Squaramide-catalysed Asymmetric Friedel-Crafts Alkylation of Naphthol and Unsaturated Pyrazolones

Dedicated to The 100th Anniversary of Chemistry at Nankai University

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Content

General information.

Commercially available compounds were used without further purification. The solvents and reagents were purified according to standard procedures. The silica gel used in the column was 200-300 mesh. The melting point was determined by an XT-4 micro melting point analyzer without calibration. The ^{1}H NMR spectra were collected at 400 and 600 MHz, while the ^{13}C NMR spectra were collected at 101 and 151 MHz correspondingly, using the Bruker Avance II spectrometer. IR spectra were obtained on the Thermo Scientific Nicolet iS5 by the ATR mode. HRMS was measured by ESI-TOF on the Bruker APEX IV mass spectrometer. HPLC analysis was performed using a Chiralpak IC on a Shimadzu SPD-20A detector (eluent = n-hexane/anhydrous ethanol or n-hexane/iso-P ropyl alcohol). XRD analysis of a single crystal was performed on the D8 Venture X-ray single-crystal diffractometer.

Synthesis of organocatalysts I−XIX.

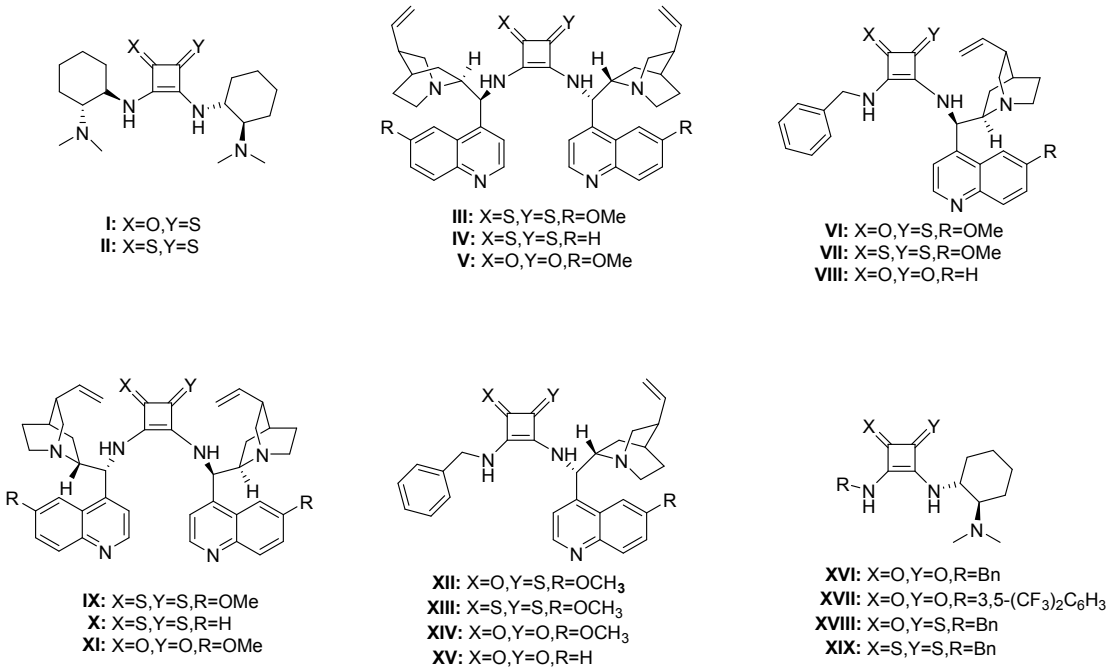
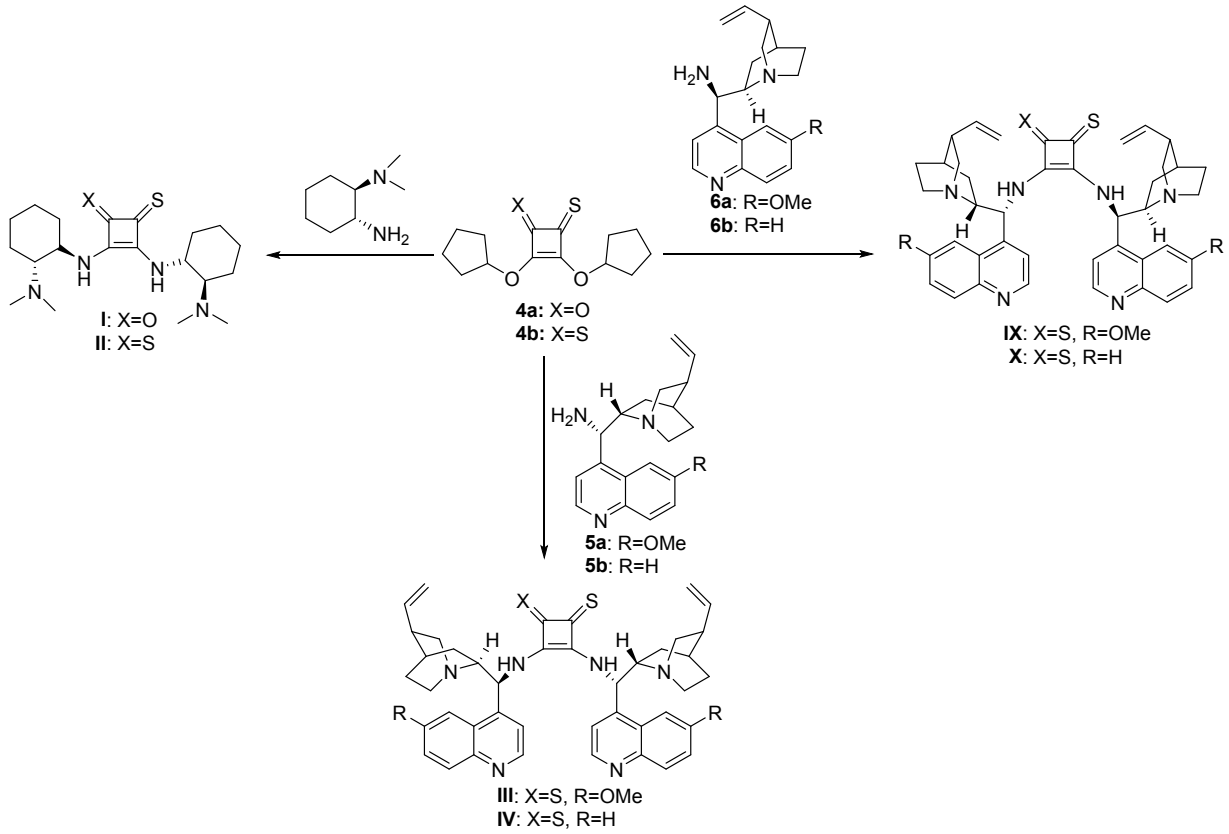


Figure S1. Structures of **I-XIX.**

Organocatalysts **V**,[1] **VI−VII**,[2] **VIII**,[3] **XI**,[4] **XII-XIII** and **XVIII**,[5] **XIV-XV**,[6] **XVI** and **XIX**,[7] **XVII**[8] were prepared according to the literature procedures. Organocatalysts **I-IV**, **IX** and **X** were prepared according to the synthetic routes (**Scheme S1**). Intermediates **4a** and **4b** were prepared according to the literature.[9] **5a**, **5b**, **6a** and **6b** were prepared according to the literature.[10]



Scheme S1. Synthetic routes of **I-IV** , **IX** and **X**.

*3-(((1R,2R)-2-(dimethylamino)cyclohexyl)amino)-2-(((1S,2R)-2-(dimethylamino)cyclohexyl)amino)-4-thioxocyclobut-2-en-1-one(**I**)*. (1R,2R)-N, N-dimethylcyclohexane- 1,2-diamine (308 mg, 2.2 mmol, commercially available) was dissolved in 5 mL of MeOH, then prepare a solution of **4a** (266 mg, 1.0 mmol) in MeOH (3 mL) and added dropwise to above solution at room temperature. The mixture was stirred at room temperature for 12 h. After full conversion, the reaction mixture was concentrated and purified by silica gel column chromatography using CH_2Cl_2 and MeOH (gradient 100:1-25:1) as an eluent to afford **I** as an yellow solid: 189 mg, 50% yield, decomposition temperature 208.6 ℃, [α]25 D-240.50 (c = 0.10, CH_2Cl_2). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.41 - 8.15 (d, J = 7.3 Hz, 1H), 7.80 (d, J = 7.3 Hz, 1H), 2.46 - 2.31 (m, 2H), 2.19 (s, 6H), 2.17 (s, 6H), 2.10 (dd, J = 8.4, 4.5 Hz, 2H), 1.93 - 1.55 (m, 7H), 1.37 (dd, J = 15.6, 7.3 Hz, 1H), 1.32 - 1.02 (m, 8H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 180.1, 171.9, 169.3, 138.2, 66.4, 55.7, 53.4, 36.6, 35.0, 24.8, 24.6, 21.6. IR 3176, 3063, 2924, 2853, 1762, 1611, 1239, 113 cm^{-1}. HRMS (ESI) m/z calcd for $C_{20}H_{35}N_4OS$ $[M+H]^+$ 379.2526, found 379.2544.

*3-(((1R,2R)-2-(dimethylamino)cyclohexyl)amino)-4-(((1S,2R)-2-(dimethylamino)cyclohexyl)amino)cyclobut-3-ene-1,2-dithione (**II**)*. (1R,2R)-N, N-dimethylcyclohexane-1,2-diamine (308 mg, 2.2 mmol, commercially available) was dissolved in 5 mL of MeOH, then prepare a solution of **4b** (282

mg, 1.0 mmol) in MeOH (3 mL) and added dropwise to above solution at room temperature. The mixture was stirred at room temperature for 6 h. After full conversion, the reaction mixture was concentrated and purified by silica gel column chromatography using CH_2Cl_2 and MeOH (gradient 120:1−30:1) as an eluent to afford **II** as an yellow solid: 211 mg, 54% yield, decomposition temperature 240.5 ℃, [α]25 D-325.00 (c = 0.004, CH_2Cl_2). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.70-8.49 (d, J = 10.8 Hz, 2H), 4.89-4.77 (m, 2H), 2.48-2.43 (m, 2H), 2.20 (s, 12H), 1.85 (d, J = 12.0 Hz, 2H), 1.74 (m, 2H), 1.67-1.63 (m, 2H), 1.41-1.34 (m, 2H), 1.28-1.12 (m, 8H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 203.0, 170.4, 66.1, 54.3, 40.0, 36.1, 24.7, 24.7, 21.5. IR 3159, 3122, 2924, 2854, 1709, 1578, 1238 cm^{-1}. HRMS (ESI) m/z calcd for $C_{20}H_{35}N_4S_2$ $[M+H]^+$ 395.2298, found 395.2304.

*3,4-bis(((1S)-(6-methoxyquinolin-4-yl)((2S)-5-vinylquinuclidin-2-yl)methyl)amino)cyclobut-3-ene-1,2-dithione (**III**).* Compound **5a** (296 mg, 0.92 mmol) was dissolved in 10 mL of MeOH, then prepare a solution of **4b** (130 mg, 0.46 mmol) in MeOH (3 mL) and added dropwise to above solution at room temperature. The mixture was stirred at room temperature for 12 h. After full conversion, the reaction mixture was concentrated and purified by silica gel column chromatography using CH_2Cl_2 and MeOH and $NH_3{\cdot}H_2O$ (gradient 100:1:1-100:3:1) as an eluent to afford **III** as an yellow solid: 148 mg, 43% yield, decomposition temperature 192.8 ℃, [α]25 D-234.00 (c = 0.10, CH_2Cl_2). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.76 (d, J = 4.6 Hz, 1H), 8.07 (dd, J = 32.8, 9.9 Hz, 1H), 7.93 (d, J = 34.7 Hz, 4H), 7.50-7.35 (m, 4H), 5.84-5.65 (m, 2H), 5.15 (d, J = 20.3 Hz, 1H), 5.06 (d, J = 7.9 Hz, 1H), 5.01 (d, J = 17.3 Hz, 2H), 4.98 (d, J = 10.6 Hz, 2H), 4.91 (s, 1H), 4.78 (s, 1H), 4.05 (s, 3H), 3.98 (s, 3H), 3.29 (d, J = 3.8 Hz, 4H), 2.89-2.75 (m, 4H), 2.37-2.24 (m, 3H), 1.74-1.67 (m, 3H), 1.67-1.60 (m, 4H), 1.60-1.50 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 181.4, 157.6, 147.8, 141.5, 133.0, 131.8, 128.6, 127.3, 121.2, 114.4, 110.9, 101.6, 91.5, 56.1, 55.5, 40.9, 39.6, 29.6, 28.0, 27.5, 25.9. IR 1712, 1620, 1580, 1506, 1474, 1432, 1357, 1288, 1222, 1136, 1096, 1024, 909 cm^{-1}. HRMS (ESI) m/z calcd for $C_{44}H_{49}N_6O_2S_2$ $[M+H]^+$ 757.3353, found 757.3367.

*3,4-bis(((1S)-quinolin-4-yl((2S)-5-vinylquinuclidin-2-yl)methyl)amino)cyclobut-3-ene-1,2-dithione (**IV**).* Compound **5b** (268 mg, 0.92 mmol) was dissolved in 10 mL of MeOH, then prepare a solution of **4b** (130 mg, 0.46 mmol) in MeOH (3 mL) and added dropwise to above solution at room temperature. The mixture was stirred at room temperature for 6 h. After full conversion, the reaction mixture was concentrated and purified by silica gel column chromatography using CH_2Cl_2 and MeOH and $NH_3{\cdot}H_2O$ (gradient 100:1:1−90:30:1) as an eluent to afford **IV** as an yellow solid: 150 mg, 47% yield, decomposition temperature 205.3 ℃, [α]25 D-57.60 (c = 0.10,

CH_2Cl_2). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.99 - 8.79 (d, 2H), 8.55 - 8.20 (m, 2H), 8.11 (dd, *J* = 39.9, 11.1 Hz, 2H), 7.77 - 7.54 (m, 4H), 5.88 - 5.59 (m, 2H), 5.35 (q, *J* = 4.6 Hz, 2H), 5.18 - 4.94 (m, 4H), 4.00 (d, *J* = 48.4 Hz, 2H), 3.38 - 3.18 (m, 2H), 3.18 - 2.95 (m, 2H), 2.94 - 2.74 (m, 3H), 2.69 (dd, *J* = 24.1, 11.3 Hz, 1H), 2.63 - 2.41 (m, 2H), 2.26 - 2.19 (m, 1H), 2.01 (q, *J* = 6.5 Hz, 2H), 1.75 - 1.54 (m, 6H), 1.43 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.0, 150.9, 148.6, 146.0, 141.6, 130.3, 130.1, 127.5, 126.6, 125.4, 120.9, 115.3, 60.9, 55.3, 53.6, 41.2, 38.8, 27.4, 26.8, 25.5. IR 1687, 1635, 1582, 1508, 1462, 1353, 1290, 1228, 1191, 1172, 1082, 1024, 925 cm^{-1}. HRMS (ESI) m/z calcd for $C_{42}H_{43}N_6S_2$ $[M-H]^-$ 695.2996, found 695.2999.

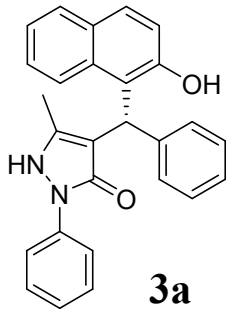
*3-(((R)-(6-methoxyquinolin-4-yl)((1R,2R,4R,5S)-5-vinylquinuclidin-2-yl)methyl)amino)-4-(((R)-(6-methoxyquinolin-4-yl)((1S,2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)amino)cyclobut-3-ene-1,2-dithione(**IX**).* Compound **6a** (296 mg, 0.92 mmol) was dissolved in 10 mL of MeOH, then prepare a solution of **4b** (130 mg, 0.46 mmol) in MeOH (3 mL) and added dropwise to above solution at room temperature. The mixture was stirred at room temperature for 6 h. After full conversion, the reaction mixture was concentrated and purified by silica gel column chromatography using CH_2Cl_2 and MeOH and $NH_3{\cdot}H_2O$ (gradient 100:1:1-90:30:1) as an eluent to afford **IX** as an yellow solid: 138 mg, 40% yield, decomposition temperature 227.0 ℃, [α]25 D+292.13 (*c* = 0.10, CH_2Cl_2). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.85 (s, 2H), 8.19 (s, 2H), 7.95 (d, *J* = 9.1 Hz, 2H), 7.84 (s, 2H), 7.39 (dd, *J* = 38.0, 8.5 Hz, 4H), 5.82 (ddd, *J* = 16.8, 10.6, 5.7 Hz, 2H), 5.18 (dd, *J* = 102.3, 13.3 Hz, 4H), 4.02 (s, 6H), 3.73 (s, 2H), 2.92 (s, 2H), 2.76 (d, *J* = 39.2 Hz, 4H), 2.21 (d, *J* = 69.6 Hz, 3H), 2.01 - 1.65 (m, 1H), 1.65 - 1.31 (m, 7H), 1.29 - 1.01 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.3, 158.3, 148.1, 144.8, 140.3, 131.8, 127.8, 122.9, 120.9, 115.5, 103.0, 56.6, 49.2, 46.2, 38.3, 27.5, 25.6, 24.5. IR 1682, 1620, 1591, 1507, 1476, 1359, 1257, 1236, 1220, 1092, 1024, 985 cm^{-1}. HRMS (ESI) m/z calcd for $C_{44}H_{49}N_6O_2S_2$ $[M+H]^+$ 757.3353. found 757.3376.

*3-(((R)-quinolin-4-yl((1R,2R,4R,5S)-5-vinylquinuclidin-2-yl)methyl)amino)-4-(((R)-quinolin-4-yl((1S,2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)amino)cyclobut-3-ene-1,2-dithione (**X**).* Compound **6b** (268 mg, 0.92 mmol) was dissolved in 10 mL of MeOH, then prepare a solution of **4b** (130 mg, 0.46 mmol) in MeOH (3 mL) and added dropwise to above solution at room temperature. The mixture was stirred at room temperature for 6 h. After full conversion, the reaction mixture was concentrated and purified by silica gel column chromatography using CH_2Cl_2 and MeOH and $NH_3{\cdot}H_2O$ (gradient 100:1:1−90:30:1) as an eluent to afford **X** as an yellow solid: 143mg, 45% yield, decomposition temperature 207.3 ℃, [α]25 D-87.40 (*c* = 0.10, CH_2Cl_2). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.01-8.89 (m, 1H), 8.70 (d, *J* = 34.6 Hz, 2H),

8.18-8.11 (m, 1H), 8.01 (d, *J* = 14.7 Hz, 2H), 7.77-7.68 (m, 2H), 7.59 (dd, *J* = 16.9, 9.1 Hz, 4H), 5.87 (s, 2H), 5.42-5.19 (m, 2H), 5.16 (d, *J* = 24.9 Hz, 2H), 4.09 (d, *J* = 49.7 Hz, 2H), 3.12-3.00 (m, 3H), 2.99-2.80 (m, 4H), 2.79-2.55 (m, 4H), 2.09 (s, 3H), 1.81-1.67 (m, 2H), 1.67-1.53 (m, 4H), 1.47 (d, *J* = 14.8 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.3, 148.5, 144.8, 140.3, 130.4, 129.7, 129.0, 127.7, 126.4, 114.7, 50.7, 49.4, 47.2, 39.3, 29.6, 27.5, 26.4, 24.9. IR 1689, 1567, 1508, 1457, 1285, 1236, 1169, 1081, 1028, 987, 911 cm^{-1}. HRMS (ESI) m/z calcd for $C_{42}H_{45}N_6S_2$ $[M+H]^+$ 697.3142, found 697.3160.

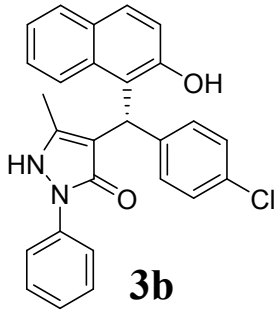
General procedure for the Asymmetric Friedel-Crafts alkylation of naphthol and unsaturated pyrazolones

The unsaturated pyrazolones **1** (0.1 mmol, 1 equiv) and **XV** (2.4 mg, 0.005 mmol) were dissolved in MeCN (3 mL) at 35 ℃. The mixture was stirred for 1 h; then 2-Naphthol **2** (19 mg, 0.13 mmol, 1.3 equiv) was added, and the mixture was stirred for 120 h. The reaction was monitored by TLC (petroleum ether/ethyl acetate = 2:1-1:1). The reaction mixture was concentrated and purified by silica gel column chromatography with petroleum ether and ethyl acetate.



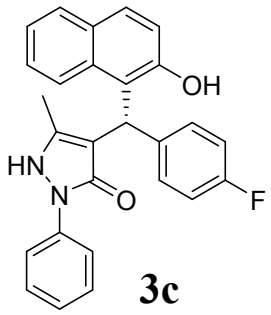
3a

The product was obtained as a white solid: 37 mg, 91%; mp 114.5-116.6 ℃; [α]25 D+41.00 (*c* = 0.10, CH_2Cl_2); ee 88%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 6.275 min, t_R (2) = 15.660 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.59 (s, 1H), 10.75 (s, 1H), 8.22 (d, *J* = 5.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.72 (dd, *J* = 18.0, 8.3 Hz, 3H), 7.44 (q, *J* = 12.4, 10.1 Hz, 3H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24 - 7.19 (m, 3H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.08 (dd, *J* = 14.3, 8.4 Hz, 3H), 6.19 (s, 1H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.1, 141.4, 136.4, 133.5, 132.7, 131.3, 128.9, 128.6, 128.5, 127.7, 127.3, 126.1, 125.3, 125.0, 122.8, 122.2, 120.9, 120.5, 119.1, 106.6, 35.9, 11.5. IR 3063, 3020, 2357, 1618, 1601, 1542, 1495, 1402, 1369, 1345, 1310, 1251, 1225, 1158, 1506, 950, 860, 747, 709, 629, 612 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{23}N_2O_2$ $[M+H]^+$ 407.1754, found 407.1761.



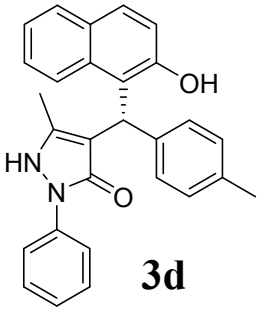
3b

The product was obtained as a white solid: 43 mg, 98%; mp 135.1-136.0 ℃; [α]25 D+47.80 (c = 0.10, CH_2Cl_2); ee 80%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 4.993 min, t_R (2) = 6.101 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.70 (s, 1H), 10.78 (s, 1H), 8.28 - 8.14 (m, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.72 (dd, J = 24.4, 8.3 Hz, 3H), 7.44 (q, J = 9.7, 8.9 Hz, 3H), 7.31 - 7.21 (m, 4H), 7.08 (dd, J = 21.6, 8.5 Hz, 3H), 6.17 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.2, 153.8, 148.2, 140.7, 136.5, 133.5, 130.0, 129.4, 129.0, 128.8, 128.7, 128.6, 127.7, 126.4, 125.3, 122.9, 122.5, 121.0, 120.3, 119.4, 106.3, 35.6, 11.5. IR 3058, 2924, 1619, 1592, 1573, 1498, 1489, 1463, 1404, 1367, 1304, 1244, 1090, 851, 766, 738, 616 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{22}ClN_2O_2$ $[M+H]^+$ 441.1364, found 441.1375.



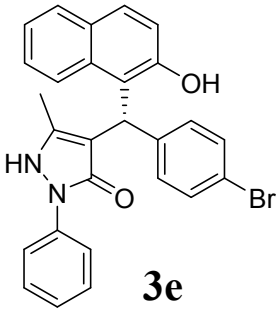
3c

The product was obtained as a white solid: 35 mg, 83%; mp 49.0-50.7 ℃; [α]25 D+48.80 (c = 0.10, CH_2Cl_2); ee 58%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 5.357 min, t_R (2) = 6.994 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.65 (s, 1H), 10.72 (s, 1H), 8.30 - 8.16 (m, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.72 (dd, J = 20.1, 8.3 Hz, 3H), 7.44 (q, J = 8.2 Hz, 3H), 7.29 (t, J = 7.4 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.07 (ddt, J = 25.2, 17.7, 8.8 Hz, 5H), 6.18 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.7, 161.7, 160.1, 154.3, 148.6, 138.0, 136.9, 133.9, 129.7, 129.6, 129.5, 129.2, 129.1, 126.8, 125.7, 123.4, 122.9, 121.5, 121.0, 119.8, 115.0, 114.8, 107.1, 35.9, 12.0. IR 3142, 3065, 1610, 1602, 1507, 1498, 1413, 1370, 1341, 1318, 1306, 1254, 1224, 1159, 861, 809, 752, 640 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{22}FN_2O_2$ $[M + H]^+$ 425.1660, found 425.1649.



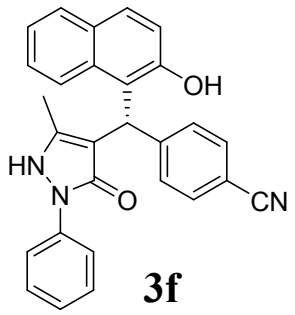
3d

The product was obtained as a white solid: 38 mg, 90%; mp 49.2-51.0 ℃; [α]25 D+41.40 (c = 0.10, CH_2Cl_2); ee 62%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 5.742 min, t_R (2) = 10.906 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.57 (s, 1H), 10.71 (s, 1H), 8.21 (d, J = 7.5 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.71 (dd, J = 11.7, 8.4 Hz, 3H), 7.48 - 7.37 (m, 3H), 7.25 (dt, J = 38.1, 7.4 Hz, 2H), 7.09 (d, J = 8.6 Hz, 1H), 6.98 (dd, J = 41.0, 8.0 Hz, 4H), 6.14 (s, 1H), 2.24 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.0, 154.3, 148.6, 138.8, 137.0, 134.7, 134.1, 129.5, 129.1, 129.0, 129.0, 128.9, 127.8, 126.7, 125.6, 123.4, 122.8, 121.5, 121.1, 119.7, 107.4, 36.1, 21.0, 12.1. IR 2920, 2850, 1619, 1591, 1554, 1497, 1462, 1423, 1396, 1346, 1321, 1307, 1293, 1247, 1223, 1157, 1138, 763, 750, 688, 617 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{25}N_2O_2$ $[M+H]^+$ 421.1911, found 421.1933.



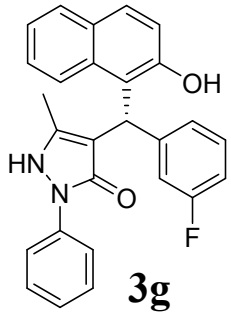
3e

The product was obtained as a white solid: 45 mg, 93%; mp 57.0-60.6 ℃; [α]25 D+56.60 (c = 0.10, CH_2Cl_2); ee 72%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 5.055 min, t_R (2) = 6.044 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.68 (s, 1H), 10.74 (s, 1H), 8.21 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.72 (dd, J = 23.6, 8.3 Hz, 3H), 7.46 - 7.39 (m, 5H), 7.29 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 8.3 Hz, 2H), 6.15 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.6, 154.2, 148.6, 141.6, 136.9, 133.9, 131.1, 130.2, 129.5, 129.3, 129.2, 129.1, 126.8, 125.7, 123.4, 122.9, 121.3, 120.7, 119.8, 118.9, 36.1, 11.9. IR 3149, 3034, 2358, 1619, 1591, 1552, 1498, 1485, 1462, 1400, 1366, 1346, 1317, 1303, 1244, 1222, 1157, 1049, 1010, 885, 851, 751, 738, 687, 634, 615cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{22}BrN_2O_2$ $[M+H]^+$ 485.0859, found 485.0861.



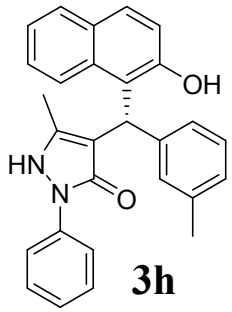
3f

The product was obtained as a white solid: 42 mg, 97%; mp 85.8-87.6 ℃; [α]25 D+53.20 (c = 0.10, CH_2Cl_2); ee 74%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 8.402 min, t_R (2) = 10.812 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.74 (s, 1H), 10.79 (s, 1H), 8.21 (s, 1H), 7.88 - 7.80 (m, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.69 (t, J = 8.7 Hz, 4H), 7.45 (q, J = 9.2, 8.6 Hz, 3H), 7.30 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 7.4 Hz, 3H), 7.11 (d, J = 8.7 Hz, 1H), 6.25 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.7, 133.8, 132.1, 129.4, 129.2, 129.1, 129.0, 126.9, 125.8, 123.4, 123.0, 119.8, 119.6, 108.6, 36.8, 11.8. IR 3328, 3050, 2922, 2850, 2227, 1618, 1602, 1566, 1499, 1459, 1422, 1379, 1315, 1262, 1231, 1051, 1012, 856, 816, 796, 748, 701, 690, 614, 558 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{22}N_3O_2$ $[M+H]^+$ 432.1707, found 432.1710.



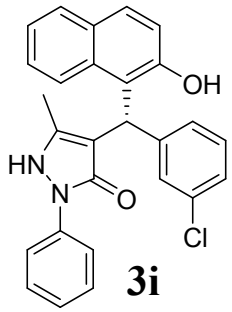
3g

The product was obtained as a white solid: 42 mg, 99%; mp 98.2-99.8 ℃; [α]25 D+85.00 (c = 0.10, CH_2Cl_2); ee 80%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 5.370 min, t_R (2) = 10.137 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.70 (s, 1H), 10.78 (s, 1H), 8.22 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.73 (dd, J = 27.3, 8.6 Hz, 3H), 7.44 (q, J = 7.8 Hz, 3H), 7.27 (ddt, J = 28.1, 13.9, 7.3 Hz, 3H), 7.12 (d, J = 8.6 Hz, 1H), 6.98 (t, J = 9.4 Hz, 1H), 6.86 (dd, J = 63.0, 9.3 Hz, 2H), 6.21 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.5, 161.9, 154.2, 148.7, 145.4, 136.9, 133.9, 130.1, 130.0, 129.5, 129.3, 129.2, 129.1, 126.8, 125.7, 124.0, 123.4, 122.9, 121.3, 120.6, 119.8, 114.7, 114.5, 112.7, 112.6, 36.4, 11.9. IR 3146, 3066, 2922, 2850, 1618, 1603, 1589, 1527, 1497, 1493, 1441, 1369, 1275, 1266, 1250, 1223, 967, 785, 767, 750, 687, 623 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{22}FN_2O_2$ $[M+H]^+$ 425.1660, found 425.1653.



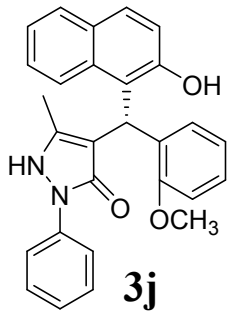
3h

The product was obtained as a white solid: 37 mg, 88%; mp 74.3-76.5 ℃; [α]25 D+65.60 (c = 0.10, CH_2Cl_2); ee 66%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 5.705 min, t_R (2) = 15.754 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.58 (s, 1H), 10.72 (s, 1H), 8.21 (s, 1H), 7.88 - 7.64 (m, 4H), 7.44 (m, 3H), 7.25 (d, J = 40.0 Hz, 2H), 7.10 (m, 2H), 6.92 (d, J = 46.8 Hz, 3H), 6.15 (s, 1H), 2.21 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.9, 154.4, 148.7, 141.9, 137.1, 134.1, 129.5, 129.1, 129.0, 128. 4, 128.2, 126.7, 125.6, 125.1, 123.3, 122.8, 121.5, 121.1, 119.7, 107.5, 36.4, 21.7, 12.1. IR 3139, 3010, 2950, 1619, 1604, 1545, 1496, 1462, 1422, 1405, 1370, 1318, 1301, 1273, 1252, 1221, 1160, 1137, 1117, 849, 825, 752, 741, 717, 690, 623, 549 cm^{-1}； HRMS (ESI) m/z calcd for $C_{28}H_{25}N_2O_2$ $[M+H]^+$ 421.1911, found 421.1935.



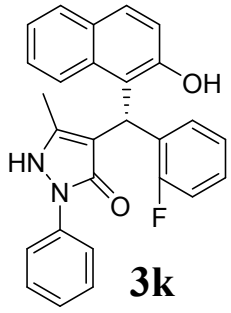
3i

The product was obtained as a white solid: 43 mg,98%; mp 69.9-73.1 ℃; [α]25 D+34.80 (c = 0.10, CH_2Cl_2); ee 72%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 5.152 min, t_R (2) = 12.917 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.68 (s, 1H), 10.80 (s, 1H), 8.22 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.45 (q, J = 6.7, 5.7 Hz, 3H), 7.32 - 7.21 (m, 4H), 7.11 (d, J = 8.7 Hz, 1H), 7.04 (d, J = 11.5 Hz, 2H), 6.20 (s, 1H), 2.23 (s, 3H).^{13}C NMR (151 MHz, DMSO-d_6) δ 148.7, 133.9, 133.0, 130.1, 129.5, 129.3, 129.2, 129.1, 127.6, 126.9, 126.8, 125.9, 125.7, 123.3, 122.9, 121.4, 120.5, 119.8, 36.4, 11.9. IR 3062, 2921, 2849, 2620, 1708, 1620, 1604, 1593, 1556, 1499, 1472, 1412, 1371, 1256, 1225, 1118, 1077, 957, 818, 748, 738, 680, 616 cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{22}ClN_2O_2$ $[M+H]^+$ 441.1364, found 441.1374.



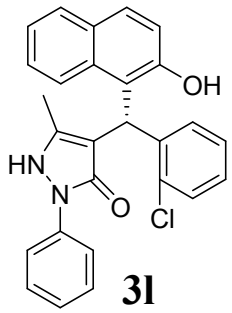
3j

The product was obtained as a white solid: 37 mg, 85%; mp 65.0-67.9 ℃; [α]25 D+36.80 (c = 0.10, CH_2Cl_2); ee 58%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 8.130 min, t_R (2) = 13.484 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.02 (s, 1H), 10.18 (s, 1H), 8.03 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.69 (dd, J = 23.0, 8.4 Hz, 3H), 7.40 (dt, J = 16.0, 7.9 Hz, 3H), 7.25 (t, J = 7.4 Hz, 1H), 7.20 - 7.05 (m, 4H), 6.93 (d, J = 8.1 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.23 (s, 1H), 3.61 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 157.5, 153.9, 148.5, 134.1, 130.0, 129.3, 129.1, 128.9, 128.5, 127.6, 126.4, 125.0, 123.3, 122.5, 120.5, 120.2, 119.1, 111.4, 56.1, 32.5, 11.9. IR 3071, 2991, 2951, 2930, 2827, 1620, 1603, 1544, 1498, 1486, 1463, 1455, 1382, 1337, 1306, 1240, 1155, 1120, 1028, 948, 885, 835, 744, 708, 692, 631 cm^{-1}. HRMS (ESI) m/z calcd for $C_{28}H_{25}N_2O_3$ $[M+H]^+$ 437.1860, found 437.1869.



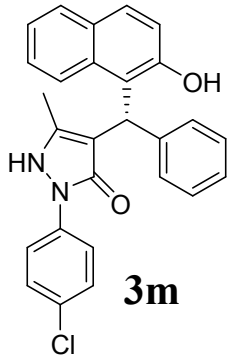
3k

The product was obtained as a white solid: 39 mg, 92%; mp 44.9-46.7 ℃; [α]25 D+28.40 (c = 0.10, CH_2Cl_2); ee 96%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 6.457 min, t_R (2) = 7.279 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.24 (s, 1H), 10.27 (s, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.71 (dd, J = 8.3, 3.6 Hz, 3H), 7.41 (dt, J = 17.4, 7.7 Hz, 3H), 7.29 - 7.13 (m, 4H), 7.12 - 7.02 (m, 3H), 6.23 (s, 1H), 2.00 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.9, 160.3, 153.8, 148.5, 133.7, 130.8, 129.4, 129.1, 129.0, 129.0, 128.1, 128.1, 126.7, 125.3, 124.0, 123.4, 122.8, 120.3, 119.5, 115.2, 115.1, 32.0, 11.9. IR 3063, 2551, 1619, 1599, 1577, 1544, 1499, 1484, 1452, 1406, 1370, 1278, 1266, 1252, 1226, 1049, 952, 812, 787, 748, 691, 626 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{22}FN_2O_2$ $[M+H]^+$ 425.1660, found 425.1675.



3l

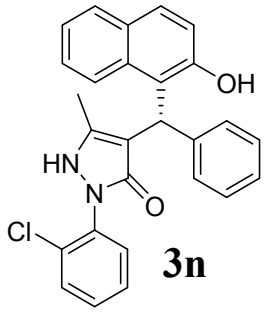
The product was obtained as a white solid: 41 mg, 93%; mp 55.6-57.2 ℃; [α]25 D+6.20 (c = 0.10, CH_2Cl_2); ee 48%; HPLC Chiralpak IC column (n-hexane/iso-Propyl alcohol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 24.788 min, t_R (2) = 35.039 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.99 (s, 1H), 10.05 (s, 1H), 8.01 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.72 (dd, J = 14.9, 8.4 Hz, 3H), 7.41 (q, J = 8.1 Hz, 3H), 7.36 (dd, J = 5.6, 3.6 Hz, 1H), 7.31 - 7.24 (m, 2H), 7.23 - 7.16 (m, 3H), 7.09 (d, J = 8.8 Hz, 1H), 6.17 (s, 1H), 1.91 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.9, 148.8, 140.5, 137.8, 134.0, 133.5, 131.3, 129.5, 129.4, 129.1, 129.1, 129.0, 128.0, 126.8, 126.8, 125.0, 123.2, 122.7, 120.1, 119.1, 36.4, 12.0. IR 3075, 2922, 2360, 1618, 1600, 1529, 1499, 1472, 1399, 1374, 1345, 1307, 1252, 1223, 1155, 1113, 1030, 951, 817, 746, 728, 684, 630 cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{22}ClN_2O_2$ $[M+H]^+$ 441.1364, found 441.1378.



3m

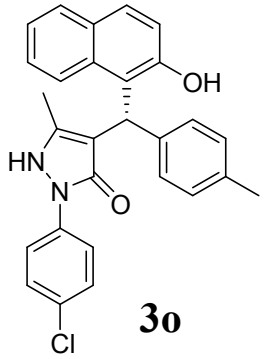
The product was obtained as a white solid: 39 mg, 89%; mp 52.9-55.0 ℃; [α]25 D+40.20(c = 0.10, CH_2Cl_2); ee 76%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 5.281 min, t_R (2) = 10.749 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.48 (s, 1H), 10.46 (s, 1H), 8.19 (d, J = 7.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.74 (dd, J = 14.2, 8.9 Hz, 3H), 7.50 (d, J = 8.8 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.5 Hz, 2H), 7.13 (dd, J = 18.4, 8.0 Hz, 2H), 7.08 (d, J = 7.7 Hz, 2H), 6.20 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.0, 154.1, 149.5, 142.0, 136.0, 134.0, 129.4, 129.2, 129.1, 129.0, 128.3, 128.0, 126.6, 125.9, 123.6, 122.8, 120.9, 120.7, 107.6, 36.6, 12.3. IR 3638, 3055, 3974, 1614, 1595, 1490, 1466, 1363, 1261, 1172, 1154, 1089, 1028, 1011, 829,

823, 749, 713, 697, 603, 544 cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{22}ClN_2O_2$ $[M+H]^+$ 441.1364, found 441.1368.



3n

The product was obtained as a white solid: 39mg, 89%; mp 57.1-59.8 ℃; [α]25 D+58.80 (c = 0.10, CH_2Cl_2); ee 53%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 7.937 min, t_R (2) = 14.821 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.89 (s, 1H), 11.08 (s, 1H), 8.26 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.49 (ddd, J = 28.8, 14.4, 6.9 Hz, 4H), 7.30 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 7.6 Hz, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 7.7 Hz, 3H), 6.18 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.3, 142.2, 134.1, 132.3, 131.3, 130.9, 130.7, 129.2, 129.0, 129.0, 128.5, 128.2, 127.8, 126.7, 125.8, 123.2, 122.8, 121.8, 36.3, 11.9. IR 3538, 3363, 3058, 2883, 2816, 1621, 1606, 1565, 1519, 1484, 1467, 1447, 1251, 1224, 1156, 1045, 953, 787, 739, 708, 693, 612 cm^{-1}； HRMS (ESI) m/z calcd for $C_{27}H_{22}FN_2O_2$ $[M+H]^+$ 441.1364, found 441.1363.



3o

The product was obtained as a white solid: 43 mg, 95%; mp 65.7-67.6 ℃; [α]25 D+28.80 (c = 0.10, CH_2Cl_2); ee 52%; HPLC Chiralpak IC column (n-hexane/EtOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R (1) = 5.120 min, t_R (2) = 8.200 min; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.46 (s, 1H), 10.44 (s, 1H), 8.17 (d, J = 8.1 Hz, 1H), 7.84 - 7.69 (m, 4H), 7.44 (dd, J = 67.2, 8.3 Hz, 3H), 7.27 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 8.8 Hz, 1H), 7.05 - 6.89 (m, 4H), 6.14 (s, 1H), 2.24 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.1, 154.2, 149.5, 138.8, 136.2, 134.8, 134.0, 129.4, 129.3, 129.1, 129.0, 128.9, 127.9, 126.6, 123.6, 122.7, 120.8, 36.3, 21.0,

12.2. IR 3083, 2920, 1620, 1598, 1488, 1455, 1403, 1372, 1328, 1302, 1286, 1247, 1225, 1093, 952, 851, 825, 799, 763, 734, 715, 618 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{24}ClN_2O_2$ $[M+H]^+$ 455.1521, found 455.1530.

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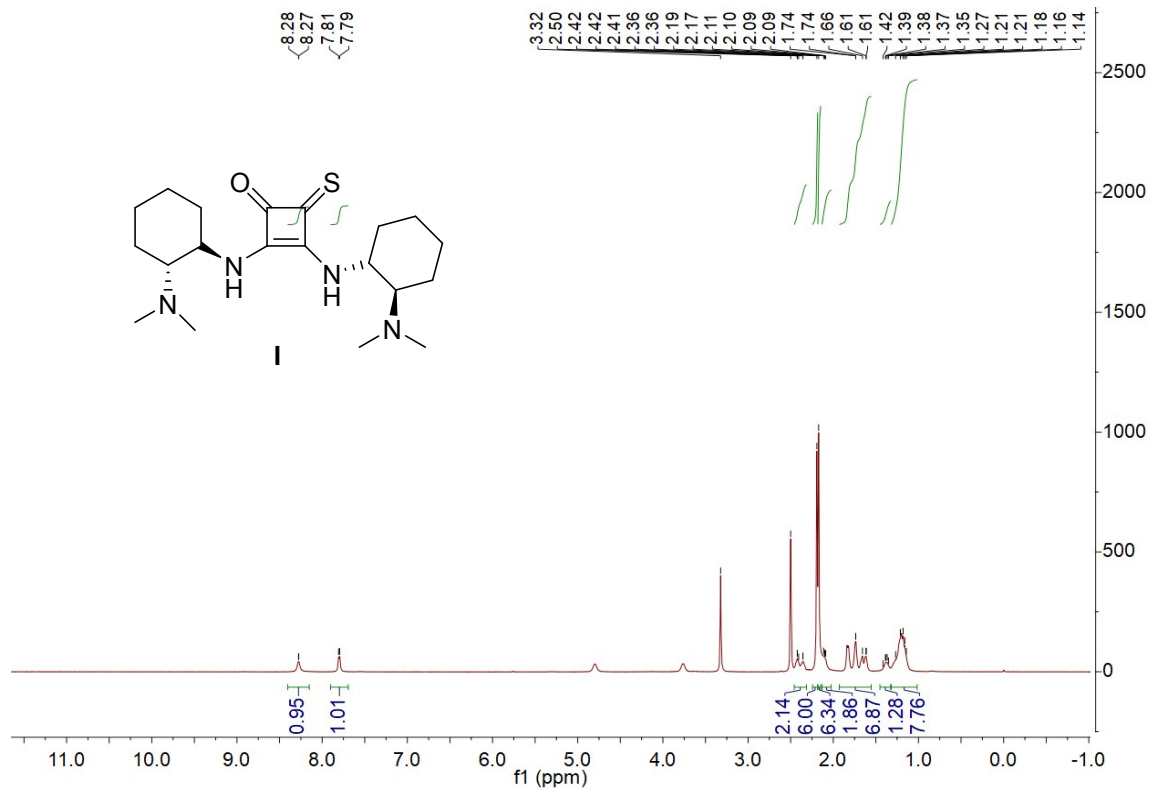
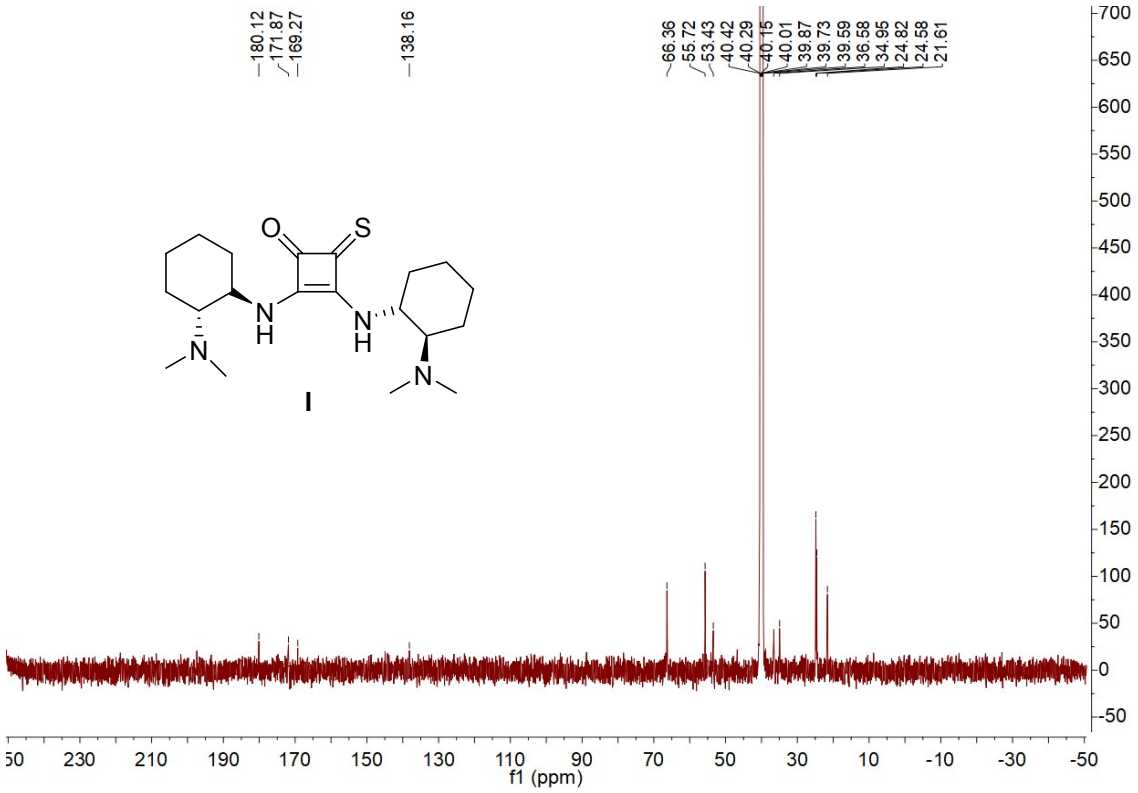
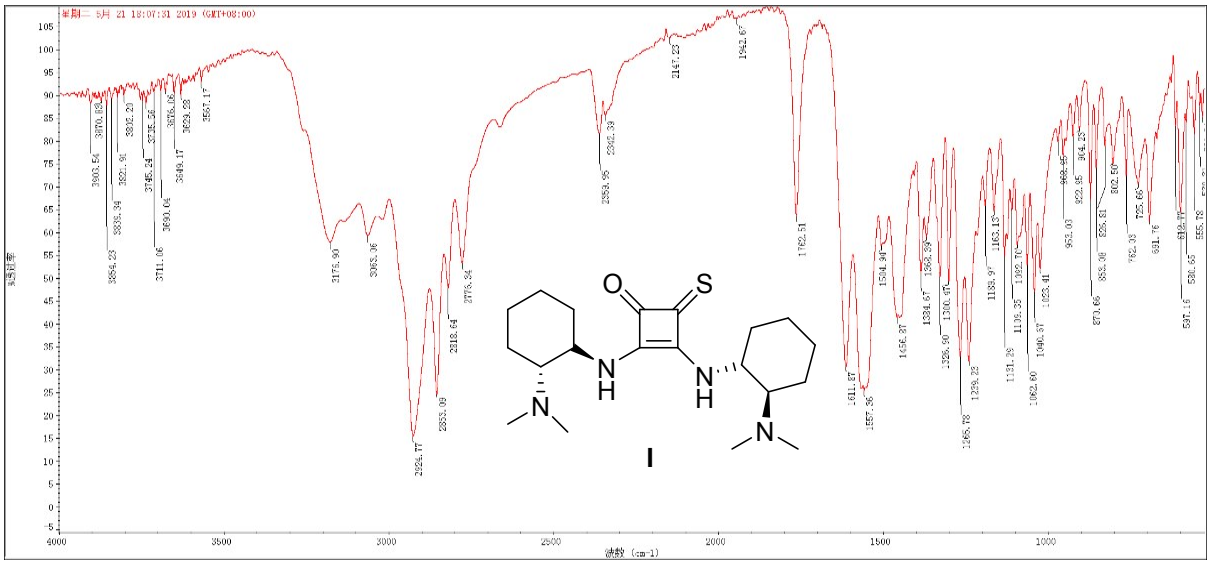
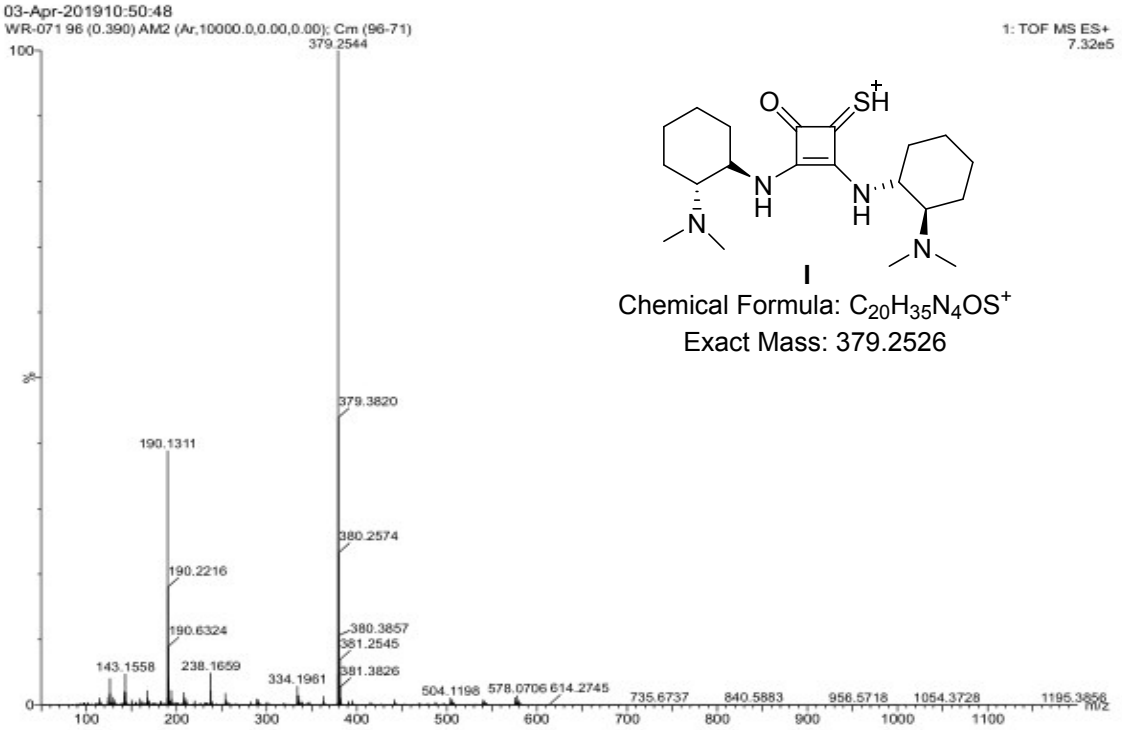
Copies of ^{1}H NMR, ^{13}C NMR, IR and HRMS spectra of organocatalysts







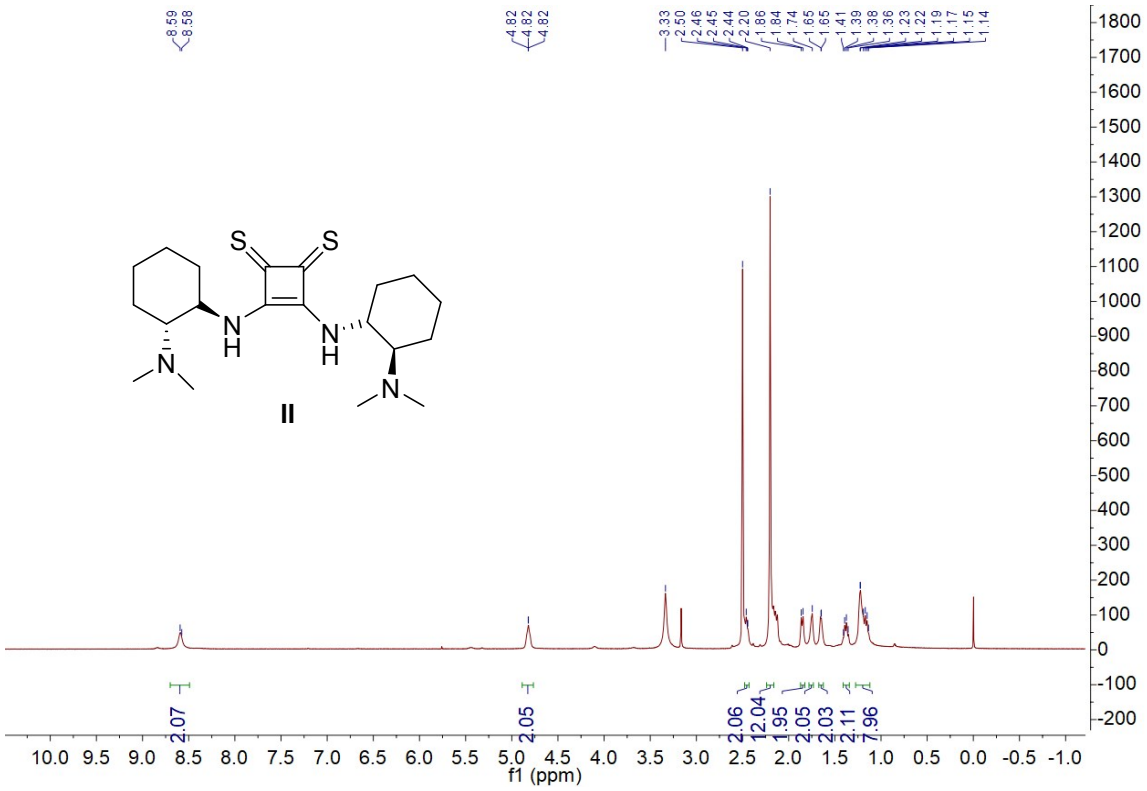
I

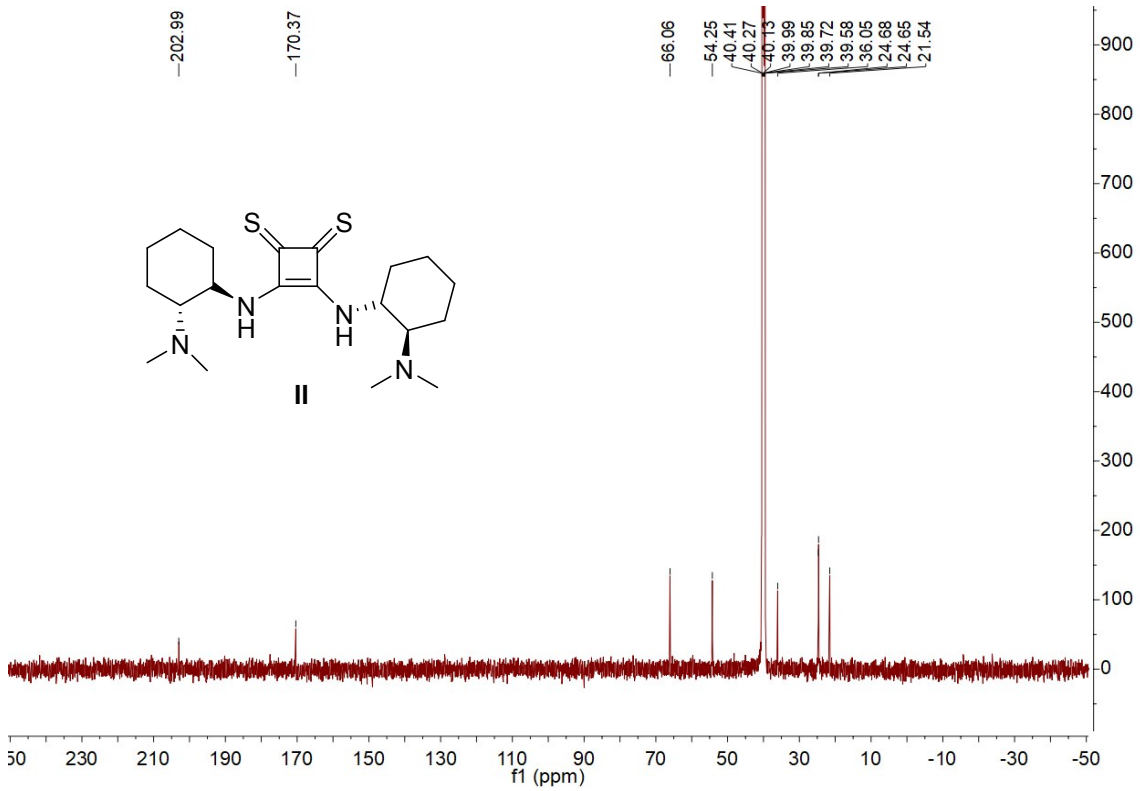


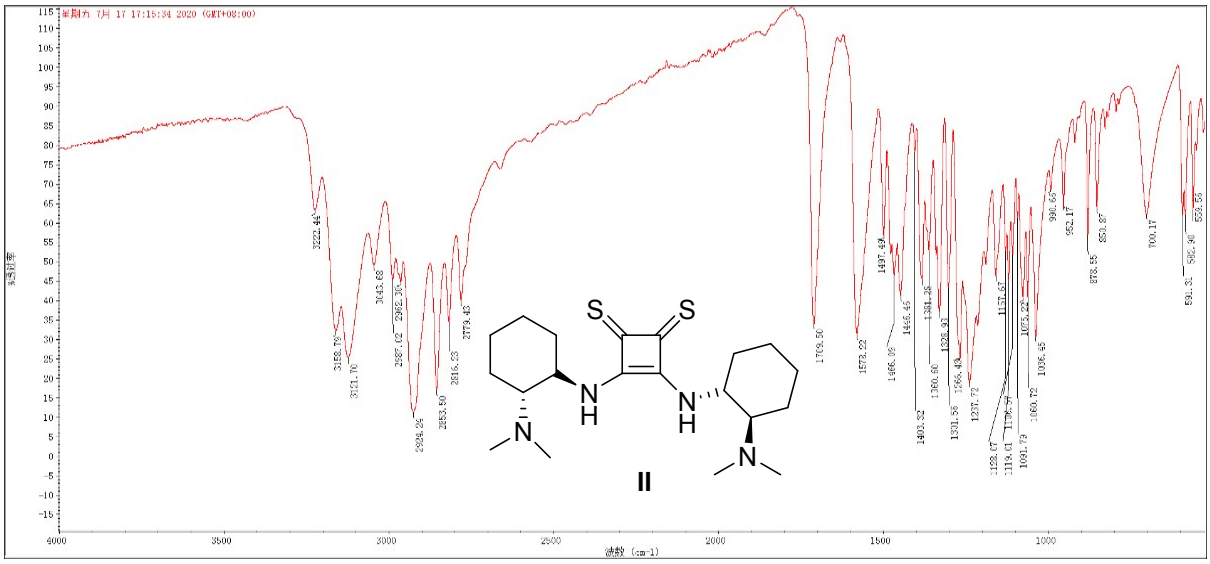
I

Chemical Formula: $C_{20}H_{35}N_4OS^+$

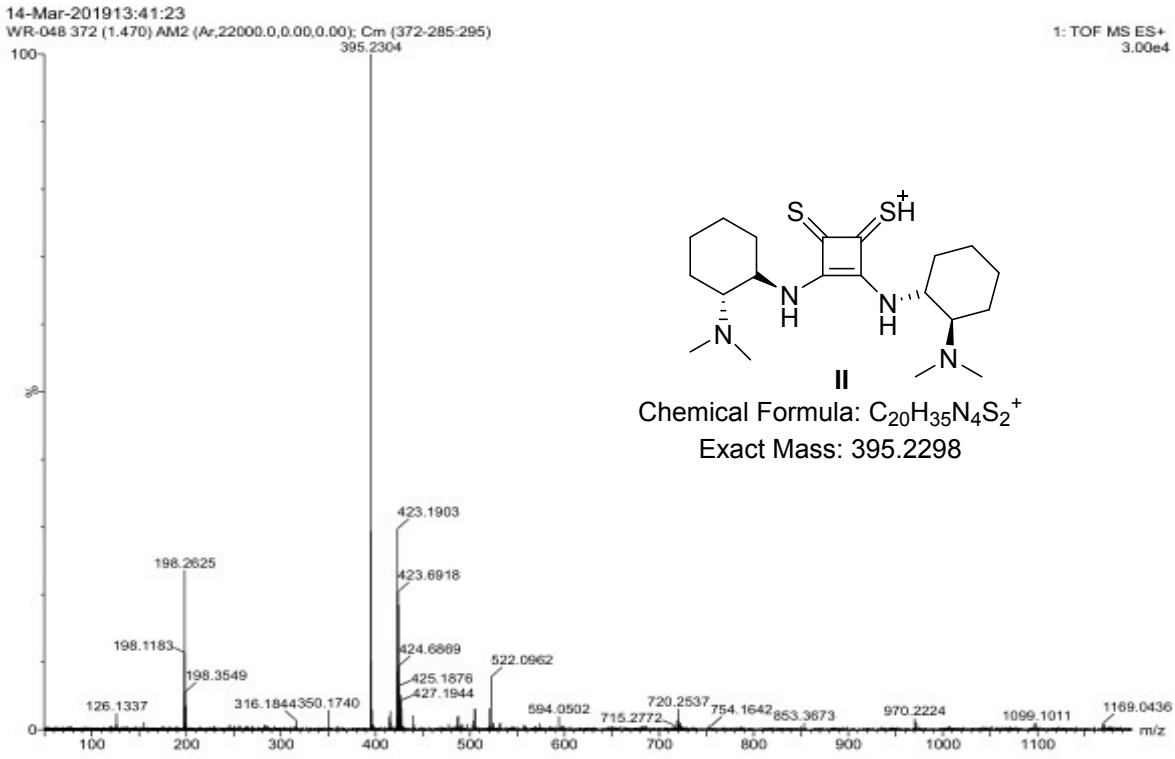
Exact Mass: 379.2526


8.59
8.58
4.82
4.82
4.82
3.33
2.50
2.46
2.45
2.44
2.20
1.86
1.84
1.74
1.65
1.65
1.41
1.39
1.38
1.36
1.23
1.22
1.19
1.17
1.15
1.14
S
S
N
H
N
H
N
N
II
2.07
2.05
2.06
12.04
1.95
2.05
2.03
2.11
7.96
f1 (ppm)


202.99
170.37
66.06
54.25
40.41
40.27
40.13
39.99
39.85
39.72
39.58
36.05
24.68
24.65
21.54
S
S
N
H
N
H
N
N
II
f1 (ppm)



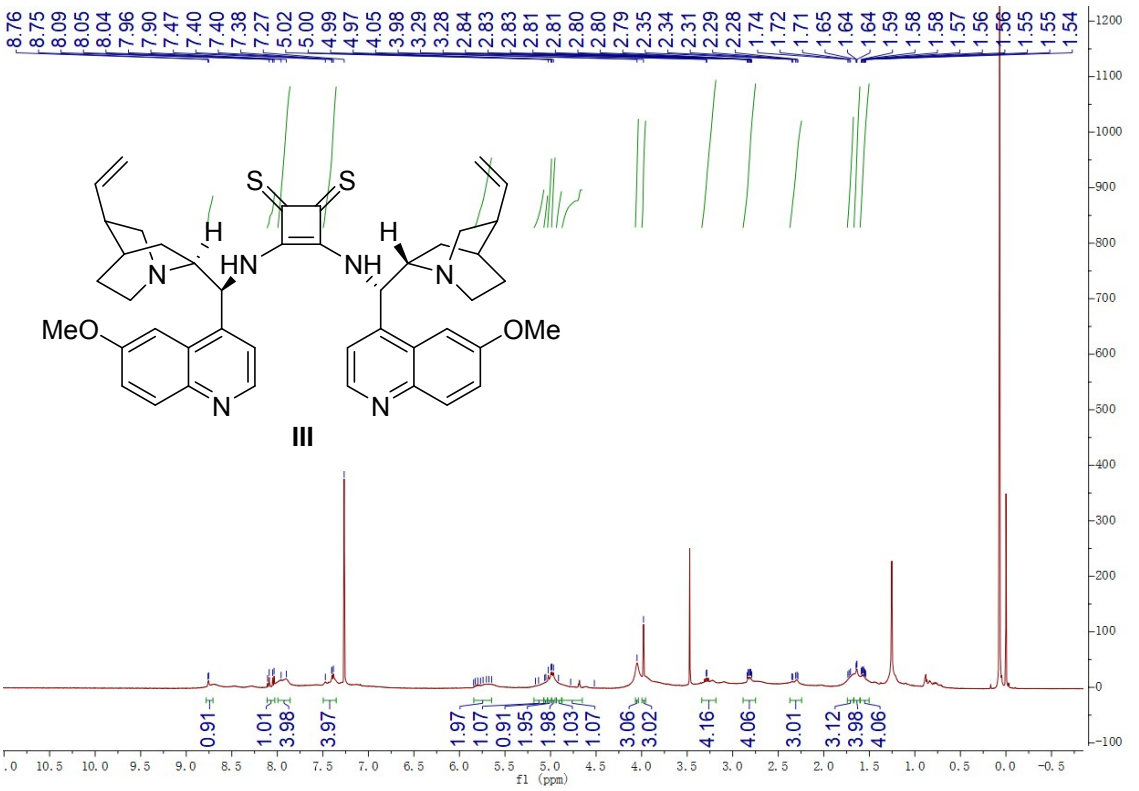
II

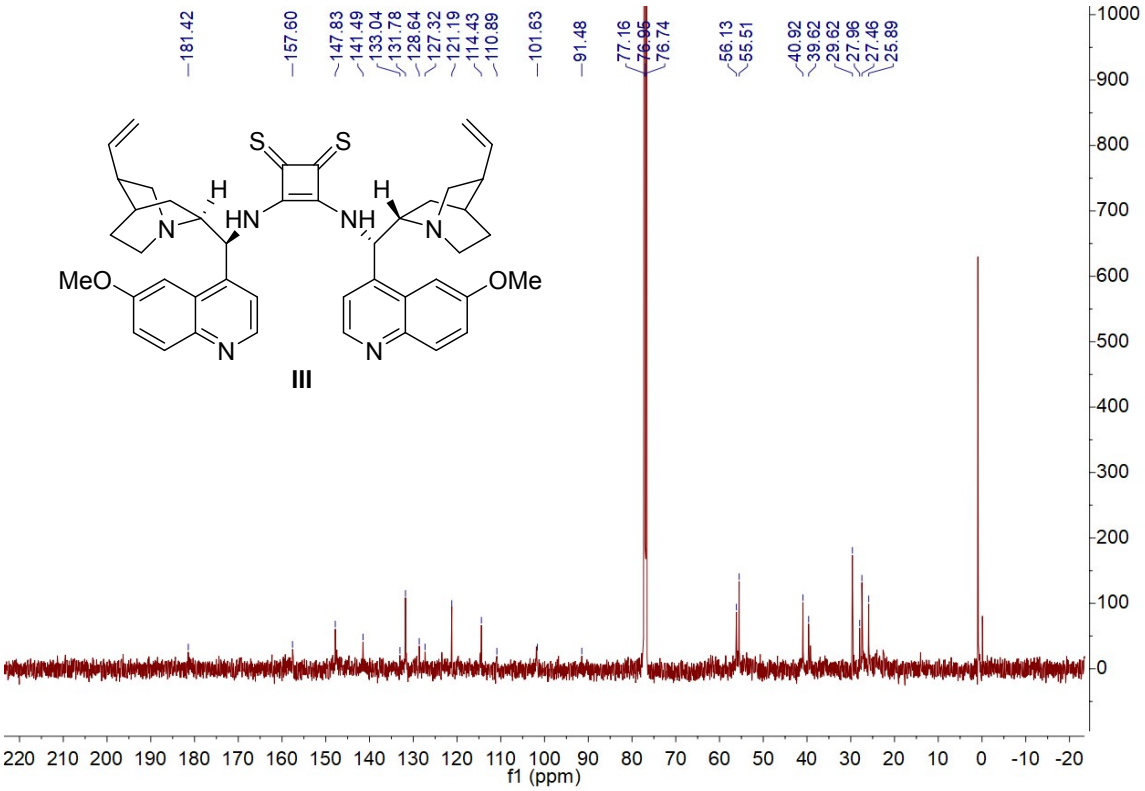


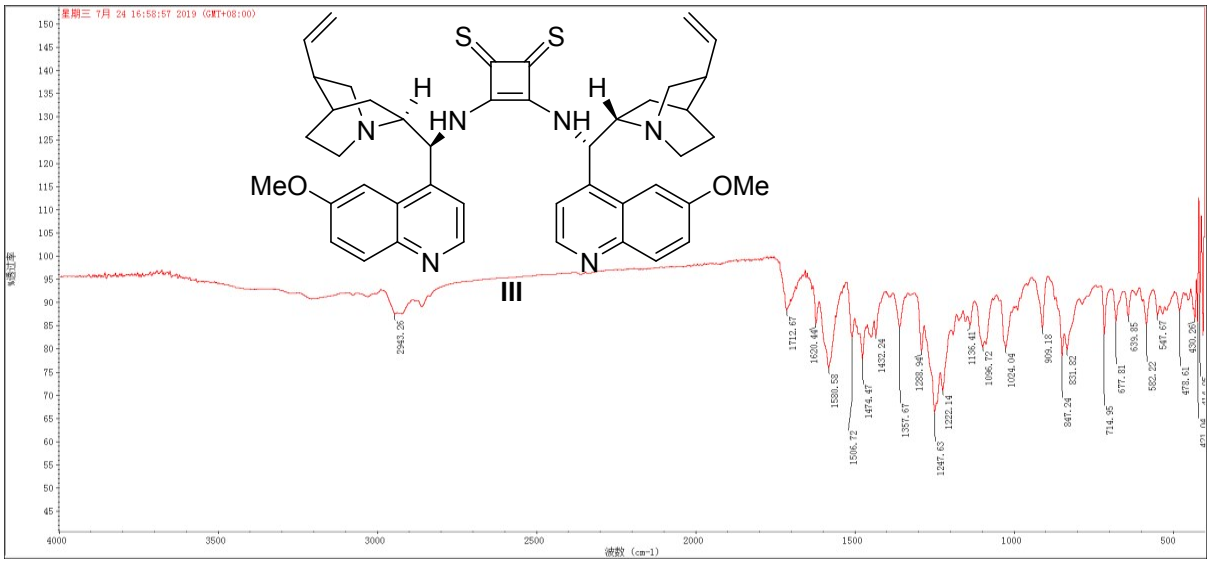
II

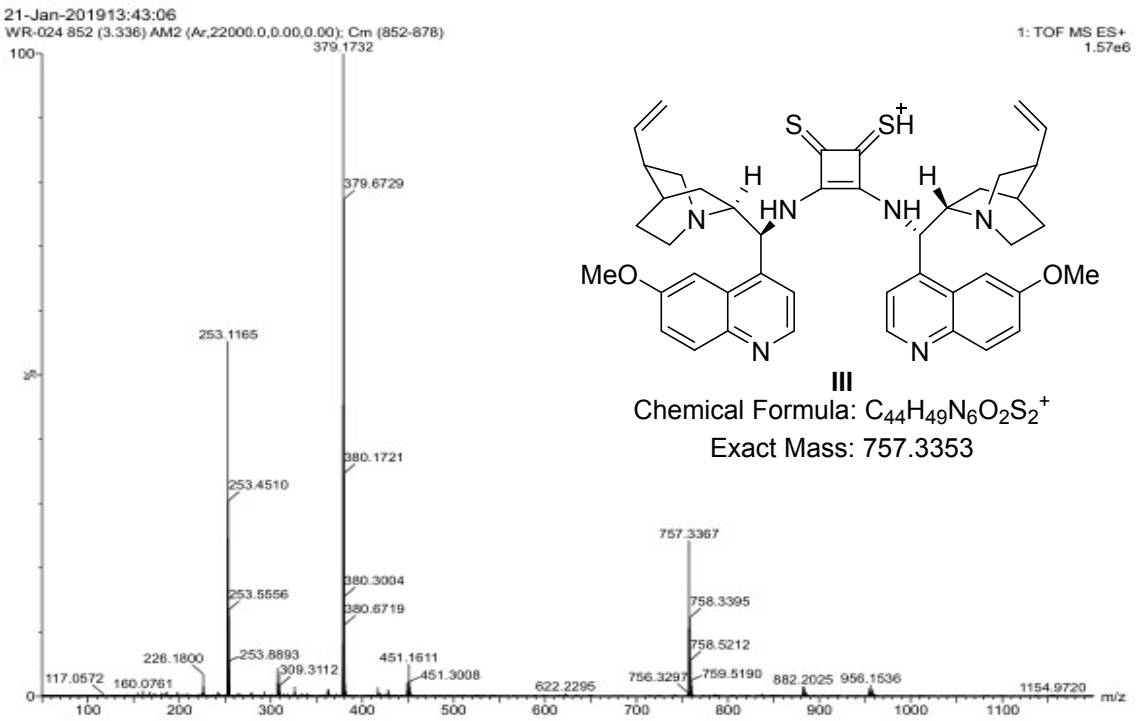
Chemical Formula: $C_{20}H_{35}N_4S_2^+$

Exact Mass: 395.2298


8.76 8.75 8.09 8.05 8.04 7.96 7.90 7.47 7.40 7.40 7.38 7.27 5.02 5.00 4.99 4.97 4.05 3.98 3.29 3.28 2.84 2.83 2.83 2.81 2.81 2.80 2.80 2.79 2.35 2.34 2.31 2.29 2.28 1.74 1.72 1.71 1.65 1.64 1.64 1.59 1.58 1.58 1.57 1.56 1.56 1.55 1.55 1.54
S
S
H
HN
NH
H
N
N
MeO
OMe
N
N
III
0.91 1.01 3.98 3.97 1.97 1.07 0.91 1.95 1.98 1.03 1.07 3.06 3.02 4.16 4.06 3.01 3.12 3.98 4.06
f1 (ppm)


181.42 157.60 147.83 141.49 133.04 131.78 128.64 127.32 121.19 114.43 110.89 101.63 91.48 77.16 76.96 76.74 56.13 55.51 40.92 39.62 29.62 27.96 27.46 25.89
S
S
H
HN
NH
H
N
N
MeO
OMe
N
N
III
f1 (ppm)

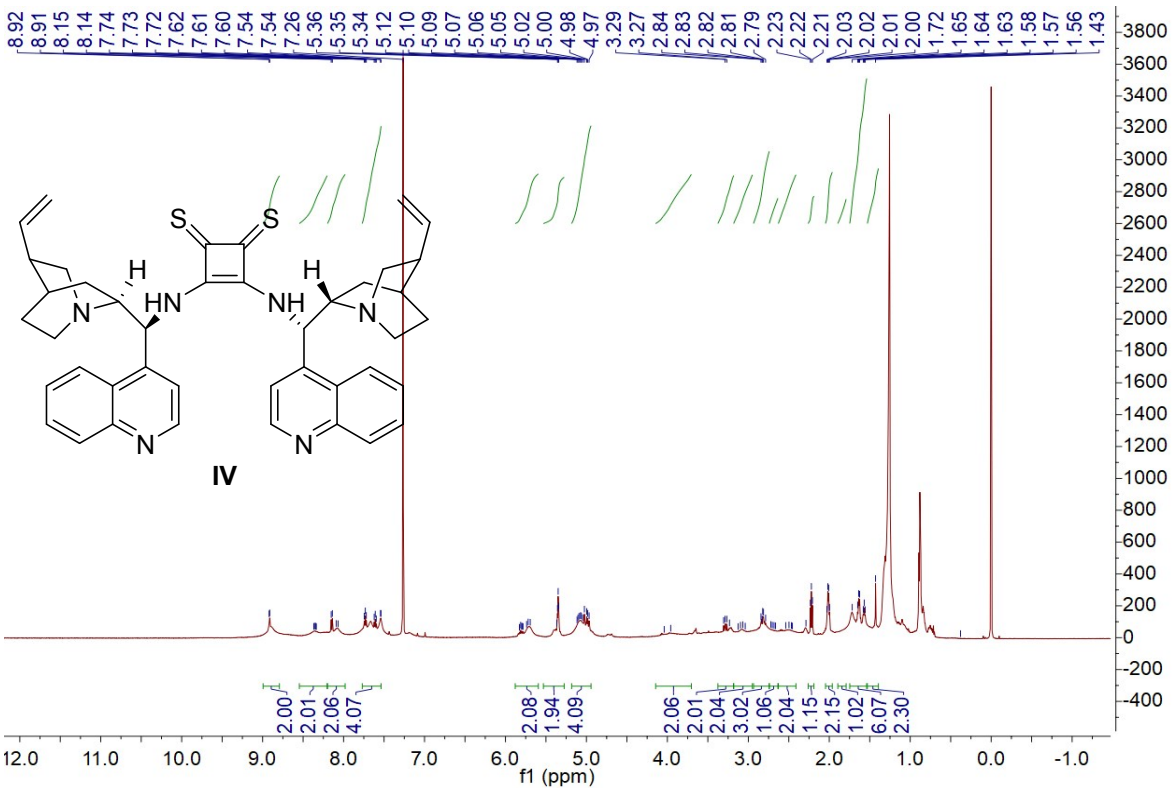




III

Chemical Formula: $C_{44}H_{49}N_6O_2S_2^+$

Exact Mass: 757.3353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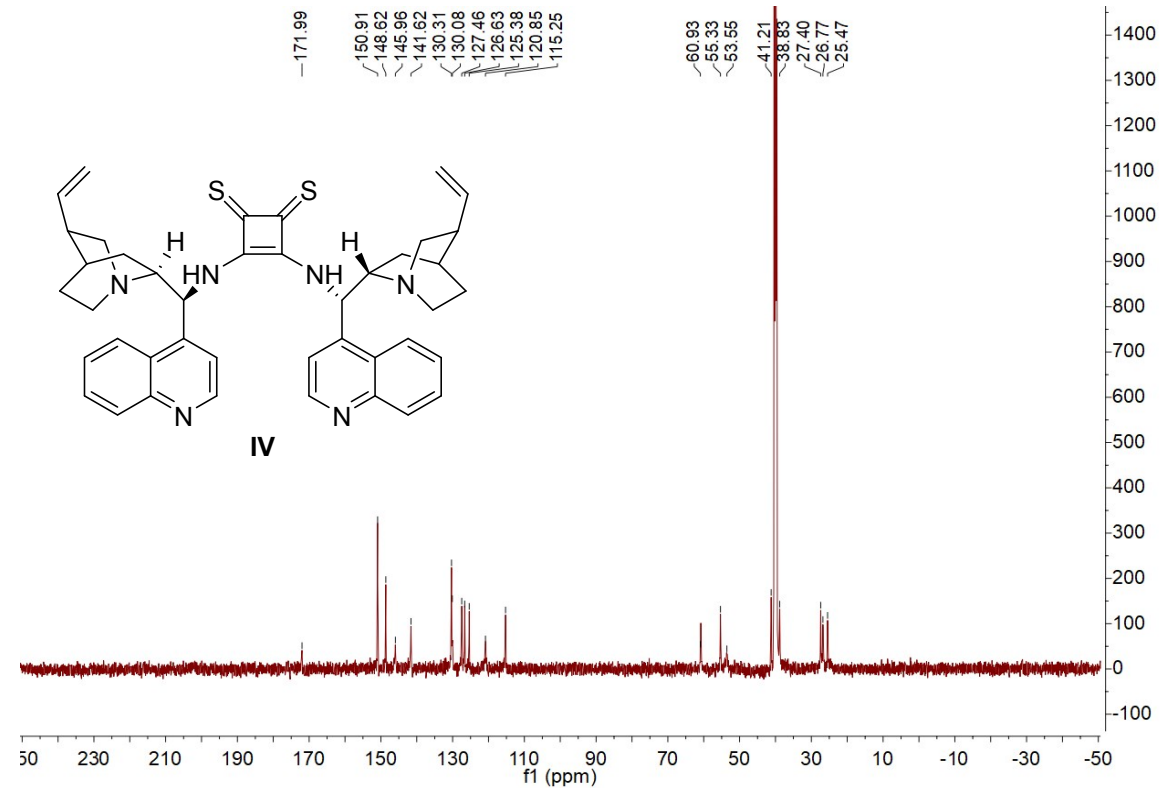
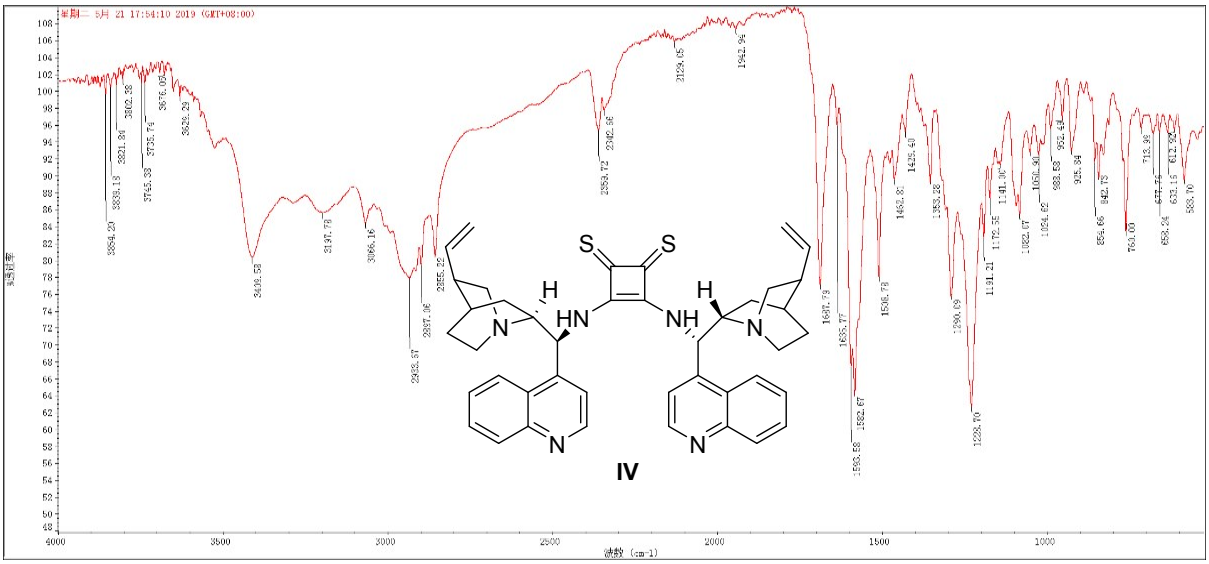
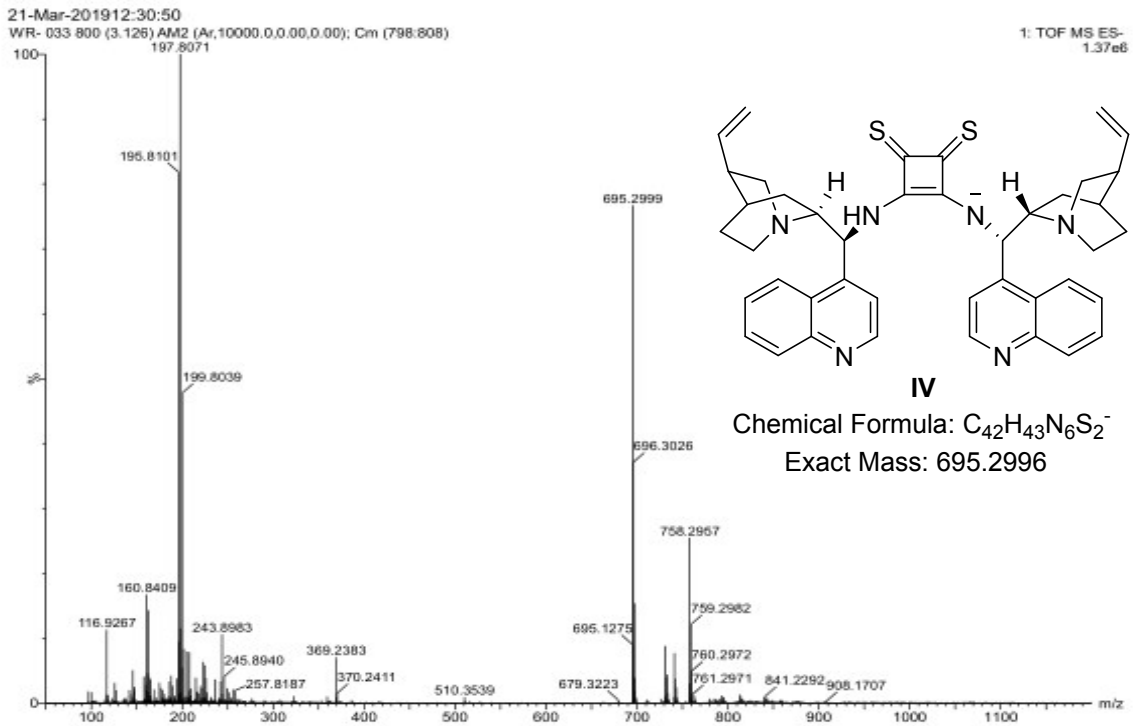
8.91
8.15
8.14
7.74
7.73
7.72
7.62
7.61
7.60
7.54
7.54
7.26
5.36
5.35
5.34
5.12
5.10
5.09
5.07
5.06
5.05
5.02
5.00
4.98
4.97
3.29
3.27
2.84
2.83
2.82
2.81
2.79
2.23
2.22
2.21
2.03
2.02
2.01
2.00
1.72
1.65
1.64
1.63
1.58
1.57
1.56
1.43
S
S
H
HN
NH
H
N
N
N
N
IV
2.00
2.01
2.06
4.07
2.08
1.94
4.09
2.06
2.01
2.04
3.02
1.06
2.04
1.15
2.15
1.02
6.07
2.30
f1 (ppm)


171.99
150.91
148.62
145.96
141.62
130.31
130.08
127.46
126.63
125.38
120.85
115.25
60.93
55.33
53.55
41.21
38.83
27.40
26.77
25.47
S
S
H
HN
NH
H
N
N
N
N
IV
f1 (ppm)



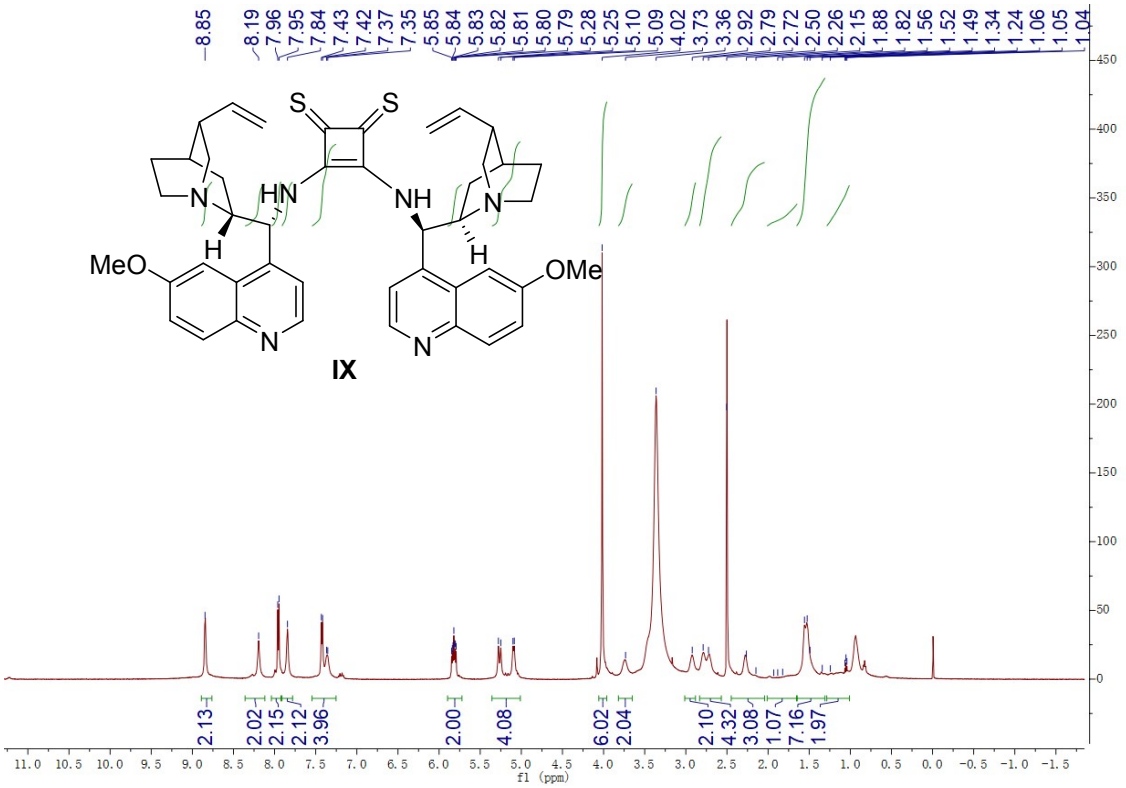
IV

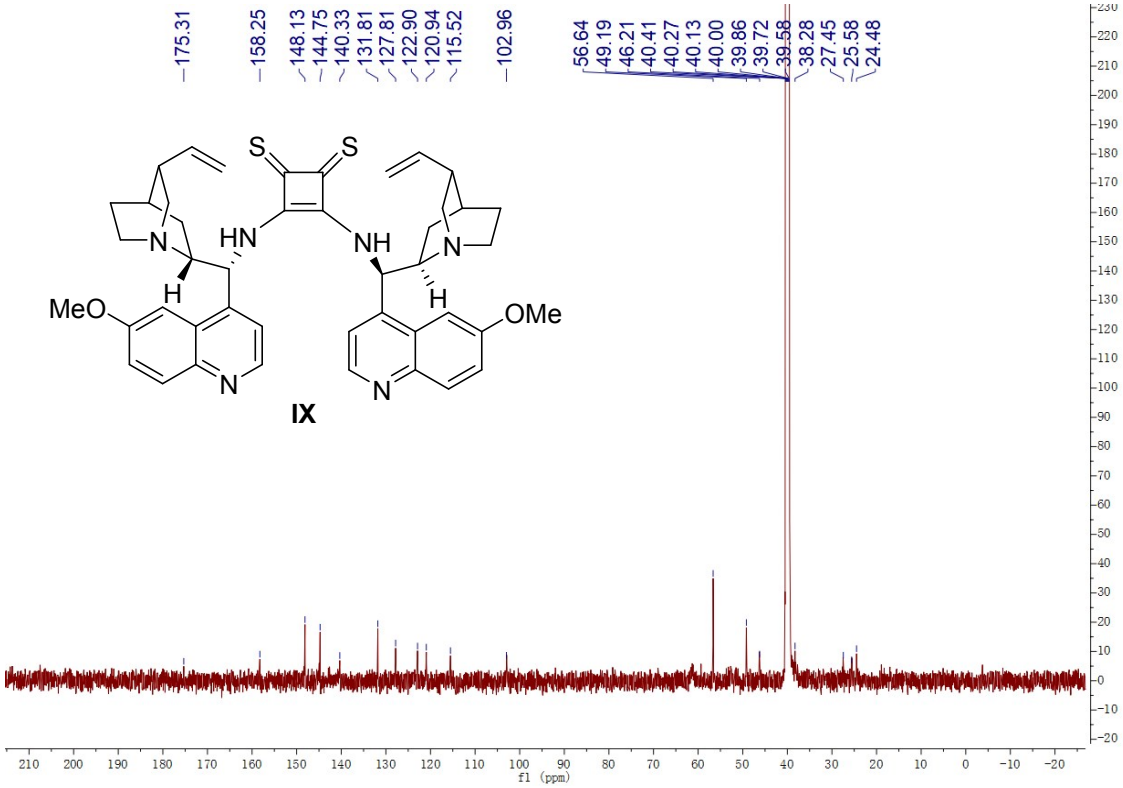


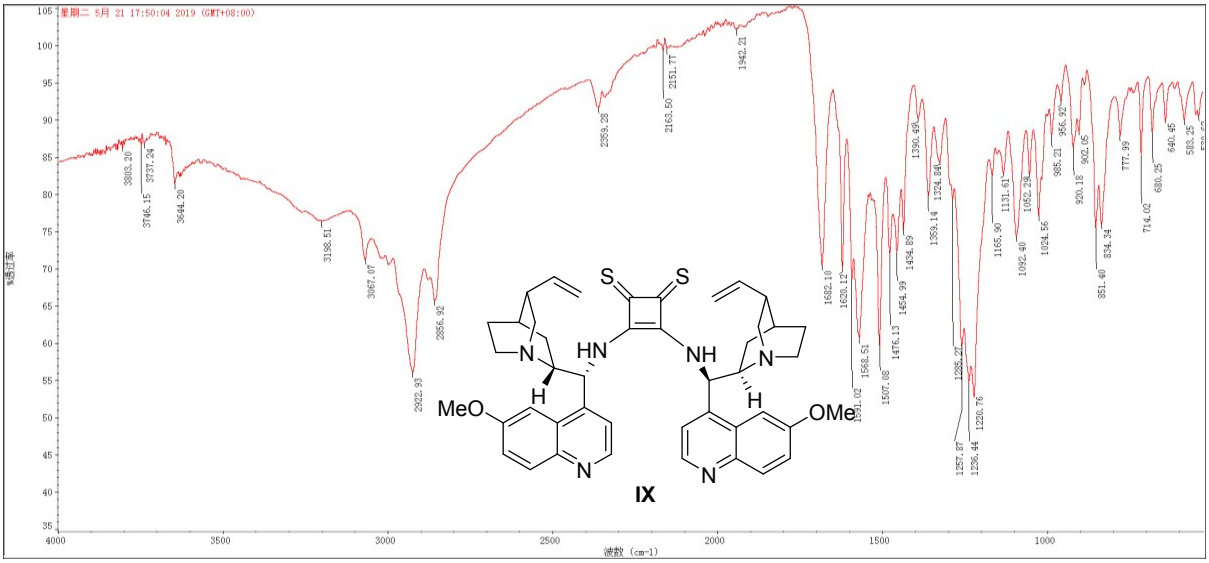
IV

Chemical Formula: $C_{42}H_{43}N_6S_2^-$

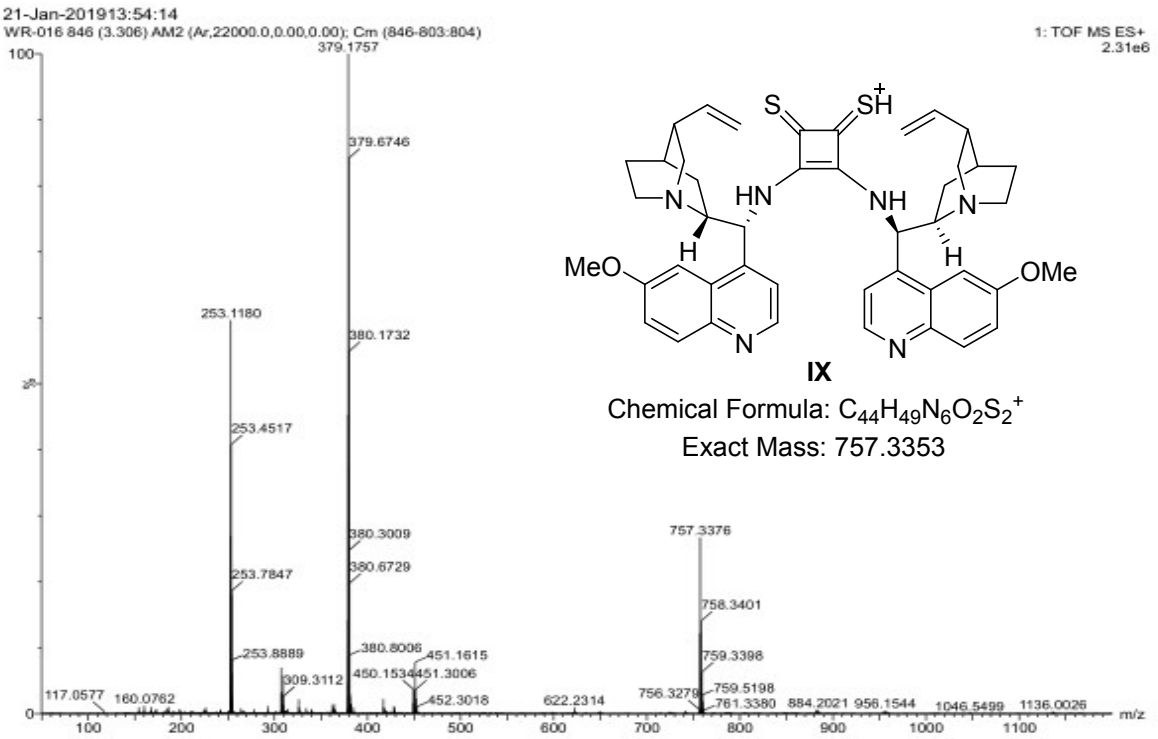
Exact Mass: 695.2996


8.85
8.19
7.96
7.95
7.84
7.43
7.42
7.37
7.35
5.85
5.84
5.83
5.82
5.81
5.80
5.79
5.28
5.25
5.10
5.09
4.02
3.73
3.36
2.92
2.79
2.72
2.50
2.26
2.15
1.88
1.82
1.56
1.52
1.49
1.34
1.24
1.06
1.05
1.04
S
S
HN
NH
N
N
H
H
MeO
OMe
N
N
IX
2.13
2.02
2.15
2.12
3.96
2.00
4.08
6.02
2.04
2.10
4.32
3.08
1.07
7.16
1.97
f1 (ppm)


175.31
158.25
148.13
144.75
140.33
131.81
127.81
122.90
120.94
115.52
102.96
56.64
49.19
46.21
40.41
40.27
40.13
40.00
39.86
39.72
39.58
38.28
27.45
25.58
24.48
S
S
HN
NH
N
N
H
H
MeO
OMe
N
N
IX
f1 (ppm)



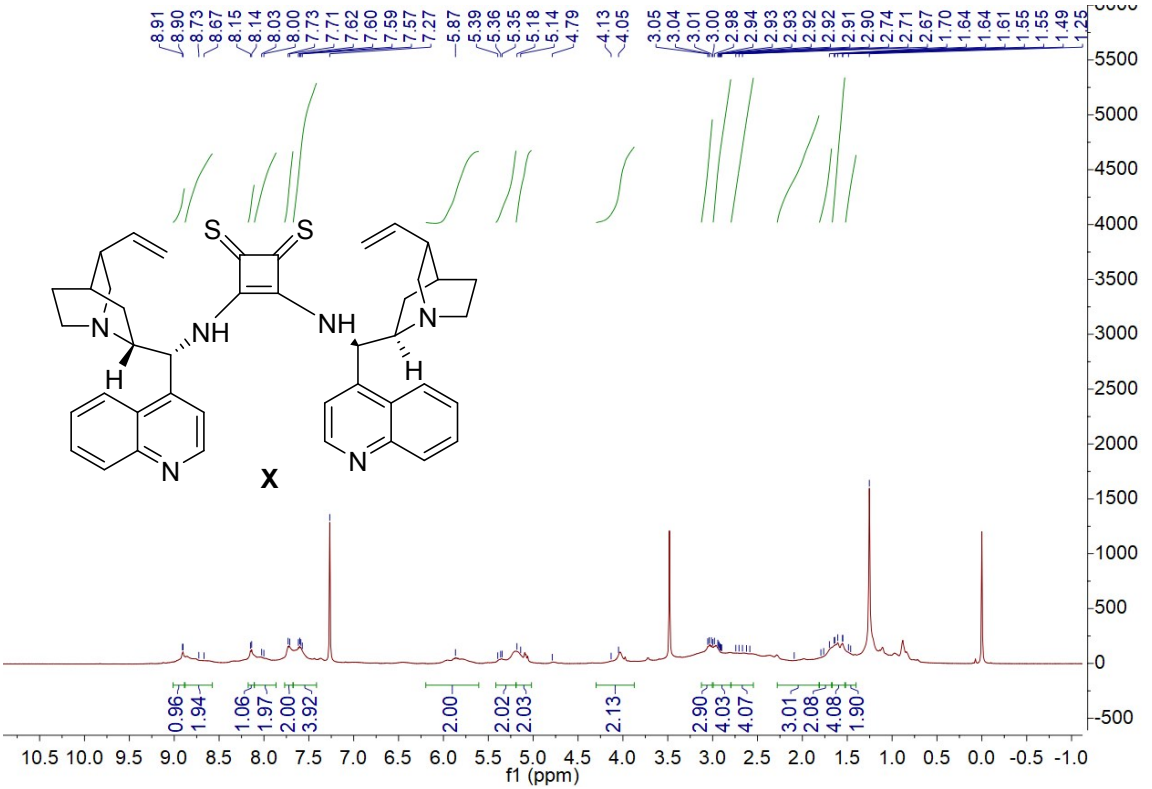
IX

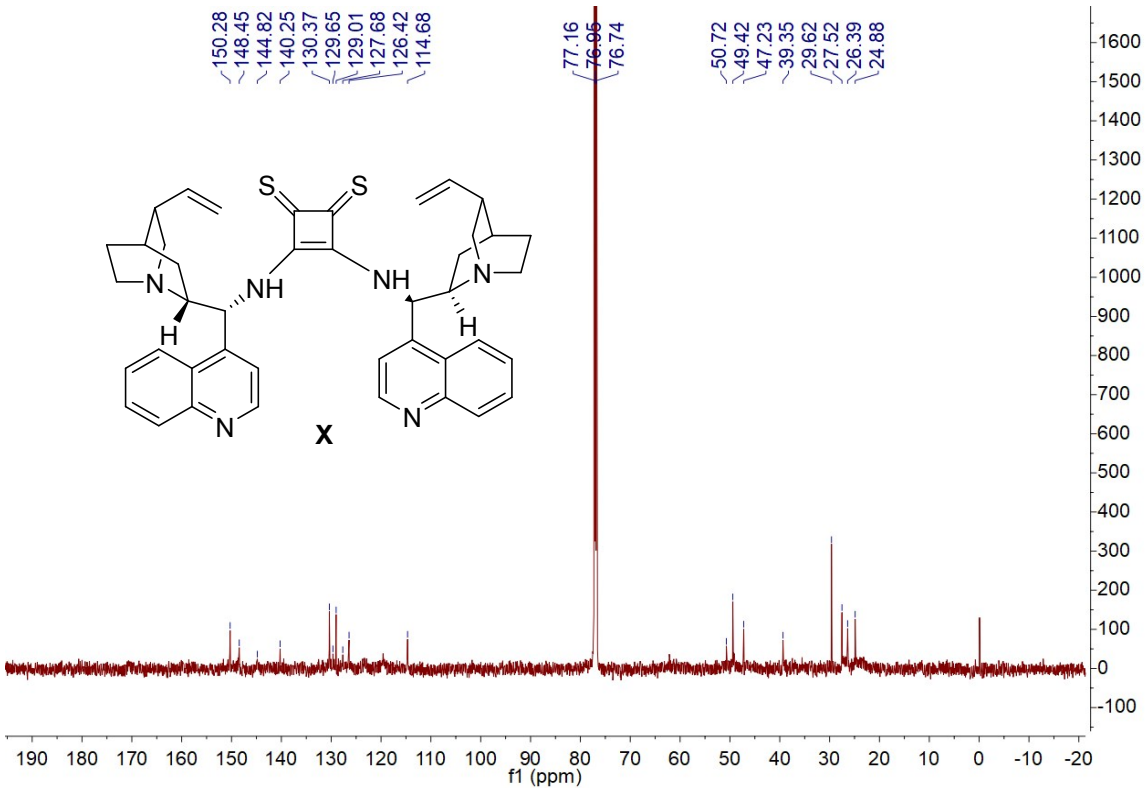


IX

Chemical Formula: $C_{44}H_{49}N_6O_2S_2^+$

Exact Mass: 757.3353


8.91
8.90
8.73
8.67
8.15
8.14
8.03
8.00
7.73
7.71
7.62
7.60
7.59
7.57
7.27
5.87
5.39
5.36
5.35
5.18
5.14
4.79
4.13
4.05
3.05
3.04
3.01
3.00
2.98
2.94
2.93
2.93
2.92
2.92
2.91
2.90
2.74
2.71
2.67
1.70
1.64
1.64
1.61
1.55
1.55
1.49
1.25
S
S
NH
NH
N
N
H
H
N
N
X
0.96
1.94
1.06
1.97
2.00
3.92
2.00
2.02
2.03
2.13
2.90
4.03
4.07
3.01
2.08
4.08
1.90
f1 (ppm)


150.28
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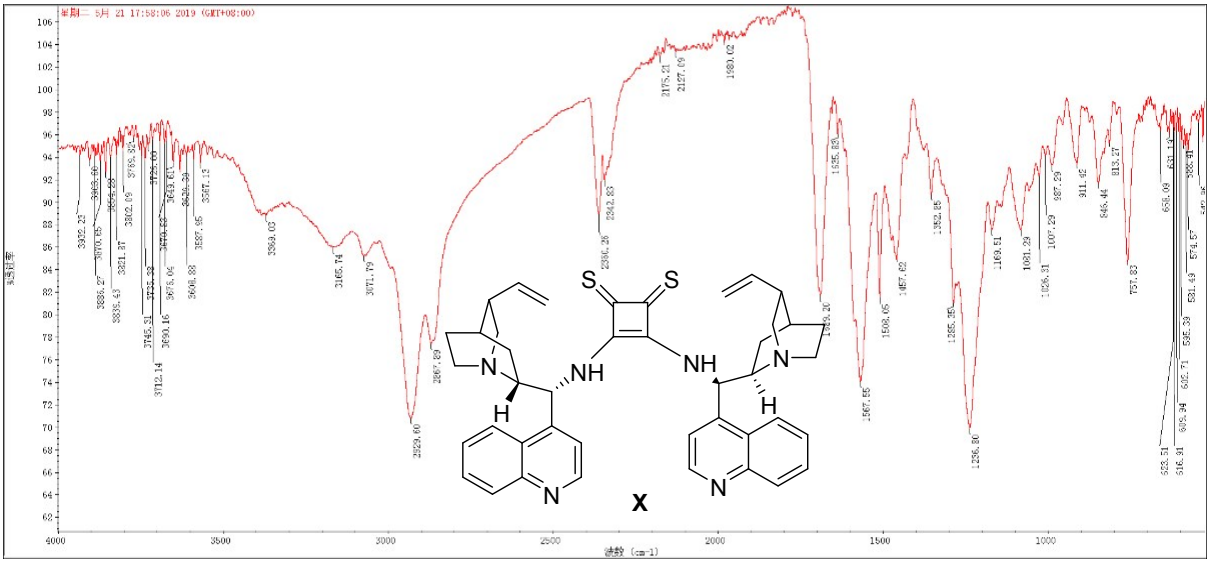
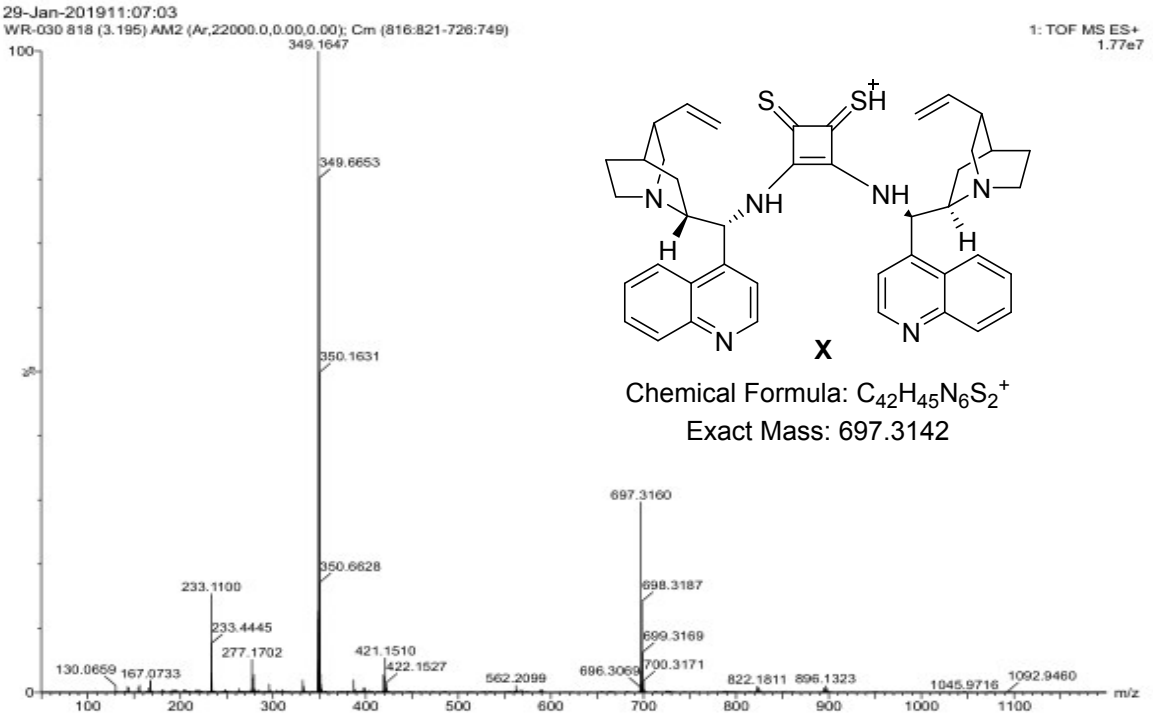
144.82
140.25
130.37
129.65
129.01
127.68
126.42
114.68
77.16
76.06
76.74
50.72
49.42
47.23
39.35
29.62
27.52
26.39
24.88
S
S
NH
NH
N
N
H
H
N
N
X
f1 (ppm)

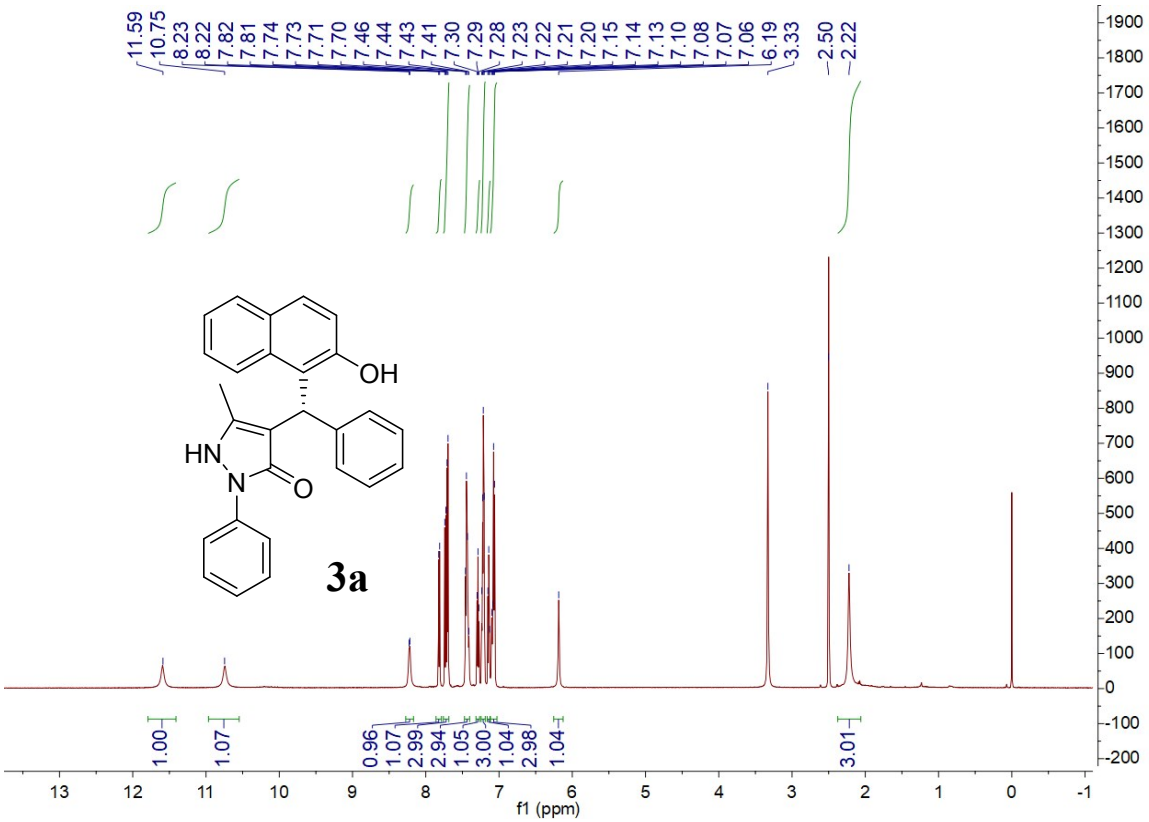


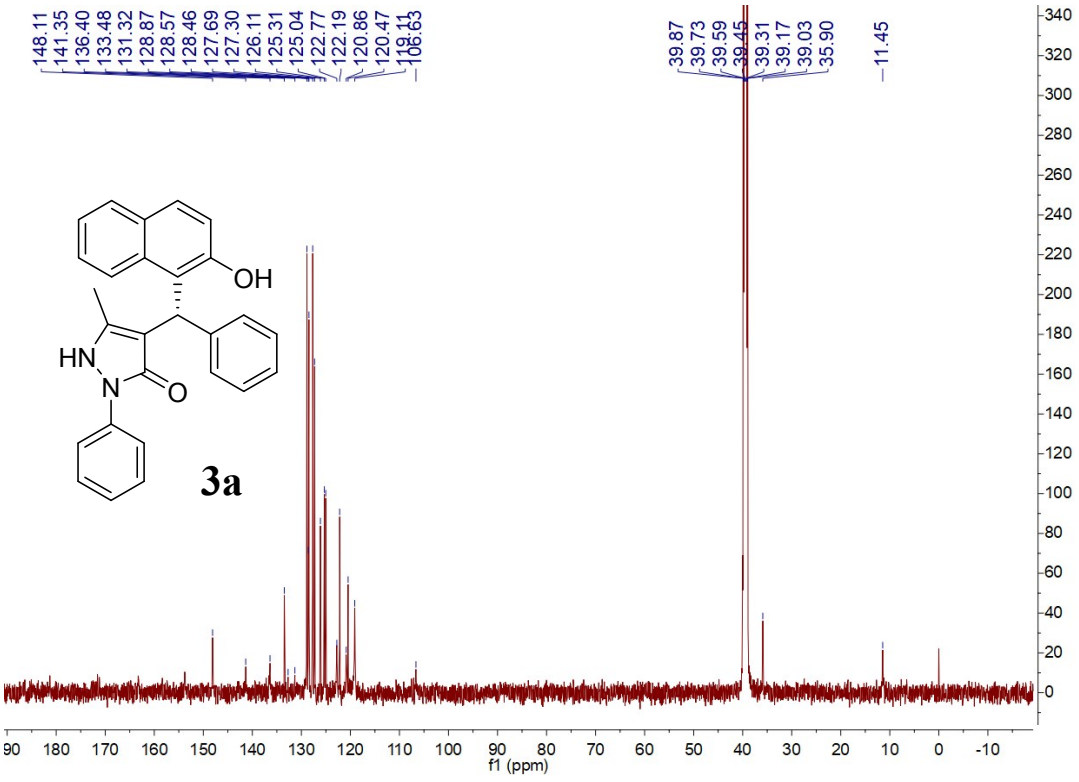


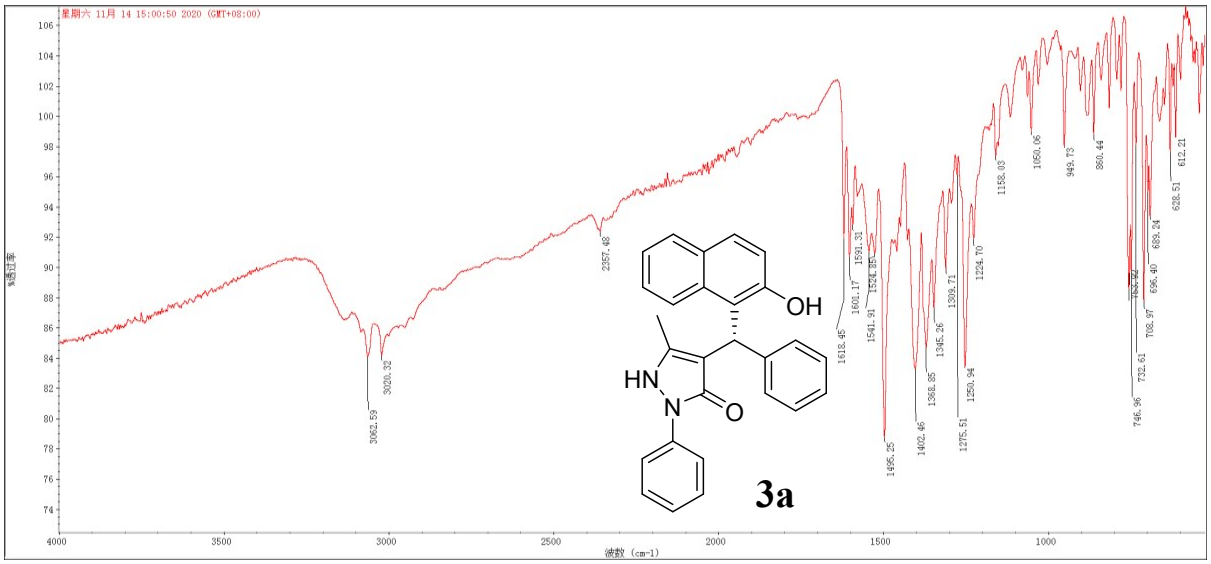
Chemical Formula: $C_{42}H_{45}N_6S_2^+$

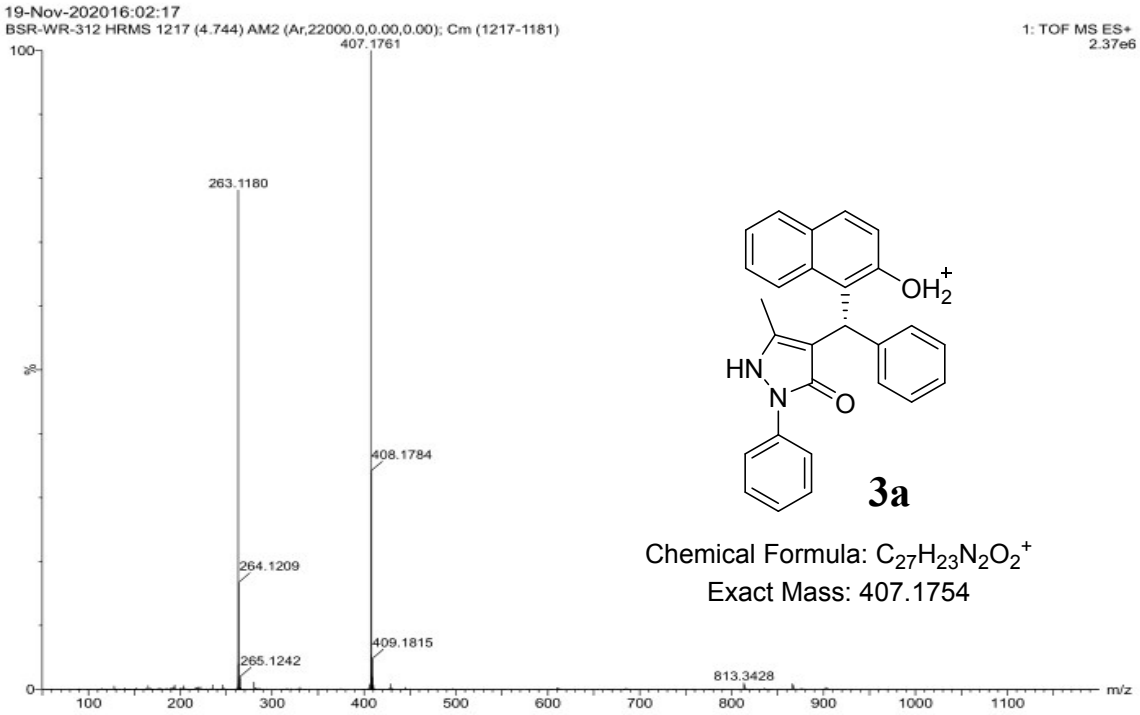
Exact Mass: 697.3142

Copies of ^{1}H NMR, ^{13}C NMR, IR and HRMS spectra of 3



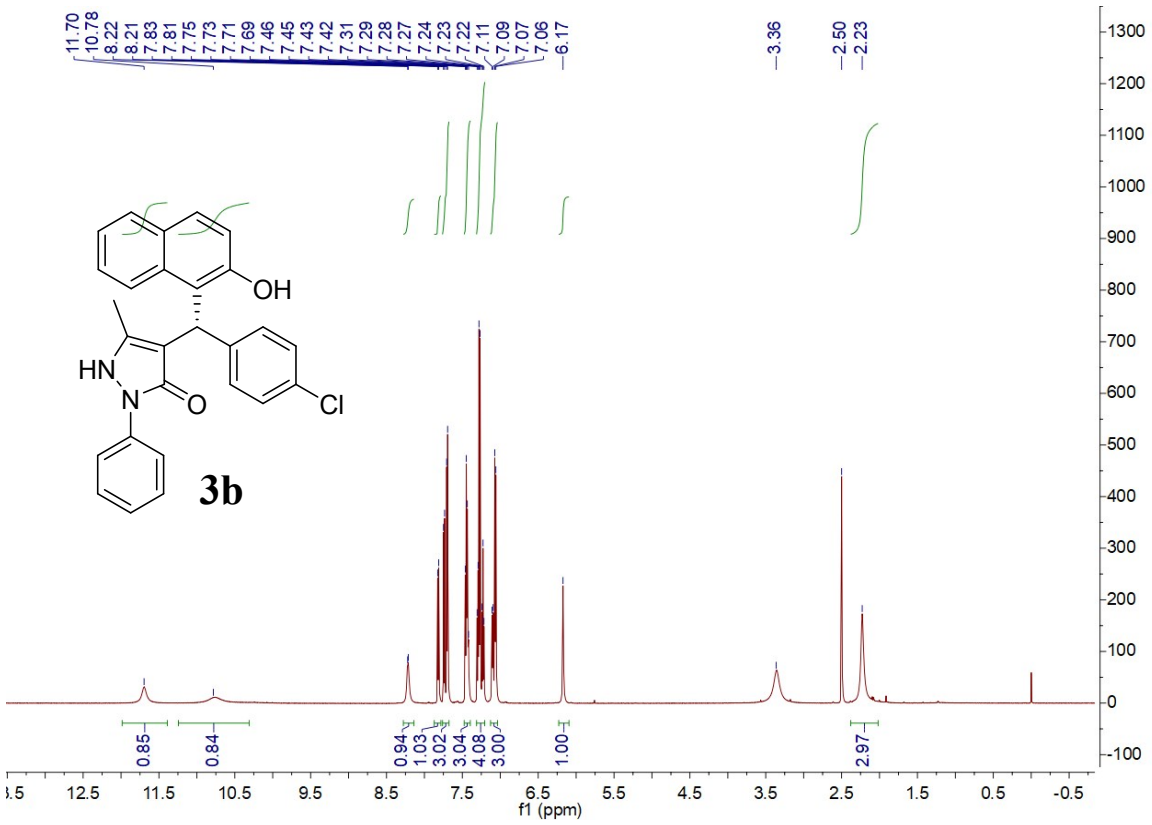






Chemical Formula: $C_{27}H_{23}N_2O_2^+$

Exact Mass: 407.1754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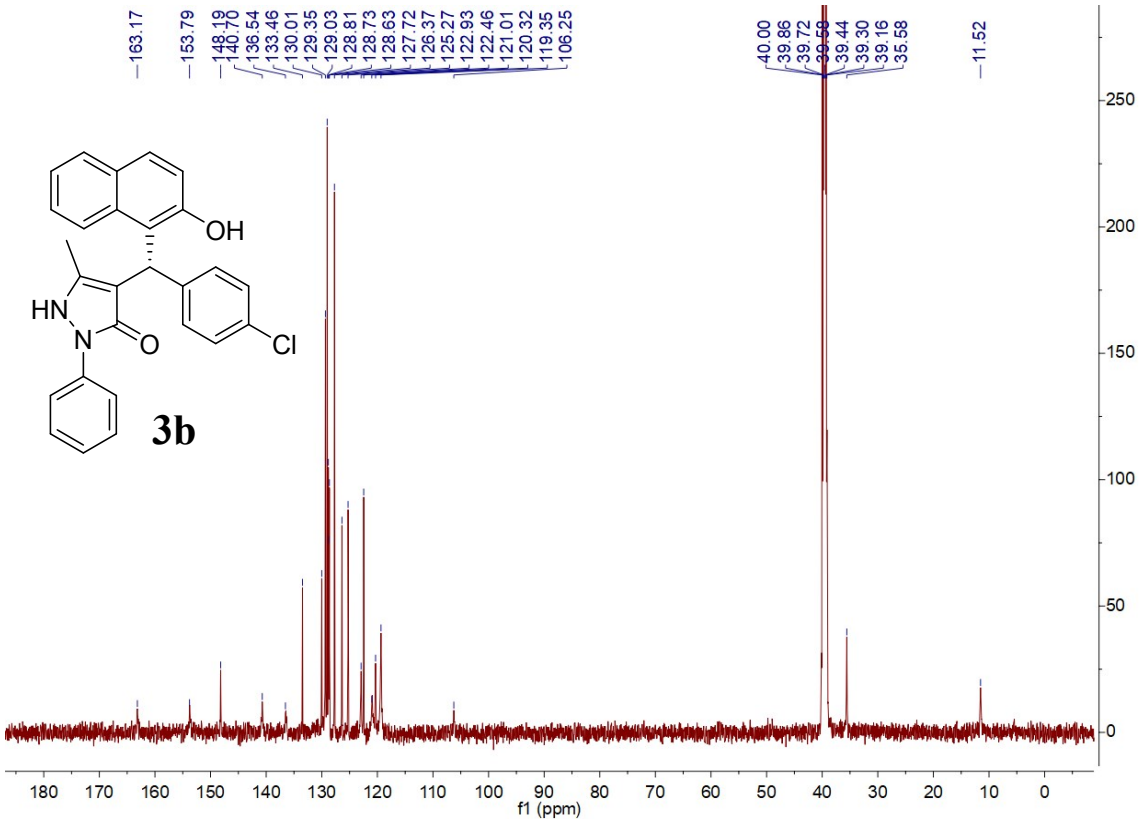
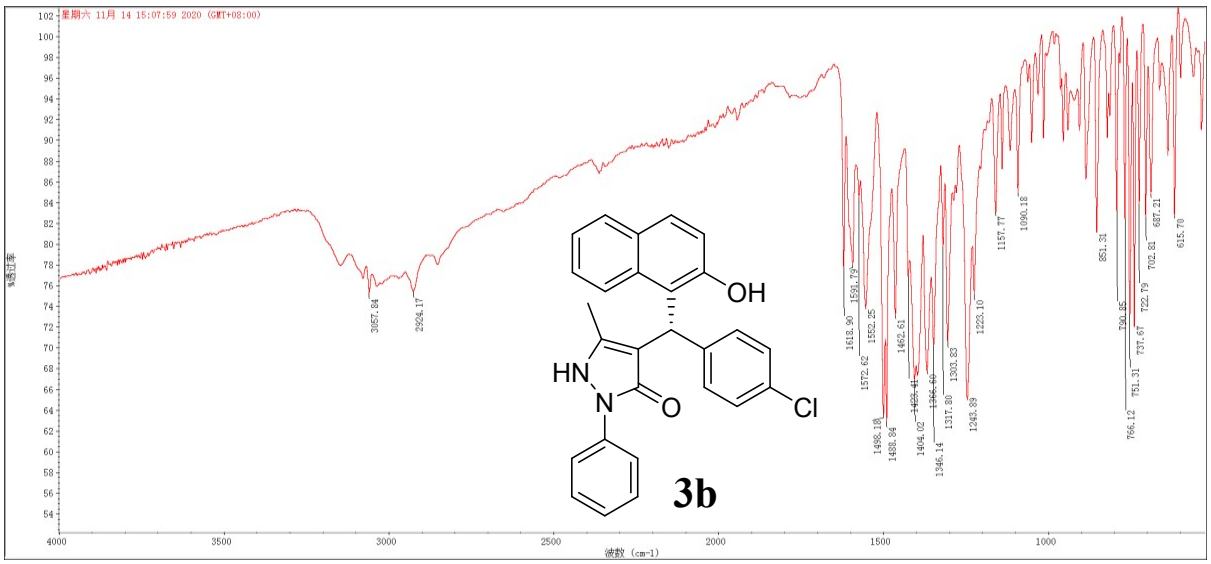
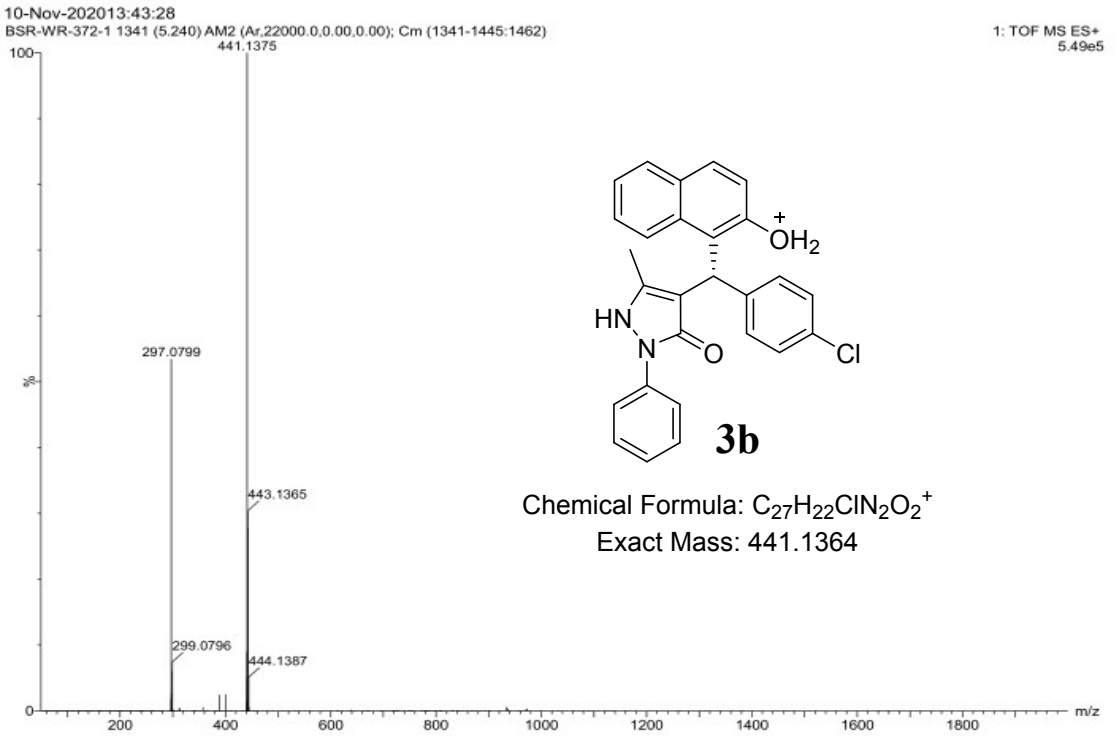
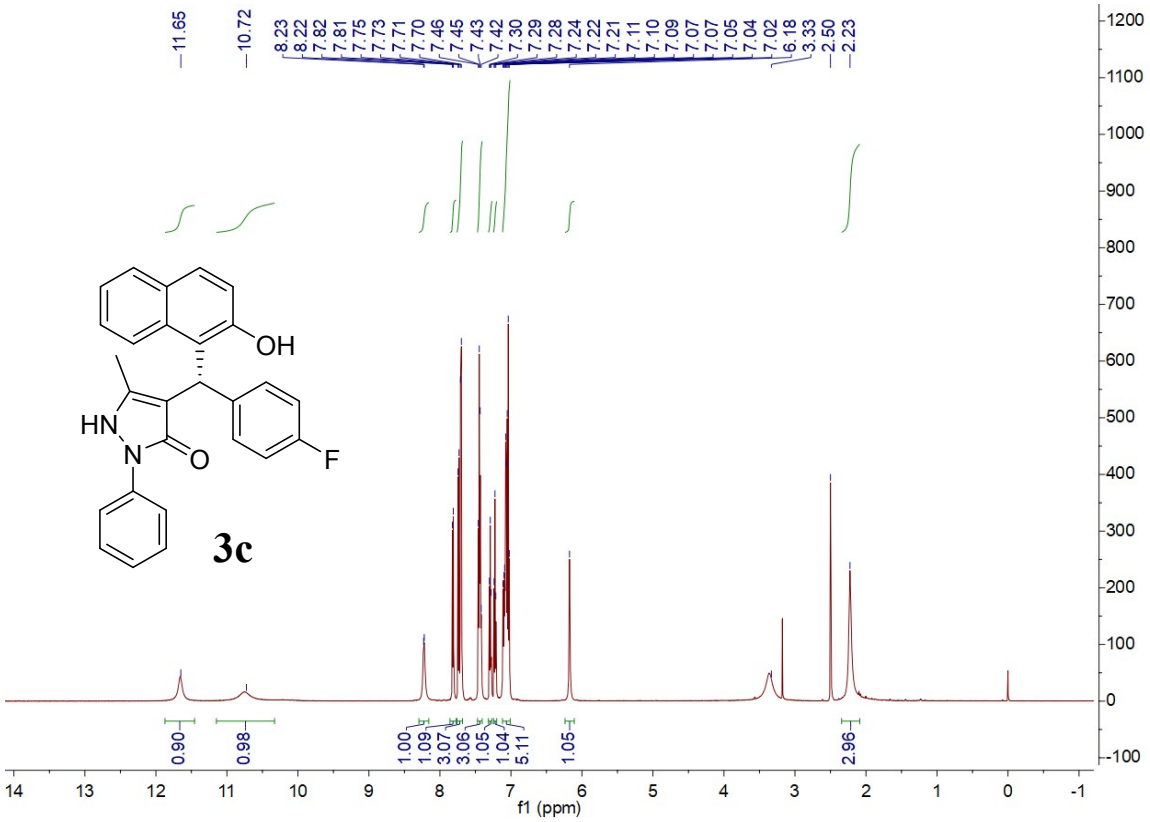
8.22
8.21
7.83
7.81
7.75
7.73
7.71
7.69
7.46
7.45
7.43
7.42
7.31
7.29
7.28
7.27
7.24
7.23
7.22
7.11
7.09
7.07
7.06
6.17
3.36
2.50
2.23
OH
HN
N
O
Cl
3b
0.85
0.84
0.94
1.03
3.02
3.04
4.08
3.00
1.00
2.97
f1 (ppm)

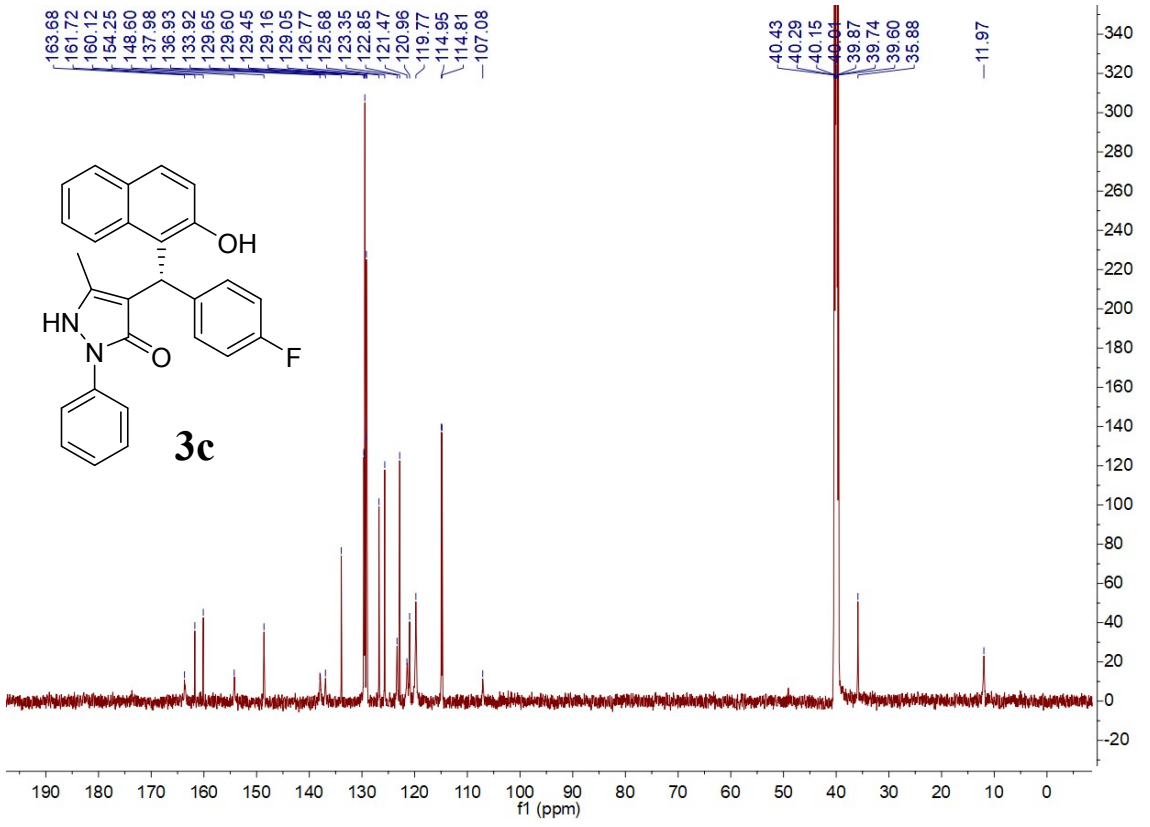

163.17
153.79
148.19
140.70
136.54
133.46
130.01
129.35
129.03
128.81
128.73
128.63
127.72
126.37
125.27
122.93
122.46
121.01
120.32
119.35
106.25
40.00
39.86
39.72
39.58
39.44
39.30
39.16
35.58
11.52
OH
HN
N
O
Cl
3b
f1 (ppm)

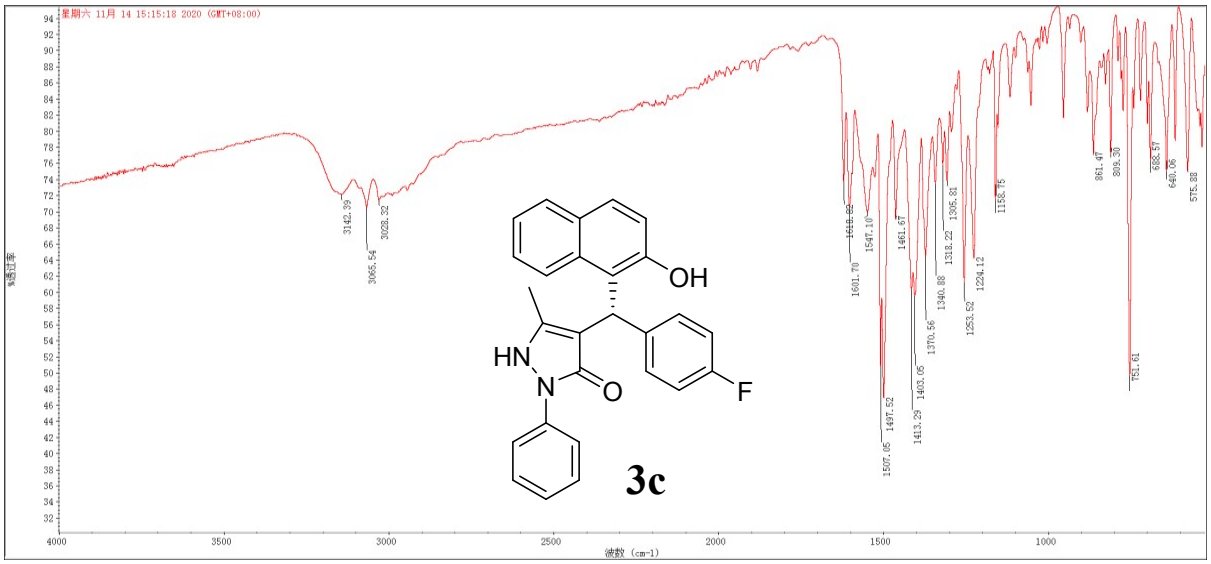


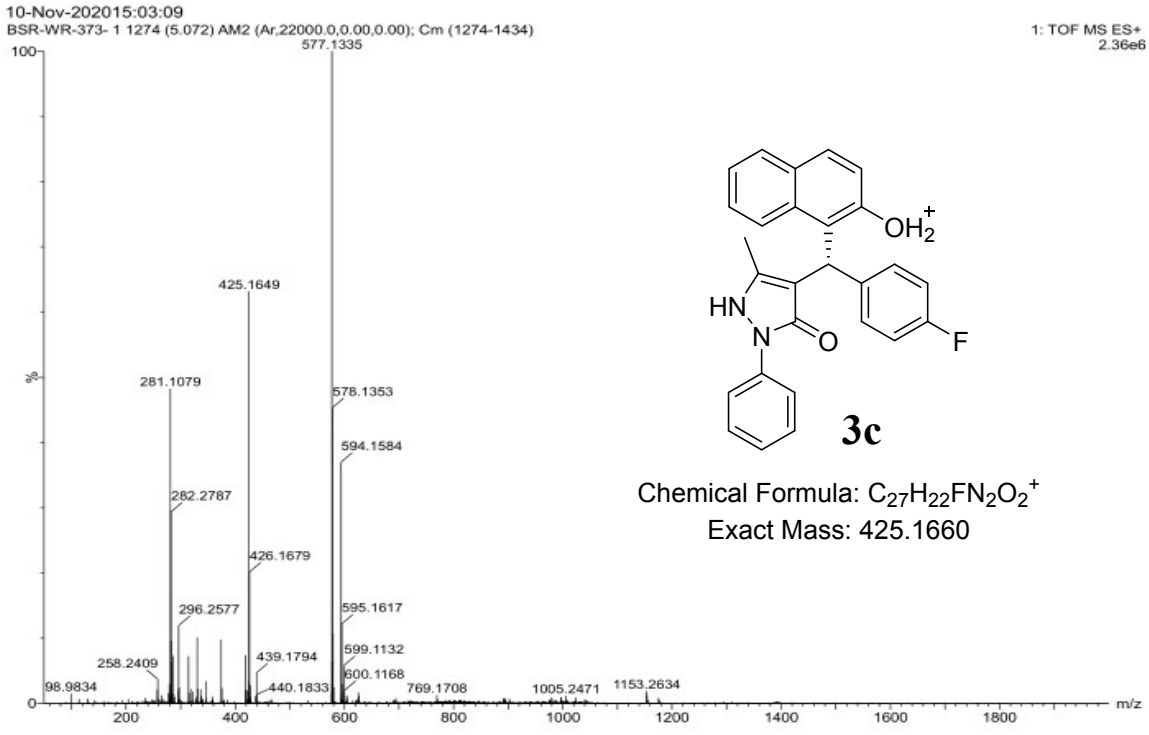


Chemical Formula: $C_{27}H_{22}ClN_2O_2^+$
Exact Mass: 441.1364


11.65
10.72
8.23
8.22
7.82
7.81
7.75
7.73
7.71
7.70
7.46
7.45
7.43
7.42
7.30
7.29
7.28
7.24
7.22
7.21
7.11
7.10
7.09
7.07
7.07
7.05
7.04
7.02
6.18
3.33
2.50
2.23
OH
HN
N
O
F
3c
0.90
0.98
1.00
1.09
3.07
3.06
1.05
1.04
5.11
1.05
2.96
f1 (ppm)

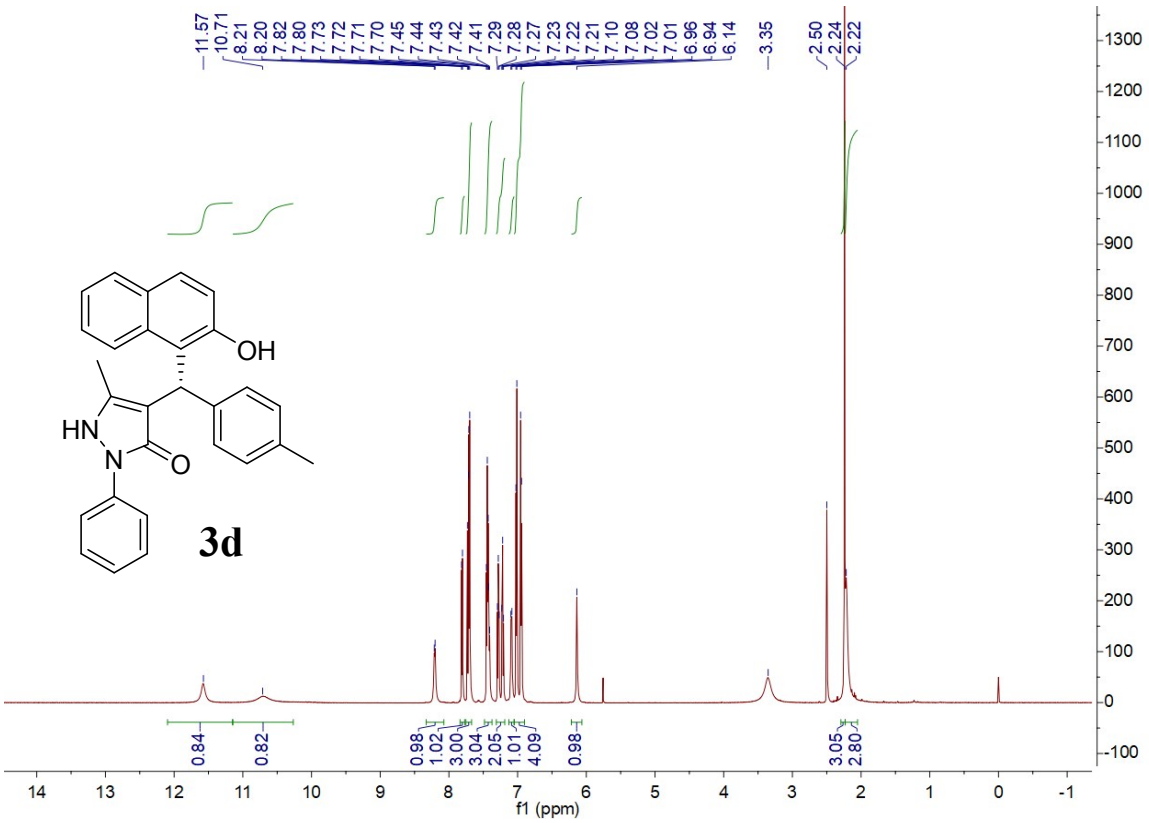

163.68
161.72
160.12
154.25
148.60
137.98
136.93
133.92
129.65
129.60
129.45
129.16
129.05
126.77
125.68
123.35
122.85
121.47
120.96
119.77
114.95
114.81
107.08
40.43
40.29
40.15
40.01
39.87
39.74
39.60
35.88
11.97
OH
HN
N
O
F
3c
f1 (ppm)

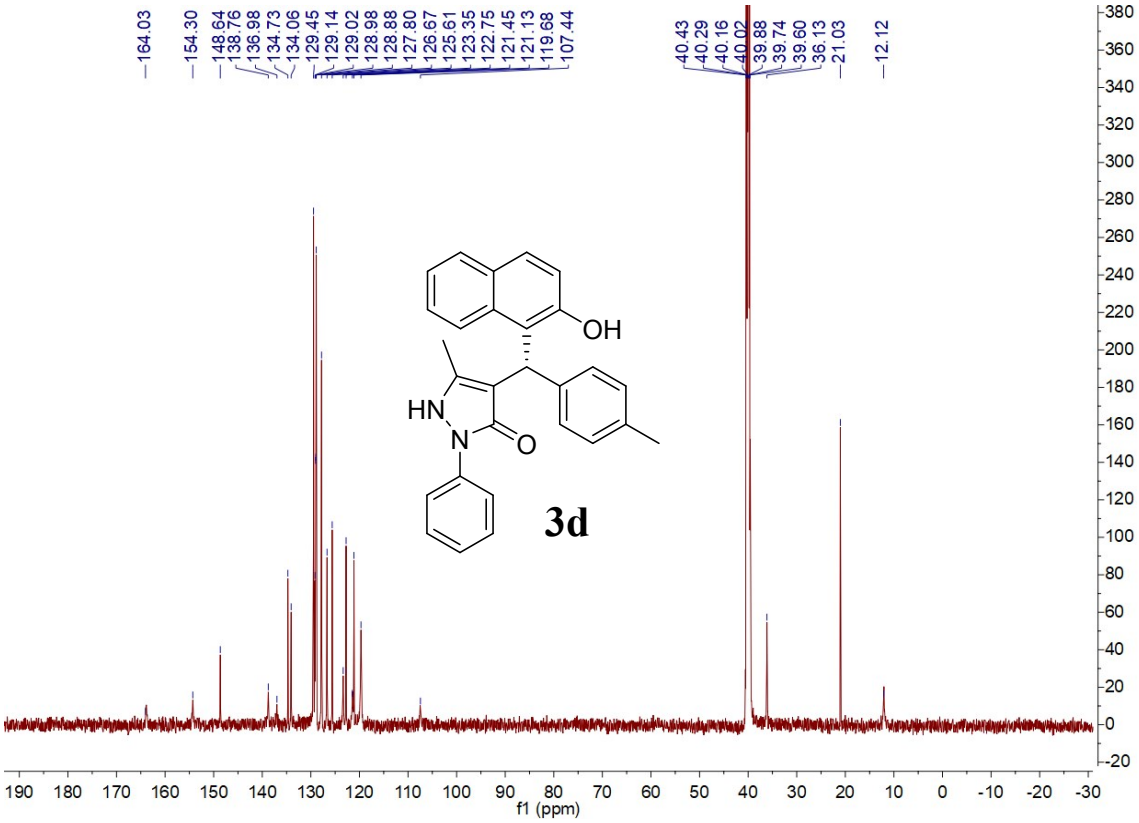


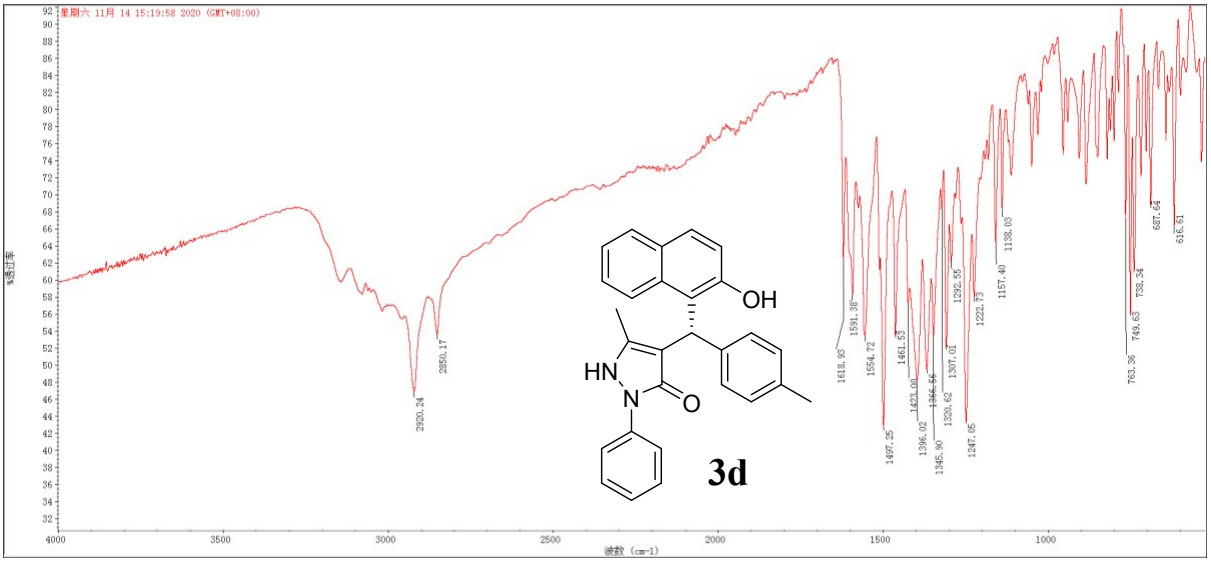


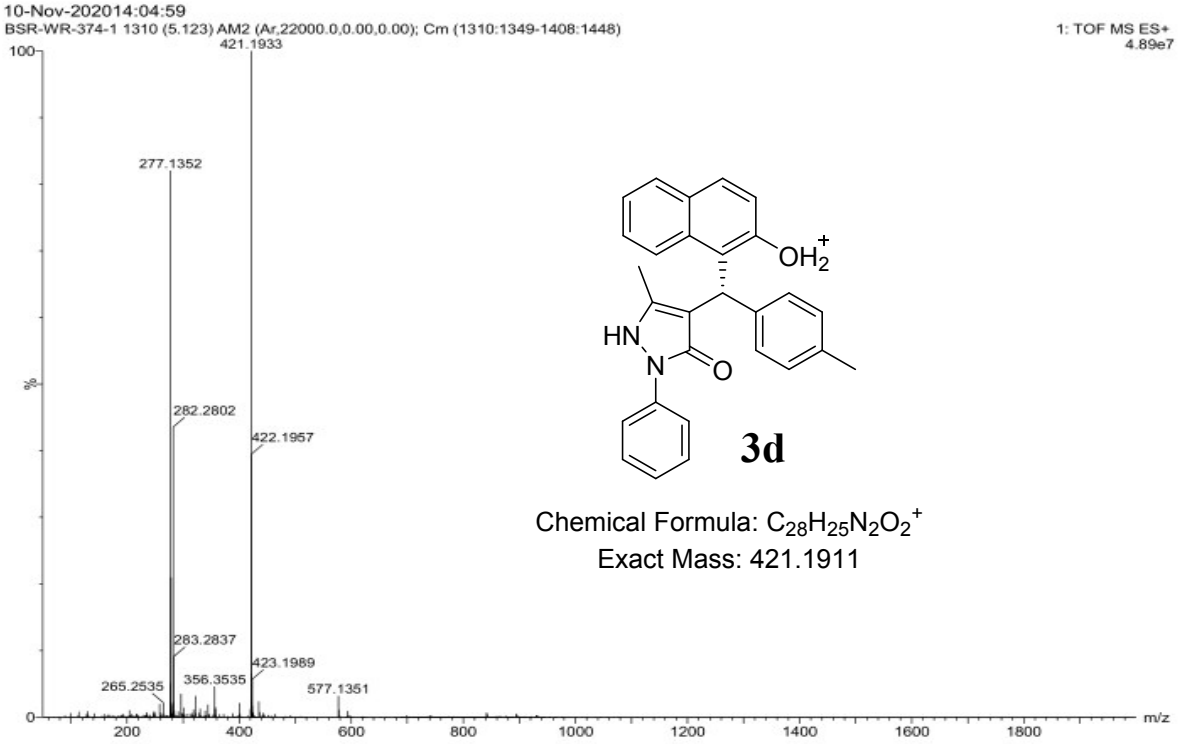
Chemical Formula: $C_{27}H_{22}FN_2O_2^+$

Exact Mass: 425.1660

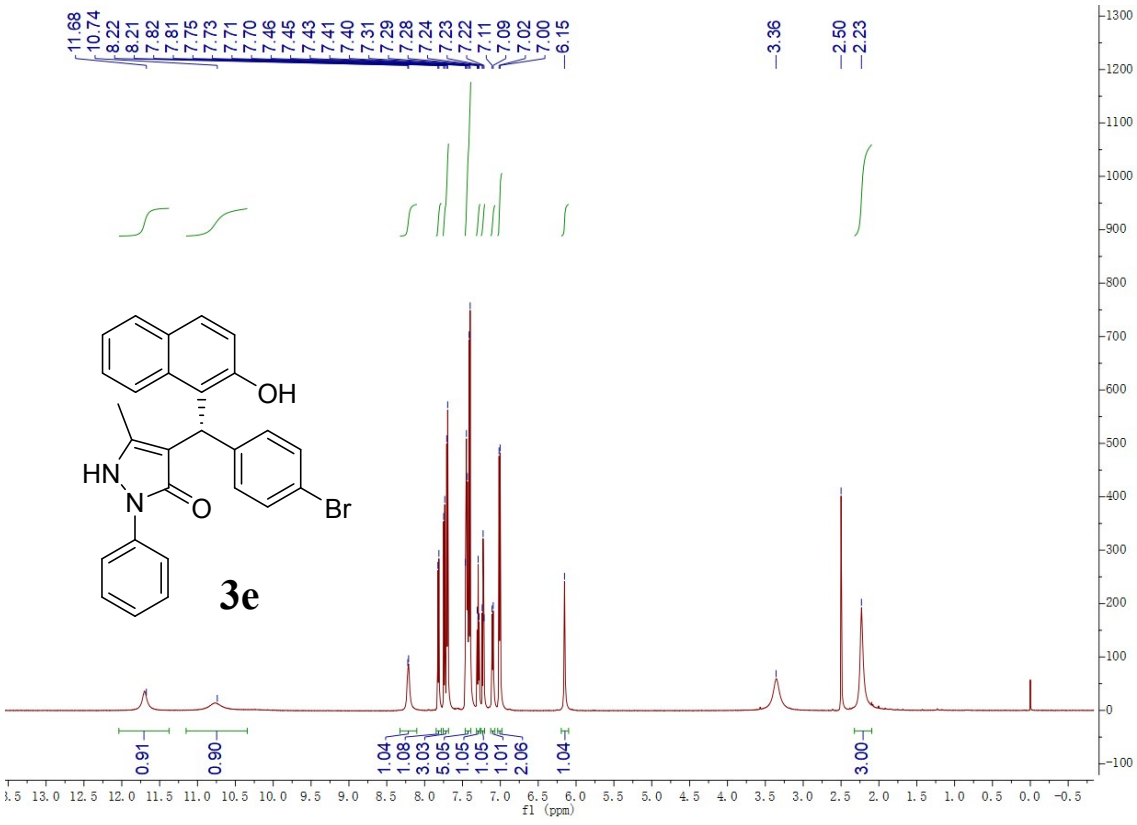

11.57
10.71
8.21
8.20
7.82
7.80
7.73
7.72
7.71
7.70
7.45
7.44
7.43
7.42
7.41
7.29
7.28
7.27
7.23
7.22
7.21
7.10
7.08
7.02
7.01
6.96
6.94
6.14
3.35
2.50
2.24
2.22
OH
HN
N
O
3d
0.84
0.82
0.98
1.02
3.00
3.04
2.05
1.01
4.09
0.98
3.05
2.80
f1 (ppm)

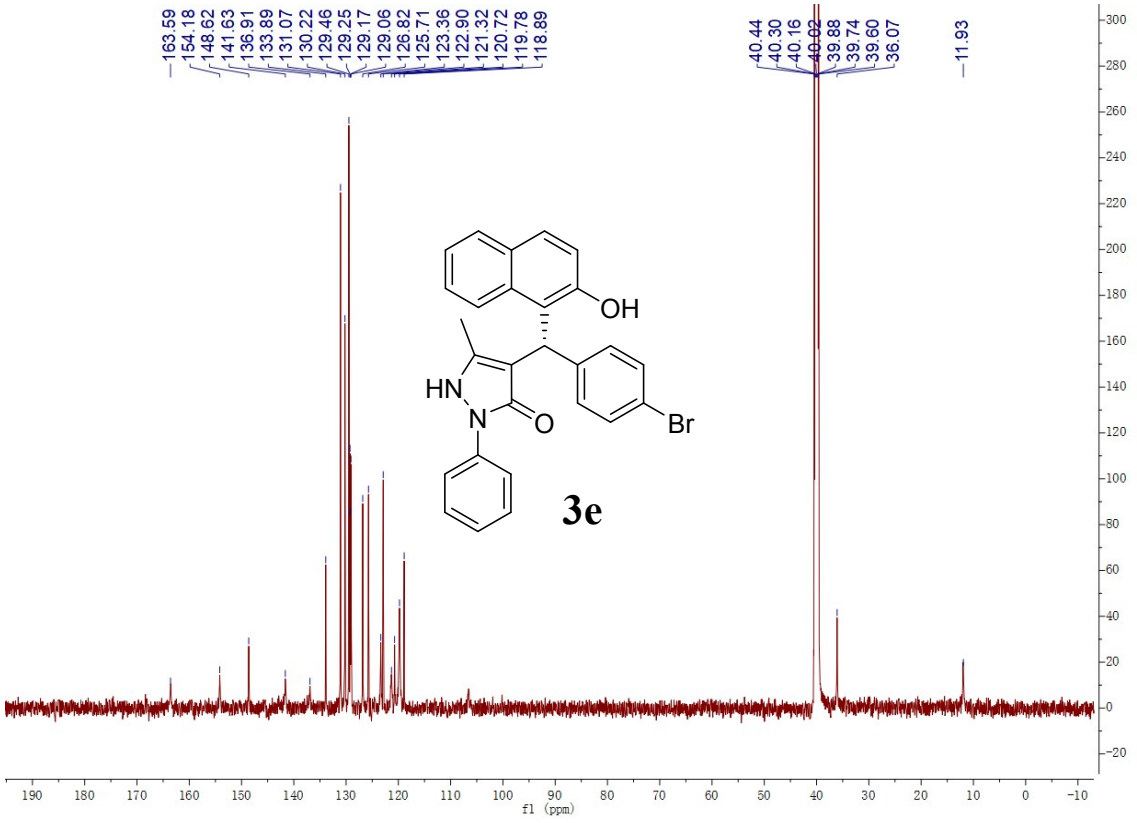

164.03
154.30
148.64
138.76
136.98
134.73
134.06
129.45
129.14
129.02
128.98
128.88
127.80
126.67
125.61
123.35
122.75
121.45
121.13
119.68
107.44
40.43
40.29
40.16
40.02
39.88
39.74
39.60
36.13
21.03
12.12
OH
HN
N
O
3d
f1 (ppm)

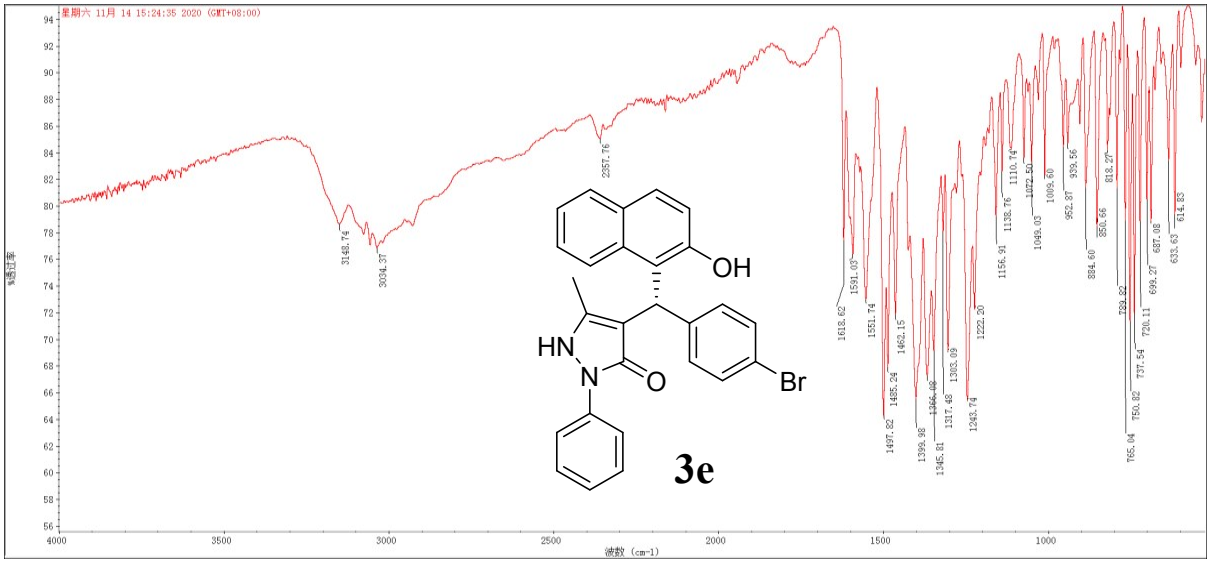


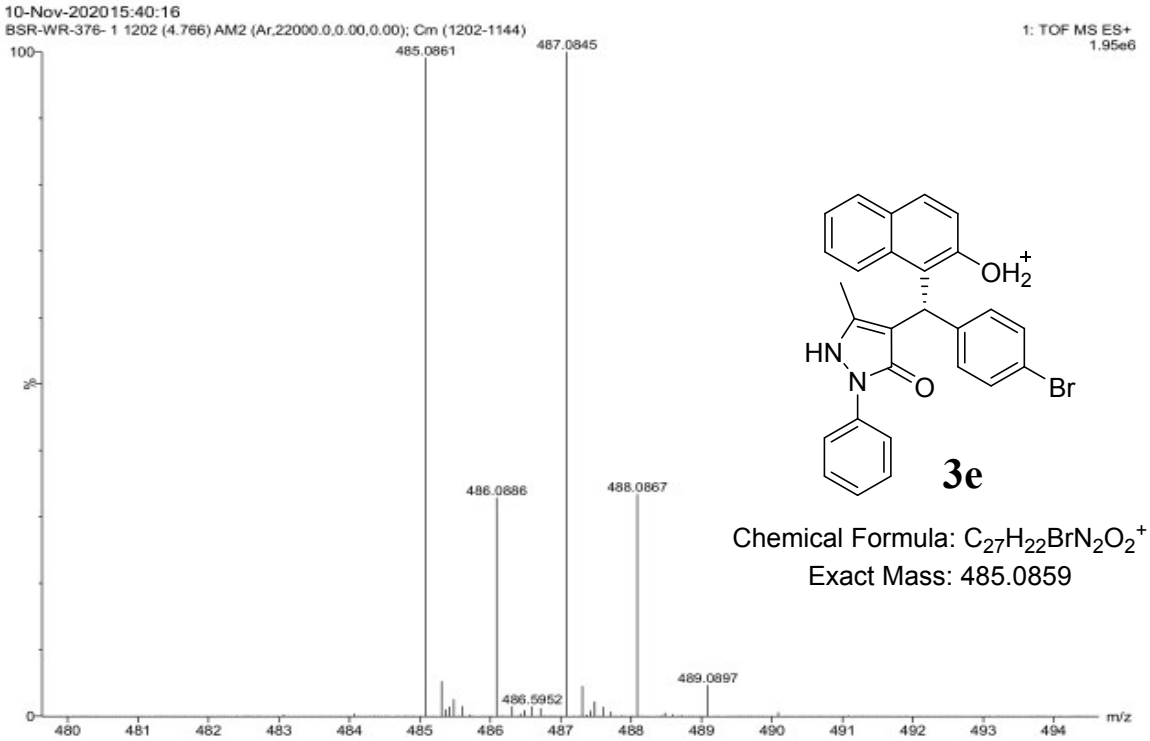


Chemical Formula: $C_{28}H_{25}N_2O_2^+$
Exact Mass: 421.1911

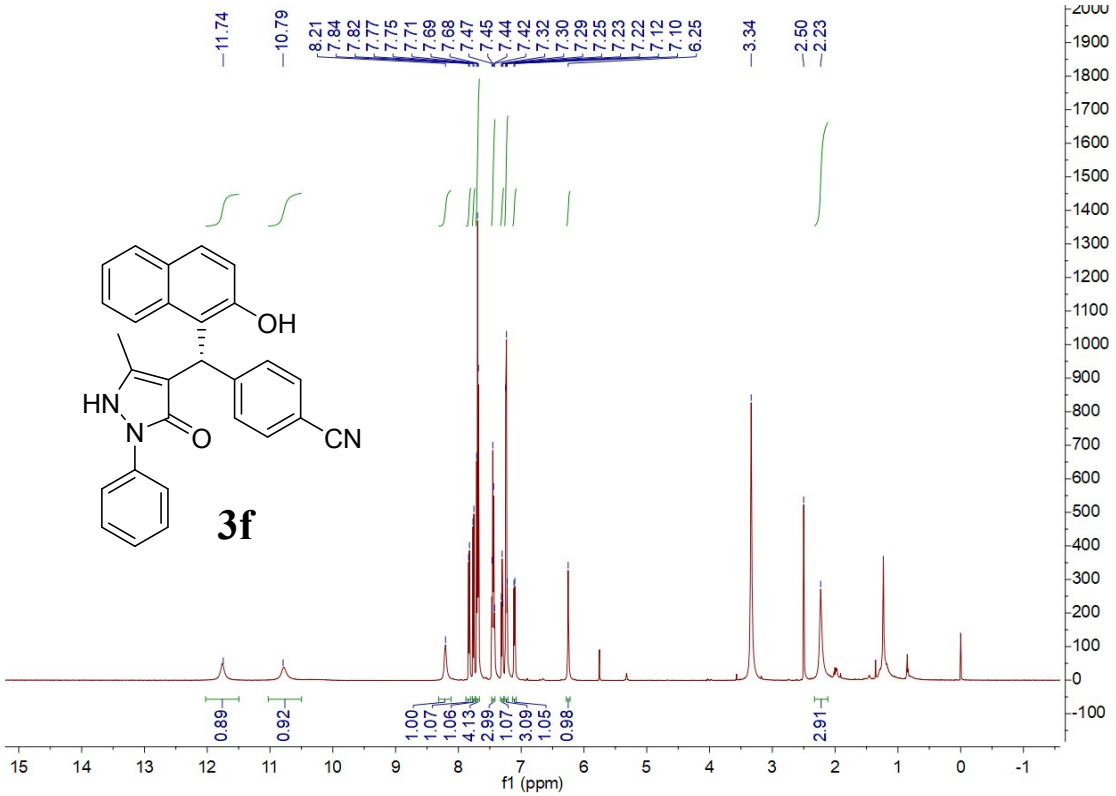

11.68
10.74
8.22
8.21
7.82
7.81
7.75
7.73
7.71
7.70
7.46
7.45
7.43
7.41
7.40
7.31
7.29
7.28
7.24
7.23
7.22
7.11
7.09
7.02
7.00
6.15
3.36
2.50
2.23
OH
HN
N
O
Br
3e
0.91
0.90
1.04
1.08
3.03
5.05
1.05
1.05
1.01
2.06
1.04
3.00
f1 (ppm)

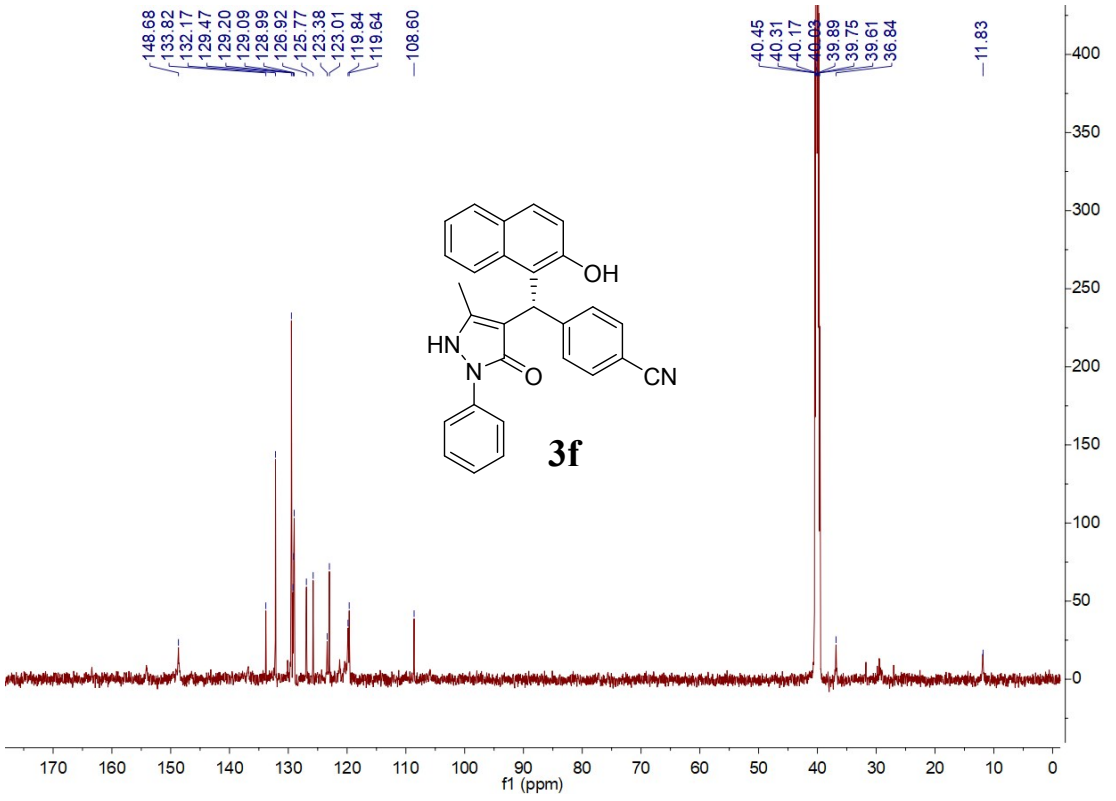

163.59
154.18
148.62
141.63
136.91
133.89
131.07
130.22
129.46
129.25
129.17
129.06
126.82
125.71
123.36
122.90
121.32
120.72
119.78
118.89
40.44
40.30
40.16
40.02
39.88
39.74
39.60
36.07
11.93
OH
HN
N
O
Br
3e
f1 (ppm)

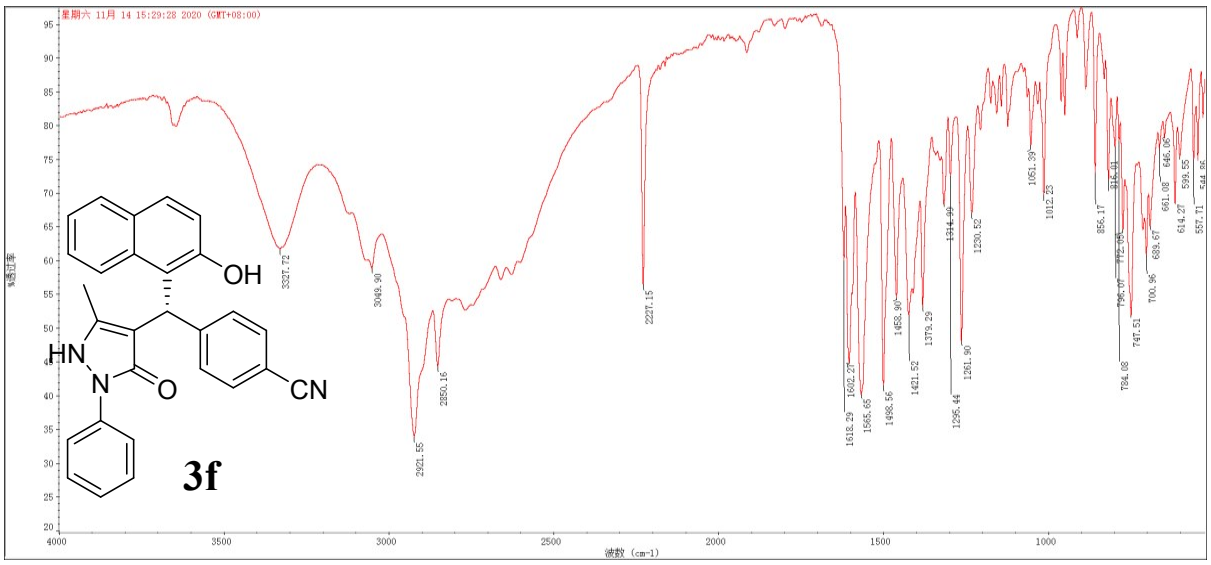


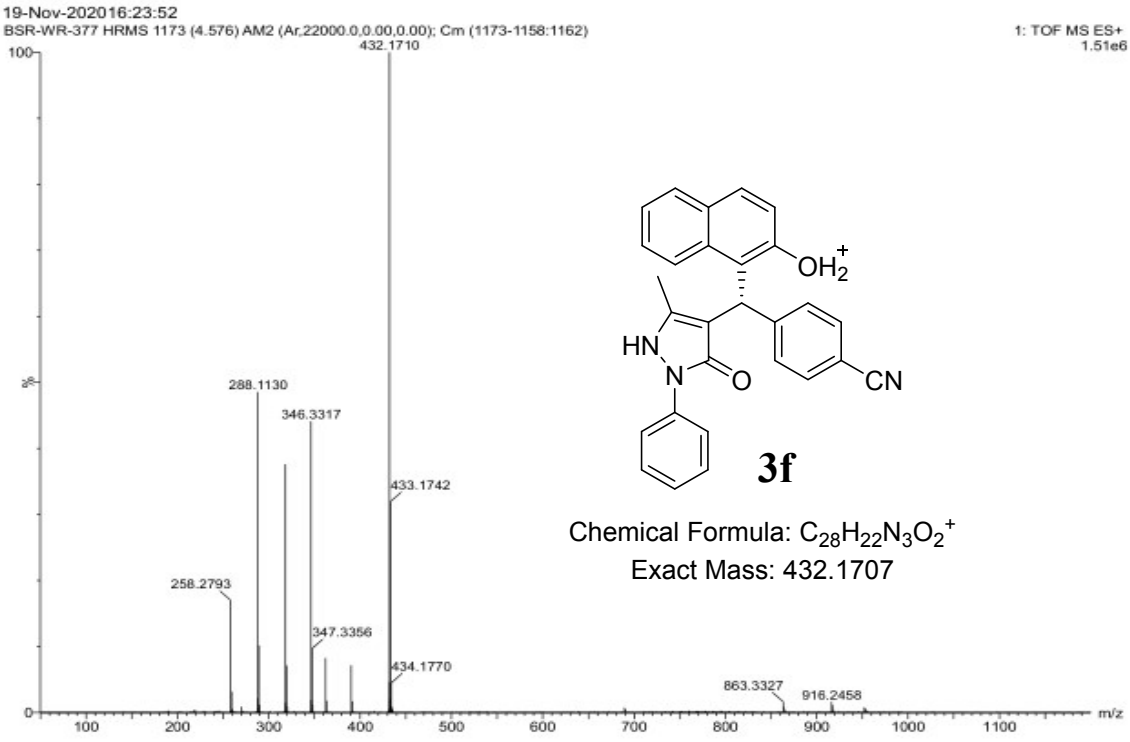


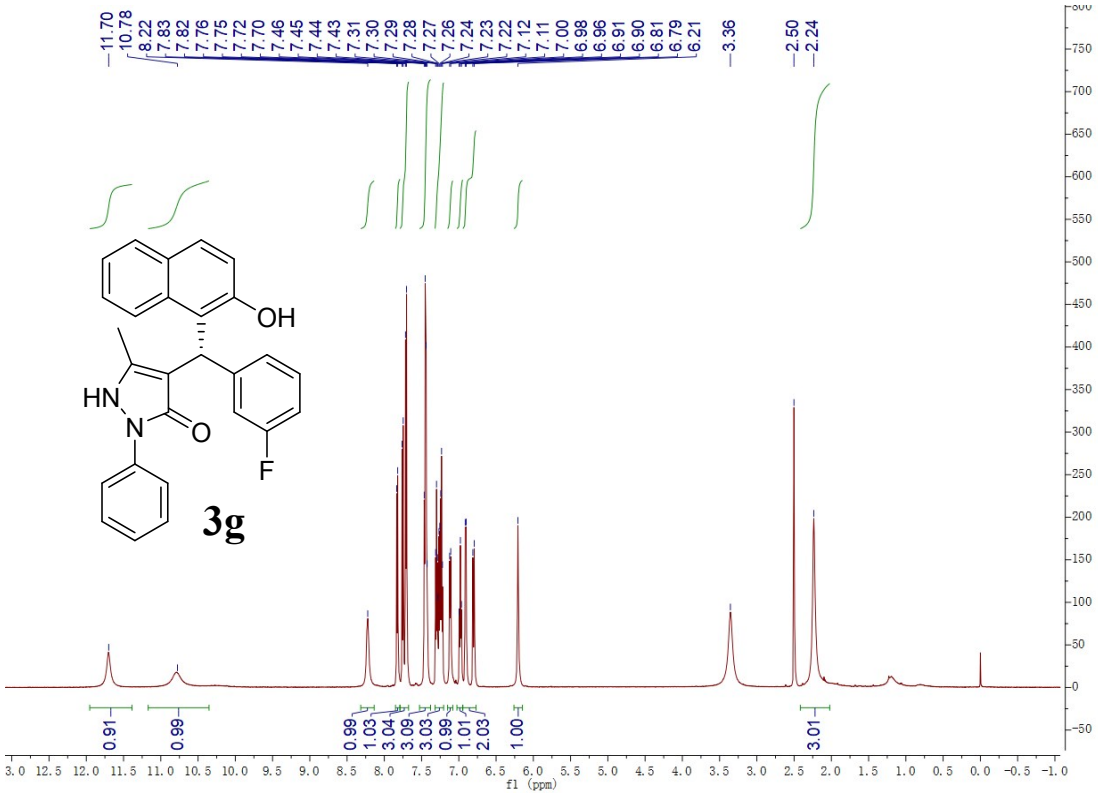
Chemical Formula: $C_{27}H_{22}BrN_2O_2^+$
Exact Mass: 485.0859

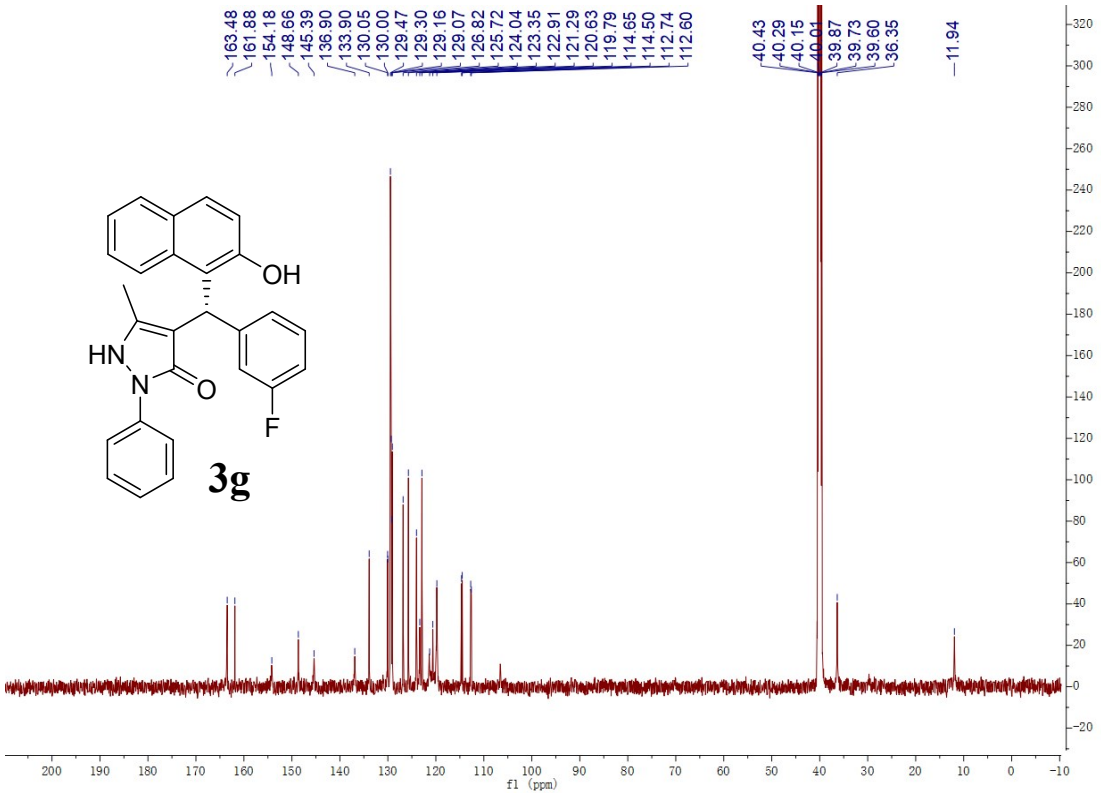

11.74
10.79
8.21
7.84
7.82
7.77
7.75
7.71
7.69
7.68
7.47
7.45
7.44
7.42
7.32
7.30
7.29
7.25
7.23
7.22
7.12
7.10
6.25
3.34
2.50
2.23
OH
HN
N
O
CN
3f
0.89
0.92
1.00
1.07
1.06
4.13
2.99
1.07
3.09
1.05
0.98
2.91
f1 (ppm)

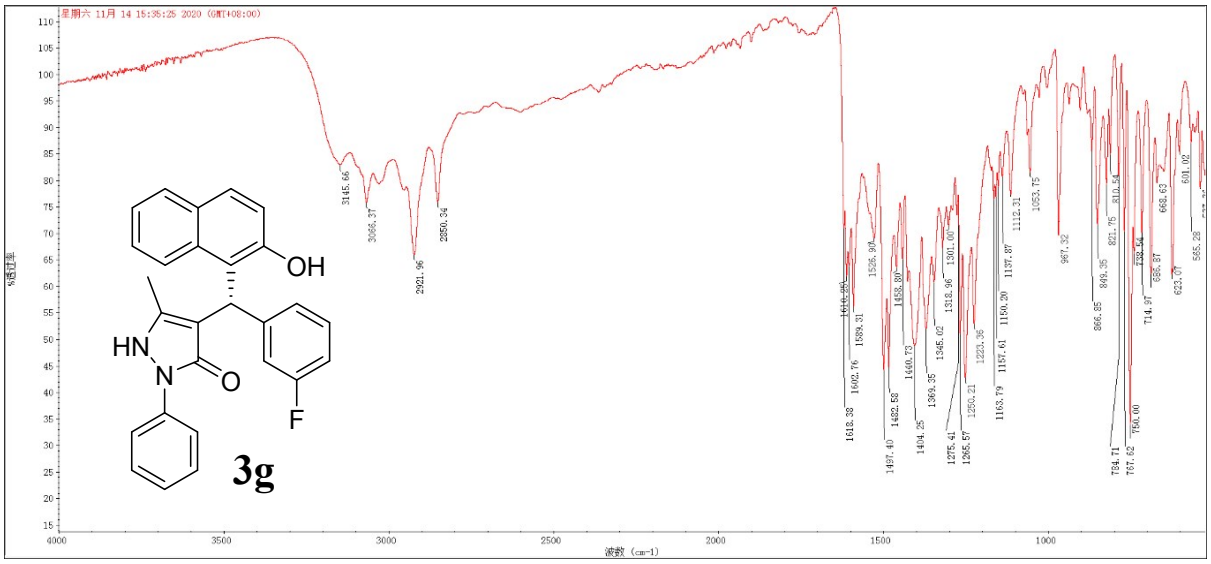

148.68
133.82
132.17
129.47
129.20
129.09
128.99
126.92
125.77
123.38
123.01
119.84
119.64
108.60
40.45
40.31
40.17
40.03
39.89
39.75
39.61
36.84
11.83
OH
HN
N
O
CN
3f
f1 (ppm)

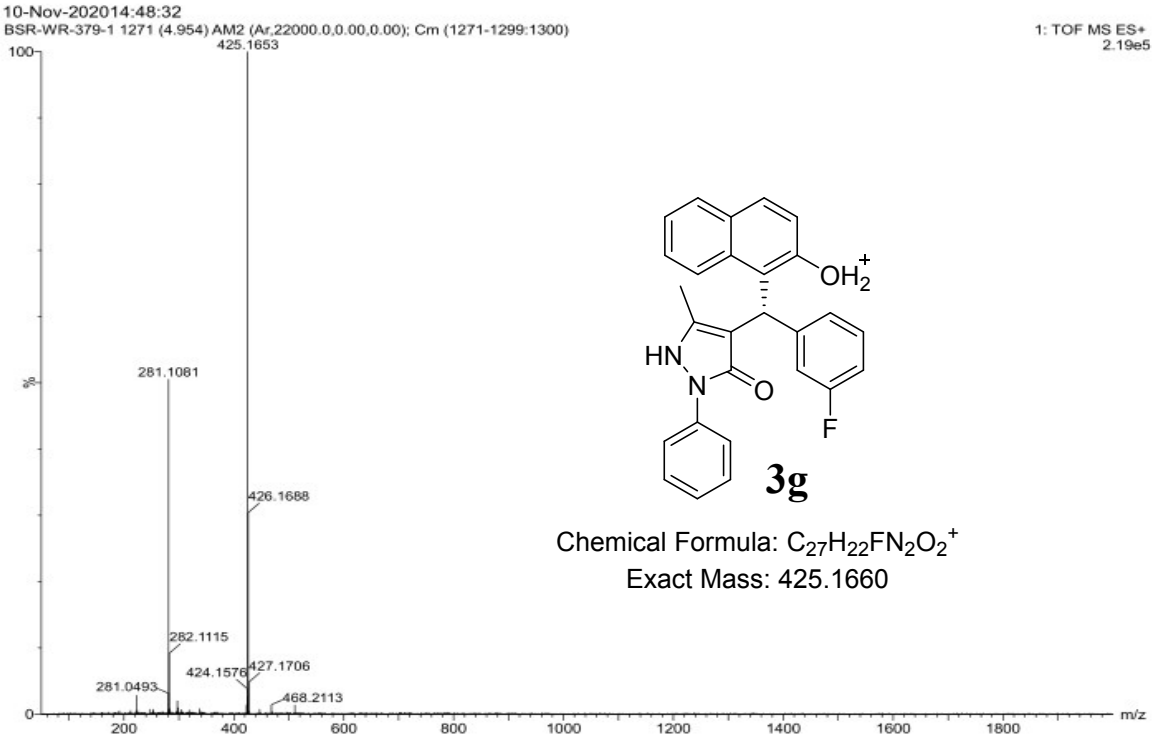

星期六 11月 14 15:29:28 2020 (GMT+08:00)
OH
HN
N
O
CN
3f
3327.72
3069.90
2921.55
2850.16
2227.15
1618.29
1602.27
1565.65
1498.56
1458.90
1421.52
1379.29
1314.49
1296.44
1261.90
1200.52
1051.39
1012.23
856.17
796.07
784.08
747.51
700.96
689.67
681.08
646.06
614.27
599.55
557.71
544.86
4000
3500
3000
2500
2000
1500
1000
波数 (cm-1)


19-Nov-202016:23:52
BSR-WR-377 HRMS 1173 (4.576) AM2 (Ar,22000.0,0.00,0.00); Cm (1173-1158:1162)
1: TOF MS ES+
1.51e6
100
%
0
432.1710
288.1130
346.3317
433.1742
258.2793
347.3356
434.1770
863.3327
916.2458
100
200
300
400
500
600
700
800
900
1000
1100
m/z
OH2+
HN
N
O
CN
3f
Chemical Formula: C28H22N3O2+
Exact Mass: 432.1707


11.70
10.78
8.22
7.83
7.82
7.76
7.75
7.72
7.70
7.46
7.45
7.44
7.43
7.31
7.30
7.29
7.28
7.27
7.26
7.24
7.23
7.22
7.12
7.11
7.00
6.98
6.96
6.91
6.90
6.81
6.79
6.21
3.36
2.50
2.24
OH
HN
N
O
F
3g
0.91
0.99
0.99
1.03
3.04
3.09
3.03
0.99
1.01
2.03
1.00
3.01
f1 (ppm)

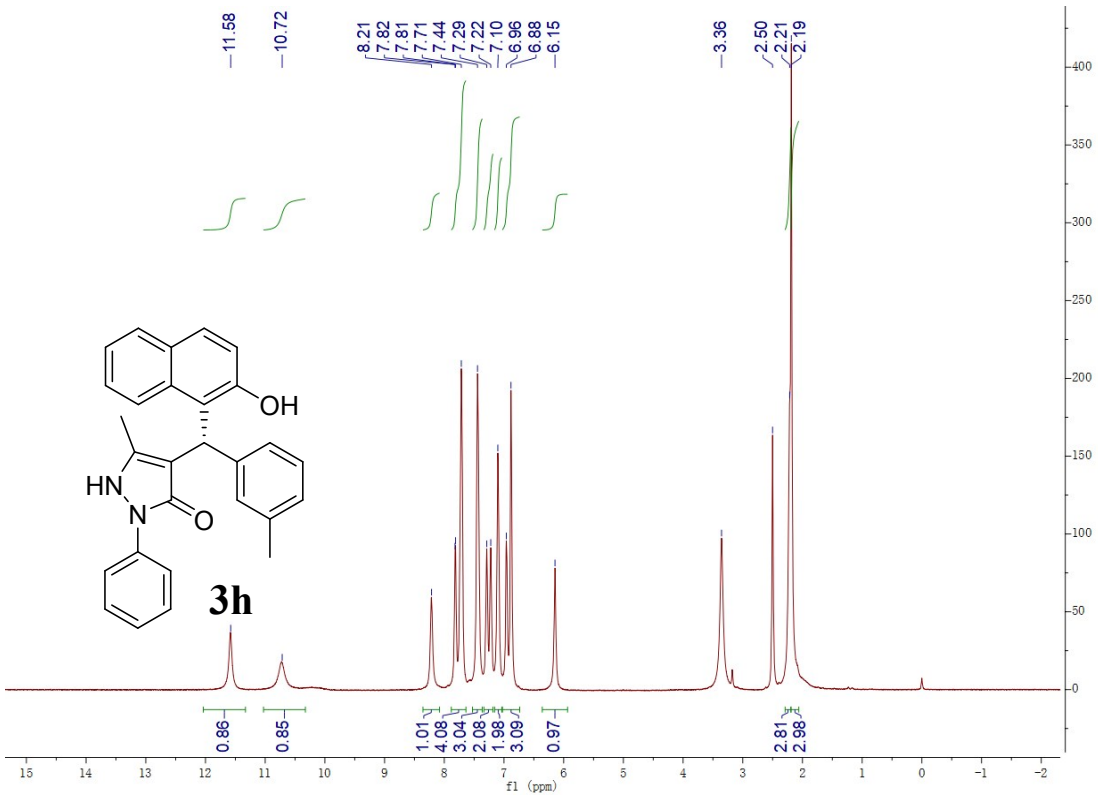

163.48
161.88
154.18
148.66
145.39
136.90
133.90
130.05
130.00
129.47
129.30
129.16
129.07
126.82
125.72
124.04
123.35
122.91
121.29
120.63
119.79
114.65
114.50
112.74
112.60
40.43
40.29
40.15
40.01
39.87
39.73
39.60
36.35
11.94
OH
HN
N
O
F
3g
f1 (ppm)

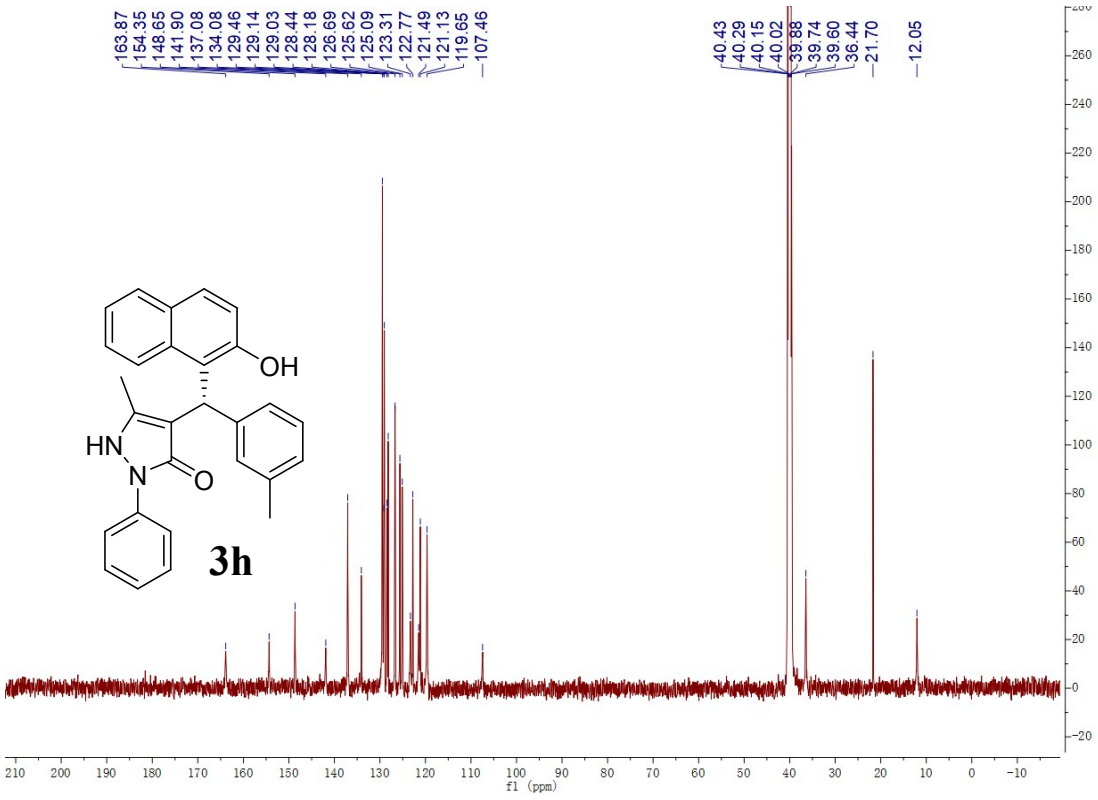


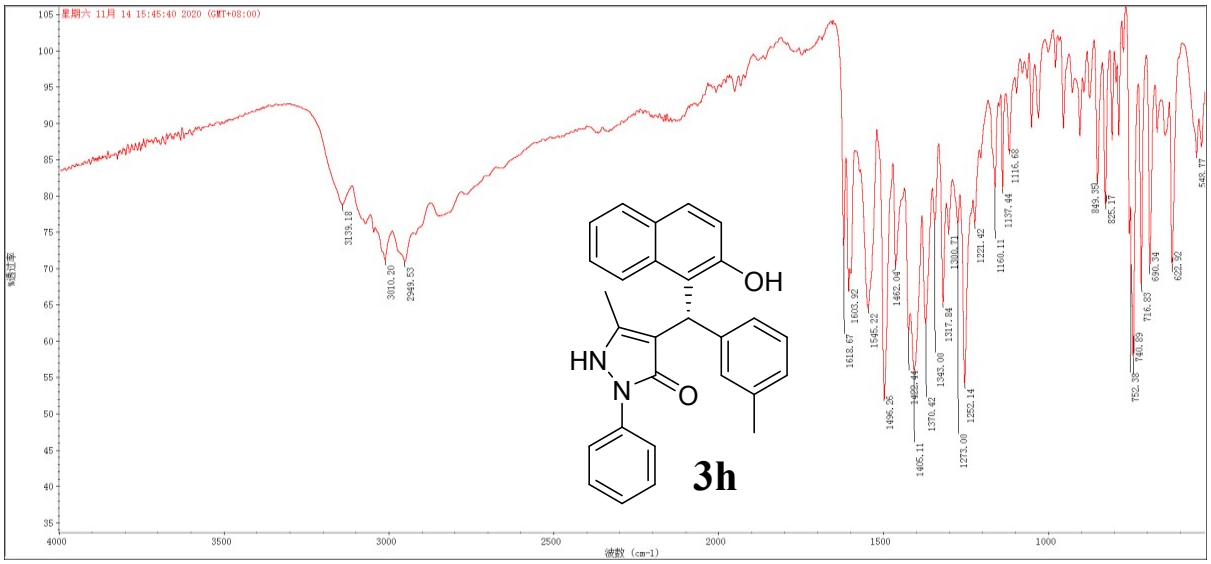


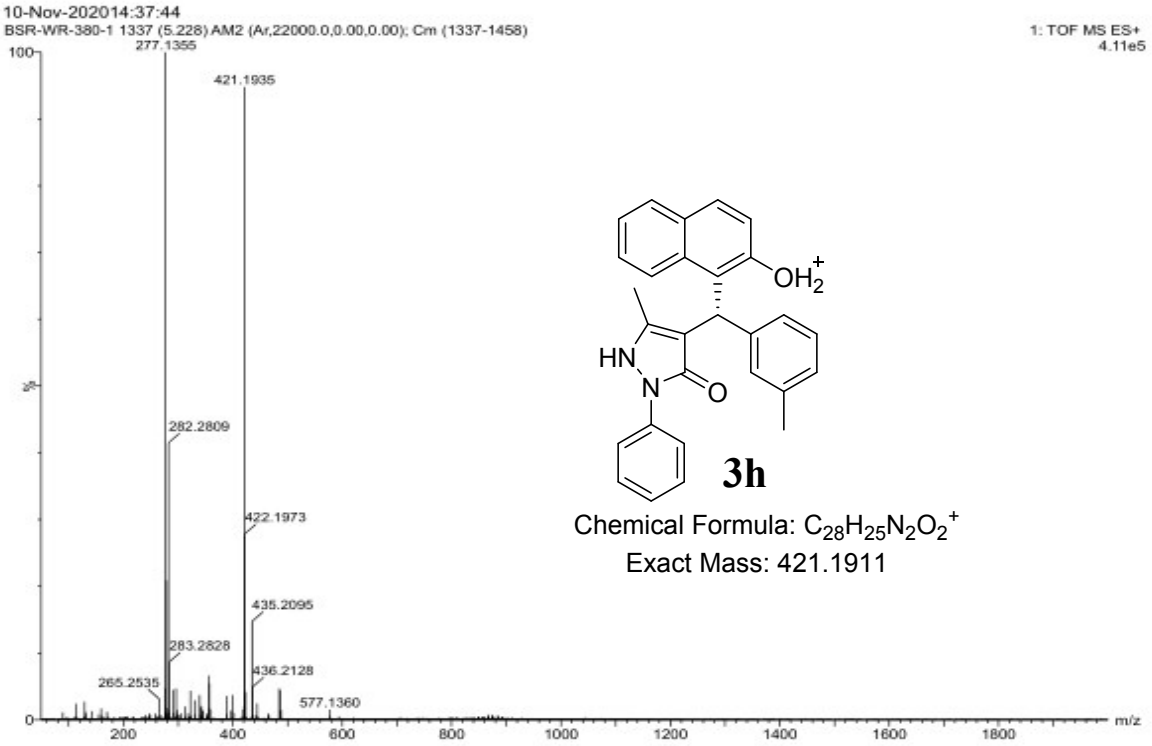
Chemical Formula: $C_{27}H_{22}FN_2O_2^+$

Exact Mass: 425.1660


11.58
10.72
8.21
7.82
7.81
7.71
7.44
7.29
7.22
7.10
6.96
6.88
6.15
3.36
2.50
2.21
2.19
OH
HN
N
O
3h
0.86
0.85
1.01
4.08
3.04
2.08
1.98
3.09
0.97
2.81
2.98
f1 (ppm)

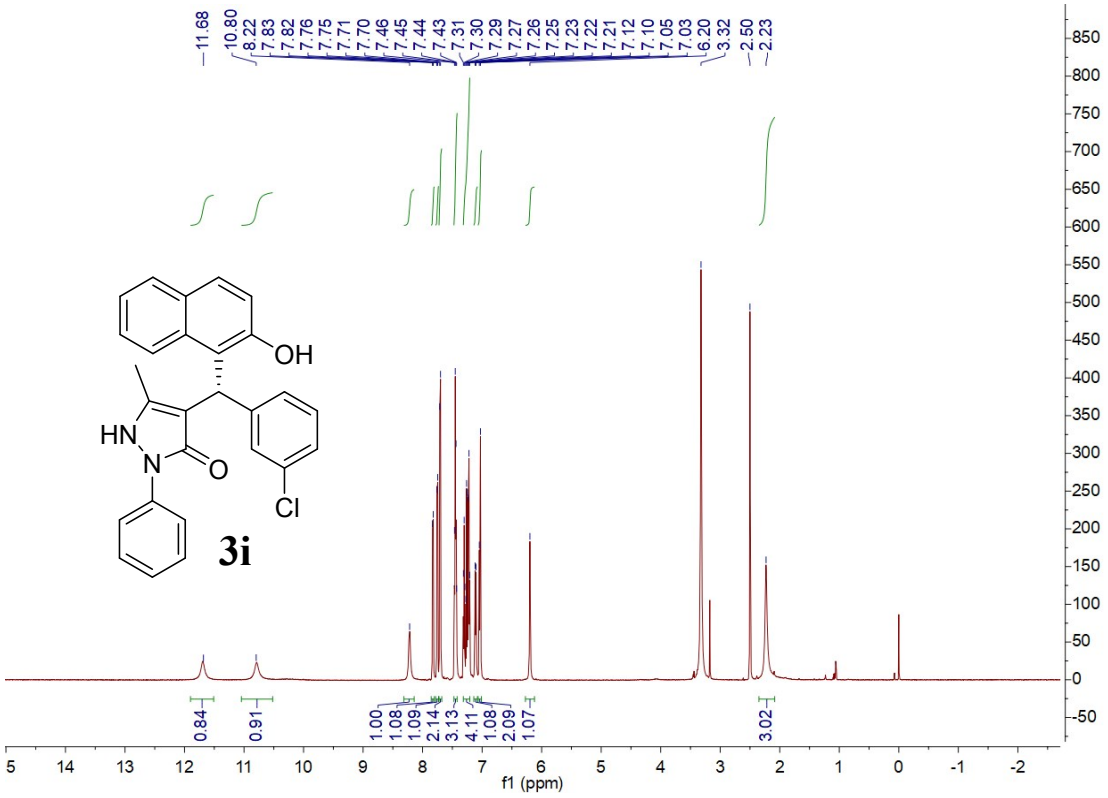

163.87
154.35
148.65
141.90
137.08
134.08
129.46
129.14
129.03
128.44
128.18
126.69
125.62
125.09
123.31
122.77
121.49
121.13
119.65
107.46
40.43
40.29
40.15
40.02
39.88
39.74
39.60
36.44
21.70
12.05
OH
HN
N
O
3h
f1 (ppm)

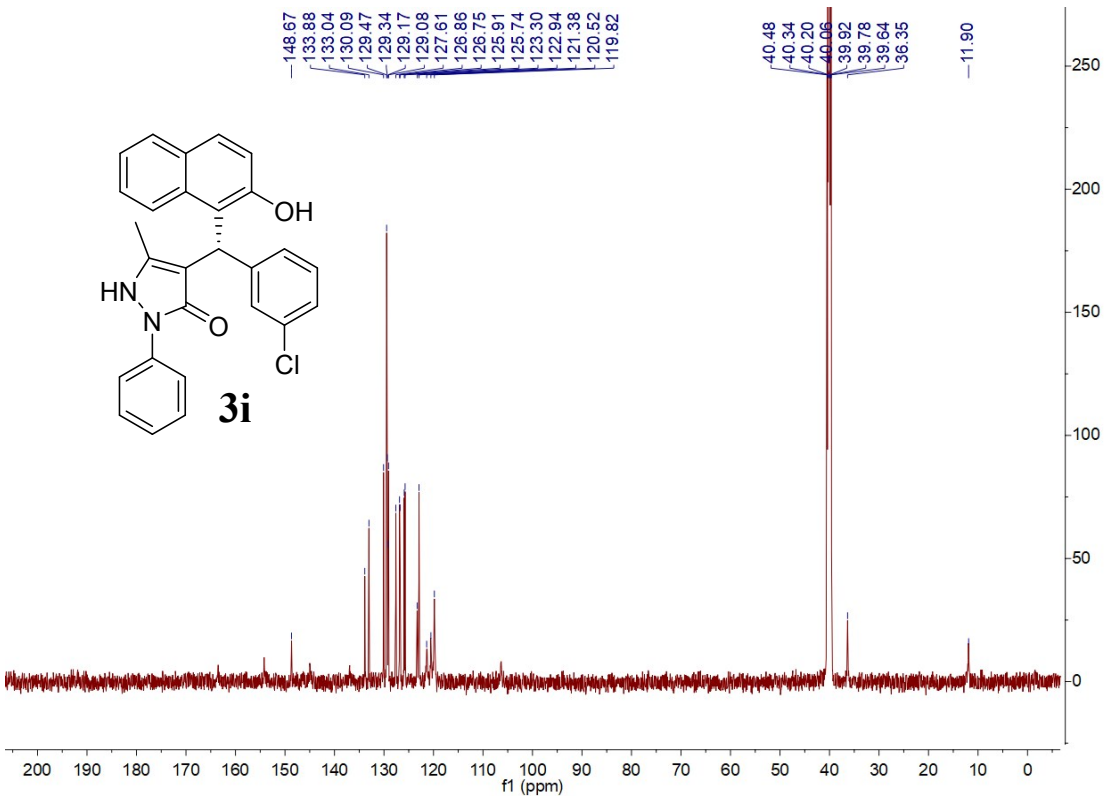


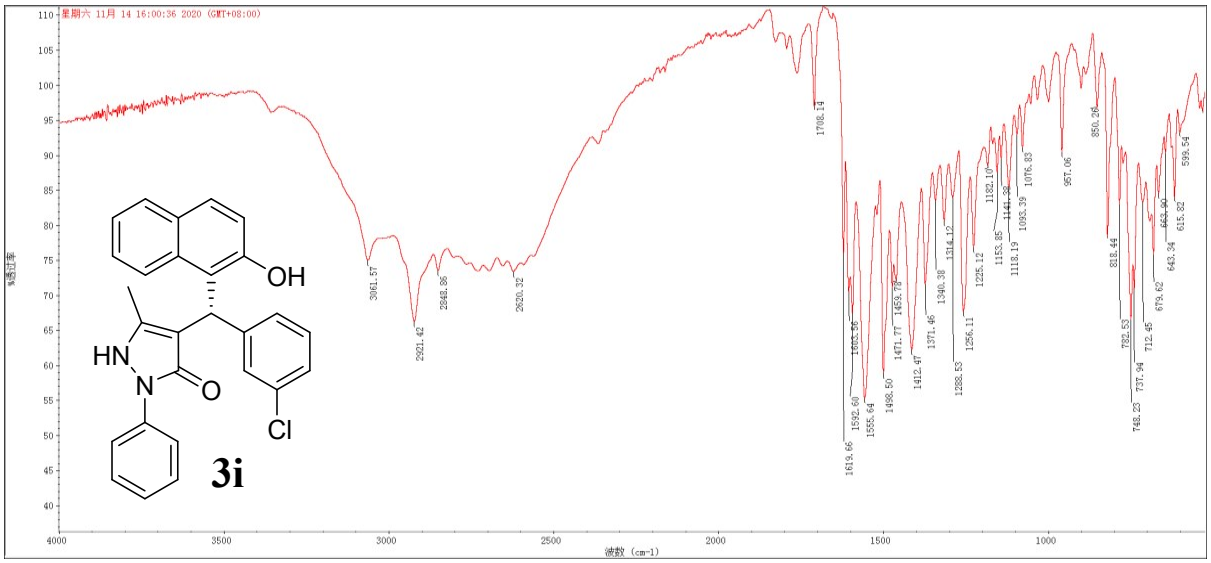


Chemical Formula: $C_{28}H_{25}N_2O_2^+$

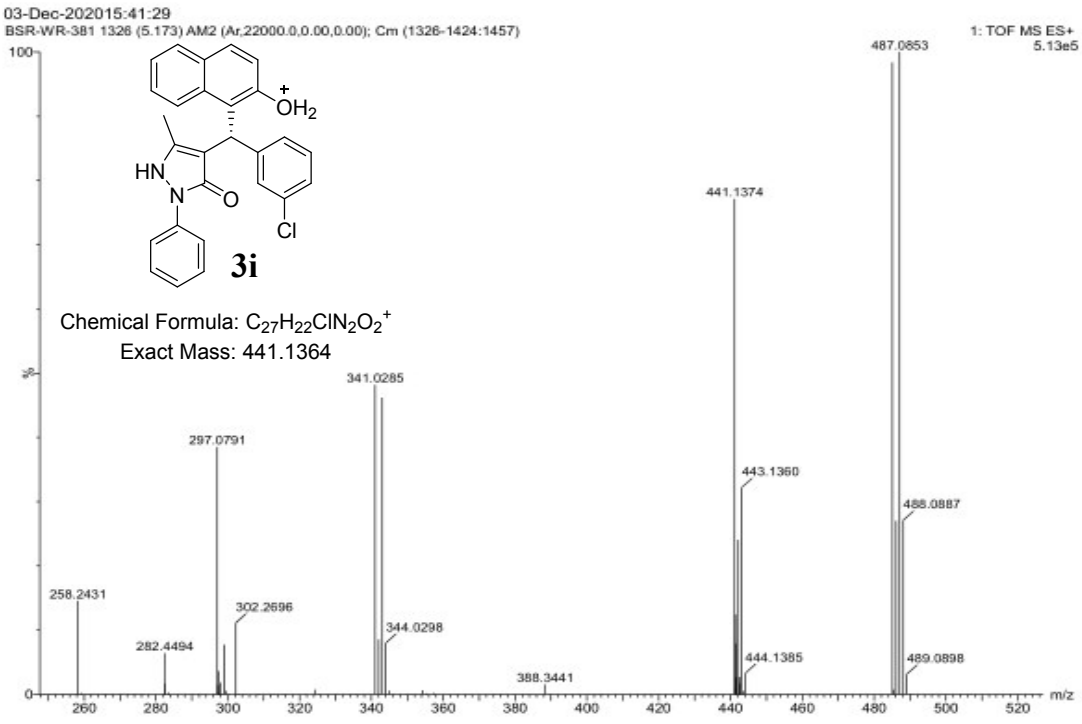
Exact Mass: 421.1911

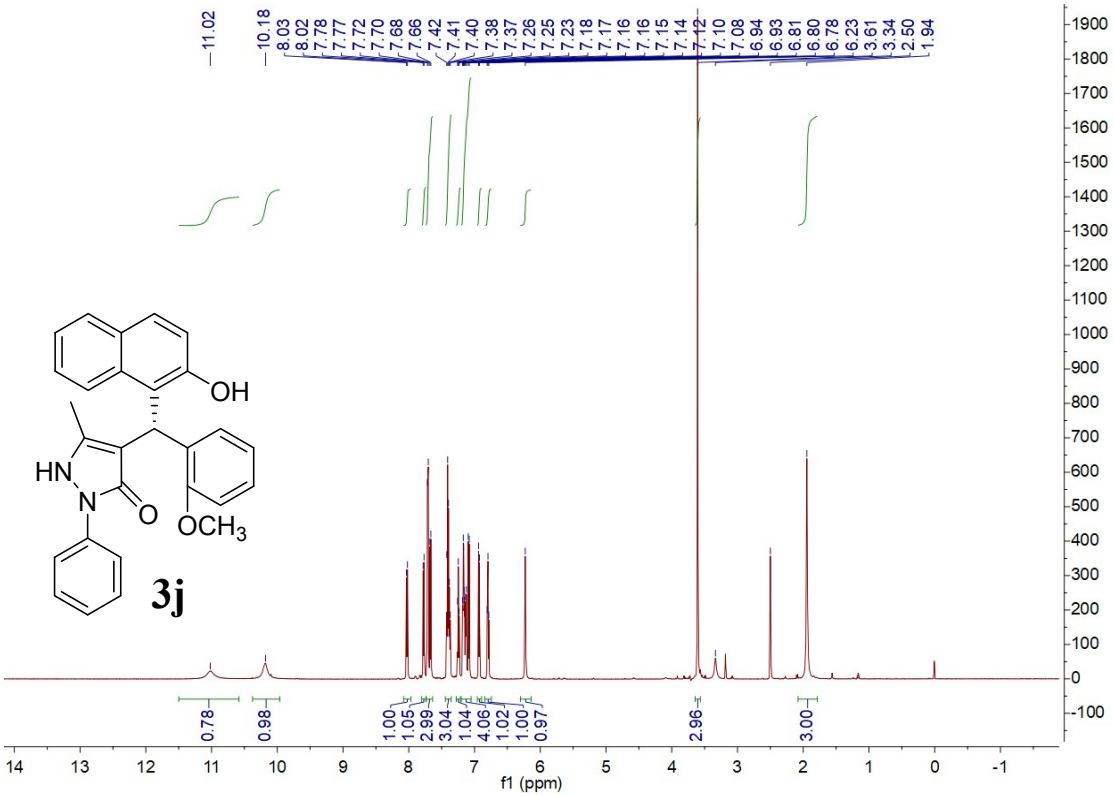

11.68
10.80
8.22
7.83
7.82
7.76
7.75
7.71
7.70
7.46
7.45
7.44
7.43
7.31
7.30
7.29
7.27
7.26
7.25
7.23
7.22
7.21
7.12
7.10
7.05
7.03
6.20
3.32
2.50
2.23
OH
HN
N
O
Cl
3i
0.84
0.91
1.00
1.08
1.09
2.14
3.13
4.11
1.08
2.09
1.07
3.02
f1 (ppm)

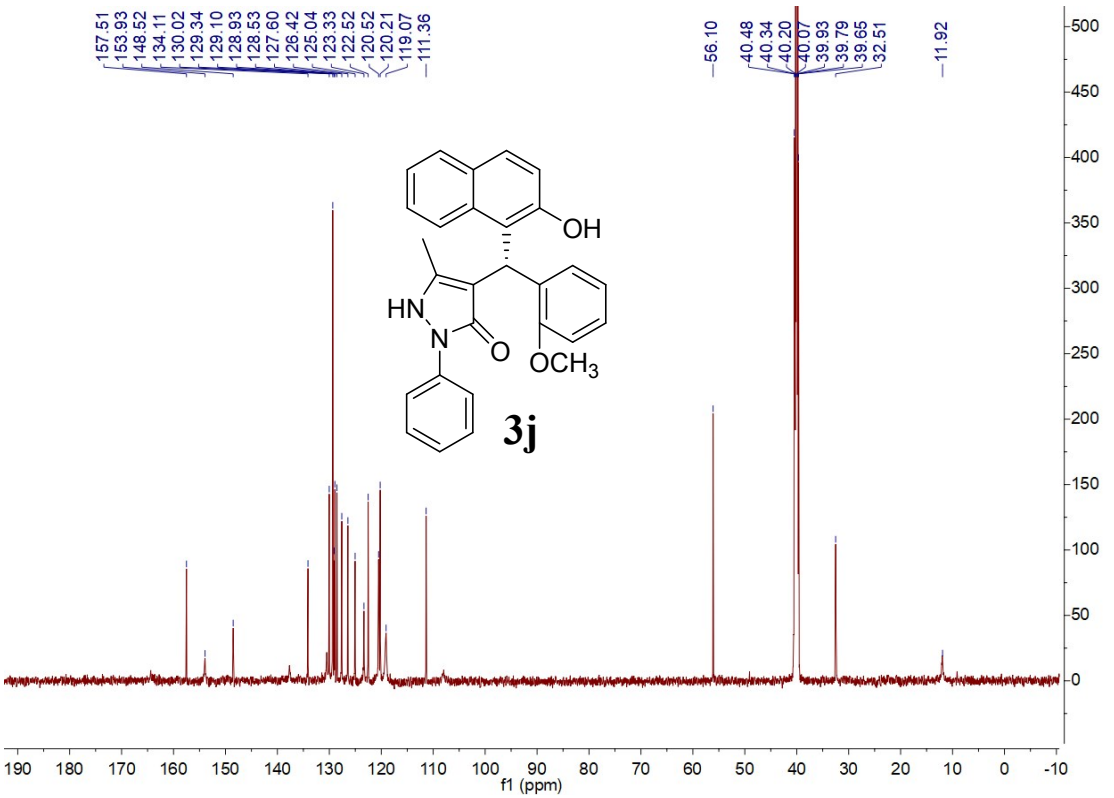

148.67
133.88
133.04
130.09
129.47
129.34
129.17
129.08
127.61
126.86
126.75
125.91
125.74
123.30
122.94
121.38
120.52
119.82
40.48
40.34
40.20
40.06
39.92
39.78
39.64
36.35
11.90
OH
HN
N
O
Cl
3i
f1 (ppm)

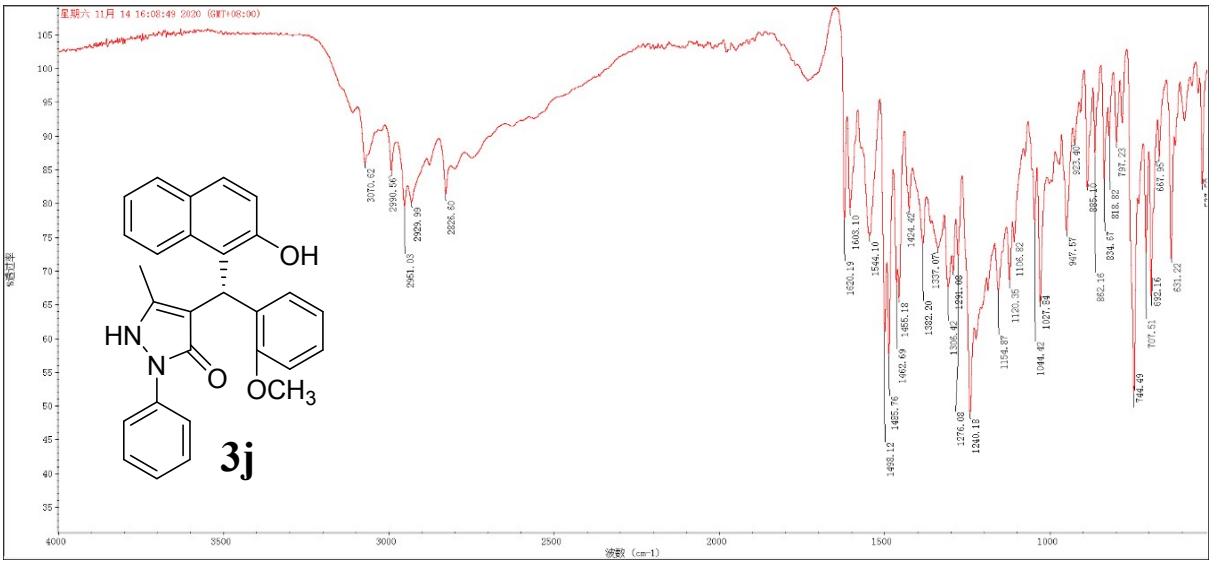

OH
HN
N
O
Cl
3i

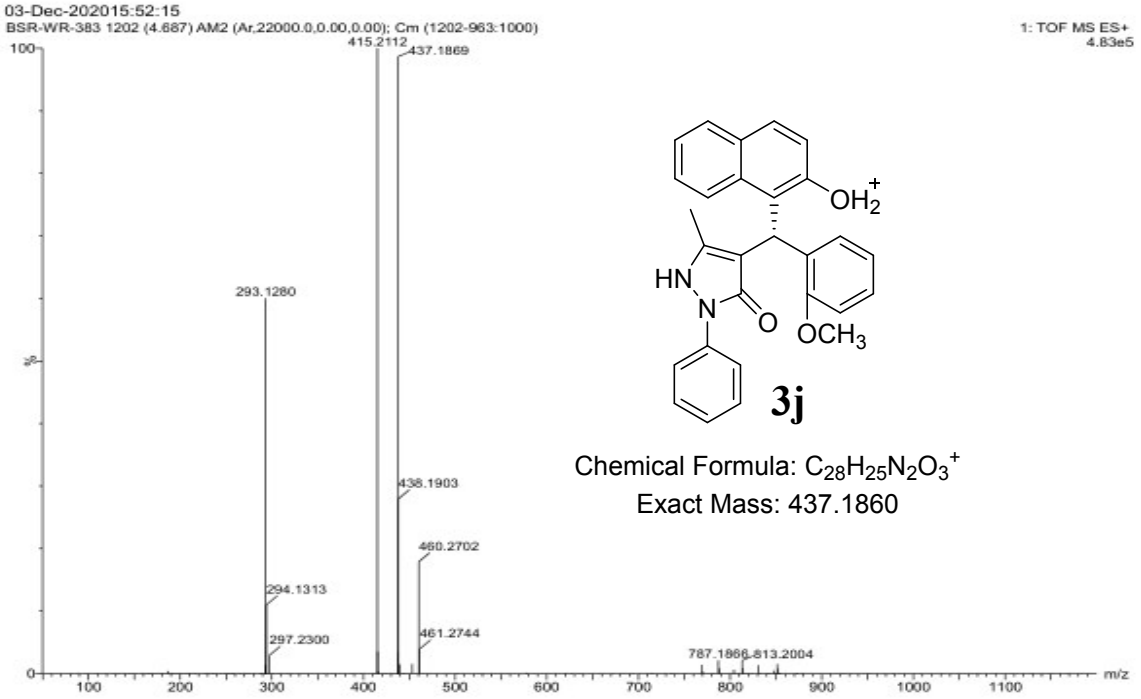
、


03-Dec-202015:41:29
BSR-WR-381 1326 (5.173) AM2 (Ar,22000.0,0.00,0.00); Cm (1326-1424:1457)
1: TOF MS ES+
5.13e5
OH2
HN
N
O
Cl
3i
Chemical Formula: C27H22ClN2O2+
Exact Mass: 441.1364
487.0853
441.1374
443.1360
488.0887
444.1385
489.0898
341.0285
297.0791
258.2431
302.2696
344.0298
282.4494
388.3441
m/z


11.02
10.18
8.03
8.02
7.78
7.77
7.72
7.70
7.68
7.66
7.42
7.41
7.40
7.38
7.37
7.26
7.25
7.23
7.18
7.17
7.16
7.16
7.15
7.14
7.12
7.10
7.08
6.94
6.93
6.81
6.80
6.78
6.23
3.61
3.34
2.50
1.94
OH
HN
N
O
OCH3
3j
0.78
0.98
1.00
1.05
2.99
3.04
1.04
4.06
1.02
1.00
0.97
2.96
3.00
f1 (ppm)

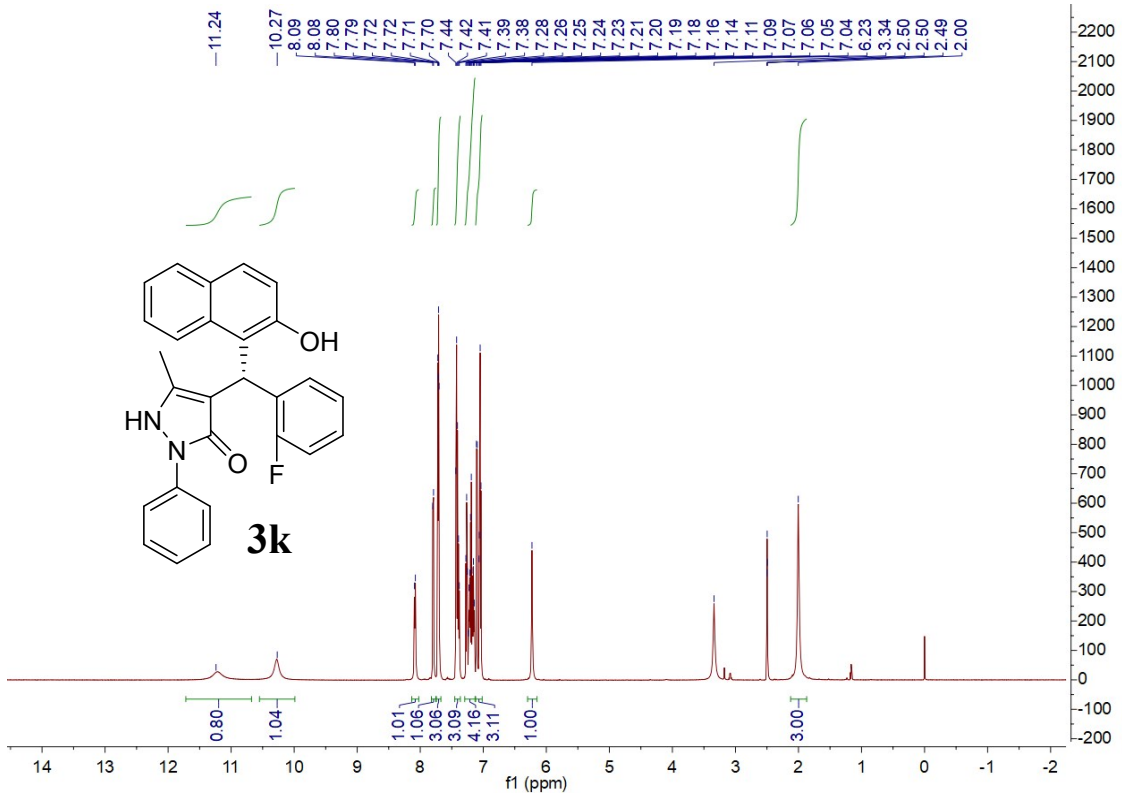

157.51
153.93
148.52
134.11
130.02
129.34
129.10
128.93
128.53
127.60
126.42
125.04
123.33
122.52
120.52
120.21
119.07
111.36
56.10
40.48
40.34
40.20
40.07
39.93
39.79
39.65
32.51
11.92
OH
HN
N
O
OCH3
3j
f1 (ppm)

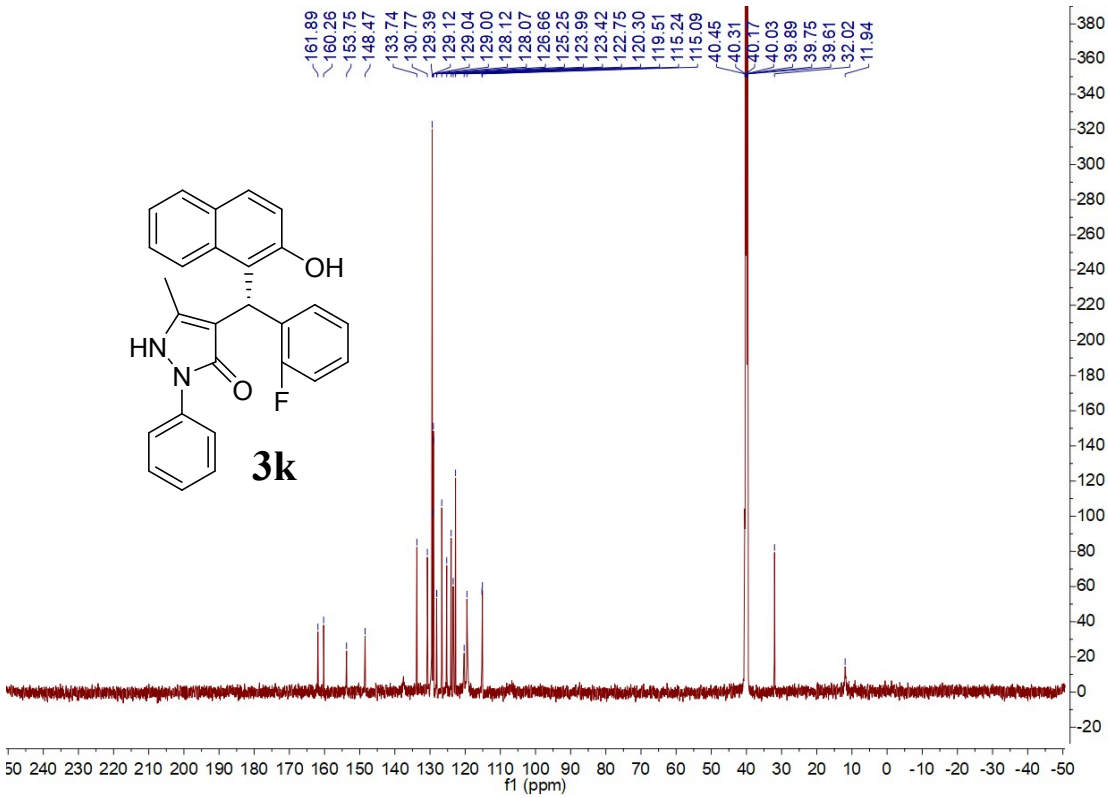


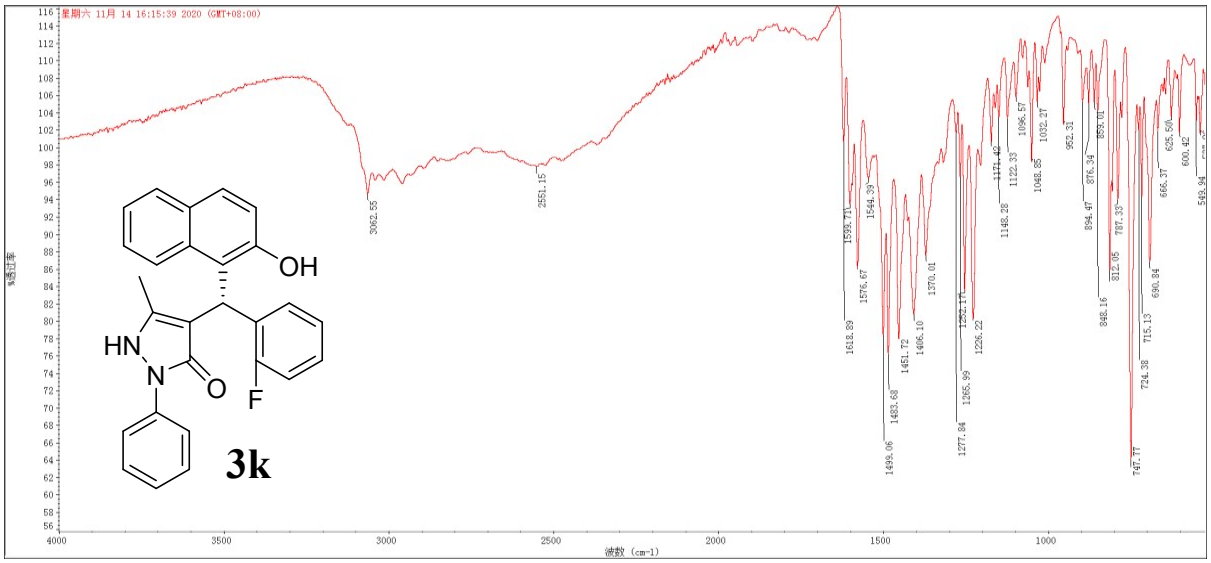


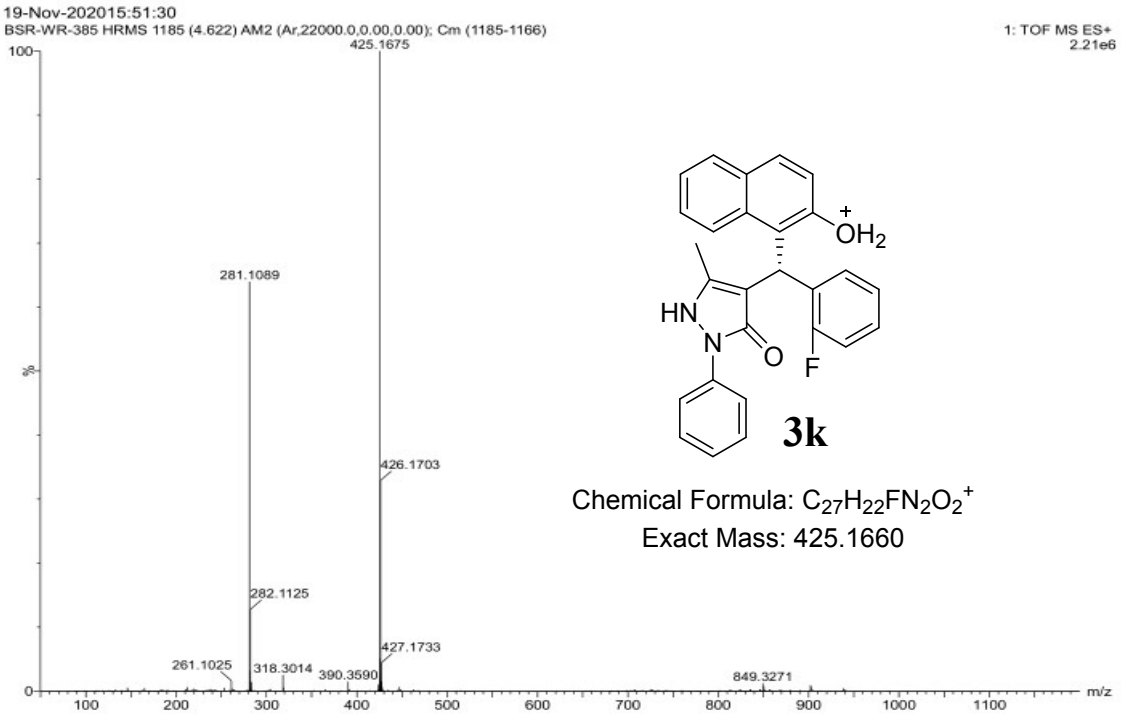
Chemical Formula: $C_{28}H_{25}N_2O_3^+$

Exact Mass: 437.1860


11.24
10.27
8.09
8.08
8.80
7.79
7.72
7.72
7.71
7.70
7.44
7.42
7.41
7.39
7.38
7.28
7.26
7.25
7.24
7.23
7.21
7.20
7.19
7.18
7.16
7.14
7.11
7.09
7.07
7.06
7.05
7.04
6.23
3.34
2.50
2.50
2.49
2.00
OH
HN
N
O
F
3k
0.80
1.04
1.01
1.06
3.06
3.09
4.16
3.11
1.00
3.00
f1 (ppm)

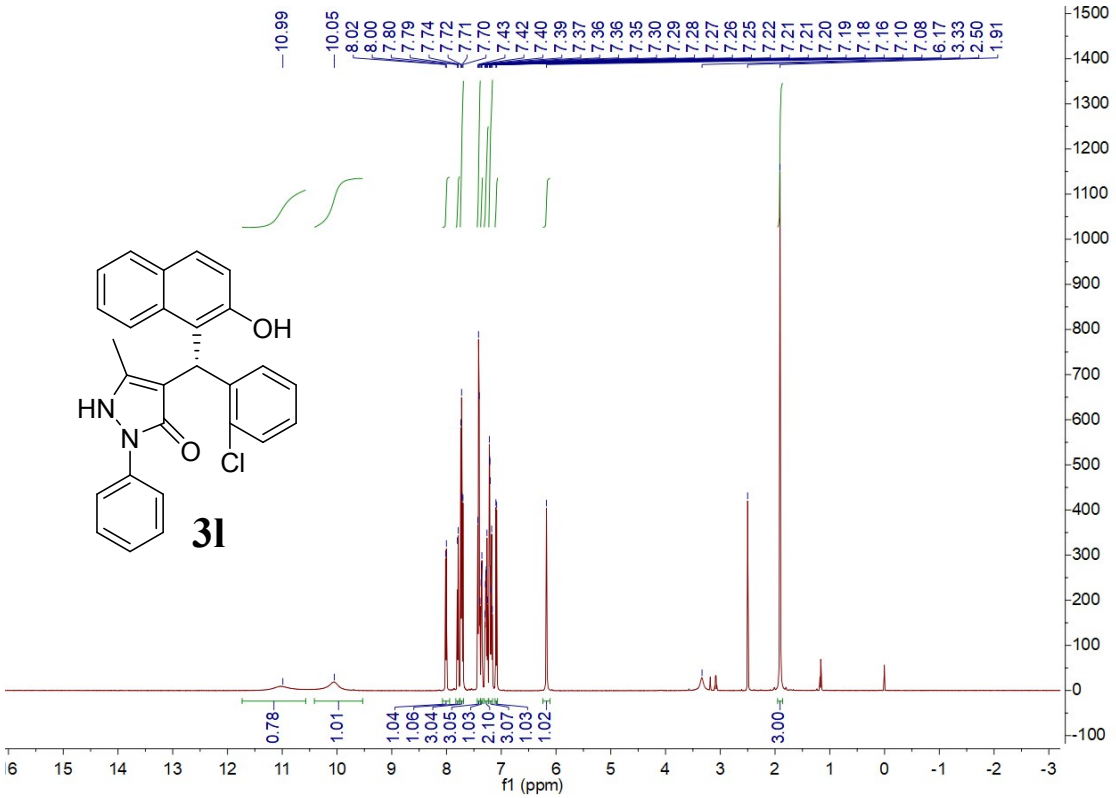

161.89
160.26
153.75
148.47
133.74
130.77
129.39
129.12
129.04
129.00
128.12
128.07
126.66
125.25
123.99
123.42
122.75
120.30
119.51
115.24
115.09
40.45
40.31
40.17
40.03
39.89
39.75
39.61
32.02
11.94
OH
HN
N
O
F
3k
f1 (ppm)





Chemical Formula: $C_{27}H_{22}FN_2O_2^+$

Exact Mass: 425.1660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7.37
7.36
7.36
7.35
7.30
7.29
7.28
7.27
7.26
7.25
7.22
7.21
7.21
7.20
7.19
7.18
7.16
7.10
7.08
6.17
3.33
2.50
1.91
OH
HN
N
O
Cl
3l
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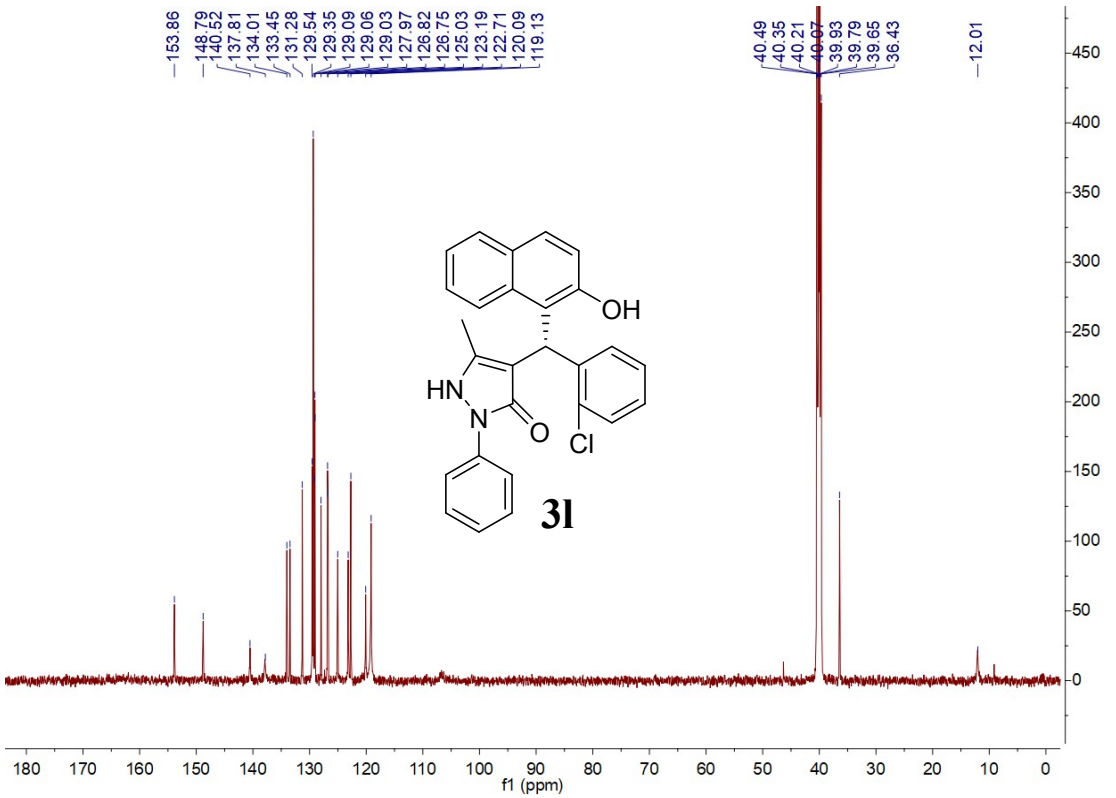
3.00
f1 (ppm)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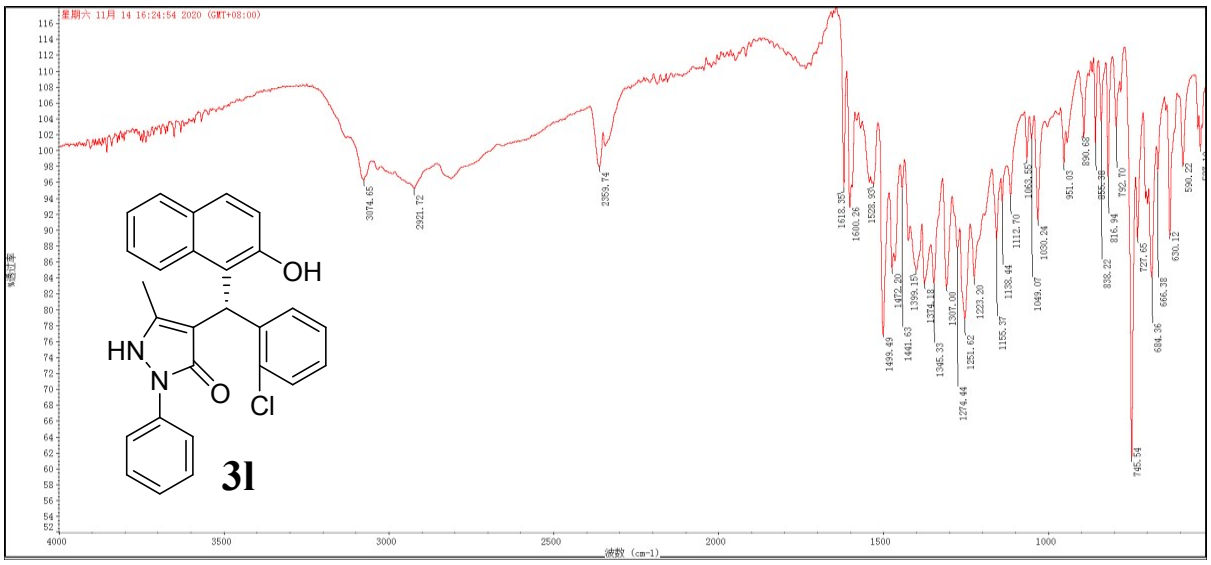
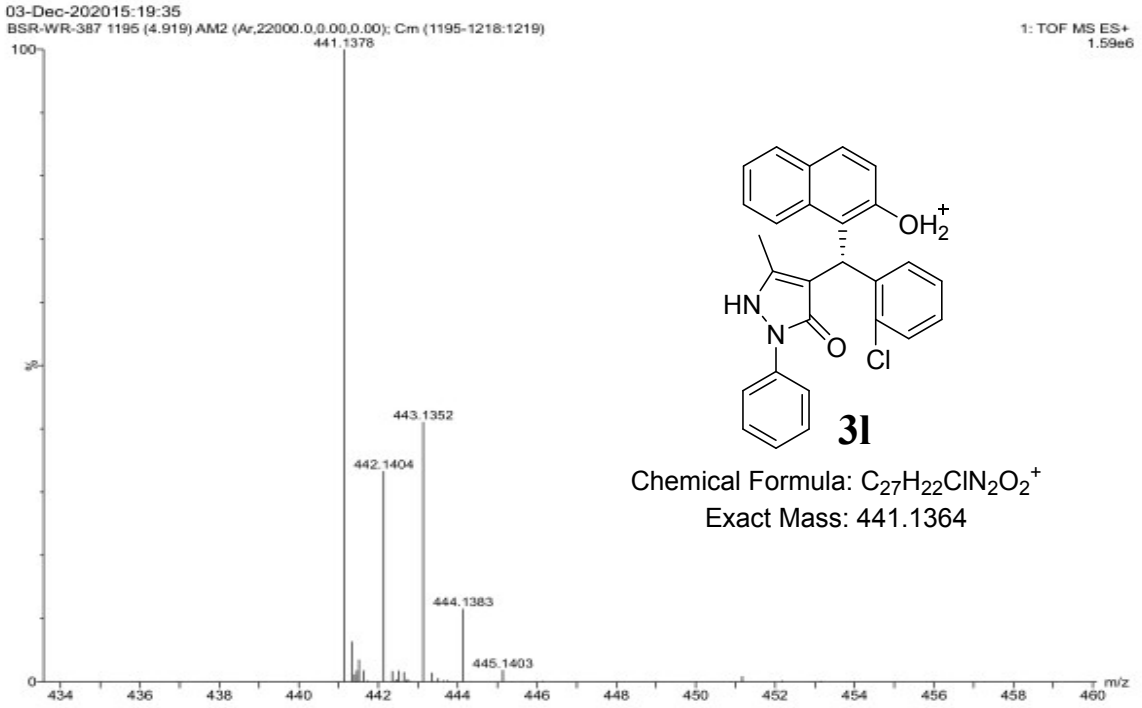
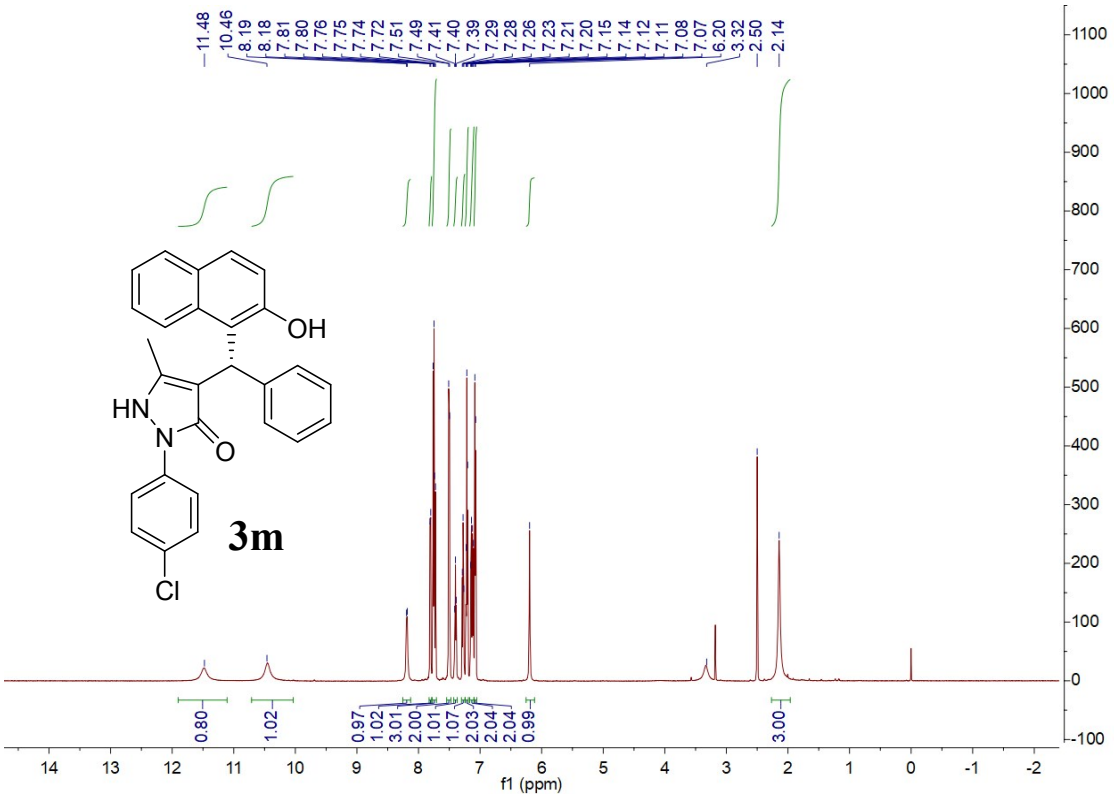
Cl
3l
f1 (ppm)





Chemical Formula: $C_{27}H_{22}ClN_2O_2^+$

Exact Mass: 441.1364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7.80
7.76
7.75
7.74
7.72
7.51
7.49
7.41
7.40
7.39
7.29
7.28
7.26
7.23
7.21
7.20
7.15
7.14
7.12
7.11
7.08
7.07
6.20
3.32
2.50
2.14
OH
HN
N
O
Cl
3m
0.80
1.02
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2.04
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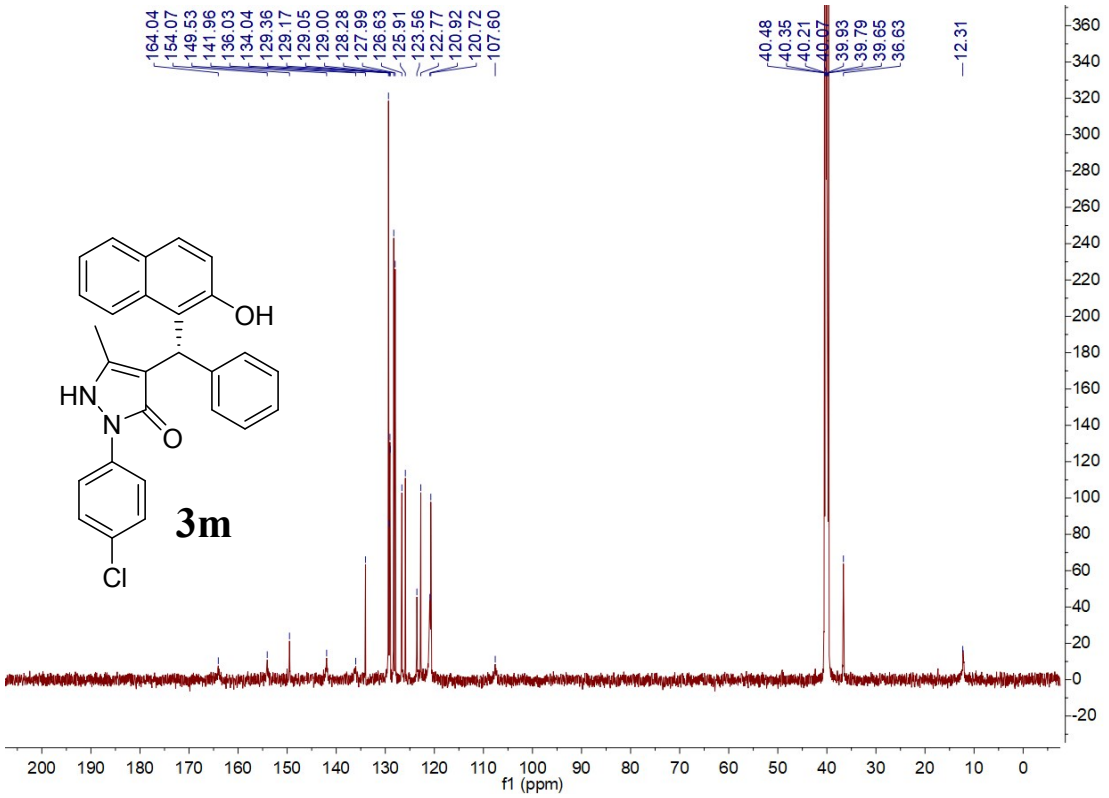
3.00
f1 (ppm)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107.60
40.48
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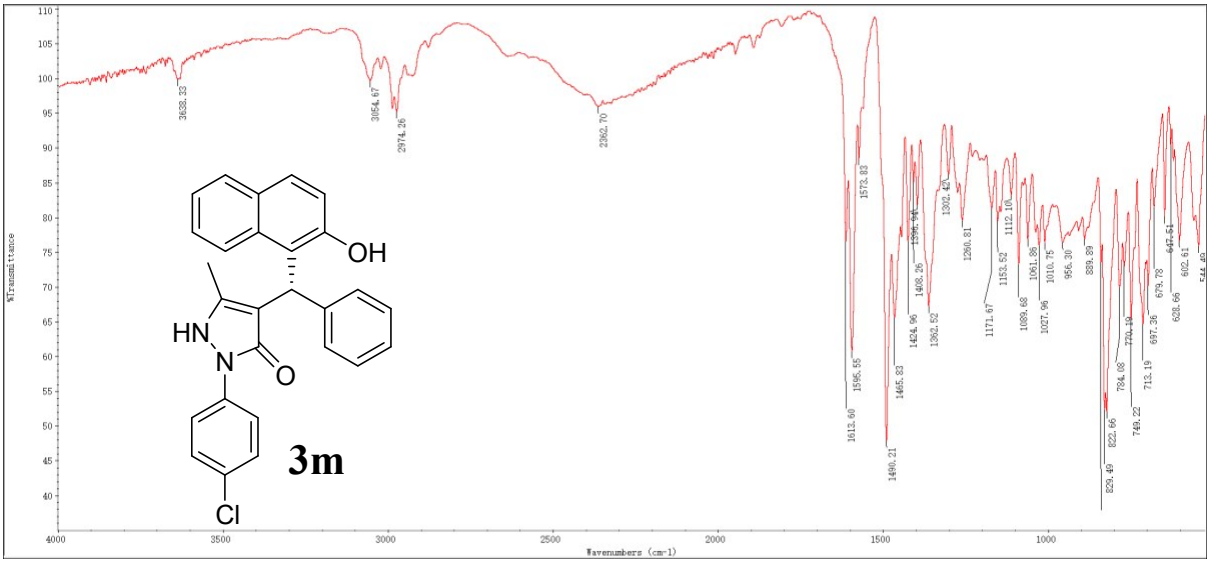
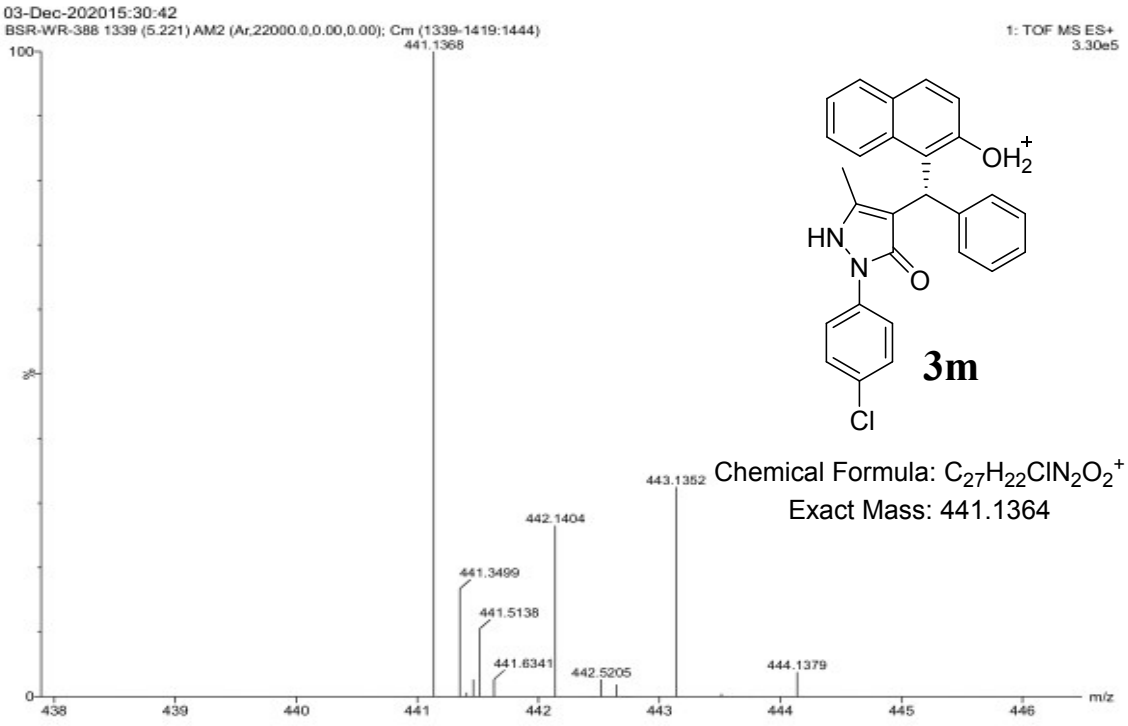
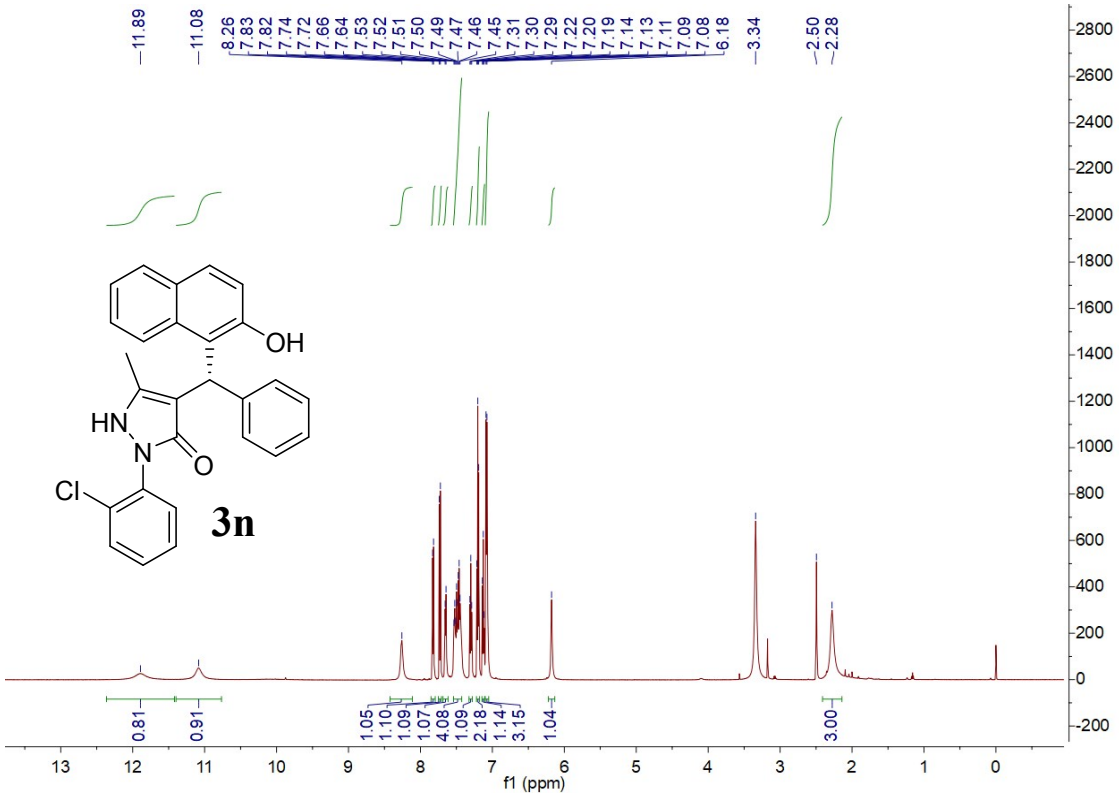
3m
f1 (ppm)





Chemical Formula: $C_{27}H_{22}ClN_2O_2^+$

Exact Mass: 441.1364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7.47
7.46
7.45
7.31
7.30
7.29
7.22
7.20
7.19
7.14
7.13
7.11
7.09
7.08
6.18
3.34
2.50
2.28
OH
HN
N
O
Cl
3n
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0.91
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1.10
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1.07
4.08
1.09
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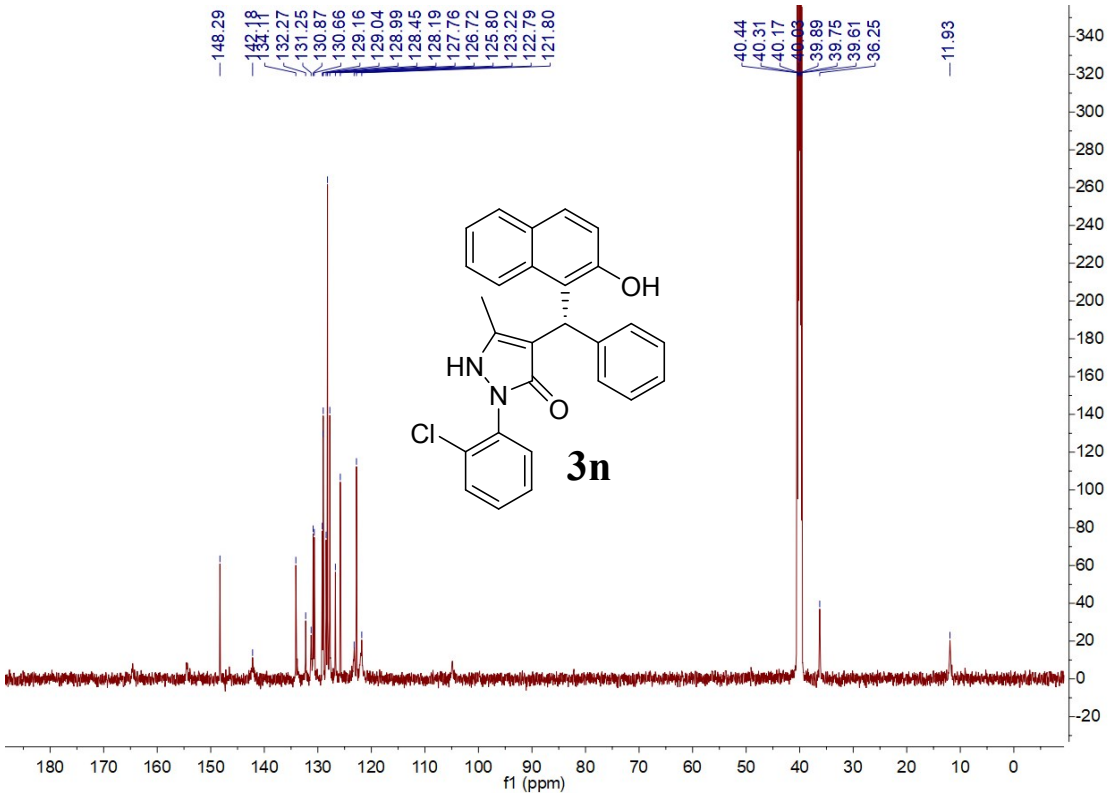
3.15
1.04
3.00
f1 (ppm)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121.80
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40.31
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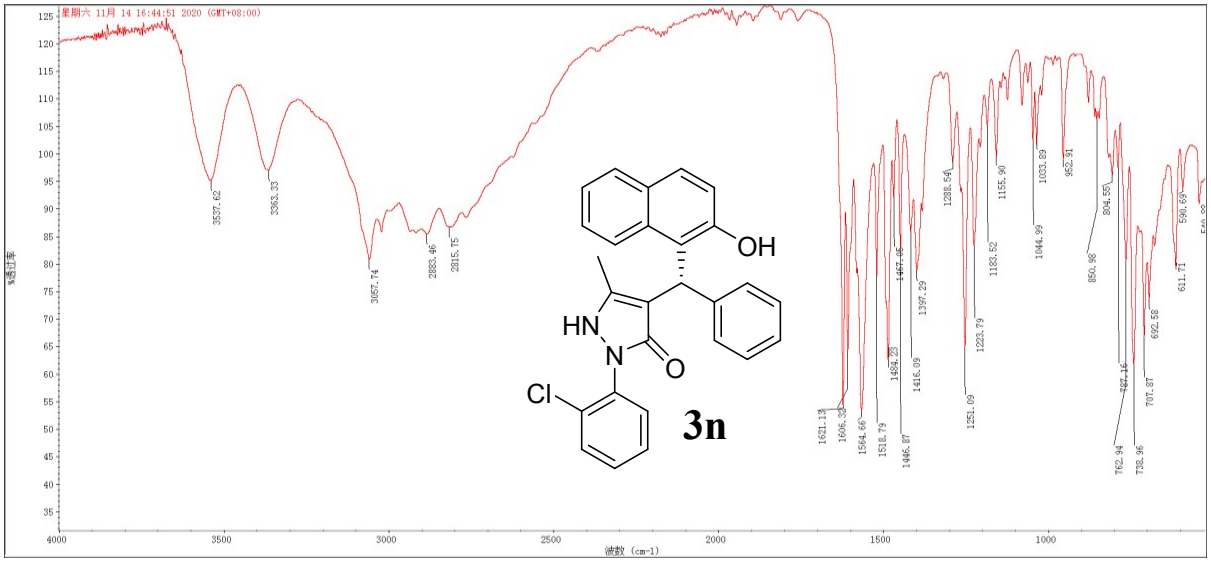
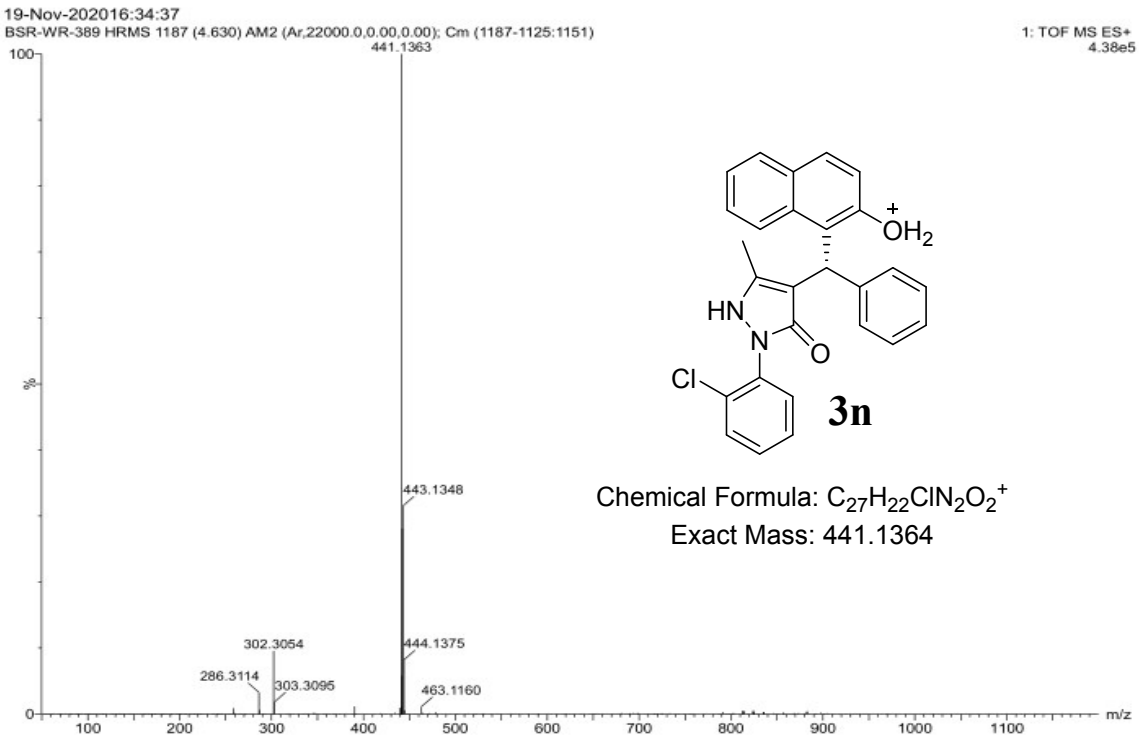
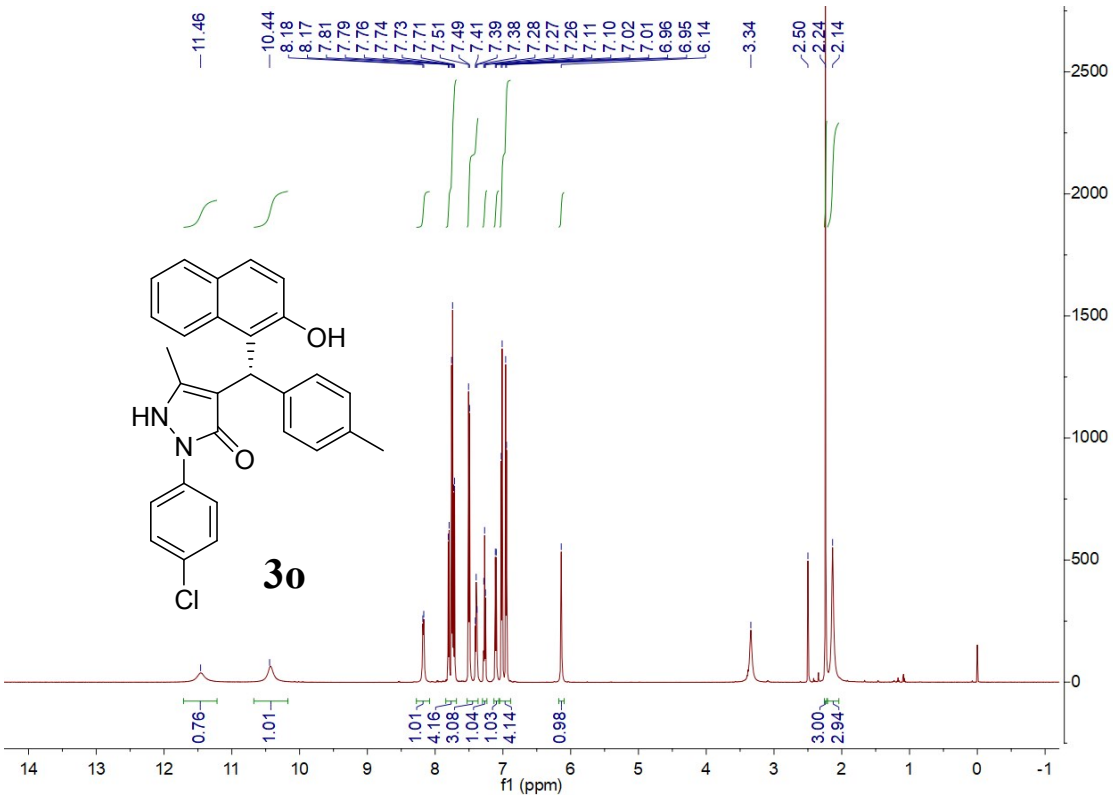
OH
HN
N
O
Cl
3n
f1 (ppm)





Chemical Formula: $C_{27}H_{22}ClN_2O_2^+$

Exact Mass: 441.1364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10.44
8.18
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7.81
7.79
7.76
7.74
7.73
7.71
7.51
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7.38
7.28
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7.26
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HN
N
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Cl
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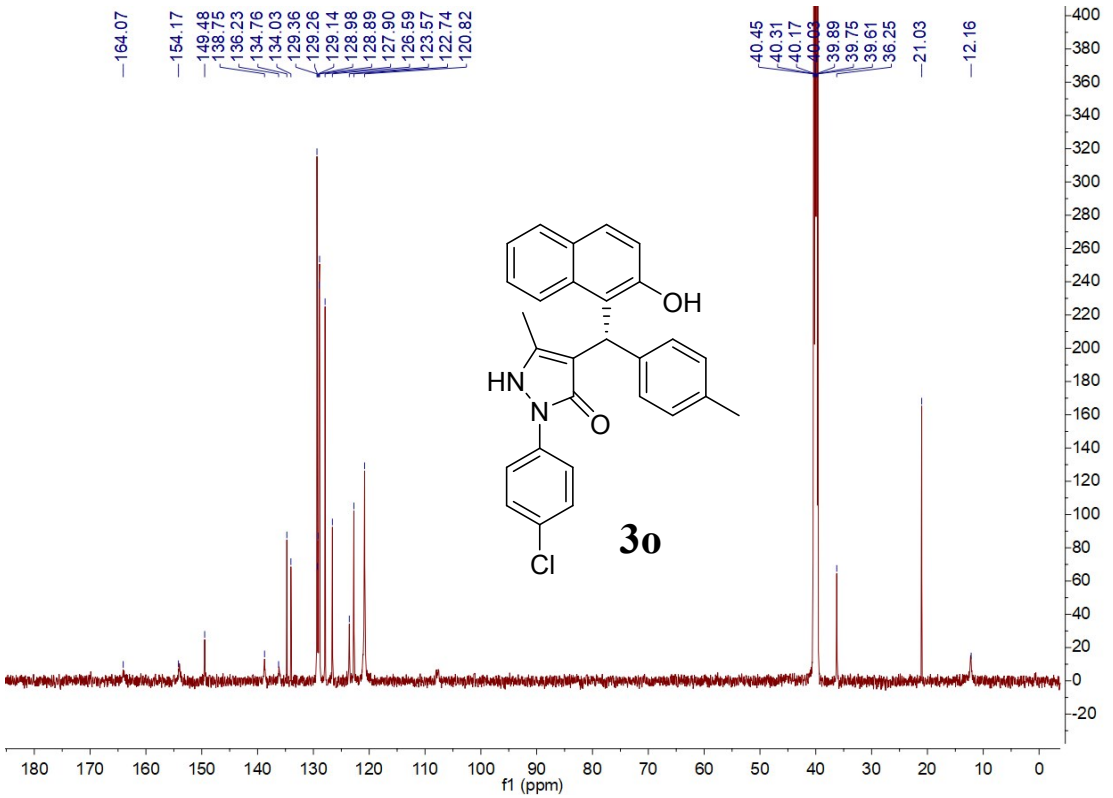
f1 (ppm)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HN
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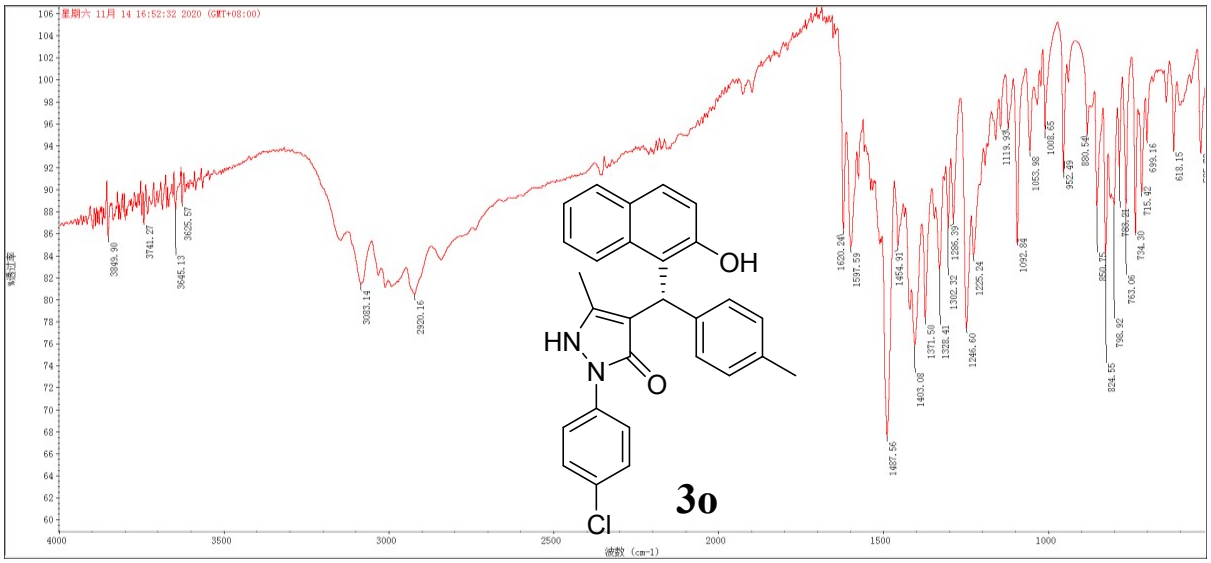
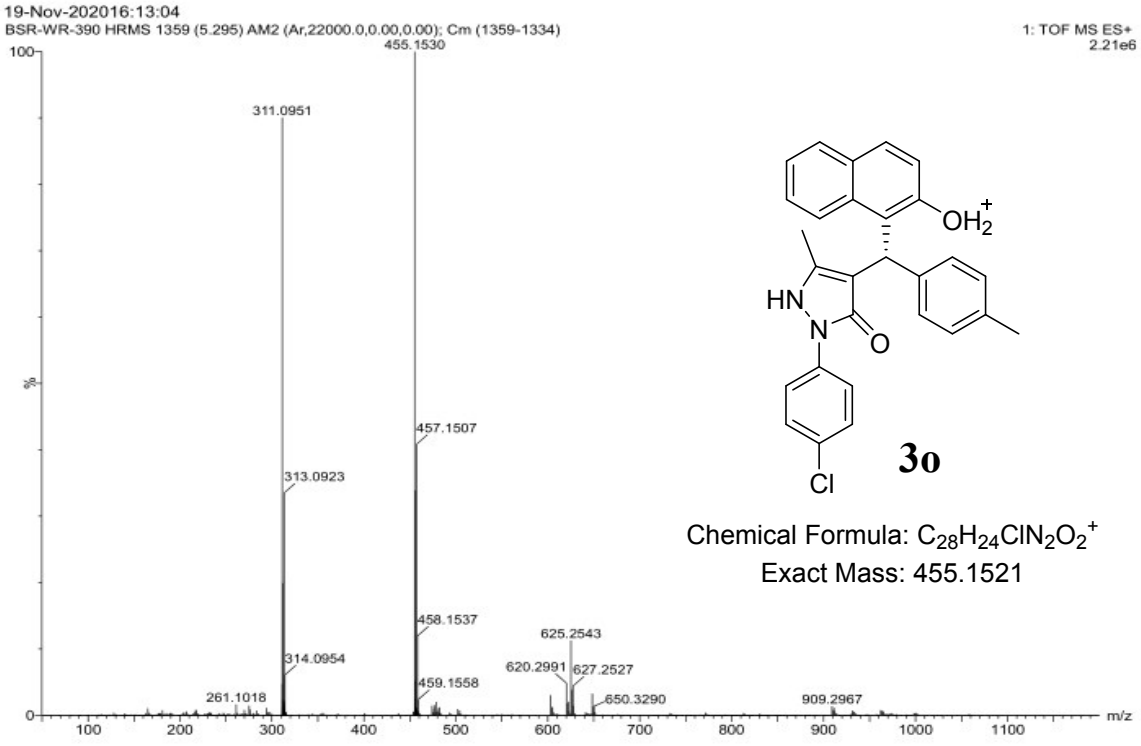
O
Cl
3o
f1 (ppm)

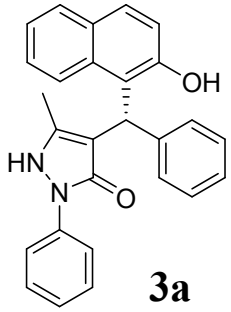




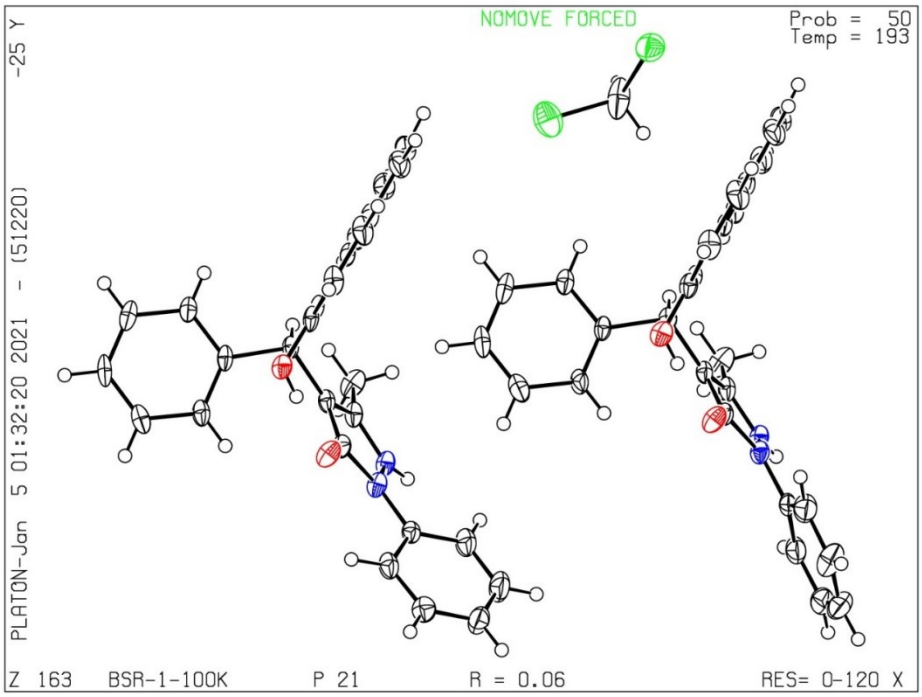
Chemical Formula: $C_{28}H_{24}ClN_2O_2^+$

Exact Mass: 455.1521

Crystallographic data for 3a



3a



CheckCIF/PLATON report

Structure factors have been supplied for datablock(s) BSR-1-100K

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: BSR-1-100K

Bond precision: C-C = 0.0050 A Wavelength=1.54178

Cell:	a=15.2574(2)	b=8.0550(1)	c=18.4264(4)
	alpha=90	beta=96.396(2)	gamma=90
Temperature:	193 K		

Calculated	Reported Volume 2250.48(6)	2250.48(6)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	2(C27 H22 N2 O2), C H2 Cl22(C27 H22 N2 O2), C H2 Cl2	
Sum formula	C55 H46 Cl2 N4 O4	C55 H46 Cl2 N4 O4
Mr	897.86	897.86
Dx,g cm-3	1.325	1.325
Z	2	2
Mu (mm-1)	1.721	1.721
F000	940.0	940.0
F000'	943.96	
h,k,lmax	19,10,23	19,10,23
Nref	9385[5041]	8936
Tmin,Tmax	0.940,0.966	0.996,0.998
Tmin'	0.857	

Correction method= # Reported T Limits: Tmin=0.996 Tmax=0.998 AbsCorr = MULTI-SCAN

Data completeness= 1.77/0.95 Theta(max)= 75.962 R(reflections)= 0.0613(7555) wR2(reflections)= 0.1680(8936)
S = 1.082 Npar= 586

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for mre details of the test.

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.18 Report PLAT112_ALERT_2_C ADDSYM Detects New (Pseudo) Symm. Elem C 87 %Fit
PLAT230_ALERT_2_C Hirshfeld Test Diff for C21A --C22A . 5.5 s.u.
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.2 Note PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.2 Note PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00498 Ang. PLAT410_ALERT_2_C Short Intra H...H Contact H1AB ..H11B . 1.92 Ang.
x,y,z = 1_555 Check
PLAT410_ALERT_2_C Short Intra H...H Contact H1BB ..H11A . 1.93 Ang.
x,y,z = 1_555 Check
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1 Note
C27 H22 N2 O2
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.382 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 16 Report
PLAT987_ALERT_1_C The Flack x is >> 0 - Do a BASF/TWIN Refinement Please Check

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 4 Report
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero . 0.037 Note
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C27A Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C27B Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 14 Note
PLAT791_ALERT_4_G Model has Chirality at C11A (Sohnke SpGr) S Verify
PLAT791_ALERT_4_G Model has Chirality at C11B (Sohnke SpGr) S Verify
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 86 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 26 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..... 4.9 Low
PLAT953_ALERT_1_G Reported (CIF) and Actual (FCF) Hmax Differ by . 1 Units
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 0 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
12 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
14 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
10 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
8 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

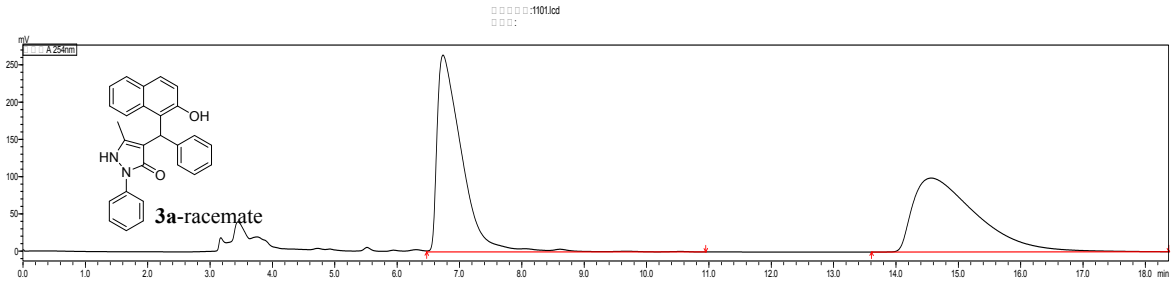
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/12/2020; check.def file version of 05/12/2020

Copies of HPLC profiles of 3



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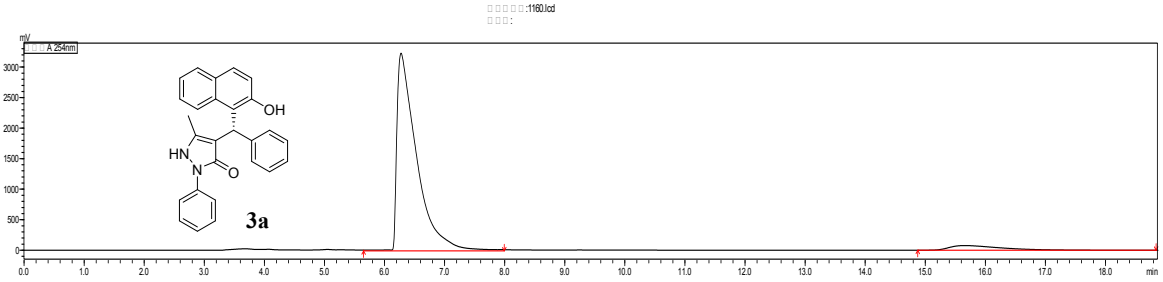

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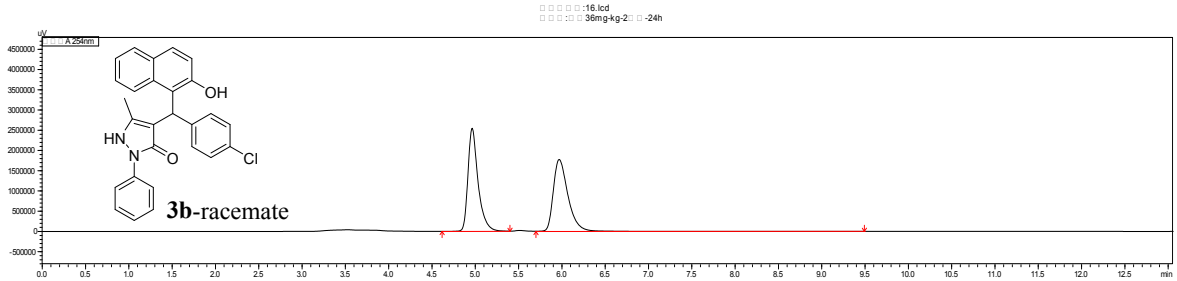

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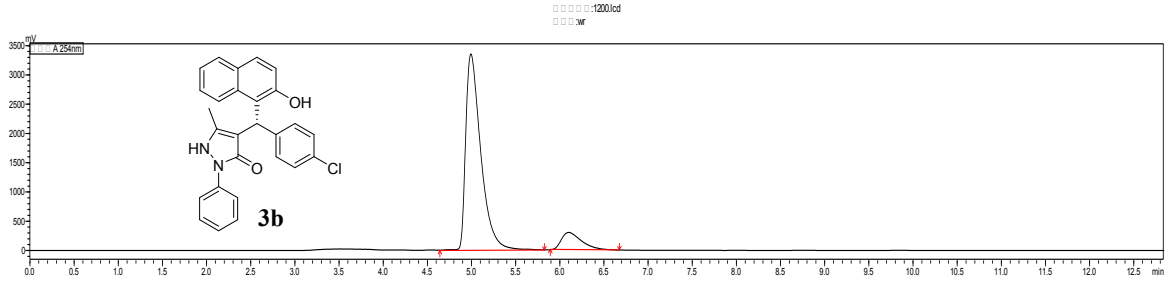

NO.	Name	Time（min）	Area	Height	Area%
1	-	4.993	39955703	3357332	89.720
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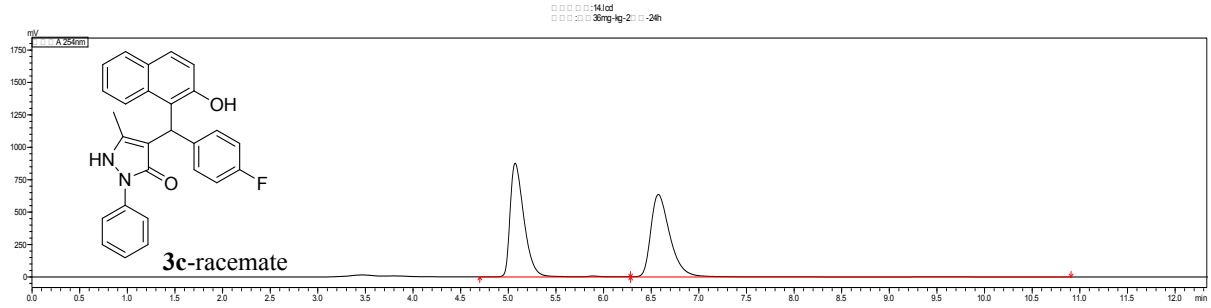

NO.	Name	Time（min）	Area	Height	Area%
1	-	5.072	8941173	876840	49.952
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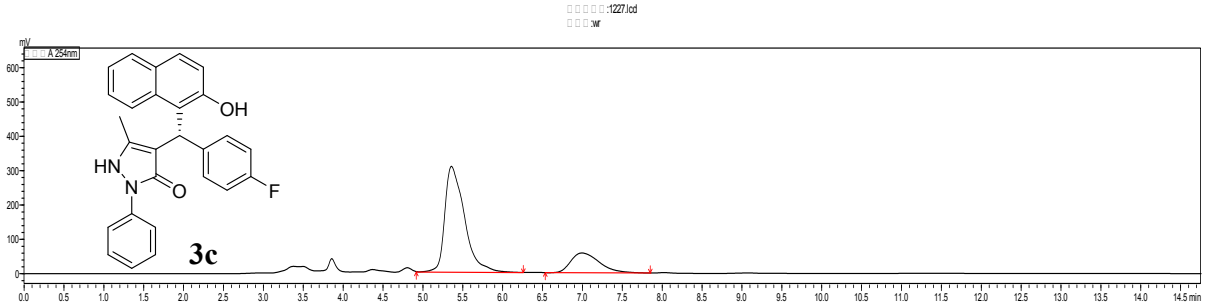

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1	-	5.357	5291464	308231	78.828
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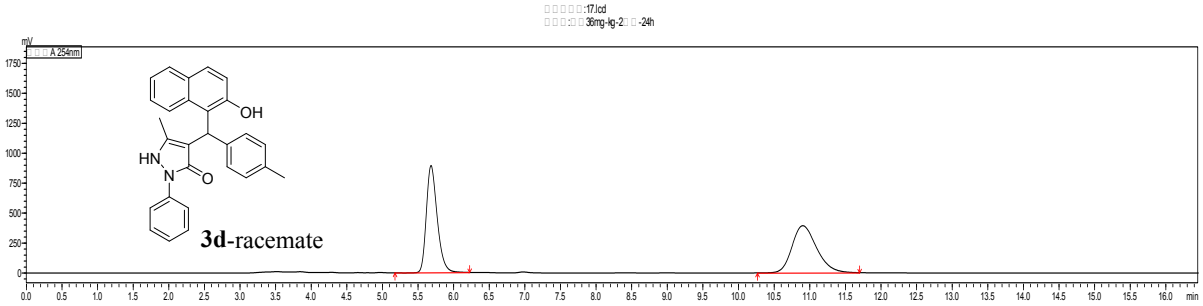

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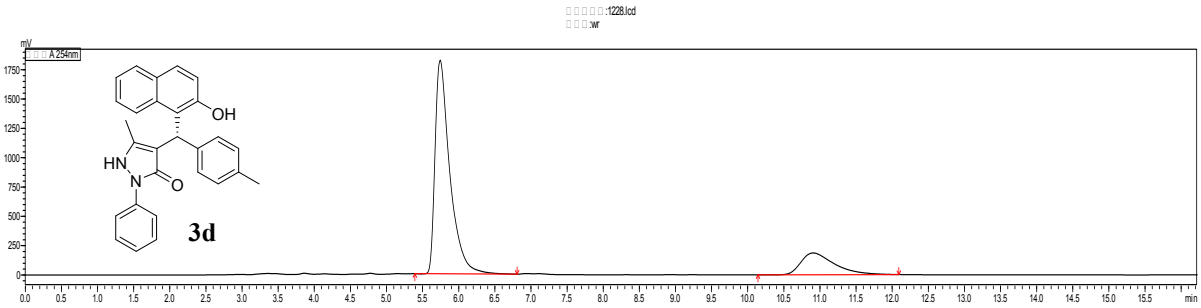

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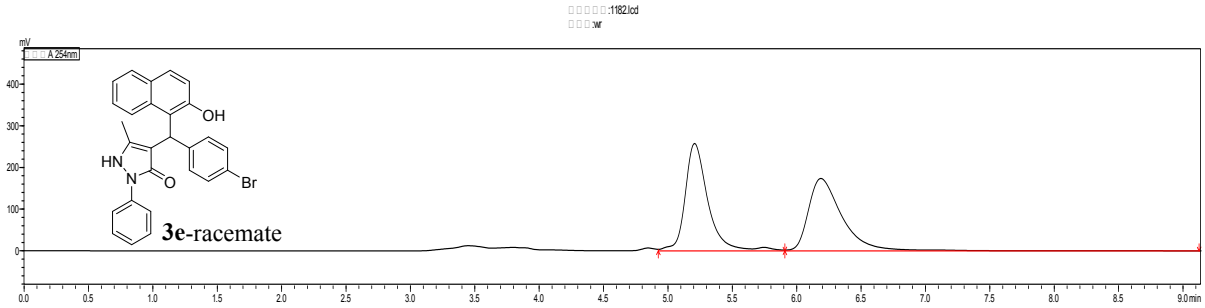

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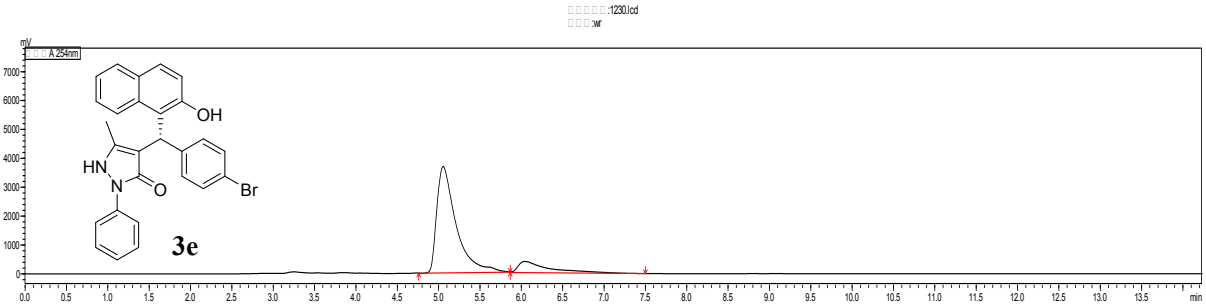
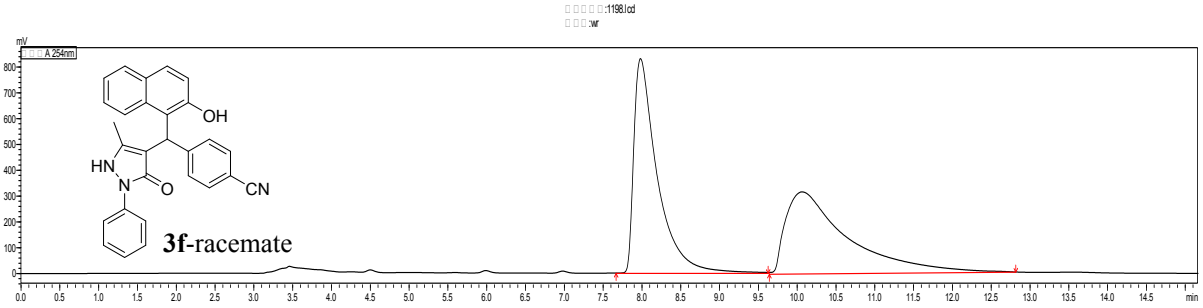
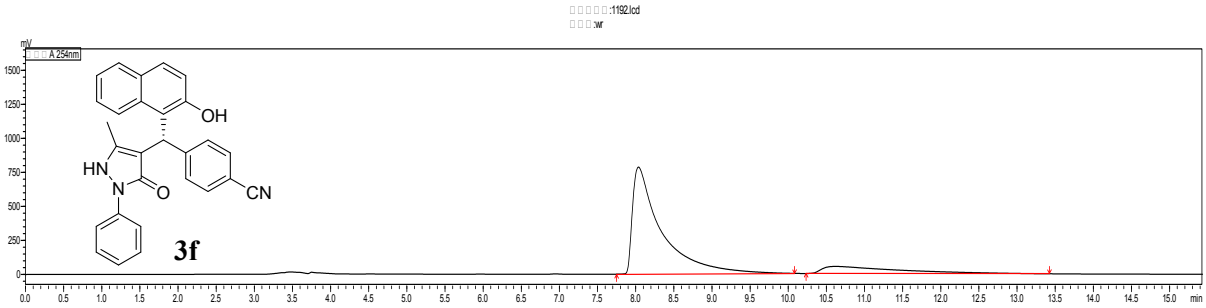
1	-	5.207	3187954	257915	50.012
2	-	6.188	3186456	173630	49.988



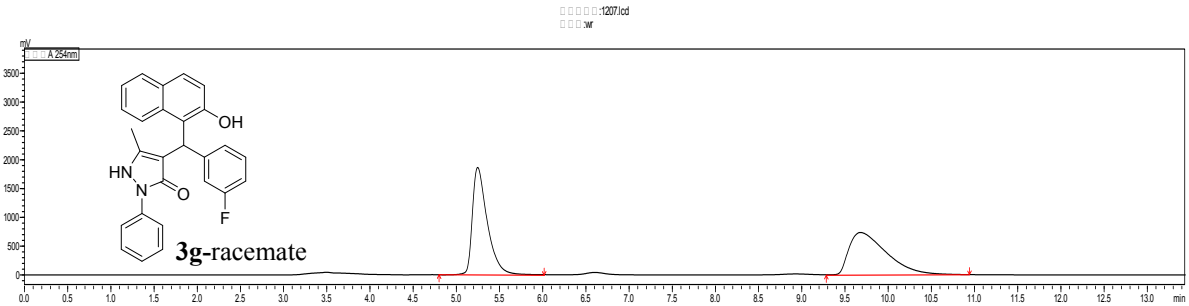
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.055	60187560	3688889	85.917
2	-	6.044	9865434	384553	14.083



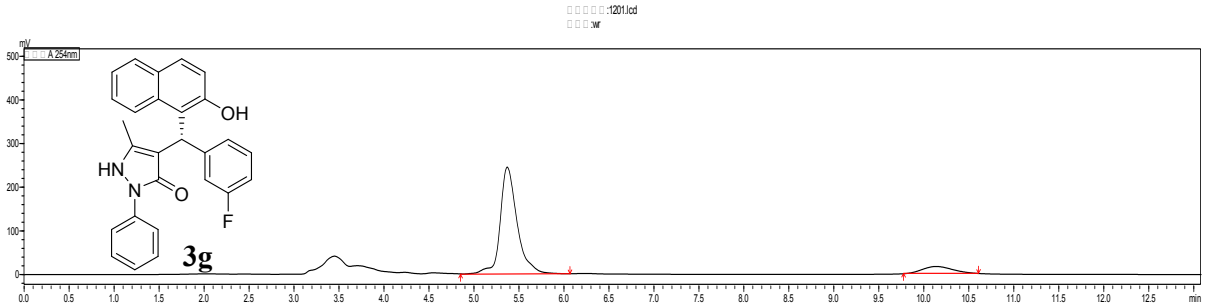
NO.	Name	Time（min）	Area	Height	Area%
1	-	8.516	23960740	847100	49.679
2	-	10.610	24270124	503699	50.321



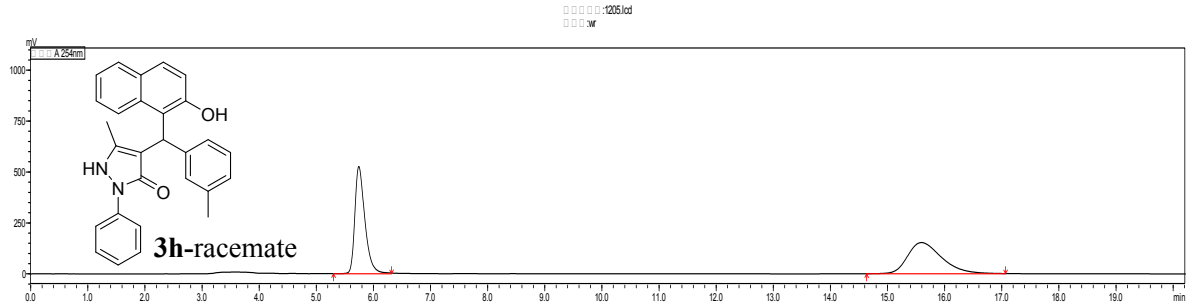
NO.	Name	Time（min）	Area	Height	Area%
1	-	8.402	34137966	1080758	86.884
2	-	10.812	5153632	123425	13.116



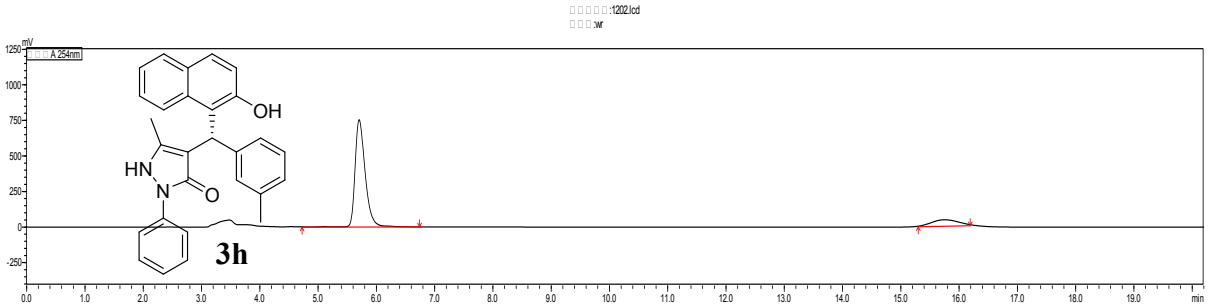
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.247	22714744	1866252	50.059
2	-	9.681	22660952	741360	49.941



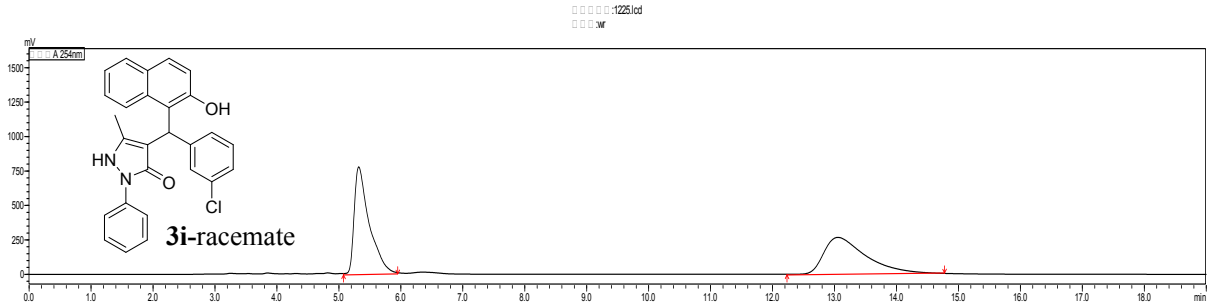
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.370	3210363	244750	89.819
2	-	10.137	363910	15892	10.181



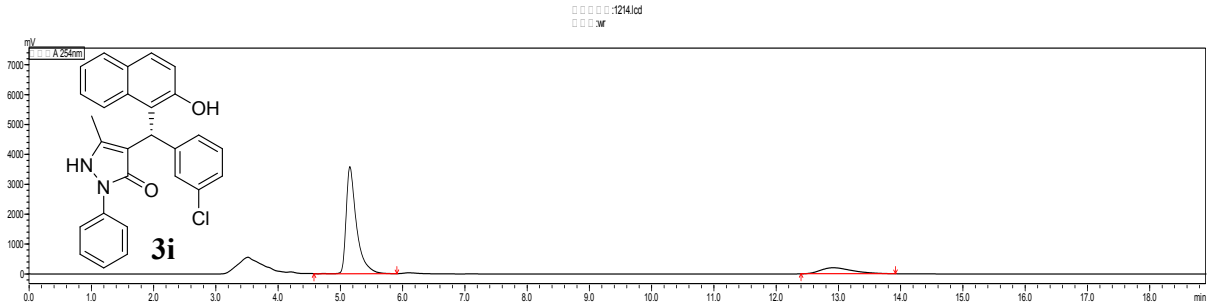
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.744	6487014	527170	50.304
2	-	15.595	6408700	153149	49.696



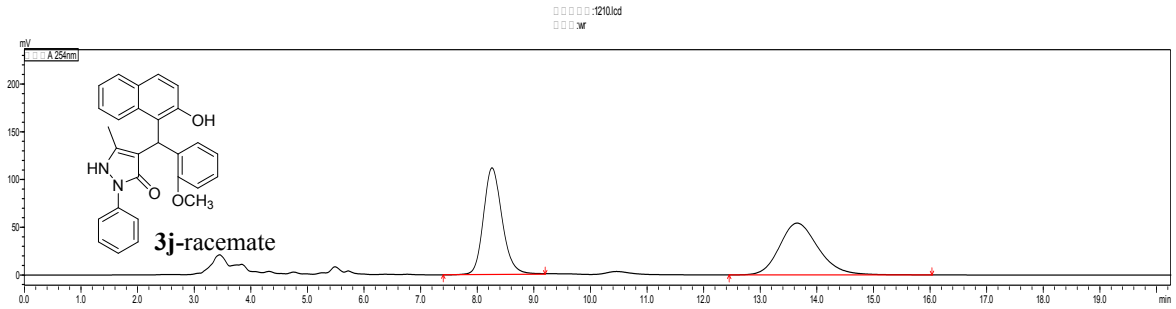
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.705	9041838	753847	82.913
2	-	15.754	1863319	50023	17.087



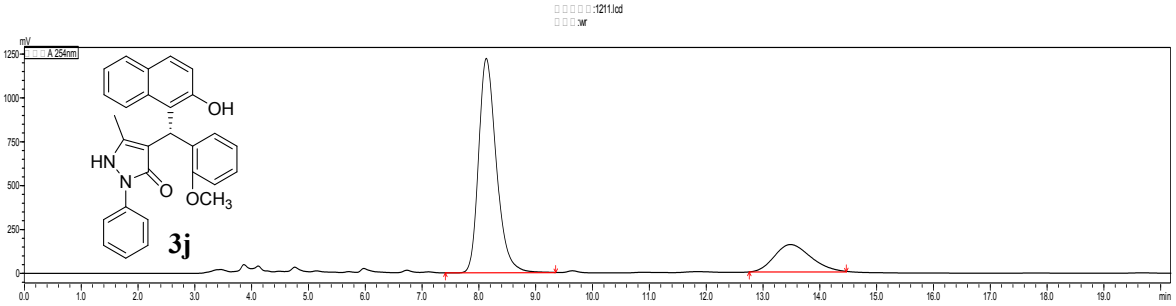
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.320	13309660	781971	51.317
2	-	13.055	12626704	267767	48.683



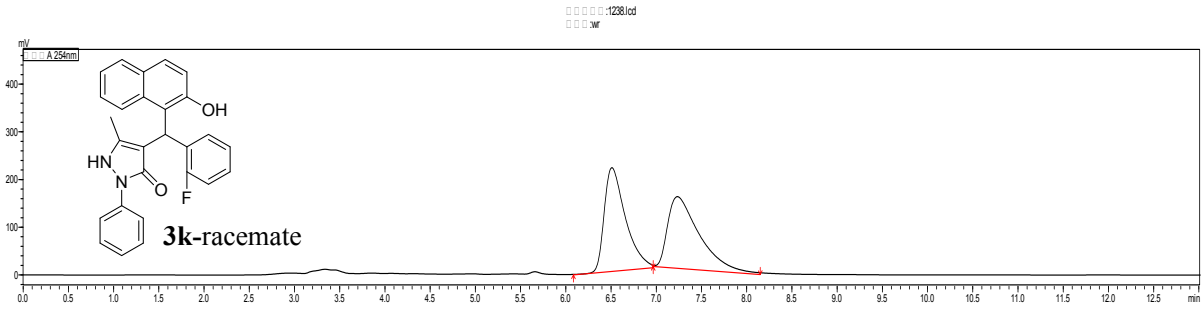
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.152	41308934	3590356	85.913
2	-	12.917	6773142	197403	14.087



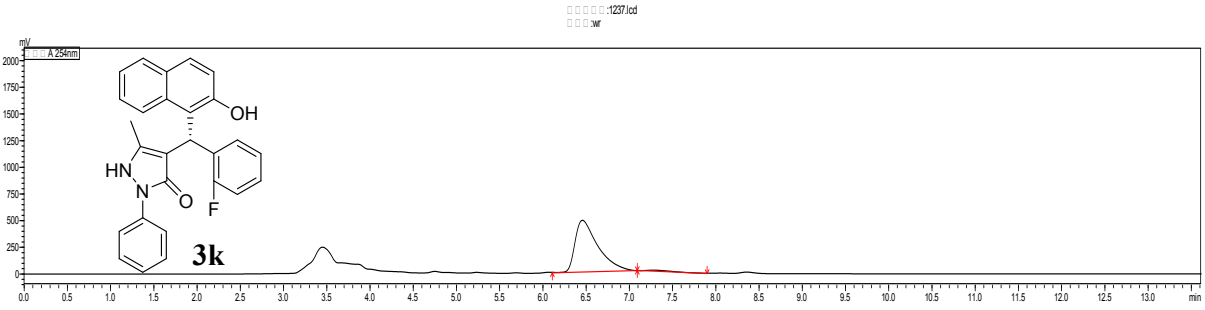
NO.	Name	Time（min）	Area	Height	Area%
1	-	8.261	2554447	111619	49.706
2	-	13.651	2584691	54265	50.294



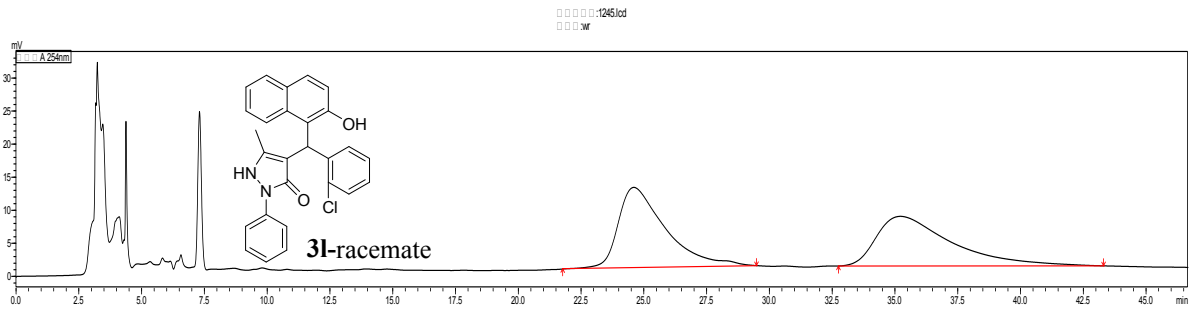
NO.	Name	Time（min）	Area	Height	Area%
1	-	8.130	26491829	1221438	78.933
2	-	13.484	7070525	156902	21.067



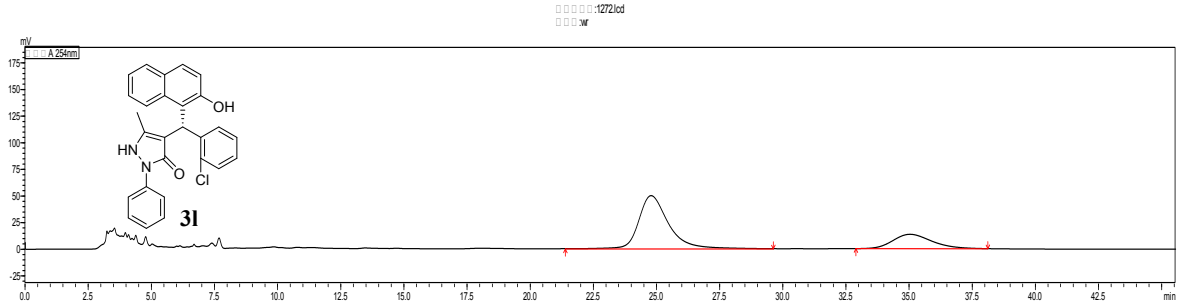
NO.	Name	Time（min）	Area	Height	Area%
1	-	6.509	3566888	217590	49.209
2	-	7.234	3681568	150240	50.791



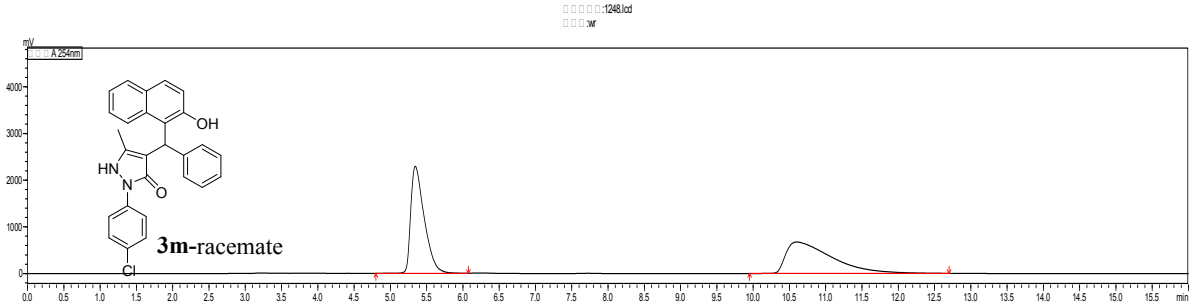
NO.	Name	Time（min）	Area	Height	Area%
1	-	6.457	8929279	485506	98.067
2	-	7.279	175974	8582	1.933



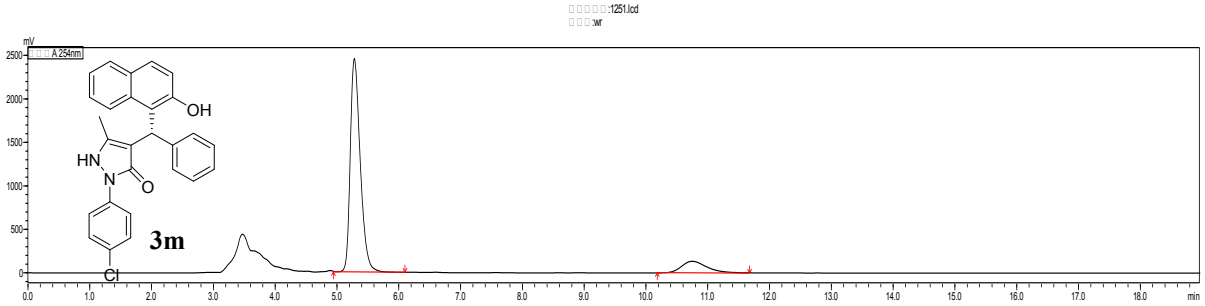
NO.	Name	Time（min）	Area	Height	Area%
1	-	24.604	1583119	12123	50.424
2	-	35.221	1556477	7507	49.576



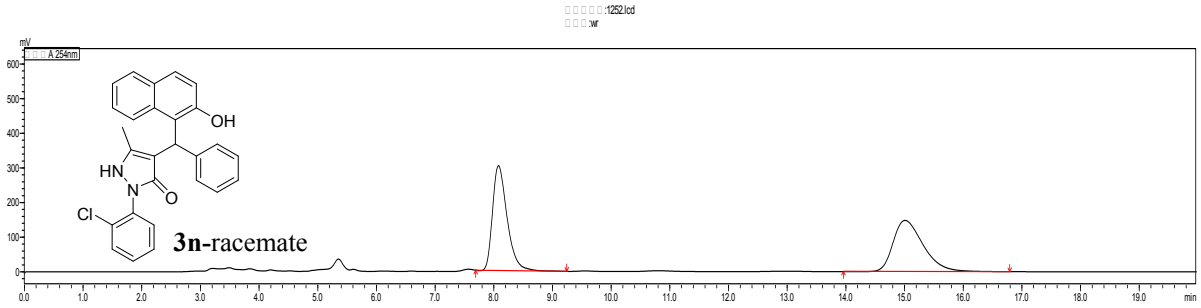
NO.	Name	Time（min）	Area	Height	Area%
1	-	24.788	4178105	50074	73.854
2	-	35.039	1479164	13554	26.146



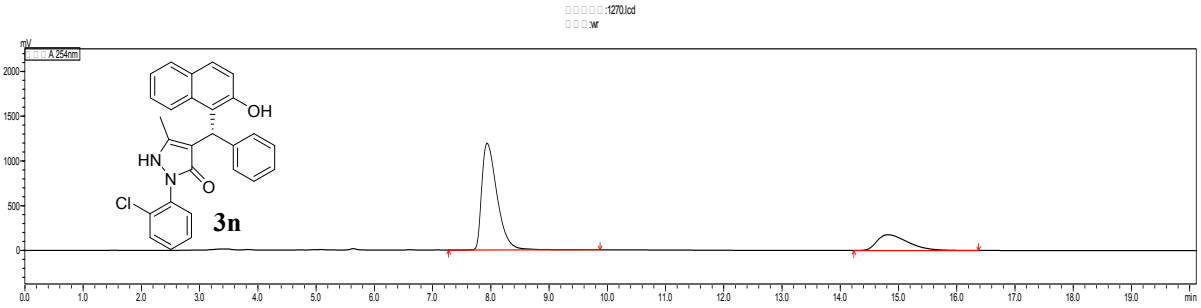
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.344	29842814	2294572	50.264
2	-	10.601	29528974	673065	49.736



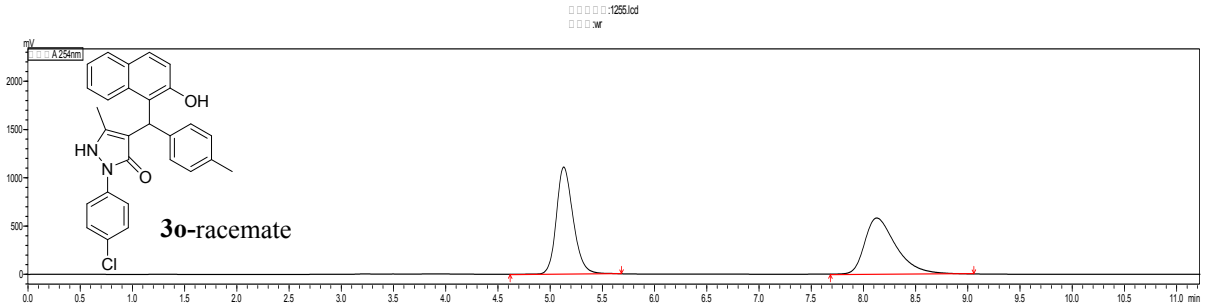
NO.	Name	Time（min）	Area	Height	Area%
1	-	5.281	27494672	2452938	88.100
2	-	10.749	3713946	131541	11.900



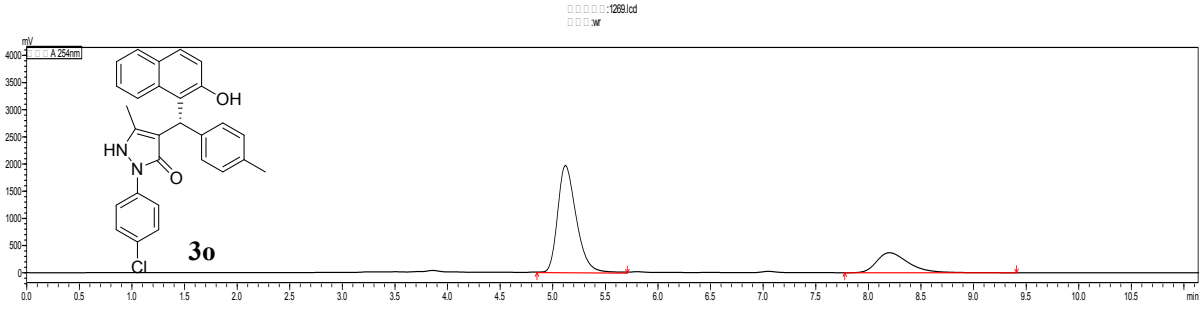
NO.	Name	Time（min）	Area	Height	Area%
1	-	8.080	5190765	302528	50.075
2	-	15.009	5175283	147248	49.925



NO.	Name	Time（min）	Area	Height	Area%
1	-	7.937	21756771	1191767	76.618
2	-	14.821	6639655	177384	23.382



NO.	Name	Time（min）	Area	Height	Area%
1	-	5.130	12482775	1109286	50.539
2	-	8.128	12216380	583110	49.461



NO.	Name	Time（min）	Area	Height	Area%
1	-	5.120	24489472	1973587	75.940
2	-	8.200	7759138	368824	24.060