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Chiral Cobalt(II) Complex Catalyzed Enantioselective Aza-Piancatelli Rearrangment/Diels-Alder Cascade Reaction

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Content

1. General remarks 2

2. General procedure for the synthesis of chiral *N,N'*-dioxides 2

3. General procedure for the preparation of the racemic products 3

4. Optimization of the asymmetric reaction conditions 4

5. Typical procedure for the catalytic asymmetric reactions 7

6. Scale-up version of the asymmetric reaction 7

7. The analytical and spectral characterization data of products 8

8. Product derivatizations 36

9. X-ray structure of **3m** 39

10. Control experiments 41

11. Copies of NMR spectra 45

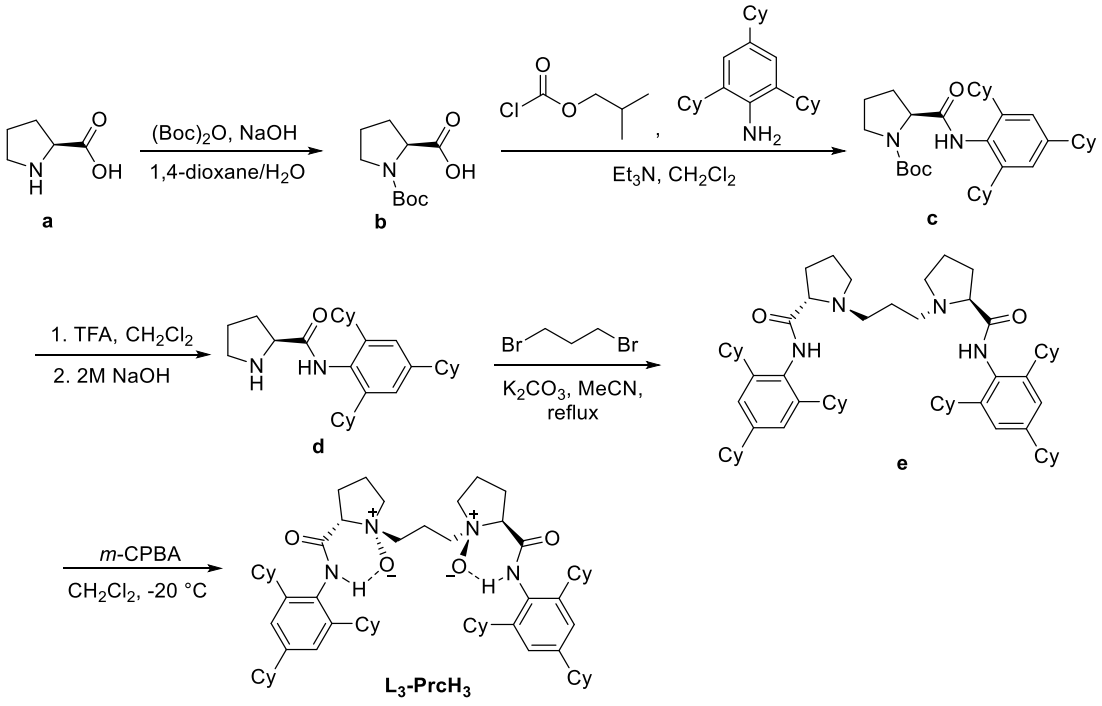
12. Copies of CD spectra 79

13. References 91

1. General remarks

Reactions were carried out with commercially available reagent in dried apparatus. *o*-Xylene was purchased from CHRON CHEMICALS. THF was pretreated under the potassium hydroxide, and then distilled from the sodium benzophenone under nitrogen atmosphere before use. The yield was the purified state by flash chromatography in silica gel. Enantiomeric excesses were determined by HPLC analysis using the corresponding commercial chiral column (chiralcel IB, IF column) as stated in the experimental procedures at 23 °C with the UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]^{T}_{D}$ (*c* g/100 mL, in solvent). The melting points of hexahydro-2a,5-epoxy-cyclopenta[*cd*]isoindole were determined by OptiMelt. ^{1}H NMR spectra were recorded on Bruker ASCEND^{TM} 400M (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet), coupling constants (Hz), integration and assignment. $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker ASCEND^{TM} 400M (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.0). $^{19}F\{^{1}H\}$ NMR spectra were recorded on Bruker ASCEND^{TM} 400M (376 MHz) with complete proton decoupling. chemical shifts δ are given relative to $CFCl_3$ (external reference, δ $^{19}F(CFCl_3)$ = 0), HRMS was recorded on a Thermo Q-Exactive Focus (FTMS+c ESI). All the reactions were carried out under an atmosphere of nitrogen in over-dried apparatus. TLC was performed on glass-backed silica plates. 2-Furfuryl carbinol derivatives were prepared according to reported procedure.[1] *N*-(Furan-2-ylmethyl)aniline derivatives were prepared according to reported procedure.[2]

2. General procedure for the synthesis of chiral *N,N'*-dioxides



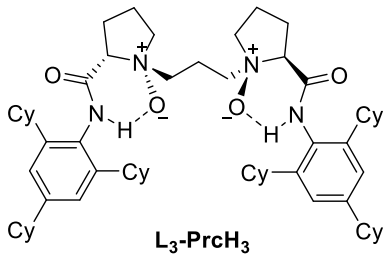
To the solution of *L*-proline **a** (5.76 g, 50 mmol) in 1,4-dioxane (80 mL) was added NaOH (2.20 g, 55 mmol), H_2O (105 mL) at 0 °C. After stirring for 20 min, $(Boc)_2O$ (11.5 mL, 50 mmol) was added. The reaction mixture was stirred at rt and detected by TLC until the reaction was finished. Next, the mixture was washed with 1 M $KHSO_4$ solution, saturated $NaHCO_3$ solution, brine, dried over anhydrous Na_2SO_4, concentrated in vacuo, and directly used for the next step (10.75 g, 99% yield).

To solution of **b** (2.15 g, 10 mmol) in CH_2Cl_2 (20 mL) was added Et_3N (1.54 mL, 11 mmol), isobutyl carbonochloridate (1.43 mL, 11 mmol) at 0 °C under stirring. After 30 min, 2,4,6-tricyclohexylaniline[3] (3.73 g, 11 mmol) was added. The reaction was stirred at rt and detected by TLC. After 12 h, the mixture was washed with 1 M $KHSO_4$ solution, saturated $NaHCO_3$ solution, brine, dried over anhydrous Na_2SO_4, concentrated in vacuo, and directly used for the next step.

TFA (10 mL) was added to the solution of the amide **c** (5.36 g, 10 mmol) in CH_2Cl_2 (10 mL) and stirred at rt until reaction was finished (30 min). Then, CH_2Cl_2 (20 mL) was added. The pH value of the mixture was brought into the range of 10–12 by the addition of 2 M NaOH solution. The aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, concentrated and the residue was subjected to column chromatography on silica gel and eluted with EtOAc/petroleum ether (1:1, v/v) to give the white solid **d** (3.60 g, 82% yield).

K_2CO_3 (5.62 g, 41 mmol) and 1,3-dibromopropane (0.42 mL, 4.1 mmol) was added to a solution of **d** (3.60 g, 8.2 mmol) in CH_3CN (10 mL) under stirring. The resulting reaction mixture was refluxed and monitored by TLC (8 h). Then, CH_2Cl_2 (20 mL) was added, the solid was removed by filtration and washed with CH_2Cl_2. The filtrate was concentrated and the residue was subjected to column chromatography on silica gel and eluted with EtOAc/petroleum ether (1:3 and 1:2, v/v) to give the desired product **e** as a white solid (3.02 g, 81% yield).

Finally, *m*-CPBA (1.42 g, 8.3 mmol) was added to the solution of compound **e** (3.02 g, 3.3 mmol) in CH_2Cl_2 (10 mL) at −20 °C, the resulting reaction mixture was stirred at −20 °C for 30 min. the solvent was removed in vacuo, and the residue was subjected to column chromatography on silica gel and eluted with EtOAc/MeOH (1:1, v/v) to provide the desired *N,N*'-dioxide ligand **L-PrcH$_3$** as a white solid (1.21 g, 39% yield). Other *N,N*'-dioxide ligands were prepared by the similar procedure.[4]



White solid. 130–132 °C; $[\alpha]^{19}_D$ = –38.1 (*c* 0.20, CH_2Cl_2), **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 12.33 (s, 2H), 6.98 (s, 4H), 3.71 – 3.85 (m, 6H), 3.28 – 3.40 (m, 4H), 2.97 – 3.03 (m, 2H), 2.68 – 2.78 (m, 2H), 2.60 – 2.63 (m, 6H), 2.44 – 2.54 (m, 4H), 2.06 – 2.15 (m, 2H), 1.72 – 1.84 (m, 30H), 1.26 – 1.45 (m, 30H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 166.4, 147.0, 128.7, 122.5, 68.1, 64.0, 44.8, 39.9, 34.5, 27.9, 27.4, 27.0, 26.2, 26.2, 20.4, 19.6; **HRMS** (FTMS+c ESI): Calcd for $C_{61}H_{92}N_4O_4H^+$ [M+H$^+$] 945.7197, found 945.7194.

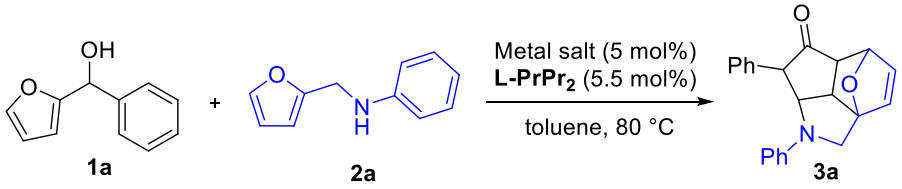
3. General procedure for the preparation of the racemic products

An oven-dried reaction tube was charged with 2-furfuryl carbinol **1** (0.10 mmol), *N*-(furan-2-ylmethyl)aniline **2** (0.10 mmol), $Co(BF_4)_2{\cdot}6H_2O$ (3.4 mg, 0.01 mmol) and *o*-xylene (1.0 mL)

subsequently. The reaction mixture was stirred at 65 °C for 1 h and then subjected to column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (3:1, v/v) to afford the desired racemic product **3** as a white solid.

4. Optimization of the asymmetric reaction conditions

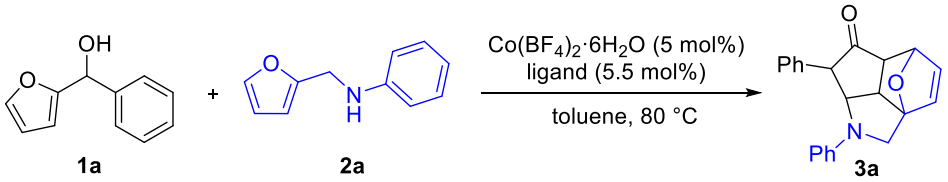
Table S1. Screening of the metal salts[a]

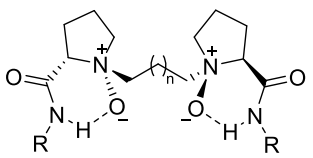


Entry	Metal salt	Yield (%)[b]	dr[c]	ee (%)[d]
1	$Zn(OTf)_2$	12	> 19:1	31
2	$Cu(OTf)_2$	69	> 19:1	0
3	$Yb(OTf)_3$	14	> 19:1	0
4	$In(OTf)_3$	47	> 19:1	4
5	$Dy(OTf)_3$	<10	> 19:1	–3
6	$Co(OTf)_2$	10	> 19:1	57
7	$Co(BF_4)_2{\cdot}6H_2O$	36	> 19:1	65
8	$Co(ClO_4)_2{\cdot}6H_2O$	50	> 19:1	11
9	$Co(NTf_2)_2$	trace	> 19:1	67

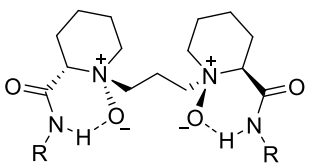
[a] All reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and metal salt/**L-PrPr$_2$** (1:1.1, 5 mol%) in toluene (1.0 mL) at 80 °C for 15 h. [b] Yield of the isolated products. [c] Determined by ^{1}H NMR. [d] Determined by HPLC analysis on a chiral stationary phase.

Table S2. Screening of the ligands[a]

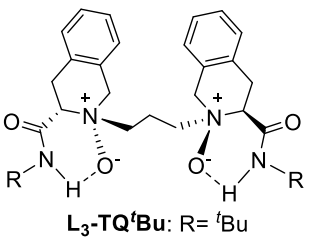




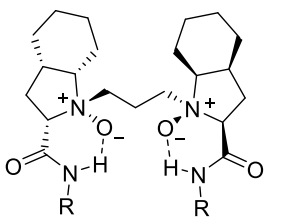
L$_3$-PrPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$, n = 1
L$_2$-PrPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$, n = 0
L$_3$-PrMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$, n = 1
L$_3$-PrEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 1
L$_3$-PrPr$_3$: R = 2,4,6-*i*Pr$_3$C$_6$H$_2$, n = 1
L$_3$-PrPr$_2$Ad: R = 2,6-*i*Pr$_2$-4-(1-Ad)C$_6$H$_2$, n = 1
L$_3$-PrcH$_3$: R = 2,4,6-Cy$_3$C$_6$H$_2$, n = 1



L$_3$-PiPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$



L$_3$-TQ^{t}Bu: R= ^{t}Bu

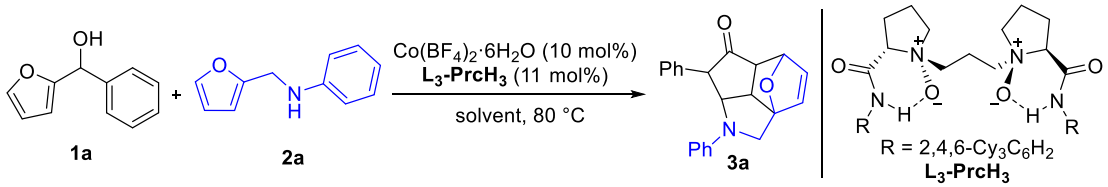


L$_3$-PePr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$

Entry	ligand	Yield (%)[b]	dr[c]	ee (%)[d]
1	**L_3-PrPr$_2$**	36	> 19:1	65
2	**L_3-PiPr$_2$**	10	> 19:1	62
3	**L_3-PePr$_2$**	48	> 19:1	3
4	**L_3-TQtBu**	46	> 19:1	3
5	**L_2-PrPr$_2$**	39	> 19:1	38
6	**L_3-PrMe$_2$**	50	> 19:1	7
7	**L_3-PrEt$_2$**	60	> 19:1	8
8	**L_3-PrPr$_3$**	14	> 19:1	81
9	**L_3-PrPr$_2$Ad**	42	> 19:1	82
10	**L_3-PrcH$_3$**	40	> 19:1	83
11[e]	**L_3-PrcH$_3$**	55	> 19:1	83

[a] All reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and $Co(BF_4)_2{\cdot}6H_2O$/ligand (1:1.1, 5 mol%) in toluene (1.0 mL) at 80 °C for 15 h. [b] Yield of the isolated products. [c] Determined by ^1H NMR. [d] Determined by HPLC analysis on a chiral stationary phase. [e] $Co(BF_4)_2{\cdot}6H_2O$/**L_3-PrcH$_3$** (1:1.1, 10 mol%).

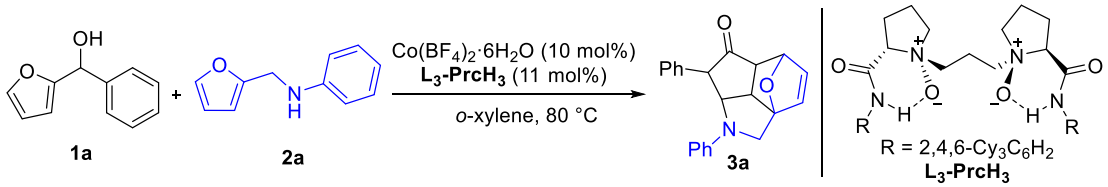
Table 3. Screening of the solvents[a]



Entry	solvent	Yield (%)[b]	dr[c]	ee (%)[d]
1	$CHCl_2CHCl_2$	79	> 19:1	25
2	$MeNO_2$	65	> 19:1	5
3	*o*-xylene	63	> 19:1	85
4	*m*-xylene	58	> 19:1	81
5	*p*-xylene	73	> 19:1	51
6	mesitylene	37	> 19:1	82
7	bromobenzene	67	> 19:1	55
8	benzotrifluoride	24	> 19:1	77
9	4-methylanisole	48	> 19:1	74
10	toluene	55	> 19:1	83

[a] All reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and $Co(BF_4)_2{\cdot}6H_2O$/**L_3-PrcH$_3$** (1:1.1, 10 mol%) in solvent (1.0 mL) at 80 °C for 15 h. [b] Yield of the isolated products. [c] Determined by ^1H NMR. [d] Determined by HPLC analysis on a chiral stationary phase.

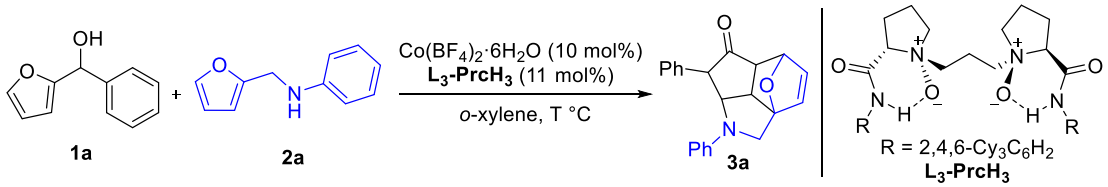
Table 4. Screening of the reaction concentration[a]



Entry	***o*-xylene [mL]**	Yield[b] (%)	dr[c]	ee (%)[d]
1	0.5	35	> 19:1	85
2	1.0	63	> 19:1	85
3	1.5	47	> 19:1	80
4	2.0	36	> 19:1	83

[a] All reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and $Co(BF_4)_2{\cdot}6H_2O$/**L_3-PrcH$_3$** (1:1.1, 10 mol%) in *o*-xylene at 80 ℃ for 15 h. [b] Yield of the isolated products. [c] Determined by ^{1}H NMR. [d] Determined by HPLC analysis on a chiral stationary phase.

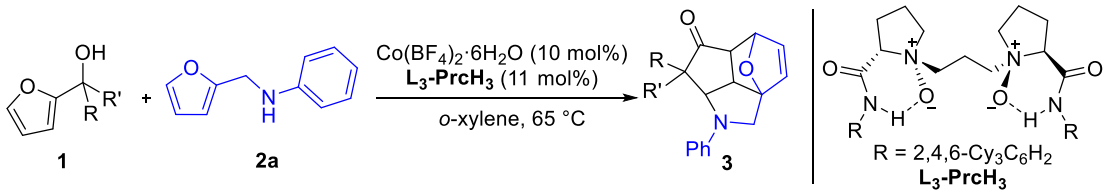
Table 5. Screening of the temperature[a]

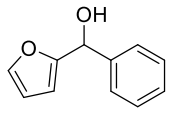


Entry	T (℃)	Yield (%)[b]	dr[c]	ee (%)[d]
1	90	62	> 19:1	63
2	80	63	> 19:1	85
3	70	47	> 19:1	87
4	65	20	> 19:1	92
5	60	trace	> 19:1	91

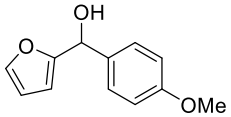
[a] All reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and $Co(BF_4)_2{\cdot}6H_2O$/**L_3-PrcH$_3$** (1:1.1, 10 mol%) in *o*-xylene (1.0 mL). [b] Yield of the isolated products. [c] Determined by ^{1}H NMR. [d] Determined by HPLC analysis on a chiral stationary phase.

Table 6. Screening of different of 2-furfuryl carbinols[a]

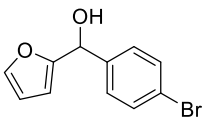




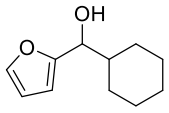
1a: 20 yield, > 19:1 dr, 92% ee



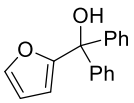
1b: 88 yield, > 19:1 dr, 90% ee



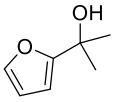
1l[e]: 57% yield, > 19:1 dr 70% ee



1m: NR



1n: NR

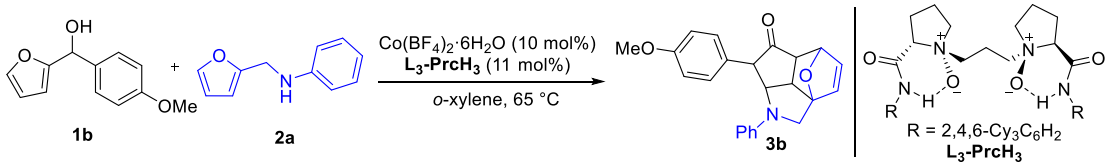


1o: 32 yield, 39% ee

[a] All reactions were carried out with **1** (0.10 mmol), **2a** (0.10 mmol) and $Co(BF_4)_2{\cdot}6H_2O$/**L_3-PrcH$_3$** (1:1.1, 10 mol%) in *o*-xylene (1.0 mL) at 65 ℃ for 16 h. [b] Yield of the isolated products. [c] Determined by ^{1}H NMR. [d] Determined by HPLC analysis on a chiral stationary phase. [e] The reaction

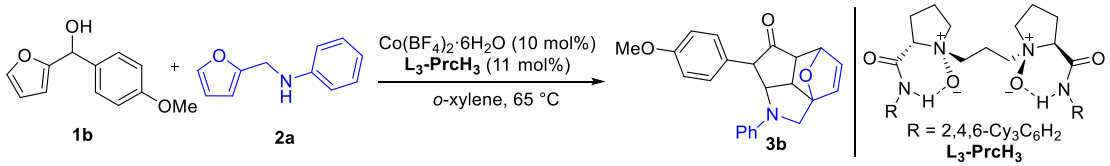
was carried out at 70 ℃.

5. Typical procedure for the catalytic asymmetric reactions



Typical Procedure: To an oven-dried reaction tube under nitrogen atmosphere was added $Co(BF_4)_2·6H_2O$ (3.4 mg, 10 mol%), **L_3-PrcH$_3$** (10.4 mg, 11 mol%) and THF (0.3 mL). The mixture was stirred at 35 °C for 30 min. Then the solvent was removed in vacuo and dinitrogen atmosphere was introduced. Then furan-2-yl(4-methoxyphenyl)methanol **1b** (20.3 mg, 0.10 mmol), *N*-(furan-2-ylmethyl)aniline **2a** (17.3 mg, 0.10 mmol) and *o*-xylene (1.0 mL) were added subsequently. After completion of the addition, the reaction mixture was stirred at 65 °C for 16 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (3:1, v/v) to afford the desired product **3b** as a white solid (88% yield, 90% ee).

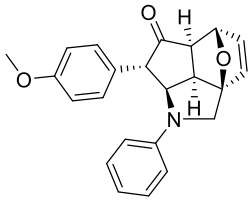
6. Scale-up version of the asymmetric reaction



To an oven-dried reaction tube under nitrogen atmosphere was added $Co(BF_4)_2·6H_2O$ (136.0 mg, 10 mol%), **L_3-PrcH$_3$** (416.0 mg, 11 mol%) and THF (12 mL). The mixture was stirred at 35 °C overnight. Then the solvent was removed in vacuo and nitrogen atmosphere was introduced. After that, furan-2-yl(4-methoxyphenyl)methanol **1b** (812.0 mg, 4.0 mmol), *N*-(furan-2-ylmethyl)aniline **2a** (692.0 mg, 4.0 mmol) and *o*-xylene (40.0 mL) were added subsequently. After completion of the addition, the reaction mixture was stirred at 65 °C for 26 h. Then the solvent was removed in vacuo and the residue was subjected to column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (3:1, v/v) to afford the desired product **3b** as a white solid (79% yield, 91% ee).

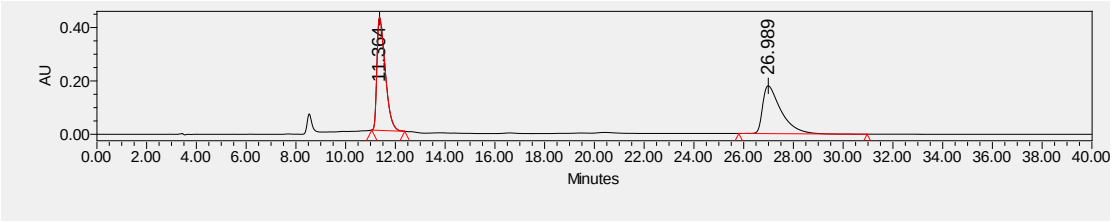
7. The analytical and spectral characterization data of products

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-7-(4-Methoxyphenyl)-1-phenyl-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3b)

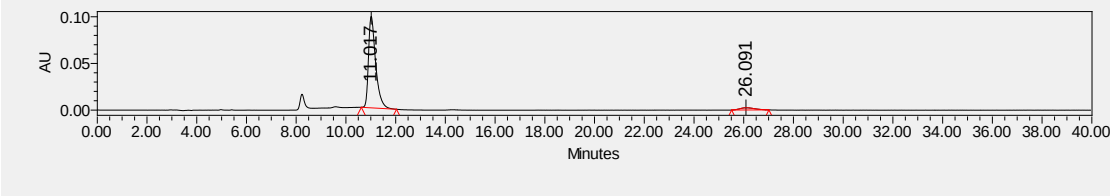


3b

White solid, 132 – 134 °C, 31.6 mg, 88% yield, 90% ee, >19:1 dr for the isolated product. t: 16 h. $[\alpha]^{19}_D$ = +180.3 (*c* 0.14, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 11.02 min, $t_{R(minor)}$ = 26.09 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.00 – 7.06 (m, 4H), 6.89 – 6.93 (m, 2H), 6.75 (d, *J* = 6.0 Hz, 1H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.49 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.24 (d, *J* = 8.0 Hz, 2H), 5.29 (d, *J* = 1.6 Hz, 1H), 4.35 (dd, *J* = 6.0 Hz, *J* = 8.8 Hz, 1H), 3.96 (dd, *J* = 10.8 Hz, *J* = 89.2 Hz, 2H), 3.84 (s, 3H), 3.09 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.76 (d, *J* = 76.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.5, 158.7, 146.9, 137.1, 136.3, 131.5, 129.9, 129.1, 116.6, 114.4, 112.2, 96.2, 84.5, 65.6, 65.1, 55.3, 54.1, 52.8, 50.1; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{21}NO_3H^+$ [M+H$^+$] 360.1594, found 360.1592. **IR** (neat): 2948, 2909, 2833, 1725, 1599, 1505, 1462, 1346, 1299, 1248, 1028, 828, 745, 690 cm^{-1}.

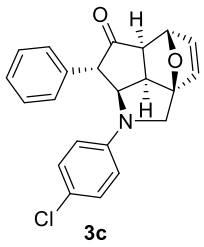


	Retention Time	Area	% Area
1	11.364	9820549	51.71
2	26.989	9171490	48.29



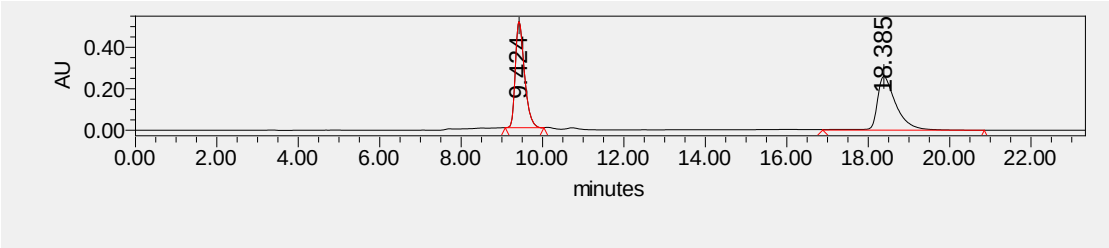
	Retention Time	Area	% Area
1	11.017	1960832	95.22
2	26.091	98428	4.78

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Chlorophenyl)-7-phenyl-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3c)

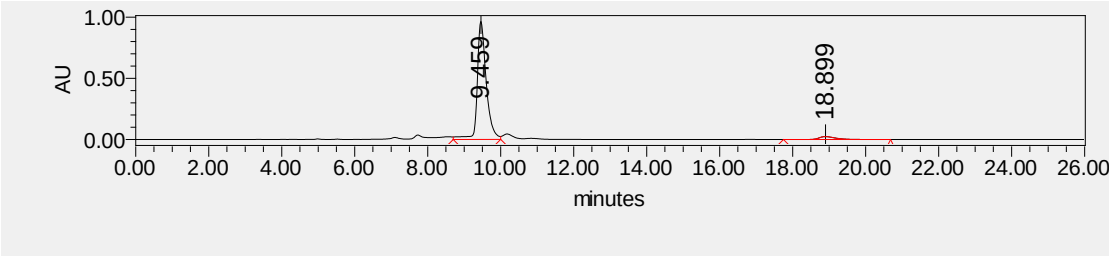


3c

White solid, 139 – 141 °C, 15.2 mg, 42% yield, 91% ee, >19:1 dr for the isolated product. t: 73 h. $[\alpha]^{17}_D$ = +190.9 (*c* 0.21, CH_2Cl_2); HPLC (Daicel chiralcel IF, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 9.46 min, $t_{R(minor)}$ = 18.90 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 – 7.39 (m, 3H), 7.10 – 7.12 (m, 2H), 6.93 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 5.6 Hz, 1H), 6.50 (d, *J* = 5.6 Hz, 1H), 6.08 – 6.10 (m, 2H), 5.30 (s, 1H), 4.35 (dd, *J* = 6.0 Hz, *J* = 8.8 Hz, 1H), 3.93 (dd, *J* = 10.8 Hz, *J* = 86.0 Hz, 2H), 3.77 (d, *J* = 6.4 Hz, 1H), 3.12 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.78 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.6, 145.4, 139.3, 137.0, 136.4, 129.1, 128.9, 128.8, 127.5, 121.5, 113.3, 96.2, 84.6, 65.7, 54.3, 53.0, 50.1; **HRMS** (FTMS+c ESI): Calcd for $C_{22}H_{18}{}^{34.9689}ClNO_2H^+$ [M+H$^+$] 364.1099, found 364.1096, Calcd for $C_{22}H_{18}{}^{36.9659}ClNO_2H^+$ [M+H$^+$] 366.1069, found 366.1065; **IR** (neat): 2924, 2863, 1729, 1594, 1494, 1454, 1353, 1130, 1072, 1009, 865, 804, 748, 696, 617, 503 cm^{-1}.

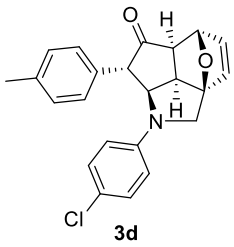


	Retention Time	Area	% Area
1	9.424	7939806	48.98
2	18.385	8271145	51.02



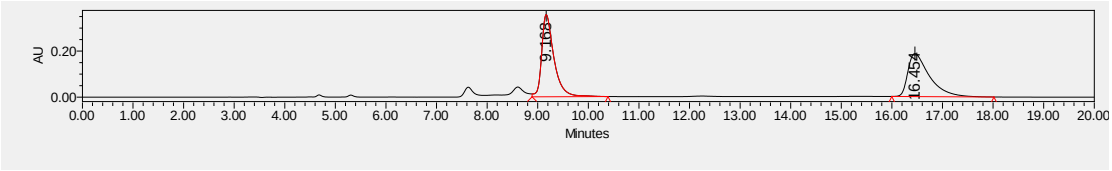
	Retention Time	Area	% Area
1	9.459	16508983	95.48
2	18.899	781544	4.52

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Chlorophenyl)-7-(p-tolyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3d)

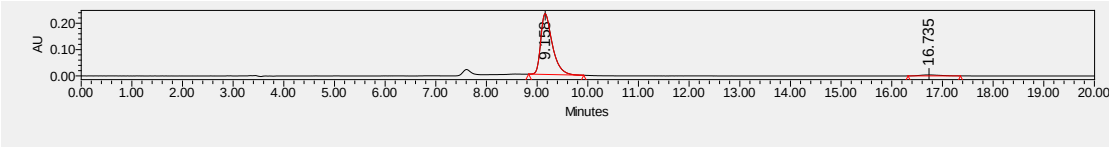


3d

White solid, 82 – 84 °C, 18.9 mg, 50% yield, 94% ee, >19:1 dr for the isolated product. t: 70 h. $[\alpha]^{17}_D$ = +169.8 (*c* 0.22, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 9.16 min, $t_{R(minor)}$ = 16.74 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7,17 – 7.18 (m, 2H), 6.94 – 7.00 (m, 4H), 6.74 (d, *J* = 6.0 Hz, 1H), 6.49 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.12 – 6.14 (m, 2H), 5.92 (d, *J* = 1.2 Hz, 1H), 4.33 (dd, *J* = 6.4 Hz, *J* = 8.8 Hz, 1H), 3.93 (dd, *J* = 11.2 Hz, *J* = 85.6 Hz, 2H), 3,72 (d, *J* = 6.4 Hz, 1H), 3.11 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.77 (d, *J* = 6.8 Hz, 1H), 2.37 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.9, 145.4, 137.1, 137.0, 136.4, 136.2, 129.8, 128.8, 128.6, 121.4, 113.3, 96.1, 84.6, 65.7, 65.4, 54.2, 53.0, 50.3, 21.2; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{20}{}^{34.9689}ClNO_2H^+$ [M+H$^+$] 378.1255, found 378.1270, Calcd for $C_{23}H_{20}{}^{36.9659}ClNO_2H^+$ [M+H$^+$] 380.1226, found 380.1237; **IR** (neat): 2916, 2848, 1730, 1596, 1495, 1459, 1352, 1186, 1149, 887, 811, 769, 691, 661, 506 cm^{-1}.

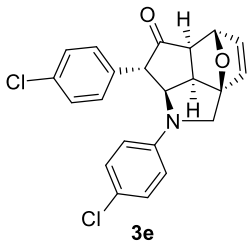


	Retention Time	Area	% Area
1	9.168	5999386	52.18
2	16.454	5498136	47.82



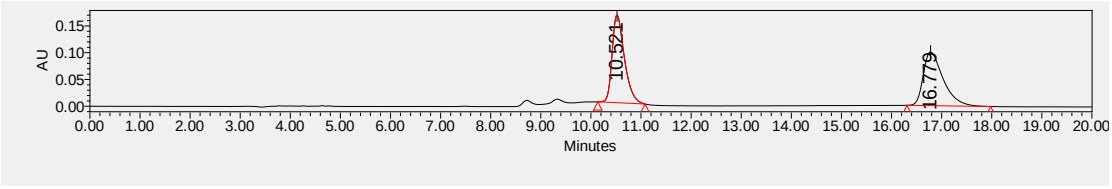
	Retention Time	Area	% Area
1	9.158	3664170	97.26
2	16.735	103183	2.74

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1,7-Bis(4-chlorophenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3e)

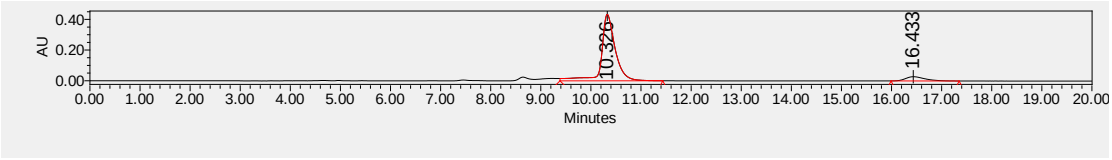


3e

White solid, 124 – 126 °C, 19.1 mg, 48% yield, 83% ee, >19:1 dr for the isolated product. t: 73 h. $[\alpha]^{20}_D$ = +107.7 (*c* 0.18, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 10.33 min, $t_{R(minor)}$ = 16.43 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 5.6 Hz, 1H), 6.50 (dd, *J* = 1.6 Hz, *J* = 6.0 Hz, 1H), 6.09 (d, *J* = 9.2 Hz, 2H), 5.29 (d, *J* = 1.2 Hz, 1H), 4.31 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 3.94 (dd, *J* = 11.2 Hz, *J* = 84.0 Hz, 2H), 3.77 (d, *J* = 6.4 Hz, 1H), 3.11 (d, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.77 (d, *J* = 6.4 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.1, 145.2, 137.7, 137.0, 136.4, 133.4, 130.2, 129.3, 128.9, 121.7, 113.2, 96.2, 84.5, 65.4, 65.1, 54.3, 53.0, 50.3; **HRMS** (FTMS+c ESI): Calcd for $C_{22}H_{17}{}^{34.9689}Cl_2NO_2H^+$ [M+H$^+$] 398.0709, found 398.0721, Calcd for $C_{22}H_{17}{}^{34.9689}Cl{}^{36.9659}ClNO_2H^+$ [M+H$^+$] 400.0680, found 400.0690, Calcd for $C_{20}H_{17}{}^{36.9659}Cl_2NO_2H^+$ [M+H$^+$] 402.0650, found 402.0656; **IR** (neat): 2928, 2856, 2835, 1732, 1597, 1494, 1460, 1144, 1089, 1073, 991, 865, 829, 804, 741, 653, 503 cm^{-1}.

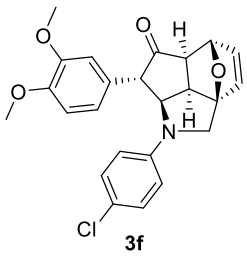


	Retention Time	Area	% Area
1	10.521	2789118	50.20
2	16.779	2766576	49.80



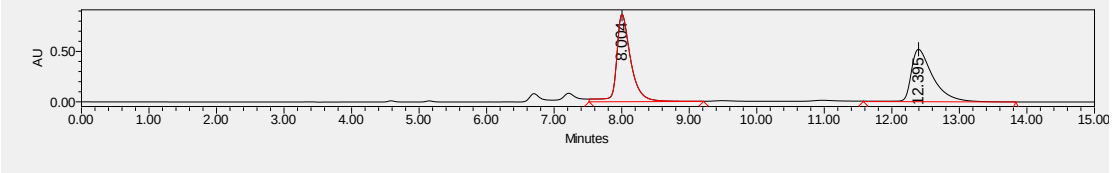
	Retention Time	Area	% Area
1	10.326	8241847	91.74
2	16.433	742306	8.26

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Chlorophenyl)-7-(3,4-dimethoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3f)

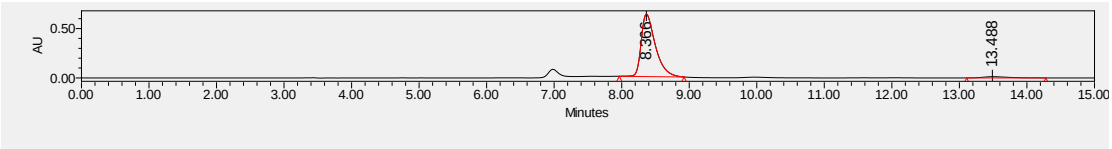


3f

White solid, 76 – 78 °C, 28.8 mg, 68% yield, 93% ee, >19:1 dr for the isolated product. t: 65 h. $[\alpha]^{16}_D$ = +98.0 (*c* 0.25, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 8.37 min, $t_{R(minor)}$ = 13.49 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.12 (d, *J* = 7.2 Hz, 1H), 6.93 – 6.96 (m, 2H), 6.82 – 6.86 (m, 2H), 6.74 (d, *J* = 5.6 Hz, 1H), 6.49 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.12 – 6.17 (m, 2H), 5.29 (d, *J* = 1.6 Hz, 1H), 4.33 (dd, *J* = 6.0 Hz, *J* = 9.2 Hz, 1H), 3.92 (dd, *J* = 10.8 Hz, *J* = 84.8 Hz, 2H), 3.68 (d, *J* = 6.0 Hz, 1H), 3.11 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.77 (d, *J* = 6.8 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.2, 145.5, 137.2, 137.0, 136.6, 136.4, 135.7, 130.3, 130.0, 128.8, 126.1, 121.4, 113.4, 96.1, 84.6, 65.7, 65.4, 54.3, 53.0, 50.3, 19.9, 19.5; **HRMS** (FTMS+c ESI): Calcd for $C_{24}H_{22}{}^{34.9689}ClNO_4H^+$ [M+Na$^+$] 446.1130, found 446.1134, Calcd for $C_{24}H_{22}{}^{36.9659}ClNO_4H^+$ [M+Na$^+$] 448.1100, found 448.1111; **IR** (neat): 2917, 2854, 1733, 1597, 1497, 1457, 1354, 1144, 1069, 991, 866, 810, 688, 660, 506 cm^{-1}.

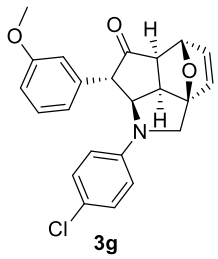


	Retention Time	Area	% Area
1	8.004	12708411	52.39
2	12.395	11547871	47.61



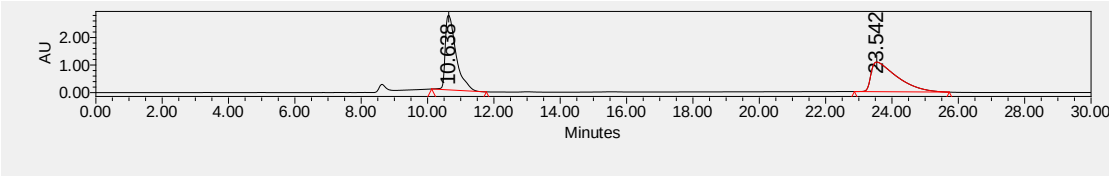
	Retention Time	Area	% Area
1	8.366	9213028	96.76
2	13.488	308101	3.24

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Chlorophenyl)-7-(3-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3g)

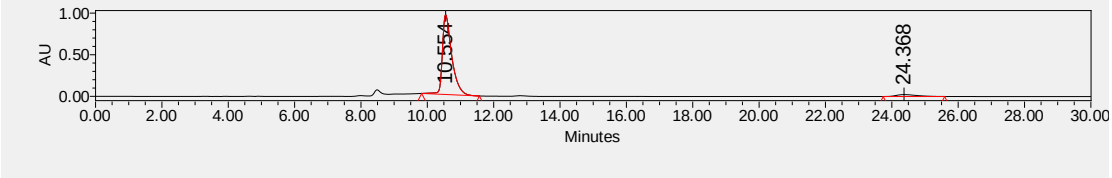


3g

White solid, 63 – 65 °C, 22.8 mg, 58% yield, 90% ee, >19:1 dr for the isolated product. t: 140 h. $[\alpha]^{16}_D$ = +180.3 (*c* 0.23, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 10.56 min, $t_{R(minor)}$ = 24.34 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 (t, *J* = 8.0 Hz, 1H), 6.94 – 6.97 (m, 2H), 6.87 (dd, *J* = 2.4 Hz, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 5.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.63 – 6.64 (m, 1H), 6.49 (dd, *J* = 1.6 Hz, *J* = 6.0 Hz, 1H), 6.12 – 6.14 (m, 2H), 5.30 (d, *J* = 1.2 Hz, 1H), 4.36 (dd, *J* = 2.0 Hz, *J* = 6.0 Hz, 1H), 3.93 (dd, *J* = 10.8 Hz, *J* = 85.6 Hz, 2H), 3.79 (s, 3H), 3.73 (d, *J* = 6.0 Hz, 1H), 3.11 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.78 (d, *J* = 6.8 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.4, 156.0, 145.4, 140.7, 137.0, 136.4, 130.1, 128.8, 121.5, 121.1, 114.7, 113.3, 112.8, 96.2, 84.6, 65.7, 65.6, 55.2, 54.3, 53.0, 50.2; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{20}{}^{34.9689}ClNO_3H^+$ [M+H$^+$] 394.1204, found 394.1205, Calcd for $C_{23}H_{20}{}^{36.9659}ClNO_3H^+$ [M+H$^+$] 396.1175, found 396.1174; **IR** (neat): 2913, 2839, 1733, 1597, 1495, 1459, 1354, 1244, 1142, 1039, 991, 867, 810, 766, 689, 660, 507 cm^{-1}.

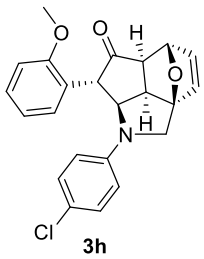


	Retention Time	Area	% Area
1	10.638	61437860	51.30
2	23.542	58317258	48.70



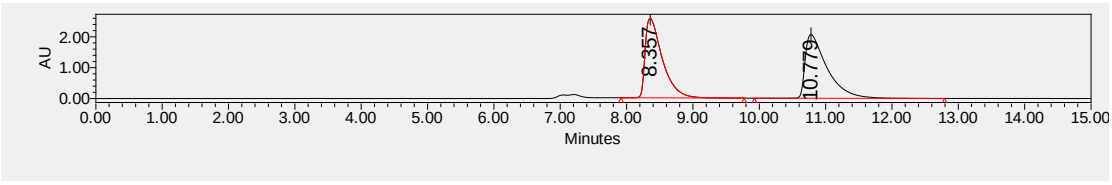
	Retention Time	Area	% Area
1	10.554	18724762	95.18
2	24.368	948184	4.82

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Chlorophenyl)-7-(2-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3h)

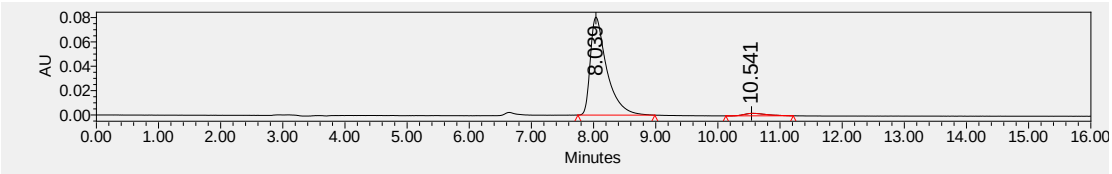


3h

White solid, 117 – 120 °C, 31.1 mg, 79% yield, 93% ee, >19:1 dr for the isolated product. t: 64 h. $[\alpha]^{19}_D$ = +198.4 (*c* 0.31, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 8.04 min, $t_{R(minor)}$ = 10.54 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 – 7.34 (m, 1H), 7.12 – 7.14 (m, 1H), 6.92 – 6.98 (m, 4H), 6.73 (d, *J* = 5.6 Hz, 1H), 6.48 – 6.50 (m, 1H), 6.20 – 6.22 (m, 2H), 5.28 (d, *J* = 1.6 Hz, 1H), 4.29 (dd, *J* = 5.2 Hz, *J* = 9.2 Hz, 1H), 3.88 (dd, *J* = 10.4 Hz, *J* = 102.0 Hz, 2H), 3.76 (s, 3H), 3.55 (d, *J* = 2.8 Hz, 1H), 3.11 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.82 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.7, 155.6, 145.6, 136.9, 136.3, 132.5, 129.6, 129.1, 128.8, 121.2, 121.2, 113.1, 111.3, 95.8, 84.6, 64.9, 55.3, 54.4, 53.6, 50.3; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{20}{}^{34.9689}ClNO_3H^+$ [M+H$^+$] 394.1204, found 394.1203, Calcd for $C_{23}H_{20}{}^{36.9659}ClNO_3H^+$ [M+H$^+$] 396.1175, found 396.1172; **IR** (neat): 2936, 2916, 2857, 2840, 1731, 1593, 1493, 1458,1350, 1270, 1147, 1025, 992, 866, 757, 729, 700 cm^{-1}.

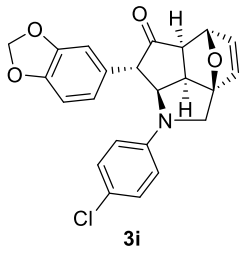


	Retention Time	Area	% Area
1	8.357	46223035	49.49
2	10.779	47179866	50.51



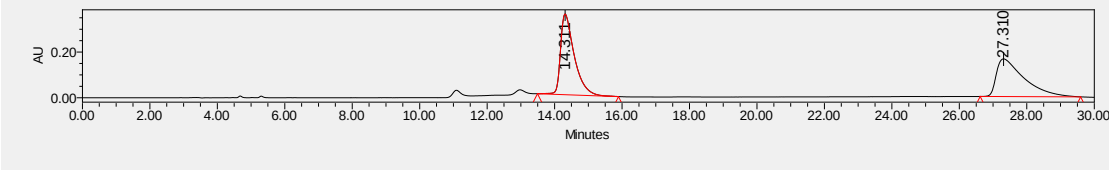
	Retention Time	Area	% Area
1	8.039	1479828	96.77
2	10.541	49397	3.23

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-7-(Benzo[*d*][1,3]dioxol-5-yl)-1-(4-chlorophenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3i)

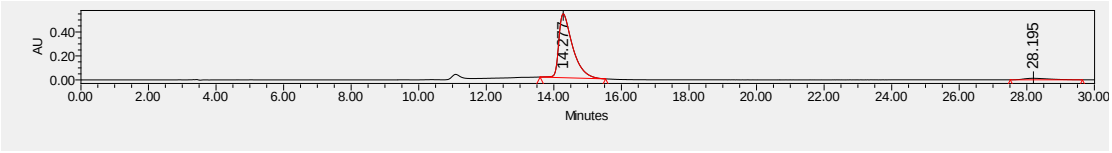


3i

White solid, 84 – 86 °C, 27.7 mg, 68% yield, 91% ee, >19:1 dr for the isolated product. t: 65 h. $[\alpha]^{16}_D$ = +112.2 (*c* 0.34, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 14.28 min, $t_{R(minor)}$ = 28.20 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.97 – 7.01 (m, 2H) 6.79 – 6.81 (m, 1H), 6.73 – 6.75 (m, 1H), 6.57 – 6.59 (m, 2H), 6.49 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.15 – 6.19 (m, 2H), 5.99 (d, *J* = 4.4 Hz, 2H), 5.28 (d, *J* = 1.2 Hz, 1H), 4.29 (dd, *J* = 6.4 Hz, *J* = 9.6 Hz, 1H), 3.92 (dd, *J* = 11.2 Hz, *J* = 84.0 Hz, 2H), 3.69 (d, *J* = 6.0 Hz, 1H), 3.09 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2,75 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.7, 148.2, 146.9, 145.4, 136.9, 136.3, 132.8, 128.9, 122.5, 121.5, 113.3, 108.8, 96.1, 84.5, 65.6, 65.4, 54.1, 52.8, 50.3; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{18}{}^{34.9689}ClNO_4H^+$ [M+H$^+$] 408.0997, found 408.1013, Calcd for $C_{23}H_{18}{}^{36.9659}ClNO_4H^+$ [M+H$^+$] 410.0968, found 410.0983; **IR** (neat): 2901, 2853, 1732, 1597, 1495, 1441, 1354, 1240, 1143, 1035, 928, 867, 808, 660, 506 cm^{-1}.

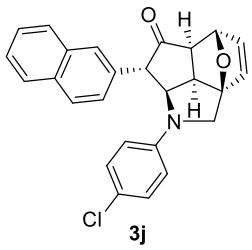


	Retention Time	Area	% Area
1	14.311	9970009	51.48
2	27.310	9396462	48.52



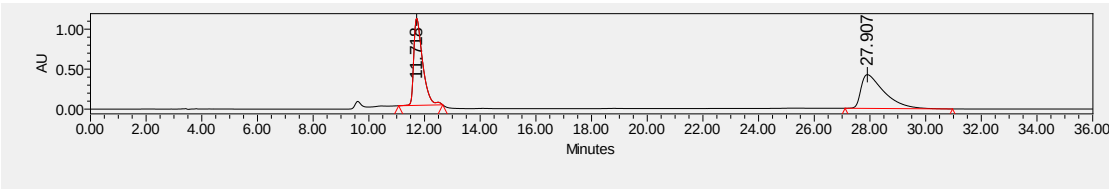
	Retention Time	Area	% Area
1	14.277	15119753	95.76
2	28.195	669792	4.24

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Chlorophenyl)-7-(naphthalen-2-yl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3j)

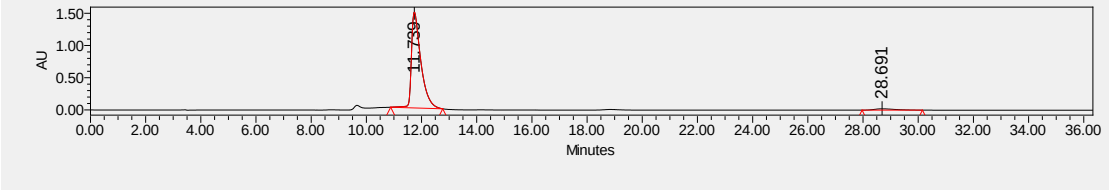


3j

White solid, 148 – 150 °C, 13.6 mg, 31% yield, 94% ee, >19:1 dr for the isolated product. t: 71 h. $[\alpha]^{16}_D$ = +132.8 (*c* 0.13, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 11.74 min, $t_{R(minor)}$ = 28.69 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.85 – 7.88 (m, 2H), 7.76 – 7.79 (m, 1H), 7.60 (s, 1H), 7.47 – 7.52 (m, 2H), 7.21 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 1H), 6.84 – 6.88 (m, 2H), 6.77 (d, *J* = 6.0 Hz, 1H), 6.52 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 5.33 (d, *J* = 1.6 Hz, 1H), 4.49 (dd, *J* = 6.0 Hz, *J* = 9.2 Hz, 1H), 3.96 (dd, *J* = 11.2 Hz, *J* = 90.0 Hz, 2H), 3.94 (d, *J* = 6.0 Hz, 1H), 3.19 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.84 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.7, 145.4, 137.0, 136.6, 136.4, 133.6, 132.6, 129.0, 128.9, 128.1, 127.8, 127.7, 126.4, 126.4, 126.0, 121.5, 113.3, 96.2, 84.7, 65.9, 65.6, 54.4, 53.2, 50.3; **HRMS** (FTMS+c ESI): Calcd for $C_{26}H_{20}{}^{34.9689}ClNO_2H^+$ [M+H$^+$] 414.1255, found 414.1266, Calcd for $C_{26}H_{20}{}^{36.9659}ClNO_2H^+$ [M+H$^+$] 416.1226, found 416.1236; **IR** (neat): 2907, 2847, 1736, 1596, 1495, 1459, 1354, 1269, 1148, 1125, 861, 805, 746, 685, 654, 506, 475 cm^{-1}.

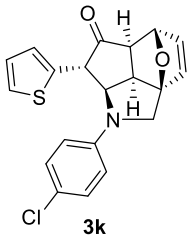


	Retention Time	Area	% Area
1	11.718	23990487	49.67
2	27.907	24311296	50.33



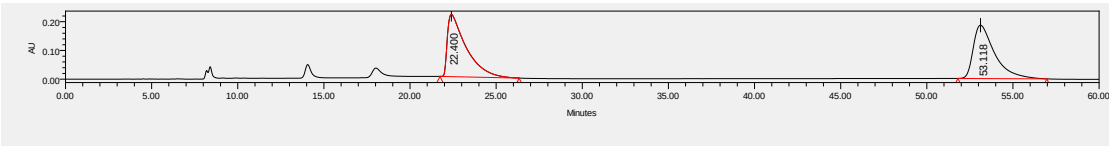
	Retention Time	Area	% Area
1	11.739	35109544	97.07
2	28.691	1060800	2.93

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Chlorophenyl)-7-(thiophen-2-yl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3k)

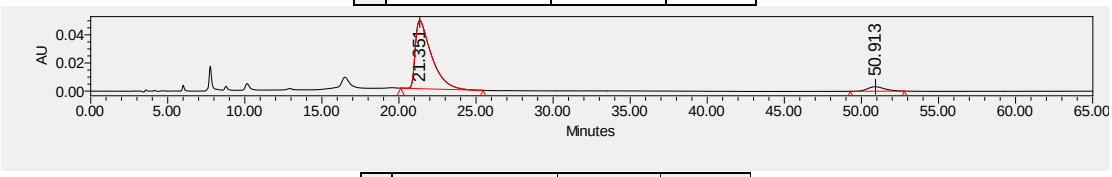


3k

White solid, 124 – 126 °C, 22.5 mg, 61% yield, 87% ee, >19:1 dr for the isolated product. t: 22 h. $[\alpha]^{16}_D$ = +167.6 (*c* 0.24, CH_2Cl_2); HPLC (Daicel chiralcel IF, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 21.35 min, $t_{R(minor)}$ = 50.91 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 2.8 Hz, 1H), 6.99 – 7.04 (m, 3H), 6.89 – 6.90 (m, 1H), 6.74 (d, *J* = 6.0 Hz, 1H), 6.50 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.23 (d, *J* = 8.8 Hz, 2H), 5.28 (d, *J* = 1.2 Hz, 1H), 4.36 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 4.11 (d, *J* = 6.0 Hz, 1H), 3.93 (dd, *J* = 11.2 Hz, *J* = 81.2 Hz, 2H), 3.09 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.77 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 212.6, 150.5, 145.4, 142.4, 136.9, 136.4, 128.9, 121.7, 112.8, 110.8, 109.6, 96.2, 84.5, 61.8, 58.5, 53.7, 52.6, 50.1; **HRMS** (FTMS+c ESI): Calcd for $C_{20}H_{16}{}^{34.9689}ClNO_2SH^+$ [M+H$^+$] 370.0663, found 370.0666, Calcd for $C_{20}H_{16}{}^{36.9659}ClNO_2SH^+$ [M+H$^+$] 372.0634, found 372.0632; **IR** (neat): 2922, 2858, 1730, 1594, 1494, 1355, 1328, 1308, 1150, 1069, 866, 802, 687, 651,501 cm^{-1}.

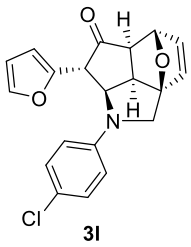


	Retention Time	Area	% Area
1	22.400	16358400	50.53
2	53.118	16014838	49.47



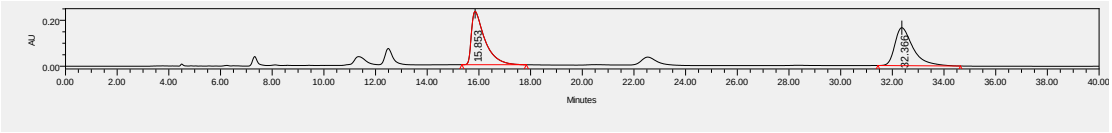
	Retention Time	Area	% Area
1	21.351	3544669	93.51
2	50.913	245905	6.49

(2a*R*,2a^1*R*,5*S*,5a*R*,7*R*,7a*R*)-1-(4-Chlorophenyl)-7-(furan-2-yl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3l)

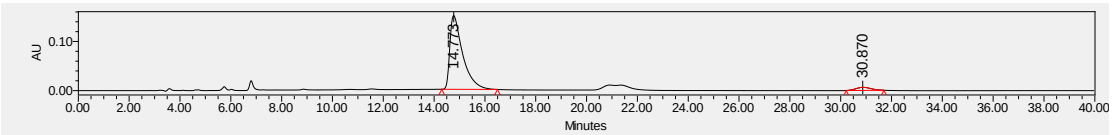


3l

White solid, 124 – 126 °C, 18.0 mg, 51% yield, 91% ee, >19:1 dr for the isolated product. t: 22 h. $[\alpha]^{16}_D$ = +149.4 (*c* 0.18, CH_2Cl_2); HPLC (Daicel chiralcel IF, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 14.78 min, $t_{R(minor)}$ = 30.87 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 0.8 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 6.0 Hz, 1H), 6.49 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.40 – 6.41 (m, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 6.19 (d, *J* = 9.2 Hz, 2H), 5.26 (d, *J* = 1.2 Hz, 1H), 4.56 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 3.92 (d, *J* = 6.8 Hz, 1H), 3.91 (dd, *J* = 11.2 Hz, *J* = 68.0 Hz, 2H), 3.09 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.75 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 212.6, 150.5, 145.4, 142.4, 136.9, 136.4, 128.9, 121.7, 112.8, 110.8, 109.6, 96.2, 84.5, 61.8, 58.5, 53.7, 52.6, 50.1; **HRMS** (FTMS+c ESI): Calcd for $C_{20}H_{16}^{34.9689}ClNO_3H^+$ [M+H$^+$] 354.0891, found 354.0895, Calcd for $C_{20}H_{16}^{36.9659}ClNO_3H^+$ [M+H$^+$] 356.0862, found 356.0862; **IR** (neat): 2919, 2855, 1732, 1699, 1594, 1495, 1458, 1355, 1337, 1308, 1150, 1067, 1010, 868, 806, 739, 691, 657, 508 cm^{-1}.

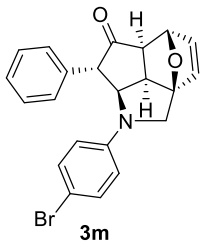


	Retention Time	Area	% Area
1	15.853	8375252	50.90
2	32.366	8078781	49.10



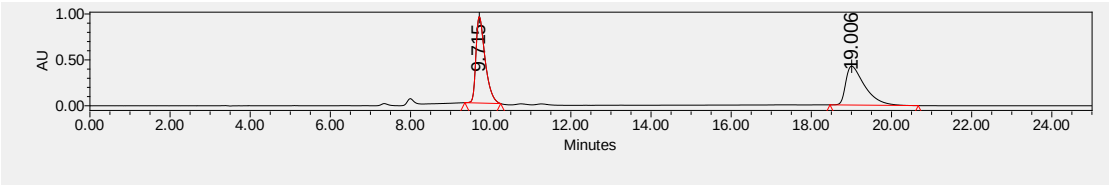
	Retention Time	Area	% Area
1	14.773	5261915	95.34
2	30.870	256915	4.66

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Bromophenyl)-7-phenyl-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3m)

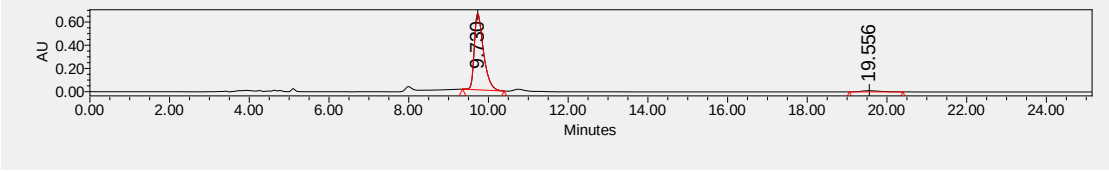


3m

White solid, 158 – 160 °C, 13.8 mg, 34% yield, 94% ee, >19:1 dr for the isolated product. t: 72 h. $[\alpha]^{20}_D$ = +174.5 (*c* 0.11, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 9.73 min, $t_{R(minor)}$ = 19.56 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 – 7.39 (m, 3H), 7.10 (d, *J* = 6.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 6.0 Hz, 1H), 6.49 – 6.51 (m, 1H), 6.05 (d, *J* = 8.8 Hz, 2H), 5.30 (s, 1H), 4.34 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 3.93 (dd, *J* = 11.2 Hz, *J* = 86.4 Hz, 2H), 3.77 (d, *J* = 6.0 Hz, 1H), 3.12 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.78 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.5, 145.7, 139.3, 137.0, 136.4, 131.7, 129.1, 128.8, 127.5, 113.9, 108.6, 96.1, 84.6, 65.7, 54.3, 53.0, 50.2; **HRMS** (FTMS+c ESI): Calcd for $C_{22}H_{18}{}^{78.9183}BrNO_2H^+$ [M+H$^+$] 408.0594, found 408.0594; Calcd for $C_{22}H_{18}{}^{80.9163}BrNO_2H^+$ [M+H$^+$] 410.0573, found 410.0573; **IR** (neat): 2999, 2921, 2849, 1733, 1586, 1493, 1452, 1351, 1260, 1138, 1072, 990, 858, 805, 742, 695, 645, 618, 545, 503 cm^{-1}.

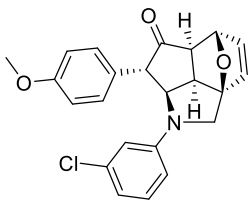


	Retention Time	Area	% Area
1	9.715	14969108	51.94
2	19.006	13852798	48.06



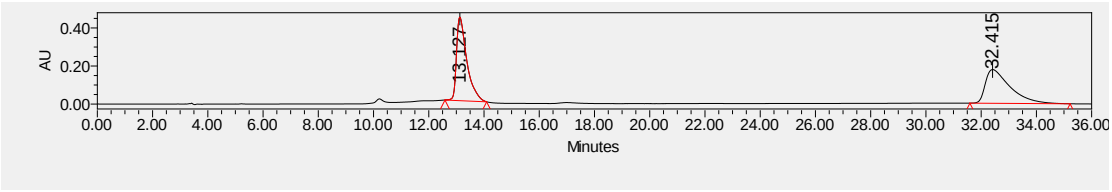
	Retention Time	Area	% Area
1	9.730	10524290	96.95
2	19.556	330595	3.05

(2a*R*,2a^1*R*,5*S*,5aR,7*S*,7a*R*)-1-(3-Chlorophenyl)-7-(4-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3n)

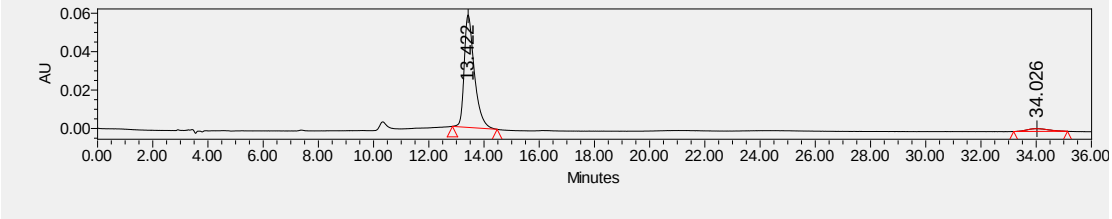


3n

White solid, 141 – 143 °C, 25.2 mg, 64% yield, 90% ee, >19:1 dr for the isolated product. t: 22h. $[\alpha]^{20}_D$ = +188.3 (*c* 0.32, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 13.42 min, $t_{R(minor)}$ = 34.03 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.02 – 7.05 (m, 2H), 6.89 – 6.93 (m, 3H), 6.74 (d, *J* = 5.6 Hz, 1H), 6.58 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 1H), 6.49 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.17 (t, *J* = 2.4 Hz, 1H), 6.09 (dd, *J* = 2.4 Hz, *J* = 8.0 Hz, 1H), 5.28 (d, *J* = 1.6 Hz, 1H), 4.31 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 3.94 (dd, *J* = 10.8 Hz, *J* = 77.2 Hz, 2H), 3.83 (s, 3H), 3.73 (d, *J* = 6.0 Hz, 1H), 3.08 (dd, *J* = 2.8 Hz, *J* = 6.8 Hz, 1H), 2.76 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ= 216.0, 159.0, 147.8, 136.9, 136.4, 134.9, 131.3, 129.9, 129.9, 116.4, 114.6, 112.5, 110.4, 96.0, 84.5, 65.8, 64.8, 53.3, 54.1, 52.7, 50.1; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{20}{}^{34.9689}ClNO_3H^+$ [M+H$^+$] 394.1204, found 394.1214, Calcd for $C_{23}H_{20}{}^{36.9659}ClNO_3H^+$ [M+H$^+$] 396.1175, found 396.1183; **IR** (neat): 2932, 2910, 2836, 1729, 1590, 1491, 1462, 1362, 1246, 1141, 985, 825, 752, 691 cm^{-1}.

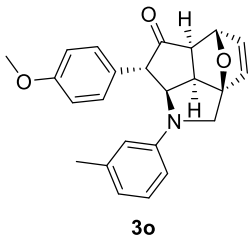


	Retention Time	Area	% Area
1	13.127	11370339	50.82
2	32.415	11001240	49.18



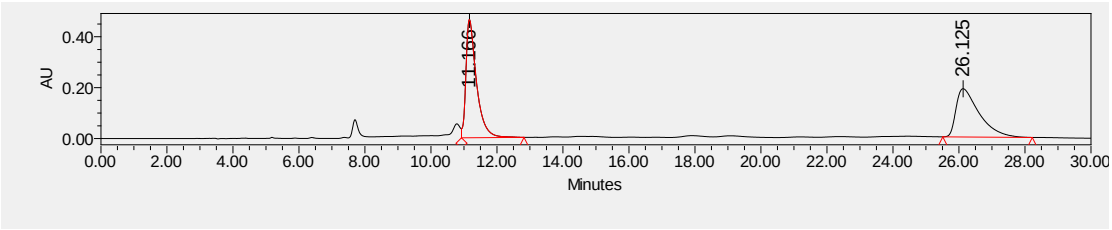
	Retention Time	Area	% Area
1	13.422	1496139	95.04
2	34.026	78104	4.96

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-7-(4-Methoxyphenyl)-1-(m-tolyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3o)

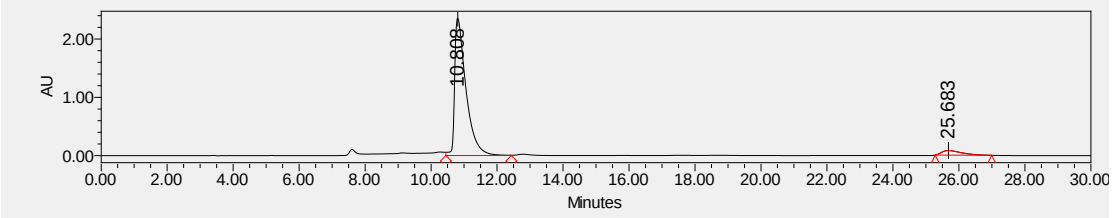


3o

White solid, 125 – 127 °C, 28.0 mg, 75% yield, 89% ee, >19:1 dr for the isolated product. t: 20 h. $[\alpha]^{19}_D$ = +166.3 (*c* 0.25, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 10.81 min, $t_{R(minor)}$ = 25.68 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.04 – 7.07 (m, 2H), 6.91 – 6.98 (m, 3H), 6,74 (d, *J* = 5.6 Hz, 1H), 6.48 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.45 (d, *J* = 7.6 Hz,1H), 6.12 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 5.95 (s, 1H), 4.33 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 3.95 (dd, *J* = 11.2 Hz, *J* = 81.2 Hz, 2H), 3.84 (s, 3H), 3.76 (d, *J* = 6.4 Hz, 1H), 3.06 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.75 (d, *J* = 6.8 Hz, 1H), 2.01 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.6, 158.8, 146.9, 138.8, 137.1, 136.2, 130.0, 129.0, 117.4, 114.4, 113.6, 109.1, 96.2, 84.4, 65.8, 65.2, 55.3, 54.2, 52.7, 50.0, 21.5; **HRMS** (FTMS+c ESI): Calcd for $C_{24}H_{23}NO_3H^+$ [M+H$^+$] 374.1751, found 374.1754; **IR** (neat): 2955, 2910, 2855, 2837, 1726, 1602, 1579, 1504, 1459, 1356, 1301, 1242, 1174, 1145, 1028, 866, 827, 764, 689, 587 cm^{-1}.

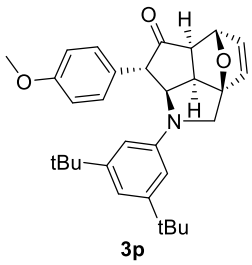


	Retention Time	Area	% Area
1	11.166	10291893	52.79
2	26.125	9204462	47.21



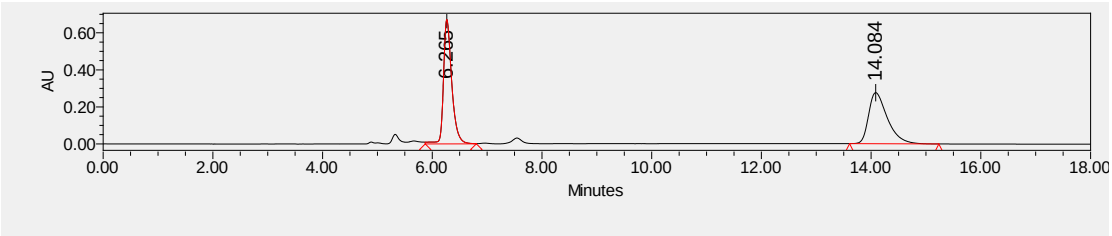
	Retention Time	Area	% Area
1	10.808	56438170	94.30
2	25.683	3413739	5.70

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(3,5-Di-tert-butylphenyl)-7-(4-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3p)

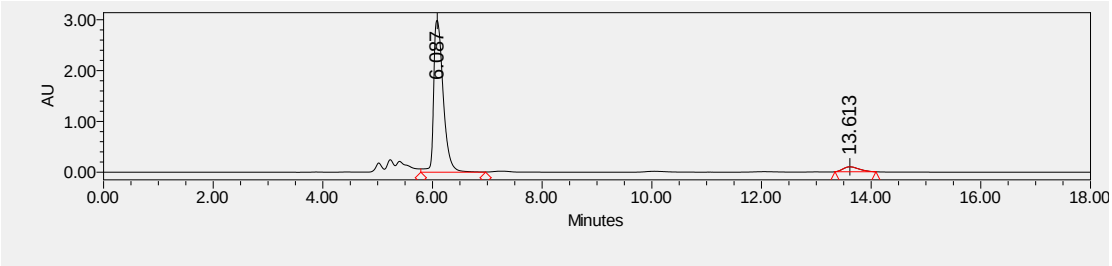


3p

White solid, 164 – 166 °C, 31.1 mg, 66% yield, 90% ee, >19:1 dr for the isolated product. t: 21 h. $[\alpha]^{19}_D$ = +117.0 (*c* 0.19, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 6.09 min, $t_{R(minor)}$ = 13.61 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.10 – 7.12 (m,2H), 6.92 – 6.94 (m, 2H), 6.75 – 6.76 (m, 2H), 6.48 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.22 (d, *J* = 1.2 Hz, 1H), 5.03 (d, *J* = 1.2 Hz, 1H), 4.55 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 4.01 (dd, *J* = 10.8 Hz, *J* = 84.0 Hz, 2H), 3.78 – 3.82 (m, 4H), 3.07 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.74 (d, *J* = 8.4 Hz, 1H), 1.11 (s, 18H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.7, 158.9, 151.7, 146.7, 137.2, 136.2, 131.4, 129.8, 114.9, 111.6, 107.0, 96.2, 84.7, 65.7, 65.3, 55.3, 54.0, 52.8, 50.4, 34.7, 31.2; **HRMS** (FTMS+c ESI): Calcd for $C_{31}H_{37}NO_3H^+$ [M+H$^+$] 472.2864, found 472.2864; **IR** (neat): 2961, 2926, 2865, 1726, 1590, 1511, 1437, 1341, 1245, 1177, 1128, 1024, 870, 848, 751, 732, 685, 590 cm^{-1}.

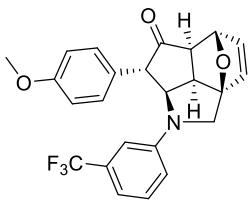


	Retention Time	Area	% Area
1	6.265	7046031	51.84
2	14.084	6544934	48.16



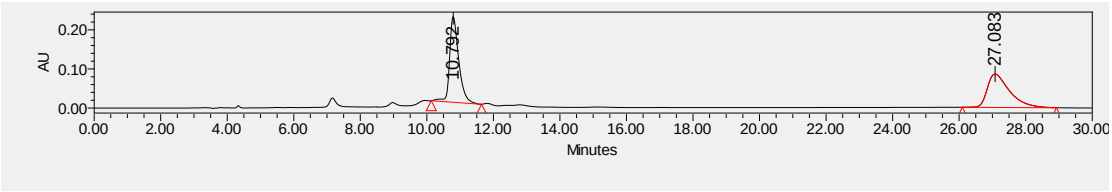
	Retention Time	Area	% Area
1	6.087	36208047	94.82
2	13.613	1979134	5.18

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-7-(4-Methoxyphenyl)-1-(3-(trifluoromethyl)phenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3q)

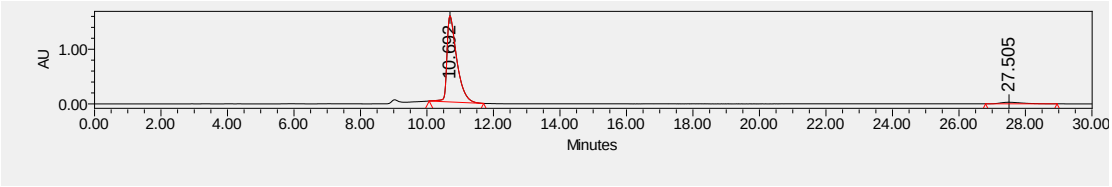


3q

White solid, 76 – 78 °C, 32.9 mg, 77% yield, 92% ee, >19:1 dr for the isolated product. t: 29 h. $[\alpha]^{19}_D$ = +150.5 (*c* 0.20, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 10.69 min, $t_{R(minor)}$ = 27.50 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.12 (t, *J* = 8.0 Hz, 1H), 7.02 – 7.04 (m, 2H), 6.91 – 6.93 (m, 2H), 6.83 – 6.85 (m, 1H), 6.74 – 6.76 (m, 1H), 6.50 – 6.51 (m, 1H), 6.38 – 6.42 (m, 2H), 5.30 (s, 1H), 4.37 (dd, *J* = 6.4 Hz, *J* = 8.8 Hz, 1H), 3.99 (dd, *J* = 11.2 Hz, *J* = 82.0 Hz, 2H), 3.83 (s, 3H), 3.75 (d, *J* = 6.4 Hz, 1H), 3.11 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.78 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.8, 159.1, 146.9, 136.8, 136.4, 131.4 (d, *J* = 31.7 Hz, 1C), 131.0, 129.9, 129.4, 124.4 (q, *J* = 272.0 Hz, 1C), 115.0, 114.7, 123.0 (q, *J* = 3.7 Hz, 1C), 108.9 (q, *J* = 4.2 Hz, 1C), 96.0, 84.5, 65.8, 64.8, 55.3, 54.1, 52.7, 50.2; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ = –63.0; **HRMS** (FTMS+c ESI): Calcd for $C_{24}H_{20}F_3NO_3H^+$ [M+H$^+$] 428.1468, found 428.1474; **IR** (neat): 2918, 2844, 1732, 1610, 1509, 1456, 1366, 1252, 1160, 1115, 1072, 1031, 1001, 860, 832, 759, 691 cm^{-1}.

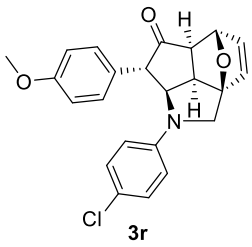


	Retention Time	Area	% Area
1	10.792	4174782	51.36
2	27.083	3953573	48.64



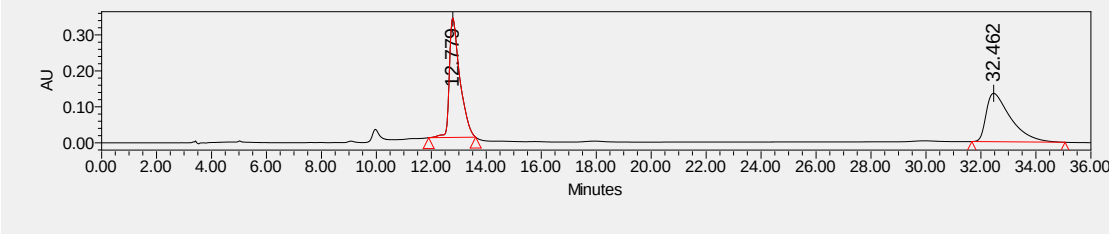
	Retention Time	Area	% Area
1	10.692	32360477	96.06
2	27.505	1327752	3.94

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Chlorophenyl)-7-(4-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3r)

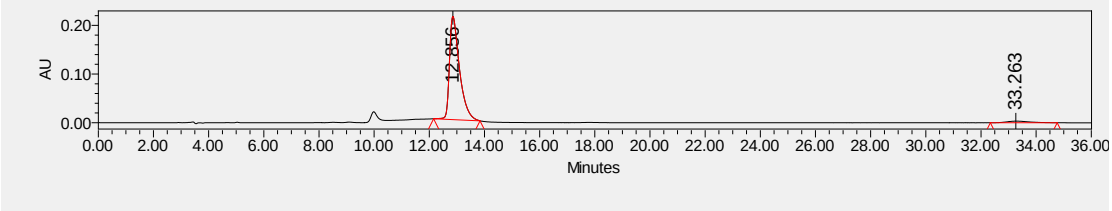


3r

White solid, 145 – 147 °C, 31.1 mg, 79% yield, 93% ee, >19:1 dr for the isolated product. t: 16h. $[\alpha]^{19}_D$ = +157.1 (*c* 0.29, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 12.86 min, $t_{R(minor)}$ = 33.26 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.01 – 7.04 (m, 2H), 6.94 – 6.97 (m, 2H), 6.90 – 6.92 (m, 2H), 6.74 (d, *J* = 6.0 Hz, 1H), 6.49 (dd, *J* = 1.6 Hz, *J* = 6.0 Hz, 1H), 6.13 (d, *J* = 8.8 Hz, 2H), 5.29 (d, *J* = 1.2 Hz, 1H), 4.30 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 3.80 – 4.04 (m, 2H), 3.83 (s, 3H), 3.72 (d, *J* = 6.0 Hz, 1H), 3.09 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.76 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.1, 158.8, 145.4, 136.9, 136.4, 131.3, 129.9, 128.8, 121.4, 114.5, 113.3, 96.1, 84.5, 65.7, 64.9, 55.3, 54.1, 52.8, 50.2; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{20}{}^{34.9689}ClNO_3H^+$ [M+H$^+$] 394.1204, found 394.1208, Calcd for $C_{23}H_{20}{}^{36.9659}ClNO_3H^+$ [M+H$^+$] 396.1175, found 396.1177; **IR** (neat): 2906, 2840, 1735, 1598, 1497, 1463, 1352, 1247, 1180, 1150, 1126, 1026, 867, 828, 805, 656, 544, 509 cm^{-1}.

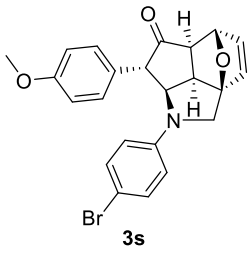


	Retention Time	Area	% Area
1	12.779	8809260	51.45
2	32.462	8311806	48.55



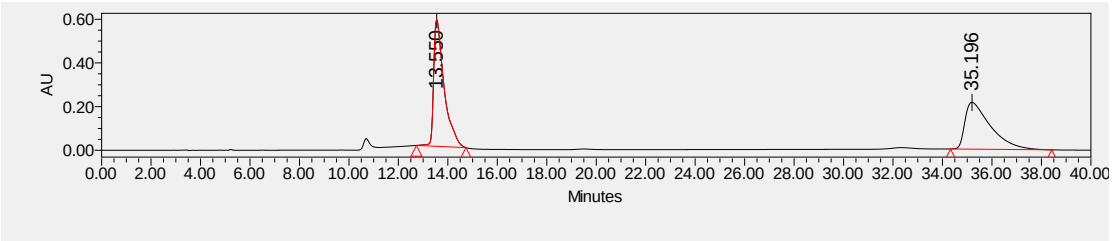
	Retention Time	Area	% Area
1	12.856	5344764	96.56
2	33.263	190321	3.44

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Bromophenyl)-7-(4-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3s)

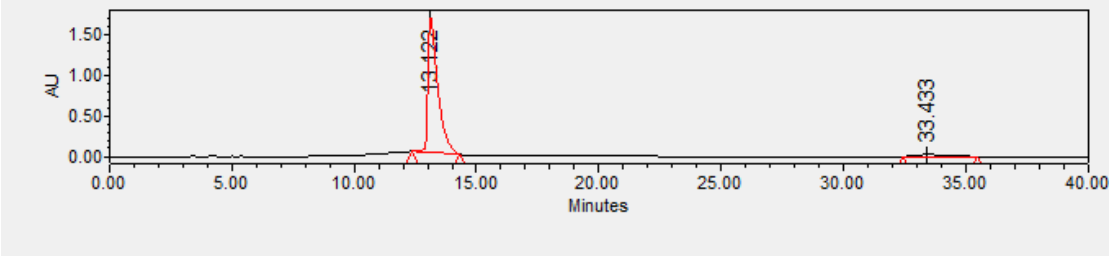


3s

White solid, 146 – 148 °C, 31.0 mg, 71% yield, 93% ee, >19:1 dr for the isolated product. t: 25 h. $[\alpha]^{19}_D$ = +139.3 (*c* 0.42, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 13.21 min, $t_{R(minor)}$ = 33.43 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.07 – 7.10 (m, 2H), 7.01 – 7.03 (m, 2H), 6.89 – 6.92 (m, 2H), 6.74 (d, *J* = 6.0 Hz,1H), 6.49 (dd, *J* = 2.0 Hz, *J* = 4.0 Hz, 1H), 6.09 (d, *J* = 8.8 Hz, 2H), 5.28 (d, *J* = 1.6 Hz, 1H), 4.29 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 3.91 (dd, *J* = 10.8 Hz, *J* = 84.8 Hz, 2H), 3.83 (s, 3H), 3.09 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.75 (d, *J* = 7.6 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.0, 158.8, 145.8, 136.9, 136.4, 131.7, 131.2, 129.8, 114.5, 113.9, 108.5, 96.1, 84.5, 65.7, 64.8, 55.2, 54.1, 52.8, 50.2; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{20}{}^{78.9183}BrNO_3H^+$ [M+H$^+$] 438.0699, found 438.0700; Calcd for $C_{23}H_{20}{}^{80.9163}BrNO_3H^+$ [M+H$^+$] 440.0679, found 440.0680; **IR** (neat): 2959, 2906, 2839, 1733, 1589, 1494, 1461, 1352, 1248, 1180, 1027, 865, 829, 804, 756, 689, 504 cm^{-1}.

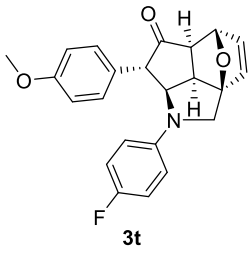


	Retention Time	Area	% Area
1	13.550	16983310	52.43
2	35.196	15406194	47.57



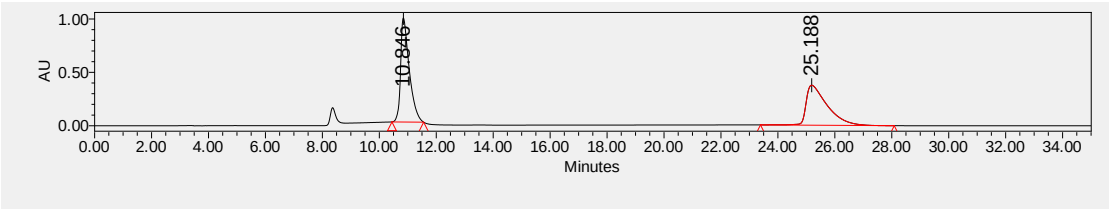
	Retention Time	Area	% Area
1	13.122	46477652	96.79
2	33.433	1540077	3.21

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-Fluorophenyl)-7-(4-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3t)

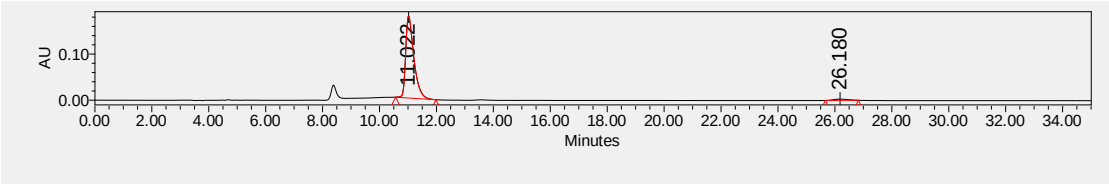


3t

White solid, 134 – 136 °C, 27.9 mg, 74% yield, 95% ee, >19:1 dr for the isolated product. t: 12h. $[\alpha]^{17}_D$ = +163.3 (*c* 0.16, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 11.02 min, $t_{R(minor)}$ = 26.18 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.02 – 7.05 (m, 2H), 6.90 – 6.93 (m, 2H), 6.71 – 6.75 (m, 3H), 6.49 (dd, *J* = 1.6 Hz, *J* = 6.0 Hz, 1H), 6.11 – 6.15 (m, 2H), 5.29 (d, *J* = 1.6 Hz, 1H), 4.28 (d, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 3.92 (dd, *J* = 10.8 Hz, *J* = 87.2 Hz, 2H), 3.83 (s, 3H), 3.73 (d, *J* = 6.4 Hz, 1H), 3.10 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.75 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.3, 157.6 (d, *J* = 239.8 Hz, 1C), 143.4 (d, *J* = 1.5 Hz, 1C), 137.0, 136.3, 131.4, 129.9, 115.4 (d, *J* = 21.9 Hz, 1C), 114.5, 112.6 (d, *J* = 7.1 Hz, 1C), 96.2, 84.5, 66.0, 65.1, 55.3, 54.1, 52.9, 50.5; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ = –129.5; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{20}FNO_3H^+$ [M+H$^+$] 378.1500, found 378.1502; **IR** (neat): 2947, 2909, 2832, 1724, 1608, 1508, 1463, 1345, 1249, 1067, 1027, 863, 821, 755, 678, 556, 495 cm^{-1}.

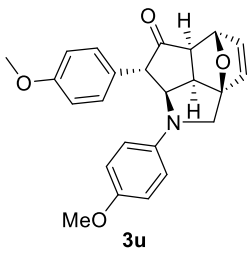


	Retention Time	Area	% Area
1	10.846	20602647	51.72
2	25.188	19230578	48.28



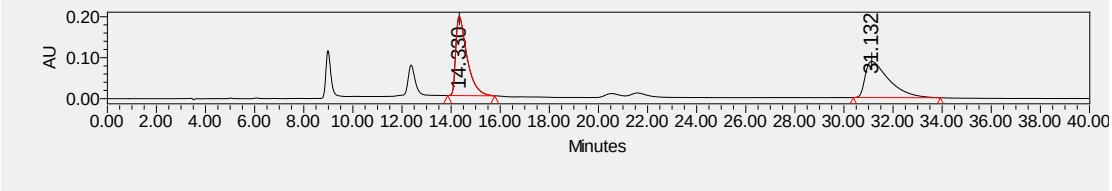
	Retention Time	Area	% Area
1	11.022	3535257	97.36
2	26.180	96040	2.64

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1,7-Bis(4-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3u)

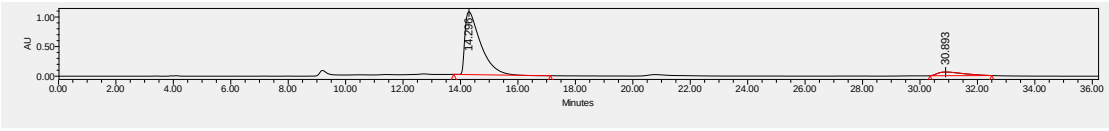


3u

White solid, 115 – 117 °C, 24.1 mg, 62% yield, 82% ee, >19:1 dr for the isolated product. t: 16 h. $[\alpha]^{20}_D$ = +126.6 (*c* 0.40, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 14.30 min, $t_{R(minor)}$ = 30.89 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.05 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 5.6 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.48 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.17 (d, *J* = 8.8 Hz, 2H), 5.29 (d, *J* = 1.2 Hz, 1H), 4.27 (dd, *J* = 6.0 Hz, *J* = 9.2 Hz, 1H), 3.92 (dd, *J* = 10.8 Hz, *J* = 91.2 Hz, 2H), 3.84 (s, 3H), 3.74 (d, *J* = 6.0 Hz, 1H), 3.68 (s, 3H), 3.08 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.74 (d, *J* = 6.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.7, 158.7, 151.3, 141.6, 137.1, 136.2, 131.5, 129.9, 114.8, 114.5, 112.8, 96.3, 84.5, 66.1, 65.4, 55.8, 55.3, 54.2, 52.9, 50.5; **HRMS** (FTMS+c ESI): Calcd for $C_{24}H_{23}NO_4H^+$ [M+H$^+$] 390.1700, found 390.1702; **IR** (neat): 2991, 2934, 2905, 2833, 1726, 1705, 1610, 1509, 1461, 1346, 1240, 1177, 1133, 1029, 815, 789, 674, 521 cm^{-1}.

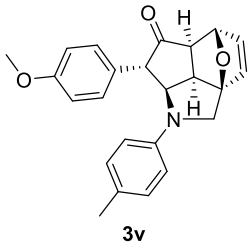


	Retention Time	Area	% Area
1	14.330	6161404	50.96
2	31.132	5928961	49.04



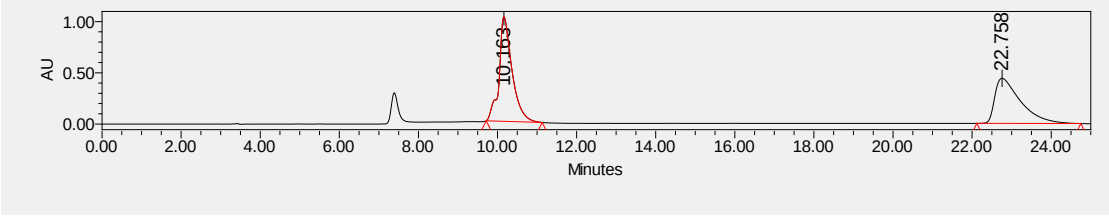
	Retention Time	Area	% Area
1	14.296	40501799	91.20
2	30.893	3908759	8.80

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-7-(4-Methoxyphenyl)-1-(p-tolyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3v)

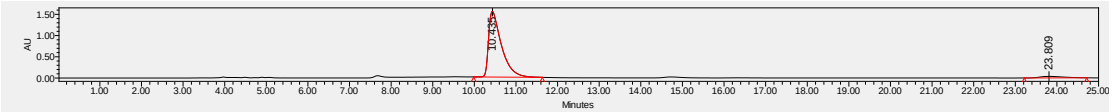


3v

White solid, 115 – 117 °C, 29.8 mg, 80% yield, 92% ee, >19:1 dr for the isolated product. t: 16 h. $[\alpha]^{17}_D$ = +156.7 (*c* 0.42, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 10.44 min, $t_{R(minor)}$ = 23.81 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.05 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 6.0 Hz, 1H), 6.48 (dd, *J* = 1.6 Hz, *J* = 6.0 Hz, 1H), 6.15 (d, *J* = 8.4 Hz, 2H), 5.29 (d, *J* = 1.2 Hz, 1H), 4.31 (dd, *J* = 6.0 Hz, *J* = 9.2 Hz, 1H), 3.94 (dd, *J* = 10.8 Hz, *J* = 93.2 Hz, 2H), 3.84 (s, 3H), 3.74 (d, *J* = 6.0 Hz, 1H), 3.07 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.74 (d, *J* = 6.8 Hz, 1H), 2.17 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.6, 158.7, 144.8, 137.2, 136.2, 131.6, 129.9, 129.6, 125.6, 114.4, 112.2, 96.2, 84.5, 65.8, 65.3, 55.3, 54.2, 52.8, 50.2, 20.1; **HRMS** (FTMS+c ESI): Calcd for $C_{24}H_{23}NO_3H^+$ [M+H$^+$] 374.1751, found 374.1761; **IR** (neat): 2912, 2839, 1726, 1612, 1513, 1460, 1346, 1135, 1068, 1030, 862, 806, 762, 680 cm^{-1}.

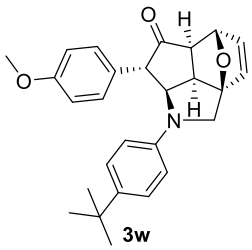


	Retention Time	Area	% Area
1	10.163	23245124	53.85
2	22.758	19921885	46.15

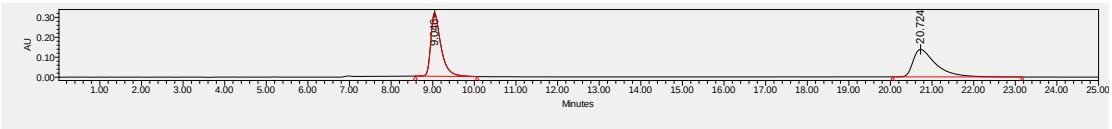


	Retention Time	Area	% Area
1	10.435	33087397	95.89
2	23.809	1417600	4.11

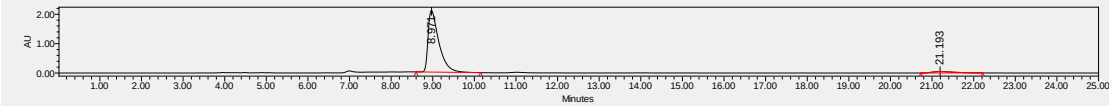
(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-1-(4-(Tert-butyl)phenyl)-7-(4-methoxyphenyl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3w)



White solid, 132- 134 °C, 30.7 mg, 74% yield, 91% ee, >19:1 dr for the isolated product. t: 16 h. $[\alpha]^{19}_D$ = +137.3 (*c* 0.24, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 8.97 min, $t_{R(minor)}$ = 21.19 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.06 – 7.09 (m, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 5.6 Hz, 1H), 6.48 (dd, *J* = 5.6 Hz, *J* = 1.6 Hz, *J* = 6.0 Hz, 1H), 6.22 (d, *J* = 8.8 Hz, 2H), 5.29 (d, *J* = 1.2 Hz, 1H), 4.32 (dd, *J* = 6.0 Hz, *J* = 9.2 Hz, 1H), 3.95 (dd, *J* = 11.2 Hz, *J* = 88.8 Hz, 2H), 3.85 (s, 3H), 3.75 (s, *J* = 6.0 Hz, 1H), 3.06 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 1H), 2.75 (d, *J* = 6.4 Hz, 1H), 1.23 (s, 9H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.6, 158.7, 144.8, 139.3, 137.2, 136.2, 131.6, 129.9, 125.9, 114.5, 111.8, 96.2, 84.6, 65.9, 65.2, 55.3, 54.2, 52.9, 50.2, 33.7, 31.5; **HRMS** (FTMS+c ESI): Calcd for $C_{27}H_{29}NO_3H^+$ [M+H$^+$] 416.2220, found 416.2207; **IR** (neat): 2957, 2837, 1729, 1610, 1515, 1461, 1343, 1254, 1134, 1032, 862, 824, 770, 686, 589, 554 cm^{-1}.

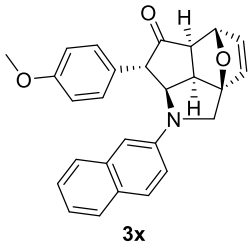


	Retention Time	Area	% Area
1	9.046	5386736	50.62
2	20.724	5254209	49.38



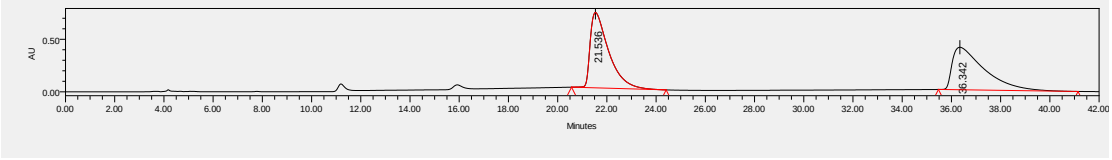
	Retention Time	Area	% Area
1	8.971	37807973	95.58
2	21.193	1746995	4.42

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-7-(4-Methoxyphenyl)-1-(naphthalen-2-yl)-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3x)

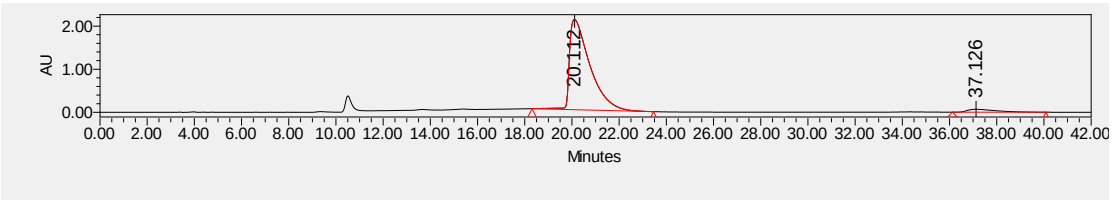


3x

White solid, 125 – 127 °C, 22.9 mg, 56% yield, 91% ee, >19:1 dr for the isolated product. t: 21 h. $[\alpha]^{19}_D$ = +190.2 (*c* 0.50, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 20.11 min, $t_{R(minor)}$ = 37.13 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.22 – 7.29 (m, 2H), 7.14 – 7.16 (m, 1H), 7.08 – 7.12 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 5.6 Hz, 1H), 6.62 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 6.51 (dd, *J* = 1.6 Hz, *J* = 6.0 Hz, 1H), 6.14 (d, *J* = 2.0 Hz, 1H), 5.32 (d, *J* = 1.2 Hz, 1H), 4.47 (dd, *J* = 6.4 Hz, *J* = 9.2 Hz, 1H), 4.09 (dd, *J* = 11.2 Hz, *J* = 86.8 Hz, 2H), 3.87 (s, 3H), 3.82 (s, 1H), 3.13 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.79 (d, *J* = 6.4 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 216.4, 158.9, 144.6, 137.1, 136.3, 134.7, 131.7, 130.1, 128.8, 127.3, 126.6, 126.2, 126.0, 121.8, 115.5, 114.5, 106.4, 96.2, 84.5, 65.9, 65.1, 55.4, 54.2, 52.8, 50.3; **HRMS** (FTMS+c ESI): Calcd for $C_{27}H_{23}NO_3H^+$ [M+H$^+$] 410.1751, found 410.1758; **IR** (neat): 2954, 2913, 2839, 1726, 1625, 1600, 1509, 1463, 1391, 1366, 1246, 1143, 1031, 861, 828, 808, 741, 678, 469 cm^{-1}.

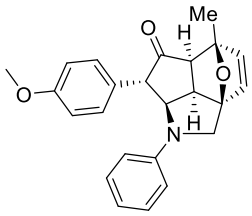


	Retention Time	Area	% Area
1	21.536	37491783	50.54
2	36.342	36687280	49.46



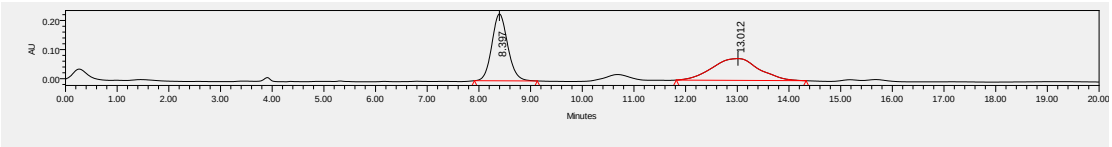
	Retention Time	Area	% Area
1	20.112	125922071	95.72
2	37.126	5628920	4.28

(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-7-(4-Methoxyphenyl)-5-methyl-1-phenyl-1,2,5,5a,7,7a-hexahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (3y)

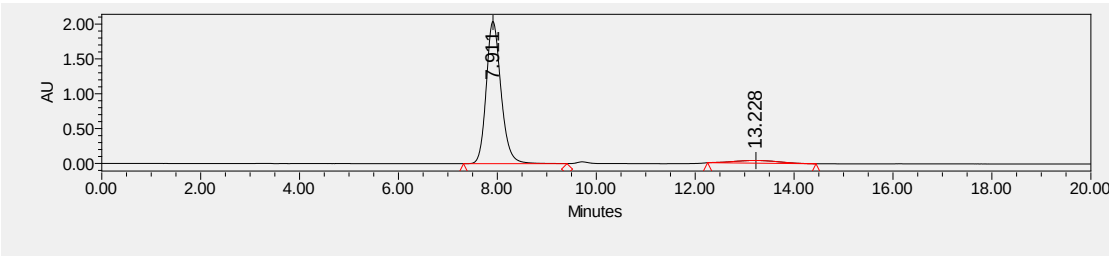


3y

White solid, 112 – 114 °C, 33.6 mg, 90% yield, 89% ee, >19:1 dr for the isolated product. t: 20 h. $[\alpha]^{20}_D$ = +190.7 (*c* 0.30, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 7.91 min, $t_{R(minor)}$ = 13.23 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.00 – 7.04 (m, 4H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 5.6 Hz, 1H), 6.60 (t, *J* = 6.8 Hz, 1H), 6.31 (d, *J* = 5.6 Hz, 1H), 6.19 (d, *J* = 8.4 Hz, 2H), 4.28 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 3.92 (dd, *J* = 10.8 Hz, *J* = 93.2 Hz, 2H), 3.84 (s, 3H), 3.16 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H), 2.60 (d, *J* = 6.4 Hz, 1H), 1.67 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 215.1, 158.7, 147.0, 140.1, 137.3, 131.5, 130.2, 129.0, 116.5, 114.4, 112.2, 95.4, 90.8, 65.3, 65.1, 56.9, 55.5, 55.3, 50.6, 15.7; **HRMS** (FTMS+c ESI): Calcd for $C_{24}H_{23}NO_3H^+$ [M+H$^+$] 374.1751, found 374.1753; **IR** (neat): 3054, 3040, 2974, 2910, 2838, 1723, 1597, 1506, 1462, 1350, 1250, 1181, 1140, 1030, 867, 836, 743, 689, 587, 549, 507 cm^{-1}.

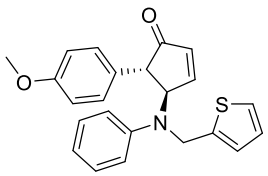


	Retention Time	Area	% Area
1	8.397	4901449	50.98
2	13.012	4713826	49.02



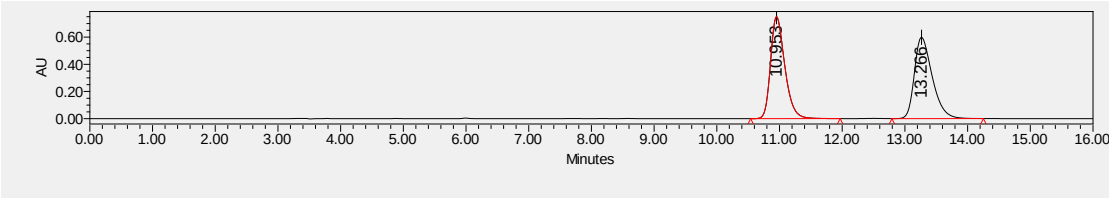
	Retention Time	Area	% Area
1	7.911	42381827	94.58
2	13.228	2429912	5.42

(4*R*,5*S*)-5-(4-Methoxyphenyl)-4-(phenyl(thiophen-2-ylmethyl)amino)cyclopent-2-en-1-one (4bn)

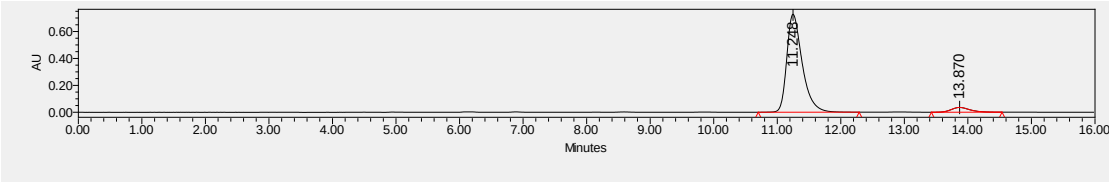


4bn

White solid, 120 – 122 °C, 35.6 mg, 95% yield, 89% ee, >19:1 dr for the isolated product. t: 25 h. $[\alpha]^{19}_{D}$ = –156.6 (*c* 0.49, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 11.25 min, $t_{R(minor)}$ = 13.87 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.76 (dd, *J* = 2.4 Hz, *J* = 6.0 Hz, 1H), 7.19 – 7.21 (m, 1H), 7.13 – 7.17 (m, 2H), 7.00 – 7.03 (m, 2H), 6.93 – 6.95 (m, 1H), 6.86 – 6.89 (m, 3H), 6.79 – 6.82 (m, 1H), 6.74 – 6.76 (m, 2H), 6.42 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 5.11 (q, *J* = 2.4 Hz, 1H), 4.57 (dd, *J* = 16.8 Hz, *J* = 5.2 Hz, *J* = 59.2 Hz, 2H), 3.81 (s, 3H), 3.54 (d, *J* = 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 206.6, 162.7, 158.8, 147.9, 143.6, 135.1, 130.2, 129.2, 129.2, 126.9, 124.7, 124.5, 119.4, 115.8, 114.5, 69.2, 56.2, 55.2, 47.6; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{21}NO_2SH^+$ [M+H$^+$] 376.1366, found 376.1366. **IR** (neat): 2925, 2830, 1700, 1597, 1505, 1255, 1172, 1032, 805, 749, 691, 607, 515 cm^{-1}.

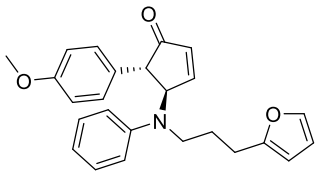


	Retention Time	Area	% Area
1	10.953	11836757	50.07
2	13.266	11802425	49.93



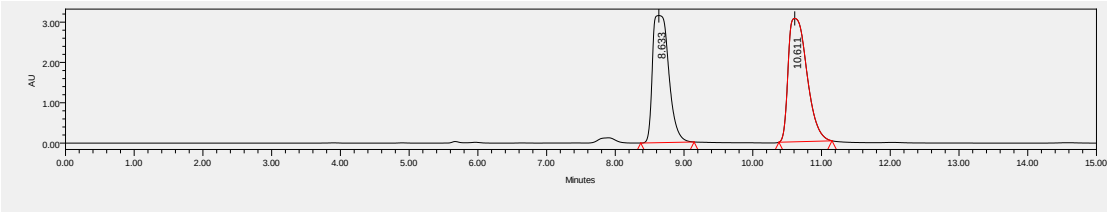
	Retention Time	Area	% Area
1	11.248	12263542	94.48
2	13.870	717042	5.52

(4*R*,5*S*)-4-((3-(Furan-2-yl)propyl)(phenyl)amino)-5-(4-methoxyphenyl)cyclopent-2-en-1-one (4bo)

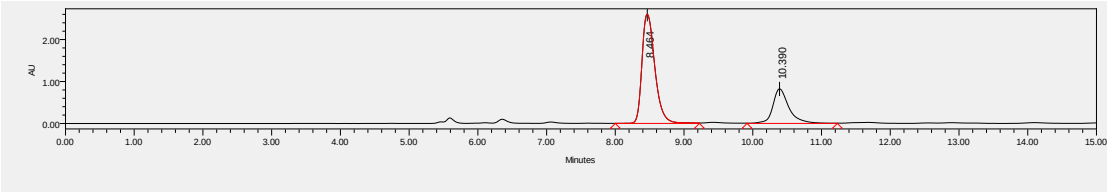


4bo

Yellow oil, 32.0 mg, 83% yield, 43% ee, >19:1 dr for the isolated product. t: 16 h. $[\alpha]^{17}_{D}$ = –70.1 (*c* 0.32, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 8.46 min, $t_{R(minor)}$ = 10.39 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.70 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 7.31 (d, *J* = 1.2 Hz, 1H), 7.13 (dd, *J* = 7.6 Hz, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.40 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 6.29 (dd, *J* = 2.0 Hz, *J* = 2.8 Hz, 1H), 5.98 (d, *J* = 2.8 Hz, 1H), 4.94 (d, *J* = 2.4 Hz, 1H), 3.97 (s, 3H), 3.46 (d, *J* = 2.8 Hz, 1H), 3.24 – 3.30 (m, 1H), 3.10 – 3.23 (m, 1H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.99 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 206.7, 163.1, 158.7, 154.9, 147.7, 141.0, 134.8, 130.2, 129.2, 129.2, 118.8, 115.7, 114.4, 110.2, 105.3, 70.6, 56.4, 55.2, 46.4, 27.1, 25.2; **HRMS** (FTMS+c ESI): Calcd for $C_{25}H_{25}NO_3H^+$ [M+H$^+$] 388.1907, found 388.1898. **IR** (neat): 2952, 2360, 1710, 1598, 1508, 1251, 1178, 750 cm^{-1}.

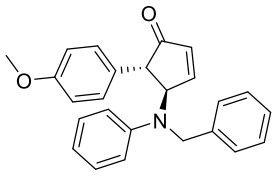


	Retention Time	Area	% Area
1	8.633	51999170	47.32
2	10.611	57897191	52.68



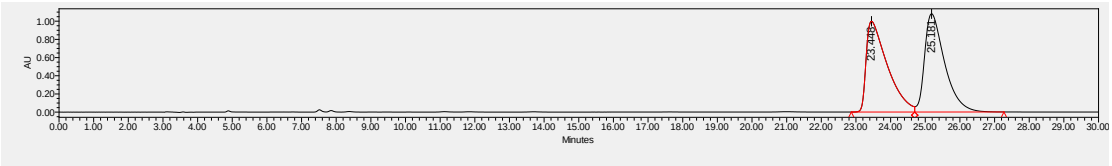
	Retention Time	Area	% Area
1	8.464	34007595	71.53
2	10.390	13538578	28.47

(4*R*,5*S*)-4-(Benzyl(phenyl)amino)-5-(4-methoxyphenyl)cyclopent-2-en-1-one (4bp)

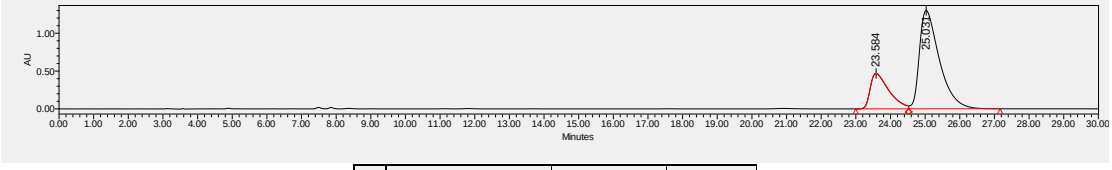


4bp

Yellow oil, 26.9 mg, 73% yield, 50% ee, >19:1 dr for the isolated product. t: 16 h. $[\alpha]^{20}_{D}$ = –74.5 (*c* 0.42, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min) $t_{R(minor)}$ = 23.58 min, $t_{R(major)}$ = 25.03 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.69 (dd, *J* = 2.0 Hz, *J* = 6.0 Hz, 2H), 7.32 – 7.35 (m, 2H), 7.25 – 7.28 (m, 2H), 7.11 (dd, *J* = 7.6 Hz, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.41 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 5.23 (d, *J* = 2.0 Hz, 1H), 4.44 (dd, *J* = 17.2 Hz, *J* = 51.6 Hz, 2H), 3.81 (s, 3H), 3.49 (d, J = 4.0 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 206.7, 162.5, 158.8, 148.6, 139.1, 135.3, 130.2, 129.2, 129.2, 128.7, 127.1, 126.3, 118.5, 114.5, 114.5, 68.7, 56.4, 55.3, 51.1; **HRMS** (FTMS+c ESI): Calcd for $C_{25}H_{23}NO_2H^+$ [M+H$^+$] 370.1801, found 370.1792; **IR** (neat): 3032, 2931, 2361, 1710, 1599, 1508, 1251, 1032, 751, 695 cm^{-1}.

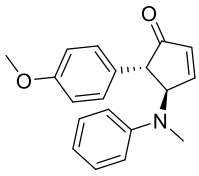


	Retention Time	Area	% Area
1	23.448	42286656	49.30
2	25.181	43493935	50.70



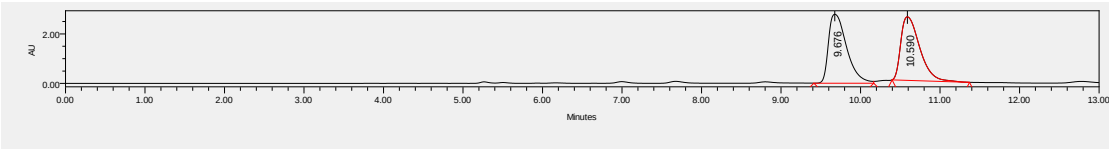
	Retention Time	Area	% Area
1	23.584	17473894	25.13
2	25.031	52063157	74.87

(4*R*,5*S*)-5-(4-Methoxyphenyl)-4-(methyl(phenyl)amino)cyclopent-2-en-1-one (4bq)

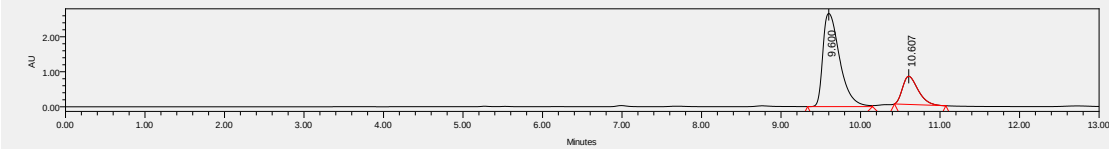


4bq

Yellow oil, 26.1 mg, 89% yield, 56% ee, >19:1 dr for the isolated product. t: 16 h. $[\alpha]^{19}_{D}$ = –80.5 (*c* 0.46, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 9.60 min, $t_{R(minor)}$ = 10.61 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.70 (dd, *J* = 2.4 Hz, *J* = 5.6 Hz, 1H), 7.12 – 7.16 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.46 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 5.08 (d, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 3.48 (d, *J* = 2.8 Hz, 1H), 2.85 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 206.8, 163.1, 158.7, 149.2, 135.0, 130.2, 129.1, 118.3, 114.4, 114.3, 69.8, 55.4, 55.2, 33.2; **HRMS** (FTMS+c ESI): Calcd for $C_{19}H_{19}NO_2H^+$ [M+H$^+$] 294.1489, found 294.1483; **IR** (neat): 2932, 2362, 1710, 1599, 1508, 1376, 1250, 1179, 1108, 1033, 824, 752, 693 cm^{-1}.

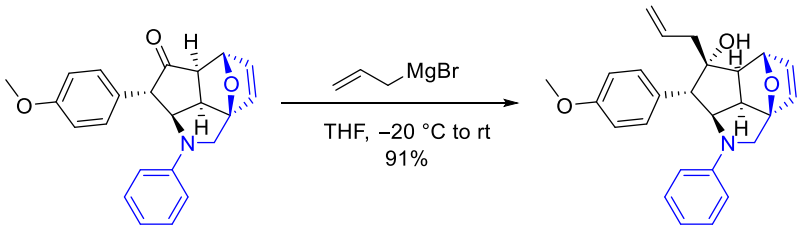


	Retention Time	Area	% Area
1	9.676	44268959	50.84
2	10.590	42810188	49.16



	Retention Time	Area	% Area
1	9.600	39152684	78.14
2	10.607	10954539	21.86

8. Product derivatizations

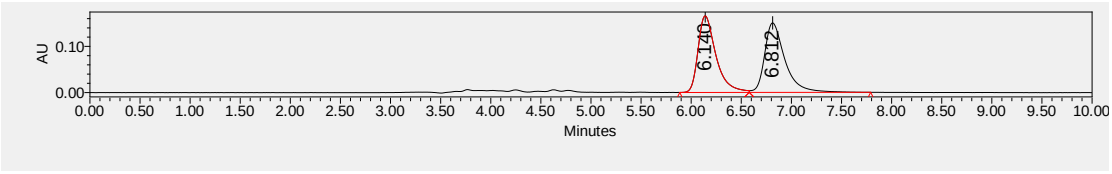


3b (95% ee) **5** (94% ee)

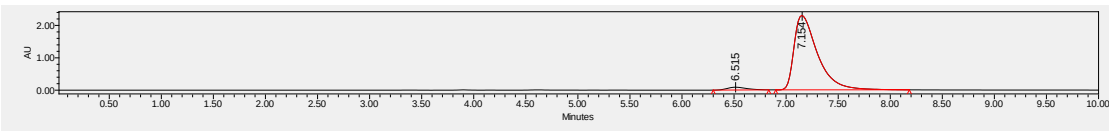
(2a*R*,2a^1*R*,5*S*,5a*R*,6*S*,7*S*,7a*R*)-6-Allyl-7-(4-methoxyphenyl)-1-phenyl-1,2,2a1,5,5a,6,7,7a-octahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6-ol (5)

At –20 °C, a solution of allylmagnesium bromide (0.30 mL, 0.30 mmol, 1.0 M in ether) was slowly added to a solution of compound **3b** (35.9 mg, 0.10 mmol, 95% ee) in THF (1 mL). The reaction was allowed to warm up to rt. The progress was monitored by thin layer chromatography. Upon completion, a saturated aqueous solution of NH_4Cl (1 mL) was added. The layers were separated, and the aqueous layer was extracted with EtOAc (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The residue was subjected to column chromatography on silica gel and eluted with EtOAc/petroleum ether (1:3, v/v) to give the product **5** as a white solid (91% yield, > 19:1 dr, 94% ee).

White solid, 97 – 99 °C, 36.3 mg, 91% yield, 94% ee, >19:1 dr for the isolated product. t: 6 h. $[\alpha]^{19}_D$ = –92.4 (*c* 0.33, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(minor)}$ = 6.52 min, $t_{R(major)}$ = 7.15 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 8.8 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 6.0 Hz, 1H), 6.56 (t, *J* = 7.2 Hz, 1H), 6.48 (dd, *J* = 1.6 Hz, *J* = 5.6 Hz, 1H), 6.36 (d, *J* = 8.4 Hz, 2H), 5.81 – 5.92 (m, 1H), 5.35 (d, *J* = 1.2 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 5.07 (d, *J* = 17.2 Hz, 1H), 4.23 (t, *J* = 8.8 Hz, 1H), 3.98 (d, *J* = 11.2 Hz, 1H), 3.72 – 3.75 (m, 5H), 2.72 – 2.76 (m, 1H), 2.34 (d, *J* = 6.8 Hz, 1H), 2.05 – 2.16 (m, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ= 158.6, 147.9, 137.1, 136.2, 134.0, 131.1, 129.8, 128.8, 119.2, 116.1, 113.6, 112.4, 94.2, 82.2, 81.3, 64.4, 64.0, 55.2, 54.2, 51.1, 48.5, 43.4; **HRMS** (FTMS+c ESI): Calcd for $C_{26}H_{27}NO_3H^+$ [M+H$^+$] 402.2064, found 402.2061; **IR** (neat): 3463, 2954, 2905, 2836, 1638, 1505, 1343, 1246, 1067, 1031, 995, 869, 835, 750, 690, 553 cm^{-1}.

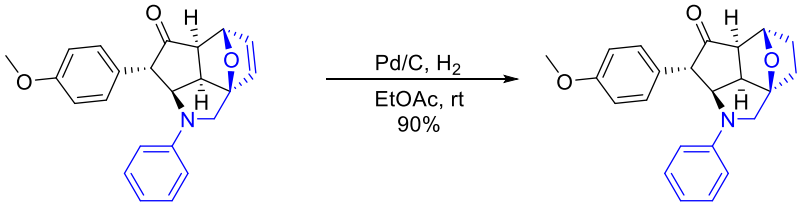


	Retention Time	Area	% Area
1	6.140	2059371	49.31
2	6.812	2116720	50.69



	Retention Time	Area	% Area

1	6.515	1111538	3.00
2	7.154	35992651	97.00

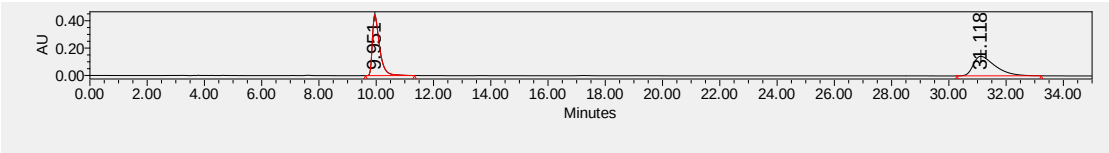


3b (95% ee) **6** (95% ee)

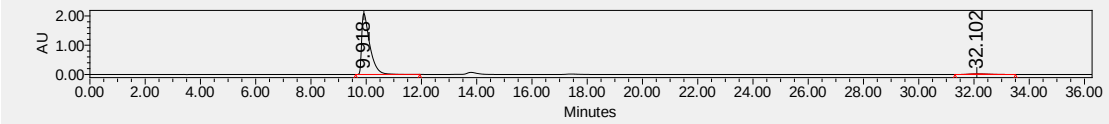
(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-7-(4-Methoxyphenyl)-1-phenyloctahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6(2a^1*H*)-one (6)

At room temperature, a flask was charged with a solution of the compound **3b** (35.9 mg, 0.10 mmol, 95% ee) in EtOAc (4 mL), Pd/C (10.0 mg) was added in one portion to the above solution. The flask was evacuated and refilled with H_2 with a ballon. The reaction mixture was stirred under H_2 atmosphere for 5 h. Then the reaction mixture was filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was subjected to column chromatography on silica gel and eluted with EtOAc/petroleum ether (1:3, v/v) to give the product **6** as a white solid (90% yield, > 19:1 dr, 95% ee).

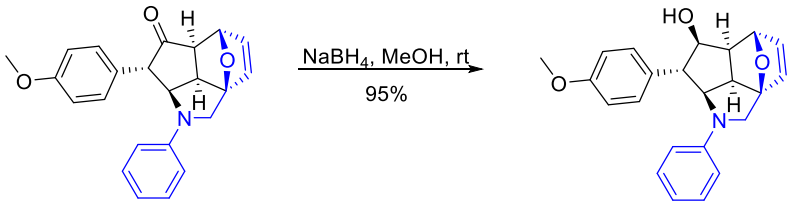
White solid, 168 – 170 °C, 32.5 mg, 90% yield, 95% ee, >19:1 dr for the isolated product. t: 5 h. $[\alpha]^{20}_D$ = +128.7 (*c* 0.42, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 9.92 min, $t_{R(minor)}$ = 32.10 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.01 – 7.05 (m, 4H), 6.89 – 6.91 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 7.2 Hz, 1H), 6.24 (d, *J* = 8.0 Hz, 2H), 4.83 (d, *J* = 5.2 Hz, 1H), 4.32 (dd, *J* = 6.0 Hz, *J* = 9.2 Hz, 1H), 3.83 (s, 3H), 3,80 (dd, *J* = 10.8 Hz, *J* = 157.2 Hz, 2H), 3.53 (d, *J* = 6.0 Hz, 1H), 3.09 – 3.13 (m, 1H), 2.87 (d, *J* = 7.2 Hz, 1H), 1.97 – 2.10 (m, 2H), 1.84 – 1.89 (m, 1H), 1.72 – 1.78 (m, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 218.4, 158.7, 147.0, 131.5, 129.8, 129.0, 116.4, 114.5, 112.3, 93.7, 82.0, 68.1, 64.2, 59.1, 55.3, 51.7, 51.3, 29.2, 29.1; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{23}NO_3H^+$ [M+H$^+$] 362.1751, found 362.1759; **IR** (neat): 2950, 2915, 2832, 1731, 1594, 1504, 1347, 1246, 1171, 1131, 1030, 812, 750, 690, 517 cm^{-1}.



	Retention Time	Area	% Area
1	9.951	7765255	50.47
2	31.118	7620598	49.53



	Retention Time	Area	% Area
1	9.918	42481673	97.41
2	32.102	1127975	2.59

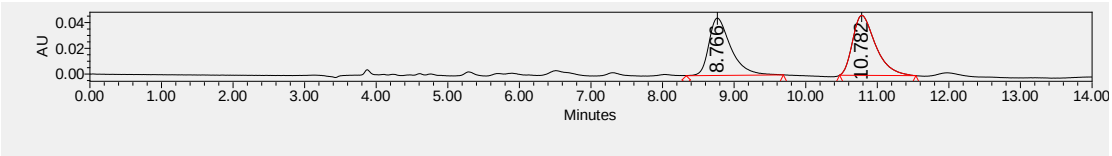


3b (95% ee) **7** (97% ee)

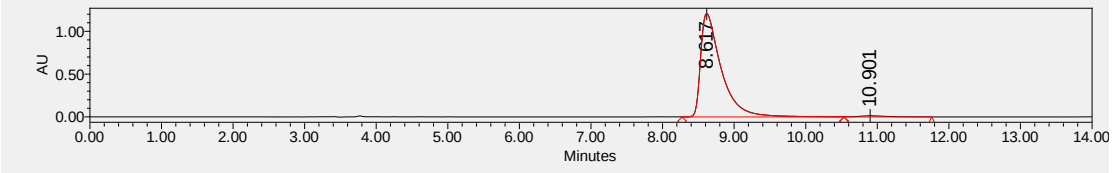
(2a*R*,2a^1*R*,5*S*,5a*S*,6*R*,7*S*,7a*S*)-7-(4-Methoxyphenyl)-1-phenyl-1,2,2a1,5,5a,6,7,7a-octahydro-2a,5-epoxycyclopenta[*cd*]isoindol-6-ol (7)

At room temperature, to a flask charged with a solution of the compound **3b** (117.2 mg, 0.33 mmol, 95% ee) in MeOH (4 mL) was added $NaBH_4$ (12.4 mg) in one portion. The resultant reaction mixture was stirred at room temperature. After completion of the reaction, methanol was removed under reduced pressure and the residue was purified by silica gel flash chromatography (ethyl acetate: petroleum ether = 1:1 to 3:1) to give the product **7** as a white solid (95% yield, > 19:1 dr, 97% ee).

White solid, 188 – 190 °C, 112.0 mg, 95% yield, 97% ee, >19:1 dr for the isolated product. t: 3 h. $[\alpha]^{20}_D$ = +49.1 (*c* 0.22, CH_2Cl_2); HPLC (Daicel chiralcel IB, λ = 254 nm, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min) $t_{R(major)}$ = 8.62 min, $t_{R(minor)}$ = 10.90 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 6.0 Hz, 1H), 6.53 (t, *J* = 7.2 Hz, 1H), 6.47 (dd, *J* = 1.2 Hz, *J* = 6.0 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 2H), 5.44 (d, *J* = 0.8 Hz, 1H), 4.42 – 4.48 (m, 1H), 4.01 (t, *J* = 8.0 Hz, 1H), 3.83 (dd, *J* = 11.2 Hz, *J* = 88.4 Hz, 2H), 3.81 (s, 3H), 3.37 (dd, *J* = 8.0 Hz, *J* = 10.4 Hz, 1H), 2.71 (dd, *J* = 6.8 Hz, *J* = 8.4 Hz, 1H), 2.42 (t, *J* = 7.2 Hz, 1H), 1.94 (d, *J* = 5.6 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ=158.7, 147.4, 136.9, 135.9, 134.9, 129.0, 128.8 115.8, 114.5, 111.9, 94.4, 81.0, 79.9, 66.8, 60.6, 55.3, 54.1, 50.4, 45.9; **HRMS** (FTMS+c ESI): Calcd for $C_{23}H_{23}NO_3H^+$ [M+H$^+$] 362.1751, found 362.1747; **IR** (neat): 3336, 2954, 2902, 2837, 1597, 1505, 1461, 1344, 1245, 1079, 1027, 866, 834, 808, 749, 688, 548 cm^{-1}.

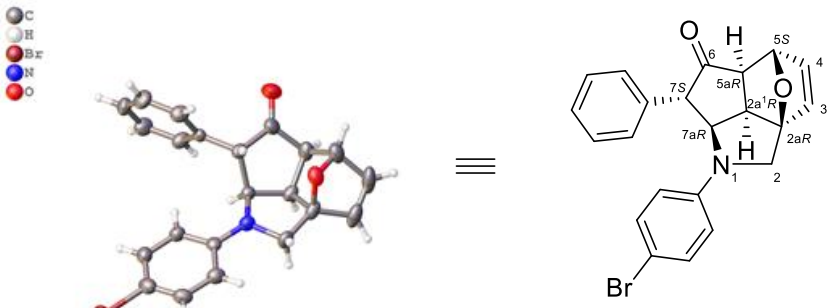


	Retention Time	Area	% Area
1	8.766	948451	47.64
2	10.782	1042575	52.36



	Retention Time	Area	% Area
1	8.617	24162182	98.60
2	10.901	343657	1.40

9. X-ray structure of 3m



(2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*)-**3m**

Single crystal of **3m** was obtained from the mixed solvents of petroleum ether and dichloromethane. The absolute configuration was shown above. CCDC 1971783 (**3m**) was assigned to be (2a*R*,2a^1*R*,5*S*,5a*R*,7*S*,7a*R*) respectively. These data can be obtained free from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_requst/cif.

Crystal data and structure refinement for.

Empirical formula	$C_{22}H_{18}BrNO_2$
Formula weigh	408.28
Temperature/K	300(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	5.8675(3)
b/Å	12.4208(7)
c/Å	24.4967(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1785.30(17)
Z	4
ρ_{calc}g/cm^3	1.519
μ/mm^{-1}	2.319
F(000)	832.0
Crystal size/mm^3	
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.97 to 49.454
Index ranges	$-6 \le h \le 6$, $-14 \le k \le 14$, $-28 \le l \le 28$
Reflections collected	9416
Independent reflections	2964 [R_{int} = 0.0269, R_{sigma} = 0.0486]
Data/restraints/parameters	2964/0/235
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0300, wR_2 = 0.0660

Final R indexes [all data]	$R_1 = 0.0374$, $wR_2 = 0.0705$
Largest diff. peak/hole / e Å	0.49/-0.52
Flack parameter	0.002(5)

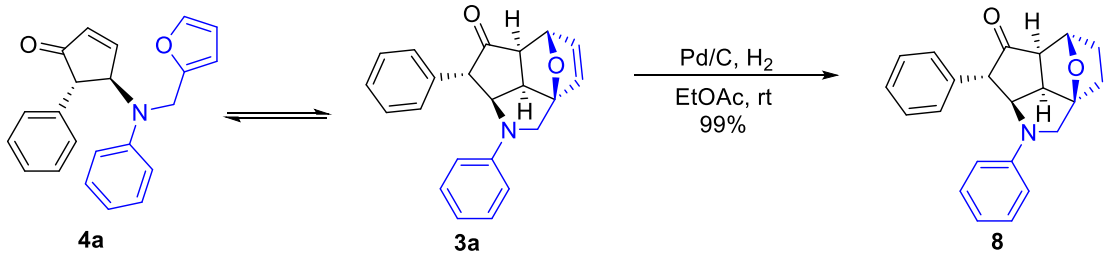
10. Control experiments

As described in the previous literature[2], it was found that there was always minor isomers related to the corresponding uncyclized intermediates according to the spectra of the desired products. We rationalized that there is an equilibrium between uncyclized intermediate **4** and the [4+2] cycloaddition product **3**. To confirmed this assumption, several control experiments were carried out.

Firstly, we recrystallized the product **3a** and analyzed it by ^{1}H NMR. After preparing the sample, we measured the ^{1}H NMR spectrum of crystals in $CDCl_3$. Pure ^{1}H NMR spectra of **3a** was obtained (a). However, rescan the sample with 0.5-2 hours, new peaks related to the uncyclized intermediate 4aa was detected. The ratio between **4a** and **3a** increased from <1:19, to 1:7.1, 1:6 and 1:6 after 0.5 h, 1 h, and 2 h.

Secondly, the ratio of [4+2] cycloaddition product **3a** to uncyclized intermediate **4a** changed when the ^{1}H NMR spectra was detected with *d*-DMSO as the solvent. It was found that the ratio between the product **3a** and the uncyclized intermediate 4aa decreased to 5.3:1 in *d*-DMSO, indicating a reversable [4+2] cycloaddition process.

It was interesting to found that hydrogenation of the mixture of the product **3a/4a** (6:1) afforded pure product **8** in 99% yield, which again indicated that the exist of the dynamic equilibrium between the product **3a** and the uncyclized intermediate **4a** was responsible for the impurity in our spectra of final products.



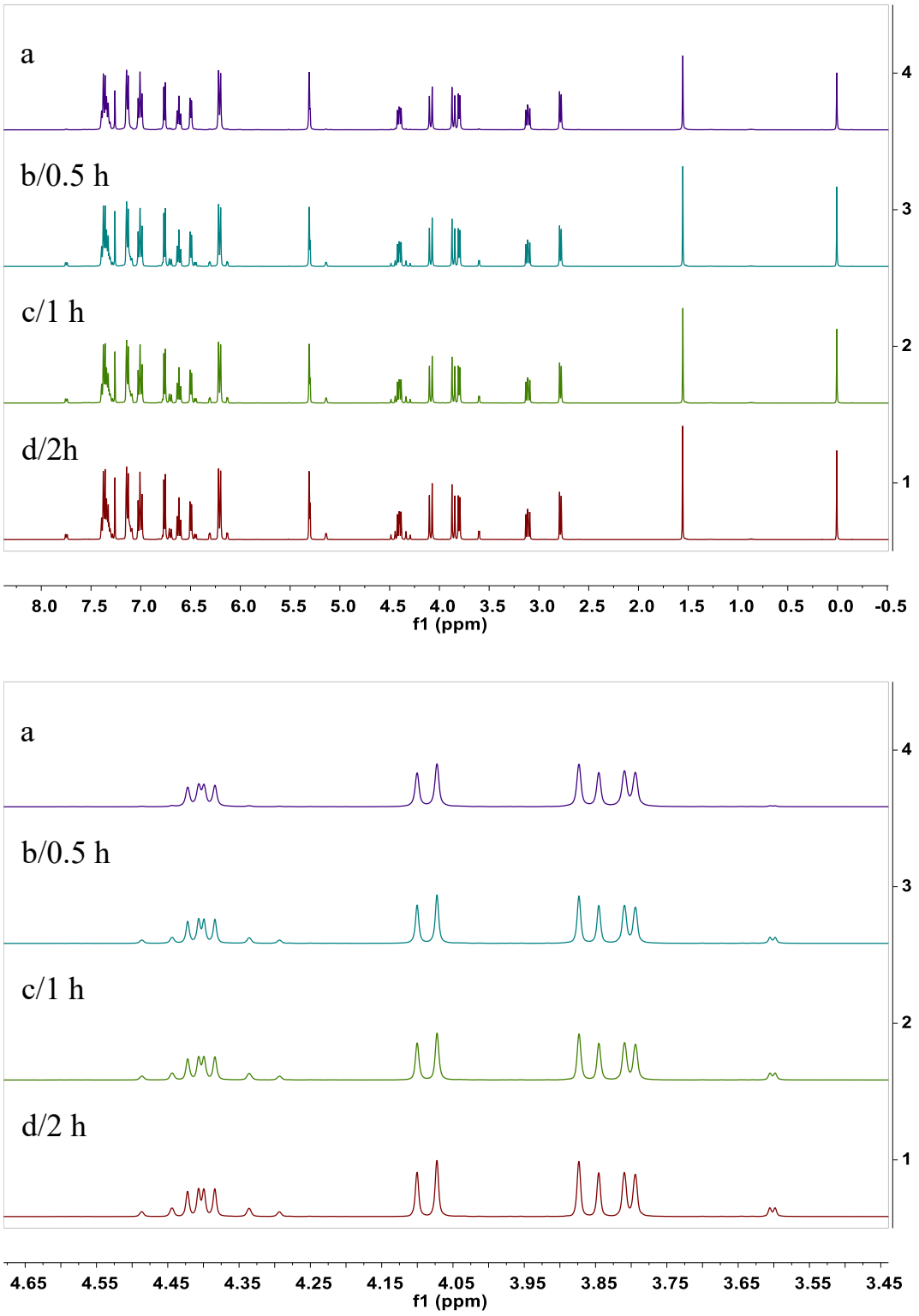
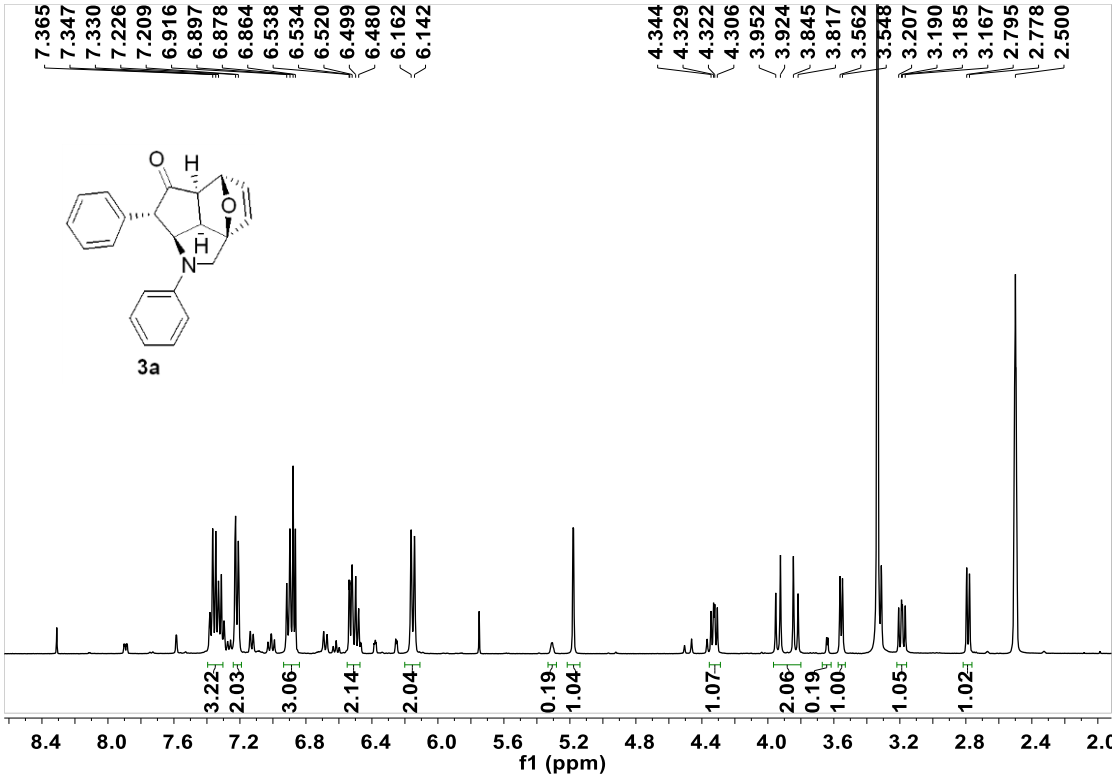


Figure S1. Different time ^{1}H NMR spectra of the product **3a** after recrystallized. From top to bottom, newly recrystallized product **3a**, the ratio of product **3a** to **4a** changed: 19:1 (a); 7.1:1 (b/0.5 h); 6:1 (c/1 h); and 6:1 (d/2 h).

In *d*-DMSO, the ratio of product **3a** to uncyclized intermediate **4a** is 5.3:1.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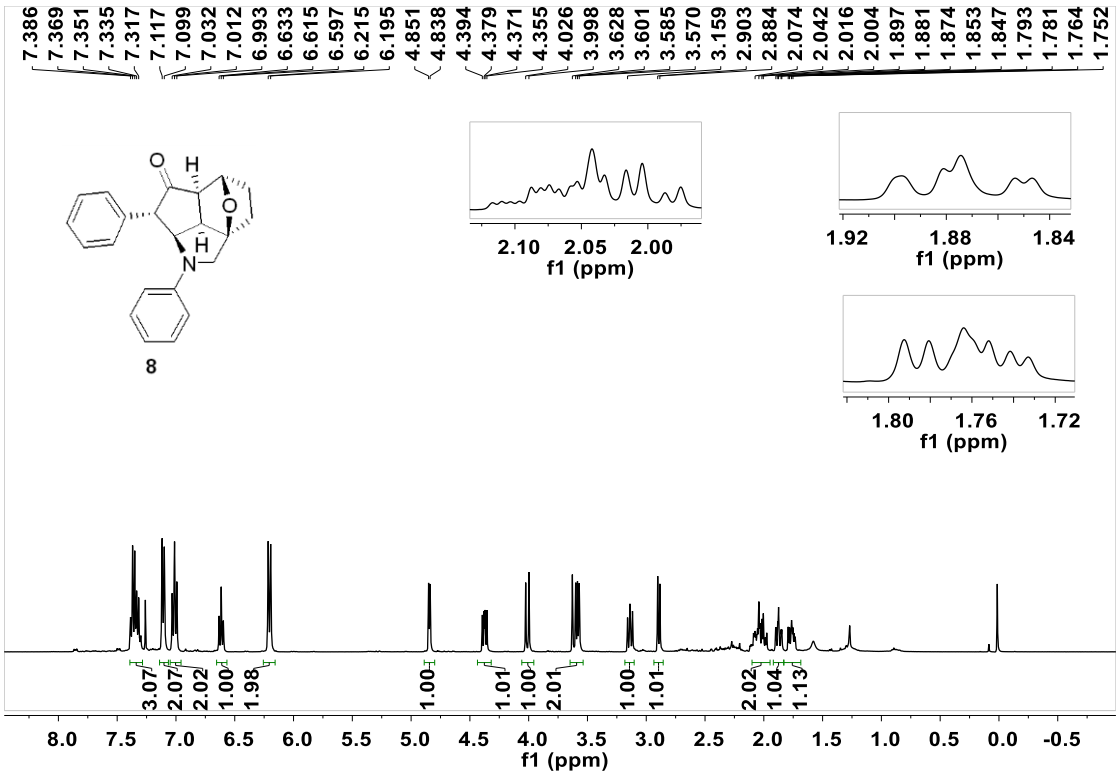
4.344 4.329 4.322 4.306 3.952 3.924 3.845 3.817 3.562 3.548 3.207 3.190 3.185 3.167 2.795 2.778 2.500
3a
3.22 2.03 3.06 2.14 2.04 0.19 1.04 1.07 2.06 0.19 1.00 1.05 1.02
f1 (ppm)

Product **8**


7.386 7.369 7.351 7.335 7.317 7.117 7.099 7.032 7.012 6.993 6.633 6.615 6.597 6.215 6.195 4.851 4.838 4.394 4.379 4.371 4.355 4.026 3.998 3.628 3.601 3.585 3.570 3.159 2.903 2.884 2.074 2.042 2.016 2.004 1.897 1.881 1.874 1.853 1.847 1.793 1.781 1.764 1.752
8
2.10 2.05 2.00
f1 (ppm)
1.92 1.88 1.84
f1 (ppm)
1.80 1.76 1.72
f1 (ppm)
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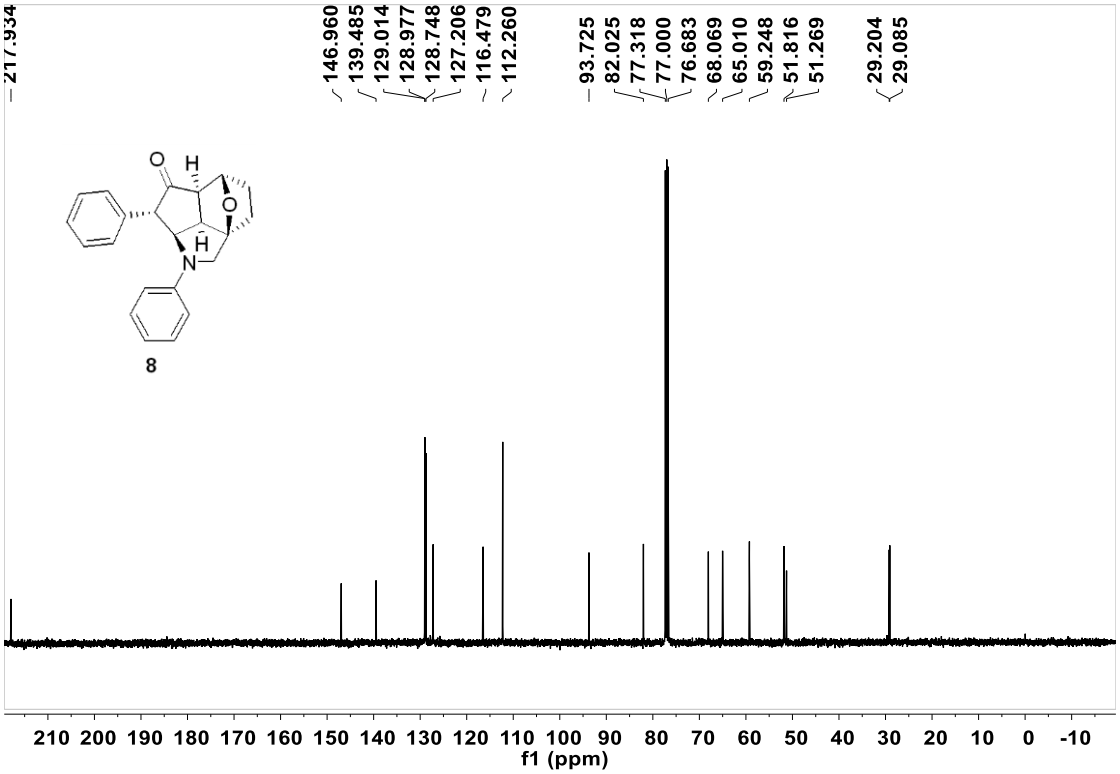
f1 (ppm)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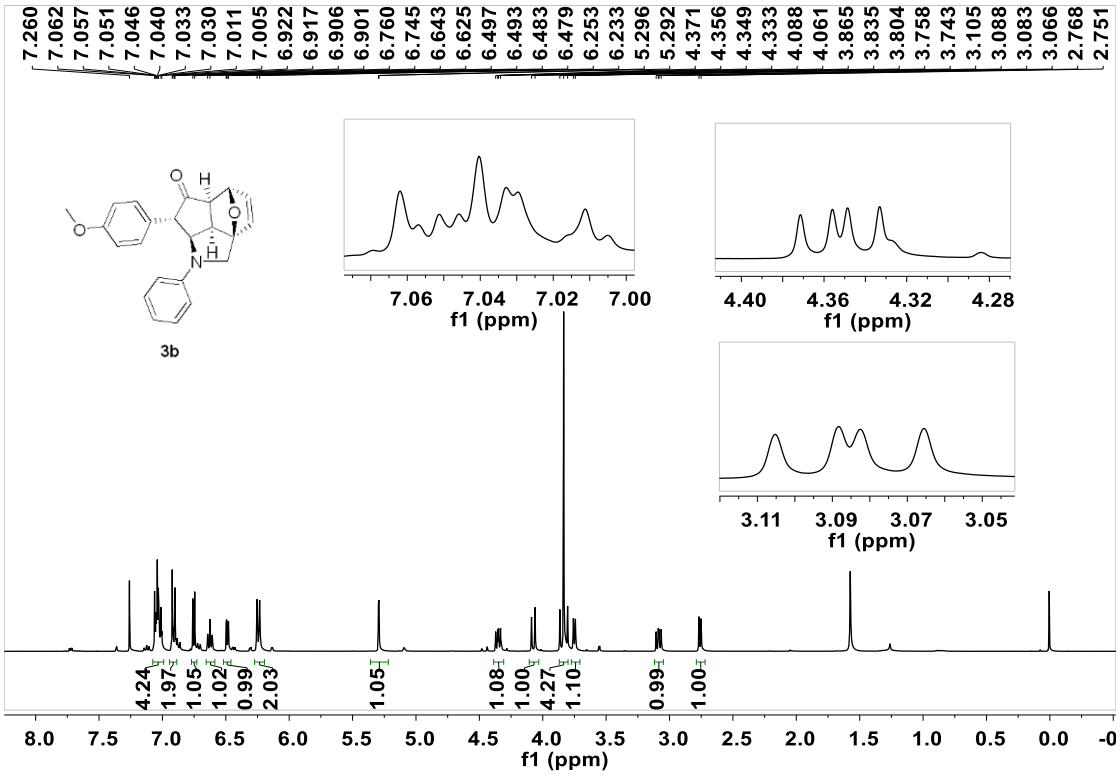
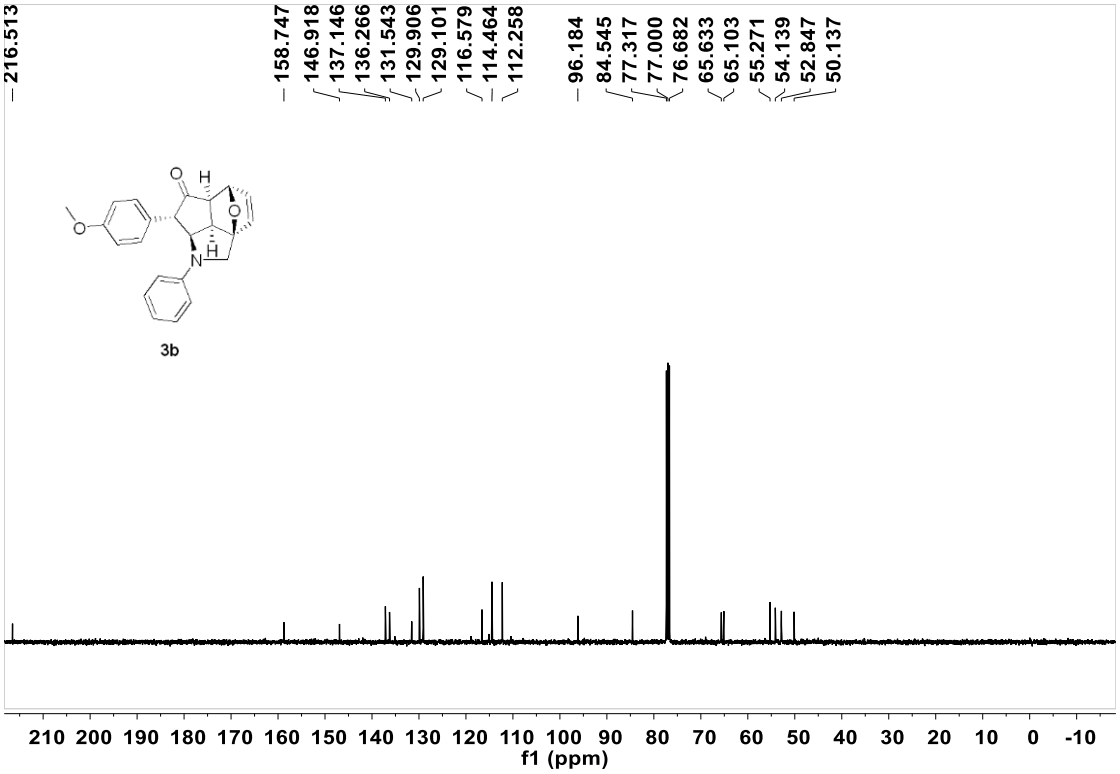
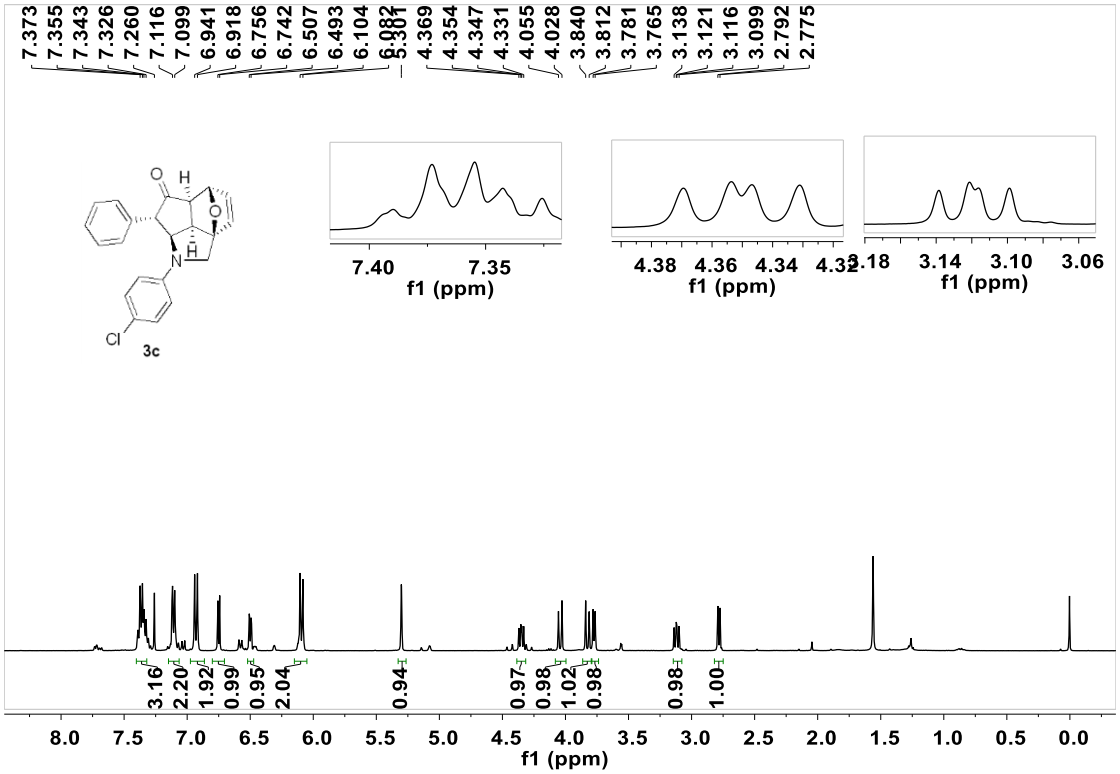
139.485
129.014
128.977
128.748
127.206
116.479
112.260
93.725
82.025
77.318
77.000
76.683
68.069
65.010
59.248
51.816
51.269
29.204
29.085
O
H
O
H
N
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

11. Copies of NMR spectra



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7.116
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6.941
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6.742
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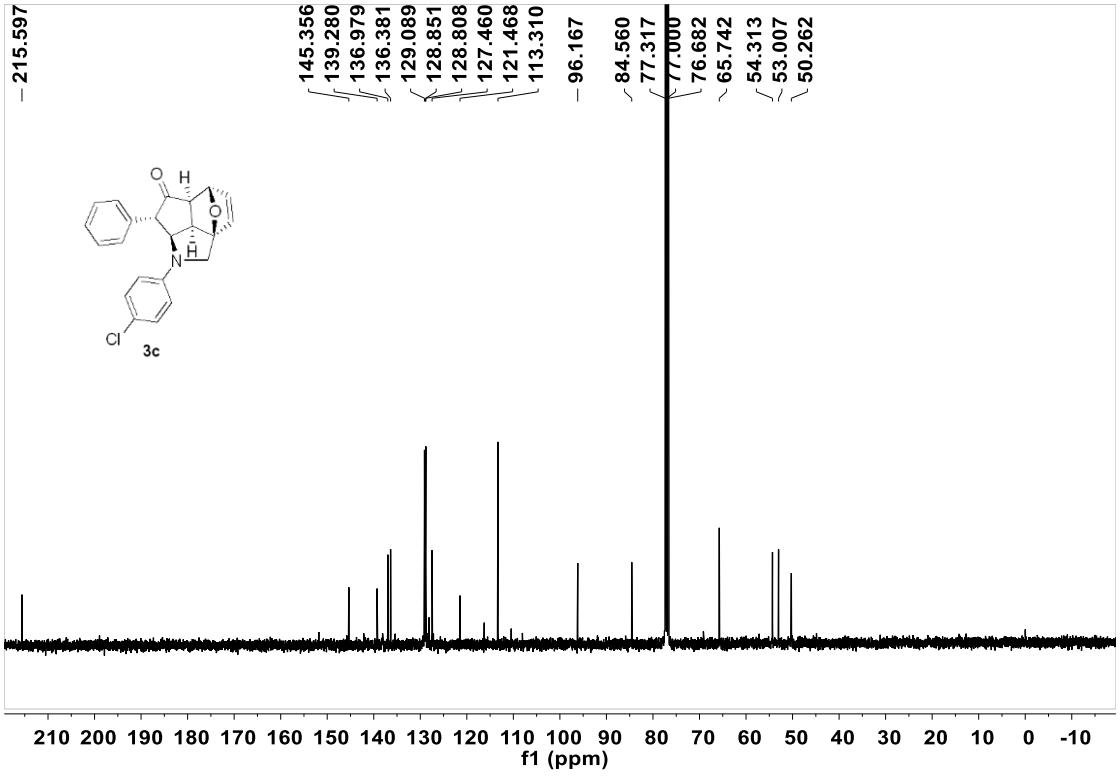
6.493
6.104
6.082
5.301
4.369
4.354
4.347
4.331
4.055
4.028
3.840
3.812
3.781
3.765
3.138
3.121
3.116
3.099
2.792
2.775
3c
7.40
7.35
f1 (ppm)
4.38
4.36
4.34
4.32
f1 (ppm)
3.18
3.14
3.10
3.06
f1 (ppm)
3.16
2.20
1.92
0.99
0.95
2.04
0.94
0.97
0.98
1.02
0.98
0.98
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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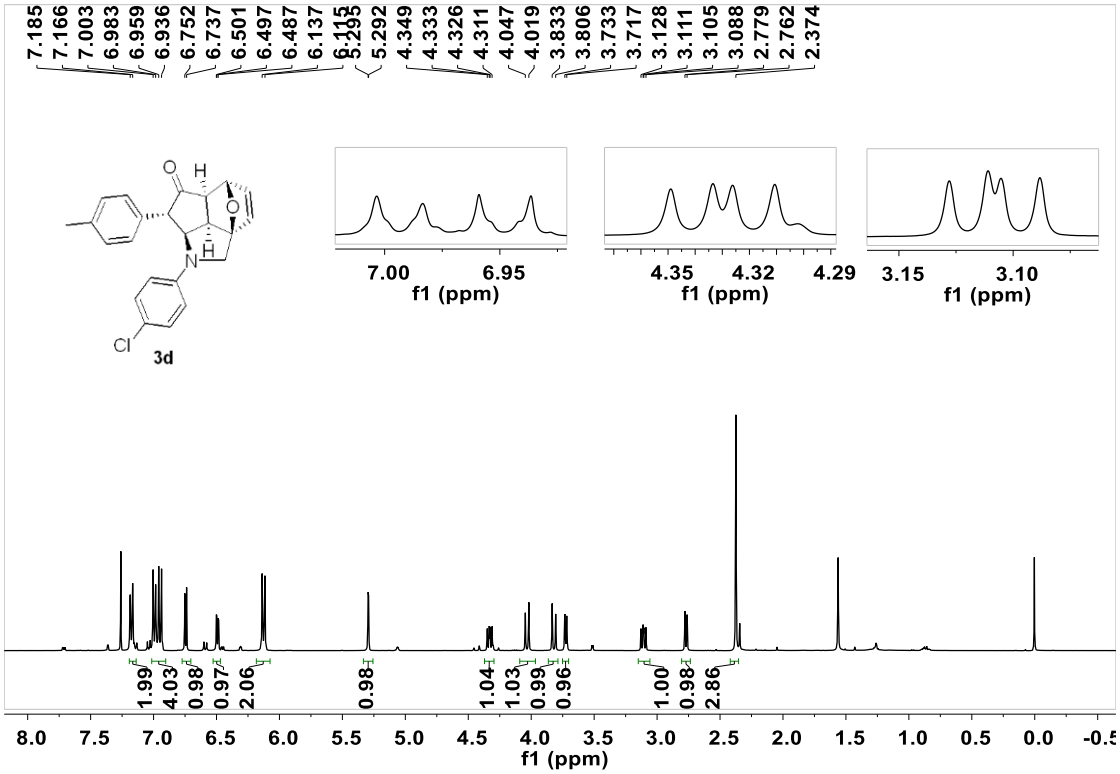
139.280
136.979
136.381
129.089
128.851
128.808
127.460
121.468
113.310
96.167
84.560
77.317
77.000
76.682
65.742
54.313
53.007
50.262
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.166
7.003
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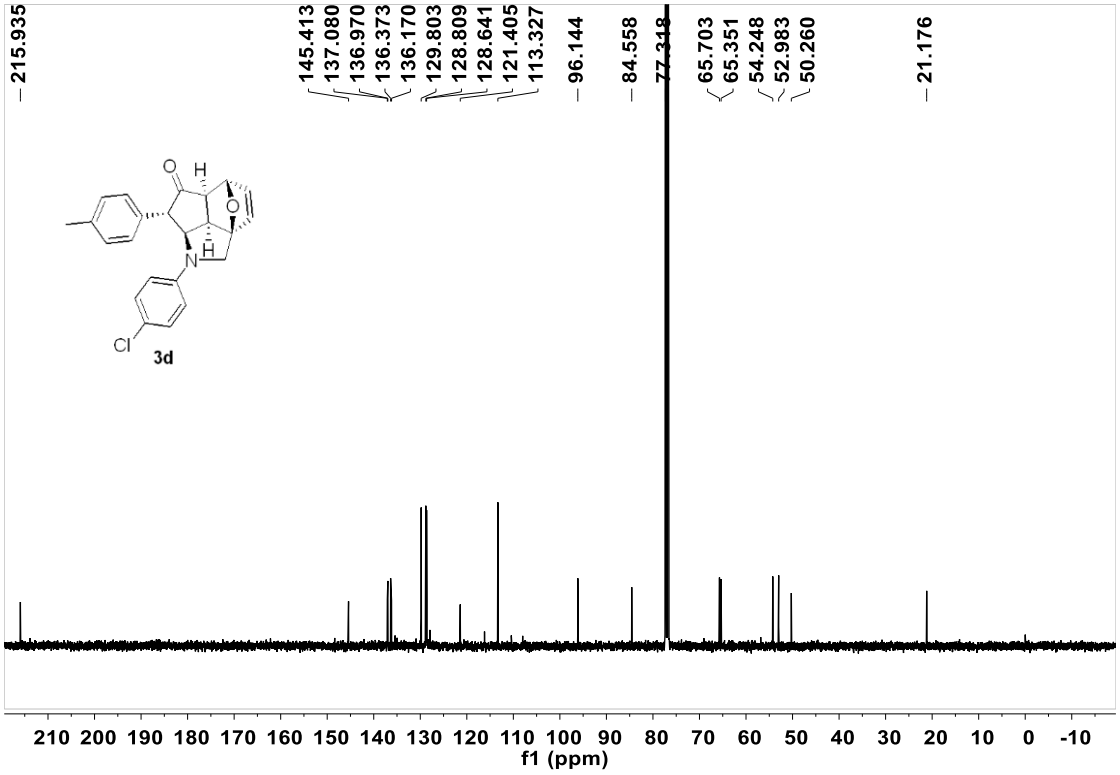
6.959
6.936
6.752
6.737
6.501
6.497
6.487
6.137
5.292
4.349
4.333
4.326
4.311
4.047
4.019
3.833
3.806
3.733
3.717
3.128
3.111
3.105
3.088
2.779
2.762
2.374
3d
7.00
6.95
f1 (ppm)
4.35
4.32
4.29
f1 (ppm)
3.15
3.10
f1 (ppm)
1.99
4.03
0.98
0.97
2.06
0.98
1.04
1.03
0.99
0.96
1.00
0.98
2.86
f1 (ppm)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137.080
136.970
136.373
136.170
129.803
128.809
128.641
121.405
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77.348
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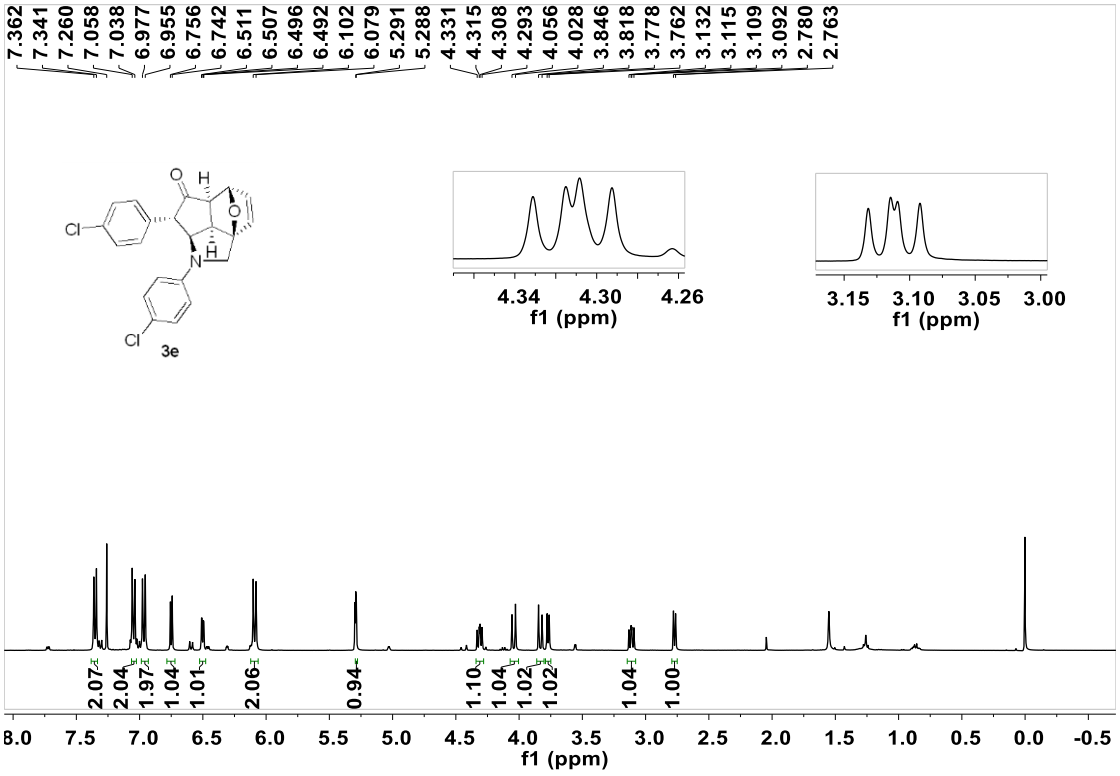
65.351
54.248
52.983
50.260
21.176
3d
f1 (ppm)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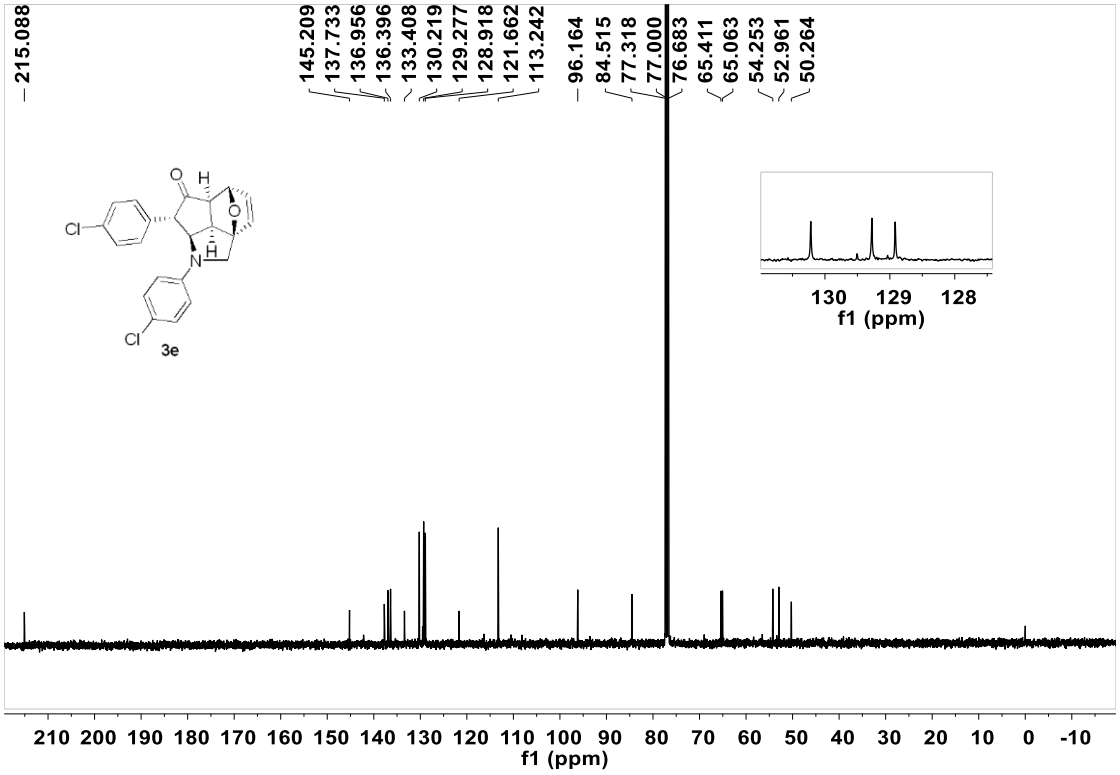
7.341
7.260
7.058
7.038
6.977
6.955
6.756
6.742
6.511
6.507
6.496
6.492
6.102
6.079
5.291
5.288
4.331
4.315
4.308
4.293
4.056
4.028
3.846
3.818
3.778
3.762
3.132
3.115
3.109
3.092
2.780
2.763
3e
4.34
4.30
4.26
f1 (ppm)
3.15
3.10
3.05
3.00
f1 (ppm)
2.07
2.04
1.97
1.04
1.01
2.06
0.94
1.10
1.04
1.02
1.02
1.04
1.00
f1 (ppm)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136.396
133.408
130.219
129.277
128.918
121.662
113.242
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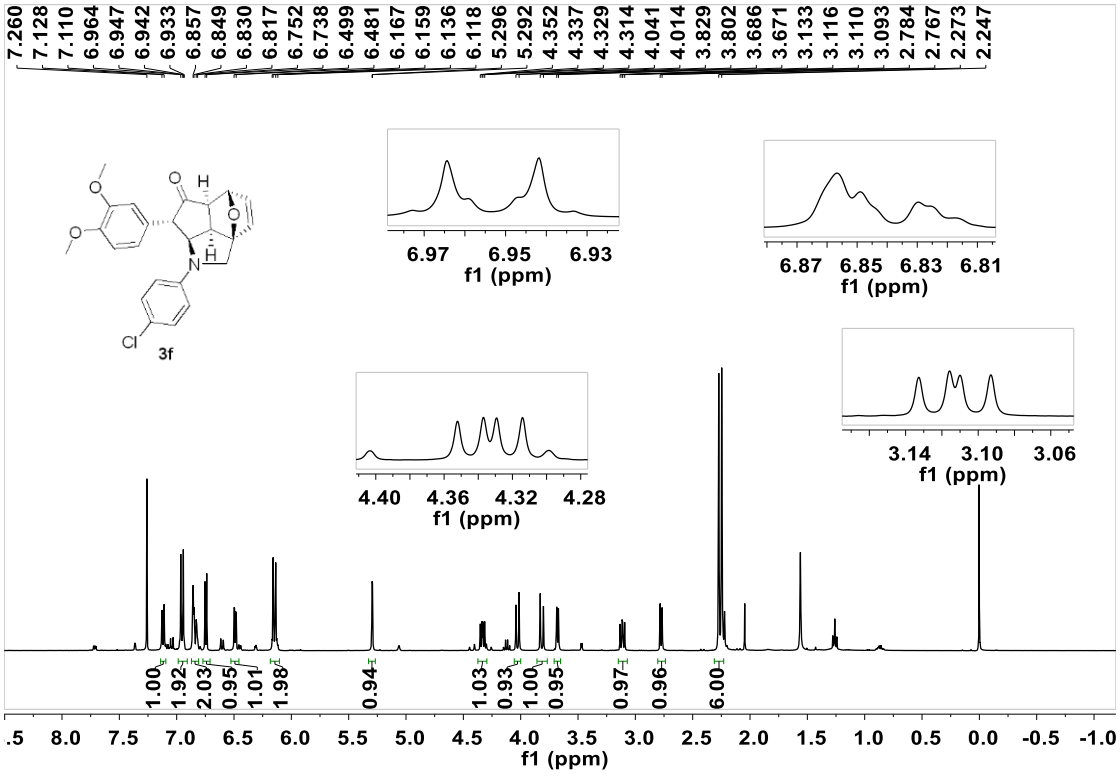
84.515
77.318
77.000
76.683
65.411
65.063
54.253
52.961
50.264
3e
130
129
128
f1 (ppm)
f1 (ppm)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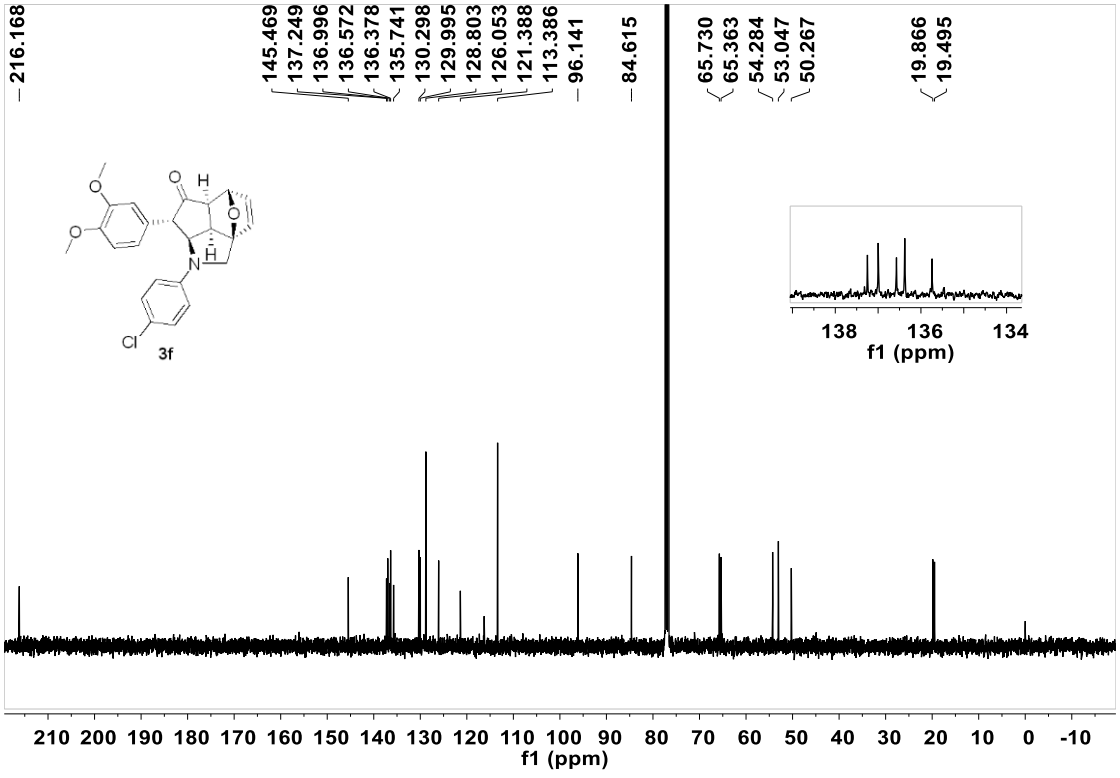
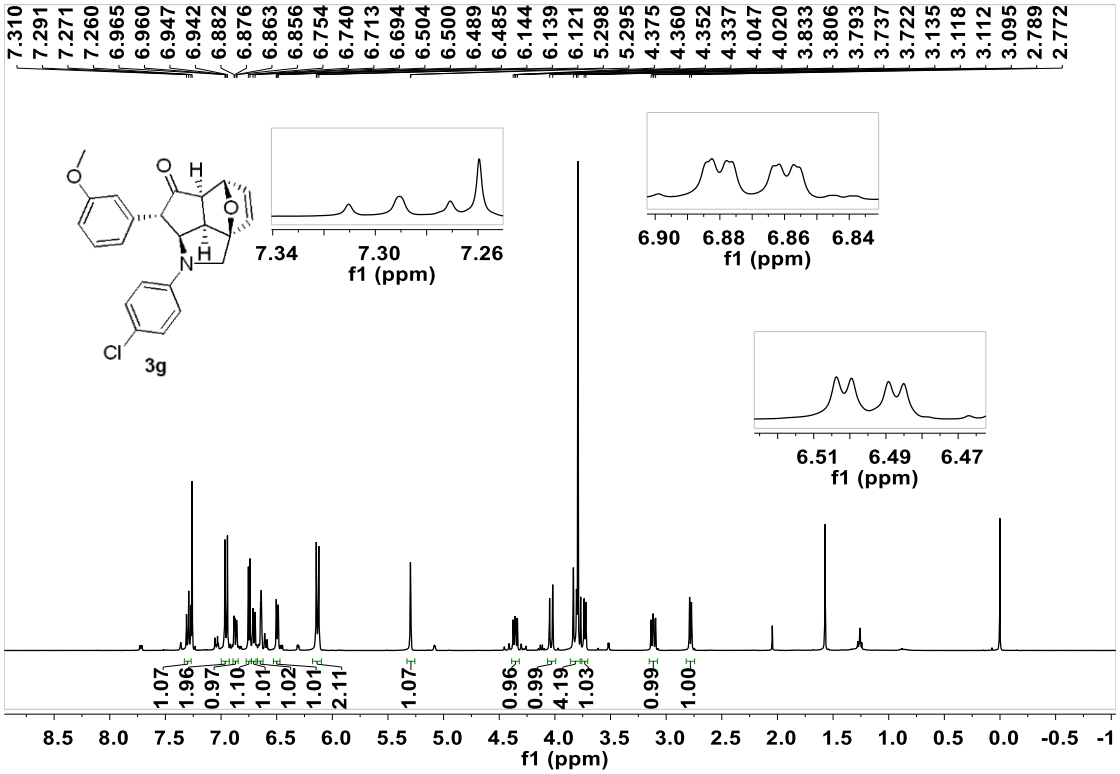
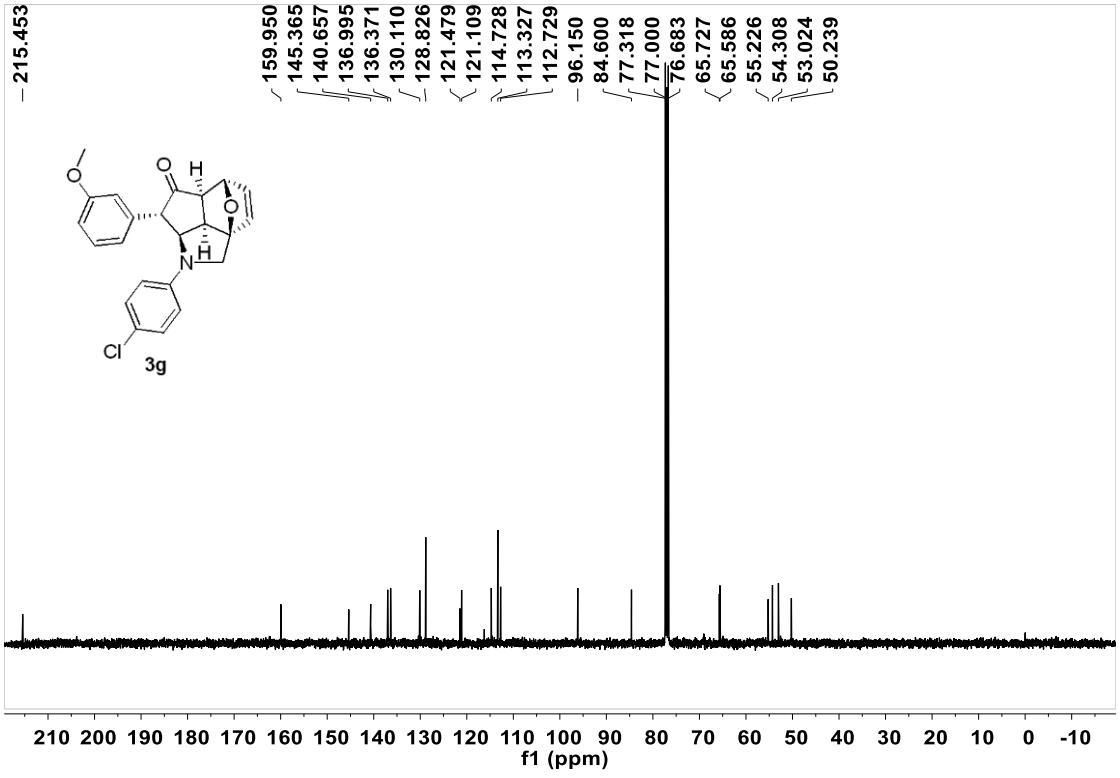
3f
6.97 6.95 6.93
f1 (ppm)
6.87 6.85 6.83 6.81
f1 (ppm)
4.40 4.36 4.32 4.28
f1 (ppm)
3.14 3.10 3.06
f1 (ppm)
1.00 1.92 2.03 0.95 1.01 1.98 0.94 1.03 0.93 1.00 0.95 0.97 0.96 6.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


216.168
145.469 137.249 136.996 136.572 136.378 135.741 130.298 129.995 128.803 126.053 121.388 113.386 96.141 84.615 65.730 65.363 54.284 53.047 50.267 19.866 19.495
3f
138 136 134
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.310 7.291 7.271 7.260 6.965 6.960 6.947 6.942 6.882 6.876 6.863 6.856 6.754 6.740 6.713 6.694 6.504 6.500 6.489 6.485 6.144 6.139 6.121 5.298 5.295 4.375 4.360 4.352 4.337 4.047 4.020 3.833 3.806 3.793 3.737 3.722 3.135 3.118 3.112 3.095 2.789 2.772
3g
7.34 7.30 7.26
f1 (ppm)
6.90 6.88 6.86 6.84
f1 (ppm)
6.51 6.49 6.47
f1 (ppm)
1.07 1.96 0.97 1.10 1.01 1.02 1.01 2.11 1.07 0.96 0.99 4.19 1.03 0.99 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


215.453
159.950 145.365 140.657 136.995 136.371 130.110 128.826 121.479 121.109 114.728 113.327 112.729 96.150 84.600 77.318 77.000 76.683 65.727 65.586 55.226 54.308 53.024 50.239
3g
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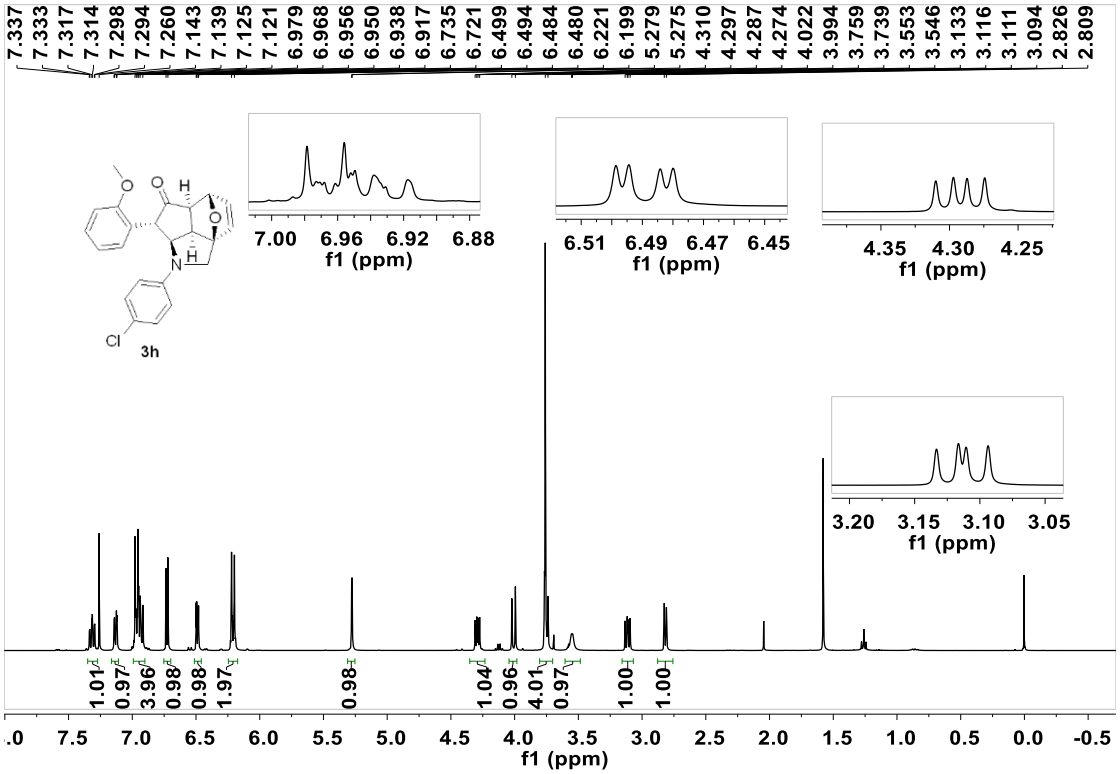
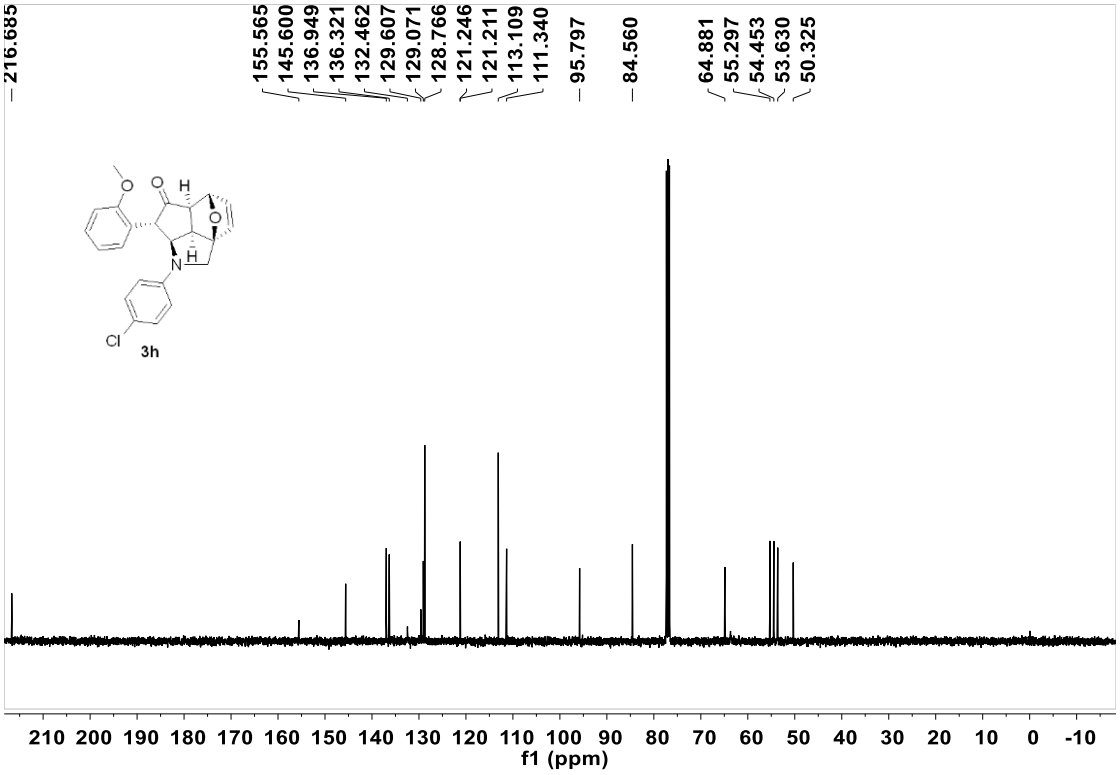
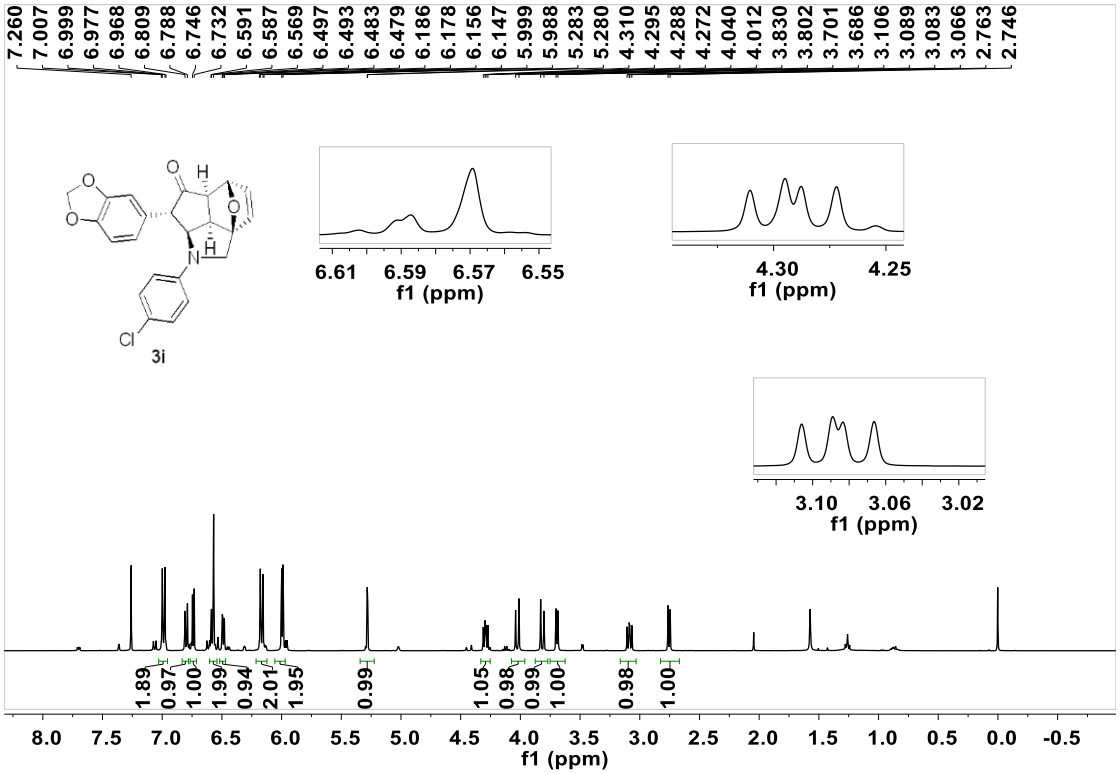
f1 (ppm)


7.337 7.333 7.317 7.314 7.298 7.294 7.260 7.143 7.139 7.125 7.121 6.979 6.968 6.956 6.950 6.938 6.917 6.735 6.721 6.499 6.494 6.484 6.480 6.221 6.199 5.279 5.275 4.310 4.297 4.287 4.274 4.022 3.994 3.759 3.739 3.553 3.546 3.133 3.116 3.111 3.094 2.826 2.809
7.00 6.96 6.92 6.88
f1 (ppm)
6.51 6.49 6.47 6.45
f1 (ppm)
4.35 4.30 4.25
f1 (ppm)
3.20 3.15 3.10 3.05
f1 (ppm)
3h
1.01 0.97 3.96 0.98 0.98 1.97 0.98 1.04 0.96 4.01 0.97 1.00 1.00
f1 (ppm)


216.685
155.565 145.600 136.949 136.321 132.462 129.607 129.071 128.766 121.246 121.211 113.109 111.340 95.797 84.560 64.881 55.297 54.453 53.630 50.325
3h
f1 (ppm)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7.007
6.999
6.977
6.968
6.809
6.788
6.746
6.732
6.591
6.587
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6.497
6.493
6.483
6.479
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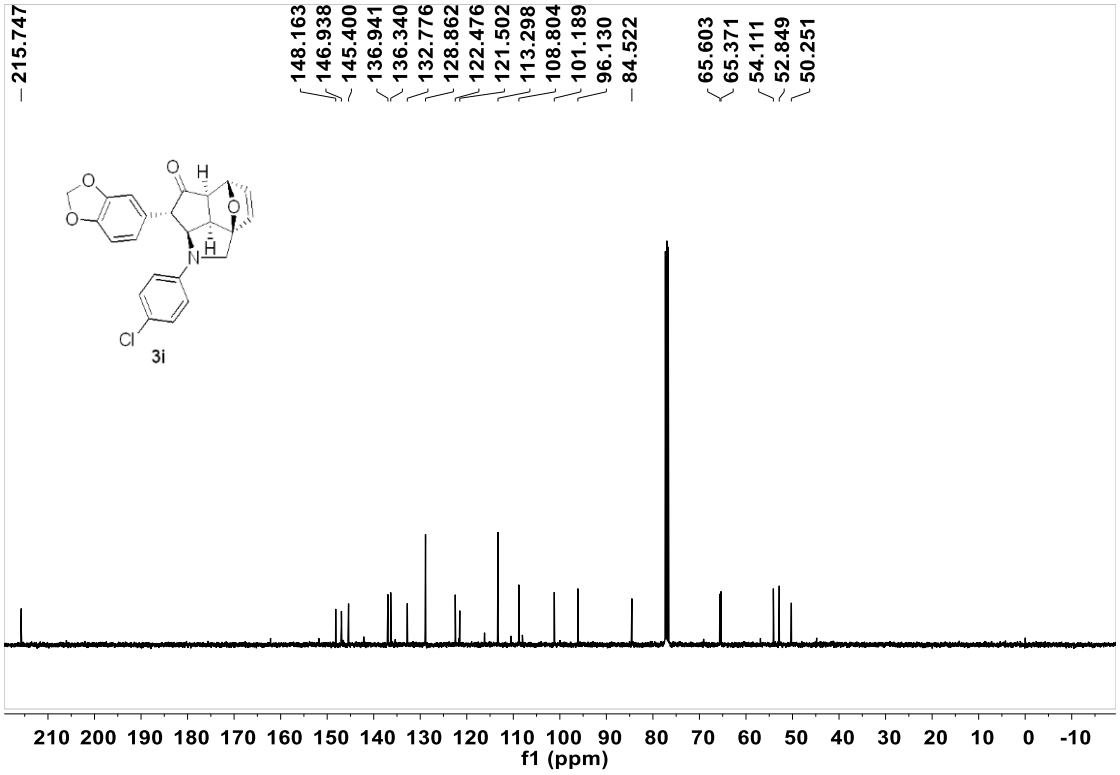
5.988
5.283
5.280
4.310
4.295
4.288
4.272
4.040
4.012
3.830
3.802
3.701
3.686
3.106
3.089
3.083
3.066
2.763
2.746
3i
6.61 6.59 6.57 6.55
f1 (ppm)
4.30 4.25
f1 (ppm)
3.10 3.06 3.02
f1 (ppm)
1.89 0.97 1.00 1.99 0.94 2.01 1.95 0.99 1.05 0.98 0.99 1.00 0.98 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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146.938
145.400
136.941
136.340
132.776
128.862
122.476
121.502
113.298
108.804
101.189
96.130
84.522
65.603
65.371
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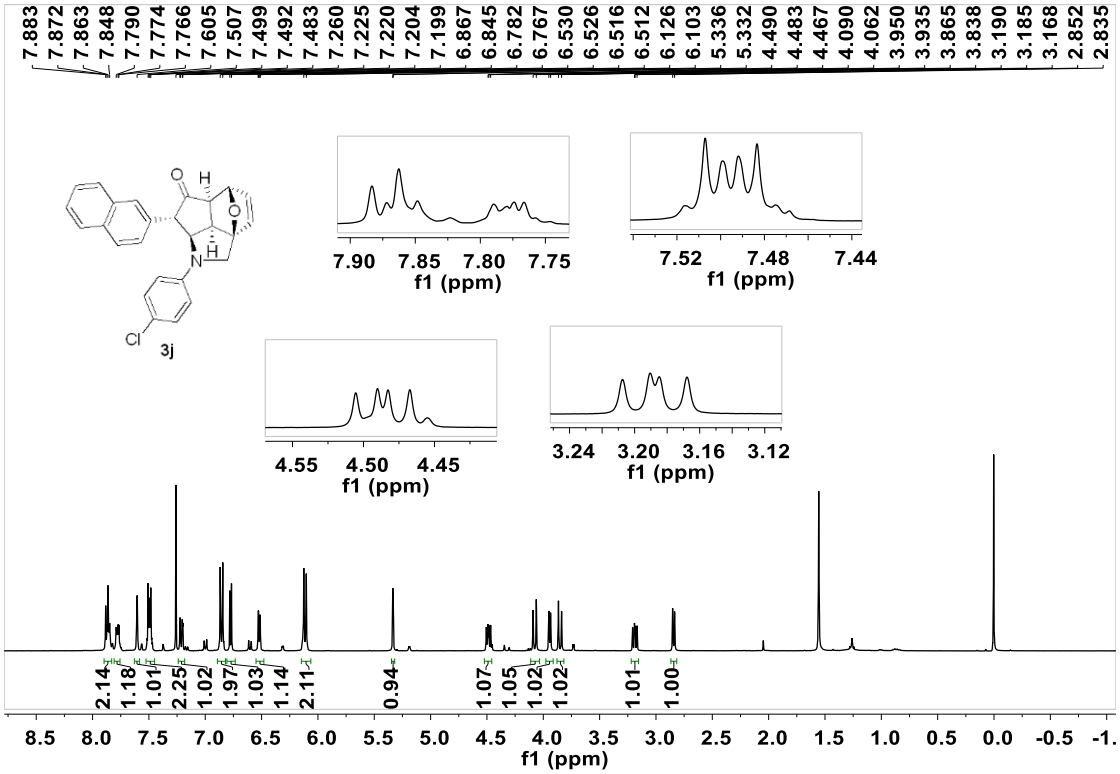
52.849
50.251
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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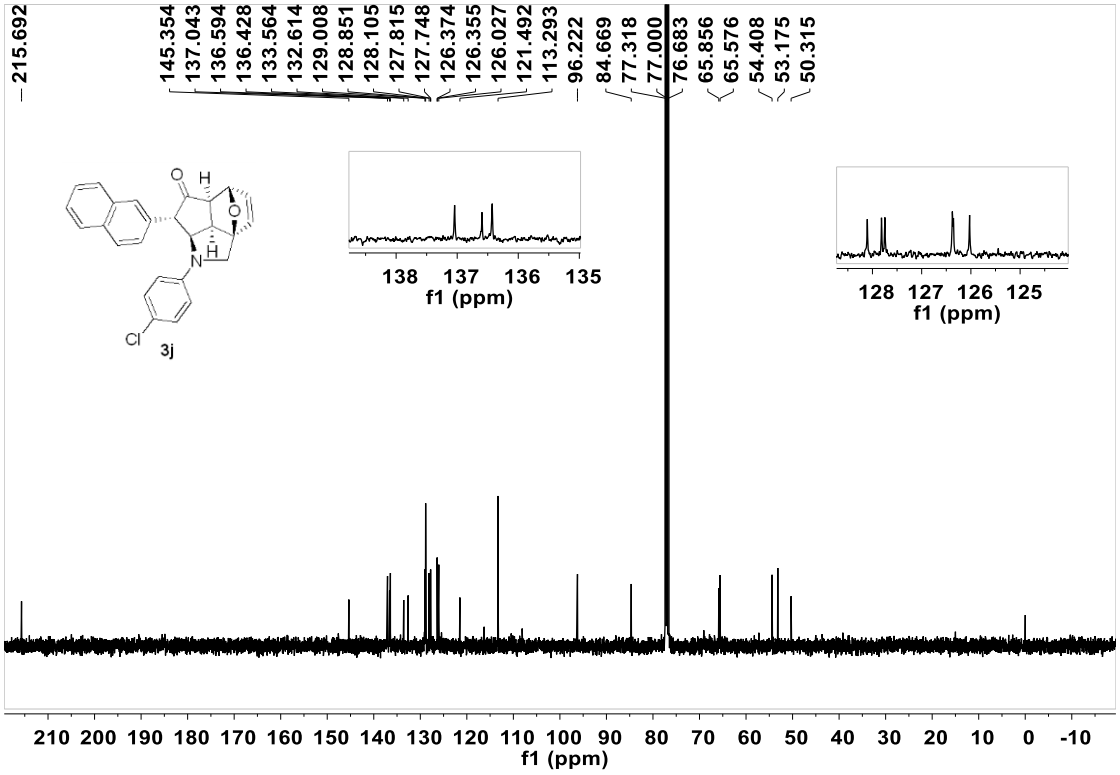
3j
7.90 7.85 7.80 7.75
f1 (ppm)
7.52 7.48 7.44
f1 (ppm)
4.55 4.50 4.45
f1 (ppm)
3.24 3.20 3.16 3.12
f1 (ppm)
2.14 1.18 1.01 2.25 1.02 1.97 1.03 1.14 2.11 0.94 1.07 1.05 1.02 1.02 1.01 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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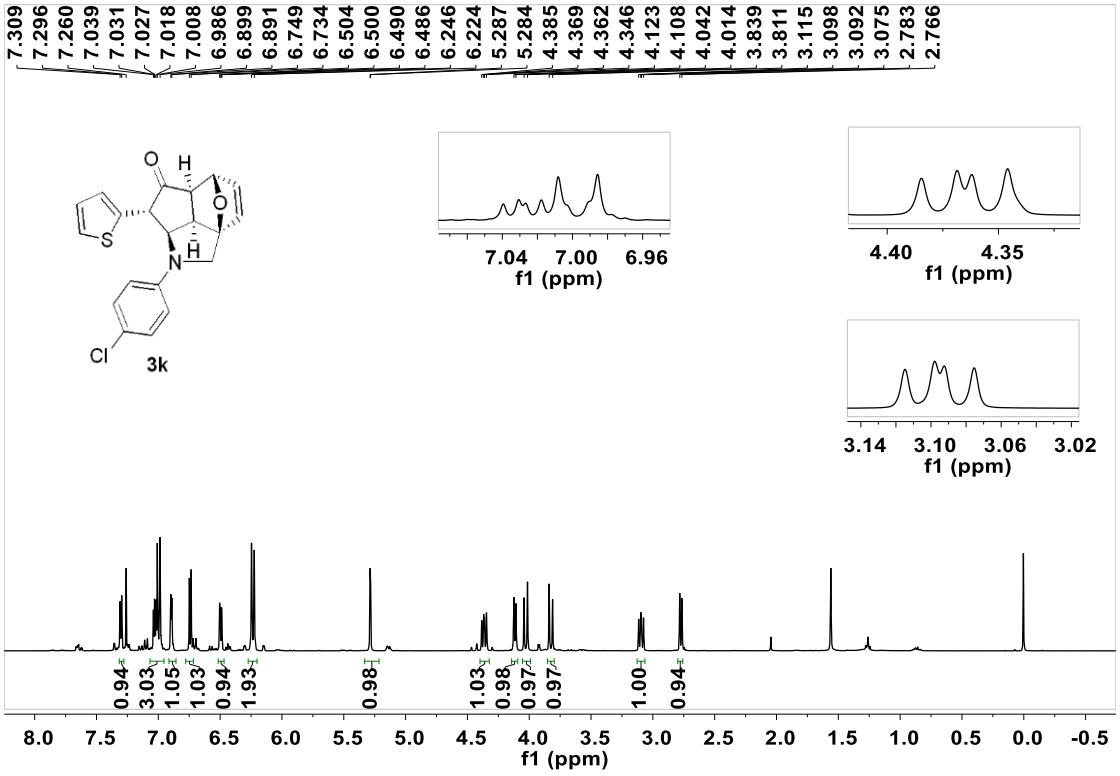
96.222
84.669 77.318 77.000 76.683 65.856 65.576 54.408 53.175 50.315
3j
138 137 136 135
f1 (ppm)
128 127 126 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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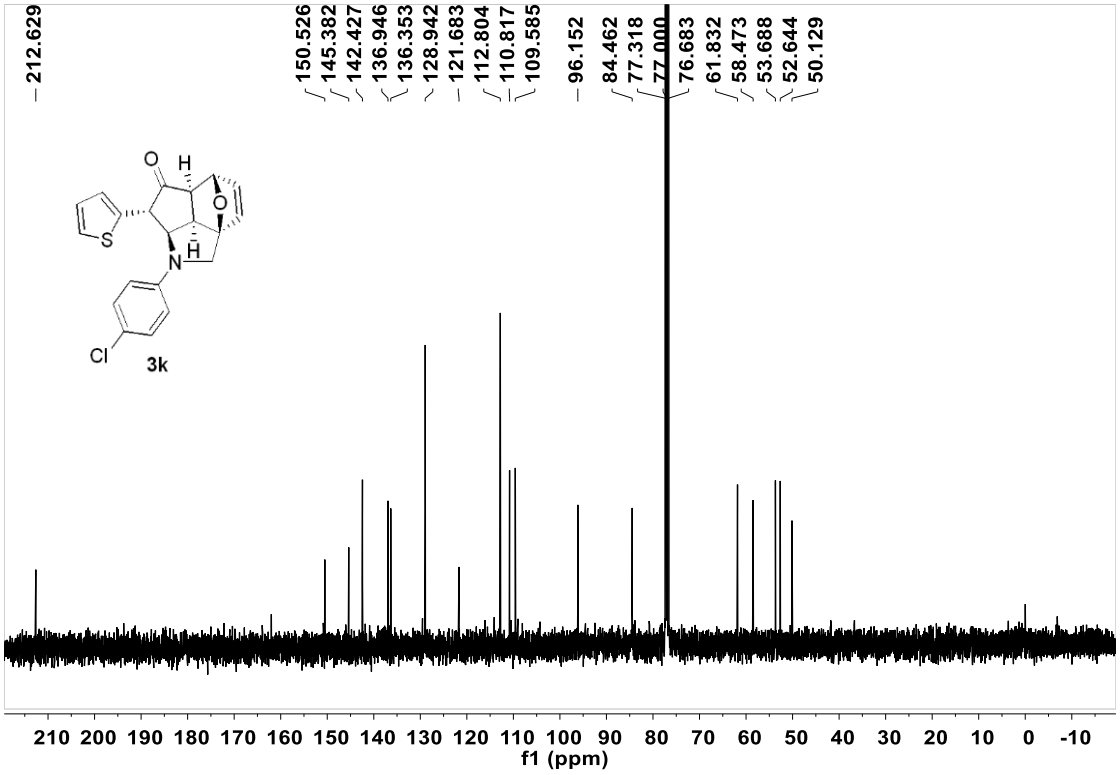
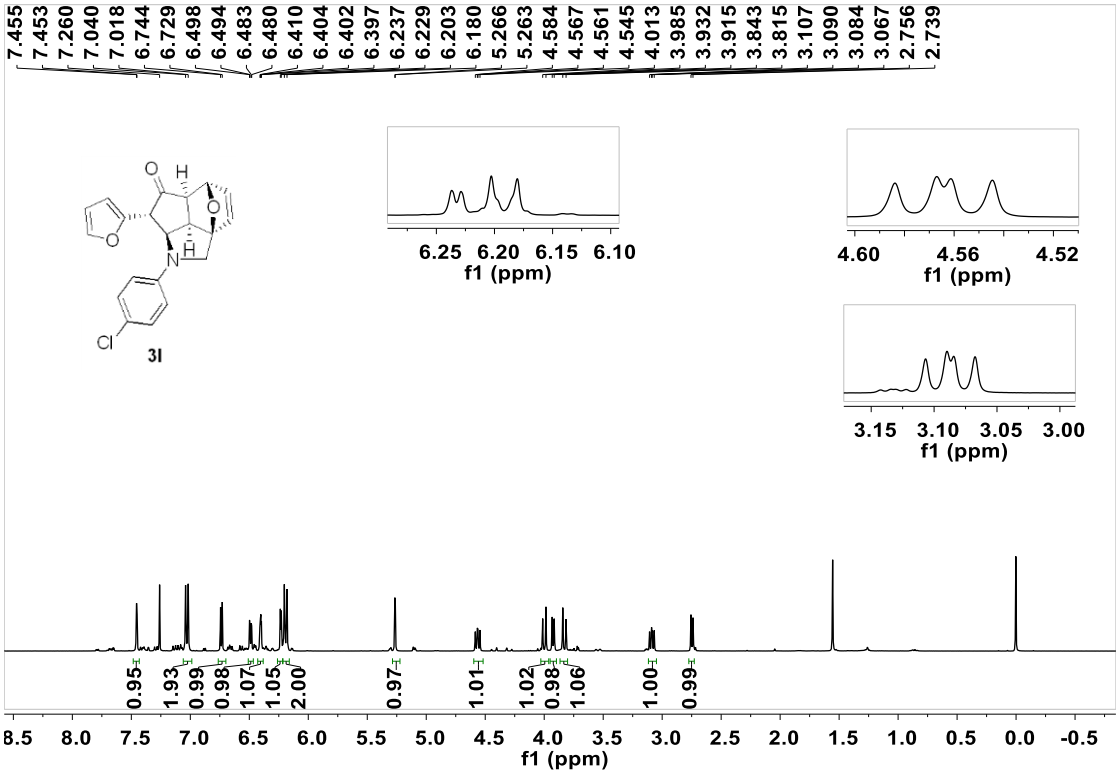
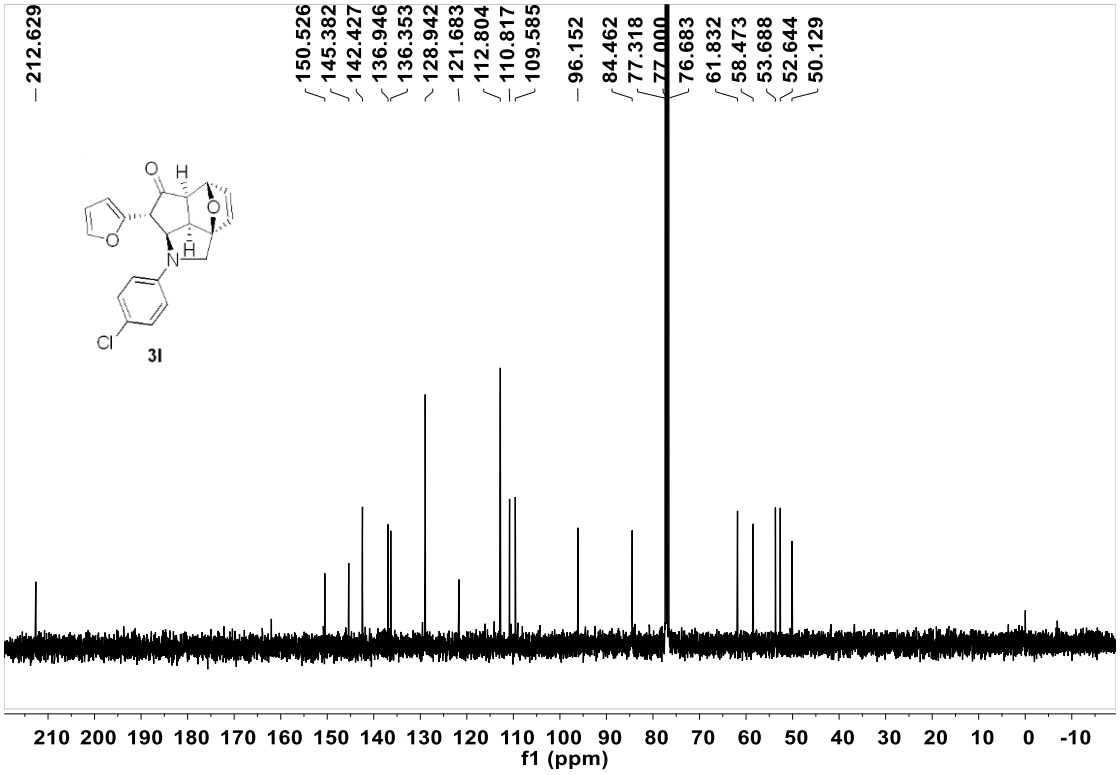
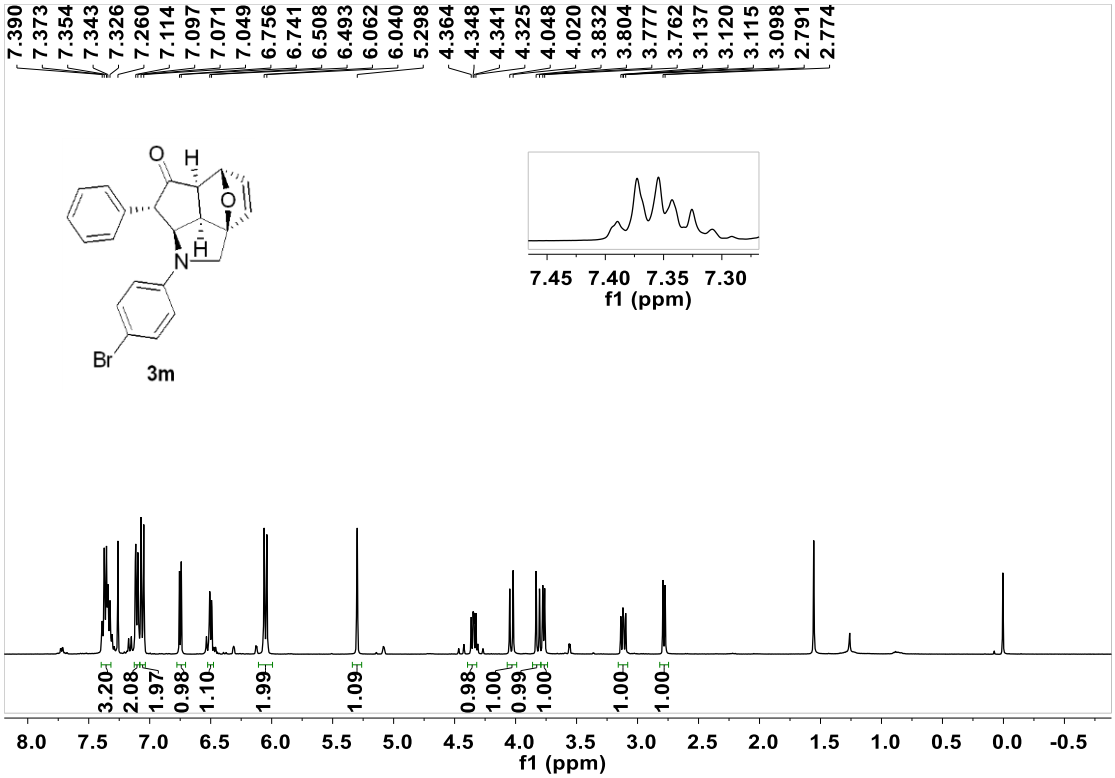
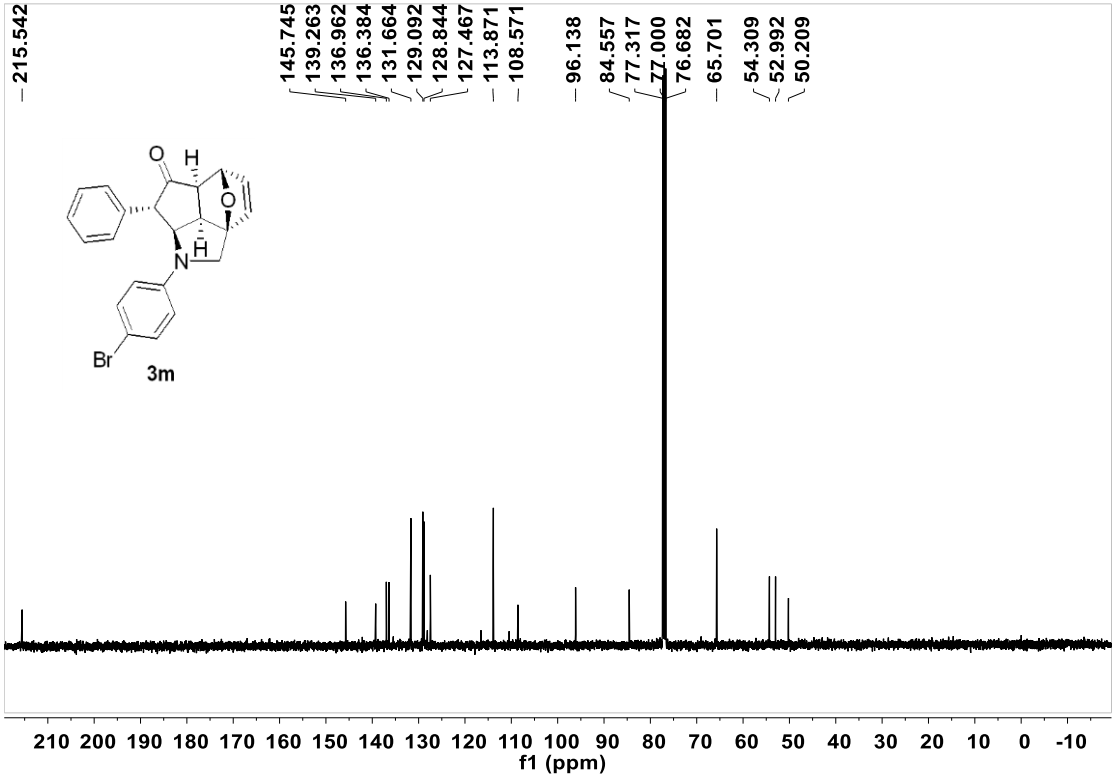
3k
7.04 7.00 6.96
f1 (ppm)
4.40 4.35
f1 (ppm)
3.14 3.10 3.06 3.02
f1 (ppm)
0.94 3.03 1.05 1.03 0.94 1.93 0.98 1.03 0.98 0.97 0.97 1.00 0.94
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

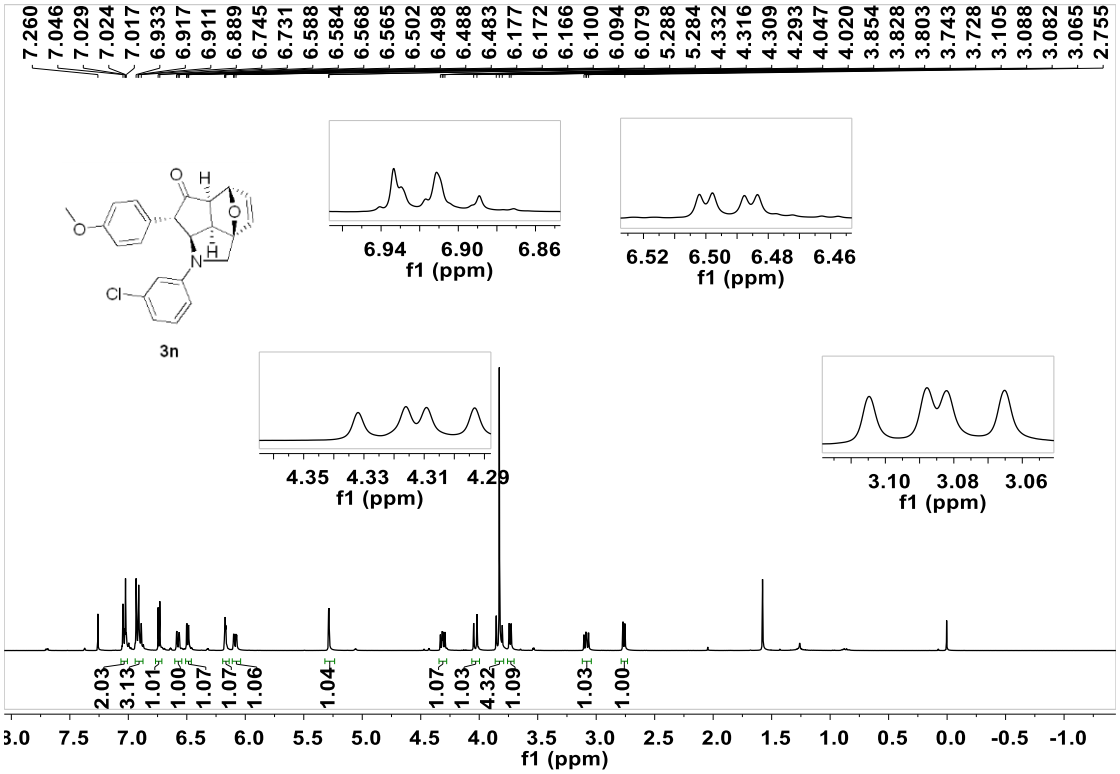

212.629
150.526 145.382 142.427 136.946 136.353 128.942 121.683 112.804 110.817 109.585
96.152
84.462 77.318 77.000 76.683 61.832 58.473 53.688 52.644 50.129
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

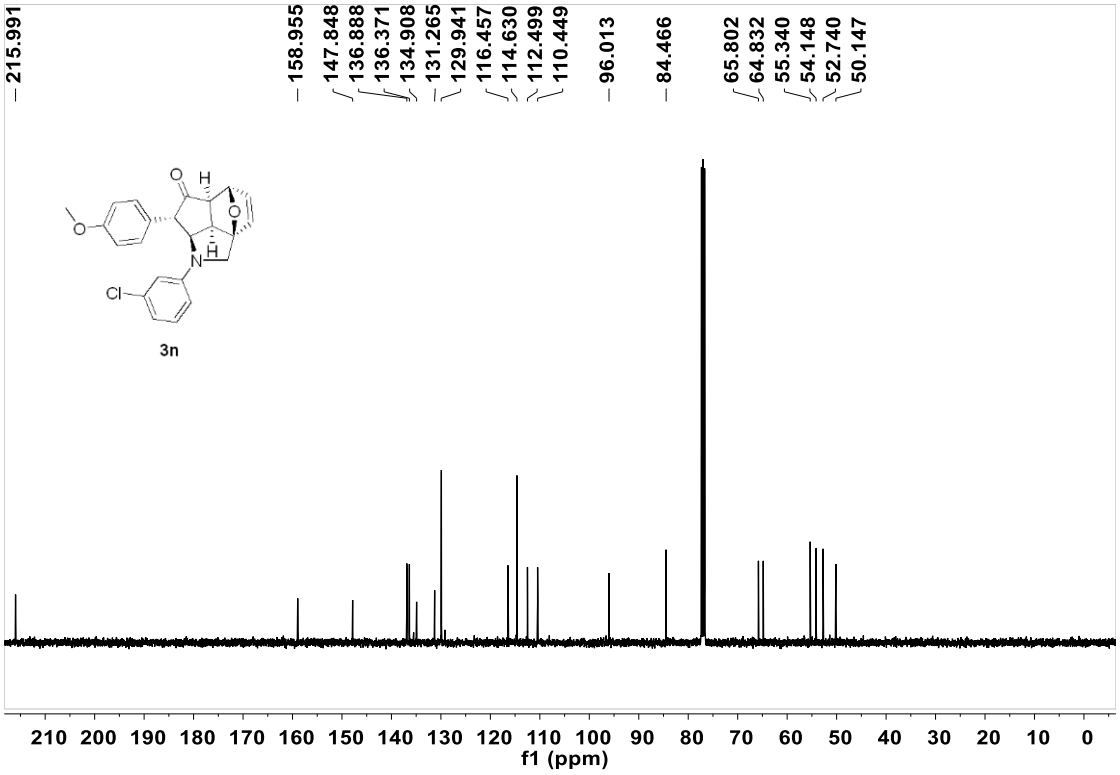

7.455 7.453 7.260 7.040 7.018 6.744 6.729 6.498 6.494 6.483 6.480 6.410 6.404 6.402 6.397 6.237 6.229 6.203 6.180 5.266 5.263 4.584 4.567 4.561 4.545 4.013 3.985 3.932 3.915 3.843 3.815 3.107 3.090 3.084 3.067 2.756 2.739
3l
6.25 6.20 6.15 6.10
f1 (ppm)
4.60 4.56 4.52
f1 (ppm)
3.15 3.10 3.05 3.00
f1 (ppm)
0.95 1.93 0.99 0.98 1.07 1.05 2.00 0.97 1.01 1.02 0.98 1.06 1.00 0.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

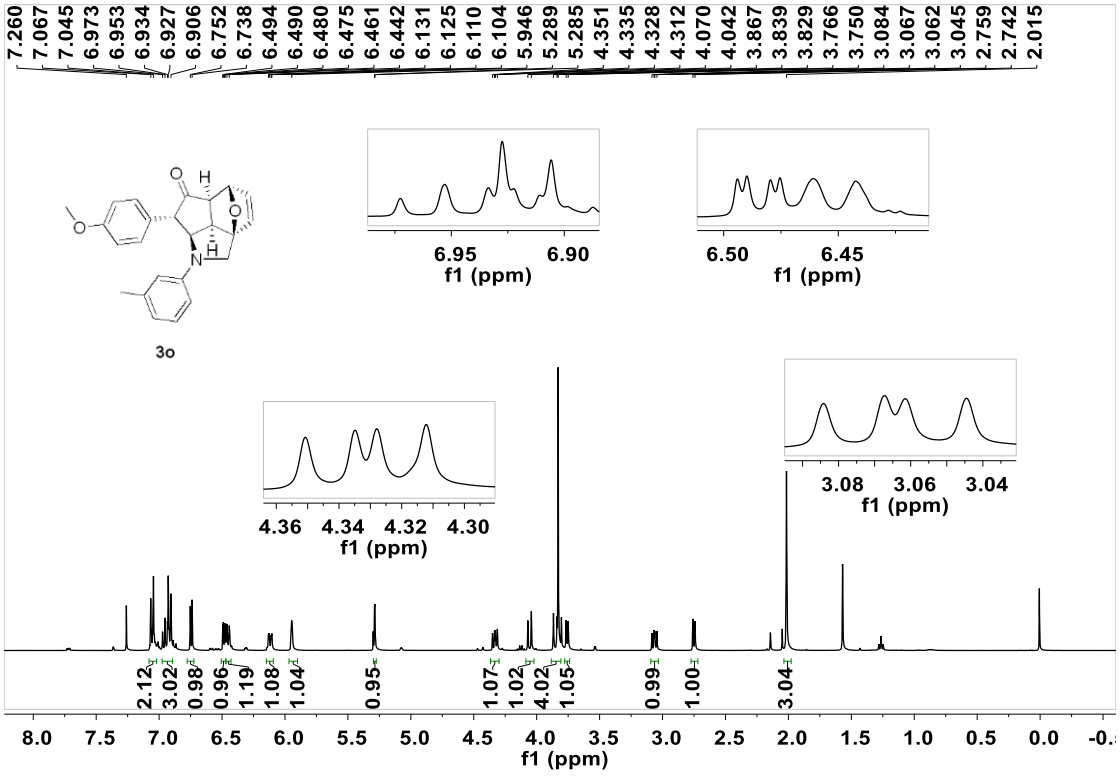

212.629
150.526 145.382 142.427 136.946 136.353 128.942 121.683 112.804 110.817 109.585 96.152 84.462 77.318 77.000 76.683 61.832 58.473 53.688 52.644 50.129
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

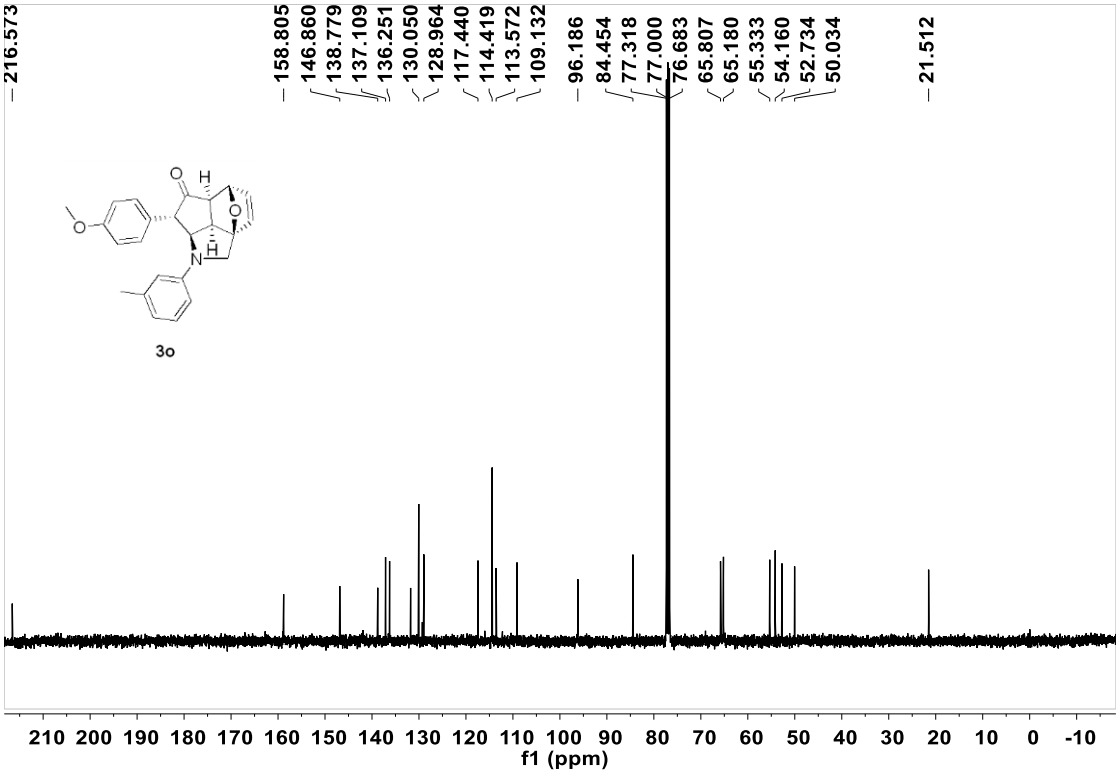

7.390
7.373
7.354
7.343
7.326
7.260
7.114
7.097
7.071
7.049
6.756
6.741
6.508
6.493
6.062
6.040
5.298
4.364
4.348
4.341
4.325
4.048
4.020
3.832
3.804
3.777
3.762
3.137
3.120
3.115
3.098
2.791
2.774
O
H
O
N
H
Br
3m
7.45 7.40 7.35 7.30
f1 (ppm)
3.20
2.08
1.97
0.98
1.10
1.99
1.09
0.98
1.00
0.99
1.00
1.00
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

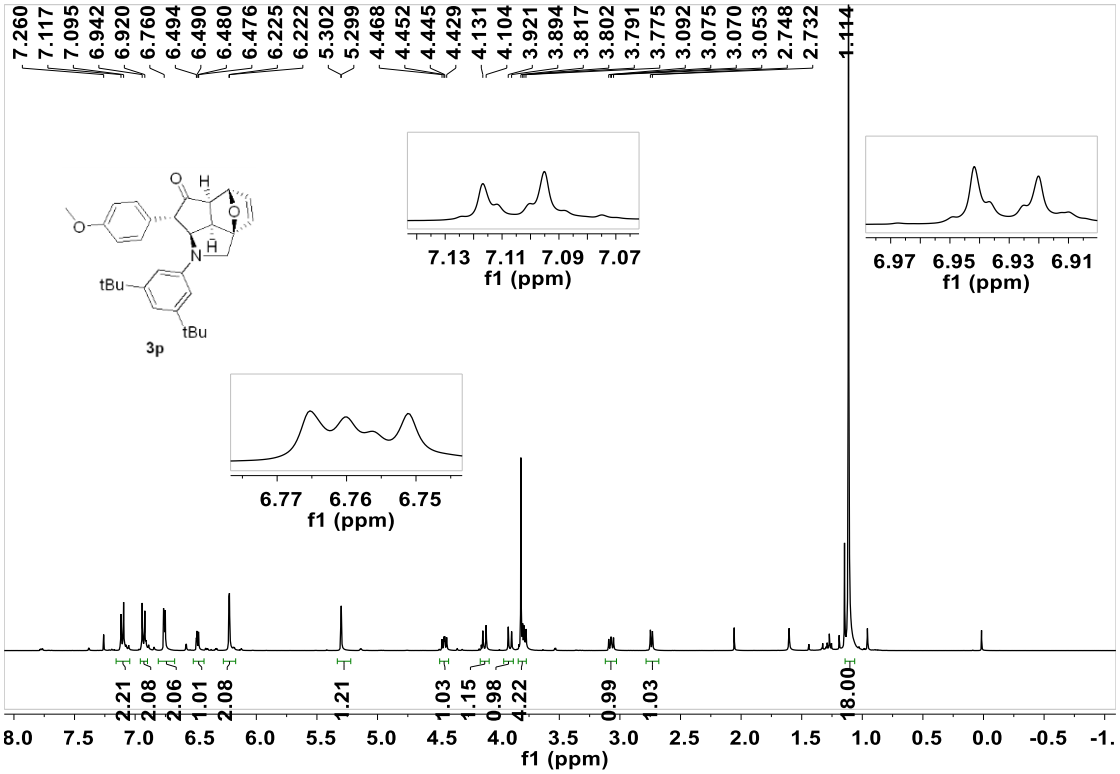

215.542
145.745
139.263
136.962
136.384
131.664
129.092
128.844
127.467
113.871
108.571
96.138
84.557
77.317
77.000
76.682
65.701
54.309
52.992
50.209
O
H
O
N
H
Br
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

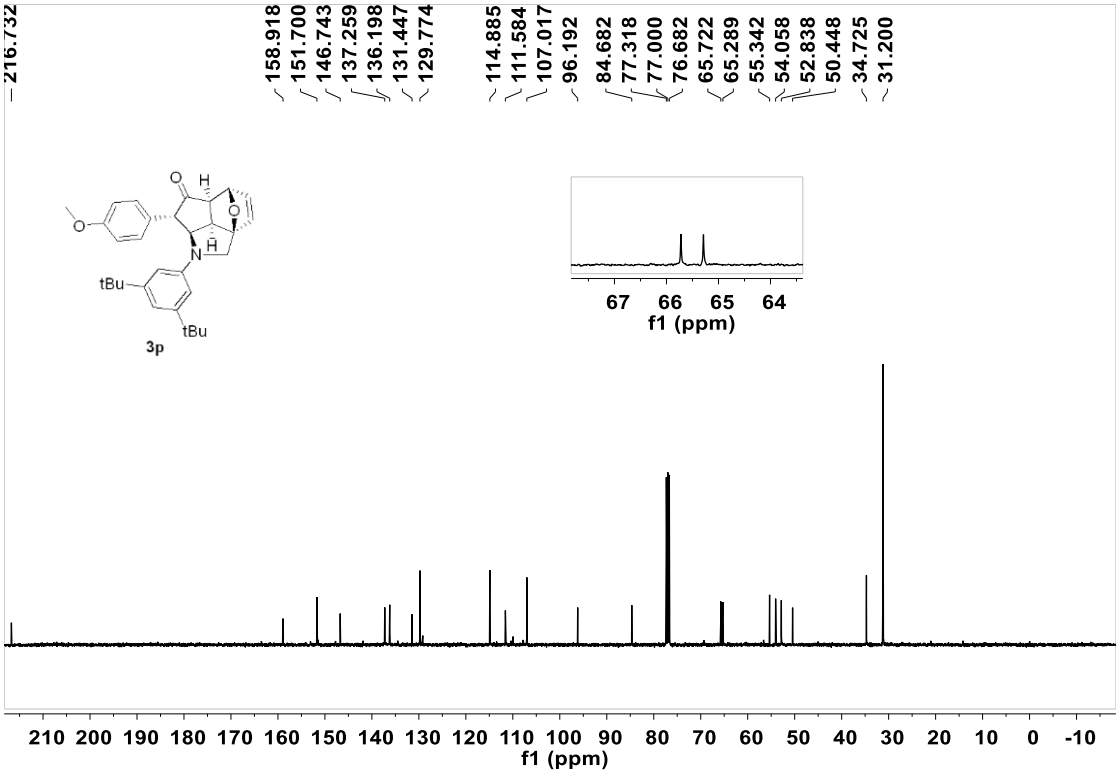

7.260 7.046 7.029 7.024 7.017 6.933 6.917 6.911 6.889 6.745 6.731 6.588 6.584 6.568 6.565 6.502 6.498 6.488 6.483 6.177 6.172 6.166 6.100 6.094 6.079 5.288 5.284 4.332 4.316 4.309 4.293 4.047 4.020 3.854 3.828 3.803 3.743 3.728 3.105 3.088 3.082 3.065 2.755
3n
6.94 6.90 6.86
f1 (ppm)
6.52 6.50 6.48 6.46
f1 (ppm)
4.35 4.33 4.31 4.29
f1 (ppm)
3.10 3.08 3.06
f1 (ppm)
2.03 3.13 1.01 1.00 1.07 1.07 1.06 1.04 1.07 1.03 4.32 1.09 1.03 1.00
f1 (ppm)

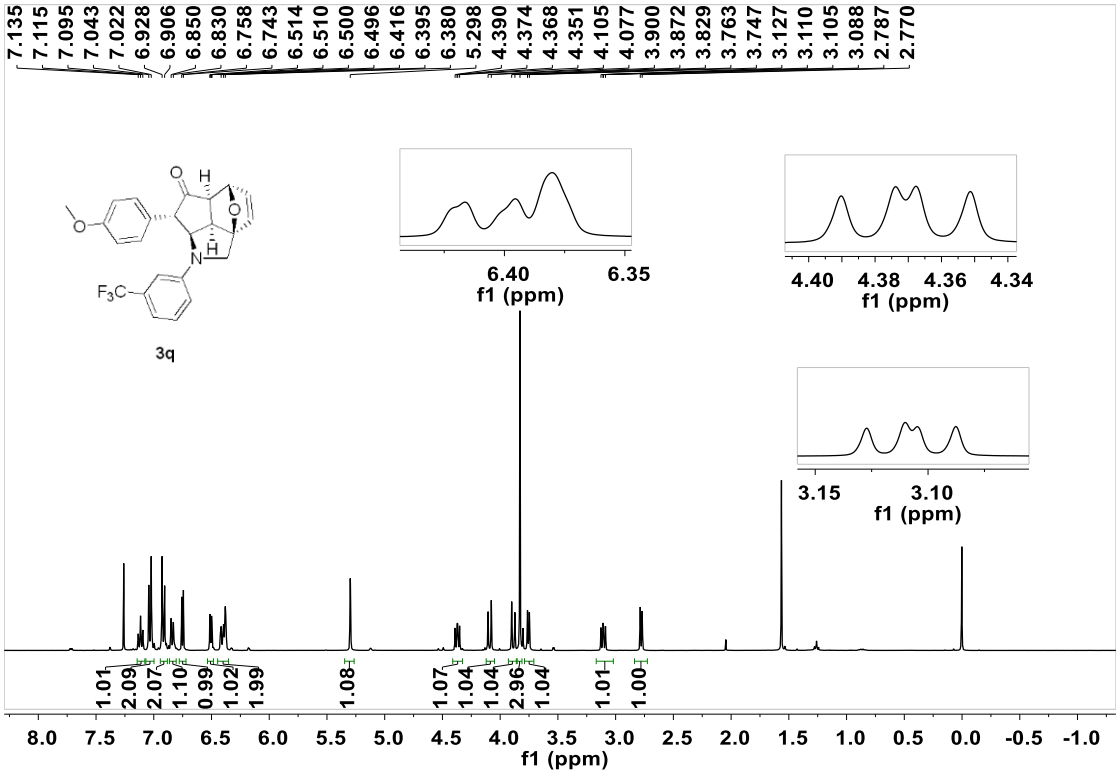

215.991
158.955 147.848 136.888 136.371 134.908 131.265 129.941 116.457 114.630 112.499 110.449 96.013 84.466 65.802 64.832 55.340 54.148 52.740 50.147
3n
f1 (ppm)

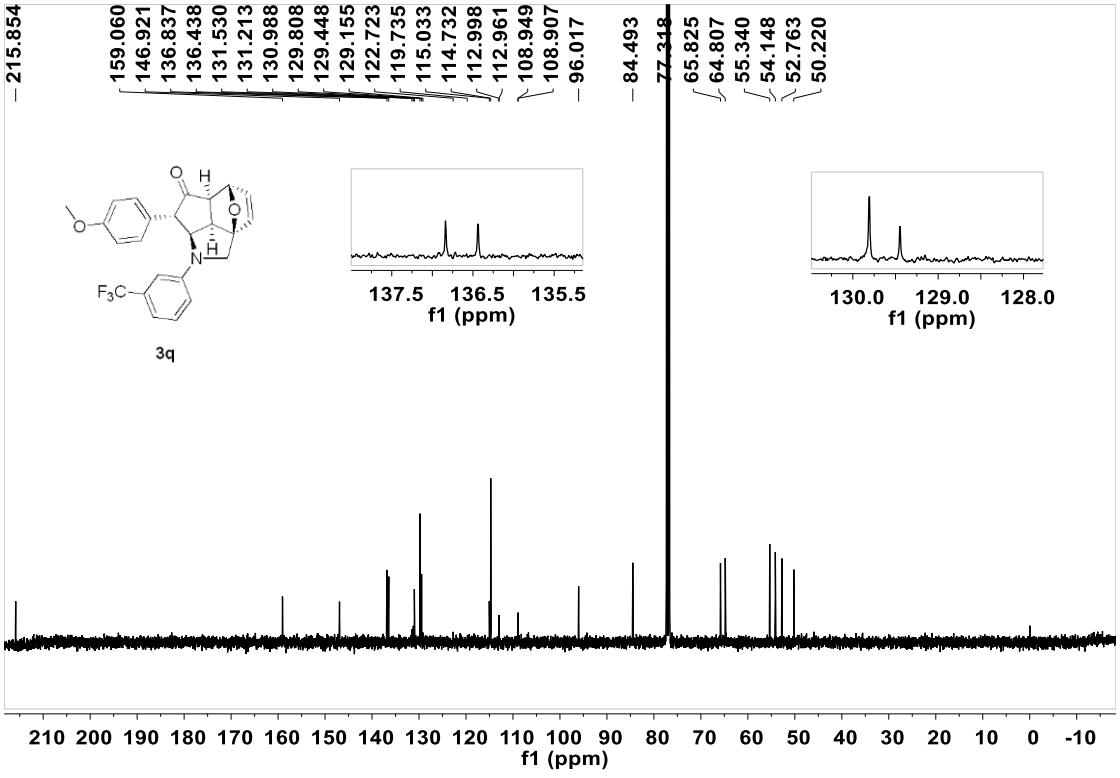

7.260 7.067 7.045 6.973 6.953 6.934 6.927 6.906 6.752 6.738 6.494 6.490 6.480 6.475 6.461 6.442 6.131 6.125 6.110 6.104 5.946 5.289 5.285 4.351 4.335 4.328 4.312 4.070 4.042 3.867 3.839 3.829 3.766 3.750 3.084 3.067 3.062 3.045 2.759 2.742 2.015
3o
6.95 6.90 f1 (ppm)
6.50 6.45 f1 (ppm)
4.36 4.34 4.32 4.30 f1 (ppm)
3.08 3.06 3.04 f1 (ppm)
2.12 3.02 0.98 0.96 1.19 1.08 1.04 0.95 1.07 1.02 4.02 1.05 0.99 1.00 3.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

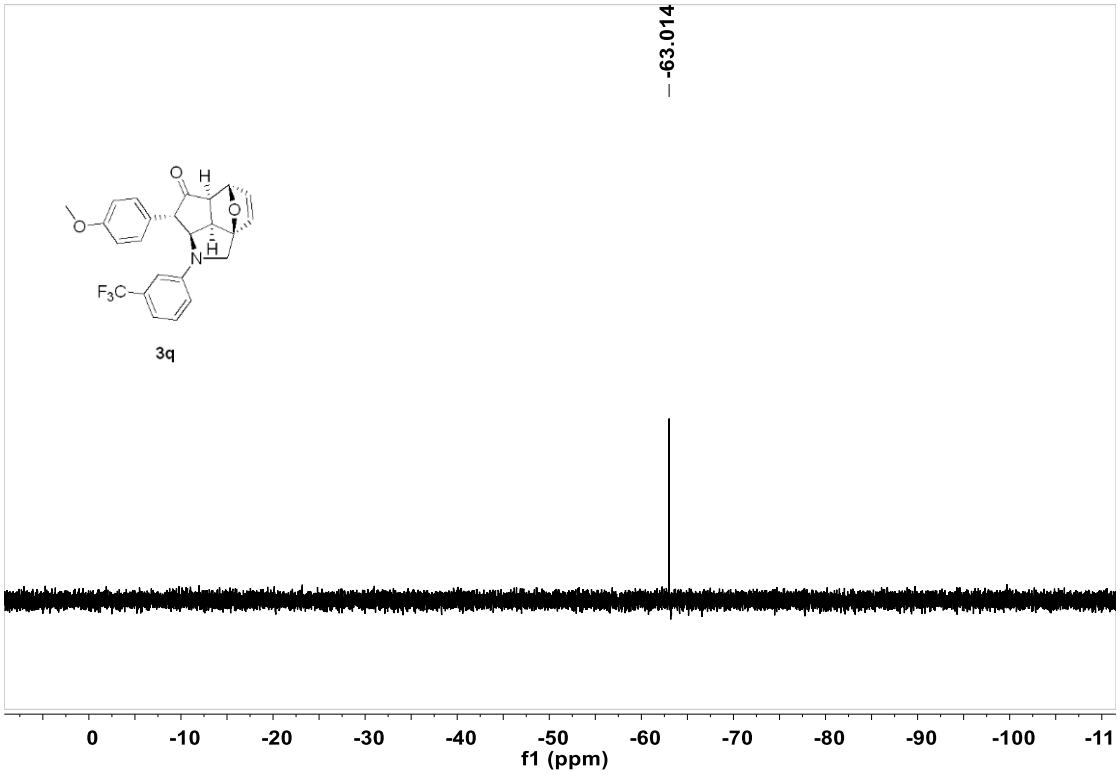

216.573 158.805 146.860 138.779 137.109 136.251 130.050 128.964 117.440 114.419 113.572 109.132 96.186 84.454 77.318 77.000 76.683 65.807 65.180 55.333 54.160 52.734 50.034 21.512
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

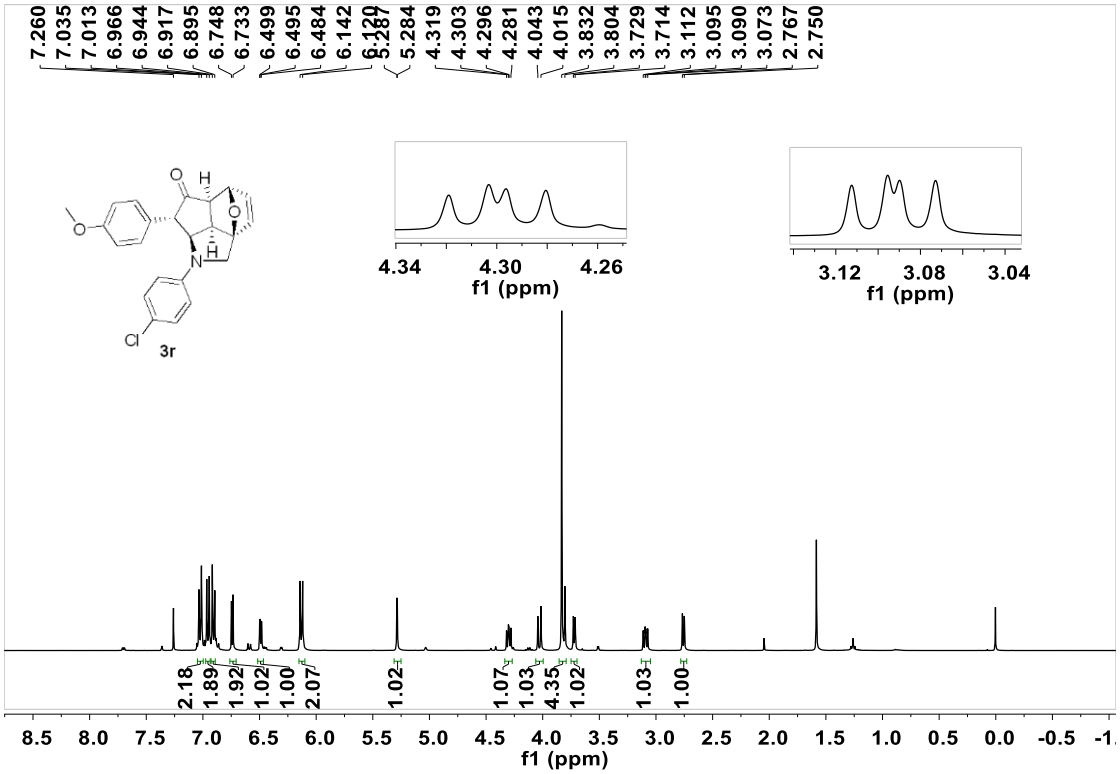

7.260
7.117
7.095
6.942
6.920
6.760
6.494
6.490
6.480
6.476
6.225
6.222
5.302
5.299
4.468
4.452
4.445
4.429
4.131
4.104
3.921
3.894
3.817
3.802
3.791
3.775
3.092
3.075
3.070
3.053
2.748
2.732
1.114
tBu
tBu
3p
7.13 7.11 7.09 7.07
f1 (ppm)
6.97 6.95 6.93 6.91
f1 (ppm)
6.77 6.76 6.75
f1 (ppm)
2.21
2.08
2.06
1.01
2.08
1.21
1.03
1.15
0.98
4.22
0.99
1.03
18.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

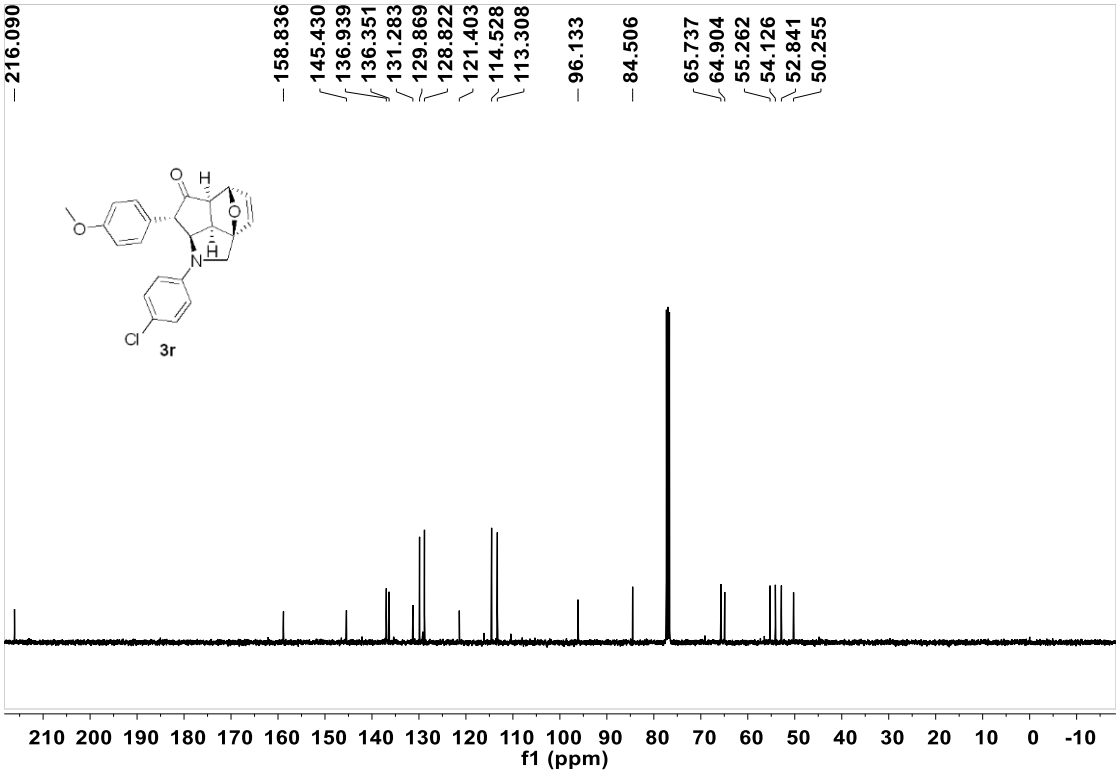

216.732
158.918
151.700
146.743
137.259
136.198
131.447
129.774
114.885
111.584
107.017
96.192
84.682
77.318
77.000
76.682
65.722
65.289
55.342
54.058
52.838
50.448
34.725
31.200
tBu
tBu
3p
67 66 65 64
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

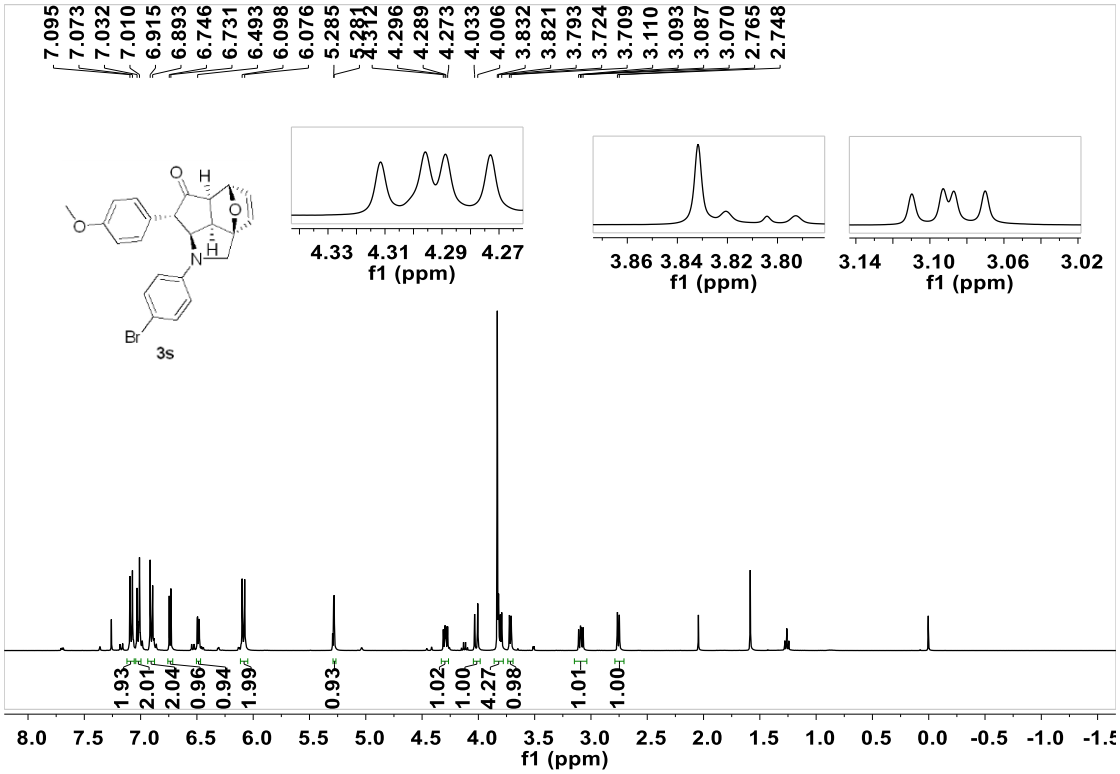

7.135
7.115
7.095
7.043
7.022
6.928
6.906
6.850
6.830
6.758
6.743
6.514
6.510
6.500
6.496
6.416
6.395
6.380
5.298
4.390
4.374
4.368
4.351
4.105
4.077
3.900
3.872
3.829
3.763
3.747
3.127
3.110
3.105
3.088
2.787
2.770
3q
6.40
6.35
f1 (ppm)
4.40
4.38
4.36
4.34
f1 (ppm)
3.15
3.10
f1 (ppm)
1.01
2.09
2.07
1.10
0.99
1.02
1.99
1.08
1.07
1.04
1.04
2.96
1.04
1.01
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

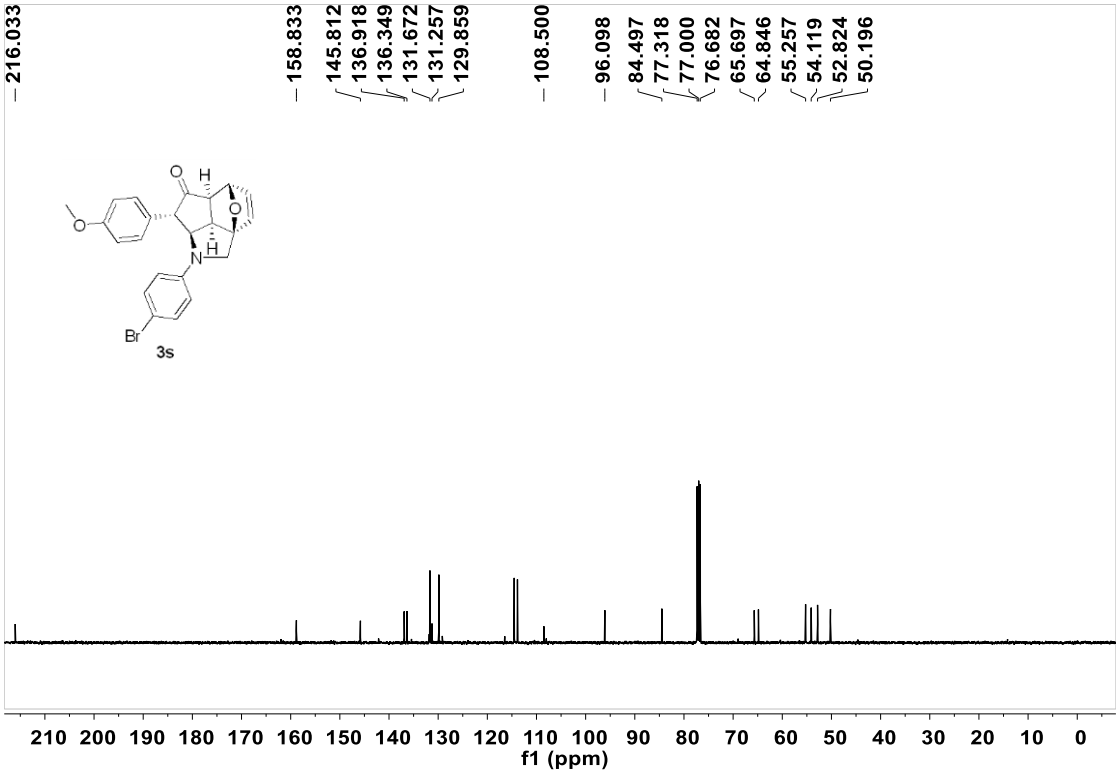

215.854
159.060
146.921
136.837
136.438
131.530
131.213
130.988
129.808
129.448
129.155
122.723
119.735
115.033
114.732
112.998
112.961
108.949
108.907
96.017
84.493
77.348
65.825
64.807
55.340
54.148
52.763
50.220
3q
137.5
136.5
135.5
f1 (ppm)
130.0
129.0
128.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

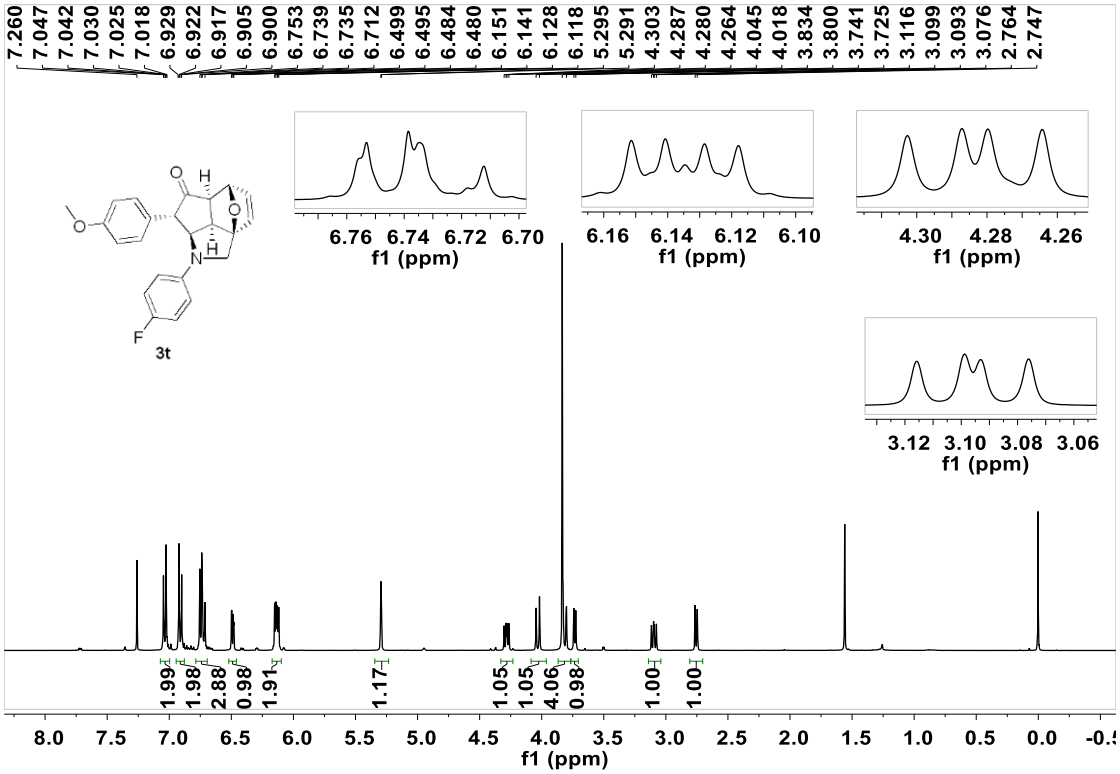

-63.014
O
H
O
O
N
H
F3C
3q
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-11
f1 (ppm)

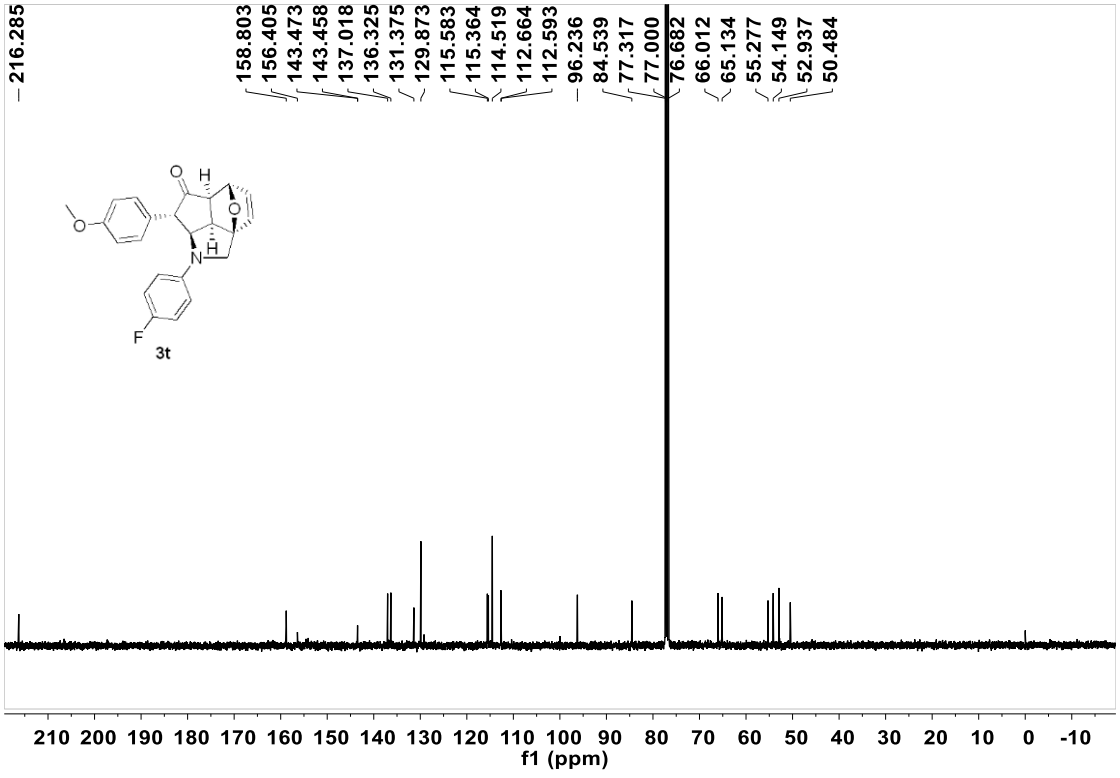

7.260
7.035
7.013
6.966
6.944
6.917
6.895
6.748
6.733
6.499
6.495
6.484
6.142
5.287
5.284
4.319
4.303
4.296
4.281
4.043
4.015
3.832
3.804
3.729
3.714
3.112
3.095
3.090
3.073
2.767
2.750
3r
4.34
4.30
4.26
f1 (ppm)
3.12
3.08
3.04
f1 (ppm)
2.18
1.89
1.92
1.02
1.00
2.07
1.02
1.07
1.03
4.35
1.02
1.03
1.00
f1 (ppm)

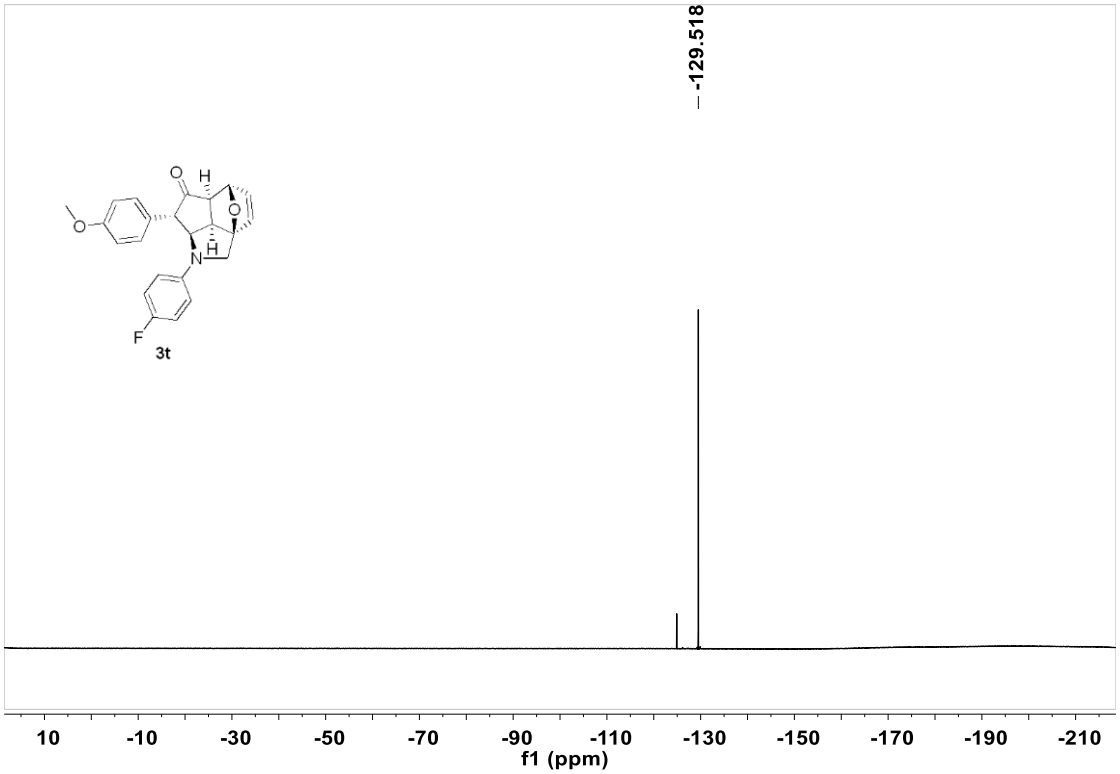

216.090
158.836
145.430
136.939
136.351
131.283
129.869
128.822
121.403
114.528
113.308
96.133
84.506
65.737
64.904
55.262
54.126
52.841
50.255
3r
f1 (ppm)

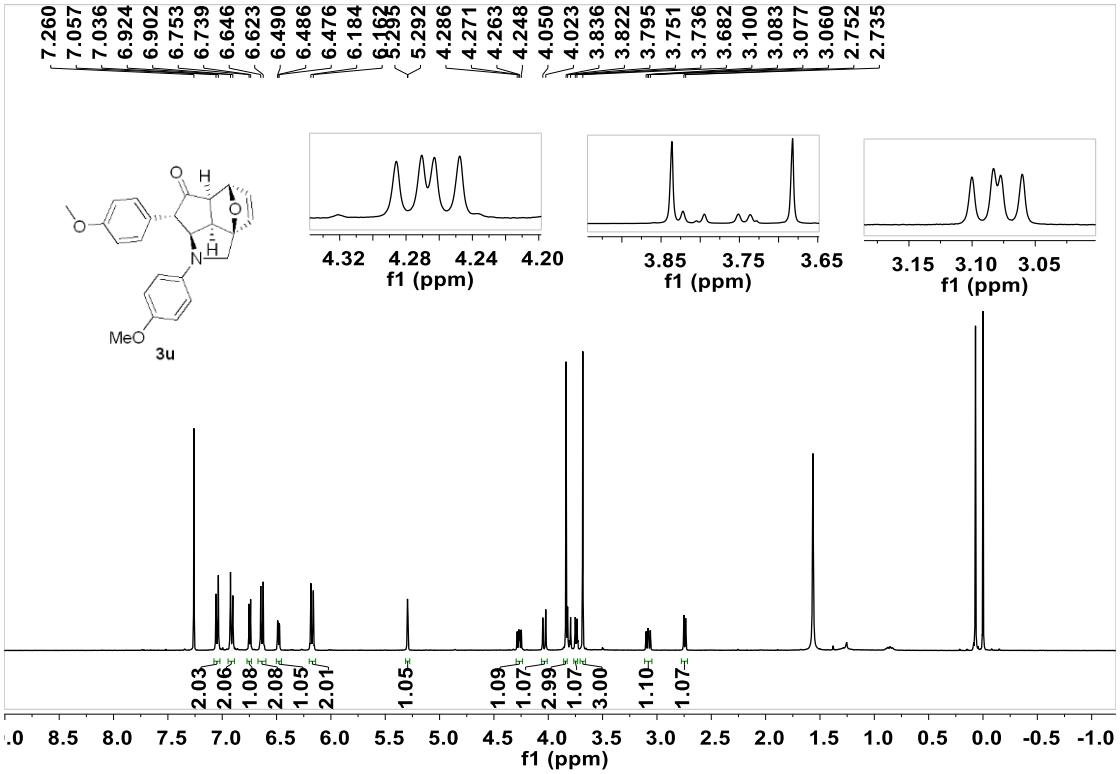

7.095
7.073
7.032
7.010
6.915
6.893
6.746
6.731
6.493
6.098
6.076
5.285
5.281
4.312
4.296
4.289
4.273
4.033
4.006
3.832
3.821
3.793
3.724
3.709
3.110
3.093
3.087
3.070
2.765
2.748
4.33 4.31 4.29 4.27
f1 (ppm)
3.86 3.84 3.82 3.80
f1 (ppm)
3.14 3.10 3.06 3.02
f1 (ppm)
3s
1.93
2.01
2.04
0.96
0.94
1.99
0.93
1.02
1.00
4.27
0.98
1.01
1.00
f1 (ppm)

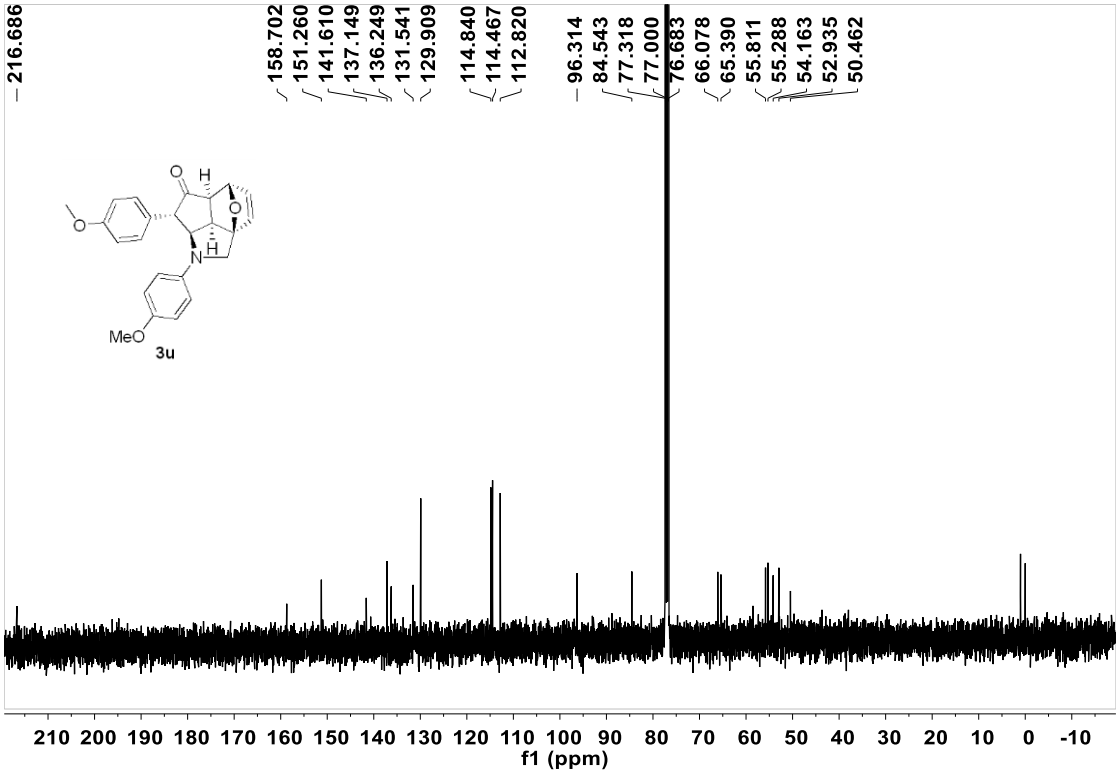

216.033
158.833
145.812
136.918
136.349
131.672
131.257
129.859
108.500
96.098
84.497
77.318
77.000
76.682
65.697
64.846
55.257
54.119
52.824
50.196
3s
f1 (ppm)

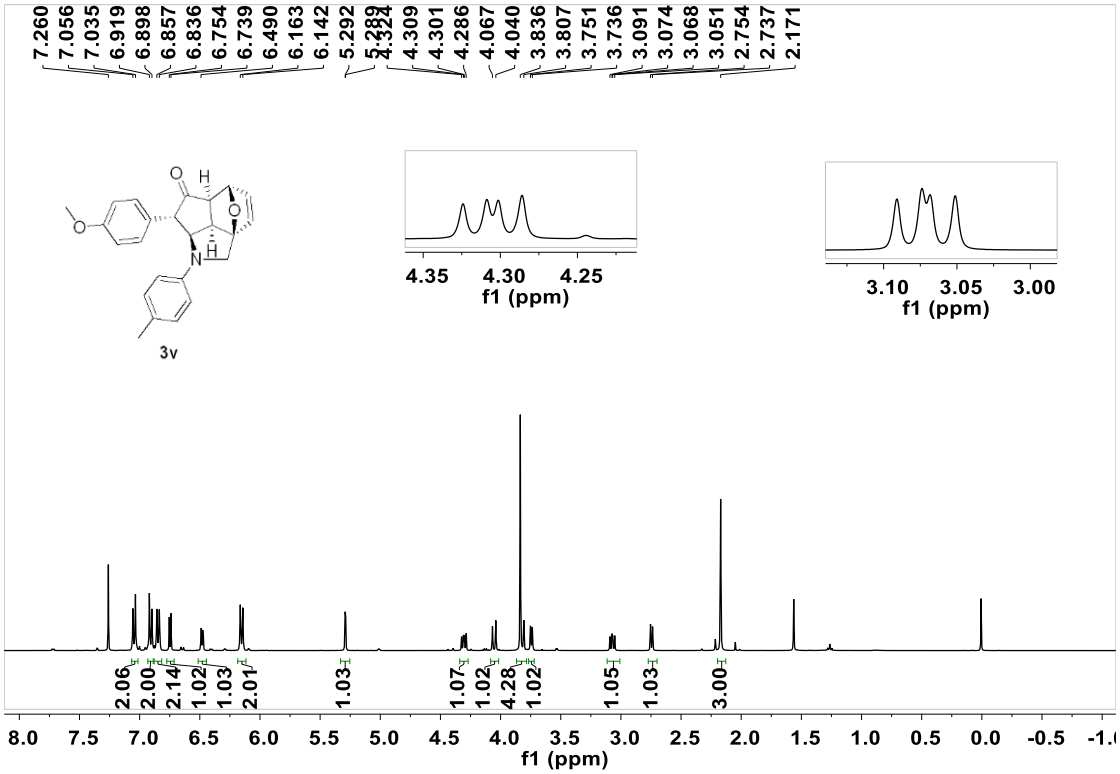

7.260 7.047 7.042 7.030 7.025 7.018 6.929 6.922 6.917 6.905 6.900 6.753 6.739 6.735 6.712 6.499 6.495 6.484 6.480 6.151 6.141 6.128 6.118 5.295 5.291 4.303 4.287 4.280 4.264 4.045 4.018 3.834 3.800 3.741 3.725 3.116 3.099 3.093 3.076 2.764 2.747
6.76 6.74 6.72 6.70
f1 (ppm)
6.16 6.14 6.12 6.10
f1 (ppm)
4.30 4.28 4.26
f1 (ppm)
3.12 3.10 3.08 3.06
f1 (ppm)
3t
1.99 1.98 2.88 0.98 1.91 1.17 1.05 1.05 4.06 0.98 1.00 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

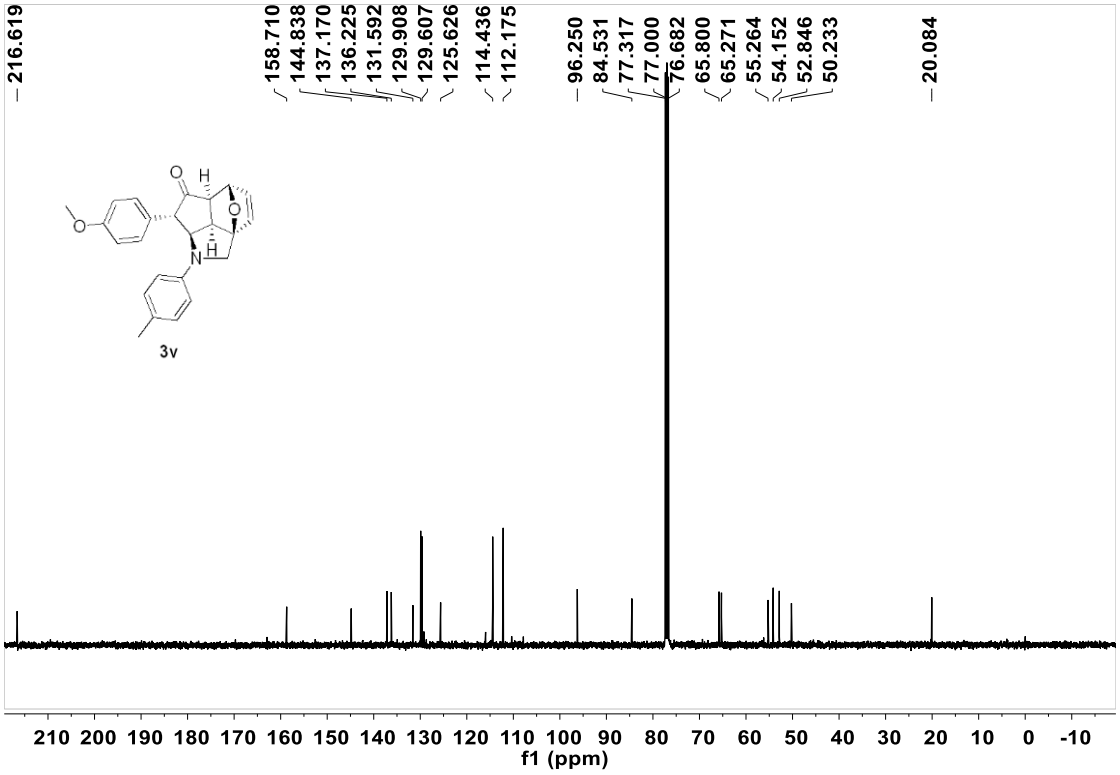

216.285
158.803 156.405 143.473 143.458 137.018 136.325 131.375 129.873 115.583 115.364 114.519 112.664 112.593 96.236 84.539 77.317 77.000 76.682 66.012 65.134 55.277 54.149 52.937 50.484
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

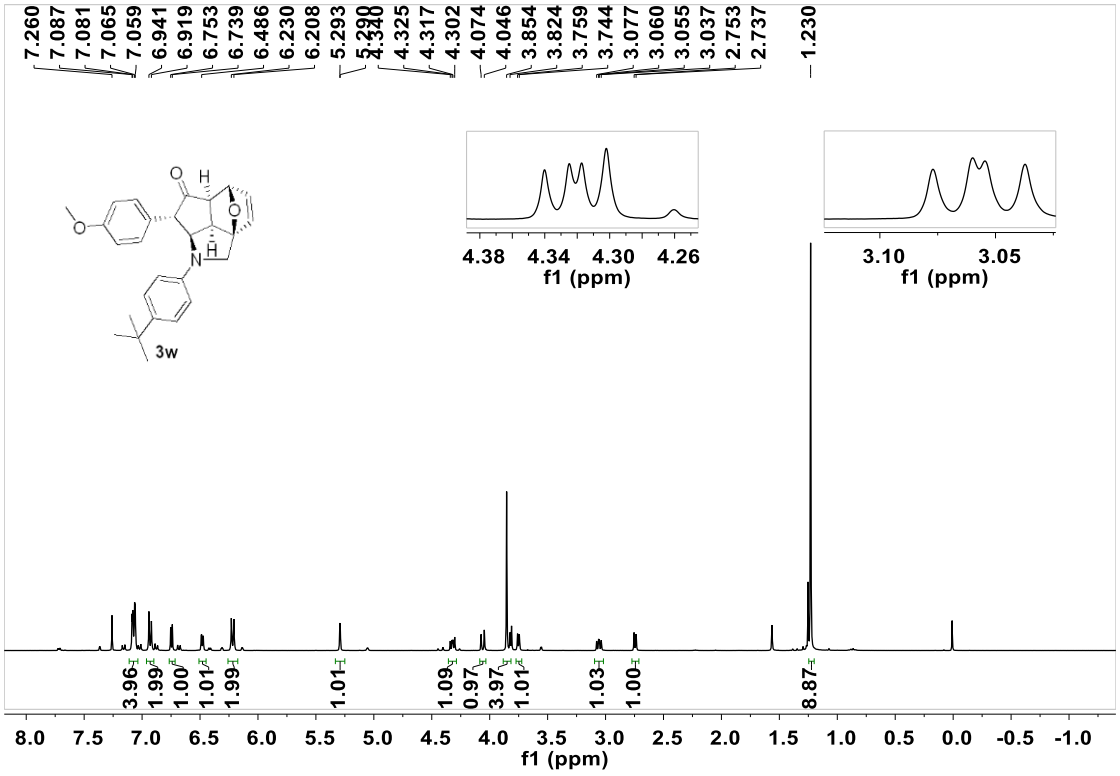

-129.518
O
H
O
O
N
H
F
3t
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

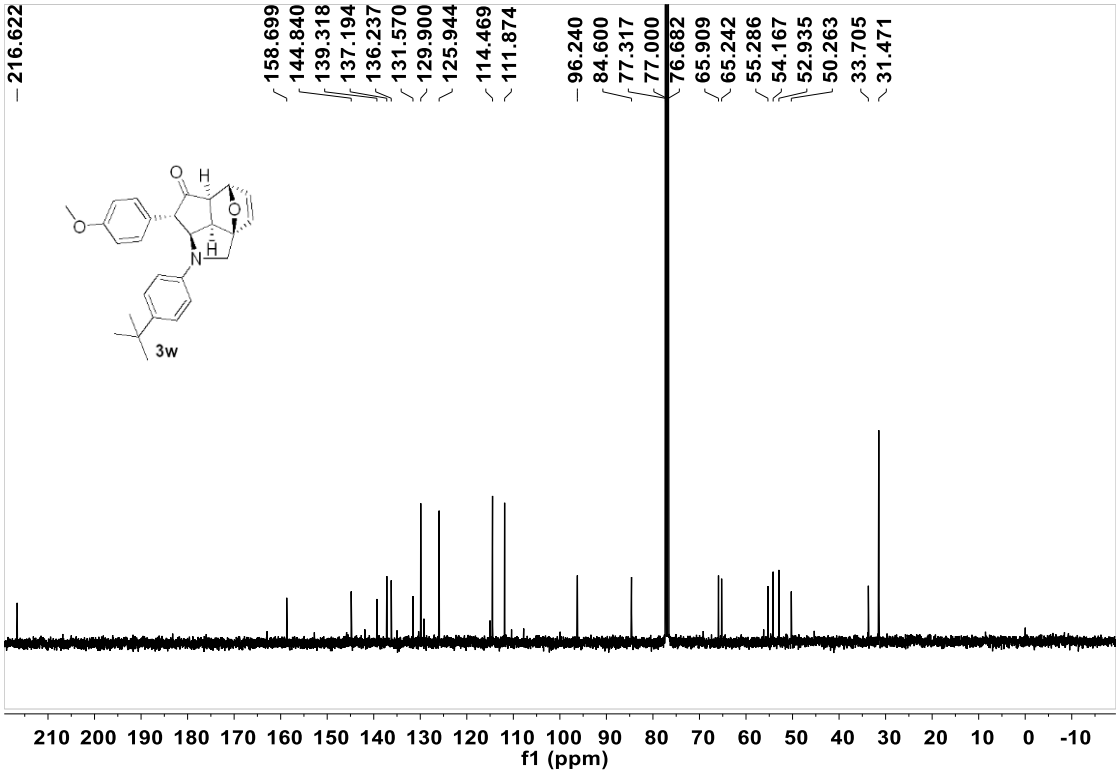

7.260
7.057
7.036
6.924
6.902
6.753
6.739
6.646
6.623
6.490
6.486
6.476
6.184
5.295
5.292
4.286
4.271
4.263
4.248
4.050
4.023
3.836
3.822
3.795
3.751
3.736
3.682
3.100
3.083
3.077
3.060
2.752
2.735
MeO
3u
4.32 4.28 4.24 4.20
f1 (ppm)
3.85 3.75 3.65
f1 (ppm)
3.15 3.10 3.05
f1 (ppm)
2.03 2.06 1.08 2.08 1.05 2.01 1.05 1.09 1.07 2.99 1.07 3.00 1.10 1.07
f1 (ppm)

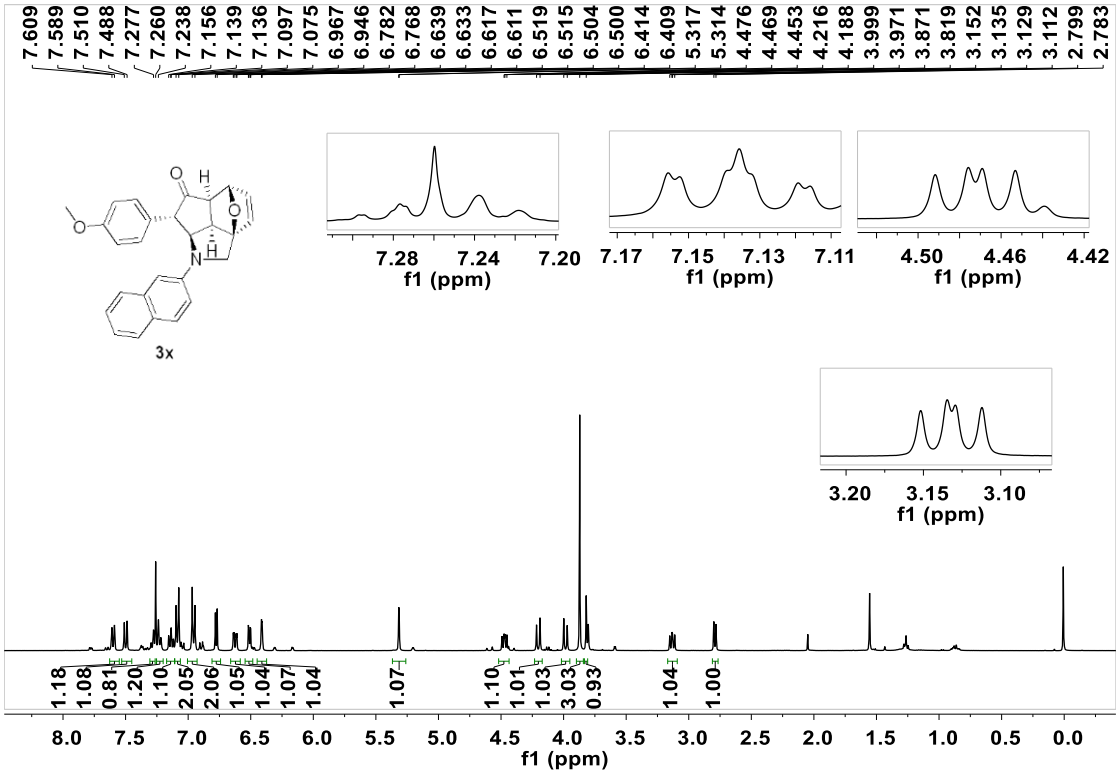

216.686
158.702
151.260
141.610
137.149
136.249
131.541
129.909
114.840
114.467
112.820
96.314
84.543
77.318
77.000
76.683
66.078
65.390
55.811
55.288
54.163
52.935
50.462
MeO
3u
f1 (ppm)

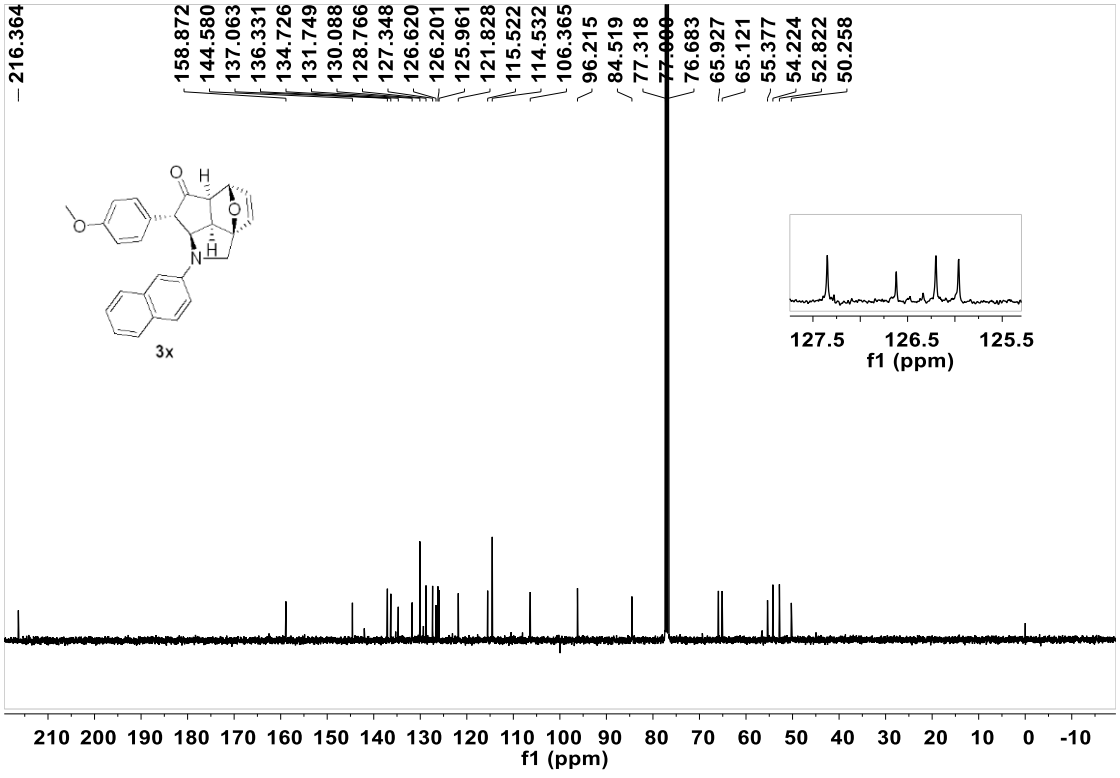

7.260
7.056
7.035
6.919
6.898
6.857
6.836
6.754
6.739
6.490
6.163
6.142
5.292
4.309
4.301
4.286
4.067
4.040
3.836
3.807
3.751
3.736
3.091
3.074
3.068
3.051
2.754
2.737
2.171
3v
4.35 4.30 4.25
f1 (ppm)
3.10 3.05 3.00
f1 (ppm)
2.06 2.00 2.14 1.02 1.03 2.01 1.03 1.07 1.02 4.28 1.02 1.05 1.03 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

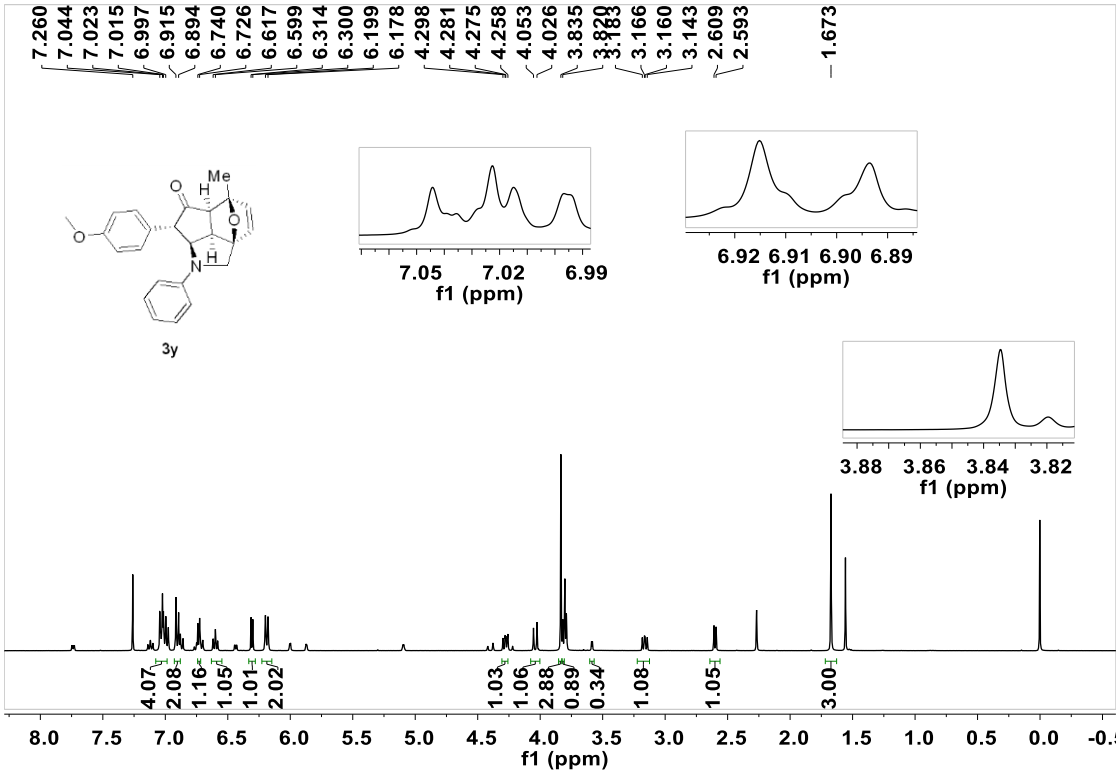

216.619
158.710
144.838
137.170
136.225
131.592
129.908
129.607
125.626
114.436
112.175
96.250
84.531
77.317
77.000
76.682
65.800
65.271
55.264
54.152
52.846
50.233
20.084
3v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

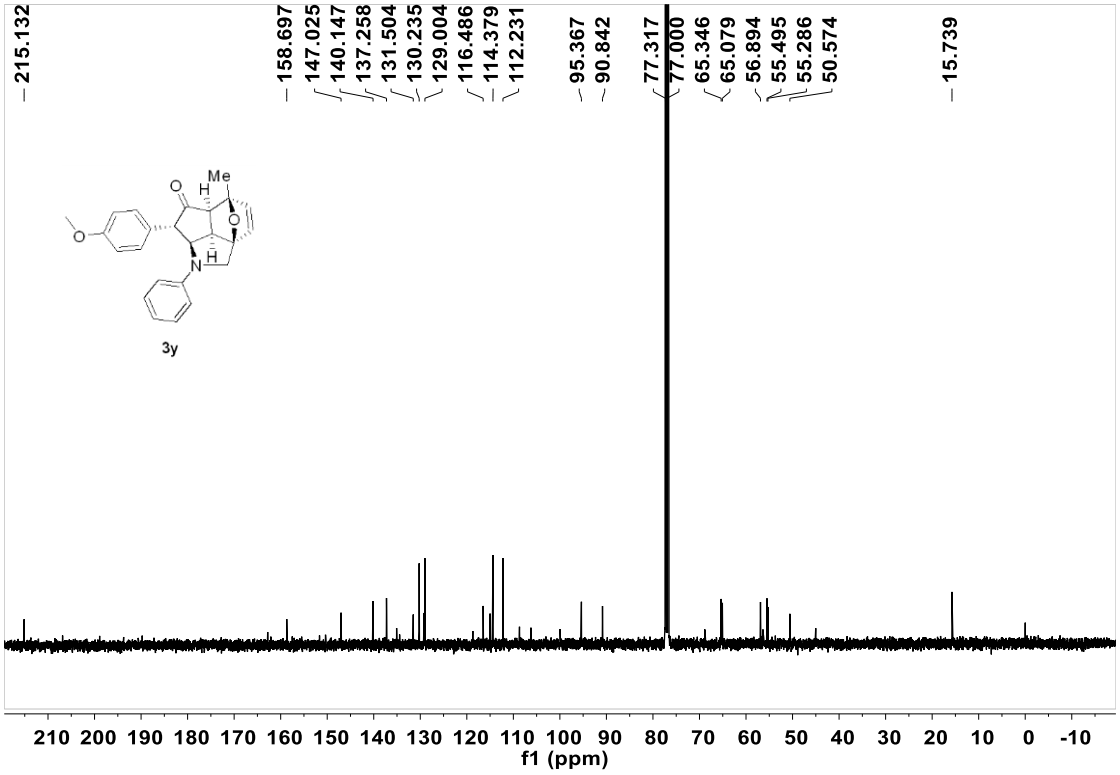

7.260
7.087
7.081
7.065
7.059
6.941
6.919
6.753
6.739
6.486
6.230
6.208
5.293
5.290
4.325
4.317
4.302
4.074
4.046
3.854
3.824
3.759
3.744
3.077
3.060
3.055
3.037
2.753
2.737
1.230
3w
4.38 4.34 4.30 4.26
f1 (ppm)
3.10 3.05
f1 (ppm)
3.96 1.99 1.00 1.01 1.99 1.01 1.09 0.97 3.97 1.01 1.03 1.00 8.87
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

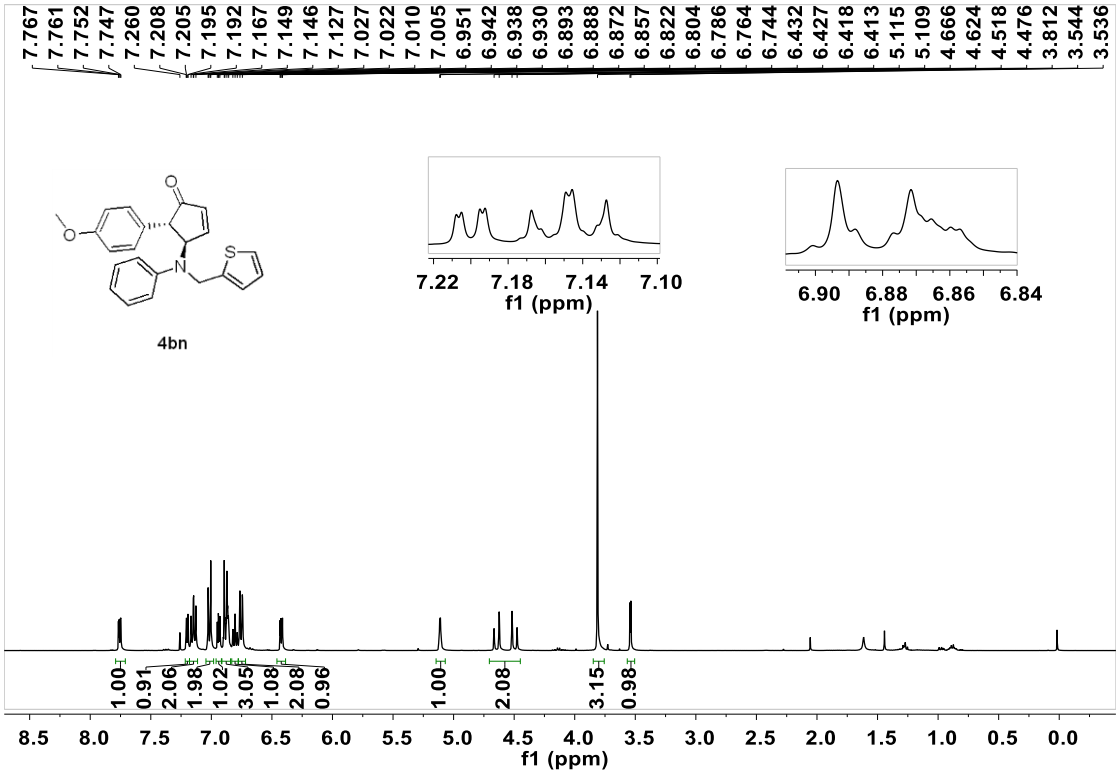

216.622
158.699
144.840
139.318
137.194
136.237
131.570
129.900
125.944
114.469
111.874
96.240
84.600
77.317
77.000
76.682
65.909
65.242
55.286
54.167
52.935
50.263
33.705
31.471
3w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

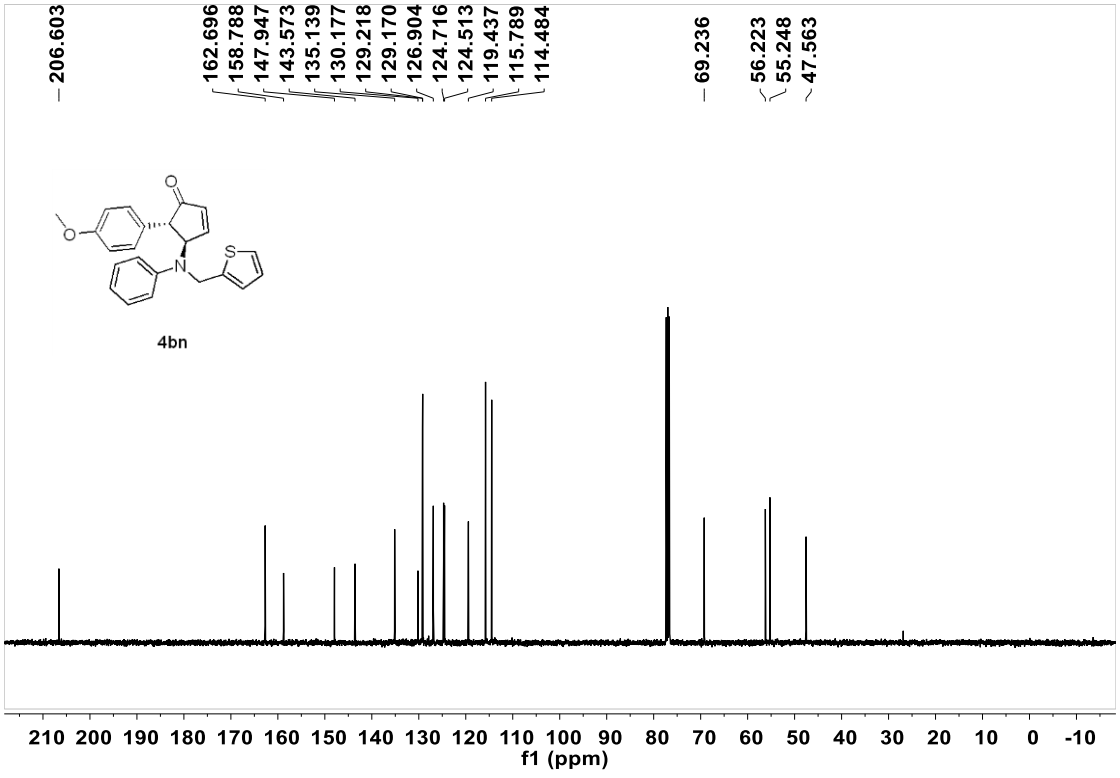

7.609 7.589 7.510 7.488 7.277 7.260 7.238 7.156 7.139 7.136 7.097 7.075 6.967 6.946 6.782 6.768 6.639 6.633 6.617 6.611 6.519 6.515 6.504 6.500 6.414 6.409 5.317 5.314 4.476 4.469 4.453 4.216 4.188 3.999 3.971 3.871 3.819 3.152 3.135 3.129 3.112 2.799 2.783
3x
7.28 7.24 7.20 f1 (ppm)
7.17 7.15 7.13 7.11 f1 (ppm)
4.50 4.46 4.42 f1 (ppm)
3.20 3.15 3.10 f1 (ppm)
1.18 1.08 0.81 1.20 1.10 2.05 2.06 1.05 1.04 1.07 1.04 1.07 1.10 1.01 1.03 3.03 0.93 1.04 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)

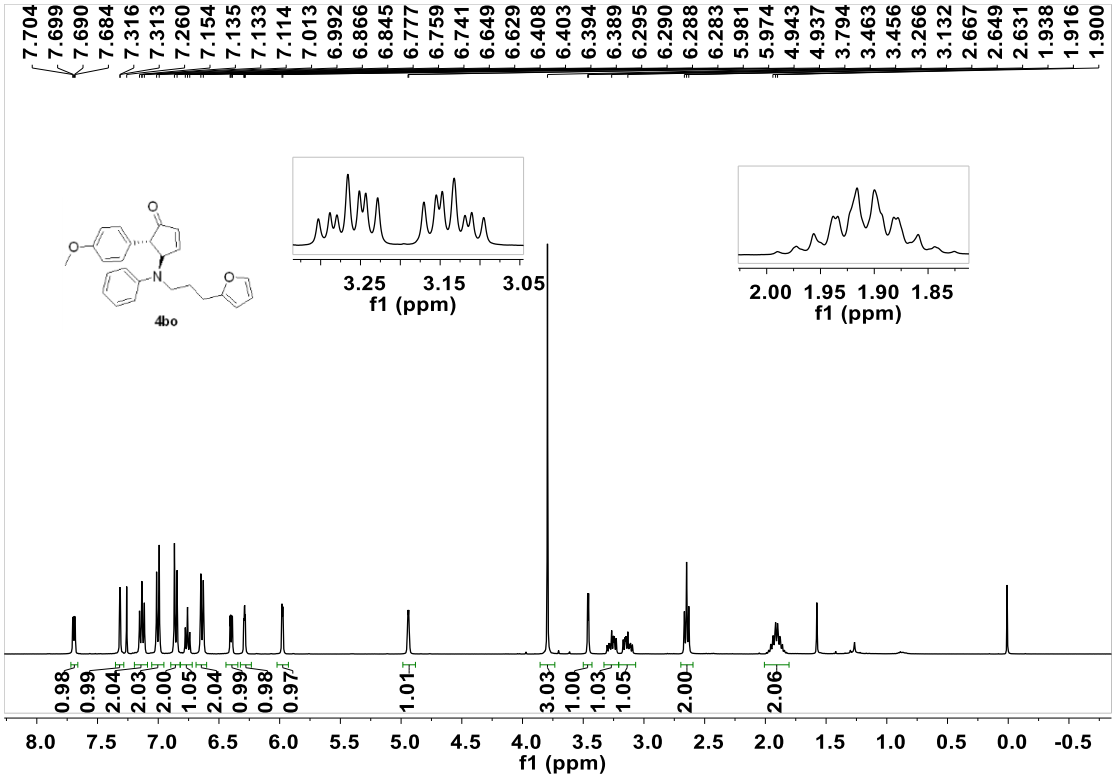

216.364
158.872 144.580 137.063 136.331 134.726 131.749 130.088 128.766 127.348 126.620 126.201 125.961 121.828 115.522 114.532 106.365 96.215 84.519 77.318 77.000 76.683 65.927 65.121 55.377 54.224 52.822 50.258
3x
127.5 126.5 125.5 f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

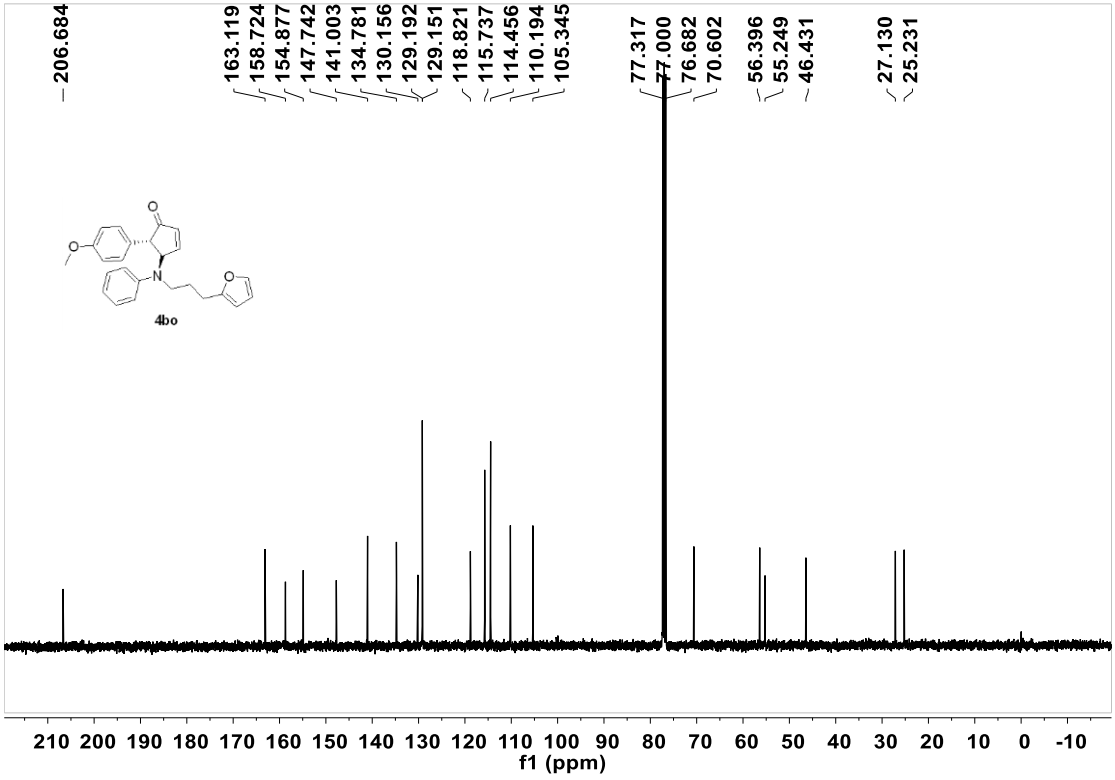

7.260
7.044
7.023
7.015
6.997
6.915
6.894
6.740
6.726
6.617
6.599
6.314
6.300
6.199
6.178
4.298
4.281
4.275
4.258
4.053
4.026
3.835
3.820
3.183
3.166
3.160
3.143
2.609
2.593
1.673
3y
7.05 7.02 6.99
f1 (ppm)
6.92 6.91 6.90 6.89
f1 (ppm)
3.88 3.86 3.84 3.82
f1 (ppm)
4.07 2.08 1.16 1.05 1.01 2.02 1.03 1.06 2.88 0.89 0.34 1.08 1.05 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

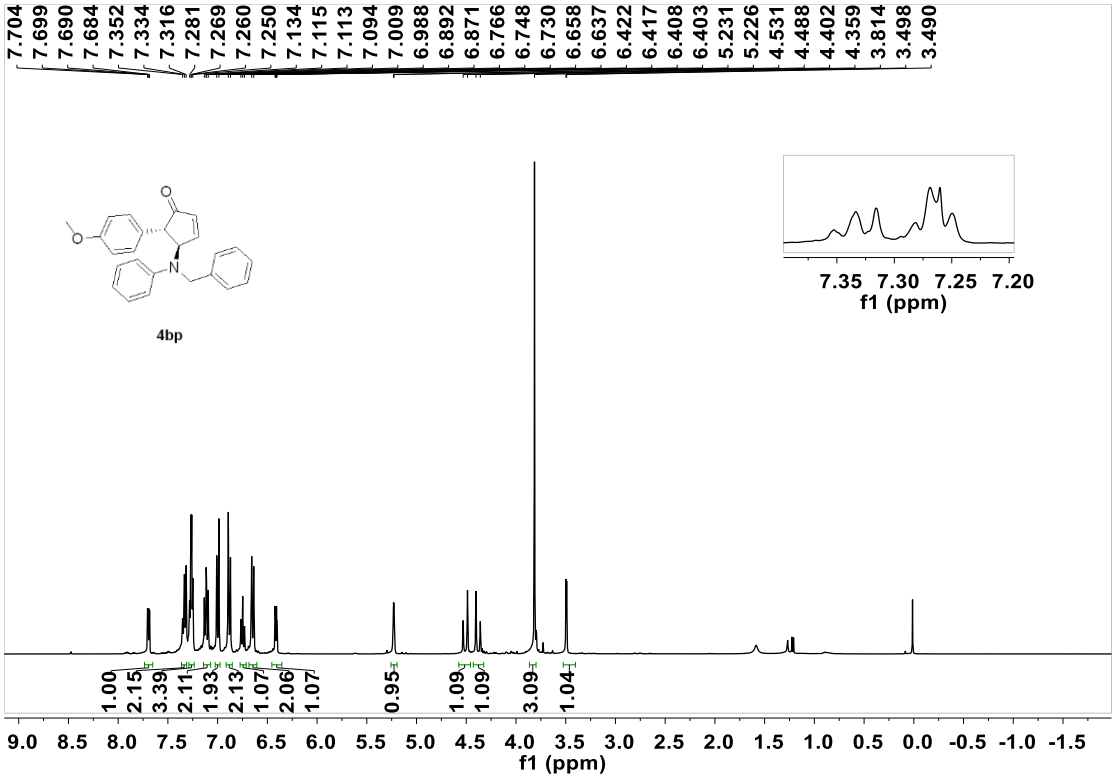

215.132
158.697
147.025
140.147
137.258
131.504
130.235
129.004
116.486
114.379
112.231
95.367
90.842
77.317
77.000
65.346
65.079
56.894
55.495
55.286
50.574
15.739
3y
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

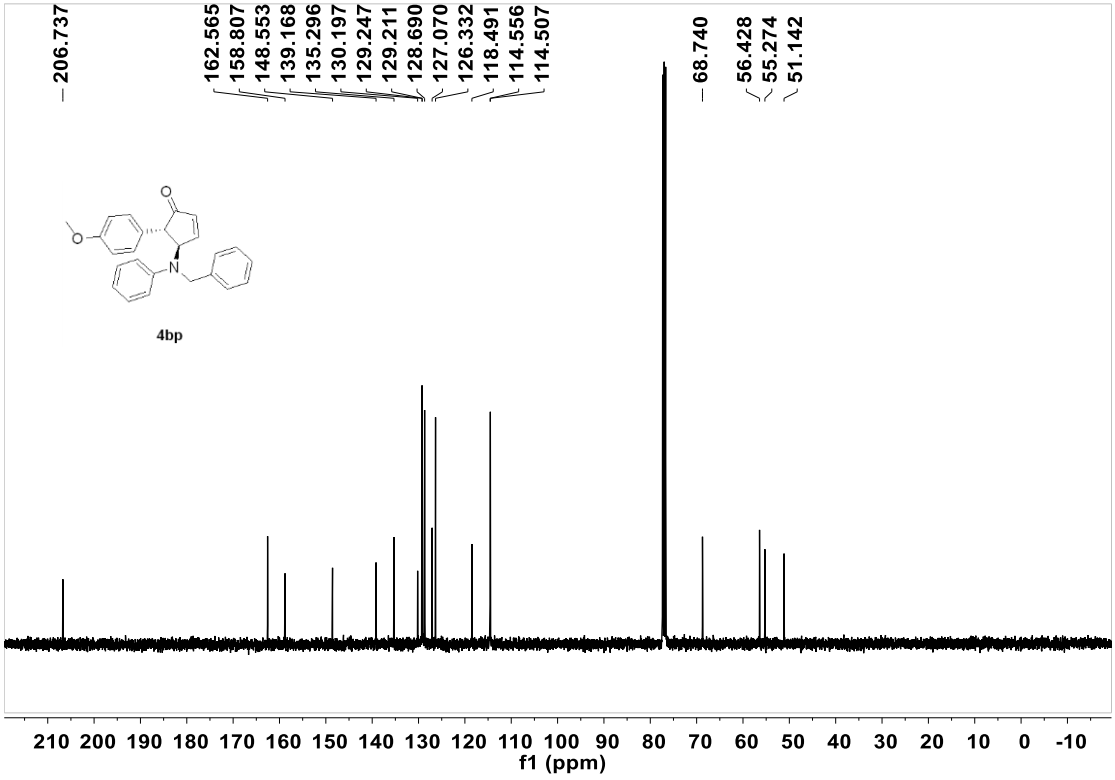

7.767
7.761
7.752
7.747
7.260
7.208
7.205
7.195
7.192
7.167
7.149
7.146
7.127
7.027
7.022
7.010
7.005
6.951
6.942
6.938
6.930
6.893
6.888
6.872
6.857
6.822
6.804
6.786
6.764
6.744
6.432
6.427
6.418
6.413
5.115
5.109
4.666
4.624
4.518
4.476
3.812
3.544
3.536
4bn
7.22 7.18 7.14 7.10
f1 (ppm)
6.90 6.88 6.86 6.84
f1 (ppm)
1.00 0.91 2.06 1.98 1.02 3.05 1.08 2.08 0.96 1.00 2.08 3.15 0.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

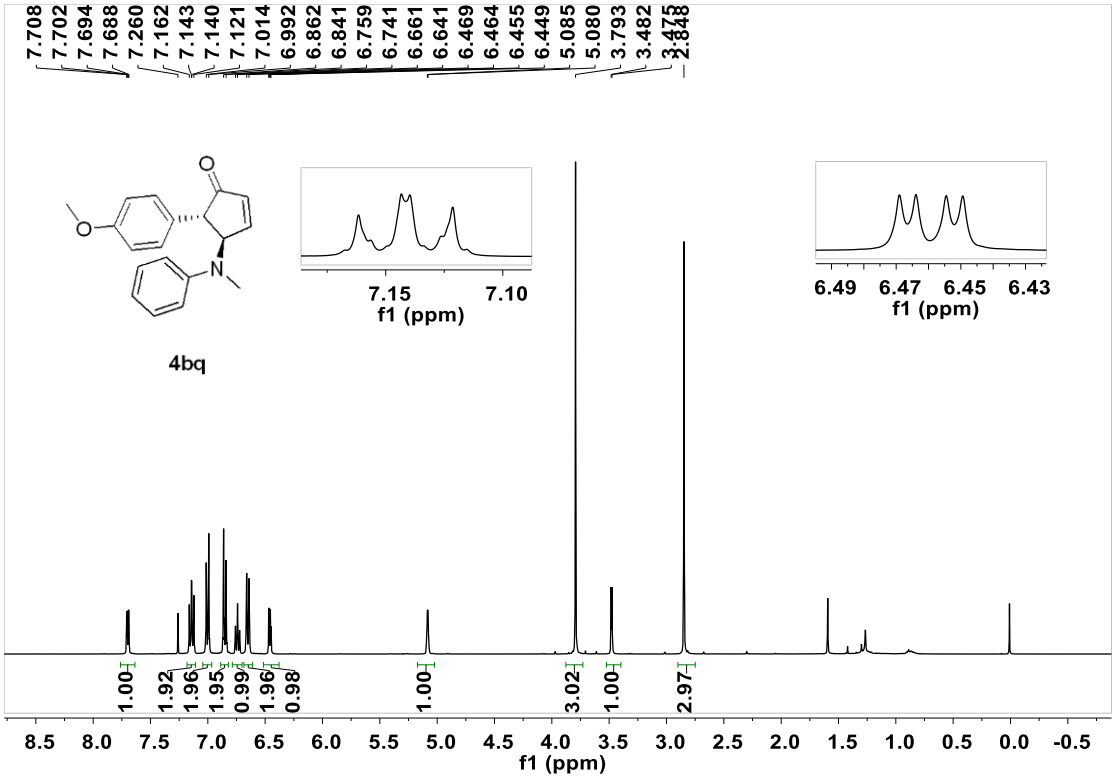

206.603
162.696
158.788
147.947
143.573
135.139
130.177
129.218
129.170
126.904
124.716
124.513
119.437
115.789
114.484
69.236
56.223
55.248
47.563
4bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

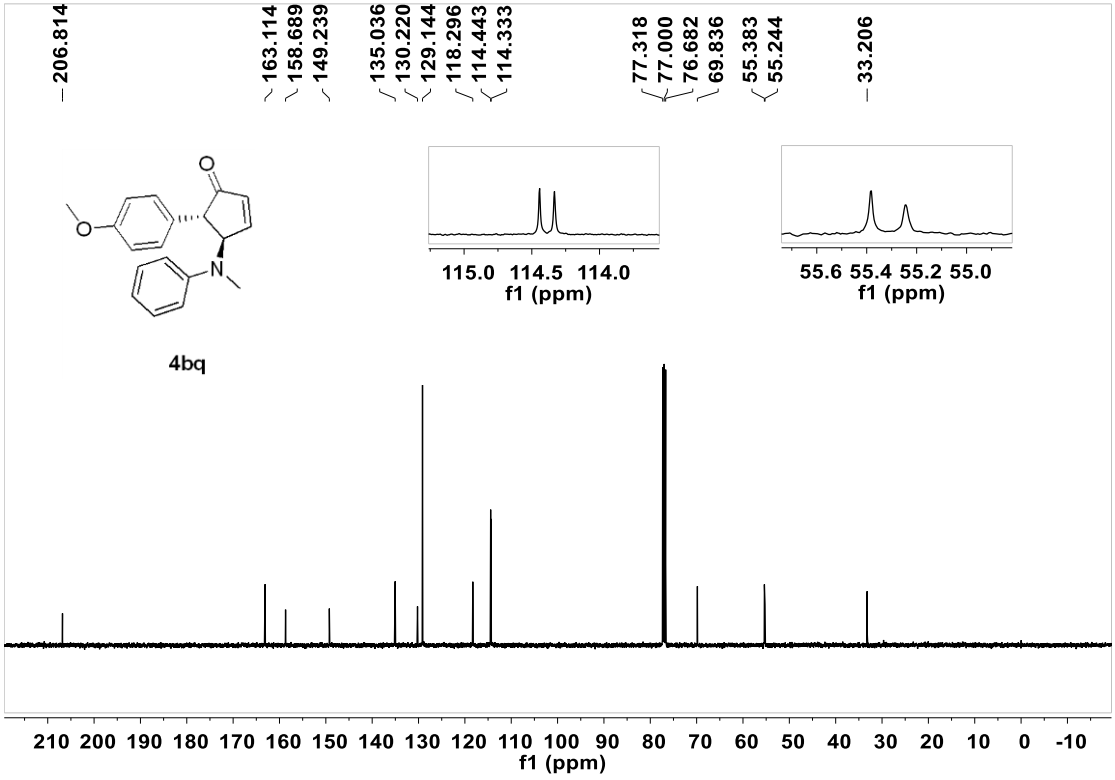

7.704 7.699 7.690 7.684 7.316 7.313 7.260 7.154 7.135 7.133 7.114 7.013 6.992 6.866 6.845 6.777 6.759 6.741 6.649 6.629 6.408 6.403 6.394 6.389 6.295 6.290 6.288 6.283 5.981 5.974 4.943 4.937 3.794 3.463 3.456 3.266 3.132 2.667 2.649 2.631 1.938 1.916 1.900
4bo
3.25 3.15 3.05
f1 (ppm)
2.00 1.95 1.90 1.85
f1 (ppm)
0.98 0.99 2.04 2.03 2.00 1.05 2.04 0.99 0.98 0.97 1.01 3.03 1.00 1.03 1.05 2.00 2.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

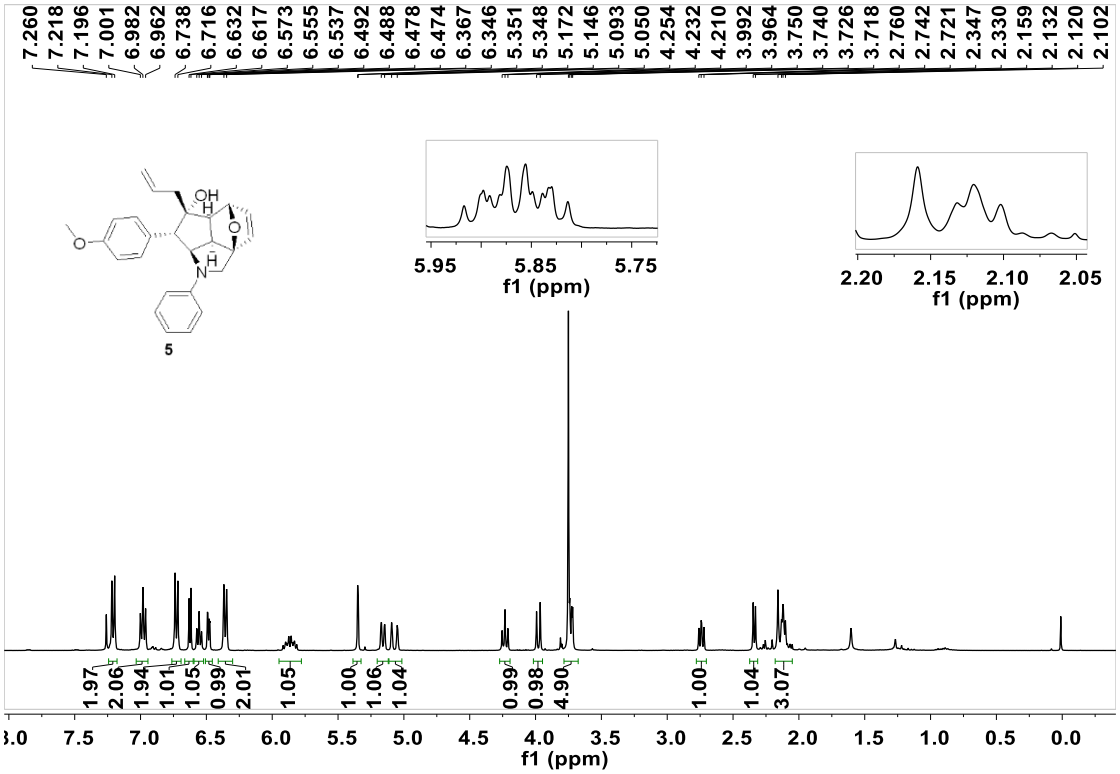

206.684
163.119 158.724 154.877 147.742 141.003 134.781 130.156 129.192 129.151 118.821 115.737 114.456 110.194 105.345
77.317 77.000 76.682 70.602 56.396 55.249 46.431 27.130 25.231
4bo
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

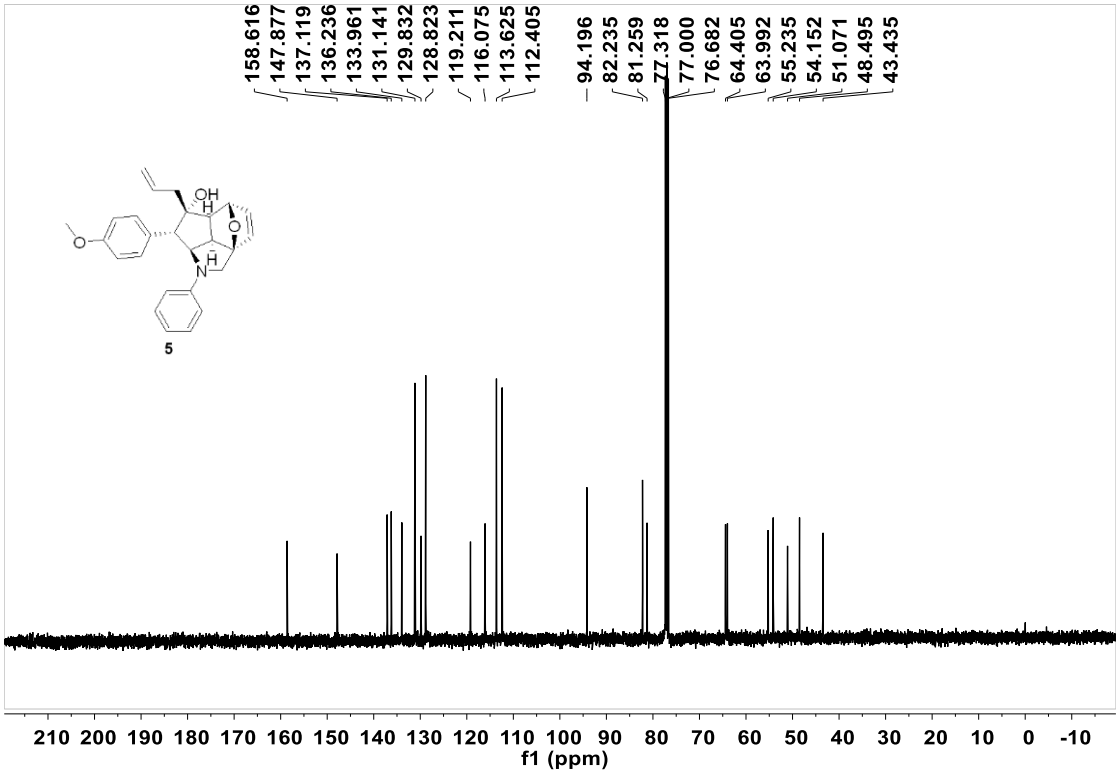

7.704
7.699
7.690
7.684
7.352
7.334
7.316
7.281
7.269
7.260
7.250
7.134
7.115
7.113
7.094
7.009
6.988
6.892
6.871
6.766
6.748
6.730
6.658
6.637
6.422
6.417
6.408
6.403
5.231
5.226
4.531
4.488
4.402
4.359
3.814
3.498
3.490
4bp
7.35 7.30 7.25 7.20
f1 (ppm)
1.00
2.15
3.39
2.11
1.93
2.13
1.07
2.06
1.07
0.95
1.09
1.09
3.09
1.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

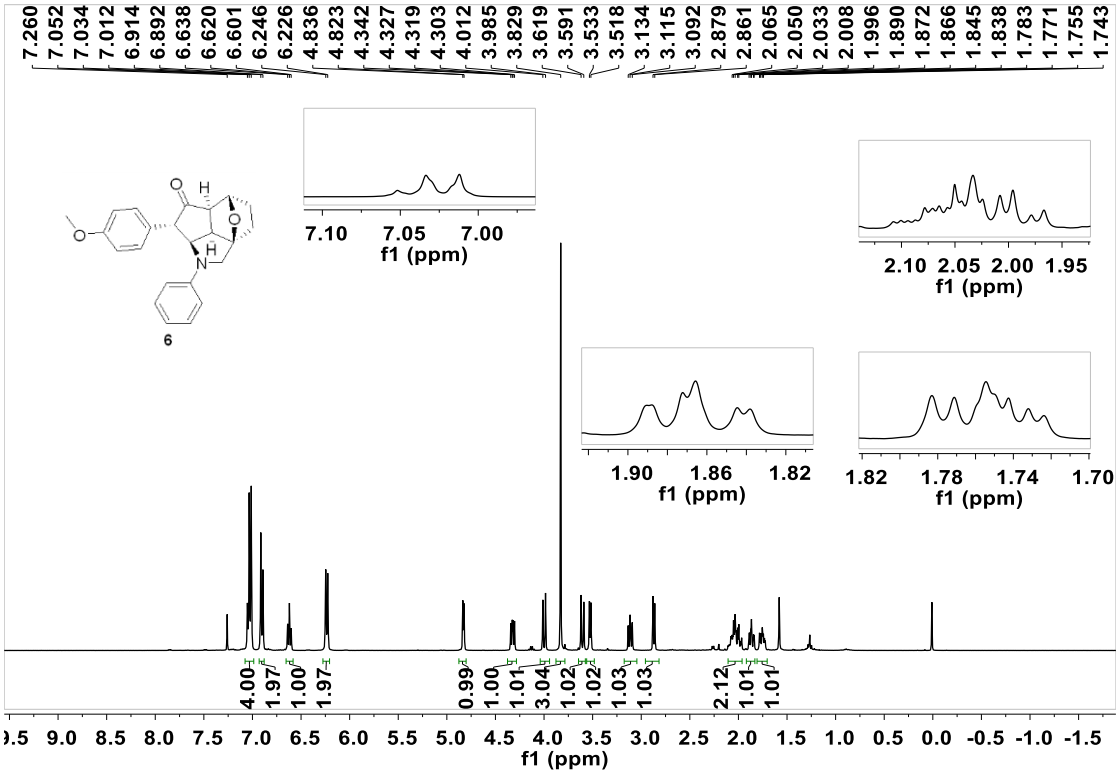

206.737
162.565
158.807
148.553
139.168
135.296
130.197
129.247
129.211
128.690
127.070
126.332
118.491
114.556
114.507
68.740
56.428
55.274
51.142
4bp
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

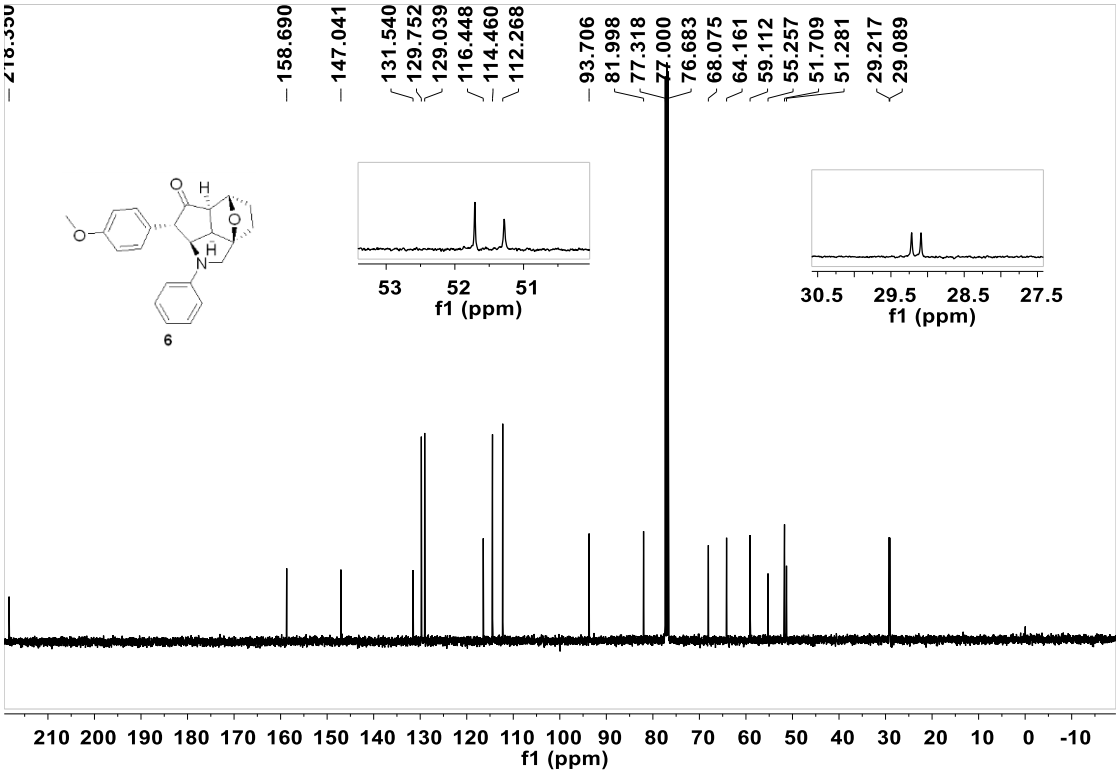

7.708
7.702
7.694
7.688
7.260
7.162
7.143
7.140
7.121
7.014
6.992
6.862
6.841
6.759
6.741
6.661
6.641
6.469
6.464
6.455
6.449
5.085
5.080
3.793
3.482
3.475
2.848
4bq
7.15
7.10
f1 (ppm)
6.49
6.47
6.45
6.43
f1 (ppm)
1.00
1.92
1.96
1.95
0.99
1.96
0.98
1.00
3.02
1.00
2.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

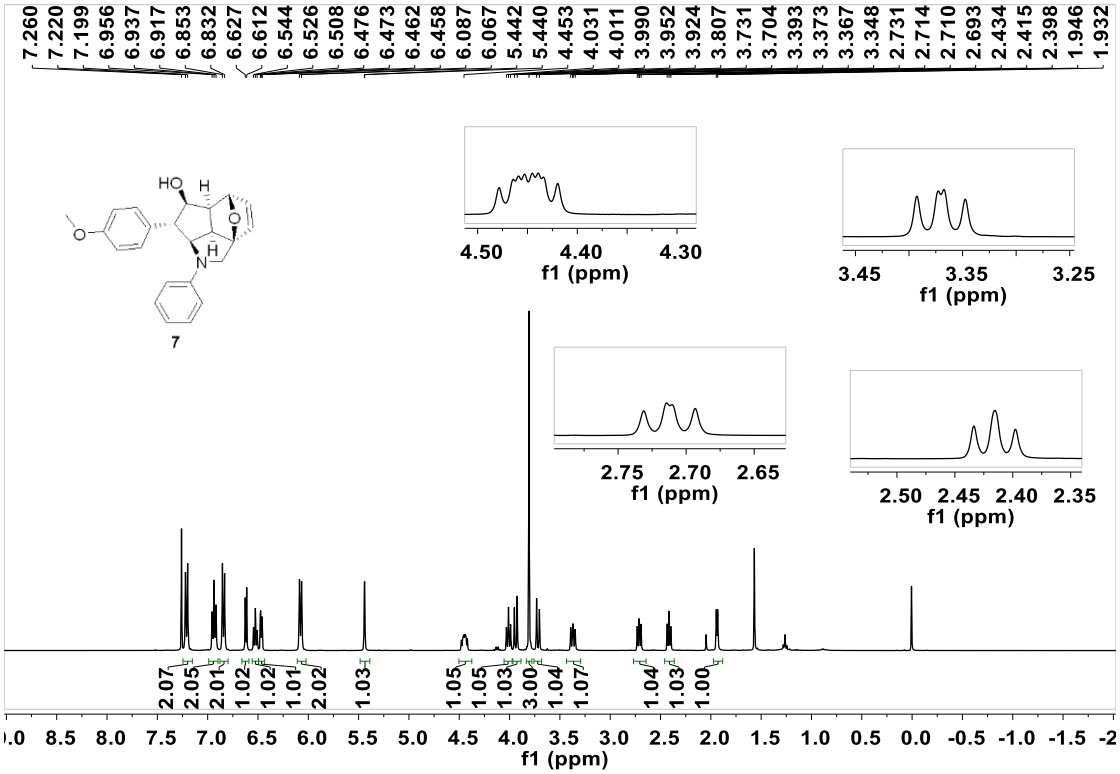

206.814
163.114
158.689
149.239
135.036
130.220
129.144
118.296
114.443
114.333
77.318
77.000
76.682
69.836
55.383
55.244
33.206
4bq
115.0 114.5 114.0
f1 (ppm)
55.6 55.4 55.2 55.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

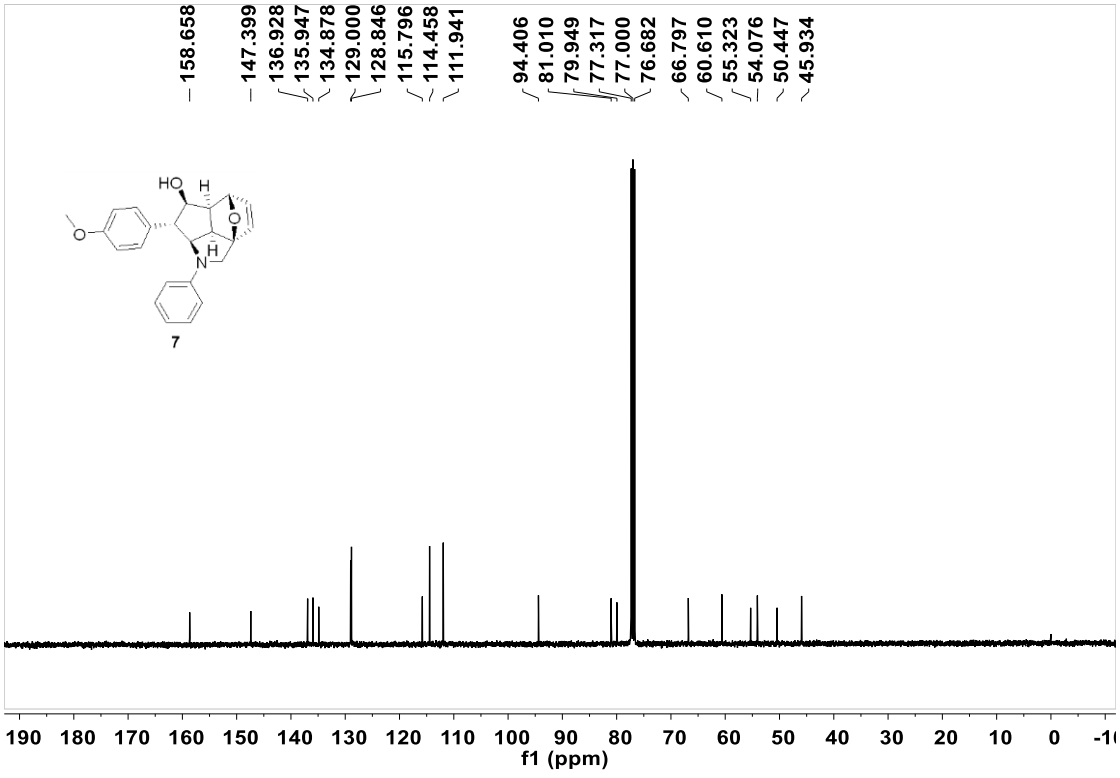

7.260 7.218 7.196 7.001 6.982 6.962 6.738 6.716 6.632 6.617 6.573 6.555 6.537 6.492 6.488 6.478 6.474 6.367 6.346 5.351 5.348 5.172 5.146 5.093 5.050 4.254 4.232 4.210 3.992 3.964 3.750 3.740 3.726 3.718 2.760 2.742 2.721 2.347 2.330 2.159 2.132 2.120 2.102
OH
H
O
N
H
O
5
5.95 5.85 5.75
f1 (ppm)
2.20 2.15 2.10 2.05
f1 (ppm)
1.97 2.06 1.94 1.01 1.05 0.99 2.01 1.05 1.00 1.06 1.04 0.99 0.98 4.90 1.00 1.04 3.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

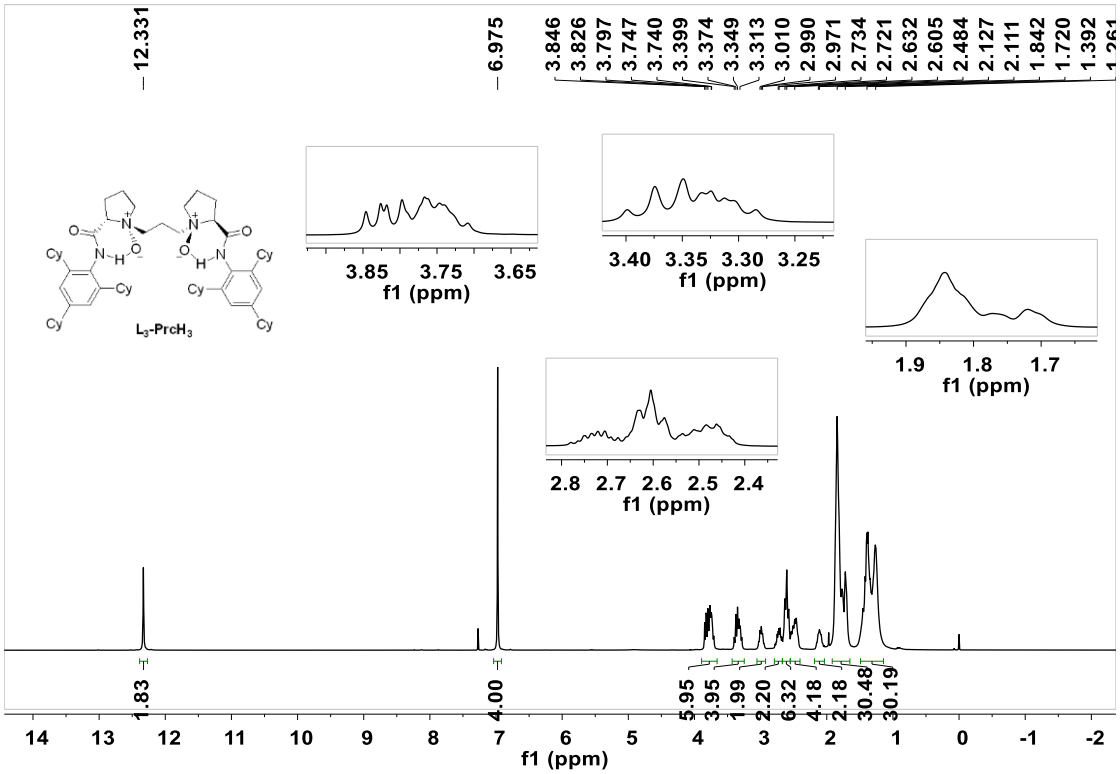

158.616 147.877 137.119 136.236 133.961 131.141 129.832 128.823 119.211 116.075 113.625 112.405
94.196 82.235 81.259 77.318 77.000 76.682 64.405 63.992 55.235 54.152 51.071 48.495 43.435
OH
H
O
N
H
O
5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.260 7.052 7.034 7.012 6.914 6.892 6.638 6.620 6.601 6.246 6.226 4.836 4.823 4.342 4.327 4.319 4.303 4.012 3.985 3.829 3.619 3.591 3.533 3.518 3.134 3.115 3.092 2.879 2.861 2.065 2.050 2.033 2.008 1.996 1.890 1.872 1.866 1.845 1.838 1.783 1.771 1.755 1.743
7.10 7.05 7.00
f1 (ppm)
2.10 2.05 2.00 1.95
f1 (ppm)
1.90 1.86 1.82
f1 (ppm)
1.82 1.78 1.74 1.70
f1 (ppm)
6
4.00 1.97 1.00 1.97 0.99 1.00 1.01 3.04 1.02 1.02 1.03 1.03 2.12 1.01 1.01
f1 (ppm)


158.690 147.041 131.540 129.752 129.039 116.448 114.460 112.268 93.706 81.998 77.318 77.000 76.683 68.075 64.161 59.112 55.257 51.709 51.281 29.217 29.089
53 52 51
f1 (ppm)
30.5 29.5 28.5 27.5
f1 (ppm)
6
f1 (ppm)


7.260 7.220 7.199 6.956 6.937 6.917 6.853 6.832 6.627 6.612 6.544 6.526 6.508 6.476 6.473 6.462 6.458 6.087 6.067 5.442 5.440 4.453 4.031 4.011 3.990 3.952 3.924 3.807 3.731 3.704 3.393 3.373 3.367 3.348 2.731 2.714 2.710 2.693 2.434 2.415 2.398 1.946 1.932
HO
H
O
N
H
O
7
4.50 4.40 4.30
f1 (ppm)
3.45 3.35 3.25
f1 (ppm)
2.75 2.70 2.65
f1 (ppm)
2.50 2.45 2.40 2.35
f1 (ppm)
2.07 2.05 2.01 1.02 1.02 1.01 2.02 1.03 1.05 1.05 1.03 3.00 1.04 1.07 1.04 1.03 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


158.658 147.399 136.928 135.947 134.878 129.000 128.846 115.796 114.458 111.941 94.406 81.010 79.949 77.317 77.000 76.682 66.797 60.610 55.323 54.076 50.447 45.934
HO
H
O
N
H
O
7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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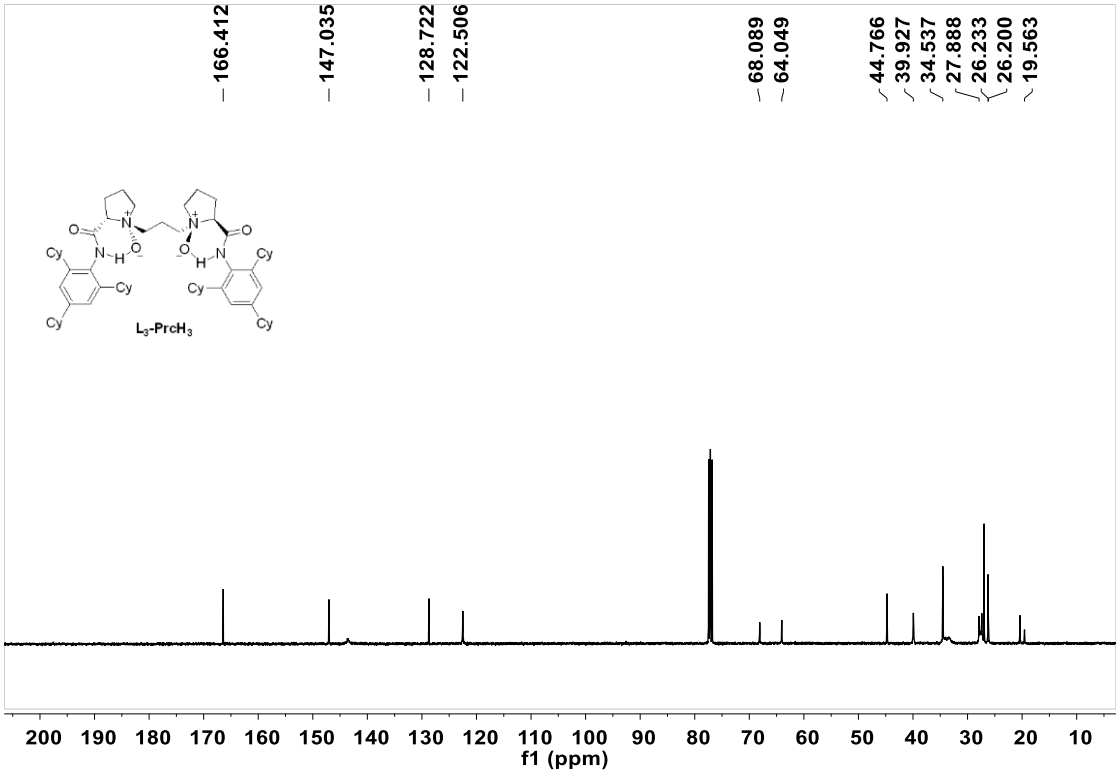
6.975
3.846
3.826
3.797
3.747
3.740
3.399
3.374
3.349
3.313
3.010
2.990
2.971
2.734
2.721
2.632
2.605
2.484
2.127
2.111
1.842
1.720
1.392
L3-PrcH3
3.85 3.75 3.65
f1 (ppm)
3.40 3.35 3.30 3.25
f1 (ppm)
1.9 1.8 1.7
f1 (ppm)
2.8 2.7 2.6 2.5 2.4
f1 (ppm)
1.83
4.00
5.95
3.95
1.99
2.20
6.32
4.18
2.18
30.48
30.19
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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27.888
26.233
26.200
19.563
L3-PrcH3
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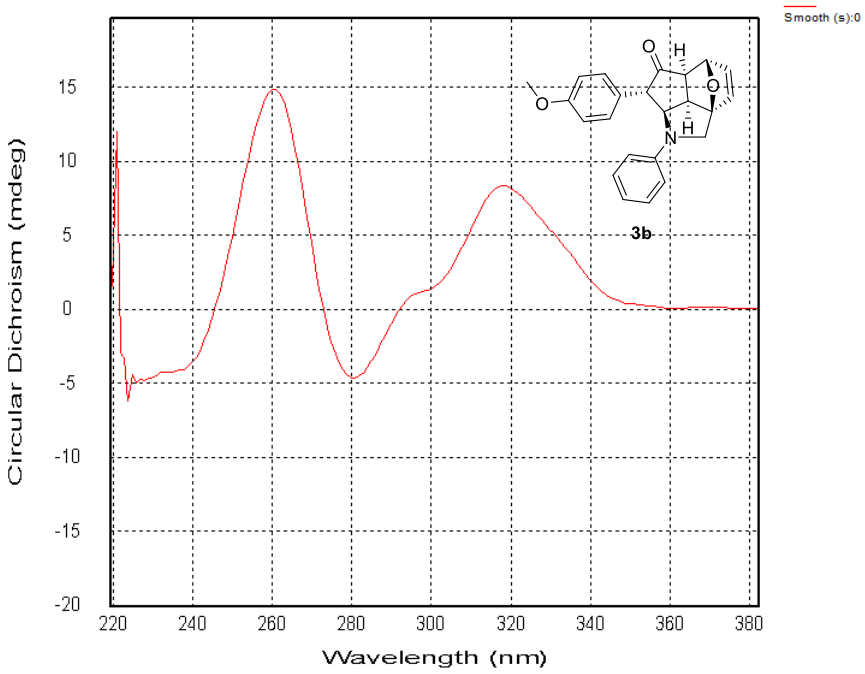
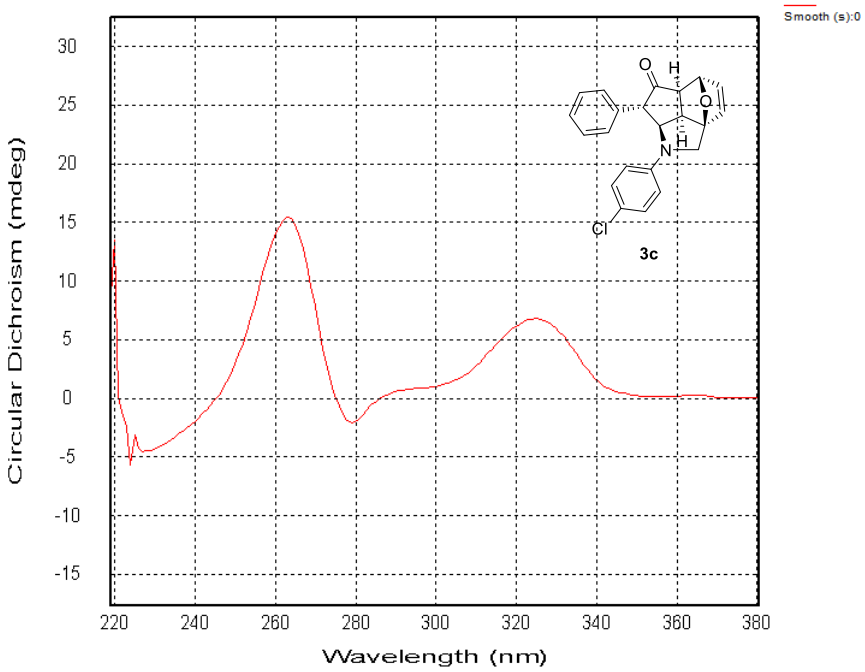
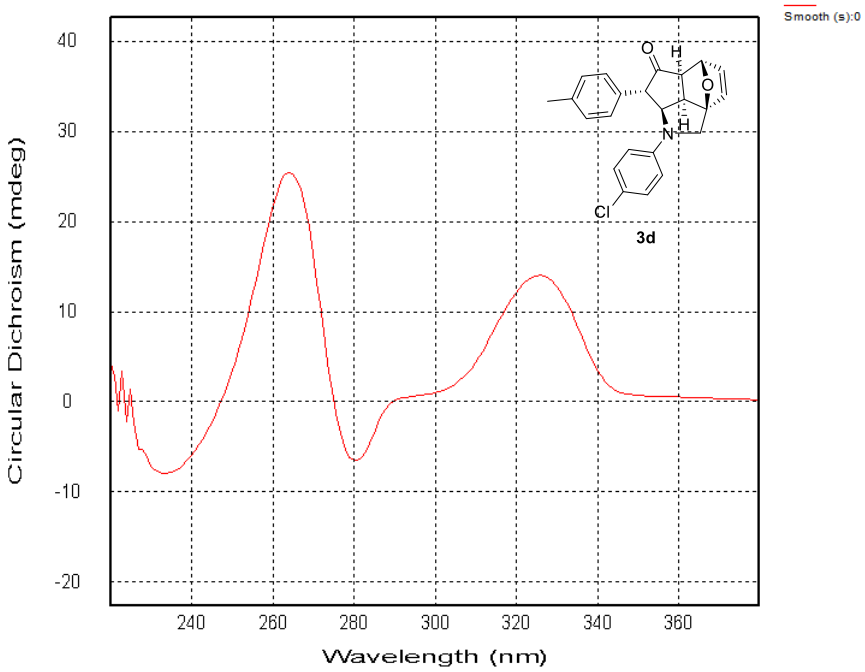
f1 (ppm)

12. Copies of CD spectra



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Wavelength (nm)
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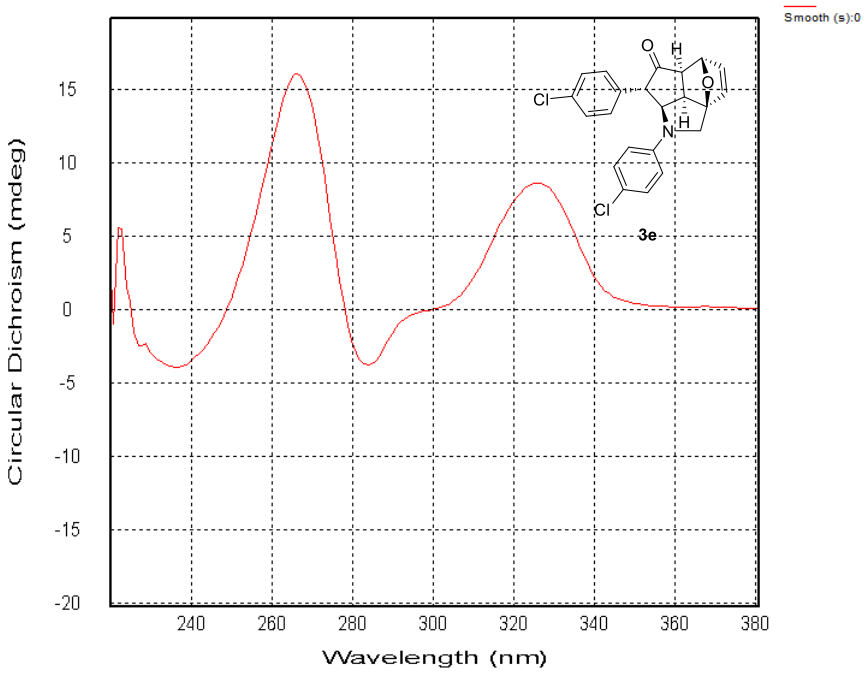
H
O
N
H
Cl
3d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Wavelength (nm)
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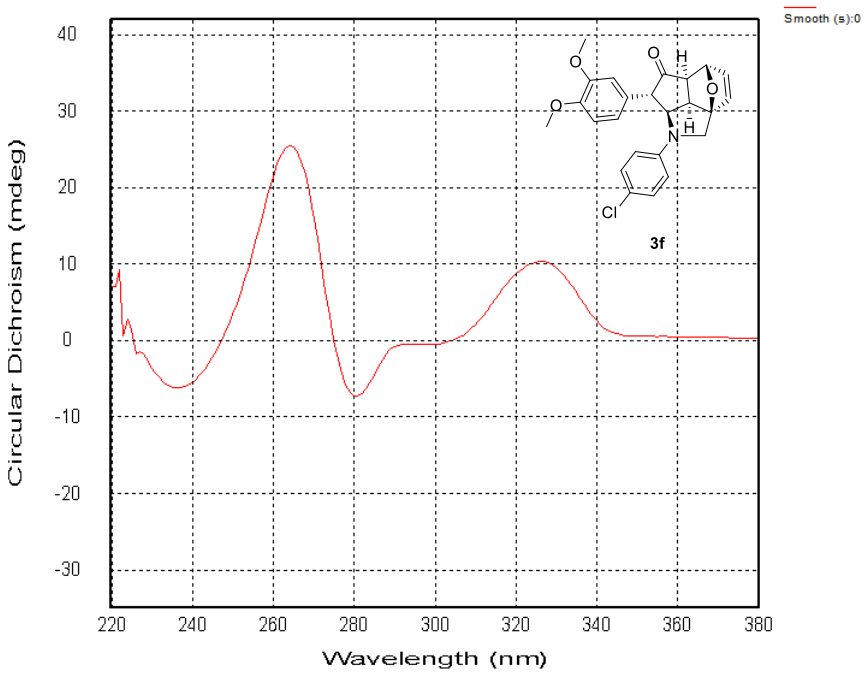
Cl
O
N
H
Cl
3e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Wavelength (nm)
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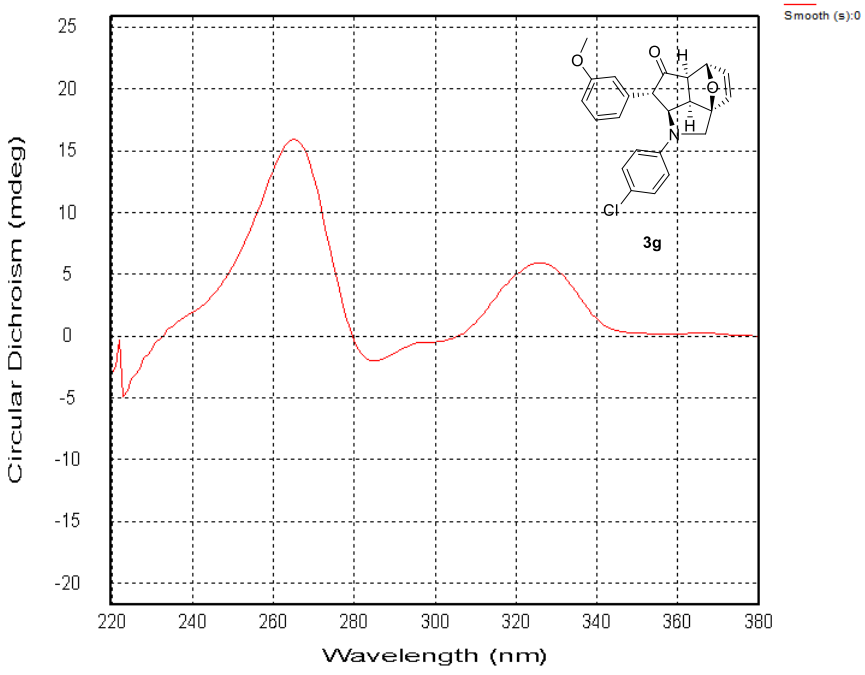
H
O
N
H
Cl
3f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360
380
Wavelength (nm)
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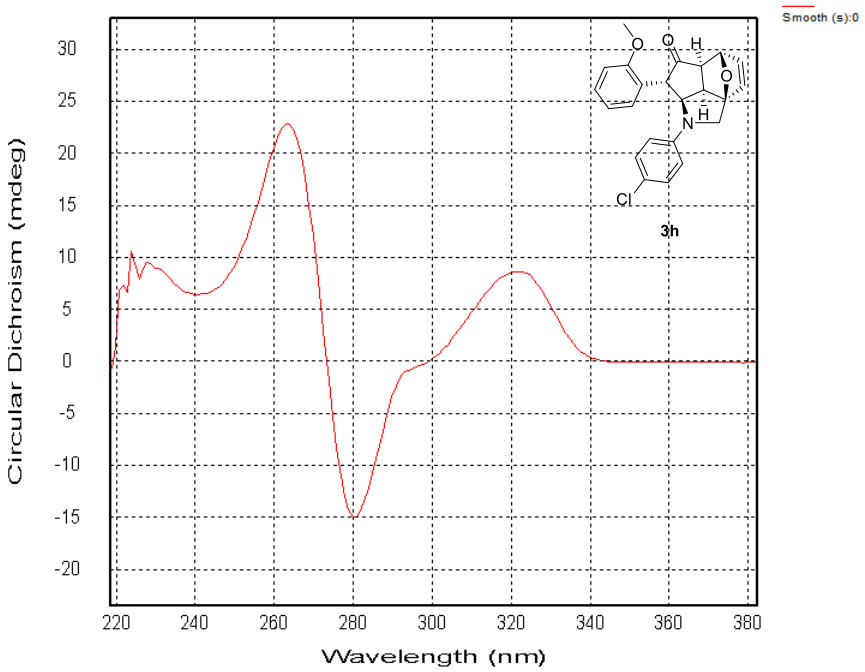
H
O
N
H
Cl
3g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-15
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300
320
340
360
380
Wavelength (nm)
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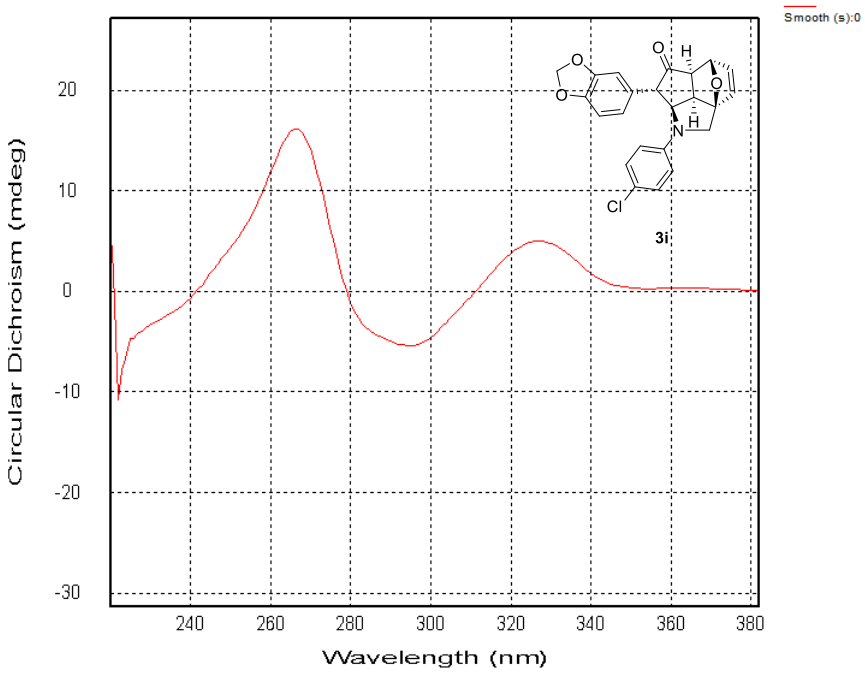
O
H
O
N
H
Cl
3h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Wavelength (nm)
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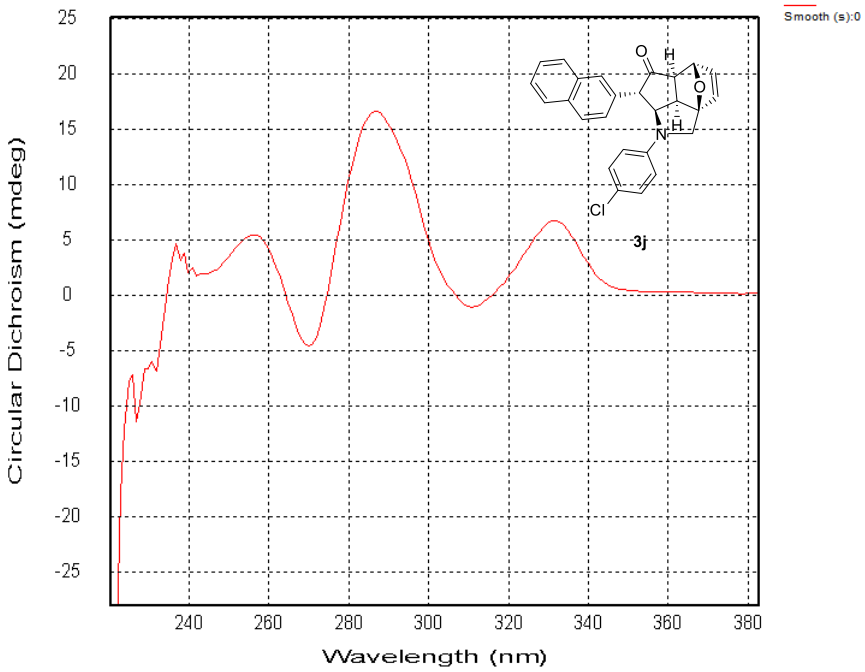
O
O
H
O
N
H
Cl
3i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-10
-15
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300
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340
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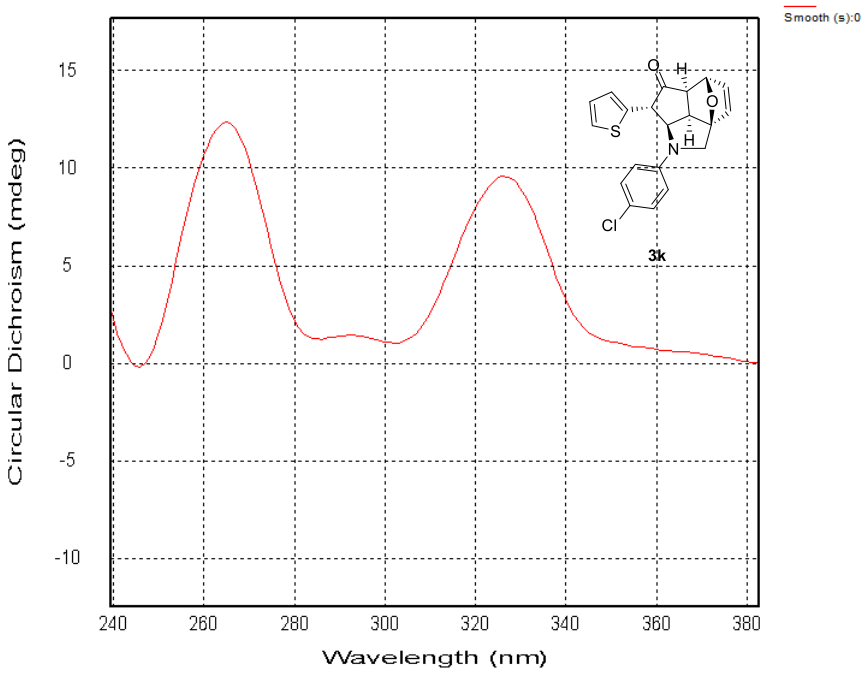
380
Wavelength (nm)
O
H
O
N
H
Cl
3j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O
S
N
H
Cl
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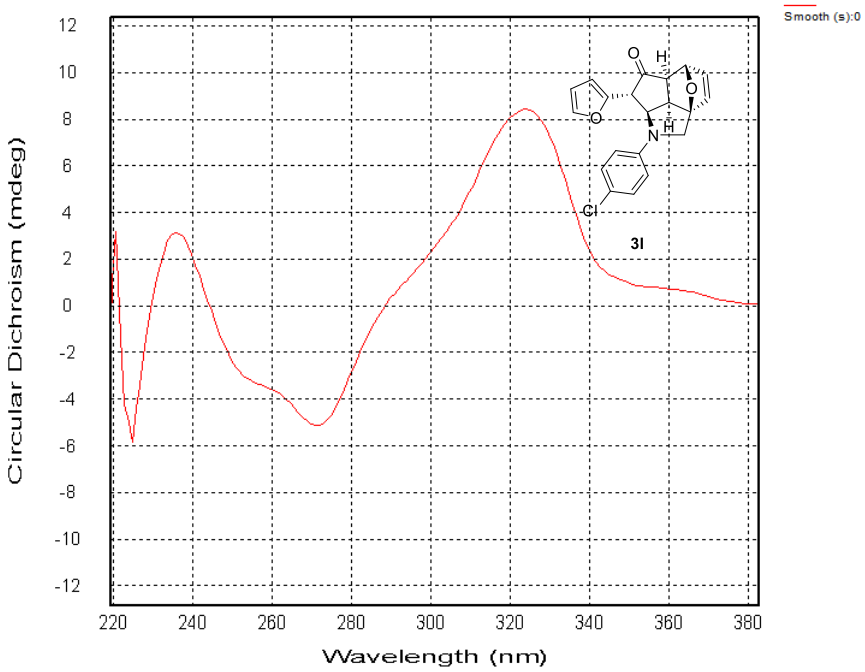
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6
4
2
0
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-4
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-10
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240
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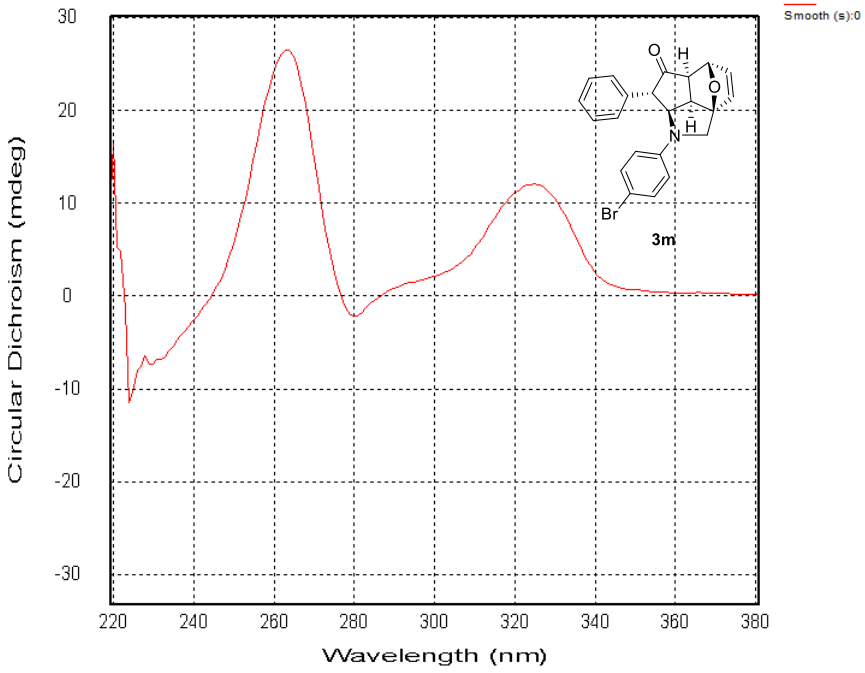
300
320
340
360
380
Wavelength (nm)
O
H
O
O
N
H
Cl
3l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300
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Wavelength (nm)
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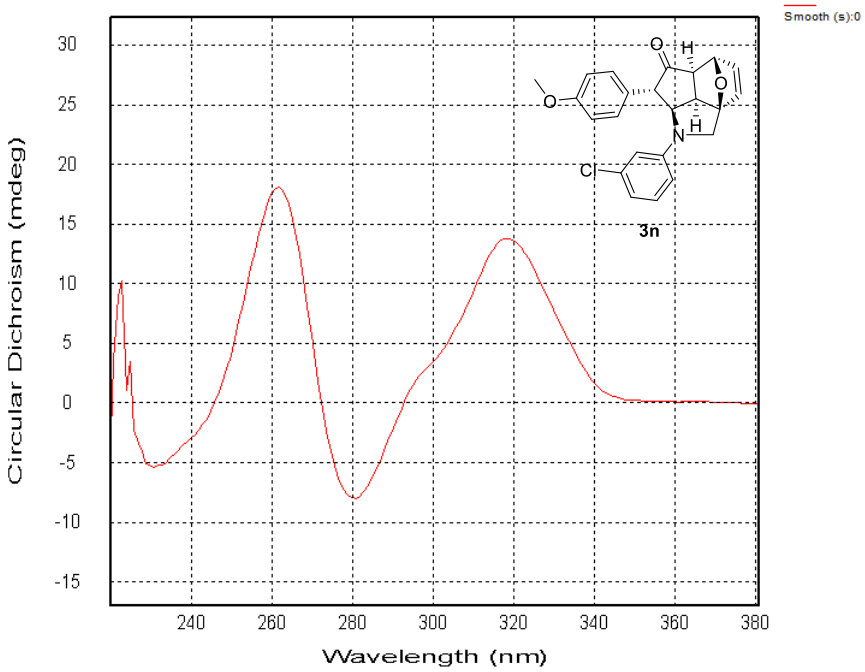
H
O
N
H
Br
3m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300
320
340
360
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Wavelength (nm)
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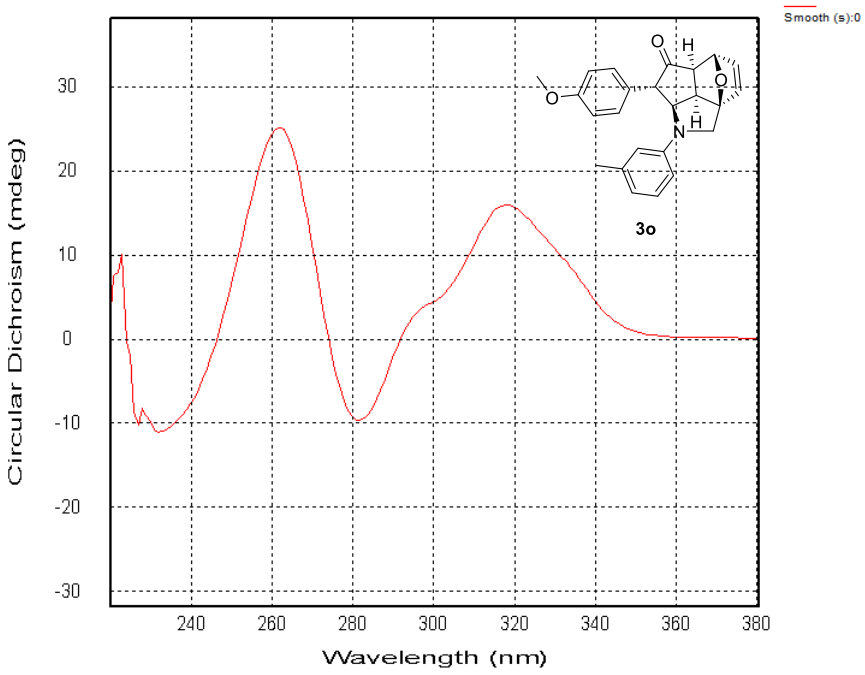
H
O
O
H
N
Cl
3n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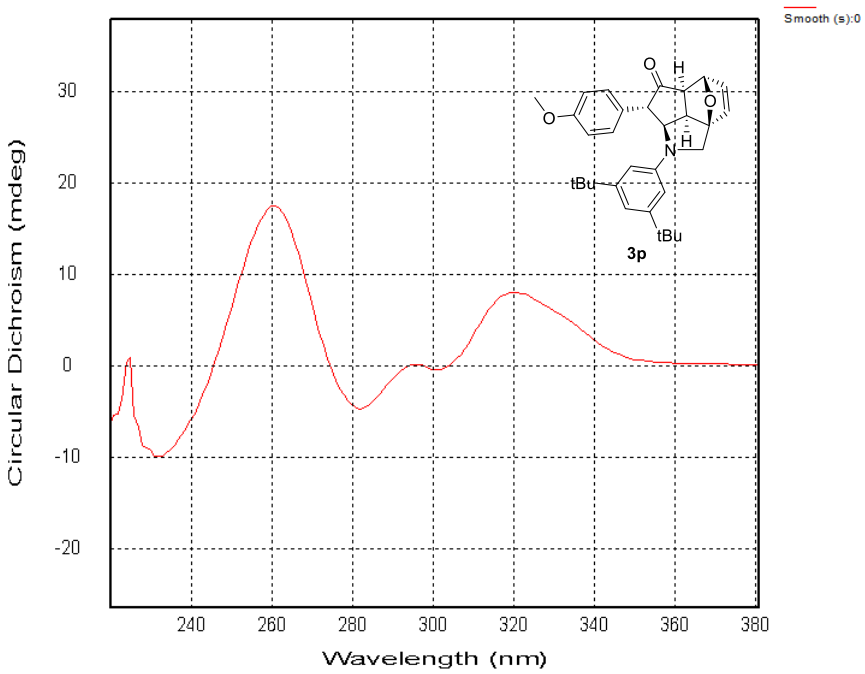
Wavelength (nm)
O
H
O
O
H
N
3o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-20
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O
O
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tBu
tBu
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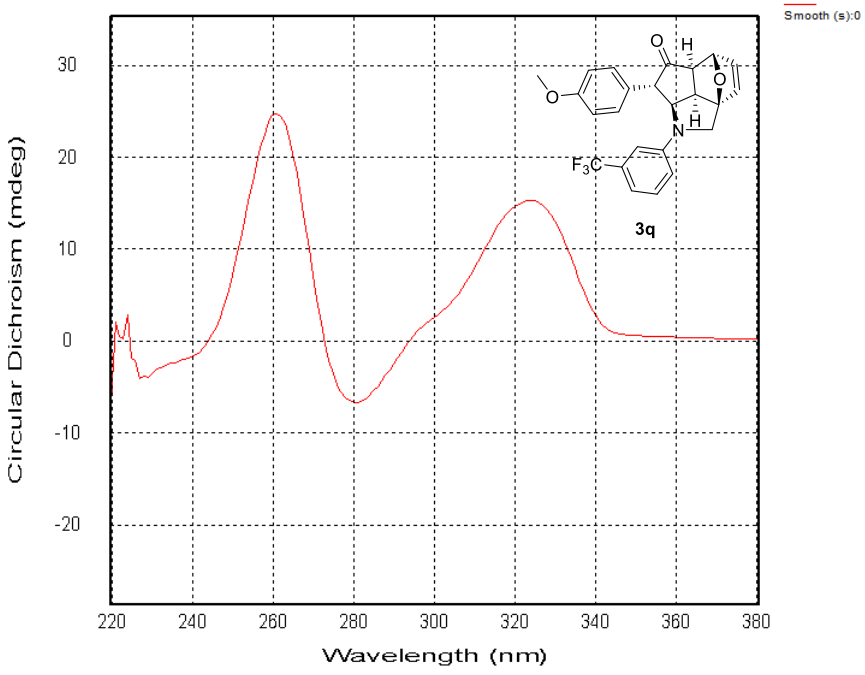
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380
Wavelength (nm)
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H
O
O
N
H
F3C
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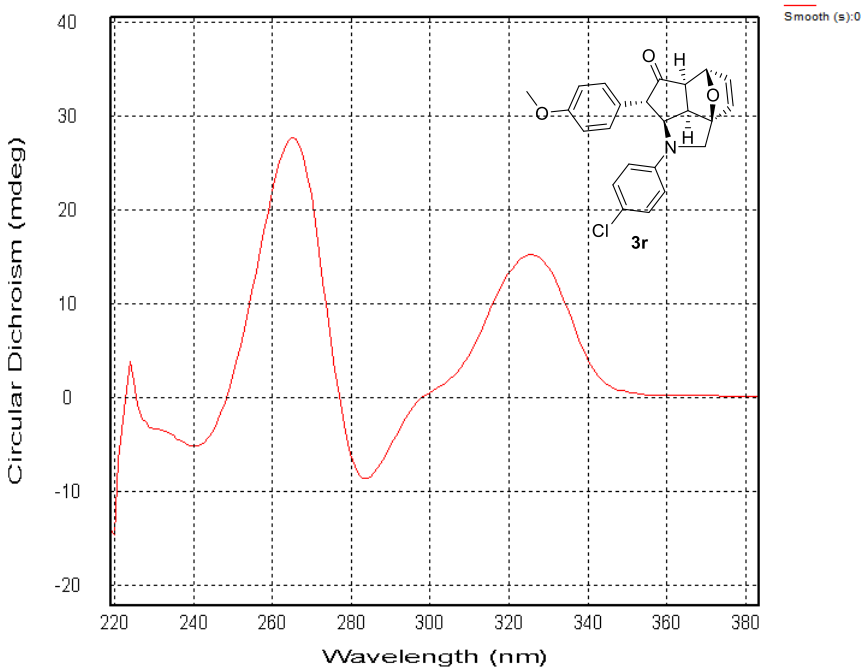
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H
O
O
H
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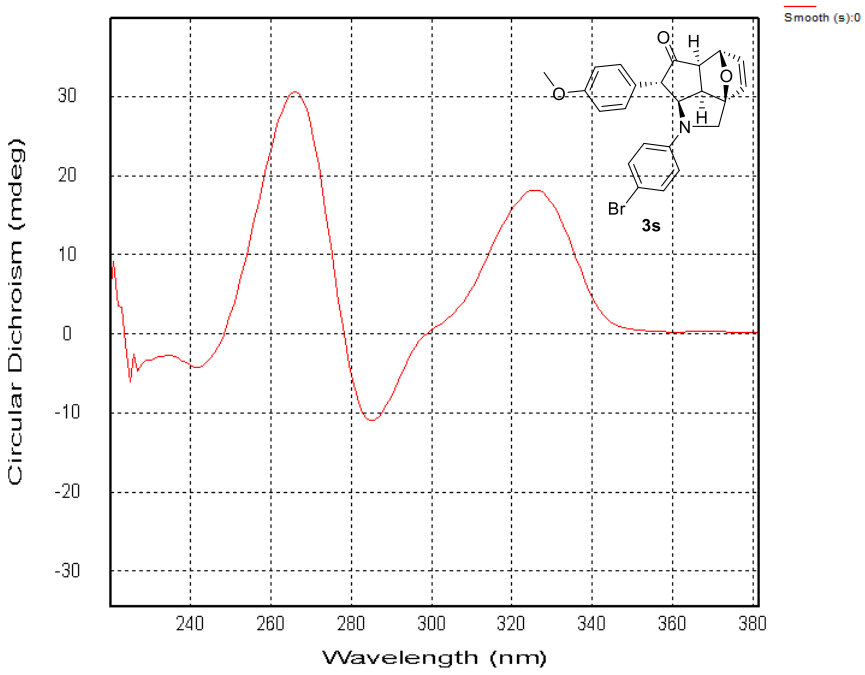
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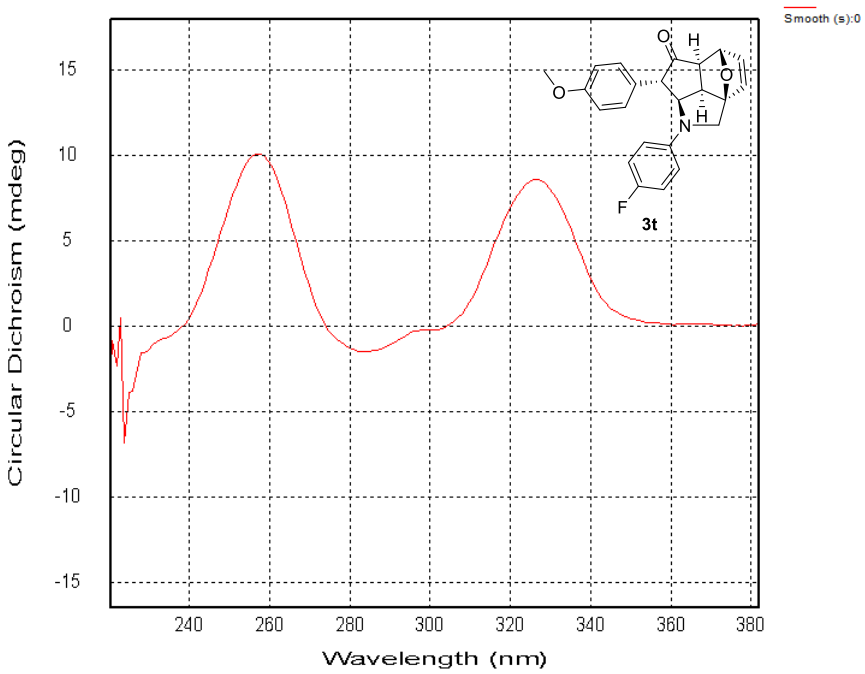
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360
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Wavelength (nm)
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H
O
O
N
H
F
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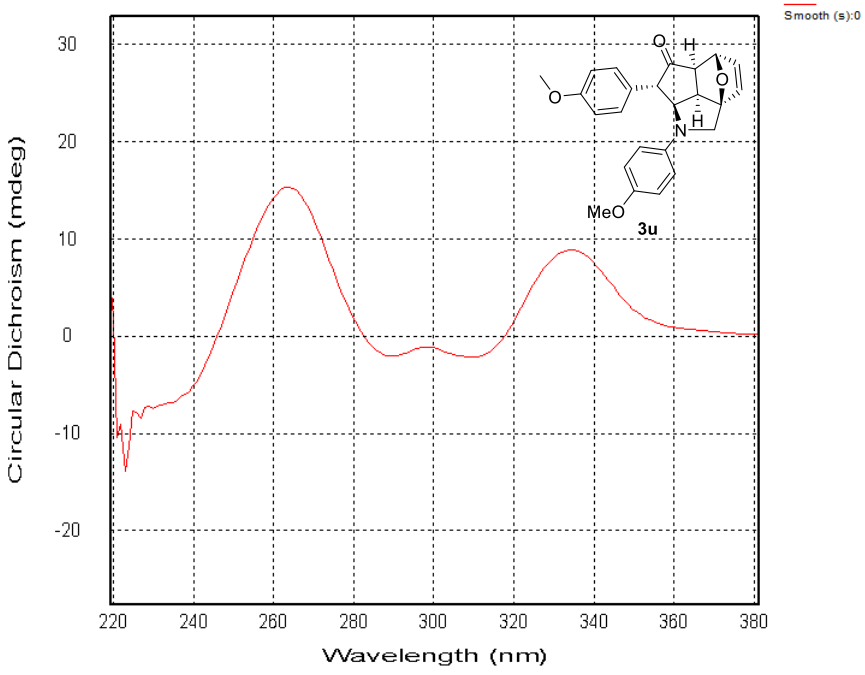
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H
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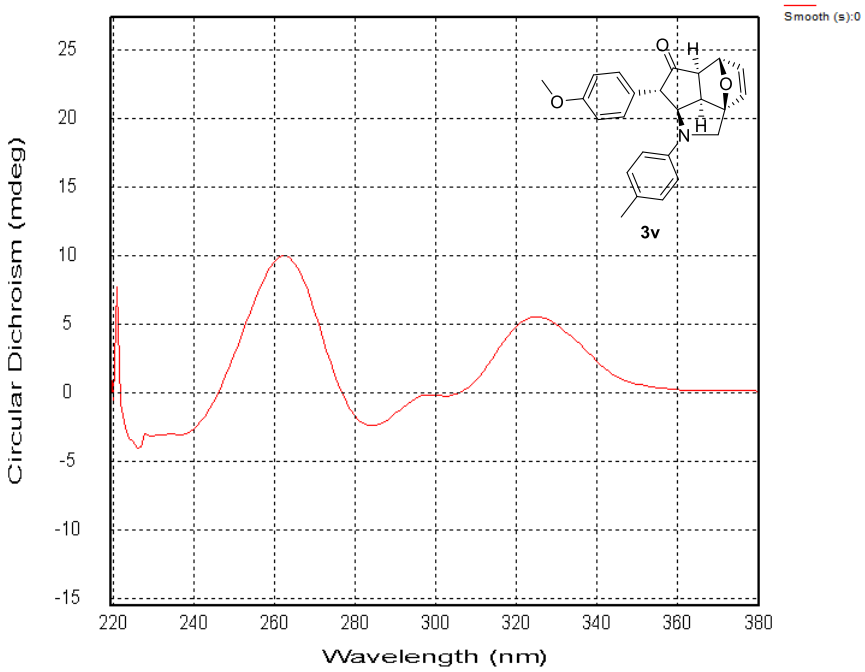
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Wavelength (nm)
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O
O
H
N
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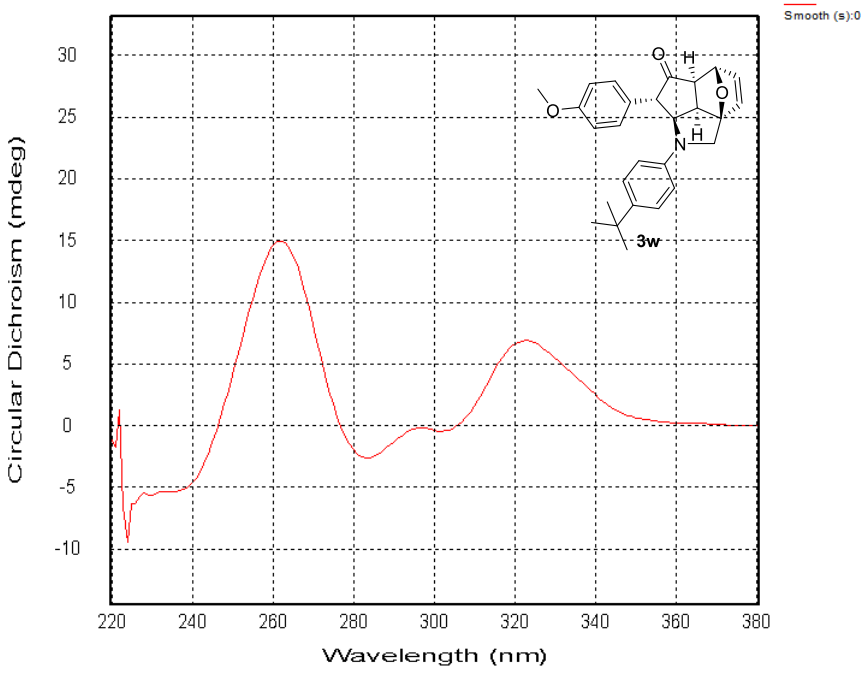
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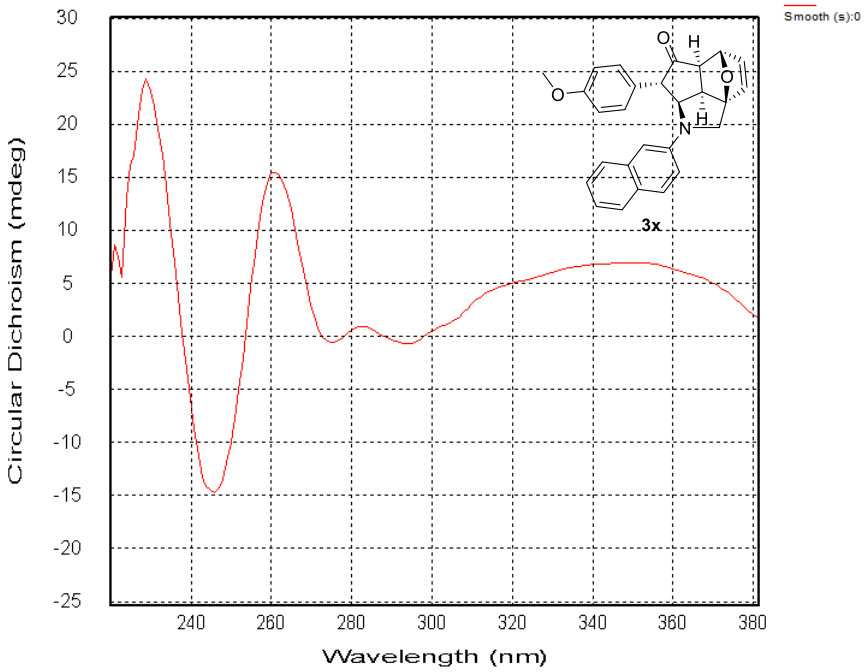
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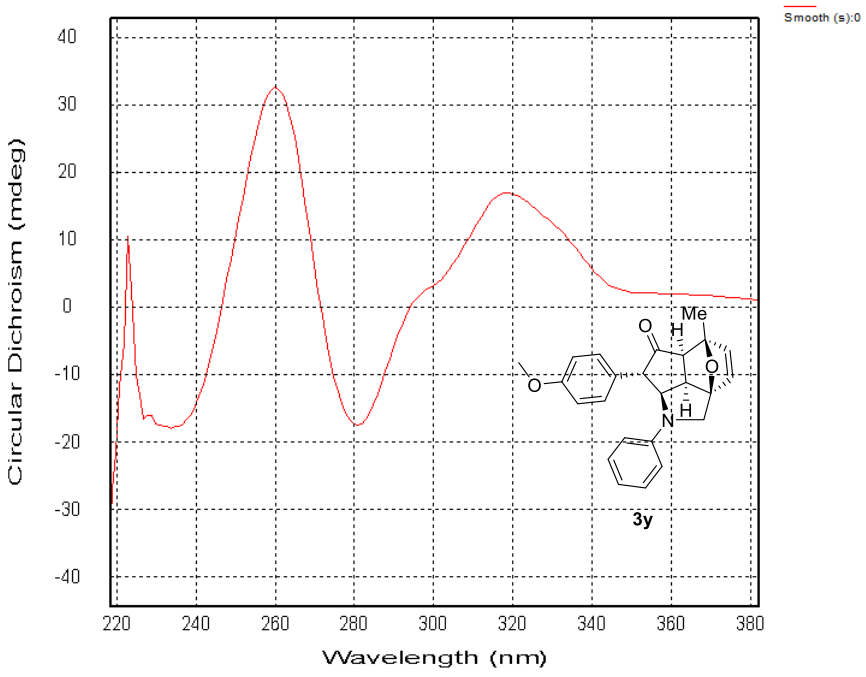
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300
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340
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380
Wavelength (nm)
Me
O
H
O
O
H
N
3y

13. References

[1] B. Martin-Matute, C. Nevado, D. J. Cardenas and A. M. Echavarren, *J. Am. Chem. Soc*., 2003, **125**, 5757.
[2] S. Gouse, N. R. Reddy and S. Baskaran, *Org. Lett.,* 2019, **21**, 3822.
[3] R. Savka and H. Plenio, *Eur. J. Inorg. Chem.* 2014, 6246.
[4] (a) X. H. Liu, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2011, **44**, 574; (b) X. H. Liu, L. L. Lin and X. M. Feng, *Org. Chem. Front.*, 2014, **1**, 298.