Electronic Supplementary Material (ESI) for ChemComm.

Palladium-catalysed Cyclisation of Vinylethylene Carbonates and Anhydrides: A New Approach to Diverse Medium-sized Bislactones

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Supporting Information

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1. General Information

General Procedures

- All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under an atmosphere of argon if needed. Gas-tight syringes with stainless steel needles were used to transfer air- and moisture-sensitive liquids. All moisture and/or air sensitive solid compounds were manipulated inside normal desiccators. Flash column chromatography was performed using silica gel (40–63 μm, 230–400 mesh).
- Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and I_2.
- Organic solutions were concentrated at 30–50 °C on rotary evaporators at ~10 torr followed by drying on vacuum pump at ~1 torr. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Materials

- Commercial reagents and solvents were purchased from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin and Energy Chemical and used as received with the following exceptions: THF, Et_2O and toluene were purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.[1] The isatoic anhydrides **1**[2] and vinylethylene carbonates **2**[3] were prepared according to literature procedure.

Instrumentation

- Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with JEOL-600M. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant(s) (Hz), integration].
- Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with JEOL 150 MHz spectrometers. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon resonances of the solvent (δ 77.0 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (C_q = fully substituted carbon)].
- High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2 using an electrospray (ESI) ionisation source.
- Melting points were recorded on WRX-X-4A melting point apparatus.

2. Bioactive Molecules Bearing a (Bis-)Lactone Skeleton and its Synthetic Motivation

The medium-sized lactones including bislactones are prevalent in several bioactive molecules (for deatail, see Figure S1).[4] However, medium-sized skeletons are rarely found in the current approved drug list. A main reason is probably the difficulty in developing efficient catalytic system to establish diverse medium-sized compound(especially for lactones or bislactones) libraries for drug-leads screening. Therefore, a general protocol for the rapid and diversity-oriented synthesis of medium-sized bislactones in a single-step reaction is significant and highly desirable.

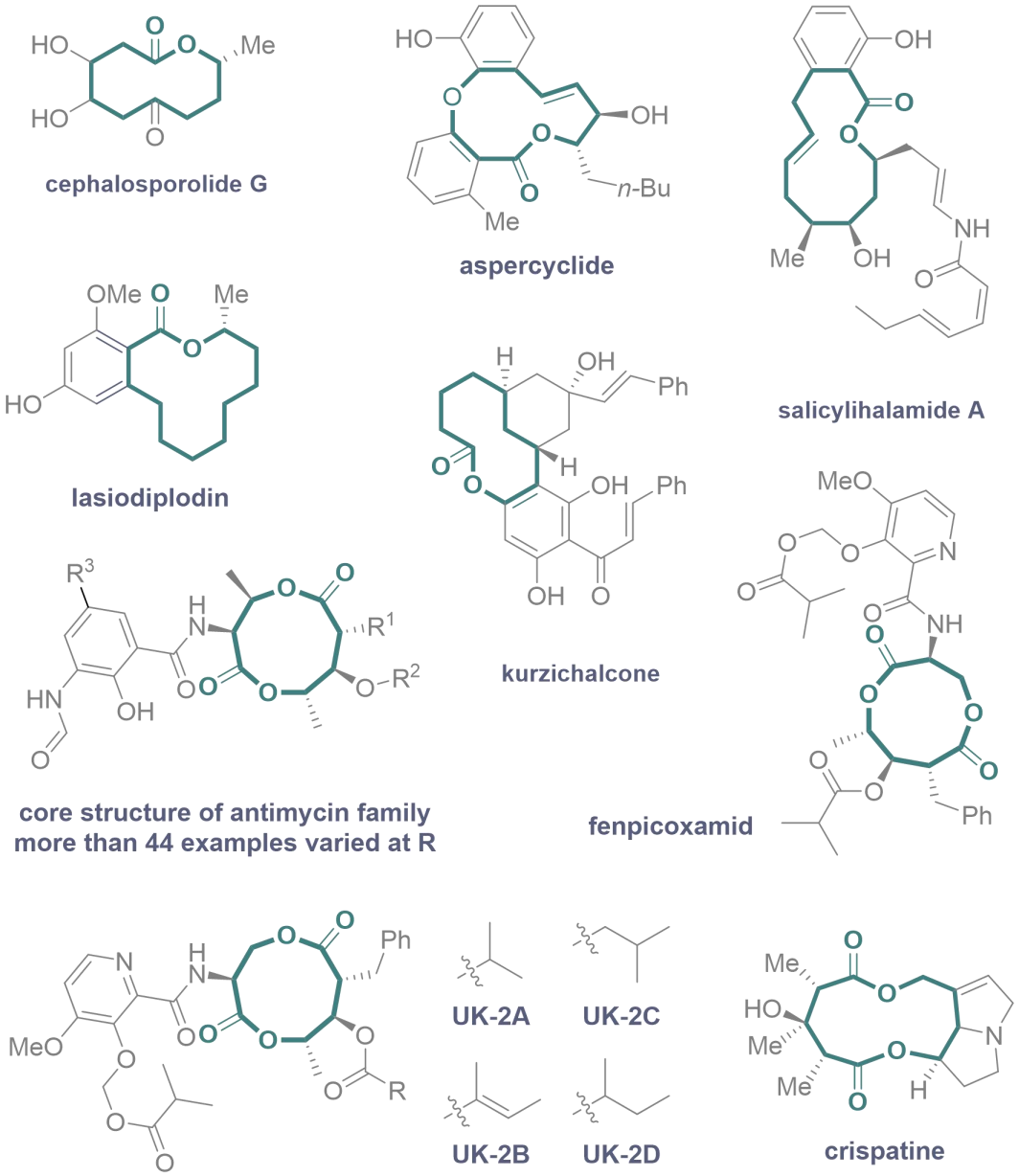
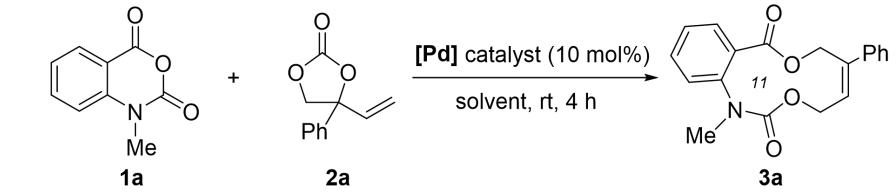


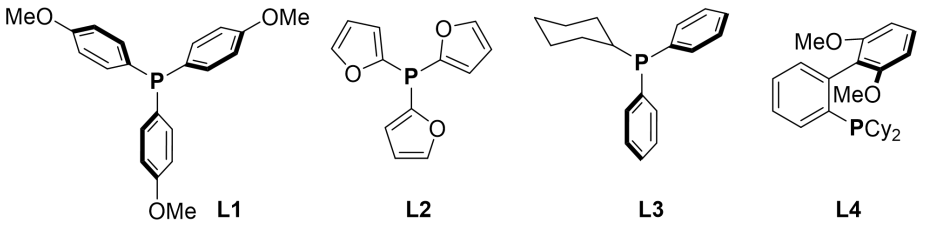
Figure S1. Bioactive molecules bearing a (bis-)lactone skeleton.

3. Optimisation Studies

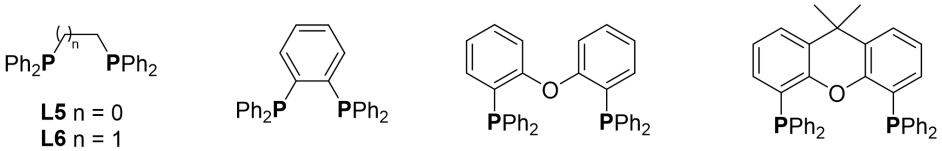
Table S1. Optimisation of the cyclisation reaction of isatoic anhydride **1a** and VEC **2a** with 10 mol% of the palladium catalyst.[a]



1a **2a** **3a**



L1 **L2** **L3** **L4**



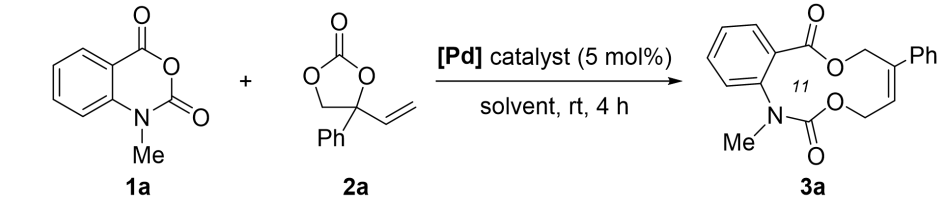
L5 n = 0
L6 n = 1
L7 n = 2

L8 **L9** **L10**

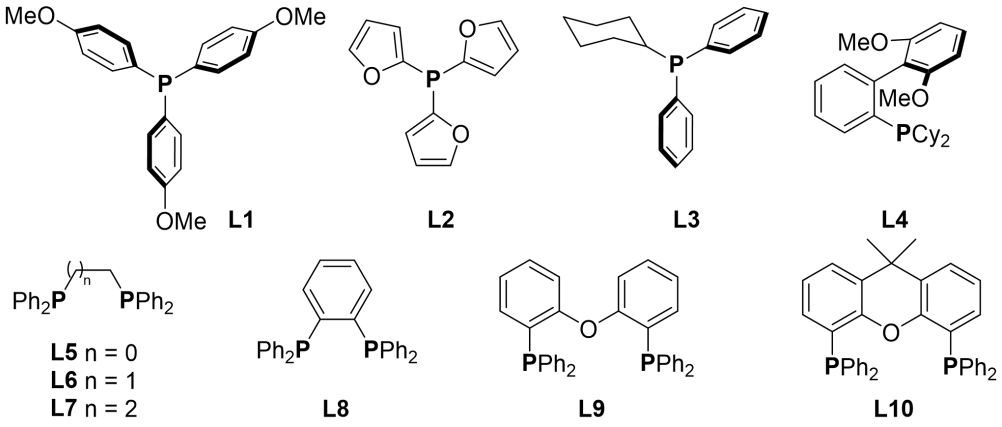
Entry	[Pd]	Ligand	Solvent	Yield (%)[b]
1	$Pd(PPh_3)_4$	-	THF	33
2	$Pd(PPh_3)_4$	-	MeCN	-
3	$Pd(PPh_3)_4$	-	PhCl	-
4	$Pd(PPh_3)_4$	-	DCM	62
5	$Pd(PPh_3)_4$	-	$CHCl_3$	58
6	$Pd(PPh_3)_4$	-	toluene	45
7	$Pd_2(dba)_3{\cdot}CHCl_3$	**L1**	DCM	19
8	$Pd_2(dba)_3{\cdot}CHCl_3$	**L2**	DCM	16
9[c]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L3-8**	DCM	<5
10	$Pd_2(dba)_3{\cdot}CHCl_3$	**L9**	DCM	56
11	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	DCM	59

[a] Unless otherwise noted, reactions were performed with 0.10 mmol of **1a**, 0.15 mmol of **2a**, 10 mol% of the palladium catalyst in 1.0 mL of solvent at room temperature for 4 hours, the Pd/ligand complex was pre-prepared with $Pd_2(dba)_3{\cdot}CHCl_3$ and ligand in solvent at rt for 1 h. [b] Isolated yield. [c] The reaction was performed for 12 hours. $Pd_2(dba)_3$: tris(dibenzylideneacetone)dipalladium.

Table S2. Optimisation of the cyclisation reaction of isatoic anhydride **1a** and VEC **2a** with 5 mol% of the palladium catalyst.[a]



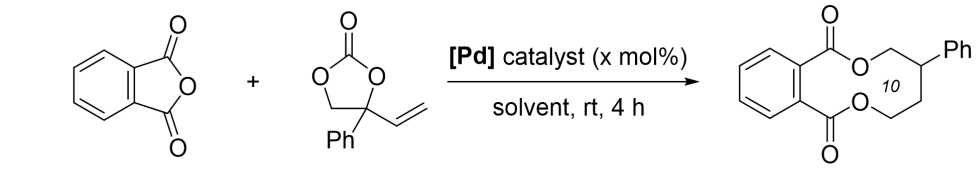
1a **2a** **3a**



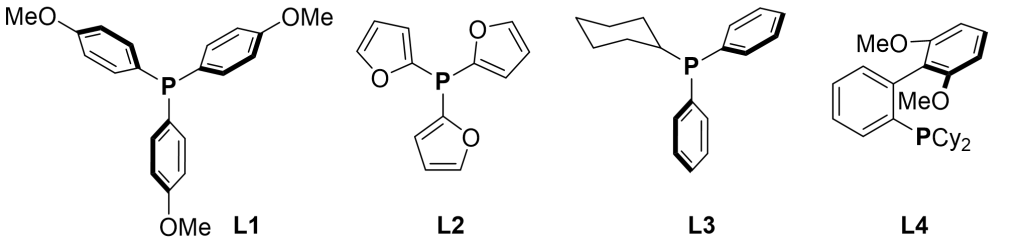
Entry	[Pd]	Ligand	Solvent	Yield (%)[b]
1	$Pd_2(dba)_3{\cdot}CHCl_3$	**L1**	DCM	28
2	$Pd_2(dba)_3{\cdot}CHCl_3$	**L2**	DCM	14
3[c]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L3-8**	DCM	<5
4	$Pd_2(dba)_3{\cdot}CHCl_3$	**L9**	DCM	42
5	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	DCM	62
6[d]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	DCM	49
7[e]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	DCM	47
8[f]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	DCM	61
9[g]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	DCM	59
10	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**/Mg(*t*BuO)$_2$	DCM	58
11	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**/Al(*i*PrO)$_3$	DCM	62
12	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**/Ti(*i*PrO)$_4$	DCM	14
13	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	toluene	95
14	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	PhCl	68
15	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	$CHCl_3$	56
16[c]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	MeCN	<5
17[c]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	THF	<5
18[f]	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	toluene	72
19	$Pd_2(dba)_3$	**L10**	toluene	49
20	$Pd(OAc)_2$	**L10**	toluene	59
21	$Pd_2(dba)_3{\cdot}CHCl_3$	-	toluene	-

[a] Unless otherwise noted, reactions were performed with 0.10 mmol of **1a**, 0.15 mmol of **2a**, 5 mol% of the palladium catalyst in 1.0 mL of solvent at room temperature for 4 hours, the Pd/ligand complex was pre-prepared with $Pd_2(dba)_3{\cdot}CHCl_3$ and ligand in solvent at rt for 1 h. [b] Isolated yield. [c] The reaction was performed for 12 hours. [d] The reaction was performed at 40 °C. [e] The reaction was performed at 60 °C. [f] 0.5 mL of solvent was used. [g] 0.25 mL of solvent was used.

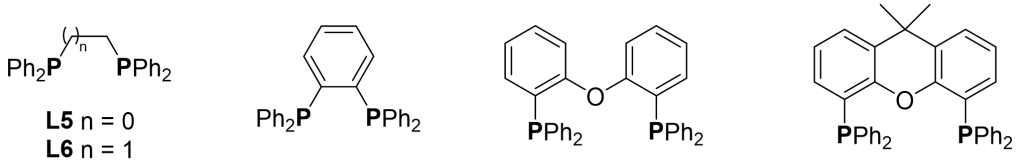
Table S3. Optimisation of the cyclisation reaction of isatoic anhydride **1a** and VEC **2a**.[a]



4a **2a** **5a**



L1 **L2** **L3** **L4**



L5 n = 0
L6 n = 1
L7 n = 2

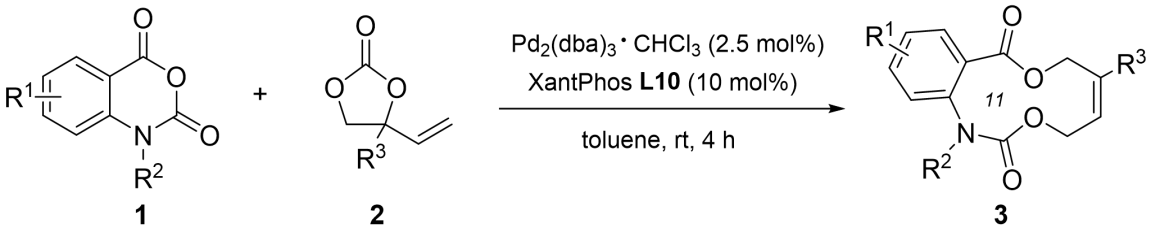
L8 **L9** **L10**

Entry	[Pd]	x mol%	Ligand	Solvent	Yield (%)[b]
1	$Pd(PPh_3)_4$	5	-	THF	-
2	$Pd(PPh_3)_4$	5	-	MeCN	-
3	$Pd(PPh_3)_4$	5	-	PhCl	-
4	$Pd(PPh_3)_4$	5	-	DCM	<5
5	$Pd(PPh_3)_4$	5	-	toluene	<5
6	$Pd(PPh_3)_4$	5	-	$CHCl_3$	
7[c]	$Pd_2(dba)_3{\cdot}CHCl_3$	2.5	**L1-8**	toluene	-
8	$Pd_2(dba)_3{\cdot}CHCl_3$	2.5	**L9**	toluene	59
9	$Pd_2(dba)_3{\cdot}CHCl_3$	2.5	**L10**	toluene	80
10	$Pd_2(dba)_3{\cdot}CHCl_3$	2.5	**L10**	THF	42
11	$Pd_2(dba)_3{\cdot}CHCl_3$	2.5	**L10**	MeCN	-
12	$Pd_2(dba)_3{\cdot}CHCl_3$	2.5	**L10**	PhCl	14
13	$Pd_2(dba)_3{\cdot}CHCl_3$	2.5	**L10**	DCM	-
14	$Pd_2(dba)_3{\cdot}CHCl_3$	2.5	**L10**	$CHCl_3$	-

[a] Unless otherwise noted, reactions were performed with 0.10 mmol of **4a**, 0.15 mmol of **2a**, 2.5 mol% of the palladium catalyst and 10 mol% of the ligand in 1.0 mL of solvent at room temperature for 4 hours. [b] Isolated yield. [c] The reaction was performed for 12 hours.

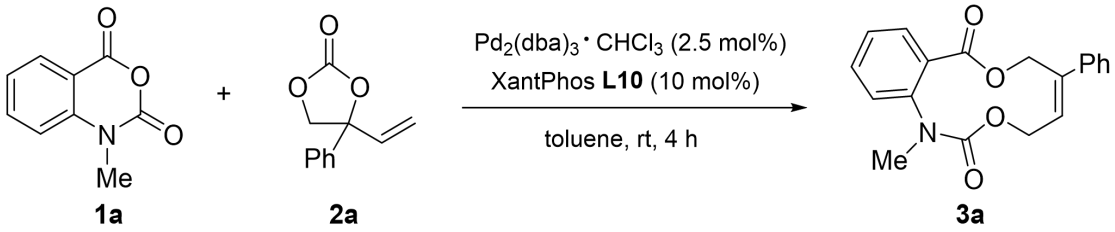
4. General Procedure for the Cyclisation of Isatoic Anhydrides and VECs

*General procedure for the synthesis of 11-membered lactones **3***



To an oven-dried Schlenk tube was added $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%) and XantPhos (10 mol%), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, isatoic anhydrides **1** (0.10 mmol) and vinylethylene carbonates **2** (0.15 mmol) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 3/1, then petroleum ether/ethyl acetate = 10/1 to 3/1) to afford the corresponding **3** in 68–95% yields, which were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*. Influenced by the flexibility of medium-sized rings, the NMR analysis of the following compounds at room temperature met some spin splitting problems and couldn't provide the clear NMR spectra.

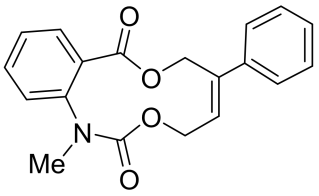
*Gram-scale synthesis of the eleven-membered lactone **3a***



To an oven-dried 100 mL Schlenk flask, was added $Pd_2(dba)_3 \cdot CHCl_3$ (0.225 mmol, 0.233 g) and XantPhos (0.90 mmol, 0.521 g), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (10 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, isatoic anhydride **1a** (6.00 mmol, 1.06 g) and vinylethylene carbonate **2a** (9.00 mmol, 1.71 g) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/

dichloromethane = 3/1, then petroleum ether/ethyl acetate = 10/1) to afford **3a** (0.81 g) as white solid in 76% yields.

(*Z*)-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3a



Prepared according to the general procedure to afford **3a** (30.7 mg, m. p. = 115 – 117 °C) in 95% yield as white solid.

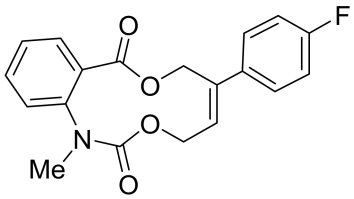
NMR and HRMS data for the product **3a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.44 (m, 3H), 7.38 – 7.35 (m, 2H), 7.33 – 7.31 (m, 1H), 7.24 – 7.23 (m, 2H), 6.08 (t, *J* = 7.2 Hz, 1H), 5.23 (br s, 2H), 4.67 (s, 2H), 3.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.8, 154.1, 145.7, 141.0, 140.7, 131.2, 130.0, 128.5, 128.1, 127.4, 126.7, 125.4, 124.5, 64.1, 61.5, 38.1.

HRMS (ESI) m/z calculated for $C_{19}H_{17}NO_4$+Na^+: 346.1050, found: 346.1047.

(*Z*)-6-(4-fluorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3b



Prepared according to the general procedure to afford **3b** (26.6 mg) in 78% yield as colorless semisolid.

NMR and HRMS data for the product **3b**:

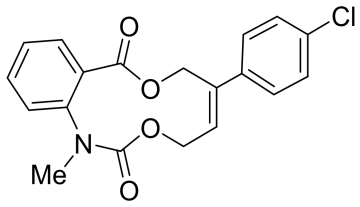
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.25 – 7.22 (m, 2H), 7.07 – 7.03 (m, 2H), 6.04 (t, *J* = 7.2 Hz, 1H), 5.19 (br s, 2H), 4.65 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.8, 162.7 (d, *J* = 245.6 Hz, 1C), 154.0, 144.7, 140.8,

137.1, 131.2, 130.0, 128.6 (d, J = 7.2 Hz, 1C), 127.4, 125.4, 124.4 (d, J = 28.7 Hz, 1C), 115.4 (d, J = 21.5 Hz, 1C), 64.3, 61.3, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}FNO_4$+Na^+: 364.0956, found: 364.0952.

(*Z*)-6-(4-chlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3c



Prepared according to the general procedure to afford **3c** (32.9 mg, m. p. = 120 – 123 °C) in 92% yield as white solid.

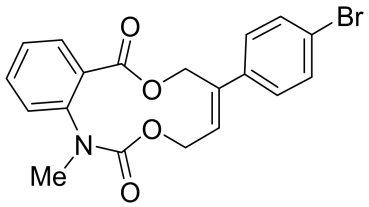
NMR and HRMS data for the product **3c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 6.06 (t, J = 6.6 Hz, 1H), 5.18 (br s, 2H), 4.65 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.8, 154.0, 144.5, 140.8, 139.5, 134.1, 131.3, 129.9, 128.7, 128.2, 127.4, 125.4, 124.9, 124.6, 64.1, 61.3, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}ClNO_4$+Na^+: 380.0660(^{35}Cl), 382.0631 (^{37}Cl), found: 380.0667, 382.0636.

(*Z*)-6-(4-bromophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3d



Prepared according to the general procedure to afford **3d** (35.0 mg, m. p. = 114 – 118 °C) in 87% yield as yellowish solid.

NMR and HRMS data for the product **3d**:

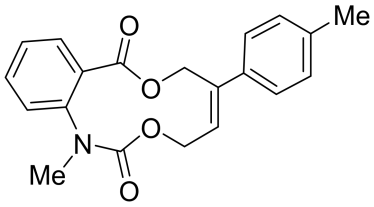
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, J = 7.2 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.34 (d, J = 7.2 Hz, 2H), 7.25 – 7.21 (m, 2H), 6.06 (t, J = 6.6 Hz, 1H), 5.17 (br s, 2H), 4.65 (s, 2H), 3.41

(s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.7, 154.0, 144.5, 140.8, 140.0, 131.6, 131.3, 129.9, 128.5, 127.4, 125.4, 124.9, 124.6, 122.3, 64.0, 61.2, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}BrNO_4$+Na^+:424.0155 (^{79}Br), 426.0134 (^{81}Br), found: 424.0159, 426.0141.

(*Z*)-1-methyl-6-(*p*-tolyl)-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3e



Prepared according to the general procedure to afford **3e** (31.3 mg, m. p. = 97 – 100 °C) in 93% yield as white solid.

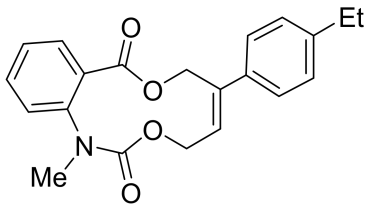
NMR and HRMS data for the product **3e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.06 (t, *J* = 7.2 Hz, 1H), 5.22 (br s, 2H), 4.65 (s, 2H), 3.42 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 154.1, 145.7, 140.7, 138.0, 131.1, 130.0, 129.2, 128.0, 127.4, 126.6, 125.3, 124.5, 123.6, 64.0, 61.6, 38.1, 21.1.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_4$+Na^+: 360.1206, found: 360.1215.

(*Z*)-6-(4-ethylphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3f



Prepared according to the general procedure to afford **3f** (31.6 mg) in 90% yield as colorless semisolid.

NMR and HRMS data for the product **3f**:

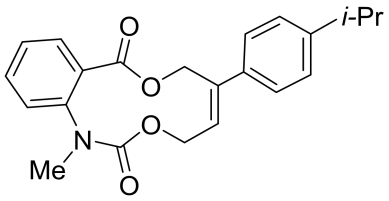
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.54 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.40

(d, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.07 (t, *J* = 7.2 Hz, 1H), 5.22 (br s, 2H), 4.65 (s, 2H), 3.41 (s, 3H), 2.65 (q, *J* = 7.8 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 154.2, 145.7, 144.5, 140.7, 138.3, 131.2, 130.0, 128.0, 127.4, 126.7, 125.4, 124.5, 123.7, 64.0, 61.6, 38.1, 28.5, 15.5.

HRMS (ESI) m/z calculated for $C_{21}H_{21}NO_4$+Na^+: 374.1363, found: 374.1360.

(*Z*)-6-(4-*iso*-propylphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3g



Prepared according to the general procedure to afford **3g** (32.5 mg) in 89% yield as colorless semisolid.

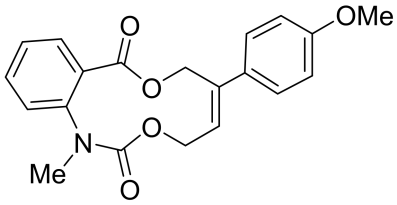
NMR and HRMS data for the product **3g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.54 (d, *J* = 6.6 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.24 – 7.21 (m, 4H), 6.07 (t, *J* = 6.0 Hz, 1H), 5.23 (br s, 2H), 4.66 (s, 2H), 3.41 (s, 3H), 2.95 – 2.87 (m, 1H), 1.25 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 154.2, 149.1, 145.7, 140.8, 138.4, 131.1, 130.1, 127.4, 126.7, 126.6, 125.3, 124.5, 123.7, 64.0, 61.6, 38.1, 33.8, 23.9.

HRMS (ESI) m/z calculated for $C_{22}H_{23}NO_4$+Na^+: 388.1519, found: 388.1519.

(*Z*)-6-(4-methoxyphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3h



Prepared according to the general procedure to afford **3h** (32.8 mg) in 93% yield as colorless semisolid.

NMR and HRMS data for the product **3h**:

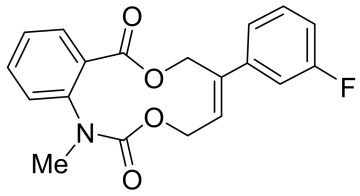
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.53 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.23 (d, *J*

= 7.8 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.03 (t, *J* = 7.2 Hz, 1H), 5.20 (br s, 2H), 4.64 (s, 2H), 3.81 (s, 3H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 159.6, 154.2, 145.5, 140.7, 133.4, 131.1, 130.0, 127.9, 127.4, 125.3, 124.5, 122.8, 113.9, 64.0, 61.6, 55.3, 38.1.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_5$+Na^+: 376.1155, found: 376.1158.

(*Z*)-6-(3-fluorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3i



Prepared according to the general procedure to afford **3i** (28.0 mg) in 82% yield as colorless semisolid.

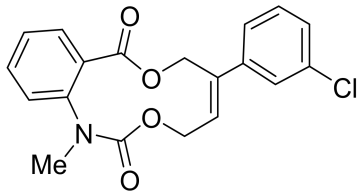
NMR and HRMS data for the product **3i**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.56 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.25 – 7.23 (m, 3H), 7.19 (d, *J* = 9.6 Hz, 1H), 7.01 (td, *J* = 8.4, 2.4 Hz, 1H), 6.10 (t, *J* = 7.2 Hz, 1H), 5.19 (br s, 2H), 4.66 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.8, 165.5 (d, *J* = 224.2 Hz, 1C), 154.0, 144.5, 143.3 (d, *J* = 8.6 Hz, 1C), 140.8, 131.3, 130.0 (d, *J* = 8.6 Hz, 1C), 129.9, 127.5, 125.4 (d, *J* = 8.6 Hz, 1C), 124.6, 122.5, 115.1 (d, *J* = 20.1 Hz, 1C), 113.9 (d, *J* = 21.5 Hz, 1C), 64.0, 61.2, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}FNO_4$+H^+: 342.1136, found: 342.1133.

(*Z*)-6-(3-chlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3j



Prepared according to the general procedure to afford **3j** (32.6 mg, m. p. = 121 – 127 °C) in 91% yield as yellowish solid.

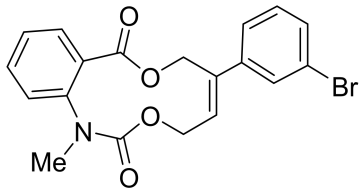
NMR and HRMS data for the product **3j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.56 (d, *J* = 7.2 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.38 – 7.32 (m, 1H), 7.31 – 7.28 (m, 2H), 7.25 – 7.22 (m, 2H), 6.08 (t, *J* = 7.2 Hz, 1H), 5.18 (br s, 2H), 4.66 (s, 2H), 3.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.8, 154.0, 144.3, 142.9, 140.8, 134.4, 131.3, 129.9, 129.8, 128.2, 127.5, 127.0, 125.5, 125.1, 124.6, 64.0, 61.2, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}ClNO_4$+Na^+: 380.0660(^{35}Cl), 382.0631 (^{37}Cl), found: 380.0656, 382.0618.

(*Z*)-6-(3-bromophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3k



Prepared according to the general procedure to afford **3k** (35.0 mg, m. p. = 123 – 127 °C) in 87% yield as white solid.

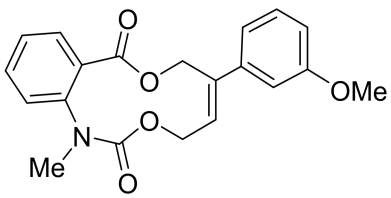
NMR and HRMS data for the product **3**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.62 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.21 (m, 3H), 6.07 (t, *J* = 7.2 Hz, 1H), 5.17 (br s, 2H), 4.65 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.7, 154.0, 144.1, 143.1, 140.8, 131.3, 131.1, 130.0, 129.9, 127.5, 125.5, 125.4, 124.5, 122.5, 64.0, 61.2, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}BrNO_4$+Na^+:424.0155 (^{79}Br), 426.0134 (^{81}Br), found: 424.0154, 426.0138.

(*Z*)-6-(3-methoxyphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3l



Prepared according to the general procedure to afford **3l** (31.8 mg) in 90% yield as colorless

semisolid.

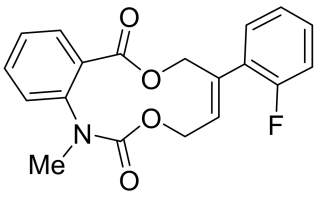
NMR and HRMS data for the product **3l**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.56 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.01 (s, 1H), 6.87 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.09 (t, *J* = 6.0 Hz, 1H), 5.22 (br s, 2H), 4.66 (s, 2H), 3.83 (s, 3H), 3.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.8, 159.6, 154.1, 145.5, 142.5, 140.8, 131.2, 129.9, 129.5, 127.5, 125.4, 124.5, 119.2, 113.5, 112.5, 64.1, 61.5, 55.3, 38.1.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_5$+Na^+: 376.1155, found: 376.1150.

(*Z*)-6-(2-fluorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3m



Prepared according to the general procedure to afford **3m** (29.3 mg) in 86% yield as colorless semisolid.

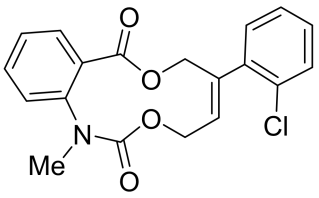
NMR and HRMS data for the product **3m**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.54 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 9.0 Hz, 1H), 6.08 (t, *J* = 6.6 Hz, 1H), 5.15 (br s, 2H), 4.67 (s, 2H), 3.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.6, 159.5 (d, *J* = 245.6 Hz, 1C), 154.0, 140.8 (d, *J* = 15.8 Hz, 1C), 131.2, 130.5, 130.1, 129.7 (d, *J* = 14.4 Hz, 1C), 129.2 (d, *J* = 14.4 Hz, 1C), 127.4, 127.2, 125.4, 124.5, 124.4, 115.5 (d, *J* = 21.6 Hz, 1C), 64.2 (d, *J* = 4.2 Hz, 1C), 61.2, 37.9.

HRMS (ESI) m/z calculated for $C_{19}H_{16}FNO_4$+Na^+: 364.0956, found: 364.0958.

(*Z*)-6-(2-chlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3n



Prepared according to the general procedure to afford **3n** (27.9 mg) in 78% yield as colorless semisolid.

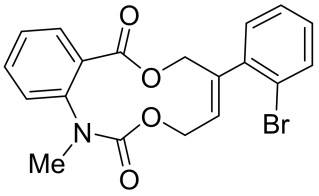
NMR and HRMS data for the product **3n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.20 (m, 4H), 5.94 (t, *J* = 6.6 Hz, 1H), 5.12 (br s, 2H), 4.68 (s, 2H), 3.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.6, 154.0, 143.5, 141.0, 131.8, 131.3, 131.2, 130.1, 129.2, 129.1, 127.7, 127.3, 127.1, 125.4, 124.6, 64.4, 61.2, 37.9.

HRMS (ESI) m/z calculated for $C_{19}H_{16}ClNO_4$+Na^+: 380.0660(^{35}Cl), 382.0631 (^{37}Cl), found: 380.0656, 382.0618.

(*Z*)-6-(2-bromophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3o



Prepared according to the general procedure to afford **3o** (30.2 mg) in 75% yield as colorless semisolid.

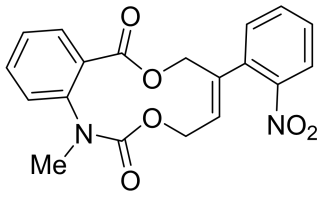
NMR and HRMS data for the product **3o**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 5.90 (t, *J* = 6.6 Hz, 1H), 5.11 (br s, 2H), 4.68 (s, 2H), 3.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.6, 154.0, 144.6, 142.9, 141.0, 132.3, 131.3, 131.3, 130.0, 129.2, 127.7, 127.6, 127.1, 125.4, 124.5, 121.6, 64.4, 61.1, 37.9.

HRMS (ESI) m/z calculated for $C_{19}H_{16}BrNO_4$+H^+: 402.0335 (^{79}Br), 404.0315 (^{81}Br), found: 402.0342, 404.0306.

(*Z*)-1-methyl-6-(2-nitrophenyl)-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3p



Prepared according to the general procedure to afford **3p** (34.2 mg) in 93% yield as colorless semisolid.

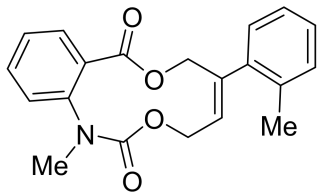
NMR and HRMS data for the product **3p**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.00 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.55 – 7.42 (m, 3H), 7.27 – 7.21 (m, 2H), 5.88 (t, *J* = 7.2 Hz, 1H), 5.12 (br s, 2H), 4.61 (s, 2H), 3.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 153.9, 147.5, 143.2, 140.9, 137.3, 133.7, 132.5, 131.2, 130.6, 128.8, 127.2, 125.5, 125.3, 124.5, 124.1, 65.1, 60.8, 37.7

HRMS (ESI) m/z calculated for $C_{19}H_{16}N_2O_6$+Na^+: 391.0901, found: 391.0902.

(*Z*)-1-methyl-6-(*o*-tolyl)-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3q



Prepared according to the general procedure to afford **3q** (25.6 mg) in 76% yield as colorless semisolid.

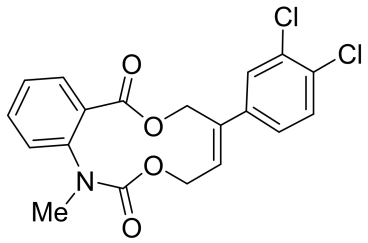
NMR and HRMS data for the product **3q**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.63 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.22 – 7.16 (m, 3H), 5.70 (t, *J* = 6.0 Hz, 1H), 5.01 (br s, 2H), 4.68 (s, 2H), 3.45 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.6, 154.1, 143.5, 141.3, 135.3, 131.6, 130.3, 129.4, 128.9, 128.3, 127.7, 125.8, 125.5, 125.4, 124.5, 64.7, 61.6, 38.0, 19.8.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_4$+Na^+: 360.1206, found: 360.1207.

(*Z*)-6-(3,4-dichlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3r



Prepared according to the general procedure to afford **3r** (34.5 mg) in 88% yield as colorless semisolid.

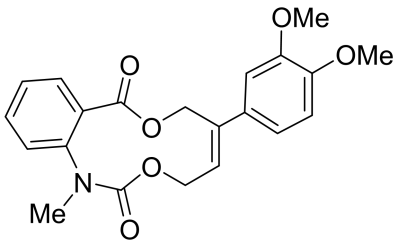
NMR and HRMS data for the product **3r**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.52 (m, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.08 (t, *J* = 6.6 Hz, 1H), 5.14 (br s, 2H), 4.65 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.7, 153.9, 143.3, 141.1, 140.8, 132.6, 132.2, 131.4, 130.4, 129.8, 128.8, 127.4, 126.3, 125.8, 125.5, 124.6, 64.0, 61.0, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{15}Cl_2NO_4$+Na^+: 414.0270 (^{35}Cl), 416.0241 (^{37}Cl), found: 414.0273, 416.0249.

(*Z*)-6-(3,4-dimethoxyphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3s



Prepared according to the general procedure to afford **3s** (27.6 mg) in 72% yield as colorless semisolid.

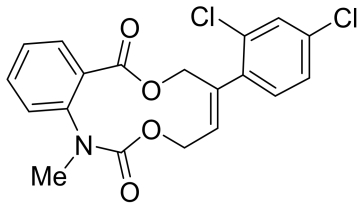
NMR and HRMS data for the product **3s**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.54 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.08 – 6.96 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.04 (t, *J* = 6.6 Hz, 1H), 5.21 (br s, 2H), 4.65 (s, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 154.1, 149.2, 148.8, 145.5, 140.7, 133.8, 131.2, 130.0, 127.4, 125.4, 124.5, 123.0, 119.4, 110.9, 110.0, 64.2, 61.6, 55.9, 38.0, 29.7.

HRMS (ESI) m/z calculated for $C_{21}H_{21}NO_6$+Na^+: 406.1261, found: 406.1257.

(*Z*)-6-(2,4-dichlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3t



Prepared according to the general procedure to afford **3t** (28.2 mg, m. p. = 112 – 117 °C) in 72% yield as white solid.

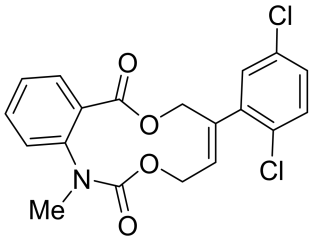
NMR and HRMS data for the product **3t**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.54 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.29 – 7.23 (m, 3H), 5.93 (t, *J* = 6.6 Hz, 1H), 5.06 (br s, 2H), 4.66 (s, 2H), 3.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.6, 154.0, 142.3, 141.0, 139.5, 134.3, 132.6, 132.1, 131.4, 130.1, 129.0, 127.8, 127.6, 127.4, 125.5, 124.6, 64.4, 61.0, 37.8.

HRMS (ESI) m/z calculated for $C_{19}H_{15}Cl_2NO_4$+Na^+: 414.0270 (^{35}Cl), 416.0241 (^{37}Cl), found: 414.0274, 416.0248.

(*Z*)-6-(2,5-dichlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3u



Prepared according to the general procedure to afford **3u** (26.7 mg) in 68% yield as colorless semisolid.

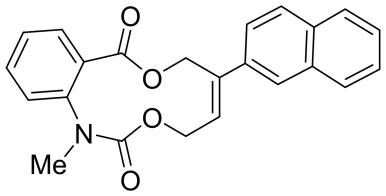
NMR and HRMS data for the product **3u**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.56 (d, *J* = 6.6 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 5.93 (t, *J* = 6.0 Hz, 1H), 5.07 (br s, 2H), 4.67 (s, 2H), 3.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.5, 154.0, 142.3, 142.1, 141.0, 132.9, 131.4, 130.9, 130.4, 130.3, 129.8, 129.2, 128.0, 127.8, 125.5, 124.6, 64.1, 60.9, 37.9.

HRMS (ESI) m/z calculated for $C_{19}H_{15}Cl_2NO_4$+Na^+: 414.0270 (^{35}Cl), 416.0241 (^{37}Cl), found: 414.0274, 416.0253.

(*Z*)-1-methyl-6-(naphthalen-2-yl)-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3v



Prepared according to the general procedure to afford **3v** (29.8 mg, m. p. = 118 – 122 °C) in 80% yield as white solid.

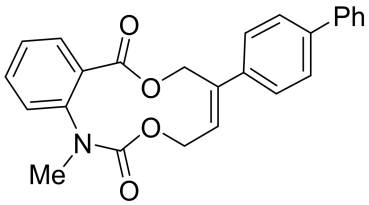
NMR and HRMS data for the product **3v**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.92 (s, 1H), 7.89 – 7.80 (m, 4H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.51 – 7.43 (m, 3H), 7.24 – 7.21 (m, 1H), 6.22 (t, *J* = 6.6 Hz, 1H), 5.34 (br s, 2H), 4.73 (s, 2H), 3.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 154.2, 145.6, 140.8, 138.3, 133.2, 133.0, 131.2, 130.0, 128.2, 127.6, 126.4, 126.3, 125.8, 125.4, 124.9, 124.8, 124.6, 64.1, 61.6, 38.1.

HRMS (ESI) m/z calculated for $C_{23}H_{19}NO_4$+Na^+: 396.1206, found: 396.1216.

(*Z*)-6-([1,1'-biphenyl]-4-yl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3w



Prepared according to the general procedure to afford **3w** (33.9 mg, m. p. = 177 – 179 °C) in 85% yield as white solid.

NMR and HRMS data for the product **3w**:

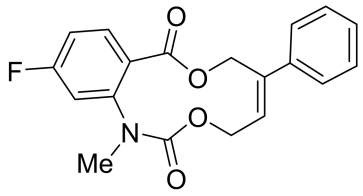
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.64 – 7.59 (m, 4H), 7.56 – 7.55 (m, 3H), 7.46 – 7.44 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.15 (t, *J* = 6.6 Hz, 1H), 5.28 (br s, 2H),

4.69 (s, 2H), 3.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 154.1, 145.3, 141.0, 140.8, 140.5, 139.9, 131.2, 130.0, 128.8, 127.5, 127.2, 127.2, 127.0, 125.4, 124.6, 124.4, 64.0, 61.5, 38.1.

HRMS (ESI) m/z calculated for $C_{25}H_{21}NO_4$+Na^+: 422.1363, found: 422.1359.

(*Z*)-12-fluoro-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3x



Prepared according to the general procedure to afford **3x** (30.7 mg) in 90% yield as colorless semisolid.

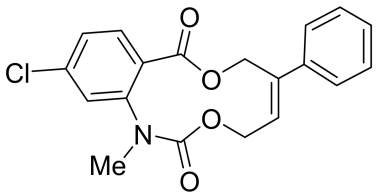
NMR and HRMS data for the product **3x**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.58 (br s, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.31 (m, 1H), 6.97 – 6.92 (m, 2H), 6.05 (br s, 1H), 5.23 (br s, 2H), 4.68 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.1, 163.9 (d, *J* = 249.9 Hz, 1C), 153.9, 145.6, 143.0, 140.9, 129.6, 128.5, 128.2, 126.7, 125.9, 124.3, 112.3 (d, *J* = 21.5 Hz, 1C), 112.00 (d, *J* = 23.1 Hz, 1C), 64.1, 61.7, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}FNO_4$+Na^+: 364.0956, found: 364.0952.

(*Z*)-12-chloro-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3y



Prepared according to the general procedure to afford **3y** (31.1 mg) in 87% yield as colorless semisolid.

NMR and HRMS data for the product **3y**:

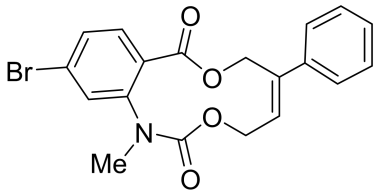
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.51 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.39

– 7.31 (m, 3H), 7.24 – 7.18 (m, 2H), 6.07 (br s, 1H), 5.23 (br s, 2H), 4.67 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.1, 153.8, 145.6, 142.2, 140.9, 136.9, 128.8, 128.6, 128.2, 126.7, 125.5, 124.9, 124.3, 64.2, 61.7, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}ClNO_4$+Na^+: 380.0660(^{35}Cl), 382.0631 (^{37}Cl), found: 380.0659, 382.0635.

(*Z*)-12-bromo-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3z



Prepared according to the general procedure to afford **3z** (34.6 mg) in 86% yield as colorless semisolid.

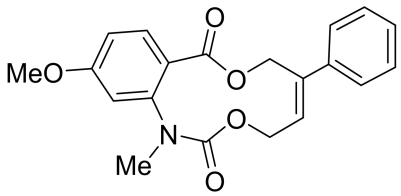
NMR and HRMS data for the product **3z**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.50 – 7.42 (m, 3H), 7.40 – 7.35 (m, 4H), 7.34 – 7.28 (m, 1H), 6.07 (t, *J* = 6.0 Hz, 1H), 5.22 (br s, 2H), 4.66 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.2, 153.8, 145.7, 142.1, 140.8, 128.8, 128.7, 128.5, 128.4, 128.2, 127.7, 126.7, 124.9, 124.2, 64.2, 61.7, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}BrNO_4$+Na^+:424.0155 (^{79}Br), 426.0134 (^{81}Br), found: 424.0155, 426.0138.

(*Z*)-12-methoxy-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3aa



Prepared according to the general procedure to afford **3aa** (28.9 mg) in 82% yield as colorless semisolid.

NMR and HRMS data for the product **3aa**:

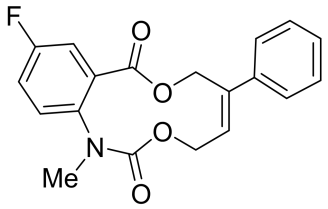
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.63 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.36

(t, *J* = 7.2 Hz, 2H), 7.33 – 7.29 (m, 1H), 6.82 – 6.72 (m, 2H), 5.98 (t, *J* = 7.2 Hz, 1H), 5.21 (br s, 2H), 4.71 (s, 2H), 3.84 (s, 3H), 3.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.5, 162.1, 154.5, 144.8, 143.0, 141.4, 130.1, 128.5, 128.0, 126.8, 124.8, 121.7, 111.2, 110.3, 63.9, 61.7, 55.6, 38.3.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_5$+Na^+: 376.1155, found: 376.1156.

(*Z*)-11-fluoro-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3ab



Prepared according to the general procedure to afford **3ab** (30.7 mg, m. p. = 124 – 126 °C) in 90% yield as white solid.

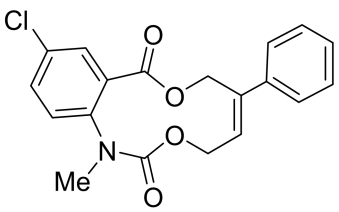
NMR and HRMS data for the product **3ab**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.47 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.28 – 7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 1H), 6.10 (t, *J* = 6.6 Hz, 1H), 5.22 (br s, 2H), 4.66 (s, 2H), 3.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.6, 159.0 (d, *J* = 245.7 Hz, 1C), 154.0, 145.6, 140.9, 136.9, 131.6 (d, *J* = 4.2 Hz, 1C), 128.6, 128.3, 126.7, 126.5 (d, *J* = 7.2 Hz, 1C), 124.5, 118.1 (d, *J* = 24.5 Hz, 1C), 114.6 (d, *J* = 24.5 Hz, 1C), 64.4, 61.5, 38.3.

HRMS (ESI) m/z calculated for $C_{19}H_{16}FNO_4$+Na^+: 364.0956, found: 364.0954.

(*Z*)-11-chloro-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3ac



Prepared according to the general procedure to afford **3ac** (29.7 mg, m. p. = 121 – 124 °C) in 83% yield as yellowish solid.

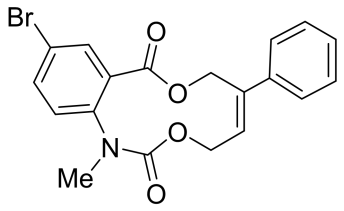
NMR and HRMS data for the product **3ac**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.52 (s, 1H), 7.46 (d, *J* = 6.6 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.35 – 7.31 (m, 1H), 7.17 (d, *J* = 9.0 Hz, 1H), 6.10 (t, *J* = 6.6 Hz, 1H), 5.23 (br s, 2H), 4.65 (s, 2H), 3.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.6, 153.9, 145.8, 140.8, 139.4, 131.3, 131.1, 130.9, 128.6, 128.3, 127.5, 126.7, 125.8, 124.3, 64.3, 61.6, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}ClNO_4+H^+$: 358.0841 (^{35}Cl), 360.0811 (^{37}Cl), found: 358.0836, 360.0801.

(*Z*)-11-bromo-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3ad



Prepared according to the general procedure to afford **3ad** (36.6 mg, m. p. = 117 – 123 °C) in 91% yield as white solid.

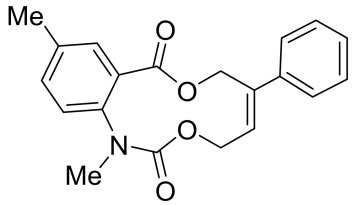
NMR and HRMS data for the product **3ad**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.66 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.11 (d, *J* = 9.0 Hz, 1H), 6.10 (t, *J* = 6.6 Hz, 1H), 5.24 (br s, 2H), 4.65 (s, 2H), 3.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.5, 153.8, 145.9, 140.8, 139.8, 134.1, 131.6, 130.3, 128.6, 128.4, 128.3, 126.7, 126.1, 124.3, 118.5, 64.3, 61.6, 38.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}BrNO_4+H^+$:402.0335 (^{79}Br), 404.0315 (^{81}Br), found: 402.0331, 404.0307.

(*Z*)-1,11-dimethyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3ae



Prepared according to the general procedure to afford **3ae** (24.9 mg, m. p. = 83 – 90 °C) in 74% yield as yellowish solid.

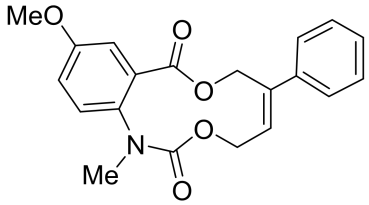
NMR and HRMS data for the product **3ae**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.48 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.33 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.08 (t, *J* = 7.2 Hz, 1H), 5.22 (br s, 2H), 4.66 (s, 2H), 3.39 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 154.3, 145.6, 141.0, 138.2, 135.4, 131.8, 129.7, 128.5, 128.1, 127.9, 126.8, 124.5, 124.5, 64.0, 61.4, 38.1, 20.7.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_4$+Na^+: 360.1206, found: 360.1194.

(*Z*)-11-methoxy-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3af



Prepared according to the general procedure to afford **3af** (25.4 mg) in 72% yield as colorless semisolid.

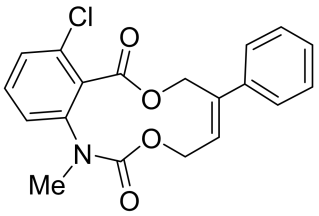
NMR and HRMS data for the product **3af**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.48 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 6.6 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 3.0 Hz, 1H), 6.98 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.08 (t, *J* = 7.2 Hz, 1H), 5.21 (br s, 2H), 4.66 (s, 2H), 3.82 (s, 3H), 3.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.5, 156.8, 154.4, 145.3, 141.1, 133.8, 130.9, 128.5, 128.1, 126.8, 126.1, 124.7, 116.8, 112.5, 64.2, 61.4, 55.6, 38.3.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_5$+Na^+: 376.1155, found: 376.1149.

(*Z*)-10-chloro-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3ag



Prepared according to the general procedure to afford **3ag** (32.2 mg, m. p. = 74 – 82 °C) in 90% yield as yellowish solid.

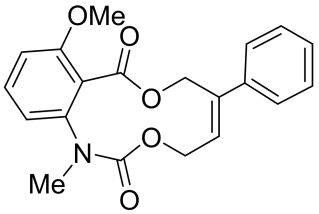
NMR and HRMS data for the product **3ag**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.52 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.31 (m, 4H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.17 (t, *J* = 7.2 Hz, 1H), 5.22 (br s, 2H), 4.65 (s, 2H), 3.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.7, 153.3, 145.4, 142.1, 140.6, 131.6, 131.0, 130.8, 128.5, 128.2, 127.1, 127.0, 124.1, 123.4, 65.4, 61.4, 38.1.

HRMS (ESI) m/z calculated for $C_{19}H_{16}ClNO_4$+Na^+: 380.0660(^{35}Cl), 382.0631 (^{37}Cl), found: 380.0662, 382.0636.

(*Z*)-10-methoxy-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3ah



Prepared according to the general procedure to afford **3ah** (31.1 mg) in 88% yield as colorless semisolid.

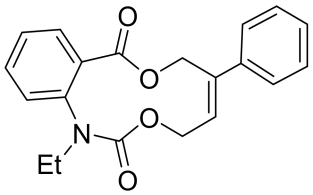
NMR and HRMS data for the product **3ah**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.52 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.32 – 7.28 (m, 1H), 6.83 (dd, *J* = 12.0, 8.4 Hz, 2H), 6.14 (t, *J* = 7.2 Hz, 1H), 5.19 (br s, 2H), 4.66 (s, 2H), 3.87 (s, 3H), 3.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.9, 156.4, 153.6, 145.0, 141.7, 141.0, 130.9, 128.4, 128.1, 127.1, 124.2, 121.6, 117.2, 108.9, 65.5, 61.4, 56.2, 37.9.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_5$+Na^+: 376.1155, found: 376.1151.

(*Z*)-1-ethyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3ai



Prepared according to the general procedure to afford **3ai** (28.6 mg, m. p. = 109 – 113 °C) in 85% yield as yellowish solid.

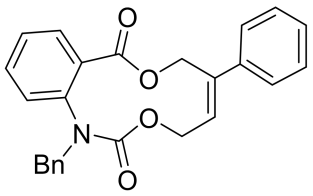
NMR and HRMS data for the product **3ai**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.57 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H),7.29 – 7.21 (m, 2H), 6.08 (t, *J* = 7.2 Hz, 1H), 5.21 (br s, 2H), 4.66 (s, 2H), 3.89 (br s, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.6, 153.7, 145.6, 141.1, 139.5, 131.2, 130.8, 128.5, 128.1, 127.6, 126.7, 125.5, 124.9, 124.6, 64.0, 61.4, 46.0, 13.2.

HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_4$+Na^+: 360.1206, found: 360.1204.

(*Z*)-1-benzyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3aj



Prepared according to the general procedure to afford **3aj** (27.1 mg, m. p. = 170 – 173 °C) in 68% yield as white solid.

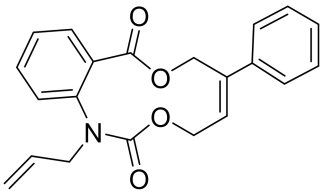
NMR and HRMS data for the product **3aj**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.28 (m, 7H), 7.25 – 7.23 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.09 (t, *J* = 7.2 Hz, 1H), 5.40 – 4.91 (m, 4H), 4.73 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.7, 154.5, 145.8, 141.0, 140.0, 137.5, 131.2, 129.8, 128.5, 128.4, 128.2, 127.8, 127.6, 127.3, 126.7, 125.5, 124.4, 124.2, 63.8, 61.8, 54.4.

HRMS (ESI) m/z calculated for $C_{25}H_{21}NO_4$+Na^+: 422.1363, found: 422.1362.

(*Z*)-1-allyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3ak



Prepared according to the general procedure to afford **3ak** (25.8 mg, m. p. = 108 – 110 °C) in 74% yield as white solid.

NMR and HRMS data for the product **3ak**:

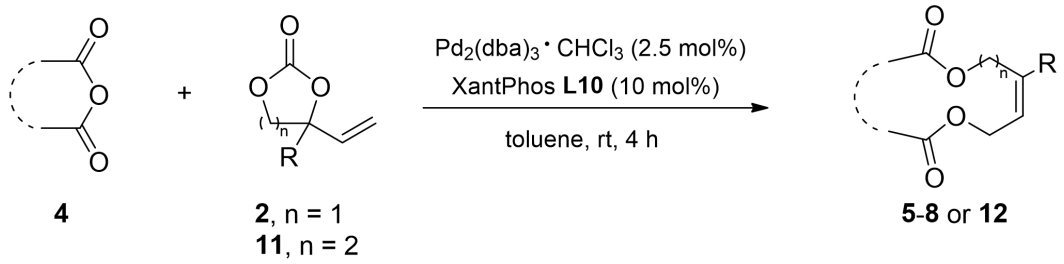
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.56 (d, *J* = 6.6 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.10 – 6.00 (m, 2H), 5.37 – 5.05 (m, 4H), 4.68 (br s, 2H), 4.43 (br s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.7, 153.8, 145.8, 141.0, 139.9, 133.9, 131.1, 130.0, 128.5, 128.1, 127.5, 126.7, 125.4, 124.4, 116.9, 63.9, 61.6, 53.7.

HRMS (ESI) m/z calculated for $C_{21}H_{19}NO_4$+Na^+: 372.1206, found: 372.1211.

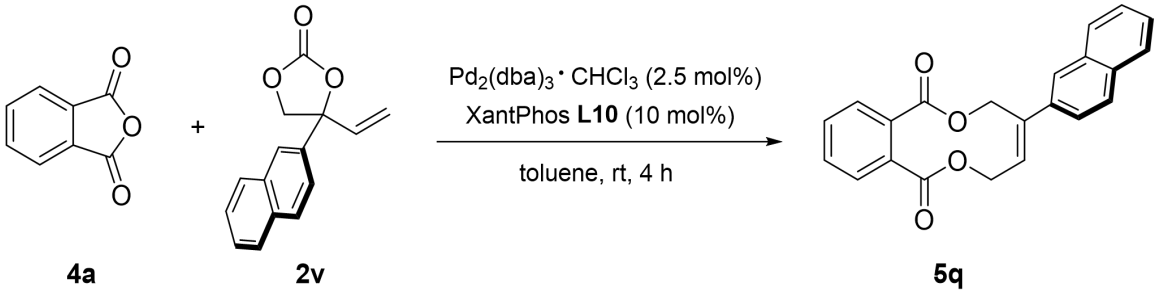
5. General Procedure for the Cyclisation of Cyclic Anhydride and VECs

*General procedure for the synthesis of 10-, 11- or 12-membered products **5**, **6** or **7***



To an oven-dried Schlenk tube was added $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%) and XantPhos (10 mol%), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, cyclic anhydrides **4** or **8** (0.10 mmol) and vinylethylene carbonates **2** or **12** (0.15 mmol) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 3/1, then petroleum ether/ethyl acetate = 30/1 to 10/1) to afford the corresponding products in 52–88% yields, which were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

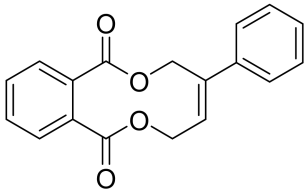
*Gram-scale synthesis of the 10-membered lactone **5q***



To an oven-dried 100 mL Schlenk flask, was added $Pd_2(dba)_3 \cdot CHCl_3$ (0.225 mmol, 0.233 g) and XantPhos (0.90 mmol, 0.521 g), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (10 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, phthalic anhydride **1a** (6.00 mmol, 0.89 g) and vinylethylene carbonate **2v** (9.00 mmol, 2.16 g) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/

dichloromethane = 3/1, then petroleum ether/ethyl acetate = 30:1) to afford **5q** (0.51 g) as white solid in 57% yields.

(*Z*)-4-phenyl-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5a



Prepared according to the general procedure to afford **5a** (23.5 mg, m. p. = 82 – 90 °C) in 80% yield as white solid.

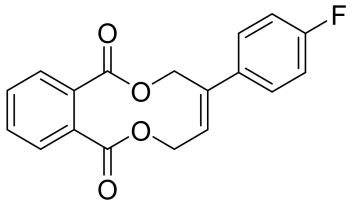
NMR and HRMS data for the product **5a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.62 – 7.58 (m, 2H), 7.51 – 7.48 (m, 2H), 7.39 – 7.35 (m, 2H), 7.34 – 7.30 (m, 1H), 6.27 (t, *J* = 6.6 Hz, 1H), 5.19 (s, 2H), 4.95 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 168.0, 143.8, 140.8, 132.7, 132.6, 131.6, 129.1, 129.1, 128.6, 128.2, 126.7, 126.5, 124.8, 66.2, 62.1.

HRMS (ESI) m/z calculated for $C_{18}H_{14}O_4$+Na^+: 317.0784, found: 317.0783.

(*Z*)-4-(4-fluorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5b



Prepared according to the general procedure to afford **5b** (25.6 mg, m. p. = 150 – 152 °C) in 82% yield as white solid.

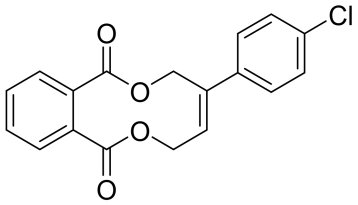
NMR and HRMS data for the product **5b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.58 (m, 2H), 7.50 – 7.46 (m, 2H), 7.05 (t, *J* = 9.0 Hz, 2H), 6.22 (t, *J* = 6.6 Hz, 1H), 5.14 (s, 2H), 4.93 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.3, 168.1, 162.7 (d, *J* = 247.1 Hz, 1C), 143.1, 136.9 (d, *J* = 4.4 Hz, 1C), 132.8, 132.5, 131.7 (d, *J* = 11.6 Hz, 1C), 129.1, 129.1, 128.6,128.5, 126.3, 115.5 (d, *J* = 21.6 Hz, 1C), 66.2, 62.1.

HRMS (ESI) m/z calculated for $C_{18}H_{13}FO_4$+Na^+: 335.0690, found: 335.0682.

(*Z*)-4-(4-chlorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5c



Prepared according to the general procedure to afford **5c** (26.3 mg, m. p. = 132 – 138 °C) in 80% yield as white solid.

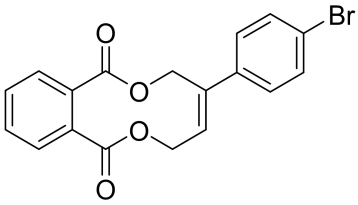
NMR and HRMS data for the product **5c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.59 (m, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.26 (t, *J* = 6.0 Hz, 1H), 5.14 (s, 2H), 4.94 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.3, 168.0, 143.0, 139.3, 132.7, 132.5, 131.8, 131.7, 129.1, 128.8, 128.1, 127.0, 125.7, 66.0, 62.0.

HRMS (ESI) m/z calculated for $C_{18}H_{13}ClO_4$+Na^+: 351.0395(^{35}Cl), 353.0365 (^{37}Cl), found: 351.0401, 353.0367.

(*Z*)-4-(4-bromophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5d



Prepared according to the general procedure to afford **5d** (26.9 mg, m. p. = 139 – 141 °C) in 72% yield as white solid.

NMR and HRMS data for the product **5d**:

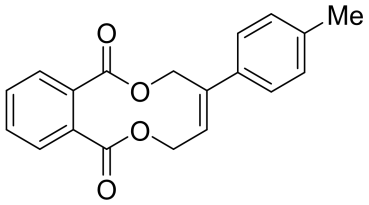
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.64 – 7.58 (m, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 6.26 (t, *J* = 6.6 Hz, 1H), 5.13 (s, 2H), 4.93 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.3, 168.0, 143.0, 139.7, 132.7, 132.4, 131.7, 131.7, 131.7, 129.1, 128.4, 127.0, 122.4, 65.9, 62.0.

HRMS (ESI) m/z calculated for $C_{18}H_{13}BrO_4$+Na^+: 394.9889 (^{79}Br), 396.9869 (^{81}Br), found:

394.9892, 396.9875.

(*Z*)-4-(*p*-tolyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5e



Prepared according to the general procedure to afford **5e** (25.6 mg, m. p. = 101 – 105 °C) in 83% yield as white solid.

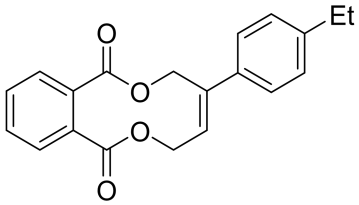
NMR and HRMS data for the product **5e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.62 – 7.58 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.24 (t, *J* = 6.0 Hz, 1H), 5.17 (s, 2H), 4.94 (d, *J* = 6.6 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 168.1, 143.8, 138.2, 137.9, 132.8, 132.7, 131.6, 129.3, 129.1, 126.6, 125.8, 125.6, 124.9, 66.3, 62.2, 21.1.

HRMS (ESI) m/z calculated for $C_{19}H_{16}O_4$+Na^+: 331.0941, found: 331.0935.

(*Z*)-4-(4-ethylphenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5f



Prepared according to the general procedure to afford **5f** (26.1 mg, m. p. = 63 – 66 °C) in 81% yield as white solid.

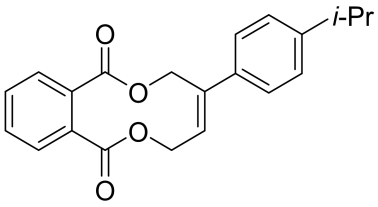
NMR and HRMS data for the product **5f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.76 (m, 2H), 7.62 – 7.57 (m, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.23 (t, *J* = 6.6 Hz, 1H), 5.18 (s, 2H), 4.94 (d, *J* = 6.0 Hz, 2H), 2.65 (q, *J* = 7.8 Hz, 2H), 1.24 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 168.0, 144.5, 143.8, 138.1, 132.8, 132.6, 131.6, 129.1, 128.1, 126.7, 125.6, 66.3, 62.2, 28.5, 15.5.

HRMS (ESI) m/z calculated for $C_{20}H_{18}O_4$+Na^+: 345.1097, found: 345.1095.

(*Z*)-4-(4-*iso*-propylphenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5g



Prepared according to the general procedure to afford **5g** (25.5 mg, m. p. = 54 – 58 °C) in 76% yield as white solid.

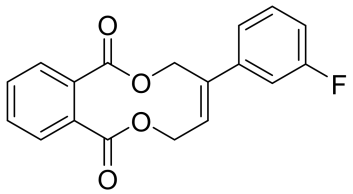
NMR and HRMS data for the product **5g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.58 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.25 (t, *J* = 6.6 Hz, 1H), 5.18 (s, 2H), 4.94 (d, *J* = 6.0 Hz, 2H), 2.95 – 2.87 (m, 1H), 1.25 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 168.0, 149.1, 143.8, 138.2, 136.0, 132.8, 132.7, 131.6, 129.1, 126.7, 126.7, 125.7, 66.3, 62.2, 33.8, 23.9.

HRMS (ESI) m/z calculated for $C_{21}H_{20}O_4$+Na^+: 359.1254, found: 359.1259.

(*Z*)-4-(3-fluorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5h



Prepared according to the general procedure to afford **5h** (23.1 mg, m. p. = 81 – 85 °C) in 74% yield as white solid.

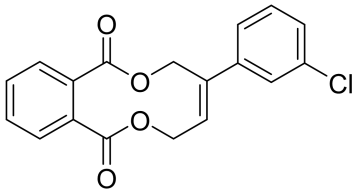
NMR and HRMS data for the product **5h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.59 (m, 2H), 7.36 – 7.30 (m,2H), 7.22 (dt, *J* = 10.2, 2.4 Hz, 1H), 7.02 (td, *J* = 8.4, 3.0 Hz, 1H), 6.30 (t, *J* = 6.0 Hz, 1H), 5.15 (s, 2H), 4.94 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 167.9, 162.8 (d, *J* = 244.1 Hz, 1C), 143.0 (d, *J* = 7.2 Hz, 1C), 142.7, 132.7, 132.5, 131.7 (d, *J* = 2.9 Hz, 1C), 130.1 (d, *J* = 7.2 Hz, 1C), 129.2, 129.1, 127.6, 125.7, 122.4 (d, *J* = 5.7 Hz, 1C), 115.1 (d, *J* = 21.6 Hz, 1C), 113.8 (d, *J* = 21.5 Hz, 1C), 66.0, 61.9.

HRMS (ESI) m/z calculated for $C_{18}H_{13}FO_4$+Na^+: 335.0690, found: 335.0699.

(*Z*)-4-(3-chlorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5i



Prepared according to the general procedure to afford **5i** (25.0 mg, m. p. = 91 – 93 °C) in 76% yield as white solid.

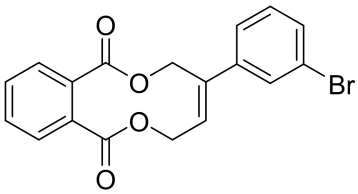
NMR and HRMS data for the product **5i**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.58 (m, 2H), 7.48 (s, 1H), 7.40 – 7.36 (m, 1H), 7.31 – 7.28 (m, 2H), 6.29 (t, *J* = 6.0 Hz, 1H), 5.14 (s, 2H), 4.94 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 167.9, 142.6, 134.5, 132.6, 132.4, 131.7, 131.7, 129.8, 129.2, 129.1, 128.3, 127.7, 126.9, 124.9, 65.9, 61.9.

HRMS (ESI) m/z calculated for $C_{18}H_{13}ClO_4$+Na^+: 351.0395(^{35}Cl), 353.0365 (^{37}Cl), found: 351.0392, 353.0356.

(*Z*)-4-(3-bromophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5j



Prepared according to the general procedure to afford **5j** (26.5 mg, m. p. = 91 – 94 °C) in 71% yield as white solid.

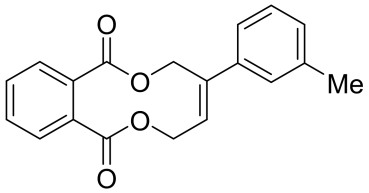
NMR and HRMS data for the product **5j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.65 – 7.58 (m, 3H), 7.45 (t, *J* = 9.6 Hz, 2H), 7.24 (t, *J* = 8.4 Hz, 1H), 6.29 (t, *J* = 6.0 Hz, 1H), 5.13 (s, 2H), 4.94 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 167.9, 142.9, 142.5, 132.6, 132.4, 131.7, 131.2, 130.1, 129.8, 129.2, 129.1, 127.8, 125.4, 122.7, 65.9, 61.9.

HRMS (ESI) m/z calculated for $C_{18}H_{13}BrO_4$+H^+:373.0070 (^{79}Br), 375.0050 (^{81}Br), found: 373.0083, 375.0042.

(*Z*)-4-(*m*-tolyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5k



Prepared according to the general procedure to afford **5k** (22.2 mg, m. p. = 75 – 78 °C) in 72% yield as white solid.

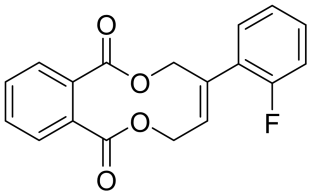
NMR and HRMS data for the product **5k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.57 (m, 2H), 7.32 – 7.23 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.26 (t, *J* = 6.0 Hz, 1H), 5.18 (s, 2H), 4.94 (d, *J* = 5.4 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.5, 168.0, 143.8, 140.8, 138.2, 132.8, 132.7, 131.6, 129.2, 129.1, 129.0, 128.5, 127.4, 126.3, 123.8, 66.3, 62.1, 21.4.

HRMS (ESI) m/z calculated for $C_{19}H_{16}O_4$+Na^+: 331.0941, found: 331.0941.

(*Z*)-4-(2-fluorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5l



Prepared according to the general procedure to afford **5l** (22.2 mg) in 71% yield as colorless semisolid.

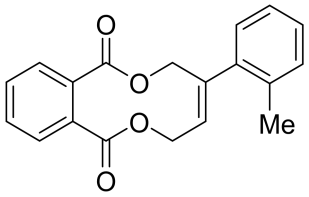
NMR and HRMS data for the product **5l**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.76 (m, 2H), 7.62 – 7.58 (m, 2H), 7.39 (td, *J* = 7.8, 1.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.25 (t, *J* = 6.0 Hz, 1H), 5.12 (s, 2H), 4.96 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.3, 167.9, 159.6 (d, *J* = 244.2 Hz, 1C), 138.7, 132.6 (d, *J* = 4.4 Hz, 1C), 131.7 (d, *J* = 5.7 Hz, 1C), 130.1(d, *J* = 4.4 Hz, 1C), 129.8, 129.8, 129.1, 129.1, 129.0, 124.4 (d, *J* = 2.9 Hz, 1C), 115.7 (d, *J* = 21.5 Hz, 1C), 65.8 (d, *J* = 5.9 Hz, 1C), 61.9.

HRMS (ESI) m/z calculated for $C_{18}H_{13}FO_4$+Na^+: 335.0690, found: 335.0700.

(*Z*)-4-(*o*-tolyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5m



Prepared according to the general procedure to afford **5m** (16.0 mg) in 52% yield as colorless semisolid.

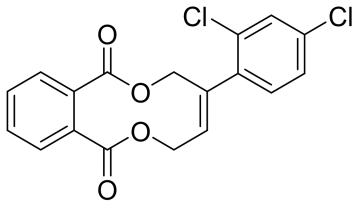
NMR and HRMS data for the product **5m**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.84 – 7.78 (m, 2H), 7.63 – 7.58 (m, 2H), 7.24 – 7.16 (m, 4H), 5.96 (t, *J* = 6.0 Hz, 1H), 5.02 (s, 2H), 4.98 (d, *J* = 6.0 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 167.9, 143.1, 141.5, 135.0, 132.7, 132.7, 131.7, 131.7, 130.3, 129.2, 129.1, 128.8, 128.1, 127.8, 125.9, 66.2, 61.9, 20.0.

HRMS (ESI) m/z calculated for $C_{19}H_{16}O_4$+Na^+: 331.0941, found: 331.0945.

(*Z*)-4-(2,4-dichlorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5n



Prepared according to the general procedure to afford **5n** (27.2 mg, m. p. = 58 – 65 °C) in 75% yield as white solid.

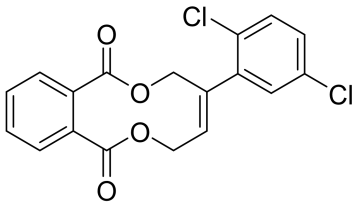
NMR and HRMS data for the product **5n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.75 (m, 2H), 7.63 – 7.58 (m, 2H), 7.40 (d, *J* = 1.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.09 (t, *J* = 6.6 Hz, 1H), 5.06 (s, 2H), 4.95 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.0, 168.0, 141.4, 139.3, 134.5, 132.7, 132.7, 132.5, 131.7, 131.7, 131.6, 130.2, 129.2, 129.1, 129.0, 127.4, 65.4, 61.8.

HRMS (ESI) m/z calculated for $C_{18}H_{12}Cl_2O_4$+Na+: 385.0005(^{35}Cl), 386.9975 (^{37}Cl), found: 385.0000, 386.9964.

(*Z*)-4-(2,5-dichlorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5o



Prepared according to the general procedure to afford **5o** (30.5 mg, m. p. = 106 – 108 °C) in 84% yield as yellowish solid.

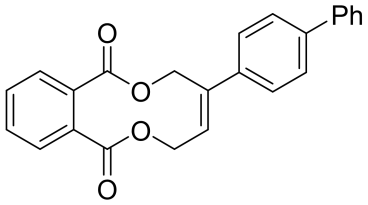
NMR and HRMS data for the product **5o**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.76 (m, 2H), 7.63 – 7.57 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.12 (t, *J* = 6.0 Hz, 1H), 5.07 (s, 2H), 4.95 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.0, 167.9, 143.3, 142.1, 141.1, 132.9, 132.6, 132.4, 131.7, 130.6, 130.5, 130.3, 129.3, 129.1, 128.4, 125.4, 65.3, 61.7.

HRMS (ESI) m/z calculated for $C_{18}H_{12}Cl_2O_4$+Na+: 385.0005(^{35}Cl), 386.9975 (^{37}Cl), found: 385.0011, 386.9982.

(*Z*)-4-([1,1'-biphenyl]-4-yl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5p



Prepared according to the general procedure to afford **5p** (28.5 mg, m. p. = 143 – 147 °C) in 77% yield as white solid.

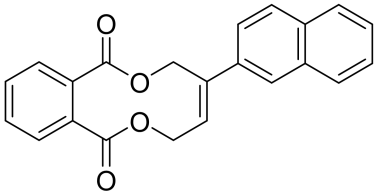
NMR and HRMS data for the product **5p**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.84 – 7.79 (m, 2H), 7.64 – 7.57 (m, 8H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 6.35 (t, *J* = 6.0 Hz, 1H), 5.22 (s, 2H), 4.98 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.5, 168.0, 143.4, 141.1, 140.4, 139.6, 132.8, 132.6, 131.7, 131.7, 129.1, 129.1, 128.8, 127.5, 127.3, 127.1, 127.0, 126.4, 66.1, 62.2.

HRMS (ESI) m/z calculated for $C_{24}H_{18}O_4$+Na^+: 393.1097, found:393.1103 .

(*Z*)-4-(naphthalen-2-yl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5q



Prepared according to the general procedure to afford **5q** (25.1 mg, m. p. = 80 – 85 °C) in 73% yield as yellowish solid.

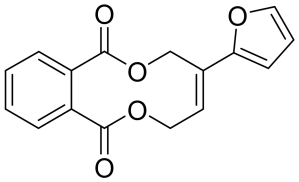
NMR and HRMS data for the product **5q**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.04 – 8.01 (m, 1H), 7.94 (s, 1H), 7.92 – 7.88 (m, 1H), 7.86 – 7.80 (m, 4H), 7.64 – 7.59 (m, 2H), 7.50 – 7.46 (m, 2H), 6.42 (t, *J* = 6.6 Hz, 1H), 5.29 (s, 2H), 5.01 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.6, 168.0, 143.7, 138.1, 136.0, 133.0, 132.8, 132.6, 131.7, 129.2, 129.1, 128.3, 128.2, 127.6, 127.0, 126.4, 126.3, 125.8, 125.7, 124.6, 66.3, 62.2.

HRMS (ESI) m/z calculated for $C_{22}H_{16}O_4$+H^+: 345.1121, found: 345.1120.

(*E*)-4-(furan-2-yl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5r



Prepared according to the general procedure to afford **5r** (19.9 mg, m. p. = 145 – 150 °C) in 70% yield as white solid.

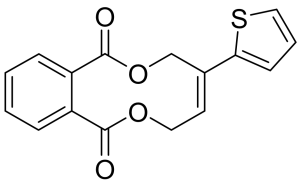
NMR and HRMS data for the product **5r**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.81 – 7.76 (m, 2H), 7.61 – 7.57 (m, 2H), 7.40 (s, 1H), 6.63 (t, *J* = 6.0 Hz, 1H), 6.52 (d, *J* = 3.6 Hz, 1H), 6.42 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.13 (s, 2H), 4.99 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.6, 167.6, 152.5, 143.1, 132.7, 132.4, 131.7, 131.6, 131.3, 129.3, 128.9, 122.6, 111.7, 107.7, 63.2, 61.9.

HRMS (ESI) m/z calculated for $C_{16}H_{12}O_5$+H^+: 285.0757, found: 285.0757.

(*E*)-4-(thiophen-2-yl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5s



Prepared according to the general procedure to afford **5s** (18.9 mg, m. p. = 136 – 138 °C) in 63% yield as white solid.

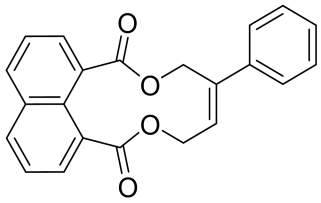
NMR and HRMS data for the product **5s**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.78 (m, 2H), 7.62 – 7.58 (m, 2H), 7.24 (d, *J* = 4.8 Hz, 2H), 7.03 – 7.00 (m, 1H), 6.45 (t, *J* = 6.6 Hz, 1H), 5.22 (s, 2H), 4.93 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.4, 167.9, 143.5, 136.7, 132.7, 132.4, 131.7, 131.7, 129.2, 129.1, 127.8, 125.7, 124.9, 124.3, 65.4, 62.1.

HRMS (ESI) m/z calculated for $C_{16}H_{12}O_4S+Na^+$: 323.0349(^{34}S), 324.0382 (^{32}S), found: 323.0354, 324.0377.

(*Z*)-4-phenyl-3,6-dihydro-1H,8H-naphtho[1,8-hi][1,6]dioxacycloundecine-1,8-dione 6a



Prepared according to the general procedure to afford **6a** (29.6 mg, m. p. = 174 – 177 °C) in 86% yield as white solid.

NMR and HRMS data for the product **6a**:

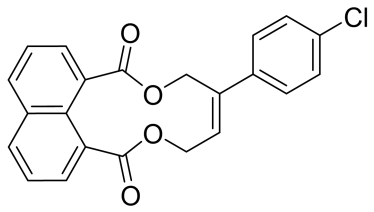
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.02 – 7.99 (m, 2H), 7.93 – 7.89 (m, 2H), 7.58 – 7.52 (m, 2H), 7.46 – 7.42 (m, 2H), 7.37 – 7.33 (m, 2H), 7.32 – 7.29 (m, 1H), 6.46 (t, *J* = 7.2 Hz, 1H), 5.39 (s, 2H), 5.11 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.6, 169.4, 145.8, 140.6, 134.1, 132.3, 132.3, 129.5, 129.4, 129.4, 129.1, 128.6, 128.3, 127.7, 126.7, 126.1, 125.3, 125.3, 62.5, 59.5.

HRMS (ESI) m/z calculated for $C_{22}H_{16}O_4+Na^+$: 367.0941, found: 367.0940.

(*Z*)-4-(4-chlorophenyl)-3,6-dihydro-1H,8H-naphtho[1,8-hi][1,6]dioxacycloundecine-1,8-di

one 6b



Prepared according to the general procedure to afford **6b** (32.2 mg, m. p. = 142 – 147 °C) in 85% yield as white solid.

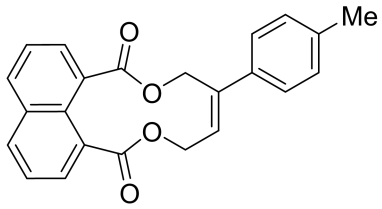
NMR and HRMS data for the product **6b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.02 – 7.99 (m, 2H), 7.93 – 7.89 (m, 2H), 7.58 – 7.54 (m, 2H), 7.37 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.44 (t, *J* = 7.8 Hz, 1H), 5.33 (s, 2H), 5.09 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.5, 169.3, 144.6, 139.0, 134.3, 134.0, 132.4, 129.4, 129.3, 129.2, 128.8, 128.2, 127.5, 126.7, 125.3, 125.3, 62.3, 59.3.

HRMS (ESI) m/z calculated for $C_{22}H_{15}ClO_4$+Na^+: 401.0551(^{35}Cl), 403.0522 (^{37}Cl), found: 401.0549, 403.0523.

(*Z*)-4-(*p*-tolyl)-3,6-dihydro-1H,8H-naphtho[1,8-hi][1,6]dioxacycloundecine-1,8-dione 6c



Prepared according to the general procedure to afford **6c** (31.5 mg, m. p. = 123 – 130 °C) in 88% yield as white solid.

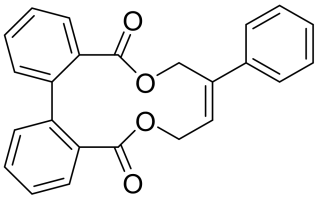
NMR and HRMS data for the product **6c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.99 – 7.97 (m, 2H), 7.94 – 7.88 (m, 2H), 7.58 – 7.50 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.18 – 7.15 (m, 2H), 6.43 (t, *J* = 7.2 Hz, 1H), 5.38 (s, 2H), 5.10 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.6, 169.3, 145.6, 138.2, 137.6, 134.0, 132.2, 132.2, 129.4, 129.4, 129.2, 129.2, 129.0, 126.6, 126.0, 125.2, 125.2, 62.4, 59.6, 21.1.

HRMS (ESI) m/z calculated for $C_{23}H_{18}O_4$+Na^+: 381.1097, found: 381.1103.

(*Z*)-8-phenyl-7,10-dihydrodibenzo[h,j][1,6]dioxacyclododecine-5,12-dione 7a



Prepared according to the general procedure to afford **7a** (31.1 mg, m. p. = 146 – 153 °C) in 84% yield as white solid.

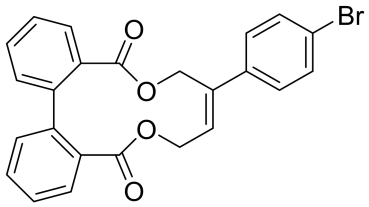
NMR and HRMS data for the product **7a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.48 – 7.41 (m, 2H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.38 – 7.32 (m, 5H), 7.32 – 7.28 (m, 1H), 5.98 (t, *J* = 4.8 Hz, 1H), 5.62 (d, *J* = 13.2 Hz, 1H), 5.23 – 5.17 (m, 1H), 4.86 (d, *J* = 15.0 Hz, 1H), 4.71 (q, *J* = 6.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 167.3, 140.9, 140.6, 140.5, 140.3, 132.7, 131.5, 131.2, 131.0, 130.8, 128.8, 128.5, 127.9, 127.5, 127.4, 127.4, 126.7, 124.2, 64.9, 61.1.

HRMS (ESI) m/z calculated for $C_{24}H_{18}O_4$+Na^+: 393.1097, found: 393.1097.

(*Z*)-8-(4-bromophenyl)-7,10-dihydrodibenzo[h,j][1,6]dioxacyclododecine-5,12-dione 7b



Prepared according to the general procedure to afford **7b** (23.3 mg, m. p. = 143 – 144 °C) in 52% yield as white solid.

NMR and HRMS data for the product **7b**:

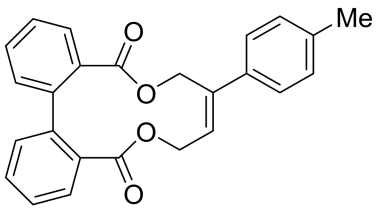
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.48 – 7.41 (m, 4H), 7.40 – 7.34 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.97 (t, *J* = 4.8 Hz, 1H), 5.54 (d, *J* = 15.0 Hz, 1H), 5.23 – 5.17 (m, 1H), 4.81 (d, *J* = 15.0 Hz, 1H), 4.69 (dd, *J* = 14.4, 6.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.8, 167.2, 140.6, 140.5, 139.9, 139.1, 132.4, 131.6, 131.3, 131.0, 131.0, 130.8, 128.9, 128.4, 127.6, 127.5, 127.5, 125.1, 122.0, 64.5, 61.0.

HRMS (ESI) m/z calculated for $C_{24}H_{17}BrO_4$+Na^+:471.0202 (^{79}Br), 473.0182 (^{81}Br), found:

471.0191, 473.0174.

(*Z*)-8-(*p*-tolyl)-7,10-dihydrodibenzo[h,j][1,6]dioxacyclododecine-5,12-dione 7c



Prepared according to the general procedure to afford **7c** (24.2 mg, m. p. = 136 – 137 °C) in 63% yield as white solid.

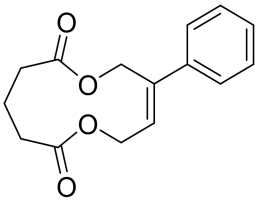
NMR and HRMS data for the product **7c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.34 (m, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 5.97 (t, *J* = 6.6 Hz, 1H), 5.63 (d, *J* = 15.0 Hz, 1H), 5.23 – 5.17 (m, 1H), 4.85 (d, *J* = 15.0 Hz, 1H), 4.69 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 167.9, 167.3, 140.5, 140.4, 140.3, 137.9, 137.8, 132.8, 131.5, 131.1, 131.0, 130.8, 129.1, 128.8, 127.5, 127.4, 126.6, 123.3, 65.0, 61.1, 21.1.

HRMS (ESI) m/z calculated for $C_{25}H_{20}O_4+H^+$: 385.1434, found: 385.1438.

(*Z*)-3-phenyl-1,6-dioxacycloundec-3-ene-7,11-dione 8a



Prepared according to the general procedure to afford **8a** (19.0 mg) in 73% yield as colorless liquid.

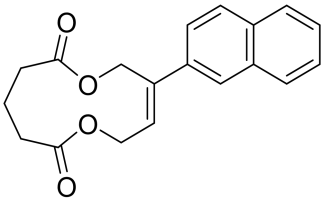
NMR and HRMS data for the product **8a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.45 – 7.42 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 6.37 (t, *J* = 7.8 Hz, 1H), 4.98 (s, 2H), 4.72 (d, *J* = 7.8 Hz, 2H), 2.46 – 2.41 (m, 4H), 2.15 – 2.10 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.9, 172.5, 144.4, 140.6, 128.6, 128.2, 127.5, 126.1, 62.3, 59.1, 34.7, 34.5, 21.9.

HRMS (ESI) m/z calculated for $C_{15}H_{16}O_4$+Na^+: 283.0941, found: 283.0940.

(*Z*)-3-(naphthalen-2-yl)-1,6-dioxacycloundec-3-ene-7,11-dione 8b



Prepared according to the general procedure to afford **8b** (26.7 mg, m. p. = 105 – 108 °C) in 86% yield as white solid.

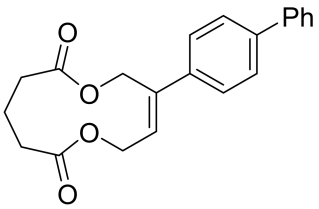
NMR and HRMS data for the product **8b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.88 (s, 1H), 7.86 – 7.81 (m, 3H), 7.59 – 7.56 (m, 1H), 7.52 – 7.47 (m, 2H), 6.52 (t, *J* = 7.2 Hz, 1H), 5.09 (s, 2H), 4.78 (d, *J* = 6.6 Hz, 2H), 2.50 – 2.44 (m, 4H), 2.18 – 2.13 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 173.0, 172.5, 144.2, 137.8, 133.2, 133.0, 128.3, 128.2, 127.9, 127.6, 126.5, 126.4, 125.2, 124.1, 62.2, 59.2, 34.7, 34.5, 21.9.

HRMS (ESI) m/z calculated for $C_{19}H_{18}O_4$+Na^+: 333.1097, found: 333.1103.

(*Z*)-3-([1,1'-biphenyl]-4-yl)-1,6-dioxacycloundec-3-ene-7,11-dione 8c



Prepared according to the general procedure to afford **8c** (26.2 mg, m. p. = 135 – 137 °C) in 78% yield as white solid.

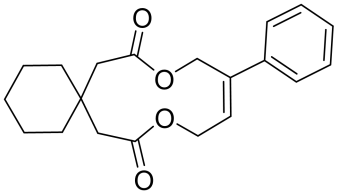
NMR and HRMS data for the product **8c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.63 – 7.58 (m, 4H), 7.54 – 7.51 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 6.44 (t, *J* = 7.2 Hz, 1H), 5.02 (s, 2H), 4.75 (d, *J* = 7.2 Hz, 2H), 2.49 – 2.42 (m, 4H), 2.17 – 2.11 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 172.9, 172.5, 143.9, 141.1, 140.4, 139.4, 128.8, 127.5, 127.4, 127.3, 127.0, 126.6, 62.1, 59.2, 34.7, 34.5, 21.9.

HRMS (ESI) m/z calculated for $C_{21}H_{20}O_4$+Na^+: 359.1254, found: 359.1260.

(*Z*)-11-phenyl-9,14-dioxaspiro[5.10]hexadec-11-ene-8,15-dione 8d



Prepared according to the general procedure to afford **8d** (23.0 mg) in 70% yield as colorless liquid.

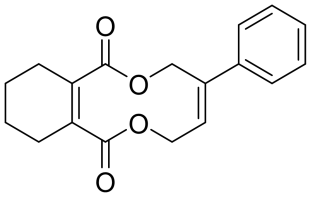
NMR and HRMS data for the product **8d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.43 – 7.38 (m, 2H), 7.37 – 7.33 (m, 2H), 7.32 – 7.29 (m, 1H), 6.22 (t, *J* = 6.6 Hz, 1H), 4.99 (s, 2H), 4.74 (d, *J* = 7.2 Hz, 2H), 2.41 (s, 2H), 2.39 (s, 2H), 1.66 – 1.63 (m, 4H), 1.53 – 1.49 (m, 4H), 1.45 – 1.42 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 171.6, 171.3, 143.1, 140.9, 128.5, 128.0, 127.0, 126.2, 62.5, 59.2, 43.5, 43.1, 37.7, 37.5, 25.8, 21.6.

HRMS (ESI) m/z calculated for $C_{20}H_{24}O_4$+Na^+: 351.1567, found: 351.1567.

(*Z*)-4-phenyl-3,6,9,10,11,12-hexahydrobenzo[c][1,6]dioxecine-1,8-dione 8e



Prepared according to the general procedure to afford **8e** (21.2 mg, m. p. = 82 – 87 °C) in 71% yield as pink solid.

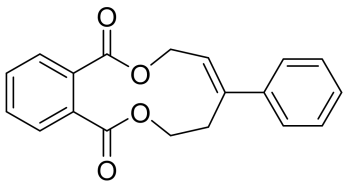
NMR and HRMS data for the product **8e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.45 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.29 (m, 1H), 6.16 (t, *J* = 6.0 Hz, 1H), 5.02 (s, 2H), 4.79 (d, *J* = 6.0 Hz, 2H), 2.45 – 2.41 (m, 4H), 1.82 – 1.79 (m, 1H), 1.71 – 1.67 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.9, 168.5, 143.3, 140.9, 137.7, 137.4, 128.5, 128.1, 126.7, 126.1, 65.7, 61.5, 25.7, 21.2, 20.8, 20.7.

HRMS (ESI) m/z calculated for $C_{18}H_{18}O_4$+Na^+: 321.1097, found: 321.1093.

(*Z*)-6-phenyl-4,7-dihydro-3H-benzo[c][1,6]dioxacycloundecine-1,9-dione 12



Prepared according to the general procedure to afford **12** (19.7 mg) in 64% yield as colorless liquid.

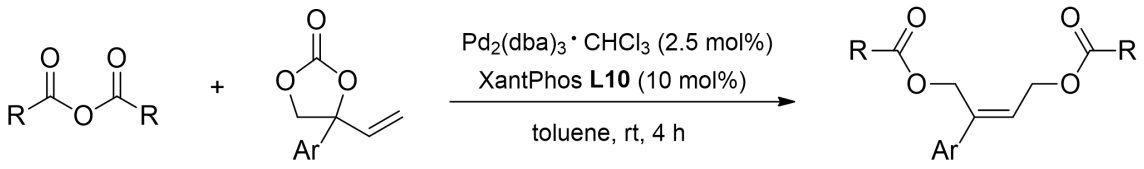
NMR and HRMS data for the product **12**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.87 – 7.83 (m, 1H), 7.63 – 7.59 (m, 1H), 7.58 – 7.53 (m, 2H), 7.40 – 7.38 (m, 2H), 7.36 – 7.28 (m, 3H), 6.40 (t, *J* = 6.6 Hz, 1H), 4.83 (d, *J* = 6.6 Hz, 2H), 4.37 (br s, 2H), 3.02 (br s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.6, 166.9, 145.8, 140.4, 133.5, 131.7, 130.9, 130.8, 129.6, 128.6, 128.4, 128.1, 126.9, 124.8, 61.2, 60.3, 30.8.

HRMS (ESI) m/z calculated for $C_{19}H_{16}O_4$+H^+: 309.1121, found: 309.1123.

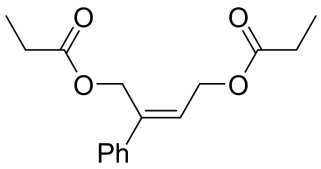
6. General Procedure for the Reactions of Linear Anhydrides and VECs



9 **2** **10**

To an oven-dried Schlenk tube was added $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%) and XantPhos (10 mol%), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, linear anhydrides **9** (0.10 mmol) and vinylethylene carbonates **2** (0.15 mmol) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 3/1) to afford the corresponding **10** in 55–57% yields, which were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

(*Z*)-2-phenylbut-2-ene-1,4-diyl dipropionate 10a



Prepared according to the general procedure to afford **10a** (15.7 mg) in 57% yield as colorless semisolid.

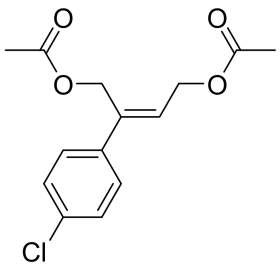
NMR and HRMS data for the product **10a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.28 (m, 1H), 6.07 (t, *J* = 6.6 Hz, 1H), 5.07 (s, 2H), 4.88 (d, *J* = 7.2 Hz, 2H), 2.36 (q, *J* = 7.8 Hz, 2H), 2.27 (q, *J* = 7.8 Hz, 2H), 1.16 (t, *J* = 7.8 Hz, 3H), 1.07 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 174.2, 174.1, 139.4, 138.7, 128.4, 127.9, 127.3, 126.4, 60.9, 60.7, 27.5, 27.4, 9.0, 9.0.

HRMS (ESI) m/z calculated for $C_{16}H_{20}O_4$+Na^+: 299.1254, found: 299.1255.

(*Z*)-2-(4-chlorophenyl)but-2-ene-1,4-diyl diacetate 10b



Prepared according to the general procedure to afford **10b** (15.6 mg, m. p. = 51 – 55 °C) in 55% yield as white solid.

NMR and HRMS data for the product **10b**:

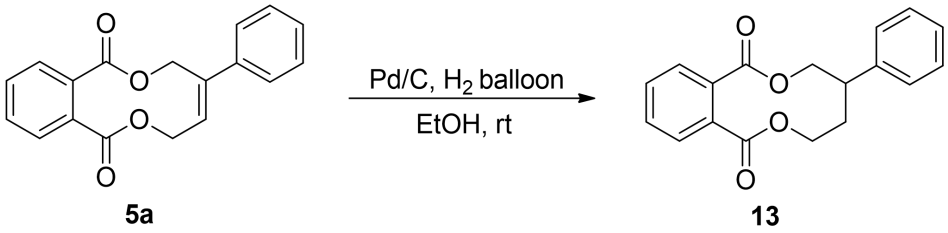
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.32 – 7.29 (m, 2H), 7.28 – 7.25 (m, 2H), 6.02 (t, *J* = 6.6 Hz, 1H), 4.99 (s, 2H), 4.83 (d, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.5, 170.4, 137.6, 137.4, 133.7, 128.4, 127.6, 127.5, 60.5, 60.5, 20.7, 20.6.

HRMS (ESI) m/z calculated for $C_{14}H_{15}ClO_4$+Na^+: 305.0551(^{35}Cl), 307.0522 (^{37}Cl), found: 305.0564, 307.0504.

7. Synthetic Transformation of 5a and 10b

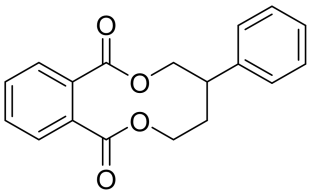
*7.1 Procedure for the hydrogenation of lactone **3a***



5a **13**

The ten-membered lactone **3a** (0.1 mmol, 29.4 mg) was dissolved in in dry ethanol (1.0 mL). This mixture was degassed of dissolved air and purged with an argon atmosphere. To it 5% Pd/C (8.0 mg) was carefully added. The above reaction mixture was degassed and purged with hydrogen. Then the reaction was stirred for 12 hours at room temperature with hydrogen balloon. After the completion of the reaction, the mixture was filtered through a plug of silica (eluting with DCM) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 50/1 to 40/1) to afford **13** (12.4 mg) as white solid in 42% yields, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

4-phenyl-3,4,5,6-tetrahydrobenzo[c][1,6]dioxecine-1,8-dione 13



Purification of the crude product *via* column chromatography delivered **13** (12.4 mg, m. p. = 135 – 136 °C) in 42% yield as white solid.

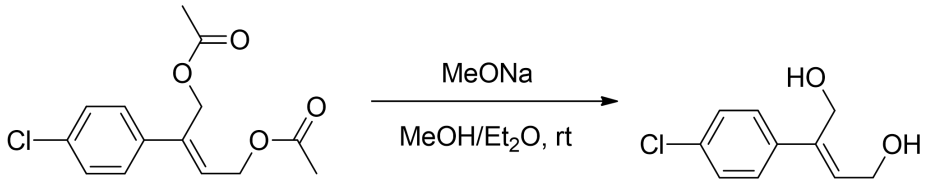
NMR and HRMS data for the product **13**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 – 7.75 (m, 2H), 7.60 – 7.56 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.23 (m, 3H), 4.92 – 4.87 (m, 1H), 4.76 (dd, *J* = 11.4, 4.8 Hz, 1H), 4.11 – 4.06 (m, 1H), 3.94 (t, *J* = 10.8 Hz, 1H), 3.32 – 3.27 (m, 1H), 2.61 – 2.54 (m, 1H), 2.06 (d, *J* = 13.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.0, 167.7, 142.2, 133.0, 132.8, 131.5, 131.5, 128.9, 128.9, 128.7, 127.5, 127.2, 69.9, 65.2, 43.8, 34.3.

HRMS (ESI) m/z calculated for $C_{18}H_{16}O_4+H^+$: 297.1121, found: 297.1126.

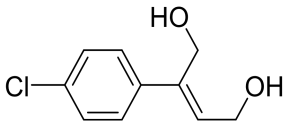
*7.2 Procedure for the hydrolysis of the linear ester **10b***



10b **14**

The linear ester **10b** (0.1mmol, 28.2 mg) was dissolved in the mixture of MeOH/Et_2O (2 mL, v/v = 1/1) and stirred at room temperature. To this solution was slowly added MeONa (0.02 mmol, 1 mg). The mixture was was stirred for 5 h at the same temperature and quenched with 5 mL of saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1 to 1/1) to afford **14** (19.1 mg) as colorless semisolid in 96% yields, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

(*Z*)-2-(4-chlorophenyl)but-2-ene-1,4-diol 14



Purification of the crude product *via* column chromatography delivered **14** (19.1 mg) in 96% yield as colorless semisolid .

NMR and HRMS data for the product **14**:

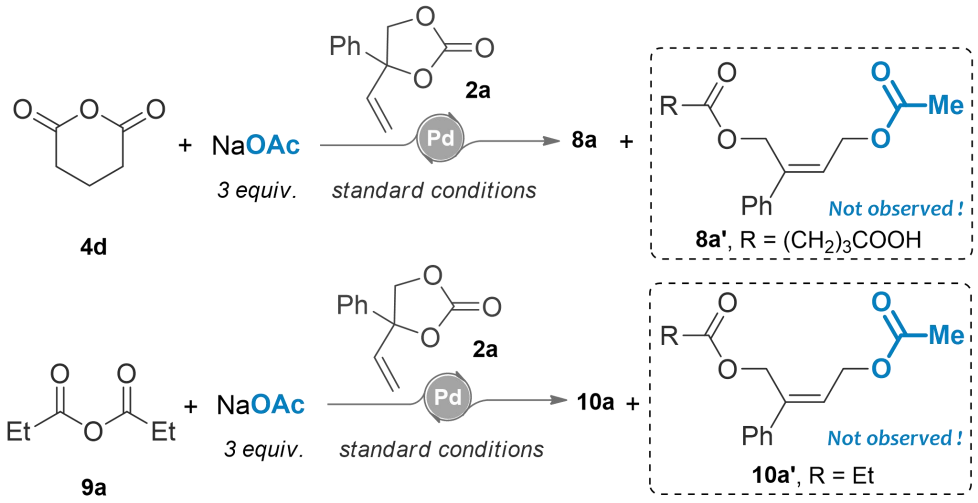
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 6.07 (t, *J* = 6.6 Hz, 1H), 4.50 (s, 2H), 4.34 (d, *J* = 7.2 Hz, 2H), 2.82 (br s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 141.5, 138.9, 133.6, 130.1, 128.6, 127.6, 60.0, 58.7.

HRMS (ESI) m/z calculated for $C_{10}H_{11}ClO_2$+Na^+: 221.0340 (^{35}Cl), 223.0310 (^{37}Cl), found: 221.0339, 223.0304.

8. Experiments for Mechanism Studies

8.1 The competition experiments



To explore the reaction mechanism, we performed several competition experiments based on the rection of vinylethylene carbonate **2a** with cyclic anhydride **4d** or linear anhydride **9a**

To three oven-dried Schlenk tubes were added $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%) and XantPhos (10 mol%), after which the tubes were evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, anhydride **4d** or **9a** (0.10 mmol), sodium acetate and vinylethylene carbonate **2a** (0.15 mmol) were added. The amounts of sodium acetate in the three reactions respectively refer to 0.10 mmol, 0.20 mmol and 0.30 mmol.

Then, the three reactions were stirred at room temperature for 4 hours, respectively. After then, the mixtures were filtered through a plug of silica (eluting with ethyl acetate) and concentrated, which were dried under vacuum further analyzed by ^{1}H NMR.

Even when three equivalents of the sodium acetate was added into the reaction mixture, the competitive product **8a'** or **10a'** was not observed, probably because the in-situ generated carboxylate is more likely to coordinate with palladium catalyst and then triggered an intramolecular attack of the π-allyl palladium moiety to deliver **8a** or **10a**.

8.2 Proposed reaction mechanism

Based on the results of competition experiments, a plausible mechanism for the catalytic cyclisation was proposed. As shown in Firure S1, the reaction was initiated by the palladium-catalysed decarboxylation of VEC **2a** to generate the zwitterionic π-allyl palladium intermediate **I**. Subsequently, the anhydride substrate was attacked by the alkoxide to form the intermediate **II**, in which the carboxylate moiety might be coordinated with palladium catalyst. Finally, a regioselective intramolecular allylation of the carboxylate and π-allyl palladium moieties occurred, which delivered diverse medium-sized lactone products.

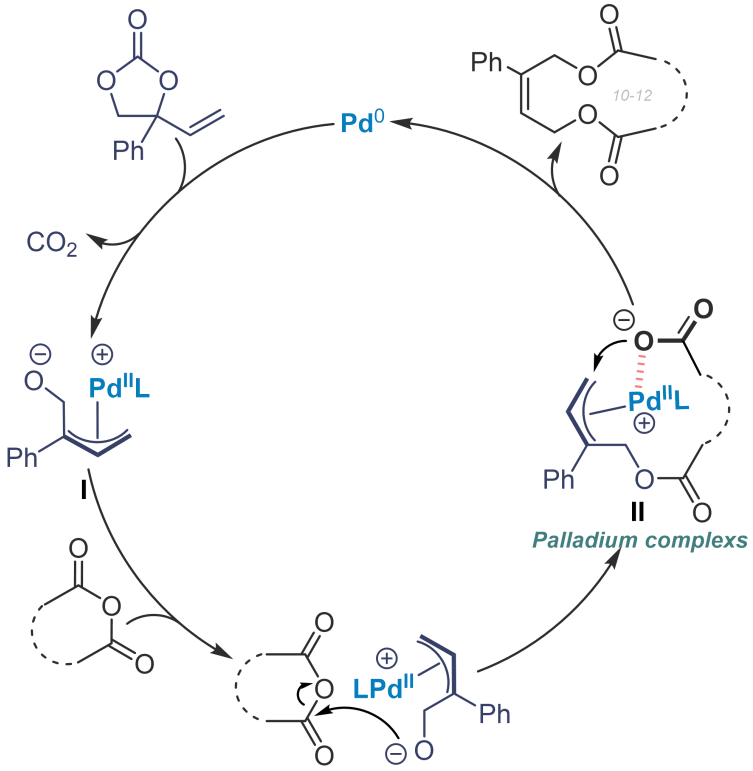
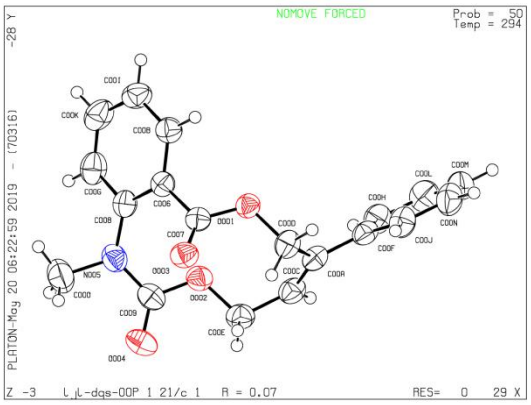
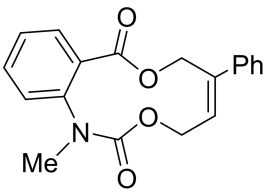


Figure S1. Proposed mechanism.

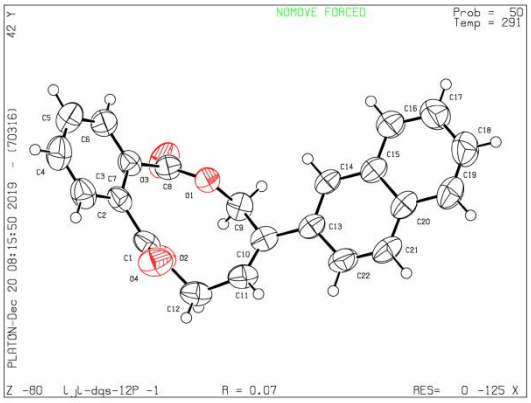
9. Crystal Data and Structure Refinement





3a
CCDC 1967378

Identification code	**3a**
Empirical formula	$C_{19}H_{17}NO_4$
Formula weight	323.33
Temperature/K	294(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.6331(7)
b/Å	8.0735(3)
c/Å	12.5699(4)
α/°	90
β/°	92.556(3)
γ/°	90
Volume/Å^3	1584.92(11)
Z	4
ρ_{calc}g/cm^3	1.355
μ/mm^{-1}	0.784
F(000)	680.0
Crystal size/mm^3	0.5 × 0.4 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.332 to 143.58
Index ranges	$-17 \le h \le 19$, $-9 \le k \le 7$, $-15 \le l \le 15$
Reflections collected	7262
Independent reflections	3046 [R_{int} = 0.0470, R_{sigma} = 0.0466]
Data/restraints/parameters	3046/0/218
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0698, wR_2 = 0.1807
Final R indexes [all data]	R_1 = 0.0845, wR_2 = 0.2040
Largest diff. peak/hole / e Å^{-3}	0.29/-0.40



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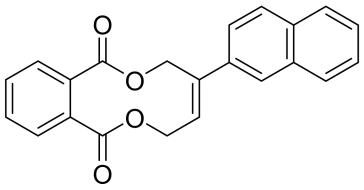
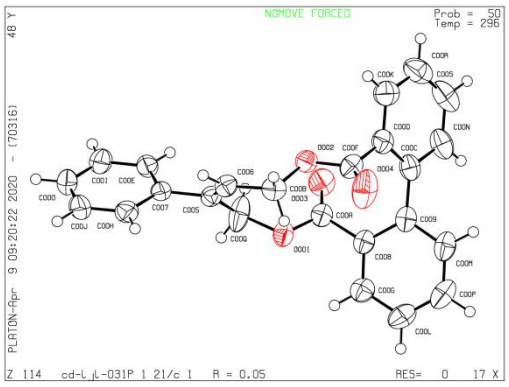


5q
CCDC 1973658

Identification code	**5q**
Empirical formula	$C_{22}H_{16}O_4$
Formula weight	344.35
Temperature/K	291.3(6)
Crystal system	triclinic
Space group	P-1
a/Å	4.8570(4)
b/Å	13.6775(14)
c/Å	14.0943(12)
α/°	114.792(9)
β/°	97.894(7)
γ/°	91.103(7)
Volume/Å^3	838.88(14)
Z	2
ρ_{calc}g/cm^3	1.363
μ/mm^{-1}	0.764
F(000)	360.0
Crystal size/mm^3	0.6 × 0.3 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.998 to 142.692
Index ranges	$-4 \le h \le 5$, $-16 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	6278
Independent reflections	3145 [R_{int} = 0.0334, R_{sigma} = 0.0416]
Data/restraints/parameters	3145/0/235
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0745, wR_2 = 0.2093
Final R indexes [all data]	R_1 = 0.0846, wR_2 = 0.2242
Largest diff. peak/hole / e Å^{-3}	0.27/-0.32



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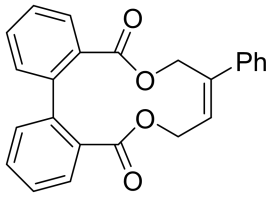
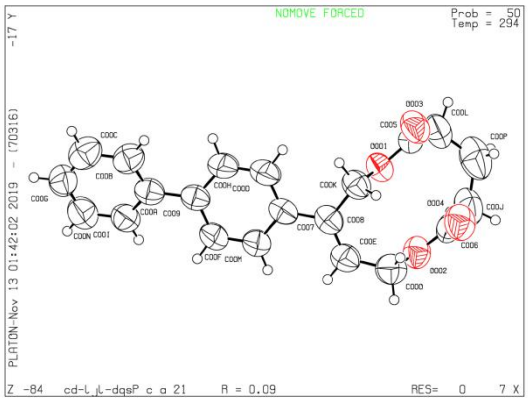
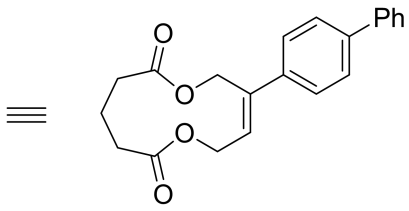


7a
CCDC 1995990

Identification code	**7a**
Empirical formula	$C_{24}H_{18}O_4$
Formula weight	370.38
Temperature/K	295.9(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.2786(3)
b/Å	10.8706(4)
c/Å	15.3317(4)
α/°	90
β/°	97.475(3)
γ/°	90
Volume/Å^3	1863.77(10)
Z	4
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	0.727
F(000)	776.0
Crystal size/mm^3	0.65 × 0.6 × 0.5
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.906 to 142.576
Index ranges	$-8 \le h \le 13$, $-8 \le k \le 13$, $-18 \le l \le 18$
Reflections collected	11540
Independent reflections	3544 [R_{int} = 0.0521, R_{sigma} = 0.0303]
Data/restraints/parameters	3544/0/253
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1376
Final R indexes [all data]	R_1 = 0.0603, wR_2 = 0.1443
Largest diff. peak/hole / e Å^{-3}	0.25/-0.33





8c
CCDC 1966143

Identification code	**8c**
Empirical formula	$C_{21}H_{20}O_4$
Formula weight	336.37
Temperature/K	293.9(5)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	10.5308(10)
b/Å	18.5025(16)
c/Å	8.7370(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1702.4(3)
Z	4
ρ_{calc}g/cm^3	1.312
μ/mm^{-1}	0.732
F(000)	712.0
Crystal size/mm^3	0.5 × 0.3 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.56 to 143.526
Index ranges	$-12 \le h \le 12$, $-22 \le k \le 21$, $-10 \le l \le 8$
Reflections collected	5135
Independent reflections	2438 [R_{int} = 0.0394, R_{sigma} = 0.0340]
Data/restraints/parameters	2438/1/226
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0879, wR_2 = 0.2521
Final R indexes [all data]	R_1 = 0.1008, wR_2 = 0.2838
Largest diff. peak/hole / e Å^{-3}	0.60/-0.29

10. References and Notes

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2 (a) F. Pin, S. Comesse and A. Daïch, *Tetrahedron*, 2011, **67**, 5564; (b) R. L. Clark, C. J. Clements, M. P. Barrett, S. P. Mackay, R. P. Rathnam, G. Owusu-Dapaah, J. Spencer and J. K. Huggan, *Bioorg. Med. Chem.*, 2012, **20**, 6019.

3 A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing and Y. J. Zhang, *Angew. Chem. Int. Ed.*, 2014, **53**, 6439.

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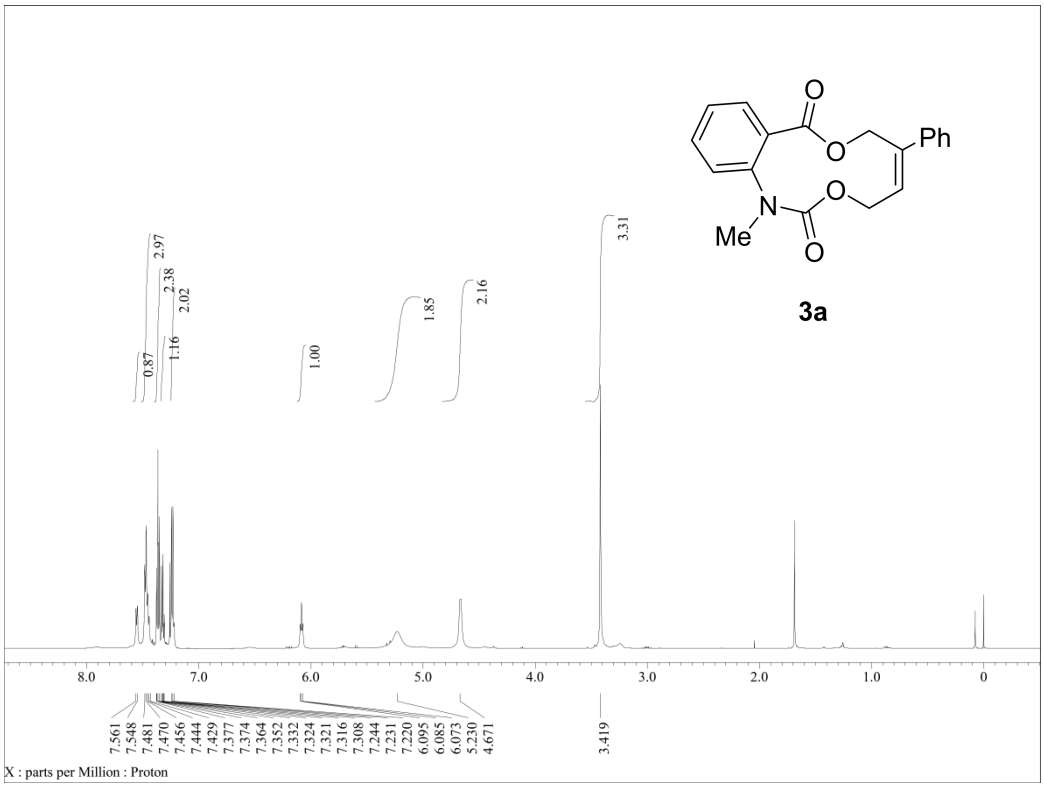
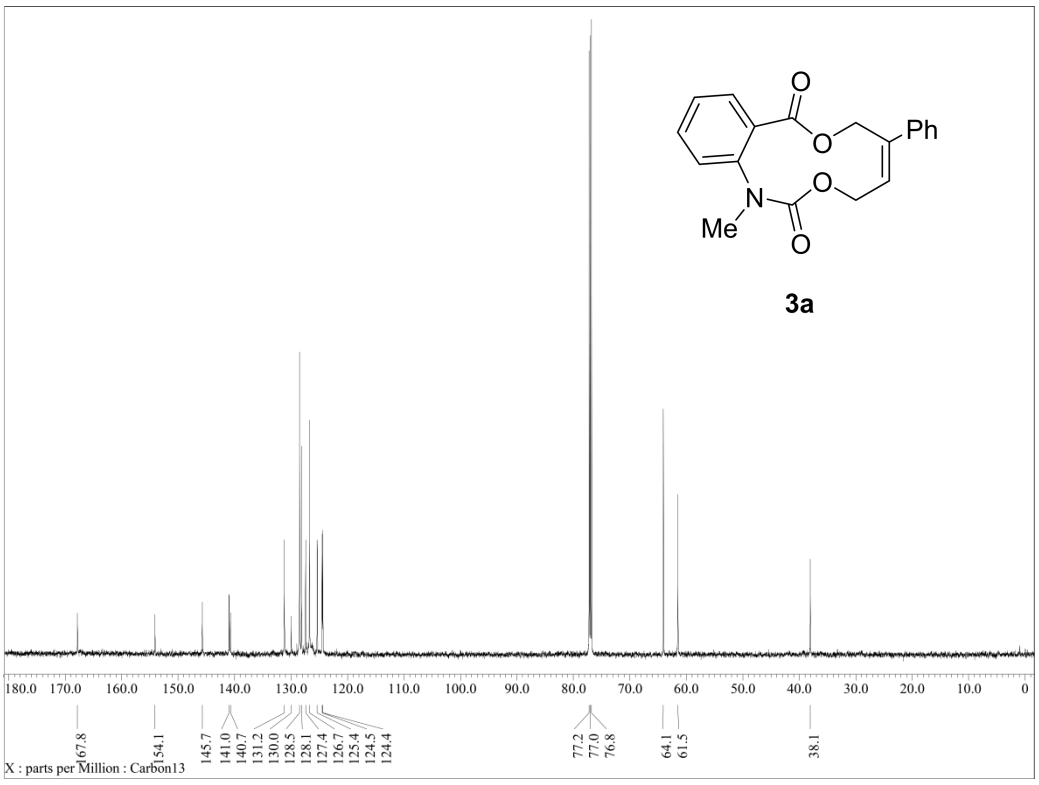
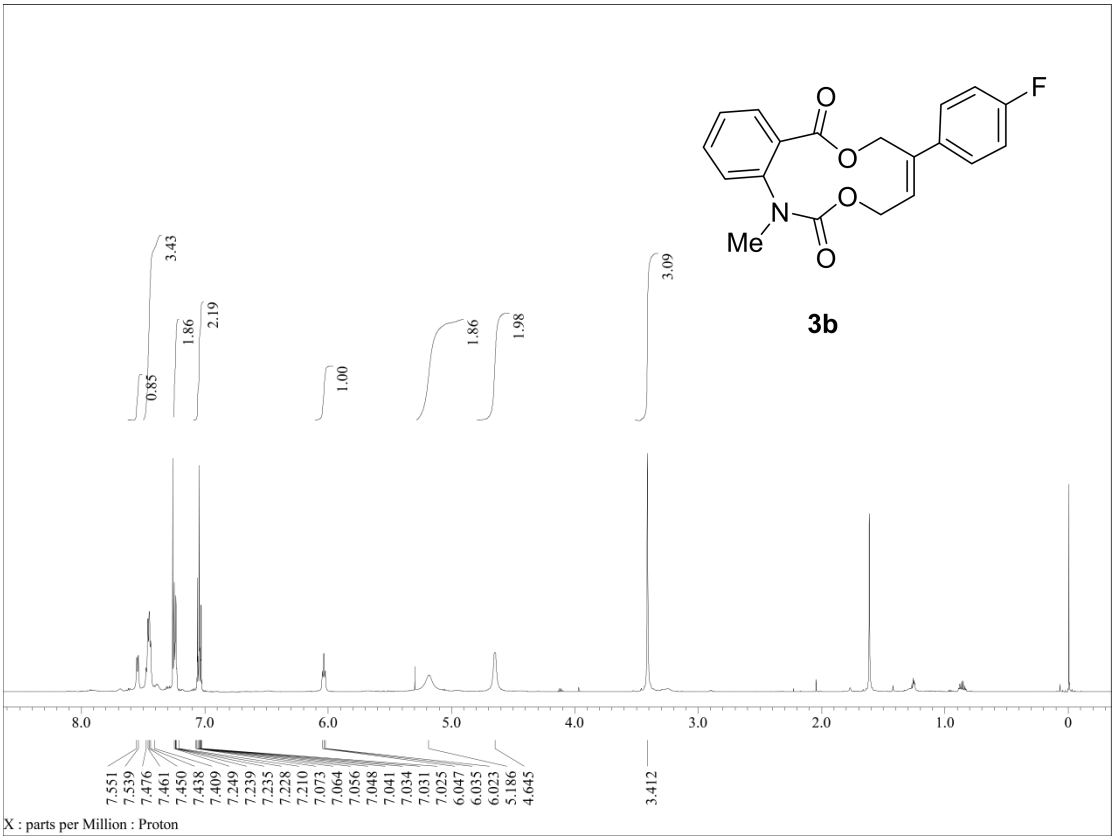
11. NMR Spectra






F
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O
O
N
Me
O
3b
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1.86
2.19
0.85
1.00
1.86
1.98
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.551
7.539
7.476
7.461
7.450
7.438
7.409
7.249
7.239
7.235
7.228
7.210
7.073
7.064
7.056
7.048
7.041
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7.025
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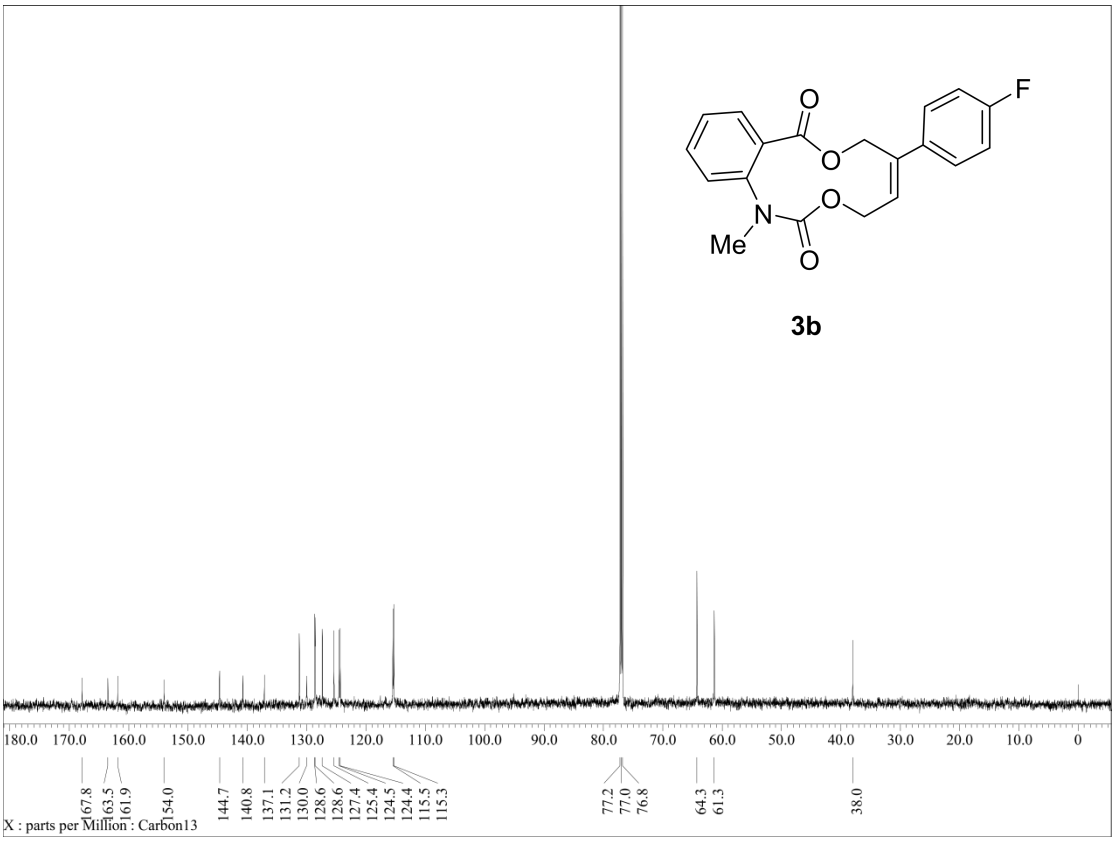
6.035
6.023
5.186
4.645
3.412
X : parts per Million : Proton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O
O
N
Me
O
3b
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170.0
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150.0
140.0
130.0
120.0
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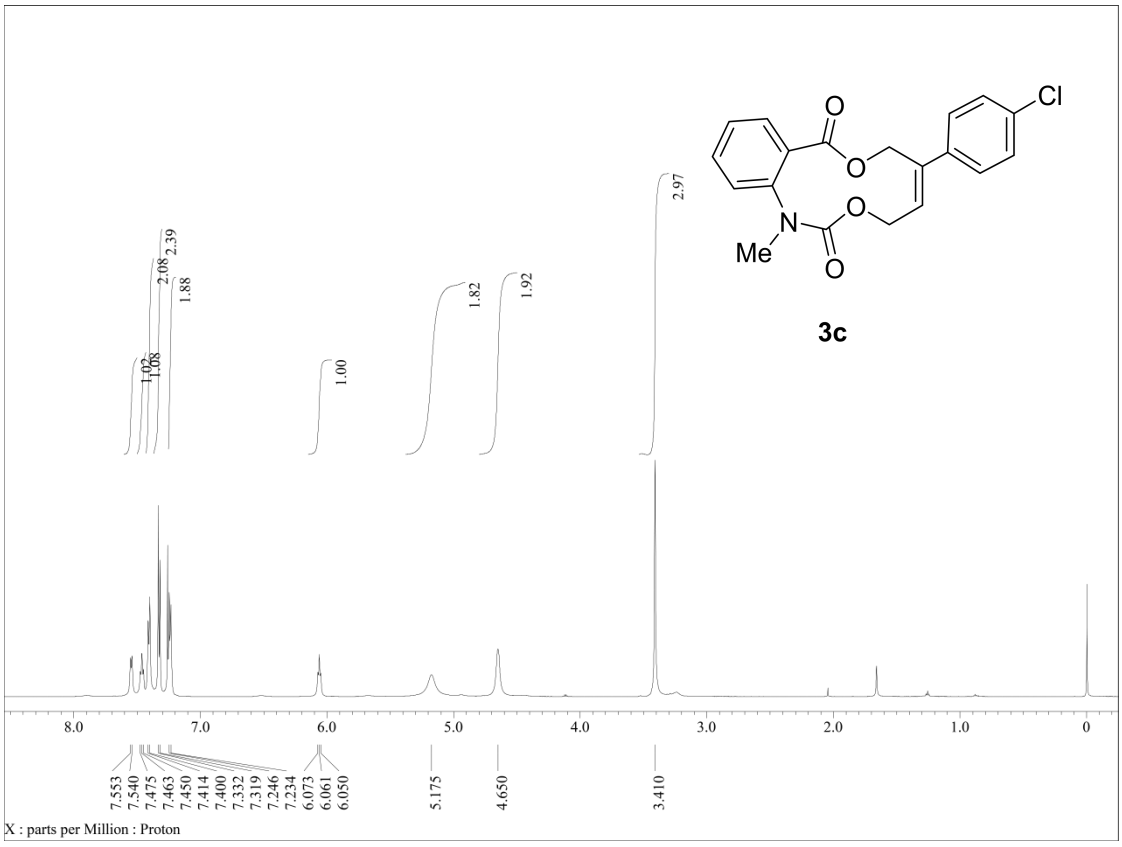
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.8
163.5
161.9
154.0
144.7
140.8
137.1
131.2
130.0
128.6
128.6
127.4
125.4
124.5
124.4
115.5
115.3
77.2
77.0
76.8
64.3
61.3
38.0
X : parts per Million : Carbon13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O
O
N
Me
O
3c
2.97
2.39
2.08
1.88
1.82
1.92
1.00
1.02
1.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.553
7.540
7.475
7.463
7.450
7.414
7.400
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7.234
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6.050
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4.650
3.410
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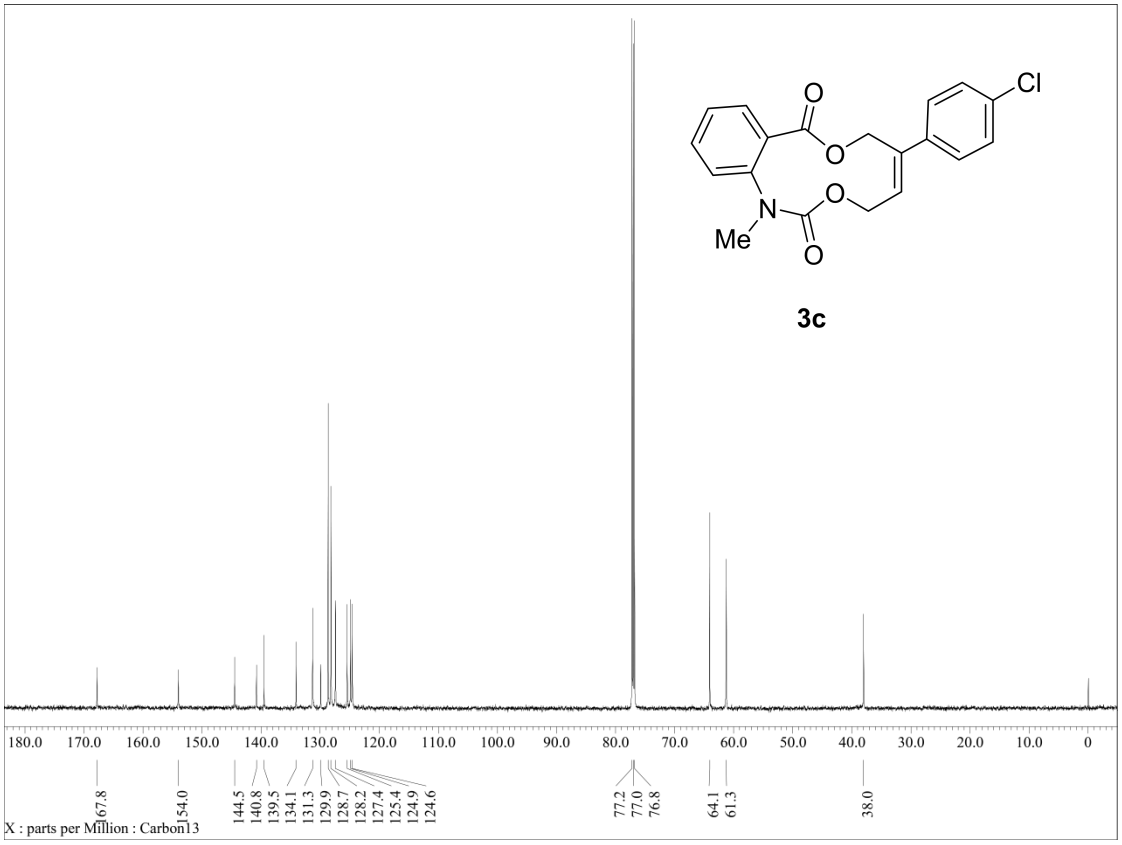
Cl
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O
O
N
Me
O
3c
180.0
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.8
154.0
144.5
140.8
139.5
134.1
131.3
129.9
128.7
128.2
127.4
125.4
124.9
124.6
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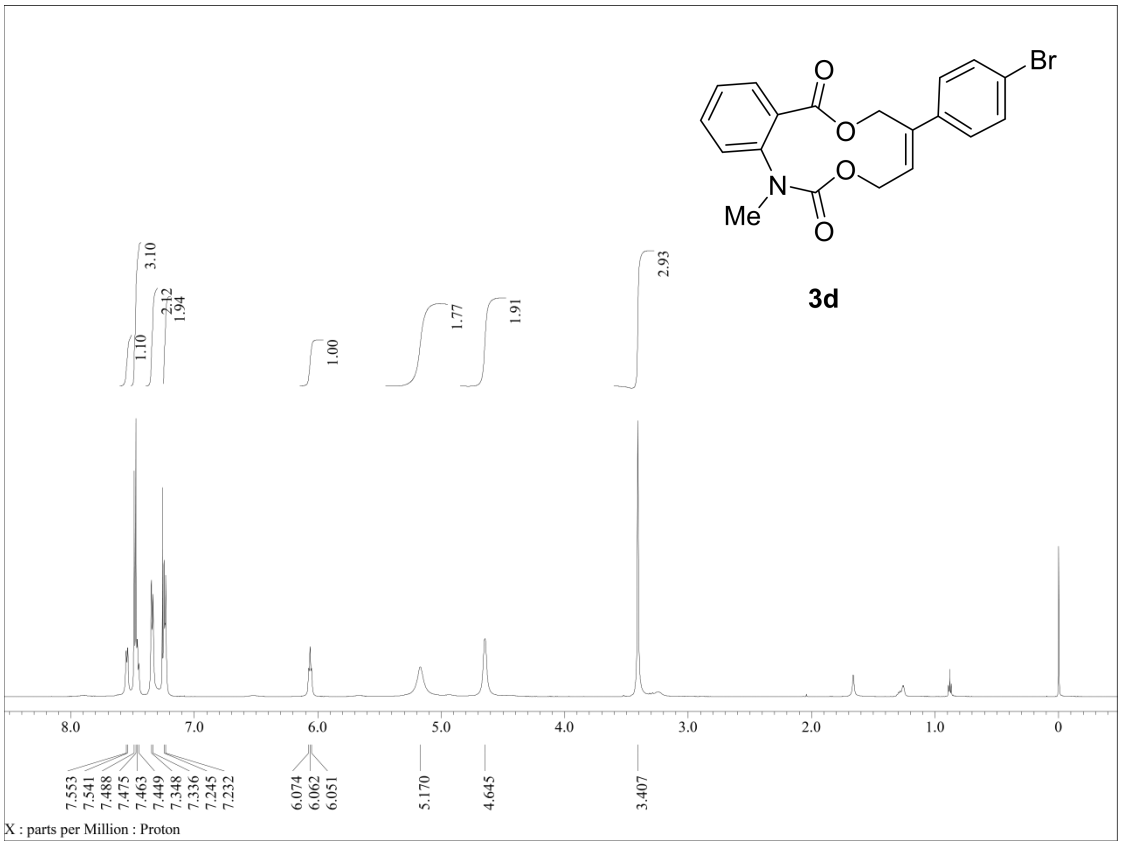
76.8
64.1
61.3
38.0
X : parts per Million : Carbon13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O
O
N
Me
O
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1.10
1.00
1.77
1.91
2.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.553
7.541
7.488
7.475
7.463
7.449
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7.232
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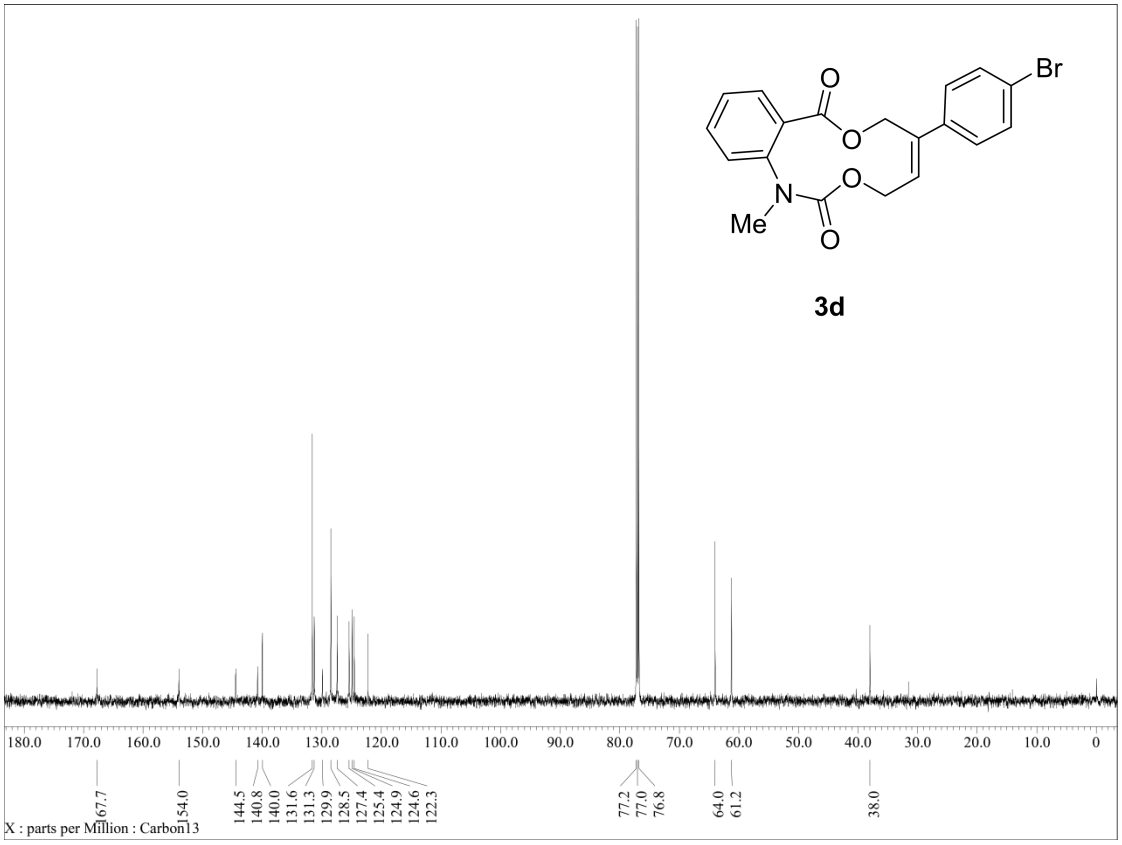
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O
O
N
Me
O
3d
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
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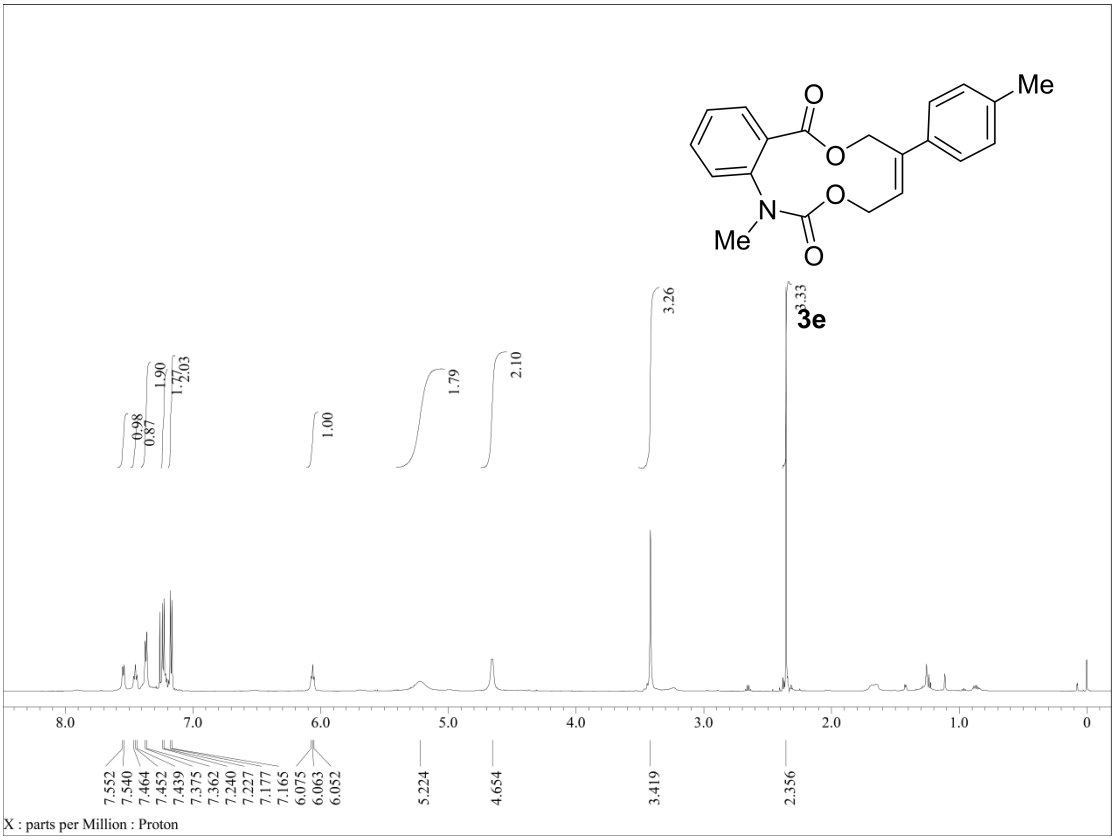
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.7
154.0
144.5
140.8
140.0
131.6
131.3
129.9
128.5
127.4
125.4
124.9
124.6
122.3
77.2
77.0
76.8
64.0
61.2
38.0
X : parts per Million : Carbon13


Me
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O
O
N
Me
O
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1.00
1.79
2.10
3.26
3.33
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.552
7.540
7.464
7.452
7.439
7.375
7.362
7.240
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6.063
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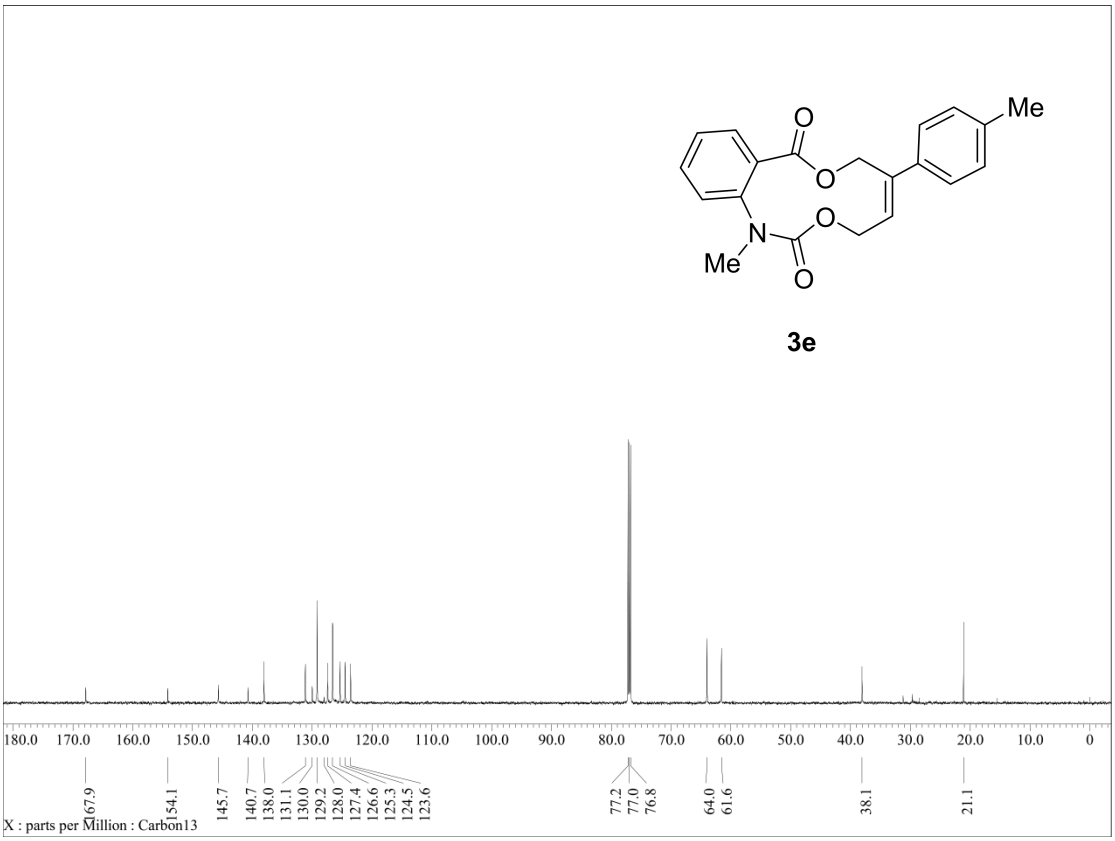
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O
O
N
Me
O
3e
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150.0
140.0
130.0
120.0
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131.1
130.0
129.2
128.0
127.4
126.6
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61.6
38.1
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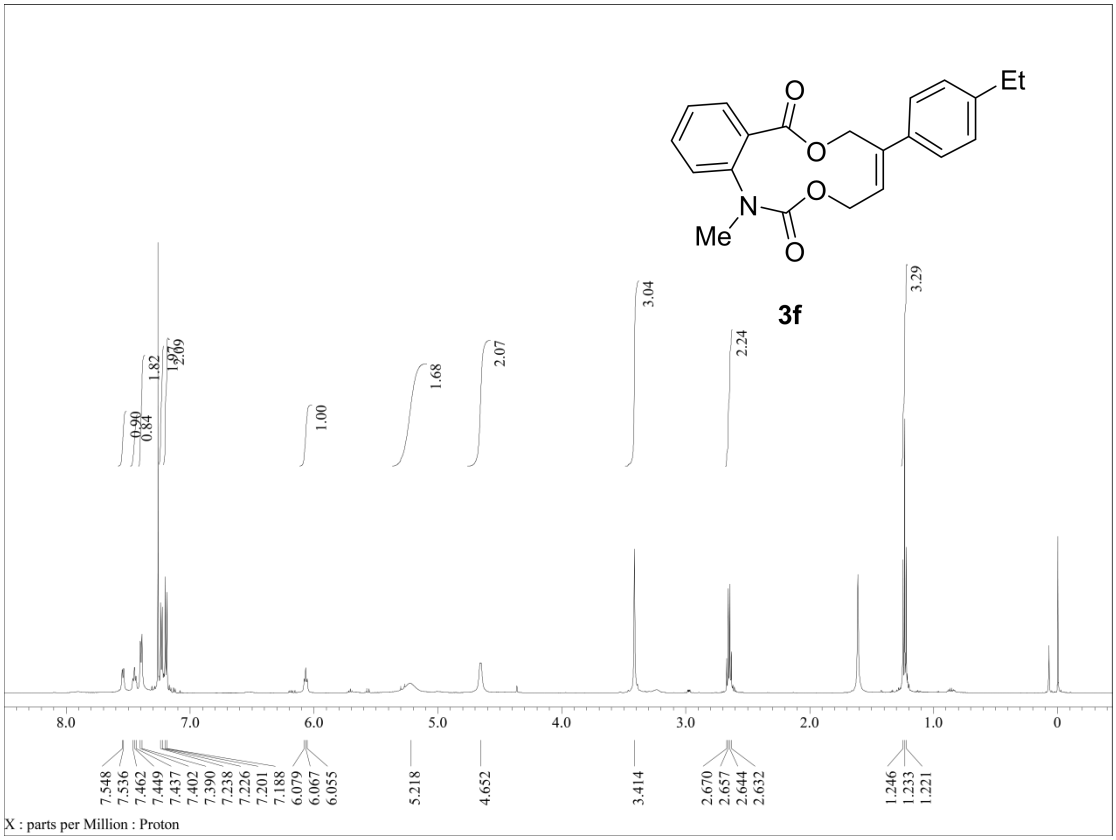
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O
N
Me
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2.07
3.04
2.24
3.29
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7.0
6.0
5.0
4.0
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2.0
1.0
0
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7.536
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7.449
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7.238
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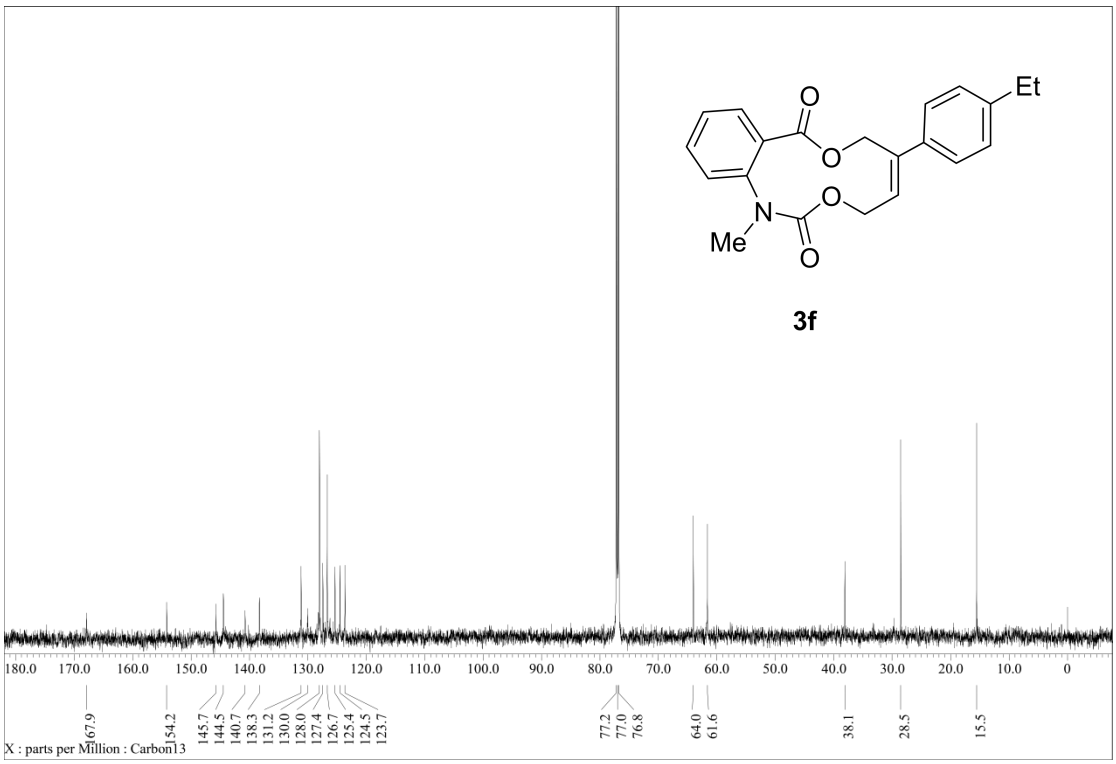
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O
O
N
Me
O
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140.0
130.0
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110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.9
154.2
145.7
144.5
140.7
138.3
131.2
130.0
128.0
127.4
126.7
125.4
124.5
123.7
77.2
77.0
76.8
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61.6
38.1
28.5
15.5
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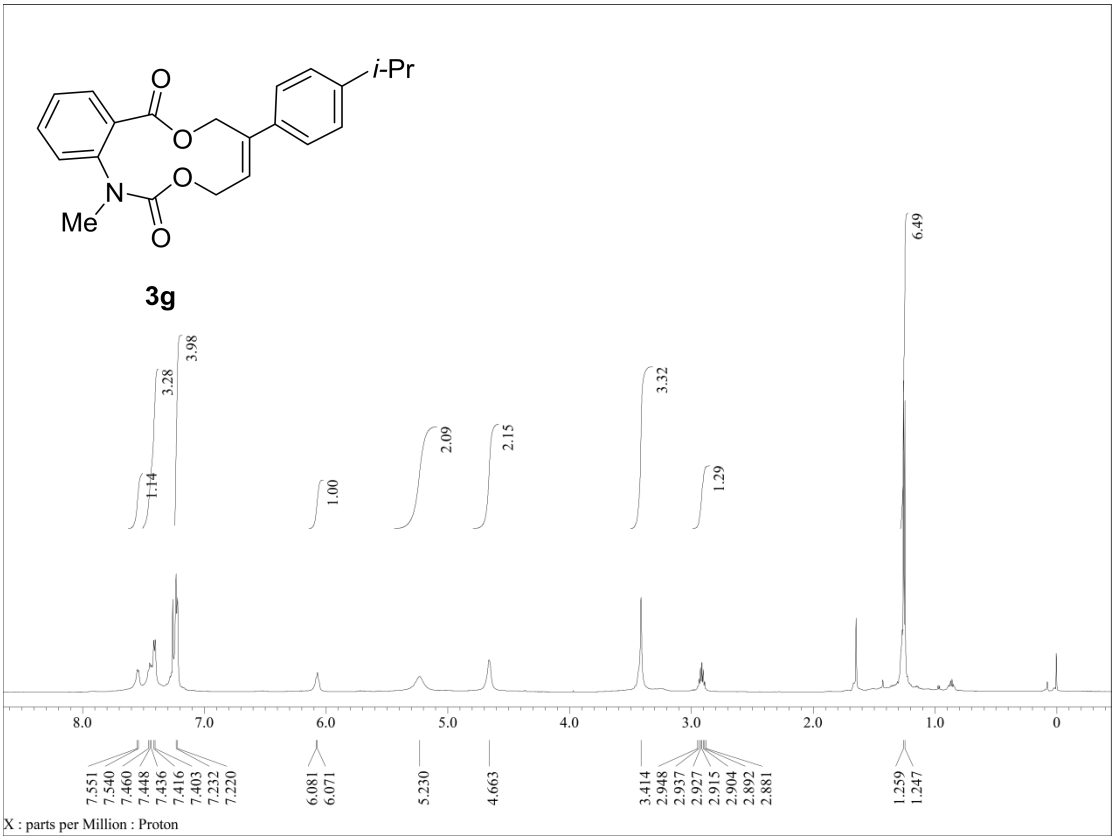
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O
O
N
Me
O
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1.14
1.00
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
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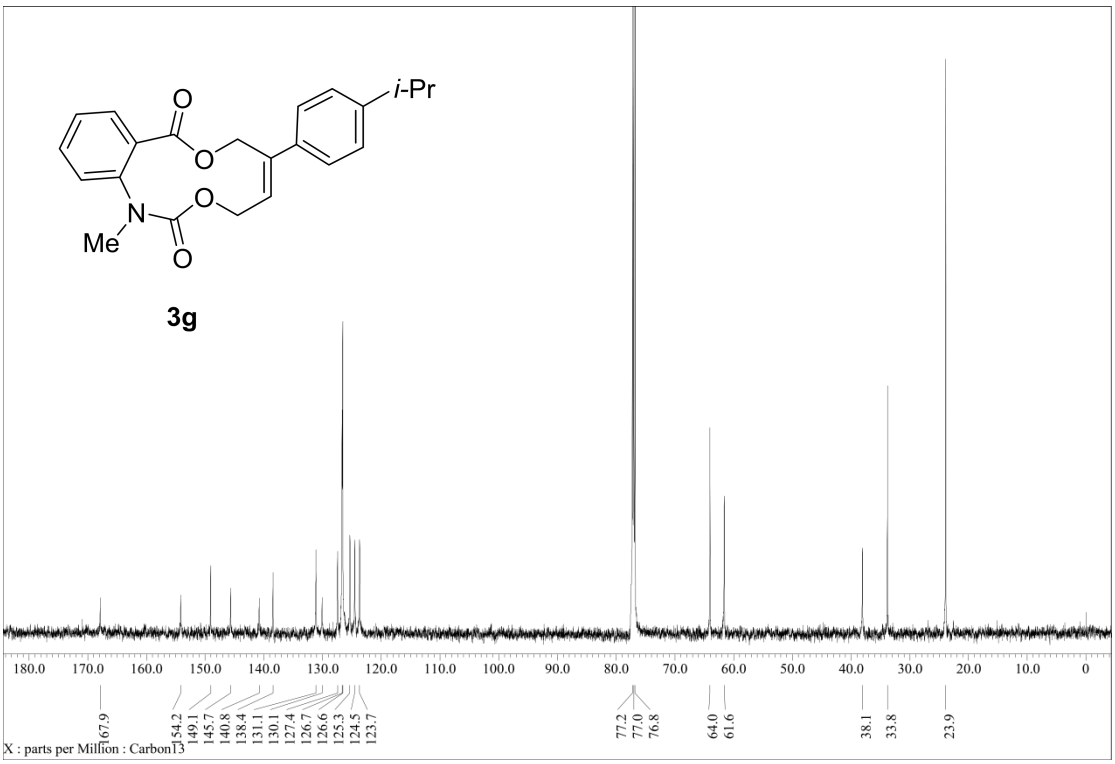
X : parts per Million : Proton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O
O
N
Me
O
3g
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140.0
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138.4
131.1
130.1
127.4
126.7
126.6
125.3
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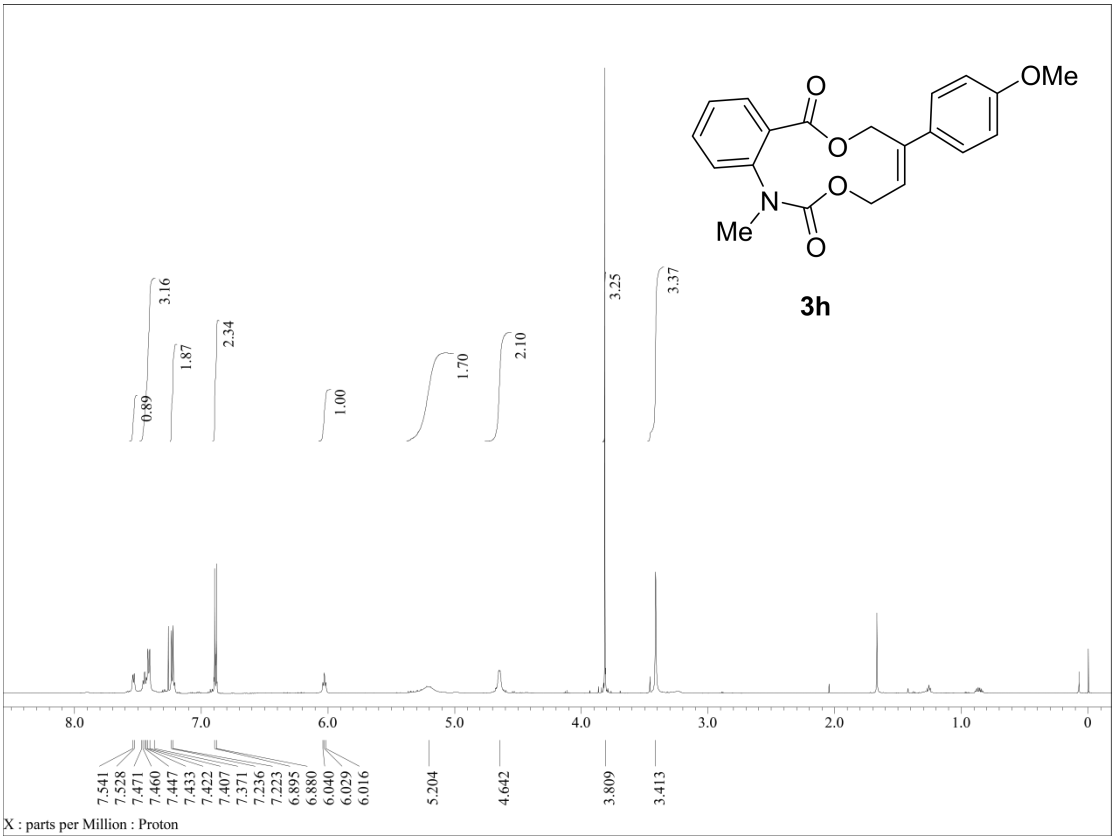
23.9
X : parts per Million : Carbon13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O
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Me
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3.25
3.37
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.528
7.471
7.460
7.447
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7.422
7.407
7.371
7.236
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6.040
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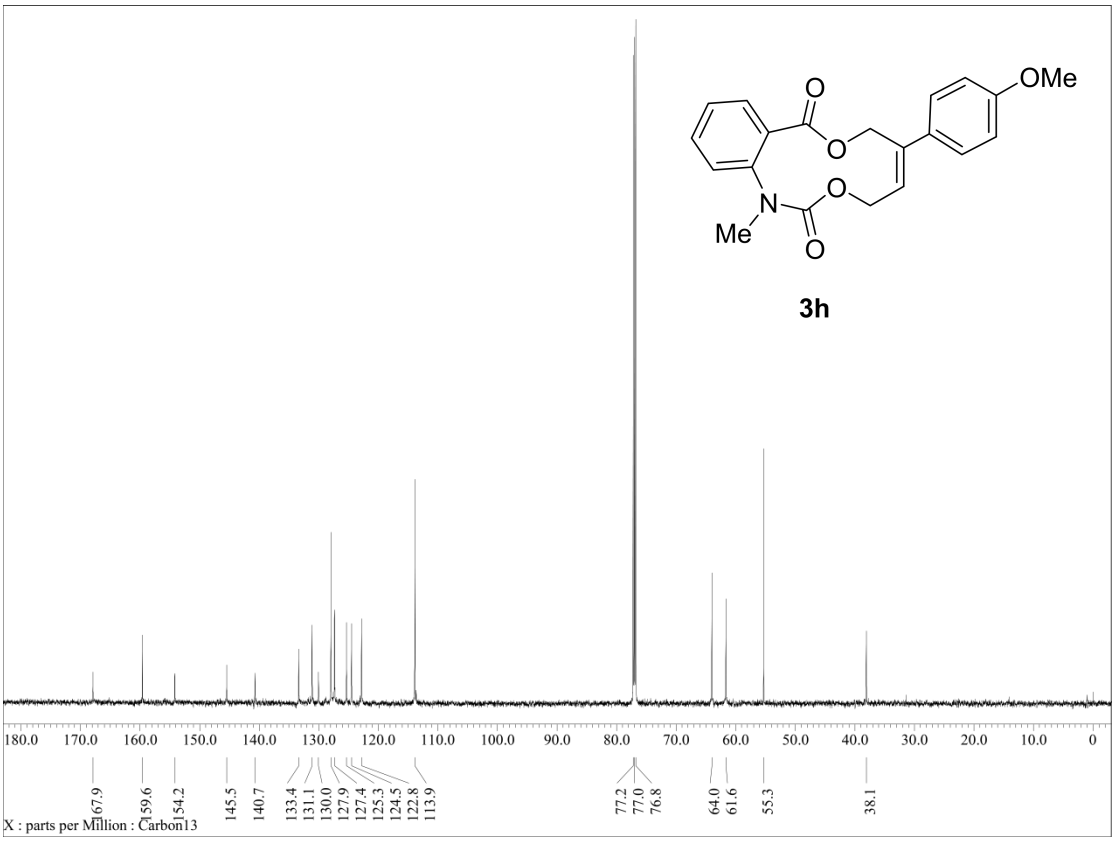
3.413
X : parts per Million : Proton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Me
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3h
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140.0
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159.6
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133.4
131.1
130.0
127.9
127.4
125.3
124.5
122.8
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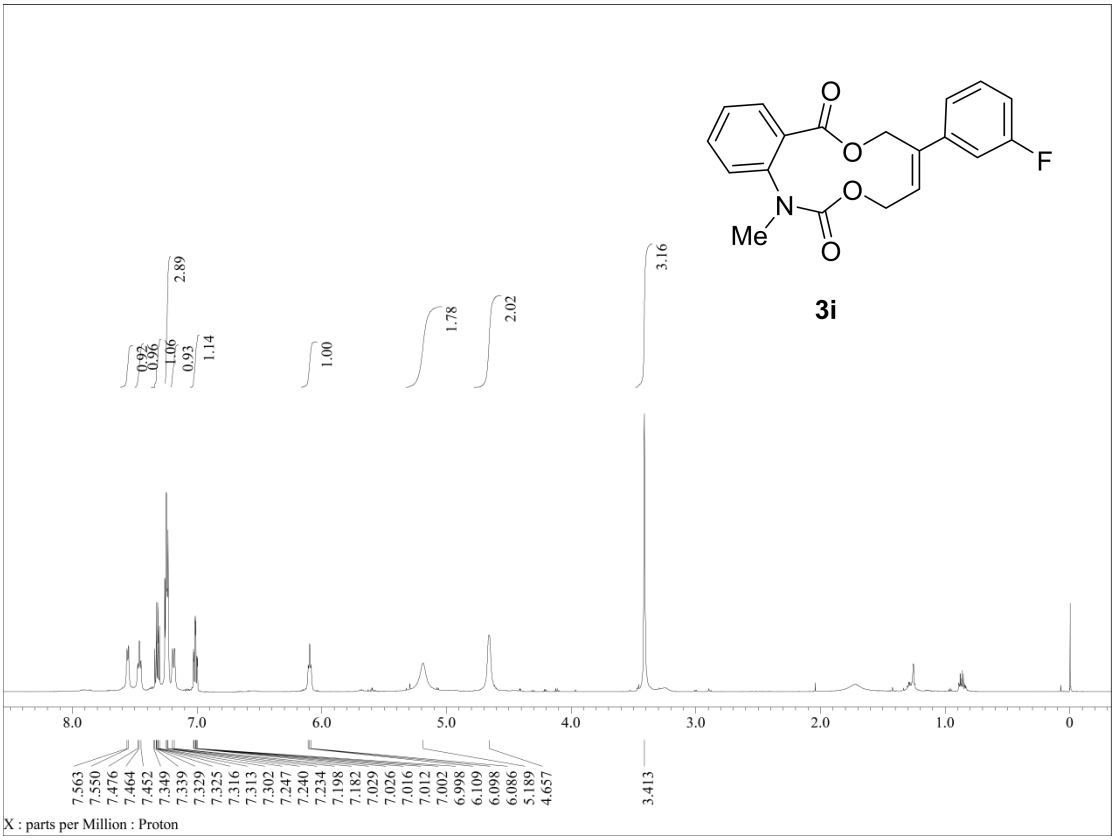
76.8
64.0
61.6
55.3
38.1
X : parts per Million : Carbon13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0.93
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2.02
3.16
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3.0
2.0
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7.550
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7.464
7.452
7.349
7.339
7.329
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7.316
7.313
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7.240
7.234
7.198
7.182
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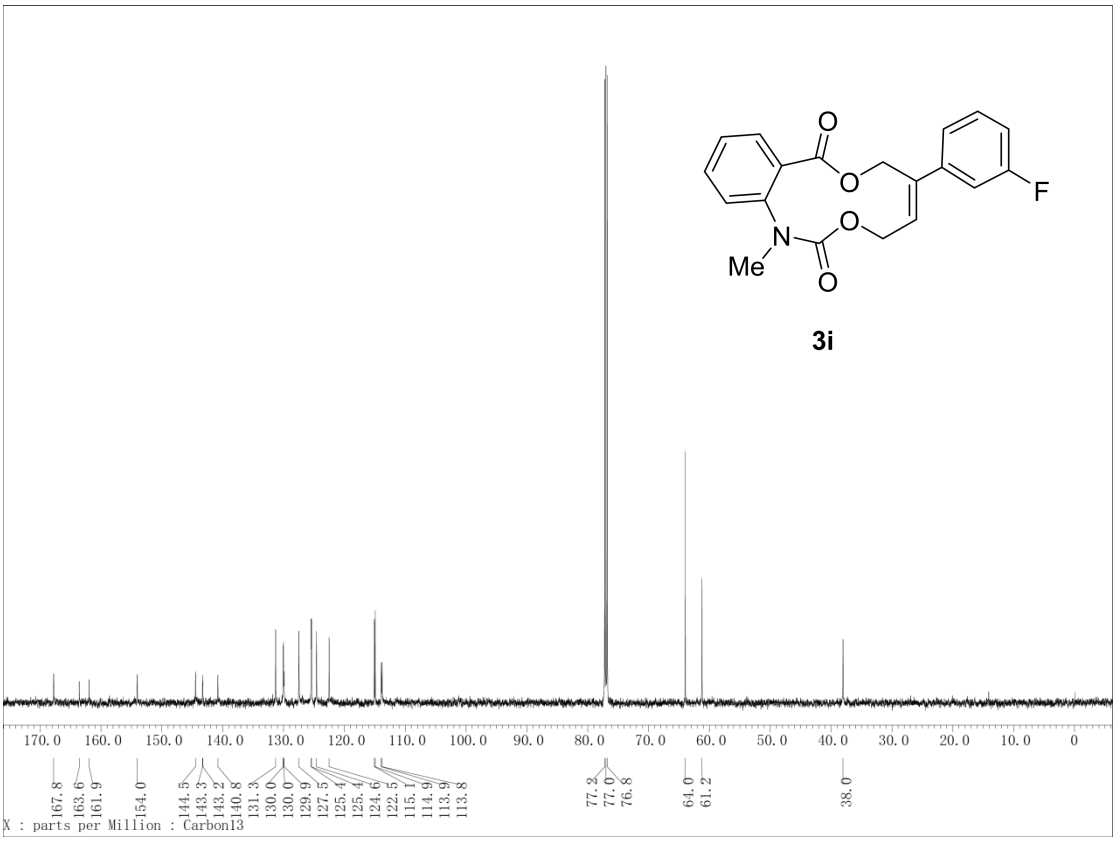
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140.0
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110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.8
163.6
161.9
154.0
144.5
143.3
143.2
140.8
131.3
130.0
130.0
129.9
127.5
125.4
125.4
124.6
122.5
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113.9
113.8
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64.0
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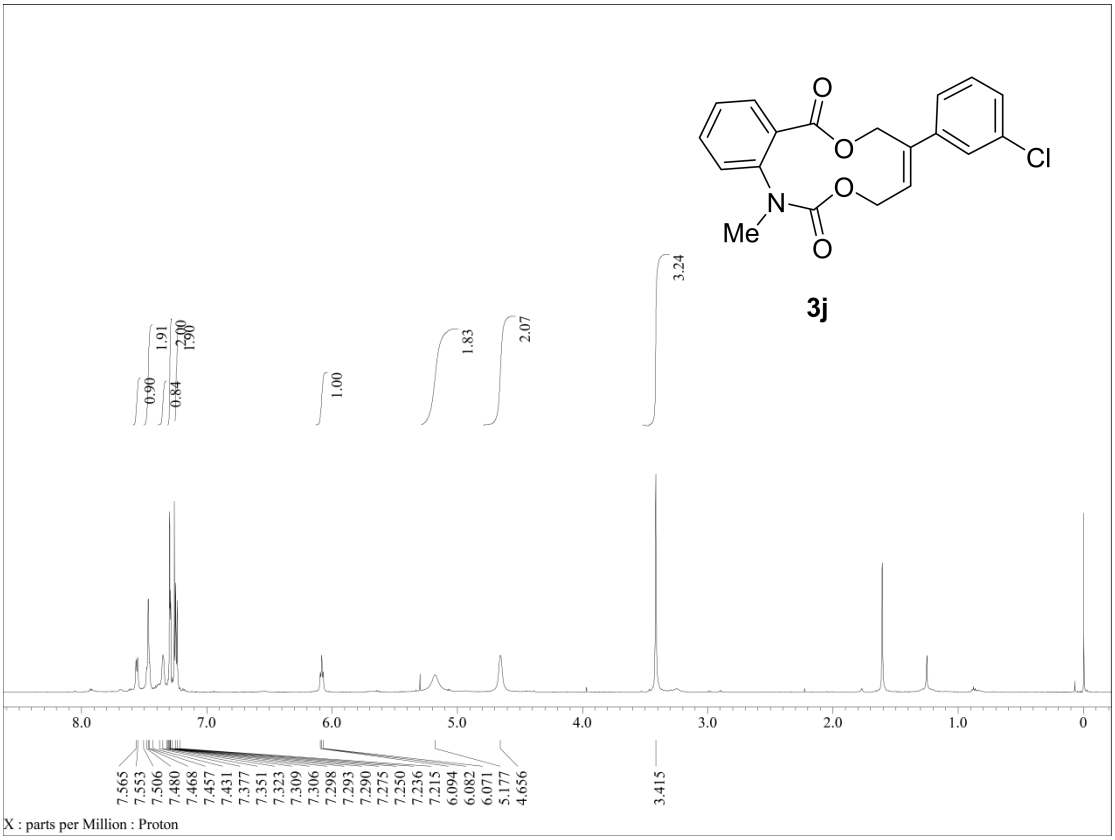
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Cl
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7.0
6.0
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3.0
2.0
1.0
0
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7.298
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7.290
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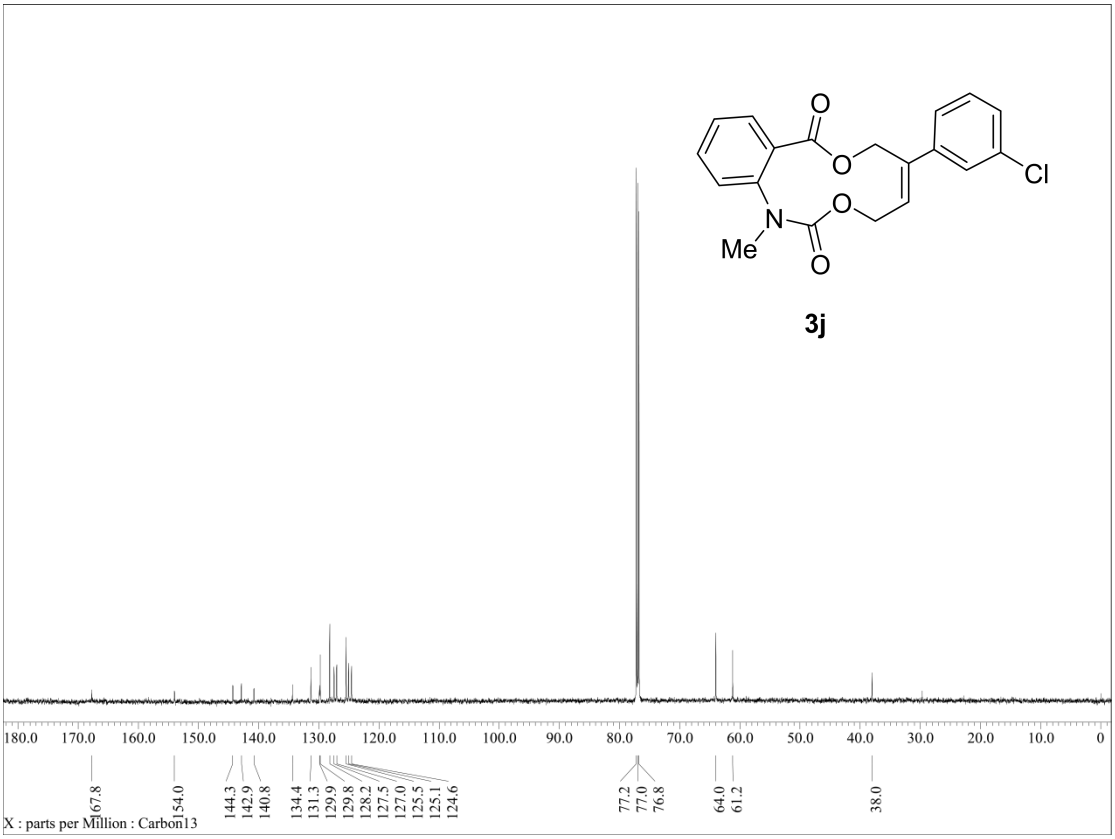
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Me
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3j
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170.0
160.0
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110.0
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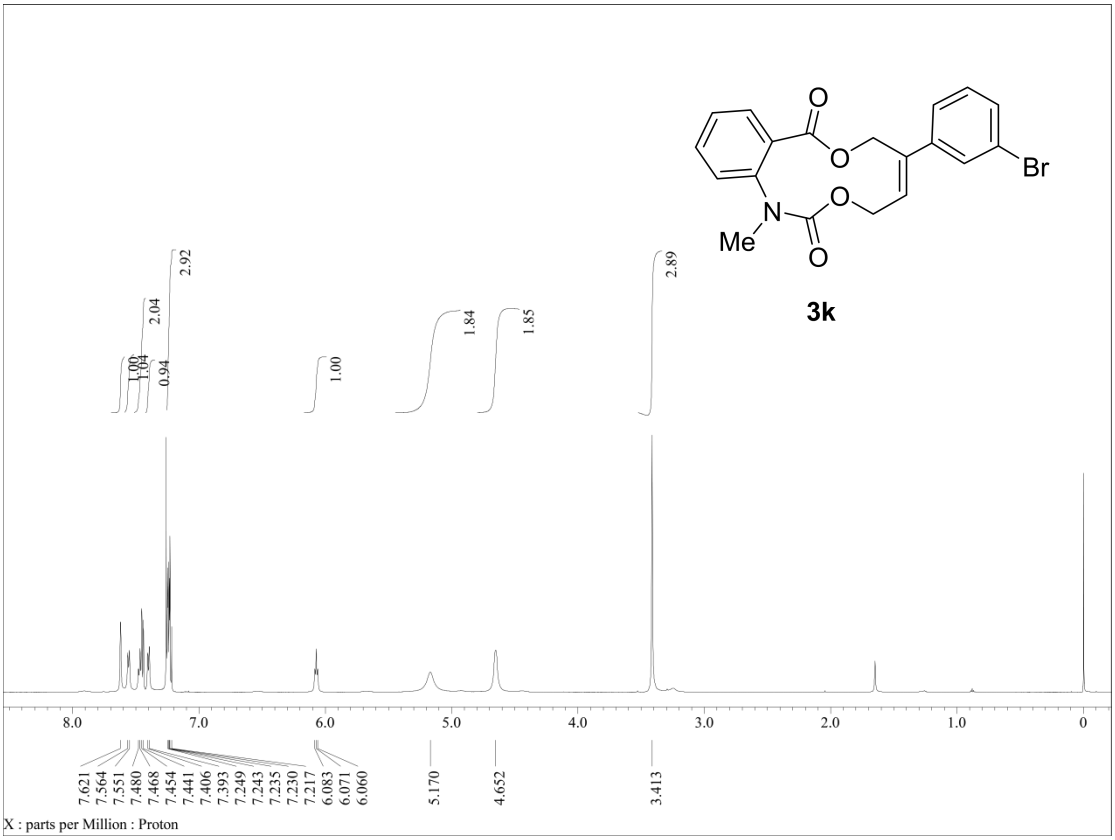
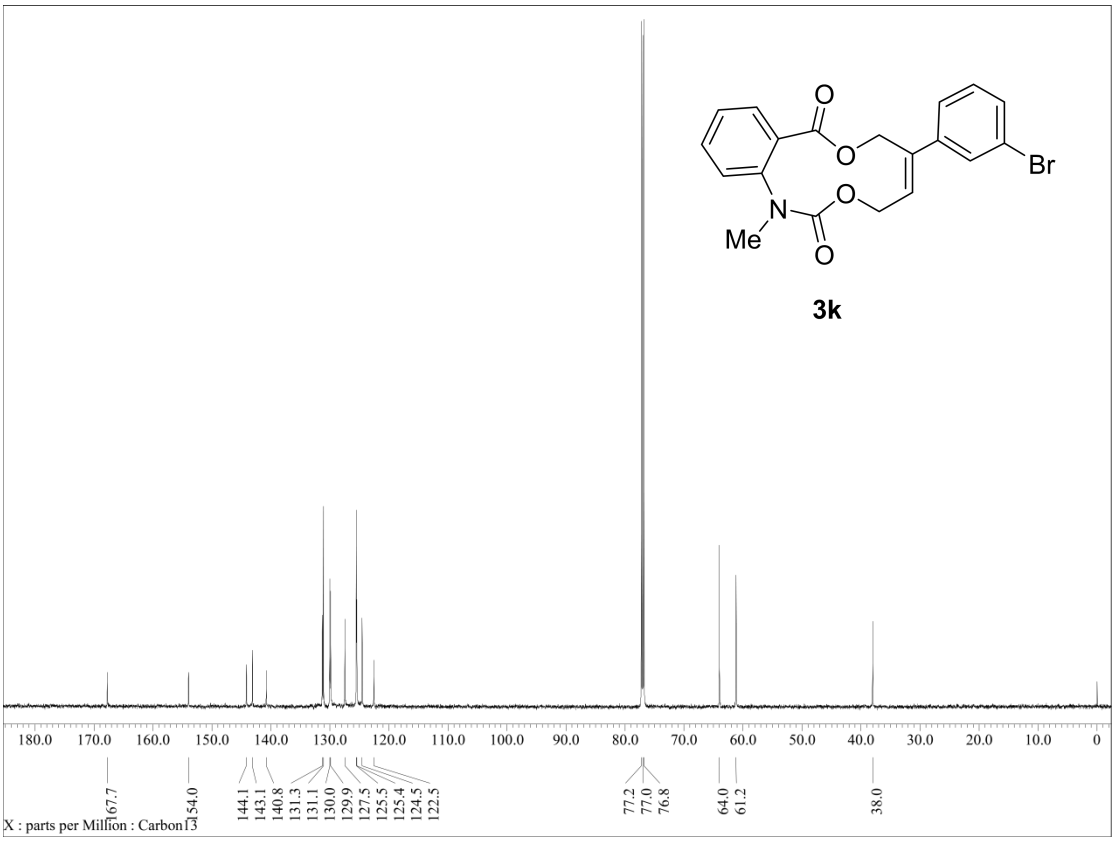
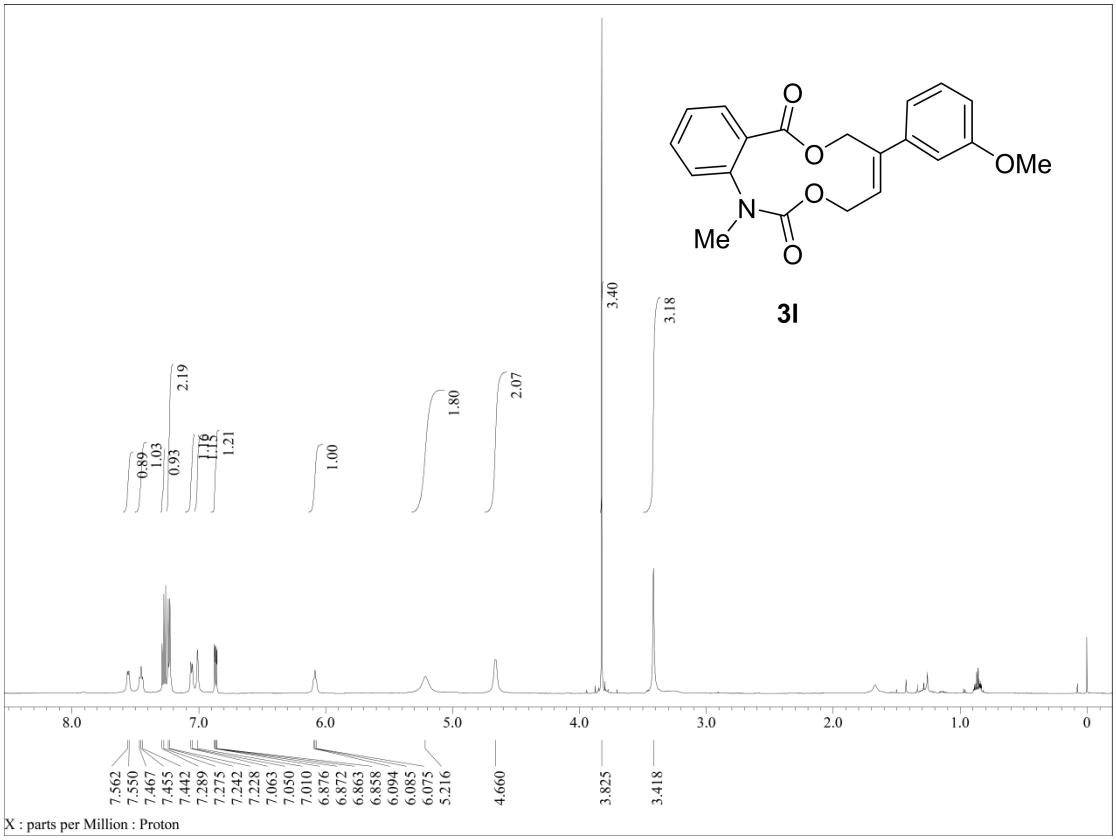
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.8
154.0
144.3
142.9
140.8
134.4
131.3
129.9
129.8
128.2
127.5
127.0
125.5
125.1
124.6
77.2
77.0
76.8
64.0
61.2
38.0
X : parts per Million : Carbon13


O
O
Br
O
N
Me
O
3k
2.92
2.04
1.00
1.04
0.94
1.00
1.84
1.85
2.89
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.621
7.564
7.551
7.480
7.468
7.454
7.441
7.406
7.393
7.249
7.243
7.235
7.230
7.217
6.083
6.071
6.060
5.170
4.652
3.413
X : parts per Million : Proton


O
O
Br
O
N
Me
O
3k
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.7
154.0
144.1
143.1
140.8
131.3
131.1
130.0
129.9
127.5
125.4
124.5
122.5
77.2
77.0
76.8
64.0
61.2
38.0
X : parts per Million : Carbon13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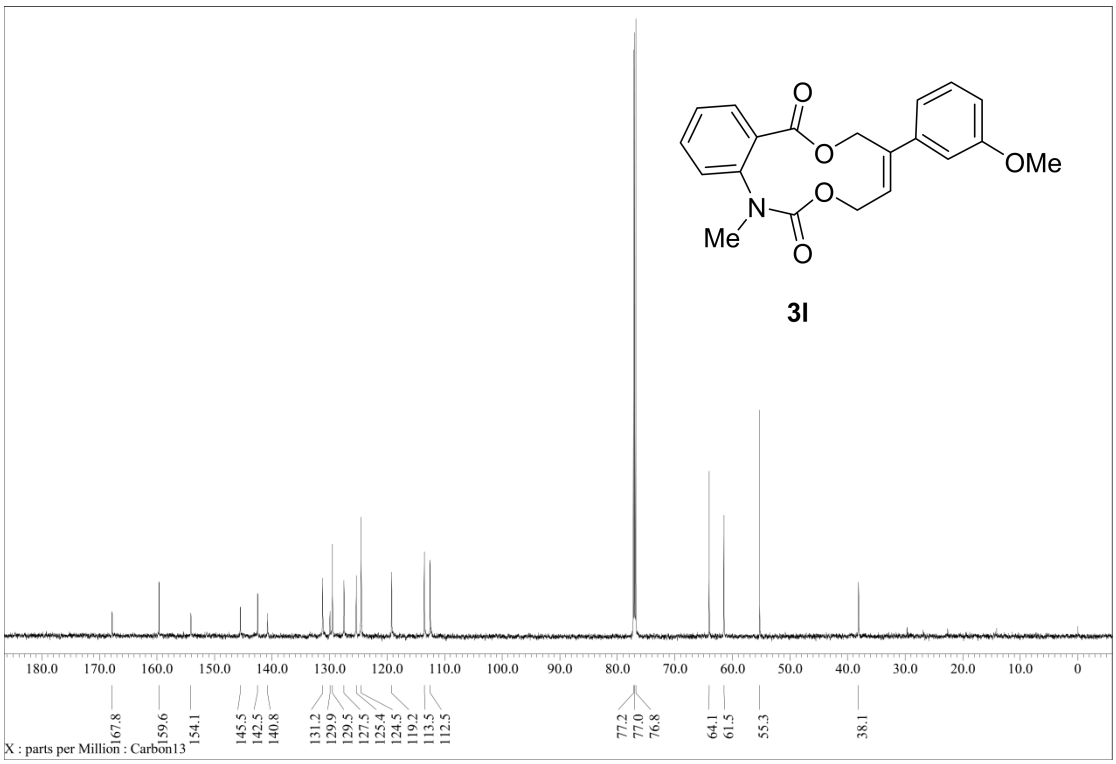
O
OMe
N
Me
O
O
3l
3.40
3.18
2.19
2.07
1.80
1.21
1.15
1.16
1.03
1.00
0.93
0.89
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.562
7.550
7.467
7.455
7.442
7.289
7.275
7.242
7.228
7.063
7.050
7.010
6.876
6.872
6.863
6.858
6.094
6.085
6.075
5.216
4.660
3.825
3.418
X : parts per Million : Proton


O
O
OMe
N
Me
O
O
3l
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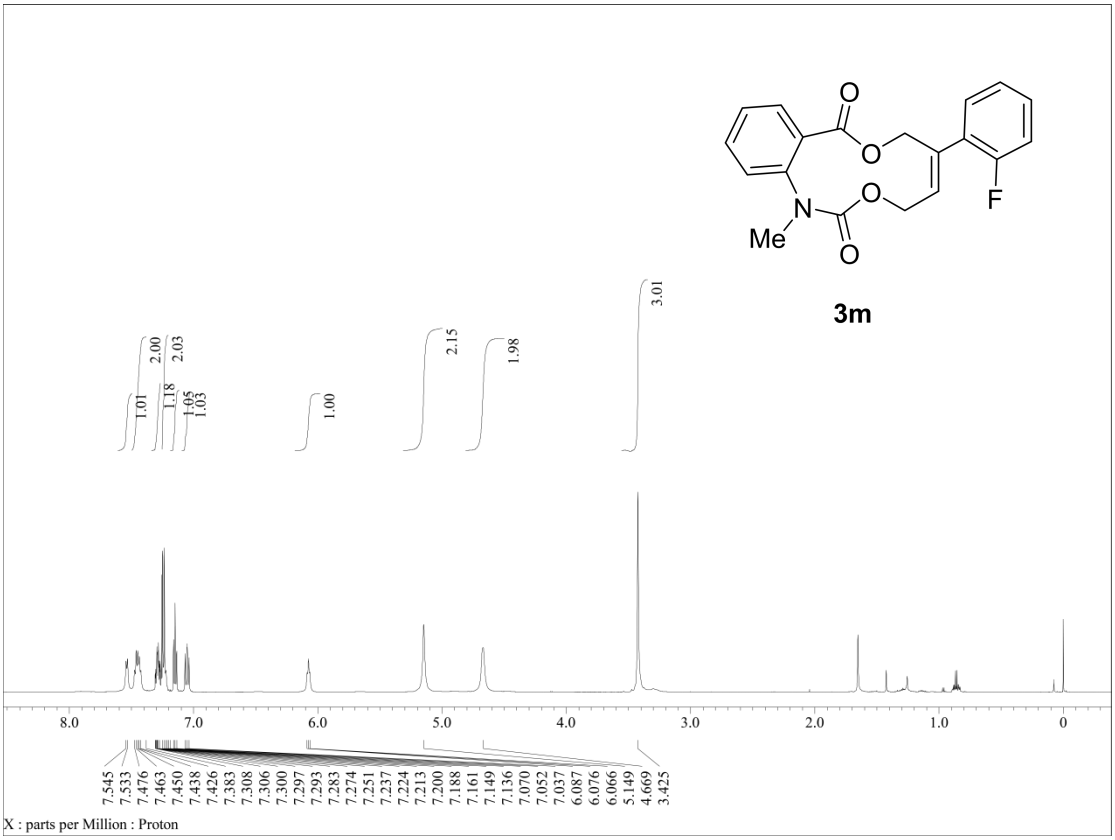
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.8
159.6
154.1
145.5
142.5
140.8
131.2
129.9
129.5
127.5
125.4
124.5
119.2
113.5
112.5
77.2
77.0
76.8
64.1
61.5
55.3
38.1
X : parts per Million : Carbon13


O
O
O
N
Me
O
F
3m
3.01
2.15
2.00
2.03
1.98
1.01
1.18
1.05
1.03
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.545
7.533
7.476
7.463
7.450
7.438
7.426
7.383
7.308
7.306
7.300
7.297
7.293
7.283
7.274
7.251
7.237
7.224
7.213
7.200
7.188
7.161
7.149
7.136
7.070
7.052
7.037
6.087
6.076
6.066
5.149
4.669
3.425
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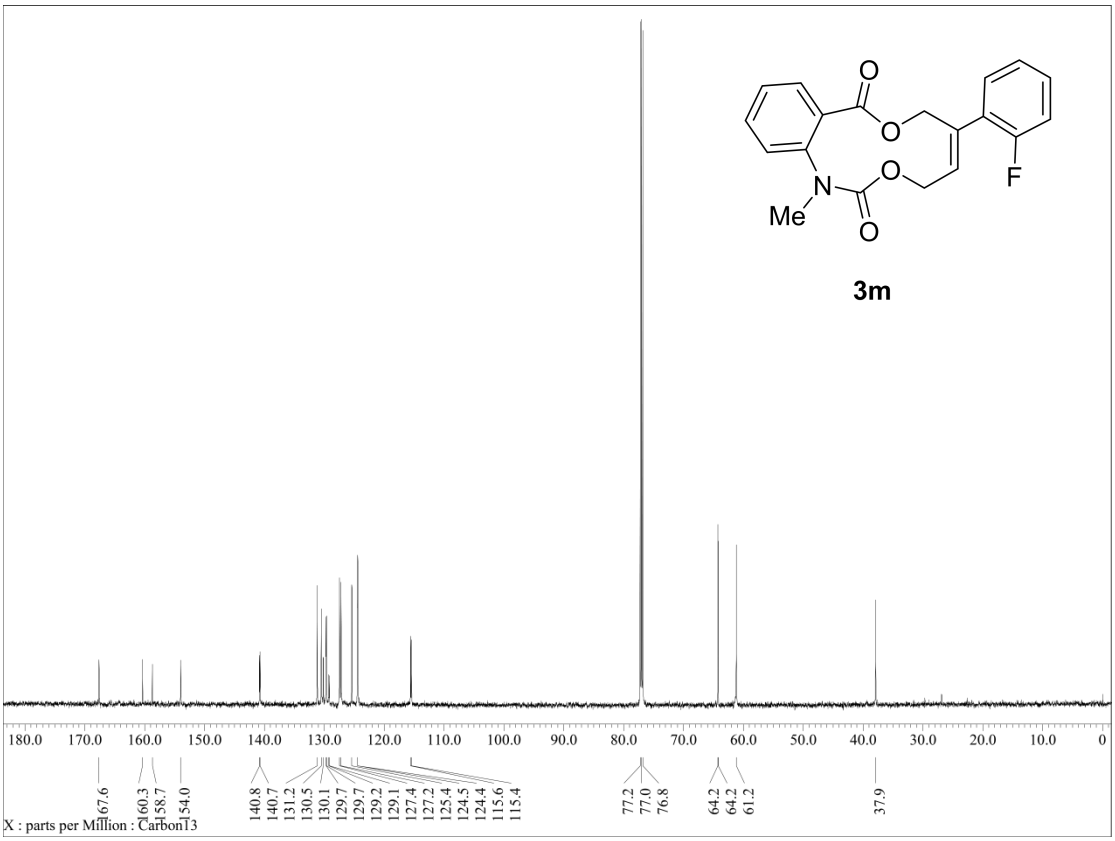
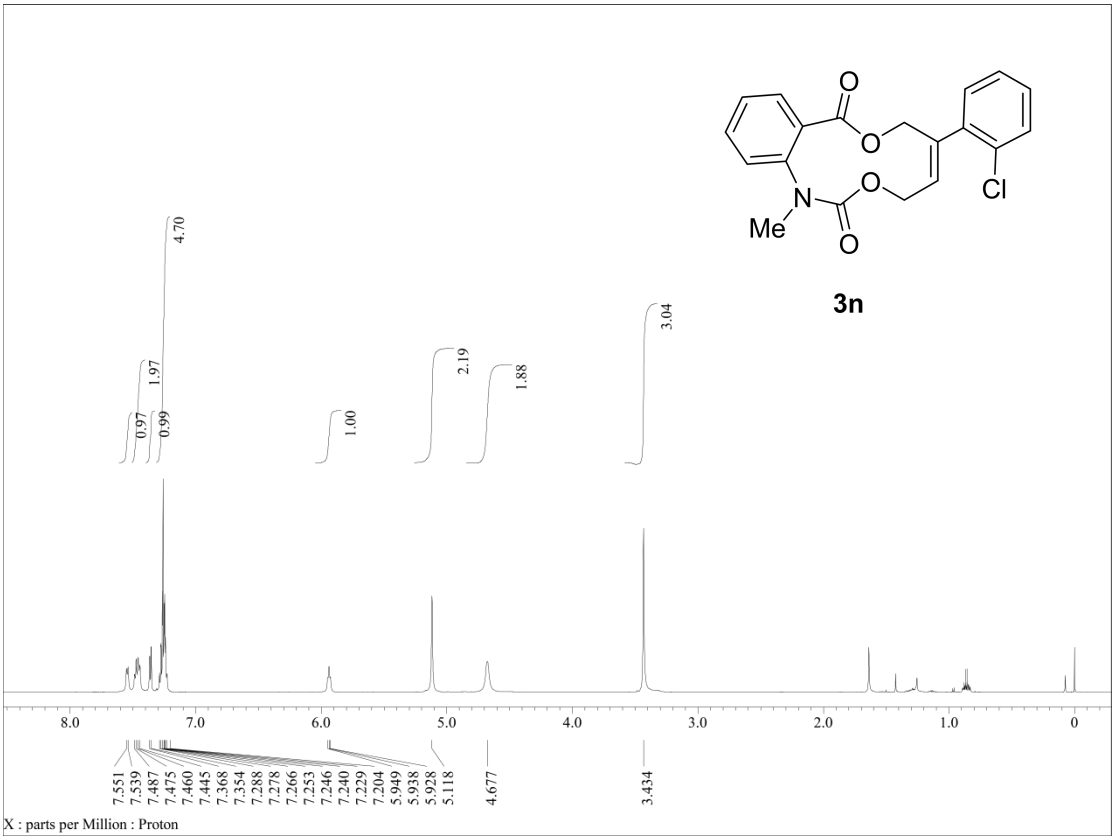
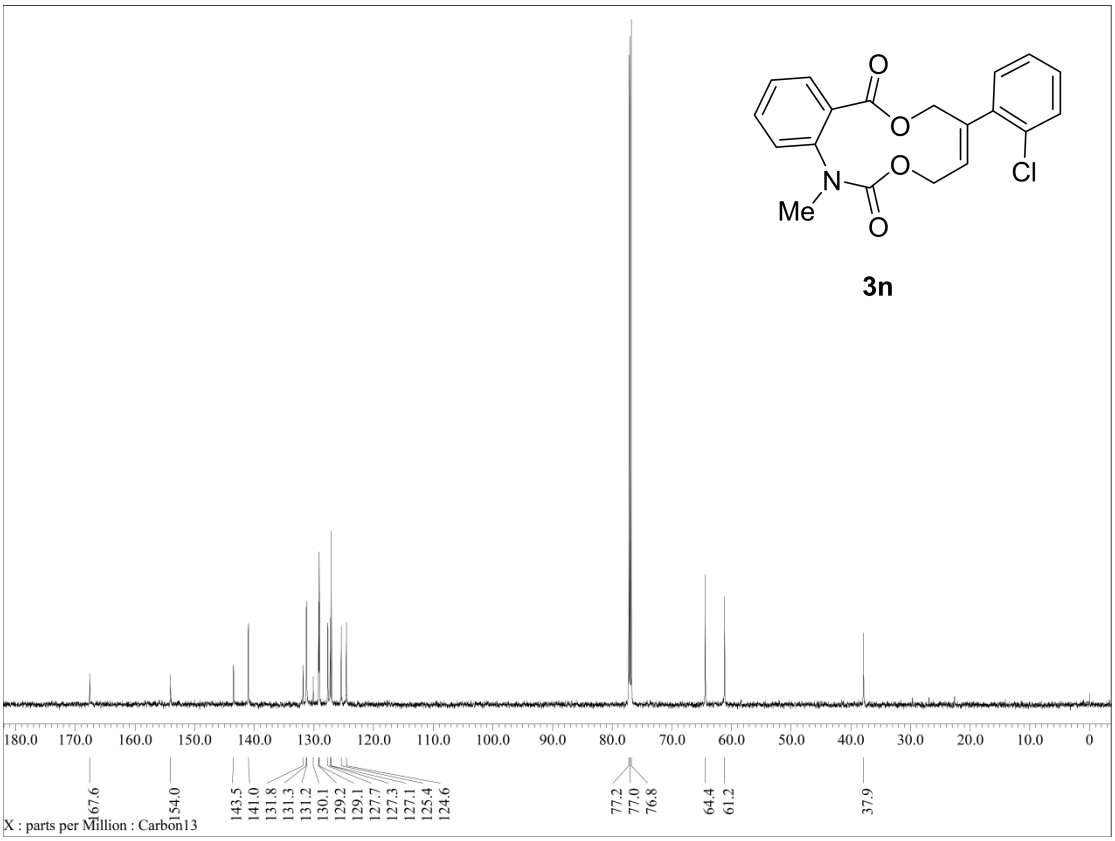
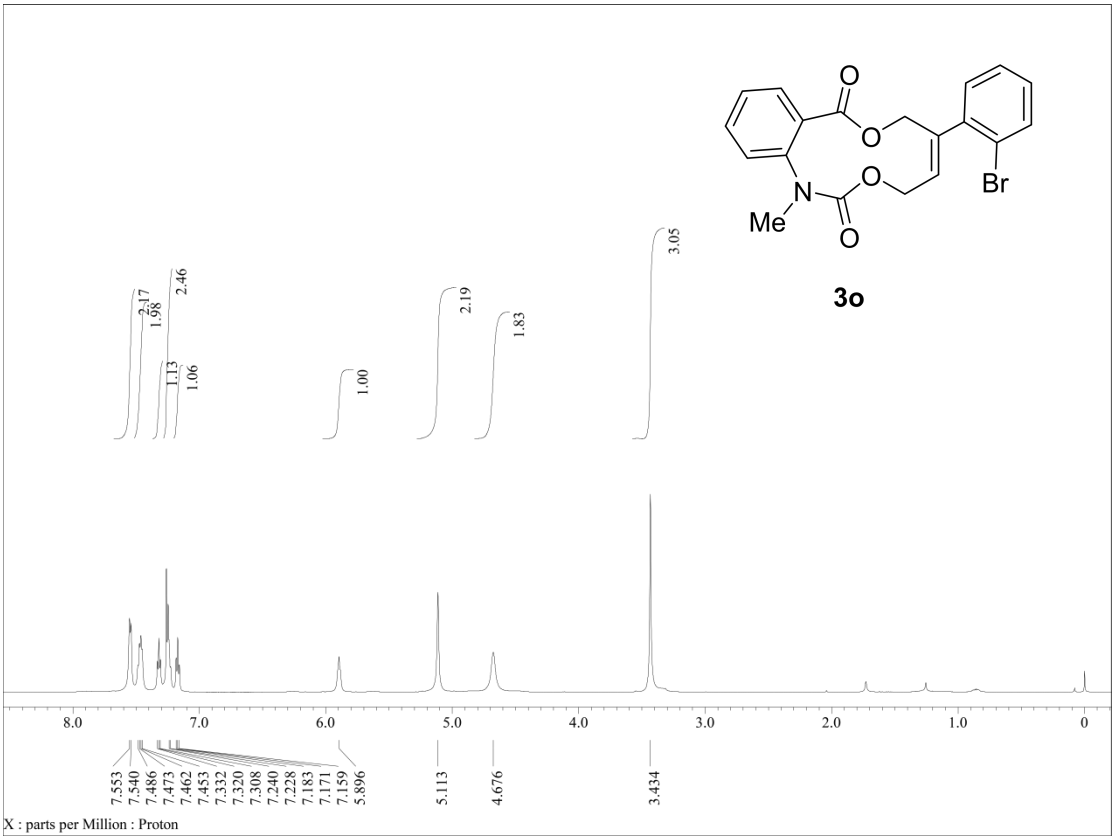
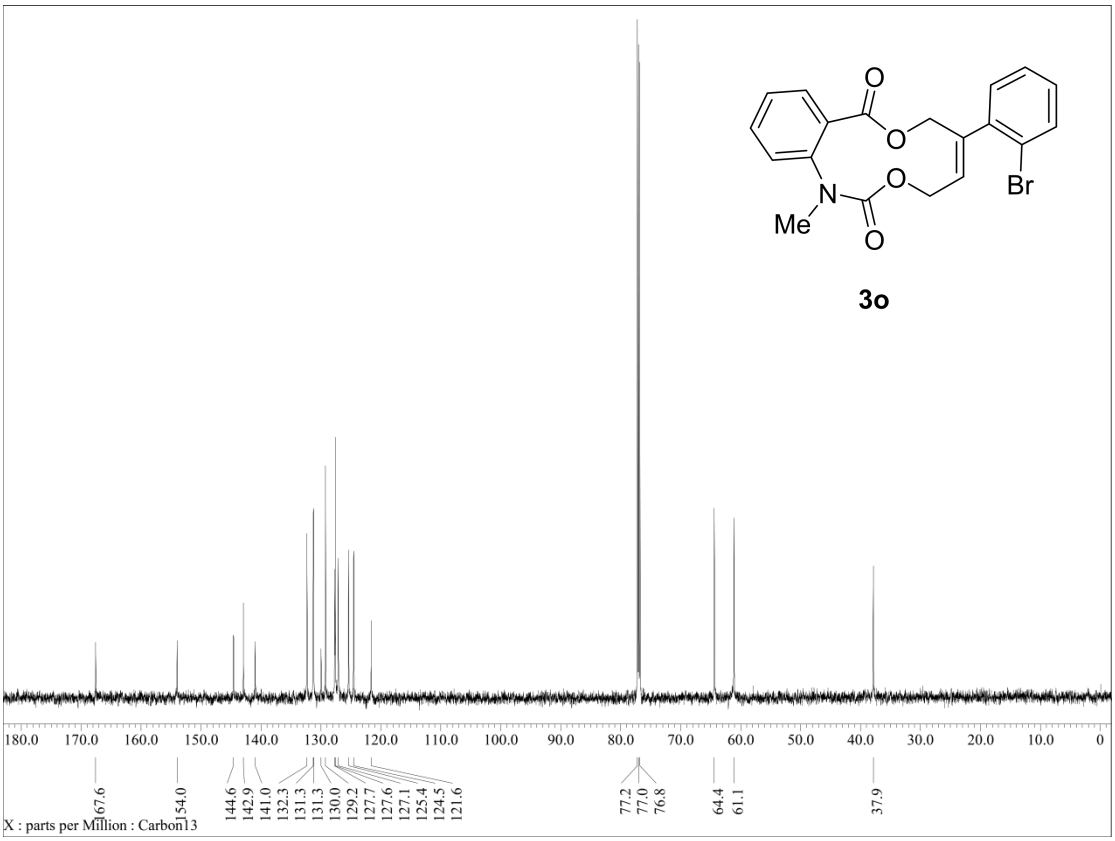
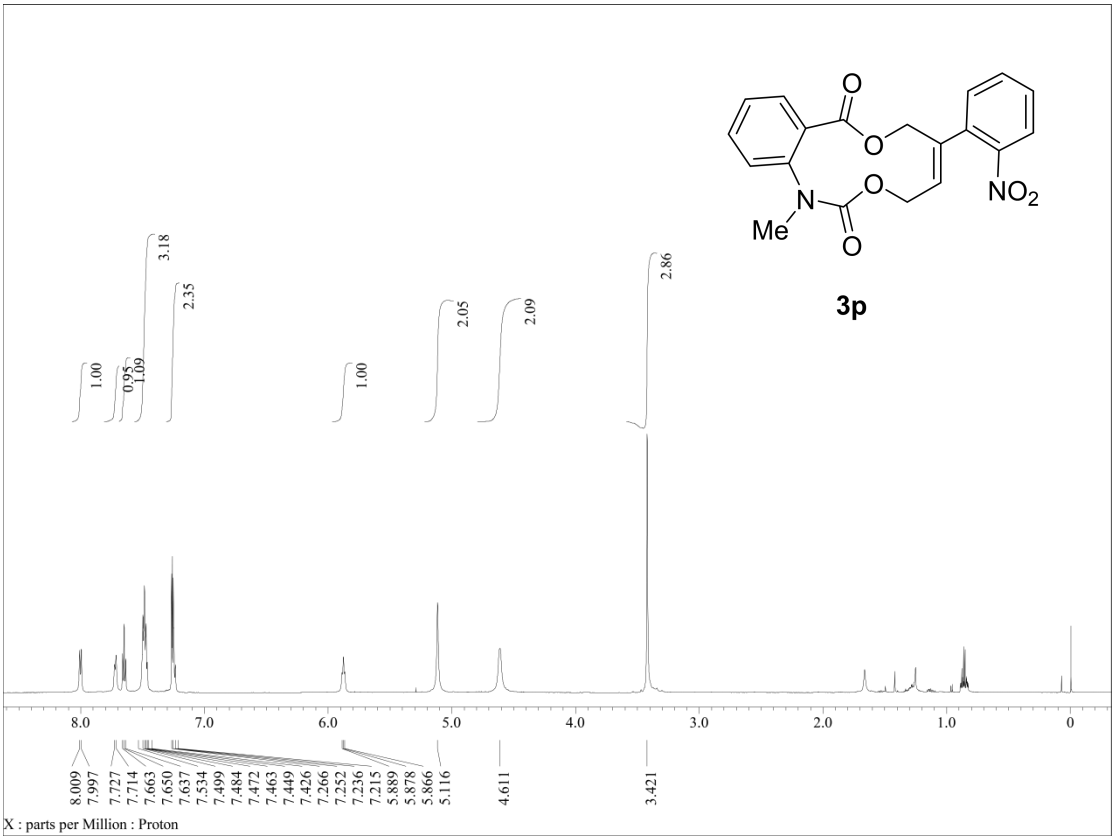

O
O
O
N
Me
O
F
3m
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.6
160.3
158.7
154.0
140.8
140.7
131.2
130.5
130.1
129.7
129.7
129.2
129.1
127.4
127.2
125.4
124.5
124.4
115.6
115.4
77.2
77.0
76.8
64.2
64.2
61.2
37.9
X : parts per Million : Carbon13

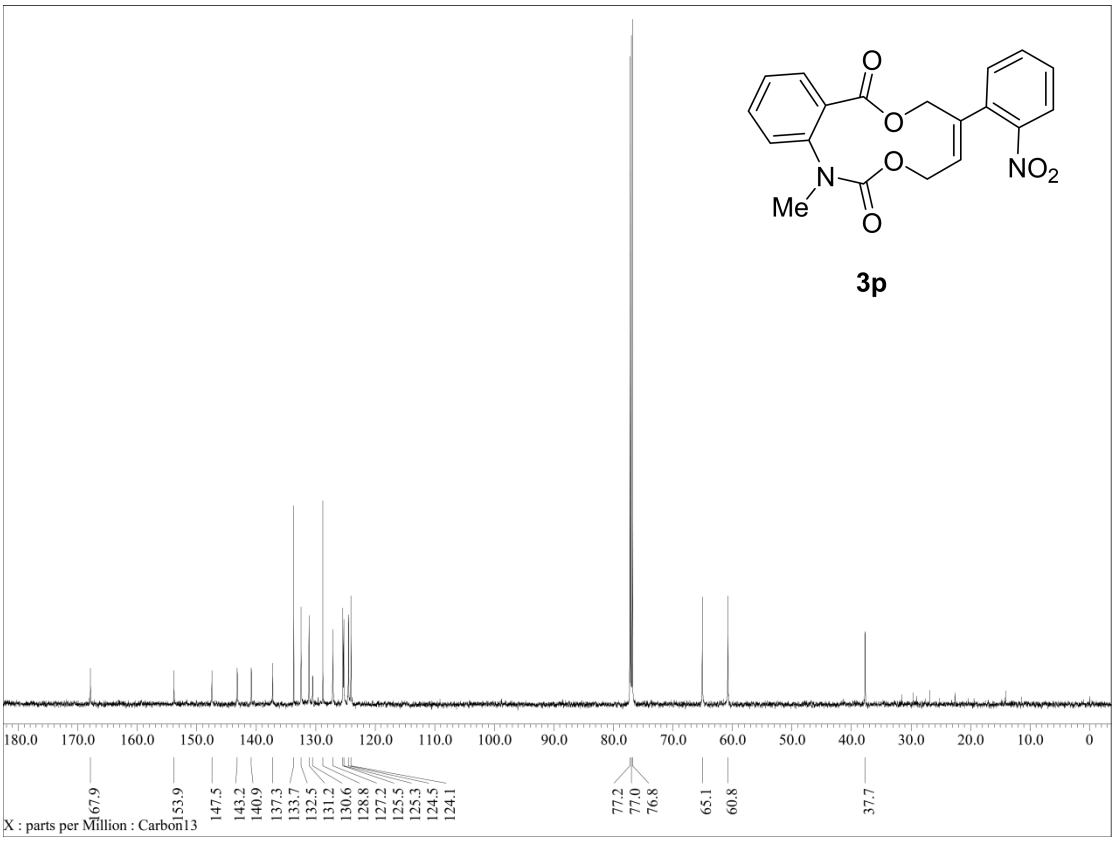

O
O
O
N
Me
O
Cl
3n
4.70
1.97
0.97
0.99
1.00
2.19
1.88
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.551
7.539
7.487
7.475
7.460
7.445
7.368
7.354
7.288
7.278
7.266
7.253
7.246
7.240
7.229
7.204
5.949
5.938
5.928
5.118
4.677
3.434
X : parts per Million : Proton

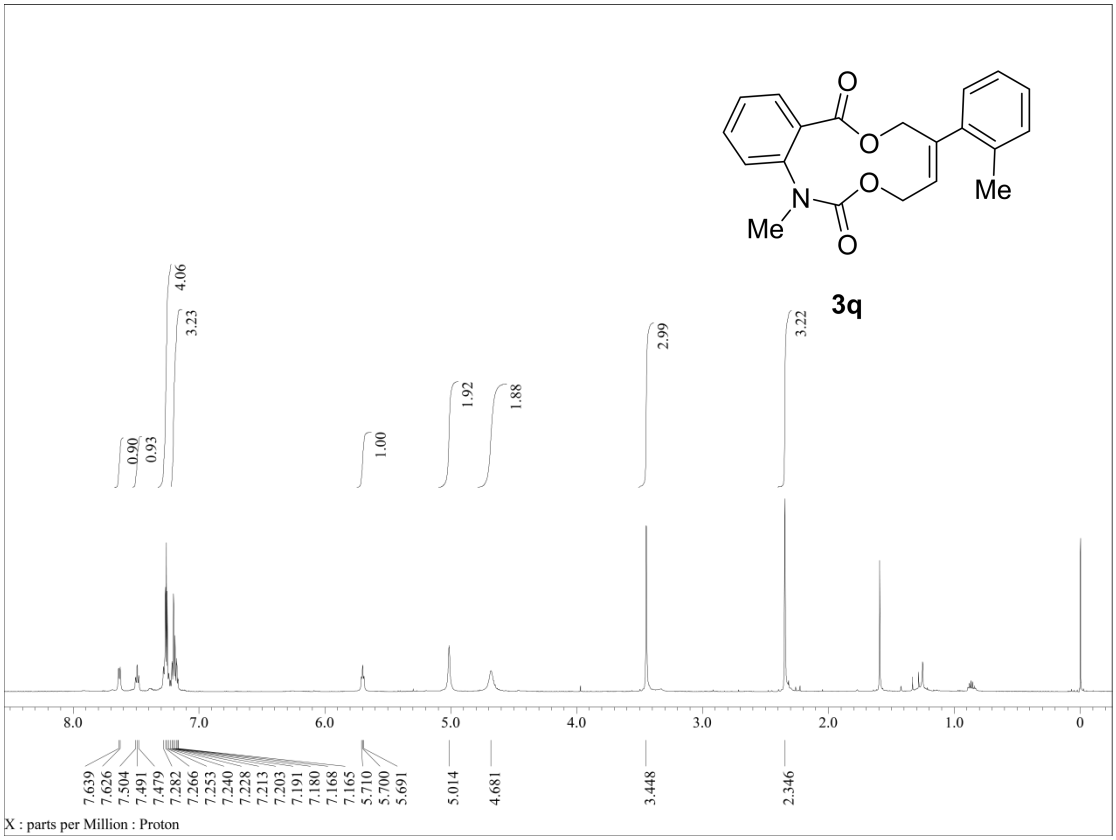

O
O
O
N
Me
O
Cl
3n
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.6
154.0
143.5
141.0
131.8
131.3
131.2
130.1
129.2
129.1
127.7
127.3
127.1
125.4
124.6
77.2
77.0
76.8
64.4
61.2
37.9
X : parts per Million : Carbon13


O
O
O
N
Me
O
Br
3o
2.17
1.98
2.46
1.13
1.06
1.00
2.19
1.83
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.553
7.540
7.486
7.473
7.462
7.453
7.332
7.320
7.308
7.240
7.228
7.183
7.171
7.159
5.896
5.113
4.676
3.434
X : parts per Million : Proton


O
O
O
N
Me
O
Br
3o
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.6
154.0
144.6
142.9
141.0
132.3
131.3
131.3
130.0
129.2
127.7
127.6
127.1
125.4
124.5
121.6
77.2
77.0
76.8
64.4
61.1
37.9
X : parts per Million : Carbon13


3p
1.00
0.95
1.09
3.18
2.35
1.00
2.05
2.09
2.86
8.009
7.997
7.727
7.714
7.663
7.650
7.637
7.534
7.499
7.484
7.472
7.463
7.449
7.426
7.266
7.252
7.236
7.215
5.889
5.878
5.866
5.116
4.611
3.421
X : parts per Million : Proton


3p
167.9
153.9
147.5
143.2
140.9
137.3
133.7
132.5
131.2
130.6
128.8
127.2
125.5
125.3
124.5
124.1
77.2
77.0
76.8
65.1
60.8
37.7
X : parts per Million : Carbon13


O
O
O
N
Me
Me
O
3q
4.06
3.23
2.99
3.22
1.92
1.88
0.90
0.93
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.639
7.626
7.504
7.491
7.479
7.282
7.266
7.253
7.240
7.228
7.213
7.203
7.191
7.180
7.168
7.165
5.710
5.700
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5.014
4.681
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2.346
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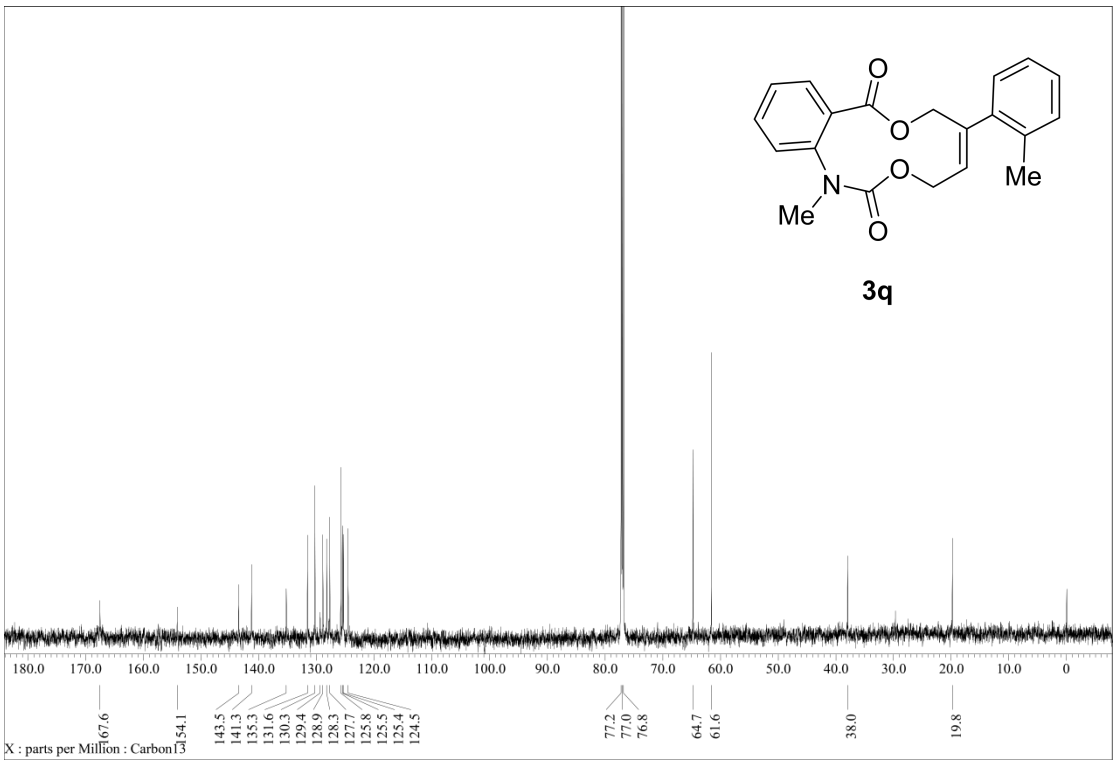
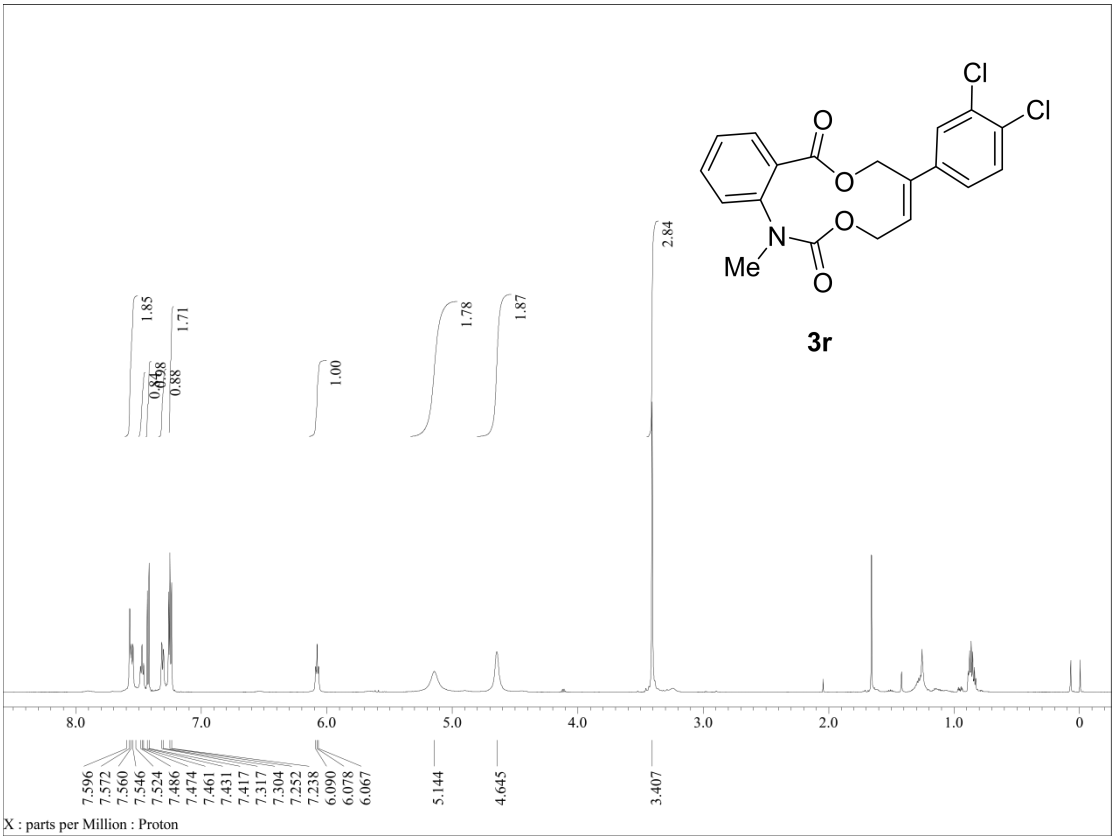
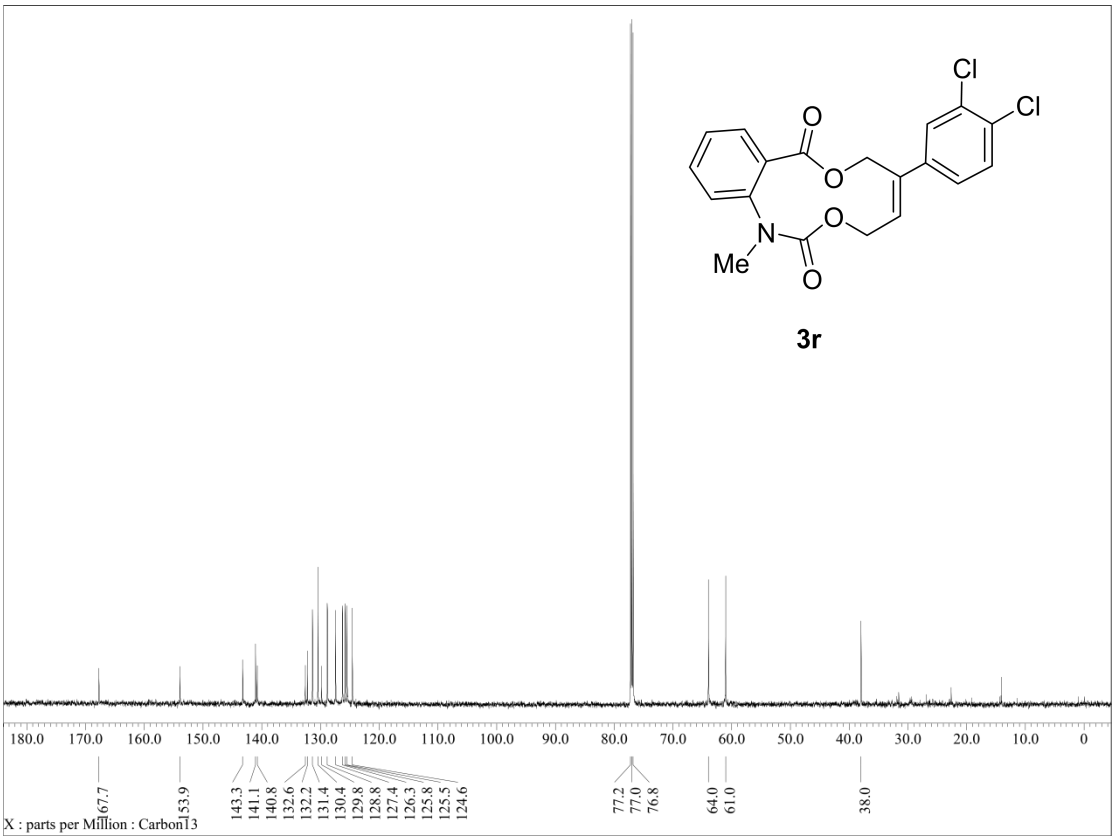
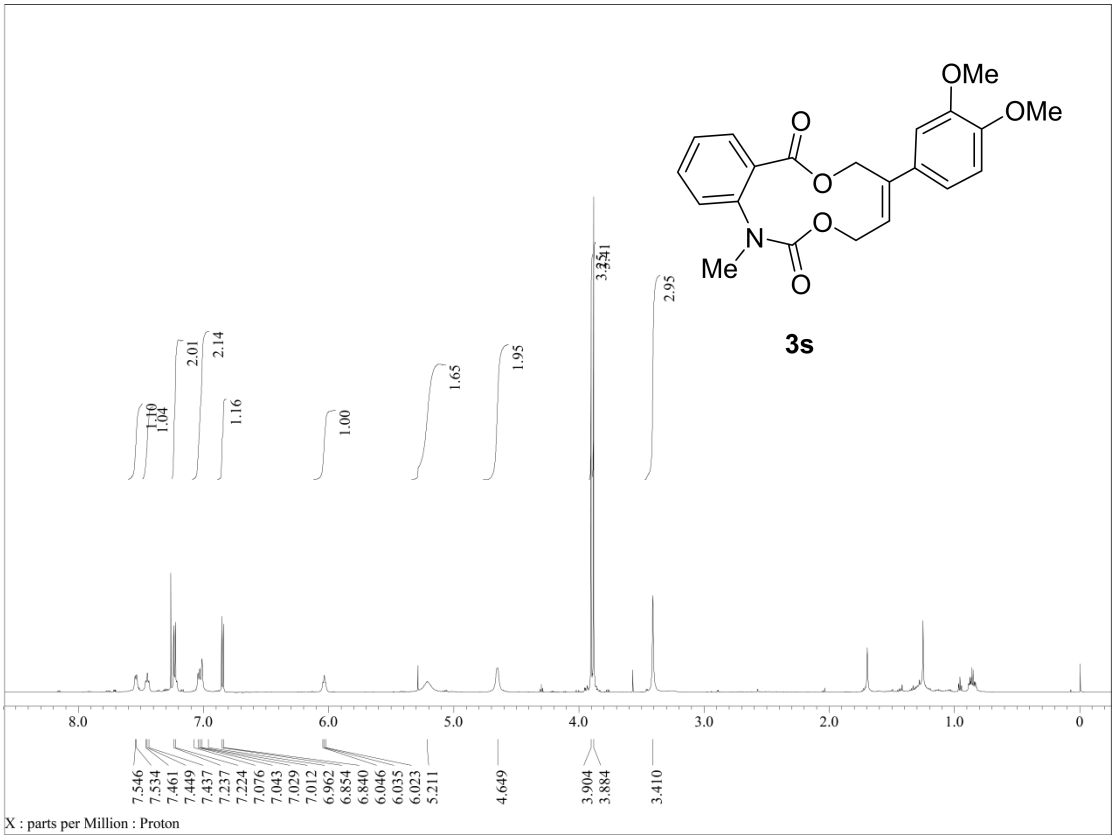
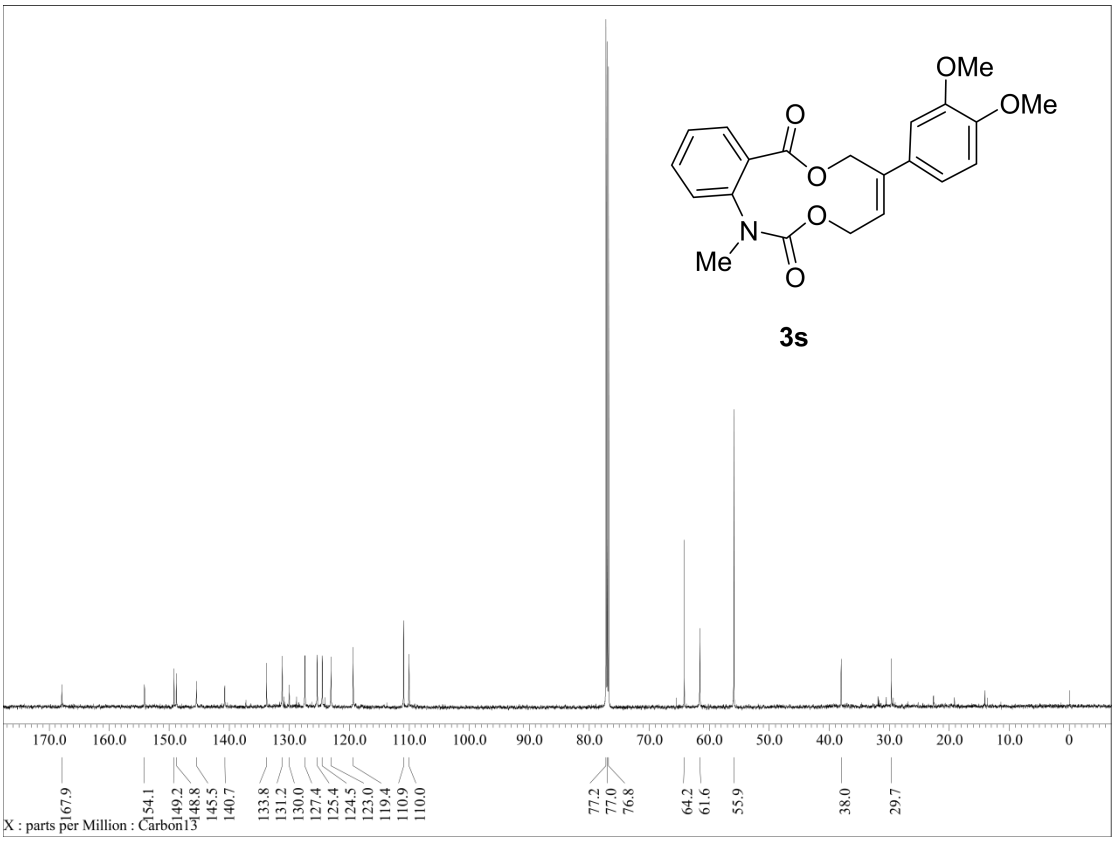
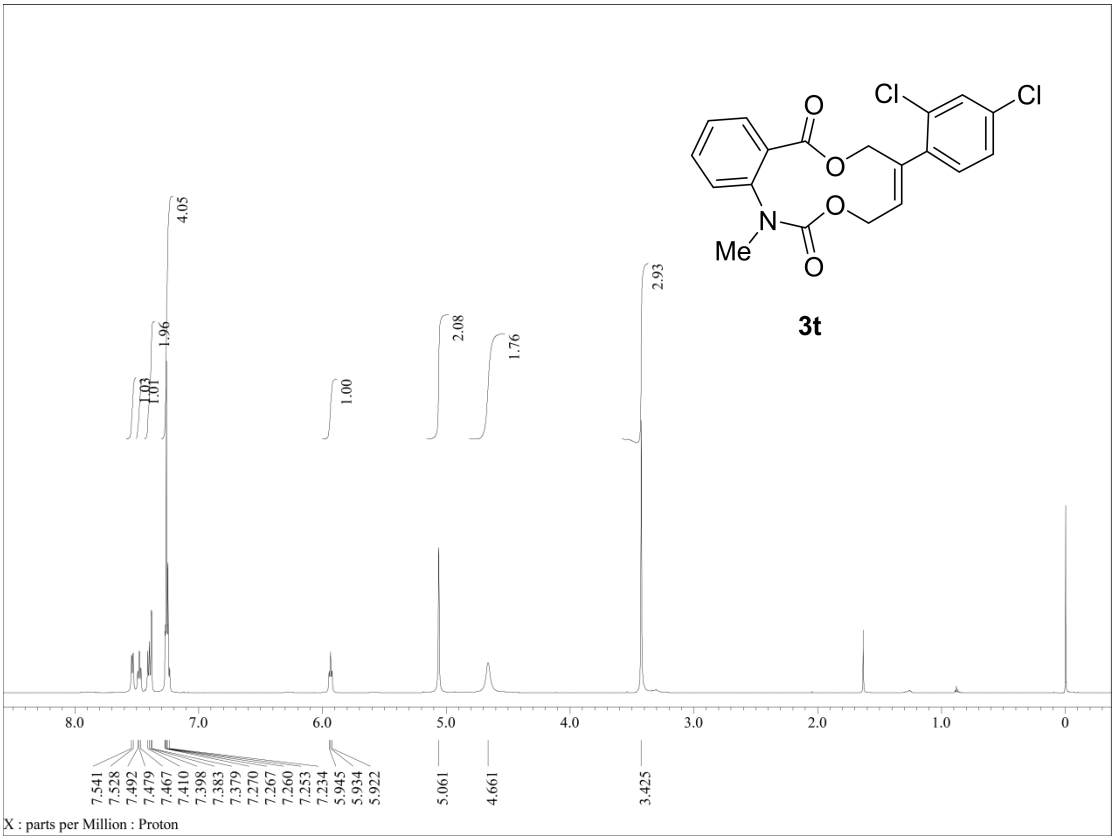

O
O
O
N
Me
Me
O
3q
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.6
154.1
143.5
141.3
135.3
131.6
130.3
129.4
128.9
128.3
127.7
125.8
125.5
125.4
124.5
77.2
77.0
76.8
64.7
61.6
38.0
19.8
X : parts per Million : Carbon13

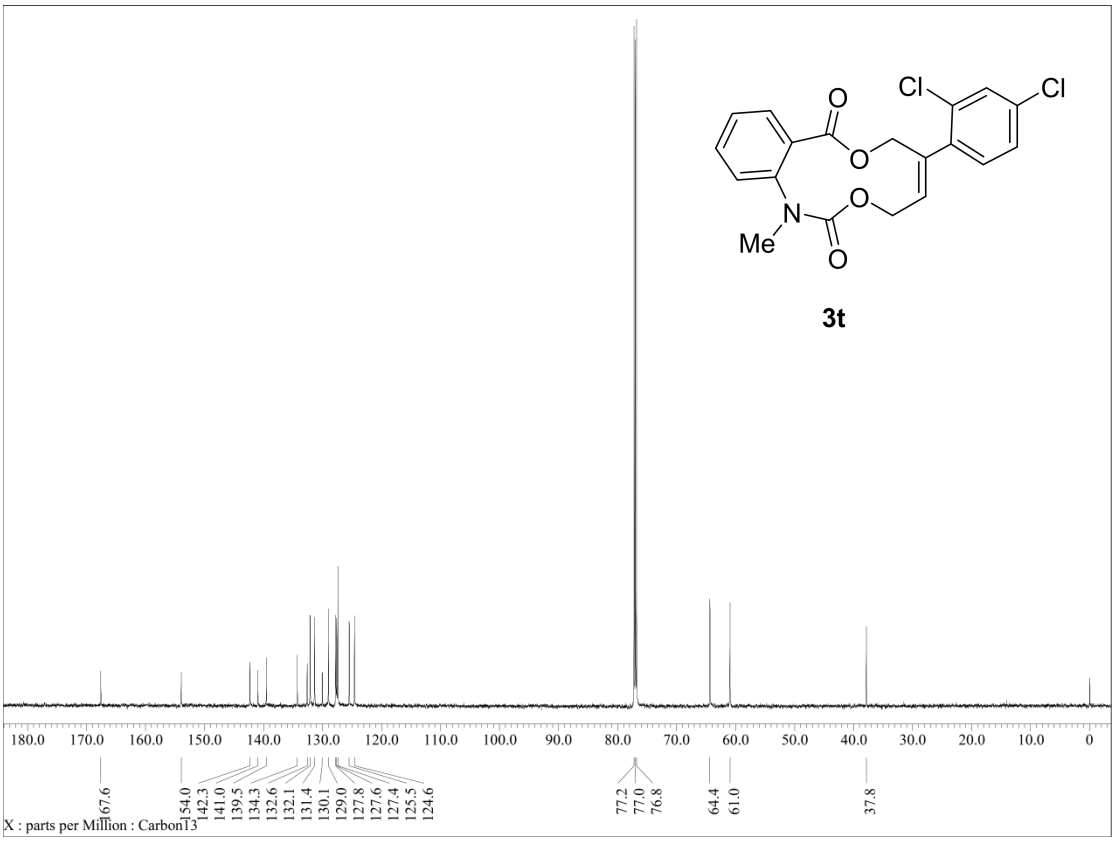

Cl
Cl
O
O
O
N
Me
O
3r
1.85
1.71
0.84
0.88
1.00
1.78
1.87
2.84
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.596
7.572
7.560
7.546
7.524
7.486
7.474
7.461
7.431
7.417
7.317
7.304
7.252
7.238
6.090
6.078
6.067
5.144
4.645
3.407
X : parts per Million : Proton

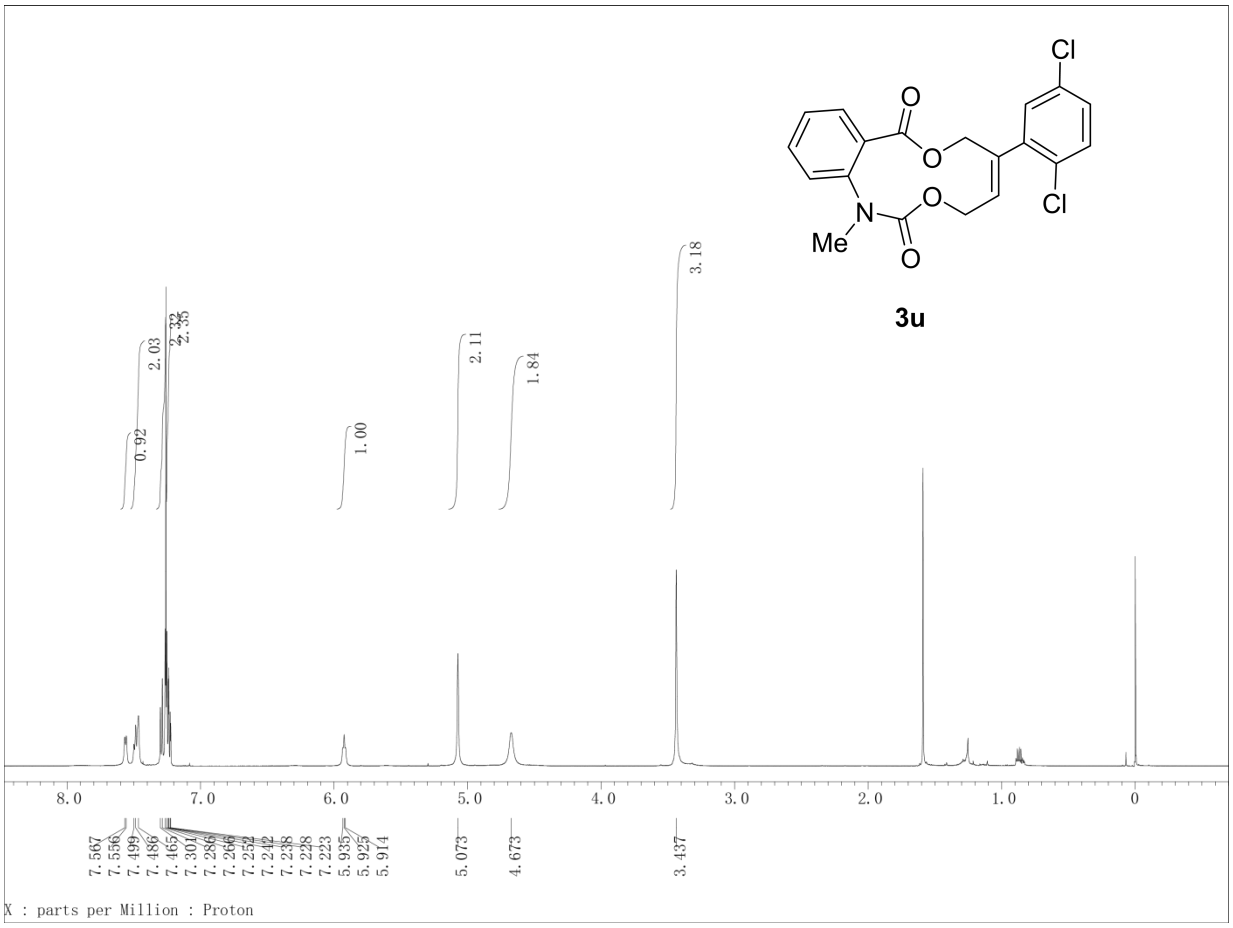

Cl
Cl
O
O
O
N
Me
O
3r
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.7
153.9
143.3
141.1
140.8
132.6
132.2
131.4
130.4
129.8
128.8
127.4
126.3
125.8
125.5
124.6
77.2
77.0
76.8
64.0
61.0
38.0
X : parts per Million : Carbon13

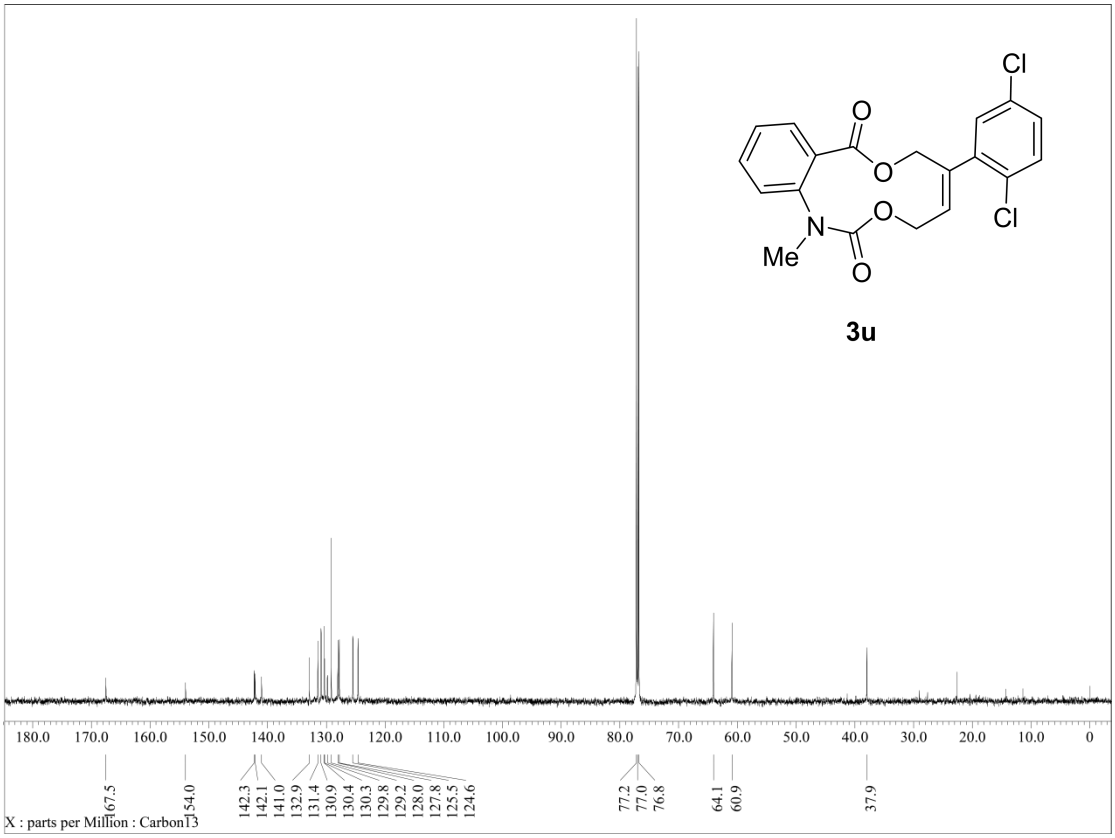

OMe
OMe
O
O
O
N
Me
O
3s
1.10
1.04
2.01
2.14
1.16
1.00
1.65
1.95
3.41
2.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.546
7.534
7.461
7.449
7.437
7.237
7.224
7.076
7.043
7.029
7.012
6.962
6.854
6.840
6.046
6.035
6.023
5.211
4.649
3.904
3.884
3.410
X : parts per Million : Proton

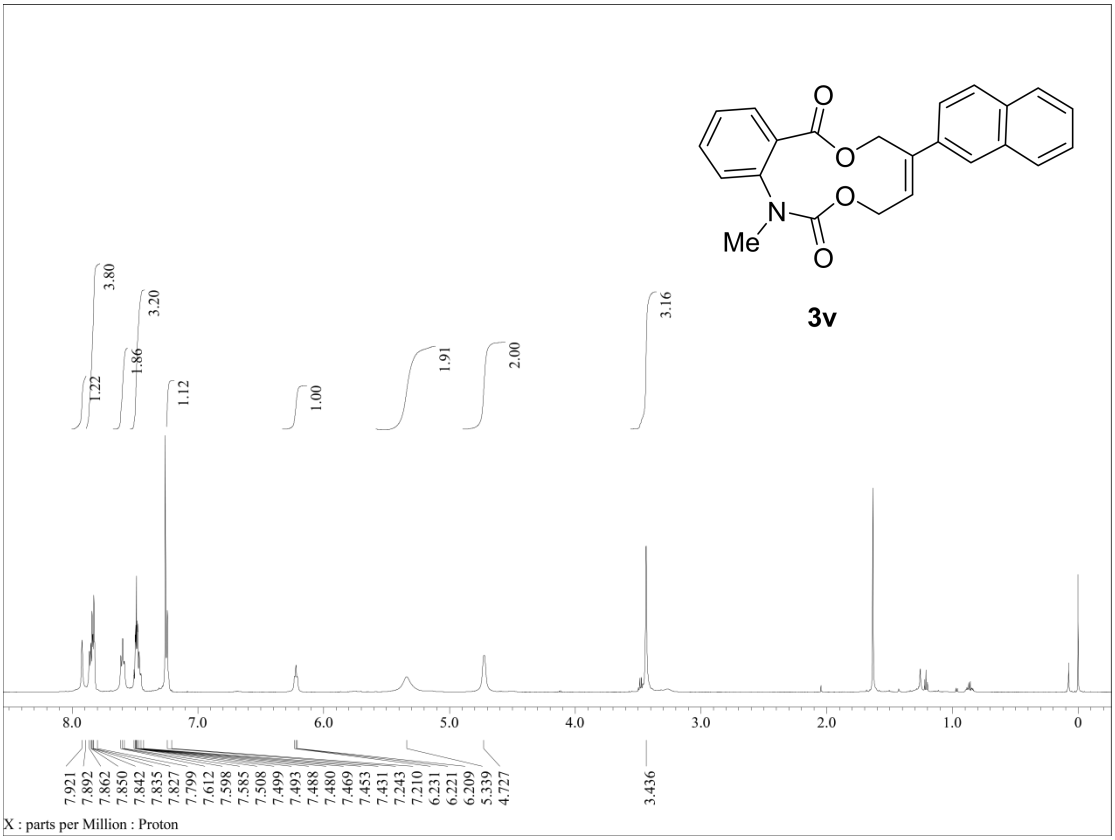

OMe
OMe
O
O
O
N
Me
O
3s
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.9
154.1
149.2
148.8
145.5
140.7
133.8
131.2
130.0
127.4
125.4
124.5
123.0
119.4
110.9
110.0
77.2
77.0
76.8
64.2
61.6
55.9
38.0
29.7
X : parts per Million : Carbon13

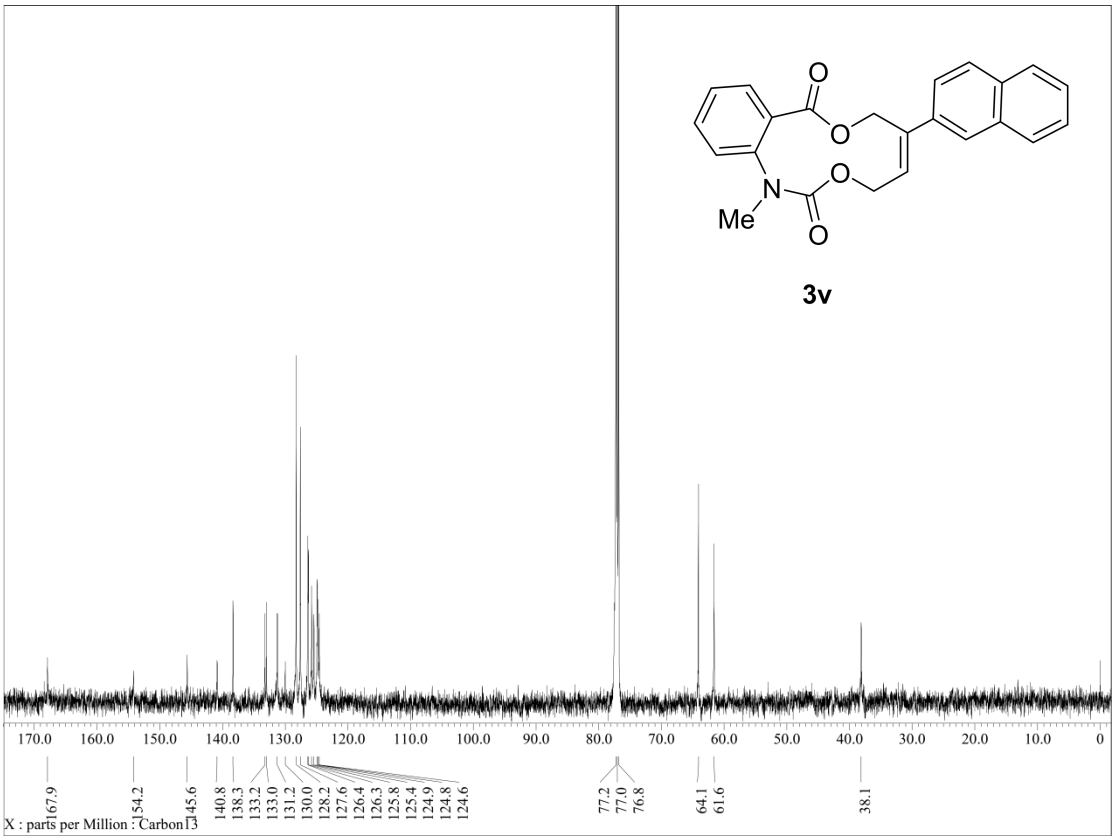

Cl
Cl
O
O
O
N
Me
O
3t
4.05
1.96
1.03
1.01
1.00
2.08
1.76
2.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.541
7.528
7.492
7.479
7.467
7.410
7.398
7.383
7.379
7.270
7.267
7.260
7.253
7.234
5.945
5.934
5.922
5.061
4.661
3.425
X : parts per Million : Proton

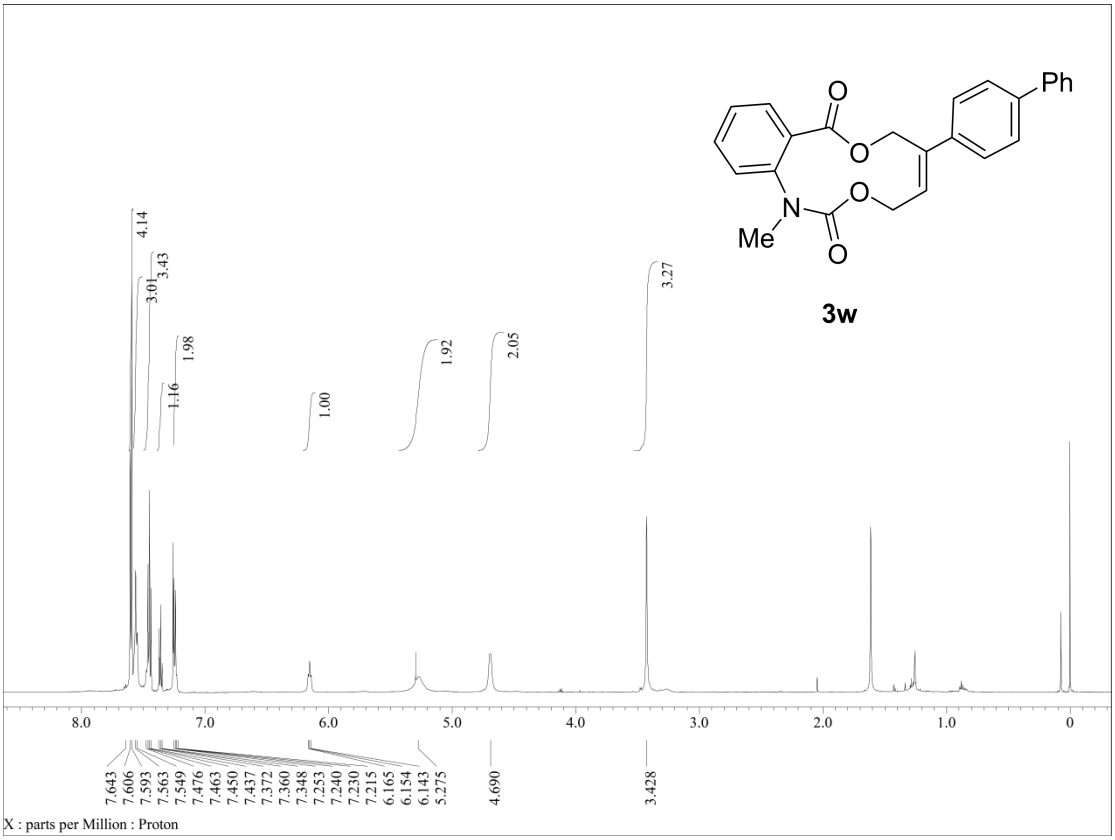

Cl
Cl
O
O
O
N
Me
O
3t
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.6
154.0
142.3
141.0
139.5
134.3
132.6
132.1
131.4
130.1
129.0
127.8
127.6
127.4
125.5
124.6
77.2
77.0
76.8
64.4
61.0
37.8
X : parts per Million : Carbon13

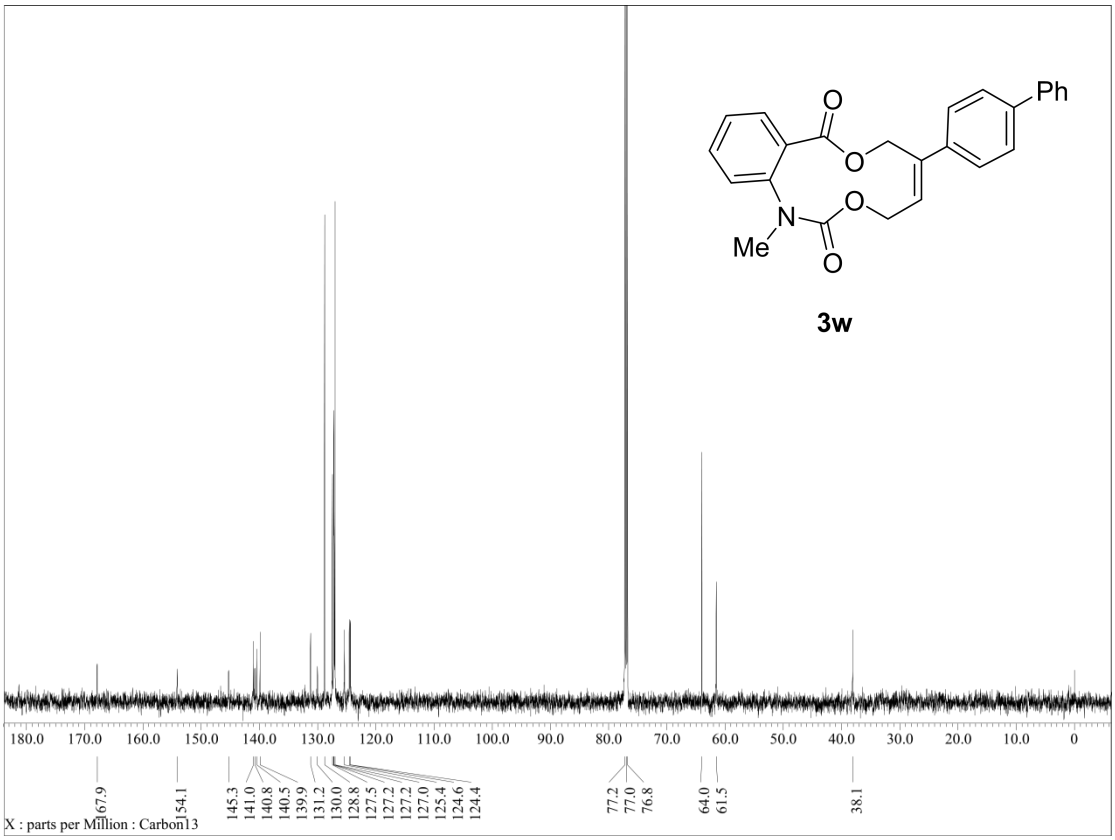

Cl
O
O
O
Cl
N
Me
O
3u
3.18
2.03
2.11
1.84
0.92
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.567
7.556
7.499
7.486
5.935
5.925
5.914
5.073
4.673
3.437
X : parts per Million : Proton

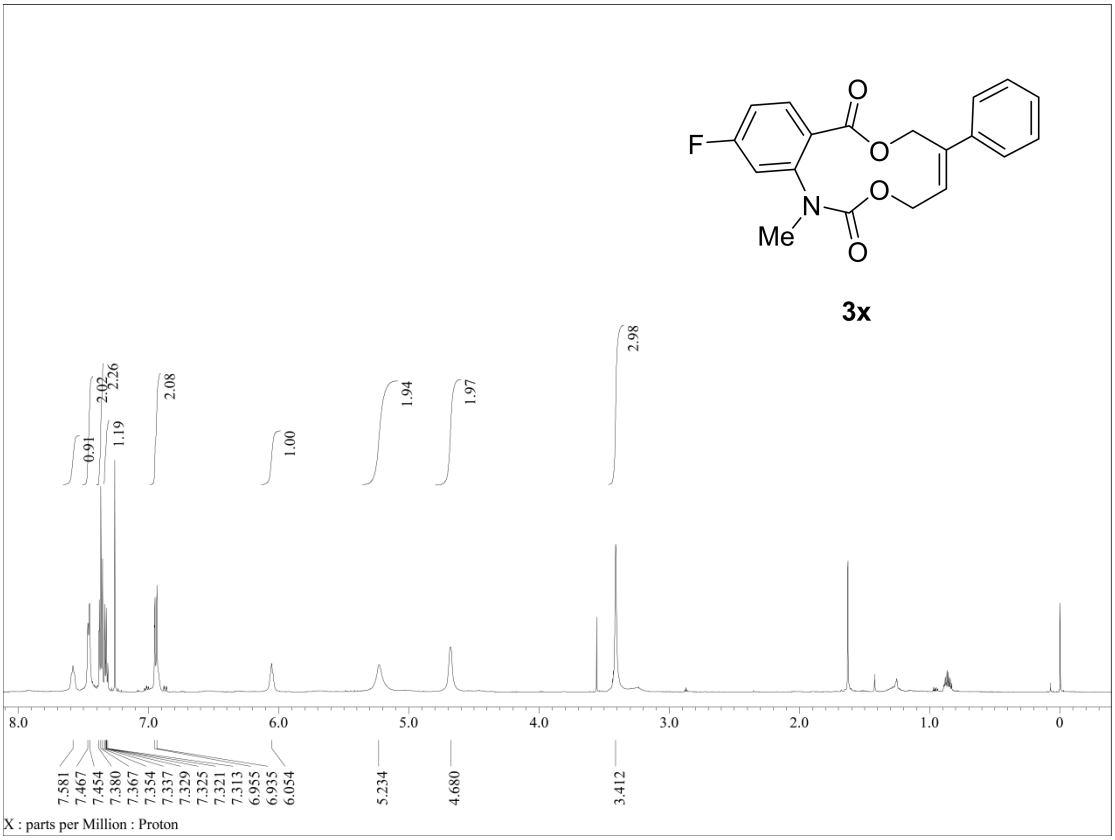

Cl
O
O
O
Cl
N
Me
O
3u
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.5
154.0
142.3
142.1
141.0
132.9
131.4
130.9
130.4
130.3
129.8
129.2
128.0
127.8
125.5
124.6
77.2
77.0
76.8
64.1
60.9
37.9
X : parts per Million : Carbon13

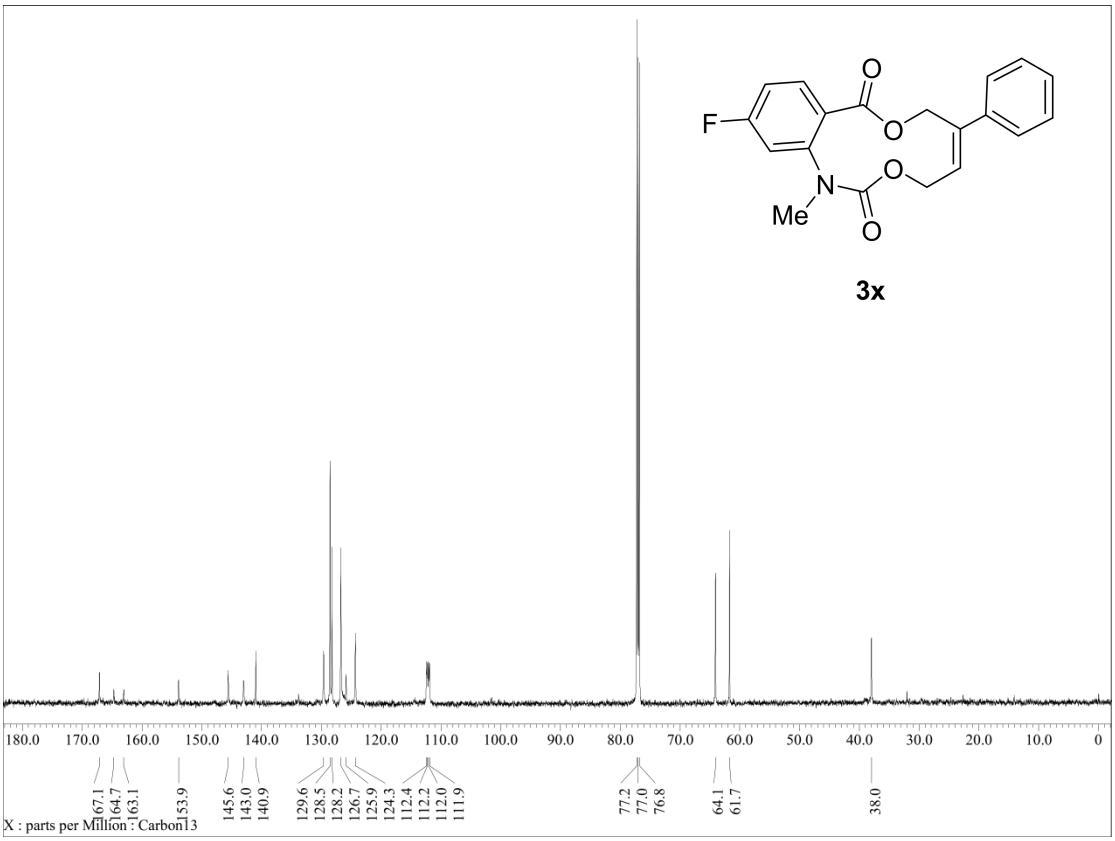

3v
3.80
3.20
1.86
1.22
1.12
1.00
1.91
2.00
3.16
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.921
7.892
7.862
7.850
7.842
7.835
7.827
7.799
7.612
7.598
7.585
7.508
7.499
7.493
7.488
7.480
7.469
7.453
7.431
7.243
7.210
6.231
6.221
6.209
5.339
4.727
3.436
X : parts per Million : Proton

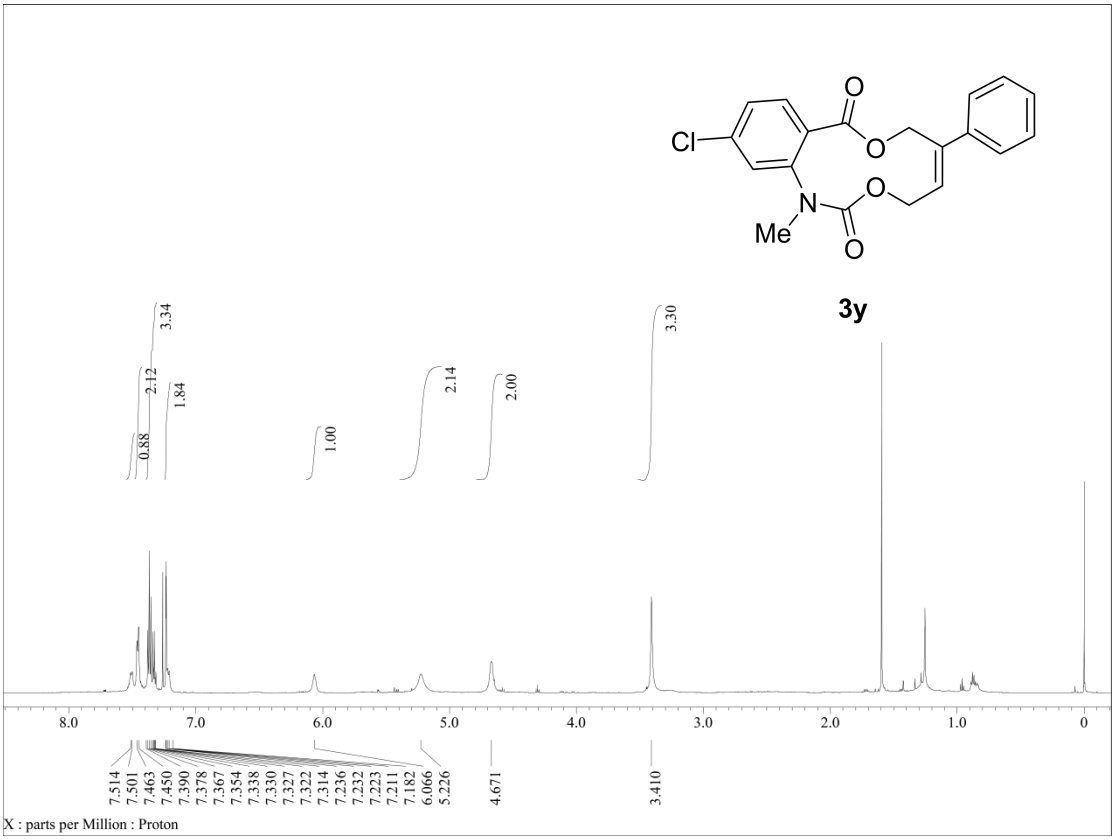

3v
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.9
154.2
145.6
140.8
138.3
133.2
133.0
131.2
130.0
128.2
127.6
126.4
126.3
125.8
125.4
124.9
124.8
124.6
77.2
77.0
76.8
64.1
61.6
38.1
X : parts per Million : Carbon13

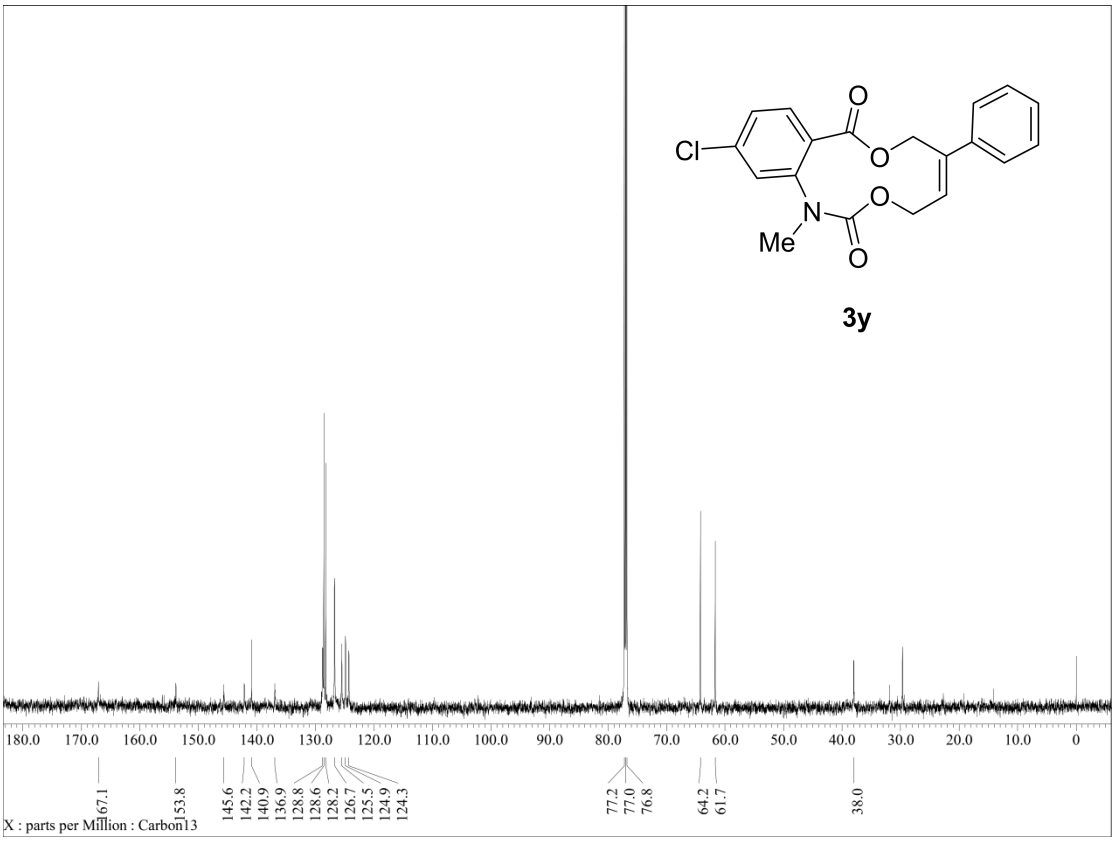

Ph
O
O
O
N
Me
O
3w
4.14
3.01
3.43
1.98
1.16
1.00
1.92
2.05
3.27
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.643
7.606
7.593
7.563
7.549
7.476
7.463
7.450
7.437
7.372
7.360
7.348
7.253
7.240
7.230
7.215
6.165
6.154
6.143
5.275
4.690
3.428
X : parts per Million : Proton

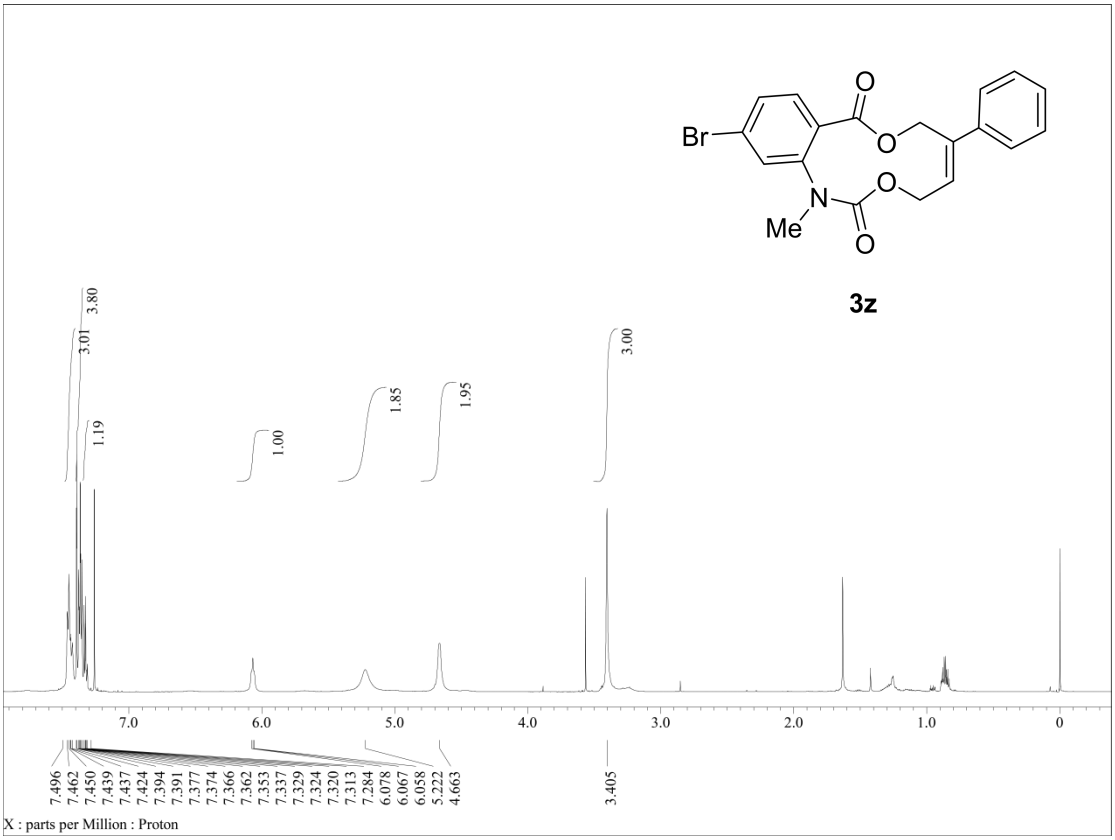

Ph
O
O
O
N
Me
O
3w
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.9
154.1
145.3
141.0
140.8
140.5
139.9
131.2
130.0
128.8
127.5
127.2
127.2
127.0
125.4
124.6
124.4
77.2
77.0
76.8
64.0
61.5
38.1
X : parts per Million : Carbon13

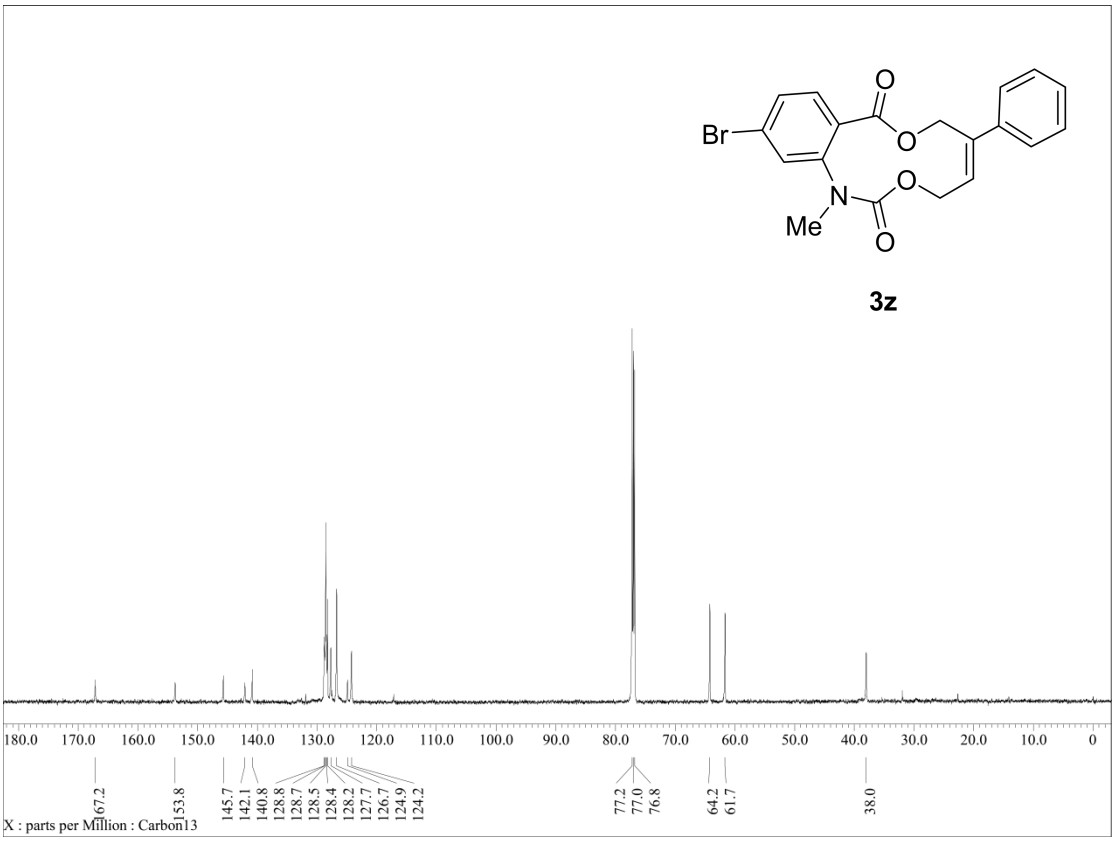

F
O
O
N
Me
O
O
3x
0.91
2.02
2.26
1.19
2.08
1.00
1.94
1.97
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.581
7.467
7.454
7.380
7.367
7.354
7.337
7.329
7.325
7.321
7.313
6.955
6.935
6.054
5.234
4.680
3.412
X : parts per Million : Proton

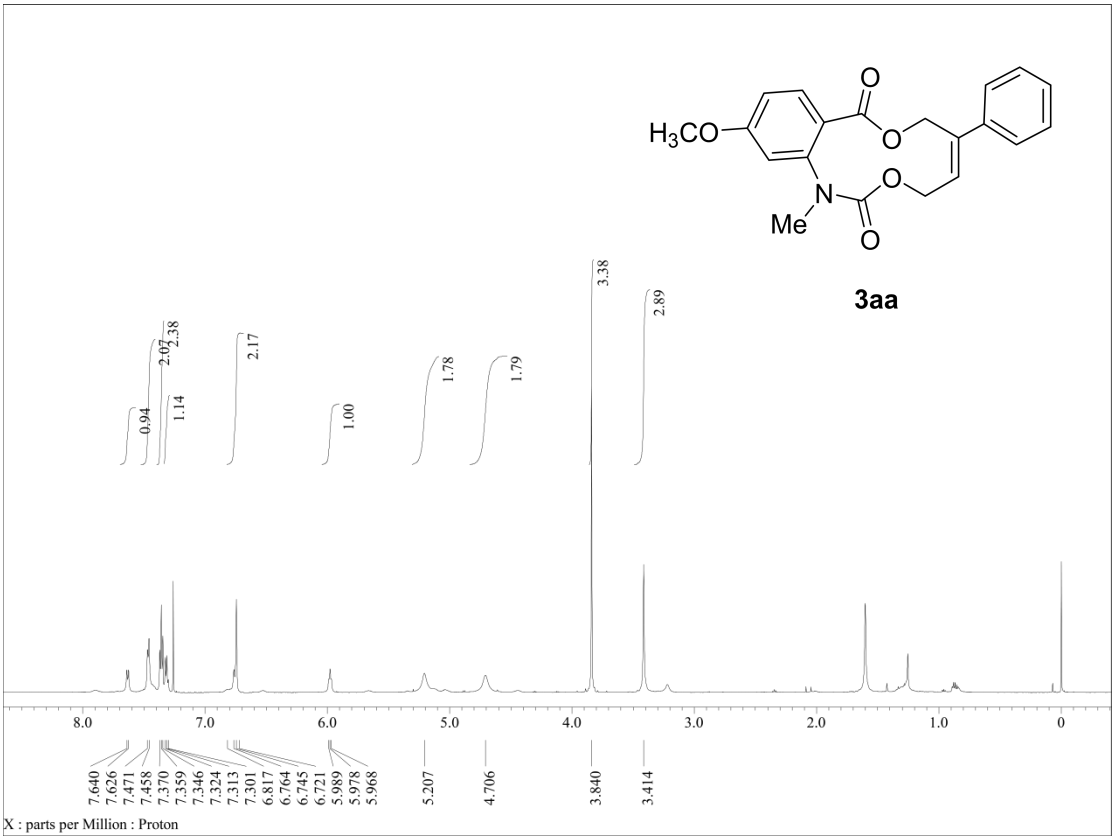

F
O
O
N
Me
O
O
3x
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.1
164.7
163.1
153.9
145.6
143.0
140.9
129.6
128.5
128.2
126.7
125.9
124.3
112.4
112.2
112.0
111.9
77.2
77.0
76.8
64.1
61.7
38.0
X : parts per Million : Carbon13

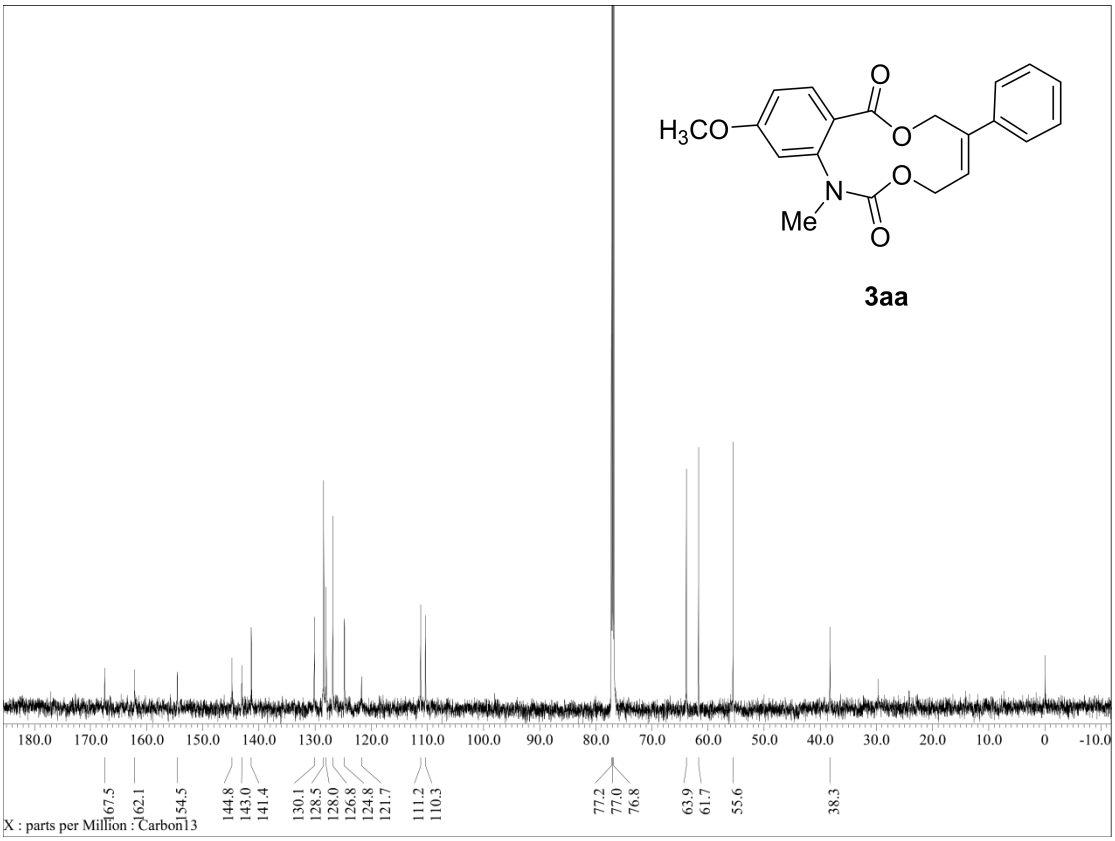

Cl
O
O
N
Me
O
O
3y
3.34
2.12
1.84
0.88
1.00
2.14
2.00
3.30
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.514
7.501
7.463
7.450
7.390
7.378
7.367
7.354
7.338
7.330
7.327
7.322
7.314
7.236
7.232
7.223
7.211
7.182
6.066
5.226
4.671
3.410
X : parts per Million : Proton

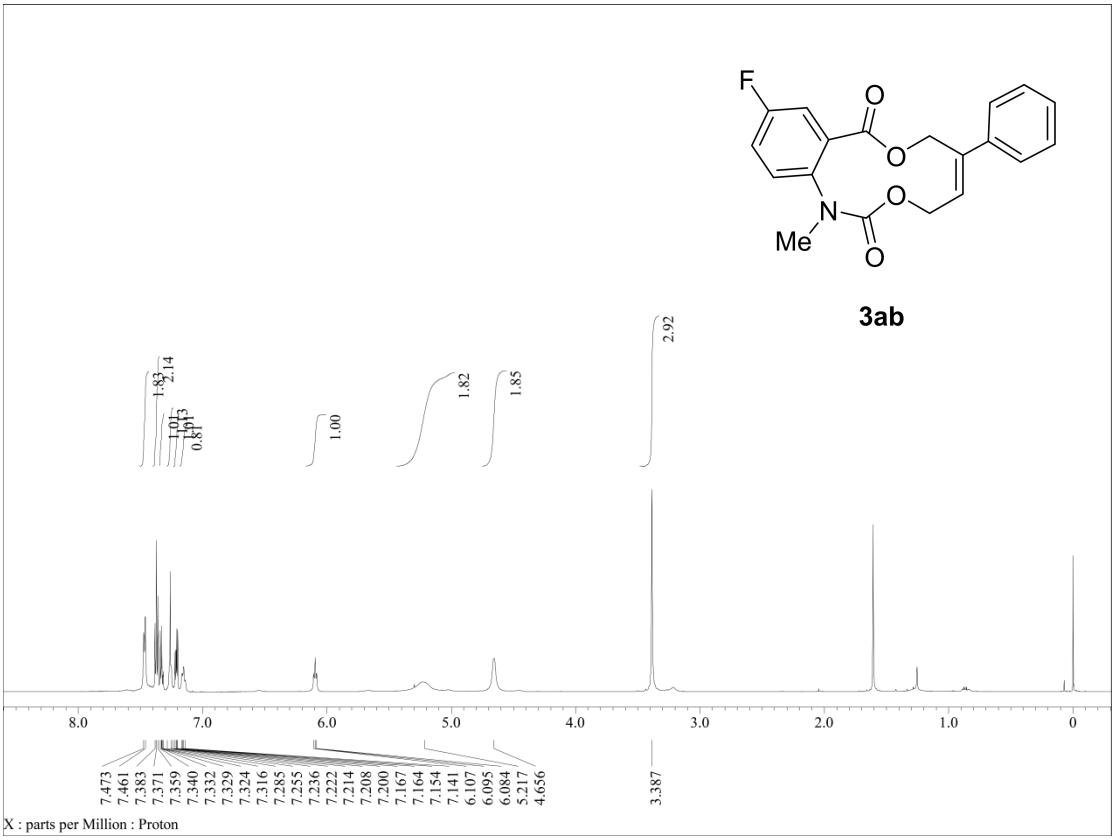

Cl
O
O
N
Me
O
O
3y
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.1
153.8
145.6
142.2
140.9
136.9
128.8
128.6
128.2
126.7
125.5
124.9
124.3
77.2
77.0
76.8
64.2
61.7
38.0
X : parts per Million : Carbon13

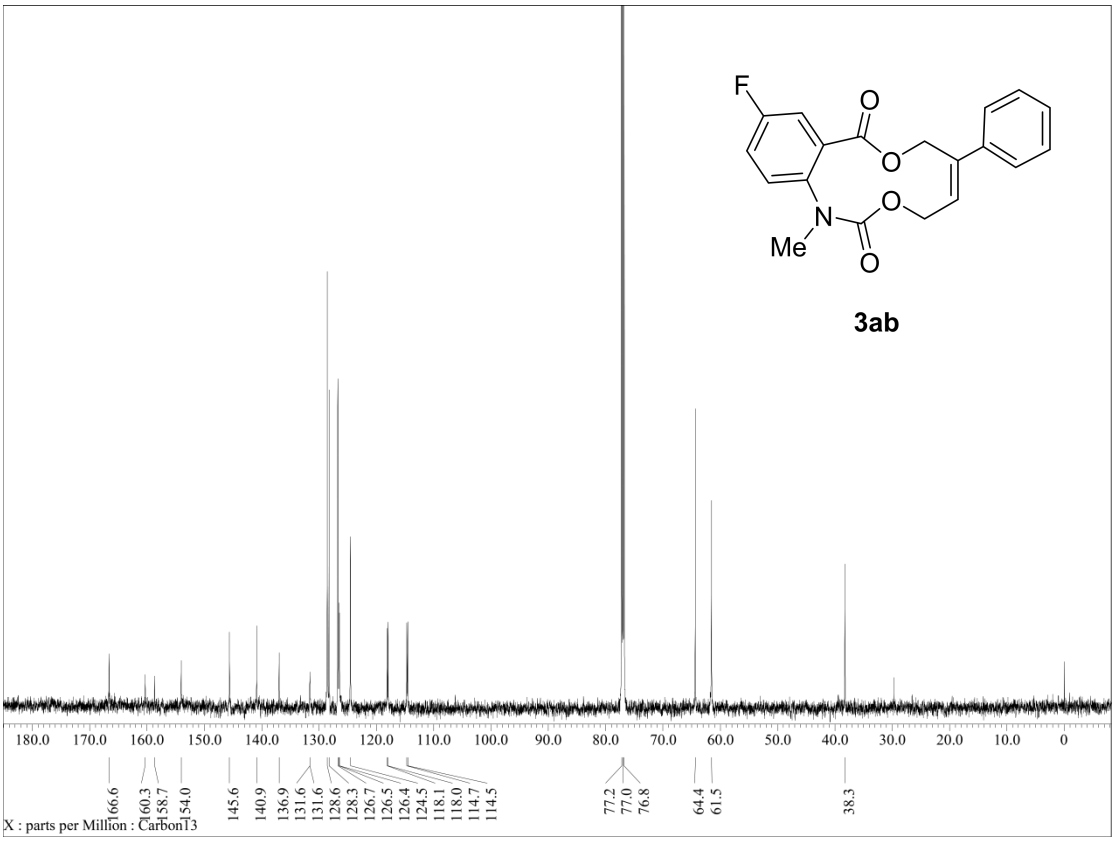

Br
O
O
O
N
Me
O
3z
3.80
3.01
1.19
1.00
1.85
1.95
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.496
7.462
7.450
7.439
7.437
7.424
7.394
7.391
7.377
7.374
7.366
7.362
7.353
7.337
7.329
7.324
7.320
7.313
7.284
6.078
6.067
6.058
5.222
4.663
3.405
X : parts per Million : Proton

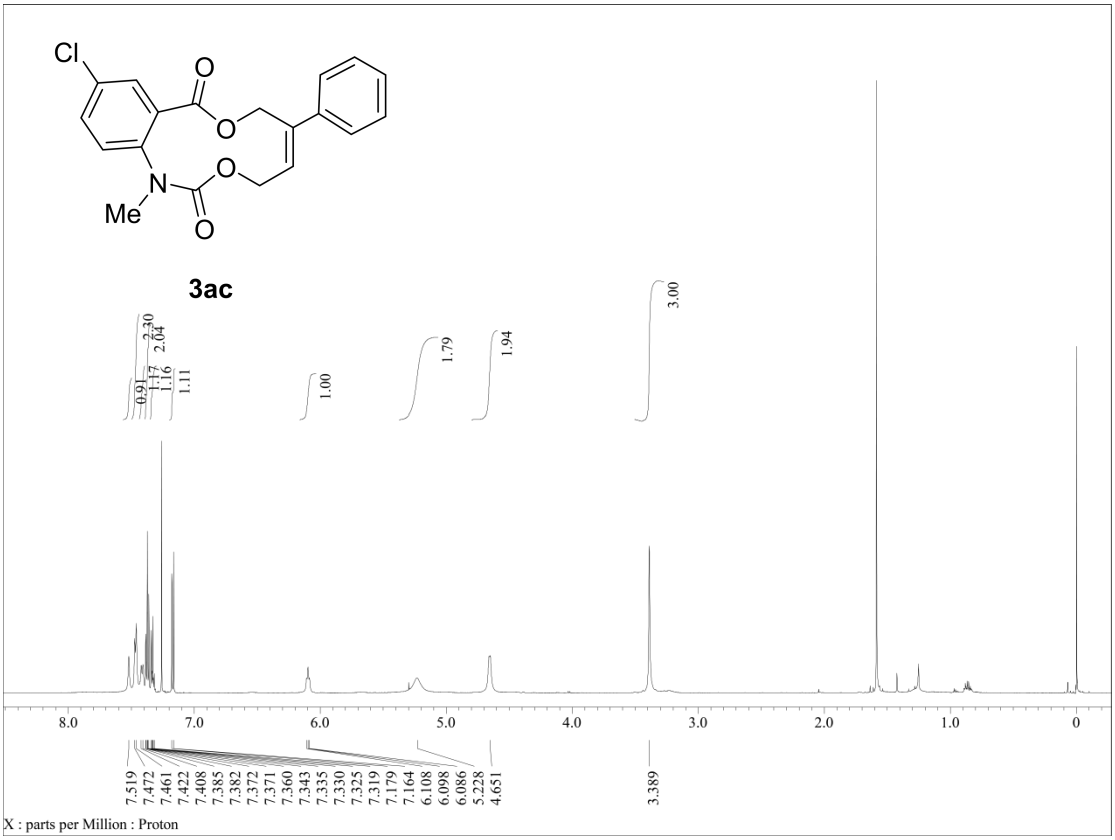

Br
O
O
O
N
Me
O
3z
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.2
153.8
145.7
142.1
140.8
128.8
128.7
128.5
128.4
128.2
127.7
126.7
124.9
124.2
77.2
77.0
76.8
64.2
61.7
38.0
X : parts per Million : Carbon13

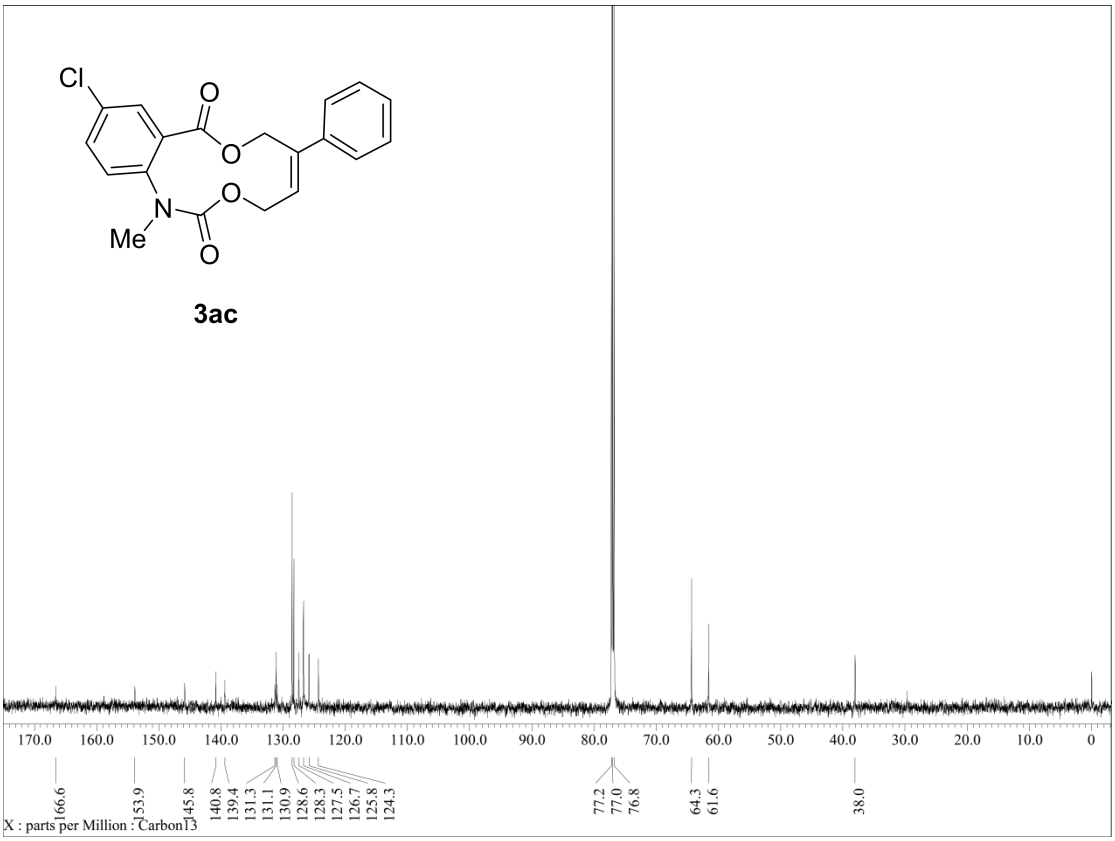

H3CO
O
O
O
N
Me
O
3aa
3.38
2.89
2.38
2.07
2.17
1.78
1.79
0.94
1.14
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.640
7.626
7.471
7.458
7.370
7.359
7.346
7.324
7.313
7.301
6.817
6.764
6.745
6.721
5.989
5.978
5.968
5.207
4.706
3.840
3.414
X : parts per Million : Proton

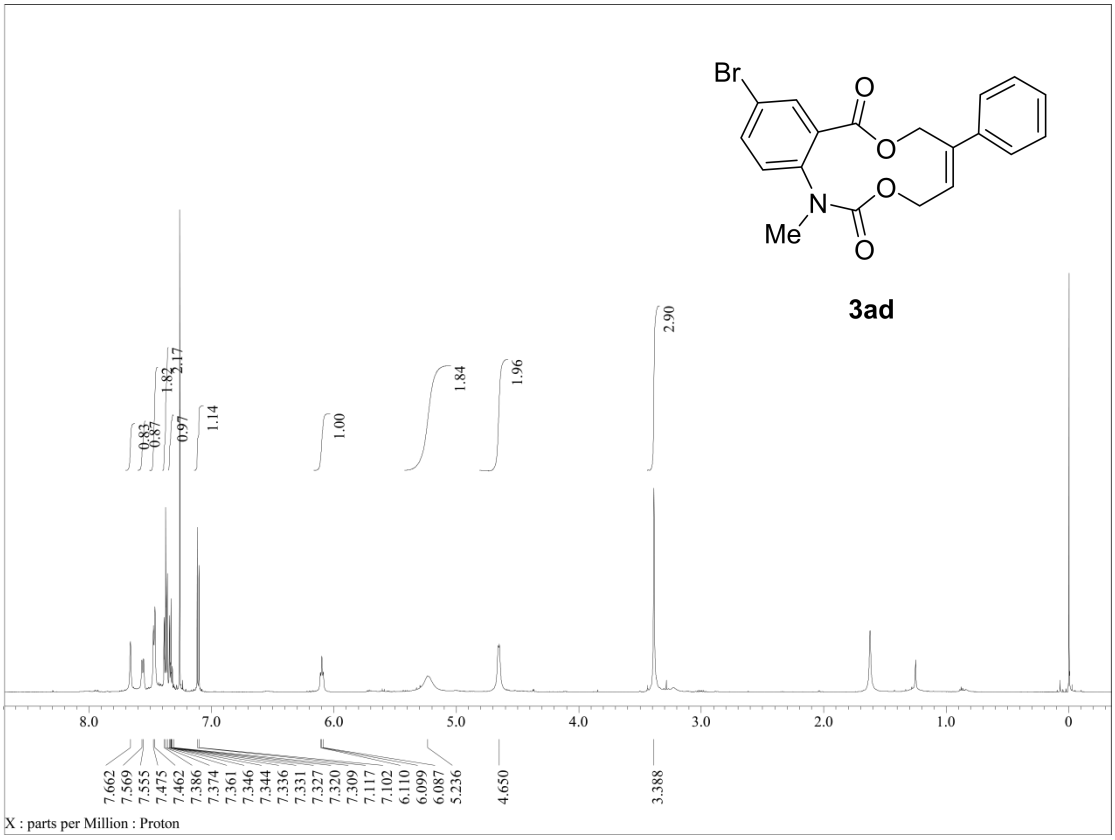

H3CO
O
O
O
N
Me
O
3aa
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
167.5
162.1
154.5
144.8
143.0
141.4
130.1
128.5
128.0
126.8
124.8
121.7
111.2
110.3
77.2
77.0
76.8
63.9
61.7
55.6
38.3
X : parts per Million : Carbon13

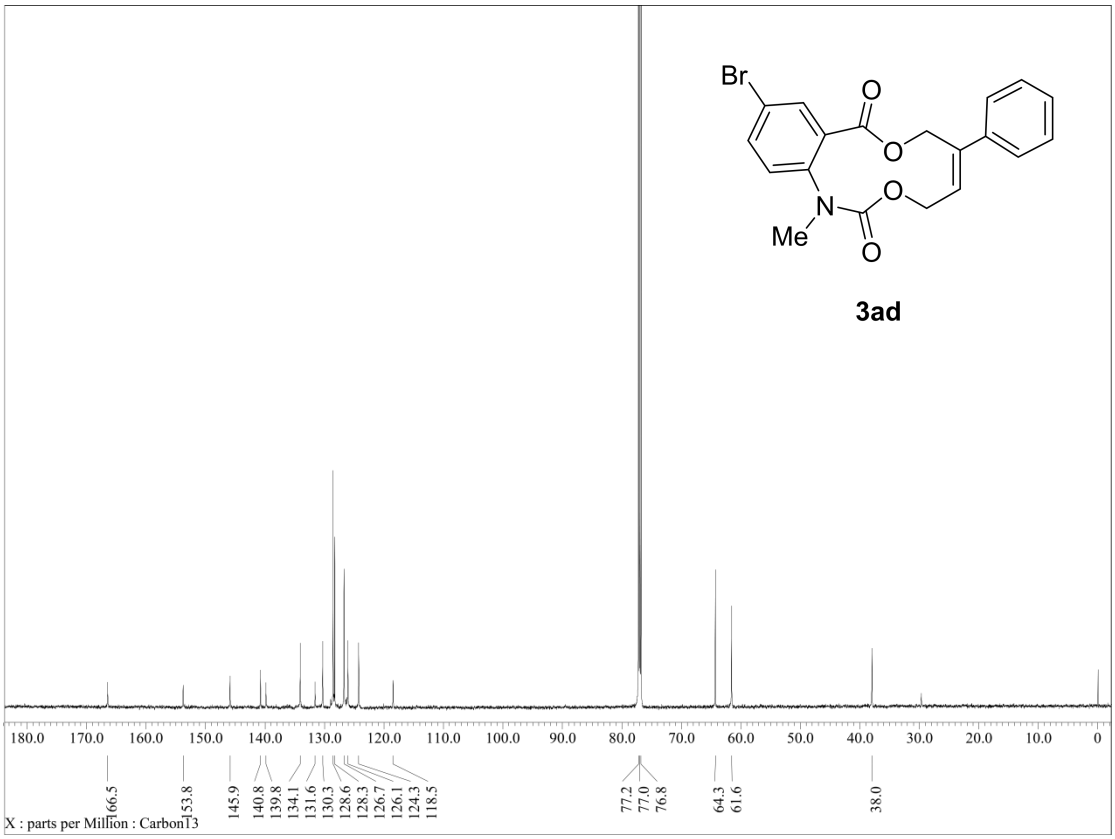

F
O
O
O
N
Me
O
3ab
2.92
2.14
1.83
1.82
1.85
1.07
1.03
0.81
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.473
7.461
7.383
7.371
7.359
7.340
7.332
7.329
7.324
7.316
7.285
7.255
7.236
7.222
7.214
7.208
7.200
7.167
7.164
7.154
7.141
6.107
6.095
6.084
5.217
4.656
3.387
X : parts per Million : Proton

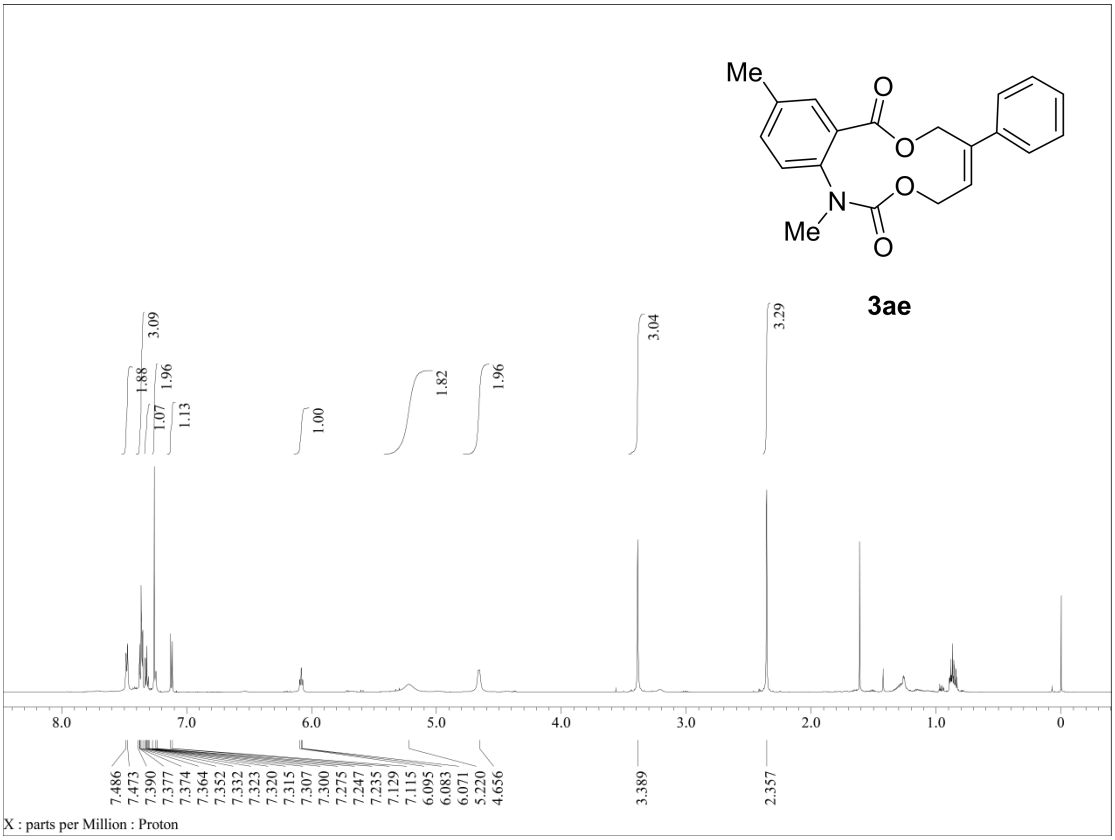

F
O
O
O
N
Me
O
3ab
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
166.6
160.3
158.7
154.0
145.6
140.9
136.9
131.6
131.6
128.6
128.3
126.7
126.5
126.4
124.5
118.1
118.0
114.7
114.5
77.2
77.0
76.8
64.4
61.5
38.3
X : parts per Million : Carbon13

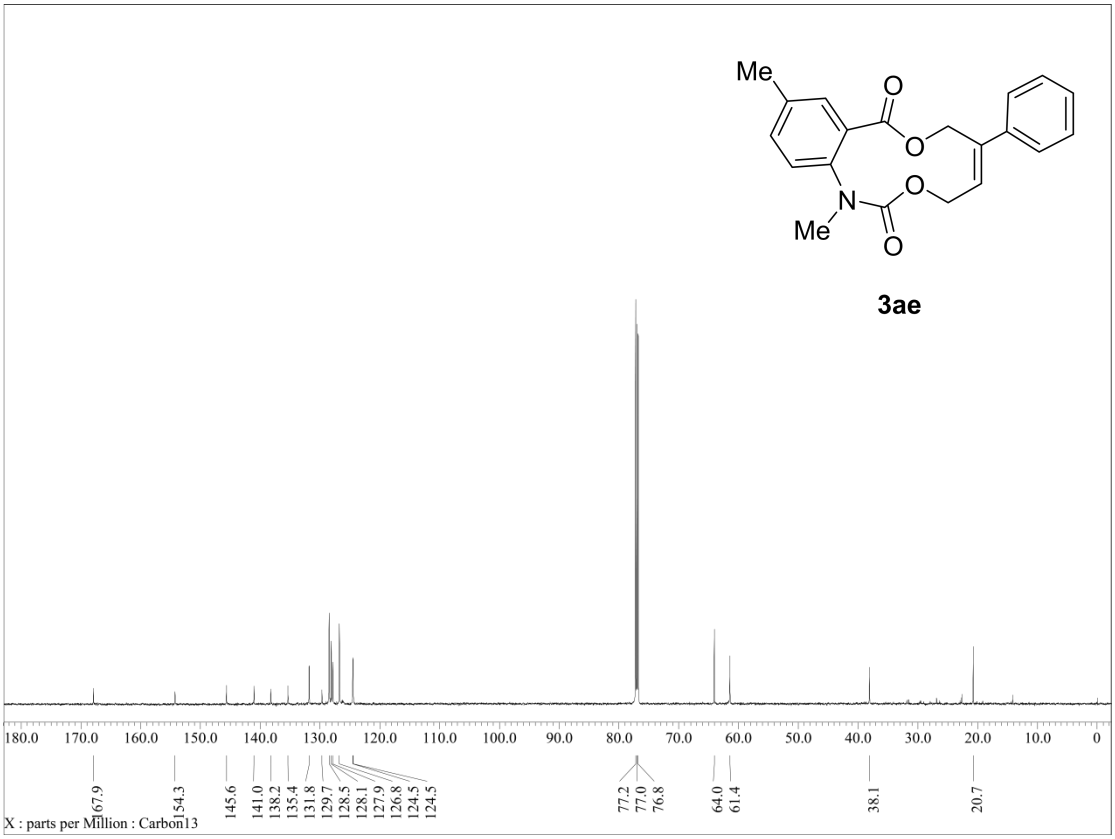

Cl
O
O
O
N
Me
O
3ac
0.91
1.17
1.16
2.30
2.04
1.11
1.00
1.79
1.94
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.519
7.472
7.461
7.422
7.408
7.385
7.382
7.372
7.371
7.360
7.343
7.335
7.330
7.325
7.319
7.179
7.164
6.108
6.098
6.086
5.228
4.651
3.389
X : parts per Million : Proton

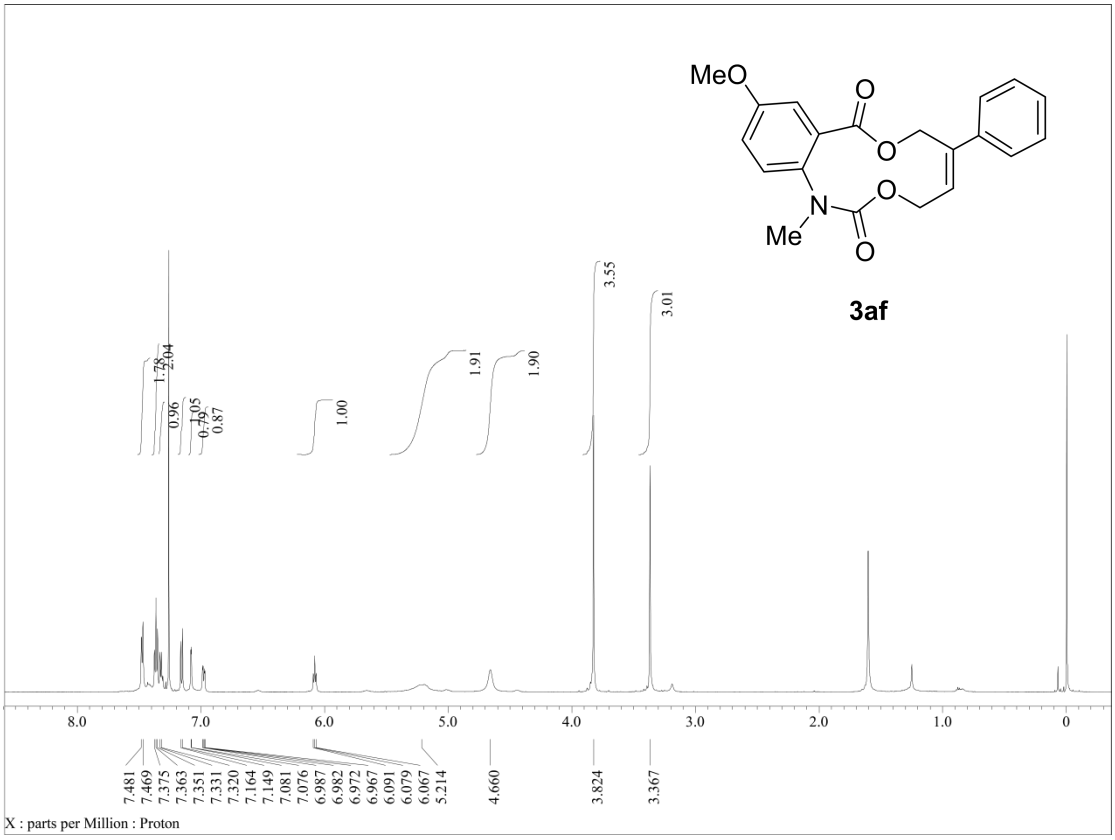

Cl
O
O
O
N
Me
O
3ac
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
166.6
153.9
145.8
140.8
139.4
131.3
131.1
130.9
128.6
128.3
127.5
126.7
125.8
124.3
77.2
77.0
76.8
64.3
61.6
38.0
X : parts per Million : Carbon13

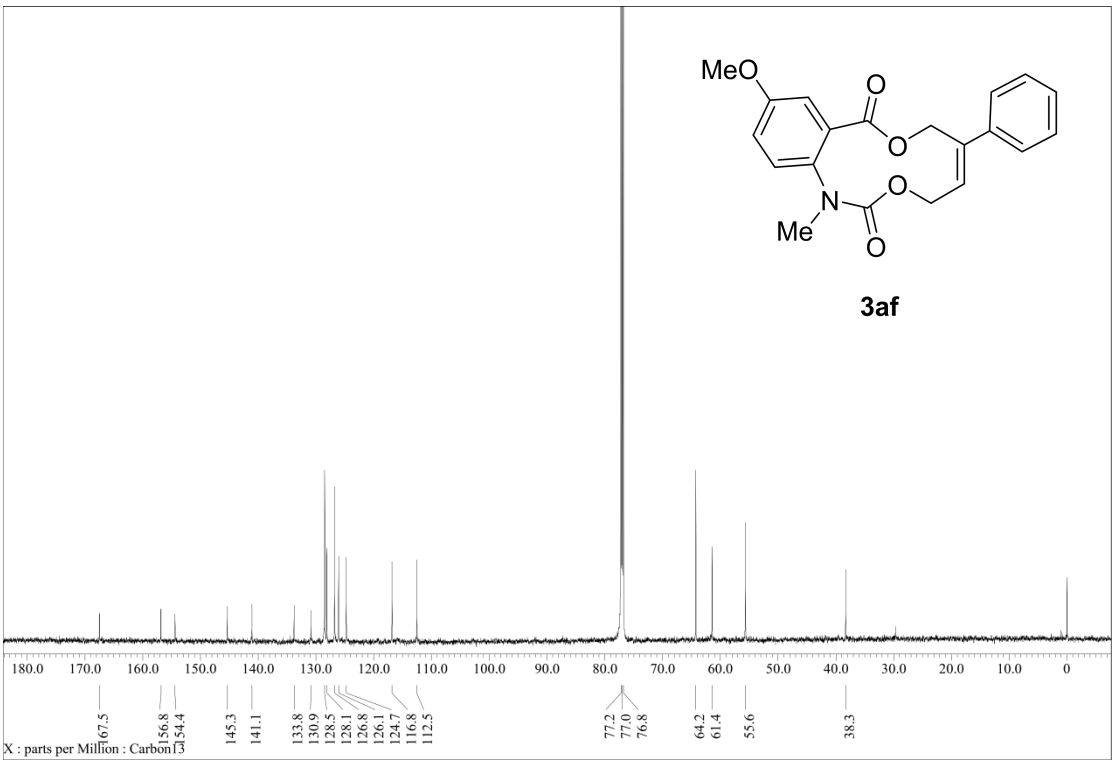

Br
O
O
O
N
Me
O
3ad
2.90
1.84
1.96
1.82
2.17
1.14
1.00
0.97
0.83
0.87
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.662
7.569
7.555
7.475
7.462
7.386
7.374
7.361
7.346
7.344
7.336
7.331
7.327
7.320
7.309
7.117
7.102
6.110
6.099
6.087
5.236
4.650
3.388
X : parts per Million : Proton

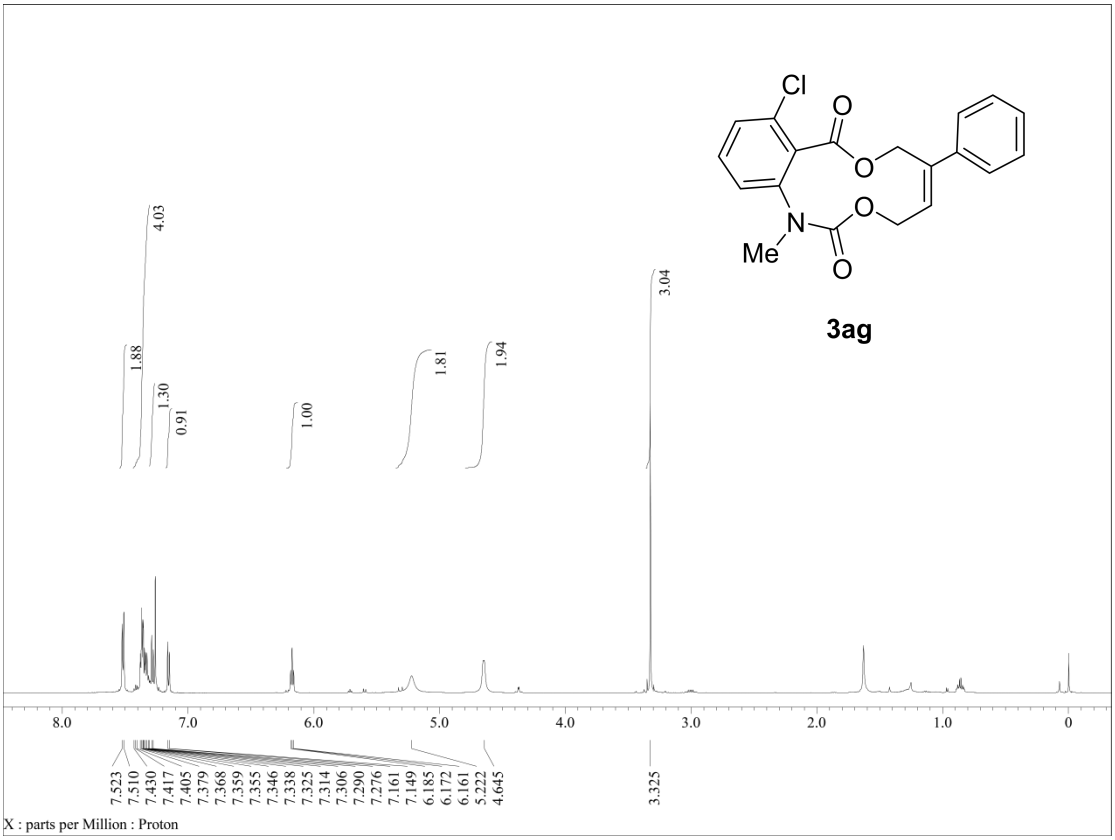

Br
O
O
O
N
Me
O
3ad
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
166.5
153.8
145.9
140.8
139.8
134.1
131.6
130.3
128.6
128.3
126.7
126.1
124.3
118.5
77.2
77.0
76.8
64.3
61.6
38.0
X : parts per Million : CarbonI3

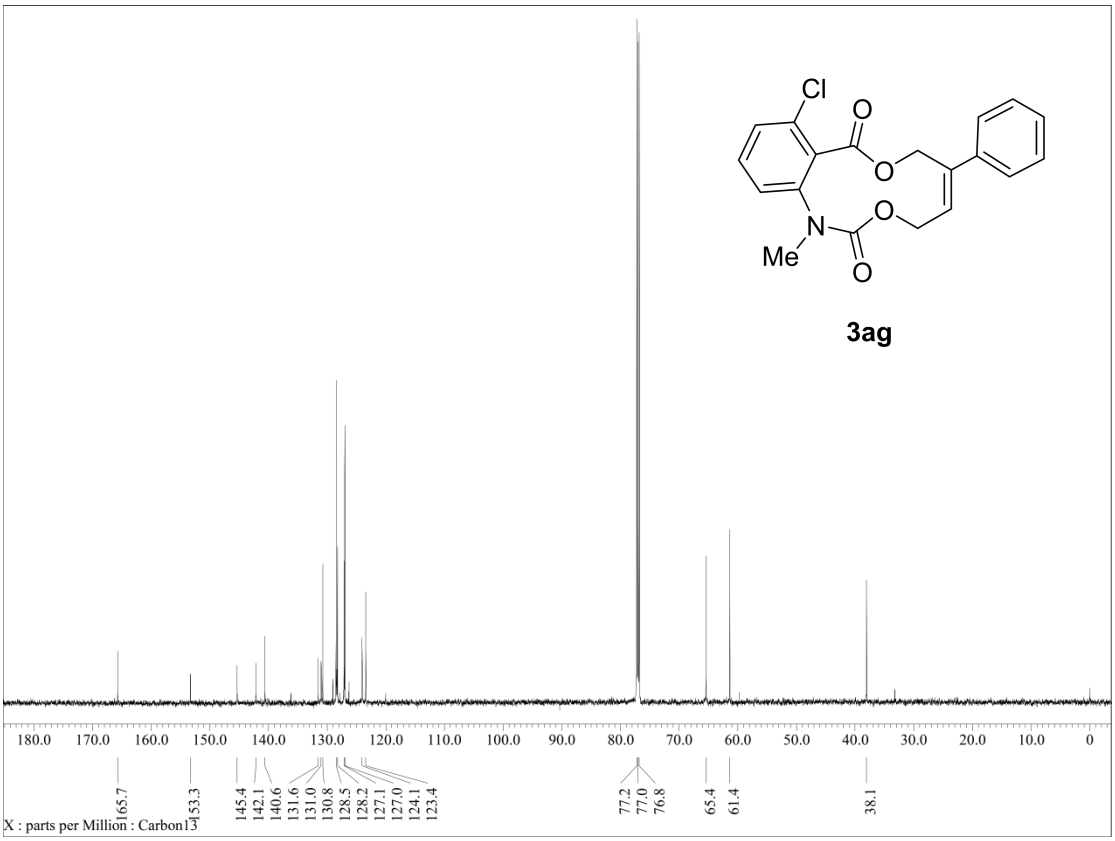

Me
O
O
O
N
Me
O
3ae
3.09
1.88
1.96
1.07
1.13
1.00
1.82
1.96
3.04
3.29
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.486
7.473
7.390
7.377
7.374
7.364
7.352
7.332
7.323
7.320
7.315
7.307
7.300
7.275
7.247
7.235
7.129
7.115
6.095
6.083
6.071
5.220
4.656
3.389
2.357
X : parts per Million : Proton


Me
O
O
O
N
Me
O
3ae
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.9
154.3
145.6
141.0
138.2
135.4
131.8
129.7
128.5
128.1
127.9
126.8
124.5
124.5
77.2
77.0
76.8
64.0
61.4
38.1
20.7
X : parts per Million : Carbon13


MeO
O
O
O
N
Me
O
3af
3.55
3.01
1.91
1.90
1.00
0.96
1.05
0.79
0.87
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.481
7.469
7.375
7.363
7.351
7.331
7.320
7.164
7.149
7.081
7.076
6.987
6.982
6.972
6.967
6.091
6.079
6.067
5.214
4.660
3.824
3.367
X : parts per Million : Proton


MeO
O
O
O
N
Me
O
3af
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.5
156.8
154.4
145.3
141.1
133.8
130.9
128.5
128.1
126.8
126.1
124.7
116.8
112.5
77.2
77.0
76.8
64.2
61.4
55.6
38.3
X : parts per Million : Carbon13


Cl
O
O
O
N
Me
O
3ag
4.03
3.04
1.88
1.30
0.91
1.00
1.81
1.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.523
7.510
7.430
7.417
7.405
7.379
7.368
7.359
7.355
7.346
7.338
7.325
7.314
7.306
7.290
7.276
7.161
7.149
6.185
6.172
6.161
5.222
4.645
3.325
X : parts per Million : Proton


Cl
O
O
O
N
Me
O
3ag
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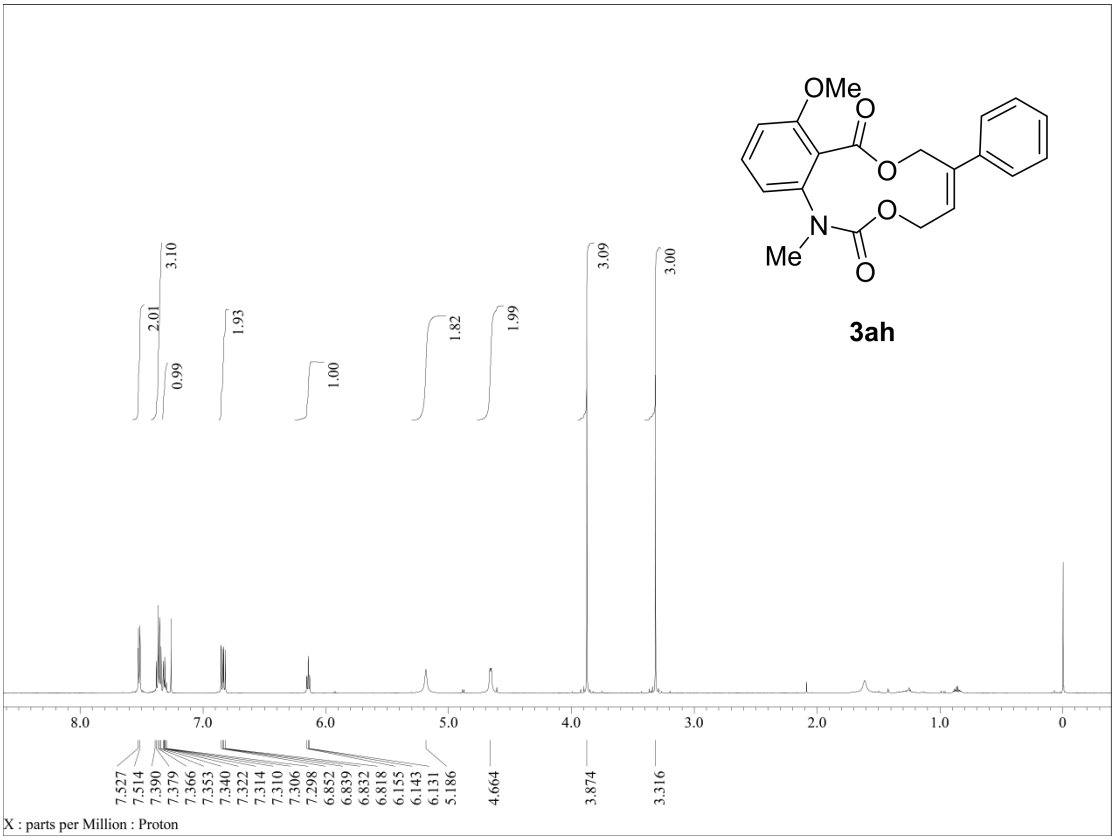
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.7
153.3
145.4
142.1
140.6
131.6
131.0
130.8
128.5
128.2
127.1
127.0
124.1
123.4
77.2
77.0
76.8
65.4
61.4
38.1
X : parts per Million : Carbon13


OMe
O
O
O
N
Me
O
3ah
3.10
2.01
0.99
1.93
1.00
1.82
1.99
3.09
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.527
7.514
7.390
7.379
7.366
7.353
7.340
7.322
7.314
7.310
7.306
7.298
6.852
6.839
6.832
6.818
6.155
6.143
6.131
5.186
4.664
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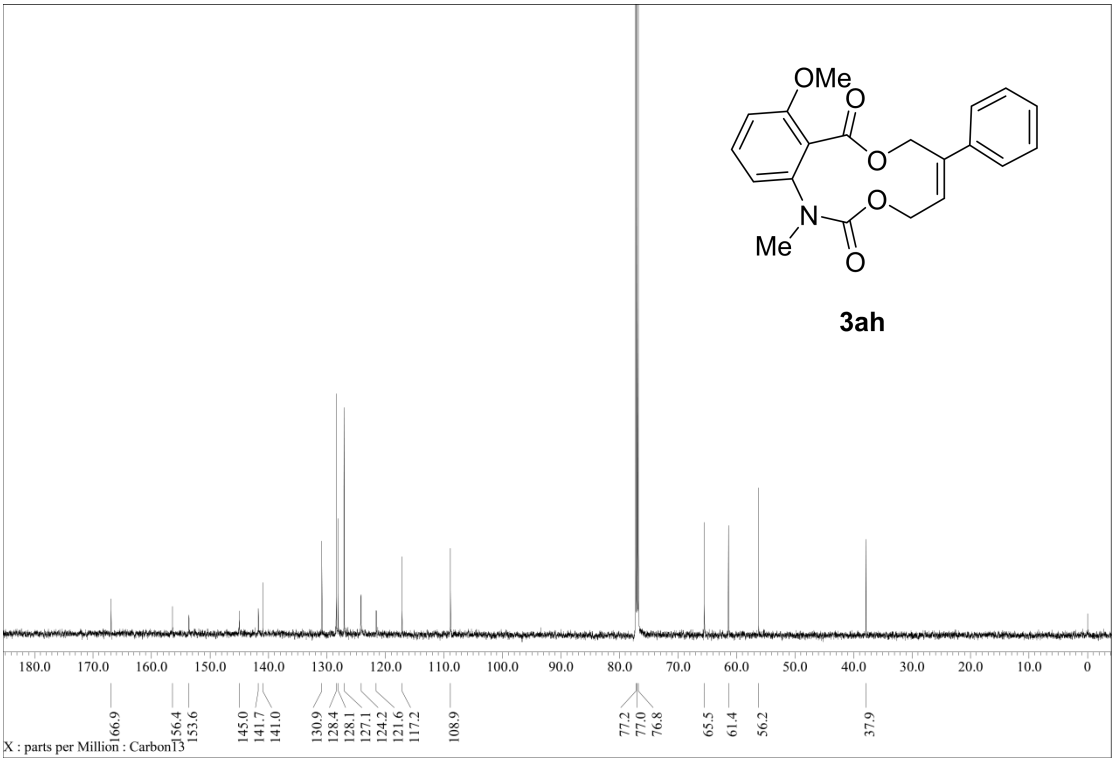
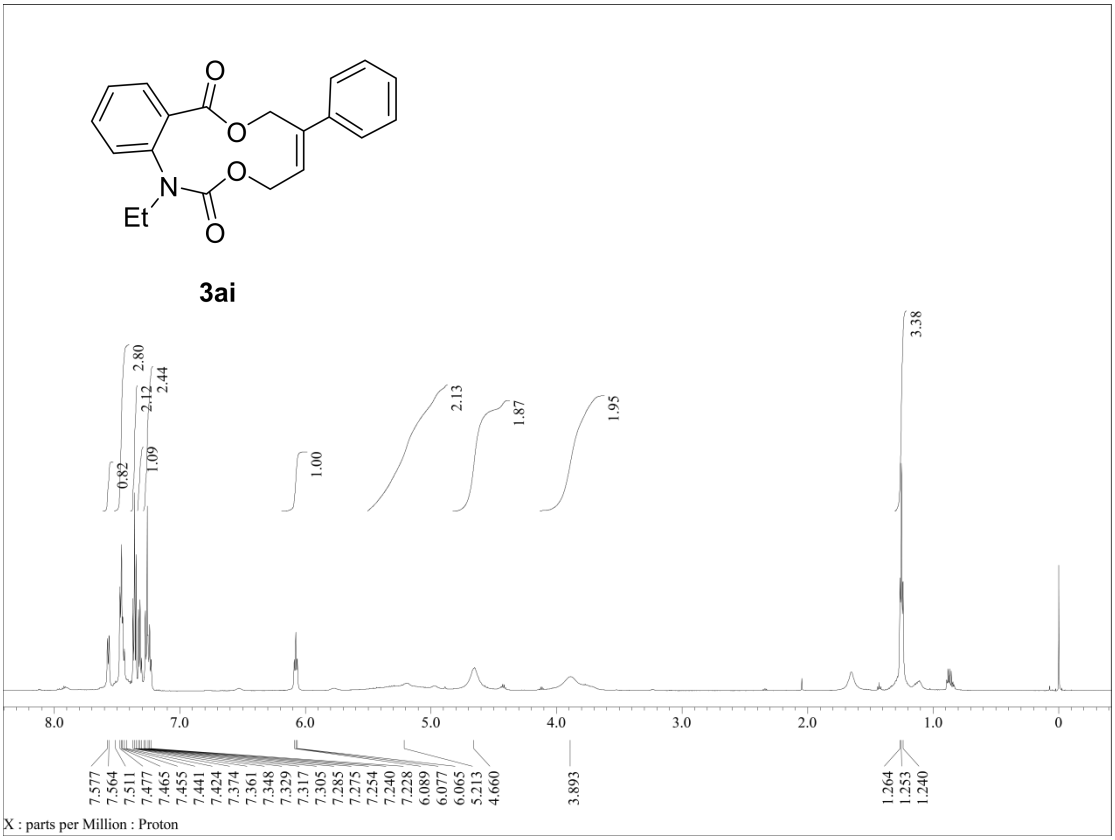
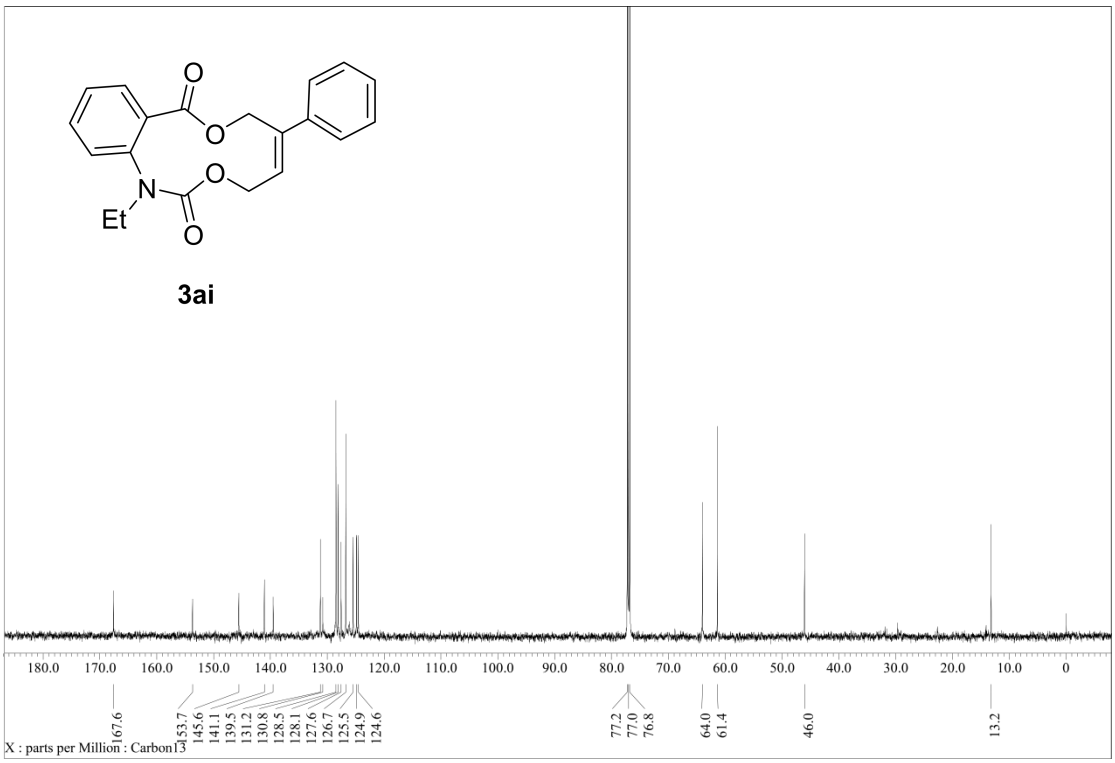
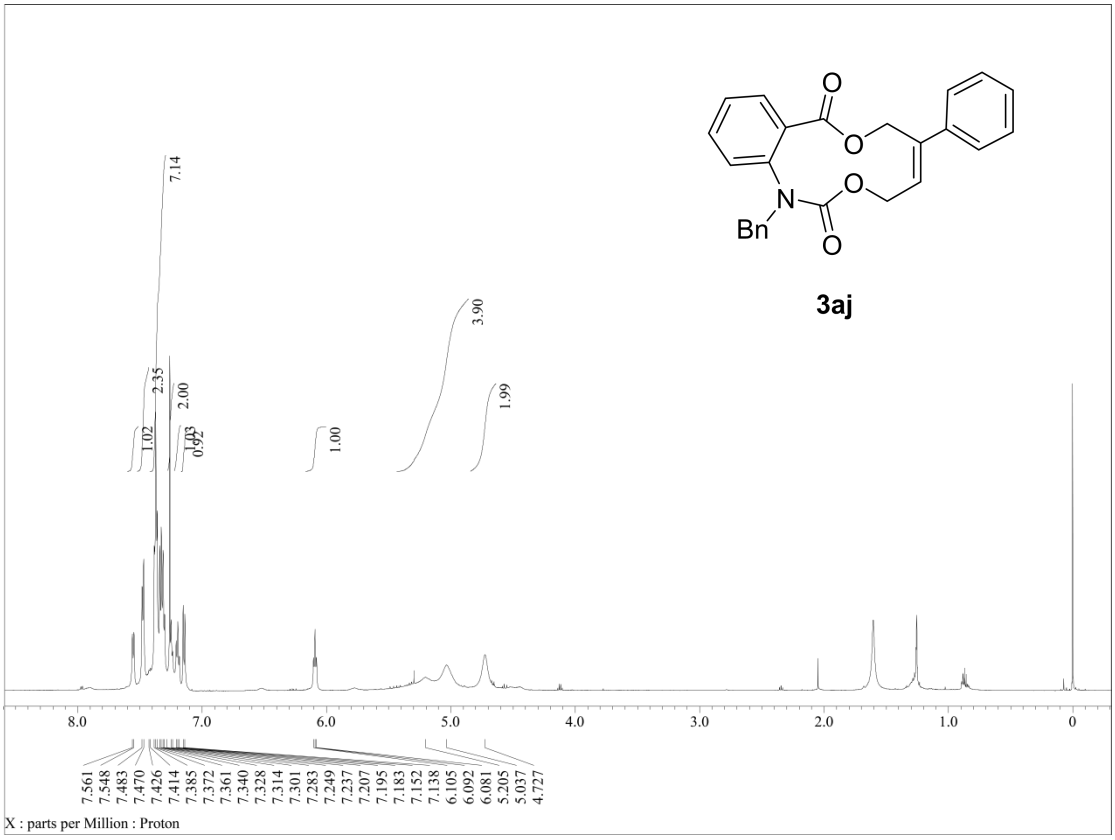
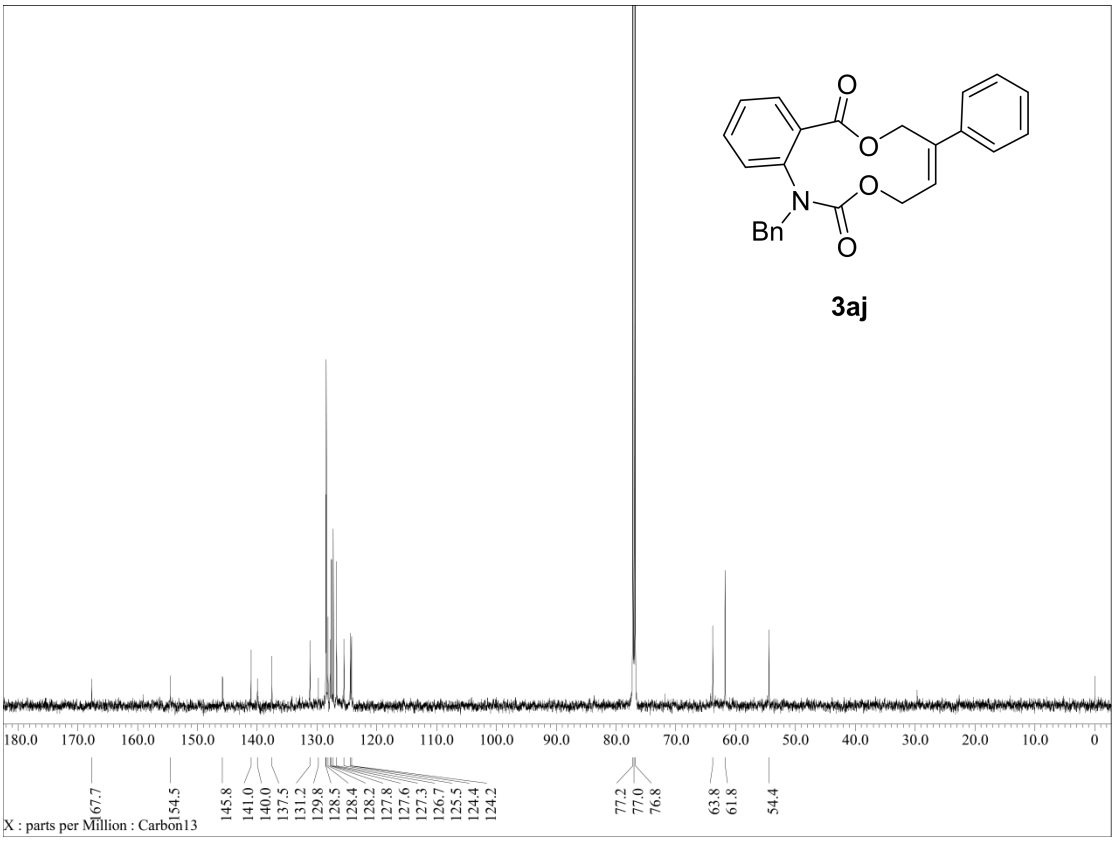
X : parts per Million : Proton

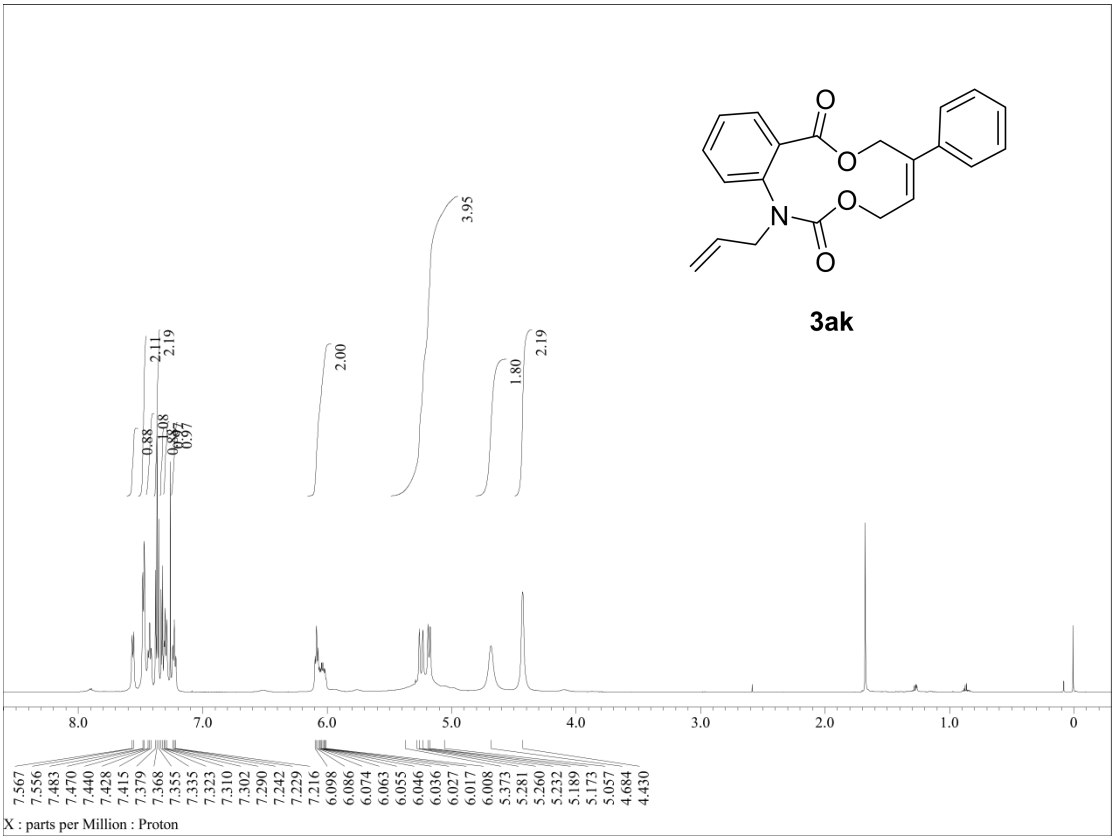

OMe
O
O
O
N
Me
O
3ah
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
166.9
156.4
153.6
145.0
141.7
141.0
130.9
128.4
128.1
127.1
124.2
121.6
117.2
108.9
77.2
77.0
76.8
65.5
61.4
56.2
37.9
X : parts per Million : Carbon13

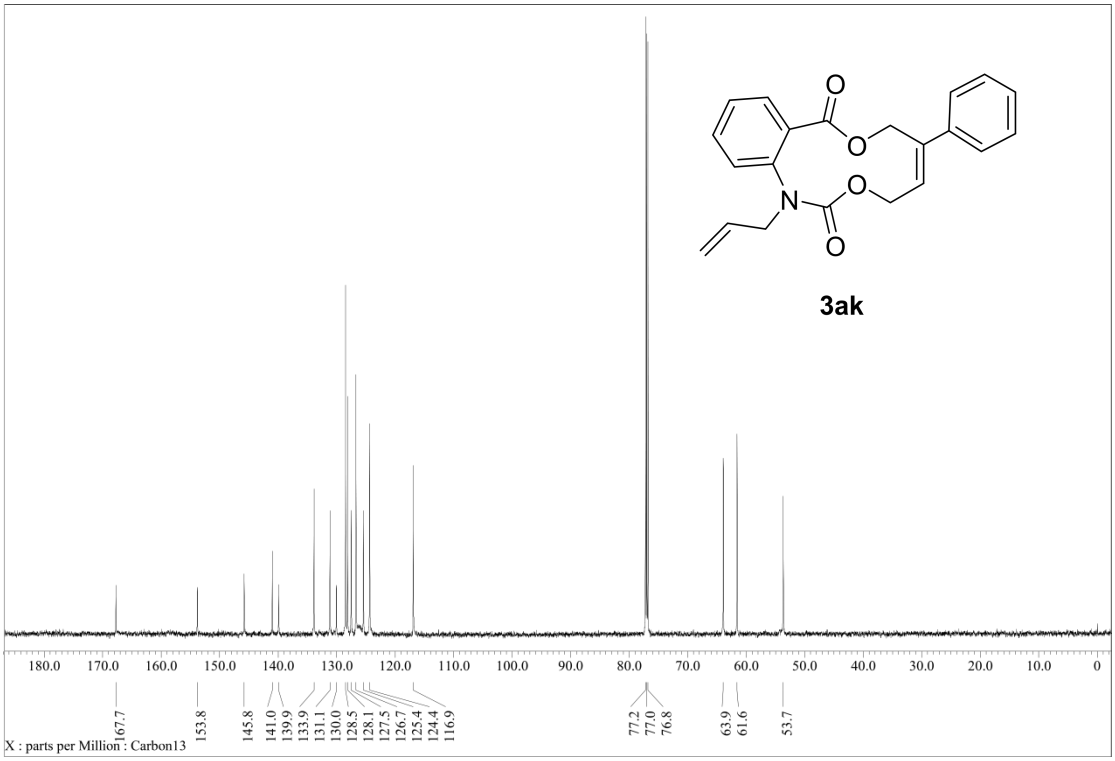

O
O
O
N
Et
O
3ai
3.38
2.80
2.44
2.12
2.13
1.87
1.95
1.09
1.00
0.82
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.577
7.564
7.511
7.477
7.465
7.455
7.441
7.424
7.374
7.361
7.348
7.329
7.317
7.305
7.285
7.275
7.254
7.240
7.228
6.089
6.077
6.065
5.213
4.660
3.893
1.264
1.253
1.240
X : parts per Million : Proton

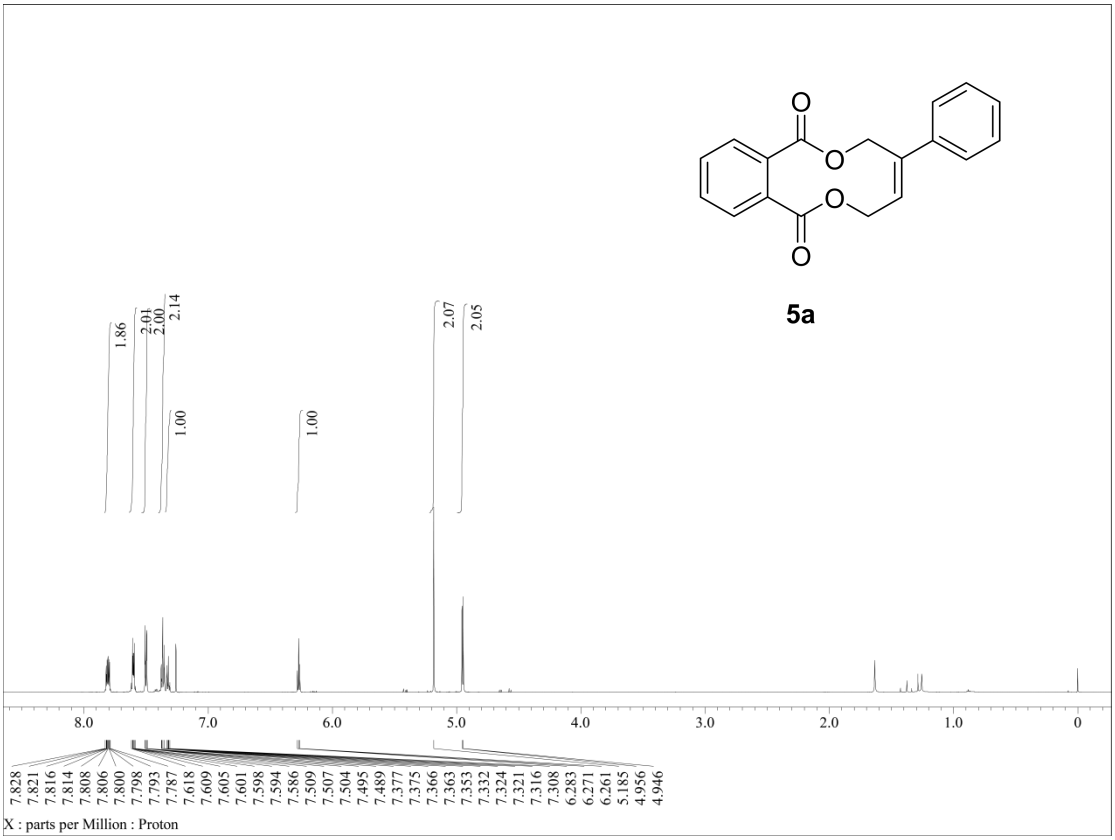

O
O
O
N
Et
O
3ai
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.6
153.7
145.6
141.1
139.5
131.2
130.8
128.5
128.1
127.6
126.7
125.5
124.9
124.6
77.2
77.0
76.8
64.0
61.4
46.0
13.2
X : parts per Million : Carbon13

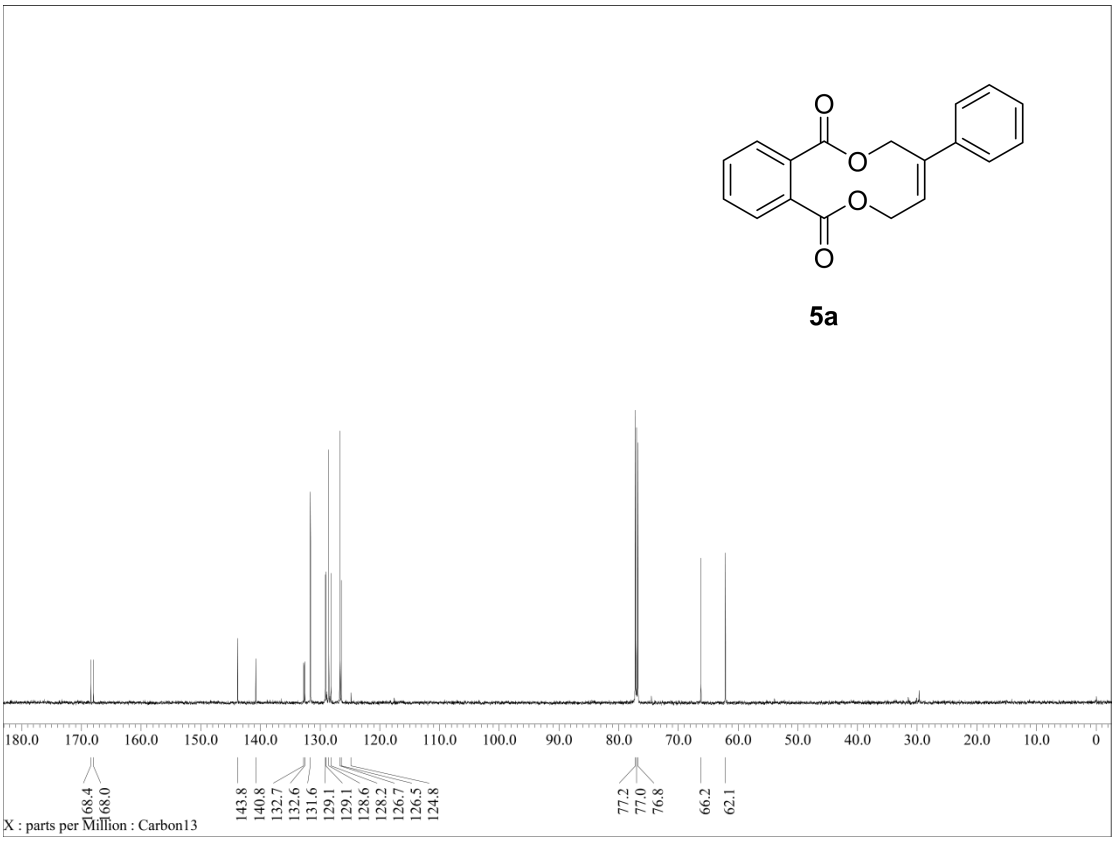

3aj
7.14
2.35
2.00
1.02
0.92
1.00
3.90
1.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.561
7.548
7.483
7.470
7.426
7.414
7.385
7.372
7.361
7.340
7.328
7.314
7.301
7.283
7.249
7.237
7.207
7.195
7.183
7.152
7.138
6.105
6.092
6.081
5.205
5.037
4.727
X : parts per Million : Proton

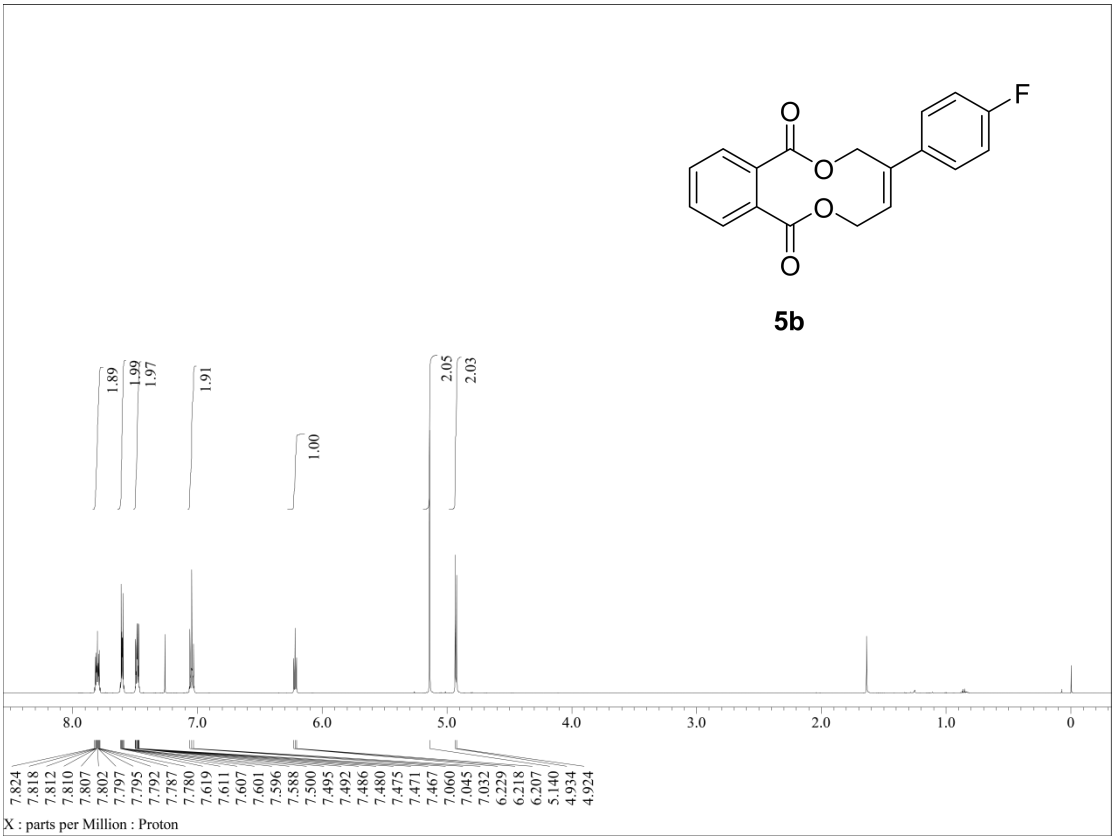

3aj
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.7
154.5
145.8
141.0
140.0
137.5
131.2
129.8
128.5
128.4
128.2
127.8
127.6
127.3
126.7
125.5
124.4
124.2
77.2
77.0
76.8
63.8
61.8
54.4
X : parts per Million : Carbon13

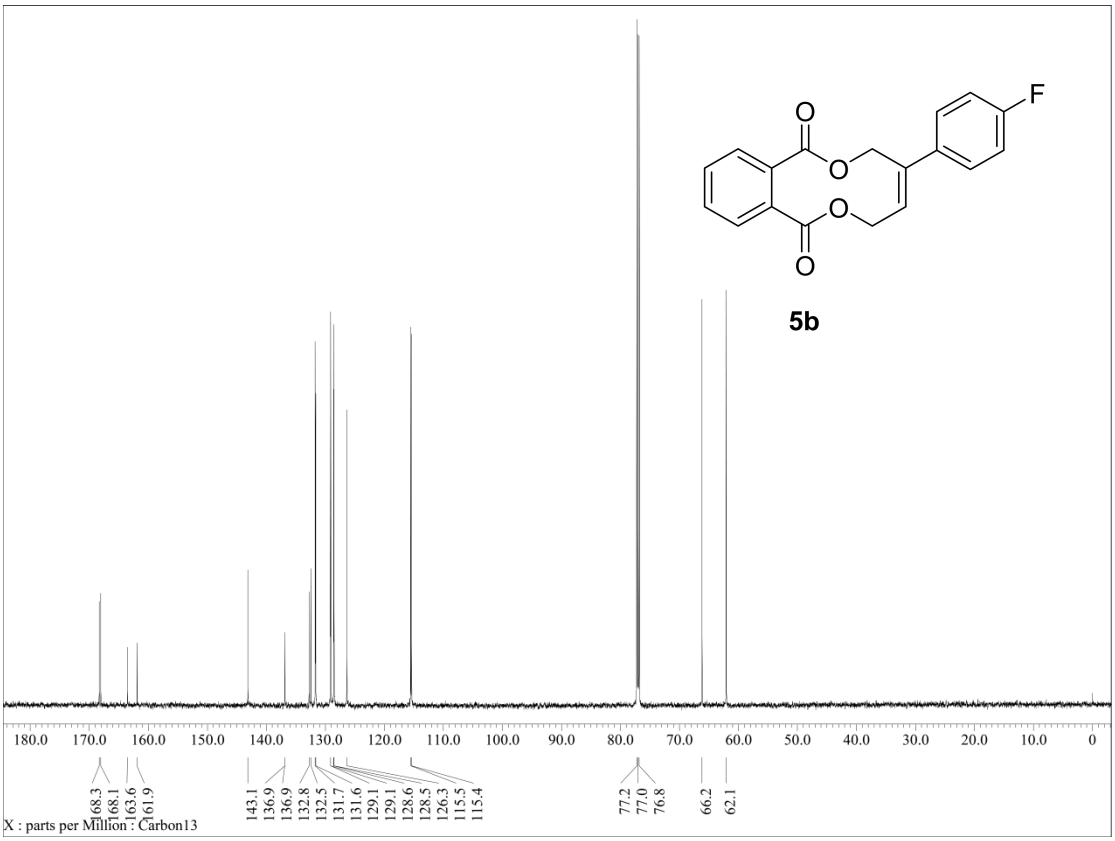

3ak
2.11
2.19
2.00
3.95
1.80
2.19
0.88
1.08
0.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.567
7.556
7.483
7.470
7.440
7.428
7.415
7.379
7.368
7.355
7.335
7.323
7.310
7.302
7.290
7.242
7.229
7.216
6.098
6.086
6.074
6.063
6.055
6.046
6.036
6.027
6.017
6.008
5.373
5.281
5.260
5.232
5.189
5.173
5.057
4.684
4.430
X : parts per Million : Proton

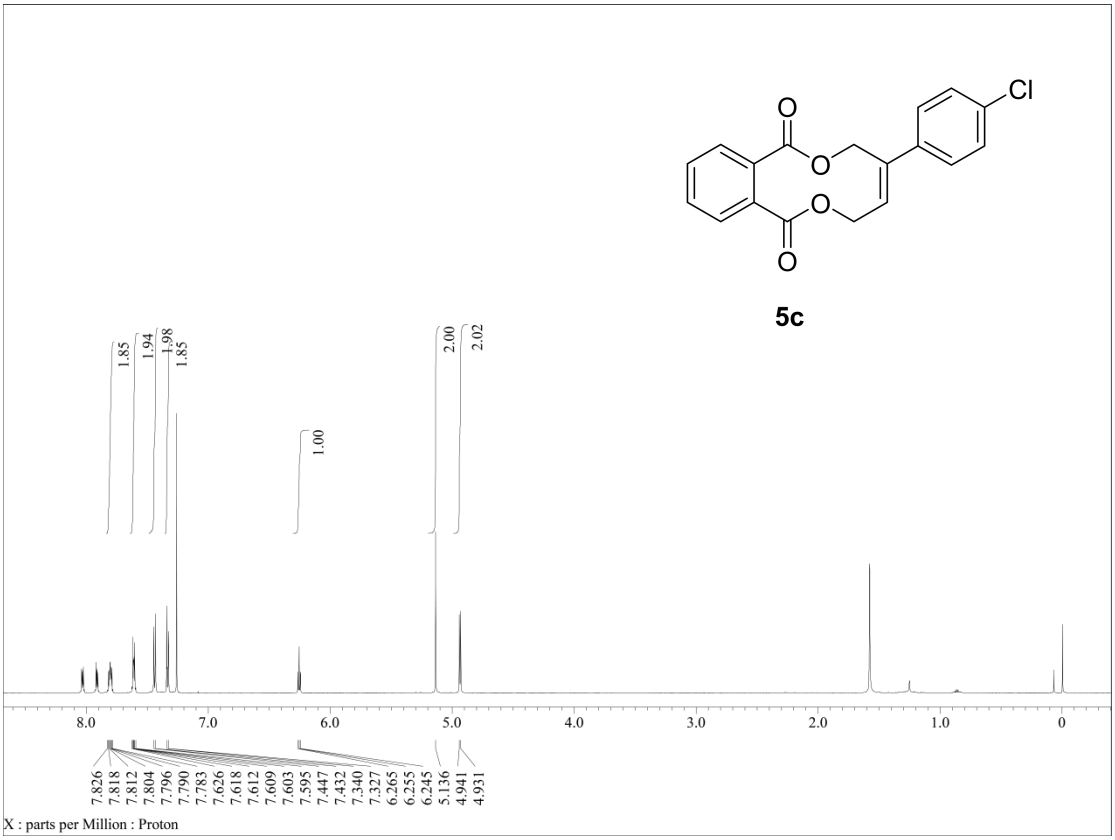

3ak
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.7
153.8
145.8
141.0
139.9
133.9
131.1
130.0
128.5
128.1
127.5
126.7
125.4
124.4
116.9
77.2
77.0
76.8
63.9
61.6
53.7
X : parts per Million : Carbon13

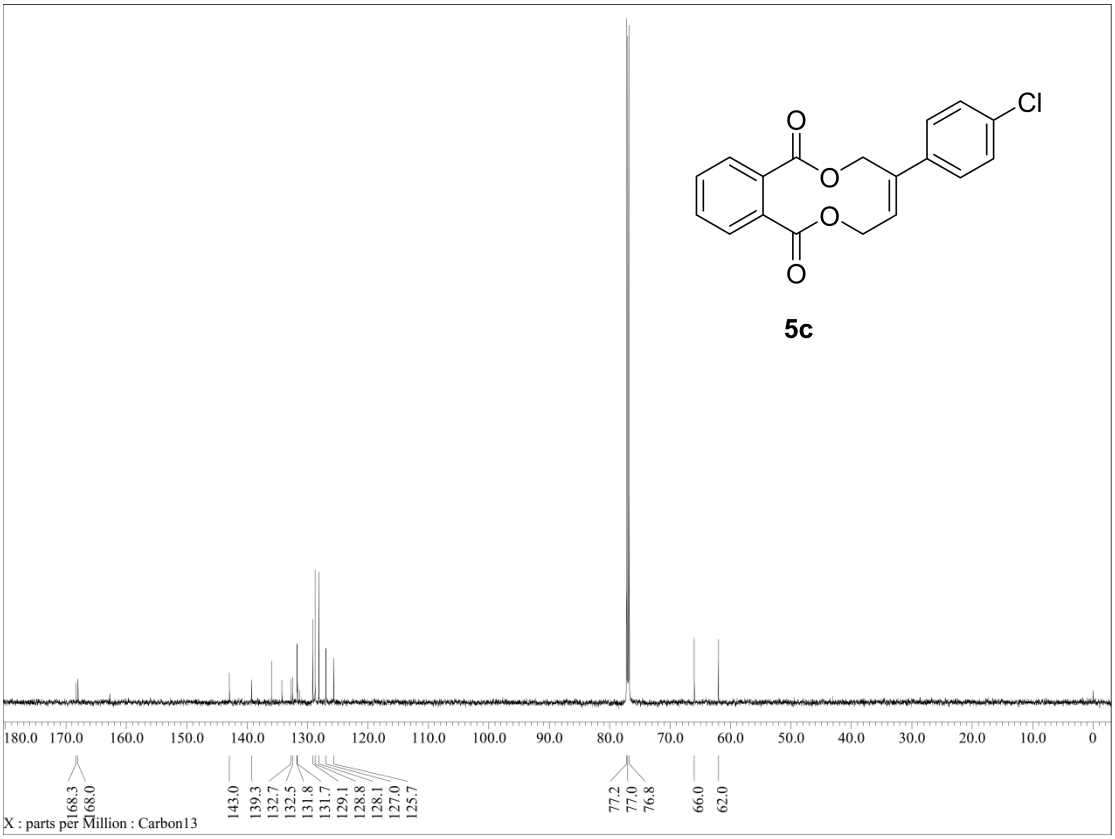

5a
1.86
2.01
2.00
2.14
1.00
1.00
2.07
2.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.828
7.821
7.816
7.814
7.808
7.806
7.800
7.798
7.793
7.787
7.618
7.609
7.605
7.601
7.598
7.594
7.586
7.509
7.507
7.504
7.495
7.489
7.377
7.375
7.366
7.363
7.353
7.332
7.324
7.321
7.316
7.308
6.283
6.271
6.261
5.185
4.956
4.946
X : parts per Million : Proton

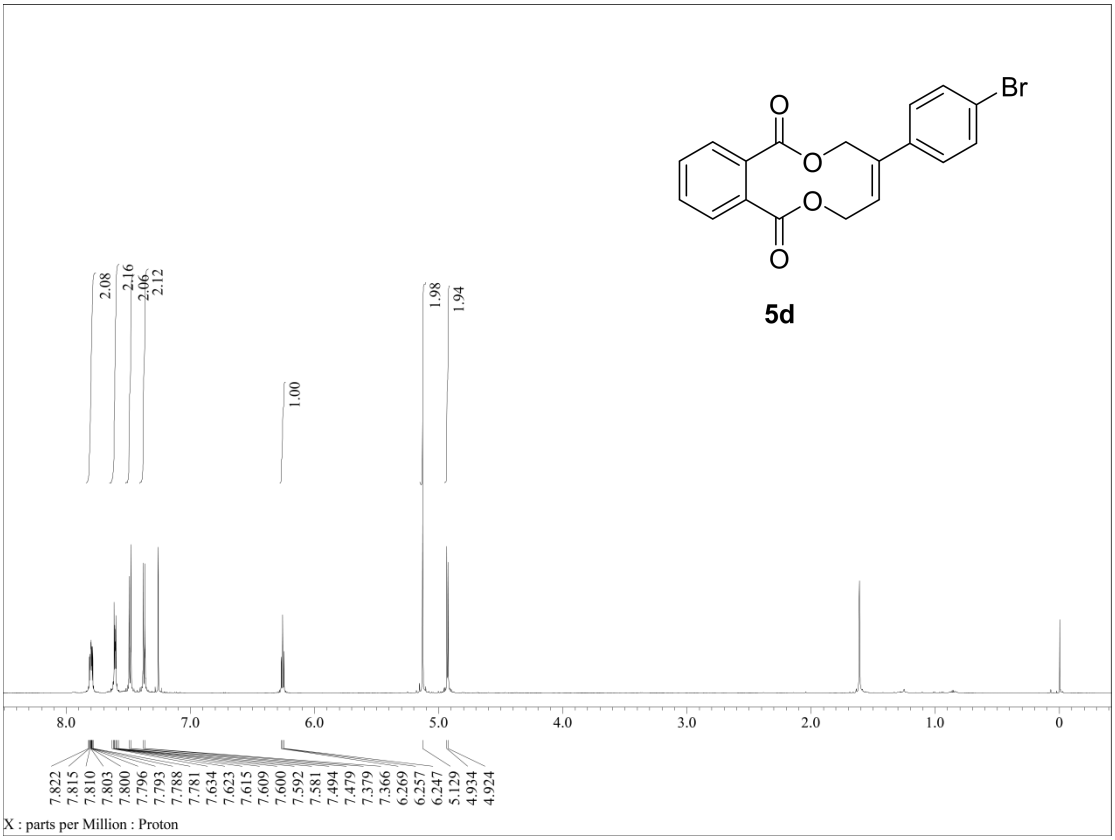

5a
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
168.0
143.8
140.8
132.7
132.6
131.6
129.1
129.1
128.6
128.2
126.7
126.5
124.8
77.2
77.0
76.8
66.2
62.1
X : parts per Million : Carbon13


F
O
O
O
O
5b
1.89
1.99
1.97
1.91
1.00
2.05
2.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.824
7.818
7.812
7.810
7.807
7.802
7.797
7.795
7.792
7.787
7.780
7.619
7.611
7.607
7.601
7.596
7.588
7.500
7.495
7.492
7.486
7.480
7.475
7.471
7.467
7.060
7.045
7.032
6.229
6.218
6.207
5.140
4.934
4.924
X : parts per Million : Proton

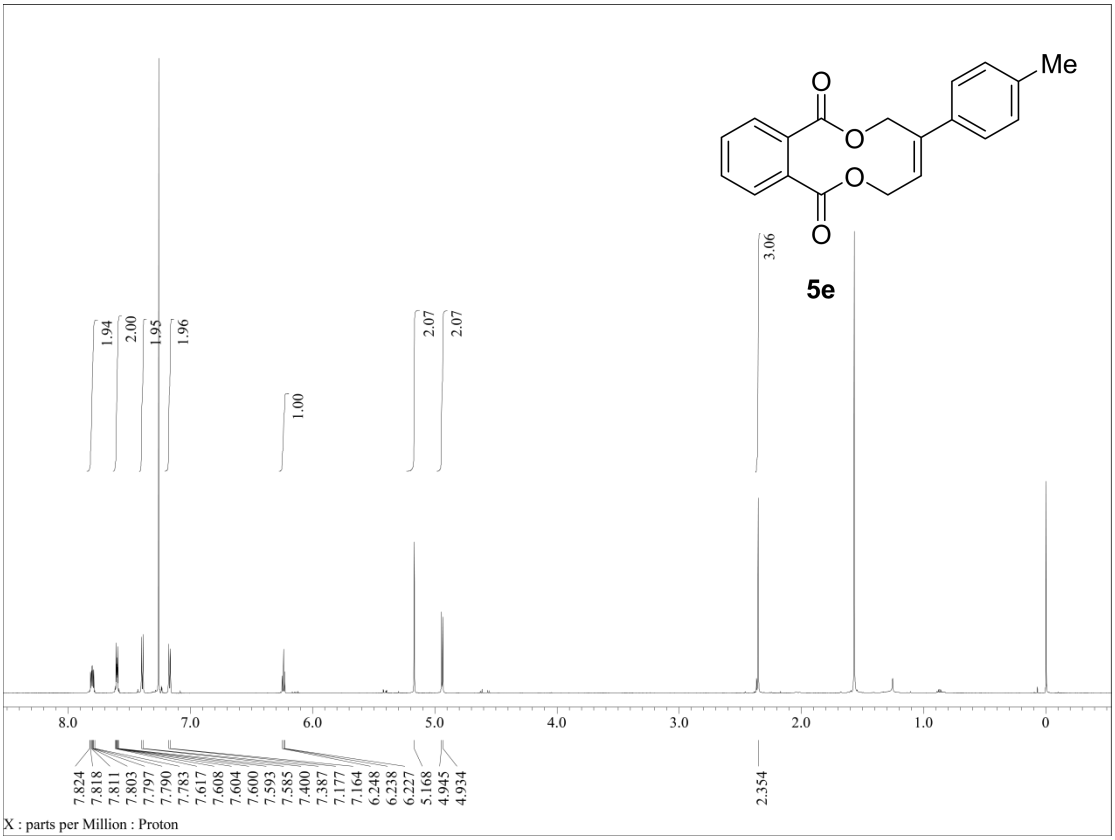

F
O
O
O
O
5b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.3
168.1
163.6
161.9
143.1
136.9
136.9
132.8
132.5
131.7
131.6
129.1
129.1
128.6
128.5
126.3
115.5
115.4
77.2
77.0
76.8
66.2
62.1
X : parts per Million : Carbon13

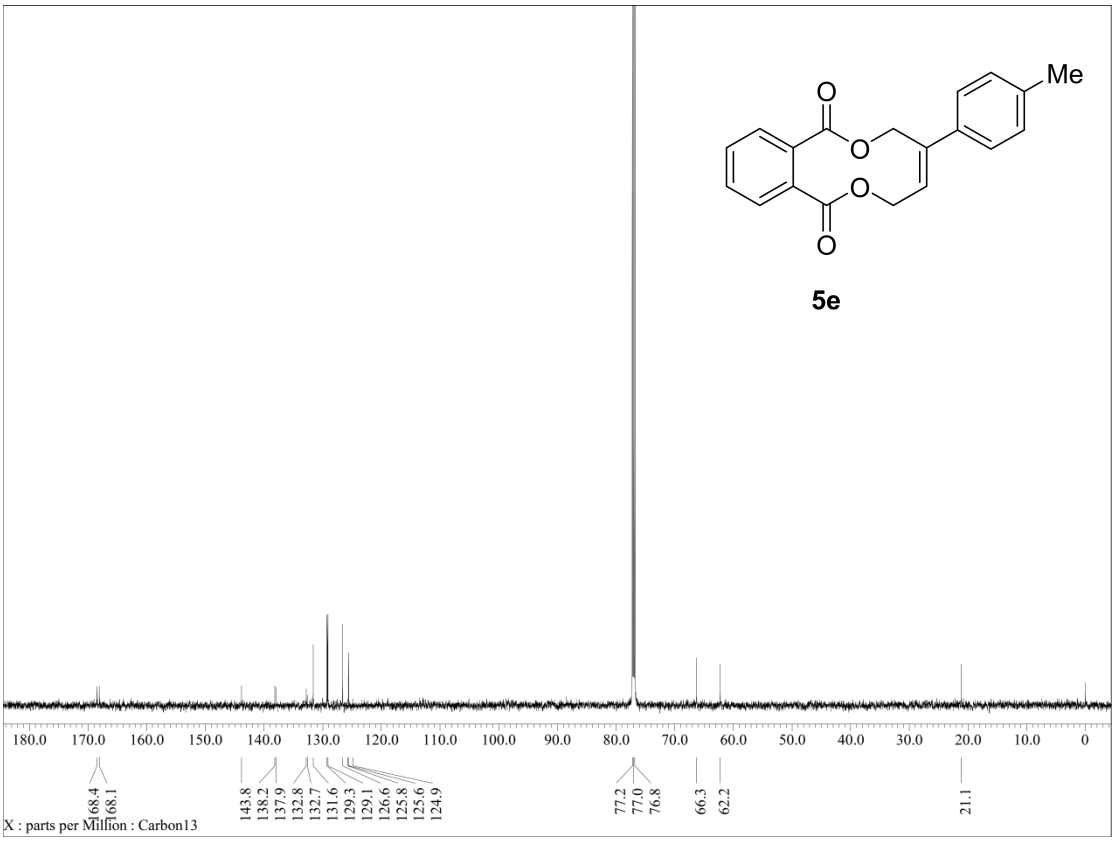

Cl
O
O
O
O
5c
1.85
1.94
1.98
1.85
1.00
2.00
2.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.826
7.818
7.812
7.804
7.796
7.790
7.783
7.626
7.618
7.612
7.609
7.603
7.595
7.447
7.432
7.340
7.327
6.265
6.255
6.245
5.136
4.941
4.931
X : parts per Million : Proton

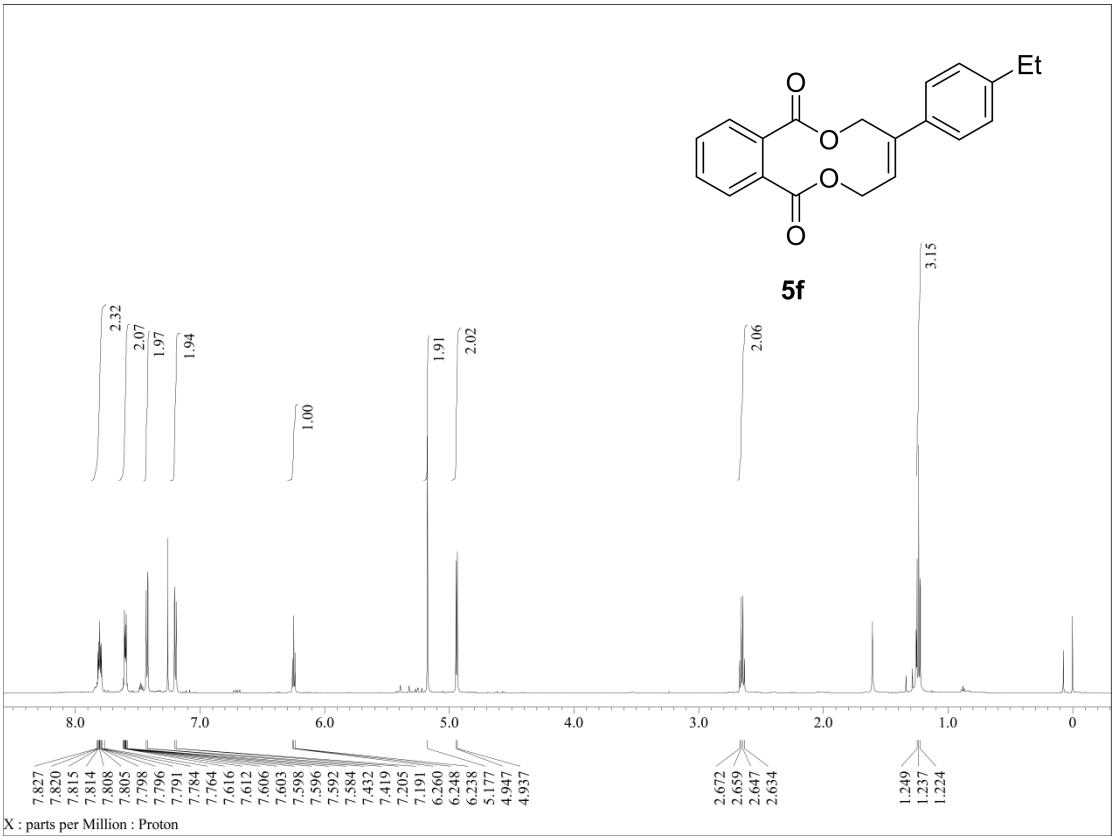

Cl
O
O
O
O
5c
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.3
168.0
143.0
139.3
132.7
132.5
131.8
131.7
129.1
128.8
128.1
127.0
125.7
77.2
77.0
76.8
66.0
62.0
X : parts per Million : Carbon13

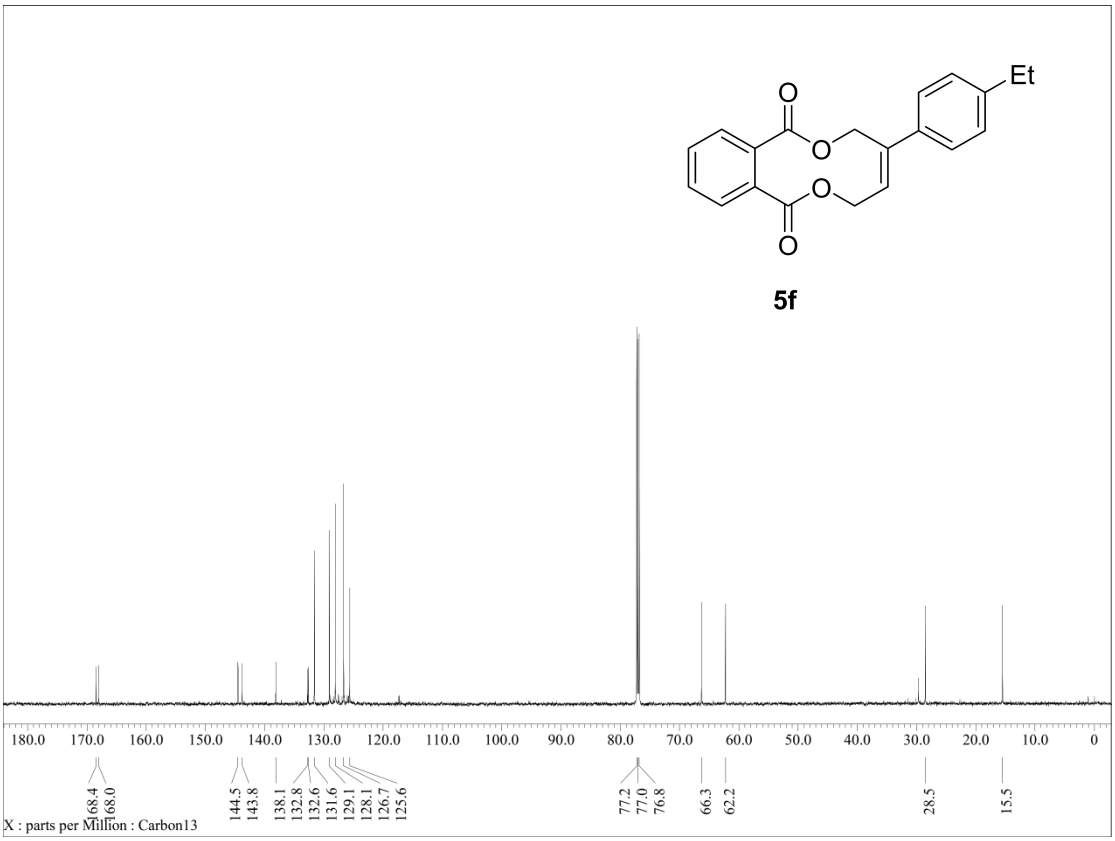

Br
O
O
O
O
5d
2.08
2.16
2.06
2.12
1.00
1.98
1.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.822
7.815
7.810
7.803
7.800
7.796
7.793
7.788
7.781
7.634
7.623
7.615
7.609
7.600
7.592
7.581
7.494
7.479
7.379
7.366
6.269
6.257
6.247
5.129
4.934
4.924
X : parts per Million : Proton

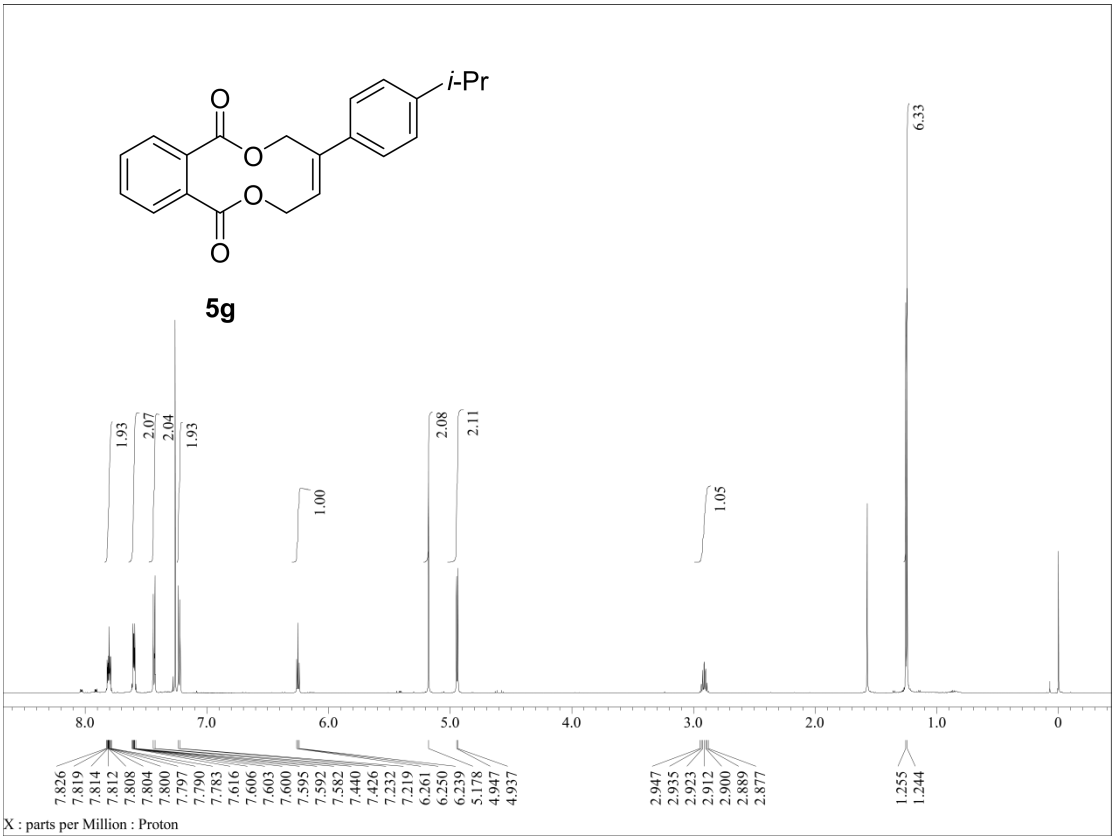

Br
O
O
O
O
5d
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.3
168.0
143.0
139.7
132.7
132.4
131.7
131.7
131.7
129.1
128.4
127.0
122.4
77.2
77.0
76.8
65.9
62.0
X : parts per Million : Carbon13

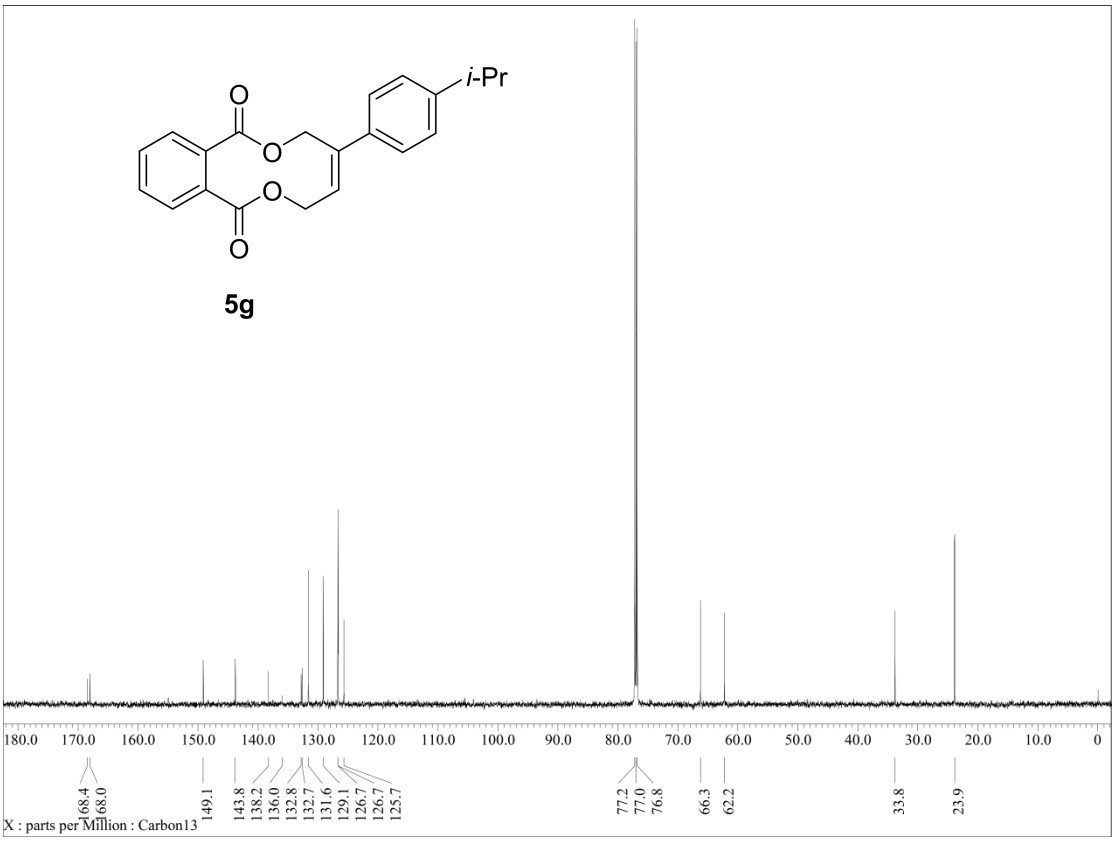

Me
O
O
O
O
3.06
5e
1.94
2.00
1.95
1.96
1.00
2.07
2.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.824
7.818
7.811
7.803
7.797
7.790
7.783
7.617
7.608
7.604
7.600
7.593
7.585
7.400
7.387
7.177
7.164
6.248
6.238
6.227
5.168
4.945
4.934
2.354
X : parts per Million : Proton

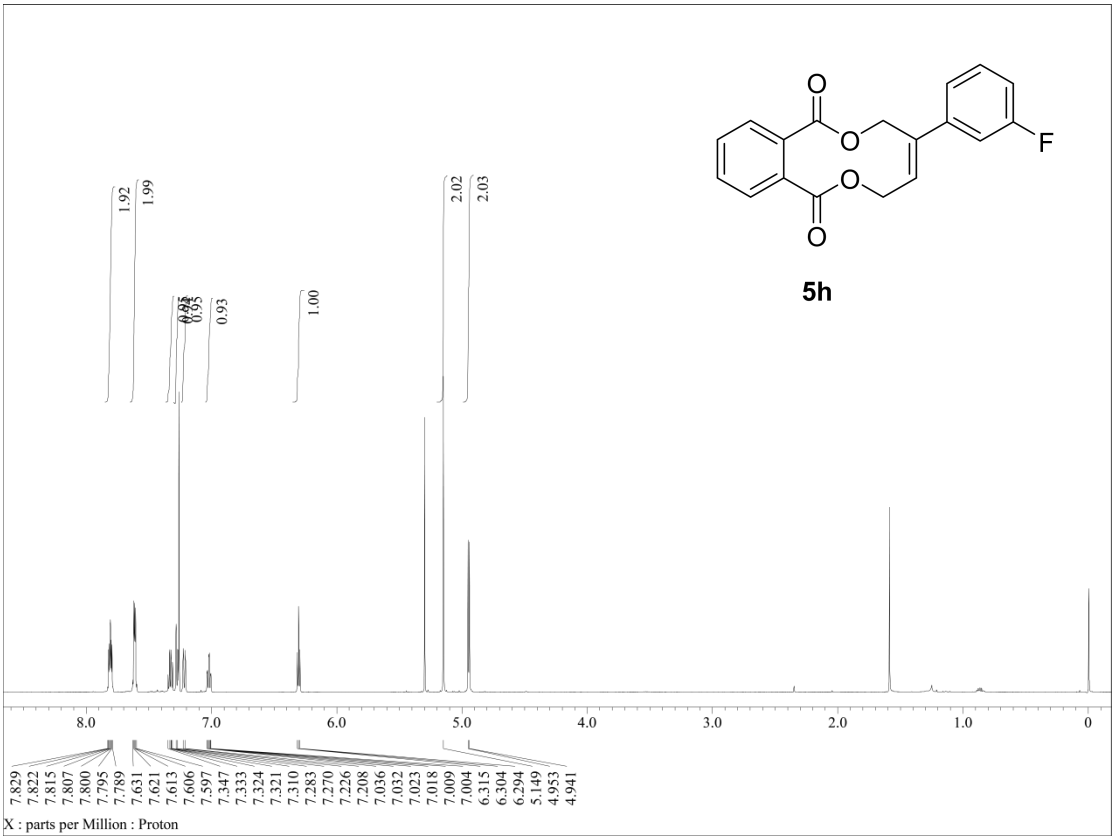

Me
O
O
O
O
5e
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
168.1
143.8
138.2
137.9
132.8
132.7
131.6
129.3
129.1
126.6
125.8
125.6
124.9
77.2
77.0
76.8
66.3
62.2
21.1
X : parts per Million : Carbon13


Et
O
O
O
O
5f
2.32
2.07
1.97
1.94
1.00
1.91
2.02
2.06
3.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.827
7.820
7.815
7.814
7.808
7.805
7.798
7.796
7.791
7.784
7.764
7.616
7.612
7.606
7.603
7.598
7.596
7.592
7.584
7.432
7.419
7.205
7.191
6.260
6.248
6.238
5.177
4.947
4.937
2.672
2.659
2.647
2.634
1.249
1.237
1.224
X : parts per Million : Proton


Et
O
O
O
O
5f
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
168.0
144.5
143.8
138.1
132.8
132.6
131.6
129.1
128.1
126.7
125.6
77.2
77.0
76.8
66.3
62.2
28.5
15.5
X : parts per Million : Carbon13

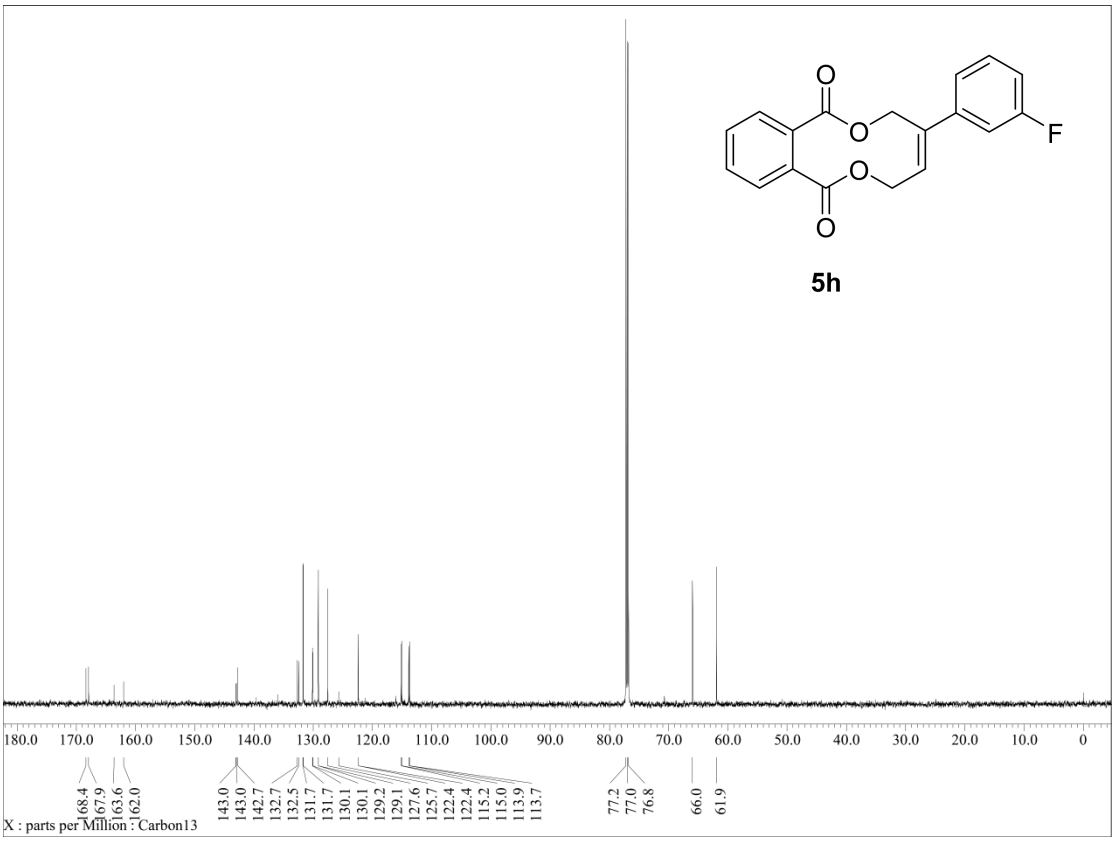

i-Pr
O
O
O
O
5g
1.93
2.07
2.04
1.93
1.00
2.08
2.11
1.05
6.33
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.826
7.819
7.814
7.812
7.808
7.804
7.800
7.797
7.790
7.783
7.616
7.606
7.603
7.600
7.595
7.592
7.582
7.440
7.426
7.232
7.219
6.261
6.250
6.239
5.178
4.947
4.937
2.947
2.935
2.923
2.912
2.900
2.889
2.877
1.255
1.244
X : parts per Million : Proton


i-Pr
O
O
O
O
5g
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
168.0
149.1
143.8
138.2
136.0
132.8
132.7
131.6
129.1
126.7
126.7
125.7
77.2
77.0
76.8
66.3
62.2
33.8
23.9
X : parts per Million : Carbon13


1.92
1.99
0.93
1.00
2.02
2.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.829
7.822
7.815
7.807
7.800
7.795
7.789
7.631
7.621
7.613
7.606
7.597
7.347
7.333
7.324
7.321
7.310
7.283
7.270
7.226
7.208
7.036
7.032
7.023
7.018
7.009
7.004
6.315
6.304
6.294
5.149
4.953
4.941
X : parts per Million : Proton

O
O
O
F

5h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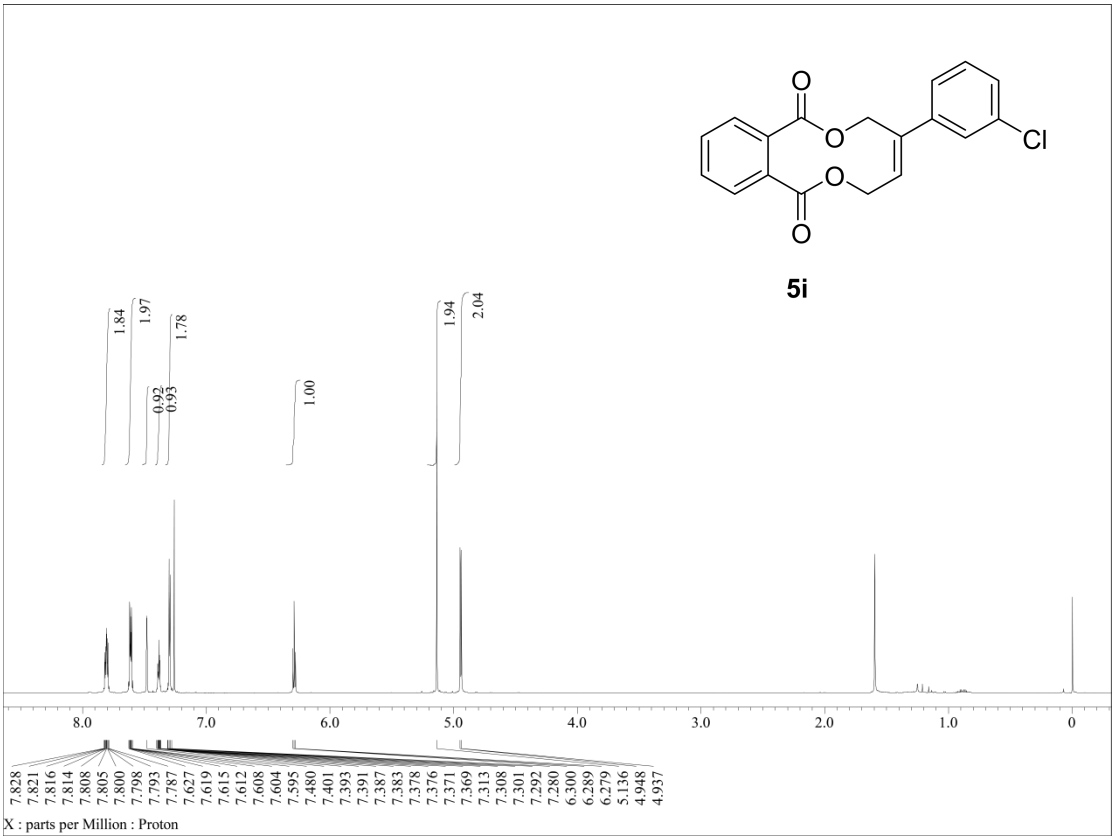
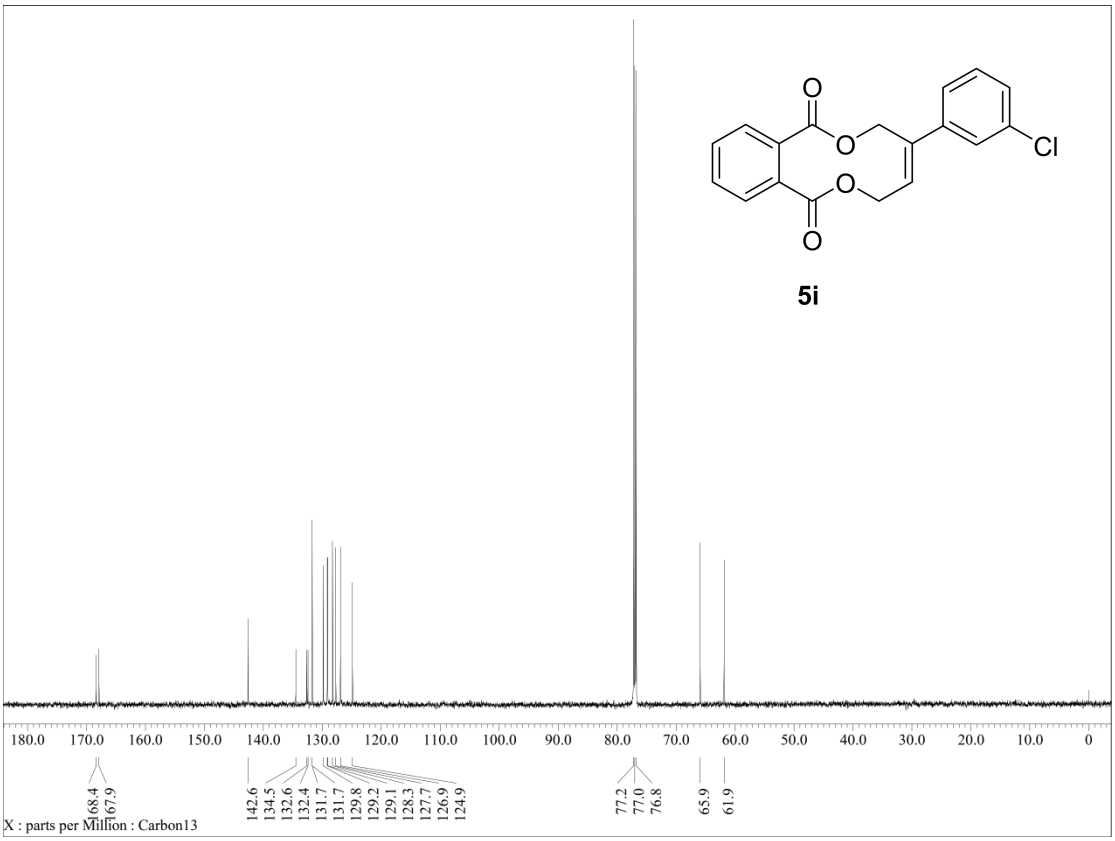
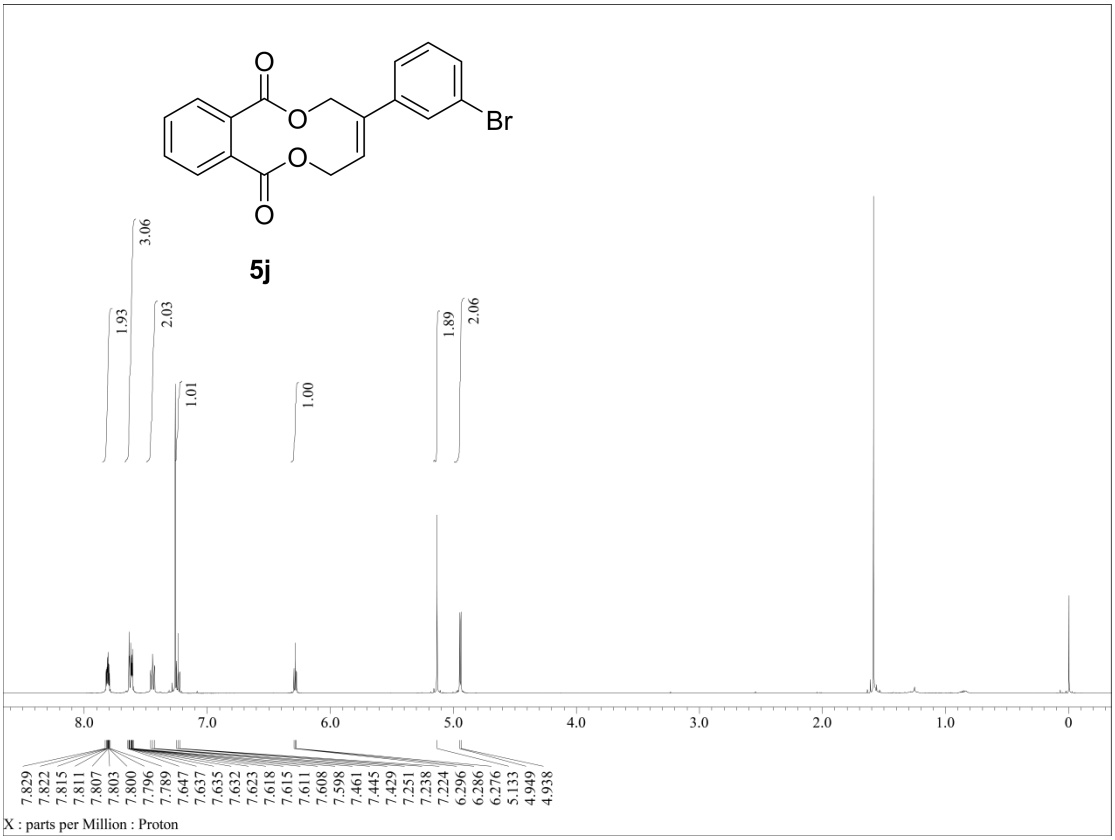
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
167.9
163.6
162.0
143.0
143.0
142.7
132.7
132.5
131.7
131.7
130.1
130.1
129.2
129.1
127.6
125.7
122.4
122.4
115.2
115.0
113.9
113.7
77.2
77.0
76.8
66.0
61.9
X : parts per Million : Carbon13

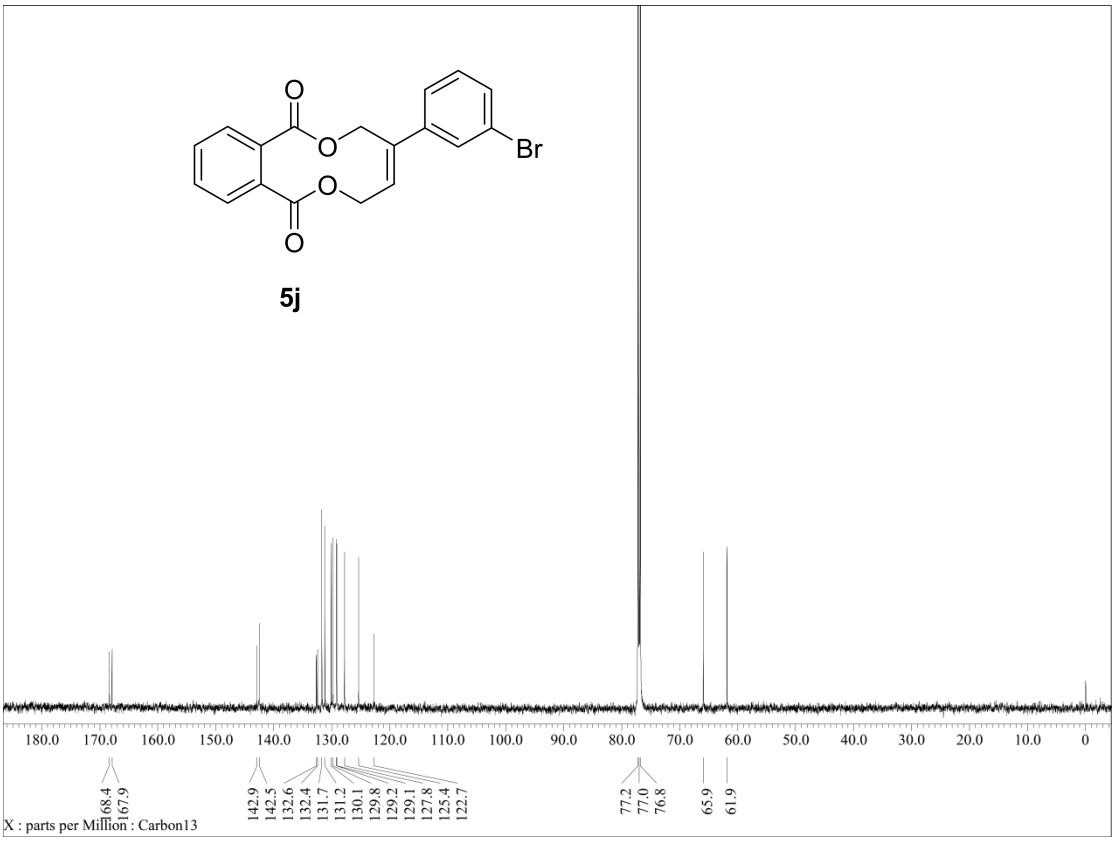
O
O
O
F

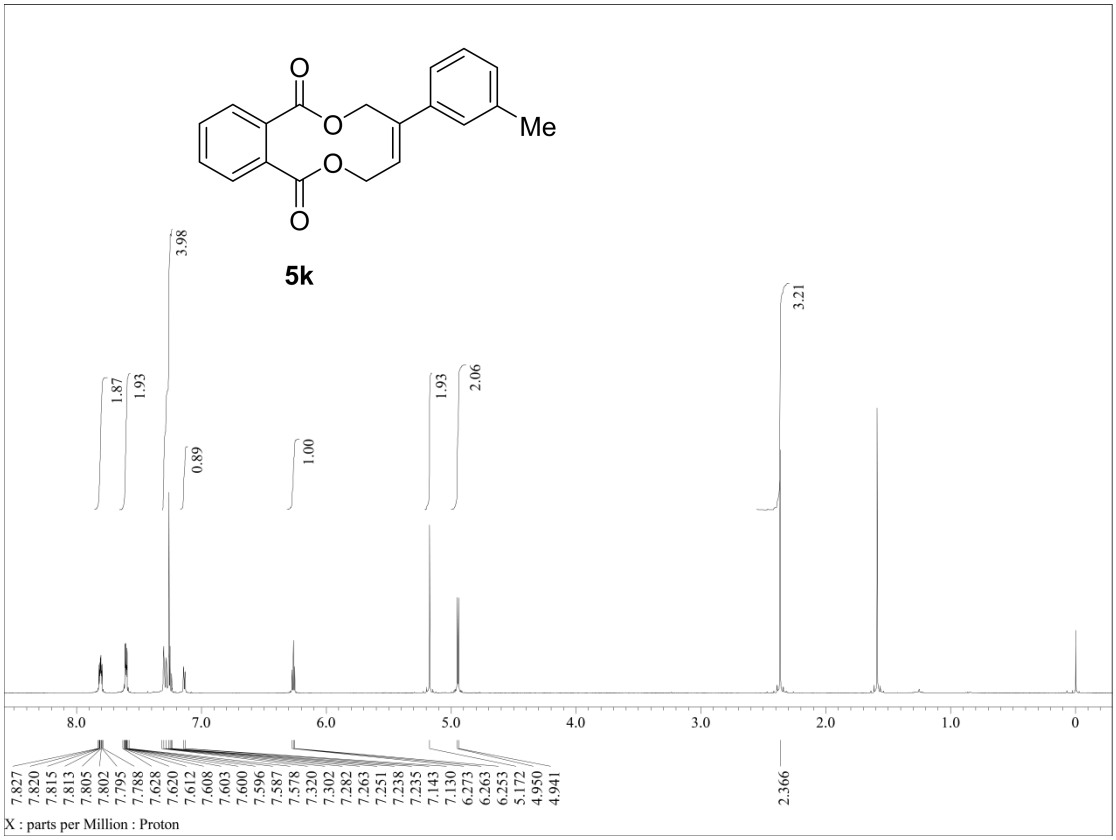
5h

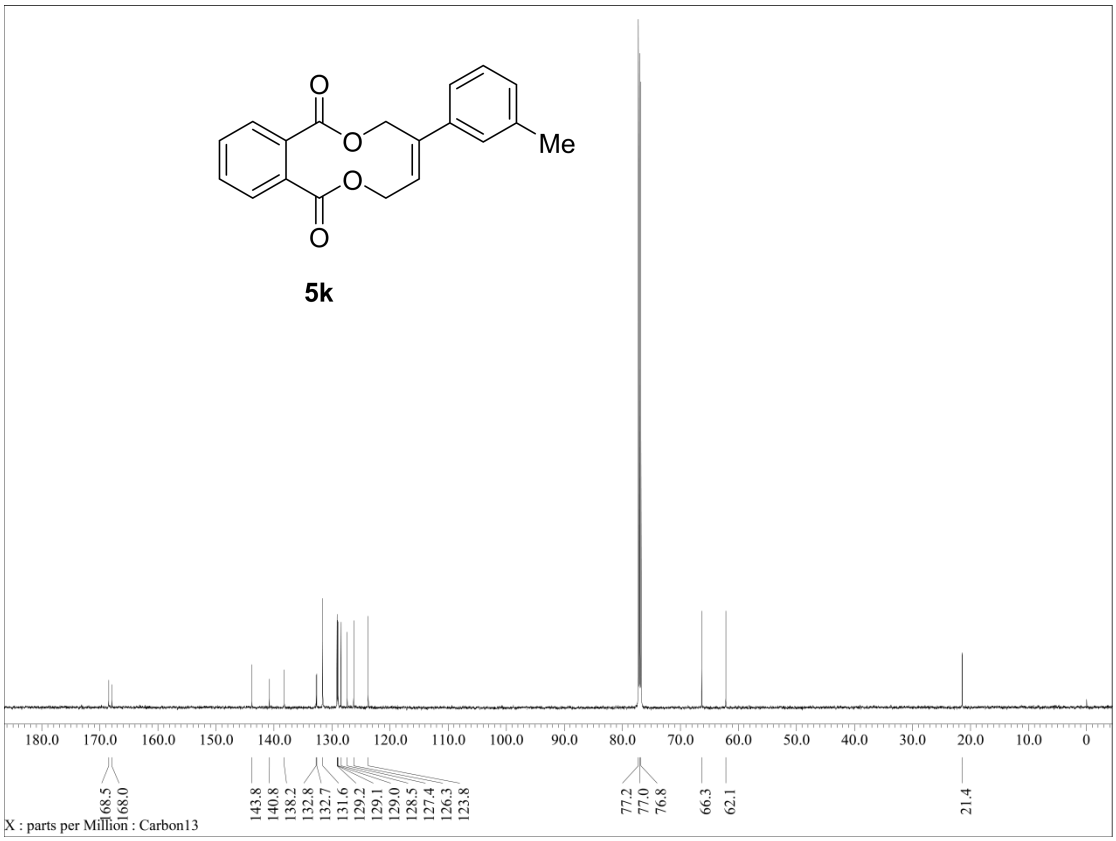

O
O
O
O
Cl
5i
1.84
1.97
0.92
0.93
1.78
1.00
1.94
2.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.828
7.821
7.816
7.814
7.808
7.805
7.800
7.798
7.793
7.787
7.627
7.619
7.615
7.612
7.608
7.604
7.595
7.480
7.401
7.393
7.391
7.387
7.383
7.378
7.376
7.371
7.369
7.313
7.308
7.301
7.292
7.280
6.300
6.289
6.279
5.136
4.948
4.937
X : parts per Million : Proton

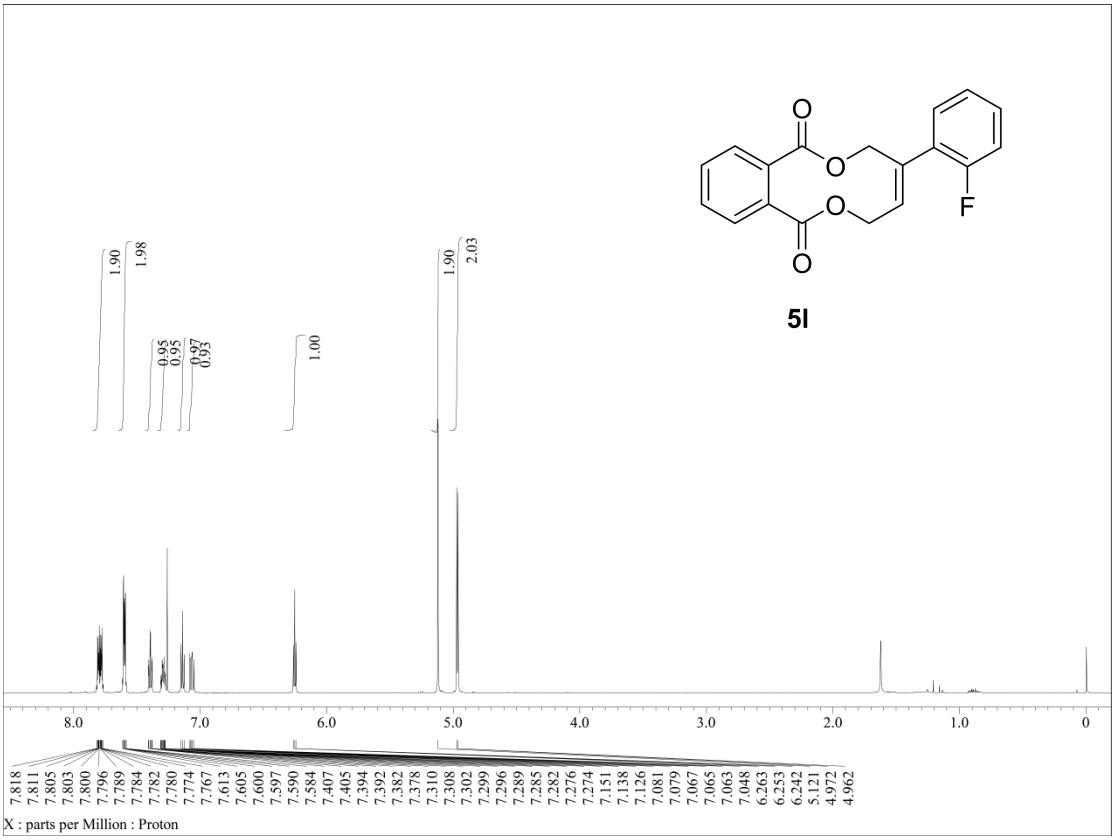

O
O
O
O
Cl
5i
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
167.9
142.6
134.5
132.6
132.4
131.7
131.7
129.8
129.2
129.1
128.3
127.7
126.9
124.9
77.2
77.0
76.8
65.9
61.9
X : parts per Million : Carbon13

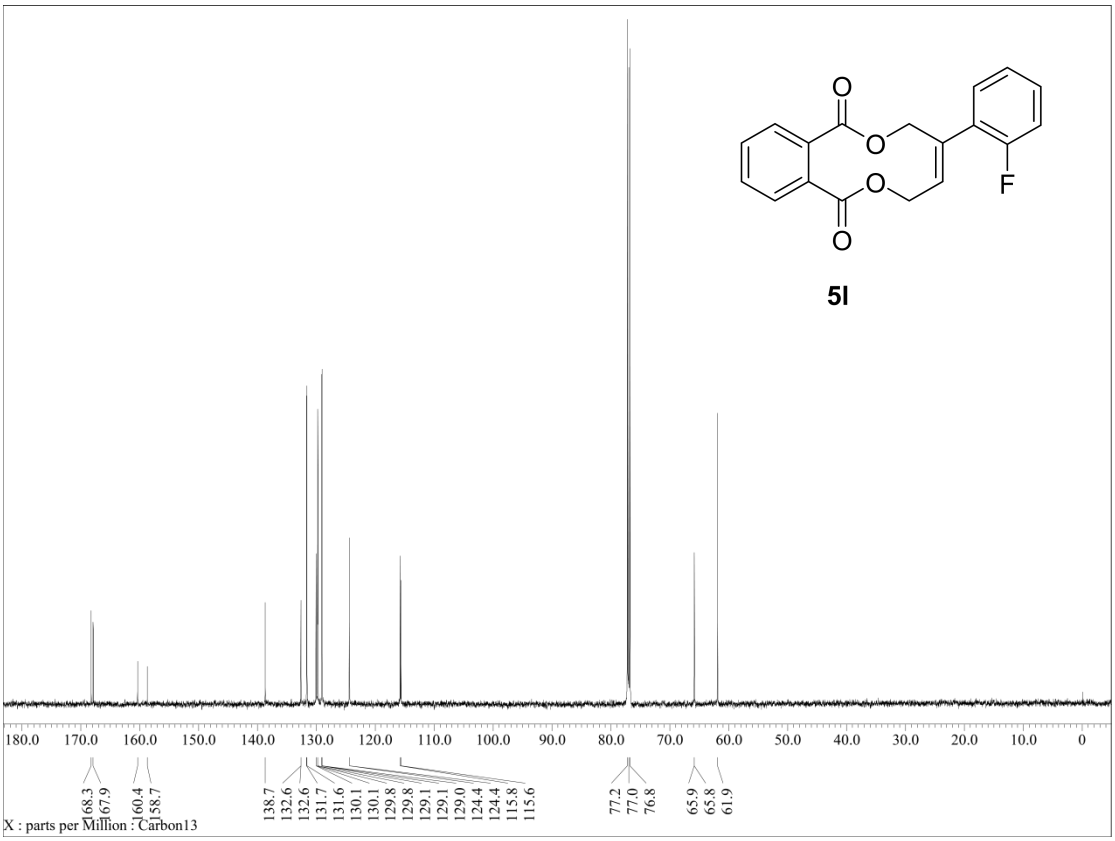

O
O
O
O
Br
5j
3.06
1.93
2.03
1.01
1.00
1.89
2.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.829
7.822
7.815
7.811
7.807
7.803
7.800
7.796
7.789
7.647
7.637
7.635
7.632
7.623
7.618
7.615
7.611
7.608
7.598
7.461
7.445
7.429
7.251
7.238
7.224
6.296
6.286
6.276
5.133
4.949
4.938
X : parts per Million : Proton

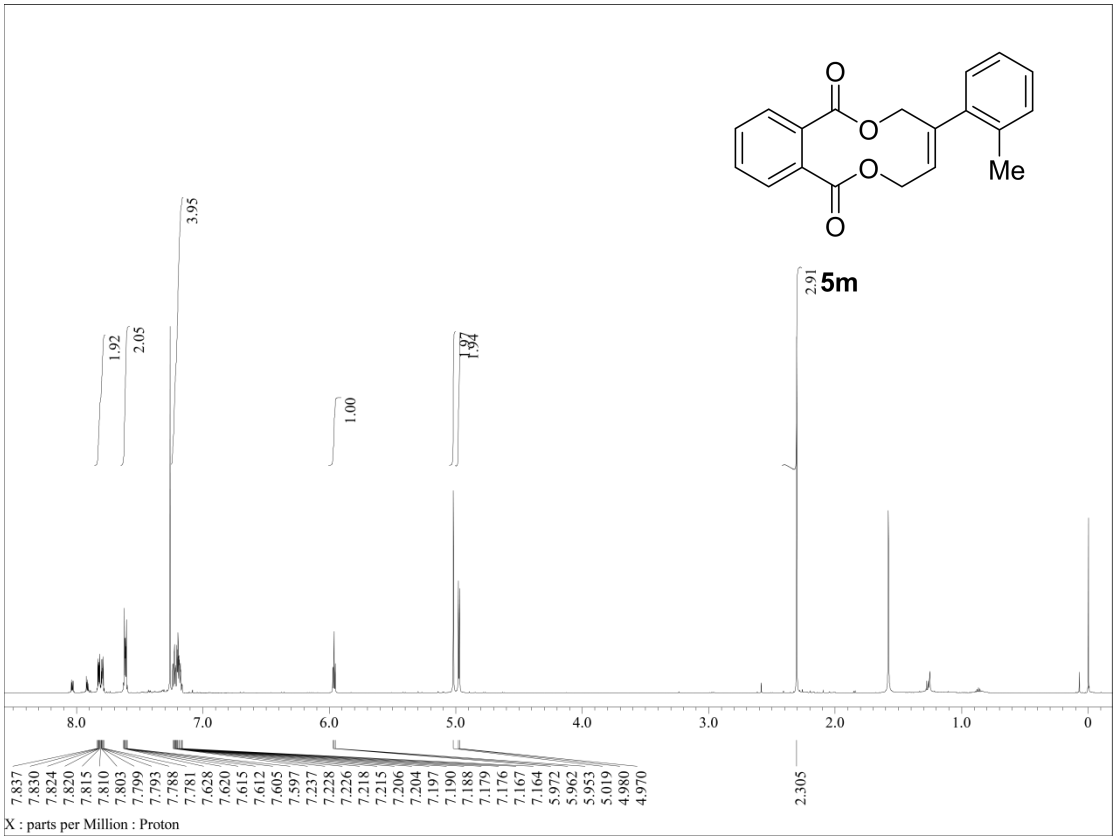

O
O
O
O
Br
5j
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
167.9
142.9
142.5
132.6
132.4
131.7
131.2
130.1
129.8
129.2
129.1
127.8
125.4
122.7
77.2
77.0
76.8
65.9
61.9
X : parts per Million : Carbon13

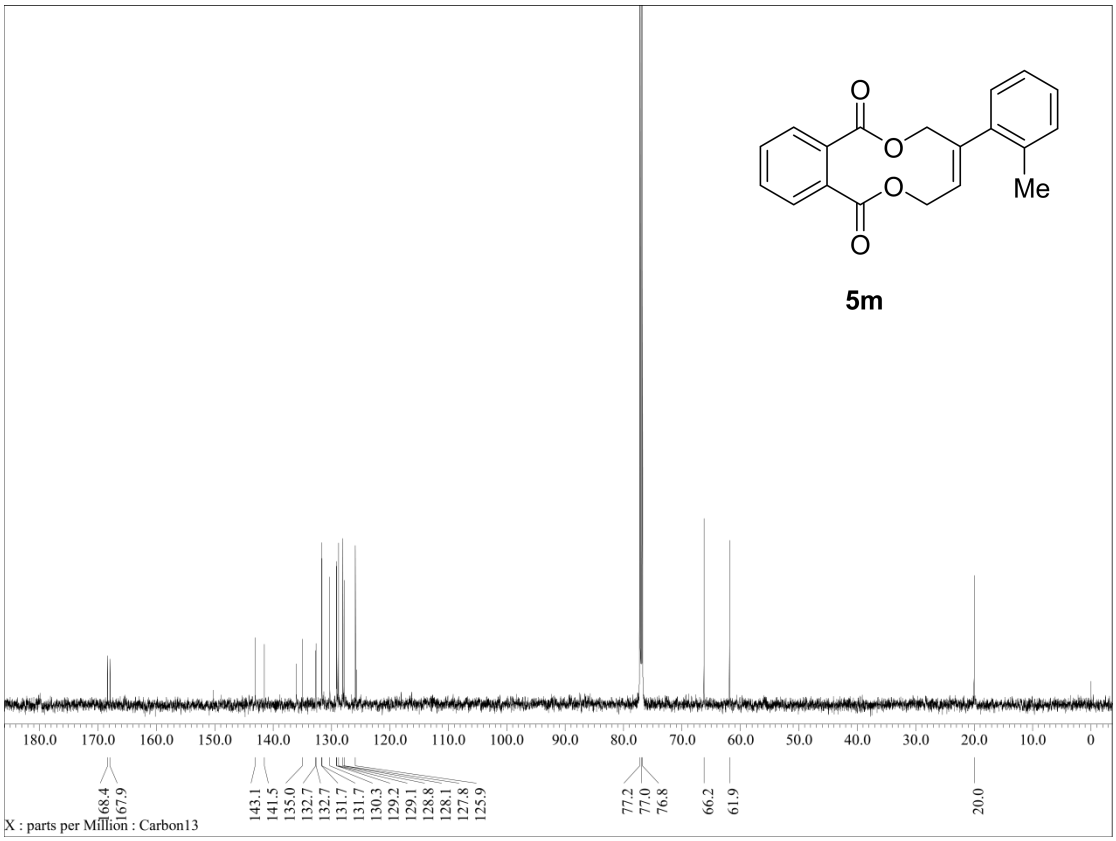

O
O
O
O
Me
5k
3.98
1.87
1.93
0.89
1.00
1.93
2.06
3.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.827
7.820
7.815
7.813
7.805
7.802
7.795
7.788
7.628
7.620
7.612
7.608
7.603
7.600
7.596
7.587
7.578
7.320
7.302
7.282
7.263
7.251
7.238
7.235
7.143
7.130
6.273
6.263
6.253
5.172
4.950
4.941
2.366
X : parts per Million : Proton

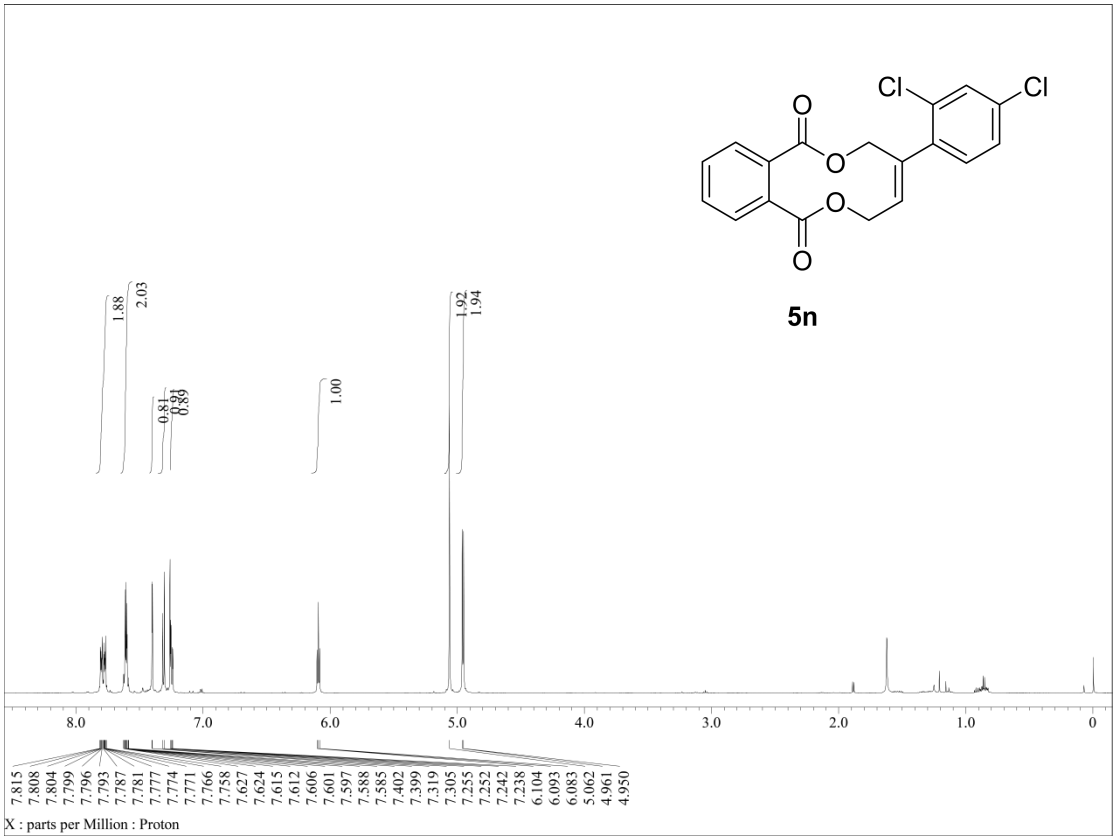

O
O
O
O
Me
5k
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.5
168.0
143.8
140.8
138.2
132.8
132.7
131.6
129.2
129.1
129.0
128.5
127.4
126.3
123.8
77.2
77.0
76.8
66.3
62.1
21.4
X : parts per Million : Carbon13

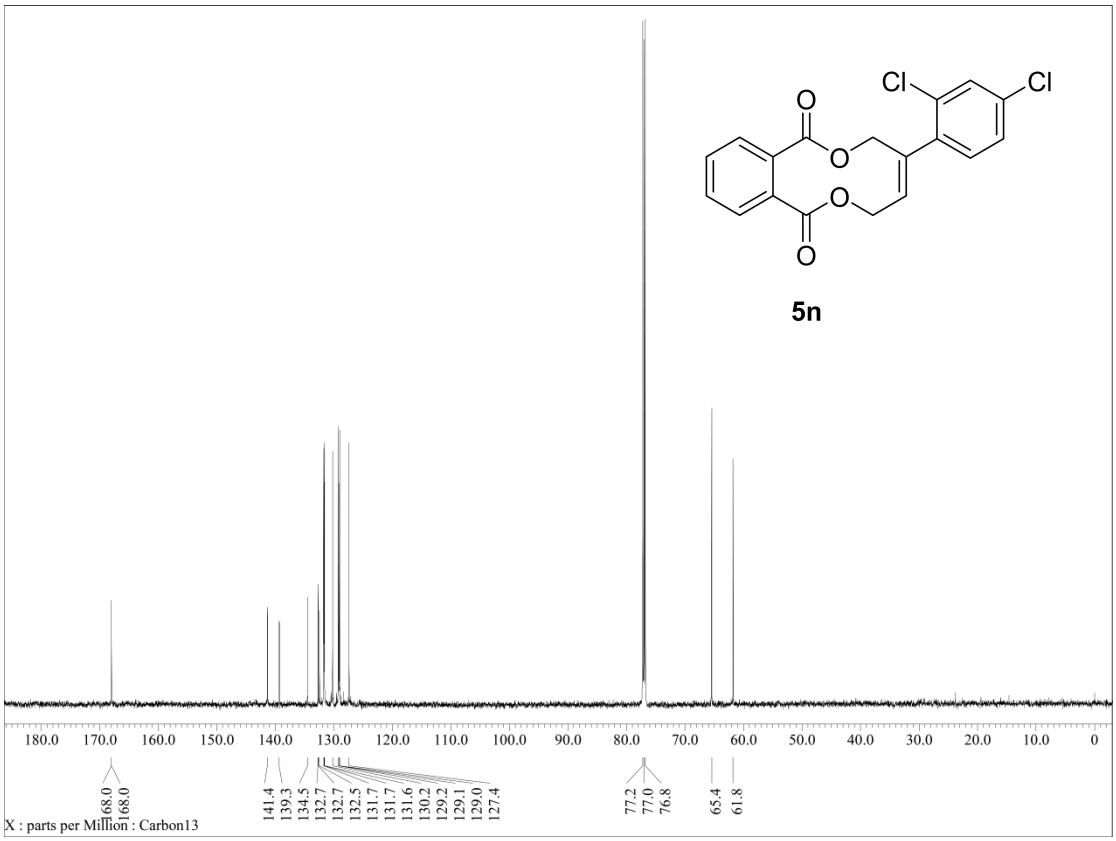

O
O
O
O
F
5l
1.90
1.98
0.95
0.95
0.97
0.93
1.00
1.90
2.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.818
7.811
7.805
7.803
7.800
7.796
7.789
7.784
7.782
7.780
7.774
7.767
7.613
7.605
7.600
7.597
7.590
7.584
7.407
7.405
7.394
7.392
7.382
7.378
7.310
7.308
7.302
7.299
7.296
7.289
7.285
7.282
7.276
7.274
7.151
7.138
7.126
7.081
7.079
7.067
7.065
7.063
7.048
6.263
6.253
6.242
5.121
4.972
4.962
X : parts per Million : Proton

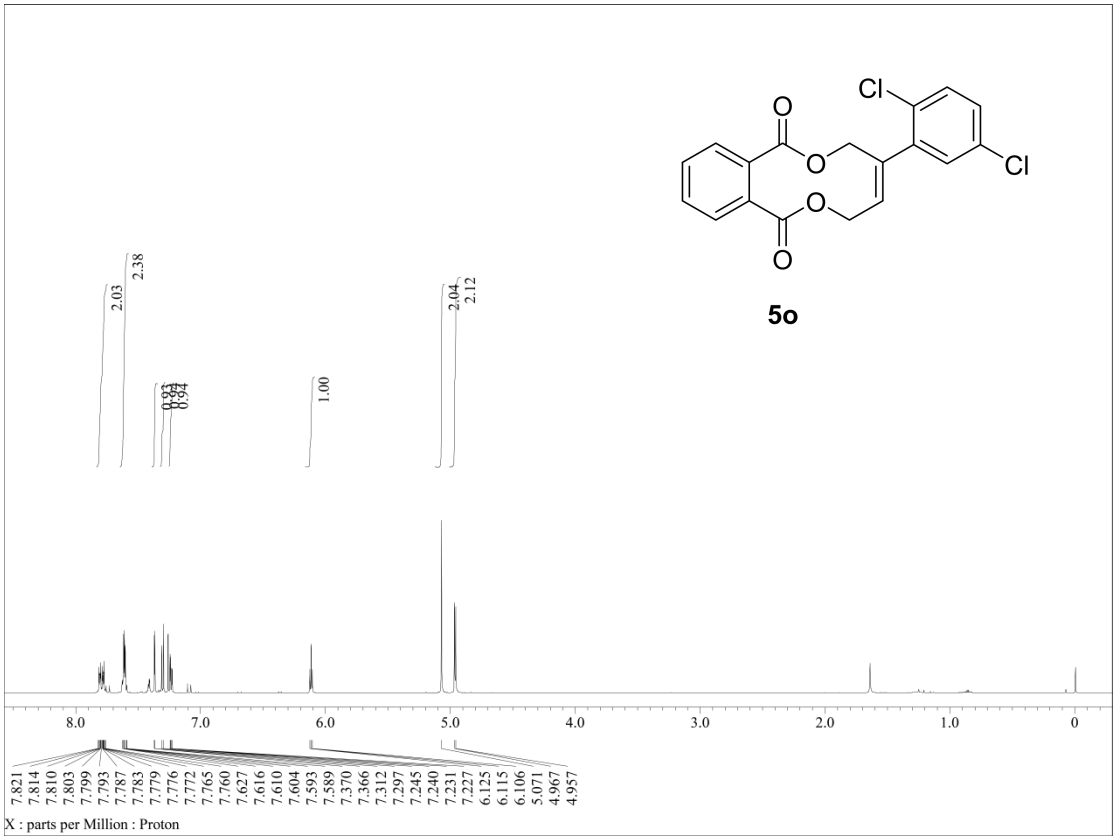

O
O
O
O
F
5l
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.3
167.9
160.4
158.7
138.7
132.6
132.6
131.7
131.6
130.1
130.1
129.8
129.8
129.1
129.1
129.0
124.4
124.4
115.8
115.6
77.2
77.0
76.8
65.9
65.8
61.9
X : parts per Million : Carbon13

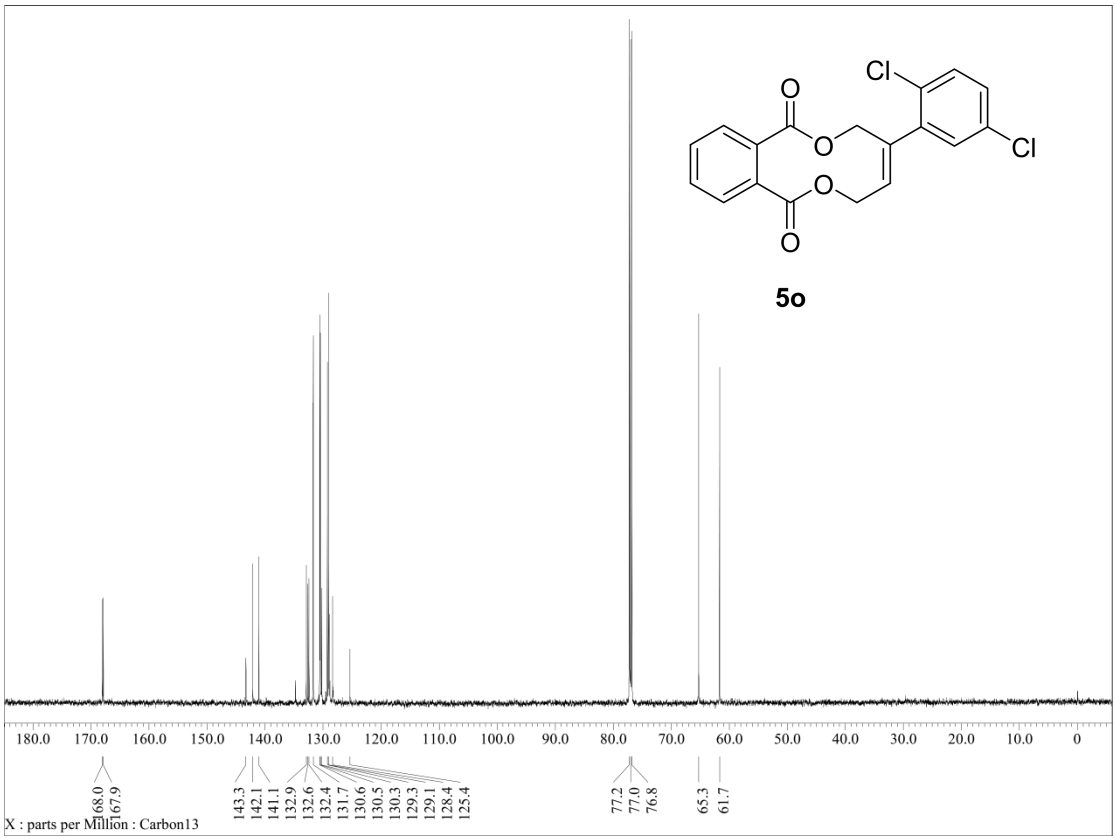

O
O
O
O
Me
5m
3.95
2.91
1.92
2.05
1.00
1.97
1.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.837
7.830
7.824
7.820
7.815
7.810
7.803
7.799
7.793
7.788
7.781
7.628
7.620
7.615
7.612
7.605
7.597
7.237
7.228
7.226
7.218
7.215
7.206
7.204
7.197
7.190
7.188
7.179
7.176
7.167
7.164
5.972
5.962
5.953
5.019
4.980
4.970
2.305
X : parts per Million : Proton

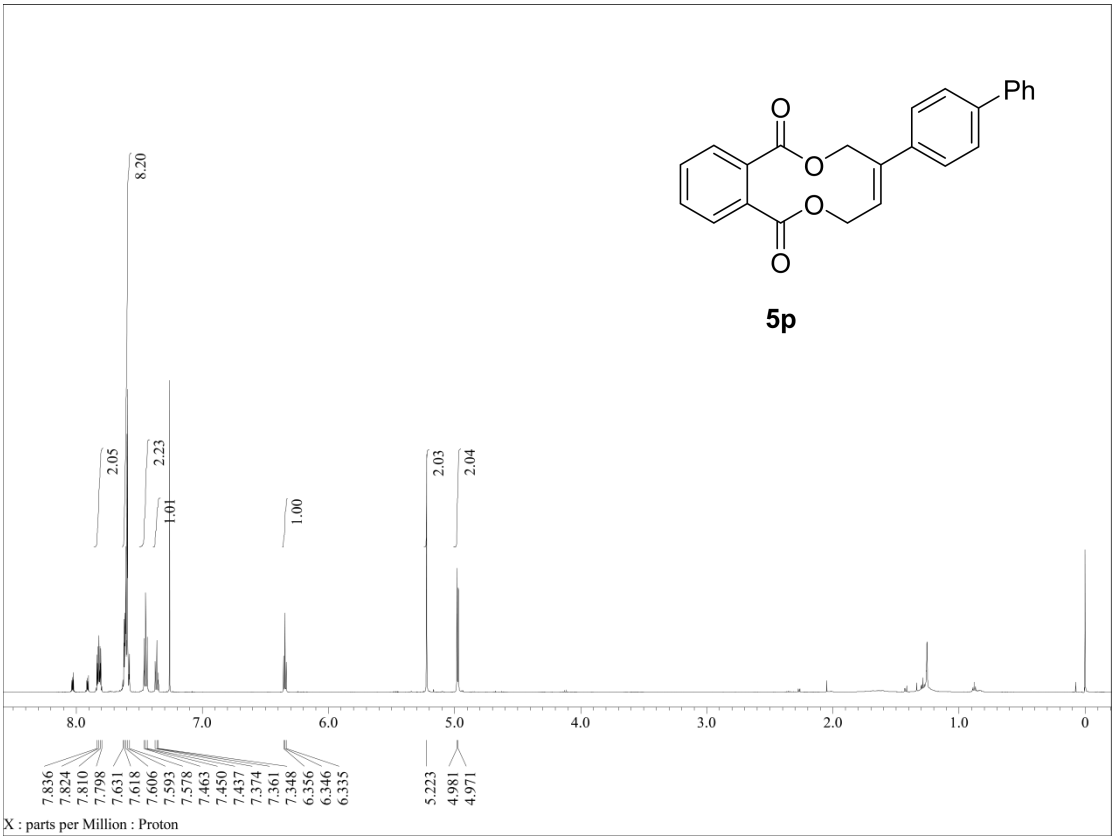

O
O
O
O
Me
5m
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
167.9
143.1
141.5
135.0
132.7
132.7
131.7
131.7
130.3
129.2
129.1
128.8
128.1
127.8
125.9
77.2
77.0
76.8
66.2
61.9
20.0
X : parts per Million : Carbon13

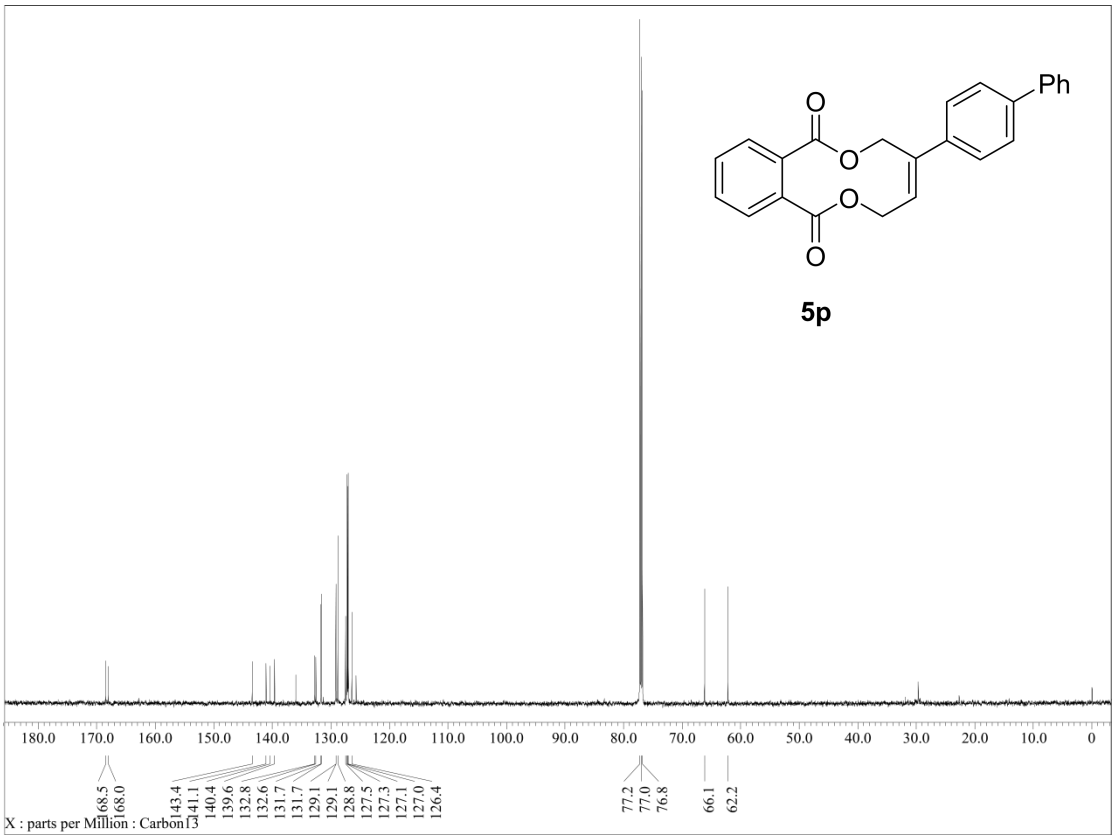

Cl
Cl
O
O
O
O
5n
1.88
2.03
0.81
0.84
0.89
1.00
1.92
1.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.815
7.808
7.804
7.799
7.796
7.793
7.787
7.781
7.777
7.774
7.771
7.766
7.758
7.627
7.624
7.615
7.612
7.606
7.601
7.597
7.588
7.585
7.402
7.399
7.319
7.305
7.255
7.252
7.242
7.238
6.104
6.093
6.083
5.062
4.961
4.950
X : parts per Million : Proton

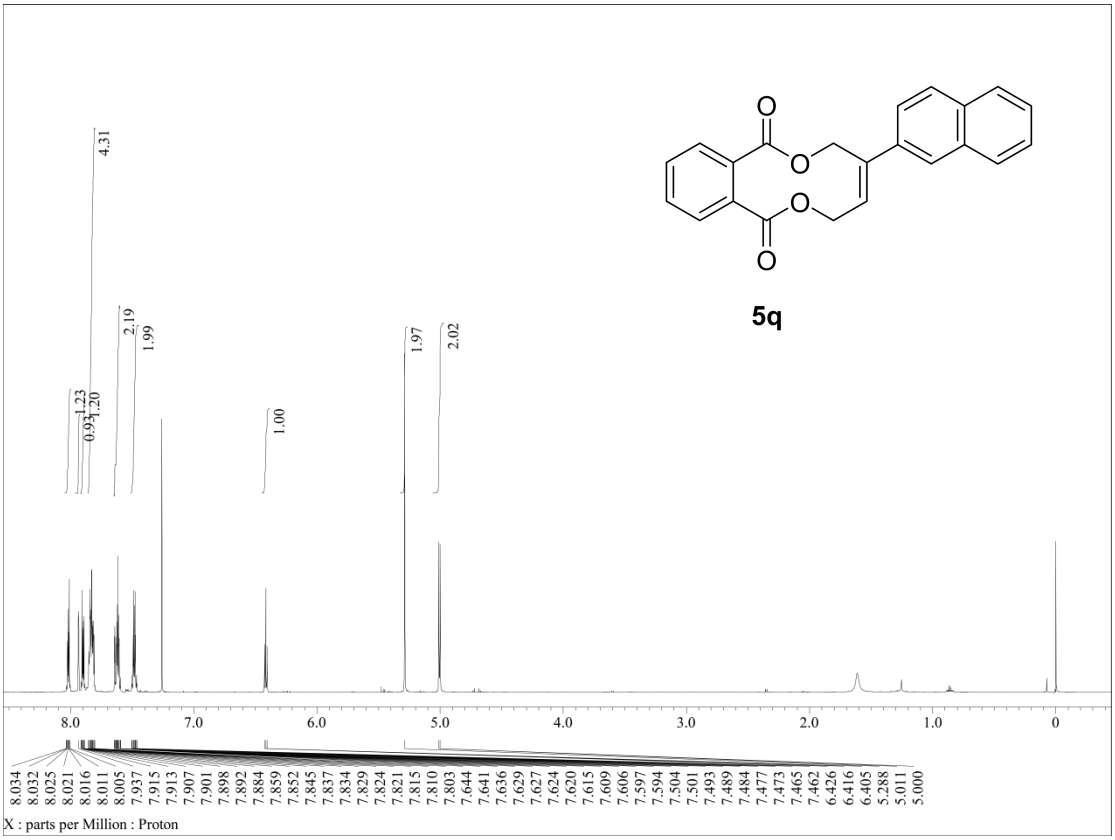

Cl
Cl
O
O
O
O
5n
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.0
168.0
141.4
139.3
134.5
132.7
132.5
131.7
131.7
131.6
130.2
129.2
129.1
129.0
127.4
77.2
77.0
76.8
65.4
61.8
X : parts per Million : Carbon13


Cl
Cl
O
O
O
O
5o
2.38
2.03
2.04
2.12
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.821
7.814
7.810
7.803
7.799
7.793
7.787
7.783
7.779
7.776
7.772
7.765
7.760
7.627
7.616
7.610
7.604
7.593
7.589
7.370
7.366
7.312
7.297
7.245
7.240
7.231
7.227
6.125
6.115
6.106
5.071
4.967
4.957
X : parts per Million : Proton

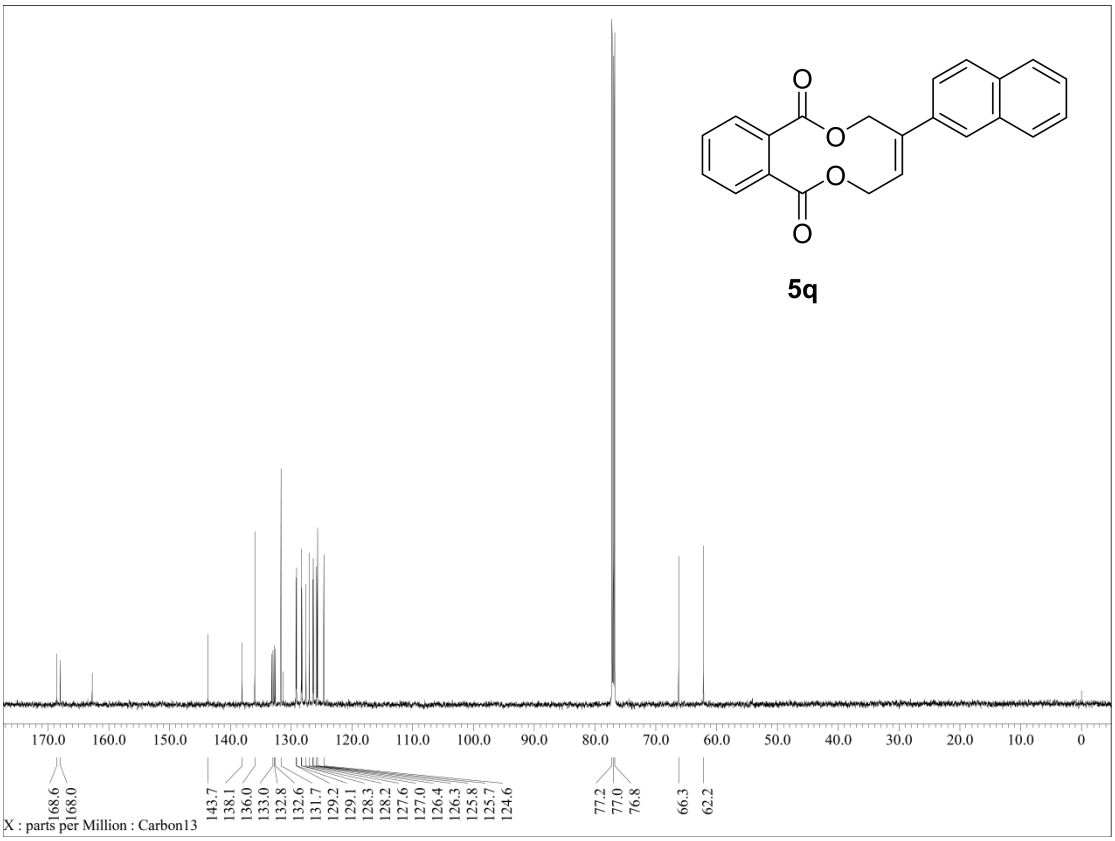

Cl
Cl
O
O
O
O
5o
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.0
167.9
143.3
142.1
141.1
132.9
132.6
132.4
131.7
130.6
130.5
130.3
129.3
129.1
128.4
125.4
77.2
77.0
76.8
65.3
61.7
X : parts per Million : Carbon13


Ph
O
O
O
O
5p
8.20
2.05
2.23
1.01
1.00
2.03
2.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.836
7.824
7.810
7.798
7.631
7.618
7.606
7.593
7.578
7.463
7.450
7.437
7.374
7.361
7.348
6.356
6.346
6.335
5.223
4.981
4.971
X : parts per Million : Proton

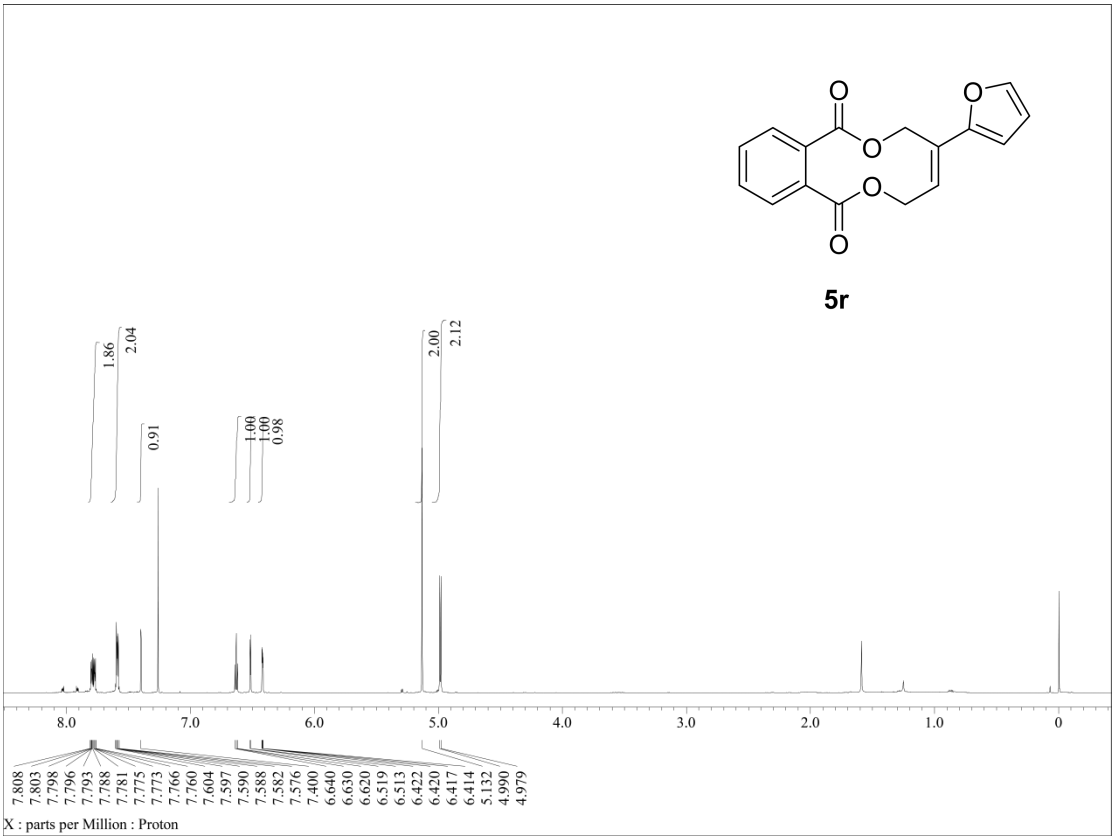

Ph
O
O
O
O
5p
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.5
168.0
143.4
141.1
140.4
139.6
132.8
132.6
131.7
131.7
129.1
129.1
128.8
127.5
127.3
127.1
127.0
126.4
77.2
77.0
76.8
66.1
62.2
X : parts per Million : Carbon13

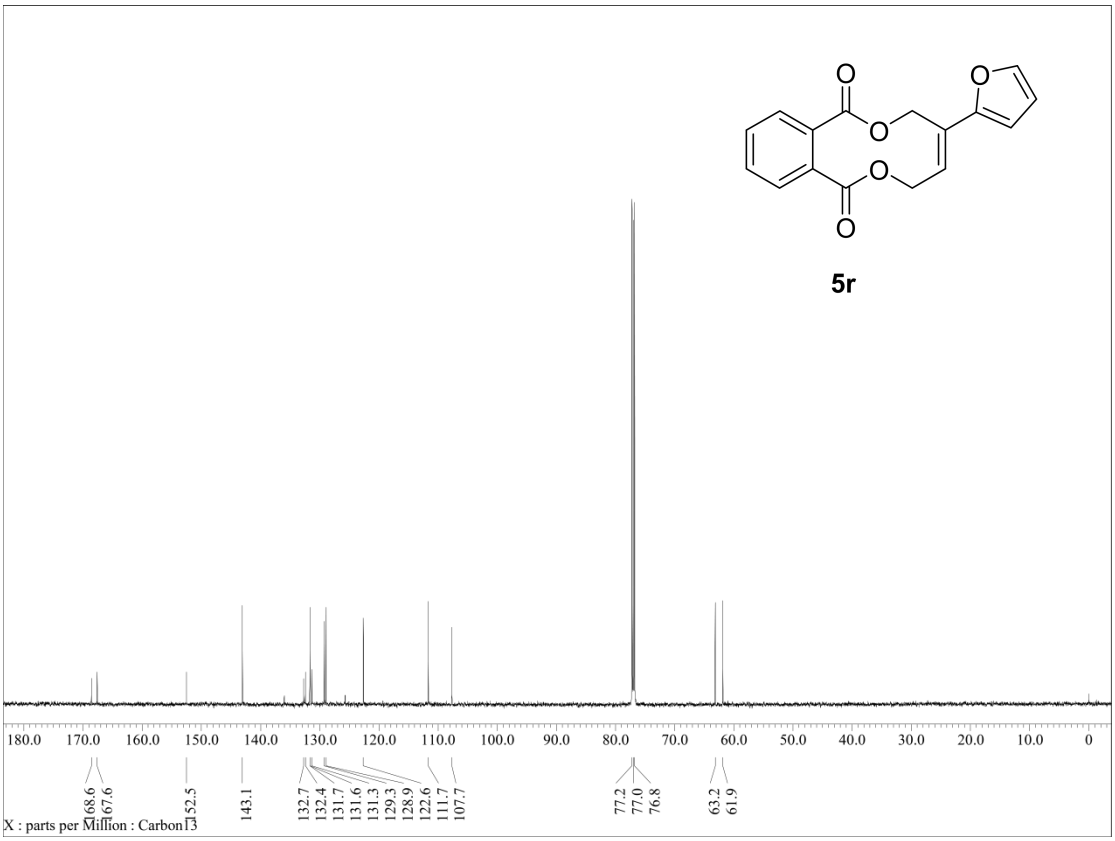

4.31
2.19
1.99
1.97
2.02
1.23
0.93
1.20
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.034
8.032
8.025
8.021
8.016
8.011
8.005
7.937
7.915
7.913
7.907
7.901
7.898
7.892
7.884
7.859
7.852
7.845
7.837
7.834
7.829
7.824
7.821
7.815
7.810
7.803
7.644
7.641
7.636
7.629
7.627
7.624
7.620
7.615
7.609
7.606
7.597
7.594
7.504
7.501
7.493
7.489
7.484
7.477
7.473
7.465
7.462
6.426
6.416
6.405
5.288
5.011
5.000
X : parts per Million : Proton

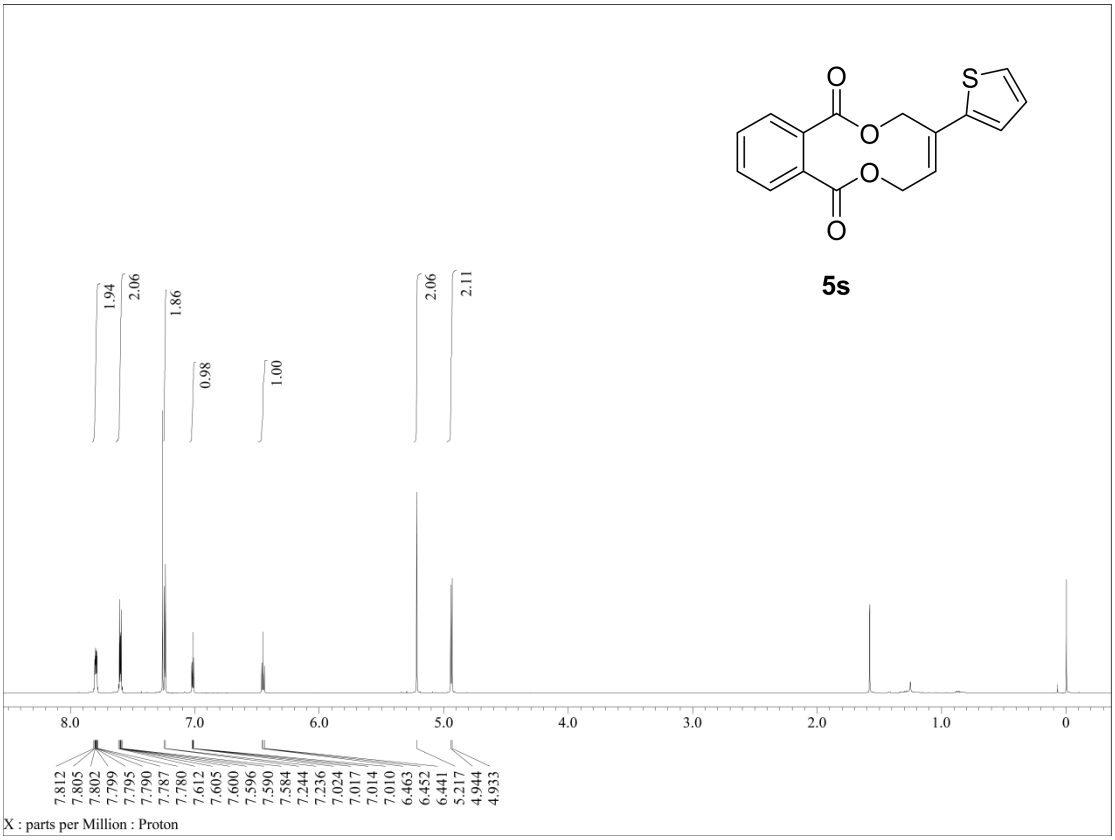
5q

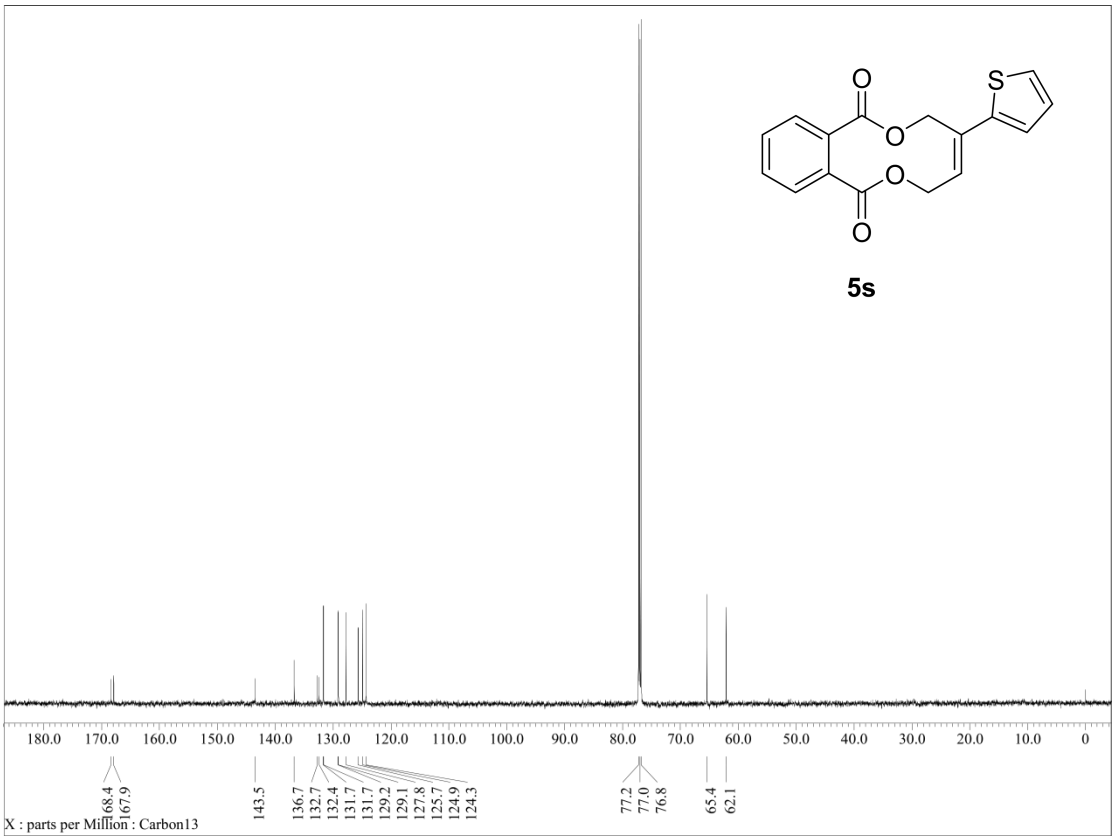

170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.6
168.0
143.7
138.1
136.0
133.0
132.8
132.6
131.7
129.2
129.1
128.3
128.2
127.6
127.0
126.4
126.3
125.8
125.7
124.6
77.2
77.0
76.8
66.3
62.2
X : parts per Million : Carbon13

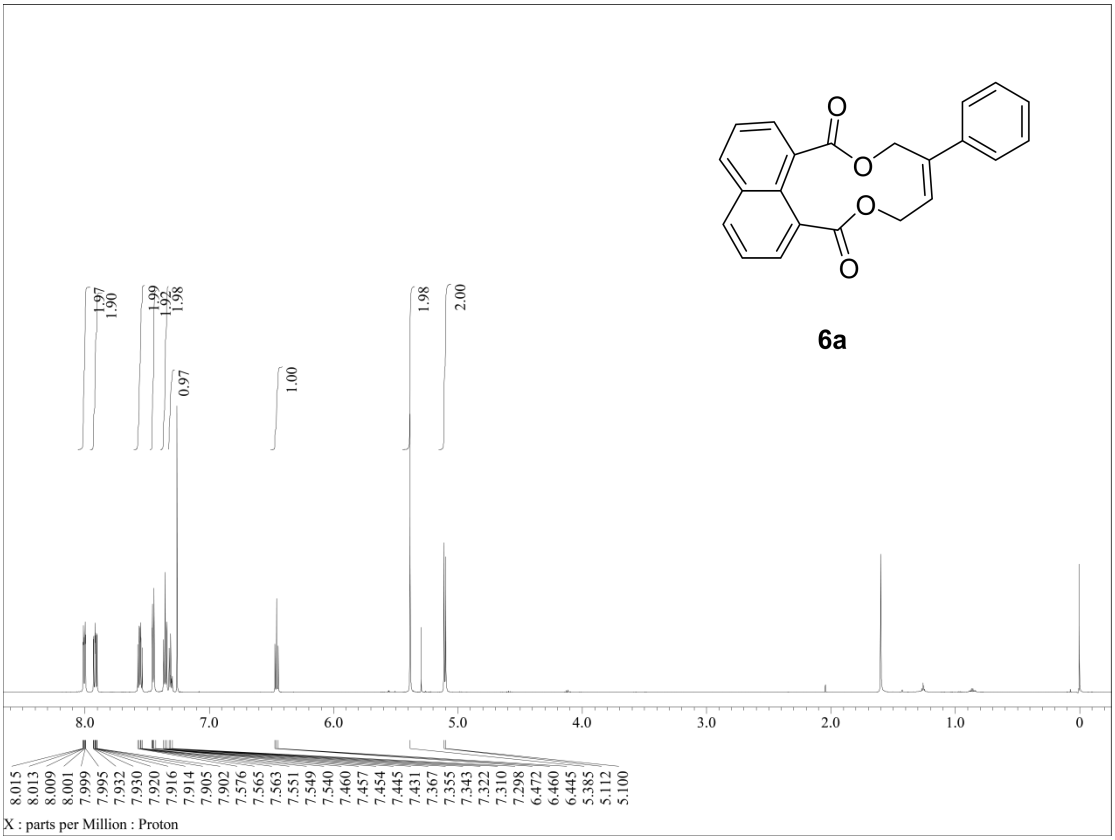
5q

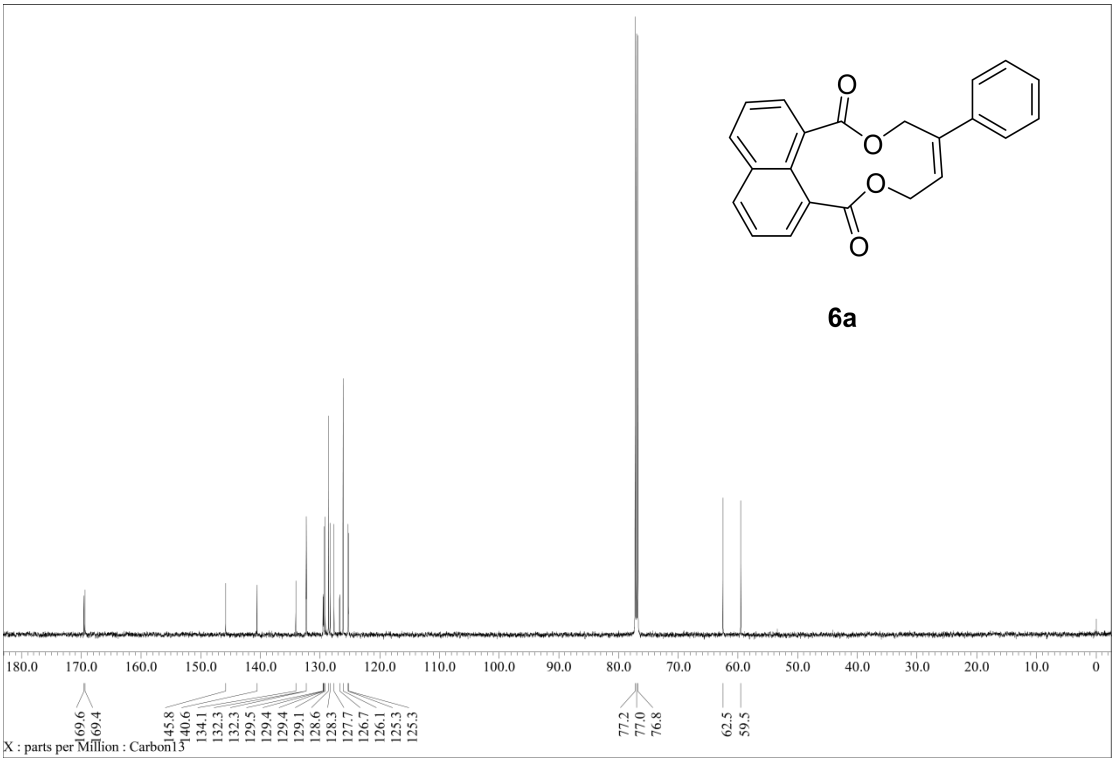

5r
1.86
2.04
0.91
1.00
1.00
0.98
2.00
2.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.808
7.803
7.798
7.796
7.793
7.788
7.781
7.775
7.773
7.766
7.760
7.604
7.597
7.590
7.588
7.582
7.576
7.400
6.640
6.630
6.620
6.519
6.513
6.422
6.420
6.417
6.414
5.132
4.990
4.979
X : parts per Million : Proton

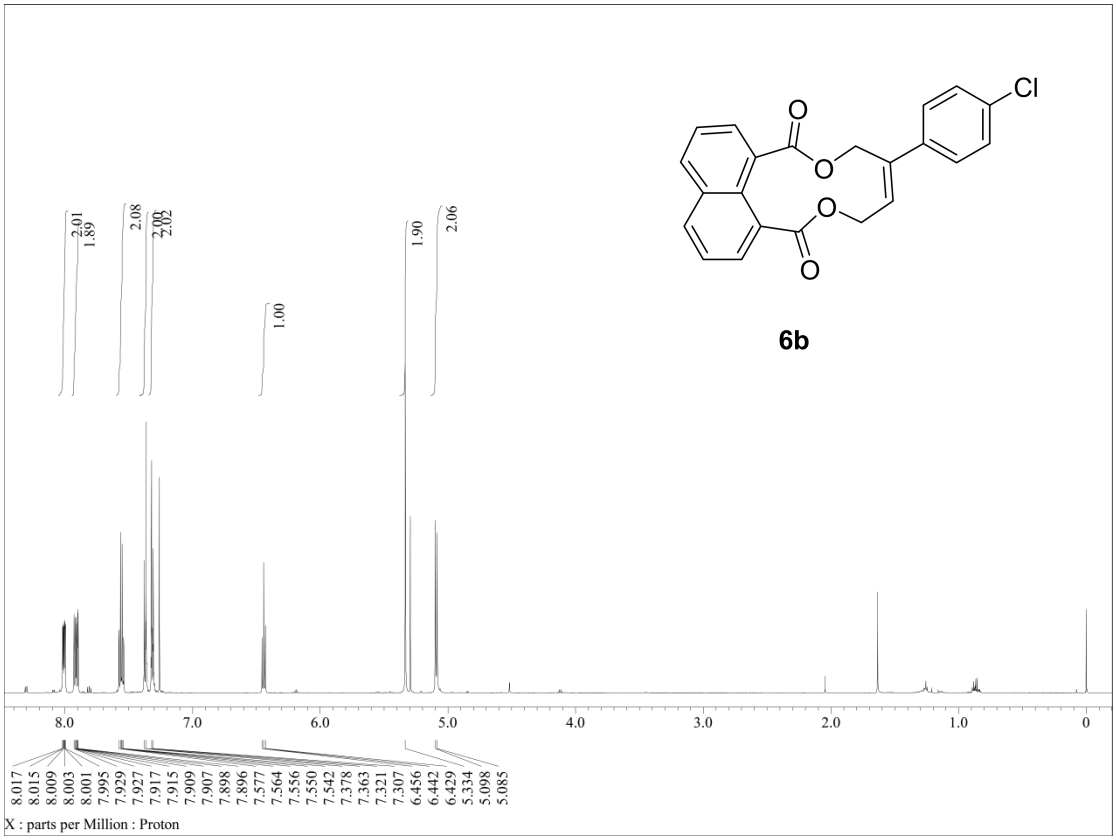

5r
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.6
167.6
152.5
143.1
132.7
132.4
131.7
131.6
131.3
129.3
128.9
122.6
111.7
107.7
77.2
77.0
76.8
63.2
61.9
X : parts per Million : Carbon13

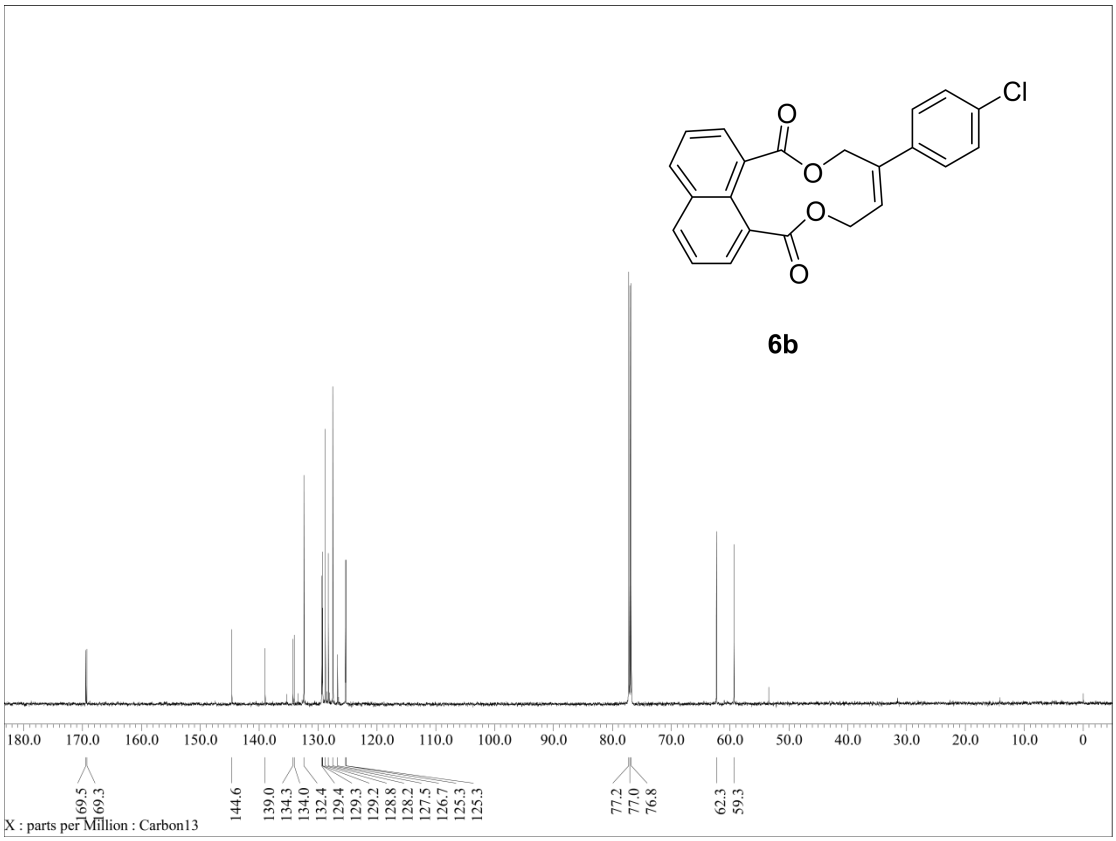

O
S
O
O
O
5s
1.94
2.06
1.86
0.98
1.00
2.06
2.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.812
7.805
7.802
7.799
7.795
7.790
7.787
7.780
7.612
7.605
7.600
7.596
7.590
7.584
7.244
7.236
7.024
7.017
7.014
7.010
6.463
6.452
6.441
5.217
4.944
4.933
X : parts per Million : Proton

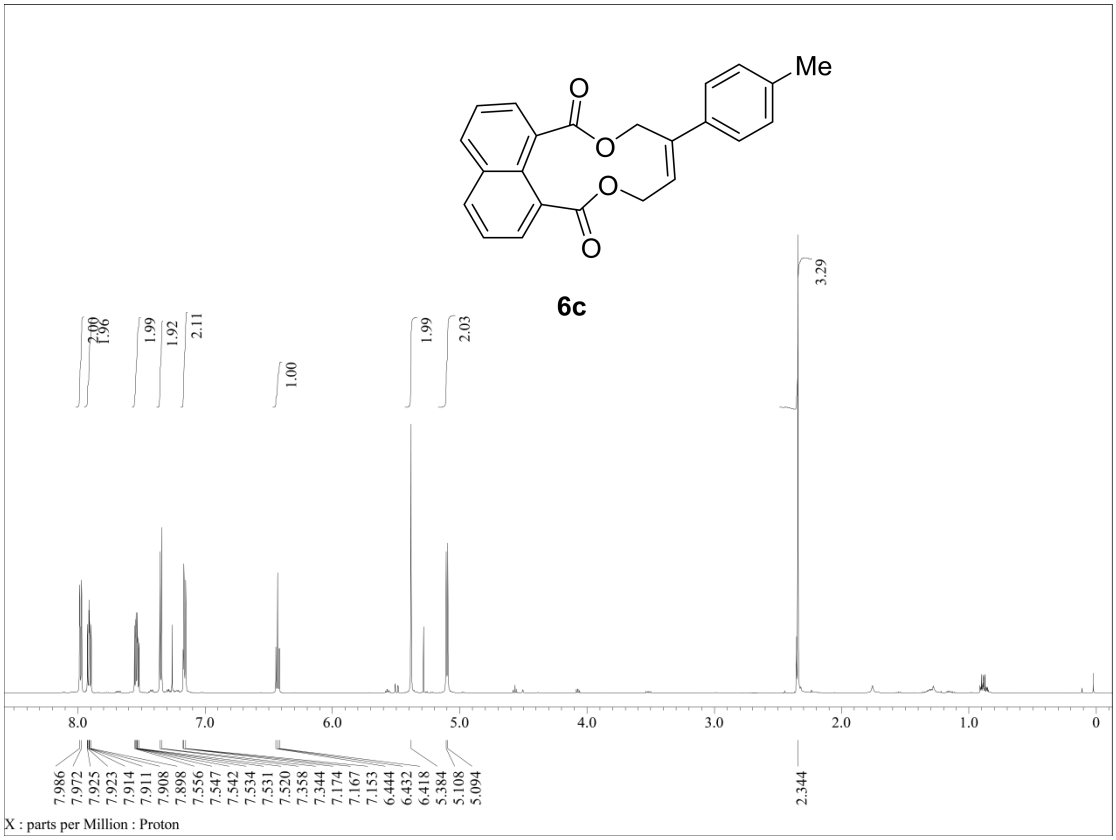

O
S
O
O
O
5s
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.4
167.9
143.5
136.7
132.7
132.4
131.7
131.7
129.2
129.1
127.8
125.7
124.9
124.3
77.2
77.0
76.8
65.4
62.1
X : parts per Million : Carbon13

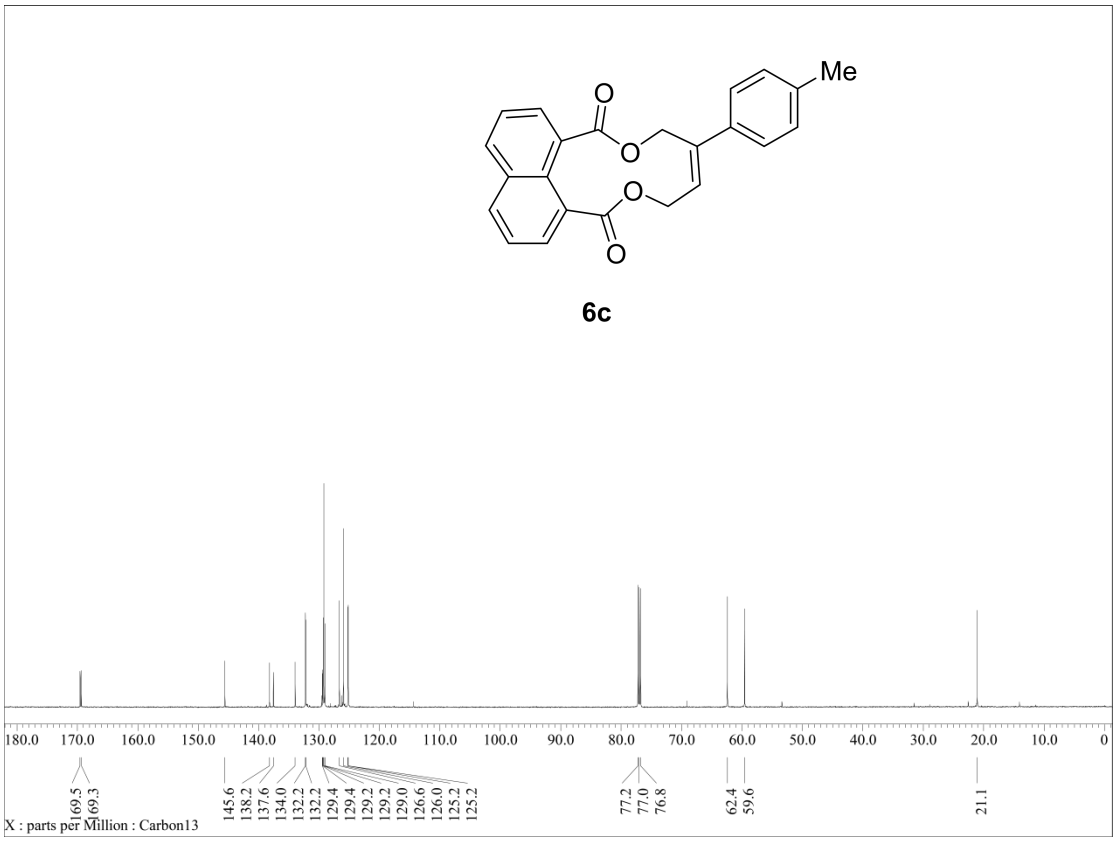

6a
1.97
1.90
1.99
1.92
1.98
0.97
1.00
1.98
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.015
8.013
8.009
8.001
7.999
7.995
7.932
7.930
7.920
7.916
7.914
7.905
7.902
7.576
7.565
7.563
7.551
7.549
7.540
7.460
7.457
7.454
7.445
7.431
7.367
7.355
7.343
7.322
7.310
7.298
6.472
6.460
6.445
5.385
5.112
5.100
X : parts per Million : Proton

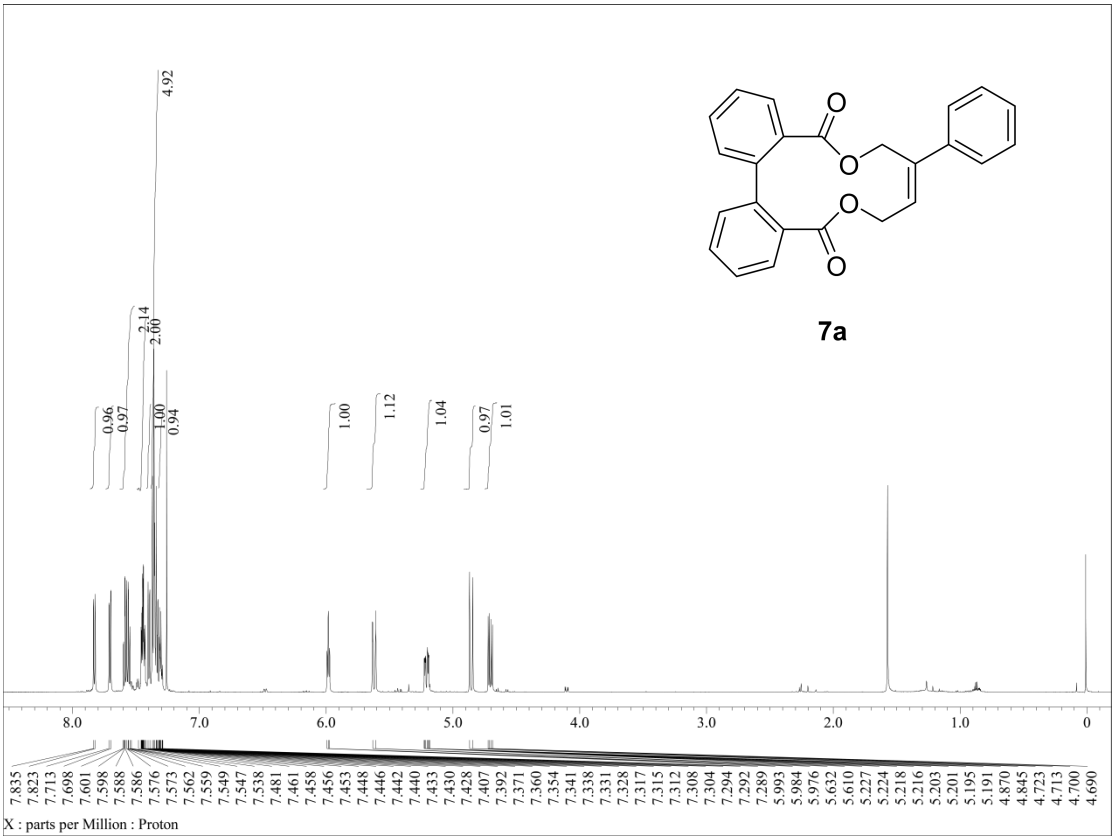

6a
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.6
169.4
145.8
140.6
134.1
132.3
132.3
129.5
129.4
129.4
129.1
128.6
128.3
127.7
126.7
126.1
125.3
125.3
77.2
77.0
76.8
62.5
59.5
X : parts per Million : Carbon13

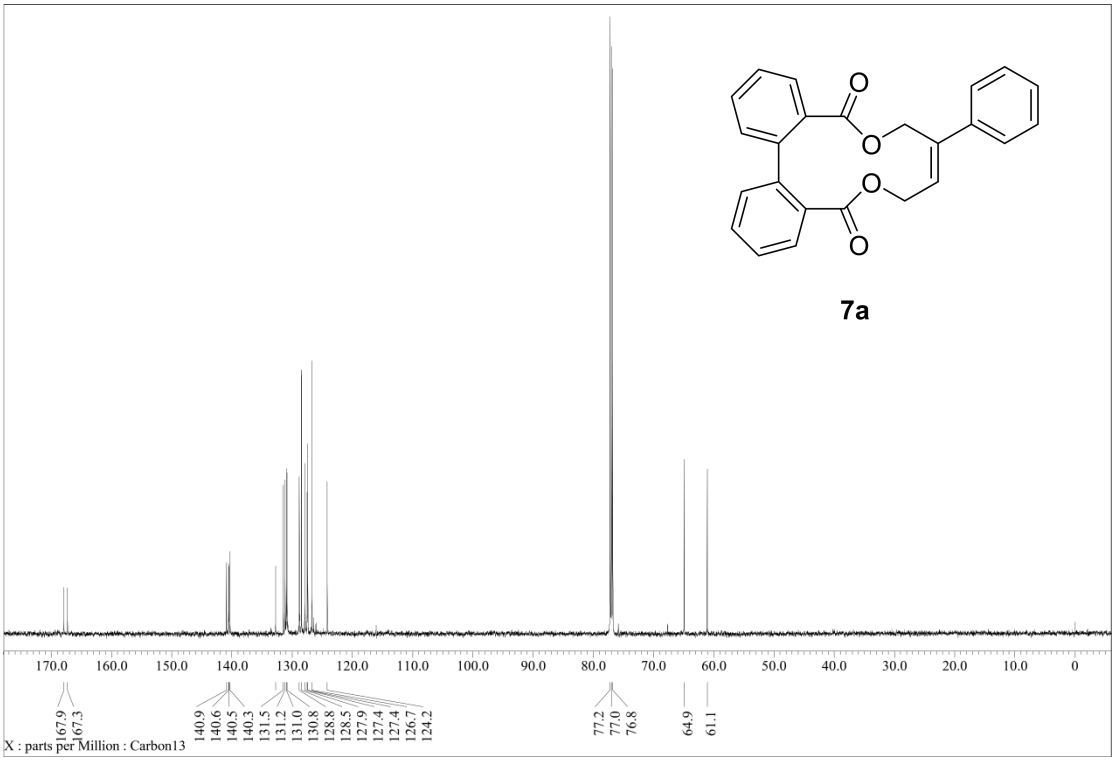

Cl
O
O
O
O
6b
2.01
1.89
2.08
2.00
2.02
1.00
1.90
2.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.017
8.015
8.009
8.003
8.001
7.995
7.929
7.927
7.917
7.915
7.909
7.907
7.898
7.896
7.577
7.564
7.556
7.550
7.542
7.378
7.363
7.321
7.307
6.456
6.442
6.429
5.334
5.098
5.085
X : parts per Million : Proton

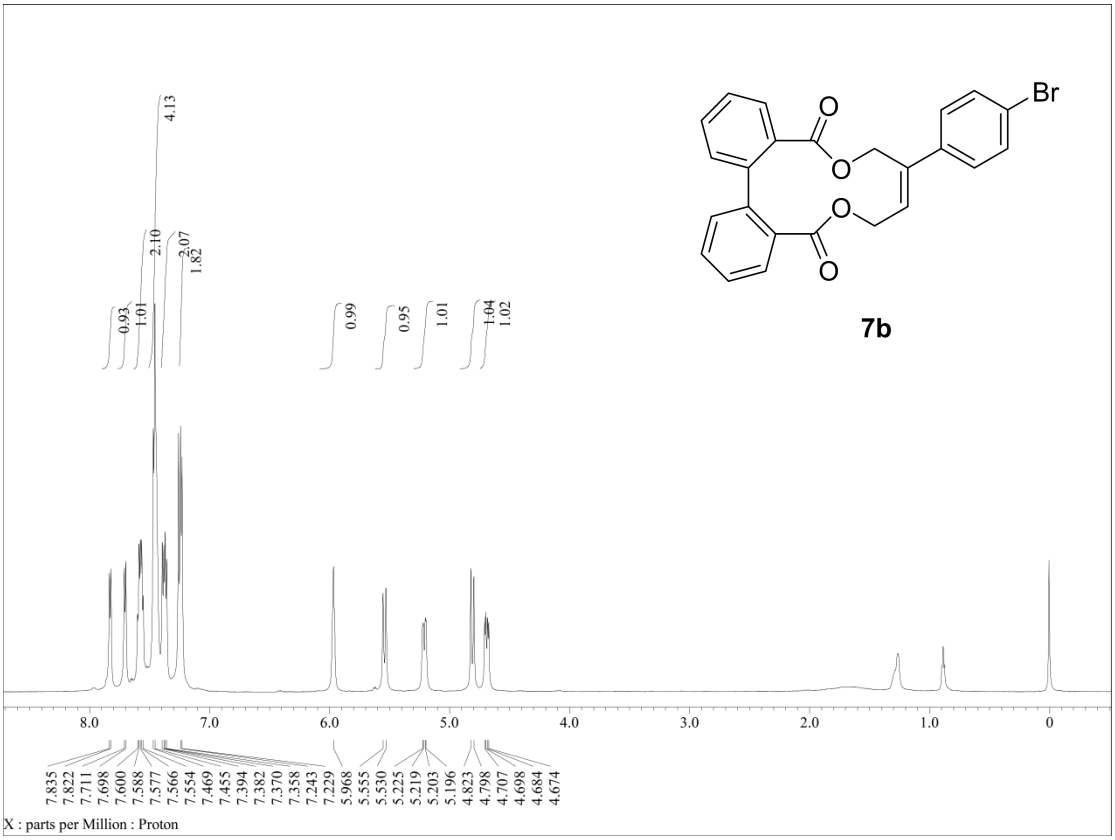

Cl
O
O
O
O
6b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.5
169.3
144.6
139.0
134.3
134.0
132.4
129.4
129.3
129.2
128.8
128.2
127.5
126.7
125.3
125.3
77.2
77.0
76.8
62.3
59.3
X : parts per Million : Carbon13

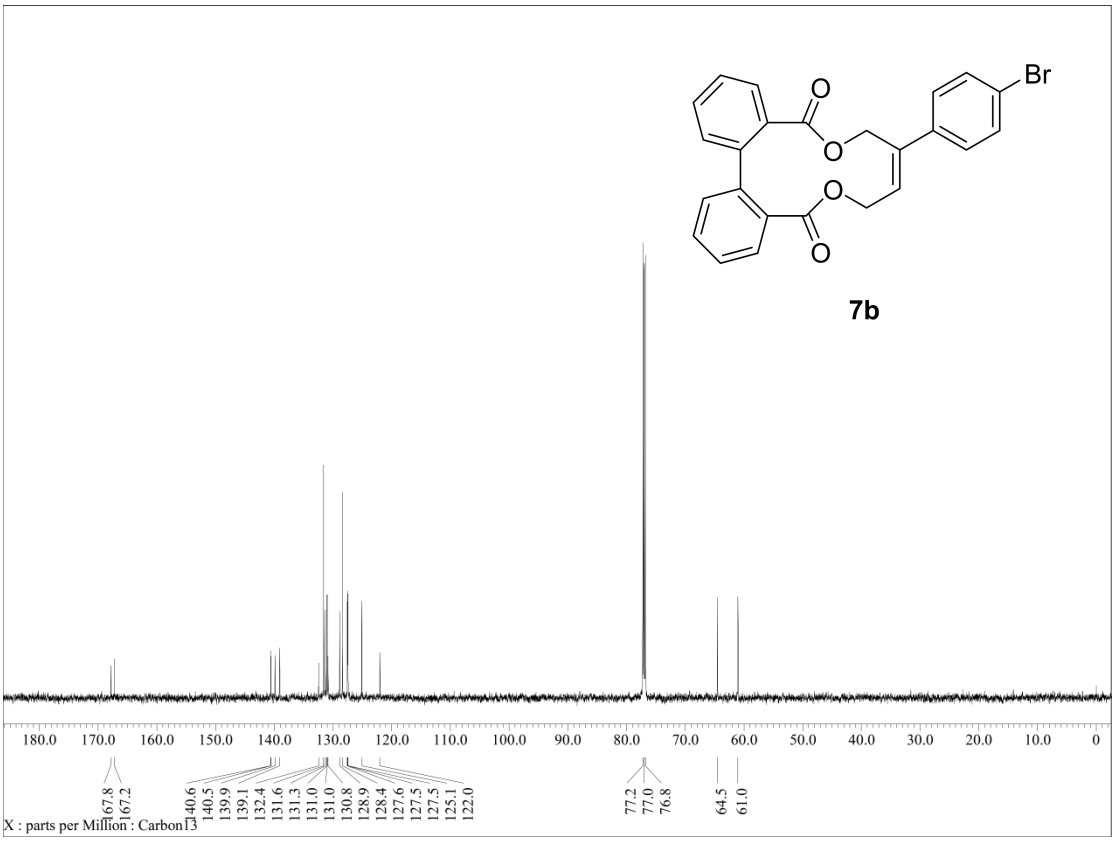

Me
O
O
O
O
6c
2.00
1.96
1.99
1.92
2.11
1.00
1.99
2.03
3.29
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.986
7.972
7.925
7.923
7.914
7.911
7.908
7.898
7.556
7.547
7.542
7.534
7.531
7.520
7.358
7.344
7.174
7.167
7.153
6.444
6.432
6.418
5.384
5.108
5.094
2.344
X : parts per Million : Proton

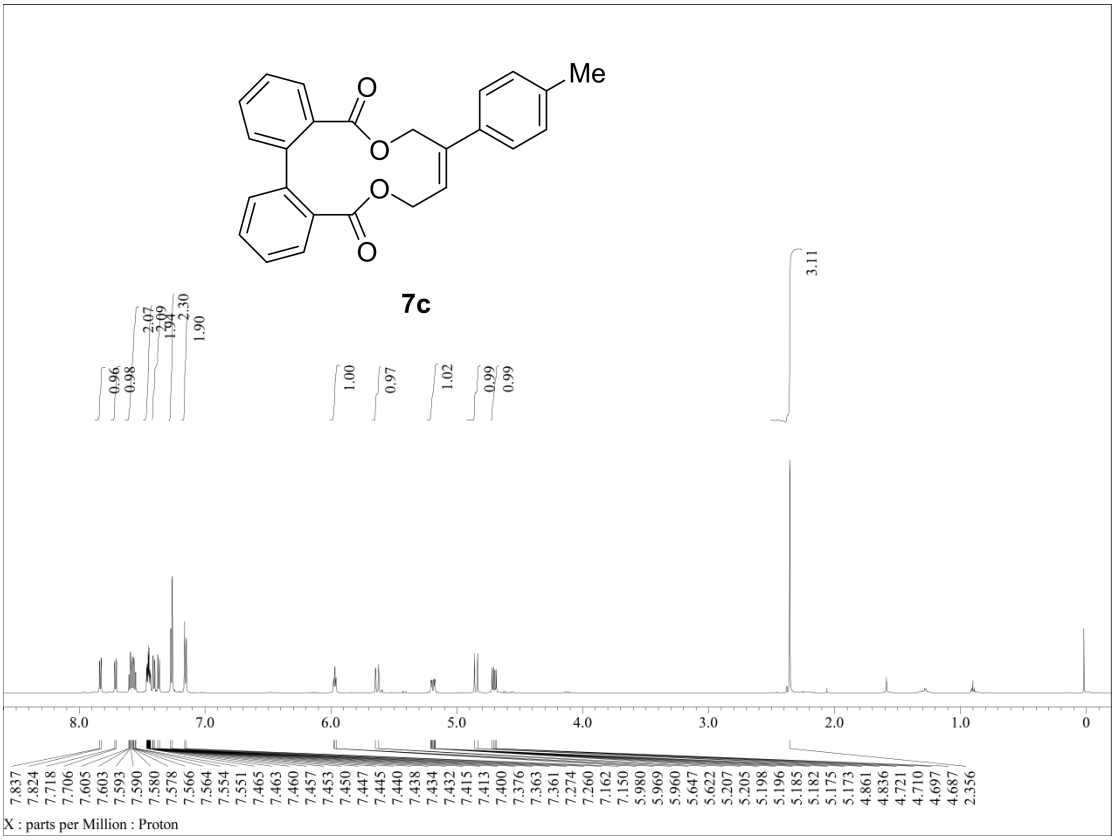

Me
O
O
O
O
6c
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.5
169.3
145.6
138.2
137.6
134.0
132.2
132.2
129.4
129.4
129.2
129.2
129.0
126.6
126.0
125.2
125.2
77.2
77.0
76.8
62.4
59.6
21.1
X : parts per Million : Carbon13

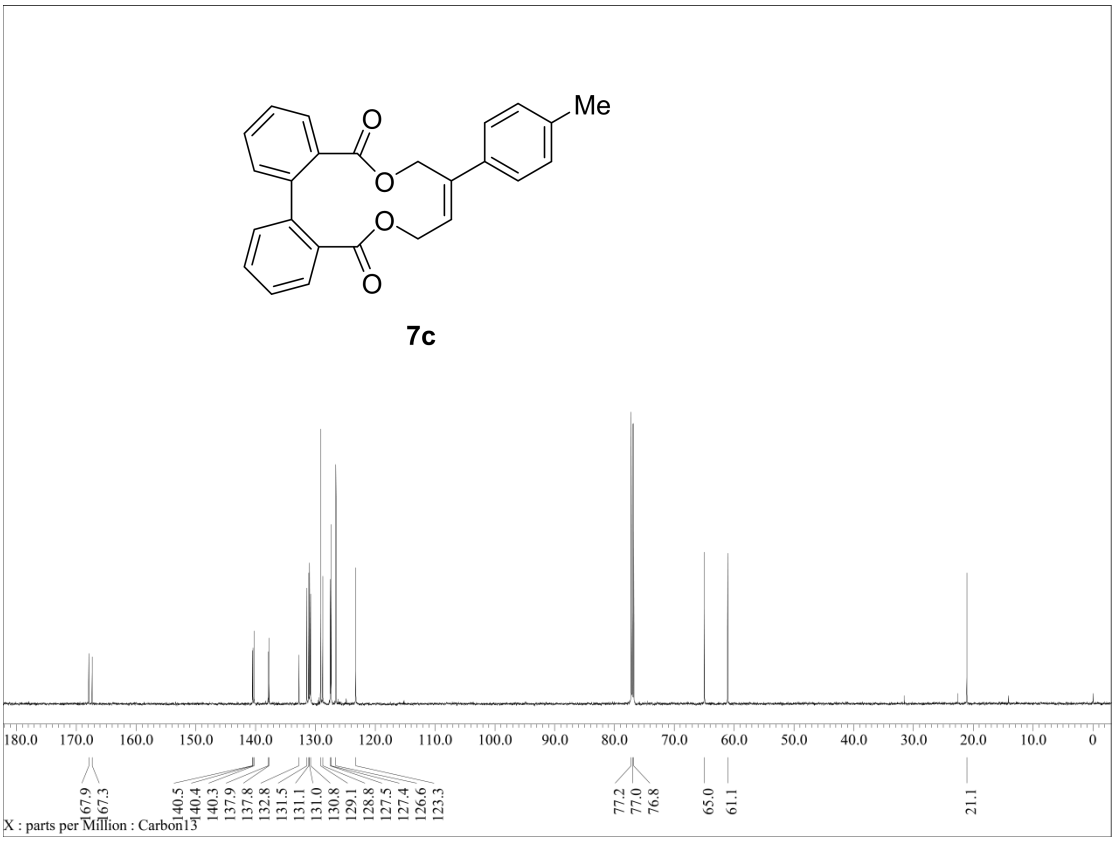

4.92
2.14
2.00
0.96
0.97
1.00
0.94
1.00
1.12
1.04
0.97
1.01
O
O
O
O
7a
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.835
7.823
7.713
7.698
7.601
7.598
7.588
7.586
7.576
7.573
7.562
7.559
7.549
7.547
7.538
7.481
7.461
7.458
7.456
7.453
7.448
7.446
7.442
7.440
7.433
7.430
7.428
7.407
7.392
7.371
7.360
7.354
7.341
7.338
7.331
7.328
7.317
7.315
7.312
7.308
7.304
7.294
7.292
7.289
5.993
5.984
5.976
5.632
5.610
5.227
5.224
5.218
5.216
5.203
5.201
5.195
5.191
4.870
4.845
4.723
4.713
4.700
4.690
X : parts per Million : Proton

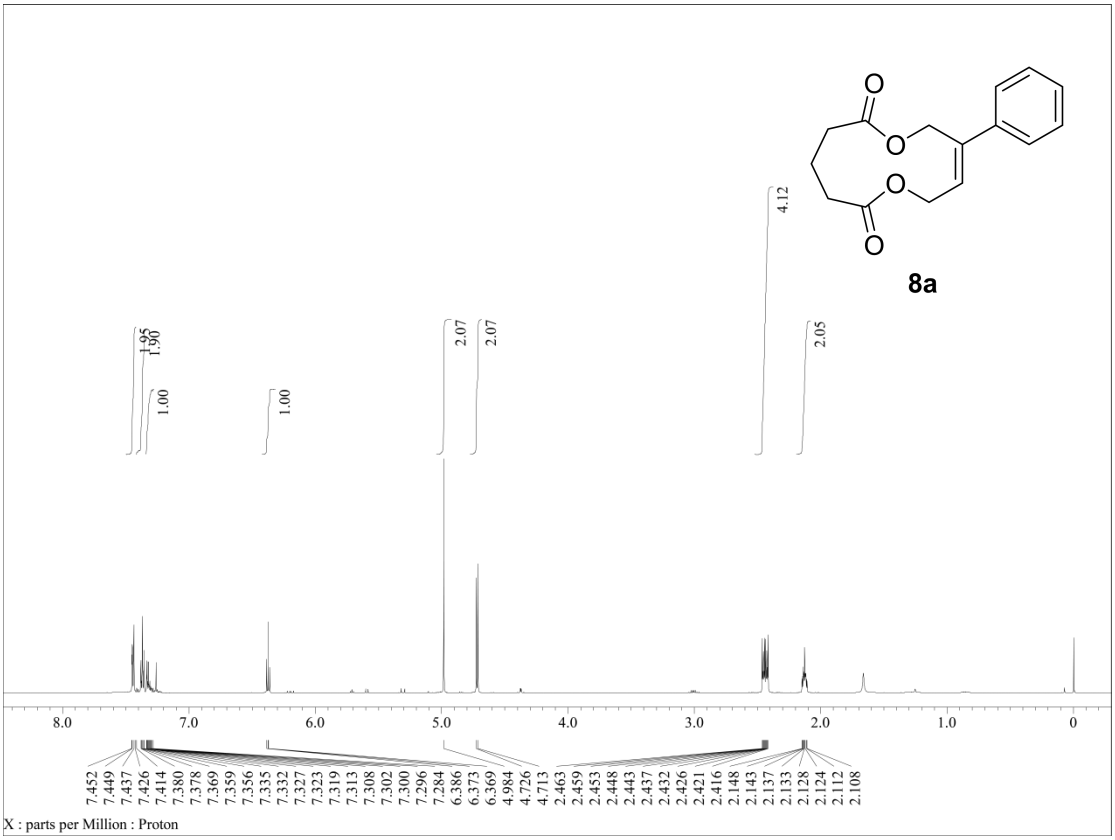

O
O
O
O
7a
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.9
167.3
140.9
140.6
140.5
140.3
131.5
131.2
131.0
130.8
128.8
128.5
127.9
127.4
127.4
126.7
124.2
77.2
77.0
76.8
64.9
61.1
X : parts per Million : Carbon13

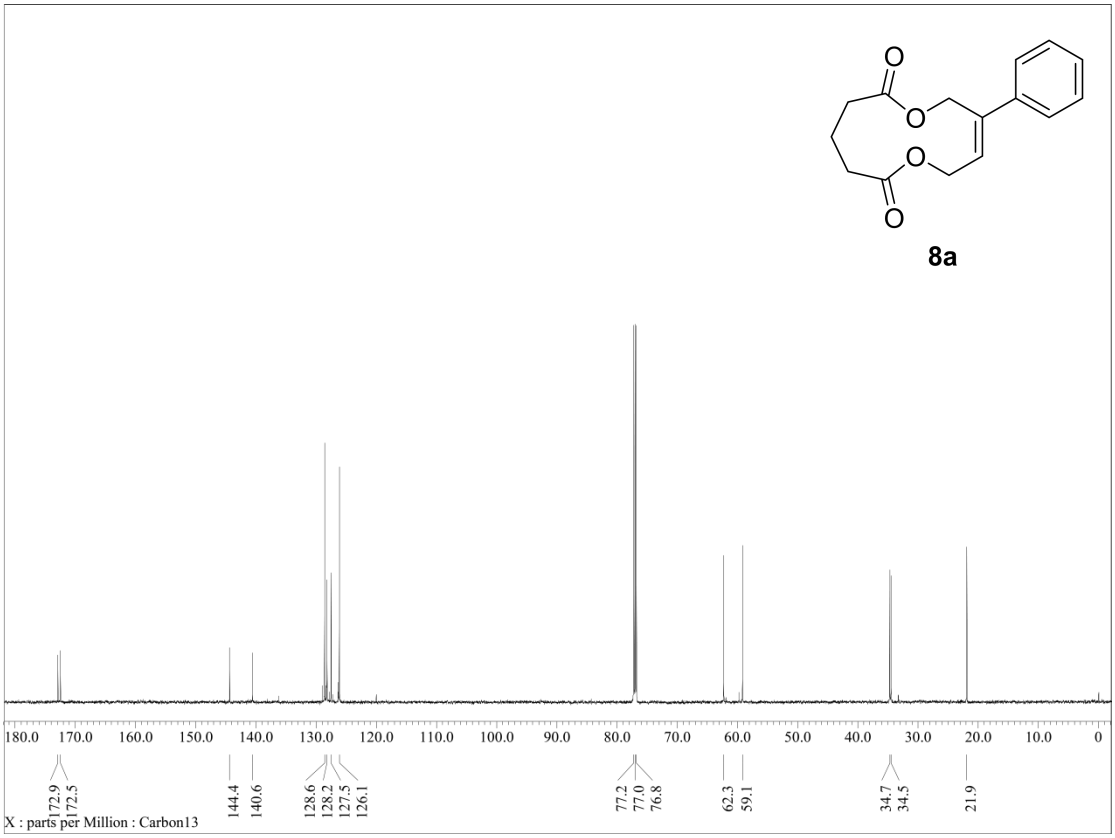

Br
O
O
O
O
7b
4.13
2.10
2.07
1.82
0.93
1.01
0.99
0.95
1.01
1.04
1.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.835
7.822
7.711
7.698
7.600
7.588
7.577
7.566
7.554
7.469
7.455
7.394
7.382
7.370
7.358
7.243
7.229
5.968
5.555
5.530
5.225
5.219
5.203
5.196
4.823
4.798
4.707
4.698
4.684
4.674
X : parts per Million : Proton

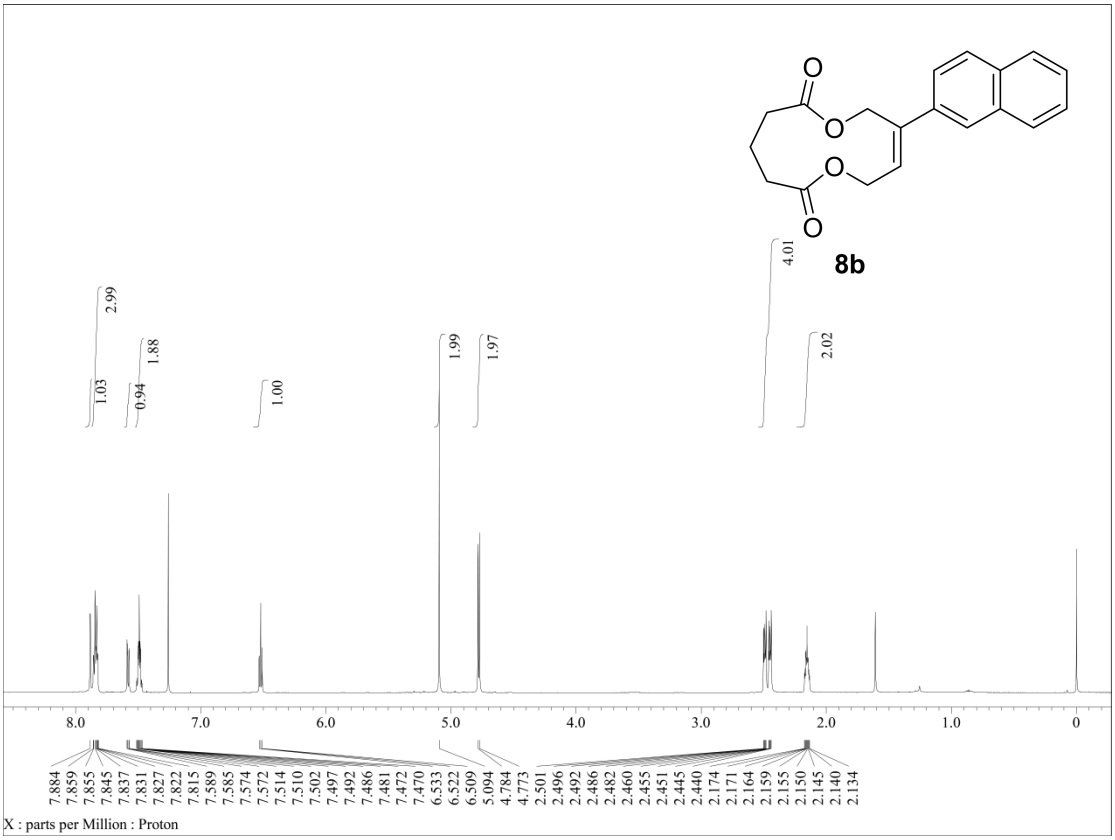

Br
O
O
O
O
7b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.8
167.2
140.6
140.5
139.9
139.1
132.4
131.6
131.3
131.0
131.0
130.8
128.9
128.4
127.6
127.5
127.5
125.1
122.0
77.2
77.0
76.8
64.5
61.0
X : parts per Million : Carbon13

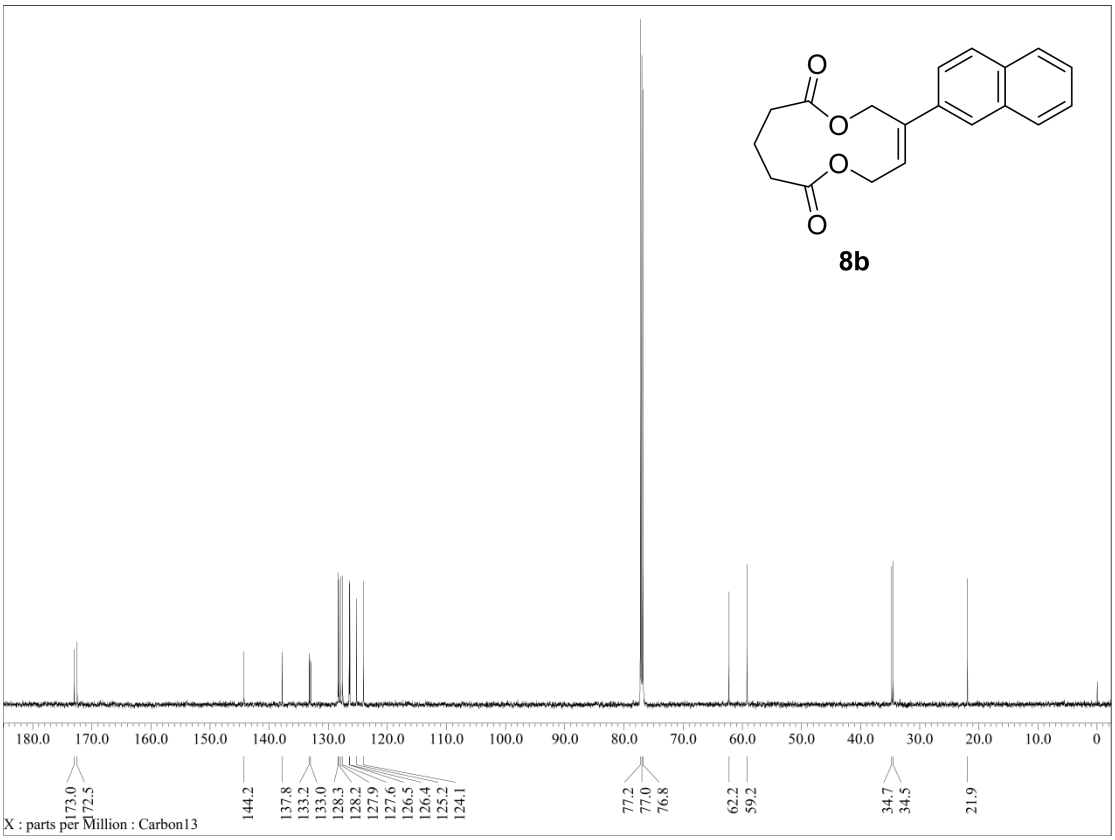

Me
O
O
O
O
7c
3.11
2.07
2.09
1.94
2.30
1.90
0.96
0.98
1.00
0.97
1.02
0.99
0.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.837
7.824
7.718
7.706
7.605
7.603
7.593
7.590
7.580
7.578
7.566
7.564
7.554
7.551
7.465
7.463
7.460
7.457
7.453
7.450
7.447
7.445
7.440
7.438
7.434
7.432
7.415
7.413
7.400
7.376
7.363
7.361
7.274
7.260
7.162
7.150
5.980
5.969
5.960
5.647
5.622
5.207
5.205
5.198
5.196
5.185
5.182
5.175
5.173
4.861
4.836
4.721
4.710
4.697
4.687
2.356
X : parts per Million : Proton

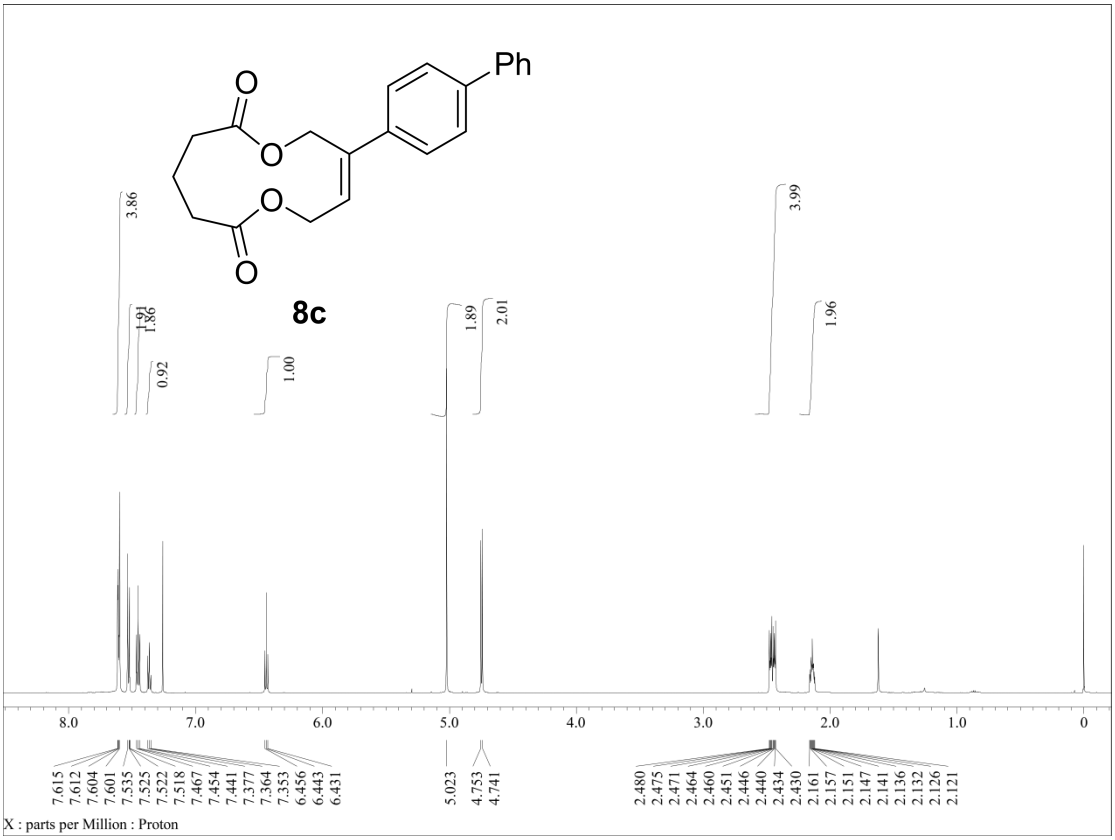

Me
O
O
O
O
7c
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.9
167.3
140.5
140.4
140.3
137.9
137.8
132.8
131.5
131.1
131.0
130.8
129.1
128.8
127.5
127.4
126.6
123.3
77.2
77.0
76.8
65.0
61.1
21.1
X : parts per Million : Carbon13

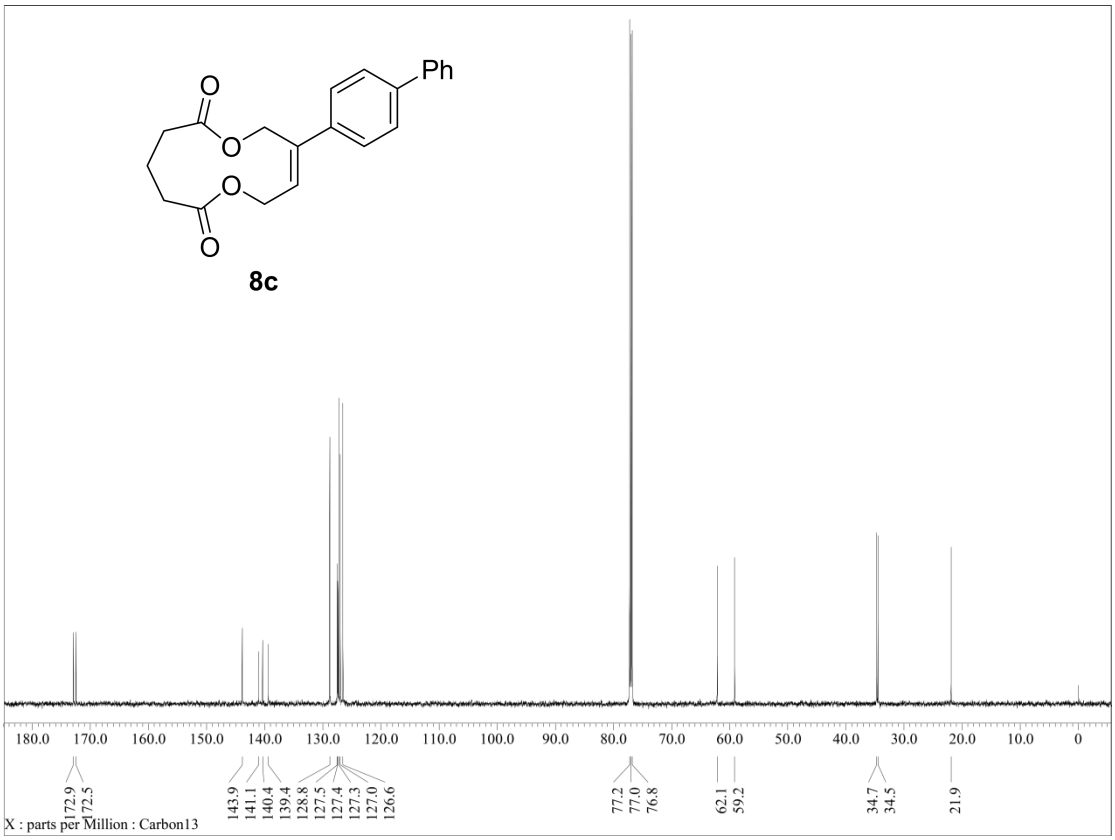

8a
4.12
2.07
2.07
2.05
1.00
1.00
1.00
1.00
X : parts per Million : Proton

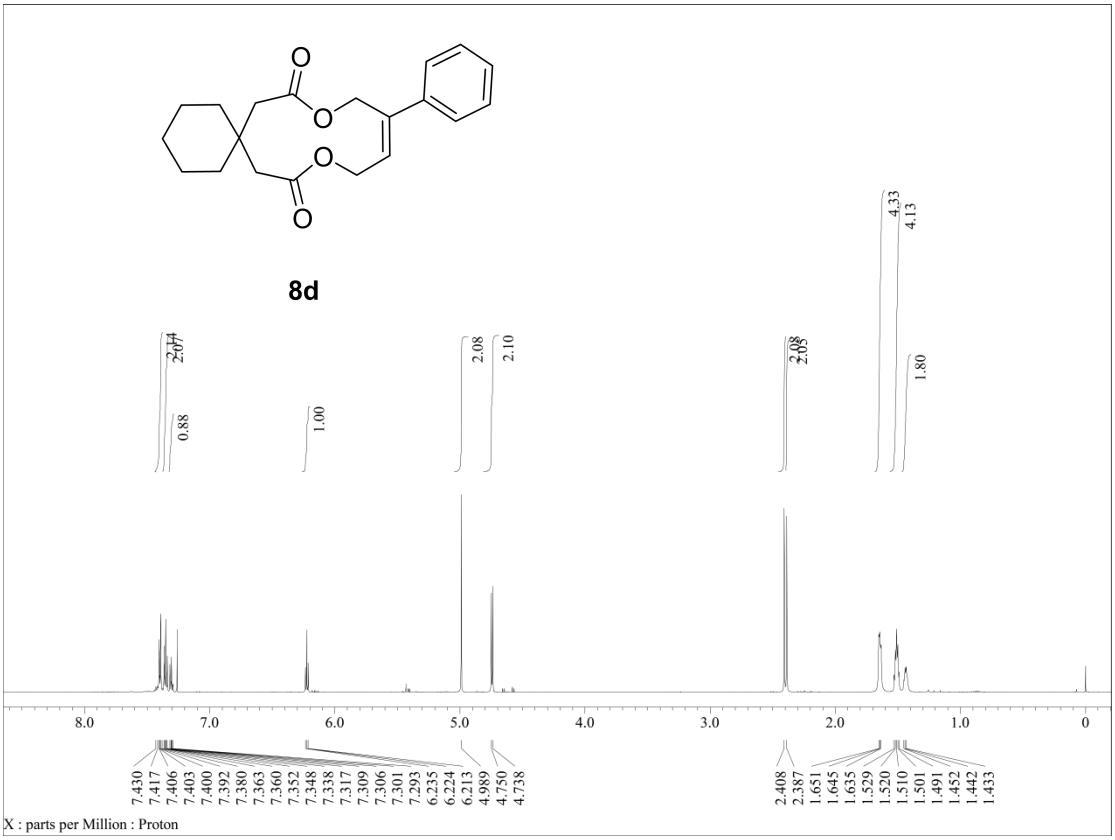

8a
X : parts per Million : Carbon13

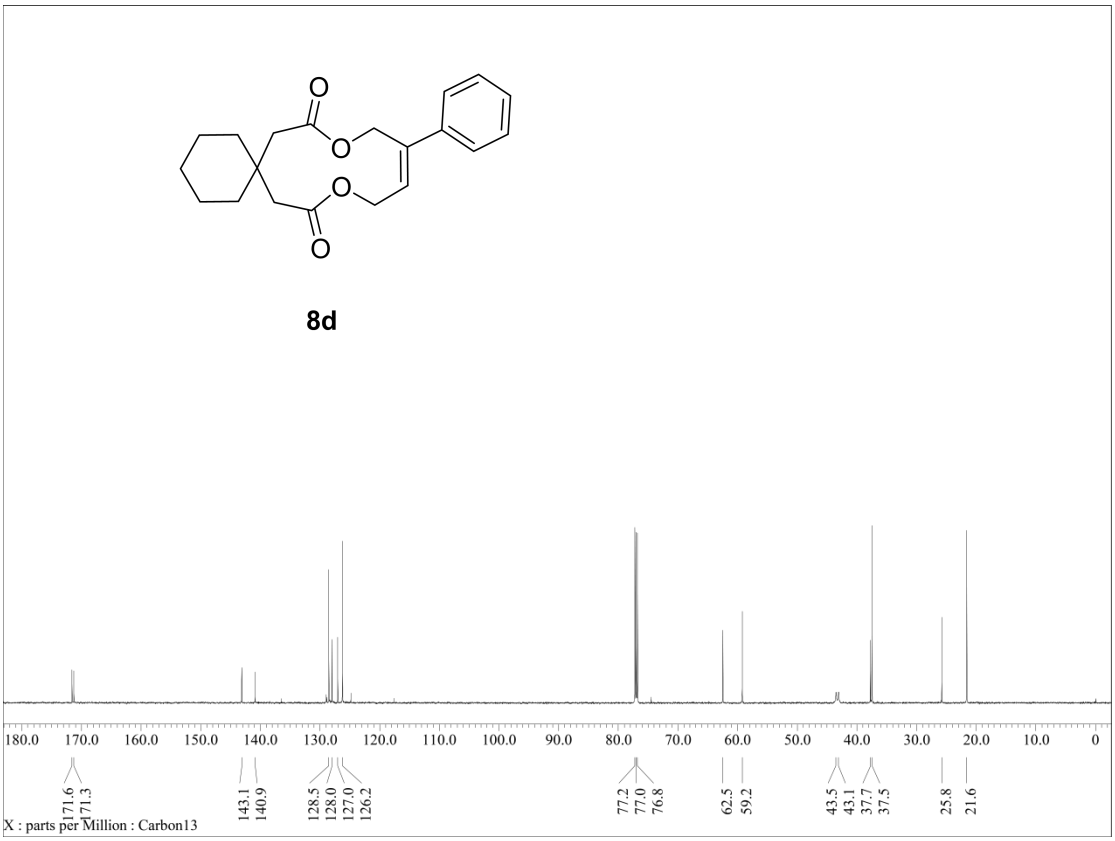

8b
4.01
2.99
2.02
1.99
1.97
1.88
1.03
0.94
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.884
7.859
7.855
7.845
7.837
7.831
7.827
7.822
7.815
7.589
7.585
7.574
7.572
7.514
7.510
7.502
7.497
7.492
7.486
7.481
7.472
7.470
6.533
6.522
6.509
5.094
4.784
4.773
2.501
2.496
2.492
2.486
2.482
2.460
2.455
2.451
2.445
2.440
2.174
2.171
2.164
2.159
2.155
2.150
2.145
2.140
2.134
X : parts per Million : Proton

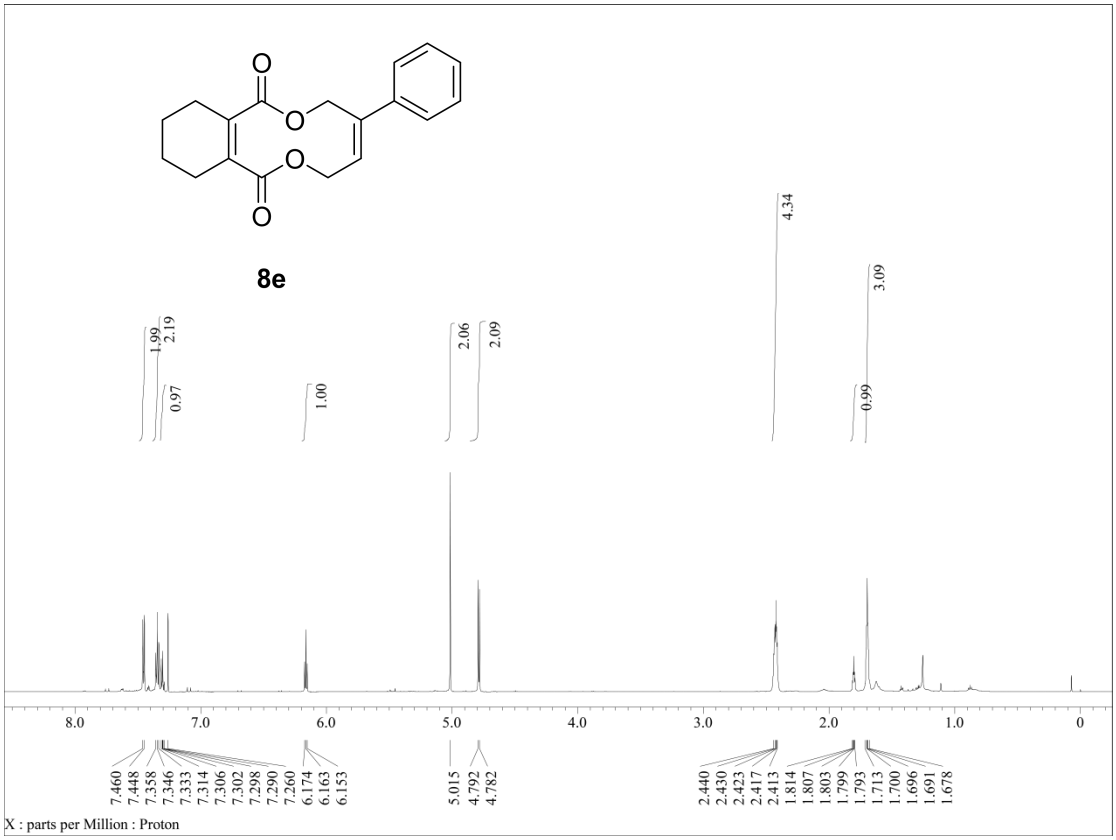

8b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.0
172.5
144.2
137.8
133.2
133.0
128.3
128.2
127.9
127.6
126.5
126.4
125.2
124.1
77.2
77.0
76.8
62.2
59.2
34.7
34.5
21.9
X : parts per Million : Carbon13

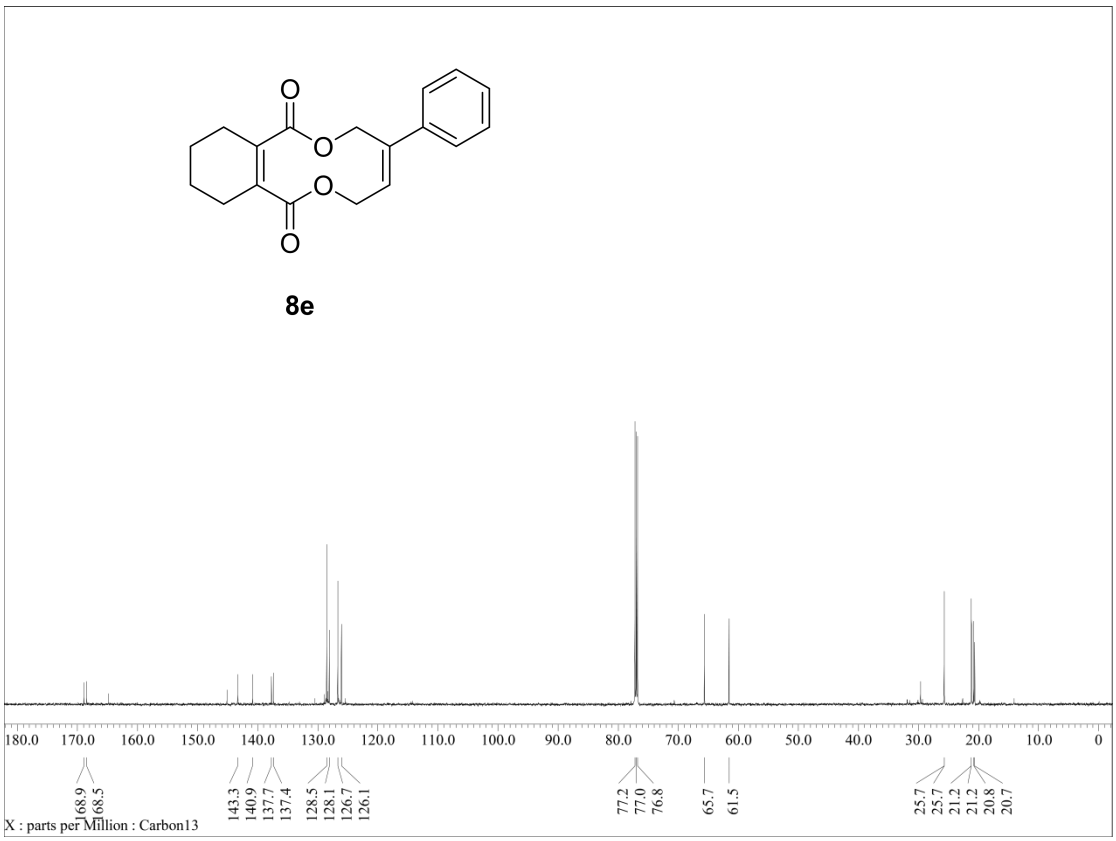

Ph
O
O
O
O
8c
3.86
1.91
1.86
0.92
1.00
1.89
2.01
3.99
1.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.615
7.612
7.604
7.601
7.535
7.525
7.522
7.518
7.467
7.454
7.441
7.377
7.364
7.353
6.456
6.443
6.431
5.023
4.753
4.741
2.480
2.475
2.471
2.464
2.460
2.451
2.446
2.440
2.434
2.430
2.161
2.157
2.151
2.147
2.141
2.136
2.132
2.126
2.121
X : parts per Million : Proton

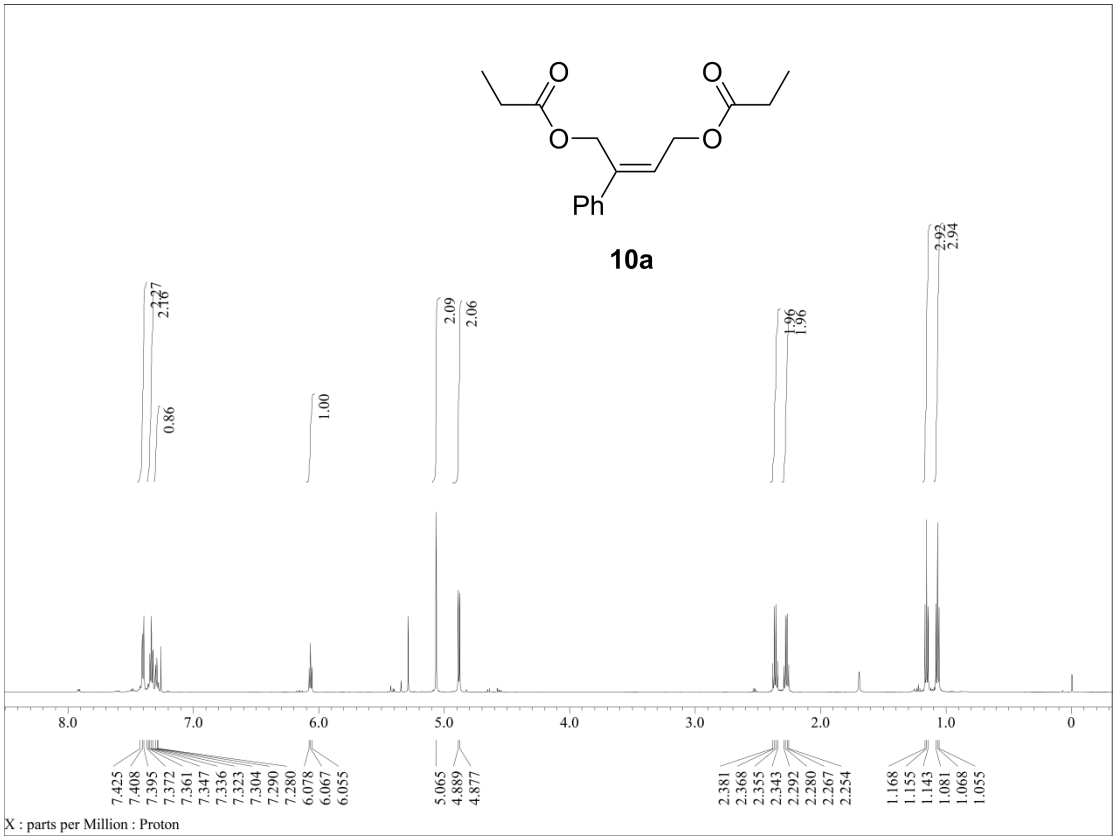

Ph
O
O
O
O
8c
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.9
172.5
143.9
141.1
140.4
139.4
128.8
127.5
127.4
127.3
127.0
126.6
77.2
77.0
76.8
62.1
59.2
34.7
34.5
21.9
X : parts per Million : Carbon13

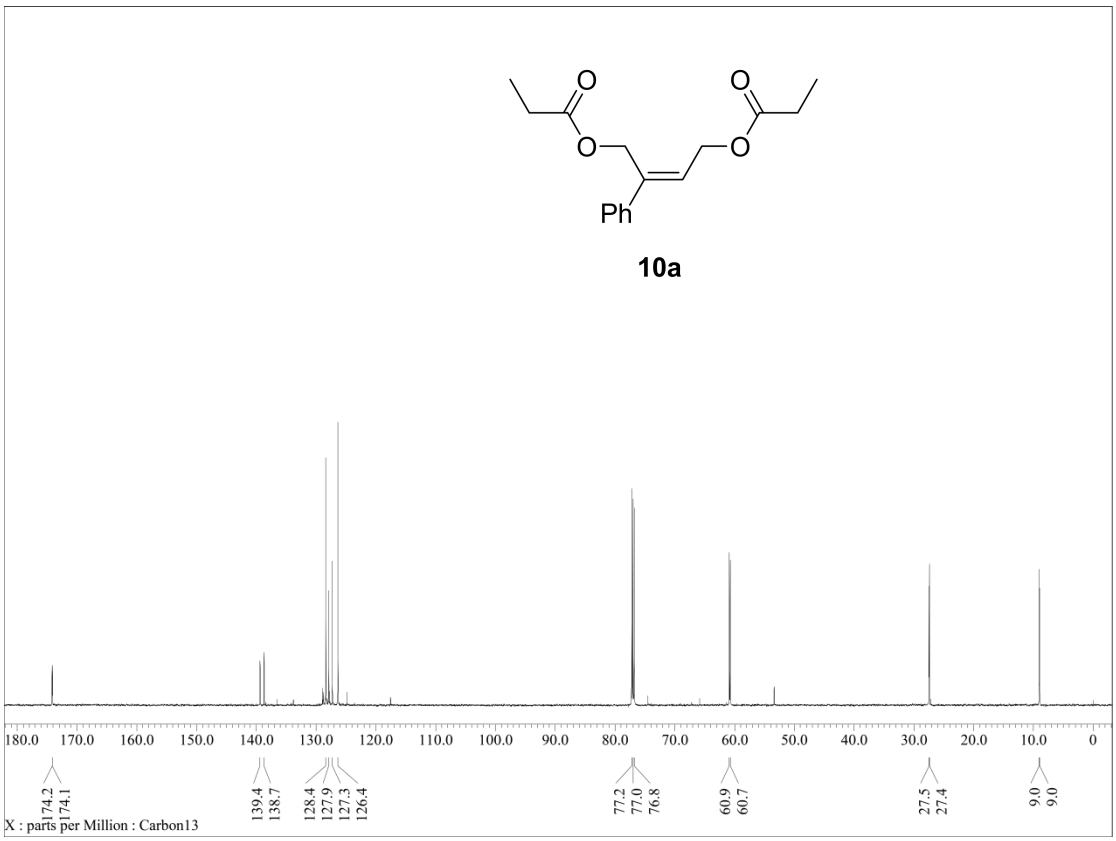

8d
4.33
4.13
2.08
2.10
1.80
1.00
0.88
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.430
7.417
7.406
7.403
7.400
7.392
7.380
7.363
7.360
7.352
7.348
7.338
7.317
7.309
7.306
7.301
7.293
6.235
6.224
6.213
4.989
4.750
4.738
2.408
2.387
1.651
1.645
1.635
1.529
1.520
1.510
1.501
1.491
1.452
1.442
1.433
X : parts per Million : Proton

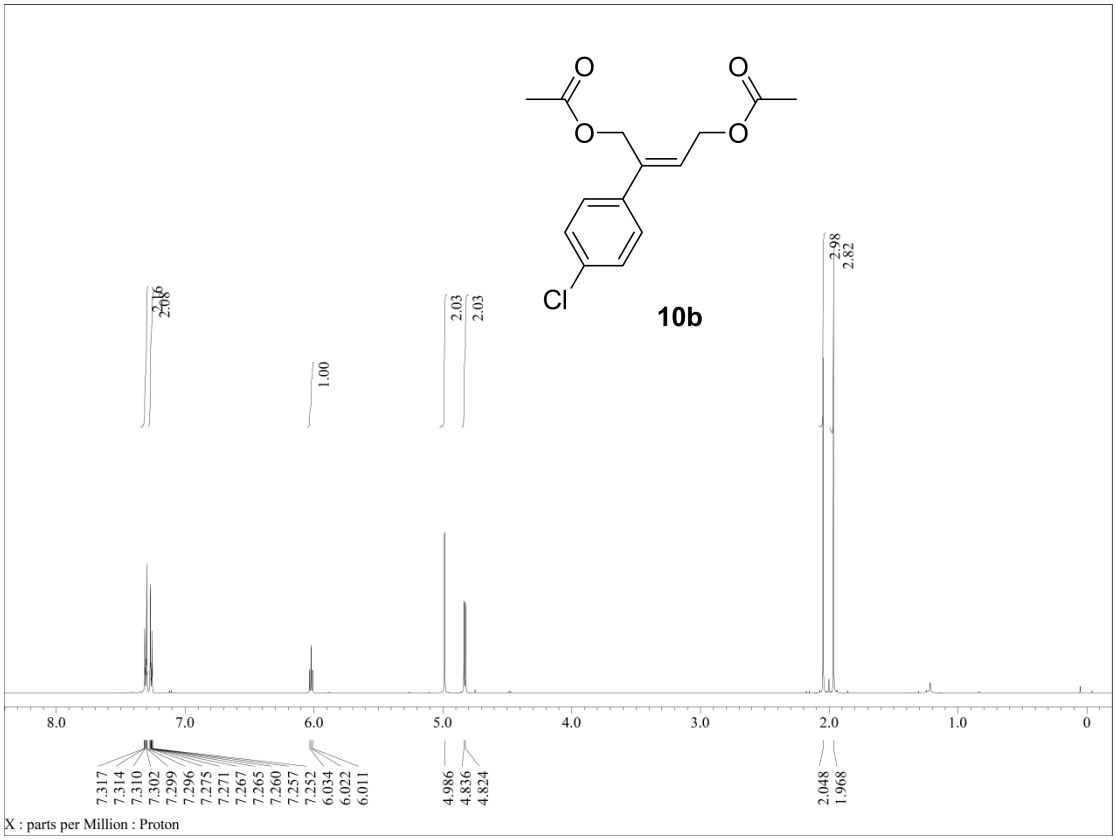

8d
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.6
171.3
143.1
140.9
128.5
128.0
127.0
126.2
77.2
77.0
76.8
62.5
59.2
43.5
43.1
37.7
37.5
25.8
21.6
X : parts per Million : Carbon13

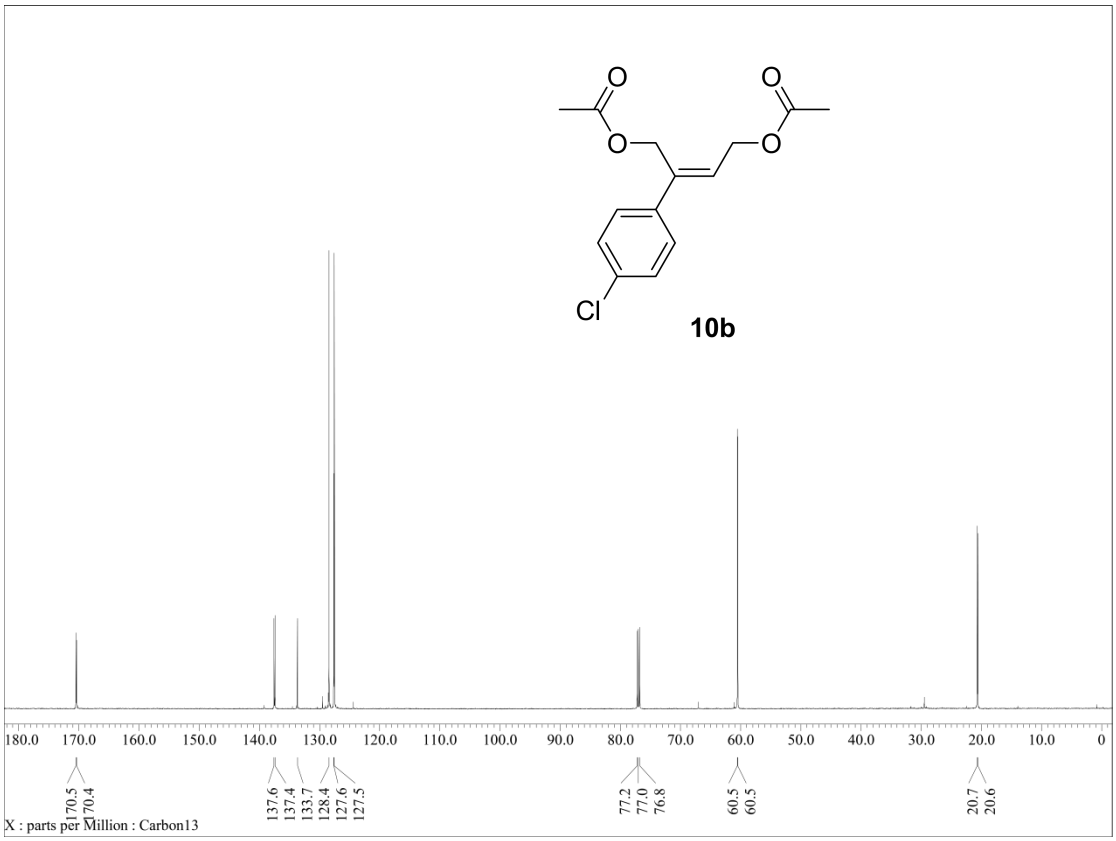

8e
1.99
2.19
0.97
1.00
2.06
2.09
4.34
3.09
0.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.460
7.448
7.358
7.346
7.333
7.314
7.306
7.302
7.298
7.290
7.260
6.174
6.163
6.153
5.015
4.792
4.782
2.440
2.430
2.423
2.417
2.413
1.814
1.807
1.803
1.799
1.793
1.713
1.700
1.696
1.691
1.678
X : parts per Million : Proton

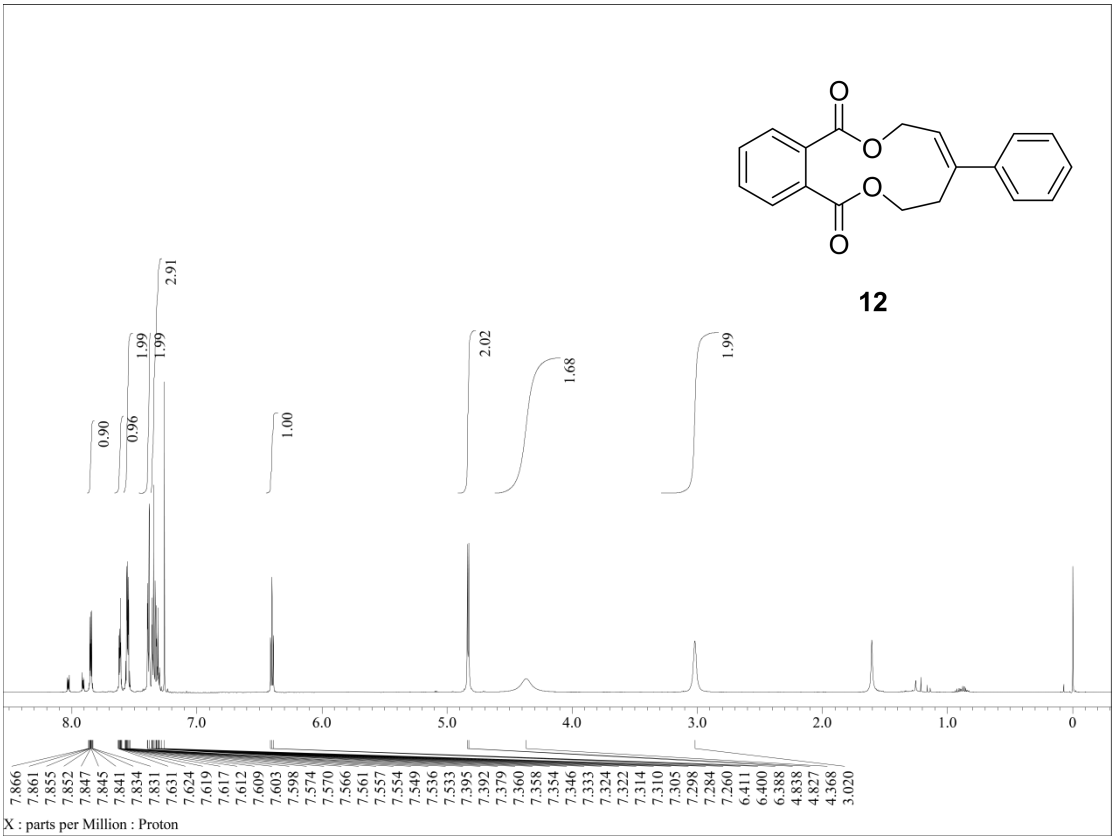

8e
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.9
168.5
143.3
140.9
137.7
137.4
128.5
128.1
126.7
126.1
77.2
77.0
76.8
65.7
61.5
25.7
25.7
21.2
21.2
20.8
20.7
X : parts per Million : Carbon13

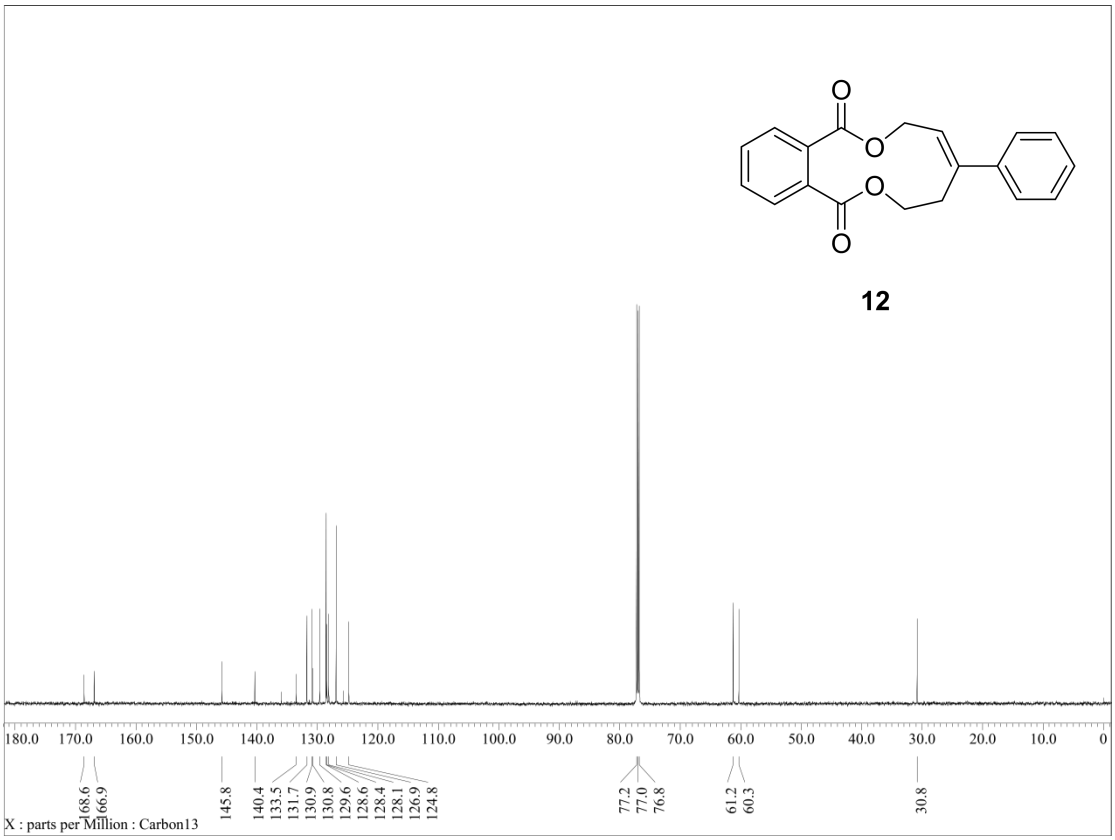

10a
2.27
2.16
0.86
1.00
2.09
2.06
1.96
1.96
2.93
2.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.425
7.408
7.395
7.372
7.361
7.347
7.336
7.323
7.304
7.290
7.280
6.078
6.067
6.055
5.065
4.889
4.877
2.381
2.368
2.355
2.343
2.292
2.280
2.267
2.254
1.168
1.155
1.143
1.081
1.068
1.055
X : parts per Million : Proton

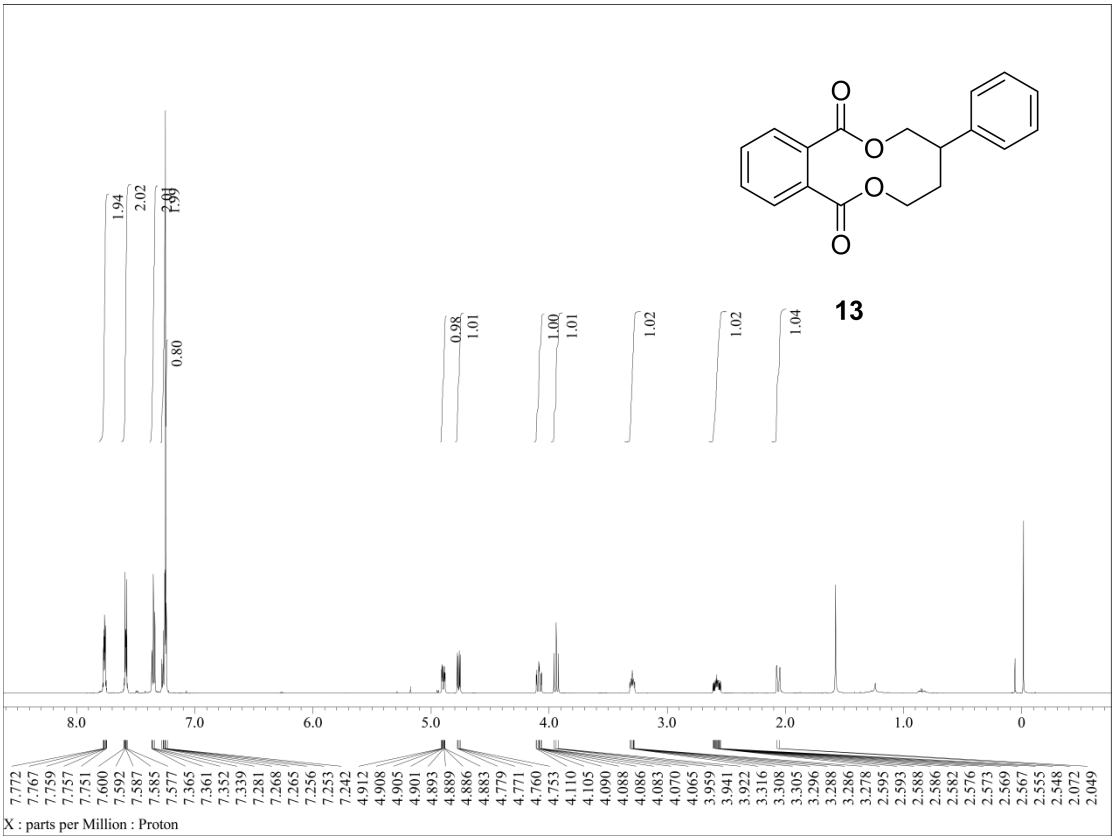

10a
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.2
174.1
139.4
138.7
128.4
127.9
127.3
126.4
77.2
77.0
76.8
60.9
60.7
27.5
27.4
9.0
9.0
X : parts per Million : Carbon13

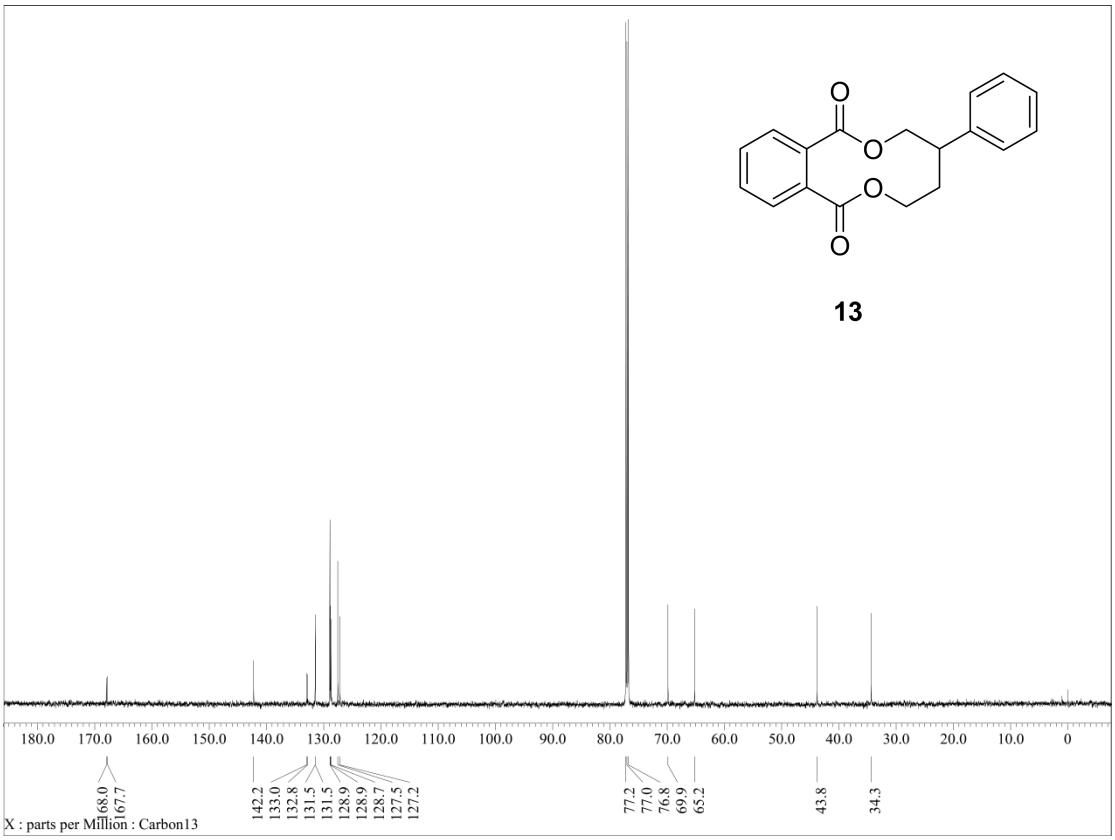

10b
2.16
2.08
1.00
2.03
2.03
2.98
2.82
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.317
7.314
7.310
7.302
7.299
7.296
7.275
7.271
7.267
7.265
7.260
7.257
7.252
6.034
6.022
6.011
4.986
4.836
4.824
2.048
1.968
X : parts per Million : Proton

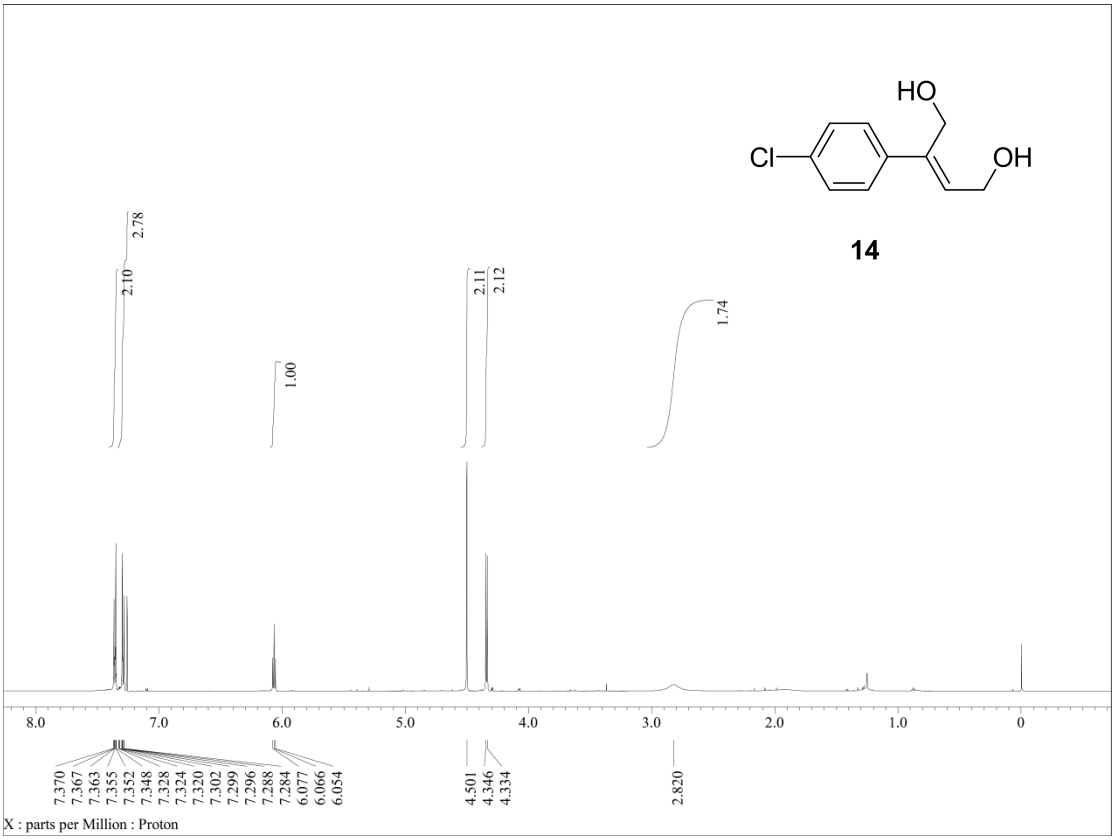

10b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.5
170.4
137.6
137.4
133.7
128.4
127.6
127.5
77.2
77.0
76.8
60.5
60.5
20.7
20.6
X : parts per Million : Carbon13

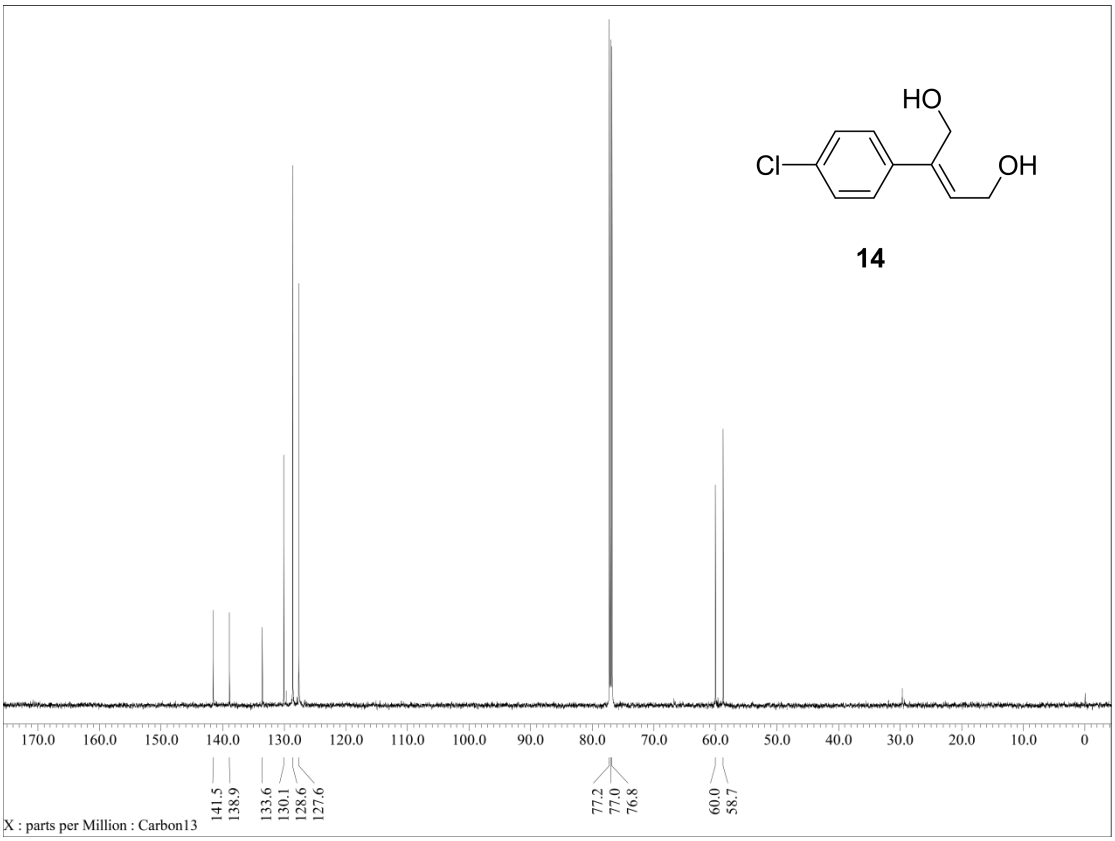

12
0.90
0.96
1.99
1.99
2.91
1.00
2.02
1.68
1.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.866
7.861
7.855
7.852
7.847
7.845
7.841
7.834
7.831
7.631
7.624
7.619
7.617
7.612
7.609
7.603
7.598
7.574
7.570
7.566
7.561
7.557
7.554
7.549
7.536
7.533
7.395
7.392
7.379
7.360
7.358
7.354
7.346
7.333
7.324
7.322
7.314
7.310
7.305
7.298
7.284
7.260
6.411
6.400
6.388
4.838
4.827
4.368
3.020
X : parts per Million : Proton


12
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.6
166.9
145.8
140.4
133.5
131.7
130.9
130.8
129.6
128.6
128.4
128.1
126.9
124.8
77.2
77.0
76.8
61.2
60.3
30.8
X : parts per Million : Carbon13

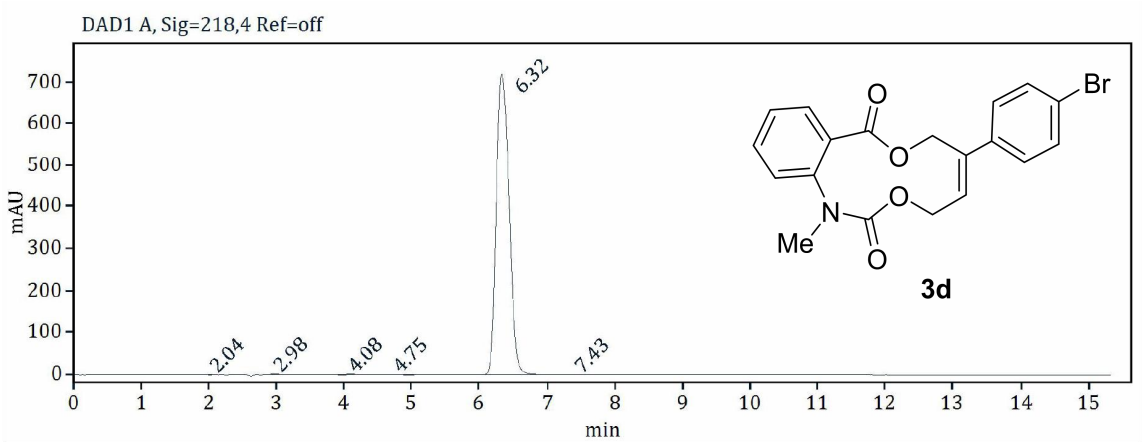

13
1.94
2.02
2.01
1.91
0.80
0.98
1.01
1.00
1.01
1.02
1.02
1.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.772
7.767
7.759
7.757
7.751
7.600
7.592
7.587
7.585
7.577
7.365
7.361
7.352
7.339
7.281
7.268
7.265
7.256
7.253
7.242
4.912
4.908
4.905
4.901
4.893
4.889
4.886
4.883
4.779
4.771
4.760
4.753
4.110
4.105
4.090
4.088
4.086
4.083
4.070
4.065
3.959
3.941
3.922
3.316
3.308
3.305
3.296
3.288
3.286
3.278
2.595
2.593
2.588
2.586
2.582
2.576
2.573
2.569
2.567
2.555
2.548
2.072
2.049
X : parts per Million : Proton


13
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.0
167.7
142.2
133.0
132.8
131.5
131.5
128.9
128.9
128.7
127.5
127.2
77.2
77.0
76.8
69.9
65.2
43.8
34.3
X : parts per Million : Carbon13

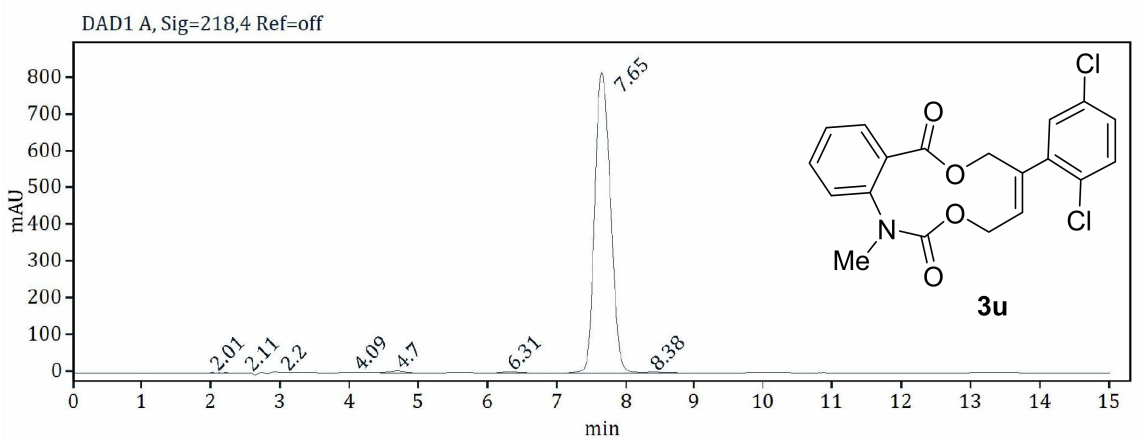

HO
Cl
OH
14
2.78
2.10
1.00
2.11
2.12
1.74
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.370
7.367
7.363
7.355
7.352
7.348
7.328
7.324
7.320
7.302
7.299
7.296
7.288
7.284
6.077
6.066
6.054
4.501
4.346
4.334
2.820
X : parts per Million : Proton


HO
Cl
OH
14
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.5
138.9
133.6
130.1
128.6
127.6
77.2
77.0
76.8
60.0
58.7
X : parts per Million : Carbon13

PS: The purity of the compound **3d** and **3u** determined by HPLC.



Peak#	Ret. Time[min]	Area[mAU*s]	Height[mAU]	Rel. Area [%]
1	2.04	3.958	1.0301	0.0414
2	2.98	15.655	2.4083	0.1638
3	4.08	21.322	1.6707	0.2231
4	4.75	17.843	0.9887	0.1867
5	6.32	9491.991	720.8486	99.3013
6	7.43	8.004	0.393	0.0837



Peak#	Ret. Time[min]	Area[mAU*s]	Height[mAU]	Rel. Area [%]
1	2.01	3.862	1.579	0.0296
2	2.11	2.309	0.7374	0.0177
3	2.2	5.065	1.5223	0.0389
4	4.09	16.071	1.2893	0.1234
5	4.7	75.925	5.1397	0.5828
6	6.31	38.917	2.9185	0.2987
7	7.65	12849.223	814.7239	98.6323
8	8.38	36.021	1.8596	0.2765