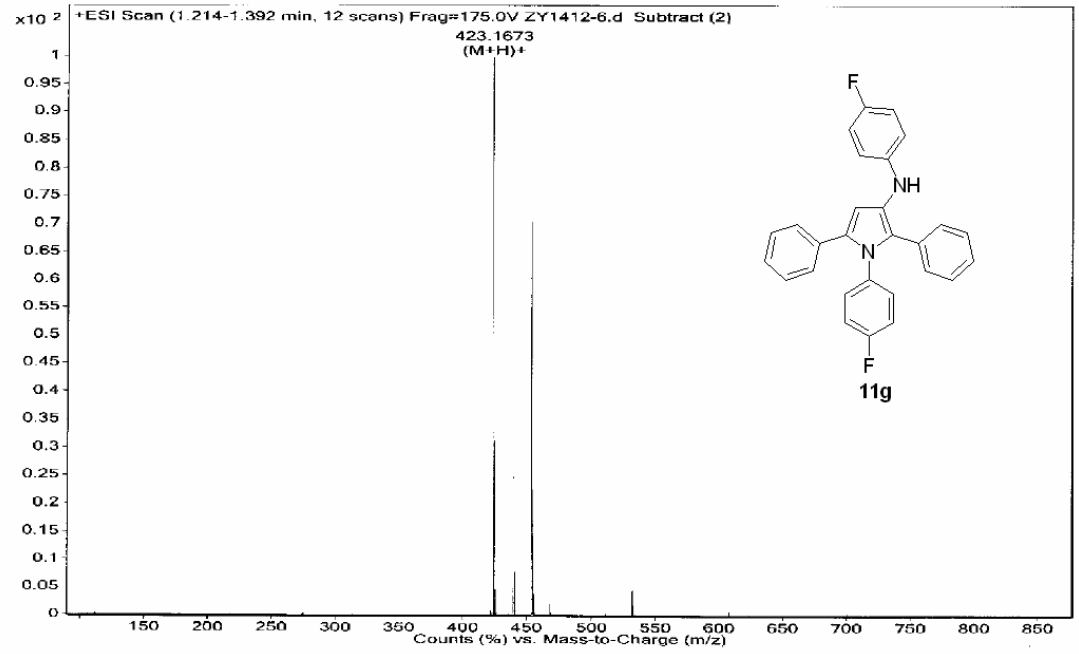
11e

Sample Name	A1	**Position**	P1-A1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY1412-2.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 9:40:20 AM

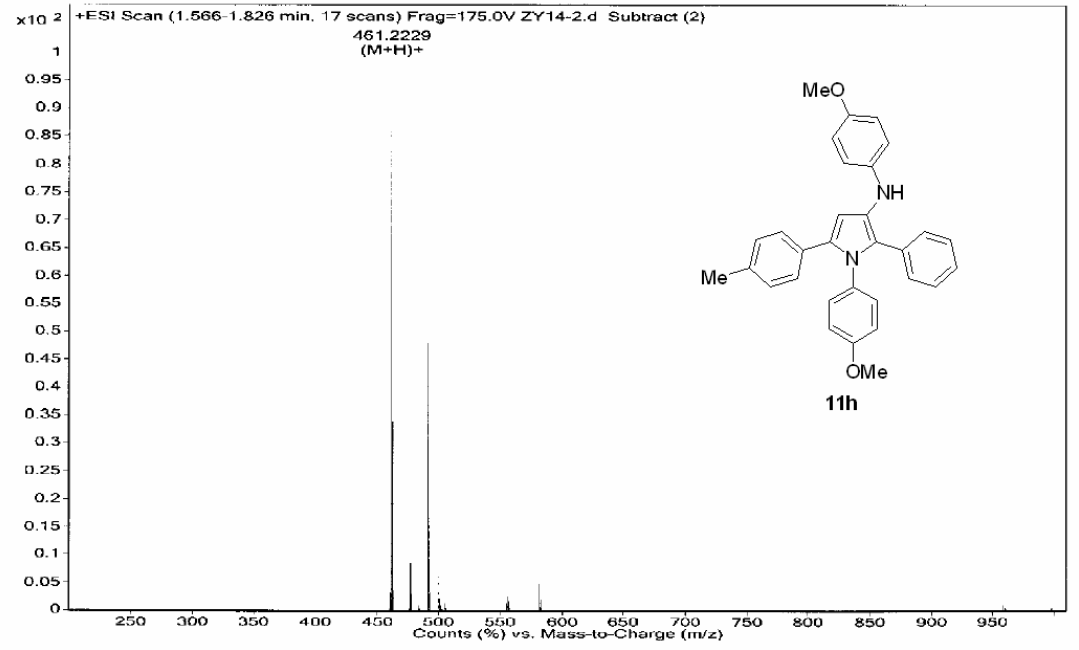


11f

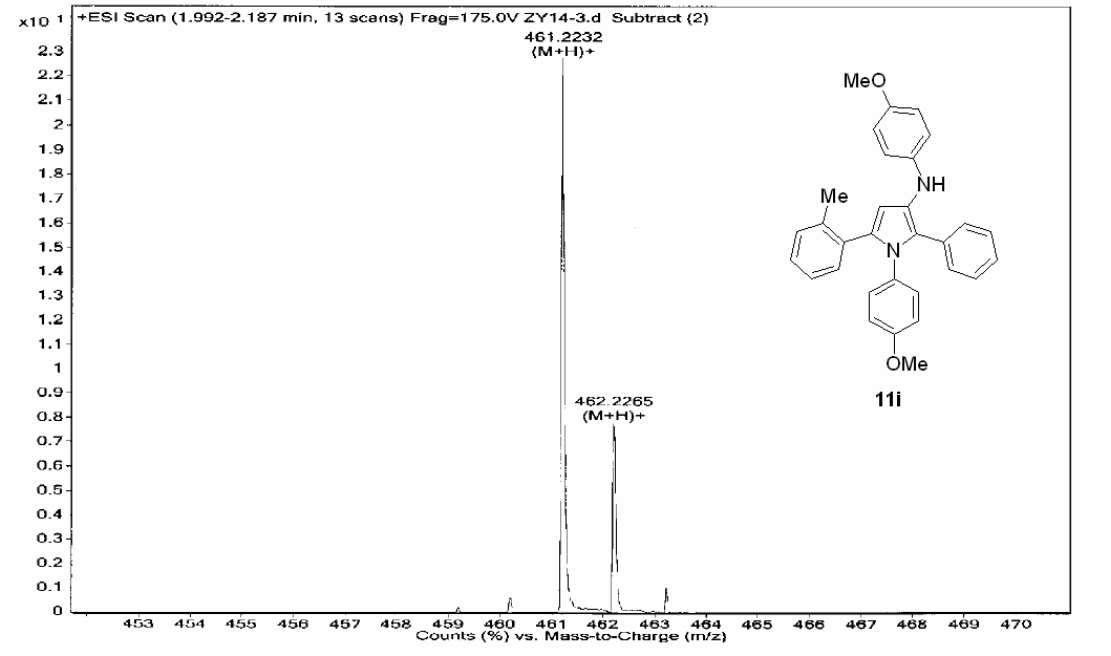
Sample Name	A4	**Position**	P1-A4	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRN Calibration Status**	Some Ions Missed
Data Filename	ZY1412-6.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 9:54:34 AM



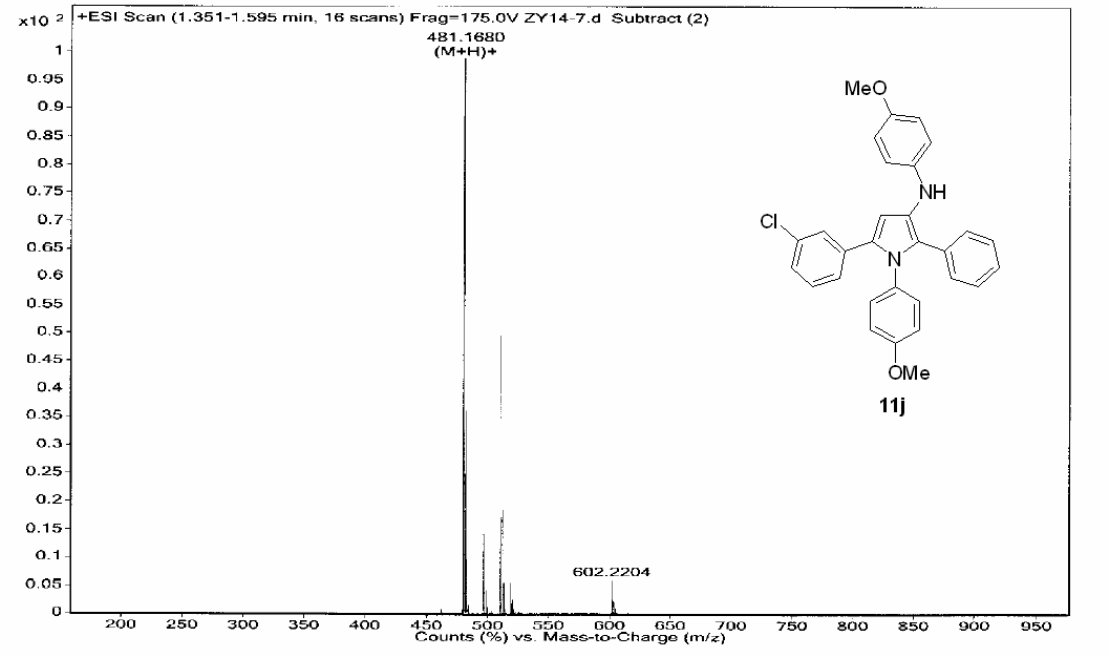
Sample Name	A7	**Position**	P1-A7	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRN Calibration Status**	Some Ions Missed
Data Filename	ZY14-2.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:08:49 AM



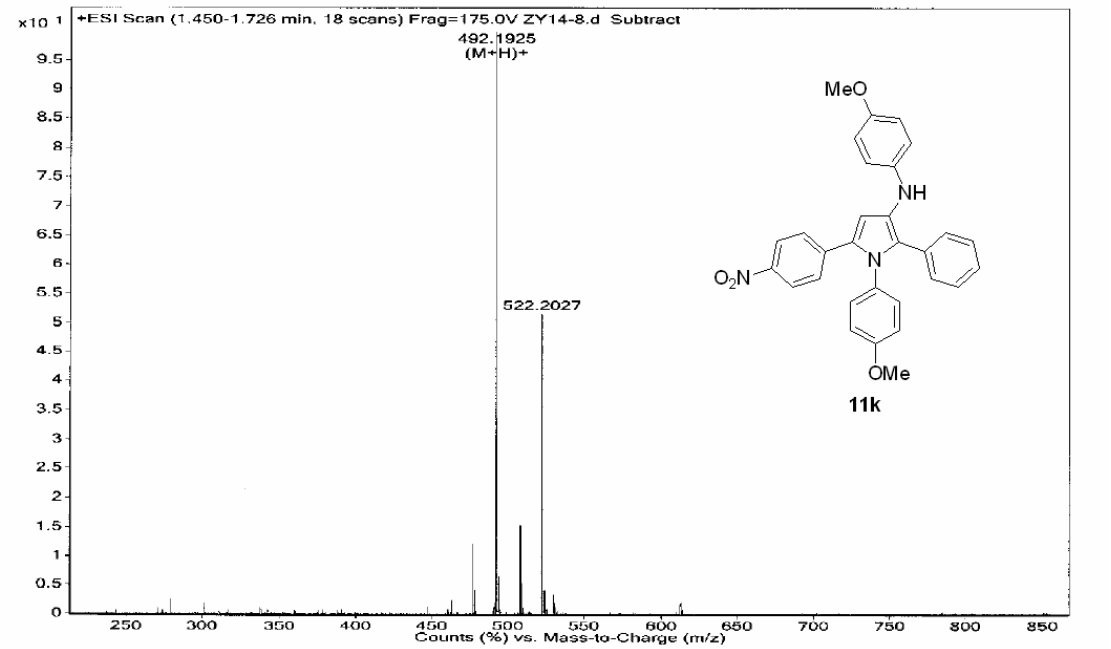
Sample Name	A8	**Position**	P1-A8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY14-3.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:13:34 AM



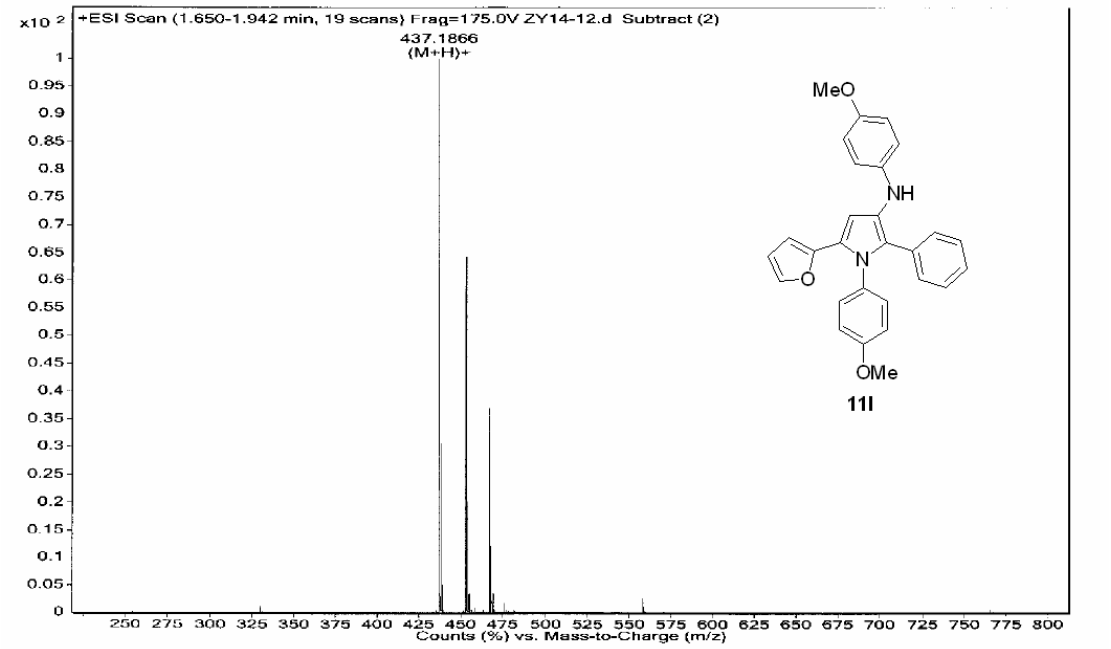
Sample Name	A9	**Position**	P1-A9	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY14-7.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:18:18 AM



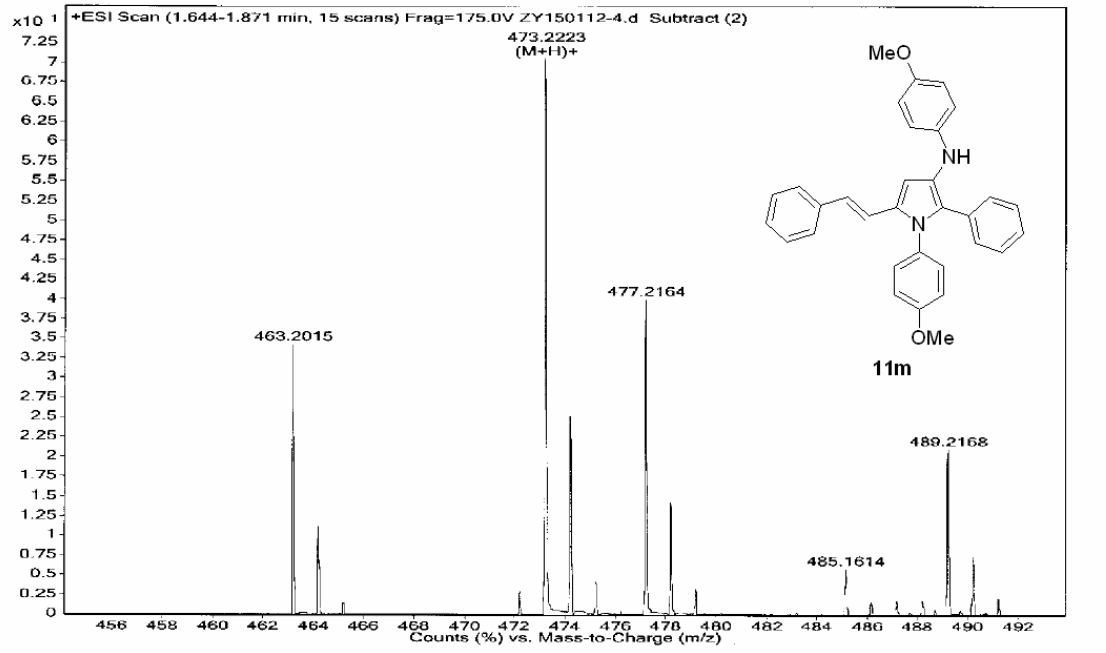
Sample Name	A10	**Position**	P1-B1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY14-8.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:23:03 AM



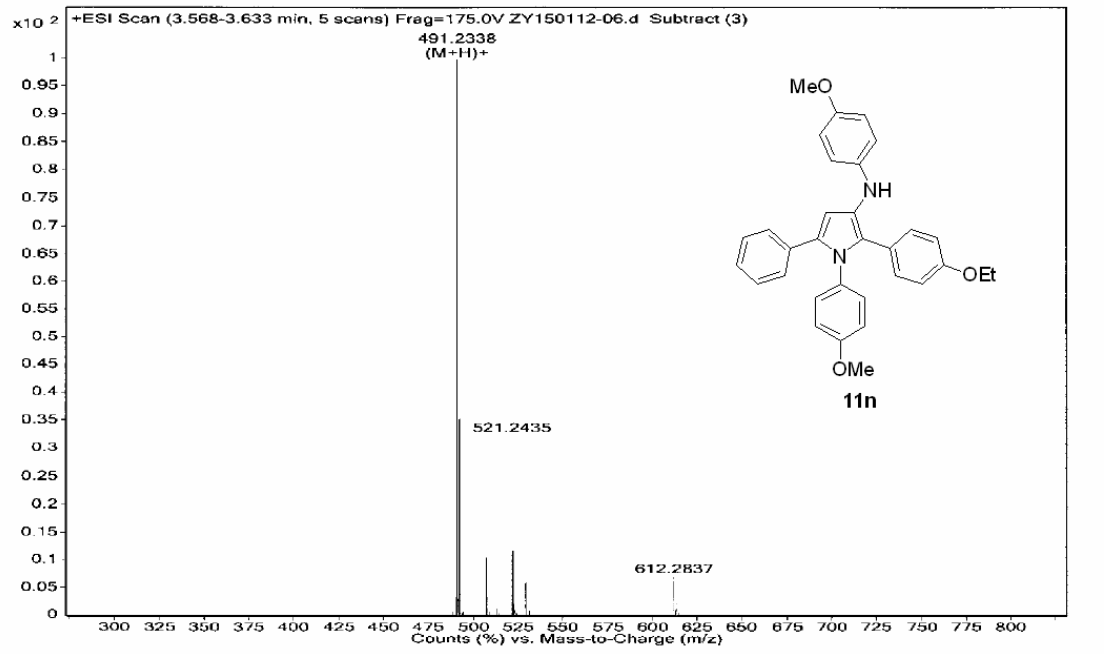
Sample Name	A11	**Position**	P1-B2	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY14-12.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:27:49 AM



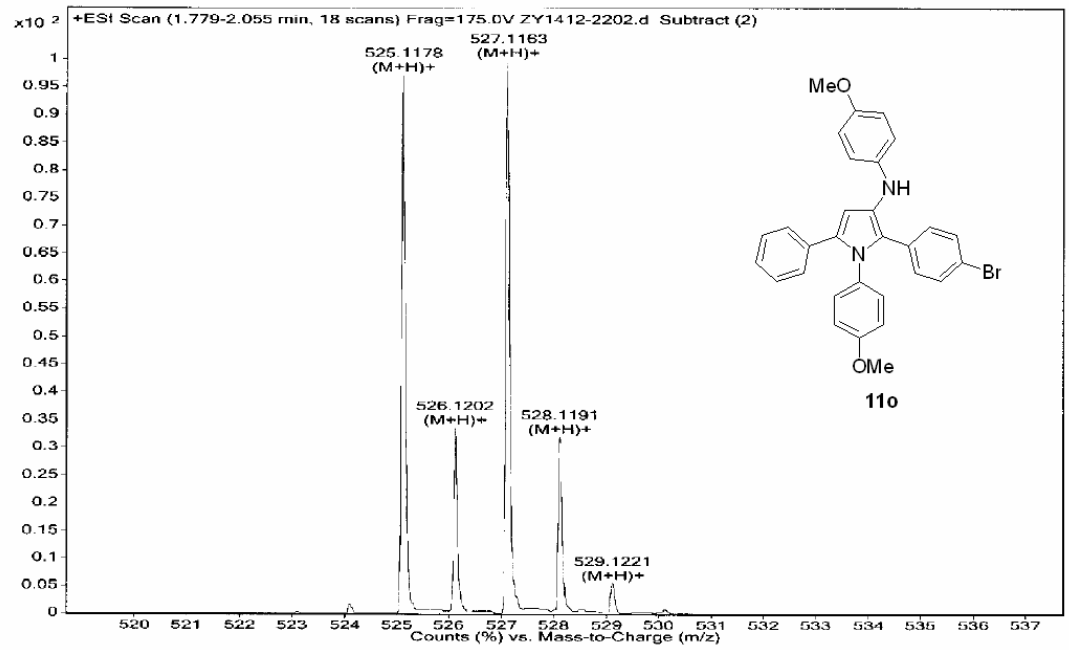
Sample Name	A12	**Position**	P1-B3	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY150112-4.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:32:34 AM



Sample Name	A17	**Position**	P1-B8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY150112-06.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:56:20 AM

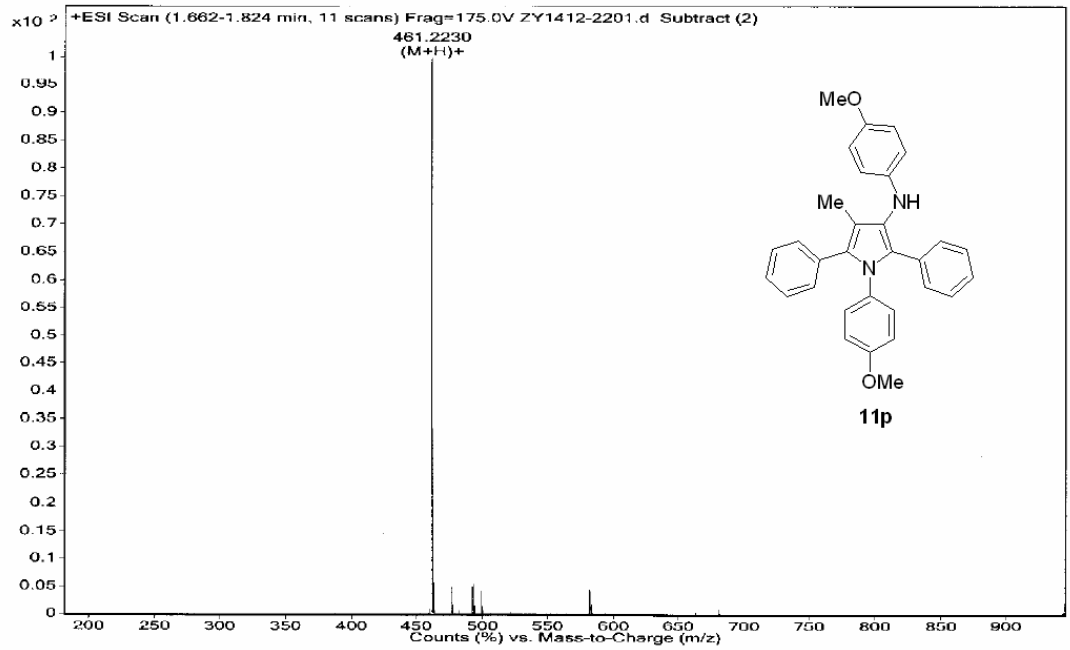


Sample Name	A14	**Position**	P1-B5	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY1412-2202.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:42:04 AM



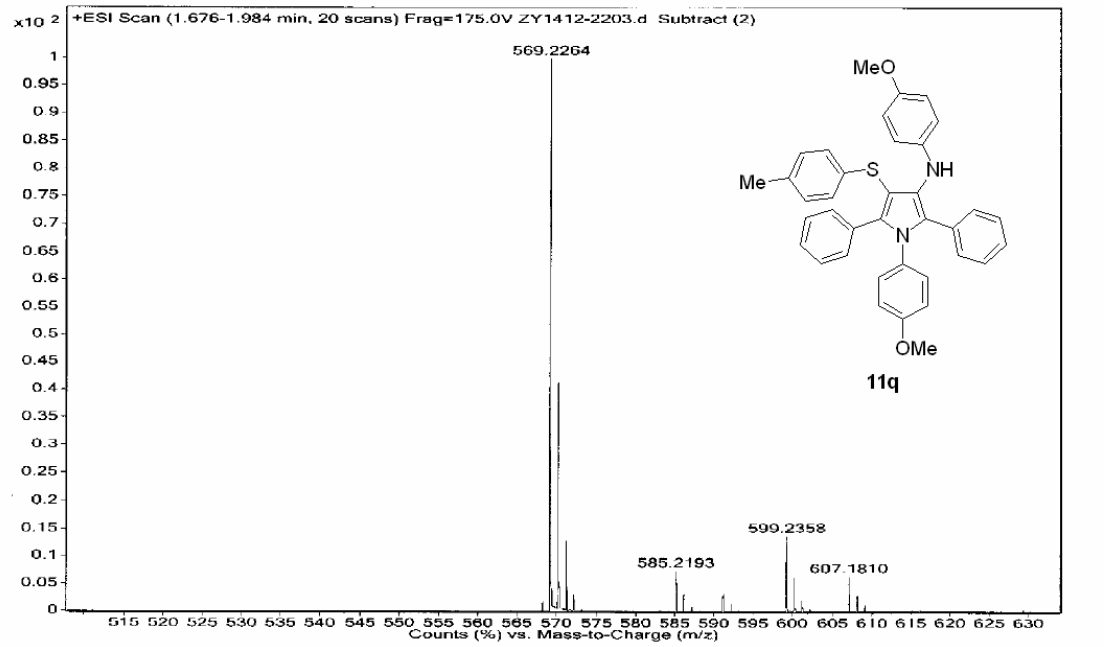
11o

Sample Name	A13	**Position**	P1-B4	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY1412-2201.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:37:19 AM



11p

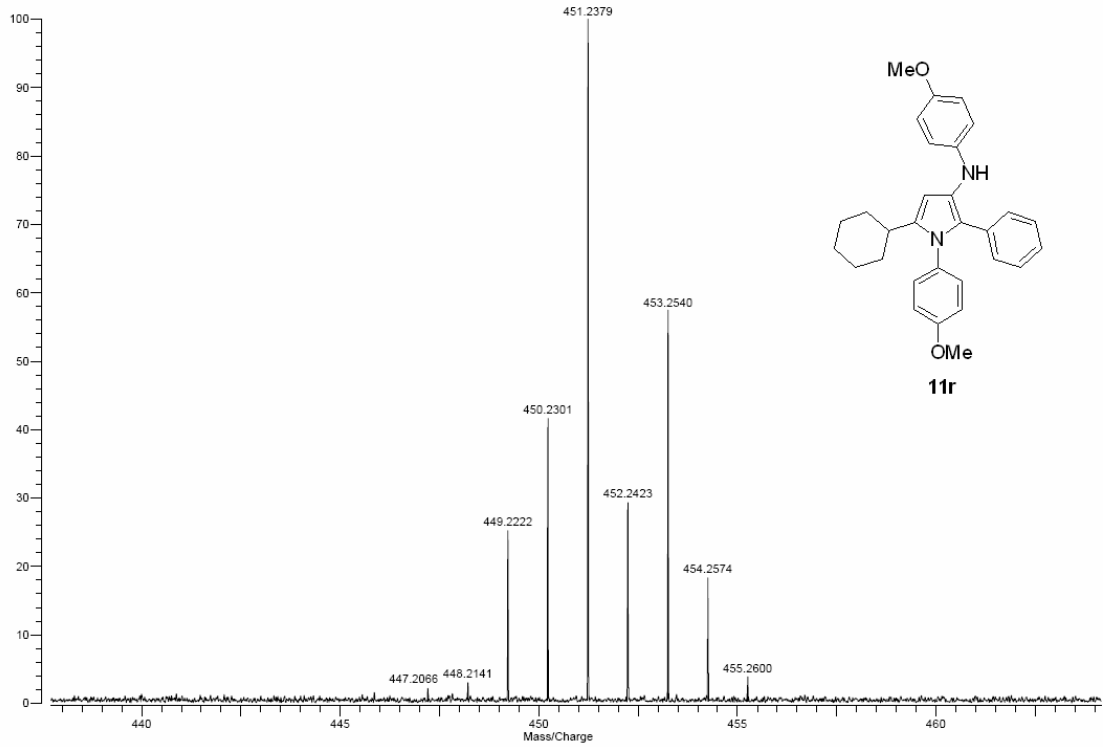
Sample Name	A15	**Position**	P1-B6	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY1412-2203.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	3/13/2015 10:46:50 AM



Varian ProMALDI
File: zy0810-1_MALDI.trans

Mode: Positive
Scans: 1

Date: 10-AUG-2015
Time: 15:50:10
Scale: 17.1978



Sample Name	lc/ms	**Position**	P1-A1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	ZY01.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	5/22/2015 9:54:24 AM