Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rh(III)-Catalyzed Mild Straightforward Synthesis of Quinoline-Braced Cyclophane Macrocycles via Migratory Insertion

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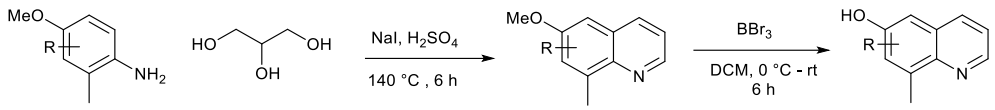
Experimental Section

General information: All commercially available compounds were used without further purification. Solvents for elution in column were distilled. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254. Visualization on TLC was achieved using UV light (254 nm). Column chromatography was undertaken on silica gel (230-400 mesh). 1H and 13C NMR spectra were recorded on BRUKER ULTRA SHIELD and BRUKER ASCEND (400 MHz and 600 MHz) instruments. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br= broad, s= singlet, d= doublet, t= triplet, q= quartet, dd= doublet of doublet, td= triplet of doublet, ddd= doublet of doublet of doublet, m= multiplet. Coupling constants, J, were reported in hertz unit (Hz). ^{13}C NMR spectra were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the centre of a triplet at 77.16 ppm of $CDCl_3$. Infrared (IR) spectra were recorded using Spectrum BX FT-IR instrument from Perkin Elmer. Frequencies are given in reciprocal centimetres (cm-1) and only selected absorbance peaks are reported. High resolution mass spectra were recorded in ESI(+ve) method using a time-of-flight (TOF) mass analyser. LC-MS were obtained from Agilent Technologies A6120BW (single quadruple mass analyzer). Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted.

1. General procedure for the synthesis of substituted 8-methylquinolin-6-ol:

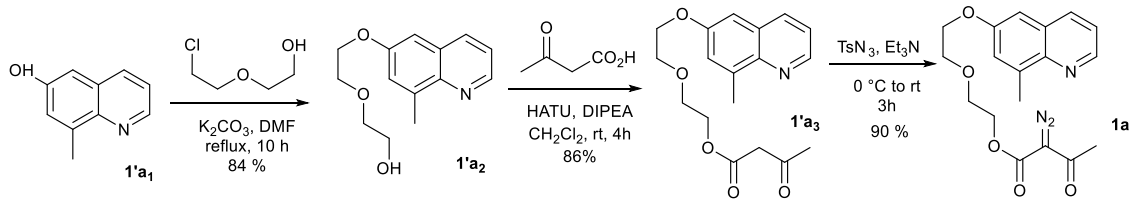


6-Methoxy-8-methylquinoline derivatives were prepared following the procedure described by O'Murchu[1]. Glycerine (1.2 mmol) was added over a period of 0.5 h to a solution of substituted 4-methoxy-2-methylaniline (1 mmol), NaI (0.013 mmol) and 80% H_2SO_4 (4.5 mmol) at 140 °C. The reaction mixture was allowed to stir at the same temperature for 6 h. The mixture was then neutralized with 25% aq. NaOH solution and *p*H was adjusted to 9 - 10 and extracted with toluene (30 mL × 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluant. Pure substituted 6-methoxy-8-methylquinoline derivatives were obtained with 80 - 90% yield.

To a stirred solution of 6-methoxy-8-methylquinoline (1 mmol) in anhydrous CH_2Cl_2 (10 mL), excess BBr_3 (1.5 mmol, 1M in DCM) was added at 0 °C. The mixture was stirred for 6 h. The reaction mixture was then quenched by slow addition of *aq*. ammonium hydroxide. The pure solid product formed was collected by filtration. Further the filtrate was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel with EtOAc/hexane as eluent to give pure substituted 8-methylquinolin-6-ol.

2. Synthetic procedures for the preparation of starting pre-macrocyclized diazo compounds:

2.1 General synthetic procedure for the preparation of pre-macrocyclized scaffold 1a and related starting materials:



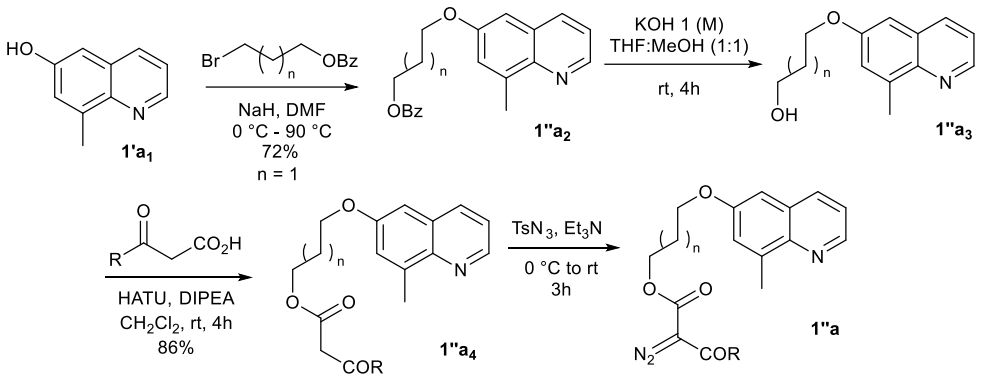
To a stirred solution of 8-methylquinolin-6-ol **1′a₁** (1 mmol) in DMF (10 mL), K_2CO_3 (2 mmol) was added at 0 °C under nitrogen atmosphere. After 5 min, 2-(2-chloroethoxy)ethanol (1.2 mmol) was added in one portion. The mixture was then stirred at 90 °C for 10 h. After completion of the reaction, it was diluted with H_2O and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **1′a₂** in 84 % of isolated yield.

To a stirred solution of **1′a₂** (1 mmol) in CH_2Cl_2 (10 mL), HATU (1.5 mmol), DIPEA (2 mmol) and acetoacetic acid (2 mmol) were added at room temperature under nitrogen atmosphere. The mixture was stirred for 4 h at the room temperature while the reaction progress was monitored by TLC. After completion, it was diluted with H_2O and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **1′a₃** in 86 % of isolated yield.

Tosyl azide (1.2 mmol) and triethylamine (2 mmol) were added to a solution of **1′a₃** (1 mmol) in acetonitrile (10 mL) at 0 °C. The reaction mixture was allowed to stir at rt for 3 h while the reaction progress was monitored by TLC. After completion, the reaction mixture was diluted with H_2O and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **1a** in 90 % of isolated yield.

Compounds **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1r** were prepared using the same procedure.

2.2 General synthetic procedure for the preparation of pre-macrocyclized scaffolds 1′′a and related starting materials:



To a stirred suspension of sodium hydride (1.5 equiv) in DMF was added 8-methylquinolin-6-ol **1′a₁** (1 mmol) at 0 °C under nitrogen atmosphere. After 30 min, required benzoyl protected bromoalkene (1.2 mmol) was added and the mixture was then stirred at 90 °C for 10 h. After completion of the reaction, saturated solution of aq. NH_4Cl was added, the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed with H_2O, brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **1′′a₂** in 72 % of isolated yield.

The product obtained was then treated with 5 mL 1(M) KOH in a 10 mL 1:1 (THF : MeOH) solvent mixture for 4 h. After completion of the reaction, MeOH was evaporated, and the aqueous part was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over anhydrous

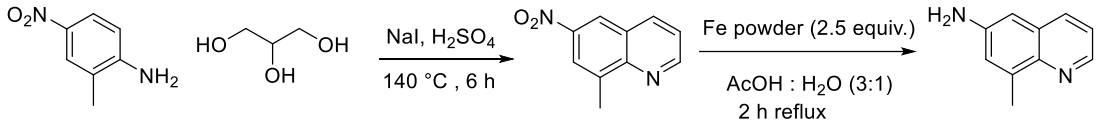
Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography to obtain pure **1′′a$_3$**.

To a stirred solution of **1′′a$_3$** (1 mmol) in CH_2Cl_2 (10 mL), HATU (1.5 mmol), DIPEA (2 mmol) and substituted acetoacetic acid (2 mmol) was added at room temperature under nitrogen atmosphere. The mixture was stirred for 4 h at room temperature while the reaction progress was monitored by TLC. After completion of the reaction, it was diluted with H_2O and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **1′′a$_4$**.

Tosyl azide (1.2 mmol) and triethylamine (2 mmol) were added to a solution of **1′′a$_4$** (1 mmol) in acetonitrile (10 mL) at 0 °C. The reaction mixture was allowed to stir at room temperature for 3 h while the reaction progress was monitored by TLC. After completion of the reaction, acetonitrile was evaporated, and it was diluted with H_2O. It was then extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **1′′a**.

Compound **1b**, **1c**, **1d**, **1e**, **1n**, **1o**, **1p**, **1q**, **1s**, **1t**, **1u** were prepared following this procedure.

2.3 General procedure for the synthesis of 8-methylquinolin-6-amine (1m$_1$):

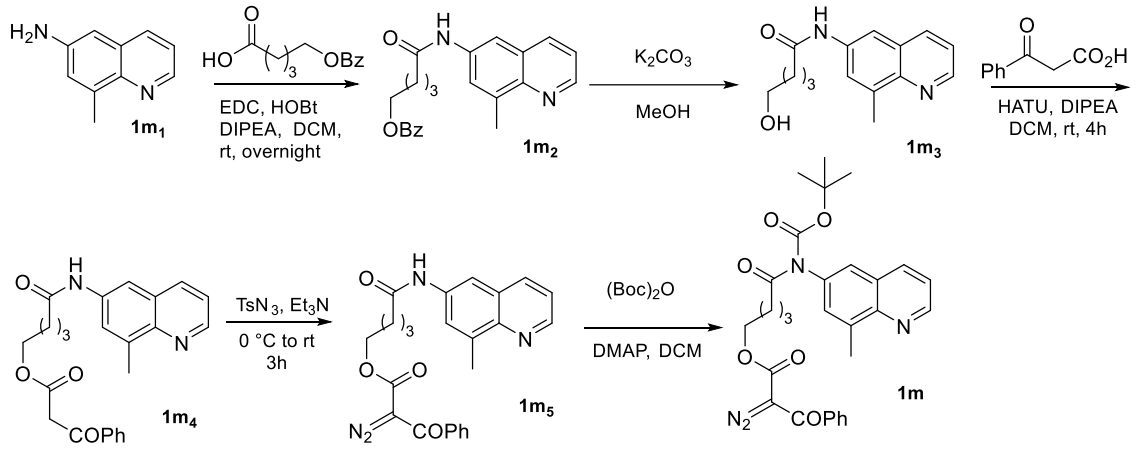


Glycerol (1.2 mmol) was added over a period of 0.5 h to a solution of substituted 2-methyl-4-nitroaniline (1 mmol), NaI (0.013 mmol) and 80% H_2SO_4 (4.5 mmol) at 140 °C. The reaction mixture was allowed to stir at the same temperature for 6 h. The mixture was then neutralized with 25% aq. NaOH solution and pH was adjusted to 9 - 10 and extracted with toluene (30 mL × 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent. Pure 8-methyl-6-nitroquinoline derivative was obtained in 85% yield.

Iron powder (1.4 g, 25.5 mmol) was added in portions to a suspension of 8-methyl-6-nitroquinoline (820 mg, 5.1 mmol) in a mixture of 15 ml of acetic acid and 5 ml of water at room temperature. Then, the reaction mixture was refluxed for 2 hours. After completion (by TLC), reaction mixture was cooled to 40 °C and then quenched by slow addition of (2N) sodium hydroxide solution. Next, the reaction mixture was diluted with water and EtOAc. The aq. layer separated off

and extracted twice with EtOAc. The organic phases were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was further purified by column chromatography on silica gel with EtOAc/hexane as eluent to give pure 8-methylquinolin-6-amine with 70% yield.[2]

2.4 Synthetic procedure for the pre-macrocyclized scaffold 1m:



To a stirred solution of **$1m_1$** (1 mmol) in DCM (10 mL), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) (1.1 mmol), 1-Hydroxybenzotriazole (HOBt) (1.1 mmol), *N,N*-diisopropylethylamine (DIPEA) (3.0 mmol) and aliphatic acid (1.5 mmol) was added at the room temperature under nitrogen atmosphere. The mixture was stirred for overnight at room temperature while the reaction progress was monitored by TLC. After completion of the reaction, it was diluted with H_2O and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **$1m_2$**.

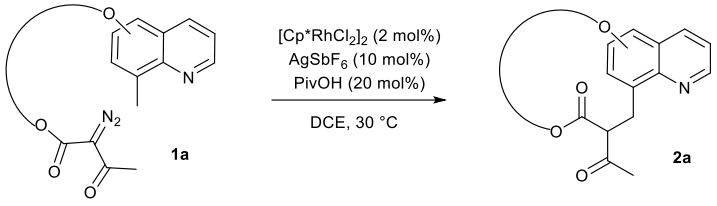
The product obtained was then treated with anhydrous K_2CO_3 (2 equiv) in 10 mL MeOH for 18h at room temperature. After completion of the reaction, MeOH was evaporated and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed with water, brine and dried over anhydrous Na_2SO_4. Next, it was filtered and concentrated under vacuum. The residue was purified by column chromatography to obtain pure **$1m_3$**.

To a stirred solution of **$1m_3$** (1 mmol) in DCM (10 mL), HATU (1.5 mmol), DIPEA (2 mmol) and 3-*oxo*-3-phenylpropanoic acid (2 mmol) were added at room temperature under nitrogen atmosphere. The mixture was stirred for 4 h at room temperature while the reaction progress was monitored by TLC. After completion of the reaction, it was diluted with H_2O and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **$1m_4$**.

Tosyl azide (1.2 mmol) and triethylamine (2 mmol) were added to a solution of **1m$_4$** (1 mmol) in acetonitrile (10 mL) at 0 °C. The reaction mixture was allowed to stir at room temperature for 3 h while the reaction progress was monitored by TLC. After completion of the reaction, acetonitrile was evaporated, and it was diluted with H_2O. Next, it was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **1m$_5$**.

Next, to a stirred solution of **1m$_5$** (1 mmol) in DCM (10 mL), 4-(*N*,*N*-dimethylamino)pyridine (10 mol%) and di-*tert*-butyl decarbonate (2 mmol) were added and the mixture was allowed to stir at room temperature for 20 h while the reaction progress was monitored by TLC. After completion, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **1m**.

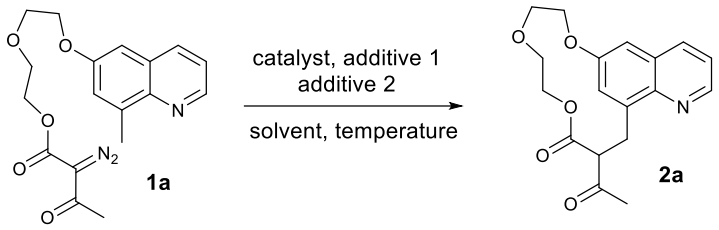
3. General procedure for the Rh(III)-catalyzed macrocyclization:



In a 10 mL screw cap vial equipped with magnetic stirring bar, pre-macrocyclic scaffold **1a** (0.10 mmol), $[Cp^*RhCl_2]_2$ (1.2 mg, 2.0 mol%), $AgSbF_6$ (2.7 mg, 8.0 mol%) and pivalic acid (2.04 mg, 20 mol%) were taken in dry 1,2-dichloroethane (1 mL). The reaction mixture was stirred at 30 °C temperature for 6 h. After the completion, the reaction mixture was purified directly through silica gel column chromatography with ethyl acetate/hexane as eluent to give the desired macrocyclic product **2a**.

4. Optimization Table

4.1 Table S1: Detail optimization of the macrocyclization[a]

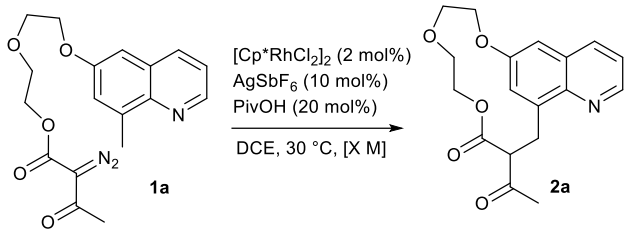


Entries	Catalyst	Solvent	Additive 1	Additive 2	Temp (° C)	Isolated Yield (%)[b]
1	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	PivOH	60	48
2	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	PivOH	80	35
3	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	PivOH	40	70
4	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	PivOH	30	72
5	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	PivOH	20	30
6	$[Cp^*RhCl_2]_2$	toluene	$AgSbF_6$	PivOH	30	<10
7	$[Cp^*RhCl_2]_2$	MeCN	$AgSbF_6$	PivOH	30	32
8	$[Cp^*RhCl_2]_2$	dioxane	$AgSbF_6$	PivOH	30	23
9	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$	PivOH	30	15
10	$[Cp^*RhCl_2]_2$	^{t}AmOH	$AgSbF_6$	PivOH	30	Trace
11	$[Cp^*RhCl_2]_2$	DCM	$AgSbF_6$	PivOH	30	61
12	$[Cp^*RhCl_2]_2$	DME	$AgSbF_6$	PivOH	30	Trace
13	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	AcOH	30	55
14	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	$AdCO_2H$	30	31
15	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	*p*-NO_2-$C_6H_4CO_2H$	30	<10
16	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	*o*-OMe-$C_6H_4CO_2H$	30	Trace
17	$[Cp^*RhCl_2]_2$	DCE	$AgNTf_2$	PivOH	30	52
18	$[Cp^*RhCl_2]_2$	DCE	AgOAc	PivOH	30	Trace
19	$[Cp^*RhCl_2]_2$	DCE	$AgBF_4$	PivOH	30	58
20	$[Cp^*RhCl_2]_2$	DCE	AgOTf	PivOH	30	34
21[c]	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$	PivOH	30	68
22	$[Cp^*IrCl_2]_2$	DCE	$AgSbF_6$	PivOH	30	0

23	$Cp^*Co(CO)I_2$	DCE	$AgSbF_6$	PivOH	30	0
24	[Ru(*p*-cymene)Cl_2]$_2$	DCE	$AgSbF_6$	PivOH	30	0
25	[Cp^*RhCl_2]$_2$	DCE	$AgSbF_6$	-	30	0
26	[Cp^*RhCl_2]$_2$	DCE	-	PivOH	30	0
27	-	DCE	$AgSbF_6$	PivOH	30	0

[a] Reaction conditions: **1a** (0.1 mmol), [Cp^*RhCl_2]$_2$ (2 mol%), $AgSbF_6$ (10 mol%), Ag salt (10 mol%), carboxylic acid (20 mol%), solvent (0.1 M), 6-8 h. [b]Isolated yields. [c]Reaction conditions: [Cp^*RhCl_2]$_2$ (1 mol%), $AgSbF_6$ (5 mol%), pivalic acid (20 mol%), solvent (0.1 M), 20 h.

4.2 Table S2: Determination of optimized reaction concentration[a]



Entries	**Concentration [M]**	**Yield(%)[b]**
1	0.001	n.d.
2	0.01	n.d.
3	0.025	66
4	0.05	70
5	0.1	72
6	0.2	67

[a] Reaction conditions: **1a** (0.1 mmol), [Cp^*RhCl_2]$_2$ (2 mol%), $AgSbF_6$ (10 mol%), pivalic acid (20 mol%), solvent (X M), 6 h. [b]Isolated yields.

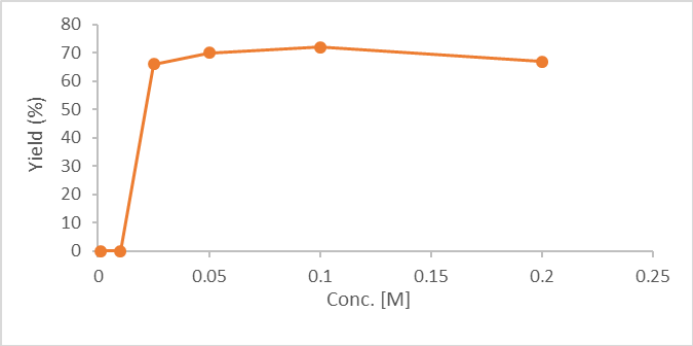
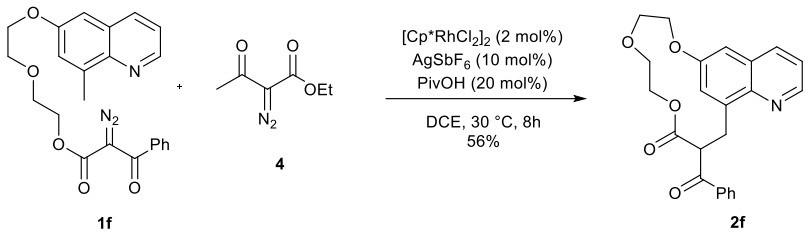


Figure S1: Line diagram of yield (%) vs concentration [M]

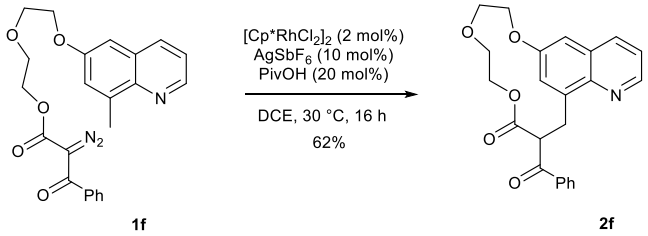
5. Control Experiments:

5.1 Procedure for intra and intermolecular competition reaction:



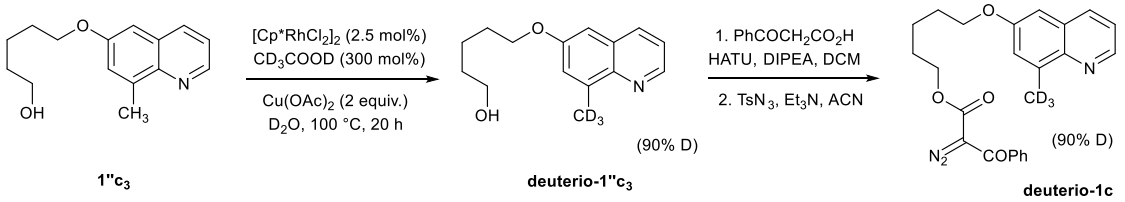
In a 10 mL screw cap vial equipped with magnetic stirring bar, pre-macrocyclic scaffold **1f** (0.10 mmol), ethyl 2-diazo-3-oxobutanoate **4** (0.1 mmol), $[Cp^*RhCl_2]_2$ (1.2 mg, 2.0 mol%), $AgSbF_6$ (2.7 mg, 8.0 mol%) and pivalic acid (2.04 mg, 20 mol%) were taken in dry 1,2-dichloroethane (1 mL). The reaction mixture was stirred at 30 °C temperature for 8 h. After the completion, the reaction mixture was purified directly through silica gel column chromatography with ethyl acetate/hexane as eluent to give the corresponding macrocyclic product **2f** in 56% of isolated yield.

5.2 Scale up experiment:



Pre-macrocyclized scaffold **1f** (500 mg, 1.2 mmol) was taken in a 30 mL screw cap vial equipped with magnetic stirring bar and dissolved in 10 mL dry 1,2-dichloroethane. Then $[Cp^*RhCl_2]_2$ (14 mg, 2 mol%), $AgSbF_6$ (32 mg, 8 mol%) and PivOH (25 mg, 20 mol%) were added to the reaction mixture and stirred at 30 °C for 16 h. After completion, the reaction mixture was passed through a short plug of Celite and washed with 10 mL dichloromethane. The combined organic layer was concentrated under reduced pressure and purified by flash silica gel column chromatography to isolate the compound **2f** in 62% yield (300 mg).

5.3 Preparation of deuterio-pre macrocyclized quinoline scaffold:[3]



To an oven-dried sealed tube, **1′′c$_3$** (245 mg, 1 mmol) was taken in 3 ml D_2O. Then $[Cp^*RhCl_2]_2$ (15 mg, 0.0075 mmol, 2.5 mol%) and CD_3COOD (180 mg, 3 mmol) and $Cu(OAc)_2$ (363.0 mg, 2 mmol) were added at room temperature. The reaction mixture was allowed to stir at 100 °C for 20 h, and then cooled to room temperature. Next, it was extracted with EtOAc (30 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (*n*-hexane/EtOAc = 10:1) to afford **deuterio-1′′c$_3$** in 90% yield (221 mg). **Deuterio-1c** was then prepared using the general protocol as mentioned above.

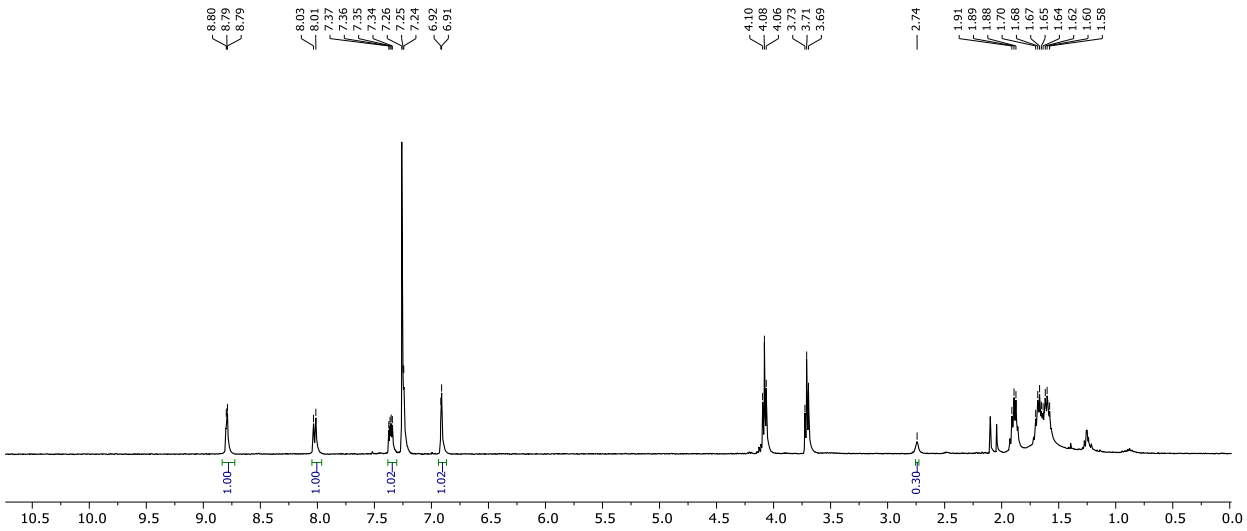
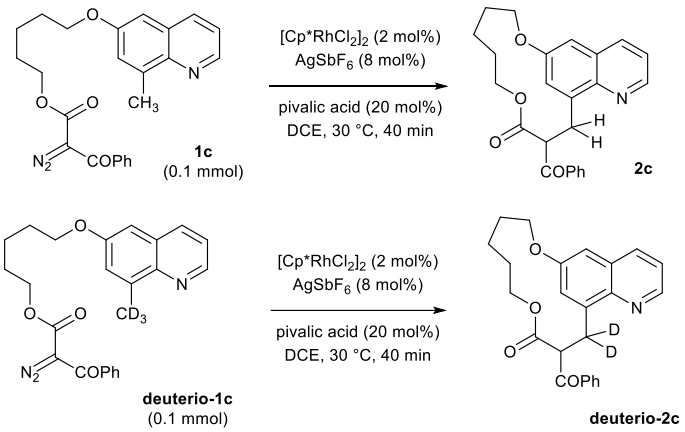


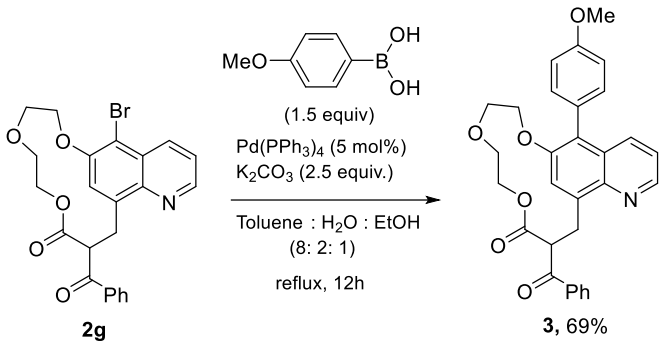
Figure S2: ^{1}H NMR of deuterio-pre macrocyclized quinoline scaffold

5.4 Determination of Kinetic Isotope Effect through parallel reactions:

The competitive macrocyclization of **1c** and **deuterio-1c** were carried out under optimized reaction conditions in parallel fashion separately. The experiments were repeated three times, and calculated KIE values found 5.78, 5.83 and 5.80. The average k_H/k_D= 5.8 was calculated based on the isolated yields.



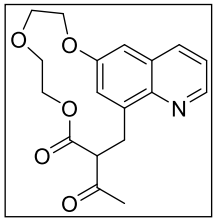
6 Procedure for the synthesis of compound 3



Compound **2g** (20 mg, 0.04 mmol), was taken in a 50 mL round bottom flask containing toluene, water and ethanol in 8:2:1 ratio. Then, K_2CO_3 (2.5 equiv.) and 4-methoxy phenylboronic acid (1.5 equiv.) was added to the reaction mixture. The reaction mixture was degassed by passing through a steady stream of argon for 30 minutes. $Pd(PPh_3)_4$ (5 mol%) was added and refluxed for 12h. After completion of the reaction, reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate as eluent to obtain pure **3.**

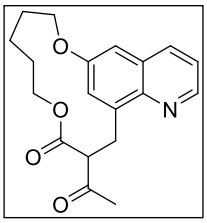
7.1 Analytical data of the products:

10-Acetyl-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (**2a**):



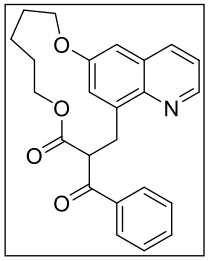
Off-white semisolid, 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.97 (t, *J* = 8.7 Hz, 1H), 7.35 – 7.33 (m, 2H), 6.92 (m, 1H), 4.33 – 4.25 (m, 3H), 4.18 – 4.06 (m, 2H), 3.94 (m, 1H), 3.78 – 3.73 (m, 2H), 3.70 – 3.64 (m, 2H), 3.48 (m, 1H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) for one conformer: 202.9, 169.6, 156.3, 147.1, 142.9, 138.4, 135.3, 129.6, 123.2, 121.6, 105.4, 69.3, 67.2, 64.1, 60.5, 30.5, 29.1; FT-IR: $\tilde{\nu}$ = 2928, 1732, 1680, 1622, 1455, 1224, 1120, 1050 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{20}NO_5^+$ $[M+H]^+$ 330.1336; found 330.1348.

10-Acetyl-2,8-dioxa-1(6,8)-quinolinacycloundecaphan-9-one (2b):



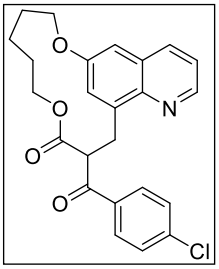
White semisolid, 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (m, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.37 (dt, *J* = 8.5, 4.4 Hz, 1H), 7.22 (m, 1H), 6.88 (dd, *J* = 21.3, 2.5 Hz, 1H), 4.34 (m, 1H), 4.18 (m, 1H), 4.09 – 3.96 (m, 3H), 3.86 (m, 1H), 3.37 (m, 1H), 2.36 (s, 3H), 1.79 – 1.68 (m, 2H), 1.62 – 1.52 (m, 2H), 1.29 – 1.17 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) for one conformer: δ 202.8, 169.9, 156.6, 147.1, 143.0, 138.4, 135.2, 129.8, 123.5, 121.6, 104.3, 67.8, 65.1, 60.7, 30.9, 29.05, 28.8, 28.6, 22.3; FT-IR: $\tilde{\nu}$ = 2926, 1730, 1684, 1616, 1450, 1170, 1055 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{22}NO_4^+$ $[M+H]^+$ 328.1543; found 328.1553.

10-Benzoyl-2,8-dioxa-1(6,8)-quinolinacycloundecaphan-9-one (2c):



White semisolid, 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (m, 1H), 8.33 – 8.27 (m, 2H), 8.03 (m, 1H), 7.58 (m, 1H), 7.53 – 7.48 (m, 2H), 7.39 (m, 1H), 7.32 (m, 1H), 6.91 (m, 1H), 5.28 (m, 1H), 4.16 – 4.02 (m, 3H), 3.97 – 3.84 (m, 2H), 3.52 (m, 1H), 1.81 – 1.74 (m, 2H), 1.63 – 1.51 (m, 2H), 1.31 – 1.19 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) for one conformer: δ 195.5, 169.9, 156.6, 147.0, 143.3, 138.6, 136.0, 135.2, 133.6, 129.8, 129.3, 128.8, 124.0, 121.6, 104.4, 67.9, 65.1, 55.8, 32.5, 28.8, 28.5, 22.2; FT-IR: $\tilde{\nu}$ = 2945, 1708, 1644, 1586, 1472, 1249, 1161, 1069 cm^{-1}; HRMS (ESI): calcd. for $C_{24}H_{24}NO_4^+$ $[M+H]^+$ 390.1700; found 390.1710.

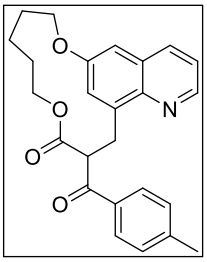
10-(4-Chlorobenzoyl)-2,8-dioxa-1(6,8)-quinolinacycloundecaphan-9-one (2d):



Brown semisolid, 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (m, 1H), 8.26 (dd, *J* = 19.7, 8.6 Hz, 2H), 8.04 (m, 1H), 7.49 – 7.36 (m, 3H), 7.33 – 7.31 (dd, *J* = 5.9, 2.5 Hz, 1H), 6.91 (m, 1H), 5.23 (m, 1H), 4.16 – 4.02 (m, 3H), 3.95 (m, 1H), 3.86 (m, 1H), 3.51 (m, 1H), 1.81 – 1.74 (m, 2H), 1.60 – 1.52 (m, 2H), 1.31 – 1.19 (m, 2H);

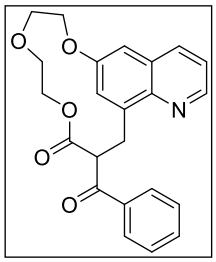
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) for one conformer: δ 194.4, 169.7, 156.7, 147.0, 143.2, 140.2, 138.4, 135.3, 134.4, 130.8, 129.8, 129.1, 128.8, 128.0, 124.2, 121.6, 104.6, 67.9, 65.2, 55.9, 32.5, 28.8, 28.6, 22.3; ; FT-IR: $\tilde{\nu}$ = 2943, 1719, 1619, 1494, 1296, 1168, 1089 cm^{-1}; HRMS (ESI): calcd. For $C_{24}H_{23}{}^{35}ClNO_4^+$ $[M+H]^+$ 424.1310; found 424.1317.

10-(4-Methylbenzoyl)-2,8-dioxa-1(6,8)-quinolinacycloundecaphan-9-one (2e):



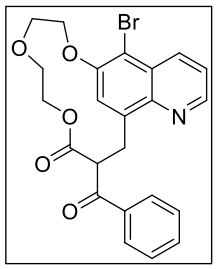
Off-white semisolid, 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (m, 1H), 8.20 (dd, *J* = 15.6, 8.2 Hz, 2H), 8.03 (dd, *J* = 7.5, 3.9 Hz, 1H), 7.40 (m, 1H), 7.32 – 7.28 (m, 3H), 6.91 (m, 1H), 5.24 (m, 1H), 4.15 – 4.01 (m, 3H), 3.96 – 3.83 (m, 2H), 3.51 (m, 1H), 2.42 (s, 3H), 1.82 – 1.74 (m, 2H), 1.61 – 1.51 (m, 2H), 1.29 – 1.23 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) for one conformer: δ 186.9, 161.2, 156.8, 153.1, 147.6, 143.6, 138.6, 137.3, 134.8, 132.3, 129.8, 128.4, 128.0, 126.5, 122.3, 118.5, 103.9, 69.8, 67.7, 65.6, 29.0, 28.7, 28.4, 22.6, 18.5; FT-IR: $\tilde{\nu}$ = 2924, 1728, 1682, 1617, 1448, 1224, 1123, 1053 cm^{-1}; HRMS (ESI): calcd. for $C_{25}H_{26}NO_4^+$ $[M+H]^+$ 404.1856; found 404.1867.

10-Benzoyl-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (2f):



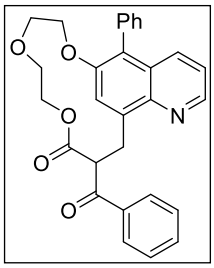
Brown semisolid, 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.32 – 8.30 (m, 2H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 2.6 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.21 (d, *J* = 2.7 Hz, 1H), 5.12 (m, 1H), 4.67 (m, 1H), 4.36 – 4.19 (m, 4H), 3.91 (m, 1H), 3.73 – 3.68 (m, 2H), 3.52 – 3.39 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) for one conformer: δ 195.3, 169.6, 156.4, 147.7, 137.6, 135.9, 133.7, 129.6, 129.4, 128.8, 123.3, 121.4, 112.9, 72.3, 69.4, 69.0, 64.1, 56.6, 32.5; FT-IR: $\tilde{\nu}$ = 2927, 1730, 1683, 1620, 1497, 1449, 1220, 1170, 1054 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{22}NO_5^+$ $[M+H]^+$ 392.1492; found 392.1510.

10-Benzoyl-15-bromo-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (2g):



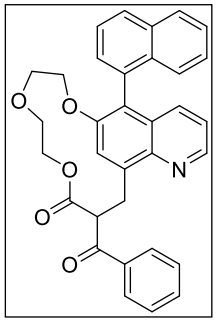
White semisolid, 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.54 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.32 – 8.30 (m, 2H), 7.88 (s, 1H), 7.61 (m, 1H), 7.54 – 7.48 (m, 3H), 5.13 (dd, *J* = 12.1, 3.3 Hz, 1H), 4.69 (dd, *J* = 13.7, 6.6 Hz, 1H), 4.43 – 4.35 (m, 2H), 4.24 – 4.15 (m, 2H), 3.97 (m, 1H), 3.76 – 3.70 (m, 2H), 3.50 – 3.42 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) for one conformer: δ 195.2, 169.4, 153.3, 148.2, 143.8, 136.9, 135.8, 135.2, 133.8, 129.3, 128.8, 128.7, 124.2, 122.3, 108.5, 72.2, 70.0, 68.8, 64.0, 56.5, 32.3; FT-IR: $\tilde{\nu}$ = 2919, 1716, 1629, 1493, 1377, 1319, 1263, 1132, 1083 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{21}{}^{79}BrNO_5^+$ $[M+H]^+$ 470.0598; found 470.0594.

10-Benzoyl-15-phenyl-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (2h):



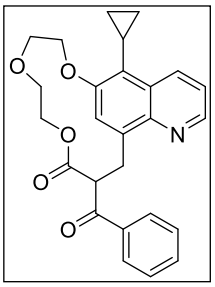
White solid, 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.83 (m, 1H), 8.38 (d, *J* = 8.2 Hz, 2H), 7.92 – 7.87 (m, 2H), 7.62 (t, *J* = 6.9 Hz, 1H), 7.56 – 7.48 (m, 4H), 7.45 – 7.41 (t, *J* = 7.1 Hz, 1H), 7.37 (d, *J* = 4.5 Hz, 2H), 7.29 (m, 1H), 5.23 (m, 1H), 4.48 – 4.37 (m, 2H), 4.30 (dd, *J* = 13.0, 2.9 Hz, 1H), 4.23 (m, 1H), 3.94 (dd, *J* = 13.7, 5.2 Hz, 1H), 3.83 (dd, *J* = 12.1, 5.2 Hz, 1H), 3.73 (m, 1H), 3.60 – 3.44 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) for one conformer: δ 195.5, 169.9, 153.5, 147.5, 143.3, 137.2, 136.0, 134.3, 133.7, 129.4, 128.8, 128.5, 128.2, 126.2, 125.8, 125.5, 124.0, 123.2, 121.2, 72.3, 68.9, 68.3, 64.2, 56.7, 32.7; FT-IR: $\widetilde{\nu}$ = 2950, 1720, 1680, 1592, 1498, 1449, 1311, 1232, 1133 cm^{-1}; HRMS (ESI): calcd. for $C_{29}H_{26}NO_5^+$ $[M+H]^+$ 468.1805; found 468.1824.

10-Benzoyl-15-(naphthalen-1-yl)-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (2i):



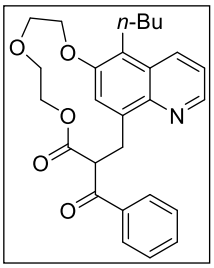
White solid, 78%; m.p. 178-180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (m, 1H), 8.40 – 8.37 (m, 2H), 7.93 – 8.00 (m, 3H), 7.65 – 7.60 (m, 2H), 7.56 – 7.42 (m, 5H), 7.34 – 7.31 (m, 2H), 7.17 (m, 1H), 5.27 (m, 1H), 4.49 – 4.45 (m, 2H), 4.38 – 4.23 (m, 2H), 3.90 – 3.67 (m, 5H), 3.46 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) for one conformer: δ 195.4, 169.8, 153.7, 147.3, 136.0, 133.9, 133.7, 133.0, 129.5, 128.9, 128.8, 128.5, 128.3, 126.3, 126.2, 126.0, 125.8, 125.5, 124.0, 123.5, 121.2, 72.3, 69.2, 68.5, 64.2, 56.7, 32.7; FT-IR: $\widetilde{\nu}$ = 2955, 1729, 1682, 1596, 1499, 1449, 1399, 1235, 1133 cm^{-1}; HRMS (ESI): calcd. for $C_{33}H_{28}NO_5^+$ $[M+H]^+$ 518.1962; found 518.1988.

10-Benzoyl-15-cyclopropyl-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (2j):



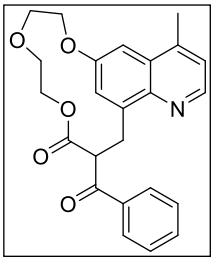
Off-white semisolid, 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.77 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.35 – 8.33 (m, 2H), 7.71 (s, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42 (dd, *J* = 8.6, 4.1 Hz, 1H), 5.19 (dd, *J* = 12.1, 3.2 Hz, 1H), 4.56 (dd, *J* = 13.5, 6.1 Hz, 1H), 4.41 (m, 1H), 4.29 (dd, *J* = 13.6, 6.0 Hz, 1H), 4.22 – 4.14 (m, 2H), 3.91 (dd, *J* = 11.9, 6.0 Hz, 1H), 3.74 (m, 1H), 3.67 (m, 1H), 3.48 – 3.41 (m, 2H), 1.88 (m, 1H), 1.20 – 1.12 (m, 2H), 0.94 (m, 1H), 0.59 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.7, 169.8, 155.6, 147.3, 143.7, 135.8, 133.7, 130.4, 129.4, 128.8, 125.5, 124.0, 120.7, 72.3, 70.3, 68.9, 64.1, 56.6, 32.4, 8.4, 7.7, 7.1; FT-IR: $\widetilde{\nu}$ = 2954, 1723, 1680, 1568, 1490, 1442, 1220, 1128, 1050 cm^{-1}; HRMS (ESI): calcd. for $C_{26}H_{26}NO_5^+$ $[M+H]^+$ 432.1805; found 432.1817.

10-Benzoyl-15-butyl-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (2k):



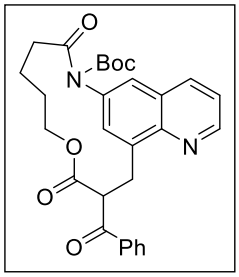
Off-white liquid, 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.37 – 8.35 (m, 2H), 8.29 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.85 (s, 1H), 7.60 – 7.58 (m, 1H), 7.54 – 7.50 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.40 (dd, *J* = 8.6, 4.1 Hz, 1H), 5.15 (dd, *J* = 12.1, 3.3 Hz, 1H), 4.68 (dd, *J* = 13.8, 7.0 Hz, 1H), 4.46 – 4.42 (m, 1H), 4.27 – 4.16 (m, 3H), 3.96 (dd, *J* = 12.5, 4.2 Hz, 1H), 3.73 – 3.65 (m, 2H), 3.49 – 3.30 (m, 2H), 3.01 (t, *J* = 7.8 Hz, 2H), 1.60 – 1.55 (m, 2H), 1.45 (dd, *J* = 14.7, 7.3 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.6, 169.7, 152.9, 146.9, 143.4, 135.8, 134.7, 133.7, 132.3, 129.4, 128.8, 128.2, 124.5, 122.8, 120.8, 72.5, 68.8, 63.9, 56.8, 32.8, 32.5, 27.1, 24.6, 23.1, 14.1; FT-IR: $\widetilde{\nu}$ = 2955, 1729, 1681, 1594, 1503, 1449, 1230, 1120, 1054 cm^{-1}; HRMS (ESI): calcd. for $C_{27}H_{30}NO_5^+$ $[M+H]^+$ 448.2118; found 448.2127.

10-Benzoyl-14-methyl-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (2l):



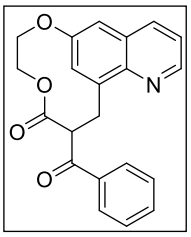
Off-white semisolid, 78%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.4 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 2.8 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 2.7 Hz, 1H), 7.21 (d, *J* = 4.3 Hz, 1H), 5.13 (dd, *J* = 12.1, 3.5 Hz, 1H), 4.69 (dd, *J* = 13.9, 7.3 Hz, 1H), 4.38 – 4.28 (m, 2H), 4.24 – 4.18 (m, 2H), 3.94 – 3.90 (m, 1H), 3.74 – 3.70 (m, 2H), 3.51 – 3.39 (m, 2H), 2.64 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.37, 169.69, 156.18, 147.26, 138.03, 136.01, 133.66, 129.70, 129.42, 128.83, 122.75, 122.16, 109.45, 72.42, 69.29, 69.03, 64.09, 56.84, 32.91, 19.15; FT-IR: $\widetilde{\nu}$ = 2924, 1729, 1682, 1617, 1508, 1448, 1220, 1165, 1053 cm^{-1}; HRMS (ESI): calcd. for $C_{24}H_{24}NO_5^+$ $[M+H]^+$ 406.1649; found 406.1663.

***tert*-Butyl 10-benzoyl-3,9-dioxo-8-oxa-2-aza-1(6,8)-quinolinacycloundecaphane-2-carboxylate (2m):**



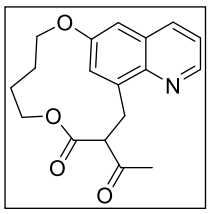
Colourless oil, 40%; for one conformer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.2 Hz, 1H), 8.23 (t, *J* = 8.1 Hz, 2H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.35 (s, 1H), 5.27 (m, 1H), 4.21 – 4.08 (m, 1H), 4.08 – 3.95 (m, 1H), 3.93 – 3.77 (m, 1H), 3.65 – 3.50 (m, 1H), 3.04 – 2.74 (m, 2H), 1.57 – 1.46 (m, 4H), 1.36 (s, 9H).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.06, 175.44, 169.64, 152.98, 149.90, 137.88, 136.90, 136.16, 133.61, 131.83, 129.24, 129.03, 128.80, 128.63, 127.39, 126.18, 121.54, 83.49, 66.45, 56.71, 37.48, 32.06, 28.07, 27.97, 21.44. FT-IR: $\widetilde{\nu}$ = 2979, 2924, 1729, 1686, 1585, 1365, 1245, 1150, 1092. HRMS (ESI): calcd. for $C_{29}H_{31}N_2O_6^+$ $[M+H]^+$ 503.2177; found 503.2162.

12-Benzoyl-8,9,12,13-tetrahydro-11*H*-6,14-(metheno)[1,4]dioxacyclododecino[8,7-b]pyridin-11-one (2n):



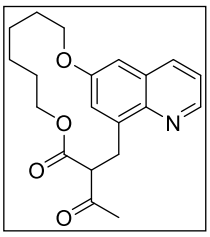
Off-white semisolid, 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.45 (d, *J* = 7.4 Hz, 2H), 8.18 (d, *J* = 2.6 Hz, 1H), 8.12 – 8.09 (m, 1H), 7.65 – 7.61 (m, 1H), 7.57 – 7.52 (m, 2H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.00 (d, *J* = 2.6 Hz, 1H), 5.16 (dd, *J* = 12.2, 3.0 Hz, 1H), 4.63 – 4.49 (m, 2H), 4.34 – 4.21 (m, 3H), 3.57 – 3.47 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) for one conformer: δ 195.4, 169.6, 156.8, 147.3, 138.7, 135.8, 135.5, 133.8, 129.8, 129.7, 128.9, 128.8, 124.7, 121.6, 104.1, 65.0, 64.3, 57.7, 32.0; FT-IR: $\widetilde{\nu}$ = 2930, 1733, 1619, 1494, 1441, 1377, 1220, 1170, 1050 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{18}NO_4^+$ $[M+H]^+$ 348.1230; found 348.1246.

9-Acetyl-2,7-dioxa-1(6,8)-quinolinacyclodecaphan-8-one (2o):

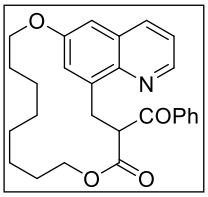


Off-white liquid, 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (m, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.35 (dd, *J* = 8.1, 4.1 Hz, 1H), 7.22 (m, 1H), 6.93 (dd, *J* = 19.6, 2.7 Hz, 1H), 4.36 (m, 1H), 4.20 (m, 1H), 4.07 – 3.86 (m, 4H), 3.40 (m, 1H), 2.39 (s, 3H), 1.74 – 1.58 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) for one conformer: δ 202.6, 169.9, 156.6, 147.2, 143.1, 138.5, 135.1, 129.7, 123.0, 121.6, 105.5, 67.7, 65.0, 61.0, 31.0, 28.9, 26.0, 25.6; FT-IR: $\widetilde{\nu}$ = 2954, 1714, 1620, 1504, 1436, 1379, 1220, 1170, 1048 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{20}NO_4^+$ $[M+H]^+$ 314.1387; found 314.1393.

11-Acetyl-2,9-dioxa-1(6,8)-quinolinacyclododecaphan-10-one (2p):

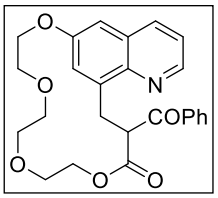


Off-white semisolid, 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (m, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.35 (dd, *J* = 8.1, 4.1 Hz, 1H), 7.25 (m, 1H), 6.94 (dd, *J* = 6.0, 2.7 Hz, 1H), 4.35 (m, 1H), 4.12 (m, 1H), 4.06 – 3.94 (m, 4H), 3.36 (m, 1H), 2.36 (s, 3H), 1.77 – 1.74 (m, 2H), 1.52 – 1.41 (m, 4H), 1.25 – 1.19 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) for one conformer: δ 202.8, 169.9, 156.7, 147.0, 142.9, 138.4, 135.2, 129.7, 123.1, 121.5, 105.1, 68.2, 65.1, 60.8, 30.9, 29.2, 29.0, 28.6, 25.9, 25.8; FT-IR: $\widetilde{\nu}$ = 2939, 1714, 1620, 1495, 1439, 1376, 1221, 1170, 1048 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{24}NO_4^+$ $[M+H]^+$ 342.1700; found 342.1716.



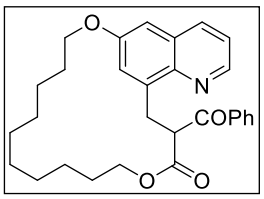
13-Benzoyl-2,11-dioxa-1(6,8)-quinolinacyclotetradecaphan-12-one (**2q**): Grey semisolid, 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.33 (d, *J* = 7.2 Hz, 2H), 8.03 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.36 (m, 2H), 6.98 (d, *J* = 2.7 Hz, 1H), 5.11 (dd, *J* = 11.9, 2.9 Hz, 1H), 4.27 – 4.14 (m, 4H), 3.88 (m, 1H), 3.51 (m, 1H), 1.93 (m, 1H), 1.80 – 1.66 (m, 2H), 1.46 – 1.31 (m, 5H), 1.30 – 1.16 (m, 4H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.4, 169.9, 156.7, 147.0, 143.2, 138.6, 136.0, 135.2, 133.6, 129.9, 129.4, 128.7, 124.3, 121.5, 105.3, 67.7, 65.4, 56.0, 32.0, 28.2, 27.1, 26.1, 24.6, 24.2; HRMS (ESI): calcd. for $C_{27}H_{30}NO_4^+$ $[M+H]^+$ 432.2169; found 432.2185.

13-Benzoyl-2,5,8,11-tetraoxa-1(6,8)-quinolinacyclotetradecaphan-12-one (2r):



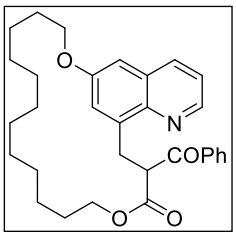
White semisolid, 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, 1H), 8.33 (d, *J* = 7.4 Hz, 2H), 8.03 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.61 (m, 1H), 7.53 – 7.50 (m, 3H), 7.38 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.25 (s, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 5.25 (dd, *J* = 12.0, 2.9 Hz, 1H), 4.37 – 4.36 (m, 2H), 4.28 (m, 1H), 4.15 – 4.04 (m, 2H), 3.89 – 3.83 (m, 3H), 3.71 (m, 1H), 3.64 (m, 1H), 3.59 – 3.52 (m, 4H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.5, 169.8, 156.8, 147.3, 143.3, 138.4, 135.8, 135.4, 133.7, 129.6, 129.4, 128.8, 124.4, 121.5, 108.1, 71.6, 70.5, 69.5, 69.3, 69.0, 64.2, 55.9, 32.1; FT-IR: $\widetilde{\nu}$ = 2931, 1717, 1657, 1620, 1497, 1313, 1252, 1161, 1076 cm^{-1}; HRMS (ESI): calcd. for $C_{25}H_{26}NO_6^+$ $[M+H]^+$ 436.1755; found 436.1773.

15-Benzoyl-2,13-dioxa-1(6,8)-quinolinacyclohexadecaphan-14-one (2s):



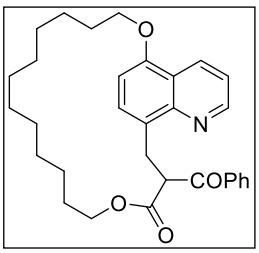
Off-white semisolid, 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.31 (d, *J* = 7.5 Hz, 2H), 8.03 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.32 (d, *J* = 2.6 Hz, 1H), 6.95 (d, *J* = 2.7 Hz, 1H), 5.20 (dd, *J* = 11.9, 3.0 Hz, 1H), 4.13 – 4.08 (m, 3H), 4.04 (m, 1H), 3.92 (m, 1H), 3.52 (m, 1H), 1.88 (m, 1H), 1.77 (m, 1H), 1.64 (m, 1H), 1.57 – 1.49 (m, 2H), 1.47 – 1.37 (m, 6H), 1.31 – 1.21 (m, 5H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.4, 169.8, 156.9, 146.8, 143.2, 138.6, 136.0, 135.2, 133.5, 129.9, 129.4, 128.7, 123.9, 121.4, 104.5, 67.1, 65.5, 56.0, 32.1, 28.2, 28.0, 27.6, 27.2, 27.1, 26.5, 24.7, 24.0; FT-IR: $\widetilde{\nu}$ = 2929, 1732, 1683, 1620, 1439, 1338, 1243, 1171 cm^{-1}; HRMS (ESI): calcd. for $C_{29}H_{34}NO_4^+$ $[M+H]^+$ 460.2482; found 460.2504.

7-Benzoyl-2,15-dioxa-1(6,8)-quinolinacyclooctadecaphan-16-one (2t):



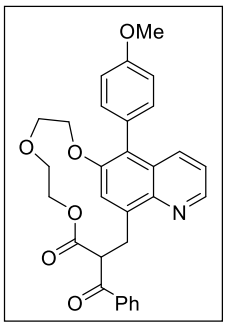
White semisolid, 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.2 Hz, 1H), 8.29 (d, *J* = 7.4 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.36 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 6.95 (d, *J* = 2.6 Hz, 1H), 5.18 (dd, *J* = 11.6, 3.2 Hz,1H), 4.15 – 4.07 (m, 3H), 4.04 – 3.91 (m, 2H), 3.50 (m, 1H), 1.87 – 1.77 (m, 2H), 1.52 – 1.54 (m, 6H), 1.42 – 1.39 (m, 2H), 1.35 – 1.25 (m, 10H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ195.4, 169.8, 157.0, 146.8, 140.4, 136.1, 133.5, 129.3, 128.7, 123.7, 121.4, 104.9, 67.9, 65.4, 56.1, 32.2, 28.6, 28.2, 27.9, 27.8, 27.3, 27.2, 26.7, 24.9; FT-IR: $\widetilde{\nu}$ = 2928, 1729, 1642, 1592, 1463, 1395, 1267, 1154, 1080 cm^{-1}; FT-IR: $\widetilde{\nu}$ = 2924, 1722, 1628, 1591, 1467, 1389, 1294, 1164, 1084 cm^{-1}; HRMS (ESI): calcd. for $C_{31}H_{38}NO_4^+$ $[M+H]^+$ 488.2795; found 488.2845.

17-Benzoyl-2,15-dioxa-1(5,8)-quinolinacyclooctadecaphan-16-one (2u):



Grey semisolid, 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.63 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.36 – 8.34 (m, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.42 (dd, *J* = 8.4, 4.1 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.31 (dd, *J* = 11.8, 3.2 Hz, 1H), 4.18 – 4.16 (m, 2H), 4.03 – 3.95 (m, 2H), 3.71 (m, 1H), 3.47 (m, 1H), 2.08 (m, 1H), 1.81 – 1.74 (m, 2H), 1.50 (m, 1H), 1.42 – 1.29 (m, 5H), 1.27 – 1.20 (m, 4H), 1.10 – 0.91 (m, 7H), 0.71 – 0.63 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 170.3, 153.9, 149.7, 147.6, 136.2, 133.5, 131.3, 130.8, 129.3, 128.7, 128.0, 121.3, 120.0, 104.3, 66.8, 64.9, 55.7, 32.7, 28.9, 28.5, 28.4, 28.0, 27.8, 27.5, 27.3, 26.1, 25.1, 23.9; HRMS (ESI): calcd. for $C_{31}H_{38}NO_4^+$ $[M+H]^+$ 488.2795; found 488.2763.

10-Benzoyl-15-(4-methoxyphenyl)-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (3):



Colourless oil, 69%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.35 (d, *J* = 7.5 Hz, 1H), 8.30 (d, *J* = 7.4 Hz, 1H), 8.02 – 7.79 (m, 2H), 7.60 (m, 1H), 7.54 – 7.49 (m, 2H), 7.36 – 7.20 (m, 4H), 7.05 (d, *J* = 7.1 Hz, 2H), 5.19 (m, 1H), 4.68 (m, 1H), 4.43 (m, 1H), 4.30 (m, 1H), 4.26 – 4.14 (m, 2H), 3.96 (m, 1H), 3.90 (s, 2H), 3.71 (m, 2H), 3.60–3.56 (m, 2H), 3.51–3.33 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) for one conformer: δ 195.29, 169.66, 159.20, 135.96, 133.71, 132.39, 132.16, 129.49, 129.39, 128.85, 125.90, 121.42, 121.00, 114.15, 113.97, 112.96, 72.21, 69.37, 68.88, 64.12, 56.62, 55.45, 32.42. FT-IR: $\tilde{\nu}$ = 2927, 2859, 1733, 1690, 1596, 1519, 1450, 1245, 1133; HRMS (ESI): calcd. for $C_{29}H_{31}N_2O_6^+$ $[M+H]^+$ 498.1911; found 498.1896.

References:

1 C. O'Murchu, *Synthesis*, 1989, **11**, 880.

2 T. Lan, X. X. Yuan, J. H. Yu, C. Jia, Y. S. Wang, H. J. Zhang, Z. F. Ma and W. D. Ye, *Chin Chem Lett*. 2011, **22**, 253.

3 S. Kim, S. Han, J. Park, S. Sharma, N. K. Mishra, H. Oh, J. H. Kwak and I. S. Kim, *Chem. Commun.*, 2017, **53**, 3006.

7.2 Table S3: Crystal data and structure refinement for 10-benzoyl-15-(naphthalen-1-yl)-2,5,8-trioxa-1(6,8)-quinolinacycloundecaphan-9-one (**2i**, **CCDC: 2004156**):

Bond precision: C-C = 0.0048 A Wavelength=0.71073

Cell: a=8.649(4) b=11.578(5) c=13.602(7)
alpha=89.58(5) beta=77.17(3) gamma=77.71(4)
Temperature: 296 K

	Calculated	Reported
Volume	1296.5(11)	1296.5(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C33 H27 N O5	C33 H27 N O5
Sum formula	C33 H27 N O5	C33 H27 N O5
Mr	517.56	517.55
Dx,g cm-3	1.326	1.326
Z	2	2
Mu (mm-1)	0.089	0.089
F000	544.0	544.0
F000'	544.26	
h,k,lmax	14,19,22	14,19,22
Nref	12789	10966
Tmin,Tmax	0.975,0.982	0.975,0.982
Tmin'	0.975	

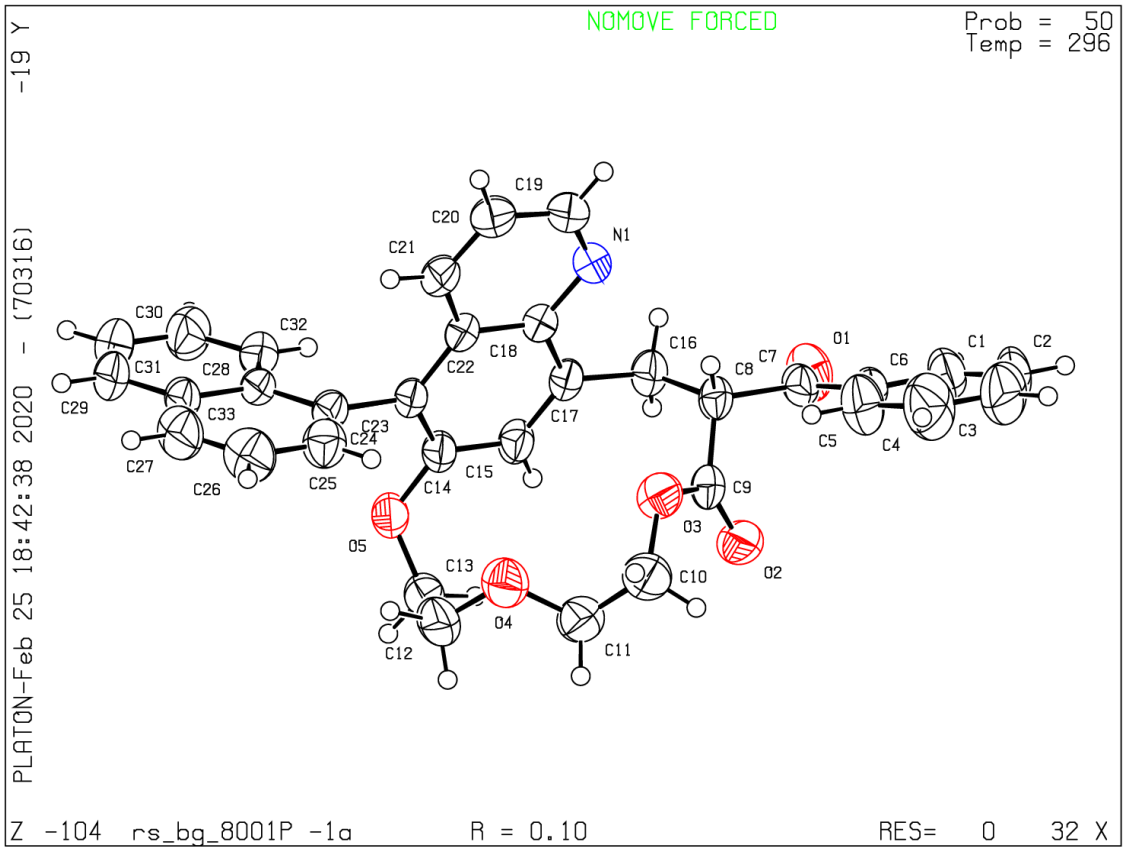
Correction method= # Reported T Limits: Tmin=0.975 Tmax=0.982
AbsCorr = MULTI-SCAN

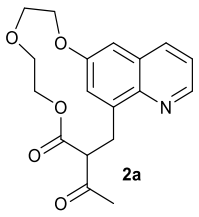
Data completeness= 0.857 Theta(max)= 36.547

R(reflections)= 0.0993(3722) wR2(reflections)= 0.3292(10966)

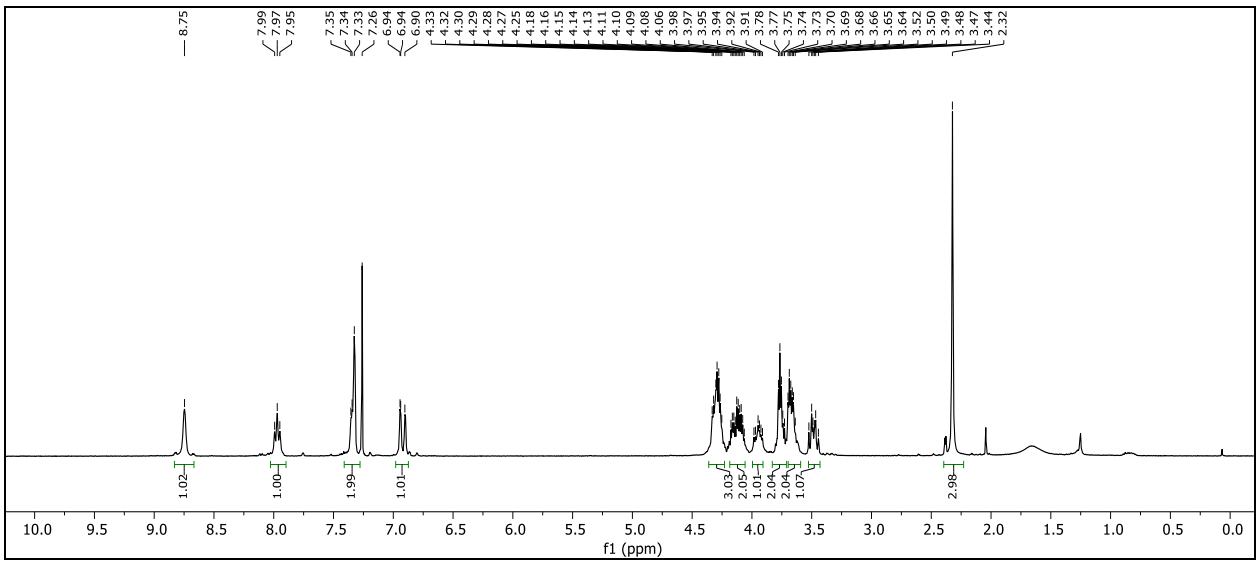
S = 0.911 Npar= 353

Figure S3: ORTEP-representation of the crystal structure of compound **2i**. Colour code: N, blue; O, red; C, light grey; H, white. Ellipsoid probability level 50%




O
O
O
O
O
N
O

2a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7.34
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4.27
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4.15
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4.09
4.08
4.06
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3.94
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3.50
3.49
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3.47
3.44
2.32
1.02
1.00
1.99
1.01
3.03
2.05
1.01
2.04
2.04
1.07
2.98
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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4.5
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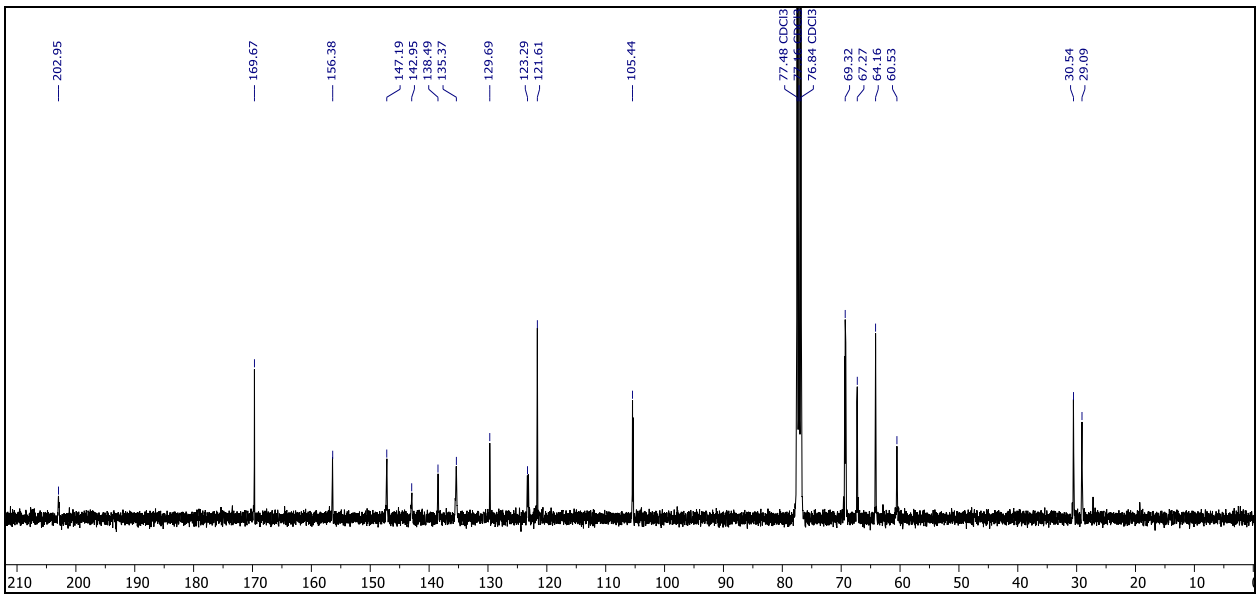
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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138.49
135.37
129.69
123.29
121.61
105.44
77.48 CDCl3
76.84 CDCl3
69.32
67.27
64.16
60.53
30.54
29.09
210
200
190
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170
160
150
140
130
120
110
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90
80
70
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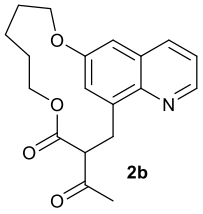
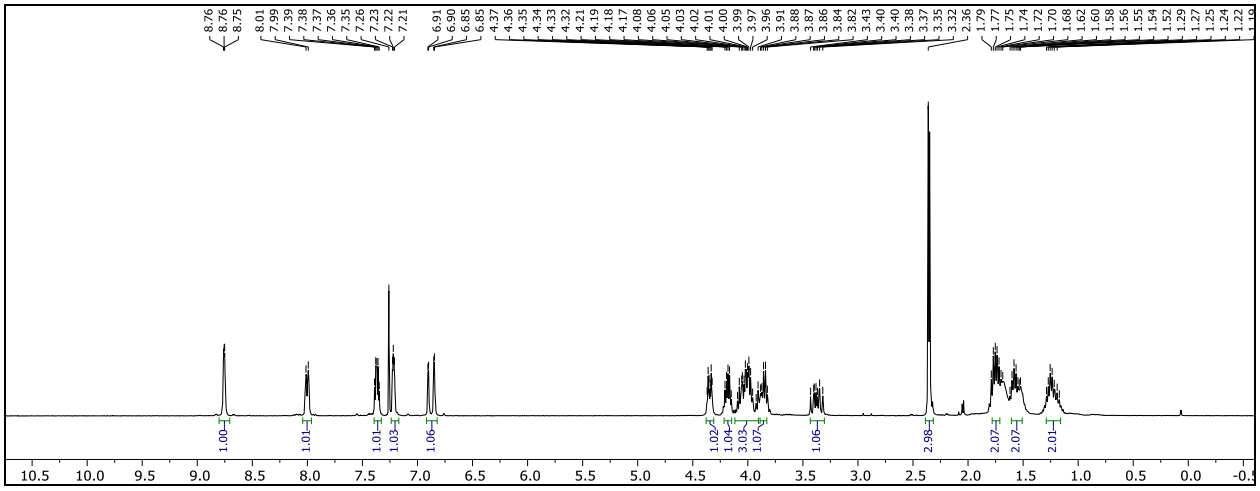
30
20
10


O
O
N
O
O
O

2b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1.02
1.04
3.03
1.07
1.06
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2.07
2.07
2.01
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9.0
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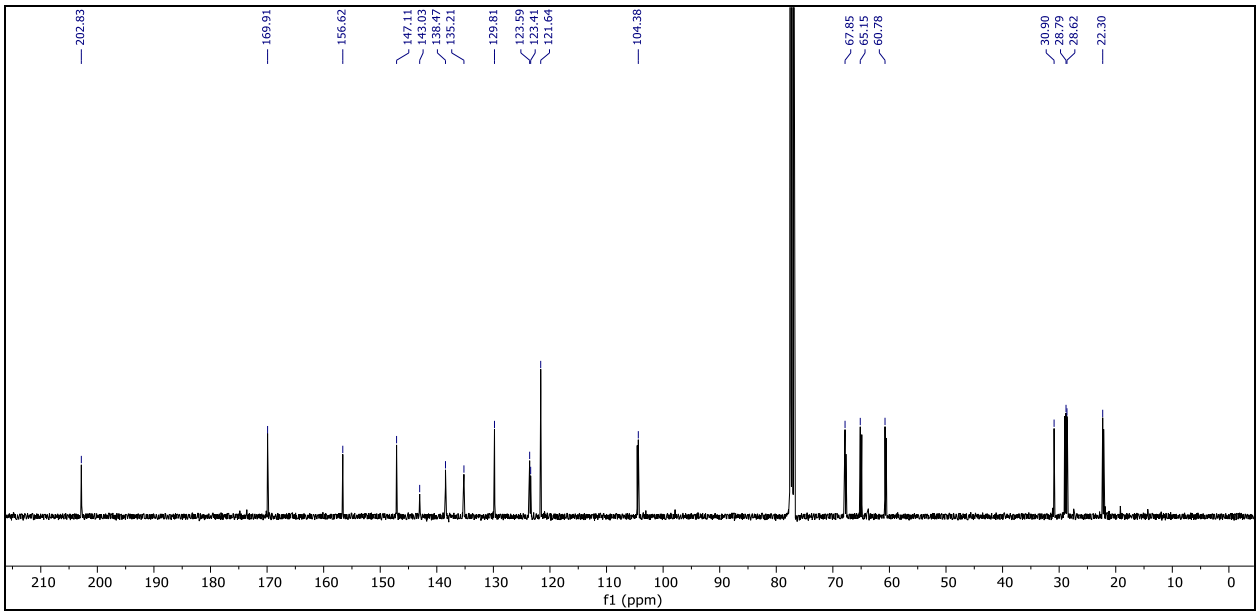
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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129.81
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123.41
121.64
104.38
67.85
65.15
60.78
30.90
28.79
28.62
22.30
210
200
190
180
170
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110
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90
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50
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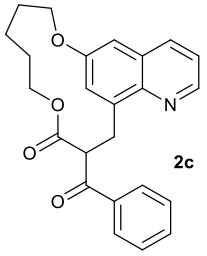
10
0
f1 (ppm)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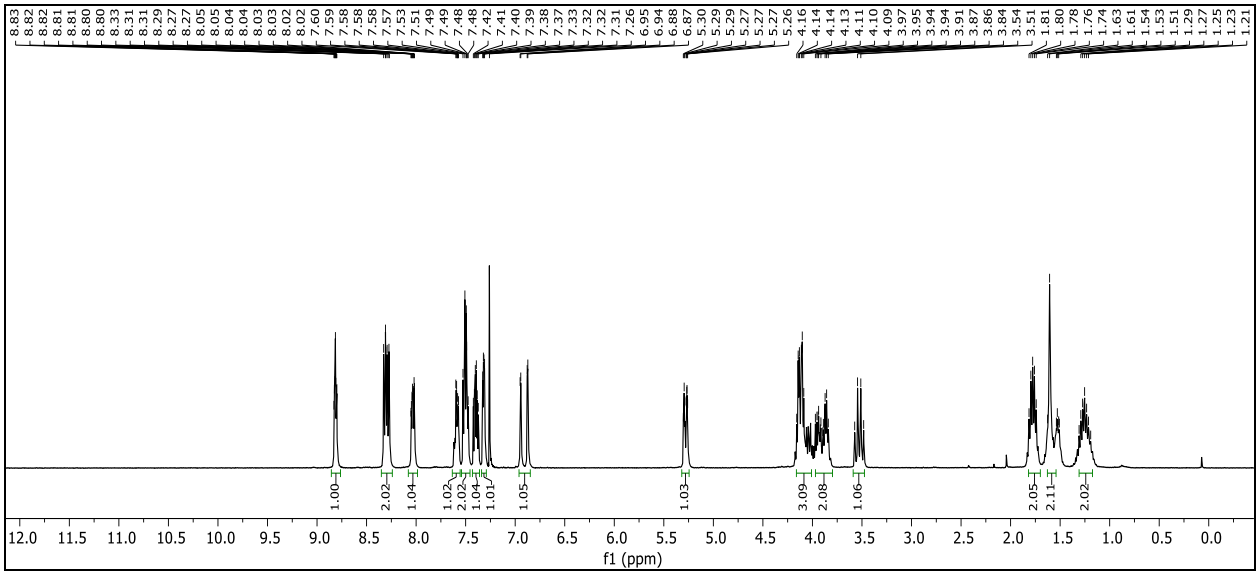
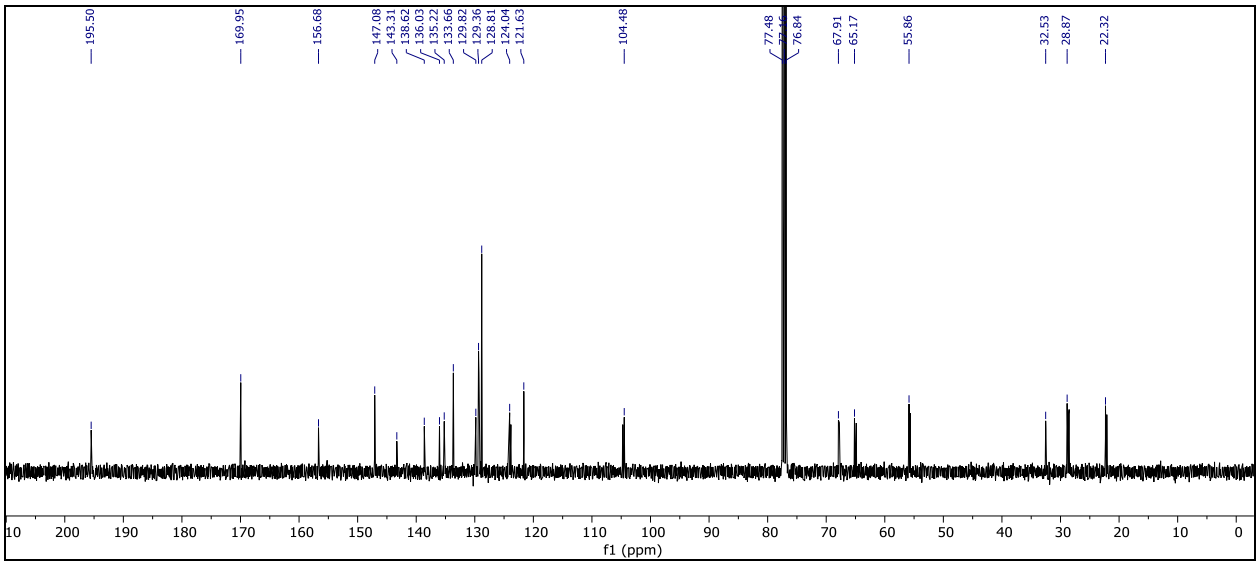
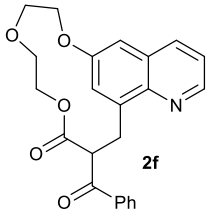
O
O

2c


8.83 8.82 8.82 8.81 8.81 8.80 8.80 8.33 8.31 8.31 8.29 8.27 8.27 8.05 8.05 8.04 8.04 8.03 8.03 8.02 8.02 7.60 7.59 7.58 7.58 7.58 7.57 7.53 7.51 7.49 7.49 7.48 7.48 7.42 7.41 7.40 7.39 7.38 7.37 7.33 7.32 7.31 7.26 6.95 6.94 6.88 6.87 5.30 5.29 5.29 5.27 5.27 5.27 5.26 4.16 4.14 4.14 4.13 4.11 4.10 4.09 3.97 3.95 3.94 3.94 3.91 3.87 3.86 3.84 3.54 3.51 1.81 1.80 1.78 1.76 1.74 1.63 1.61 1.54 1.53 1.51 1.29 1.27 1.25 1.23 1.21
1.00 2.02 1.04 1.02 2.02 1.04 1.01 1.05 1.03 3.09 2.08 1.06 2.05 2.11 2.02
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
f1 (ppm)


195.50 169.95 156.68 147.08 143.31 138.62 136.03 135.22 133.66 129.82 129.36 128.81 124.04 121.63 104.48 77.48 76.84 67.91 65.17 55.86 32.53 28.87 22.32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
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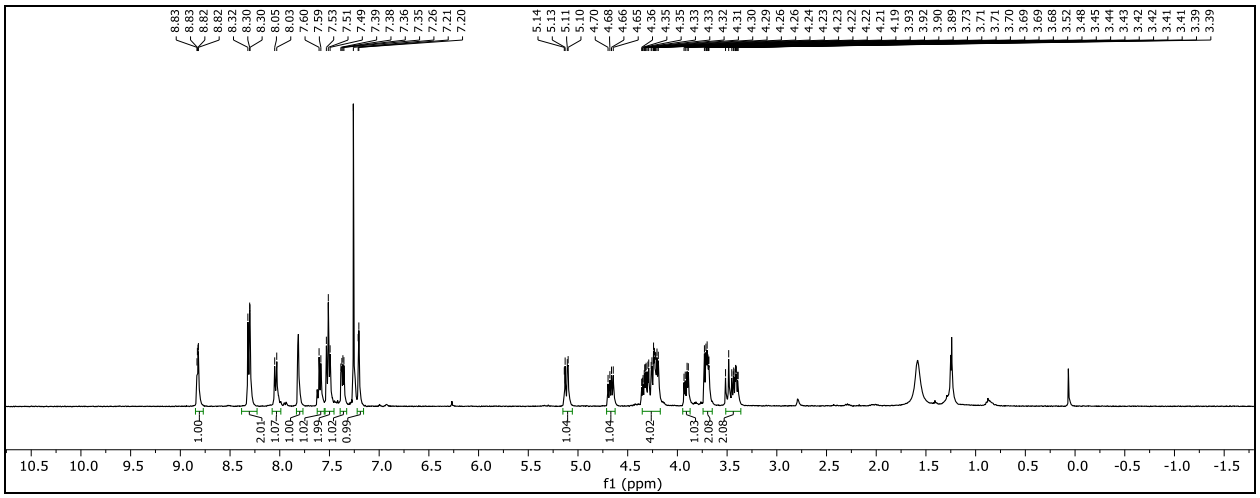
N
O
O
Ph

2f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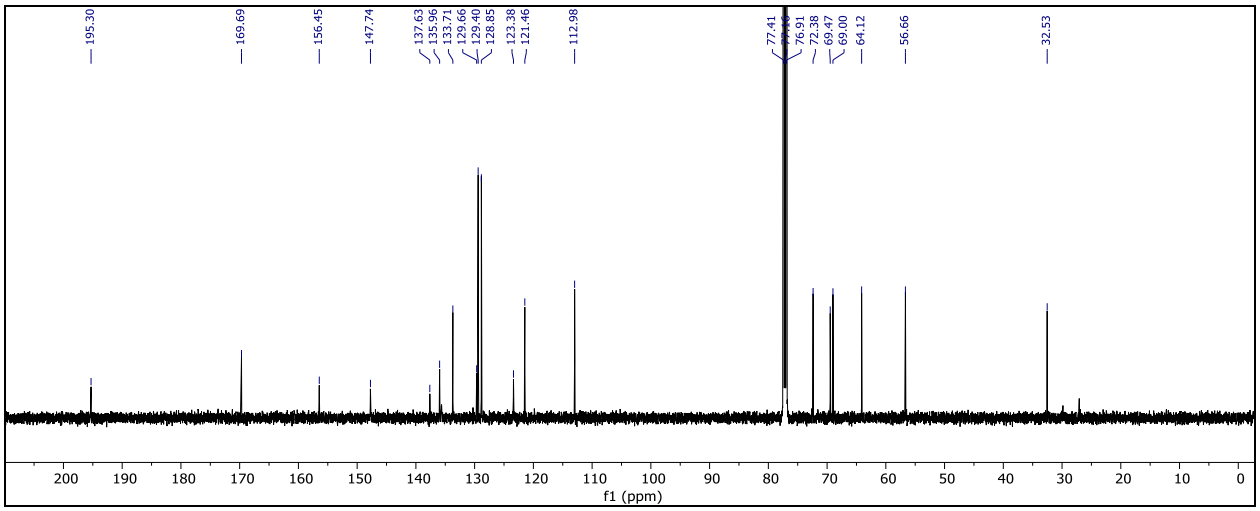
8.83
8.82
8.82
8.32
8.30
8.30
8.05
8.03
7.60
7.59
7.53
7.51
7.49
7.39
7.38
7.36
7.35
7.26
7.21
7.20
5.14
5.13
5.11
5.10
4.70
4.68
4.66
4.65
4.36
4.35
4.35
4.33
4.33
4.32
4.31
4.30
4.29
4.26
4.26
4.24
4.23
4.23
4.22
4.22
4.21
4.19
3.93
3.92
3.90
3.89
3.73
3.71
3.71
3.70
3.69
3.69
3.68
3.52
3.48
3.45
3.44
3.43
3.42
3.42
3.41
3.41
3.39
3.39
1.00
2.01
1.07
1.00
1.02
1.99
1.02
0.99
1.04
1.04
4.02
1.03
2.08
2.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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135.96
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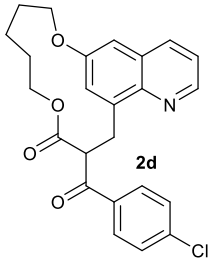
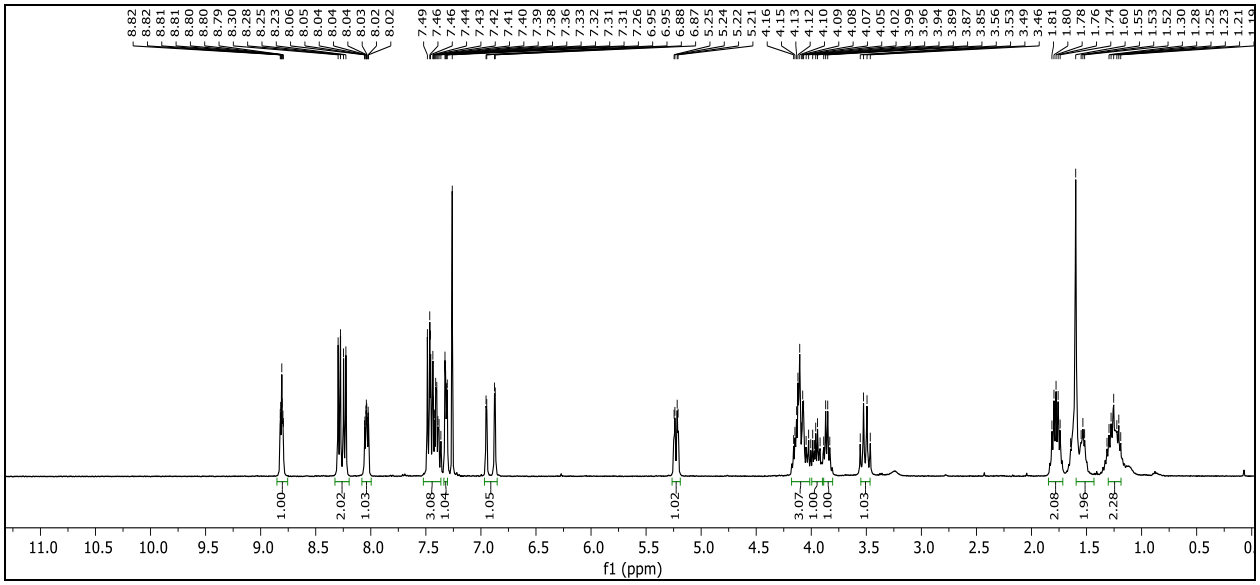
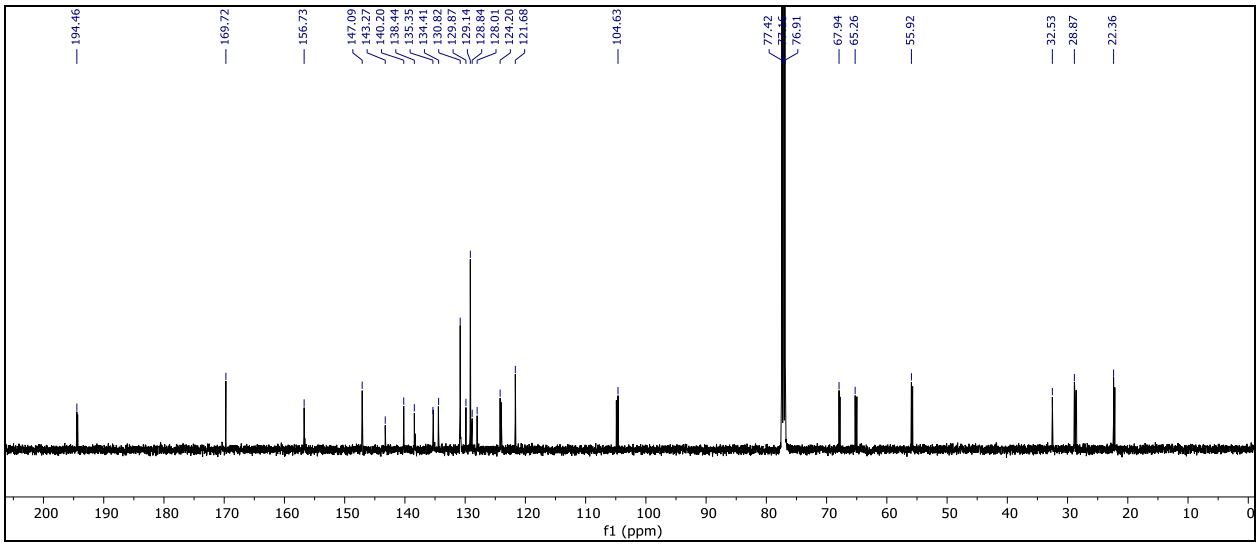
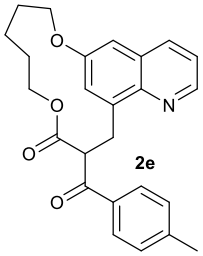
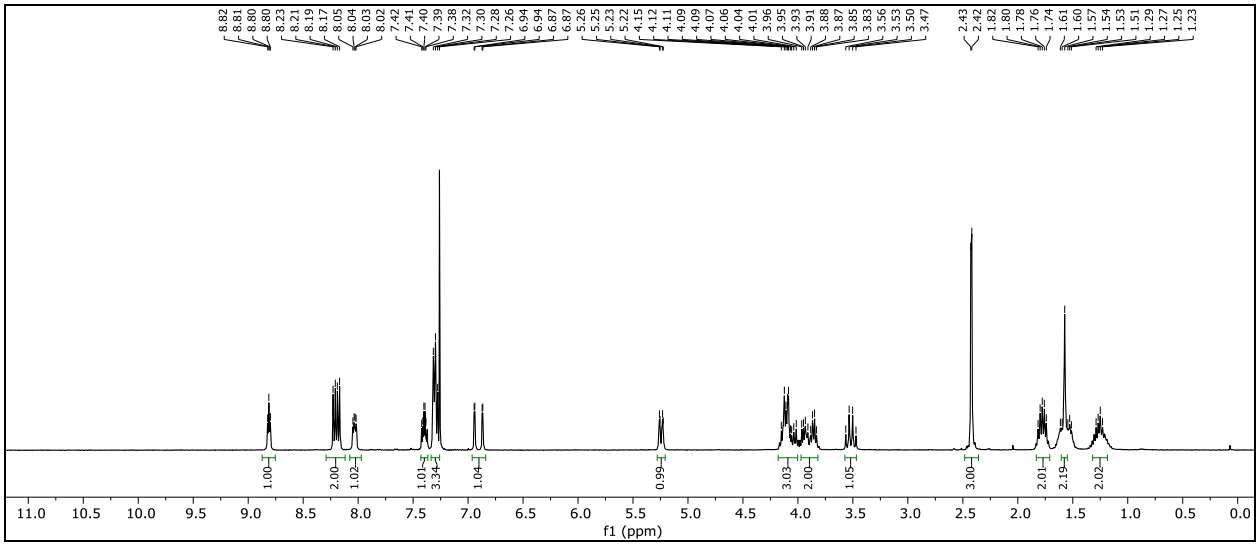
129.66
129.40
128.85
123.38
121.46
112.98
77.41
76.91
72.38
69.47
69.00
64.12
56.66
32.53
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
N
O
O
2d
Cl


f1 (ppm)


f1 (ppm)


O
O
N
O
O
2e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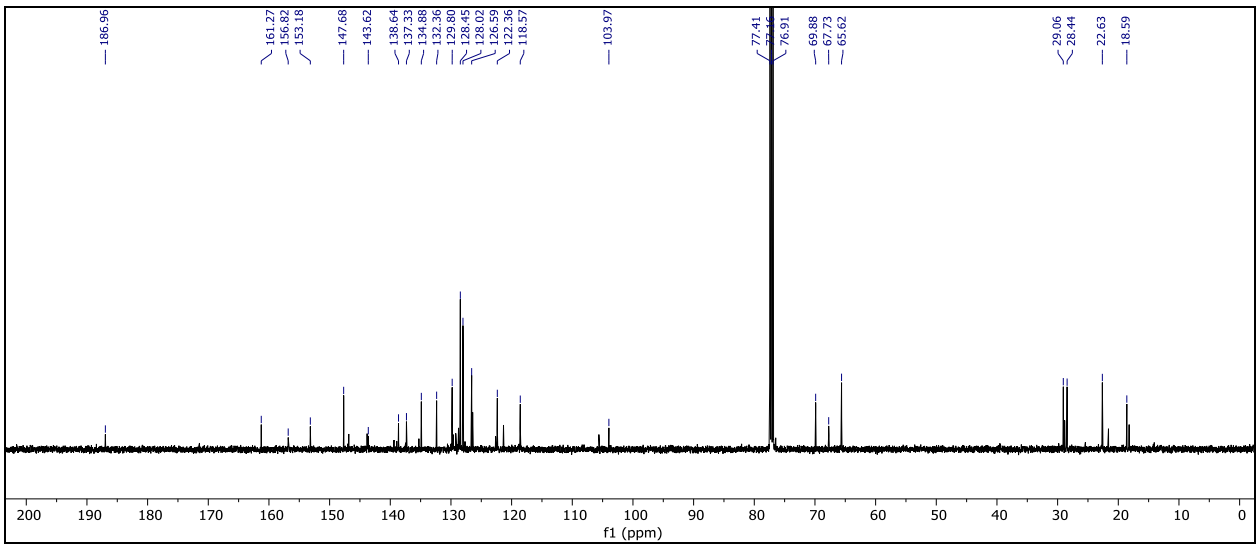
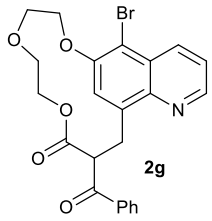
1.00 2.00 1.02 1.01 3.34 1.04 0.99 3.03 2.00 1.05 3.00 2.01 2.19 2.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


186.96
161.27 156.82 153.18 147.68 143.62 138.64 137.33 134.88 132.36 129.80 128.45 128.02 126.59 122.36 118.57 103.97 77.41 77.16 76.91 69.88 67.73 65.62 29.06 28.44 22.63 18.59
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
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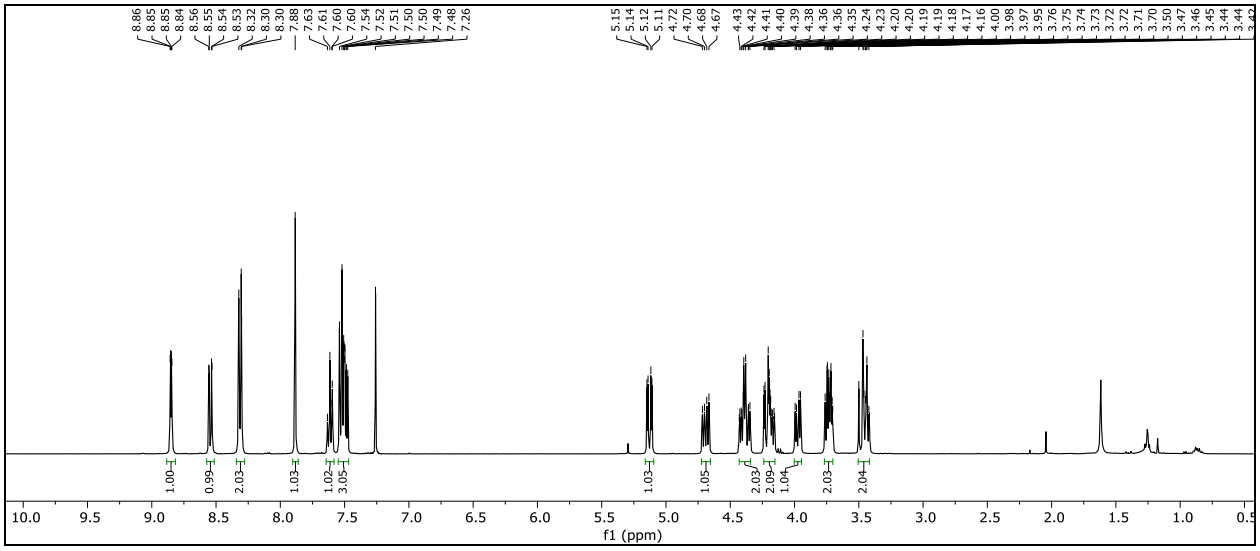
O
O
O
N
O
Ph

2g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8.53
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7.63
7.61
7.60
7.60
7.54
7.52
7.51
7.50
7.50
7.49
7.48
7.26
5.15
5.14
5.12
5.11
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4.68
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4.41
4.40
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4.36
4.36
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4.19
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4.16
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3.97
3.95
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3.73
3.72
3.72
3.71
3.70
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3.46
3.45
3.44
3.44
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2.03
1.03
1.02
3.05
1.03
1.05
2.03
2.09
1.04
2.03
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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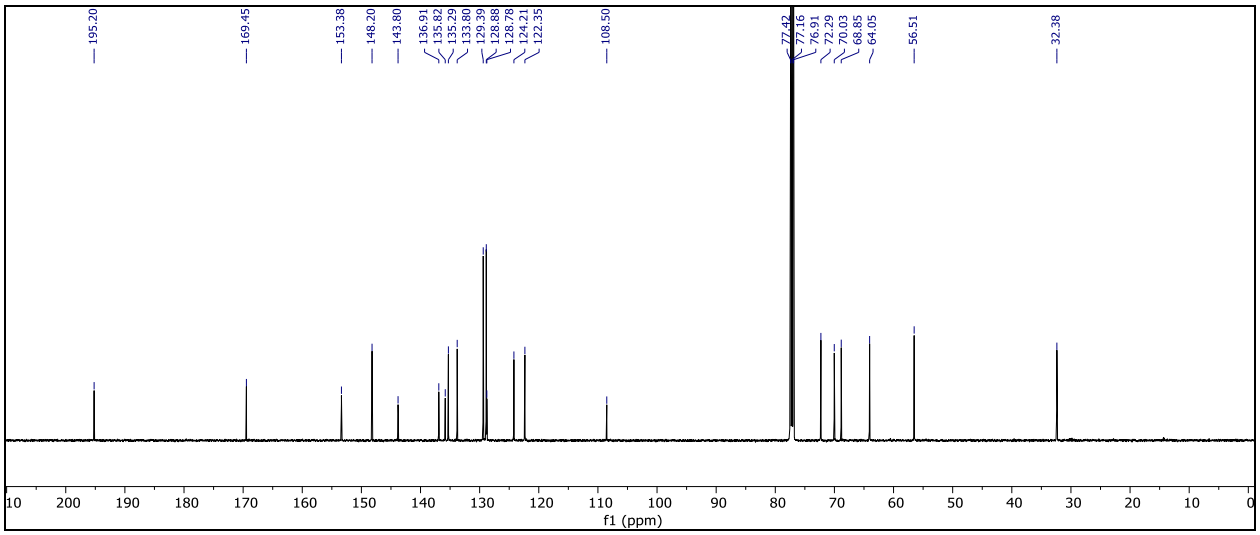
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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135.29
133.80
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124.21
122.35
108.50
77.42
77.16
76.91
72.29
70.03
68.85
64.05
56.51
32.38
10
200
190
180
170
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130
120
110
100
90
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70
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50
40
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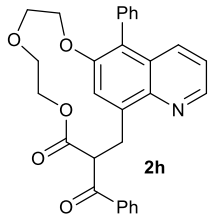
20
10
0
f1 (ppm)


Ph
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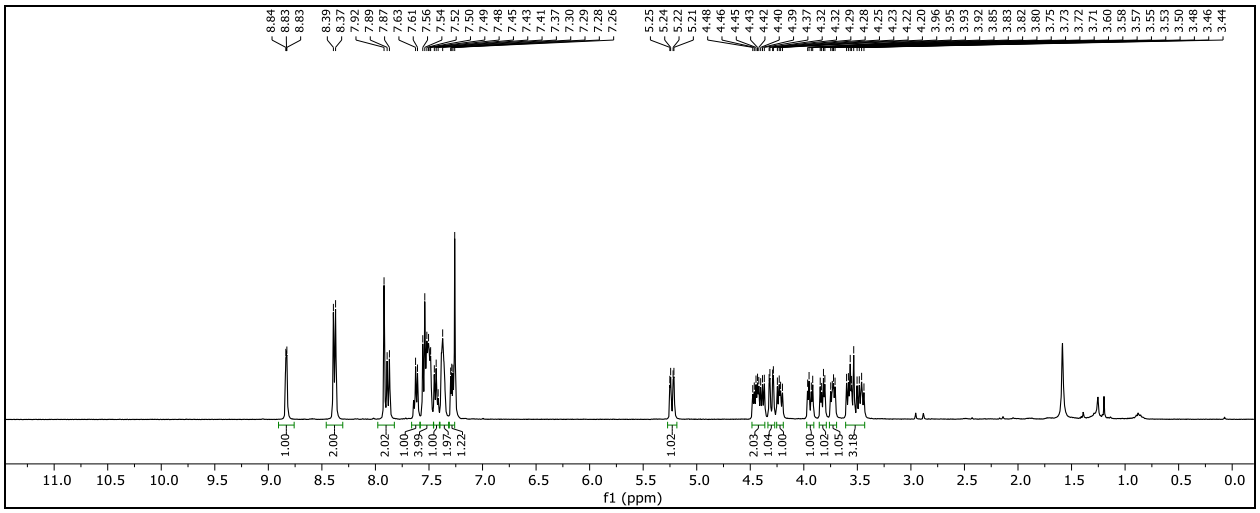
O
O
O
N
O
O
Ph

2h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7.52
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7.49
7.48
7.45
7.43
7.41
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7.30
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7.28
7.26
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5.24
5.22
5.21
4.48
4.46
4.45
4.43
4.42
4.40
4.39
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3.57
3.55
3.53
3.50
3.48
3.46
3.44
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2.00
2.02
1.00
3.99
1.00
1.97
1.22
1.02
2.03
1.04
1.00
1.00
1.02
1.05
3.18
11.0
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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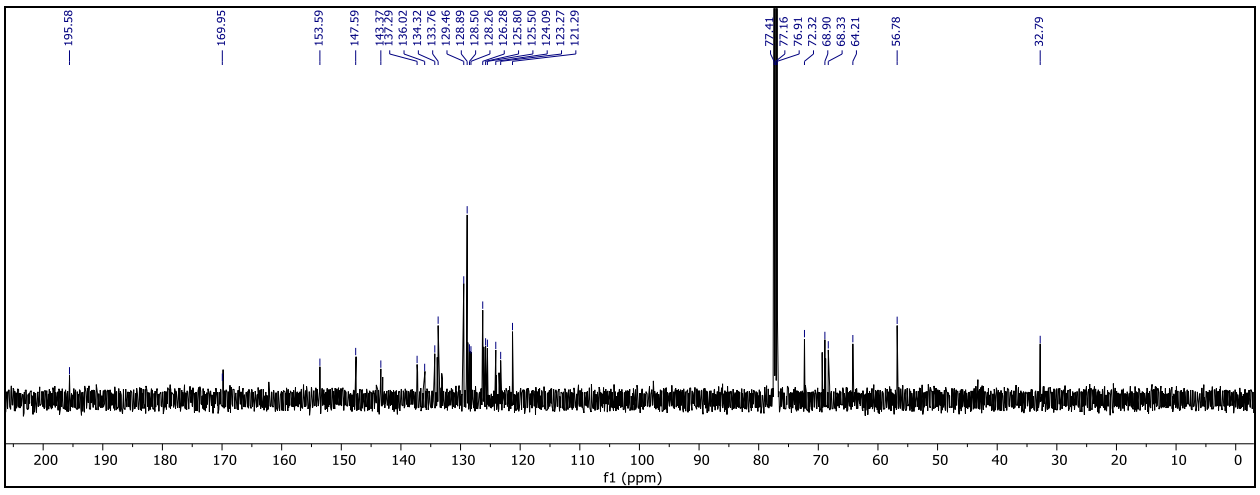
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.26
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125.80
125.50
124.09
123.27
121.29
77.41
77.16
76.91
72.32
68.90
68.33
64.21
56.78
32.79
200
190
180
170
160
150
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130
120
110
100
90
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70
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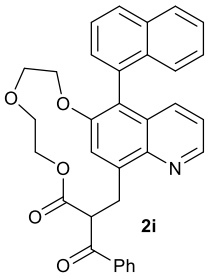
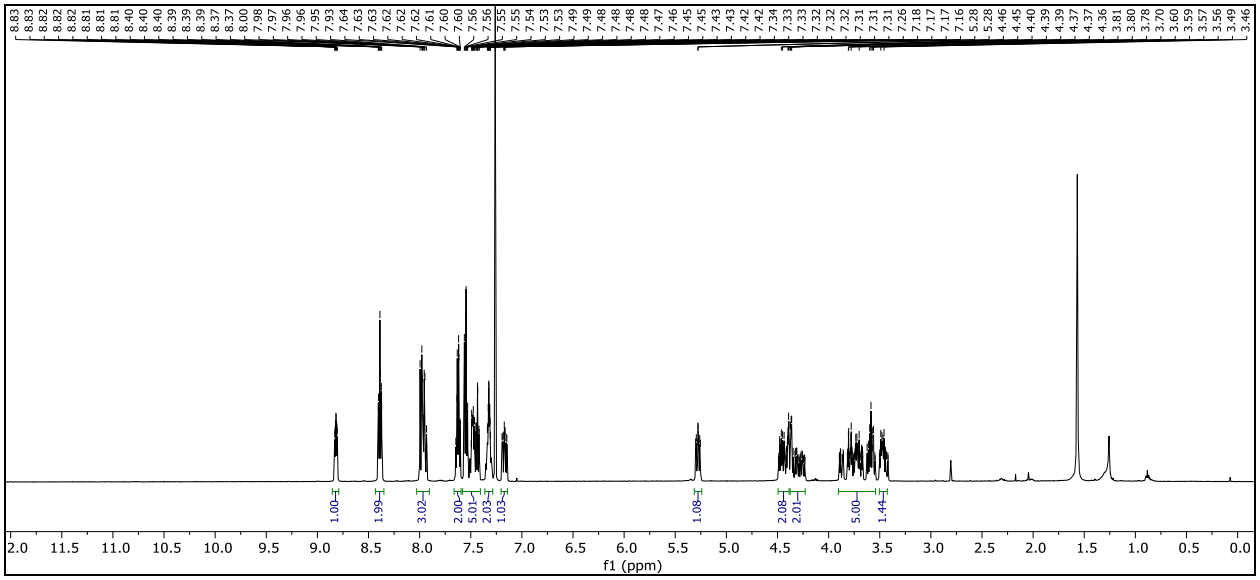
50
40
30
20
10
0
f1 (ppm)


O
O
O
O
O
N
O
Ph

2i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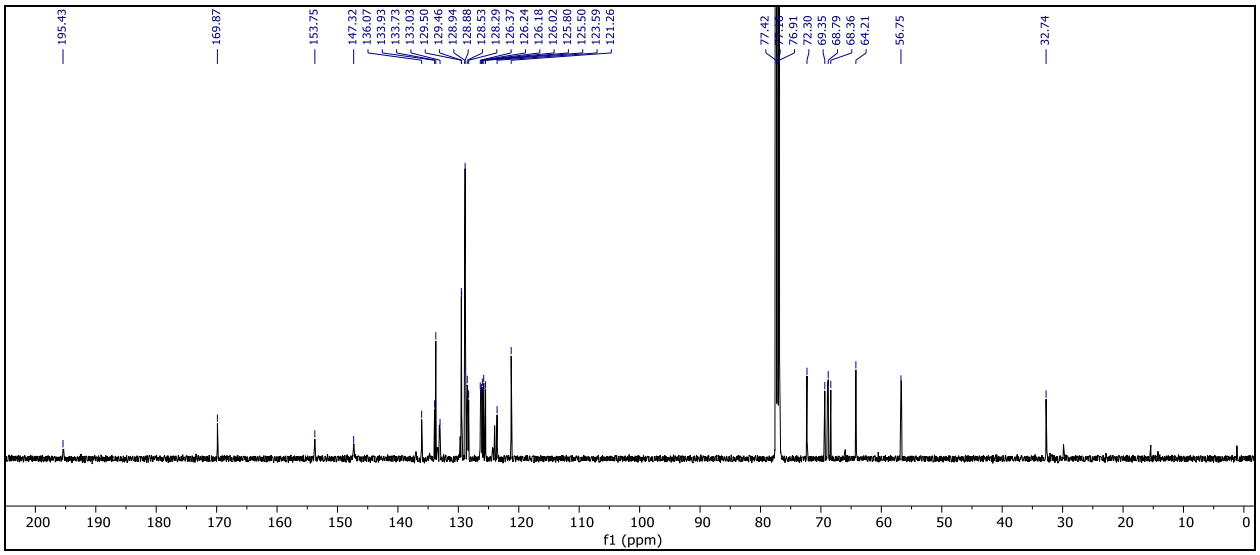
2.03
1.03
1.08
2.08
2.01
5.00
1.44
f1 (ppm)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126.24
126.18
126.02
125.80
125.50
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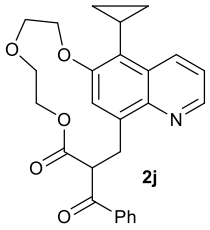
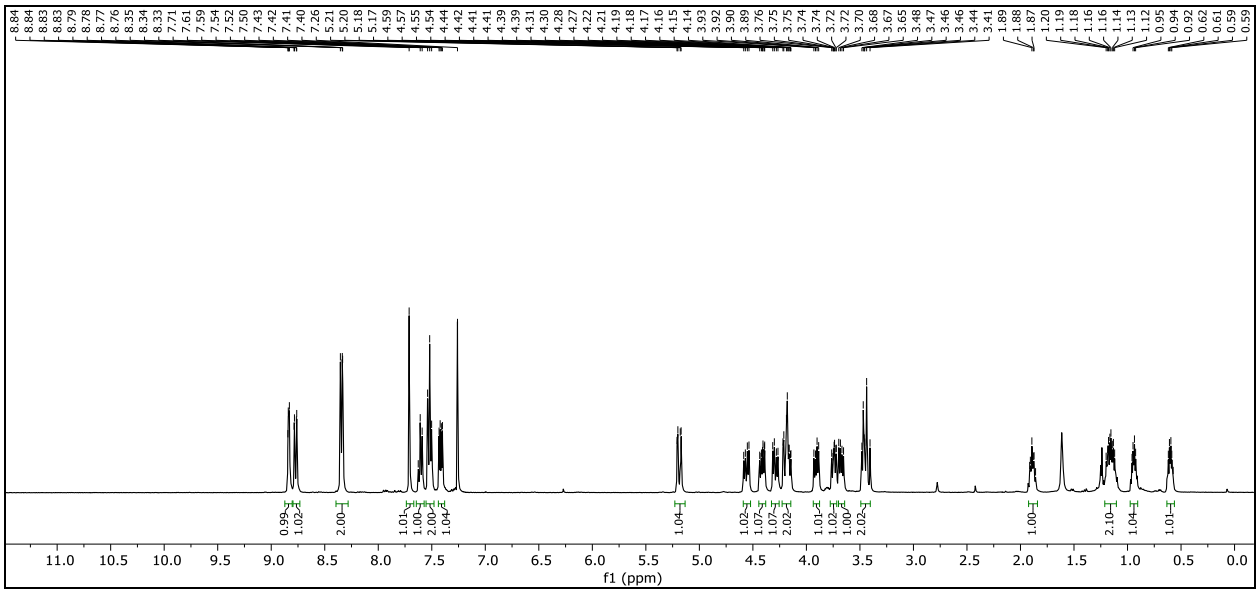
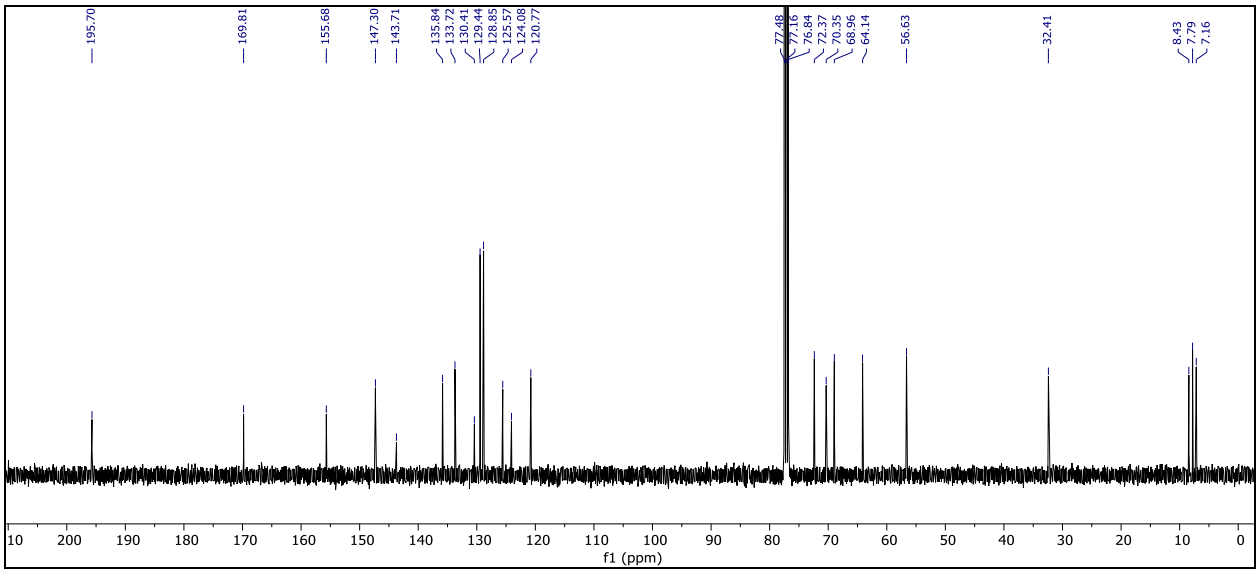
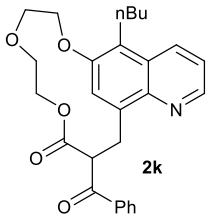
32.74
f1 (ppm)



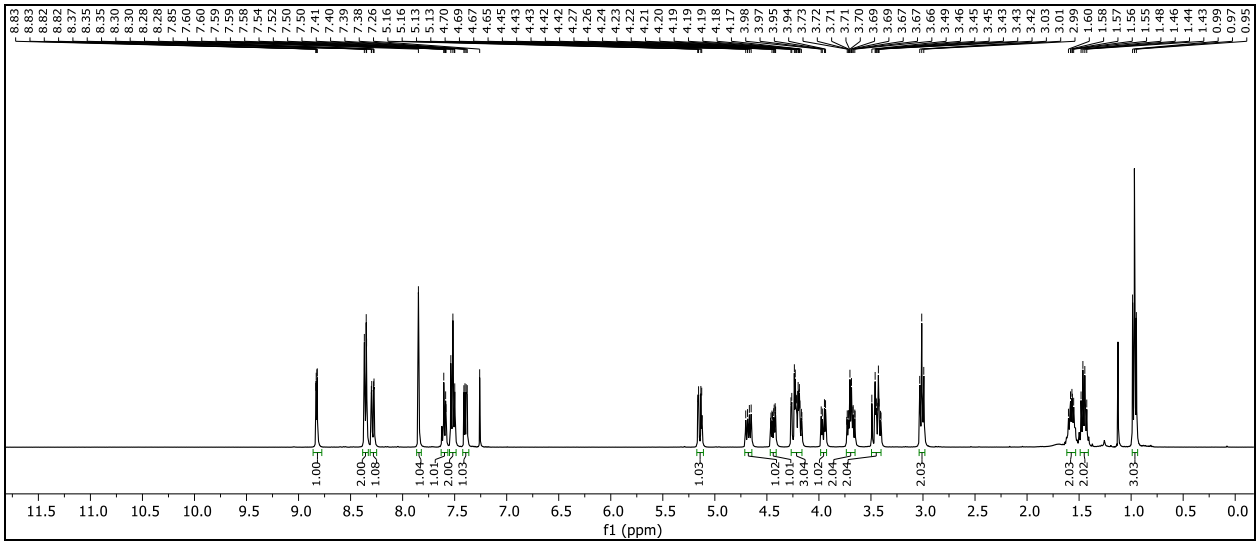
2j

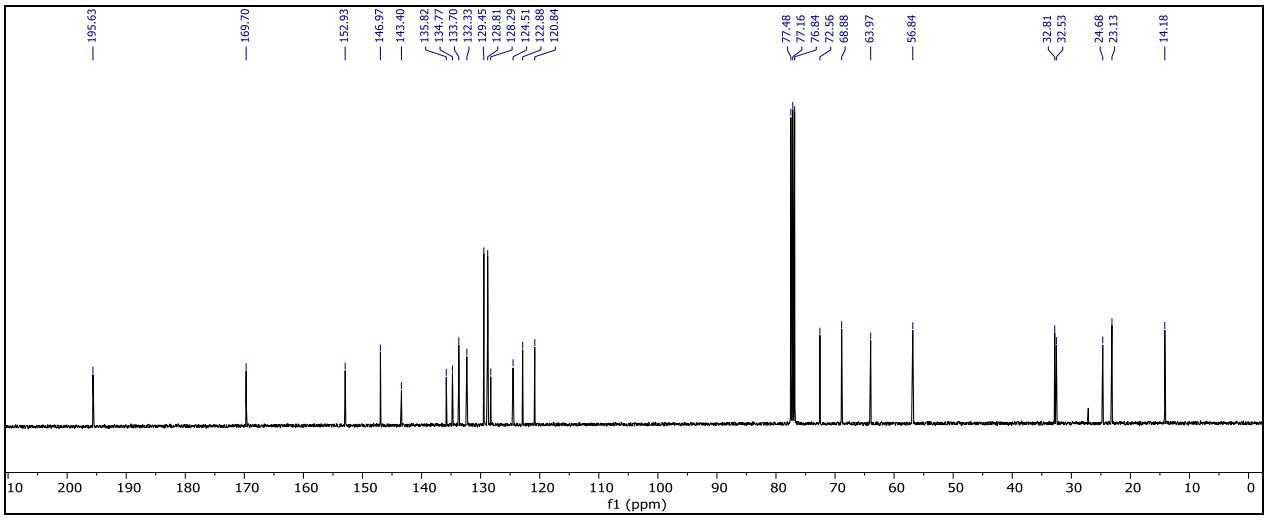





nBu
O
O
O
O
N
O
O
Ph

2k


f1 (ppm)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122.88
120.64
77.48
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68.88
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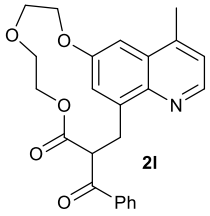
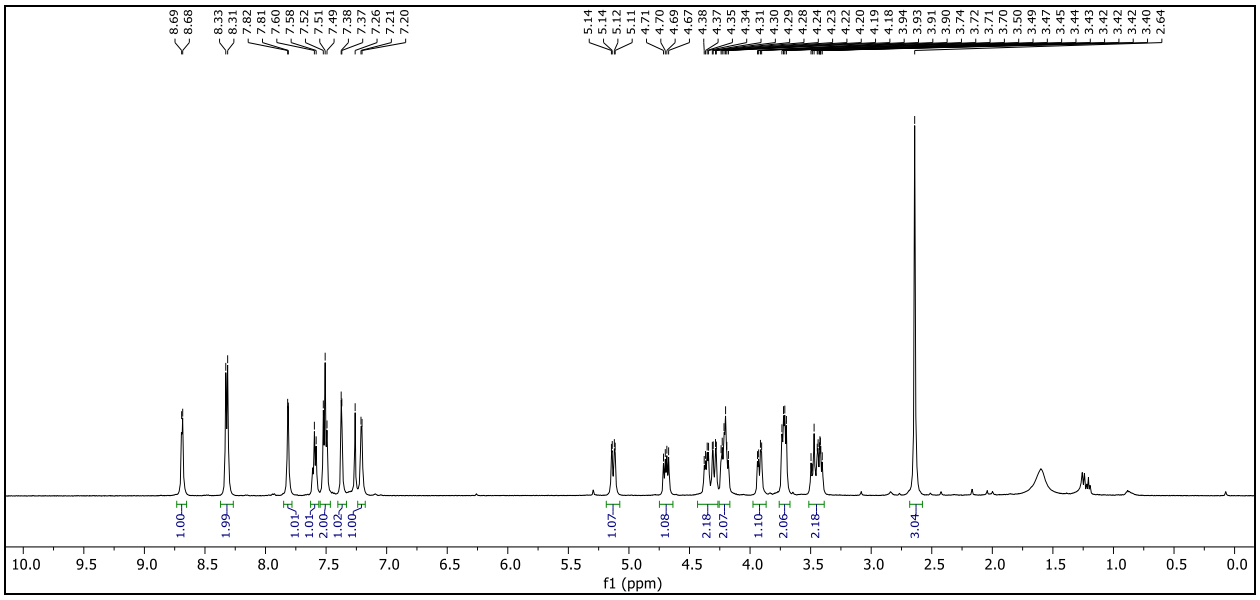
56.84
32.81
32.53
24.68
23.13
14.18
f1 (ppm)


O
O
O
O
N
O
O
Ph

2l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7.37
7.26
7.21
7.20
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5.14
5.12
5.11
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4.37
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3.47
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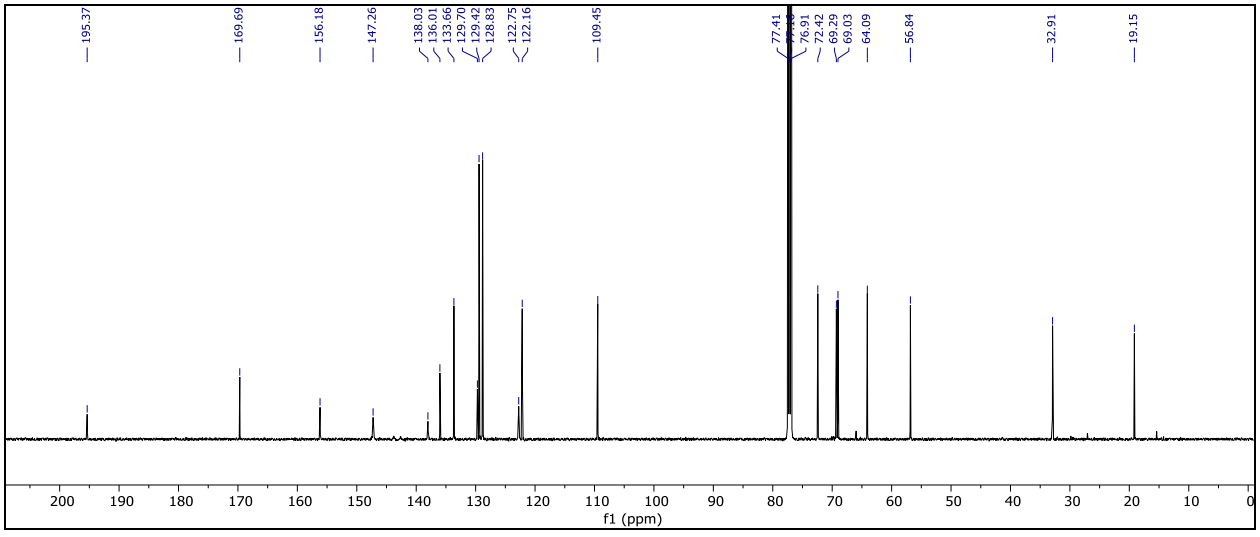
2.00
1.02
1.00
1.07
1.08
2.18
2.07
1.10
2.06
2.18
3.04
f1 (ppm)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122.75
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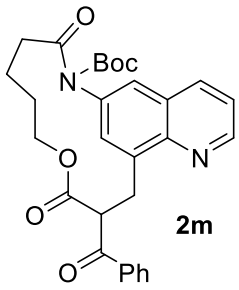
76.91
72.42
69.29
69.03
64.09
56.84
32.91
19.15
f1 (ppm)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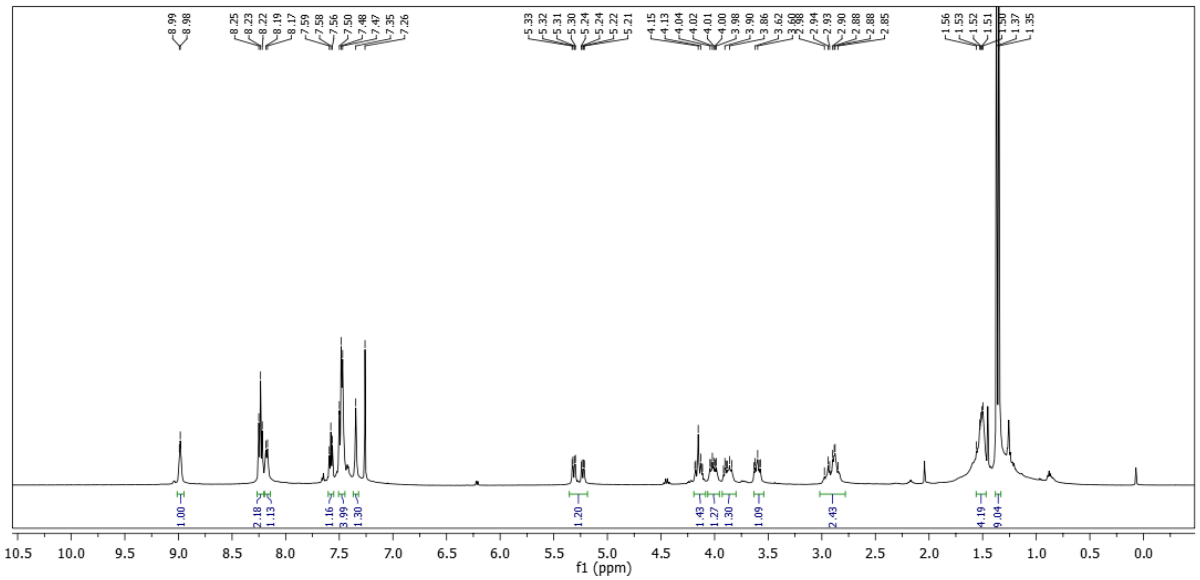
O
O
Ph

2m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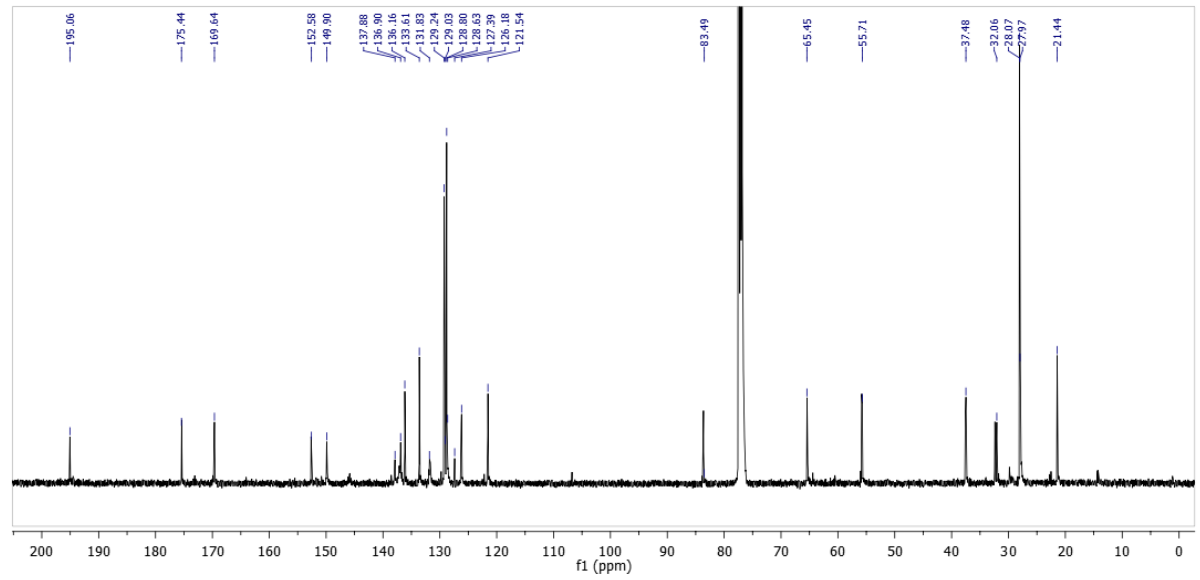
7.26
5.33
5.32
5.31
5.30
5.24
5.22
5.21
4.15
4.13
4.04
4.02
4.01
4.00
3.98
3.90
3.86
3.62
3.60
2.94
2.93
2.90
2.88
2.88
2.85
1.56
1.53
1.52
1.51
1.50
1.37
1.35
1.00
2.18
1.13
1.16
3.99
1.30
1.20
1.43
1.27
1.30
1.09
2.48
4.19
9.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.39
126.18
121.54
83.49
65.45
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28.07
27.97
21.44
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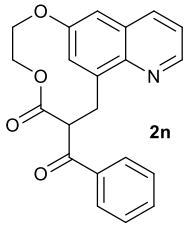
f1 (ppm)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O
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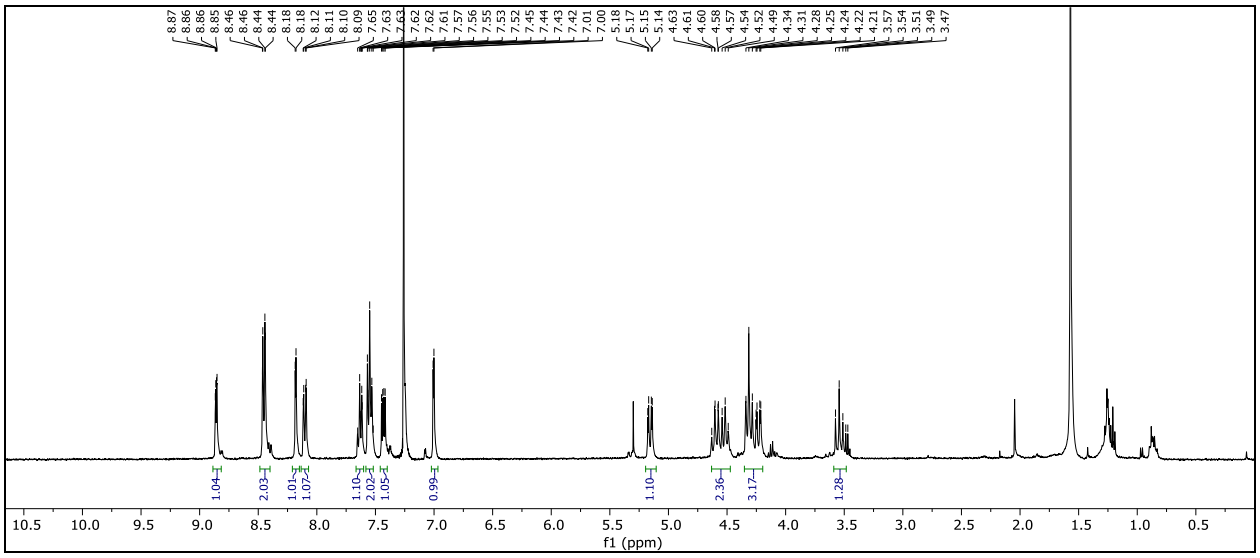
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7.56
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7.53
7.52
7.45
7.44
7.43
7.42
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7.00
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4.22
4.21
3.57
3.54
3.51
3.49
3.47
1.04
2.03
1.01
1.07
1.10
2.02
1.05
0.99
1.10
2.36
3.17
1.28
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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2.0
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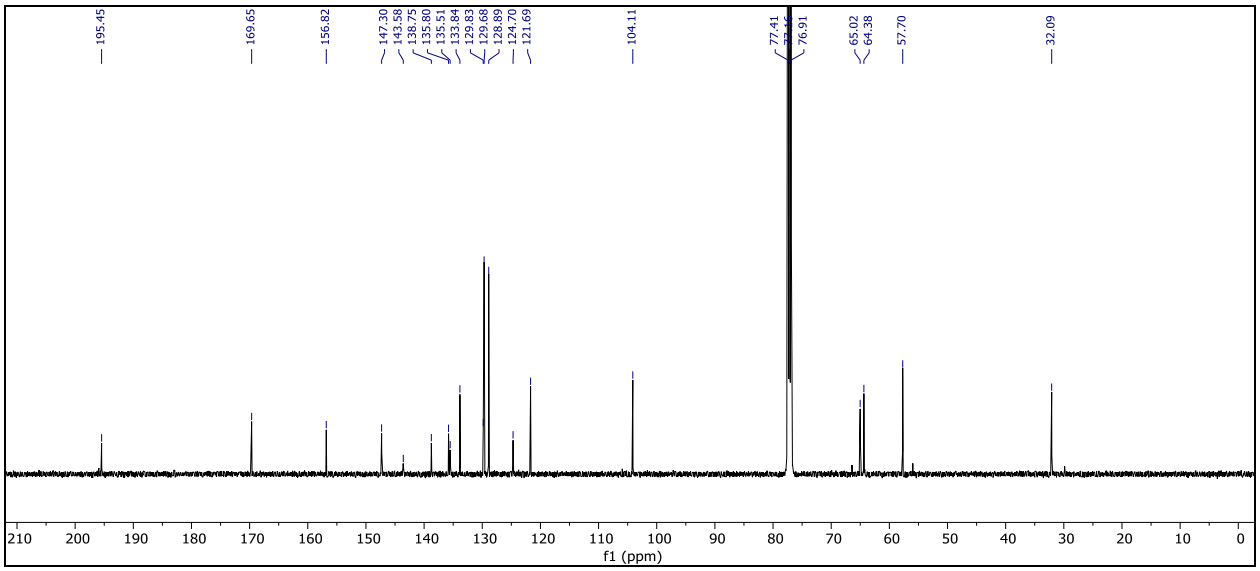
0.5
f1 (ppm)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128.89
124.70
121.69
104.11
77.41
77.16
76.91
65.02
64.38
57.70
32.09
210
200
190
180
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130
120
110
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90
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70
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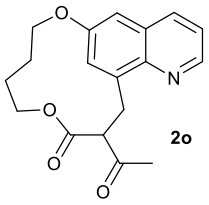
50
40
30
20
10
0
f1 (ppm)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O

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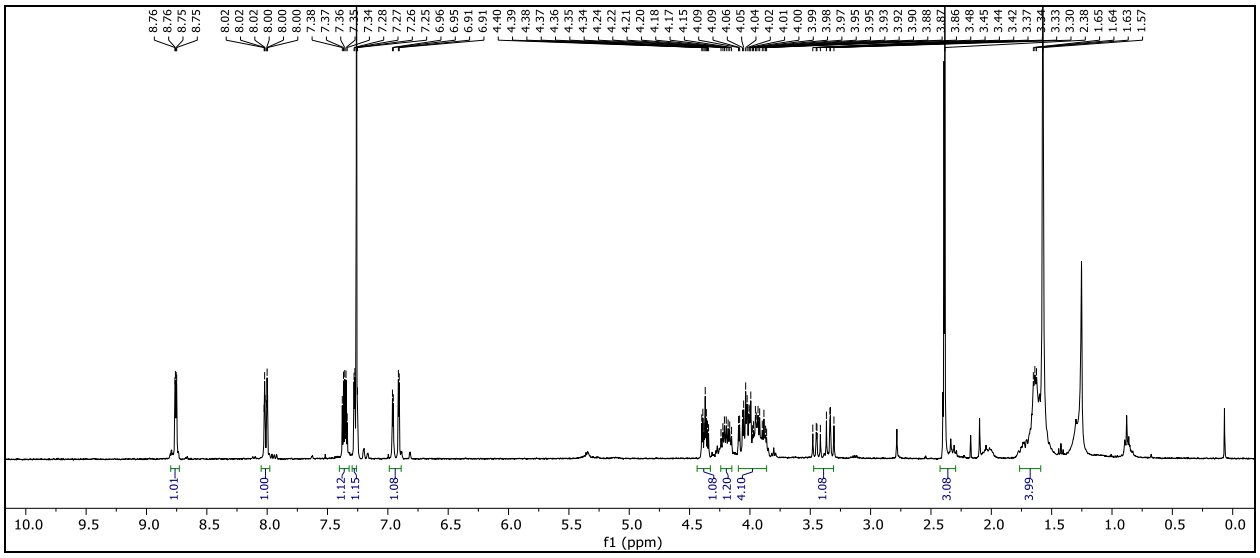
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7.25
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6.95
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6.91
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4.36
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4.09
4.09
4.06
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4.04
4.02
4.01
4.00
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3.93
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3.87
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3.44
3.42
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1.64
1.63
1.57
1.01
1.00
1.12
1.15
1.08
1.08
1.20
4.10
1.08
3.08
3.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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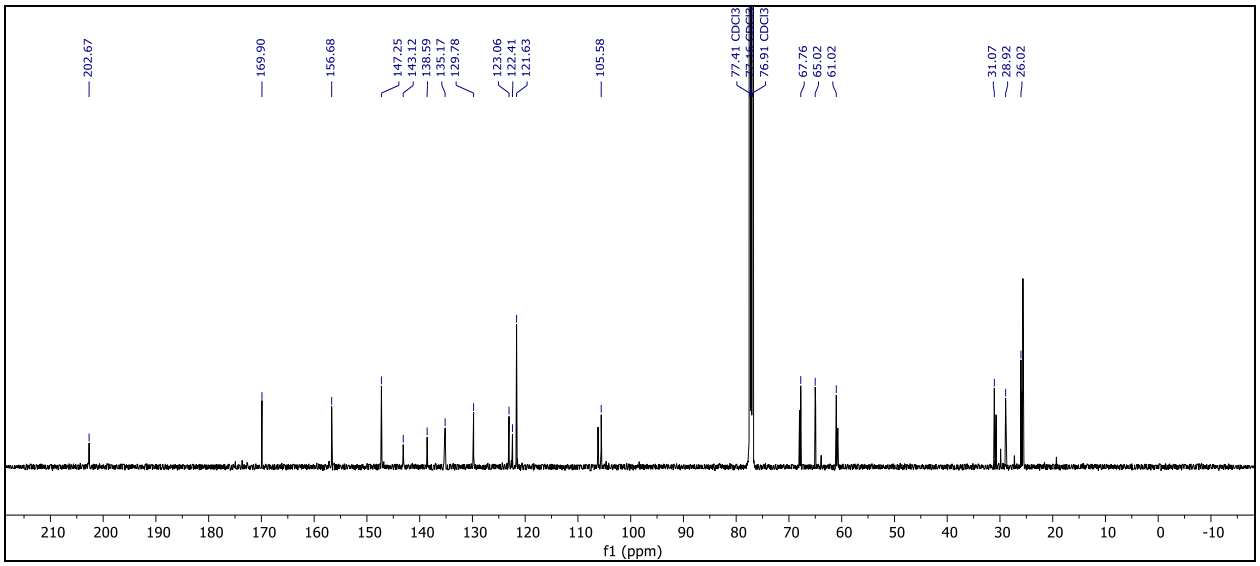
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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123.06
122.41
121.63
105.58
77.41 CDCl3
76.91 CDCl3
67.76
65.02
61.02
31.07
28.92
26.02
210
200
190
180
170
160
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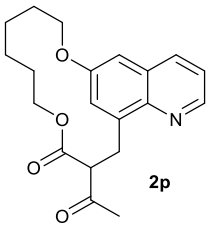
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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O
O
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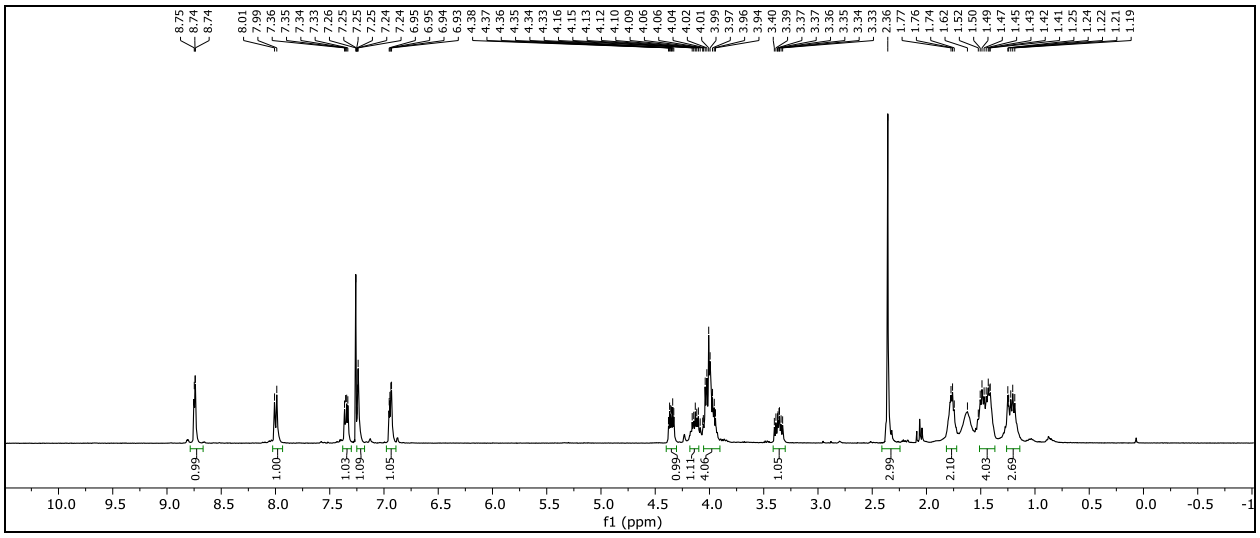
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7.24
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4.37
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4.34
4.33
4.16
4.15
4.13
4.12
4.10
4.09
4.06
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4.02
4.01
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1.42
1.41
1.25
1.24
1.22
1.21
1.19
0.99
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0.99
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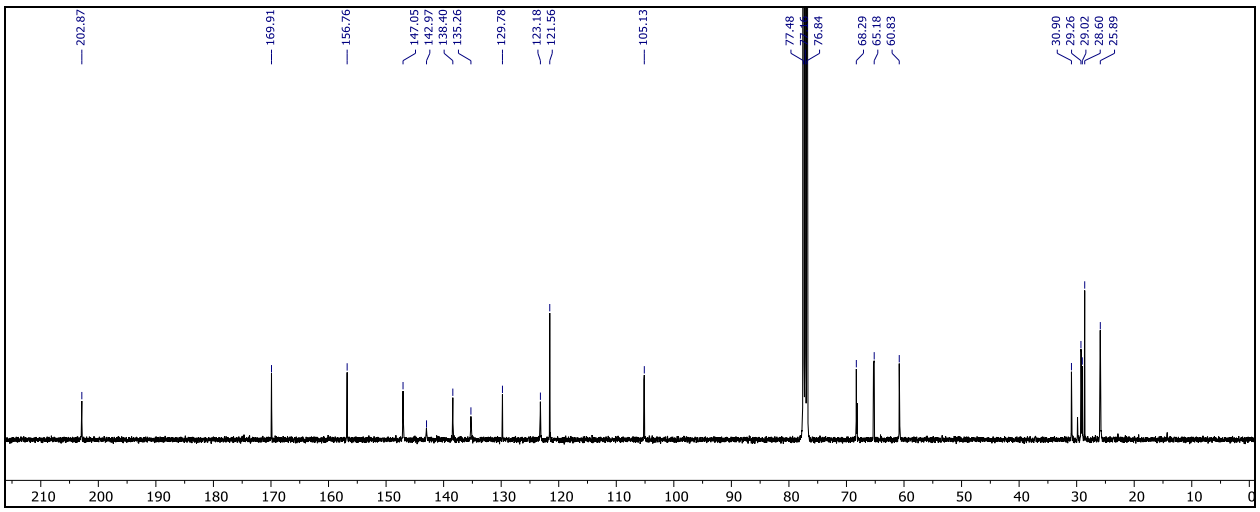
2.10
4.03
2.69
f1 (ppm)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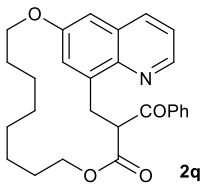
60.83
30.90
29.26
29.02
28.60
25.89



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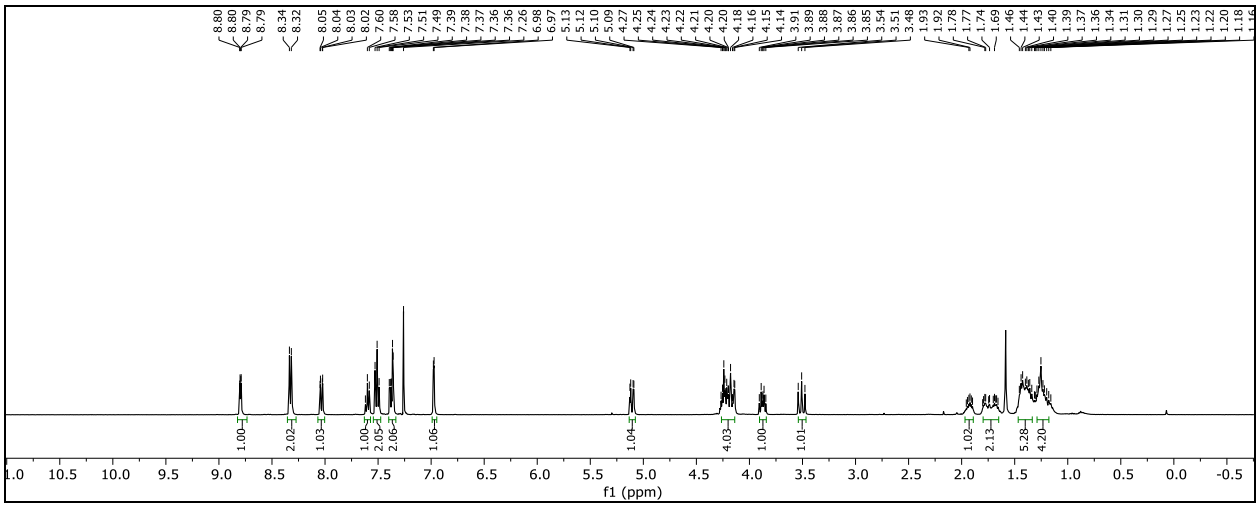

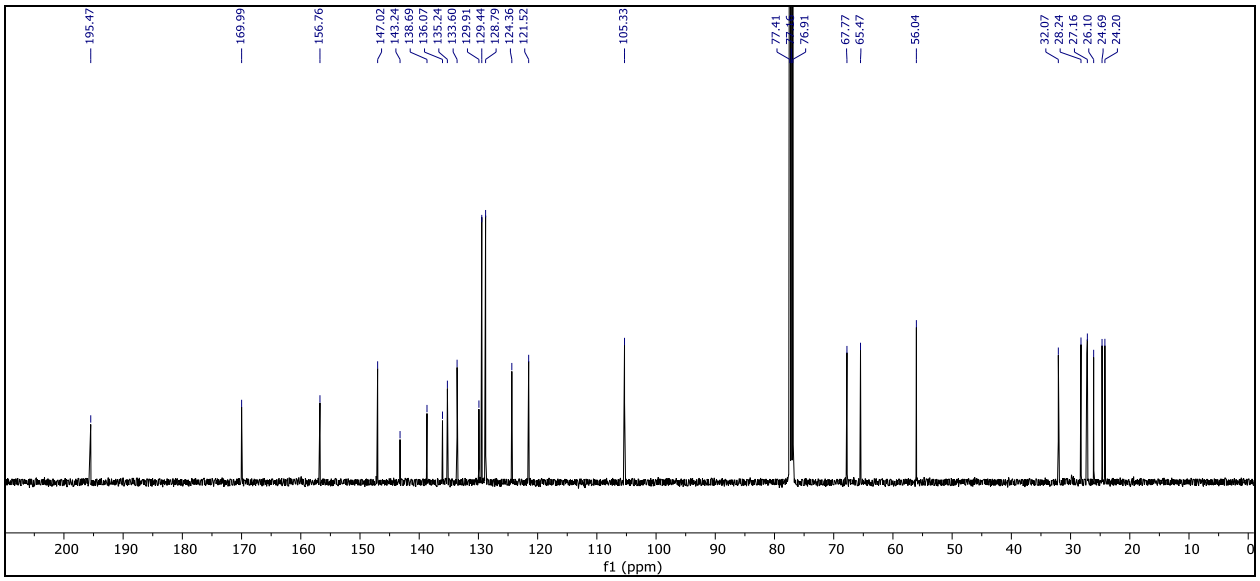

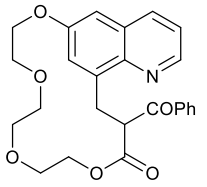
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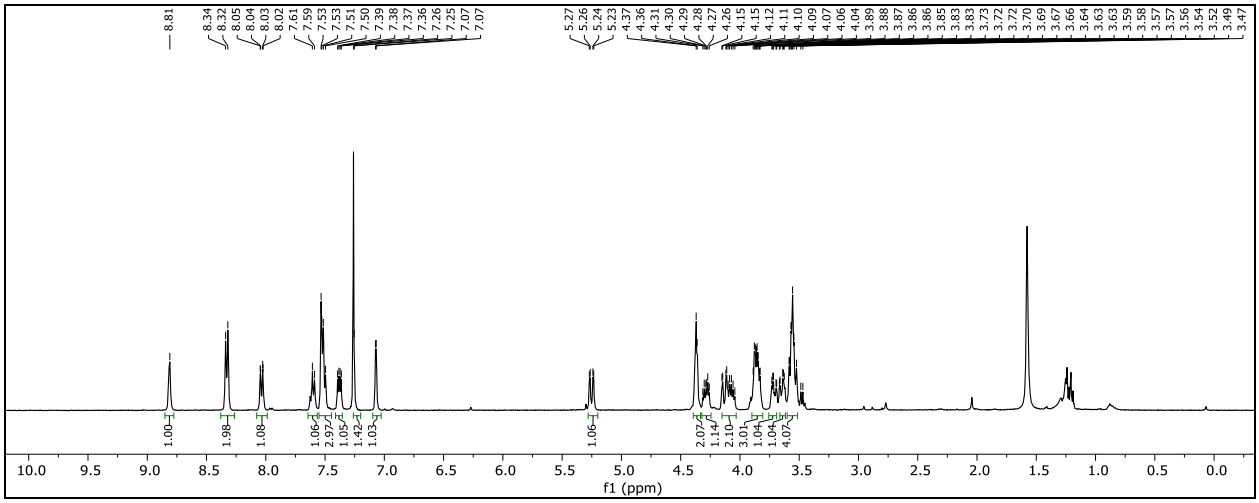
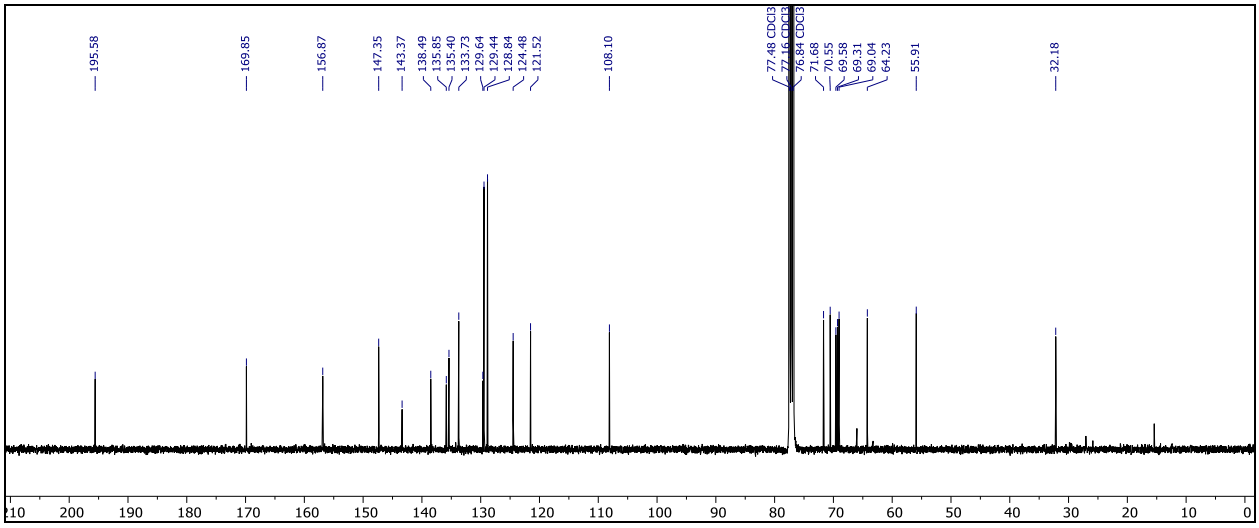
N
COPh
O
O
O

2r


f1 (ppm)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108.10
77.48 CDCl3
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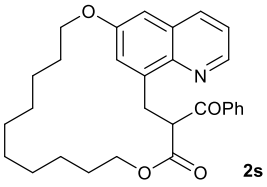
69.31
69.04
64.23
55.91
32.18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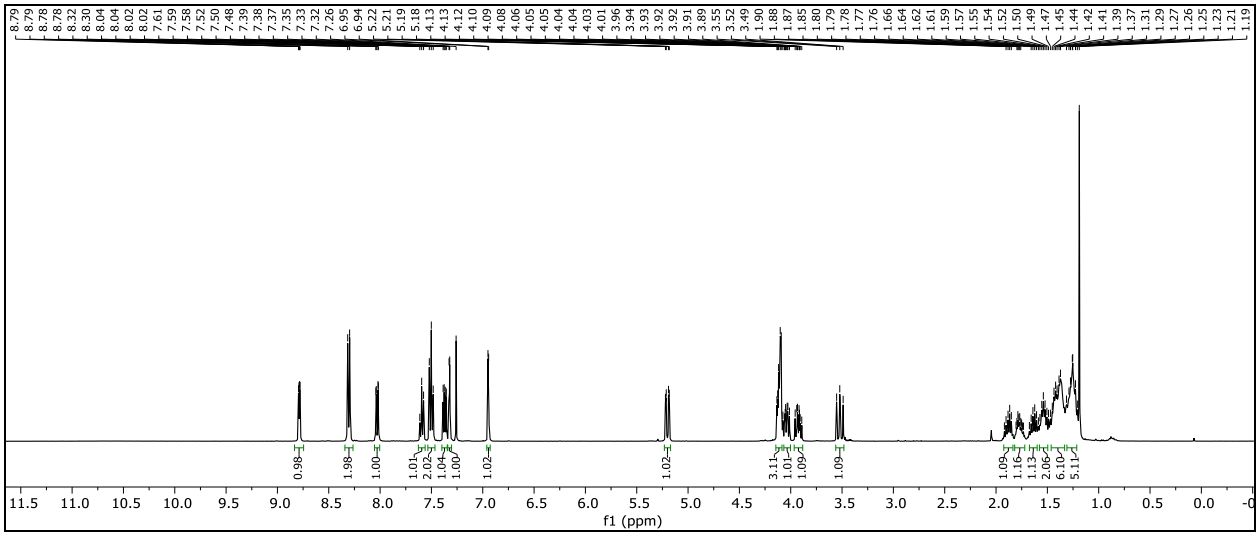
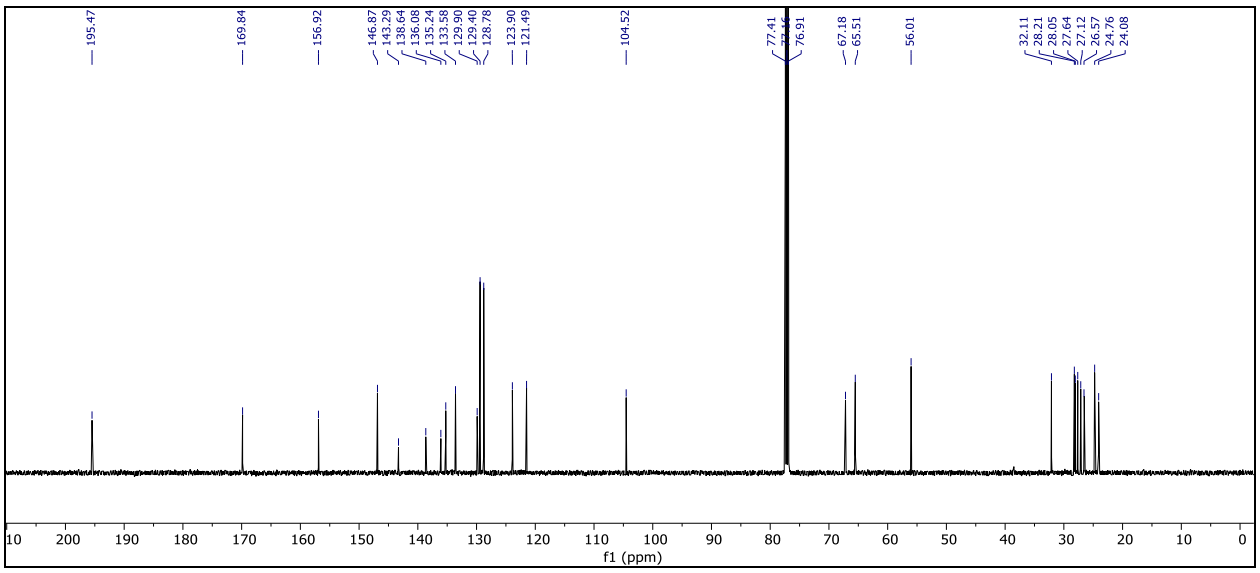
N
COPh
O
O

2s


f1 (ppm)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121.49
104.52
77.41
76.91
67.18
65.51
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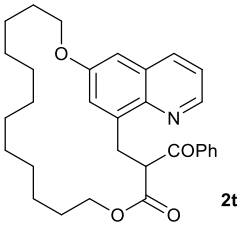
28.21
28.05
27.64
27.12
26.57
24.76
24.08
f1 (ppm)



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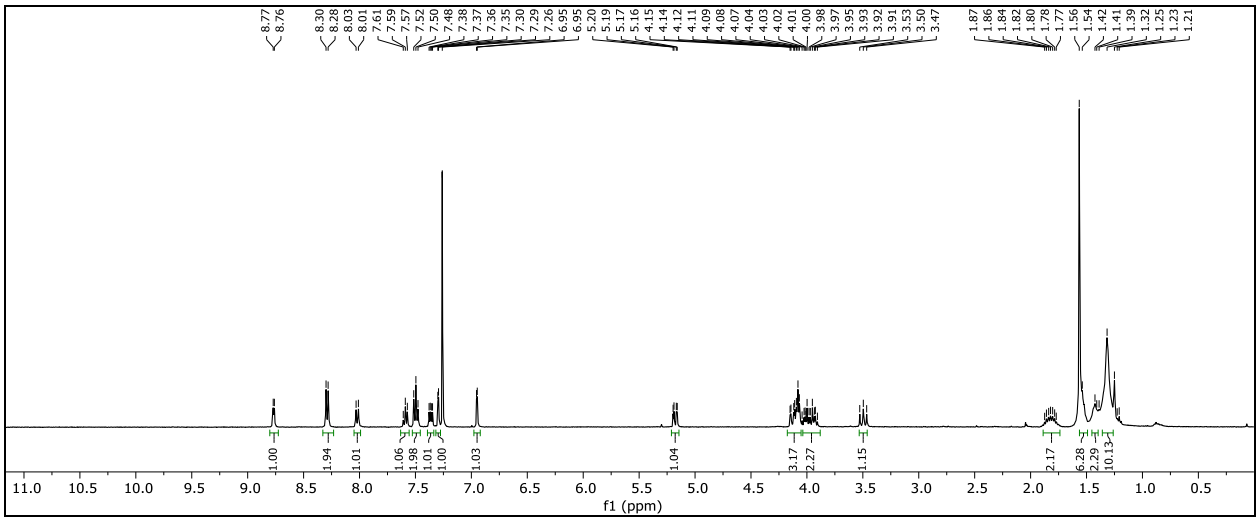

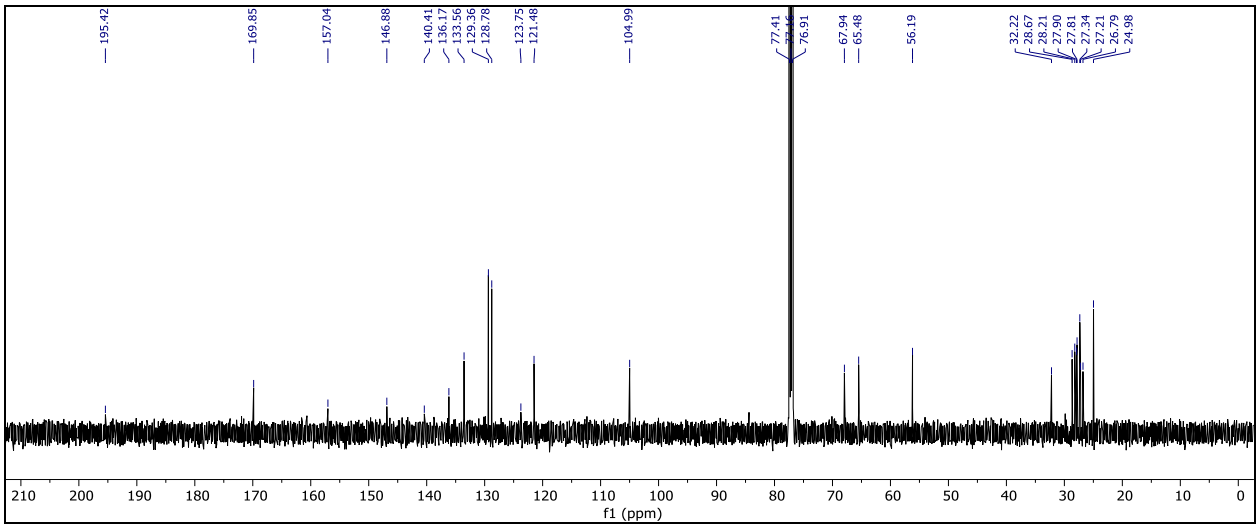

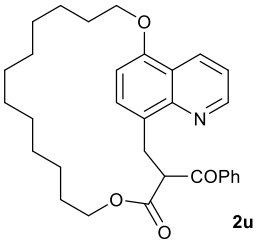

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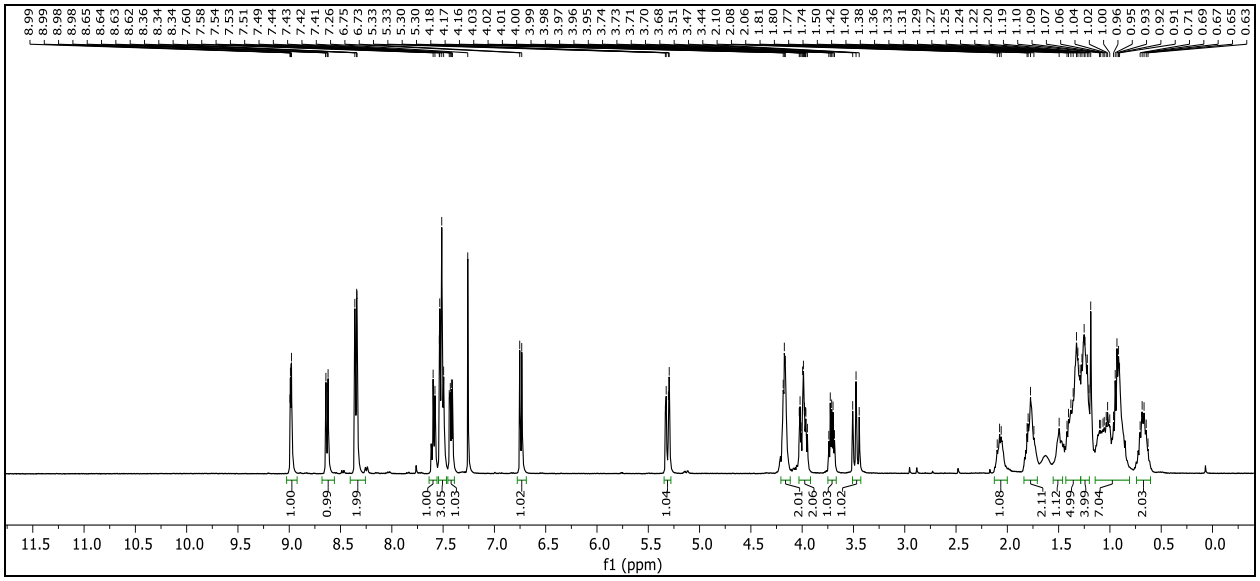

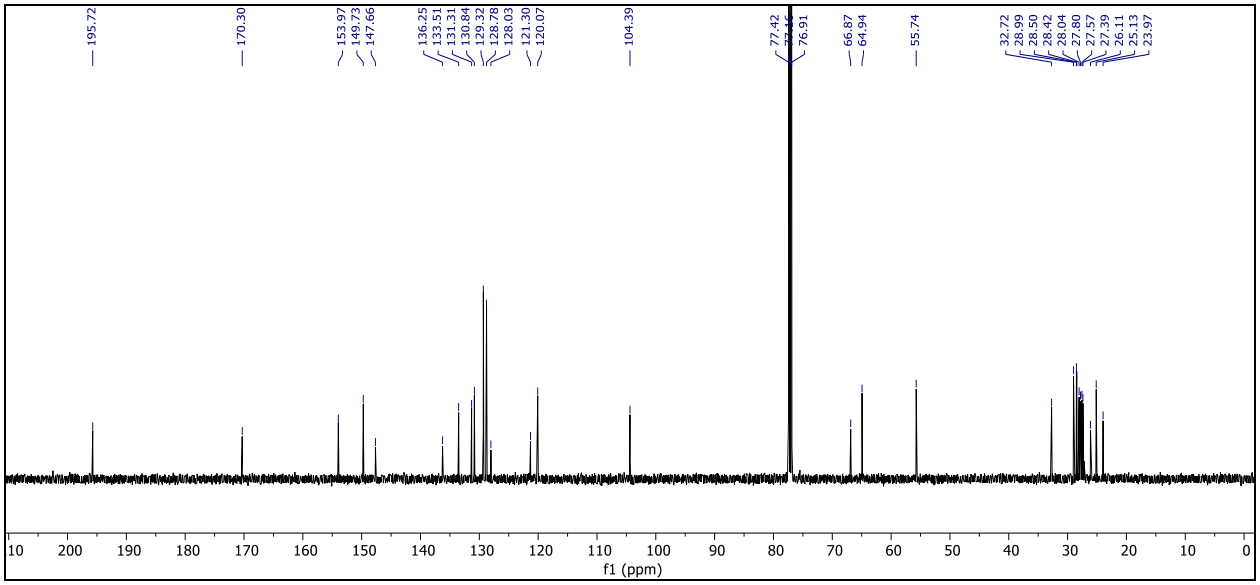

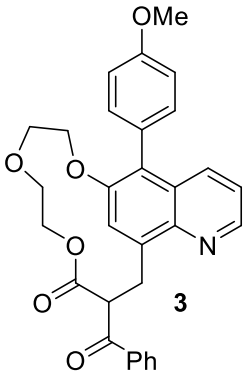

3