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Supporting information

Single step incorporation of isatin to enaminone: a recyclable catalyst towards assembly of diverse four ring fused pyrrolo[2,3,4-*kl*]acridin-1-ones

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Materials and Methods. The reagents were purchased from Aladdin and Aldrich and were not purified before use. Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF254 plates. Melting points were measured on an X-4 melting point apparatus. ^{1}HNMR spectra were recorded on a 400 MHz instrument (Bruker Avance 400 Spectrometer). Chemical shifts (δ) are given in ppm relative to TMS as the internal reference, with coupling constants (J) in Hz. ^{13}C NMR spectra were recorded at 100 MHz. Chemical shift were reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Elemental analysis was carried out on EuroEA elemental analyzer.

Preparation and characterization of the carbonaceous material (C-SO_3H) catalyst

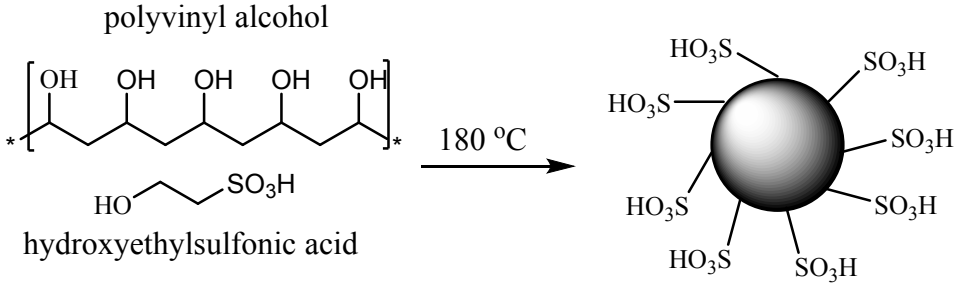


Fig. 1. The preparation of the carbon functinalized material

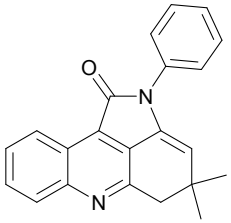
According to literature method,[1] the polyvinyl alcohol (5.0 g), hydroxyethylsulfuric acid (3.5 g) and deionized water (50 mL) was mixed in Teflon-lined stainless steel autoclaves, which was heated at 180 °C for 4 h. Then, the resulting mixture were filtered, washed with water and methanol, and dried in a vacuum oven at 100 °C for 4 h. The goal product was obtained as black solid with 50% yield according to polyvinyl alcohol (Fig. 1).

The acidity of the sulfonated carbonaceous materials was 2.4 mmol/g by neutralization titration. According to XPS analysis, the S content of 7.6% indicated almost all the S existed in the forms of sulfonic acid groups and the O content was as high as 24% indicated that many oxygen-containing groups besides the carbonyl acid groups were exist. The BET surface of the solid acid was 146 m^2/g. The 1040 and 1195 cm^{-1} absorbability of IR spectra indicated the existence of the sulfuric acid groups. FT-IR spectra showed that the sulfonated carbonaceous materials contains resident functionalities such as hydroxyl (3500 cm^{-1}), carboxylate (1704 cm^{-1}), C=C groups (1604 cm^{-1}) and C-O groups (1204 cm^{-1}).

General procedure for the synthesis of 3

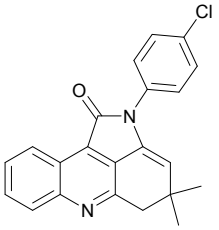
Enaminone (1.0 mmol) was introduced in a 10-mL reaction vial, isatin (1.0 mmol) and carbonaceous material (10 mg), and water (3 mL), were then successively added. Then, the reaction vial was closed and stirred on an oil bath at 80 ^{o}C for the appropriate time. The mixture was stirred until TLC revealed that the conversion of the starting material was complete. Then, the mixture was cooled to room temperature and the catalyst and the product were filtered. The filtered solid catalyst was washed with water and methanol, and dried in vacuum oven at 100 ^{o}C for 4 h. The resulting solution was concentrated and recrystallized from EtOH (95%) to give the pure products.

Spectral data of the compounds



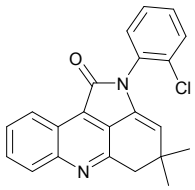
4,4-dimethyl-2-phenyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3a)

Yellow solid; mp 187-188 ^{o}C (lit:[2] mp 188-190 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, 1H, J = 7.2 Hz, ArH), 8.19 (d, 1H, J = 8.4 Hz, ArH), 7.76-7.80 (m, 1H, ArH), 7.68 (t, 1H, J = 7.2 Hz, ArH), 7.51-7.58 (m, 4H, ArH), 7.42 (t, 1H, J = 7.2 Hz, ArH), 5.64 (s, 1H, CH), 3.23 (s, 2H, CH_2), 1.34 (s, 6H, CH_3).



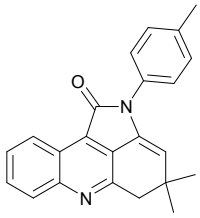
2-(4-chlorophenyl)-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3b)

Yellow solid; mp 178-180 ^{o}C (lit:[2] mp 182-183 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, 1H, J = 8.0 Hz, ArH), 8.32 (d, 1H, J = 8.4 Hz, ArH), 7.82 (t, 1H, J = 7.6 Hz, ArH), 7.73 (t, 1H, J = 7.2 Hz, ArH), 7.54 (d, 2H, J = 8.8 Hz, ArH), 7.47 (d, 2H, J = 8.8 Hz, ArH), 5.66 (s, 1H, CH), 3.32 (s, 2H, CH_2), 1.36 (s, 6H, CH_3).



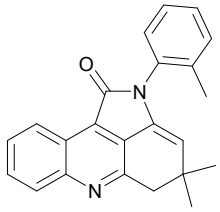
2-(2-chlorophenyl)-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3c)

Yellow solid; mp 137-138 °C (lit:[3] mp 136-138 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, 1H, J = 8.0 Hz, ArH), 8.19 (d, 1H, J = 8.4 Hz, ArH), 7.77 (t, 1H, J = 7.2 Hz, ArH), 7.68 (t, 1H, J = 7.6 Hz, ArH), 7.61-7.63 (m, 1H, ArH), 7.44-7.47 (m, 3H, ArH), 5.29 (s, 1H, CH), 3.23 (d, 2H, J = 1.6 Hz, CH_2), 1.32 (s, 6H, CH_3).



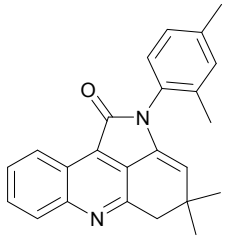
4,4-dimethyl-2-(p-tolyl)-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3d)

Yellow solid; mp 183-184 °C (lit:[4] mp 182-183 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, 1H, J = 8.8 Hz, ArH), 8.56 (d, 1H, J = 7.6 Hz, ArH), 7.86-7.94 (m, 2H, ArH), 7.38-7.46 (m, 4H, ArH), 5.82 (s, 1H, CH), 2.47 (s, 2H, CH_2), 1.53 (s, 6H, CH_3).



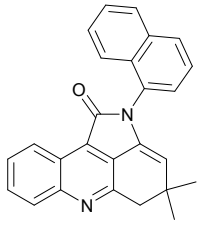
4,4-dimethyl-2-(*o*-tolyl)-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3e)

Yellow solid; mp 118-120 °C (lit:[5] no report); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, 1H, J = 8.4 Hz, ArH), 8.19 (d, 1H, J = 8.4 Hz, ArH), 7.77 (t, 1H, J = 7.2 Hz, ArH), 7.67 (t, 1H, J = 8.0 Hz, ArH), 7.35-7.41 (m, 3H, ArH), 7.30 (s, 1H, ArH), 5.27 (s, 1H, CH) , 3.23 (s, 2H, CH_2), 2.23 (s, 3H, CH_3), 1.32 (d, 6H, J = 6.4 Hz, CH_3).



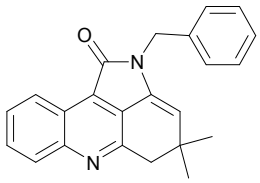
2-(2,4-dimethylphenyl)-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3f)

Yellow solid; mp 137-138 ^{o}C; IR (KBr): 2959, 1700, 1646, 1600, 1509, 1490, 1442, 1342, 1207, 1152, 1086, 1069, 892 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (dd, 1H, J = 2.0, 8.0 Hz, ArH), 8.19 (d, 1H, J = 8.4 Hz, ArH), 7.75-7.79 (m, 1H, ArH), 7.65-7.69 (m, 1H, ArH), 7.25 (s, 1H, ArH), 7.17-7.18 (m, 2H, ArH), 5.27(s, 1H, CH), 3.22 (s, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 1.31 (d, 6H, J = 6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 154.6, 149.7, 139.0, 136.4, 133.9, 132.0, 130.6, 129.5, 129.4, 128.5, 127.6, 127.5, 126.7, 125.3, 124.3, 122.8, 117.8, 44.3, 37.1, 30.8, 31.0, 21.2, 17.9; ESI m/z 355.21 $(M + H)^+$; anal. calcd for $C_{24}H_{22}N_2O$: C, 81.33; H, 6.26; N, 7.90 found: C, 81.30; H, 5.98; N, 8.13%.



4,4-dimethyl-2-(naphthalen-1-yl)-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3g)

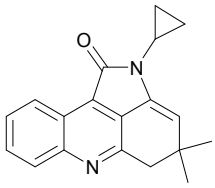
Brown solid; mp 114-116 ^{o}C; IR (KBr): 2956, 1704, 1653, 1603, 1513, 1490, 1445, 1355, 1198, 1089, 1060, 895 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, 1H, J = 8.0 Hz, ArH), 8.23 (d, 1H, J = 8.4 Hz, ArH), 8.01 (t, 2H, J = 8.8 Hz, ArH), 7.78-7.82 (m, 1H, ArH), 7.63-7.71 (m, 3H, ArH), 7.48-7.58 (m, 3H, ArH), 5.23 (s, 1H, CH), 3.26 (s, 2H, CH_2), 1.29 (d, 6H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 134.6, 129.6, 129.4, 128.5, 127.8, 127.1, 127.0, 126.6, 125.6, 124.4, 123.0, 122.8, 118.5, 44.3, 37.1, 30.8, 30.7; ESI m/z 377.20 $(M + H)^+$; anal. calcd for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.36; N, 7.44 found: C, 82.87; H, 5.51; N, 7.49%.



2-benzyl-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3h)

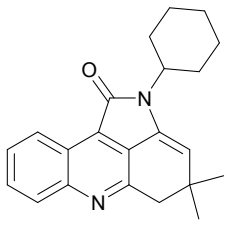
Brown solid; mp 134-136 ^{o}C (lit:[6] mp 136-138 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (dd, 1H, J = 1.2, 8.0 Hz, ArH), 8.15 (d, 1H, J = 8.4 Hz, ArH), 7.73-7.77 (m, 1H,

ArH), 7.64-7.68 (m, 1H, ArH), 7.27-7.37 (m, 5H, ArH), 5.45 (s, 1H, CH), 5.03 (s, 2H, CH_2), 3.15 (s, 2H, CH_2), 1.27 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 134.6, 129.5, 129.4, 128.7, 127.8, 127.3, 127.1, 126.4, 124.2, 117.7, 44.4, 43.8, 37.1, 30.9.



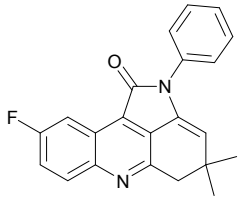
2-cyclopropyl-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3i)

Yellow solid; mp 137-138 ^oC; IR (KBr): 3035, 2941, 1698, 1661, 1467, 1441, 1339, 1153, 793 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.67 (dd, 1H, J = 1.2, 8.0 Hz, ArH), 8.13 (d, 1H, J = 8.4 Hz, ArH), 7.70-7.74 (m, 1H, ArH), 7.61-7.65 (m, 1H, ArH), 5.73 (s, 1H, CH), 3.15 (s, 2H, CH_2), 2.81-2.86 (m, 1H, CH), 1.35 (s, 6H, CH_3), 1.07-1.10 (m, 2H, CH_2), 1.00-1.03 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 135.2, 135.0, 133.8, 129.3, 127.6, 124.2, 122.6, 117.6, 44.1, 37.1, 31.0, 22.8, 5.8; ESI m/z 291.22 $(M + H)^+$; anal. calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65 found: C, 78.44; H, 6.52; N, 9.28%.



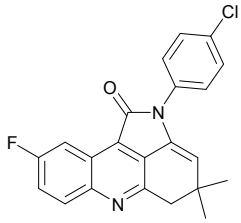
2-cyclohexyl-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3j)

Yellow solid; mp 159-160 ^oC; IR (KBr): 3027, 2943, 1699, 1453, 1339, 1059, 892 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, 1H, J = 7.6 Hz, ArH), 8.13 (d, 1H, J = 8.4Hz, ArH), 7.71-7.75 (m, 1H, ArH), 7.64 (t, 1H, J = 7.2 Hz, ArH), 5.68 (s, 1H, CH), 3.15 (s, 2H, CH_2), 2.01-2.11 (m, 2H, CH_2), 1.91 (t, 3H, J = 16.0 Hz, CH_2), 1.76-1.80 (m, 1H, CH_2), 1.46-1.50 (m, 2H, CH_2) , 1.35 (s, 6H, CH_3), 1.21-1.24 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 154.3, 149.5, 132.2, 129.3, 127.5, 126.5, 124.1, 122.6, 118.4, 52.2, 43.9, 37.1, 31.0, 30.9, 26.1, 25.4; ESI m/z 333.28 $(M + H)^+$; anal. calcd for $C_{22}H_{24}N_2O$: C, 79.48; H,7.28; N, 8.43 found: C, 79.57; H, 6.98; N, 8.78%.



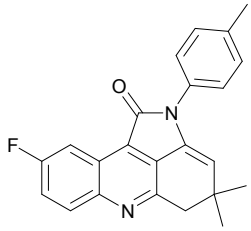
9-fluoro-4,4-dimethyl-2-phenyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3k)

Yellow solid; mp 163-164 °C (lit:[2] mp 160-161 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (dd, 1H, *J* = 2.8, 8.8 Hz, ArH), 8.15-8.19 (m, 1H, ArH), 7.49-7.58 (m, 5H, ArH), 7.41-7.45 (m, 1H, ArH), 5.67 (s, 1H, CH), 3.21 (s, 2H, CH_2), 1.34 (s, 6H, CH_3).



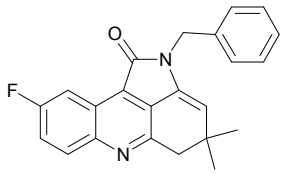
2-(4-chlorophenyl)-9-fluoro-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3l)

Yellow solid; mp 191-193 °C (lit:[7] mp 190-192 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (dd, 1H, *J* = 2.8, 8.8 Hz, ArH), 8.15-8.19 (m, 1H, ArH), 7.47-7.55 (m, 3H, ArH), 7.45-7.47 (m, 2H, ArH), 5.65 (s, 1H, CH), 3.21 (s, 2H, CH_2), 1.34 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 153.7, 146.7, 133.2, 133.1, 132.9, 131.8, 131.7, 129.6, 127.5, 119.5, 119.1, 108.4, 43.9, 37.2, 34.8.



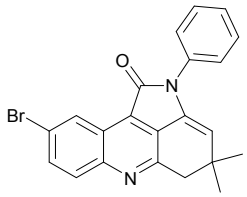
9-fluoro-4,4-dimethyl-2-(*p*-tolyl)-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3m)

Yellow solid; mp 174-176 °C (lit:[2] mp 172-173 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (dd, 1H, *J* = 3.2, 9.2 Hz, ArH), 8.15-8.18 (m, 1H, ArH), 7.49-7.54 (m, 1H, ArH), 7.34 -7.39 (m, 4H, ArH), 5.63 (s, 1H, CH), 3.20 (s, 2H, CH_2), 2.45 (s, 3H, CH_3), 1.33 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 154.2, 137.6, 133.4, 131.9, 131.7, 131.6, 130.0, 126.9, 126.2, 119.4, 118.9, 108.4, 108.2, 44.0, 37.1, 30.9, 21.2.



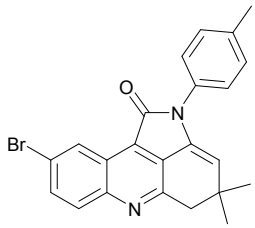
2-benzyl-9-fluoro-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3n)

Yellow solid; mp 163-164 ^{o}C; IR (KBr): 3020, 2947, 1701, 1665, 1468, 1445, 1329, 1148, 890 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (dd, 1H, J = 2.8, 8.8 Hz, ArH), 8.11-8.15 (m, 1H, ArH), 7.46-7.54 (m, 1H, ArH), 7.27-7.37 (m, 5H, ArH), 5.47 (s, 1H, CH), 5.01 (s, 2H, CH_2), 3.13 (s, 2H, CH_2), 1.27 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 154.3, 146.6, 136.6, 132.7, 131.7, 131.6, 128.8, 127.7, 127.4, 127.1, 119.3, 119.0, 118.4, 108.4, 108.1, 43.9, 37.1, 30.9; ESI m/z 359.10 $(M + H)^{+}$; anal. calcd for $C_{23}H_{19}FN_2O$: C, 77.08; H, 5.34; N, 7.82 found: C, 76.82; H, 4.99; N, 8.11%.



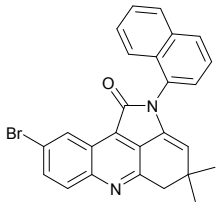
9-bromo-4,4-dimethyl-2-phenyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3o)

Yellow solid; mp 165-166 ^{o}C (lit:[2] mp 164-165 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, 1H, J = 2.4 Hz, ArH), 7.79 (d, 1H, J = 8.8 Hz, ArH), 7.60 (dd, 1H, J = 2.4, 9.2 Hz, ArH), 7.33 (t, 1H, J = 8.0 Hz, ArH), 7.26-7.28 (m, 2H, ArH), 7.18 (t, 1H, J = 7.2 Hz, ArH), 5.44 (s, 1H, CH), 2.96 (s, 2H, CH_2), 1.10 (s, 6H, CH_3).



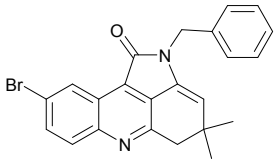
9-bromo-4,4-dimethyl-2-(*p*-tolyl)-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3p)

Yellow solid; mp 195-196 ^{o}C (lit:[2] mp 192-194 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (d, 1H, J = 2.0 Hz, ArH), 8.03 (d, 1H, J = 8.8 Hz, ArH), 7.83 (dd, 1H, J = 2.4, 8.8 Hz, ArH), 7.35-7.39 (m, 4H, ArH), 5.64 (s, 1H, CH), 3.19 (s, 2H, CH_2), 2.45 (s, 3H, CH_3), 1.33 (s, 6H, CH_3).



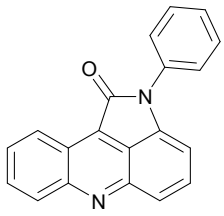
9-bromo-4,4-dimethyl-2-(naphthalen-1-yl)-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3q)

Yellow solid; mp 176-178 °C (lit:[2] mp 174-176 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, 1H, J = 2.4 Hz, ArH), 8.07 (d, 1H, J = 9.2 Hz, ArH), 7.99-8.04 (m, 2H, ArH), 7.86 (dd, 1H, J = 2.4, 9.2 Hz, ArH), 7.64 (d, 2H, J = 8.4 Hz, ArH), 7.49-7.58 (m, 3H, ArH), 5.27 (s, 1H, CH), 3.23 (s, 2H, CH_2), 1.29 (s, 6H, J = 8.4 Hz, CH_3).



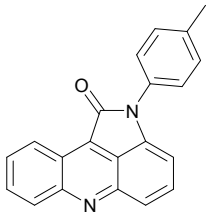
2-benzyl-9-bromo-4,4-dimethyl-4,5-dihydropyrrolo[2,3,4-kl]acridin-1(2H)-one (3r)

Yellow solid; mp 201-202 °C; IR (KBr): 3021, 2945, 1700, 1663, 1466, 1450, 1331, 1149, 899 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, 1H, J = 2.4 Hz, ArH), 7.99 (d, 1H, J = 8.8 Hz, ArH), 7.80 (dd, 1H, J = 2.0, 8.8 Hz, ArH), 7.28-7.35 (m, 5H, ArH), 5.49 (s, 1H, CH), 5.01 (s, 2H, CH_2), 3.12 (s, 2H, CH_2), 1.27 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 154.8, 148.1, 136.6, 132.9, 132.6, 130.9, 128.8, 127.7, 127.4, 126.5, 123.6, 122.0, 118.6, 44.0, 43.9, 37.1, 30.9; ESI m/z 419.02 $(M + H)^+$; anal. calcd for $C_{23}H_{19}BrN_2O$: C, 65.88; H,4.57; N, 6.68 found: C, 66.12; H,4.85; N, 6.47%.



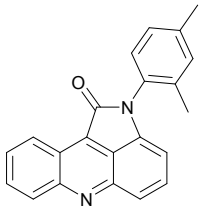
2-phenylpyrrolo[2,3,4-kl]acridin-1(2H)-one (3s)

Red brown solid; mp 295-296 °C (lit:[2] mp 298-300 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96 (d, 1H, J = 8.0 Hz, ArH), 8.47 (d, 1H, J = 8.8 Hz, ArH), 7.91-7.98 (m, 2H, ArH), 7.84 (t, 1H, J = 8.4 Hz, ArH), 7.72 (t, 1H, J = 6.8 Hz, ArH), 7.59-7.67 (m, 3H, ArH), 7.45-7.49 (m, 1H, ArH), 7.04 (d, 1H, J = 7.2 Hz, ArH).



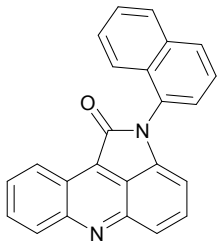
2-(*p*-tolyl)pyrrolo[2,3,4-kl]acridin-1(2H)-one (3t)

Red brown solid; mp 232-234°C (lit:[5] no report); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96 (d, 1H, *J* = 8.4 Hz, ArH), 8.46 (d, 1H, *J* = 8.8 Hz, ArH), 7.95-7.97 (m, 1H, ArH), 7.90 (d, 1H, *J* = 8.8 Hz, ArH), 7.81-7.86 (m, 1H, ArH), 7.69-7.73 (m, 1H, ArH), 7.52 (d, 2H, *J* = 8.4 Hz, ArH), 7.40 (d, 2H, *J* = 8.0 Hz, ArH), 6.99 (d, 1H, *J* = 7.2 Hz, ArH), 2.48 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 151.9, 146.6, 140.3, 137.7, 132.8, 130.8, 130.6, 130.2, 129.2, 127.7, 125.8, 124.2, 123.1, 122.6, 119.8, 105.9, 21.2.



2-(2,4-dimethylphenyl)pyrrolo[2,3,4-kl]acridin-1(2H)-one(3u)

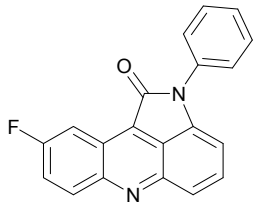
Red brown solid; mp 175-176 °C (lit:[2] mp 172-173 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (d, 1H, *J* = 8.4 Hz, ArH), 8.46 (d, 1H, *J* = 8.4 Hz, ArH), 7.92-7.97 (m, 1H, ArH), 7.88 (d, 1H, *J* = 9.2 Hz, ArH), 7.30 (t, 1H, *J* = 7.6 Hz, ArH), 7.64-7.68 (m, 1H, ArH), 7.19-7.30 (m, 1H, ArH), 6.65 (d, 1H, *J* = 6.8 Hz, ArH), 2.45 (s, 3H, CH_3), 2.25 (s, 3H, CH_3).



2-(naphthalen-1-yl)pyrrolo[2,3,4-kl]acridin-1(2H)-one (3v)

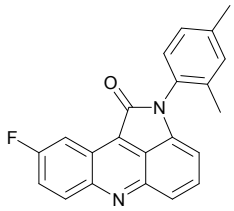
Red brown solid; mp 211-212 °C (lit:[2] mp 208-210 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (d, 1H, *J* = 8.0 Hz, ArH), 8.50 (d, 1H, *J* = 8.8 Hz, ArH), 8.06 (t, 1H, *J* = 4.8 Hz, ArH), 8.02 (d, 1H, *J* = 8.0 Hz, ArH), 7.96-8.00 (m, 1H, ArH), 7.93 (d, 1H, *J* = 8.8 Hz,

ArH), 7.84-7.88 (m, 1H, ArH), 7.77 (d, 1H, *J* = 8.4 Hz, ArH), 7.68-7.69 (m, 2H, ArH), 7.62-7.66 (m, 1H, ArH), 7.56-7.60 (m, 1H, ArH), 7.47-7.51 (m, 1H, ArH), 7.50 (d, 1H, *J* = 6.8 Hz, ArH).



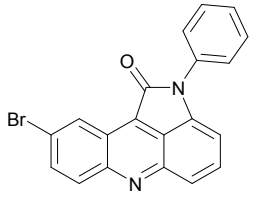
9-fluoro-2-phenylpyrrolo[2,3,4-kl]acridin-1(2H)-one (3w)

Red brown solid; mp 226-228 ^{o}C (lit:[8] mp 228-230 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (dd, 1H, *J* = 2.8, 8.8 Hz, ArH), 8.44-8.48 (m, 1H, ArH), 7.89 (d, 1H, *J* = 8.8 Hz, ArH), 7.69-7.76 (m, 2H, ArH), 7.59-7.65 (m, 4H, ArH), 7.48 (t, 1H, *J* = 7.2 Hz, ArH), 7.05 (d, 1H, *J* = 6.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8, 167.2, 151.7, 149.3, 134.6, 133.5, 132.6, 129.6, 127.8, 125.8, 122.7, 122.4, 115.4, 107.0, 106.6.



2-(2,4-dimethylphenyl)-9-fluoropyrrolo[2,3,4-kl]acridin-1(2H)-one (3x)

Red brown solid; mp 161-163 ^{o}C (lit:[2] mp 162-165 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (dd, 1H, *J* = 2.8, 8.8 Hz, ArH), 8.45-8.49 (m, 1H, ArH), 7.87 (d, 1H, *J* = 9.2 Hz, ArH), 7.70-7.76 (m, 1H, ArH), 7.64-7.68 (m, 1H, ArH), 7.22-7.29 (m, 2H, ArH), 7.19-7.21 (m, 2H, ArH), 6.68 (d, 1H, *J* = 6.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.6, 160.9, 151.5, 149.3, 140.5, 139.3, 136.4, 133.6, 133.5, 132.8, 132.3, 130.4, 128.2, 127.9, 122.3, 122.0, 120.2, 107.3, 106.1, 21.2, 18.0.



9-bromo-2-phenylpyrrolo[2,3,4-kl]acridin-1(2H)-one (3y)

Red brown solid; mp 212-214 °C (lit:[2] mp 208-210 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (d, 1H, J = 2.0 Hz, ArH), 8.31 (d, 1H, J = 9.2 Hz, ArH), 7.99 (dd, 1H, J = 2.4, 9.6 Hz, ArH), 7.89 (d, 1H, J = 9.2 Hz, ArH), 7.71-7.75 (m, 1H, ArH), 7.59-7.66 (m, 3H, ArH), 7.46-7.50 (m, 1H, ArH), 7.05 (d, 1H, J = 6.8 Hz, ArH).

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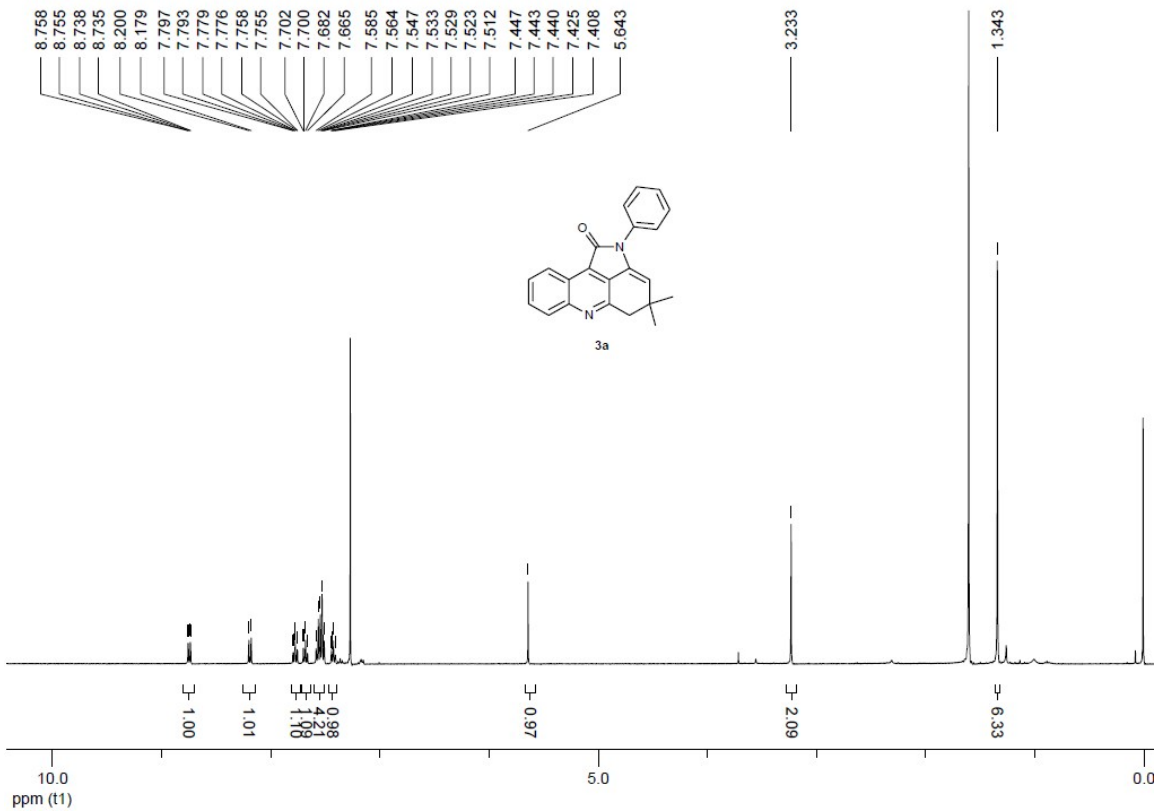
^{1}H and ^{13}C NMR Spectra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7.702
7.700
7.682
7.665
7.585
7.564
7.547
7.533
7.529
7.523
7.512
7.447
7.443
7.440
7.425
7.408
5.643
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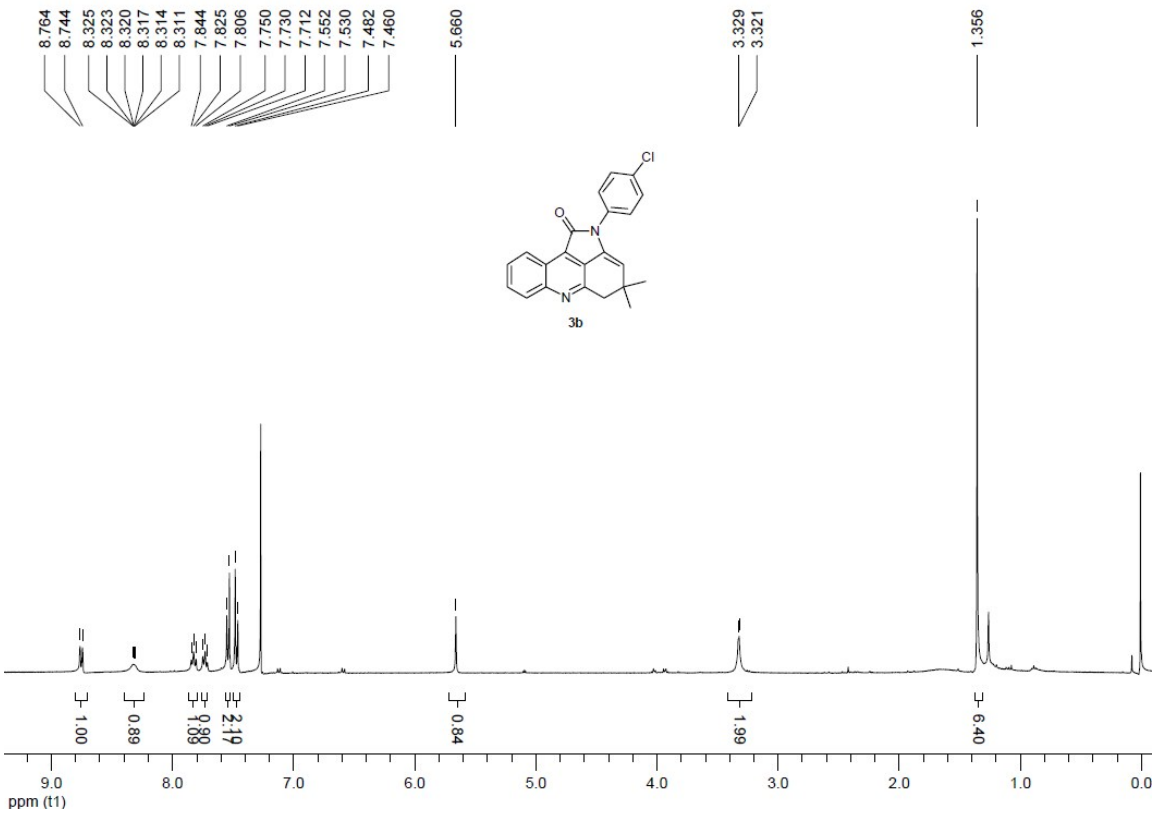
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7.730
7.712
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7.530
7.482
7.460
5.660
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3.321
1.356
Cl
3b
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1.00
0.84
1.99
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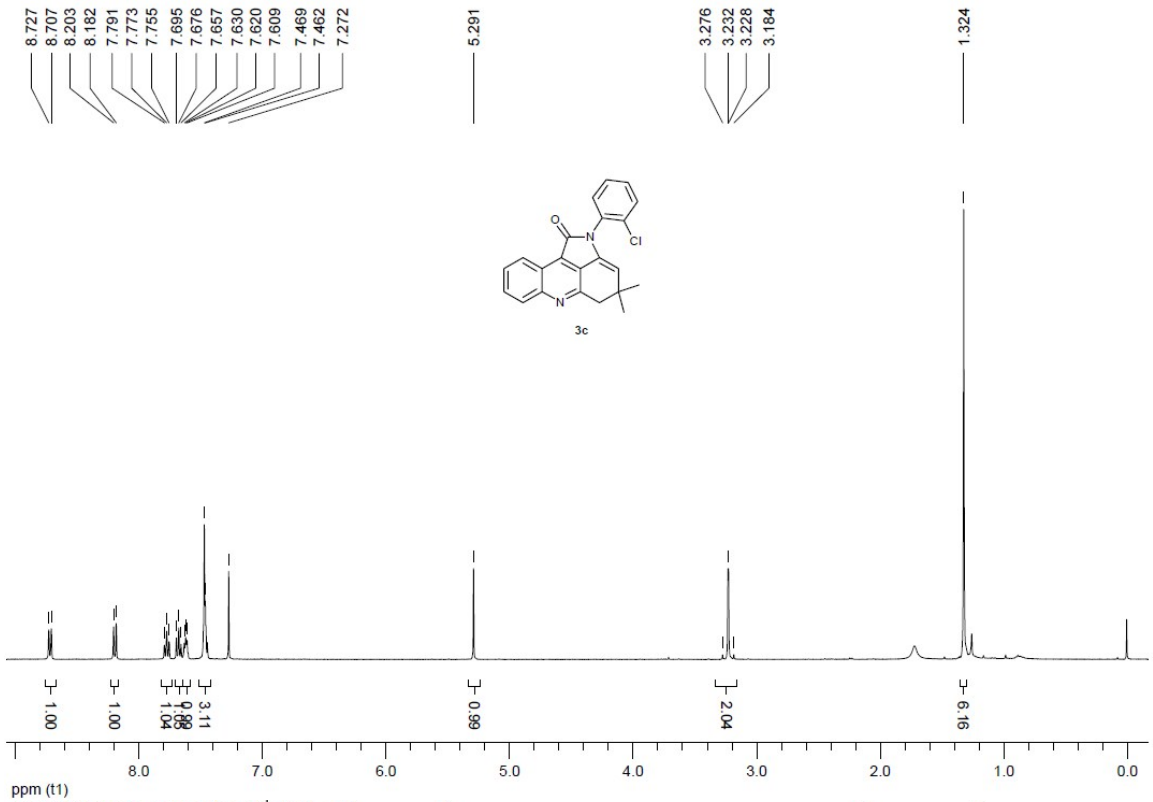
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1.08
3.11
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5.0
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2.0
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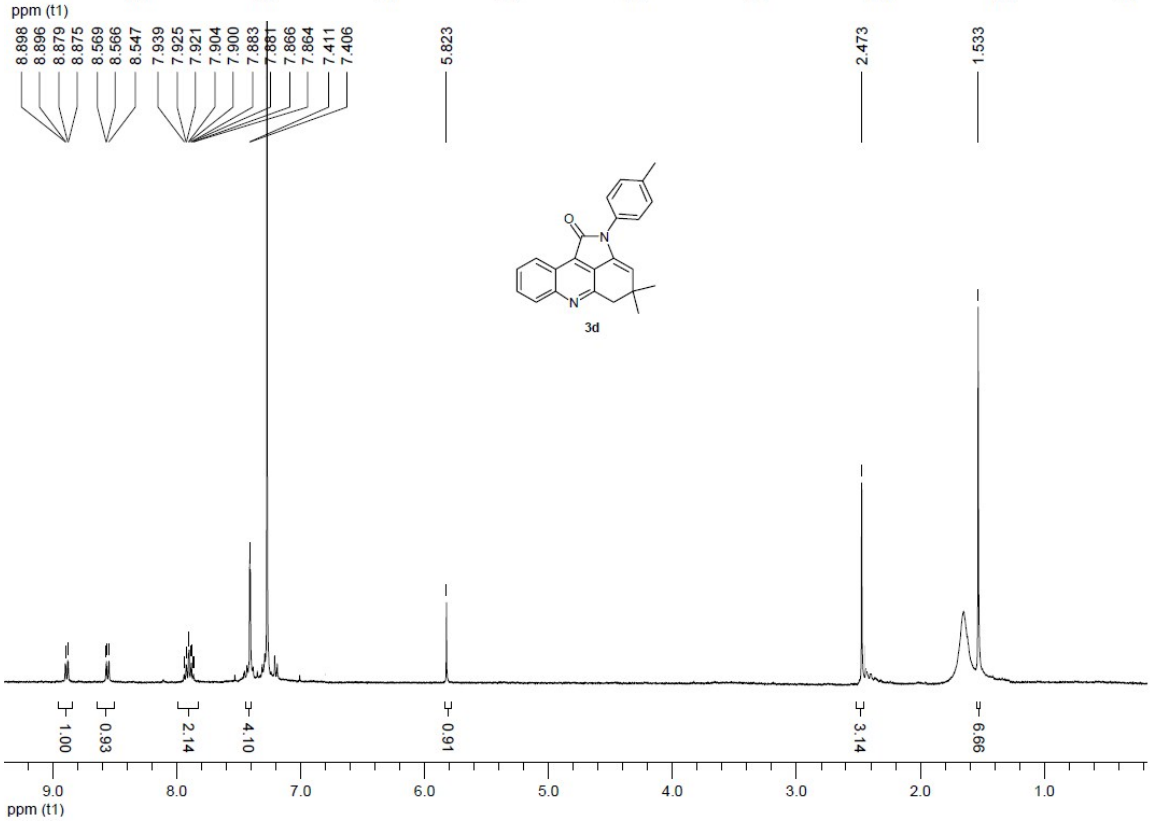
0.0
ppm (t1)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7.900
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7.881
7.866
7.864
7.411
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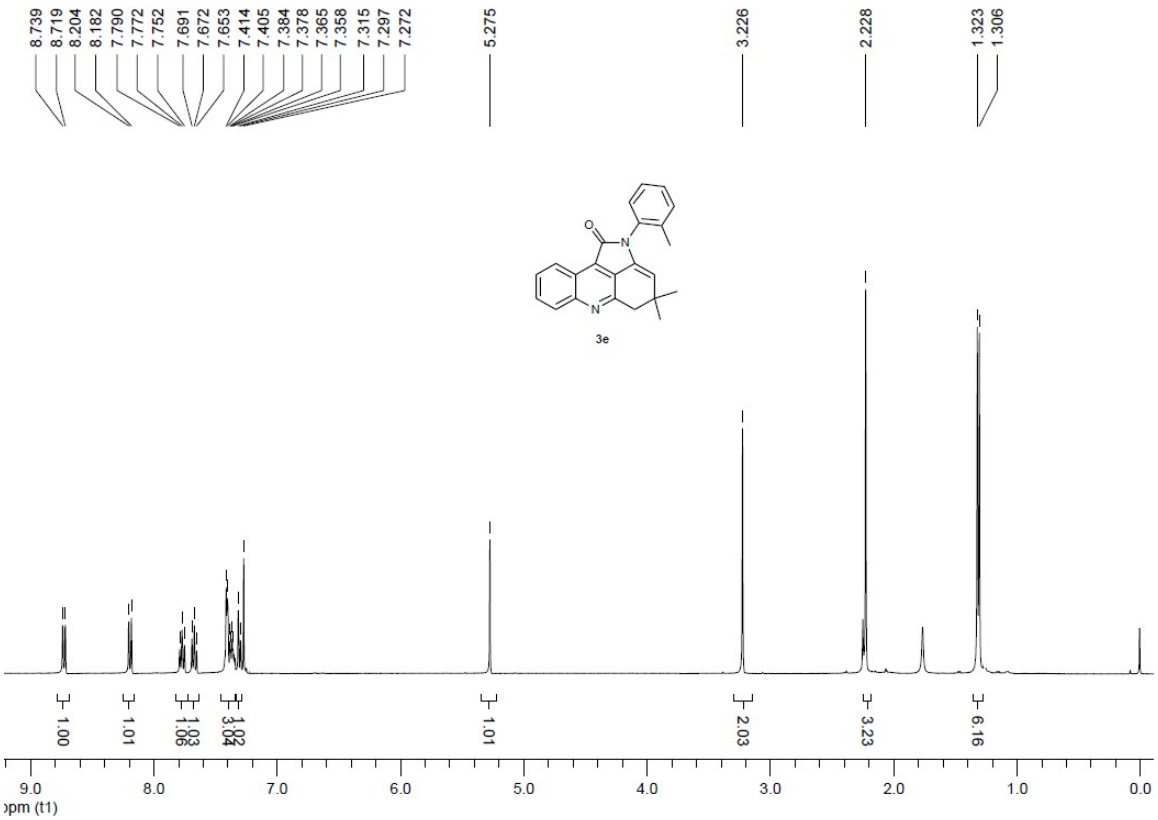
ppm (t1)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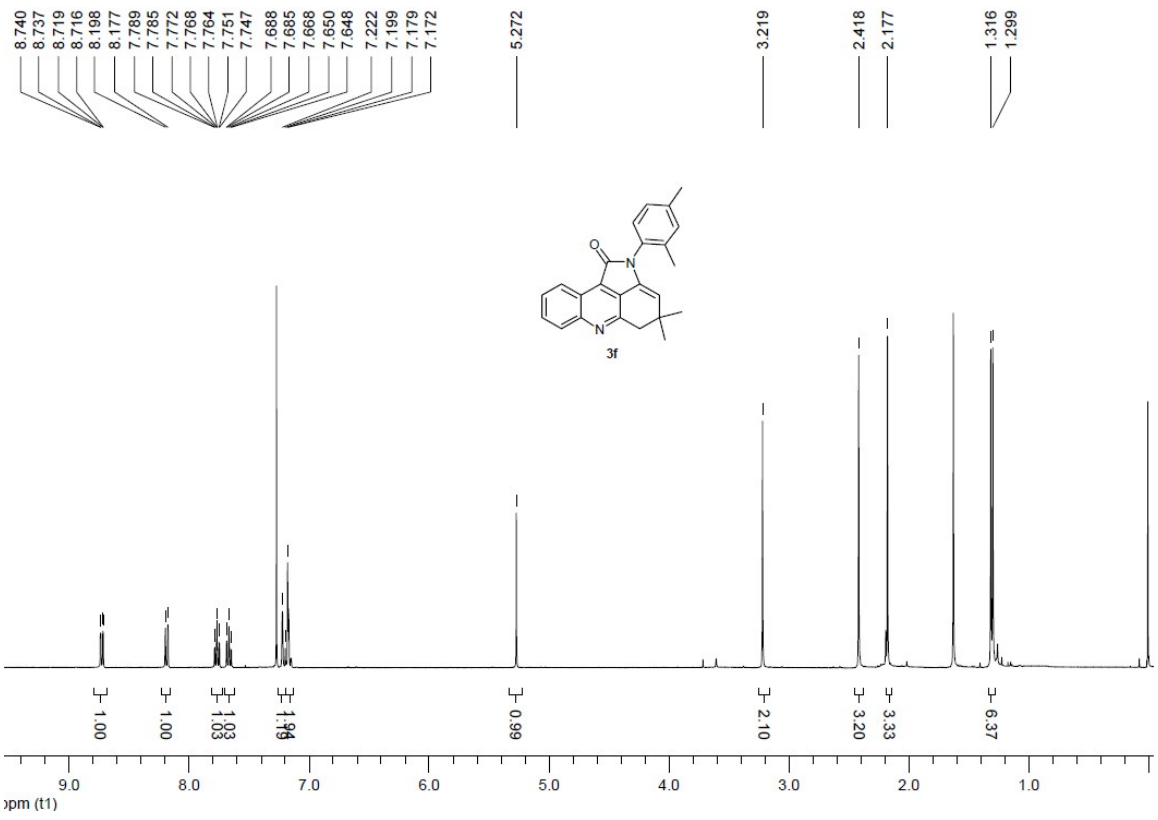
ppm (t1)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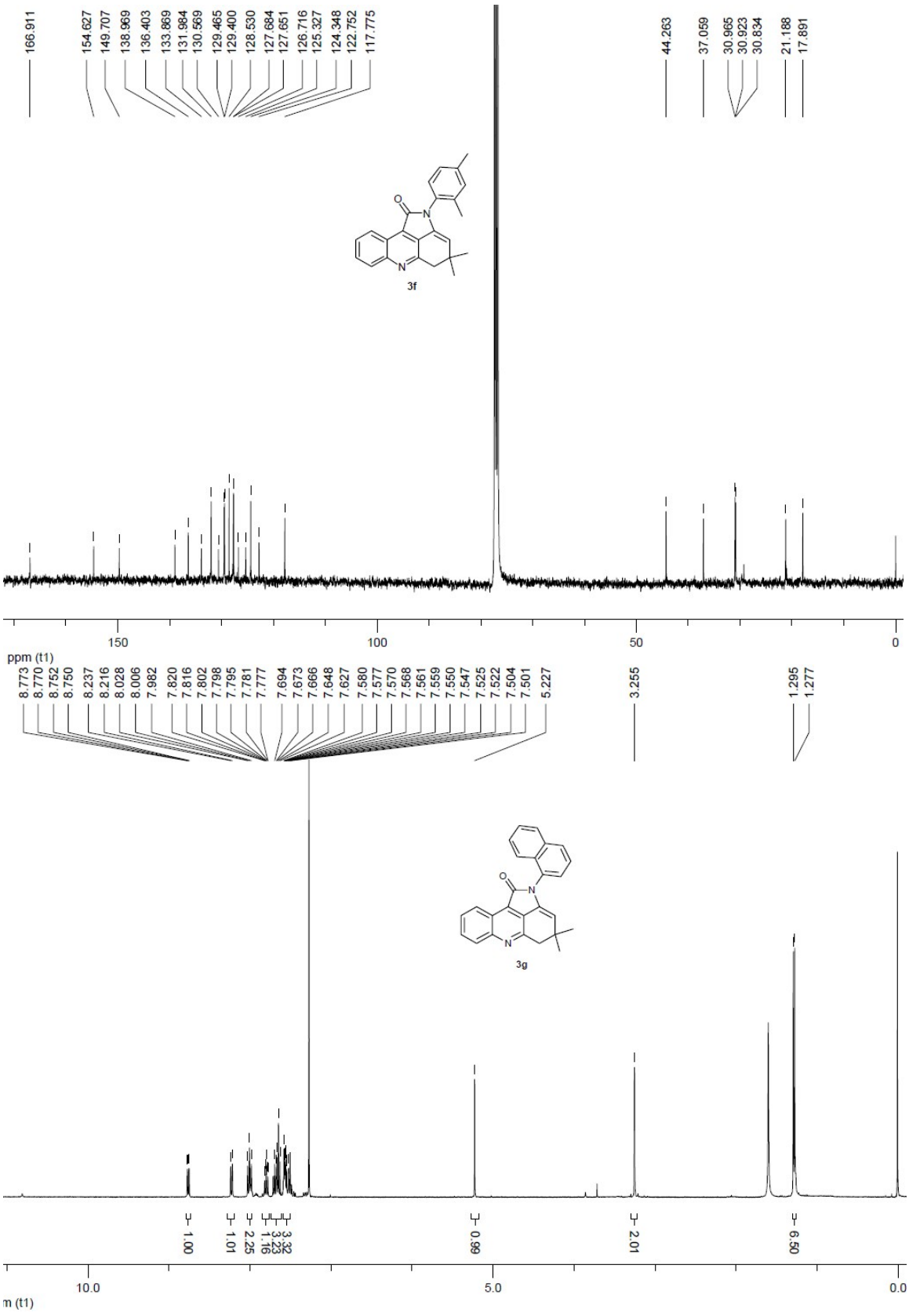
ppm (t1)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ppm (t1)
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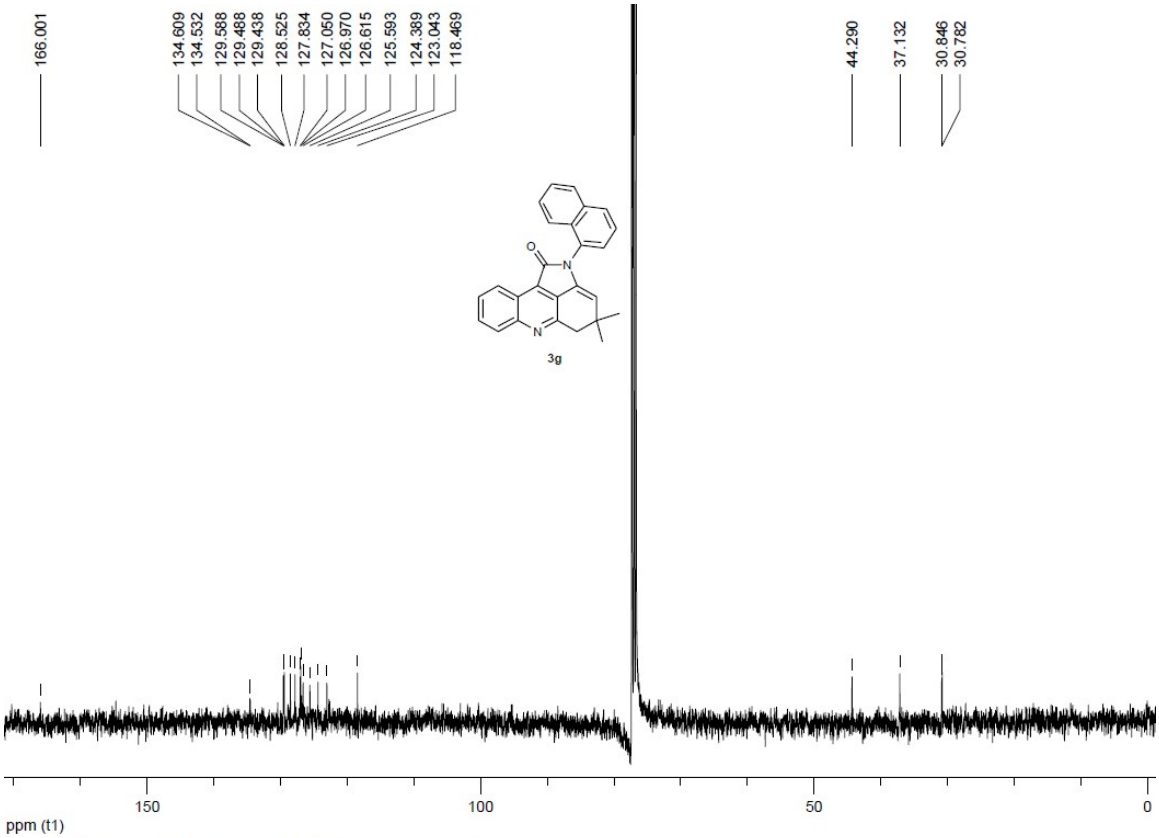
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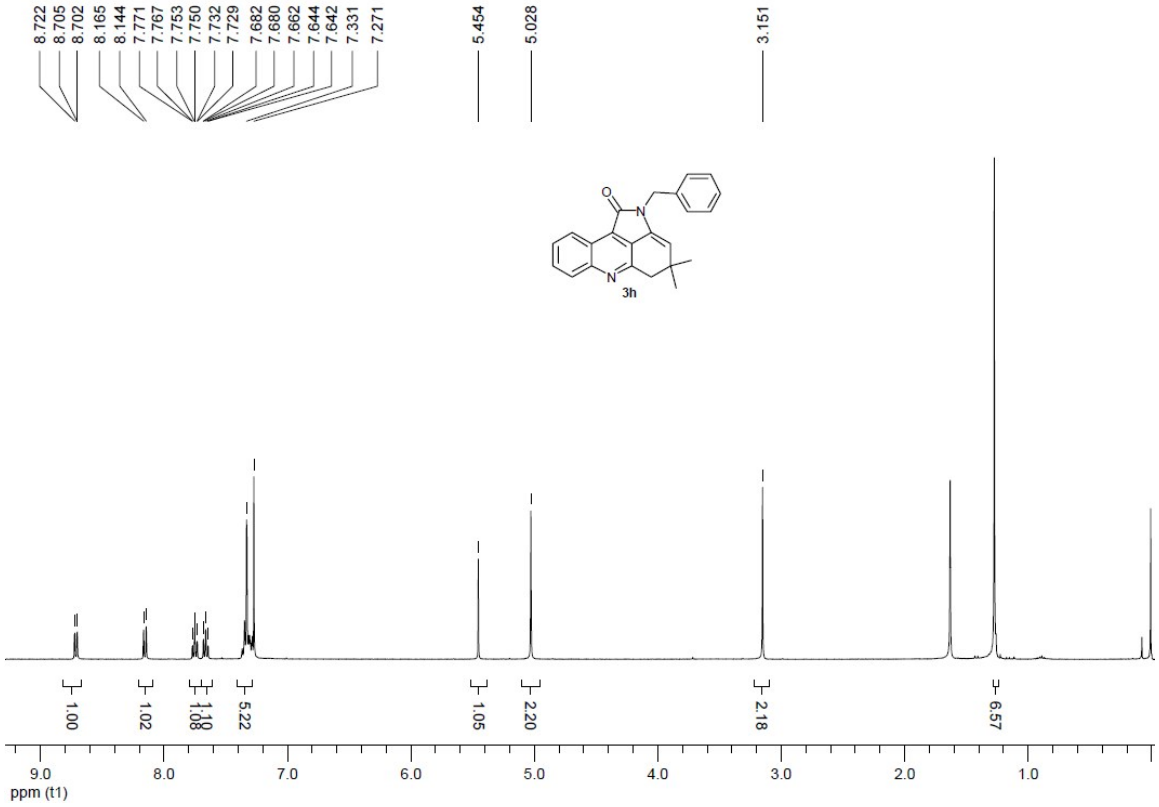
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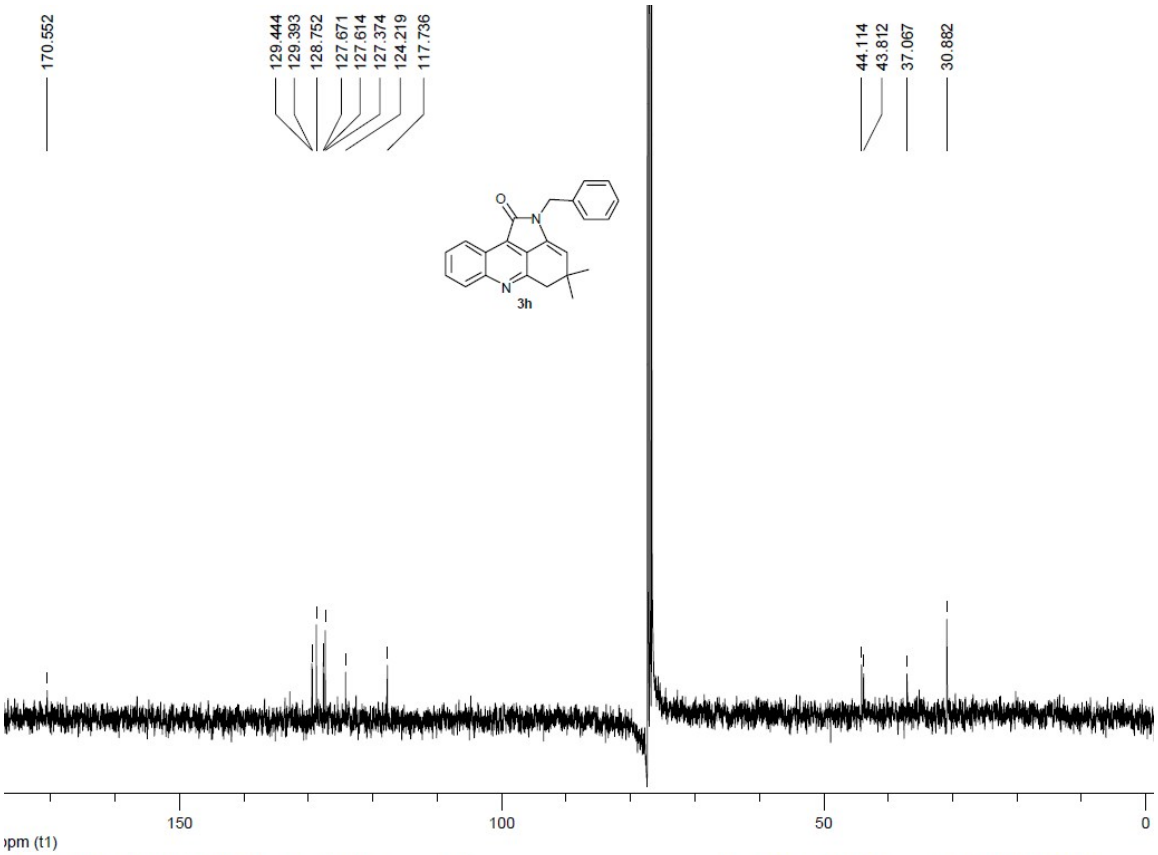
ppm (t1)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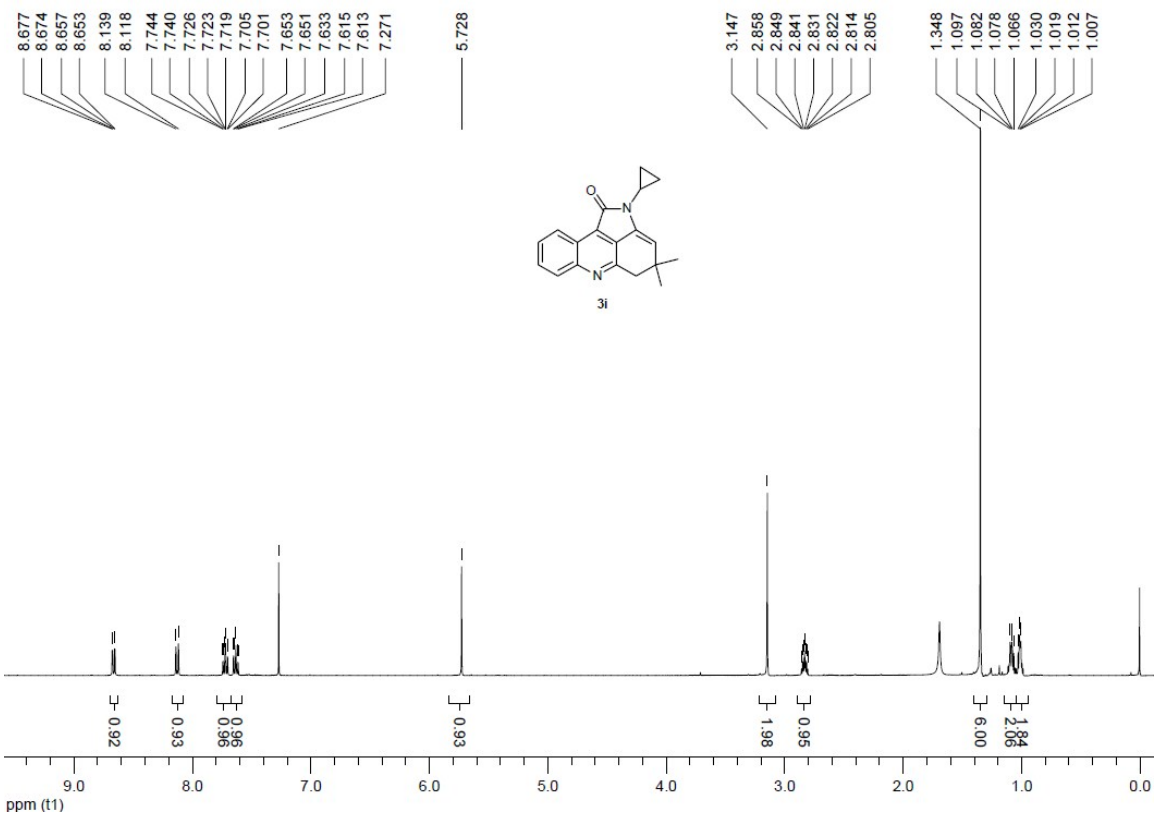
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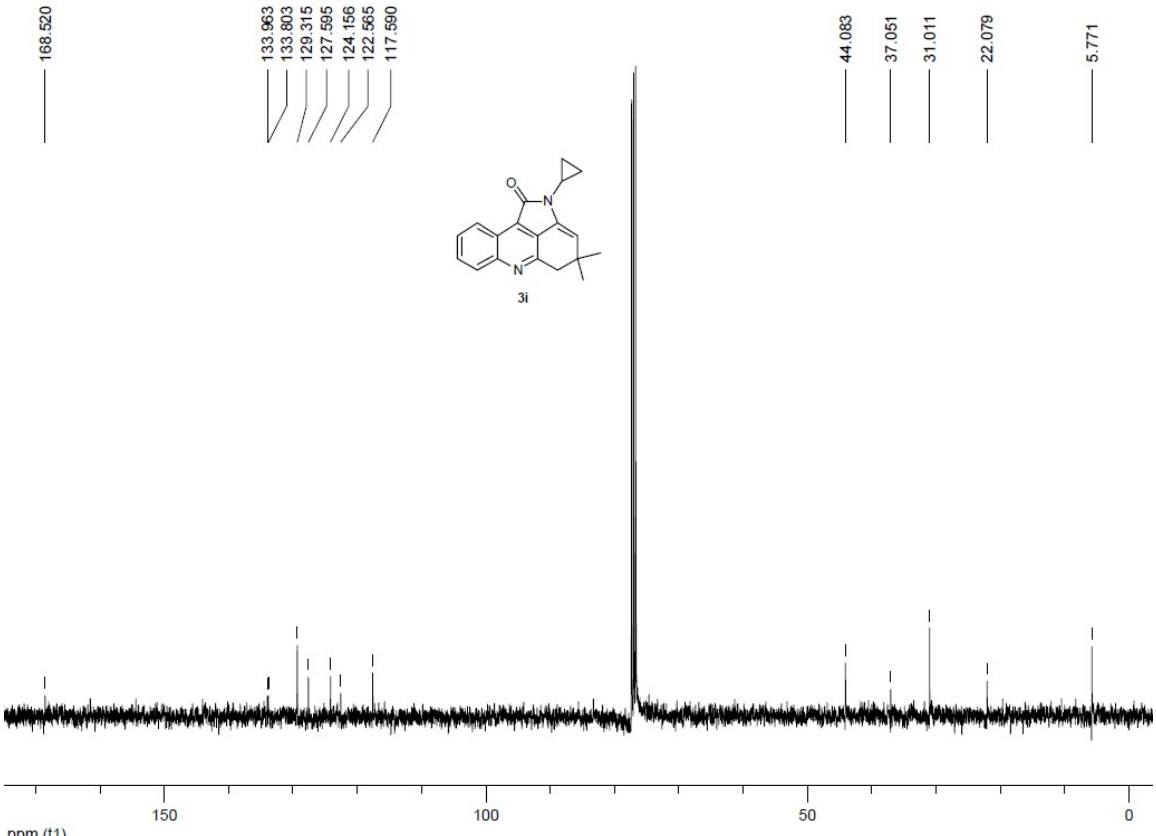
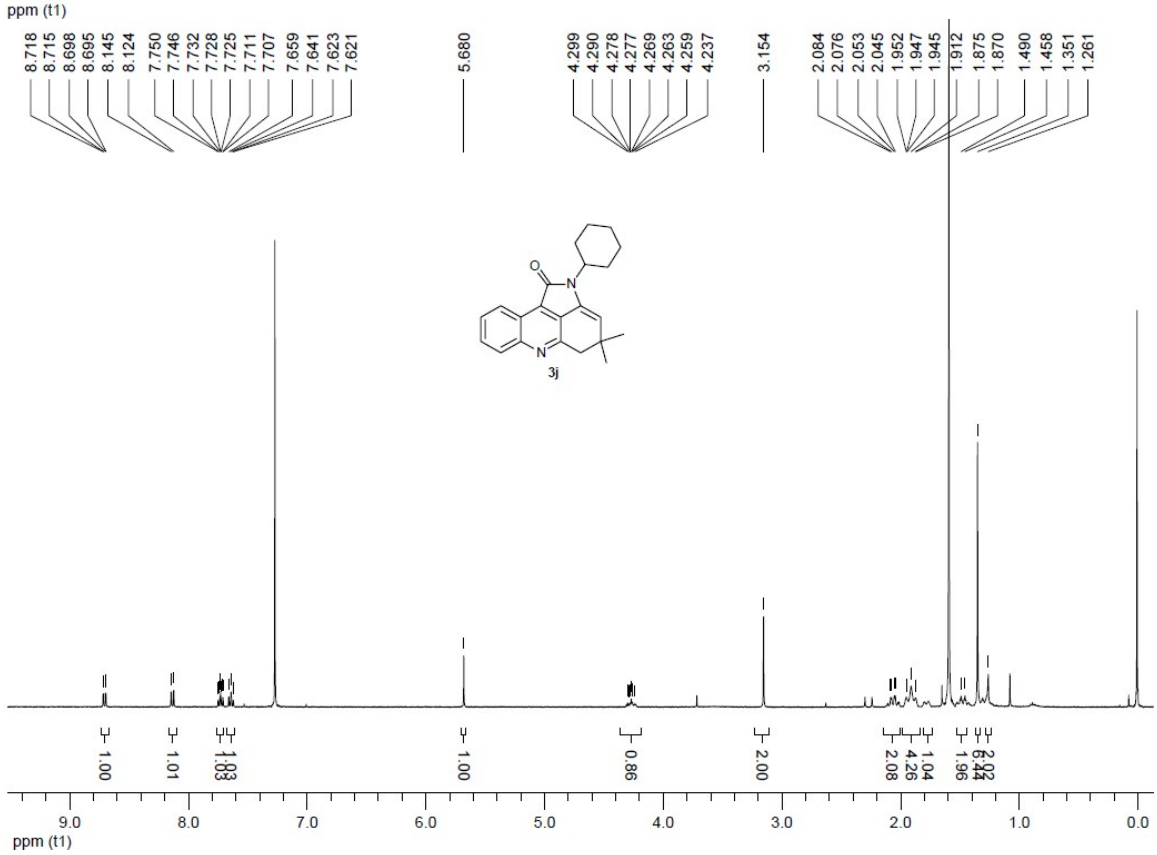
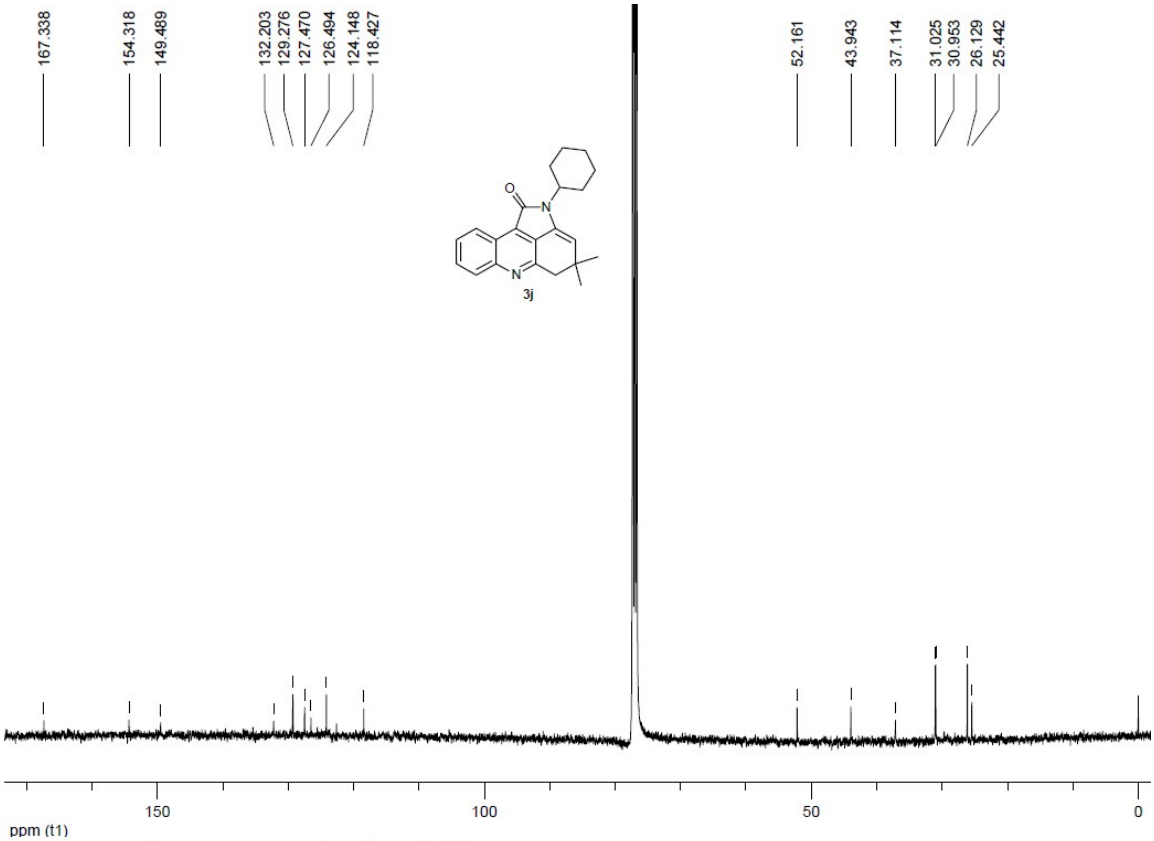
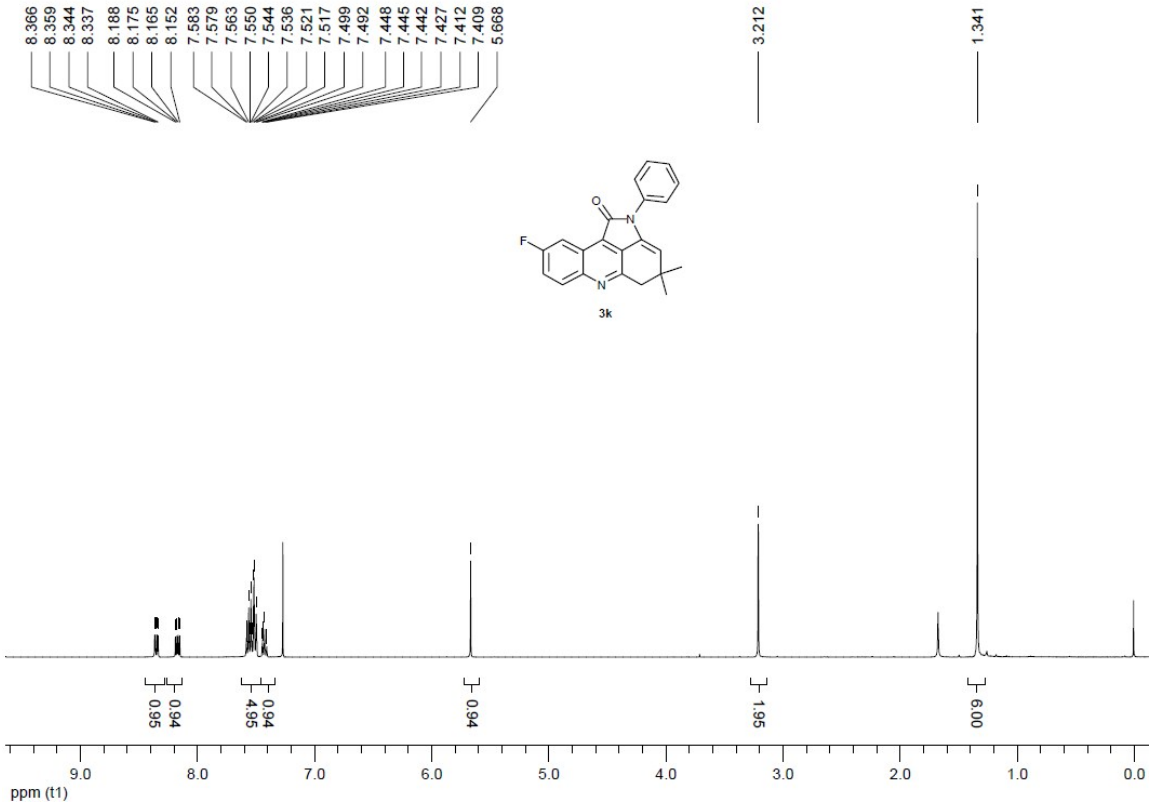
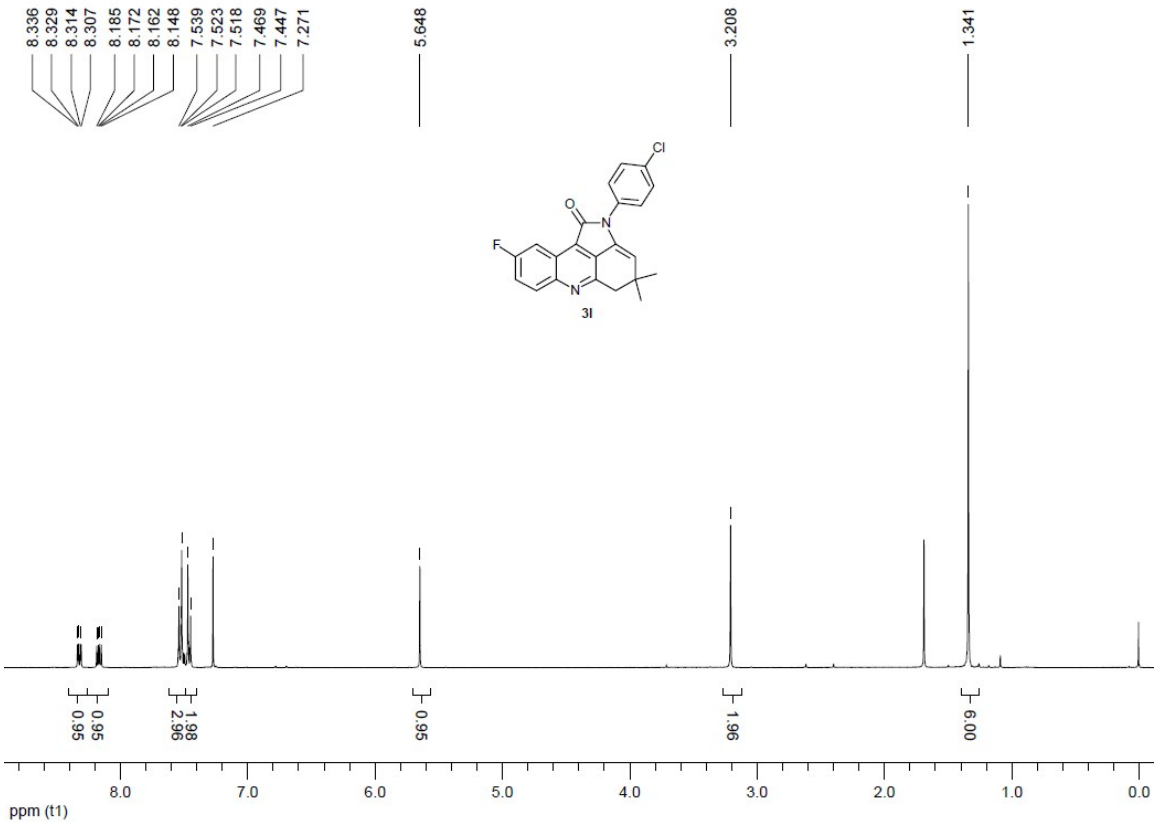
ppm (t1)

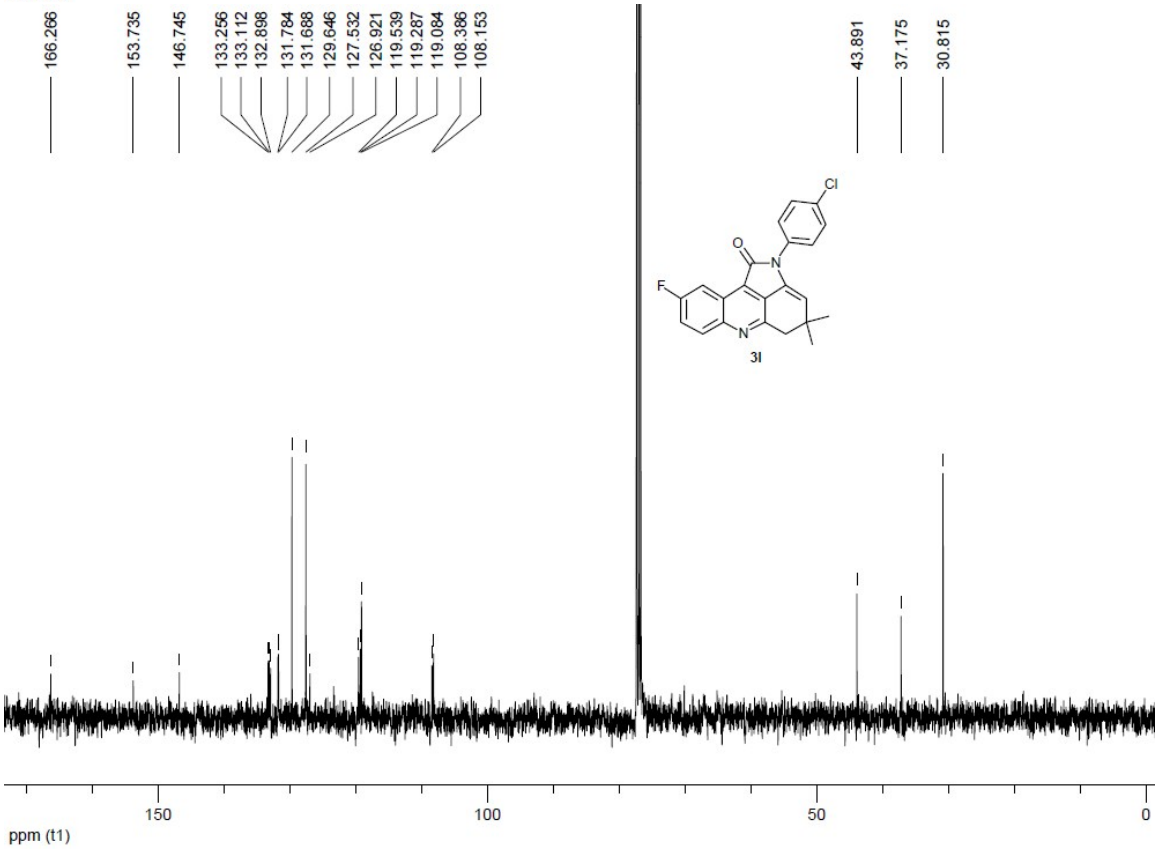

168.520
133.963
133.803
129.315
127.595
124.156
122.565
117.590
44.083
37.051
31.011
22.079
5.771
3i
150
100
50
0
ppm (t1)

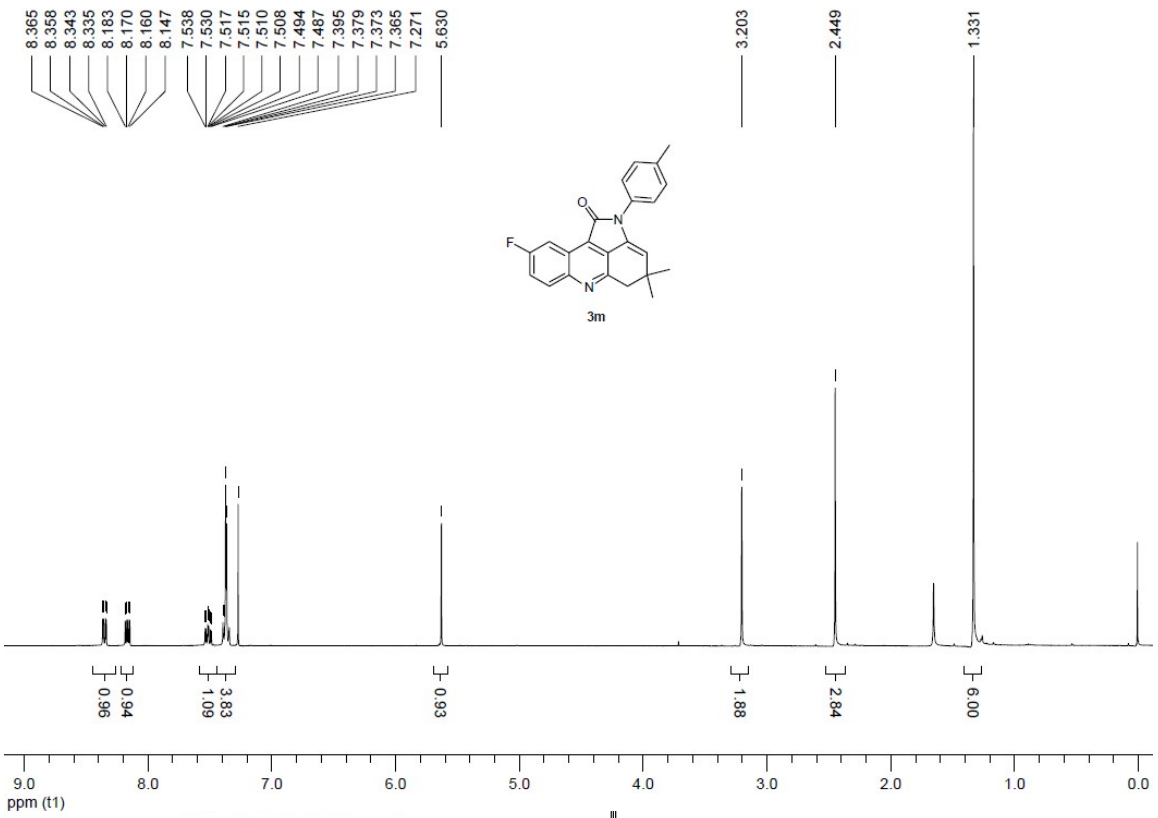

8.718
8.715
8.698
8.695
8.145
8.124
7.750
7.746
7.732
7.728
7.725
7.711
7.707
7.659
7.641
7.623
7.621
5.680
4.299
4.290
4.278
4.277
4.269
4.263
4.259
4.237
3.154
2.084
2.076
2.053
2.045
1.952
1.947
1.945
1.912
1.875
1.870
1.490
1.458
1.351
1.261
3j
1.00
1.01
1.03
1.00
0.86
2.00
2.08
4.26
1.04
1.96
2.02
6.44
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

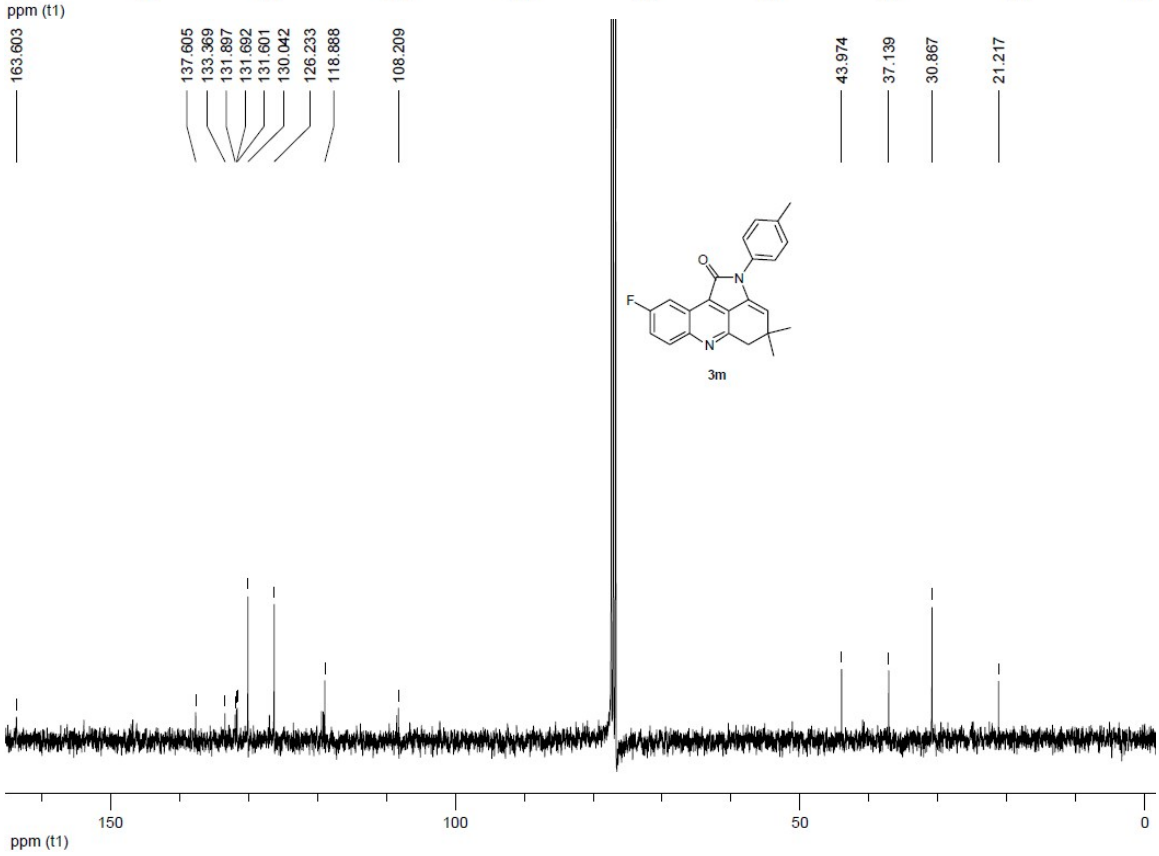

167.338
154.318
149.489
132.203
129.276
127.470
126.494
124.148
118.427
52.161
43.943
37.114
31.025
30.953
26.129
25.442
3j
150
100
50
0
ppm (t1)

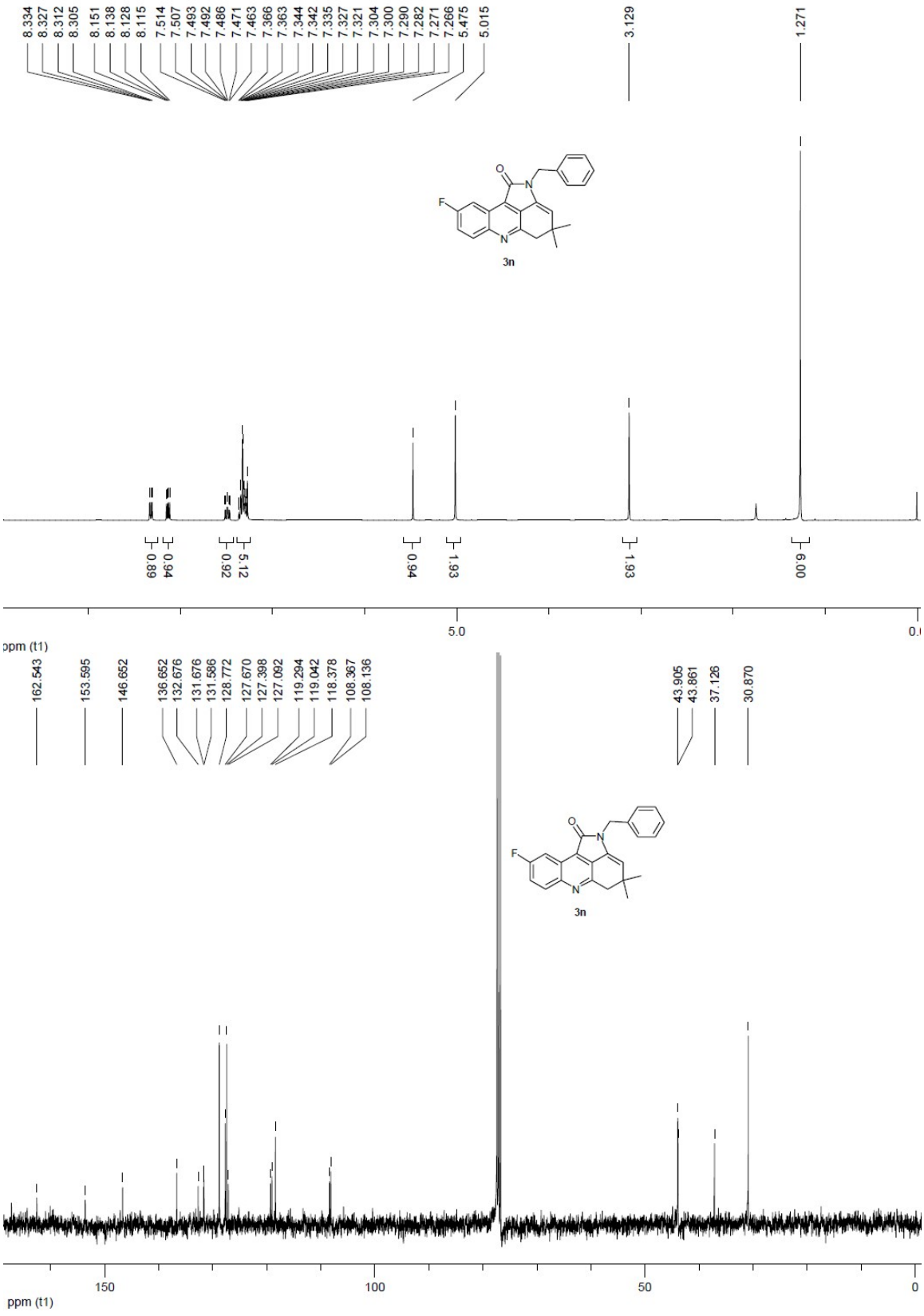

8.366
8.359
8.344
8.337
8.188
8.175
8.165
8.152
7.583
7.579
7.563
7.550
7.544
7.536
7.521
7.517
7.499
7.492
7.448
7.445
7.442
7.427
7.412
7.409
5.668
3.212
1.341
3k
0.95
0.94
4.95
0.94
0.94
1.95
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

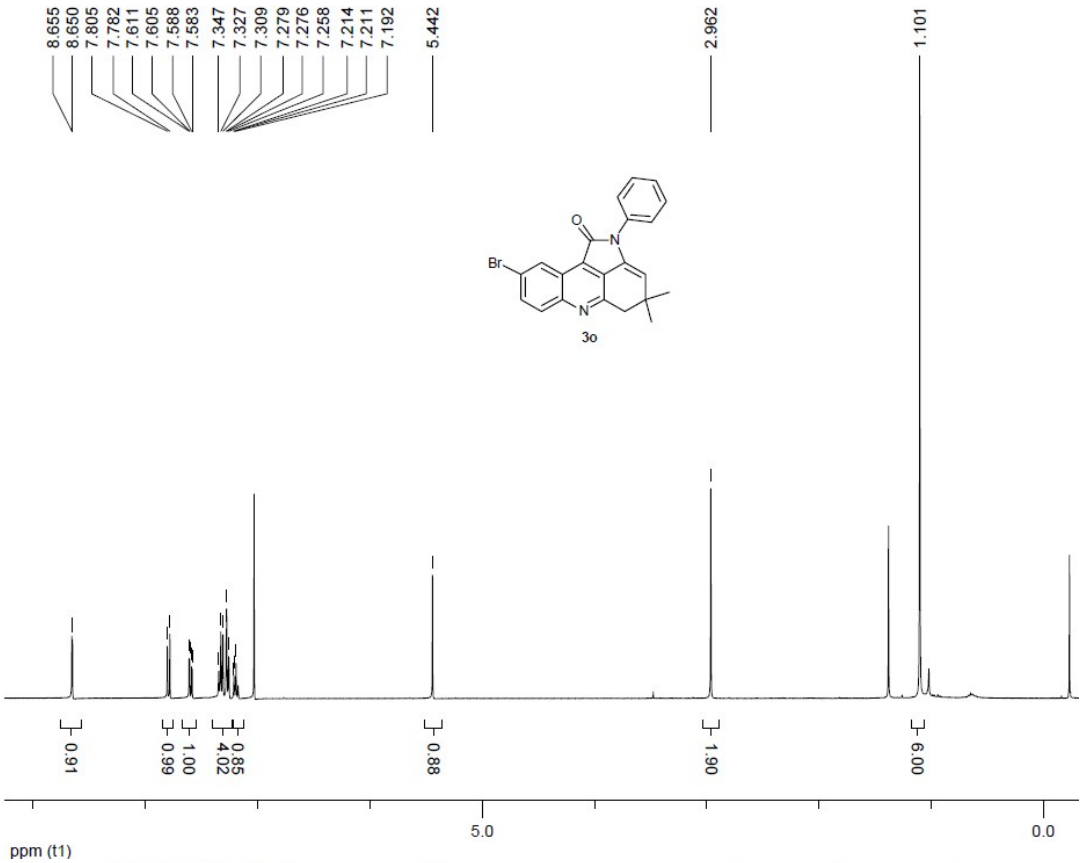

8.336
8.329
8.314
8.307
8.185
8.172
8.162
8.148
7.539
7.523
7.518
7.469
7.447
7.271
5.648
3.208
1.341
Cl
O
N
F
N
3l
0.96
0.96
1.98
2.96
0.95
1.96
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

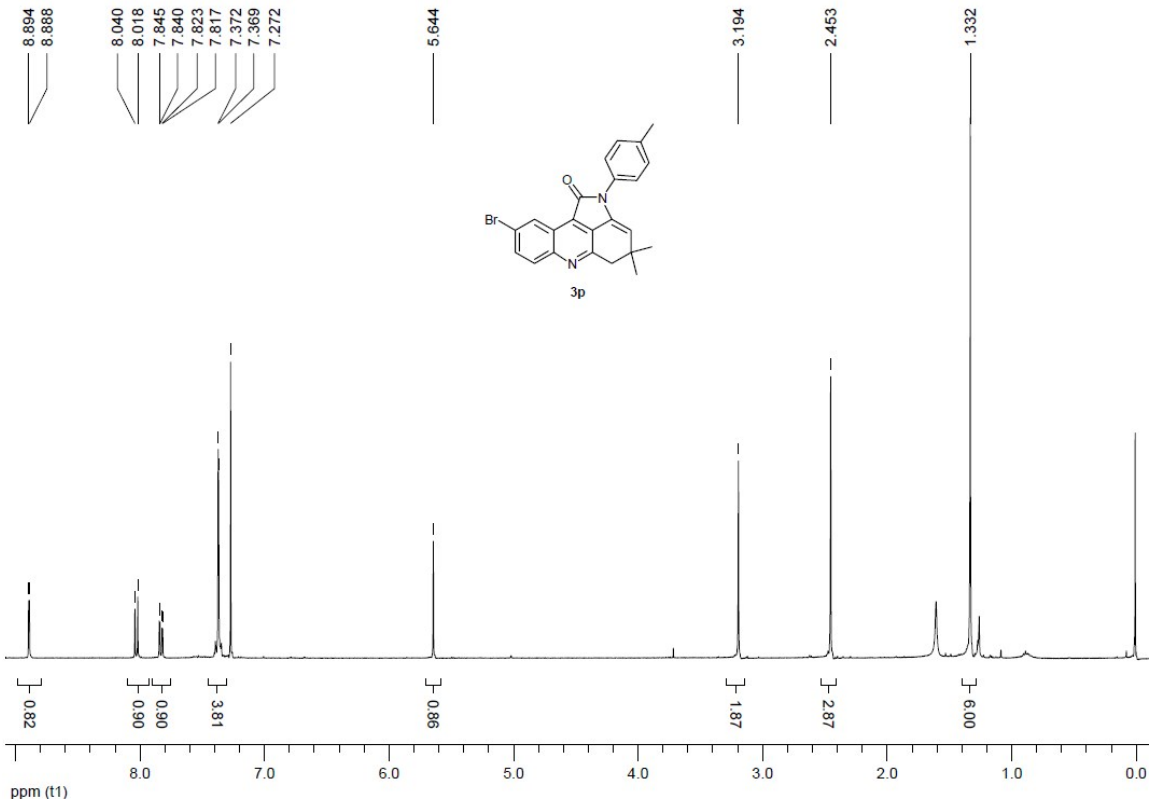

166.266
153.735
146.745
133.256
133.112
132.898
131.784
131.688
129.646
127.532
126.921
119.539
119.287
119.084
108.386
108.153
43.891
37.175
30.815
Cl
O
N
F
N
3l
150
100
50
0
ppm (t1)

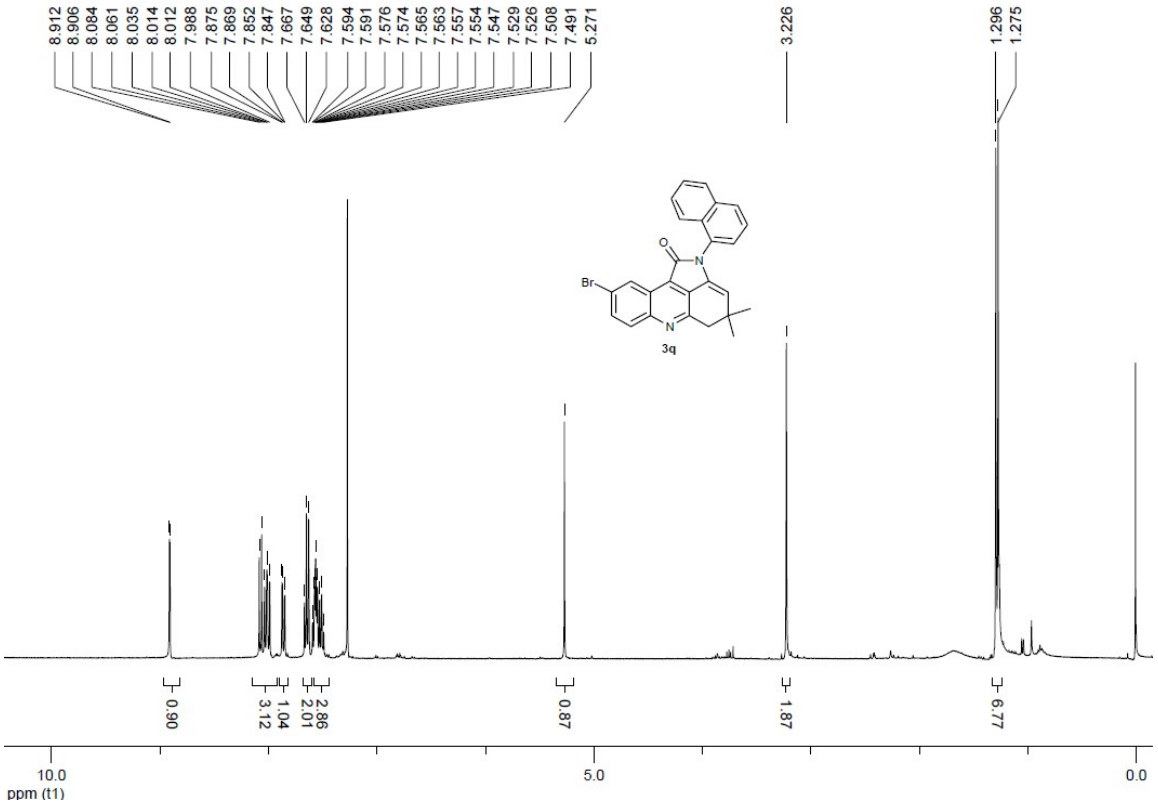

8.365
8.358
8.343
8.335
8.183
8.170
8.160
8.147
7.538
7.530
7.517
7.515
7.510
7.508
7.494
7.487
7.395
7.379
7.373
7.365
7.271
5.630
3.203
2.449
1.331
3m
0.96
0.94
3.83
1.09
0.93
1.88
2.84
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

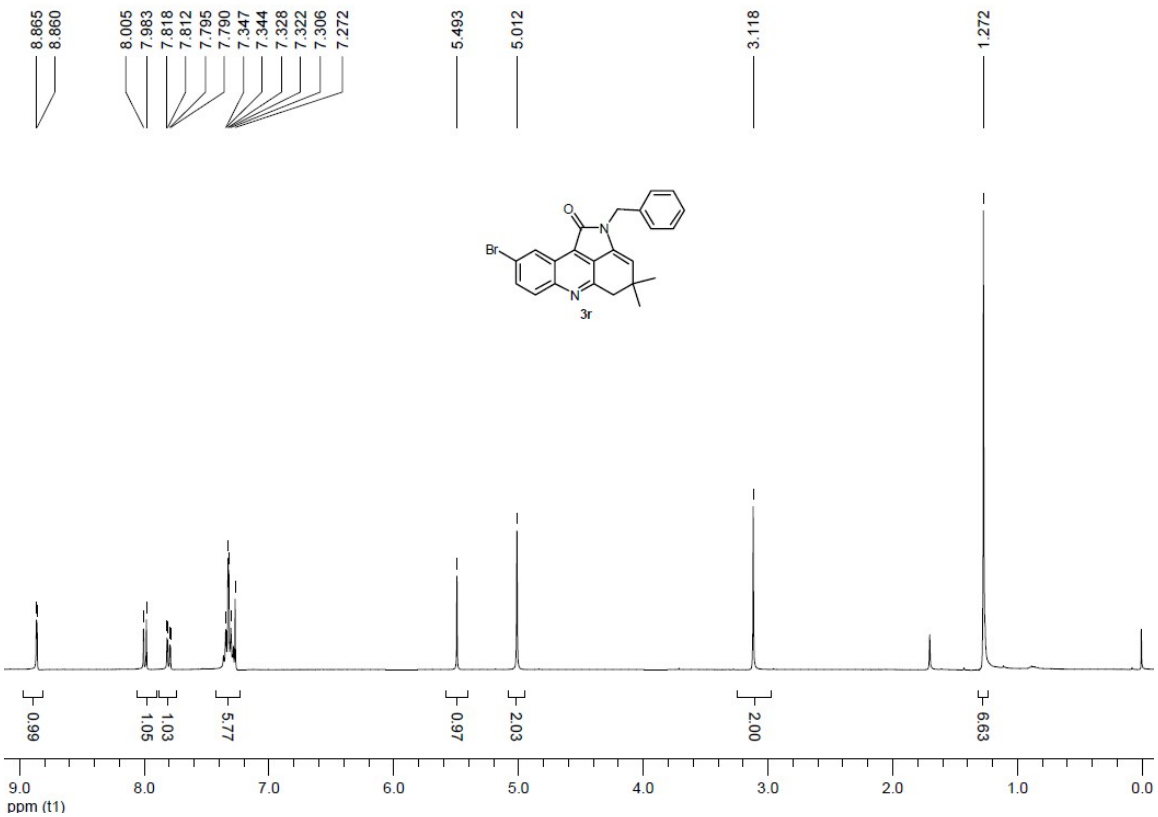

163.603
137.605
133.369
131.897
131.692
131.601
130.042
126.233
118.888
108.209
43.974
37.139
30.867
21.217
3m
150
100
50
0
ppm (t1)

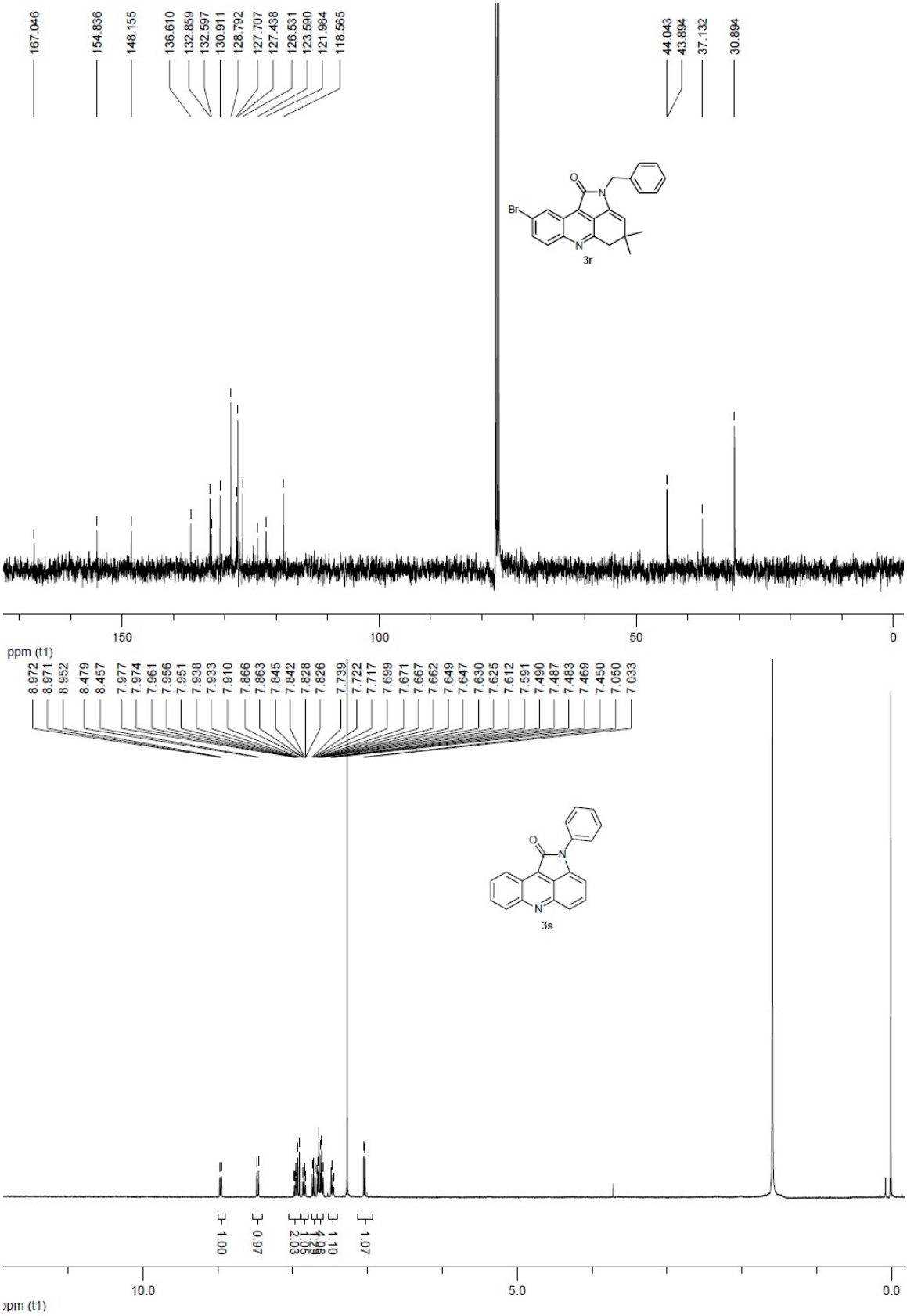

8.334
8.327
8.312
8.305
8.151
8.138
8.128
8.115
7.514
7.507
7.493
7.492
7.486
7.471
7.463
7.366
7.363
7.344
7.342
7.335
7.327
7.321
7.304
7.300
7.290
7.282
7.271
7.266
5.475
5.015
3.129
1.271
3n
0.89
0.94
0.92
5.12
0.94
1.93
1.83
6.00
5.0
ppm (t1)
162.543
153.595
146.652
136.652
132.676
131.676
131.586
128.772
127.670
127.398
127.092
119.294
119.042
118.378
108.367
108.136
43.905
43.861
37.126
30.870
3n
150
100
50
0
ppm (t1)

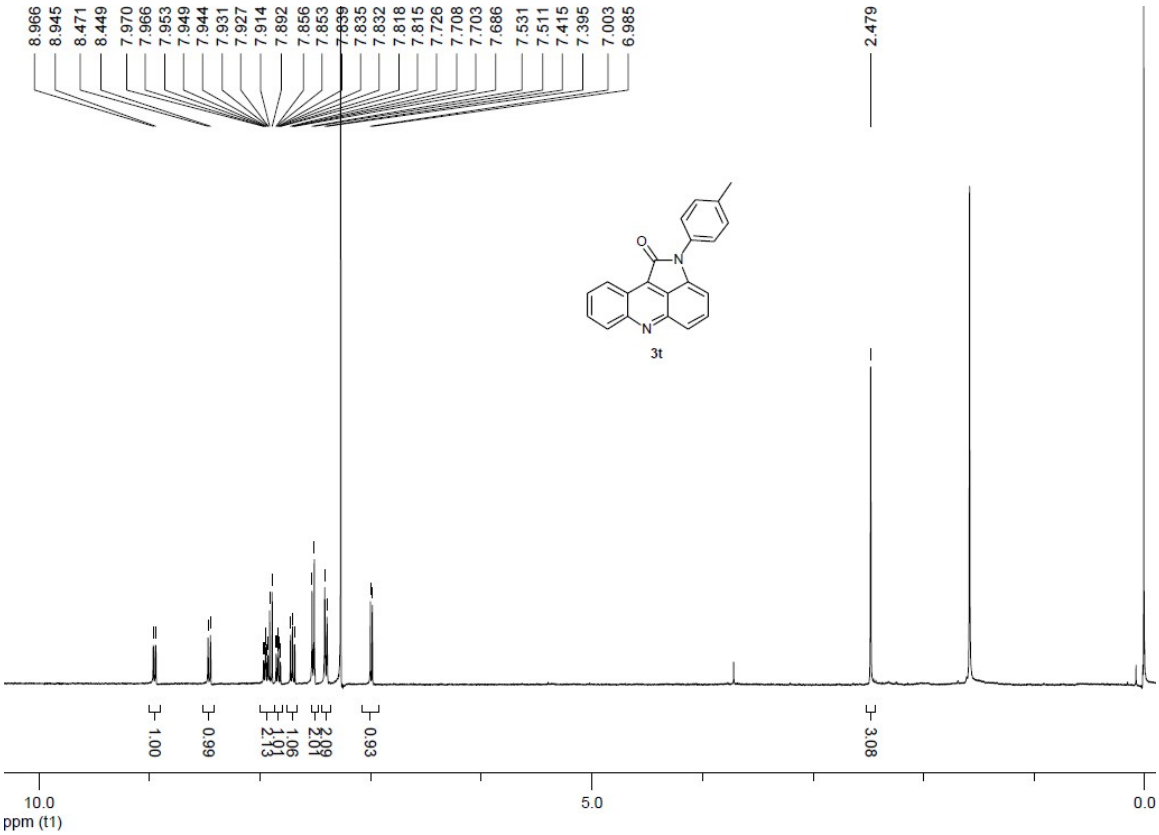

8.655
8.650
7.805
7.782
7.611
7.605
7.588
7.583
7.347
7.327
7.309
7.279
7.276
7.258
7.214
7.211
7.192
5.442
2.962
1.101
Br
O
N
N
3o
0.91
0.99
1.00
4.02
0.85
0.88
1.90
6.00
5.0
0.0
ppm (t1)

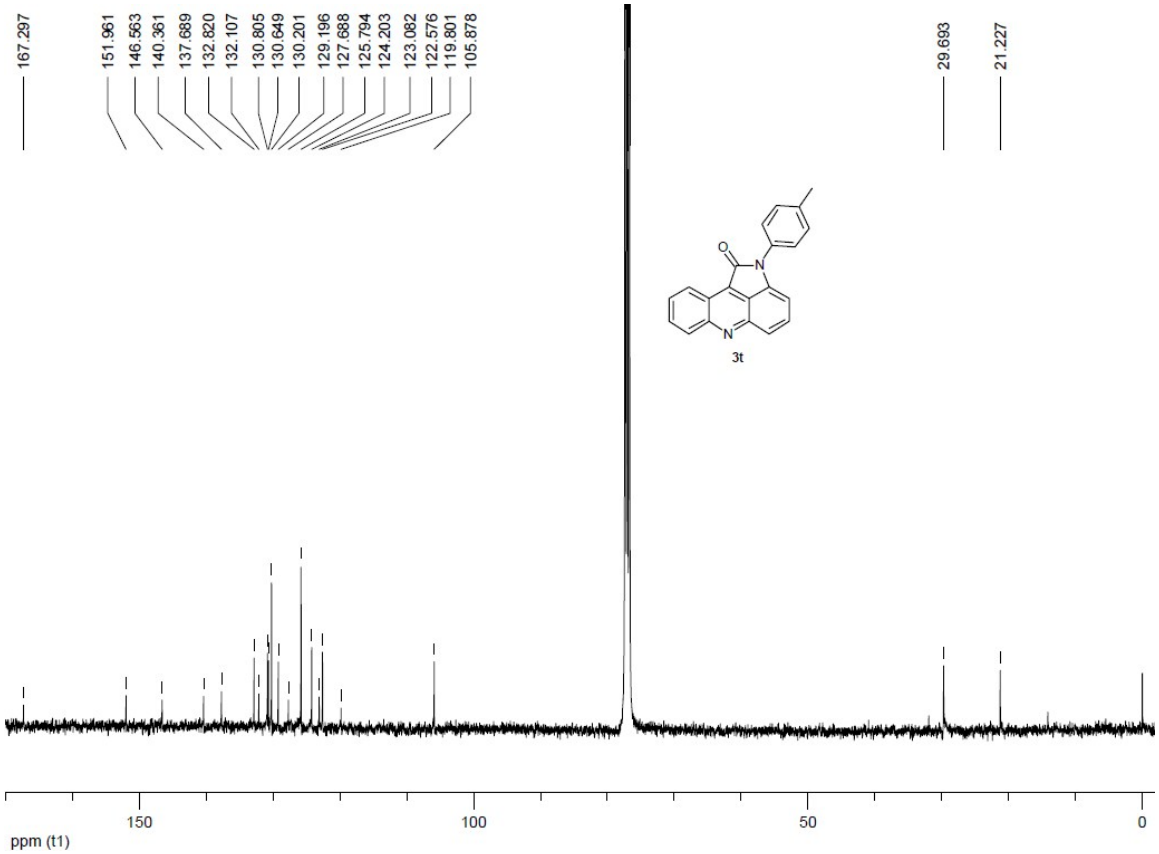

8.894
8.888
8.040
8.018
7.845
7.840
7.823
7.817
7.372
7.369
7.272
5.644
3.194
2.453
1.332
Br
O
N
N
3p
0.82
0.90
0.90
3.81
0.86
1.87
2.87
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

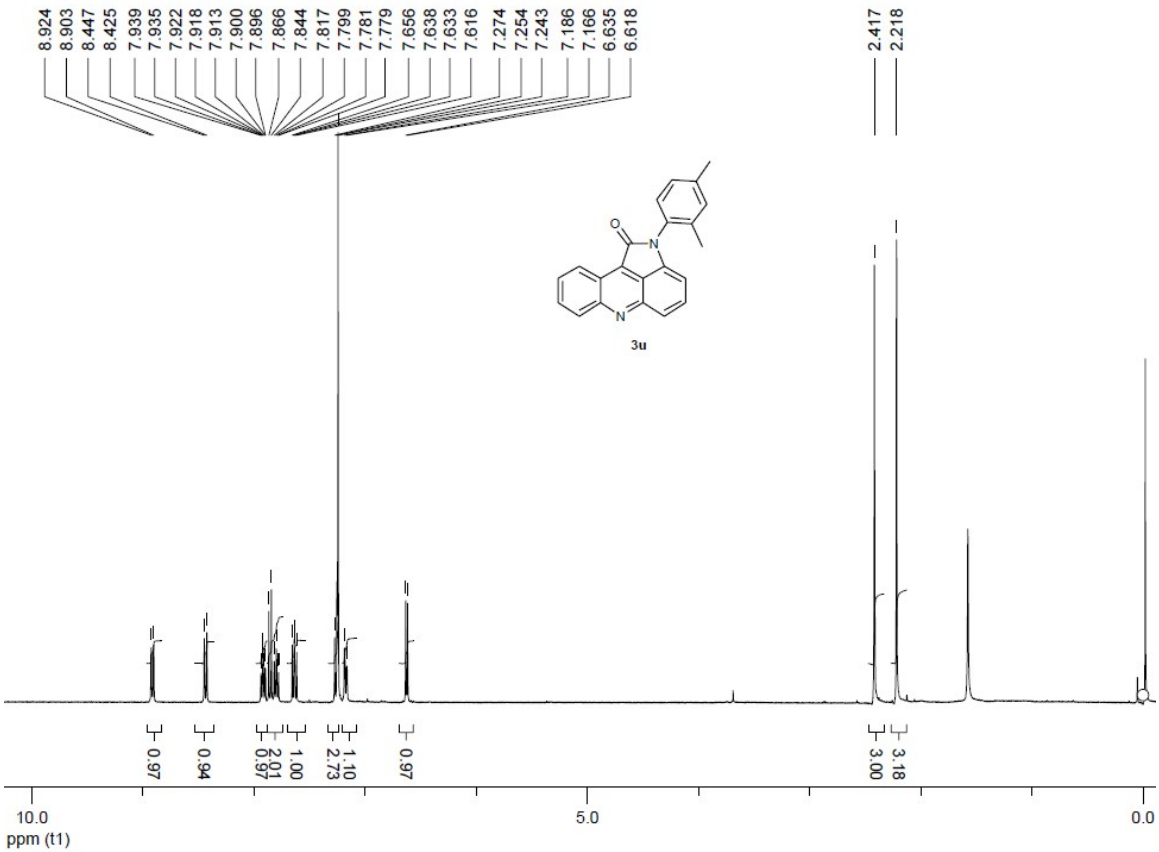

8.912
8.906
8.084
8.061
8.035
8.014
8.012
7.988
7.875
7.869
7.852
7.847
7.667
7.649
7.628
7.594
7.591
7.576
7.574
7.565
7.563
7.557
7.554
7.547
7.529
7.526
7.508
7.491
5.271
3.226
1.296
1.275
Br
O
N
3q
0.90
3.12
1.04
2.86
2.01
0.87
1.87
6.77
10.0
5.0
0.0
ppm (t1)

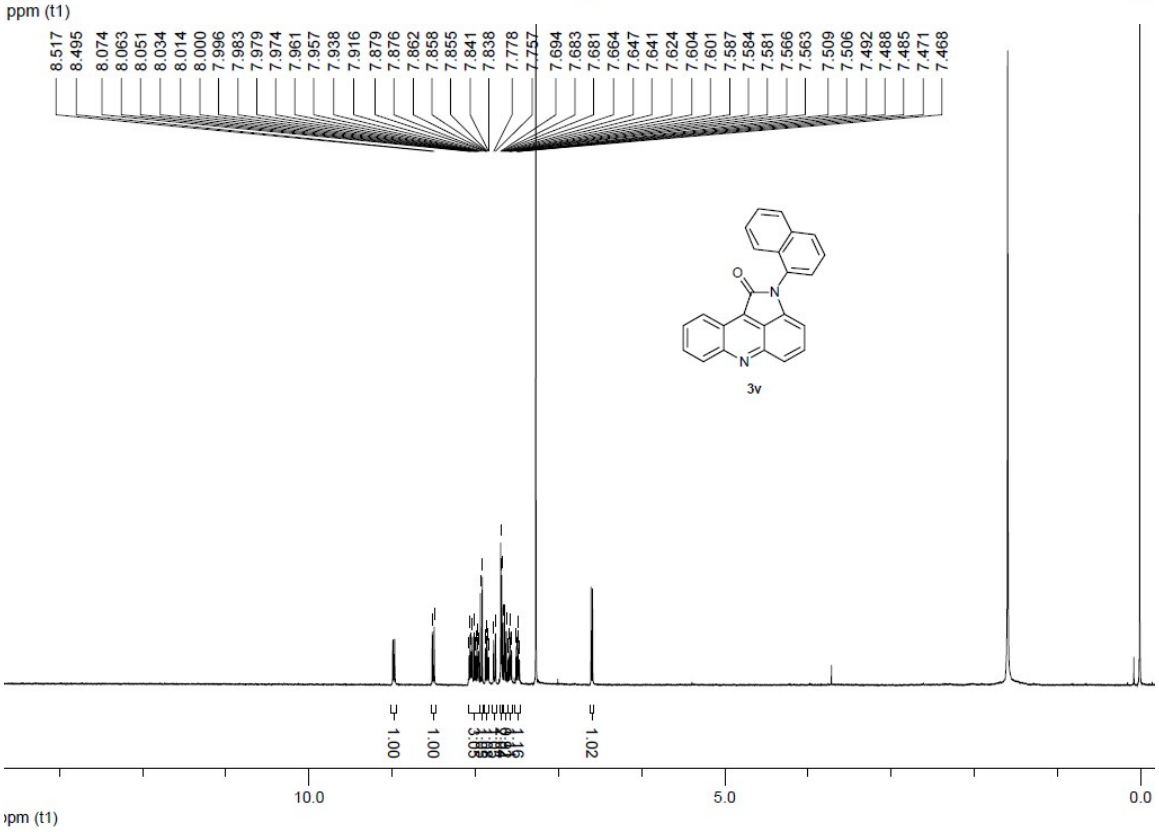

8.865
8.860
8.005
7.983
7.818
7.812
7.795
7.790
7.347
7.344
7.328
7.322
7.306
7.272
5.493
5.012
3.118
1.272
Br
O
N
3r
0.99
1.05
1.03
5.77
0.97
2.03
2.00
9.63
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

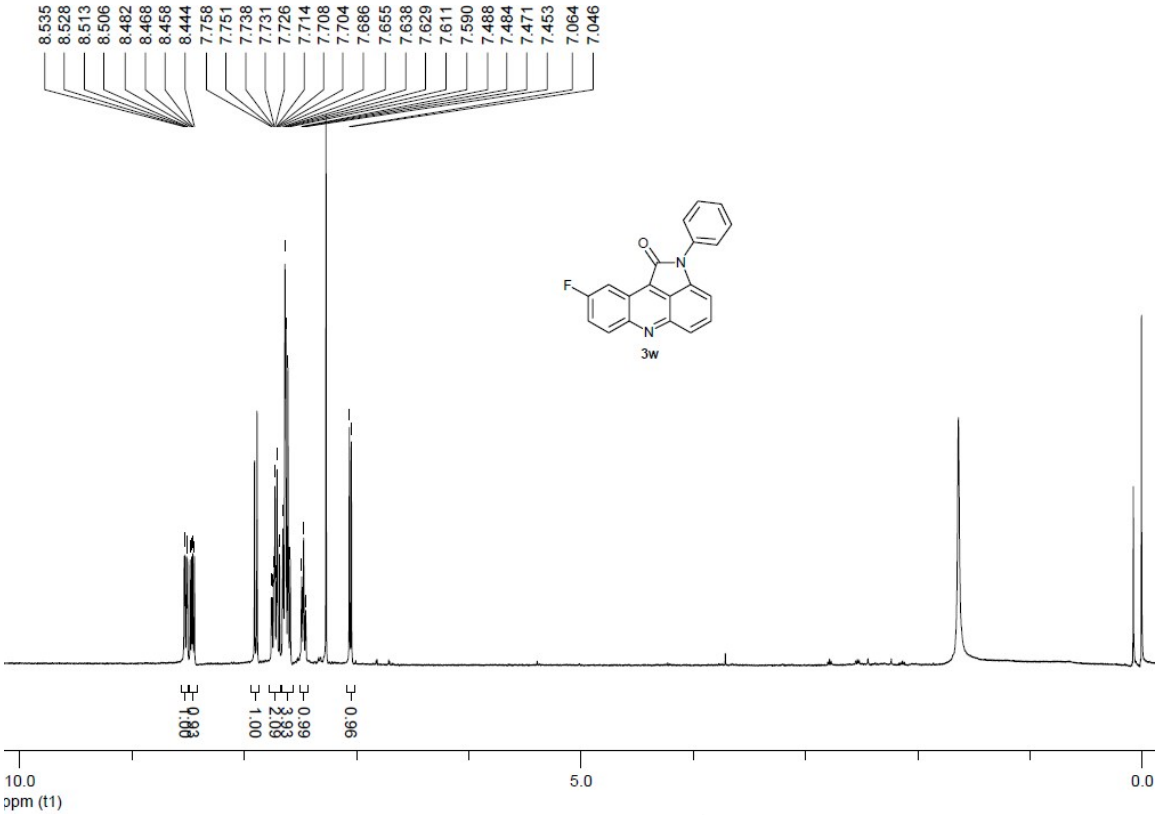

167.046
154.836
148.155
136.610
132.859
132.597
130.911
128.792
127.707
127.438
126.531
123.590
121.984
118.565
44.043
43.894
37.132
30.894
Br
O
N
3r
150
100
50
0
ppm (t1)
8.972
8.971
8.952
8.479
8.457
7.977
7.974
7.961
7.956
7.951
7.938
7.933
7.910
7.866
7.863
7.845
7.842
7.828
7.826
7.739
7.722
7.717
7.699
7.671
7.667
7.662
7.649
7.647
7.630
7.625
7.612
7.591
7.490
7.487
7.483
7.469
7.450
7.050
7.033
O
N
3s
1.00
0.97
2.03
1.05
4.69
4.68
1.10
1.07
10.0
5.0
0.0
ppm (t1)

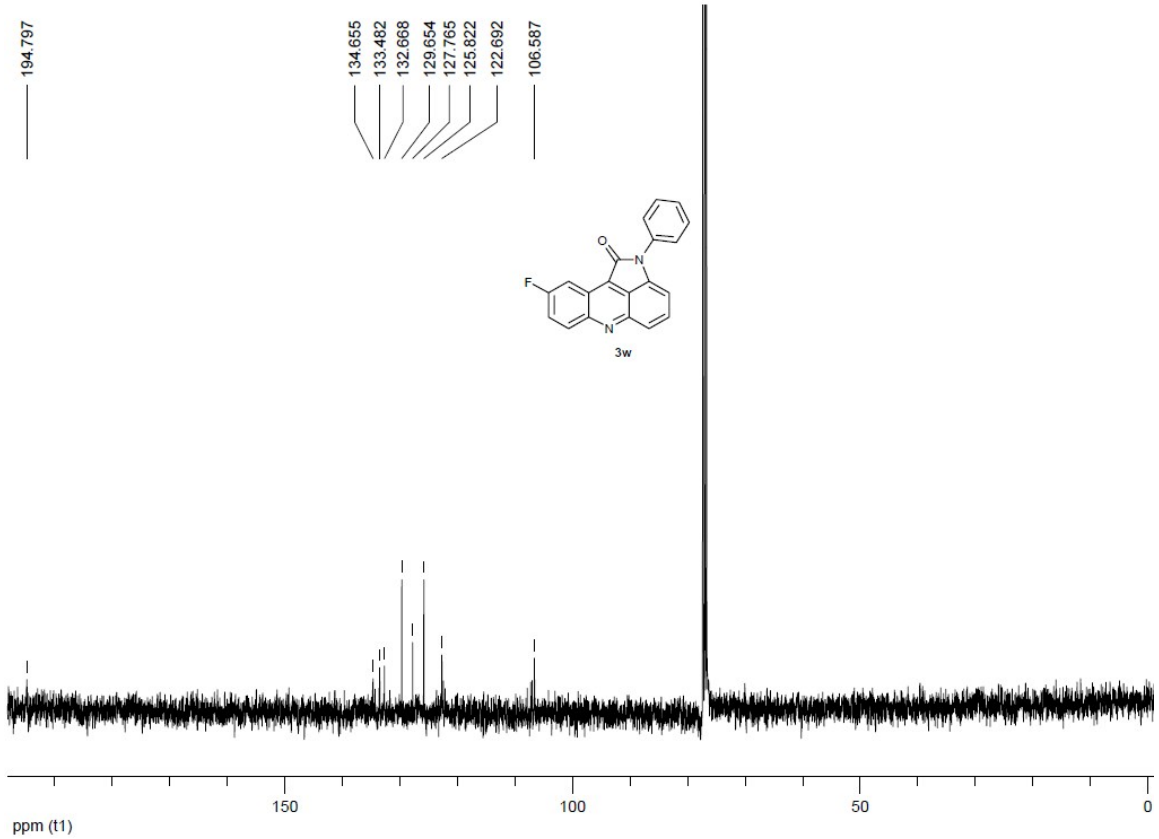

8.966
8.945
8.471
8.449
7.970
7.966
7.953
7.949
7.944
7.931
7.927
7.914
7.892
7.856
7.853
7.839
7.835
7.832
7.818
7.815
7.726
7.708
7.703
7.686
7.531
7.511
7.415
7.395
7.003
6.985
2.479
3t
1.00
0.99
2.17
1.06
2.09
2.07
0.93
3.08
10.0
5.0
0.0
ppm (t1)

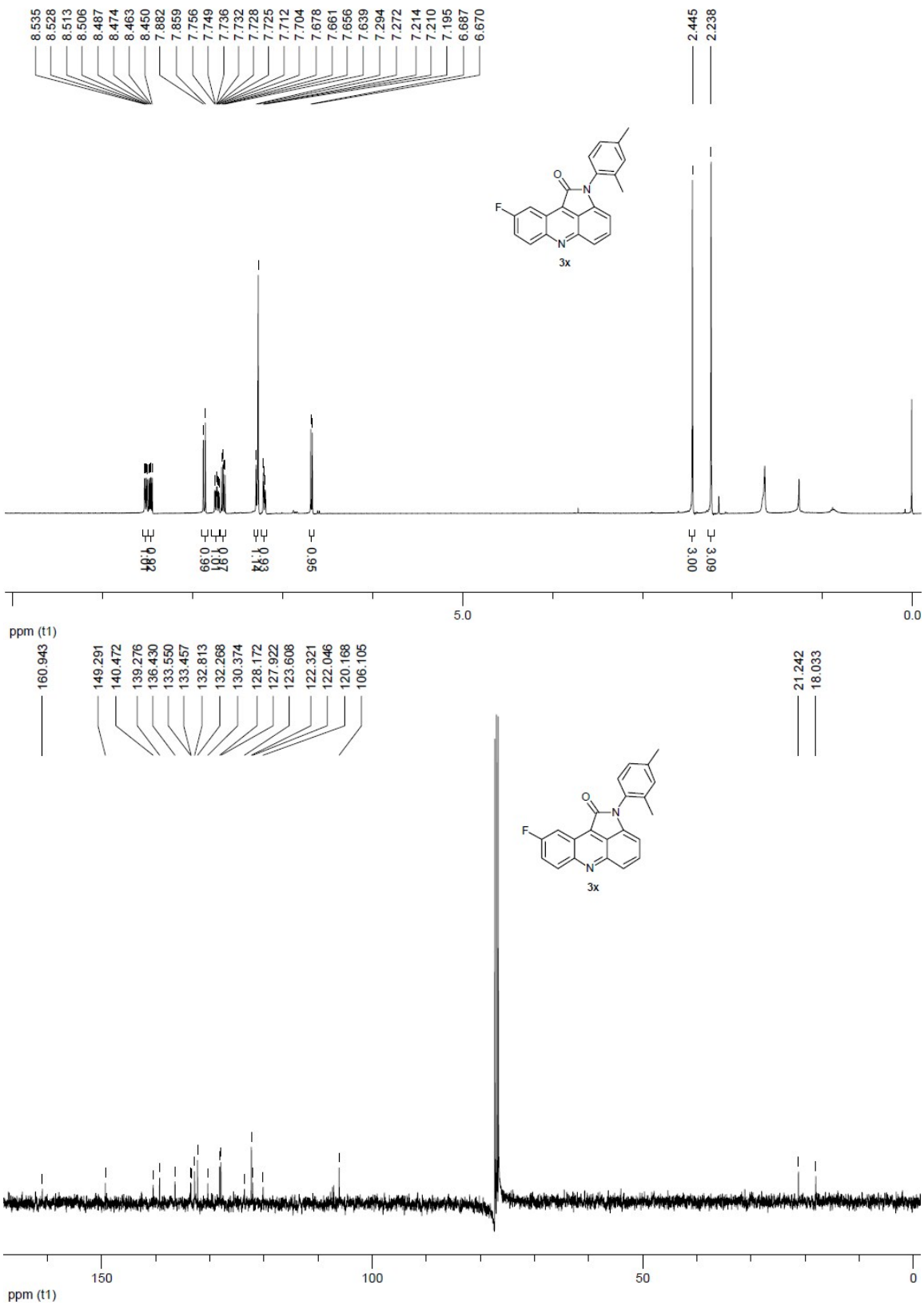

167.297
151.961
146.563
140.361
137.689
132.820
132.107
130.805
130.649
130.201
129.196
127.688
125.794
124.203
123.082
122.576
119.801
105.878
29.693
21.227
3t
150
100
50
0
ppm (t1)

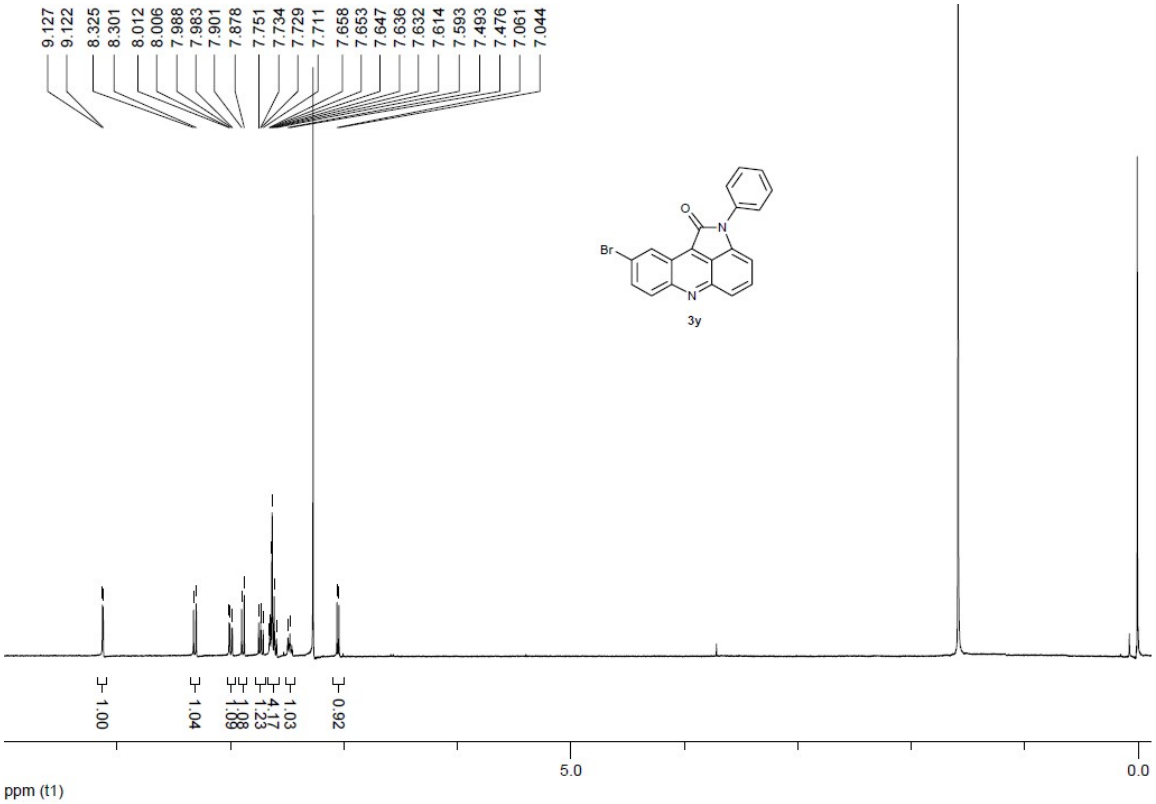

8.924
8.903
8.447
8.425
7.939
7.935
7.922
7.918
7.913
7.900
7.896
7.866
7.844
7.817
7.799
7.781
7.779
7.656
7.638
7.633
7.616
7.274
7.254
7.243
7.186
7.166
6.635
6.618
2.417
2.218
3u
0.97
0.94
2.01
1.00
2.73
1.10
0.97
3.00
3.18
10.0
5.0
0.0
ppm (t1)


8.517
8.495
8.074
8.063
8.051
8.034
8.014
8.000
7.996
7.983
7.979
7.974
7.961
7.957
7.938
7.916
7.879
7.876
7.862
7.858
7.855
7.841
7.838
7.778
7.757
7.694
7.683
7.681
7.664
7.647
7.641
7.624
7.604
7.601
7.587
7.584
7.581
7.566
7.563
7.509
7.506
7.492
7.488
7.485
7.471
7.468
3v
1.00
1.00
1.02
10.0
5.0
0.0
ppm (t1)


8.535
8.528
8.513
8.506
8.482
8.468
8.458
8.444
7.758
7.751
7.738
7.731
7.726
7.714
7.708
7.704
7.686
7.655
7.638
7.629
7.611
7.590
7.488
7.484
7.471
7.453
7.064
7.046
F
O
N
N
3w
1.00
1.00
2.09
3.83
2.09
0.99
0.96
10.0
5.0
0.0
ppm (t1)


194.797
134.655
133.482
132.668
129.654
127.765
125.822
122.692
106.587
F
O
N
N
3w
150
100
50
0
ppm (t1)


8.535
8.528
8.513
8.506
8.487
8.474
8.463
8.450
7.882
7.859
7.756
7.749
7.736
7.732
7.728
7.725
7.712
7.704
7.678
7.661
7.656
7.639
7.294
7.272
7.214
7.210
7.195
6.687
6.670
2.445
2.238
3x
0.84
0.99
0.97
1.00
1.17
0.93
0.95
3.00
3.09
5.0
0.0
ppm (t1)
160.943
149.291
140.472
139.276
136.430
133.550
133.457
132.813
132.268
130.374
128.172
127.922
123.608
122.321
122.046
120.168
106.105
21.242
18.033
3x
150
100
50
0
ppm (t1)


9.127
9.122
8.325
8.301
8.012
8.006
7.988
7.983
7.901
7.878
7.751
7.734
7.729
7.711
7.658
7.653
7.647
7.636
7.632
7.614
7.593
7.493
7.476
7.061
7.044
O
N
Br
N
3y
1.00
1.04
1.08
1.08
1.23
4.17
1.03
0.92
5.0
0.0
ppm (t1)