Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Harnessing structurally unbiased *ortho*-benzoquinone monoimine for biomimetic oxidative [4+2] cycloaddition with enamines

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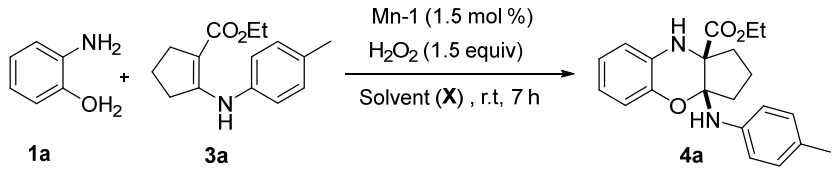
(A) General Informations

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products.^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts of ^{1}H NMR were reported in part per million relatives to the $CDCl_3$ residual peak (δ 7.26). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16) or CD_3OD (δ 49.00). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint. (quintet), m (multiplet), br (broad). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (*virt.*). High resolution mass spectra (HRMS) data were measured on a ESI-microTOF Ⅱ. Melting points were measured on a SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Further visualization was achieved by staining with iodine, or $KMnO_4$ followed by heating on a hot plate. Flash column chromatography was performed on silica gel 60 Å, 10-40 μm.

Enamine substrates **3** were prepared by using following literature methods.[1,2] (salen)Mn(III)Cl complex was prepared according to known procedure.[3,4]

(B) Optimization of reaction conditions

Table S1. The reaction of **1a** with **3a** in different solvents.[a]

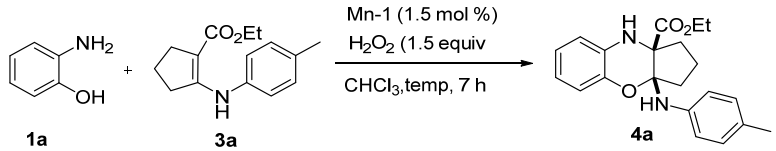


Entry	Solvent	Yield (4a,%) [b]
1	DCM	85
2	DCE	61
3	Chloroform	**89**
4	CCl_4	38
5	Methanol	10
6	Ethanol	10
7	Toluene	76
8	Et_2O	Traces

9	Benzene	71%
10	THF	Traces
11	Acetone	Traces
12	DMF	Traces
13	MeCN	Traces

[a]**Reaction conditions**: Reactions were performed with **1a** (0.1 mmol, 10.91 mg, 1 equiv.), **3a** (0.3 mmol, 73.54 mg, 3 equiv.), and H_2O_2 (1.5 equiv., 17 μL), and Mn-1 (1.5 mol %., 0.7 mg) in solvent (5.0 mL) for 7 hours. [b] Isolated yield.

Table S2 The reaction of **1a** with **3a** under different temperatures.[a]



1a **3a** **4a**

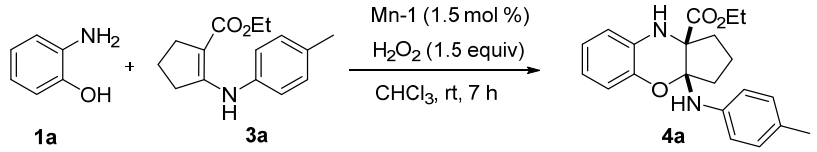
Entry	Temperature (°C)	Yield (4a,%)[b]
1	70	35
2	40	64
3	r.t	**89**
4	0	59
5	-10	50

[a]**Reaction conditions**: Reactions were performed with **1a** (0.1 mmol, 10.91 mg, 1 equiv.), **3a** (0.3 mmol, 73.54 mg, 3 equiv.), and H_2O_2 (1.5 equiv., 17 μL) and **Mn-1** (1.5 mol %., 0.7 mg) in solvent (5.0 mL) for 7 hours. [b]Isolated yield.

(C) Representative procedure for catalytic oxidative [4+2] cycloaddition

General procedure： Unless specified otherwise, a 25 mL round bottom flask were charged with 2-aminophenol **1** (0.1 mmol, 1.0 equiv), ethyl 2-(p-tolylamino)cyclopent-1-ene-1-carboxylate **3** (0.3 mmol, 3.0 equiv), **Mn-1** (0.7 mg, 1.5 mol%), and then added chloroform ($CHCl_3$) 5 mL, and H_2O_2 (17 μL, 1.5 equiv., 30%) the mixture was stirred at room temperature and monitored by TLC until the full conversion of the 2-aminophenol **1a**. After the reaction completed, the reaction was quenched by adding saturated $Na_2S_2O_3$ solution (3 mL) and then water (5 mL). The organic solvent was separated and the aqueous phase was extracted with CH_2Cl_2 (2*5 mL). The combined organic phase was evaporated. Purification of the crude product was performed by column chromatography using hexane/EtOAc (100:1 to 30:1) as the eluents to afford cycloadduct **4**.

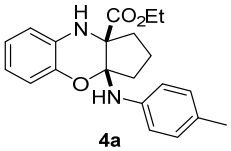
Gram-scale [4+2] Cycloaddition Reaction of 2-aminophenol 1a with enamine 3a.



A 500 mL round bottom flask were charged with 2-aminophenol **1a** (5.4 mmol, 590 mg, 1.0 equiv), ethyl 2-(p-tolylamino)cyclopent-1-ene-1-carboxylate **3a** (16.2 mmol, 3971 mg, 3.0 equiv), and **Mn-1** (1.5 mol%, 37.9 mg), and then added chloroform ($CHCl_3$) 200 mL, and H_2O_2 (0.92 mL, 1.5 equiv.) the mixture was stirred at room temperature and monitored by TLC until the full conversion of the 2-aminophenol **1a**. After the reaction completed, the reaction was quenched by adding saturated $Na_2S_2O_3$ solution (30 mL) and then water (100 mL). The organic solvent was separated and the aqueous phase was extracted with CH_2Cl_2 (2*50 mL). The combined organic phase was evaporated, Purification of the crude product was performed by column chromatography using hexane/EtOAc (100:1 to 30:1) as the eluents to afford ethyl 3a-(p-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate **4a** (85%, 16.2 g).

(D) Analytical data of the desired products

Ethyl-3a-(p-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4a



4a

A dark brown oil, 31.4 mg, 89% yield.

TLC: R_f = 0.45 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

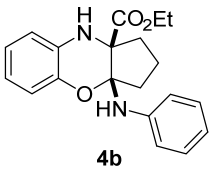
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.0 Hz, 2H), 6.87 – 6.70 (m, 5H), 6.70 – 6.60 (m, 1H), 4.81 (s, 1H), 4.39 – 4.22 (m, 2H), 4.16 (s, 1H), 2.77 – 2.63 (m, 1H), 2.50 – 2.37 (m, 1H), 2.23 (s, 3H), 2.20 – 2.09 (m, 1H), 2.05 – 1.89 (m, 2H), 1.88 – 1.77 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 141.1, 139.7, 130.2, 129.5, 129.3, 122.0, 119.1, 119.1, 118.3, 115.3, 89.0, 69.1, 62.4, 34.4, 33.8, 20.6, 19.2, 14.1.

IR (ATR/cm^{-1}) 3389.2, 2977.0, 1721.1, 1613.1, 1517.9, 1328.4, 1297.9, 1080.5, 744.9.

HRMS (ESI): $C_{21}H_{25}N_2O_3^+$ [$(M+H)^+$]: calcd.: 353.1860; found: 353.1869.

Ethyl-3a-(phenylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4b



4b

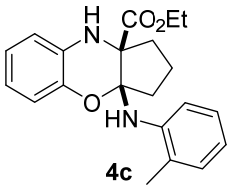
A brown solid, 21 mg, 62% yield.

m.p.: 113– 115 °C.

TLC: R_f = 0.71 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.87 – 6.80 (m, 2H), 6.83 – 6.75 (m, 2H), 6.72 – 6.66 (m, 1H), 4.83 (s, 1H), 4.45 – 4.27 (m, 3H), 2.90 – 2.74 (m, 1H), 2.53 – 2.38 (m, 1H), 2.25 – 2.38 (m, 1H), 2.11 – 1.93 (m, 2H), 1.93 – 1.82 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 143.7, 139.7, 129.5, 128.9, 122.1, 120.5, 119.2, 118.3, 118.3, 115.4, 88.6, 69.2, 62.5, 34.4, 33.7, 19.2, 14.2.
IR (ATR/cm^{-1}) 3386.0, 2953.8, 2854.5, 1711.8, 1497.9, 1366.5, 1291.1, 1184.0, 902.2, 850.5, 793.6,
HRMS (ESI): $C_{20}H_{23}N_2O_3^+$ [$(M+H)^+$]: calcd.: 339.1703; found: 339.1708.

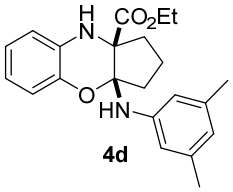
Ethyl-3a-(o-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4c



4c

A pale yellow solid, 28 mg, 79% yield.
m.p.: 75–77 °C.
TLC: R_f = 0.83 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.88 – 6.72 (m, 4H), 6.70 – 6.61 (m, 1H), 4.79 (s, 1H), , 4.30 (q, *J* = 7.1 Hz, 2H), 4.18 (s, 1H), 2.94 – 2.79(m, 1H), 2.43 – 2.26 (m, 1H), 2.24 – 2.13 (m, 1H), 2.07 – 1.93 (m, 2H), 1.90 (s, 3H), 1.88 – 1.80 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 142.0, 139.8, 130.2, 129.5, 126.7, 125.8, 122.1, 120.1, 119.2, 118.3, 117.0, 115.4, 88.6, 69.4, 62.6, 34.2, 33.7, 19.3, 17.6, 14.2.
IR (ATR/cm^{-1}) 3375.1, 3052.3, 2922.7, 1719.3, 1451.4, 1301.0, 1249.3, 993.4.
HRMS (ESI): $C_{21}H_{25}N_2O3^+$ [$(M+H)^+$]: calcd.: 353.1860; found: 353.1858.

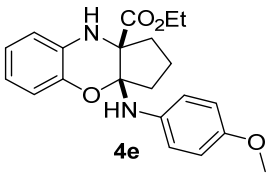
Ethyl-3a-((3,5-dimethylphenyl)amino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4d



4d

A brown oil, 30 mg, 82% yield.
TLC: R_f = 0.57 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 – 6.76 (m, 2H), 6.73 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.68 – 6.62 (m, 1H), 6.52 (s, 2H), 6.48 (s, 1H), 4.78 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.21 (s, 1H), 2.95 – 2.69 (m, 1H), 2.52 – 2.30 (m, 1H), 2.21 (s, 6H), 2.18 – 2.08 (m, 1H), 2.08 – 1.92 (m, 2H), 1.90 – 1.77 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 143.6, 139.8, 138.5, 129.5, 122.2, 122.1, 119.1, 118.3, 115.9, 115.3, 88.5, 69.2, 62.4, 34.4, 33.7, 21.5, 19.2, 14.2.
IR (ATR/cm^{-1}) 3389.1, 2960.4, 2866.7, 1720.2, 1500.9, 1368.5, 1298.9, 1117.0, 1082, 999.9, 830.5,
HRMS (ESI): $C_{22}H_{27}N_2O_3$+ [$(M+H)^+$]: calcd.: 367.2016; found: 367.2013.

Ethyl-3a-((4-methoxyphenyl)amino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4] oxazine-9a(9H)-carboxylate 4e



4e

A brown oil, 34.1 mg, 93% yield.

TLC: R_f = 0.83 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

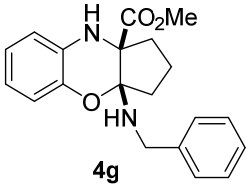
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 – 6.81 (m, 3H), 6.81 – 6.64 (m, 5H), 4.83 (s, 1H), 4.45 – 4.22 (m, 2H), 3.97 (s, 1H), 3.74 (s, 3H), 2.59 – 2.37 (m, 2H), 2.22 – 2.10 (m, 1H), 2.05 – 1.78 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 155.06, 139.7, 136.7, 129.7, 122.4, 122.1, 119.1, 118.3, 115.3, 114.1, 89.8, 69.1, 62.37, 55.6, 34.51, 34.2, 19.1, 14.2.

IR (ATR/cm^{-1}) 3387.1, 2956.2, 1723.0, 1609.6, 1367.5, 1243.0, 1117.6, 1036.4, 848.1.

HRMS (ESI): $C_{21}H_{25}N_2O_4^+$ [(M+H)$^+$]: calcd.: 369.1809; found: 369.1801.

Methyl-3a-(benzylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4g



4g

A brown solid, 23.5 mg, 71% yield.

m.p.: 78– 80 °C.

TLC: R_f = 0.70 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

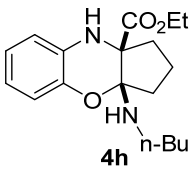
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 2H), 7.24 – 7.16 (m, 3H), 6.91 – 6.81 (m, 2H), 6.71 (t, *J* = 7.7 Hz, 2H), 4.77 (s, 1H), 3.93 (s, 2H), 3.87 (s, 3H), 2.39 – 2.29 (m, 2H), 2.26 – 2.11 (m, 2H), 2.05 – 1.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 140.5, 139.7, 130.0, 128.3, 127.7, 126.8, 122.1, 118.9, 118.2, 115.3, 91.8, 69.1, 52.9, 46.3, 35.2, 34.0, 18.9.

IR (ATR/cm^{-1}) 3400.1, 3302.4, 3064.6, 2951.4, 1728.2, 1591.1, 1408.0, 12381, 1075.2,

HRMS (ESI): m/z: [M + H]$^+$ $C_{20}H_{23}N_2O_3^+$ calcd.: 339.1703; found: 339.1700.

Ethyl 3a-(butylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4h



4h

A brown oil, 23.8 mg, 70% yield.

TLC: R_f = 0.75 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

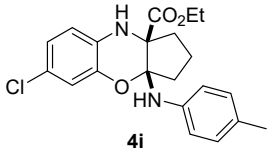
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 – 6.81 (m, 2H), 6.78 – 6.68 (m, 2H), 4.80 (s, 1H), 4.47 – 4.09 (m, 2H), 2.88 – 2.69 (m, 1H), 2.65 – 2.53 (m, 1H), 2.41 – 2.24 (m, 2H), 2.18 – 2.08 (m, 1H), 2.04 – 1.79 (m, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.32 – 1.14 (m, 4H), 0.83 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 140.0, 130.1, 121.8, 118.8, 118.2, 115.3, 91.9, 69.0, 61.9, 42.03, 35.2, 34.1, 32.6, 20.2, 18.9, 14.1, 13.8.

IR (ATR/cm^{-1}) 3359.3, 3063.4, 2960.7, 2871.7, 1637.1, 1453.8, 1401, 1310.1, 1105.2, 923.0.

HRMS (ESI): $C_{20}H_{23}N_2O_3^+$ [$(M+H)^+$]: calcd.: 319.4245; found: 319.4251.

Ethyl-6-chloro-3a-(p-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4i



4i

A dark brown solid, 33.2 mg, 85% yield.

m.p.: 99– 101 °C.

TLC: R_f = 0.68 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

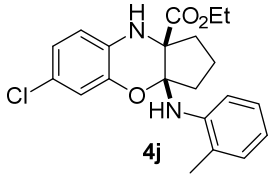
^{1}H NMR (600 MHz, $CDCl_3$), δ 7.01 (d, *J* = 8.1 Hz, 2H) 6.85 – 6.78 (m, 4H), 6.71 – 6.56 (m, 1H), 4.83 (s, 1H), 4.46 – 4.22 (m, 2H), 4.13 (s, 1H), 2.81 – 2.65 (m, 1H), 2.48 – 2.33 (m, 1H), 2.24 (s, 3H), 2.18 – 2.08 (m, 1H), 2.07 – 1.86 (m, 2H), 1.83 – 1.71 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 140.8, 140.4, 130.4, 129.5, 128.2, 123.2, 122.0, 118.9, 118.3, 116.0, 89.5, 69.0, 62.5, 34.3, 33.6, 20.6, 19.1, 14.1.

IR (ATR/cm^{-1}) 3394.2, 3332.9, 2975.9, 2869.0, 1721.5, 1589.6, 1468.5, 1369.8, 1189.2, 994.5.

HRMS (ESI): $C_{21}H_{24}ClN_2O_3^+$ [$(M+H)^+$]: calcd.: 387.1470; found: 387.1478.

Ethyl-6-chloro-3a-(o-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4j



4j

A brown solid, 30 mg, 78% yield.

m.p.: 127– 129 °C.

TLC: R_f = 0.75 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

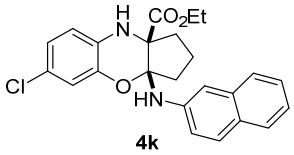
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 1H), 7.13 (td, *J* = 7.8, 1.6 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H) 6.86 – 6.72 (m, 3H), 6.66 (d, *J* = 8.2 Hz, 1H) 4.79 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 1H), 2.91 – 2.77 (m, 1H), 2.41 – 2.25 (m, 1H), 2.22 – 2.12 (m, 1H), 2.06 – 1.95 (m, 2H), 1.93 (s, 3H), 1.83 – 1.72 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 141.6, 140.4, 130.3, 128.2, 126.8, 125.7, 123.3, 122.0, 120.3, 118.3, 116.8, 116.0, 89.0, 69.2, 62.7, 34.0, 33.4, 19.2, 17.6, 14.1.

IR (ATR/cm^{-1}) 3368.1, 2969.6, 2922.6, 1722.1, 1495.6, 1370.5, 1252.1, 850.1, 750.2.

HRMS (ESI): $C_{21}H_{24}ClN_2O_3^+$ [$(M+H)^+$]: calcd.: 387.1470; found: 387.1477.

Ethyl-6-chloro-3a-(naphthalen-2-ylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e] [1,4]oxazine-9a(9H)-carboxylate 4k



4k

A white solid, 33 mg, 78% yield.

m.p.: 117– 119 °C.

TLC: R_f = 0.63 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

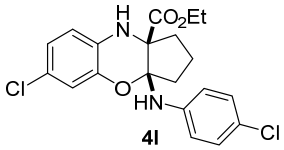
^{1}H NMR (600 MHz, $CDCl_3$) δ, 7.76 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.53 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.48 – 7.33 (m, 4H), 6.87 (d, *J* = 2.3 Hz, 1H), (dd, *J* = 8.5, 2.3 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 4.89 (s, 1H), 4.79 (s, 1H), 4.46 – 4.23 (m, 2H) 4.35 (qq, *J* = 7.3, 3.7 Hz, 2H), 2.95 – 2.82 (m, 1H), 2.41 – 2.29 (m, 1H), 2.29 – 2.20 (m, 1H), 2.07 – 1.94 (m, 2H), 1.94 – 1.82 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 140.5, 138.6, 134.2, 128.6, 128.2, 126.5, 126.1, 125.8, 125.4, 123.4, 122.1, 121.3, 120.9, 118.3, 116.1, 113.5, 69.3, 62.8, 33.7, 33.5, 19.3, 14.2.

IR (ATR/cm^{-1}) 3367.1, 3063.2, 2969.2, 1721.3, 1585.4, 1493.2, 1297.8, 1129.6, 1074, 798.1.

HRMS (ESI): $C_{24}H_{24}ClN_2O_3^+$ [$(M+H)^+$]: calcd.: 423.1470; found: 423.1479.

Ethyl-6-chloro-3a-((4-chlorophenyl)amino)-1,2,3,3a tetrahydrobenzo[b]cyclopenta[e] [1,4]oxazine-9a(9H)-carboxylate 4l



4l

A brown solid, 32.9 mg, 81% yield.

m.p.: 90– 92 °C.

TLC: R_f = 0.69 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

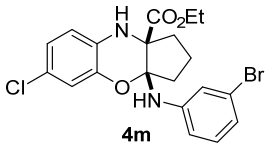
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 – 7.05 (m, 2H), 6.88 – 6.72 (m, 4H), 6.64 (d, *J* = 8.3 Hz, 1H), 4.78 (s, 1H), 4.41 – 4.16 (m, 3H), 2.79 – 2.66 (m, 1H), 2.42 – 2.27 (m, 1H), 2.21 – 2.10 (m, 1H), 2.05 – 1.87 (m, 1H), 1.83 – 1.70 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 142.0, 140.1, 128.9, 128.1, 125.6, 123.3, 122.2, 119.3, 119.2, 118.2, 116.0, 89.0, 68.8, 62.7, 34.1, 33.4, 19.1, 14.1.

IR (ATR/cm^{-1}) 3389.3, 2966.8, 2853.1, 1708.8, 1327.3, 1296.0, 1126.2, 982.2.

HRMS (ESI): $C_{20}H_{21}Cl_2N_2O_3$+ [$(M+H)^+$]: calcd.: 407.0924; found: 407.0920.

Ethyl-3a-((3-bromophenyl)amino)-6-chloro-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4] oxazine-9a(9H)-carboxylate 4m



4m

A brown oil, 33 mg, 73% yield.

TLC: R_f = 0.67 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

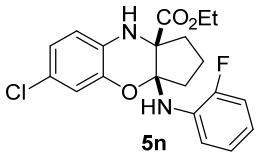
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (t, *J* = 2.0 Hz, 1H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.95 (dt, *J* = 8.0, 1.3 Hz, 1H), 6.84 – 6.77 (m, 3H), 6.68 – 6.62 (m, 1H), 4.76 (s, 1H), 4.38 (s, 1H), 4.32 (qt, *J* = 7.1, 3.3 Hz, 2H), 2.86 – 2.75 (m, 1H), 2.41 – 2.28 (m, 1H), 2.21 – 2.10 (m, 1H), 2.09 – 1.88 (m, 2H), 1.85 – 1.73 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 144.9, 140.1, 130.3, 128.0, 123.4, 123.2, 122.8, 122.3, 120.2, 118.2, 116.1, 116.0, 88.6, 68.9, 62.8, 34.0, 33.2, 19.1, 14.2.

IR (ATR/cm^{-1}) 3387.1, 2959.6, 2855.6, 1718.8, 1496.2, 1386.1, 1188.1, 855.1.

HRMS (ESI): $C_{20}H_{21}{}^{79}BrClN_2O_3^+$ [$(M+H)^+$]: calcd.: 451.0419; found: 451.0411.

Ethyl-6-chloro-3a-((2-fluorophenyl)amino)-1,2,3,3a tetrahydrobenzo[b]cyclopenta[e] [1,4]oxazine-9a(9H)-carboxylate 4n



5n

A brown oil, 26 mg, 66% yield.

TLC: R_f = 0.82 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

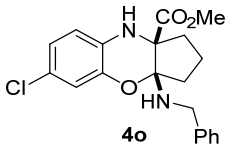
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 1H), 7.07 – 6.97 (m, 1H), 6.95 – 6.86 (m, 1H), 6.84 – 6.72 (m, 3H), 6.70 – 6.64 (m, 1H), 4.78 (s, 1H), 4.63 – 4.47 (m, 1H), 4.43 – 4.22 (m, 2H), 2.88 – 2.72 (m, 1H), 2.44 – 2.28 (m, 1H), 2.24 – 2.13 (m, 1H), 2.09 – 1.88 (m, 2H), 1.86 – 1.74 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 152.8 (d, *J* = 240.1 Hz), 140.2, 132.9 (d, *J* = 10.7 Hz), 128.2, 124.3 (d, *J* = 3.5 Hz), 123.3, 122.2, 120.2 (d, *J* = 7.4 Hz), 118.2, 118.1 (d, *J* = 2.1 Hz), 116.3, 114.9 (d, *J* = 19.4 Hz), 88.5, 69.0, 62.8, 34.0, 33.4, 19.0, 14.1.

IR (ATR/cm^{-1}) 3397.9, 2960.3, 1723.4, 1619.7, 1590.8, 1368.3, 1238.6, 999.5, 800.5.

HRMS (ESI): $C_{20}H_{21}ClFN_2O_3^+$ [$(M+H)^+$]: calcd.: 391.1219; found: 391.1225.

Methyl-3a-(benzylamino)-6-chloro-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4o



4o

A brown oil, 33 mg, 86% yield.

TLC: R_f = 0.73 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

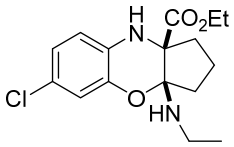
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 3H), 7.23 – 7.17 (m, 2H), 6.84 (d, *J* = 2.3 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 4.81 (s, 1H), 3.92 (s, 2H), 3.87 (s, 3H), 2.36 – 2.21 (m, 2H), 2.21 – 2.07 (m, 2H), 2.20 – 2.07 (m, 2H), 2.00 – 1.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 140.4, 140.3, 128.6, 128.3, 127.7, 127.0, 123.1, 121.9, 118.2, 115.9, 92.4, 68.9, 53.0, 46.4, 34.9, 33.8, 18.8.

IR (ATR/cm^{-1}) 3400.3, 3302.5, 3064.7, 2951.7, 1728.8, 1642.3, 1591.9, 1302.9, 1188.9, 699.

HRMS (ESI): $C_{20}H_{22}ClN_2O_3^+$ [$(M+H)^+$]: calcd.: 373.1313; found: 373.1319.

Ethyl-6-chloro-3a-(ethylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4p



4p

A brown oil, 26 mg, 80% yield.

TLC: R_f = 0.76 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

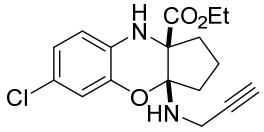
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (d, *J* = 2.3 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 4.77 (s, 1H), 4.36 – 4.18 (m, 2H), 2.88 – 2.76 (m, 1H), 2.69 – 2.56 (m, 1H), 2.37 – 2.22 (m, 2H), 2.18 – 2.00 (m, 1H), 2.00 – 1.72 (m, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 140.7, 128.8, 122.9, 121.6, 118.2, 115.9, 92.6, 68.7, 62.1, 36.99, 34.9, 34.0, 18.9, 16.0, 14.1.

IR (ATR/cm^{-1}) 3344, 2926, 2855, 1731, 1599, 1488, 1416, 1371, 1258, 1178, 1083, 1007, 906, 856, 569.

HRMS (ESI): $C_{16}H_{22}ClN_2O_3^+$ [$(M+H)^+$]: calcd.: 325.1313; found: 325.1317.

Ethyl-6-chloro-3a-(prop-2-yn-1-ylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4] oxazine-9a(9H)-carboxylate 4q



4q

A dark brown oil, 29 mg, 86% yield.

TLC: R_f = 0.91 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

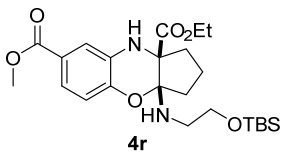
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (d, *J* = 2.3 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.79 (s, 1H), 4.38 – 4.22 (m, 2H), 3.50 (dt, *J* = 9.2, 2.6 Hz, 2H), 2.44 – 2.27 (m, 2H), 2.19 – 2.05 (m, 3H), 2.01 – 1.86 (m, 1H), 1.82 – 1.72 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 140.2, 128.4, 123.1, 122.0, 118.3, 116.0, 92.0, 82.2, 71.0, 68.43, 62.3, 34.6, 33.6, 32.0, 18.8, 14.1.

IR (ATR/cm^{-1}) 3386.5, 3297.7, 2956.4, 1724.3, 1589.5, 1302.1, 1186.3, 927.1, 853.9.

HRMS (ESI): $C_{17}H_{20}ClN_2O_3^+$ [$(M+H)^+$]: calcd.: 335.1157; found: 335.1151.

9a-Ethyl-7-methyl-3a-(((tert-butyldimethylsilyl)oxy)amino)-1,2,3,3a-tetrahydrobenzo[b] cyclopenta[e][1,4]oxazine-7,9a(9H)-dicarboxylate 4r



4r

A colorless oil, 38 mg, 79% yield.

TLC: R_f = 0.90 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

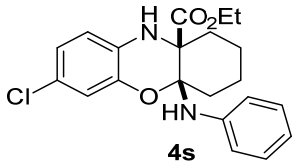
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 4.91 (s, 1H), 4.36 – 4.20 (m, 2H), 3.85 (s, 3H), 3.63 – 3.46 (m, 2H), 3.00 – 2.87 (m, 1H), 2.77 – 2.58 (m, 1H), 2.30 (dd, *J* = 8.6, 6.5 Hz, 2H), , 2.21 (dd, *J* = 9.6, 3.5 Hz, 1H), 2.16 – 2.06 (m, 1H), 2.01 – 1.83 (m, 2H), 1.82 – 1.69 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.70 (s, 9H), -0.09 (s, 3H), -0.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 167.1, 144.3, 129.6, 123.5, 120.8, 117.7, 116.4, 93.0, 68.4, 62.5, 61.9, 51.7, 44.4, 34.8, 33.8, 25.6, 18.7, 18.0, 14.0, -5.4, -5.5.

IR (ATR/cm^{-1}) 3383.1, 2953.4, 2931.6, 2858.6, 1722.2, 1593.4, 1472.2, 1307.5, 1231.7, 1078.8, 837.9.

HRMS (ESI): $C_{24}H_{39}N_2O_6Si^+$ [(M+H)$^+$]: calcd.: 479.2572; found: 479.2579.

Ethyl-7-chloro-4a-(phenylamino)-2,3,4,4a-tetrahydro-1H-phenoxazine-10a(10H)-carboxylate 4s



4s

A colorless oil, 30 mg, 79% yield.

TLC: R_f = 0.65 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

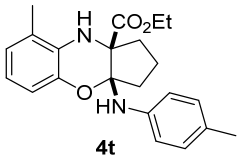
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.04 – 6.92 (m, 3H), 6.87 (d, *J* = 2.3 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.66 – 6.61 (m, 1H) 6.64 (d, *J* = 8.4 Hz, 1H), 4.57 (s, 1H), 4.46 – 4.25 (m, 2H), 2.56 – 2.29 (m, 2H), 1.94 – 1.47 (m, 6H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.7, 123.3, 121.9, 121.8, 121.5, 117.4, 62.1, 61.3, 33.1, 21.3, 21.1, 14.2, 14.1.

IR (ATR/cm^{-1}) 3386.1, 2920.8, 2850.5, 1721.3, 1601.9, 1443.0, 1297.4, 1152.8.

HRMS (ESI): $C_{21}H_{24}ClN_2O_3^+$ [(M+H)$^+$]: calcd.: 387.1470; found: 387.1480.

Ethyl 8-methyl-3a-(p-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4t



4t

A white solid, 21.9 mg, 61% yield.

m.p.: 99– 101 °C.

TLC: R_f = 0.78 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

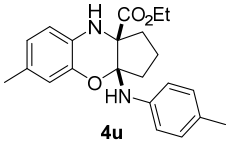
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.0 Hz, 2H), 6.83 – 6.77 (m, 2H), 6.73 (d, *J* = 7.4 Hz, 1H),6.68 (d, *J* = 8.6 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H),, 4.78 (s, 1H), 4.36 – 4.25 (m, 2H), 4.21 (s, 1H), 2.88 – 2.75 (m, 1H), 2.49 – 2.34 (m, 1H), 2.21 (s, 6H), 2.18 – 2.08 (m, 1H), 2.08 – 1.90 (m, 2H), 1.91 – 1.75 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 141.2, 139.4, 130.2, 129.4, 127.8, 123.3, 119.3, 118.4, 116.2, 88.3, 69.4, 62.4, 34.6, 34.3, 20.6, 19.2, 16.9, 14.2.

IR (ATR/cm^{-1}) 3381.8, 3355.4, 3031.3, 2919.5, 1710.7, 1613.9, 1588.3, 1370.3, 1241.6, 897.8, 807.1.

HRMS (ESI): $C_{22}H_{27}N_2O_3^+$ [(M+H)$^+$]: calcd.: 367.2016; found: 367.2011

Ethyl-6-methyl-3a-(p-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4u



4u

A pale yellow solid, 23.2 mg, 63% yield.

m.p.: 77– 79 °C.

TLC: R_f = 0.53 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

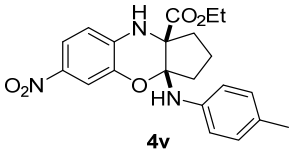
^{1}H NMR (400 MHz, $CDCl_3$) 6.97 (d, *J* = 8.0 Hz, 2H), 6.85 – 6.78 (m, 2H), 6.69 – 6.60 (m, 3H), 4.68 (s, 1H), 4.41 – 4.22 (m, 2H), 4.17 (s, 1H), 2.79 – 2.64 (m, 1H), 2.44 – 2.28 (m, 1H), 2.24 (s, 3H), 2.18 (s, 3H), 2.05 – 1.88 (m, 2H), 1.88 – 1.71 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 141.3, 139.8, 130.0, 129.4, 128.9, 126.7, 122.6, 118.9, 118.7, 115.6, 88.9, 69.2, 62.4, 34.4, 33.5, 20.7, 20.6, 19.24, 14.2.

IR (ATR/cm^{-1}) 3353.7, 3000.3, 2968.4, 1709.4, 1617.3, 1515.3, 1441.7, 1369.3, 1303.9, 995.7, 806.8.

HRMS (ESI): $C_{22}H_{27}N_2O_3^+$ [(M+H)$^+$]: calcd.: 367.2016; found: 367.2019

Ethyl-6-nitro-3a-(p-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-9a(9H)-carboxylate 4v



4v

A yellow solid, 37 mg, 93% yield.

m.p: 87– 89 °C

TLC: R_f = 0.40 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

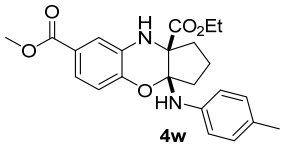
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.86 – 6.78 (m, 2H), 6.73 (d, *J* = 8.8 Hz, 1H), 5.52 (s, 1H), 4.47 – 4.20 (m, 2H), 4.07 (s, 1H), 2.87 – 2.74 (m, 1H), 2.56 – 2.41 (m, 1H), 2.27 (s, 3H), 2.27 – 2.22 (m, 1H), 2.13 – 1.92 (m, 2H), 1.92 – 1.81 (m, 1H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 140.2, 139.4, 138.5, 136.5, 131.0, 129.7, 119.4, 119.0, 114.7, 113.1, 90.4, 69.20, 63.0, 34.8, 34.3, 20.6, 19.2, 14.2.

IR (ATR/cm^{-1}) 3373.7, 2957.5, 2877.1, 1726.7, 1607.4, 1481.0, 1328.6, 1236.6, 1186.4, 852.51, 804.4,.

HRMS (ESI): $C_{21}H_{24}N_3O_5^+$ [(M+H)$^+$]: calcd.: 398.1710; found: 398.1690.

9a-ethyl-7-methyl-3a-(p-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine-7,9a(9H)-dicarboxylate 4w



4w

A brown oil, 38.8 mg, 94% yield.

TLC: R_f = 0.55 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

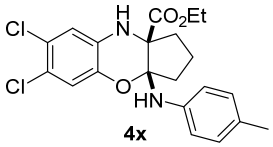
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.0 Hz, 1H), 7.37 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.84 – 6.70 (m, 3H), 4.91 (s, 1H), 4.32 (p, *J* = 7.0 Hz, 2H), 4.17 (s, 1H), 3.86 (s, 3H), 2.82 – 2.64 (m, 1H), 2.55 – 2.38 (m, 1H), 2.24 (s, 3H), 2.23 – 2.10 (m, 1H), 2.10 – 1.87 (m, 2H), 1.86 – 1.72 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 167.1, 144.1, 140.7, 130.5, 129.5, 129.3, 123.9, 121.1, 119.2, 118.0, 116.6, 90.3, 68.8, 62.5, 51.9, 34.3, 33.7, 20.6, 19.1, 14.2.

IR (ATR/cm^{-1}) 3381.0, 2953.9, 2869.9, 1718.1, 1516.7, 1439.4, 1258.7, 1230.3, 898.2, 812.9.

HRMS (ESI): $C_{23}H_{27}N_2O_5^+$ [$(M+H)^+$]: calcd.: 411.1914; found: 411.1915.

Ethyl-6,7-dichloro-3a-(p-tolylamino)-1,2,3,3a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazine 9a(9H)-carboxylate 4x



4x

A pale yellow solid, 38.4 mg, 91% yield.

m.p.: 120–122 °C.

TLC: R_f = 0.68 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 6.84 – 6.78 (m, 3H), 4.91 (s, 1H), 4.44 – 4.26 (m, 2H), 4.13 (s, 1H), 2.79 – 2.68 (m, 1H), 2.51 – 2.36 (m, 1H), 2.28 (s, 3H), 2.23 – 2.13 (m, 1H), 2.09 – 1.88 (m, 2H), 1.85 – 1.74 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 140.5, 139.0, 130.6, 129.6, 129.5, 124.8, 121.0, 119.6, 118.9, 115.8, 89.9, 68.9, 62.7, 34.3, 33.9, 20.7, 19.1, 14.2.

IR (ATR/cm^{-1}) 3401.0, 3363.9, 2964.38, 2866.6, 1720.0, 1610.3, 1370.4, 1305.8 1119.1, 1083.4, 704.3

HRMS (ESI): $C_{21}H_{23}Cl_2N_2O_3^+$ [$(M+H)^+$]: calcd.: 421.1080; found: 421.1079.

(E) X-Ray crystallographic analysis of 4v

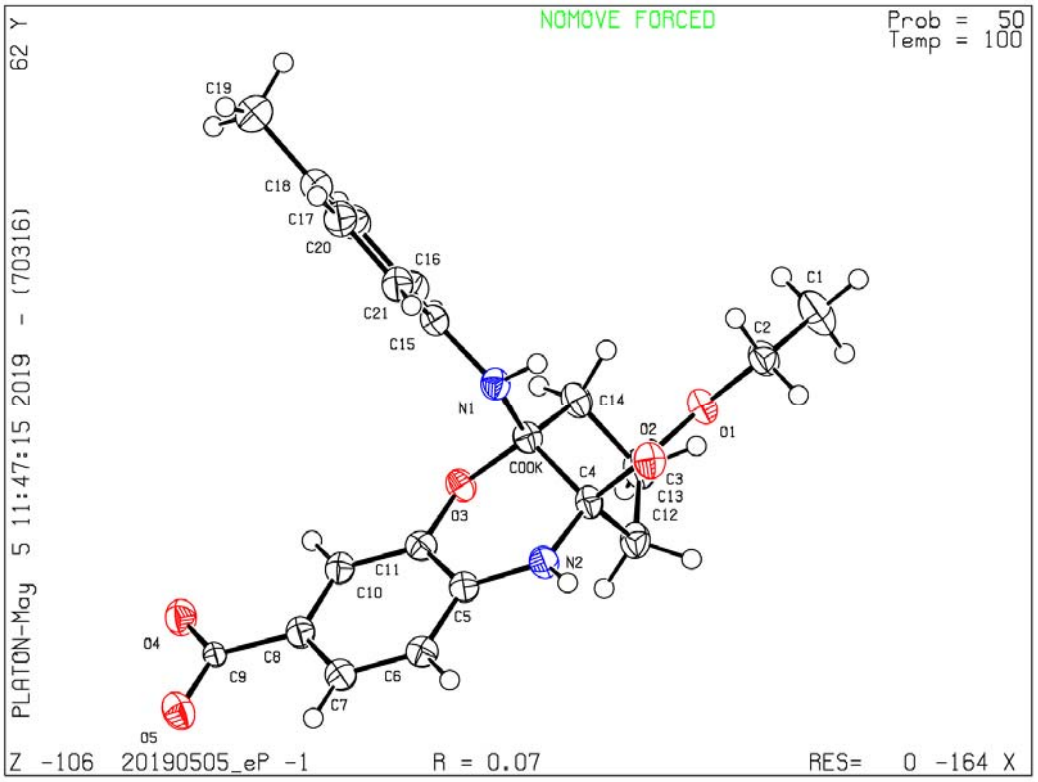
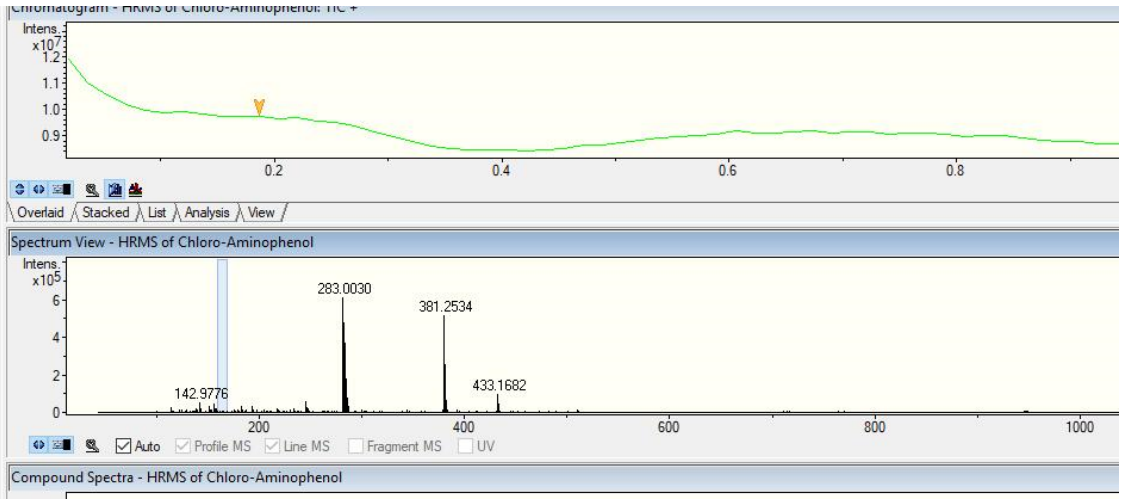


Table 1. Crystal data and structure refinement for **4v**

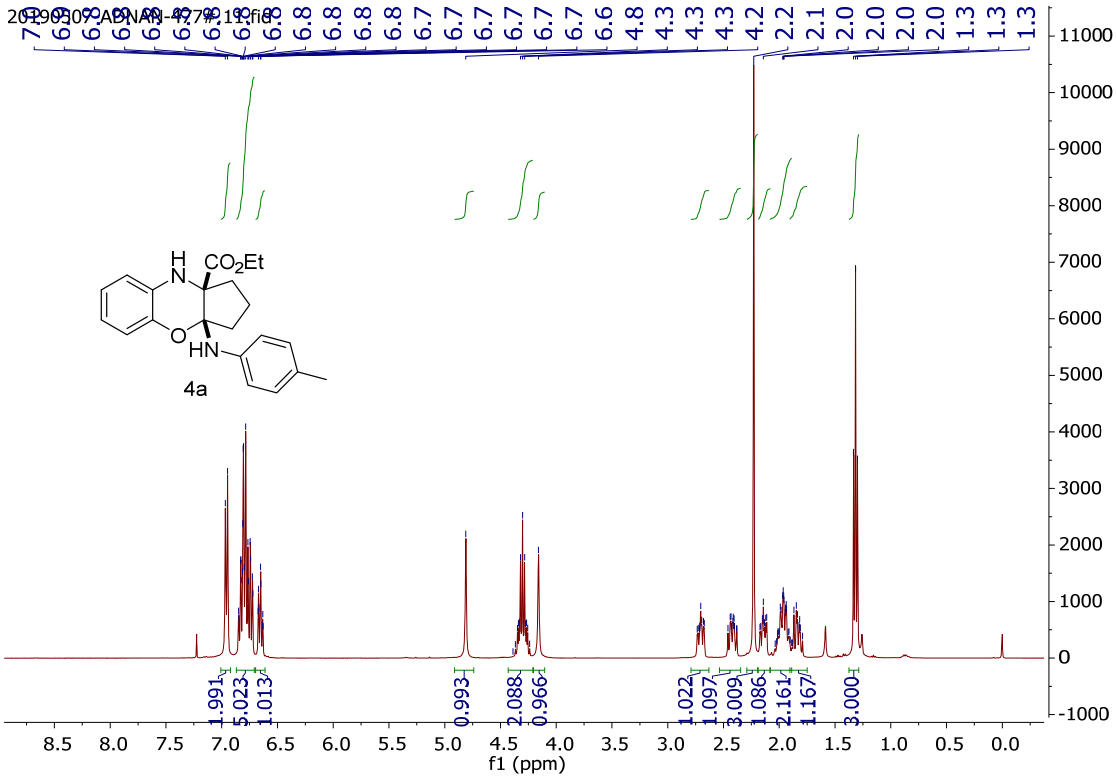
Identification code	20190505_EA
Empirical formula	$C_{22}H_{23}N_2O_5$
Formula weight	395.42
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.9699(3)
b/Å	10.2021(3)
c/Å	14.9823(8)
α/°	72.265(4)
β/°	77.347(4)
γ/°	82.211(4)
Volume/Å^3	987.37(8)
Z	2
ρ_{calc}g/cm^3	1.330
μ/mm^{-1}	0.782
F(000)	418.0

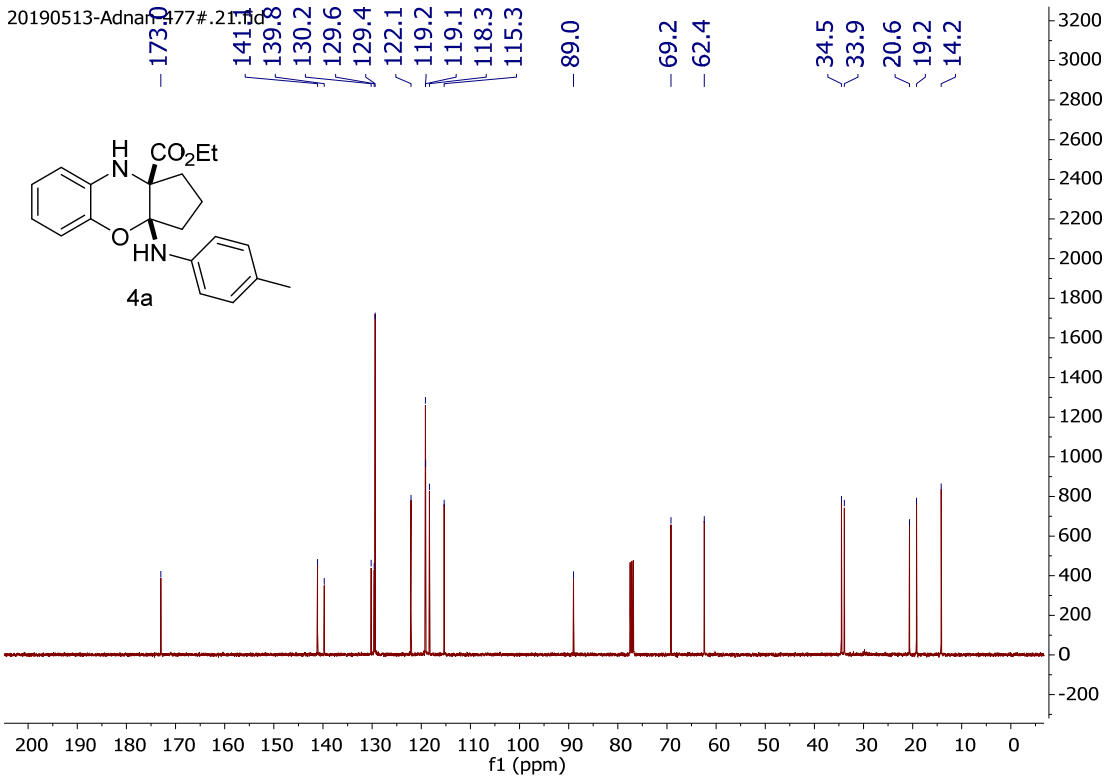
Crystal size/mm^3	? × ? × ?
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.306 to 147.962
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 11, -18 ≤ l ≤ 18
Reflections collected	19112
Independent reflections	3926 [R_{int} = 0.0692, R_{sigma} = 0.0331]
Data/restraints/parameters	3926/0/264
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0683, wR_2 = 0.1926
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1957
Largest diff. peak/hole/ e Å^{-3}	0.67/-0.78

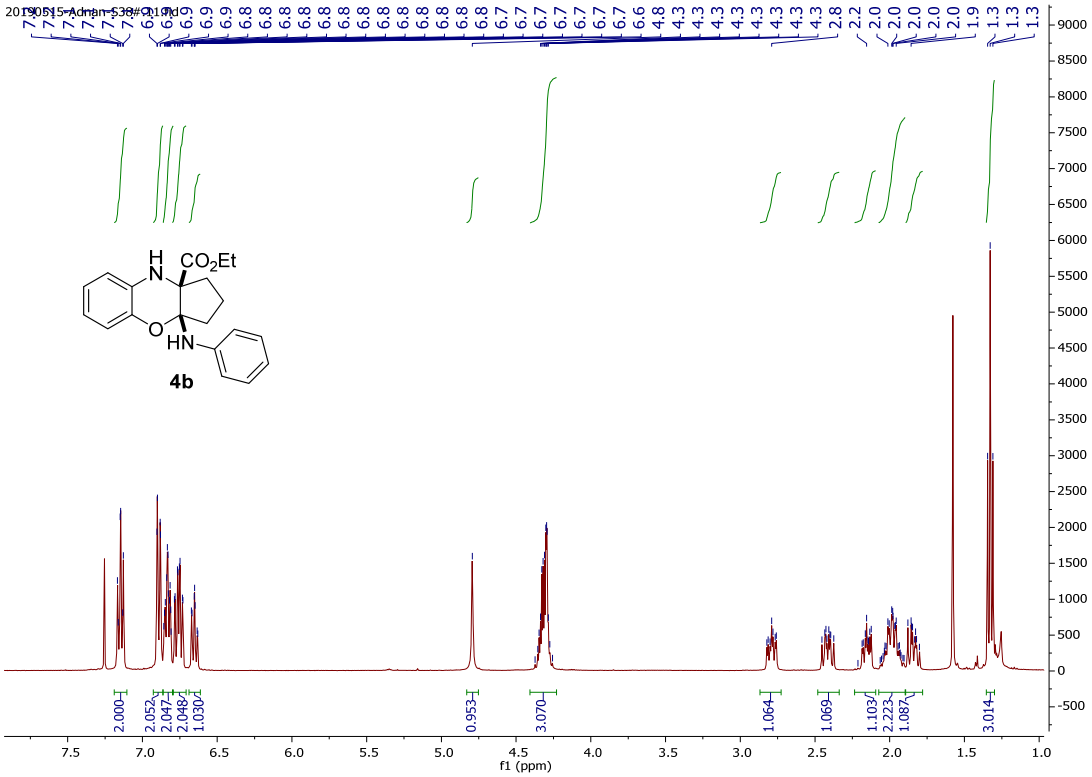
(F) HRMS spectrum of dimer of oQMI 5b



(G) NMR spectra of cycloadducts



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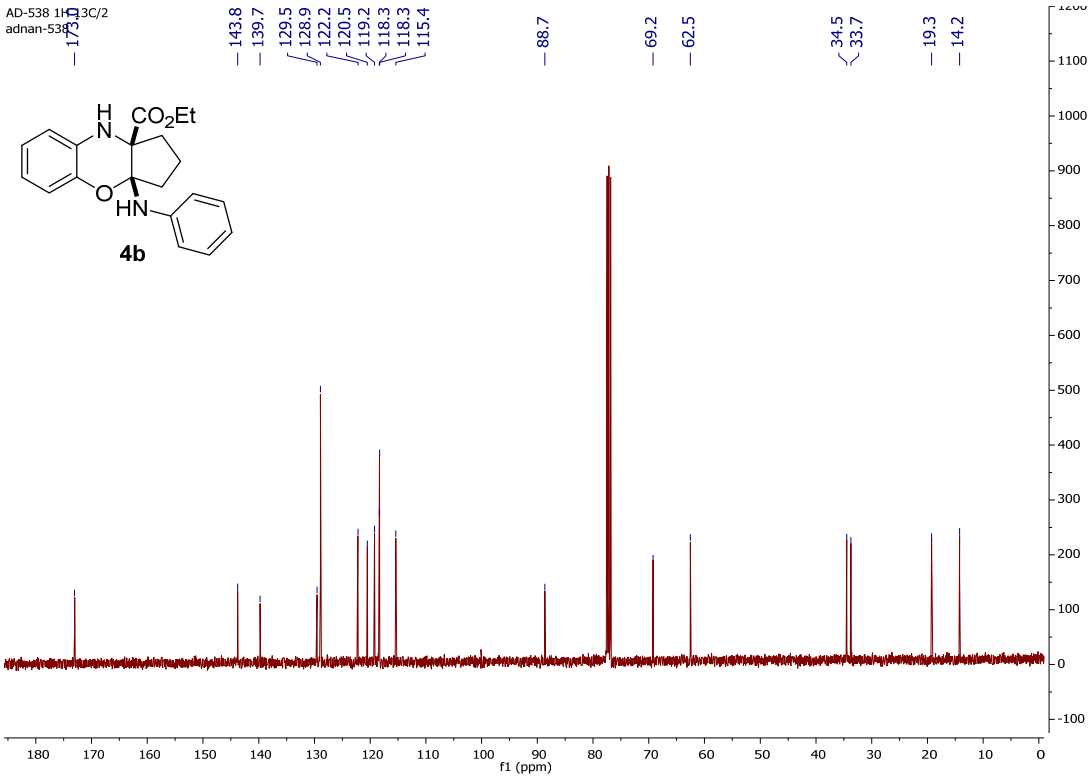
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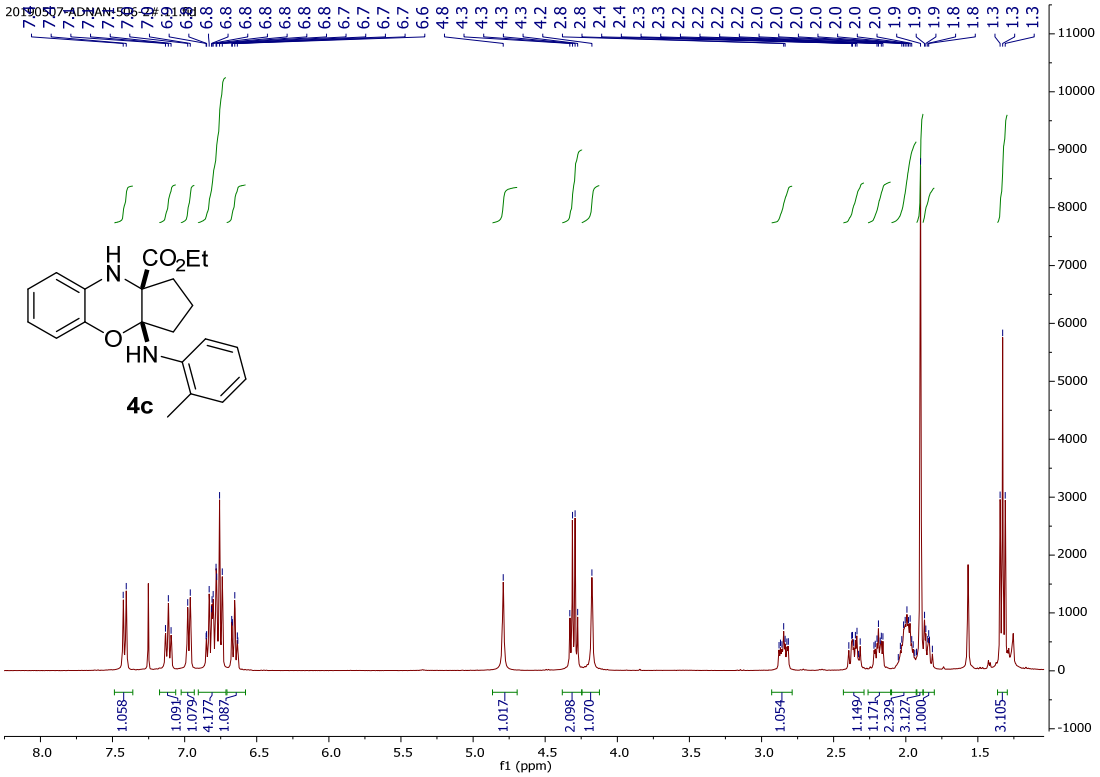
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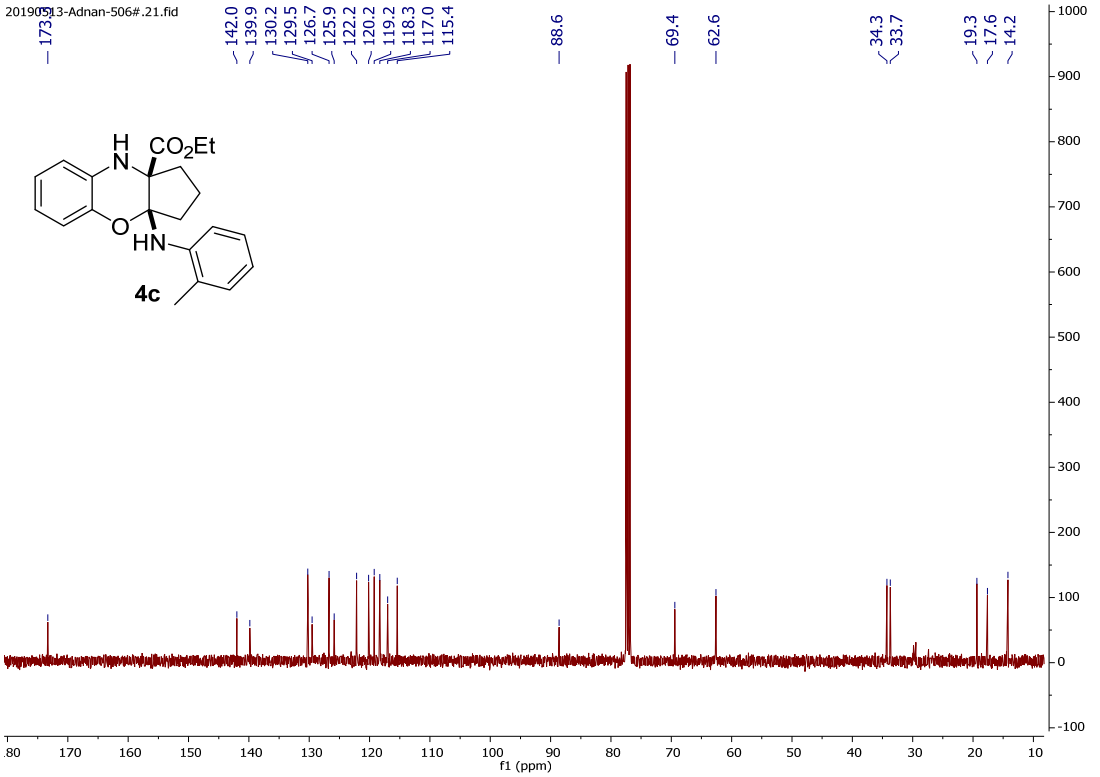
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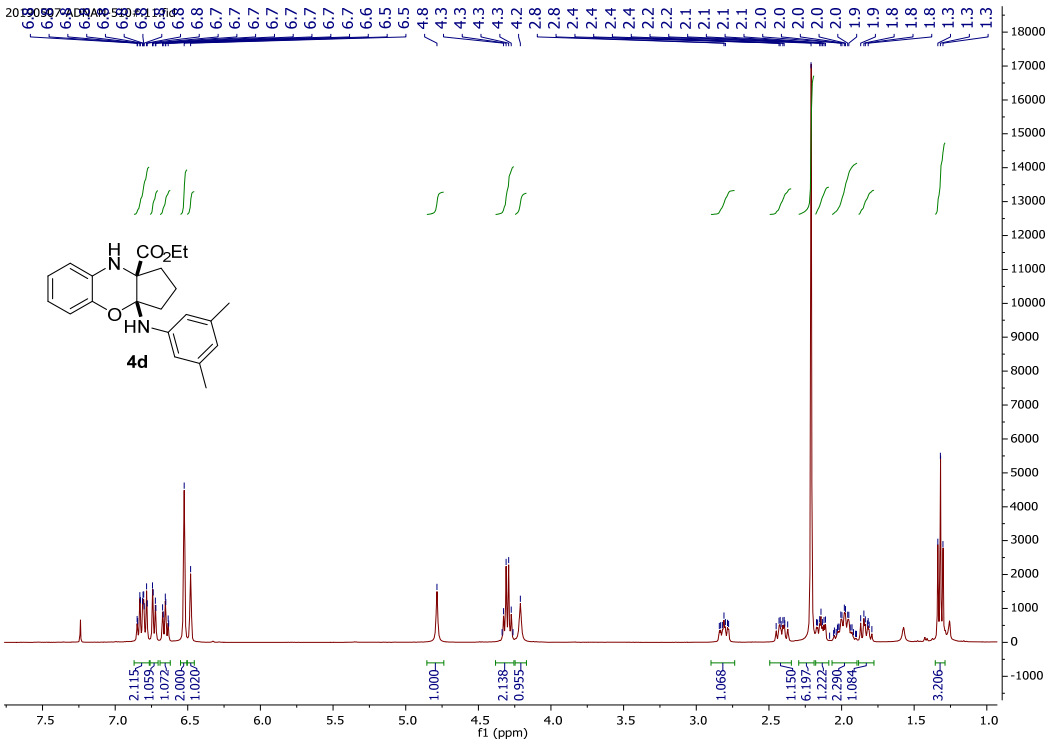
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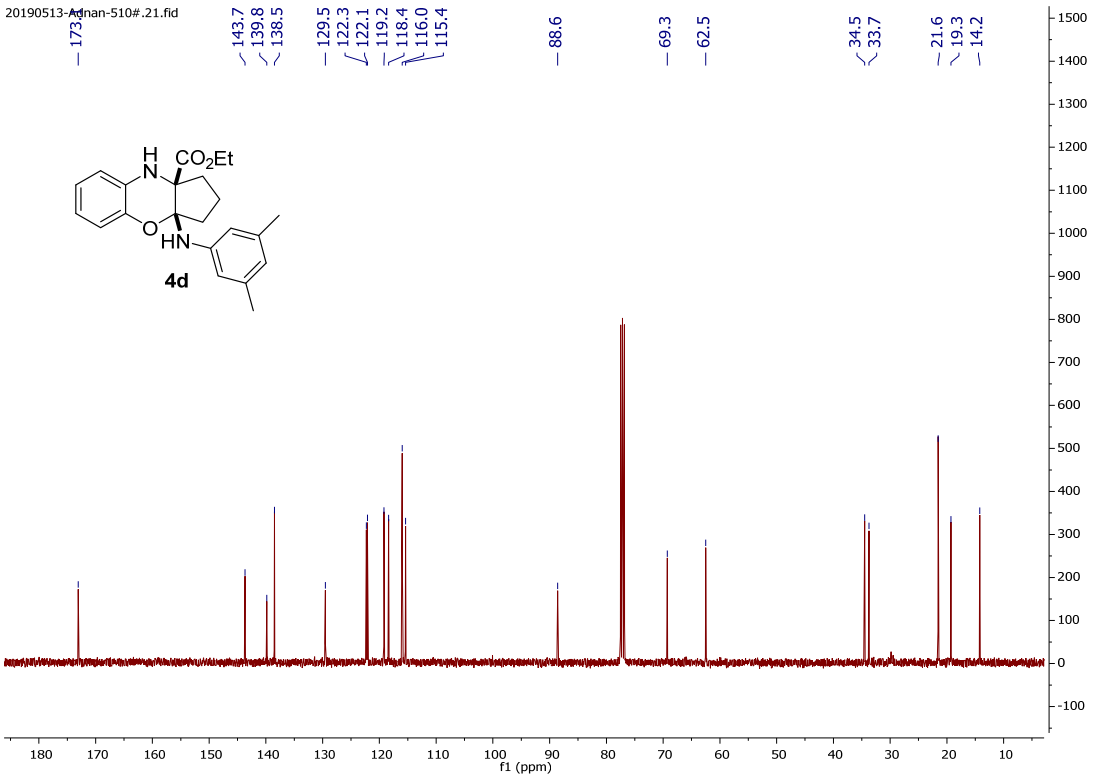
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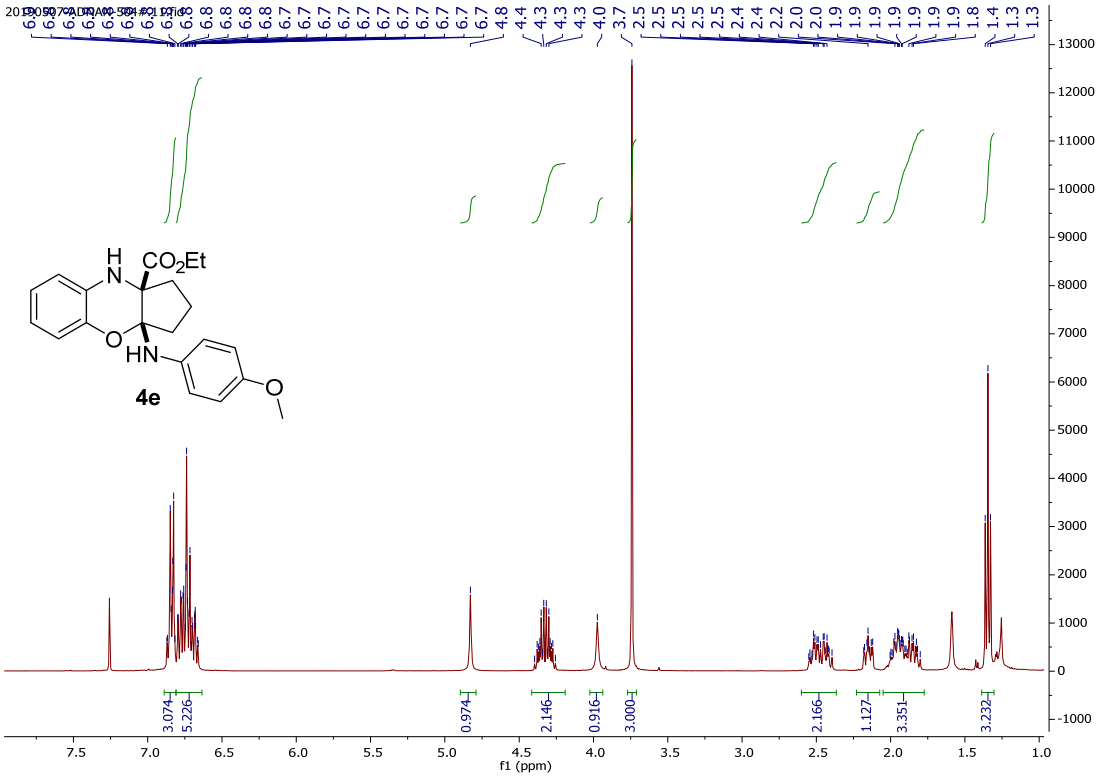
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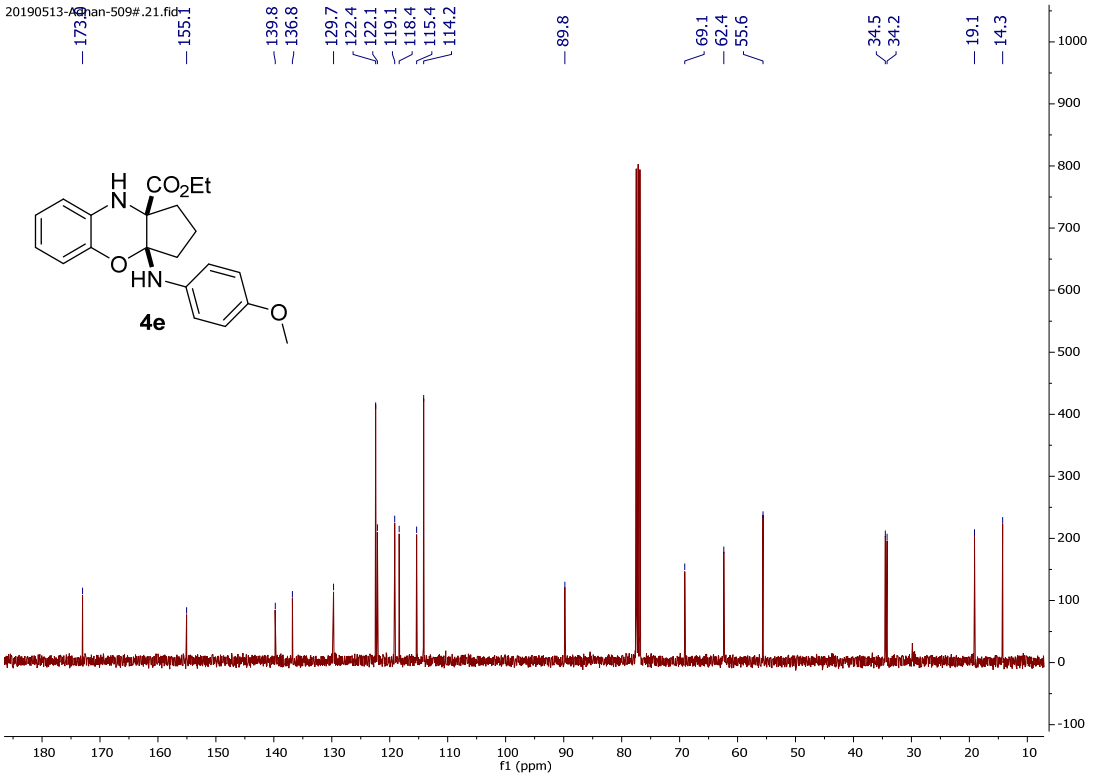
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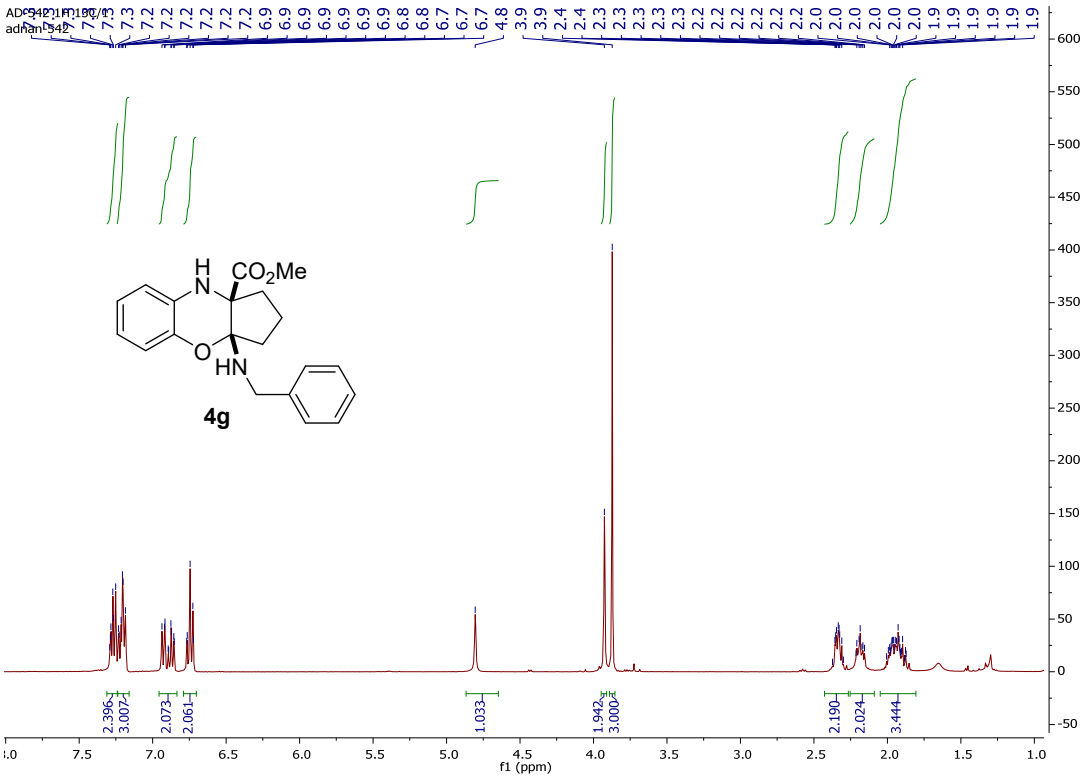
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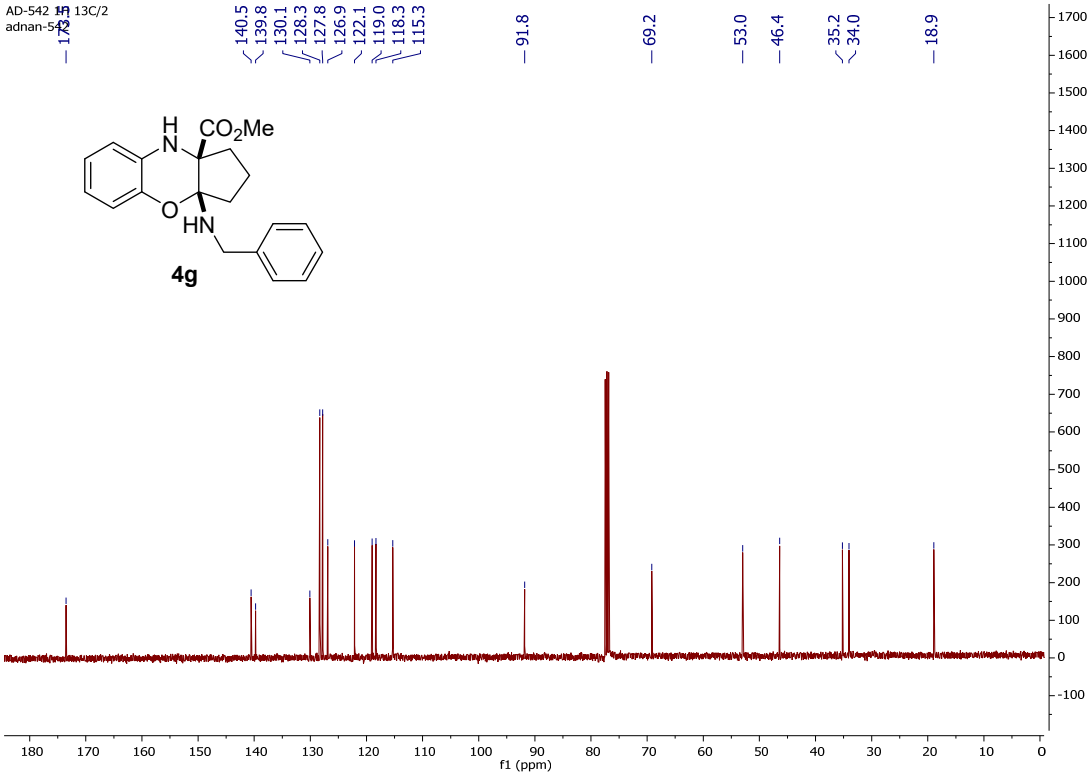
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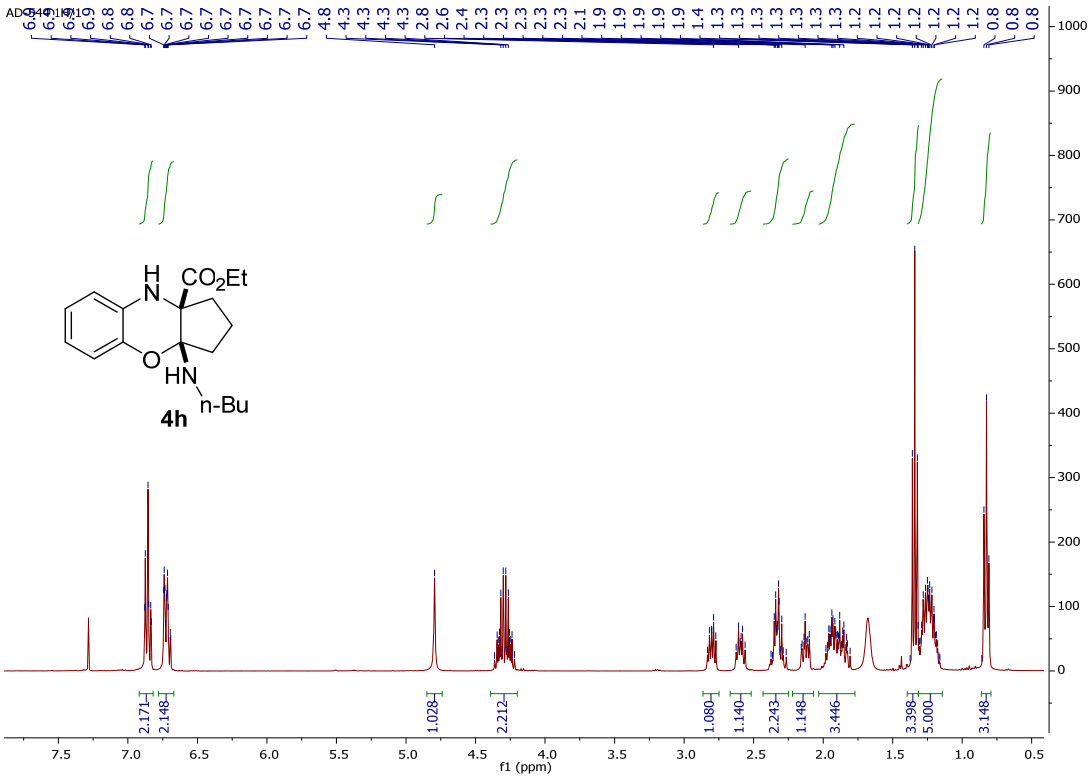
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n-Bu
4h
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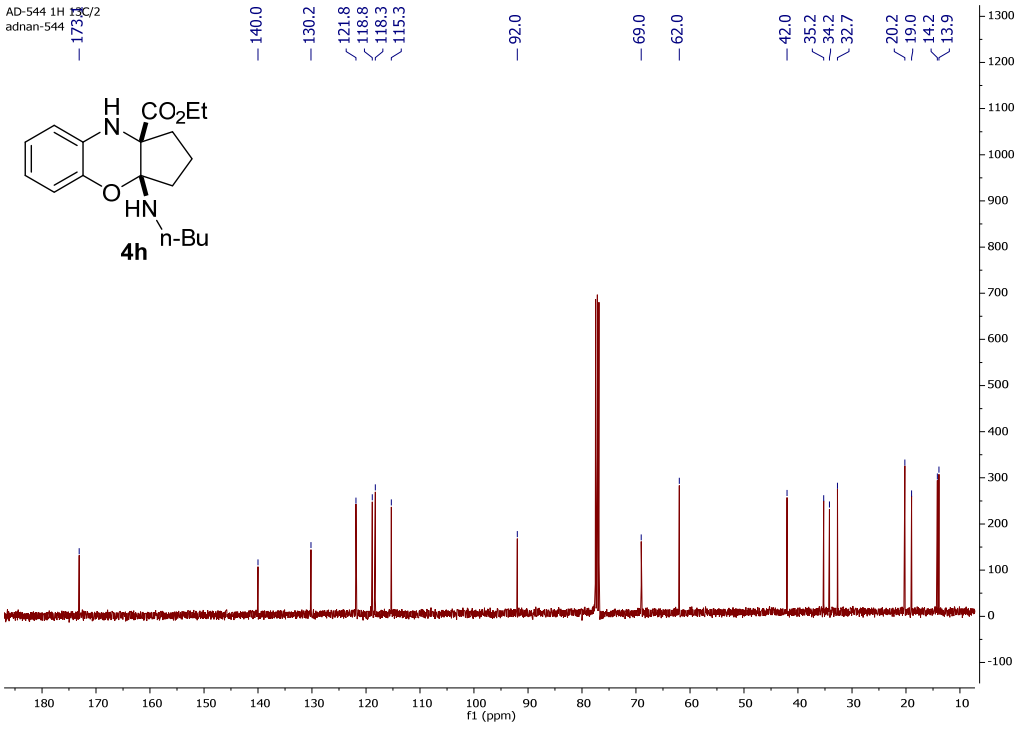
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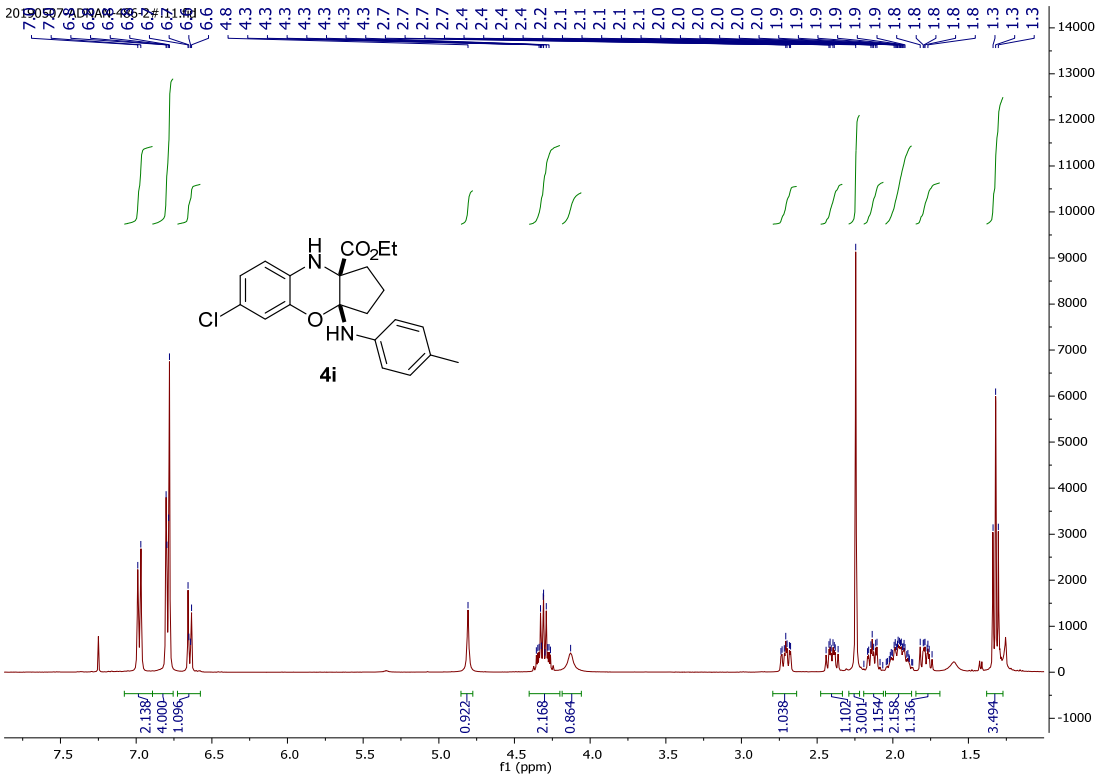
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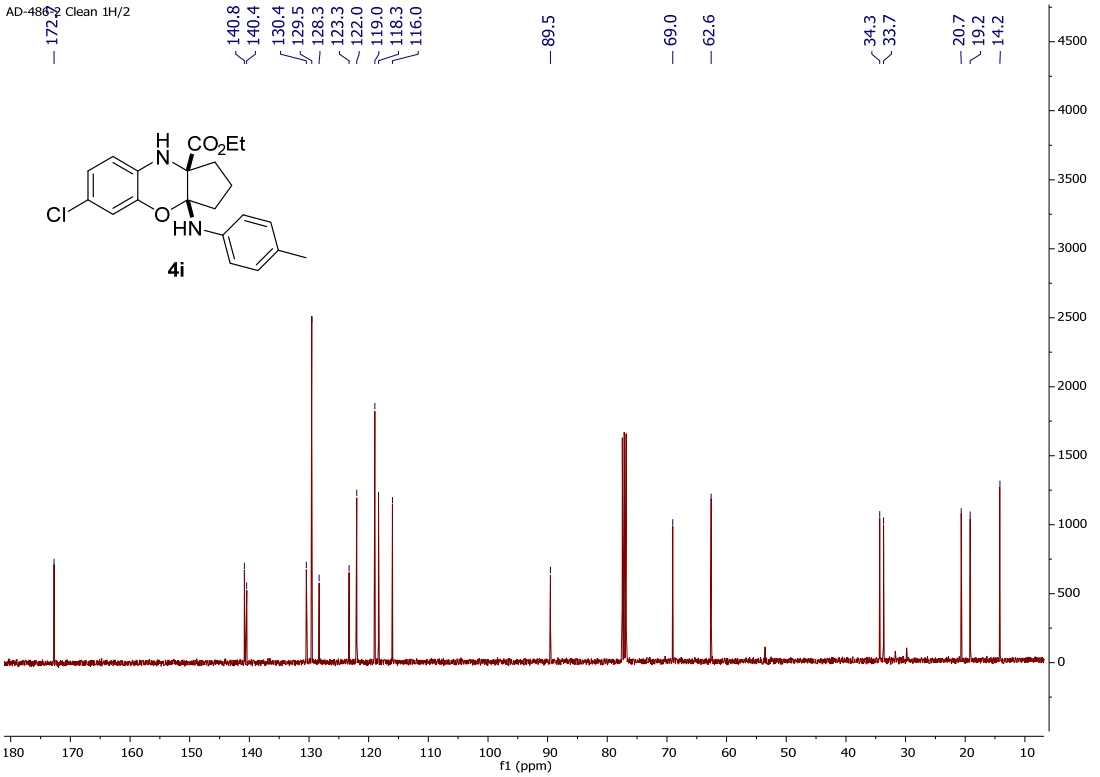
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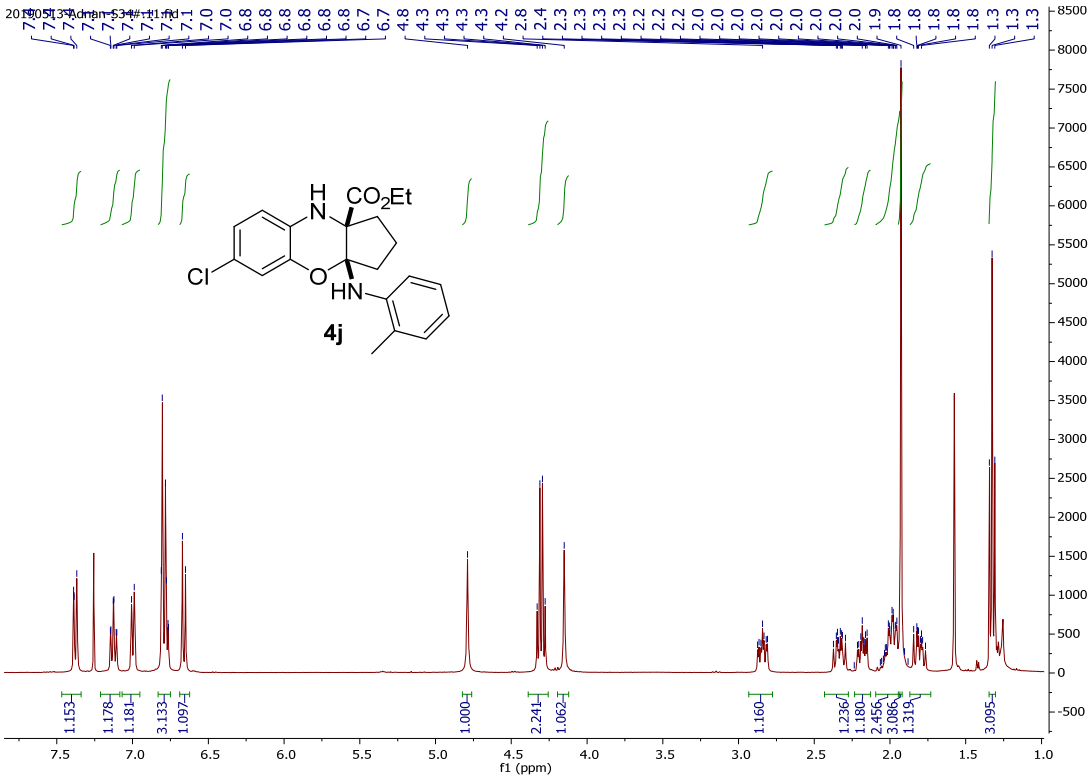
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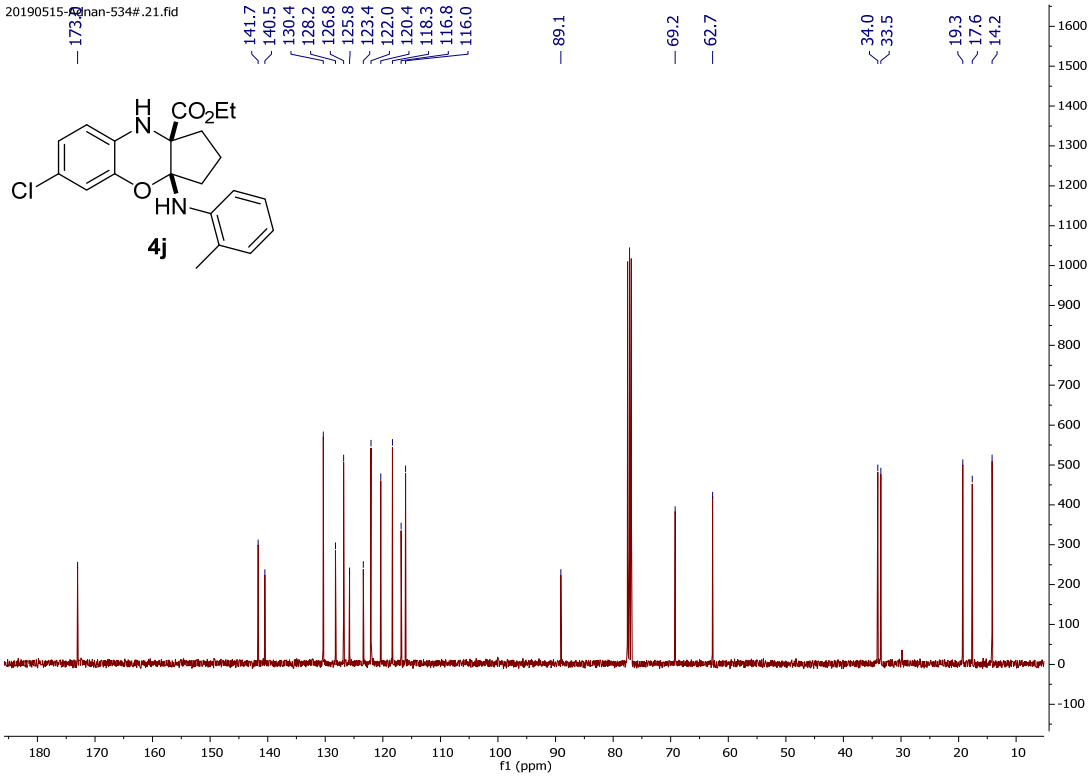
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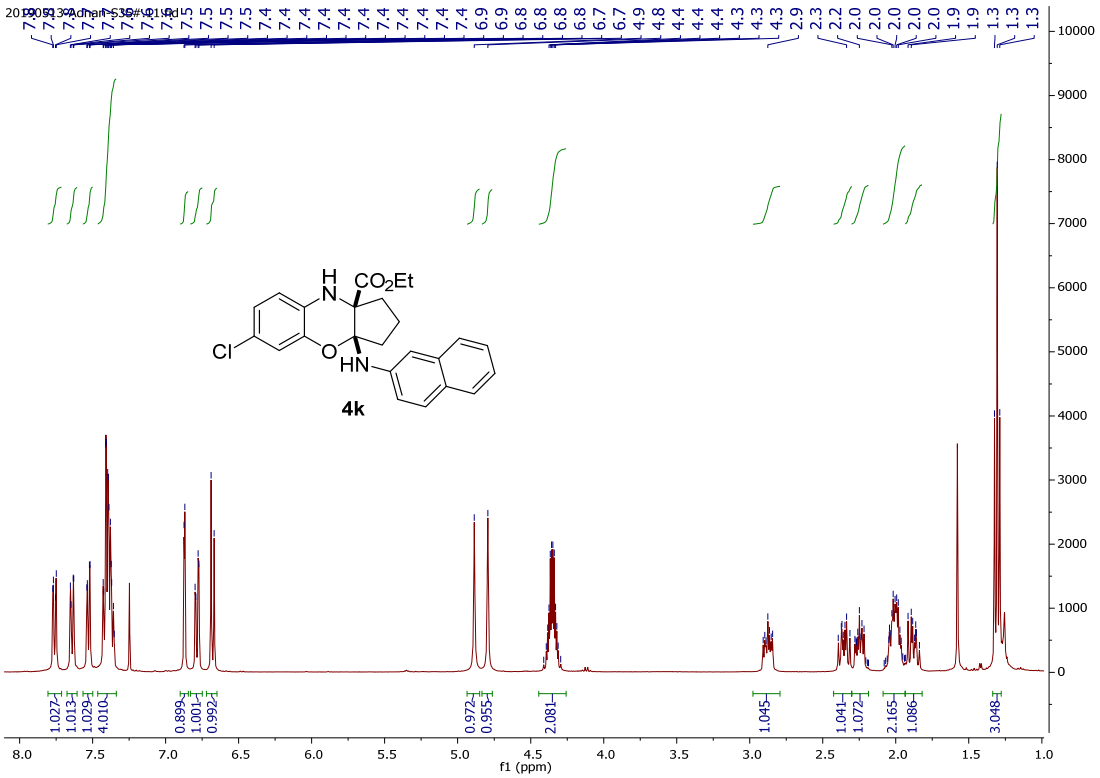
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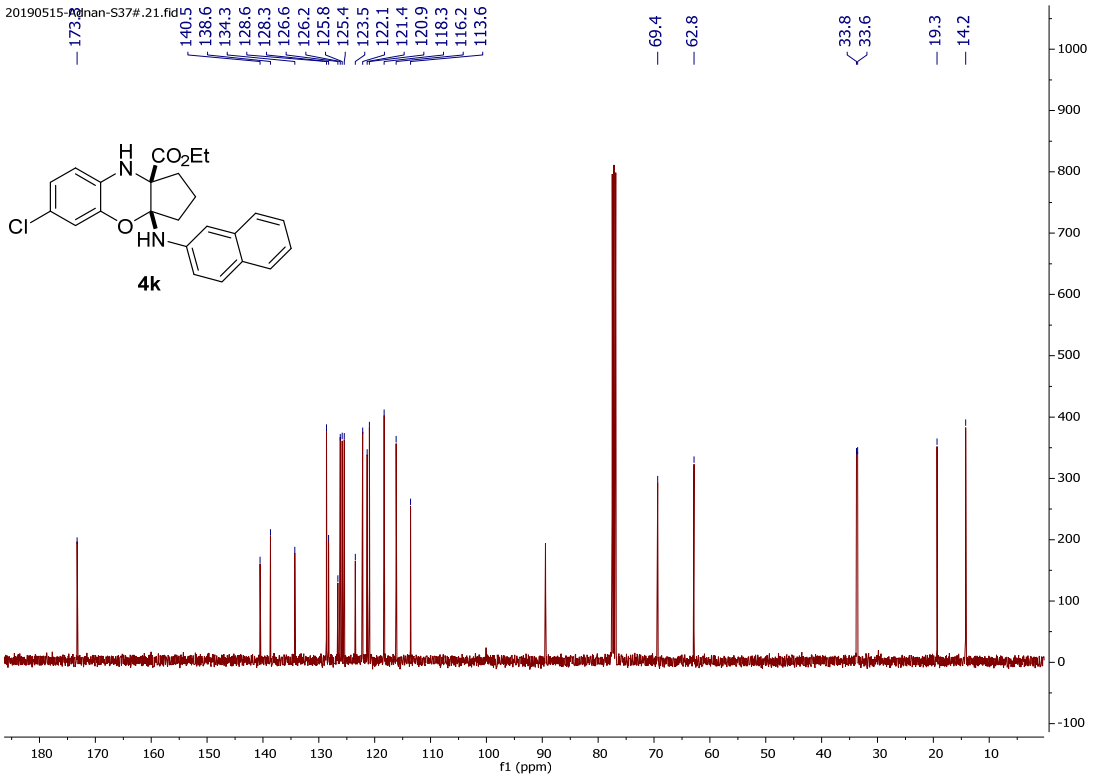
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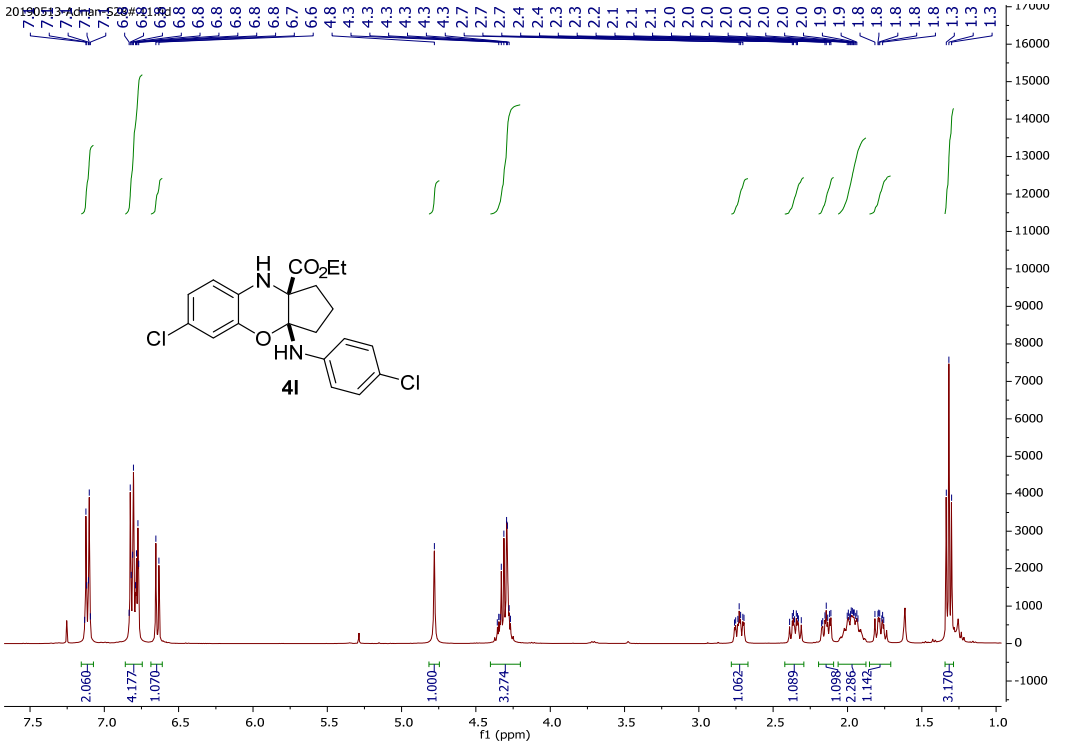
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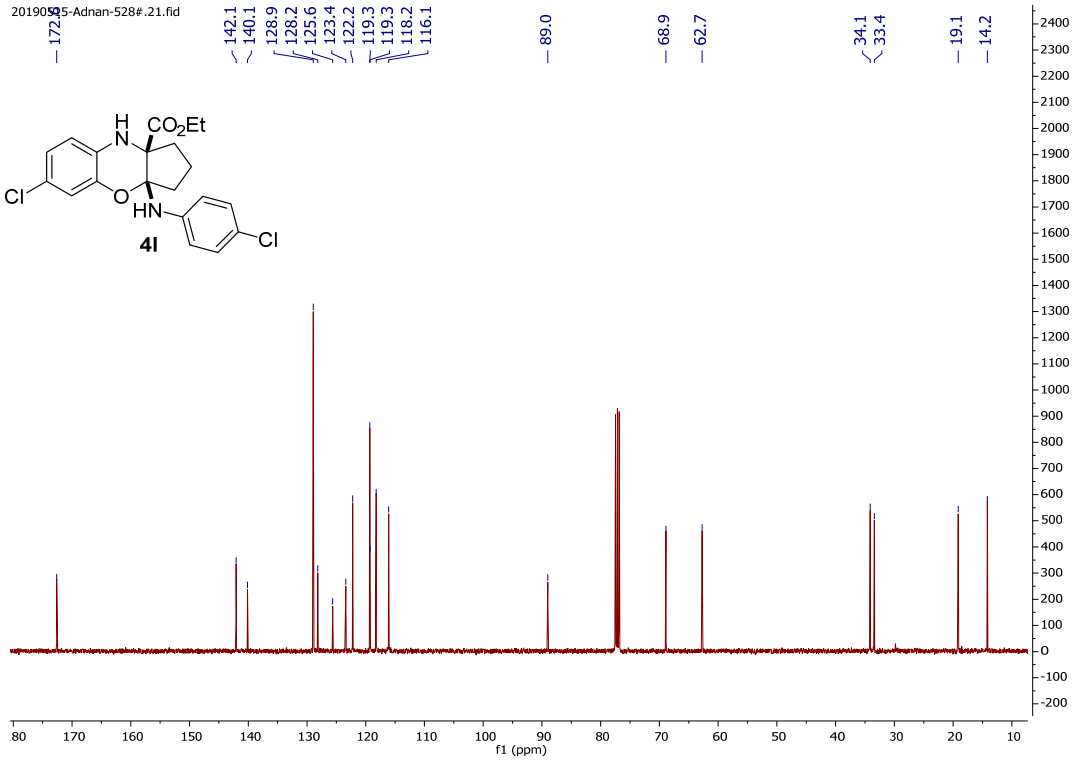
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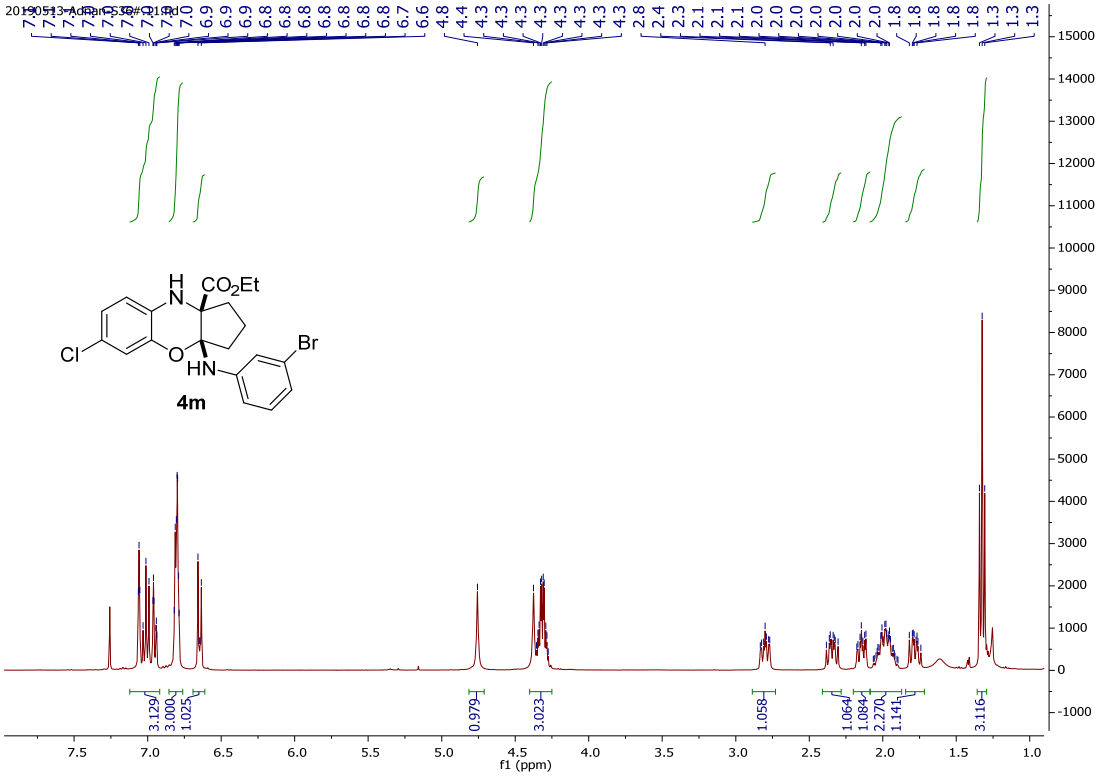
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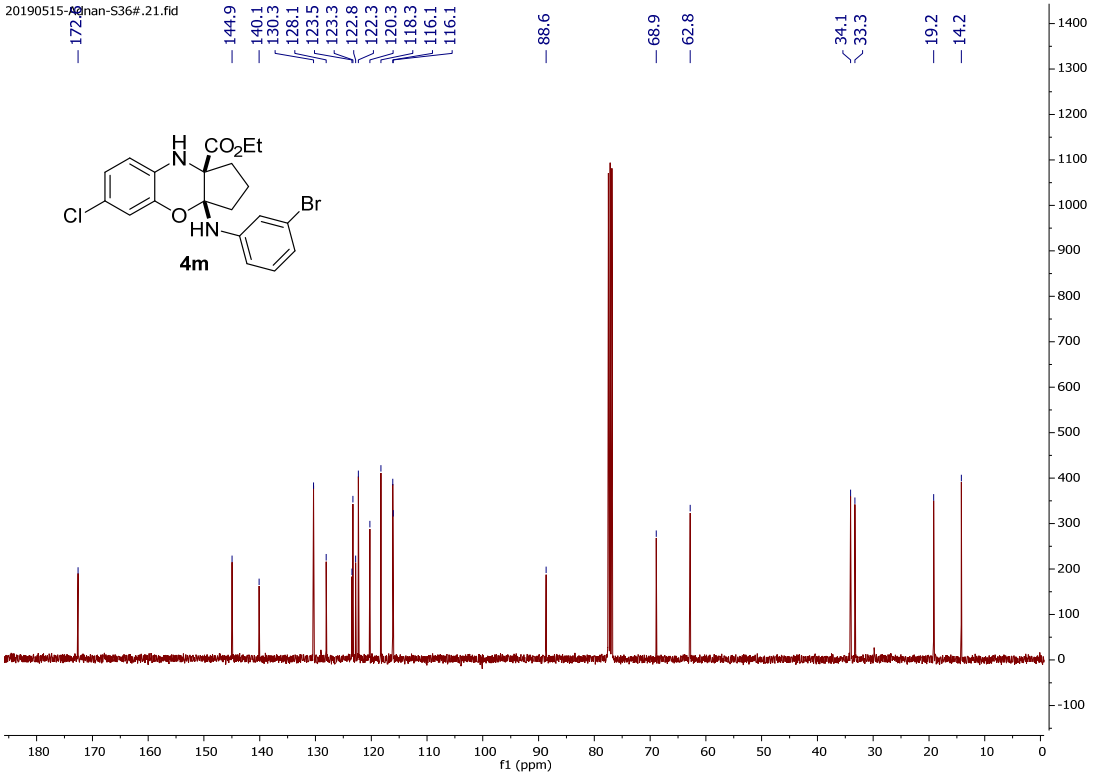
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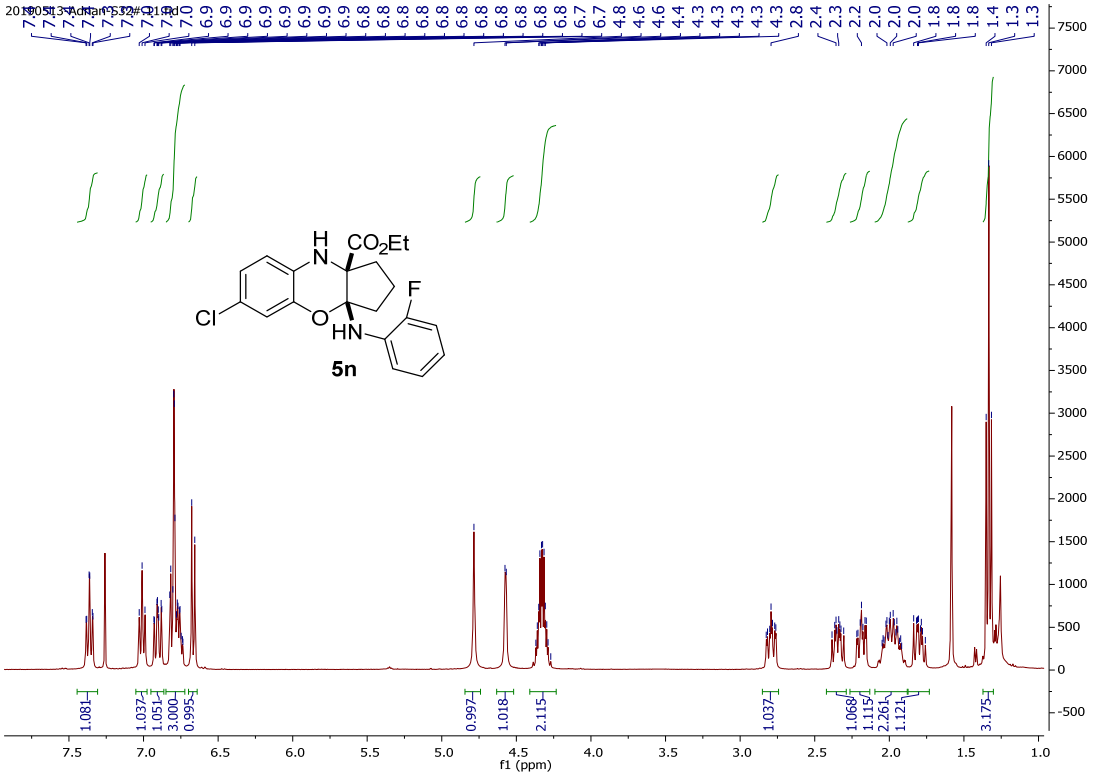
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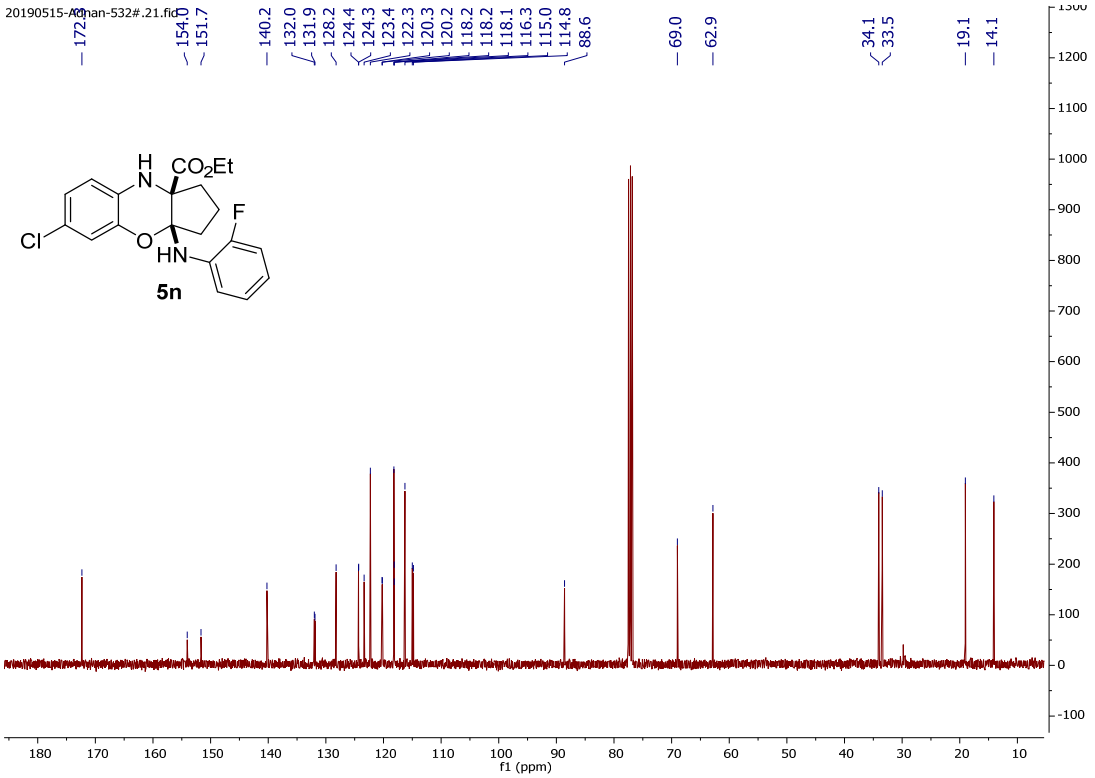
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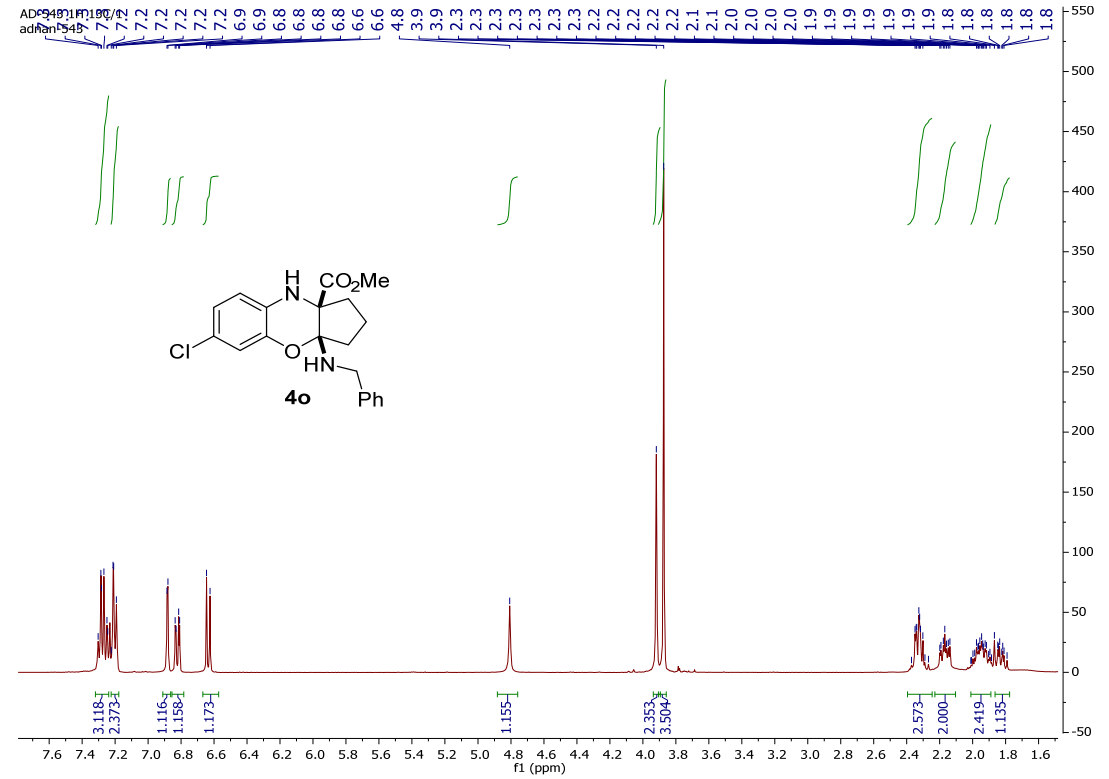
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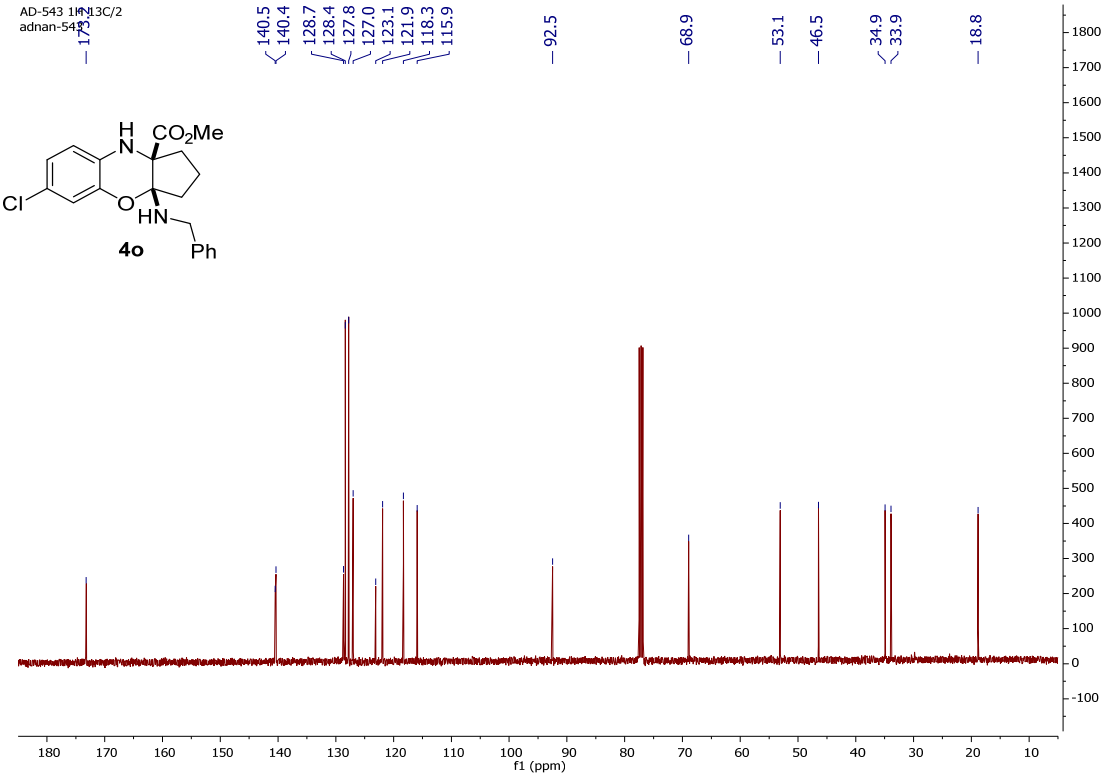
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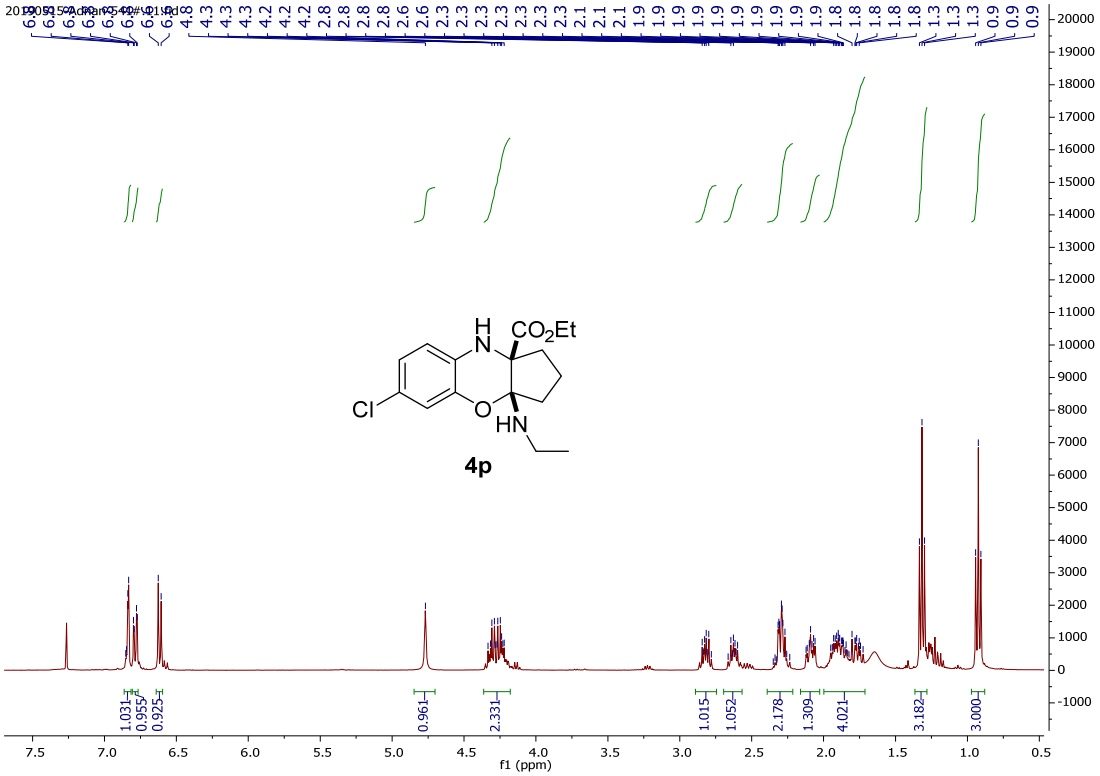
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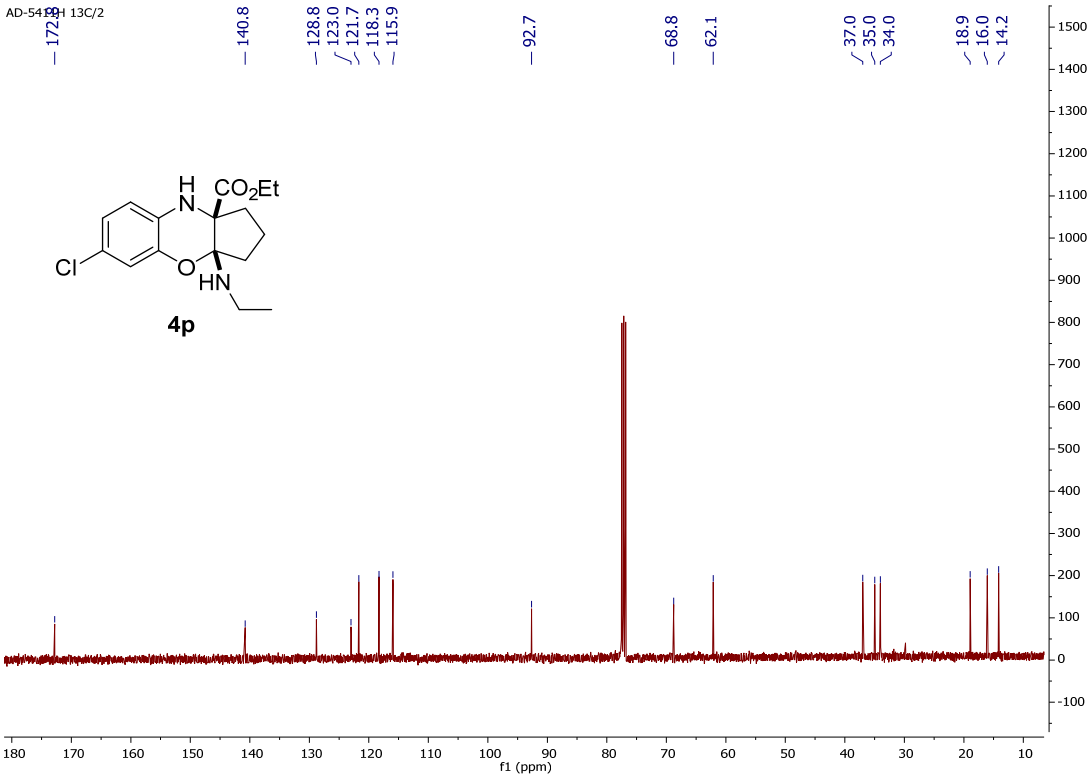
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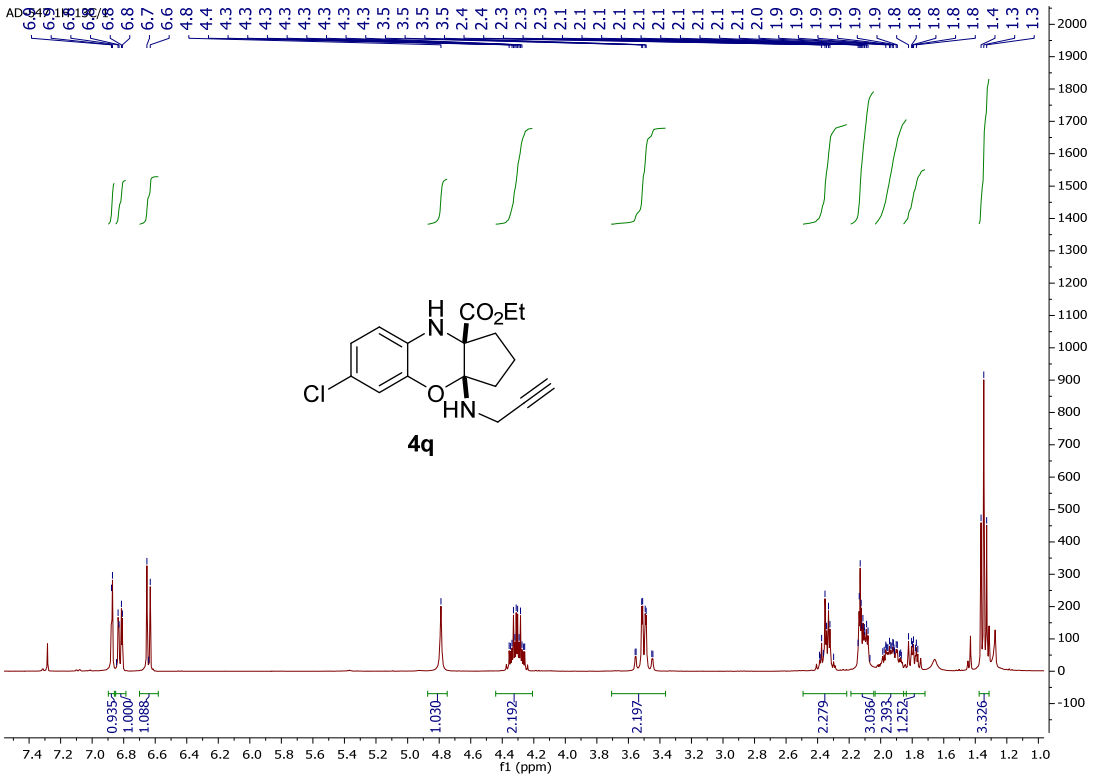
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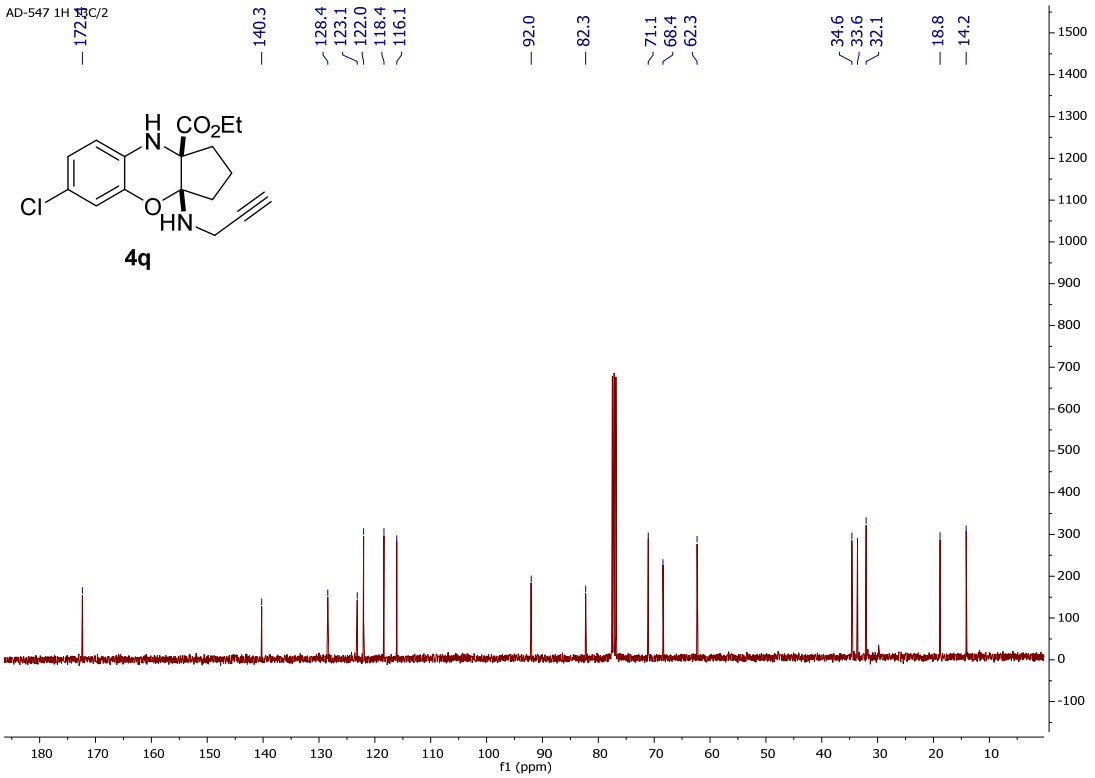
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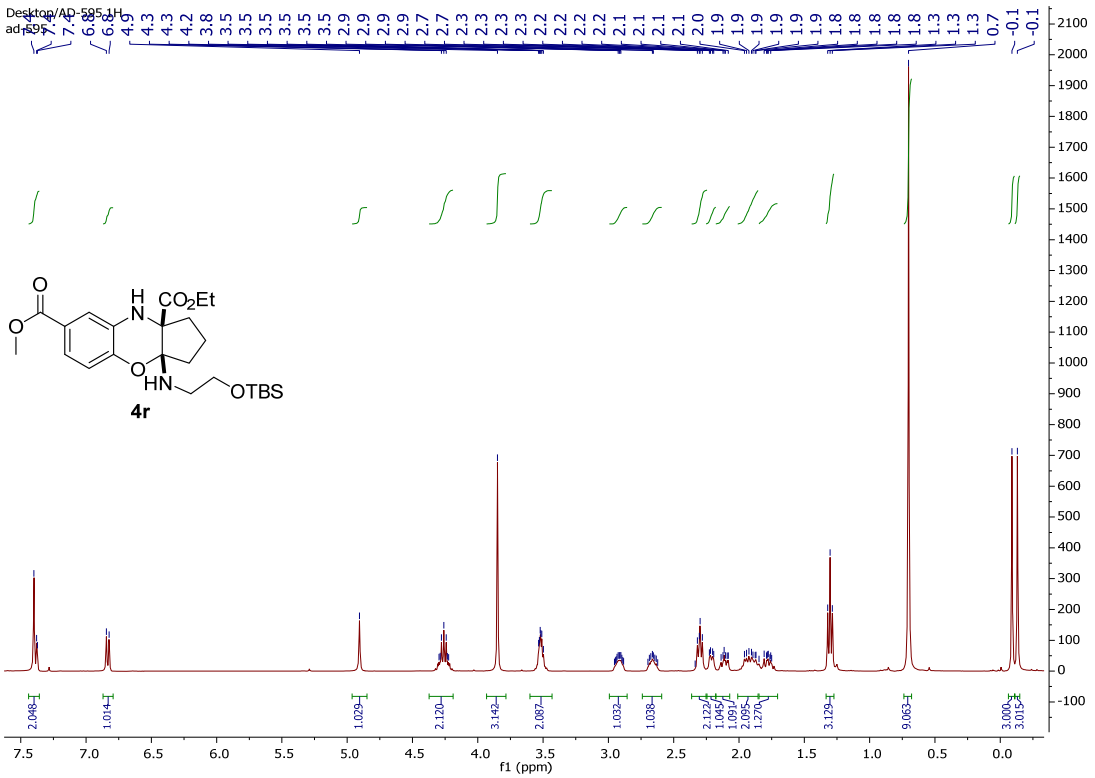
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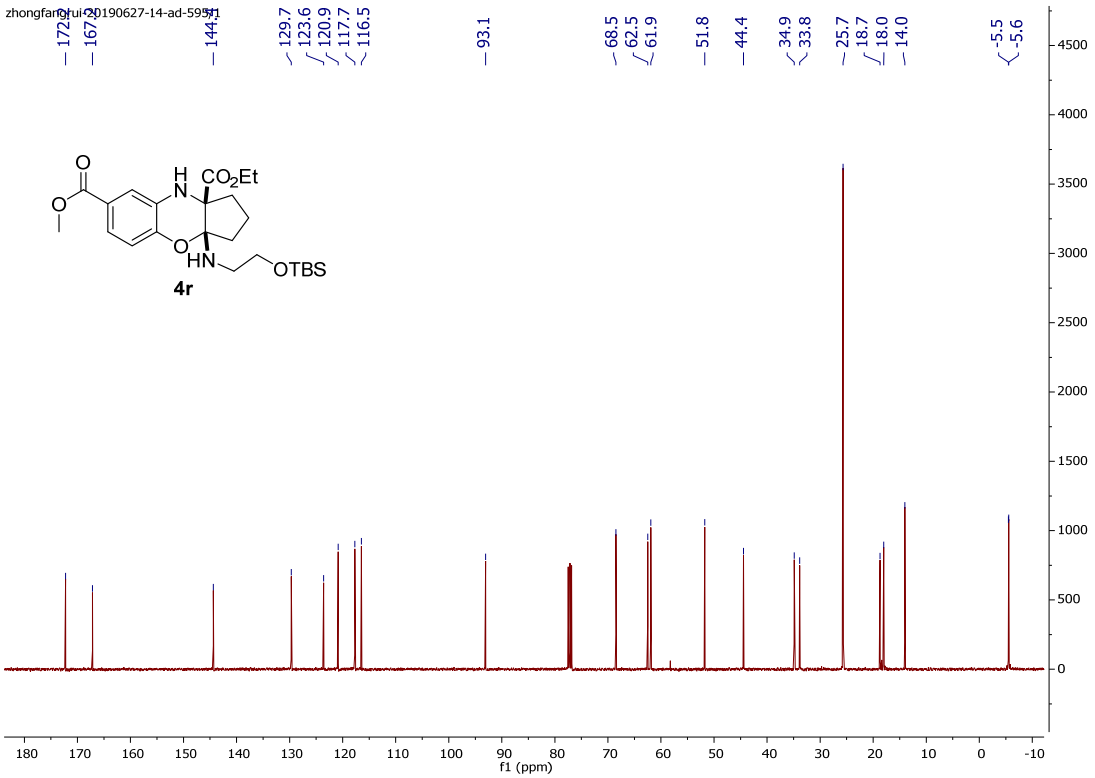
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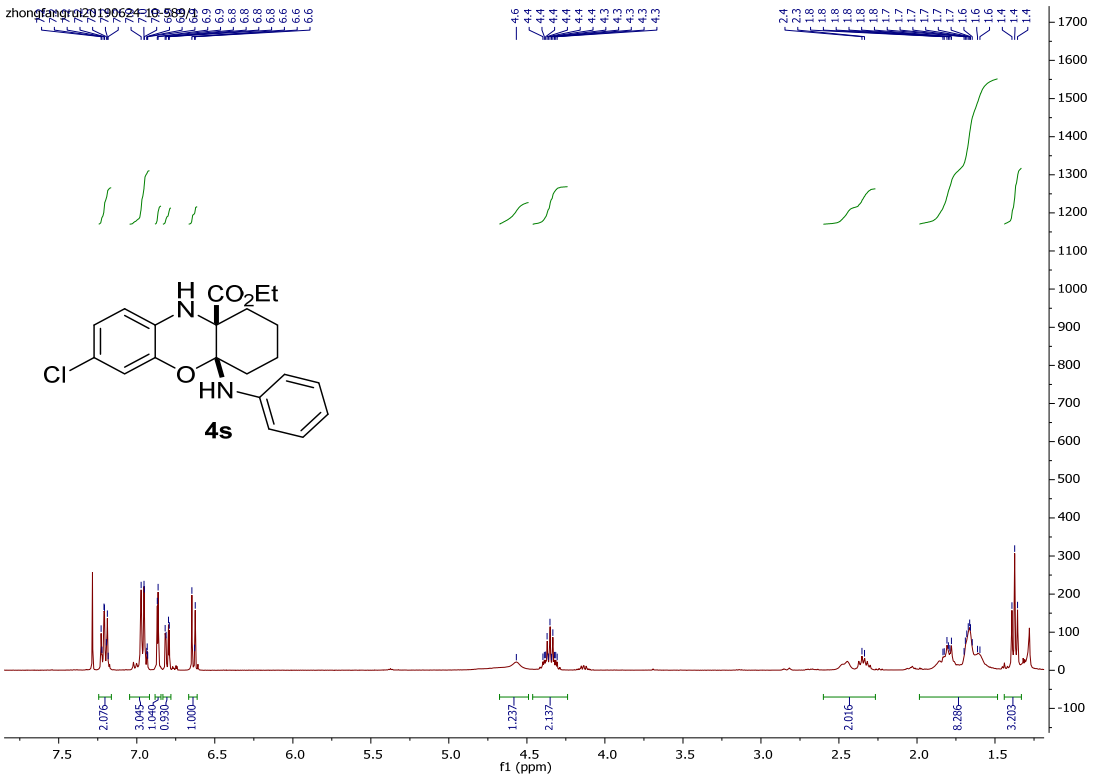
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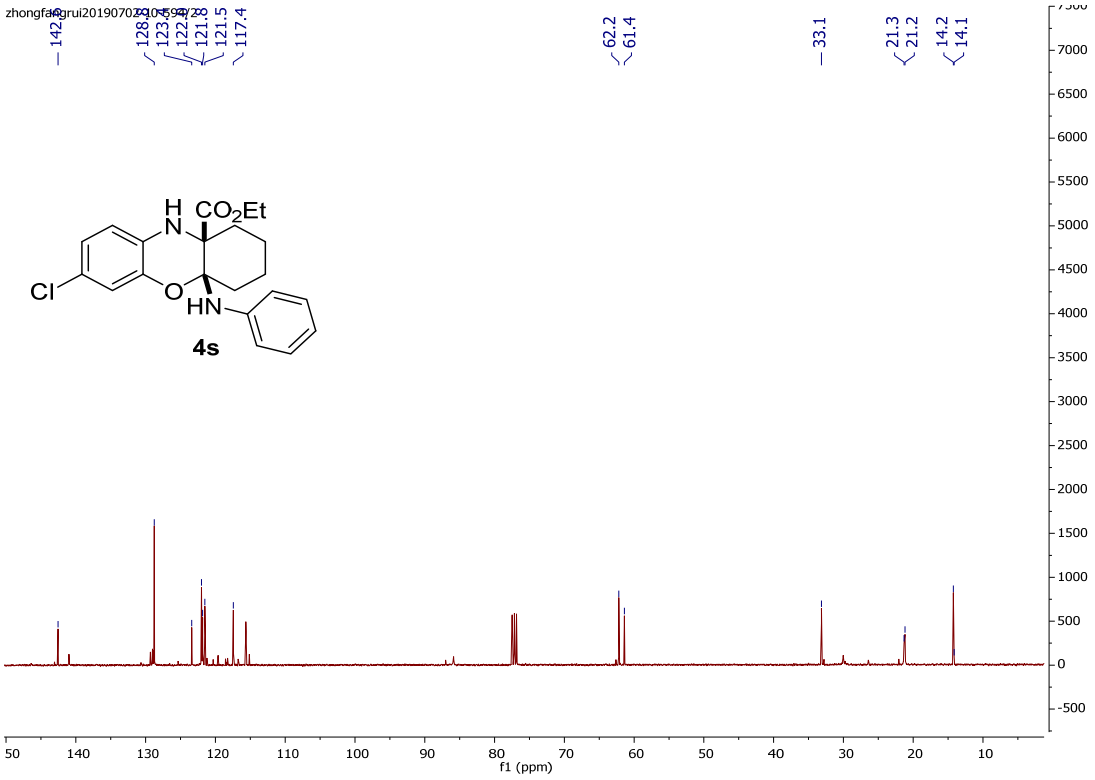
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14.1
H
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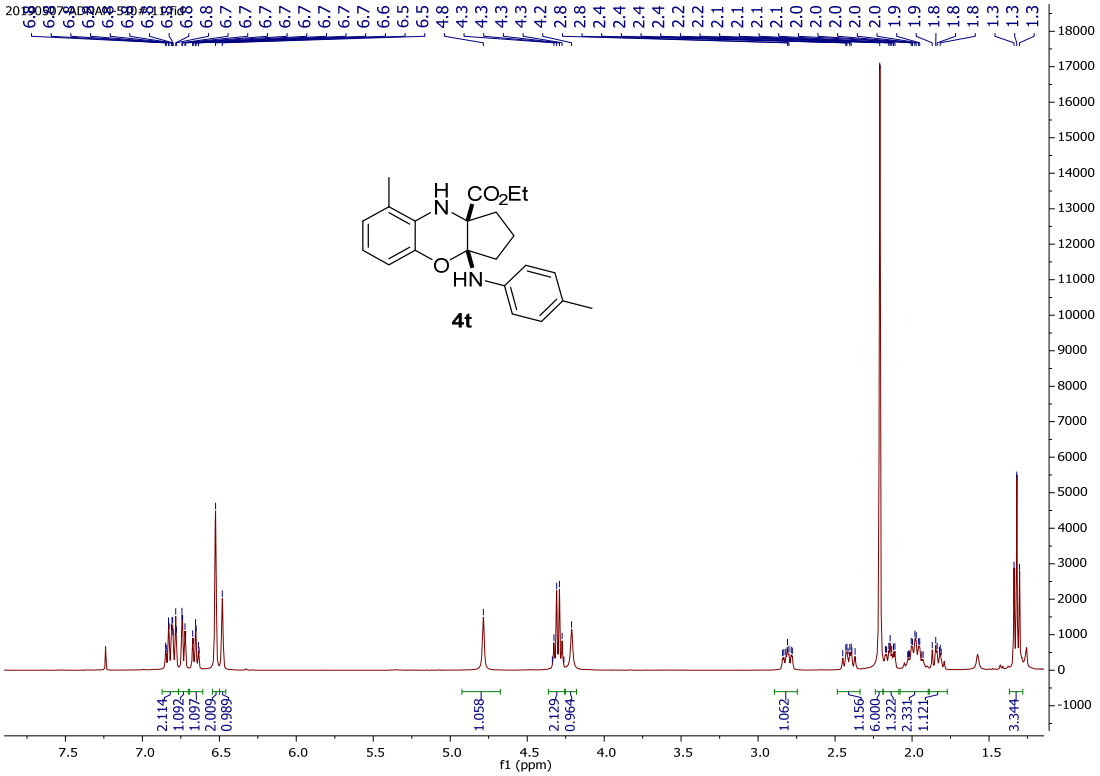
CO2Et
Cl
O
HN
4s
f1 (ppm)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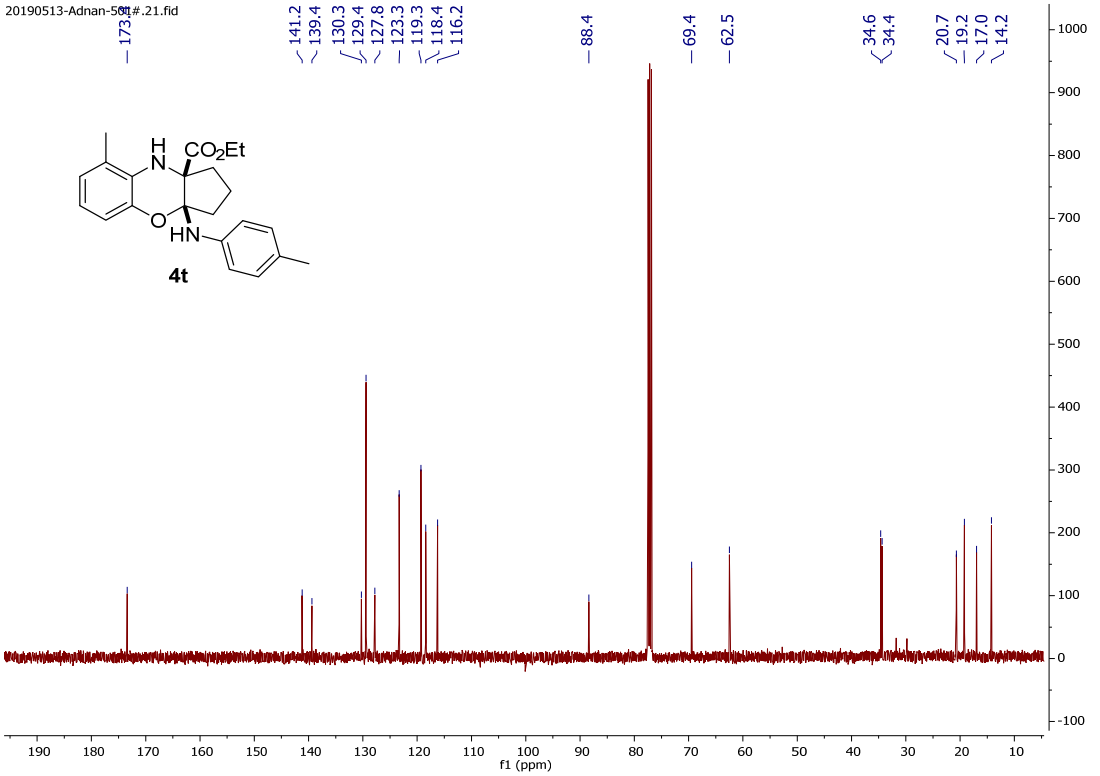
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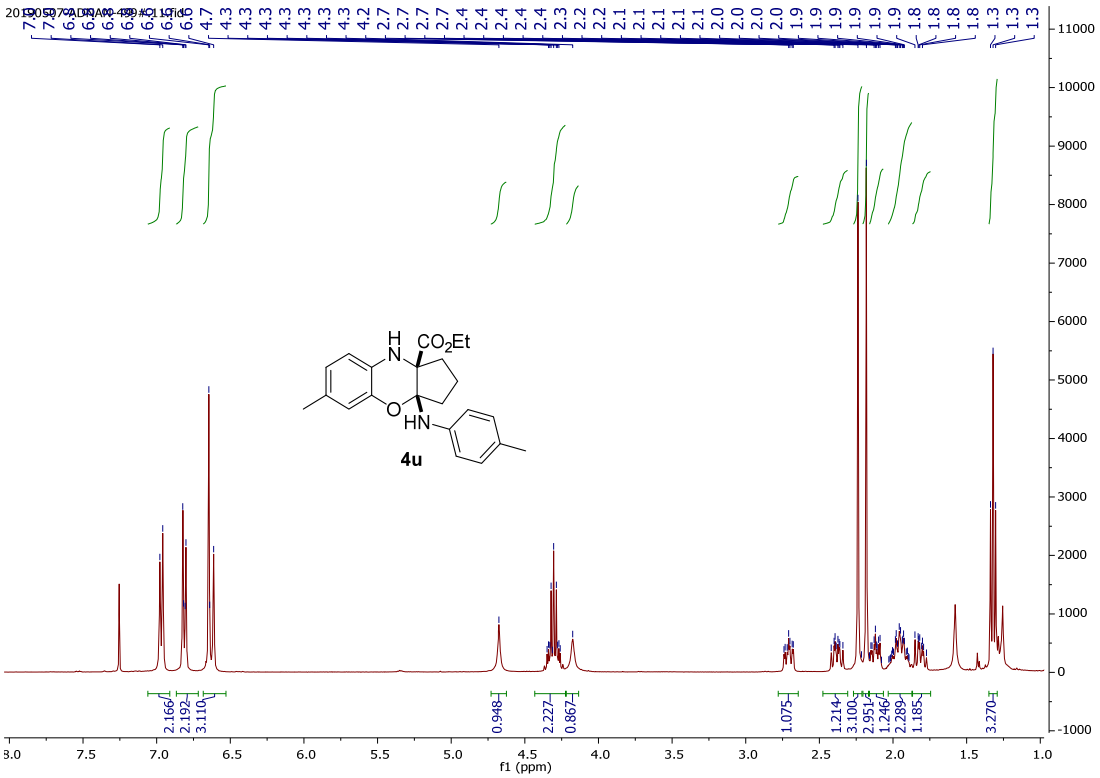
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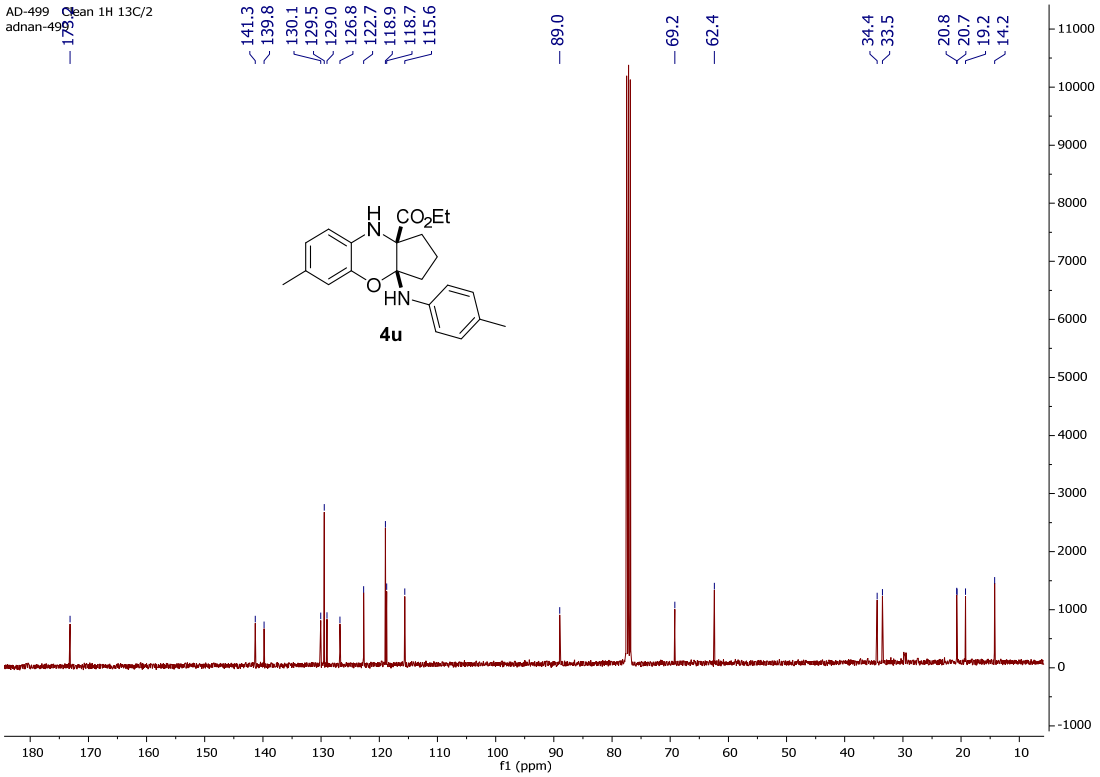
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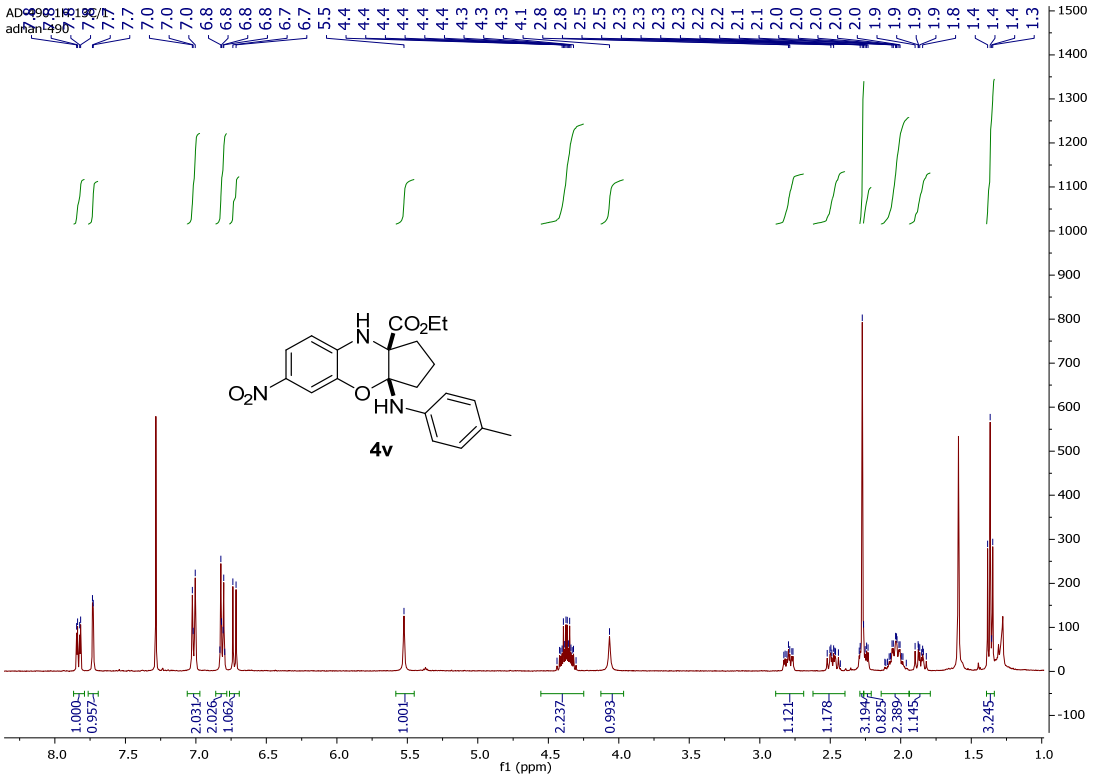
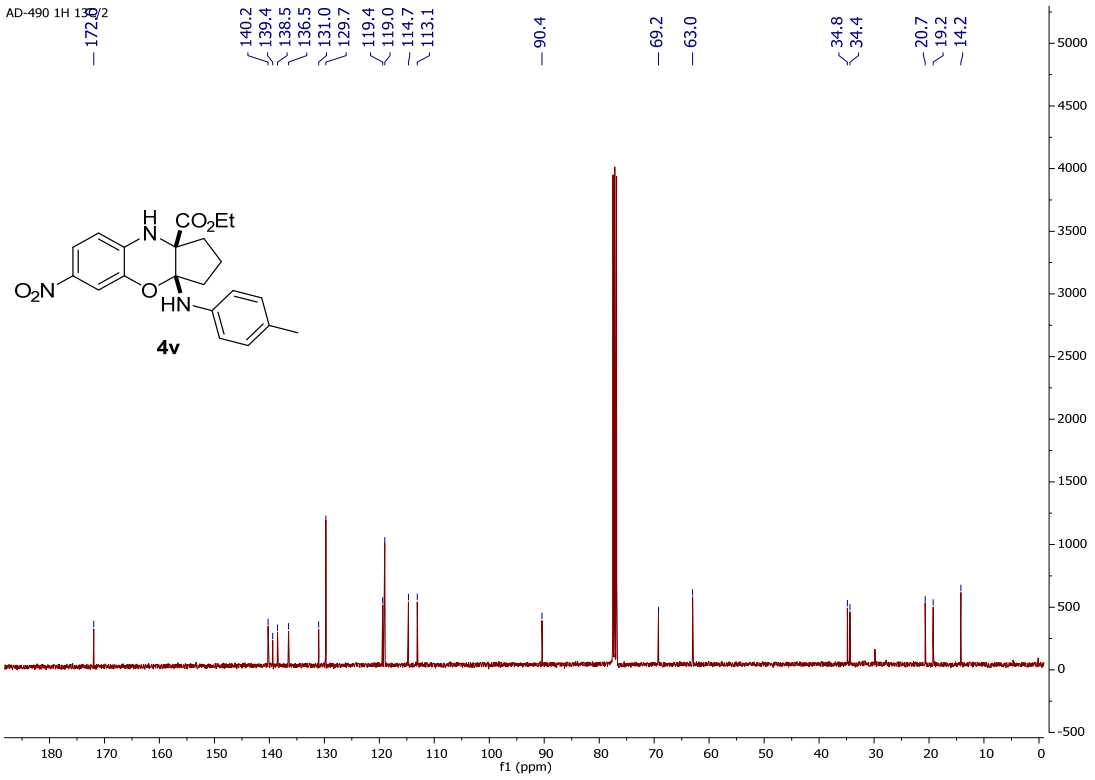
4u
f1 (ppm)


AD-490 1H 13C/1
adnan c490
7.7 7.7 7.0 7.0 6.8 6.8 6.8 6.8 6.7 6.7 5.5 4.4 4.4 4.4 4.4 4.4 4.3 4.3 4.3 4.1 2.8 2.8 2.5 2.5 2.3 2.3 2.3 2.3 2.2 2.2 2.1 2.1 2.0 2.0 2.0 2.0 2.0 1.9 1.9 1.9 1.9 1.8 1.4 1.4 1.4 1.3
1.000 0.957 2.031 2.026 1.062 1.001 2.237 0.993 1.121 1.178 3.194 0.825 2.389 1.145 3.245
f1 (ppm)

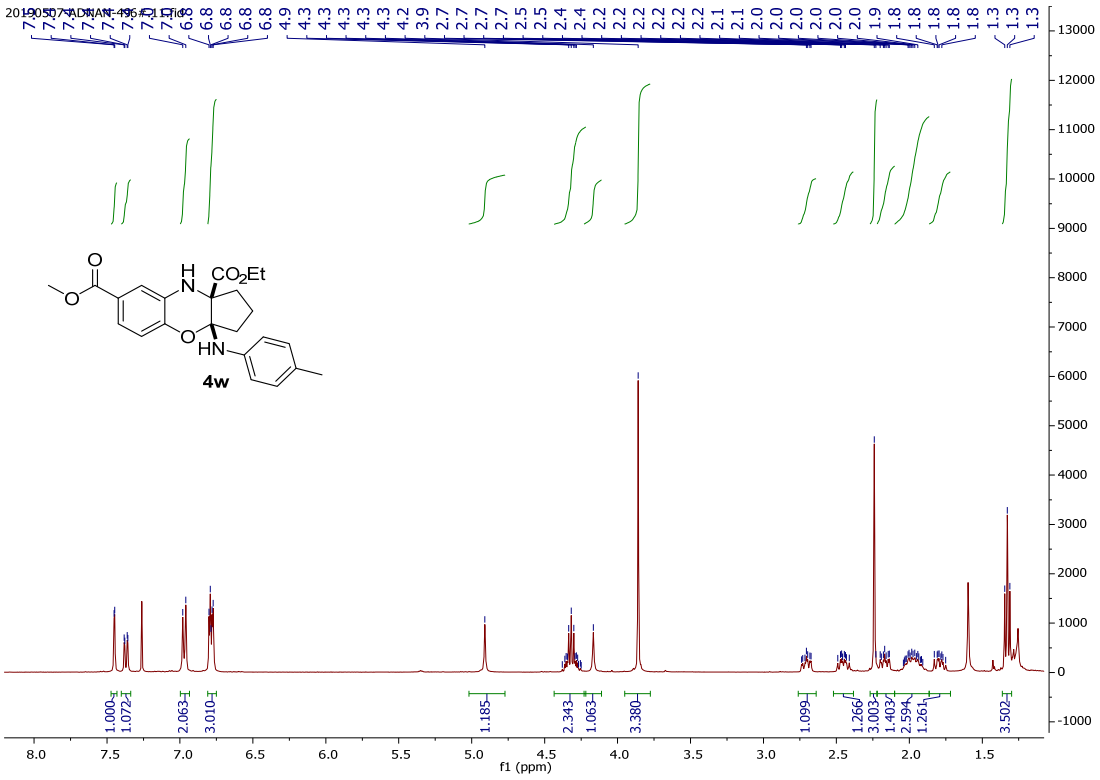
H
N
CO2Et
O2N
O
HN

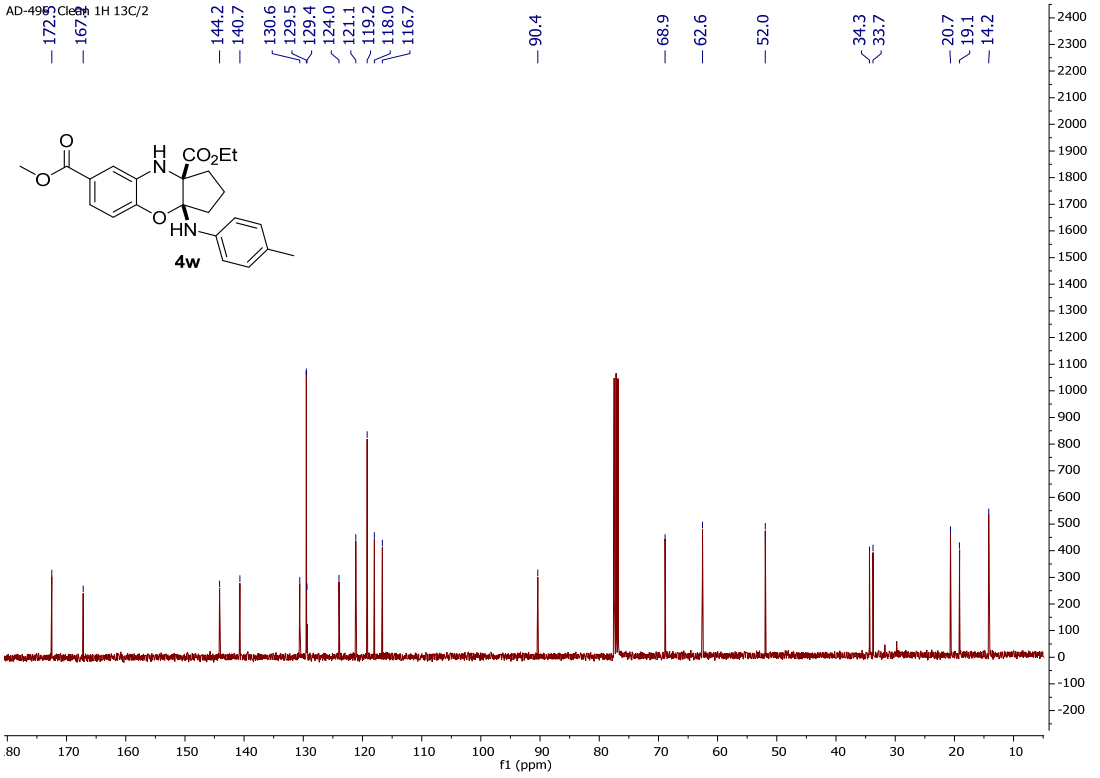
4v

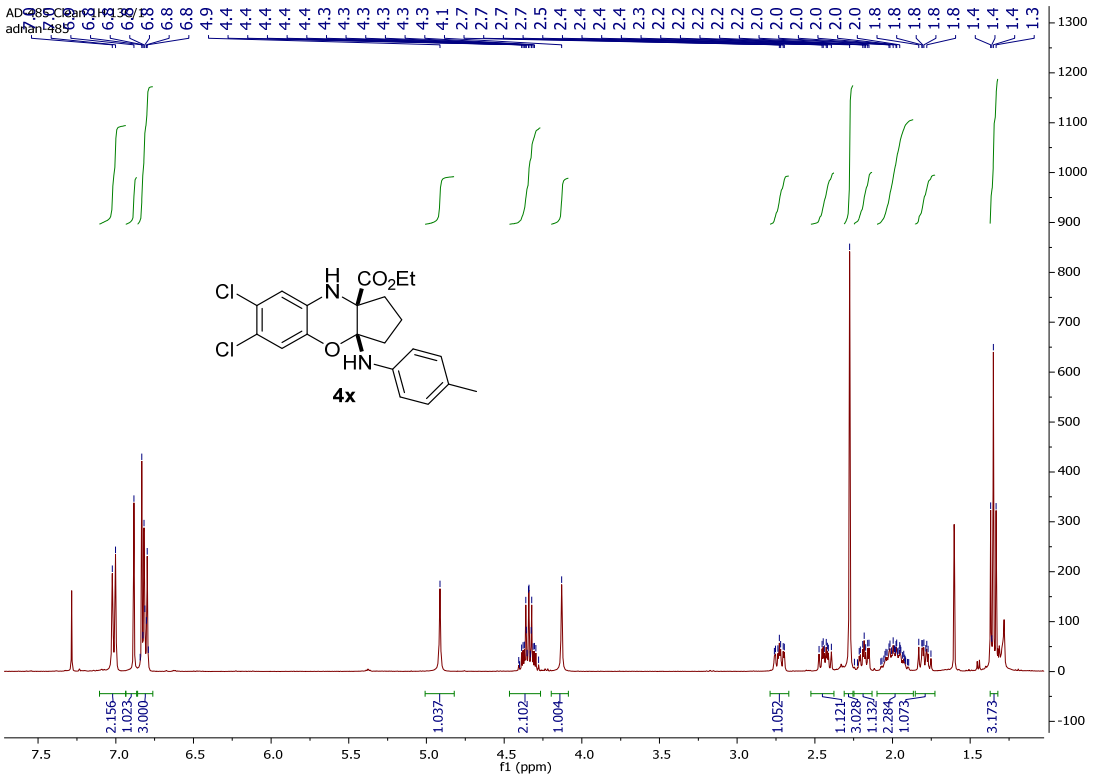

AD-490 1H 13C/2
172.2
140.2 139.4 138.5 136.5 131.0 129.7 119.4 119.0 114.7 113.1
90.4
69.2
63.0
34.8 34.4
20.7 19.2 14.2
f1 (ppm)

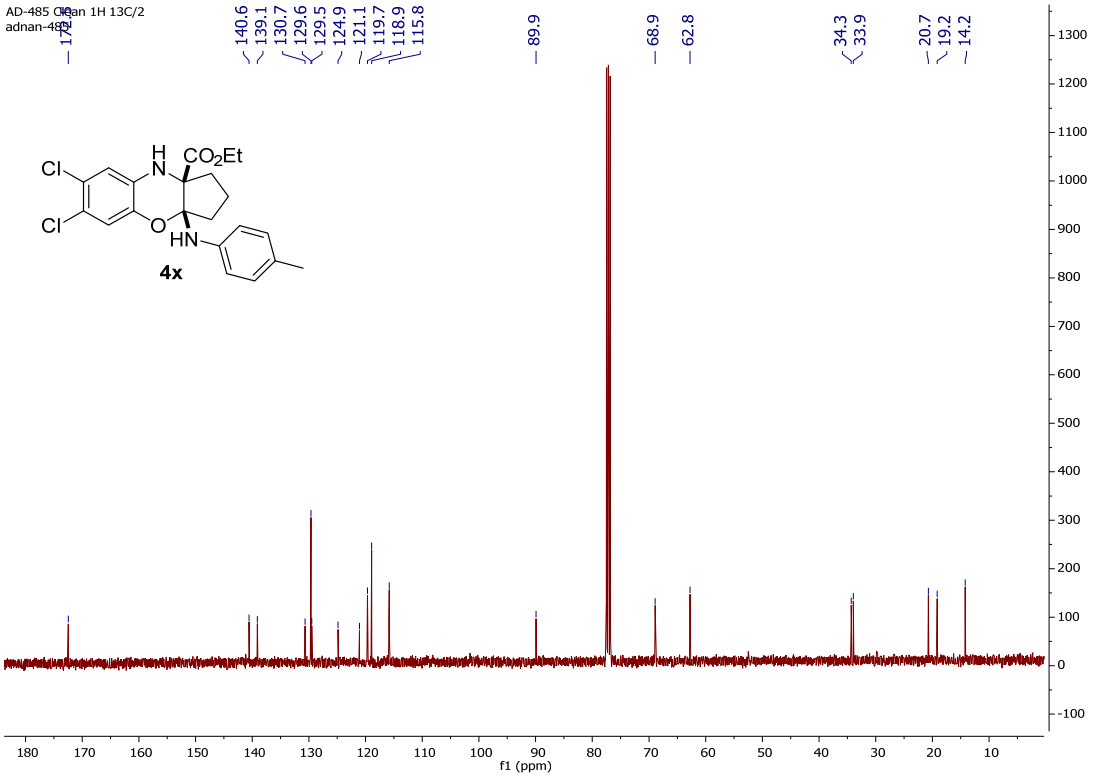
H
N
CO2Et
O2N
O
HN

4v


4w
f1 (ppm)


4w
f1 (ppm)


AD-485 Clean 1H 13C/2
adnan-485
4x
f1 (ppm)


AD-485 Clean 1H 13C/2
adnan-485
140.6
139.1
130.7
129.6
129.5
124.9
121.1
119.7
118.9
115.8
89.9
68.9
62.8
34.3
33.9
20.7
19.2
14.2
4x
f1 (ppm)

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1. V. Sridharan, C. Avendaño and J. C. Menéndez, *Synlett*, **2007**, 0881-0884.
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3. J. Larrow and E. Jacobsen, *Org. Synth*.,**1998**, *75*, 1-11.