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A General, Simple and Green Access to Pyrrolo[2,1-a]isoquinolines Using KI/TBHP Catalytic System

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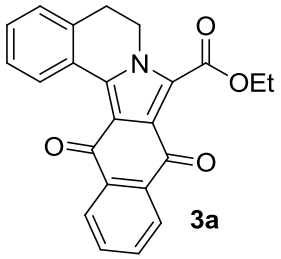
1. General information: All solvents were purified and dried using standard methods prior to use. Commercially available reagents were used without further purification. ^{1}H NMR spectra were recorded on an NMR instrument operated at 500 MHz. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). ^{13}C NMR spectra were recorded on an NMR instrument operated at 125 MHz with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 77.1 ppm). MS and HRMS were measured in EI or ESI mode and the mass analyzer of the HRMS was TOF. Thin layer chromatography was performed on pre-coated glass back plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel.

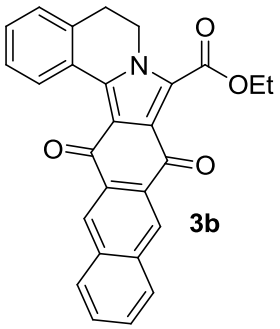
2. Representative procedure for the synthesis of 3a: A dipolarophile **1a** (1.0 mmol) was added to a mixture of a tetrahydroisoquinoline **2a** (1.7 mmol), 70% aq TBHP (3-6 mmol), and potassium iodide (0.2 mmol) in DMF (5.0 mL). The solution was stirred for 9 h at 80 ℃. After **1a** was completely consumed (as indicated by TLC and GC-MS), the reaction mixture was washed with aq $Na_2S_2O_3$, dried over magnesium sulfate, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel with CH_2Cl_2 as the eluent provided desired products **3a**.

3. Characterization of **3**



3a

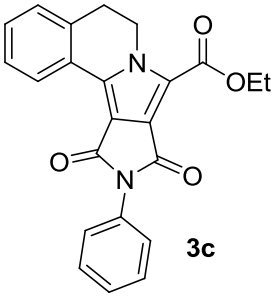
Ethyl 9,14-dioxo-5,6,9,14-tetrahydrobenzo[5,6]isoindolo[1,2-a] isoquinoline-8 -carboxylate (3a) [1]**:** yellow solid, yield 87% (0.323 g), mp 144-145^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.01 (d, *J* = 8.0 Hz, 1H), 8.31-8.30 (m, 1H), 8.23-8.21 (m, 1H), 7.75-7.69 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 6.5 Hz, 1H), 7.29-7.27 (m, 1H), 4.56 (q, *J* = 7.0 Hz, 2H), 4.30 (t, *J* = 6.5 Hz, 2H), 3.12 (t, *J* = 6.5 Hz, 2H), 1.51 (t, *J* = 7.0 Hz, 3H); IR ν/cm^{-1} (KBr) 1704, 1660, 1524, 1465, 1413, 1384, 1311, 1268, 1227, 1141, 1108, 1047, 1010, 984, 790, 729, 711; GC-MS *m/z* 372.0 $[M+1]^{+}$, 326.7, 301.0, 243.6, 77.8, 51.0.



3b

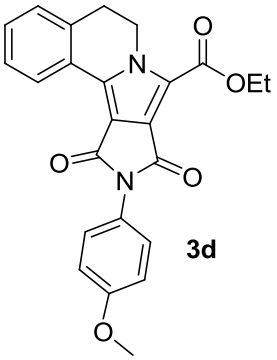
Ethyl 9,16-dioxo-5,6,9,16-tetrahydronaphtho[5,6]isoindolo[1,2-a]isoquinoline -8-carboxylate (3b) [3]**:** orange solid, yield 93% (0.392 g), mp 234-235^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.00 (d, *J* = 8.0 Hz, 1H), 8.71 (s, 1H), 8.63 (s, 1H), 7.95-7.94 (m, 2H), 7.55-7.54 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 4.57 (q, *J* = 7.0 Hz, 2H), 4.22 (t, *J* = 6.5 Hz, 2H),

3.06 (t, J = 6.5 Hz, 2H), 1.54 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.4, 179.2, 161.6, 135.5, 134.8, 134.6, 133.5, 132.1, 131.2, 129.9, 129.8, 129.7, 129.2, 129.0, 128.8, 128.7, 128.5, 127.3, 127.3, 126.4, 126.1, 124.0, 118.2, 62.5, 43.1, 29.1, 14.1; IR ν/cm^{-1} (KBr) 1665, 1461, 1267, 1016, 751; HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{20}NO_4$ $[M+H]^+$ 422.1392, found 422.1388.



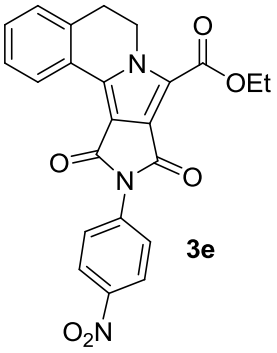
3c

Ethyl 9,11-dioxo-10-phenyl-6,9,10,11-tetrahydro-5H-pyrrolo[3',4':3,4]pyrrolo [2,1-a]isoquinoline-8-carboxylate (3c) [1]**:** white solid, yield 94% (0.363 g), mp 190-191^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.59 (d, J = 8.5 Hz, 1H), 7.50 (t, J = 7.0 Hz, 2H), 7.43-7.36 (m, 5H), 7.29 (d, J = 7.5 Hz, 1H), 4.77 (q, J = 8.0 Hz, 2H), 4.44 (q, J = 7.0 Hz, 2H), 3.18 (t, J = 7.0 Hz, 2H), 1.48 (t, J = 8.0 Hz, 3H); IR ν/cm^{-1} (KBr) 1759, 1709, 1551, 1482, 1421, 1384, 1341, 1301, 1279, 1198, 1155, 1111, 1090, 1051, 945, 895, 862, 823, 759; GC-MS *m/z* 386.8 $[M+1]^+$, 385.8, 339.9, 314.0, 270.1, 139.1.



3d

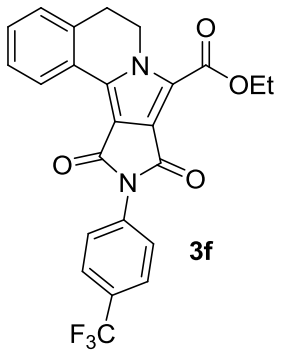
Ethyl 10-(4-methoxyphenyl)-9,11-dioxo-6,9,10,11-tetrahydro-5*H*-pyrrolo-[3',4':3,4] pyrrolo[2,1-*a*]isoquinoline-8-carboxylate (3d) [2]**:** white solid, yield 74% (0.308 g), mp 168-169^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.57 (d, *J* = 7.5 Hz, 1H), 7.41-7.35 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.28-7.27 (m, 1H), 7.00 (d, *J* = 9.0 Hz, 2H), 4.75 (t, *J* = 7.0 Hz, 2H), 4.42 (q, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 3.17 (t, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.5 Hz, 3H); IR *v*/cm^{-1} (KBr) 1761, 1707, 1514, 1385, 1280, 1250, 1194, 1159, 1111, 1031, 809, 743; GC-MS *m/z* 417.3 $[M+1]^{+}$, 385.1, 325.6, 288.2, 236.1, 156.7, 71.1.



3e

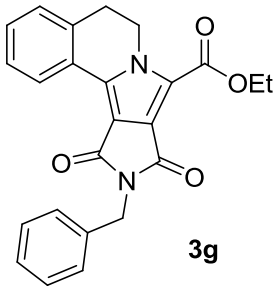
Ethyl 10-(4-nitrophenyl)-9,11-dioxo-6,9,10,11-tetrahydro-5*H*-pyrrolo-[3',4':3,4] pyrrolo[2,1-*a*]isoquinoline-8-carboxylate (3e) [2]**:** yellow solid, yield 81% (0.349 g), mp 206-207^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.55 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J*= 9.5 Hz, 2H), 7.46-7.40 (m, 2H),

7.32 (d, *J* = 7.0 Hz, 1H), 4.80 (t, *J* = 6.5 Hz, 2H), 4.46 (q, *J* = 7.5 Hz, 2H), 3.21 (t, *J* = 6.5 Hz, 2H), 1.49 (t, *J* = 7.5 Hz, 3H); IR *v*/cm^{-1} (KBr) 1761, 1713, 1524, 1384, 1321, 1277, 1194, 1138, 1109, 1040, 1011, 893, 853, 817, 777; GC-MS *m/z* 432.5 $[M+1]^+$, 400.2, 333.8, 263.9, 200.9, 184.5, 85.1.



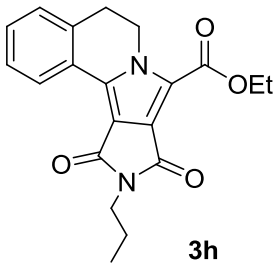
3f

Ethyl 10-(4-trifluoromethylphenyl)-9,11-dioxo-6,9,10,11-tetrahydro-5*H*-pyrrolo- [3',4':3,4]pyrrolo[2,1-*a*]isoquinoline-8-carboxylate (3f) [3]**:** white solid, yield 83% (0.377 g), mp 203-204^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.49-8.47 (m, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J*= 8.5 Hz, 2H), 7.36-7.34 (m, 2H), 7.25 (t, *J* = 4.5 Hz, 1H), 4.70 (t, *J* = 7.0 Hz, 2H), 4.39 (q, *J* = 7.0 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 162.2, 160.6, 159.1, 135.8, 134.2, 133.5, 132.3, 130.3, 127.7, 127.6, 127.5, 126.8, 125.7, 125.6, 125.5, 125.1, 124.5, 122.8, 118.8, 115.6, 61.5, 43.2, 27.9, 13.9; IR *v*/cm^{-1} (KBr) 1762, 1712, 1477, 1417, 1385, 1325, 1277, 1196, 1162, 1117, 1068, 1019, 947, 895, 845, 815; GC-MS *m/z* 454.7 $[M+1]^+$, 453.8, 371.0, 408.8, 381.8, 338.0, 139.0; HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{18}F_3N_2O_4$ $[M+H]^+$ 455.1219, found 455.1216.



3g

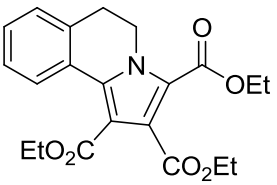
Ethyl 10-benzyl)-9,11-dioxo-6,9,10,11-tetrahydro-5*H*-pyrrolo-[3',4':3,4] pyrrolo [2,1-*a*] isoquinoline-8-carboxylate (3g) [2]**:** white solid, yield 88% (0.352 g), mp 200-201^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.49 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.38-7.30 (m, 3H), 7.27-7.23 (m, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 4.77 (s, 2H), 4.68 (t, *J* = 7.0 Hz, 2H), 4.43 (q, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 3H); GC-MS *m/z* 401.0 $[M+1]^{+}$, 400.0, 371.0, 353.9, 325.9, 224.2, 195.1.



3h

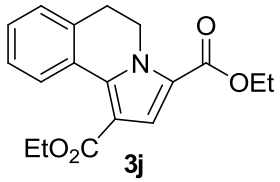
Ethyl 10-propyl-9,11-dioxo-6,9,10,11-tetrahydro-5*H*-pyrrolo[3',4':3,4]pyrrolo [2,1-*a*] isoquinoline-8-carboxylate (**3h**) [3]: white solid, yield 91% (0.321 g), mp 188-189^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.53 (d, *J* = 8.5 Hz, 1H), 7.42-7.39 (m, 1H), 7.38-7.34 (m, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 4.72 (t, *J* = 7.0 Hz, 2H), 4.43 (q, *J* = 7.0 Hz, 2H), 3.59 (t, *J* = 7.0 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H),

1.72-1.67 (m, 2H), 1.49 (t, J = 7.0 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 164.2, 162.7, 159.7, 132.8, 132.4, 130.1, 127.9, 127.9, 127.6, 125.9, 125.7, 118.1, 116.7, 61.5, 43.3, 39.9, 28.4, 22.0, 14.2, 11.4; IR ν/cm^{-1} (KBr) 1752, 1700, 1471, 1385, 1330, 1280, 1199, 1123, 1012, 779, 746; GC-MS *m/z* 353.0 $[M+1]^+$, 352.0, 323.1, 278.1, 266.2, 222.2, 139.2, 103.0; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{21}N_2O_4$ $[M+H]^+$ 353.1501, found 353.1498.



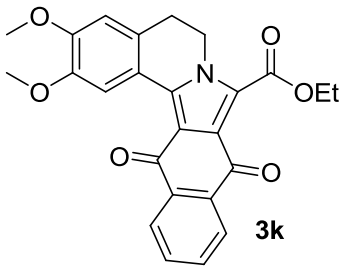
3i

3-Ethyl 1,2-diethyl 5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1,2,3-tricarboxylate (**3i**) [3]: white solid, yield 78% (0.301 g), mp 112-113^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.20-8.18 (m, 1H), 7.32-7.30 (m, 2H), 7.25-7.24 (m, 1H), 4.54 (t, J = 7.0 Hz, 2H), 4.38 (q, J = 7.0 Hz, 2H), 4.34-4.30 (m, 4H), 3.00 (t, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H), 1.37-1.32 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 166.0, 163.4, 159.9, 136.6, 134.3, 129.2, 128.5, 127.3, 126.9, 126.9, 126.5, 119.0, 110.8, 61.4, 61.0, 60.7, 42.6, 29.4, 14.12, 14.09, 14.05; IR ν/cm^{-1} (KBr) 1673, 1581, 1431, 1366, 1155, 1043, 886; GC-MS *m/z* 385.5 $[M]^+$, 384.7, 339.7, 312.8, 265.7, 221.9, 139.0, 129.9; HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{24}NO_6$ $[M+H]^+$ 386.1604, found 386.1598.



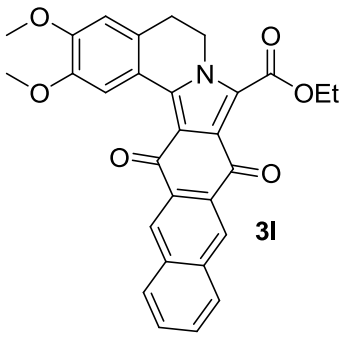
3j

Diethyl 5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1,3-dicarboxylate (**3j**) [2]: yellow solid, yield 50% (0.157 g), mp 100-101°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.45 (d, *J* = 8.5 Hz, 1H), 7.50 (s, 1H), 7.36-7.30 (m, 2H), 7.25 (d, *J* = 6.0 Hz, 1H), 4.61 (t, *J* = 6.5 Hz, 2H), 4.37-4.32 (m, 4H), 3.03 (t, *J* = 6.5 Hz, 2H), 1.41-1.38 (m, 6H); GC-MS *m/z* 314.2 $[M+1]^+$, 312.9, 283.5, 155.9,73.5.

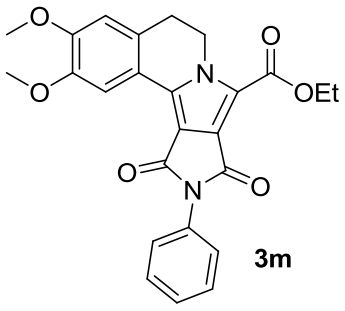


3k

Ethyl 2,3-dimethoxy-9,14-dioxo-5,6,9,14-tetrahydrobenzo[5,6]isoindolo[1,2-a] isoquinoline-8-carboxylate (3k) [3]**:** orange solid, yield 90% (0.388 g), mp 194-195°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.88 (s, 1H), 8.23 (t, *J* = 2.0 Hz, 1H), 8.12-8.10 (m, 1H), 7.66-7.60 (m, 2H), 6.67 (s, 1H), 4.51 (q, *J* = 7.0 Hz, 2H), 4.21 (t, *J* = 7.0 Hz, 2H), 4.06 (s, 3H), 3.89 (s, 3H), 3.01 (t, *J* = 7.0 Hz, 2H), 1.48 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.5, 179.4, 161.5, 150.2, 147.6, 136.2, 135.8, 134.6, 133.1, 132.7, 127.3, 126.9, 126.4, 125.9, 122.9, 119.1, 116.3, 112.4, 110.2, 62.4, 54.3, 55.9, 43.3, 28.5, 14.0; IR *v*/cm^{-1} (KBr) 1718, 1657, 1479, 1385, 1282, 1257, 1217, 1152, 1132, 1045, 1015, 705; HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{22}NO_6$ $[M+H]^+$ 432.1447, found 432.1444.

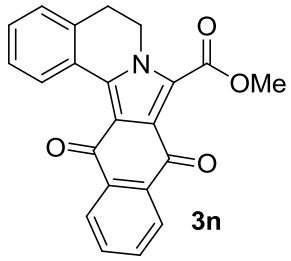


Ethyl 2,3-dimethoxy-9,16-dioxo-5,6,9,16-tetrahydronaphtho[5,6]isoindolo [1,2-a] isoquinoline-8-carboxylate (3l) [3]**:** orange solid, yield 80% (0.433 g), mp 271-272^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.98 (s, 1H), 8.80 (s, 1H), 8.68 (s, 1H), 8.04-8.00 (m, 2H), 7.63-7.61 (m, 2H), 6.73 (s, 1H), 4.57 (q, *J* = 7.5 Hz, 2H), 4.26 (t, *J* = 7.0 Hz, 2H), 4.13 (s, 3H), 3.93 (s, 3H), 3.06 (t, *J* = 7.0 Hz, 2H), 1.54 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.6, 179.4, 161.8, 150.2, 147.7, 136.3, 134.9, 134.6, 132.4, 131.3, 129.83, 129.77, 129.3, 128.82, 128.76, 128.4, 127.0, 126.1, 123.8, 119.3, 117.2, 112.6, 110.2, 62.5, 56.3, 56.0, 43.3, 28.6, 14.1; IR *v*/cm^{-1} (KBr) 1719, 1659, 1479, 1384, 1271, 1240, 1222, 1186, 1133, 1038, 914, 763; HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{24}NO_6$ $[M+H]^+$ 482.1604, found 482.1600.



Ethyl 2,3-dimethoxy-9,11-dioxo-10-phenyl-6,9,10,11-tetrahydro-5*H*-pyrrolo

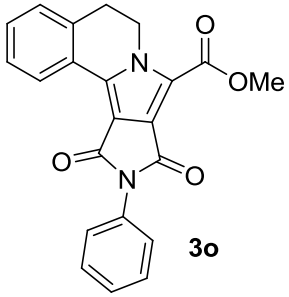
[3',4':3,4] pyrrolo[2,1-*a*]isoquinoline-8-carboxylate (**3m**) [2]: orange solid, yield 80% (0.357 g), mp 230-231°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.24 (s, 1H), 7.49-7.47 (m, 2H), 7.40-7.36 (m, 3H), 6.75 (s, 1H), 4.73 (t, *J* = 7.0 Hz, 2H), 4.41 (q, *J* = 7.0 Hz, 2H), 3.97 (s, 3H), 3.93 (s, 3H), 3.11 (t, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 163.46, 161.59, 159.59, 150.67, 148.57, 134.01, 132.60128.97 (2C), 127.84, 127.28 (2C), 125.55, 125.03, 118.29, 118.08, 114.75, 110.48, 110.26, 61.48, 56.14, 55.97, 43.42, 27.81, 14.12; GC-MS *m/z* 447.1 $[M+1]^+$, 445.0, 411.3, 385.4, 301.9, 254.3, 100.1, 56.4.



3n

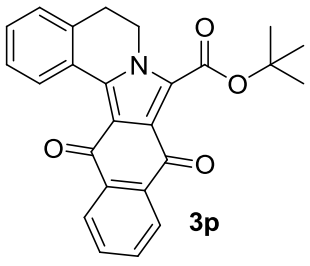
Methyl 2,3-dimethoxy-9,14-dioxo-5,6,9,14-tetrahydrobenzo[5,6]isoindolo [1,2-a] isoquinoline-8-carboxylate (3n) [3]**:** orange solid, yield 92% (0.329 g), mp 205-206°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.95 (s, *J* = 8.0 Hz, 1H), 8.27-8.25 (m, 1H), 8.17-8.16 (m, 1H), 7.71-7.65 (m, 2H), 7.42 (t, *J* = 6.5 Hz, 1H), 7.36-7.33 (m, 1H), 7.23 (s, *J* = 7.0 Hz, 1H), 4.26 (t, *J* = 6.5 Hz, 2H), 4.06 (s, 3H), 3.08 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.51, 179.47, 161.8, 135.8, 135.6, 134.6, 133.7, 133.3, 132.9, 130.1, 128.9, 127.4 (2C), 127.2, 126.5, 126.3, 125.4, 123.4, 117.5, 53.0, 43.2, 29.0; IR *ν*/cm^{-1} (KBr) 1712, 1656, 1466, 1412, 1385, 1314, 1269, 1224, 1140, 1113, 1060, 1012, 799, 734; GC-MS

m/z 358.1 $[M+1]^+$, 356.8, 333.6, 276.5, 139.8, 73.9; HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{16}NO_4$ $[M+H]^+$ 358.1079, found 358.1077.



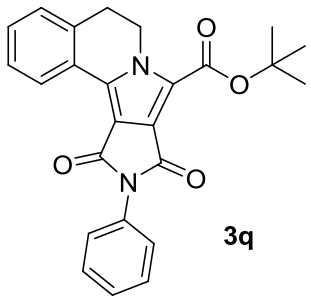
3o

Methyl 2,3-dimethoxy-9,11-dioxo-10-phenyl-6,9,10,11-tetrahydro-5*H*-pyrrolo [3',4':3,4] pyrrolo[2,1-*a*]isoquinoline-8-carboxylate (**3o**) [3]: orange solid, yield 71% (0.264 g), mp 217-218°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.58-8.57 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.43-7.36 (m, 5H), 7.29-7.28 (m, 1H), 4.77 (t, *J* = 7.0 Hz, 2H), 3.98 (s, 3H), 3.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 163.0, 161.5, 160.0, 133.6, 132.6, 132.4, 130.4, 128.8 (2C), 128.0, 127.9, 127.70, 127.65, 127.0 (2C), 125.5, 125.3, 118.2, 116.3, 52.3, 43.4, 28.3; IR *v*/cm^{-1} (KBr) 1497, 1385, 1199, 756, 694, 620; GC-MS *m/z* 373.6 $[M+1]^+$, 372.1, 348.6, 303.2, 256.4, 202.1, 154.1, 54.6; HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{17}N_2O_4$ $[M+H]^+$ 373.1188, found 373.1184.



3p

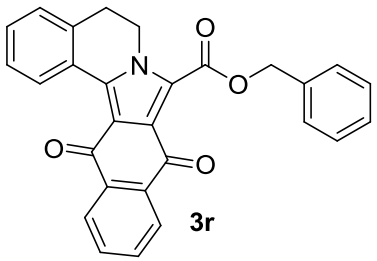
***Tert*-butyl 2,3-dimethoxy-9,14-dioxo-5,6,9,14-tetrahydrobenzo[5,6]isoindolo [1,2-a] isoquinoline-8-carboxylate** (**3p**) [3]: orange solid, yield 61% (0.244 g), mp 170-171°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.02 (d, J = 7.5 Hz, 1H), 8.30 (dd, J_1 = 2.0 Hz, J_2 = 6.5 Hz, 1H), 8.23 (dd, J_1 = 2.0 Hz, J_2 = 6.5 Hz, 1H), 7.72-7.69 (m, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 8.5 Hz, 1H), 4.27 (t, J = 7.0 Hz, 2H), 3.11 (t, J = 7.0 Hz, 2H), 1.72 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.8, 179.3, 160.6, 135.8, 135.0, 134.9, 133.5, 133.1, 132.9 (2C), 129.9, 128.8, 127.7, 127.4, 127.4, 127.2, 126.5, 122.4, 117.2, 84.1, 43.0, 29.1, 28.1 (3C); IR ν/cm^{-1} (KBr) 1660, 1467, 1385, 1266, 1229, 1141, 1010, 714; HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{21}NO_4Na$ $[M+Na]^+$ 422.1369, found 422.1365.



3q

***Tert*-butyl 2,3-dimethoxy-9,11-dioxo-10-phenyl-6,9,10,11-tetrahydro-5*H*-pyrrolo [3',4':3,4]pyrrolo[2,1-*a*]isoquinoline-8-carboxylate** (**3q**) [3]: orange solid, yield 58% (0.240 g), mp 234-235°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.59 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.43-7.35 (m, 5H), 7.28 (t, J = 6.5 Hz, 1H), 4.75 (t, J = 6.5 Hz, 2H), 3.16 (t, J = 6.5 Hz, 2H), 1.68 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 163.2, 161.6, 159.0, 133.0, 132.8, 132.4,

130.1, 128.9 (2C), 127.9, 127.9, 127.7, 127.6, 127.3 (2C), 125.7, 124.7, 120.2, 116.0, 83.4, 43.3, 28.4, 28.3 (3C); IR ν/cm^{-1} (KBr) 1759, 1703, 1481, 1415, 1385, 1349, 1305, 1289, 1154, 1135, 1112, 1089, 1051, 950, 889, 843, 762; HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{22}N_2O_4Na$ $[M+Na]^+$ 437.1478, found 437.1475.

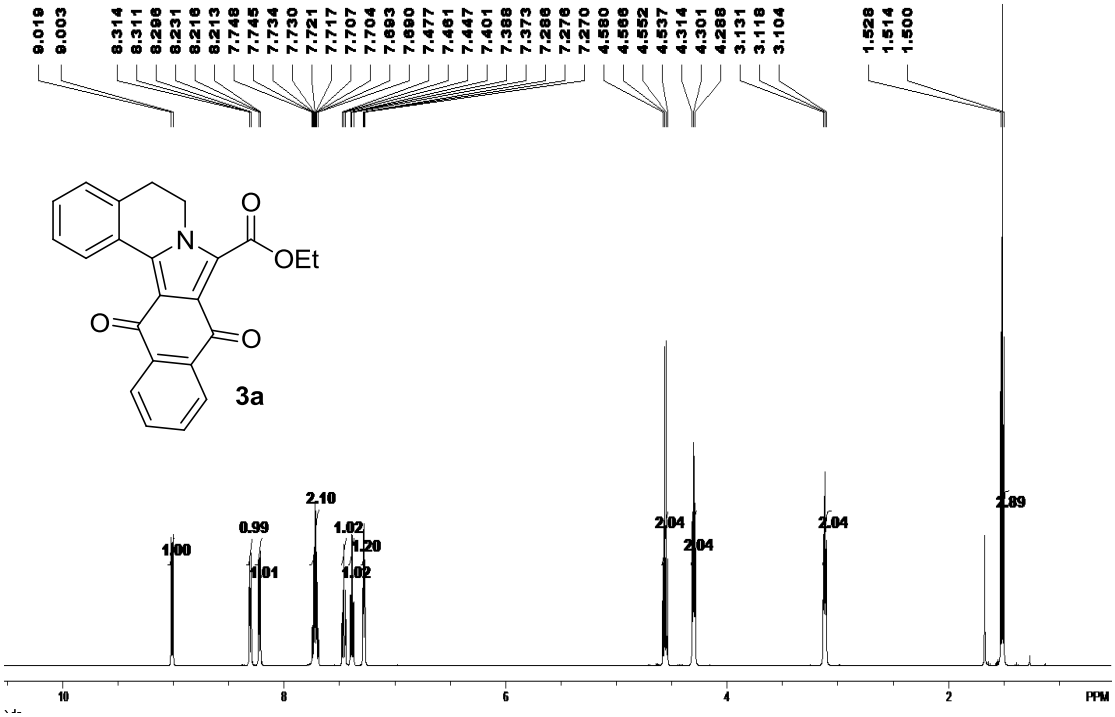


3r

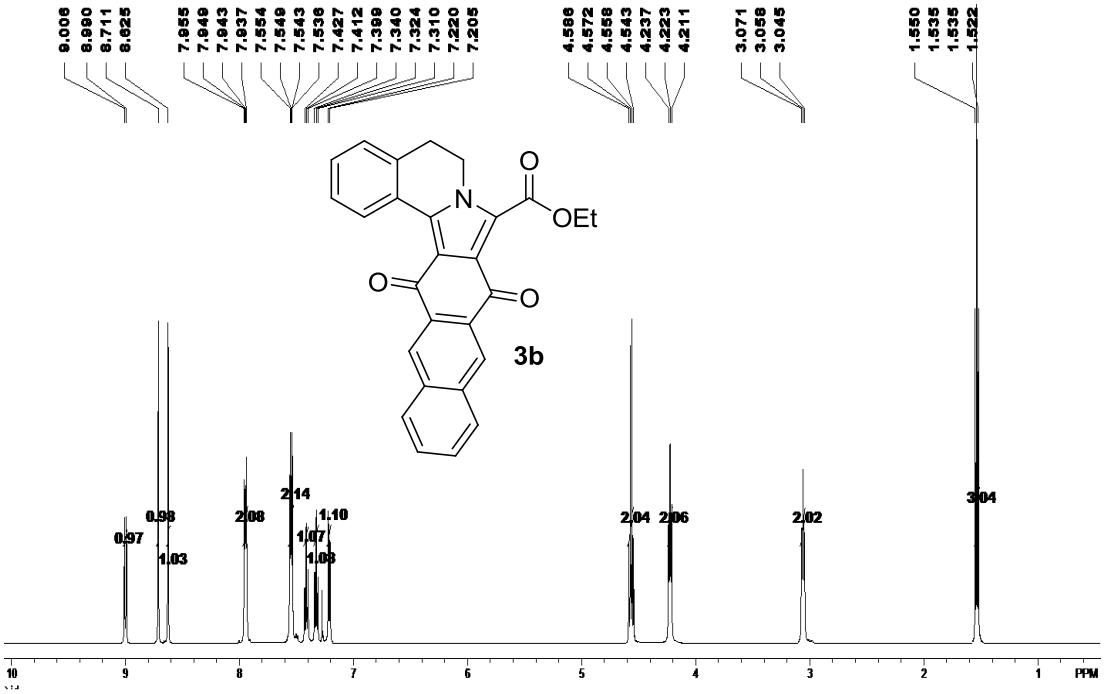
Benzyl 2,3-dimethoxy-9,11-dioxo-10-phenyl-6,9,10,11-tetrahydro-5*H*-pyrrolo [3',4':3,4] pyrrolo[2,1-*a*]isoquinoline-8-carboxylate (**3r**) [3]: orange solid, yield 90% (0.390 g), mp 198-199^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.00 (d, J = 7.5 Hz, 1H), 8.30 (dd, J_1 = 2.5 Hz, J_2 = 6.0 Hz, 1H), 8.24 (dd, J_1 = 3.0 Hz, J_2 = 6.5 Hz, 1H), 7.74-7.70 (m, 2H), 7.57 (d, J = 6.5 Hz, 2H), 7.47-7.36 (m, 5H), 7.27 (d, J = 8.5 Hz, 1H), 5.53 (s, 2H), 4.26 (t, J = 6.5 Hz, 2H), 3.08 (t, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.8, 179.5, 161.4, 135.9, 135.8, 135.2, 134.9, 133.7, 133.4, 133.1, 130.2, 129.0, 128.8 (2C), 128.7 (2C), 128.7, 127.5, 127.5, 127.3, 126.7, 126.4, 125.5, 123.7, 117.7, 68.4, 43.3, 29.2; IR ν/cm^{-1} (KBr) 1642, 1384, 1262, 1097, 802; HRMS (ESI-TOF) *m/z* Calcd for $C_{28}H_{20}NO_4$ $[M+H]^+$ 434.1392, found 434.1390.

4. NMR Spectra

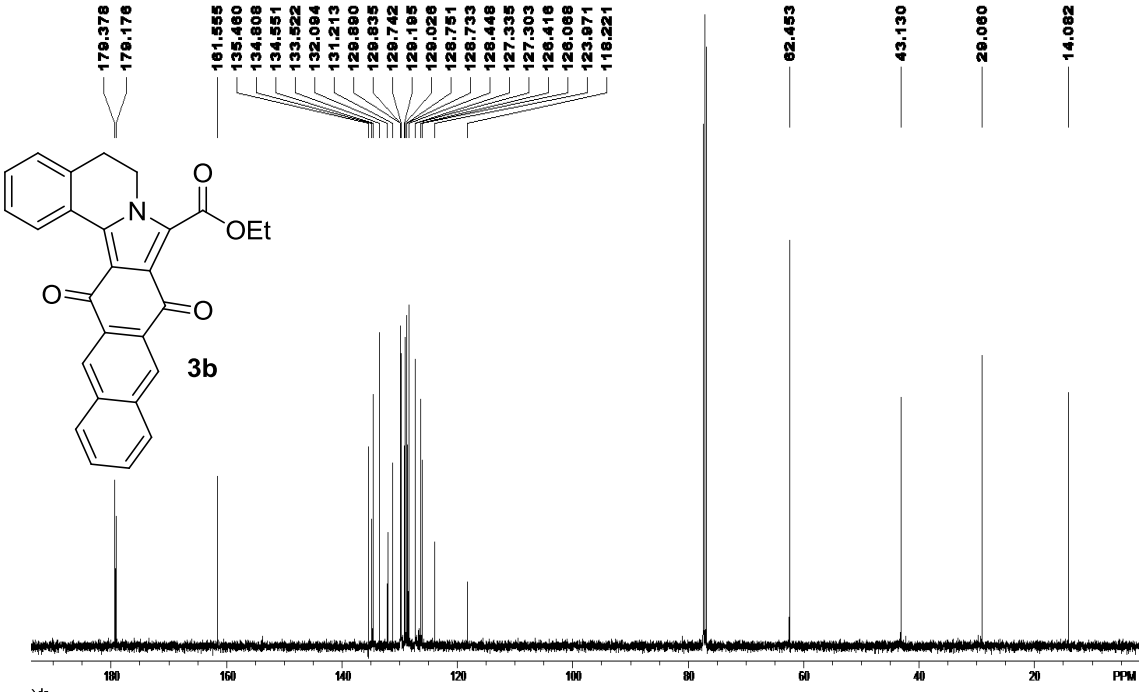
^{1}H NMR (500 MH_Z, $CDCl_3$)



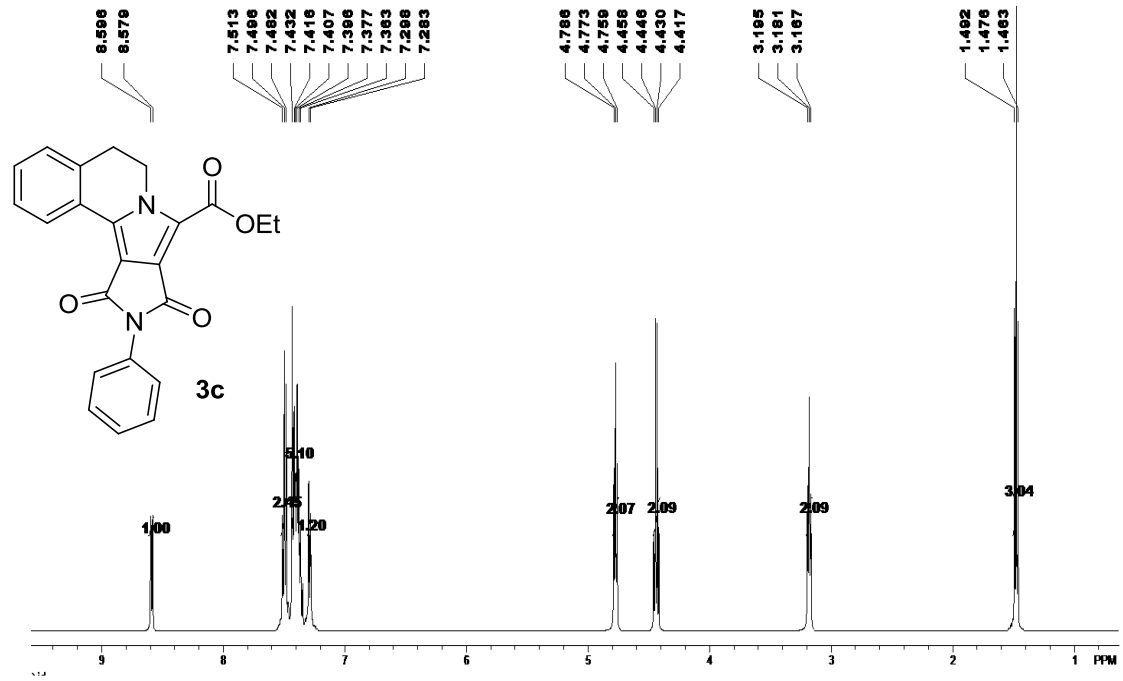
^{1}H NMR (500 MH_Z, $CDCl_3$)



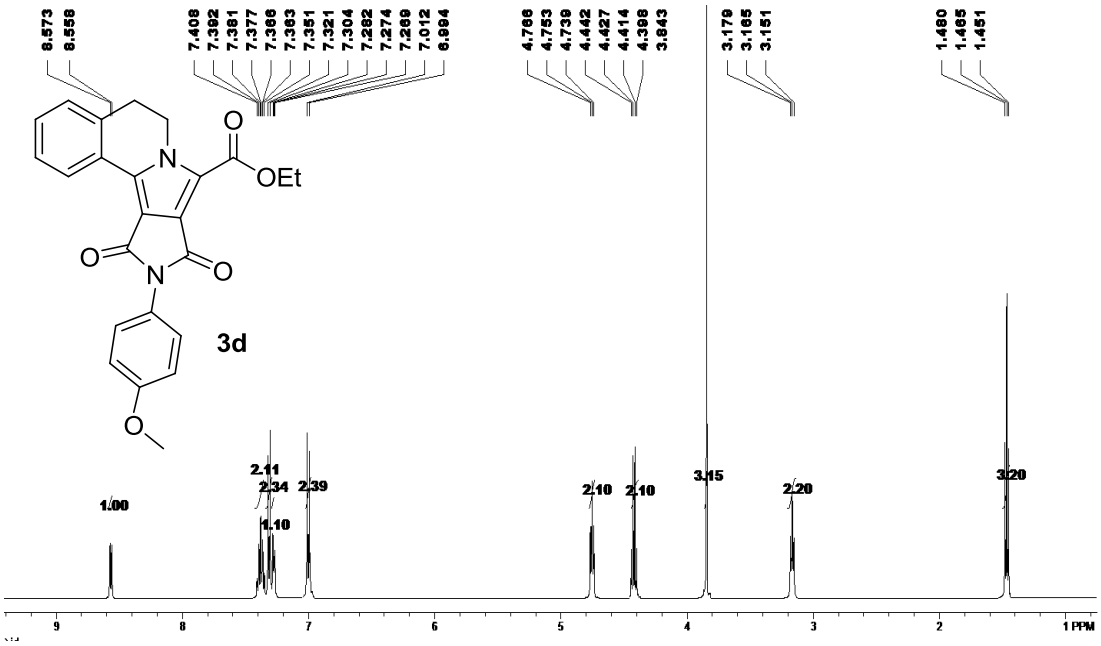
^{13}C NMR (125MHz, $CDCl_3$)



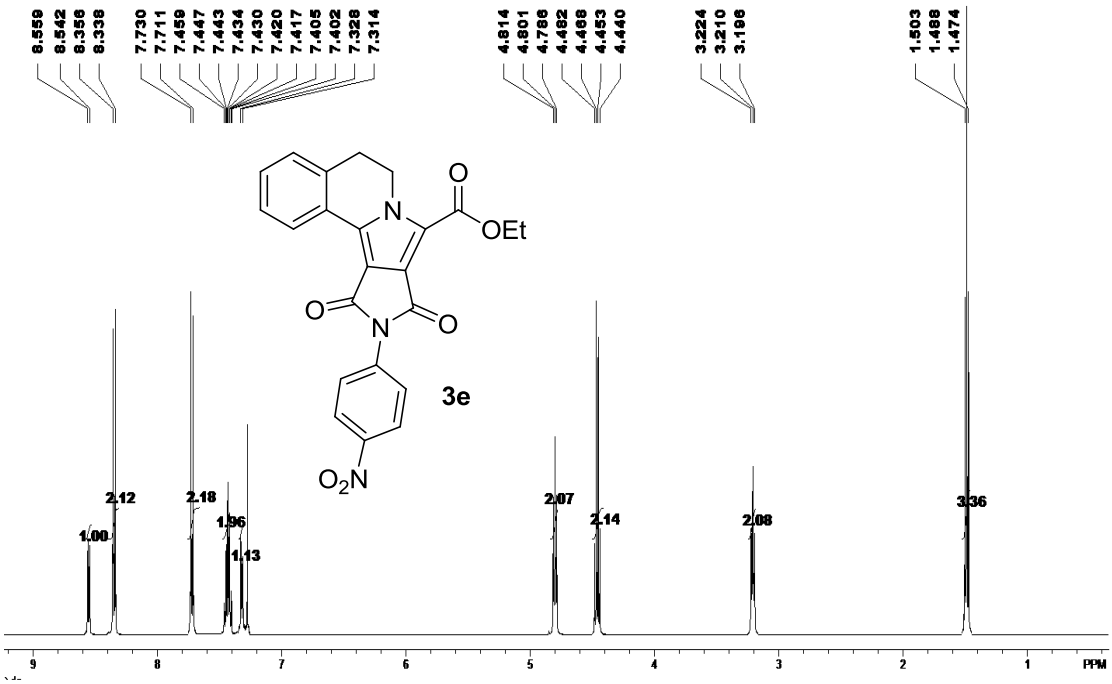
^{1}H NMR (500 MH_Z, $CDCl_3$)



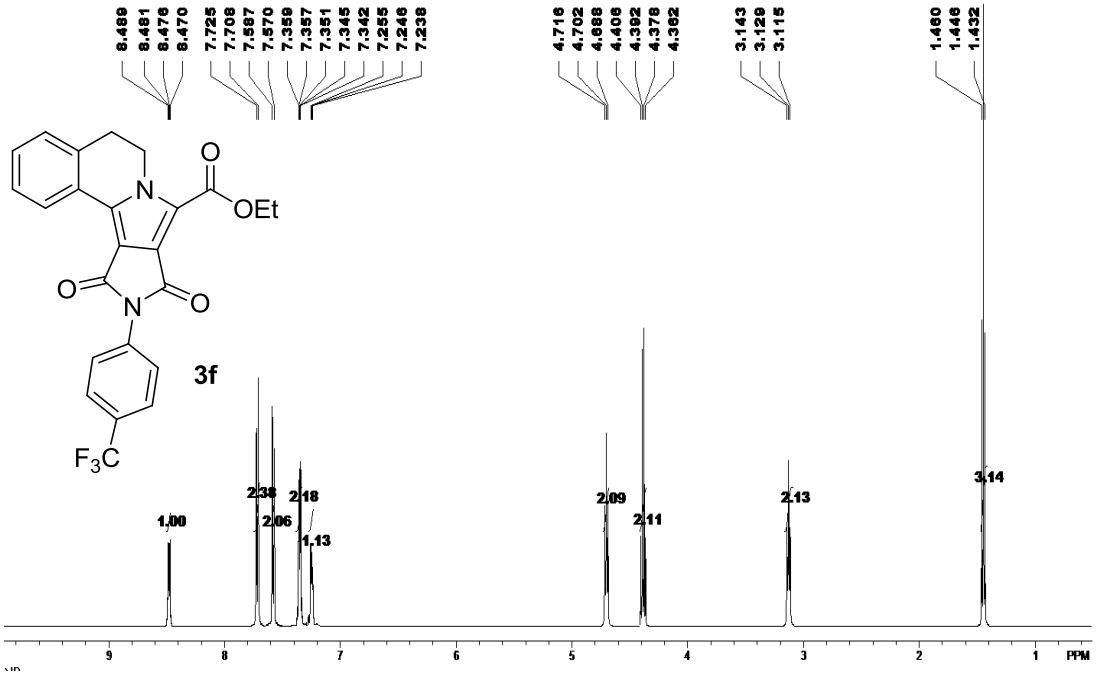
^{1}H NMR (500 MH_Z, $CDCl_3$)



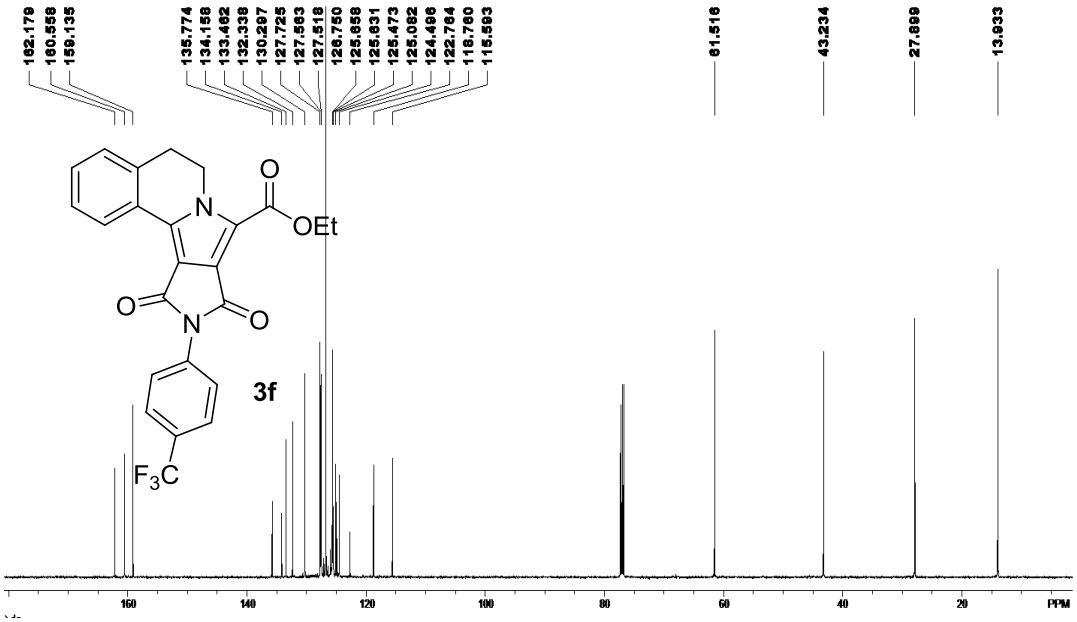
^{1}H NMR (500 MH_Z, $CDCl_3$)



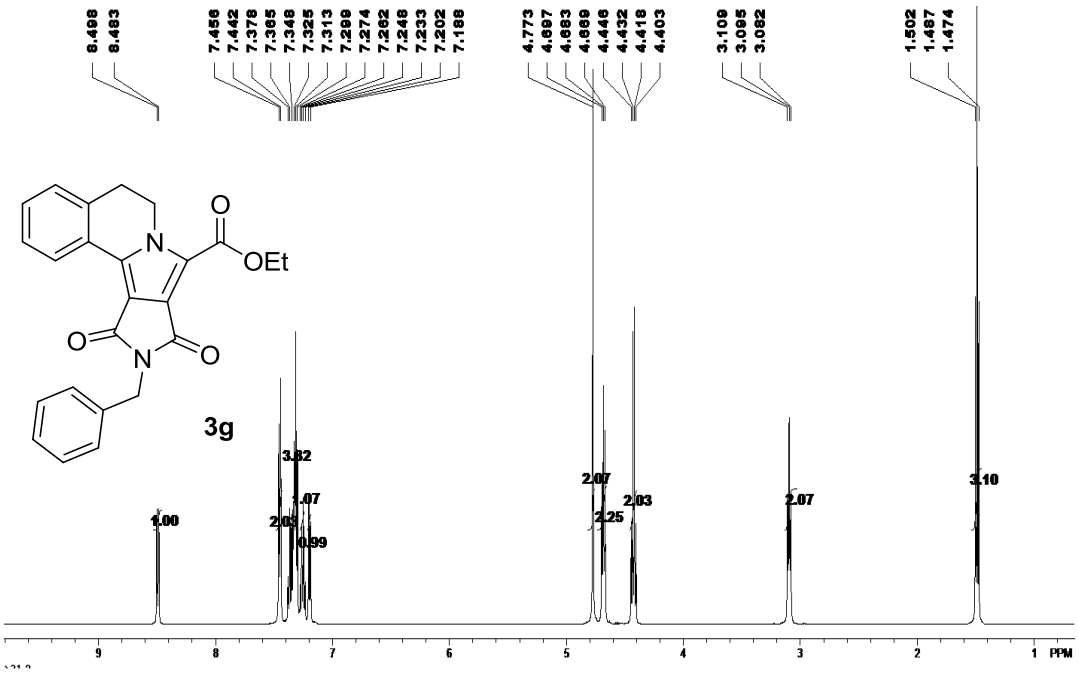
^{1}H NMR (500 MH_Z, $CDCl_3$)



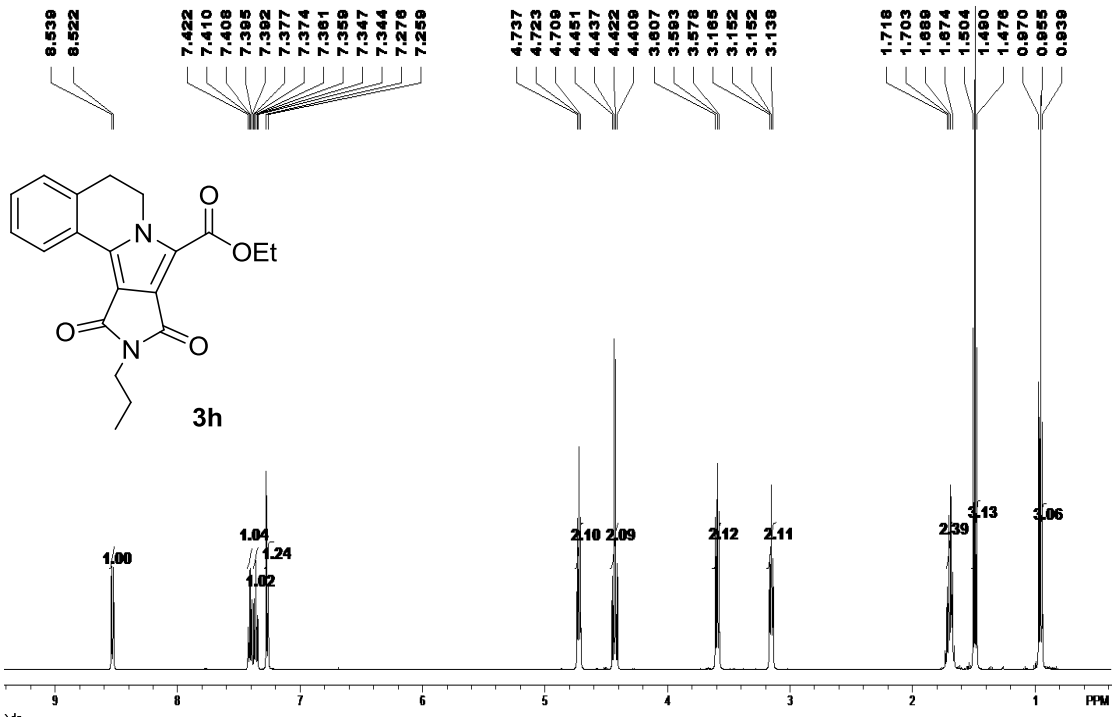
^{13}C NMR (125MHz, $CDCl_3$)



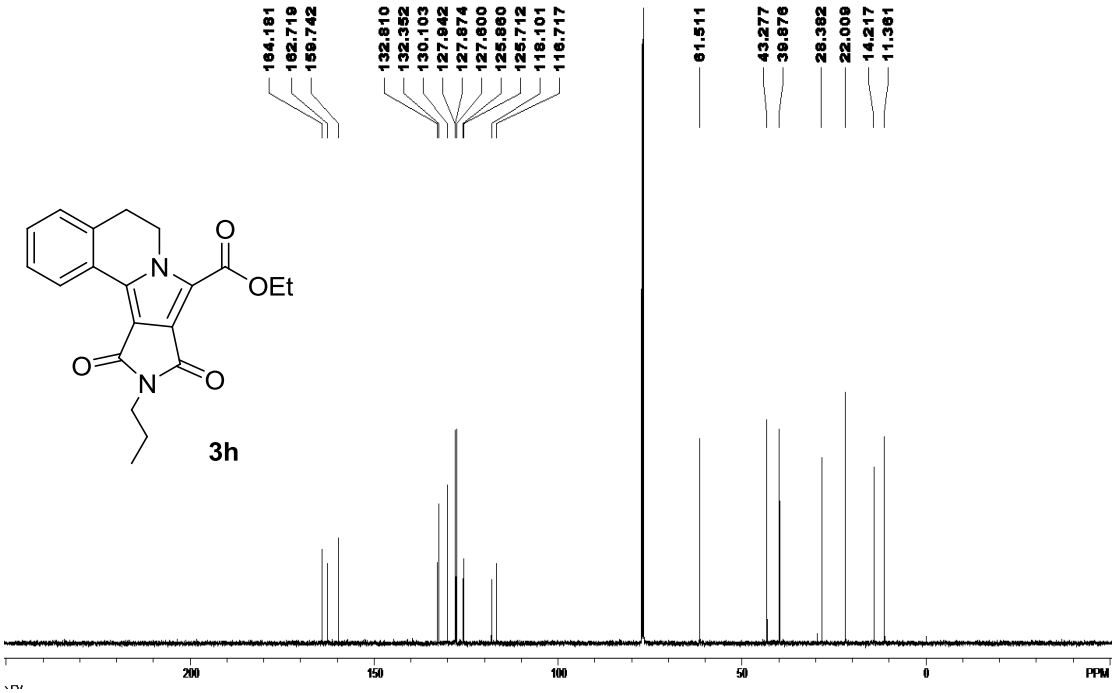
^{1}H NMR (500 MH_Z, $CDCl_3$)



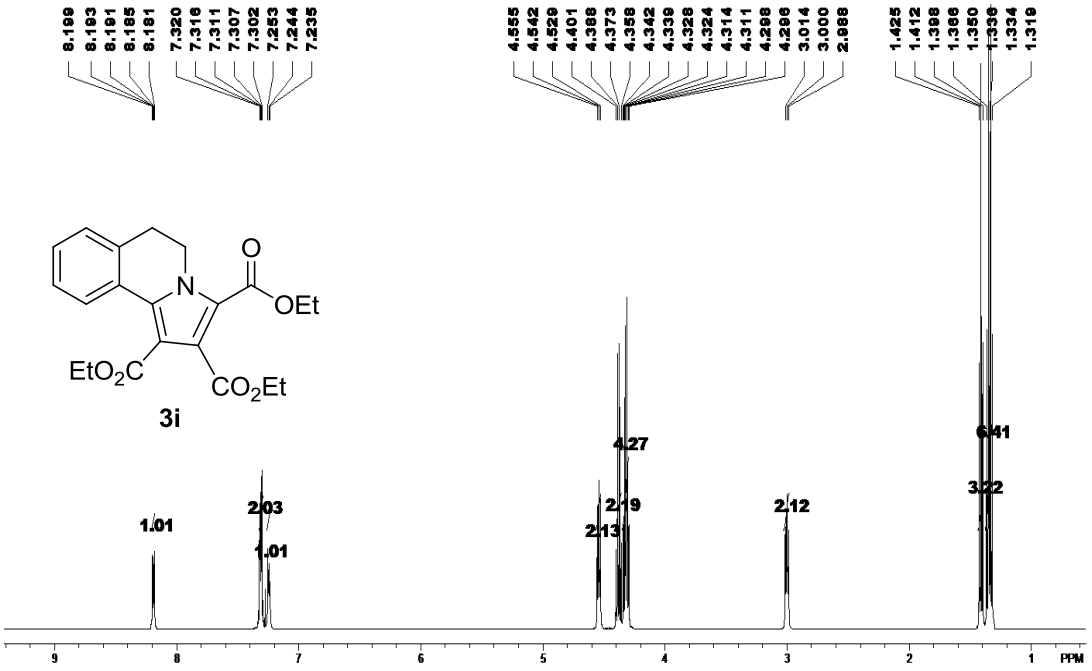
^{1}H NMR (500 MH_Z, $CDCl_3$)



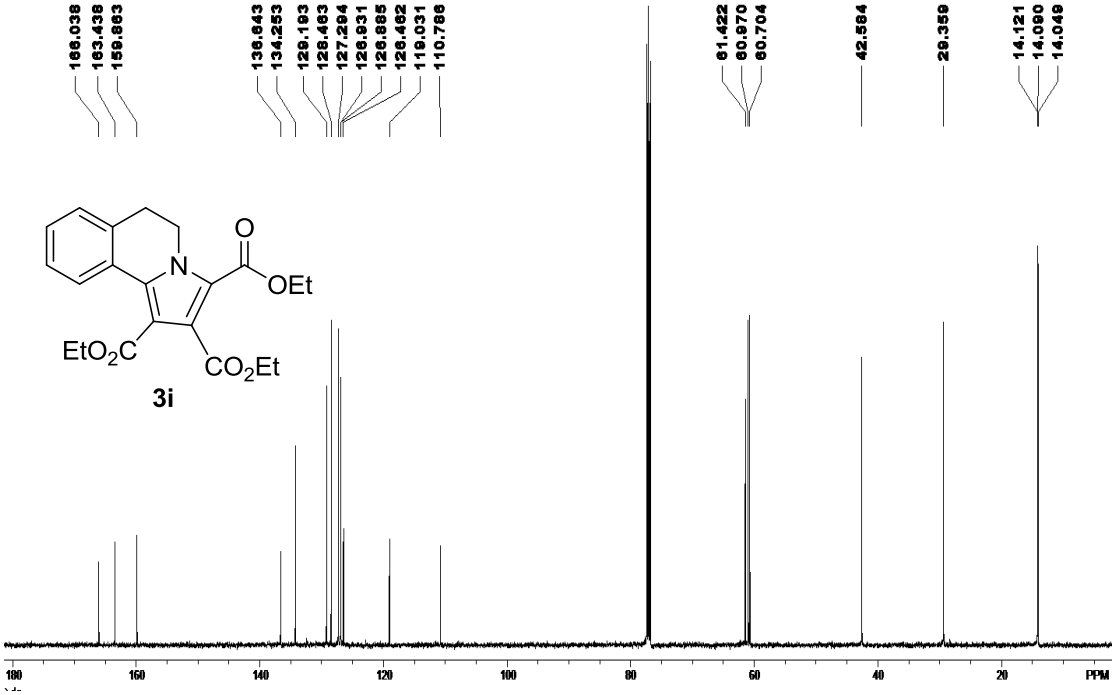
^{13}C NMR (125MHz, $CDCl_3$)



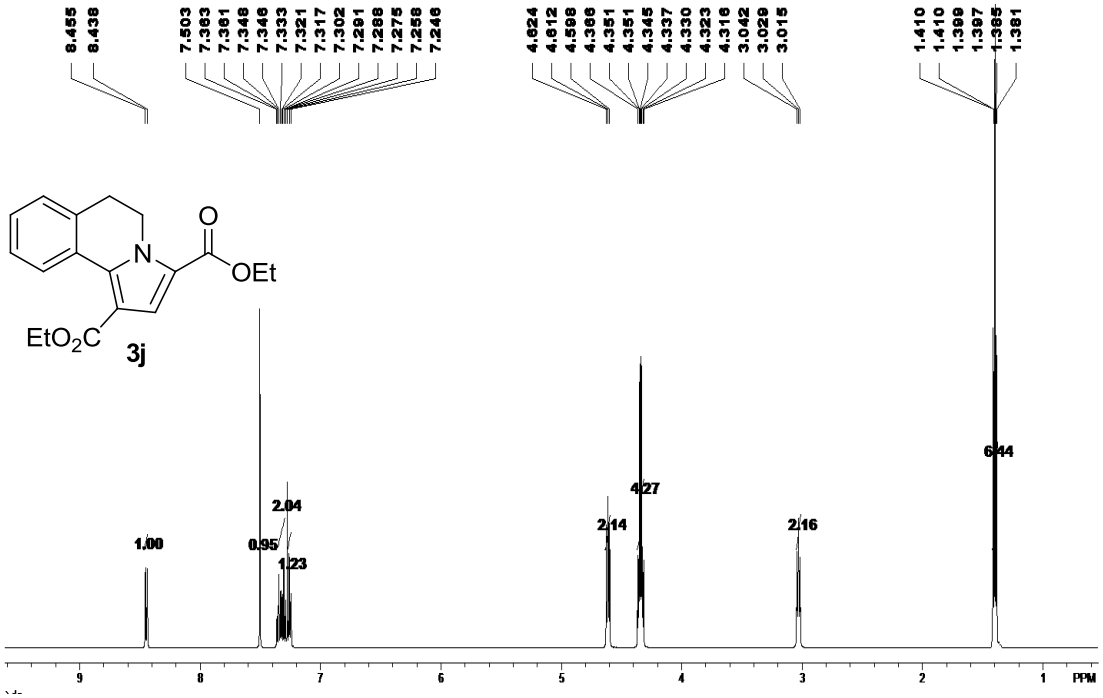
^{1}H NMR (500 MH_Z, $CDCl_3$)



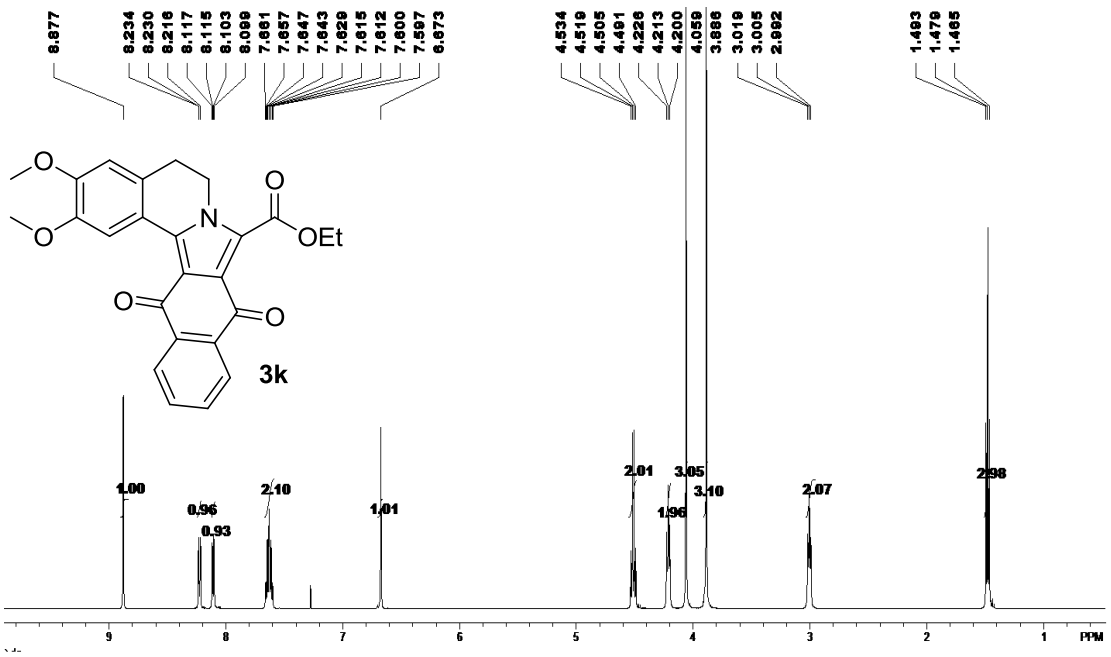
^{13}C NMR (125MHz, $CDCl_3$)



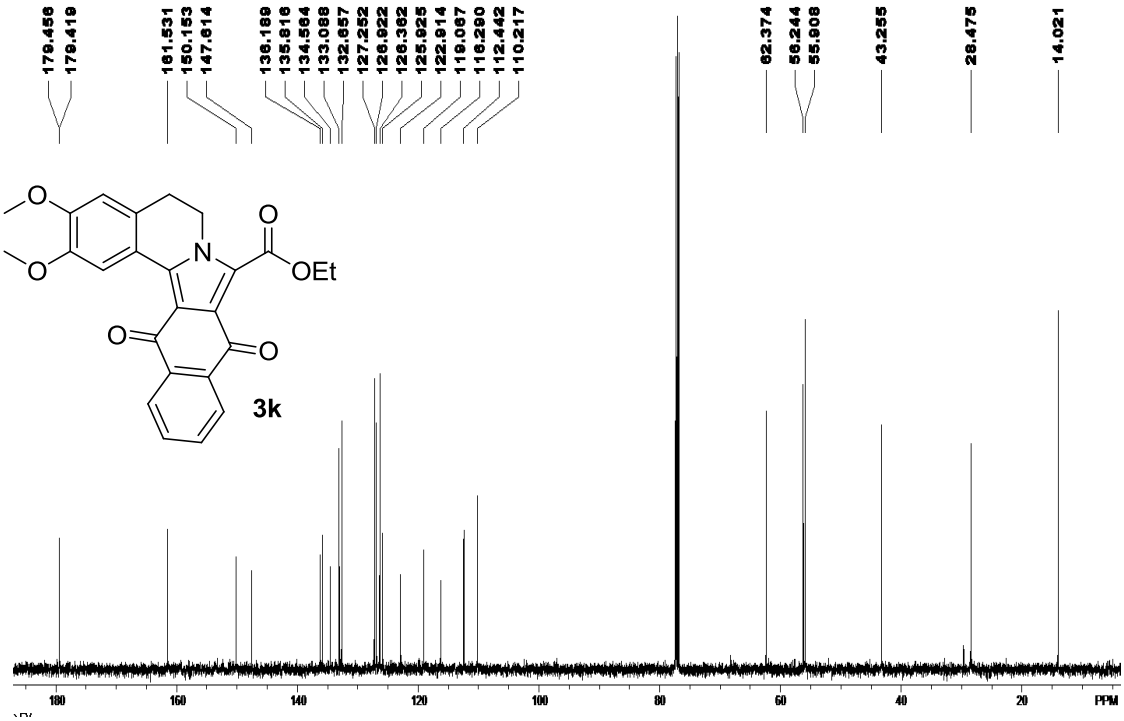
^{1}H NMR (500 MH_Z, $CDCl_3$)



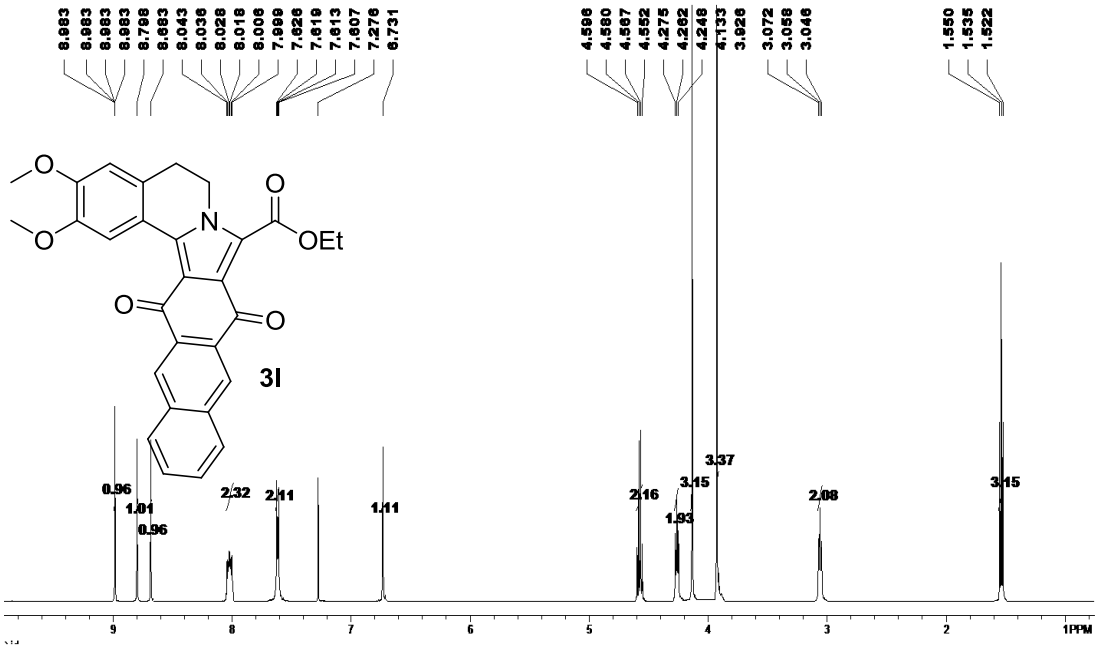
^{1}H NMR (500 MH_Z, $CDCl_3$)



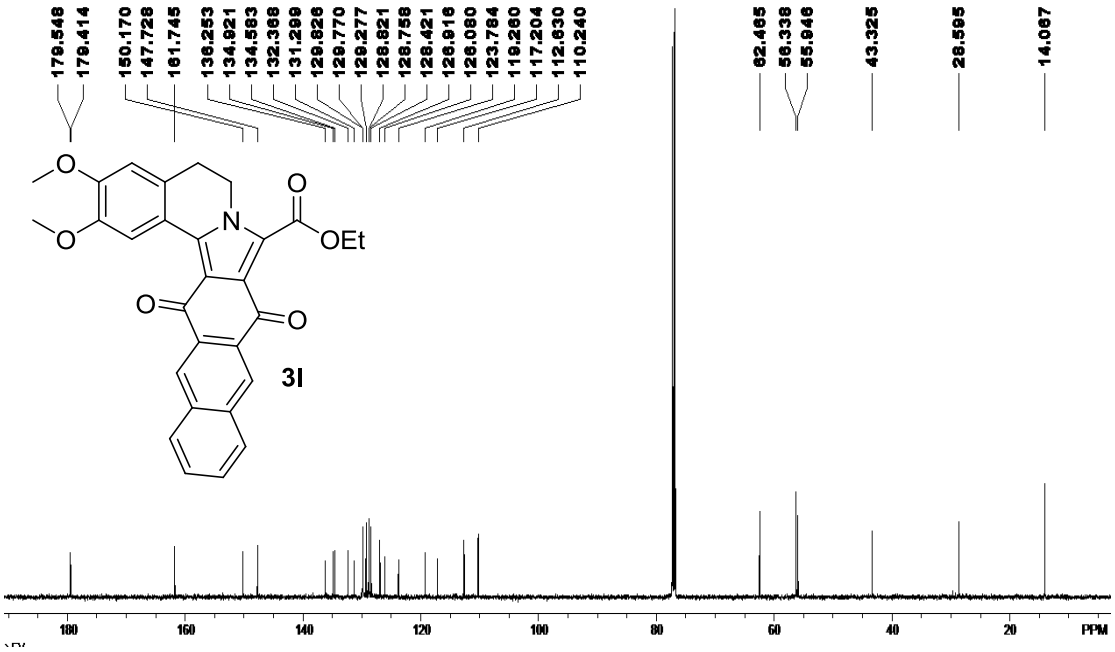
^{13}C NMR (125MHz, $CDCl_3$)



^{1}H NMR (500 MH_Z, $CDCl_3$)



^{13}C NMR (125MHz, $CDCl_3$)



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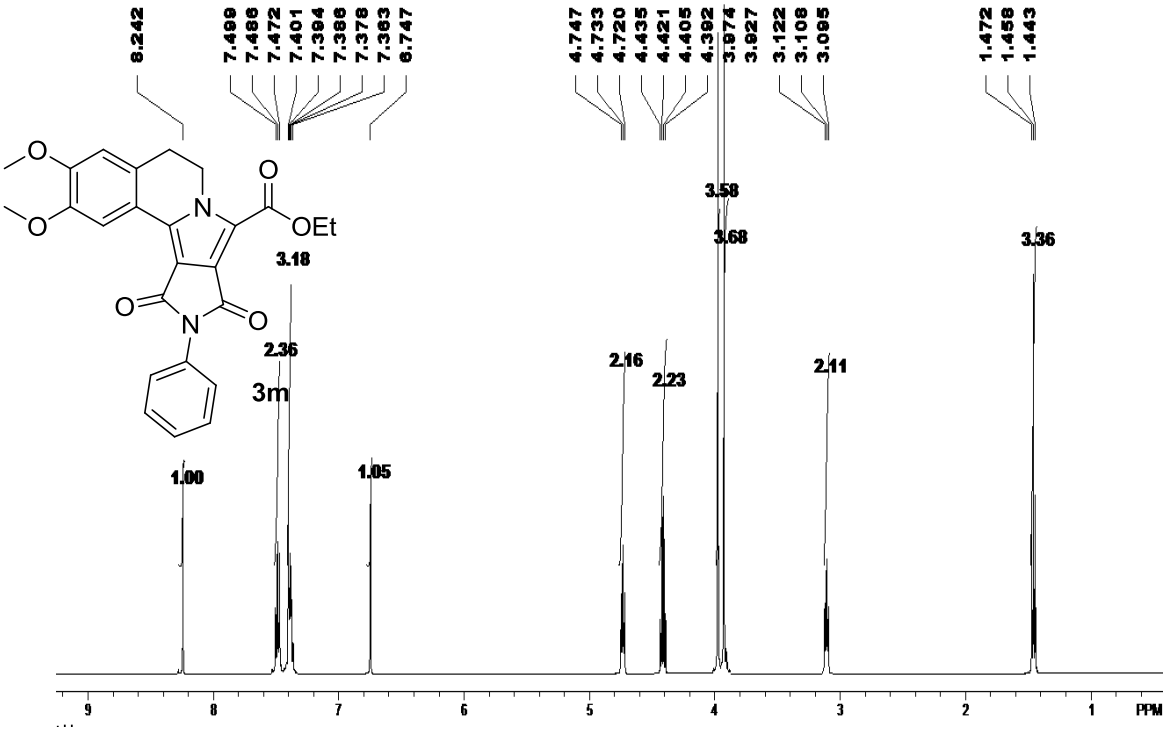
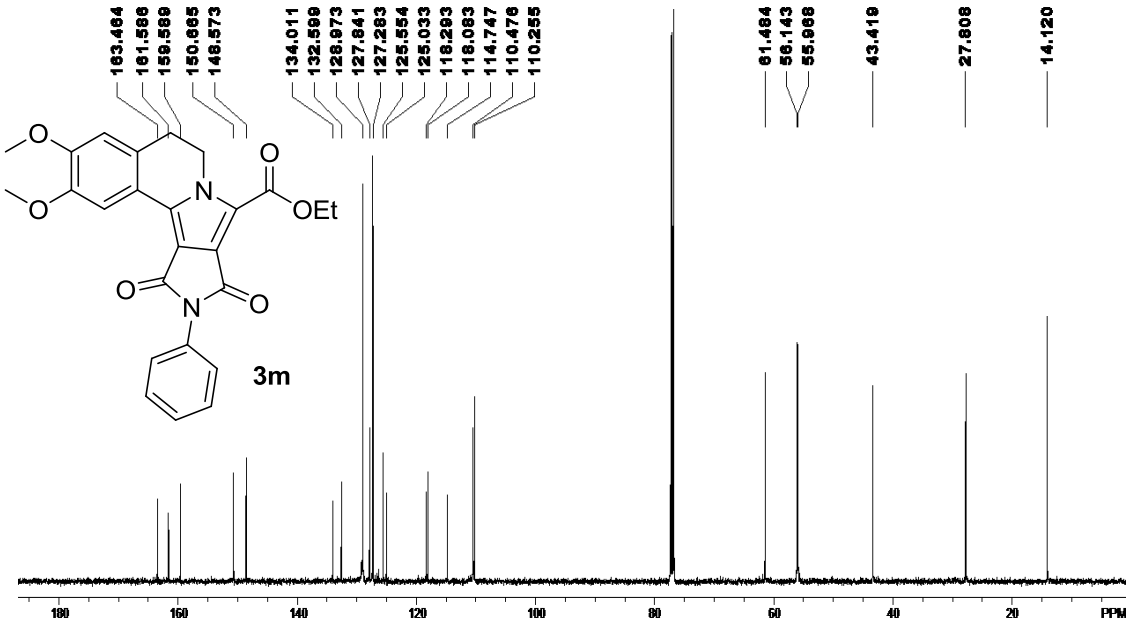


^{13}C NMR (125MHz, $CDCl_3$)



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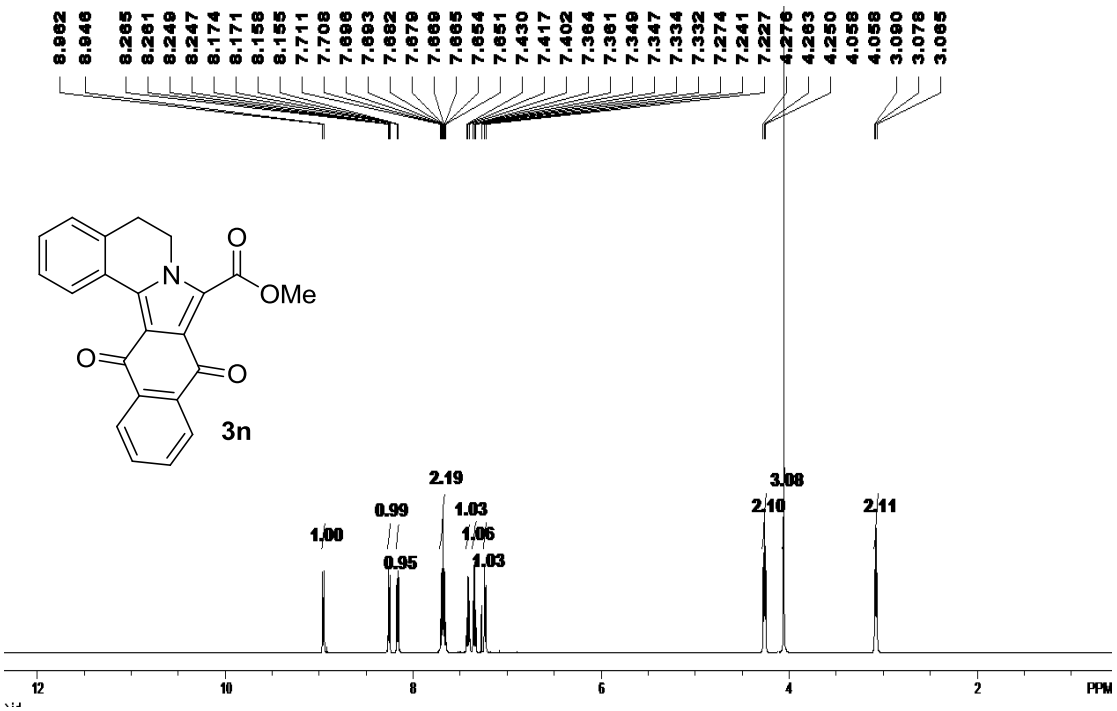
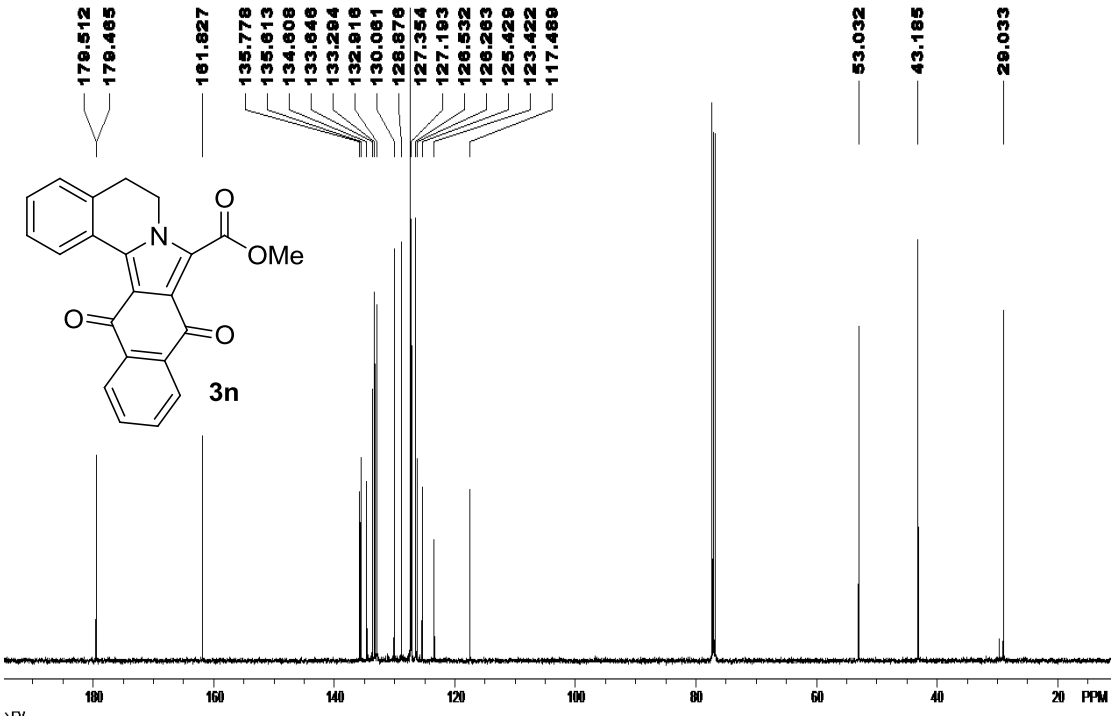
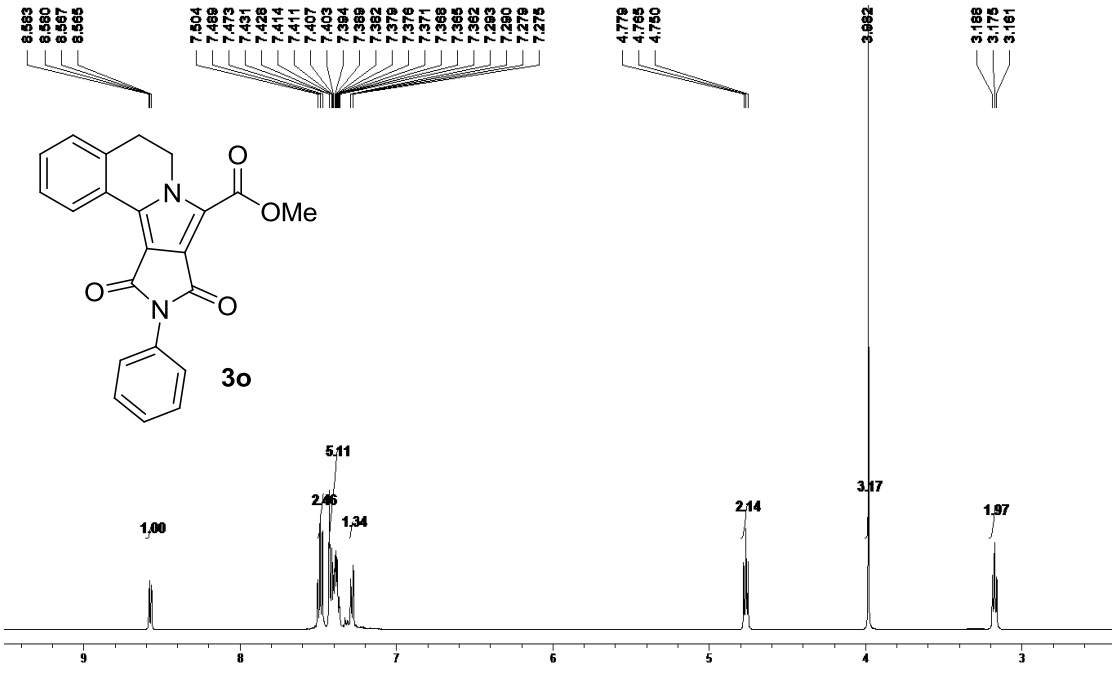


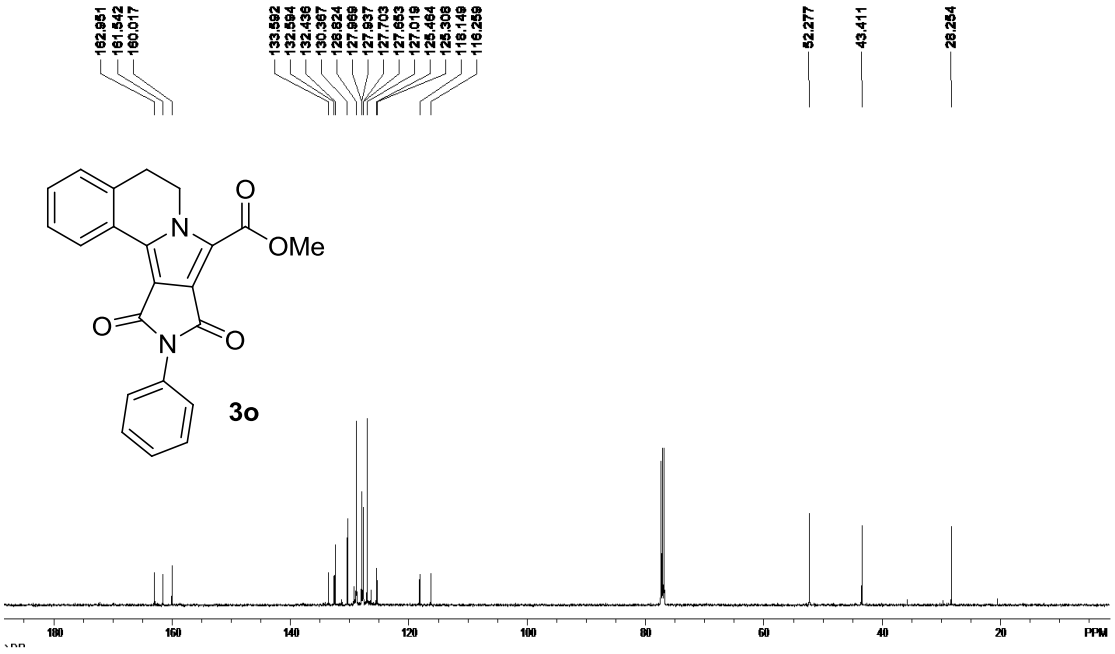
^{13}C NMR (125MHz, $CDCl_3$)



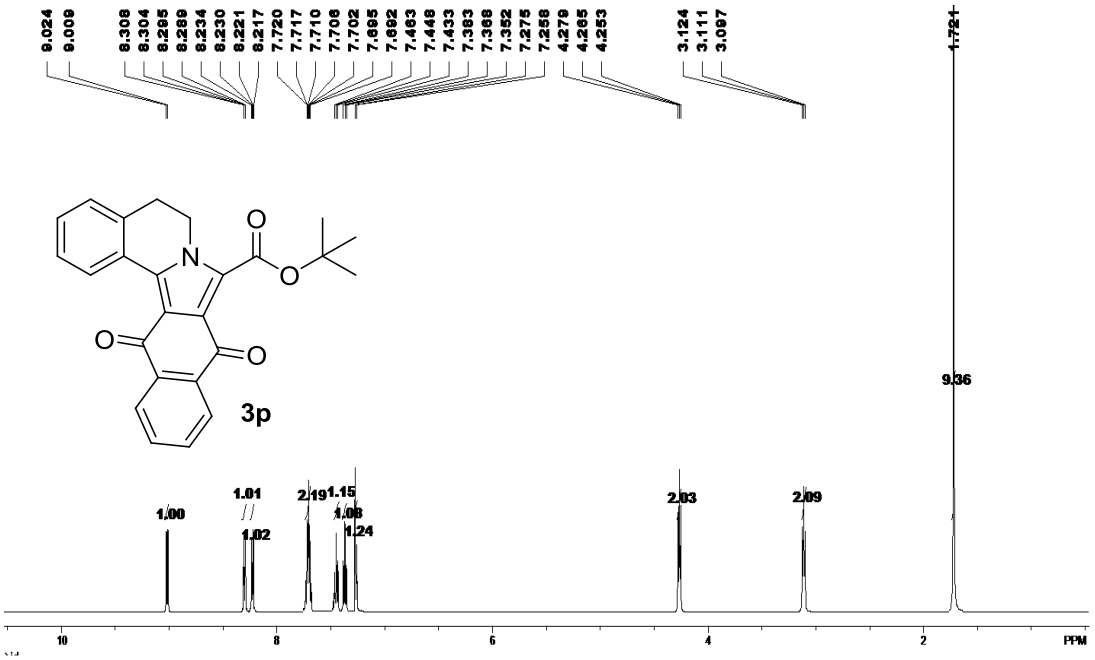
^{1}H NMR (500 MH$_Z$, CDCl$_3$)



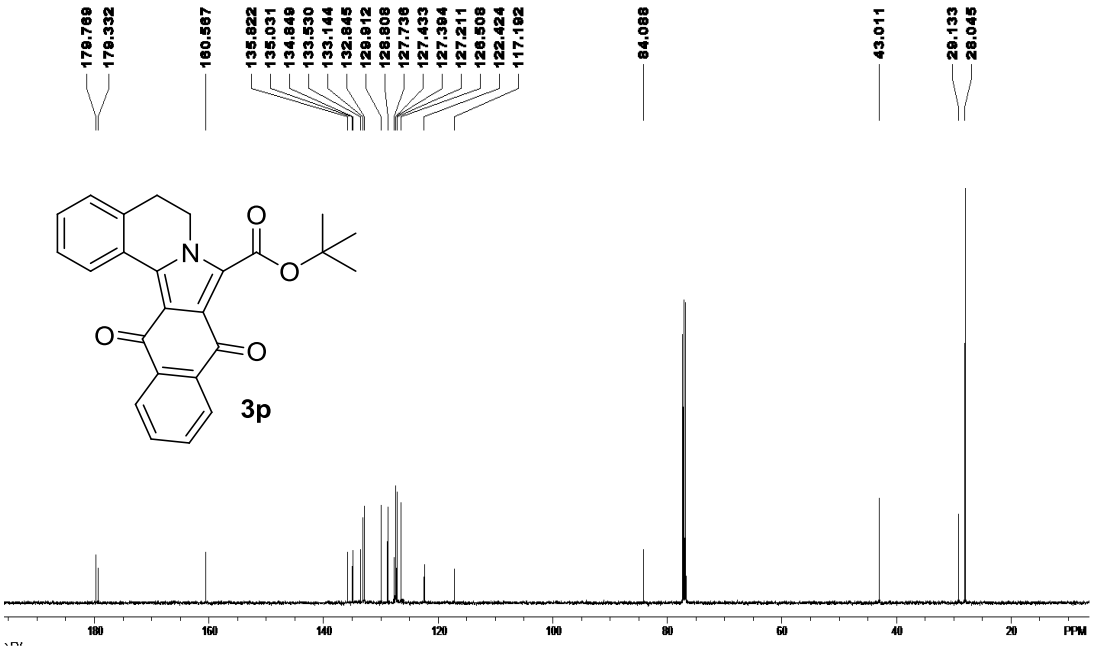
^{13}C NMR (125MHz, CDCl$_3$)



^{1}H NMR (500 MH_Z, $CDCl_3$)



^{13}C NMR (125MHz, $CDCl_3$)



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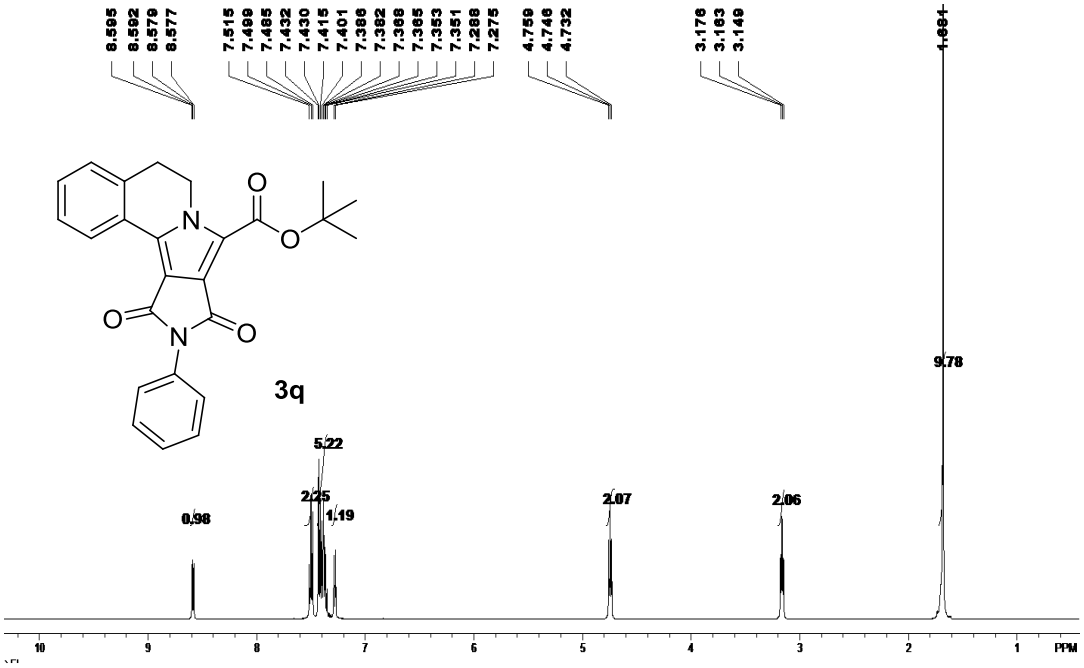

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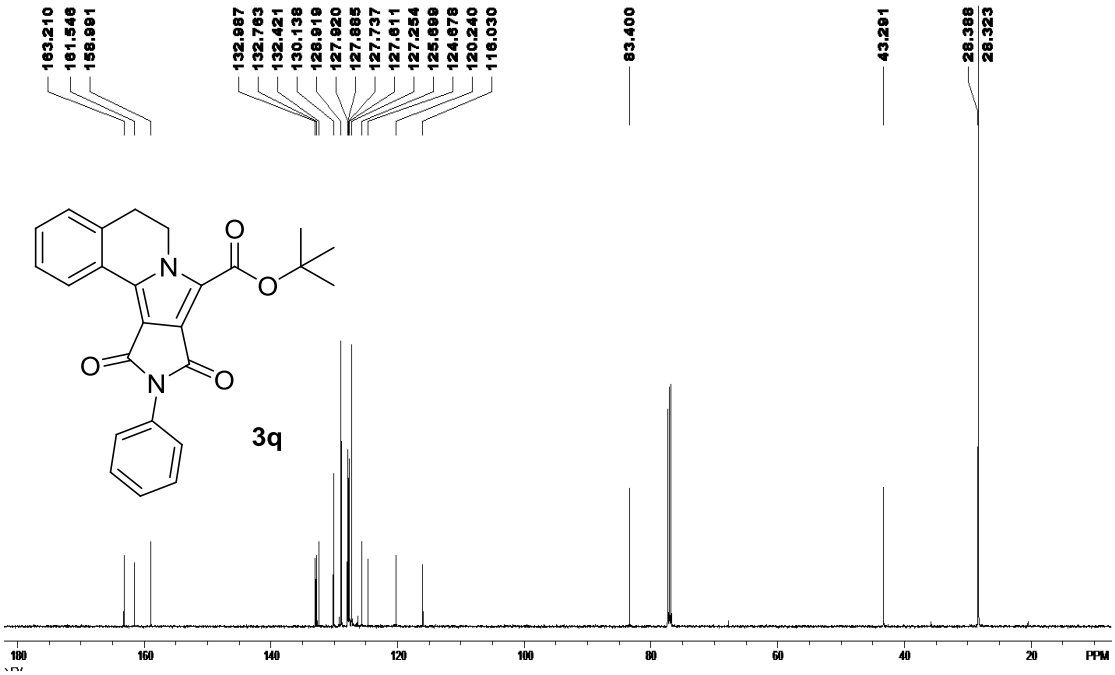

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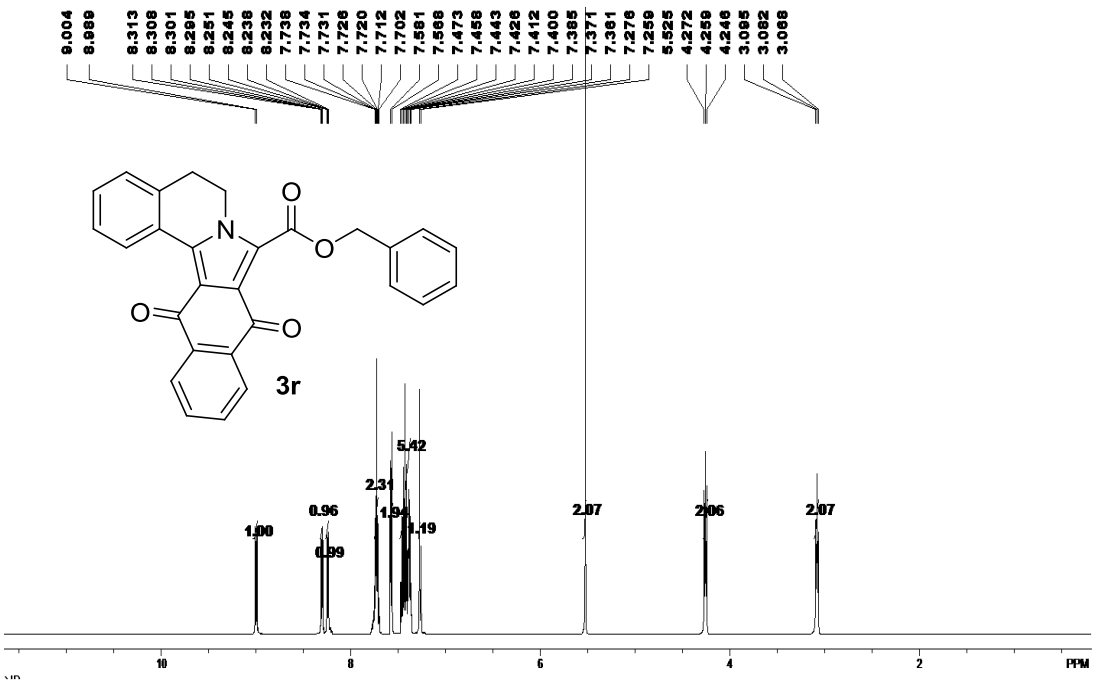
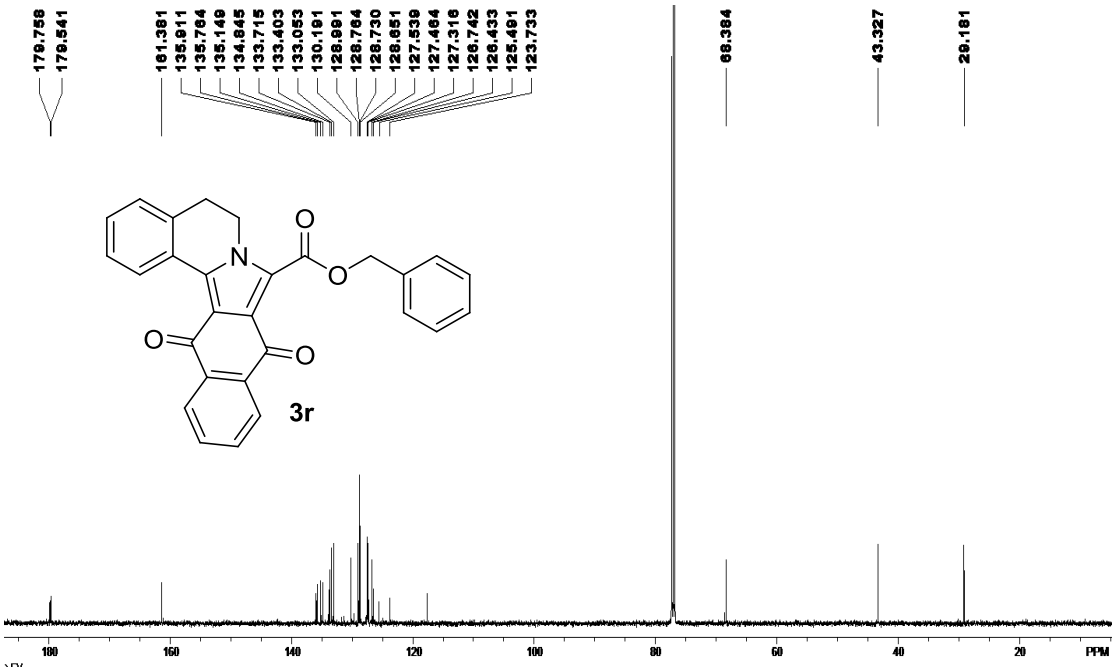


^{13}C NMR (125MHz, $CDCl_3$)



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1. C. Yu; Y. Zhang; S. Zhang; H. Li; W. Wang, *Chem. Commun.* 2011, **47**, 1036-1038.

2. Y.-Q. Zou; L.-Q. Lu; L. Fu; N.-J. Chang; J. Rong; J.-R. Chen; W.-J. Xiao, *Angew. Chem. Int. Ed.* 2011, **50**, 7171-7175.

3. H.-M. Huang, Y.-J. Li, Q. Ye, W.-B. Yu, L. Han, J.-H. Jia and J.-R. Gao, *J. Org. Chem.* 2014, **79**, 1084-1092.