Supporting Information

Cascade Michael/Aldol//Rearrangement between Phenacylmalononitriles and Maleimides: Highly Diastereoselective Access to Functionalized Bicyclic Cyclopentenes Containing a CN-substituted All-Carbon Quaternary Center

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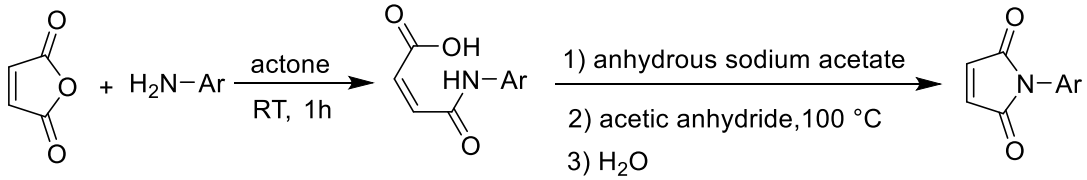
Content

1. General Information.

Commercially available compounds were used without further purification. The solvents and reagents were purified and dried according to standard procedures. Column chromatography was carried out using silica gel (200–300 mesh). All reactions were monitored by analytical thin-layer chromatography using silica gel plates with F254 indicator. Melting points were measured on an XT-4 melting point apparatus without correction. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on BRUKER AVANCE II 400MHz and 600MHz spectrometer. Infrared spectra were obtained on Thermo Scientific Nicolet iS5 or Bruker tensor II spectrometer. The ESI-HRMS spectra were obtained on Bruker APEX IV mass spectrometer and Bruker micrOTOF-Q III mass spectrometer. The crystal structure of **3k** and intermediate **C-3a** was confirmed by D8 Venture X-ray crystal diffractometer.

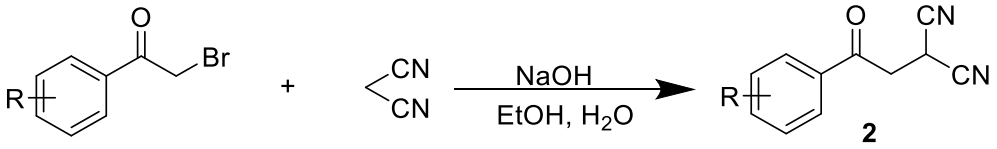
2. Preparation of N-Aryl maleimide

N-Aryl maleimides were prepared using the reported procedure from the corresponding anilines[1].



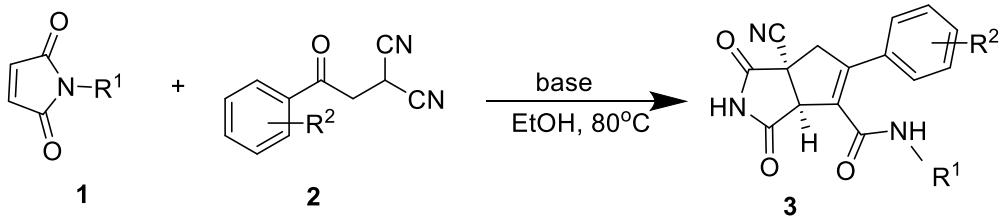
To a solution of maleic anhydride (10 mmol) dissolved in acetone (15 mL) was added the appropriate aryl amine (10 mmol) dissolved in acetone (5 mL). The reaction was stirred at RT for 1 h. The precipitated solid was isolated by filtration and washed with acetone. This solid was immediately used in the next step and add anhydrous sodium acetate (5 mmol) and acetic anhydride (10 mL) sequentially. This mixture was heated to 100 ºC for 0.5 h, after which the mixture was cooled in ice water. The crude product was obtained by precipitation with a large amount of water. Then filtered and washed with water and recrystallized in ethanol.

3. Synthesis of the substrate 2



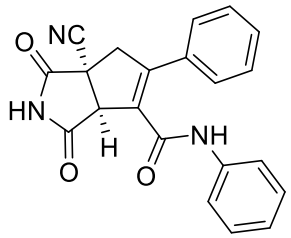
Substrate **2** were prepared according to literature procedures.[1] A series of 2-bromoacetophenone (25 mmol, 1.0 equiv) and malononitrile (25 mmol, 1.0 equiv) were dissolved in EtOH (25 mL), and then sodium hydroxide (25 mmol, 1.0 equiv) dissolved in 25 mL of water was slowly added dropwise to the above solution. In the mixed solution, add water (25 mL) to dilute, stir at room temperature for 1.5 hours, precipitate out, filter to obtain crude product, recrystallize with ethanol to obtain pure product, and obtain benzoylmalononitrile products after drying.

4. General synthetic procedure for bicyclic cyclopentene 3



To a stirred suspension of maleimides (0.22 mmol, 1.1 equiv) in EtOH (2.5 mL) was added phenacylmalononitriles (0.20 mmol, 1.0 equiv) and base(0.2 mmol, 1.0 equiv), and the mixture was heated for 1.5 h at 80 °C in the sealed tube. After the reaction is completed, the mixture was concentrated and purified by silica gel column chromatography (CH_2Cl_2/MeOH) to afford the desired pure product.

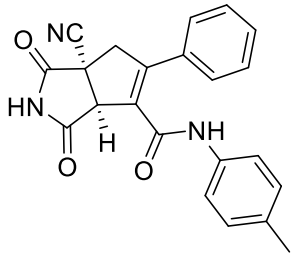
6a-cyano-1,3-dioxo-*N*,5-diphenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide（3a）



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3a** (90%) as a white solid, mp 120-122 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 10.26 (s, 1H), 7.53 (d, J = 7.9 Hz,

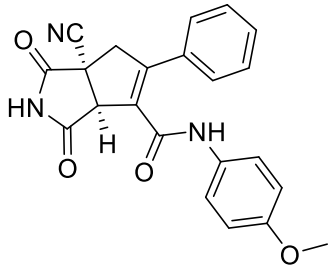
2H), 7.46 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.38-7.26 (m, 5H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.87 (d, *J* = 2.8 Hz, 1H), 3.86 (dd, *J* = 18.1, 3.1 Hz, 1H), 3.61 (d, *J* = 18.1 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.6, 173.3, 163.3, 140.9, 139.1, 133.4, 129.5, 129.4, 129.2, 128.9, 128.0, 124.3, 120.0, 118.7, 61.9, 46.1, 45.6. IR (ATR): 3059, 2919, 2849, 1790, 1716, 1651, 1537, 1443, 1337, 1172, 752, 690, 633, 504 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{16}N_3O_3$ $[M+H]^+$: 358.1186, found 358.1205.

6a-cyano-1,3-dioxo-5-phenyl-*N*-(p-tolyl)-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3aa)



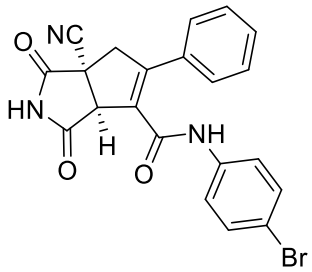
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3aa** (53%) as a white solid, mp 120-122 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 10.21 (s, 1H), 7.46 – 7.43 (m, 2H), 7.43 – 7.39 (m, 2H), 7.37 – 7.29 (m, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.85 (d, *J* = 2.9 Hz, 1H), 3.86 (dd, *J* = 18.1, 3.1 Hz, 1H), 3.60 (d, *J* = 18.1 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.7, 173.4, 163.1, 140.6, 136.6, 133.4, 133.3, 129.6, 129.5, 128.9, 128.9, 128.0, 120.0, 118.7, 61.9, 46.1, 45.6, 21.0. IR (ATR): 3354, 3182, 2919, 2849, 1784, 1701, 1604, 1541, 1470, 1409, 1355, 1254, 1178, 1080, 816, 763, 641, 508, 495, 436 cm^{-1}; HRMS ESI (m/z): calcd for $C_{22}H_{18}N_3O_3$ $[M+H]^+$: 372.1343, found 372.1358.

6a-cyano-*N*-(4-methoxyphenyl)-1,3-dioxo-5-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3ab)



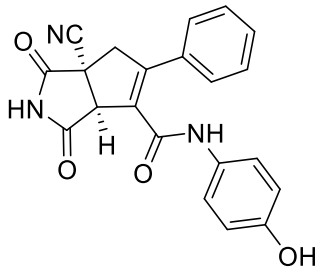
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3ab** (76%) as a white solid, mp 129-134 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 10.15 (s, 1H), 7.50 – 7.40 (m, 4H), 7.39 – 7.29 (m, 3H), 6.95 – 6.81 (m, 2H), 4.85 (s, 1H), 3.86 (dd, *J* = 18.1, 3.1 Hz, 1H), 3.73 (s, 3H), 3.60 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.6, 173.4, 162.8, 156.1, 140.5, 133.4, 132.3, 129.5, 129.0, 128.9, 128.0, 121.5, 118.7, 114.4, 61.9, 55.7, 46.1, 45.6. IR (ATR): 3063, 2921, 2850, 1790, 1719, 1509, 1443, 1338, 1300, 1171, 828, 764, 694, 524, 507, 418 cm^{-1}; HRMS ESI (m/z): calcd for $C_{22}H_{16}N_3O_4$ $[M+H]^+$: 386.1146, found 386.1147.

N-(4-bromophenyl)-6a-cyano-1,3-dioxo-5-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3ac)



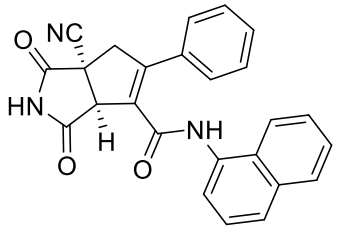
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3ac** (98%) as a white solid, mp 148-150 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.12 (s, 1H), 10.47 (s, 1H), 7.51 (s, 4H), 7.46 – 7.41 (m, 2H), 7.37 – 7.31 (m, 3H), 4.86 (s, 1H), 3.87 (d, *J* = 18.0 Hz, 1H), 3.61 (d, *J* = 18.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.2, 173.8, 163.4, 141.5, 138.5, 133.4, 132.1, 129.6, 128.9, 128.6, 128.0, 121.9, 118.8, 115.9, 61.9, 46.1, 45.7. IR (ATR): 3265, 3061, 2763, 1791, 1717, 1660, 1487, 1304, 1247, 1009, 822, 693, 623, 503, 435, 421 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{15}BrN_3O_3$ $[M+H]^+$: 436.0291, found 436.0305.

6a-cyano-*N*-(4-hydroxyphenyl)-1,3-dioxo-5-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3ad)



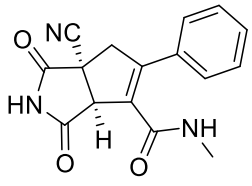
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3ad** (85%) as a white solid, mp 167-170 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 10.04 (s, 1H), 9.29 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.34 (dt, *J* = 17.5, 7.4 Hz, 5H), 6.71 (d, *J* = 8.4 Hz, 2H), 4.84 (d, *J* = 3.0 Hz, 1H), 3.85 (dd, *J* = 18.1, 3.2 Hz, 1H), 3.59 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.7, 173.4, 162.6, 154.3, 140.2, 133.5, 130.8, 129.4, 129.1, 128.9, 128.0, 121.8, 118.7, 115.6, 61.9, 46.0, 45.5. IR (ATR): 3289, 3061, 2767, 1790, 1627, 1436, 1339, 1212, 1168, 1033, 828, 760, 695, 630, 521, 503, 477 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{16}N_3O_4$ $[M+H]^+$: 374.1135, found 374.1152.

6a-cyano-*N*-(naphthalen-1-yl)-1,3-dioxo-5-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3ae)



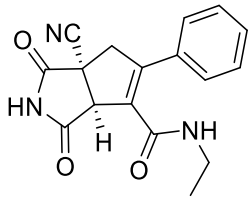
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3ae** (52%) as a white solid, mp 116-118 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.18 (s, 1H), 10.27 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.53 (dt, *J* = 15.0, 7.6 Hz, 4H), 7.40 (h, *J* = 7.2 Hz, 4H), 4.96 (d, *J* = 3.0 Hz, 1H), 3.92 (dd, *J* = 18.1, 3.1 Hz, 1H), 3.64 (d, *J* = 17.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.0, 173.5, 164.3, 141.2, 134.1, 133.7, 133.3, 130.1, 129.5, 129.1, 128.9, 128.4, 128.2, 126.6, 126.2, 126.2, 126.0, 123.4, 122.3, 118.7, 62.0, 46.2, 45.7. IR (ATR): 3187, 3053, 2921, 2850, 1790, 1647, 1534, 1444, 1398, 1212, 1034, 794, 764, 695, 642, 505 cm^{-1}; HRMS ESI (m/z): calcd for $C_{25}H_{18}N_3O_3$ $[M+H]^+$: 408.1343, found 408.1367.

6a-cyano-*N*-methyl-1,3-dioxo-5-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*] pyrrole-4-carboxamide(3b)



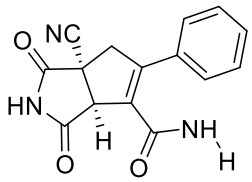
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3b** (50%) as a white solid, mp 130-131 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.01 (s, 1H), 8.13 (s, 1H), 7.54 – 7.18 (m, 5H), 4.70 (s, 1H), 3.76 (d, *J* = 17.6 Hz, 1H), 3.53 (d, *J* = 18.1 Hz, 1H), 2.61 (s, 3H).^{13}C NMR (151 MHz, DMSO-d_6) δ 174.5, 173.3, 165.1, 139.8, 133.6, 129.3, 129.0, 128.8, 128.0, 118.7, 61.8, 46.0, 45.5, 26.1. IR (ATR): 3308, 2917, 2849, 2759, 1789, 1718, 1615, 1545, 1388, 1297, 762, 694, 632, 498 cm^{-1}; HRMS ESI (m/z): calcd for $C_{16}H_{14}N_3O_3$ $[M+H]^+$: 296.1030, found: 296.1037.

6a-cyano-*N*-ethyl-1,3-dioxo-5-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*] pyrrole-4-carboxamide(3c)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3c** (55%) as a white solid, mp 119-121 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.01 (s, 1H), 8.18 (t, *J* = 5.7 Hz, 1H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 3H), 4.70 (s, 1H), 3.76 (d, *J* = 18.0 Hz, 1H), 3.52 (d, *J* = 17.9 Hz, 1H), 3.11 (ddp, *J* = 27.0, 13.8, 6.7 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (151 MHz, DMSO-d_6) δ 174.4, 173.3, 164.3, 139.5, 133.5, 129.3, 128.7, 128.1, 118.7, 61.8, 46.0, 45.5, 33.9, 14.6. IR (ATR): 3270, 2930, 2758, 1789, 1719, 1617, 1541, 1337, 1173, 762, 694, 632, 499 cm^{-1}; HRMS ESI (m/z): calcd for $C_{17}H_{16}N_3O_3$ $[M+H]^+$: 310.1186, found 310.1187.

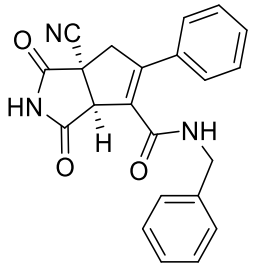
6a-cyano-1,3-dioxo-5-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3d)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3d** (54%) as a white solid, mp 127-129 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.98 (s, 1H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.36-7.32 (m, 1H), 6.35 (s, 1H), 4.55 (s, 1H), 3.62 (d, *J* = 17.4 Hz, 1H), 3.56 (d, *J* = 17.5 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 176.0, 173.8, 142.3, 133.4, 129.2, 129.1, 126.8,

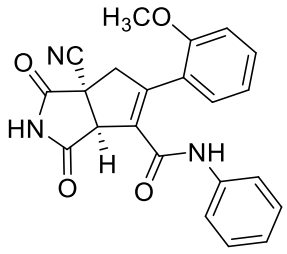
120.2, 119.0, 60.2, 46.9, 43.4. IR (ATR): 3242, 3092, 2940, 1796, 1702, 1445, 1349, 1209, 1178, 1051, 765, 747, 689, 618 cm^{-1}; HRMS ESI (m/z): calcd for $C_{15}H_{12}N_3O_3$ $[M+H]^+$: 282.0873, found: 282.2808.

N-benzyl-6a-cyano-1,3-dioxo-5-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*] pyrrole-4-carboxamide(3e)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3e** (78%) as a white solid, mp 105-106 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.03 (s, 1H), 8.73 (t, *J* = 5.9 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.31-7.27 (m, 4H), 7.25 (d, *J* = 7.3 Hz, 3H), 4.77 (d, *J* = 2.9 Hz, 1H), 4.32 (d, *J* = 5.9 Hz, 2H), 3.77 (dd, *J* = 18.0, 3.1 Hz, 1H), 3.53 (d, *J* = 17.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.6, 173.3, 164.7, 140.1, 139.1, 133.5, 129.2, 129.0, 128.7, 128.6, 128.1, 128.0, 127.3, 118.7, 61.9, 46.1, 45.6, 42.7. IR (ATR): 3881, 3201, 3059, 2925, 1786, 1702, 1519, 1388, 1211, 1178, 1075, 750, 683, 600 cm^{-1}; HRMS ESI (m/z): calcd for $C_{22}H_{18}N_3O_3$ $[M+H]^+$: 372.1343, found: 372.1356.

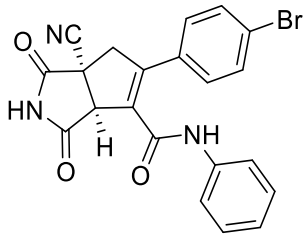
6a-cyano-5-(2-methoxyphenyl)-1,3-dioxo-*N*-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3f)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3f** (65%) as a white solid, mp 61-63 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.06 (s, 1H), 9.93 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.29 (s, 4H), 7.07 – 6.86 (m, 3H), 4.95 (s, 1H), 3.83 (d, *J* = 18.3 Hz, 1H), 3.65 (s, 3H), 3.45 (d, *J* =

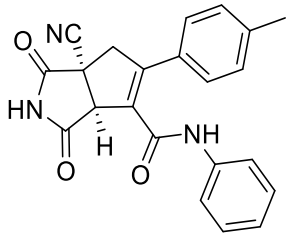
18.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.0, 173.4, 162.6, 156.8, 140.3, 139.3, 132.0, 130.7, 130.3, 129.8, 129.1, 123.9, 122.7, 120.6, 119.8, 118.8, 111.9, 61.0, 55.8, 46.6, 46.3. IR (ATR): 2859, 2918, 2848, 1789, 1717, 1664, 1597, 1491, 1443, 1340, 1284, 1256, 1170, 1020, 798, 751, 691, 501 cm^{-1}; HRMS ESI (m/z): calcd for $C_{22}H_{18}N_3O_4$ $[M+H]^+$: 388.1292, found: 388.1301.

5-(4-bromophenyl)-6a-cyano-1,3-dioxo-*N*-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3g)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3g** (90%) as a white solid, mp 126-127 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.17 (s, 1H), 10.55 (s, 1H), 7.59-7.51 (m, 4H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.94 (s, 1H), 3.80 (dd, *J* = 18.1, 2.9 Hz, 1H), 3.59 (d, *J* = 17.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.8, 174.2, 163.0, 140.4, 139.1, 132.9, 131.8, 130.2, 129.8, 129.2, 124.3, 122.7, 120.1, 118.8, 62.1, 46.1, 45.5. IR (ATR): 2918, 2849, 1790, 1720, 1654, 1597, 1541, 1491, 1444, 1442, 1343, 1257, 1173, 1073, 822, 752, 713, 691 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{15}BrN_3O_3$ $[M+H]^+$: 436.0291, found: 436.0295.

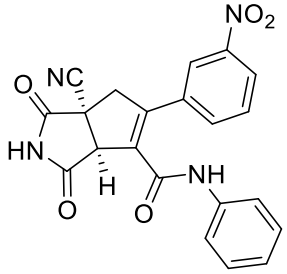
6a-cyano-1,3-dioxo-*N*-phenyl-5-(p-tolyl)-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*] pyrrole-4-carboxamide(3h)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3h** (80%) as a white solid, mp 113-114 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 10.28 (s, 1H), 7.54 (d, *J* = 6.9 Hz, 2H), 7.35 (d, *J* = 6.9 Hz, 2H), 7.31 (s, 2H), 7.15 (d, *J* = 6.7 Hz, 2H), 7.11 – 7.05 (m, 1H), 4.84 (s, 1H), 3.83 (d, *J* = 17.3 Hz, 1H), 3.57 (d, *J* = 17.9 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, DMSO-

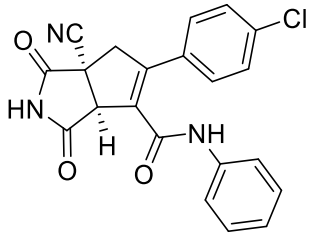
d_6) δ 174.7, 173.4, 163.5, 140.6, 139.2, 130.5, 129.5, 129.2, 128.1, 127.9, 124.2, 120.0, 118.7, 61.9, 46.0, 45.6, 21.3. IR (ATR): 3059, 2918, 2849, 1790, 1717, 1652, 1596, 1538, 1442, 1340, 1318, 1172, 1034, 817, 752, 690, 504 cm^{-1}; HRMS ESI (m/z): calcd for $C_{22}H_{18}N_3O_3$ $[M+H]^+$: 372.1343, found: 372.1346.

6a-cyano-5-(3-nitrophenyl)-1,3-dioxo-*N*-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3i)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3i** (99%) as a white solid, mp 132-133 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.58 (s, 1H), 8.26 (t, *J* = 2.0 Hz, 1H), 8.15 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 4.55 – 4.44 (m, 1H), 3.69 (d, *J* = 18.4 Hz, 1H), 3.28 (dd, *J* = 18.5, 2.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 192.0, 186.2, 162.6, 147.9, 142.4, 139.4, 136.9, 135.2, 132.3, 130.0, 129.3, 124.1, 123.4, 123.3, 121.6, 119.9, 64.7, 47.7, 45.7. IR (ATR): 3083, 2917, 2848, 1790, 1719, 1655, 1526, 1493, 1443, 1345, 1257, 1172, 736, 718, 690, 633 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{15}N_4O_5$ $[M+H]^+$: 403.1037, found: 403.1046.

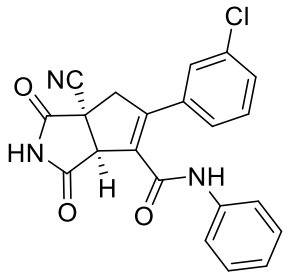
5-(4-chlorophenyl)-6a-cyano-1,3-dioxo-*N*-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3j)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3j** (75%) as a white solid, mp 120-122 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 10.27 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.3 Hz,

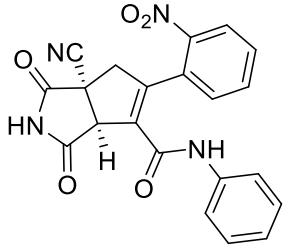
1H), 4.87 (s, 1H), 3.85 (dd, *J* = 18.2, 3.2 Hz, 1H), 3.60 (d, *J* = 18.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.6, 173.2, 163.0, 140.2, 139.0, 134.1, 132.4, 129.9, 129.5, 129.3, 128.9, 124.4, 120.1, 118.6, 61.8, 46.1, 45.6. IR (ATR): 3064, 2924, 2852, 1790, 1719, 1655, 1595, 1541, 1443, 1340, 1208, 1173, 1092, 1013, 828, 753, 691, 501 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{15}ClN_3O_3$ $[M+H]^+$: 392.0796, found: 392.0808.

5-(3-chlorophenyl)-6a-cyano-1,3-dioxo-*N*-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3k)



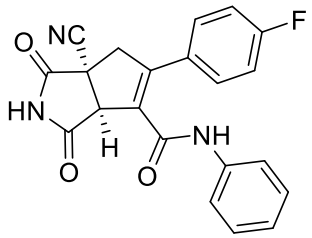
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3k** (82%) as a white solid, mp 130-131 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.11 (s, 1H), 10.28 (s, 1H), 7.54 (s, 1H), 7.51 (d, *J* = 6.9 Hz, 2H), 7.35-7.43 (m, 3H), 7.28-7.35 (m, 2H), 7.09 (t, *J* = 6.5 Hz, 1H), 4.90 (s, 1H), 3.89 (d, *J* = 18.1 Hz, 1H), 3.63 (d, *J* = 18.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.5, 173.2, 162.9, 140.1, 138.9, 135.6, 133.6, 130.7, 130.1, 129.3, 127.9, 126.7, 124.4, 120.1, 118.6, 61.8, 46.1, 45.6. IR (ATR): 3064, 2916, 2848, 1790, 1717, 1654, 1596, 1540, 1443, 1338, 1313, 1172, 1081, 785, 751, 688, 634 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{15}ClN_3O_3$ $[M+H]^+$: 392.0796, found: 392.0801.

6a-cyano-5-(2-nitrophenyl)-1,3-dioxo-*N*-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3l)



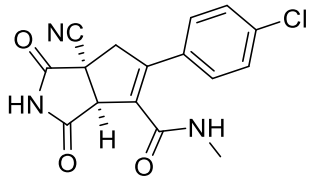
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3l** (65%) as a white solid, mp 137-139 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.27 (s, 1H), 9.94 (s, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.27 (q, *J* = 9.3, 7.4 Hz, 3H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.24 (s, 1H), 3.70 (d, *J* = 19.2 Hz, 1H), 3.59 (d, *J* = 17.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 175.7, 173.3, 160.7, 147.9, 138.7, 134.3, 130.5, 130.3, 130.0, 129.2, 129.0, 128.3, 124.7, 124.4, 120.1, 118.5, 59.5, 47.7, 46.2. IR (ATR): 3082, 2916, 2849, 1790, 1720, 1664, 1523, 1443, 1374, 1341, 1207, 1173, 853, 753, 691 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{15}N_4O_5$ $[M+H]^+$: 403.1037, found: 403.1050.

6a-cyano-5-(4-fluorophenyl)-1,3-dioxo-*N*-phenyl-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3m)



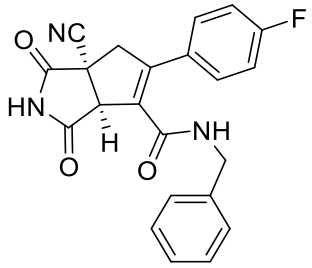
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3m** (75%) as a white solid, mp 119-120 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 10.28 (s, 1H), 7.52 (q, *J* = 7.7, 6.7 Hz, 4H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 8.7 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.88 (s, 1H), 3.86 (d, *J* = 18.2 Hz, 1H), 3.61 (d, *J* = 18.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.6, 173.3, 162.7 (d, *J* = 244.4 Hz), 163.1, 140.2, 139.1, 130.4 (d, *J* = 7.2 Hz, 2C), 130.0 (d, *J* = 2.4 Hz), 129.3, 128.8, 124.3, 120.1, 118.7, 115.8 (d, *J* = 21.3 Hz, 2C), 61.8, 46.0, 45.7. ^{19}F NMR (377 MHz, DMSO-d_6) δ -111.9. IR (ATR): 3067, 2918, 2849, 1791, 1719, 1654, 1598, 1541, 1509, 1443, 1341, 1234, 1161, 836, 753, 691 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{15}FN_3O_3$ $[M+H]^+$: 376.1092, found: 376.1095.

5-(4-chlorophenyl)-6a-cyano-*N*-methyl-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3n)



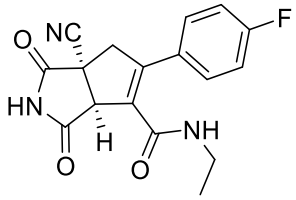
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3n** (83%) as a white solid, mp 225-226 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.03 (s, 1H), 8.15 (d, J = 4.8 Hz, 1H), 7.46 – 7.38 (m, 4H), 4.72 (d, J = 2.9 Hz, 1H), 3.76 (dd, J = 18.0, 3.1 Hz, 1H), 3.53 (d, J = 18.0 Hz, 1H), 2.61 (d, J = 4.7 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.6, 173.3, 164.8, 139.1, 133.9, 132.6, 129.9, 129.7, 128.8, 118.7, 61.8, 46.0, 45.5, 26.2. IR (ATR): 3301, 2919, 2850, 2748, 2252, 1781, 1705, 1635, 1571, 1493, 1340, 1178, 1093, 1015, 831, 764, 669, 633, 616, 485, 465 cm^{-1}; HRMS ESI (m/z): calcd for $C_{16}H_{13}ClN_3O_3$ $[M+H]^+$:330.0640, found:330.0641.

***N*-benzyl-6a-cyano-5-(4-fluorophenyl)-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3o)**



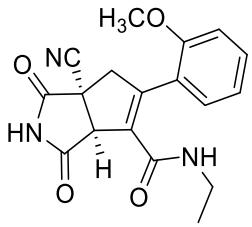
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3o** (54%) as a white solid, mp 231-232 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.04 (s, 1H), 8.73 (t, J = 5.9 Hz, 1H), 7.42 (dd, J = 8.6, 5.4 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.27-7.22 (m, 3H), 7.11 (t, J = 8.7 Hz, 2H), 4.78 (d, J = 2.9 Hz, 1H), 4.33 (q, J = 7.4, 5.6 Hz, 2H), 3.76 (dd, J = 18.0, 3.1 Hz, 1H), 3.54 (d, J = 18.0 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.6, 173.3, 164.5, 162.6 (d, J = 245.2 Hz), 139.4, 139.0, 130.4 (d, J = 8.2 Hz, 2C), 130.0 (d, J = 3.5 Hz), 128.9, 128.6, 128.0, 127.3, 118.7, 115.6 (d, J = 21.4 Hz, 2C), 61.8, 46.0, 45.7, 42.7. ^{19}F NMR (377 MHz, DMSO-d_6) δ -112.3. IR (ATR): 3381, 3202, 3084, 2931, 2258, 1788, 1702, 1634, 1606, 1513, 1494, 1437, 1379, 1243, 1164, 825, 811, 788, 750, 695, 604, 502 cm^{-1}; HRMS ESI (m/z): calcd for $C_{22}H_{17}FN_3O_3$ $[M+H]^+$: 390.1248, found: 390.1252.

6a-cyano-*N*-ethyl-5-(4-fluorophenyl)-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3p)



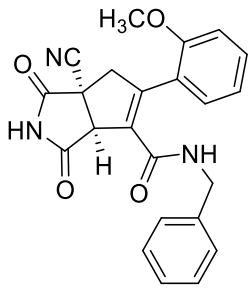
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3p** (80%) as a white solid, mp 238-240 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.01 (s, 1H), 8.20 (t, *J* = 5.6 Hz, 1H), 7.50-7.45 (m, 2H), 7.23-7.17 (m, 2H), 4.72 (dd, *J* = 3.1, 1.2 Hz, 1H), 3.76 (dd, *J* = 18.0, 3.1 Hz, 1H), 3.53 (dd, *J* = 18.0, 1.3 Hz, 1H), 3.21-3.01 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.4, 173.3, 164.1, 162.6 (d, *J* = 245.2 Hz), 138.7, 130.4 (d, *J* = 8.3 Hz, 2C), 130.1 (d, *J* = 2.3 Hz), 129.2, 118.7, 115.6 (d, *J* = 21.4 Hz, 2C), 61.8, 46.0, 45.6, 34.0, 14.6. ^{19}F NMR (377 MHz, DMSO-d_6) δ -112.3. IR (ATR): 3266, 2976, 2932, 2750, 2248, 1779, 1704, 1603, 1566, 1505, 1348, 1221, 1186, 1158, 1038, 845, 834, 685, 635, 490 cm^{-1}; HRMS ESI (m/z): calcd for $C_{17}H_{15}FN_3O_3$ $[M+H]^+$: 328.1092, found:328.1098.

6a-cyano-*N*-ethyl-5-(2-methoxyphenyl)-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3q)



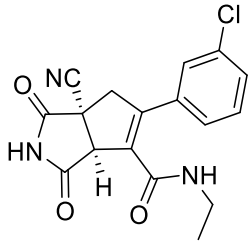
Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3q** (90%) as a white solid, mp 160-161 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.99 (s, 1H), 7.77 (t, *J* = 5.7 Hz, 1H), 7.36-7.27 (m, 1H), 7.19 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.92-6.87 (m, 1H), 4.75 (dd, *J* = 2.9, 1.1 Hz, 1H), 3.73 (s, 3H), 3.70 (dd, *J* = 18.2, 3.0 Hz, 1H), 3.38 (dd, *J* = 18.2, 1.2 Hz, 2H), 3.15-2.92 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.9, 173.4, 163.4, 156.9, 139.7, 130.6, 130.5, 130.0, 122.9, 120.5, 118.8, 111.8, 60.7, 55.8, 46.4, 46.3, 33.8, 14.7. IR (ATR): 3307, 2930, 2756, 2249, 1788, 1719, 1618, 1597, 1541, 1491, 1435, 1339, 1250, 1212, 1172, 1022, 935, 755, 630, 503 cm^{-1}; HRMS ESI (m/z): calcd for $C_{18}H_{18}N_3O_4$ $[M+H]^+$: 340.1292, found: 340.1299.

_N_-benzyl-6a-cyano-5-(2-methoxyphenyl)-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[_c_]pyrrole-4-carboxamide(3r)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3r** (64%) as a white solid, mp 144-145 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.02 (s, 1H), 8.36 (t, *J* = 6.0 Hz, 1H), 7.31 (ddd, *J* = 8.7, 7.4, 1.7 Hz, 1H), 7.25 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.23-7.14 (m, 4H), 7.02-6.96 (m, 1H), 6.86 (td, *J* = 7.4, 1.0 Hz, 1H), 4.83 (dd, *J* = 2.9, 1.1 Hz, 1H), 4.29 (dd, *J* = 15.3, 6.1 Hz, 1H), 4.23 (dd, *J* = 15.3, 5.8 Hz, 1H), 3.73-3.69 (m, 1H), 3.68 (s, 3H), 3.42-3.36 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.0, 173.4, 163.8, 156.8, 140.3, 139.4, 130.5, 130.4, 130.0, 128.5, 127.6, 127.1, 122.9, 120.6, 118.8, 111.8, 60.8, 55.8, 46.5, 46.4, 42.5. IR (ATR): 3307, 2924, 2758, 2248, 1789, 1721, 1621, 1493, 1455, 1338, 1292, 1250, 1171, 1022, 753, 697, 630, 501, 432 cm^{-1}; HRMS ESI (m/z): calcd for $C_{23}H_{20}N_3O_4$ $[M+H]^+$: 402.1448, found: 402.1454.

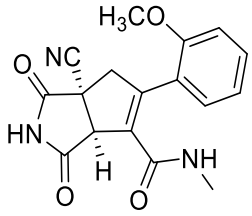
5-(3-chlorophenyl)-6a-cyano-_N_-ethyl-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[_c_]pyrrole-4-carboxamide(3s)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3s** (68%) as a white solid, mp 273-274 °C; ^{1}H NMR (600 MHz, DMSO-d6) δ 12.01 (s, 1H), 8.24 (t, *J* = 5.7 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.43-7.34 (m, 3H), 4.73 (dd, *J* = 3.1, 1.2 Hz, 1H), 3.79 (dd, *J* = 18.0, 3.1 Hz, 1H), 3.55 (dd, *J* = 18.0, 1.2 Hz, 1H), 3.22-3.01 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.3, 173.2, 163.9, 138.6, 135.7, 133.4, 130.6, 130.5, 129.0, 127.9, 126.8, 118.6, 61.7, 46.0, 45.4, 33.9, 14.6. IR (ATR): 3277, 2966, 2924, 2733, 2245, 1778, 1704, 1636, 1610, 1574,

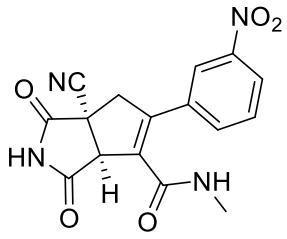
1471, 1348, 1187, 1154, 899, 784, 725, 678, 635, 511 cm^{-1}; HRMS ESI (m/z): calcd for $C_{17}H_{15}ClN_3O_3$ $[M+H]^+$: 344.0796, found: 344.0805.

6a-cyano-5-(2-methoxyphenyl)-*N*-methyl-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3t)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3t** (85%) as a light yellow solid, mp 172-173 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.99 (s, 1H), 7.76 (q, *J* = 4.6 Hz, 1H), 7.30 (td, *J* = 7.8, 1.7 Hz, 1H), 7.17 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 4.74 (d, *J* = 2.7 Hz, 1H), 3.72 (s, 3H), 3.69 (dd, *J* = 18.2, 2.9 Hz, 1H), 3.37 (d, *J* = 18.2 Hz, 1H), 2.53 (d, *J* = 4.7 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.0, 173.4, 164.3, 156.9, 139.8, 130.5, 130.4, 129.9, 123.0, 120.6, 118.8, 111.9, 60.8, 55.8, 55.4, 46.4, 46.4, 26.1. IR (ATR): 2919, 2850, 2756, 2249, 1788, 1718, 1615, 1462, 1434, 1410, 1340, 1250, 1170, 1021, 755, 694, 629, 501 cm^{-1}; HRMS ESI (m/z): calcd for $C_{17}H_{16}N_3O_4$ $[M+H]^+$: 326.1135, found: 326.1132.

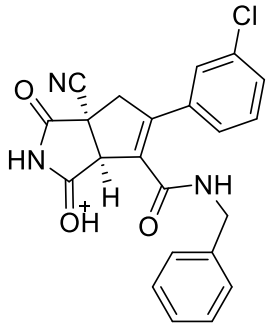
6a-cyano-*N*-methyl-5-(3-nitrophenyl)-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide (3u)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3u** (75%) as a white solid, mp 240-241 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.07 (s, 1H), 8.27 (t, *J* = 2.0 Hz, 1H), 8.22 (q, *J* = 4.7 Hz, 1H), 8.19 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.81 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 4.80 (dd, *J* = 3.1, 1.1 Hz, 1H), 3.89 (dd, *J* = 18.1, 3.1 Hz, 1H), 3.63 (dd, *J* = 18.1, 1.2 Hz, 1H), 2.62 (d, *J* = 4.6 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.4, 173.0, 164.3, 148.0, 139.2, 135.5, 134.7, 131.1, 130.3, 123.8, 122.9, 118.6, 61.6, 46.1, 45.6, 26.1. IR (ATR): 3283, 3126, 2942,

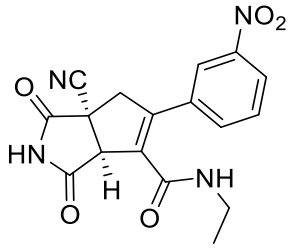
2755, 2250, 1778, 1710, 1523, 1346, 1309, 1264, 1184, 1038, 873, 806, 703, 683, 634, 510 cm^{-1}; HRMS ESI (m/z): calcd for $C_{16}H_{13}N_4O_5$ $[M+H]^+$: 341.0880, found: 341.0882.

N-benzyl-5-(3-chlorophenyl)-6a-cyano-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3v)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3v** (88%) as a white solid, mp 257-258 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.05 (s, 1H), 8.76 (t, *J* = 5.9 Hz, 1H), 7.49 (s, 1H), 7.39 (dq, *J* = 6.5, 4.0, 3.3 Hz, 1H), 7.33-7.27 (m, 4H), 7.26-7.20 (m, 3H), 4.80 (d, *J* = 2.9 Hz, 1H), 4.36-4.27 (m, 2H), 3.79 (dd, *J* = 18.1, 3.1 Hz, 1H), 3.56 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.5, 173.2, 164.3, 139.4, 139.0, 135.8, 133.5, 130.5, 130.2, 129.0, 128.7, 127.9, 127.8, 127.3, 126.8, 118.6, 61.8, 46.0, 45.6, 42.7. IR (ATR): 3384, 3200, 3082, 2927, 2257, 1788, 1703, 1637, 1519, 1439, 1380, 1259, 1179, 817, 784, 753, 699, 680, 603 cm^{-1}; HRMS ESI (m/z): calcd for $C_{22}H_{17}ClN_3O_3$ $[M+H]^+$: 406.0953, found: 406.0955.

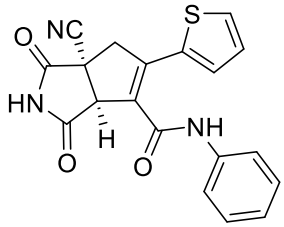
6a-cyano-*N*-ethyl-5-(3-nitrophenyl)-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta [*c*]pyrrole-4-carboxamide(3w)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3w** (65%) as a light yellow solid, mp 267-268 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.06 (s, 1H), 8.29 (t, *J* = 5.6 Hz, 1H), 8.27 (t, *J* = 2.1 Hz, 1H), 8.19 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 4.80 (d, *J* = 3.0 Hz, 1H), 3.89 (dd, *J* = 18.0, 3.1 Hz, 1H), 3.62 (d, *J* = 18.0 Hz, 1H), 3.20-3.04

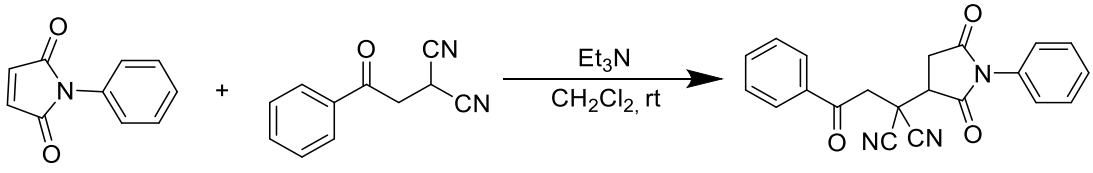
(m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.4, 173.1, 163.6, 148.0, 138.7, 135.4, 134.7, 131.4, 130.3, 123.8, 122.9, 118.6, 61.6, 46.1, 45.5, 34.0, 14.6. IR (ATR): 3269, 3108, 2924, 2738, 2248, 1779, 1644, 1609, 1580, 1523, 1470, 1346, 1186, 915, 805, 717, 683, 636, 511, 444 cm^{-1}; HRMS ESI (m/z): calcd for $C_{17}H_{15}N_4O_5$ $[M+H]^+$: 355.1037, found: 355.1042.

6a-cyano-1,3-dioxo-*N*-phenyl-5-(thiophen-2-yl)-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxamide(3x)



Isolation by column chromatography (CH_2Cl_2: MeOH= 50/1 v/v) yielded **3x** (72%) as a white solid, mp 127-130 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.13 (s, 1H), 10.52 (s, 1H), 7.67 – 7.59 (m, 3H), 7.40 – 7.32 (m, 3H), 7.14 – 7.10 (m, 1H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.85 (s, 1H), 3.81 (d, *J* = 17.4 Hz, 1H), 3.75 (dd, *J* = 17.7, 2.7 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.5, 173.4, 162.7, 139.2, 134.7, 133.6, 130.4, 130.1, 129.3, 127.7, 126.3, 124.4, 120.0, 118.6, 63.4, 61.7, 45.8. IR (ATR): 3260, 2926, 2766, 1719, 1541, 1444, 1333, 1254, 1175, 1078, 952, 850, 754, 691, 623, 503, 479 cm^{-1}; HRMS ESI (m/z): calcd for $C_{19}H_{14}N_3O_3S$ $[M+H]^+$: 364.0750, found 364.0763.

5. Characterization data of 4a

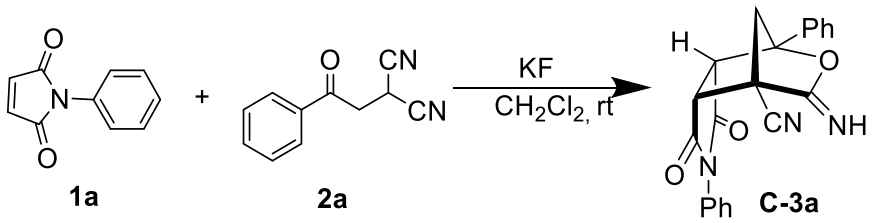


1a **2a** **4a**

White solid, mp 126-128 °C; ^{1}H NMR (600 MHz, DMSO-d6) δ 8.05 (dd, *J* = 8.0, 0.7 Hz, 2H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.30 (dd, *J* = 8.0, 0.6 Hz, 2H), 4.54 (d, *J* = 18.5 Hz, 1H), 4.33 (d, *J* = 18.5 Hz, 1H), 4.21 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.25 (dd, *J* = 18.3, 9.2 Hz, 1H), 3.18 (dd, *J* = 18.3, 5.6 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 194.5, 173.8, 173.7, 135.2, 134.9, 132.2, 129.6, 129.5, 129.3, 128.8, 127.4, 114.8,

114.5, 44.9, 43.4, 34.0, 32.1. IR (ATR): 3357, 2956, 2918, 2849, 1711, 1659, 1631, 1498, 1469, 1424, 1396, 1356, 1230, 1206, 757, 694, 628 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{16}N_3O_3$ $[M+H]^+$: 358.1186, found 358.1186.

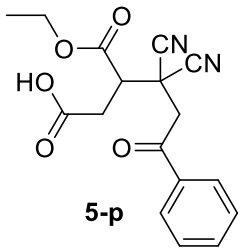
6. Synthesis of the intermediate C-3a



To a stirred suspension of N-Phenylmaleimide (0.55 mmol, 1.1 equiv) in CH_2Cl_2 (2 mL) was added phenacylmalononitrile (0.5 mmol, 1.0 equiv) and KF (1.5 mmol, 3 equiv), and the mixture was stirred at RT for 48h (monitored by TLC). After the reaction is completed, the mixture is filtered and washed to afford the desired pure product. 53% yield, white solid, mp 227-228 °C; ^{1}H NMR (600 MHz, Methanol-d_4) δ 7.99 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.85 (t, J = 7.6 Hz, 2H), 7.73 (q, J = 7.8 Hz, 3H), 7.53 (t, J = 7.3 Hz, 1H), 4.39 (d, J = 7.2 Hz, 1H), 4.20 (d, J = 7.2 Hz, 1H), 3.38 (d, J = 15.4 Hz, 1H), 3.15 (d, J = 15.8 Hz, 1H). ^{13}C NMR (151 MHz, MeOD) δ 172.2, 171.3, 168.4, 143.6, 134.0, 130.6, 128.7, 128.3, 128.1, 127.1, 125.9, 124.6, 124.1, 120.3, 108.5, 82.5, 55.6, 50.4, 49.8, 48.0, 47.9, 47.7, 47.6, 47.5, 47.3, 47.2, 43.8. IR (ATR): 3269, 2982, 1711, 1495, 1454, 1377, 1337, 1281, 1244, 1168, 1090, 981, 881, 731, 683, 591, 563 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{16}N_3O_3$ $[M+H]^+$: 358.1186, found 358.1184.

7. Synthesis of the 5-p and 6-p

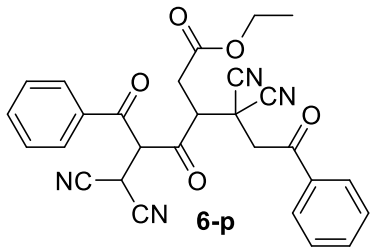
4,4-dicyano-3-(ethoxycarbonyl)-6-oxo-6-phenylhexanoic acid (5-p)



5-p

To a stirred suspension of maleic anhydride **5** (0.22 mmol, 1.1 equiv) in EtOH (2.5 mL) was added phenacylmalononitriles **2a** (0.20 mmol, 1.1 equiv) and $NaHCO_3$(0.2 mmol, 1.0 equiv), and the mixture was heated for 1.0 h at 80 ºC in the sealed tube. After the reaction is completed, the mixture was concentrated and purified by silica gel column chromatography (CH_2Cl_2/MeOH) to afford the product. 51% yield, white solid, mp 64-68 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.04 – 7.98 (m, 2H), 7.75 – 7.70 (m, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 4.38 – 4.28 (m, 2H), 4.21 (qd, *J* = 7.2, 1.8 Hz, 2H), 3.69 (dd, *J* =10.8, 3.6 Hz, 1H), 3.00 (dd, *J* = 16.8, 3.7 Hz, 1H), 2.81 (dd, *J* = 16.8, 10.9 Hz, 1H), 1.20 (t, *J* = 7.1Hz, 3H). ^{13}C NMR (151 MHz, DMSO-*d*6) δ 194.4, 171.5, 169.5, 135.3, 134.8, 129.4, 128.7, 114.6, 114.5, 62.2, 45.6, 43.5, 34.8, 33.8, 29.5, 14.2. IR (ATR): 3009, 2914, 2848, 1688, 1597, 1471, 1449, 1260, 1225, 1183, 1104, 1068, 1012, 799, 755, 687, 577, 475, 449, 422 cm^{-1}; MS ESI (m/z): calcd for $C_{17}H_{15}N_2O_5$ [M-H]-: 327.10, found 328.01.

ethyl 5-benzoyl-6,6-dicyano-3-(1,1-dicyano-3-oxo-3-phenylpropyl)-4-oxohexanoate (6-p)

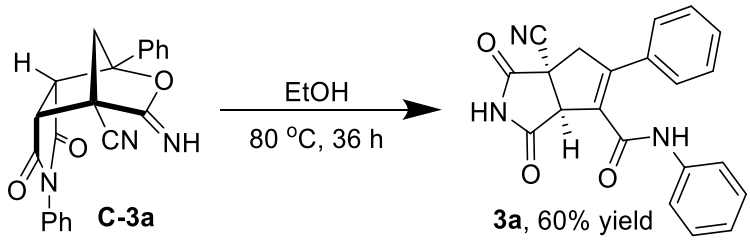


6-p

To a stirred suspension of unsaturated ester **6** (0.50 mmol, 1.0 equiv) in EtOH (2.5 mL) was added phenacylmalononitriles **2a** (0.55 mmol, 1.1 equiv) and $NaHCO_3$ (0.5 mmol, 1.0 equiv), and the mixture was heated for 1.0 h at 80 ºC in the sealed tube. After thereaction is completed, the mixture was concentrated and purified by silica gel column chromatography (CH_2Cl_2/MeOH) to afford the product. 48% yield, white solid, mp 64-66 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.03 – 7.90 (m, 4H), 7.74 – 7.70 (m, 1H), 7.65 (tq, *J* = 7.3, 1.6 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.56 – 7.49 (m, 2H), 4.42 (d, *J* = 18.6 Hz, 1H), 4.30 (d, *J* = 18.6 Hz, 1H), 4.14 – 4.02 (m, 4H), 3.82 – 3.68 (m, 1H), 2.91 (dd, *J* = 15.9, 8.7 Hz, 1H), 2.78 (dd, *J* = 6.8, 3.1Hz, 1H), 2.71 (dd, *J* = 15.9, 4.8 Hz, 1H), 1.21

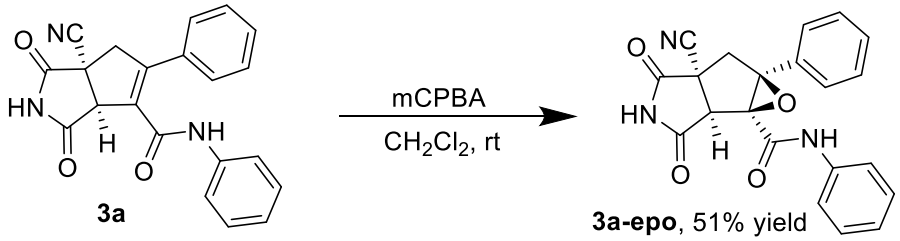
(t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6)δ 196.9, 195.0, 172.0, 171.3, 136.6, 135.7, 134.6, 134.0, 129.4, 129.2, 129.2, 128.5, 128.4, 120.1, 116.6, 116.3, 60.7, 48.2, 47.8, 44.0, 35.4, 35.2, 34.7, 14.5. IR (ATR): 3227, 2921, 1793, 1717, 1682, 1596, 1580, 1449, 1398, 1355, 1192, 1096, 1024, 1001, 919, 852, 755, 687, 654, 602, 560, 497, 417 cm^{-1}; MS ESI (m/z): calcd for $C_{28}H_{23}N_4O_5$ [M-H]$^-$ 495.17, found 496.39.

8. Control experiment



To a stirred suspension of intermediate **C-3a** (0.55 mmol, 1.1 equiv) directly in EtOH (2.5 mL) at 80 °C for 36 in the sealed tube (monitored by TLC). After the reaction is completed, the mixture was concentrated and purified by silica gel column chromatography (CH_2Cl_2/MeOH) to afford the desired pure product.

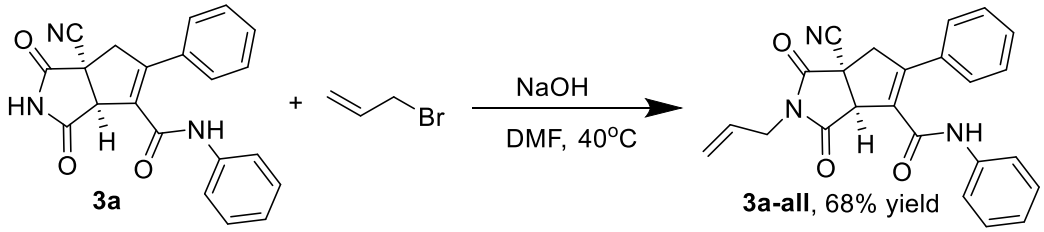
9. Epoxidation of compound 3a



To a stirred suspension of bicyclic cyclopentene (0.2 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added 3-Chloroperoxybenzoic acid (0.4 mmol, 2.0 equiv) and $NaHCO_3$ (0.4 mmol, 2.0 equiv), and the mixture was stirred at RT for 72h (monitored by TLC). After the reaction is completed, the mixture was concentrated and purified by silica gel column chromatography (CH_2Cl_2/MeOH) to afford the desired pure product. 51% yield, light yellow solid, mp 98-100 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.30 (s, 1H), 9.93 (s, 1H), 7.60 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.38 – 7.30 (m, 3H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.61 (s, 1H), 3.46 (d, *J* = 15.1 Hz, 1H), 3.06 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 173.2, 161.1, 137.7, 131.7, 129.6, 129.1,

128.8, 127.1, 124.9, 120.7, 117.0, 77.3, 72.7, 54.6, 47.7, 29.5. IR (ATR): 2951, 2851, 1793, 1734, 1681, 1599, 1587, 1446, 1338, 1237, 1177, 1096, 1055, 753, 691, 632, 538, 482 cm^{-1}; HRMS ESI (m/z): calcd for $C_{21}H_{16}N_3O_4$ $[M+H]^+$: 374.1135, found 374.1152.

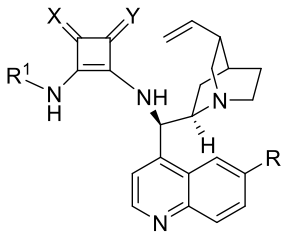
10. N-allylation of compound 3a



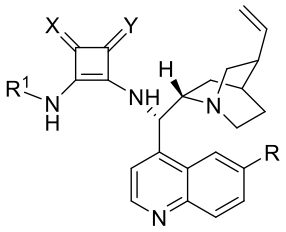
To a stirred suspension of bicyclic cyclopentene (0.2 mmol, 1.0 equiv) in DMF (2 mL) was added allyl bromide (2 mmol, 10.0 equiv) and NaOH (1.0 mmol, 5.0 equiv), and the mixture was stirred at 40 °C for 2h (monitored by TLC). After the reaction is completed, the mixture was concentrated and purified by silica gel column chromatography (CH_2Cl_2/MeOH) to afford the desired pure product. 68% yield, white solid, mp 190-191 °C; ^1H NMR (600 MHz, DMSO-d_6) δ 10.30 (s, 1H), 7.56 (d, *J* = 6.4 Hz, 2H), 7.48 (s, 2H), 7.40-7.29 (m, 5H), 7.14-7.06 (m, 1H), 5.91-5.71 (m, 1H), 5.26-5.13 (m, 2H), 5.02 (s, 1H), 4.08 (s, 2H), 3.87 (d, *J* = 17.6 Hz, 1H), 3.69 (d, *J* = 17.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.7, 171.7, 163.1, 141.0, 139.1, 133.3, 131.3, 129.6, 129.3, 128.9, 128.6, 128.0, 124.4, 120.1, 118.6, 117.9, 60.6, 45.6, 45.0, 41.9. IR (ATR): 3290, 3202, 3142, 3098, 2917, 2849, 1790, 1701, 1667, 1600, 1589, 1492, 1444, 1394, 1339, 1261, 1172, 971, 750, 696, 537, 481 cm^{-1}; HRMS ESI (m/z): calcd for $C_{24}H_{20}N_3O_3$ $[M+H]^+$: 398.1499, found 398.1506.

11.Asymmetric catalysis of 4a

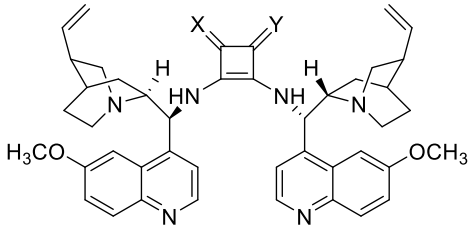
Figure S1. Bifunctional organocatalysts I- XIV used in this work.



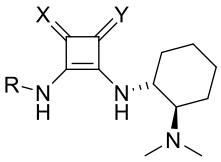
I : X=S,Y=S,R=OMe
II : X=O,Y=S,R=OMe
III :X=O,Y=O,R=OCH_3,R^1=3,5-$(CF_3)_2C_6H_3$



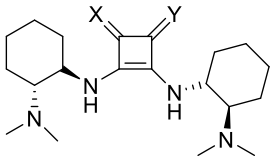
IV: X=O,Y=S,R=OCH_3,R^1=Bn
V : X=S,Y=S,R=OCH_3,R^1=Bn
VI: X=O,Y=O,R=H,R^1=Bn
VII:X=O,Y=O,R=OCH_3,R^1=Bn
VIII:X=O,Y=O,R=OCH_3,R^1=3,5-$(CF_3)_2C_6H_3$



IX: X=S,Y=S
X : X=O,Y=O

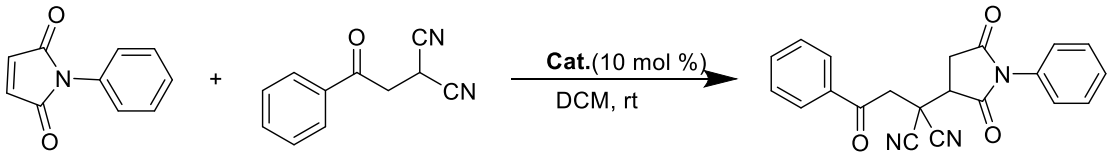


XI: X=O,Y=O,R=Bn
XII: X=S,Y=S,R=Bn
XIII: X=O,Y=S,R=Bn



XIV : X=S,Y=S

Table S1. Catalyst screening for the model reaction[a]

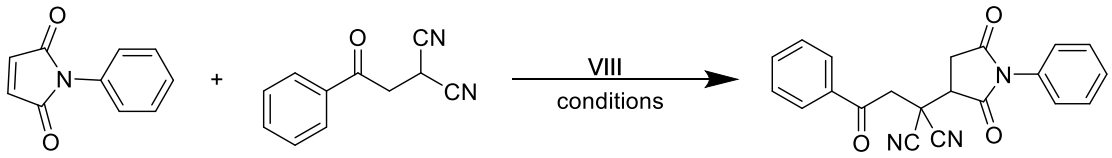


1a + 2a → 4a

Entry	Cat.	Time(h)	Yield(%)[b]	ee(%)[c]
1	**I**	10	99	4
2	**II**	10	99	8
3	**III**	10	99	27
4	**IV**	10	78	-8
5	**V**	10	99	0
6	**VI**	10	34	14
7	**VII**	10	99	0
8	**VIII**	10	99	-41
9	**IX**	12	99	-4
10	**X**	12	99	-2
11	**XI**	10	99	30
12	**XII**	10	99	8
13	**XIII**	10	99	2
14	**XIV**	12	99	0

[a] Reaction conditions: maleimide (**1a**, 17.3 mg, 0.10 mmol), phenacylmalononitrile (**2a**, 9.2 mg, 0.05 mmol), cat. (0.005 mmol), DCM (2 mL), room temperature. [b] Isolated yield. [c] The ee value determined by chiral HPLC on a Chiralpak IC column.

Table S2. Optimization of reaction conditions [a]



1a **2a** **4a**

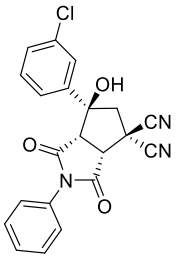
Entry	Solvent	T (°C)	Time(h)	Yield(%)[b]	ee(%)[c]
1	DCM	rt	10	99	-41
2	acetone	rt	10	99	-2
3	DCE	rt	10	99	-27
4	$CHCl_3$	rt	10	99	-7
5	MeOH	rt	10	99	-5
6	Et_2O	rt	10	67	0
7	THF	rt	10	99	0
8	toluene	rt	10	99	-5
9	EtOH	rt	10	99	-5
10	EA	rt	10	99	-3
11	trifluorotoluene	rt	10	99	-10
12	DMF	rt	10	11	0
13	h-hexane	rt	10	99	0
14	isopropanol	rt	10	99	-2
15	benzene	rt	10	99	-8
16	DMSO	rt	10	ND	
17	dioxane	rt	10	99	-13
18	DCM:DCE=7:3	rt	10	99	-31
19	DCM:DCE=1:1	rt	10	99	-3
20	DCM:DCE=3:7	rt	10	99	-39
21	CH_3CN	rt	10	99	-7
22[d]	DCM	rt	10	99	-11
23[e]	DCM	rt	10	99	-20
24[f]	DCM	rt	10	99	-32
25[g]	DCM	rt	10	99	-26
26	DCM	0	48	99	-43
27	DCM	35	6	99	-35
28	DCM	-15	48	99	-24
29	DCM	-30	76	40	-36

[a] Reaction conditions: maleimide (**1a**, 17.3 mg, 0.10 mmol), phenacylmalononitrile (**2a**, 9.2 mg, 0.05 mmol), **VIII** (3.2 mg, 0.005 mmol, 10 mol%), solvent (2 mL), room temperature. [b] Isolated yield. [c] The ee value determined by chiral HPLC on a Chiralpak IC column. [d] 2.5 mol% **VIII.** [e] 2.5 mol% **VIII**. [f] 7.5 mol% **VIII**. [g] 10 mol% **VIII**.

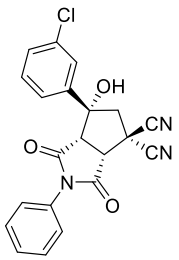
12. Hartree-Fock calculations

All calculations were performed with Gaussian 09. Molecular geometries were fully optimized with the Hartree-Fock/6-31g(d) method (#p opt freq HF/6-31g(d) iop(6/7=3,5/13=1,2/16=1)).

Table S3 Total Energies of intermediates A-3k and B-3k



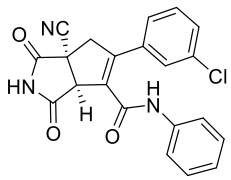
A-3k



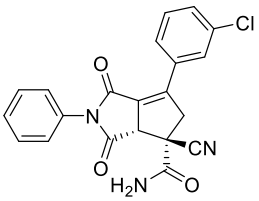
B-3k

Energies	**A-3k**	**B-3k**
E_{total}/*Hartree*	-1650.8156088	-1650.8137630
E_B-E_A	1.16kcal/mol	

Table S4 Total Energies of 3k and D-3k



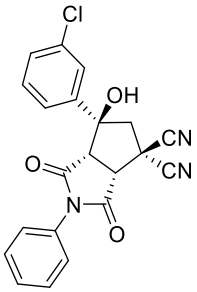
3k

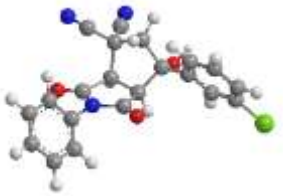


D-3k

Energies	**3k**	**D-3k**
E_{total}/*Hartree*	-1650.853288	-1650.8434513
E_D-E_{3k}	6.17kcal/mol	

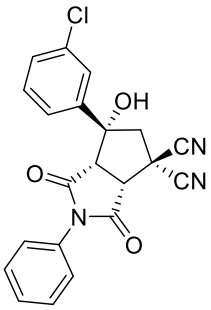
Table S5. Cartesian Coordinates of A-3k





C	0.21394100	0.50727700	-0.94279400
C	-0.84099800	1.61672400	-1.04592900
C	-0.58335100	2.56343100	0.19596900
C	0.53101600	1.84109400	1.01168100
C	1.32962000	1.06634200	-0.04193300
C	2.34614100	0.06310800	0.49078800
O	1.96059000	1.98998700	-0.89914000
O	-3.22853400	1.32852500	-1.27068700
C	-0.56890100	-0.69562000	-0.42623400
N	-1.92075500	-0.40310500	-0.53515800
C	-2.17081600	0.88168700	-0.98680800
O	-0.12245900	-1.72372300	-0.04293300
C	-2.96010900	-1.34725100	-0.25090200
C	-3.92381300	-1.03106000	0.69123000
C	-4.93347300	-1.93867100	0.96157000
C	-4.97048500	-3.15667600	0.30259000
C	-3.99836200	-3.46605600	-0.63476500
C	-2.99250800	-2.55874500	-0.91917600
C	3.33374100	-0.38331400	-0.38274000
C	4.28065300	-1.28777000	0.05178800
C	4.27840400	-1.76309600	1.35089100
C	3.30051300	-1.31466600	2.21797600
C	2.34058400	-0.40910200	1.79495100
Cl	5.50700400	-1.83525500	-1.05846500
C	-1.76549900	2.76518500	1.06238400
N	-2.63816900	2.88014100	1.77673400
C	-0.13764300	3.89924600	-0.25540800
N	0.19989500	4.93144700	-0.57973900
H	0.62489800	0.23688100	-1.90732200
H	-0.79606600	2.19101600	-1.95679000
H	1.13258500	2.53914600	1.57893900
H	0.05255900	1.16641600	1.70854000
H	2.67228800	2.42979100	-0.44956900
H	-3.89259000	-0.08408400	1.19684000
H	-5.68686900	-1.69278400	1.68735800
H	-5.75349900	-3.86111100	0.51774300
H	-4.02271000	-4.40996700	-1.14805300
H	-2.23597500	-2.79453800	-1.64339000
H	3.36793600	-0.02291700	-1.39211800
H	5.02439700	-2.46446800	1.67215700
H	3.28396700	-1.67315500	3.23080300
H	1.59451000	-0.09098900	2.49721500

Table S6. Cartesian Coordinates of B-3k



C	0.16381800	0.17390100	-0.67718800
C	-0.59503300	1.47763800	-0.93915000
C	0.13811500	2.55339600	-0.10218400
C	0.57424800	1.76720000	1.15324200
C	0.93114200	0.33564900	0.69664400
C	2.41826500	-0.00183300	0.53689200

O	0.37268900	-0.48413300	1.69502400
C	-0.92343000	-0.87274800	-0.55628700
N	-2.13397900	-0.22184900	-0.42800300
C	-2.03005400	1.15592600	-0.52311600
O	-2.91110700	1.92868400	-0.36560500
O	-0.75903200	-2.04908100	-0.54185400
C	-3.36438800	-0.89519900	-0.13739300
C	-4.36825400	-0.93159800	-1.08757100
C	-5.55720900	-1.57833100	-0.79603100
C	-5.73131200	-2.18968300	0.43493900
C	-4.71803600	-2.15056000	1.37949900
C	-3.53098500	-1.49728700	1.09708200
C	2.73311200	-1.25712900	0.01217700
C	4.04855500	-1.65370300	-0.09976500
C	5.08466500	-0.82274500	0.29247700
C	4.77428100	0.41992500	0.80508500
C	3.45355500	0.82895200	0.93236800
Cl	4.41299900	-3.22547700	-0.75402500
C	-0.64460000	3.75577800	0.25043100
N	-1.18449300	4.70313500	0.55797300
C	1.31755900	3.00931600	-0.87782500
N	2.22319400	3.33292500	-1.47822800
H	0.83608500	-0.09188900	-1.47748900
H	-0.62853300	1.75183800	-1.98625300
H	1.34431100	2.27235800	1.71243800
H	-0.28760400	1.68122400	1.80176600
H	0.63710200	-1.38827000	1.57649100
H	-4.22375000	-0.45566300	-2.03975900
H	-6.34241300	-1.60552000	-1.52919200
H	-6.65407200	-2.69398300	0.65800900
H	-4.85165000	-2.62299400	2.33544700
H	-2.73913100	-1.45444200	1.82169700
H	1.95835000	-1.92643700	-0.31778200
H	6.10375500	-1.14351400	0.19233700
H	5.56435200	1.08154600	1.10924200
H	3.26466900	1.80442100	1.33280800
C	-0.03017500	0.18646300	-0.94381400
C	-0.82173900	1.45546200	-0.95199800
C	0.16318600	2.47734800	-0.31530100
C	1.52343200	1.89350100	-0.79307800
C	1.27644500	0.38822900	-0.81421300
C	2.36567800	-0.60195200	-0.70219400
C	0.13486600	2.48374100	1.23843100
C	-0.95848400	-0.94070400	-0.72694600
N	-2.17427400	-0.34042000	-0.34708400
C	-2.14556100	1.04343800	-0.33405800
O	-0.78250000	-2.11102100	-0.80001500
O	-3.02675700	1.75468400	0.03058700
C	-3.32207100	-1.09751800	0.05069000
O	1.05397400	2.03952900	1.86374800
N	-0.95331400	3.02939900	1.80188600
C	-3.23951100	-1.95110900	1.13726600
C	-4.35144400	-2.68390000	1.51514400
C	-5.54126700	-2.55403700	0.81738000
C	-5.61746600	-1.69344000	-0.26554500
C	-4.50530100	-0.96739600	-0.65550300
C	3.43716700	-0.35674600	0.15497600
C	4.45334700	-1.28487600	0.25720400
C	4.43660900	-2.45278900	-0.48434500
C	3.37149200	-2.69290600	-1.33486000
C	2.33886300	-1.77891500	-1.44443000
Cl	5.78277300	-0.97796500	1.34144300
C	-0.05588500	3.84561800	-0.82086600
N	-0.21717500	4.89094600	-1.23136300
H	-1.05995700	1.78525600	-1.96164600
H	2.32800900	2.19509500	-0.14422300
H	1.75077400	2.23875400	-1.79772300
H	-1.02030000	2.98360700	2.79479900
H	-1.78694500	3.21094600	1.28712100
H	-2.31429700	-2.04880600	1.67313600
H	-4.28716900	-3.35175000	2.35472700
H	-6.40455400	-3.12094500	1.11575800
H	-6.53844800	-1.58860500	-0.80949600
H	-4.55796800	-0.29928000	-1.49468600
H	3.46496600	0.52691000	0.76184300
H	5.24018600	-3.15863000	-0.39430800
H	3.34697500	-3.59811500	-1.91306600
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Table S7. Cartesian Coordinates of D-3k

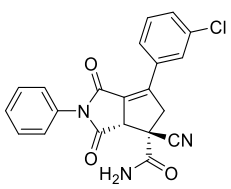
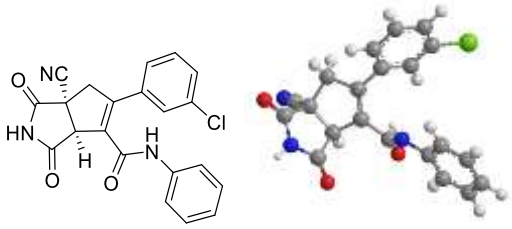


Table S8. Cartesian Coordinates of 3k



N	-3.66522300	-1.70319900	1.08751500
C	-2.70452800	-2.11782200	0.18771300
C	-2.38384000	-0.93204200	-0.71542600
C	-3.38819100	0.17121700	-0.29241100
C	-4.07631400	-0.40612500	0.95815500
C	-1.03210300	-0.32762000	-0.39723300
C	-1.11776800	0.92916400	0.02027600
C	-2.54707500	1.42837000	0.04746500
O	-4.81090400	0.17487300	1.68254800
O	-2.20863100	-3.19202900	0.17020800
C	-0.00496000	1.86336100	0.34211900
C	0.19344700	-1.13868000	-0.71990600
O	0.27924300	-1.65391800	-1.79800200
N	1.10647600	-1.22502400	0.27289800
C	2.37120100	-1.85494500	0.25347500
C	3.25162100	-1.53139800	1.28045000
C	4.49880800	-2.12321800	1.34495800
C	4.88605200	-3.04111500	0.38251500
C	4.00674100	-3.35833500	-0.63804300
C	2.75005400	-2.77845400	-0.71291200
C	1.01829100	2.08262200	-0.57463100
C	2.03294700	2.97004900	-0.26743000
C	2.05396700	3.64720900	0.93827900
C	1.03269200	3.42977100	1.84755900
C	0.00549700	2.55073400	1.55241000
Cl	3.30248200	3.24350700	-1.42449200
C	-4.41260600	0.44152600	-1.31126600
N	-5.19024500	0.64683300	-2.11115900
H	-3.99402600	-2.29337900	1.82317600
H	-2.44662200	-1.24003900	-1.75045300
H	-2.68070200	2.20424400	-0.69735300
H	-2.84365200	1.85052900	0.99952400
H	0.89609400	-0.72337400	1.10509900
H	2.96195300	-0.81172900	2.02726800
H	5.16709900	-1.86193600	2.14577400
H	5.85655200	-3.50071500	0.42809800
H	4.29338400	-4.07097300	-1.39052000
H	2.08052700	-3.03418000	-1.50592500
H	1.02110900	1.57598900	-1.52088200
H	2.85036500	4.33242700	1.15722300
H	1.03832200	3.95134900	2.78707100
H	-0.78091800	2.39489400	2.26876300

13. Reference

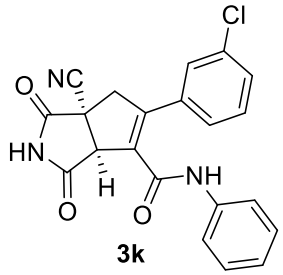
1. Q. Jia; L. Chen; G. Yang; J. Wang; J. Wei and Z. Du, DABCO-catalyzed [3+2] cycloaddition reactions of azomethine imines with N-aryl maleimides: facile access to dinitrogen-fused heterocycles. Tetrahedron Letters 2015, 56 (52), 7150-7153.

2. Al-Mousawi, S. M.; Moustafa, M. S.; Meier, H.; Kolshorn, H.; Elnagdi, M. H., Polyfunctional Nitriles in Organic Syntheses: A Novel Route to Aminopyrroles, Pyridazines and Pyrazolo 3,4-c pyridazines. Molecules 2009, 14 (2), 798-806.

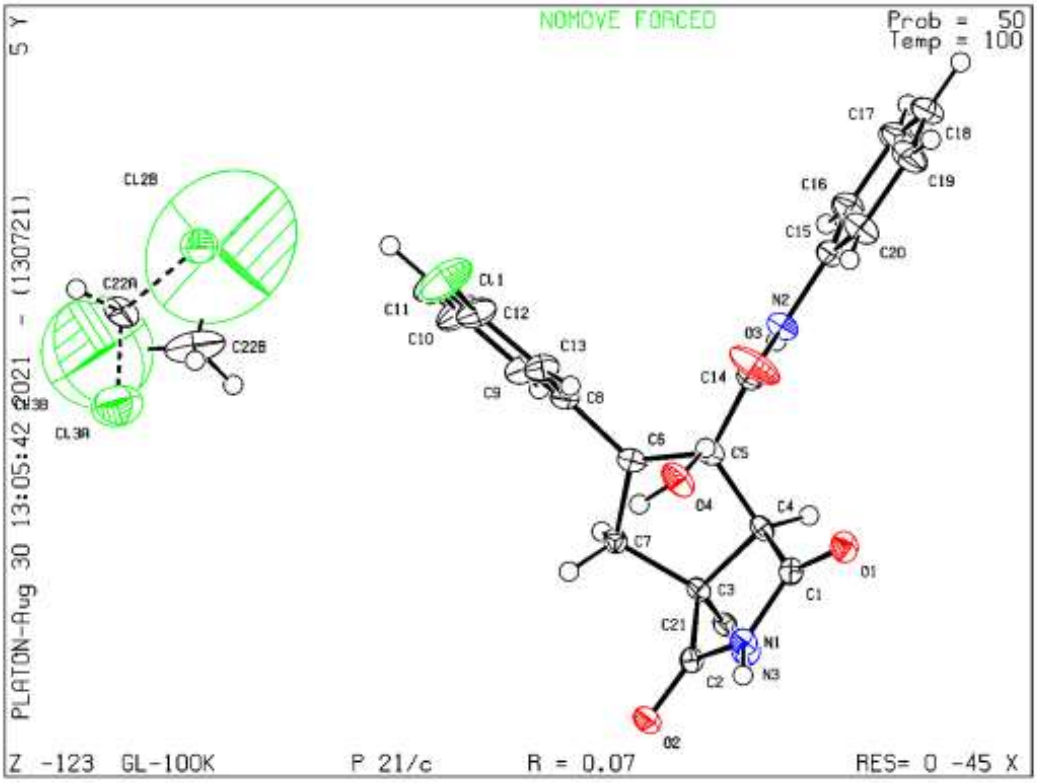
14. X-Ray Crystallography data of compound 3k and C-3a.

X-Ray Crystallography data for compound 3k(CCDC number: 2106413)

Sample preparation method: **3k** (17 mg) was dissolved in 5 mL of mixed solvent of chloroform and n-hexane toluene, filtered, and slowly volatilized at room temperature.



3k



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) GL-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: GL-100K

```
Bond precision:   C-C = 0.0033 A          Wavelength=1.54184

Cell:           a=14.82704(11)    b=9.94081(7)       c=14.20343(10)
                alpha=90          beta=93.8125(7)    gamma=90
Temperature:    100 K

                Calculated                  Reported
Volume          2088.85(3)                  2088.85(3)
Space group     P 21/c                      P 21/c
Hall group      -P 2ybc                     -P 2ybc
Moiety formula  C21 H14 Cl N3 O3, C H2 Cl2, C21H14ClN3O3, Ch2Cl2, H2O
                H2 O
Sum formula     C22 H18 Cl3 N3 O4           C22 H18 Cl3 N3 O4
Mr              494.74                      494.74
Dx,g cm-3       1.573                       1.573
Z               4                           4
Mu (mm-1)       4.298                       4.298
F000            1016.0                      1016.0
F000'           1023.03
h,k,lmax        18,12,17                    18,12,17
Nref            4358                        4291
Tmin,Tmax       0.902,0.958                 0.902,0.958
Tmin'           0.773

Correction method= # Reported T Limits: Tmin=0.902 Tmax=0.958
AbsCorr = MULTI-SCAN

Data completeness= 0.985          Theta(max)= 75.932

R(reflections)= 0.0718( 4106)                wR2(reflections)=
                                             0.2334( 4291)
S = 1.255                 Npar= 328
```

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

Alert level C

```
PLAT202_ALERT_3_C Isotropic non-H Atoms in Anion/Solvent .........          1 Check
            Cl3B
PLAT260_ALERT_2_C Large Average Ueq of Residue Including      Cl2B      0.299 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        20 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .         2 Check
PLAT977_ALERT_2_C Check Negative Difference Density on H22C             -0.41 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H22D             -0.32 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H22A             -0.60 eA-3
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          9 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          4 Report
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT142_ALERT_4_G s.u. on b - Axis Small or Missing ...............    0.00007 Ang.
PLAT143_ALERT_4_G s.u. on c - Axis Small or Missing ...............    0.00010 Ang.
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          4 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          2 Report
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )        100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  2  )       3.12 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  3  )       1.88 Check
PLAT434_ALERT_2_G Short Inter HL..HL Contact Cl1       ..Cl3A            3.36 Ang.
                                      1-x,-1/2+y,1/2-z  =      2_645 Check
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .       1.11 Ratio
PLAT793_ALERT_4_G Model has Chirality at C3          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C4          (Centro SPGR)          R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..............       32 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         47 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....         2 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...        18 Note
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.        10 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          3 Check
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  7 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 25 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
  6 ALERT type 3 Indicator that the structure quality may be low
 12 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

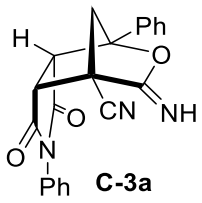
Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT202_GL-100K
;
PROBLEM: Isotropic non-H Atoms in Anion/Solvent .........          1 Check
RESPONSE: ...
;
_vrf_PLAT260_GL-100K
;
PROBLEM: Large Average Ueq of Residue Including      Cl2B      0.299 Check
RESPONSE: ...
;
_vrf_PLAT911_GL-100K
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600         20 Report
RESPONSE: ...
;
_vrf_PLAT918_GL-100K
;
PROBLEM: Reflection(s) with I(obs) much Smaller I(calc) .          2 Check
RESPONSE: ...
;
_vrf_PLAT977_GL-100K
;
PROBLEM: Check Negative Difference Density on H22C            -0.41 eA-3
RESPONSE: ...
;
# end Validation Reply Form
```

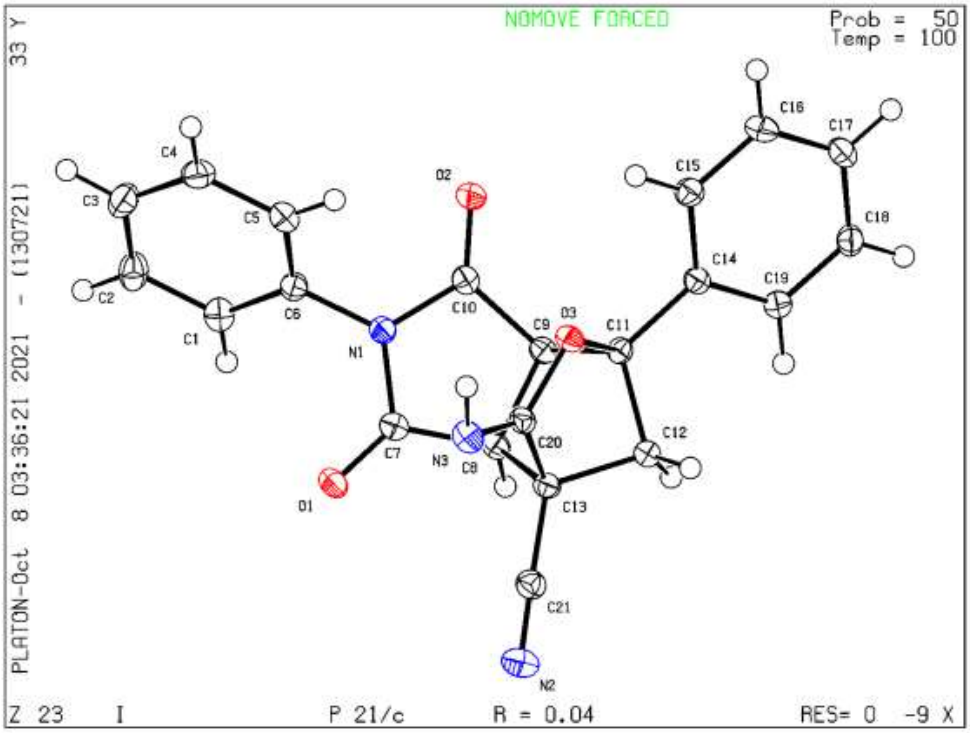
X-Ray Crystallography data for compound C-3a (CCDC number: 2114587)

Sample preparation method: The compound was separated by column chromatography, concentrated under reduced pressure, dissolved in dichloromethane, and crystals precipitated in the system.



C-3a

Datablock 1 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) I

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: I

Bond precision: C-C = 0.0017 A Wavelength=1.54178

Cell: a=13.2827(1) b=11.3775(1) c=12.2318(1)
alpha=90 beta=116.121(1) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	1659.72(3)	1659.72(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H15 N3 O3	C21 H15 N3 O3
Sum formula	C21 H15 N3 O3	C21 H15 N3 O3
Mr	357.36	357.36
Dx,g cm-3	1.430	1.430
Z	4	4
Mu (mm-1)	0.802	0.802
F000	744.0	744.0
F000'	746.34	
h,k,lmax	16,14,15	16,14,15
Nref	3454	3406
Tmin,Tmax	0.972,0.984	0.972,0.984
Tmin'	0.945	

Correction method= # Reported T Limits: Tmin=0.972 Tmax=0.984
AbsCorr = MULTI-SCAN

Data completeness= 0.986 Theta(max)= 75.889

R(reflections)= 0.0370(3216) wR2(reflections)= 0.1019(3406)

S = 1.038 Npar= 248

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

Alert level C

```
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.227 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=  0.600          9 Report
```

Alert level G

```
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT142_ALERT_4_G s.u. on b - Axis Small or Missing ...............    0.00010 Ang.
PLAT143_ALERT_4_G s.u. on c - Axis Small or Missing ...............    0.00010 Ang.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C13      --C21      .        6.1 s.u.
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O3            107.0 Degree
PLAT793_ALERT_4_G Model has Chirality at C8           (Centro SPGR)         S Verify
PLAT793_ALERT_4_G Model has Chirality at C9           (Centro SPGR)         R Verify
PLAT793_ALERT_4_G Model has Chirality at C11          (Centro SPGR)         S Verify
PLAT793_ALERT_4_G Model has Chirality at C13          (Centro SPGR)         R 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         39 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
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.         20 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          2 Check
```

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

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

checkCIF publication errors

Alert level A

```
PUBL004_ALERT_1_A  The contact author's name and address are missing,
            _publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
            _publ_contact_author_phone are all missing.
            At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
            e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
```

```
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
           Abstract of paper in English.
```

Alert level G

```
PUBL017_ALERT_1_G The _publ_section_references section is missing or
           empty.
```

7 **ALERT level A** = Data missing that is essential or data in wrong format
1 **ALERT level G** = General alerts. Data that may be required is missing

Publication of your CIF

You should 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 nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should 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.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

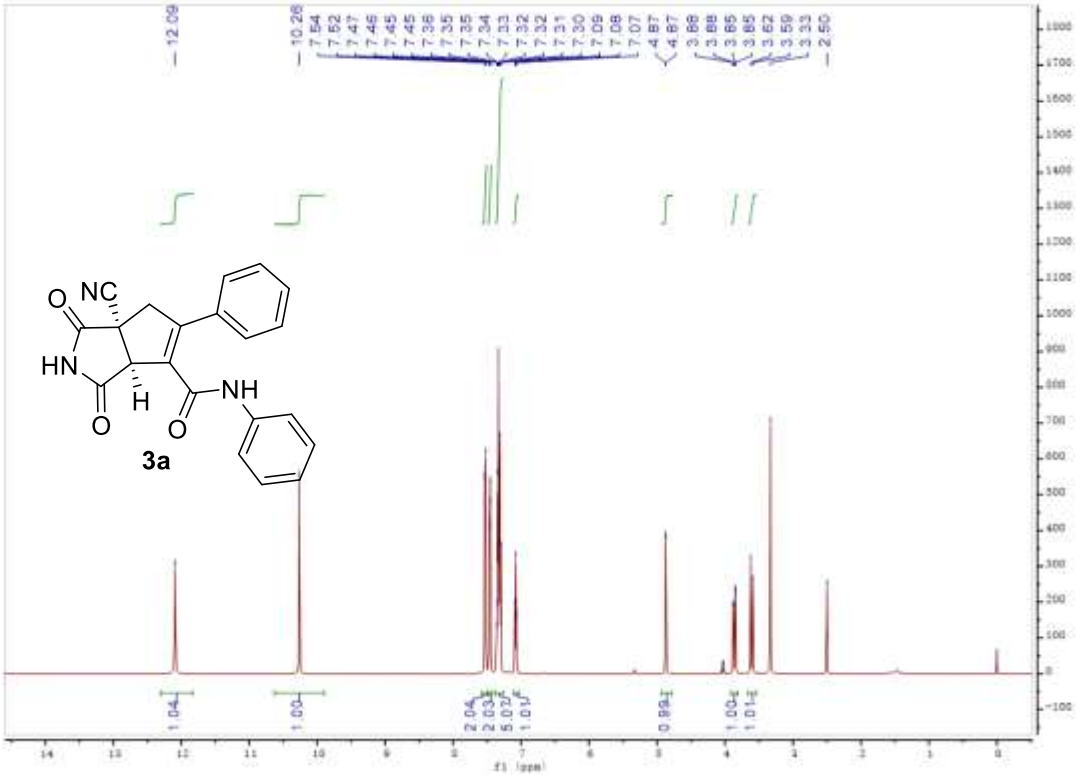
Validation response form

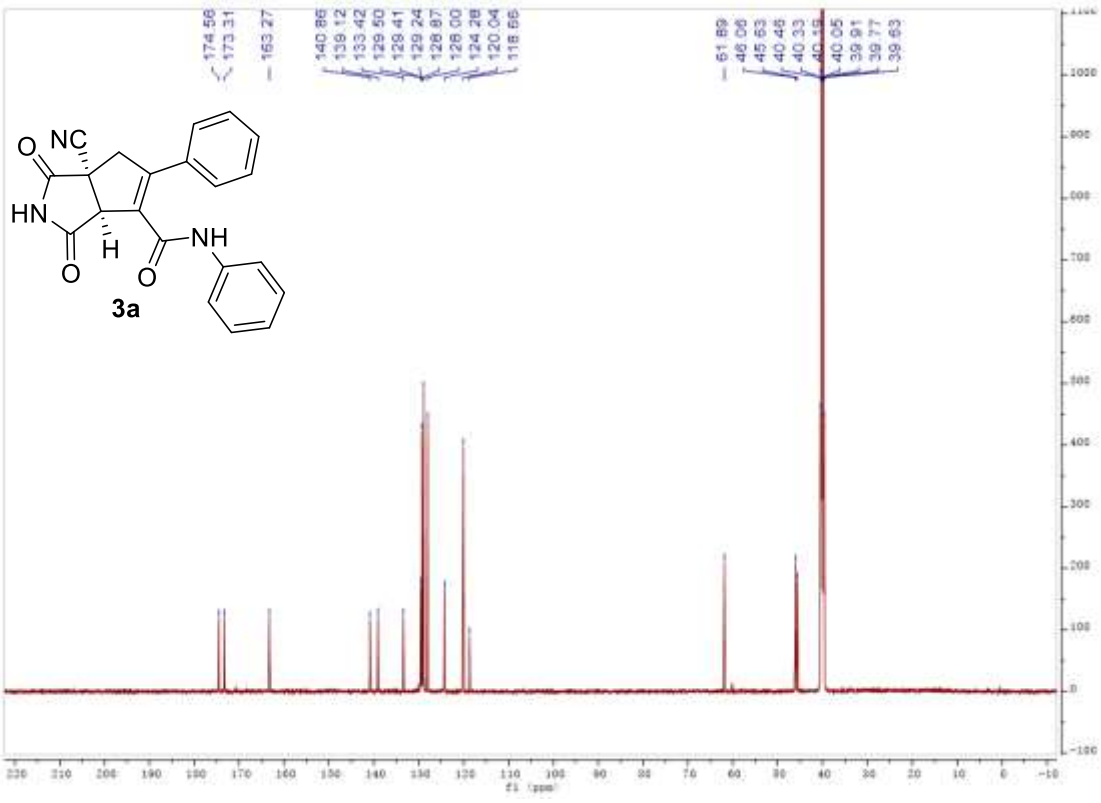
Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

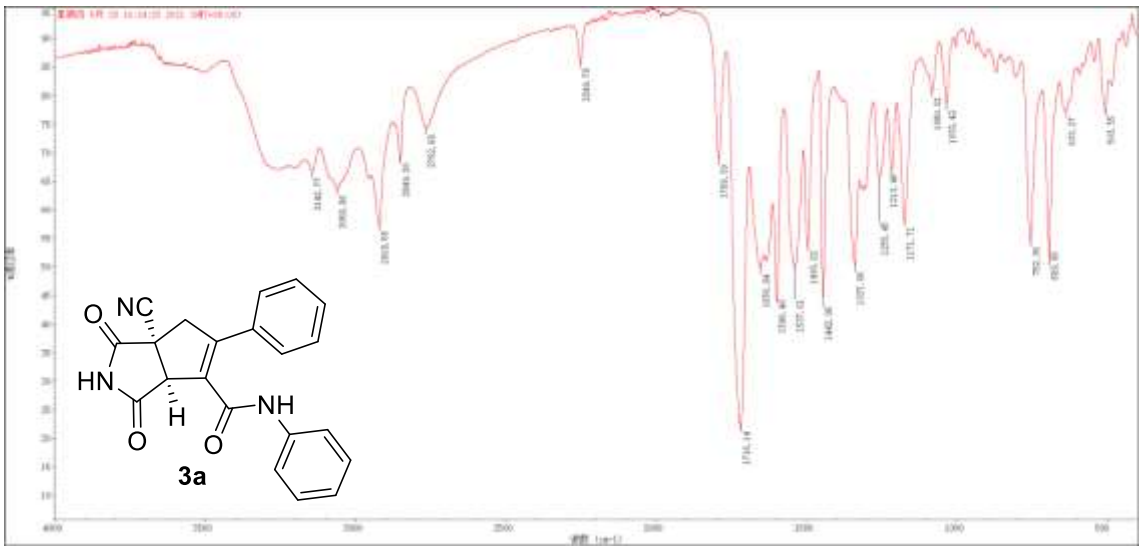
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author's name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
```

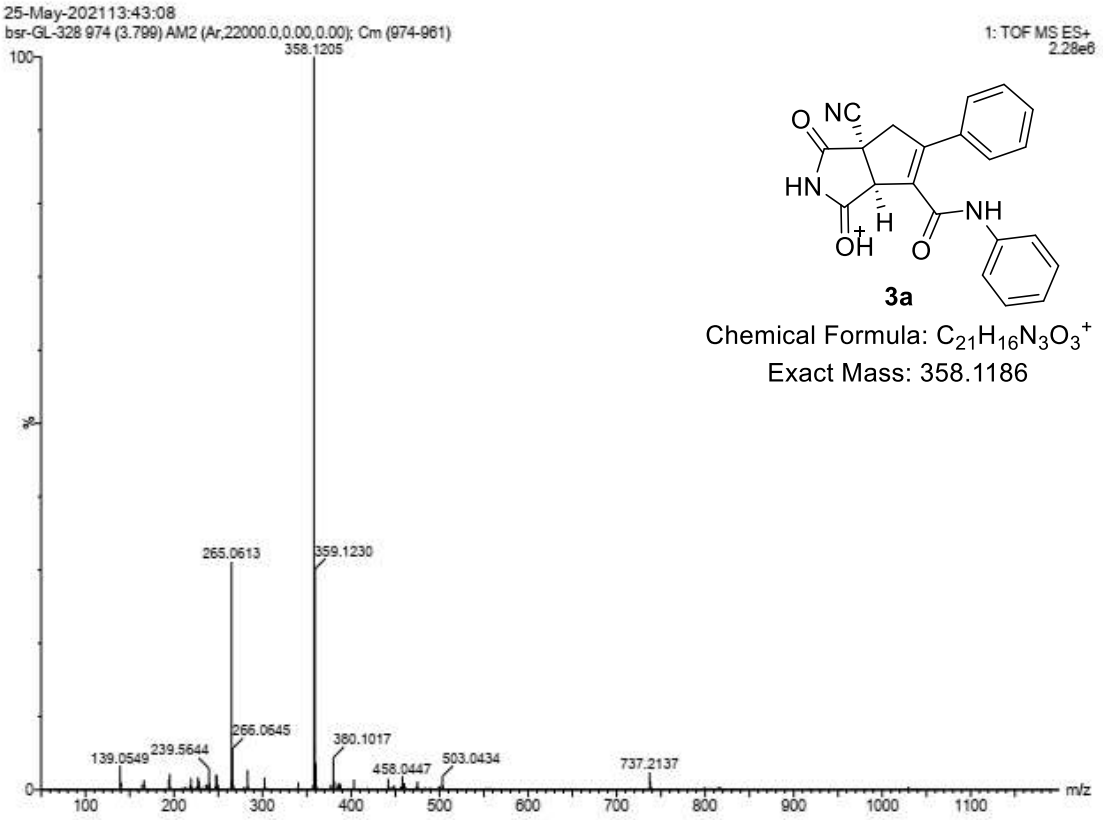
```
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

15. Copies of 1H NMR, 13C NMR, 19F NMR, IR and HRMS spectra of 3, 4a, 5-p, 6-p, intermediate C-3a, 3a-epo and 3a-all.





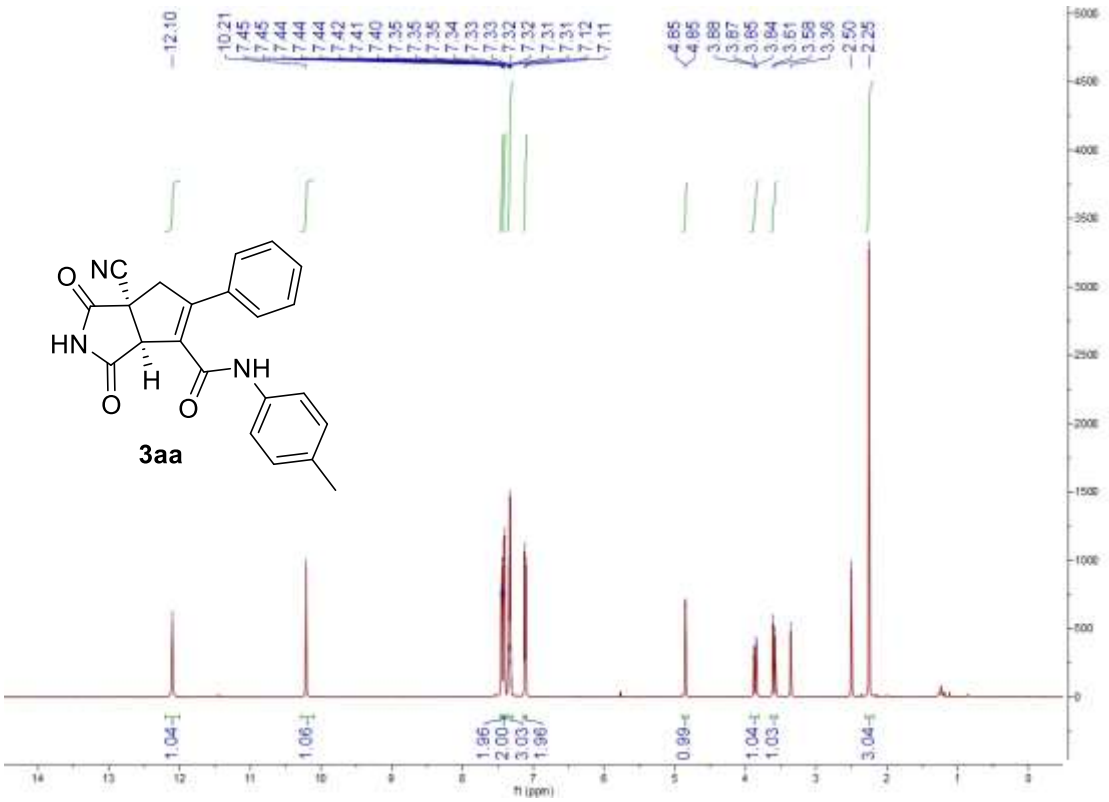


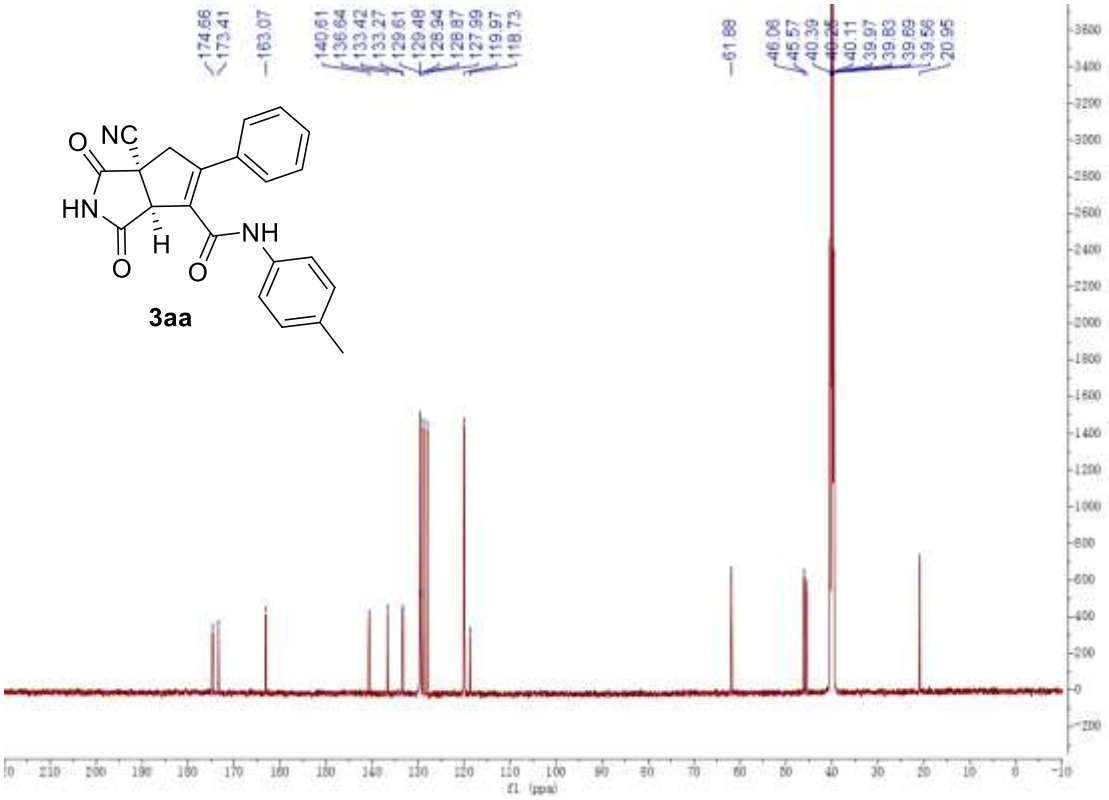


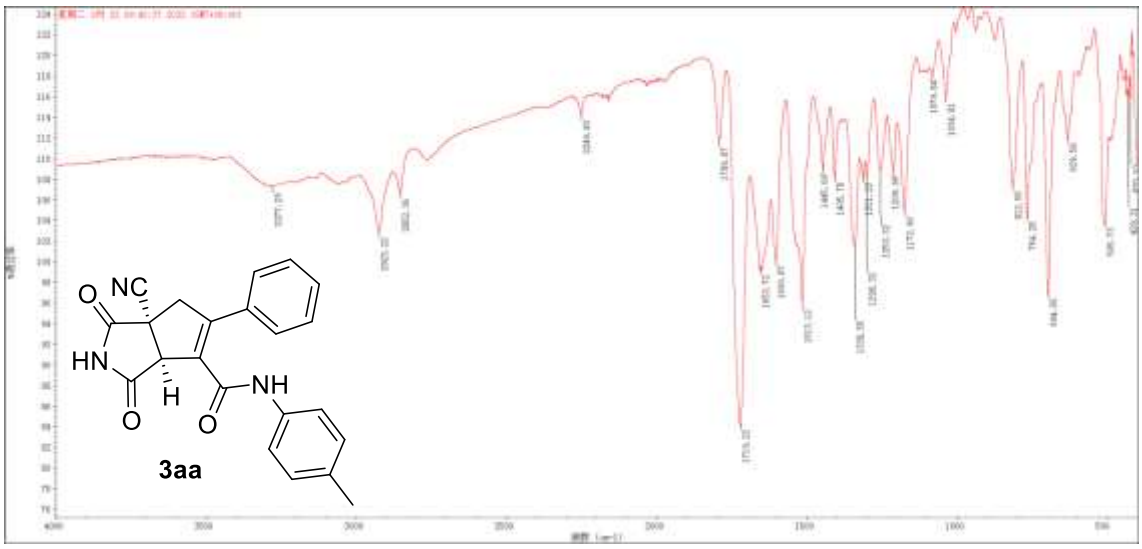
3a

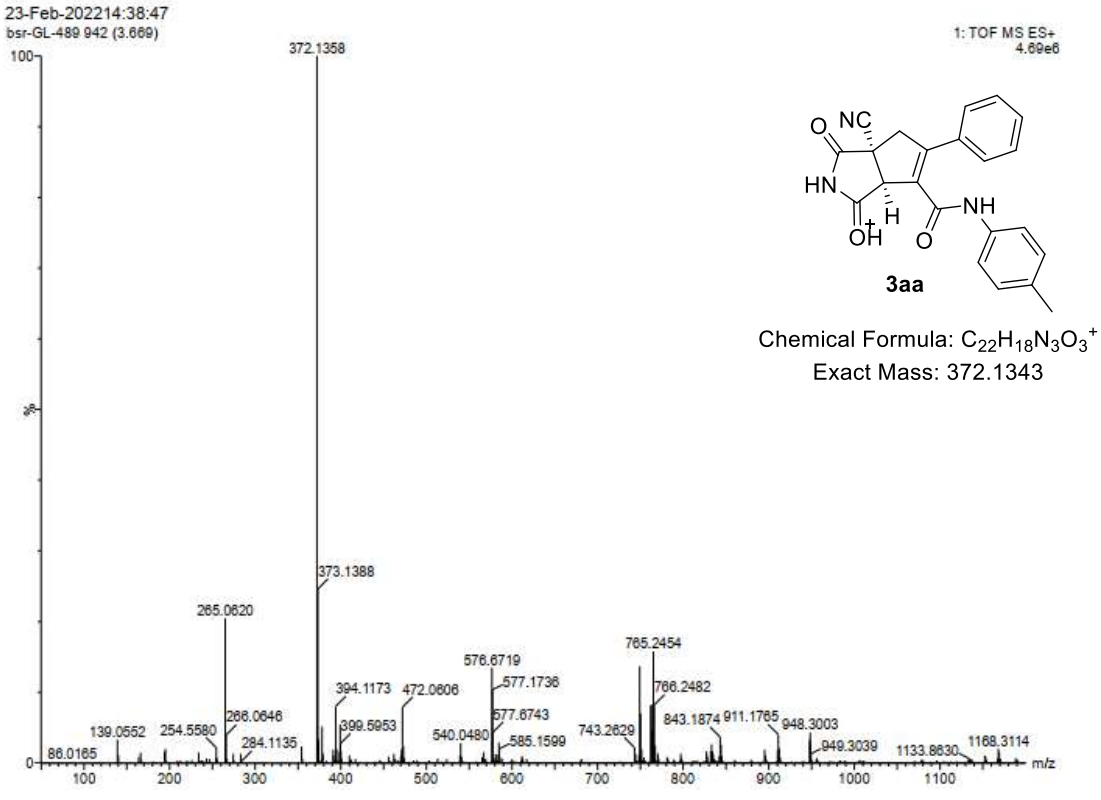
Chemical Formula: $C_{21}H_{16}N_3O_3^+$

Exact Mass: 358.1186

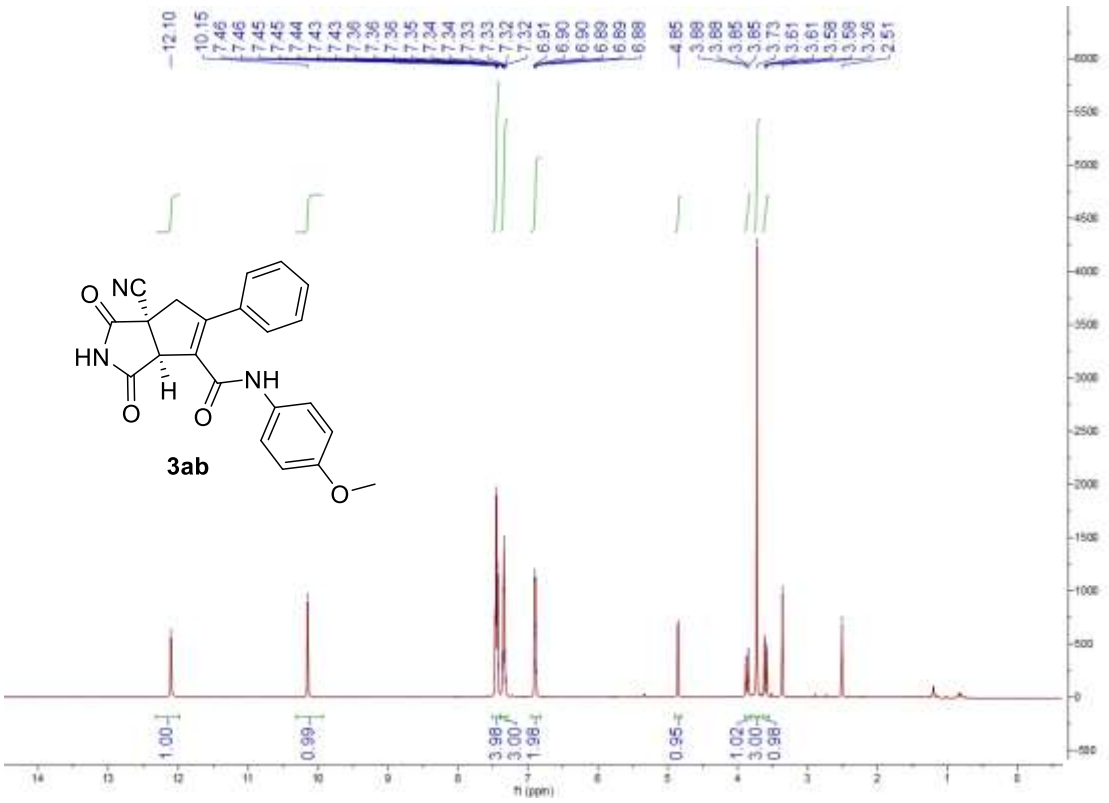

12.10
10.21
7.45
7.45
7.44
7.44
7.44
7.42
7.41
7.40
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.12
7.11
4.85
4.85
3.88
3.87
3.85
3.84
3.61
3.59
3.36
2.50
2.25
1.04
1.06
1.96
2.00
3.03
1.96
0.99
1.04
1.03
3.04
O
NC
HN
H
O
O
NH
3aa
f1 (ppm)


174.66
173.41
163.07
140.61
136.64
133.42
133.27
129.61
129.48
128.94
128.87
127.99
119.97
118.73
61.89
46.06
45.57
40.39
40.26
40.11
39.97
39.83
39.69
39.56
20.95
O
NC
HN
H
O
O
NH
3aa
f1 (ppm)





Chemical Formula: $C_{22}H_{18}N_3O_3^+$
Exact Mass: 372.1343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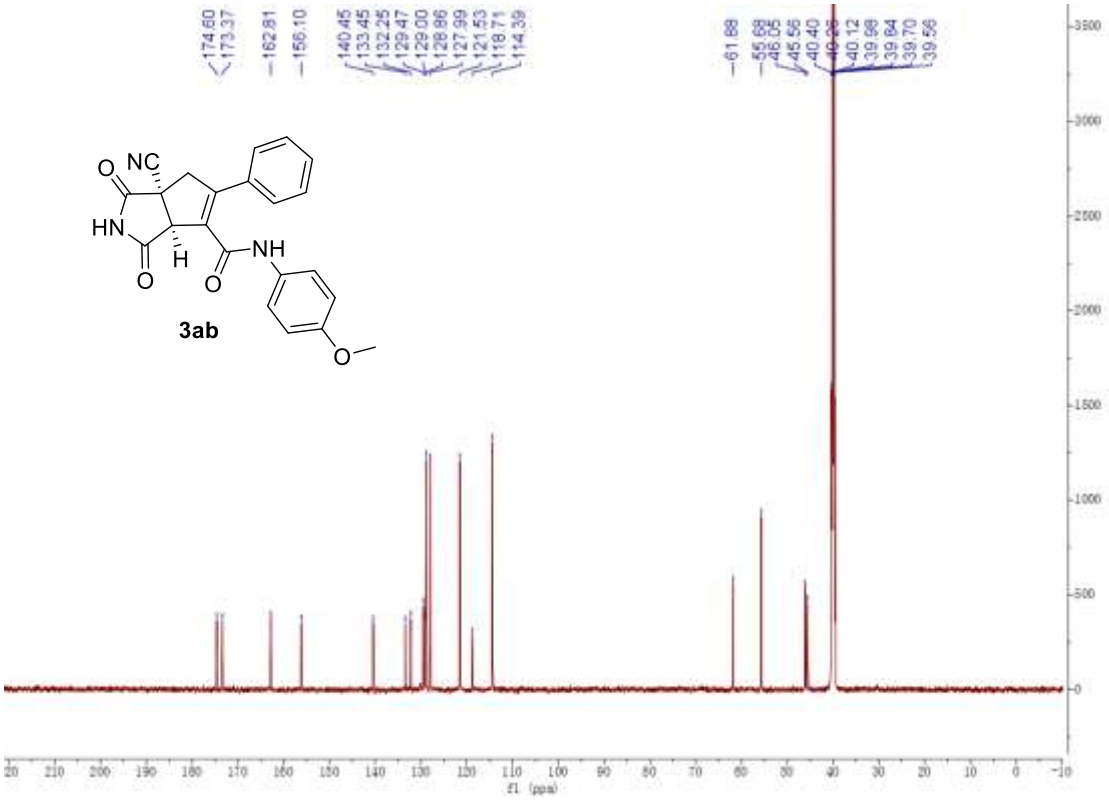
10.15
7.46
7.45
7.44
7.43
7.36
7.35
7.34
7.33
7.32
6.91
6.90
6.89
6.88
4.65
3.89
3.88
3.85
3.73
3.61
3.58
3.36
2.51
1.00
0.99
3.98
3.00
1.98
0.95
1.02
3.00
0.98
f1 (ppm)
O
NC
HN
H
O
NH
O
O
3ab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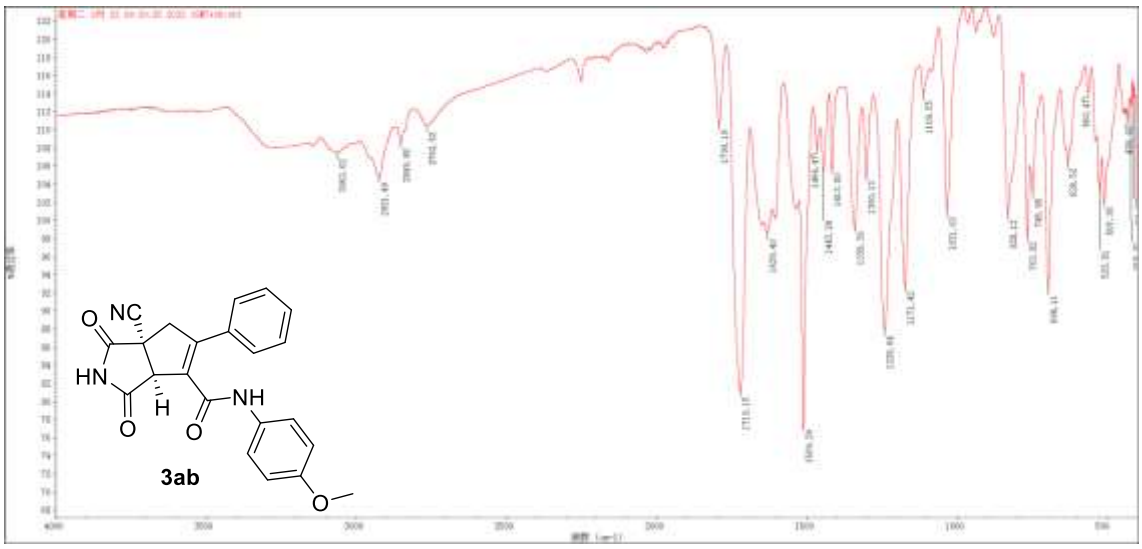
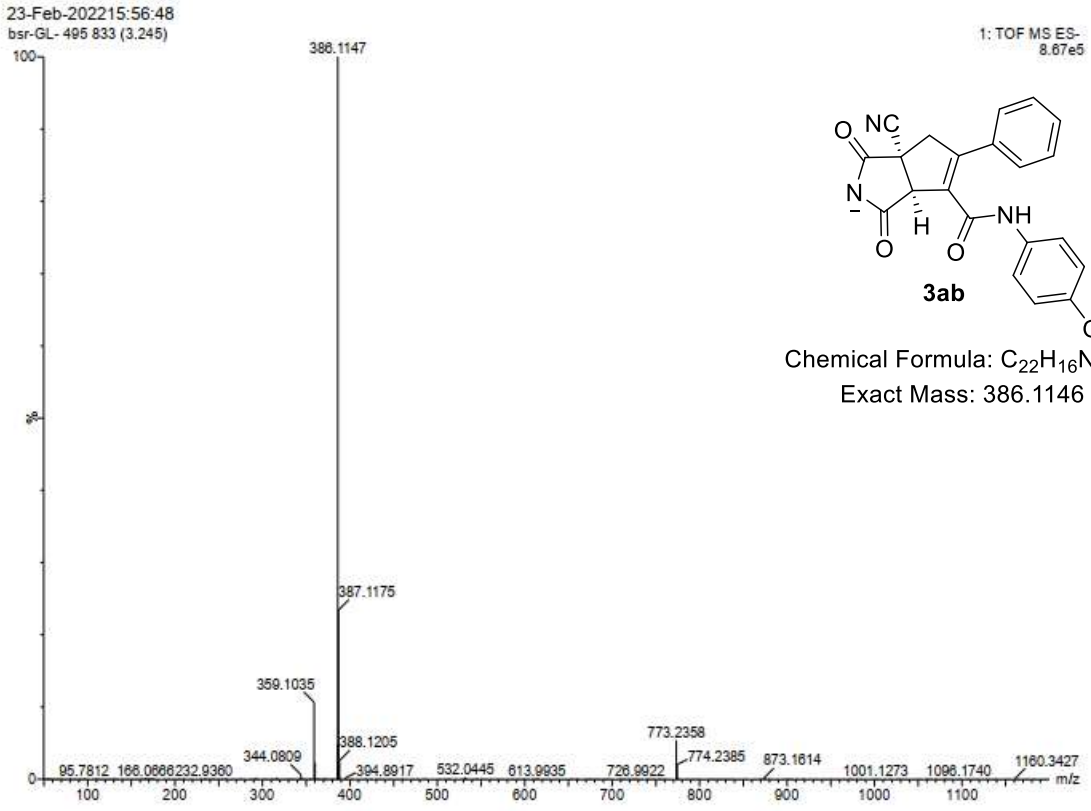
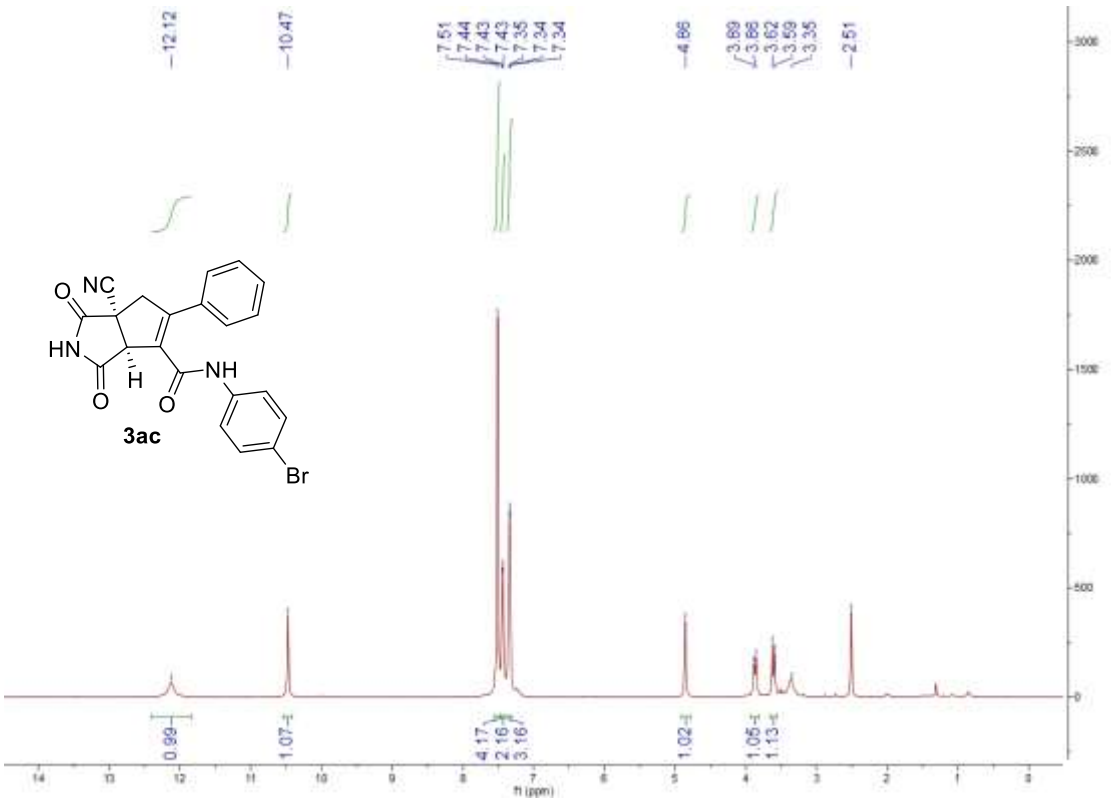
173.37
162.81
156.10
140.45
133.45
132.25
129.47
129.00
128.86
127.99
121.53
118.71
114.39
61.88
55.69
46.05
45.56
40.40
40.26
40.12
39.98
39.84
39.70
39.56
f1 (ppm)
O
NC
HN
H
O
NH
O
O
3ab





Chemical Formula: $C_{22}H_{16}N_3O_4^-$
Exact Mass: 386.1146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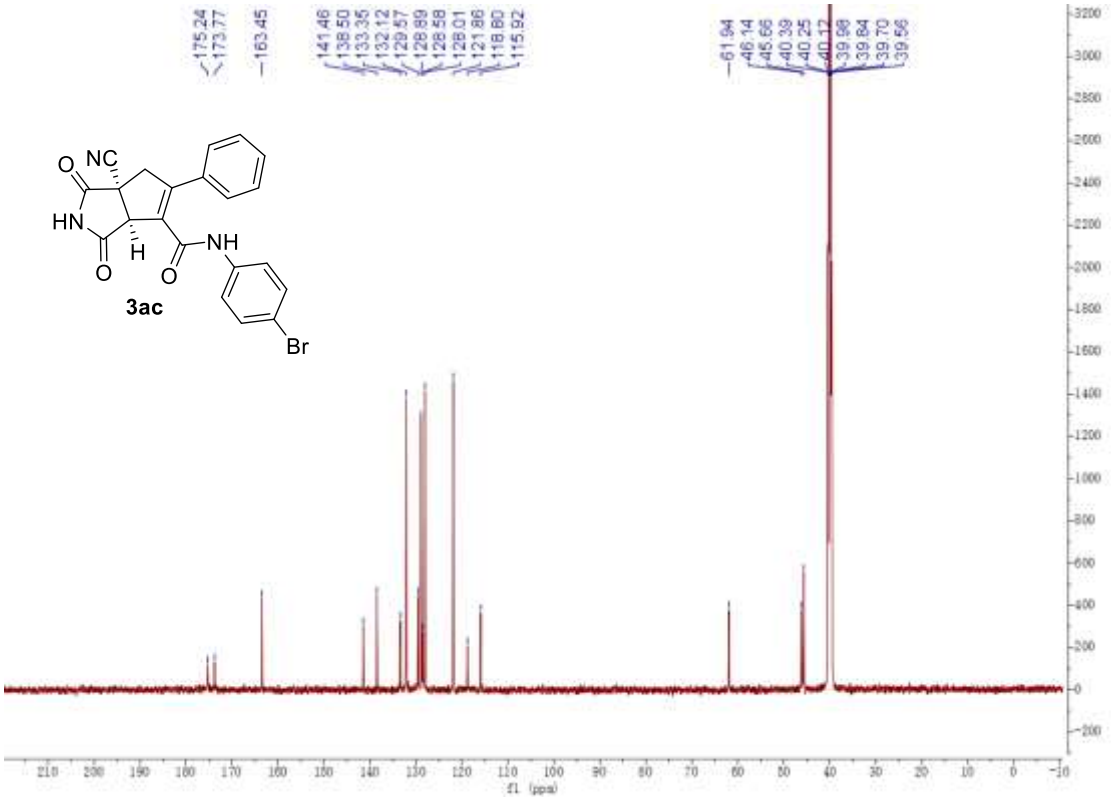
10.47
7.51
7.44
7.43
7.43
7.35
7.34
7.34
4.86
3.89
3.86
3.62
3.59
3.35
2.51
NC
O
HN
O
H
NH
O
Br
3ac
0.99
1.07
4.17
2.16
3.16
1.02
1.05
1.13
f1 (ppm)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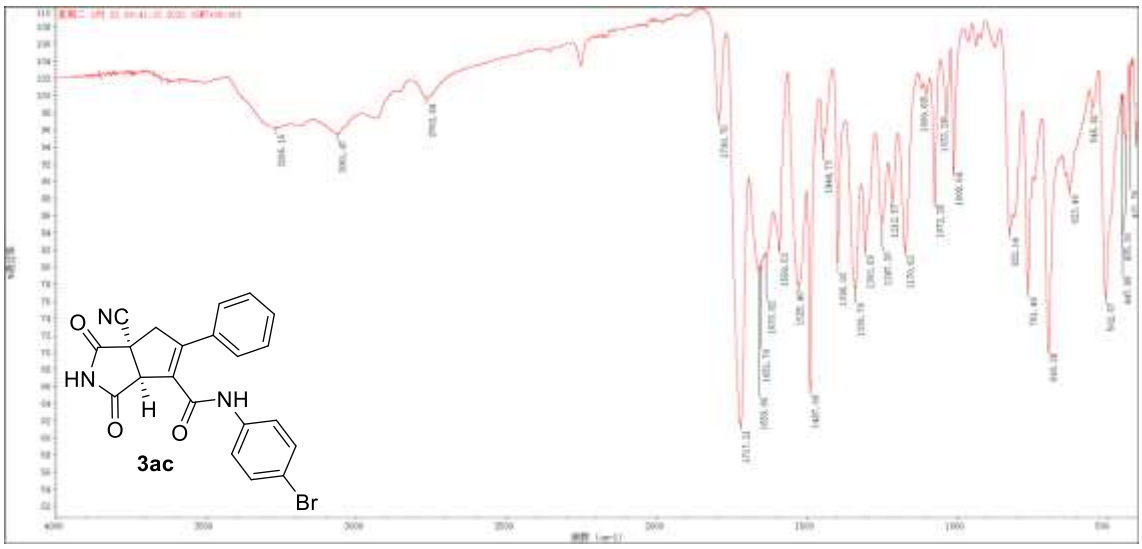
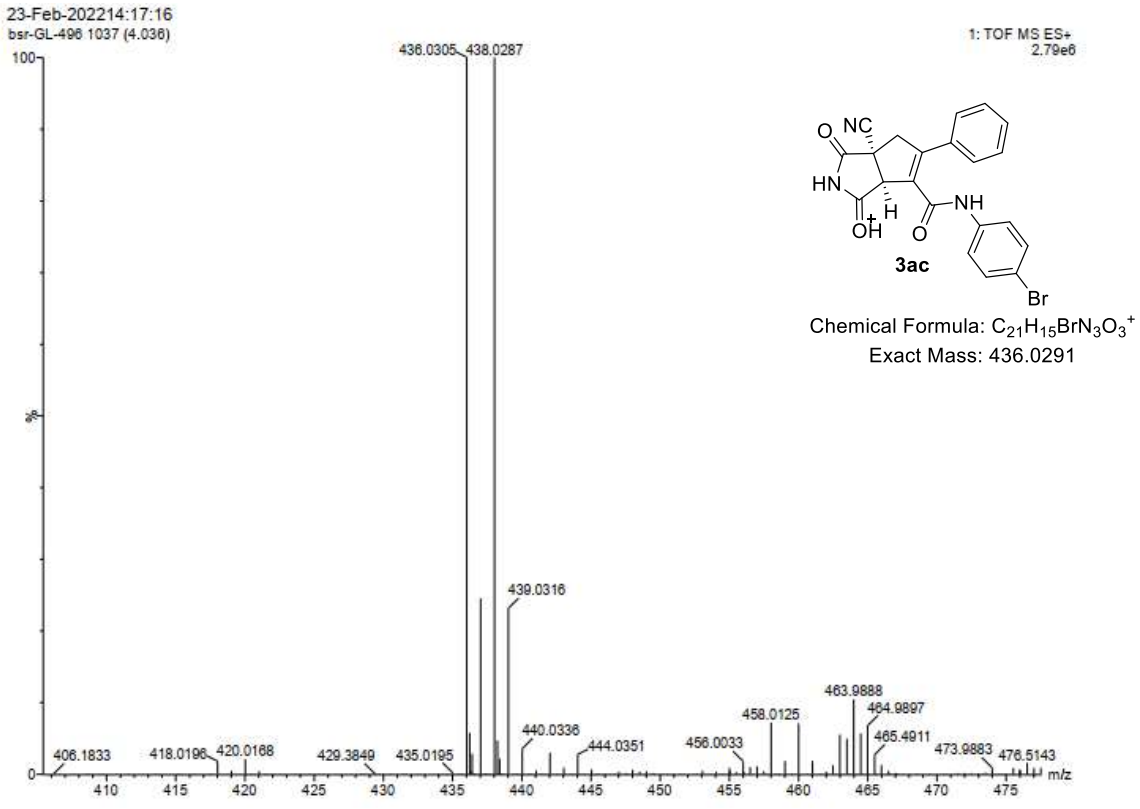
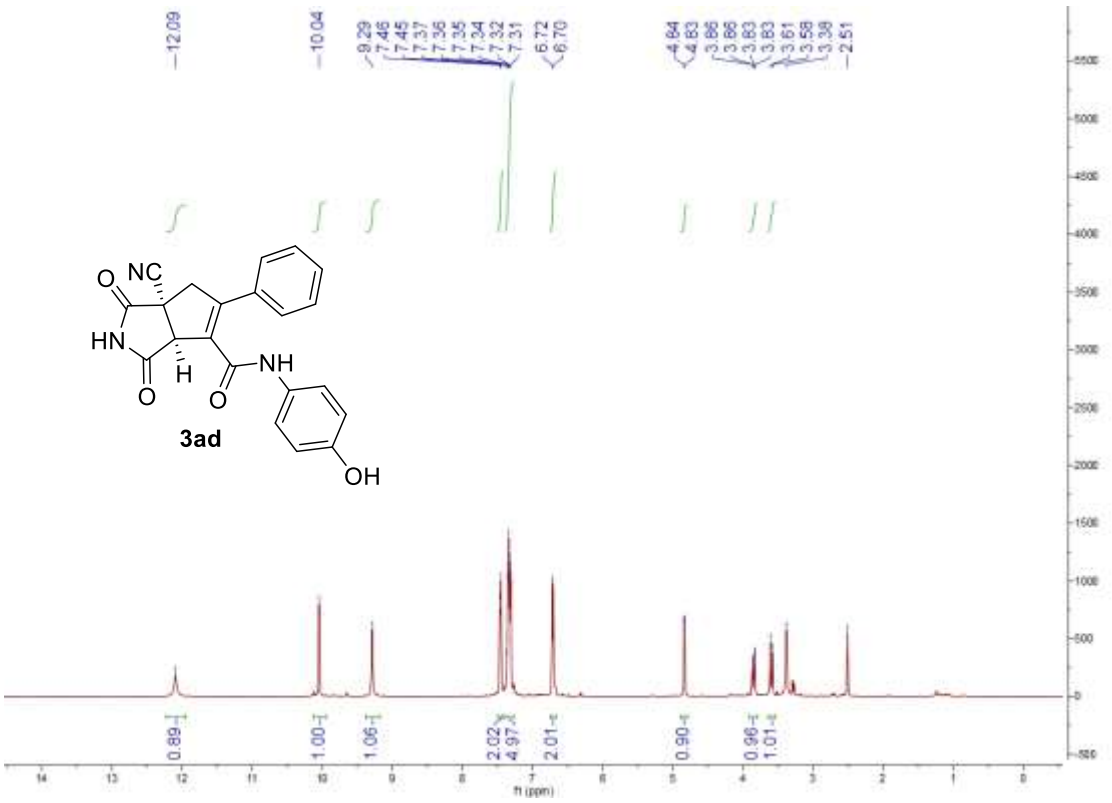
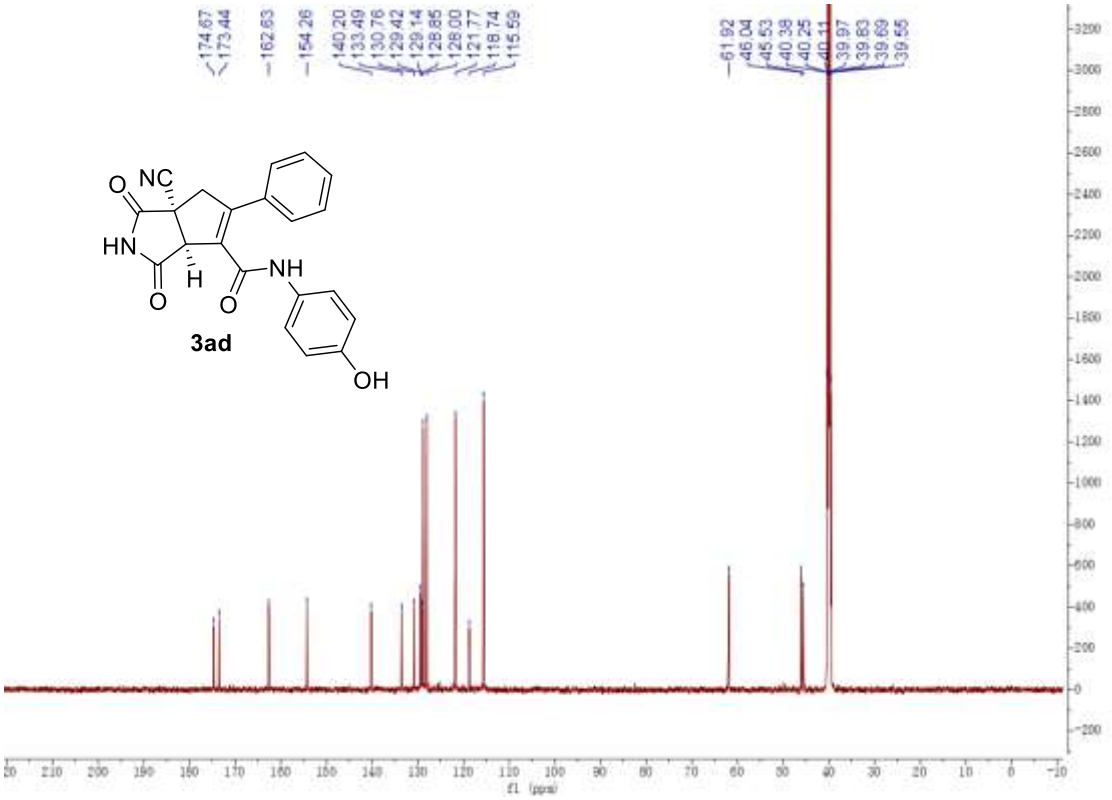
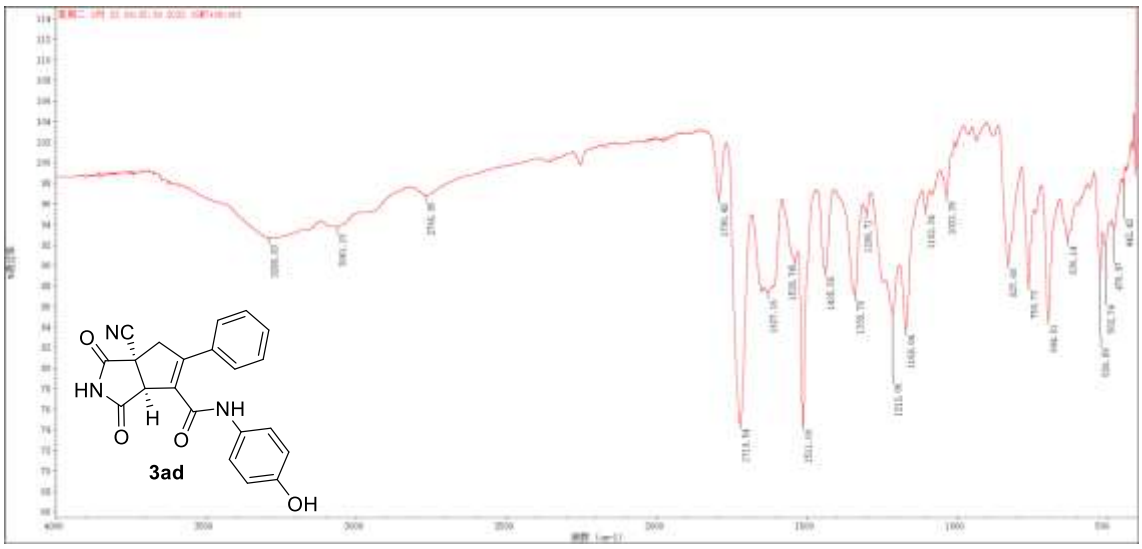
173.77
163.45
141.46
138.50
133.35
132.12
129.57
128.89
128.58
128.01
121.86
118.80
115.92
61.94
46.14
45.66
40.39
40.25
40.12
39.98
39.84
39.70
39.56
NC
O
HN
O
H
NH
O
Br
3ac
f1 (ppm)

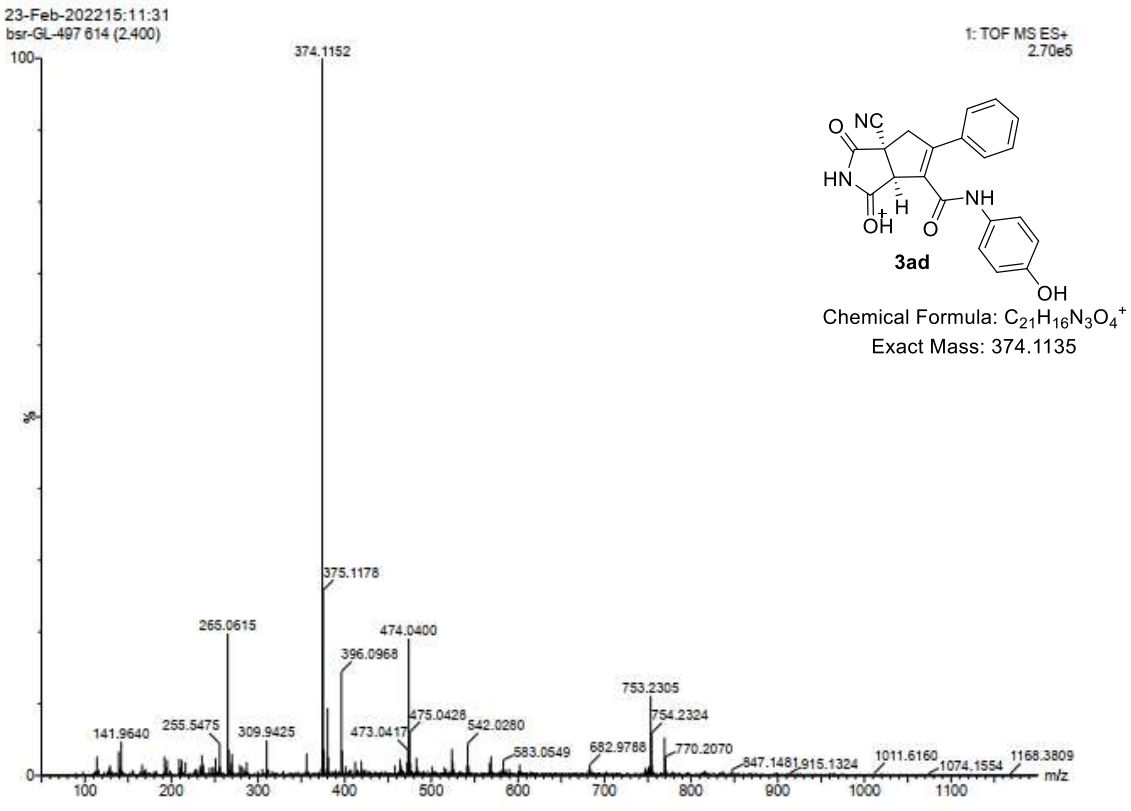

O
NC
HN
H
O
O
NH
3ac
Br


23-Feb-202214:17:16
bsr-GL-496 1037 (4.036)
1: TOF MS ES+
2.79e6
100
%
0
436.0305
438.0287
439.0316
406.1833
418.0196
420.0168
429.3849
435.0195
440.0336
444.0351
456.0033
458.0125
463.9888
464.9897
465.4911
473.9883
476.5143
410
415
420
425
430
435
440
445
450
455
460
465
470
475
m/z
O
NC
HN
H
OH
O
NH
3ac
Br
Chemical Formula: $C_{21}H_{15}BrN_3O_3^+$
Exact Mass: 436.0291


12.09
10.04
9.29
7.46
7.45
7.37
7.36
7.35
7.34
7.32
7.31
6.72
6.70
4.84
4.83
3.86
3.86
3.83
3.83
3.61
3.58
3.38
2.51
NC
O
HN
H
NH
O
O
OH
3ad
0.89
1.00
1.06
2.02
4.97
2.01
0.90
0.96
1.01
f1 (ppm)

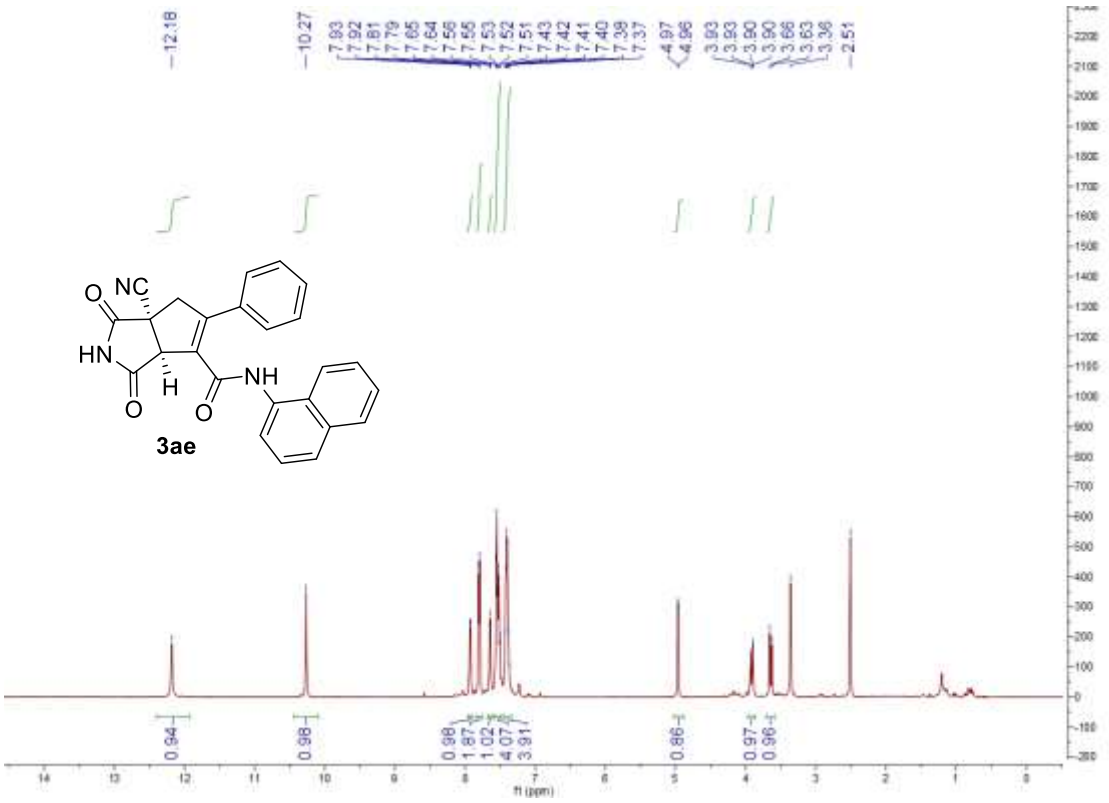

174.67
173.44
162.63
154.26
140.20
133.49
130.76
129.42
129.14
128.85
128.00
121.77
118.74
115.59
61.92
46.04
45.53
40.38
40.25
40.11
39.97
39.83
39.69
39.55
NC
O
HN
H
NH
O
O
OH
3ad
f1 (ppm)

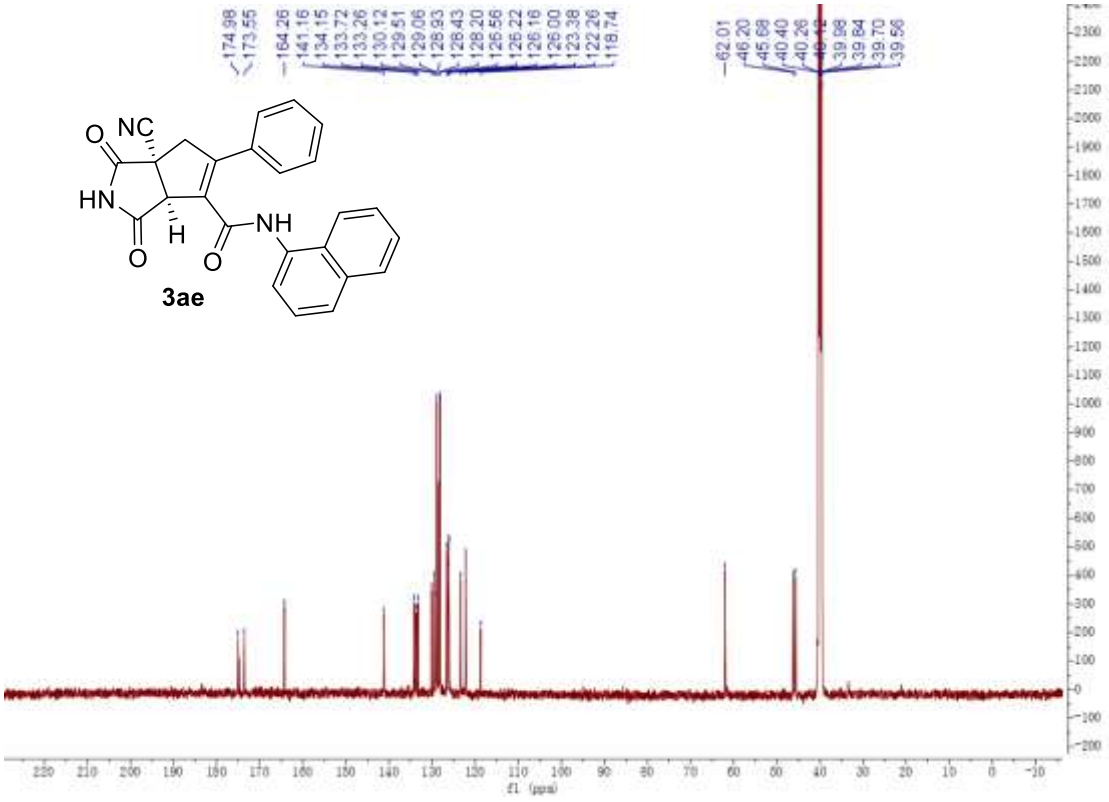




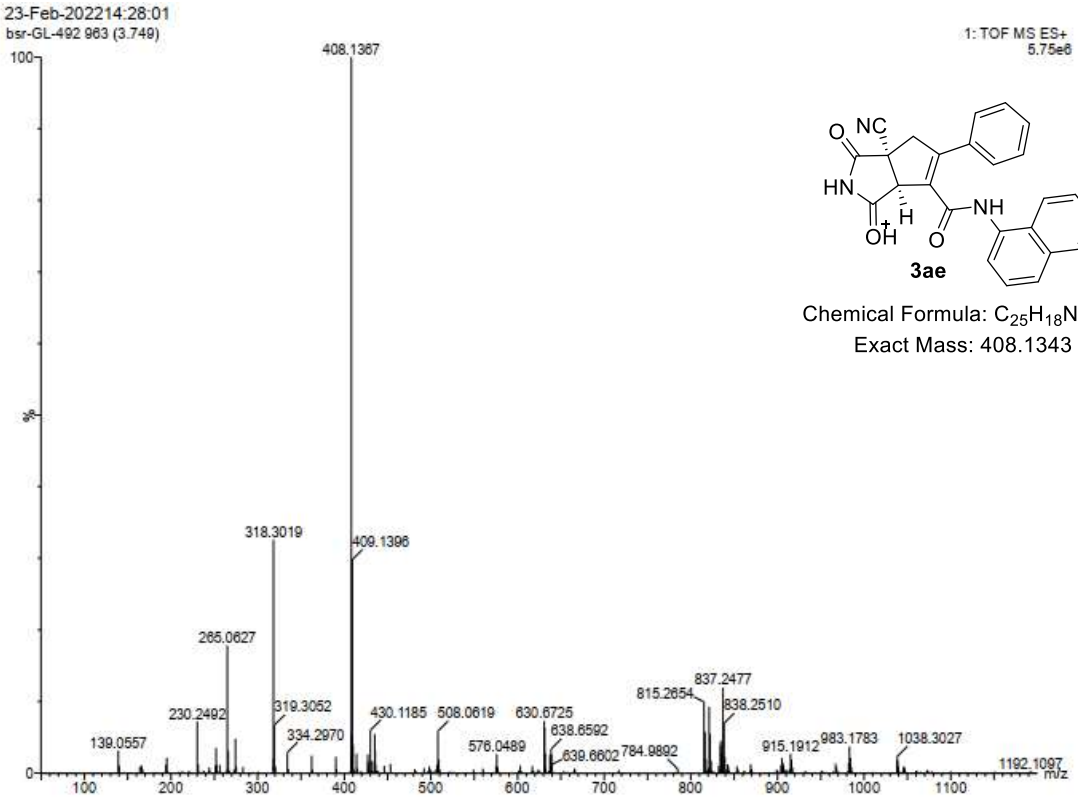
Chemical Formula: $C_{21}H_{16}N_3O_4^+$

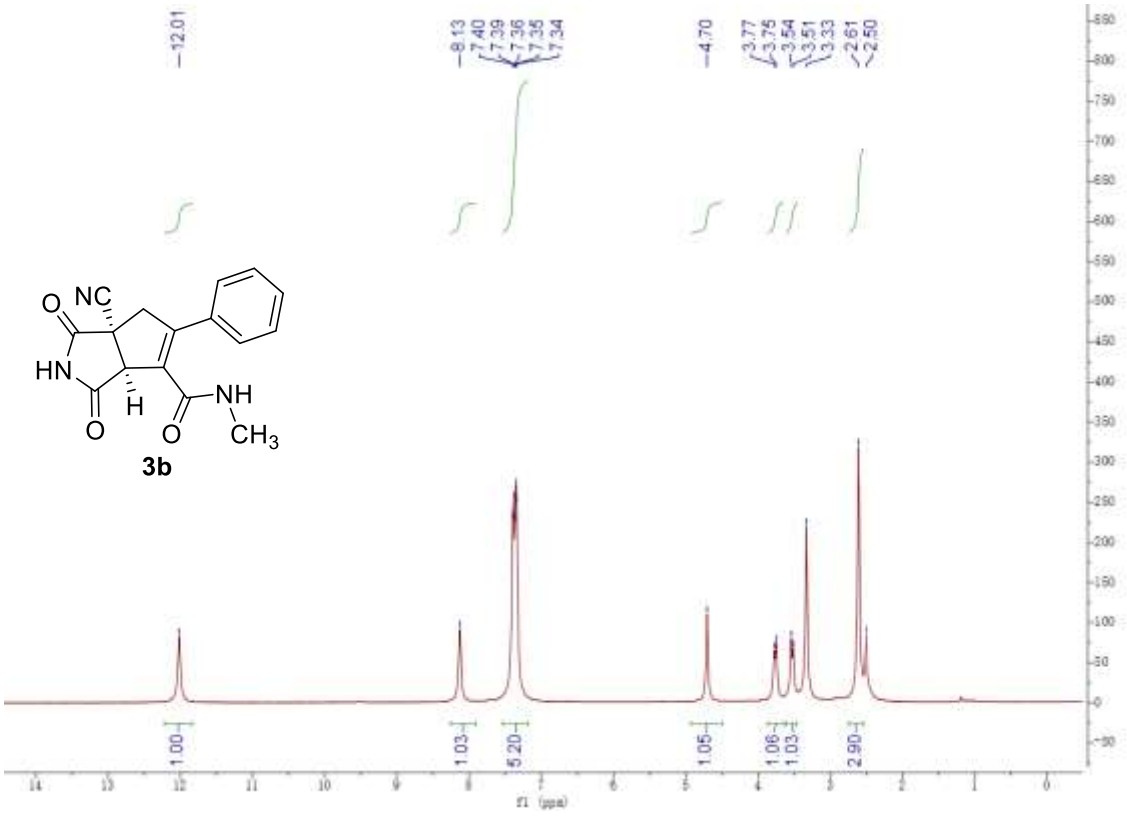
Exact Mass: 374.1135


12.18
10.27
7.93
7.92
7.81
7.79
7.65
7.64
7.56
7.55
7.53
7.52
7.51
7.43
7.42
7.41
7.40
7.39
7.37
4.97
4.96
3.93
3.93
3.90
3.90
3.66
3.63
3.36
2.51
0.94
0.98
0.98
1.87
1.02
4.07
3.91
0.86
0.97
0.96
f1 (ppm)
O
NC
HN
H
O
NH
O
3ae


174.98
173.55
164.26
141.16
134.15
133.72
133.26
130.12
129.51
129.06
128.93
128.43
128.20
126.56
126.22
126.16
126.00
123.38
122.26
118.74
62.01
46.20
45.68
40.40
40.26
39.98
39.84
39.70
39.56
f1 (ppm)
O
NC
HN
H
O
NH
O
3ae

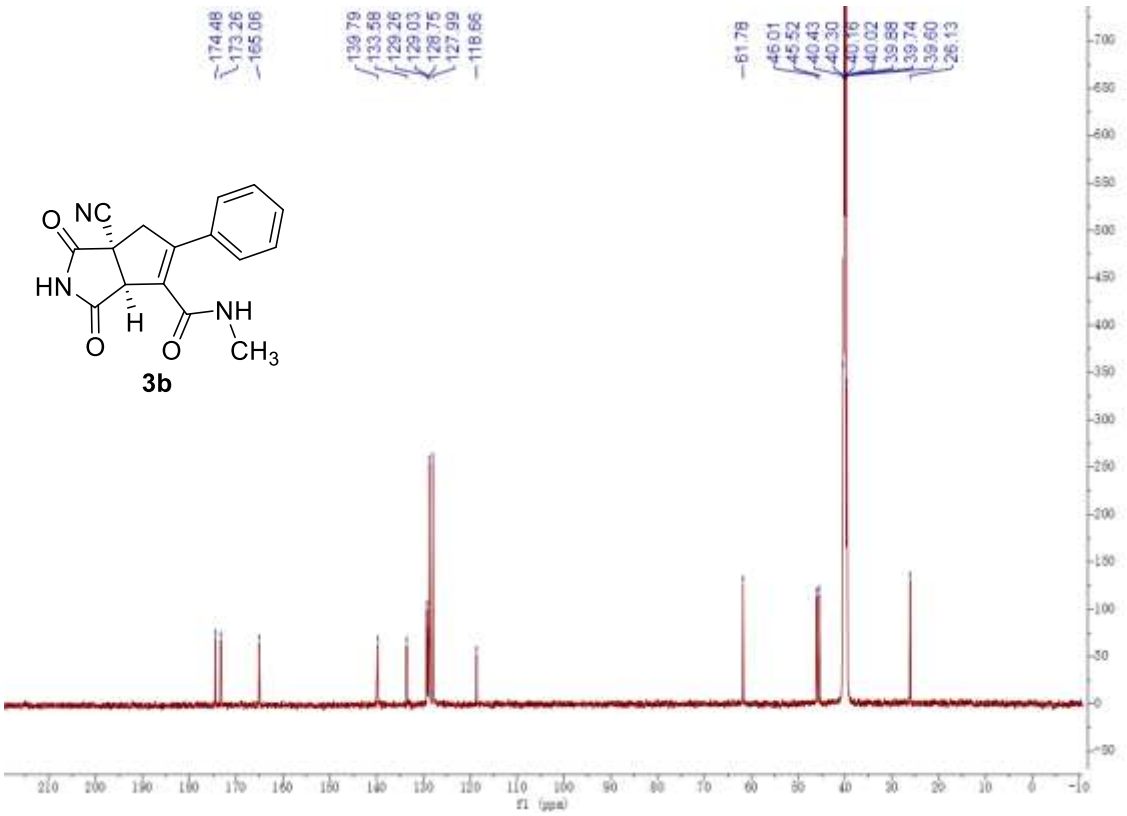

O
NC
HN
H
O
O
NH
3ae


23-Feb-202214:28:01
bsr-GL-492 963 (3.749)
1: TOF MS ES+
5.75e6
100
%
0
408.1367
409.1396
318.3019
265.0627
319.3052
230.2492
139.0557
334.2970
430.1185
508.0619
630.6725
638.6592
639.6602
576.0489
784.9892
815.2654
837.2477
838.2510
915.1912
983.1783
1038.3027
1192.1097
100
200
300
400
500
600
700
800
900
1000
1100
m/z
O
NC
HN
H
OH
O
NH
3ae
Chemical Formula: $C_{25}H_{18}N_3O_3^+$
Exact Mass: 408.1343


12.01
8.13
7.40
7.39
7.36
7.35
7.34
4.70
3.77
3.75
3.54
3.51
3.33
2.61
2.50
1.00
1.03
5.20
1.05
1.06
1.03
2.90
f1 (ppm)

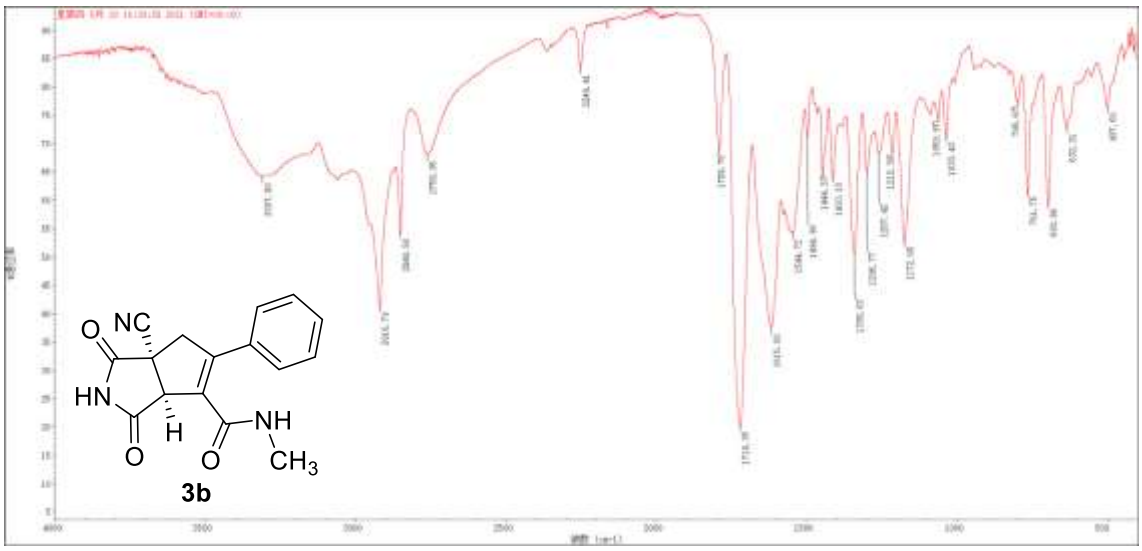
O
NC
HN
H
O
O
NH
CH3

3b

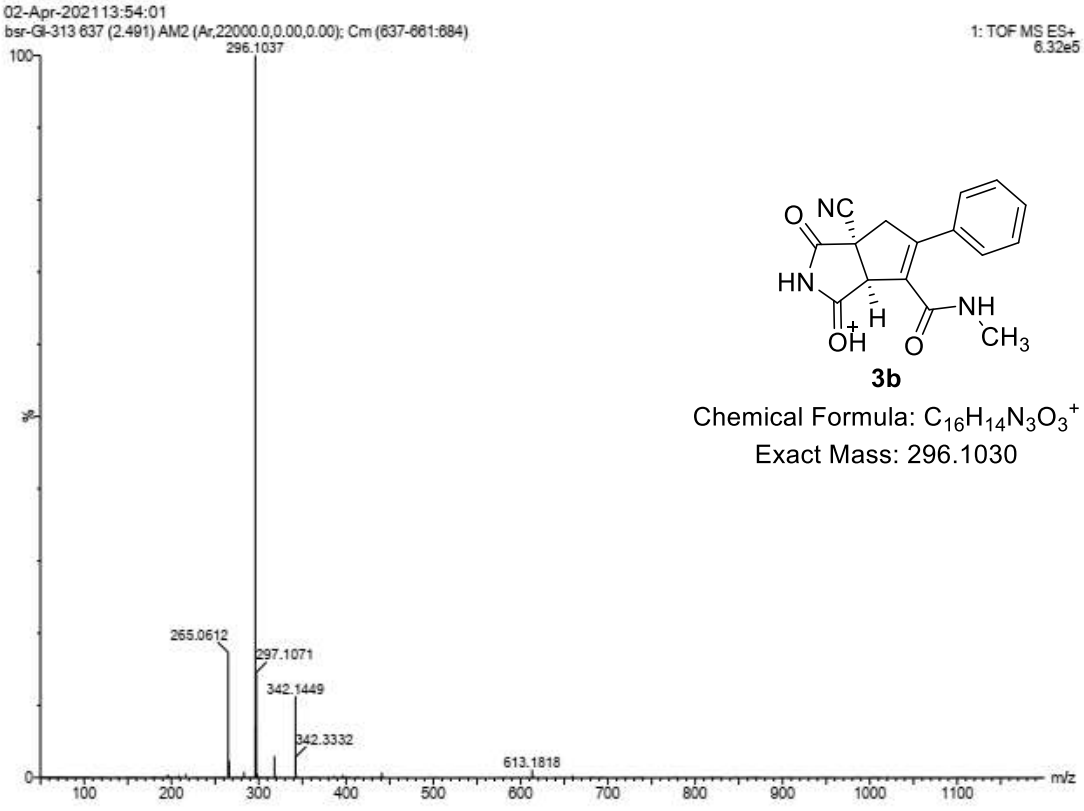

174.48
173.26
165.06
139.79
133.58
129.26
129.03
128.75
127.99
118.66
61.78
46.01
45.52
40.43
40.30
40.16
40.02
39.88
39.74
39.60
26.13
f1 (ppm)

O
NC
HN
H
O
O
NH
CH3

3b



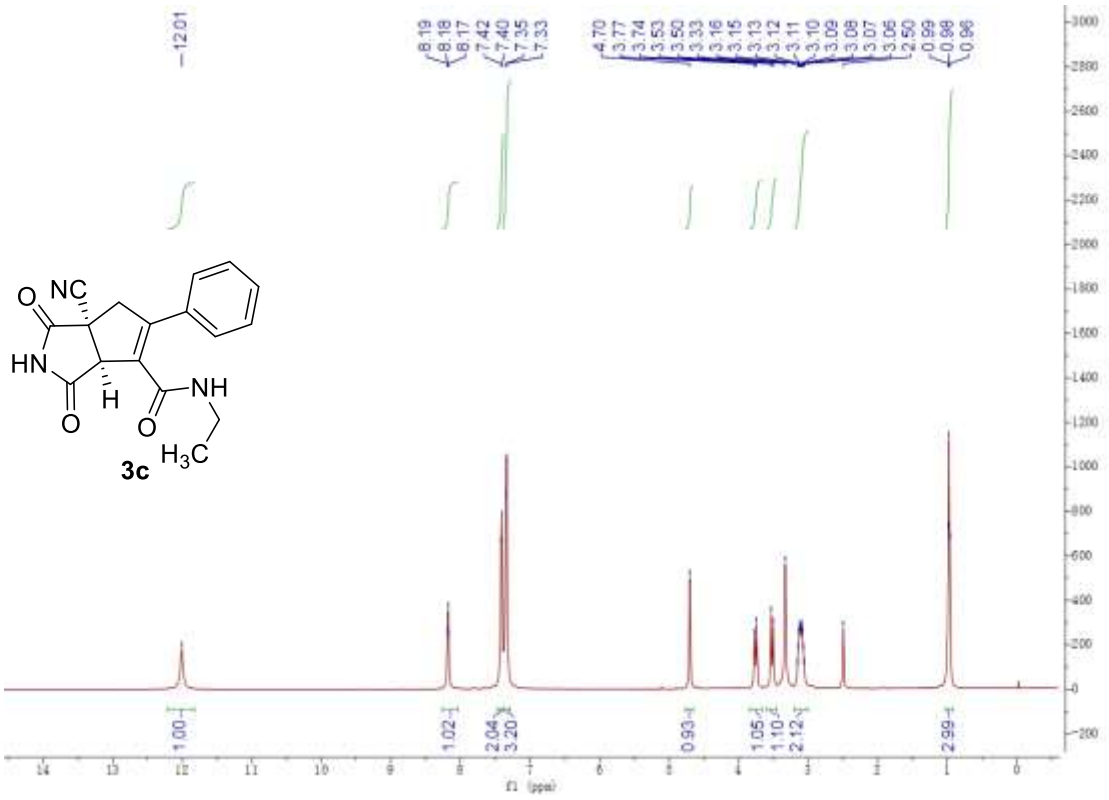
3b

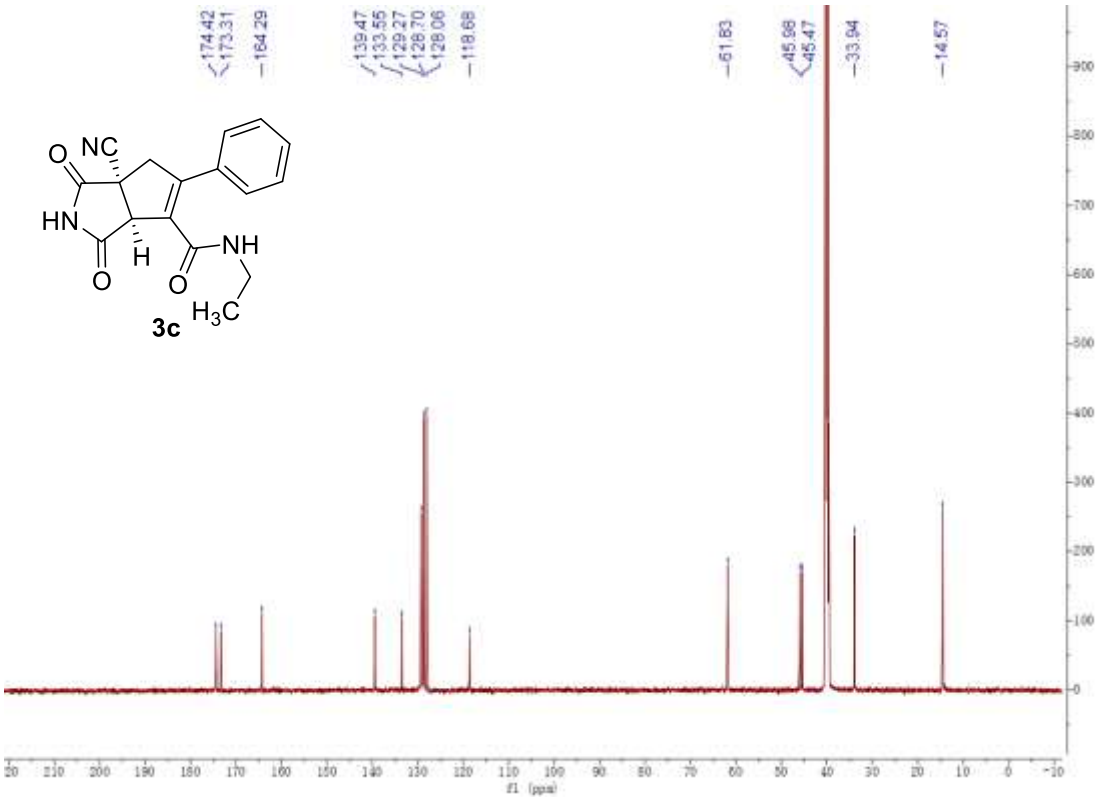


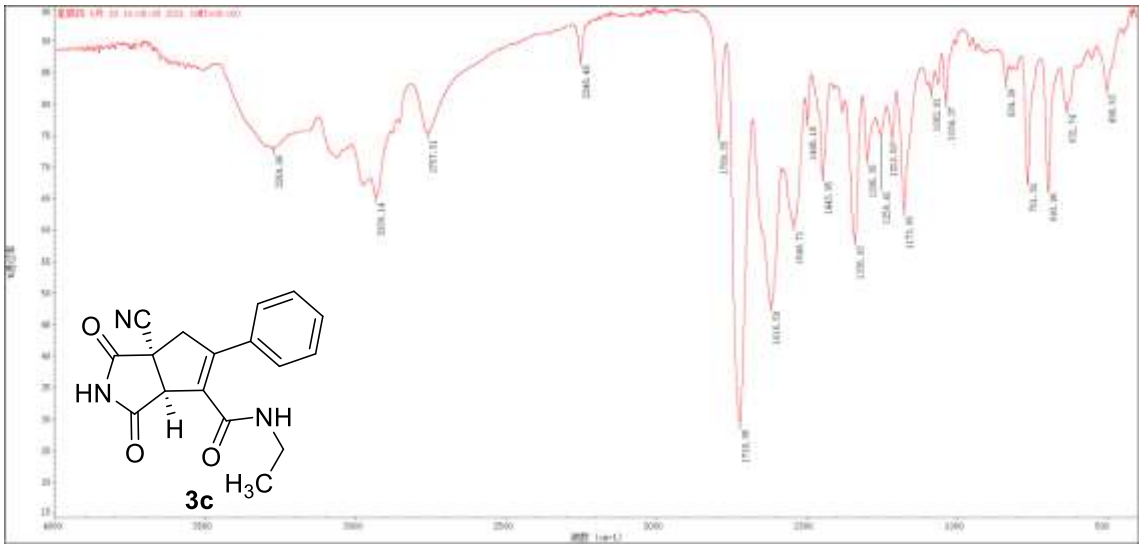
3b

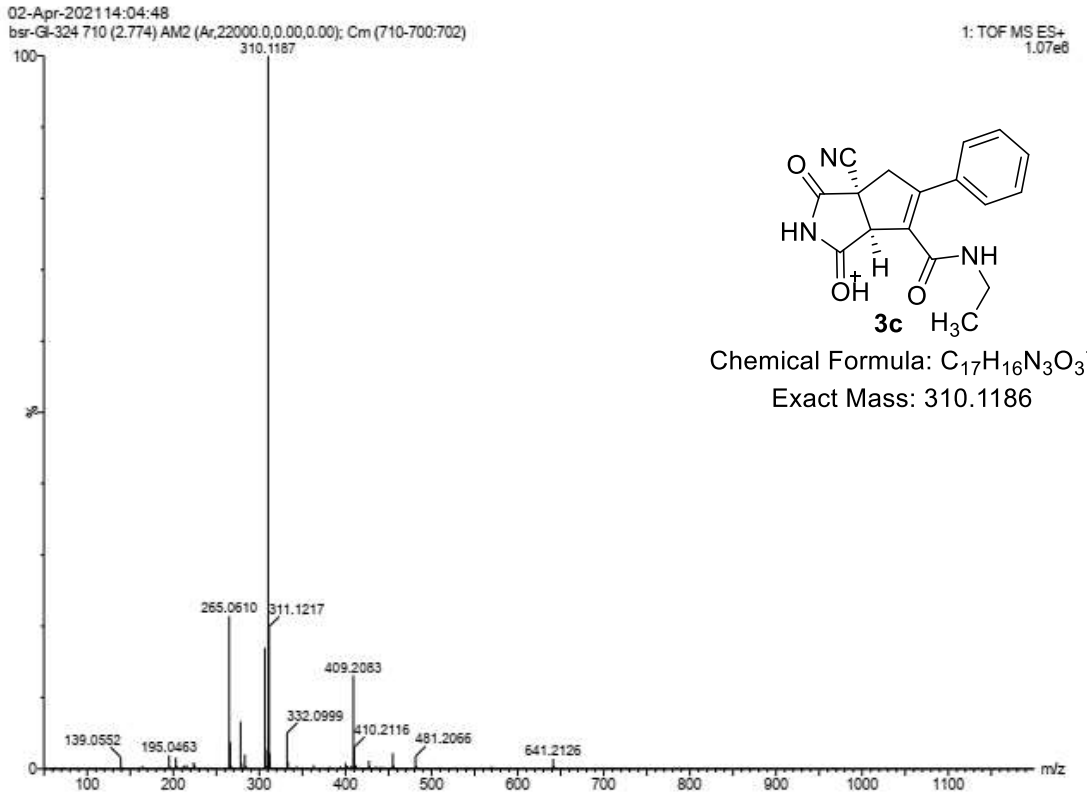
Chemical Formula: $C_{16}H_{14}N_3O_3^+$

Exact Mass: 296.1030


12.01
8.19
8.18
8.17
7.42
7.40
7.35
7.33
4.70
3.77
3.74
3.53
3.50
3.33
3.16
3.15
3.13
3.12
3.11
3.10
3.09
3.08
3.07
3.06
2.50
0.99
0.98
0.96
1.00
1.02
2.04
3.20
0.93
1.05
1.10
2.12
2.99
f1 (ppm)
3c

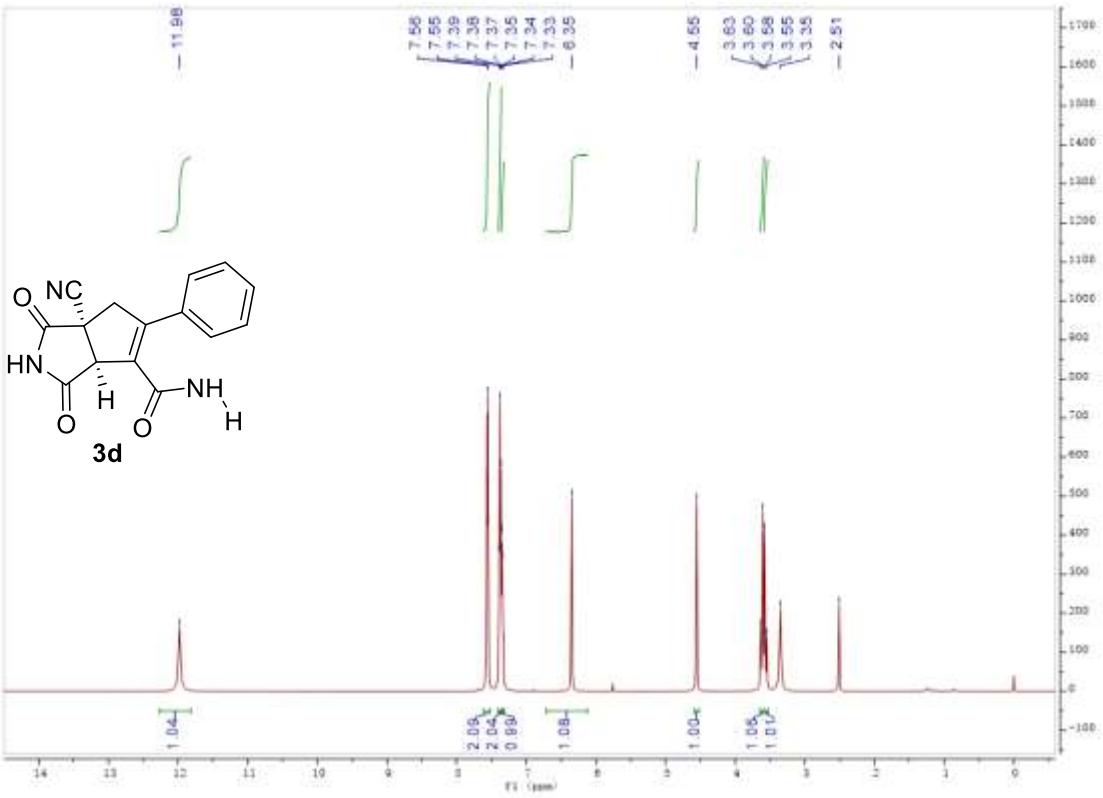

174.42
173.31
164.29
139.47
133.55
129.27
128.70
128.06
118.68
61.83
45.98
45.47
33.94
14.57
f1 (ppm)
3c

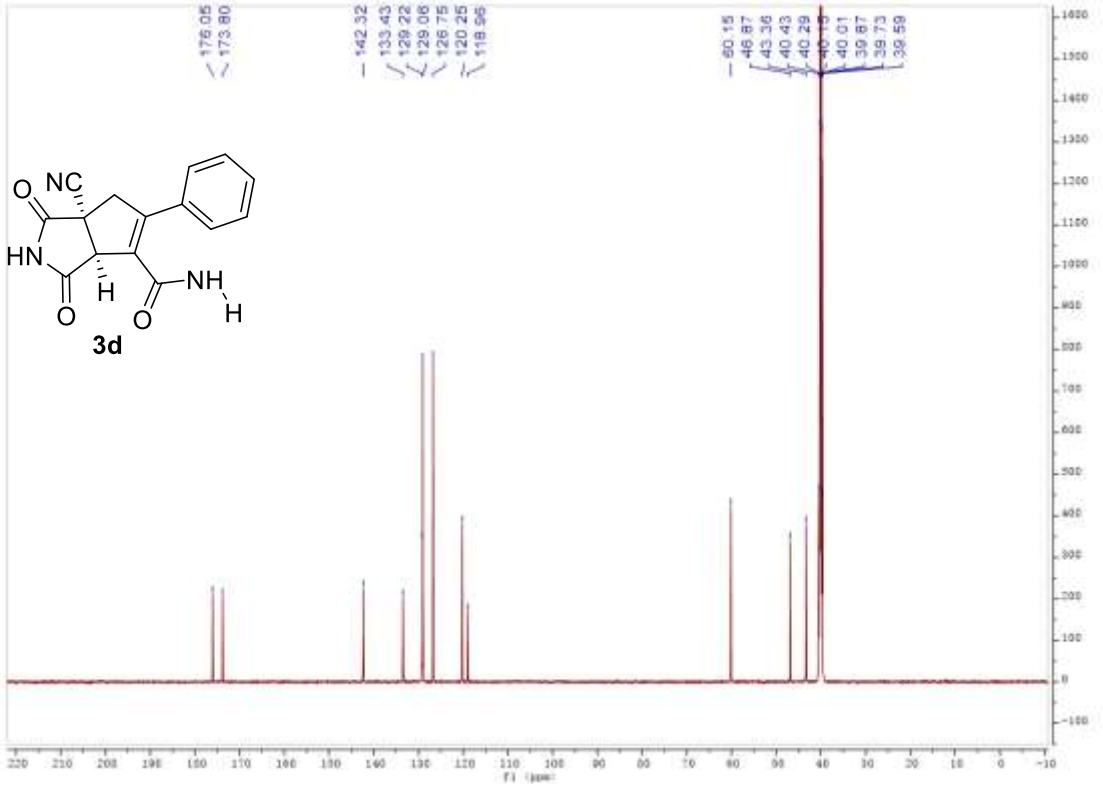


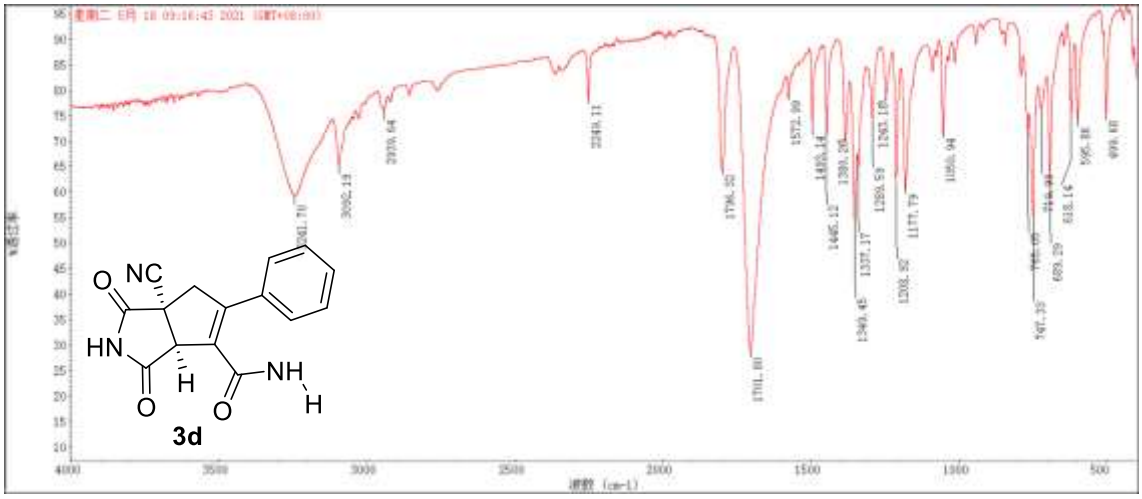


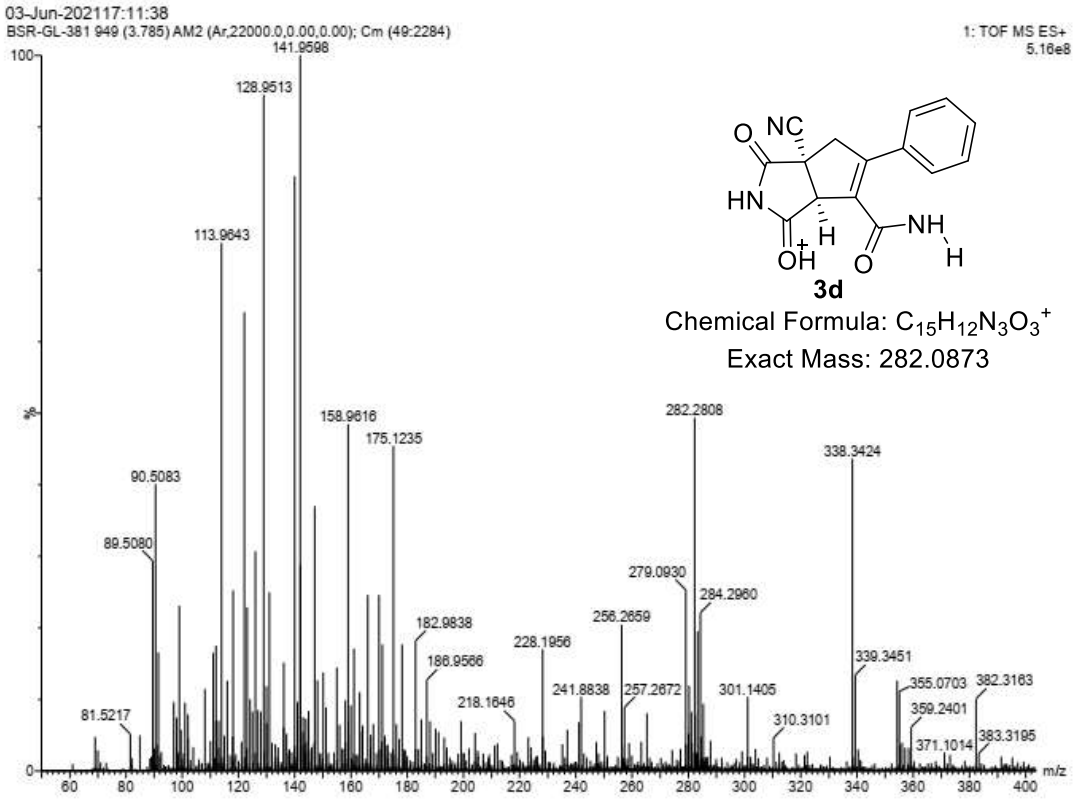
Chemical Formula: $C_{17}H_{16}N_3O_3^+$

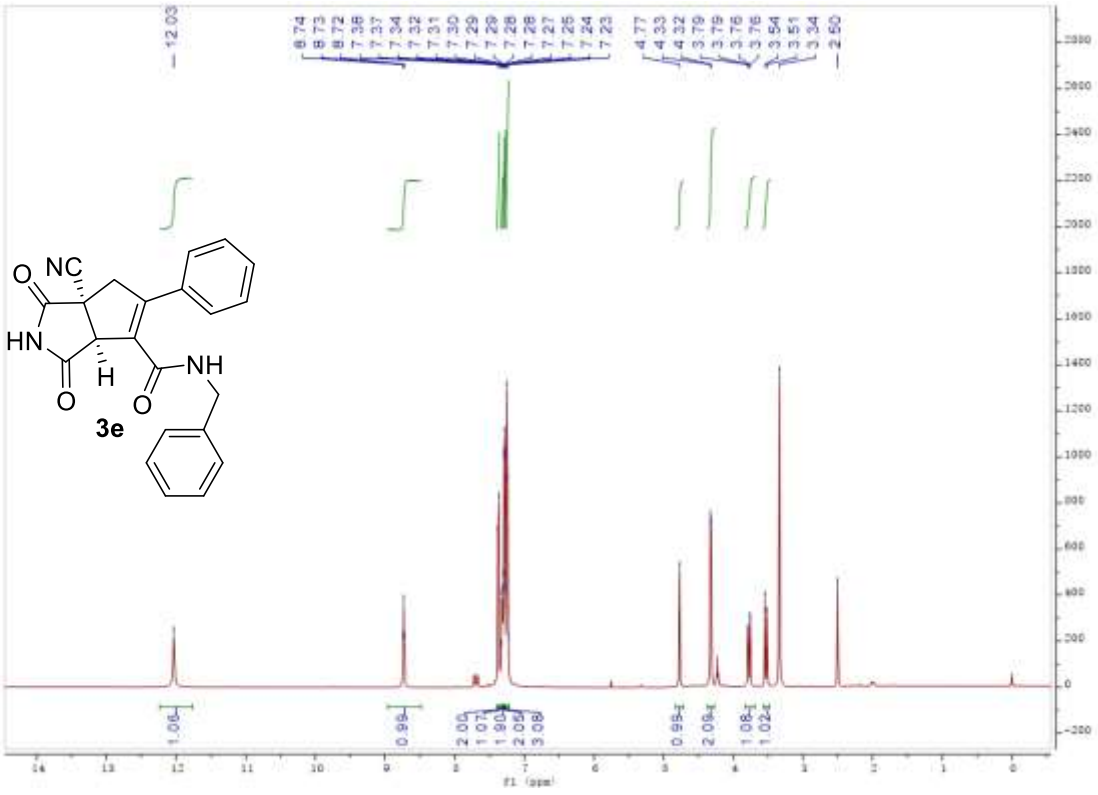
Exact Mass: 310.1186

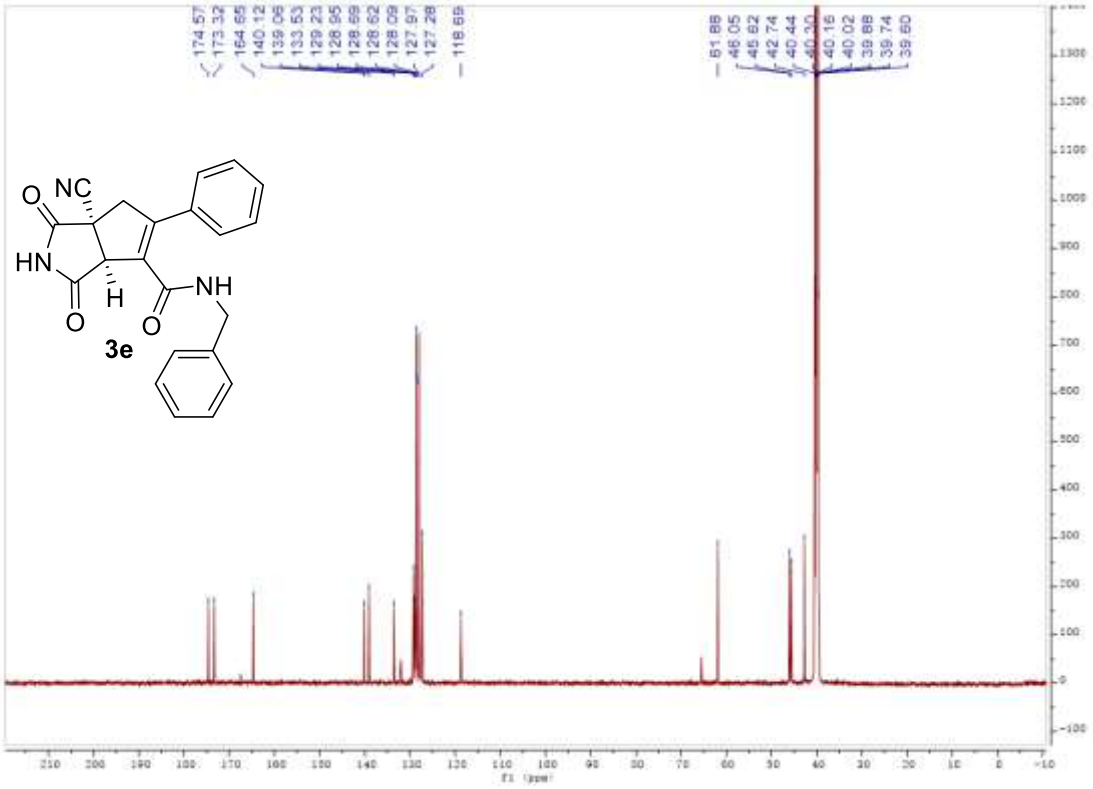

11.98
7.56
7.55
7.39
7.38
7.37
7.35
7.34
7.33
6.35
4.55
3.63
3.60
3.58
3.55
3.35
2.51
1.04
2.09
2.04
0.89
1.08
1.00
1.05
1.01
NC
O
HN
H
NH
H
O
O
3d

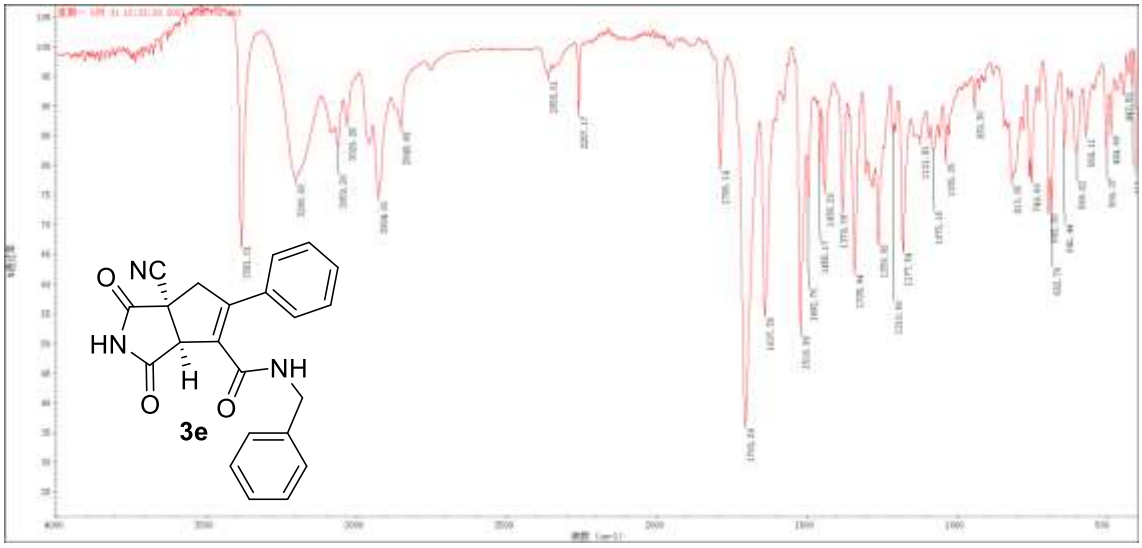

176.05
173.80
142.32
133.43
129.22
129.06
126.75
120.25
118.96
80.15
46.87
43.36
40.43
40.29
40.01
39.87
39.73
39.59
NC
O
HN
H
NH
H
O
O
3d

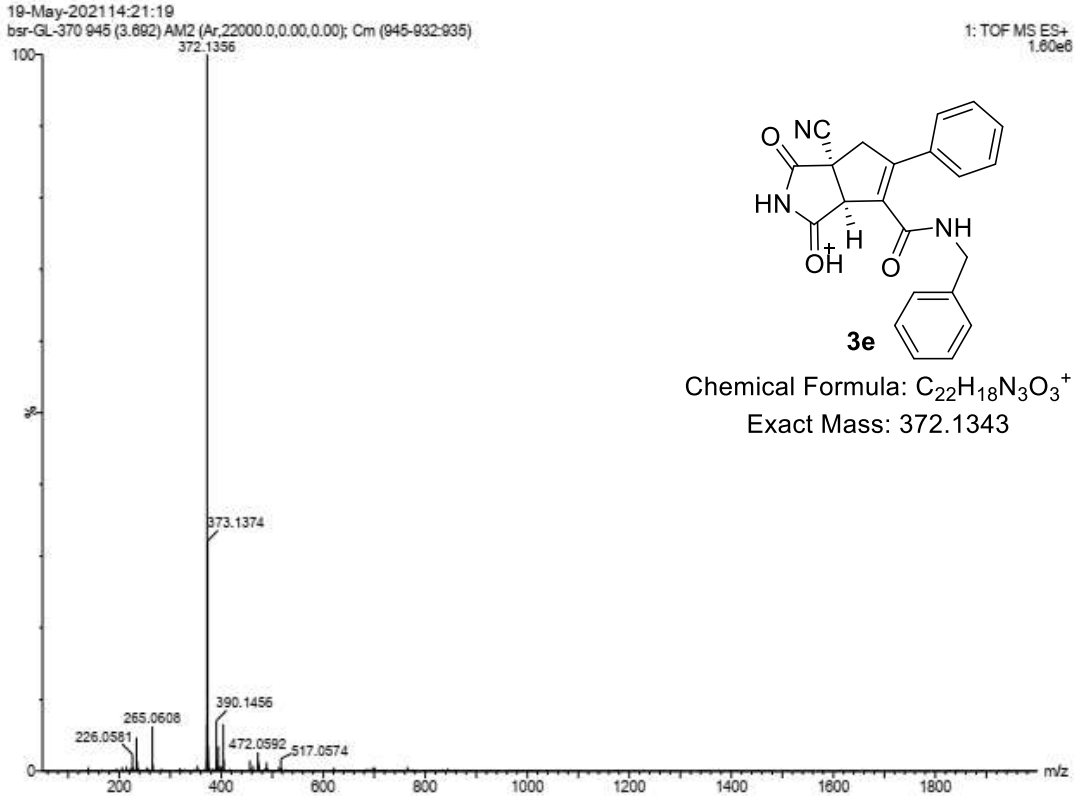

3d


03-Jun-202117:11:38
BSR-GL-381 949 (3.785) AM2 (Ar,22000.0,0.00,0.00); Cm (49:2284)
1: TOF MS ES+
5.16e8
3d
Chemical Formula: C15H12N3O3+
Exact Mass: 282.0873
m/z


12.03
8.74
8.73
8.72
7.36
7.37
7.34
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.25
7.24
7.23
4.77
4.33
4.32
3.79
3.79
3.76
3.76
3.54
3.51
3.34
2.50
1.06
0.98
2.00
1.07
1.90
2.08
3.08
0.95
2.04
1.08
1.02
NC
O
HN
H
NH
O
O
3e

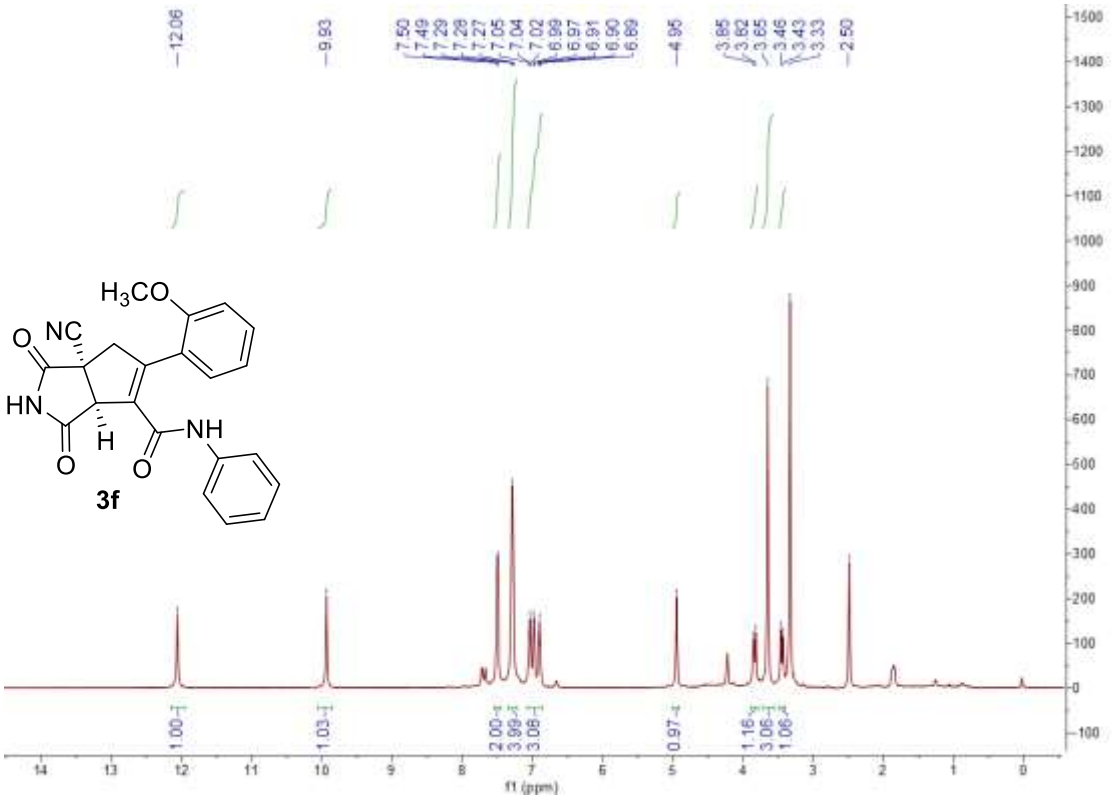

174.57
173.32
164.65
140.12
139.06
133.53
129.23
128.95
128.69
128.62
128.09
127.97
127.28
118.55
61.88
46.05
45.62
42.74
40.44
40.30
40.16
40.02
39.88
39.74
39.60
NC
O
HN
H
NH
O
O
3e

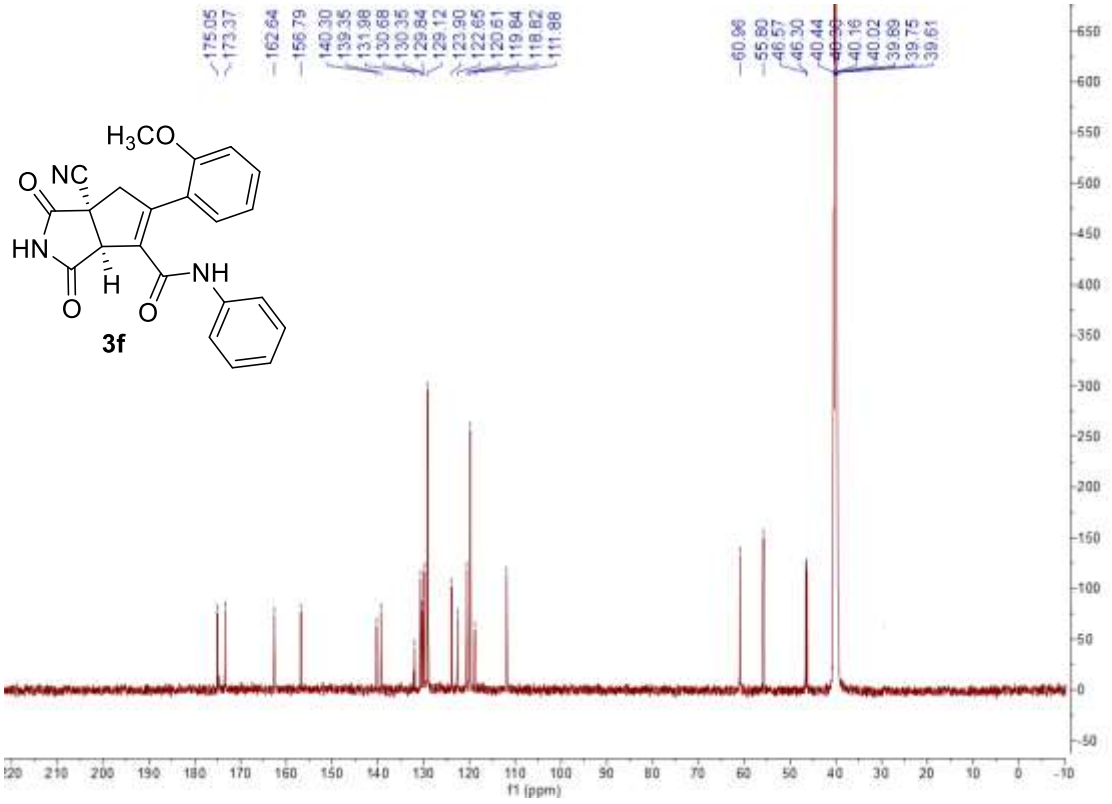


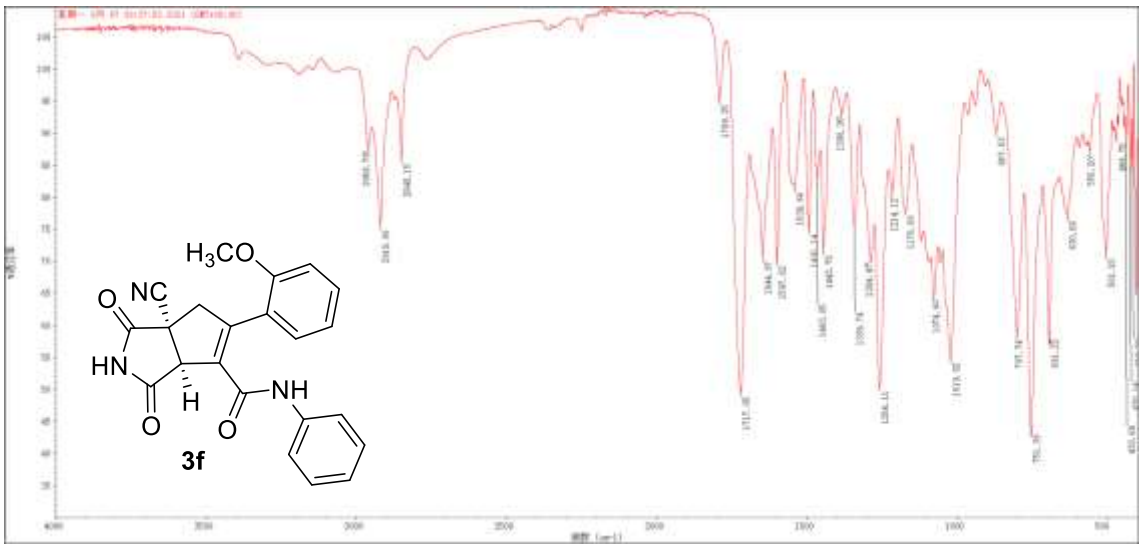


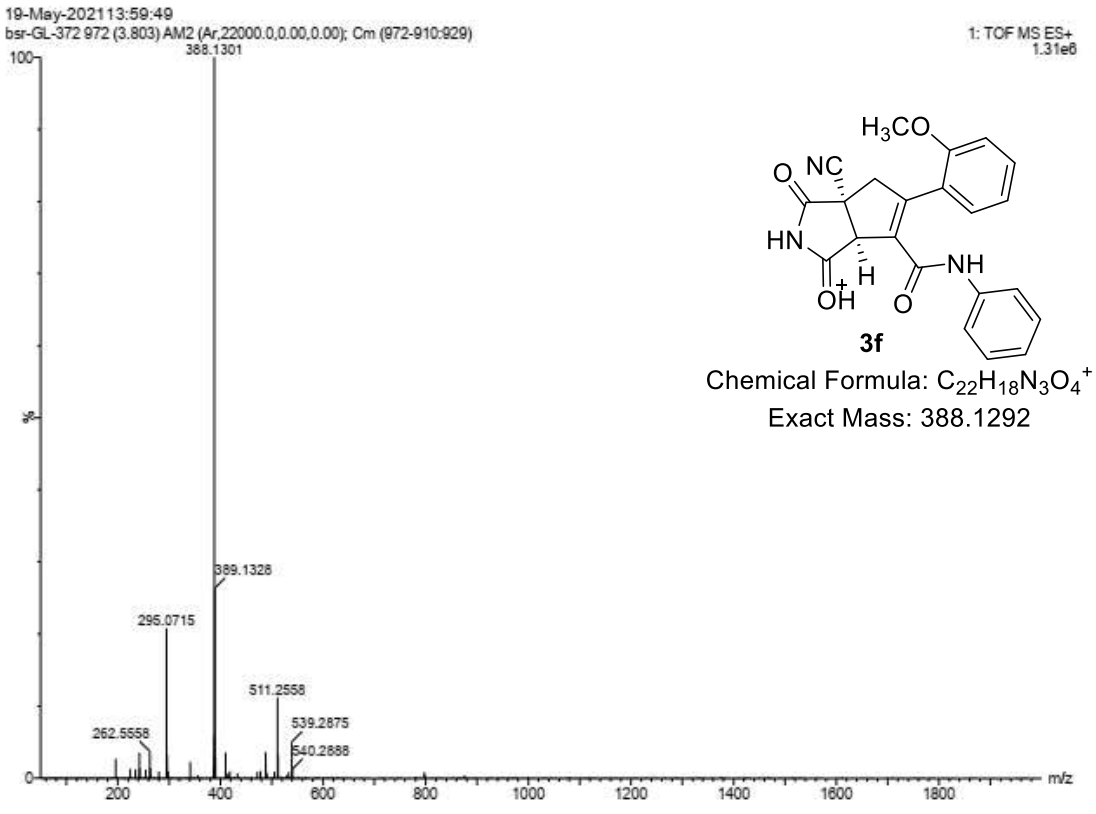
Chemical Formula: $C_{22}H_{18}N_3O_3^+$

Exact Mass: 372.1343


12.06
9.93
7.50
7.49
7.29
7.28
7.27
7.05
7.04
7.02
6.99
6.97
6.91
6.90
6.89
4.95
3.85
3.82
3.65
3.46
3.43
3.33
2.50
1.00
1.03
2.00
3.99
3.08
0.97
1.16
3.06
1.06
f1 (ppm)
H3CO
NC
O
HN
H
NH
O
O
3f

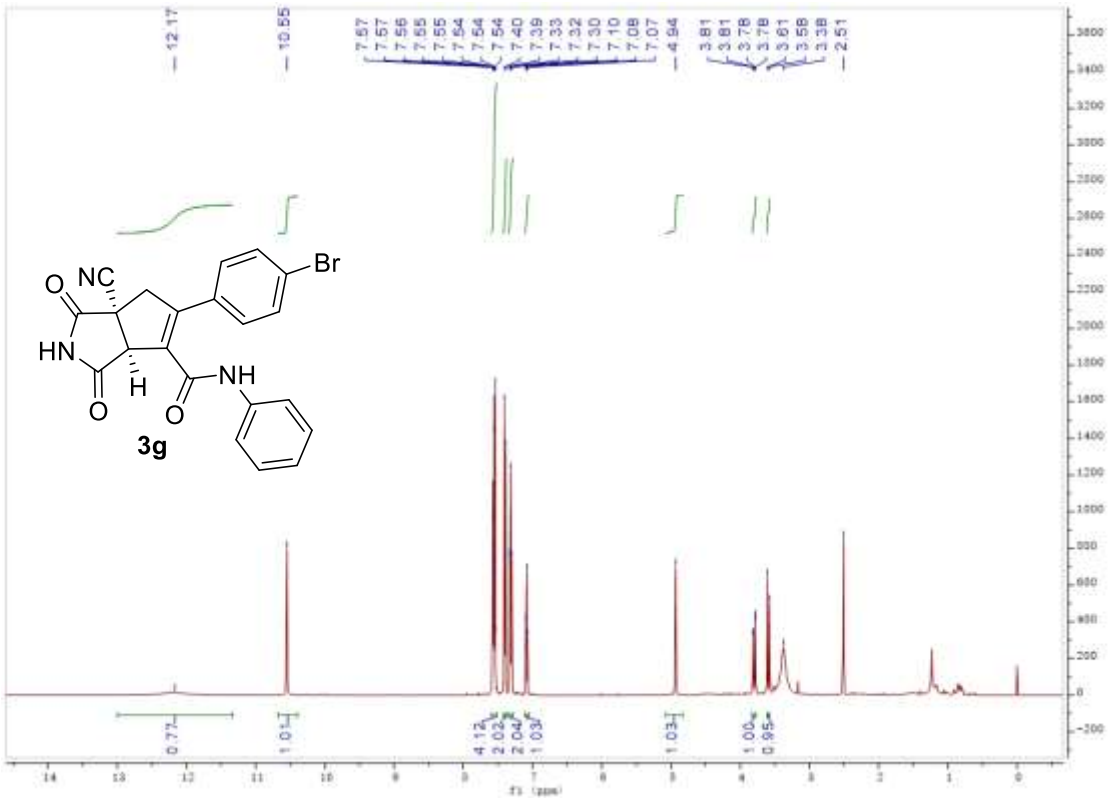

175.05
173.37
162.64
156.79
140.30
139.35
131.98
130.68
130.35
129.84
129.12
123.90
122.65
120.61
119.84
118.82
111.88
60.96
55.80
46.57
46.30
40.44
40.30
40.16
40.02
39.89
39.75
39.61
f1 (ppm)
H3CO
NC
O
HN
H
NH
O
O
3f

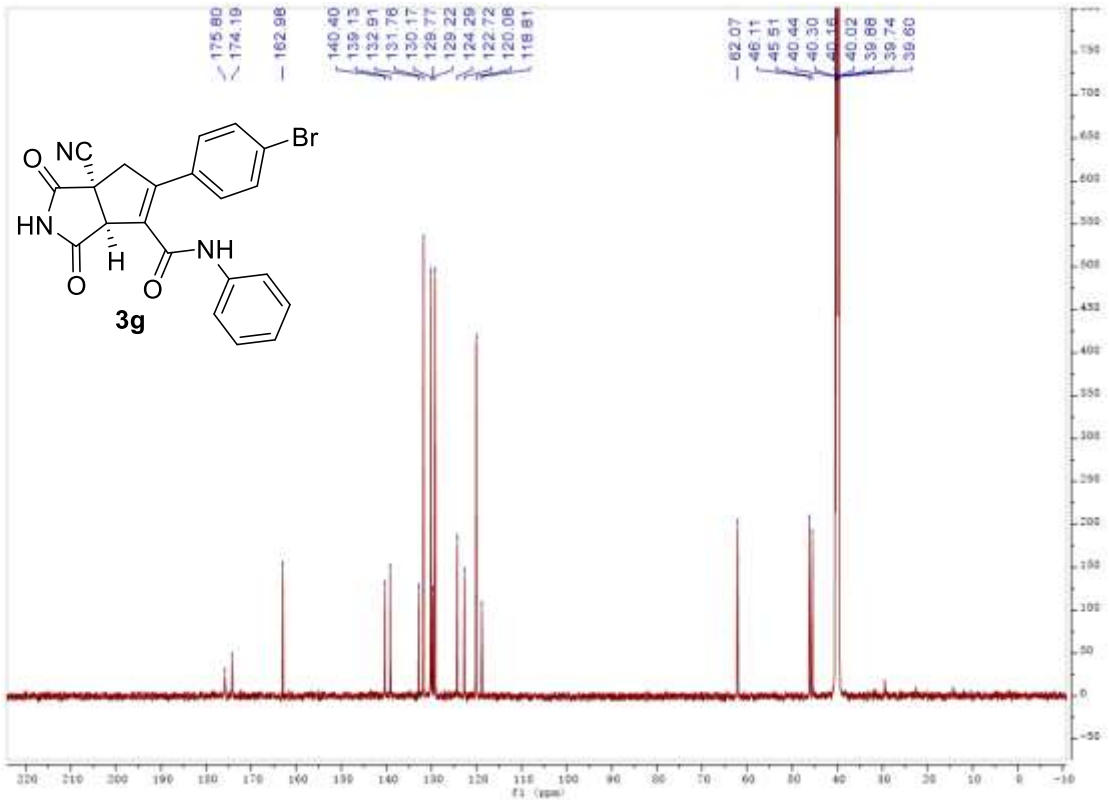


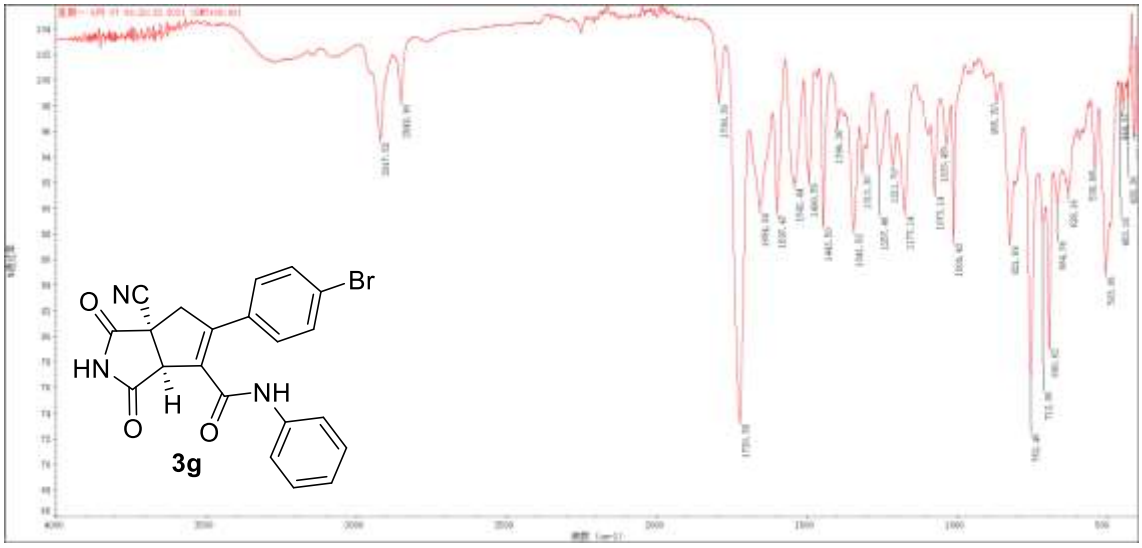


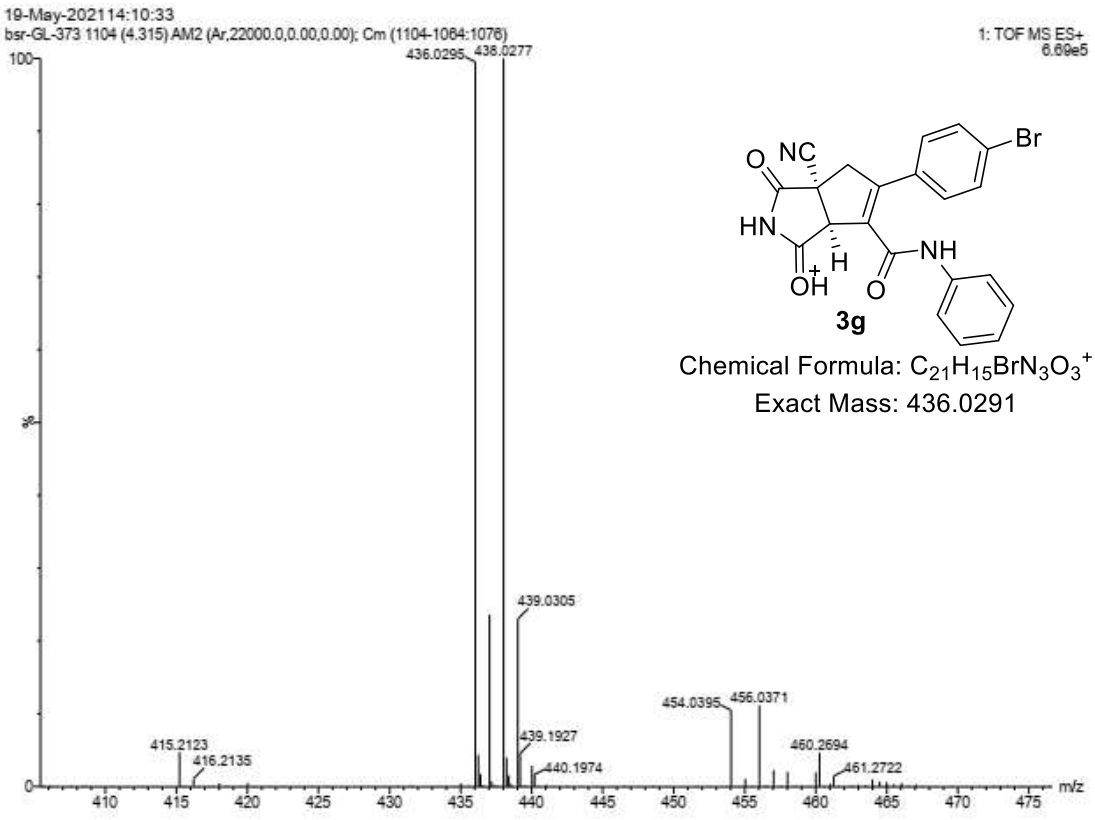
Chemical Formula: $C_{22}H_{18}N_3O_4^+$

Exact Mass: 388.1292


12.17
10.55
7.57
7.57
7.56
7.55
7.55
7.54
7.54
7.54
7.40
7.39
7.33
7.32
7.30
7.10
7.08
7.07
4.94
3.81
3.81
3.78
3.78
3.61
3.58
3.38
2.51
0.77
1.01
4.12
2.02
2.04
1.03
1.03
1.00
0.95
f1 (ppm)
O
NC
HN
O
H
NH
O
O
Br
3g

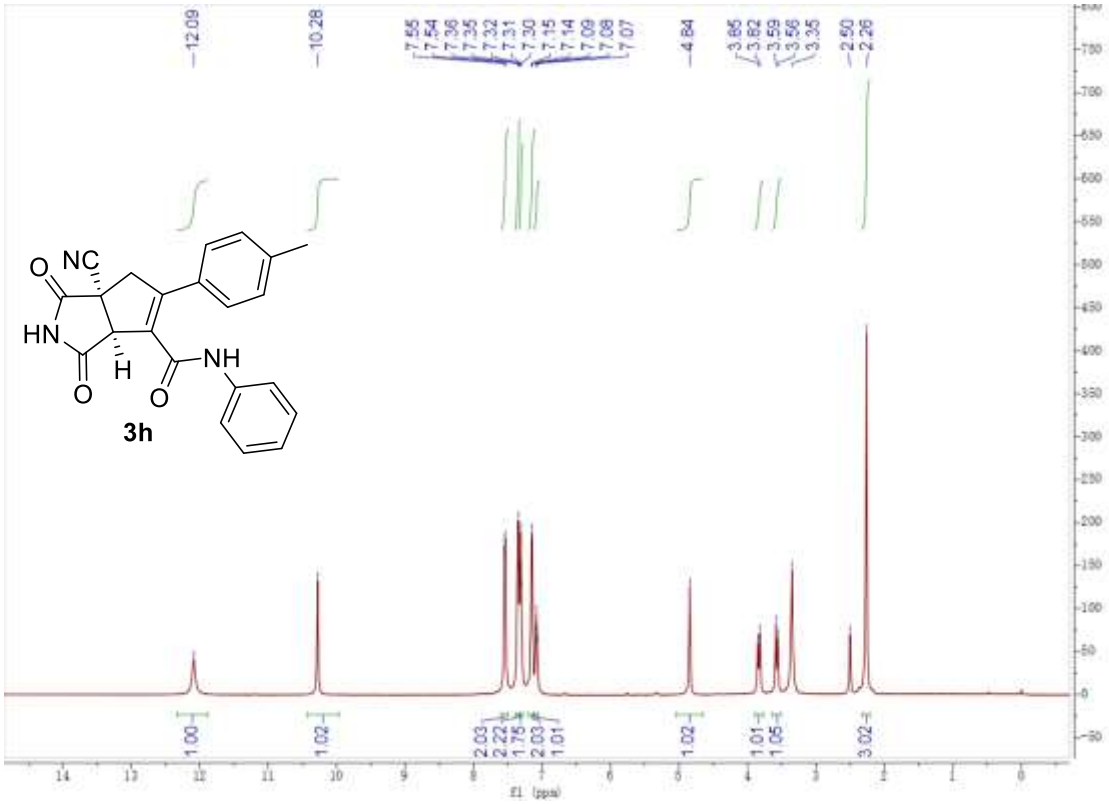

175.80
174.19
162.98
140.40
139.13
132.91
131.76
130.17
129.77
129.22
124.29
122.72
120.08
118.81
62.07
46.11
45.51
40.44
40.30
40.16
40.02
39.88
39.74
39.60
f1 (ppm)
O
NC
HN
O
H
NH
O
O
Br
3g

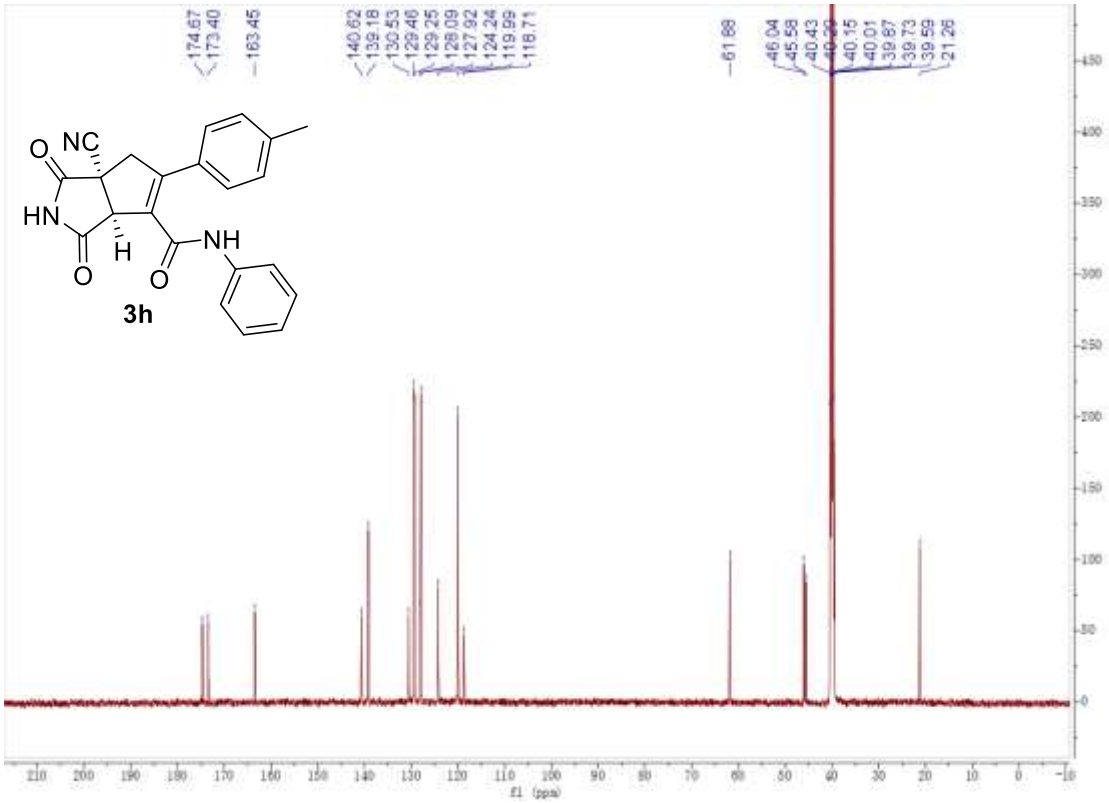


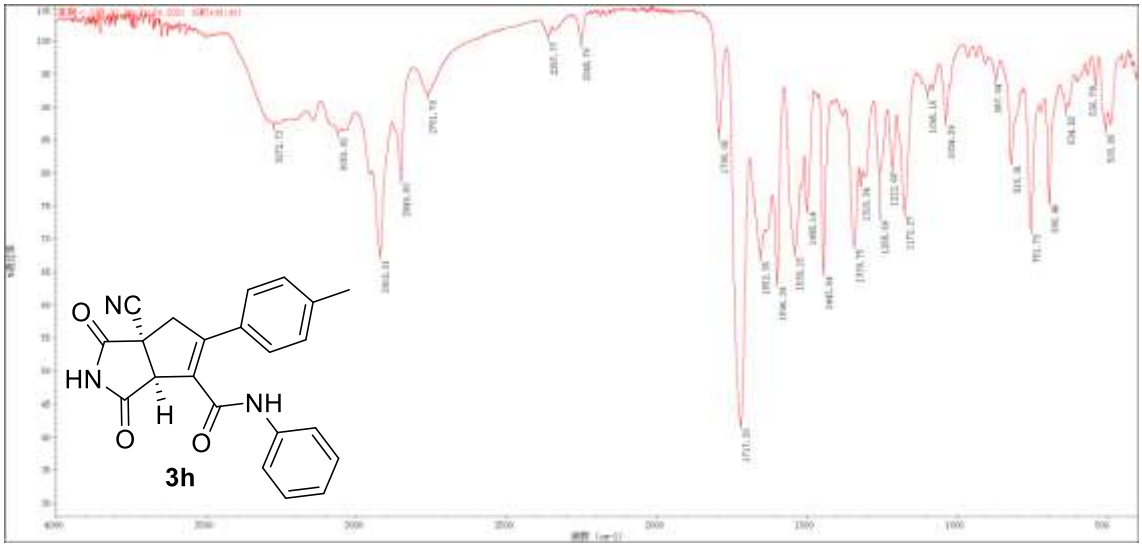


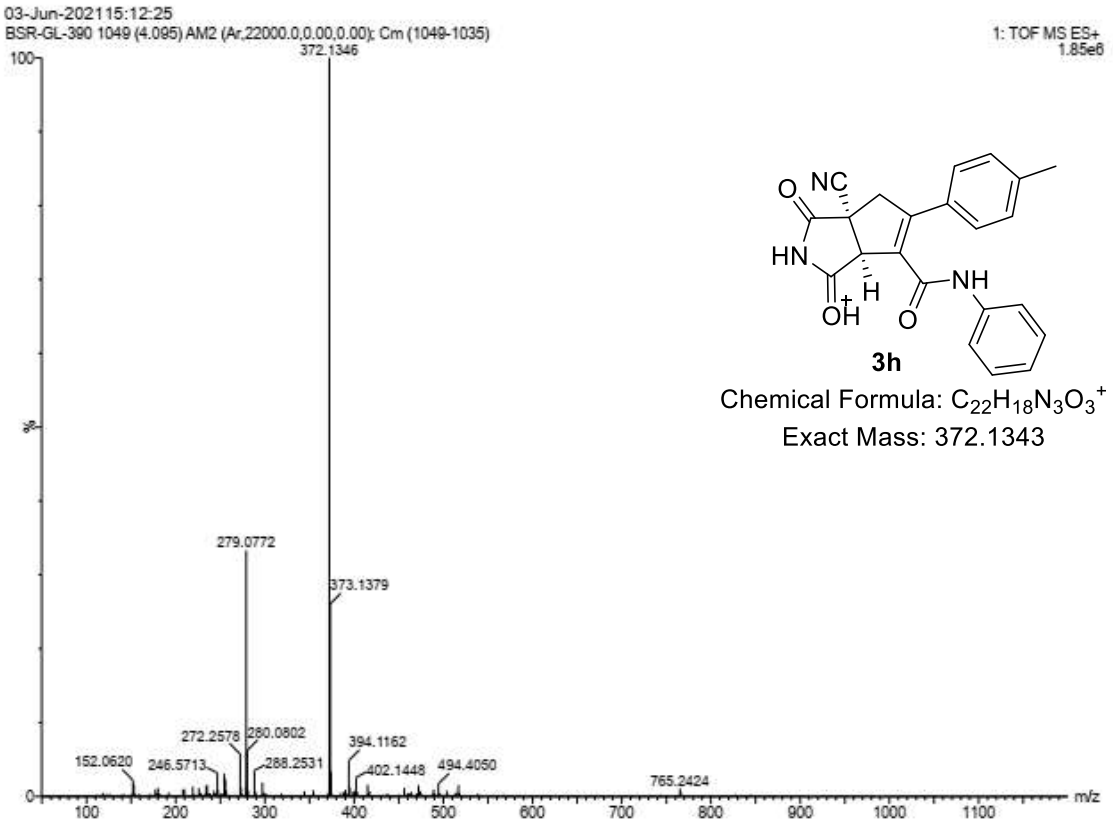
Chemical Formula: $C_{21}H_{15}BrN_3O_3^+$

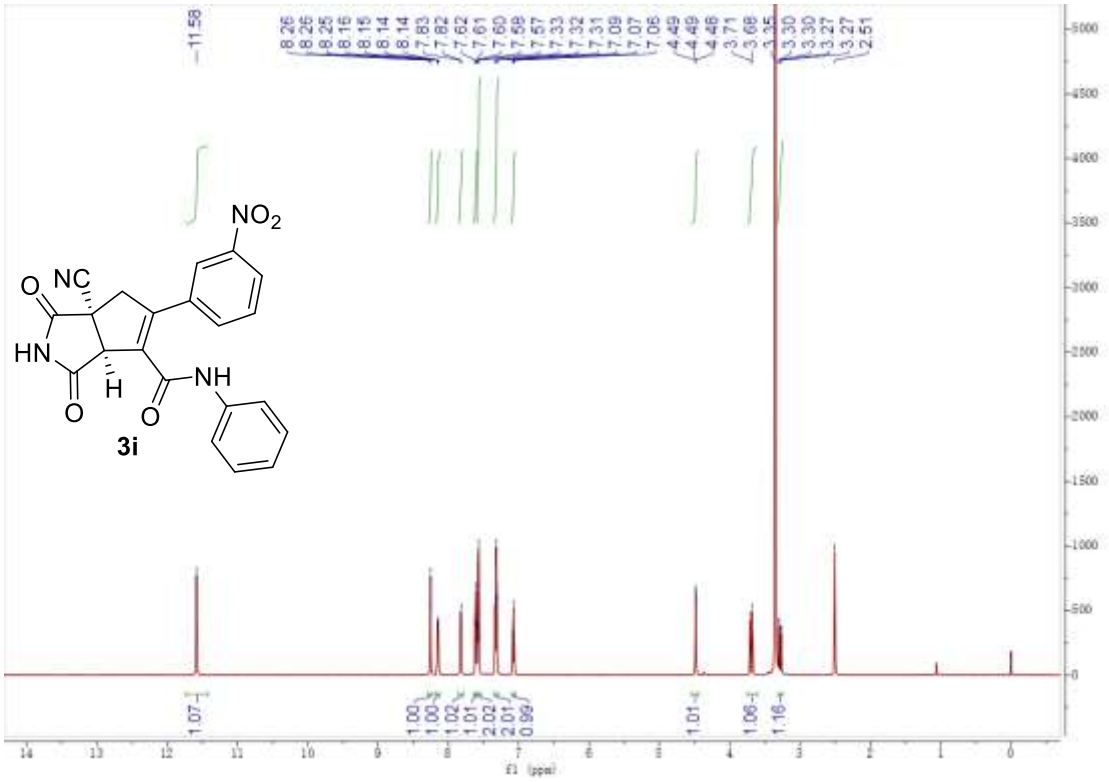
Exact Mass: 436.0291


12.09
10.28
7.55
7.54
7.36
7.35
7.32
7.31
7.30
7.15
7.14
7.09
7.08
7.07
4.84
3.85
3.82
3.59
3.56
3.35
2.50
2.26
1.00
1.02
2.03
2.22
1.75
2.03
1.01
1.02
1.01
1.05
3.02
f1 (ppm)
NC
O
HN
O
H
NH
O
3h


174.67
173.40
163.45
140.62
139.18
130.53
129.46
129.25
128.09
127.92
124.24
119.99
118.71
61.88
46.04
45.58
40.43
40.15
40.01
39.87
39.73
39.59
21.26
f1 (ppm)
NC
O
HN
O
H
NH
O
3h


O
NC
HN
H
O
NH
O
3h


03-Jun-202115:12:25
BSR-GL-390 1049 (4.095) AM2 (Ar,22000.0,0.00,0.00); Cm (1049-1035)
1: TOF MS ES+
1.85e6
100
%
0
372.1346
279.0772
373.1379
272.2578
280.0802
394.1162
152.0620
246.5713
288.2531
402.1448
494.4050
765.2424
100
200
300
400
500
600
700
800
900
1000
1100
m/z
O
NC
HN
H
OH
NH
O
3h
Chemical Formula: $C_{22}H_{18}N_3O_3^+$
Exact Mass: 372.1343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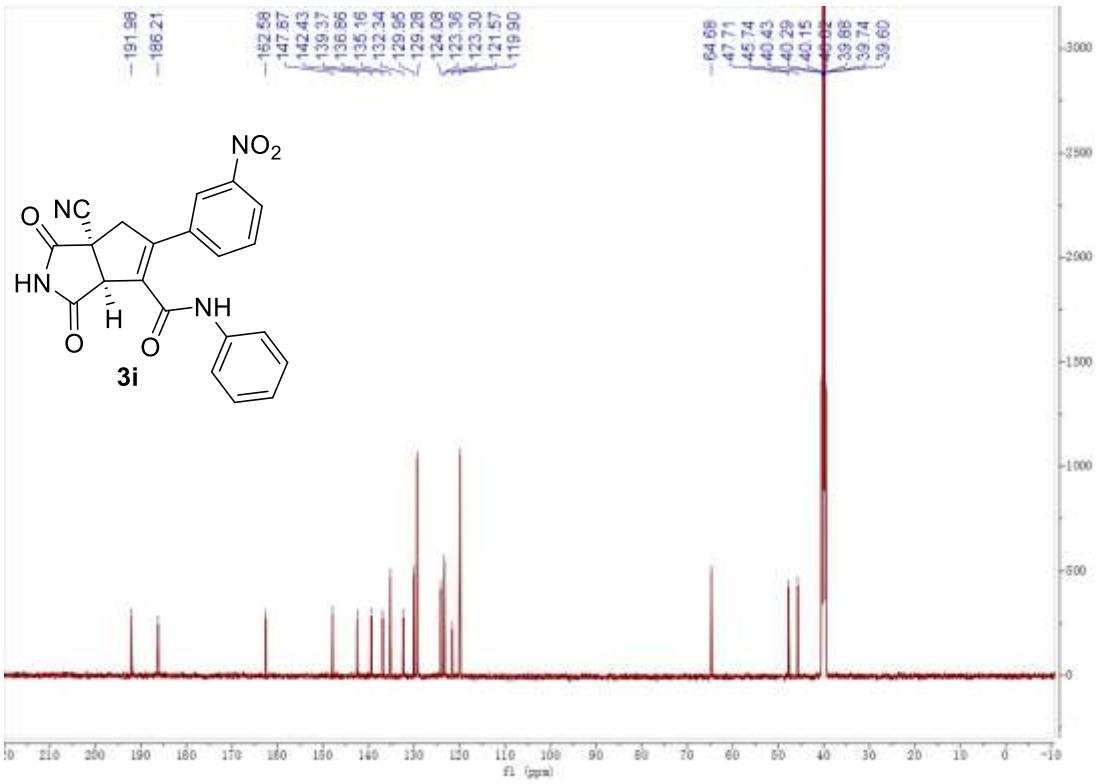
8.26
8.25
8.16
8.15
8.14
7.83
7.82
7.62
7.61
7.60
7.59
7.57
7.33
7.32
7.31
7.09
7.07
7.06
4.49
4.46
3.71
3.68
3.35
3.30
3.27
2.51
NO2
NC
O
HN
H
NH
O
O
3i
f1 (ppm)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152.58
147.67
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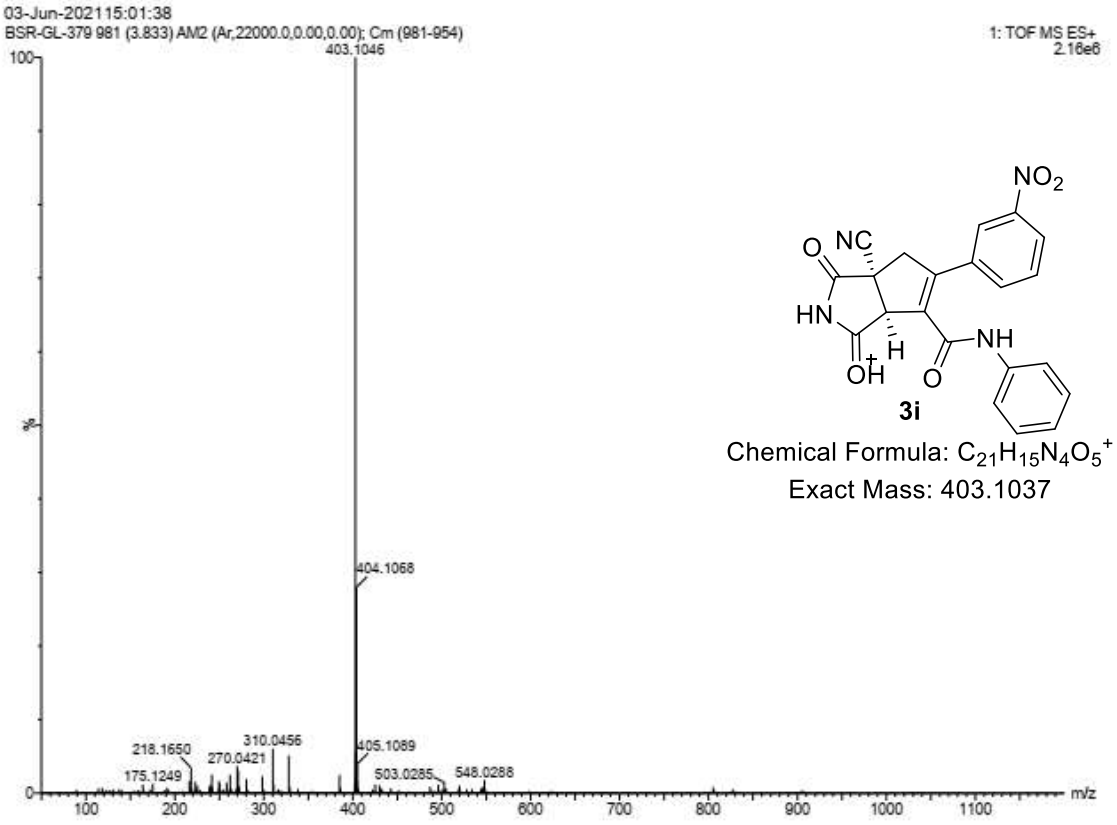
139.37
136.86
135.16
132.34
129.95
129.28
124.08
123.36
123.30
121.57
119.90
64.68
47.71
45.74
40.43
40.29
40.15
39.88
39.74
39.60
NO2
NC
O
HN
H
NH
O
O
3i
f1 (ppm)


NO2
NC
O
HN
H
O
NH
O
3i


03-Jun-202115:01:38
BSR-GL-379 981 (3.833) AM2 (Ar,22000.0,0.00,0.00); Cm (981-954)
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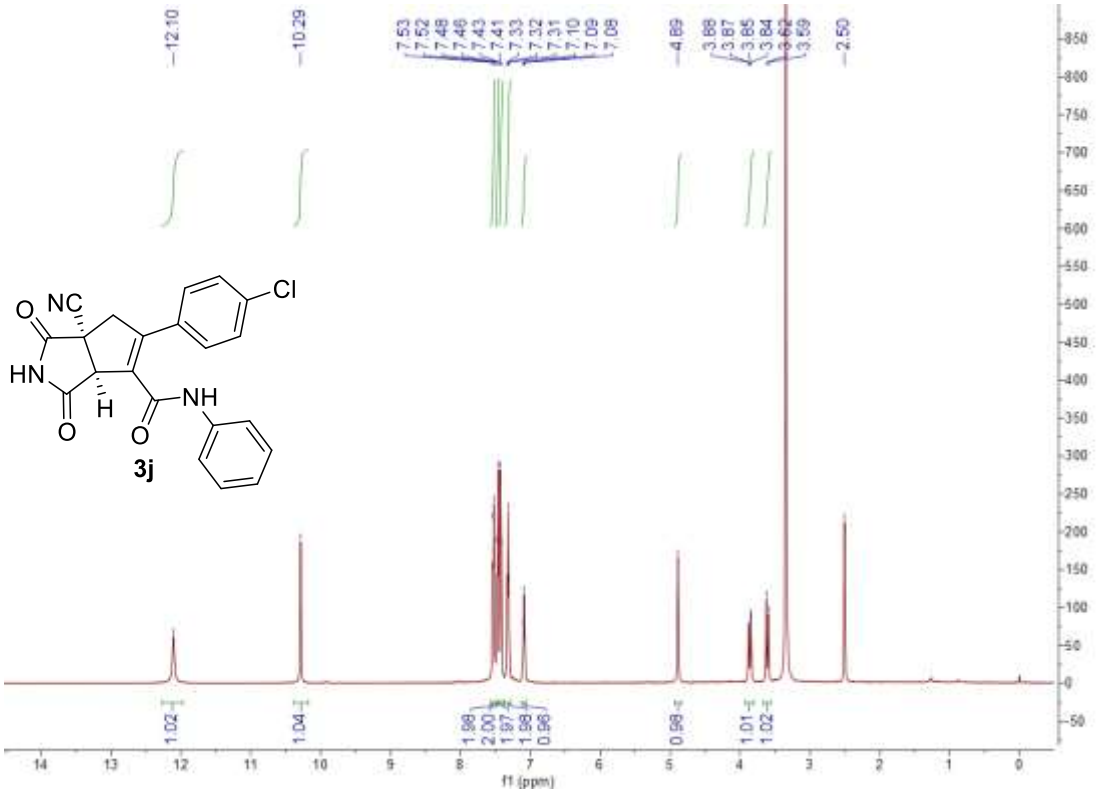
2.16e6
403.1046
404.1068
405.1089
310.0456
218.1650
270.0421
175.1249
503.0285
548.0288
%
m/z
100
200
300
400
500
600
700
800
900
1000
1100
NO2
NC
O
HN
H
OH+
NH
O
3i
Chemical Formula: C21H15N4O5+
Exact Mass: 403.1037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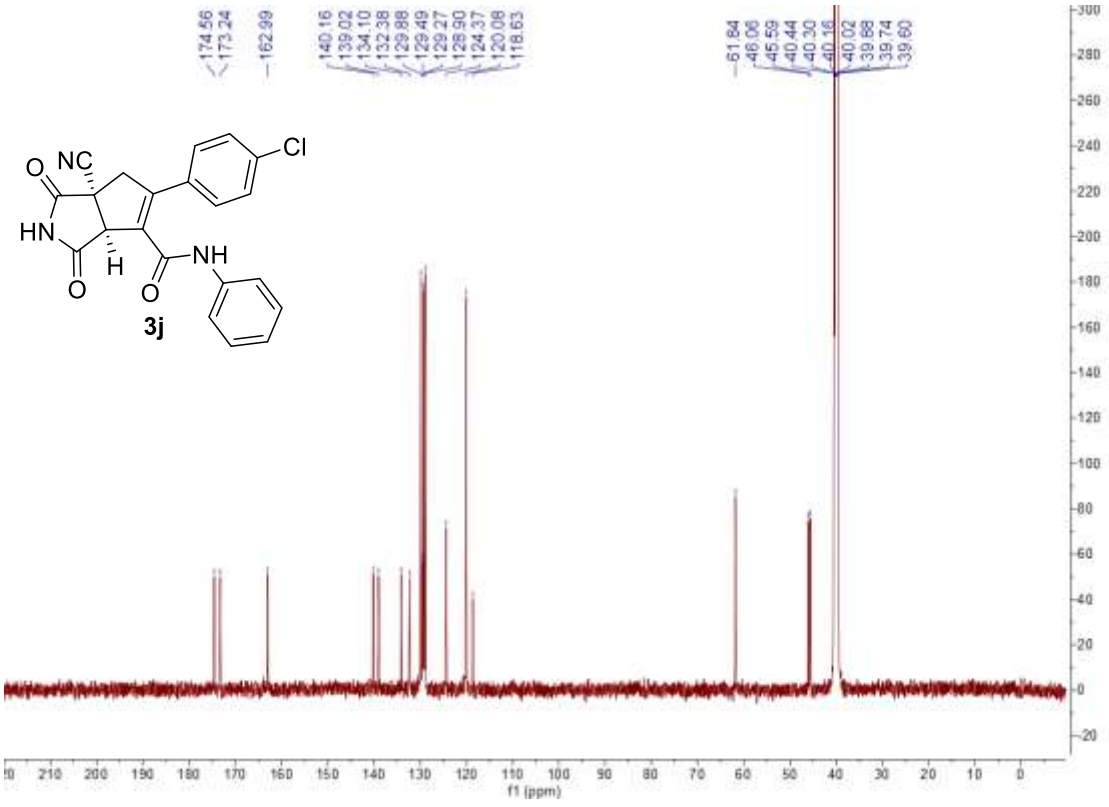
10.29
7.53
7.52
7.48
7.46
7.43
7.41
7.33
7.32
7.31
7.10
7.09
7.08
4.89
3.88
3.87
3.85
3.84
3.62
3.59
2.50
1.02
1.04
1.98
2.00
1.97
1.98
0.96
0.99
1.01
1.02
f1 (ppm)
O
NC
HN
O
H
NH
O
Cl
3j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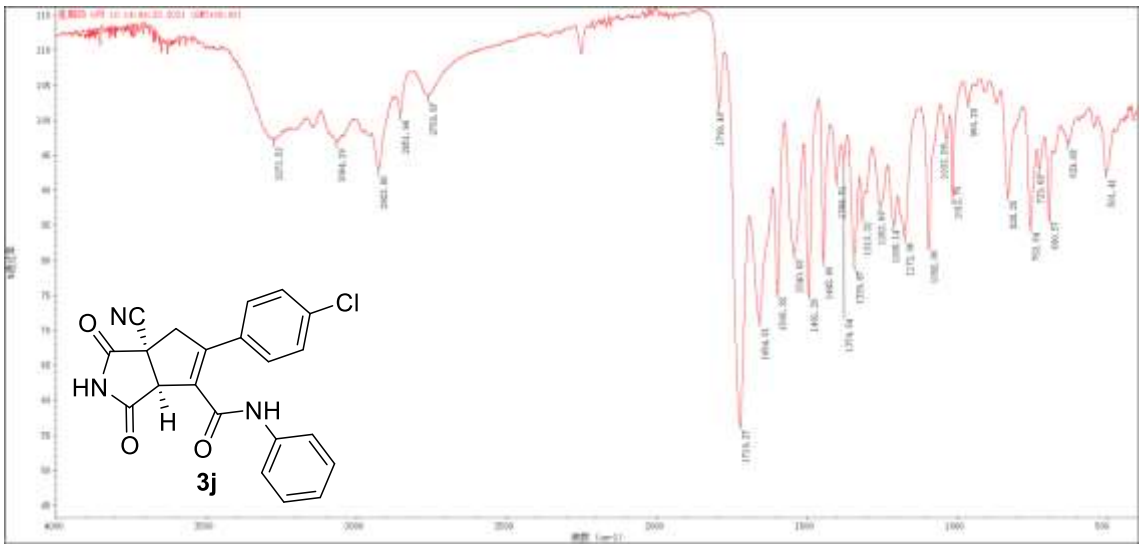
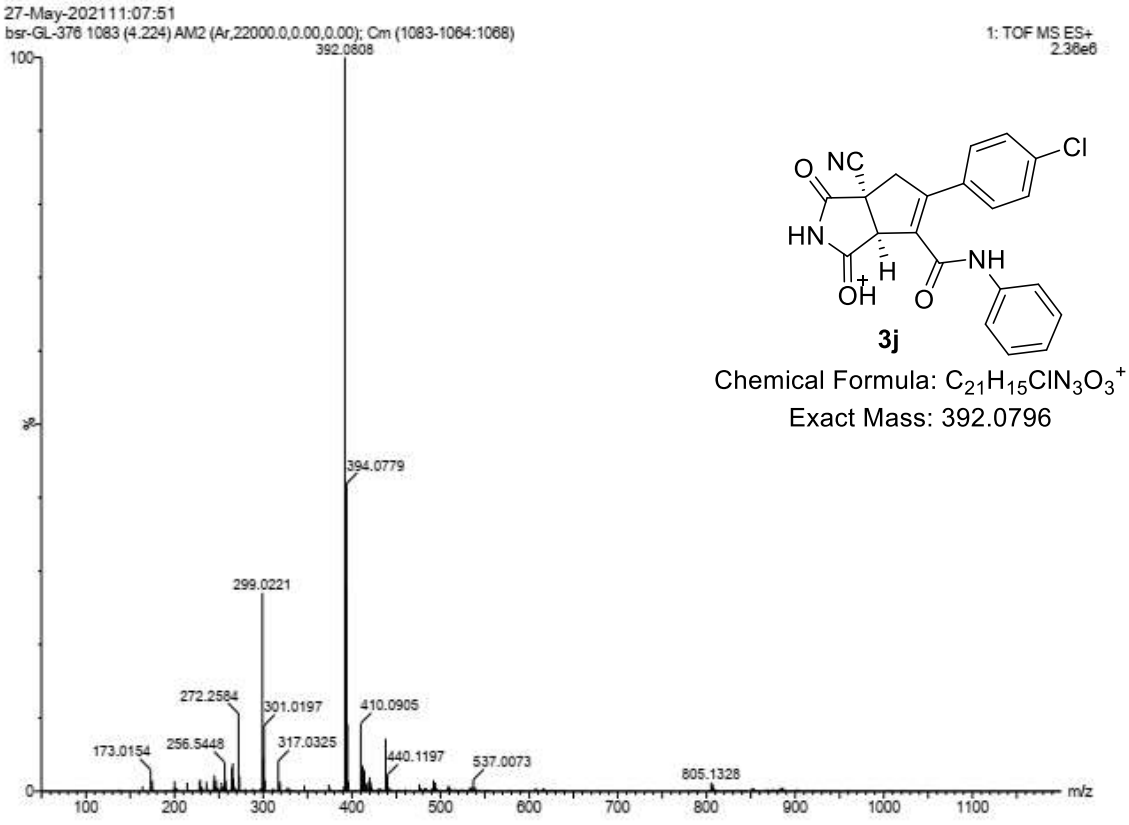
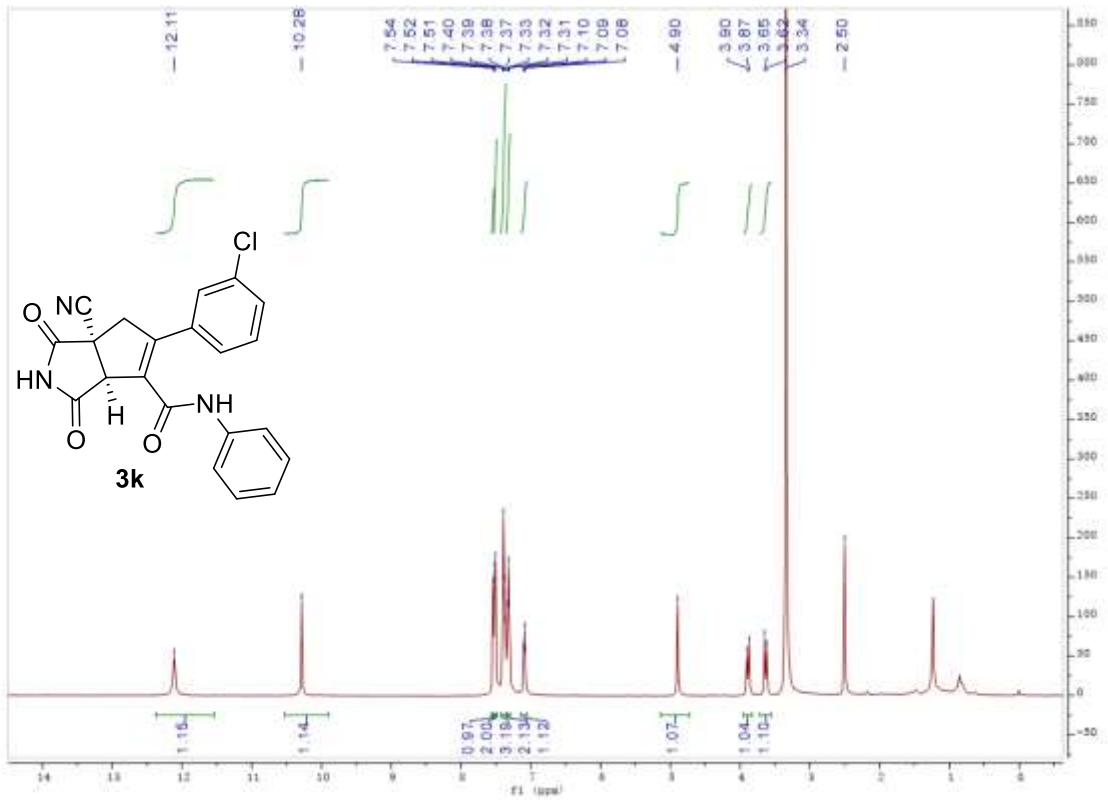
173.24
162.99
140.16
139.02
134.10
132.38
129.88
129.49
129.27
128.90
124.37
120.08
118.63
61.84
46.06
45.59
40.44
40.30
40.16
40.02
39.88
39.74
39.60
f1 (ppm)
O
NC
HN
O
H
NH
O
Cl
3j





Chemical Formula: $C_{21}H_{15}ClN_3O_3^+$

Exact Mass: 392.0796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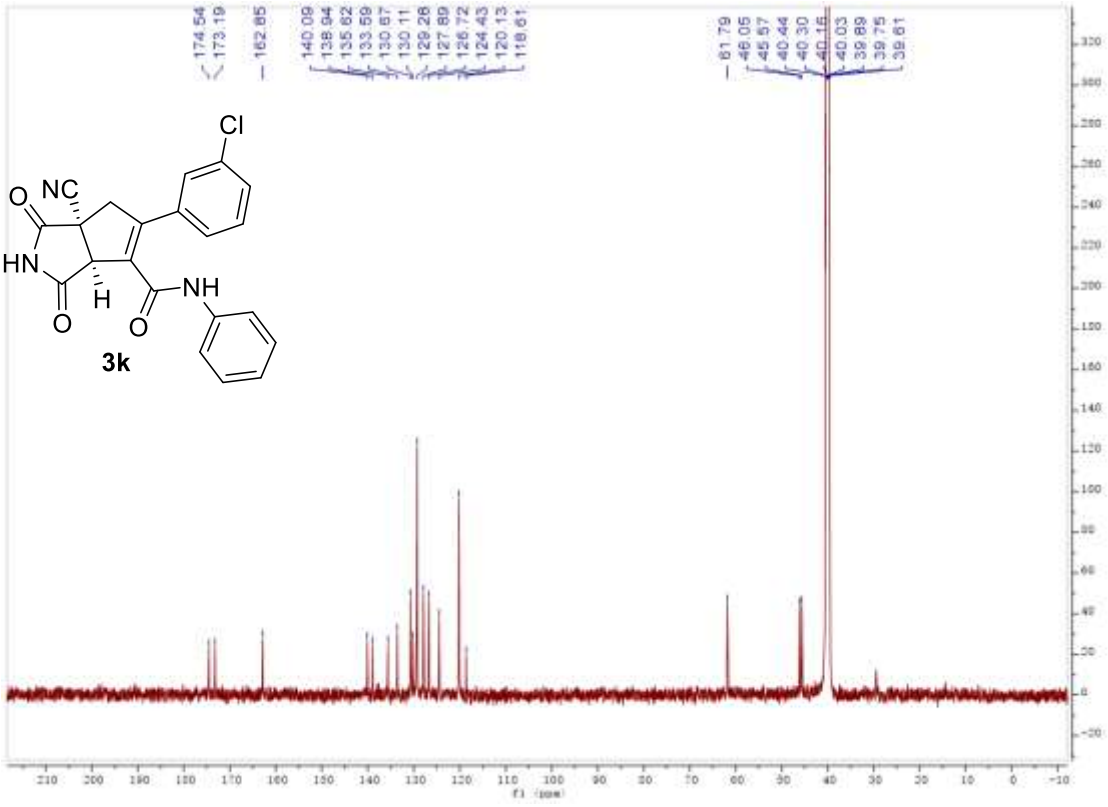
10.28
7.54
7.52
7.51
7.40
7.39
7.38
7.37
7.33
7.32
7.31
7.10
7.09
7.08
4.90
3.90
3.87
3.65
3.62
3.34
2.50
Cl
NC
O
HN
O
H
NH
O
3k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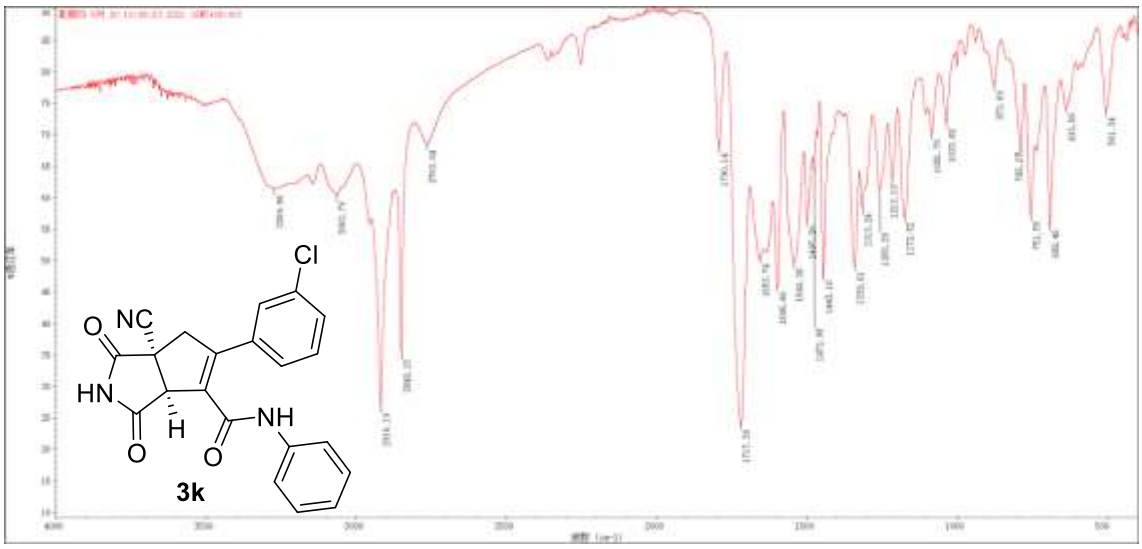
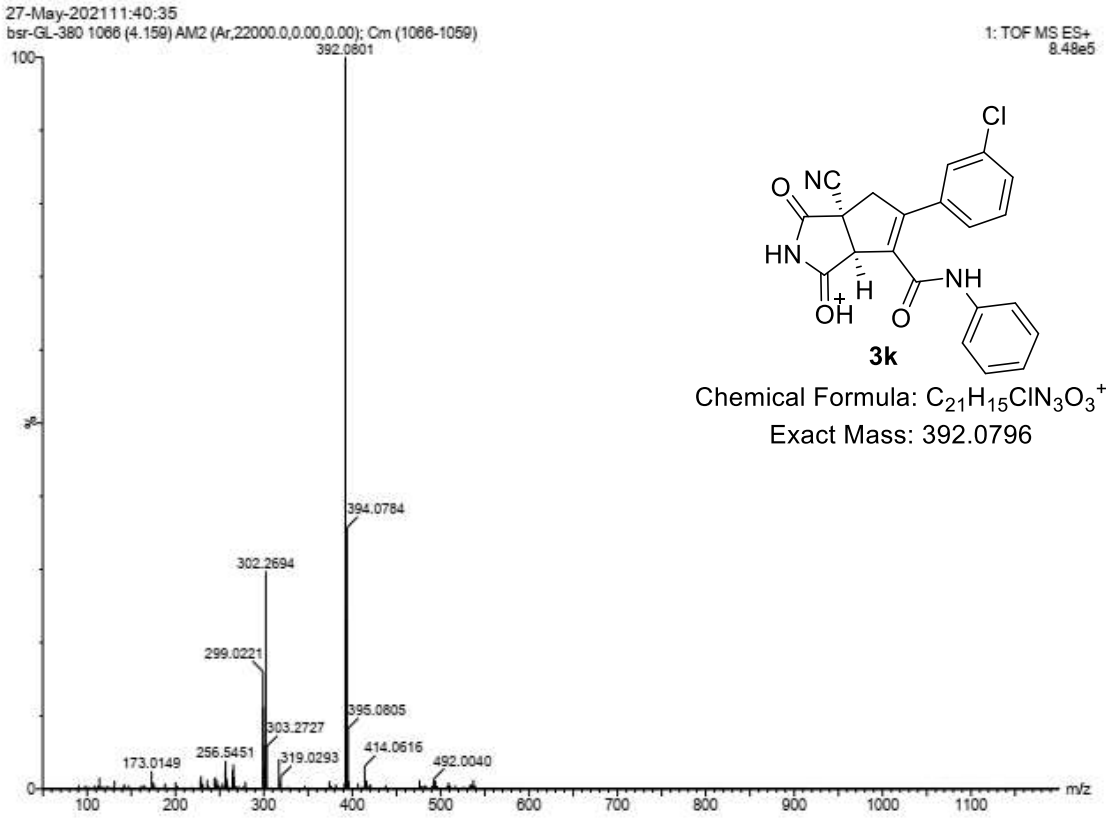
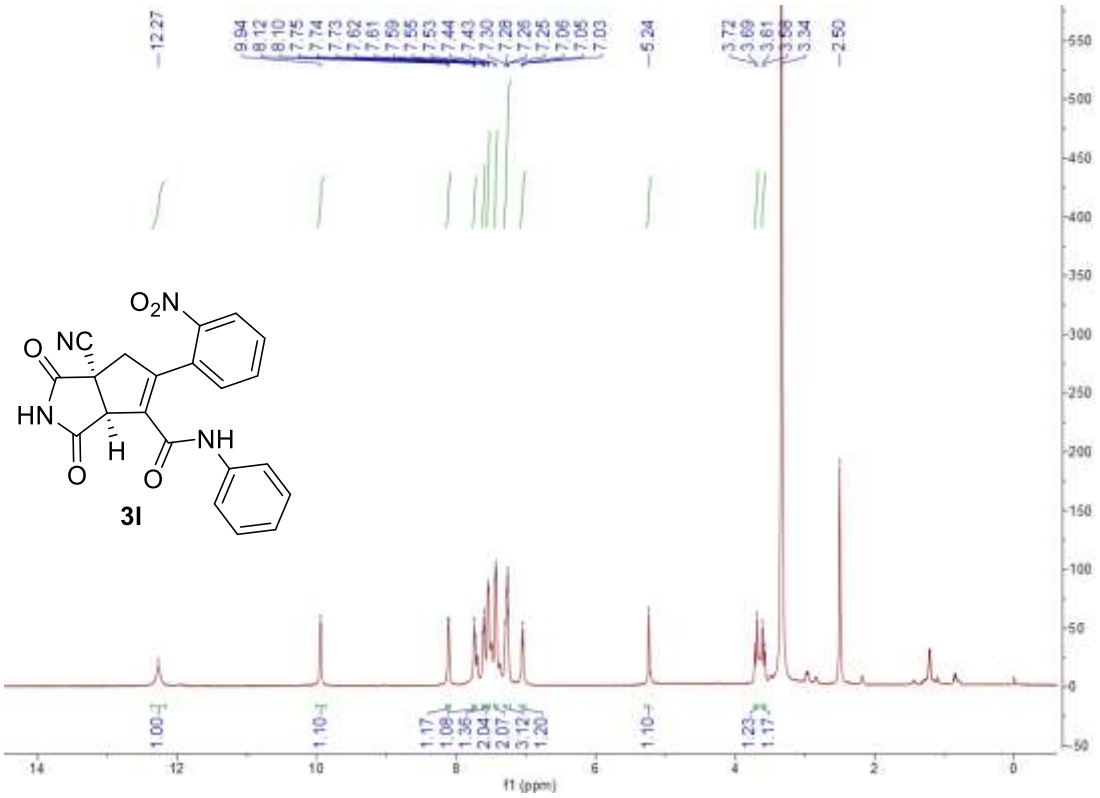
138.94
135.62
133.59
130.67
130.11
129.26
127.89
126.72
124.43
120.13
118.61
61.79
46.05
45.57
40.44
40.30
40.16
40.03
39.89
39.75
39.61
Cl
NC
O
HN
O
H
NH
O
3k





Chemical Formula: $C_{21}H_{15}ClN_3O_3^+$

Exact Mass: 392.0796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9.94
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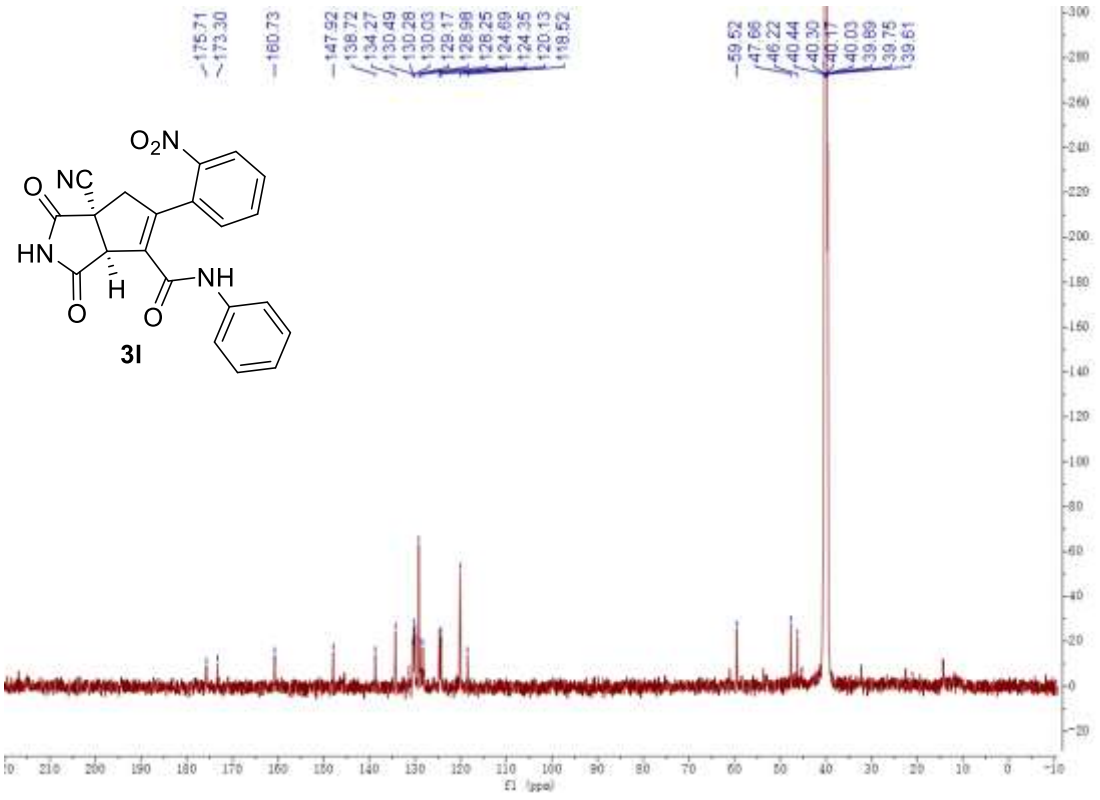
8.10
7.75
7.74
7.73
7.62
7.61
7.59
7.55
7.53
7.44
7.43
7.30
7.28
7.26
7.06
7.05
7.03
5.24
3.72
3.69
3.61
3.56
3.34
2.50
1.00
1.10
1.17
1.08
1.36
2.04
2.07
3.12
1.20
1.10
1.23
1.17
f1 (ppm)
O2N
NC
O
HN
O
H
NH
O
3l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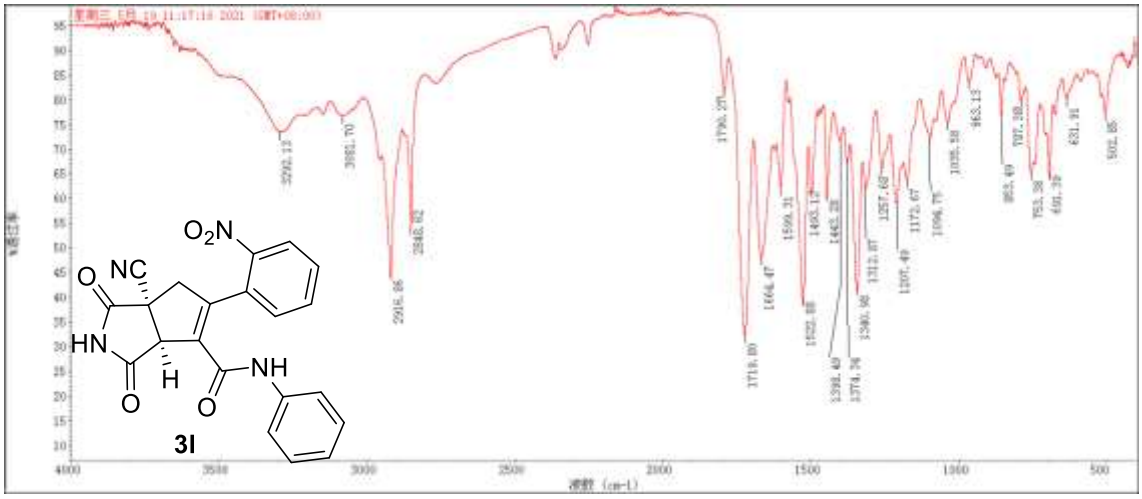
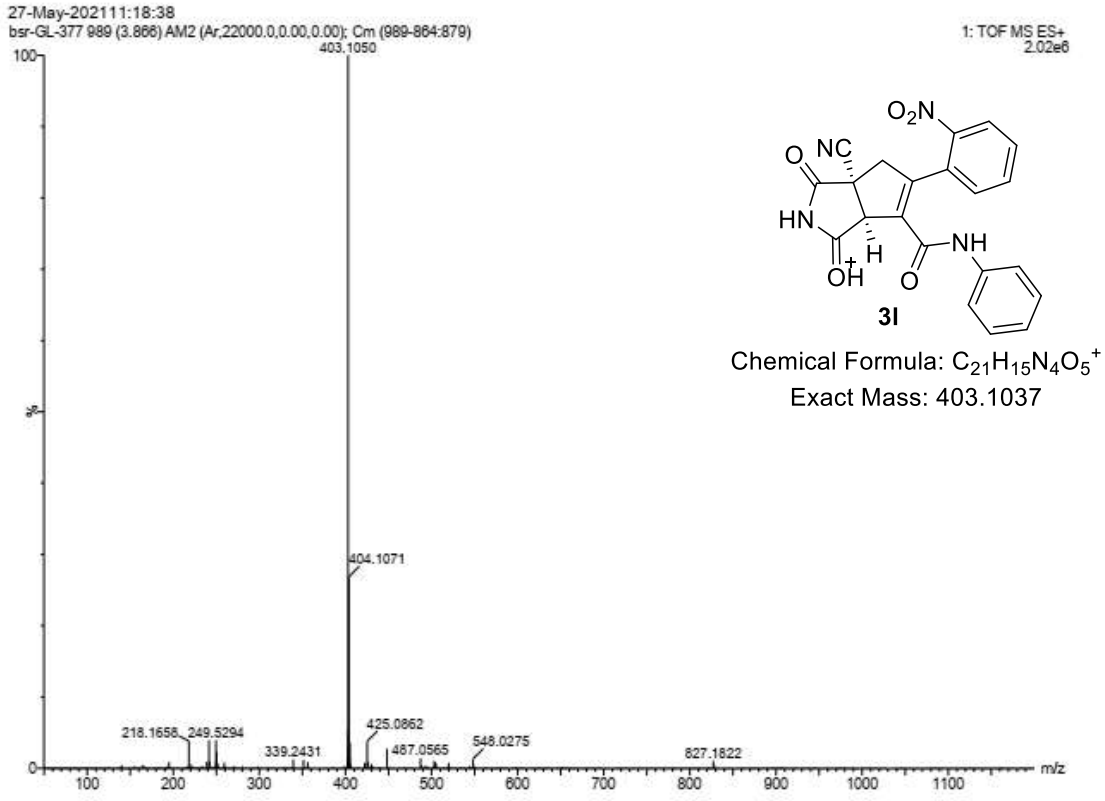
173.30
160.73
147.92
138.72
134.27
130.49
130.28
130.03
129.17
128.98
126.25
124.69
124.35
120.13
118.52
59.52
47.66
46.22
40.44
40.30
40.17
40.03
39.89
39.75
39.61
f1 (ppm)
O2N
NC
O
HN
O
H
NH
O
3l


3l


27-May-202111:18:38
bsr-GL-377 989 (3.866) AM2 (Ar,22000.0,0.00,0.00); Cm (989-864:879)
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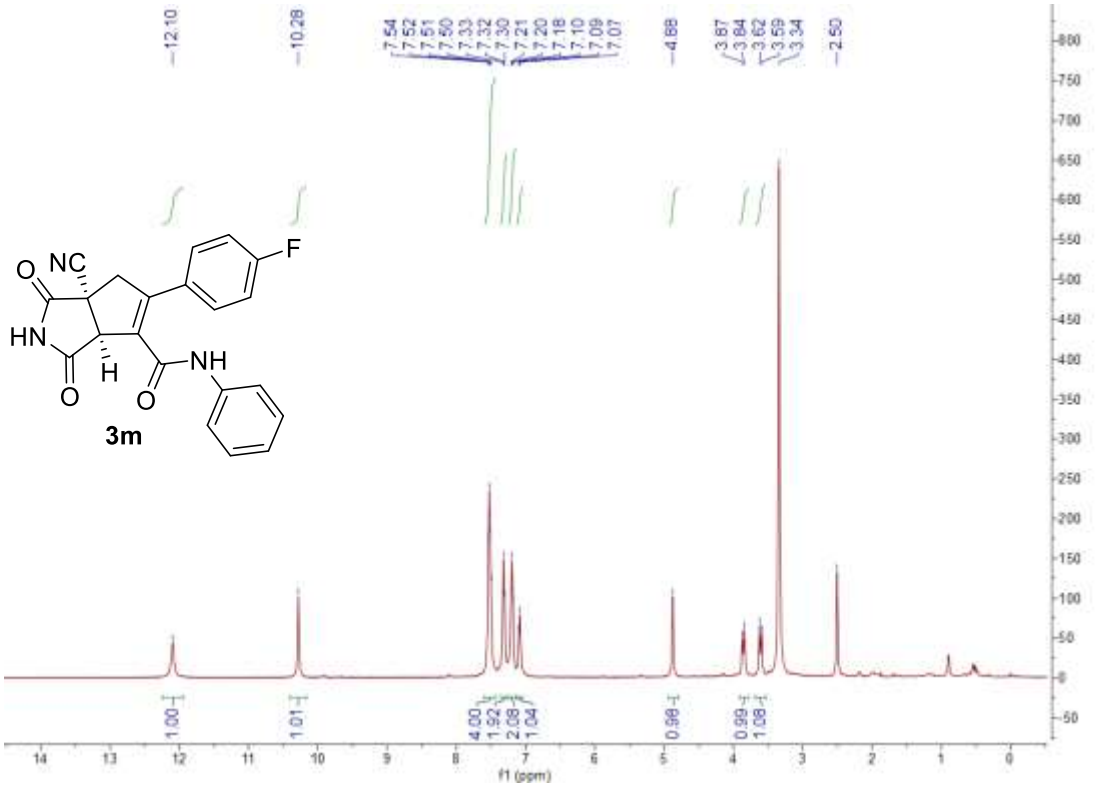
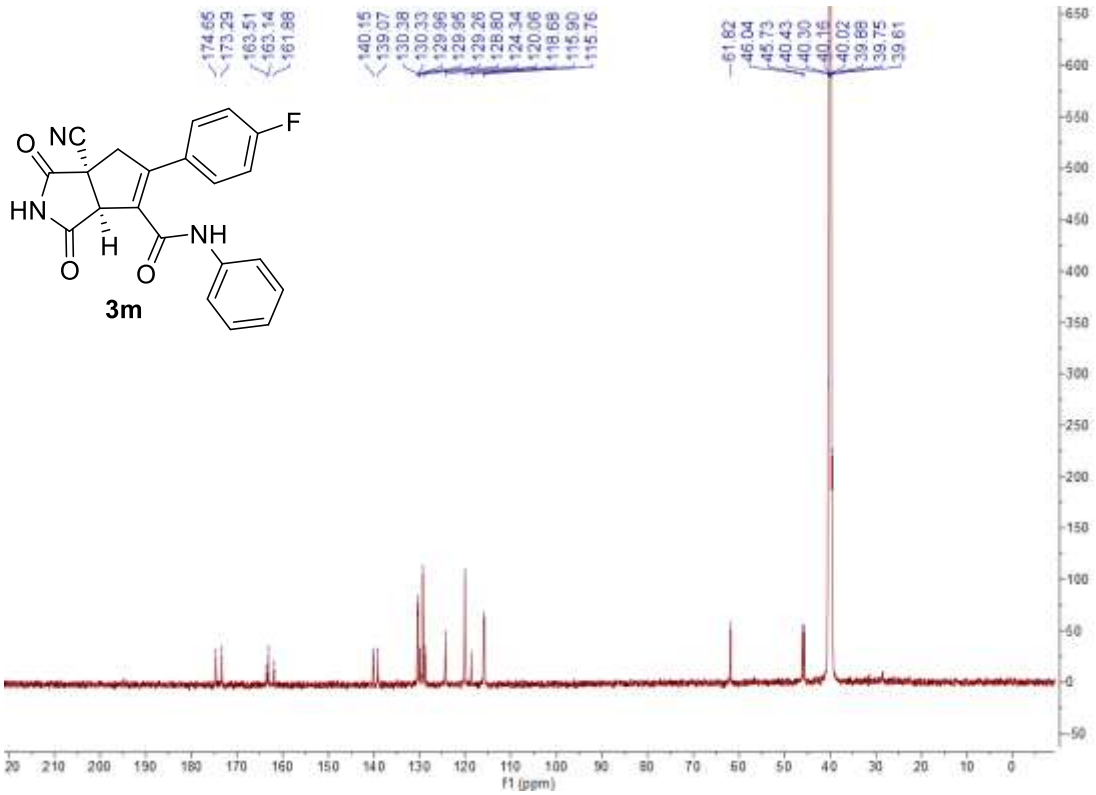
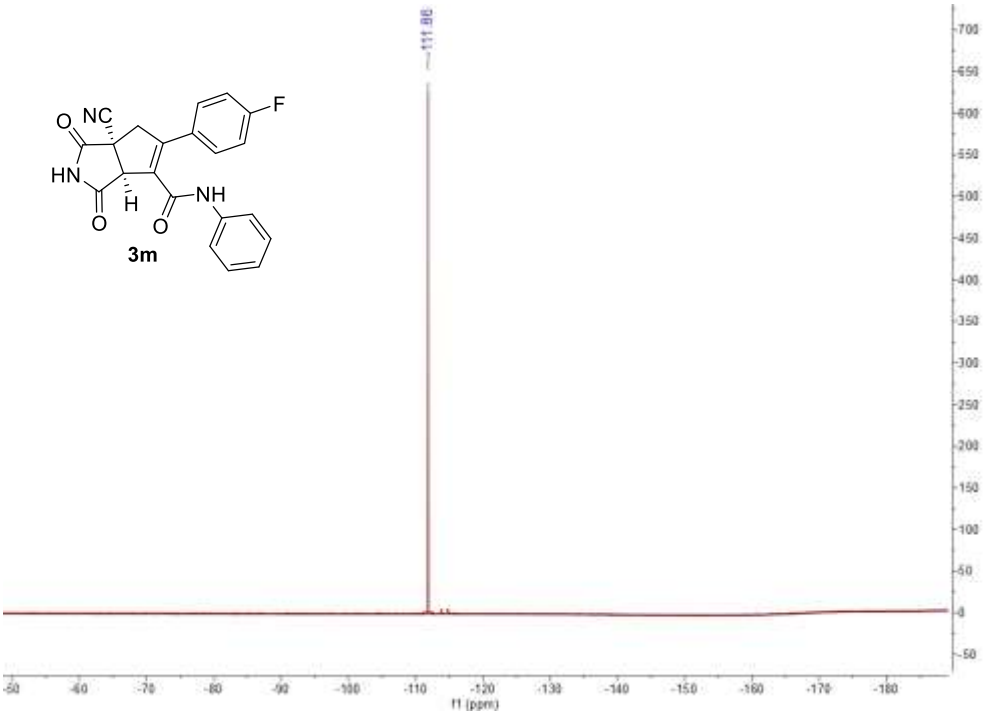
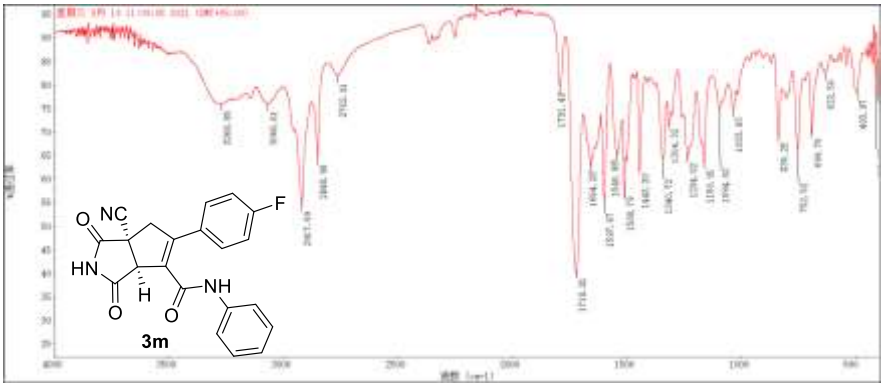
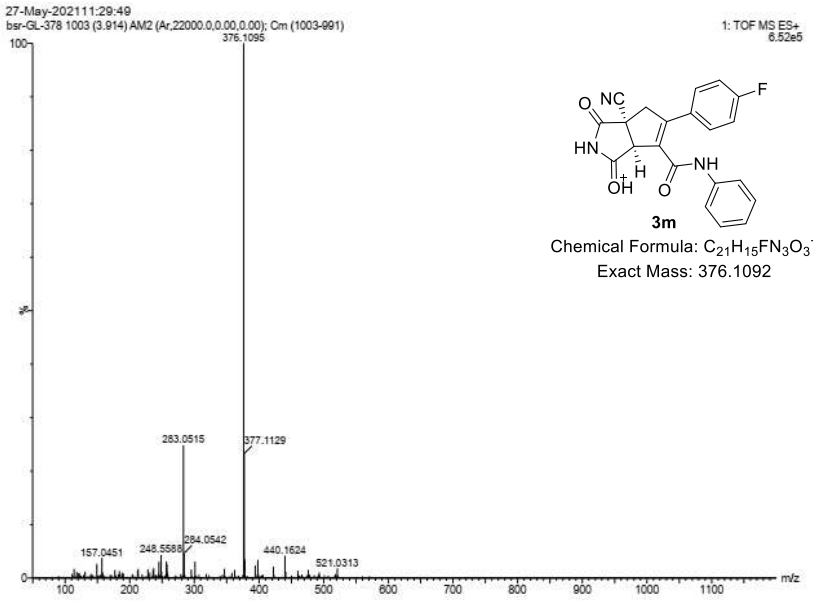
2.02e6
403.1050
404.1071
425.0862
218.1658
249.5294
339.2431
467.0565
548.0275
827.1822
%
m/z
3l
Chemical Formula: $C_{21}H_{15}N_4O_5^+$
Exact Mass: 403.1037


12.10
10.28
7.54
7.52
7.51
7.50
7.33
7.32
7.30
7.21
7.20
7.18
7.10
7.09
7.07
4.88
3.87
3.84
3.62
3.59
3.34
2.50
1.00
1.01
4.00
1.92
2.08
1.04
0.99
0.99
1.08
f1 (ppm)
O
NC
F
HN
H
NH
O
O
3m


174.65
173.29
163.51
163.14
161.88
140.15
139.07
130.38
130.33
129.96
129.95
129.26
128.80
124.34
120.06
118.68
115.90
115.76
61.82
46.04
45.73
40.43
40.30
40.16
40.02
39.88
39.75
39.61
f1 (ppm)
O
NC
F
HN
H
NH
O
O
3m



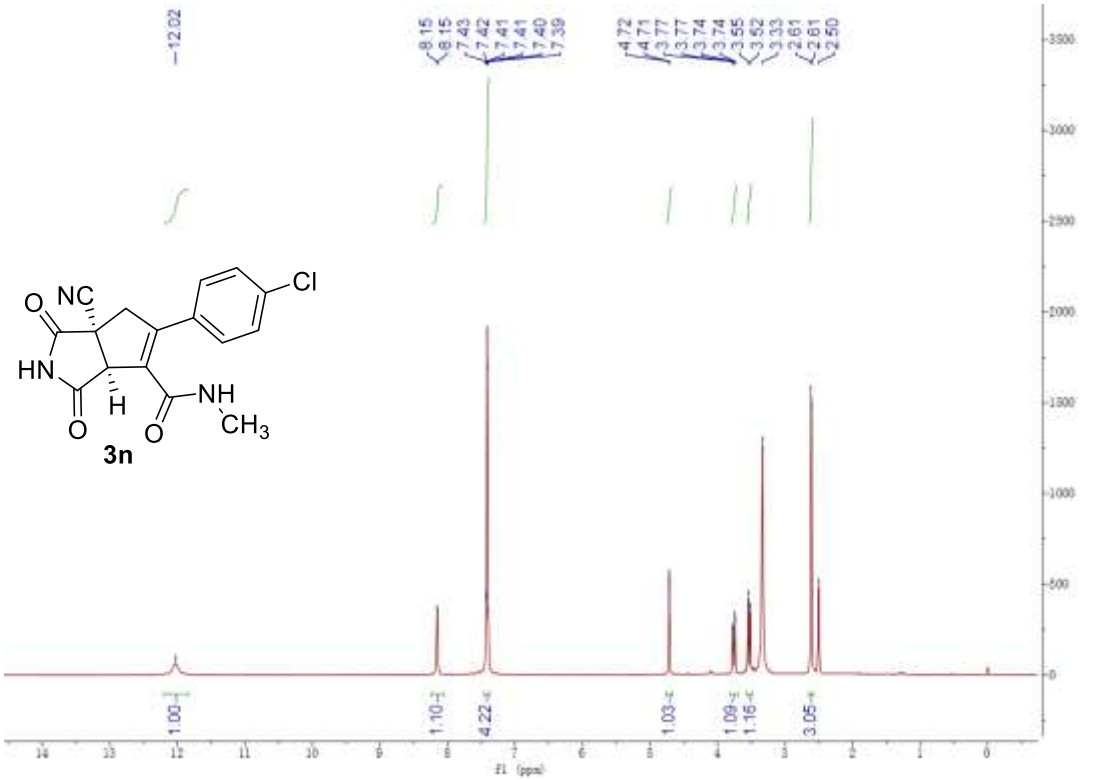




3m

Chemical Formula: $C_{21}H_{15}FN_3O_3^+$

Exact Mass: 376.1092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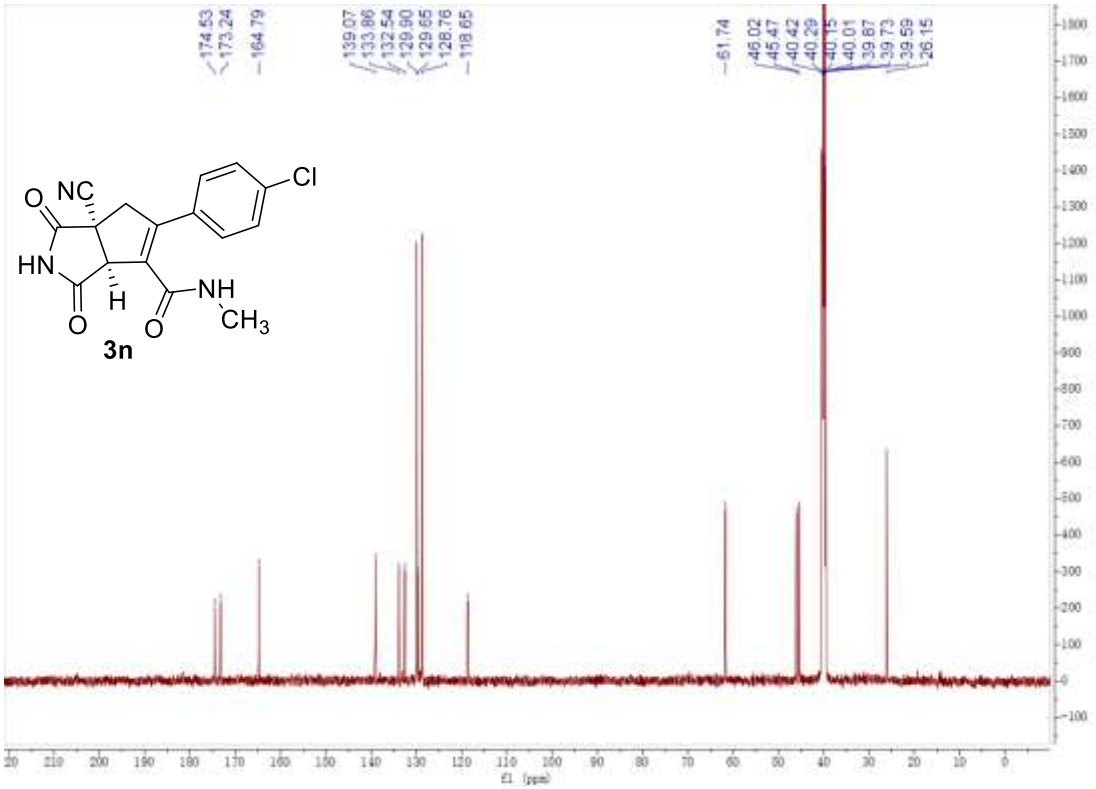
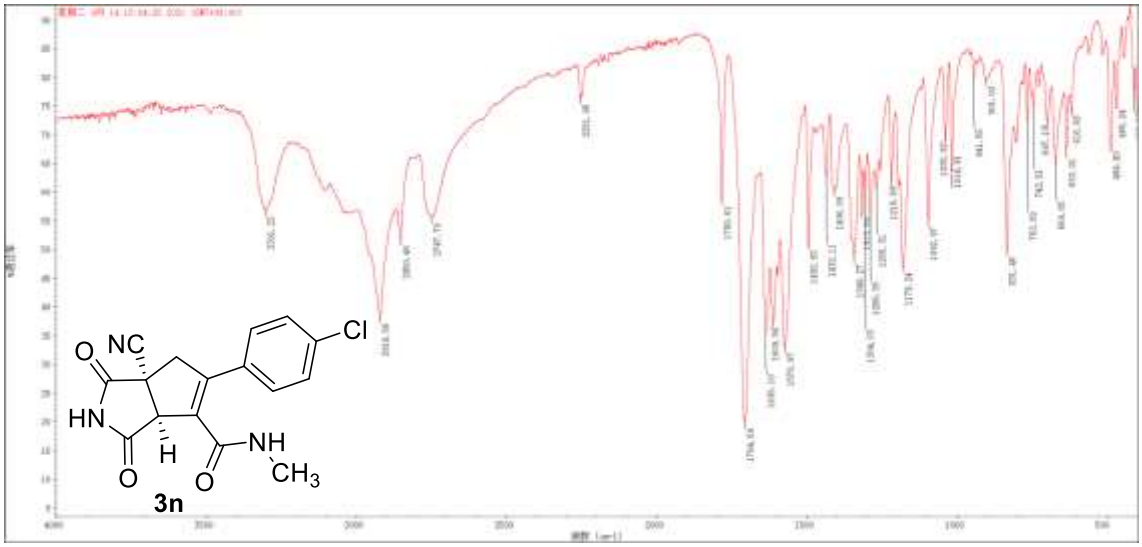
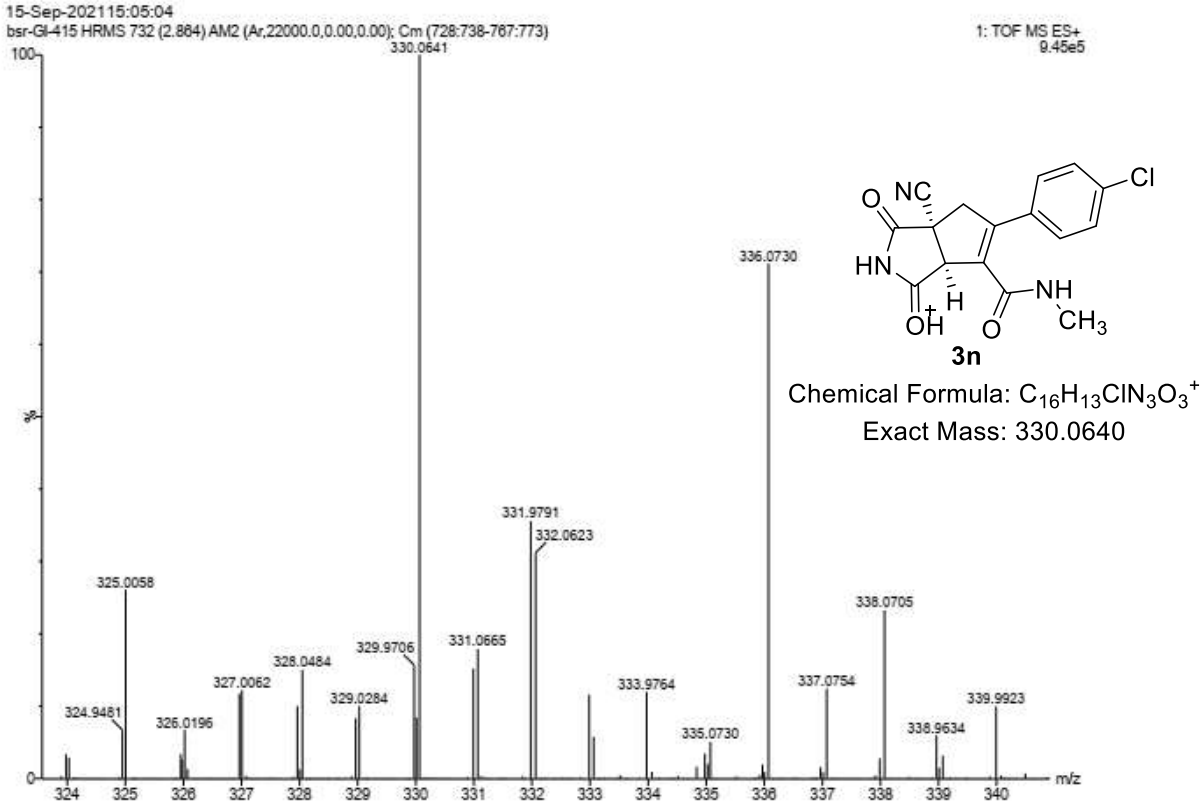
8.15
8.15
7.43
7.42
7.41
7.41
7.40
7.39
4.72
4.71
3.77
3.74
3.74
3.55
3.52
3.33
2.61
2.61
2.50
1.00
1.10
4.22
1.03
1.09
1.16
3.05
f1 (ppm)
O
NC
HN
O
H
O
NH
CH3
Cl
3n


174.53
173.24
164.79
139.07
133.86
132.54
129.90
129.65
128.76
118.65
61.74
46.02
45.47
40.42
40.29
40.15
40.01
39.87
39.73
39.59
26.15
f1 (ppm)
O
NC
HN
O
H
O
NH
CH3
Cl
3n


O
NC
Cl
HN
H
NH
CH3
O
O
O
3n


15-Sep-202115:05:04
bsr-GI-415 HRMS 732 (2.864) AM2 (Ar,22000.0,0.00,0.00); Cm (728:738-767:773)
1: TOF MS ES+
9.45e5
100
%
0
330.0641
336.0730
331.9791
332.0623
325.0058
338.0705
329.9706
331.0665
328.0484
327.0062
329.0284
333.9764
337.0754
339.9923
324.9481
326.0196
335.0730
338.9634
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
m/z
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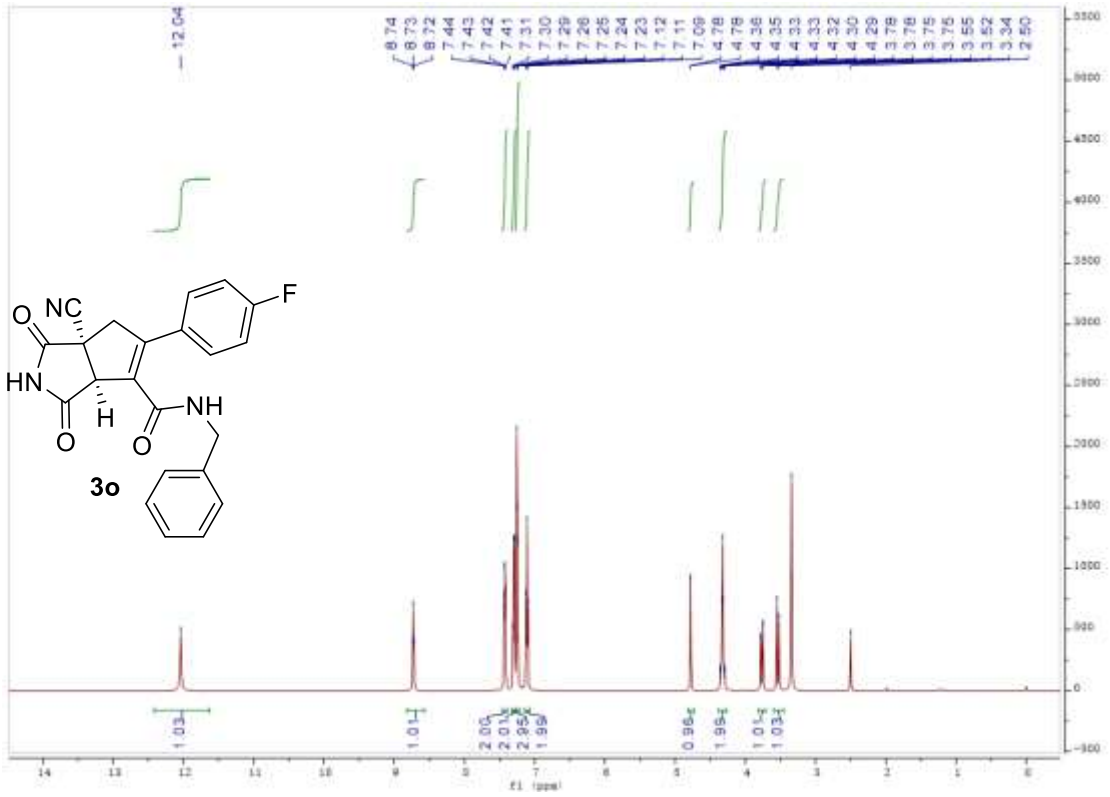
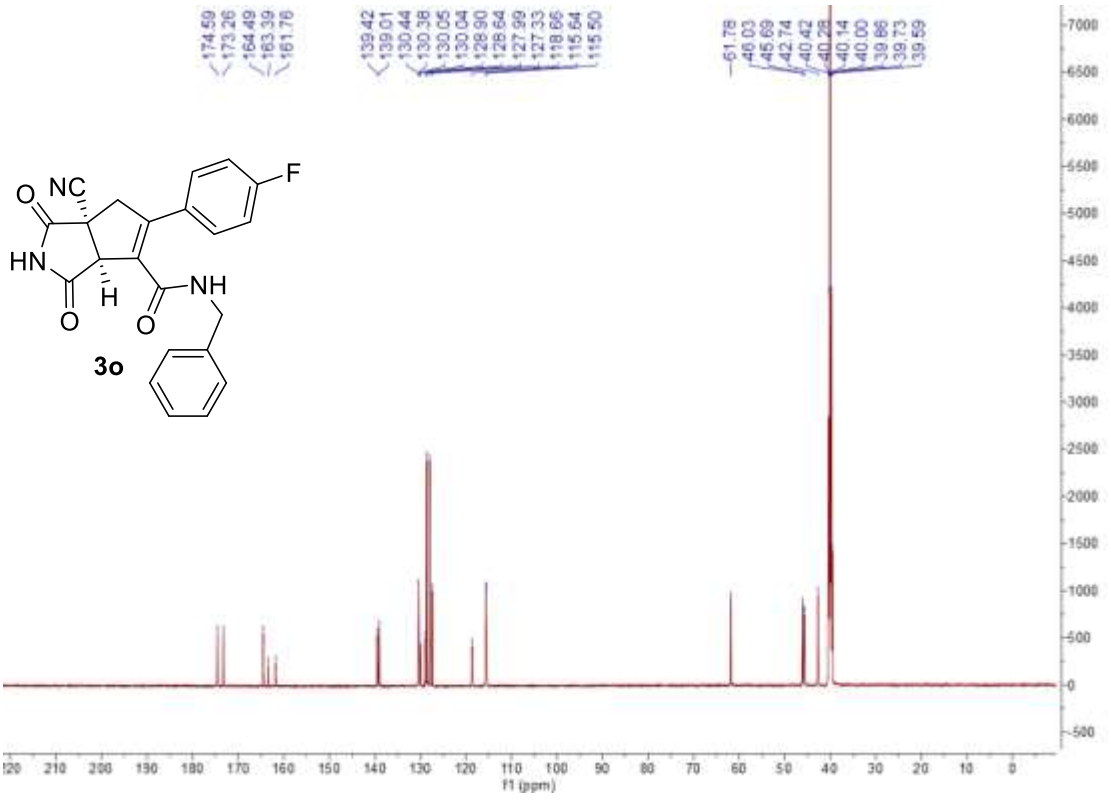
CH3
O
3n
Chemical Formula: C16H13ClN3O3+
Exact Mass: 330.0640


12.04
8.74
8.73
8.72
7.44
7.43
7.42
7.41
7.31
7.30
7.29
7.26
7.25
7.24
7.23
7.12
7.11
7.09
4.78
4.38
4.35
4.33
4.33
4.32
4.30
4.29
3.78
3.78
3.75
3.75
3.55
3.52
3.34
2.50
1.03
1.01
2.00
2.01
2.95
1.99
0.96
1.95
1.01
1.03
O
NC
HN
H
O
NH
O
F
3o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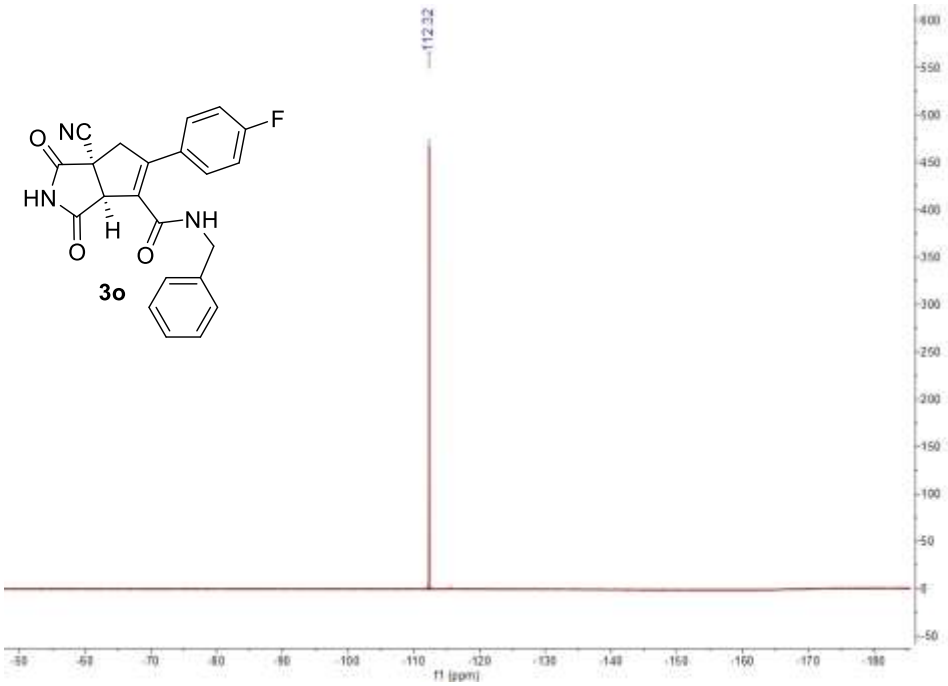
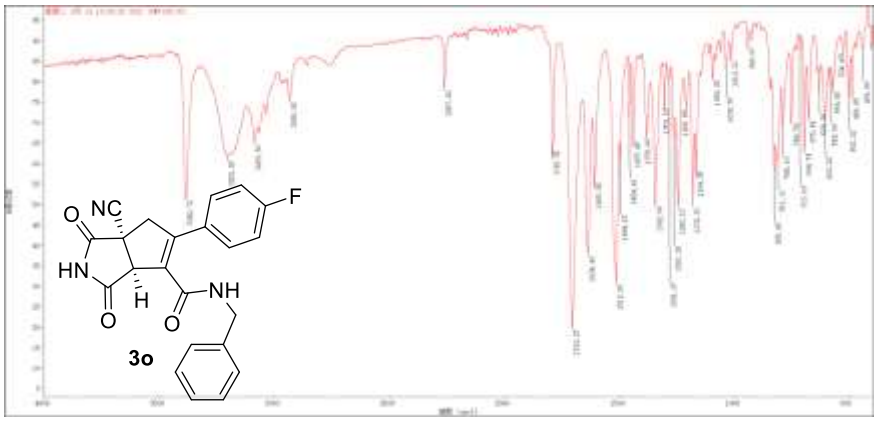
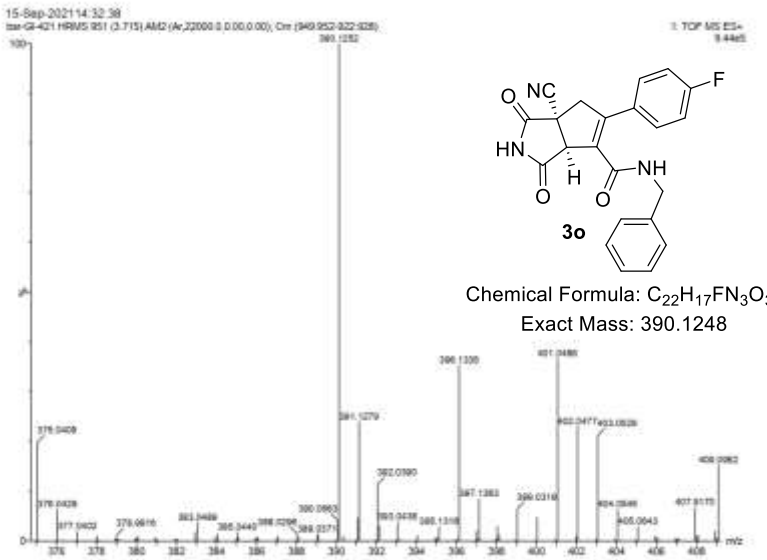
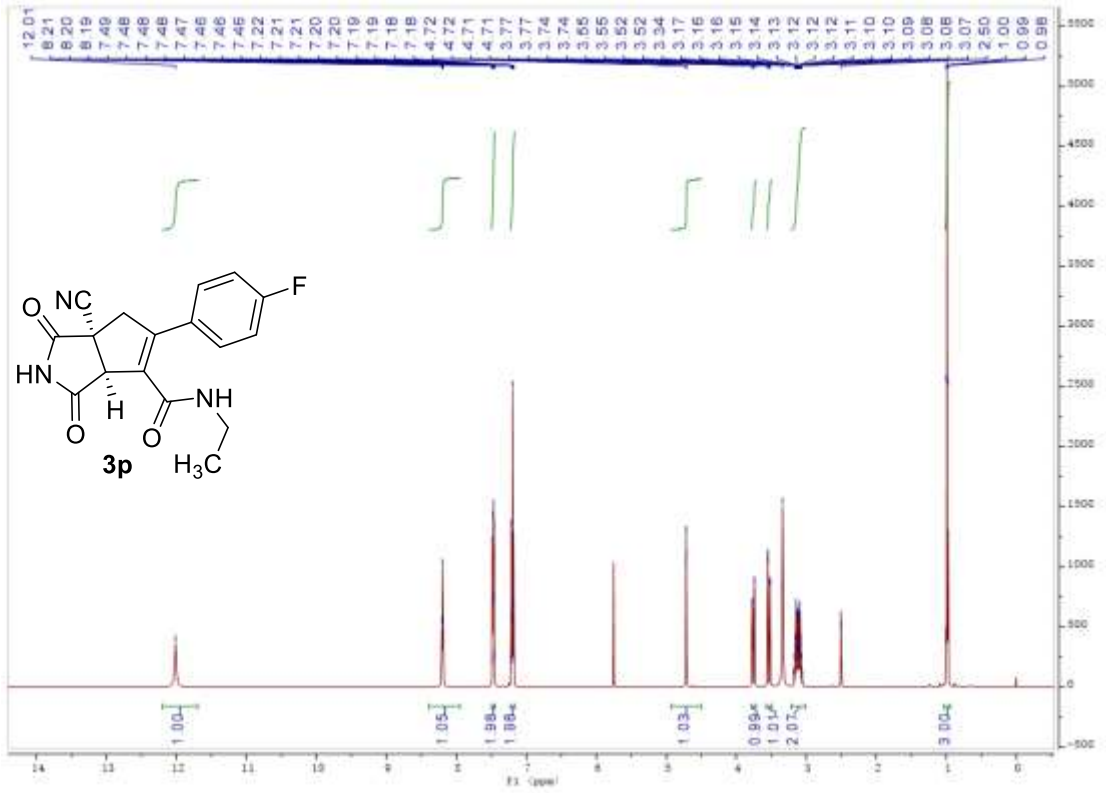
164.49
163.39
161.76
139.42
139.01
130.44
130.38
130.05
130.04
128.90
128.64
127.99
127.33
118.66
115.64
115.50
51.78
40.03
45.69
42.74
40.42
40.28
40.14
40.00
39.86
39.73
39.59
f1 (ppm)
O
NC
HN
H
O
NH
O
F
3o


NC
O
HN
H
O
NH
O
F
3o
-112.32
f1 (ppm)


NC
O
HN
H
O
NH
O
F
3o


15-Sep-202114:32:38
NC
O
HN
H
O
NH
O
F
3o
Chemical Formula: $C_{22}H_{17}FN_3O_3^+$
Exact Mass: 390.1248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7.49
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7.48
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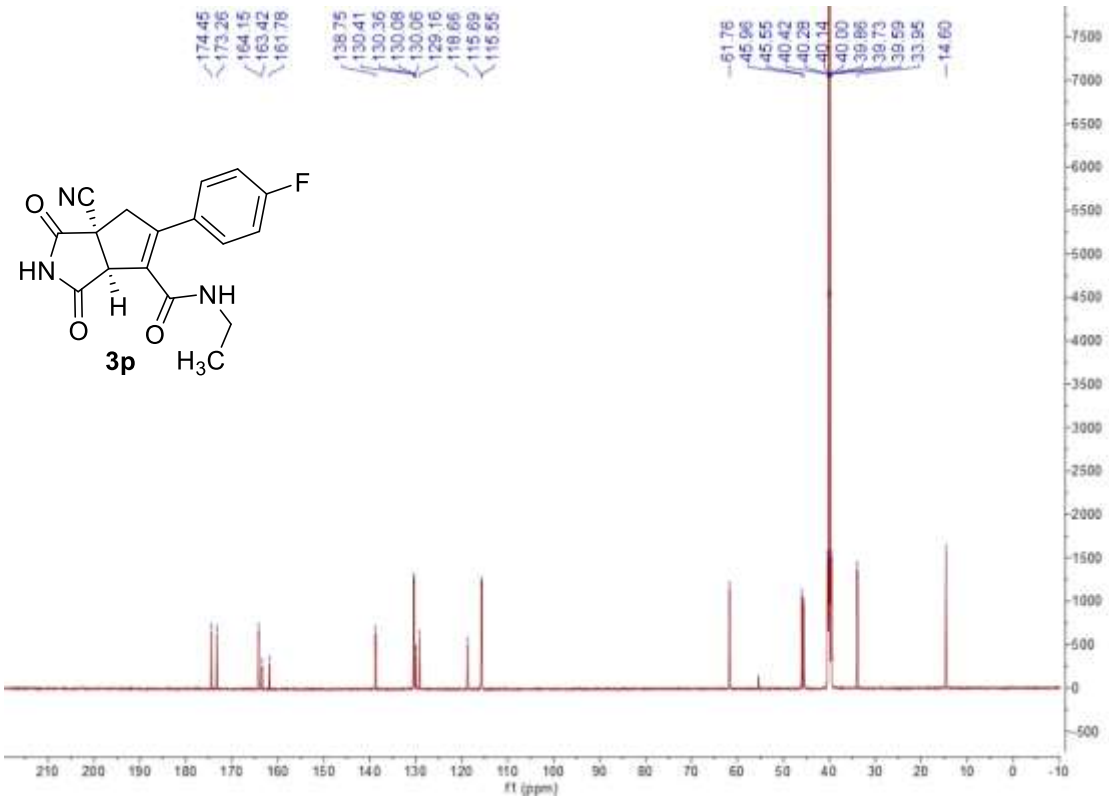
7.46
7.46
7.46
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
4.72
4.72
4.71
4.71
3.77
3.77
3.74
3.74
3.55
3.52
3.52
3.34
3.17
3.16
3.16
3.15
3.14
3.13
3.12
3.12
3.12
3.11
3.10
3.10
3.09
3.08
3.08
3.07
2.50
1.00
0.99
0.98
1.00
1.05
1.98
1.88
1.03
0.99
1.01
2.07
3.00
F1 (ppm)
O
NC
HN
O
H
O
NH
O
H3C
F
3p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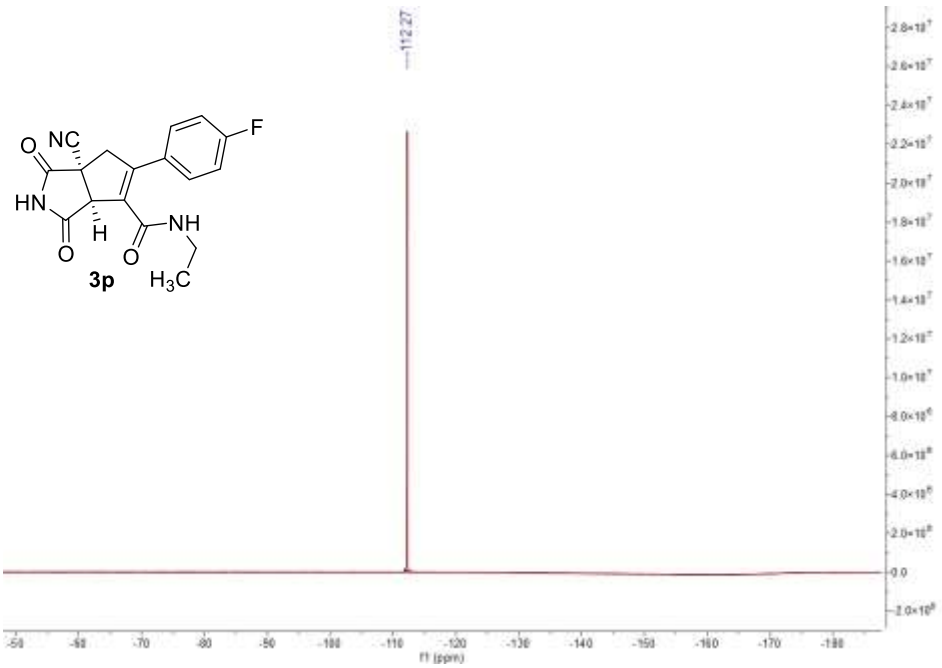
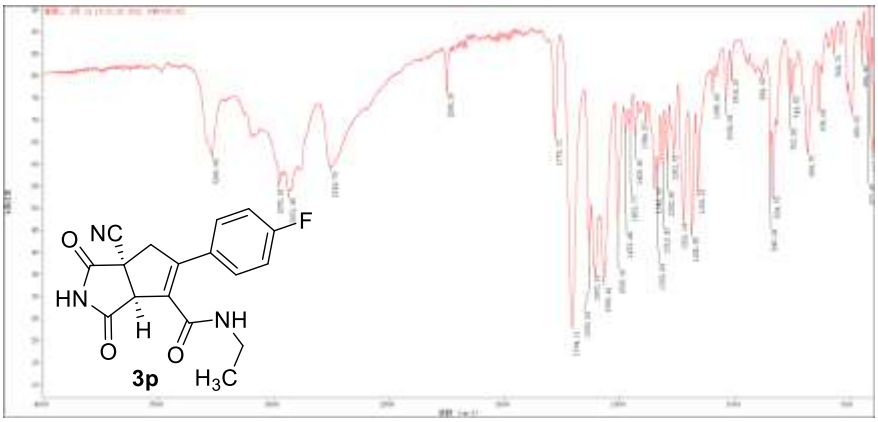
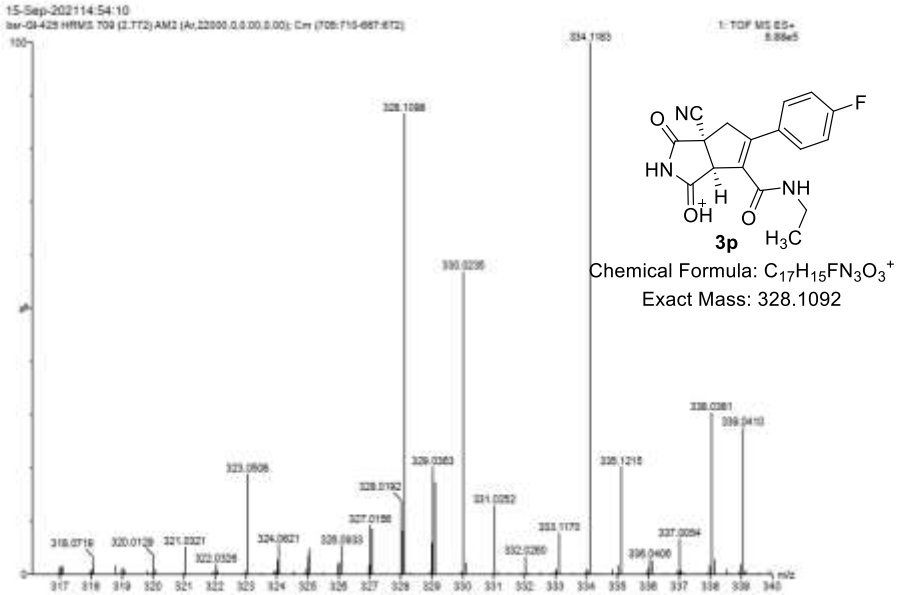
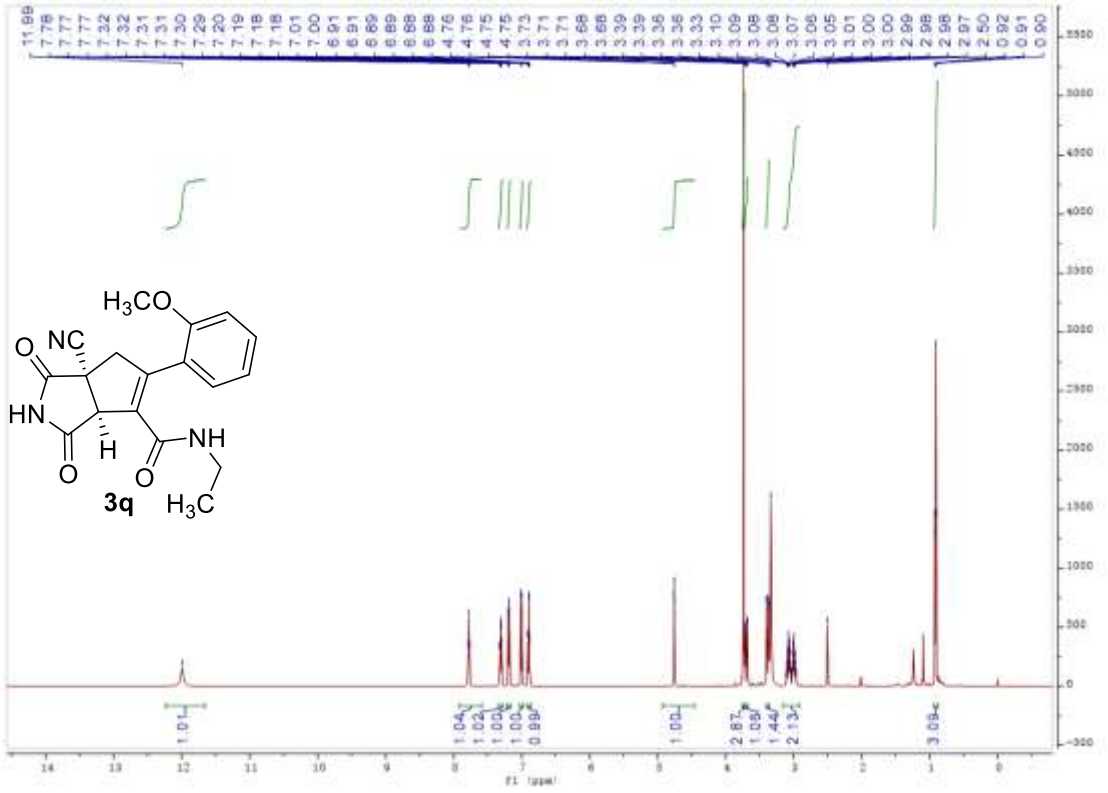
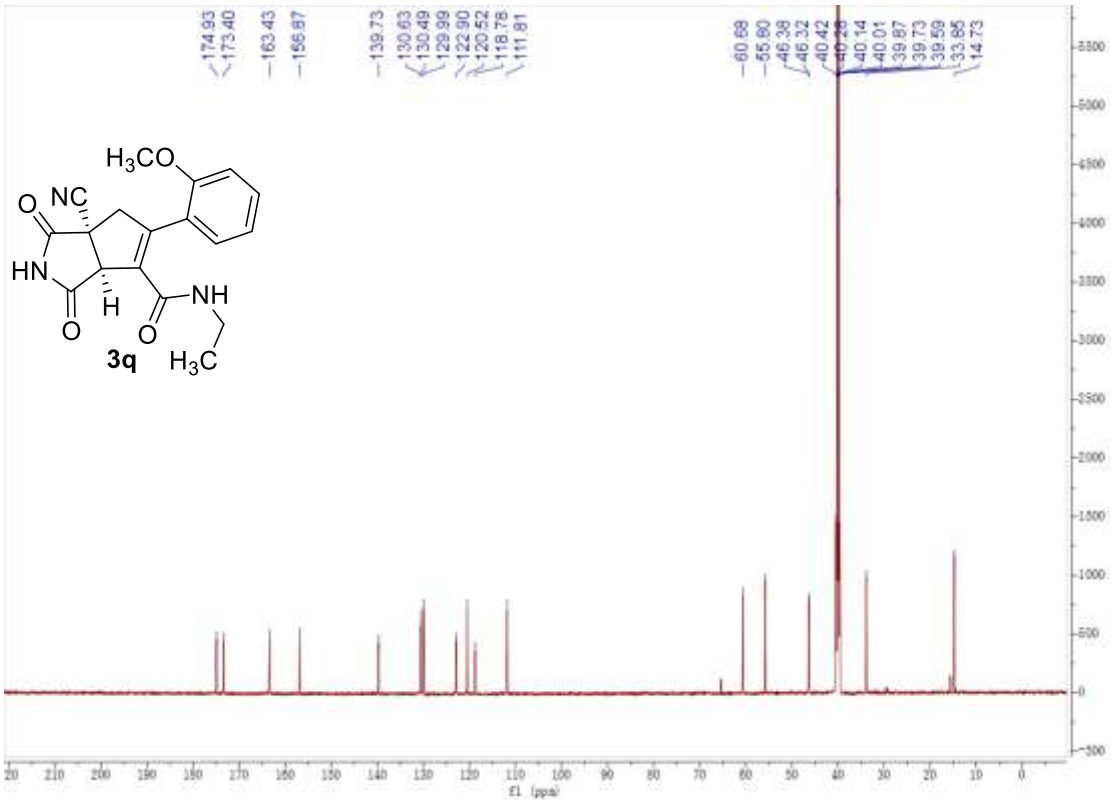
163.42
161.78
138.75
130.41
130.36
130.08
130.06
129.16
118.66
115.69
115.55
61.76
45.98
45.55
40.42
40.28
40.14
40.00
39.86
39.73
39.59
33.95
14.60
F1 (ppm)
O
NC
HN
O
H
O
NH
O
H3C
F
3p

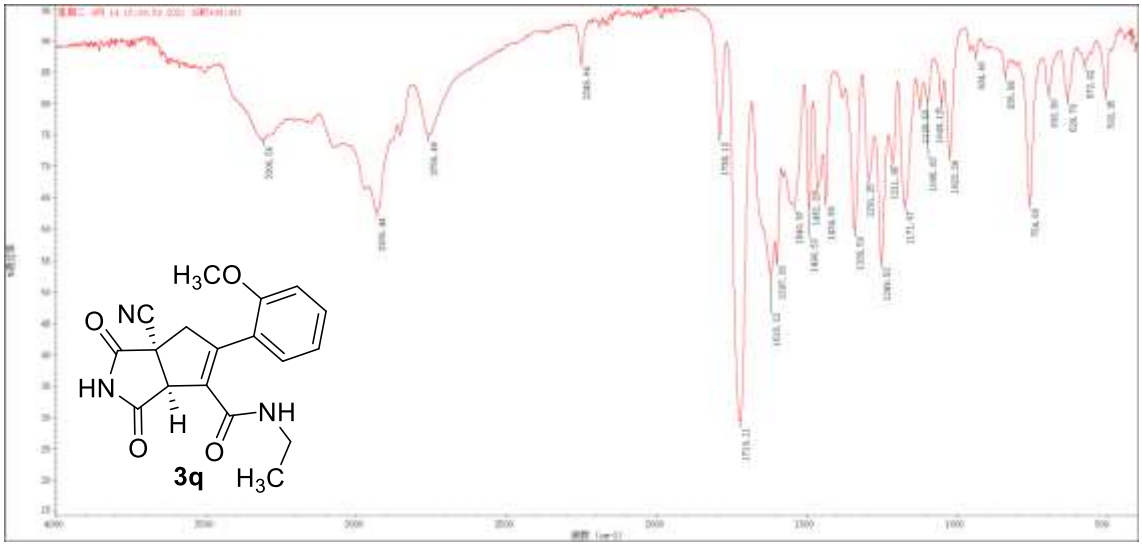

-112.27
F
O
NC
HN
H
O
NH
O
3p
H_3C
f1 (ppm)

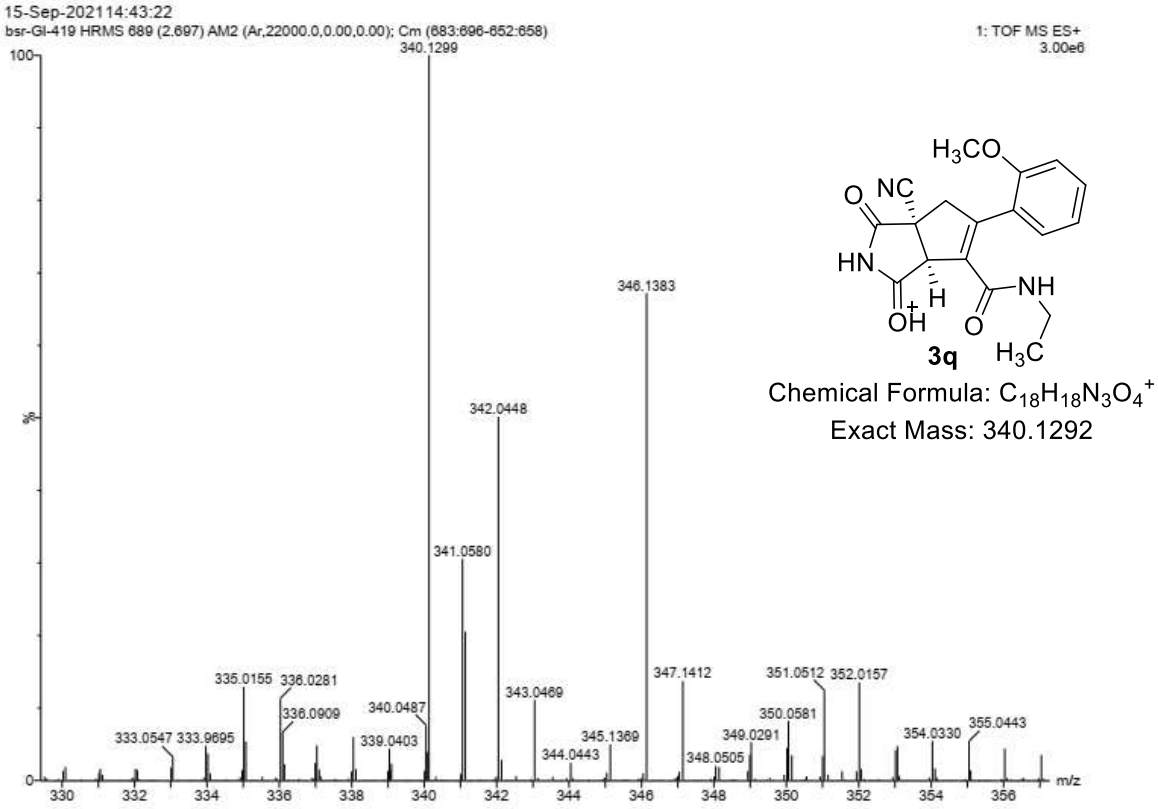

F
O
NC
HN
H
O
NH
O
3p
H_3C


15-Sep-202114:54:10
1: TOF MS ES+
334.1183
328.1098
330.0235
329.0263
323.0508
328.0192
327.0156
331.0252
333.1172
335.1215
338.0361
339.0410
337.0054
316.0716
320.0129
321.0321
322.0326
324.0621
326.0933
332.0260
336.0406
F
O
NC
HN
H
OH
NH
O
3p
H_3C
Chemical Formula: $C_{17}H_{15}FN_3O_3^+$
Exact Mass: 328.1092


H3CO
NC
O
HN
H
NH
O
O
3q
H3C

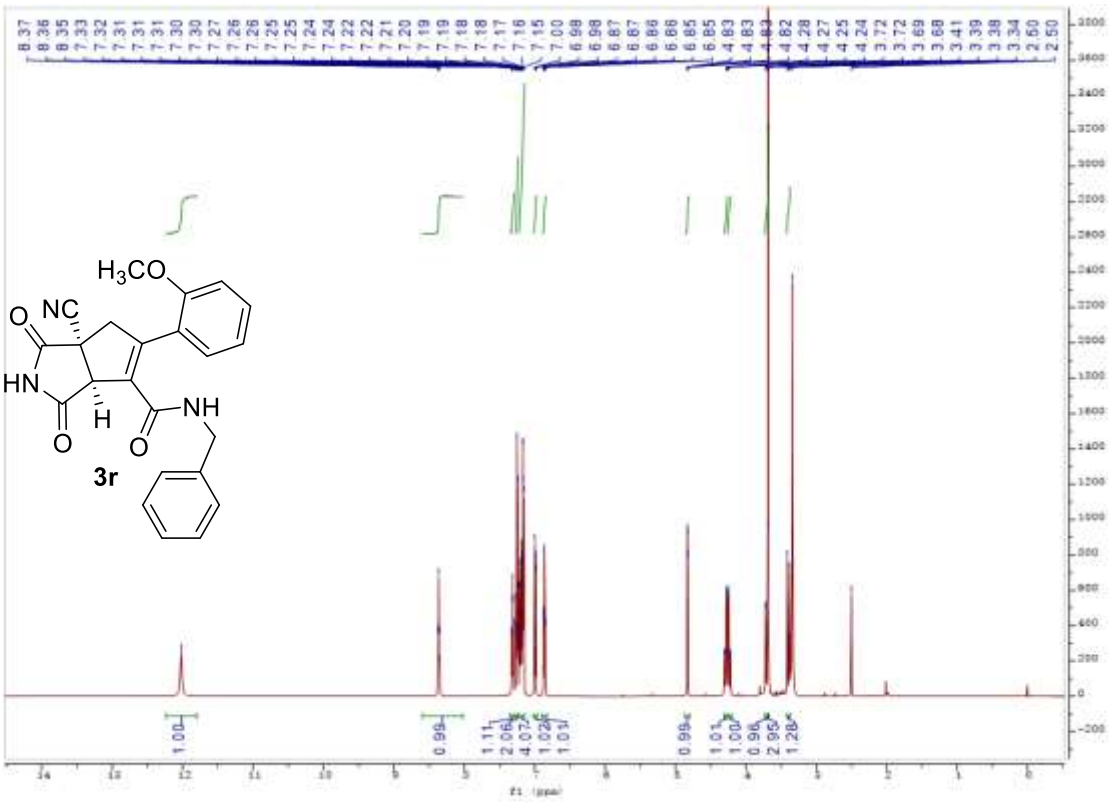

H3CO
NC
O
HN
H
NH
O
O
3q
H3C

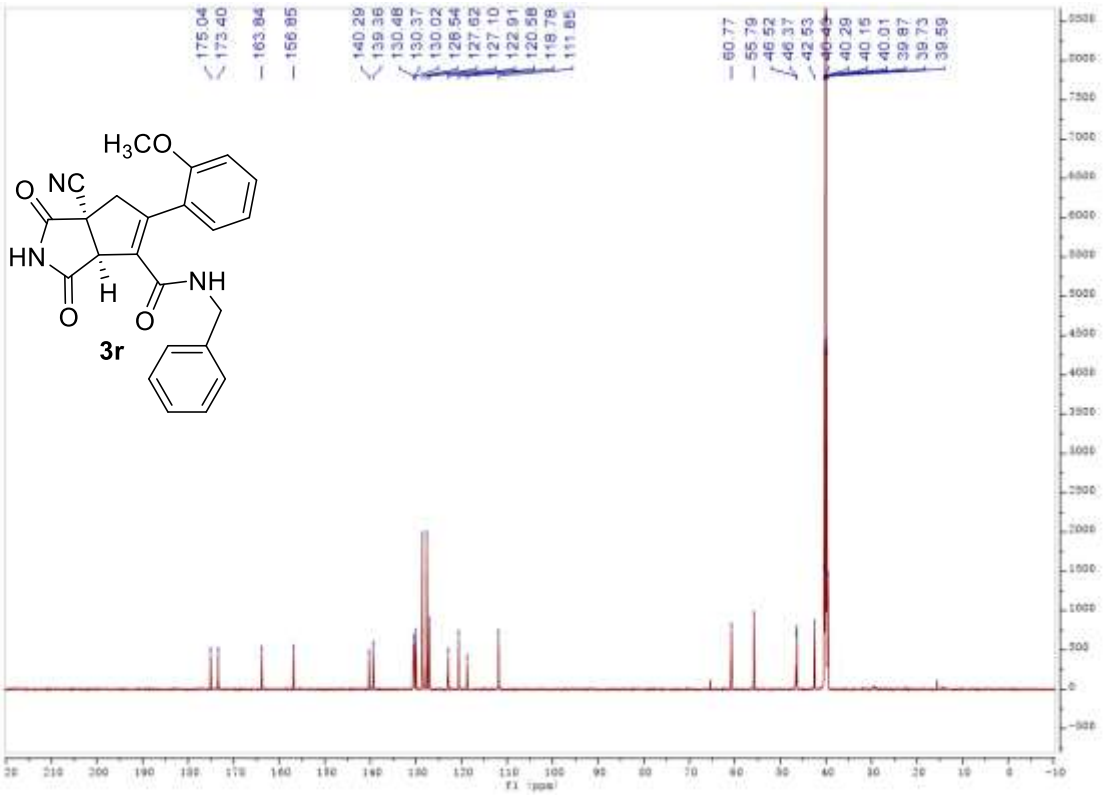


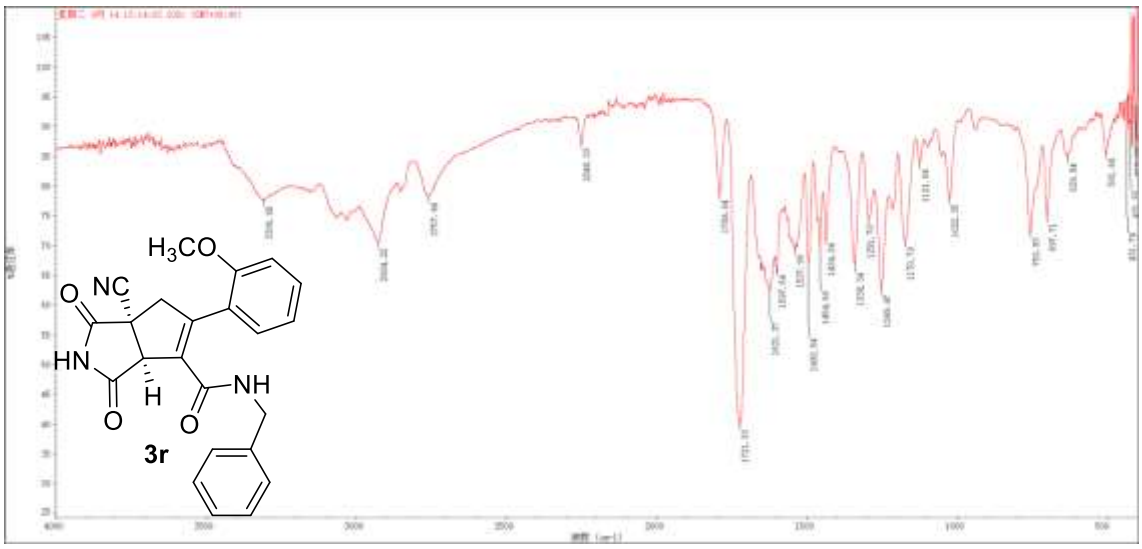


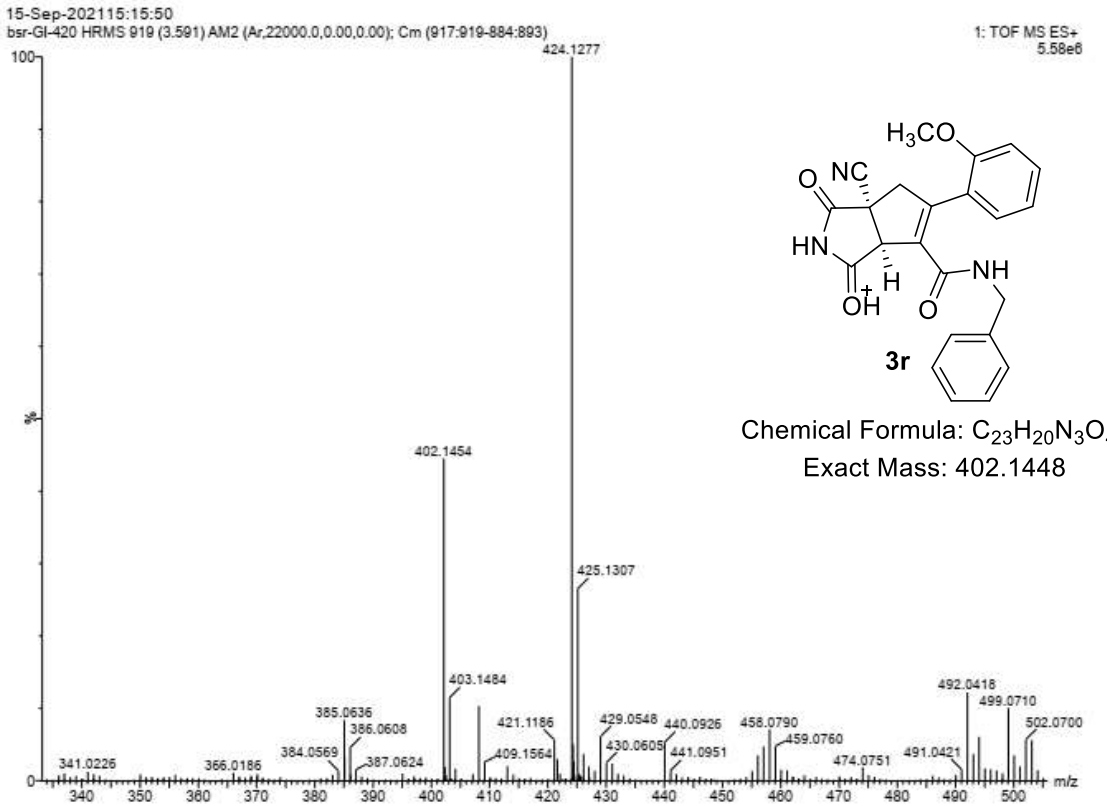
Chemical Formula: $C_{18}H_{18}N_3O_4^+$

Exact Mass: 340.1292


H3CO
NC
O
HN
O
H
NH
O
3r

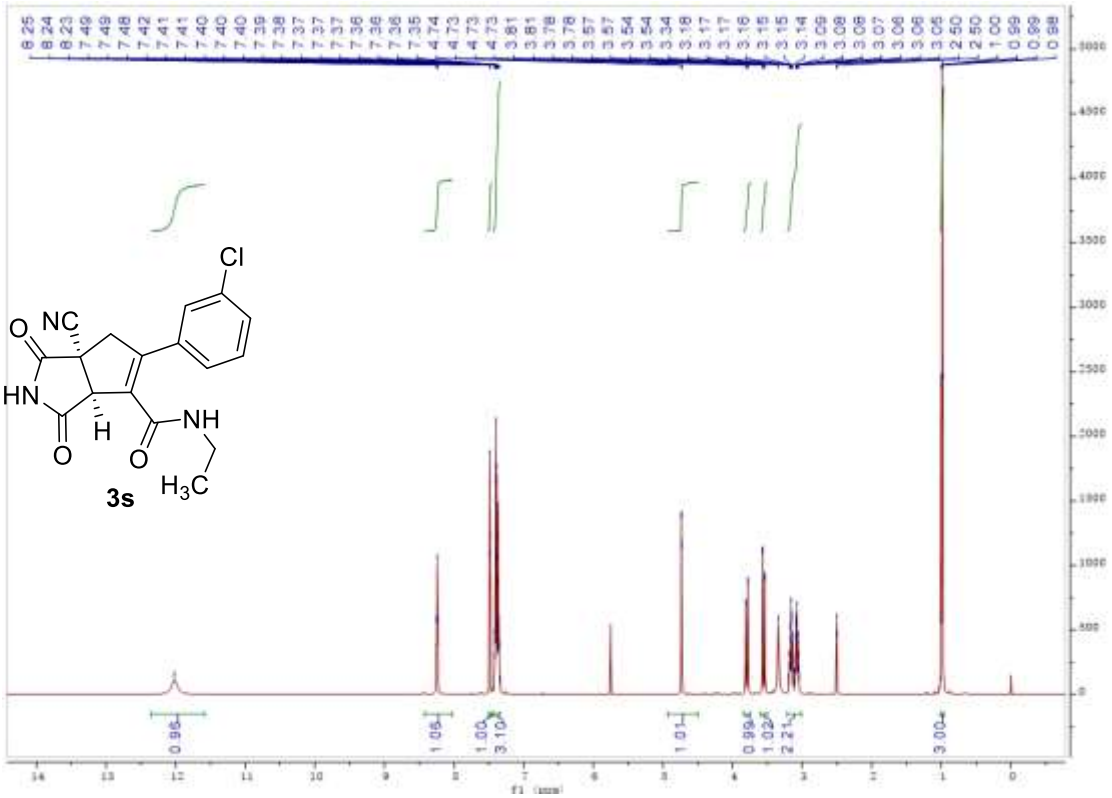

H3CO
NC
O
HN
O
H
NH
O
3r

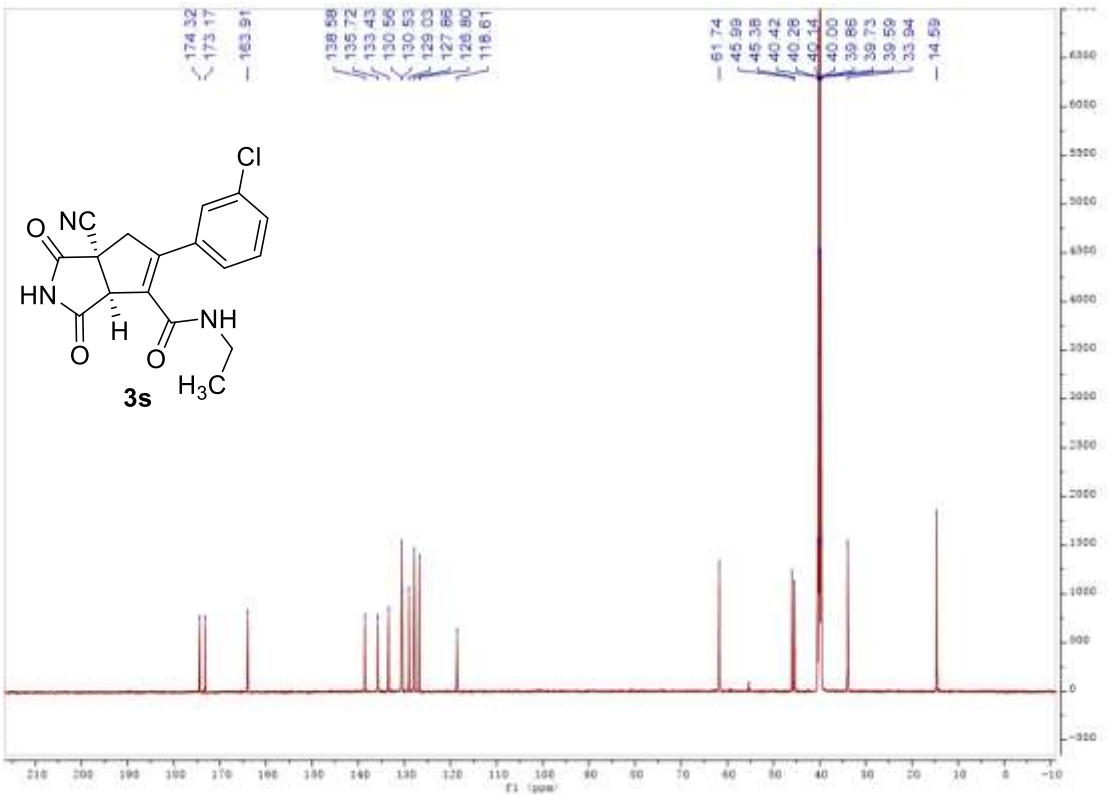


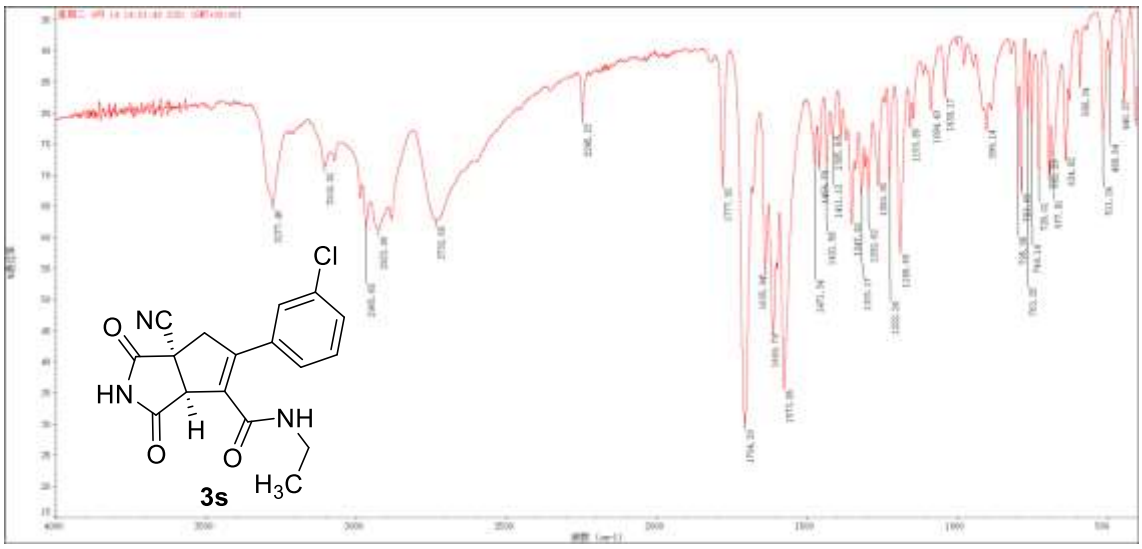


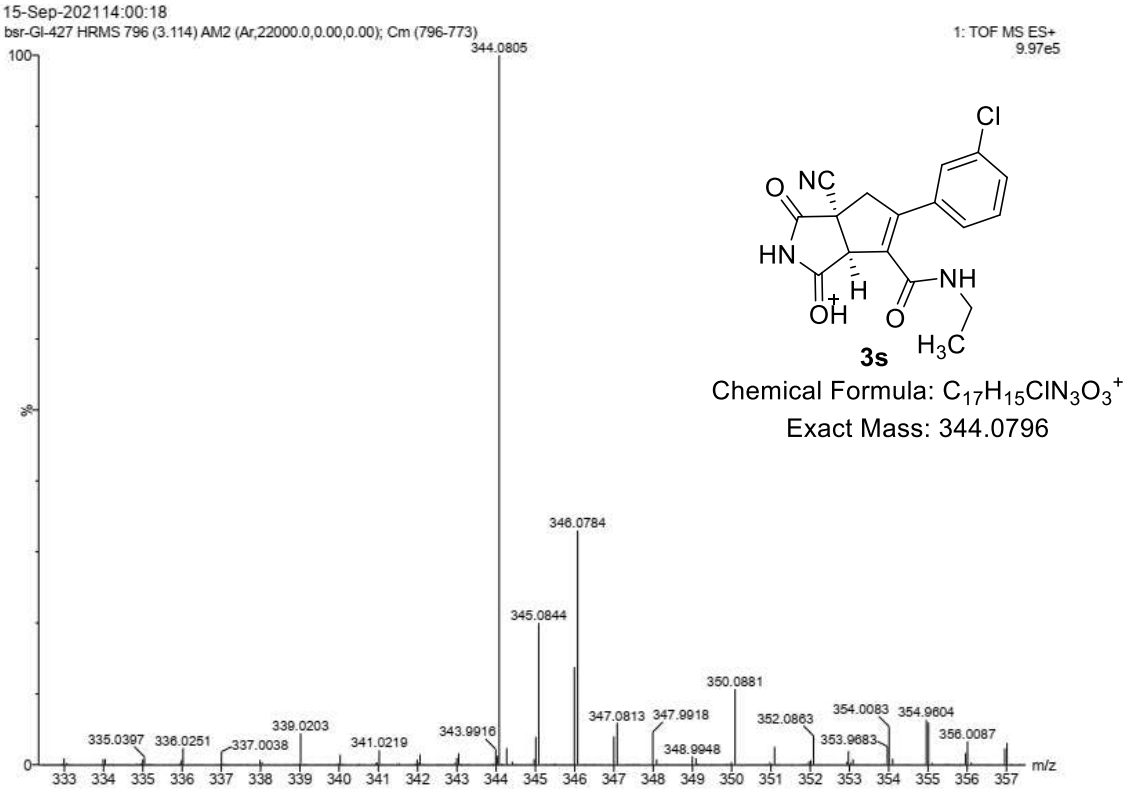
Chemical Formula: $C_{23}H_{20}N_3O_4^+$

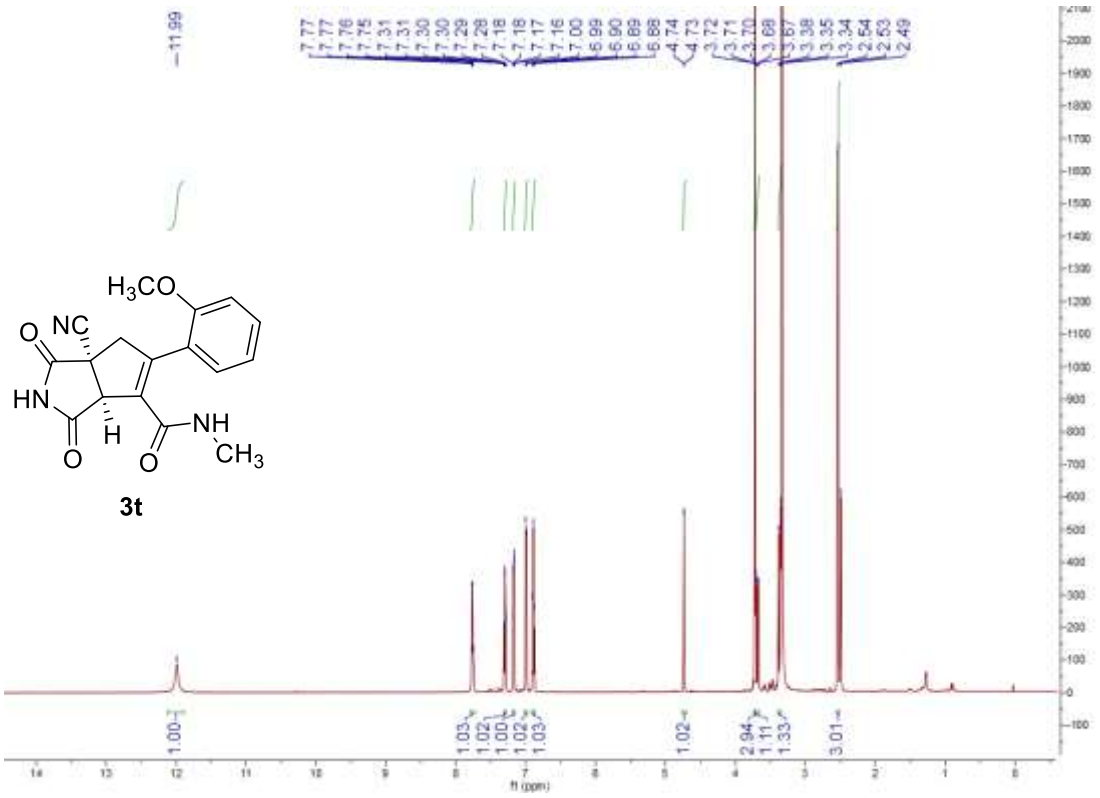
Exact Mass: 402.1448


Cl
NC
O
HN
H
O
NH
O
H3C
3s


Cl
NC
O
HN
H
O
NH
O
H3C
3s

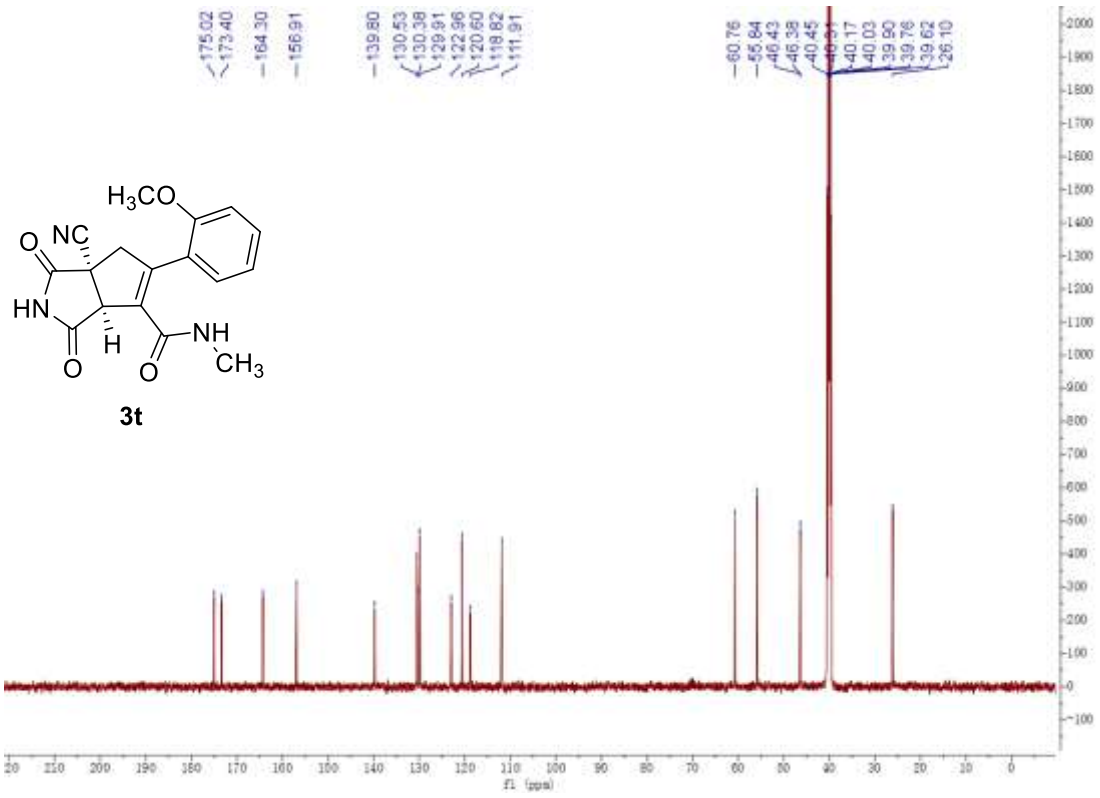

Cl
O
NC
HN
H
O
NH
O
H3C
3s


15-Sep-202114:00:18
bsr-GI-427 HRMS 796 (3.114) AM2 (Ar,22000.0,0.00,0.00); Cm (796-773)
1: TOF MS ES+
9.97e5
100
%
0
344.0805
346.0784
345.0844
350.0881
347.0813
347.9918
352.0863
354.0083
354.9604
356.0087
353.9683
348.9948
339.0203
335.0397
336.0251
337.0038
341.0219
343.9916
333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357
m/z
Cl
O
NC
HN
H
OH+
NH
O
H3C
3s
Chemical Formula: C17H15ClN3O3+
Exact Mass: 344.0796


11.99
7.77
7.77
7.76
7.75
7.31
7.31
7.30
7.30
7.29
7.28
7.18
7.18
7.17
7.16
7.00
6.99
6.90
6.89
6.88
4.74
4.73
3.72
3.71
3.70
3.68
3.67
3.38
3.35
3.34
2.54
2.53
2.49
1.00
1.03
1.02
1.00
1.02
1.03
1.02
2.94
1.11
1.33
3.01
f1 (ppm)

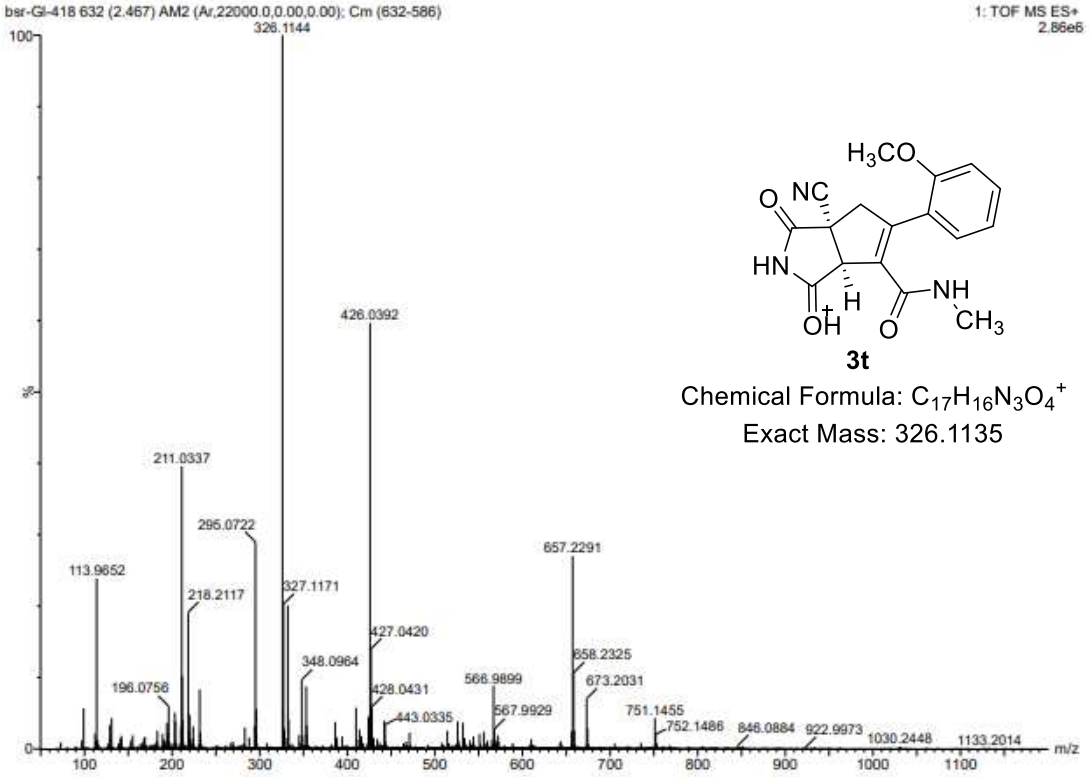
H3CO
NC
O
HN
H
NH
CH3
O
O

3t


175.02
173.40
164.30
156.91
139.80
130.53
130.38
129.91
122.96
120.60
118.82
111.91
60.76
55.84
46.43
46.38
40.45
40.17
40.03
39.90
39.76
39.62
26.10
f1 (ppm)

H3CO
NC
O
HN
H
NH
CH3
O
O

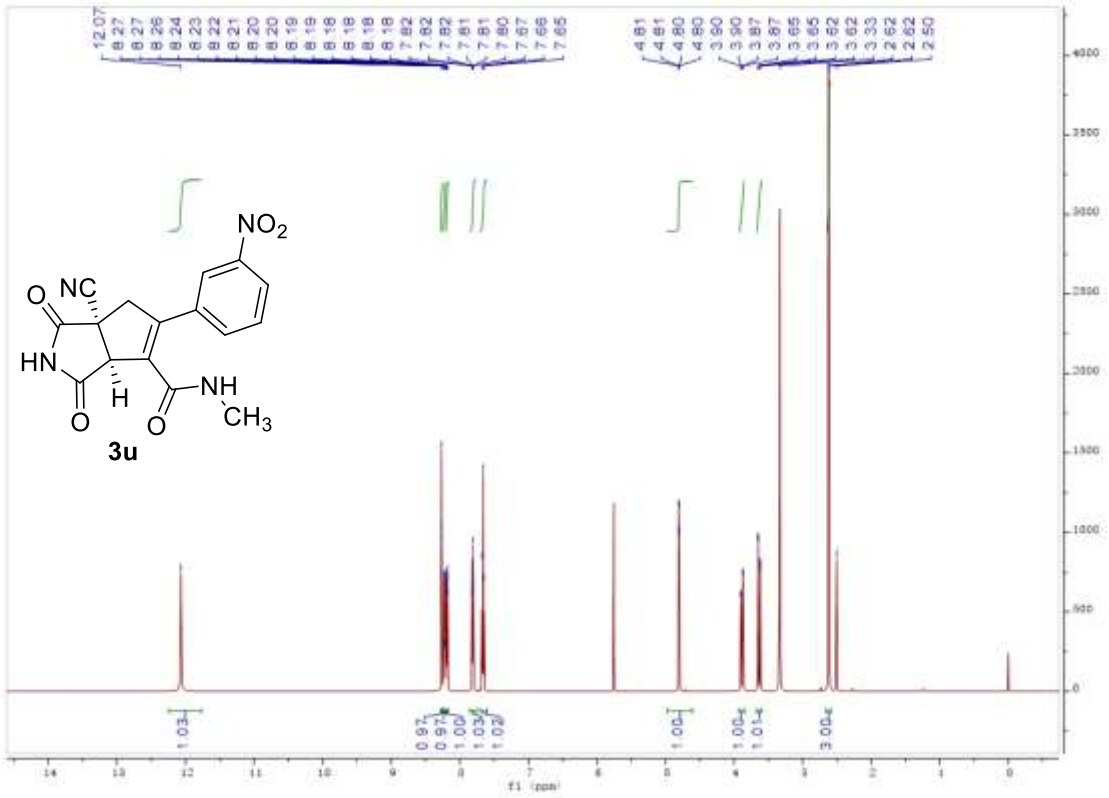
3t

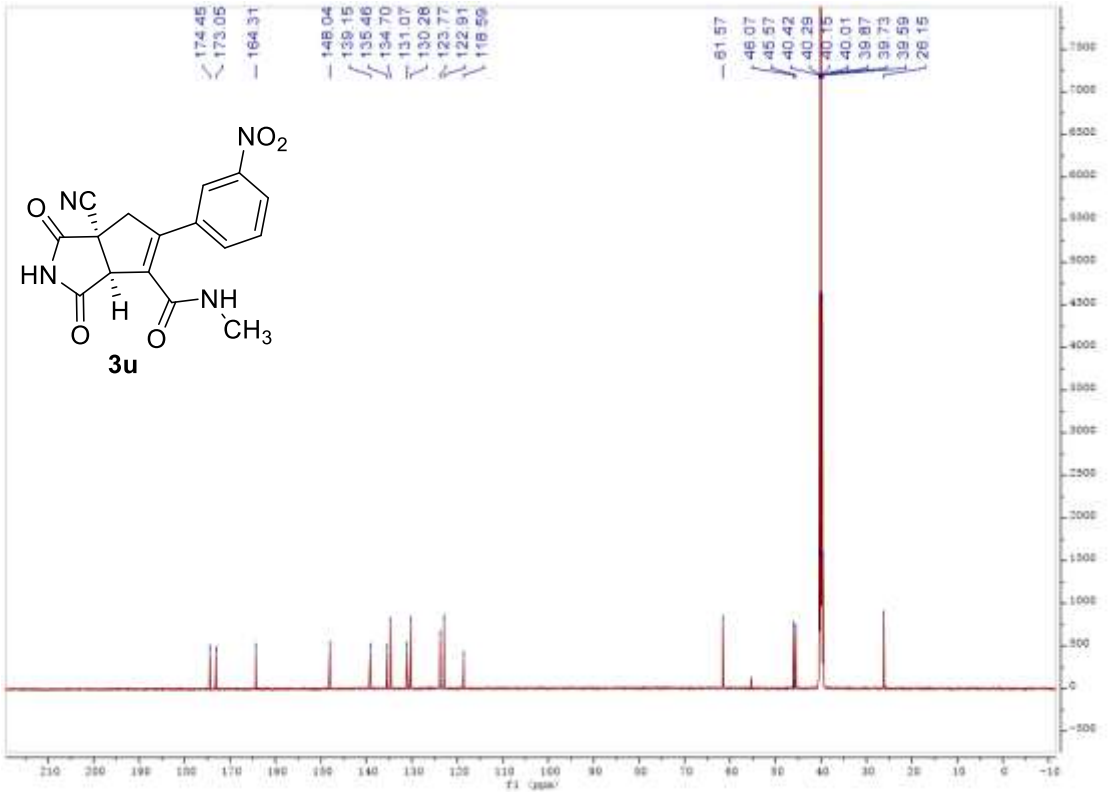


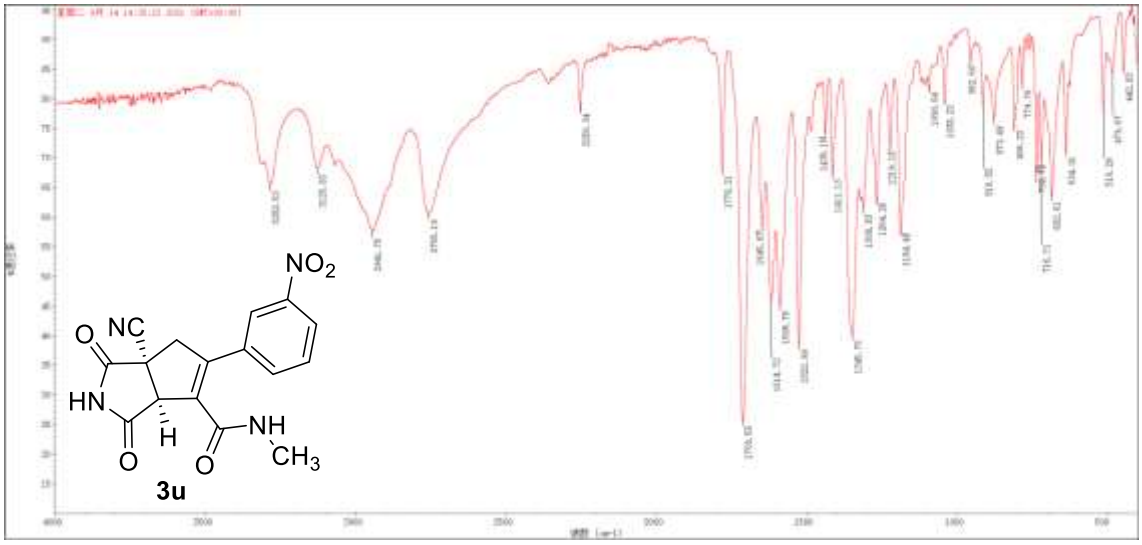
3t

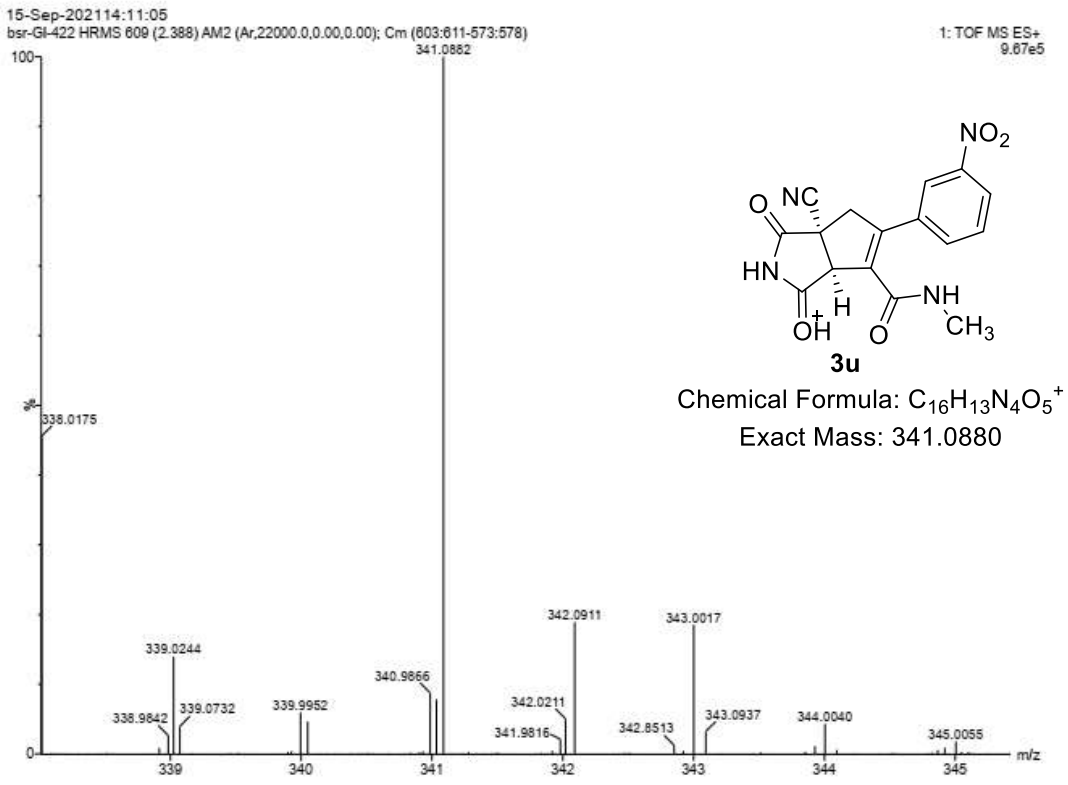
Chemical Formula: $C_{17}H_{16}N_3O_4^+$

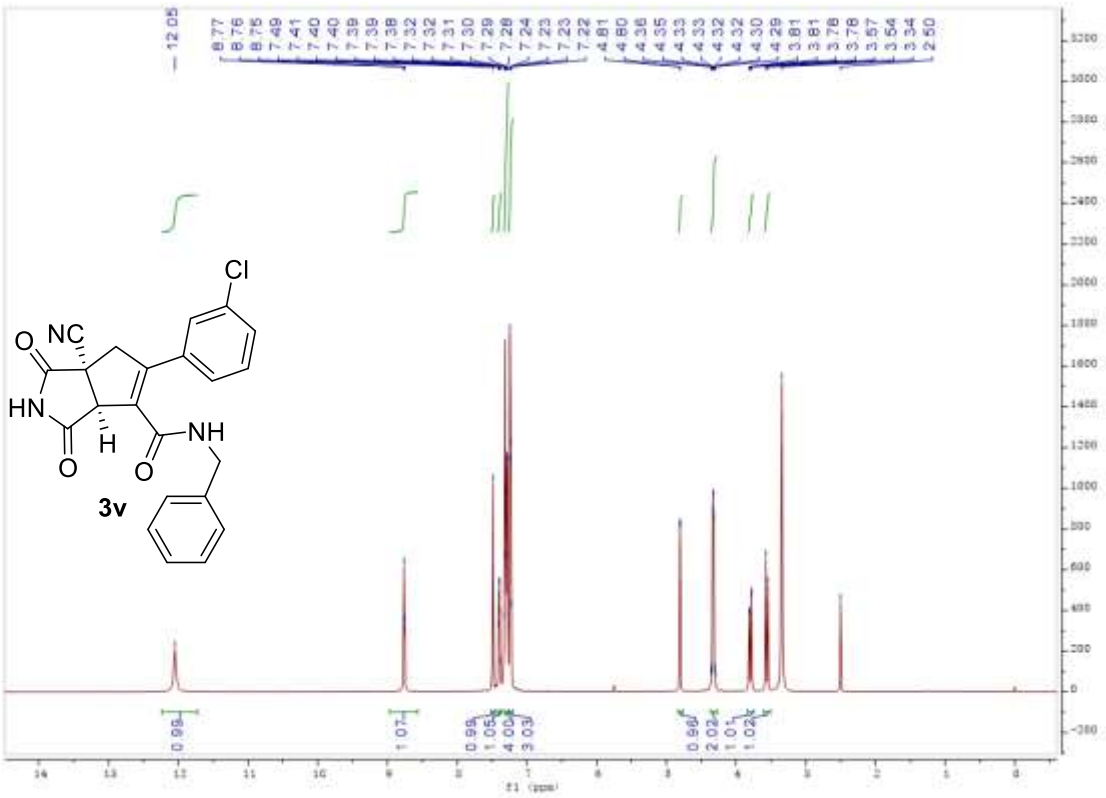
Exact Mass: 326.1135

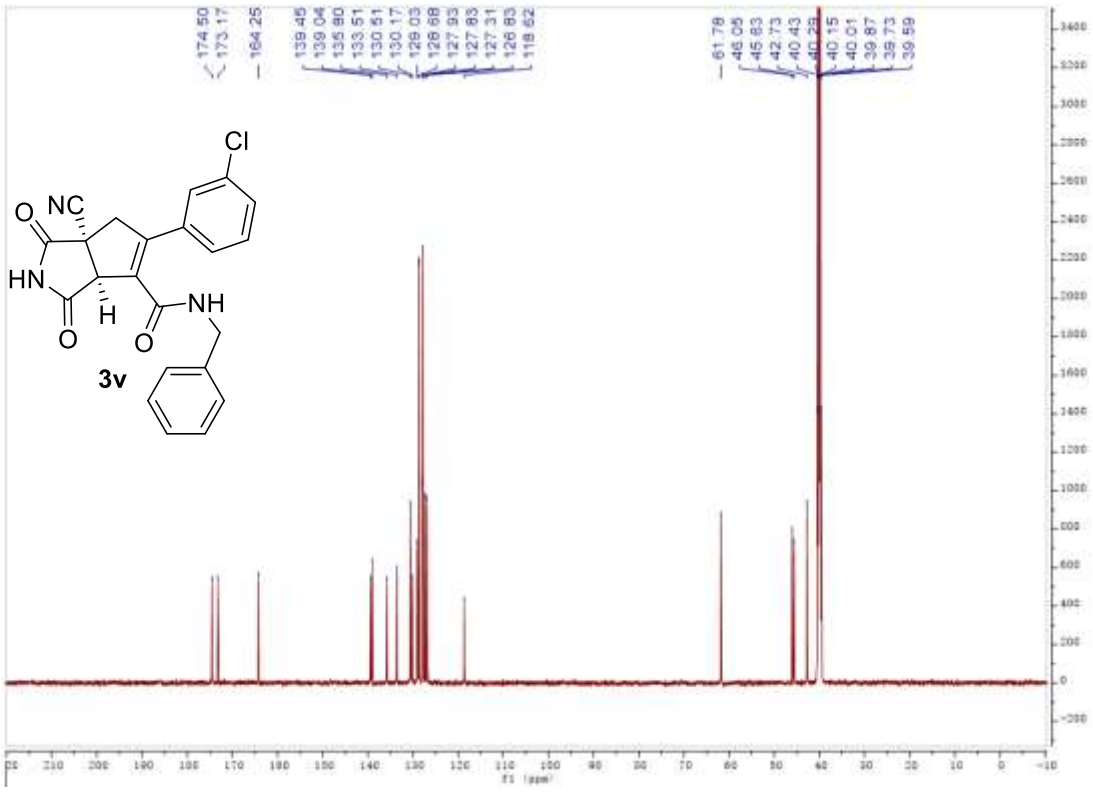

12.07
8.27
8.27
8.26
8.24
8.23
8.22
8.21
8.20
8.20
8.19
8.19
8.18
8.18
8.18
8.18
7.82
7.82
7.82
7.81
7.81
7.80
7.67
7.66
7.65
4.81
4.81
4.80
4.80
3.90
3.90
3.87
3.87
3.65
3.65
3.62
3.62
3.33
2.62
2.62
2.50
NO2
NC
O
HN
O
H
O
NH
CH3
3u
1.03
0.97
0.97
1.00
1.03
1.02
1.00
1.00
1.01
3.00
f1 (ppm)

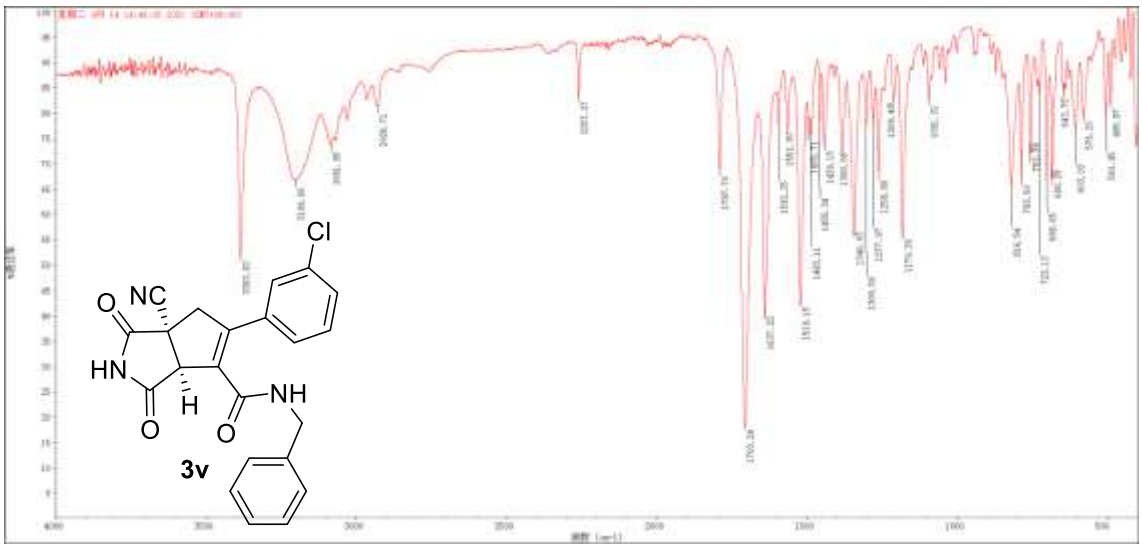

174.45
173.05
164.31
148.04
139.15
135.46
134.70
131.07
130.28
123.77
122.91
118.59
61.57
46.07
45.57
40.42
40.29
40.15
40.01
39.87
39.73
39.59
26.15
NO2
NC
O
HN
O
H
O
NH
CH3
3u
f1 (ppm)

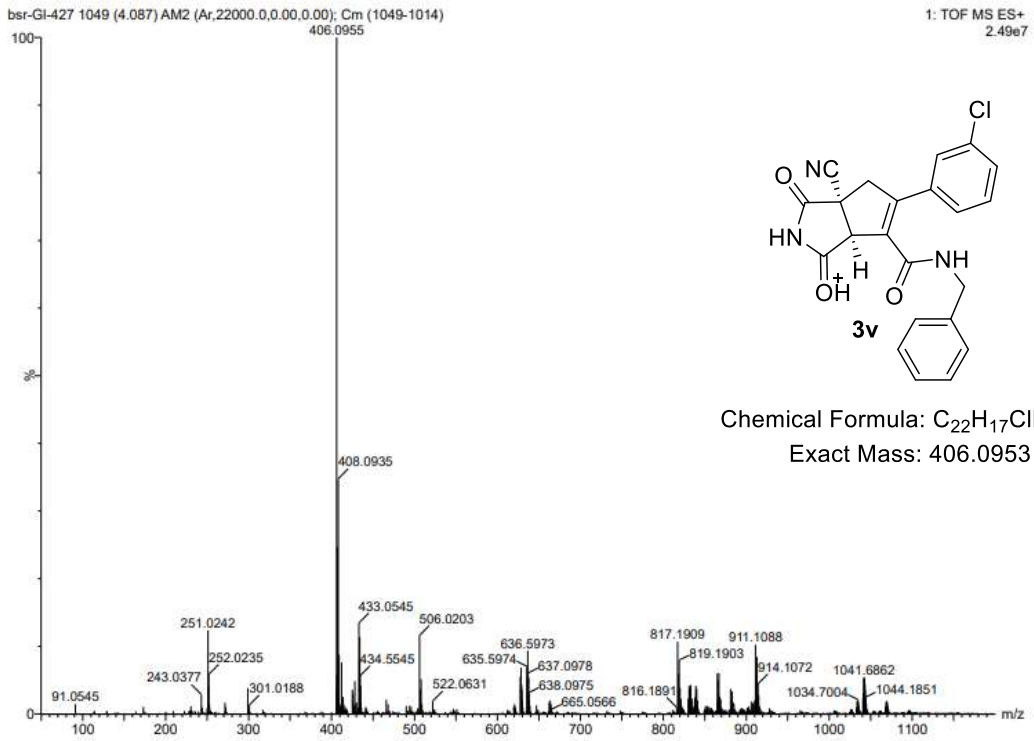

NO2
NC
O
HN
H
NH
CH3
O
O
3u


15-Sep-202114:11:05
bsr-GI-422 HRMS 609 (2.388) AM2 (Ar,22000.0,0.00,0.00); Cm (603:611-573:578)
1: TOF MS ES+
9.67e5
100
%
0
341.0882
338.0175
339.0244
338.9842
339.0732
339.9952
340.9866
342.0911
342.0211
341.9816
342.8513
343.0017
343.0937
344.0040
345.0055
339
340
341
342
343
344
345
m/z
NO2
NC
O
HN
H
OH
NH
CH3
O
3u
Chemical Formula: C16H13N4O5+
Exact Mass: 341.0880

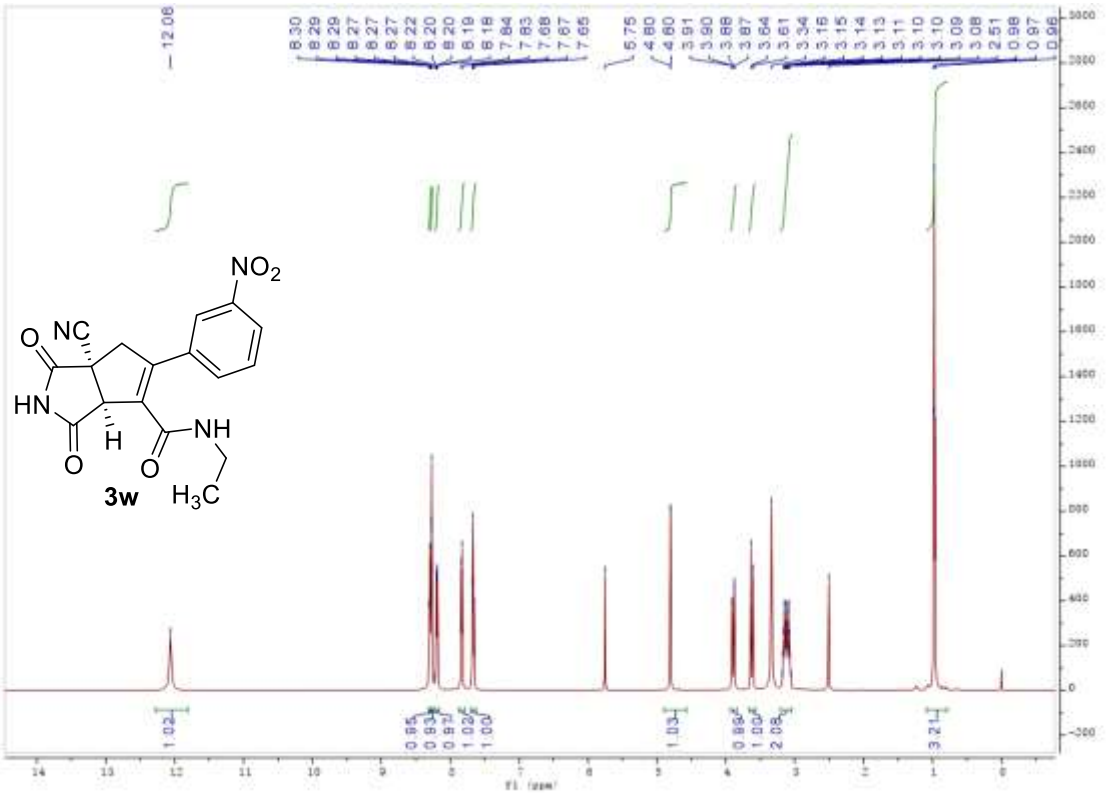

Cl
NC
O
HN
H
NH
O
O
3v

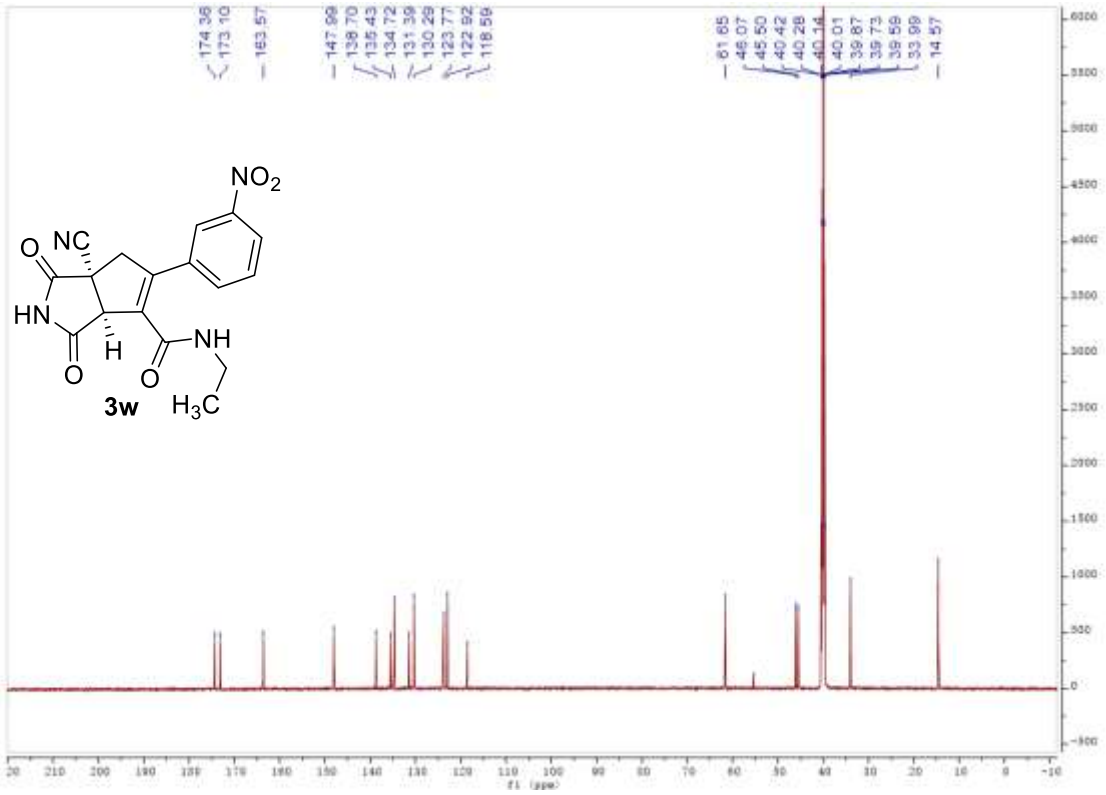

Cl
NC
O
HN
H
NH
O
O
3v

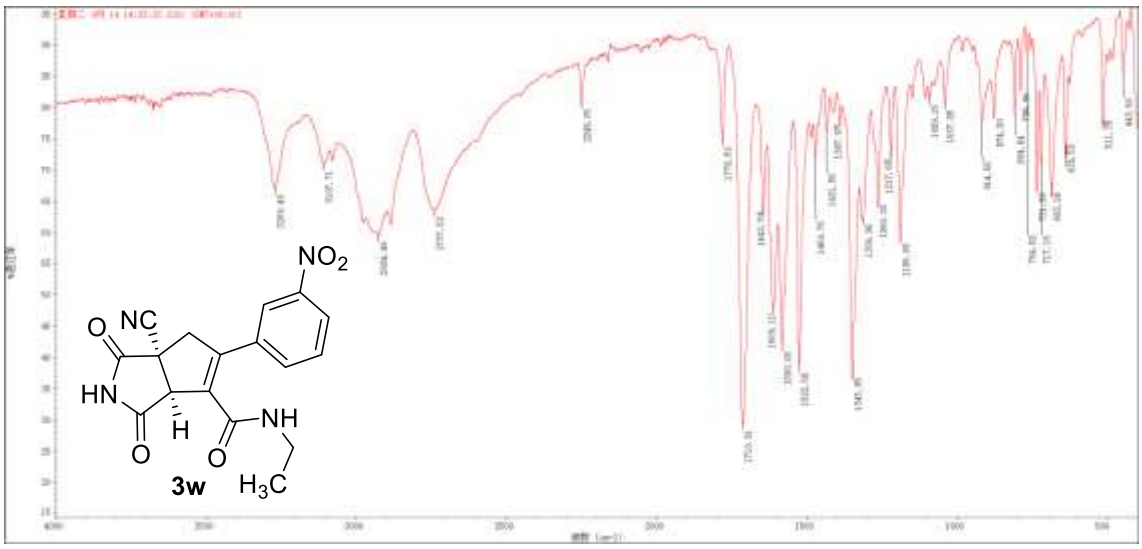


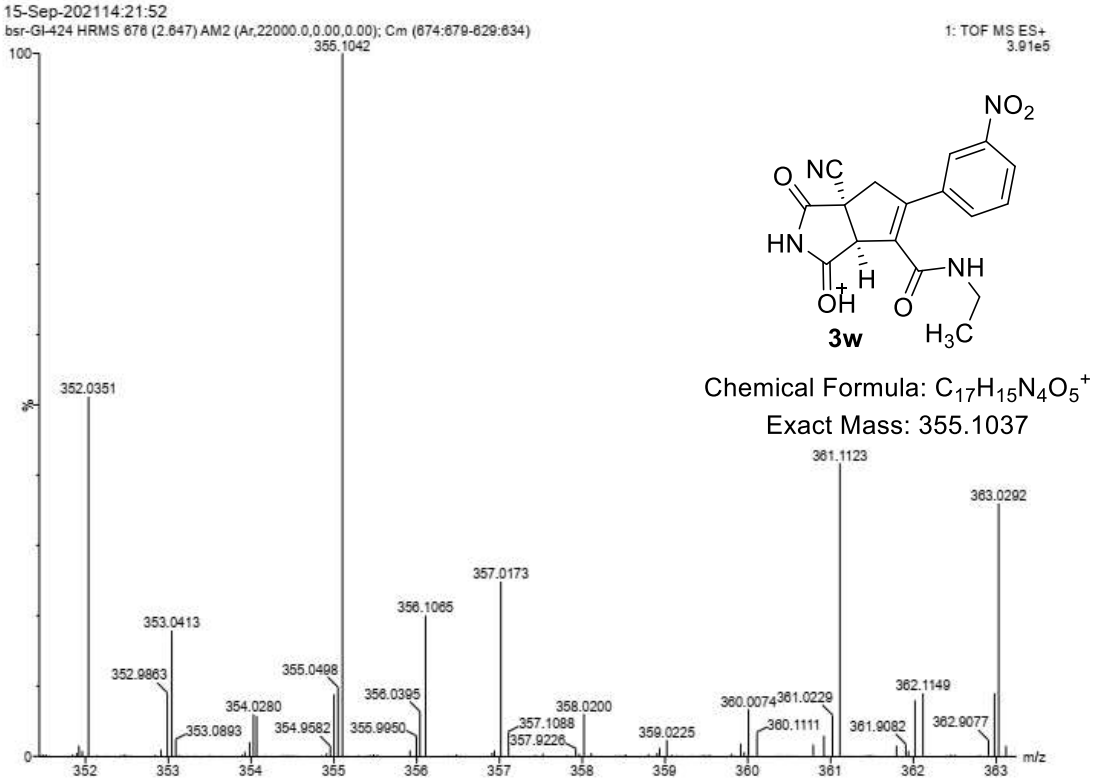


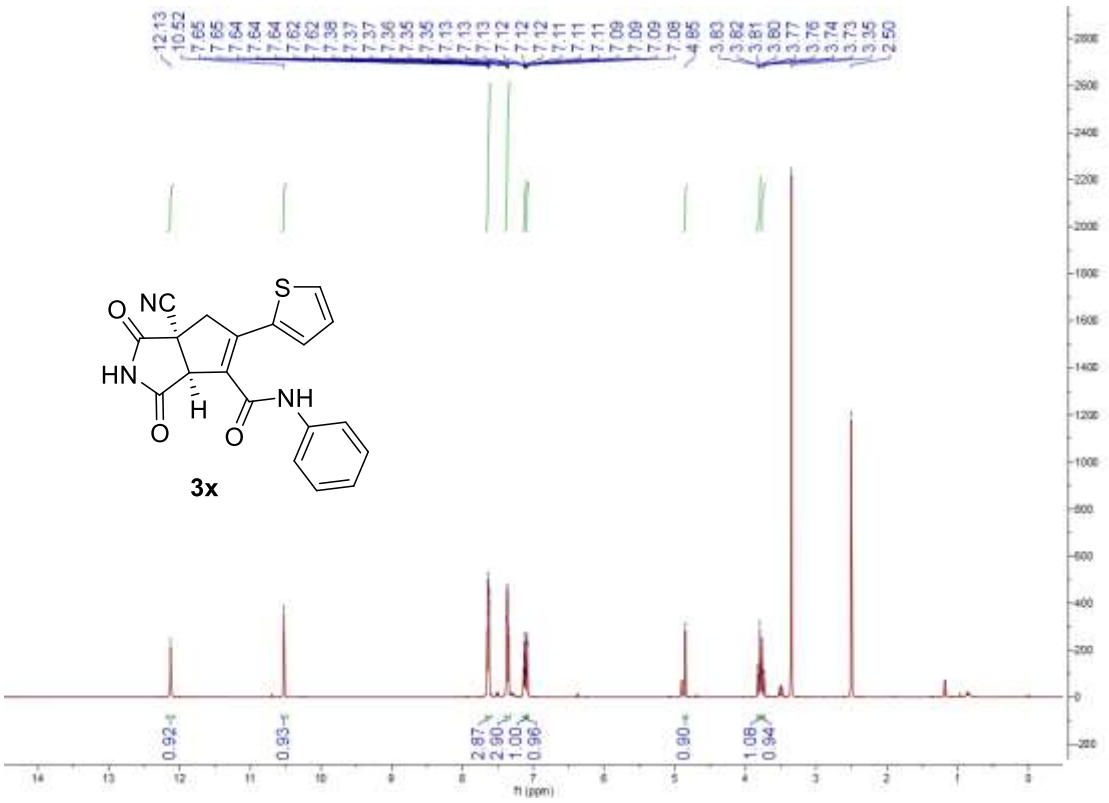
Chemical Formula: $C_{22}H_{17}ClN_3O_3^+$
Exact Mass: 406.0953

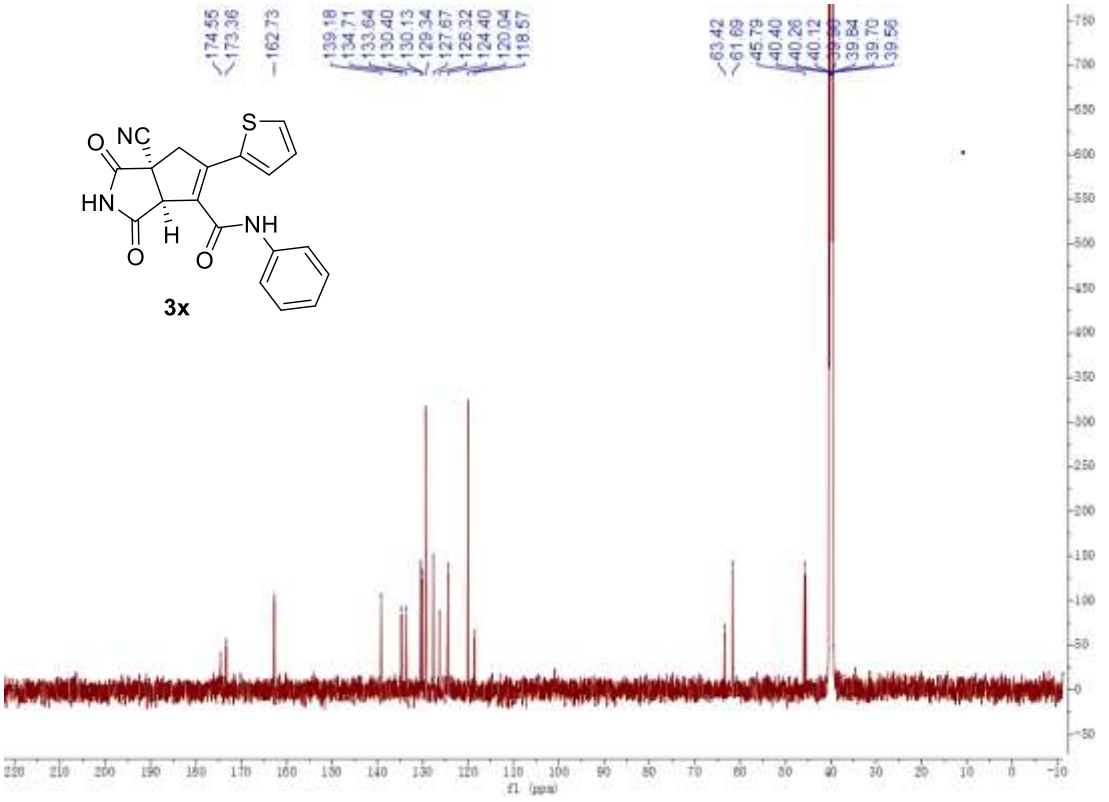

12.06
8.30
8.29
8.29
8.27
8.27
8.27
8.22
8.20
8.20
8.19
8.18
7.84
7.83
7.68
7.67
7.65
5.75
4.80
4.60
3.91
3.90
3.88
3.87
3.64
3.61
3.34
3.16
3.15
3.14
3.13
3.11
3.10
3.10
3.09
3.08
2.51
0.98
0.97
0.96
1.02
0.85
0.83
0.93
1.02
1.00
1.03
0.89
1.00
2.08
3.21
NO2
NC
O
HN
O
H
NH
O
3w
H3C

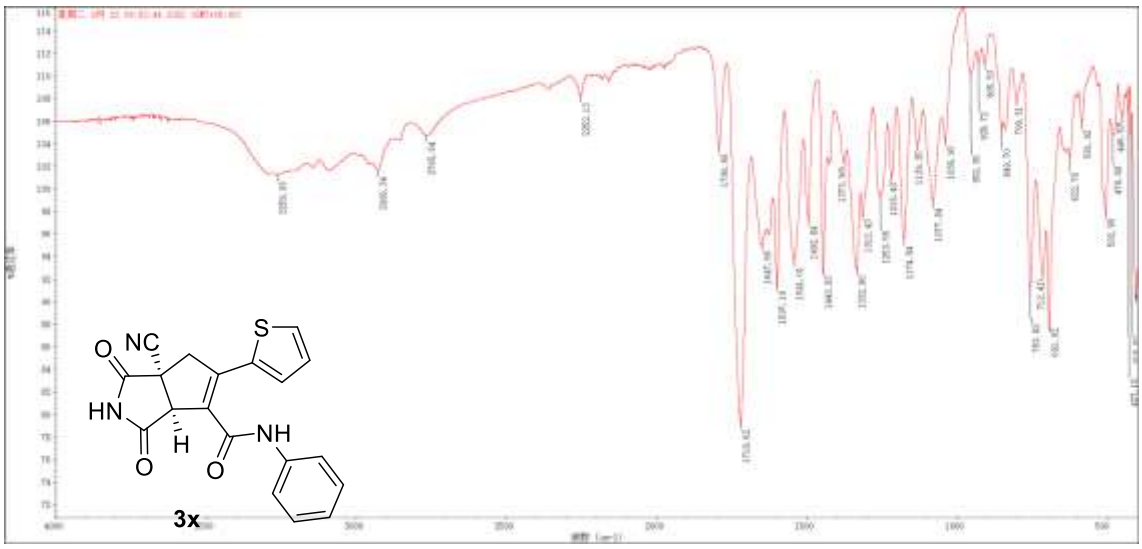

174.36
173.10
163.57
147.99
138.70
135.43
134.72
131.39
130.29
123.77
122.92
118.59
61.65
46.07
45.50
40.42
40.28
40.14
40.01
39.87
39.73
39.59
33.99
14.57
NO2
NC
O
HN
O
H
NH
O
3w
H3C

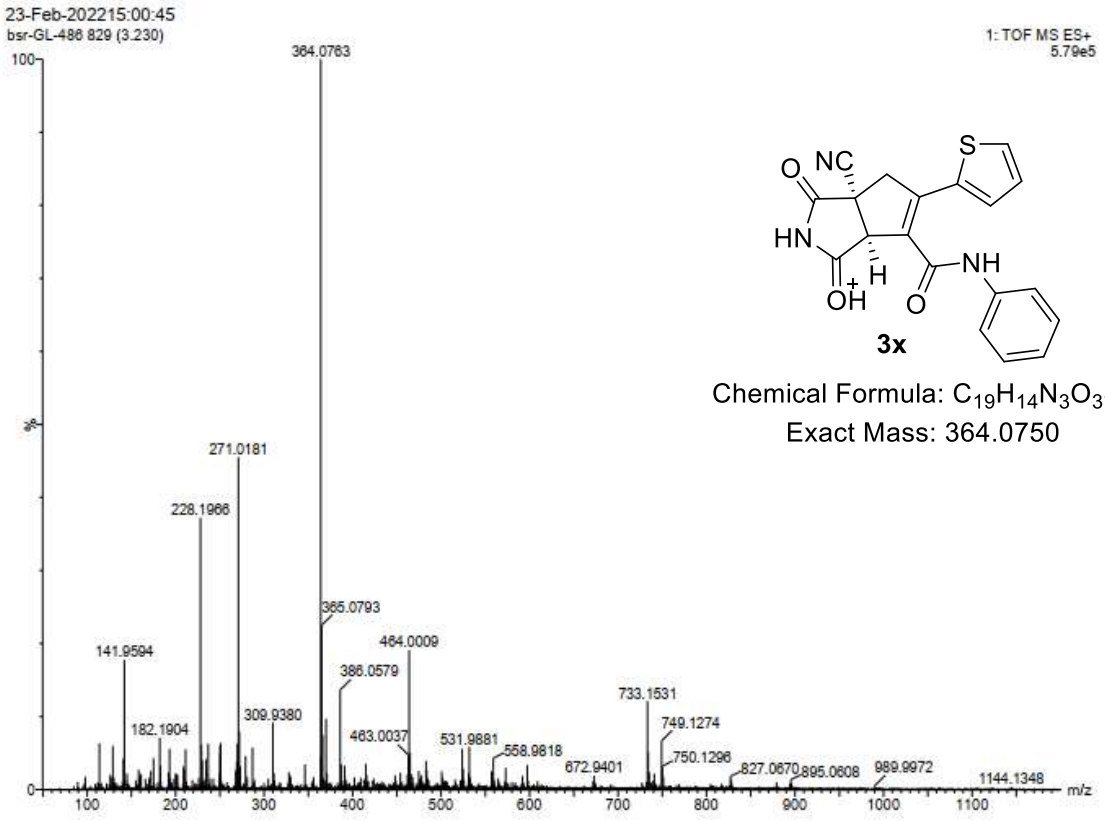

NO2
O
NC
HN
H
O
NH
O
H3C
3w


15-Sep-202114:21:52
bsr-GI-424 HRMS 676 (2.647) AM2 (Ar,22000.0,0.00,0.00); Cm (674:679-629:634)
1: TOF MS ES+
3.91e5
100
%
0
355.1042
352.0351
353.0413
352.9863
355.0498
354.0280
353.0893
354.9582
356.0395
355.9950
356.1065
357.0173
357.1088
357.9226
358.0200
359.0225
360.0074
360.1111
361.0229
361.1123
361.9082
362.1149
362.9077
363.0292
352
353
354
355
356
357
358
359
360
361
362
363
m/z
NO2
O
NC
HN
H
OH
+
O
NH
H3C
3w
Chemical Formula: C17H15N4O5+
Exact Mass: 355.1037


12.13
10.52
7.65
7.65
7.64
7.64
7.64
7.62
7.62
7.38
7.37
7.37
7.36
7.35
7.35
7.13
7.13
7.13
7.12
7.12
7.12
7.11
7.11
7.11
7.09
7.09
7.09
7.08
4.85
3.83
3.82
3.81
3.80
3.77
3.76
3.74
3.73
3.35
2.50
O
NC
S
HN
H
NH
O
O
3x
0.92
0.93
2.87
2.90
1.00
0.96
0.90
1.08
0.94
f1 (ppm)

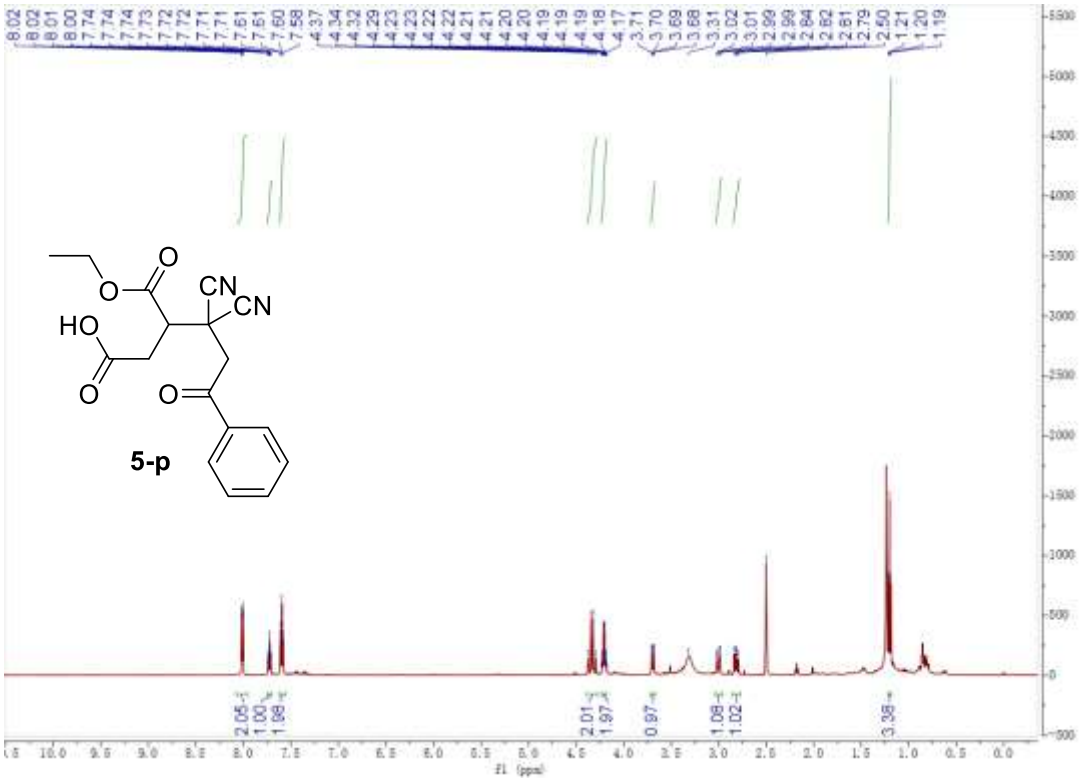

174.55
173.36
162.73
139.18
134.71
133.64
130.40
130.13
129.34
127.67
126.32
124.40
120.04
118.57
63.42
61.69
45.79
40.40
40.26
40.12
39.98
39.84
39.70
39.56
O
NC
S
HN
H
NH
O
O
3x
f1 (ppm)

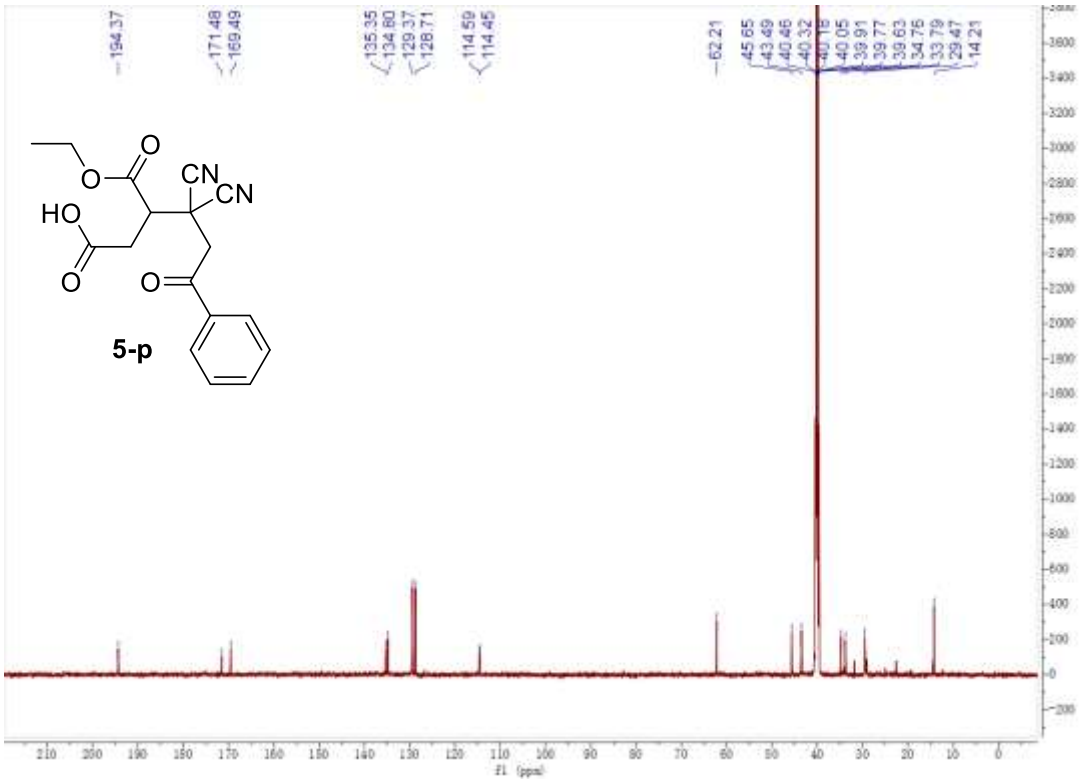


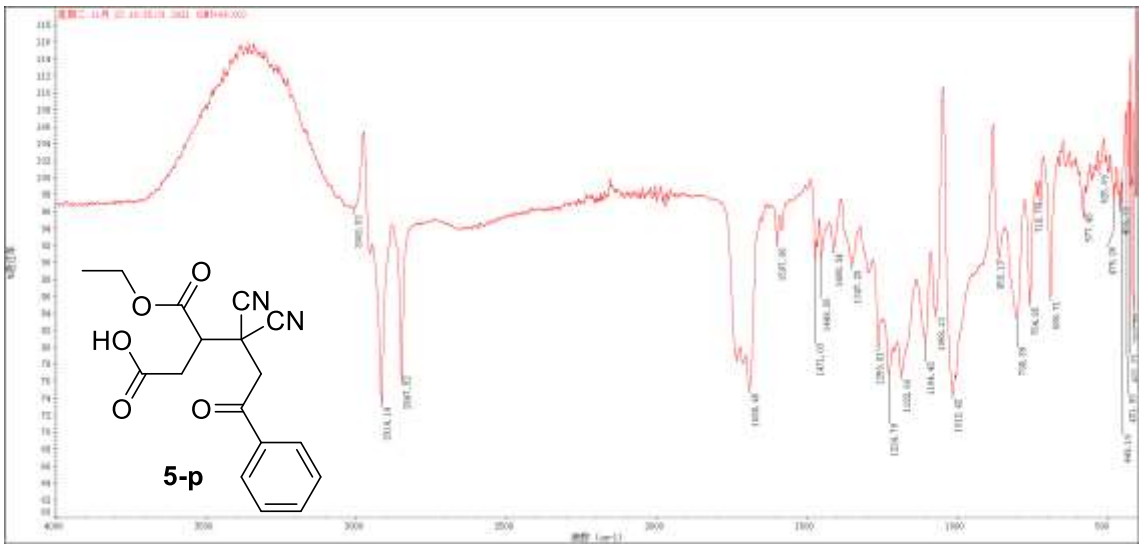


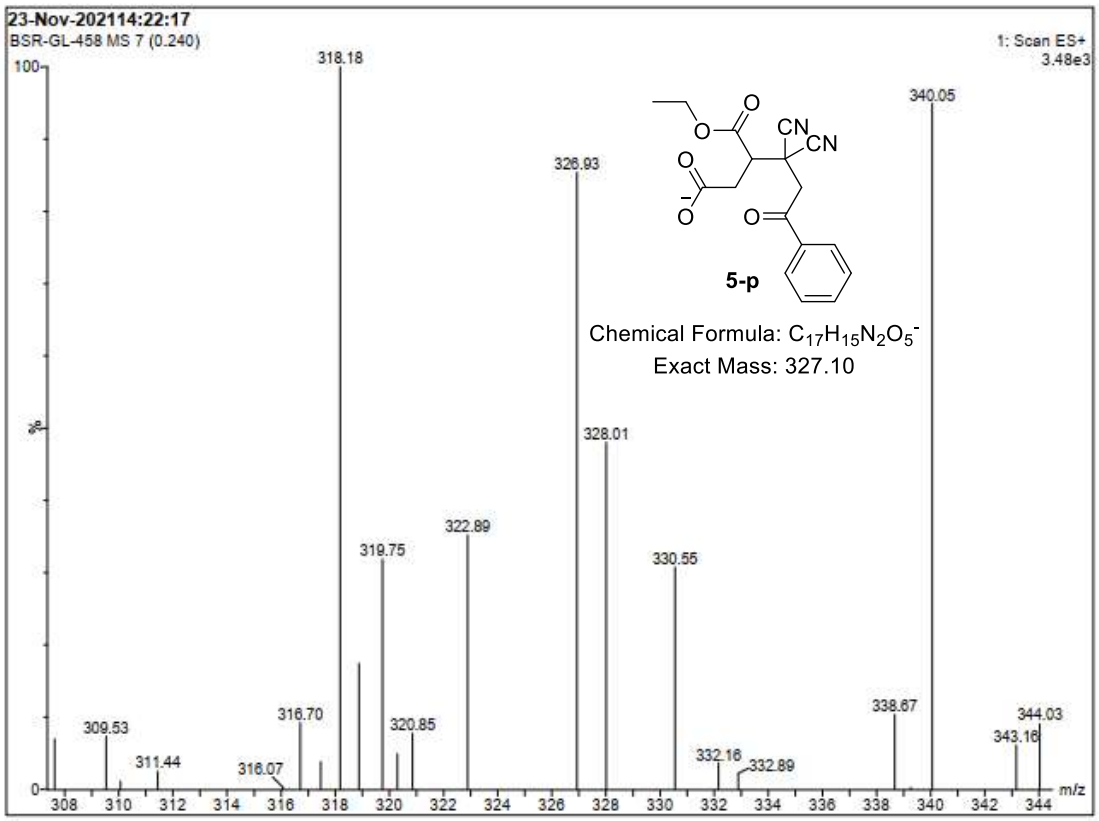
Chemical Formula: $C_{19}H_{14}N_3O_3S^+$

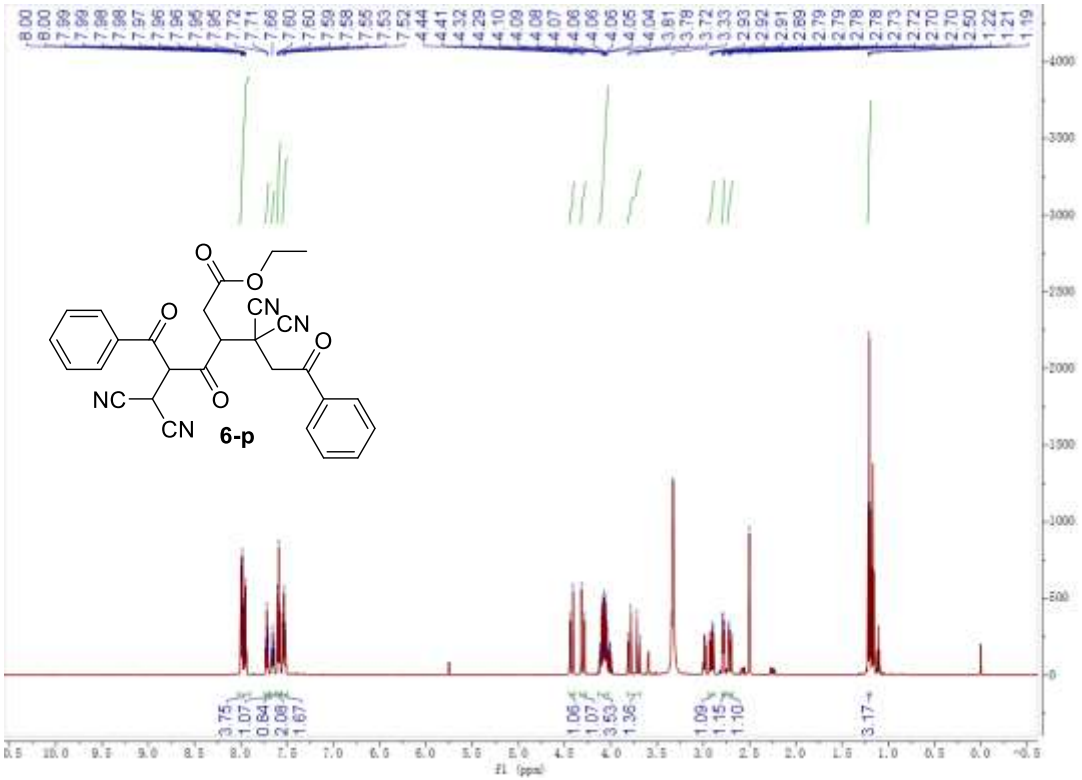
Exact Mass: 364.0750

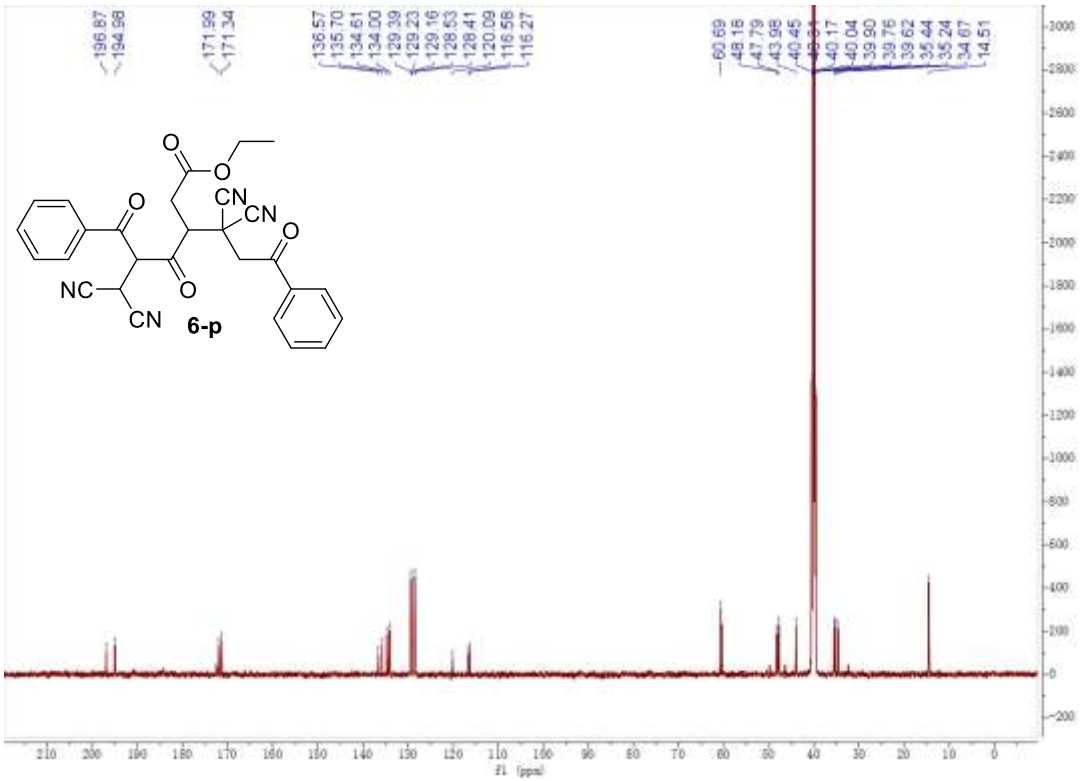

8.02
8.02
8.01
8.00
7.74
7.74
7.74
7.73
7.72
7.72
7.71
7.71
7.61
7.61
7.60
7.58
4.37
4.34
4.32
4.29
4.23
4.23
4.22
4.22
4.21
4.21
4.20
4.20
4.19
4.19
4.19
4.18
4.17
3.71
3.70
3.69
3.68
3.31
3.02
3.01
2.99
2.99
2.84
2.82
2.81
2.79
2.50
1.21
1.20
1.19
O
O
CN
CN
HO
O
O
5-p
2.05
1.00
1.98
2.01
1.97
0.97
1.08
1.02
3.38
f1 (ppm)

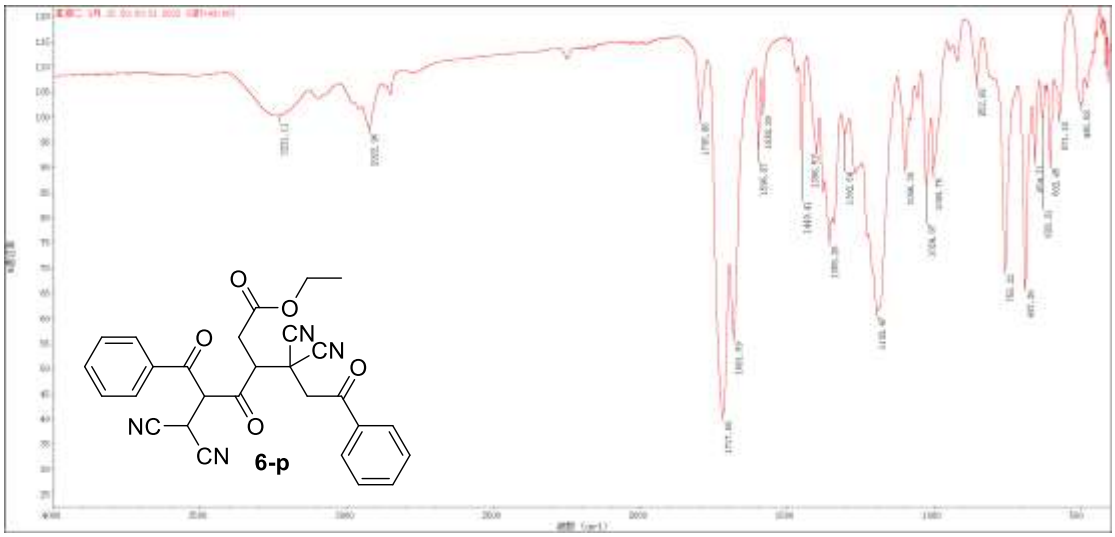

194.37
171.48
169.49
135.35
134.80
129.37
128.71
114.59
114.45
62.21
45.65
43.49
40.46
40.32
40.18
40.05
39.91
39.77
39.63
34.76
33.79
29.47
14.21
O
O
CN
CN
HO
O
O
5-p
f1 (ppm)

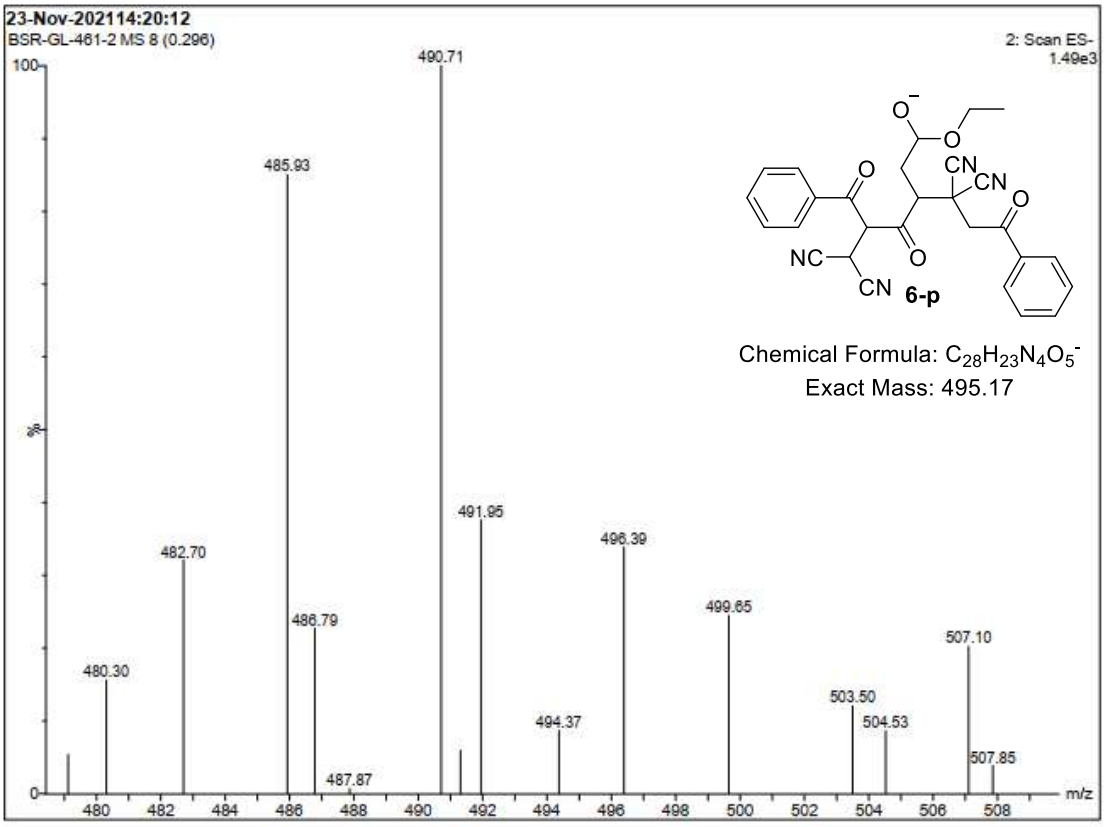

HO
O
O
O
CN
CN
O
5-p

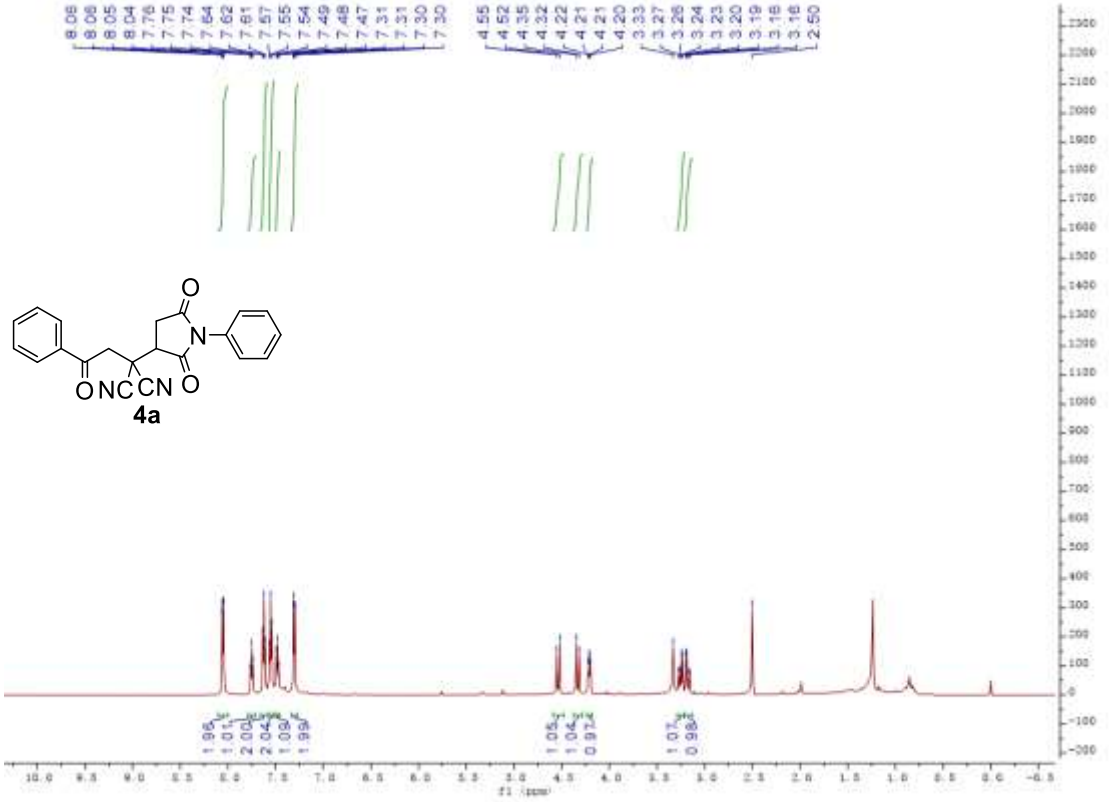

23-Nov-202114:22:17
BSR-GL-458 MS 7 (0.240)
1: Scan ES+
3.48e3
100
%
0
318.18
340.05
326.93
328.01
322.89
319.75
330.55
309.53
316.70
320.85
311.44
316.07
338.67
344.03
343.16
332.16
332.89
m/z
308
310
312
314
316
318
320
322
324
326
328
330
332
334
336
338
340
342
344
5-p
Chemical Formula: $C_{17}H_{15}N_2O_5^-$
Exact Mass: 327.10

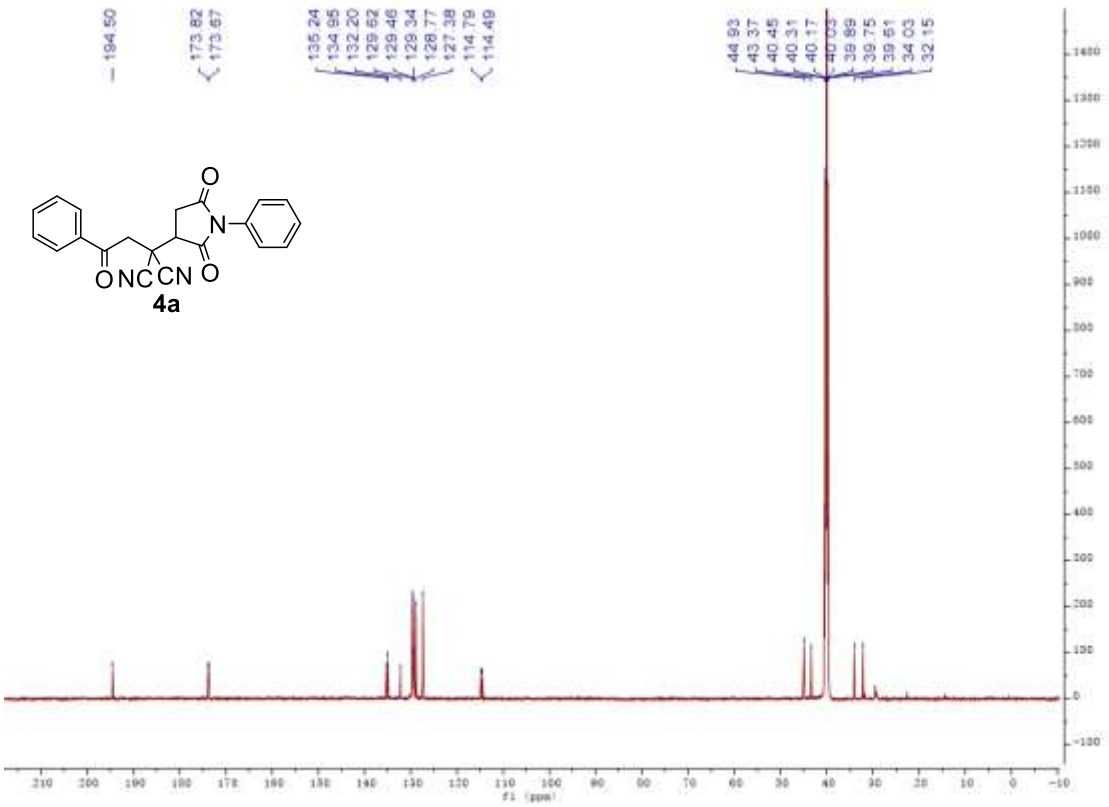

6-p

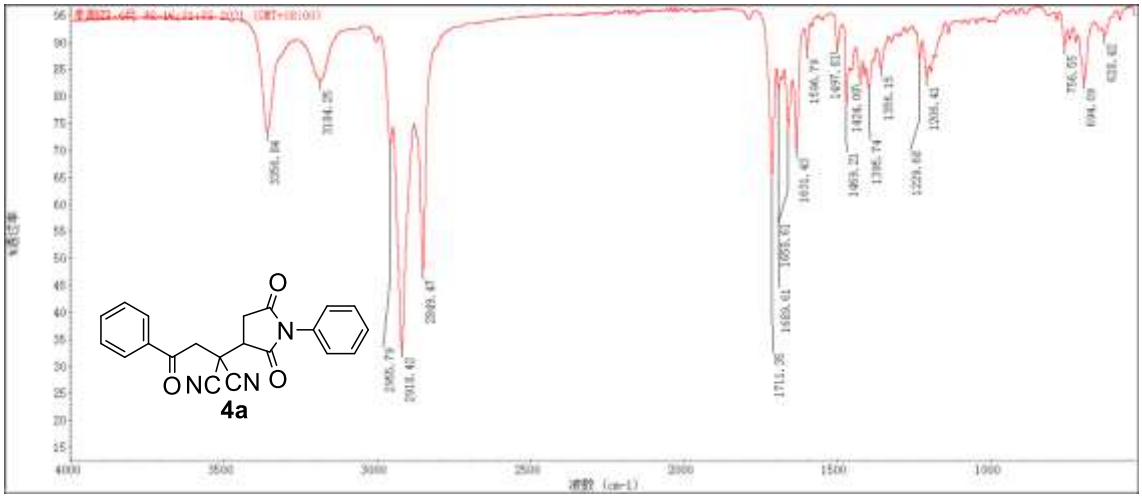

6-p

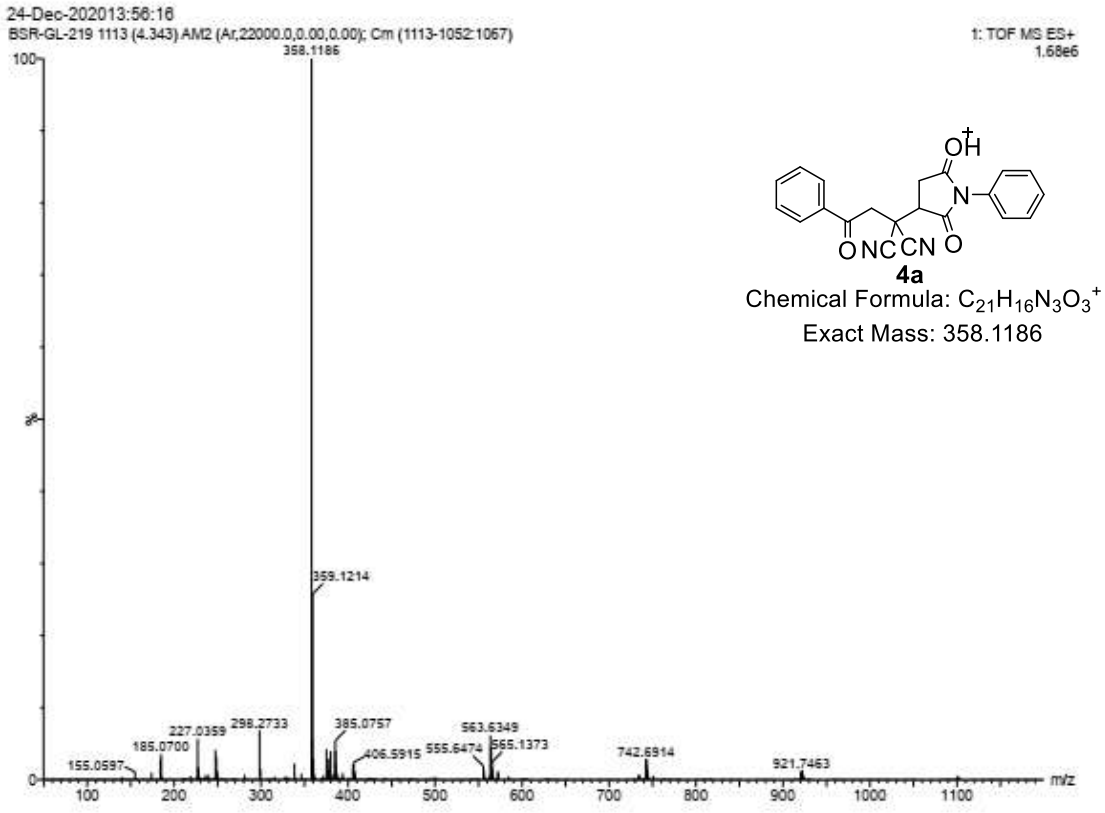

6-p

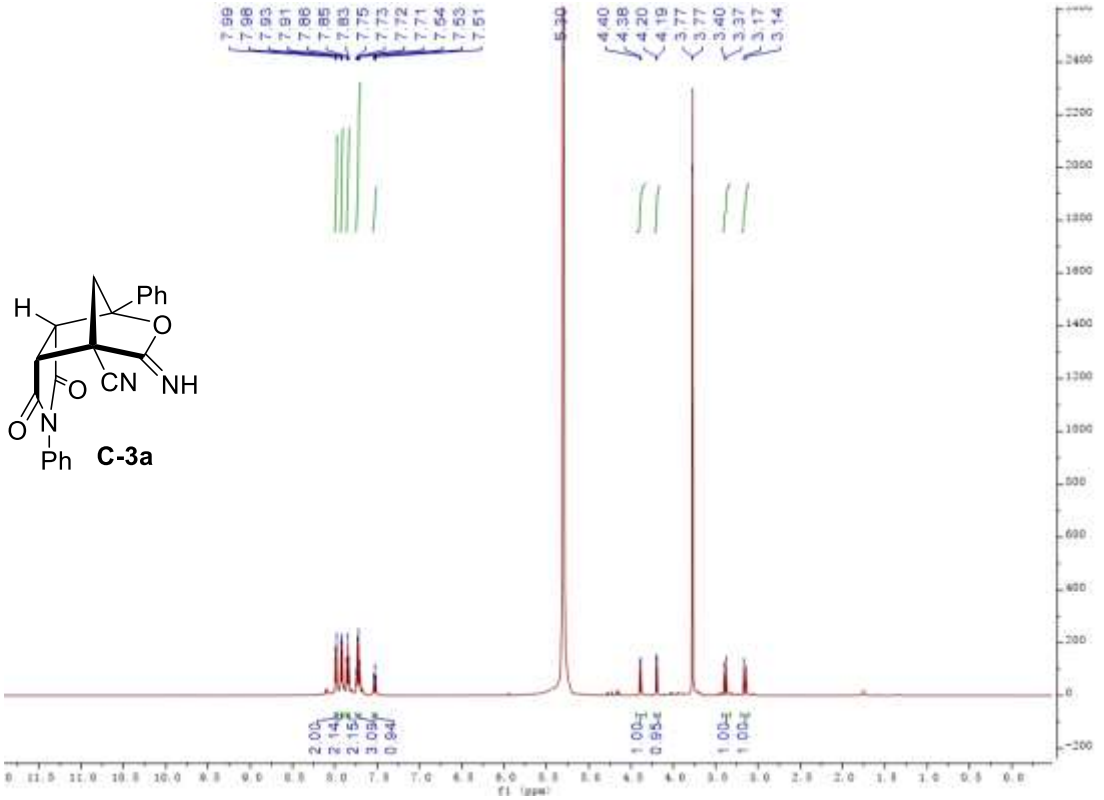

23-Nov-202114:20:12
BSR-GL-461-2 MS 8 (0.296)
2: Scan ES-
1.49e3
100
%
0
490.71
485.93
491.95
482.70
496.39
499.65
486.79
507.10
480.30
503.50
504.53
494.37
507.85
487.87
480
482
484
486
488
490
492
494
496
498
500
502
504
506
508
m/z
6-p
Chemical Formula: C28H23N4O5-
Exact Mass: 495.17


8.06
8.06
8.05
8.04
7.76
7.75
7.74
7.64
7.62
7.61
7.57
7.55
7.54
7.49
7.48
7.47
7.31
7.31
7.30
7.30
4.55
4.52
4.35
4.32
4.22
4.21
4.21
4.20
3.33
3.27
3.26
3.24
3.23
3.20
3.19
3.16
3.16
2.50
O
N
O
ONC CN O
4a
1.96
1.01
2.00
2.04
1.08
1.99
1.05
1.04
0.91
1.07
0.98


194.50
173.82
173.67
135.24
134.95
132.20
129.62
129.46
129.34
128.77
127.38
114.79
114.49
44.93
43.37
40.45
40.31
40.17
40.03
39.89
39.75
39.61
34.03
32.15
O
N
O
ONC CN O
4a

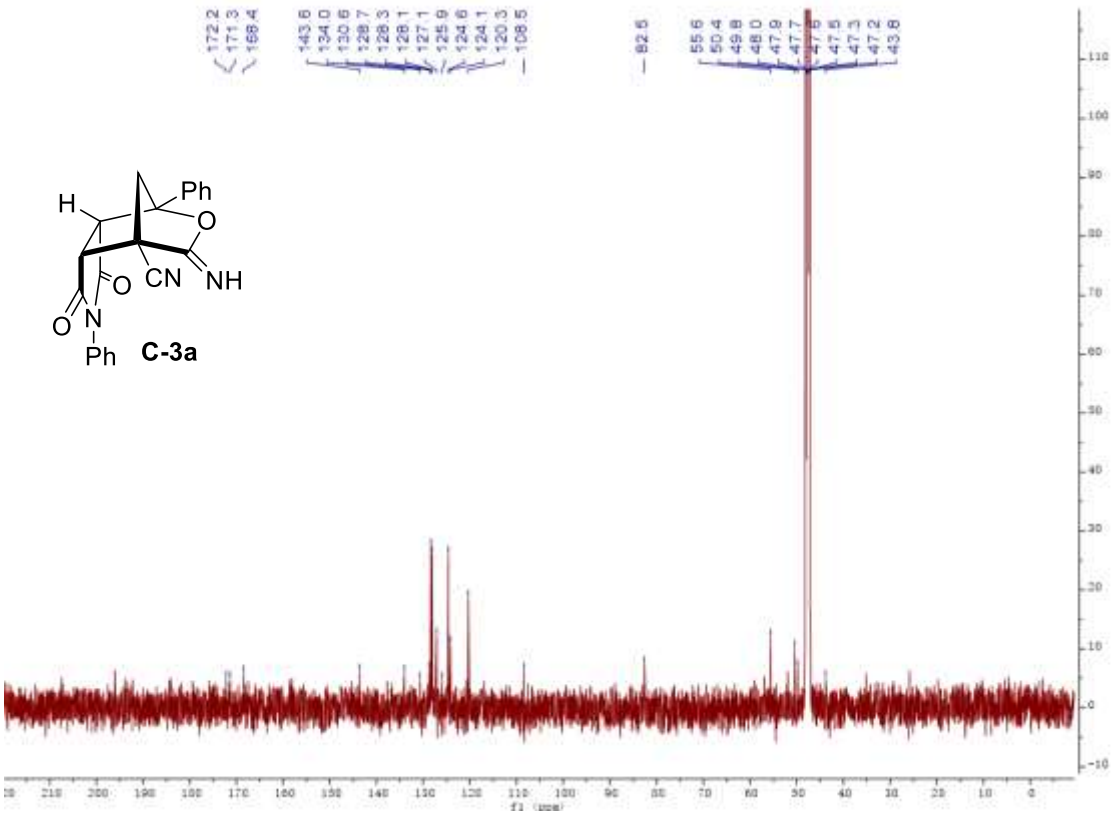

4a


24-Dec-202013:56:16
BSR-GL-219 1113 (4.343) AM2 (Ar,22000.0,0.00,0.00); Cm (1113-1052:1067)
1: TOF MS ES+
1.68e6
358.1186
359.1214
4a
Chemical Formula: C21H16N3O3+
Exact Mass: 358.1186


7.99
7.98
7.93
7.91
7.86
7.85
7.83
7.75
7.73
7.72
7.71
7.54
7.53
7.51
5.30
4.40
4.38
4.20
4.19
3.77
3.77
3.40
3.37
3.17
3.14
2.00
2.14
2.15
3.08
0.94
1.00
0.95
1.00
1.00
f1 (ppm)

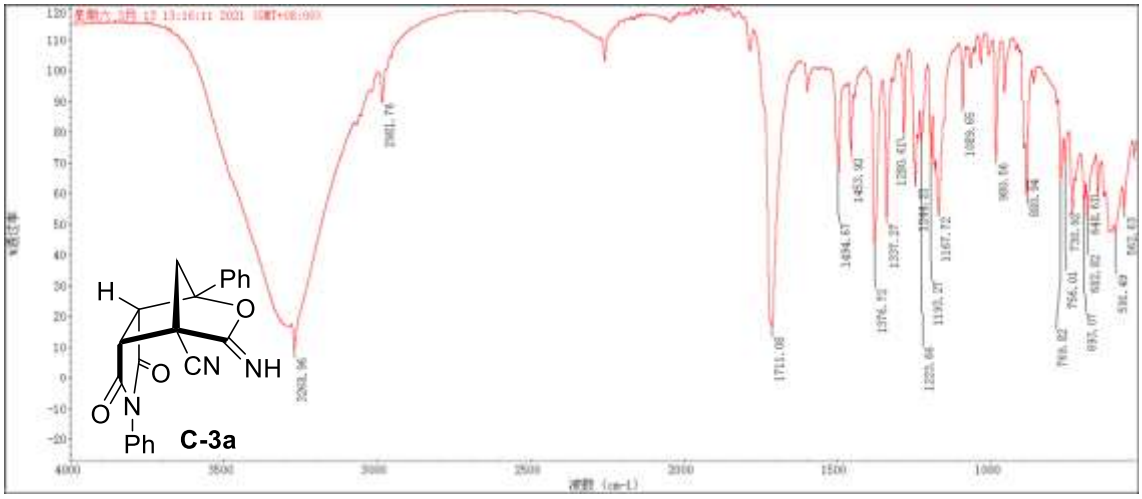
H
Ph
O
CN
NH
O
O
N
Ph

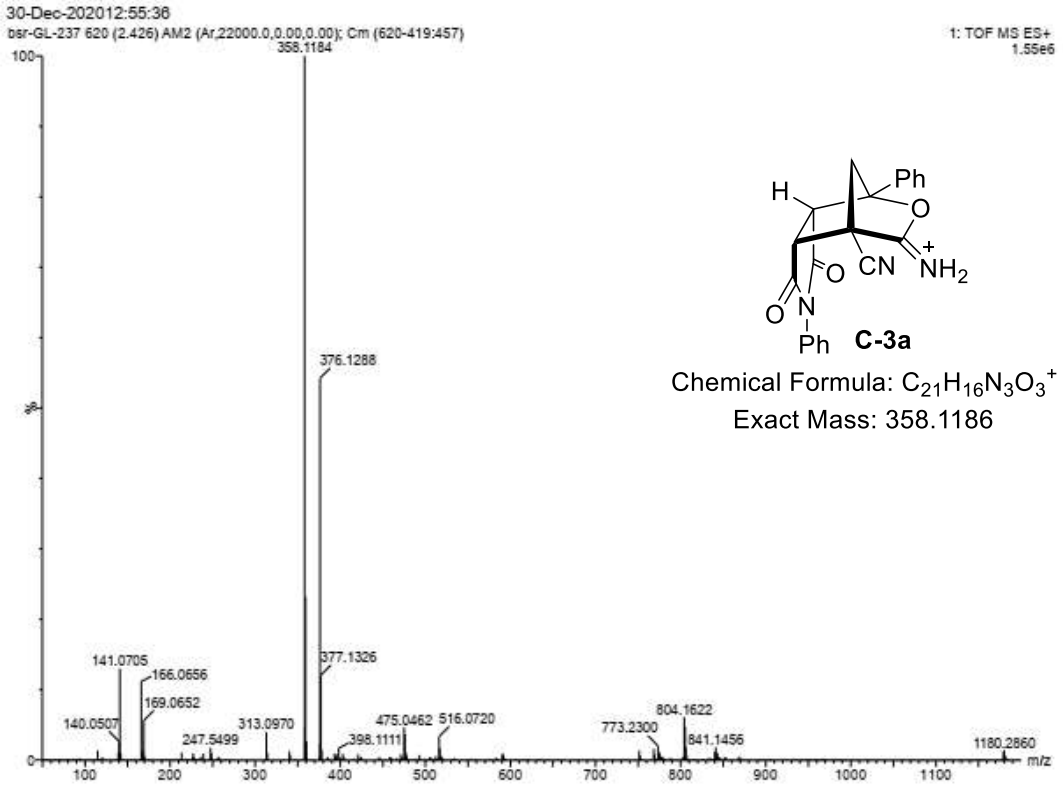
C-3a


172.2
171.3
168.4
143.6
134.0
130.6
128.7
128.3
128.1
127.1
125.9
124.6
124.1
120.3
108.5
92.5
55.6
50.4
49.8
48.0
47.9
47.7
47.5
47.3
47.2
43.8
f1 (ppm)

H
Ph
O
CN
NH
O
O
N
Ph

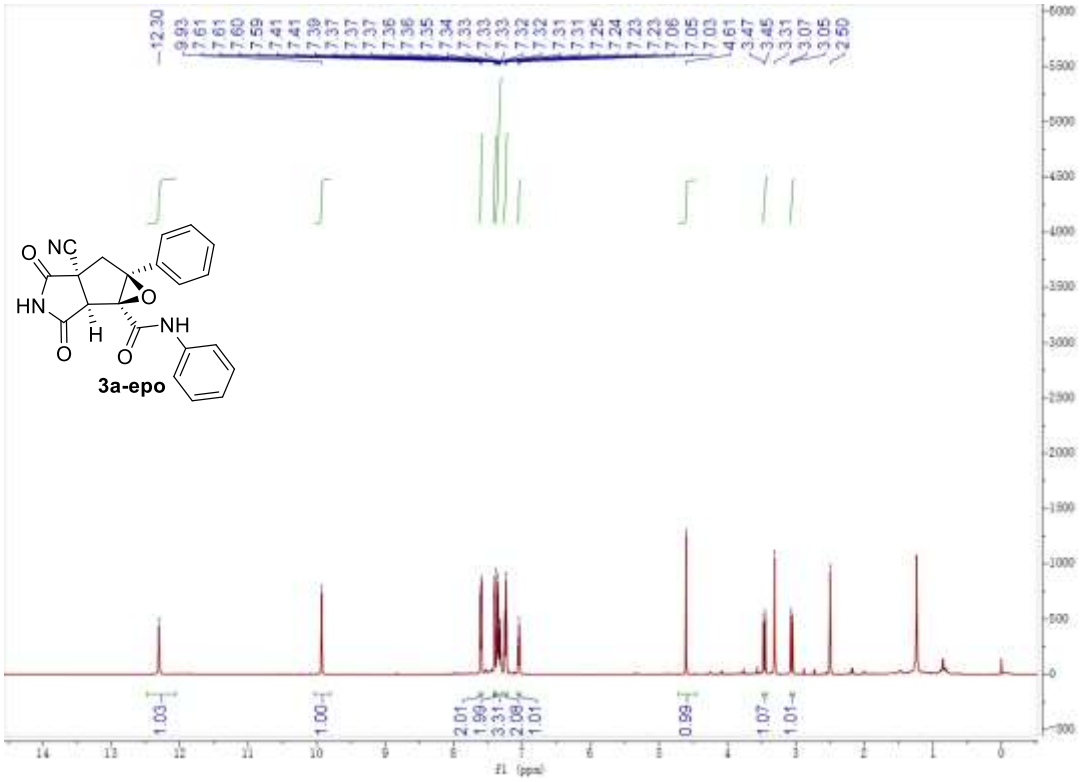
C-3a

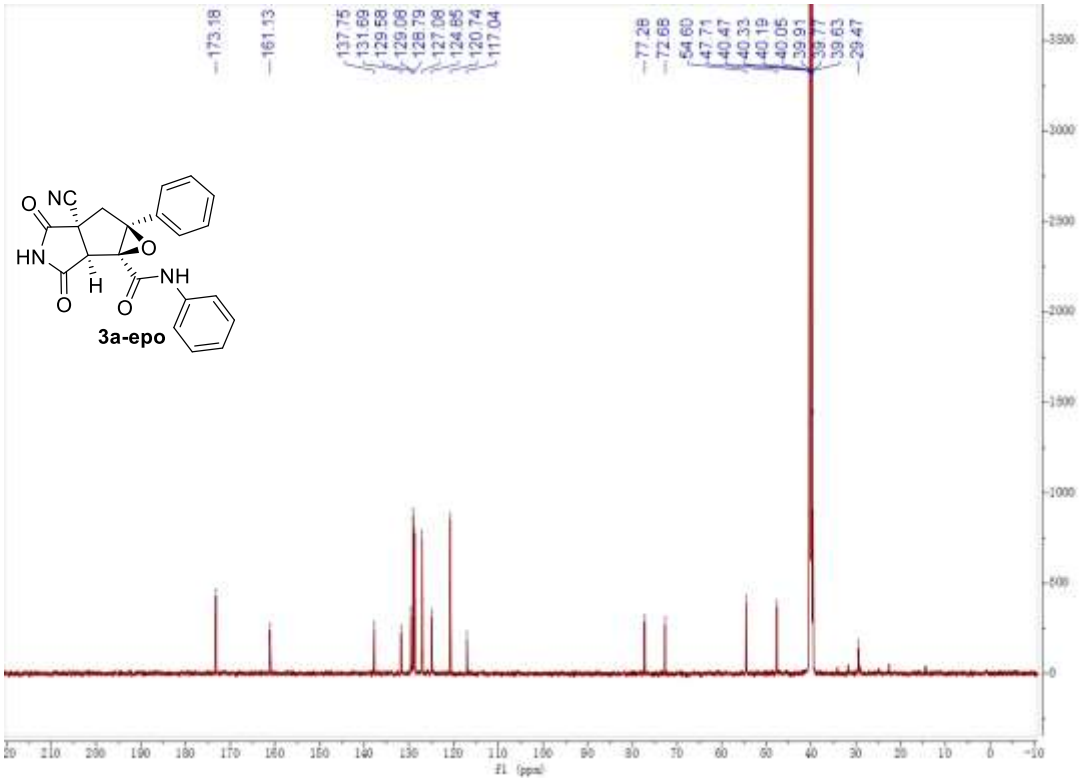


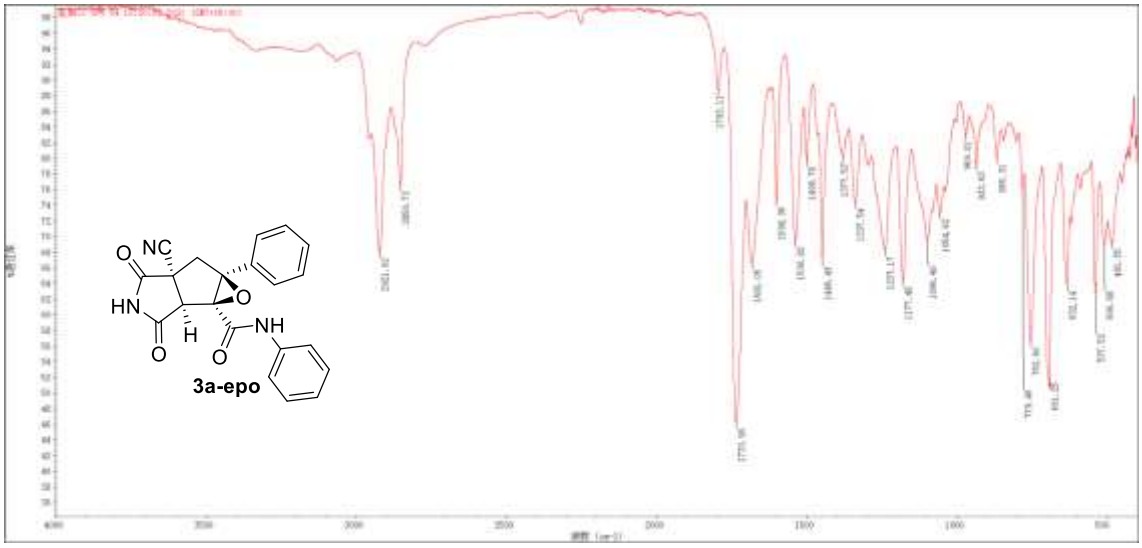


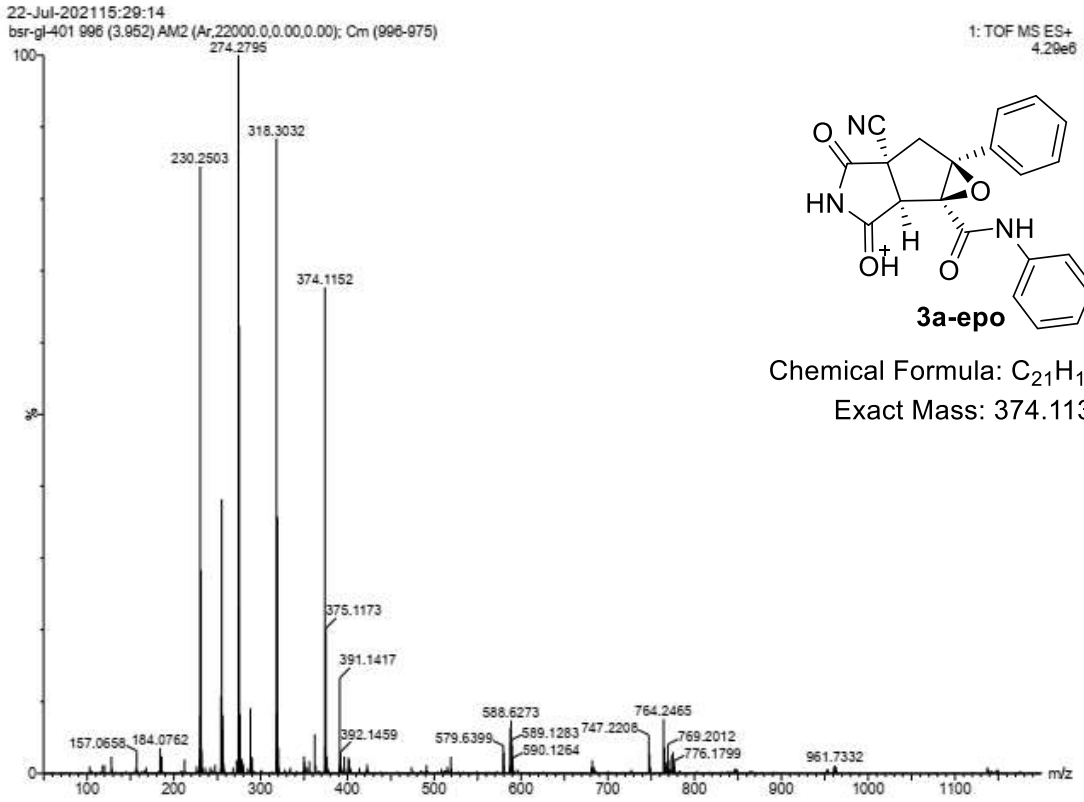
Chemical Formula: $C_{21}H_{16}N_3O_3^+$

Exact Mass: 358.1186

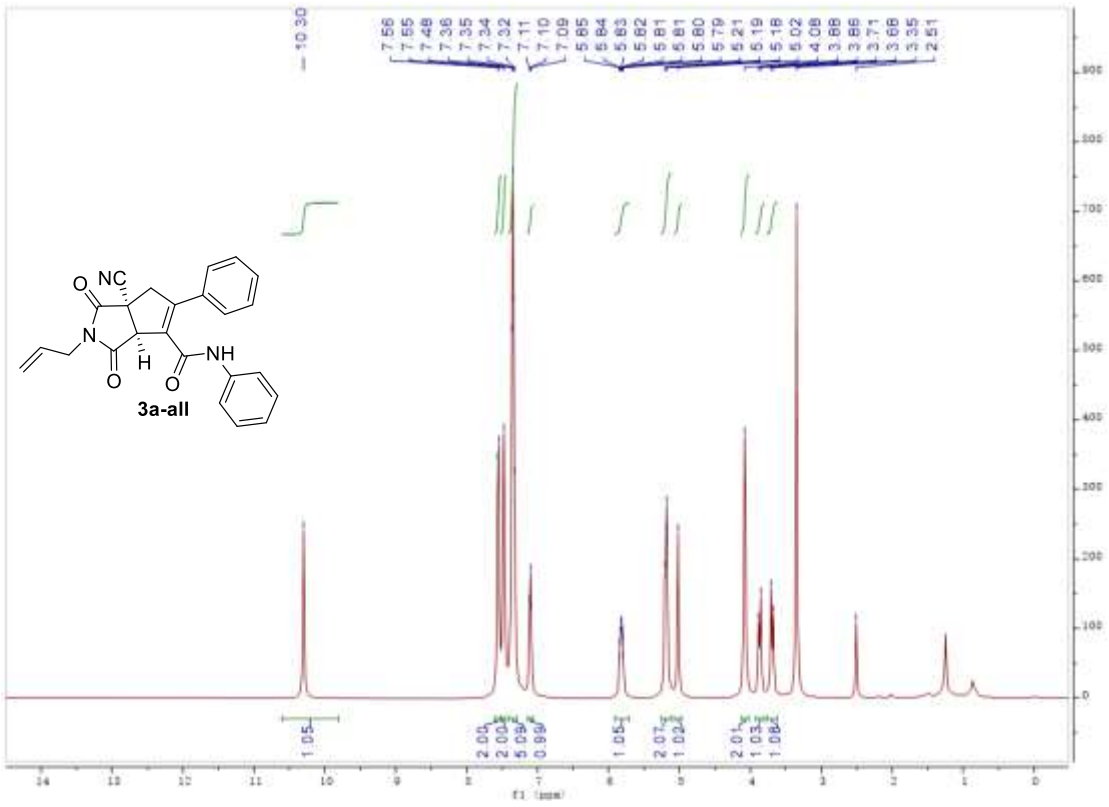

12.30
9.93
7.61
7.61
7.60
7.59
7.41
7.41
7.39
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.25
7.24
7.23
7.23
7.06
7.05
7.03
4.61
3.47
3.45
3.31
3.07
3.05
2.50
1.03
1.00
2.01
1.99
3.31
2.08
1.01
0.99
1.07
1.01
f1 (ppm)
3a-epo

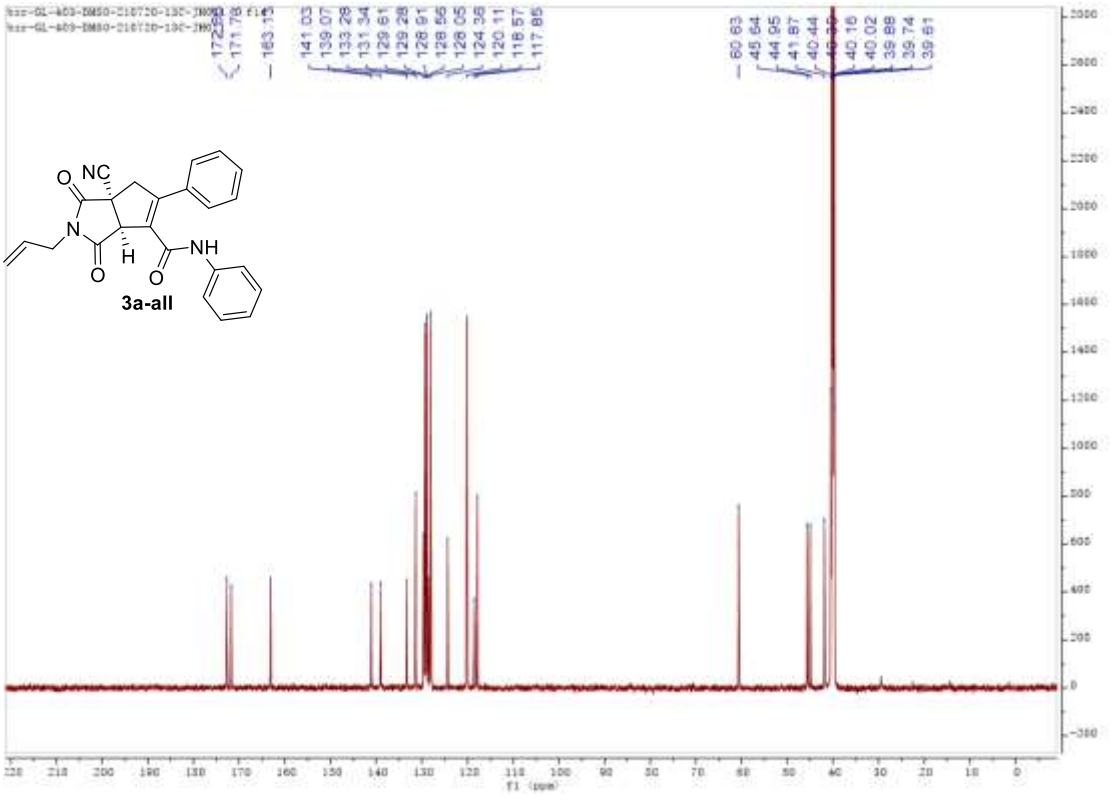

173.18
161.13
137.75
131.69
129.58
129.08
128.79
127.08
124.85
120.74
117.04
77.28
72.68
54.60
47.71
40.47
40.33
40.19
40.05
39.91
39.77
39.63
29.47
f1 (ppm)
3a-epo

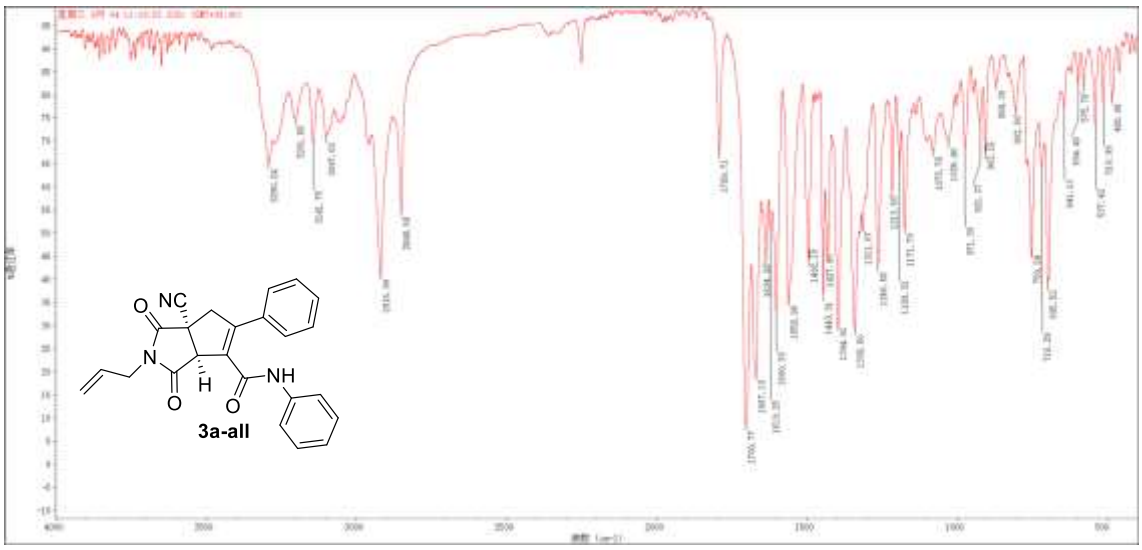


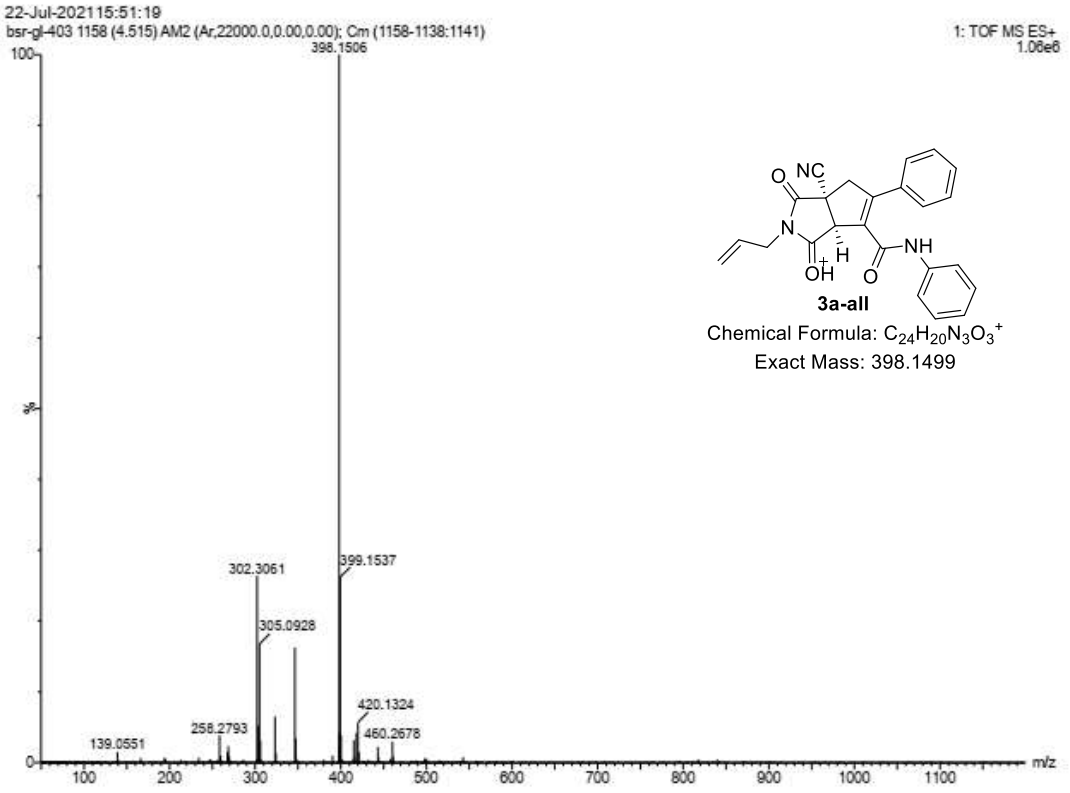


Chemical Formula: $C_{21}H_{16}N_3O_4^+$
Exact Mass: 374.1135

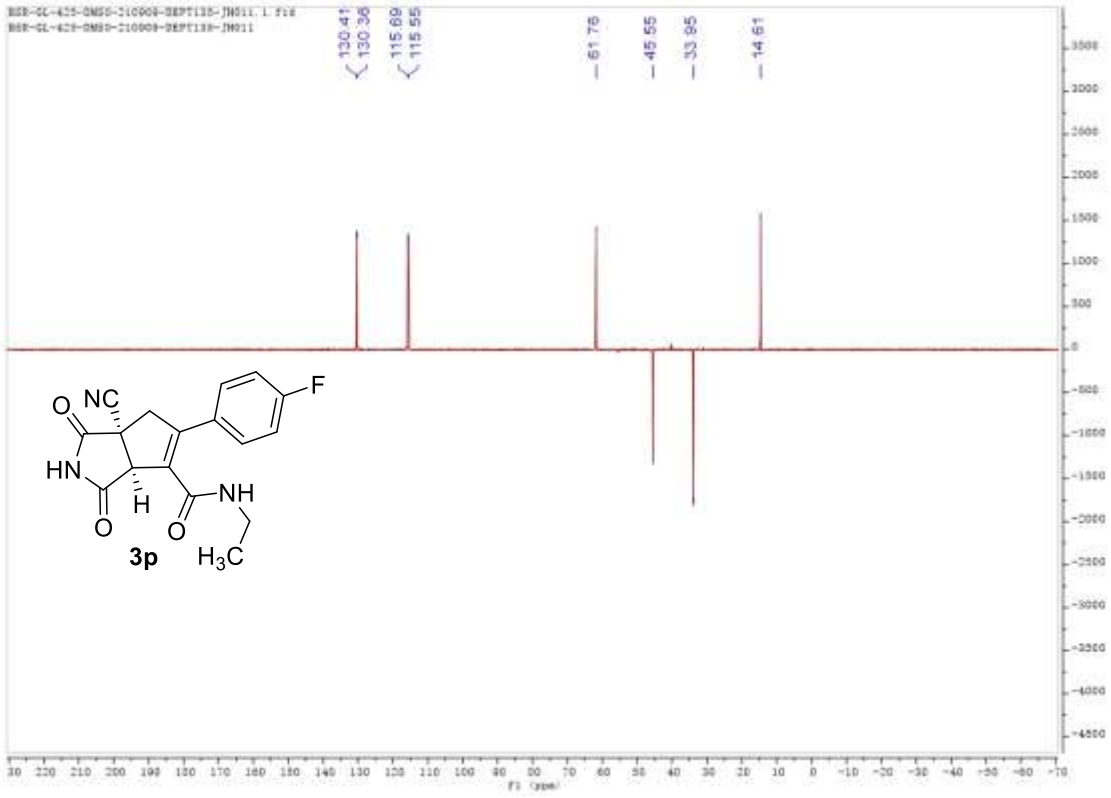

10.30
7.56
7.55
7.48
7.36
7.35
7.34
7.32
7.11
7.10
7.09
5.85
5.84
5.83
5.82
5.81
5.81
5.80
5.79
5.21
5.19
5.18
5.02
4.08
3.88
3.86
3.71
3.66
3.35
2.51
1.05
2.00
2.00
5.09
0.99
1.05
2.07
1.02
2.01
1.03
1.08
NC
O
N
H
NH
O
O
3a-all


172.58
171.78
163.15
141.03
139.07
133.28
131.34
129.61
129.28
128.91
128.55
128.05
124.38
120.11
118.57
117.85
60.63
45.64
44.95
41.87
40.44
40.30
40.16
40.02
39.88
39.74
39.61
NC
O
N
H
NH
O
O
3a-all

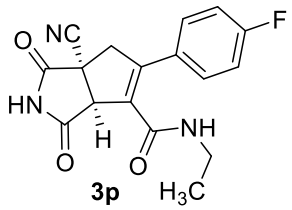

NC
O
N
H
NH
O
O
3a-all


22-Jul-202115:51:19
bsr-gl-403 1158 (4.515) AM2 (Ar,22000.0,0.00,0.00); Cm (1158-1138:1141)
1: TOF MS ES+
1.06e8
398.1506
399.1537
302.3061
305.0928
420.1324
460.2678
258.2793
139.0551
m/z
NC
O
N
H
NH
O
OH
3a-all
Chemical Formula: $C_{24}H_{20}N_3O_3^+$
Exact Mass: 398.1499

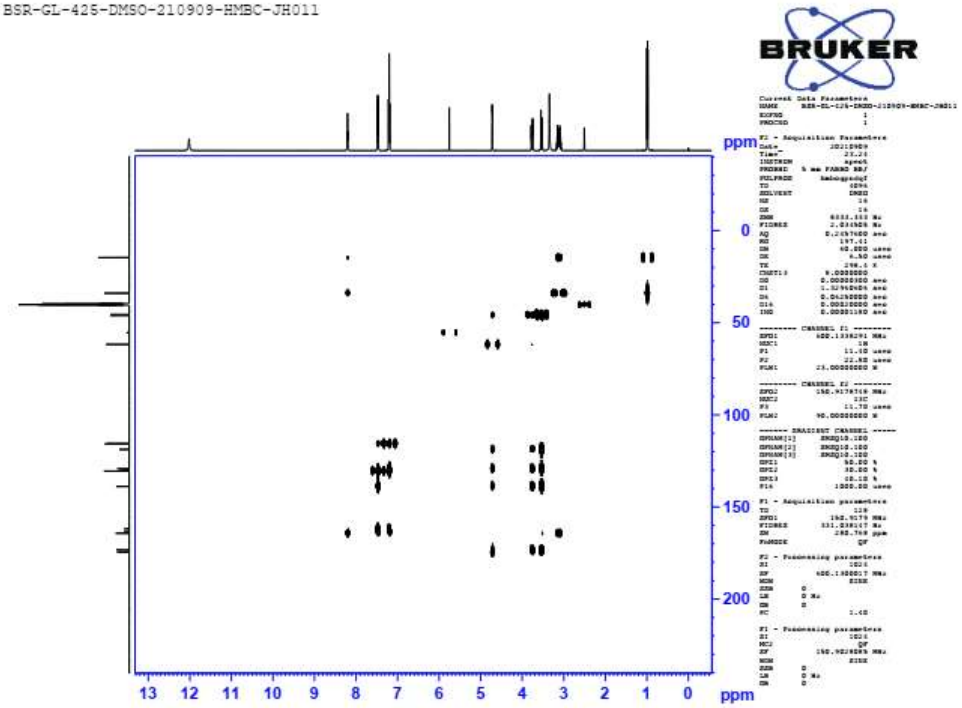
16. 135-DEPT NMR spectrum of 3p



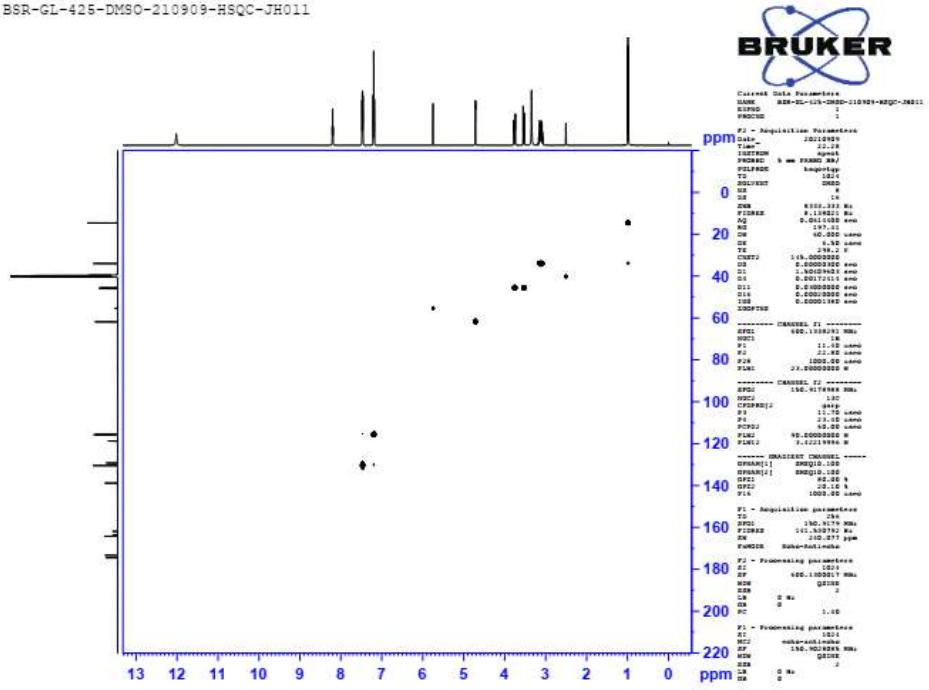
17. 2D NMR spectra of 3p and 3a-all

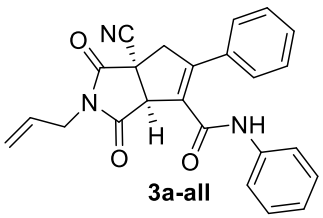


BSR-GL-425-DMSO-210909-HMBC-JH011



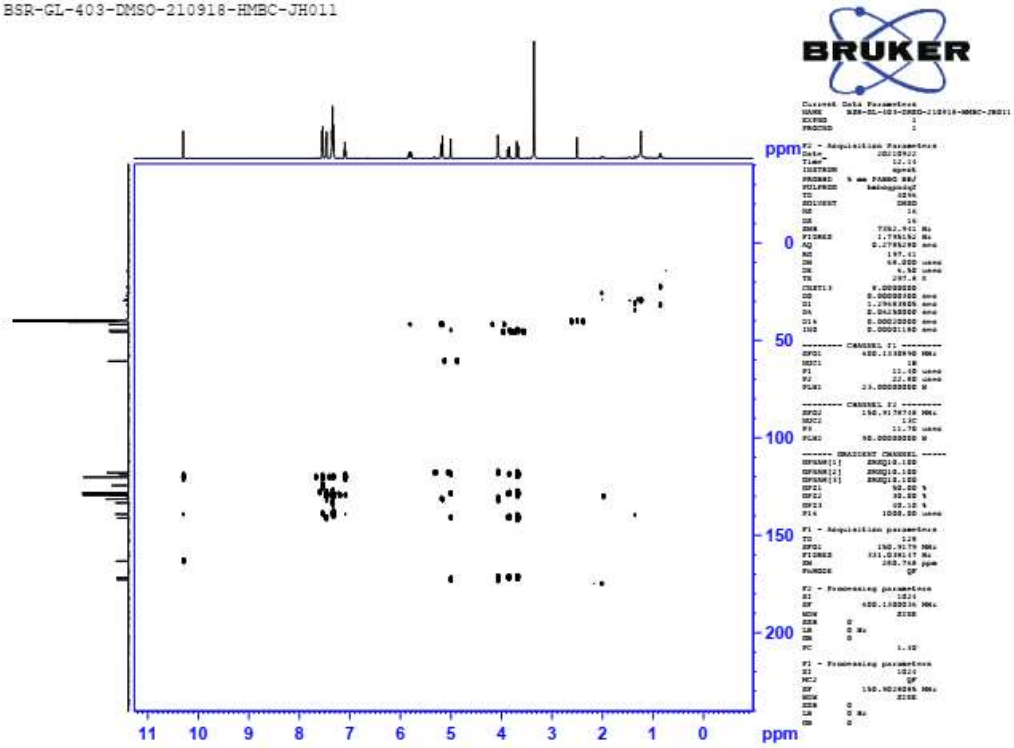
BSR-GL-425-DMSO-210909-HSQC-JH011



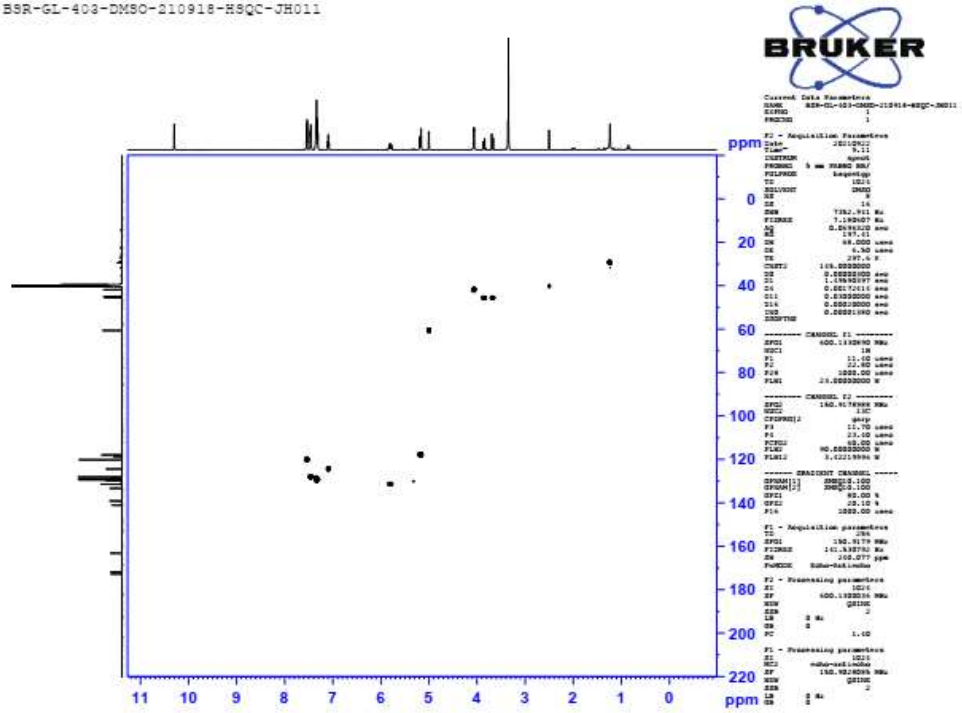


3a-all

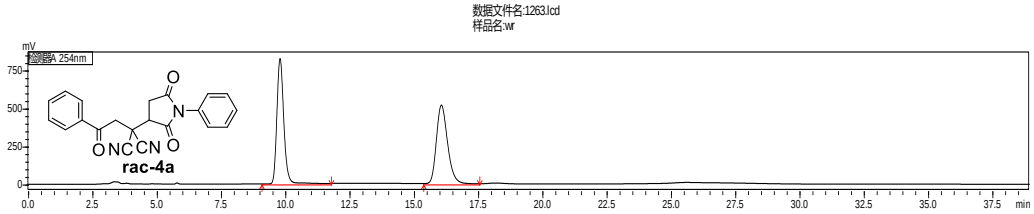
BSR-GL-403-DMSO-210918-HMBC-JH011



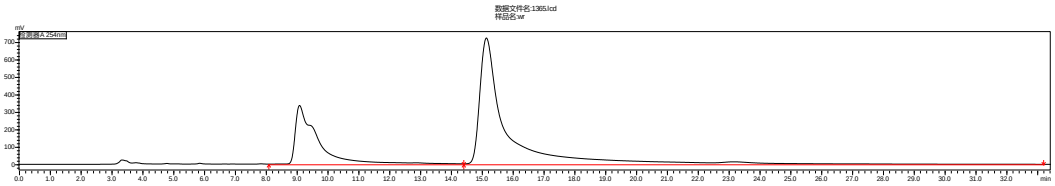
BSR-GL-403-DMSO-210918-HSQC-JH011



18. HPLC spectra of Michael adduct 4a



NO.	Name	Time(min)	Area	Height	Area%
1	--	9.803	15783036	826788	49.879
2	--	16.077	15859670	519713	50.121



NO.	Name	Time(min)	Area	Height	Area%
1	--	9.091	17276473	337279	28.467
2	--	15.147	43413653	723379	71.533

HPLC conditions: Chiralpak IC, n-hexane/EtOH = 80/20, flow rate 1 mL/min, λ = 254 nm.