Supporting Information

Base-Promoted Annulation of *α*-Hydroxy Ketones and Dimethyl But-2-ynedioate : Straightforward Access to pyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-triones and 2*H*-pyran-2,5(6*H*)-diones

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A. General methods

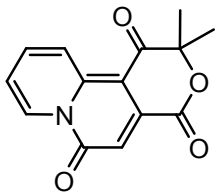
^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). GC–MS was obtained using electron ionization. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. Compounds **1a-o** were synthesized using our recently developed method.[1] Other compounds were commercially purchased and used without further purification.

B. General procedure for the preparation of pyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione and 2*H*-pyran-2,5(6*H*)-dione derivatives (3a-k, 4l-o)

To a dried 10 mL tube, the mixture of α-ketols (0.25 mmol), dimethyl but-2-ynedioate (0.35 - 0.5 mmol), DMF (1 mL) and DBU (0.25 - 0.5 mmol) was added successively. The reaction was carried out at the selected temperature under magnetic stirring for 1-2 h. As the reaction was completed, the mixture was washed with brine and extracted with ethyl acetate. The organic layer was dried ($MgSO_4$), concentrated in vacuum, and the crude residue was separated by column chromatography on silica gel with CH_2Cl_2 to give the desired product **3a-k, 4l-m** and with petroleum ether/ethyl acetate (2:1 to 5:1) to give the desired product **4n-o**.

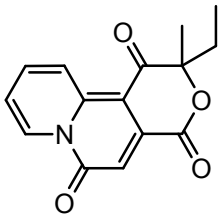
C. Analytical data

2,2-dimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3a)



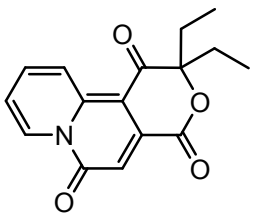
Yellow solid (60.3 mg, 94%), mp: 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81 (d, J = 9.1 Hz, 1 H), 9.49 (d, J = 7.1 Hz, 1H), 8.08 – 8.02 (m, 1 H), 7.55 (t, J = 6.9 Hz, 1 H), 7.25 (s, 1 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 161.0, 157.8, 144.6, 138.0, 136.3, 129.4, 125.7, 119.4, 106.8, 101.5, 87.0, 27.2. IR (KBr): 2987, 2924, 2362, 1713, 1648, 1478, 1381, 1272, 1141, 759 cm^{-1}. HRMS EI (m/z): calcd for $C_{14}H_{12}NO_4$, 258.0761 $[M + H]^+$; found 258.0753.

2-ethyl-2-methylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3b)



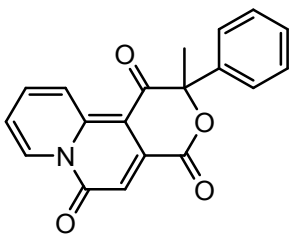
Yellow solid (58.2 mg, 86%), mp: 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (d, J = 9.1 Hz, 1 H), 9.50 (d, J = 7.1 Hz, 1 H), 8.08 – 8.02 (m, 1 H), 7.54 (t, J = 6.9 Hz, 1 H), 7.29 (s, 1 H), 2.21 (dq, J = 14.6, 7.3 Hz, 1 H), 1.92 (dq, J = 14.5, 7.4 Hz, 1 H), 1.68 (s, 3 H), 0.94 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 161.3, 157.8, 144.5, 138.1, 136. 5, 129.5, 125.8, 119.5, 106.9, 102.6, 90.1, 33.8, 25.9, 8.2. IR (KBr): 3119, 2927, 2362, 1720, 1648, 1573, 1482, 1376, 1270, 1155, 1033, 760 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{14}NO_4$, 272.0917 $[M + H]^+$; found 272.0912.

2,2-diethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3c)



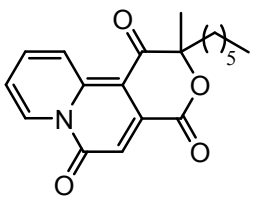
Yellow solid (57.1 mg, 80%), mp: 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.93 (d, J = 9.1 Hz, 1 H), 9.51 (d, J = 7.1 Hz, 1 H), 8.10 – 8.02 (m, 1 H), 7.56 (t, J = 7.0 Hz, 1 H), 7.31 (s, 1 H), 2.20 (dq, J = 14.5, 7.3 Hz, 2 H), 1.91 (dq, J = 14.5, 7.3 Hz, 2 H), 0.90 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 161.6, 157.8, 144.2, 138.2, 136.6, 129.5, 125.9, 119.5, 106.9, 104.0, 93.7, 32.9, 8.0. IR (KBr): 3123, 2974, 2358, 1721, 1639, 1574, 1484, 1379, 1268, 1154, 766 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{16}NO_4$, 286.1074 $[M + H]^+$; found 286.1072.

2-methyl-2-phenylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3d)



Yellow solid (70.9 mg, 89%), mp: 185-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.72 (d, J = 9.1 Hz, 1 H), 9.39 (d, J = 7.1 Hz, 1 H), 8.01 – 7.96 (m, 1 H), 7.50 – 7.41 (m, 3 H), 7.34 – 7.29 (m, 2 H), 7.27 – 7.23 (m, 1 H), 7.20 (s, 1 H), 2.01 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.7, 161.8, 157.8, 144.4, 141.0, 137.9, 136.0, 129.4, 128.9, 128.4, 125.4, 124.1, 119.3, 107.0, 102.4, 89.6, 26.9. IR (KBr): 3121, 2926, 2361, 1731, 1648, 1575, 1485, 1375, 1263, 1152, 764, 702 cm^{-1}. HRMS EI (m/z): calcd for $C_{19}H_{14}NO_4$, 320.0917 $[M + H]^+$; found 320.0912.

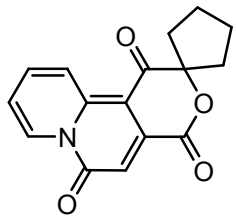
2-hexyl-2-methylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3e)



Yellow solid (73.5 mg, 90%), mp: 94-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (d, J = 9.1 Hz, 1 H), 9.50 (d, J = 7.1 Hz, 1 H), 8.09 – 8.02 (m, 1 H), 7.55 (t, J = 7.0 Hz, 1 H), 7.28 (s, 1 H), 2.20 – 2.11 (m, 1 H), 1.91 – 1.81 (m, 1 H), 1.68 (s, 3 H), 1.44 – 1.33 (m, 1 H), 1.30 – 1.19 (m, 7 H), 0.83 (t, J = 6.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 161.2, 157.8, 144.5, 138.1, 136.4, 129.5, 125.8, 119.5, 106.8, 102.5, 89.9, 40.8, 31.4, 29.1, 26.4, 23.7, 22.4, 13.9. IR (KBr): 2926, 2858, 2358, 1717, 1641, 1574, 1481, 1378, 1268, 1110, 759, 619 cm^{-1}. HRMS EI (m/z): calcd for $C_{19}H_{22}NO_4$, 328.1543 $[M + H]^+$; found

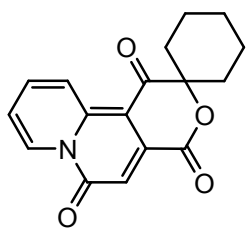
328.1542.

1*H*-spiro[cyclopentane-1,2'-pyrano[4,3-*a*]quinolizine]-1',4',6'-trione (3f)



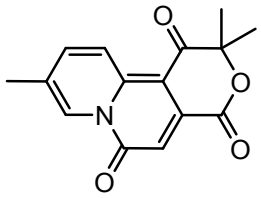
Yellow solid (52.3 mg, 74%), mp: 194-195 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (d, J = 9.1 Hz, 1 H), 9.49 (d, J = 7.1 Hz, 1 H), 8.06 – 7.99 (m, 1 H), 7.53 (t, J = 7.0 Hz, 1 H), 7.28 (s, 1 H), 2.43 – 2.33 (m, 2 H), 2.13 – 2.00 (m, 4 H), 1.94 – 1.84 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 161.1, 157.9, 144.4, 137.9, 136.4, 129.4, 125.7, 119.4, 106.9, 103.1, 96.8, 40.1, 25.1. IR (KBr): 2924, 2858, 2360, 1716, 1641, 1480, 1110, 757, 619 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{14}NO_4$, 284.0917 [M + H]$^+$; found 284.0912.

1*H*-spiro[cyclohexane-1,2'-pyrano[4,3-*a*]quinolizine]-1',4',6'-trione (3g)



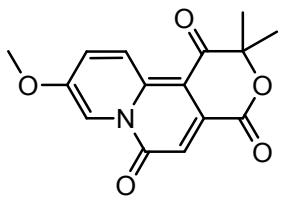
Yellow solid (61.6 mg, 83%), mp: 242-243 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (d, J = 9.1 Hz, 1 H), 9.48 (d, J = 7.1 Hz, 1 H), 8.07 – 7.98 (m, 1 H), 7.52 (t, J = 6.9 Hz, 1 H), 7.26 (s, 1 H), 2.09 – 2.01 (m, 2 H), 1.96 – 1.91 (m, 2 H), 1.89 – 1.81 (m, 2 H), 1.74 – 1.67 (m, 2 H), 1.50 – 1.15 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 161.1, 157.9, 144.6, 137.8, 136.1, 129.4, 125.7, 119.3, 106.8, 101.9, 88.2, 34.8, 24.6, 20.6. IR (KBr): 2930, 2858, 2360, 1716, 1642, 1482, 1111, 757, 619 cm^{-1}. HRMS EI (m/z): calcd for $C_{17}H_{15}NNaO_4$, 320.0893 [M + Na]$^+$; found 320.0899.

2,2,9-trimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione ($3h_1$)



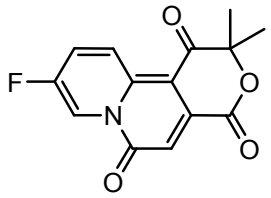
Yellow solid (46.8 mg, 69%), mp: 272-273 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.72 (d, J = 9.2 Hz, 1 H), 9.31 (s, 1 H), 7.90 (d, J = 9.2 Hz, 1 H), 7.22 (s, 1 H), 2.57 (s, 3 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 161.3, 157.7, 142.8, 140.6, 135.8, 130.4, 127.5, 125.2, 106.3, 101.5, 87.0, 27.2, 18.7. IR (KBr): 2922, 2852, 2357, 1717, 1637, 1487, 1383, 1108, 851, 759, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{14}NO_4$, 272.0917 [M + H]$^+$; found 272.0915.

9-methoxy-2,2-dimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione ($3h_2$)



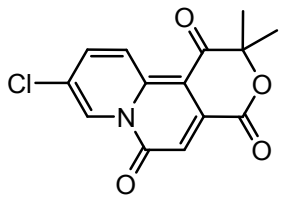
Yellow solid (42.4 mg, 59%), mp: 263-264 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (d, J = 9.9 Hz, 1 H), 9.03 (d, J = 1.7 Hz, 1 H), 7.76 (dd, J = 9.9, 2.3 Hz, 1 H), 7.23 (s, 1 H), 4.05 (s, 3 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 161.2, 157.5, 153.7, 140.2, 134.9, 131.6, 126.5, 110.4, 105.8, 102.2, 87.0, 56.5, 27.2. IR (KBr): 2992, 2923, 2850, 2393, 1717, 1640, 1466, 1381, 1245, 1137, 1021, 851, 759, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{14}NO_5$, 288.0866 [M + H]$^+$; found 288.0870.

9-fluoro-2,2-dimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3h$_3$)



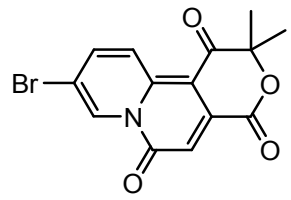
Yellow solid (57.0 mg, 83%), mp: 187-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (dd, J = 10.0, 5.6 Hz, 1 H), 9.40 (dd, J = 4.4, 2.6 Hz, 1 H), 7.97 – 7.90 (m, 1 H), 7.29 (s, 1 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 160.7, 157.1, 156.4, 142.1, 135.9, 129.2, 128.0, 116.3, 106.9, 102.2, 87.1, 27.2. IR (KBr): 3078, 2927, 2357, 1727, 1650, 1469, 1388, 1283, 1109, 750, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{14}H_{11}FNO_4$, 276.0667 $[M + H]^+$; found 276.0660.

9-chloro-2,2-dimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3h$_4$)



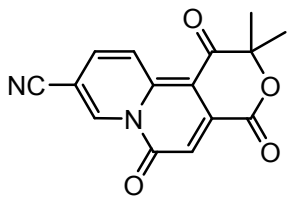
Yellow solid (50.9 mg, 70%), mp: 258-259 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (d, J = 9.7 Hz, 1 H), 9.48 (s, 1 H), 7.94 (d, J = 9.7 Hz, 1 H), 7.31 (s, 1 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 160.7, 156.8, 142.7, 138.6, 136.2, 128.4, 127.4, 126.6, 107.9, 102.0, 87.1, 27.2. IR (KBr): 3125, 3072, 2923, 2853, 2356, 1727, 1647, 1467, 1388, 1275, 1148, 841, 752, 678, 590 cm^{-1}. HRMS EI (m/z): calcd for $C_{14}H_{11}ClNO_4$, 292.0371 $[M + H]^+$; found 292.0375.

9-bromo-2,2-dimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3h$_5$)



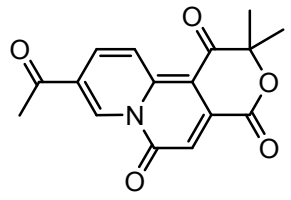
Yellow solid (33.5 mg, 40%), mp: 282-283 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.70 (d, J = 9.6 Hz, 1 H), 9.59 (s, 1 H), 8.04 (d, J = 9.6 Hz, 1 H), 7.32 (s, 1 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 160.7, 156.8, 142.8, 140.8, 136.2, 129.7, 126.5, 115.3, 108.1, 102.0, 87.2, 27.2. IR (KBr): 3123, 2922, 2851, 2357, 1726, 1646, 1466, 1384, 1274, 1111, 747, 620, 546 cm^{-1}. HRMS EI (m/z): calcd for $C_{14}H_{11}BrNO_4$, 335.9866 $[M + H]^+$; found 335.9858.

2,2-dimethyl-1,4,6-trioxo-1,2,4,6-tetrahydropyrano[4,3-*a*]quinolizine-9-carbonitrile (3h$_6$)



Yellow solid (52.9 mg, 75%), mp: 286-287 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 (d, J = 9.5 Hz, 1 H), 9.73 (s, 1 H), 7.95 (d, J = 9.5 Hz, 1 H), 7.42 (s, 1 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 160.1, 156.7, 144.4, 137.2, 135.7, 134.9, 126.6, 114.3, 110.3, 105.3, 102.3, 87.3, 27.0. IR (KBr): 3128, 3067, 2920, 2850, 2353, 1713, 1648, 1475, 1386, 1274, 1111, 748, 620, 554 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{11}N_2O_4$, 283.0713 $[M + H]^+$; found 283.0712.

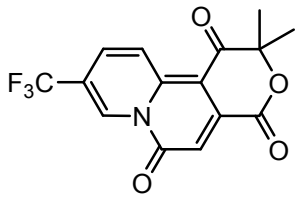
9-acetyl-2,2-dimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3h$_7$)



Yellow solid (69.5 mg, 93%), mp: 252-253 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1 H), 9.77 (d, J = 9.5 Hz, 1 H), 8.44 (dd, J = 9.3, 1.2 Hz, 1 H), 7.35 (s, 1 H), 2.77 (s, 3 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.2, 191.4, 160.6, 157.9, 145.3, 137.1, 134.8, 131.7,

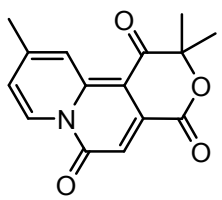
128.1, 125.6, 108.8, 102.1, 87.2, 27.1, 26.3. IR (KBr): 2926, 2850, 2362, 1648, 1385, 1110, 753, 620, 546 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{14}NO_5$, 300.0866 $[M + H]^+$; found 300.0872.

2,2-dimethyl-9-(trifluoromethyl)pyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione ($3h_8$)



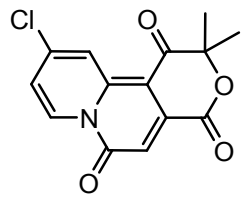
Yellow solid (76.3 mg, 94%), mp: 219-220 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.88 (d, J = 9.5 Hz, 1 H), 9.73 (s, 1 H), 8.07 (dd, J = 9.5, 1.3 Hz, 1 H), 7.38 (s, 1 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 160.4, 157.4, 145.1, 137.0, 132.6, 127.9, 126.7, 122.7, 122.1, 109.3, 102.0, 87.2, 27.0. IR (KBr): 3097, 2923, 2354, 1730, 1653, 1490, 1387, 1273, 1113, 753, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{11}F_3NO_4$, 326.0635 $[M + H]^+$; found 326.0637.

2,2,10-trimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione ($3i_1$)



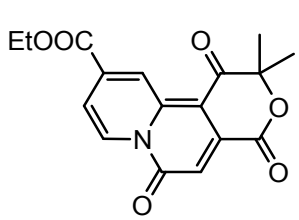
Yellow solid (58.3 mg, 86%), mp: 156-157 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.64 (s, 1 H), 9.37 (d, J = 7.2 Hz, 1 H), 7.36 (d, J = 7.3 Hz, 1 H), 7.18 (s, 1 H), 2.65 (s, 3 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 161.2, 157.9, 151.3, 144.3, 136.5, 128.9, 124.4, 121.7, 105.7, 100.7, 86.9, 27.3, 22.2. IR (KBr): 2925, 2853, 2357, 1726, 1640, 1572, 1485, 1383, 1282, 1108, 762, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{14}NO_4$, 272.0917 $[M + H]^+$; found 272.0914.

10-chloro-2,2-dimethylpyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione ($3i_2$)



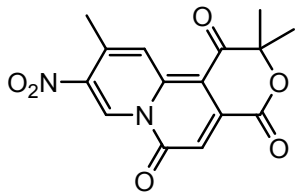
Brown solid (64.0 mg, 88%), mp: 179-180 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.86 (d, J = 2.0 Hz, 1 H), 9.37 (d, J = 7.6 Hz, 1 H), 7.46 (dd, J = 7.6, 1.9 Hz, 1 H), 7.24 (s, 1 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 160.6, 157.4, 146.6, 144.4, 136.8, 130.4, 124.3, 120.6, 107.5, 100.7, 87.1, 27.2. IR (KBr): 3116, 2927, 2855, 2360, 1712, 1649, 1480, 1279, 1112, 758, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{14}H_{11}ClNO_4$, 292.0371 $[M + H]^+$; found 292.0365.

Ethyl 2,2-dimethyl-1,4,6-trioxo-1,2,4,6-tetrahydropyrano[4,3-*a*]quinolizine-10-carboxylate ($3i_3$)



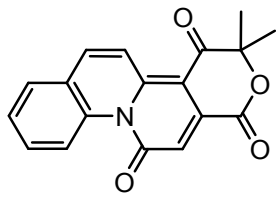
Orange solid (77.3 mg, 94%), mp: 176-177 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.31 (s, 1 H), 9.47 (d, J = 7.4 Hz, 1 H), 7.94 (dd, J = 7.4, 1.5 Hz, 1 H), 7.39 (s, 1 H), 4.53 (q, J = 7.1 Hz, 2 H), 1.73 (s, 6 H), 1.49 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 163.2, 160.7, 157.6, 138.3, 136.4, 129.7, 127.3, 117.7, 109.6, 103.0, 100.0, 87.2, 62.9, 27.1, 14.2. IR (KBr): 2925, 2850, 2360, 1722, 1645, 1478, 1112, 754, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{17}H_{16}NO_6$, 330.0972 $[M + H]^+$; found 330.0969.

2,2,10-trimethyl-9-nitropyrano[4,3-*a*]quinolizine-1,4,6(2*H*)-trione (3j)



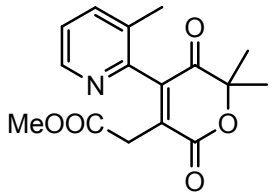
Red solid (17.4 mg, 22%), mp: 218-219 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.14 (s, 1 H), 9.73 (s, 1 H), 7.33 (s, 1 H), 2.88 (s, 3 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 160.3, 157.0, 144.3, 143.8, 142.4, 137.6, 128.8, 127.7, 108.4, 101.3, 87.2, 27.1, 21.2. IR (KBr): 2923, 2853, 2360, 1721, 1649, 1480, 1275, 1109, 755, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{13}N_2O_6$, 317.0768 $[M + H]^+$; found 317.0772.

3,3-dimethylpyrano[4',3':3,4]pyrido[1,2-*a*]quinoline-1,4,12(3*H*)-trione (3k)



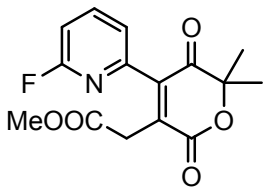
Yellow solid (61.3 mg, 80%), mp: 194-195 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.54 (d, J = 8.9 Hz, 1 H), 9.40 (d, J = 9.6 Hz, 1 H), 7.99 (d, J = 9.6 Hz, 1 H), 7.81 (d, J = 7.6 Hz, 1 H), 7.73 (t, J = 7.9 Hz, 1 H), 7.66 (t, J = 7.4 Hz, 1 H), 7.38 (s, 1 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 163.3, 161.0, 146.5, 137.8, 135.0, 134.6, 130.2, 128.2, 128.1, 126.4, 122.2, 120.7, 115.3, 102.8, 87.1, 27.0. IR (KBr): 2925, 2855, 2361, 1730, 1650, 1519, 1466, 1382, 1273, 1144, 1006, 762 cm^{-1}. HRMS EI (m/z): calcd for $C_{18}H_{14}NO_4$, 308.0917 $[M + H]^+$; found 308.0908.

methyl 2-(6,6-dimethyl-4-(6-methylpyridin-2-yl)-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate (4l$_1$)



Yellow oil (60.5 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (t, J = 7.7 Hz, 1 H), 7.19 (m, 2 H), 3.68 (s, 3 H), 3.67 (s, 2 H), 2.56 (s, 3 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 169.6, 162.2, 158.7, 149.3, 142.6, 138.4, 136.5, 123.7, 122.7, 86.6, 52.3, 34.9, 26.4, 24.3. IR (KBr): 2990, 2947, 2851, 2360, 1726, 1454, 1242, 1151, 791 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{18}NO_5$, 304.1179 $[M + H]^+$; found 304.1185.

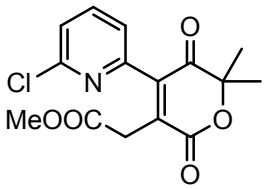
methyl 2-(4-(6-fluoropyridin-2-yl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate (4l$_2$)



Yellow oil (53.8 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (q, J = 7.9 Hz, 1 H), 7.30 (d, J = 7.4 Hz, 1 H), 7.02 (dd, J = 8.2, 1.5 Hz, 1 H), 3.70 (s, 3 H), 3.69 (s, 2 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 169.4, 162.9, 161.8, 148.2, 141.5, 141.1, 139.0, 123.4, 110.6, 86.7, 52.5, 34.7, 26.3. IR (KBr): 2927, 2854, 2365, 1716, 1453, 1109, 748, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{15}FNO_5$, 308.0929 $[M + H]^+$; found 308.0933.

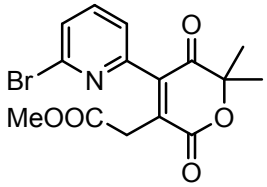
methyl 2-(4-(6-chloropyridin-2-yl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate (4l$_3$)

Brown oil (52.5 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (t, J = 7.8 Hz, 1 H), 7.40 (d, J = 8.0 Hz, 1 H), 7.35 (d, J = 7.6 Hz, 1 H), 3.71 (s, 3 H), 3.70 (s, 2 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 169.4, 161.8, 151.3,



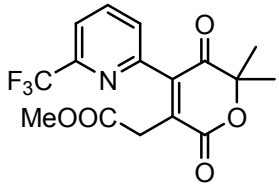
150.2, 141.1, 139.2, 138.9, 125.0, 124.5, 86.8, 52.5, 34.8, 26.4. IR (KBr): 2928, 2850, 2363, 1719, 1386, 1109, 758, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{15}ClNO_5$, 324.0633 $[M + H]^+$; found 324.0638.

methyl 2-(4-(6-bromopyridin-2-yl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4l_4$)



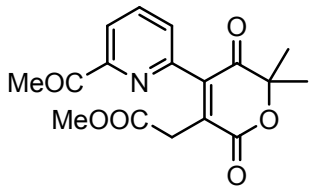
Yellow oil (71.5 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66 (t, J = 7.8 Hz, 1 H), 7.55 (d, J = 8.0 Hz, 1 H), 7.39 (d, J = 7.6 Hz, 1 H), 3.71 (s, 5 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 169.4, 161.8, 150.6, 141.7, 140.9, 139.3, 138.5, 128.8, 124.9, 86.7, 52.5, 34.7, 26.4. IR (KBr): 2945, 2853, 2361, 1720, 1554, 1436, 1296, 1114, 793, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{15}H_{15}BrNO_5$, 368.0128 $[M + H]^+$; found 368.0126.

methyl 2-(6,6-dimethyl-2,5-dioxo-4-(6-(trifluoromethyl)pyridin-2-yl)-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4l_5$)



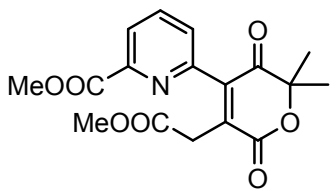
Yellow oil (72.3 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (t, J = 7.9 Hz, 1 H), 7.75 (d, J = 7.9 Hz, 1 H), 7.63 (d, J = 7.9 Hz, 1 H), 3.74 (s, 2 H), 3.68 (s, 3 H), 1.73 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.10, 169.3, 161.8, 150.6, 148.2, 140.8, 139.9, 137.8, 128.8, 121.1, 120.8, 86.7, 52.4, 34.6, 26.4. IR (KBr): 2923, 2853, 2356, 1704, 1643, 1541, 1461, 1337, 1147, 747, 549 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{15}F_3NO_5$, 358.0897 $[M + H]^+$; found 358.0898.

methyl 2-(4-(6-acetylpyridin-2-yl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4l_6$)



Brown oil (62.8 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 7.8 Hz, 1 H), 7.96 (t, J = 7.8 Hz, 1 H), 7.57 (d, J = 7.7 Hz, 1 H), 3.76 (s, 2 H), 3.68 (s, 3 H), 2.65 (s, 3 H), 1.75 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.1, 195.3, 169.3, 162.0, 153.4, 149.3, 141.7, 139.0, 137.3, 129.4, 122.0, 86.7, 77.4, 77.1, 76.7, 52.4, 34.7, 26.4, 25.5. IR (KBr): 2931, 2855, 2362, 1703, 1298, 1109, 805, 747, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{17}H_{18}NO_6$, 332.1129 $[M + H]^+$; found 332.1133.

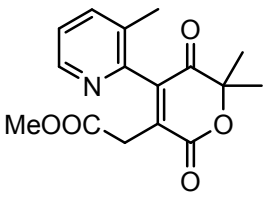
methyl 6-(5-(2-methoxy-2-oxoethyl)-2,2-dimethyl-3,6-dioxo-3,6-dihydro-2*H*-pyran-4-yl)picolinate ($4l_7$)



Brown oil (73.7 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 7.8 Hz, 1 H), 7.96 (t, J = 7.9 Hz, 1 H), 7.55 (d, J = 7.8 Hz, 1 H), 4.00 (s, 3 H), 3.75 (s, 2 H), 3.67 (s, 3 H), 1.72 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.2, 169.3, 165.0, 161.9, 150.4, 148.1, 141.8, 139.7, 137.4, 129.0, 125.4, 86.8, 53.0, 52.4, 34.6, 26.6. IR (KBr): 2923, 2853, 2359, 1726, 1642, 1301, 1139, 761, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{17}H_{18}NO_7$, 348.1078 $[M + H]^+$; found

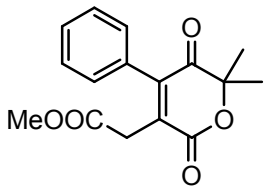
348.1072.

methyl 2-(6,6-dimethyl-4-(3-methylpyridin-2-yl)-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate (4m)



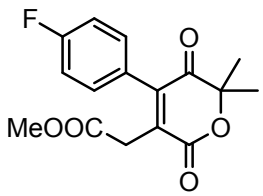
Brown oil (34.0 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, J = 4.5 Hz, 1 H), 7.60 (d, J = 7.7 Hz, 1 H), 7.32 – 7.27 (m, 1 H), 3.64 (s, 3 H), 2.16 (s, 3 H), 1.73 (s, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 169.2, 161.8, 150.1, 147.3, 144.6, 139.3, 138.4, 133.1, 124.1, 87.1, 52.4, 34.6, 26.9, 18.2. IR (KBr): 2925, 2853, 2360, 1726, 1646, 1293, 1110, 754, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{18}NO_5$, 304.1179 [M + H]$^+$; found 304.1180.

methyl 2-(6,6-dimethyl-2,5-dioxo-4-phenyl-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4n_1$)



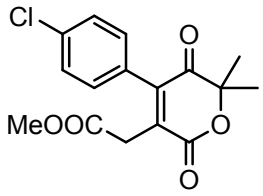
White solid (39.7 mg, 55%), mp: 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 – 7.42 (m, 3 H), 7.20 – 7.16 (m, 2 H), 3.71 (s, 3 H), 3.50 (s, 2 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 169.9, 162.1, 145.2, 136.8, 130.7, 129.6, 128.8, 128.6, 86.5, 52.5, 35.4, 26.5, 26.3. IR (KBr): 2949, 2852, 2354, 1718, 1441, 1294, 1203, 1138, 966, 759, 701 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{16}NaO_5$, 311.0890 [M + Na]$^+$; found 311.0893.

methyl 2-(4-(4-fluorophenyl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4n_2$)



Light yellow oil (48.2 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 –7.12 (m, 4 H), 3.73 (s, 3 H), 3.50 (s, 2 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 169.8, 162.2, 161.9, 144.4, 137.2, 131.0, 126.6, 115.9, 86.6, 52.6, 35.4, 26.4. IR (KBr): 2924, 2853, 2359, 1712, 1641, 1385, 1109, 753, 620, 549 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{15}FNaO_5$, 329.0796 [M + Na]$^+$; found 329.0799.

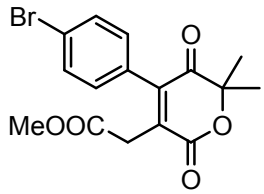
methyl 2-(4-(4-chlorophenyl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4n_3$)



White solid (57.9 mg, 72%), mp: 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 8.1 Hz, 2 H), 3.72 (s, 3 H), 3.49 (s, 2 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 169.7, 161.8, 144.2, 137.3, 136.0, 130.3, 129.0, 129.0, 86.6, 52.6, 35.4, 26.4. IR(KBr): 2942, 2853, 2357, 1717, 1296, 1133, 816, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{15}ClNaO_5$, 345.0500 [M + Na]$^+$; found 345.0506.

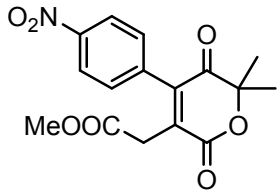
methyl 2-(4-(4-bromophenyl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4n_4$)

White solid (64.1 mg, 70%), mp: 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.1 Hz, 2 H), 7.08 (d, J = 8.1



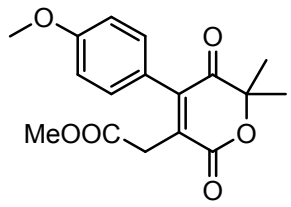
Hz, 2 H), 3.72 (s, 3 H), 3.48 (s, 2 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.3, 169.7, 161.7, 144.3, 137.2, 131.9, 130.5, 129.5, 124.3, 86.6, 52.6, 35.4, 26.4. IR (KBr): 2948, 2865, 2365, 1720, 1297, 1243, 1138, 1058, 1012, 811 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{15}BrO_5$, 367.0176 $[M + H]^+$; found 367.0175.

methyl 2-(6,6-dimethyl-4-(4-nitrophenyl)-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4n_5$)



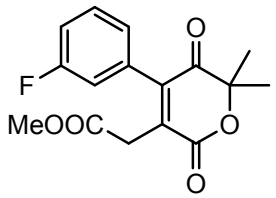
Yellow solid (67.4 mg, 81%), mp: 118-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, J = 8.5 Hz, 2 H), 7.41 (d, J = 8.3 Hz, 2 H), 3.74 (s, 3 H), 3.46 (s, 2 H), 1.72 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8, 169.4, 161.3, 148.5, 143.5, 138.2, 137.1, 130.2, 123.8, 86.9, 52.8, 35.4, 26.4. IR (KBr): 2991, 2924, 2852, 2360, 1760, 1524, 1349, 1243, 1054, 853 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{15}NNaO_7$, 356.0741 $[M + Na]^+$; found 356.0732.

methyl 2-(4-(4-methoxyphenyl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4n_6$)



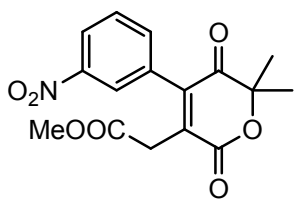
Yellow oil (19.0 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, J = 7.5 Hz, 2 H), 6.96 (d, J = 7.6 Hz, 2 H), 3.85 (s, 3 H), 3.73 (s, 3 H), 3.54 (s, 2 H), 1.69 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 170.1, 162.3, 160.7, 144.9, 136.1, 130.6, 122.7, 114.1, 86.4, 55.3, 52.5, 35.5, 26.4. IR (KBr): 2989, 2946, 2846, 2360, 1717, 1247, 1138, 1028, 829 cm^{-1}. HRMS EI (m/z): calcd for $C_{17}H_{18}NaO_6$, 341.0996 $[M + Na]^+$; found 341.0998.

methyl 2-(4-(3-fluorophenyl)-6,6-dimethyl-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4n_7$)



Light yellow oil (58.8 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 – 7.40 (m, 1 H), 7.20 – 7.12 (m, 1 H), 6.97 (d, J = 7.7 Hz, 1 H), 6.93 (d, J = 9.0 Hz, 1 H), 3.73 (s, 3 H), 3.49 (s, 2 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.2, 169.6, 163.7, 161.7, 144.1, 137.5, 132.6, 130.4, 124.6, 116.7, 116.2, 86.7, 52.6, 35.4, 26.4. IR (KBr): 2990, 2362, 1762, 1378, 1243, 1054, 789, 631 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{15}FNaO_5$, 329.0796 $[M + Na]^+$; found 329.0800.

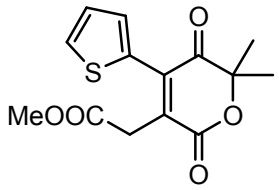
methyl 2-(6,6-dimethyl-4-(3-nitrophenyl)-2,5-dioxo-5,6-dihydro-2*H*-pyran-3-yl)acetate ($4n_8$)



Light yellow solid (65.8 mg, 79%), mp: 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.33 (d, J = 8.2 Hz, 1 H), 8.10 (s, 1 H), 7.68 (t, J = 7.9 Hz, 1 H), 7.57 (d, J = 7.7 Hz, 1 H), 3.74 (s, 3 H), 3.49 (s, 2 H), 1.73 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 194.9, 169.3, 161.3, 148.2, 143.0, 138.3, 135.0, 132.2, 129.8, 124.5, 124.2, 86.9, 52.8, 35.5, 26.4. IR(KBr): 2930, 2856, 2357, 1719, 1531, 1348, 1107, 749, 620 cm^{-1}. HRMS EI (m/z): calcd for $C_{16}H_{15}NNaO_7$, 356.0741 [M + Na]$^+$; found

356.0744.

methyl 2-(6,6-dimethyl-2,5-dioxo-4-(thiophen-2-yl)-5,6-dihydro-2*H*-pyran-3-yl)acetate (4o)



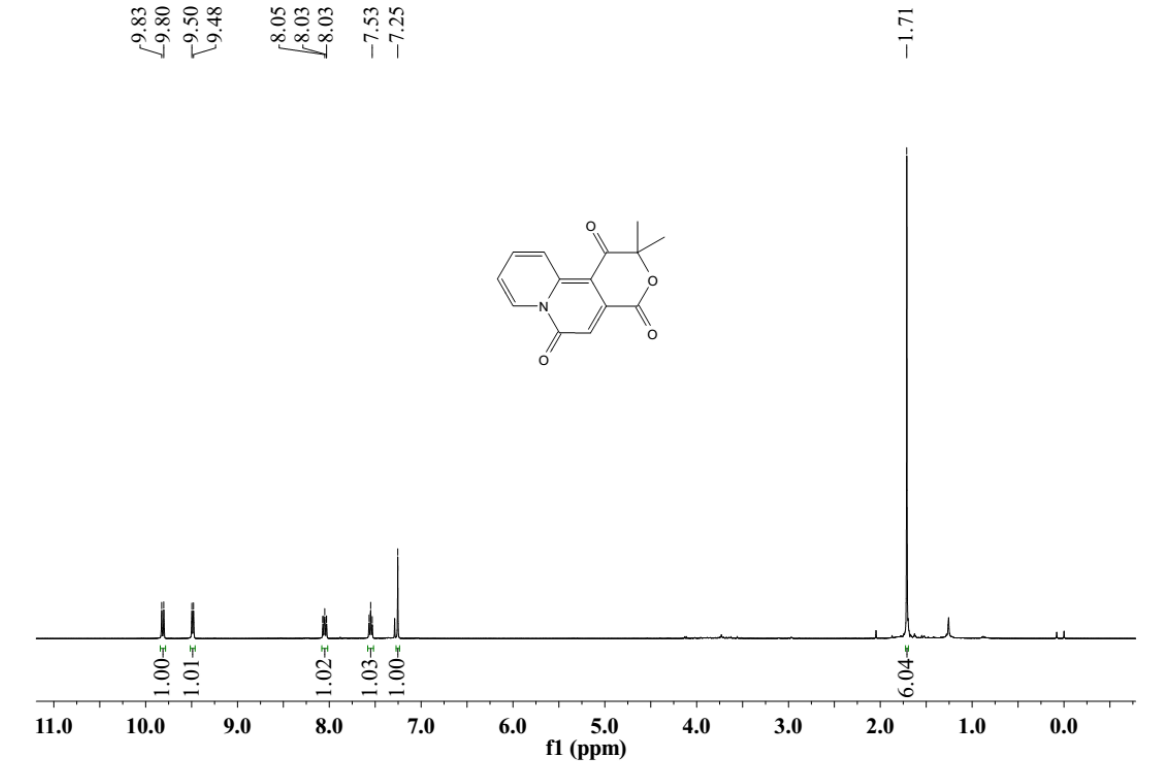
Brown oil (62.5 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 5.0 Hz, 1 H), 7.28 – 7.25 (m, 1 H), 7.17 – 7.14 (m, 1 H), 3.80 (s, 2 H), 3.77 (s, 3 H), 1.70 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.1, 169.9, 162.0, 138.3, 135.2, 131.4, 131.2, 130.1, 127.1, 85.9, 52.6, 36.0, 26.4. IR (KBr): 2989, 2949, 2851, 2357, 1708, 1427, 1243, 1117, 852, 713 cm^{-1}. HRMS EI (m/z): calcd for $C_{14}H_{15}O_5S$, 295.0635 $[M + Na]^+$; found 295.0634.

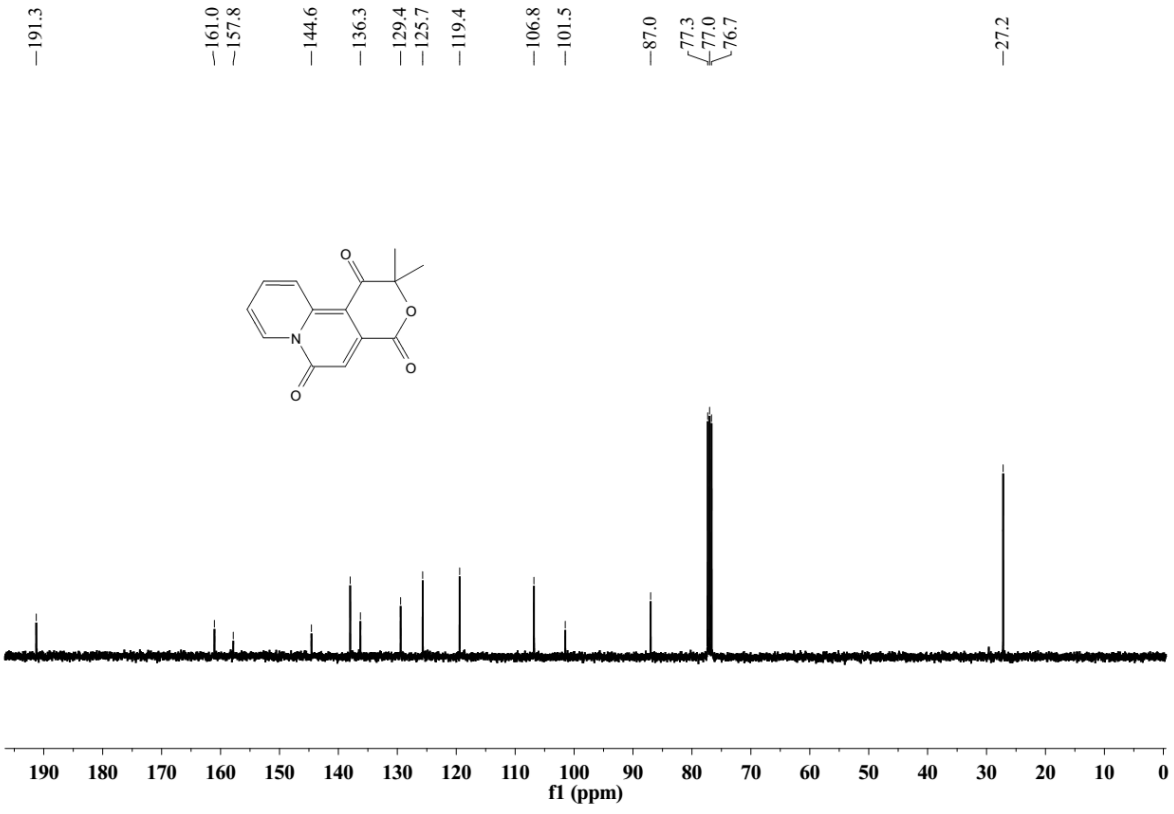
References

[1] H. He, C. Qi, X. Hu, Y. Guan, H. Jiang, *Green Chem.*, 2014, **16**, 3729.

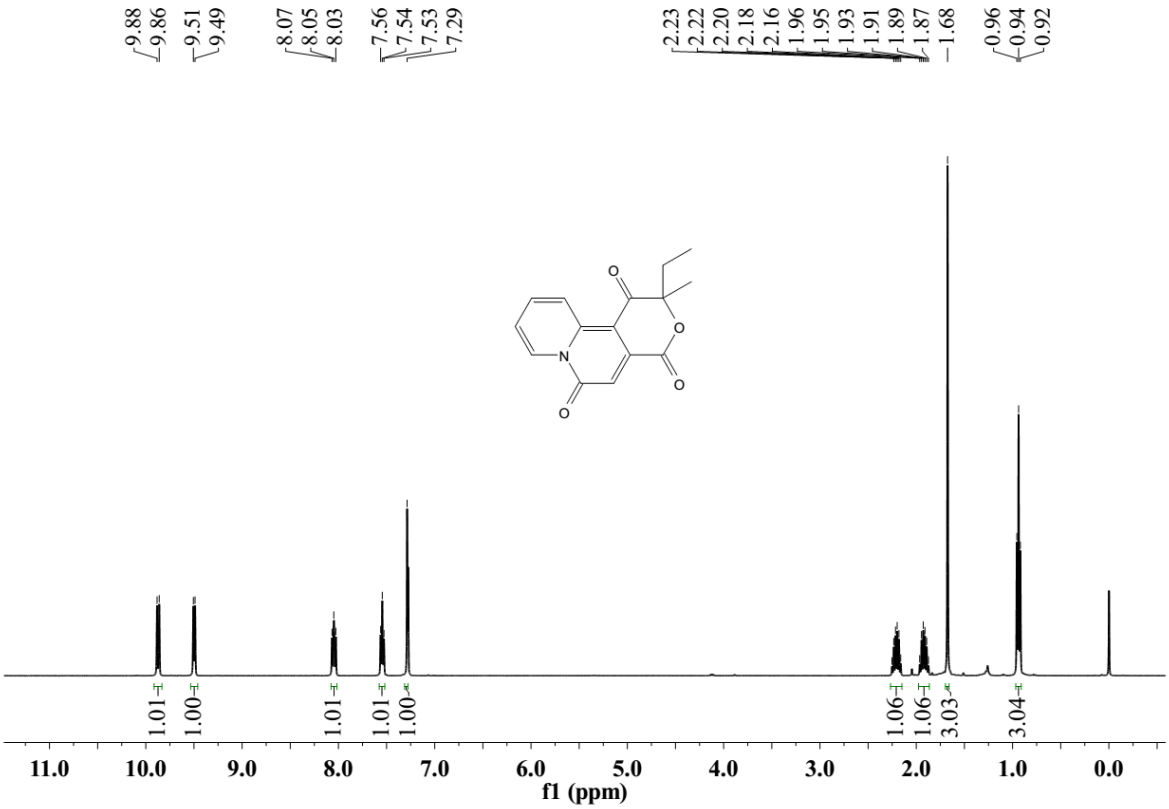
D. NMR Spectra

3a





3b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2.22
2.20
2.18
2.16
1.96
1.95
1.93
1.91
1.89
1.87
1.68
0.96
0.94
0.92
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1.00
1.01
1.01
1.00
1.06
1.06
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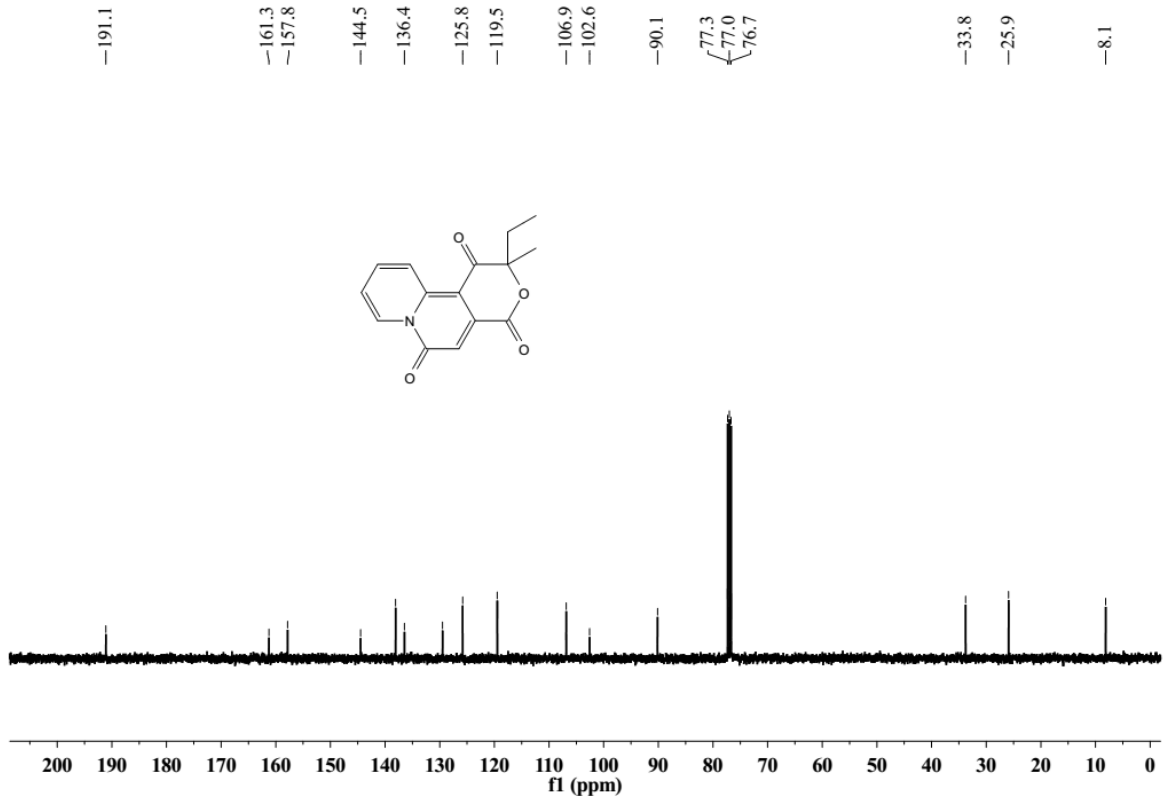
f1 (ppm)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106.9
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77.0
76.7
33.8
25.9
8.1
200
190
180
170
160
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140
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120
110
100
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80
70
60
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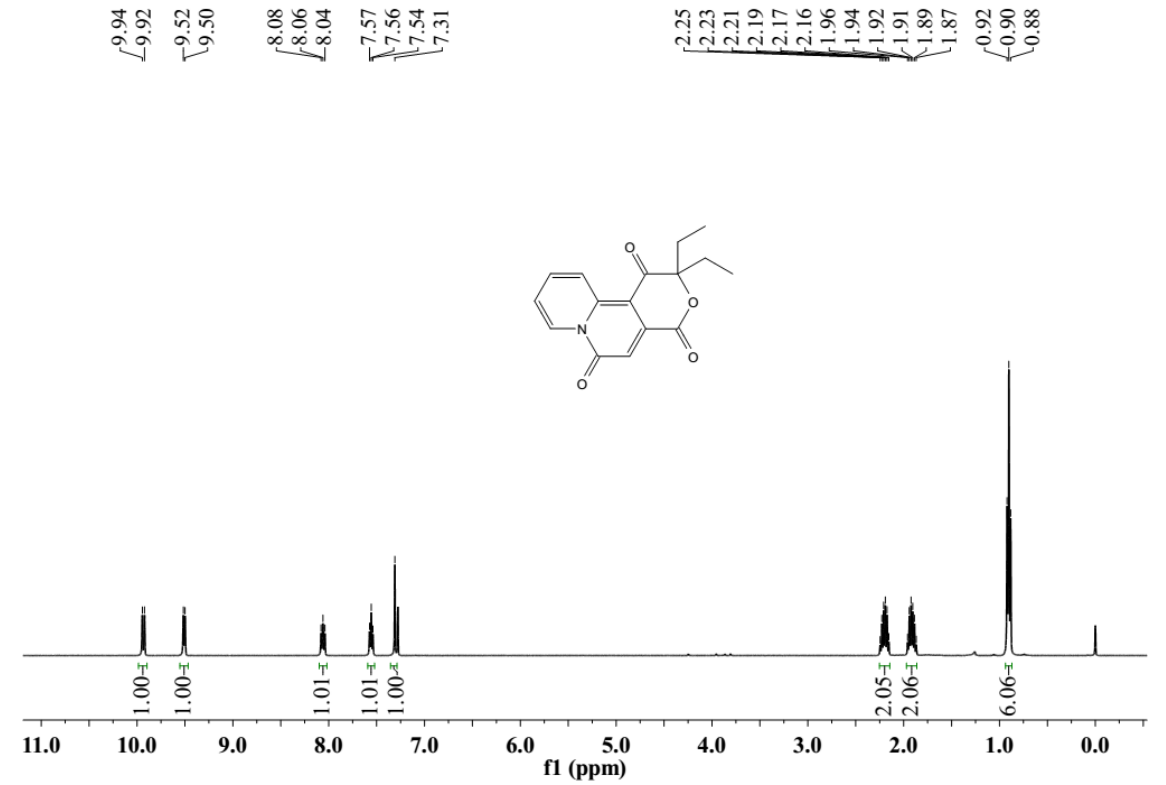
40
30
20
10
0
f1 (ppm)

3c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2.21
2.19
2.17
2.16
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1.94
1.92
1.91
1.89
1.87
0.92
0.90
0.88
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1.00
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1.01
1.00
2.05
2.06
6.06
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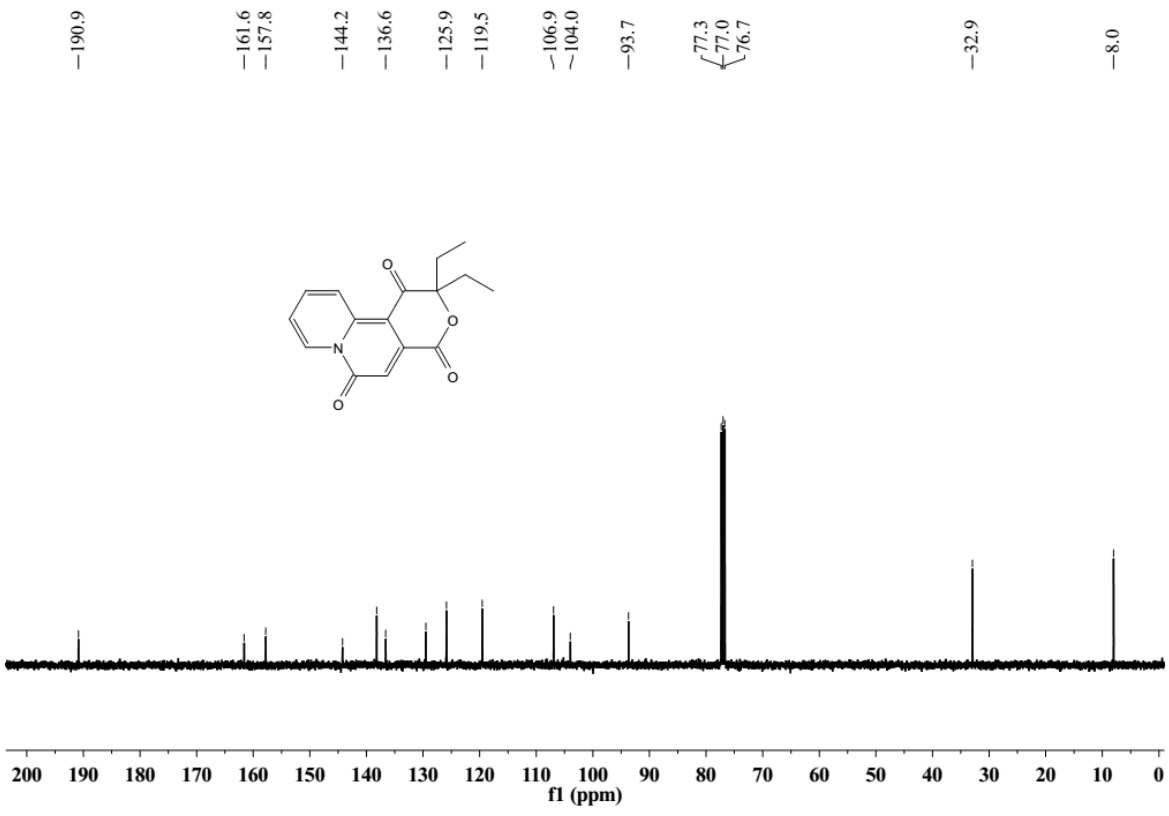
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190
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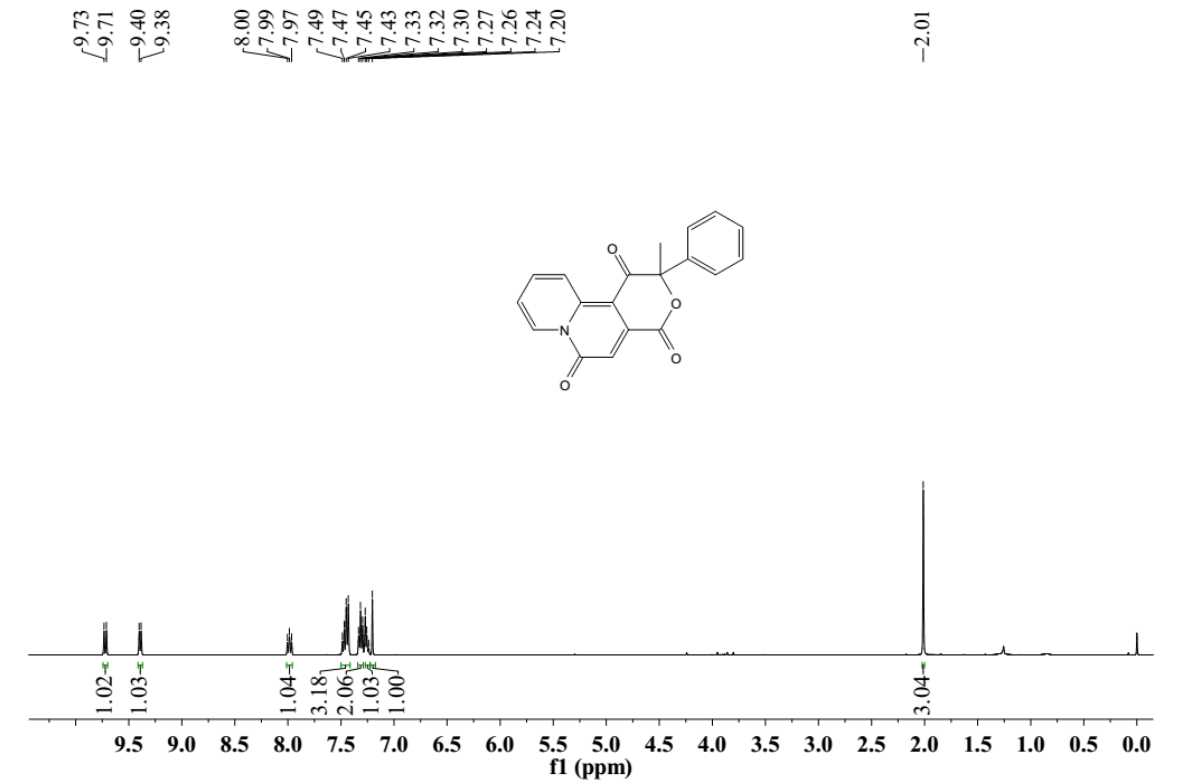
f1 (ppm)

3d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7.20
2.01
1.02
1.03
1.04
3.18
2.06
1.03
1.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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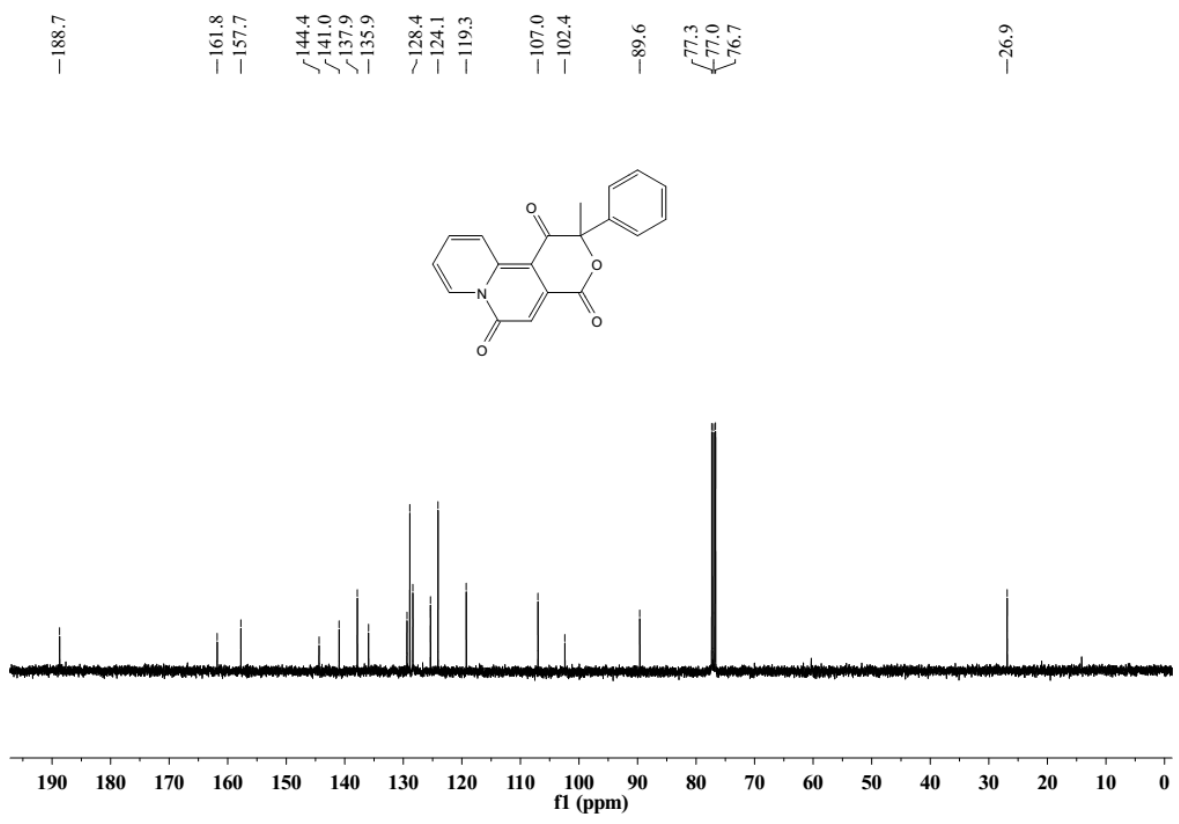
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77.0
76.7
26.9
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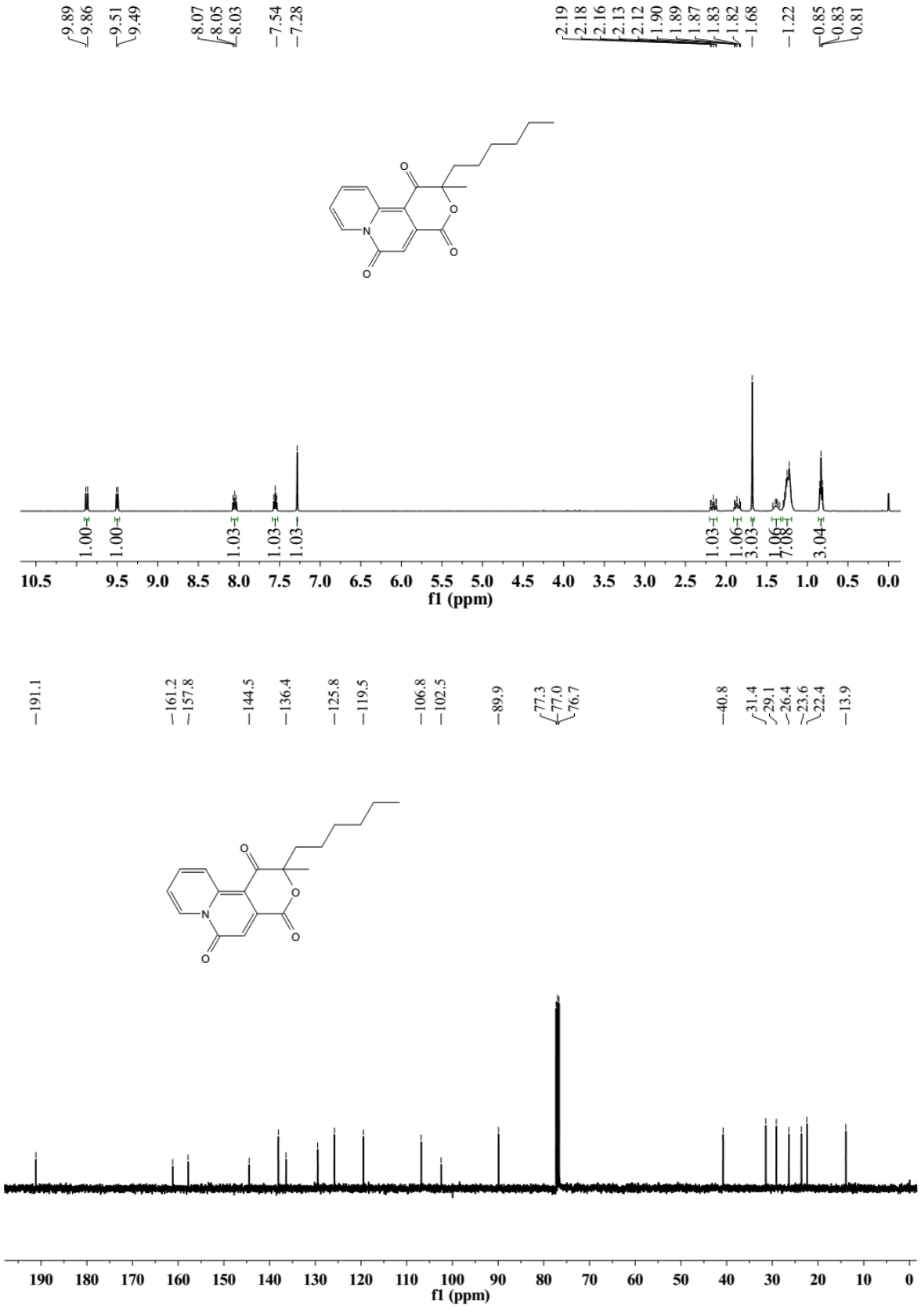
f1 (ppm)

3e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2.12
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1.87
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1.68
1.22
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1.03
1.03
1.06
3.03
1.06
1.08
3.04
f1 (ppm)
191.1
161.2
157.8
144.5
136.4
125.8
119.5
106.8
102.5
89.9
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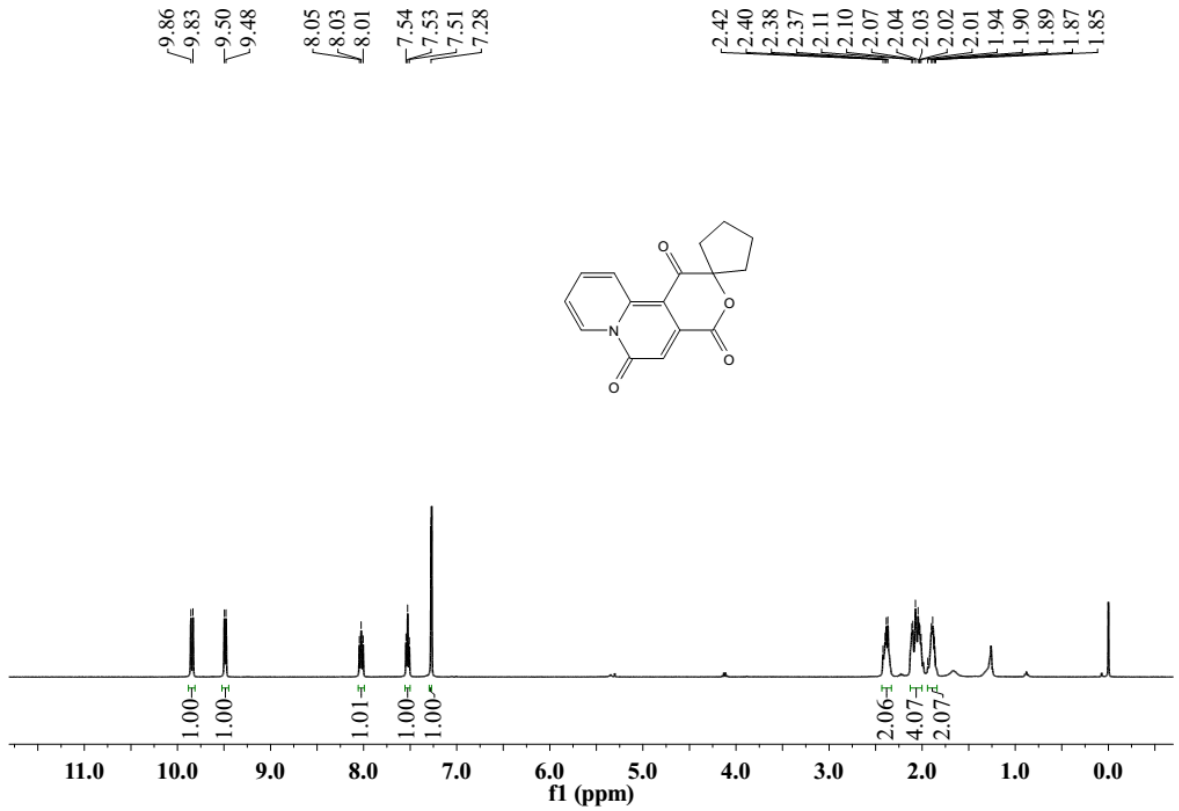
13.9
f1 (ppm)

3f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2.38
2.37
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2.10
2.07
2.04
2.03
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2.01
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2.06
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2.07
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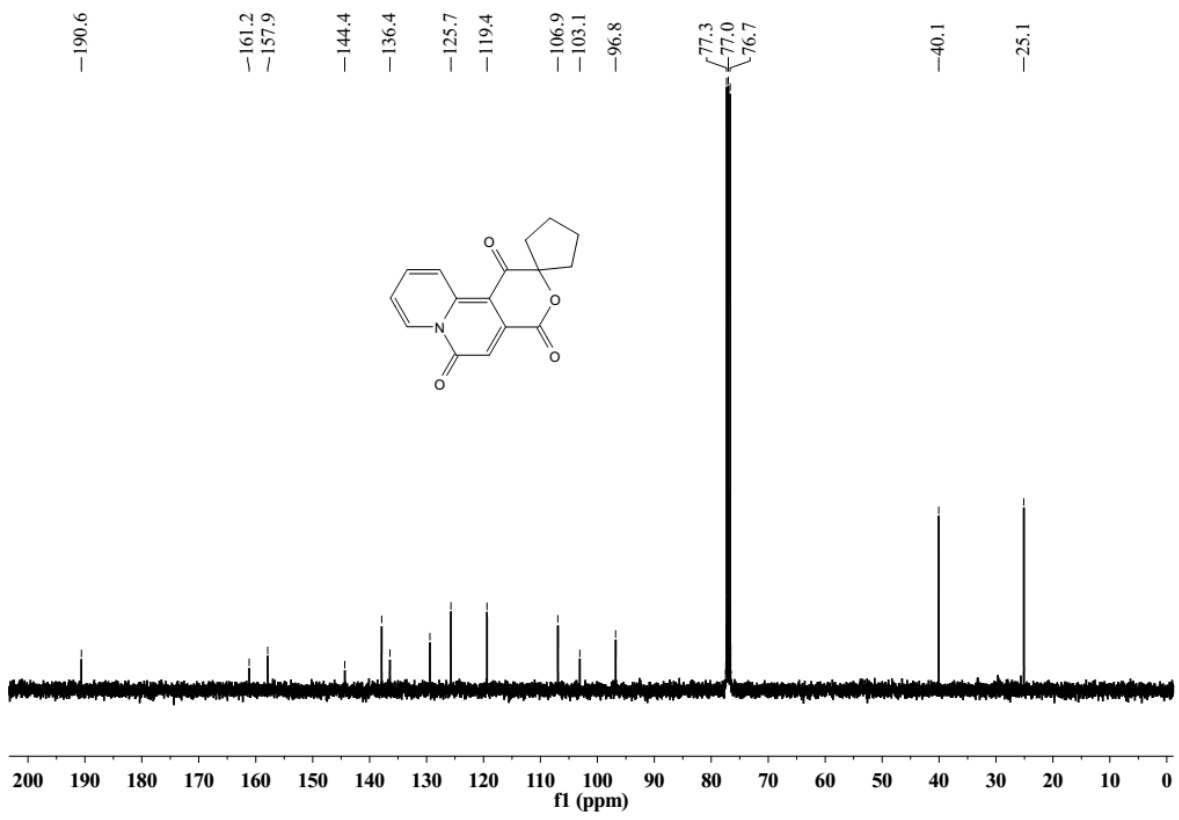
f1 (ppm)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25.1
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30
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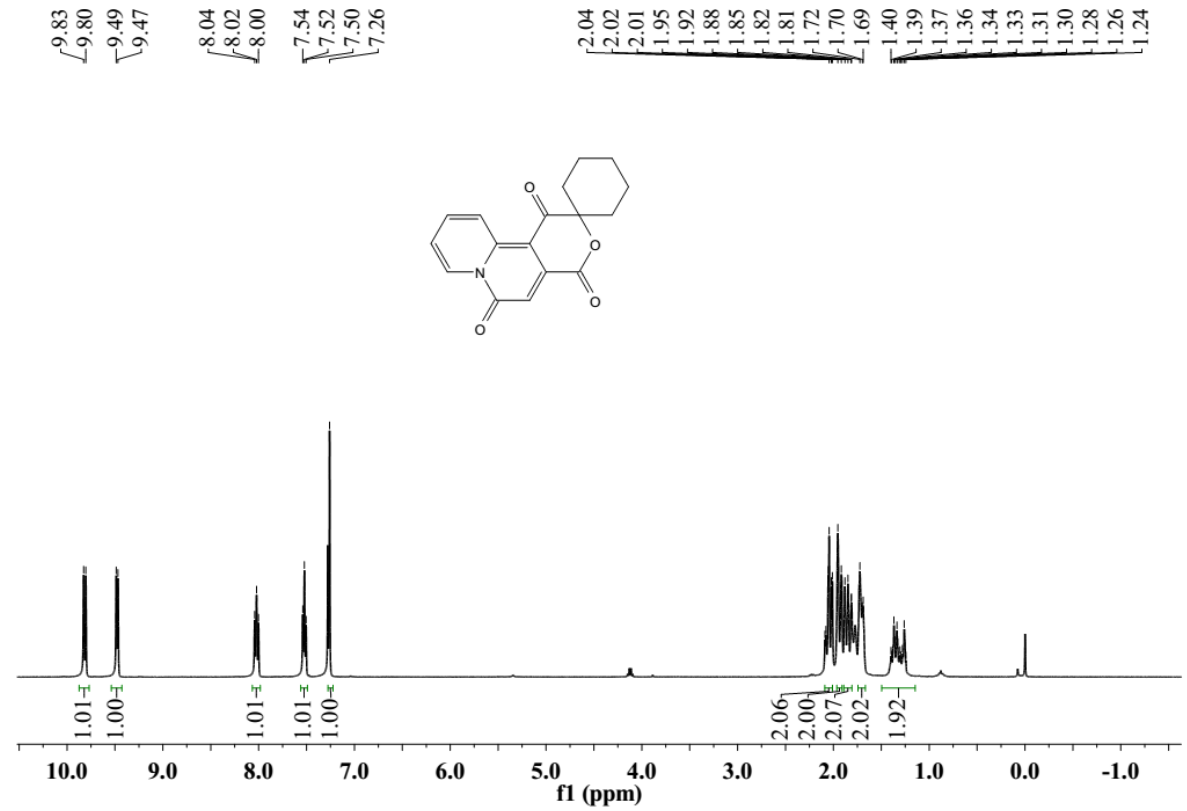
10
0
f1 (ppm)

3g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1.85
1.82
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1.69
1.40
1.39
1.37
1.36
1.34
1.33
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1.30
1.28
1.26
1.24
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1.00
1.01
1.01
1.00
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2.02
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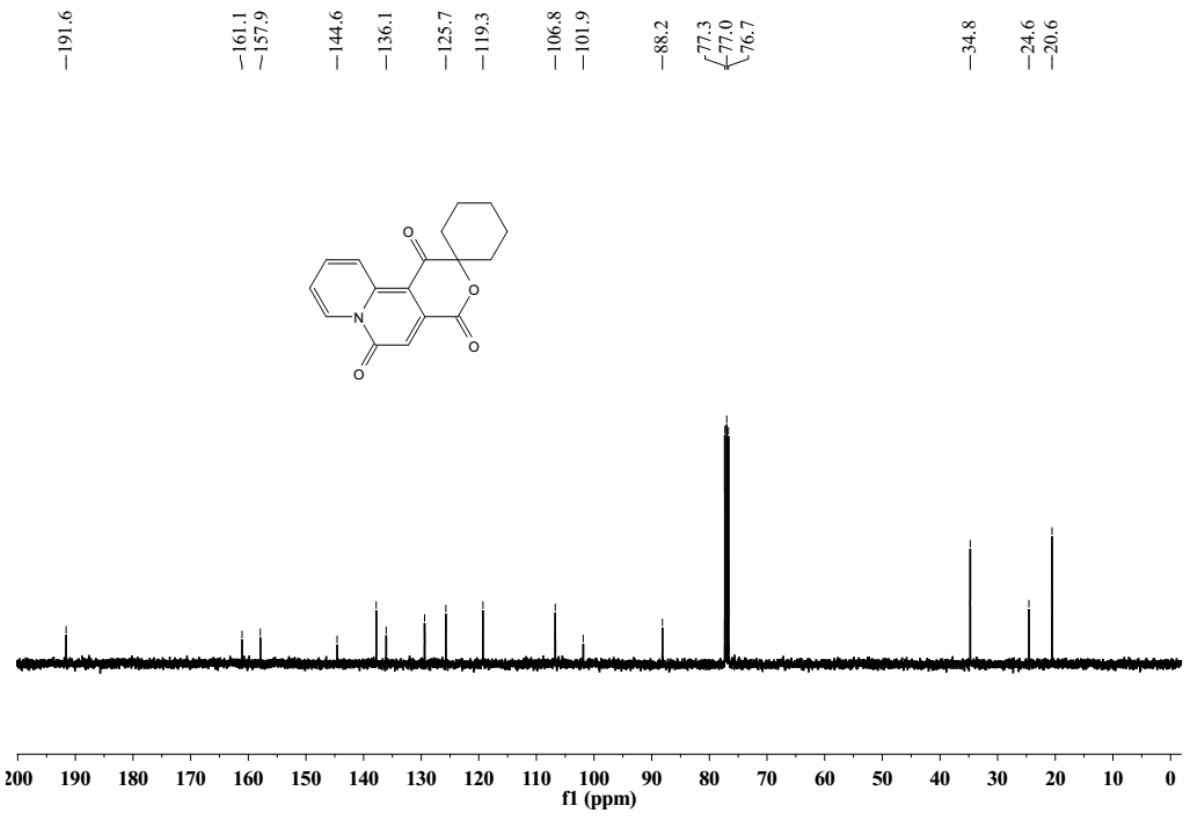
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20.6
200
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180
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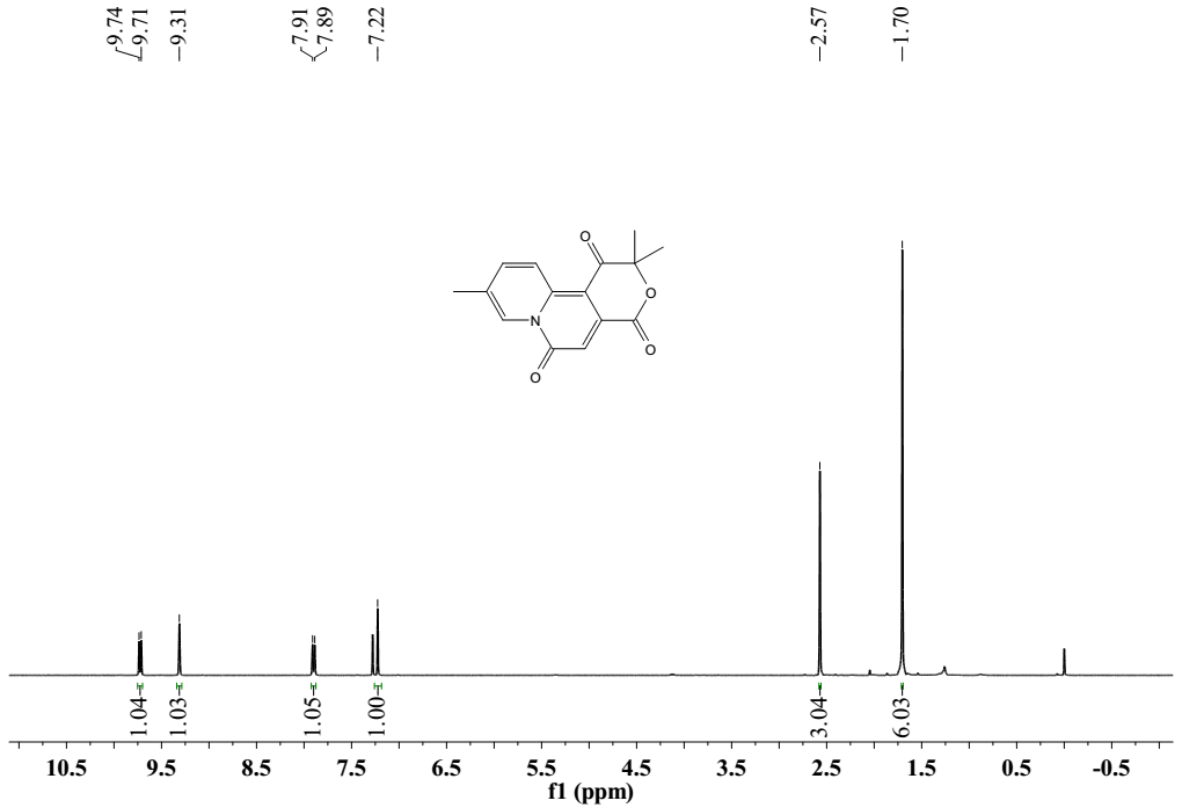
30
20
10
0
f1 (ppm)

$3h_1$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10.5
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1.5
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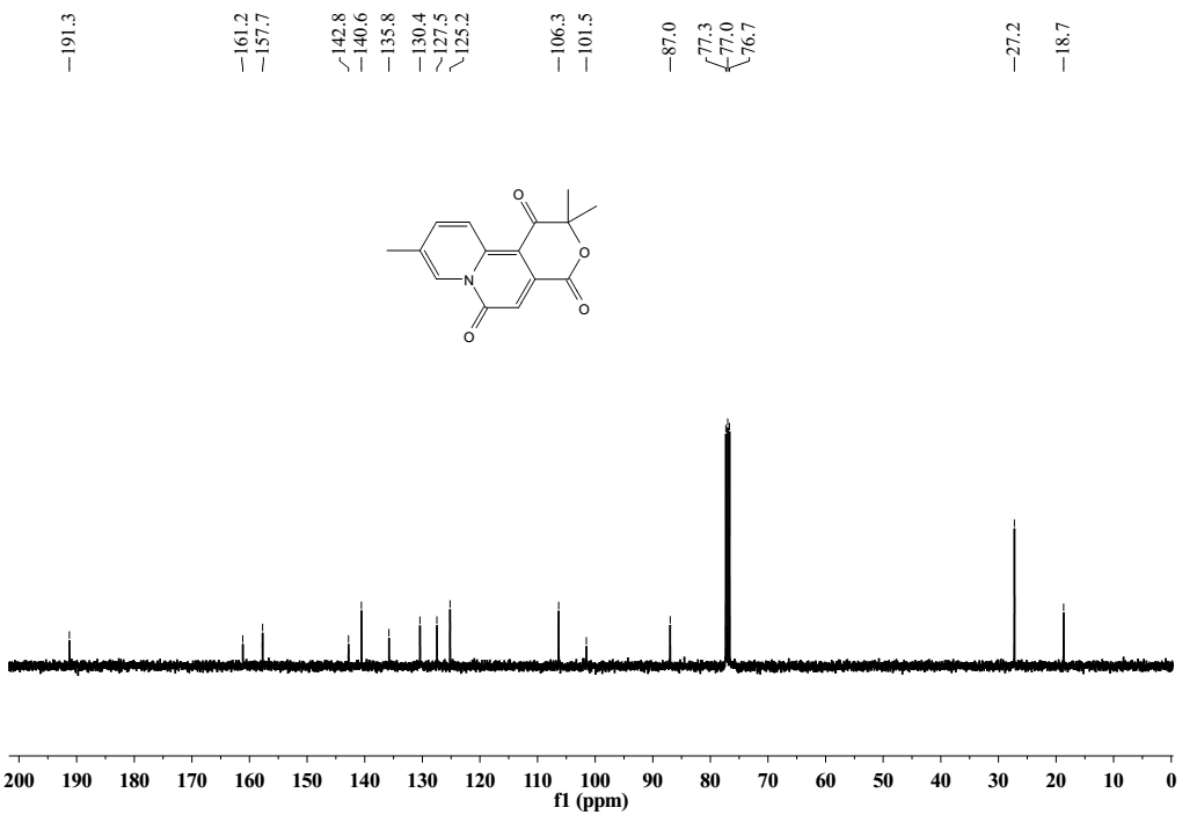
f1 (ppm)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77.0
76.7
27.2
18.7
200
190
180
170
160
150
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90
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60
50
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20
10
0
f1 (ppm)

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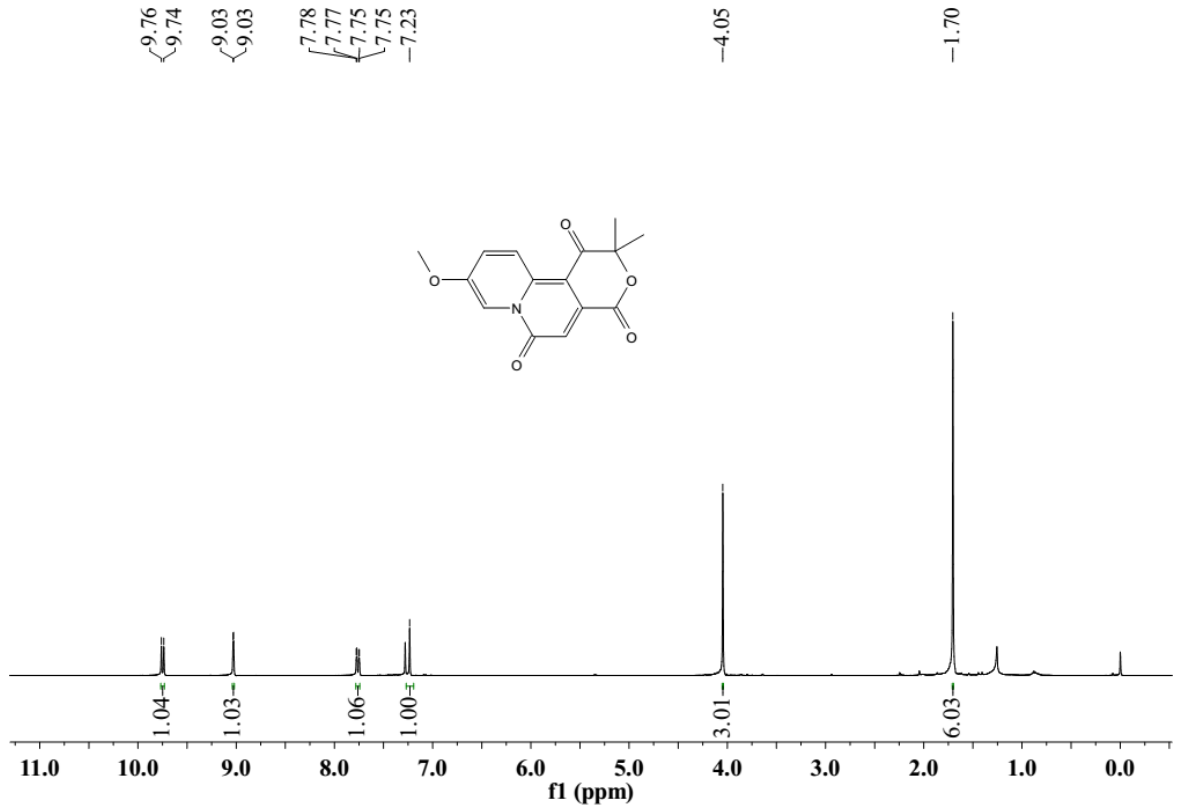
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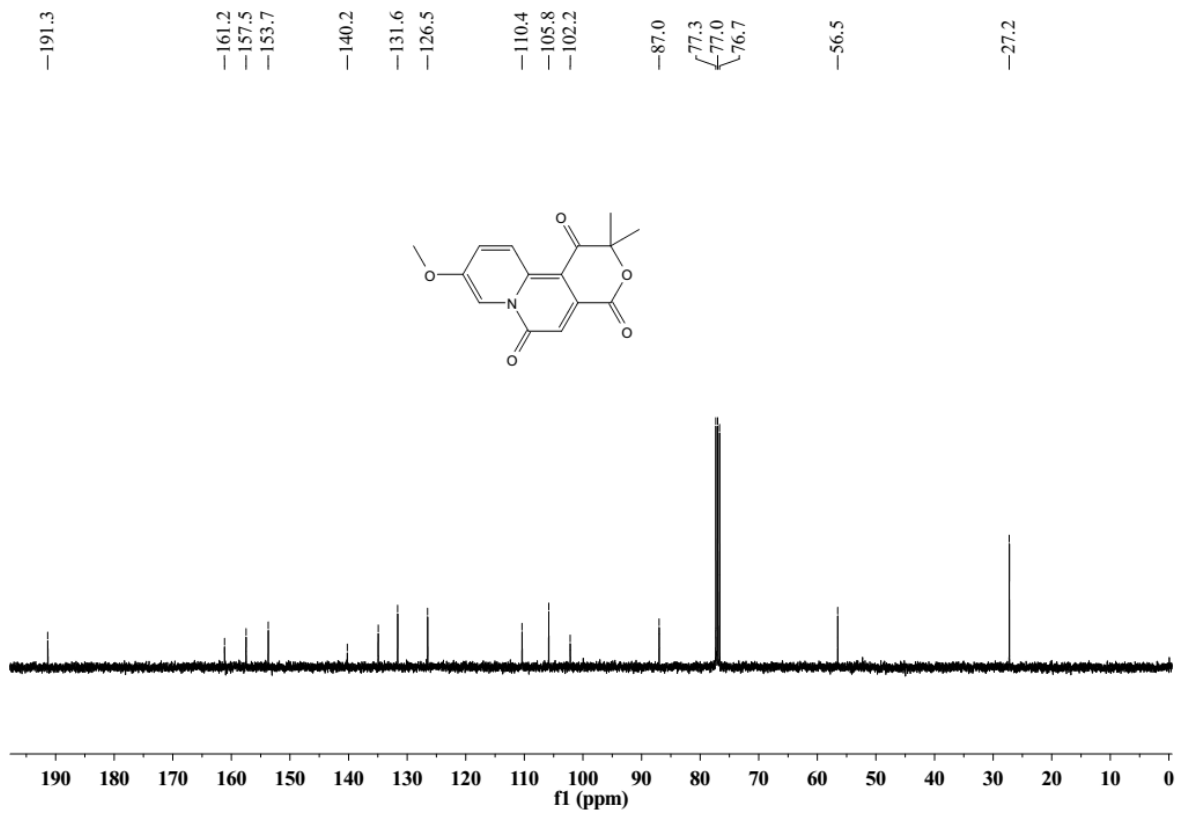
f1 (ppm)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77.0
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27.2
190
180
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160
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20
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f1 (ppm)

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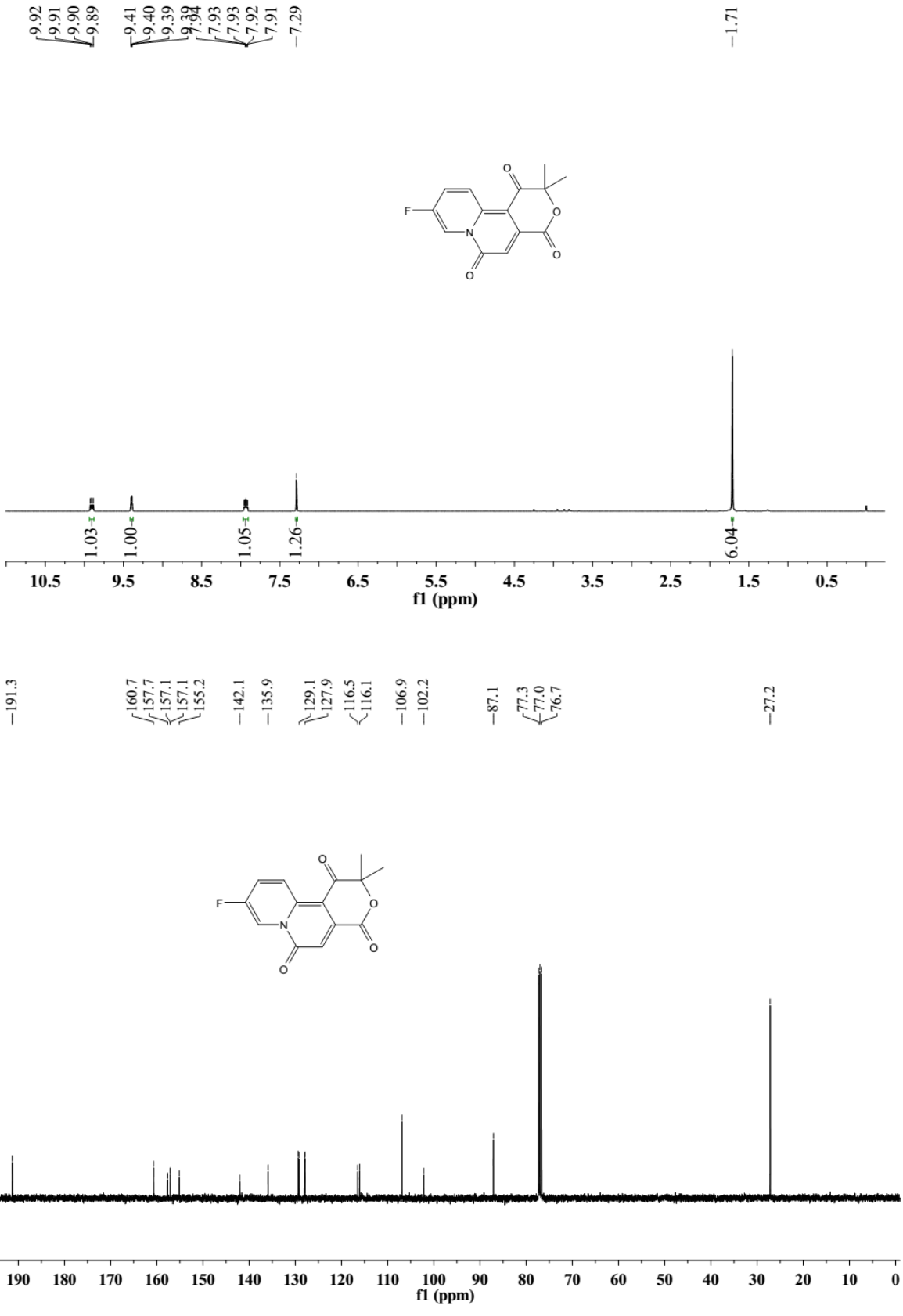
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3.5
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f1 (ppm)
191.3
160.7
157.7
157.1
157.1
155.2
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116.5
116.1
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102.2
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27.2
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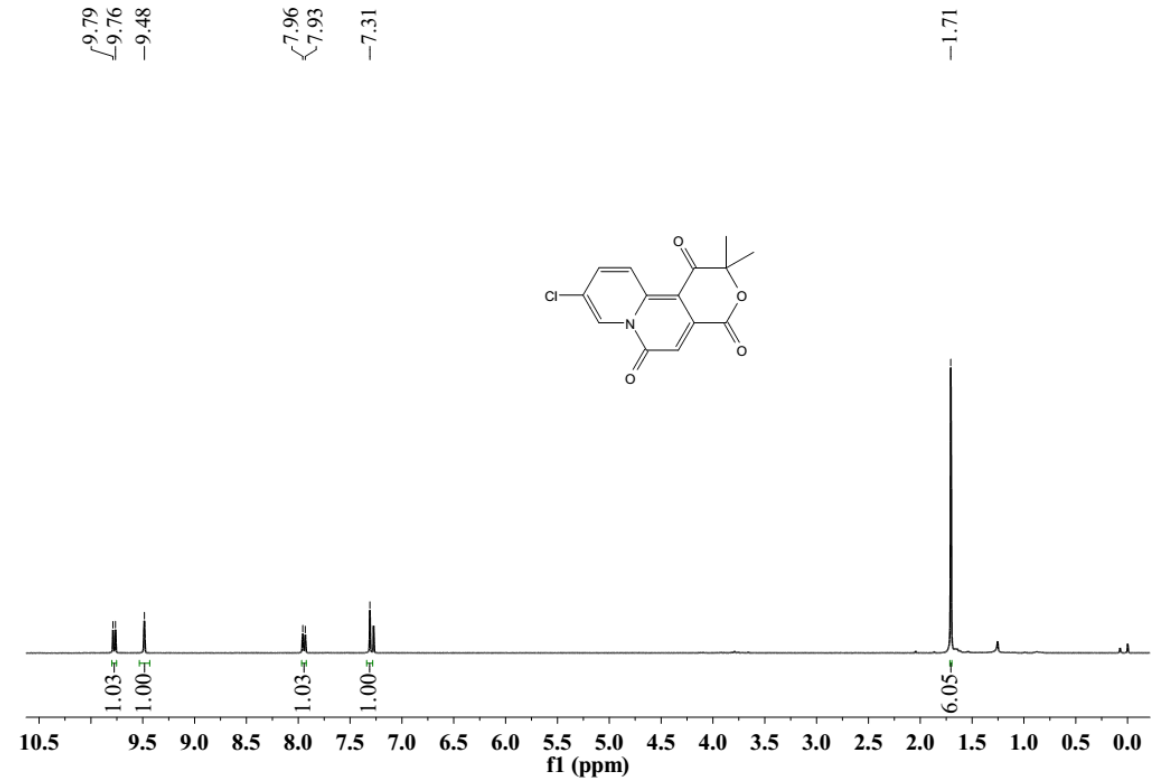
$3h_4$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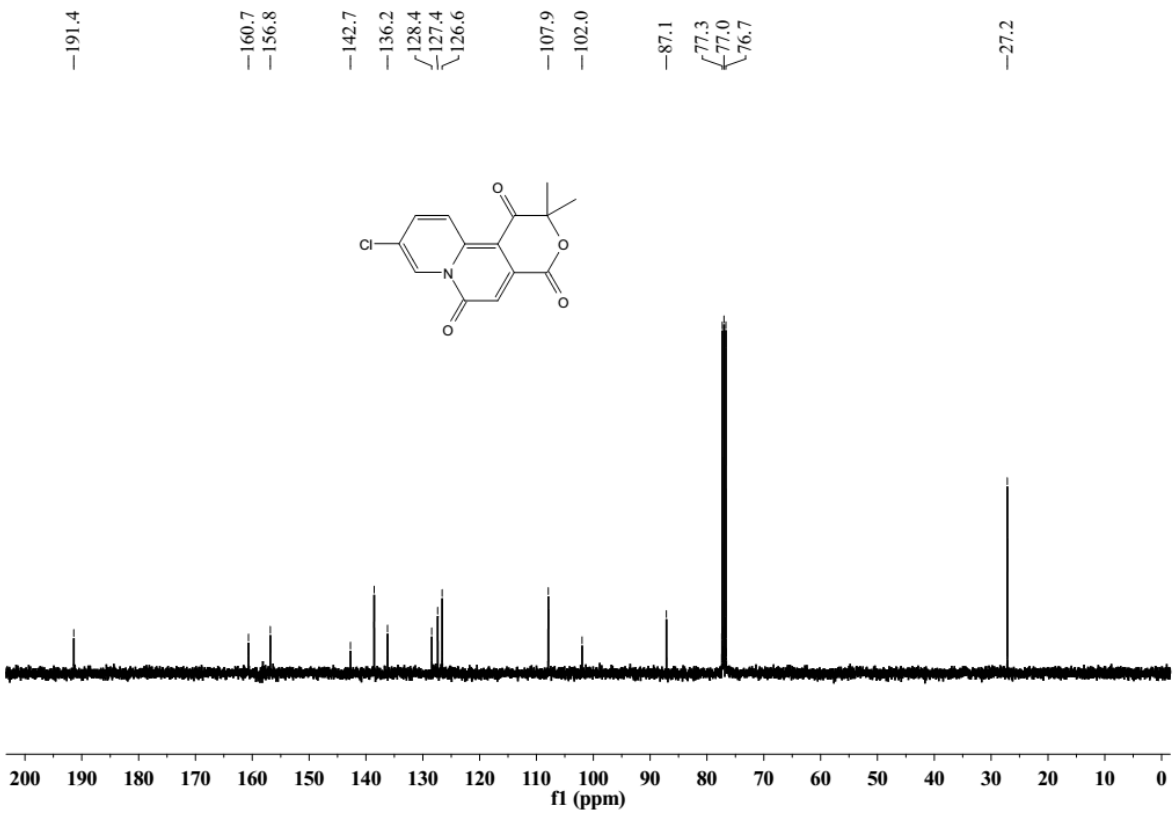
6.05
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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102.0
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76.7
27.2
Cl
O
N
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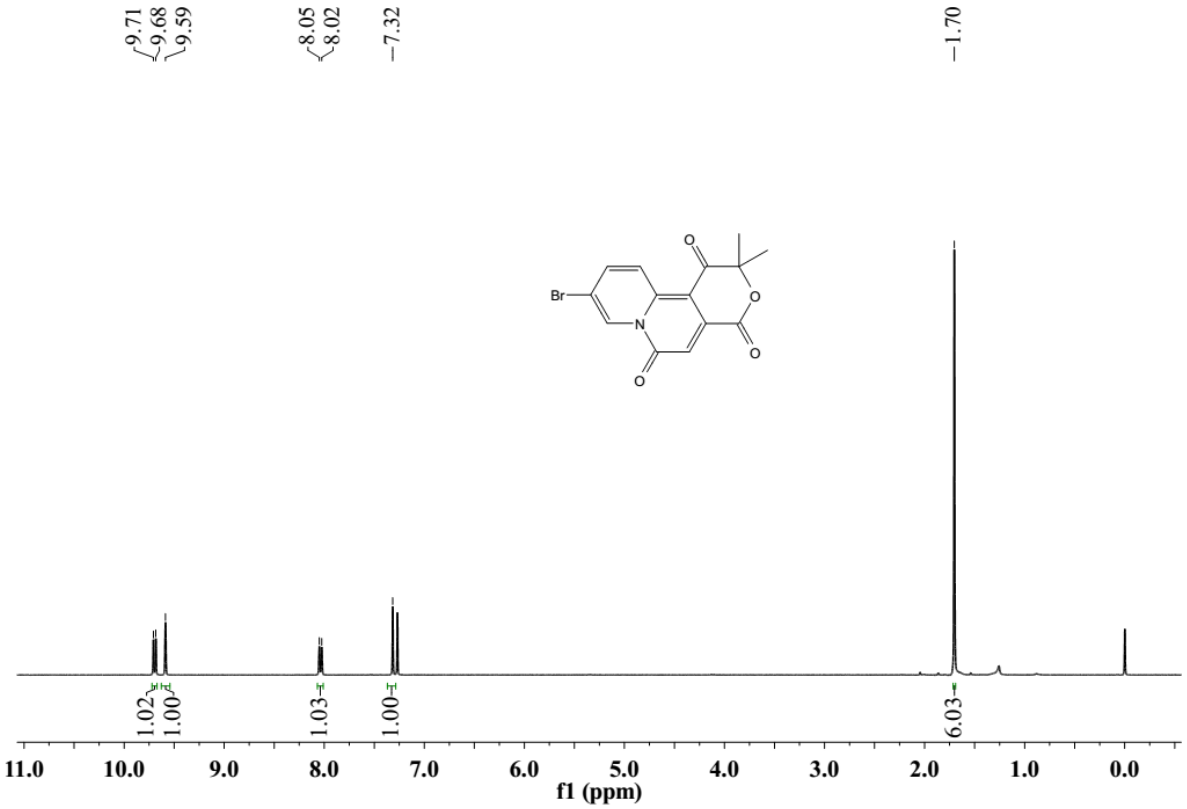
f1 (ppm)

$3h_5$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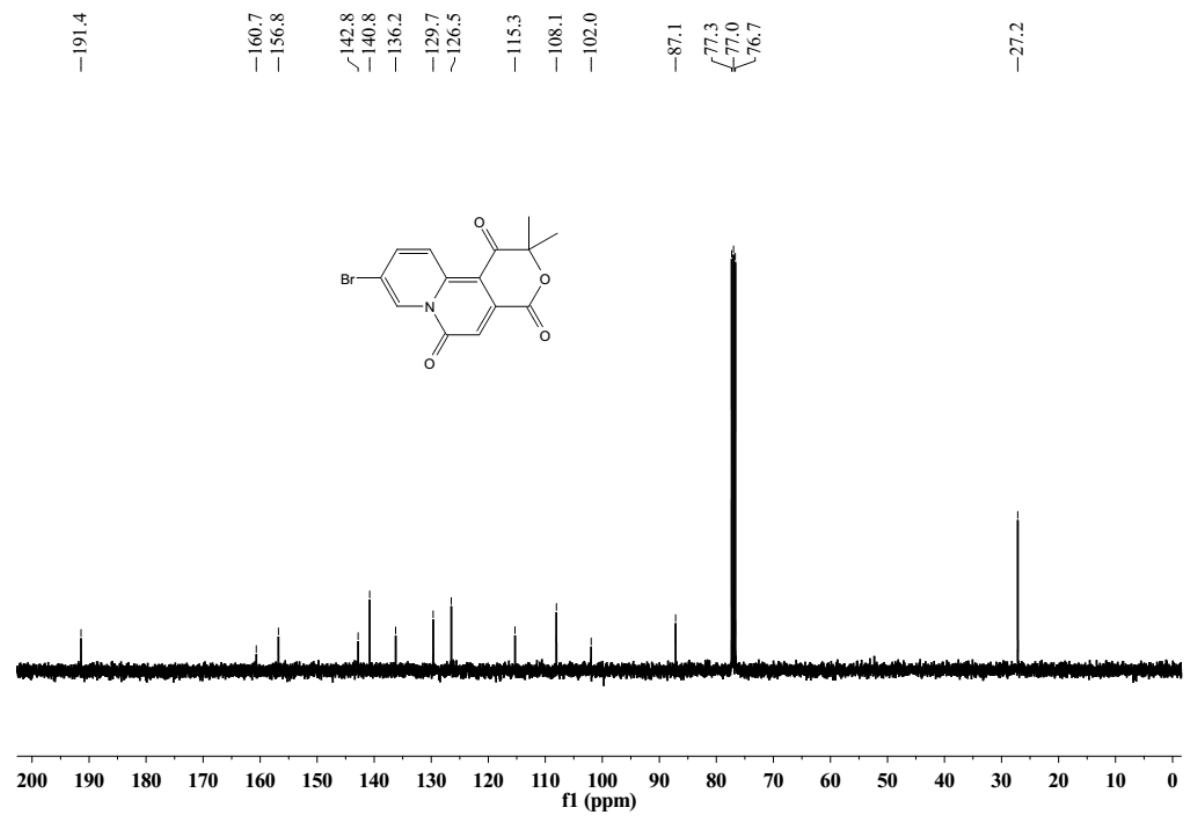
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126.5
115.3
108.1
102.0
87.1
77.3
77.0
76.7
27.2
Br
O
N
200
190
180
170
160
150
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130
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100
90
80
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60
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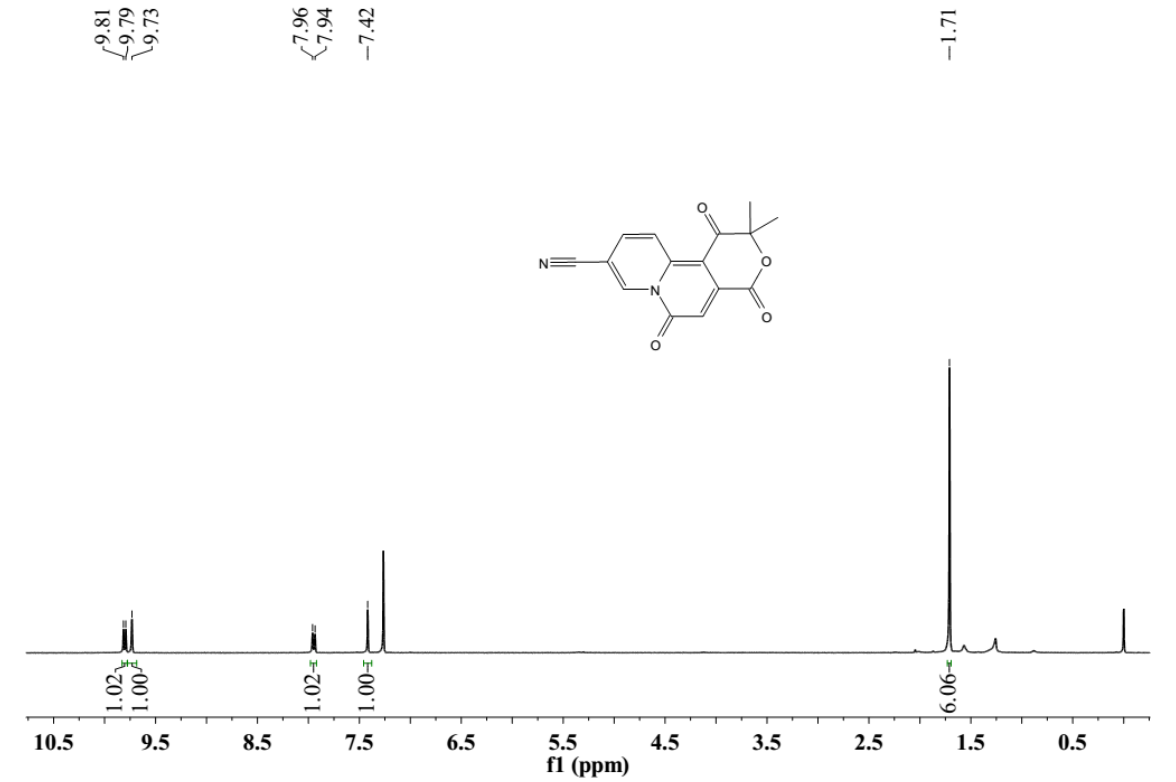
30
20
10
0
f1 (ppm)

$3h_6$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9.5
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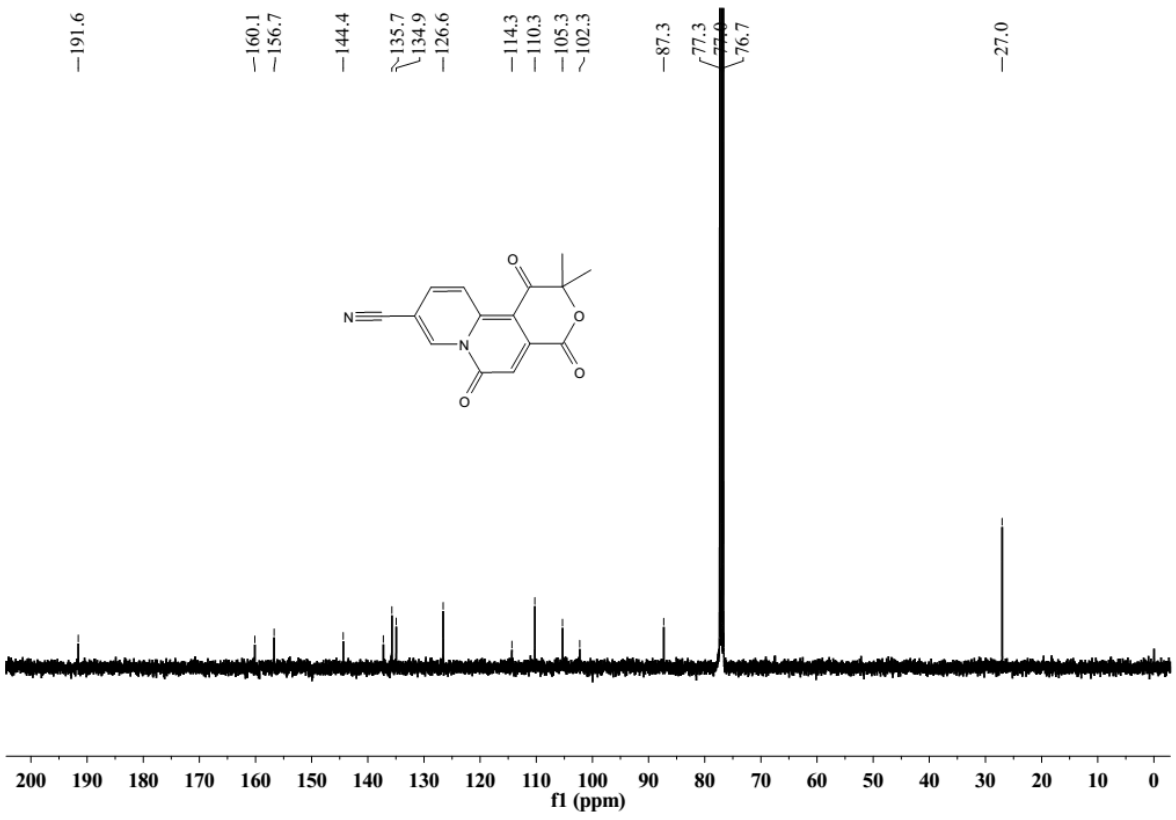
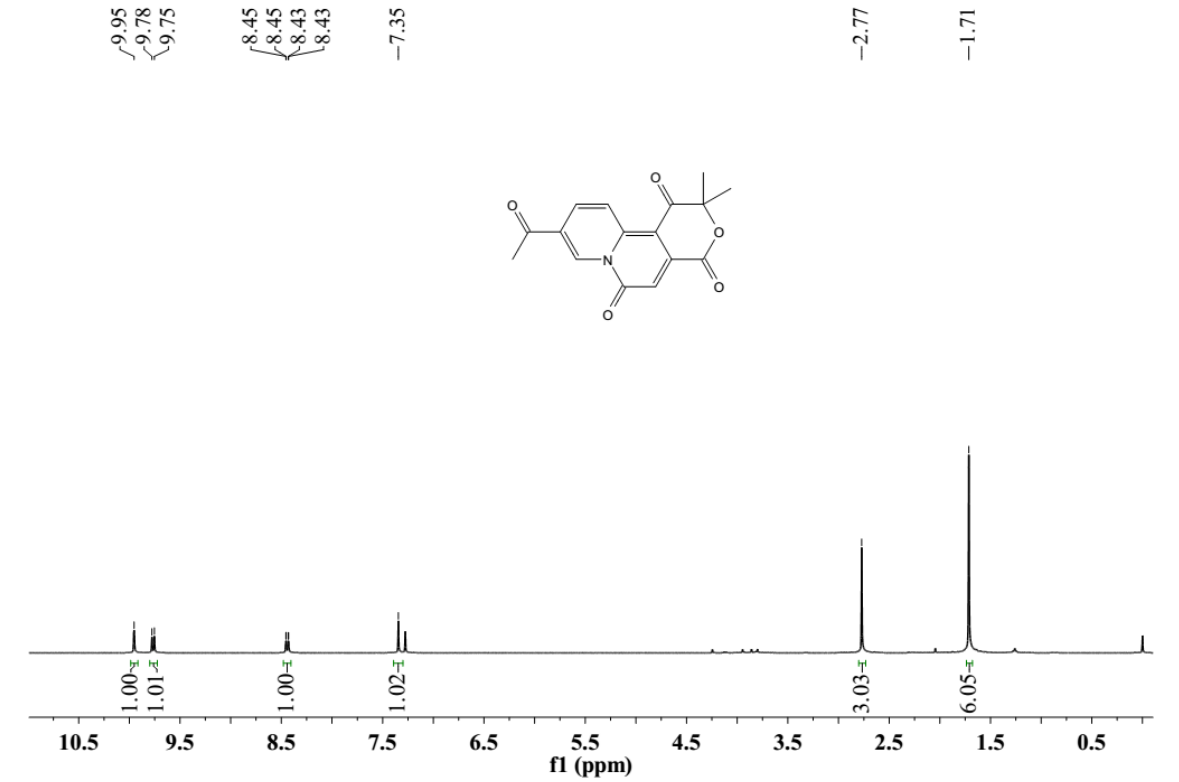
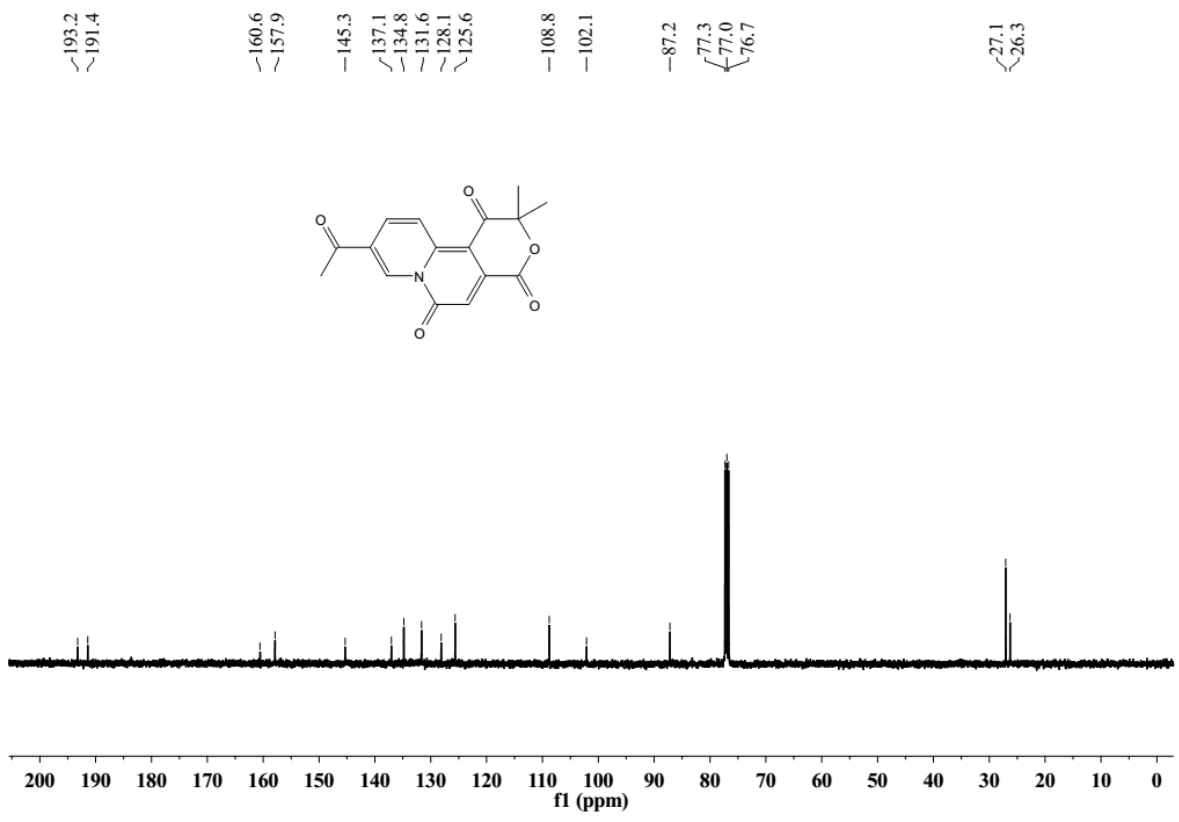
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

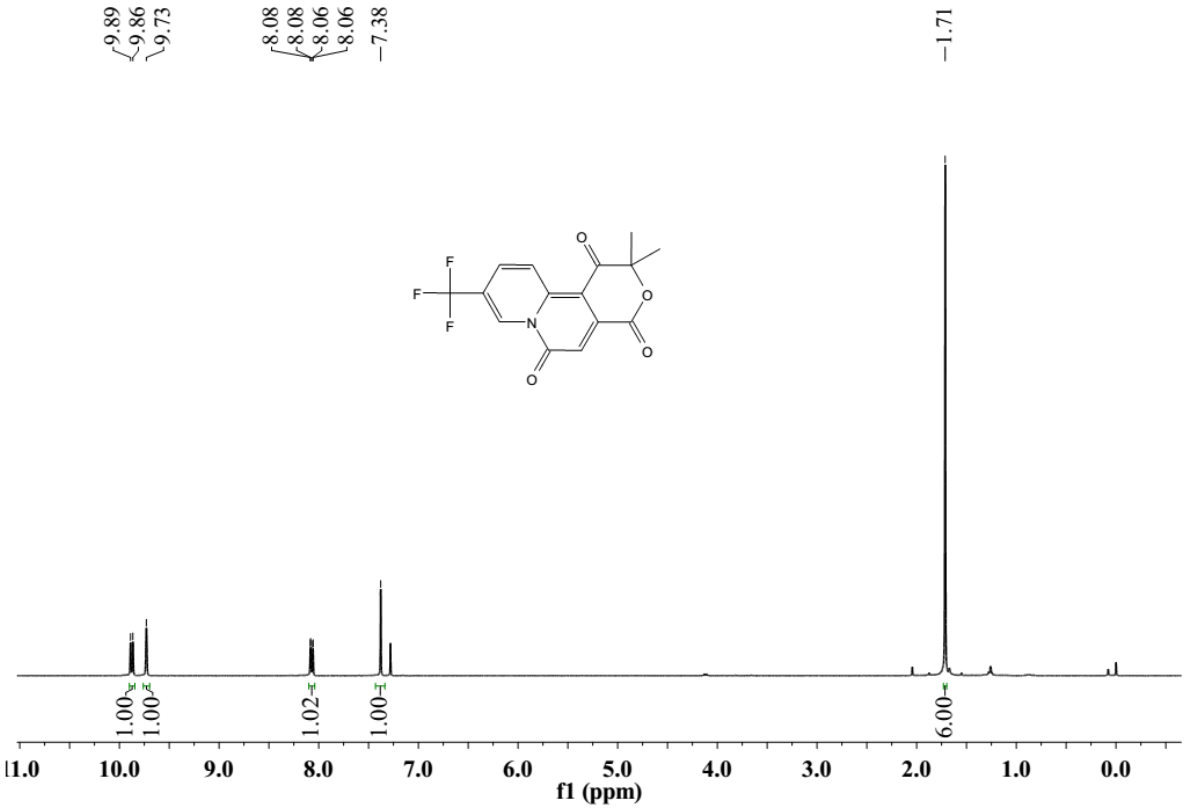

191.6
160.1
156.7
144.4
135.7
134.9
126.6
114.3
110.3
105.3
102.3
87.3
77.3
76.7
27.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

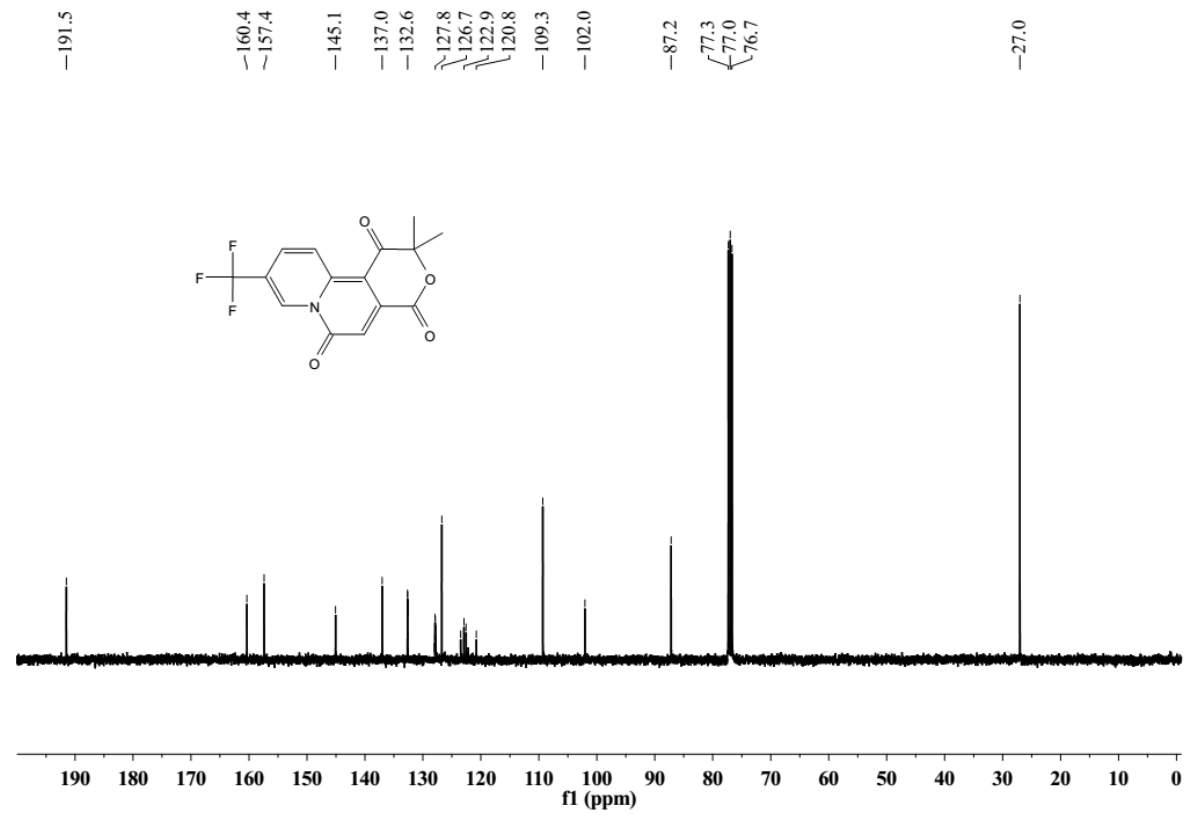
3h$_7$


9.95
9.78
9.75
8.45
8.45
8.43
8.43
7.35
2.77
1.71
1.00
1.01
1.00
1.02
3.03
6.05
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

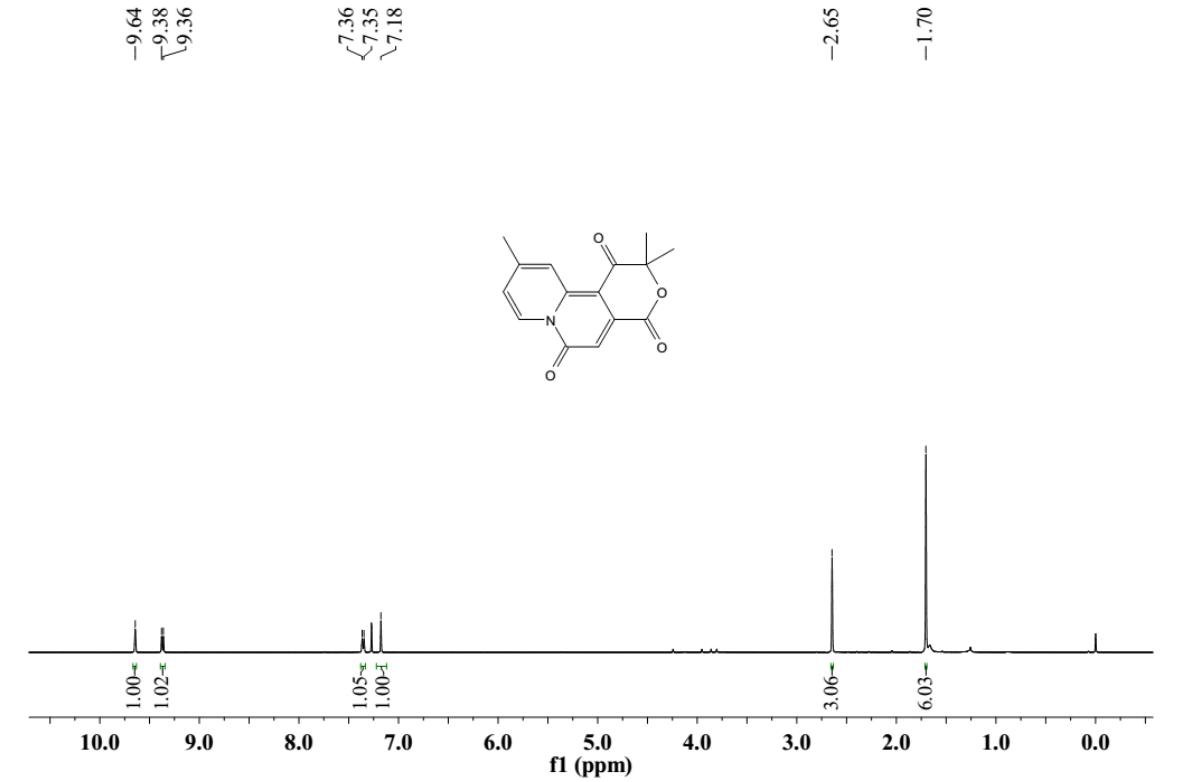

193.2
191.4
160.6
157.9
145.3
137.1
134.8
131.6
128.1
125.6
108.8
102.1
87.2
77.3
77.0
76.7
27.1
26.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

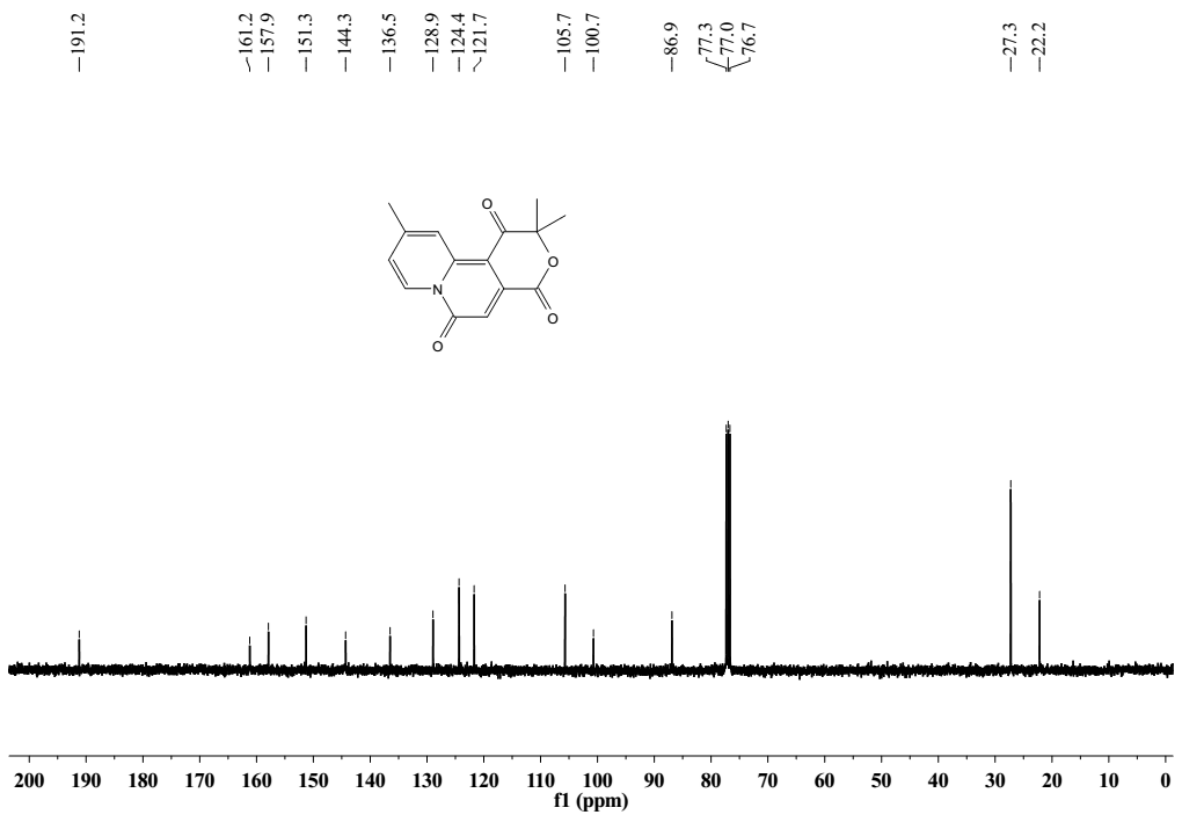
3h$_8$


9.89
9.86
9.73
8.08
8.08
8.06
8.06
7.38
1.71
1.00
1.00
1.02
1.00
6.00
f1 (ppm)

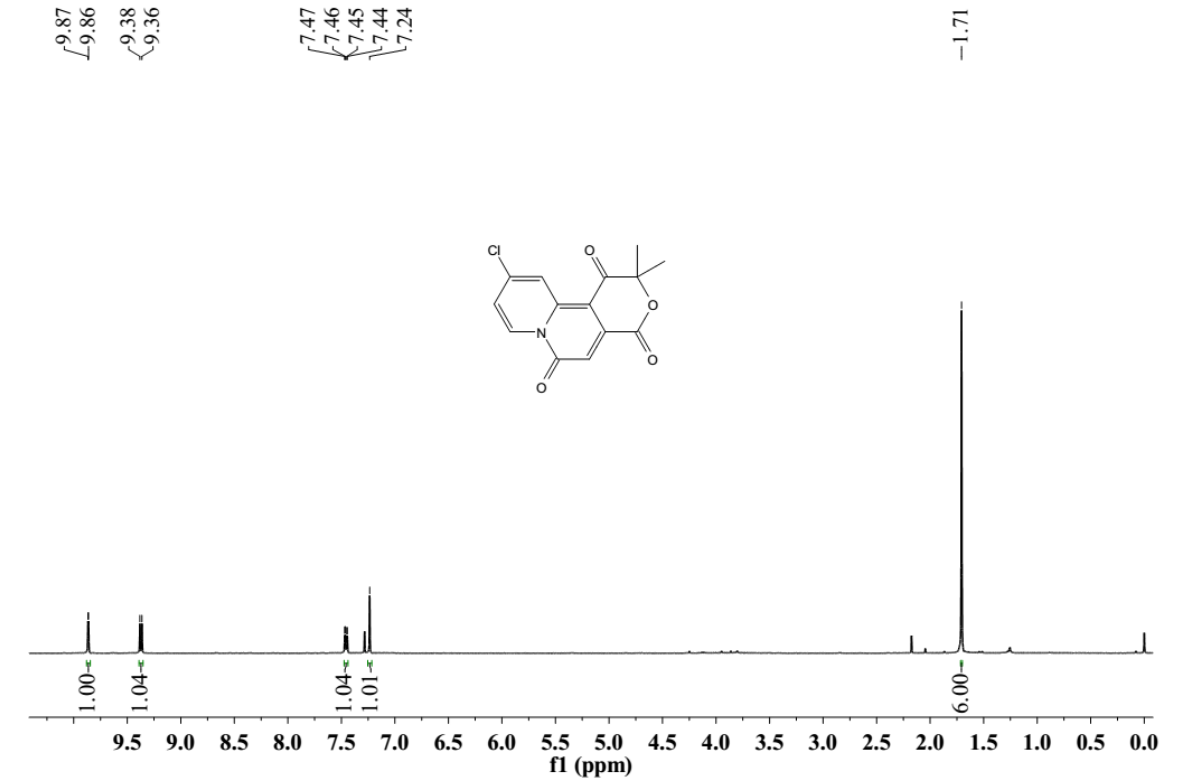

191.5
160.4
157.4
145.1
137.0
132.6
127.8
126.7
122.9
120.8
109.3
102.0
87.2
77.3
77.0
76.7
27.0
f1 (ppm)

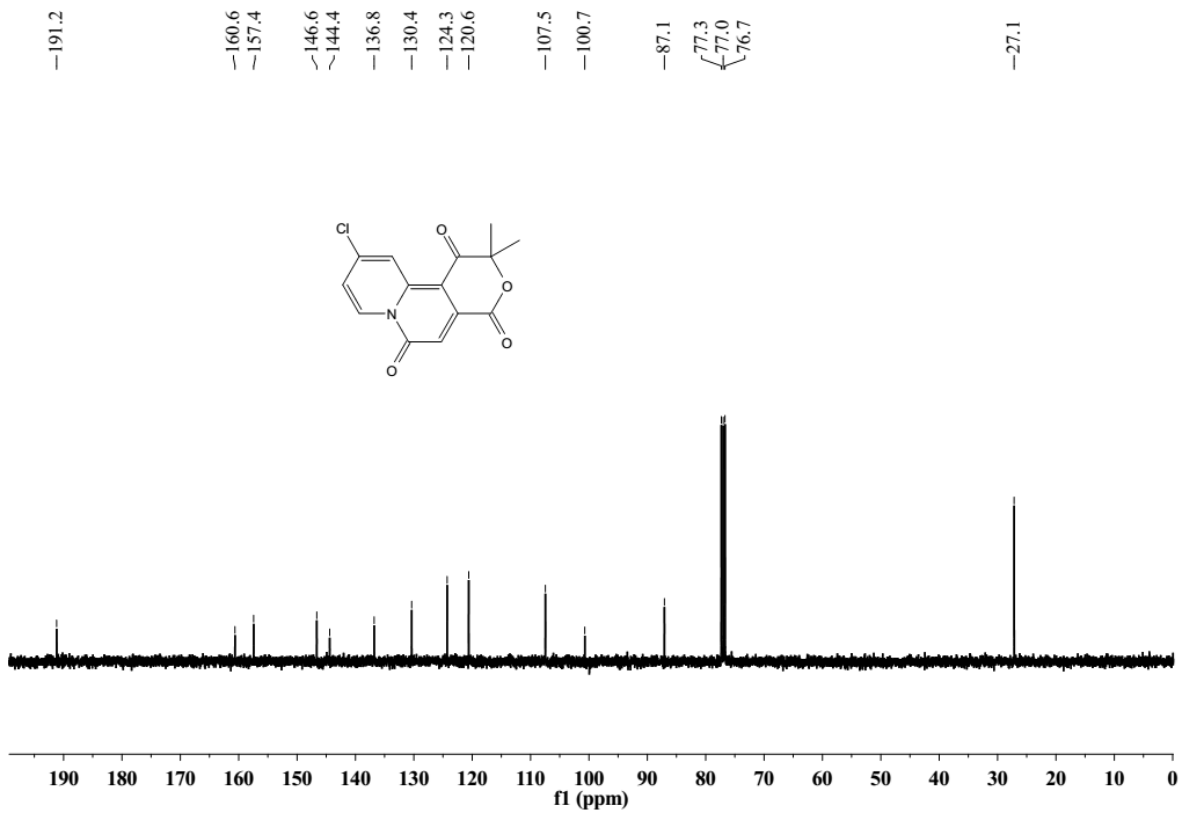
$3i_1$


9.64
9.38
9.36
7.36
7.35
7.18
2.65
1.70
1.00
1.02
1.05
1.00
3.06
6.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

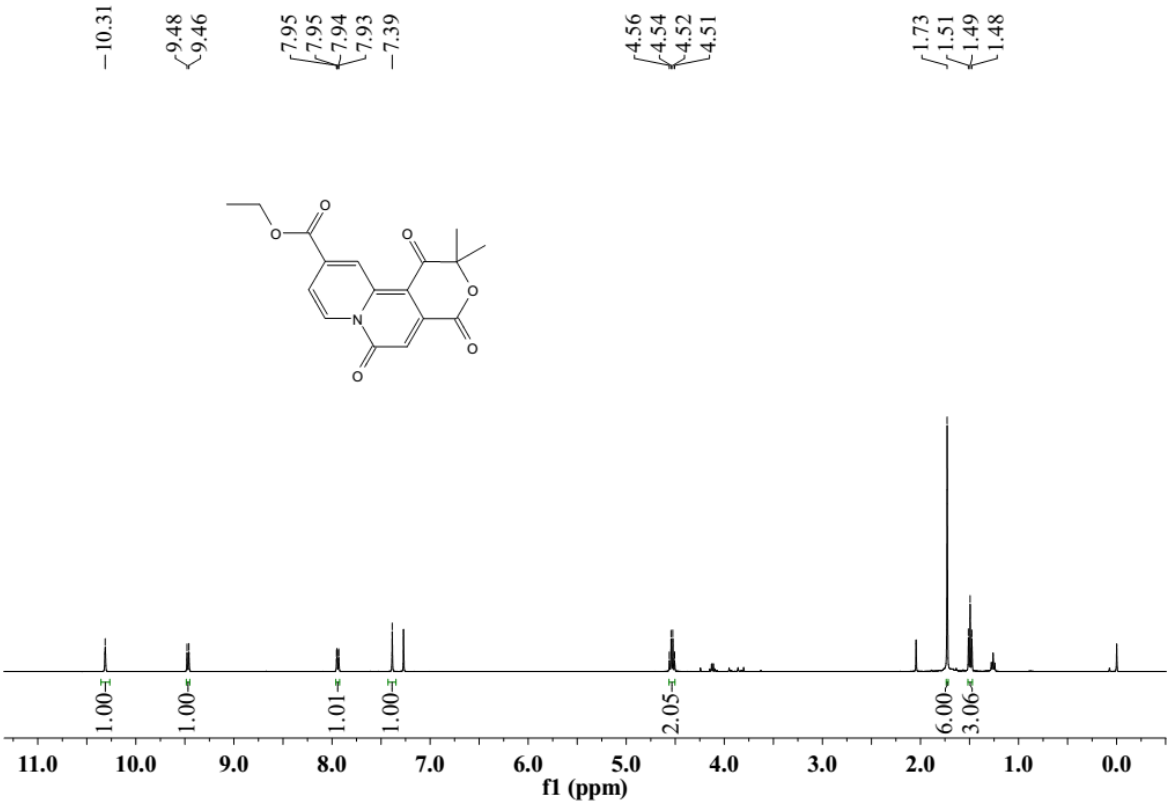

191.2
161.2
157.9
151.3
144.3
136.5
128.9
124.4
121.7
105.7
100.7
86.9
77.3
77.0
76.7
27.3
22.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

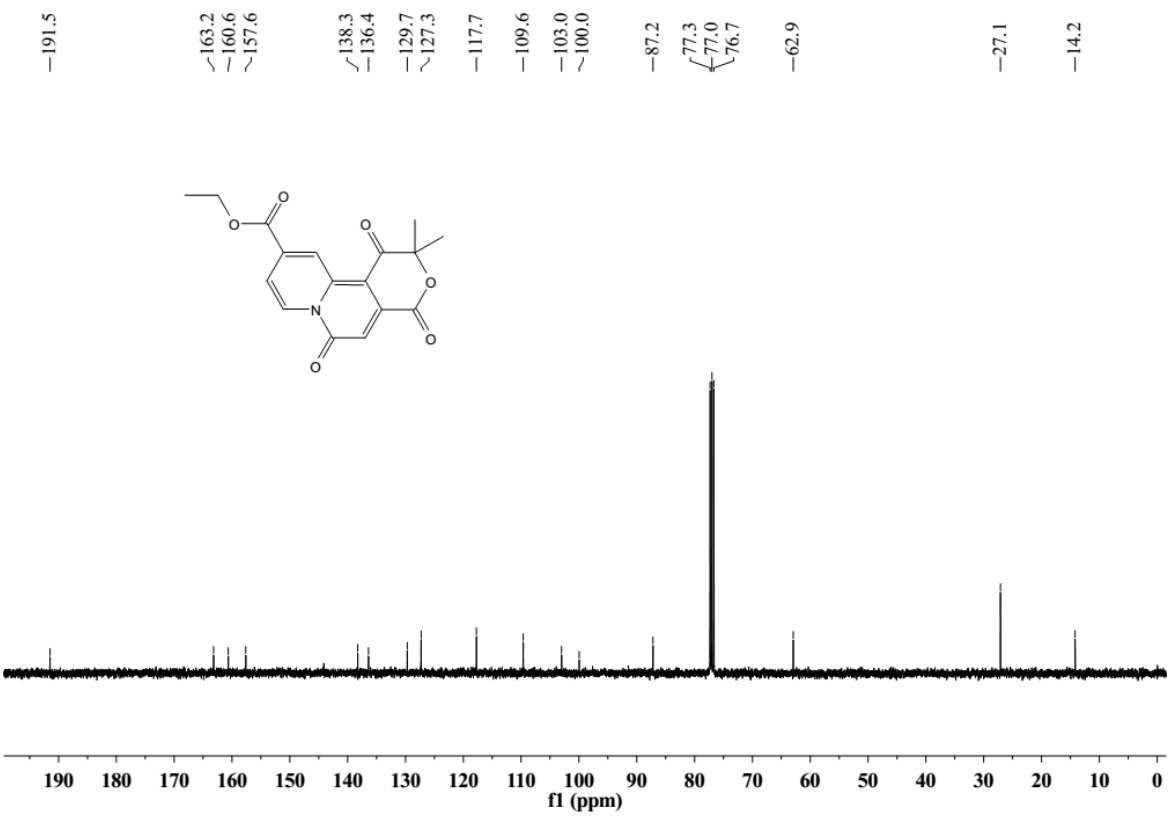
$3i_2$


9.87
9.86
9.38
9.36
7.47
7.46
7.45
7.44
7.24
1.71
Cl
O
O
O
N
O
O
1.00
1.04
1.04
1.01
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

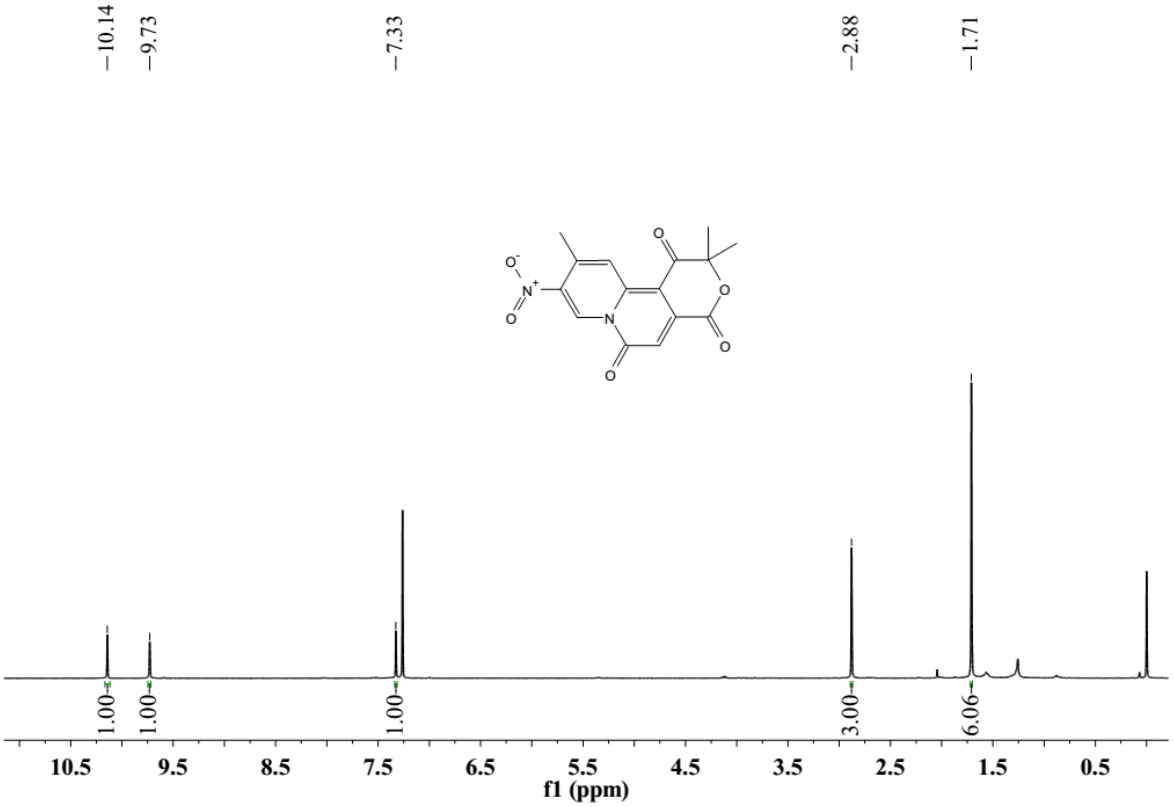

191.2
160.6
157.4
146.6
144.4
136.8
130.4
124.3
120.6
107.5
100.7
87.1
77.3
77.0
76.7
27.1
Cl
O
O
O
N
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

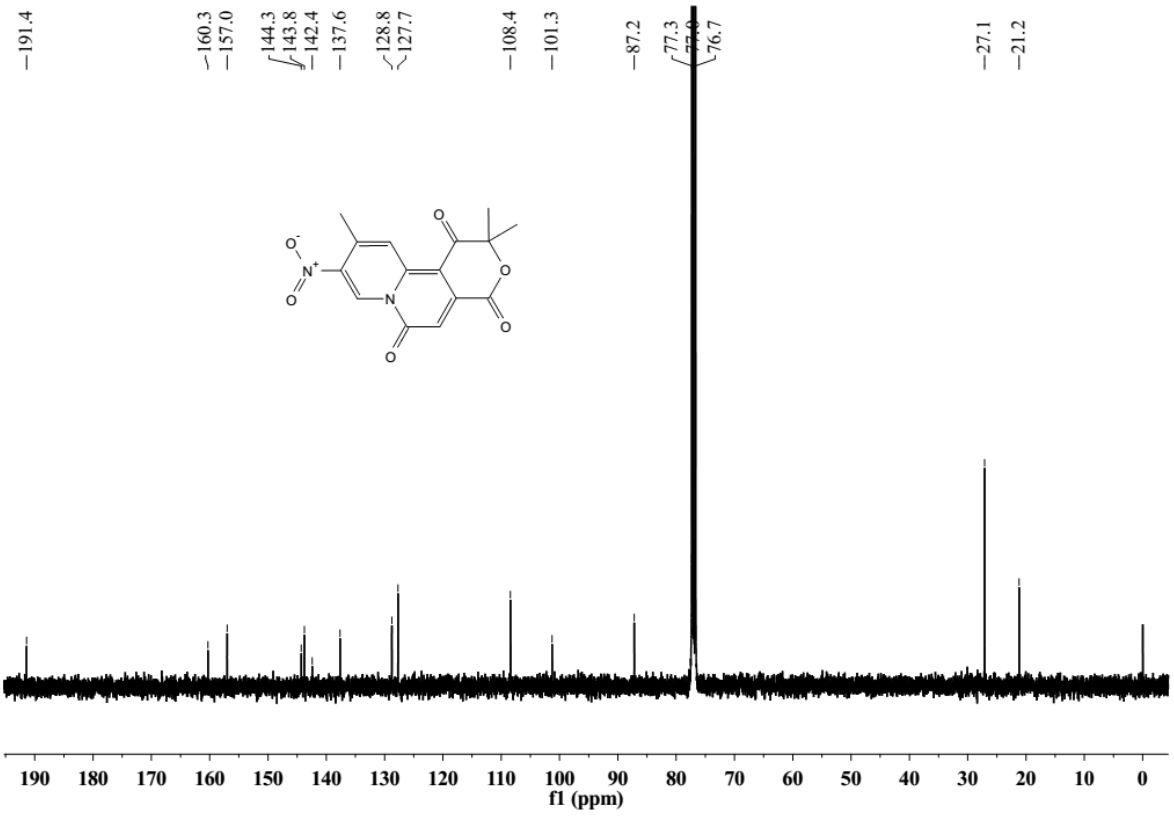
$3i_3$


10.31
9.48
9.46
7.95
7.95
7.94
7.93
7.39
4.56
4.54
4.52
4.51
1.73
1.51
1.49
1.48
1.00
1.00
1.01
1.00
2.05
6.00
3.06
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

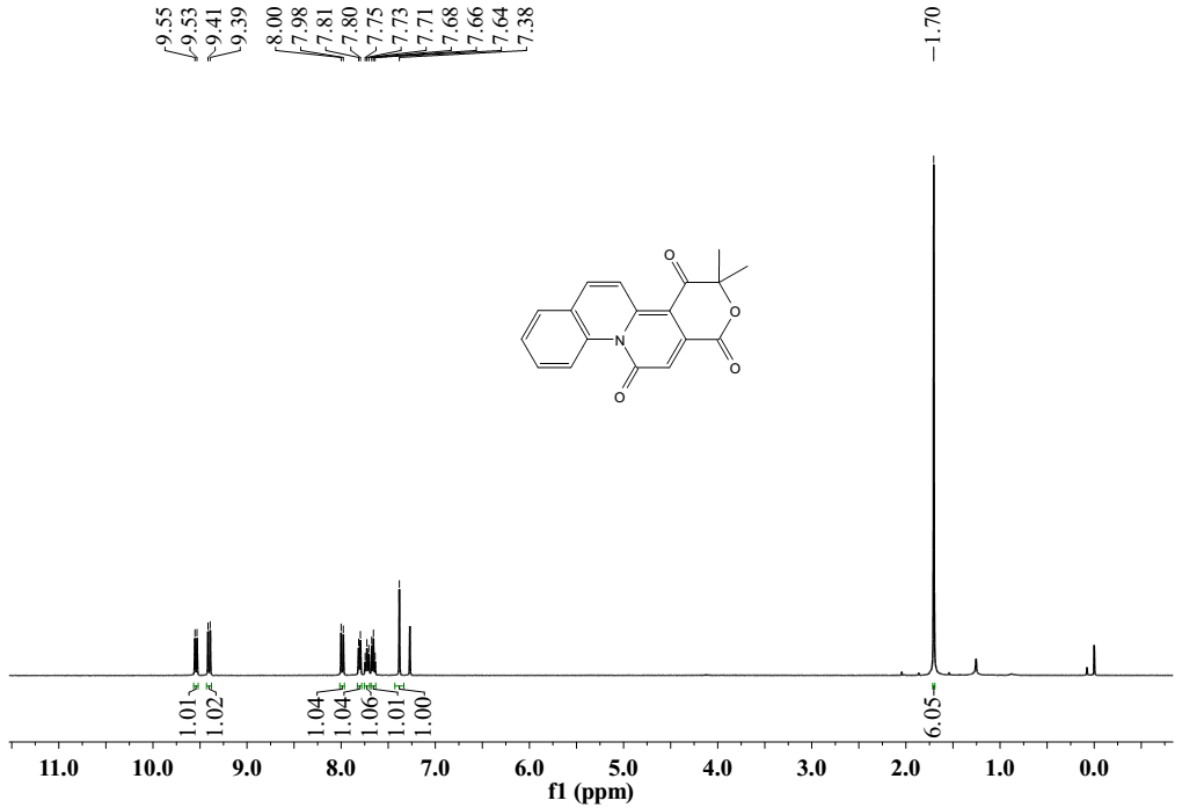

191.5
163.2
160.6
157.6
138.3
136.4
129.7
127.3
117.7
109.6
103.0
100.0
87.2
77.3
77.0
76.7
62.9
27.1
14.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

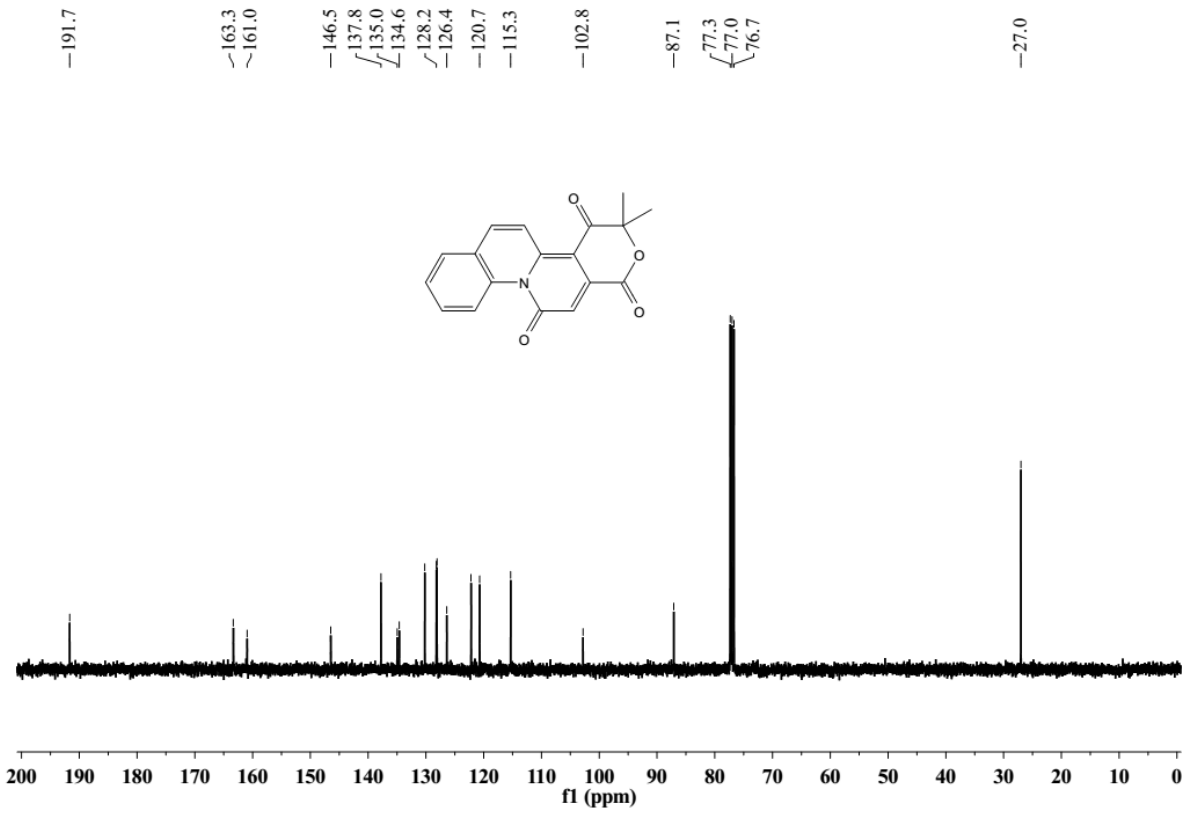
3j


10.14
9.73
7.33
2.88
1.71
1.00
1.00
1.00
3.00
6.06
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

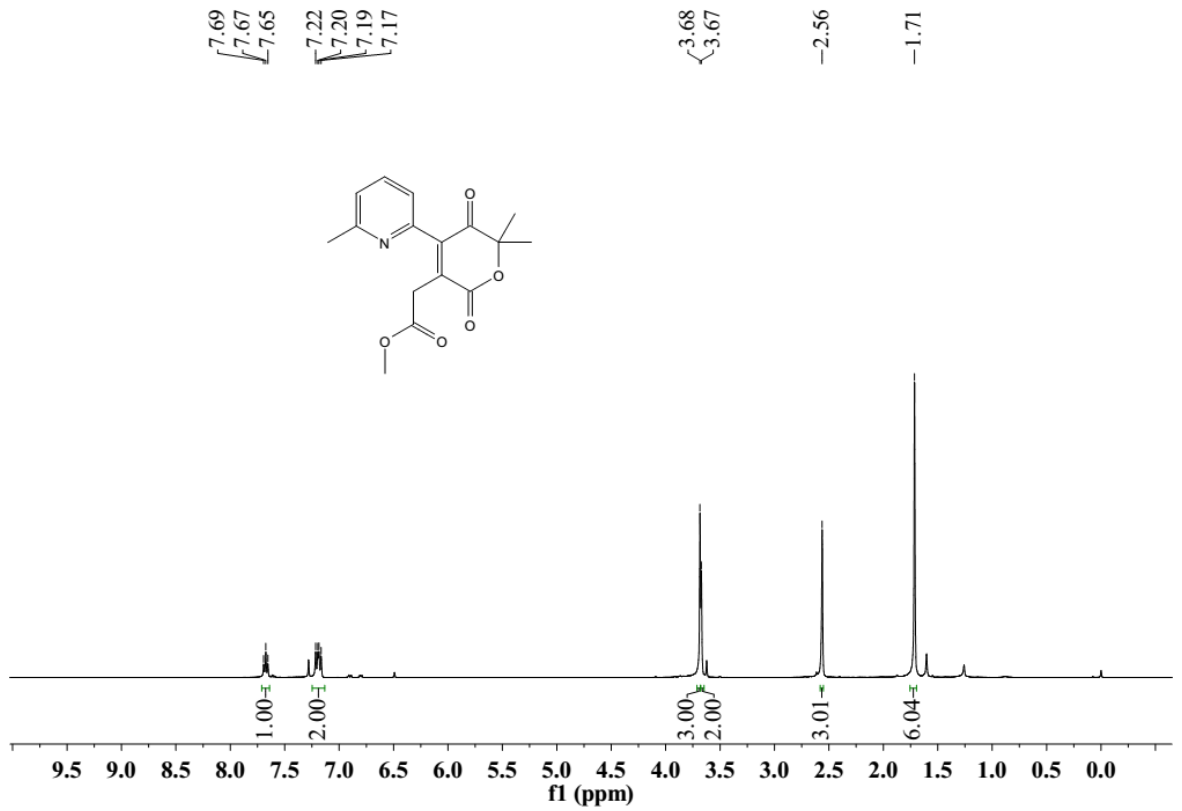

191.4
160.3
157.0
144.3
143.8
142.4
137.6
128.8
127.7
108.4
101.3
87.2
77.3
77.0
76.7
27.1
21.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

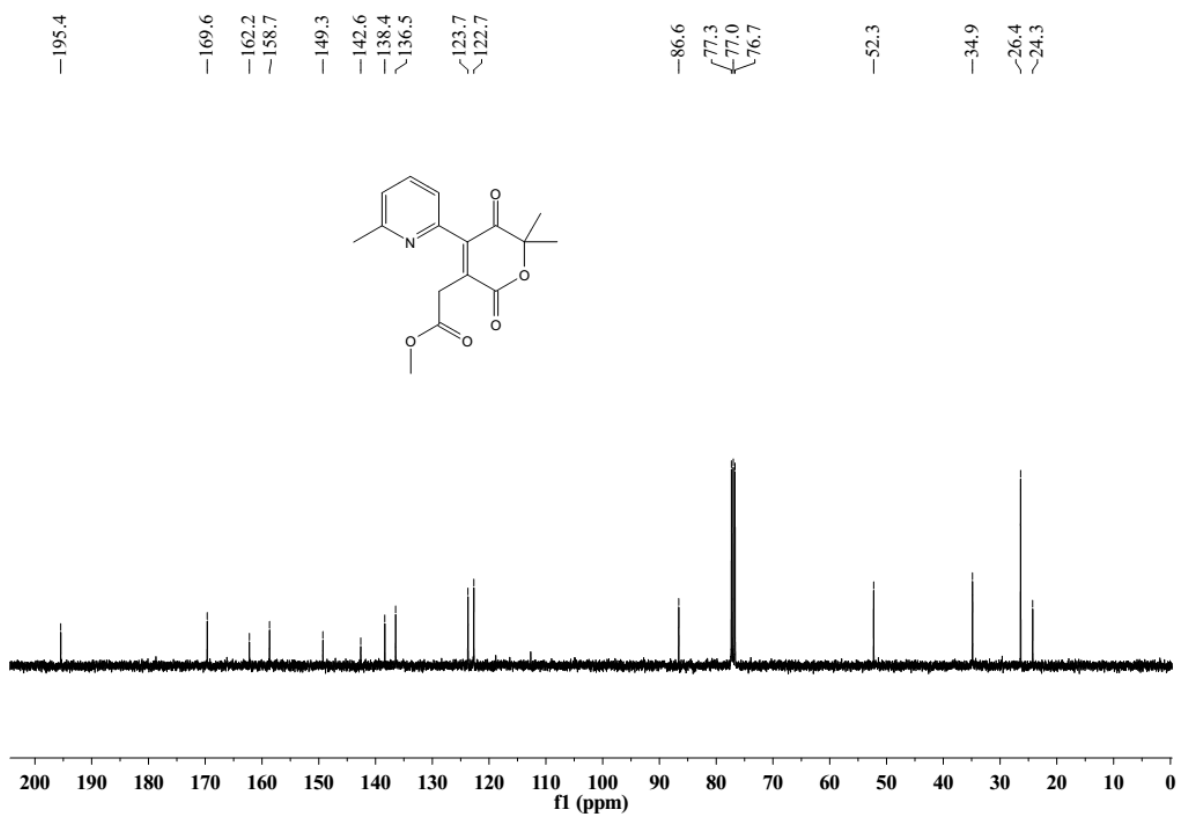
3k


9.55
9.53
9.41
9.39
8.00
7.98
7.81
7.80
7.75
7.73
7.71
7.68
7.66
7.64
7.38
1.70
1.01
1.02
1.04
1.04
1.06
1.01
1.00
6.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

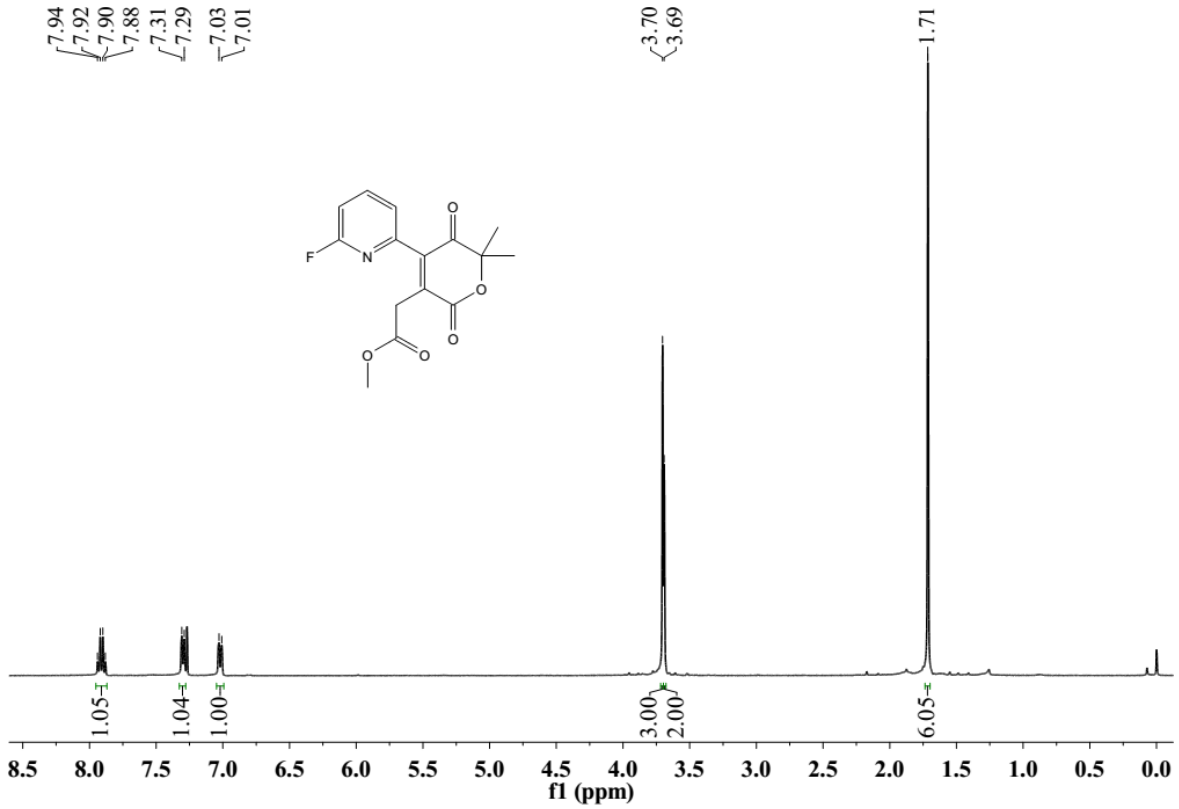

191.7
163.3
161.0
146.5
137.8
135.0
134.6
128.2
126.4
120.7
115.3
102.8
87.1
77.3
77.0
76.7
27.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

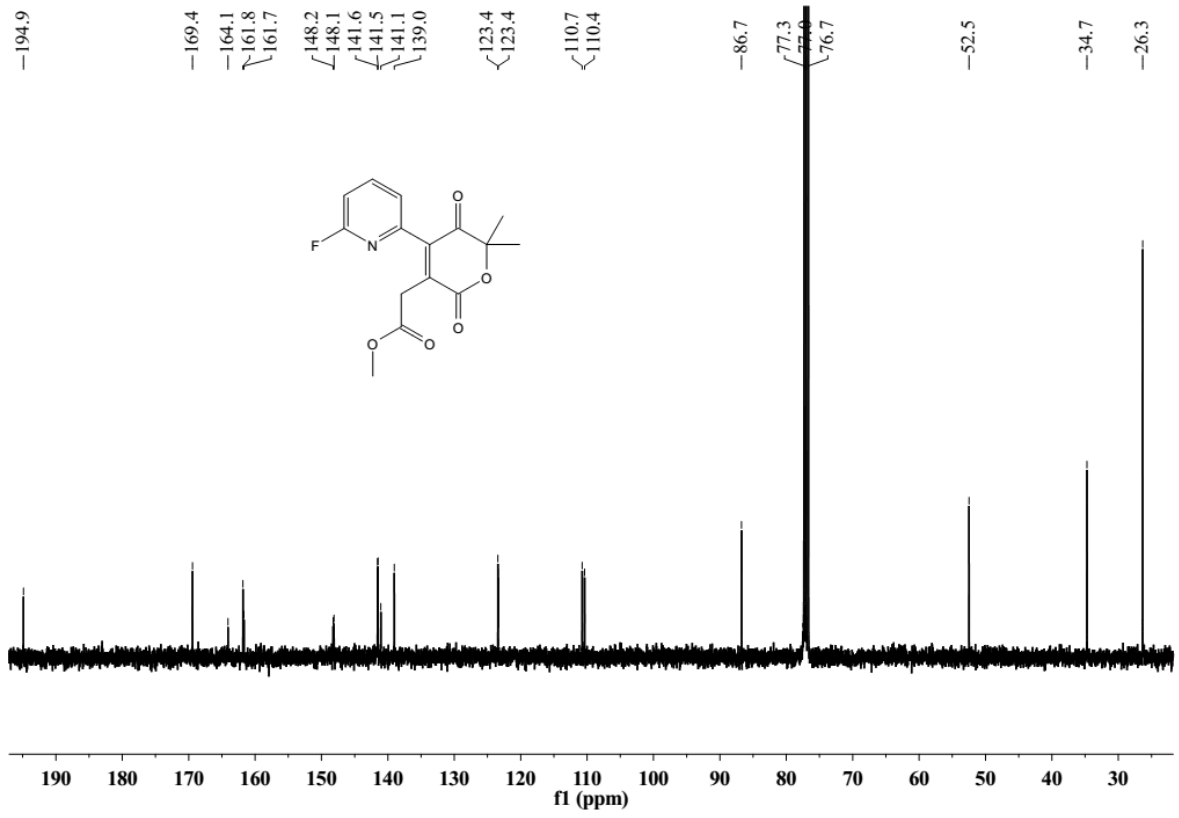
$4l_1$


7.69
7.67
7.65
7.22
7.20
7.19
7.17
3.68
3.67
2.56
1.71
1.00
2.00
3.00
2.00
3.01
6.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

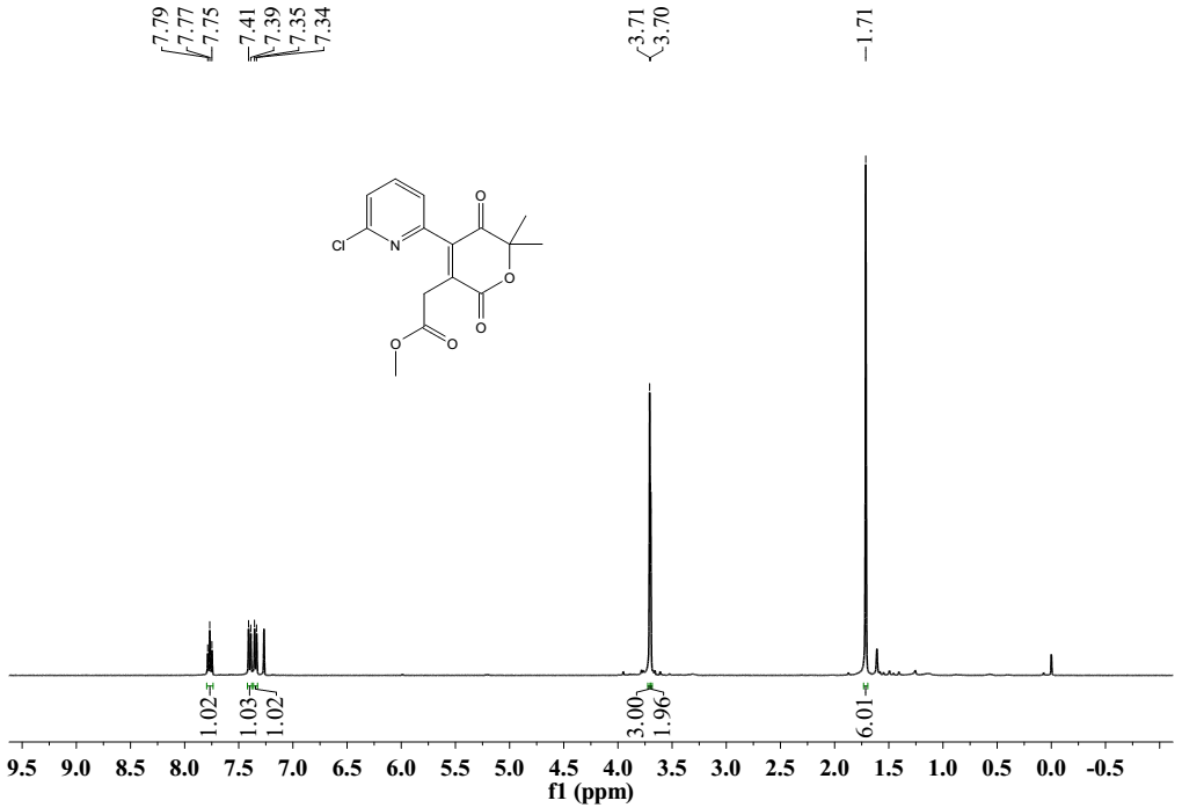

195.4
169.6
162.2
158.7
149.3
142.6
138.4
136.5
123.7
122.7
86.6
77.3
77.0
76.7
52.3
34.9
26.4
24.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

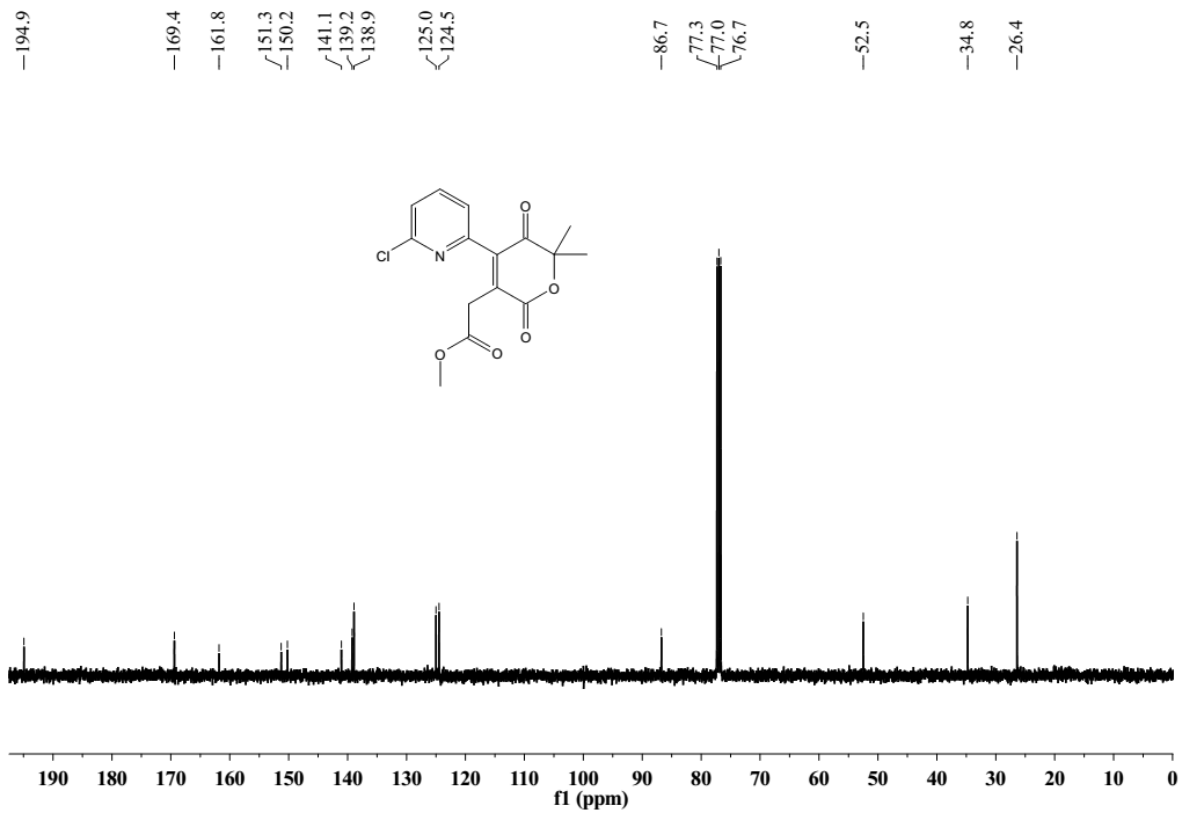
4l$_2$


7.94
7.92
7.90
7.88
7.31
7.29
7.03
7.01
3.70
3.69
1.71
1.05
1.04
1.00
3.00
2.00
6.05
f1 (ppm)

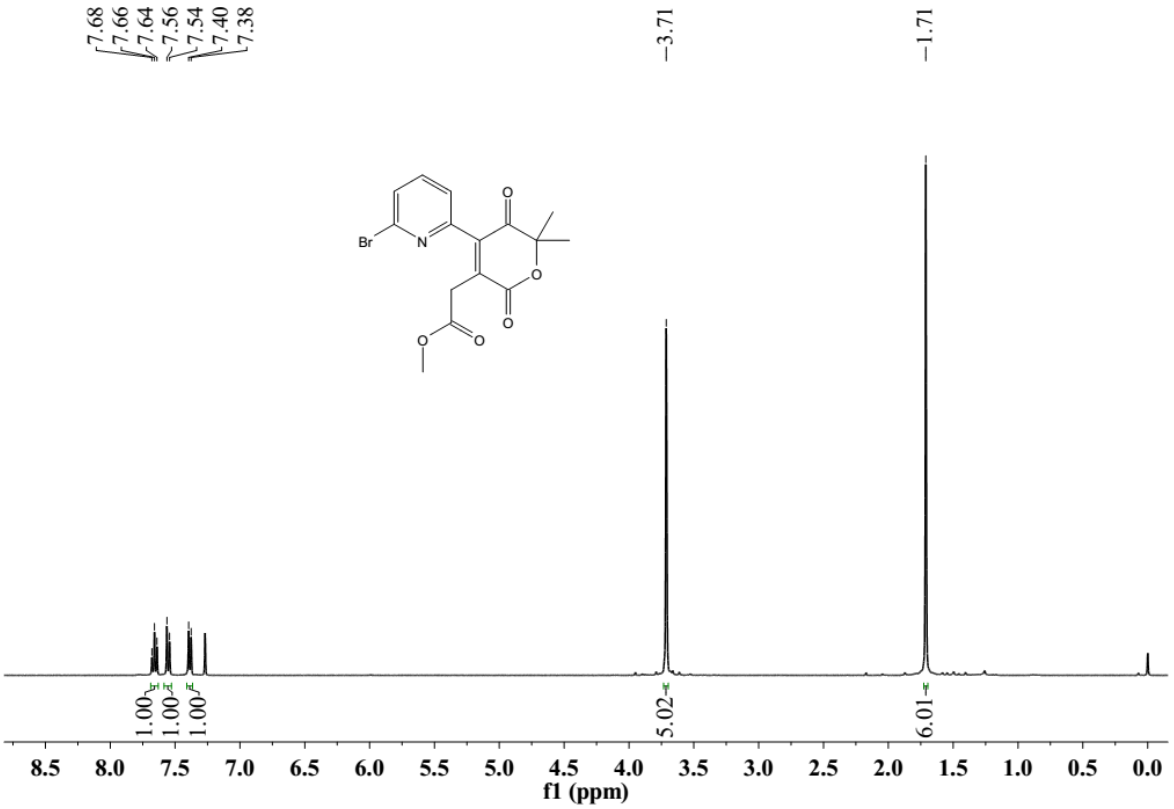

194.9
169.4
164.1
161.8
161.7
148.2
148.1
141.6
141.5
141.1
139.0
123.4
123.4
110.7
110.4
86.7
77.3
76.7
52.5
34.7
26.3
f1 (ppm)

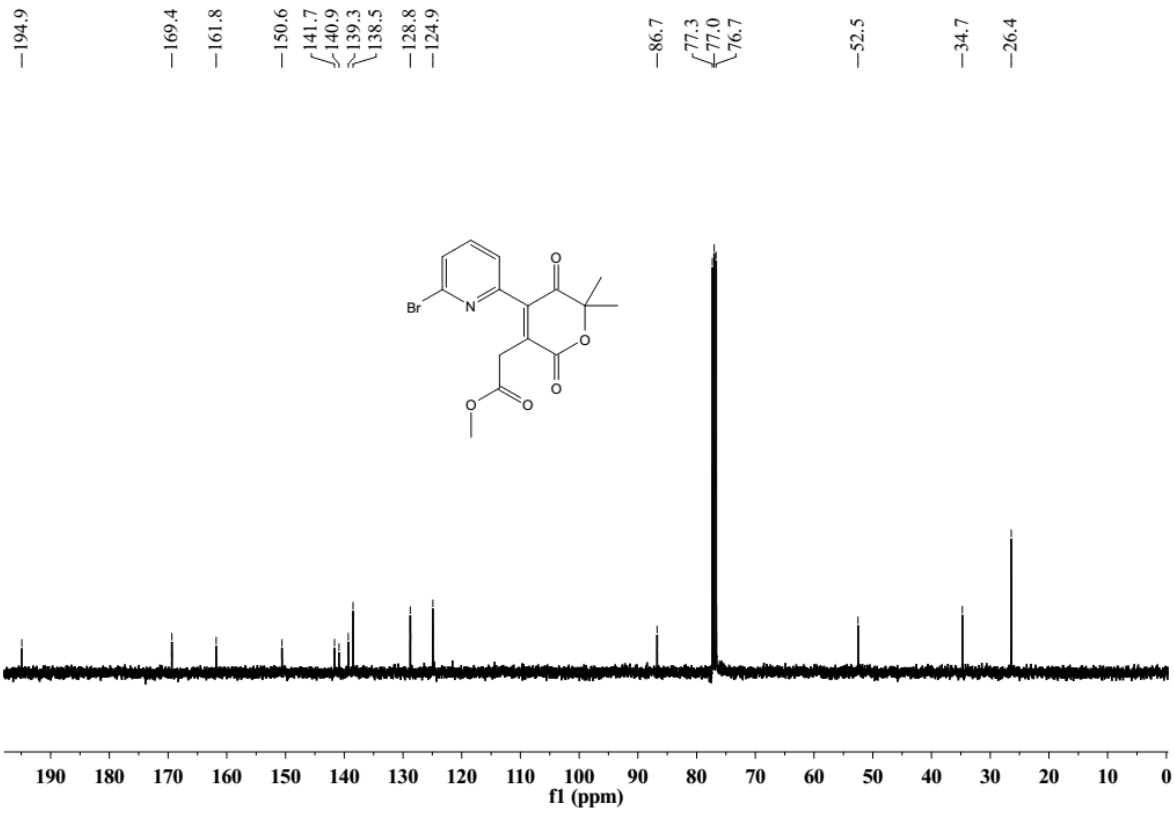
4l$_3$


7.79
7.77
7.75
7.41
7.39
7.35
7.34
3.71
3.70
1.71
1.02
1.03
1.02
3.00
1.96
6.01
f1 (ppm)

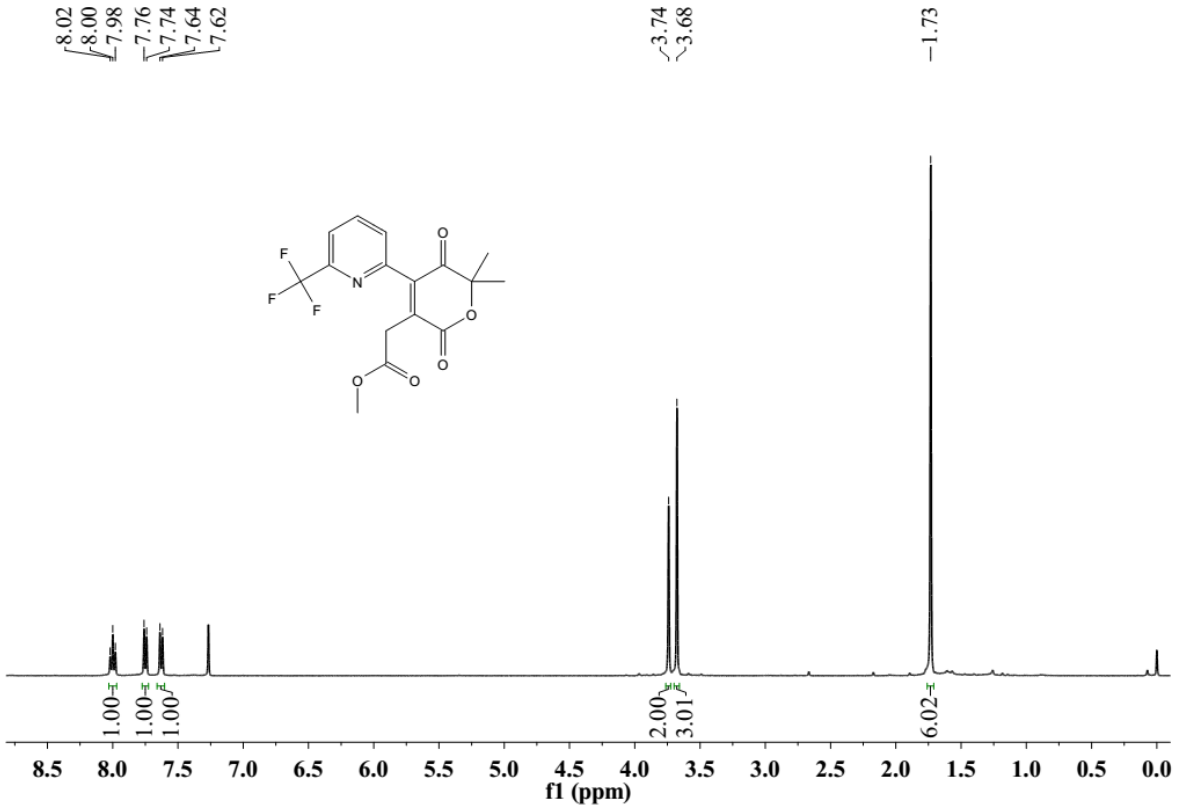

194.9
169.4
161.8
151.3
150.2
141.1
139.2
138.9
125.0
124.5
86.7
77.3
77.0
76.7
52.5
34.8
26.4
f1 (ppm)

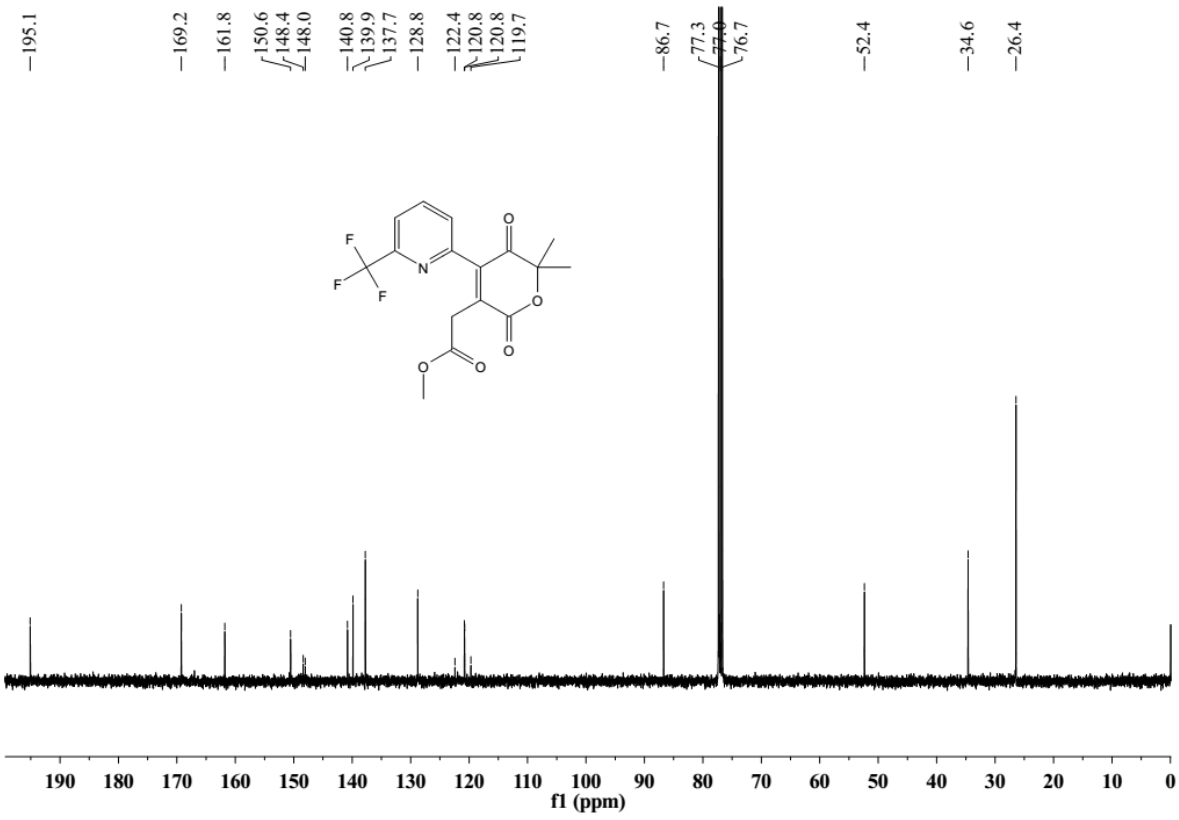
4l$_4$


7.68
7.66
7.64
7.56
7.54
7.40
7.38
3.71
1.71
Br
N
O
O
O
O
O
1.00
1.00
1.00
5.02
6.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

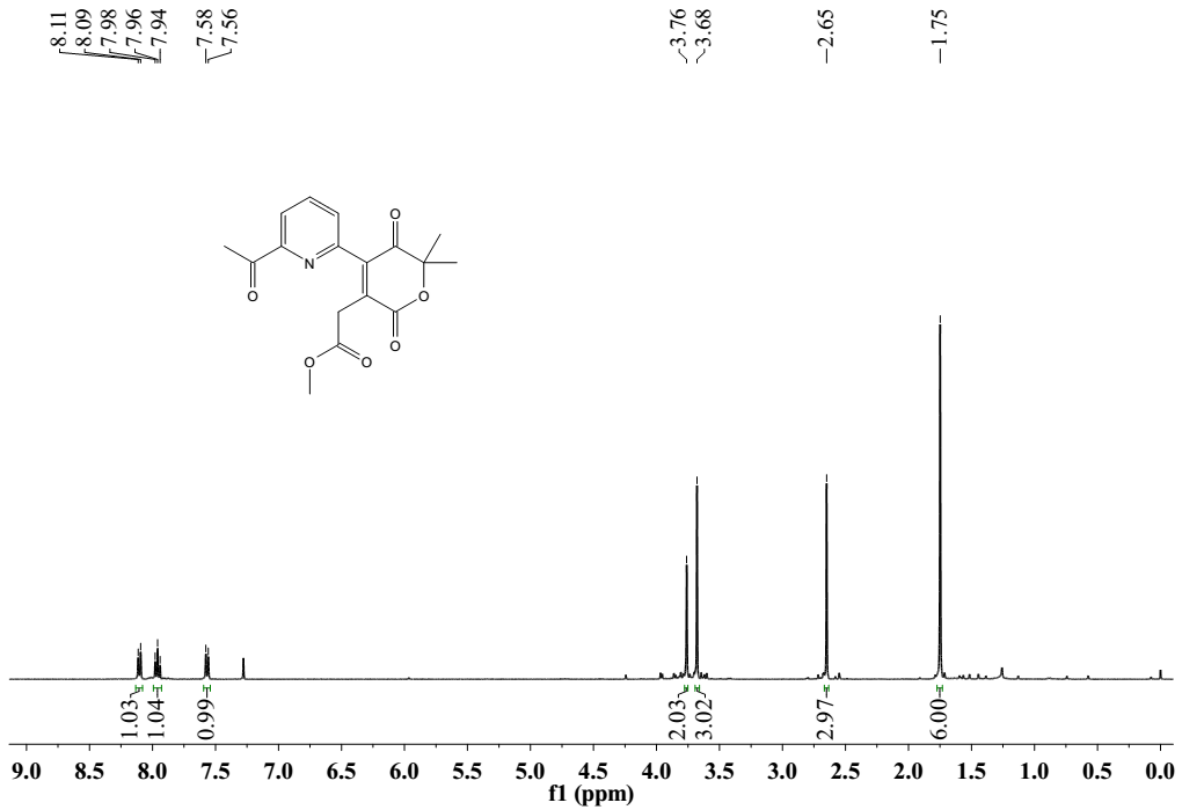

194.9
169.4
161.8
150.6
141.7
140.9
139.3
138.5
128.8
124.9
86.7
77.3
77.0
76.7
52.5
34.7
26.4
Br
N
O
O
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

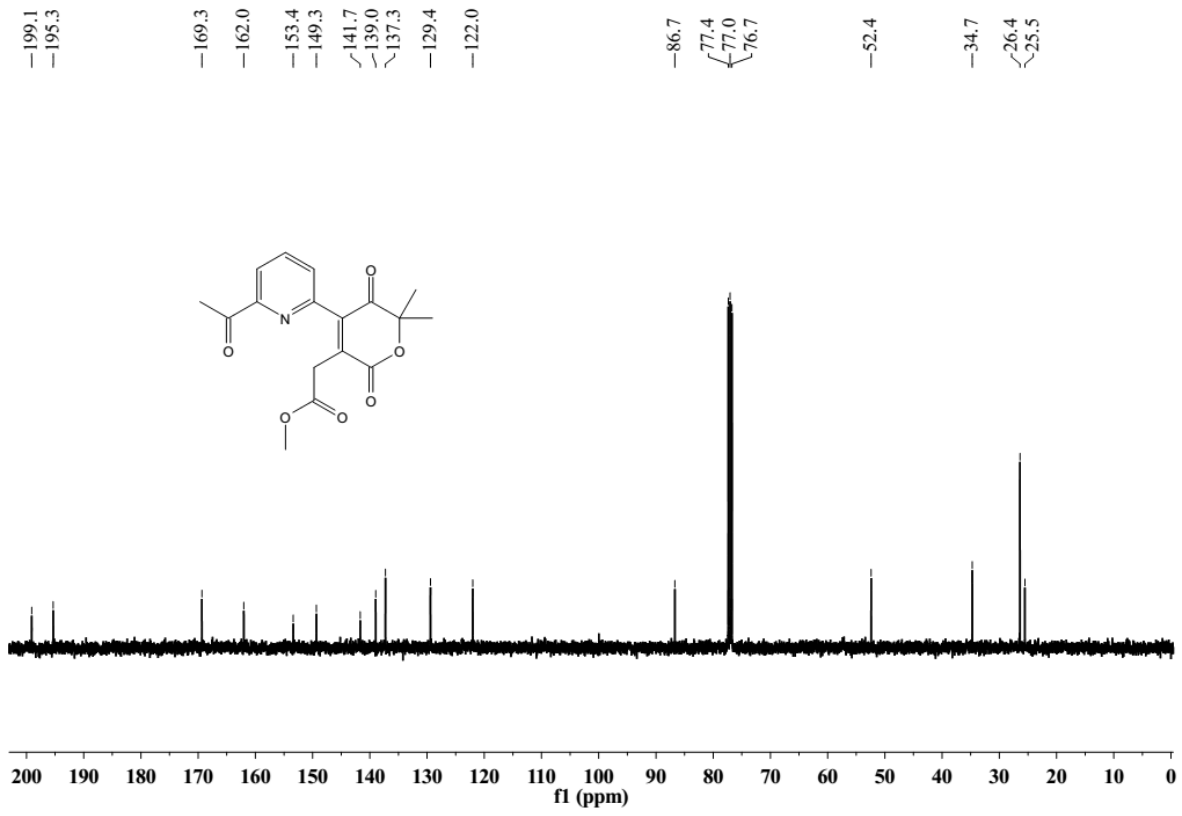
4l$_5$


8.02
8.00
7.98
7.76
7.74
7.64
7.62
3.74
3.68
1.73
1.00
1.00
1.00
2.00
3.01
6.02
f1 (ppm)

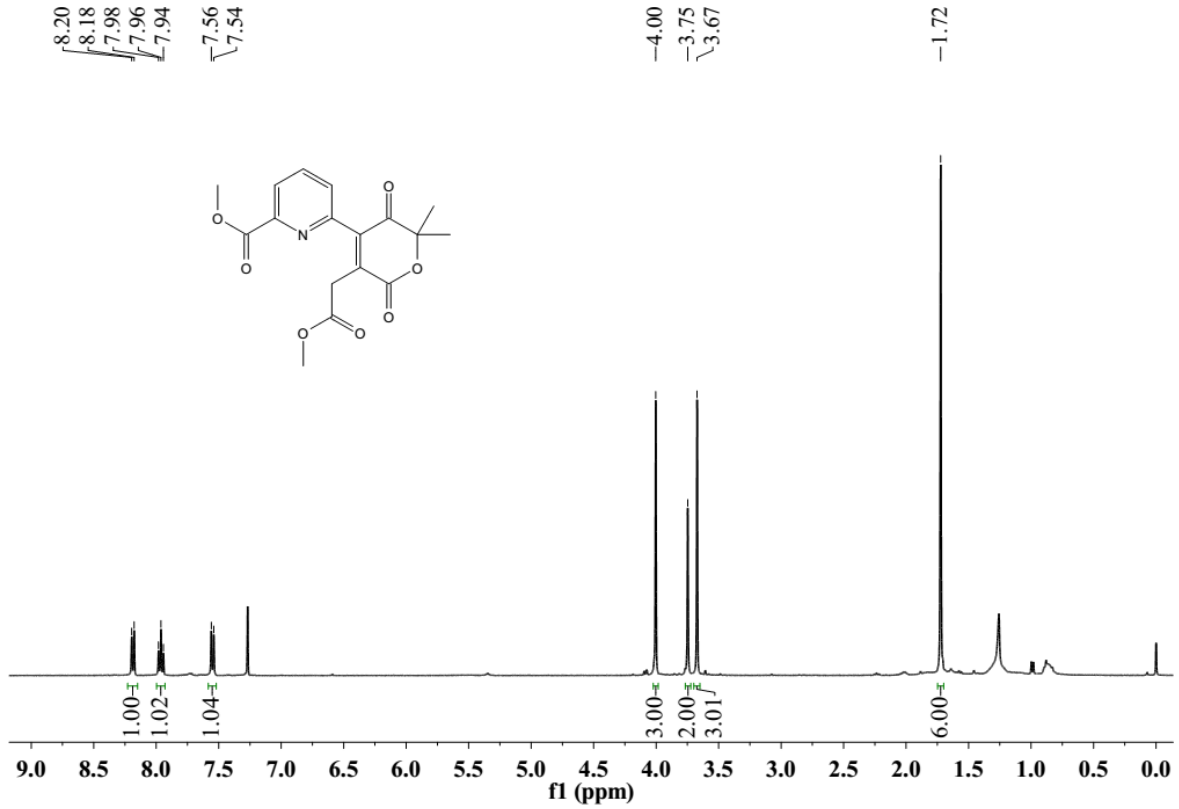

195.1
169.2
161.8
150.6
148.4
148.0
140.8
139.9
137.7
128.8
122.4
120.8
120.8
119.7
86.7
77.3
77.0
76.7
52.4
34.6
26.4
f1 (ppm)

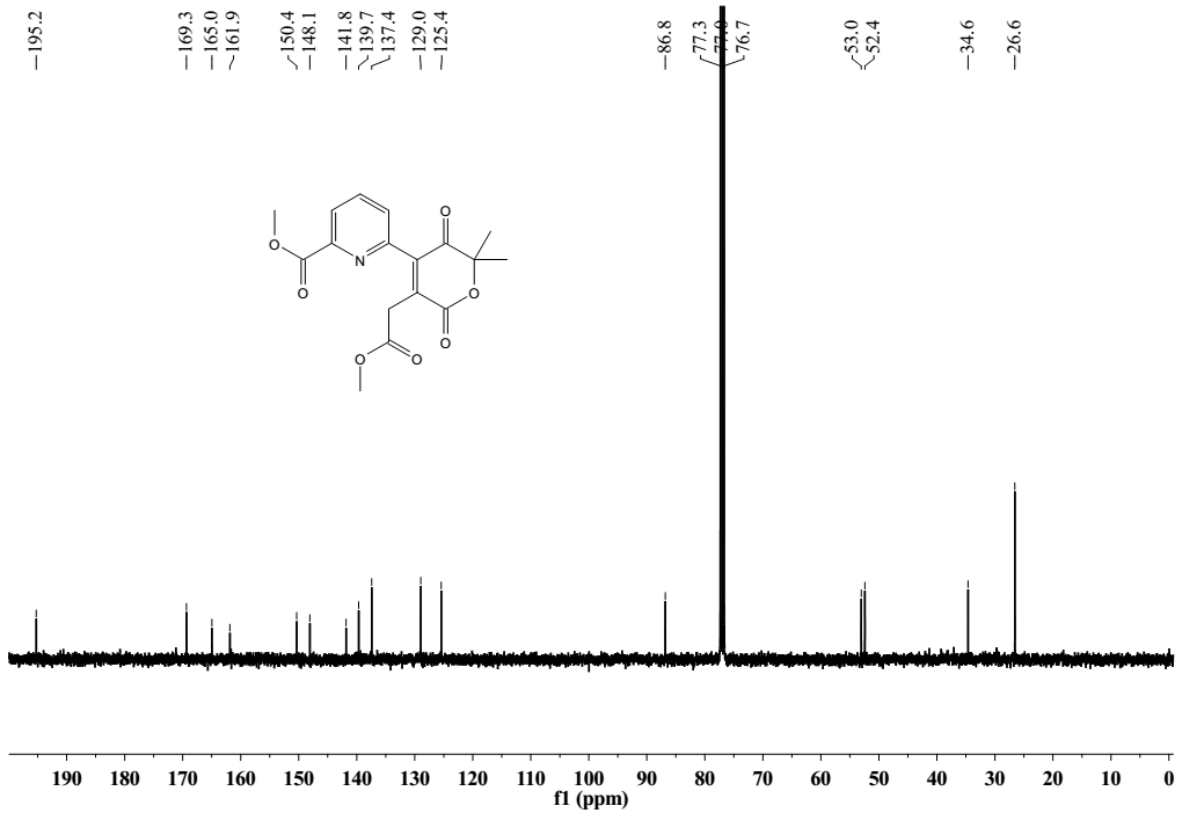
4l$_6$


8.11
8.09
7.98
7.96
7.94
7.58
7.56
3.76
3.68
2.65
1.75
1.03
1.04
0.99
2.03
3.02
2.97
6.00
f1 (ppm)

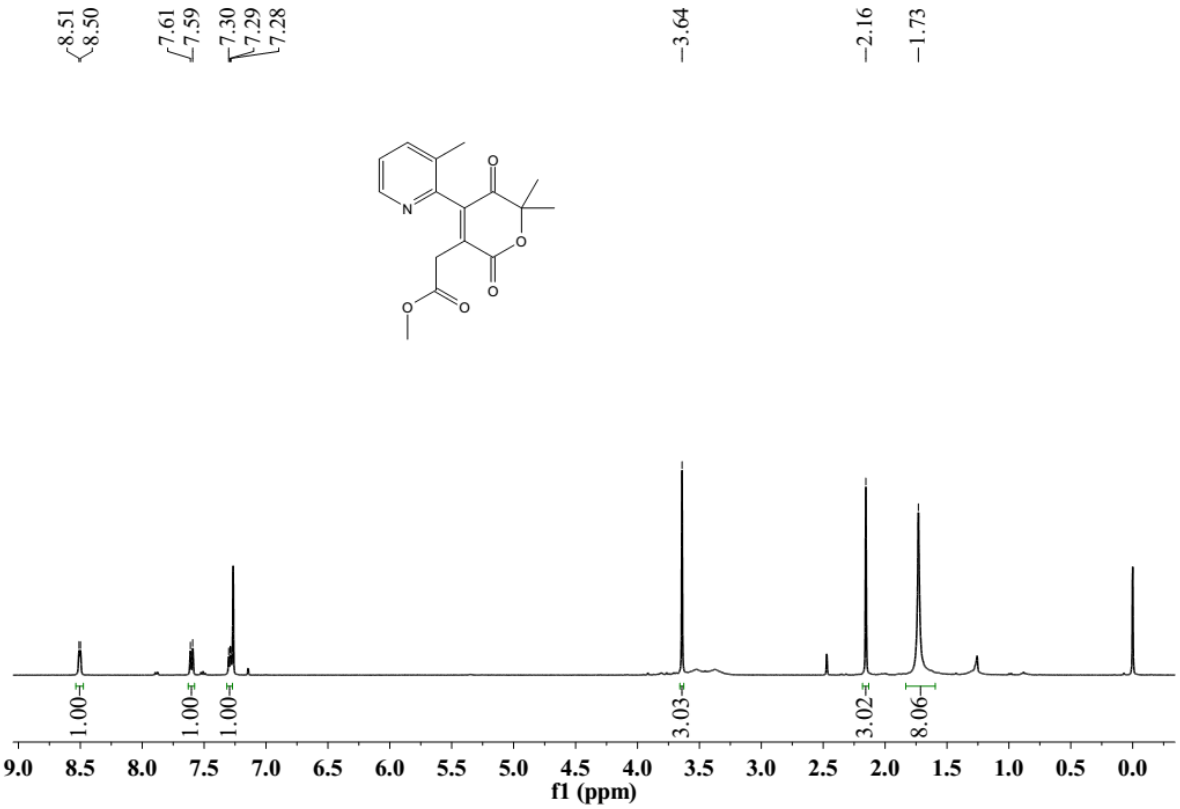

199.1
195.3
169.3
162.0
153.4
149.3
141.7
139.0
137.3
129.4
122.0
86.7
77.4
77.0
76.7
52.4
34.7
26.4
25.5
f1 (ppm)

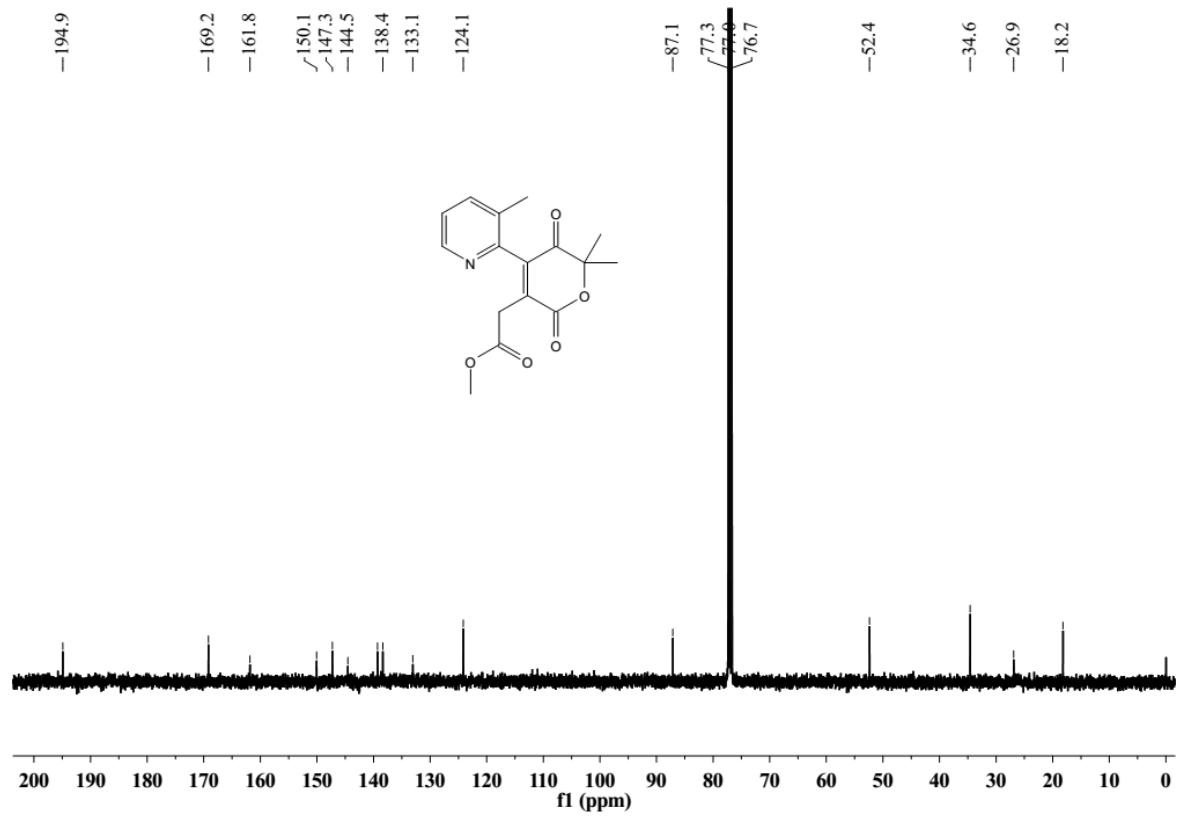
4l$_7$


8.20
8.18
7.98
7.96
7.94
7.56
7.54
4.00
3.75
3.67
1.72
1.00
1.02
1.04
3.00
2.00
3.01
6.00
f1 (ppm)

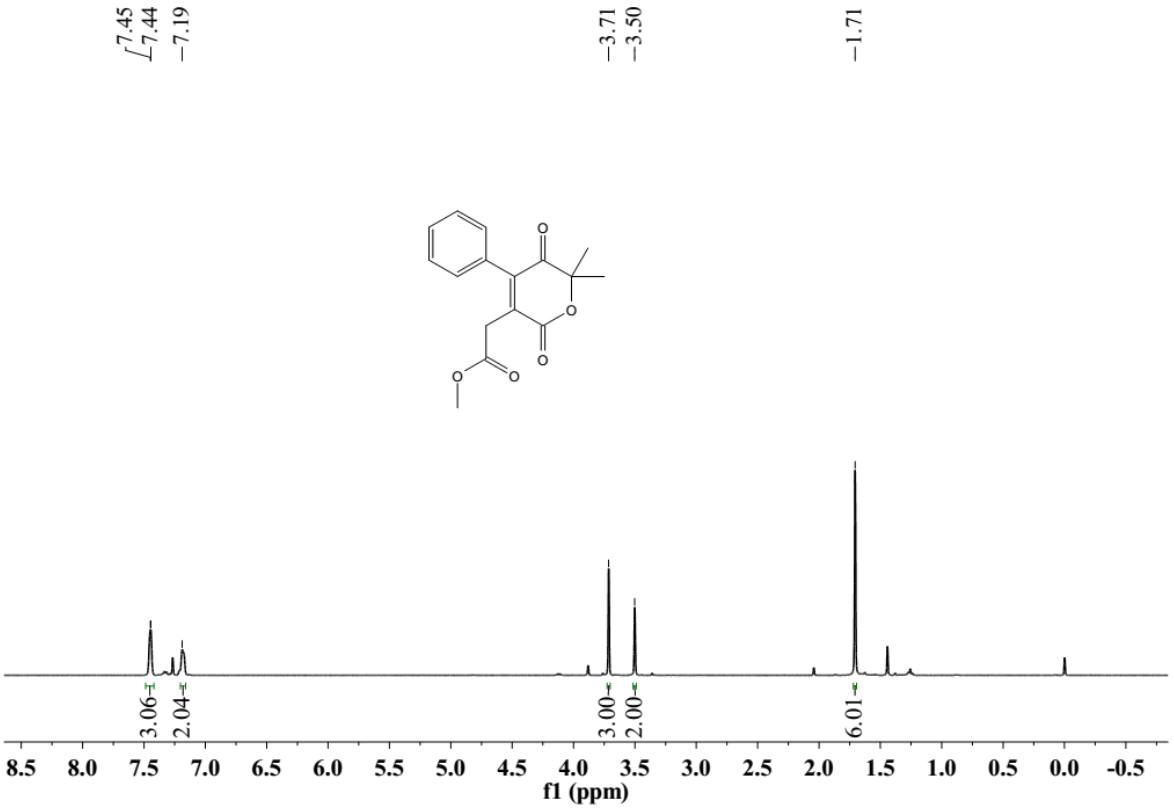

195.2
169.3
165.0
161.9
150.4
148.1
141.8
139.7
137.4
129.0
125.4
86.8
77.3
76.7
53.0
52.4
34.6
26.6
f1 (ppm)

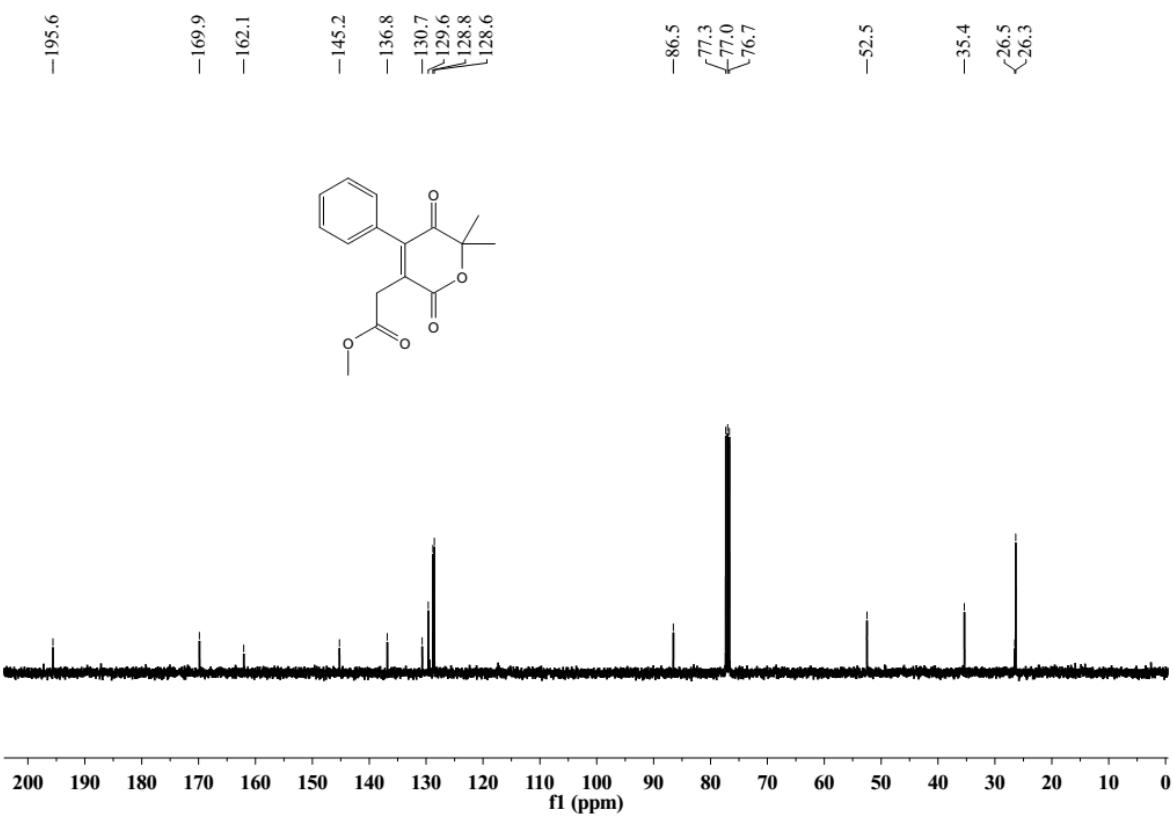
4m


8.51
8.50
7.61
7.59
7.30
7.29
7.28
3.64
2.16
1.73
1.00
1.00
1.00
3.03
3.02
8.06
f1 (ppm)

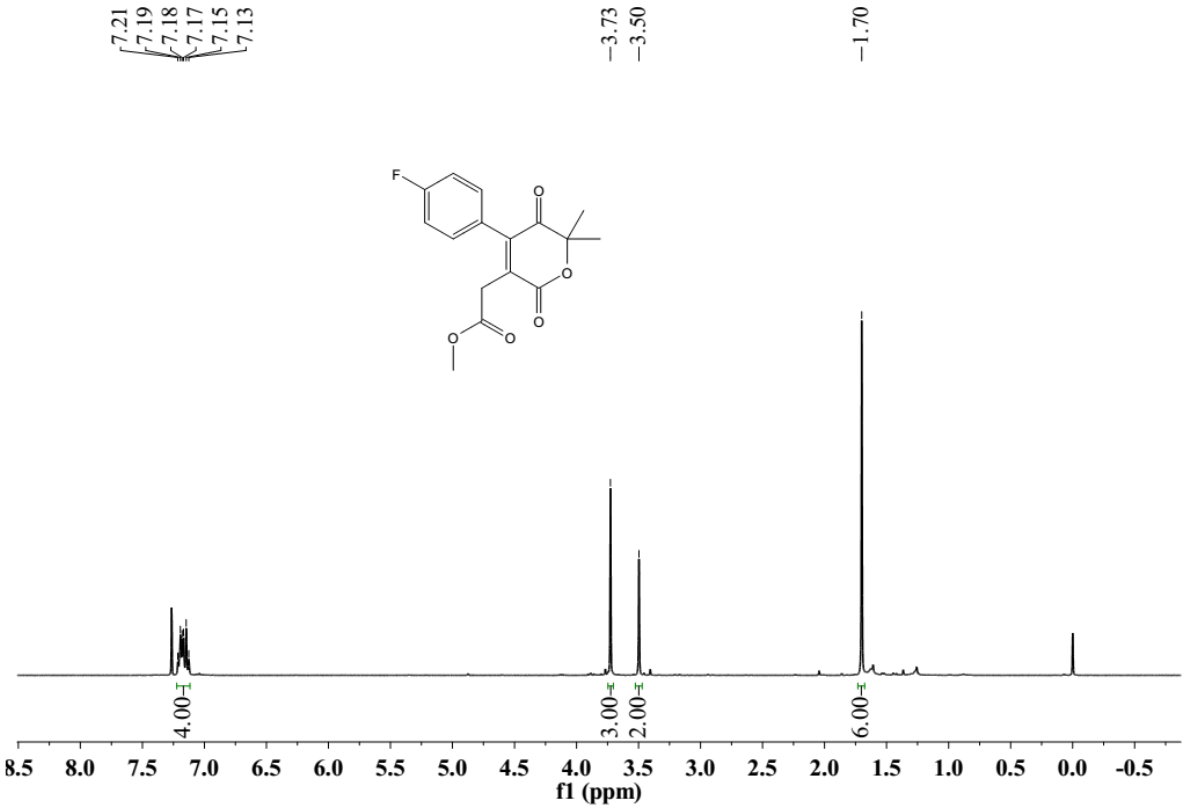

194.9
169.2
161.8
150.1
147.3
144.5
138.4
133.1
124.1
87.1
77.3
76.7
52.4
34.6
26.9
18.2
f1 (ppm)

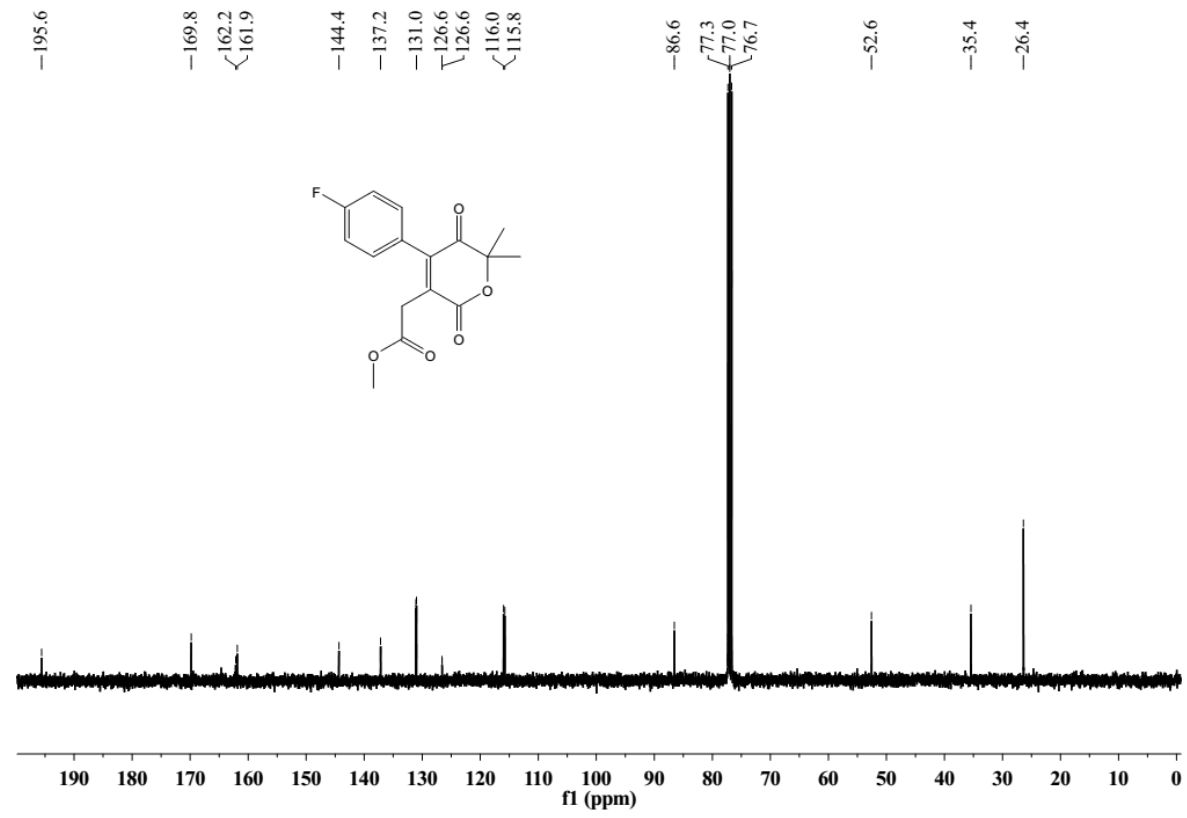
$4n_1$


7.45
7.44
7.19
3.71
3.50
1.71
3.06
2.04
3.00
2.00
6.01
f1 (ppm)

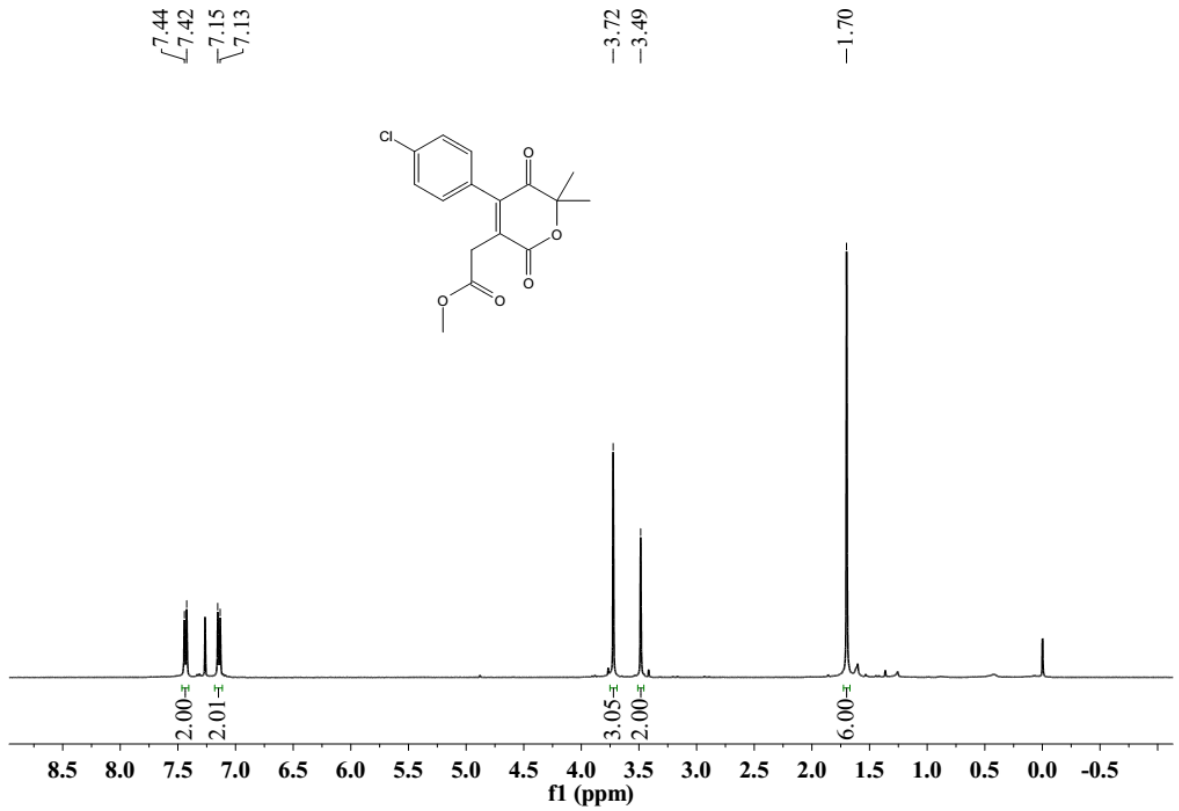

195.6
169.9
162.1
145.2
136.8
130.7
129.6
128.8
128.6
86.5
77.3
77.0
76.7
52.5
35.4
26.5
26.3
f1 (ppm)

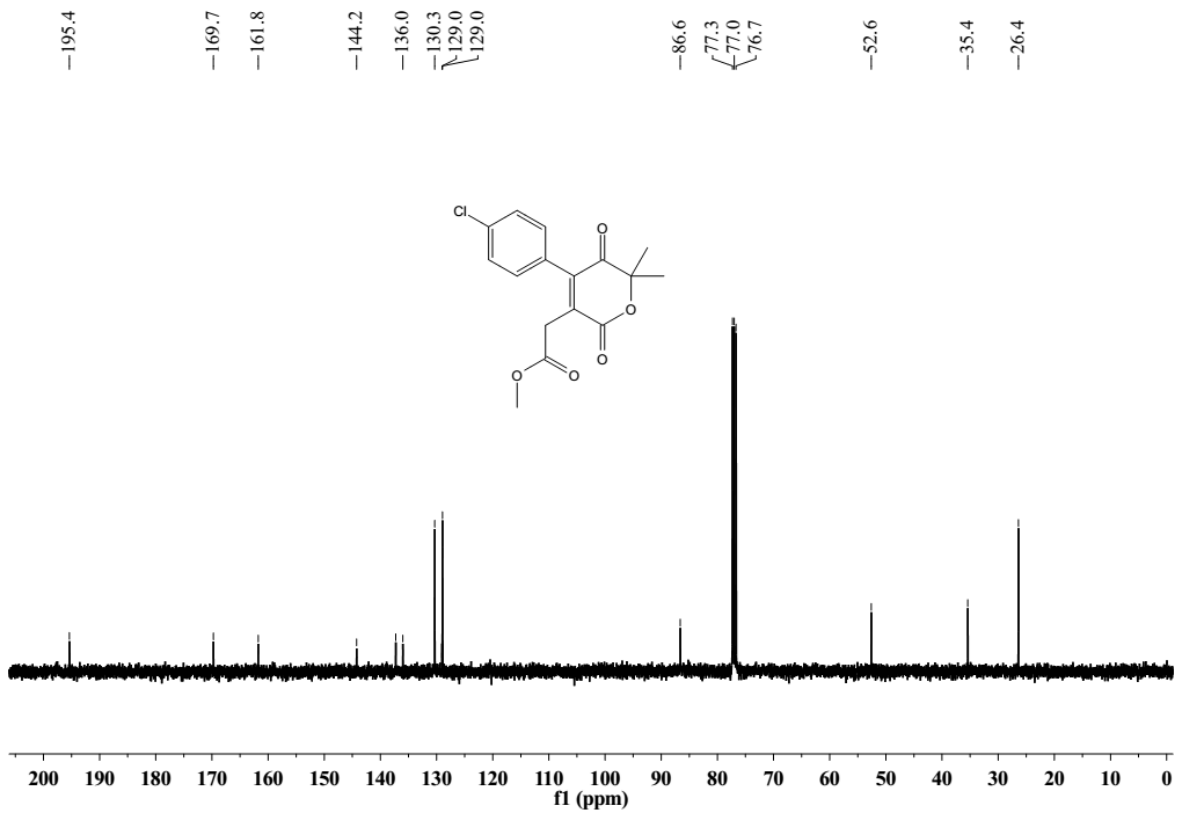
$4n_2$


7.21
7.19
7.18
7.17
7.15
7.13
3.73
3.50
1.70
F
O
O
O
O
O
O
4.00
3.00
2.00
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

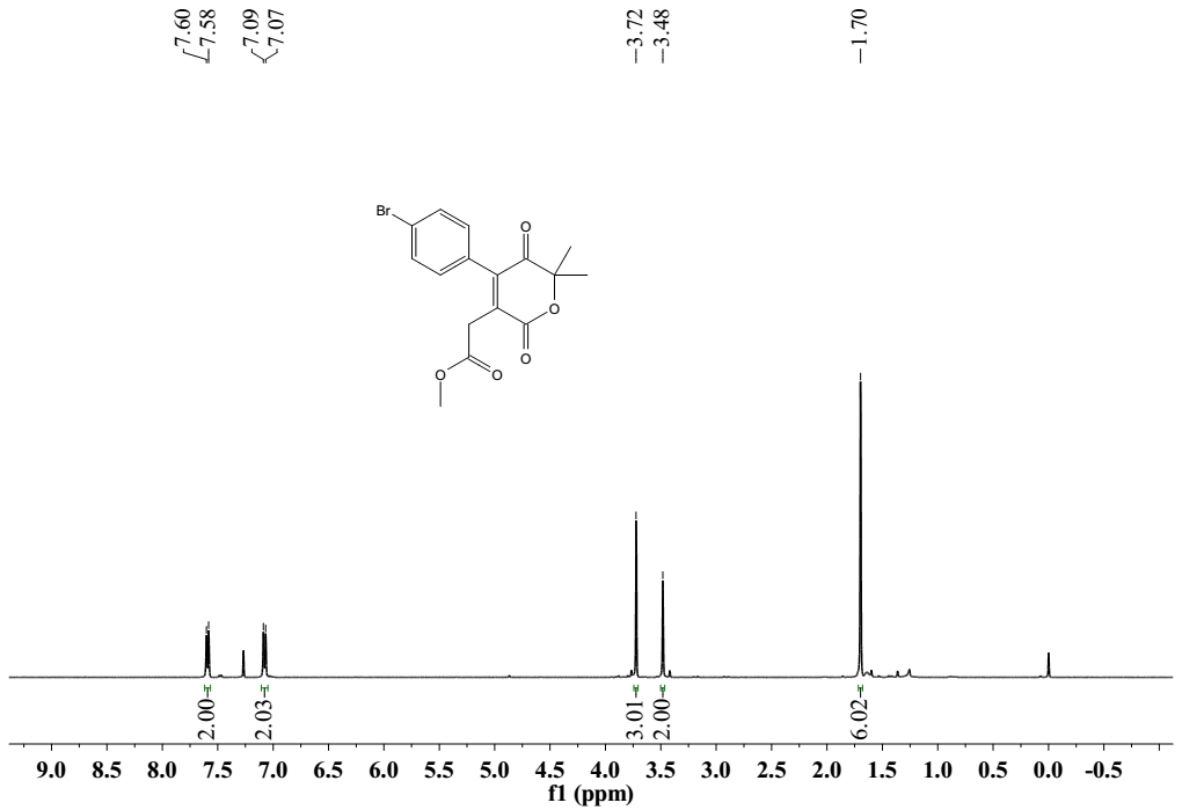

195.6
169.8
162.2
161.9
144.4
137.2
131.0
126.6
126.6
116.0
115.8
86.6
77.3
77.0
76.7
52.6
35.4
26.4
F
O
O
O
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

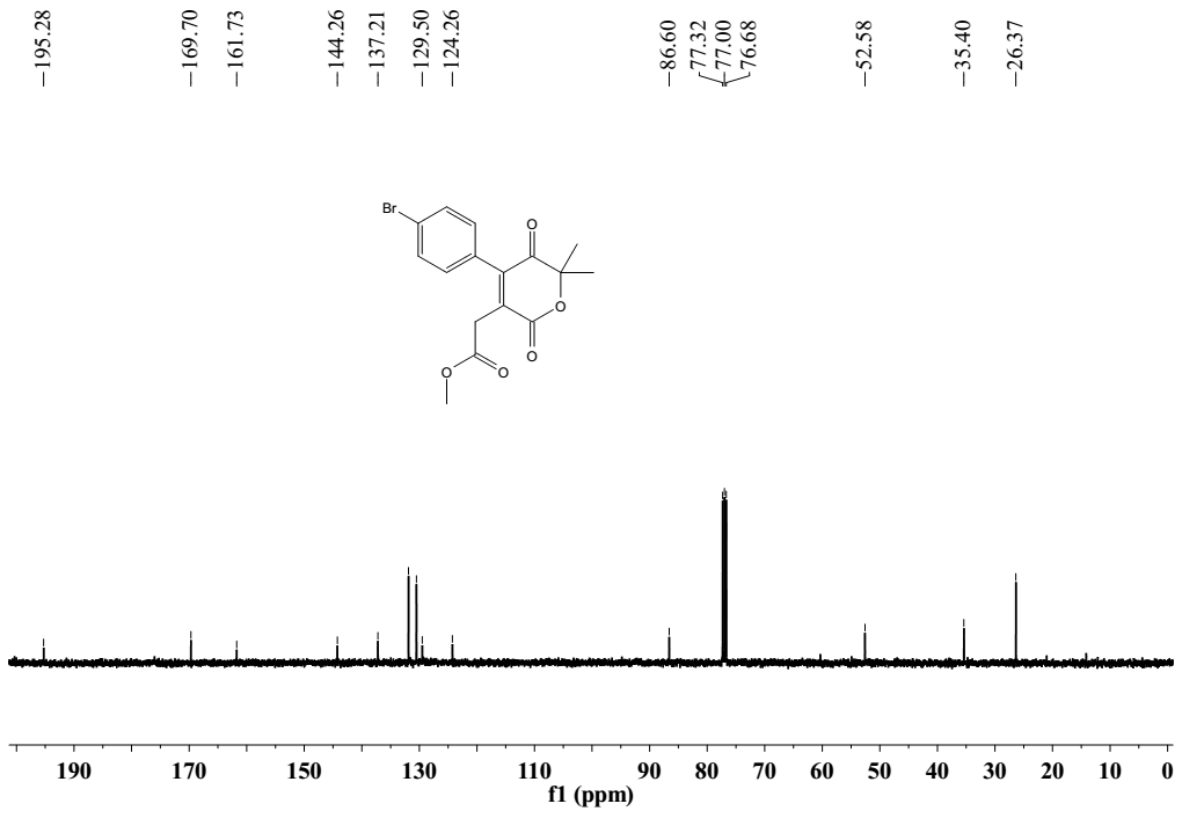
$4n_3$


7.44
7.42
7.15
7.13
3.72
3.49
1.70
Cl
O
O
O
O
O
2.00
2.01
3.05
2.00
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

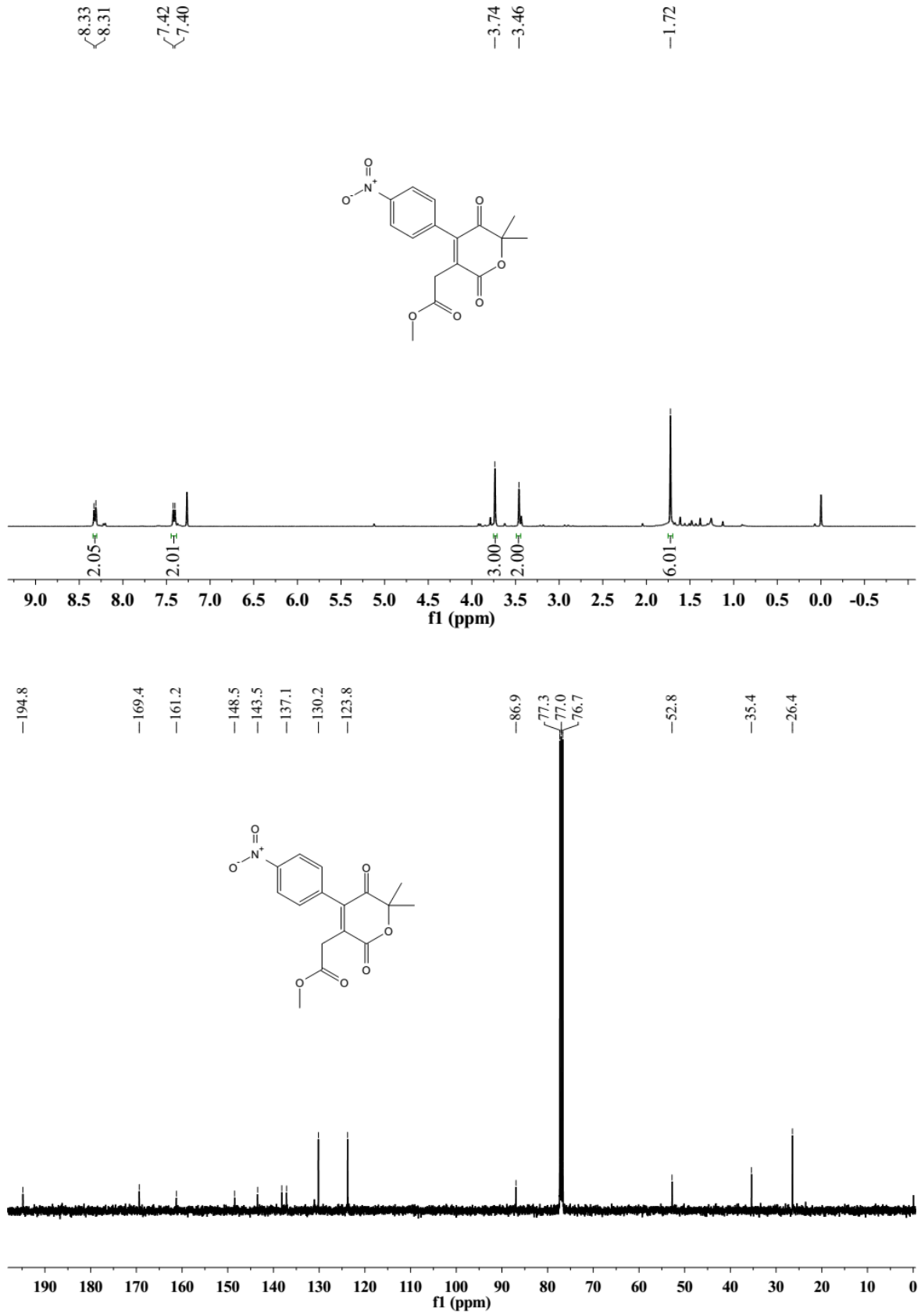

195.4
169.7
161.8
144.2
136.0
130.3
129.0
129.0
86.6
77.3
77.0
76.7
52.6
35.4
26.4
Cl
O
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4n$_4$

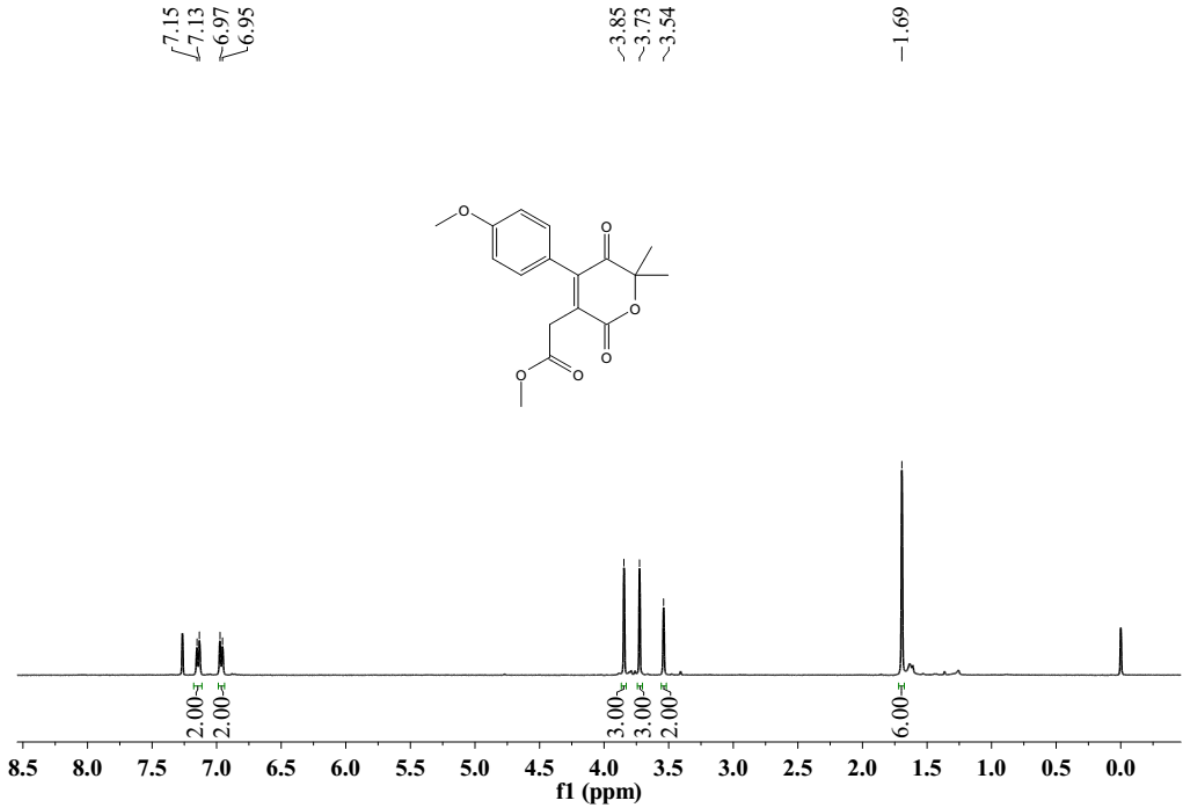

7.60
7.58
7.09
7.07
3.72
3.48
1.70
Br
O
O
O
O
O
O
2.00
2.03
3.01
2.00
6.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

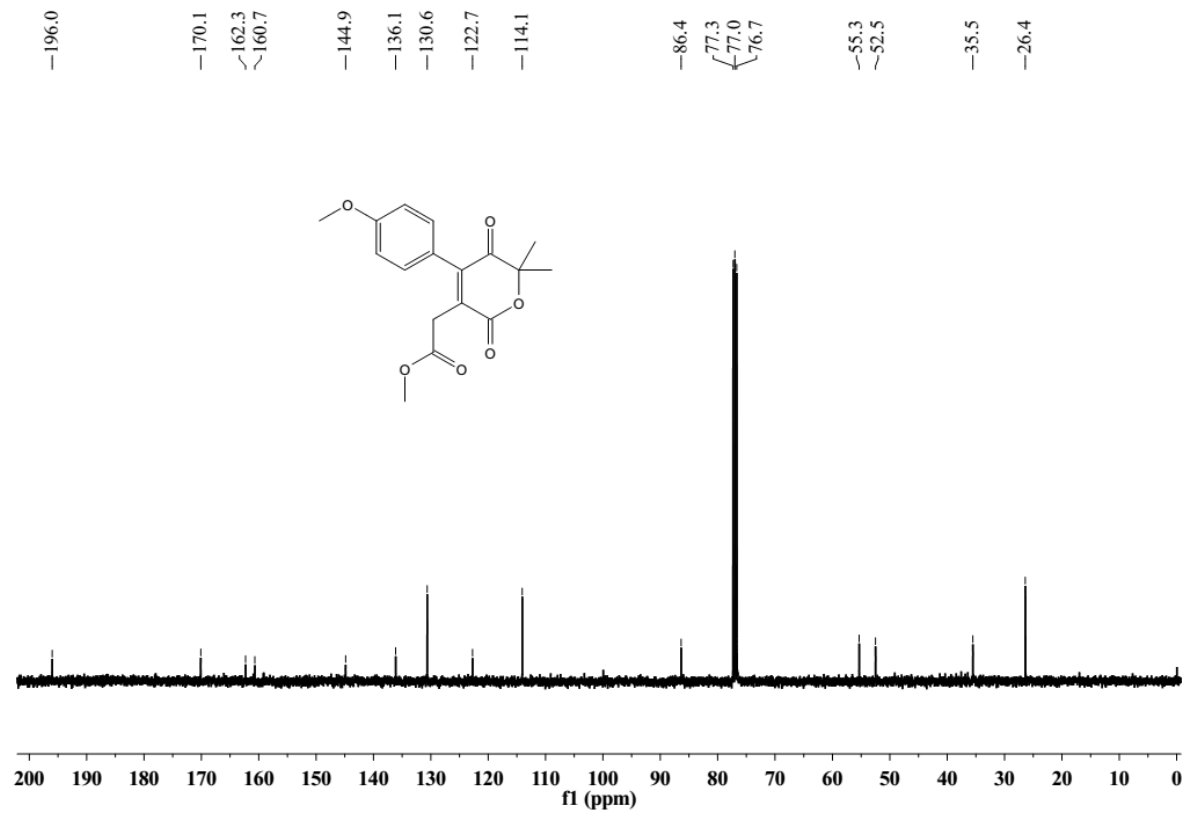

195.28
169.70
161.73
144.26
137.21
129.50
124.26
86.60
77.32
77.00
76.68
52.58
35.40
26.37
Br
O
O
O
O
O
O
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

$4n_5$

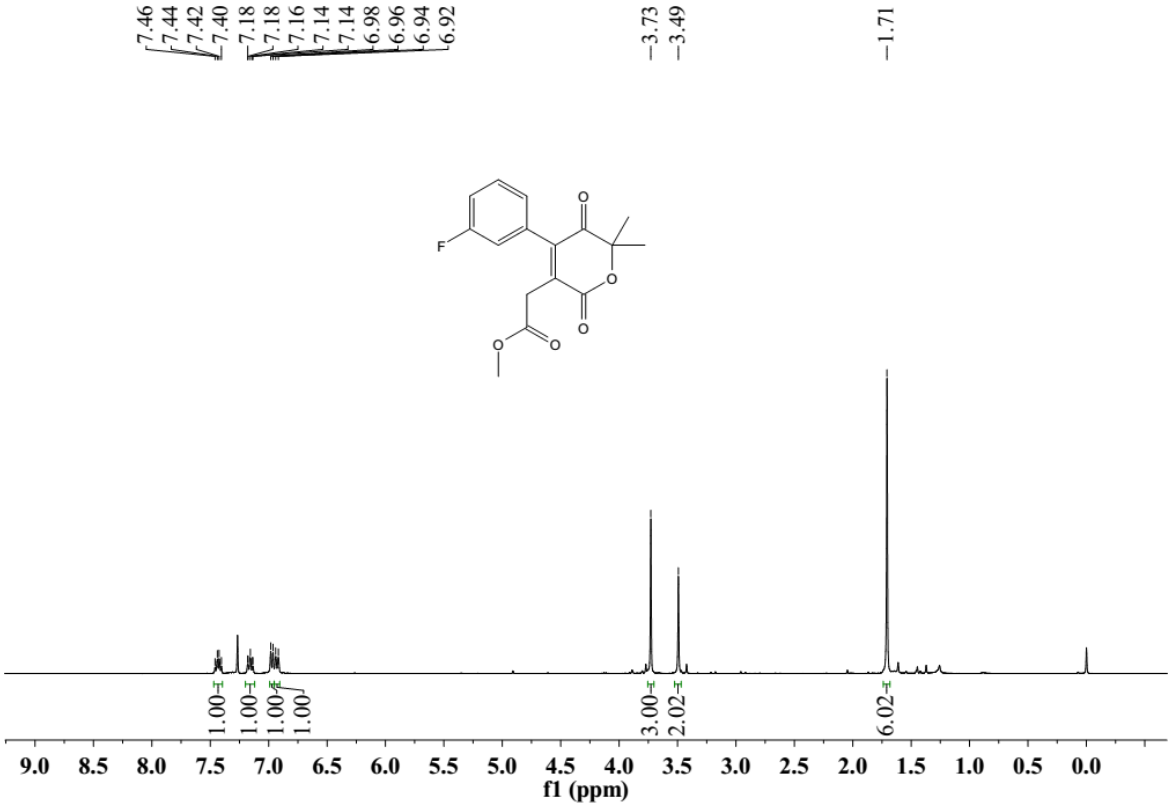

8.33
8.31
7.42
7.40
3.74
3.46
1.72
2.05
2.01
3.00
2.00
6.01
f1 (ppm)
194.8
169.4
161.2
148.5
143.5
137.1
130.2
123.8
86.9
77.3
77.0
76.7
52.8
35.4
26.4
f1 (ppm)

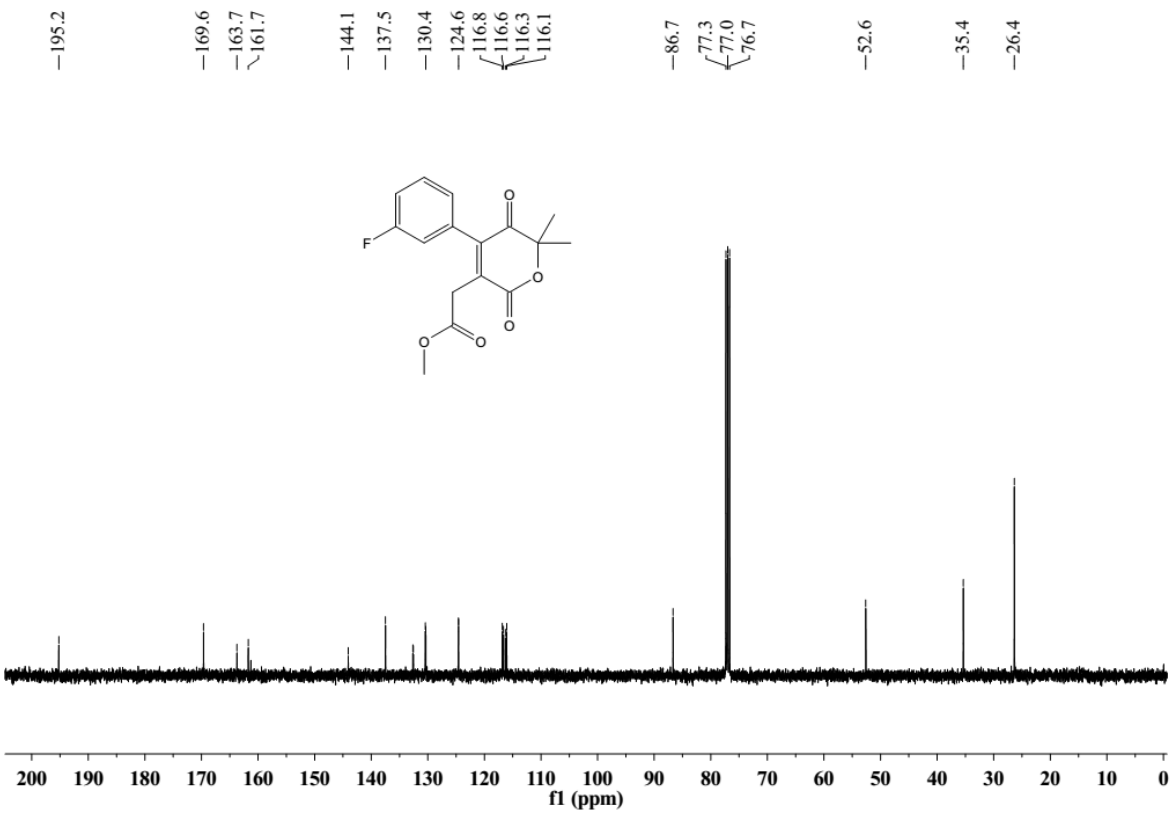
4n$_6$


7.15
7.13
6.97
6.95
3.85
3.73
3.54
1.69
2.00
2.00
3.00
3.00
2.00
6.00
f1 (ppm)

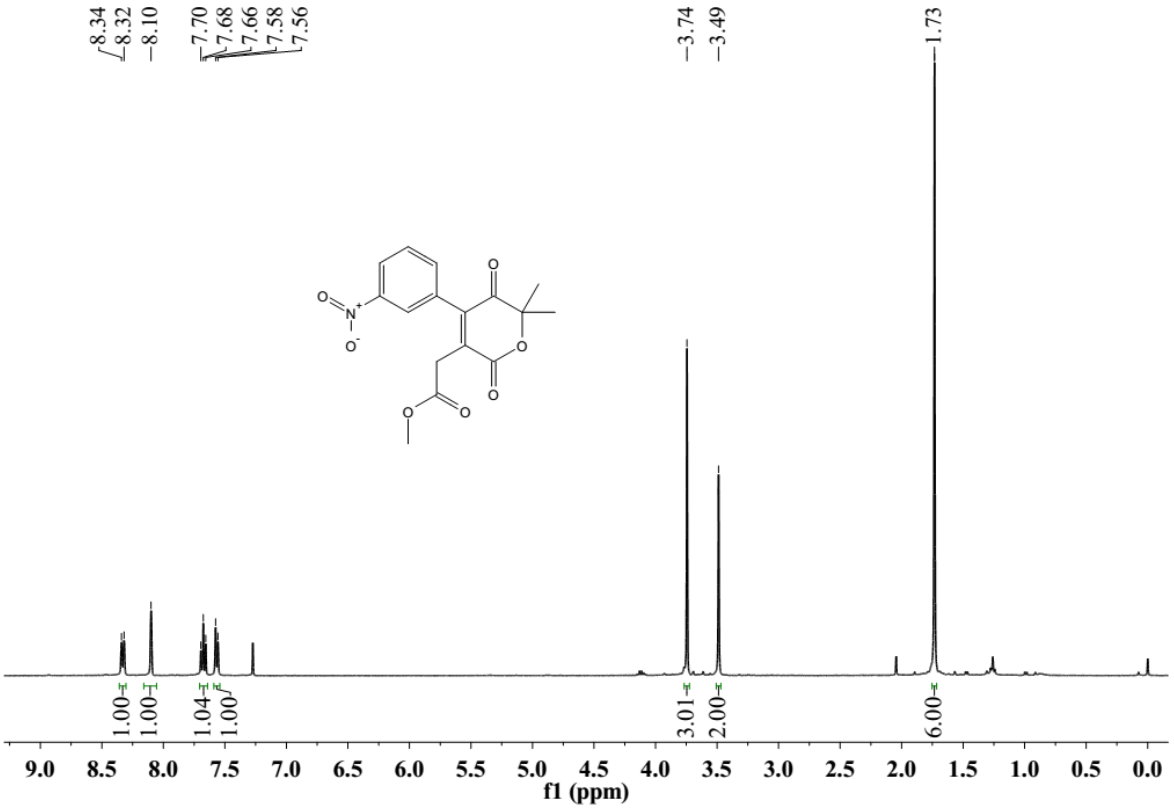

196.0
170.1
162.3
160.7
144.9
136.1
130.6
122.7
114.1
86.4
77.3
77.0
76.7
55.3
52.5
35.5
26.4
f1 (ppm)

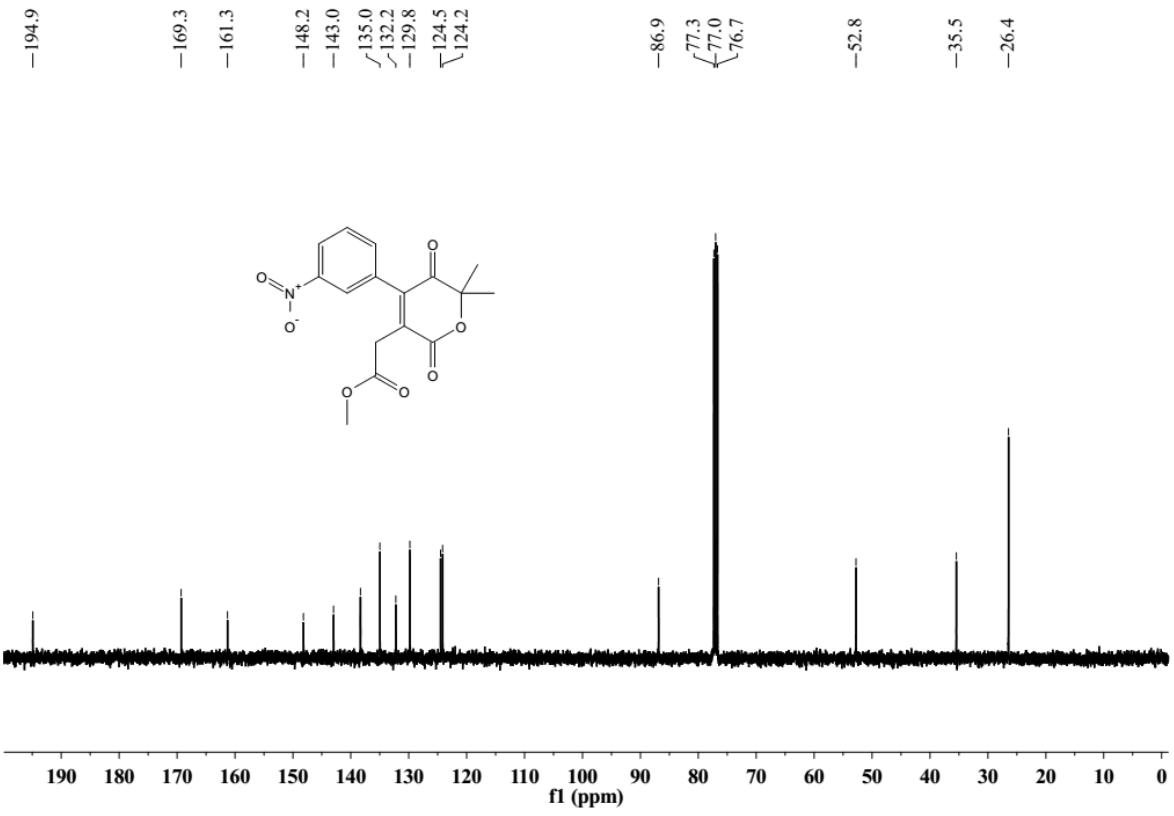
4n$_7$


7.46
7.44
7.42
7.40
7.18
7.18
7.16
7.14
7.14
6.98
6.96
6.94
6.92
3.73
3.49
1.71
F
O
O
O
O
O
1.00
1.00
1.00
1.00
3.00
2.02
6.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

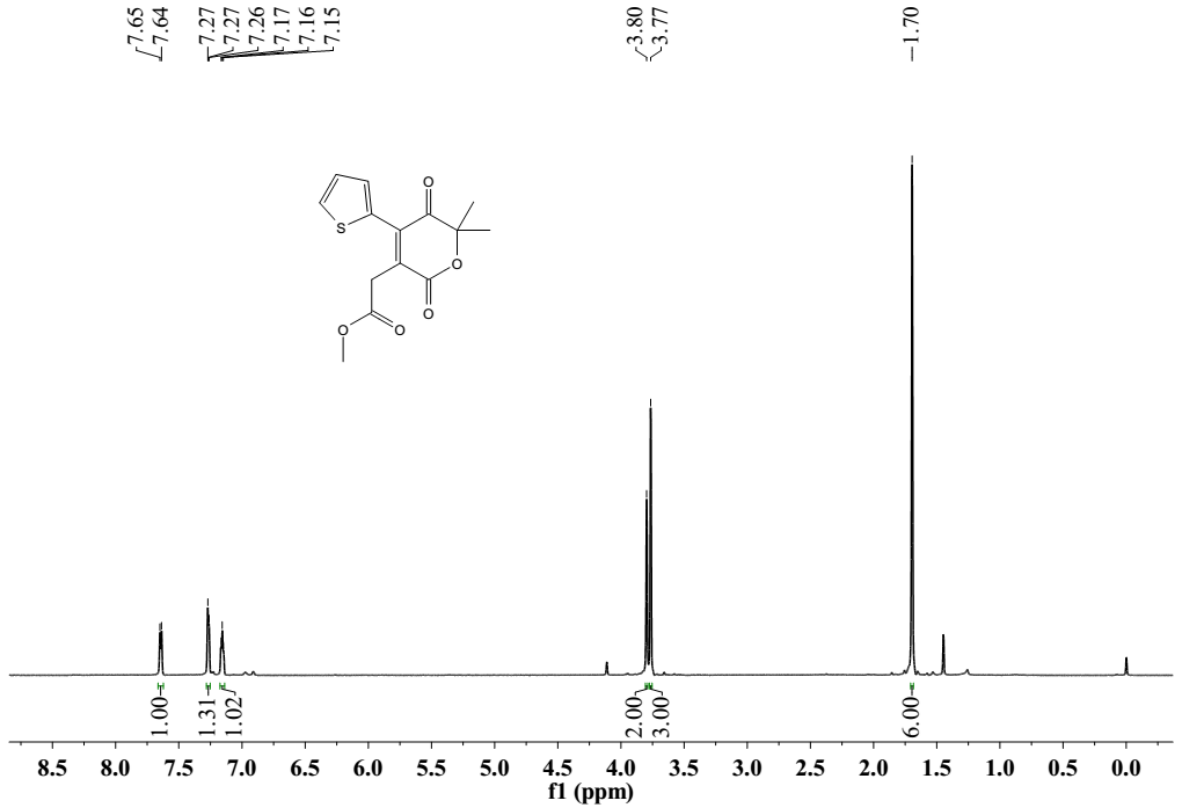

195.2
169.6
163.7
161.7
144.1
137.5
130.4
124.6
116.8
116.6
116.3
116.1
86.7
77.3
77.0
76.7
52.6
35.4
26.4
F
O
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

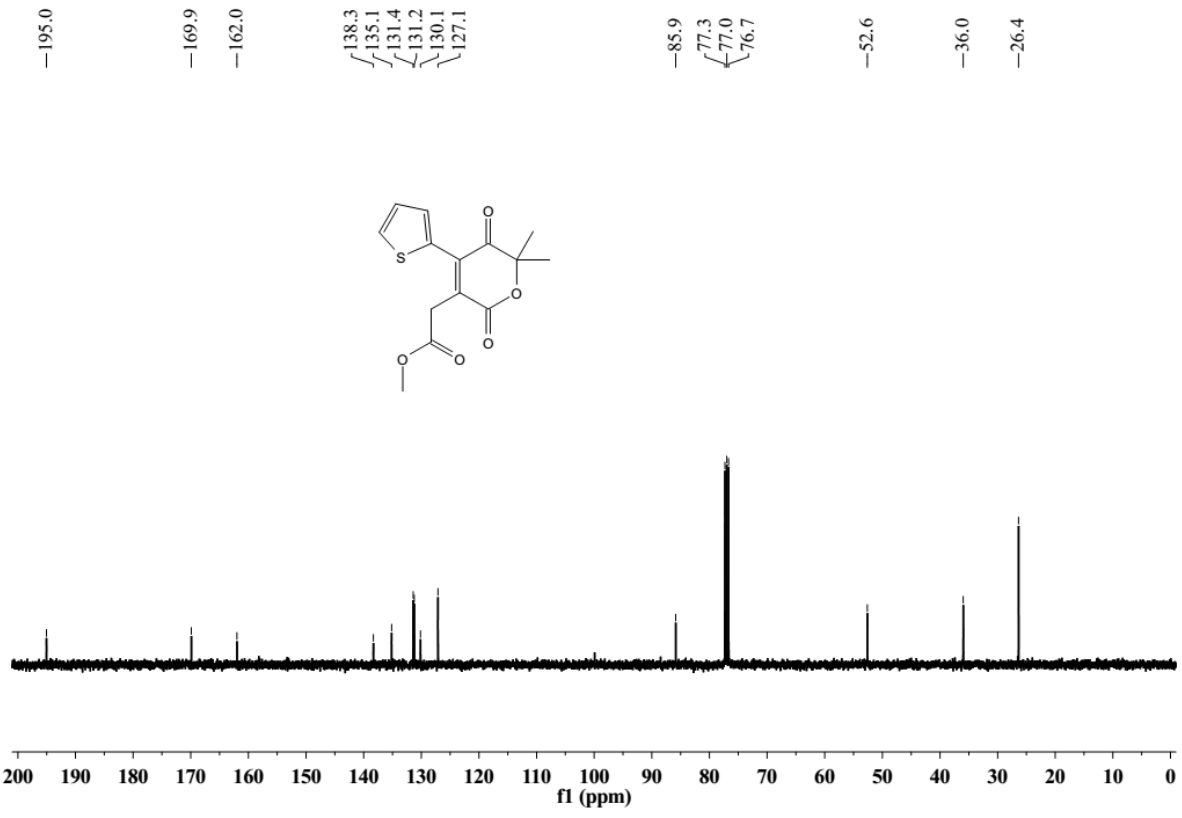
4n$_8$


8.34
8.32
8.10
7.70
7.68
7.66
7.58
7.56
3.74
3.49
1.73
1.00
1.00
1.04
1.00
3.01
2.00
6.00
f1 (ppm)


194.9
169.3
161.3
148.2
143.0
135.0
132.2
129.8
124.5
124.2
86.9
77.3
77.0
76.7
52.8
35.5
26.4
f1 (ppm)

4o


7.65
7.64
7.27
7.27
7.26
7.17
7.16
7.15
3.80
3.77
1.70
1.00
1.31
1.02
2.00
3.00
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.0
169.9
162.0
138.3
135.1
131.4
131.2
130.1
127.1
85.9
77.3
77.0
76.7
52.6
36.0
26.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)