- Electronic Supporting Information -

Photoredox cobalt dual catalysis toward C3-functionalization of quinoxalinones with alkenes and alkynes

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Table of Contents

General procedure

All non-aqueous reactions were carried out under an atmosphere of nitrogen in flame-dried glassware and were stirred using a magnetic stir plate. All reactions were carried out using commercial-grade solvent unless otherwise noted. CH_3CN, DCE, and CH_2Cl_2 were dried over calcium hydride. Dry THF was prepared by distilling over sodium ketyl.

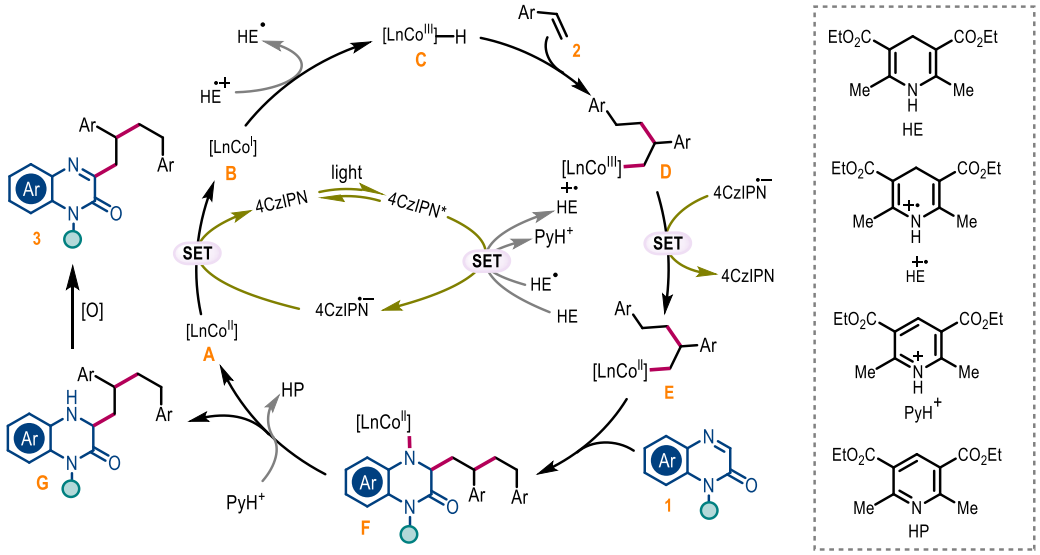
All reactions were monitored by thin layer chromatography (TLC) on WhatmanPartisil® K6F TLC plates (silica gel 60 Å, 0.25 mm thickness) and visualized using a UV lamp (366 or 254 nm) or by use of one of the following visualization reagents: PMA: 10g phosphomolybdic acid/ 100 mL ethanol; $KMnO_4$: 0.75g potassium permanganate, 5g K_2CO_3, / 100 mL water. Products were isolated by column chromatography (Merck silica gel 100-200μm). Yields refer to chromatographically and spectroscopically homogenous materials unless noted otherwise. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 or Bruker 500 MHz spectrometers. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak $CDCl_3$ δ = 7.2600 ppm for ^1H, δ = 77.16 for ^{13}C, DMSO-d6 δ = 2.500 ppm for ^1H, δ = 39.500 ppm for ^{13}C; or calibrated to tetramethylsilane (δ = 0.00 ppm). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; tt, triplet of triplet; dq, doublet of quartet; br, broad; app, apparent.

Mass spectra were recorded by electrospray ionization (ESI) method on a Q-TOF Micro with lock spray source.

The crystal data were collected and integrated using a BrukerAxs kappa apex2 CCD diffractometer, with graphite monochromated Mo-Kα radiation.

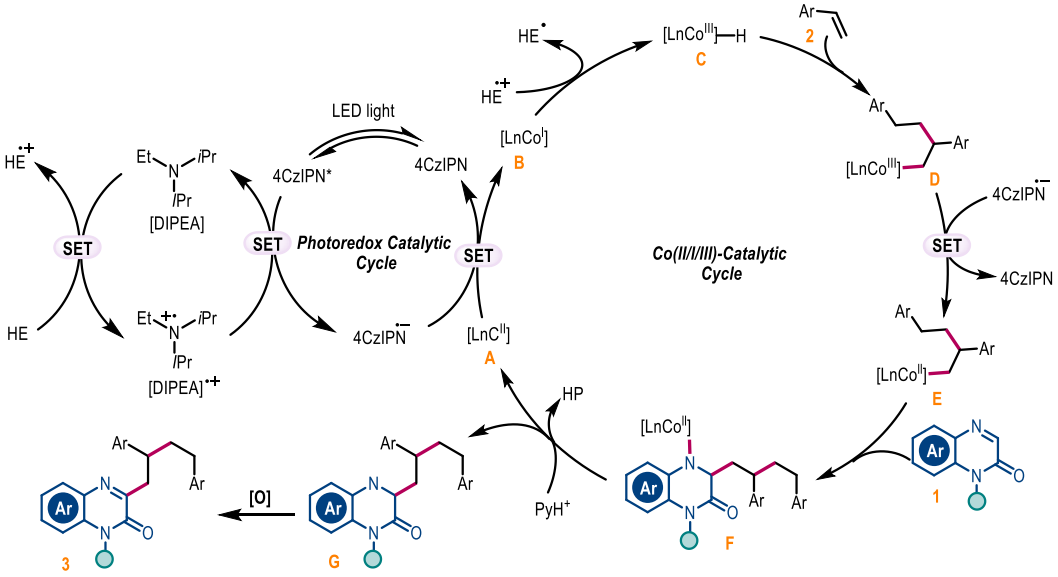
Quinoxalin-2(1*H*)-ones **1** were synthesized following literature procedures (*Org. Lett.* **2013**, *15*, 5606–5609). Compound **1c** and **1d** were prepared following the reported procedure (*Bioorg. Med. Chem.* **2023**, *78*, 117152**)**. Compound **1x** and **1y** were prepared as reported earlier (*Adv. Synth. Catal.* **2023**, *365*, 1020–1026.). Compounds **2** (styrene derivatives) were prepared following the reported procedure (*Eur. J. Med. Chem.* **2017**, *138*, 1089–1105). Styrene, 4-methylstyrene, DIPEA, cobalt bromide, and DPPP were purchased from Avra chemicals, TCI chemicals, and BLD chemicals.

Plausible reaction mechanism for product 3

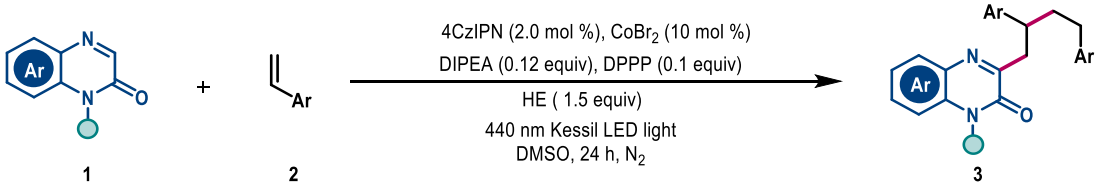


A plausible reaction mechanism is depicted here. Upon irradiation with visible light, photoexcited 4CzIPN* accepts an electron from HE to form 4CzIPN$^{\bullet-}$. This species then reduces ligand-coordinated Co(II)-complex **A** to the low valent Co(I) species **B**. Next, Co(I) species transforms to Co(III)–H species **C** through oxidative addition with proton. Subsequent reaction with styrene (**2**) generates the alkyl Co(III) species **D**. It is then reduced by 4CzIPN$^{\bullet-}$ to render alkyl Co(II) species **E**, which reacts with quinoxalin-2-one (**1**) to give intermediate **F**. Subsequent protonation yields reduced coupling product **G** and regenerates the active Co(II)-complex **A**. Further oxidation of **G** under photocatalysis furnishes the desired C3-functionalized products **3**.

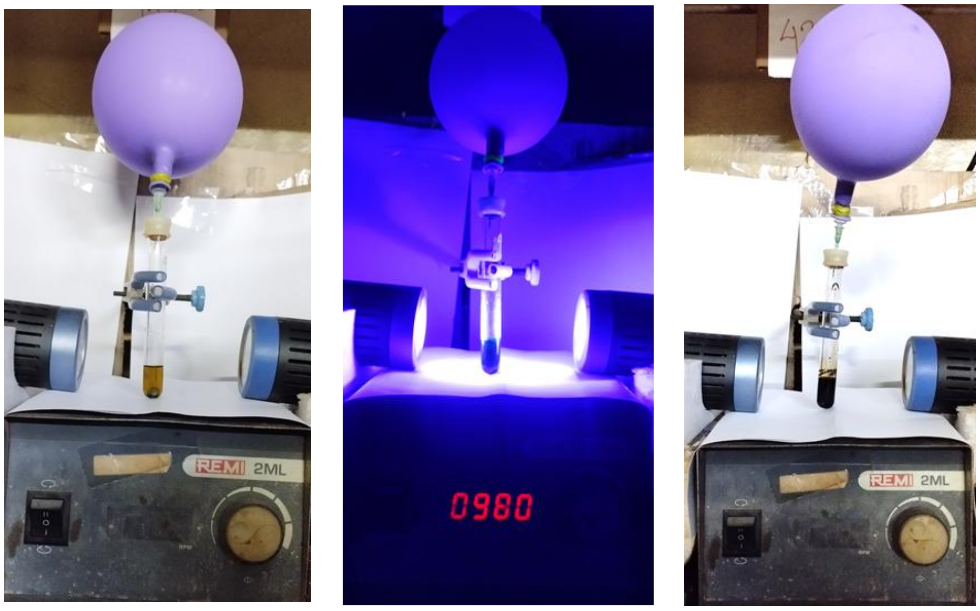
At this juncture, another alternative mechanism (for example, the one shown below) cannot be also ruled out.



General procedure for C3-selective coupling of quinoxalin-2(1*H*)-one (1) with alkene

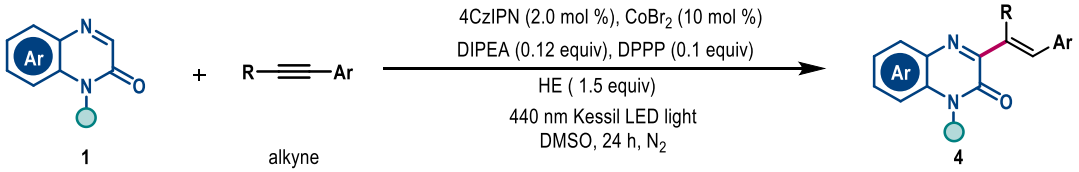


A 16×100 mm oven-dried reaction tube equipped with a magnetic stir was charged with $CoBr_2$ (10 mol %), DPPP (0.1 equiv), 4CzIPN (2.0 mol %), Hantzsch ester (HE) (1.5 equiv), quinoxalinone **1** (0.2 mmol, 1.0 equiv), and alkene **2** (0.6 mmol, 3.0 equiv) under the nitrogen atmosphere. The reaction tube was capped with a septum, and DIPEA (0.12 equiv) and dry DMSO (1.5 mL) were added via a syringe. Then, the reaction mixture was allowed to stir with irradiation of 440 nm Kessil LED light at room temperature for 24 h. After completion of the reaction (TLC monitored), brine solution was added and then extracted with ethyl acetate. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography over silica gel to get C3-alkyl quinoxalin-2(1*H*)-one (**3**).



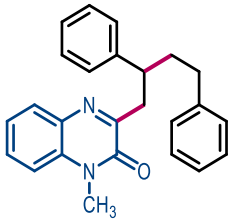
Before the reaction **During the reaction** **After the reaction**

General procedure for C3-selective coupling of quinoxalin-2(1*H*)-one (1) with alkyne



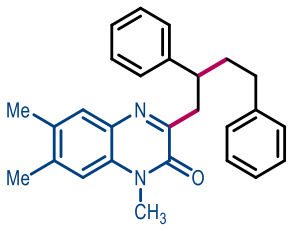
A 16×100 mm oven-dried reaction tube equipped with a magnetic stir was charged with $CoBr_2$ (10 mol %), DPPP (0.1 equiv), 4CzIPN (2.0 mol %), Hantzsch ester (HE) (1.5 equiv), quinoxalinone **1** (0.2 mmol, 1.0 equiv), and alkyne (0.6 mmol, 3.0 equiv) under the nitrogen atmosphere. The reaction tube was capped with a septum, and DIPEA (0.12 equiv) and dry DMSO (1.5 mL) were added via a syringe. Then, the reaction mixture was allowed to stir with irradiation of 440 nm Kessil LED light at room temperature for 24 h. After completion (TLC monitored), brine solution was added and then extracted with ethyl acetate. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography over silica gel to get C3-alkenyl quinoxalin-2(1*H*)-one (**4**).

Spectral Data of Synthesized Compounds



3a

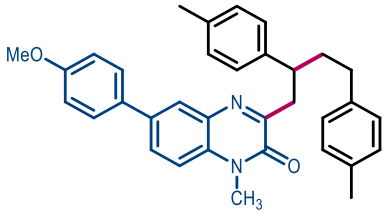
Compound, **3a**: Yellow solid; mp = 84–86 °C; eluent (20% ethyl acetate in hexane). **Yield:** 93% (68 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 – 7.76 (m, 1H), 7.52 – 7.46 (m, 1H), 7.33 – 7.28 (m, 5H), 7.24 – 7.17 (m, 3H), 7.16 – 7.12 (m, 2H), 7.10 – 7.07 (m, 2H), 3.65 (s, 3H, CH_3), 3.54 – 3.50 (m, 1H, CH), 3.31 – 3.27 (m, 2H, CH_2), 2.53 – 2.48 (m, 2H, CH_2), 2.15 – 1.98 (m, 2H, CH_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.5(C), 155.1(C), 144.9(C), 142.6(C), 133.1(C), 132.8(C), 129.9(CH), 129.7(CH), 128.51(CH), 128.45(CH), 128.3(CH), 128.1(CH), 126.3(CH), 125.7(CH), 123.6(CH), 113.6(CH), 42.8(CH), 41.1(CH_3), 37.9(CH_3), 33.9(CH_3), 29.2(CH_3). **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{25}H_{24}N_2OH^+$ 369.1961; Found 369.1964.



3b

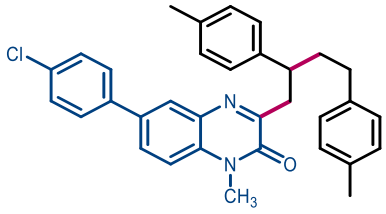
Compound, **3b**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 95% (75 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (s, 1H), 7.33 – 7.25 (m, 5H), 7.23 – 7.16 (m, 2H), 7.15 – 7.12 (m, 1H), 7.09 – 7.06 (m, 2H), 7.00 (s, 1H), 3.61 (s, 3H), 3.53 – 3.45 (m, 1H), 3.28 – 3.24 (m, 2H), 2.51 – 2.46 (m, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 2.12 – 1.96 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1(C), 155.1(C), 145.0(C), 142.6(C), 139.4(C), 132.4(C), 131.2(C), 131.1(C), 129.9(CH), 128.5(CH), 128.4(CH), 128.3(CH), 128.1(CH), 126.2(CH), 125.7(CH), 114.2(CH), 42.9(CH), 41.1(CH_2), 37.9(CH_2), 33.9(CH_2), 29.0(CH_3), 20.5(CH_3), 19.2(CH_3). **HRMS**

(ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{28}N_2OH^+$ 397.2274; Found 397.2285.



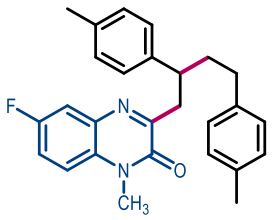
3c

Compound, **3c**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 89% (89 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 2.2 Hz, 1H), 7.70 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.60 – 7.59 (m, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.03 – 6.98 (m, 6H), 3.88 (s, 3H), 3.67 (s, 3H), 3.53 – 3.48 (m, 1H), 3.33 – 3.23 (m, 2H), 2.48 – 2.42 (m, 2H), 2.30 (s, 3H), 2.28 (s, 3H), 2.09 – 1.96 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.0, 159.6, 155.0, 141.8, 139.6, 136.4, 135.7, 135.1, 133.1, 132.2, 131.9, 129.2, 129.0, 128.4, 128.1, 128.0, 127.3, 114.6(2C), 114.0, 55.5, 42.4, 41.4, 38.1, 33.5, 29.2, 21.2, 21.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{34}H_{34}N_2O_2H^+$ 503.2693; Found 503.2694.



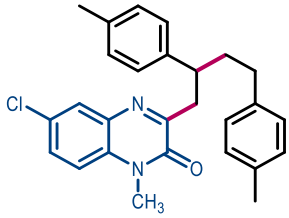
3d

Compound, **3d**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 86% (87 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, J = 2.2 Hz, 1H), 7.69 (dd, J = 8.6, 2.2 Hz, 1H), 7.59 – 7.57 (m, 2H), 7.46 – 7.44 (m, 2H), 7.31 – 7.28 (m, 1H), 7.2 (dd, J = 7.9, 1.7 Hz, 2H), 7.11 (d, J = 7.7 Hz, 2H), 7.05 – 6.99 (m, 4H), 3.66 (s, 3H), 3.55 – 3.47 (m, 1H), 3.35 – 3.23 (m, 2H), 2.54 – 2.41 (m, 2H), 2.31 – 2.29 (m, 6H), 2.10 – 1.96 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.3, 154.9, 141.7, 139.5, 138.1, 135.7, 135.4, 135.1, 133.8, 133.0, 132.5, 129.3, 129.2, 129.0, 128.4, 128.3, 127.9, 127.7, 127.1, 114.2, 42.3, 41.3, 38.1, 33.4, 29.2, 21.2, 21.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{33}H_{31}ClN_2OH^+$ 507.2198; Found 507.2206.



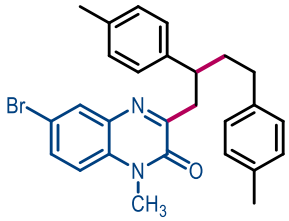
3e

Compound, **3e**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 85% (70 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.24 – 7.17 (m, 4H), 7.11 – 7.09 (m, 2H), 7.05 – 6.98 (m, 4H), 3.63 (s, 3H), 3.50 – 3.45 (m, 1H), 3.31 – 3.23 (m, 2H), 2.51 – 2.42 (m, 2H), 2.31 – 2.30 (m, 6H), 2.08 – 1.96 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.2, 158.7 (d, *J* = 243.2 Hz), 154.7, 141.7, 139.5, 135.7, 135.1, 133.3 (d, *J* = 11.2 Hz), 129.8, 129.1, 129.0, 128.4, 127.9, 117.3 (d, *J* = 23.9 Hz), 115.3 (d, *J* = 22.4 Hz), 114.6 (d, *J* = 8.8 Hz), 42.2, 41.2, 38.2, 33.4, 29.4, 21.2, 21.1. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -110.43. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{27}FN_2OH^+$ 415.2180; Found 415.2175.



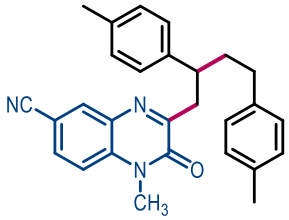
3f

Compound, **3f**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 94% (81 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, J = 2.4 Hz, 1H), 7.44 (dd, J = 8.9, 2.4 Hz, 1H), 7.21 – 7.19 (m, 2H), 7.16 (d, J = 8.9 Hz, 1H), 7.09 (d, J = 7.9 Hz, 2H), 7.05 – 6.97 (m, 4H), 3.61 (s, 3H), 3.51 – 3.43 (m, 1H), 3.29 – 3.22 (m, 2H), 2.51 – 2.39 (m, 2H), 2.30 (bs, 6H), 2.07 – 1.96 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.1, 155.0, 141.7, 139.5, 135.7, 135.1, 133.4, 131.9, 129.6, 129.3, 129.2, 129.0, 128.9, 128.4, 128.0, 114.7, 42.1, 41.1, 38.2, 33.4, 29.3, 21.15, 21.09. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{27}ClN_2OH^+$ 431.1885; Found 431.1880.



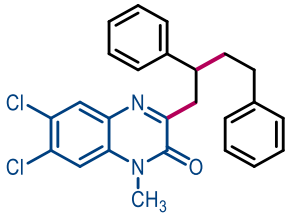
3g

Compound, **3g**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 81% (77 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 – 7.78 (m, 1H), 7.52 – 7.48 (m, 1H), 7.34 – 7.30 (m, 1H), 7.24 – 7.20 (m, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.06 – 6.98 (m, 4H), 3.65 (s, 3H), 3.55 – 3.46 (m, 1H), 3.33 – 3.24 (m, 2H), 2.53 – 2.43 (m, 2H), 2.32 – 2.30 (m, 6H), 2.10 – 1.98 (m, 2H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.6, 155.1, 141.8, 139.6, 135.7, 135.1, 133.1, 132.8, 129.9, 129.7, 129.1, 129.0, 128.4, 128.0, 123.6, 113.6, 42.4, 41.3, 38.1, 33.5, 29.2, 21.2, 21.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{27}BrN_2OH^+$ 475.1380; Found 475.1383.



3h

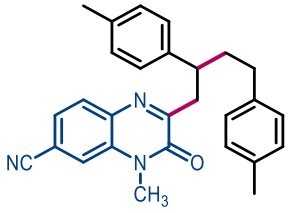
Compound, **3h**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 88% (74 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 (d, J = 2.0 Hz, 1H), 7.71 (dd, J = 8.7, 1.9 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.20 – 6.98 (m, 6H), 3.63 (s, 3H), 3.49 – 3.42 (m, 1H), 3.32 – 3.23 (m, 2H), 2.50 – 2.39 (m, 2H), 2.30 (s, 6H), 2.04 – 1.97 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.9, 154.6, 141.4, 139.4, 136.3, 135.9, 135.2, 134.1, 132.31, 132.25, 129.2, 129.0, 128.4, 127.9, 118.2, 114.7, 107.1, 42.0, 41.0, 38.3, 33.4, 29.4, 21.15, 21.11. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{28}H_{27}N_3OH^+$ 422.2227; Found 422.2223.



3i

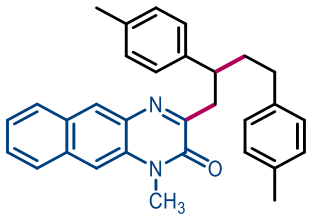
Compound, **3i**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 91% (82 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 7.33 (s, 1H), 7.29 – 7.28 (m, 4H), 7.23 (d, J = 7.3 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.09 (dd, J = 7.5, 1.6 Hz, 2H), 3.59 (s, 3H), 3.49 – 3.43 (m, 1H), 3.29 – 3.23 (m, 2H), 2.51 – 2.47 (m, 2H), 2.07 – 2.00 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.2, 154.5, 144.6, 142.5, 133.8, 132.6, 131.9, 130.7, 128.5(2C), 128.4, 128.1, 127.4, 126.5, 125.8, 115.1, 42.7, 41.0, 38.1, 33.9, 29.4. **HRMS** (ESI/TOF-Q) m/z:

$[M+H]^+$ Calculated for $C_{25}H_{22}Cl_2N_2OH^+$ 437.1182; Found 437.1180.



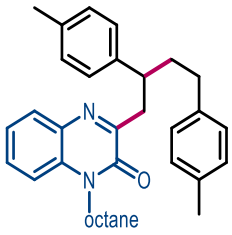
3j

Compound, **3j**: Yellow solid; mp = 112–114 °C; eluent (15% ethyl acetate in hexane). **Yield:** 91% (77 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, J = 8.1 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 7.7 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 3.63 (s, 3H), 3.50 – 3.43 (m, 1H), 3.35 – 3.23 (m, 2H), 2.50 – 2.41 (m, 2H), 2.30 (s, 6H), 2.07 – 1.94 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2, 154.3, 141.2, 139.2, 135.8, 135.1, 134.8, 133.4, 130.6, 129.1, 128.9, 128.3, 127.8, 126.4, 118.2, 117.7, 112.7, 42.1, 41.2, 38.1, 33.3, 29.2, 21.03, 20.99. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{28}H_{27}N_3OH^+$ 422.2227; Found 422.2229.



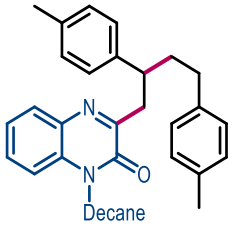
3k

Compound, **3k**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 87% (78 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (s, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.49 – 7.45 (m, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 7.03 – 6.97 (m, 4H), 3.71 (s, 3H), 3.55 – 3.48 (m, 1H), 3.32 – 3.28 (m, 2H), 2.53 – 2.43 (m, 2H), 2.29 – 2.28 (m, 6H), 2.13 – 1.98 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.2, 154.9, 141.8, 139.6, 135.7, 135.1, 133.5, 132.2, 131.9, 129.8, 129.2, 129.0, 128.8, 128.5, 128.4, 128.0, 127.7, 127.3, 125.3, 109.9, 42.5, 41.4, 38.2, 33.5, 29.2, 21.2, 21.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{31}H_{30}N_2OH^+$ 447.2431; Found 447.2433.



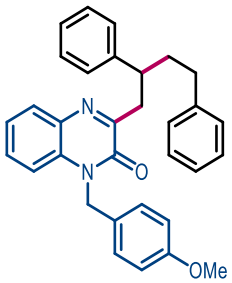
3l

Compound, **3l**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 93% (92 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.98 (m, 4H), 4.18 (t, *J* = 7.8 Hz, 2H), 3.53 – 3.44 (m, 1H), 3.34 – 3.21 (m, 2H), 2.52 – 2.43 (m, 2H), 2.303 – 2.296 (m, 6H), 2.10 – 1.98 (m, 2H), 1.72 – 1.67 (m, 2H), 1.47 – 1.36 (m, 4H), 1.33 – 1.28 (m, 6H), 0.92 – 0.88 (m, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 154.7, 141.8, 139.6, 135.6, 135.0, 133.1, 132.3, 130.1, 129.5, 129.1, 129.0, 128.4, 128.0, 123.3, 113.6, 42.5, 42.4, 41.2, 38.1, 33.5, 31.9, 29.4, 29.3, 27.4, 27.1, 22.7, 21.15, 21.08, 14.2. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{34}H_{42}N_2OH^+$ 495.3370; Found 495.3376.



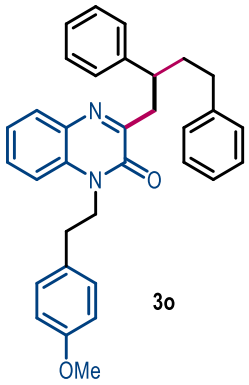
3m

Compound, **3m**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 90% (94 mg); **^{1}H NMR (400 MHz , $CDCl_3$)** δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.09 (d, J = 7.9 Hz, 1H), 7.05 – 6.98 (m, 4H), 4.18 (t, *J* = 7.8 Hz, 2H), 3.53 – 3.44 (m, 1H), 3.34 – 3.21 (m, 2H), 2.52 – 2.41 (m, 2H), 2.304 – 2.296 (m, 6H), 2.09 – 1.97 (m, 2H), 1.72 – 1.67 (m, 2H), 1.45 – 1.39 (m, 2H), 1.29 – 1.28 (m, 12H), 0.90 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 154.7, 141.8, 139.6, 135.6, 135.0, 133.1, 132.3, 130.1, 129.5, 129.1, 129.0, 128.4, 128.0, 123.3, 113.6, 42.5, 42.4, 41.3, 38.1, 33.5, 32.0, 29.6(2C), 29.44, 29.41, 27.4, 27.1, 22.8, 21.15, 21.08, 14.2. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{36}H_{46}N_2OH^+$ 523.3683; Found 523.3698.



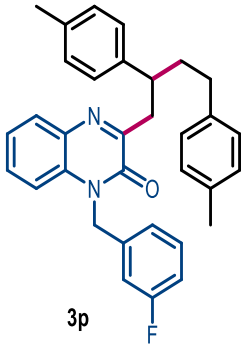
3n

Compound, **3n**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 85% (81 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (dd, J = 7.8, 1.6 Hz, 1H), 7.39 – 7.27 (m, 5H), 7.25 – 7.14 (m, 6H), 7.10 (d, J = 7.6 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 6.81 – 6.79 (m, 2H), 5.36 (s, 2H), 3.76 (s, 3H), 3.58 – 3.50 (m, 1H), 3.42 – 3.29 (m, 2H), 2.54 – 2.50 (m, 2H), 2.23 – 2.00 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 159.2, 155.1, 144.6, 142.6, 133.1, 132.5, 129.9, 129.7, 128.53, 128.45, 128.4(2C), 128.2, 127.5, 126.3, 125.8, 123.6, 114.5, 114.4, 55.4, 45.4, 43.4, 41.1, 38.2, 34.0. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{32}H_{30}N_2OH^+$ 475.2380; Found 475.2381.



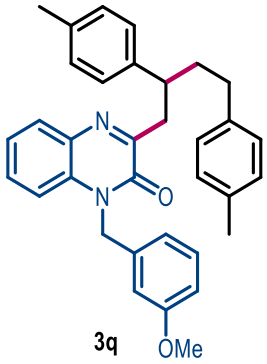
3o

Compound, **3o**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 89% (87 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.34 – 7.28 (m, 6H), 7.25 – 7.15 (m, 6H), 7.11 (d, J = 6.9 Hz, 2H), 6.86 (d, J = 7.3 Hz, 2H), 4.36 (t, J = 7.6 Hz, 2H), 3.80 (s, 3H), 3.56 – 3.50 (m, 1H), 3.37 – 3.27 (m, 2H), 2.93 – 2.90 (m, 2H), 2.57 – 2.51 (m, 2H), 2.16 – 2.03 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.5, 158.7, 154.6, 144.7, 142.6, 133.0, 132.2, 130.1, 129.9 129.7, 128.5, 128.4, 128.3, 128.1, 126.3, 125.7, 123.4, 114.3 (2C), 113.4, 55.4, 44.0, 42.9, 41.0, 38.0, 33.9, 32.6. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{33}H_{32}N_2O_2H^+$ 489.2537; Found 489.2535.



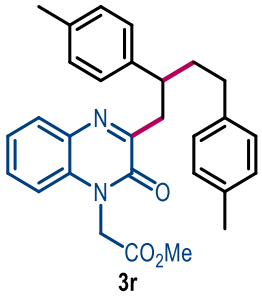
3p

Compound, **3p**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 88% (86 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (dd, J = 7.9, 1.6 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.30 – 7.28 (m, 1H), 7.25 – 7.23 (m, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.12 – 7.08 (m, 3H), 7.06 – 7.00 (m, 4H), 6.97 – 6.93 (m, 1H), 6.92 – 6.90 (m, 1H), 6.83 – 6.80 (m, 1H), 5.41 (s, 2H), 3.56 – 3.49 (m, 1H), 3.41 – 3.27 (m, 2H), 2.52 – 2.48 (m, 2H), 2.302 – 2.297 (m, 6H), 2.12 – 2.03 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2 (d, *J* = 246.8 Hz), 159.8, 154.9, 141.4, 139.4, 137.9 (d, *J* = 7.1 Hz), 135.6, 134.9, 133.0, 132.2, 130.5 (d, *J* = 8.4 Hz), 129.9, 129.6, 129.0, 128.9, 128.3, 127.9, 123.6, 122.3 (d, *J* = 3.2 Hz), 114.6 (d, *J* = 21.2 Hz), 114.0, 113.8 (d, *J* = 22.4 Hz), 45.3, 42.8, 41.0, 38.3, 33.4, 21.0, 20.9. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -110.26. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{33}H_{31}FN_2OH^+$ 491.2493; Found 491.2491.



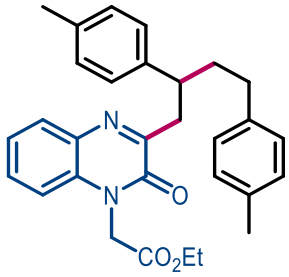
3q

Compound, **3q**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 83% (83 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.25 – 7.15 (m, 5H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.04 – 6.98 (m, 4H), 6.79 – 6.77 (m, 1H), 6.72 – 6.71 (m, 1H), 6.69 – 6.66 (m, 1H), 5.41 (s, 2H), 3.74 (s, 3H), 3.56 – 3.48 (m, 1H), 3.37 – 3.27 (m, 2H), 2.50 – 2.45 (m, 2H), 2.29 (bs, 6H), 2.10 – 1.99 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.2, 159.9, 155.1, 141.7, 139.6, 137.1, 135.7, 135.1, 133.1, 132.5, 130.1, 130.0, 129.7, 129.2, 129.0, 128.4, 128.0, 123.6, 119.1, 114.5, 113.0, 112.81, 55.3, 45.9, 42.8, 41.3, 38.4, 33.5, 21.2, 21.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{34}H_{34}N_2O_2H^+$ 503.2693; Found 503.2697.



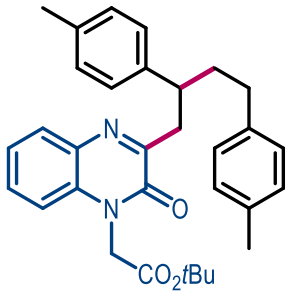
3r

Compound, **3r**: Yellow solid; mp = 84–86 °C; eluent (15% ethyl acetate in hexane). **Yield:** 92% (84 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 (d, J = 7.9 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 7.04 – 7.01 (m, 3H), 6.98 (d, J = 7.6 Hz, 2H), 5.04 – 4.93 (m, 2H), 3.75 (s, 3H), 3.50 – 3.44 (m, 1H), 3.26 (d, J = 7.4 Hz, 2H), 2.49 – 2.40 (m, 2H), 2.30 – 2.29 (m, 6H), 2.08 – 1.95 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.8, 159.5, 154.6, 141.7, 139.5, 135.7, 135.1, 132.9, 132.2, 130.2, 129.9, 129.2, 129.0, 128.4, 127.9, 124.0, 113.0, 52.9, 43.5, 42.4, 41.3, 38.0, 33.4, 21.2, 21.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{29}H_{30}N_2O_3H^+$ 455.2329; Found 455.2334.



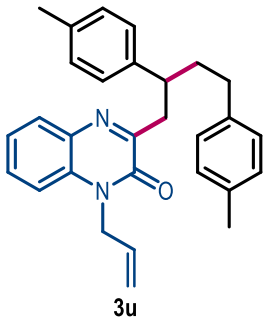
3s

Compound, **3s**: Yellow solid; mp = 88–90 °C; eluent (15% ethyl acetate in hexane). **Yield:** 93% (87 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79 (d, J = 7.9 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.20 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 7.04 – 7.01 (m, 3H), 6.98 (d, J = 7.8 Hz, 2H), 5.02 – 4.91 (m, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.50 – 3.44 (m, 1H), 3.26 (d, J = 7.2 Hz, 2H), 2.50 – 2.40 (m, 2H), 2.30 – 2.29 (m, 6H), 2.08 – 1.97 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.3, 159.5, 154.6, 141.7, 139.6, 135.7, 135.1, 132.9, 132.3, 130.2, 129.9, 129.2, 129.0, 128.4, 127.9, 123.9, 113.1, 62.1, 43.7, 42.4, 41.3, 38.0, 33.5, 21.2, 21.1, 14.2. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{30}H_{32}N_2O_3H^+$ 469.2486; Found 469.2484.



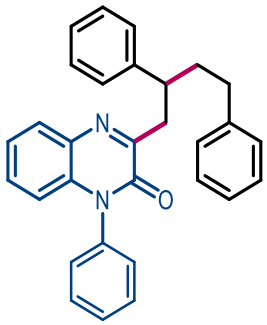
3t

Compound, **3t**: Yellow solid; mp = 80–82 °C; eluent (15% ethyl acetate in hexane). **Yield:** 95% (94 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (dd, J = 7.9, 1.5 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.21 – 7.19 (m, 2H), 7.08 (d, J = 7.8 Hz, 2H), 7.04 – 6.97 (m, 5H), 4.94 – 4.81 (m, 2H), 3.52 – 3.44 (m, 1H), 3.27 (d, J = 7.3 Hz, 2H), 2.53 – 2.40 (m, 2H), 2.30 – 2.29 (m, 6H), 2.14 – 1.95 (m, 2H), 1.43 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.3, 159.6, 154.7, 141.8, 139.6, 135.6, 135.0, 132.9, 132.5, 130.2, 129.7, 129.2, 129.0, 128.4, 128.0, 123.7, 113.1, 83.1, 44.4, 42.5, 41.2, 38.1, 33.5, 28.1, 21.12, 21.07. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{32}H_{36}N_2O_3H^+$ 497.2799; Found 497.2796.



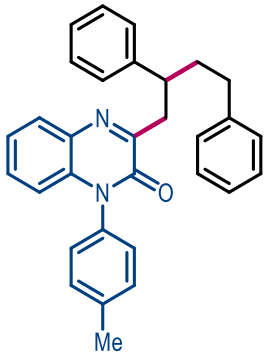
3u

Compound, **3u**: Yellow solid; mp = 85–87 °C; eluent (15% ethyl acetate in hexane). **Yield:** 90% (76 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (dd, J = 8.0, 1.6 Hz, 1H, CH), 7.48 – 7.44 (m, 1H, CH), 7.33 – 7.28 (m, 1H, CH), 7.23 – 7.20 (m, 3H, CH), 7.09 (d, J = 7.9 Hz, 2H, CH), 7.05 – 6.99 (m, 4H, CH), 5.96 – 5.84 (m, 1H, CH), 5.27 – 5.18 (m, 1H, CH), 5.07 – 5.02 (m, 1H, CH), 4.86 – 4.83 (m, 2H, CH_2), 3.54 – 3.48 (m, 1H, CH), 3.36 – 3.23 (m, 2H, CH_2), 2.53 – 2.43 (m, 2H, CH_2), 2.30 (bs, 6H, CH_3), 2.10 – 1.99 (m, 2H, CH_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.8(C), 154.6(C), 141.6(C), 139.6(C), 135.6(C), 135.1(C), 133.0(C), 132.3(C), 130.7(CH), 129.9(CH), 129.6(CH), 129.1(CH), 129.0(CH), 128.4(CH), 128.0(CH), 123.5(CH), 117.9(CH_2), 114.2(CH), 44.5(CH_2), 42.6(CH), 41.2(CH_2), 38.1(CH_2), 33.4(CH_2), 21.2(CH_3), 21.1(CH_3). **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{29}H_{30}N_2OH^+$ 423.2431; Found 423.2433.



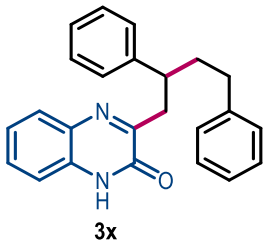
3v

Compound, **3v**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 92% (79 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.83 – 7.79(m, 1H), 7.61 – 7.56 (m, 2H), 7.55 – 7.53 (m, 1H), 7.34 – 7.31 (m, 2H), 7.30 – 7.27 (m, 5H), 7.24 – 7.21 (m, 3H), 7.19 – 7.15 (m, 2H), 7.11 – 7.10 (m, 2H), 6.63 – 6.59 (m, 1H), 3.59 – 3.54 (m, 1H), 3.36 – 3.28 (m, 2H), 2.55 – 2.48 (m, 2H), 2.19 – 2.03 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.2, 154.6, 144.6, 142.5, 135.9, 133.8, 132.5, 130.3, 129.4, 129.33, 129.27, 128.4, 128.34, 128.26, 128.2, 128.0, 126.2, 125.6, 123.7, 115.3, 42.8, 41.1, 37.8, 33.8. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{30}H_{26}N_2OH^+$ 431.2118; Found 431.2135.



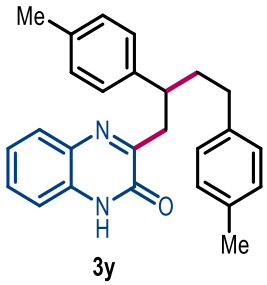
3w

Compound, **3w**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 93% (83 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 – 7.75 (m, 1H), 7.36 – 7.34 (m, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.24 – 7.20 (m, 5H), 7.19 – 7.17 (m, 2H), 7.15 – 7.10 (m, 2H), 7.07 (d, J = 8.1 Hz, 2H), 7.02 – 7.00 (m, 1H), 6.62 – 6.59 (m, 1H), 3.55 – 3.49 (m, 1H), 3.33 – 3.23 (m, 2H), 2.50 – 2.46 (m, 2H), 2.42 (s, 3H), 2.13 – 2.01 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.3, 154.9, 144.7, 142.6, 139.5, 134.1, 133.3, 132.6, 131.0, 129.4, 129.3, 128.5, 128.4, 128.3, 128.2, 128.0, 126.3, 125.7, 123.7, 115.5, 42.9, 41.2, 37.9, 33.9, 21.4. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{31}H_{28}N_2OH^+$ 445.2274; Found 445.2290.



3x

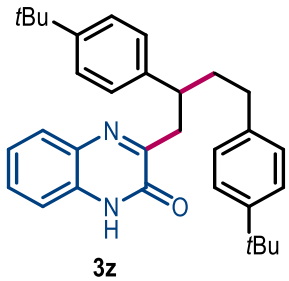
Compound, **3x**: Yellow liquid; eluent (25% ethyl acetate in hexane). **Yield:** 98% (70 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 12.40 (bs, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.34 (m, 3H), 7.32 – 7.29 (m, 3H), 7.24 – 7.20 (m, 2H), 7.19 – 7.17 (m, 1H), 7.15 – 7.11 (m, 3H), 3.59 – 3.53 (m, 1H), 3.40 – 3.30 (m, 2H), 2.60 – 2.51 (m, 2H), 2.20 – 2.07 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.9, 156.8, 144.7, 142.4, 132.9, 130.9, 129.8, 128.9, 128.5(2C), 128.3, 128.1, 126.4, 125.7, 124.2, 115.8, 42.9, 40.3, 37.8, 33.8. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{24}H_{22}N_2OH^+$ 355.1805; Found 355.1801.



3y

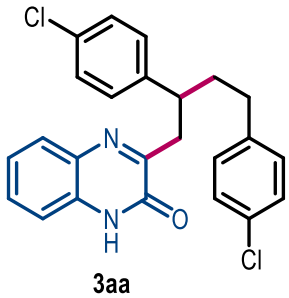
Compound, **3y**: Yellow solid; mp = 122–124 °C; eluent (20% ethyl acetate in hexane). **Yield:** 96% (73 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.33 (bs, 1H), 7.81 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.36 – 7.29 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.04 – 6.99 (m, 4H), 3.54 – 3.47 (m, 1H), 3.37 – 3.24 (m, 2H), 2.55 – 2.42 (m, 2H), 2.28 – 2.27 (s, 6H), 2.15 – 2.00 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.1, 156.8, 141.7, 139.5, 135.7, 135.1, 132.9, 130.9, 129.8,

129.2, 129.0, 128.9, 128.4, 127.9, 124.2, 115.8, 42.6, 40.5, 38.0, 33.4, 21.13, 21.07. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{26}H_{26}N_2OH^+$ 383.2118; Found 383.2112.



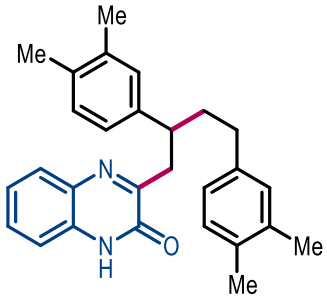
3z

Compound, **3z**: Yellow liquid; eluent (20% ethyl acetate in hexane). **Yield:** 95% (89 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.57 (bs, 1H), 7.78 (dd, J = 8.1, 1.4 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.33 – 7.29 (m, 2H), 7.28 – 7.27 (m, 2H), 7.25 – 7.22 (m, 4H), 7.05 – 7.03 (m, 2H), 3.54 – 3.47 (m, 1H), 3.30 (d, J = 7.3 Hz, 2H), 2.55 – 2.44 (m, 2H), 2.15 – 2.00 (m, 2H), 1.28 – 1.27 (m, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.3, 156.8, 149.0, 148.5, 141.7, 139.6, 133.0, 130.9, 129.8, 128.9, 128.1, 127.6, 125.3, 125.2, 124.2, 115.7, 42.6, 40.4, 37.6, 34.5, 34.4, 33.3, 31.54, 31.51. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{32}H_{38}N_2OH^+$ 467.3057; Found 467.3057.



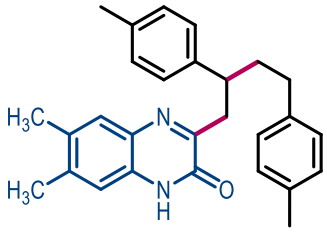
3aa

Compound, **3aa**: Yellow solid; mp = 156–158 ºC; eluent (20% ethyl acetate in hexane). **Yield:** 91% (77 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.23 (bs, 1H), 7.80 (dd, J = 8.1, 1.4 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.38 – 7.34 (m, 1H), 7.31 – 7.28 (m, 2H), 7.26 (bs, 3H), 7.20 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 3.54 – 3.47 (m, 1H), 3.33 – 3.26 (m, 2H), 2.54 – 2.44 (m, 2H), 2.18 – 1.97 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.4, 156.6, 142.9, 140.5, 132.9, 132.1, 131.6, 130.8, 130.0, 129.8, 129.4, 128.9, 128.7, 128.5, 124.4, 115.7, 42.1, 40.0, 37.6, 33.0. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{24}H_{20}Cl_2N_2OH^+$ 423.1025; Found 423.1022.



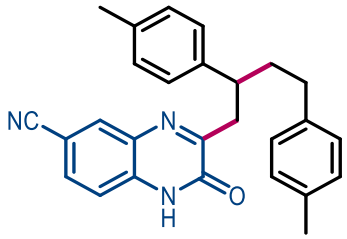
3ab

Compound, **3ab**: Yellow liquid; eluent (20% ethyl acetate in hexane). **Yield:** 93% (76 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.69 (s, 1H), 7.79 (dd, J = 8.1, 1.4 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.33 – 7.29 (m, 1H), 7.18 (dd, J = 8.2, 1.3 Hz, 1H), 7.09 – 7.04 (m, 3H), 6.95 (d, J = 7.5 Hz, 1H), 6.85 – 6.81 (m, 2H), 3.49 – 3.42 (m, 1H), 3.28 – 3.25 (m, 2H), 2.51 – 2.37 (m, 2H), 2.23 (s, 3H), 2.20 (s, 3H), 2.17 (s, 3H), 2.16 (s, 3H), 2.08 – 1.94 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.2, 156.7, 142.3, 140.0, 136.3, 136.2, 134.3, 133.6, 132.9, 130.9, 129.7, 129.64, 129.61, 129.4, 129.3, 128.8, 125.7, 125.2, 124.0, 115.6, 42.5, 40.5, 37.8, 33.3, 19.9, 19.7, 19.4, 19.2. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{28}H_{30}N_2OH^+$ 411.2431; Found 411.2430.



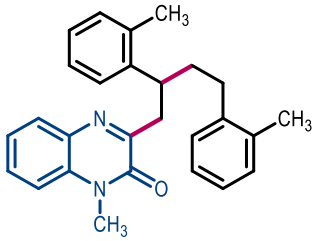
3ac

Compound, **3ac**: Yellow liquid; eluent (30% ethyl acetate in hexane). **Yield:** 85% (70 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.48 (s, 1H), 7.54 (s, 1H), 7.22 – 7.20 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.01 – 6.96 (m, 5H), 3.50 – 3.43 (m, 1H), 3.31 – 3.18 (m, 2H), 2.49 – 2.39 (m, 2H), 2.36 – 2.34 (m, 6H), 2.27 – 2.26 (m, 6H), 2.11 – 1.96 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.8, 156.5, 141.8, 139.8, 139.6, 135.7, 135.1, 133.2, 131.4, 129.2, 129.0, 128.9(2C), 128.4, 127.9, 115.8, 42.6, 40.5, 37.9, 33.4, 21.14, 21.08, 20.2, 19.6. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{28}H_{30}N_2OH^+$ 411.2431; Found 411.2430.



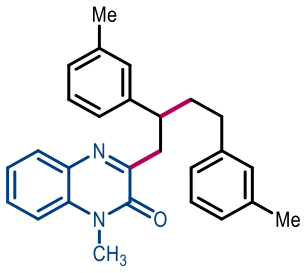
3ad

Compound, **3ad**: Yellow liquid; eluent (25% ethyl acetate in hexane). **Yield:** 89% (42 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.08 (bs, 1H), 8.07 (d, J = 1.8 Hz, 1H), 7.66 (dd, J = 8.4, 1.8 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 7.05 – 6.98 (m, 4H), 3.49 – 3.40 (m, 1H), 3.33 – 3.21 (m, 2H), 2.54 – 2.42 (m, 2H), 2.29 – 2.28 (m, 6H), 2.10 – 1.96 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.7, 156.3, 141.2, 139.3, 136.0, 135.3, 134.0, 133.7, 132.3, 129.9, 129.6, 129.3, 129.1, 128.4, 127.9, 116.7, 107.8, 42.2, 40.2, 38.2, 33.3, 21.12, 21.09. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{25}N_3OH^+$ 408.2070; Found 408.2077.



3ae

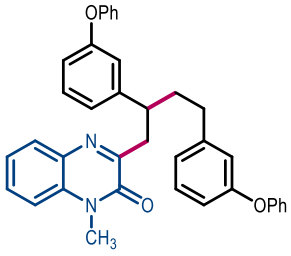
Compound, **3ae**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 92% (73 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (dd, J = 8.0, 1.5 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.19 (t, J = 7.3 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.06 – 7.02 (m, 5H), 3.93 – 3.86 (m, 1H), 3.66 (s, 3H), 3.42 – 3.37 (m, 1H), 3.23 – 3.18 (m, 1H), 2.55 – 2.46 (m, 2H), 2.43 (s, 3H) 2.13 (s, 3H), 2.06 – 1.91 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.5, 155.1, 143.3, 140.8, 136.6, 136.0, 133.1, 132.8, 130.3, 130.2, 129.8, 129.7, 128.8, 126.3, 126.02, 125.96, 125.9(2C), 123.6, 113.7, 40.9, 37.4, 36.8, 31.2, 29.2, 20.2, 19.2. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{28}N_2OH^+$ 397.2274; Found 397.2275.



3af

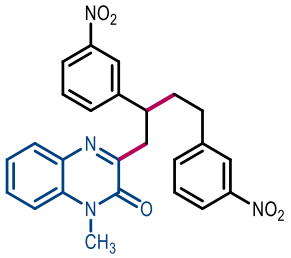
Compound, **3af**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 97% (77 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (dd, J = 8.0, 1.5 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.24 (s, 1H), 7.19 – 7.08 (m, 4H), 6.98 (d, J = 7.0 Hz, 1H), 6.94 (d, J = 7.4 Hz, 1H), 6.90 – 6.88 (m, 2H), 3.66 (s, 3H), 3.52 – 3.45 (m, 1H), 3.29 – 3.27 (m, 2H), 2.52 – 2.42 (m, 2H), 2.32 (s, 3H), 2.27 (s, 3H), 2.11 – 1.96 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6, 155.1, 145.0, 142.6, 137.9, 137.8, 133.2, 132.9, 129.9, 129.7, 129.3, 128.9, 128.3, 128.2, 127.0,

126.4, 125.5, 125.1, 123.6, 113.6, 42.8, 41.2, 37.9, 33.9, 29.1, 21.6, 21.5. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{28}N_2OH^+$ 397.2274; Found 397.2280.



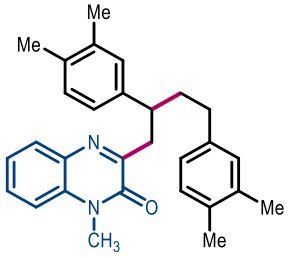
3ag

Compound, **3ag**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 91% (100 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.31 – 7.21 (m, 7H), 7.17 (t, *J* = 8.2 Hz, 1H), 7.07 – 7.03 (m, 3H), 6.99 – 6.97 (m, 3H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.85 – 6.78 (m, 4H), 3.61 (s, 3H), 3.52 – 3.47 (m, 1H), 3.26 (d, *J* = 7.4 Hz, 2H), 2.56 – 2.45 (m, 2H), 2.12 – 1.96 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.1, 157.6, 157.5, 157.2, 157.1, 154.9, 146.8, 144.5, 133.0, 132.7, 129.8, 129.74(2C), 129.71, 129.5, 123.6, 123.5, 123.1, 123.0, 119.1, 119.0, 118.8(2C), 118.6(2C), 117.1, 116.3, 113.6, 42.5, 41.0, 37.5, 33.7, 29.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{37}H_{32}N_2O_3H^+$ 553.2486; Found 553.2496.



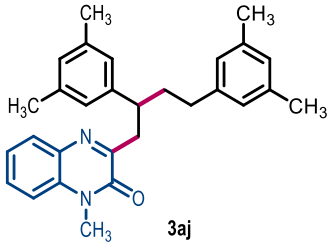
3ah

Compound, **3ah**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 78% (71 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79 – 7.77 (m, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.30 (m, 1H), 7.25 – 7.20 (m, 3H), 7.09 (d, J = 7.9 Hz, 2H), 7.03 – 6.97 (m, 4H), 3.65 (s, 3H), 3.51 – 3.45 (m, 1H), 3.31 – 3.20 (m, 2H), 2.50 – 2.40 (m, 2H), 2.07 – 1.94 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.0, 154.4, 144.5, 142.4, 133.7, 132.5, 131.8, 130.6, 128.7, 128.5(2C), 128.4(2C), 128.0(2C), 127.3, 126.5, 126.2, 125.8, 115.1, 42.5, 41.0, 38.1, 33.8, 29.4. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{25}H_{22}N_4O_5H^+$ 459.1663; Found 459.1660.



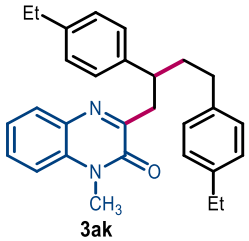
3ai

Compound, **3ai**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 87% (74 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.34 – 7.30 (m, 1H), 7.25 – 7.24 (1H), 7.11 – 7.05 (m, 3H), 6.98 – 6.96 (m, 1H), 6.85 – 6.81 (m, 2H), 3.66 (s, 3H), 3.49 – 3.42 (m, 1H), 3.29 – 3.22 (m, 2H), 2.54 – 2.34 (m, 2H), 2.24 (s, 3H), 2.21 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H), 2.05 – 1.95 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.7, 155.1, 142.5, 140.2, 136.4, 136.3, 134.3, 133.7, 133.2, 132.9, 129.9 (2C), 129.7 (2C), 129.6, 129.5, 125.8, 125.4, 123.6, 113.6, 42.4, 41.4, 38.0, 33.5, 29.2, 20.0, 19.8, 19.5, 19.4. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{29}H_{32}N_2OH^+$ 425.2587; Found 425.2590.



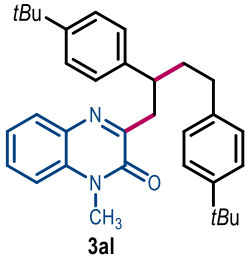
3aj

Compound, **3aj**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 95% (81 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (dd, J = 8.0, 1.5 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.34 – 7.30 (m, 1H), 7.253 – 7.249 (m, 1H), 6.95 (bs, 2H), 6.81 (s, 1H), 6.76 (s, 1H), 6.70 (bs, 2H), 3.67 (s, 3H), 3.49 – 3.40 (m, 1H), 3.25 (d, J = 7.3 Hz, 2H), 2.49 – 2.35 (m, 2H), 2.28 (s, 6H), 2.22 (s, 6H), 2.04 – 1.95 (m, 2H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.7, 155.1, 145.0, 142.6, 137.7 (2C), 133.2, 132.8, 129.9, 129.7, 127.9, 127.3, 126.3, 125.9, 123.6, 113.6, 42.7, 41.3, 37.7, 33.8, 29.1, 21.5, 21.3. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{29}H_{32}N_2OH^+$ 425.2587; Found 425.2591.



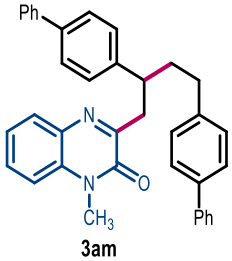
3ak

Compound, **3ak**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 92% (78 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (dd, J = 8.0, 1.5 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.33 – 7.30 (m, 1H), 7.25 – 7.23 (m, 3H), 7.11 (d, J = 7.9 Hz, 2H), 7.05 – 7.00 (m, 4H), 3.65 (s, 3H), 3.51 – 3.45 (m, 1H), 3.26 (t, J = 7.2 Hz, 2H), 2.62 – 2.56 (m, 4H), 2.51 – 2.40 (m, 2H), 2.08 – 1.96 (m, 2H), 1.22 – 1.18 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.7, 155.1, 142.1, 142.0, 141.5, 139.9, 133.1, 132.8, 129.9, 129.7, 128.4(2C), 128.0, 127.9, 127.8, 123.6, 113.6, 42.5, 41.3, 37.9, 33.5, 29.2, 28.5, 15.8, 15.6. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{29}H_{32}N_2OH^+$ 425.2587; Found 425.2587.



3al

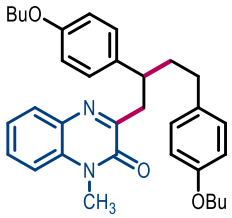
Compound, **3al**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 90% (87 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 – 7.74 (m, 1H), 7.50 – 7.45 (m, 1H), 7.31 – 7.27 (m, 2H), 7.24 – 7.21 (m, 6H), 7.02 (d, J = 7.9 Hz, 2H), 3.63 (s, 3H), 3.50 – 3.46 (m, 1H), 3.26 (d, J = 7.3 Hz, 2H), 2.50 – 2.45 (m, 2H), 2.09 – 1.97 (m, 2H), 1.28 – 1.27 (m, 18H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 155.2, 149.0, 148.5, 141.9, 139.7, 133.2, 132.9, 129.9, 129.6, 128.1, 127.7, 125.3, 125.2, 123.5, 113.6, 42.5, 41.3, 37.7, 34.5, 34.4, 33.4, 31.6(2C), 29.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{33}H_{40}N_2OH^+$ 481.3213; Found 481.3224.



3am

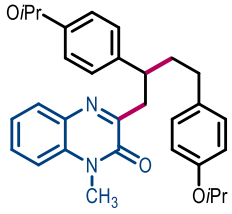
Compound, **3am**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 85% (88 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.60 – 7.52 (m, 8H), 7.48 – 7.46 (m, 1H), 7.45 – 7.40 (m, 7H), 7.34 – 7.29 (m, 3H), 7.21 – 7.19 (m, 1H), 3.65 (s, 3H), 3.64 – 3.58 (m, 1H), 3.37 – 3.31 (m, 2H), 2.65 – 2.54 (m, 2H), 2.22 – 2.05 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.3, 155.0, 143.9, 141.6, 141.2, 140.8, 139.0, 138.6, 133.0, 132.7, 129.75, 129.67, 129.1, 128.9, 128.7, 128.4, 127.13, 127.05, 127.02,

126.97, 123.6, 123.5, 113.6, 113.5, 42.3, 41.0, 35.9, 33.4, 29.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{37}H_{32}N_2OH^+$ 521.2587; Found 521.2586.



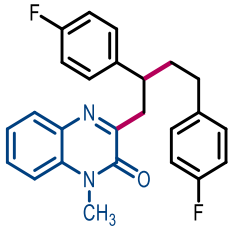
3an

Compound, **3an**: Yellow liquid; eluent (20% ethyl acetate in hexane). **Yield:** 82% (84 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (dd, J = 7.9, 1.6 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.24 (s, 1H), 7.20 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 3.94 – 3.90 (m, 4H), 3.64 (s, 3H), 3.47 – 3.41 (m, 1H), 3.29 – 3.19 (m, 2H), 2.48 – 2.36 (m, 2H), 2.05 – 1.90 (m, 2H), 1.73 (p, J = 7.2 Hz, 4H), 1.47 (h, J = 7.4 Hz, 4H), 0.96 (t, J = 7.3 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.6, 157.5, 157.2, 154.9, 136.6, 134.4, 133.0, 132.7, 129.7, 129.5, 129.2, 128.8, 123.4, 114.3(2C), 113.5, 67.7, 67.6, 41.8, 41.2, 38.2, 32.8, 31.44, 31.42, 29.0, 19.3(2C), 13.9(2C). **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{33}H_{40}N_2O_3H^+$ 513.3112; Found 513.3115.



3ao

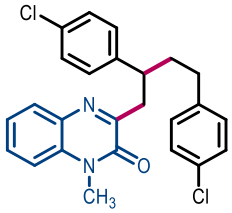
Compound, **3ao**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 91% (88 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 – 7.76 (m, 1H), 7.51 – 7.47 (m, 1H), 7.32 – 7.28 (m, 1H), 7.24 – 7.23 (m, 1H), 7.20 – 7.17 (m, 2H), 6.99 – 6.96 (m, 2H), 6.81 – 6.72 (m, 4H), 4.51 – 4.43 (m, 2H), 3.64 (s, 3H), 3.47 – 3.40 (m, 1H), 3.26 – 3.23 (m, 2H), 2.48 – 2.37 (m, 2H), 2.08 – 1.90 (m, 2H), 1.31 – 1.29 (m, 12H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 156.4, 156.1, 155.1, 136.9, 134.8, 133.2, 132.8, 129.9, 129.7, 129.4, 129.0, 123.6, 116.02, 115.98, 113.6, 70.2, 70.1, 42.1, 41.4, 38.3, 33.0, 29.1, 22.3(2C). **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{31}H_{36}N_2O_3H^+$ 485.2799; Found 485.2808.



3ap

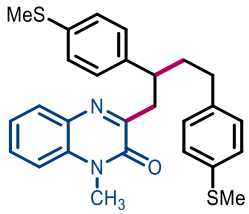
Compound, **3ap**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 84% (66 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (dd, J = 7.9, 1.5 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.30 (m, 1H), 7.273 – 7.270 (m, 1H), 7.25 – 7.22 (m, 2H), 7.05 – 7.00 (m, 2H), 6.98 – 6.93 (m, 2H), 6.92 – 6.87 (m, 2H), 3.65 (s, 3H), 3.51 – 3.44 (m, 1H), 3.25 (dd, J = 7.4, 2.2 Hz, 2H), 2.50 – 2.40 (m, 2H), 2.11 – 1.91 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.5 (d, *J* = 243.8 Hz), 161.3 (d, *J* = 243.0 Hz), 159.1, 155.0, 140.2 (d, J = 3.5 Hz), 137.9 (d, J = 3.4 Hz), 133.1, 132.7, 129.9, 129.81 (d, *J* = 7.5 Hz), 129.77, 129.4 (d, *J* = 7.5 Hz), 123.7, 115.2 (d, *J* = 21.2 Hz), , 115.0 (d, *J* = 21.2 Hz), 113.7, 41.9, 41.1, 38.2, 33.0, 29.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -117.04, -117.95. **HRMS** (ESI/TOF-Q) m/z:

$[M+H]^+$ Calculated for $C_{25}H_{22}F_2N_2OH^+$ 405.1773; Found 405.1772.



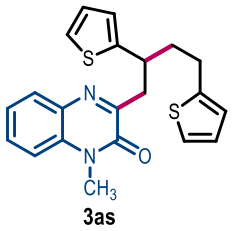
3aq

Compound, **3aq**: Yellow solid; mp = 102–104 ºC; eluent (15% ethyl acetate in hexane). **Yield:** 79% (69 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (dd, J = 8.0, 1.6 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.30 (m, 1H), 7.28 – 7.27 (m, 1H), 7.25 – 7.24 (m, 1H), 7.23 – 7.22 (m, 3H), 7.20 – 7.16 (m, 2H), 7.01 – 6.99 (m, 2H), 3.65 (s, 3H), 3.51 – 3.44 (m, 1H), 3.29 – 3.21 (m, 2H), 2.51 – 2.41 (m, 2H), 2.12 – 1.91 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.9, 155.0, 143.1, 140.6, 133.1, 132.8, 132.1, 131.6, 130.0(2C), 129.9, 129.5, 128.7, 128.5, 123.7, 113.7, 42.0, 40.8, 37.8, 33.1, 29.2. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{25}H_{22}Cl_2N_2OH^+$ 437.1182; Found 437.1182.



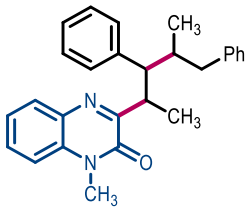
3ar

Compound, **3ar**: Yellow liquid; eluent (20% ethyl acetate in hexane). **Yield:** 90% (83 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, J = 8.0 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.35 – 7.29 (m, 2H), 7.24 – 7.22 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 3.64 (s, 3H), 3.49 – 3.43 (m, 1H), 3.30 – 3.19 (m, 2H), 2.48 – 2.40 (m, 8H), 2.08 – 1.90 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.3, 155.0, 141.9, 139.6, 135.8, 135.1, 133.1, 132.8, 129.84, 129.80, 129.1, 128.6, 127.3, 127.0, 123.6, 113.7, 42.1, 41.0, 37.9, 33.3, 29.2, 16.5, 16.2. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{28}N_2OS_2H^+$ 461.1716; Found 461.1715.



3as

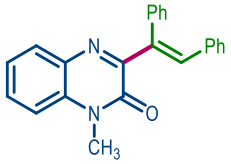
Compound, **3as**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 82% (62 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 – 7.79 (m, 1H), 7.54 – 7.50 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 7.13 – 7.11 (m, 1H), 7.08 – 7.07 (m, 1H), 6.91 – 6.88 (m, 3H), 6.753 – 6.746 (m, 1H), 3.94 – 3.88 (m, 1H), 3.67 (s, 3H), 3.37 – 3.29 (m, 2H), 2.87 – 2.76 (m, 2H), 2.23 – 2.07 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.7, 155.0, 148.4, 145.1, 133.2, 132.8, 130.0, 129.9, 126.8, 126.6, 124.4, 124.3, 123.7, 123.3, 123.0, 113.7, 41.9, 39.2, 37.7, 29.2, 27.8. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{21}H_{20}N_2OS_2H^+$ 381.1090; Found 381.1100.



3at, (1:1 dr)
with β-methylstyrene

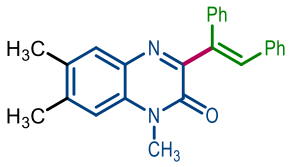
Compound, **3at**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 91% (72 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 (dd, J = 8.0, 1.6 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.53 – 7.46 (m, 2H), 7.38 – 7.33 (m, 5H), 7.30 – 7.27 (m, 5H), 7.23 – 7.20 (m, 2H), 7.18 – 7.15 (m, 5H), 7.11 – 7.07 (m, 3H), 7.05 – 7.03 (m, 2H), 6.95 (d, J = 7.2 Hz, 2H), 3.61 – 3.56 (m, 6H), 3.35 – 3.24 (m, 4H), 3.16 – 3.12 (m, 1H), 2.67 – 2.62 (m, 1H), 2.59 –

2.55 (m, 2H), 2.42 – 2.26 (m, 1H), 2.10 – 2.06 (m, 1H), 1.59 – 1.55 (m, 6H), 1.34 (d, J = 7.0 Hz, 3H), 1.14 (d, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.9, 159.1, 155.4, 155.2, 149.5, 149.4, 147.5, 147.2, 133.2, 132.6, 130.03, 129.96, 129.74, 129.68, 128.5, 128.4, 128.2, 127.9, 127.8, 127.4, 127.3, 127.2, 126.9, 126.2, 125.70, 125.66, 125.6, 125.4, 123.6, 123.4, 113.6, 113.5, 50.5, 50.2, 46.0, 44.0, 43.4, 42.4, 37.5, 37.0, 36.8, 29.3, 25.55, 25.46, 24.3, 21.9. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{27}H_{28}N_2OH^+$ 397.2274; Found 397.2279.



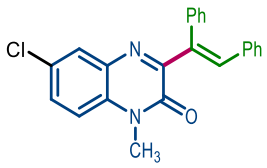
4a

Compound, **4a**: Yellow sticky liquid; eluent (10% ethyl acetate in hexane). **Yield:** 55% (37 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 – 7.79 (m, 1H), 7.51 – 7.47 (m, 2H), 7.25 – 7.22 (m, 10H), 7.21 – 7.20 (m, 1H), 7.15 (s, 1H), 3.57 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.1, 150.2, 141.5, 133.4, 133.3, 131.1, 130.6, 128.32(2C), 128.26, 128.2(2C), 127.8(2C), 123.8, 114.3(2C), 113.8, 28.8. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{23}H_{18}N_2OH^+$ 339.1492; Found 339.1495.



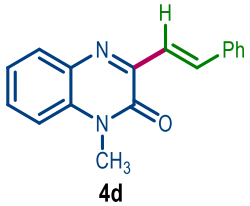
4b

Compound, **4b**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 56% (41 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.18 (s, 1H), 7.57 (s, 1H), 7.28 – 7.26 (m, 10H), 7.04 (s, 1H), 3.60 (s, 3H), 2.37 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.3, 150.2, 149.1, 141.6, 141.1, 132.9, 132.0, 131.3, 130.6, 128.4(2C), 128.29, 128.26(2C), 127.8(2C), 114.45, 114.39, 28.8, 20.7, 19.3. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{25}H_{22}N_2OH^+$ 367.1805; Found 3671801.



4c

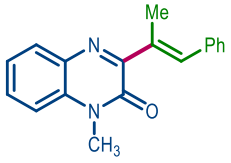
Compound, **4c**: Yellow sticky liquid; eluent (10% ethyl acetate in hexane). **Yield:** 51% (38 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.822 – 7.816 (m, 1H), 7.49 (dd, J = 8.0, 2.4 Hz, 1H), 7.29 – 7.27 (m, 10H), 7.21 (s, 1H), 7.19 (s, 1H), 3.61 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.8, 151.6(2C), 150.2, 141.6, 134.0, 132.1, 131.1, 130.0, 129.3, 128.4(2C), 128.3(2C), 127.8(2C), 115.0, 114.3, 29.0. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{23}H_{17}ClN_2ONH_4^+$ 390.1368; Found 390.1363.



4d

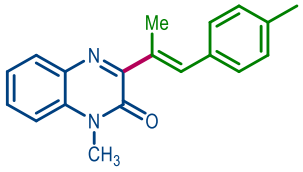
Compound, **4d**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 22% (11 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 7.4 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.36 – 7.28 (m, 5H), 7.25 – 7.24 (m, 1H), 7.07 (d, J = 14.0 Hz, 1H), 6.72 (d, J = 13.9 Hz, 1H), 3.65 (s, 3H). **^{13}C**

NMR (126 MHz, $CDCl_3$) δ 155.2, 150.3, 137.3, 136.0, 133.5, 132.4, 131.2, 130.6, 128.9, 128.4, 126.2, 123.9, 113.9, 106.6, 28.8. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{17}H_{14}N_2OH^+$ 263.1179; Found 263.1183.



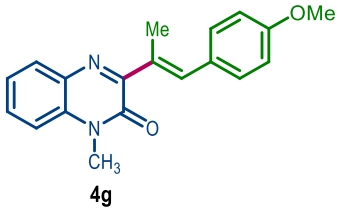
4e

Compound, **4e**: Yellow sticky liquid; eluent (10% ethyl acetate in hexane). **Yield:** 69% (38 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.61 (m, 1H), 7.51 – 7.52 (m, 1H), 7.28 – 7.26 (m, 6H), 7.21 – 7.17 (m, 1H), 6.46 (s, 1H), 3.62 (s, 3H), 2.62 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.0, 150.2, 143.3, 141.2, 133.4, 133.3, 131.1, 130.5, 128.2, 127.4, 125.5, 123.8, 113.8, 112.4, 28.7, 21.8. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{18}H_{16}N_2OH^+$ 277.1335; Found 277.1330.



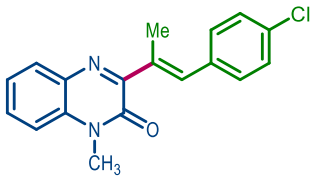
4f

Compound, **4f**: Yellow sticky liquid; eluent (7% ethyl acetate in hexane). **Yield:** 64% (37 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.54 (m, 1H), 7.24 – 7.21 (m, 4H), 7.19 – 7.18 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 6.69 (s, 1H), 3.58 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.4, 149.2, 141.2, 137.4, 136.1, 132.9, 132.1, 131.5, 130.7, 129.0, 128.5, 126.3, 114.5, 106.7, 28.9, 20.8, 19.3.**HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{19}H_{18}N_2OH^+$ 291.1492; Found 291.1498.



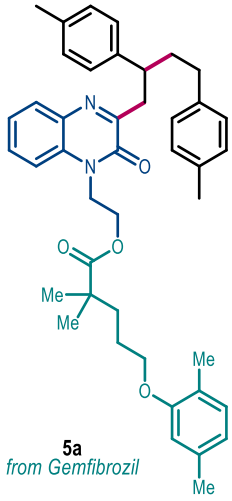
4g

Compound, **4g**: Yellow sticky liquid; eluent (7% ethyl acetate in hexane). **Yield:** 48% (32 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 – 7.75 (m, 1H), 7.49 – 7.45 (m, 1H), 7.36 (d, J = 7.3 Hz, 1H), 7.24 – 7.18 (m, 4H), 7.16 – 7.15 (m, 1H), 6.79 (s, 1H), 3.68 (s, 3H), 3.54 (s, 3H), 2.05 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.8, 154.7, 151.1, 137.5, 136.7, 134.8, 133.8, 132.6, 132.3, 129.1, 126.1, 116.4, 115.4, 112.6, 50.1, 28.8, 21.1. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{19}H_{18}N_2O_2Na^+$ 329.1260; Found 329.1262.



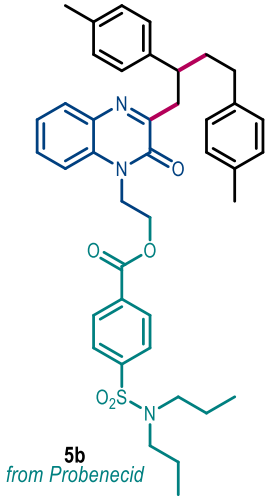
4h

Compound, **4h**: Yellow sticky liquid; eluent (7% ethyl acetate in hexane). **Yield:** 59% (37 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 – 7.80 (m, 1H), 7.54 – 7.51 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.22 (m, , 2H), 7.05 (d, J = 8.2 Hz, 1H), 6.62 (s, 1H), 3.60 (s, 3H), 2.27 (s, 3H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.0, 150.1, 137.6, 136.7, 134.8, 133.3, 133.2, 131.1, 130.5, 129.2, 126.1, 123.7, 113.8, 112.7, 28.7, 21.2. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{18}H_{15}ClN_2OH^+$ 311.0946; Found 311.0940.



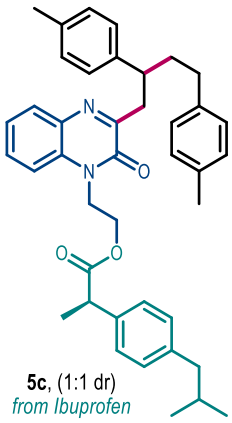
5a
from Gemfibrozil

Compound, **5a**: Yellow liquid; eluent (20% ethyl acetate in hexane). **Yield:** 94% (123 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 – 7.77 (m, 1H), 7.52 – 7.42 (m, 2H), 7.32 – 7.28 (m, 1H), 7.21 – 7.19 (m, 2H), 7.11 – 6.98 (m, 7H), 6.67 – 6.65 (m, 1H), 6.58 (bs, 1H), 4.47 – 4.44 (m, 2H), 4.37 – 4.32 (m, 2H), 3.82 – 3.79 (m, 2H), 3.51 – 3.48 (m, 1H), 3.34 – 3.19 (m, 2H), 2.49 – 2.42 (m, 2H), 2.32 (s, 3H), 2.30 (s, 6H), 2.17 (s, 3H), 2.11 – 1.96 (m, 2H), 1.68 – 1.62 (m, 4H), 1.12 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.9, 159.5, 157.0, 154.7, 141.6, 139.5, 136.6, 135.7, 135.1, 132.9, 132.6, 130.4, 130.1, 129.8, 129.1, 129.0, 128.4, 127.9, 123.7, 123.6, 120.8, 113.9, 112.1, 67.8, 60.9, 42.5, 42.2, 41.1, 40.7, 38.1, 37.1, 33.4, 25.13, 25.10, 21.5, 21.13, 21.09, 15.9. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{43}H_{50}N_2O_4H^+$ 659.3843; Found 659.3841.



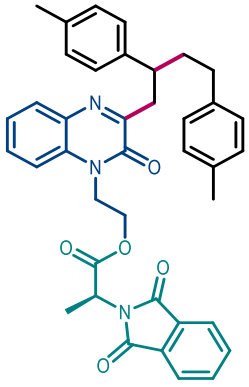
5b
from Probenecid

Compound, **5b**: Yellow liquid; eluent (25% ethyl acetate in hexane). **Yield:** 96% (42 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 – 8.00 (m, 3H), 7.85 – 7.79 (m, 2H), 7.80 – 7.72 (m, 1H), 7.62 – 7.52 (m, 2H), 7.26 – 7.19 (m, 3H), 7.15 – 6.69 (m, 5H), 4.86 – 4.52 (m, 4H), 4.43 – 4.20 (m, 2H), 3.12 – 3.08 (m, 4H), 2.43 – 2.40 (m, 1H), 2.36 – 2.30 (m, 2H), 2.19 (bs, 6H), 1.58 – 1.52 (m, 6H), 0.89 – 0.85 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.1, 155.2, 151.9, 144.5, 139.2, 139.0, 138.9, 135.9, 133.2, 130.34, 130.31, 129.1, 128.93, 128.87, 128.8, 128.7, 128.4, 126.98, 126.95, 126.6, 126.5, 63.8, 63.6, 50.0, 48.8, 27.2, 22.0, 21.03, 21.00 12.6, 11.2(2C). **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{41}H_{47}N_3O_5SH^+$ 694.3309; Found 694.3310.



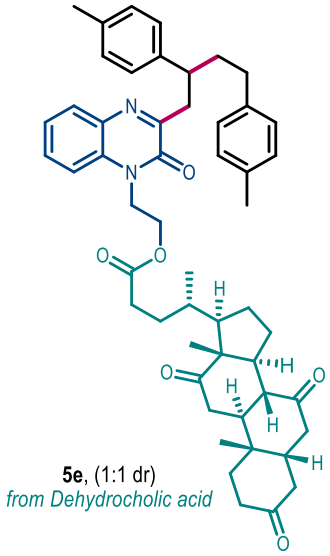
5c, (1:1 dr)
from Ibuprofen

Compound, **5c**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 88% (108 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (dd, J = 8.0, 1.6 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.32 – 7.29 (m, 2H), 7.19 – 7.16 (m, 2H), 7.09 – 6.97 (m, 10H), 4.52 – 4.23 (m, 4H), 3.60 – 3.55 (m, 1H), 3.48 – 3.40 (m, 1H), 3.31 – 3.17 (m, 2H), 2.53 – 2.45 (m, 2H), 2.43 (d, J = 7.1 Hz, 2H), 2.28 (bs, 6H), 2.08 – 1.97 (m, 2H), 1.88 – 1.81 (m, 1H), 1.40 (d, J = 7.1 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.8, 159.6, 154.8, 141.72, 141.69(C*), 140.8, 139.6, 137.4, 135.7, 135.1, 133.0, 132.7, 130.1, 129.7, 129.5, 129.1, 129.0, 128.4, 128.0, 127.2, 123.6, 113.8, 61.2, 45.21, 45.17(C*), 42.61, 42.57(C*), 41.1, 40.9, 38.1, 33.5, 30.3, 22.5, 21.12, 21.08, 18.5(2C). **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{41}H_{46}N_2O_3H^+$ 615.3581; Found 615.3585. C* is another diastereomer.



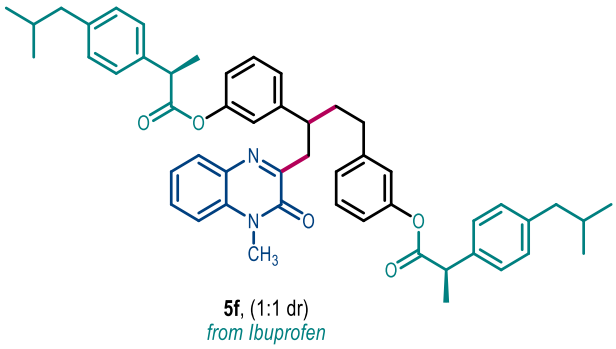
5d, (1:1 dr)
from Alanine

Compound, **5d**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 77% (96 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 – 8.09 (m, 1H), 8.04 – 7.84 (m, 1H), 7.82 – 7.70 (m, 2H), 7.68 – 7.50 (m, 5H), 7.40 – 7.28 (m, 5H), 7.24 – 7.00 (m, 2H), 4.69 – 4.49 (m, 4H), 4.40 – 4.35 (m, 1H), 2.81 – 2.73 (m, 1H), 2.35 – 2.26 (m, 2H), 1.58 (bs, 6H), 1.45 – 1.39 (m, 2H), 1.17 – 1.11 (m, 2H), 0.91 – 0.88 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 167.8, 165.3, 155.3, 139.4, 136.9, 134.3, 133.9, 131.7, 130.3, 129.1, 128.5, 127.4, 126.9, 126.4, 125.9, 124.8, 123.6, 123.4, 116.2, 107.3, 63.9, 63.5, 60.3, 57.7, 29.8, 28.8, 21.0, 19.5, 15.6, 14.6. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{39}H_{37}N_3O_5H^+$ 628.2806; Found 628.2801.



5e, (1:1 dr)
from Dehydrocholic acid

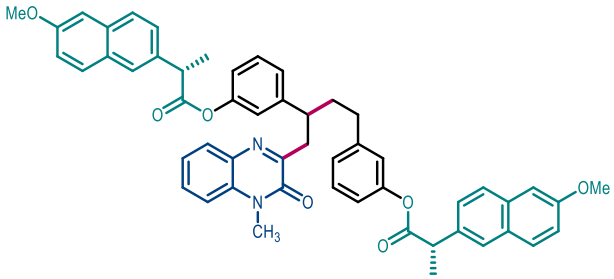
Compound, **5e**: Yellow liquid; eluent (25% ethyl acetate in hexane). **Yield:** 69% (114 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.34 – 7.28 (m, 2H), 7.22 – 7.15 (m, 3H), 7.11 – 7.05 (m, 2H), 7.03 – 6.96 (m, 3H), 3.51 – 3.41 (m, 1H), 3.30 – 3.19 (m, 2H), 2.94 – 2.86 (m, 4H), 2.48 – 2.41 (m, 2H), 2.38 – 2.32 (m, 6H), 2.31 – 2.30 (m, 2H), 2.284 – 2.278 (m, 3H), 2.25 – 2.24 (m, 2H), 2.21 – 2.19 (m, 2H), 2.17 – 2.16 (m, 2H), 2.14 – 2.12 (m, 2H), 2.06 – 2.01 (m, 6H), 1.96 – 1.94 (m, 1H), 1.89 – 1.84 (m, 4H), 1.66 – 1.59 (m, 2H), 1.40 (s, 3H), 1.08 (s, 3H), 0.87 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 212.1, 209.2, 208.8, 178.7, 160.1, 156.4, 141.6, 139.5, 135.8, 135.1, 133.0, 130.5, 129.9, 129.2, 129.1, 129.0, 128.4, 127.9, 124.3, 115.4, 57.1, 51.9, 49.1, 47.0, 45.8, 45.7, 45.1, 42.9, 42.5, 40.4, 38.8(2C), 38.1, 36.6, 36.2, 35.7, 35.4, 33.4, 31.3, 30.4, 29.8, 27.8, 25.3, 22.1, 21.2, 21.1, 18.8, 12.0. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{52}H_{62}N_2O_6H^+$ 811.4681; Found 811.4683.



5f, (1:1 dr)
from Ibuprofen

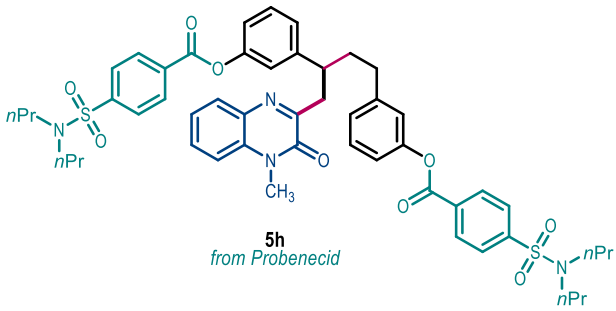
Compound, **5f**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 87% (135 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 – 7.74 (m, 1H), 7.53 – 7.47 (m, 1H), 7.32 – 7.28 (m, 6H), 7.25 – 7.21 (m, 2H), 7.18 – 7.13 (m, 6H), 6.99 – 6.91 (m, 2H), 6.85 – 6.75 (m, 2H), 3.95 – 3.88 (m, 2H), 3.63 (s, 3H), 3.52 – 3.46 (m, 1H), 3.27 – 3.24 (m, 2H), 2.49 – 2.46 (m, 6H), 2.11 – 1.92 (m, 2H), 1.91 – 1.84 (m, 2H), 1.62 – 1.58 (m, 6H), 0.93 – 0.91 (m, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.3, 173.2, 159.8(C*), 159.0, 155.0, 151.1, 151.0(C*), 144.0,

143.8(C*), 140.8, 137.5(C*), 137.4, 133.1(C*), 132.7, 129.9, 129.8, 129.61, 129.59, 129.3(C*), 129.2, 129.1, 127.4(2C), 126.1, 125.9, 125.3, 123.7, 123.6, 121.7, 121.3, 121.1, 119.4(C*), 119.3, 119.1, 118.8, 113.7, 113.6, 45.4, 45.2, 42.5, 42.4, 40.8, 40.7(C*), 37.4, 35.7, 33.5, 32.3, 30.3, 29.1, 22.5(2C), 18.74, 18.71. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{51}H_{56}N_2O_5H^+$ 777.4262; Found 777.4273. C* is another diastereomer.



5g, (1:1 dr)
from Naproxen

Compound, **5g**: Yellow liquid; eluent (30% ethyl acetate in hexane). **Yield:** 88% (145 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 – 7.84 (m, 1H), 7.83 – 7.67 (m, 6H), 7.55 – 7.46 (m, 4H), 7.36 – 7.28 (m, 4H), 7.24 – 7.10 (m, 8H), 6.83 – 6.79 (m, 1H), 4.58 – 4.54 (m, 1H), 4.40 – 4.31 (m, 1H), 4.10 – 4.05 (m, 1H), 3.92 (s, 6H), 3.61 (s, 3H), 2.35 – 2.23 (m, 2H), 2.08 – 2.01 (m, 2H), 1.72 – 1.62 (m, 2H), 0.91 – 0.87 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.2(2C), 161.0, 158.5, 157.8, 154.7, 150.9, 143.4, 142.70, 142.67, 135.4, 135.3, 133.92, 133.86, 133.1, 133.0, 132.9, 130.3, 129.9, 129.8, 129.6, 129.5(2C), 129.13, 129.08, 127.5, 126.41, 126.38, 126.35, 126.33, 126.27, 126.26, 123.8, 123.6, 121.5, 119.8, 119.7, 119.2, 113.8, 113.6, 105.8(2C), 55.5(2C), 48.9, 45.7, 29.8, 29.3, 27.3, 21.8, 18.7, 14.3, 12.5. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{53}H_{48}N_2O_7H^+$ 825.3534; Found 825.3539.



5h
from Probenecid

Compound, **5h**: Yellow liquid; eluent (15% ethyl acetate in hexane). **Yield:** 93% (174 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 – 7.73 (m, 1H), 7.51 – 7.47 (m, 1H), 7.31 – 7.27 (m, 6H), 7.24 – 7.20 (m, 2H), 7.16 – 7.12 (m, 6H), 6.96 – 6.90 (m, 2H), 6.82 – 6.73 (m, 2H), 3.93 – 3.87 (m, 2H), 3.63 (s, 3H), 3.50 – 3.47 (m, 1H), 3.25 – 3.23 (m, 2H), 2.49 – 2.46 (m, 6H), 2.10 – 1.92 (m, 2H), 1.91 – 1.82 (m, 2H), 1.61 – 1.56 (m, 8H), 0.93 – 0.91 (m, 12H). **^{13}C NMR (126**

MHz, $CDCl_3$) δ 173.3, 173.2, 159.0, 155.0, 151.0, 150.9, 146.3, 144.0, 140.9, 137.5, 137.4, 133.1, 132.7, 129.9, 129.8, 129.63, 129.61, 129.3, 129.1, 127.4(2C), 126.0, 125.4, 123.6, 121.4, 121.1, 119.39, 119.36, 118.8, 113.7, 45.4, 45.2, 42.5, 42.4(2C*), 40.81, 40.76(2C*), 37.4, 33.6, 30.3, 29.2, 22.6, 18.8, 18.7. **HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{51}H_{58}N_4O_9S_2H^+$ 935.3718; Found 935.3711.

Crystallographic experimental data

Crystallization: Crystals of compound **3a** were obtained through a slow evaporation technique at room temperature from the solution in a hexane/DCM mixture.

Crystal structure of compound **3a** (CCDC number: 2385075, Ellipsoid Probability 50%):

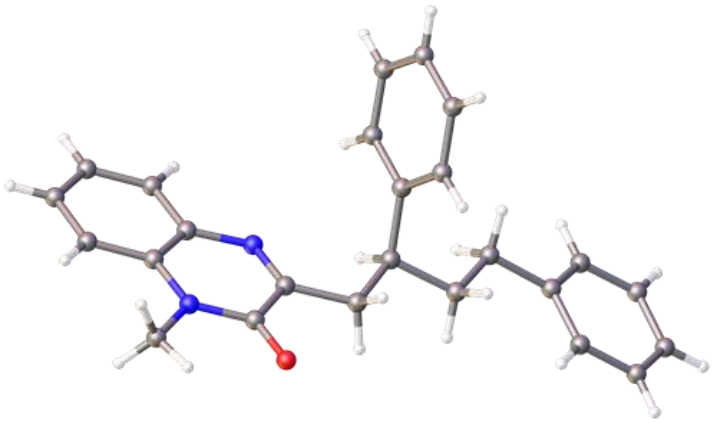


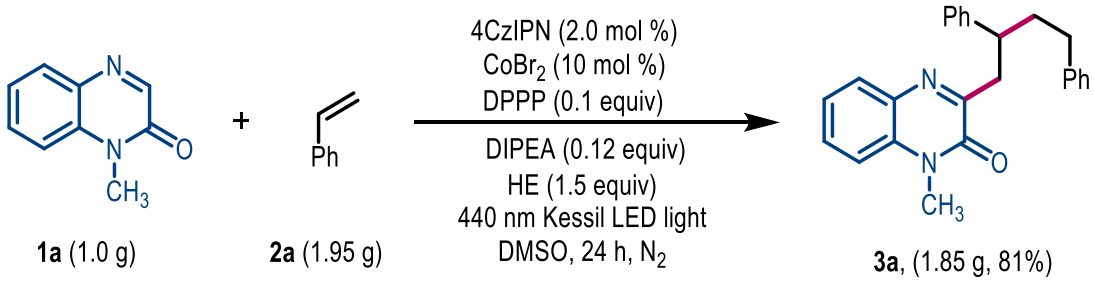
Table 1. Crystal data and structure refinement for **3a**

Identification code	**3a**	
Empirical formula	$C_{25}H_{24}N_2O$	
Formula weight	368.1889	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 13.0274(8) Å	α= 90°.

	b = 8.8918(5) Å β= 90°.
	c = 19.8864(12) Å γ = 90°.
Volume	2303.6(2) Å3
Z	8
Density (calculated)	1.218 Mg/m3
Absorption coefficient	0.077 mm-1
F(000)	896
Crystal size	0.319 x 0.234 x 0.083 mm3
Theta range for data collection	3.449 to 26.990°.
Index ranges	-16<=h<=16, -11<=k<=11, -25<=l<=25
Reflections collected	70602
Independent reflections	2508 [R(int) = 0.0461]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.986 and 0.953
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	2508 / 0 / 149
Goodness-of-fit on F2	1.099
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1287
R indices (all data)	R1 = 0.0636, wR2 = 0.1373
Extinction coefficient	n/a
Largest diff. peak and hole	0.354 and -0.287 e.Å-3

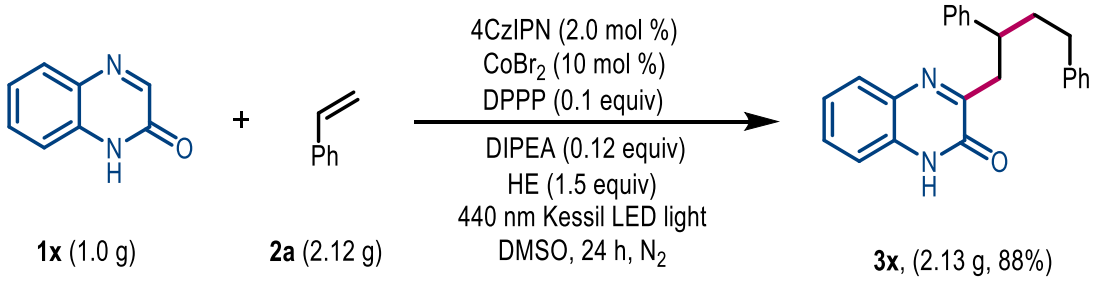
Gram scale synthesis of compound 3a and 3x

Procedure for compound 3a



A 100 mL oven-dried round bottom flask equipped with a magnetic stir was charged with $CoBr_2$ (10 mol %), DPPP (0.1 equiv), 4CzIPN (2.0 mol %), Hantzsch ester (HE) (1.5 equiv), quinoxalinone **1a** (6.2 mmol, 1.0 equiv, 1.0 g), and alkene **2a** (18.7 mmol, 3.0 equiv, 1.95 g) under nitrogen atmosphere. The reaction flask was capped with a septum, and DIPEA (0.12 equiv) and dry DMSO (30 mL) were added via a syringe. After that, the reaction mixture was allowed to stir with irradiation of 440 nm Kessil LED light at room temperature for 24 h. After completion of the reaction (TLC monitored), brine solution was added and then extracted with ethyl acetate. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography over silica gel to get product **3a** (1.85 g, 81% yield).

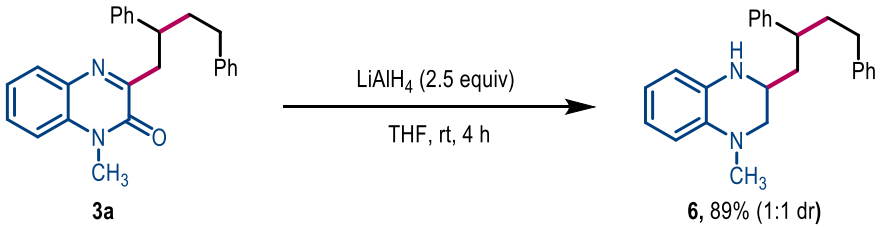
Procedure for compound 3x



A 100 mL oven-dried round bottom flask equipped with a magnetic stir was charged with $CoBr_2$ (10 mol %), DPPP (0.1 equiv), 4CzIPN (2.0 mol %), Hantzsch ester (HE) (1.5 equiv), quinoxalinone **1x** (6.8 mmol, 1.0 equiv, 1.0 g), and alkene **2a** (20.5 mmol, 3.0 equiv, 2.12 g) under nitrogen atmosphere. The reaction flask was capped with a septum, and DIPEA (0.12 equiv) and dry DMSO (30 mL) were added via a syringe. After that, the reaction mixture was allowed to stir with irradiation of 440 nm Kessil LED light at room temperature for 24 h. After completion of the reaction (TLC monitored), brine solution was added and then extracted with ethyl acetate. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography over silica gel to get product **3x** (2.13 g, 88% yield).

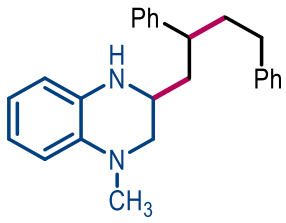
Post-synthetic manipulations

a) Synthesis of compound **6**



3a **6**, 89% (1:1 dr)

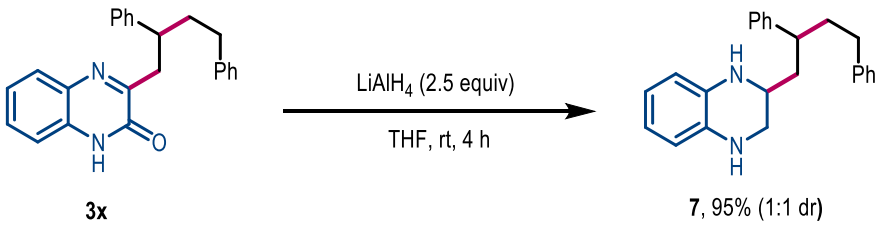
A 16×100 mm oven-dried reaction tube equipped with a magnetic stir was charged with C3-alkyl quinoxalin-2(1*H*)-one **3a** (0.1 mmol, 1.0 equiv), and $LiAlH_4$ (0.25 mmol, 2.5 equiv) under a nitrogen atmosphere. The reaction tube was capped with a septum, and dry THF (1.0 mL) was added via a syringe. After that, the reaction mixture was allowed to stir at room temperature under N_2 atmosphere for 4 h. After completion of the reaction (TLC monitored), the reaction mixture was neutralized with a saturated solution of sodium bicarbonate and then extracted with ethyl acetate. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography column over silica gel to get compound **6**.



6, (1:1 dr)

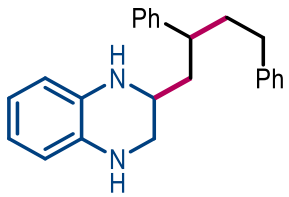
Compound, **6**: Yellow liquid; eluent (7% ethyl acetate in hexane). **Yield:** 89% (32 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.32 (m, 4H), 7.29 – 7.27 (m, 3H), 7.24 – 7.16 (m, 10H), 7.13 – 7.09 (m, 4H), 6.68 – 6.55 (m, 4H), 6.52 – 6.49 (m, 3H), 6.47 – 6.45 (m, 1H), 6.16 – 6.14 (m, 1H), 3.35 – 3.29 (m, 1H), 3.25 – 3.21 (m, 1H), 3.18 – 3.14 (m, 1H), 2.97 – 2.92 (m, 2H), 2.86 – 2.84 (m, 1H), 2.82 (s, 3H), 2.76 (s, 3H), 2.73 – 2.60 (m, 2H), 2.50 – 2.46 (m, 4H), 2.02 – 1.94 (m, 4H), 1.88 – 1.76 (m, 4H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.7, 144.4, 142.3, 142.2, 136.1, 135.9, 133.9, 133.9, 129.0, 128.9, 128.53(2C), 128.50, 128.47, 127.8(2C), 126.8, 126.7, 126.0, 125.9, 118.78, 118.75, 118.3, 118.2, 113.7, 113.6, 111.6, 111.5, 55.6, 55.5, 49.0, 48.1, 43.2, 42.1, 41.9, 41.7, 39.3, 39.3, 39.1, 38.9, 33.8, 33.6.**HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{25}H_{28}N_2H^+$ 356.2252; Found 356.2250.

b) Synthesis of compound **7**



3x **7**, 95% (1:1 dr)

A 16×100 mm oven-dried reaction tube equipped with a magnetic stir was charged with compound **3x** (0.1 mmol, 1.0 equiv), and $LiAlH_4$ (0.25 mmol, 2.5 equiv) under a nitrogen atmosphere. The reaction tube was capped with a septum, and dry THF (1.0 mL) was added via a syringe. After that, the reaction mixture was allowed to stir at room temperature under N_2 atmosphere for 4 h. After completion of the reaction (TLC monitored), the reaction mixture was neutralized with a saturated solution of sodium bicarbonate and then extracted with ethyl acetate. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel to get compound **7**.

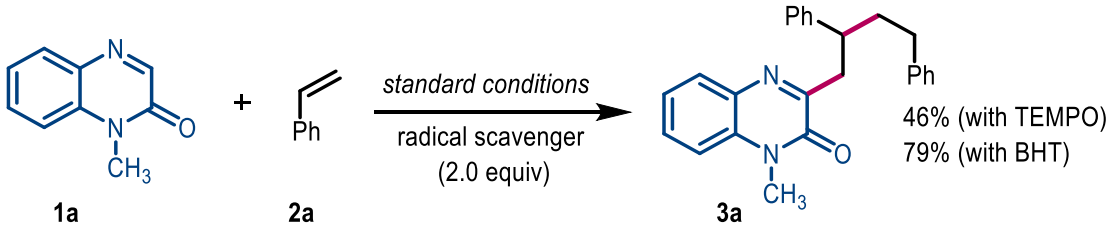


7, (1:1 dr)

Compound, **7**: Yellow liquid; eluent (10% ethyl acetate in hexane). **Yield:** 95% (33 mg); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.28 – 7.24 (m, 4H), 7.20 – 7.17 (m, 8H), 7.15 – 7.11 (m, 6H), 7.10 – 7.07 (m, 2H), 7.03 – 7.00 (m, 4H), 6.51 – 6.46 (m, 2H), 6.45 – 6.42 (m, 2H), 6.403 – 6.398 (m, 1H), 6.39 – 6.37 (m, 1H), 6.36 – 6.34 (m, 1H), 6.10 – 6.09 (m, 1H), 3.25 – 3.22 (m, 1H), 3.14 – 3.09 (m, 1H), 3.05 – 3.01 (m, 2H), 2.98 – 2.95 (m, 1H), 2.89 – 2.86 (m, 1H), 2.70 – 2.64 (m, 1H), 2.62 – 2.56 (m, 1H), 2.41 – 2.38 (m, 4H), 1.94 – 1.87 (m, 4H), 1.81 – 1.75 (m, 2H), 1.73 – 1.67 (m, 2H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.6, 144.4, 142.3, 142.2, 133.4, 133.3, 133.3, 133.2, 128.94, 128.88, 128.5(2C), 128.48, 128.45, 127.8, 127.8, 126.8, 126.7, 125.93, 125.89, 118.9, 118.73(2C), 118.70, 114.8, 114.7, 114.6, 114.4, 48.9, 48.1, 47.0, 46.7, 43.1, 42.1, 41.6, 41.3, 39.3, 39.0, 33.8, 33.6.**HRMS** (ESI/TOF-Q) m/z: $[M+H]^+$ Calculated for $C_{24}H_{26}N_2H^+$ 342.2096; Found 342.2098.

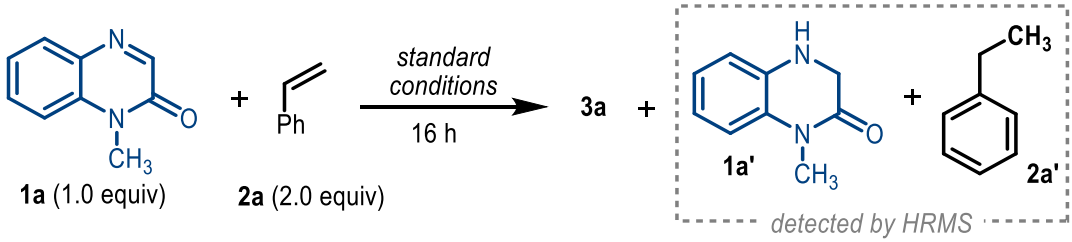
Mechanistic studies

a) Radical quenching experiments

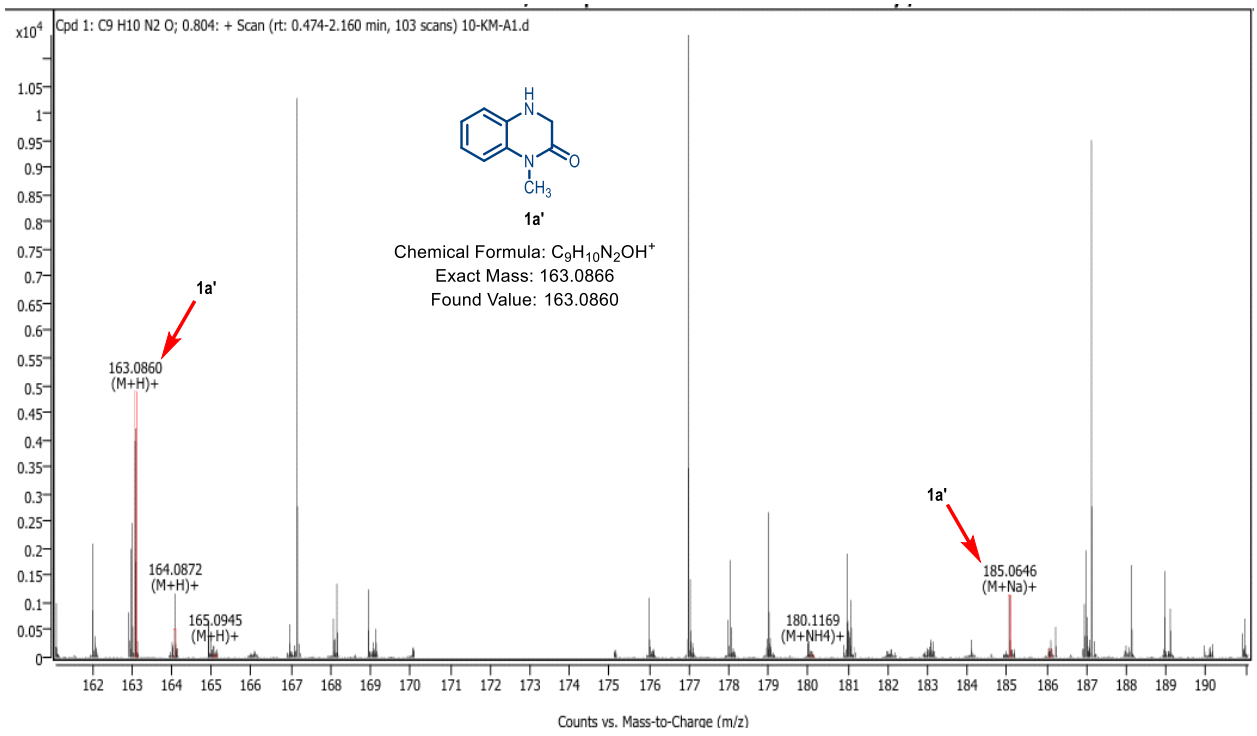


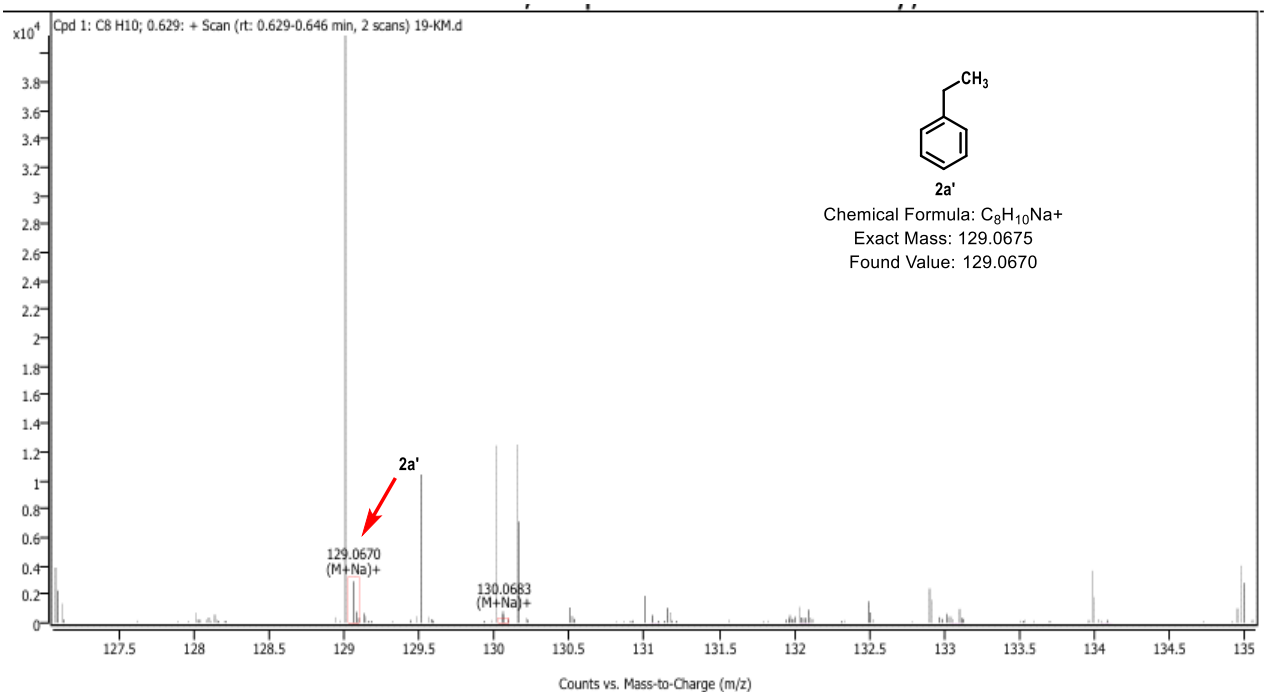
A 16×100 mm oven-dried reaction tube equipped with a magnetic stir was charged with $CoBr_2$ (10 mol %), DPPP (0.1 equiv), 4CzIPN (2.0 mol %), Hantzsch ester (HE) (1.5 equiv), quinoxalinone **1a** (0.2 mmol, 1.0 equiv), alkene **2a** (0.6 mmol, 3.0 equiv), and TEMPO or BHT (2.0 equiv, as a radical scavenger) under a nitrogen atmosphere. The reaction tube was capped with a septum, and DIPEA (0.12 equiv) and dry DMSO (1.5 mL) were added via a syringe. After that, the reaction mixture was allowed to stir with irradiation of 440 nm Kessil LED light at room temperature for 24 h. After the reaction, product **3a** was isolated following the steps described in the general procedure. For TEMPO as a radical scavenger, **3a** was obtained in 46% yield and with BHT as a radical scavenger, **3a** was obtained in 79% yield.

b) Detection of reductive products



A 16×100 mm oven-dried reaction tube equipped with a magnetic stir was charged with $CoBr_2$ (10 mol %), DPPP (0.1 equiv), 4CzIPN (2.0 mol %), Hantzsch ester (HE) (1.5 equiv), quinoxalinone **1a** (0.2 mmol, 1.0 equiv), and styrene **2a** (0.6 mmol, 3.0 equiv) under nitrogen atmosphere. The reaction tube was capped with a septum, and DIPEA (0.12 equiv) and dry DMSO (1.5 mL) were added via a syringe. After that, the reaction mixture was allowed to stir with irradiation of 440 nm Kessil LED light at room temperature for 16 h. The imine and styrene reduced products **1a'** and **2a'** respectively were detected by HRMS.


Cpd 1: C9 H10 N2 O; 0.804: + Scan (rt: 0.474-2.160 min, 103 scans) 10-KM-A1.d
x10^4
1a'
Chemical Formula: C9H10N2OH+
Exact Mass: 163.0866
Found Value: 163.0860
1a'
163.0860
(M+H)+
164.0872
(M+H)+
165.0945
(M+H)+
180.1169
(M+NH4)+
1a'
185.0646
(M+Na)+
Counts vs. Mass-to-Charge (m/z)

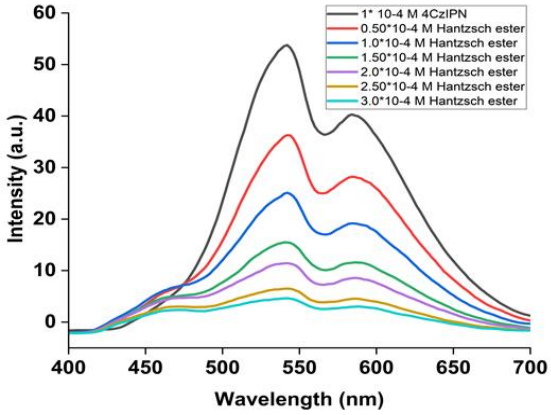

Cpd 1: C8 H10; 0.629: + Scan (rt: 0.629-0.646 min, 2 scans) 19-KM.d
x10^4
2a'
Chemical Formula: C8H10Na+
Exact Mass: 129.0675
Found Value: 129.0670
2a'
129.0670
(M+Na)+
130.0683
(M+Na)+
Counts vs. Mass-to-Charge (m/z)

c) Stern-Volmer fluorescence quenching experiments

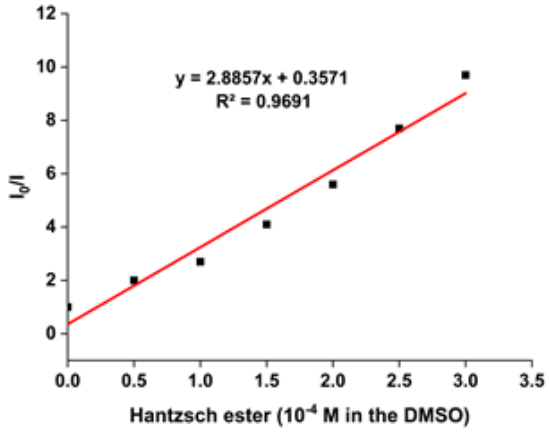
Stern-Vollmer fluorescence quenching studies were carried out using a $1*10^{-4}$ M solution of 4CzIPN in DMSO and variable concentrations of **1a** (0.01M), **2a** (0.01M), $CoBr_2$ (0.005 M), DPPP (0.005 M), HE (0.01M) and DIPEA (0.01M). **(1)** To a quartz cuvette containing 4CzIPN ($1*10^{-4}$ M) in DMSO and variable concentration of HE was added as a quencher and the emission spectra were recorded. **(2)** To a quartz cuvette containing 4CzIPN ($1*10^{-4}$ M) in DMSO and variable concentration of DIPEA was added as a quencher and the emission spectra were recorded. **(3)** To a quartz cuvette containing 4CzIPN ($1*10^{-4}$ M) in DMSO and variable concentration of Sub **1a** was added as a quencher and the emission spectra were recorded. **(4)** To a quartz cuvette containing 4CzIPN ($1*10^{-4}$ M) in DMSO and variable concentration of Sub **2a** was added as a quencher and the emission spectra were recorded. **(5)** To a quartz cuvette containing 4CzIPN ($1*10^{-4}$ M) in DMSO and variable concentration of ($CoBr_2$ + DPPP) was added as a quencher and the emission spectra were recorded. **(6)** To a quartz cuvette containing 4CzIPN ($1*10^{-4}$ M) in DMSO and variable concentration of (HE + DIPEA) was added as a quencher and the emission spectra were recorded. **(7)** To a quartz cuvette containing HE (0.01 M) in DMSO and variable concentration of DIPEA was added as a quencher and the emission spectra were recorded. Conclusion: HE quenches 4CzIPN more than the other three cases, while other components such as quinoxalinone **1a** and alkene **2a** may not react with 4CzIPN.

1) Stern-Volmer quenching experiment with 4CzIPN and HE as quencher

i) Luminescence spectra of 4CzIPN with HE

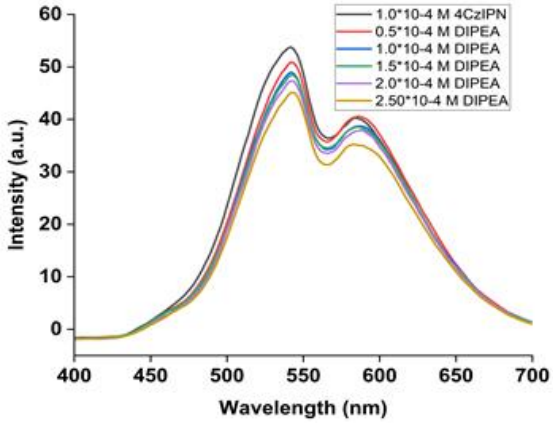


ii)Stern-Volmer Plot for 4CzIPN with HE

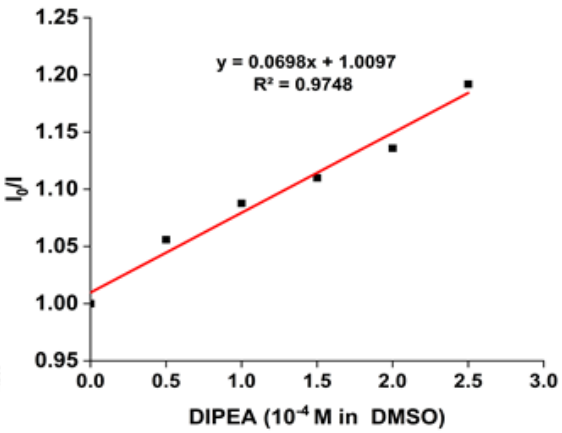


2) Stern-Volmer quenching experiment with 4CzIPN and DIPEA as quencher

i) Luminescence spectra of 4CzIPN with DIPEA

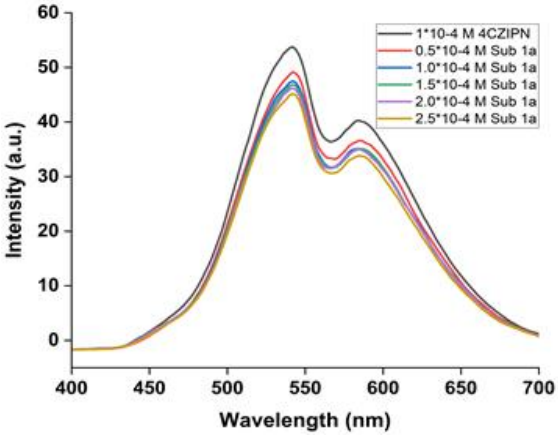


ii)Stern-Volmer Plot for 4CzIPN with DIPEA

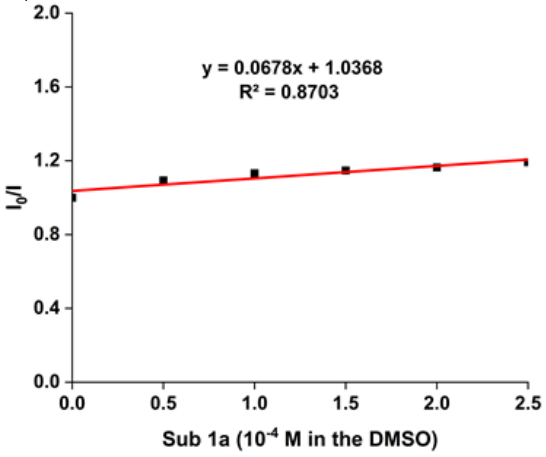


3) Stern-Volmer quenching experiment with 4CzIPN and Sub 1a as quencher

i) Luminescence spectra of 4CzIPN with **1a**

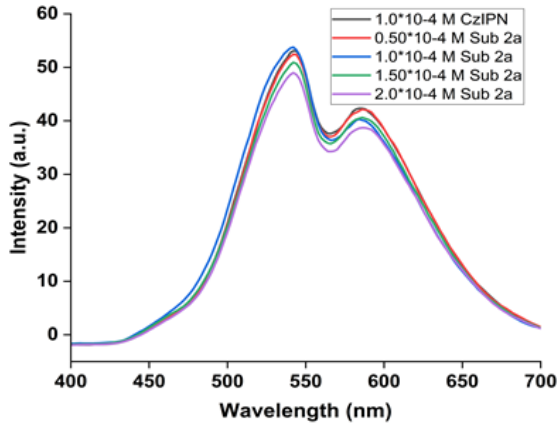


ii)Stern-Volmer Plot for 4CzIPN with **1a**

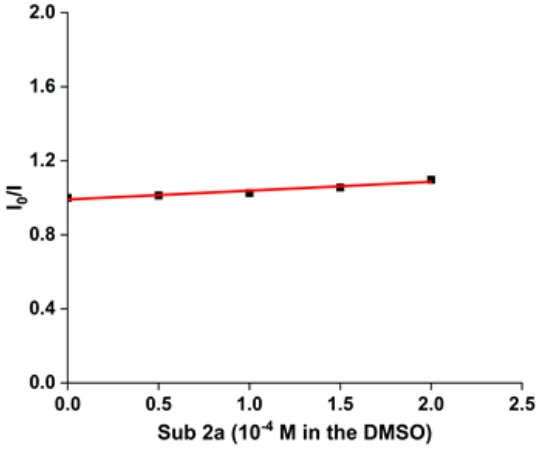


4) Stern-Volmer quenching experiment with 4CzIPN and Sub 2a as quencher

i) Luminescence spectra of 4CzIPN with **2a**

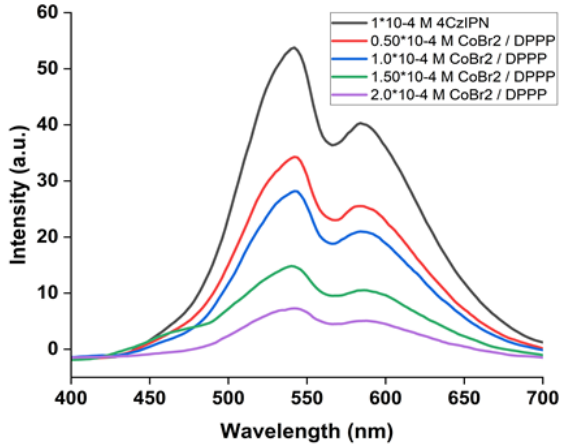


ii)Stern-Volmer Plot for 4CzIPN with **2a**

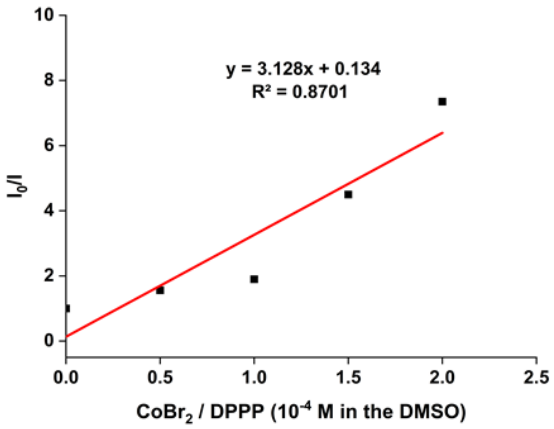


5) Stern-Volmer quenching experiment with 4CzIPN and $CoBr_2$+DPPP as quencher

i) Luminescence spectra of 4CzIPN with ($CoBr_2$+DPPP)

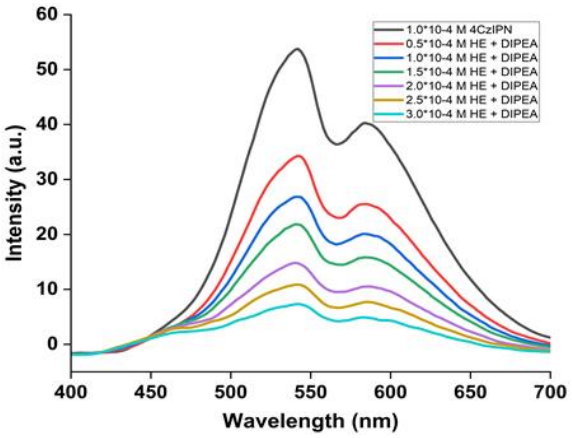


ii)Stern-Volmer Plot for 4CzIPN with ($CoBr_2$+DPPP)

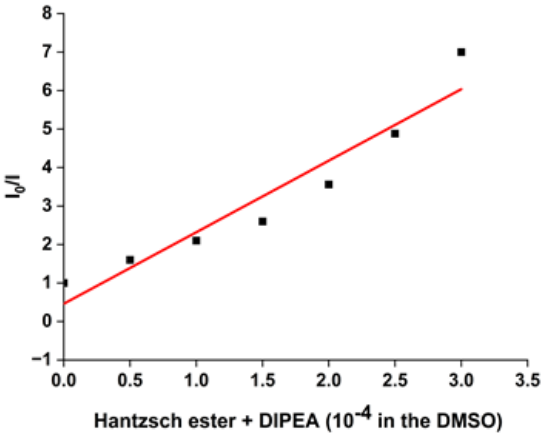


6) Stern-Volmer quenching experiment with 4CzIPN and (HE+DIPEA) as quencher

i) Luminescence spectra of 4CzIPN with (HE+DIPEA)

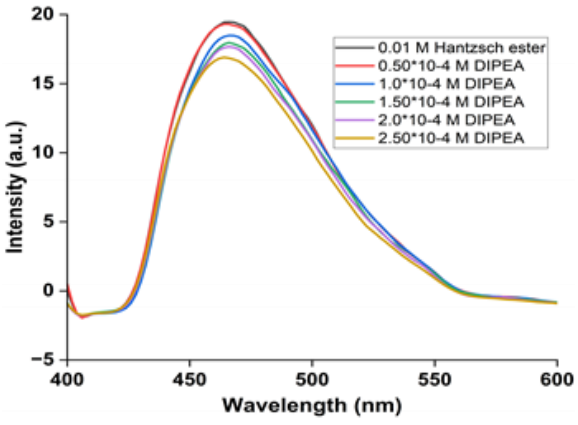


ii)Stern-Volmer Plot for 4CzIPN with (HE+DIPEA)

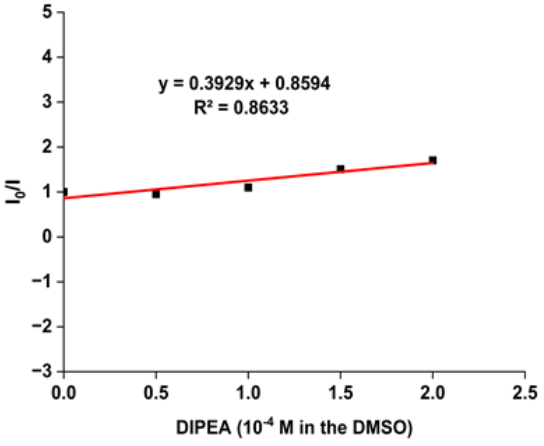


7) Stern-Volmer quenching experiment with HE and DIPEA as quencher

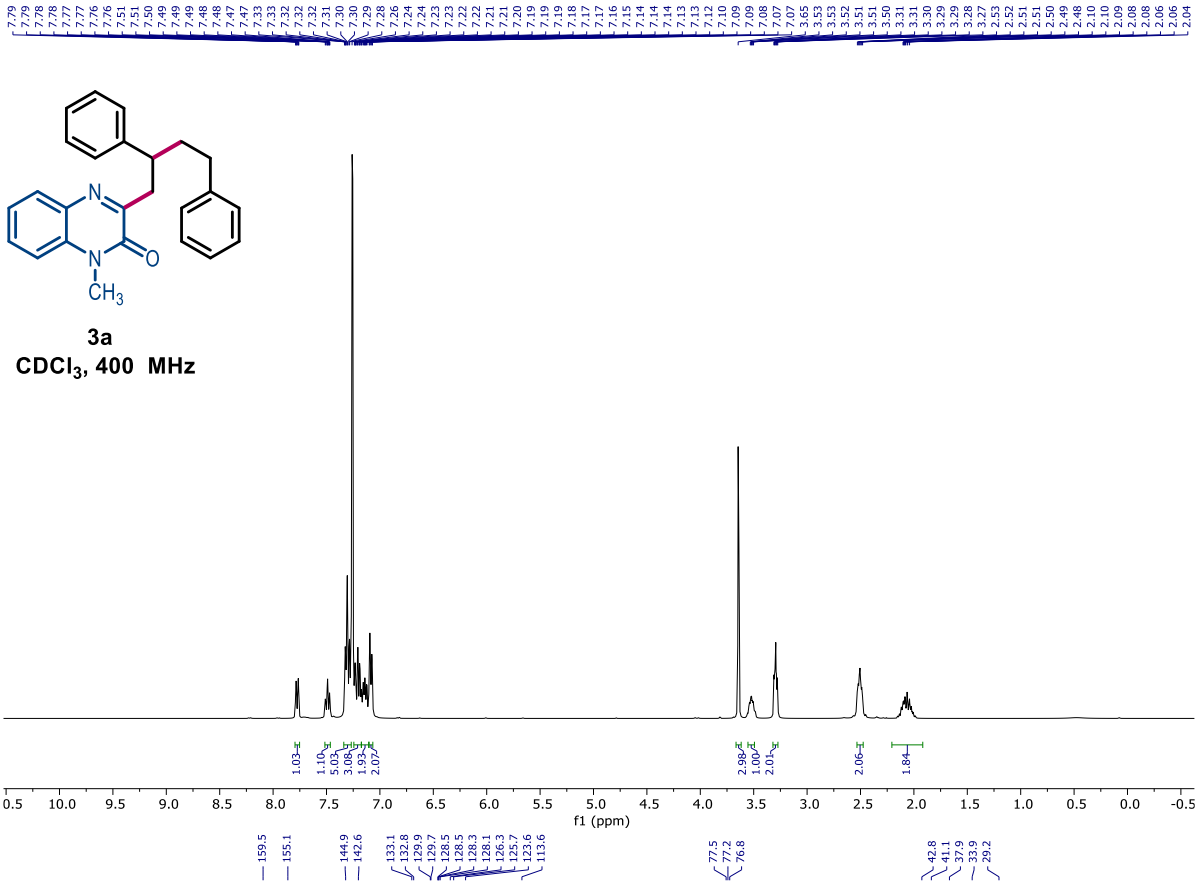
i) Luminescence spectra of HE with DIPEA

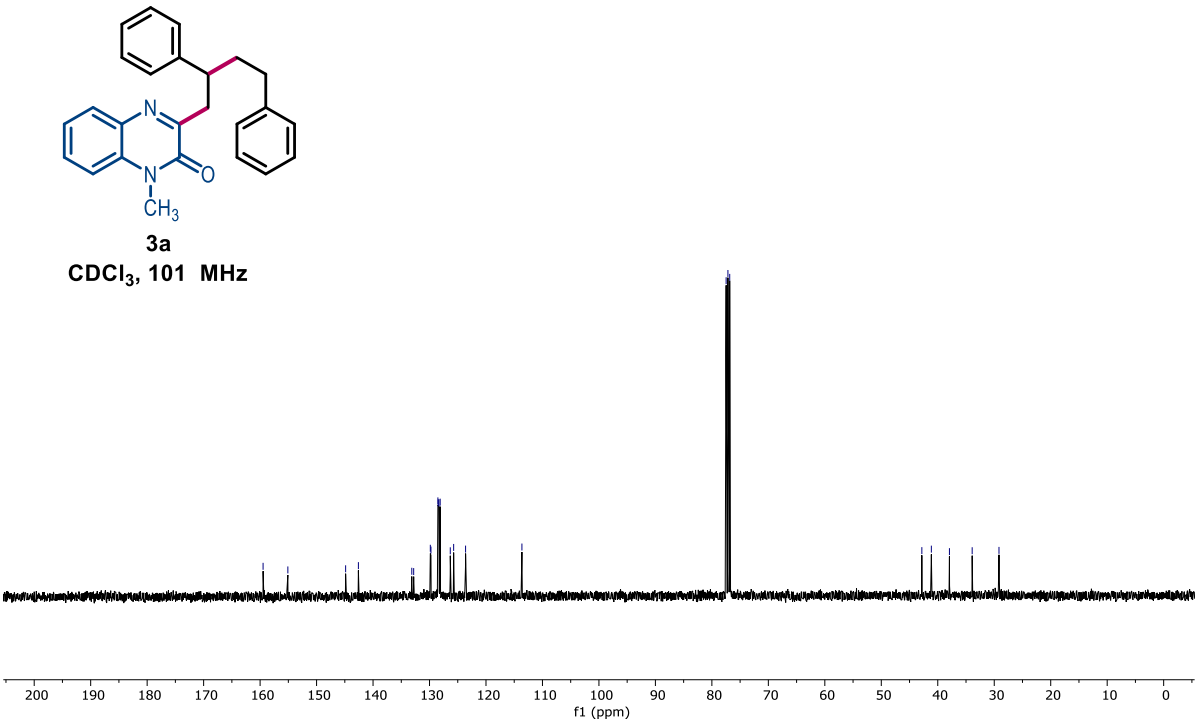


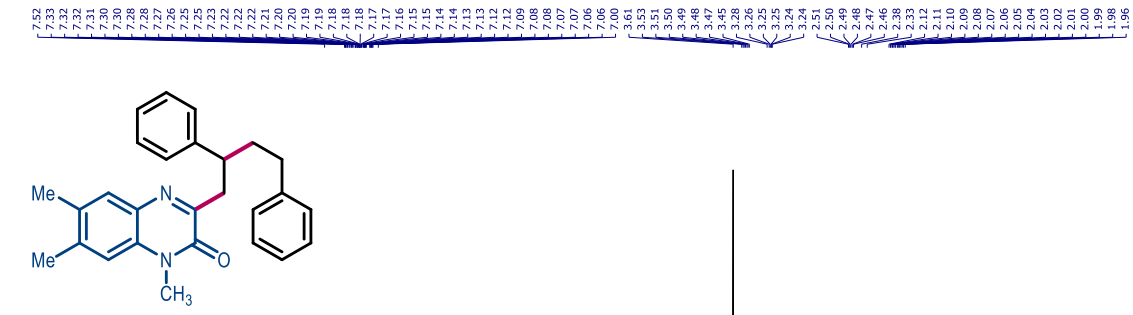
ii)Stern-Volmer Plot for HE with DIPEA



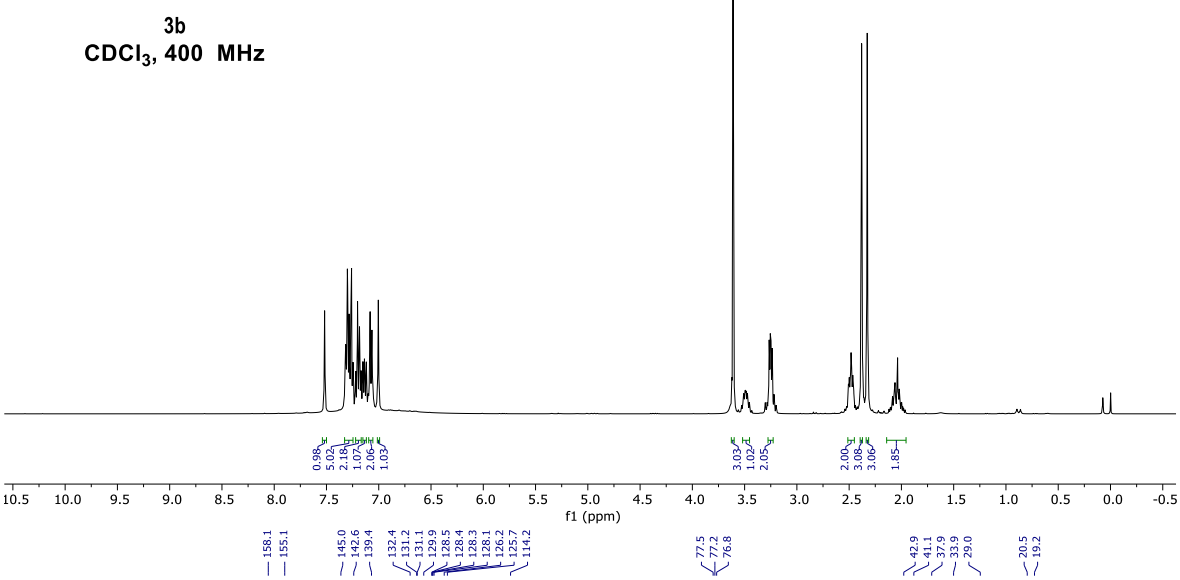
^{1}H, ^{13}C and ^{19}F NMR spectra of synthesized compounds

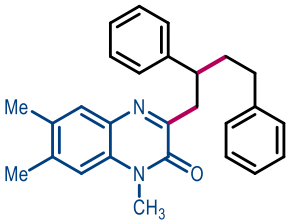




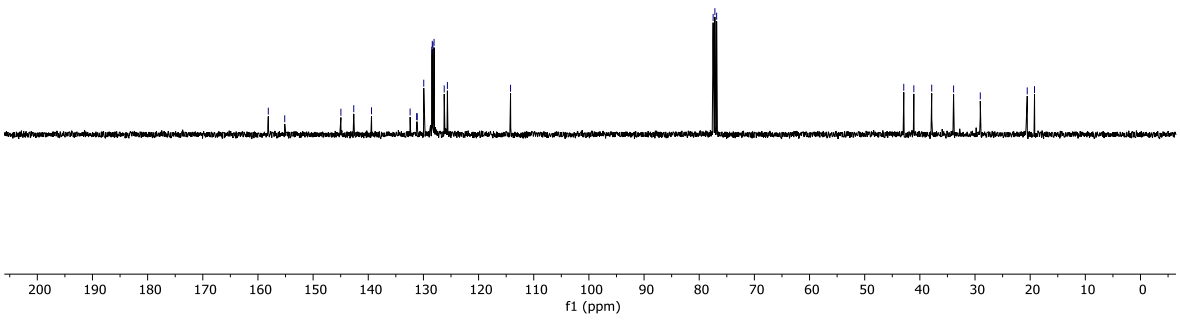


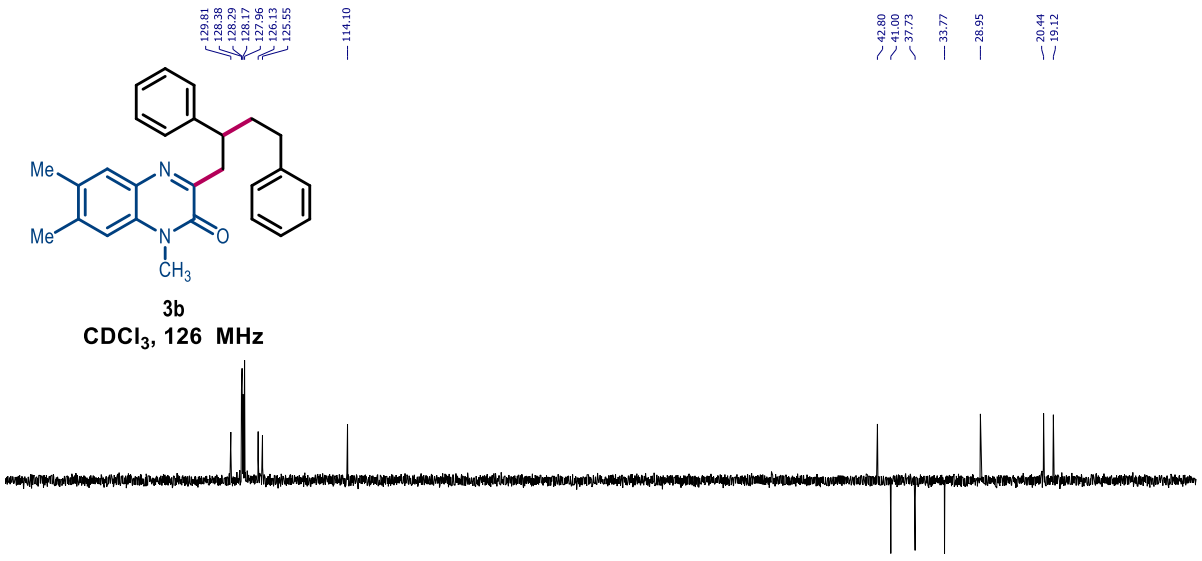
3b
$CDCl_3$, 400 MHz





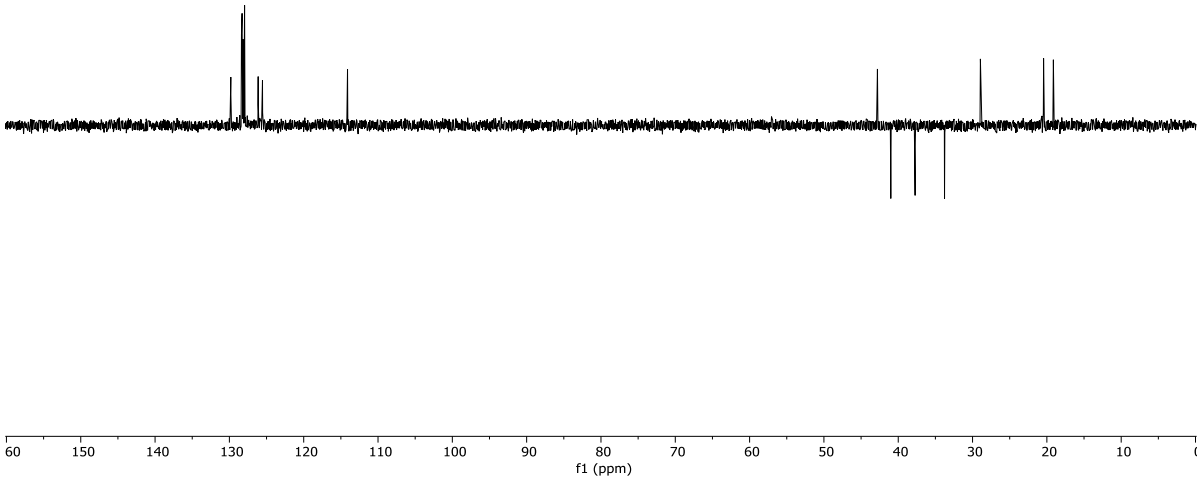
3b
$CDCl_3$, 126 MHz

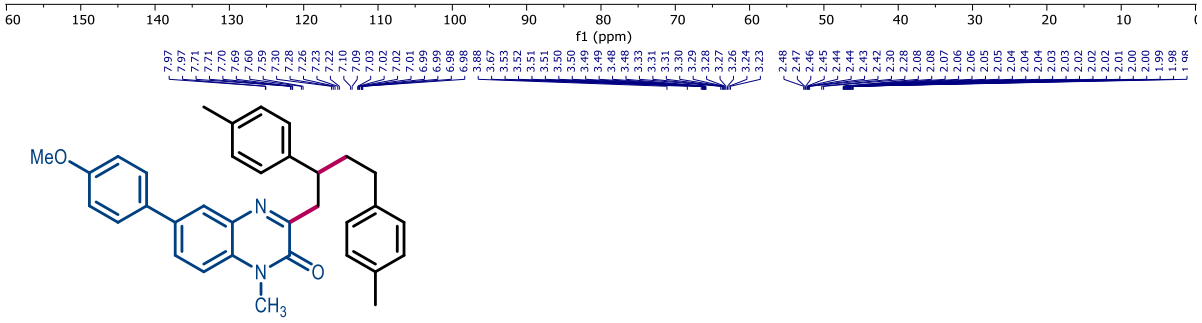




3b

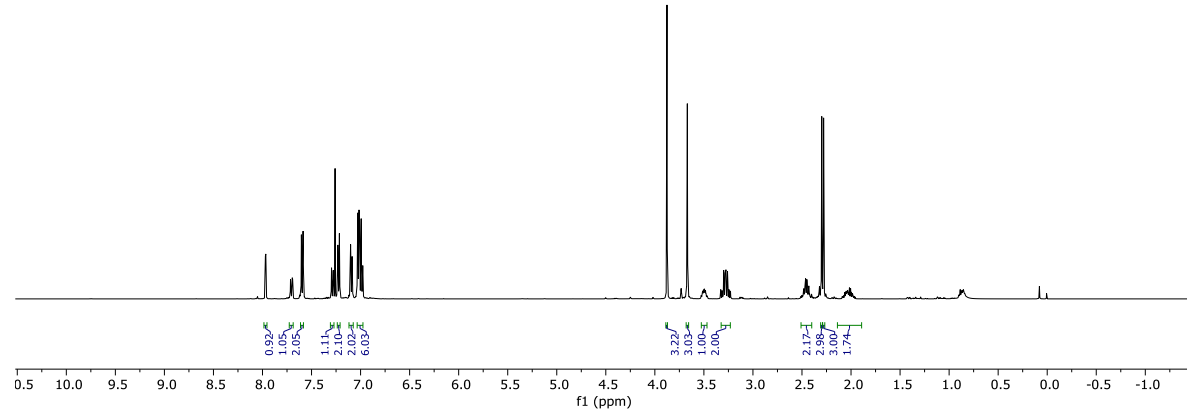
$CDCl_3$, 126 MHz

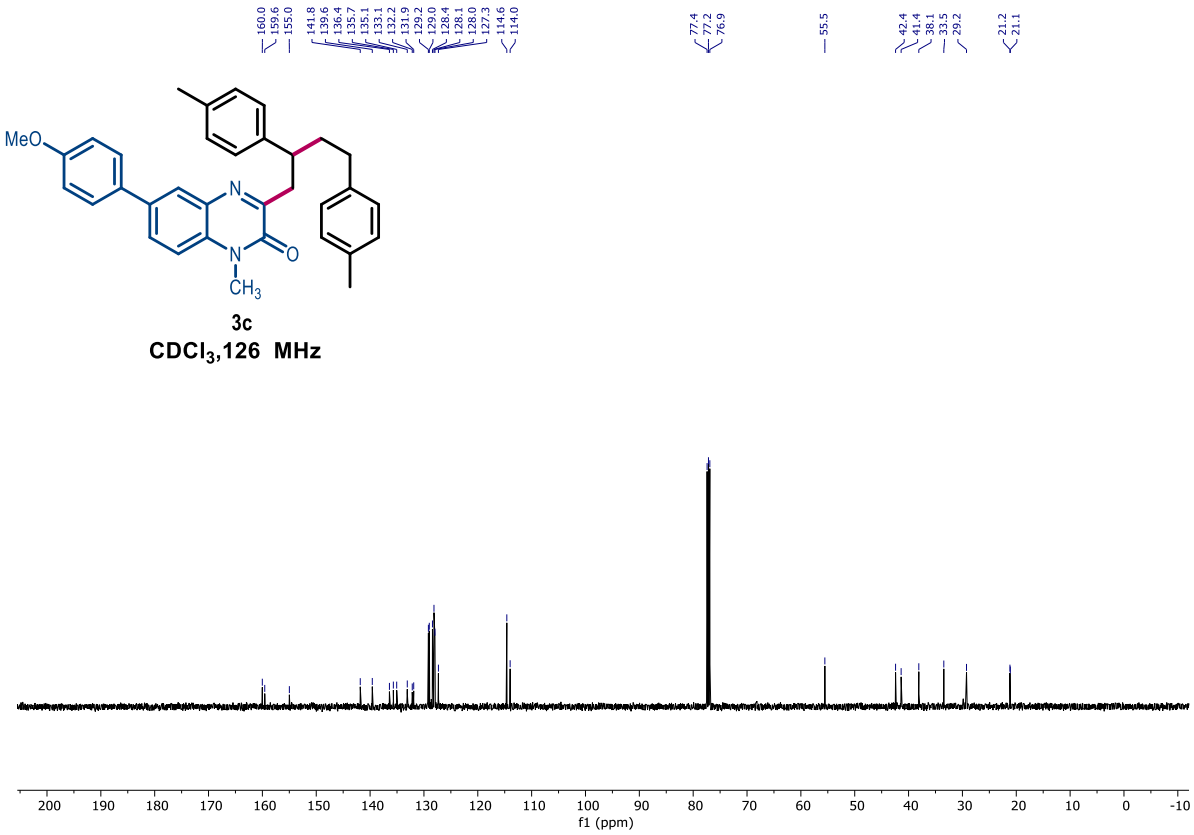




3c

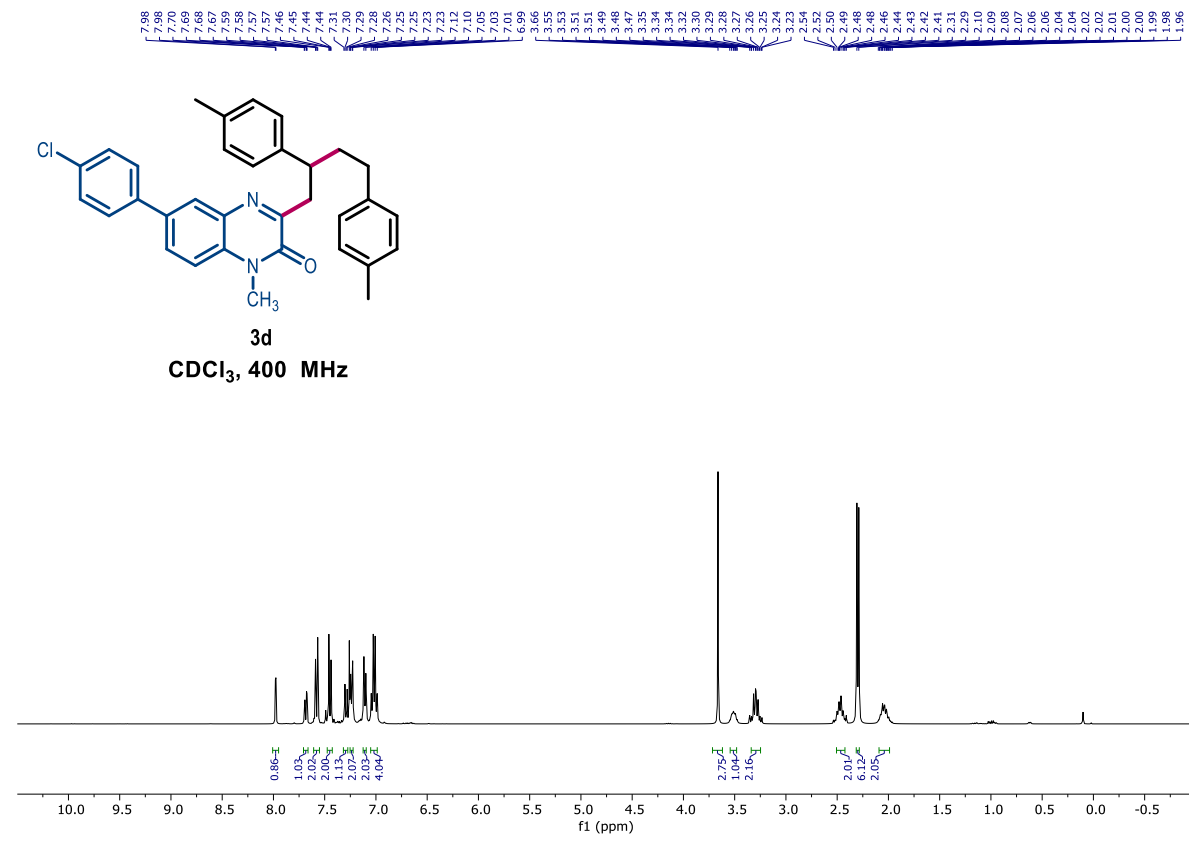
$CDCl_3$, 500 MHz





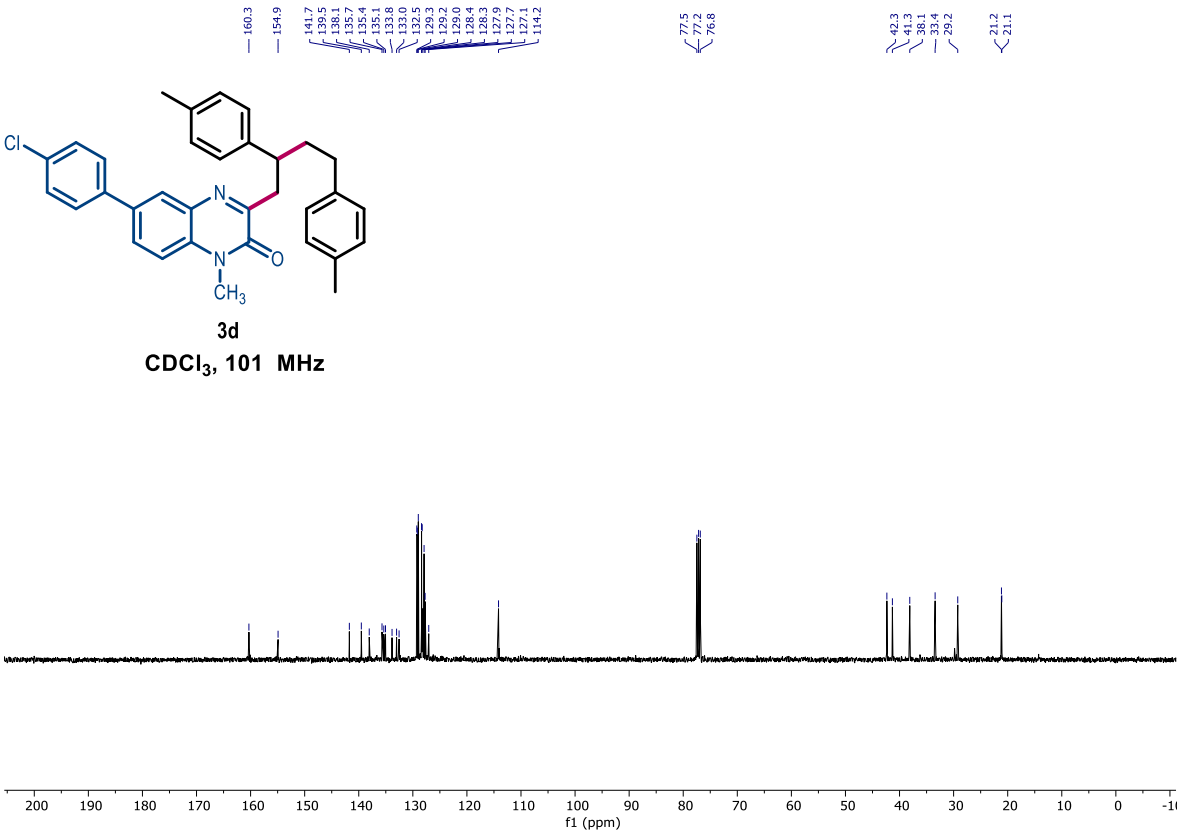
3c

$CDCl_3$,126 MHz



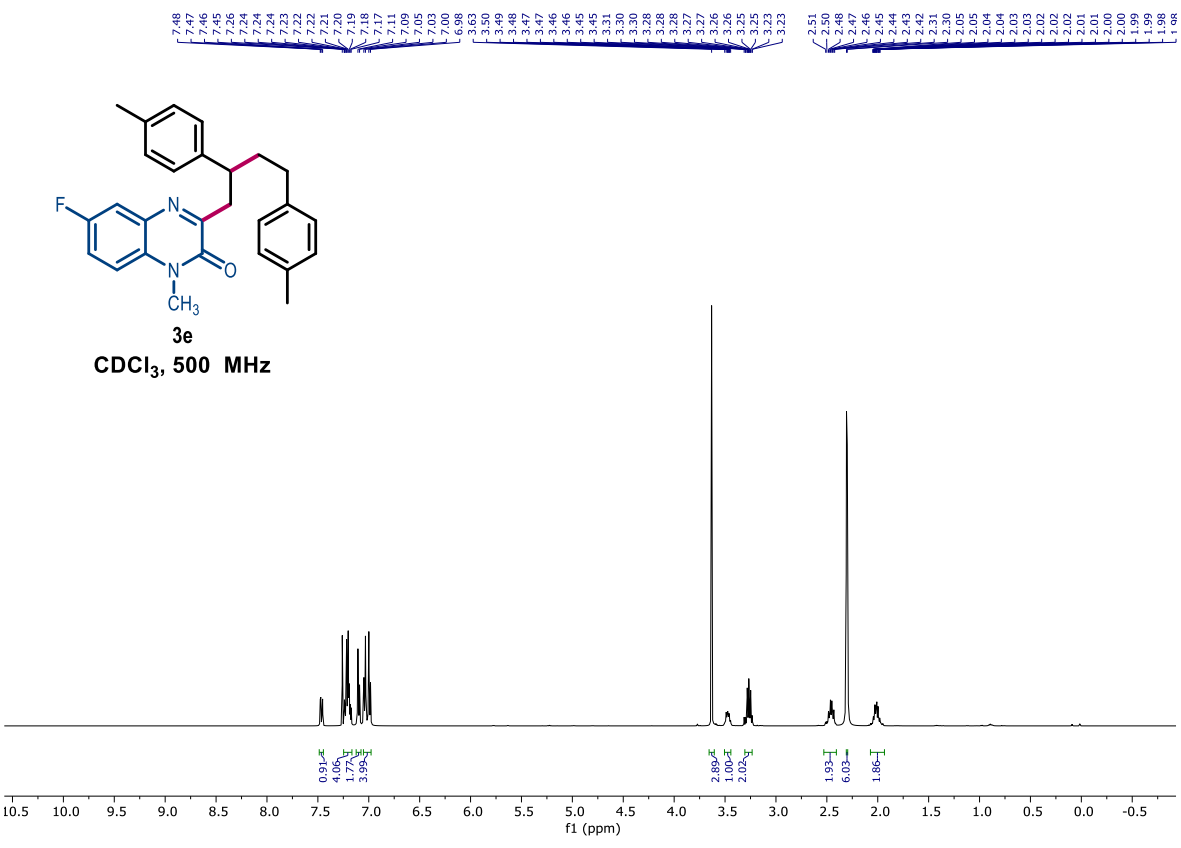
3d

$CDCl_3$, 400 MHz



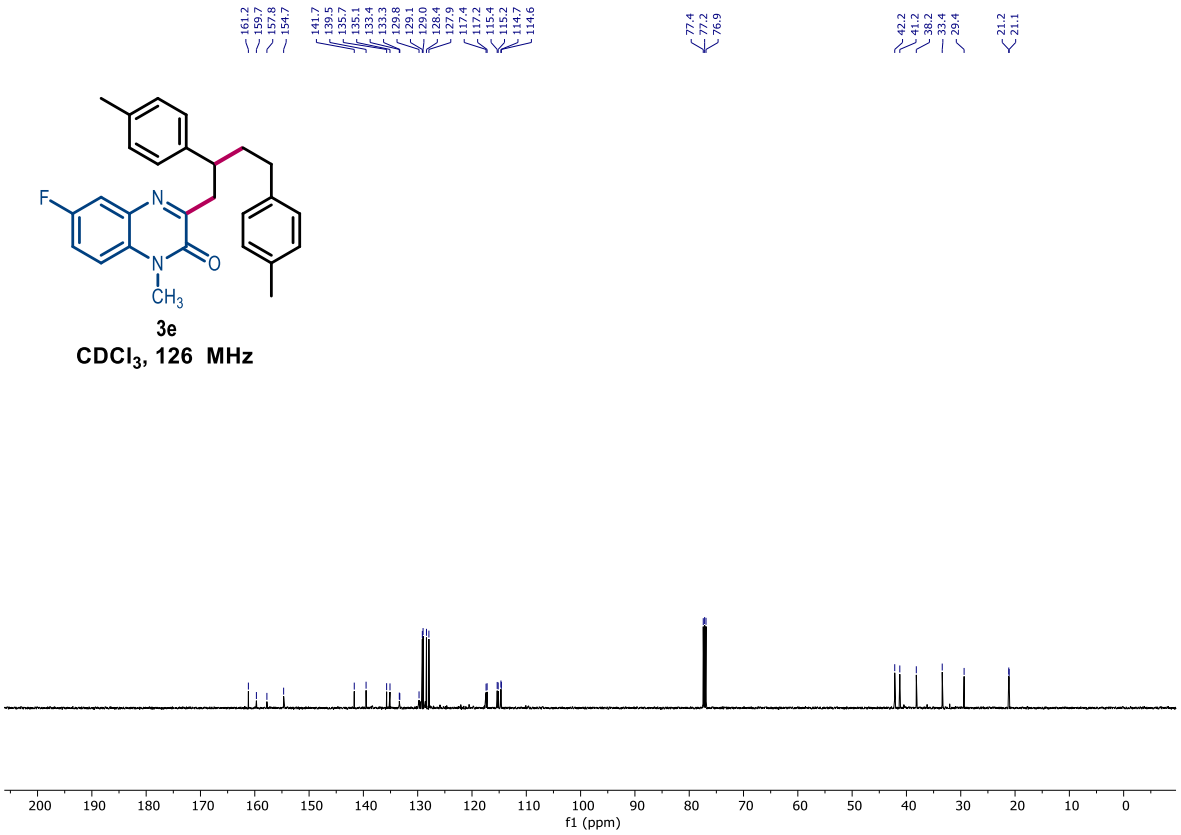
3d

$CDCl_3$, 101 MHz



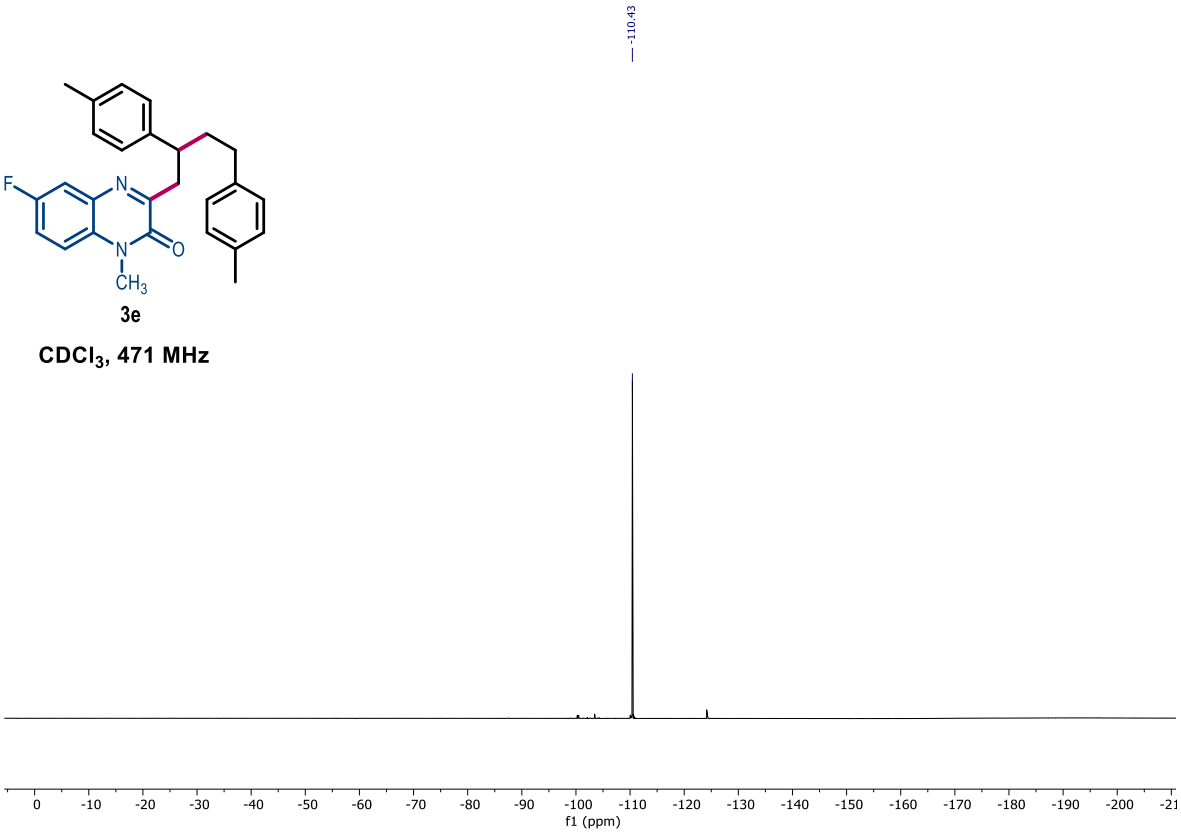
3e

$CDCl_3$, 500 MHz



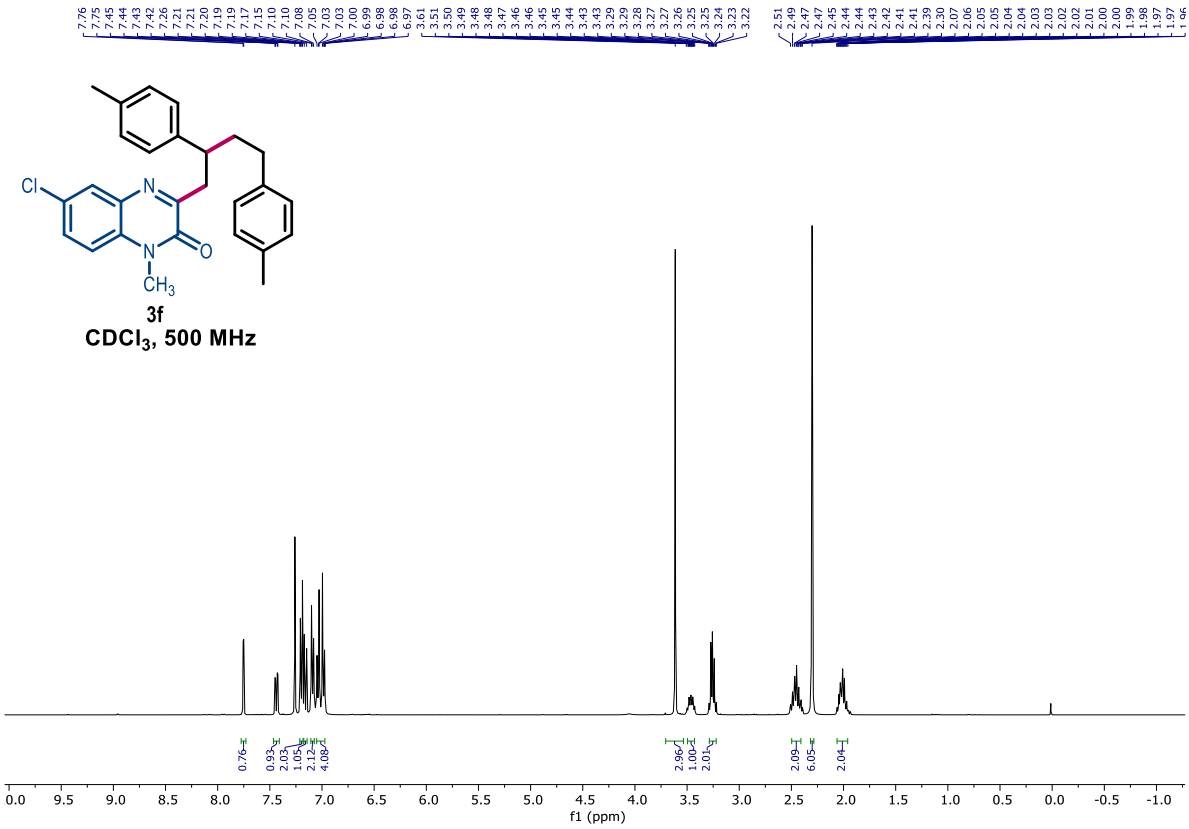
3e

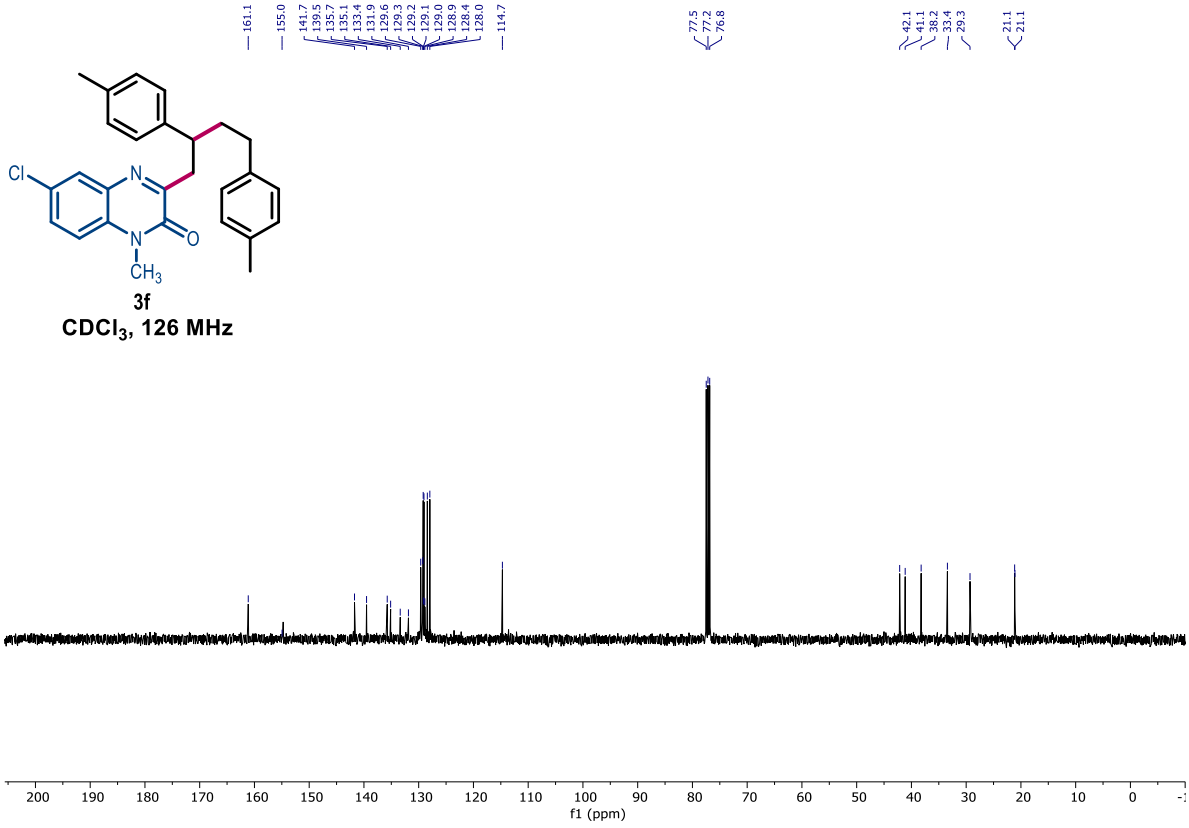
$CDCl_3$, 126 MHz

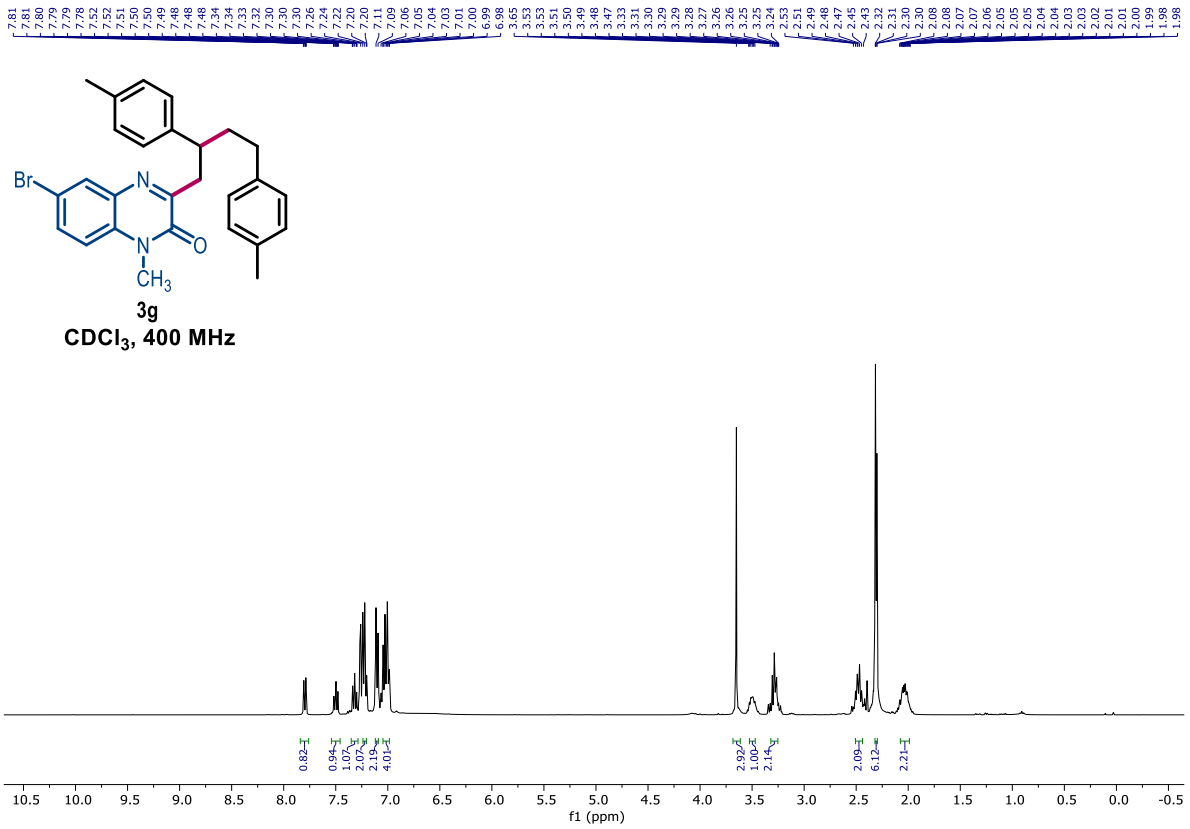


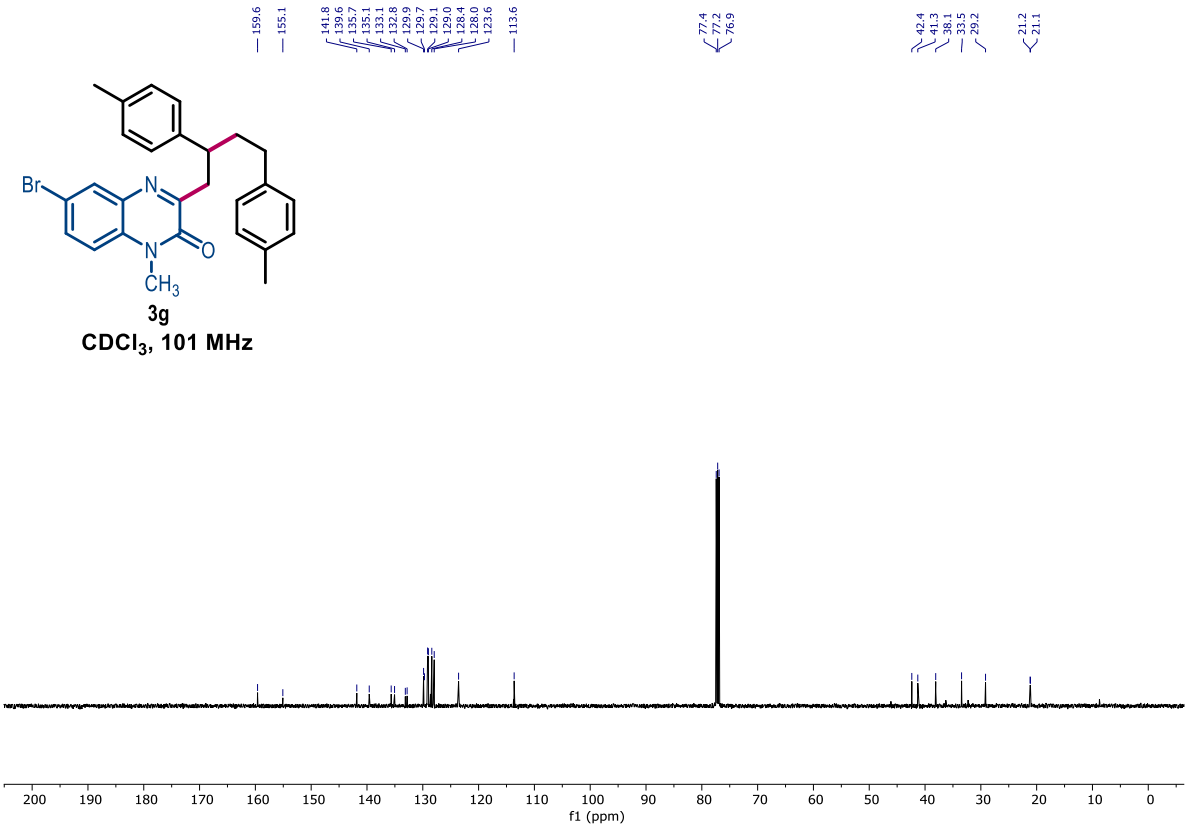
3e

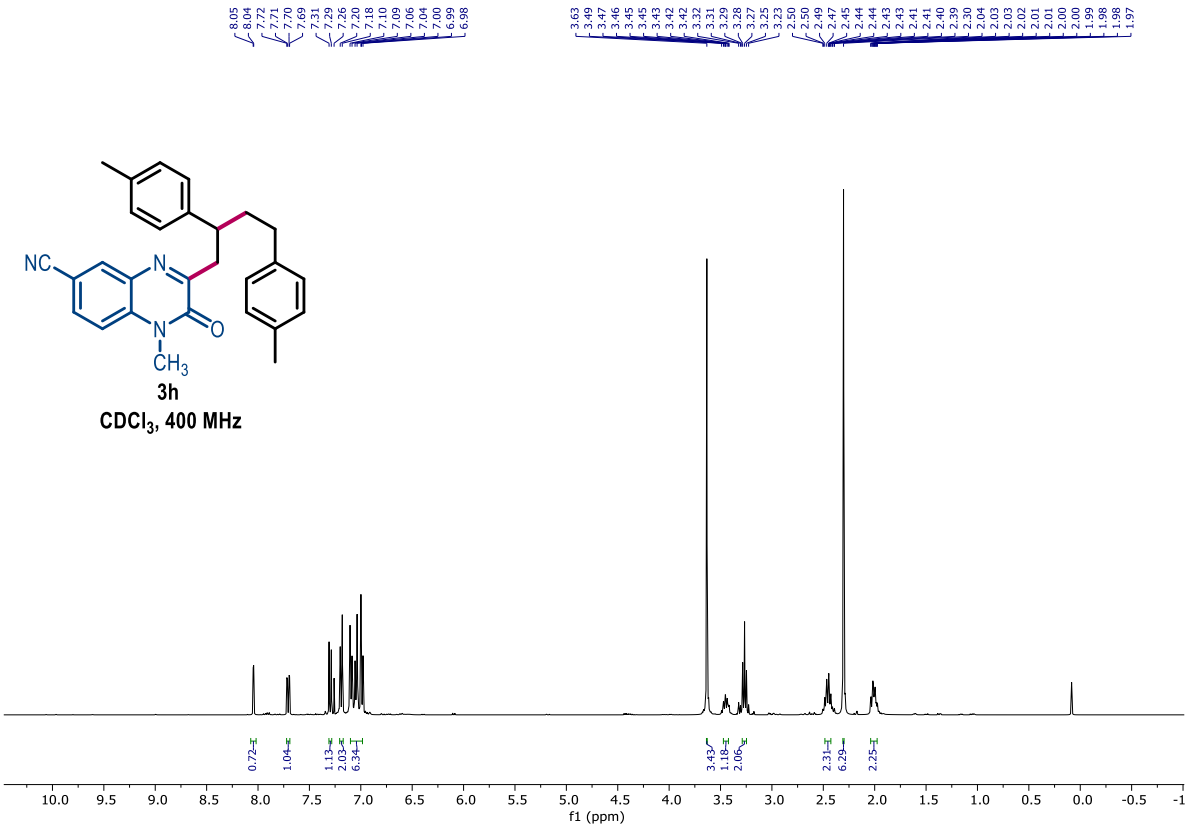
$CDCl_3$, 471 MHz


Cl
N
O
N
CH3
3f
CDCl3, 500 MHz
f1 (ppm)


Cl
N
O
N
CH3
3f
CDCl3, 126 MHz
f1 (ppm)


Br
N
O
N
CH3
3g
CDCl3, 400 MHz
f1 (ppm)


Br
N
O
N
CH3
3g
CDCl3, 101 MHz
f1 (ppm)


8.05
8.04
7.72
7.71
7.70
7.69
7.31
7.29
7.26
7.20
7.18
7.10
7.09
7.06
7.04
7.00
6.99
6.98
3.63
3.49
3.47
3.46
3.45
3.45
3.43
3.42
3.42
3.32
3.31
3.29
3.28
3.27
3.25
3.23
2.50
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2.47
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2.43
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2.40
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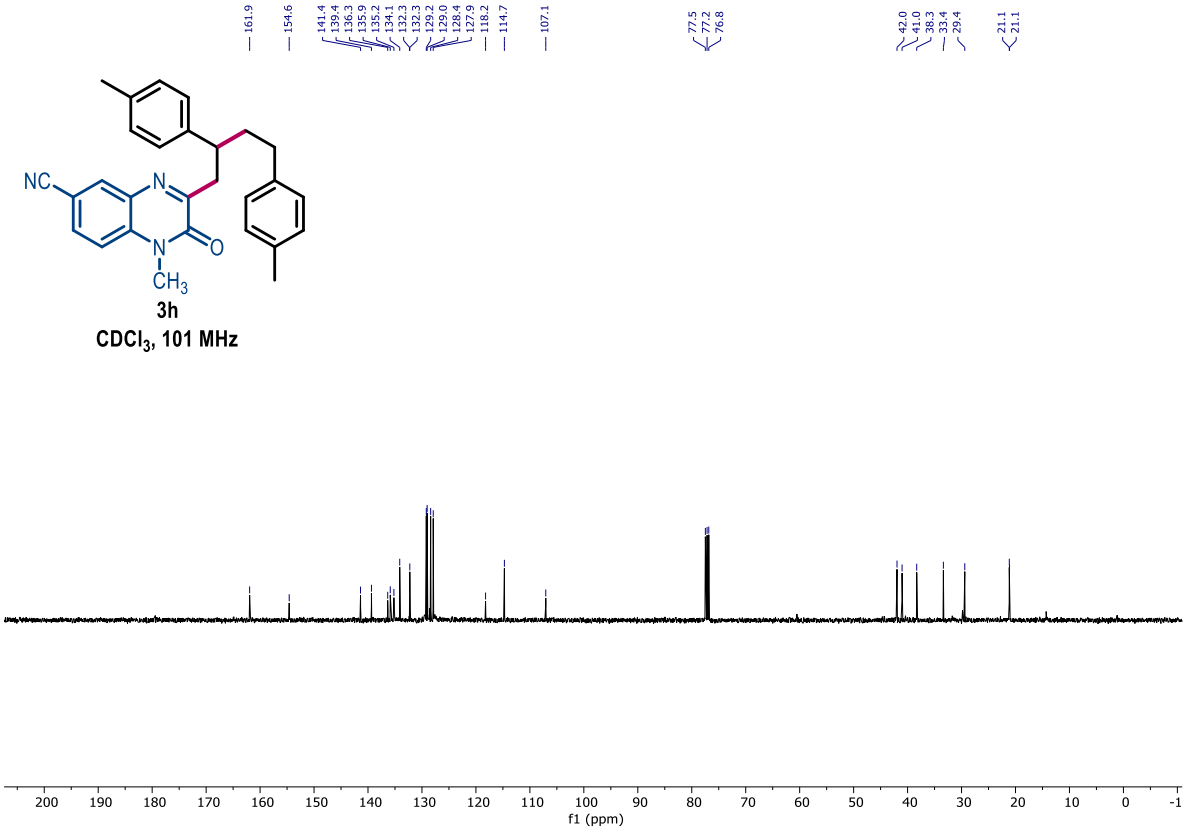
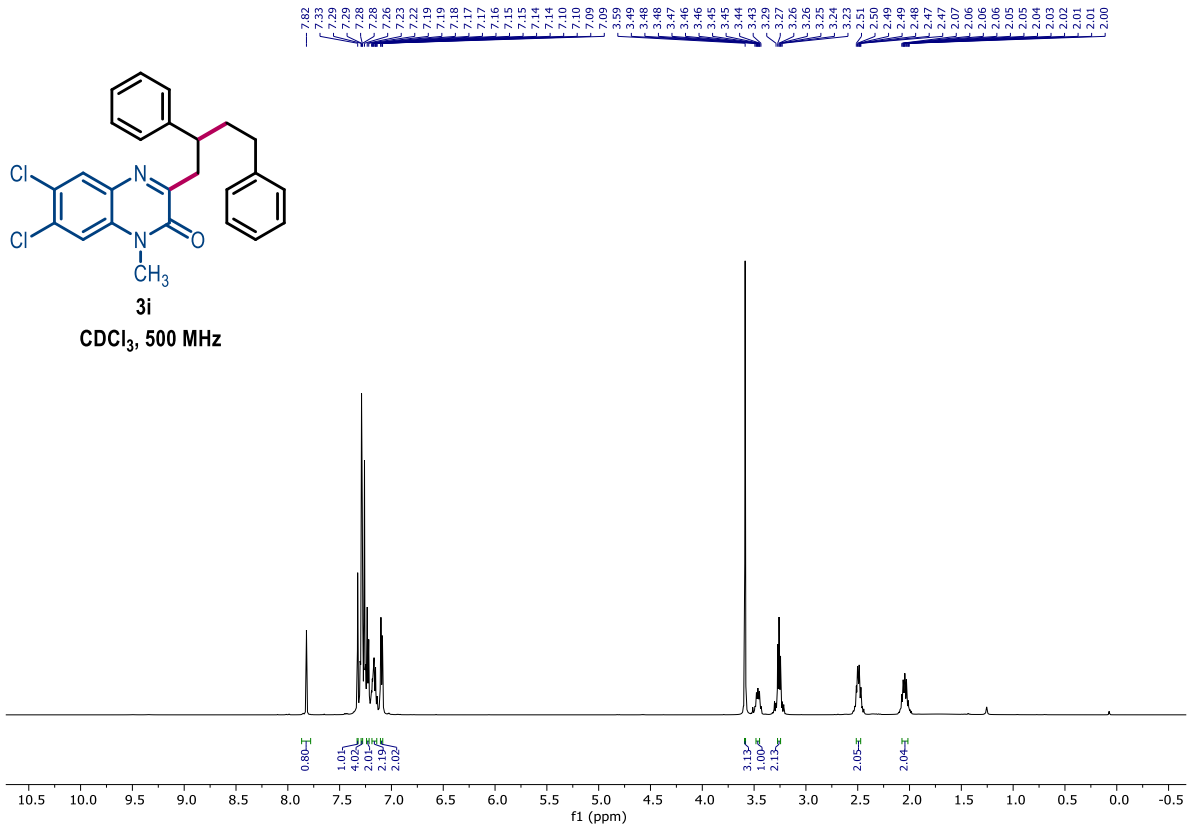
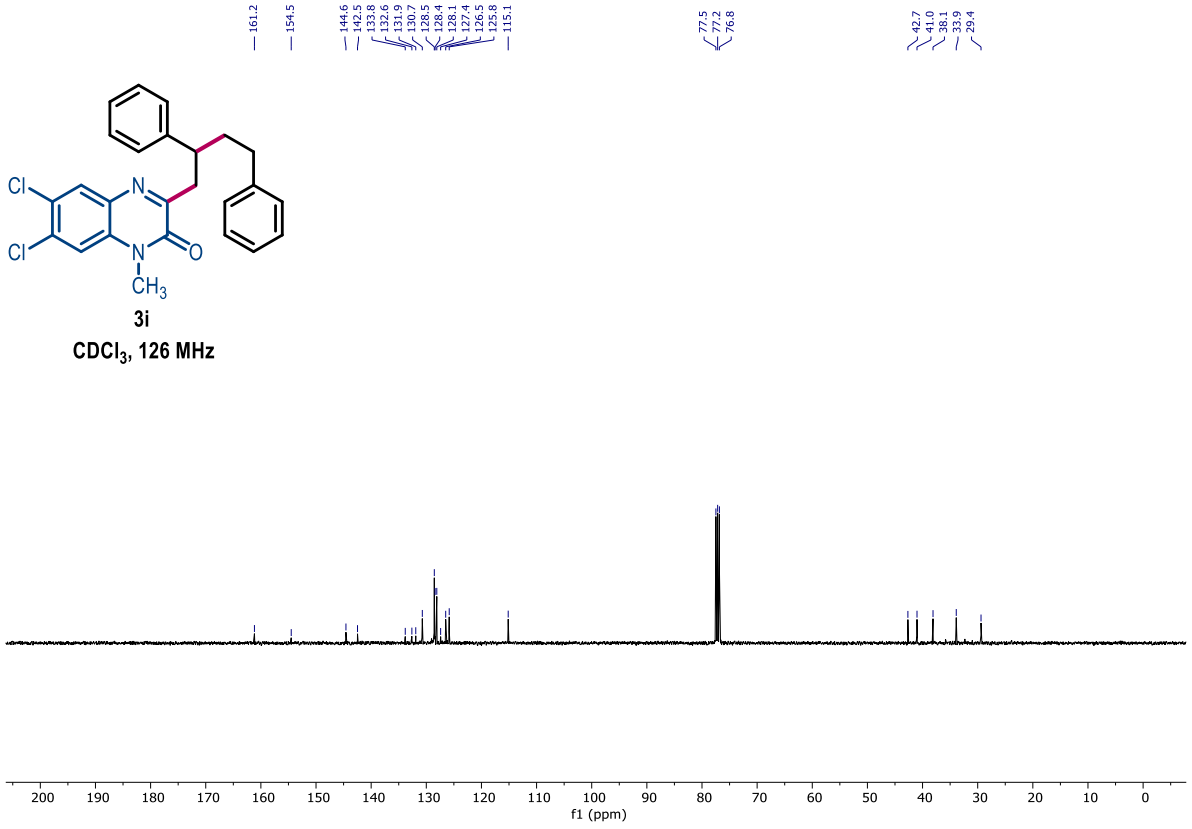
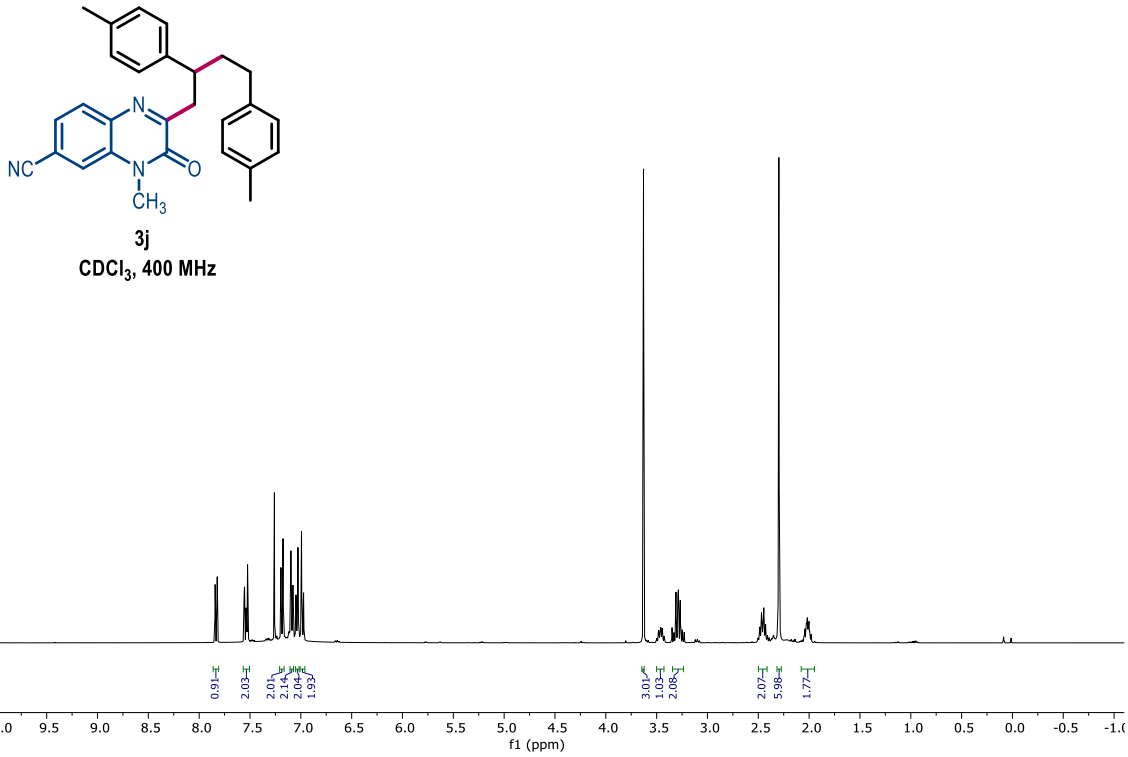
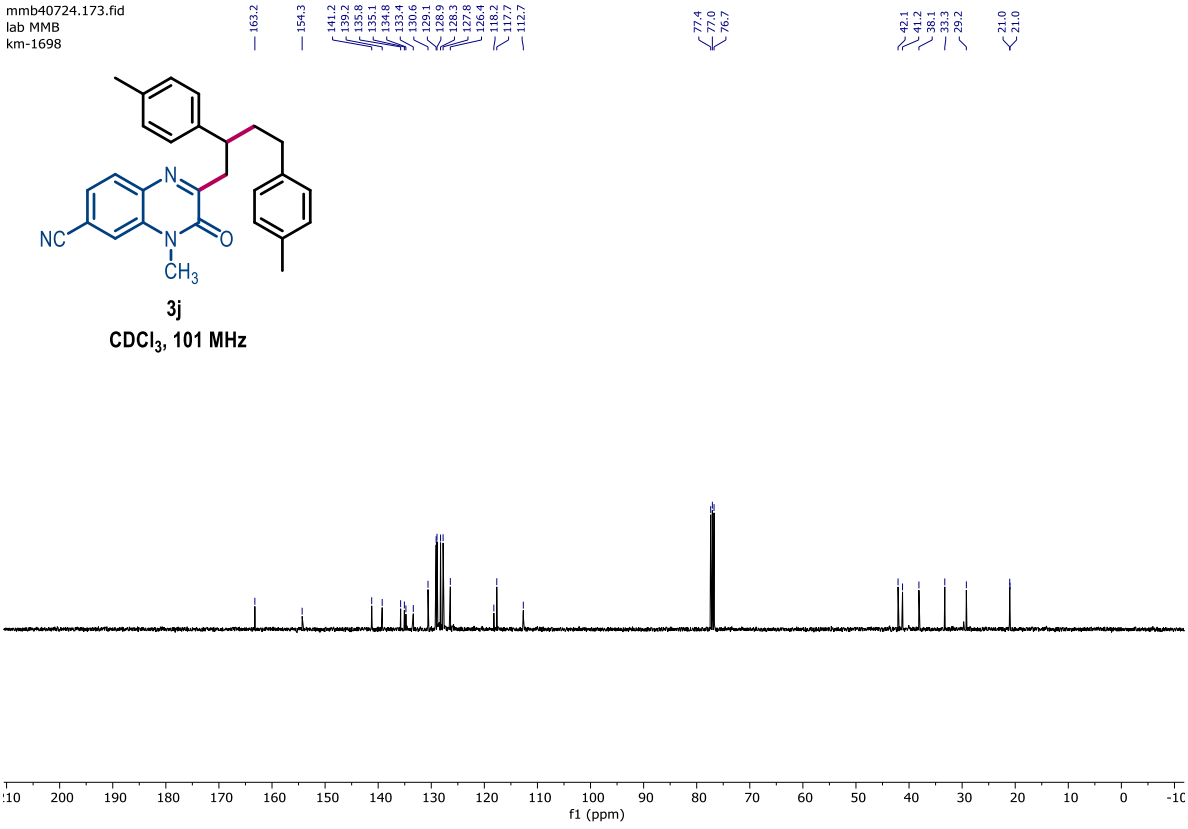
2.30
2.04
2.03
2.03
2.02
2.01
2.01
2.00
2.00
1.99
1.98
1.98
1.97
NC
N
N
O
CH3
3h
CDCl3, 400 MHz
0.72
1.04
1.13
2.03
6.34
3.43
1.18
2.06
2.31
6.29
2.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

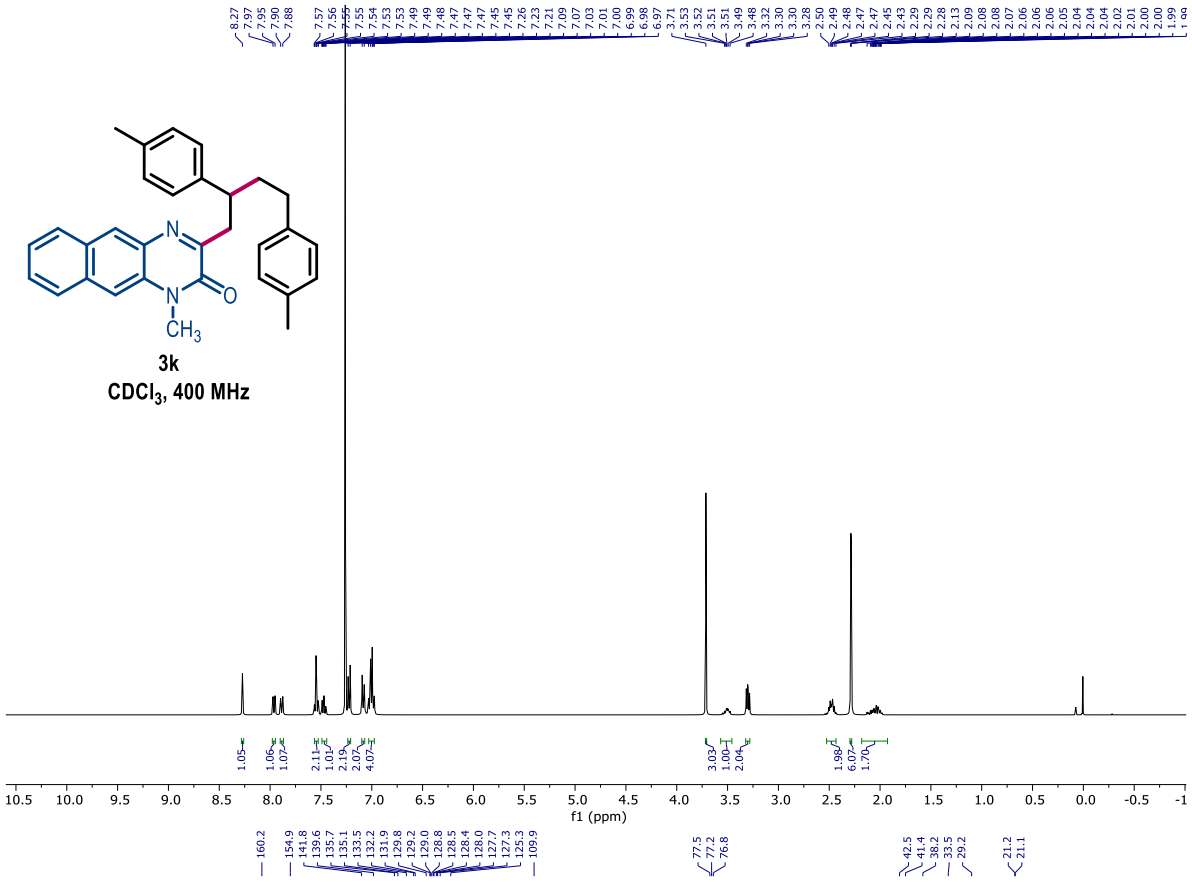

161.9
154.6
141.4
139.4
136.3
135.9
135.2
134.1
132.3
132.3
129.2
129.0
128.4
127.9
118.2
114.7
107.1
77.5
77.2
76.8
42.0
41.0
38.3
33.4
29.4
21.1
21.1
NC
N
N
O
CH3
3h
CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

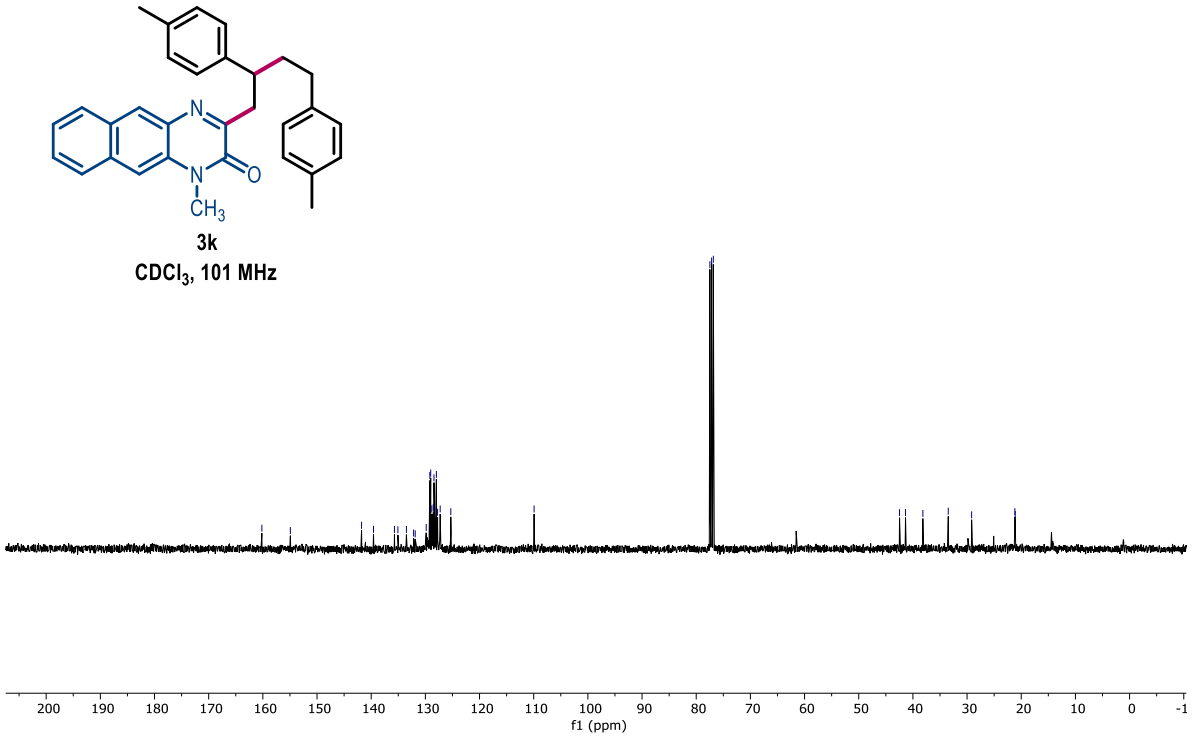

Cl
Cl
N
O
N
CH3
3i
CDCl3, 500 MHz
f1 (ppm)

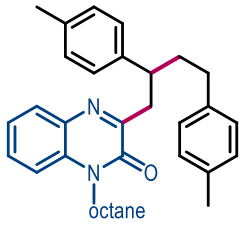

Cl
Cl
N
O
N
CH3
3i
CDCl3, 126 MHz
f1 (ppm)


NC
N
O
CH3
3j
CDCl3, 400 MHz
f1 (ppm)


mmb40724.173.fid
lab MMB
km-1698
NC
N
O
CH3
3j
CDCl3, 101 MHz
f1 (ppm)

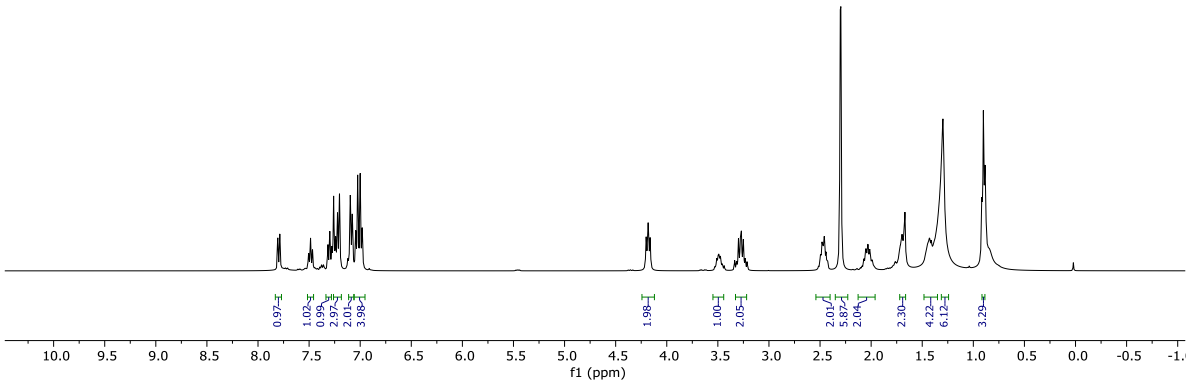

3k
CDCl3, 400 MHz
f1 (ppm)

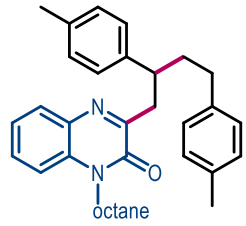

3k
CDCl3, 101 MHz
f1 (ppm)



3l

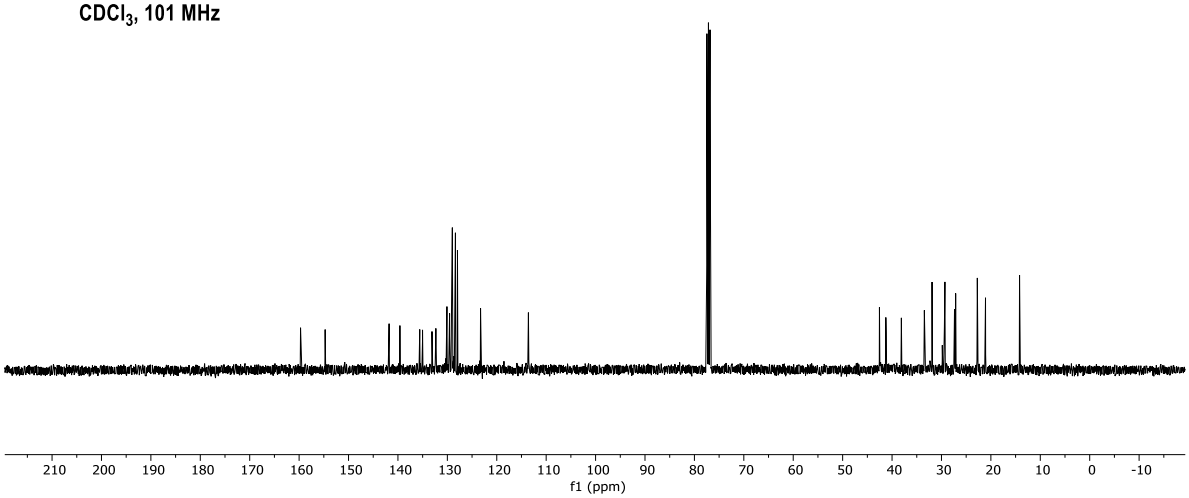
$CDCl_3$, 400 MHz

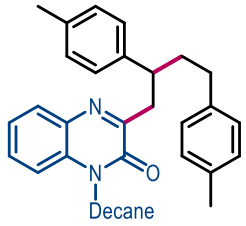




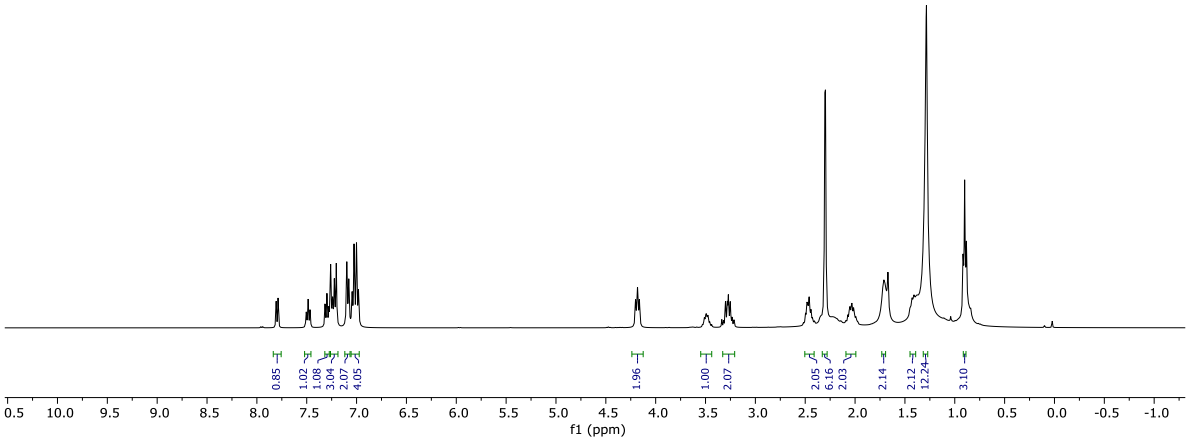
3l

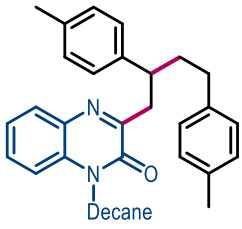
$CDCl_3$, 101 MHz



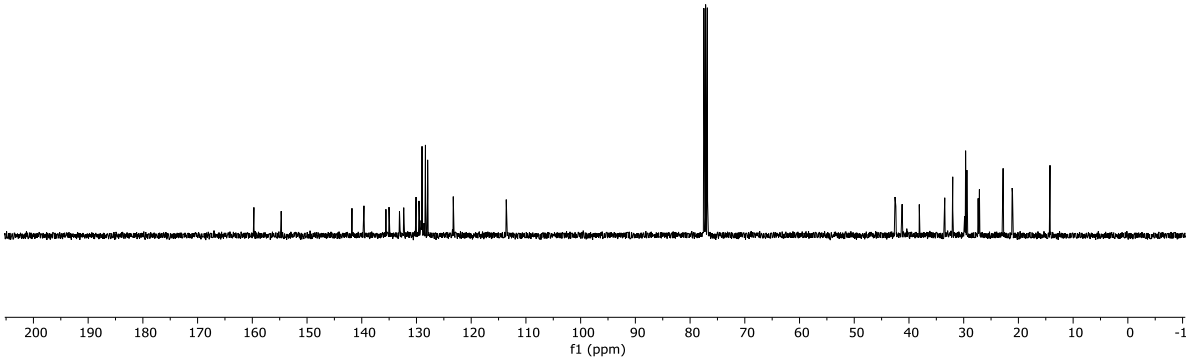


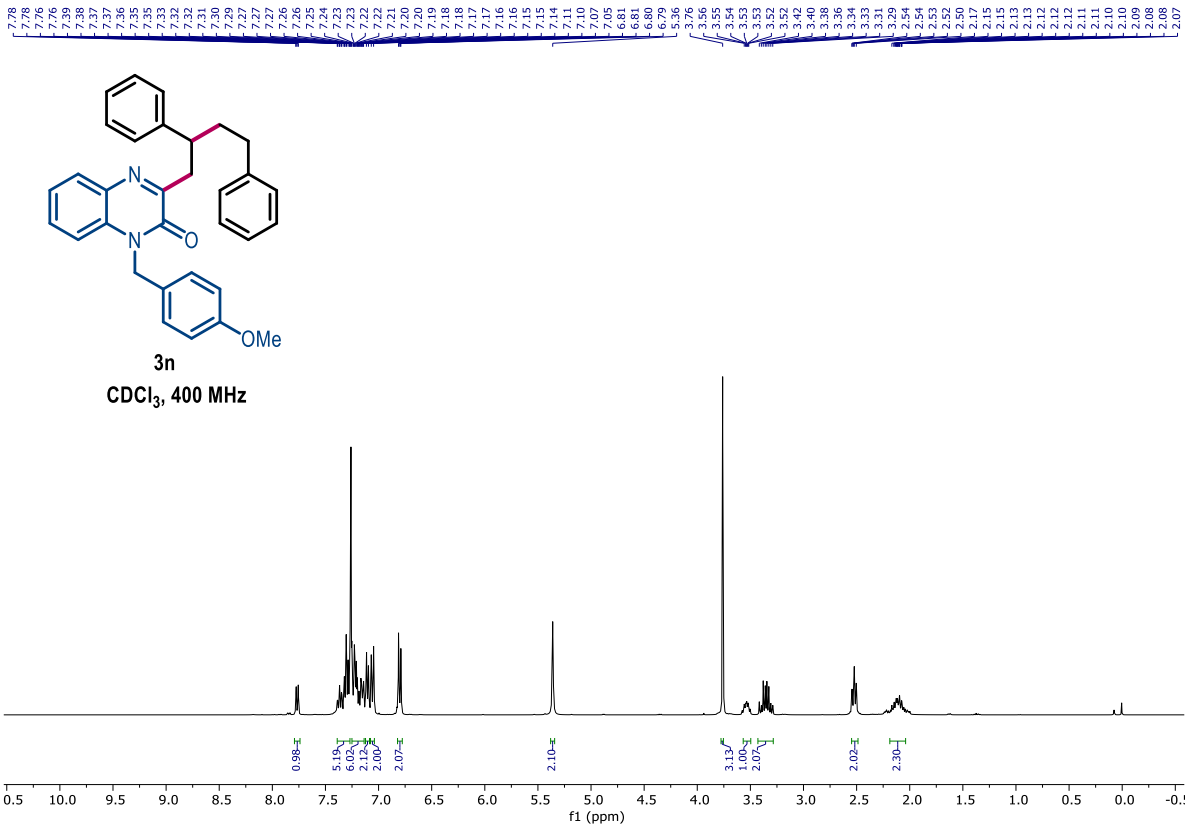
3m
$CDCl_3$, 400 MHz

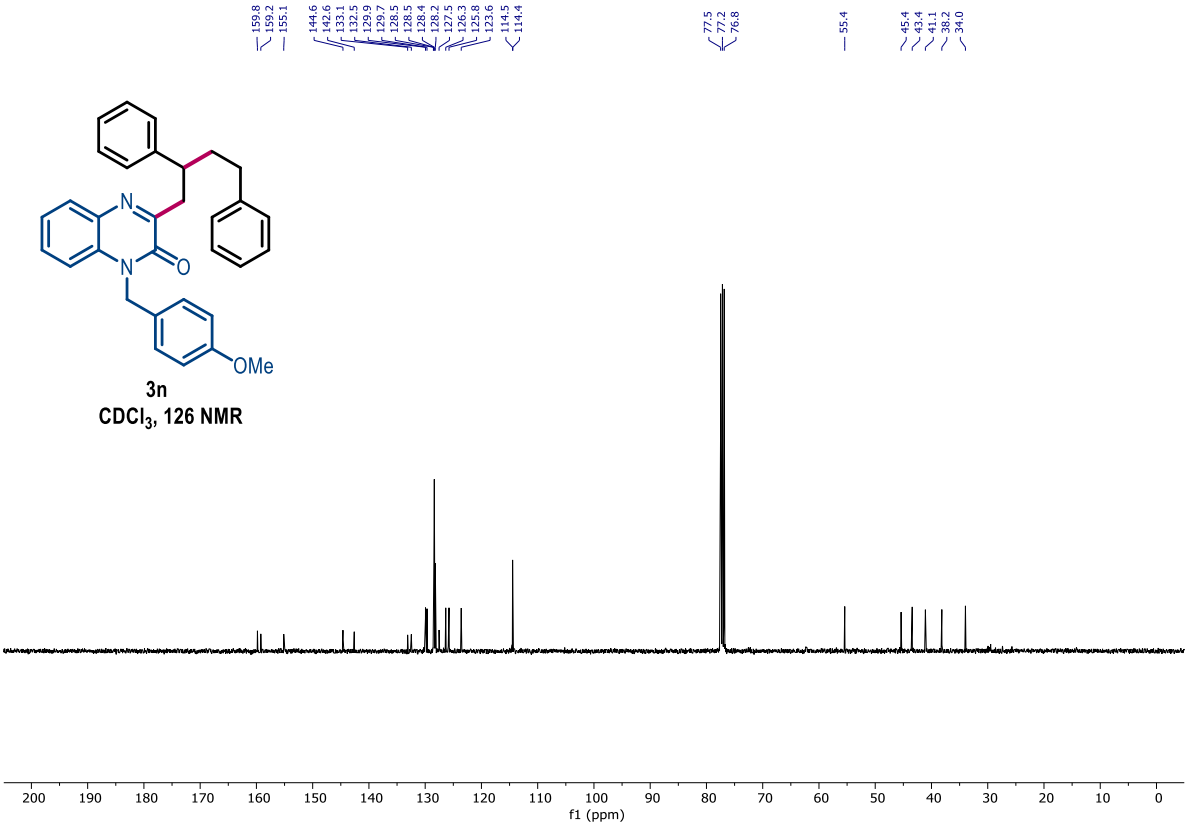


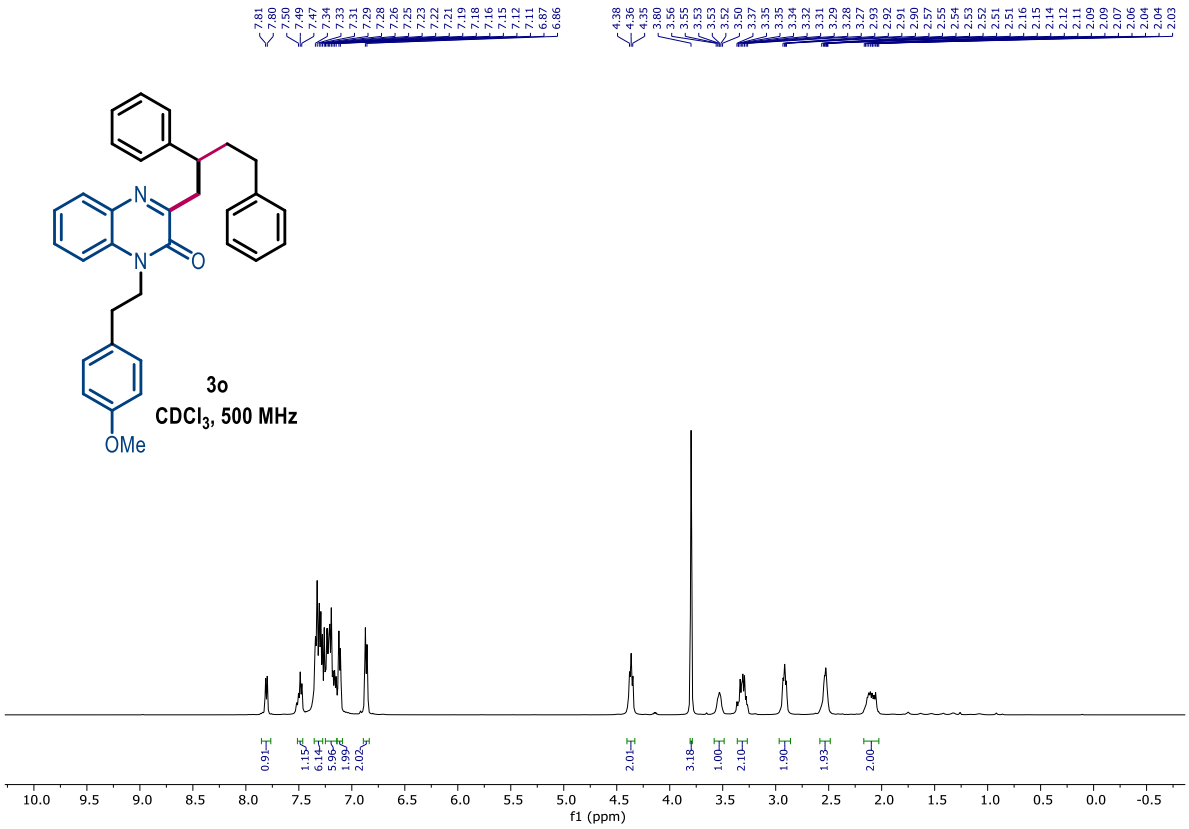


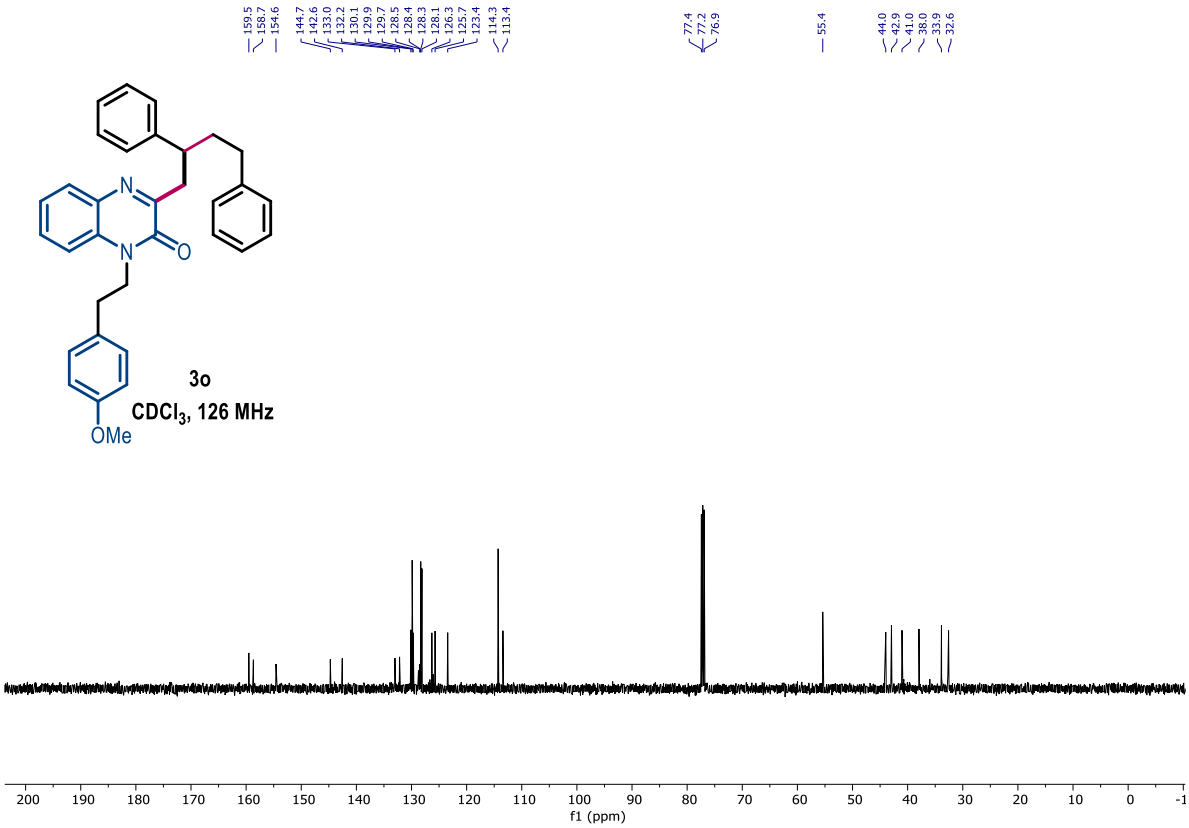
3m
$CDCl_3$, 101 MHz

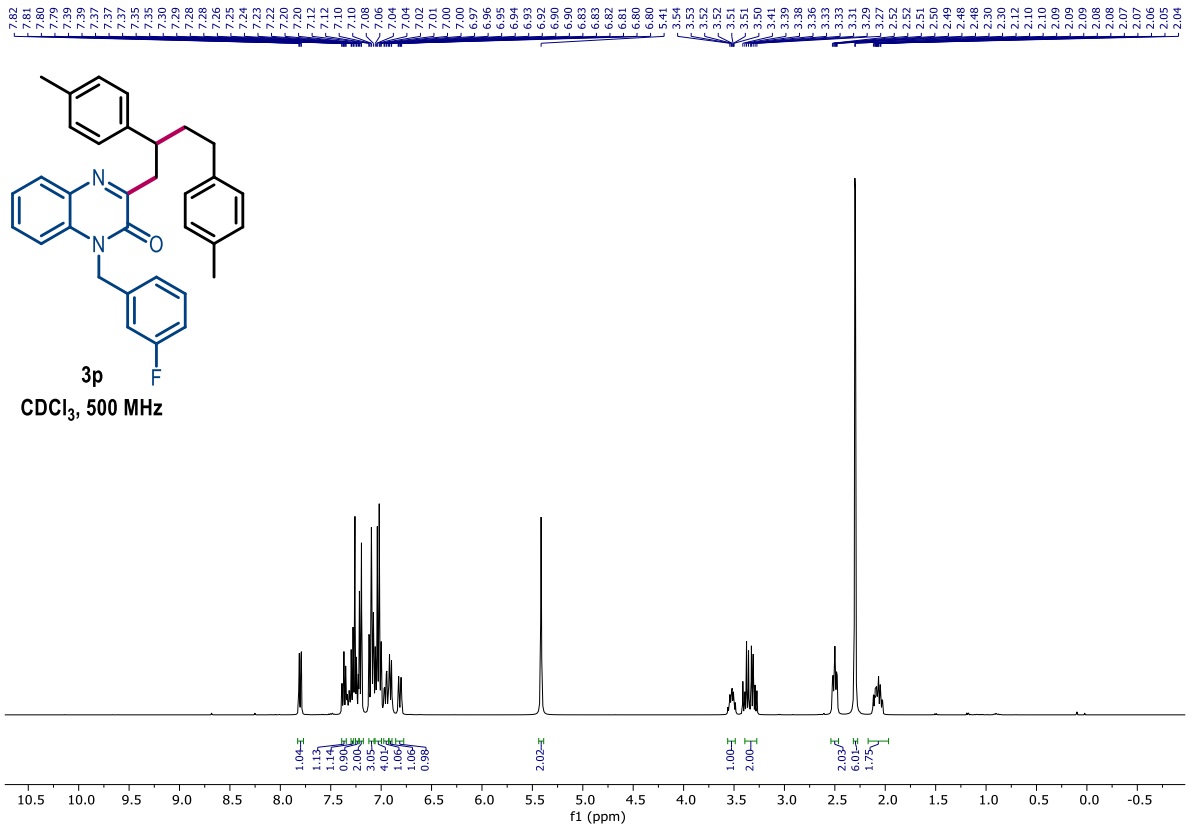


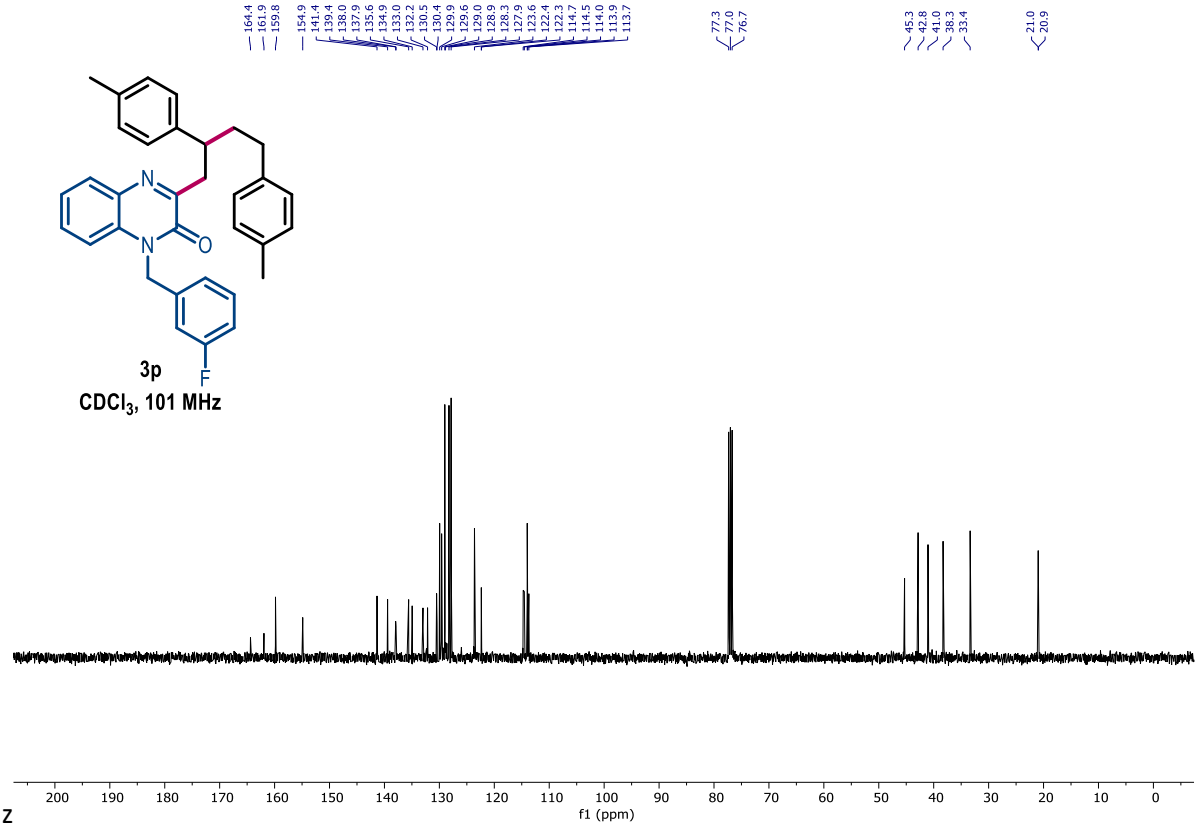

OMe
3n
CDCl3, 400 MHz
f1 (ppm)


OMe
3n
CDCl3, 126 NMR
f1 (ppm)

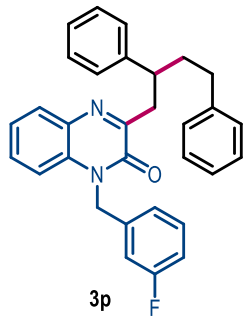

7.81 7.80 7.50 7.49 7.47 7.34 7.33 7.31 7.29 7.28 7.26 7.25 7.23 7.22 7.21 7.19 7.18 7.16 7.15 7.12 7.11 6.87 6.86
4.38 4.36 4.35 3.80 3.56 3.55 3.53 3.53 3.52 3.50 3.37 3.35 3.35 3.34 3.32 3.31 3.29 3.28 3.27 2.93 2.92 2.91 2.90 2.57 2.55 2.54 2.53 2.52 2.51 2.51 2.16 2.15 2.14 2.12 2.11 2.09 2.09 2.07 2.06 2.04 2.04 2.03
N
N
O
OMe
3o
CDCl3, 500 MHz
0.91 1.15 6.14 5.96 1.99 2.02 2.01 3.18 1.00 2.10 1.90 1.93 2.00
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
f1 (ppm)


159.5 158.7 154.6 144.7 142.6 133.0 132.2 130.1 129.9 129.7 128.5 128.4 128.3 128.1 126.3 125.7 123.4 114.3 113.4
77.4 77.2 76.9
55.4
44.0 42.9 41.0 38.0 33.9 32.6
N
N
O
OMe
3o
CDCl3, 126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



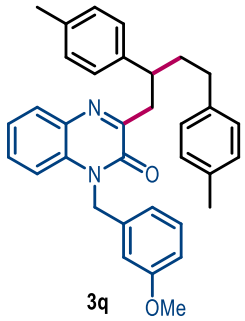


Z



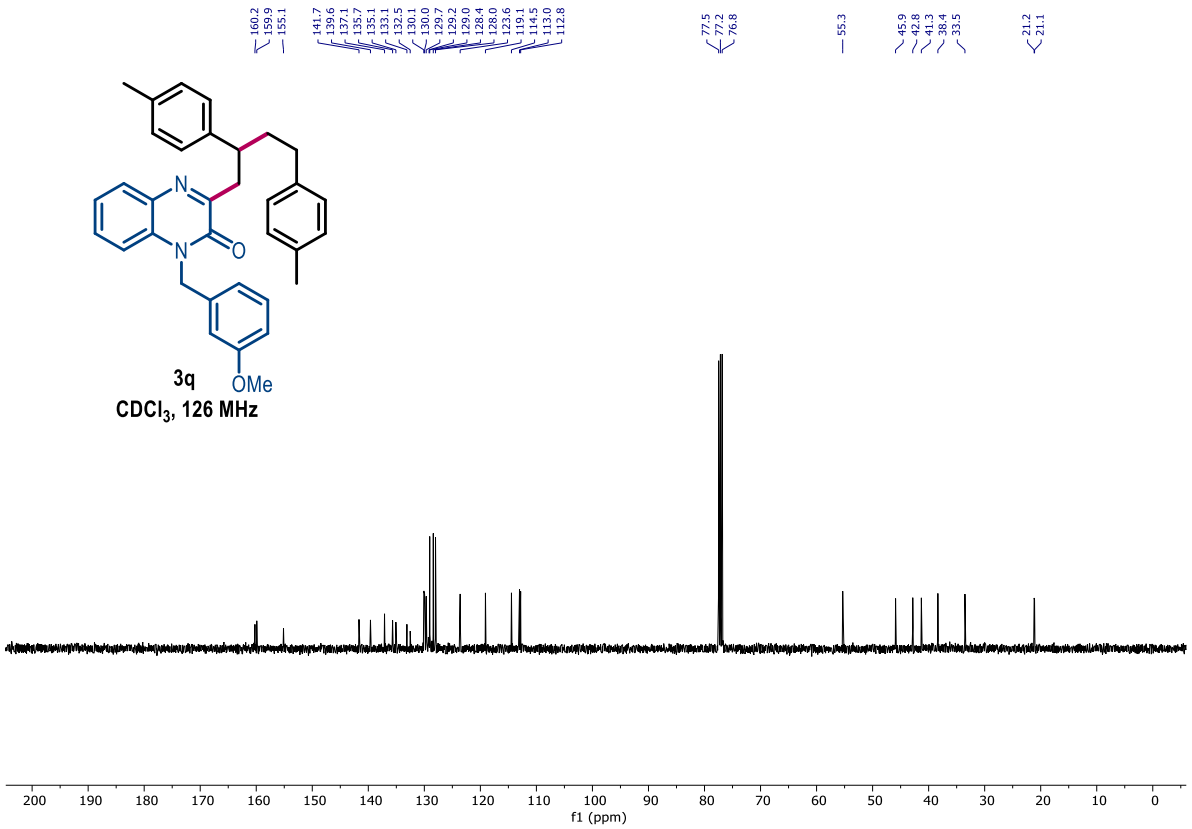
3p

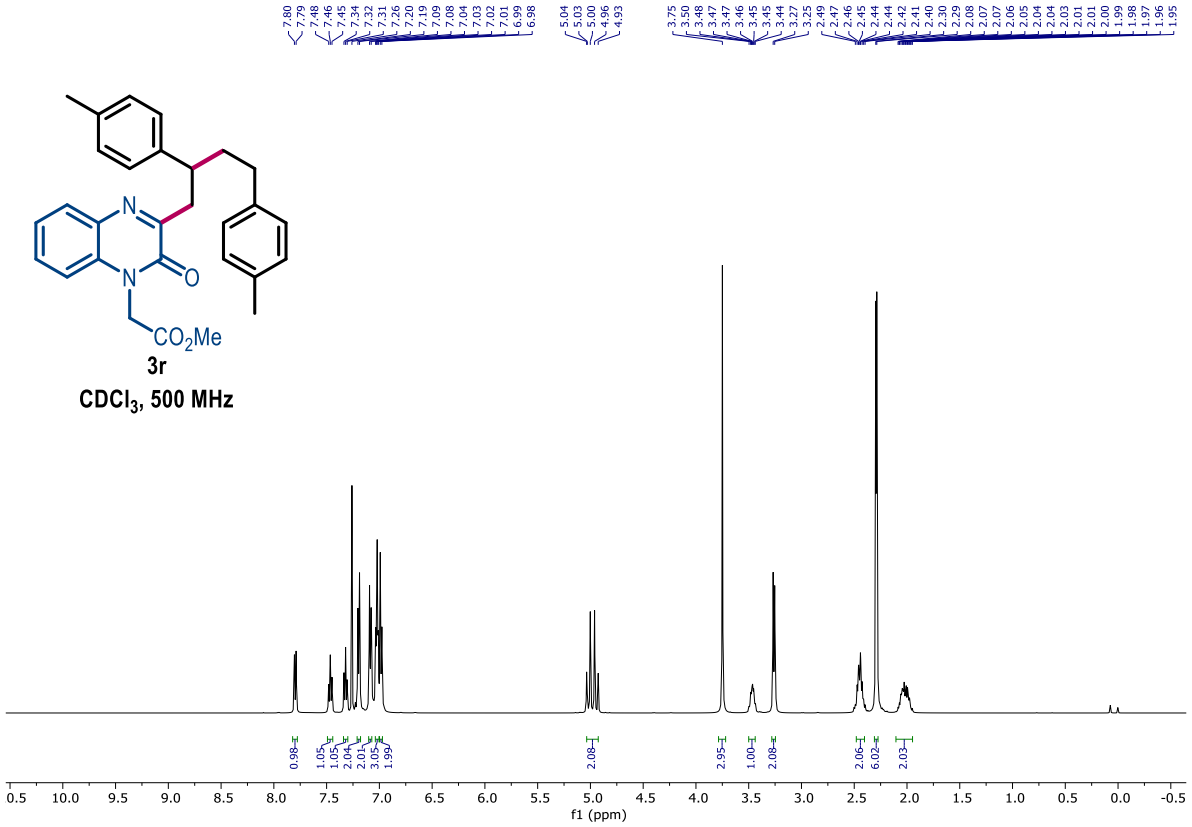
$CDCl_3$, 471 MHz

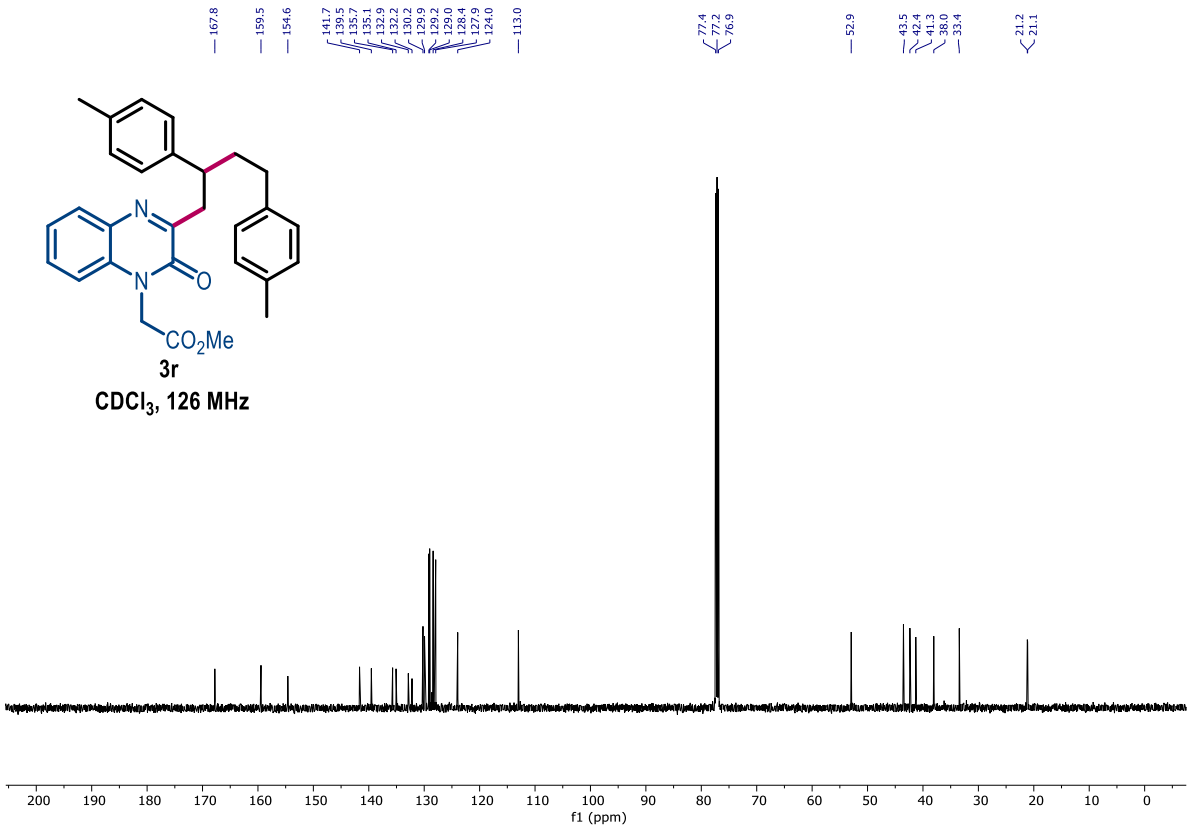


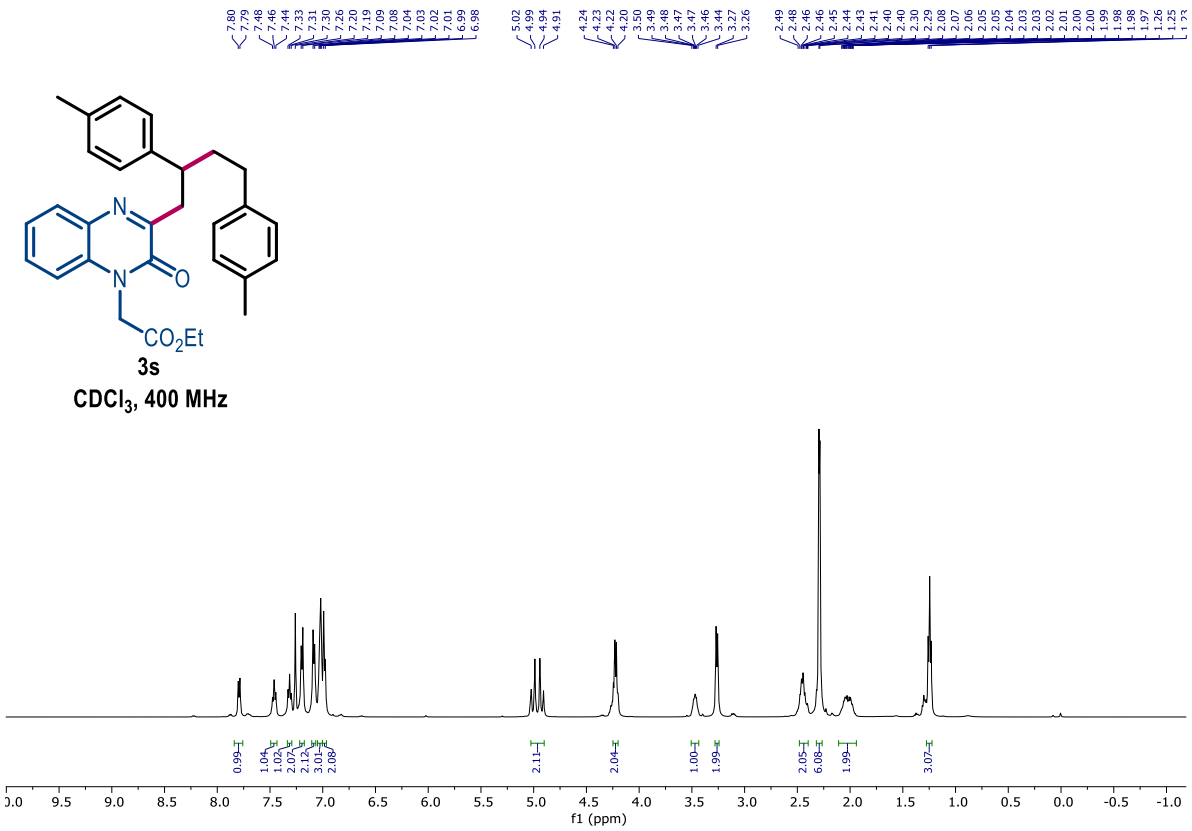
3q

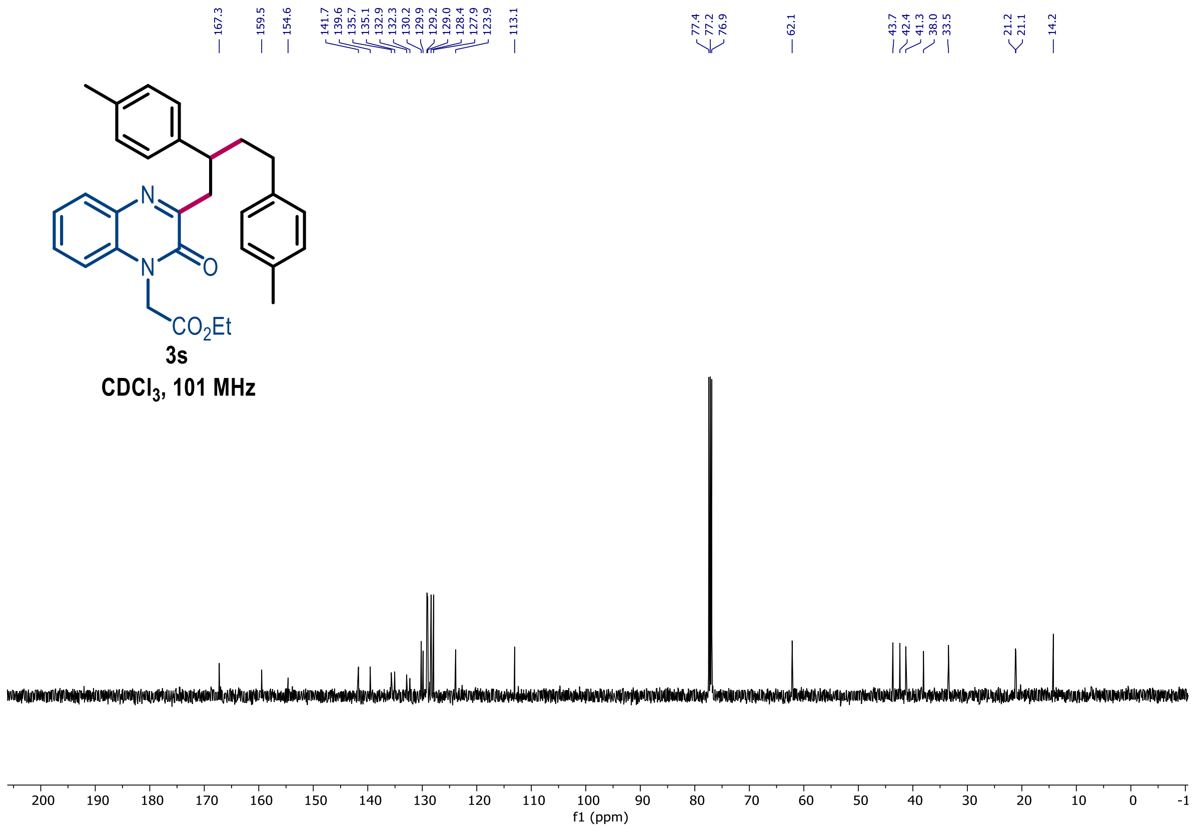
$CDCl_3$, 500 MHz


160.2
159.9
155.1
141.7
139.6
137.1
135.7
135.1
133.1
132.5
130.1
130.0
129.7
129.2
129.0
128.4
128.0
123.6
119.1
114.5
113.0
112.8
77.5
77.2
76.8
55.3
45.9
42.8
41.3
38.4
33.5
21.2
21.1
N
N
O
OMe
3q
CDCl3, 126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

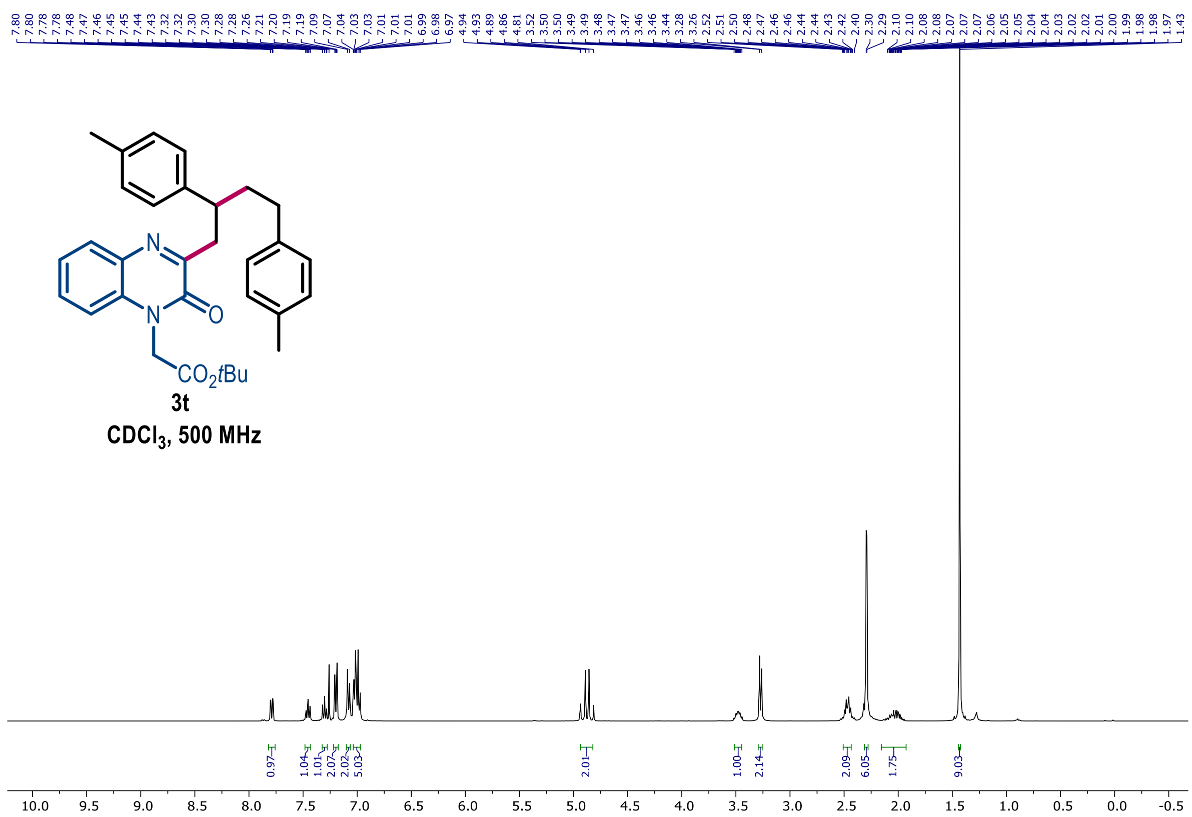

7.80
7.79
7.48
7.46
7.45
7.34
7.32
7.31
7.26
7.20
7.19
7.09
7.08
7.04
7.03
7.02
7.01
6.99
6.98
5.04
5.03
5.00
4.96
4.93
3.75
3.50
3.48
3.47
3.47
3.46
3.45
3.45
3.44
3.27
3.25
2.49
2.47
2.46
2.45
2.44
2.44
2.42
2.41
2.40
2.30
2.29
2.08
2.07
2.07
2.06
2.05
2.04
2.04
2.03
2.01
2.01
2.00
1.99
1.98
1.97
1.96
1.95
N
N
O
CO2Me
3r
CDCl3, 500 MHz
0.98
1.05
1.05
2.04
2.01
3.05
1.99
2.08
2.95
1.00
2.08
2.06
6.02
2.03
0.5 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
f1 (ppm)


167.8
159.5
154.6
141.7
139.5
138.7
135.1
132.9
132.2
130.2
129.9
129.2
129.0
128.4
127.9
124.0
113.0
77.4
77.2
76.9
52.9
43.5
42.4
41.3
38.0
33.4
21.2
21.1
N
N
O
CO2Me
3r
CDCl3, 126 MHz
f1 (ppm)

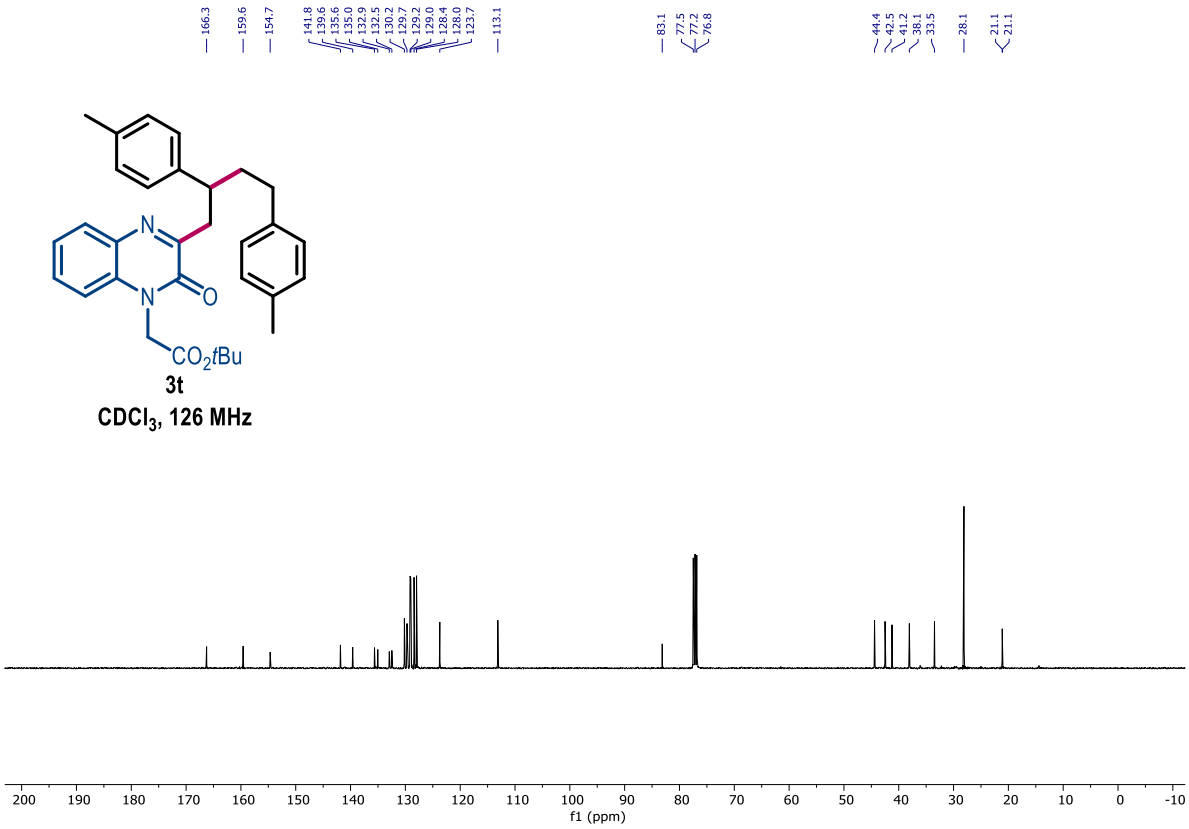

7.80
7.79
7.48
7.46
7.44
7.33
7.31
7.30
7.26
7.20
7.19
7.09
7.08
7.04
7.03
7.02
7.01
6.99
6.98
5.02
4.99
4.94
4.91
4.24
4.23
4.22
4.20
3.50
3.49
3.48
3.47
3.47
3.46
3.44
3.27
3.26
2.49
2.48
2.46
2.46
2.45
2.44
2.43
2.41
2.40
2.40
2.30
2.29
2.08
2.07
2.06
2.05
2.05
2.04
2.03
2.02
2.01
2.00
2.00
1.99
1.98
1.98
1.97
1.26
1.25
0.99
1.04
1.02
2.07
2.12
3.01
2.08
2.11
2.04
1.00
1.99
2.05
6.08
1.99
3.07
N
N
O
CO2Et
3s
CDCl3, 400 MHz
f1 (ppm)

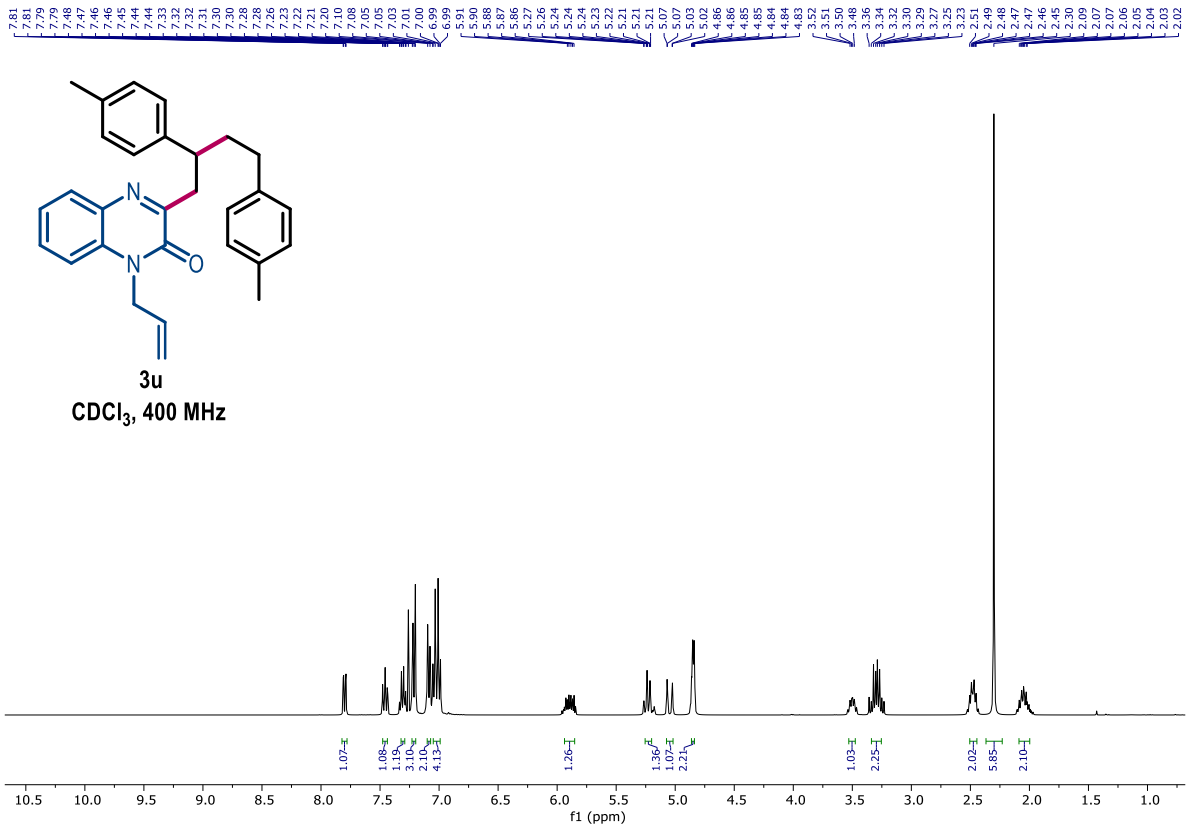


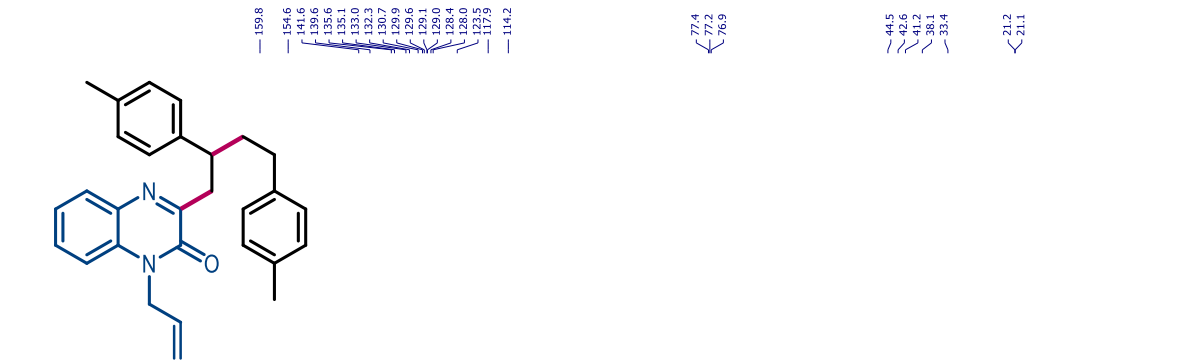
167.3
159.5
154.6
141.7
139.6
135.7
135.1
132.9
132.3
130.2
129.9
129.2
129.0
128.4
127.9
123.9
113.1
77.4
77.2
76.9
62.1
43.7
42.4
41.3
38.0
33.5
21.2
21.1
14.2
N
N
O
CO_2Et
3s
$CDCl_3$, 101 MHz
f1 (ppm)



N
N
O
CO_2tBu
3t
$CDCl_3$, 500 MHz
0.97
1.04
1.01
2.07
2.02
5.03
2.01
1.00
2.14
2.09
6.05
1.75
9.03
f1 (ppm)

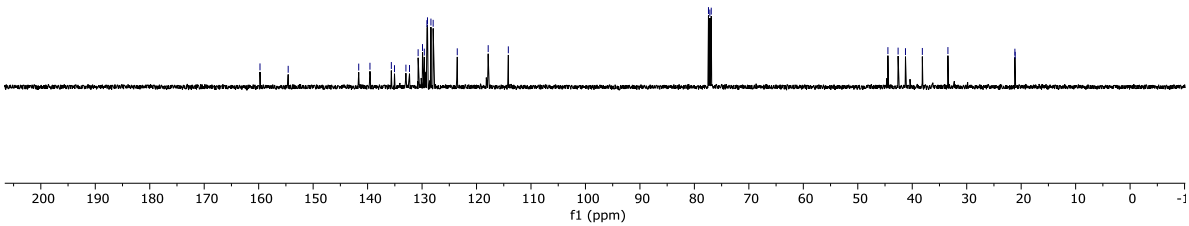

166.3
159.6
154.7
141.8
139.6
135.6
135.0
132.9
132.5
130.2
129.7
129.2
129.0
128.4
128.0
123.7
113.1
83.1
77.5
77.2
76.8
44.4
42.5
41.2
38.1
33.5
28.1
21.1
21.1
N
N
O
CO2tBu
3t
CDCl3, 126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

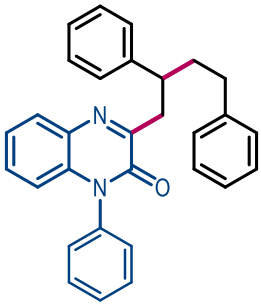

7.81 7.81 7.79 7.79 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.33 7.32 7.32 7.31 7.30 7.30 7.28 7.28 7.26 7.23 7.22 7.21 7.10 7.10 7.08 7.05 7.05 7.03 7.01 7.00 6.99 6.99
5.91 5.90 5.88 5.87 5.86 5.27 5.26 5.24 5.24 5.24 5.23 5.22 5.21 5.21 5.21 5.07 5.07 5.03 5.02 4.86 4.86 4.85 4.85 4.84 4.84 4.83
3.52 3.51 3.50 3.48 3.36 3.34 3.32 3.30 3.29 3.27 3.25 3.23
2.51 2.49 2.48 2.47 2.47 2.46 2.45 2.30 2.09 2.07 2.07 2.06 2.05 2.04 2.03 2.02
N
N
O
3u
CDCl3, 400 MHz
1.07 1.08 1.19 3.10 2.10 4.13 1.26 1.36 1.07 2.21 1.03 2.25 2.02 5.85 2.10
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
f1 (ppm)



3u

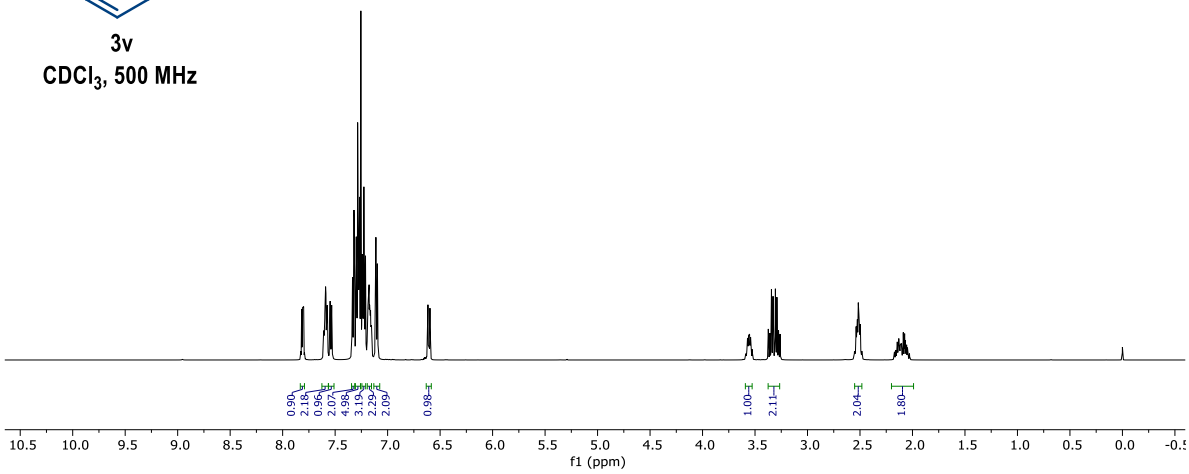
$CDCl_3$, 126 MHz

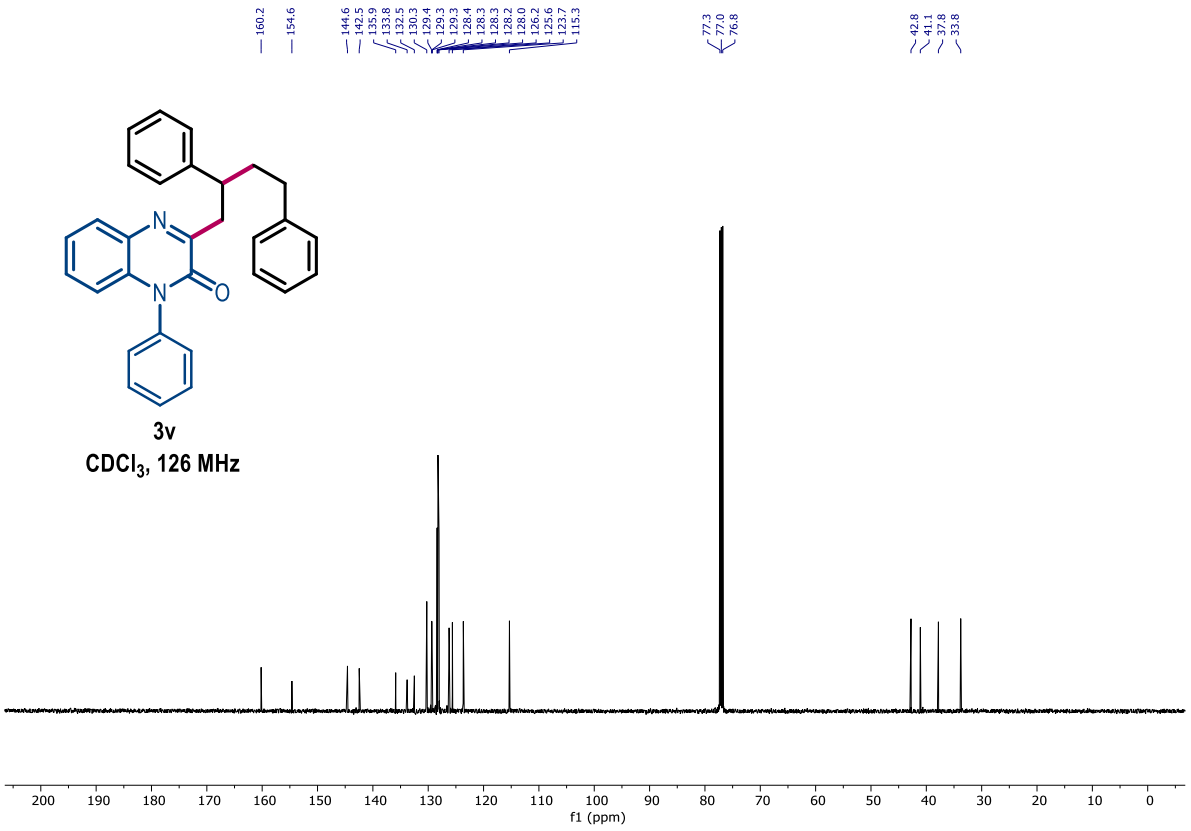


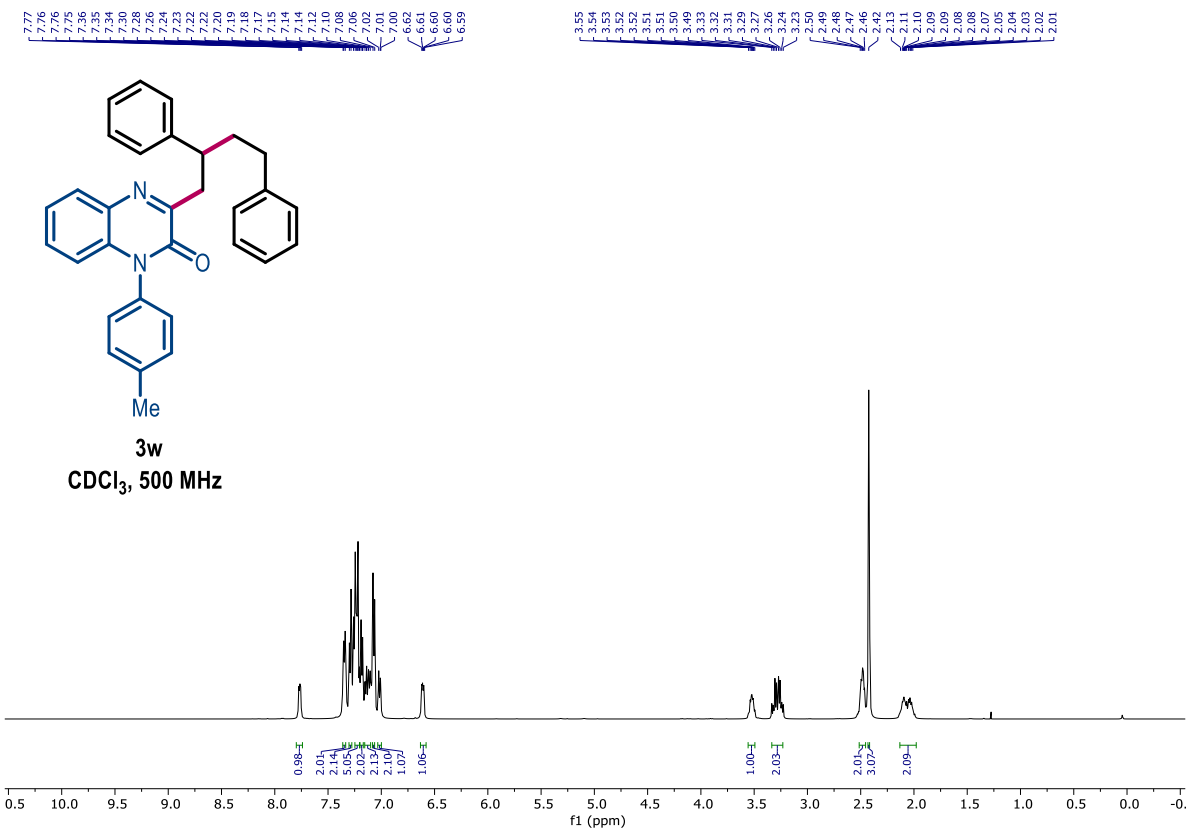


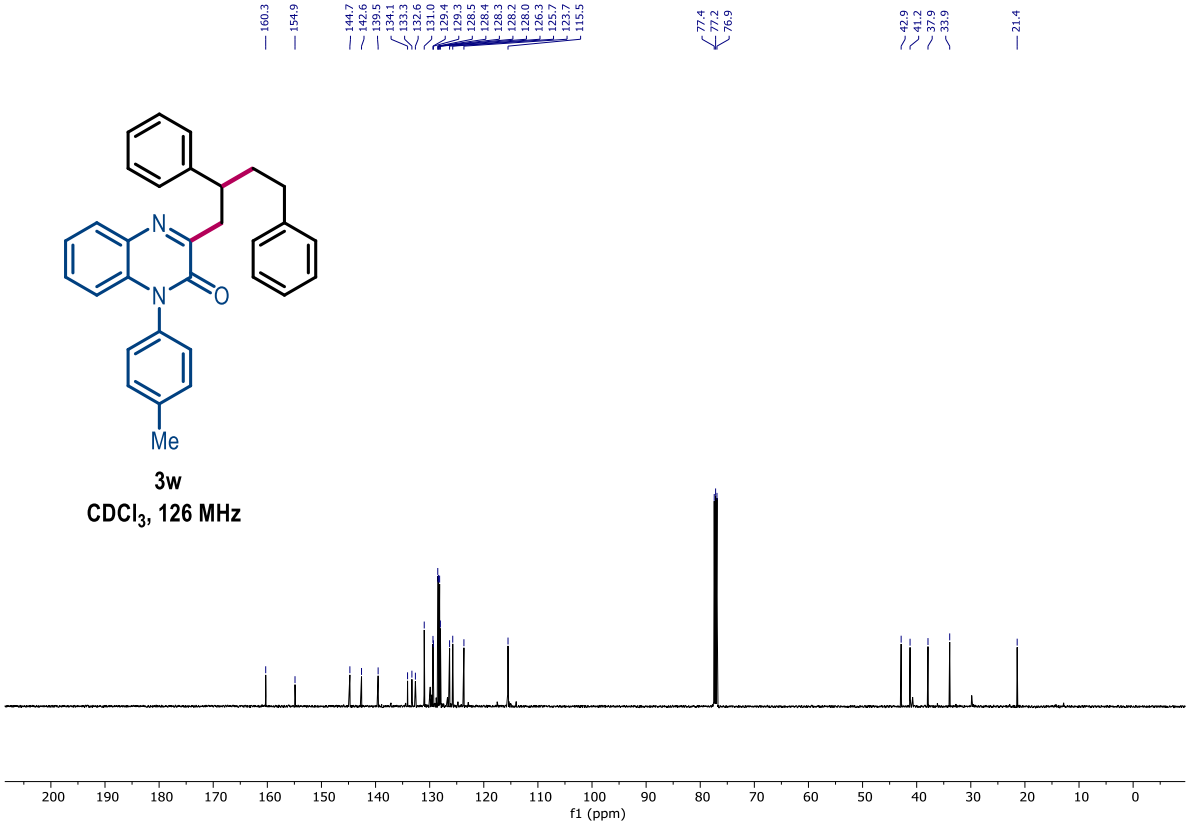
3v

$CDCl_3$, 500 MHz



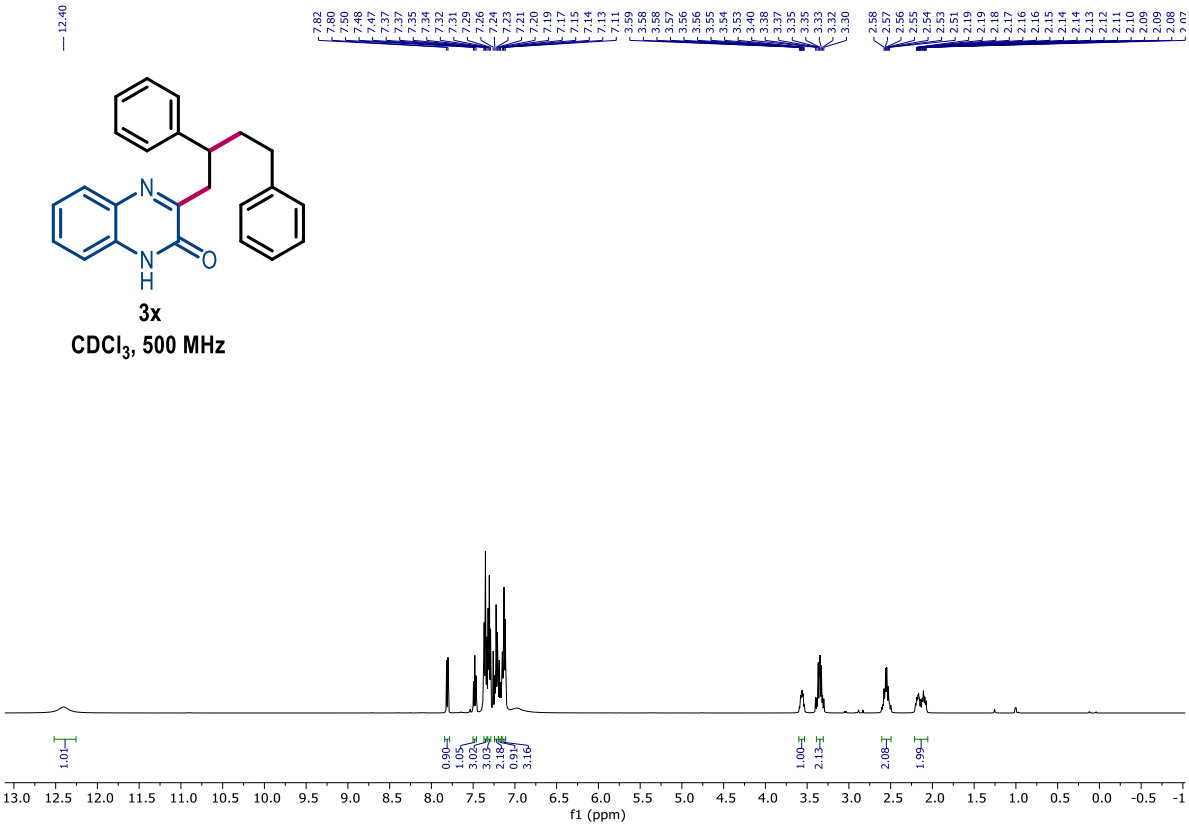

160.2
154.6
144.6
142.5
135.9
133.8
132.5
130.3
129.4
129.3
129.3
128.4
128.3
128.3
128.2
128.0
126.2
125.6
123.7
115.3
77.3
77.0
76.8
42.8
41.1
37.8
33.8
N
N
O
3v
CDCl3, 126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.77
7.76
7.76
7.75
7.75
7.36
7.35
7.34
7.30
7.28
7.26
7.24
7.23
7.22
7.22
7.20
7.19
7.18
7.17
7.15
7.14
7.14
7.12
7.10
7.08
7.06
7.02
7.01
7.00
6.62
6.61
6.60
6.60
6.59
3.55
3.54
3.53
3.52
3.52
3.51
3.50
3.49
3.33
3.32
3.31
3.29
3.27
3.26
3.24
3.23
2.50
2.49
2.48
2.47
2.46
2.42
2.13
2.11
2.10
2.09
2.09
2.08
2.08
2.07
2.05
2.04
2.03
2.02
2.01
N
N
O
Me
3w
CDCl3, 500 MHz
0.98
2.01
2.14
5.05
2.02
2.13
2.10
1.07
1.06
1.00
2.03
2.01
3.07
2.09
0.5 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.
f1 (ppm)



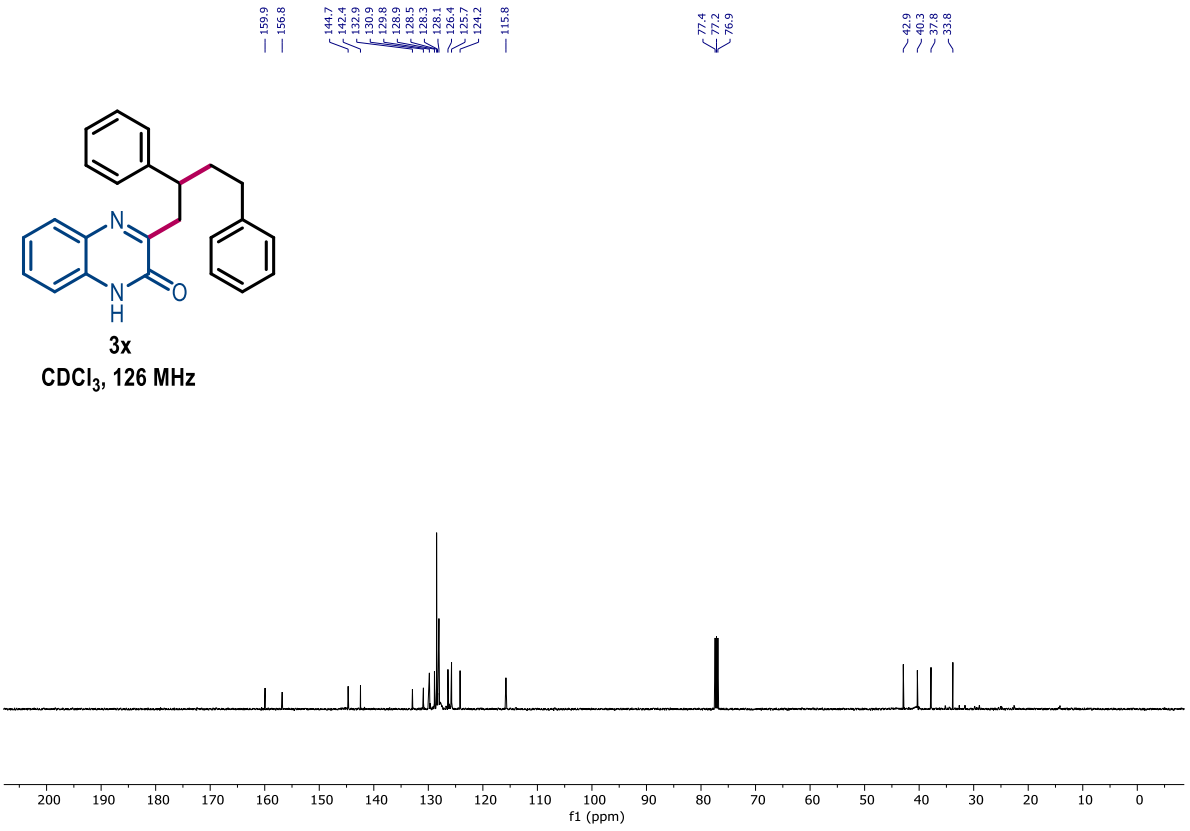
3w

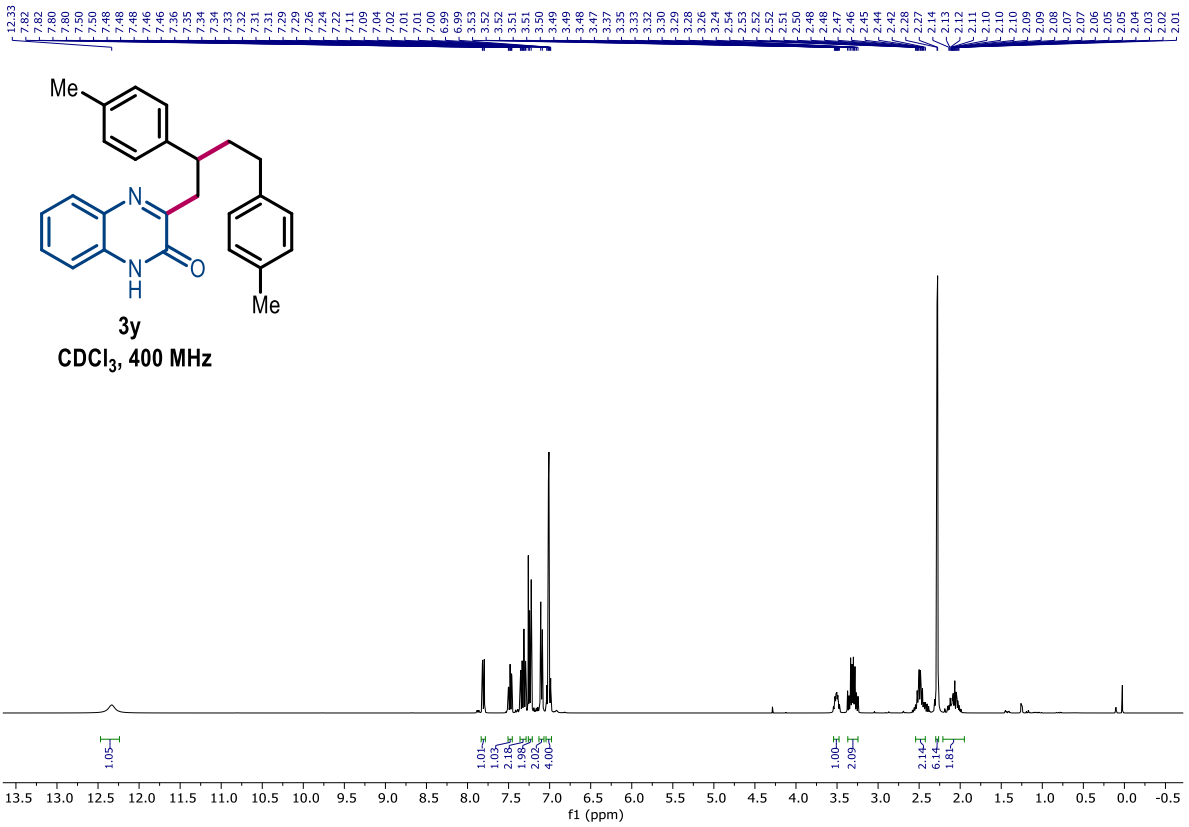
$CDCl_3$, 126 MHz

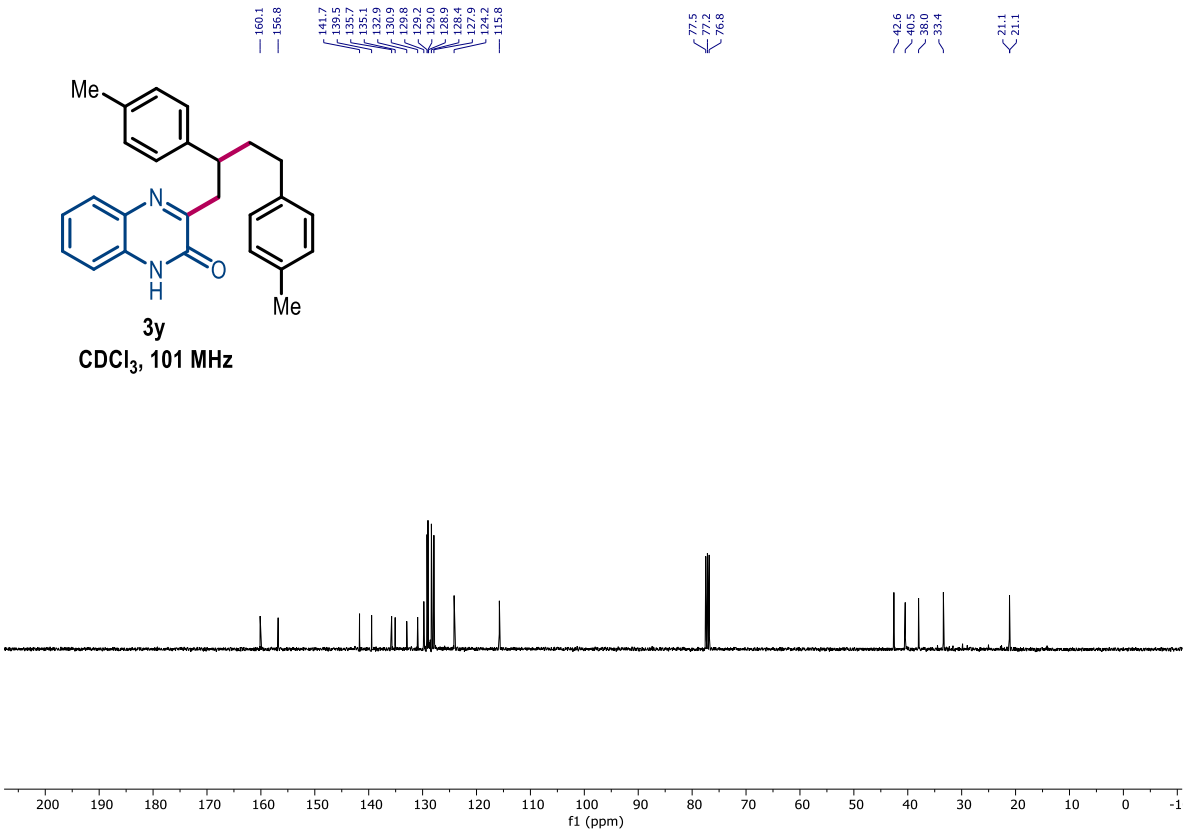


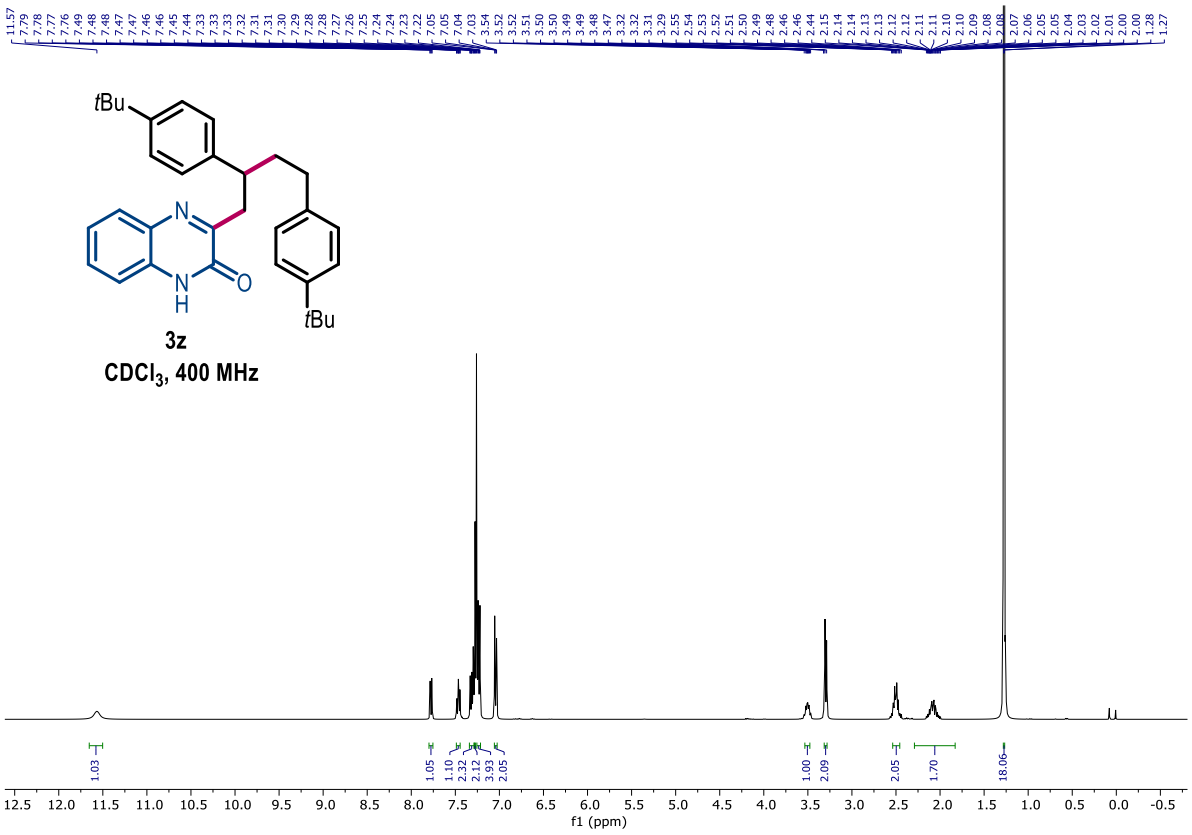
3x

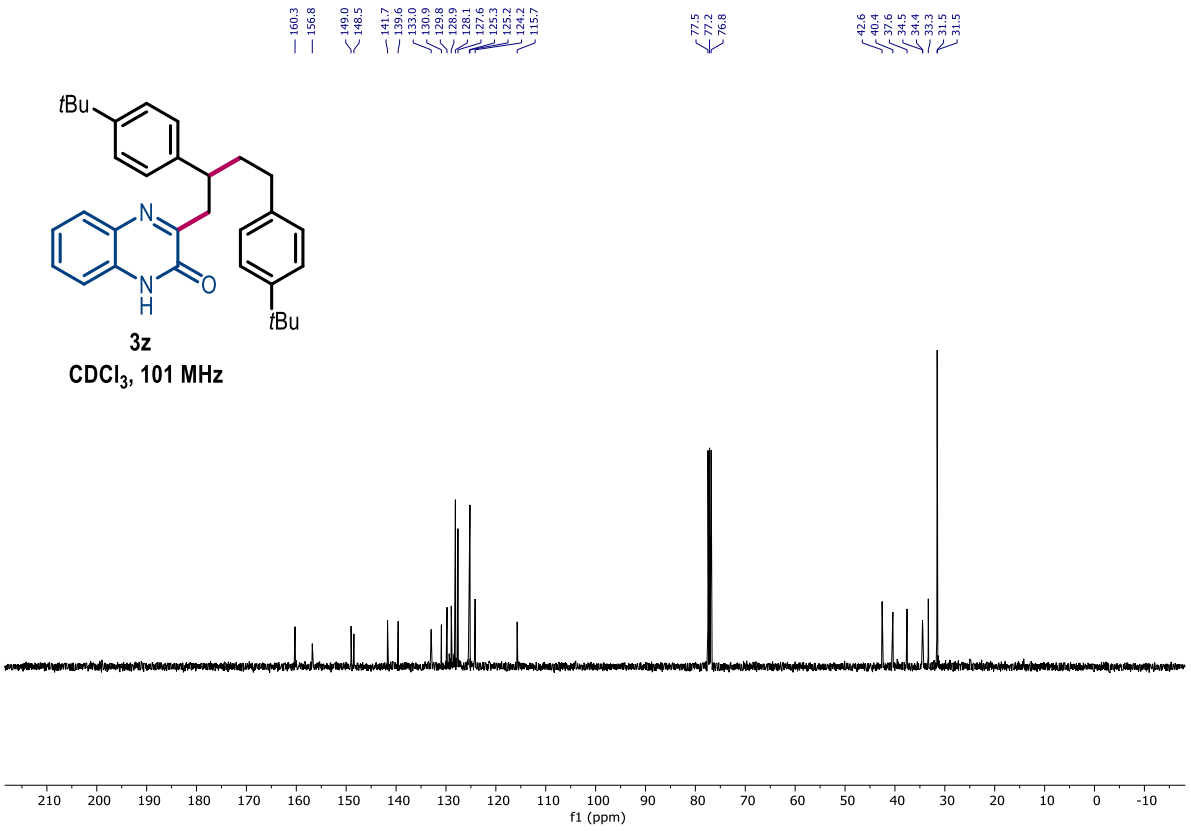
$CDCl_3$, 500 MHz

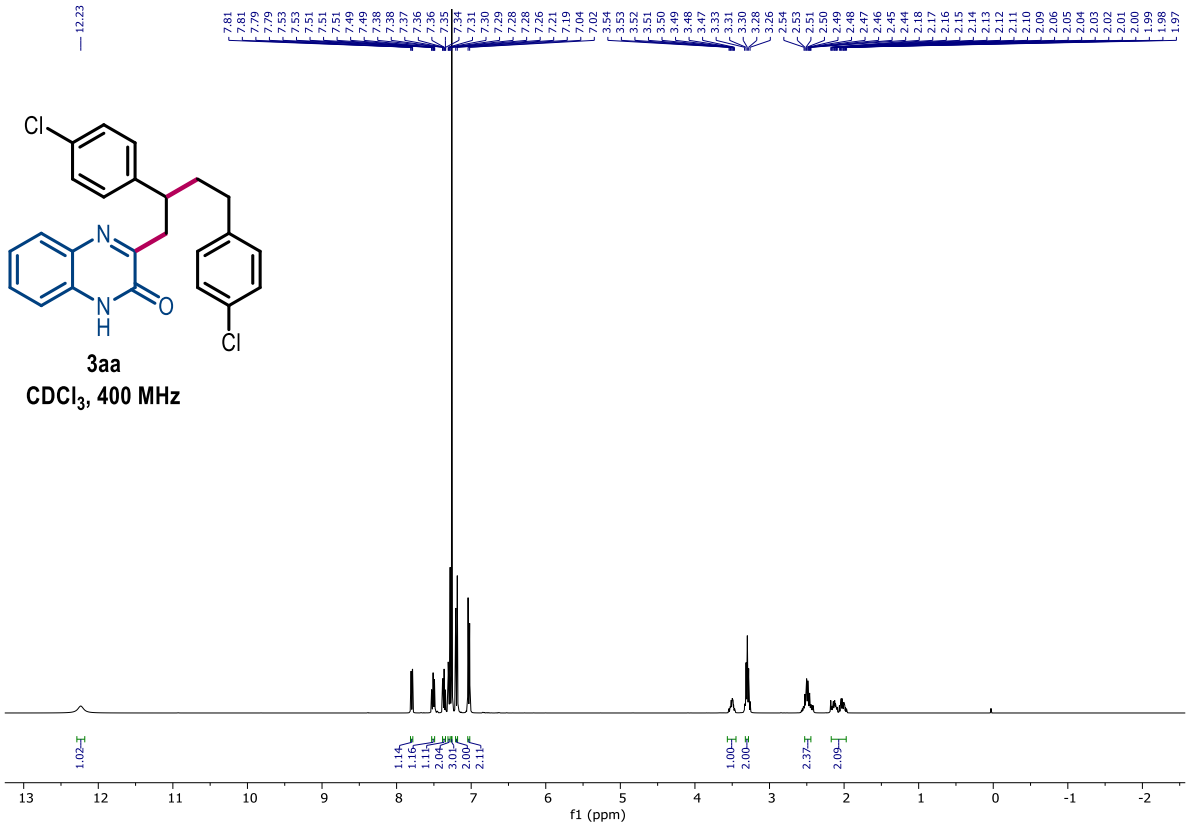

159.9
156.8
144.7
142.4
132.9
130.9
129.8
128.9
128.5
128.3
128.1
126.4
125.7
124.2
115.8
77.4
77.2
76.9
42.9
40.3
37.8
33.8
N
N
H
O
3x
CDCl3, 126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

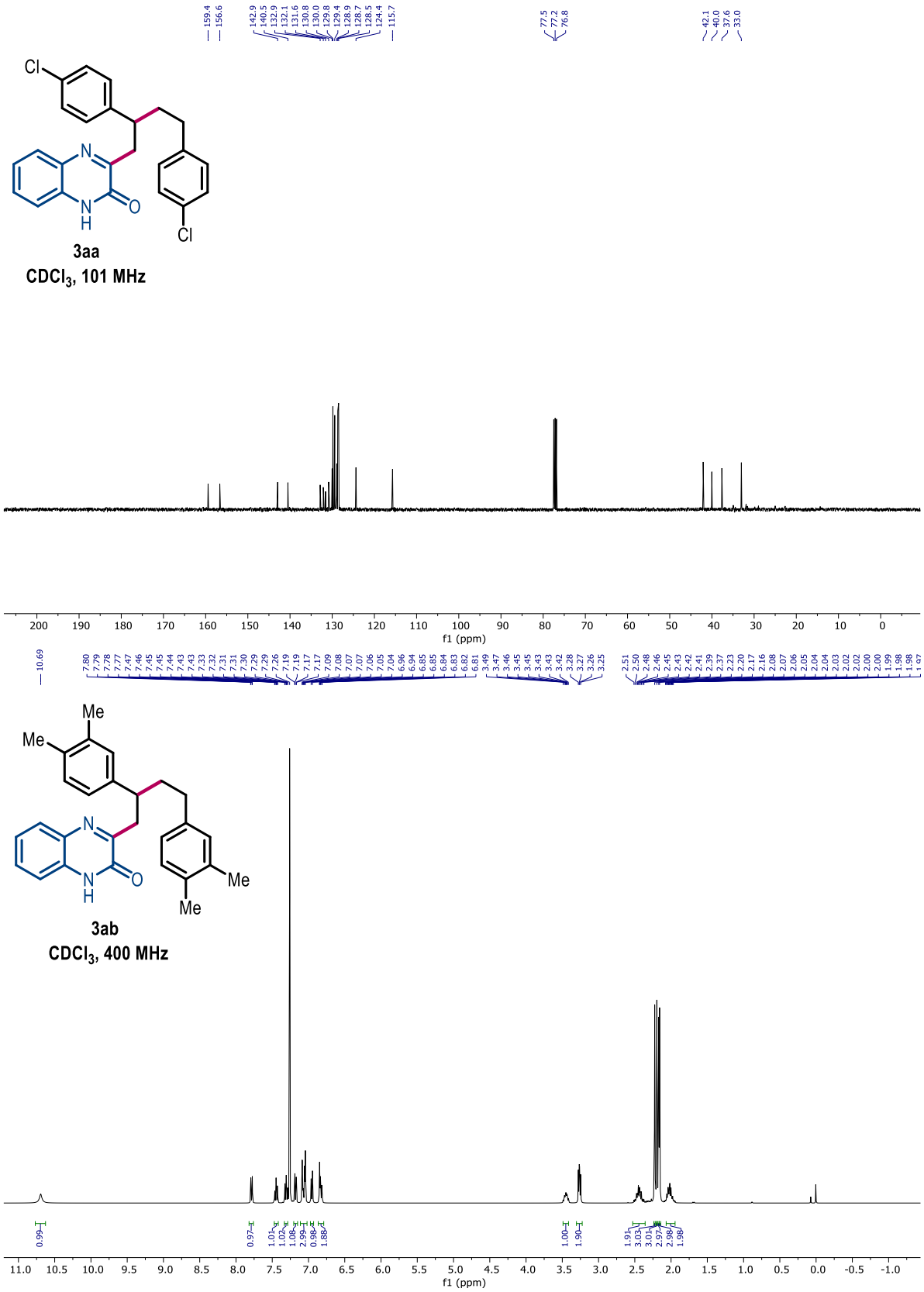

12.33
7.82
7.80
7.50
7.48
7.46
7.36
7.35
7.34
7.33
7.32
7.31
7.29
7.26
7.24
7.22
7.11
7.08
7.04
7.02
7.01
7.00
6.99
3.53
3.52
3.51
3.50
3.49
3.48
3.47
3.37
3.35
3.33
3.32
3.30
3.29
3.28
3.26
3.24
2.54
2.53
2.52
2.51
2.50
2.48
2.47
2.46
2.45
2.44
2.42
2.28
2.27
2.14
2.13
2.12
2.11
2.10
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.02
2.01
Me
N
N
H
O
Me
3y
CDCl3, 400 MHz
1.05
1.01
1.03
2.18
1.98
2.02
4.00
1.00
2.09
2.14
6.14
1.81
13.5 13.0 12.5 12.0 11.5 11.0 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
f1 (ppm)

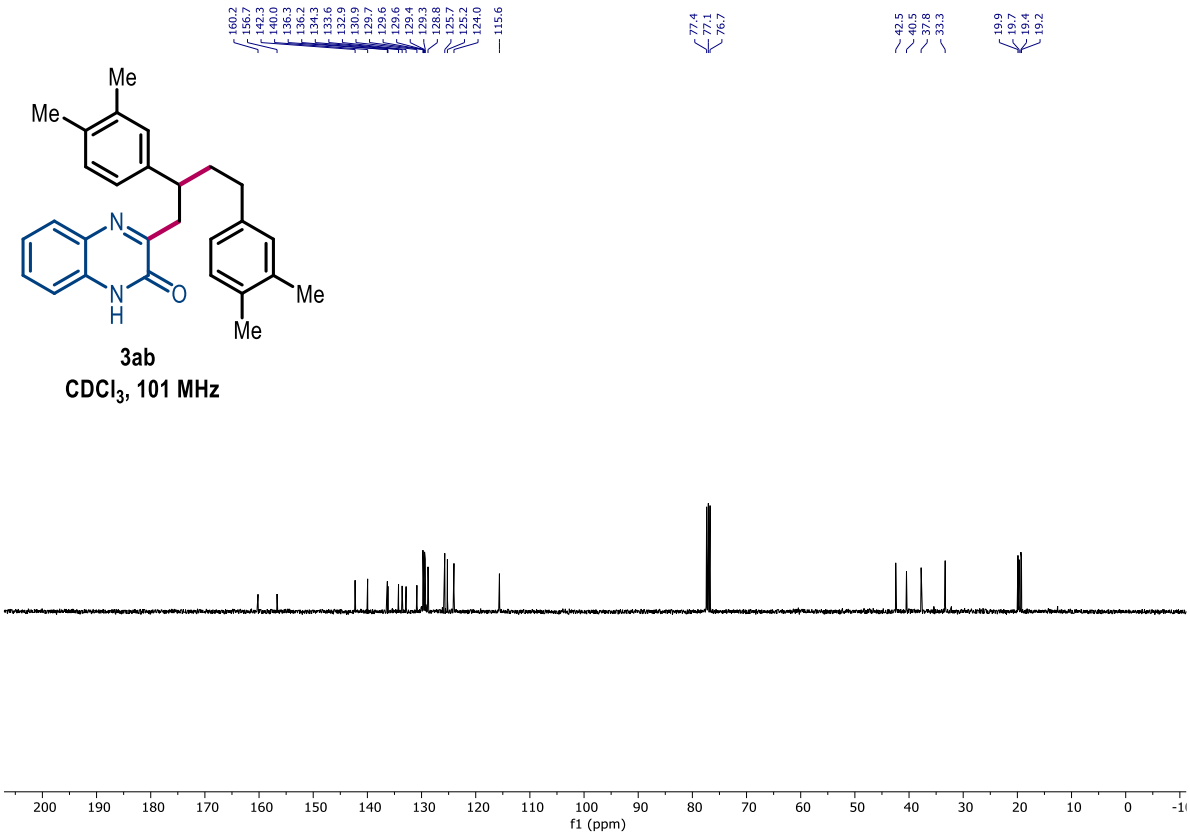

Me
N
N
H
O
Me
3y
CDCl3, 101 MHz
f1 (ppm)

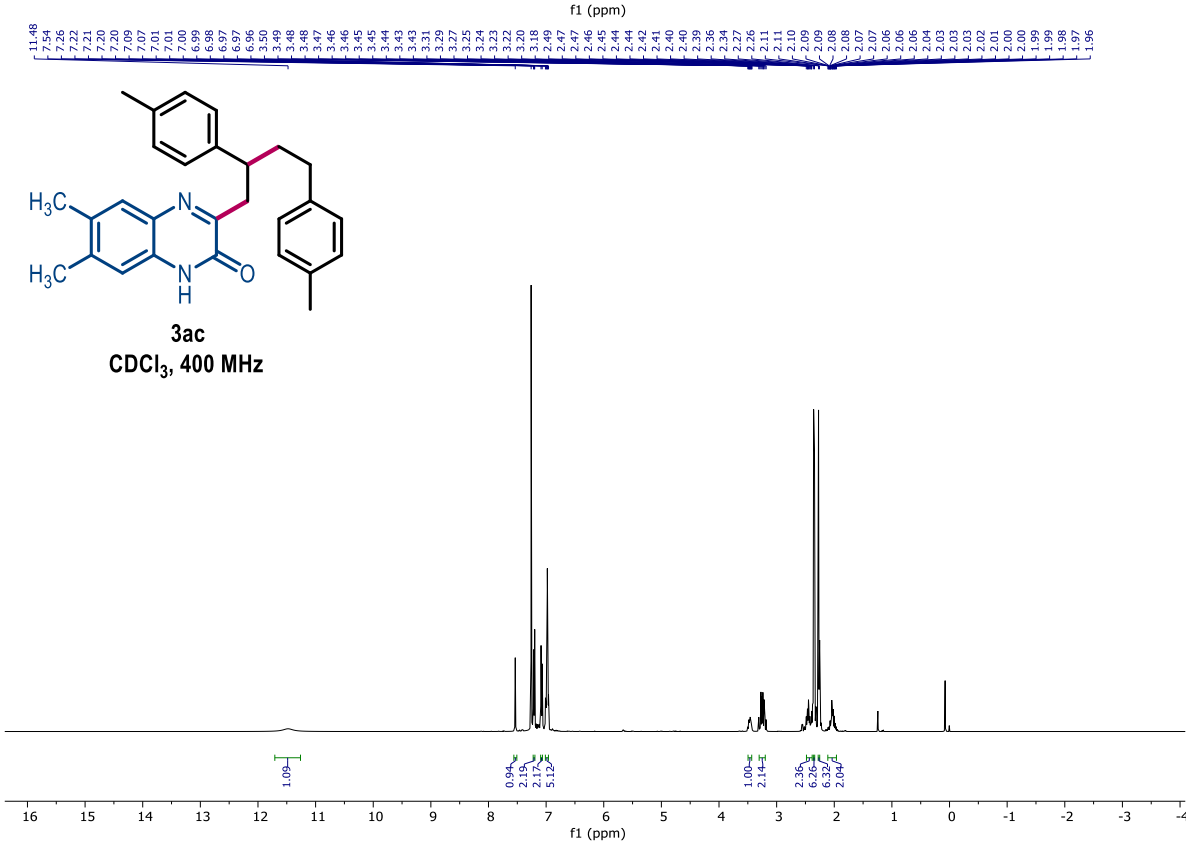

tBu
N
N
H
O
tBu
3z
CDCl3, 400 MHz
f1 (ppm)

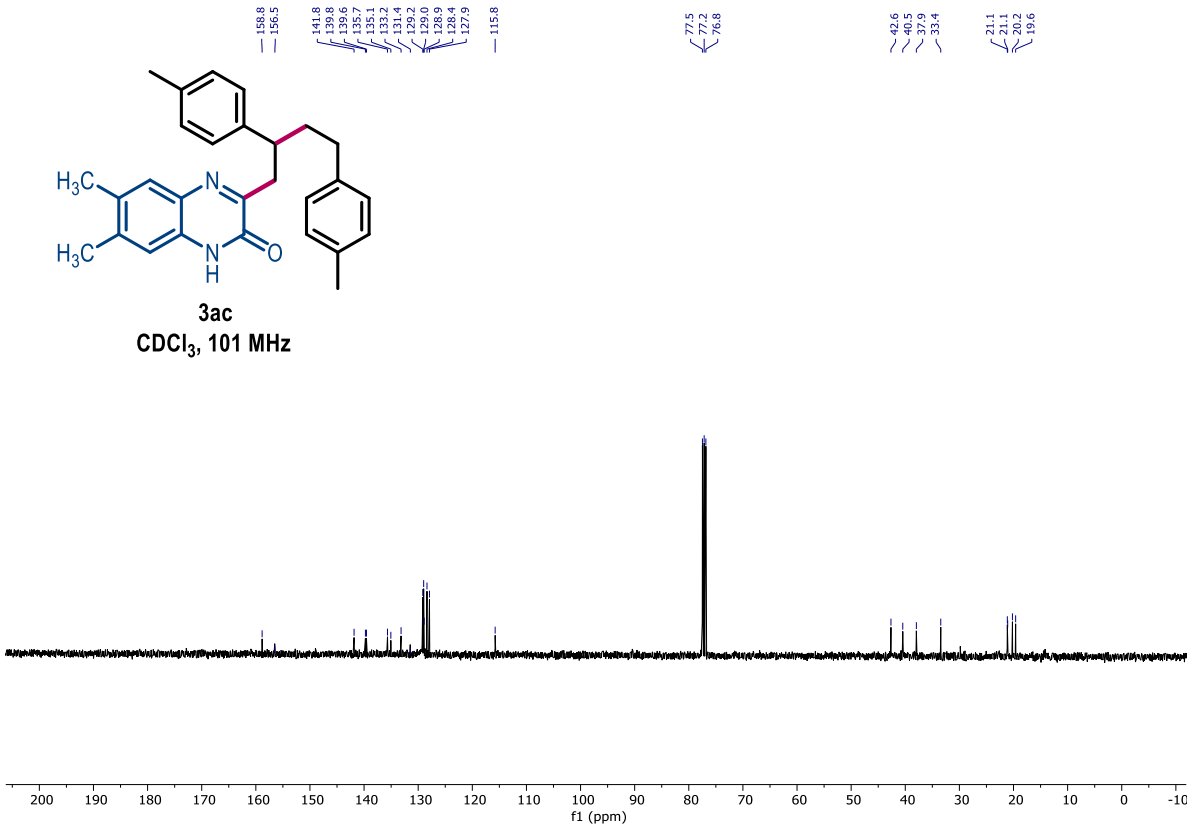

160.3
156.8
149.0
148.5
141.7
139.6
133.0
130.9
129.8
128.9
128.1
127.6
125.3
125.2
124.2
115.7
77.5
77.2
76.8
42.6
40.4
37.6
34.5
34.4
33.3
31.5
31.5
tBu
tBu
N
N
H
O
3z
CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

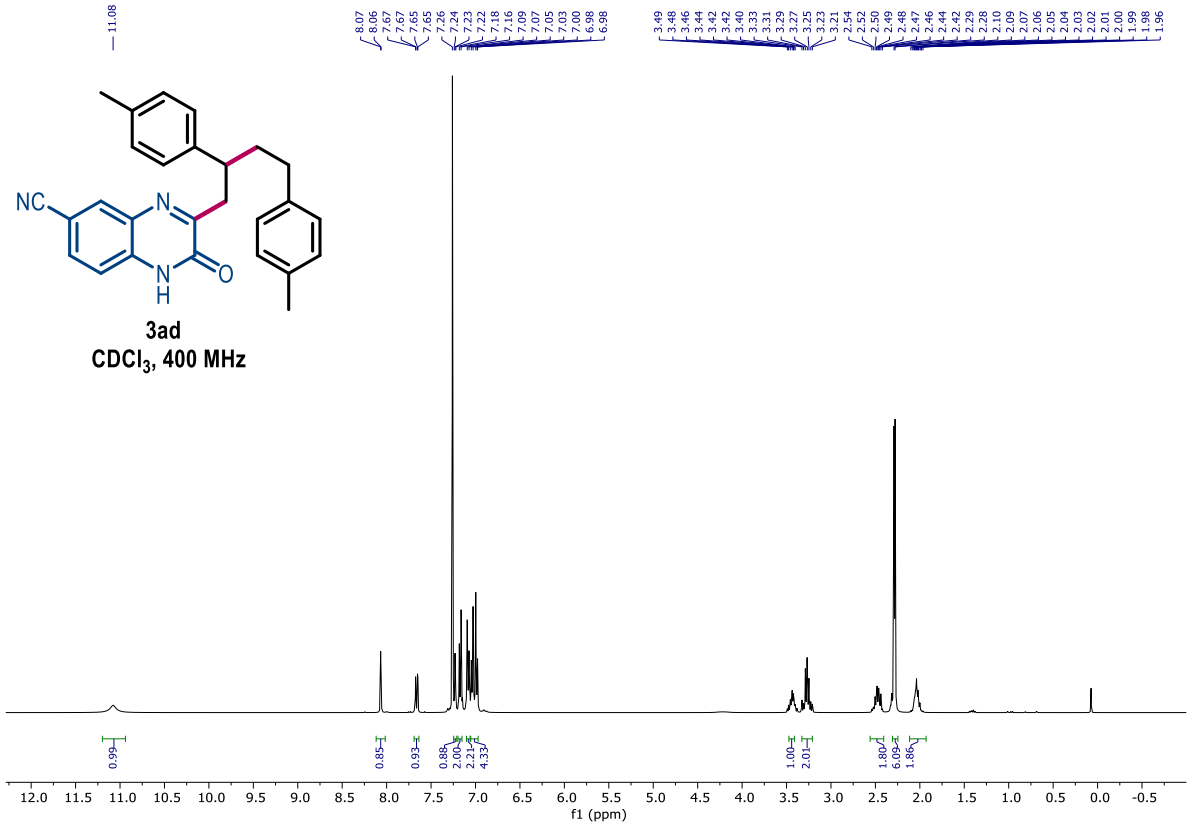

12.23
7.81
7.81
7.79
7.79
7.53
7.53
7.51
7.51
7.51
7.51
7.49
7.49
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.31
7.30
7.29
7.28
7.28
7.26
7.21
7.19
7.04
7.02
3.54
3.53
3.52
3.51
3.50
3.48
3.48
3.47
3.33
3.31
3.30
3.28
3.26
2.54
2.53
2.51
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.18
2.17
2.16
2.15
2.14
2.13
2.12
2.11
2.10
2.09
2.06
2.05
2.04
2.03
2.02
2.01
2.00
1.99
1.98
1.97
Cl
Cl
N
N
H
O
3aa
CDCl3, 400 MHz
1.02
1.14
1.16
1.11
2.04
3.01
2.00
2.11
1.00
2.00
2.37
2.09
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

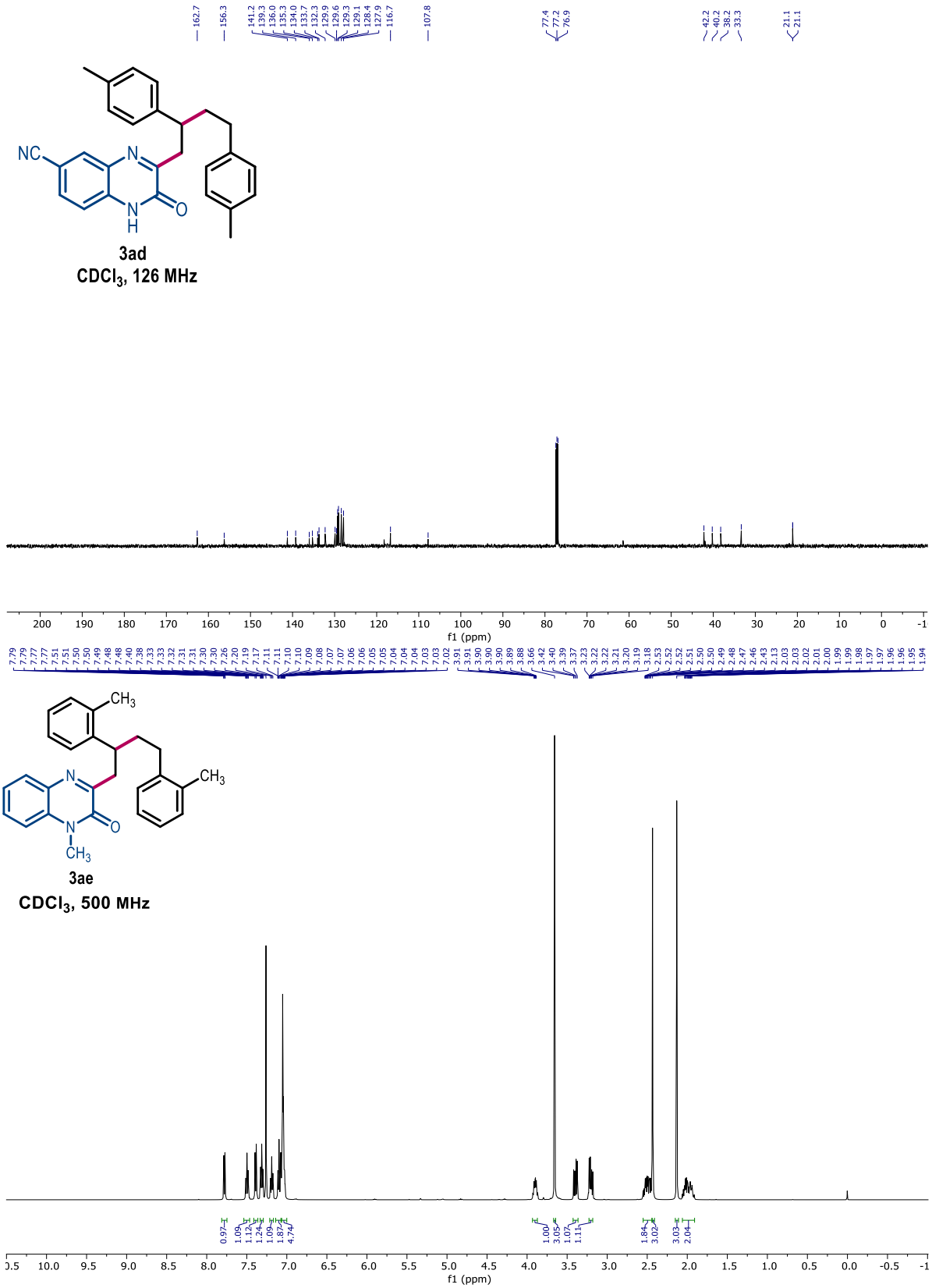

Cl
N
N
H
O
Cl
3aa
CDCl3, 101 MHz
159.4
156.6
142.9
140.5
132.9
132.1
131.6
130.8
130.0
129.8
129.4
128.9
128.7
128.5
124.4
115.7
77.5
77.2
76.8
42.1
40.0
37.6
33.0
f1 (ppm)
10.69
Me
Me
Me
Me
3ab
CDCl3, 400 MHz
f1 (ppm)

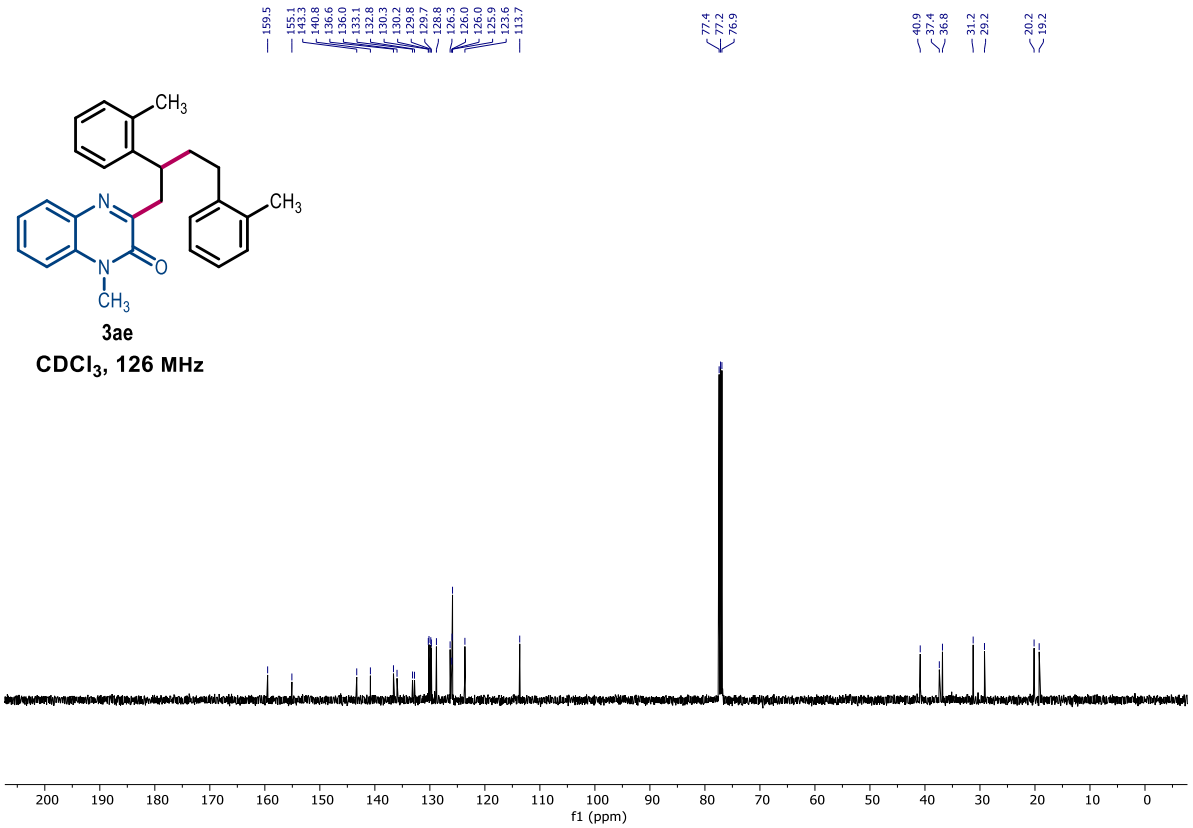

Me
Me
N
N
H
O
Me
Me
3ab
CDCl3, 101 MHz
f1 (ppm)


H3C
H3C
N
N
H
O
3ac
CDCl3, 400 MHz
f1 (ppm)


158.8
156.5
141.8
139.8
139.6
135.7
135.1
133.2
131.4
129.2
129.0
128.9
128.4
127.9
115.8
77.5
77.2
76.8
42.6
40.5
37.9
33.4
21.1
21.1
20.2
19.6
H3C
H3C
N
N
H
O
3ac
CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

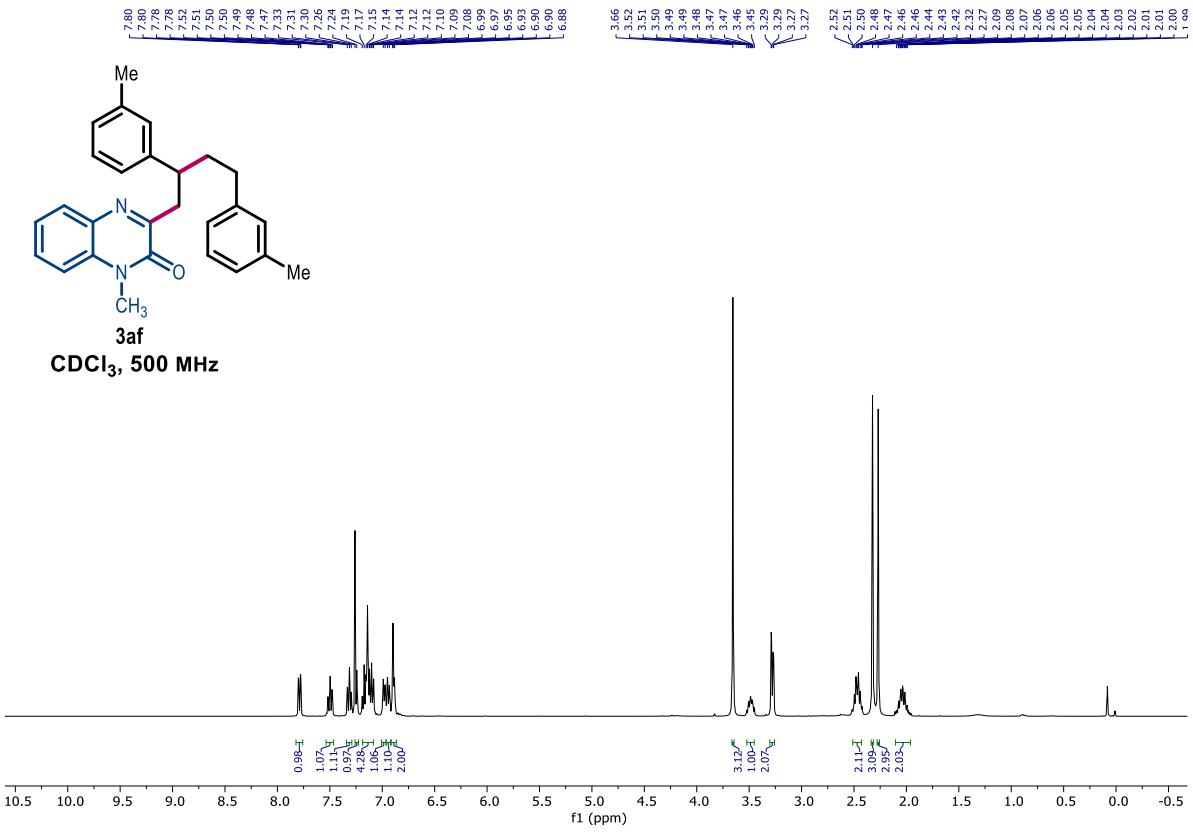

11.08
8.07
8.06
7.67
7.67
7.65
7.65
7.26
7.24
7.23
7.22
7.18
7.16
7.09
7.07
7.05
7.03
7.00
6.98
6.98
3.49
3.48
3.46
3.44
3.42
3.42
3.40
3.33
3.31
3.29
3.27
3.25
3.23
3.21
2.54
2.52
2.50
2.49
2.48
2.47
2.46
2.44
2.42
2.29
2.28
2.10
2.09
2.07
2.06
2.05
2.04
2.03
2.02
2.01
2.00
1.99
1.98
1.96
NC
N
N
H
O
3ad
CDCl3, 400 MHz
0.99
0.85
0.93
0.88
2.00
2.21
4.33
1.00
2.01
1.80
6.09
1.86
12.0
11.5
11.0
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
f1 (ppm)


NC
N
N
H
O
3ad
CDCl3, 126 MHz
f1 (ppm)
CH3
CH3
N
O
N
CH3
3ae
CDCl3, 500 MHz
f1 (ppm)



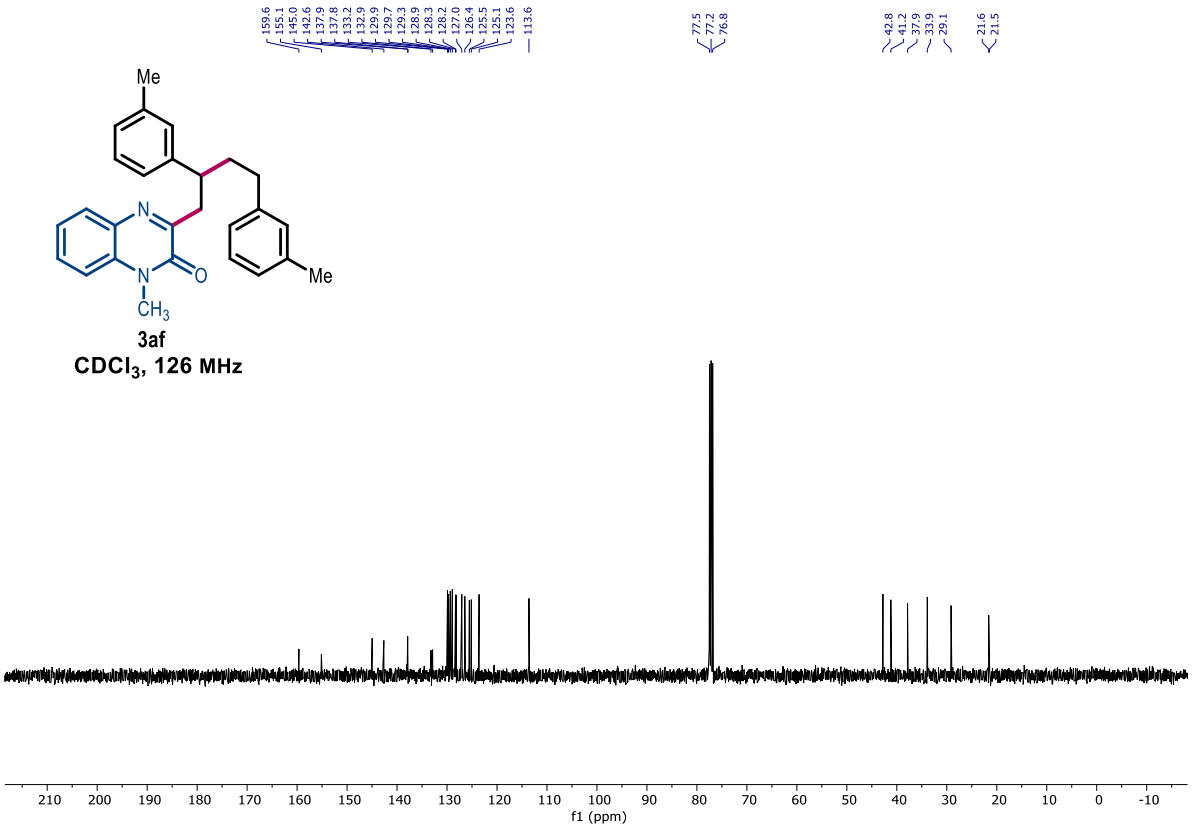
3ae

$CDCl_3$, 126 MHz



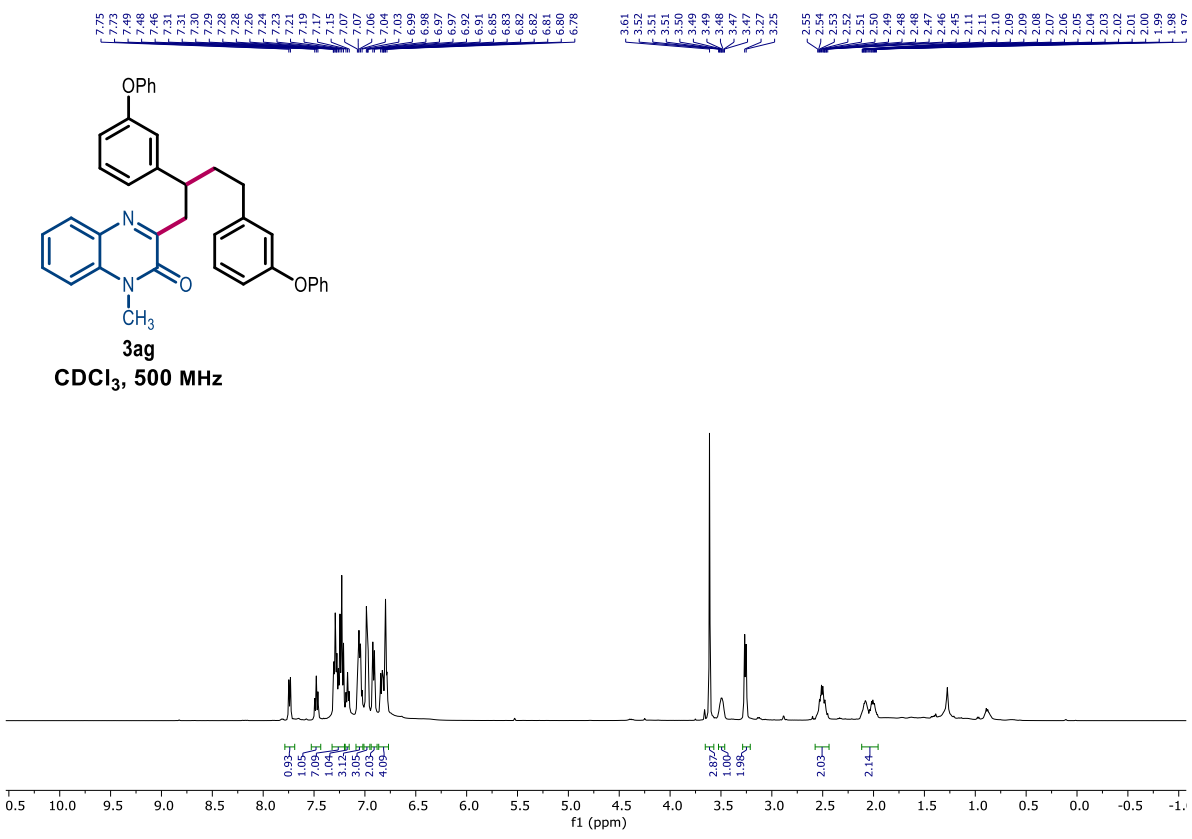
3af

$CDCl_3$, 500 MHz



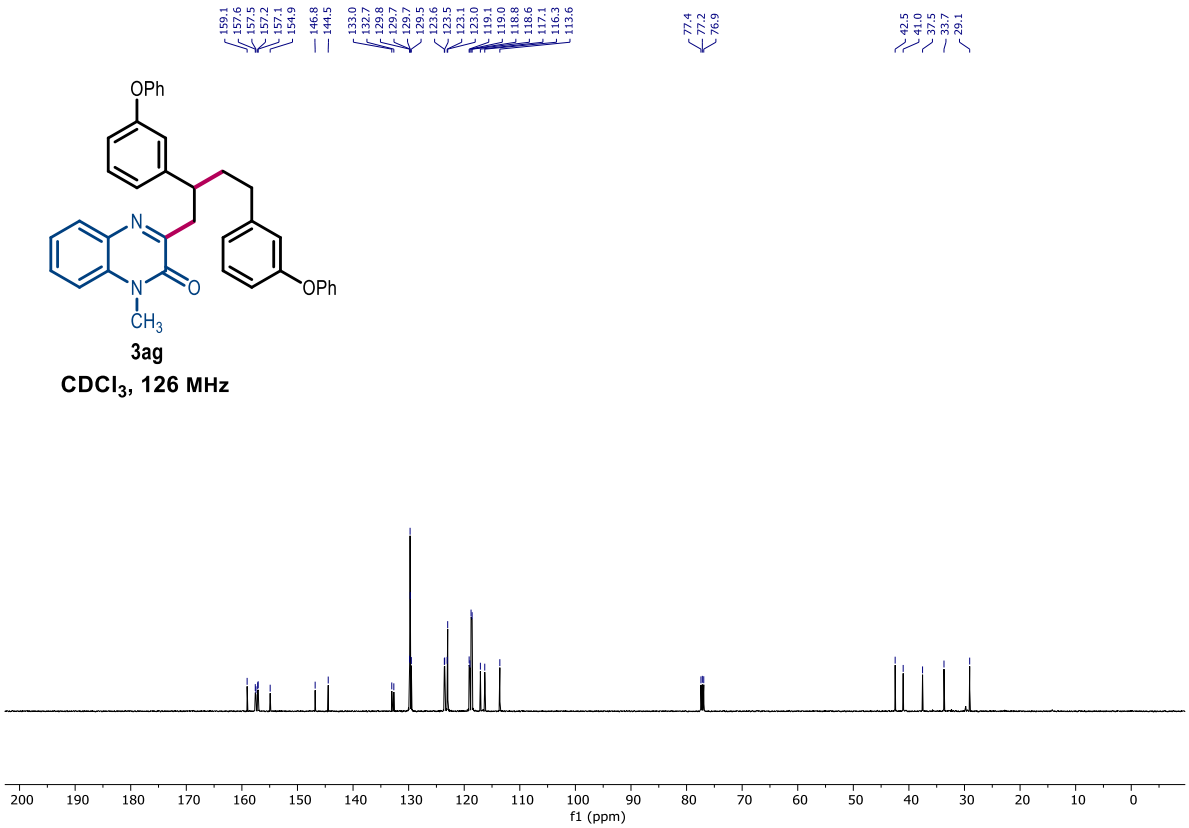
3af

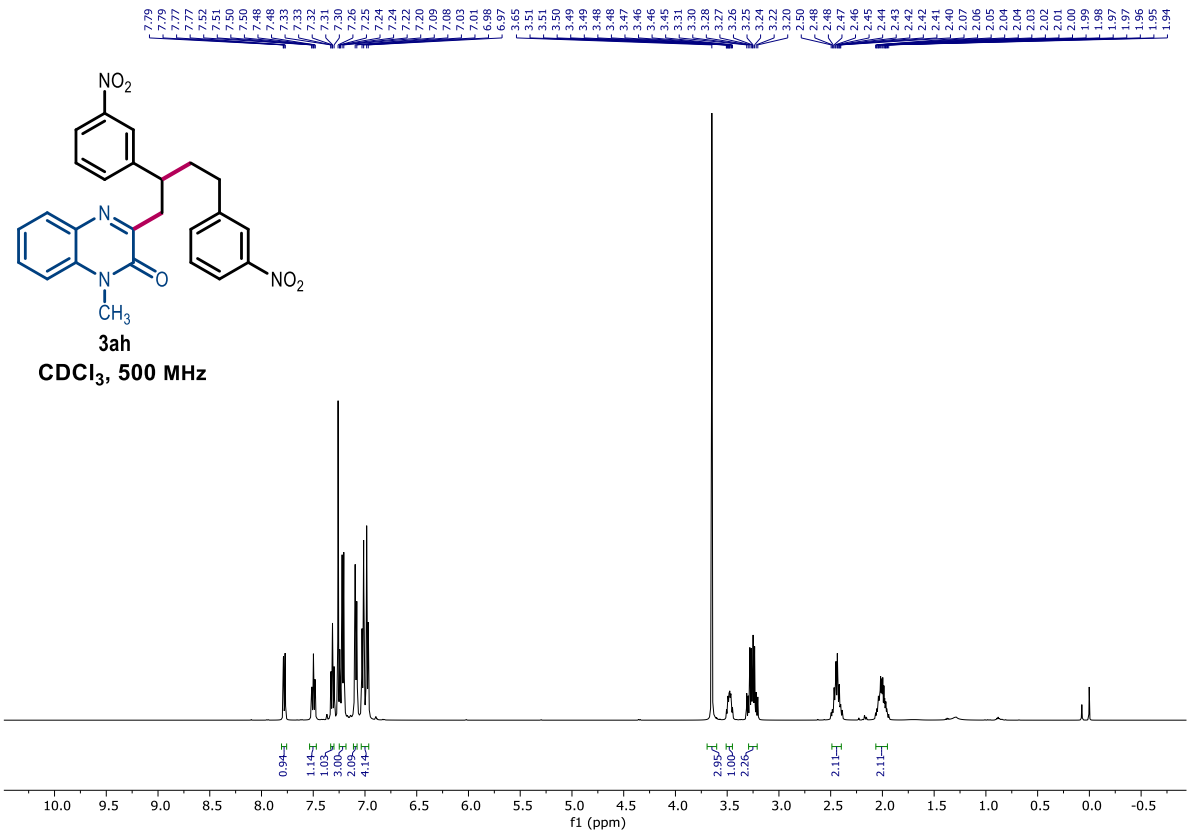
$CDCl_3$, 126 MHz

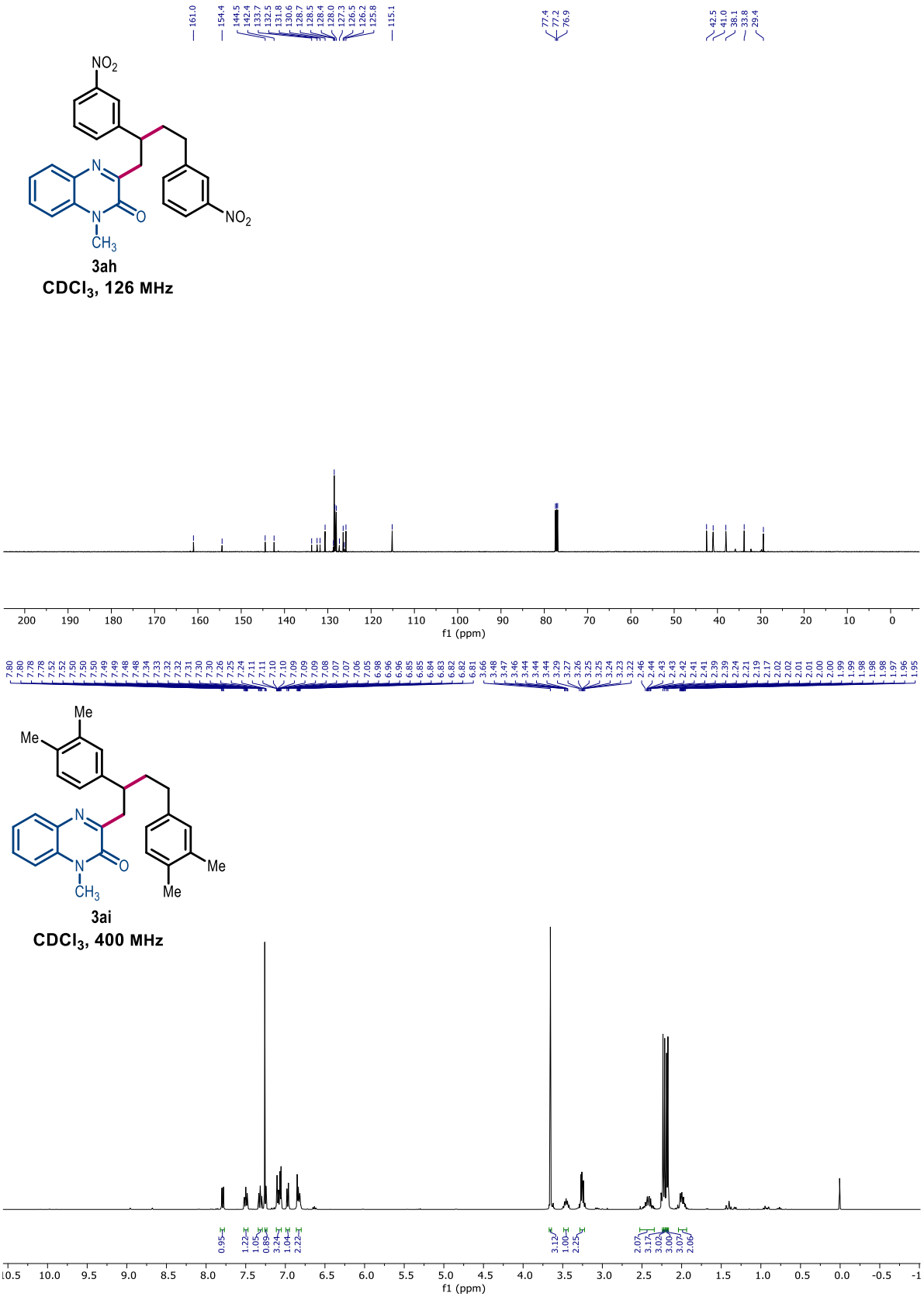


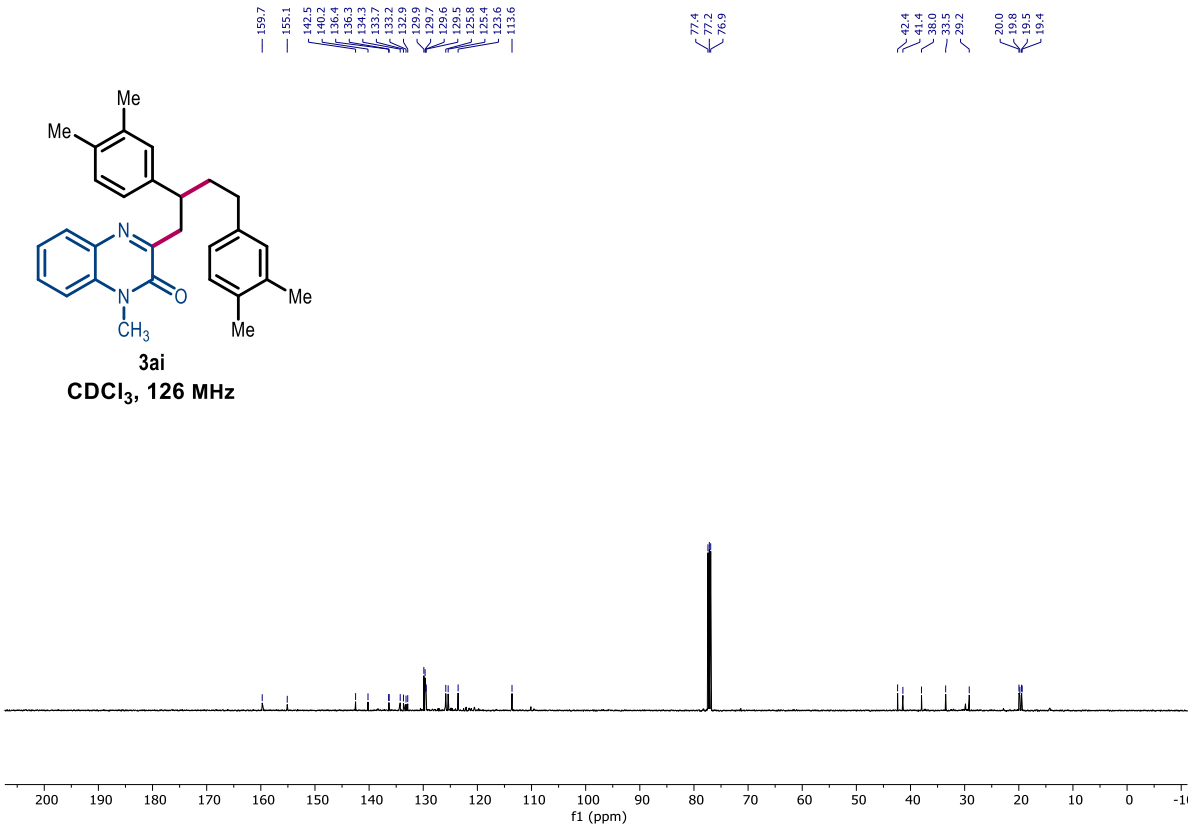
3ag

$CDCl_3$, 500 MHz


OPh
N
O
N
CH3
OPh
3ag
CDCl3, 126 MHz
f1 (ppm)

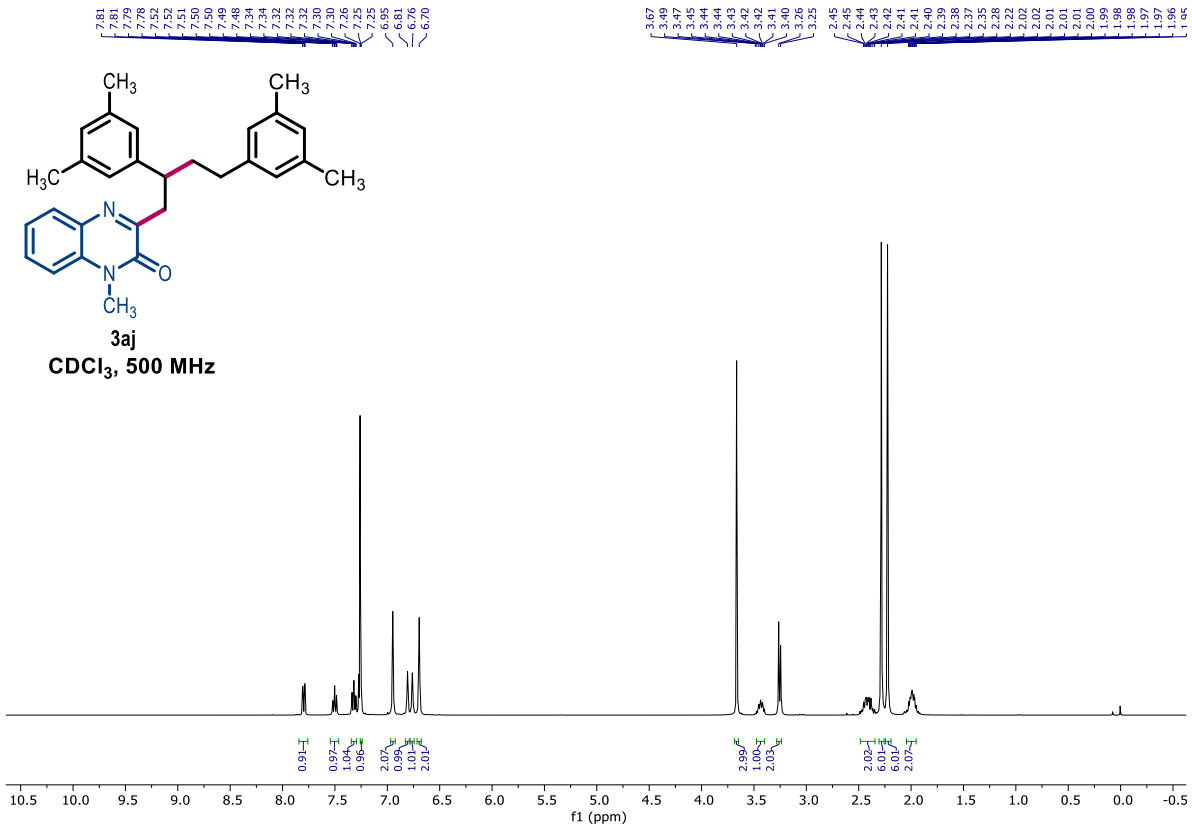

NO2
N
O
N
CH3
NO2
3ah
CDCl3, 500 MHz
f1 (ppm)


161.0
154.4
144.5
142.4
133.7
132.5
131.8
130.6
128.7
128.5
128.4
128.0
127.3
126.5
126.2
125.8
115.1
77.4
77.2
76.9
42.5
41.0
38.1
33.8
29.4
NO2
N
O
N
CH3
NO2
3ah
CDCl3, 126 MHz
f1 (ppm)
7.80
7.78
7.52
7.50
7.49
7.48
7.34
7.33
7.32
7.31
7.30
7.26
7.25
7.24
7.11
7.10
7.09
7.08
7.07
7.06
7.05
6.98
6.96
6.85
6.84
6.83
6.82
6.81
3.66
3.48
3.47
3.46
3.44
3.29
3.27
3.26
3.25
3.24
3.23
3.22
2.46
2.44
2.43
2.42
2.41
2.39
2.24
2.21
2.19
2.17
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.95
Me
Me
N
O
N
CH3
Me
Me
3ai
CDCl3, 400 MHz
0.95
1.22
1.05
0.89
3.24
1.04
2.22
3.12
1.00
2.25
2.07
3.17
3.02
3.00
3.07
2.06
f1 (ppm)



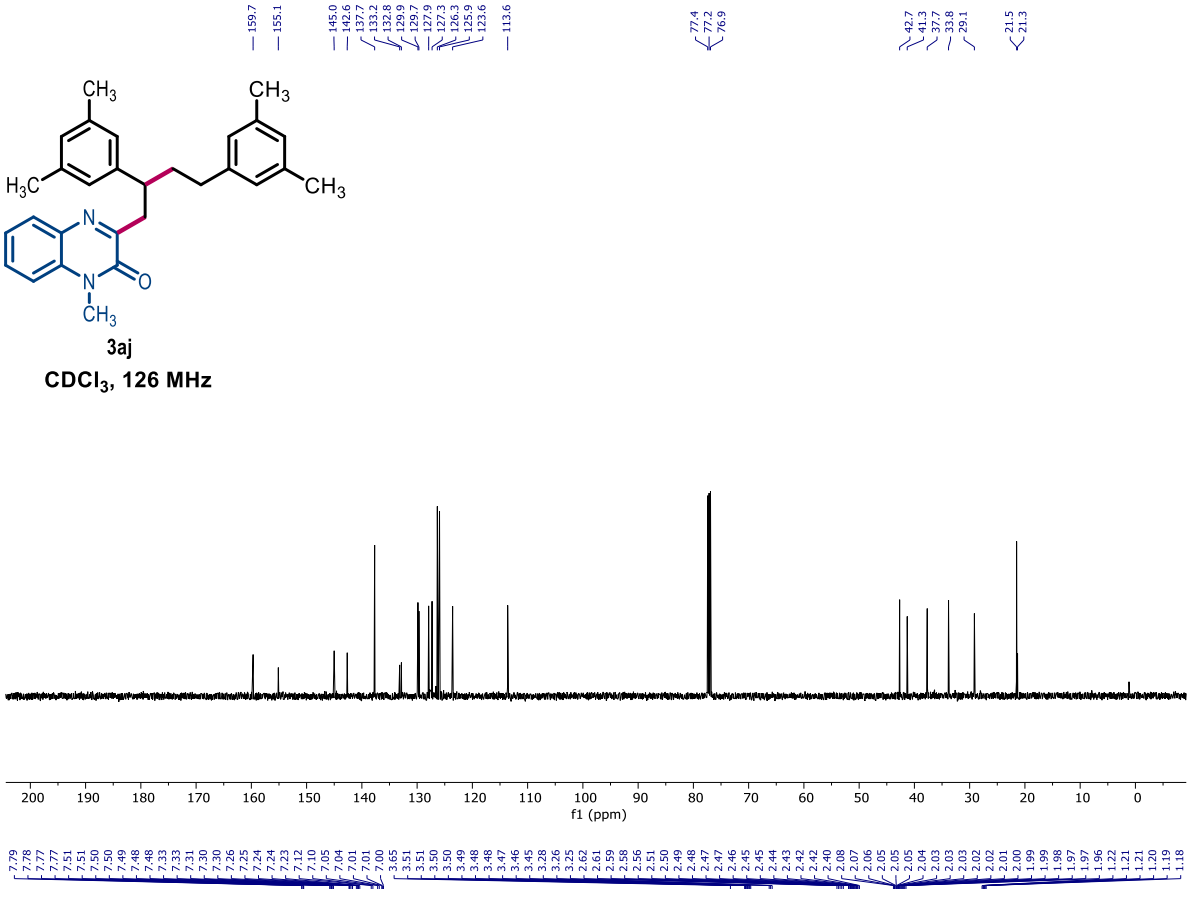
3ai

$CDCl_3$, 126 MHz



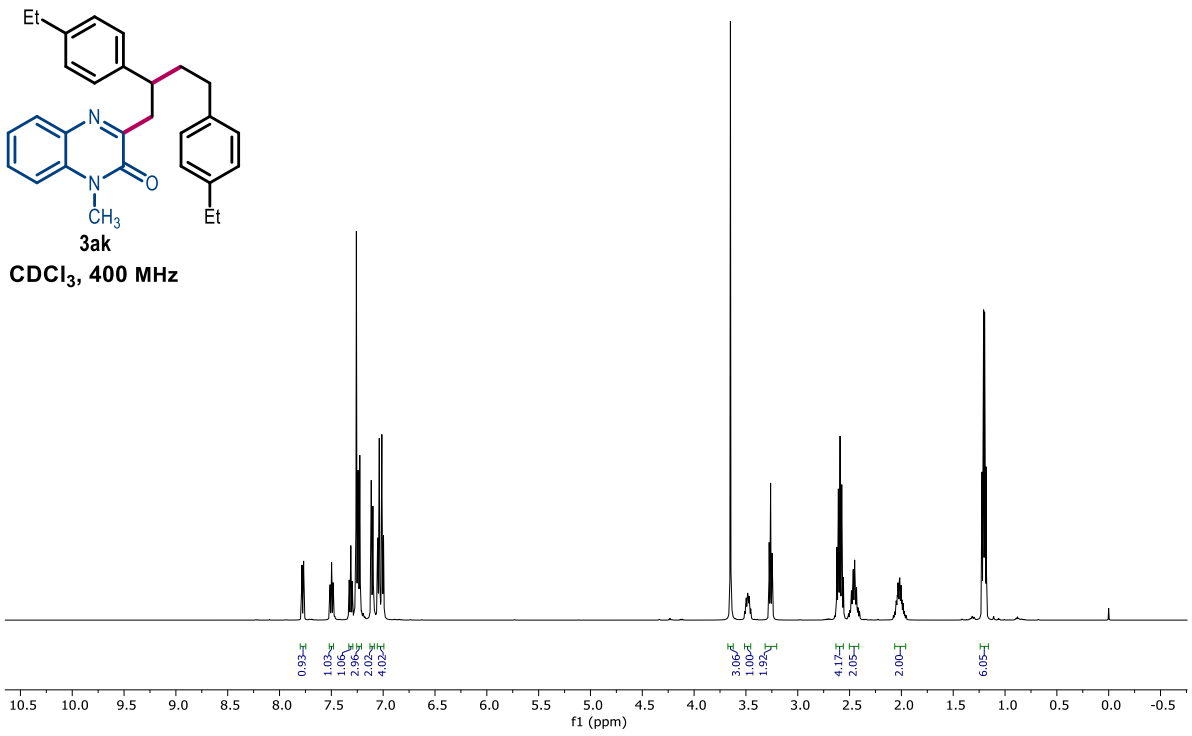
3aj

$CDCl_3$, 500 MHz



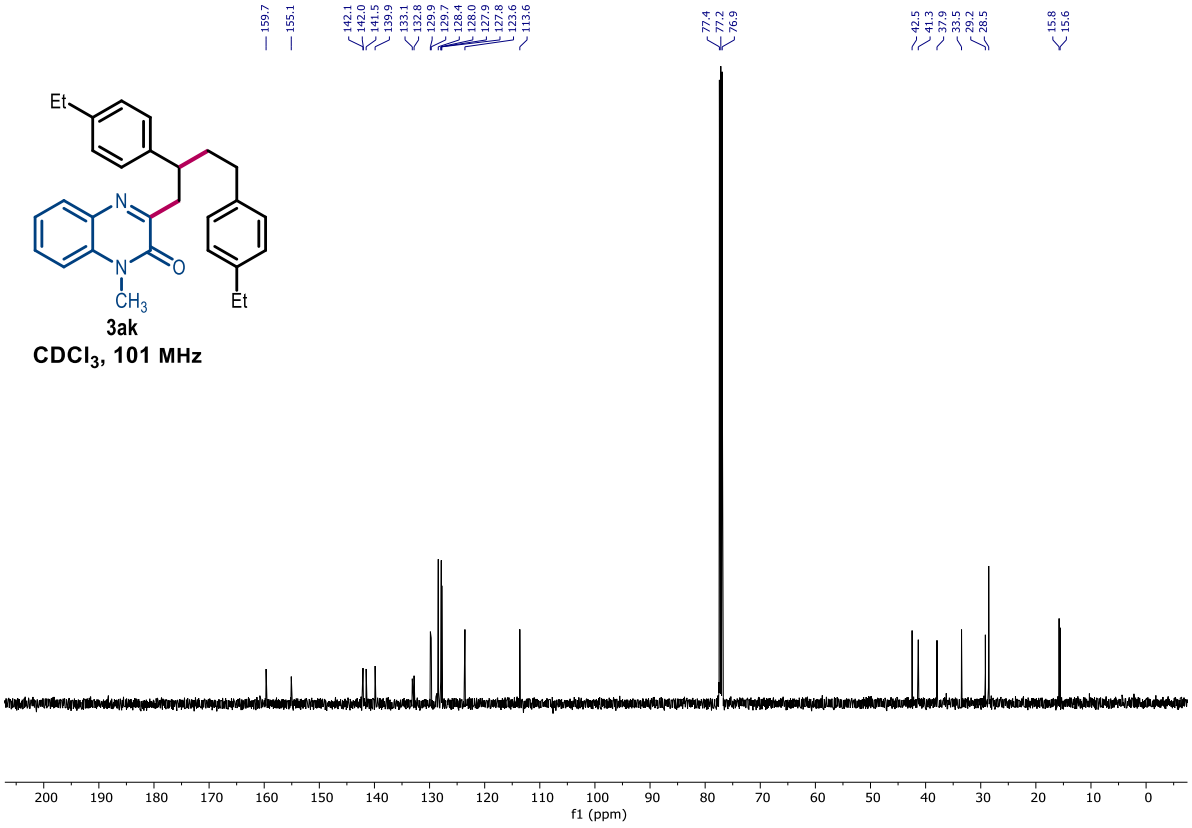
3aj

$CDCl_3$, 126 MHz



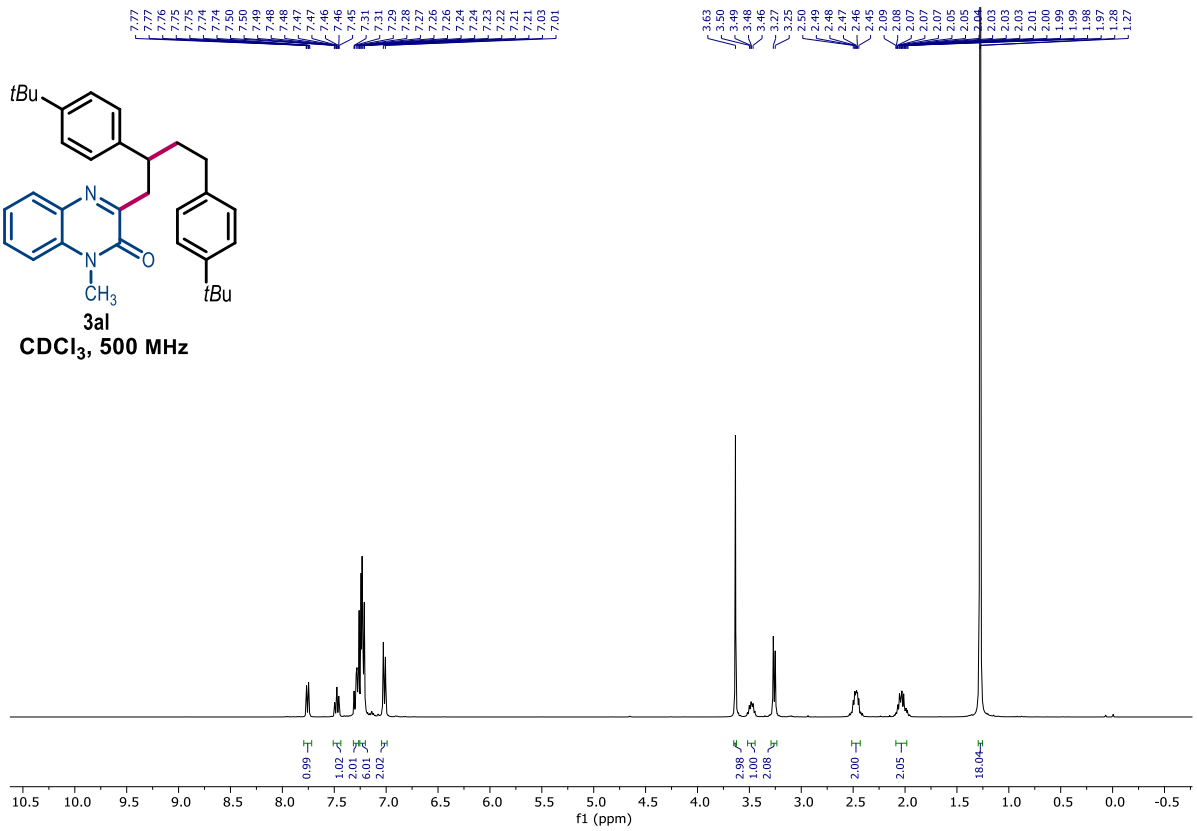
3ak

$CDCl_3$, 400 MHz



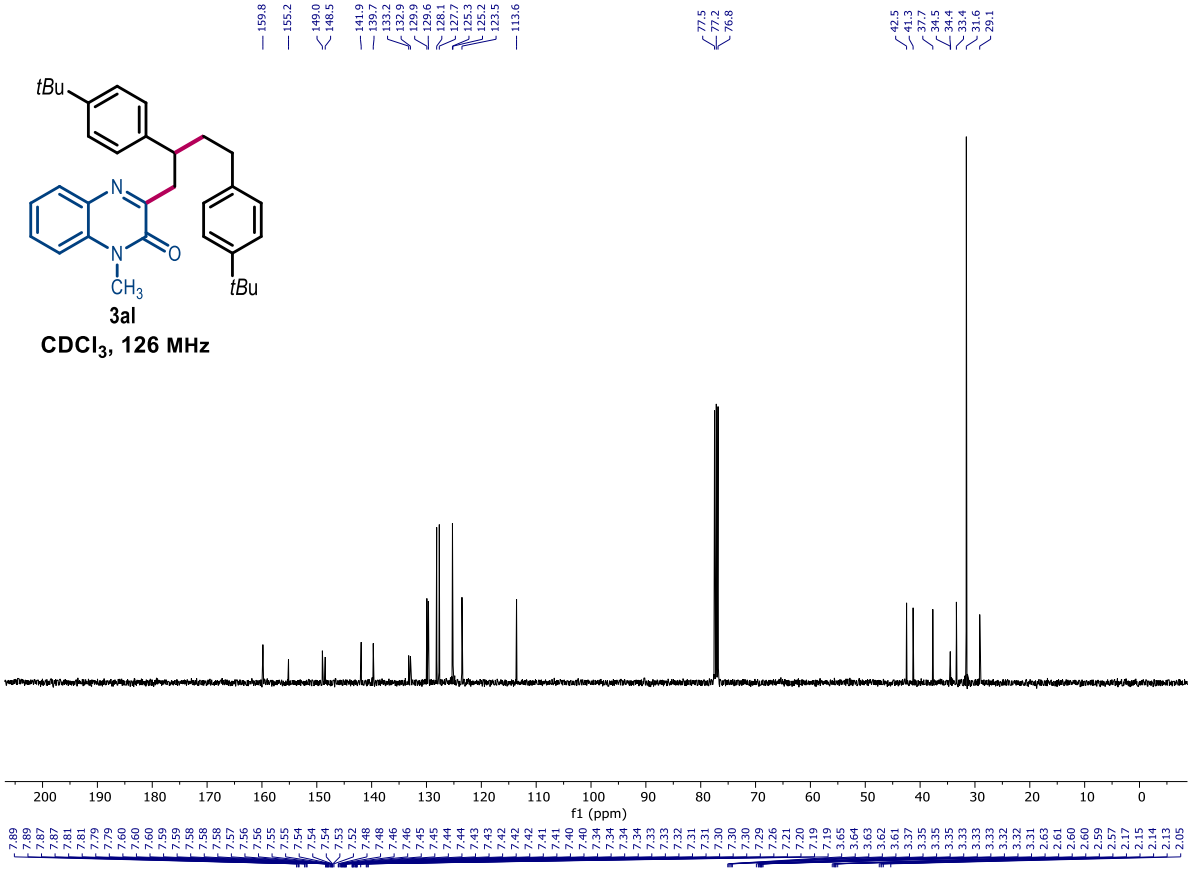
3ak

$CDCl_3$, 101 MHz



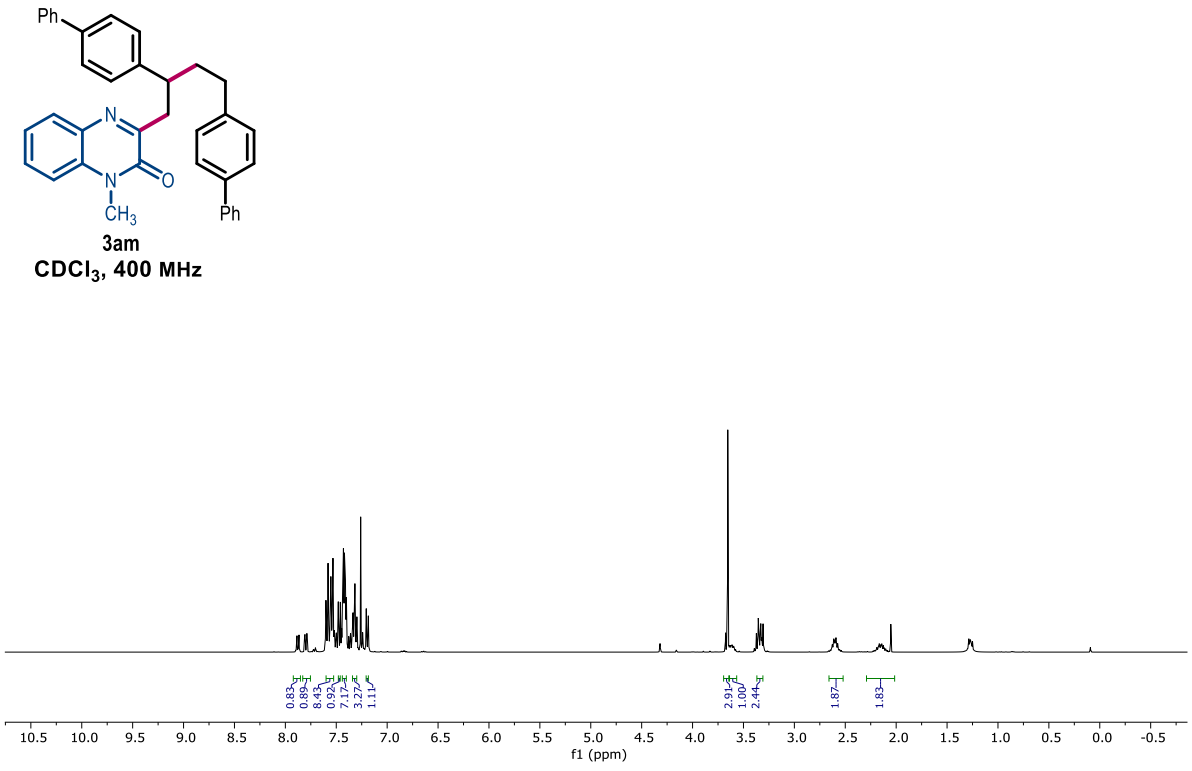
3al

$CDCl_3$, 500 MHz



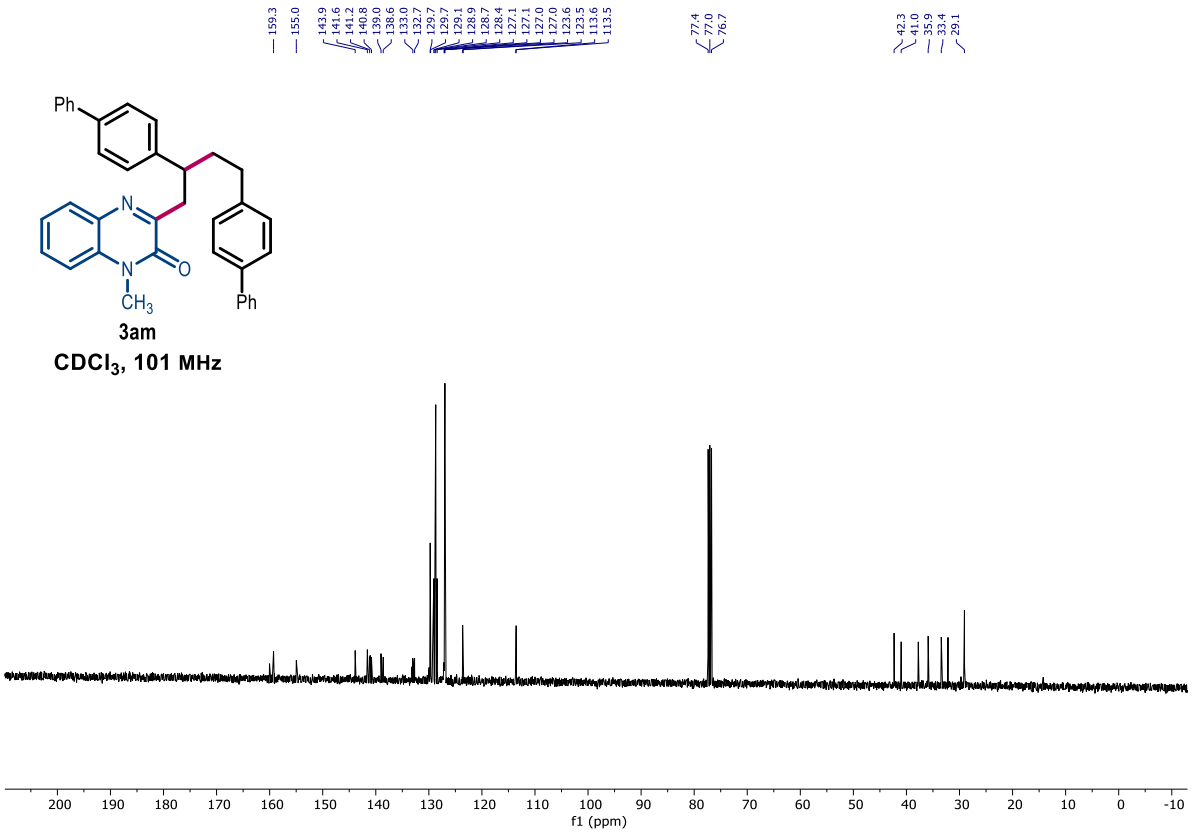
3al

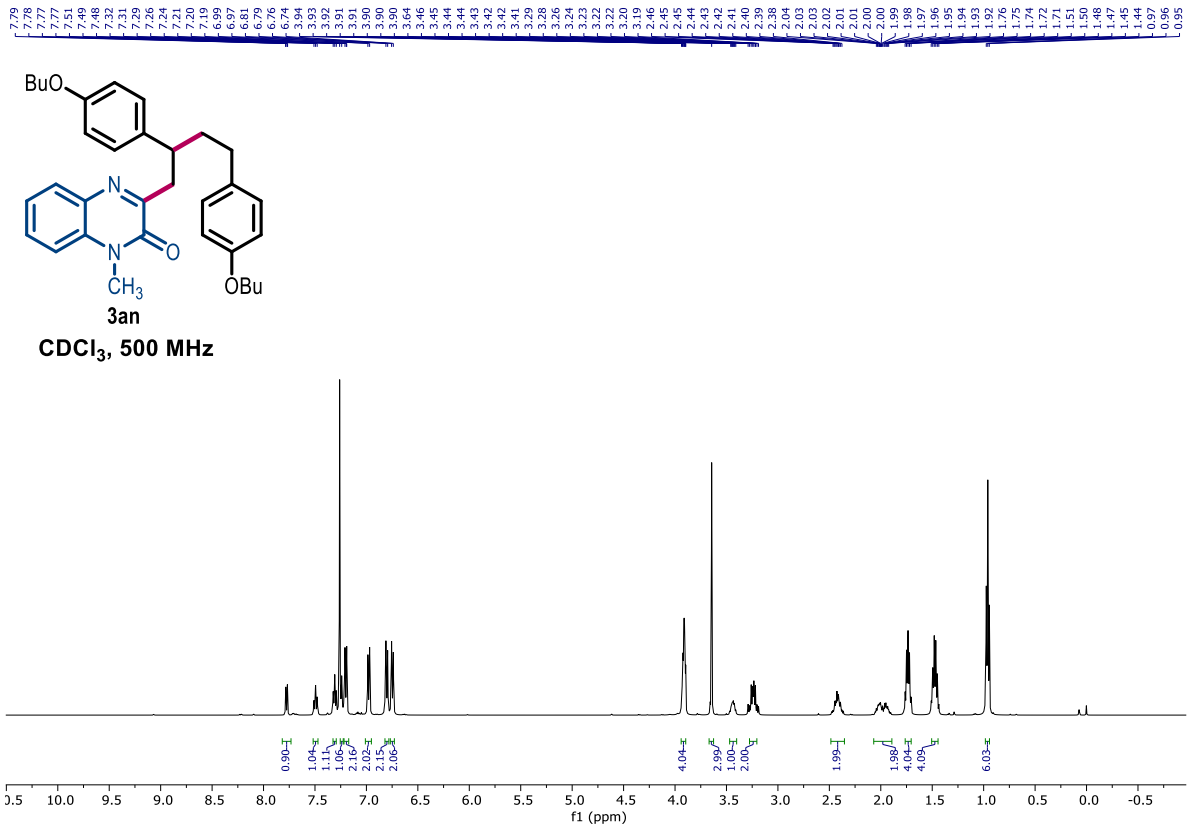
$CDCl_3$, 126 MHz

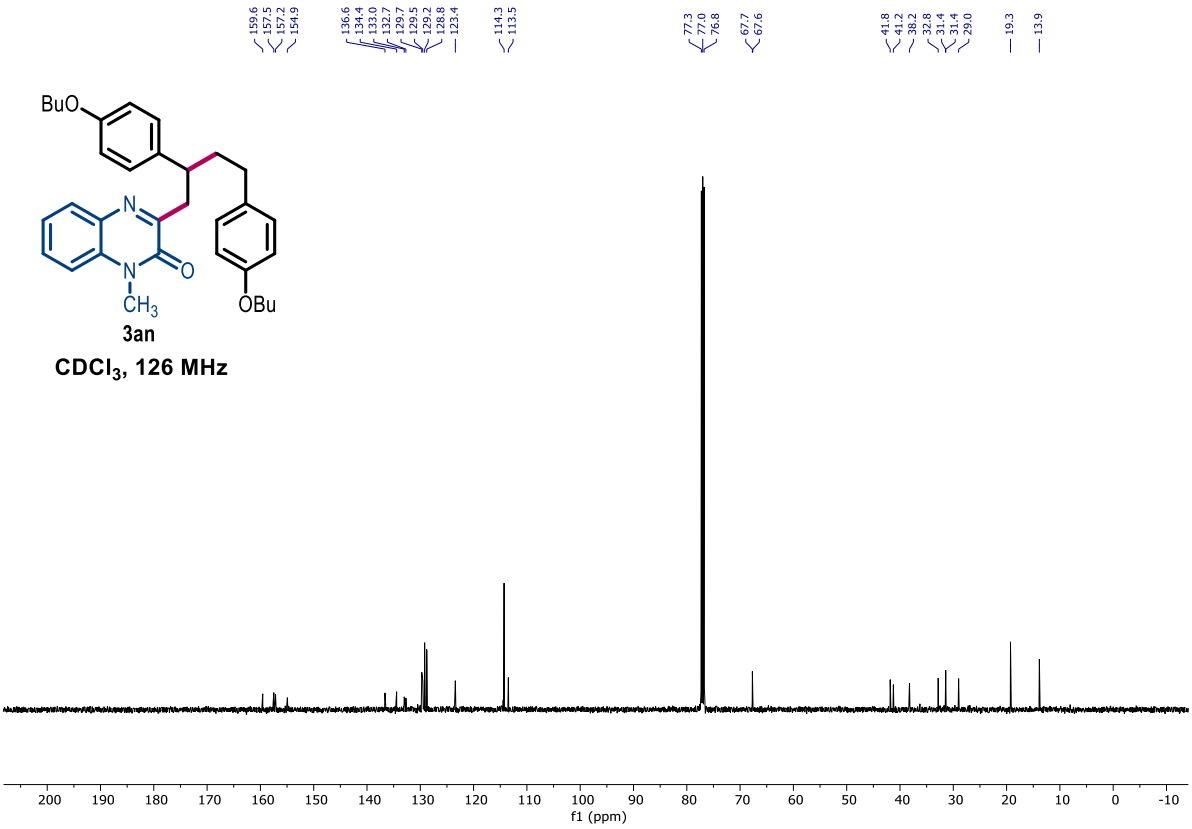


3am

$CDCl_3$, 400 MHz

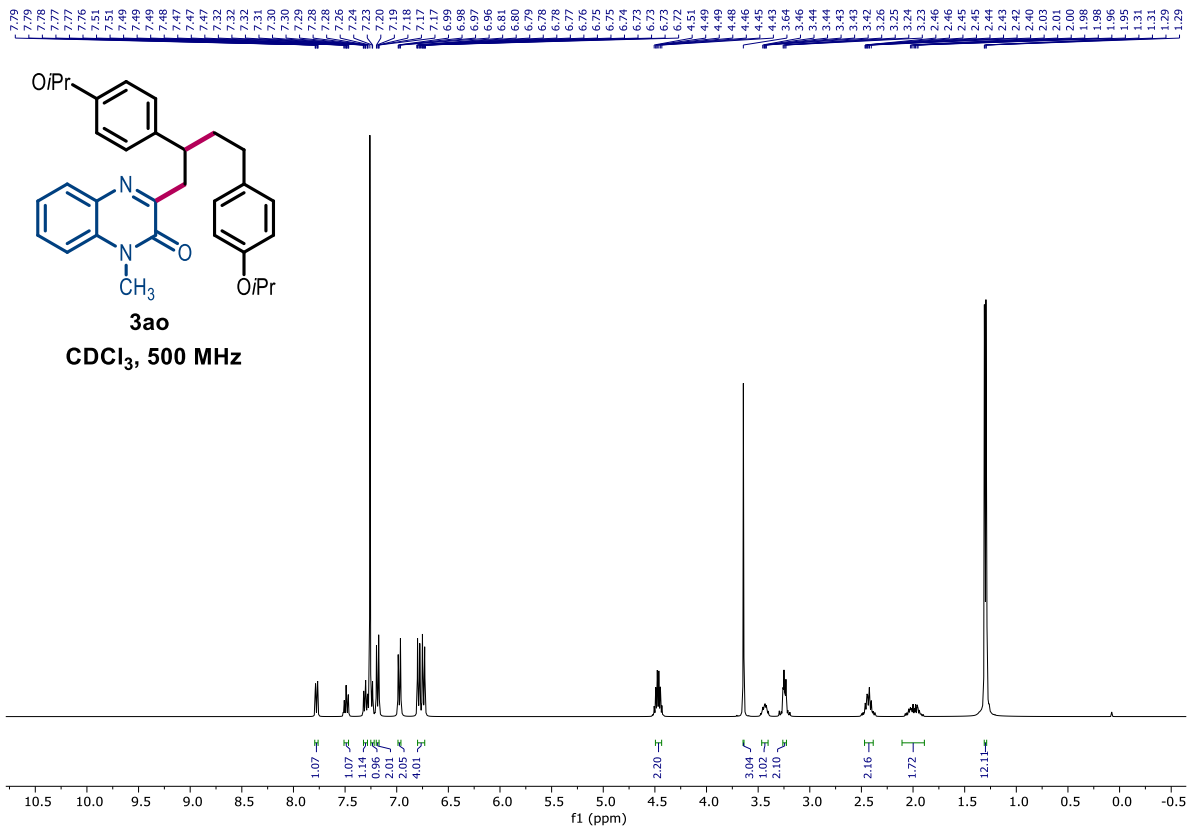

Ph
N
O
N
CH3
Ph
3am
CDCl3, 101 MHz
f1 (ppm)


BuO
N
O
N
CH3
OBu
3an
CDCl3, 500 MHz
f1 (ppm)



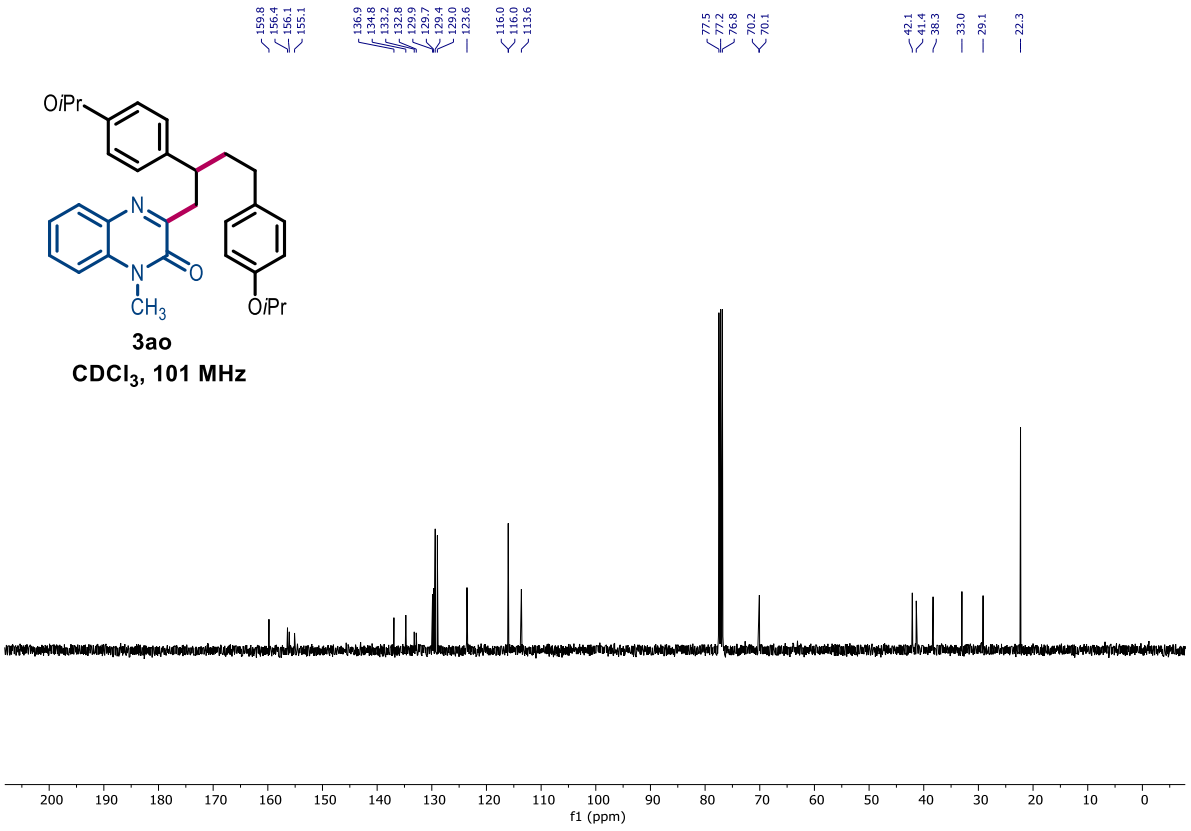
3an

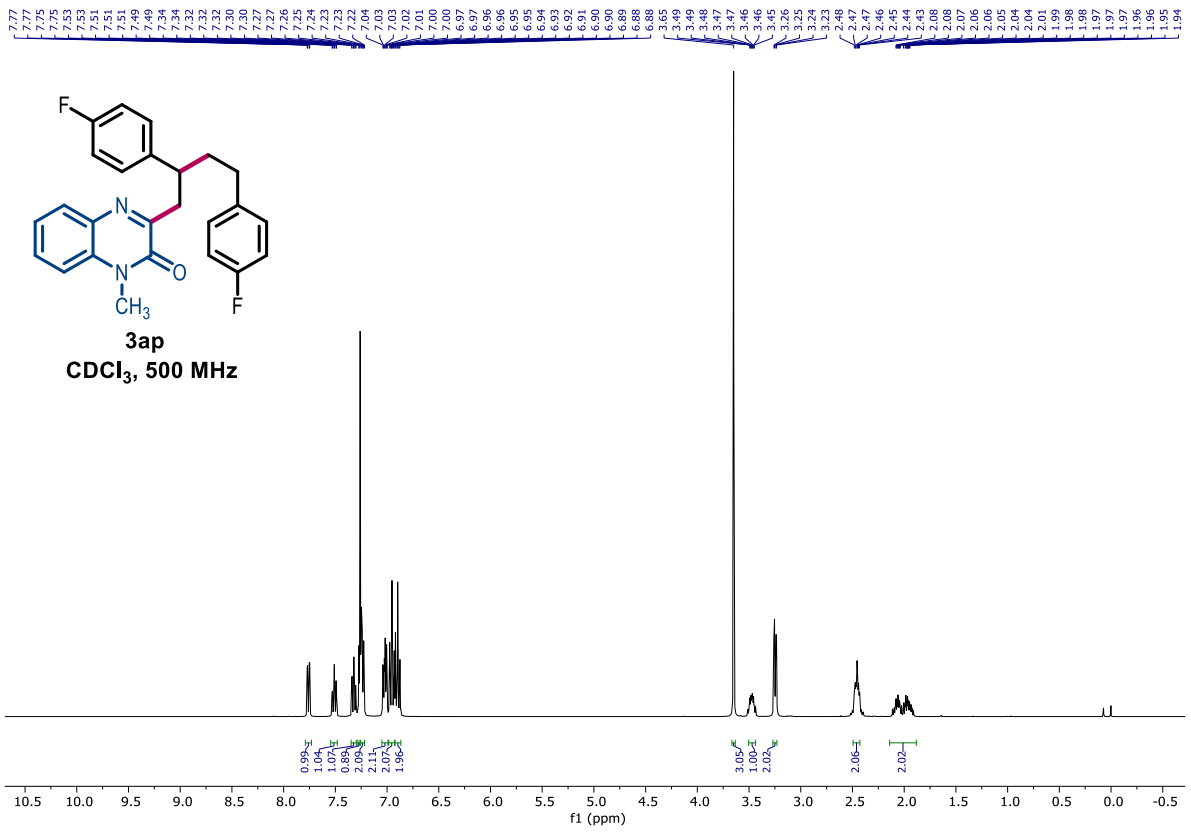
$CDCl_3$, 126 MHz

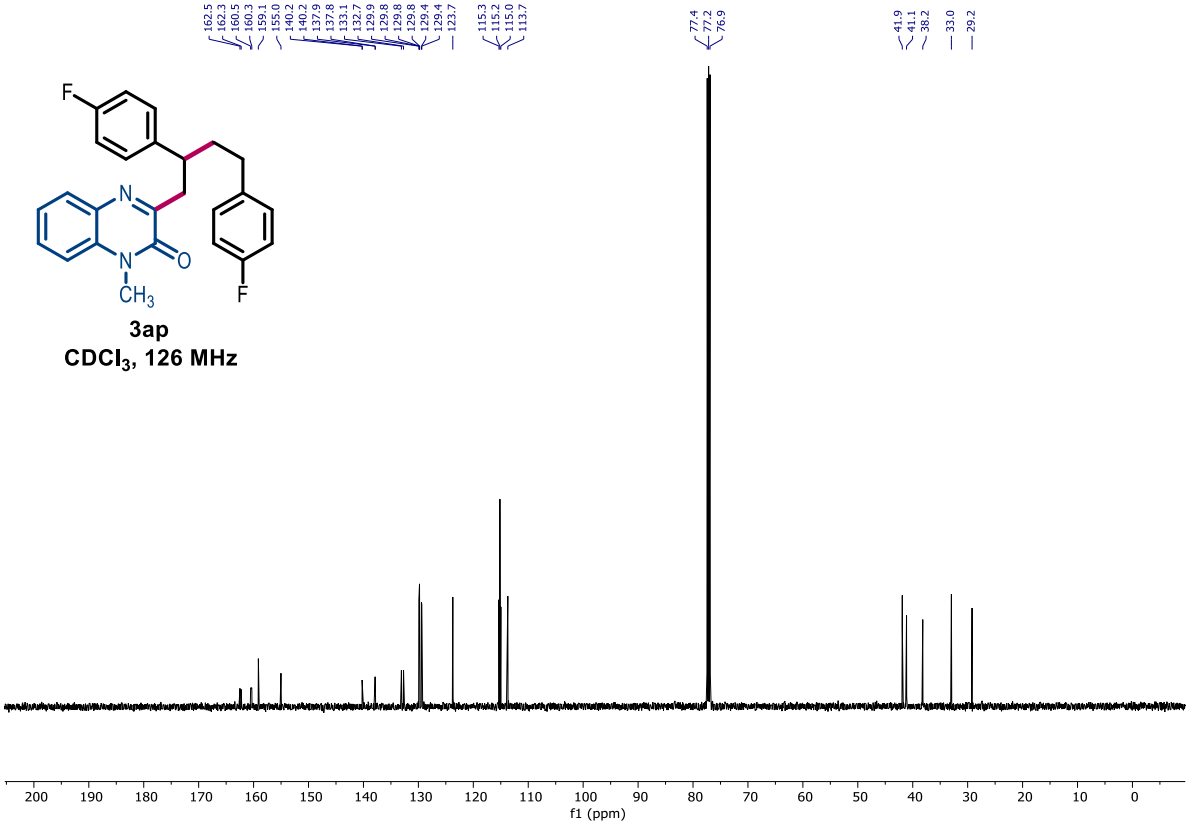


3ao

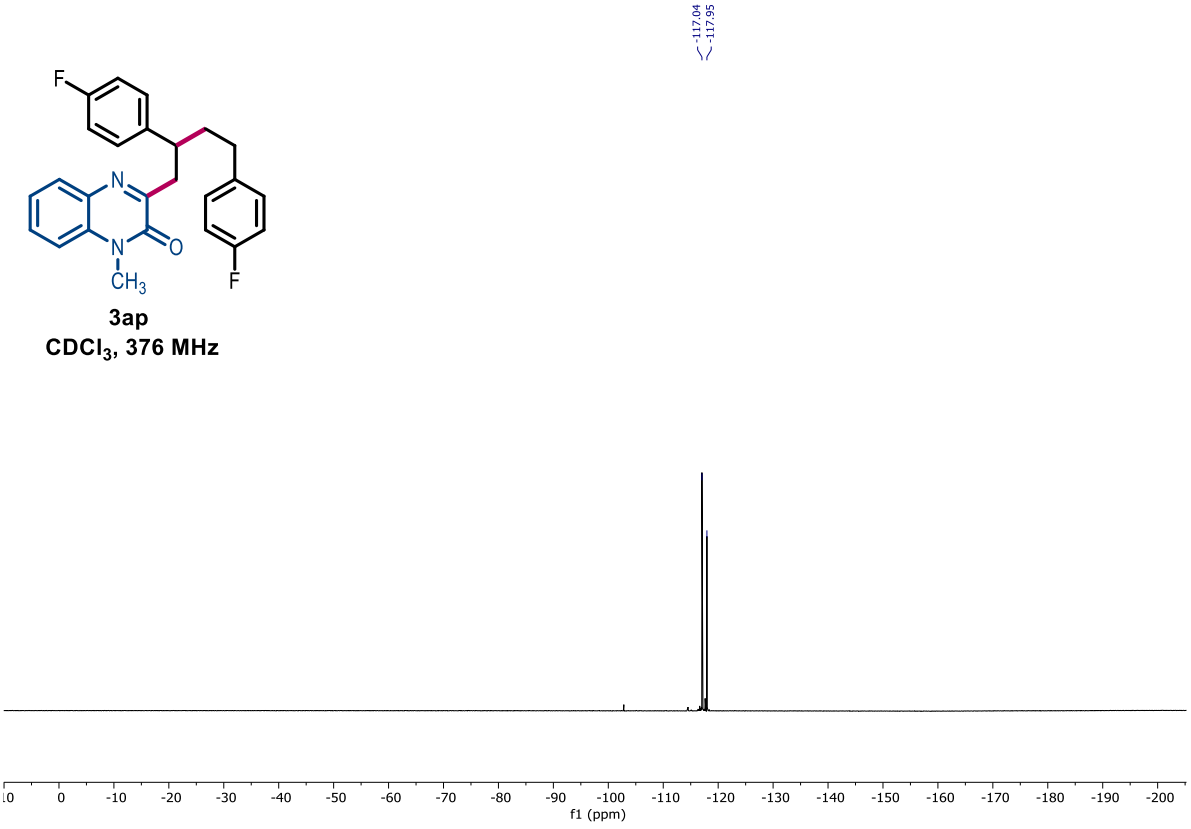
$CDCl_3$, 500 MHz


OiPr
N
N
O
CH3
OiPr
3ao
CDCl3, 101 MHz
f1 (ppm)

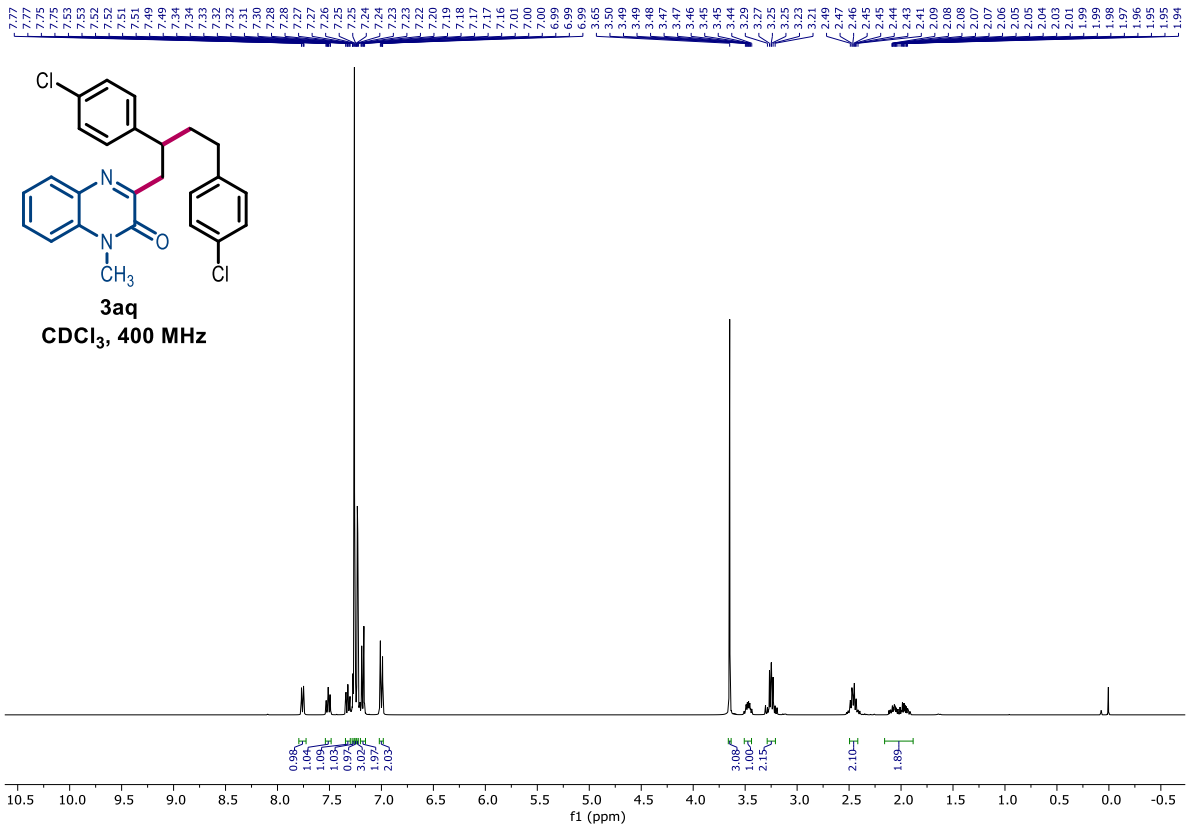

F
N
N
O
CH3
F
3ap
CDCl3, 500 MHz
f1 (ppm)

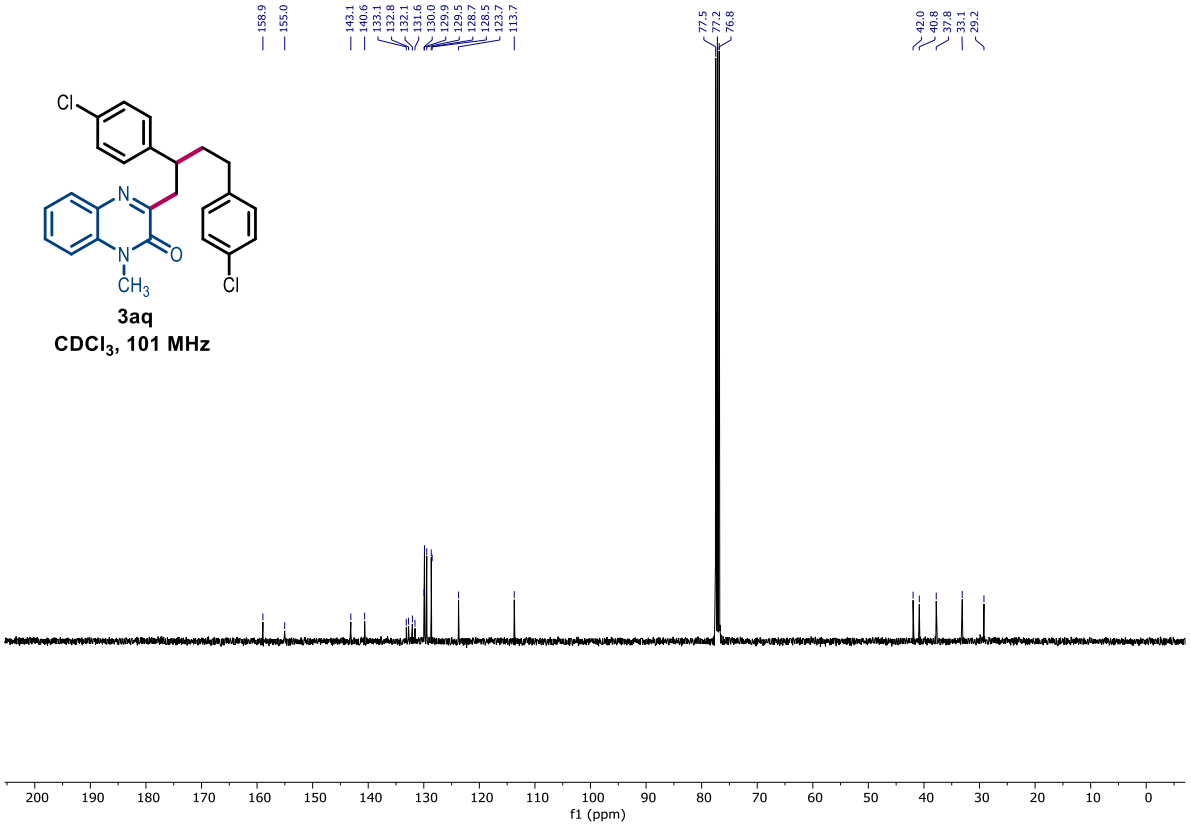


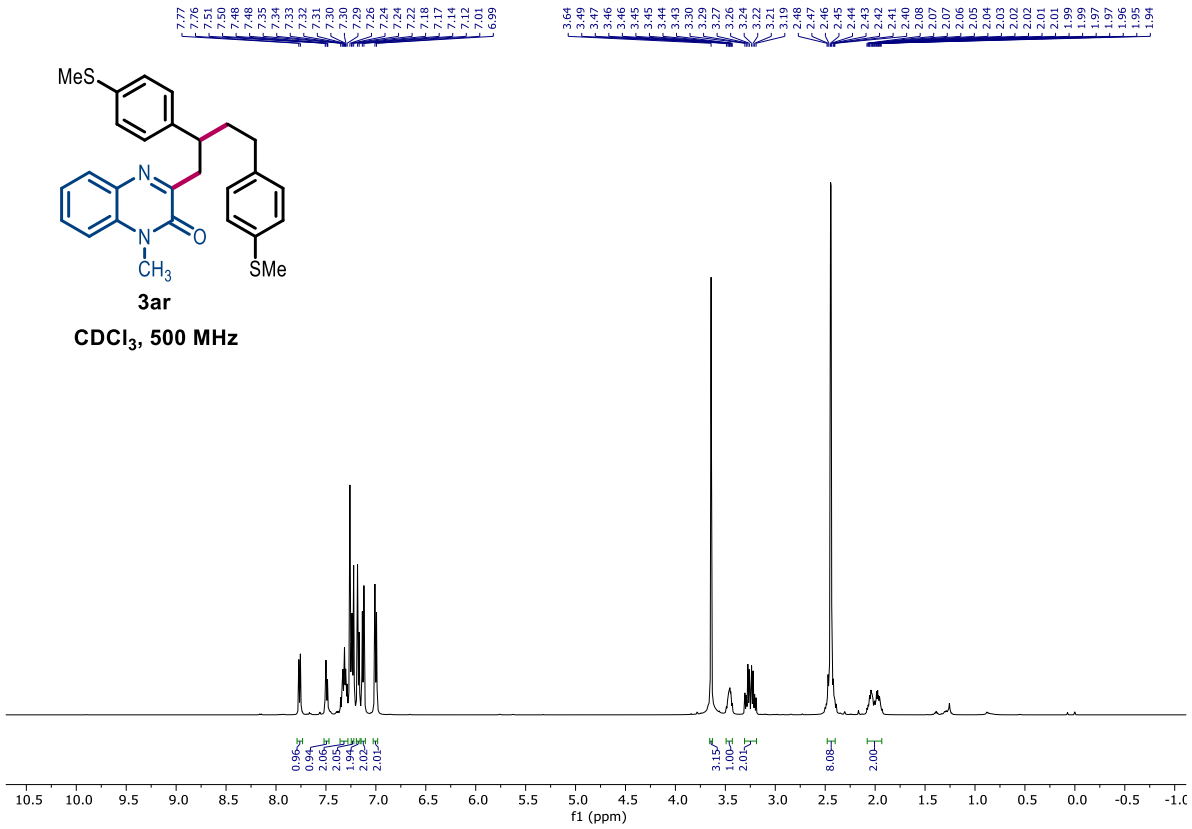
3ap
$CDCl_3$, 126 MHz

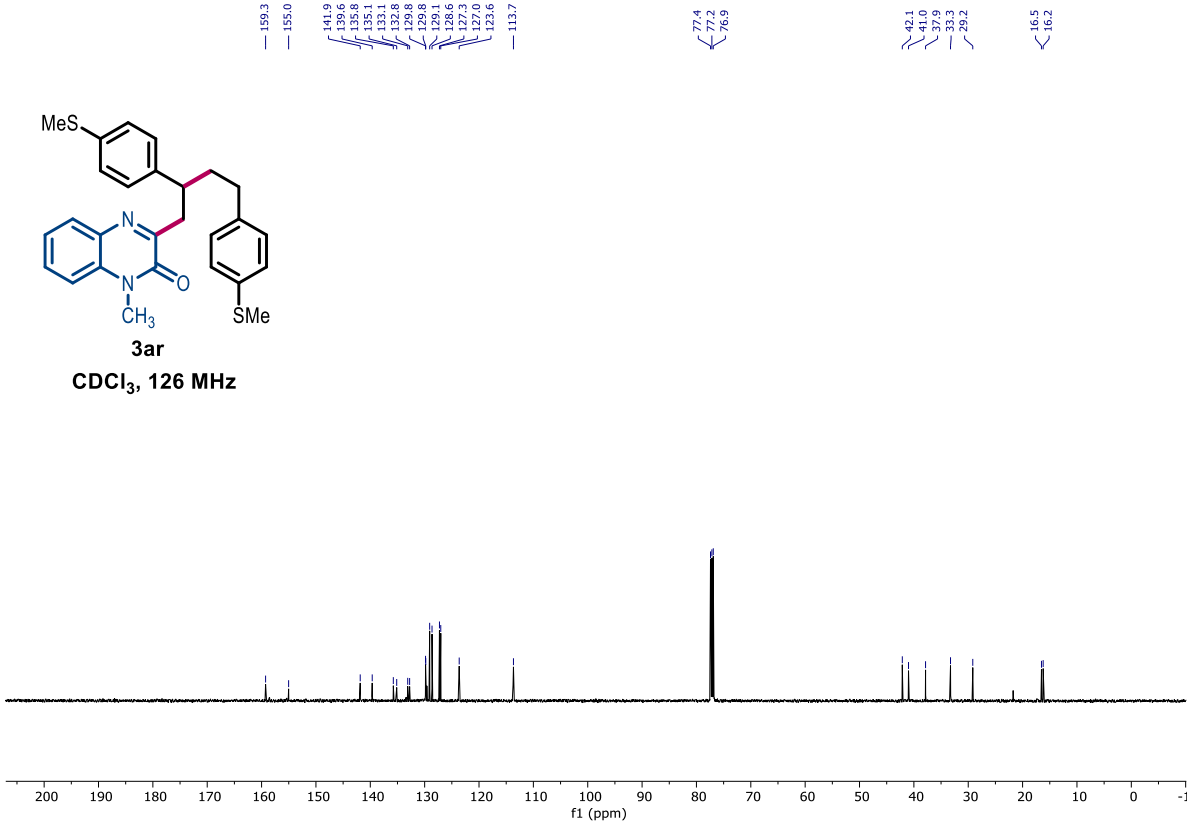


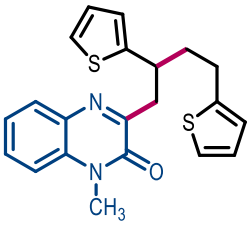
3ap
$CDCl_3$, 376 MHz


Cl
N
N
O
CH3
Cl
3aq
CDCl3, 400 MHz
f1 (ppm)


Cl
N
N
O
CH3
Cl
3aq
CDCl3, 101 MHz
f1 (ppm)

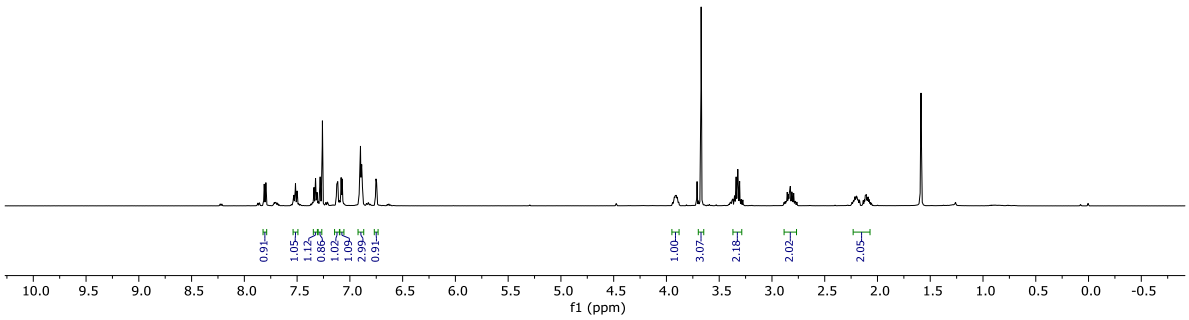

MeS
N
O
N
CH3
SMe
3ar
CDCl3, 500 MHz
f1 (ppm)

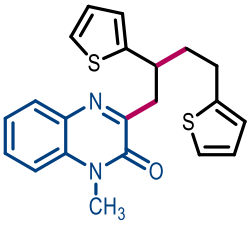

MeS
N
O
N
CH3
SMe
3ar
CDCl3, 126 MHz
f1 (ppm)



3as

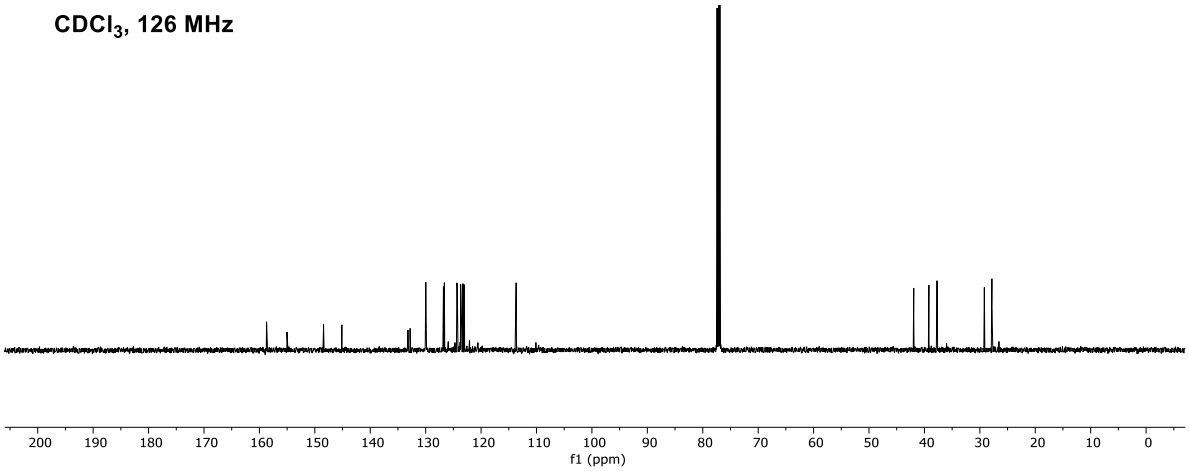
$CDCl_3$, 500 MHz

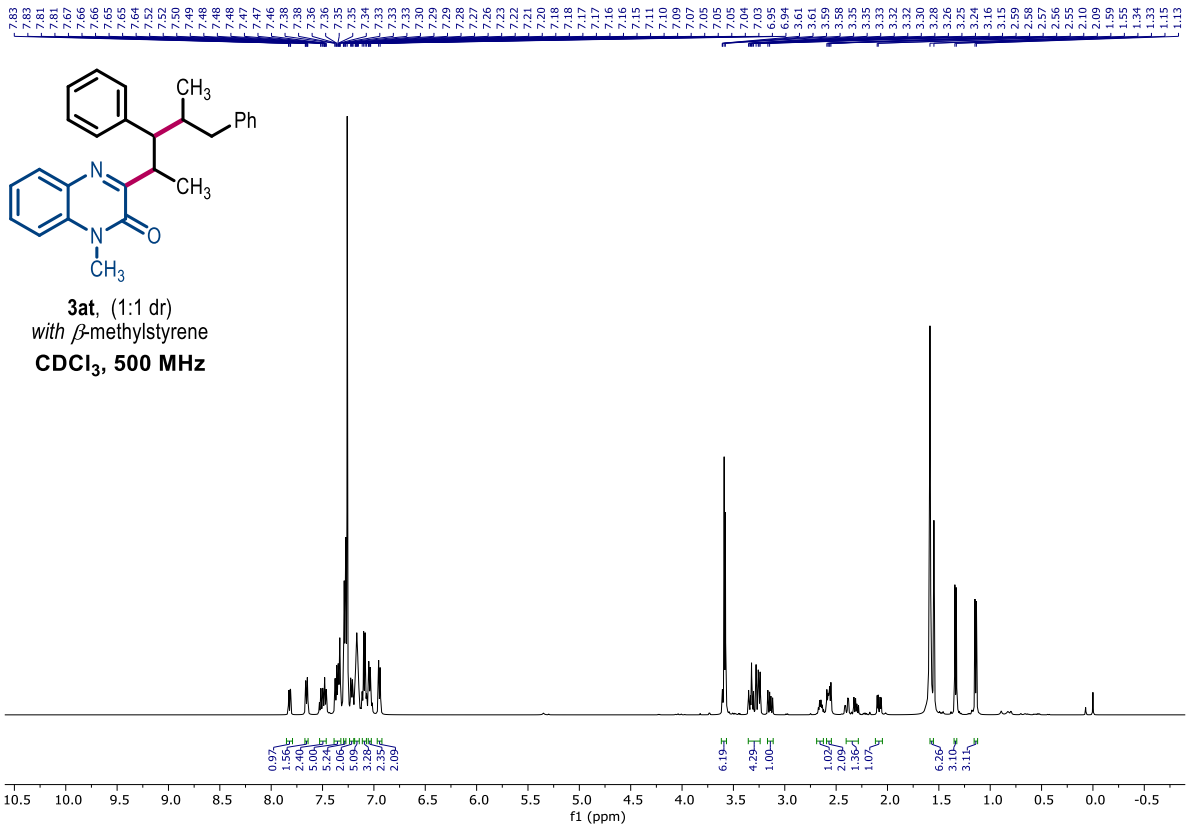




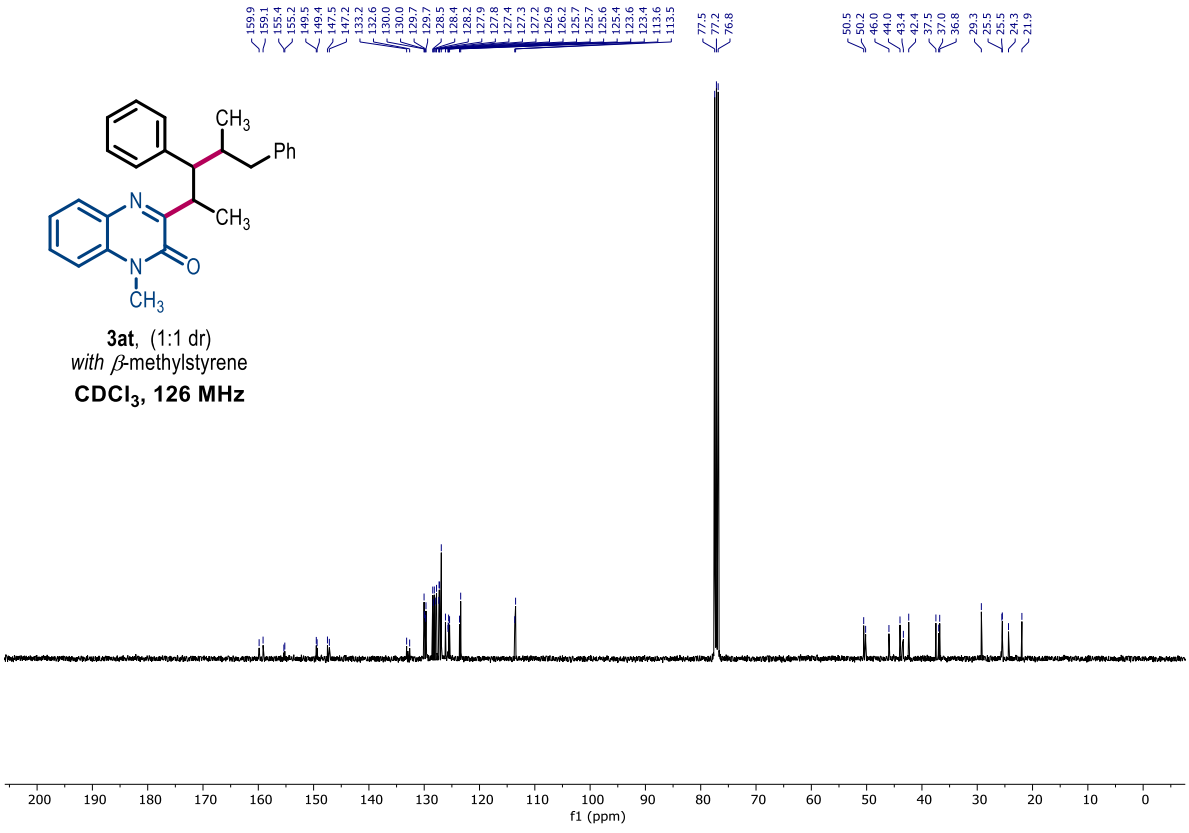
3as

$CDCl_3$, 126 MHz

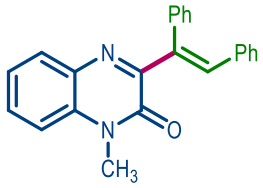




3at, (1:1 dr)
with β-methylstyrene
$CDCl_3$, 500 MHz

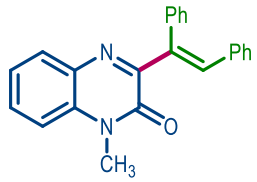


3at, (1:1 dr)
with β-methylstyrene
$CDCl_3$, 126 MHz



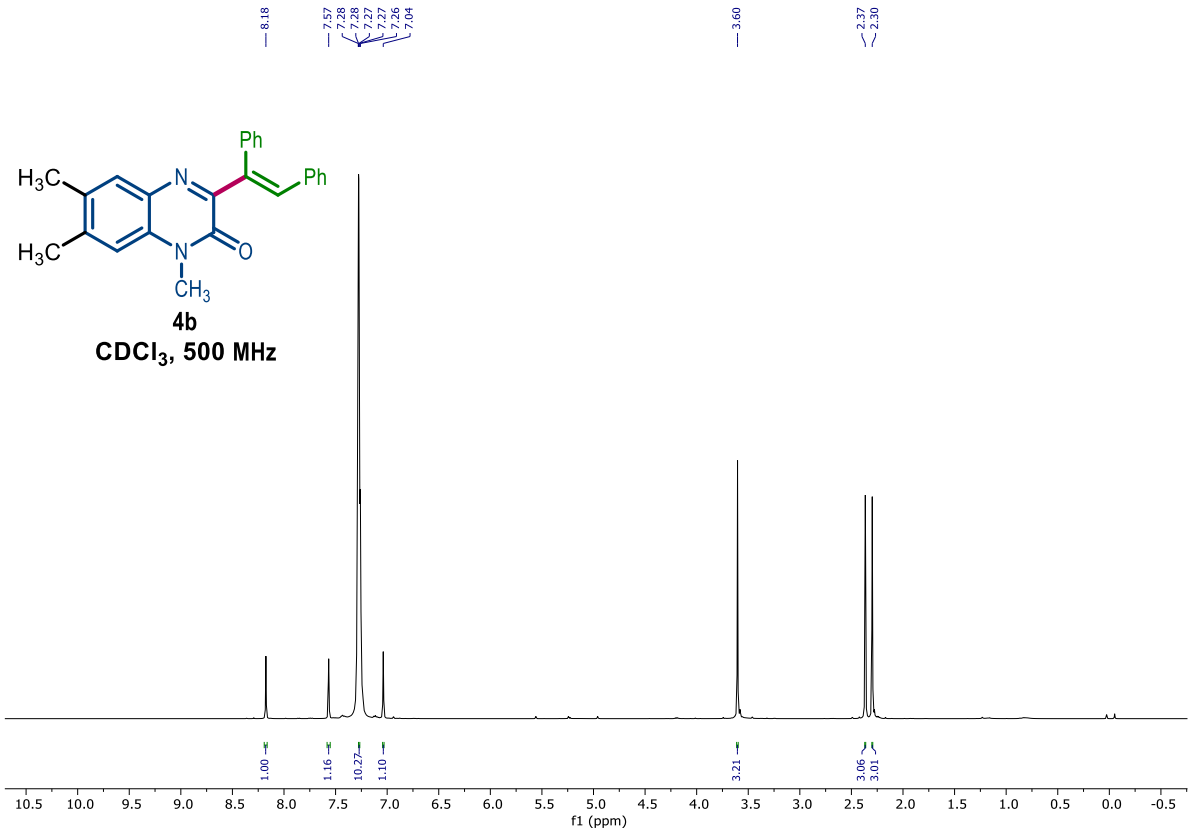
4a

$CDCl_3$, 400 MHz



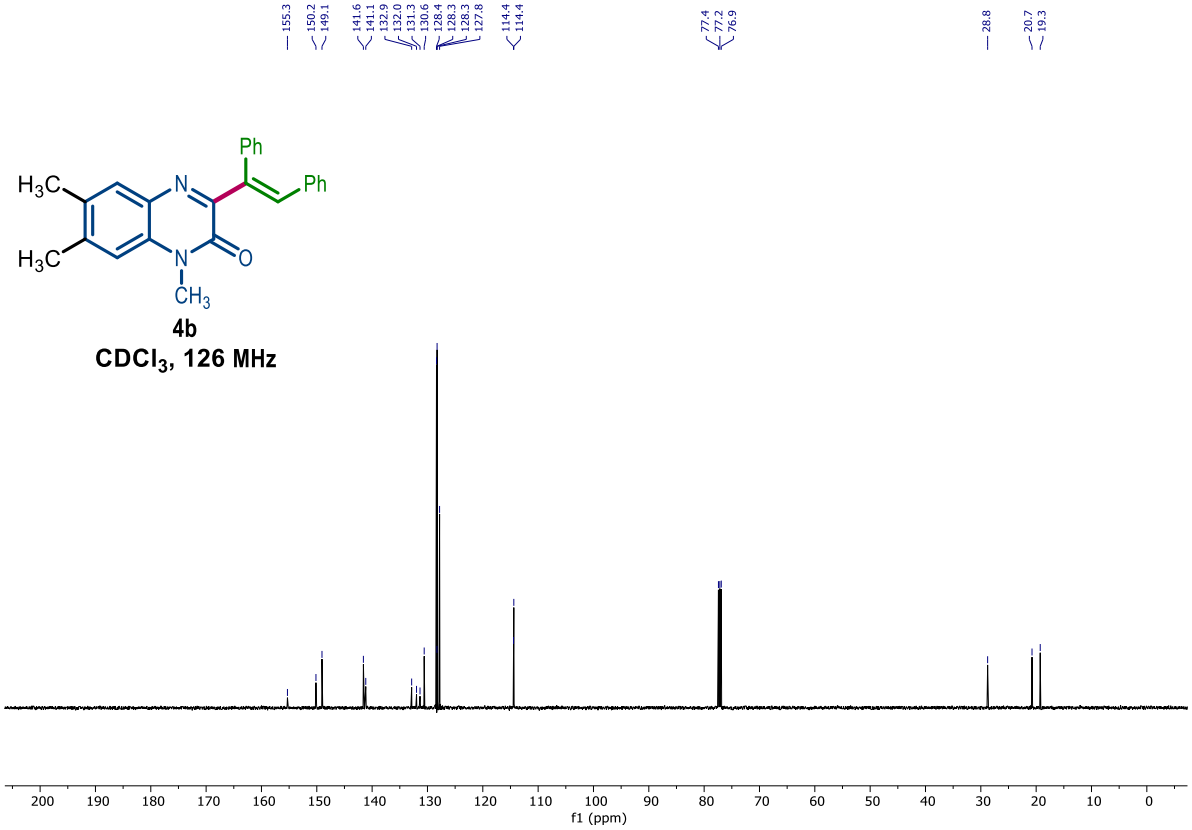
4a

$CDCl_3$, 101 MHz



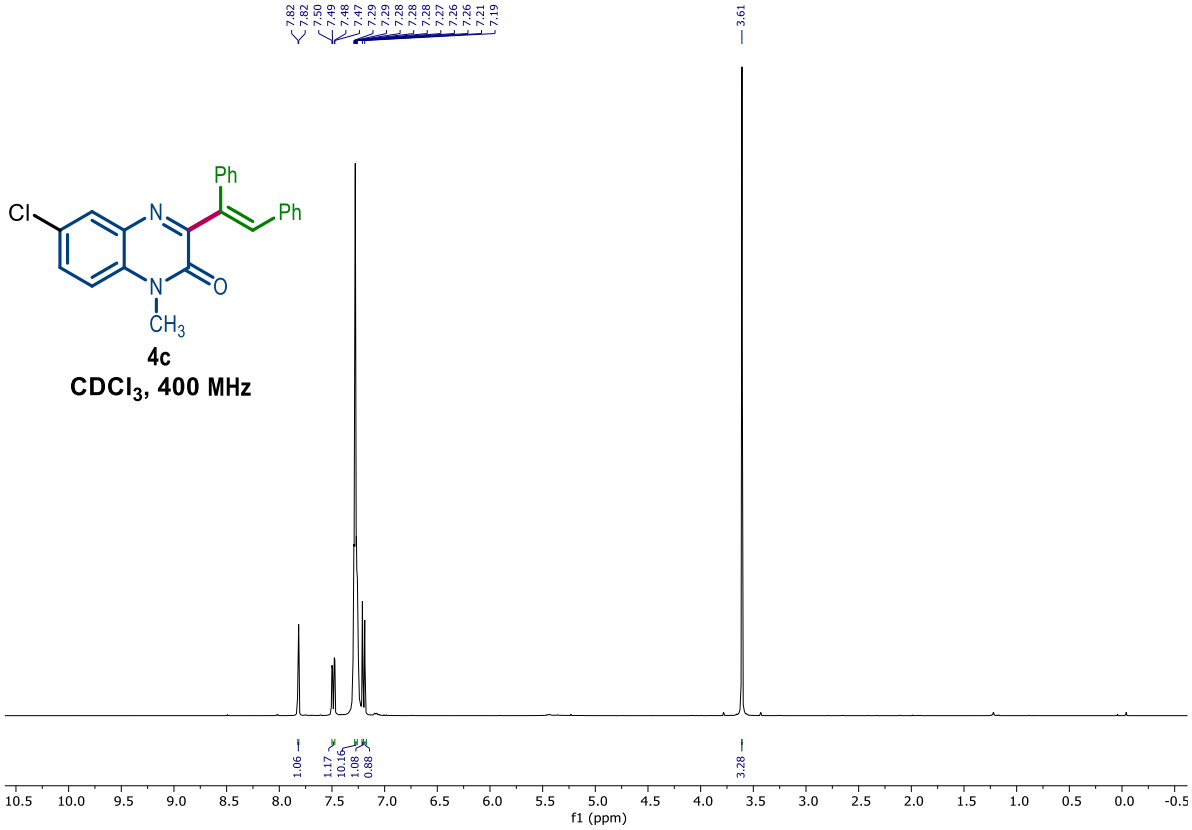
4b

$CDCl_3$, 500 MHz



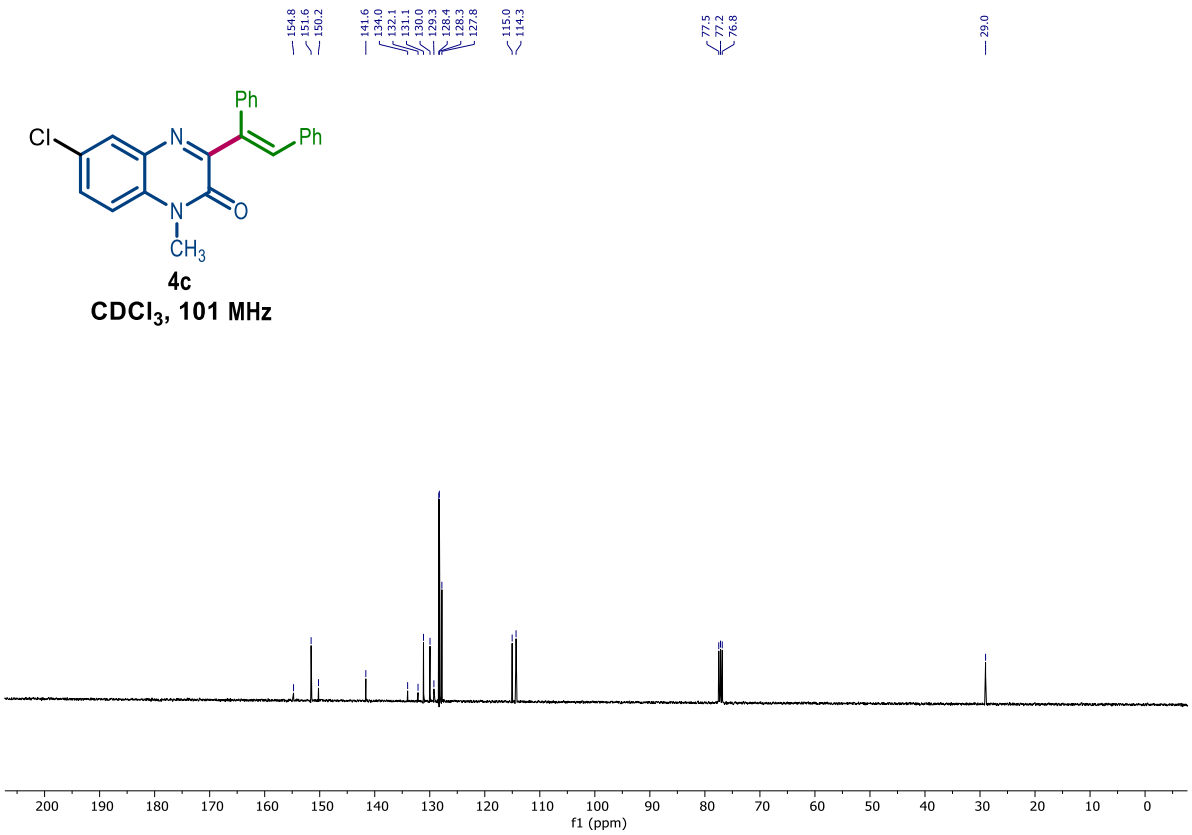
4b

$CDCl_3$, 126 MHz



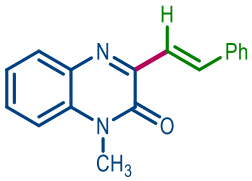
4c

$CDCl_3$, 400 MHz



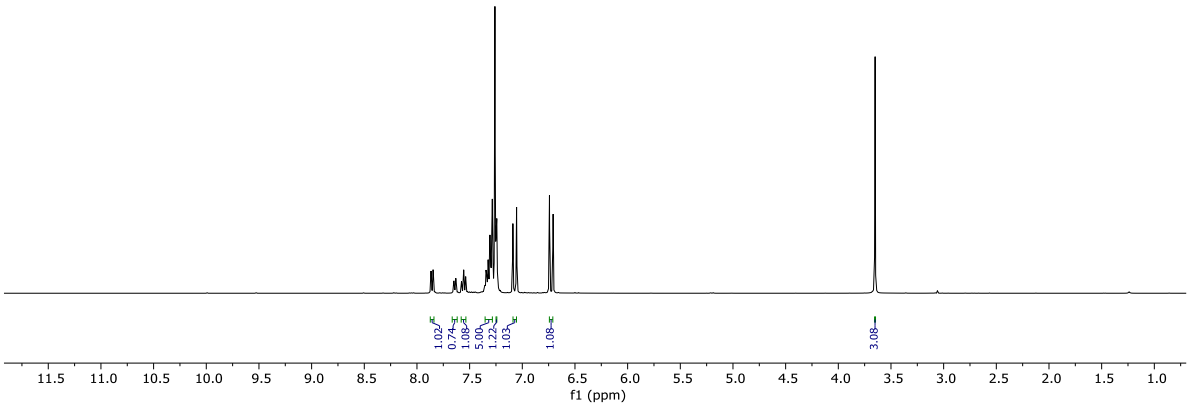
4c

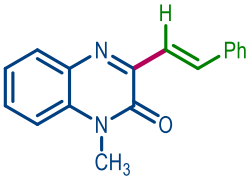
$CDCl_3$, 101 MHz



4d

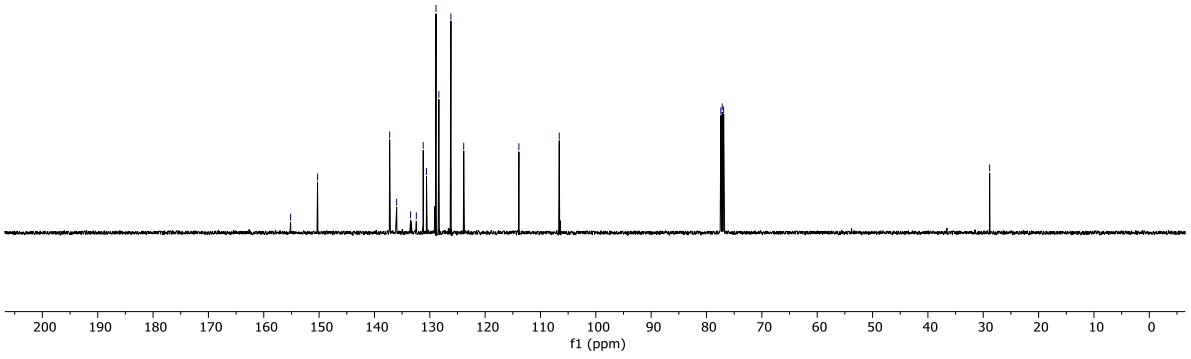
$CDCl_3$, 400 MHz

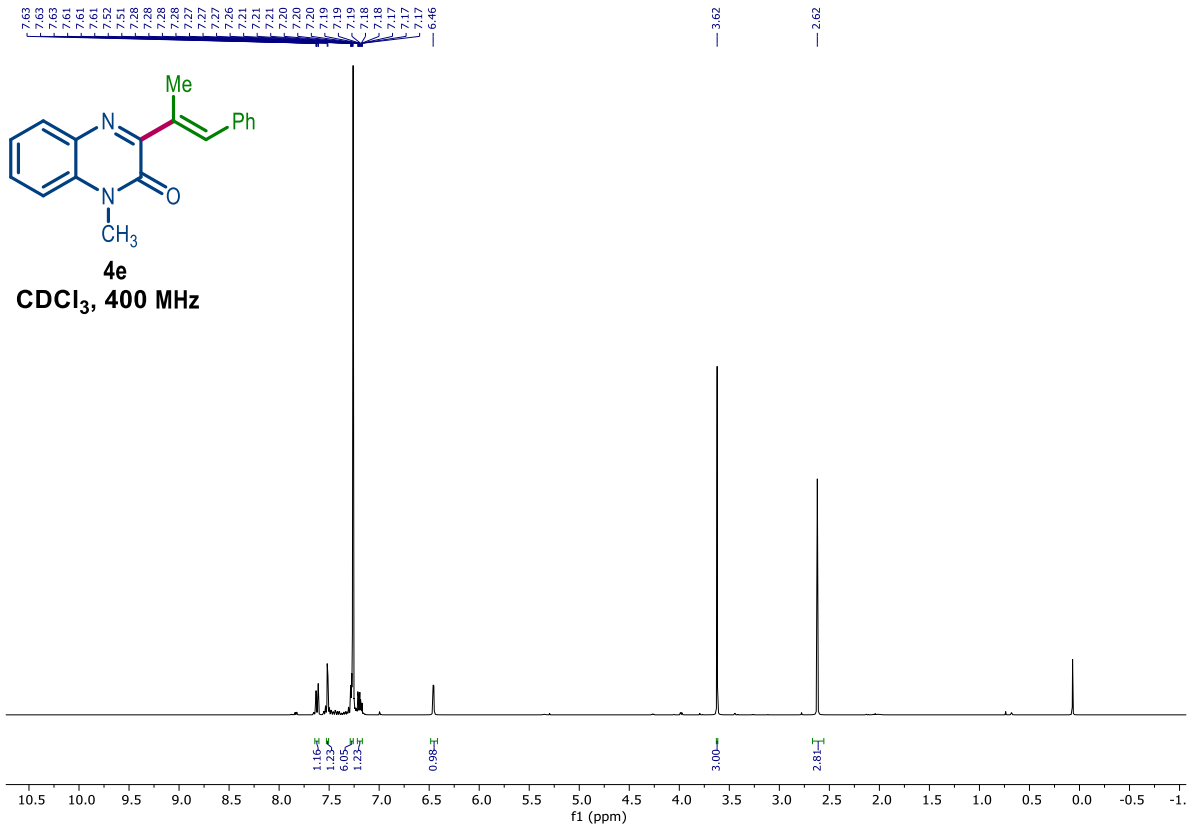




4d

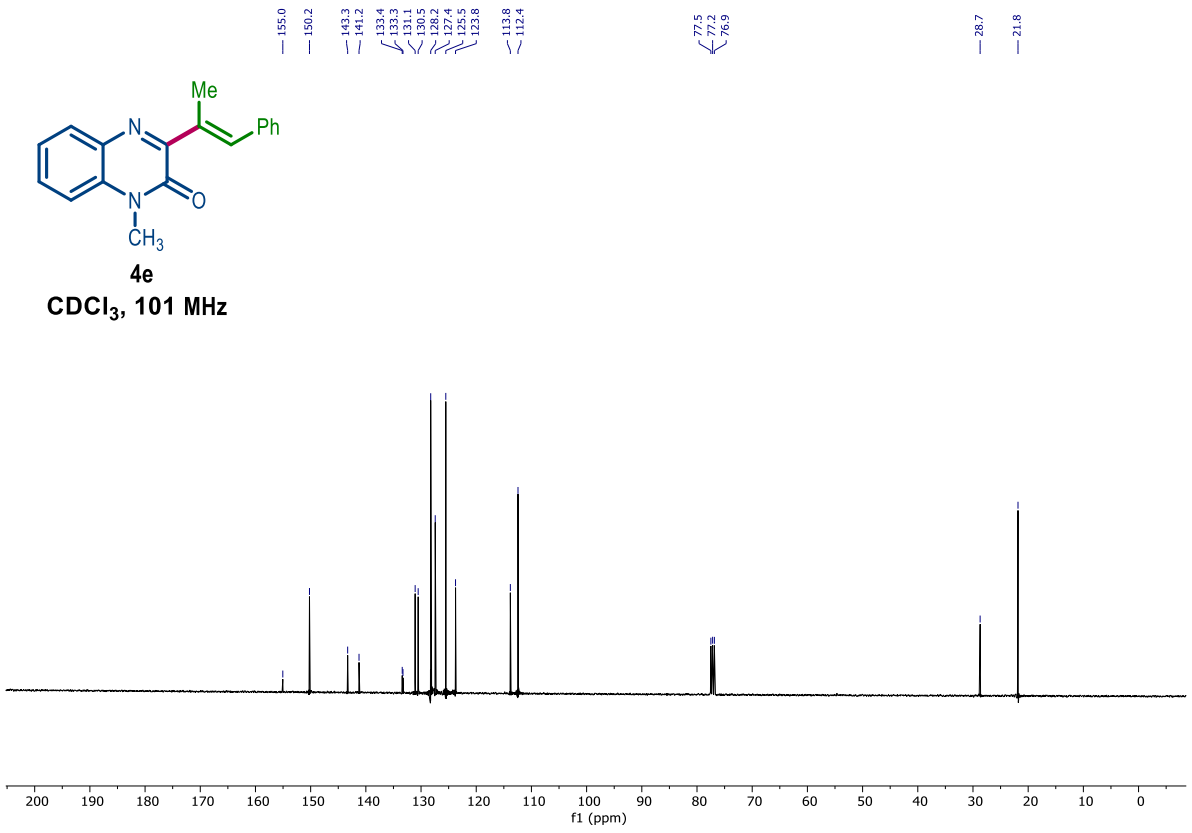
$CDCl_3$, 126 MHz





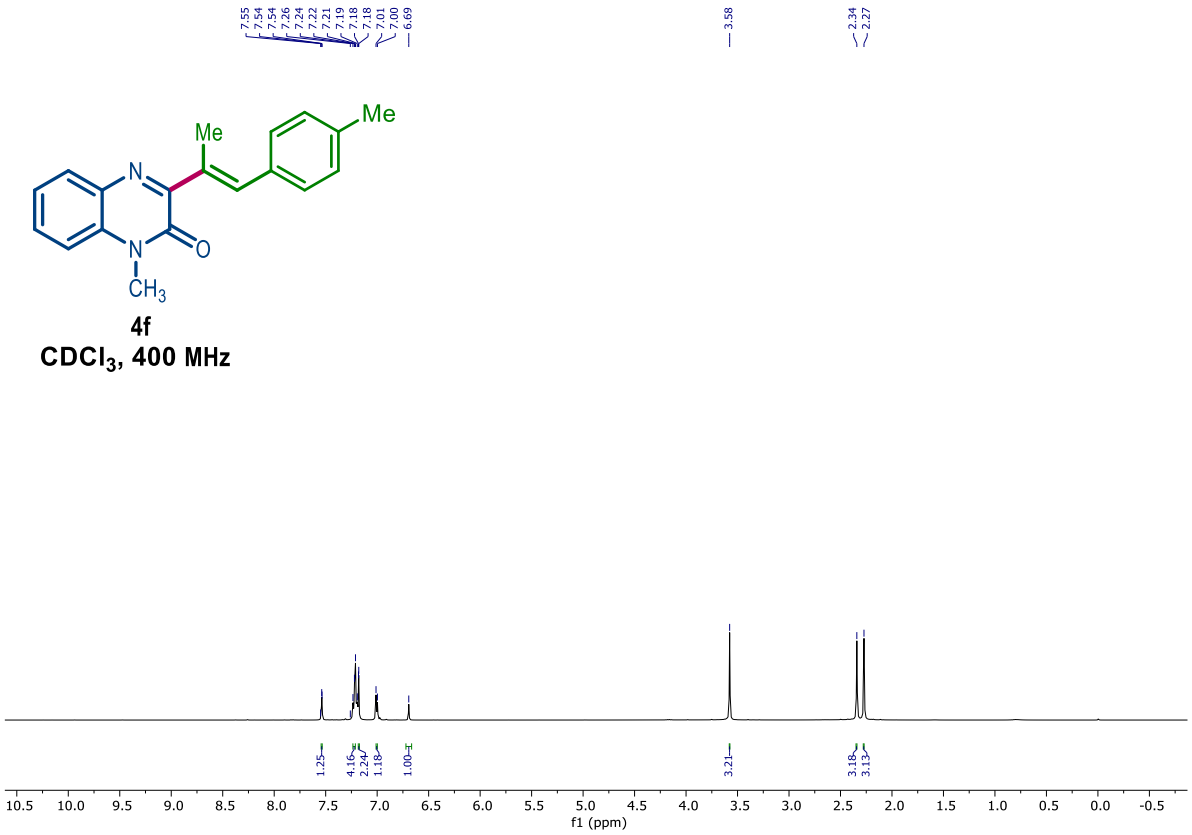
4e

$CDCl_3$, 400 MHz



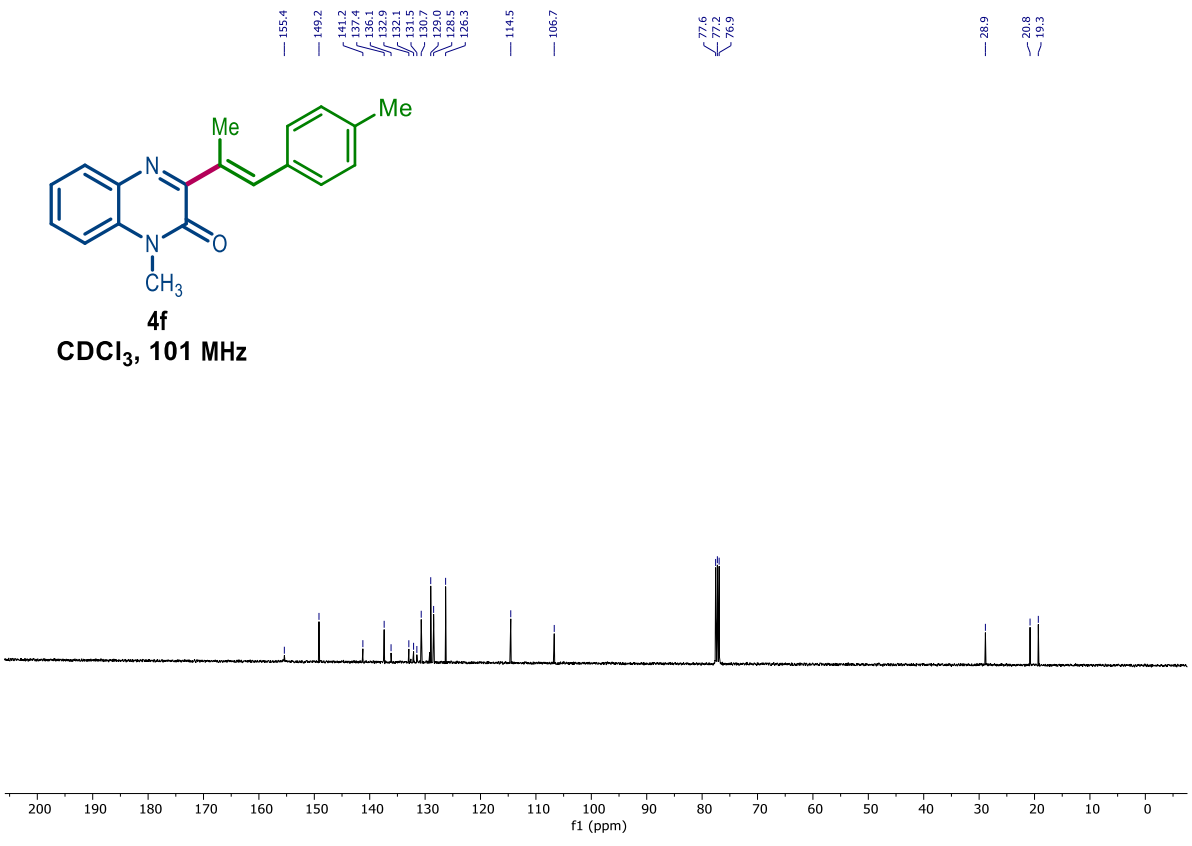
4e

$CDCl_3$, 101 MHz



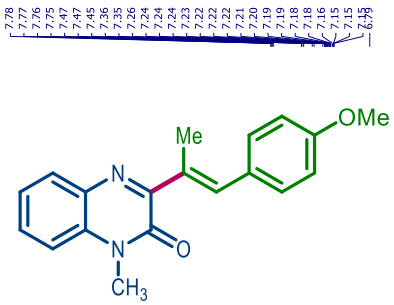
4f

$CDCl_3$, 400 MHz

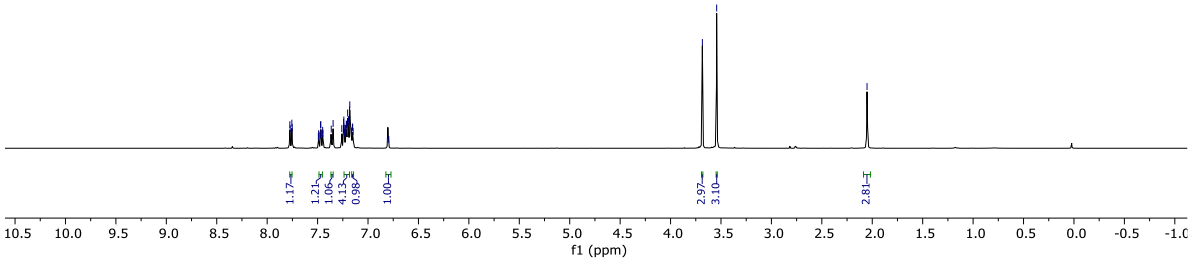


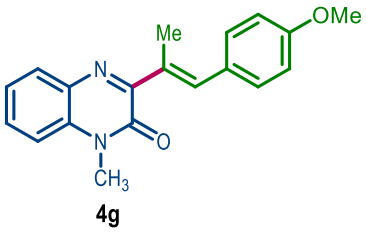
4f

$CDCl_3$, 101 MHz

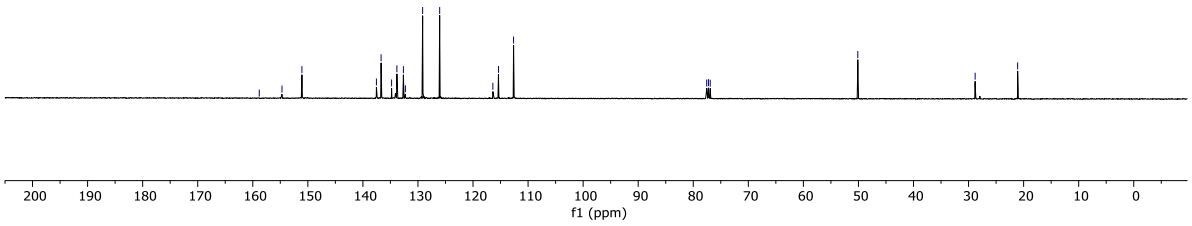


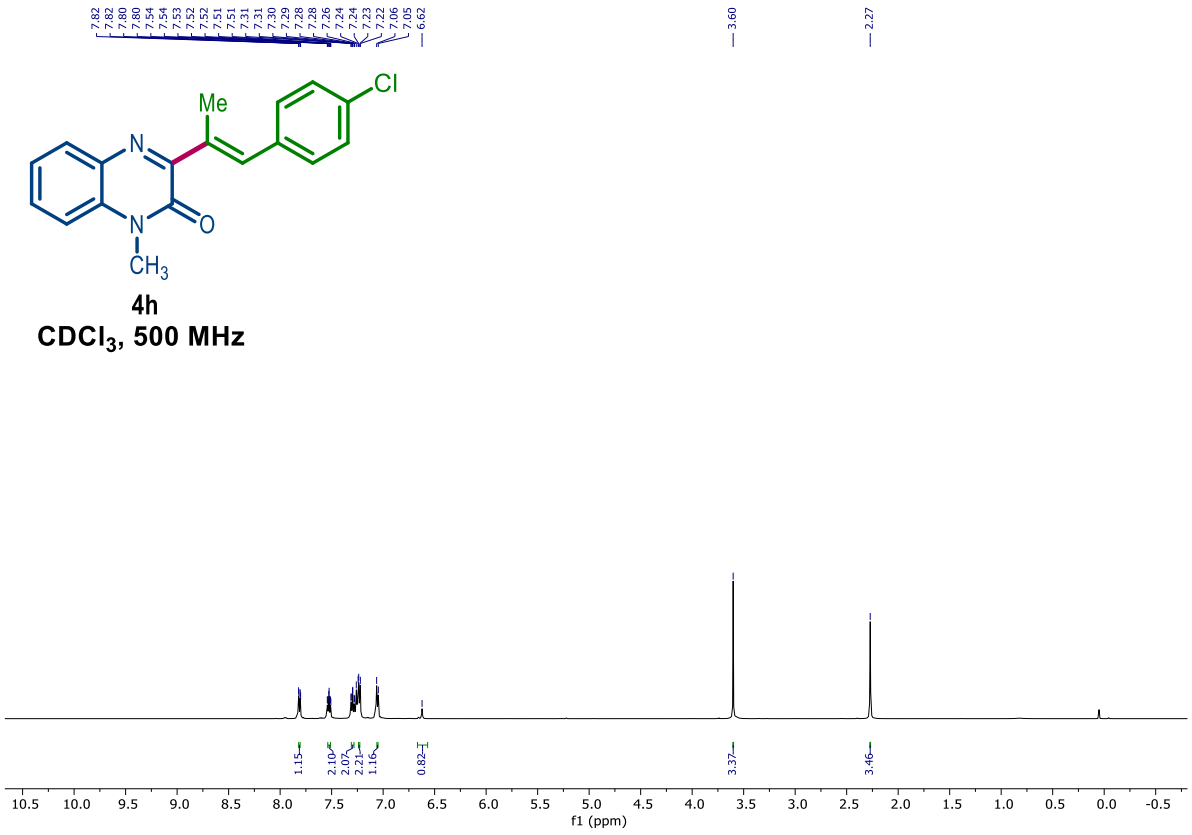
4g
$CDCl_3$, 400 MHz





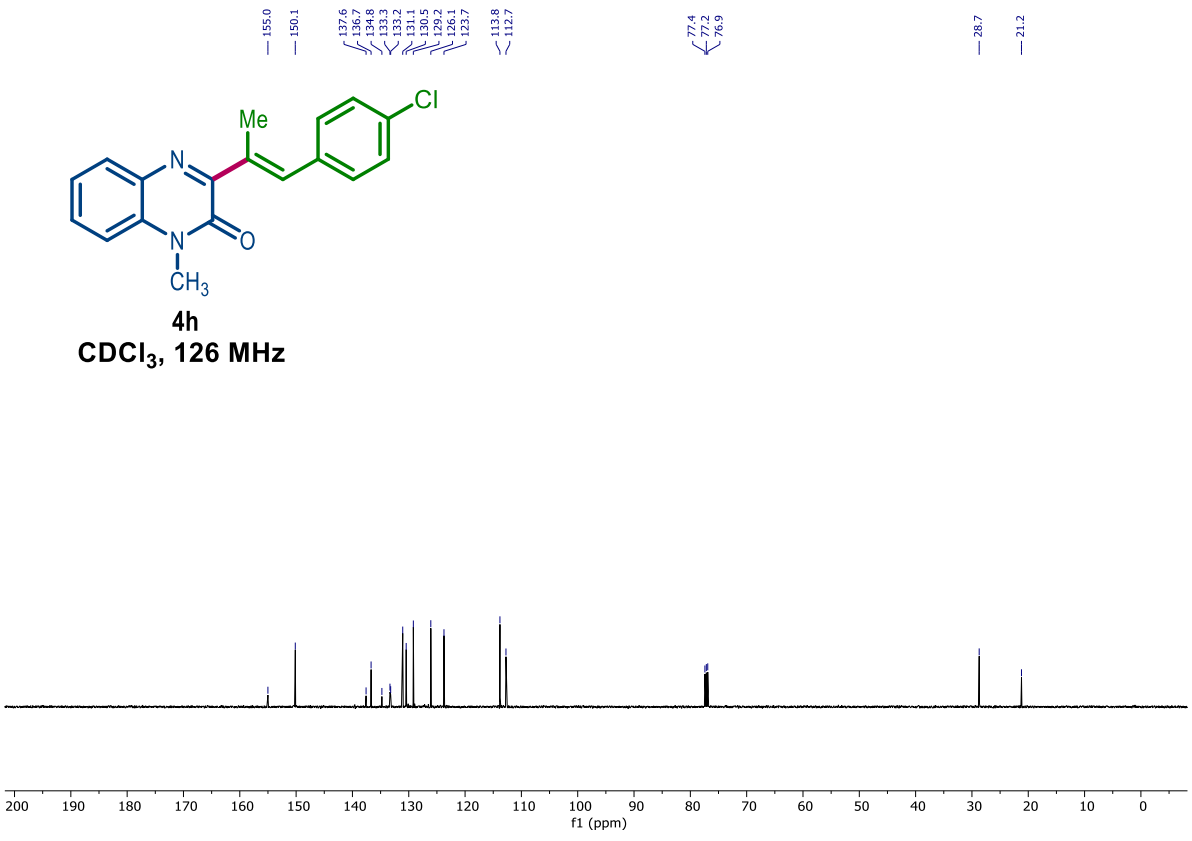
4g
$CDCl_3$, 101 MHz





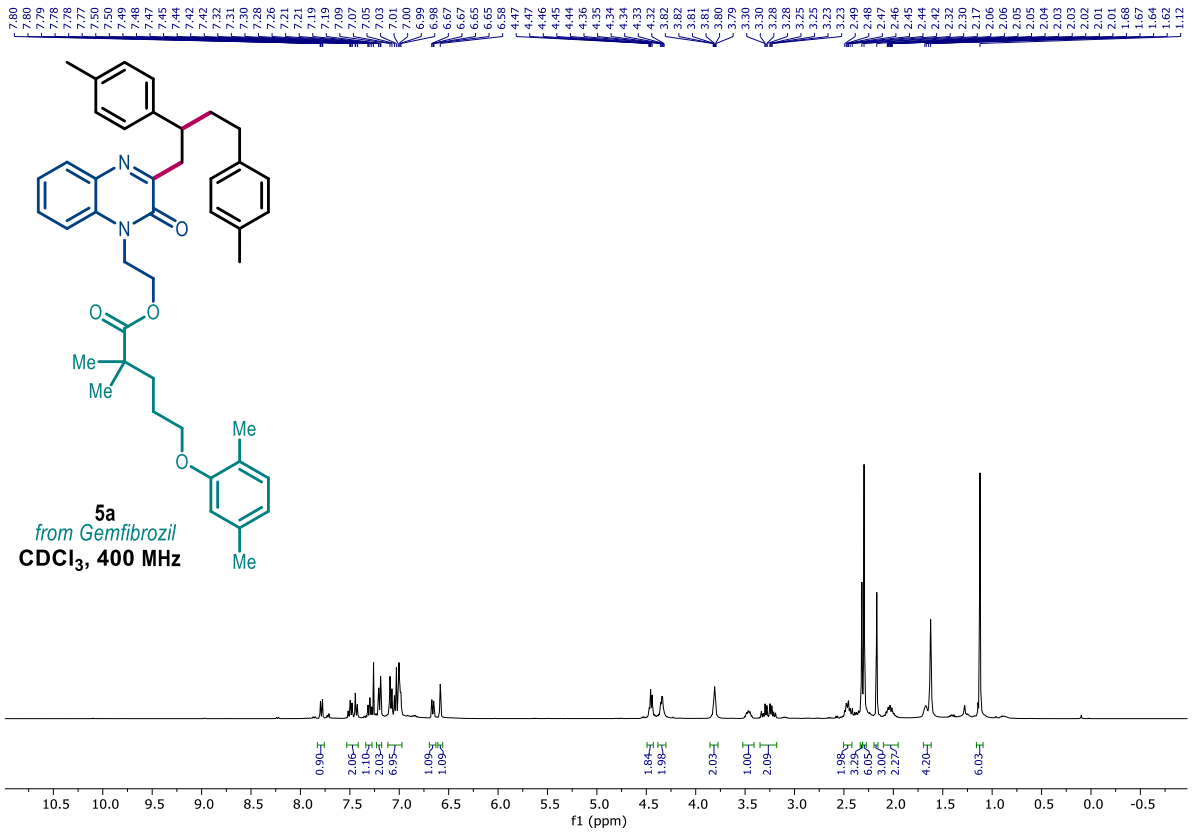
4h

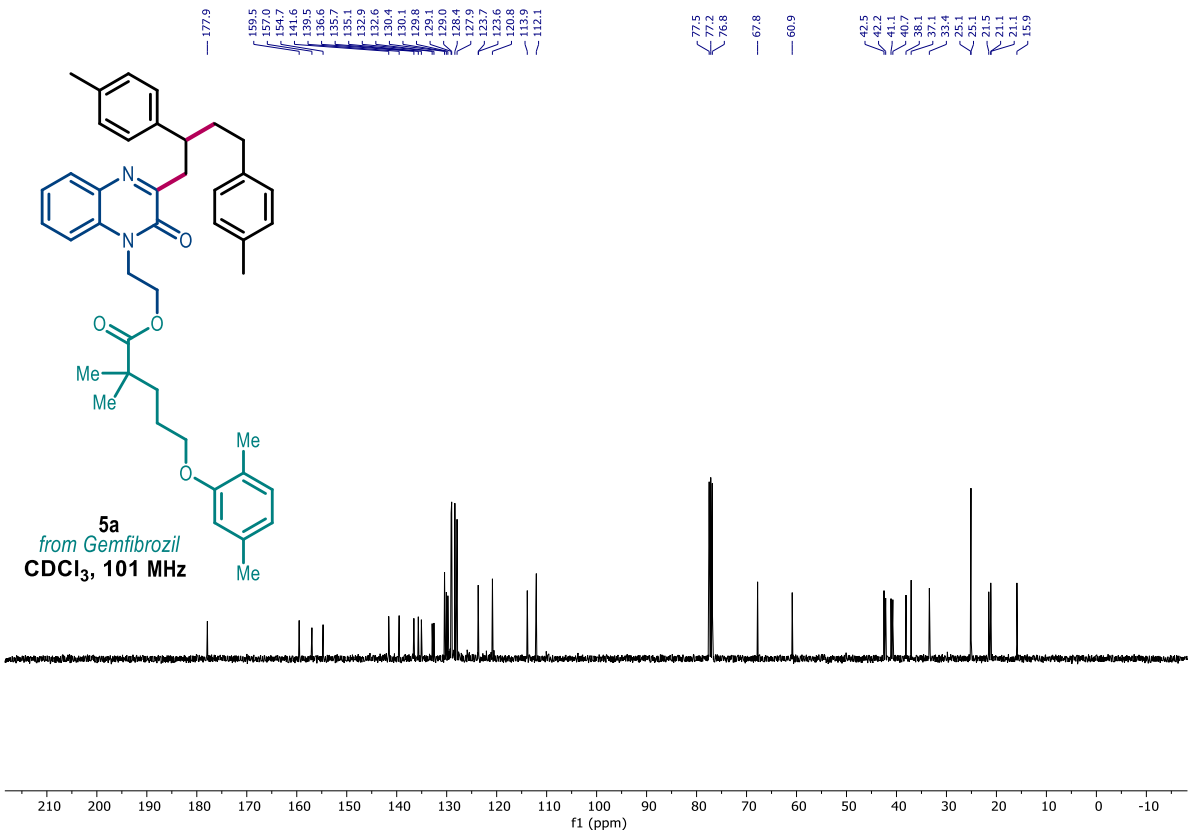
$CDCl_3$, 500 MHz

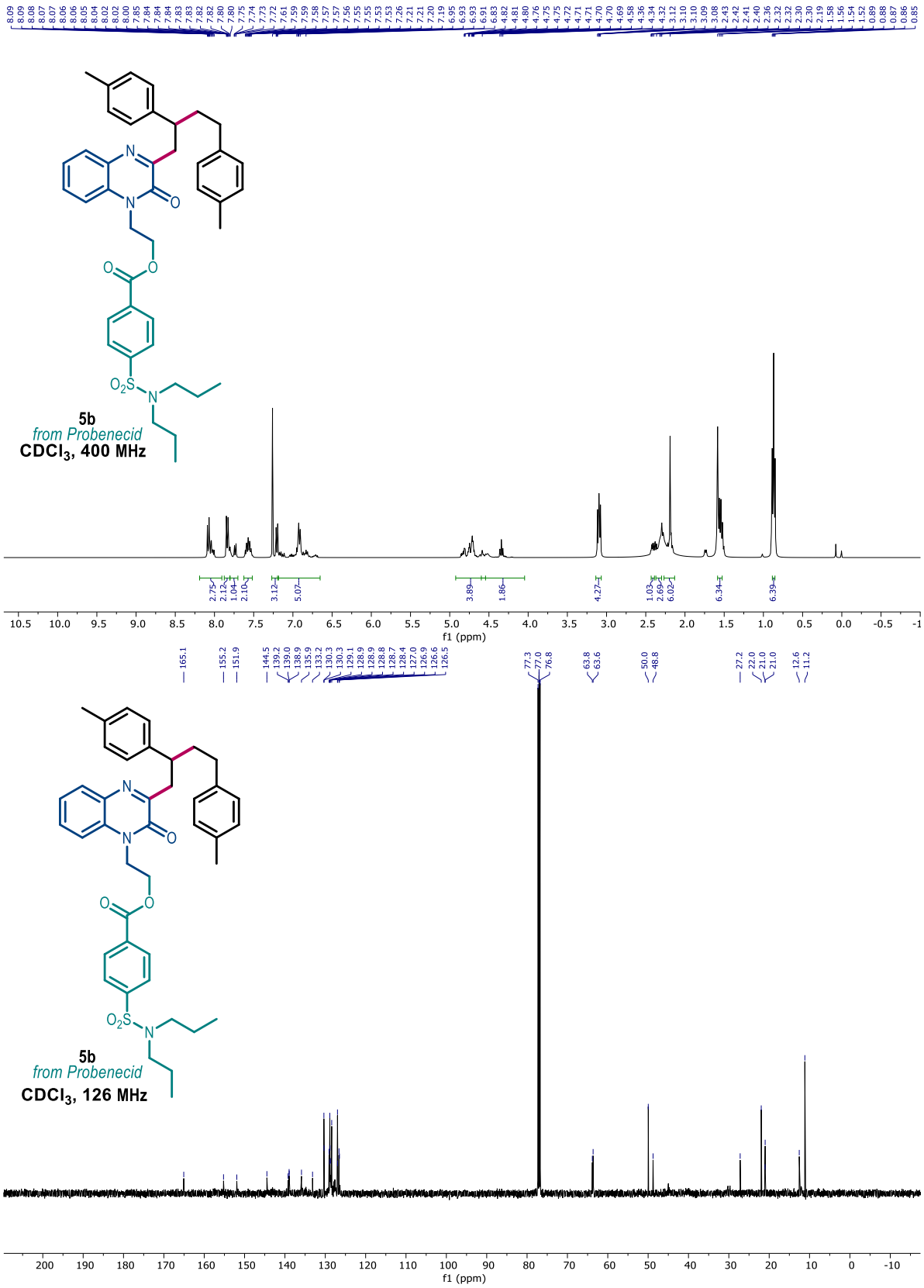


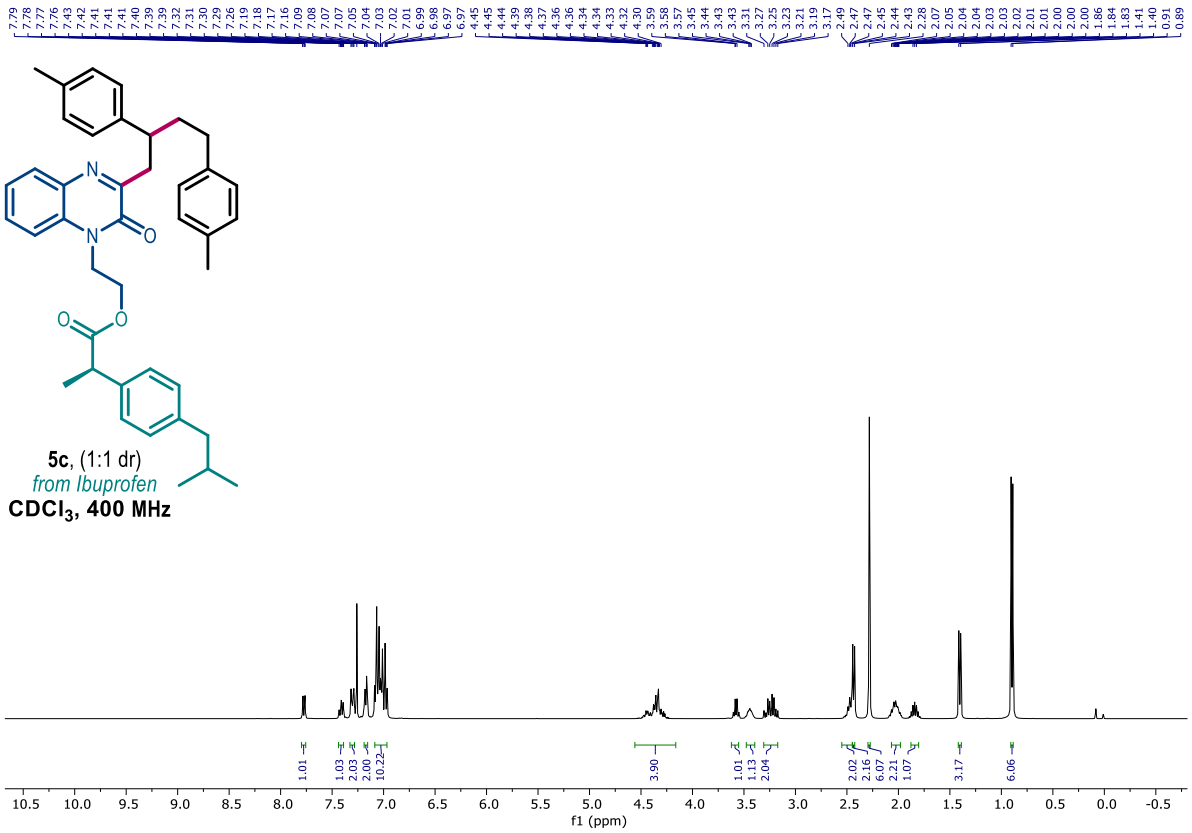
4h

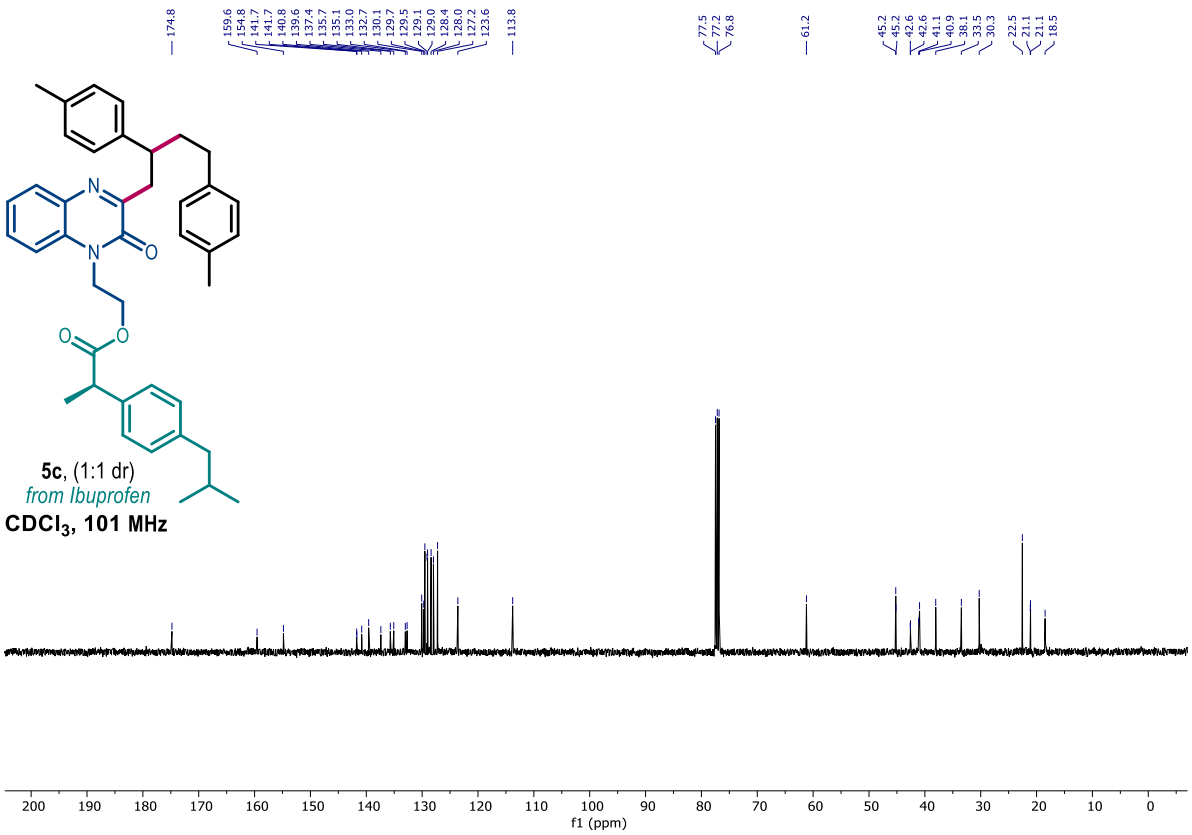
$CDCl_3$, 126 MHz

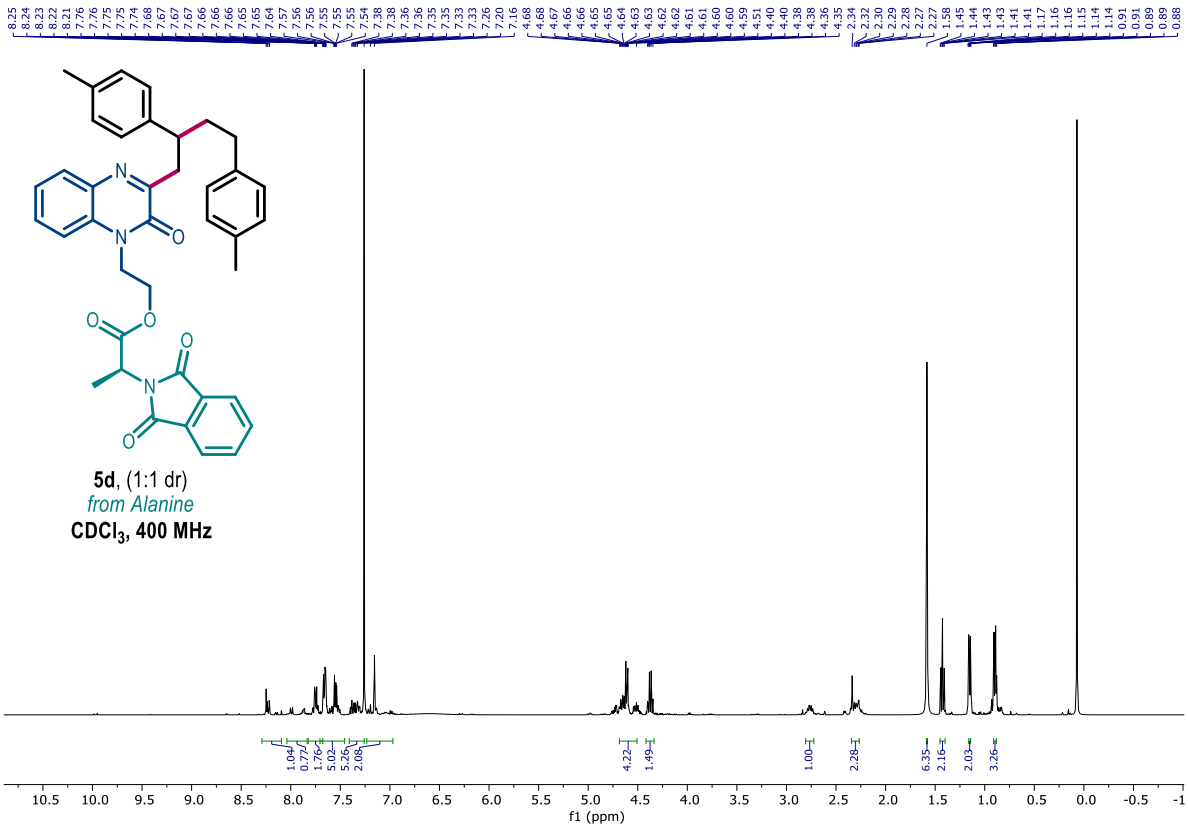

5a
from Gemfibrozil
CDCl3, 400 MHz
f1 (ppm)

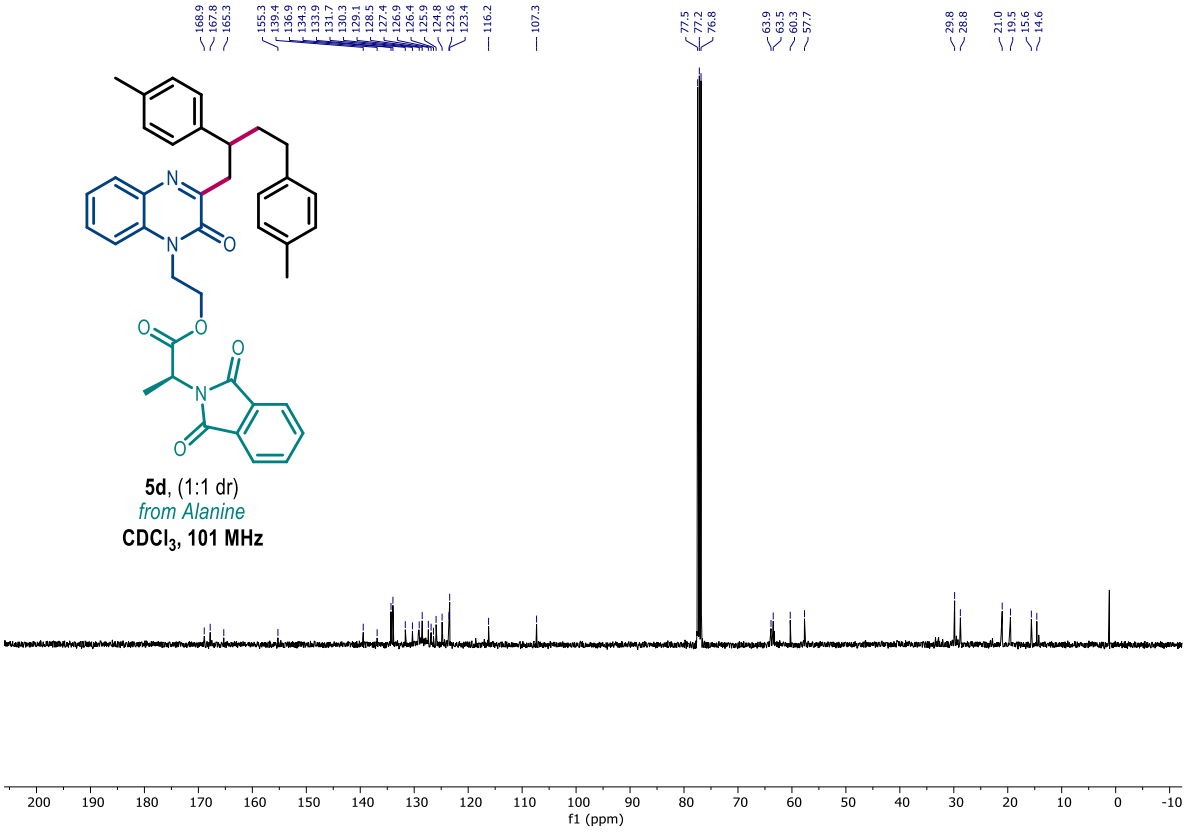

5a
from Gemfibrozil
CDCl3, 101 MHz
f1 (ppm)

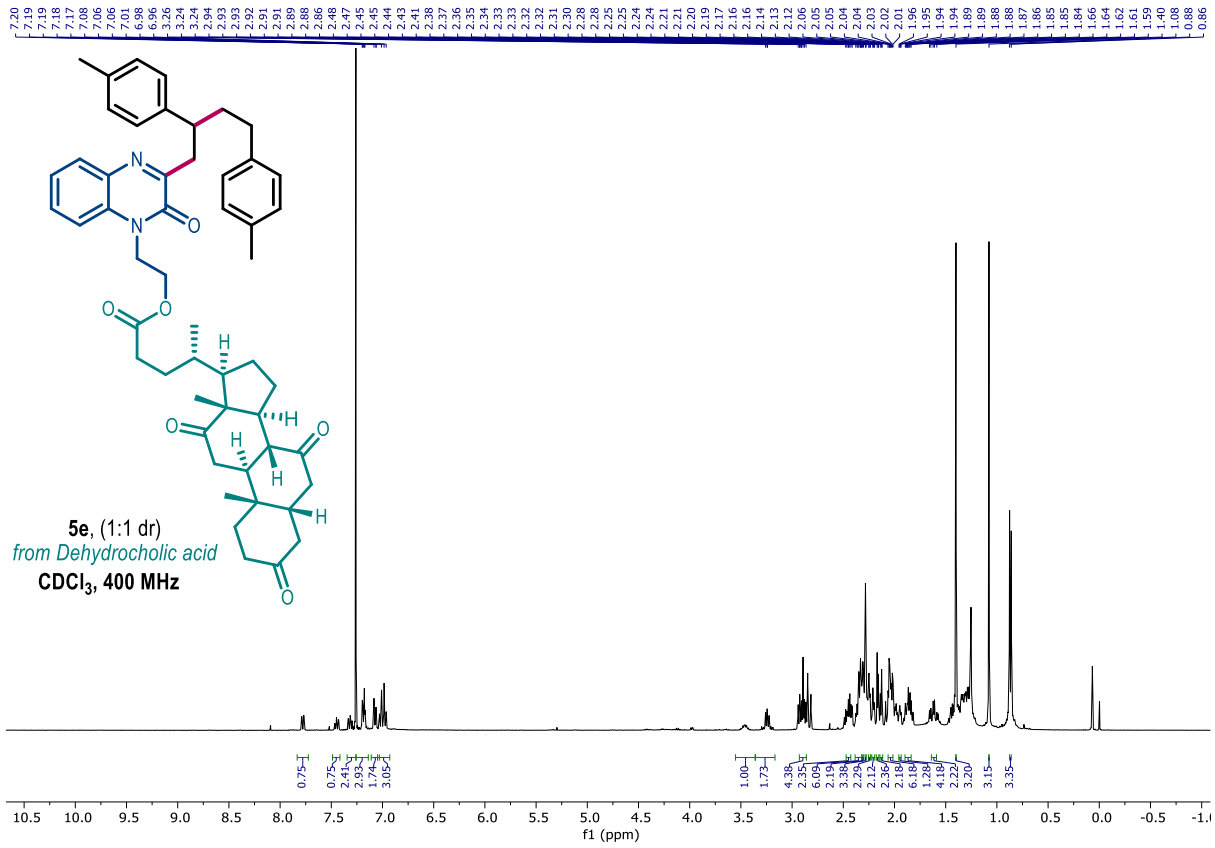

5b
from Probenecid
CDCl3, 400 MHz
f1 (ppm)
5b
from Probenecid
CDCl3, 126 MHz
f1 (ppm)

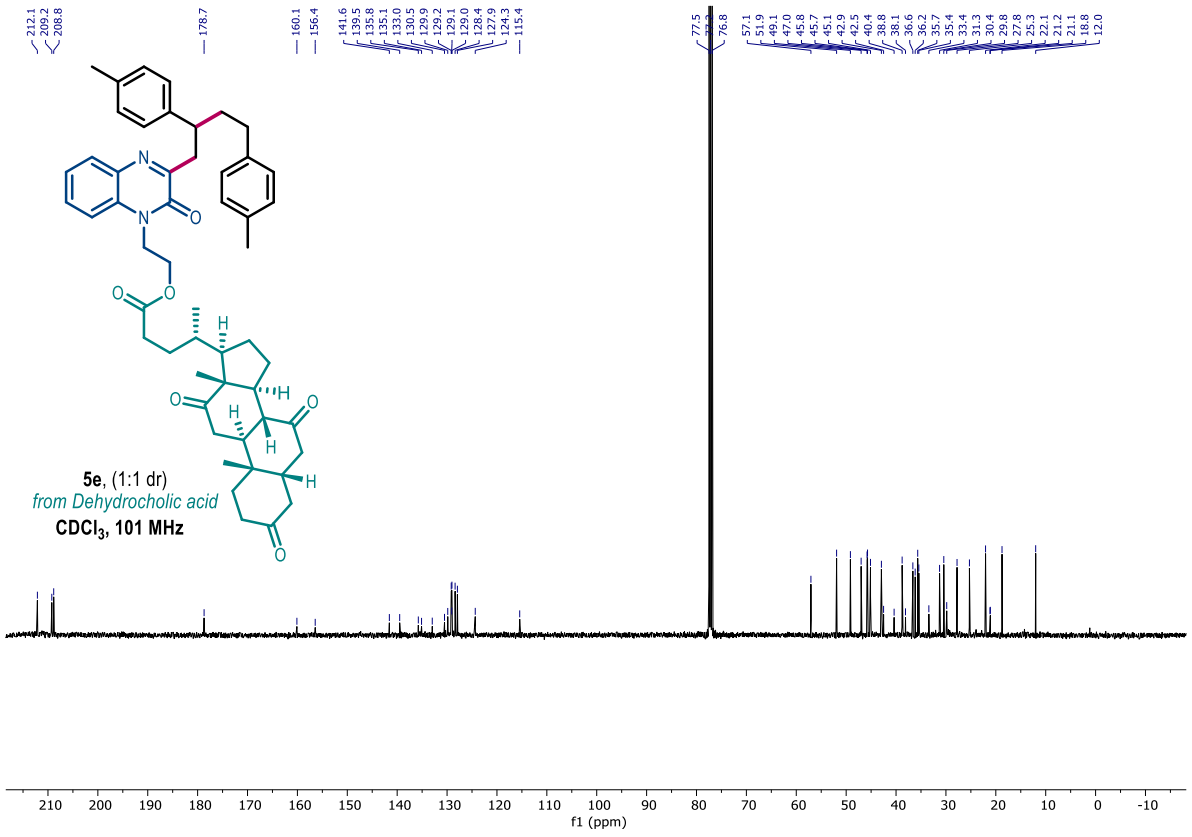

5c, (1:1 dr)
from Ibuprofen
CDCl3, 400 MHz
f1 (ppm)

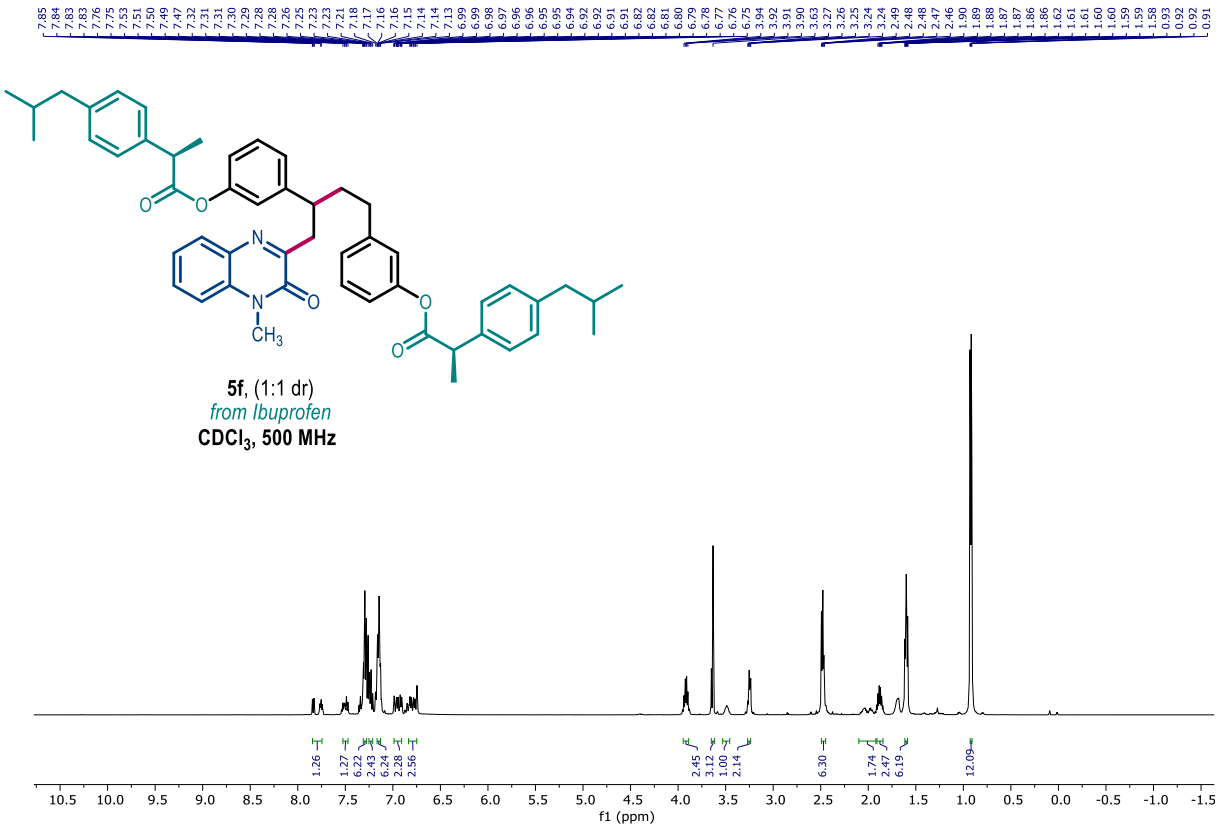

5c, (1:1 dr)
from Ibuprofen
CDCl3, 101 MHz
f1 (ppm)

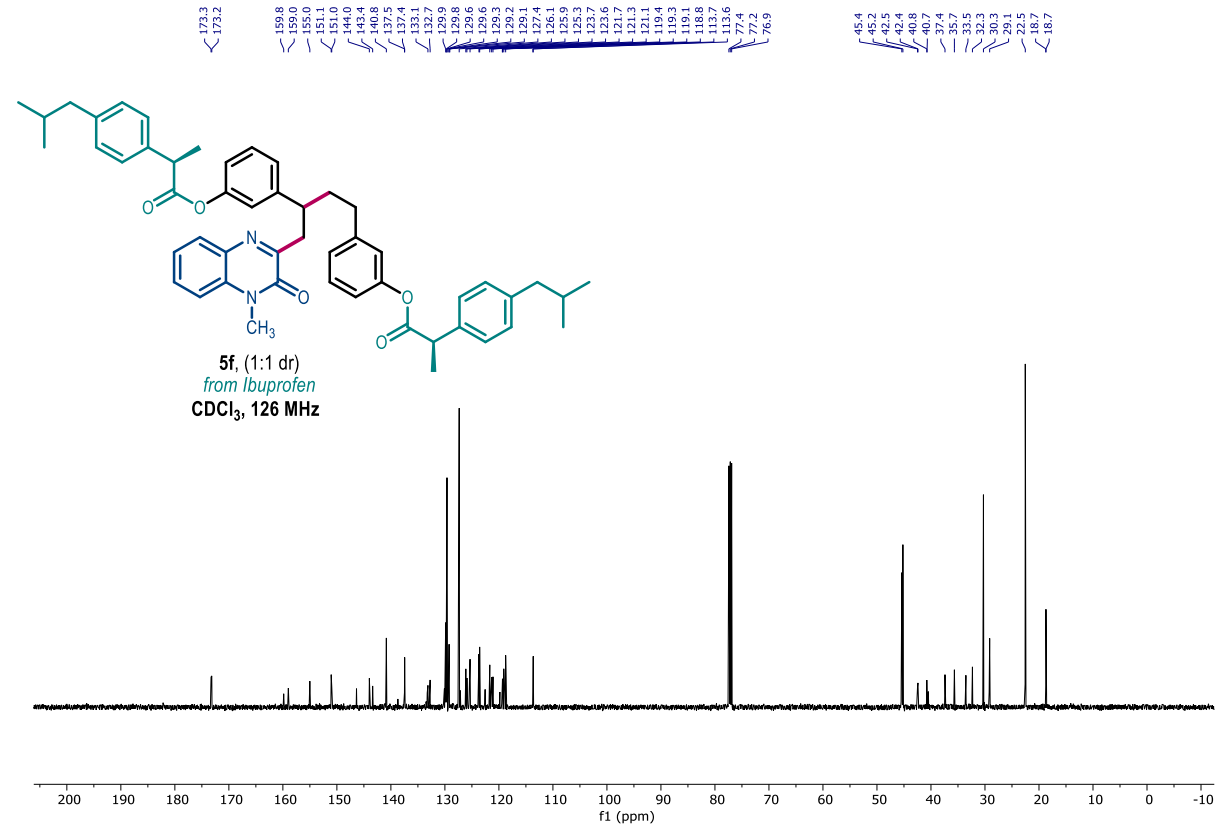

8.25 8.24 8.23 8.22 8.21 7.76 7.76 7.75 7.75 7.74 7.68 7.67 7.67 7.67 7.66 7.66 7.66 7.65 7.64 7.57 7.56 7.56 7.55 7.55 7.55 7.54 7.38 7.38 7.36 7.36 7.35 7.35 7.33 7.33 7.26 7.20 7.16 4.68 4.68 4.67 4.66 4.66 4.65 4.64 4.63 4.63 4.62 4.62 4.61 4.61 4.60 4.60 4.59 4.51 4.40 4.40 4.38 4.38 4.36 4.35 2.34 2.32 2.30 2.29 2.28 2.27 2.27 1.58 1.45 1.44 1.43 1.43 1.41 1.41 1.17 1.16 1.16 1.15 1.14 1.14 0.91 0.91 0.89 0.89 0.88
5d, (1:1 dr)
from Alanine
CDCl3, 400 MHz
1.04 0.77 1.76 5.02 5.26 2.08 4.22 1.49 1.00 2.28 6.35 2.16 2.03 3.26
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
f1 (ppm)

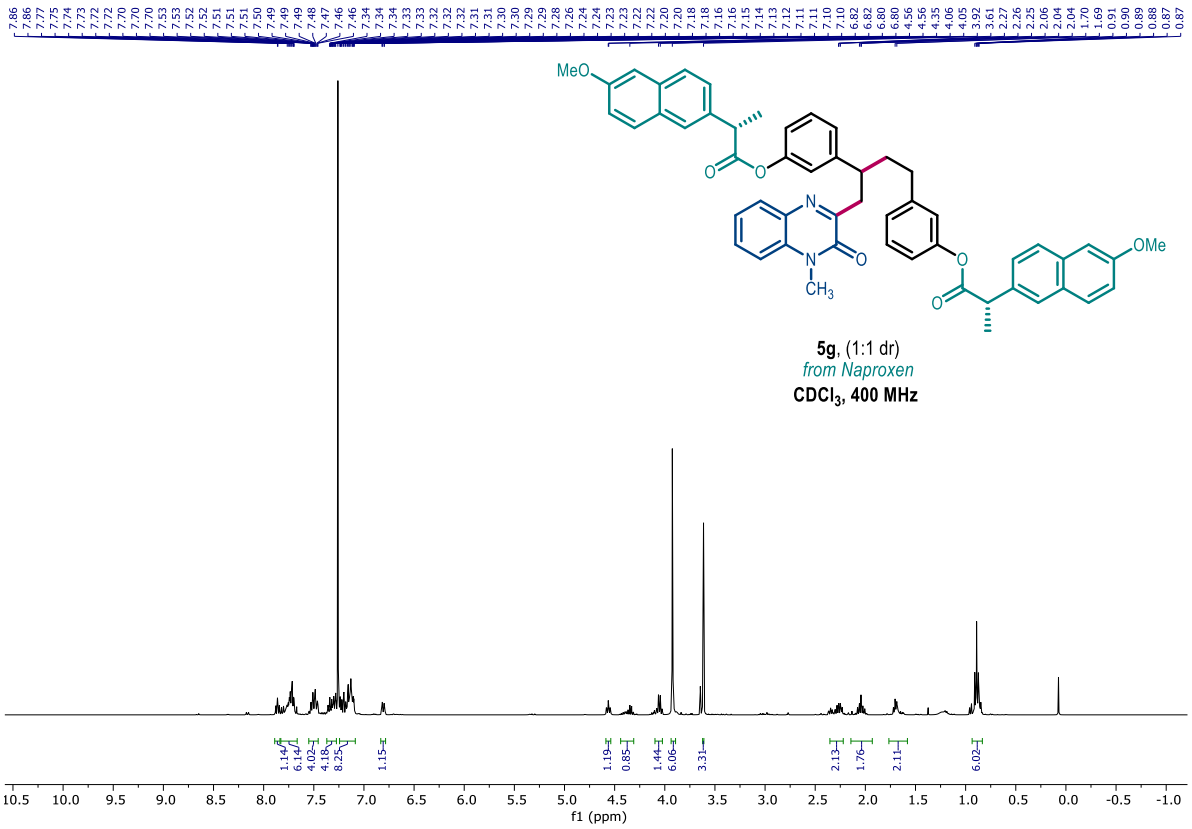

168.9 167.8 165.3 155.3 139.4 136.9 134.3 133.9 131.7 130.3 129.1 128.5 127.4 126.9 126.4 125.9 124.8 123.6 123.4 116.2 107.3 77.5 77.2 76.8 63.9 63.5 60.3 57.7 29.8 28.8 21.0 19.5 15.6 14.6
5d, (1:1 dr)
from Alanine
CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

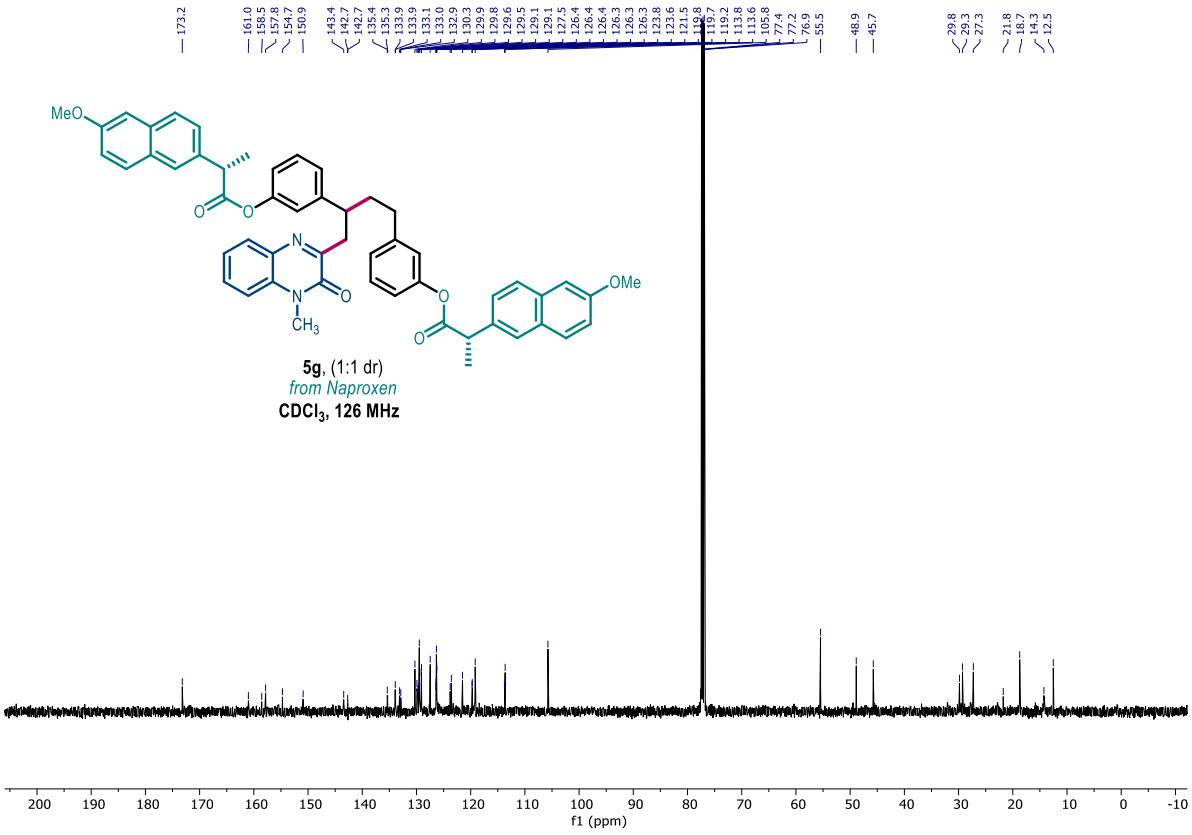

5e, (1:1 dr)
from Dehydrocholic acid
CDCl3, 400 MHz
f1 (ppm)

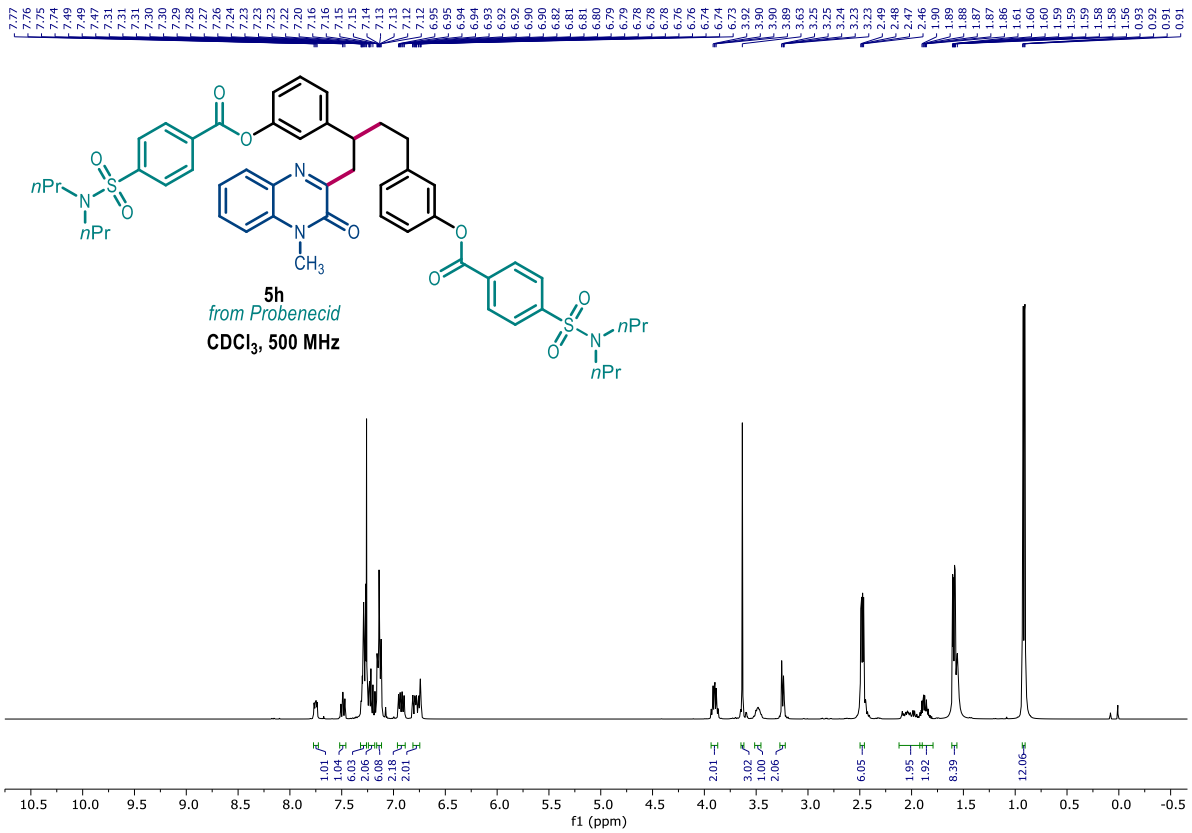

5e, (1:1 dr)
from Dehydrocholic acid
CDCl3, 101 MHz
f1 (ppm)

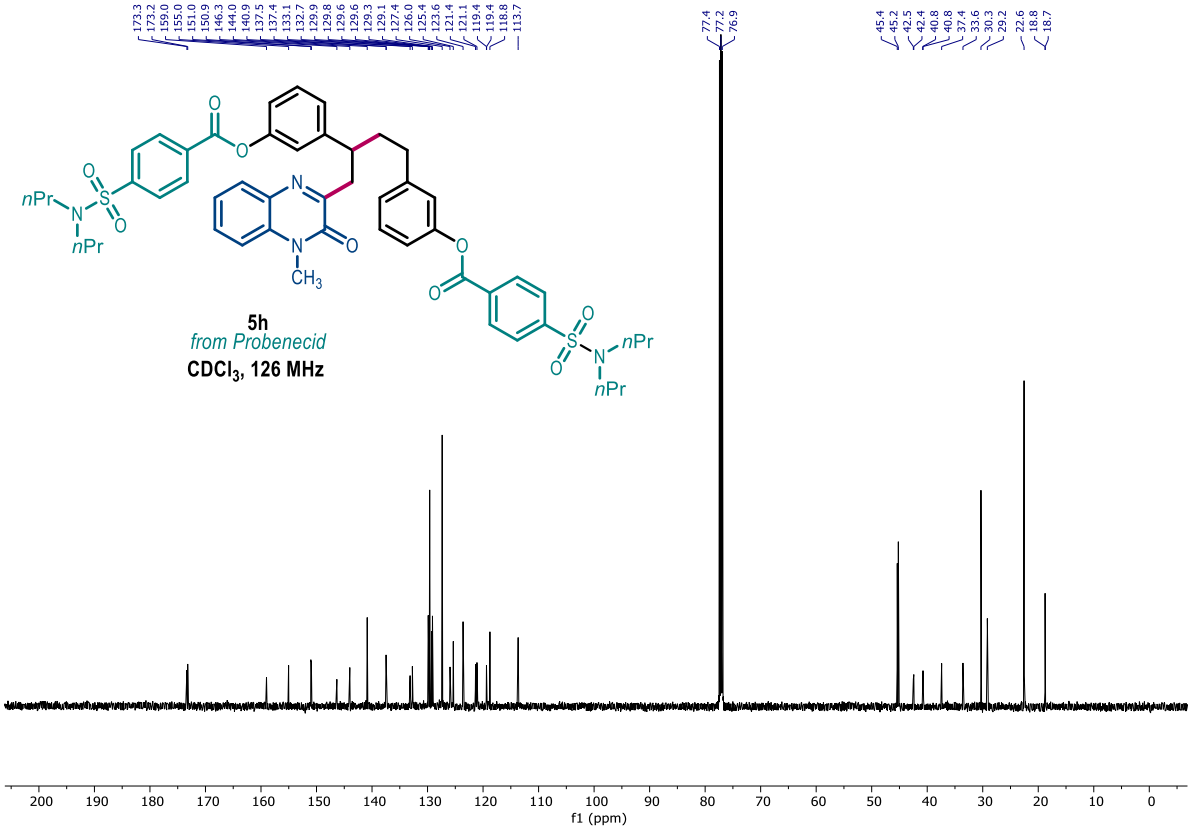

5f, (1:1 dr)
from Ibuprofen
CDCl3, 500 MHz
f1 (ppm)

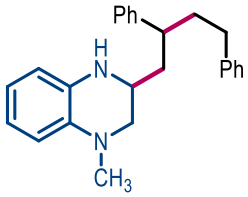

5f, (1:1 dr)
from Ibuprofen
CDCl3, 126 MHz
f1 (ppm)


MeO
OMe
N
O
CH3
5g, (1:1 dr)
from Naproxen
CDCl3, 400 MHz
f1 (ppm)

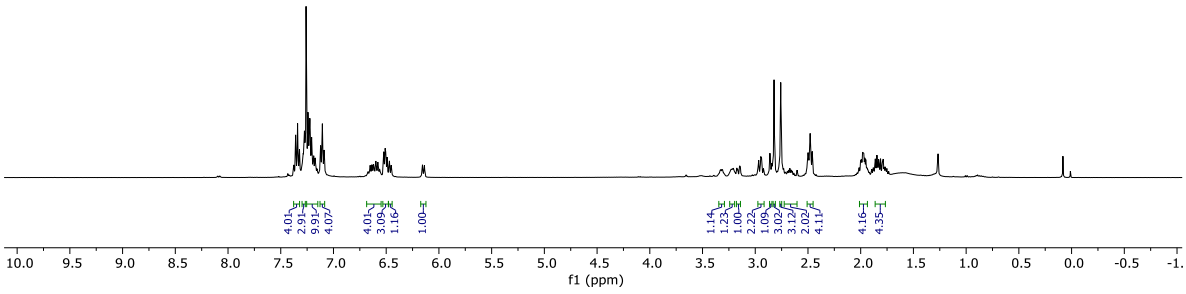

MeO
OMe
N
O
CH3
5g, (1:1 dr)
from Naproxen
CDCl3, 126 MHz
f1 (ppm)

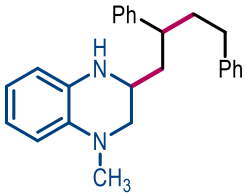

5h
from Probenecid
CDCl3, 500 MHz
f1 (ppm)


5h
from Probenecid
CDCl3, 126 MHz
f1 (ppm)

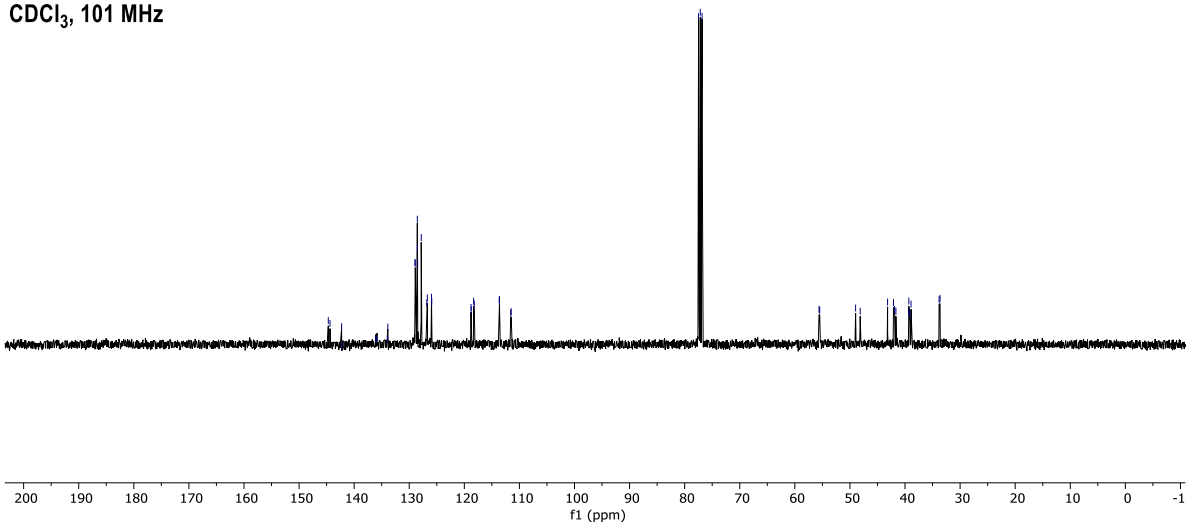


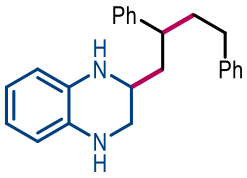
6, (1:1 dr)
$CDCl_3$, 400 MHz



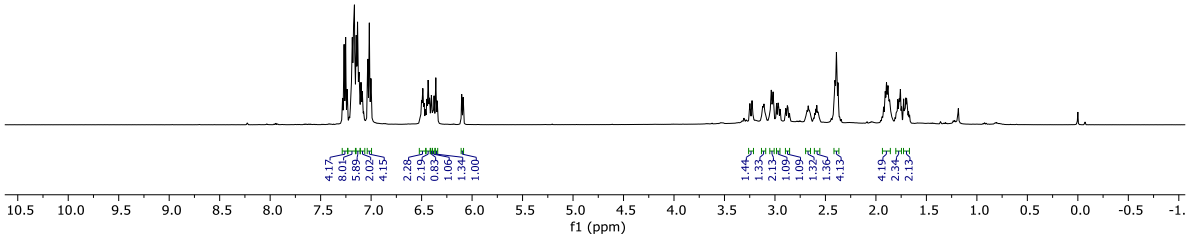


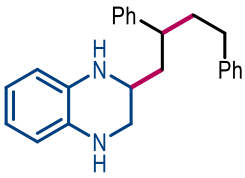
6, (1:1 dr)
$CDCl_3$, 101 MHz





7, (1:1 dr)
$CDCl_3$, 500 MHz





7, (1:1 dr)
$CDCl_3$, 126 MHz