Facile synthesis of azaarene-2-substituted chromanone derivatives via tandem sp3 C−H functionlization/ decarboxylation of azaarenes with 4-oxo-4H-chromene-3-carboxylic acid

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Supporting Information

CONTENTS

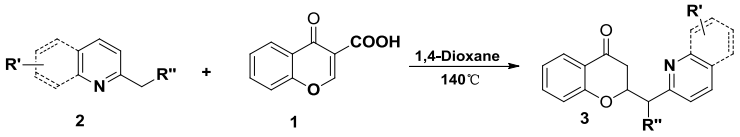
1. General Methods

All the chemical reagents were purchased from commercial companies and all the solvents were dried according to standard procedures before use. All reactions were performed in pressure-proof pipe and monitored by TLC with 0.2 mm silica gel-coated HSGF 254 plates. The reaction mixtures were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts were reported in ppm using tetramethylsilane (TMS, δ (ppm) = 0.00 ppm) as the internal standard, and relative to the signal of chloroform-d (δ 7.26, singlet). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), and multiplet (m). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were reported in parts per million using solvent $CDCl_3$ (δ (ppm) = 77.0 ppm) as an internal standard. HRMS analyses were performed on a Waters XEVO QTOF mass spectrometer. The compounds chromone-3-carbaldehyde[1, 2], chromone-3-carboxylic acid[3] and 3-acetyl-chromone[4] were prepared according the reported procedures.

2. Experimental Procedures

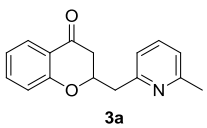
General Procedure for Synthesis of Azaarenes-Substituted Chromanones



To a 25 mL pressure tube equipped with a magnetic stirrer bar were added dioxane (1 mL), azaarenes **2** (0.75 mmol) and chromanone-3-carboxylic acids **1** (0.3 mmol). The mixture was then stirred at 140 °C and monitored by TLC until **1** was consumed up. Then the reaction was cooled to room temperature and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired product **3**.

3. Characterization of Products

3.1 2-((6-Methylpyridin-2-yl) methyl) chroman-4-one



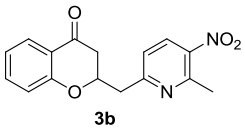
3a

Red-brown solid, yield 67%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.48-7.42 (m, 1H), 7.08-7.02 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 4.97-4.89 (m, 1H), 3.36 (dd, *J* = 13.8, 7.0 Hz, 1H), 3.15 (dd, *J* = 13.8, 6.1 Hz, 1H), 2.76 (d, *J* = 7.7 Hz, 2H), 2.53 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.2, 161.4, 158.2, 155.8, 136.7,

135.9, 126.9, 121.5, 121.2, 121.1, 121.0, 117.9, 77.4, 43.4, 42.5, 24.3. **HRMS (ESI):** calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$: 254.1176, found: 254.11776.

3.2 2-((6-Methyl-5-nitropyridin-2-yl)methyl)chroman-4-one

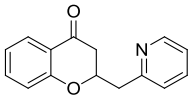


3b

Brown solid, yield 56%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49-7.44 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.05-4.97 (m, 1H), 3.41 (dd, *J* = 14.1, 7.7 Hz, 1H), 3.25 (dd, *J* = 14.1, 5.0 Hz, 1H), 2.85 (s, 3H), 2.84-2.80 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.6, 161.1, 161.0, 153.7, 144.3, 136.1, 132.9, 127.0, 122.4, 121.6, 120.9, 117.8, 76.6, 43.2, 42.6, 24.0. **HRMS (ESI):** calcd. for $C_{16}H_{15}N_2O_4$ $[M+H]^+$: 299.1027, found: 299.1025.

3.3 2-(pyridin-2-ylmethyl)chroman-4-one

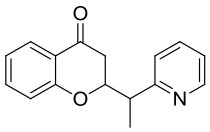


3c

Brown viscous liquid, 70%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 3.9 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.29-7.26 (m, 1H), 7.22-7.16 (m, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 5.00-4.91 (m, 1H), 3.39 (dd, *J* = 13.9, 6.9 Hz, 1H), 3.20 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.77 (dd, *J* = 6.9, 1.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.2, 161.4, 156.7, 149.6, 136.6, 136.0, 127.0, 124.3, 122.0, 121.4, 121.1, 118.0, 77.4, 43.4, 42.6. **HRMS (ESI):** calcd. for $C_{15}H_{14}NO_2$ $[M+H]^+$:240.1020, found: 240.1020.

3.4 2-(1-(pyridin-2-yl)ethyl)chroman-4-one

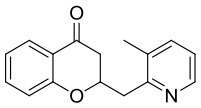


3d

Brown viscous liquid, 37%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.3 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.69-7.62 (m, 1H), 7.45-7.38 (m, 1H), 7.28-7.25 (m, 1H), 7.18 (dd, *J* = 7.0, 5.2 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 4.88-4.77 (m, 1H), 3.44-3.37 (p, *J* = 7.0 Hz, 1H), 2.75 (dd, *J* = 9.8, 8.1 Hz, 2H), 1.45 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.5, 161.5, 161.4, 149.2, 136.4, 135.8, 126.9, 123.0, 121.9, 121.2, 121.0, 117.9, 80.8, 45.6, 40.1, 15.3. **HRMS (ESI):** calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$: 254.1176, found: 254.1175.

3.5 2-((3-methylpyridin-2-yl)methyl)chroman-4-one

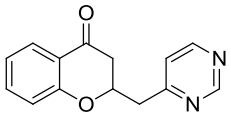


3e

Brown viscous liquid, 57%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 3.8 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.10 (dd, *J* = 7.4, 4.9 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.08-5.00 (m, 1H), 3.44 (dd, *J* = 14.2, 6.6 Hz, 1H), 3.19 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.88-2.75 (m, 2H), 2.37 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.3, 161.5, 155.2, 146.8, 137.9, 135.9, 132.1, 127.0, 121.9, 121.2, 121.1, 117.9, 77.5, 42.7, 40.0, 19.0. **HRMS (ESI):** calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$:254.1176, found: 254.1176.

3.6 2-(Pyrimidin-4-ylmethyl)chroman-4-one

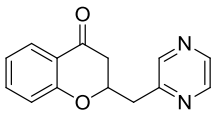


3f

Brown viscous liquid, 41%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.70 (d, *J* = 5.0 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.49-7.43 (m, 1H), 7.33 (d, *J* = 5.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 5.05-4.97 (m, 1H), 3.33 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.18 (dd, *J* = 14.3, 5.0 Hz, 1H), 2.84-2.78 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.4, 165.4, 160.9, 158.8, 156.9, 136.1, 127.0, 121.8, 121.6, 120.9, 117.8, 76.2, 42.7, 42.6. **HRMS (ESI):** calcd. for $C_{14}H_{13}N_2O_2$ $[M+H]^+$: 241.0972, found: 241.0972.

3.7 2-(Pyrazin-2-ylmethyl)chroman-4-one

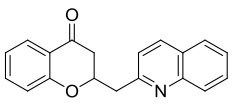


3g

Brown viscous liquid, 25%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.54 (s, 1H), 8.49 (d, *J* = 2.3 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.48-7.43 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 4.99-4.89 (m, 1H), 3.38 (dd, *J* = 14.3, 7.6 Hz, 1H), 3.23 (dd, *J* = 14.3, 5.0 Hz, 1H), 2.83-2.79 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.6, 161.1, 152.7, 145.6, 144.2, 143.1, 136.1, 127.0, 121.6, 120.9, 117.9, 76.6, 42.6, 40.6. **HRMS (ESI):** calcd. for $C_{14}H_{13}N_2O_2$ $[M+H]^+$: 241.0972, found: 241.0973.

3.8 2-(Quinolin-2-ylmethyl)chroman-4-one

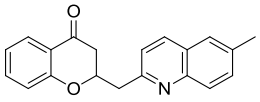


3h

Brown liquid, yield 53%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74-7.68 (m, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.46-7.37 (m, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.12-5.04 (m, 1H), 3.56 (dd, *J* = 14.0, 7.1 Hz, 1H), 3.39 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.87-2.82 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.0, 161.3, 157.2, 147.9, 136.5, 135.9, 129.6, 128.9, 127.5, 126.9, 126.2, 125.8, 122.2, 121.3, 121.0, 117.9, 77.4, 44.0, 42.6. **HRMS (ESI):** calcd. for $C_{19}H_{16}NO_2$ $[M+H]^+$: 290.1176, found: 290.1170.

3.9 2-((6-Methylquinolin-2-yl)methyl)chroman-4-one

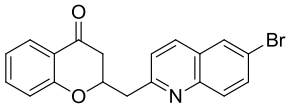


3i

Brown liquid, yield 45%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.58-7.50 (m, 2H), 7.46-7.40 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.09-5.01 (m, 1H), 3.53 (dd, *J* = 14.0, 7.1 Hz, 1H), 3.35 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.84-2.80 (m, 2H), 2.52 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.1, 161.3, 156.2, 146.5, 136.0, 135.9, 135.7, 131.8, 128.5, 126.9, 126.9, 126.3, 122.2, 121.3, 121.0, 117.9, 77.4, 43.9, 42.6, 21.4. **HRMS (ESI):** calcd. for $C_{20}H_{18}NO_2$ $[M+H]^+$: 304.1333, found: 304.1327.

3.10 2-((6-Bromoquinolin-2-yl)methyl)chroman-4-one

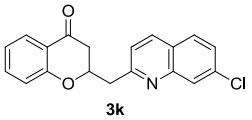


3j

Brown liquid, yield 43%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 1.9 Hz, 1H), 7.92-7.87 (m, 2H), 7.77 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.48-7.39 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.12-5.04 (m, 1H), 3.55 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.38 (dd, *J* = 14.1, 5.7 Hz, 1H), 2.87-2.83 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.9, 161.2, 157.8, 146.4, 135.9, 135.3, 133.0, 130.6, 129.5, 128.0, 126.9, 123.1, 121.4, 121.0, 120.0, 117.9, 77.1, 43.9, 42.6. **HRMS (ESI):** calcd. for $C_{19}H_{15}BrNO_2$ $[M+H]^+$:368.0281, found: 368.0275. $C_{19}H_{15}{}^{81}BrNO_2$ $[M+H+2]^+$: 370.0261, found: 370.0260.

3.11 2-((7-chloroquinolin-2-yl)methyl)chroman-4-one



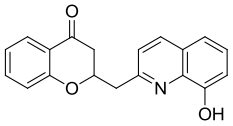
3k

Brown liquid, yield 39%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.92-7.85 (m, 2H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.46-7.38 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.19-4.98 (m, 1H), 3.55 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.39 (dd, *J* = 14.1, 5.7 Hz, 1H), 2.90-2.77 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 161.3, 158.5, 148.2, 136.0, 135.5, 133.8, 128.7, 127.0, 125.3, 125.24, 122.5, 121.4, 121.0, 118.2, 117.9, 77.2, 43.9, 42.6. **HRMS (ESI):** calcd. for $C_{19}H_{15}ClNO_2$ $[M+H]^+$:324.0786, found: 324.0781. $C_{19}H_{15}{}^{37}ClNO_2$ $[M+H+2]^+$: 326.0757, found: 326,0458.

3.12 2-((8-hydroxyquinolin-2-yl)methyl)chroman-4-one

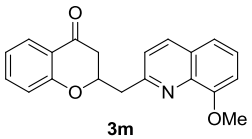


3l

Brown liquid, yield 48%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.47-7.36 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 5.11-5.02 (m, 1H), 3.53 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.36 (dd, *J* = 14.1, 5.6 Hz, 1H), 2.80 (d, *J* = 7.7 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.7, 161.2, 155.1, 151.7, 137.7, 136.6, 136.0, 127.4, 127.1, 126.9, 122.9, 121.4, 121.0, 117. 9, 117.6, 110.2, 77.1, 43.4, 42.5. **HRMS (ESI):** calcd. for $C_{19}H_{16}NO_3$ $[M+H]^+$: 306.1125, found: 306.1129.

3.13 2-((8-methoxyquinolin-2-yl)methyl)chroman-4-one

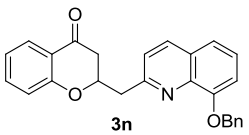


3m

Brown liquid, yield 67%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 6.6 Hz, 1H), 7.49-7.42 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.11-5.03 (m, 1H), 4.08 (s, 3H), 3.62 (dd, *J* = 13.9, 7.5 Hz, 1H), 3.47 (dd, *J* = 13.9, 5.4 Hz, 1H), 2.84 (d, *J* = 7.7 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.1, 161.4, 156.4, 155.1, 140.0, 136.3, 135.9, 128.2, 127.0, 126.4, 122.9, 121.3, 121.1, 119.5, 118.0, 108.0, 77.7, 56.1, 44.2, 42.7. **HRMS (ESI):** calcd. for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1282, found: 320.1280.

3.14 2-((8-(benzyloxy)quinolin-2-yl)methyl)chroman-4-one



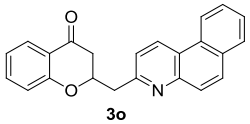
3n

Brown liquid, yield 71%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.37-7.31 (m, 4H), 7.30-7.26 (m, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.02-6.97 (m, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.40 (s, 2H), 5.16-5.07 (m, 1H), 3.61 (dd, *J* = 14.1, 7.1 Hz, 1H), 3.47 (dd, *J* = 14.1, 5.7 Hz, 1H), 2.91-2.83 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.1, 161.4, 156.3, 154.1, 140.3, 137.1, 136.3, 135.9, 129.0, 128.7, 128.5, 127.7, 126.9, 126.2, 122.8, 121.3, 121.1, 119.9, 117.9, 111.0, 77.5, 71.0, 43.9, 42.6. **HRMS**

(ESI): calcd. for $C_{26}H_{22}NO_3$ $[M+H]^+$: 396.1595, found: 396.1596.

3.15 2-(benzo[f]quinolin-3-ylmethyl)chroman-4-one

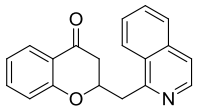


3o

Brown liquid, yield 59%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.4 Hz, 1H), 8.60 (d, *J* = 8.1 Hz, 1H), 8.05-7.85 (m, 4H), 7.72-7.57 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.18-5.06 (m, 1H), 3.59 (dd, *J* = 14.0, 7.1 Hz, 1H), 3.43 (dd, *J* = Hz, 1H), 2.92-2.75 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.1, 161.4, 156.7, 147.9, 135.9, 131.5, 131.2, 131.0, 129.5, 128.7, 127.8, 127.1, 126.9, 126.8, 124.0, 122.5, 122.2, 121.3, 121.09, 117.9, 77.4, 43.7, 42.7. **HRMS (ESI):** calcd. for $C_{23}H_{17}NO_2$ $[M+H]^+$: 339.1254, found: 339.1250.

3.16 2-(isoquinolin-1-ylmethyl)chroman-4-one

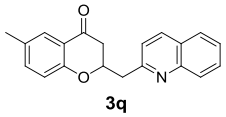


3p

Brown liquid, yield 57%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.6 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.64-7.58 (m, 1H), 7.57 (d, *J* = 5.7 Hz, 1H), 7.45-7.39 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 5.24-5.16 (m, 1H), 3.98 (dd, *J* = 14.5, 6.2 Hz, 1H), 3.66 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.89-2.83 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.2, 161.5, 156.6, 141.9, 136.4, 135.9, 130.1, 127.6, 127.5, 127.4, 127.0, 125.1, 121.4, 121.1, 120.1, 118.0, 77.3, 42.9, 40.0. **HRMS (ESI):** calcd. for $C_{19}H_{16}NO_2$ $[M+H]^+$:290.1176, found: 290.1170.

3.17 6-methyl-2-(quinolin-2-ylmethyl)chroman-4-one



3q

Brown viscous liquid, 51%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.74 - 7.70 (m, 1H), 7.68-7.65 (m, 1H), 7.55 - 7.50 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.26-7.24 (m, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.07-5.0 (m, 1H), 3.55 (dd, *J* = 13.9, 7.2 Hz, 1H), 3.38 (dd, *J* = 13.9, 5.7 Hz, 1H), 2.85 – 2.79 (m, 2H), 2.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.4, 159.4, 157.4, 147.9, 137.0, 136.5, 130.8, 129.6, 128.9, 127.5, 127.0, 126.5, 126.2, 122.3, 120.6, 117.7, 77.4, 44.1, 42.7, 20.4. **HRMS (ESI):** calcd. for $C_{20}H_{18}NO_2$ $[M+H]^+$:304.1333, found: 304.1337.

Reference

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3. Y. Machida, S. Nomoto, S. Negi, H. Ikuta, I. Saito, *Synthetic Communications*, 1980, **10**, 889.
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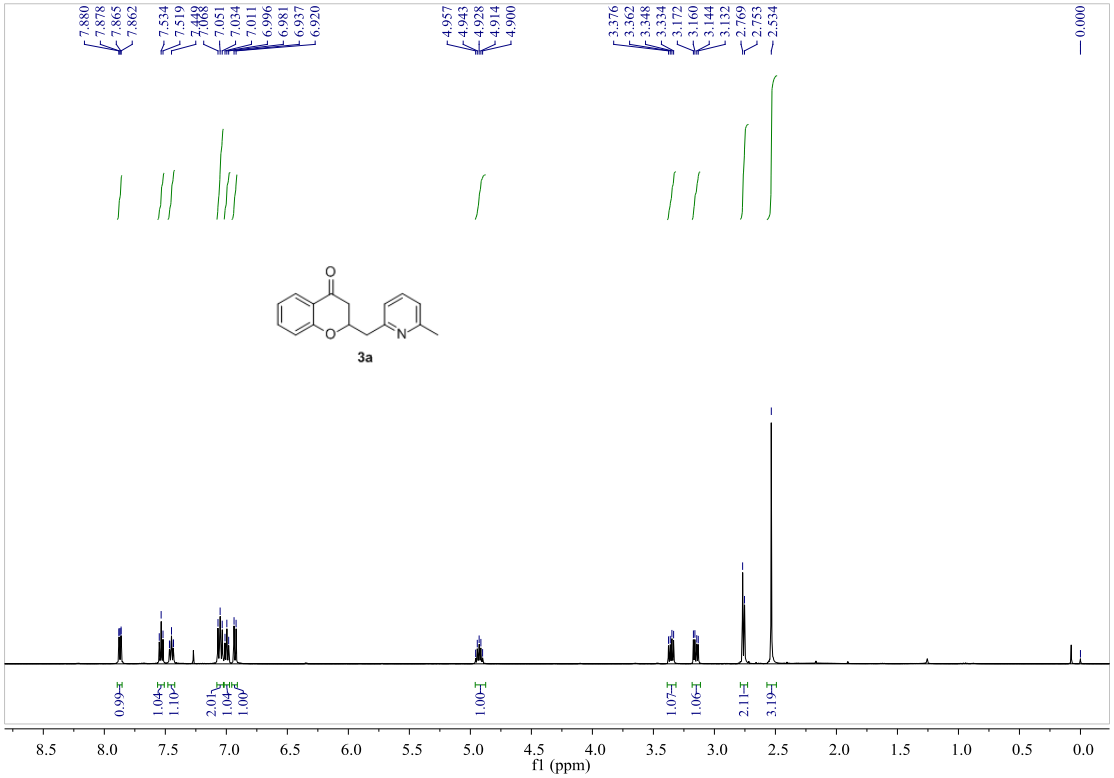
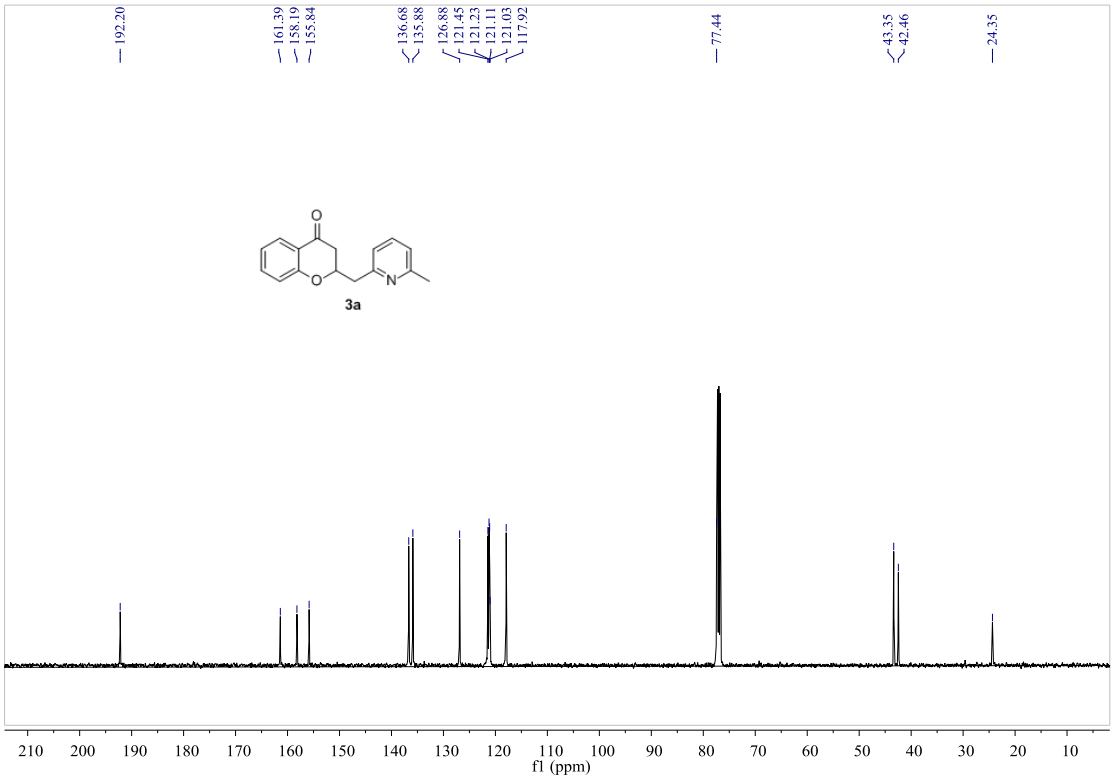
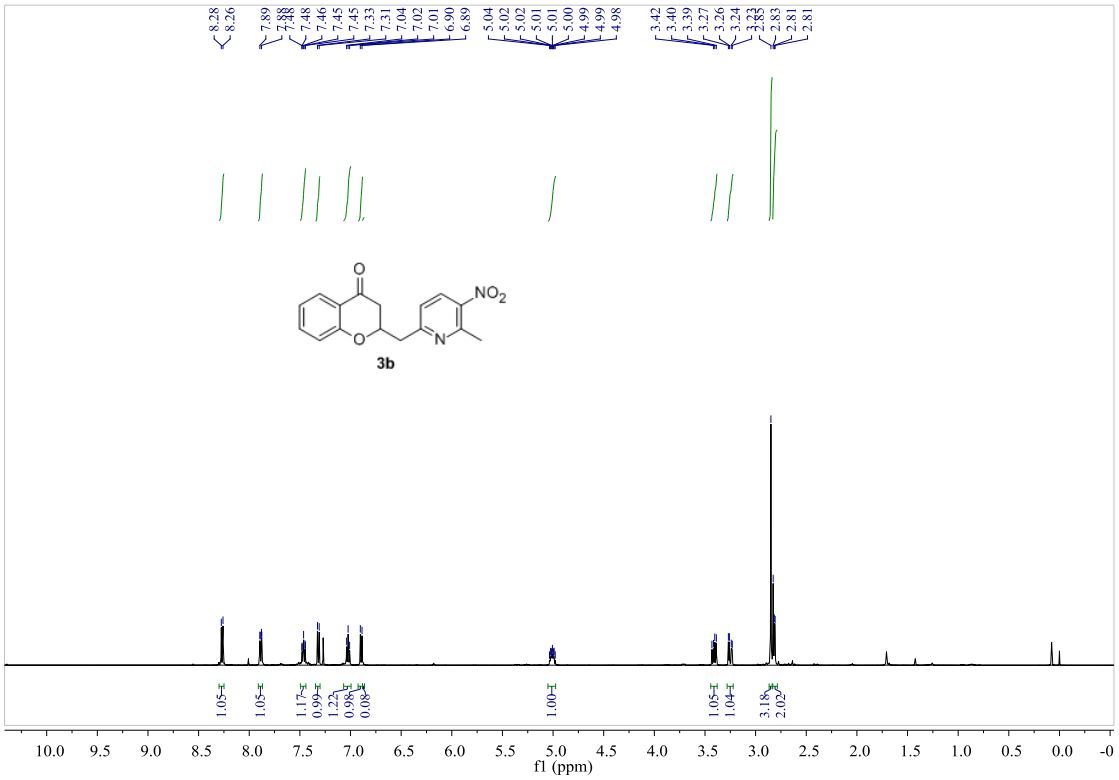
4. ^{1}H- and ^{13}C-NMR Spectras



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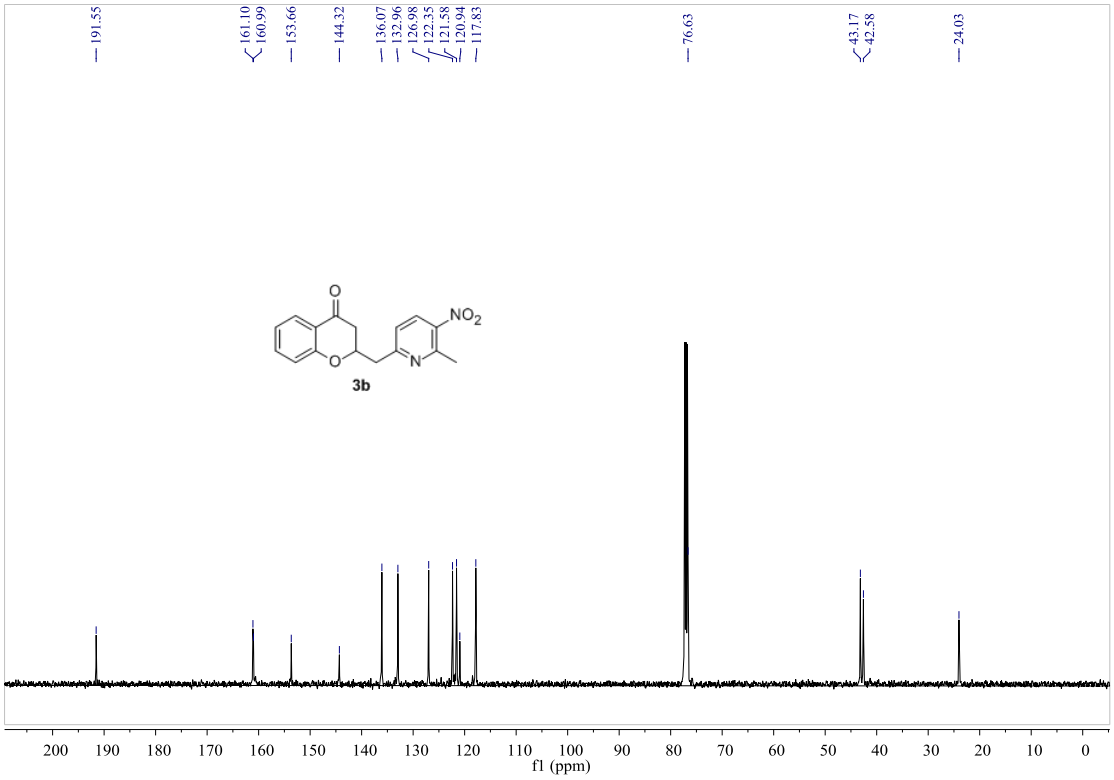
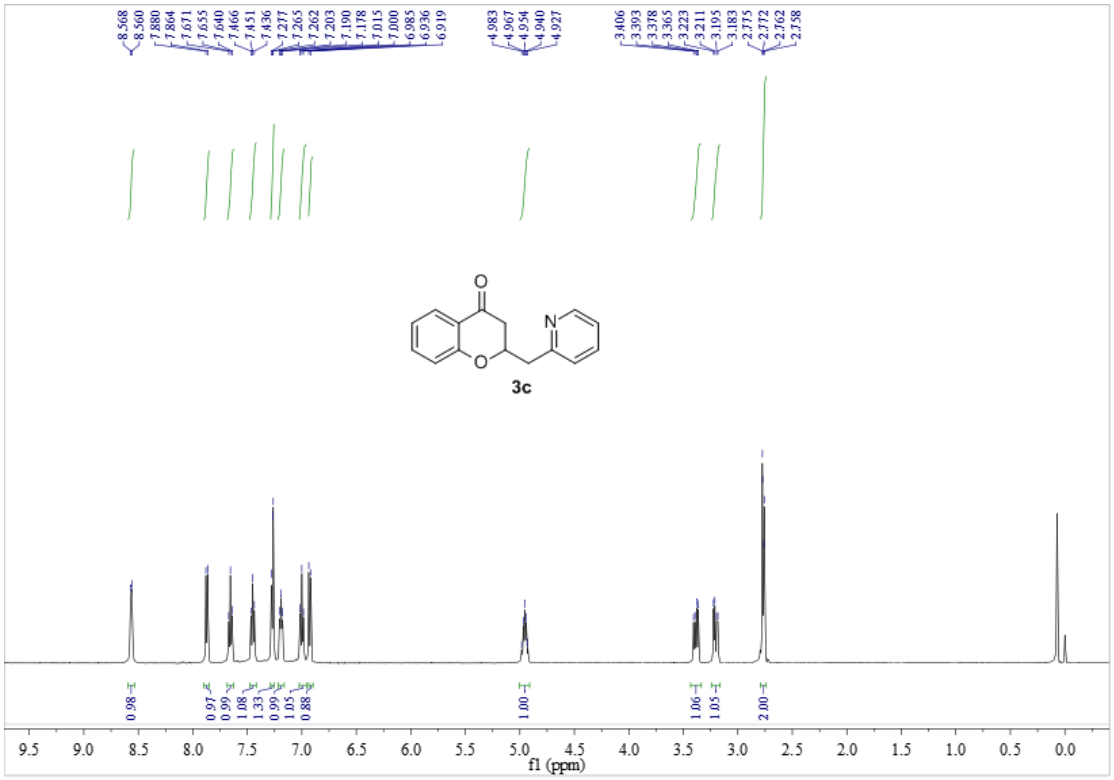
8.26
7.89
7.88
7.48
7.46
7.45
7.33
7.31
7.04
7.02
7.01
6.90
6.89
5.04
5.02
5.01
5.00
4.99
4.98
3.42
3.40
3.39
3.27
3.26
3.24
2.85
2.83
2.81
2.81
O
NO2
N
O
3b
1.05
1.05
1.17
0.99
1.22
0.98
0.08
1.00
1.05
1.04
3.18
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


191.55
161.10
160.99
153.66
144.32
136.07
132.96
126.98
122.35
121.58
120.94
117.83
76.63
43.17
42.58
24.03
O
NO2
N
O
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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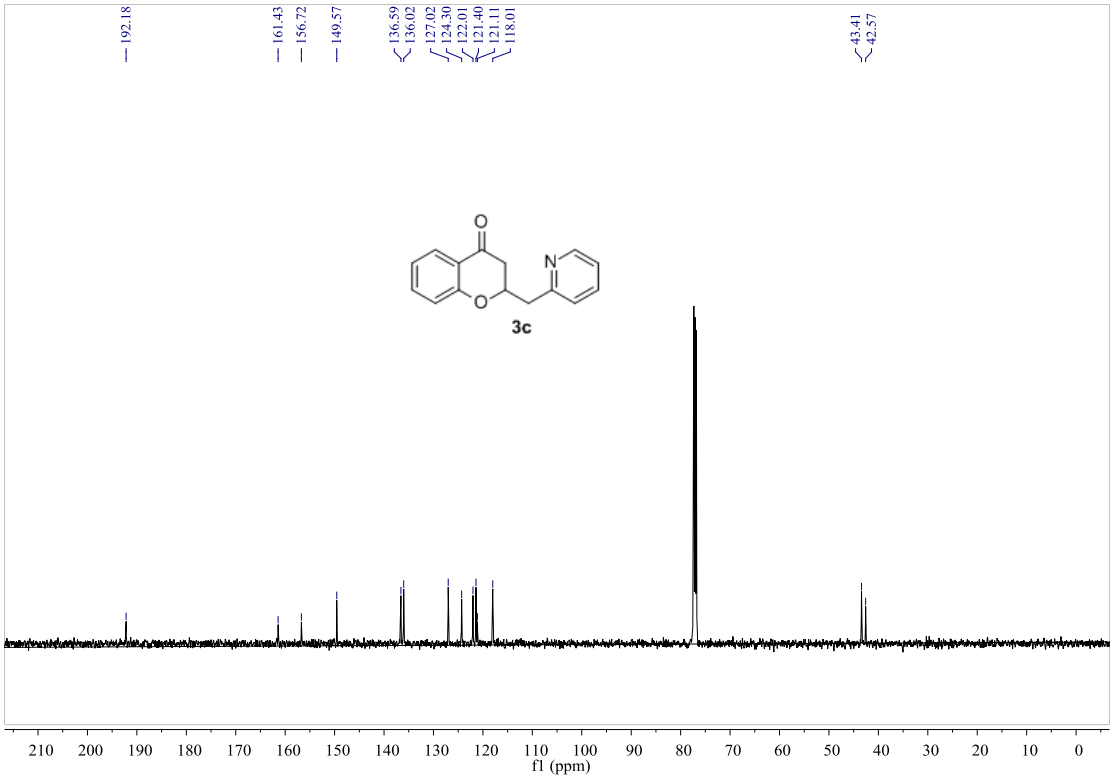
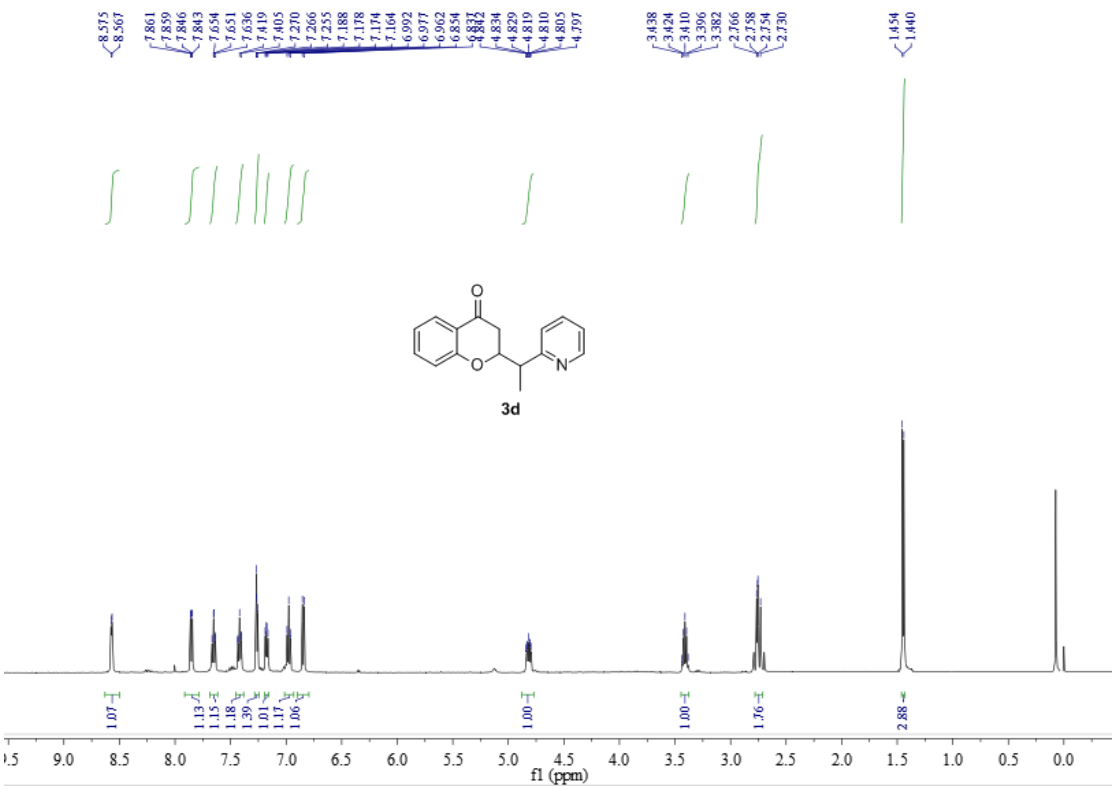
8.560
7.880
7.864
7.671
7.655
7.640
7.466
7.451
7.436
7.277
7.265
7.262
7.203
7.190
7.178
7.015
7.000
6.985
6.936
6.919
4.983
4.967
4.954
4.940
4.927
3.406
3.393
3.378
3.365
3.223
3.211
3.195
3.183
2.775
2.772
2.762
2.758
O
N
O
3c
0.98
0.97
0.99
1.08
1.33
0.99
1.05
0.88
1.00
1.06
1.05
2.00
9.5 9.0 8.5 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)


192.18
161.43
156.72
149.57
136.59
136.02
127.02
124.30
122.01
121.40
121.11
118.01
43.41
42.57
O
N
O
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.859
7.846
7.843
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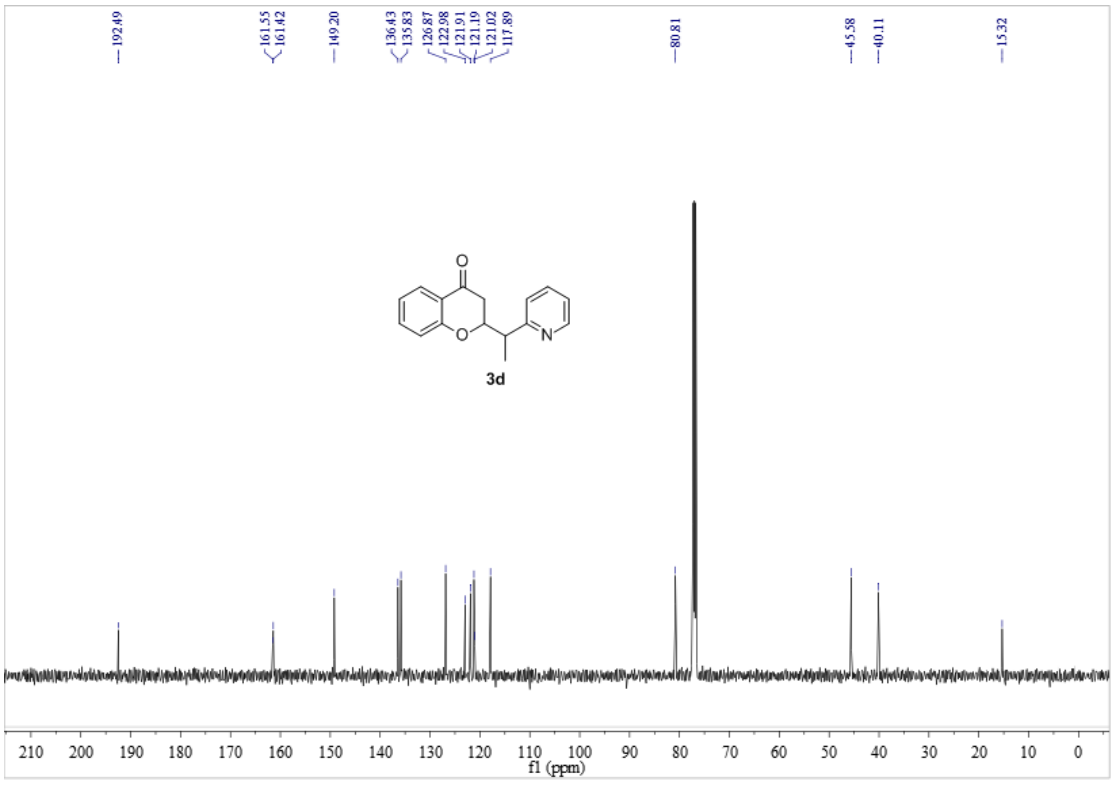
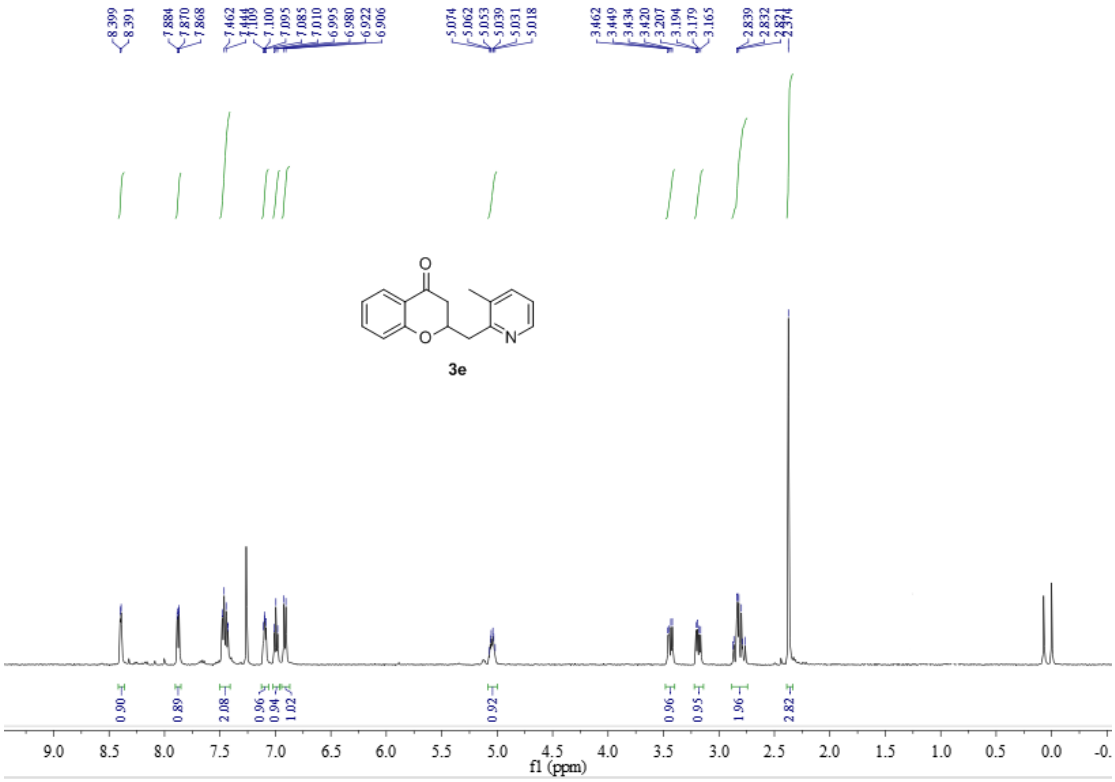
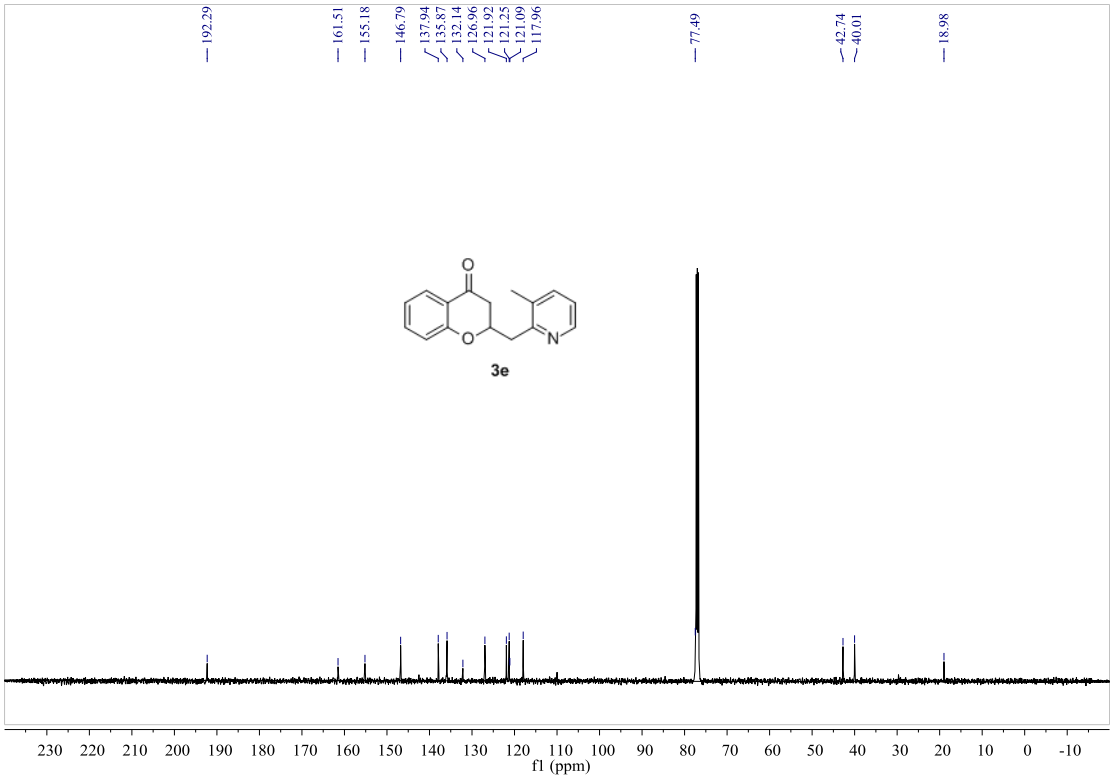
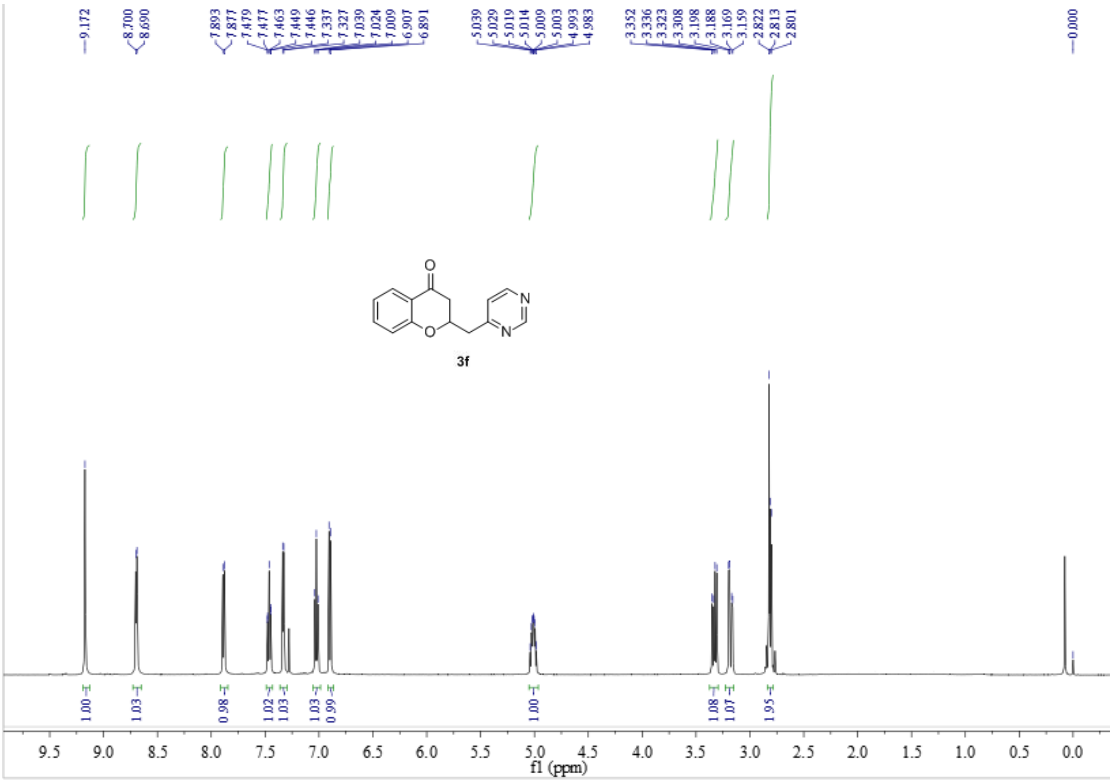
7.419
7.405
7.270
7.266
7.255
7.188
7.178
7.174
7.164
6.992
6.977
6.962
6.854
6.834
4.842
4.834
4.829
4.819
4.810
4.805
4.797
3.438
3.424
3.410
3.396
3.382
2.766
2.758
2.754
2.730
1.454
1.440
O
O
N
3d
1.07
1.13
1.15
1.18
1.39
1.01
1.17
1.06
1.00
1.00
1.76
2.88
f1 (ppm)


192.49
161.55
161.42
149.20
136.43
135.83
126.87
122.98
121.91
121.19
121.02
117.89
80.81
45.58
40.11
15.32
O
O
N
3d
f1 (ppm)


8.399
8.391
7.884
7.870
7.868
7.462
7.100
7.095
7.085
7.010
6.995
6.980
6.922
6.906
5.074
5.062
5.053
5.039
5.031
5.018
3.462
3.449
3.434
3.420
3.207
3.194
3.179
3.165
2.839
2.832
2.821
2.374
O
O
N
3e
0.90
0.89
2.08
0.96
0.94
1.02
0.92
0.96
0.93
1.96
2.82
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)


192.29
161.51
155.18
146.79
137.94
135.87
132.14
126.96
121.92
121.25
121.09
117.96
77.49
42.74
40.01
18.98
O
O
N
3e
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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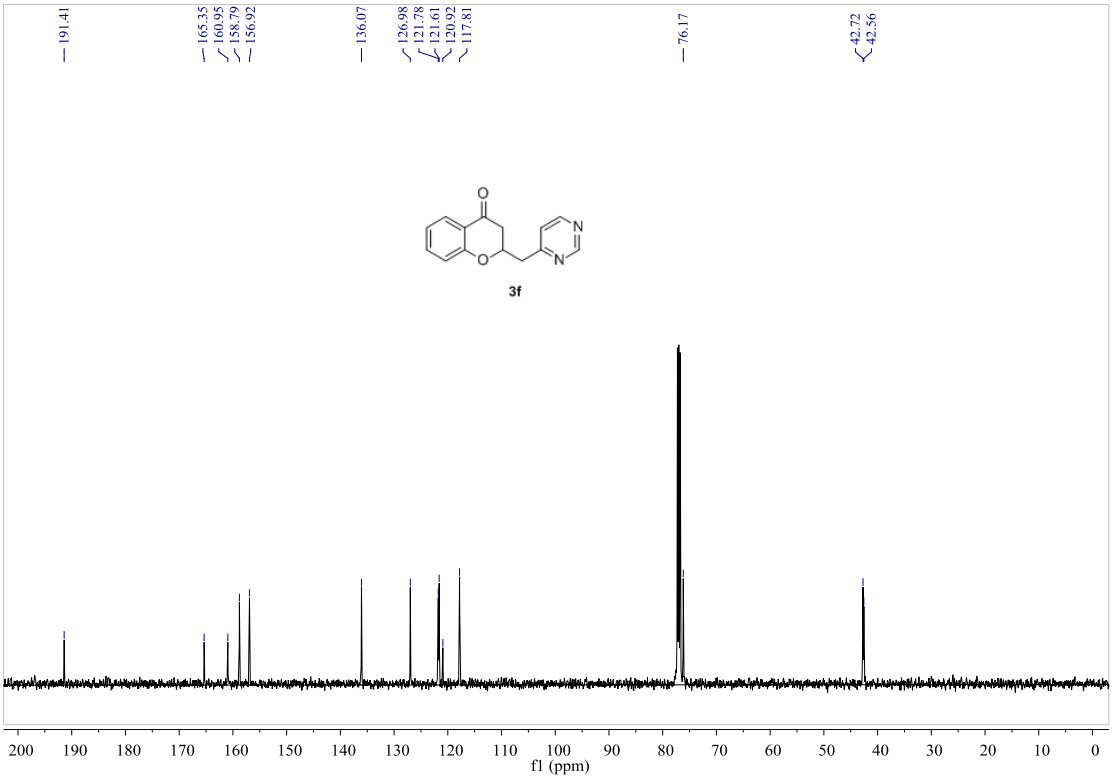
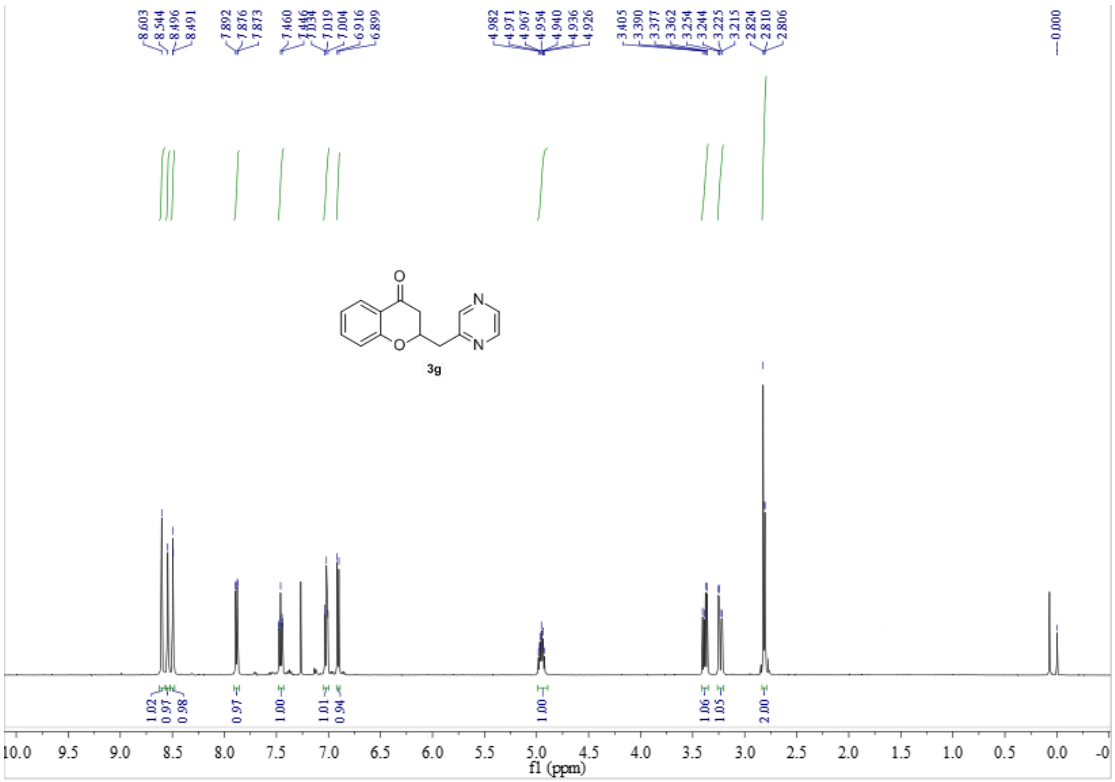
8.700
8.690
7.893
7.877
7.479
7.477
7.463
7.449
7.446
7.337
7.327
7.039
7.024
7.009
6.907
6.891
5.039
5.029
5.019
5.014
5.009
5.003
4.993
4.983
3.352
3.336
3.323
3.308
3.198
3.188
3.169
3.159
2.822
2.813
2.801
0.000
3f
1.00
1.03
0.98
1.02
1.03
1.03
0.99
1.00
1.08
1.07
1.95
f1 (ppm)


191.41
165.35
160.95
158.79
156.92
136.07
126.98
121.78
121.61
120.92
117.81
76.17
42.72
42.56
3f
f1 (ppm)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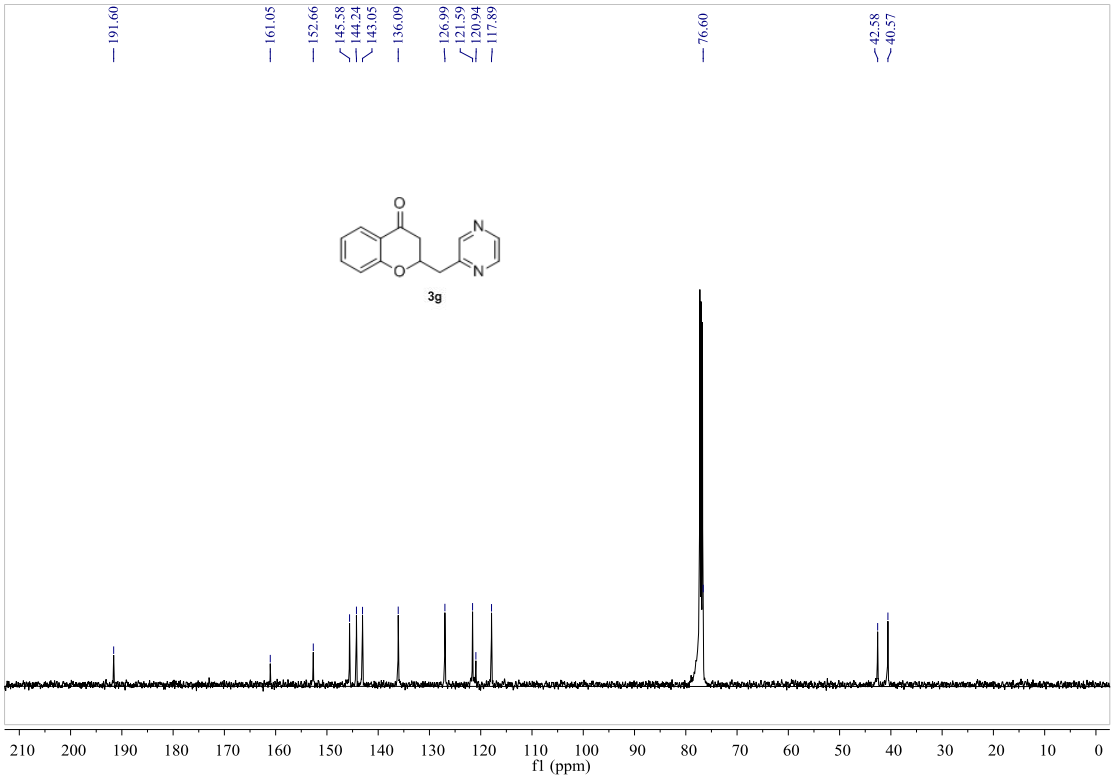
8.491
7.892
7.876
7.873
7.460
7.019
7.004
6.916
6.899
4.982
4.971
4.967
4.954
4.940
4.936
4.926
3.405
3.390
3.377
3.362
3.254
3.244
3.225
3.215
2.824
2.810
2.806
0.000
1.02
0.97
0.98
0.97
1.00
1.01
0.94
1.00
1.06
1.03
2.00
3g
f1 (ppm)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152.66
145.58
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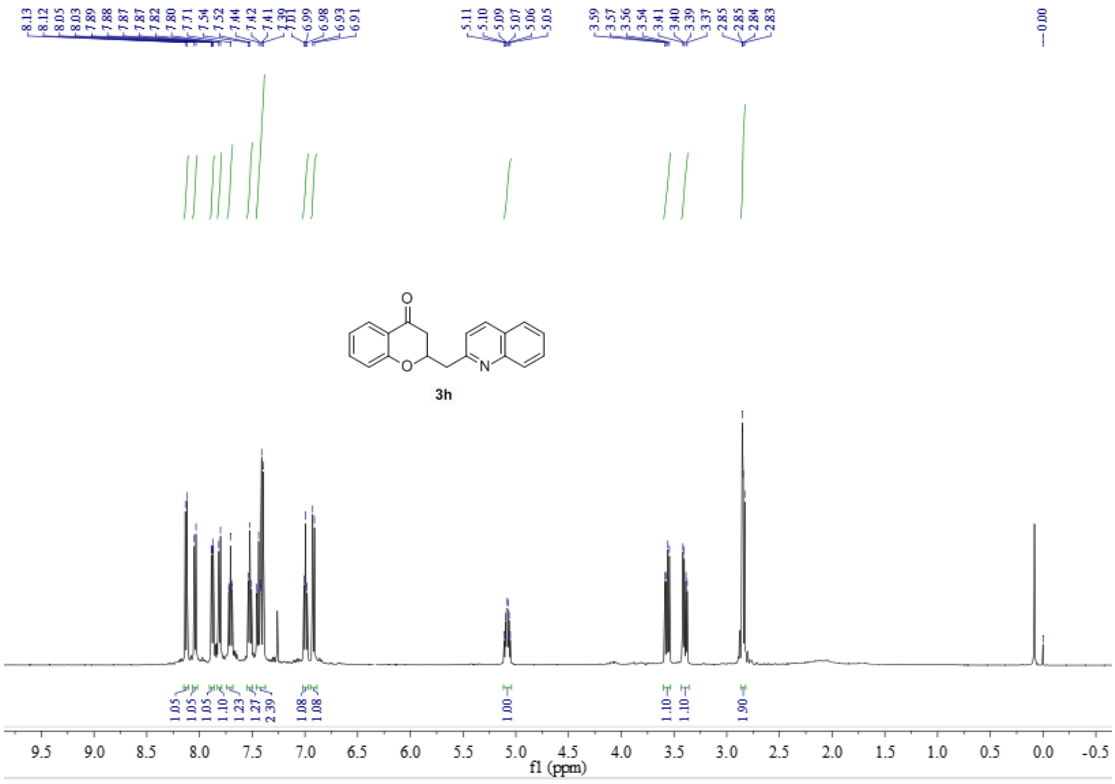
136.09
126.99
121.59
120.94
117.89
76.60
42.58
40.57
3g
f1 (ppm)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7.80
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6.91
5.11
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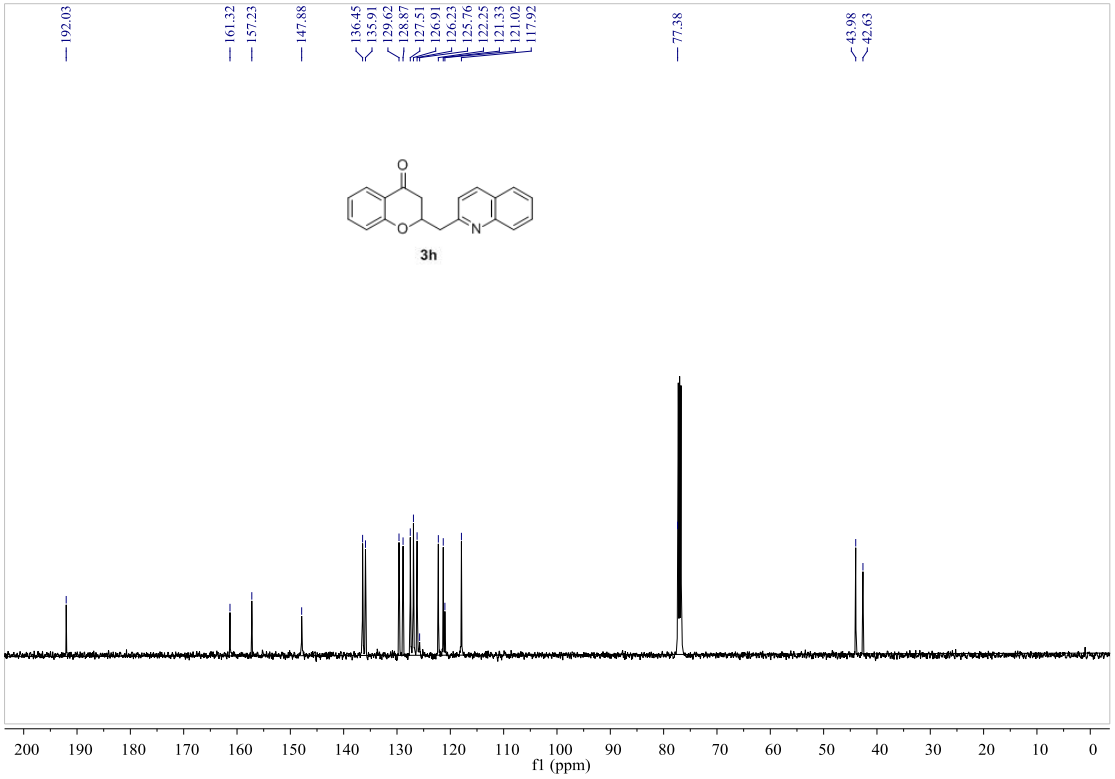
3.59
3.57
3.56
3.54
3.41
3.40
3.39
3.37
2.85
2.85
2.84
2.83
0.00
3h
1.03
1.05
1.05
1.10
1.23
1.27
2.39
1.08
1.08
1.00
1.10
1.10
1.90
f1 (ppm)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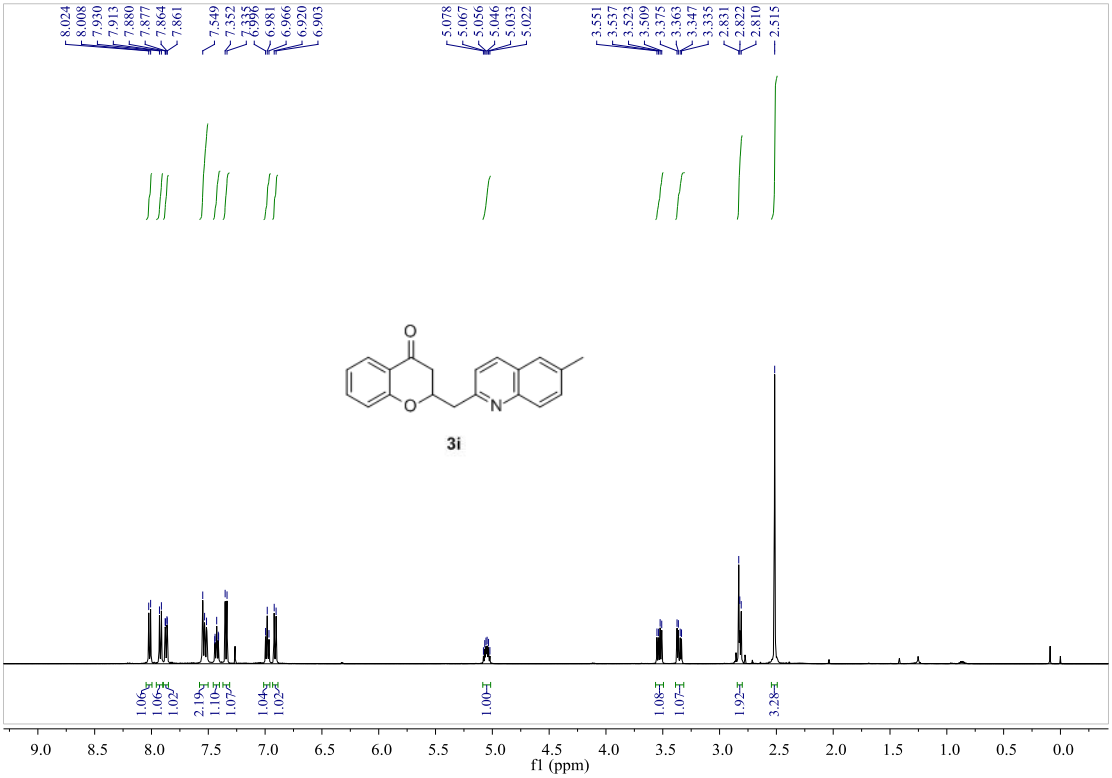
128.87
127.51
126.91
126.23
125.76
122.25
121.33
121.02
117.92
77.38
43.98
42.63
3h
f1 (ppm)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7.877
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7.352
7.335
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3.537
3.523
3.509
3.375
3.363
3.347
3.335
2.831
2.822
2.810
2.515
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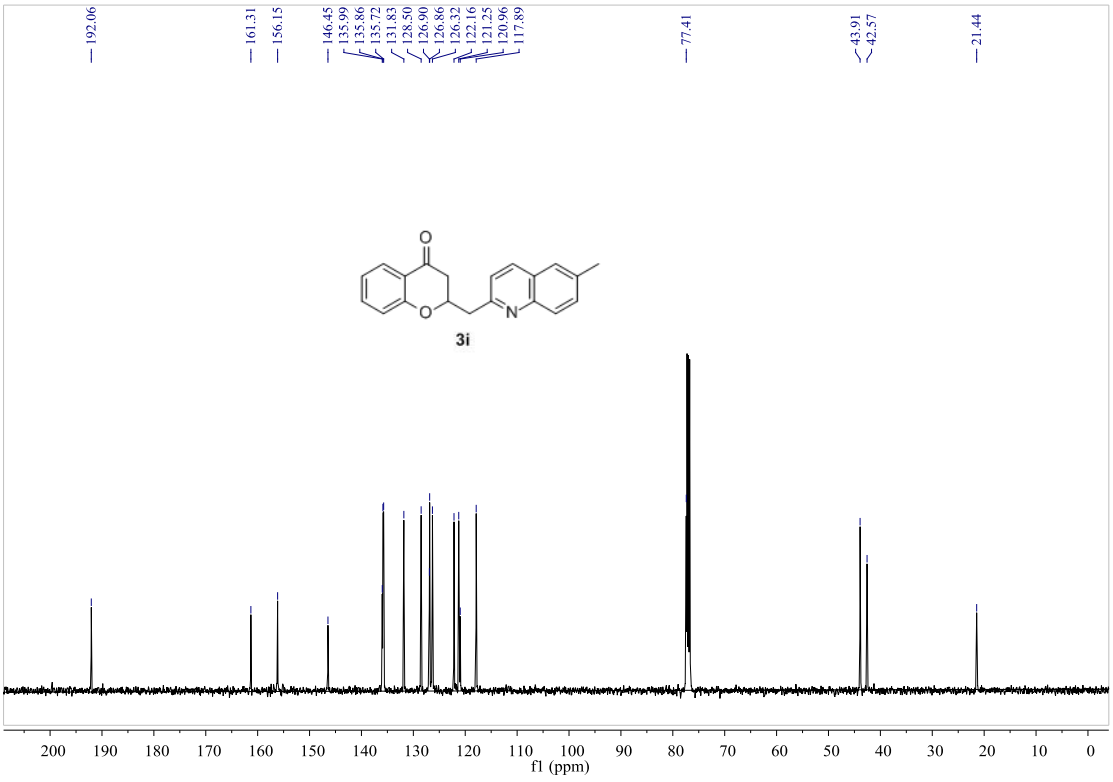
O
N
3i
1.06
1.06
1.02
2.19
1.10
1.07
1.04
1.02
1.00
1.08
1.07
1.92
3.28
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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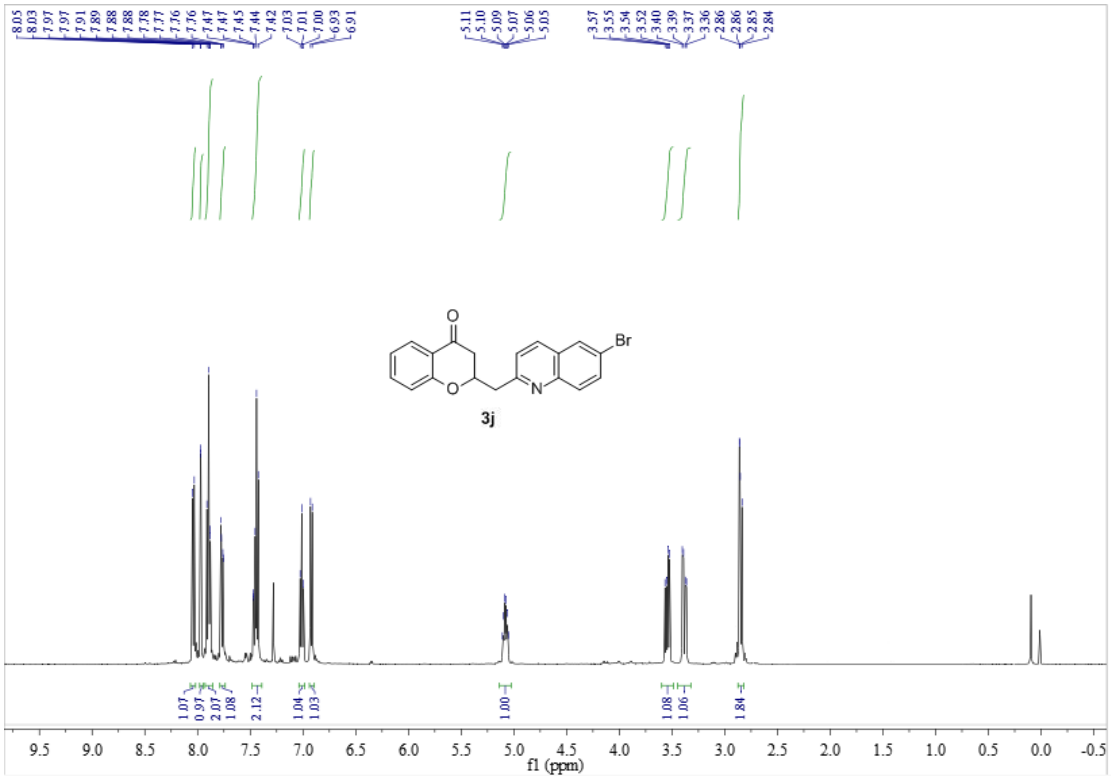
131.83
128.50
126.90
126.86
126.32
122.16
121.25
120.96
117.89
77.41
43.91
42.57
21.44
O
O
N
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.88
7.78
7.77
7.76
7.76
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7.47
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7.00
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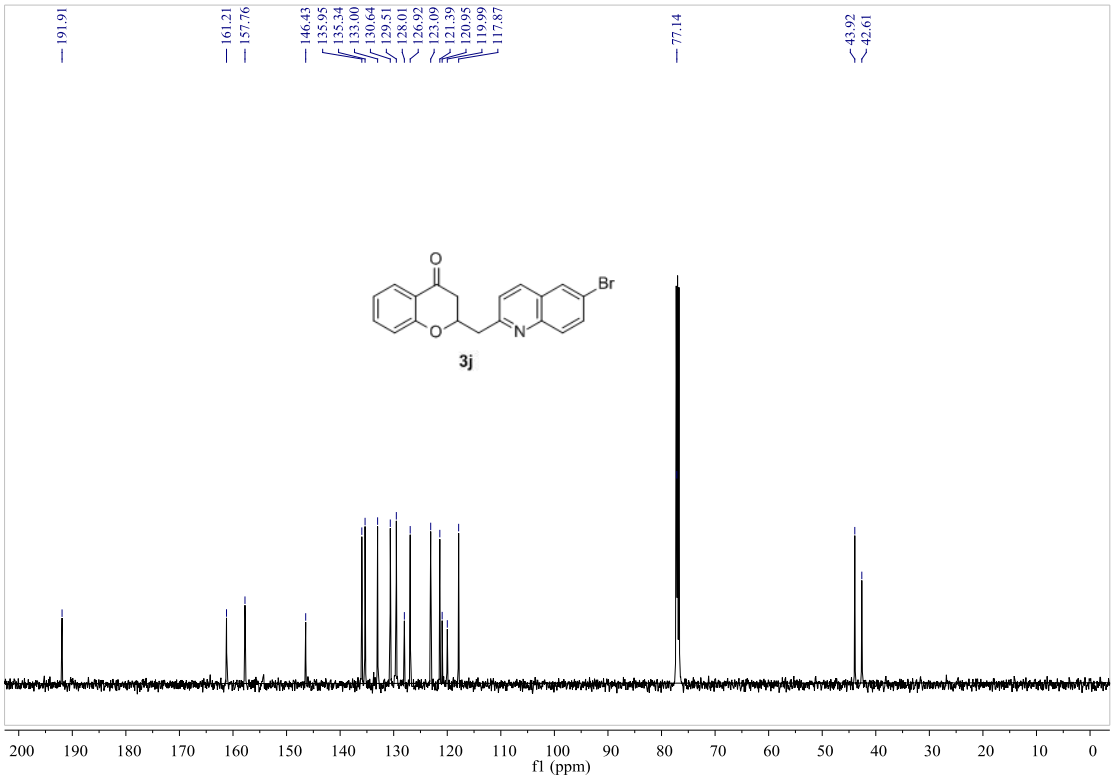
6.91
5.11
5.10
5.09
5.07
5.06
5.05
3.57
3.55
3.54
3.52
3.40
3.39
3.37
3.36
2.86
2.86
2.85
2.84
O
Br
O
N
3j
1.07
0.97
2.07
1.08
2.12
1.04
1.03
1.00
1.08
1.06
1.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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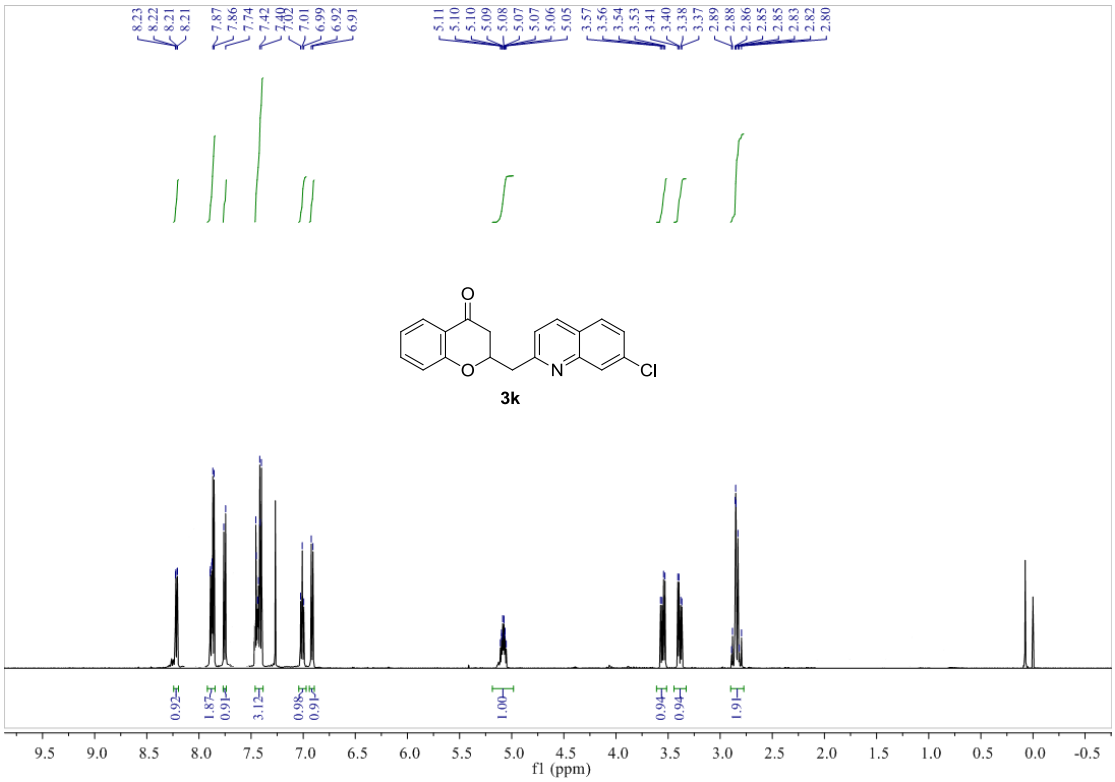
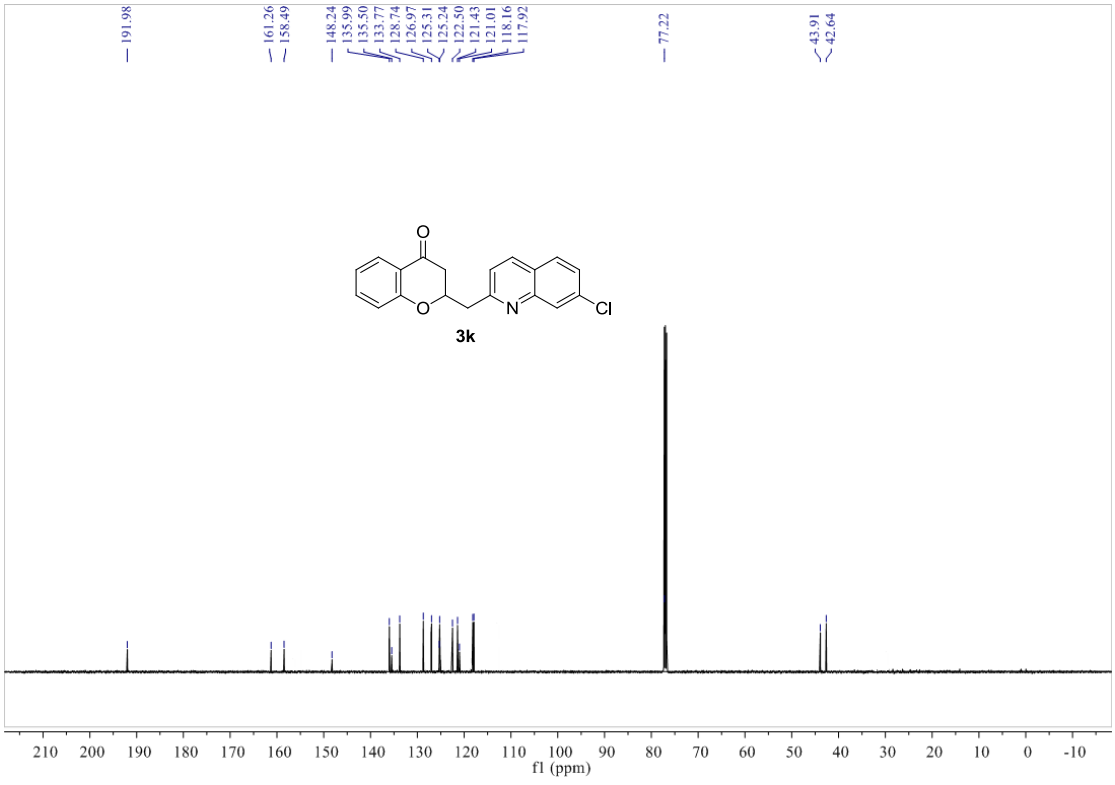
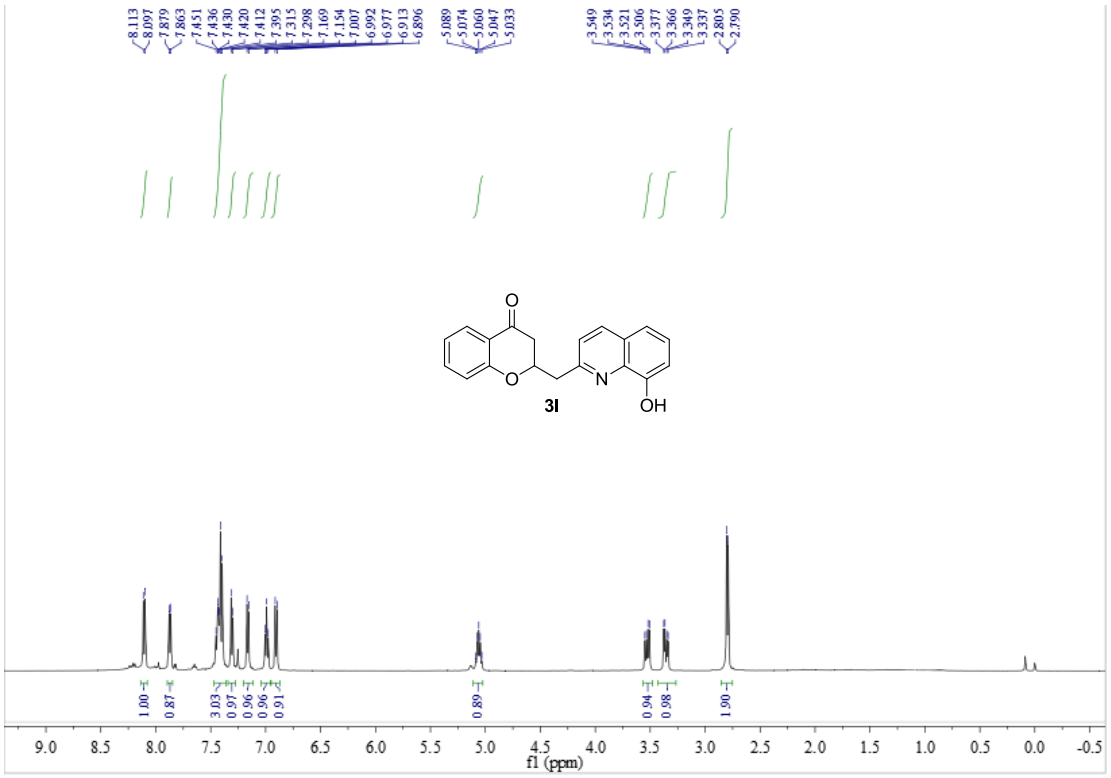
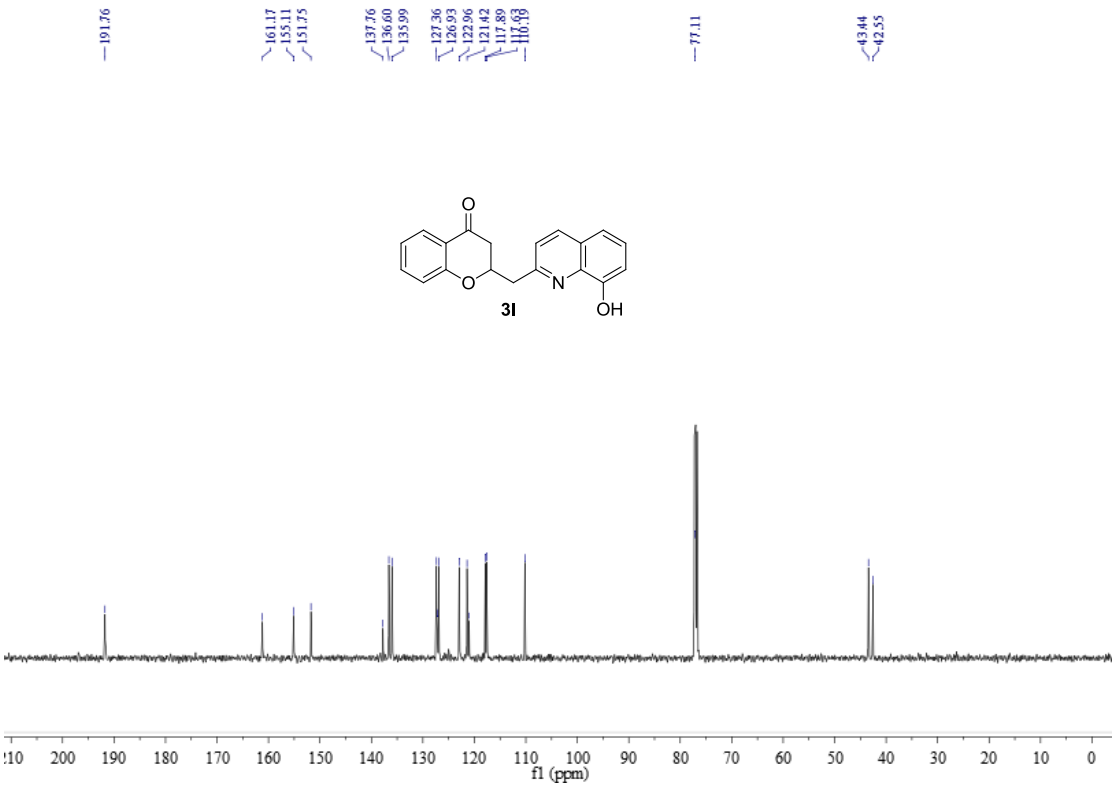
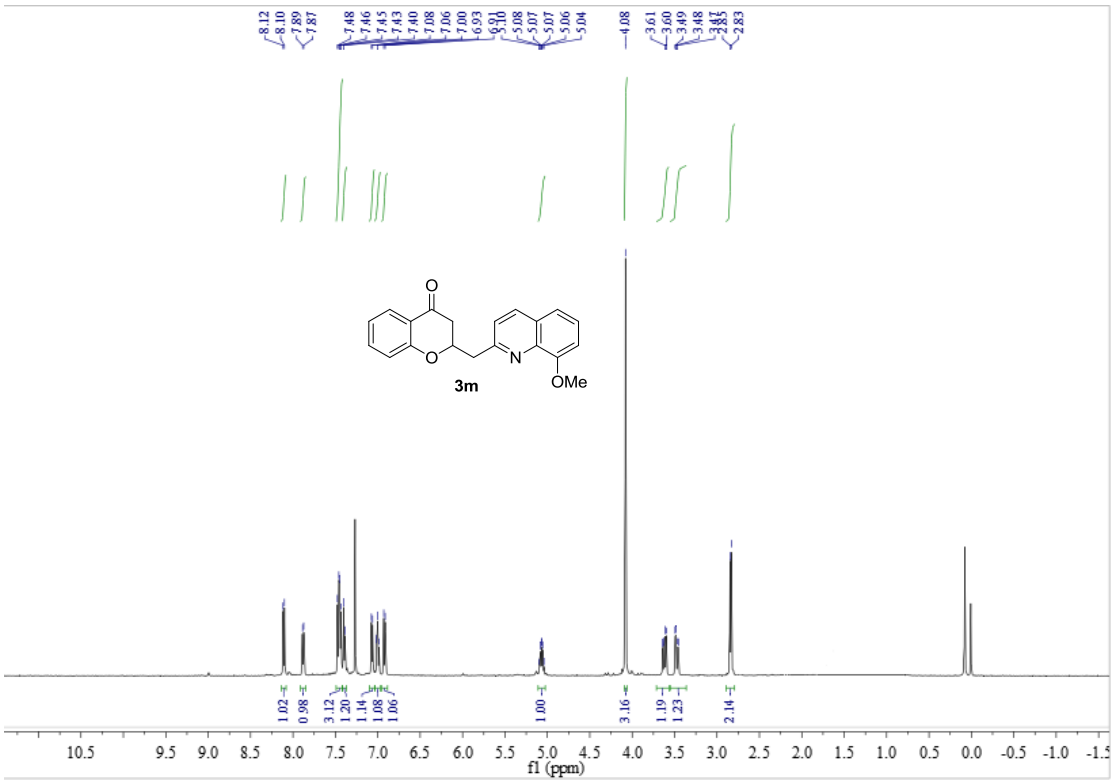
130.64
129.51
128.01
126.92
123.09
121.39
120.95
119.99
117.87
77.14
43.92
42.61
O
Br
O
N
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

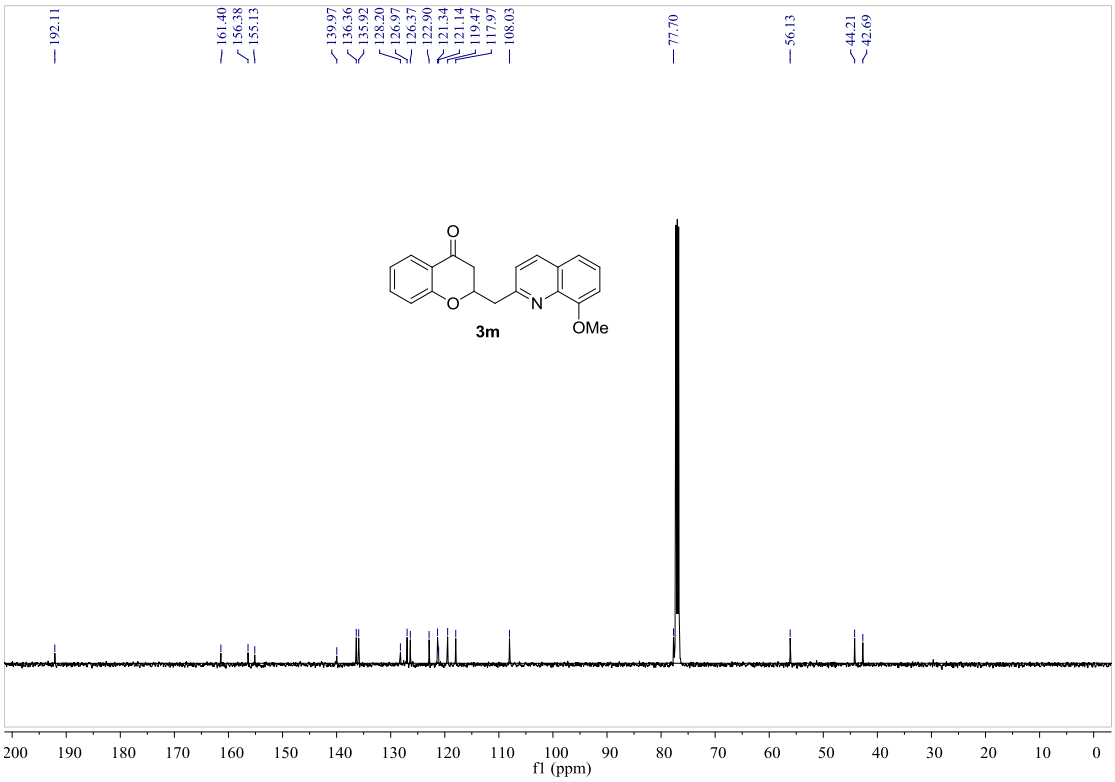

8.23
8.22
8.21
8.21
7.87
7.86
7.74
7.42
7.40
7.02
7.01
6.99
6.92
6.91
5.11
5.10
5.10
5.09
5.08
5.07
5.07
5.06
5.05
3.57
3.56
3.54
3.53
3.41
3.40
3.38
3.37
2.89
2.88
2.86
2.85
2.85
2.83
2.82
2.80
O
O
N
Cl
3k
0.92
1.87
0.91
3.12
0.98
0.91
1.00
0.94
0.94
1.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

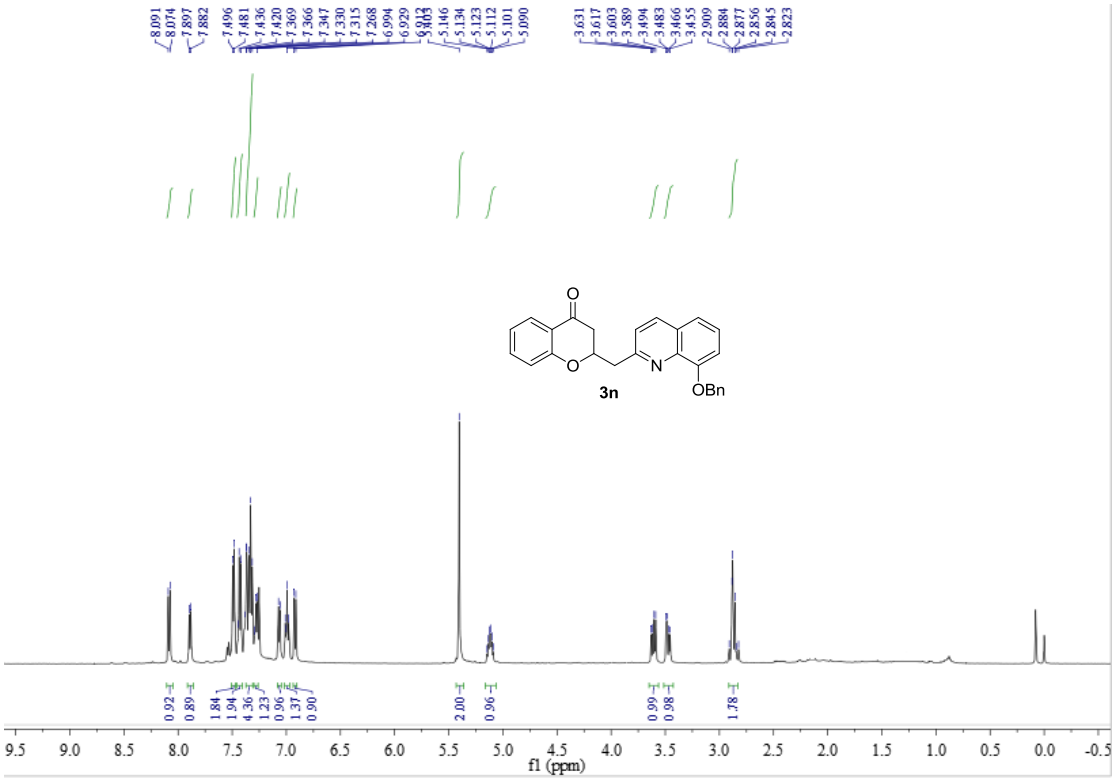

191.98
161.26
158.49
148.24
135.99
135.50
133.77
128.74
126.97
125.31
125.24
122.50
121.43
121.01
118.16
117.92
77.22
43.91
42.64
O
O
N
Cl
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

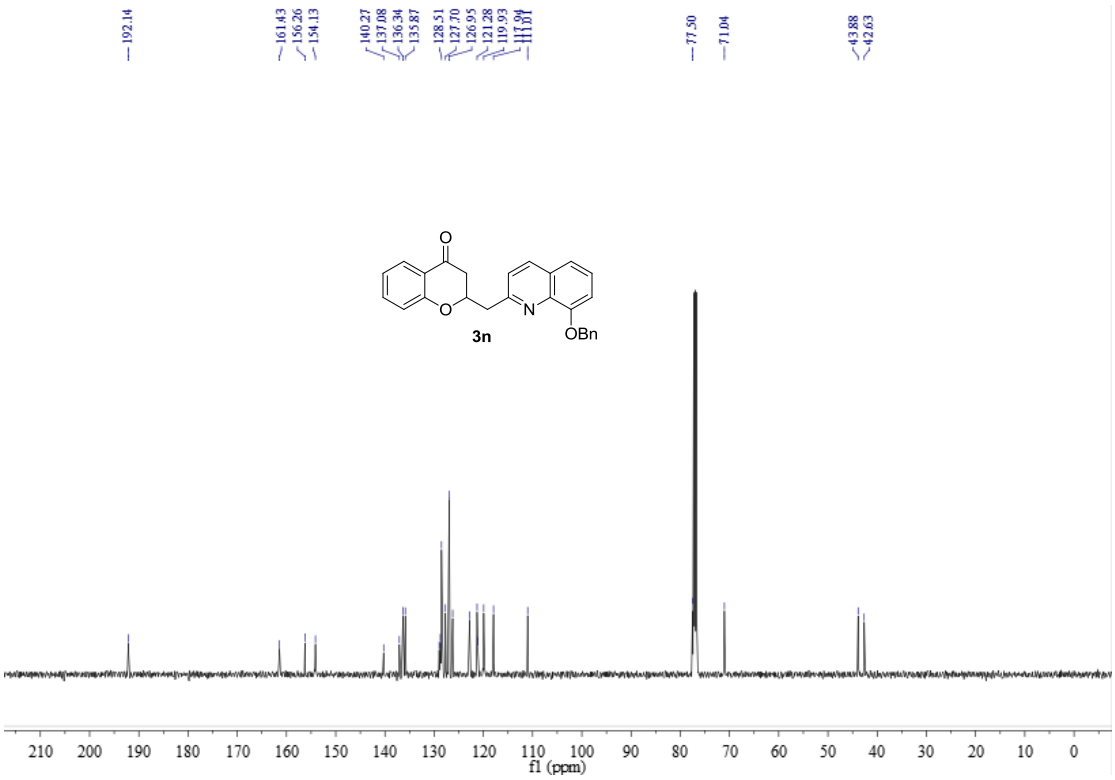

8.113
8.097
7.879
7.863
7.451
7.436
7.430
7.420
7.412
7.395
7.315
7.298
7.169
7.154
7.007
6.992
6.977
6.913
6.896
5.089
5.074
5.060
5.047
5.033
3.549
3.534
3.521
3.506
3.377
3.366
3.349
3.337
2.805
2.790
O
O
N
OH
3l
1.00
0.87
3.03
0.97
0.96
0.96
0.91
0.89
0.94
0.98
1.90
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 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)

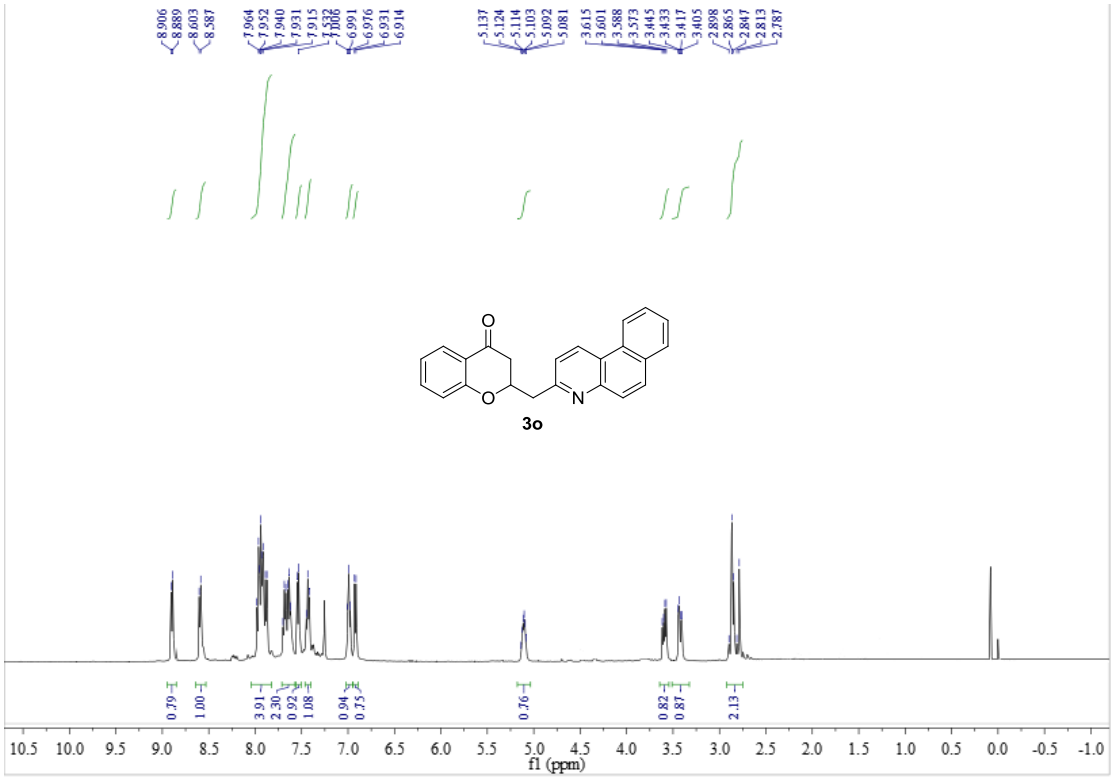

191.76
161.17
155.11
151.75
137.76
136.60
135.99
127.36
126.93
122.96
121.42
117.89
117.63
110.19
77.11
43.44
42.55
O
O
N
OH
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

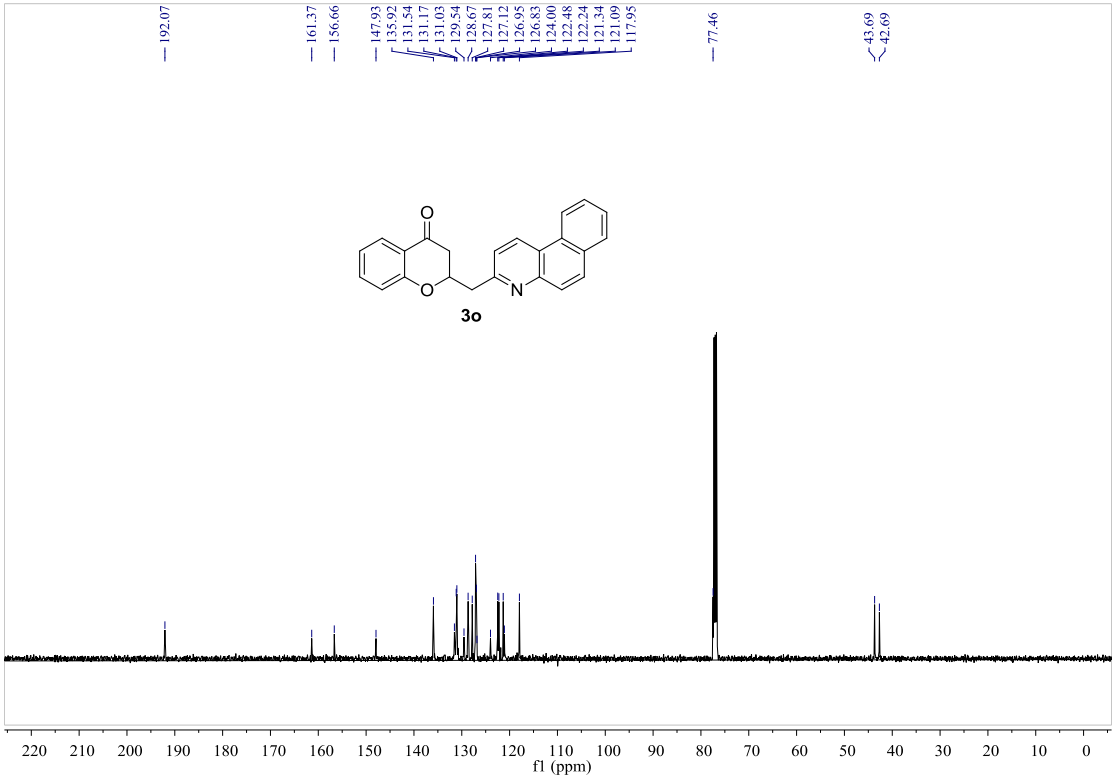

8.12
8.10
7.89
7.87
7.48
7.46
7.45
7.43
7.40
7.08
7.06
7.00
6.93
5.10
5.08
5.07
5.07
5.06
5.04
4.08
3.61
3.60
3.49
3.48
2.85
2.83
O
O
N
OMe
3m
1.02
0.98
3.12
1.20
1.14
1.08
1.06
1.00
3.16
1.19
1.23
2.14
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

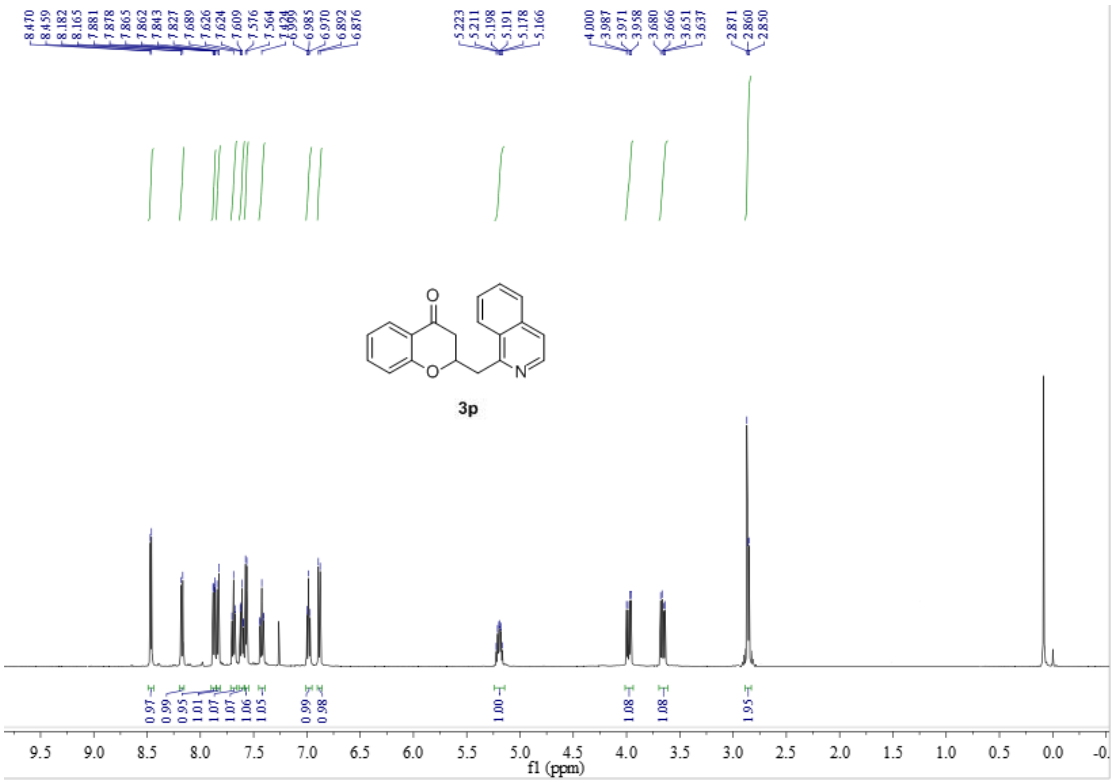

192.11
161.40
156.38
155.13
139.97
136.36
135.92
128.20
126.97
126.37
122.90
121.34
121.14
119.47
117.97
108.03
77.70
56.13
44.21
42.69
O
O
N
OMe
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

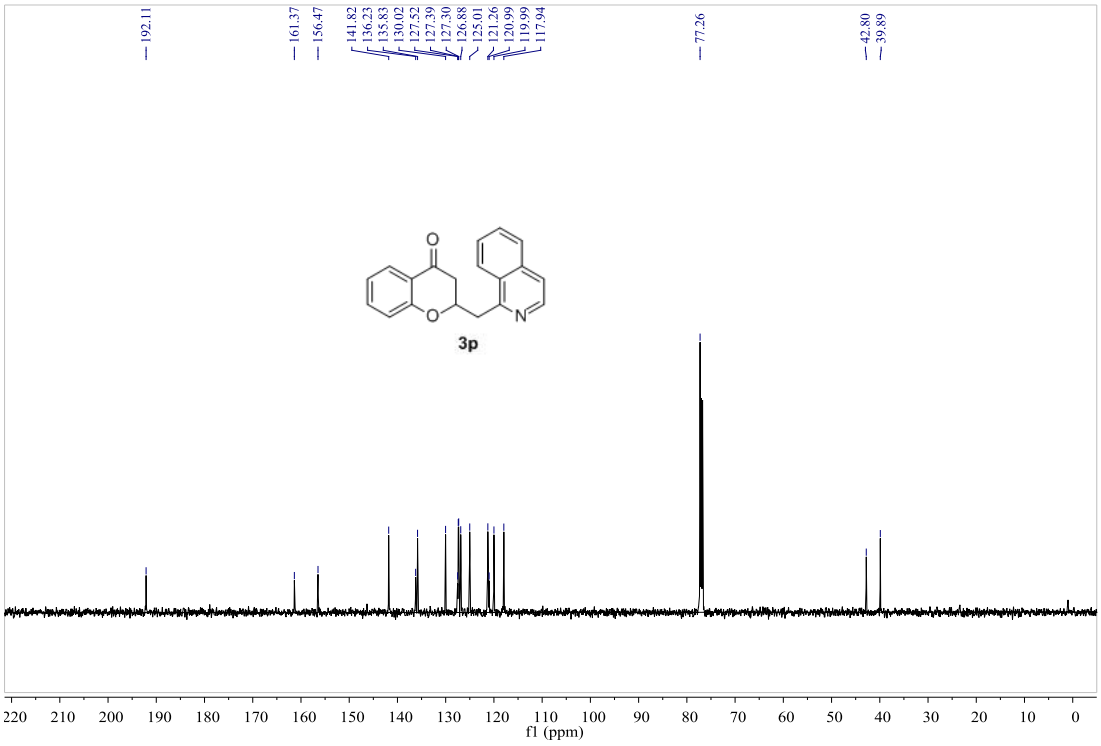

8.091
8.074
7.897
7.882
7.496
7.481
7.436
7.420
7.369
7.366
7.347
7.330
7.315
7.268
6.994
6.929
5.146
5.134
5.123
5.112
5.101
5.090
3.631
3.617
3.603
3.589
3.494
3.483
3.466
3.455
2.909
2.884
2.877
2.856
2.845
2.823
O
O
N
OBn
3n
0.92
0.89
1.84
1.94
4.36
1.23
0.96
1.37
0.90
2.00
0.96
0.99
0.98
1.78
f1 (ppm)

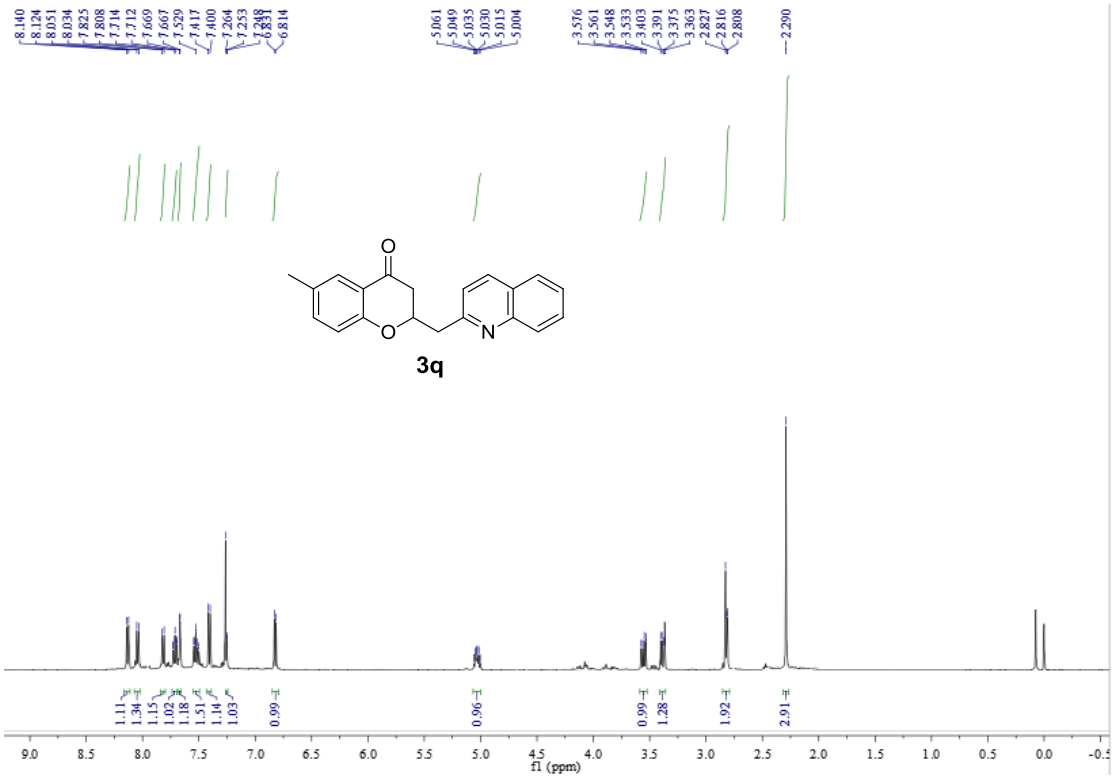

192.14
161.43
156.26
154.13
140.27
137.08
136.34
135.87
128.51
127.70
126.95
121.28
119.93
77.50
71.04
43.88
42.63
O
O
N
OBn
3n
f1 (ppm)

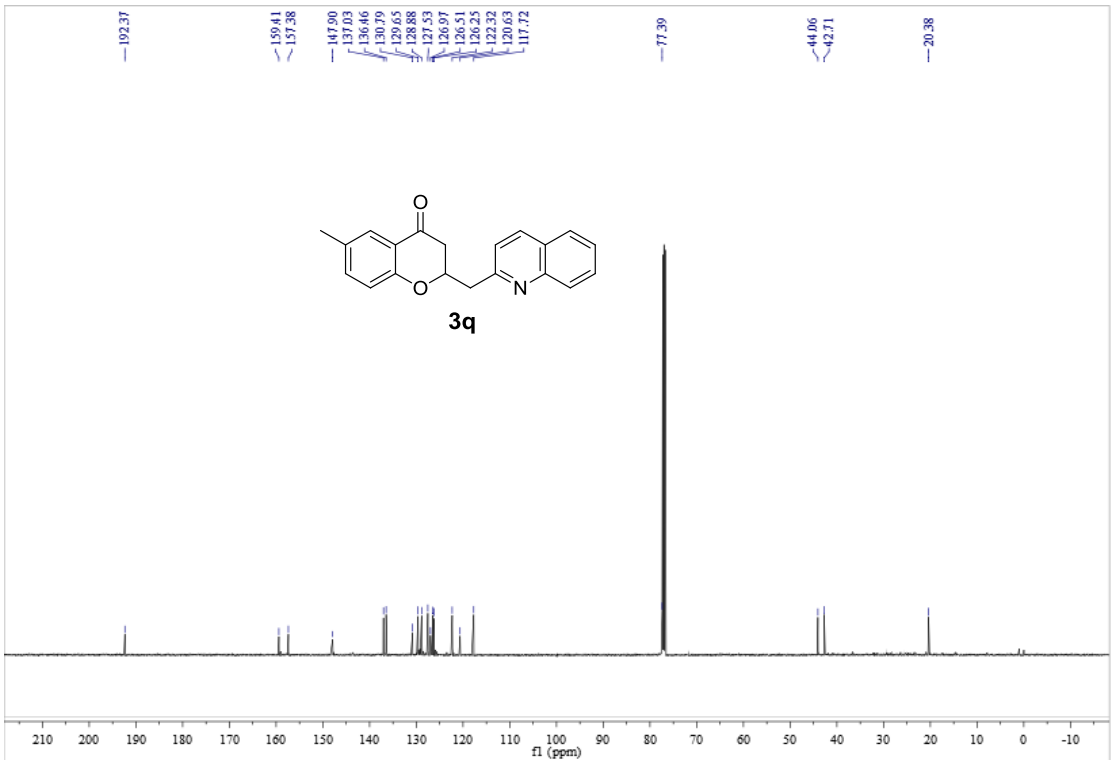

8.906
8.889
8.603
8.587
7.964
7.952
7.940
7.931
7.915
6.991
6.976
6.931
6.914
5.137
5.124
5.114
5.103
5.092
5.081
3.615
3.601
3.588
3.573
3.445
3.433
3.417
3.405
2.898
2.865
2.847
2.813
2.787
O
O
N
3o
0.79
1.00
3.91
2.30
0.92
1.08
0.94
0.75
0.76
0.82
0.87
2.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


192.07
161.37
156.66
147.93
135.92
131.54
131.17
131.03
129.54
128.67
127.81
127.12
126.95
126.83
124.00
122.48
122.24
121.34
121.09
117.95
77.46
43.69
42.69
O
O
N
3o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.470
8.459
8.182
8.165
7.881
7.878
7.865
7.862
7.843
7.827
7.689
7.626
7.624
7.609
7.576
7.564
6.985
6.970
6.892
6.876
5.223
5.211
5.198
5.191
5.178
5.166
4.000
3.987
3.971
3.958
3.680
3.666
3.651
3.637
2.871
2.860
2.850
O
O
N
3p
0.97
0.99
0.95
1.01
1.07
1.07
1.06
1.05
0.99
0.98
1.00
1.08
1.08
1.93
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)


192.11
161.37
156.47
141.82
136.23
135.83
130.02
127.52
127.39
127.30
126.88
125.01
121.26
120.99
119.99
117.94
77.26
42.80
39.89
O
O
N
3p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.140
8.124
8.051
8.034
7.825
7.808
7.714
7.712
7.669
7.667
7.529
7.417
7.400
7.264
7.253
6.814
5.061
5.049
5.035
5.030
5.015
5.004
3.576
3.561
3.548
3.533
3.403
3.391
3.375
3.363
2.827
2.816
2.808
2.290
O
O
N
3q
1.11
1.34
1.15
1.02
1.18
1.51
1.14
1.03
0.99
0.96
0.99
1.28
1.92
2.91
f1 (ppm)


192.37
159.41
157.38
147.90
137.03
136.46
130.79
129.65
128.88
127.53
126.97
126.51
126.25
122.32
120.63
117.72
77.39
44.06
42.71
20.38
O
O
N
3q
f1 (ppm)