Visible-light-accelerated amination of quinoxalin-2-ones and benzo[1,4]oxazin-2-ones with dialkyl azocarboxylates under metal and photocatalyst-free conditions.

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General Experimental Methods

Reactions were carried out in Schlenk tubes ovendried overnight at 135 ^{o}C. Commercial reagents were used as purchased. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm.

Room temperature NMR spectra were run at 300 MHz for ^{1}H and at 75 MHz for ^{13}C NMR using residual non-deuterated solvent as internal standard ($CDCl_3$: 7.26 and 77.00 ppm respectively; Acetone-d^6: 2.05 and 29.84 ppm respectively; DMSO-d^6: 2.50 and 39.52 ppm respectively) and at 282 MHz for ^{19}F NMR using $CFCl_3$ as internal standard. Hight temperature NMR spectra were run at 500 MHz for ^{1}H and at 125 MHz for ^{13}C. Chemical shifts are given in ppm. The carbon type was determined by DEPT experiments.

High resolution mass spectra (ESI) were recorded on a AB SCIEX Triple TOFTM spectrometer equipped with an electrospray source with a capillary voltage of 4.5 kV(ESI).

All photocatalysts and organic acids catalysts were commercially available. MeCN was degassed by three freeze-pump-thaw cycles and stored over 3Å MS for 48 h at least. Prior to use, MeCN was bubbled with Ar for 10 min.

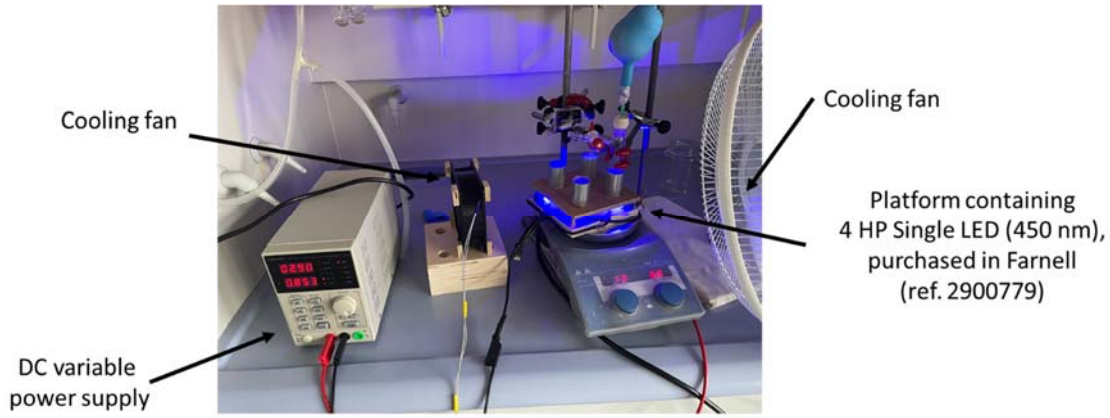
Synthesis of Starting Materials:

N-protected dihydroquinoxalin-2-ones **1** were synthetized using previously reported methodologies[1]. *N*-protected dihydrobenzoxazin-2-ones **4** were prepared using a reported methodology[2].

General Procedure for the amination of dihydroquinoxalin-2-ones and dihydrobenzoxazin-2-ones:

To an ovendried Schlenck tube containing a teflon-coated stir bar were added the proper dihydroquinoxalin-2-one or dihydrobenzoxazin-2-one (0.1 mmol, 1 eq.) and the proper diazo compound (0.13 mmol, 1.3 eq.) [if it is liquid, it was added after the MeCN]. The reaction vessel was evacuated and backfilled with argon three times. After this, freshly degassed and dried MeCN (1 mL) was added via syringe and the reaction mixture was stirred while being irradiated with HP single LED (450 nm) under a positive pressure of argon. The course of the reaction was monitored by TLC. The desired aminated product was isolated from the reaction mixture by flash column chromatography using hexane:Et_2O mixtures.

Reaction Setup:



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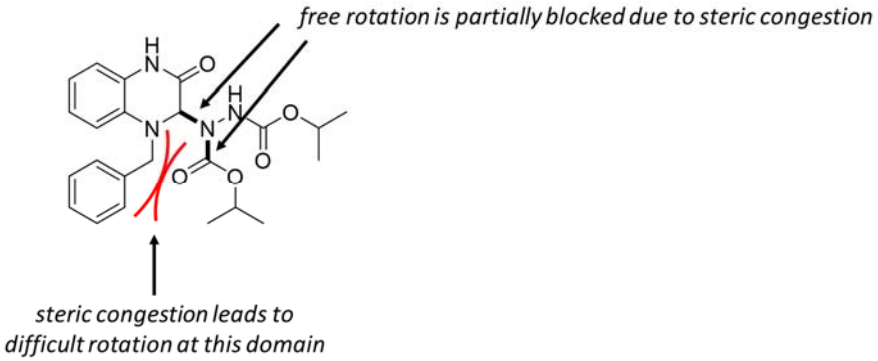
[1]*Org. Lett.* **2020**, *22*, 20, 8012–8017.

[2]*Tetrahedron*, **2008**, *64*, 5756-5761.

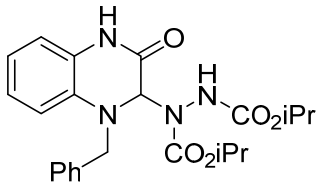
Characterization of the products

All the aminated dihydroquinoxalin-2-ones **3** and dihydrobenzoxazin-2-ones **5** exhibit high rotation energy barriers in, at least, two bonds. These energy barriers cannot be overcome at 298 K and therefore several rotameric isomers were detected by NMR. Here is an example for compound **3aa**.



As a result, NMR experiments have to be done at high temperature, trying to overcome the rotation energy barrier. All the compounds **3** and **5** have been characterized using VT-NMR at 353 K in DMSO-d^6. In most of the cases the rotamers have been resolved but, in other cases, a significant rotation barrier is still present even at 353 K.

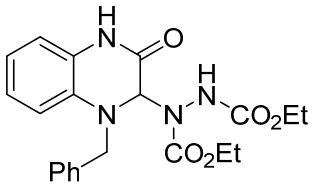
Diisopropyl 1-(1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3aa)



Using 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1a**, 23.8 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3aa** was obtained (43.6 mg, 0.099 mmol, 99% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 10.62 (bs, 1H), 8.82 (bs, 1H), 7.37 – 7.19 (m, 5H), 6.84 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.81 – 6.74 (m, 1H), 6.72 – 6.61 (m, 2H), 5.89 (s, 1H), 4.94 – 4.77 (m, 2H), 4.63 – 4.53 (m, 1H), 4.52 – 4.39 (m, 1H), 1.20 (d, *J* = 6.1 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H), 0.94 – 0.81 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 159.80 (C), 155.74 (C), 155.03 (C), 137.13 (C), 131.77 (C), 128.08 (CH), 126.82 (CH), 126.63 (CH), 125.30 (C), 122.1 (CH), 117.6 (CH), 114.4 (CH), 111.9 (CH), 71.1 (CH), 69.4 (CH), 67.7 (CH), 49.8 (CH_2), 21.3 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 21.1 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{23}H_{29}N_4O_5^+$ 441.2132; found 441.2130.

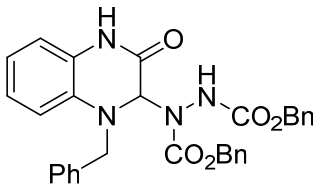
Diethyl 1-(1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ab)



Using 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1a**, 23.8 mg, 0.1 mmol) and diethyl azodicarboxylate (**2b**, 20.4 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ab** was obtained (40. mg, 0.097 mmol, 97% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 10.64 (bs, 1H), 8.94 (bs, 1H), 7.38 – 7.19 (m, 5H), 6.85 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.81 – 6.75 (m, 1H), 6.73 – 6.62 (m, 2H), 5.90 (s, 1H), 4.83 (d, *J* = 16.2 Hz, 1H), 4.45 (d, *J* = 16.2 Hz, 1H), 4.22 – 3.93 (m, 2H), 3.81 (bs, 2H), 1.16 (t, *J* = 6.6 Hz, 3H), 0.96 (bs, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 159.8 (C), 156.1 (C), 155.3 (C), 137.0 (C), 131.8 (C), 128.1 (CH), 126.9 (CH), 126.7 (CH), 125.3 (C), 122.2 (CH), 117.8 (CH), 114.4 (CH), 111.9 (CH), 71.2 (CH), 61.6 (CH_2), 60.0 (CH_2), 49.8 (CH_2), 14.0 (CH_3), 13.8 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{21}H_{25}N_4O_5^+$ 413.1819; found 413.1817.

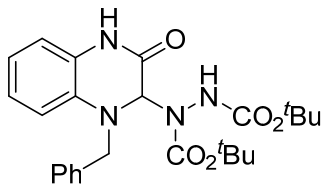
Dibenzyl 1-(1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ac)



Using 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1a**, 23.8 mg, 0.1 mmol) and dibenzyl azodicarboxylate (**3c**, 38.8 mg, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ac** was obtained (32.7 mg, 0.061 mmol, 61% yield, yellowish oil) after column chromatography using hexane-diethyl ether (from 3:7 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353K, DMSO-d_6) δ 10.70 (bs, 1H), 9.31 (bs, 1H), 7.41 – 7.17 (m, 15H), 7.11 – 7.04 (m, 1H), 6.87 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.71 – 6.67 (m, 1H), 5.98 (bs, 1H), 5.15 (s, 2H), 4.84 (m, 3H), 4.44 (s, 1H); **^{13}C NMR (126 MHz, 353 K, DMSO-d_6)** δ 159.6 (C), 156.0 (C), 155.4 (C), 136.9 (C), 136.3 (C), 135.8 (C), 135.7 (C), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 127.2 (C), 127.0 (CH), 126.8 (CH), 126.7 (CH), 125.2 (CH), 122.3 (CH), 117.9 (CH), 114.5 (CH), 111.9 (CH), 71.4 (CH), 67.0 (CH_2), 65.6 (CH_2), 49.8 (CH_2); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{31}H_{29}N_4O_5^+$ 537.2132; found 537.2135.

Di-*tert*-butyl 1-(1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ad)

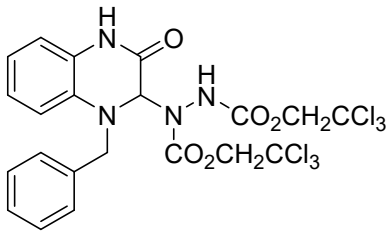


Using 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1a**, 23.8 mg, 0.1 mmol) and di-*tert*-butyl azodicarboxylate (**2d**, 29.9 µL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ad** was obtained (41.2 mg, 0.088 mmol, 88% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 4:6 to 3:7) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 10.57 (bs, 1H), 8.27 (bs, 1H), 7.39 – 7.17 (m, 5H), 6.84 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.81 – 6.67 (m, 2H), 6.66 – 6.60 (m, 1H), 5.87 (bs, 1H), 4.84 (d, *J* = 16.2 Hz, 1H), 4.48 (d, *J* = 15.4 Hz, 1H), 1.40 (s, 9H), 1.21 (s, 9H); **^{13}C NMR (126 MHz, 353 K, DMSO-d_6)** δ 159.9 (C), 155.2 (C), 154.4 (C), 137.3 (C), 132.0 (C), 128.1 (CH), 126.8 (CH), 126.6 (CH), 125.3

(C), 122.2(CH), 117.5 (CH), 114.3 (CH), 111.8 (CH), 80.3 (C), 78.5 (C), 70.6 (CH), 49.6 (CH_2), 27.5 (CH_3), 27.4 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{25}H_{33}N_4O_5^+$ 469.2445; found 469.2444.

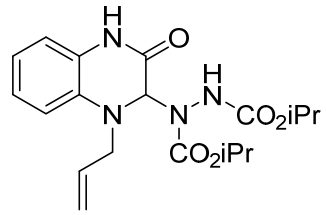
Bis(2,2,2-trichloroethyl) 1-(1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ae)



Using 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1a**, 23.8 mg, 0.1 mmol) and bis(2,2,2-trichloroethyl) azodicarboxylate (**2e**, 49.5 mg, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ae** was obtained (45.2 mg, 0.073 mmol, 73% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 10.78 (bs, 1H), 9.66 (bs, 1H), 7.45 – 7.16 (m, 5H), 7.01 – 6.56 (m, 4H), 6.06 (s, 1H), 5.03 – 4.81 (m, 3H), 4.64 – 4.41 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 163.1 (C), 154.3 (C), 153.9 (C), 136.7 (C), 131.1 (C), 128.1 (CH), 127.1 (CH), 126.7 (CH), 125.0 (C), 122.3 (CH), 118.1 (CH), 114.7 (CH), 112.1 (CH), 95.4 (C), 94.8 (C), 74.7 (CH), 73.7 (CH_2), 73.7 (CH_2), 49.9 (CH_2); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{21}H_{19}Cl_6N_4O_5^+$ 616.9481; found 616.9483.

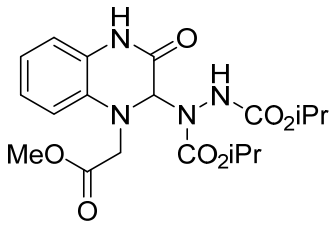
Diisopropyl 1-(1-allyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ba)



Using 4-allyl-3,4-dihydroquinoxalin-2(1*H*)-one (**3b**, 18.8 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 µL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ba** was obtained (27.1 mg, 0.069 mmol, 69% yield, yellow oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 10.56 (bs, 1H), 8.72 (bs, 1H), 6.87 – 6.78 (m, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.68 – 6.57 (m, 1H), 6.01 – 5.81 (m, 2H), 5.23 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.20 – 5.13 (m, 1H), 4.90 – 4.73 (m, 1H), 4.63 – 4.48 (m, 1H), 4.21 (dd, *J* = 16.5, 5.3 Hz, 1H), 3.89 (dd, *J* = 16.5, 5.5 Hz, 1H), 1.22 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 4.6 Hz, 3H), 1.06 (d, *J* = 6.3 Hz, 3H), 0.89 – 0.86 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO-d_6)** δ 159.7 (C), 155.7 (C), 154.9 (C), 133.5 (CH), 131.7 (C), 125.2 (C), 122.1 (CH), 117.4 (CH), 116.5 (CH_2), 114.3 (CH), 111.6 (CH), 70.8 (CH), 69.3 (CH), 68.1 (CH), 48.8 (CH_2), 21.5 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 21.1 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{27}N_4O_5^+$ 391.1976; found 391.1977.

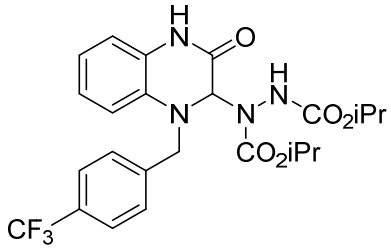
Diisopropyl 1-(1-(2-methoxy-2-oxoethyl)-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ca)



Using methyl 2-(3-oxo-3,4-dihydroquinoxalin-1(2*H*)-yl)acetate (**1c**, 20.0 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 µL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ca** was obtained (26.3 mg, 0.063 mmol, 63% yield, yellow solid) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

m.p. 178 – 183 °C;**^{1}H NMR (500 MHz, 353 K, DMSO-d_6)** δ 10.65 (bs, 1H), 8.56 (bs, 1H), 6.86 – 6.81 (m, 2H), 6.72 – 6.67 (m, 1H), 6.59 (d, *J* = 7.0 Hz, 1H), 5.93 (bs, 1H), 4.88 – 4.76 (m, 1H), 4.55 (s, 1H), 4.40 (d, *J* = 18.0 Hz, 1H), 4.17 (d, *J* = 18.0 Hz, 1H), 3.69 (s, 3H), 1.23 – 1.16 (m, 9H), 1.06 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO-d_6)** δ 169.7 (C), 159.5 (C), 155.7 (C), 155.0 (C), 131.3 (C), 125.0 (C), 122.3 (CH), 118.2 (CH), 114.5 (CH), 111.0 (CH), 69.6 (CH), 67.9 (CH), 67.5 (CH), 51.4 (CH_3), 48.0 (CH_2), 21.3 (CH_3), 21.2 (CH_3), 21.1 (CH_3), 21.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{27}N_4O_7^+$ 423.1874; found 423.1881.

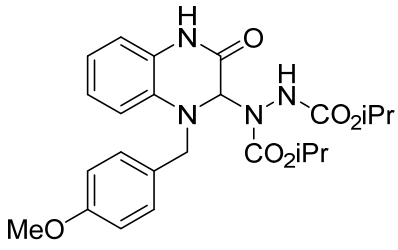
Diisopropyl 1-(3-oxo-1-(4-(trifluoromethyl)benzyl)-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3da)



Using 4-(4-(trifluoromethyl)benzyl)-3,4-dihydroquinoxalin-2(1*H*)-one (**1d**, 30.6 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3da** was obtained (44.3 mg, 0.087 mmol, 87% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 10.67 (bs, 1H), 8.87 (bs, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.77 (td, *J* = 7.7, 1.5 Hz, 1H), 6.66 (td, *J* = 7.5, 1.2 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 5.91 (bs, 1H), 4.94 (d, *J* = 16.7 Hz, 1H), 4.82 (hept, *J* = 6.3 Hz, 1H), 4.66 – 4.43 (m, 2H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H), 0.88 (bs, 3H); **^{19}F NMR (471 MHz, 353 K, DMSO d_6)** δ -61.04; **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 159.8 (2C), 155.1 (C), 142.2 (C), 131.5 (C), 127.6 (C, q, $J_{C\text{-}F}$ = 31.9 Hz), 127.6 (CH), 125.4 (C), 124.9 (CH, q, $J_{C\text{-}F}$ = 3.6 Hz), 123.9 (C, q, $J_{C\text{-}F}$ = 272.0 Hz), 122.2 (CH), 118.0 (CH), 114.5 (CH), 111.9 (CH), 71.3 (CH), 69.5 (CH), 67.8 (CH), 49.6 (CH_2), 21.3 (CH_3), 21.3 (CH_3), 21.1 (CH_3), 21.1 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{28}F_3N_4O_5^+$ 509.2006; found 509.2008.

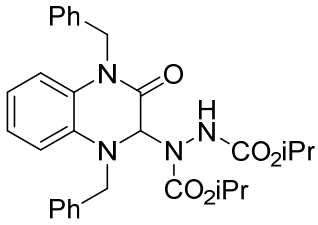
Diisopropyl-1-(1-(4-methoxybenzyl)-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ea)



Using 4-(4-methoxybenzyl)-3,4-dihydroquinoxalin-2(1*H*)-one (**1e**, 26.8 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ea** was obtained (33.7 mg, 0.072 mmol, 72% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 10.59 (bs, 1H), 8.79 (bs, 1H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.83 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.78 (td, *J* = 7.7, 1.4 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 6.64 (td, *J* = 7.5, 1.3 Hz, 1H), 5.86 (bs, 1H), 4.82 (hept, *J* = 6.3 Hz, 1H), 4.77 (s, 1H), 4.56 (s, 1H), 4.38 (d, *J* = 15.8 Hz, 1H), 3.74 (s, 3H), 1.20 (d, *J* = 6.1 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.11 – 1.03 (m, 3H), 0.88 (s, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 159.9 (C), 158.3 (C), 155.0 (C), 154.1 (C), 131.9 (C), 128.9 (C), 128.2 (CH), 125.3 (C), 122.1 (CH), 117.5 (CH), 114.3 (CH), 113.8 (CH), 111.9 (CH), 70.8 (CH), 69.3 (CH), 67.6 (CH), 54.8 (CH_3), 49.2 (CH_2), 21.3 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 21.1 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{31}N_4O_6^+$ 471.2238; found 471.2249.

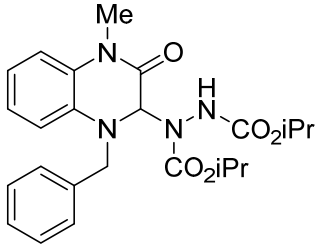
Diisopropyl 1-(1,4-dibenzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3fa)



Using 1,4-dibenzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1f**, 32.8 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3fa** was obtained (49.3 mg, 0.093 mmol, 93% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 8.85 (bs, 1H), 7.58 – 7.14 (m, 10H), 6.96 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.88 – 6.79 (m, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.69 – 6.60 (m, 1H), 6.15 (s, 1H), 5.39 (d, *J* = 16.2 Hz, 1H), 5.15 (d, *J* = 16.3 Hz, 1H), 4.90 (d, *J* = 16.0 Hz, 1H), 4.85 (hept, *J* = 6.2 Hz, 1H), 4.59-4.52 (m, 2H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H), 0.89 (bs, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 160.1 (C), 155.0 (C), 154.0 (C), 136.9 (C), 136.4 (C), 133.3 (C), 128.1 (CH), 128.0 (CH), 126.9 (CH), 126.7 (CH), 126.5 (C), 126.5 (CH), 126.3 (CH), 122.7 (CH), 118.0 (CH), 114.6 (CH), 112.8 (CH), 71.3 (CH), 69.5 (CH), 67.8 (CH), 50.2 (CH_2), 44.5 (CH_2), 21.3 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 21.1 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{30}H_{35}N_4O_5^+$ 531.2602; found 531.2600.

Diisopropyl 1-(1-benzyl-4-methyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ga)

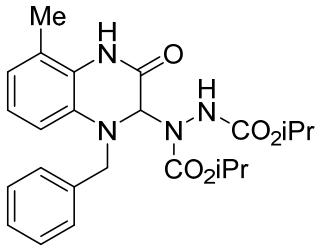


Using 4-benzyl-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1g**, 25.2 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ga** was obtained (41.3 mg, 0.091 mmol, 91% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 8.74 (bs, 1H), 7.37 – 7.18 (m, 5H), 7.03 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.86 (dt, *J* = 7.6, 4.4 Hz, 1H), 6.78 (td, *J* = 7.6, 1.4 Hz, 1H), 6.76 – 6.70 (m, 1H), 5.99 (s, 1H), 4.93 – 4.76 (m, 2H), 4.63 – 4.51 (m, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 3.37 (s, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.06 (s, 3H), 0.88 (s, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 159.7 (C), 159.1 (C), 154.8 (C), 136.8 (C), 133.1 (C), 128.1 (CH), 127.6 (C), 127.0 (CH), 126.7 (CH), 122.5 (CH), 118.0 (CH), 113.7 (CH), 112.1 (CH), 70.7 (CH), 69.4 (CH), 67.7 (CH), 50.0 (CH_2),

28.5 (CH_3), 21.4 (CH_3), 21.3 (CH_3), 21.3 (CH_3), 21.1 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{31}N_4O_5^+$ 455.2289; found 455.2292.

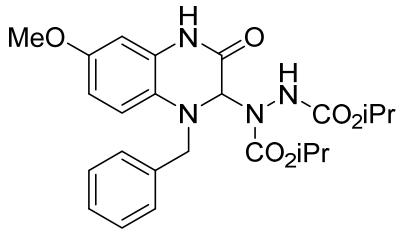
Diisopropyl 1-(1-benzyl-5-methyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ha)



Using 4-benzyl-8-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1h**, 25.2 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ha** was obtained (35.9 mg, 0.079 mmol, 79% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 9.84 (bs, 1H), 8.77 (bs, 1H), 7.37 – 7.15 (m, 5H), 6.69 (t, *J* = 7.8 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 5.89 (bs, 1H), 4.91 – 4.77 (m, 2H), 4.54 (s, 1H), 4.46 (d, *J* = 16.1 Hz, 1H), 2.23 (s, 3H), 1.19 (d, *J* = 4.6 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.90 (s, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 160.3 (C), 155.7 (C), 154.9 (C), 137.2 (C), 132.1 (C), 128.1 (CH), 126.9 (CH), 126.6 (CH), 123.5 (C), 122.6 (C), 121.8 (CH), 120.1 (CH), 110.3 (CH), 71.1 (CH), 69.3 (CH), 67.6 (CH), 50.3 (CH_2), 21.5 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 21.1 (CH_3), 16.6 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{31}N_4O_5^+$ 455.2289; found 455.2291.

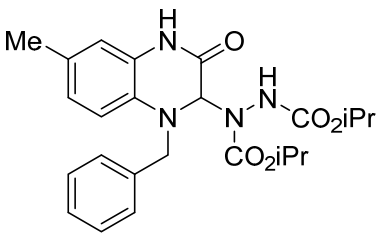
Diisopropyl 1-(1-benzyl-6-methoxy-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ia)



Using 4-benzyl-7-methoxy-3,4-dihydroquinoxalin-2(1*H*)-one (**1i**, 26.8 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 µL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ia** was obtained (26.2 mg, 0.056 mmol, 56% yield, greenish solid) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

m.p. 172 °C – 174 °C; **^{1}H NMR (500 MHz, 353 K, DMSO-d_6)** δ 10.47 (bs, 1H), 8.83 (bs, 1H), 7.36 – 7.20 (m, 5H), 6.73 (d, *J* = 9.0 Hz, 1H), 6.24 (d, *J* = 6.6 Hz, 2H), 5.87 (bs, 1H), 4.87 – 4.72 (m, 2H), 4.62 – 4.54 (m, 1H), 4.45 (d, *J* = 16.0 Hz, 1H), 3.59 (s, 3H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 5.0 Hz, 3H), 0.92 – 0.80 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO-d_6)** δ 155.7 (C), 155.2 (C), 155.0 (C), 137.0 (C), 133.0 (C), 128.1 (CH), 126.9 (CH), 126.7 (CH), 119.3 (C), 114.6 (CH), 102.4 (CH), 99.5 (CH), 71.2 (CH), 69.4 (CH), 67.8 (CH), 54.8 (CH_3), 50.0 (CH_2), 21.5 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 21.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{31}N_4O_6^+$ 471.2238; found 471.2242.

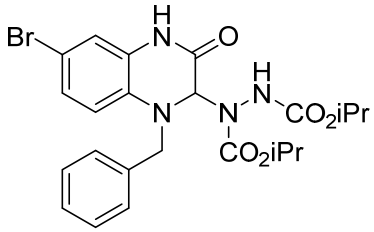
Diisopropyl 1-(1-benzyl-6-methyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ja)



Using 4-benzyl-7-methyl-3,4-dihydroquinoxalin-2(1H)-one (**1j**, 25.2 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 µL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ja** was obtained (33.1 mg, 0.073 mmol, 73% yield, yellow solid) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

m.p. 180 °C decompose**; ^{1}H NMR (500 MHz, 353 K, DMSO-*d*$_6$)** δ 10.54 (bs, 1H), 8.79 (bs, 1H), 7.42 – 7.18 (m, 5H), 6.65 (s, 1H), 6.57 (t, *J* = 7.0 Hz, 2H), 5.86 (bs, 1H), 4.87 – 4.74 (m, 2H), 4.56 (s, 1H), 4.43 (d, *J* = 16.2 Hz, 1H), 2.14 (s, 3H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.11 – 1.07 (m, 3H), 0.91 – 0.81 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO-*d*$_6$)** δ 160.0 (C), 155.7 (C), 155.0 (C), 137.3 (C), 129.5 (C), 128.0 (CH), 126.8 (CH), 126.6 (CH), 126.4 (C), 125.2 (C), 122.5 (CH), 114.9 (CH), 111.9 (CH), 71.2 (CH), 69.3 (CH), 67.6 (CH), 49.8 (CH_2), 21.34 (CH_3), 21.29 (CH_3), 21.2 (CH_3), 21.0 (CH_3), 19.6 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{31}N_4O_5^+$ 455.2289; found 455.2281.

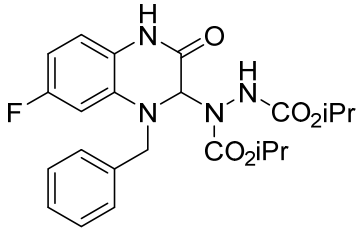
Diisopropyl 1-(1-benzyl-6-bromo-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ka)



Using 4-benzyl-7-bromo-3,4-dihydroquinoxalin-2(1*H*)-one (**1k**, 31.7 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ka** was obtained (43.1 mg, 0.083 mmol, 83% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-*d*$_6$) δ 10.76 (bs, 1H), 8.91 (bs, 1H), 7.38 – 7.22 (m, 5H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.91 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 1H), 5.88 (bs, 1H), 4.93 – 4.74 (m, 2H), 4.65 – 4.52 (m, 1H), 4.46 (d, *J* = 16.2 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H), 0.93 (s, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO *d*$_6$)** δ 159.9 (C), 159.8 (C), 155.0 (C), 136.6 (C), 131.3 (C), 128.1 (CH), 127.1 (C), 126.9 (CH), 126.8 (CH), 124.3 (CH), 116.5 (CH), 113.8 (CH), 108.8 (C), 70.7 (CH), 69.5 (CH), 67.8 (CH), 50.0 (CH_2), 21.3 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 21.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{23}H_{28}BrN_4O_5^+$ 519.1238; found 519.1249.

Diisopropyl 1-(1-benzyl-7-fluoro-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3la)

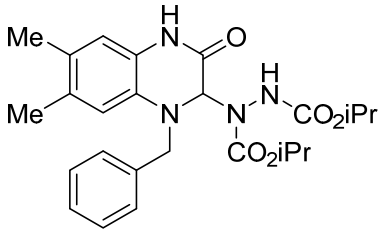


Using 4-benzyl-6-fluoro-3,4-dihydroquinoxalin-2(1*H*)-one (**1l**, 128.14 mg, 0.5 mmol) and diisopropyl azodicarboxylate (**2a**, 128 µL, 0.65 mmol, 1.3 equiv.), in accordance with General Procedure, product **3la** was obtained (171.3 mg, 0.374 mmol, 75% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-*d*$_6$) δ 10.67 (bs, 1H), 8.91 (bs, 1H), 7.38 – 7.21 (m, 5H), 6.81 (dd, *J* = 8.5, 5.7 Hz, 1H), 6.49 (d, *J* = 11.3 Hz, 1H), 6.44 (td, *J* = 8.5, 2.6 Hz, 1H), 5.87 (bs, 1H), 4.88

– 4.76 (m, 2H), 4.68 – 4.53 (m, 1H), 4.46 (d, *J* = 16.2 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 5.6 Hz, 3H), 0.99 – 0.78 (m, 3H); **^{19}F NMR (282 MHz, 353 K, DMSO-d_6)** δ -120.11 (s); **^{13}C NMR (126 MHz, 353 K, DMSO-d_6)** δ 159.4 (C), 159.4 (C), 158.2 (d, *J* = 235.3 Hz, C), 155.1 (C), 136.6 (C), 133.5 (C), 128.2 (CH), 126.9 (CH), 126.8 (CH), 121.9 (C), 114.8 (d, $J_{C–F}$ = 10.1 Hz, CH), 103.4 (d, $J_{C–F}$ = 23.0 Hz, CH), 99.5 (d, $J_{C–F}$ = 30.1 Hz, CH), 70.5 (CH), 69.5 (CH), 67.8 (CH), 50.0 (CH_2), 21.30 (CH_3), 21.27 (CH_3), 21.1 (CH_3), 21.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{23}H_{28}FN_4O_5^+$ 459.2038; found 459.2040.

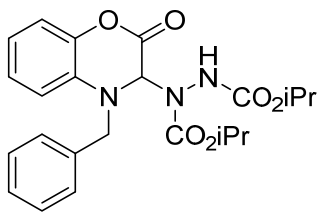
Diisopropyl 1-(1-benzyl-6,7-dimethyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)hydrazine-1,2-dicarboxylate (3ma)



Using 4-benzyl-6,7-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1m**, 26.6 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **3ma** was obtained (7.0 mg, 0.015 mmol, 15% yield, colorless oil) after column chromatography using hexane-diethyl ether (from 5:5 to 2:8) mixtures.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 10.44 (bs, 1H), 8.78 (bs, 1H), 7.36 – 7.21 (m, 5H), 6.60 (s, 1H), 6.49 (s, 1H), 5.81 (bs, 1H), 4.86 – 4.75 (m, 2H), 4.55 (bs, 1H), 4.41 (d, *J* = 16.2 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.2 Hz, 3H), 0.96 – 0.80 (m, 3H).**^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 155.7 (C), 154.9 (C), 154.2 (C), 137.4 (C), 129.7 (C), 129.2 (C), 128.0 (CH), 126.9 (CH), 126.6 (CH), 115.6 (C), 113.3 (C), 109.6 (CH), 108.6 (CH), 71.1 (CH), 69.3 (CH), 67.6 (CH), 49.6 (CH_2), 21.5 (CH_3), 21.3 (CH_3), 21.3 (CH_3), 21.2 (CH_3), 18.6 (CH_3), 17.8 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{25}H_{33}N_4O_5^+$ 469.2445; found 469.2437.

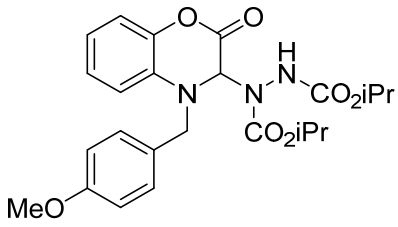
Diisopropyl 1-(4-benzyl-2-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)hydrazine-1,2-dicarboxylate (5aa)



Using 4-benzyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (**4a**, 23.9 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 µL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **5aa** was obtained (32.3 mg, 0.074 mmol, 74% yield, brown oil) after column chromatography using hexane-ethyl acetate 8:2 mixture.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 9.04 (bs, 1H), 7.41 – 7.31 (m, 4H), 7.30 – 7.22 (m, 1H), 7.05 – 6.92 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.79 (td, *J* = 7.8, 1.4 Hz, 1H), 6.09 (bs, 1H), 4.89 – 4.75 (m, 2H), 4.65 – 4.53 (m, 1H), 4.46 (d, *J* = 15.6 Hz, 1H), 1.24 – 1.13 (m, 6H), 1.07 (d, *J* = 5.8 Hz, 3H), 1.00 – 0.90 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO-d_6)** δ 159.1 (C), 154.9 (C), 153.7 (C), 140.0 (C), 136.0 (C), 131.3 (C), 128.2 (CH), 127.2 (CH), 126.9 (CH), 124.3 (CH), 118.7 (CH), 115.2 (CH), 113.2 (CH), 70.0 (CH), 68.9 (CH), 68.1 (CH), 49.7 (CH_2), 21.23 (CH_3), 21.16 (CH_3), 21.09 (CH_3), 21.05 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{23}H_{28}N_3O_6^+$ 442.1973; found 442.1983.

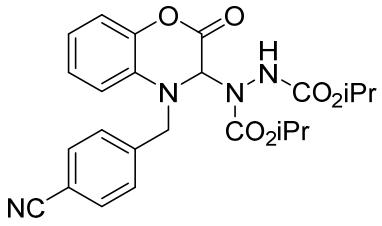
Diisopropyl 1-(4-(4-methoxybenzyl)-2-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)hydrazine-1,2-dicarboxylate (5ba)



Using 4-(4-methoxybenzyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (**4b**, 26.9 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **5ba** was obtained (27.1 mg, 0.057 mmol, 57% yield, reddish oil) after column chromatography using hexane-ethyl acetate 8:2 mixture.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 9.01 (s, 1H), 7.31 – 7.18 (m, 2H), 7.02 – 6.94 (m, 2H), 6.93 – 6.87 (m, 2H), 6.87 (dd, *J* = 5.7, 3.0 Hz, 1H), 6.79 (td, *J* = 7.7, 1.4 Hz, 1H), 6.05 (s, 1H), 4.81 (hept, *J* = 6.3 Hz, 1H), 4.74 (d, *J* = 15.3 Hz, 1H), 4.61 – 4.53 (m, 1H), 4.38 (d, *J* = 15.1 Hz, 1H), 3.75 (s, 3H), 1.21 – 1.14 (m, 6H), 1.07 (d, *J* = 5.8 Hz, 3H), 1.00 – 0.92 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 159.0 (C), 158.5 (C), 154.9 (C), 140.0 (C), 131.4 (C), 128.6 (CH), 127.7 (C), 124.3 (CH), 118.6 (CH), 115.6 (C), 115.1 (CH), 113.8 (CH), 113.2 (CH), 70.0 (CH), 68.5 (CH), 68.1 (CH), 54.8 (CH_3), 49.1 (CH_2), 21.23 (CH_3), 21.17 (CH_3), 21.11 (CH_3), 21.05 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{24}H_{30}N_3O_7^+$ 472.2078; found 472.2072.

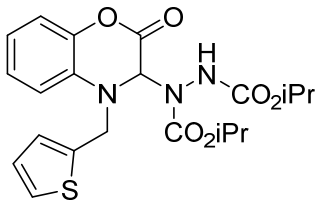
Diisopropyl 1-(4-(4-cyanobenzyl)-2-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)hydrazine-1,2-dicarboxylate (5ca)



Using 4-((2-oxo-2,3-dihydro-4*H*-benzo[*b*][1,4]oxazin-4-yl)methyl)benzonitrile (**4c**, 26.4 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **5ca** was obtained (25.5 mg, 0.055 mmol, 55% yield, reddish oil) after column chromatography using hexane-ethyl acetate 8:2 mixture.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 9.09 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.01 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.98 – 6.92 (m, 1H), 6.80 (td, *J* = 7.7, 1.3 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.16 (s, 1H), 4.90 (d, *J* = 16.6 Hz, 1H), 4.85 – 4.74 (m, 1H), 4.61 – 4.52 (m, 2H), 1.19 (d, *J* = 3.2 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H), 0.97 – 0.92 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 158.9 (C), 155.7 (C), 154.9 (C), 142.3 (C), 140.0 (C), 132.0 (CH), 130.8 (C), 128.1 (CH), 124.4 (CH), 119.0 (CH), 118.2 (CN), 115.3 (CH), 113.2 (CH), 109.9 (C), 70.1 (CH), 69.4 (CH), 68.2 (CH), 49.7 (CH_2), 21.22 (CH_3), 21.16 (CH_3), 21.1 (CH_3), 21.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{24}H_{27}N_4O_6^+$ 467.1925; found 467.1928.

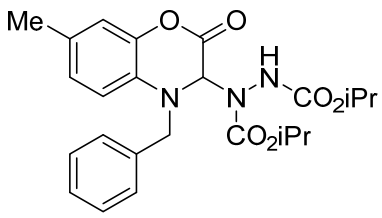
Diisopropyl 1-(2-oxo-4-(thiophen-2-ylmethyl)-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-3-yl)hydrazine-1,2-dicarboxylate (5da)



Using 4-(thiophen-2-ylmethyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (**4d**, 24.5 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **5da** was obtained (33.8 mg, 0.076 mmol, 76% yield, colorless oil) after column chromatography using hexane-ethyl acetate 8:2 mixture.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 9.04 (bs, 1H), 7.42 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.11 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.06 – 6.95 (m, 4H), 6.83 (ddd, *J* = 8.2, 7.2, 1.7 Hz, 1H), 6.11 (s, 1H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.83 (hept, *J* = 6.2 Hz, 1H), 4.64 (d, *J* = 16.0 Hz, 1H), 4.61 – 4.55 (m, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H), 0.97 (bs, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 159.1 (C), 155.0 (C), 153.8 (C), 140.0 (C), 139.1 (C), 130.8 (C), 126.6 (CH), 126.3 (CH), 125.3 (CH), 124.4 (CH), 119.0 (CH), 115.3 (CH), 113.2 (CH), 70.1 (CH), 68.2 (2CH), 44.8 (CH_2), 21.2 (CH_3), 21.2 (CH_3), 21.1 (CH_3), 21.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{21}H_{26}N_3O_6S^+$ 448.1537; found 448.1539.

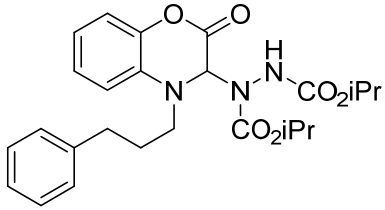
Diisopropyl 1-(4-benzyl-7-methyl-2-oxo-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)hydrazine-1,2-dicarboxylate (5ea)



Using 4-benzyl-7-methyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (**4e**, 25.3 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 µL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **5ea** was obtained (34.0 mg, 0.074 mmol, 74% yield, reddish oil) after column chromatography using hexane-ethyl acetate 8:2 mixture.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 9.01 (bs, 1H), 7.39 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 6.82 (d, *J* = 1.4 Hz, 1H), 6.80 – 6.76 (m, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.05 (bs, 1H), 4.88 – 4.72 (m, 2H), 4.62 – 4.53 (m, 1H), 4.43 (d, *J* = 15.7 Hz, 1H), 2.20 (s, 3H), 1.26 – 1.14 (m, 6H), 1.07 (d, *J* = 6.0 Hz, 3H), 1.02 – 0.89 (m, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO-d_6)** δ 159.29 (C), 159.25 (C), 154.9 (C), 139.9 (C), 136.2 (C), 128.8 (C), 128.1 (CH), 128.0 (C), 127.2 (CH), 126.9 (CH), 124.7 (CH), 115.6 (CH), 113.2 (CH), 70.0 (CH), 69.0 (CH), 68.1 (CH), 49.8 (CH_2), 21.21 (CH_3), 21.16 (CH_3), 21.1 (CH_3), 21.0 (CH_3), 19.4 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{24}H_{30}N_3O_6^+$ 456.2129; found 456.2131.

Diisopropyl 1-(2-oxo-4-(3-phenylpropyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)hydrazine-1,2-dicarboxylate (5da)



Using 4-(3-phenylpropyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (**4f**, 24.5 mg, 0.1 mmol) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.), in accordance with General Procedure, product **5fa** was obtained (23.5 mg, 0.050 mmol, 50% yield, colorless oil) after column chromatography using hexane-ethyl acetate 8:2 mixture.

^{1}H NMR (500 MHz, 353 K, DMSO-d_6) δ 8.95 (bs, 1H), 7.31 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 7.02 (td, *J* = 7.7, 1.5 Hz, 1H), 6.96 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.84 – 6.75 (m, 2H), 6.07 (bs, 1H), 4.82 (h, *J* = 6.3 Hz, 1H), 4.54 (s, 1H), 3.59 (ddd, *J* = 14.1, 8.3, 5.6 Hz, 1H), 3.25 (dt, *J* = 14.5, 7.4 Hz, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.04 (ddd, *J* = 14.4, 8.1, 6.5 Hz, 1H), 1.99 – 1.86 (m, 1H), 1.20 - 1.15 (m, 6H), 1.04 (d, *J* = 6.2 Hz, 3H), 0.94 (s, 3H); **^{13}C NMR (126 MHz, 353 K, DMSO d_6)** δ 158.9 (C), 154.8 (C), 153.7 (C), 140.9 (C), 139.9 (C), 131.2 (C), 127.8 (CH), 127.7 (CH), 125.4 (CH), 124.4 (CH), 118.2 (CH), 115.2 (CH), 112.6 (CH), 69.9 (CH), 68.8 (CH), 68.0 (CH), 45.6 (CH_2), 32.0 (CH_2), 27.0 (CH_2), 21.2 (CH_3), 21.2 (CH_3), 21.1 (CH_3), 21.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{25}H_{32}N_3O_6^+$ 470.2286; found 470.2289.

Specific Procedure for the Gram Scale reactions

Procedure for the Gram Scale Reaction between dihydroquinoxalinone 3aa and diisopropil diisopropyl azodicarboxylate (2a) under sunlight irradiation.

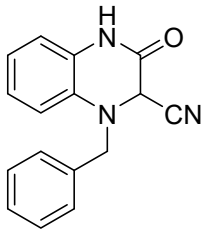
To an ovendried 250 mL-Schlenck tube containing a teflon-coated stir bar were added 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1a**, 0.92 g, 3.8 mmol, 1 eq.). The reaction vessel was evacuated and backfilled with argon three times. After this, freshly degassed and dried MeCN (20 mL) and diisopropyl azodicarboxylate (**2a**, 0.97 mL, 4.94 mmol, 1.3 equiv.) were added via syringe and the reaction mixture was placed at the upper part of the building in sunny hours under vigorous stirring and under a positive pressure of argon. The course of the reaction was monitored by TLC. The desired aminated product (**3aa**, 1.47 g, 3.34 mmol, 88% yield) was isolated from the reaction mixture by flash column chromatography using hexane:Et_2O mixtures.

Procedure for the Gram Scale Reaction between dihydroquinoxalinone 3aa and diisopropil diisopropyl azodicarboxylate (2a) under Blue LEDs (450 nm) irradiation.

To an ovendried 250 mL-Schlenck tube containing a teflon-coated stir bar were added 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1a**, 1.2 g or 1.57 g, 5.0 mmol or 6.6, 1 eq.). The reaction vessel was evacuated and backfilled with argon three times. After this, freshly degassed and dried MeCN (20 mL) and diisopropyl azodicarboxylate (**2a**, 1.28 mL or 1.68 mL, 6.5 mmol or 8.6 mmol, 1.3 equiv.) were added via syringe and the reaction mixture was irradiated with a strip of Blue LEDs (450 nm) under vigorous stirring under a positive pressure of argon. The course of the reaction was monitored by TLC. The desired aminated product (**3aa**, 1.98 g or 2.41 g, 4.5 mmol or 5.47 mmol, 90% yield or 83% yield) was isolated from the reaction mixture by flash column chromatography using hexane:Et_2O mixtures.

Specific Procedure for the derivatization of aminated dihydroquinoxalinone 3aa.

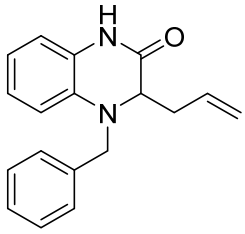
1-Benzyl-3-oxo-1,2,3,4-tetrahydroquinoxaline-2-carbonitrile (6)



In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3aa** (44.0 mg, 0.1 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. MeCN (2 mL) and TMS-CN (37.5 uL, 0.3 mmol, 3 equiv.) were sequentially added. Then, $BF_3{\cdot}OEt_2$ (13.6 uL, 0.11 mmol, 1.1 equiv.) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was directly purified by column chromatography to afford compound **6** (25.1 mg, 0.095 mmol, 95% yield) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.64 (bs, 1H), 7.57 – 7.32 (m, 5H), 7.19 – 7.08 (m, 1H), 7.04 – 6.91 (m, 3H), 4.82 (d, *J* = 13.4 Hz, 1H), 4.59 (s, 1H), 4.09 (d, *J* = 13.4 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.9 (C), 133.8 (C), 132.4 (C), 129.3 (CH), 128.8 (CH), 125.8 (C), 125.2 (CH), 122.1 (CH), 116.6 (CH), 114.4 (CH), 112.8 (CH), 52.1 (CH_2), 51.9 (CH); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{14}N_3O^+$ 264.1131; found 264.1135.

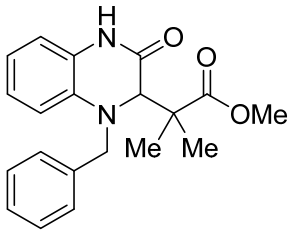
3-Allyl-4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (7)



In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3aa** (44.0 mg, 0.1 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. MeCN (2 mL) and allyl-TMS (47.8 uL, 0.3 mmol, 3 equiv.) were sequentially added. Then, $BF_3{\cdot}OEt_2$ (13.6 uL, 0.11 mmol, 1.1 equiv.) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was directly purified by column chromatography to afford compound **7** (22.7 mg, 0.082 mmol, 82% yield) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 7.47 – 7.13 (m, 5H), 6.93 (ddd, *J* = 8.0, 6.9, 2.0 Hz, 1H), 6.87 – 6.74 (m, 2H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.77 (dddd, *J* = 17.0, 10.0, 7.6, 6.9 Hz, 1H), 5.19 – 4.98 (m, 2H), 4.69 (d, *J* = 15.1 Hz, 1H), 4.32 (d, *J* = 15.1 Hz, 1H), 4.00 (td, *J* = 6.6, 0.6 Hz, 1H), 2.67 – 2.27 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 168.1 (C), 136.7 (C), 133.9 (C), 133.3 (CH), 128.7 (CH), 127.6 (CH), 127.6 (CH), 126.2 (C), 124.1 (CH), 119.1 (CH), 118.4 (CH_2), 115.5 (CH), 113.6 (CH), 62.0 (CH), 53.1 (CH_2), 34.2 (CH_2); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O^+$ 279.1492; found 279.1498.

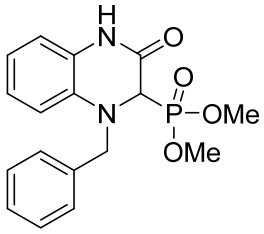
Methyl 2-(1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)-2-methylpropanoate (8)



In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3aa** (44.0 mg, 0.1 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. MeCN (2 mL) and methyl trimethylsilyl dimethylketene acetal (60.9 uL, 0.3 mmol, 3 equiv.) were sequentially added. Then, $BF_3{\cdot}OEt_2$ (13.6 uL, 0.11 mmol, 1.1 equiv.) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was directly purified by column chromatography to afford compound **8** (33.7 mg, 0.099 mmol, 99% yield) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 7.34 – 7.08 (m, 5H), 6.90 (ddd, *J* = 8.1, 5.9, 2.8 Hz, 1H), 6.84 – 6.79 (m, 1H), 6.77 – 6.70 (m, 2H), 4.86 (d, *J* = 15.8 Hz, 1H), 4.45 – 4.30 (m, 2H), 3.61 (s, 3H), 1.22 (s, 3H), 1.19 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 175.9 (C), 165.0 (C), 137.2 (C), 133.9 (C), 128.7 (CH), 127.5 (CH), 127.3 (C), 127.2 (CH), 124.2 (CH), 119.8 (CH), 116.6 (CH), 115.1 (CH), 68.9 (CH), 57.7 (CH_2), 52.2 (CH_3), 49.4 (C), 22.7 (CH_3), 22.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_3^+$ 339.1703; found 339.1700.

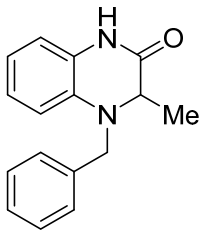
Dimethyl (1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)phosphonate (9)



In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3aa** (44.0 mg, 0.1 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. MeCN (2 mL) and dimethyl phosphite (27.5 uL, 0.3 mmol, 3 equiv.) were sequentially added. Then, $BF_3{\cdot}OEt_2$ (13.6 uL, 0.11 mmol, 1.1 equiv.) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was directly purified by column chromatography to afford compound **9** (34.3 mg, 0.099 mmol, 99% yield) as a colourless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.44 (bs, 1H), 7.44 – 7.20 (m, 5H), 6.97 (ddd, *J* = 8.1, 6.9, 1.9 Hz, 1H), 6.91 – 6.75 (m, 3H), 4.78 (dd, *J* = 14.3, 2.0 Hz, 1H), 4.50 (dd, *J* = 14.3, 4.0 Hz, 1H), 4.32 (d, *J* = 14.5 Hz, 1H), 3.68 (d, *J* = 11.0 Hz, 3H), 3.35 (d, *J* = 10.9 Hz, 3H); **^{31}P NMR (121 MHz, $CDCl_3$)** δ 20.89; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 164.1 (C, d, $J_{C\text{-}P}$ = 5.7 Hz), 135.8 (C, d, $J_{C\text{-}P}$ = 1.7 Hz), 134.1 (C), 128.8 (CH), 128.4 (CH), 127.9 (CH), 126.8 (C), 124.4 (CH), 119.9 (CH), 115.7 (CH), 113.6 (CH, d, $J_{C\text{-}P}$ = 2.0 Hz), 59.6 (CH, d, $J_{C\text{-}P}$ = 129.4 Hz), 53.0 (CH_3, d, J = 6.8 Hz), 53.0 (CH_2, d, $J_{C\text{-}P}$ = 0.8 Hz), 52.9 (CH_3, d , $J_{C\text{-}P}$ = 6.4 Hz.); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{20}N_2O_4P$ 347.1155; found 347.1156.

4-Benzyl-3-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (10)

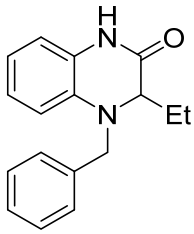


In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3aa** (44.0 mg, 0.1 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. Freshly distilled THF (2 mL) was added, and the solution was cooled down to 0 °C. MeMgBr (3 M in Et_2O, 0.11 mL, 3.3 eq.) was slowly added and the reaction mixture was stirred for 1 h at 0 °C. Then, the reaction was quenched with NH_4Cl aq. sat. (5 mL) and the mixture was extracted with DCM (x3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum to obtain a residue which

was directly purified by column chromatography using hexane:EtOAc mixtures to finally afford compound **10** (23.4 mg, 0.093 mmol, 93% yield) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.41 (bs, 1H), 7.34 – 7.16 (m, 5H), 6.85 (ddd, *J* = 8.0, 7.1, 1.9 Hz, 1H), 6.80 – 6.71 (m, 1H), 6.69 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.52 (d, *J* = 14.9 Hz, 1H), 4.12 (d, *J* = 14.9 Hz, 1H), 3.90 (q, *J* = 6.8 Hz, 1H), 1.14 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.1 (C), 136.6 (C), 133.6 (C), 128.8 (CH), 127.7 (CH), 127.6 (CH), 126.3 (C), 124.1 (CH), 119.2 (CH), 115.5 (CH), 113.7 (CH), 57.2 (CH), 51.9 (CH_2), 13.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{16}H_{17}N_2O^+$ 253.1335; found 253.1341.

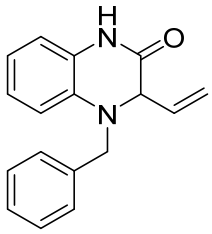
4-Benzyl-3-ethyl-3,4-dihydroquinoxalin-2(1*H*)-one (11)



In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3aa** (44.0 mg, 0.1 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. Freshly distilled THF (2 mL) was added, and the solution was cooled down to 0 °C. EtMgBr (3 M in Et_2O, 0.11 mL, 3.3 eq.) was slowly added and the reaction mixture was stirred for 1 h at 0 °C. Then, the reaction was quenched with NH_4Cl aq. sat. (5 mL) and the mixture was extracted with DCM (x3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum to obtain a residue which was directly purified by column chromatography using hexane:EtOAc mixtures to finally afford compound **11** (20.7 mg, 0.078 mmol, 78% yield) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (bs, 1H), 7.38 – 7.18 (m, 5H), 6.90 (ddd, *J* = 8.0, 7.0, 2.0 Hz, 1H), 6.80 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.80 – 6.69 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.67 (d, *J* = 15.1 Hz, 1H), 4.28 (d, *J* = 15.0 Hz, 1H), 3.83 (ddd, *J* = 7.6, 5.8, 0.7 Hz, 1H), 1.88 – 1.51 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 168.7 (C), 136.9 (C), 134.2 (C), 128.7 (CH), 127.6 (CH), 127.5 (CH), 126.3 (C), 124.0 (CH), 119.0 (CH), 115.4 (CH), 113.5 (CH), 63.1 (CH), 53.1 (CH_2), 22.6 (CH_2), 10.2 (CH_3); **HRMS (ESI$^+$)** *m/z:* [M + H]$^+$ Calcd for $C_{17}H_{19}N_2O^+$ 267.1492; found 267.1495.

4-Benzyl-3-vinyl-3,4-dihydroquinoxalin-2(1*H*)-one (12)

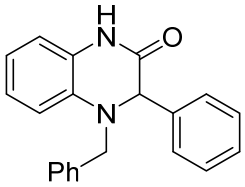


In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3aa** (44.0 mg, 0.1 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. Freshly distilled THF (2 mL) was added, and the solution was cooled down to 0 °C. Vinylmagnesium bromide (3 M in Et_2O, 0.11 mL, 3.3 eq.) was slowly added and the reaction mixture was stirred for 1 h at 0 °C. Then, the reaction was quenched with NH_4Cl aq. sat. (5 mL) and the mixture was extracted with DCM (x3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum to obtain a residue which was directly purified by column chromatography using hexane:EtOAc mixtures to finally afford compound **12** (26.1 mg, 0.099 mmol, 99% yield) as a colourless oil.

1H NMR (300 MHz, $CDCl_3$) δ 9.32 (bs, 1H), 7.37 – 7.18 (m, 5H), 6.95 (ddd, *J* = 8.0, 7.0, 1.9 Hz, 1H), 6.83 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.81 – 6.72 (m, 2H), 5.77 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.30 (dt, *J* = 17.2, 1.1 Hz, 1H), 5.27 (dt, *J* = 10.2, 1.1 Hz, 1H, 4.68 (d, *J* = 14.7 Hz, 1H), 4.34 (dt, *J* = 7.1, 1.2 Hz, 1H), 4.16 (d, *J* = 14.7 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 167.3 (C), 136.4 (C), 134.2 (C), 130.5

(CH), 128.8 (CH), 127.9 (CH), 127.6 (CH), 125.8 (C), 124.2 (CH), 120.2 (CH_2), 119.2 (CH), 115.7 (CH), 113.0 (CH), 64.1 (CH), 51.7 (CH_2); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O^+$ 265.1335; found 265.1330.

4-Benzyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (13)



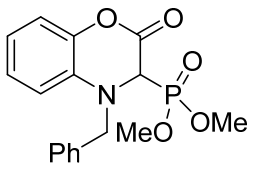
In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3aa** (44.0 mg, 0.1 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. Freshly distilled THF (2 mL) was added, and the solution was cooled down to 0 ^oC. Phenylmagnesium bromide (3 M in Et_2O, 0.11 mL, 3.3 eq.) was slowly added and the reaction mixture was stirred for 1 h at 0 ^oC. Then, the reaction was quenched with NH_4Cl aq. sat. (5 mL) and the mixture was extracted with DCM (x3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum to obtain a residue which was directly purified by column chromatography using DCM:EtOAc mixtures to finally afford compound **13** (30.8 mg, 0.098 mmol, 98% yield) as a white solid.

m.p. 167 °C – 169 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.62 (bs, 1H), 7.42 – 7.15 (m, 10H), 6.96 (ddd, *J* = 7.9, 7.3, 1.7 Hz, 1H), 6.81 (td, *J* = 7.3, 1.4 Hz, 1H), 6.80 – 6.68 (m, 2H), 4.99 (s, 1H), 4.68 (d, *J* = 15.2 Hz, 1H), 4.10 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 167.2 (C), 137.0 (C), 136.4 (C), 134.2 (C), 128.77 (CH), 128.76 (CH), 128.4 (CH), 127.7 (CH), 127.6 (CH), 127.1 (CH), 125.4 (C), 124.4 (CH), 118.7 (CH), 115.7 (CH), 112.2 (CH), 65.0 (CH), 51.6 (CH_2); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{21}H_{19}N_2O^+$ 315.1492; found 315.1490.

Specific Procedure for the One-Pot amination-phosphonylation

To an ovendried Schlenck tube containing a teflon-coated stir bar were added 4-benzyl-3,4-dihydroquinoxalin-2(1*H*)-one (**1a**, 23.8 mg, 0.1 mmol, 1 equiv.) or 4-benzyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (**4a**, 23.9 mg, 0.1 mmol, 1 equiv.). The reaction vessel was evacuated and backfilled with argon three times. After this, freshly degassed and dried MeCN (1 mL) and diisopropyl azodicarboxylate (**2a**, 25.6 uL, 0.13 mmol, 1.3 equiv.) were added via syringe and the reaction mixture was stirred while being irradiated with HP single LED (450 nm) under a positive pressure of argon. The course of the reaction was monitored by TLC. When complete consumption of 1a or 4a was observed, the reaction vessel was removed from the LED and dimethyl phosphite (27.5 uL, 0.3 mmol, 3 equiv.) and $BF_3{\cdot}OEt_2$ (13.6 uL, 0.11 mmol, 1.1 equiv.) were sequentially added and the reaction was stirred at room temperature until completion (TLC). The reaction mixture was directly purified by column chromatography to afford compound **9** (24.9 mg, 0.072 mmol, 72% yield) or compound **14** (21.9 mg, 0.063 mmol, 63% yield).

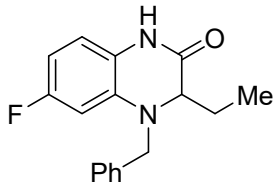
Dimethyl (4-benzyl-2-oxo-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-3-yl)phosphonate (14)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.28 (m, 5H), 7.15 – 7.05 (m, 2H), 7.03 – 6.85 (m, 2H), 4.75 (dd, *J* = 14.0, 1.9 Hz, 1H), 4.49 (dd, *J* = 14.0, 4.2 Hz, 1H), 4.42 (d, *J* = 15.7 Hz, 1H), 3.69 (d, *J* = 11.1 Hz, 3H), 3.29 (d, *J* = 11.0 Hz, 3H); **^{31}P NMR (121 MHz, $CDCl_3$)** δ 18.20; **^{13}C NMR (75 MHz, $CDCl_3$)** δ 161.90 (C, d, $J_{C\text{-}P}$ = 5.6 Hz), 142.19 (C), 135.01 (C, d, $J_{C\text{-}P}$ = 1.6 Hz), 133.09 (C), 128.95 (CH), 128.52 (CH), 128.19 (CH), 125.55 (CH), 120.56 (CH), 116.48 (CH), 114.14 (CH, d, $J_{C\text{-}P}$ = 1.7 Hz), 57.37 (CH, d, $J_{C\text{-}P}$ = 131.3 Hz), 53.29 (CH_3, d, $J_{C\text{-}P}$ = 7.2 Hz), 53.04 (CH_3, d, $J_{C\text{-}P}$ = 6.7 Hz), 52.48 (CH_2); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{19}NO_5P^+$ 348.0995; found 348.0988.

Detailed Procedures for the synthesis of *rac*-Opaviraline (17)

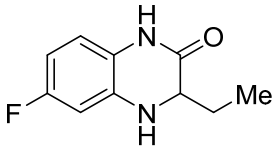
4-Benzyl-3-ethyl-6-fluoro-3,4-dihydroquinoxalin-2(1*H*)-one (15)



In a 25 mL round bottomed flask was weighted aminated dihydroquinoxalinone **3ma** (91.7 mg, 0.2 mmol). After the addition of a teflon-coated stir bar, the flask was purged with N_2. Freshly distilled THF (4 mL) was added, and the solution was cooled down to 0 °C. EtMgBr (3 M in Et_2O, 0.22 mL, 3.3 eq.) was slowly added and the reaction mixture was stirred for 1 h at 0 °C. Then, the reaction was quenched with NH_4Cl aq. sat. (5 mL) and the mixture was extracted with DCM (x3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum to obtain a residue which was directly purified by column chromatography using DCM:EtOAc mixtures to finally afford compound **15** (44.2 mg, 0.155 mmol, 78% yield) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.27 (bs, 1H), 7.42 – 7.17 (m, 5H), 6.70 (dd, *J* = 8.4, 5.5 Hz, 1H), 6.48 – 6.34 (m, 2H), 4.61 (d, *J* = 15.3 Hz, 1H), 4.29 (d, *J* = 15.1 Hz, 1H), 3.85 (dd, *J* = 7.5, 5.5 Hz, 1H), 1.79 – 1.70 (m, 1H), 1.71 – 1.61 (m, 1H), 0.93 (t, *J* = 7.6 Hz, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -117.95 (s); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.0 (C), 160.0 (d, $J_{C–F}$ = 239.9 Hz, C), 136.2 (C), 135.7 (d, $J_{C–F}$ = 11.0 Hz, C), 128.9 (CH), 127.8 (CH), 127.5 (CH), 122.1 (d, $J_{C–F}$ = 2.8 Hz, C), 115.7 (d, $J_{C–F}$ = 10.1 Hz, CH), 104.6 (d, $J_{C–F}$ = 23.0 Hz, CH), 100.8 (d, $J_{C–F}$ = 27.6 Hz, CH), 62.8 (CH), 52.9 (CH_2), 22.9 (CH_2), 10.0 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{17}H_{18}FN_2O^+$ 285.1398; found 285.1403.

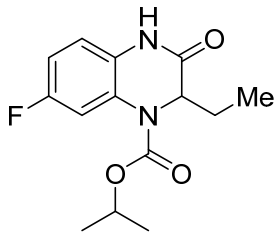
3-Ethyl-6-fluoro-3,4-dihydroquinoxalin-2(1*H*)-one (16)



In a 25 mL round bottomed flask was weighted compound **15** (44.2 mg, 0.155 mmol) and was dissolved in EtOH (6 mL). After that, Pd/C 10% (20.2 mg, 0.019 mmol) was added and the resulting suspension was stirred at room temperature under H_2 (1 atm). After complete conversion (TLC), the reaction mixture was filtered through a pad of silica. Finally, the solvent was removed under reduced pressure to afford debenzylated compound 16 (30.1 mg, 0.155 mmol, 99% yield) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (bs, 1H), 6.69 (dd, *J* = 8.2, 5.3 Hz, 1H), 6.48 – 6.35 (m, 2H), 3.88 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.66 (bs, 1H), 1.96 – 1.65 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -118.95 (s); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.8 (d, $J_{C–F}$ = 4.6 Hz, C), 159.6 (d, $J_{C–F}$ = 240.8 Hz, C), 134.2 (d, $J_{C–F}$ = 10.1 Hz, C), 121.3 (d, $J_{C–F}$ = 1.8 Hz, C), 116.0 (d, $J_{C–F}$ = 10.1 Hz, CH), 105.2 (d, $J_{C–F}$ = 23.9 Hz, CH), 101.2 (d, $J_{C–F}$ = 26.7 Hz, CH), 57.1 (CH), 25.4 (CH_2), 9.5 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{10}H_{12}FN_2O^+$ 195.0928; found 195.0930.

***rac*-Opaviraline (17)**



In a 25 mL round bottomed flask was weighted debenzylated compound 16 (30.1 mg, 0.155 mmol) and was purged with N_2. Then, freshly distilled DCM (1 mL), pyridine (20.2 uL, 0.25 mmol) and isopropyl chloroformate (0.155 mL, 2 M in toluene, 0.23 mmol) were sequentially added and the resulting mixture was stirred at room temperature for 45 minutes. After that, the reaction mixture was diluted with DCM (20 mL), washed with water (10 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography using DCM:EtOAc to afford *rac*-Opaviraline (**17**, 35.5 mg, 0.127 mmol, 82% yield) as a white solid.

m.p. 152 °C – 154 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.00 (bs, 1H), 7.50 (bs, 1H), 7.04 – 6.54 (m, 2H), 5.07 (p, *J* = 6.2 Hz, 1H), 4.97 (dd, *J* = 9.8, 5.0 Hz, 1H), 1.72 (ddd, *J* = 13.8, 7.4, 5.2 Hz, 1H), 1.54 – 1.42 (m, 1H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.30 (d, *J* = 6.2 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{19}F NMR (282 MHz, $CDCl_3$)** δ -117.90; **^{13}C NMR (75 MHz, $CDCl_3$)** δ 170.4 (C), 158.6 (d, $J_{C–F}$ = 241.6 Hz, C), 153.1 (C), 125.8 (d, $J_{C–F}$ = 11.1 Hz, C), 125.7 (d, $J_{C–F}$ = 2.2 Hz, C), 116.6 (d, $J_{C–F}$ = 9.4 Hz, CH), 112.04 (d, $J_{C–F}$ = 24.0 Hz, CH), 111.95 (d, $J_{C–F}$ = 27.8 Hz, CH), 70.9 (CH), 58.0 (CH), 23.5 (CH_2), 21.94 (CH_3), 21.90 (CH_3) , 9.8 (CH_3); **HRMS (ESI$^+$)** *m/z:* $[M + H]^+$ Calcd for $C_{14}H_{18}FN_2O_3^+$ 281.1296; found 281.1288.

Mechanistic insights

1. Reaction with TEMPO.

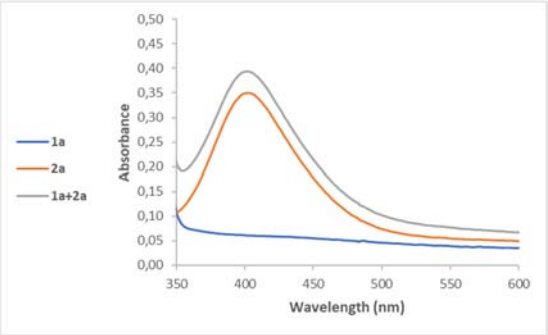
The reaction was performed according to General Procedure but also adding TEMPO (23.4 mg, 0.15 mmol, 1.5 equiv.). The desired product **3aa** was obtained in 72% yield after 8 h.

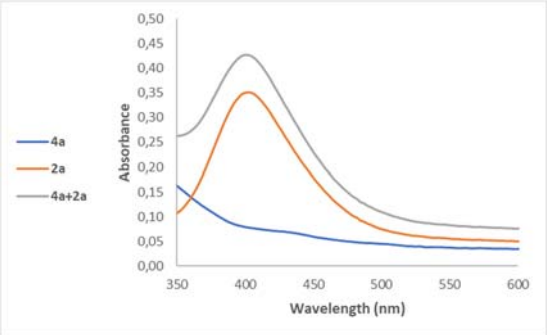
2. Reaction under a O_2 atmosphere.

The reaction was performed according to General Procedure but under a positive pressure of oxygen. The desired product **3aa** was obtained in 81% yield after 3 h.

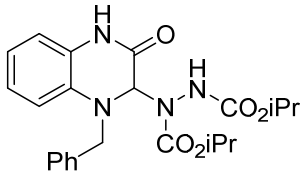
3. Investigation of the formation of an electron donor-acceptor (EDA) complex.

The UV-Vis absorption spectra of 8 mM acetonitrile solutions of quinoxalin-2-one **1a**, benzoxazin-2-one **4a** and diisopropyl azodicarboxylate (**2a**) were recorded. Then, acetonitrile solutions containing both 8 mM of **1a** and 8 mM of **2a** (and both **4a** and **2a**) were prepared and the corresponding UV-Vis absorption spectrum did not show any bathochromic shift, only an augmentation in the absorbance was observed. We think that the increased UV absorbance observed in the mixture is due to added absorbances of the two components, rather than an interaction from complexation (EDA complex for example).





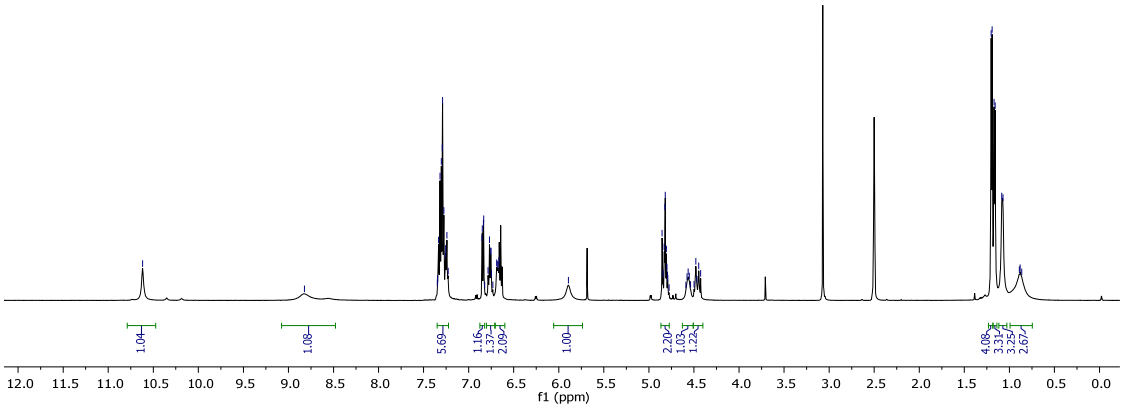
^{1}H and ^{13}C NMR Spectra

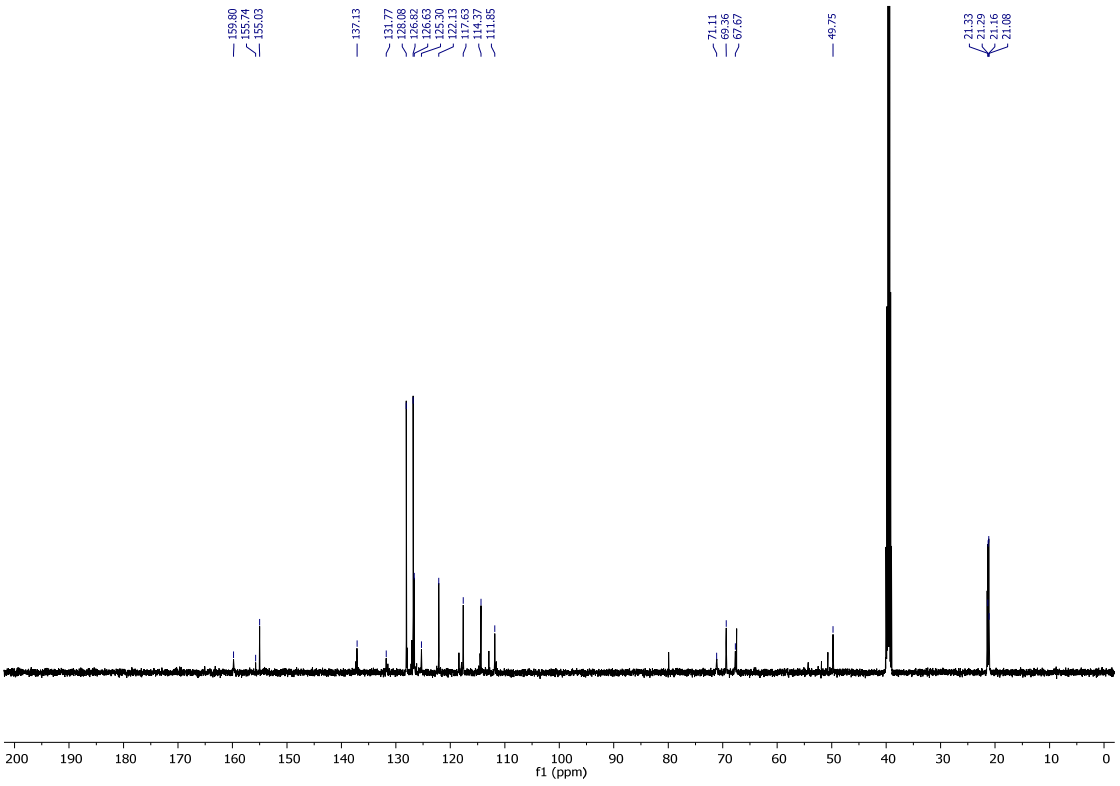


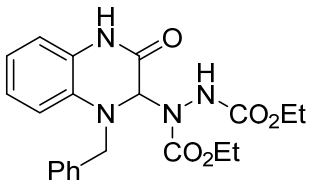
3aa

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



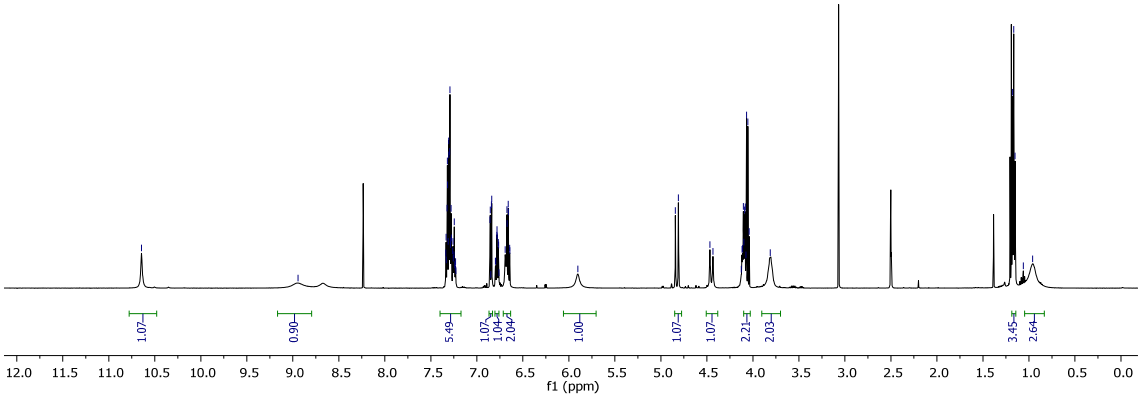


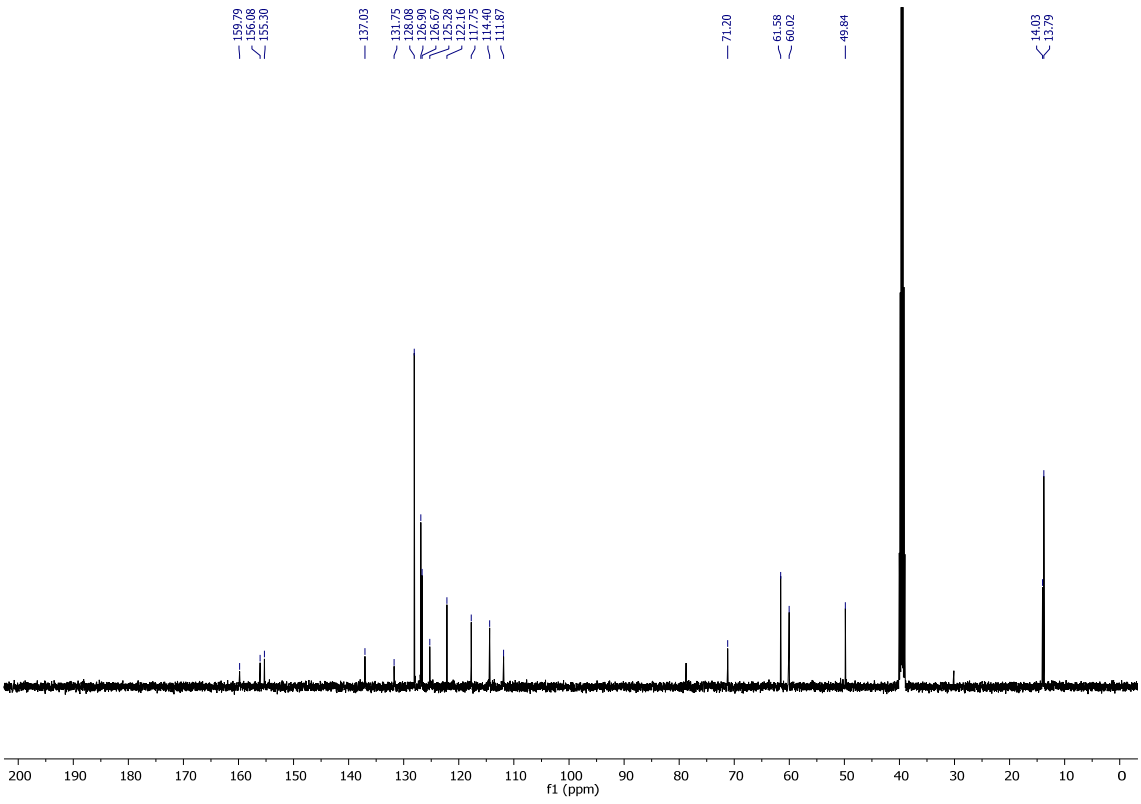


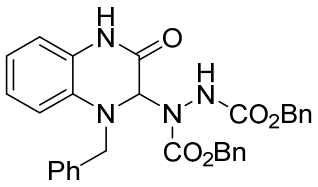
3ab

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



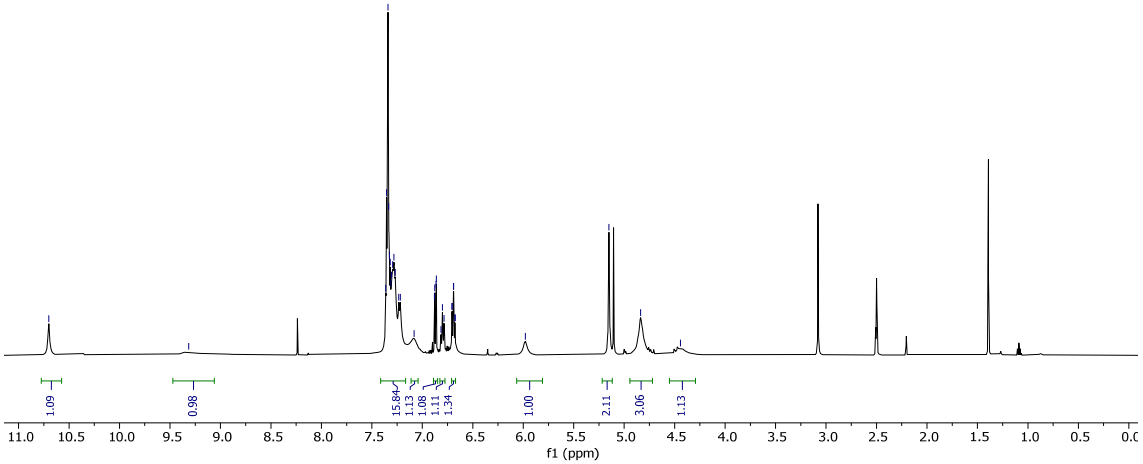


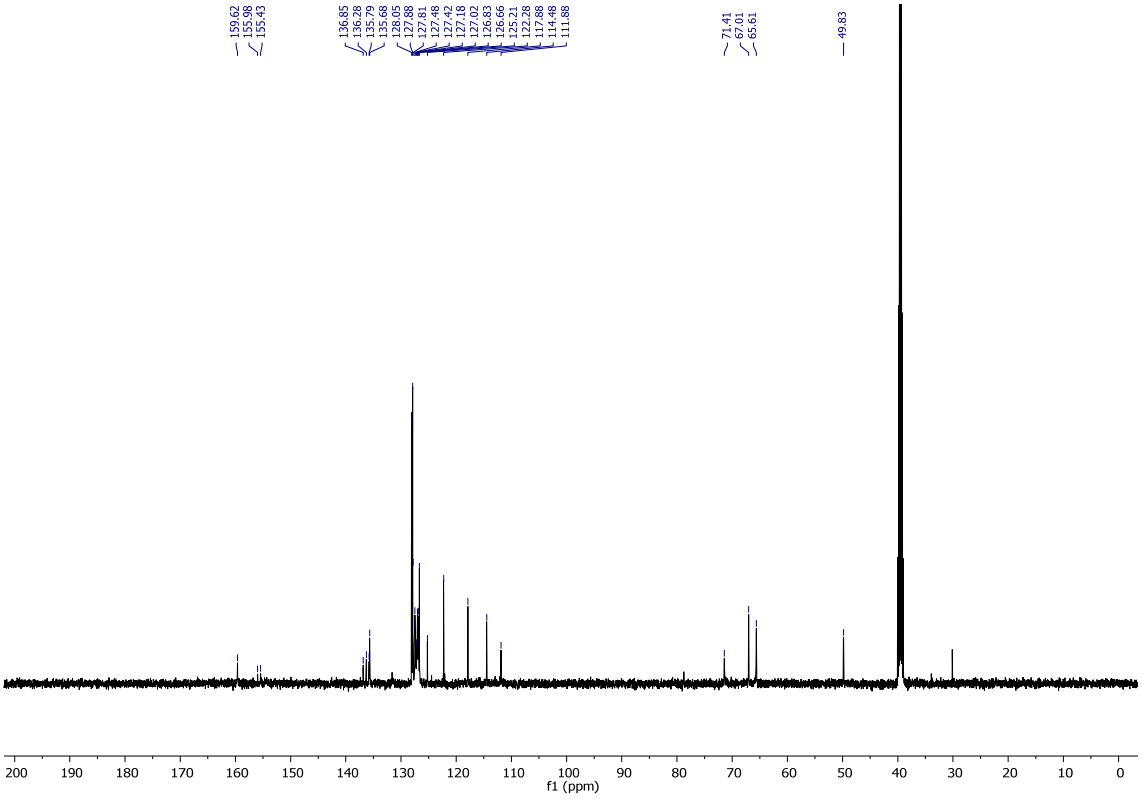


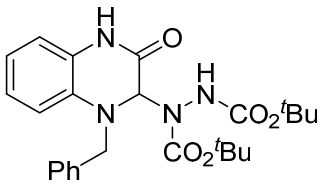
3ac

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



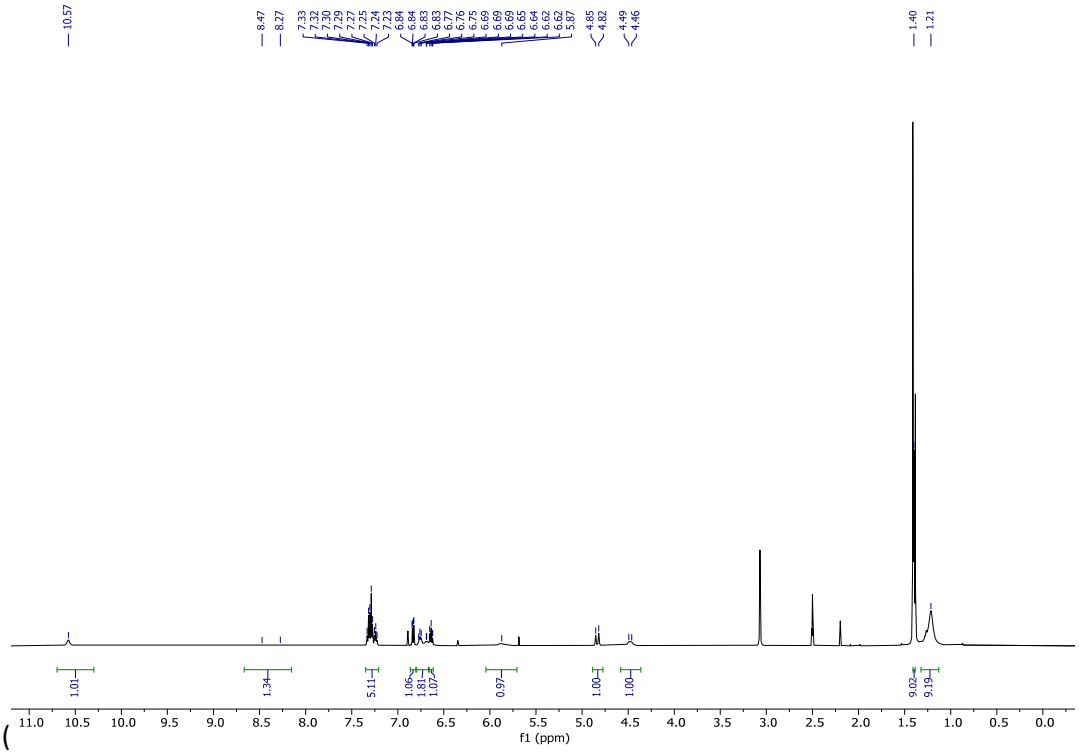




3ad

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



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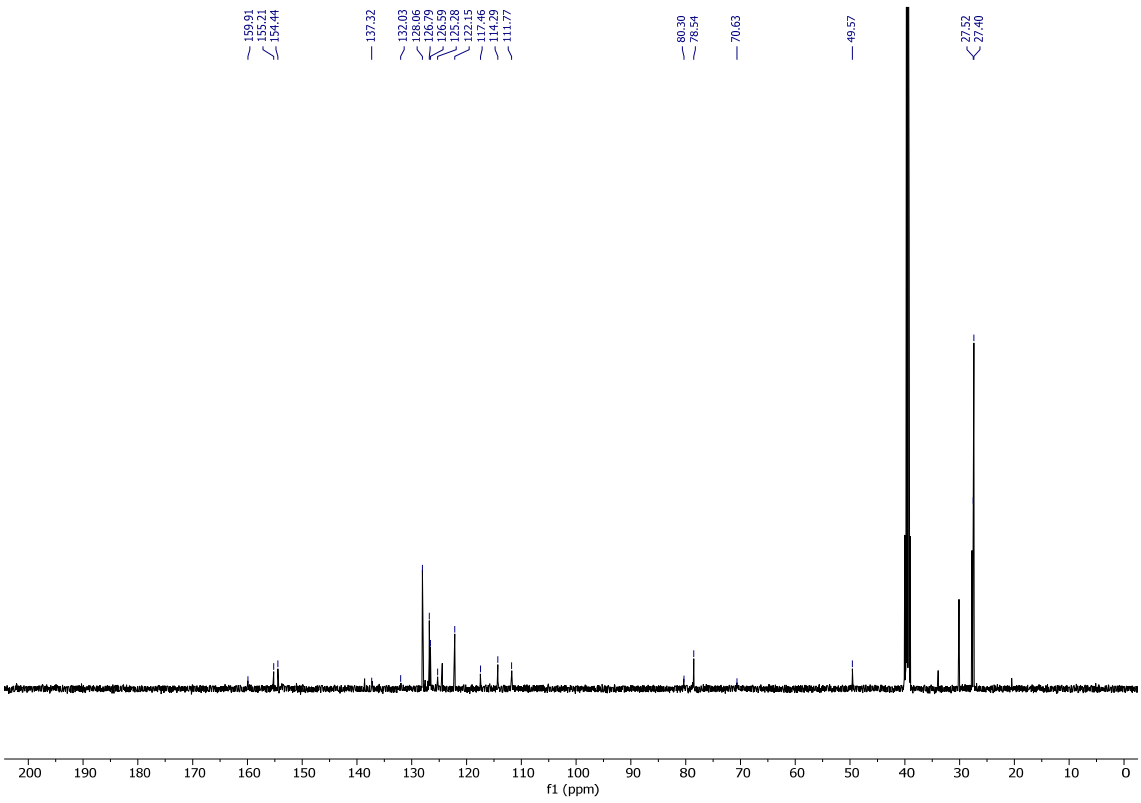
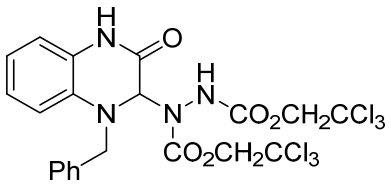
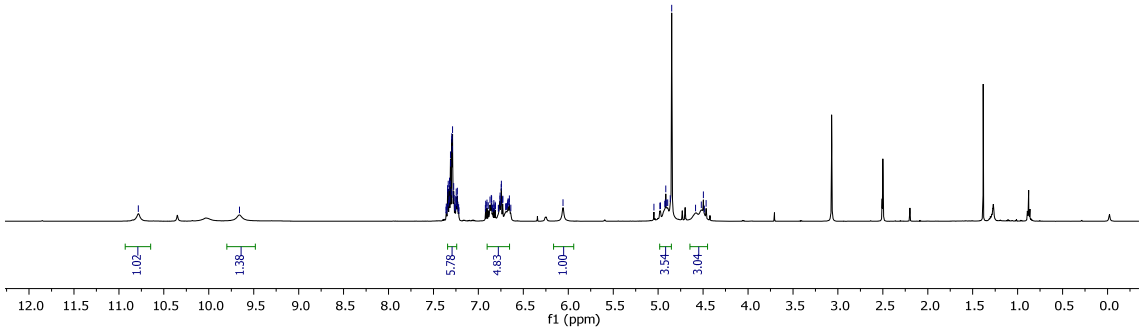


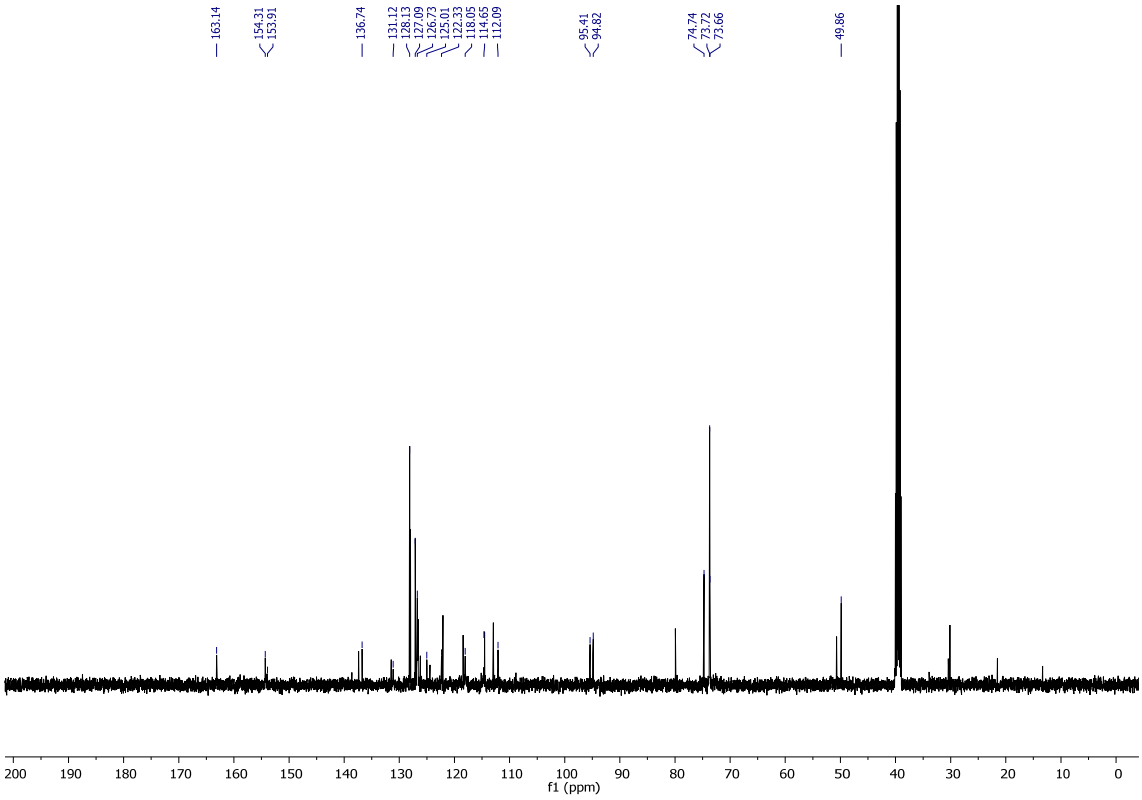


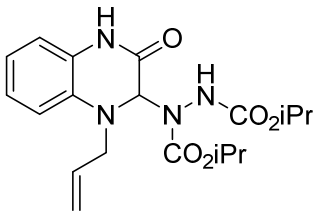
3ae

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



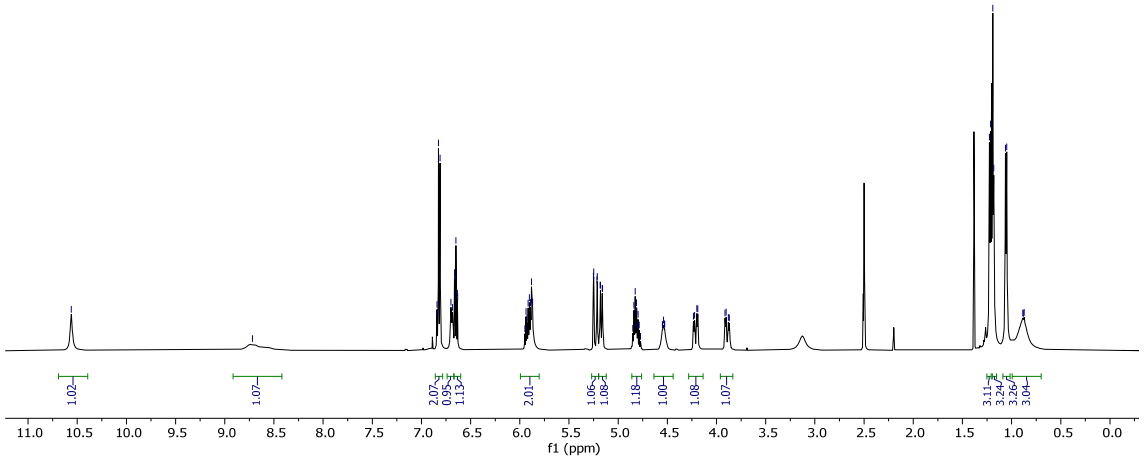


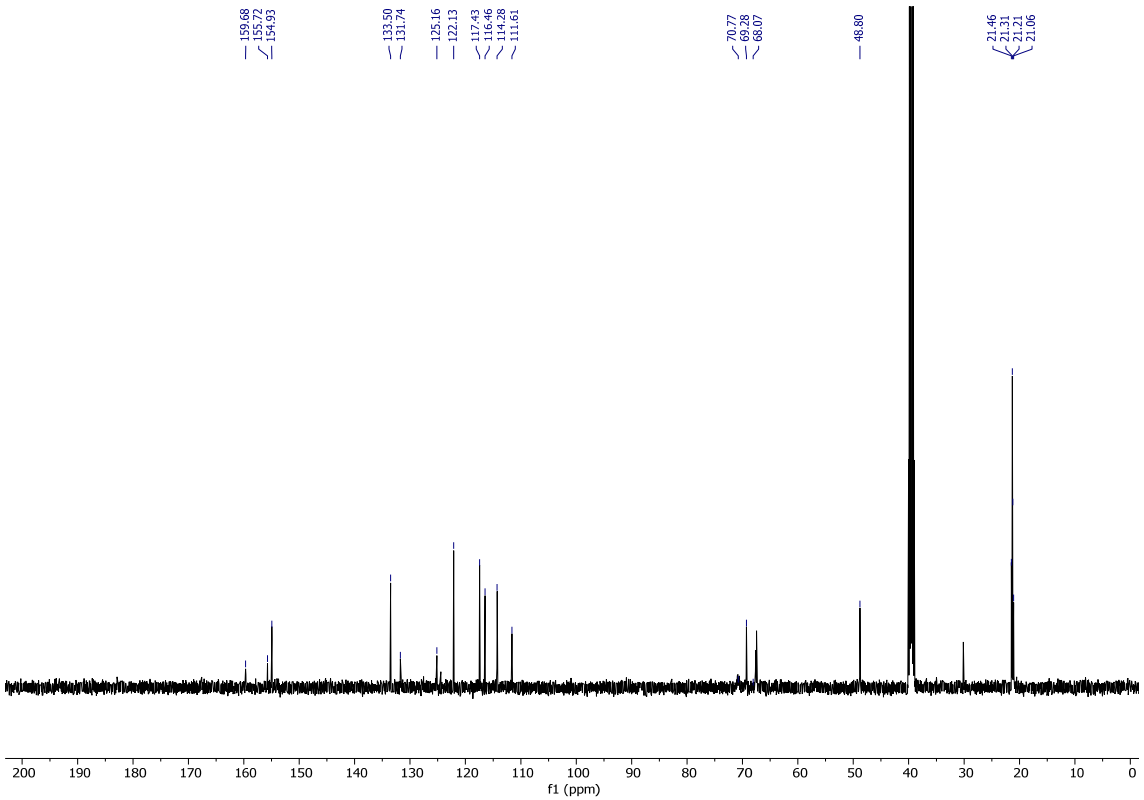


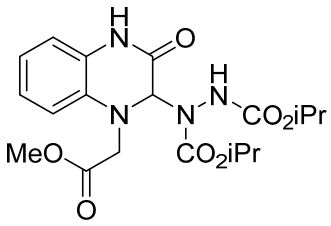
3ba

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



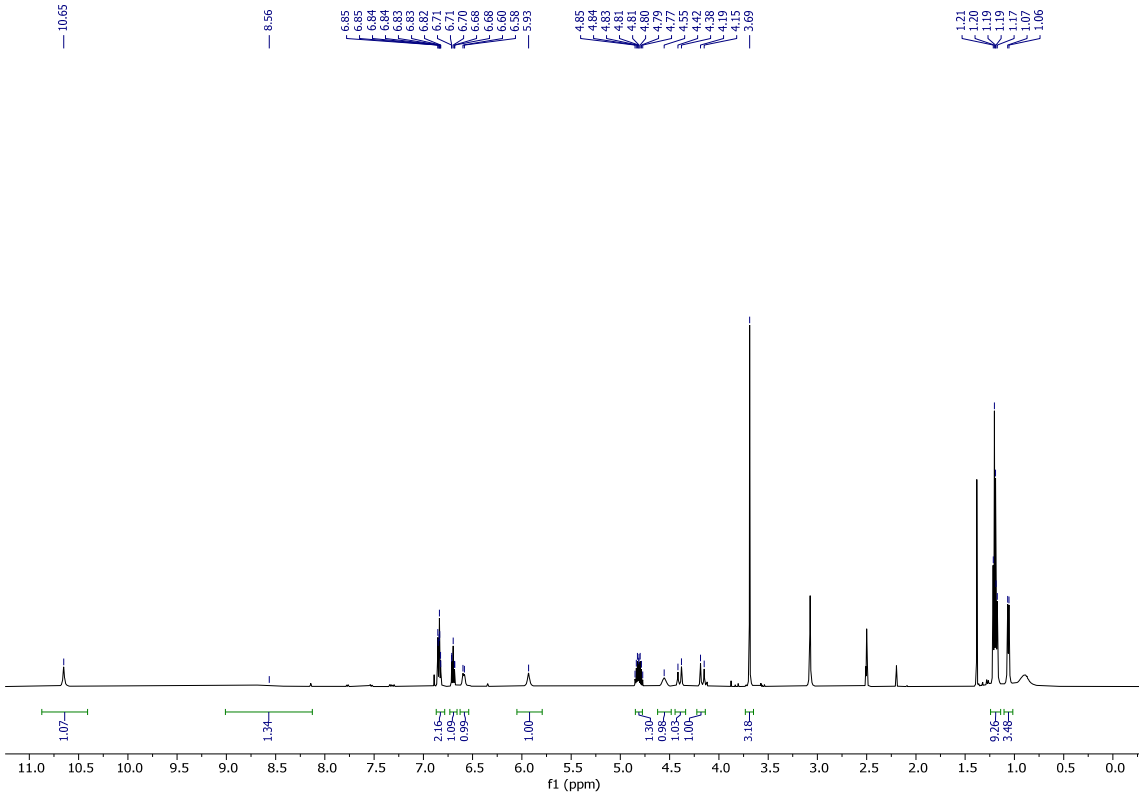


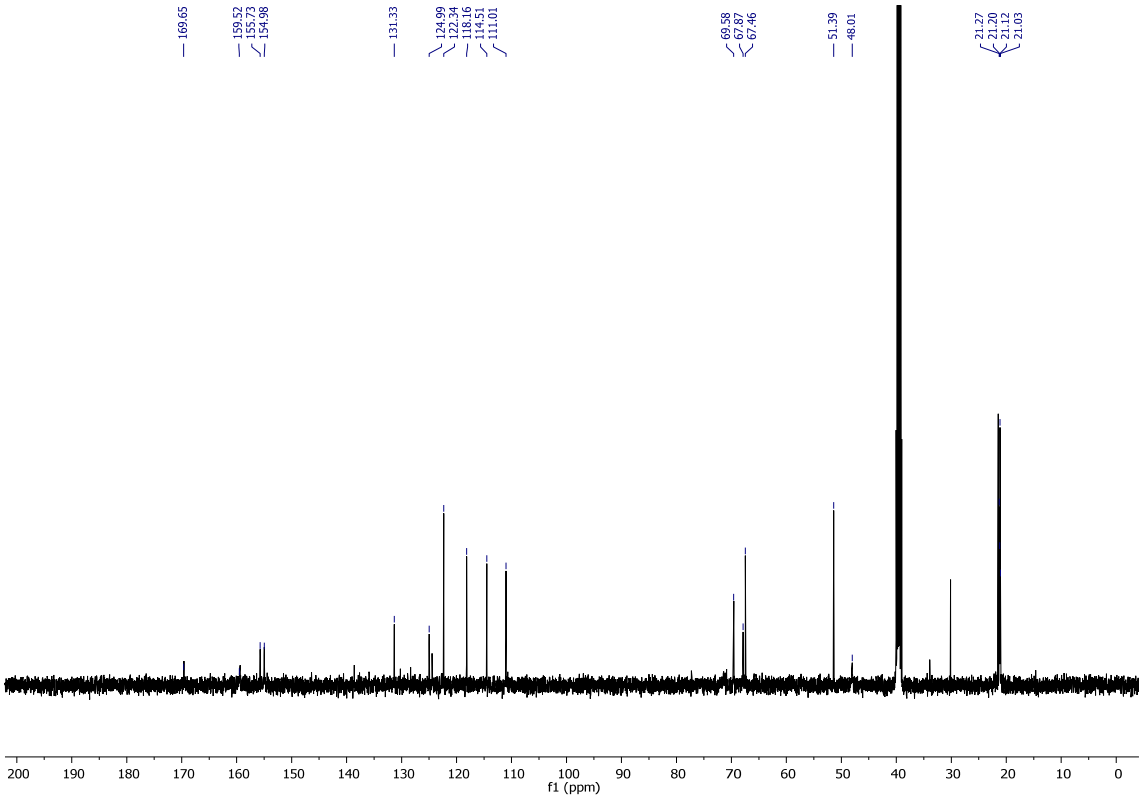


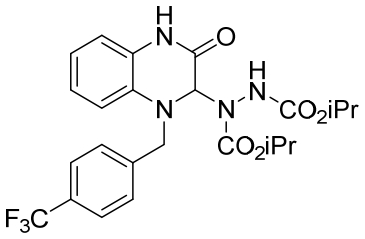
3ca

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



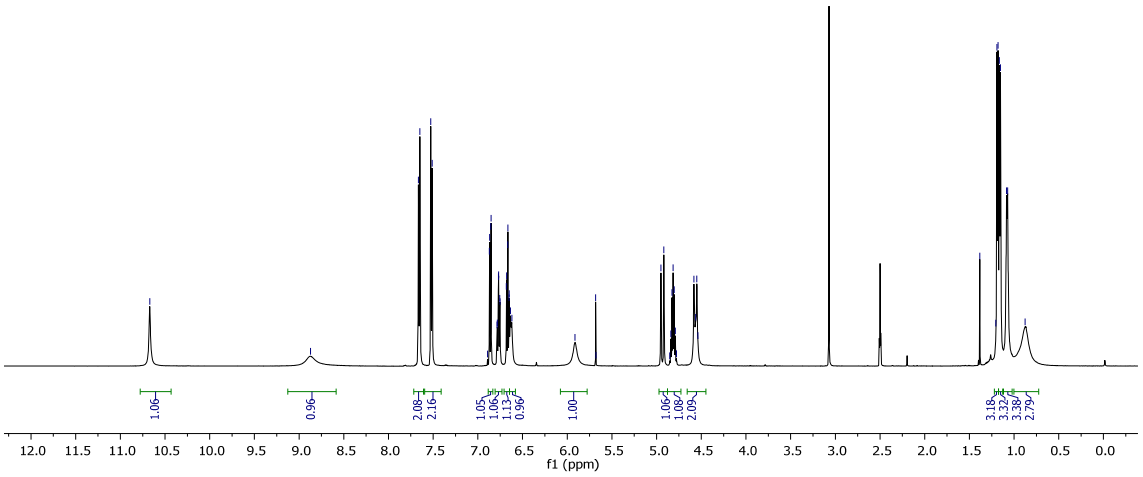


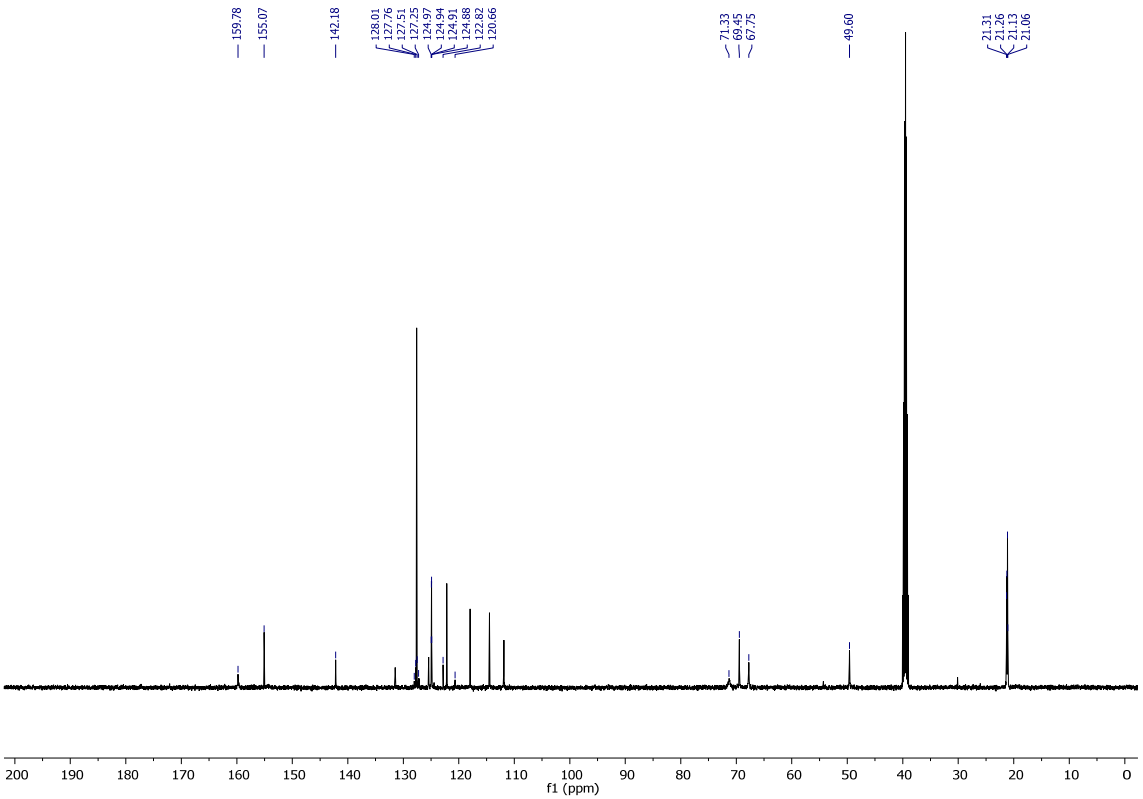


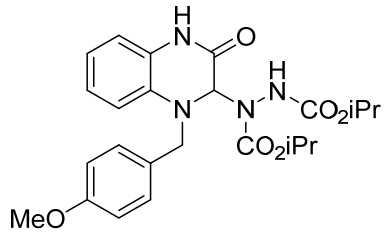
3da

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



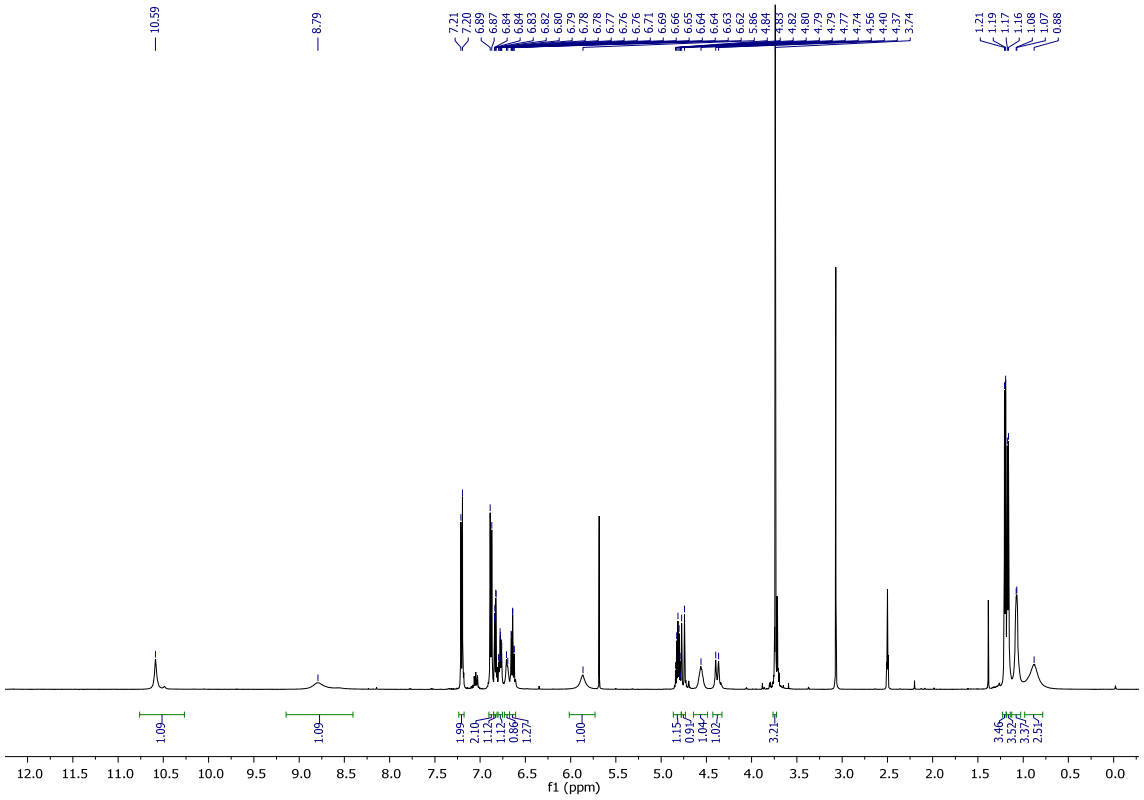


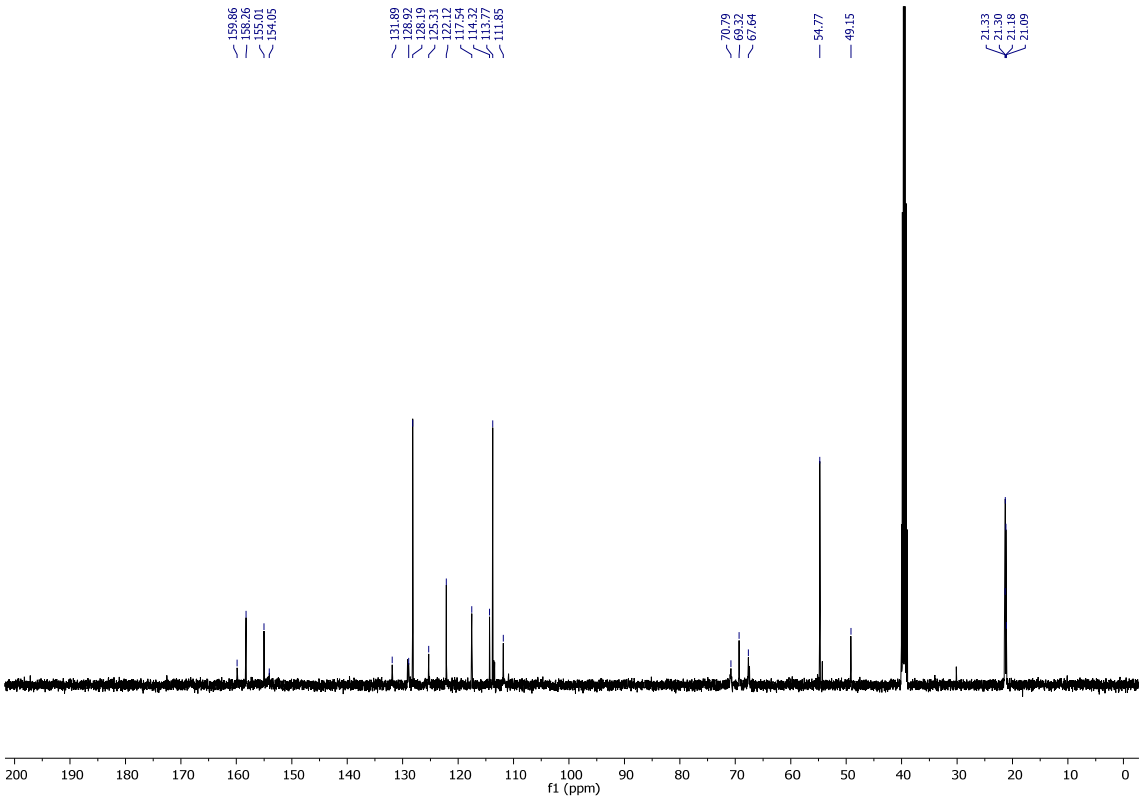


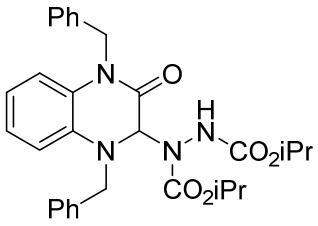
3ea

^{1}H NMR (500 MHz, 353 K, DMSO-d^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-d^{6})



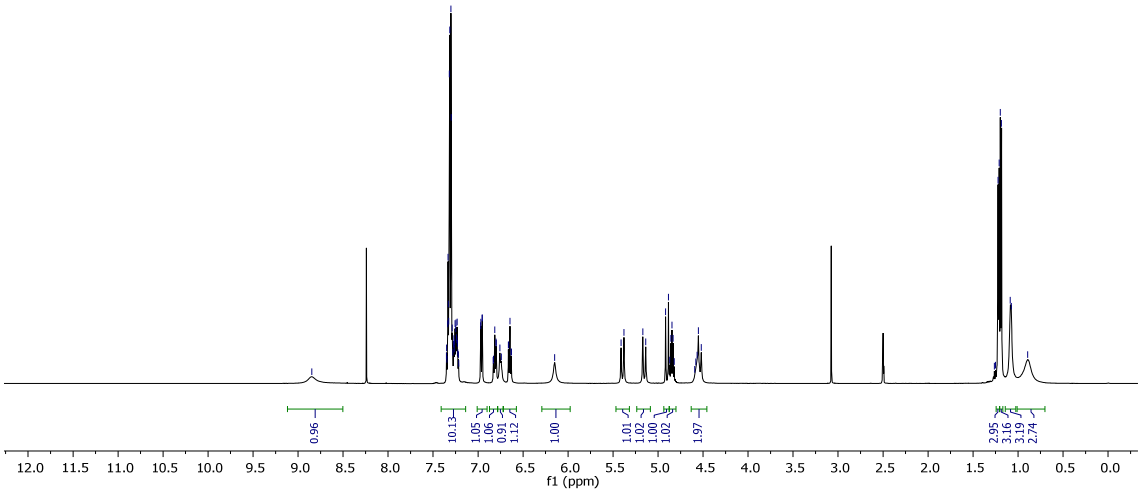


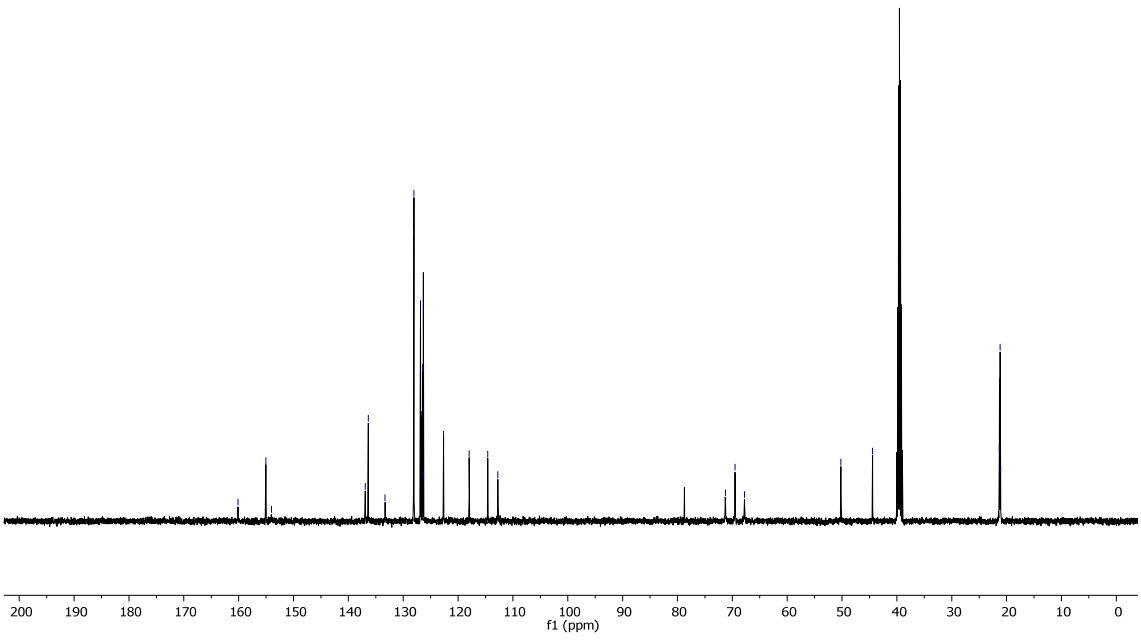


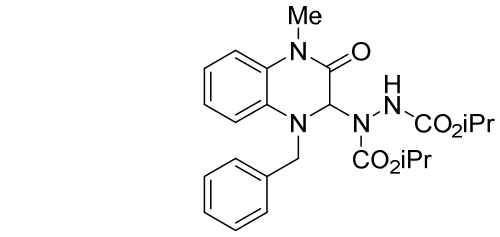
3fa

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



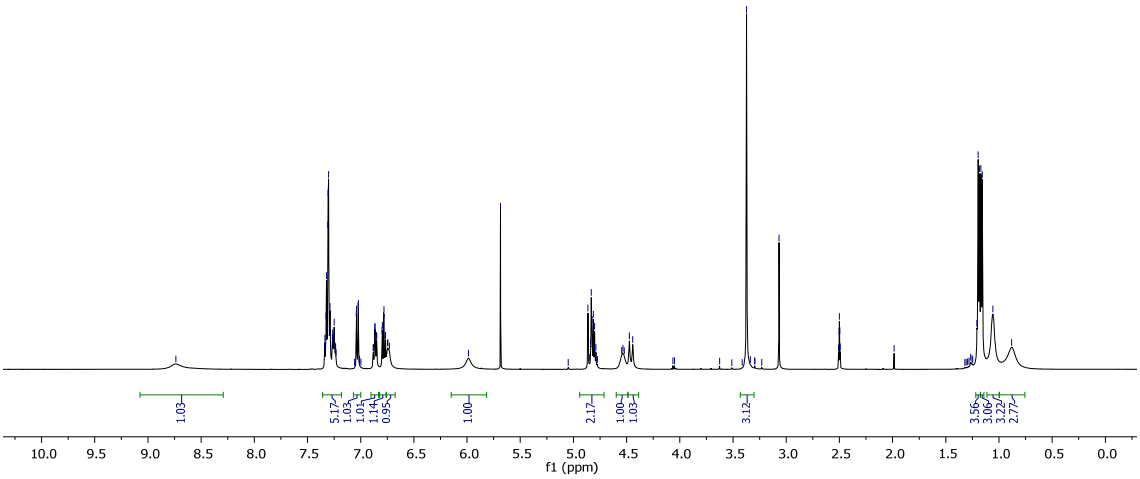


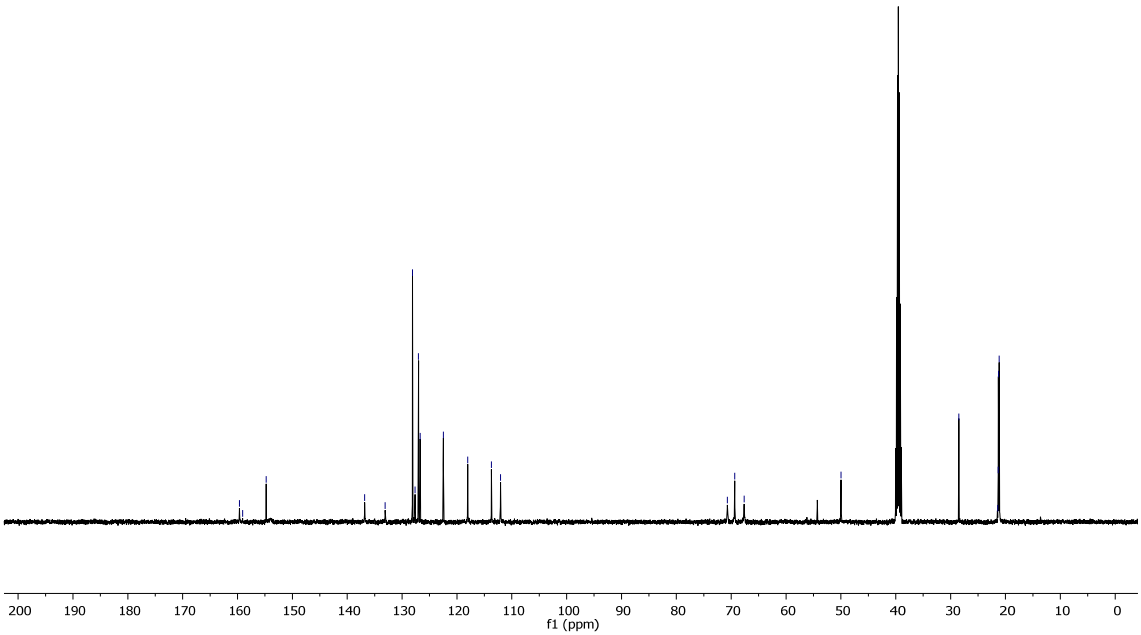


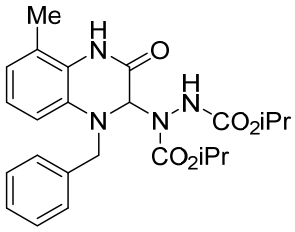
3ga

^{1}H NMR (500 MHz, 353 K, DMSO-d^6)

^{13}C NMR (125 MHz, 353 K, DMSO-d^6)



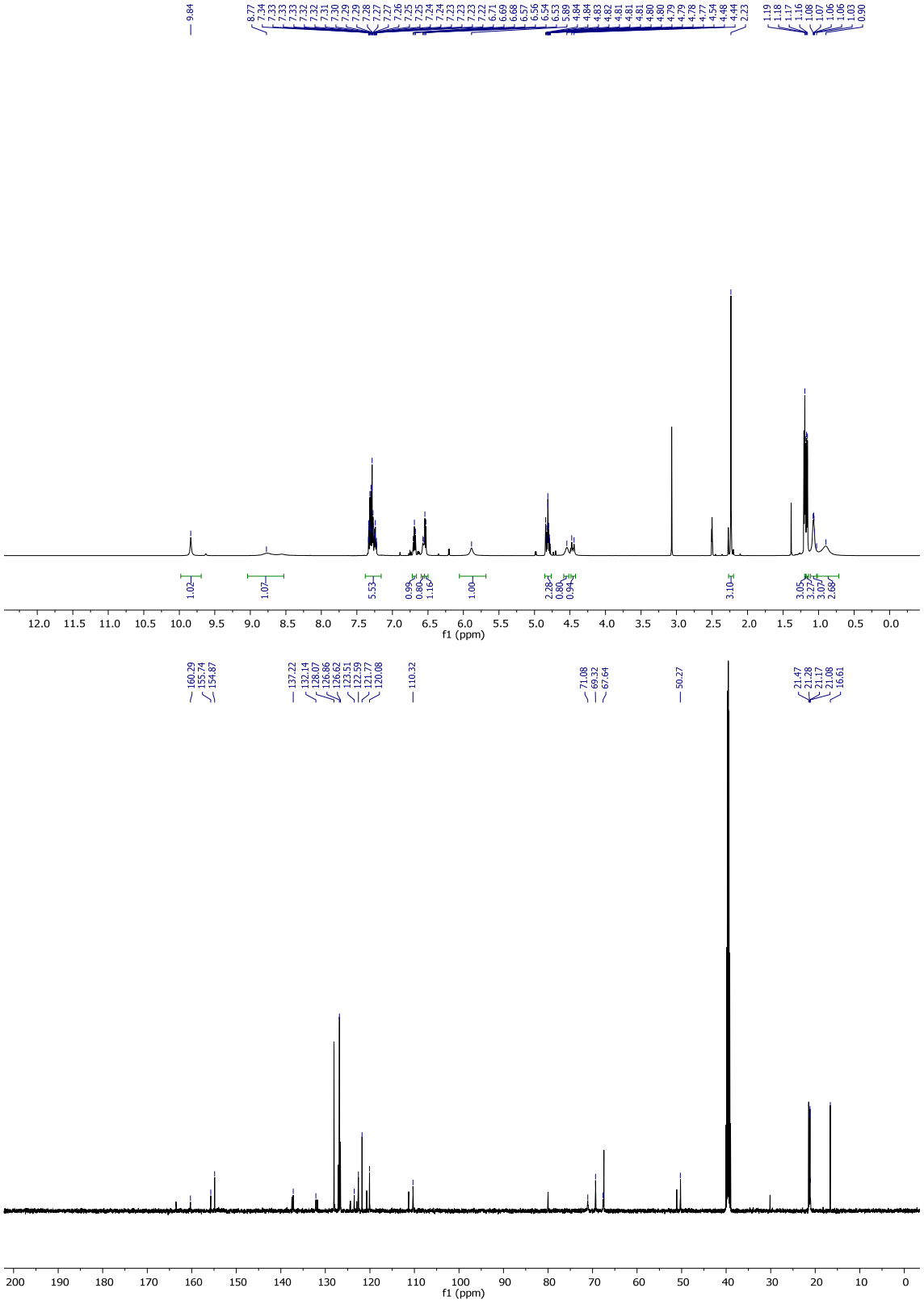


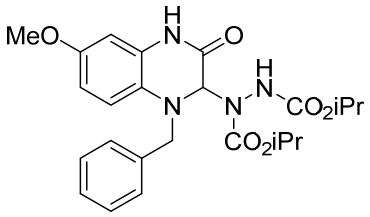


3ha

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})

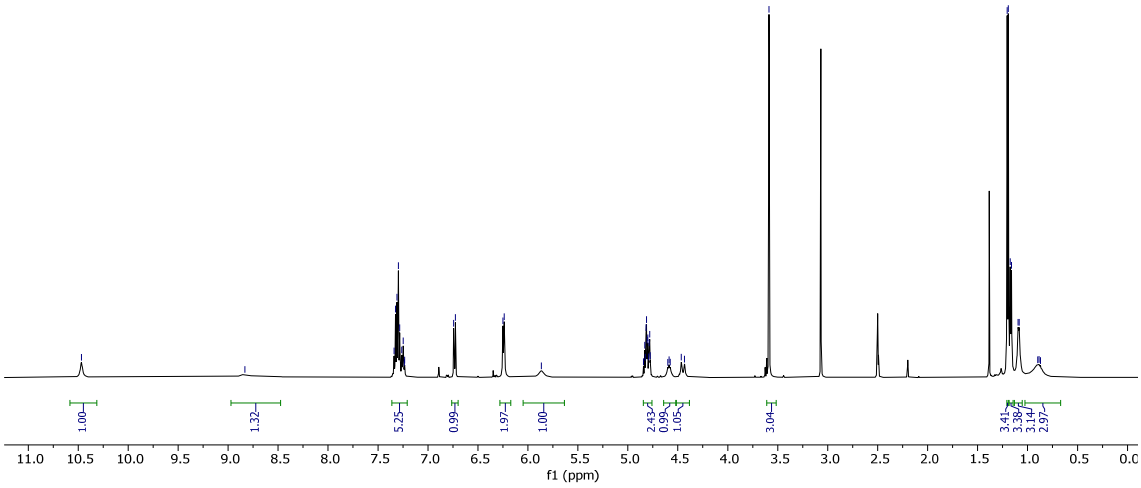


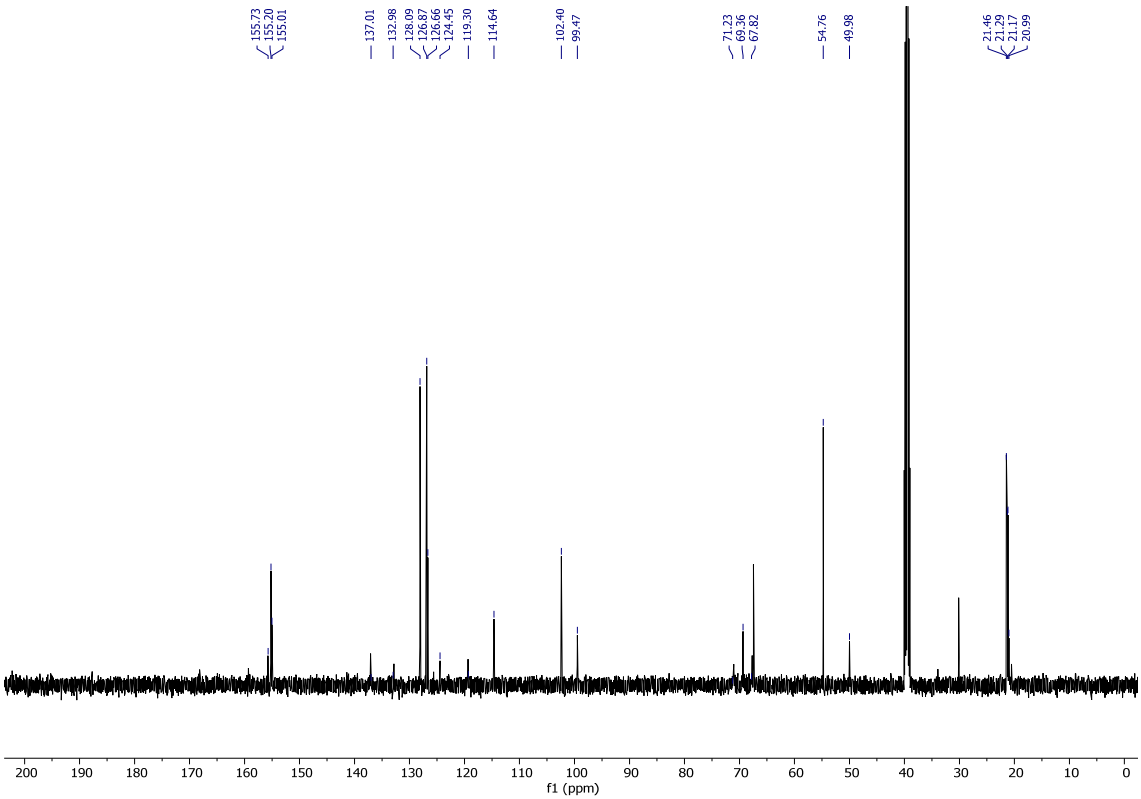


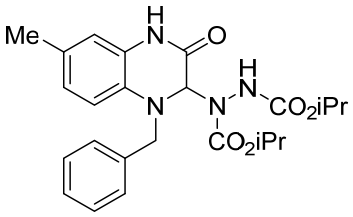
3ia

^{1}H NMR (500 MHz, 353 K, DMSO-d^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-d^{6})



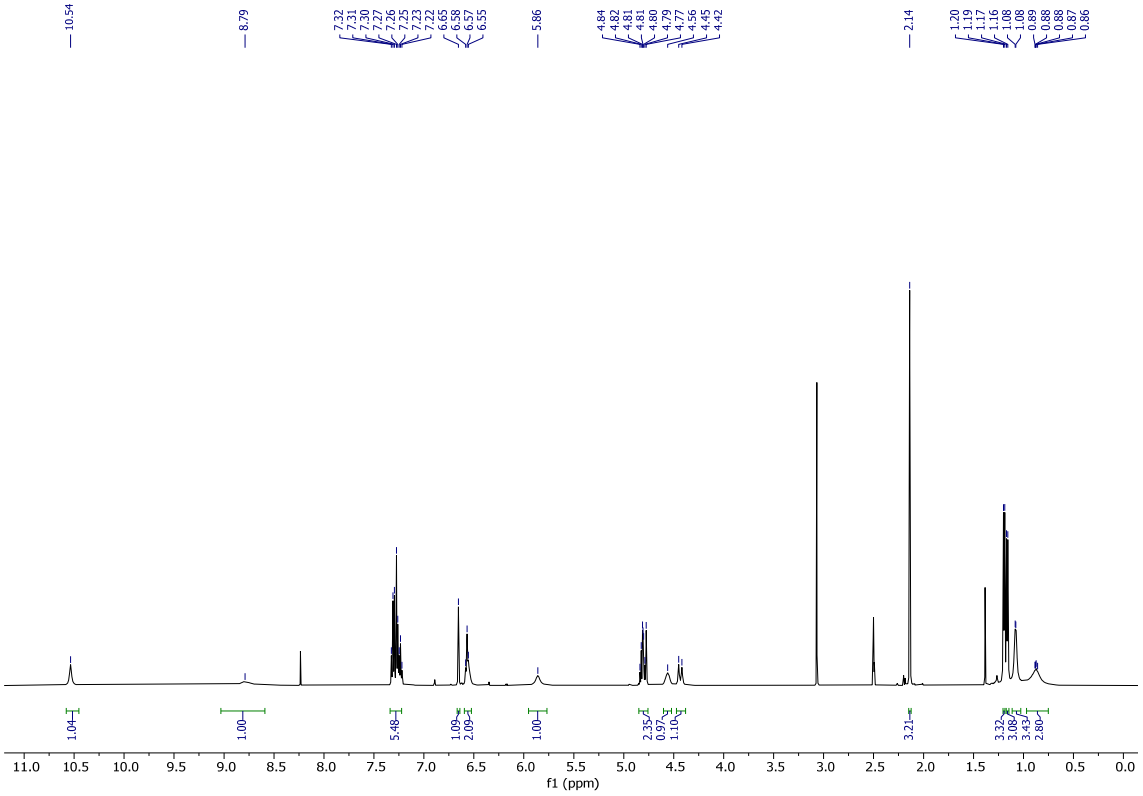


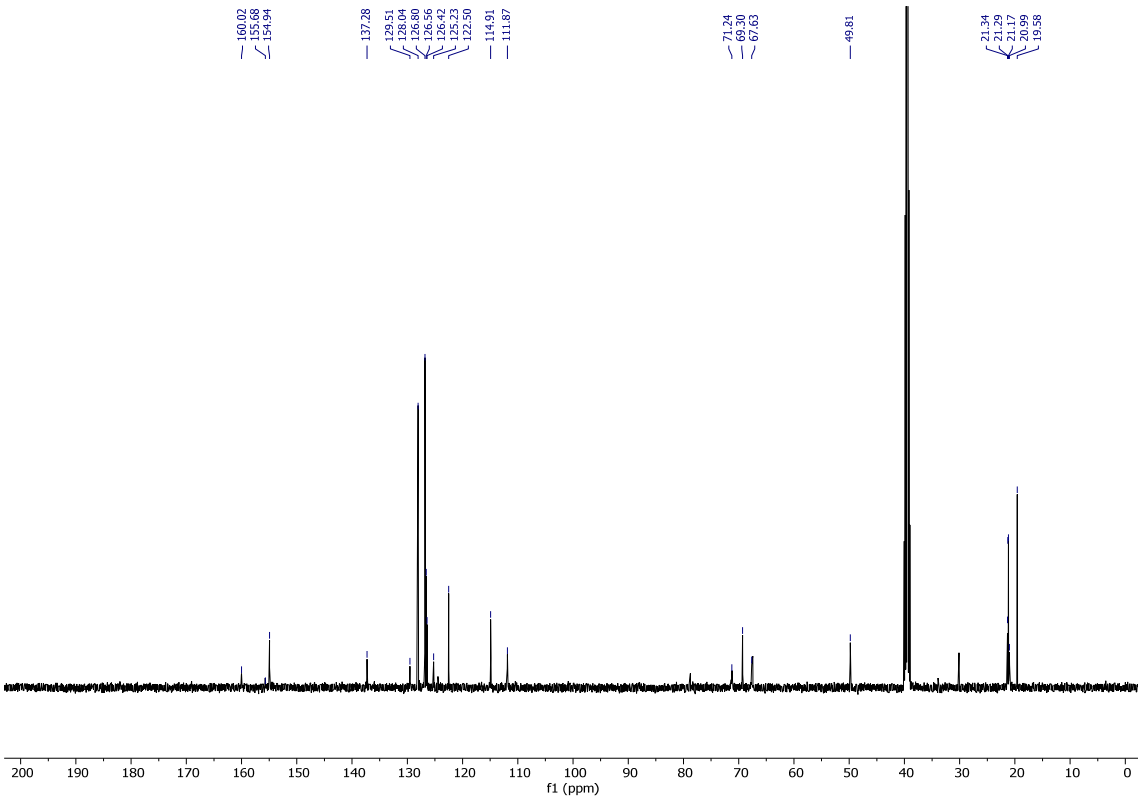


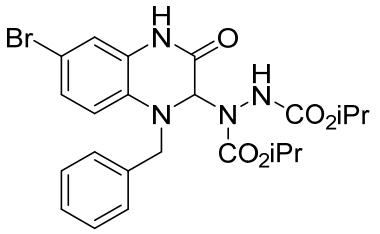
3ja

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



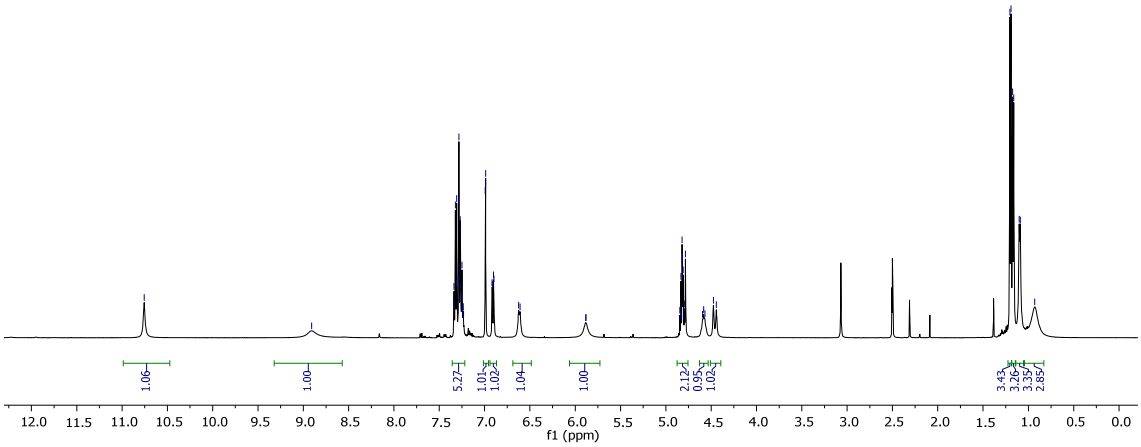


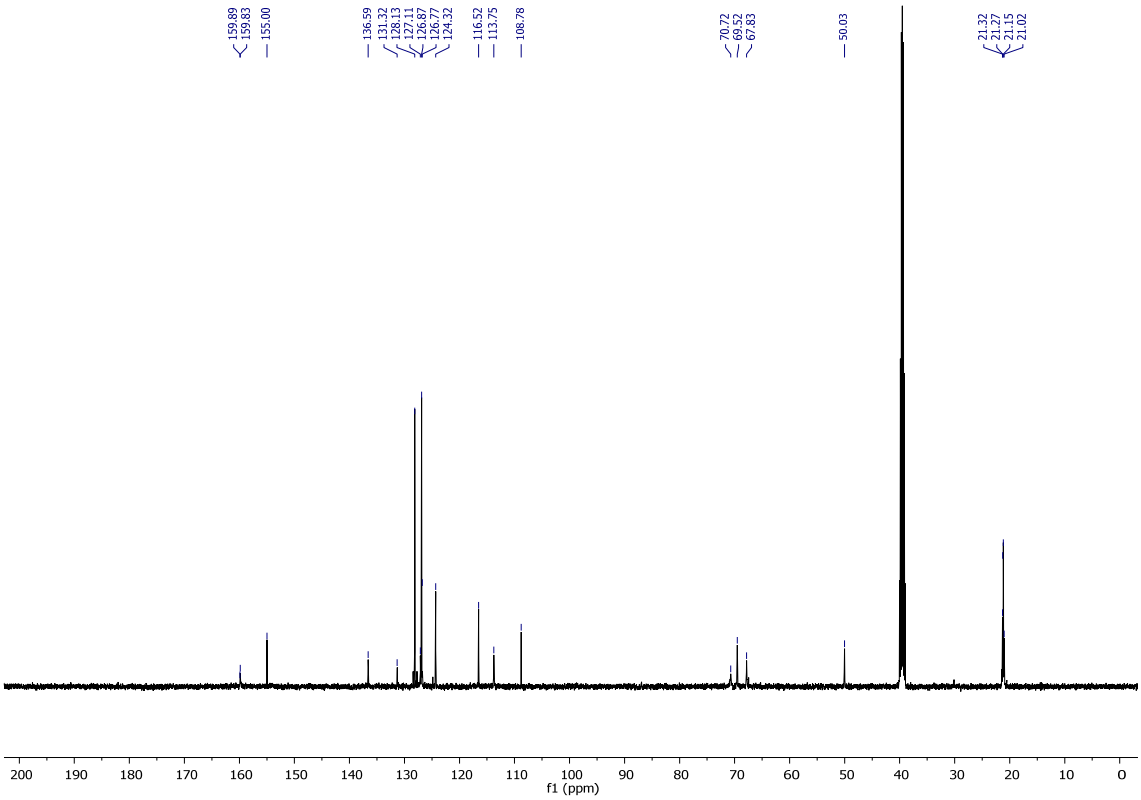


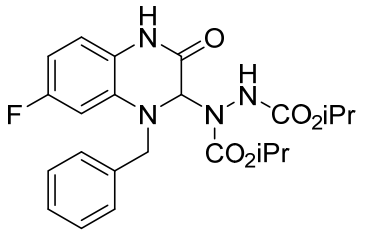
3ka

^{1}H NMR (500 MHz, 353 K, DMSO-d^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-d^{6})



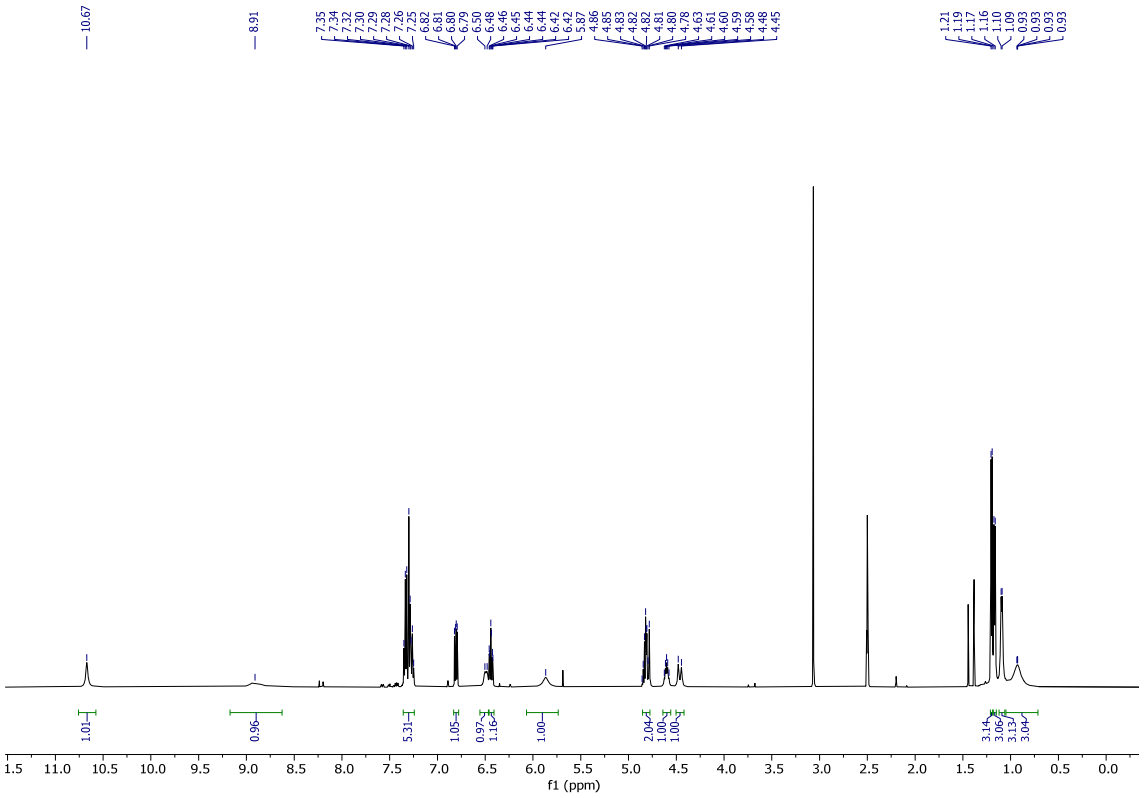


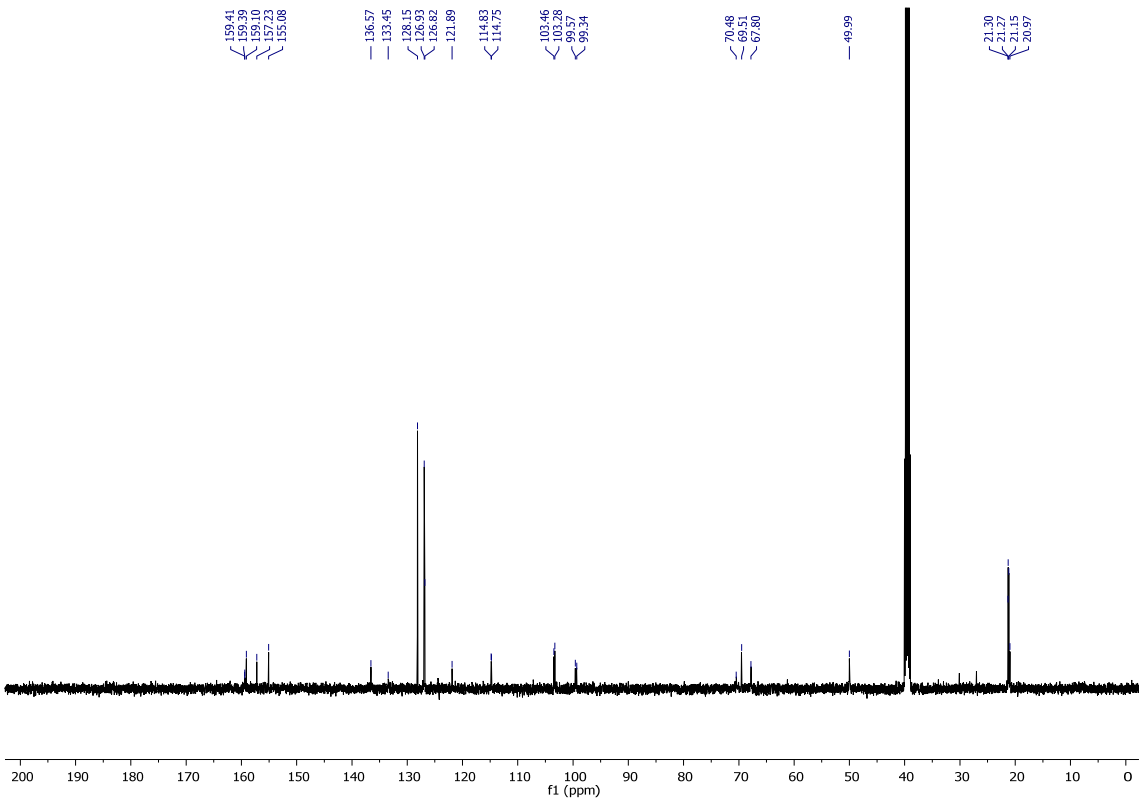


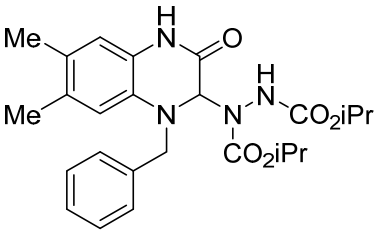
3la

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



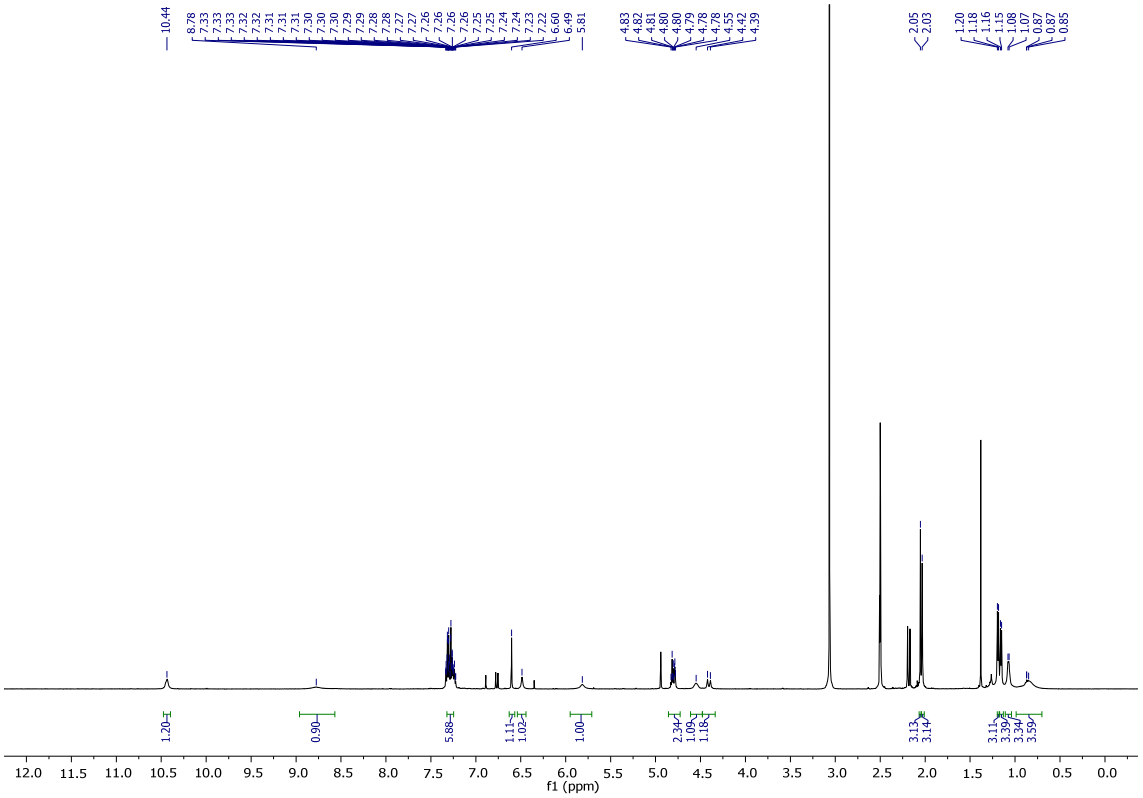


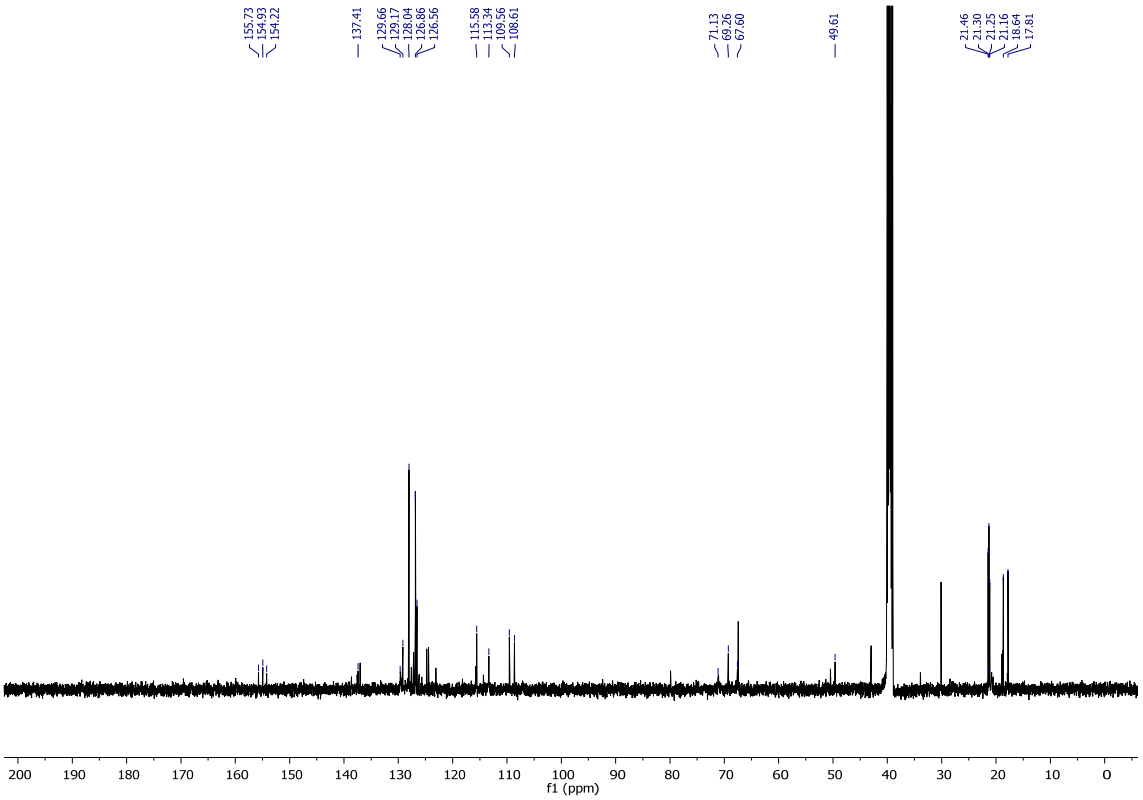


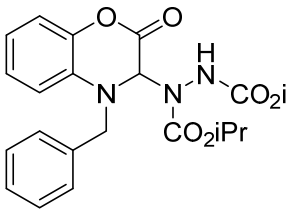
3ma

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



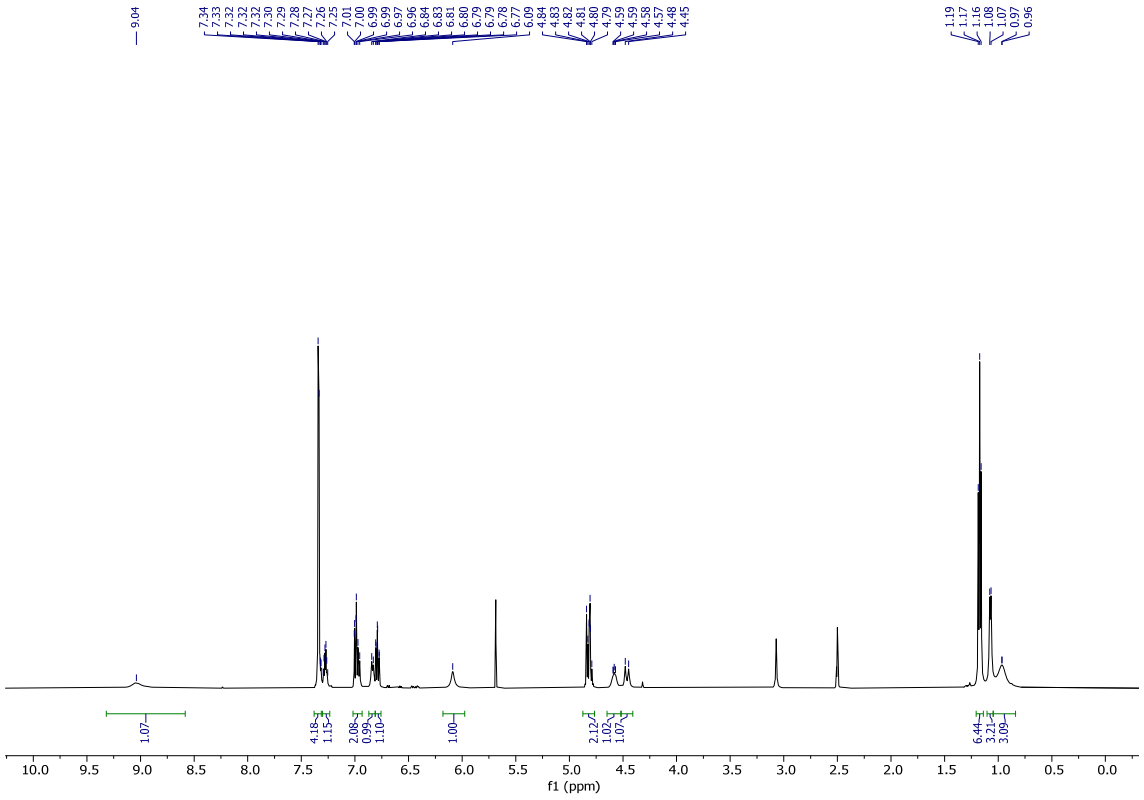


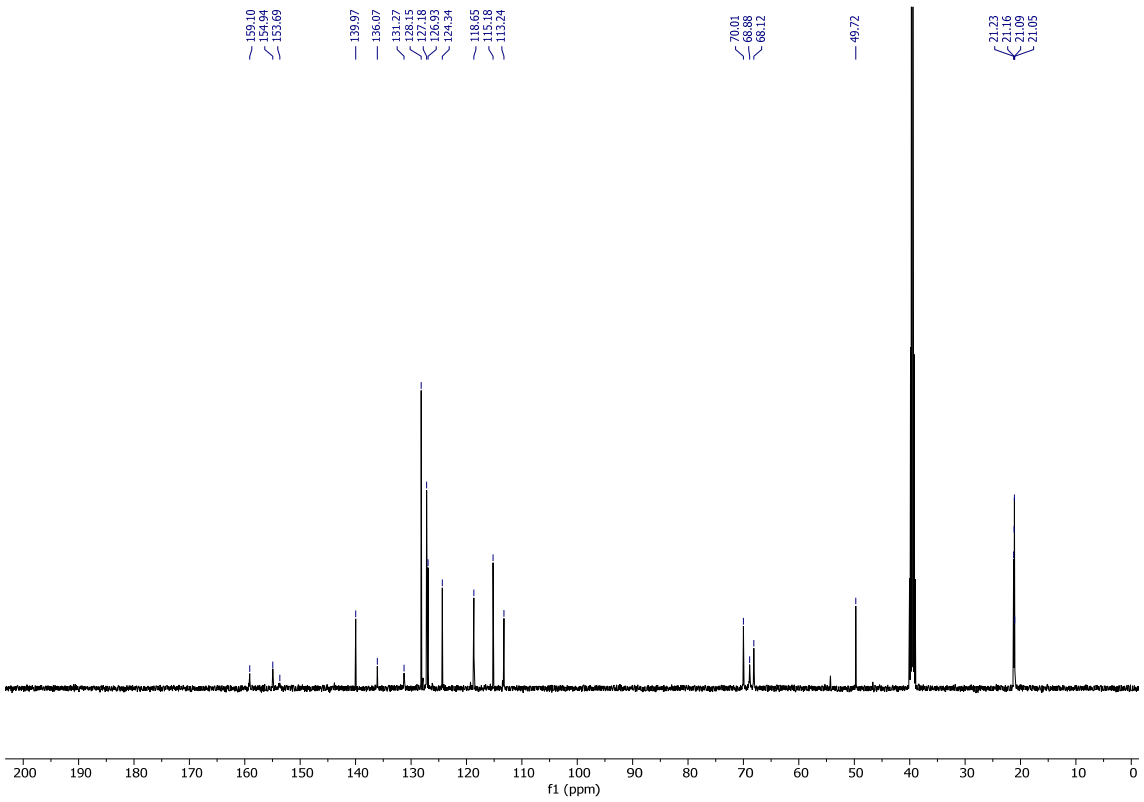


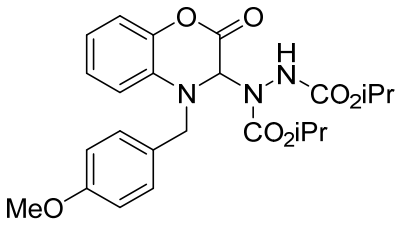
5aa

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



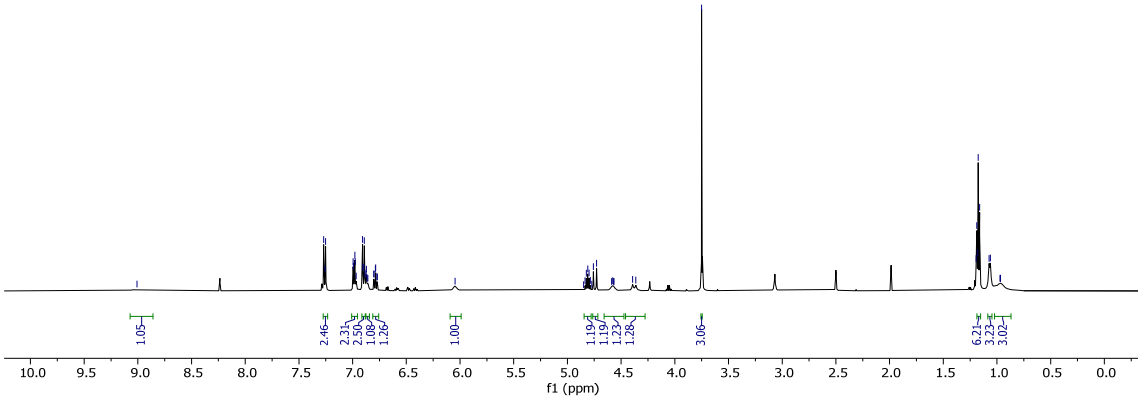


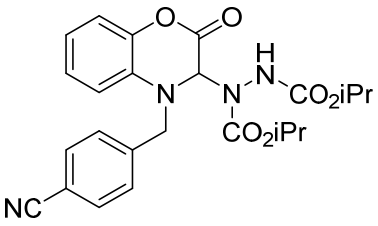


5ba

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})

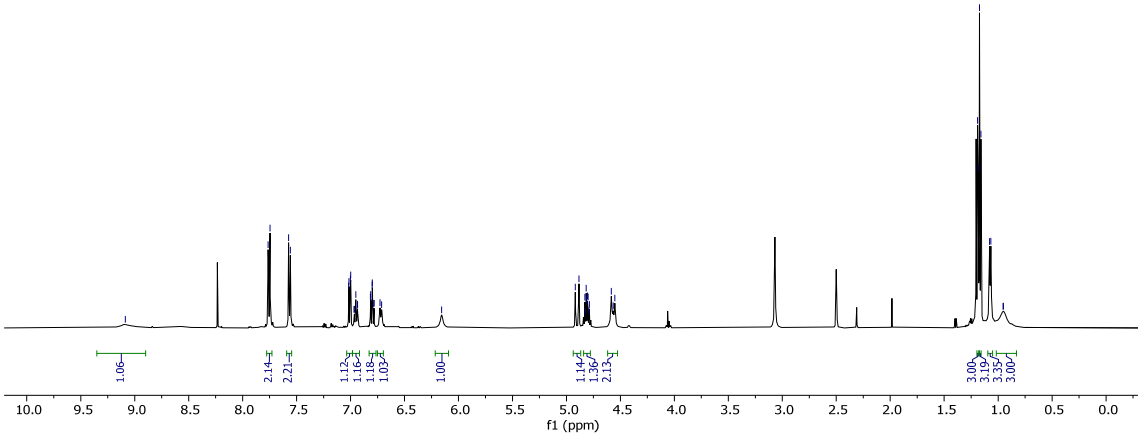


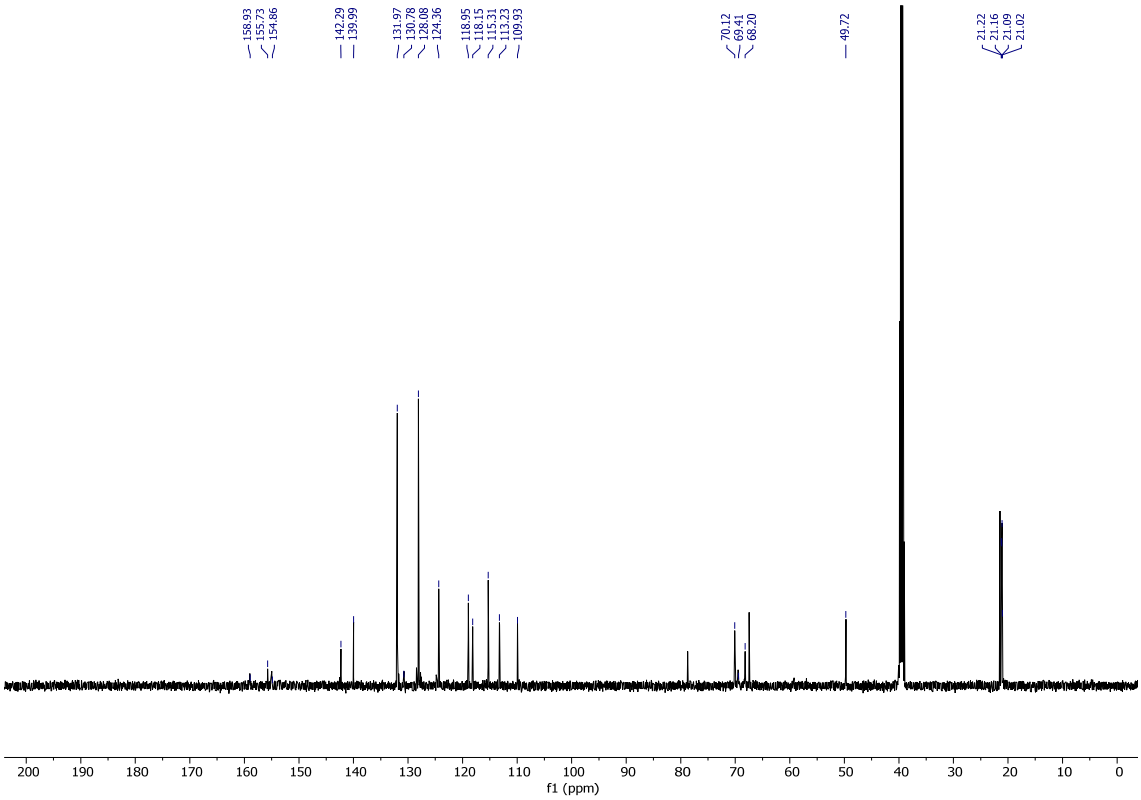


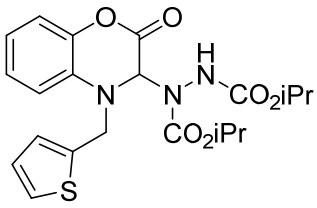
5ca

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



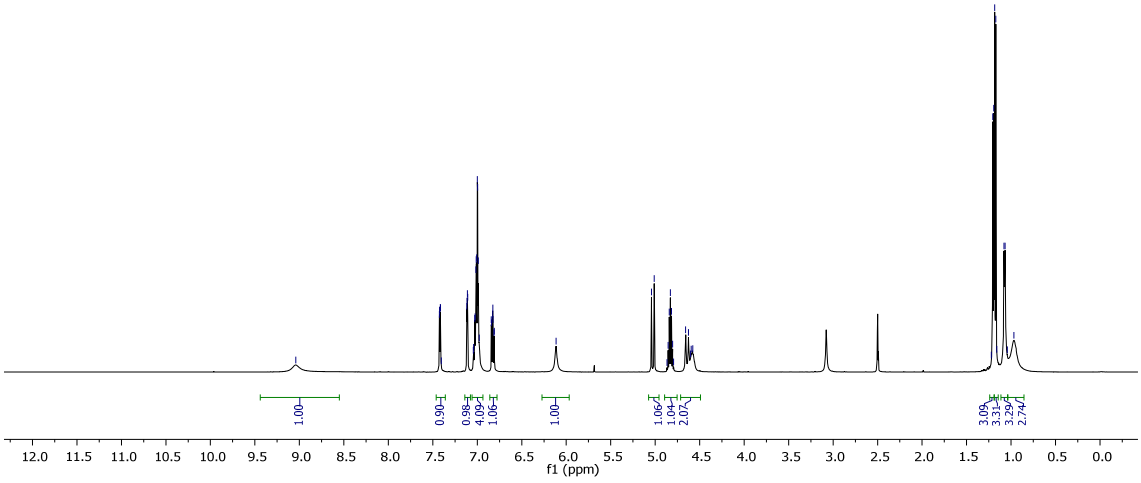


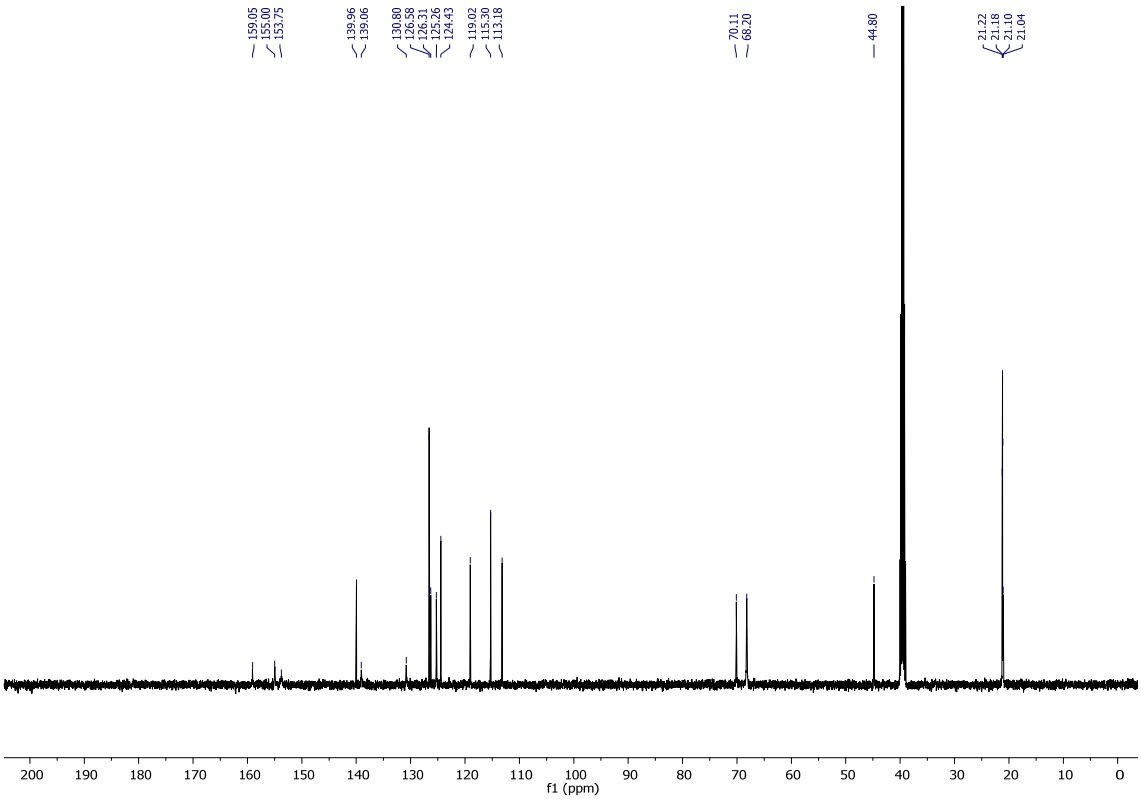


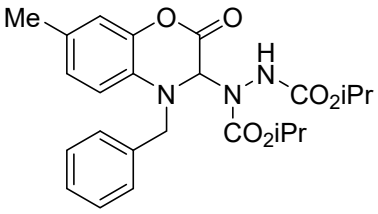
3da

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



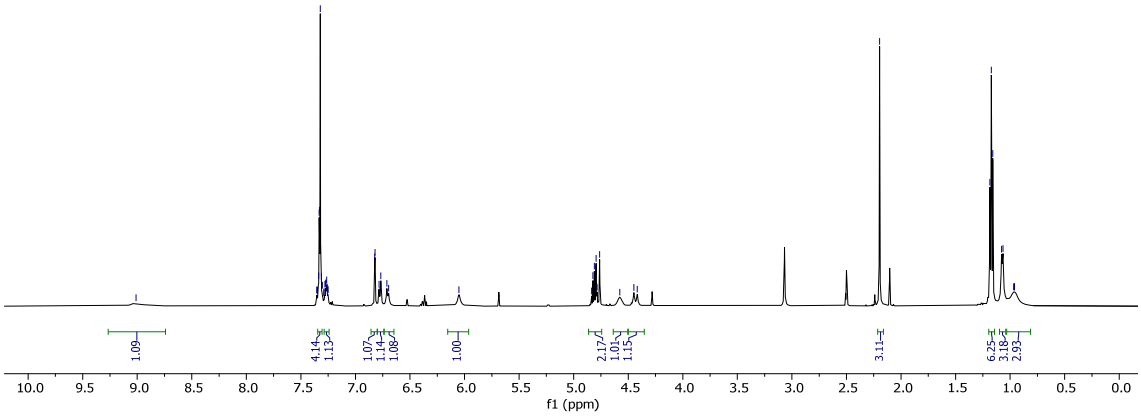


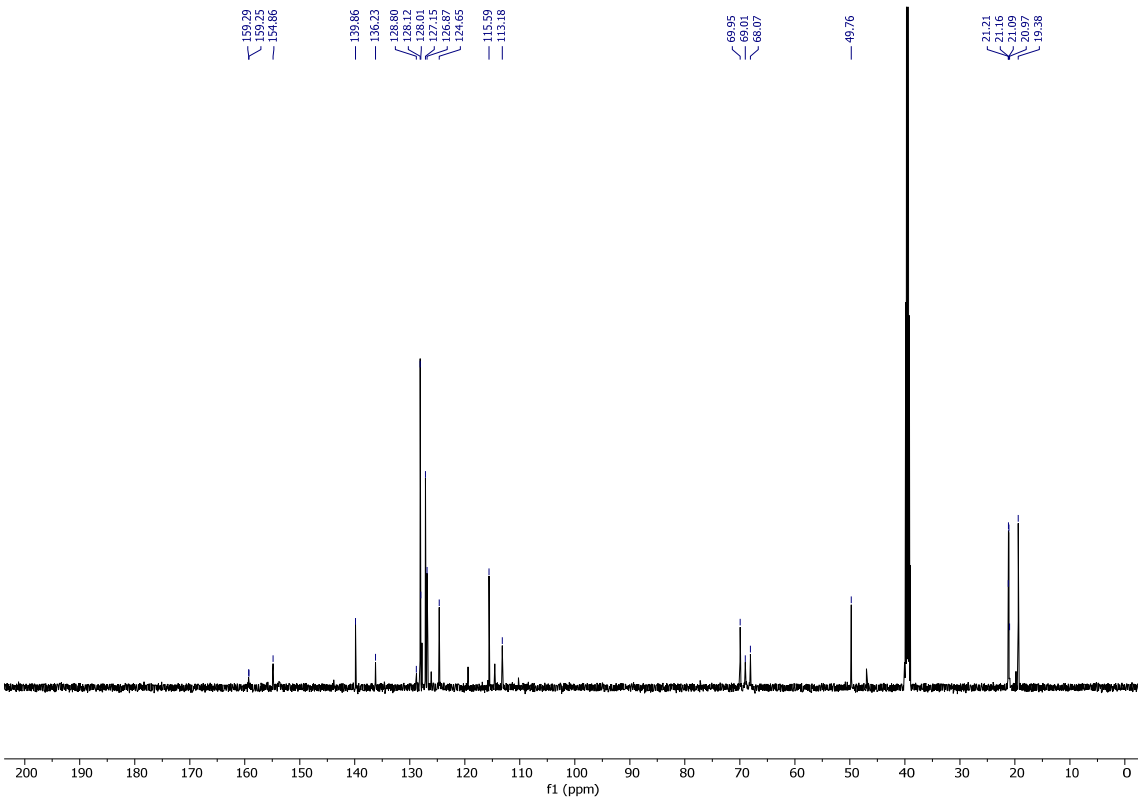


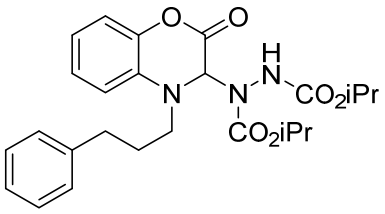
5ea

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



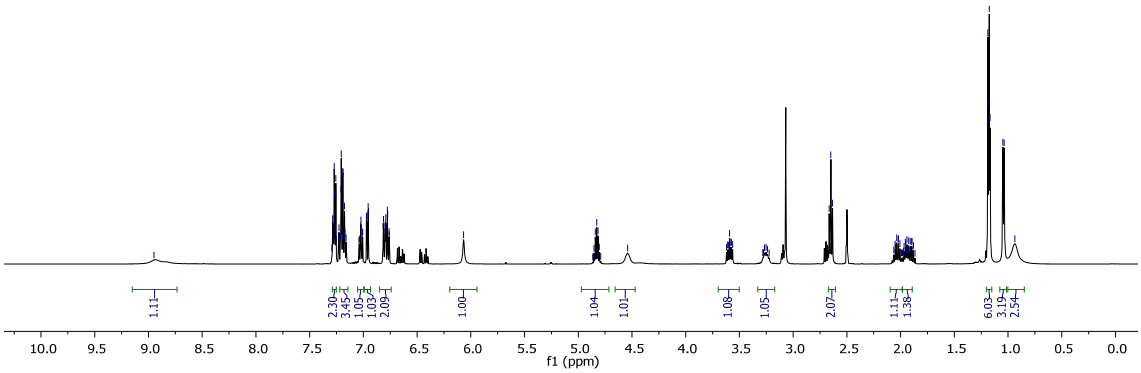


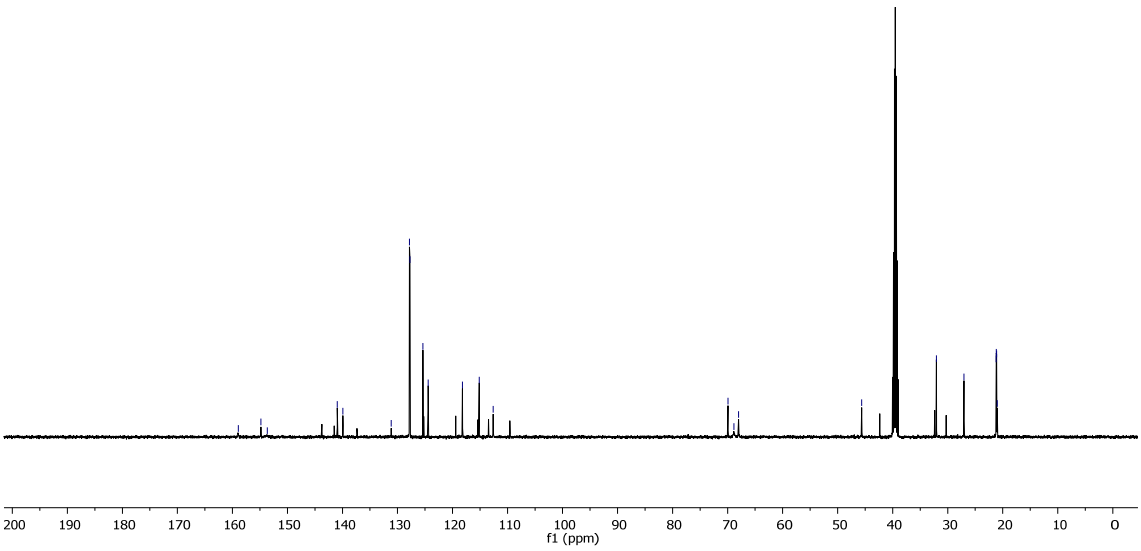


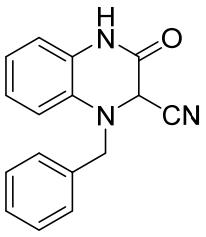
5fa

^{1}H NMR (500 MHz, 353 K, DMSO-*d*^{6})

^{13}C NMR (125 MHz, 353 K, DMSO-*d*^{6})



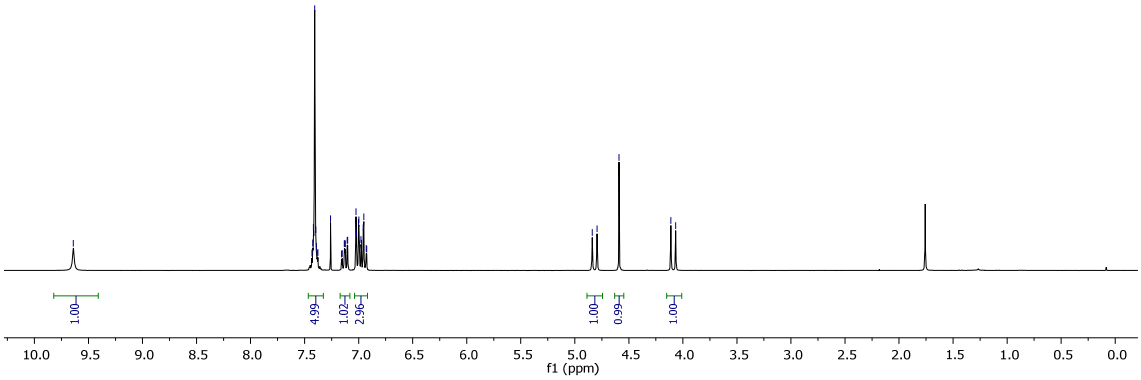


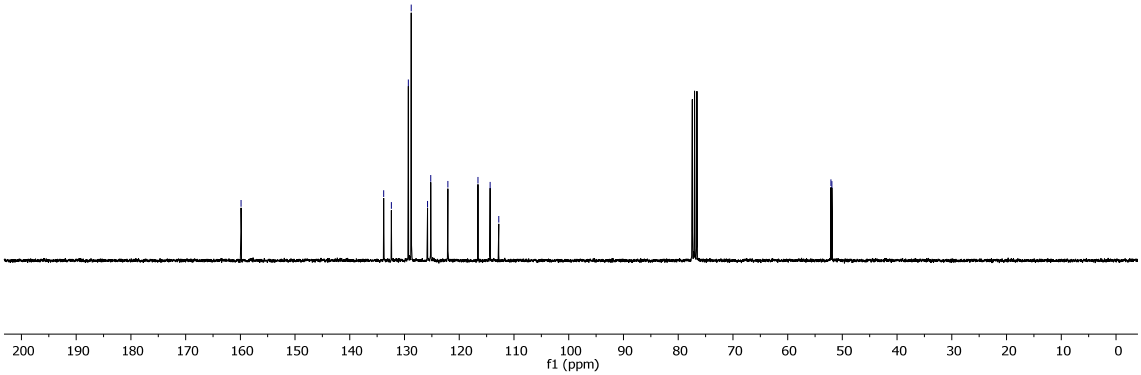


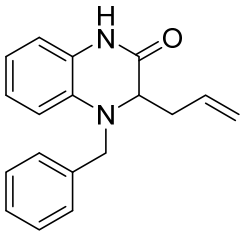
6

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



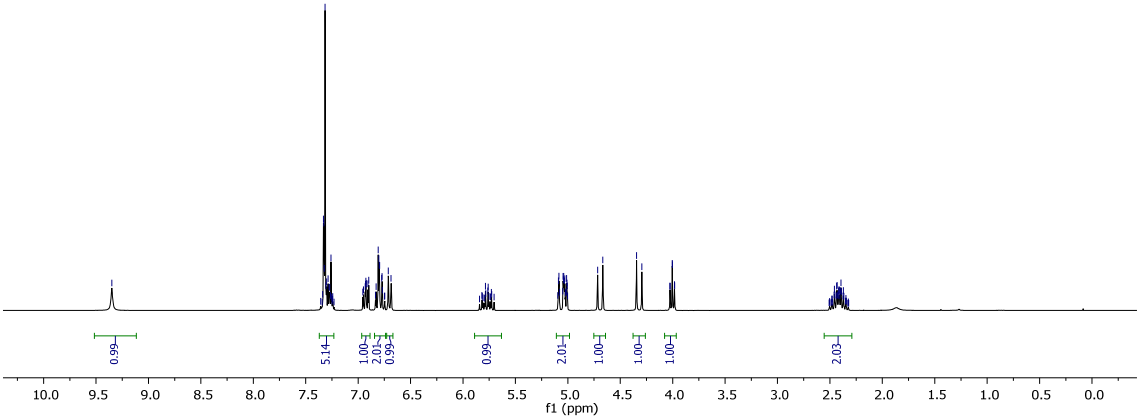


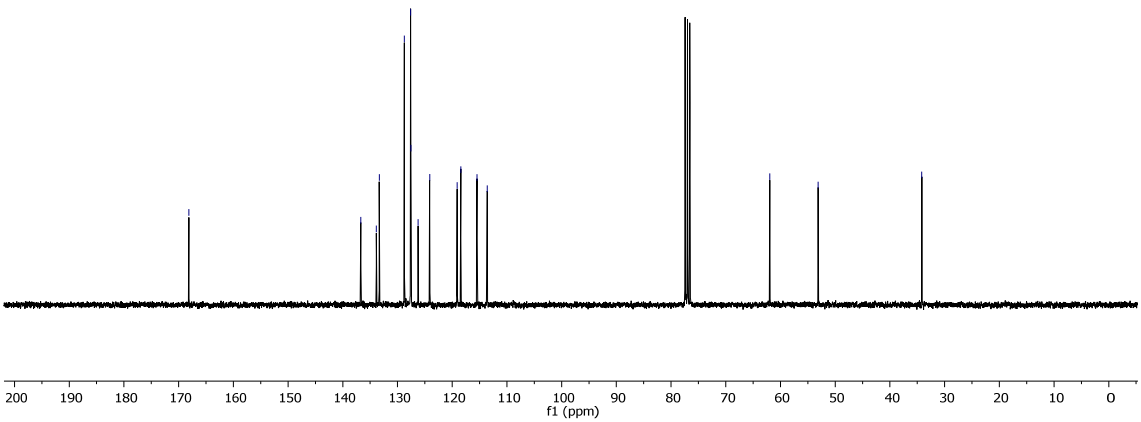


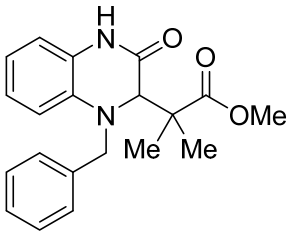
7

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



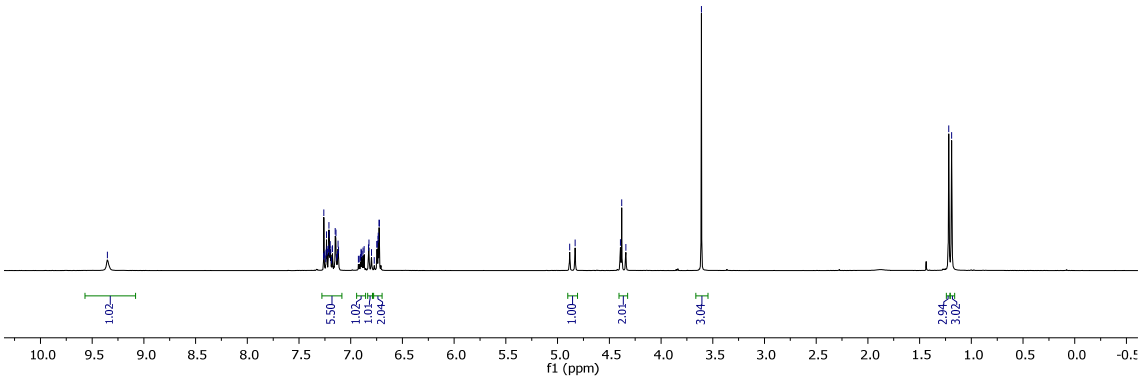


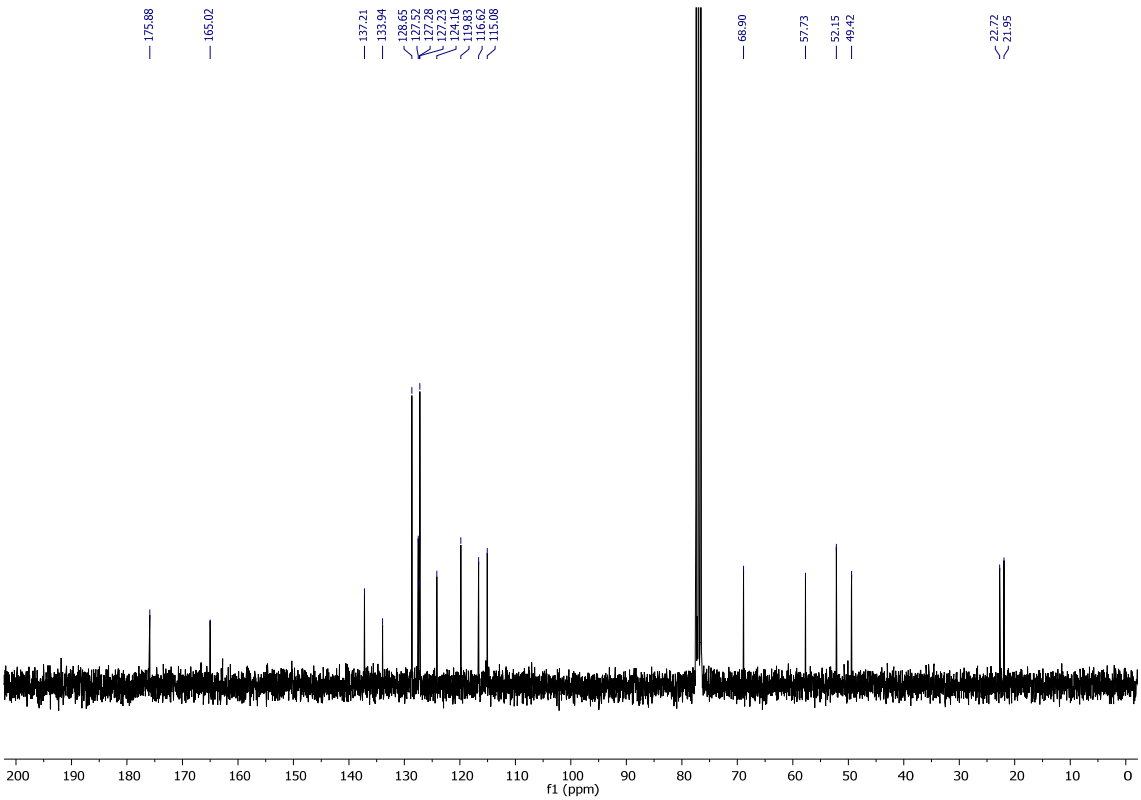


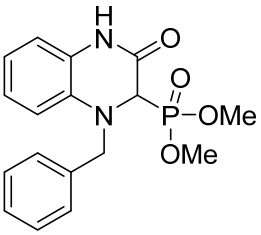
8

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



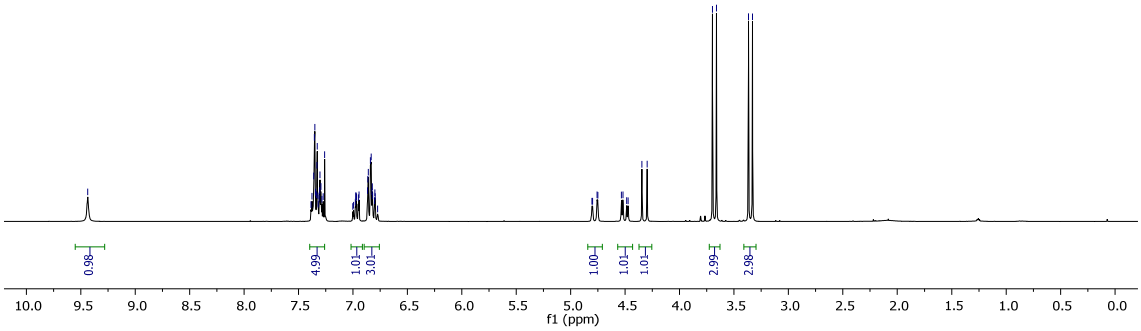


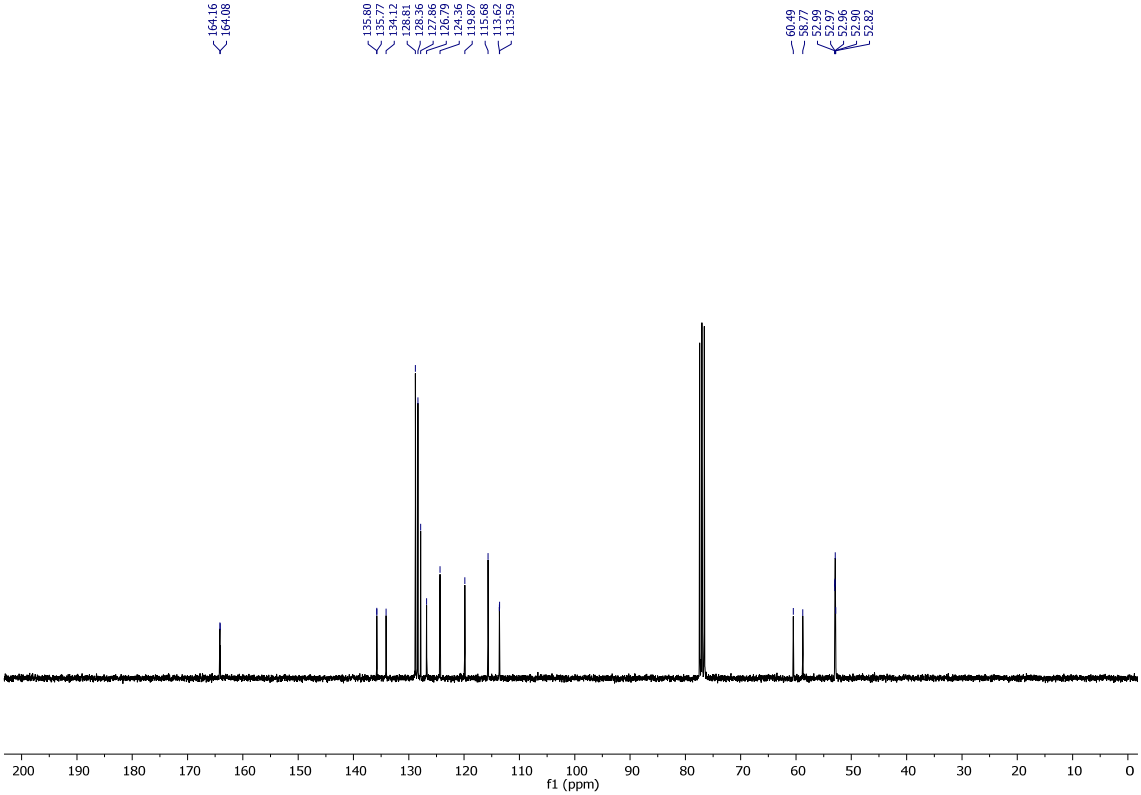


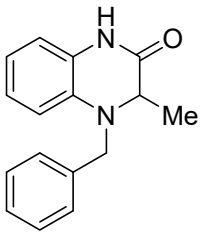
9

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



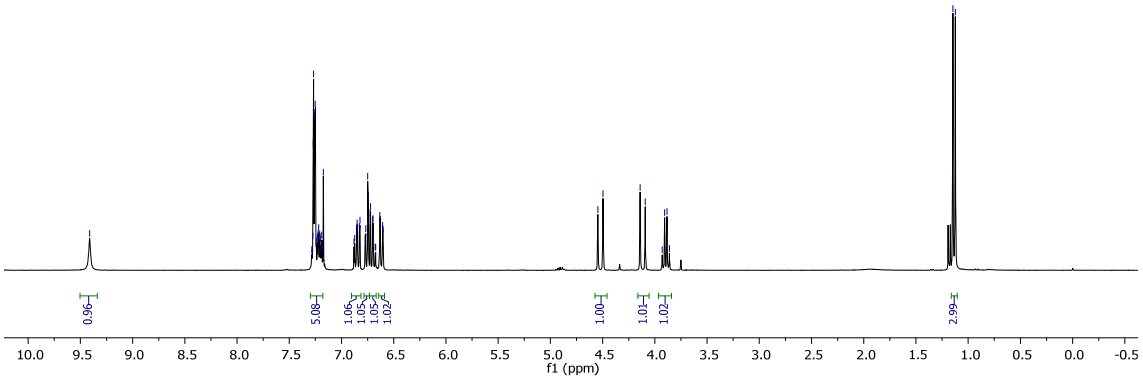


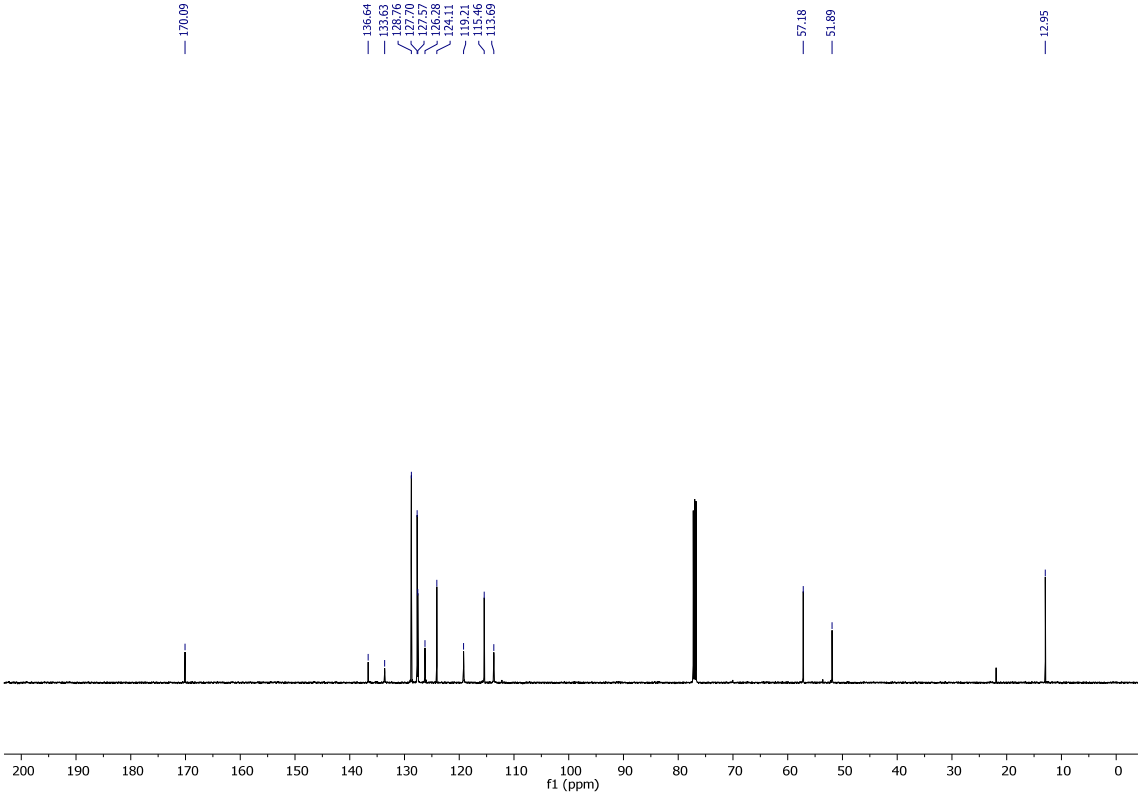


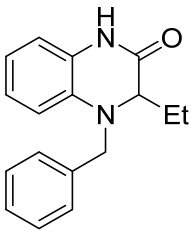
10

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



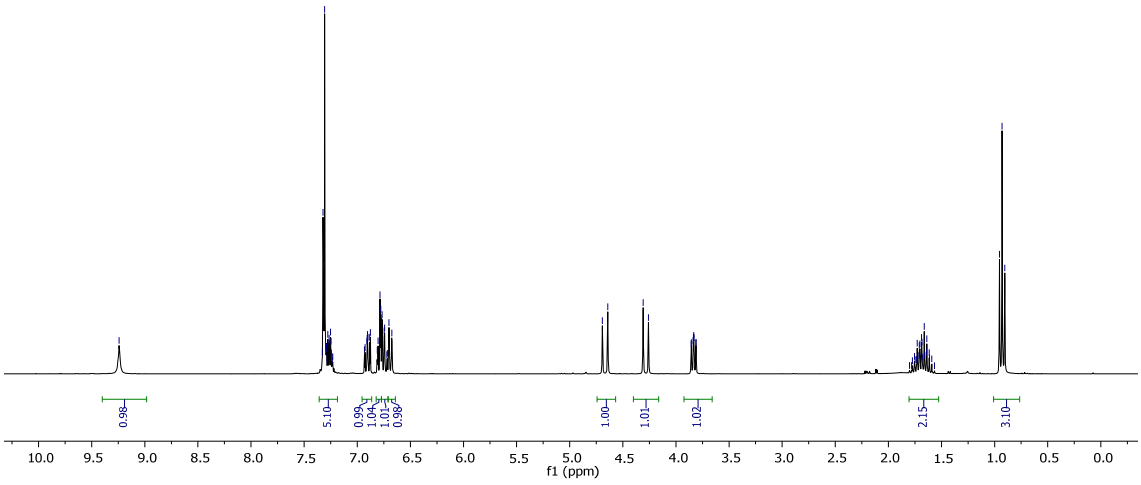


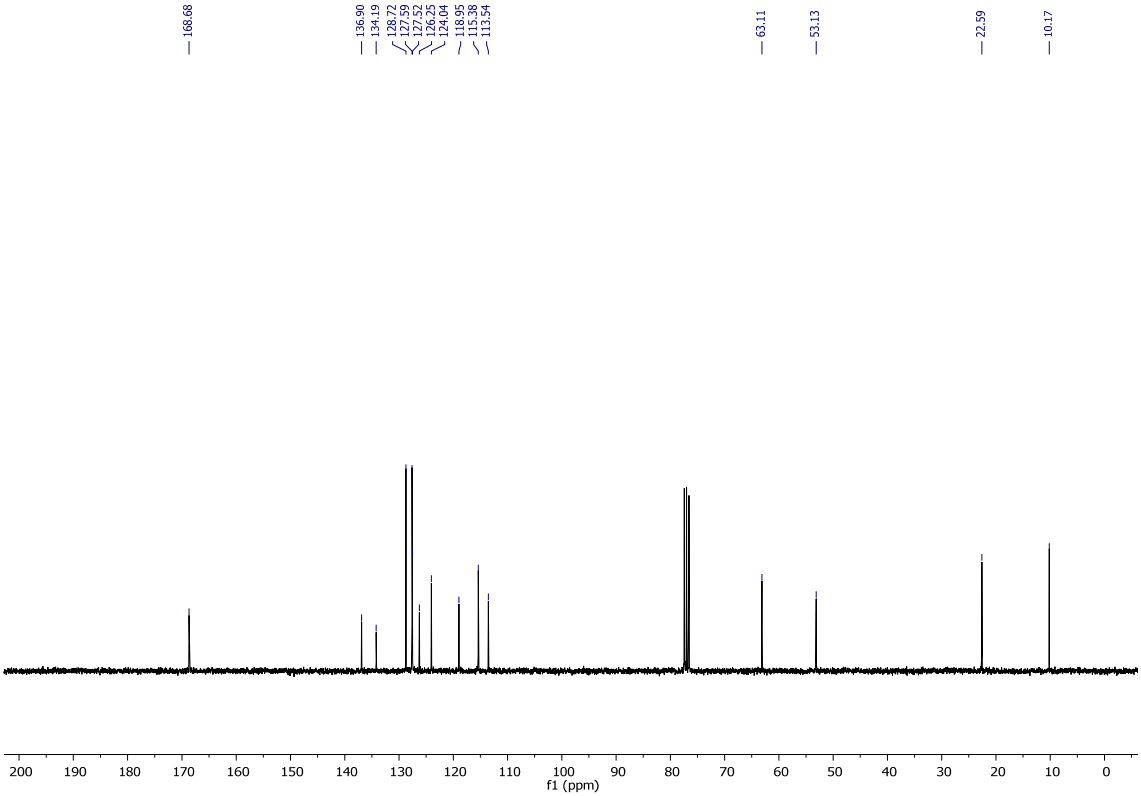


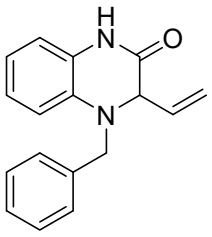
11

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



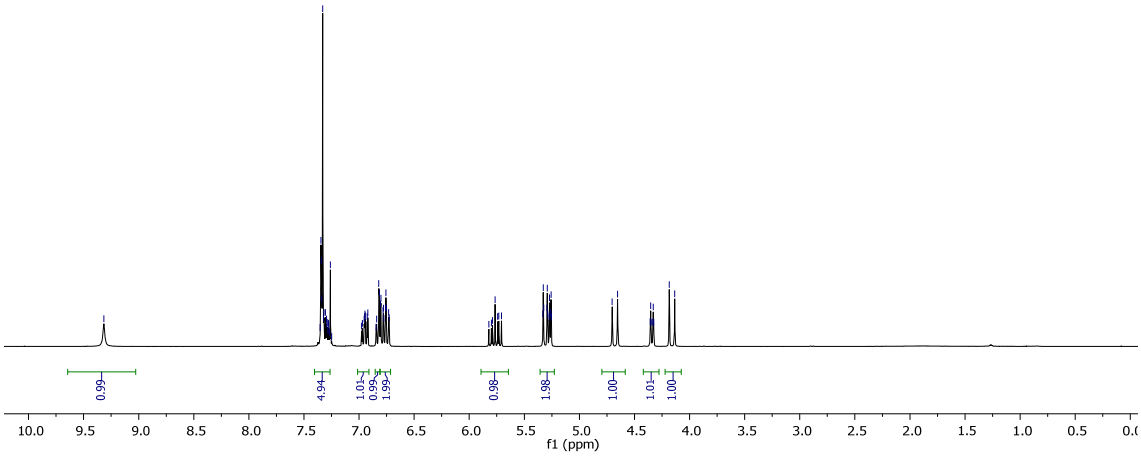


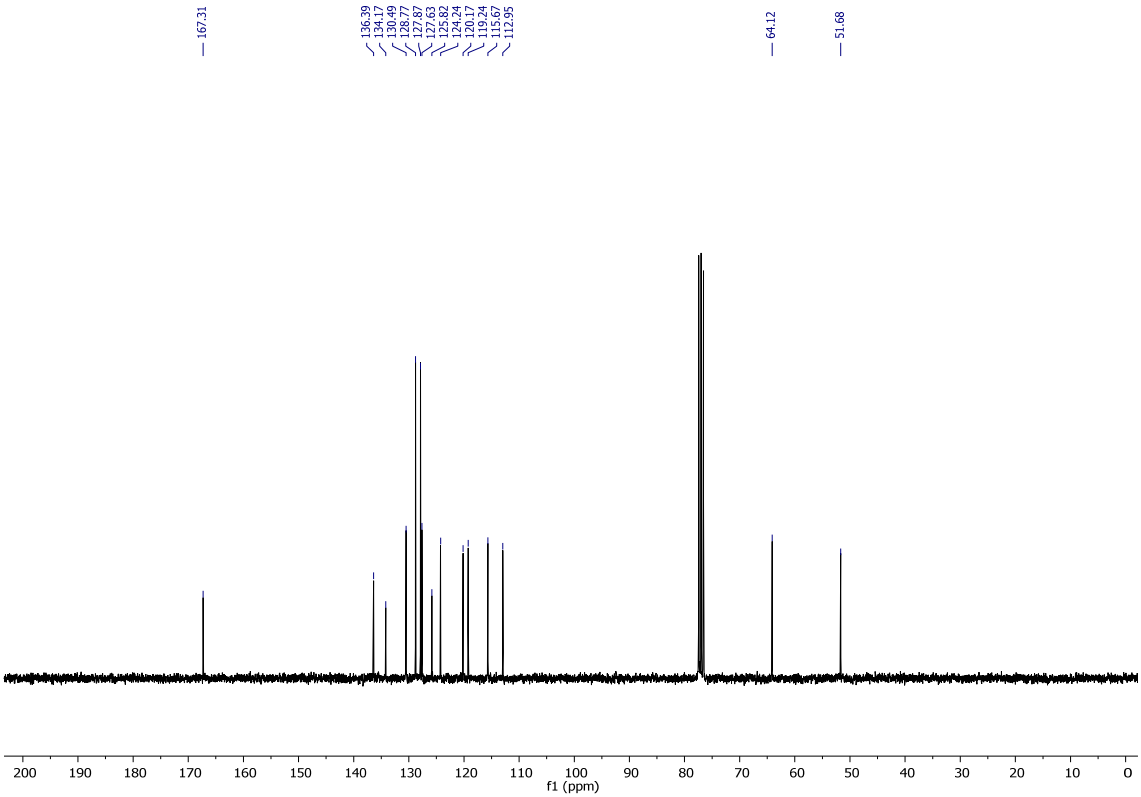


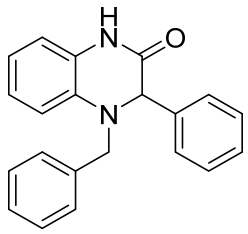
12

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



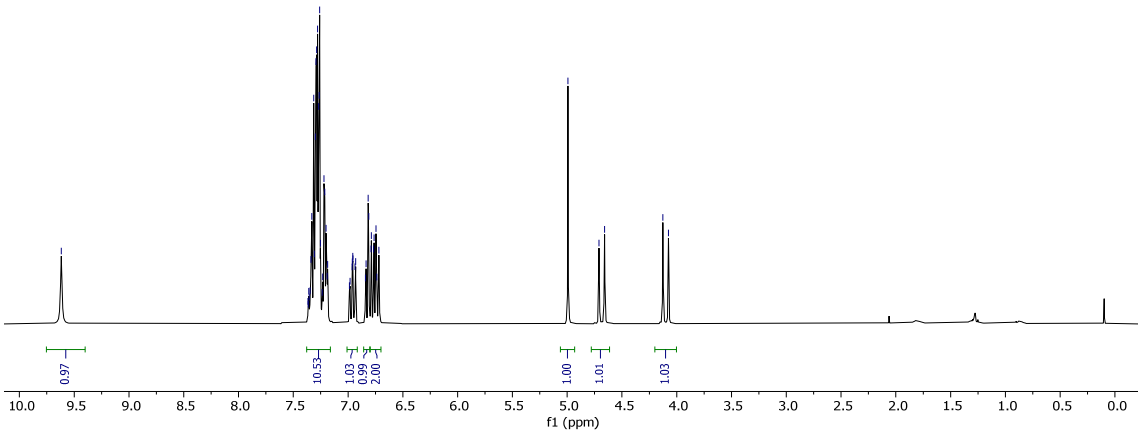


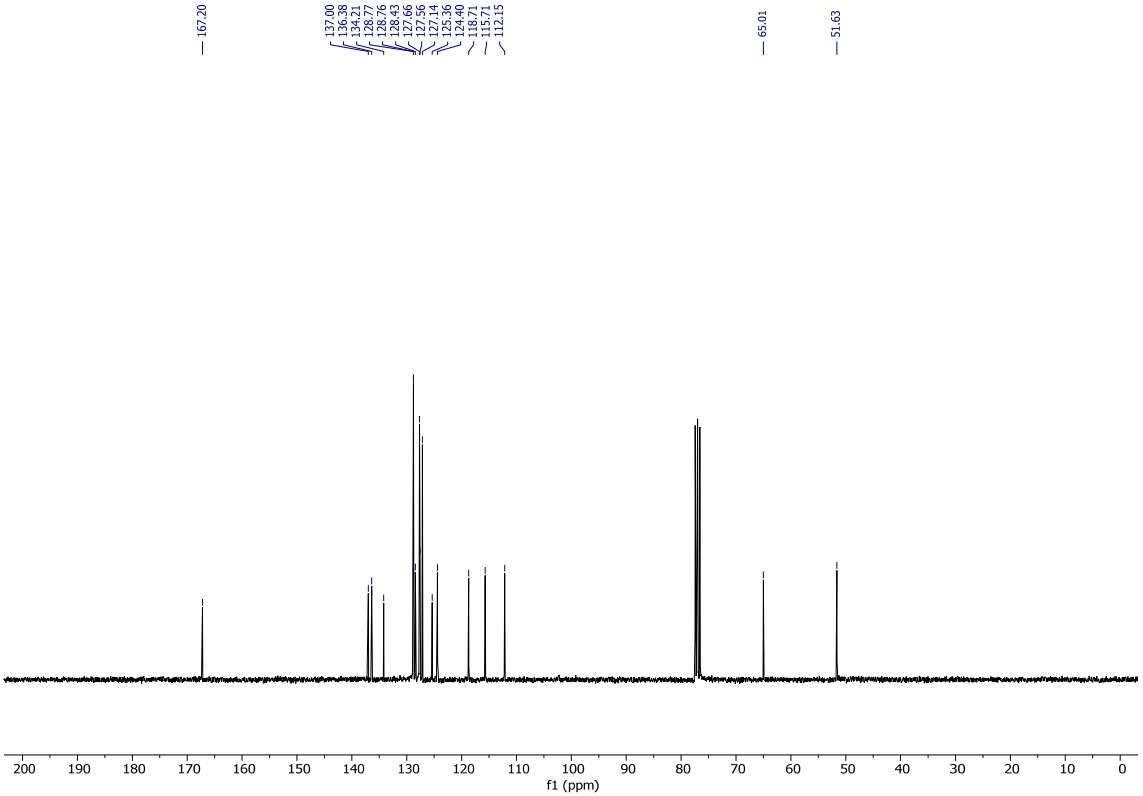


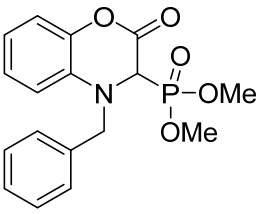
13

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



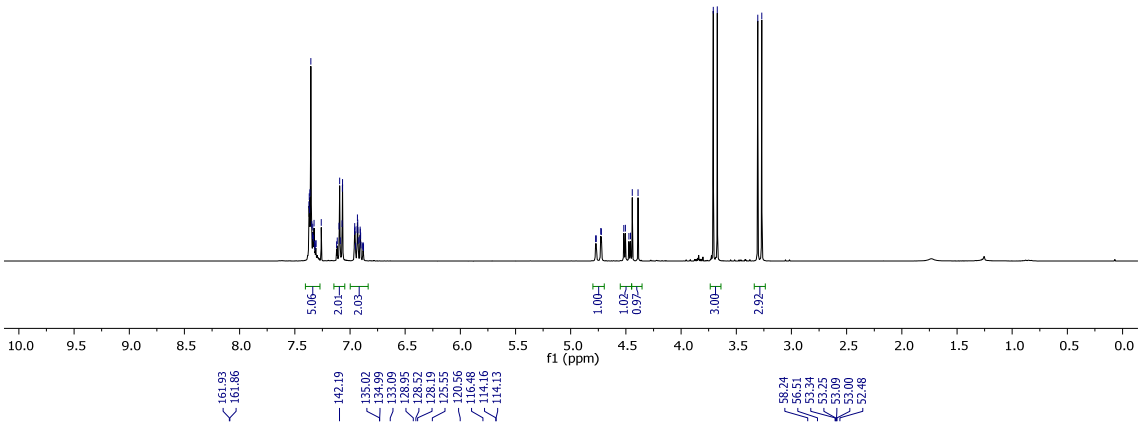


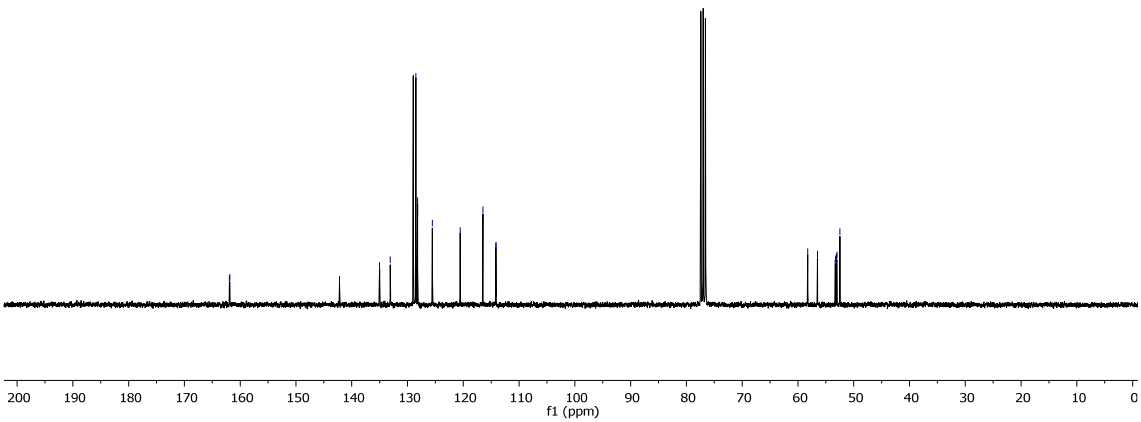


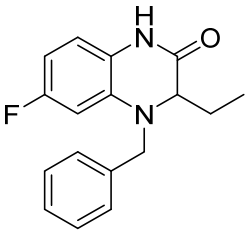
14

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



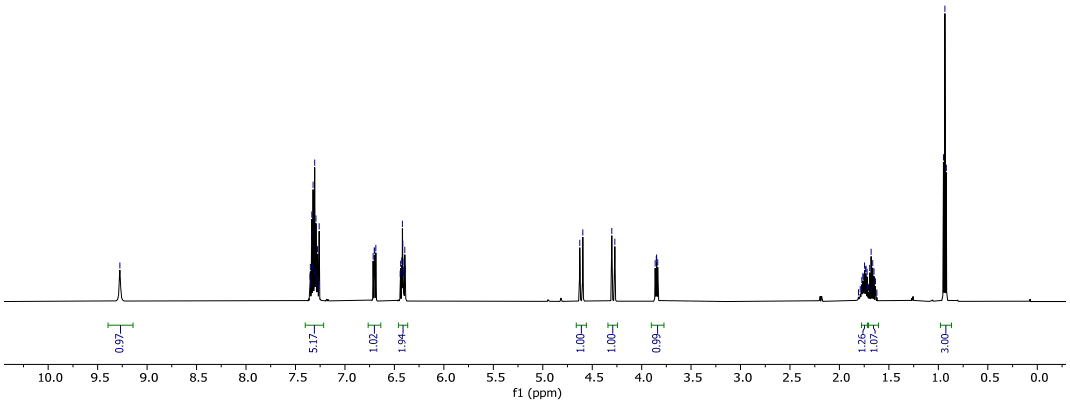


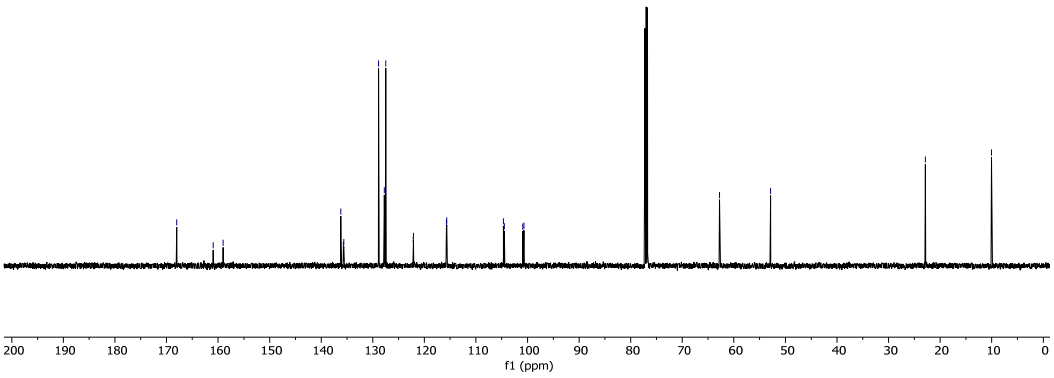


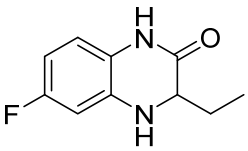
15

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)



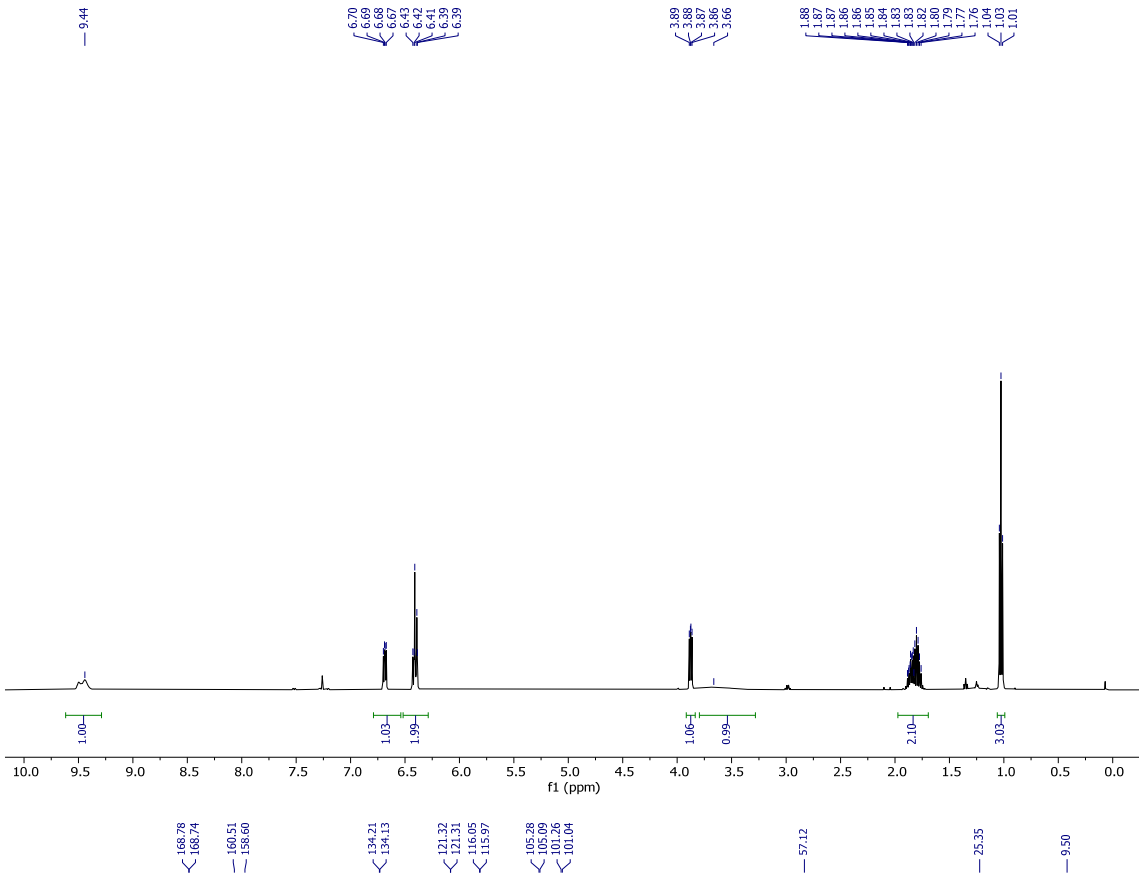


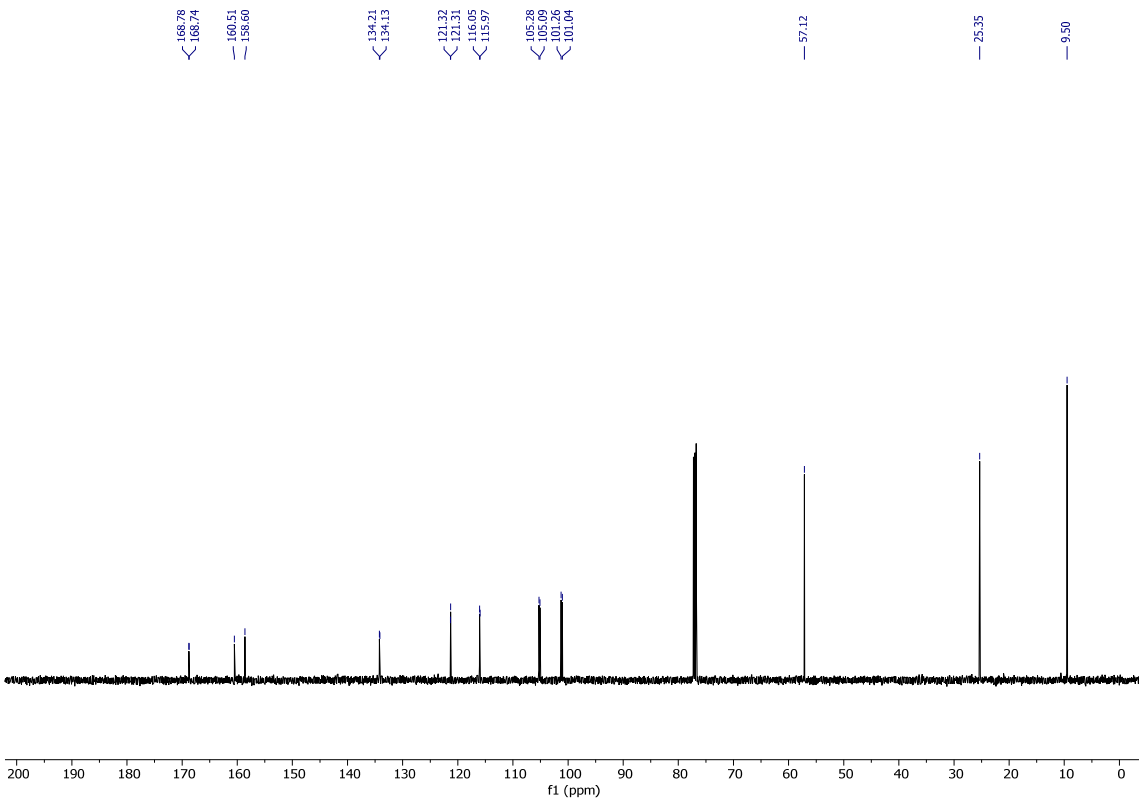


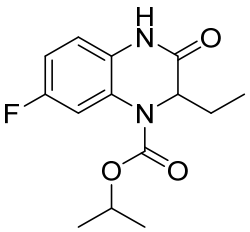
16

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$)







***rac*-Opaviraline (17)**
^{1}H NMR (300 MHz, $CDCl_3$)
^{13}C NMR (75 MHz, $CDCl_3$)