Highly Regio-, Diastereo- and Enantioselective Deracemization of Axially Chiral 3-Alkylideneoxindoles

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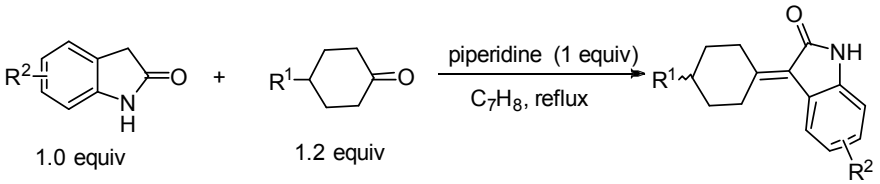
Supporting Information

CONTENTS:

(A) General remarks

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.262). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.16). Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiralcel IA, IC, or IE at 23 ^{o}C with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in CH_2Cl_2). HRMS were recorded on a commercial apparatus (ESI source). All the reactions were carried out under an atmosphere of nitrogen in over-dried apparatus. All the solvents were purified by usual methods before use. Molecular sieves were activated at 500 ^{o}C for 5h before use. The 3-(4-alkylcyclohexylidene)indolin-2-ones and substituted 3-(4-methylcyclohexylidene) indolin-2-ones were used after recrystallization with ethyl acetate and petroleum ether.

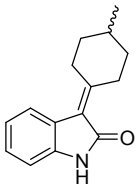
(B) General procedure for the preparation of substituted racemic 3-cyclohexylideneoxindoles



2-Oxindoles (1.0 equiv) and 4-substituted-cyclohexan-1-ones (1.2 equive) were dissolved in toluene containing piperidine (1.0 equive) in a flask. By refluxing vigorously, the water formed in the reaction was removed by a Dean and Stark trap placed under the reflux condenser. Evaporation of the toluene left a residue. The crude product was purified by flash column chromatography (ethyl acetate/dichloromethane/petroleum ether = 1:1:8) to afford a yellow solid. Recrystallization from ethanol afforded the pure compound before used.

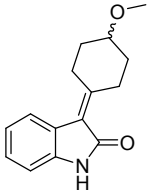
The characterization of new substituted racemic 3-cyclohexylideneoxindoles is listed

as following:



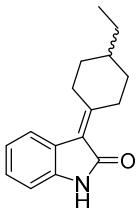
3-(4-Methylcyclohexylidene)indolin-2-one (2a)

Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (br, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.17 (td, *J* = 7.6, 0.8 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.90 – 6.80 (m, 1H), 4.51 (d, *J* = 14.0 Hz, 1H), 3.39 (dd, *J* = 14.4, 1.6 Hz, 1H), 2.39 (td, *J* = 13.6, 4.8 Hz, 1H), 2.24 (td, *J* = 13.6, 4.8 Hz, 1H), 2.08 – 1.91 (m, 2H), 1.88 – 1.70 (m, 1H), 1.38 – 1.16 (m, 2H), 0.96 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 127.7, 124.4, 123.9, 121.7, 109.5, 36.1, 35.8, 32.5), 31.9 29.4, 21.7. HRMS (ESI-TOF) calcd for $C_{15}H_{17}NONa$ ([M+Na^+]) = 250.1202, Found 250.1202.



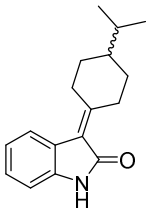
3-(4-Methoxycyclohexylidene)indolin-2-one (2b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.66 – 3.51 (m, 2H), 3.41 (s, 3H), 3.29 – 3.22 (m, 1H), 3.15 – 3.02 (m, 1H), 2.83 – 2.73 (m, 1H), 2.10 – 1.94 (m, 2H), 1.92 – 1.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 162.1, 139.7, 127.9, 124.1, 123.9, 121.7, 121.0, 109.6, 75.9, 56.0, 31.3, 31.2, 28.9, 25.5. HRMS (ESI-TOF) calcd for $C_{15}H_{17}NO_2Na$ ([M+Na^+]) = 266.1151, Found 266.1154.



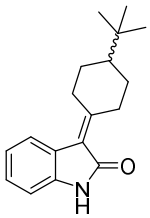
3-(4-Ethylcyclohexylidene)indolin-2-one (2c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (br, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.98 (td, *J* = 7.6, 1.2 Hz, 1H), 6.90 – 6.80 (m, 1H), 4.59 – 4.38 (m, 1H), 3.49 – 3.28 (m, 1H), 2.39 (td, *J* = 13.2, 4.8 Hz, 1H), 2.32 – 2.16 (m, 1H), 2.16 – 1.94 (m, 2H), 1.64 – 1.50 (m, 1H), 1.41 – 1.08 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 127.7, 124.4, 123.9, 121.6, 109.6, 38.4, 33.7, 33.4, 32.4, 29.3, 29.1, 11.8. HRMS (ESI-TOF) calcd for $C_{16}H_{19}NONa$ ([M+Na^+]) = 264.1359, Found 264.1365.



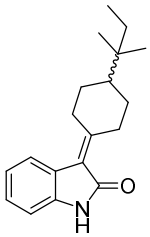
3-(4-Isopropylcyclohexylidene)indolin-2-one (2d)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.55 – 4.46 (m, 1H), 3.47 – 3.37 (m, 1H), 2.37 (td, *J* = 13.2, 4.8 Hz, 1H), 2.27 – 2.17 (m, 1H), 2.07 – 1.95 (m, 2H), 1.54 – 1.40 (m, 2H), 1.39 – 1.24 (m, 2H), 0.90 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 127.7, 123.9, 121.7, 109.4, 43.1, 32.7, 32.5, 30.9, 30.5, 29.5, 20.1. HRMS (ESI-TOF) calcd for $C_{17}H_{21}NO$ Na ([M+Na$^+$]) = 278.1515, Found 278.1523.



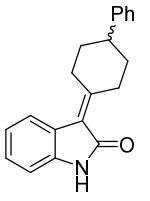
3-(4-(Tert-butyl)cyclohexylidene)indolin-2-one (2e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (br, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.17 (td, *J* = 7.6, 0.8 Hz, 1H), 6.99 (td, *J* = 7.6, 0.8 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.57 – 4.42 (m, 1H), 3.48 – 3.40 (m, 1H), 2.45 – 2.31 (m, 1H), 2.30 – 2.19 (m, 1H), 2.12 – 1.96 (m, 2H), 1.47 – 1.26 (m, 3H), 0.86 – 0.80 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 164.6, 139.4, 127.6, 124.4, 123.9, 121.7, 109.4, 47.1, 33.1, 32.8, 29.7, 28.5, 28.1, 27.6. HRMS (ESI-TOF) calcd for $C_{18}H_{24}NO^+$ ([M+H$^+$]) = 270.1852, Found 270.1856.



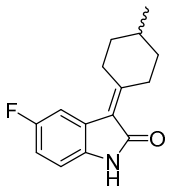
3-(4-(Tert-pentyl)cyclohexylidene)indolin-2-one (2f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.17 (td, *J* = 7.7, 0.8 Hz, 1H), 6.99 (td, *J* = 7.7, 1.1 Hz, 1H), 6.87 – 6.80 (m, 1H), 4.52 – 4.41 (m, 1H), 3.48 – 3.39 (m, 1H), 2.42 – 2.32 (m, 1H), 2.26 (ddd, *J* = 14.4, 12.2, 4.8 Hz, 1H), 1.99 (dddd, *J* = 16.8, 11.3, 7.6, 3.6 Hz, 2H), 1.56 – 1.46 (m, 1H), 1.45 – 1.22 (m, 4H), 0.87 – 0.80 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 164.7, 139.4, 127.6, 124.4, 123.9, 121.7, 120.0, 109.4, 44.4, 35.1, 33.2, 32.8, 29.7, 28.0, 27.7, 24.3, 24.2, 8.3. HRMS (ESI-TOF) calcd for $C_{19}H_{25}NONa$ ([M+Na$^+$]) = 306.1828, Found 306.1832.



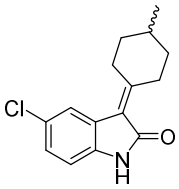
3-(4-Phenylcyclohexylidene)indolin-2-one (2g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.26 – 7.14 (m, 4H), 7.01 (td, *J* = 7.6, 1.2 Hz, 1H), 6.92 – 6.76 (m, 1H), 4.85 – 4.71 (m, 1H), 3.64 – 3.50 (m, 1H), 2.95 (tt, *J* = 12.0, 3.6 Hz, 1H), 2.53 (td, *J* = 13.6, 4.8 Hz, 1H), 2.38 – 2.08 (m, 3H), 1.91 – 1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 162.5, 146.0, 139.5, 128.7, 127.9, 127.0, 126.4, 124.3, 124.0, 121.8, 120.7, 109.5, 43.7, 35.1, 34.9, 32.9, 29.8. HRMS (ESI-TOF) calcd for $C_{20}H_{19}NONa$ ([M+Na^+]) = 312.1359, Found 312.1366.



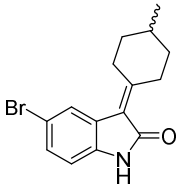
5-Fluoro-3-(4-methylcyclohexylidene)indolin-2-one (2h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.26 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.81 (td, *J* = 8.8, 2.0 Hz, 1H), 6.70 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.42 (dd, *J* = 14.0, 1.2 Hz, 1H), 3.29 – 3.09 (m, 1H), 2.32 (td, *J* = 13.2, 4.8 Hz, 1H), 2.18 (td, *J* = 13.2, 4.8 Hz, 1H), 2.01 – 1.85 (m, 2H), 1.77 – 1.68 (m, 1H), 1.29 – 1.10 (m, 2H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 166.0, 135.6, 125.3, 125.2, 120.4, 114.0, 113.7, 111.6, 111.4, 109.8, 109.7, 36.1, 35.7, 32.4, 31.8, 29.5, 21.7. HRMS (ESI-TOF) calcd for $C_{15}H_{16}FNONa$ ([M+Na^+]) = 268.1108, Found 268.1111.



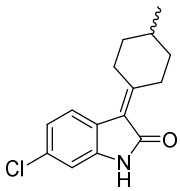
5-Chloro-3-(4-methylcyclohexylidene)indolin-2-one (2i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 14.4 Hz, 1H), 3.29 (d, *J* = 14.0 Hz, 1H), 2.40 (td, *J* = 13.2, 4.8 Hz, 1H), 2.25 (td, *J* = 13.2, 4.8 Hz, 1H), 2.10 – 1.93 (m, 2H), 1.86 – 1.74 (m, 1H), 1.37 – 1.17 (m, 3H), 0.97 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 138.0, 127.4, 126.9, 125.7, 124.0, 119.9, 110.4, 36.0, 35.7, 32.6, 31.8, 29.5, 21.7. HRMS (ESI-TOF) calcd for $C_{15}H_{16}{}^{34.9689}ClNONa$ ([M+Na^+]) = 284.0813, Found 284.0820. HRMS (ESI-TOF) calcd for $C_{15}H_{16}{}^{36.9659}ClNONa$ ([M+Na^+]) = 286.0783, Found 286.0780.



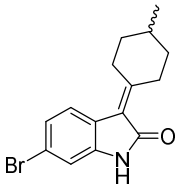
5-Bromo-3-(4-methylcyclohexylidene)indolin-2-one (2j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.68 (s, 1H), 7.26 – 7.22 (m, 1H), 6.71 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.44 (d, *J* = 14.0 Hz, 1H), 3.25 (d, *J* = 14.0 Hz, 1H), 2.37 (td, *J* = 13.6, 4.4 Hz, 1H), 2.22 (td, *J* = 13.6, 4.4 Hz, 1H), 2.07 – 1.88 (m, 2H), 1.80 – 1.73 (m, 1H), 1.34 – 1.14 (m, 2H), 0.94 (dd, *J* = 6.4, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 166.5, 138.4, 130.2, 126.8, 126.2, 119.7, 114.3), 110.9, 36.0, 35.7, 32.6, 31.7, 29.5, 21.7. HRMS (ESI-TOF) calcd for $C_{15}H_{16}{}^{78.9183}BrNONa$ ([M+Na^+]) = 328.0307, Found 328.0310. HRMS (ESI-TOF) calcd for $C_{15}H_{16}{}^{80.9163}BrNONa$ ([M+Na^+]) = 330.0287, Found 330.0287.



6-Chloro-3-(4-methylcyclohexylidene)indolin-2-one (2k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 4.45 (d, *J* = 14.4 Hz, 1H), 3.30 (d, *J* = 14.0 Hz, 1H), 2.39 (td, *J* = 13.2, 4.4 Hz, 1H), 2.23 (td, *J* = 13.2, 4.4 Hz, 1H), 2.00 (td, *J* = 13.6, 3.2 Hz, 2H), 1.87 – 1.71 (m, 1H), 1.36 – 1.15 (m, 2H), 0.96 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 165.1, 140.4, 133.1, 124.7, 121.6, 109.9, 36.0, 35.7, 32.6, 31.8, 29.5, 21.7. HRMS (ESI-TOF) calcd for $C_{15}H_{16}{}^{34.9689}ClNONa$ ([M+Na^+]) = 284.0813, Found 284.0807. HRMS (ESI-TOF) calcd for $C_{15}H_{16}{}^{36.9659}ClNONa$ ([M+Na^+]) = 286.0783, Found 286.0784.

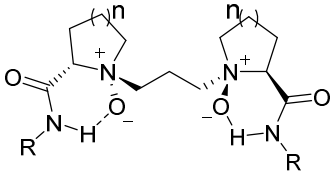


6-Bromo-3-(4-methylcyclohexylidene)indolin-2-one (2l)

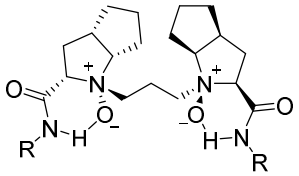
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.05 – 6.96 (m, 1H), 4.53 – 4.39 (m, 1H), 3.36 – 3.22 (m, 1H), 2.45 – 2.33 (m, 1H), 2.28 – 2.16 (m, 1H), 2.06 – 1.95 (m, 2H), 1.86 – 1.73 (m, 1H), 1.36 – 1.18 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 140.8, 124.9, 124.5, 123.3, 121.0, 119.8, 112.8, 36.0, 35.7, 32.7, 31.8, 29.5, 21.7. HRMS (ESI-TOF) calcd for $C_{15}H_{16}{}^{78.9183}BrNONa$ ([M+Na^+]) = 328.0307, Found 328.0315. HRMS (ESI-TOF) calcd for $C_{15}H_{16}{}^{80.9163}BrNONa$ ([M+Na^+]) = 330.0287, Found 330.0276.

(C) General procedure for the synthesis of chiral *N,N′*-dioxides

The *N,N′*-dioxide ligands were prepared by the similar procedure in the literatures[1].



L-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1,
L-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2,
L-PiPr$_3$: R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, n = 2,
L-PiPh: R = C_6H_5, n = 2,
L-PiBn: R = $C_6H_5CH_2$, n = 2,
L-Pi^{t}PM: R = Ph_3C, n = 2,
L-Pi*c*H: R = cyclohexyl, n = 2,
L-PiAd: R = Adamyl n = 2,

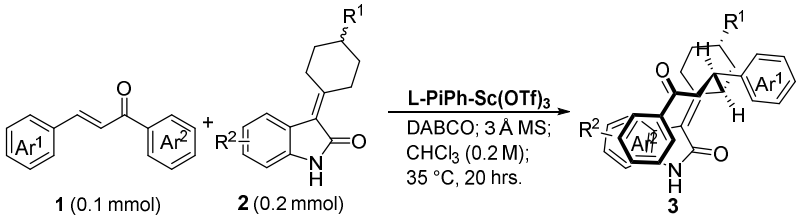


L-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$

(D) General procedure for the preparation of the racemic products

General Procedure: To an oven-dried tube under nitrogen atmosphere was added (±)-**PiPh**/Sc(OTf)$_3$ (10 mol%), chalcone (0.1 mmol), 3 Å MS 40.0 mg and $ClCH_2CH_2Cl$ (0.5 mL), respectively. After stirring at 35 °C for 30 minutes, 3-(4-substituted-cyclohexylidene)indolin-2-ones or substituted 3-(4-methylcyclo-hexylidene)indolin-2-ones (0.1 mmol) and DABCO (22.4 mg, 0.20 mmol) were added and the reaction mixture was stirred at 35 °C for 12 hrs. The reaction mixture was then directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1:9 – 1:4 or ethyl acetate/dichloromethane = 0:1 – 1:19) to afford the corresponding product.

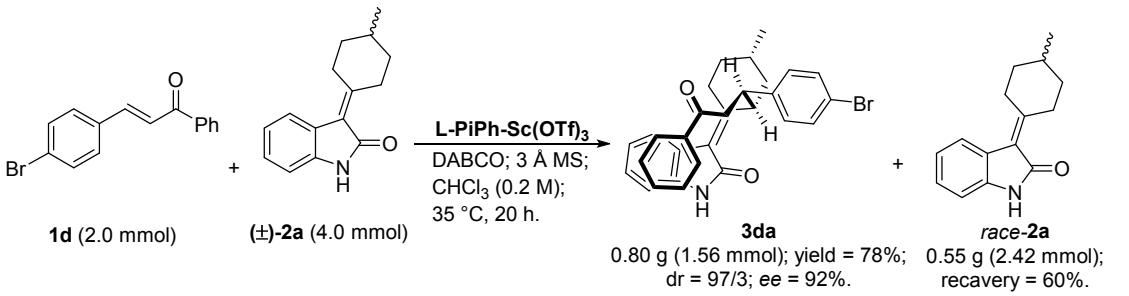
(E) General procedure for the catalytic asymmetric reactions



To an oven-dried reaction tube under nitrogen atmosphere was added Sc(OTf)$_3$ (4.9 mg, 0.01 mmol), **L-PiPh** (4.8 mg, 0.01 mmol), 3 Å MS (40.0 mg), chalcone (0.10 mmol) and $CHCl_3$ (0.5 mL). After stirring for 30 min at 35 ℃, substituted 3-cyclohexylideneoxindoles (0.2 mmol) and DABCO (22.4 mg, 0.2 mmol) were subsequently added. The reaction mixture was stirred at 35 ℃ for 20 h and directly

purified by flash column chromatography (ethyl acetate/petroleum ether = 1:9 – 1:4 or ethyl acetate/dichloromethane = 0:1 – 1:19) to afford the corresponding product.

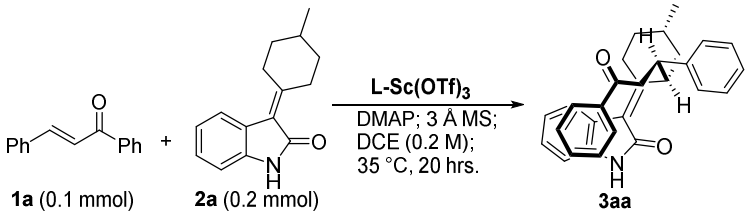
(F) Experimental procedure for the scale-up synthesis of 3da



To an oven-dried reaction tube under nitrogen atmosphere was added $Sc(OTf)_3$ (98.4 mg, 0.20 mmol), **L-PiPh** (96.0 mg, 0.20 mmol), 3 Å MS (800.0 mg), (*E*)-3-(4-bromophenyl)-1-phenylprop-2-en-1-one (574.3 mg, 2.0 mmol) and $CHCl_3$ (10.0 mL). After stirring for 30 min at 35 ℃, 3-(4-methylcyclohexylidene)-indolin-2-one (909.2 mg, 4.0 mmol) and DABCO (448.0 mg, 4.0 mmol) were subsequently added. The reaction mixture was stirred at 35 ℃ for 20 hrs and directly purified by flash column chromatography (ethyl acetate/dichloromethane = 0:1 – 1:19) to afford the desired product (0.80g, 78% yield, 97/3 dr, 92% ee) and recovery of *race*-**2a** (0.55 g, recovery 60%).

(G) Optimization of reaction conditions

Table 1: Screening of ligand.

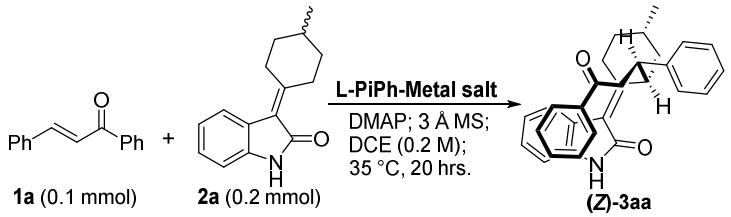


Entry[a]	Ligand	3aa			2a	
		Yield (%)[b]	dr (%)[c]	ee (%)[c]	Recov. (%)[b]	ee (%)[c]
1	**L-PiPr$_2$**	59	66/34	49/55	44	race
2	**L-RaPr$_2$**	45	63/37	16/23	59	race
3	**L-PrPr$_2$**	43	69/31	40/53	nd	nd
4	**L-PiPr$_3$**	62	57/43	39/61	50	race

5	**L-PiPh**	65	92/8	94	26	race
6	**L-PiBn**	66	93/7	88	15	race
7	**L-Pi^{t}PM**	36	69/31	race	38	race
8	**L-Pi*c*H**	68	97/3	86	32	race
9	**L-PiAd**	66	75/25	24/63	nd	nd

Unless otherwise noted, all reactions were performed with **L-Sc(OTf)$_3$** (1:1, 10 mol%), **1a** (0.1 mmol) **2a** (0.2 mmol), 3 Å MS 40.0 mg and 2.0 equiv of DMAP in DCE (0.5 mL) under N_2 at 35 ^{o}C for 20 hrs. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

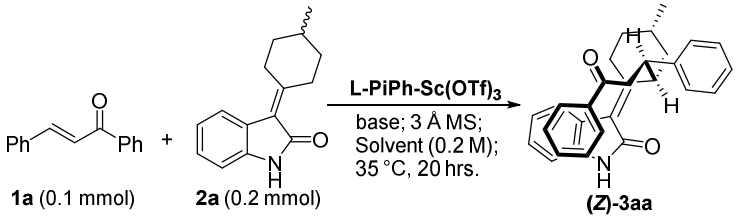
Table 2: Screening of Lewis acid.



Entry[a]	Metal salt	3aa			2a	
		Yield (%)[b]	dr (%)[c]	ee (%)[c]	Recov. (%)[b]	ee (%)[c]
1	$Lu(OTf)_3$	25	78/22	57/44	14	race
2	$Y(OTf)_3$	49	84/16	40/36	31	race
3	$Yb(OTf)_3$	33	77/23	51/47	25	race
4	$Nd(OTf)_3$	75	86/14	44/41	23	race
5	$Sm(OTf)_3$	45	79/21	15/7	12	race
6	$Sc(NTf_2)_3$	mess	--	--	16	race
7	$Sc(O^iPr)_3$	trace	--	--	48	race

Unless otherwise noted, all reactions were performed with **L-PiPh-**Metal salt (1:1, 10 mol%), **1a** (0.1 mmol) **2a** (0.2 mmol), 3 Å MS 40.0 mg and 2.0 equiv of DMAP in DCE (0.5 mL) under N_2 at 35 ^{o}C for 20 hrs. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table 3: Screening of base and solvent.

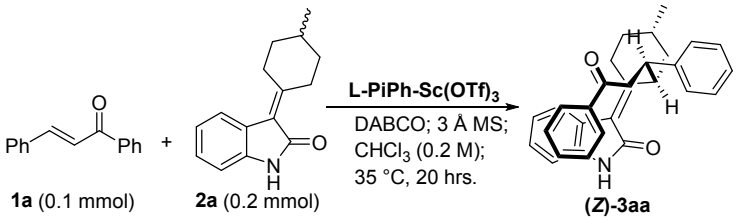


Entry[a]	base	solvent	3aa				2a
			Yield (%)[b]	dr (%)[c]	ee (%)[c]	Recov. (%)[b]	ee (%)[c]
1	DABCO	DCE	81	96/4	96	20	race
2	DIPEA	DCE	47	82/18	44/31	56	race
3	Et_3N	DCE	81	63/37	83/87	40	race

4	K_2CO_3	DCE	72	90/10	39/31	36	race
5	DABCO	$CHCl_3$	92	98/2	95	32	race
6	DABCO	DCM	73	97/3	96	36	race
7	DABCO	THF	64	97/3	91	41	race
8	DABCO	C_7H_8	81	83/17	93	62	race

Unless otherwise noted, all reactions were performed with **L-PiPh**-Sc(OTf)$_3$ (1:1, 10 mol%), **1a** (0.1 mmol) **2a** (0.2 mmol), 3 Å MS 40.0 mg and 2.0 equiv of base in solvent (0.5 mL) under N_2 at 35 ^oC for 20 hrs. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table 4: Control experiments.

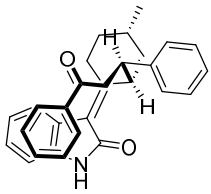


			3aa			2a	
Entry[a]	ligand	metal	Yield (%)[b]	dr (%)[c]	ee (%)[c]	Recov. (%)[b]	ee (%)[c]
1[d]	**L-PiPh**	Sc(OTf)$_3$	48	63/37	98	65	race
2[e]	**L-PiPh**	Sc(OTf)$_3$	73	89/11	96	23	race
3	**L-PiPh**	none	nr	Nd[f]	Nd[f]	80	race
4[g]	**L-PiPh**	Sc(OTf)$_3$	89	87/13	96	Nd[f]	Nd[f]
5[h]	**L-PiPh**	Sc(OTf)$_3$	91	97/3	91	25	race

[a] Unless otherwise noted, all reactions were performed with **L-PiPh**-Sc(OTf)$_3$ (1:1, 10 mol%), **1a** (0.1 mmol) **2a** (0.2 mmol), 3 Å MS 40.0 mg and 2.0 equiv of DABCO in $CHCl_3$ (0.5 mL) under N_2 at 35 ^oC for 20 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Without molecular sieves. [e] **1a/2a** = 1/1, 12 h. [f] Nd = not determined. [g] 5 mol% of **L-PiPh**/Sc(OTf)$_3$ was employed. [h] Using 1.0 equivalent of DABCO

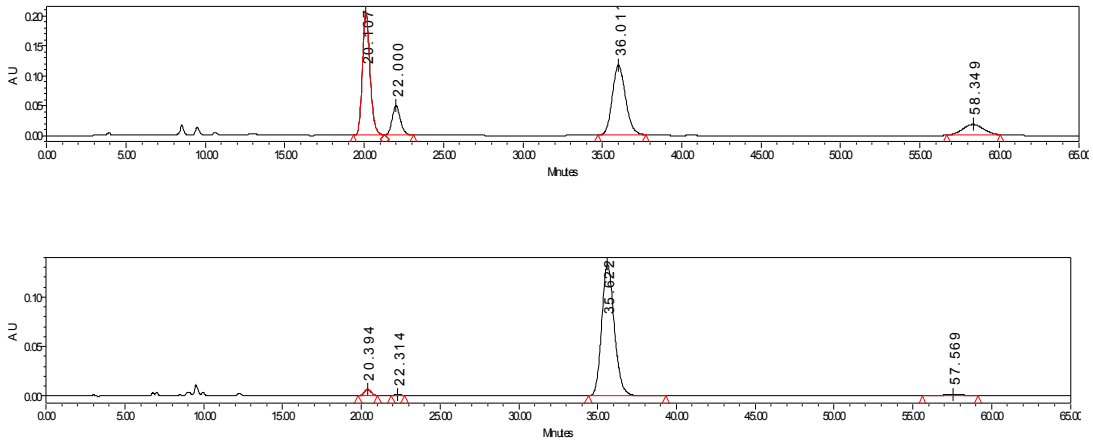
(H) The analytical and spectral characterization data of products

(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3aa)



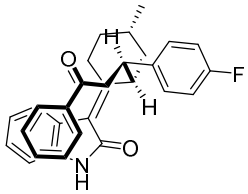
yield 40.1 mg, 92%; pale yellow solid; 95% ee, 98/2 dr; $[\alpha]_D^{19}$ = + 99.2 (c = 0.71 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 20.11 min, t_2 = 22.00 min, t_3 = 36.01 min, t_4 = 58.35 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.69 – 7.62 (m, 2H), 7.59 (d, *J*

= 7.6 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.19 (m, 2H), 7.17 – 7.10 (m, 3H), 6.96 (td, *J* = 7.6, 0.8 Hz, 1H), 6.78 (dd, *J* = 7.6, 0.8 Hz, 1H), 5.27 (dd, *J* = 11.6, 3.2 Hz, 1H), 4.04 – 3.92 (m, 1H), 3.45 – 3.24 (m, 3H), 2.73 (td, *J* = 14.0, 5.2 Hz, 1H), 2.23 – 2.03 (m, 2H), 1.51 – 1.43 (m, 1H), 1.24 (ddd, *J* = 26.0, 12.2, 3.6 Hz, 1H), 1.09 (td, *J* = 13.8, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 170.6, 166.6, 144.3, 139.5, 137.1, 132.5, 128.7, 128.5, 128.1, 128.0, 127.9, 126.6, 124.3, 123.9, 123.5, 121.8, 109.5, 43.5, 43.1, 41.6, 38.4, 36.4, 28.7, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{29}NO_2Na$ ([M+Na$^+$]) = 458.2091, Found 458.2090.



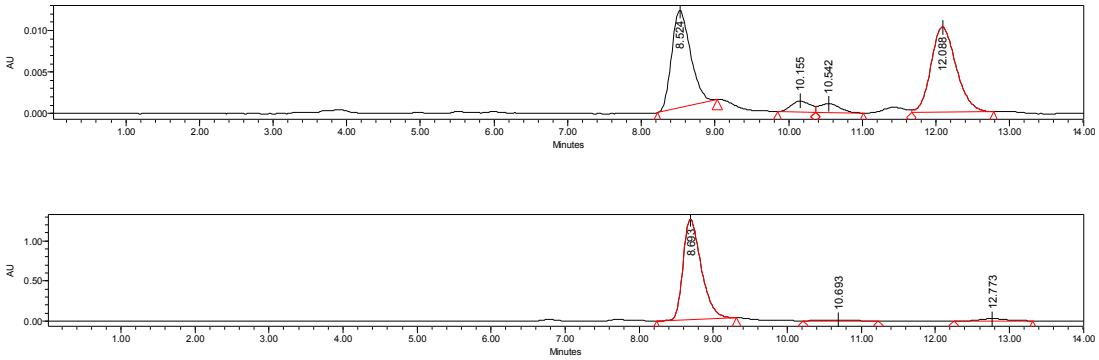
	Retention Time	Area	% Area
1	20.394	196714	2.52
2	22.314	34060	0.44
3	35.622	7419178	95.00
4	57.569	159681	2.04

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-1-(4-Fluorophenyl)-3-oxo-3-phenylpropyl)-4-methylcyclohexylidene)indolin-2-one (3ba)



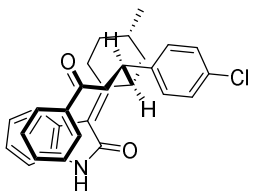
yield 36.4 mg, 80%; pale yellow solid; 95% ee, 98/2 dr; $[\alpha]_D^{22}$ = + 94.4 (c = 0.65 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 8.52 min, t_2 = 10.16 min, t_3 = 10.54 min, t_4 = 12.09 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.71 – 7.63 (m, 2H), 7.59 (d, *J*

= 8.0 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.35 – 7.28 (m, 1H), 7.20 – 7.11 (m, 3H), 7.05 – 6.94 (m, 3H), 6.84 – 6.73 (m, 1H), 5.21 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.02 – 3.90 (m, 1H), 3.42 – 3.21 (m, 3H), 2.69 (td, *J* = 14.0, 4.8 Hz, 1H), 2.16 – 1.99 (m, 2H), 1.45 (dd, *J* = 14.0, 2.4 Hz, 1H), 1.28 – 1.21 (m, 1H), 1.15 – 1.05 (m, 1H), 0.79 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 170.5, 166.2, 162.8, 160.4, 139.9, 139.9, 139.5, 137.0, 132.7, 129.8, 128.2, 128.1, 127.9, 124.3, 123.8, 123.5, 121.9, 115.6, 115.4, 109.5, 43.0, 42.7, 41.6, 38.3, 36.4, 28.6, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}FNO_2Na$ ([M+Na$^+$]) = 476.1996, Found 476.2002.



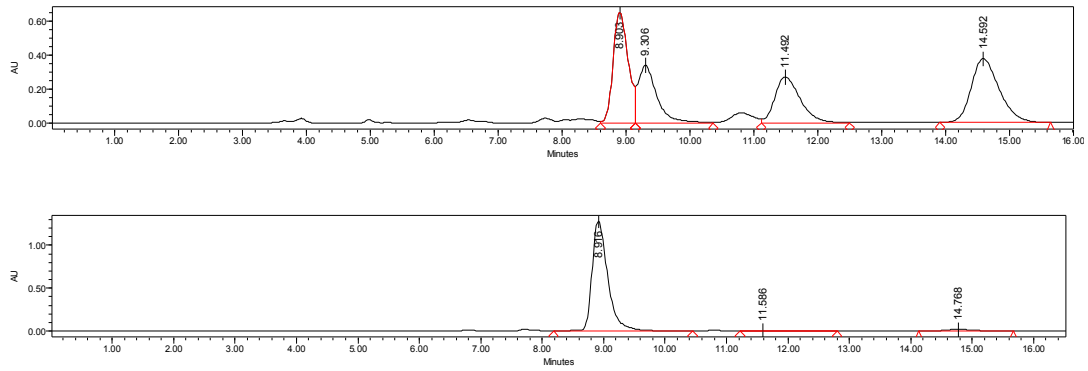
	Retention Time	Area	% Area
1	8.693	21247473	95.97
2	10.693	281520	1.27
3	12.773	609786	2.75

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-1-(4-Chlorophenyl)-3-oxo-3-phenylpropyl)-4-methylcyclohexylidene)indolin-2-one (3ca)



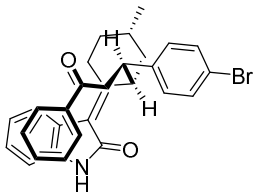
yield 38.9 mg, 83%; pale yellow solid; 95% ee, 99/1 dr; $[\alpha]_D^{22}$ = + 108.5 (c = 0.74 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 8.90 min, t_2 = 9.31 min, t_3 = 11.49 min, t_4 = 14.59 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.65 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.45 -7.43 (m, 2H), 7.35 – 7.27 (m, 3H), 7.20 – 7.11 (m, 3H), 6.96 (td, *J* = 7.6, 0.8 Hz, 1H), 6.77 (dd, *J* = 7.6, 0.4 Hz, 1H), 5.21 (dd, *J* = 11.2, 3.2 Hz, 1H), 4.02 – 3.86 (m, 1H), 3.44 – 3.19 (m, 3H), 2.67 (td, *J* = 14.0, 4.8 Hz, 1H), 2.14 – 2.03 (m, 2H), 1.44 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.24 (qd, *J* = 13.2, 3.6 Hz, 1H),

1.10 (td, J = 13.6, 4.8 Hz, 1H), 0.79 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 170.4, 165.9, 142.8, 139.5, 136.9, 132.7, 132.2, 129.8, 128.9, 128.3, 128.2, 127.9, 124.3, 123.8, 123.6, 121.9, 109.5, 42.9, 42.8, 41.4, 38.3, 36.4, 28.6, 26.2, 22.0. HRMS (ESI-TOF) calcd for $C_{30H28}{}^{34.9689}ClNONa$ ([M+Na$^+$]) = 492.1701, Found 492.1708. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{36.9659}ClNONa$ ([M+Na$^+$]) = 494.1671, Found 494.1668.



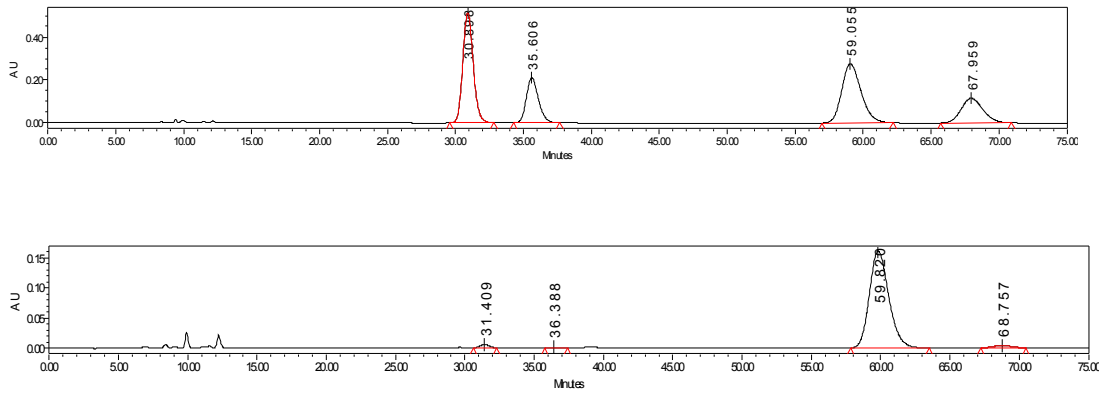
	Retention Time	Area	% Area
1	8.916	22926411	96.66
2	11.586	174199	0.73
3	14.768	619139	2.61

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-1-(4-Bromophenyl)-3-oxo-3-phenylpropyl)-4-methylcyclohexylidene)indolin-2-one (3da)



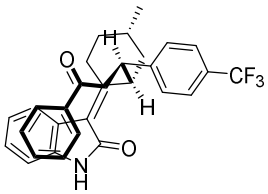
yield 45.2 mg, 88%; pale yellow solid; 97% ee, 97/3 dr; $[\alpha]_D{}^{22}$ = + 100.9 (c = 0.81 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 30.90 min, t_2 = 35.61 min, t_3 = 59.06 min, t_4 = 67.96 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.65 (dd, J = 8.0, 1.2 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.20 – 7.11 (m, 3H), 6.96 (td, J = 7.6, 1.2 Hz, 1H), 6.70 (dd, J = 7.6, 0.4 Hz, 1H), 5.21 (dd, J = 11.6, 3.2 Hz, 1H), 4.00 – 3.88 (m, 1H), 3.41 – 3.18 (m, 3H), 2.67 (td, J = 14.0, 4.4 Hz, 1H), 2.16 – 2.01 (m, 2H), 1.45 (dd, J = 14.0, 2.0 Hz, 1H), 1.24 (qd, J = 13.2, 3.6 Hz, 1H), 1.14 – 1.05 (m, 1H), 0.79 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 170.5, 165.9, 143.4, 139.5, 136.9, 132.7, 131.8, 130.2,

128.3, 128.2, 127.9, 124.3, 123.8, 123.6, 121.9, 120.3, 109.5, 42.8, 41.3, 38.3, 36.4, 28.6, 26.2, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{78.9183}BrNO_2Na$ ([M+Na$^+$]) = 536.1196, Found 536.1201. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{80.9163}BrNO_2Na$ ([M+Na$^+$]) = 538.1175, Found 538.1180.



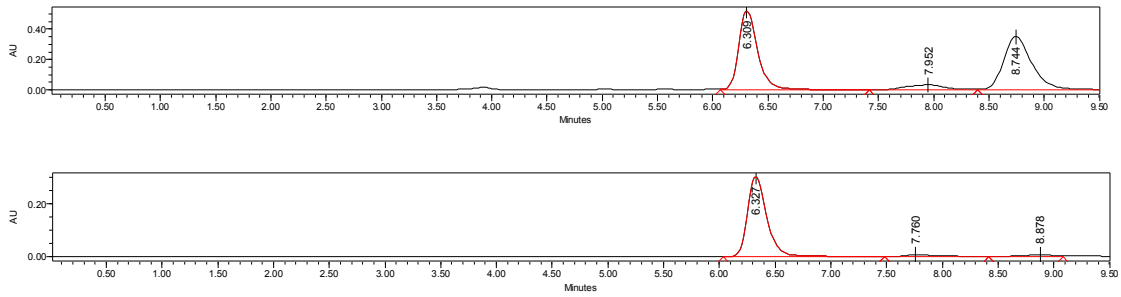
	Retention Time	Area	% Area
1	31.409	277016	1.68
2	36.388	45852	0.28
3	59.820	15724844	95.62
4	68.757	397109	2.41

(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*)-3-oxo-3-phenyl-1-(4-(trifluoromethyl)phenyl)propyl)cyclohexylidene)indolin-2-one (3ea)



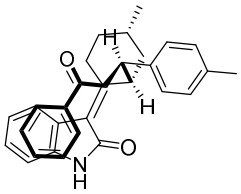
yield 39.8 mg, 79%; pale yellow solid; 93% ee, 96/4 dr; $[\alpha]_D^{22}$ = + 83.1 (c = 0.78 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 6.33 min, t_2 = 7.76 min, t_3 = 8.88 min; 1H NMR (400 MHz, CDCl3) δ 8.61 (s, 1H), 7.69 – 7.57 (m, 7H), 7.35 – 7.30 (m, 1H), 7.20 – 7.12 (m, 3H), 6.97 (td, *J* = 7.6, 0.8 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.28 (dd, *J* = 11.4, 3.4 Hz, 1H), 4.10 – 4.01 (m, 1H), 3.46 – 3.24 (m, 3H), 2.68 (td, *J* = 14.0, 4.8 Hz, 1H), 2.18 – 2.06 (m, 2H), 1.40 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.25 (dd, *J* = 13.2, 3.6 Hz, 1H), 1.11 (td, *J* = 13.8, 4.8 Hz, 1H), 0.80 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 170.5, 165.5, 148.6, 139.5, 136.8, 132.8, 129.0, 128.8, 128.7, 128.3, 128.2, 127.9, 127.8, 125.8, 125.7, 125.7, 124.3, 123.8, 123.8, 123.1, 122.0, 109.5,

43.1, 42.7, 41.3, 38.3, 36.3, 28.6, 26.2, 21.9. HRMS (ESI-TOF) calcd for $C_{31}H_{28}F_3NO_2Na$ ([M+Na$^+$]) = 526.1964, Found 526.1967.

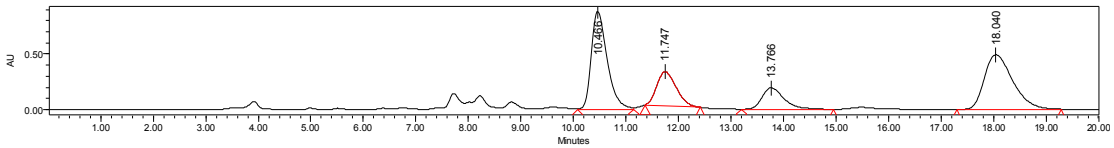


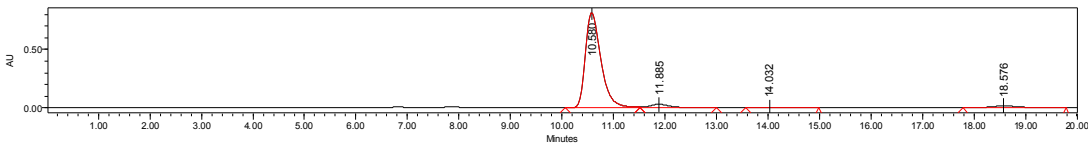
	Retention Time	Area	% Area
1	6.327	3657299	92.52
2	7.760	154708	3.91
3	8.878	140971	3.57

(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*)-3-oxo-3-phenyl-1-(*p*-tolyl)propyl)cyclohexylidene) indolin-2-one (3fa)



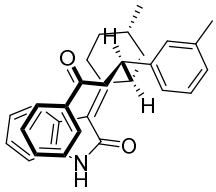
yield 39.5 mg, 88%; pale yellow solid; 93% ee, 95/5 dr; $[\alpha]_D^{22}$ = + 112.6 (c = 0.59 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 10.47 min, t_2 = 11.75 min, t_3 = 13.77 min, t_4 = 18.04 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.69 – 7.61 (m, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.18 – 7.09 (m, 5H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80 – 6.72 (m, 1H), 5.23 (dd, *J* = 11.4, 3.4 Hz, 1H), 4.02 – 3.89 (m, 1H), 3.40 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.36 – 3.29 (m, 1H), 3.25 (dd, *J* = 17.0, 7.4 Hz, 1H), 2.72 (td, *J* = 14.0, 4.8 Hz, 1H), 2.33 (s, 3H), 2.18 – 2.05 (m, 2H), 1.50 (dd, *J* = 13.8, 2.2 Hz, 1H), 1.27 – 1.21 (m, 1H), 1.08 (td, *J* = 13.6, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 170.6, 166.9, 141.2, 139.5, 137.1, 136.0, 132.5, 129.4, 128.3, 128.1, 128.0, 127.9, 124.3, 123.9, 123.4, 121.8, 109.4, 43.2, 43.1, 41.7, 38.4, 36.5, 28.7, 26.1, 22.0, 21.2. HRMS (ESI-TOF) calcd for $C_{31}H_{31}NO_2Na$ ([M+Na$^+$]) = 472.2247, Found 472.2251.



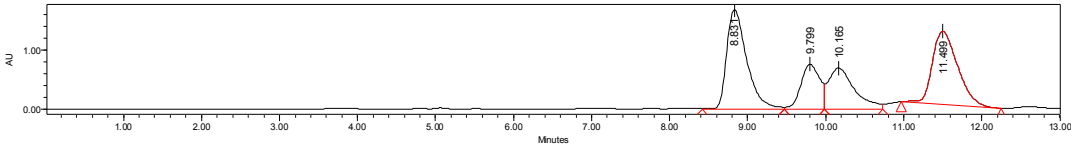


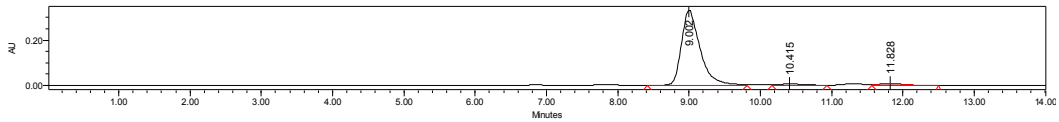
	Retention Time	Area	% Area
1	10.580	17141100	91.16
2	11.885	867082	4.61
3	14.032	178849	0.95
4	18.576	617123	3.28

(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*)-3-oxo-3-phenyl-1-(*m*-tolyl)propyl)cyclohexylidene)indolin-2-one (3ga)



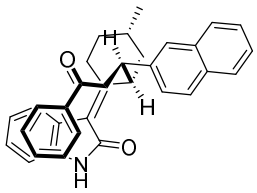
yield 43.5 mg, 97%; pale yellow solid; 94% ee, 97/3 dr; $[\alpha]_D^{22}$ = + 106.6 (c = 0.70 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 8.83 min, t_2 = 9.80 min, t_3 = 10.17 min, t_4 = 11.50 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.70 – 7.62 (m, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.20 (m, 4H), 7.17 – 7.09 (m, 3H), 7.05 – 7.01 (m, 1H), 6.96 (td, *J* = 7.6, 0.8 Hz, 1H), 6.81 – 6.73 (m, 1H), 5.25 (dd, *J* = 11.4, 3.4 Hz, 1H), 4.02 – 3.87 (m, 1H), 3.44 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.37 – 3.28 (m, 1H), 3.23 (dd, *J* = 17.0, 7.0 Hz, 1H), 2.74 (td, *J* = 14.0, 4.8 Hz, 1H), 2.38 (s, 3H), 2.19 – 2.04 (m, 2H), 1.49 (dd, *J* = 13.8, 2.0 Hz, 1H), 1.28 – 1.21 (m, 1H), 1.09 (td, *J* = 13.2, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 170.7, 166.9, 144.2, 139.5, 138.2, 137.1, 132.5, 128.9, 128.5, 128.1, 128.0, 127.9, 127.4, 125.7, 124.3, 123.9, 123.5, 121.8, 109.4, 43.5, 43.1, 41.6, 38.4, 36.4, 28.7, 26.1, 22.0, 21.7. HRMS (ESI-TOF) calcd for $C_{31}H_{31}NO_2Na$ ([M+Na^+]) = 472.2247, Found 472.2254.



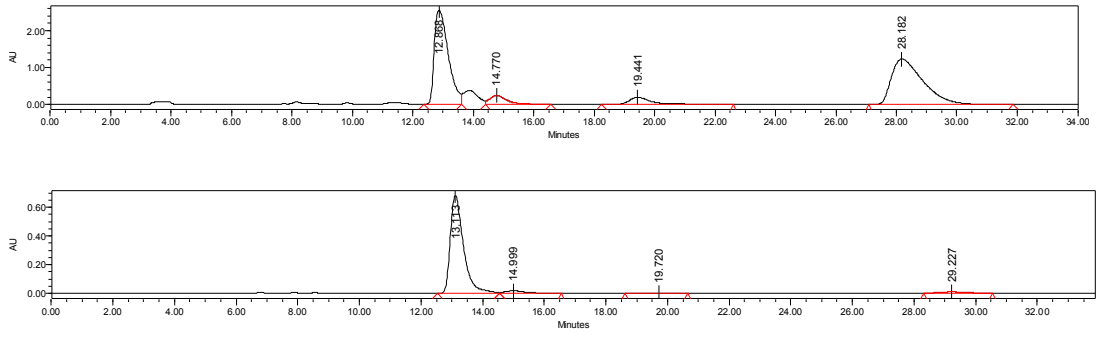


	Retention Time	Area	% Area
1	9.002	6094562	94.29
2	10.415	172883	2.67
3	11.828	196236	3.04

(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*)-1-(naphthalen-2-yl)-3-oxo-3-phenylpropyl)cyclohexylidene)indolin-2-one (3ha)



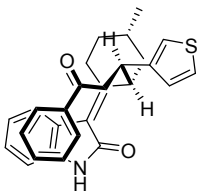
yield 45.4 mg, 94%; pale yellow solid; 94% ee, 96/4 dr; $[\alpha]_D^{22}$ = + 138.7 (c = 0.83 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 13.11 min, t_2 = 15.00 min, t_3 = 19.72 min, t_4 = 29.23 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.95 – 7.82 (m, 4H), 7.75 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.70 – 7.59 (m, 3H), 7.51 – 7.42 (m, 2H), 7.30 – 7.24 (m, 1H), 7.18 – 7.10 (m, 3H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 – 6.78 (m, 1H), 5.43 (dd, *J* = 11.4, 3.4 Hz, 1H), 4.29 – 4.14 (m, 1H), 3.53 (dd, *J* = 17.0, 5.8 Hz, 1H), 3.45 – 3.31 (m, 2H), 2.80 (td, *J* = 14.0, 4.8 Hz, 1H), 2.27 – 2.08 (m, 2H), 1.54 – 1.45 (m, 1H), 1.31 – 1.24 (m, 1H), 1.12 (td, *J* = 13.8, 4.8 Hz, 1H), 0.77 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 170.7, 166.6, 141.8, 139.6, 137.0, 133.7, 132.6, 128.6, 128.2, 128.1, 127.9, 127.7, 127.3, 126.5, 126.0, 125.5, 124.3, 123.9, 123.6, 121.8, 109.5, 43.6, 43.1, 41.4, 38.4, 36.4, 28.8, 26.2, 22.0. HRMS (ESI-TOF) calcd for $C_{34}H_{31}NO_2Na$ ([M+Na^+]) = 508.2247, Found 508.2252.



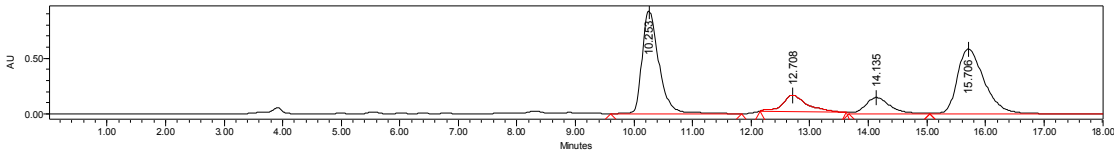
	Retention Time	Area	% Area

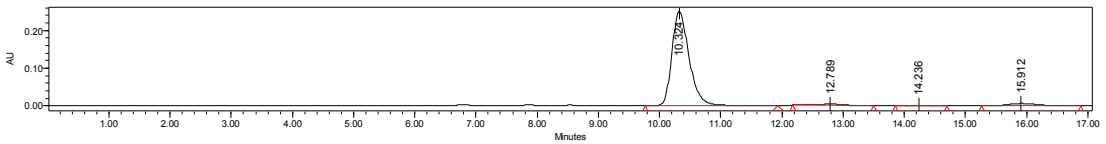
1	13.113	20159725	93.60
2	14.999	708275	3.29
3	19.720	105655	0.49
4	29.227	563731	2.62

(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*)-3-oxo-3-phenyl-1-(thiophen-3-yl)propyl)cyclohexylidene)indolin-2-one (3ia)



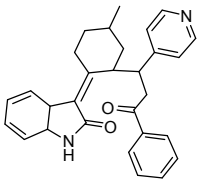
yield 34.8 mg, 79%; pale yellow solid; 93% ee, 97/3 dr; $[\alpha]_D^{22}$ = + 93.5 (c = 0.61 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 10.32 min, t_2 = 12.79 min, t_3 = 14.24 min, t_4 = 15.91 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.73 – 7.62 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.24 (m, 3H), 7.21 – 7.09 (m, 4H), 6.96 (td, *J* = 7.6, 0.8 Hz, 1H), 6.75 (d, *J* = 7.2 Hz, 1H), 5.22 (dd, *J* = 11.4, 3.4 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.39 – 3.29 (m, 2H), 3.25 (dd, *J* = 16.6, 7.4 Hz, 1H), 2.69 (td, *J* = 14.0, 4.8 Hz, 1H), 2.17 – 2.01 (m, 2H), 1.54 (dd, *J* = 13.8, 2.2 Hz, 1H), 1.28 – 1.19 (m, 1H), 1.14 (dd, *J* = 12.8, 4.4 Hz, 1H), 0.81 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 170.5, 166.3, 144.7, 139.5, 137.1, 132.6, 128.2, 128.0, 127.9, 127.1, 125.9, 124.3, 123.9, 123.5, 121.8, 121.5, 109.4, 42.9, 41.5, 39.0, 38.6, 36.4, 28.6, 26.2, 22.0. HRMS (ESI-TOF) calcd for $C_{28}H_{27}NO_2SNa$ ([M+Na$^+$]) = 464.1655, Found 464.1655.



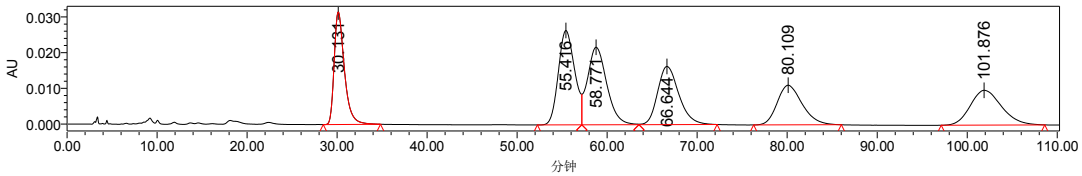


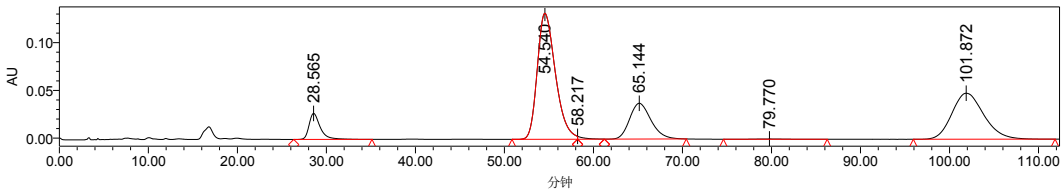
	Retention Time	Area	% Area
1	10.324	4923798	93.24
2	12.789	145378	2.75
3	14.236	28793	0.55
4	15.912	182756	3.46

(Z)-3-(4-methyl-2-(3-oxo-3-phenyl-1-(pyridin-4-yl)propyl)cyclohexylidene)-1,3,3a ,7a-tetrahydro-2H-indol-2-one (3ja)



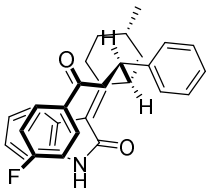
yield 39.8 mg, 91%; pale yellow solid; 45/99/99% ee, 22/48/30 dr; HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 28.57 min, t_2 = 54.54 min, t_3 = 58.22 min, t_4 = 65.14 min, t_5 = 79.77 min, t_6 = 101.87 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.23 (m, 3H), 7.89 – 7.59 (m, 2H), 7.58 – 7.28 (m, 4H), 7.22 – 7.03 (m, 2H), 7.00 – 6.83 (m, 1H), 6.79 – 6.64 (m, 1H), 5.46 – 5.01 (m, 1H), 4.38 – 3.85 (m, 1H), 3.82 – 3.43 (m, 1H), 3.41 – 2.97 (m, 2H), 2.77 – 2.38 (m, 1H), 2.12 (m, 2H), 1.95 – 1.34 (m, 2H), 1.34 – 1.00 (m, 2H), 0.94 – 0.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (for major) δ 198.3, 170.4, 164.5, 153.7, 150.1, 149.4, 139.7, 136.7, 132.9, 128.3, 128.2, 128.1, 127.9, 124.0, 123.8, 123.7, 121.9, 109.5, 47.3, 42.3, 40.6, 38.2, 36.2, 31.6, 28.5, 28.2, 27.7, 26.2, 21.9. HRMS (ESI-TOF) calcd for $C_{29}H_{29}N_2O_2$ ($[M+H^+]$) = 437.2224, Found 437.2222.



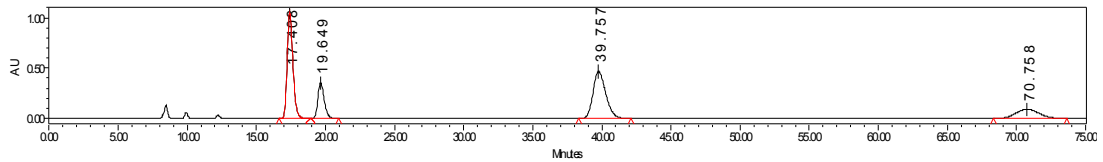


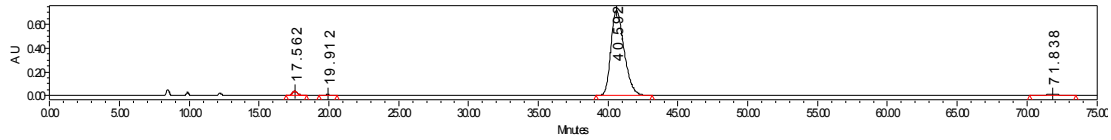
	Retention Time	Area	% Area
1	28.565	2386934	6.04
2	54.540	18638797	47.14
3	58.217	147562	0.37
4	65.144	6265817	15.85
5	79.770	58881	0.15
6	101.872	12045051	30.46

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-3-(4-Fluorophenyl)-3-oxo-1-phenylpropyl)-4-methylcyclohe xylidene)indolin-2-one (3ka)



yield 36.1 mg, 80%; pale yellow solid; 96% ee, 98/2 dr; $[\alpha]_D^{19}$ = + 107.8 (c = 0.40 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 17.41min, t_2 = 19.65 min, t_3 = 39.76 min, t_4 = 70.76 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.70 – 7.60 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 6.4 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.85 – 6.65 (m, 3H), 5.23 (d, *J* = 10.0 Hz, 1H), 4.05 – 3.89 (m, 1H), 3.50 – 3.36 (m, 1H), 3.30 (d, *J* = 14.0 Hz, 1H), 3.20 – 3.09 (m, 1H), 2.71 (td, *J* = 14.0, 3.2 Hz, 1H), 2.20 – 2.00 (m, 2H), 1.45 (d, *J* = 13.6 Hz, 1H), 1.25 – 1.16 (m, 1H), 1.07 (td, *J* = 12.8, 3.2 Hz, 1H), 0.78 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 170.4, 166.7, 164.1, 144.2, 139.3, 133.5, 130.6, 130.5, 128.8, 128.4, 128.1, 126.7, 124.3, 123.9, 123.5, 121.9, 115.2, 115.0, 109.3, 43.8, 43.0, 41.6, 38.3, 36.4, 28.8, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}FNO_2Na$ ([M+Na^+]) = 476.1996, Found 476.2001.

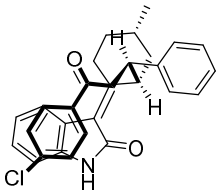




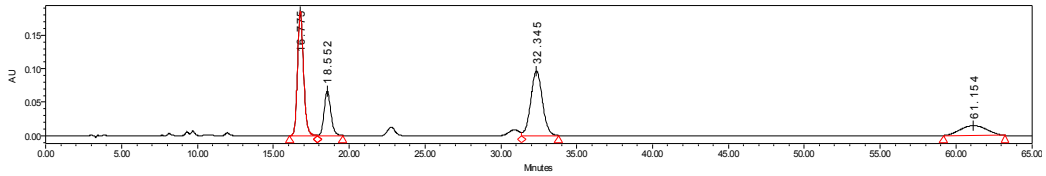
	Retention Time	Area	% Area
1	17.562	999182	2.02
2	19.912	256931	0.52
3	40.592	47410328	95.69
4	71.838	879218	1.77

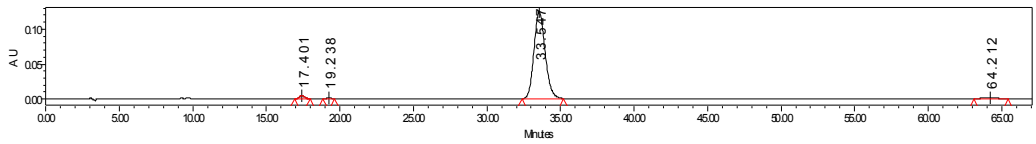
(*Z*)-3-((2*S*,4*S*)-2-((*R*)-3-(4-Chlorophenyl)-3-oxo-1-phenylpropyl)-4-methylcyclohe

xylidene)indolin-2-one (3la)



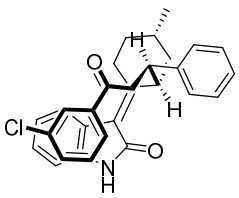
yield 35.4 mg, 75%; pale yellow solid; 96% ee, 98/2 dr; $[\alpha]_D^{19}$ = + 110.5 (c = 0.58 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 16.78 min, t_2 = 18.55 min, t_3 = 32.35 min, t_4 = 61.15 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.59 – 7.52 (m, 3H), 7.51 – 7.45 (m, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.18 – 7.12 (m, 1H), 7.11 – 7.03 (m, 2H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.24 (dd, *J* = 11.6, 3.6 Hz, 1H), 4.08 – 3.88 (m, 1H), 3.46 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.35 – 3.25 (m, 1H), 3.12 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.70 (td, *J* = 14.0, 4.8 Hz, 1H), 2.18 – 2.02 (m, 2H), 1.45 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.26 – 1.16 (m, 1H), 1.08 (td, *J* = 13.6, 4.8 Hz, 1H), 0.78 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 170.5, 166.6, 144.2, 139.4, 138.9, 135.3, 129.3, 128.8, 128.3, 128.1, 126.7, 124.3, 123.8, 123.6, 121.9, 109.4, 43.9, 43.0, 41.6, 38.3, 36.3, 28.8, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{34.9689}ClNO_2Na$ ([M+Na$^+$]) = 492.1701, Found 492.1693. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{36.9659}ClNO_2Na$ ([M+Na$^+$]) = 494.1671, Found 494.1680.



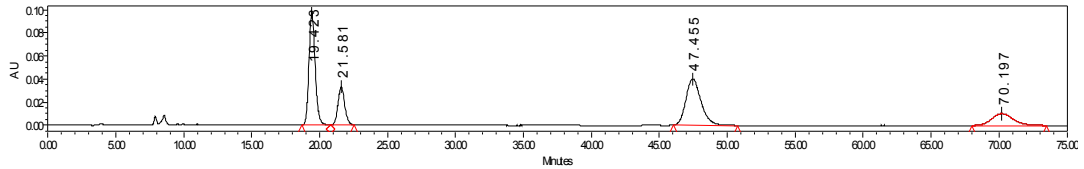


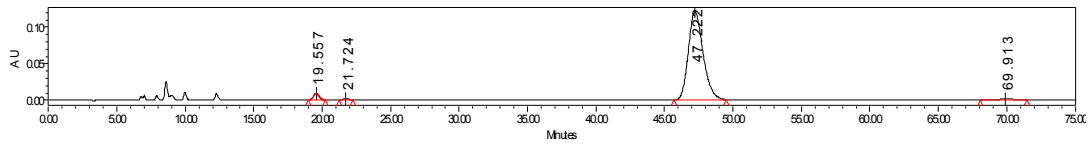
	Retention Time	Area	% Area
1	17.401	127612	1.87
2	19.238	30151	0.44
3	33.547	6573340	96.34
4	64.212	91816	1.35

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-3-(3-Chlorophenyl)-3-oxo-1-phenylpropyl)-4-methylcyclohe xylidene)indolin-2-one (3ma)



yield 37.9 mg, 81%; pale yellow solid; 94% ee, 98/2 dr; $[\alpha]_D^{19}$ = + 101.7 (c = 0.70 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 19.42 min, t_2 = 21.58 min, t_3 = 47.46 min, t_4 = 70.20 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.60 (t, *J* = 1.6 Hz, 1H), 7.55 – 7.46 (m, 4H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.26 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.52 (dd, *J* = 16.8, 6.8 Hz, 1H), 3.33 – 3.23 (m, 1H), 3.06 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.67 (td, *J* = 14.0, 4.8 Hz, 1H), 2.14 – 2.03 (m, 2H), 1.46 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.22 (dd, *J* = 12.8, 3.2 Hz, 1H), 1.08 (td, *J* = 13.2, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 170.6, 166.3, 144.2, 139.4, 138.5, 134.5, 132.4, 129.4, 128.8, 128.3, 128.2, 127.9, 126.7, 126.0, 124.3, 123.8, 123.7, 121.9, 109.4, 44.0, 43.1, 41.5, 38.1, 36.3, 28.8, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{34.9689}ClNO_2Na$ ([M+Na$^+$]) = 492.1701, Found 492.1701. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{36.9659}ClNO_2Na$ ([M+Na$^+$]) = 494.1671, Found 494.1679.

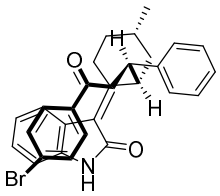




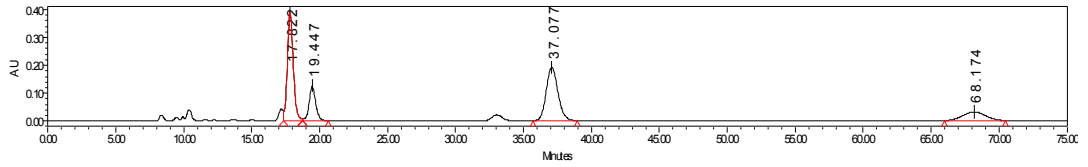
	Retention Time	Area	% Area
1	19.557	274237	2.87
2	21.724	65827	0.69
3	47.222	9072896	94.79
4	69.913	158364	1.65

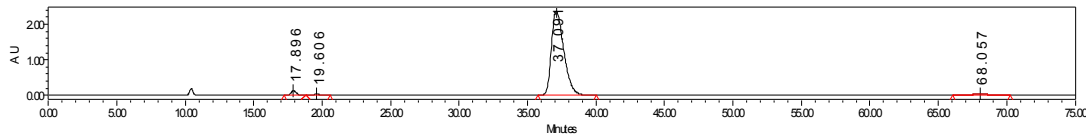
(*Z*)-3-((2*S*,4*S*)-2-((*R*)-3-(4-Bromophenyl)-3-oxo-1-phenylpropyl)-4-methylcyclohe

xylidene)indolin-2-one (3na)



yield 41.8 mg, 81%; pale yellow solid; 96% ee, 97/3 dr; $[\alpha]_D^{19}$ = + 109.6 (c = 0.59 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 17.82 min, t_2 = 19.45 min, t_3 = 37.08 min, t_4 = 68.17 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.44 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.24 (dd, *J* = 11.2, 3.2 Hz, 1H), 4.04 – 3.90 (m, 1H), 3.47 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.29 (d, *J* = 14.4 Hz, 1H), 3.10 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.70 (td, *J* = 14.0, 5.2 Hz, 1H), 2.16 – 2.00 (m, 2H), 1.45 (dd, *J* = 13.6, 1.2 Hz, 1H), 1.22 (dd, *J* = 13.2, 3.6 Hz, 1H), 1.08 (td, *J* = 13.2, 4.8 Hz, 1H), 0.78 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 170.4, 166.6, 144.2, 139.3, 135.7, 131.3, 129.4, 128.8, 128.3, 128.2, 127.7, 126.7, 124.3, 123.8, 123.6, 121.9, 109.5, 43.9, 43.0, 41.6, 38.3, 36.3, 28.8, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{78.9183}BrNO_2Na$ ([M+Na$^+$]) = 536.1196, Found 536.1196. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{80.9163}BrNO_2Na$ ([M+Na$^+$]) = 538.1175, Found 538.1182.

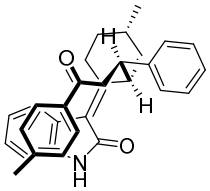




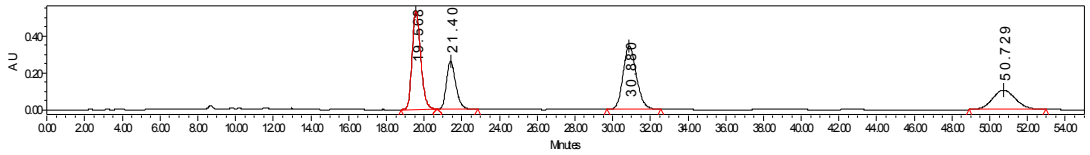
	Retention Time	Area	% Area
1	17.896	3849441	2.44
2	19.606	1295650	0.82
3	37.091	149310869	94.53
4	68.057	3498455	2.21

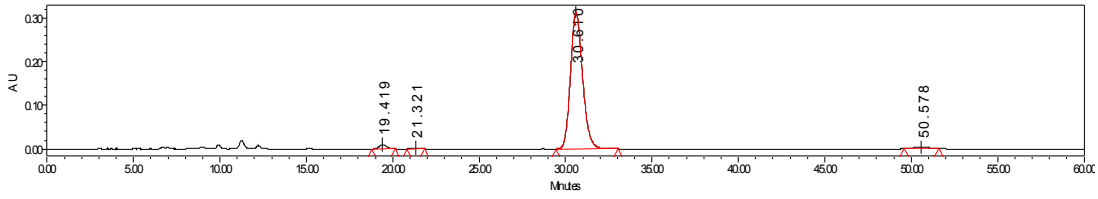
(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*)-3-oxo-1-phenyl-3-(*p*-tolyl)propyl)cyclohexylidene)

indolin-2-one (3oa)



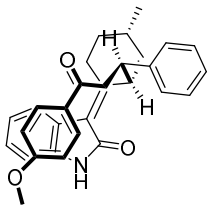
yield 40.4 mg, 90%; pale yellow solid; 96% ee, 98/2 dr; $[\alpha]_D^{19}$ = + 100.1 (c = 0.76 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 19.57 min, t_2 = 21.41 min, t_3 = 30.88 min, t_4 = 50.73 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.60 – 7.55 (m, 3H), 7.54 – 7.39 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.98 – 6.90 (m, 3H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.27 (dd, *J* = 11.2, 3.2 Hz, 1H), 4.05 – 3.93 (m, 1H), 3.44 – 3.20 (m, 3H), 2.72 (td, *J* = 14.0, 4.8 Hz, 1H), 2.22 – 2.06 (m, 5H), 1.53 – 1.41 (m, 1H), 1.31 – 1.17 (m, 1H), 1.09 (td, *J* = 13.2, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 170.7, 166.6, 144.4, 143.2, 139.6, 134.6, 128.8, 128.7, 128.5, 128.0, 127.9, 126.5, 124.3, 123.9, 123.6, 121.8, 109.4, 43.5, 42.9, 41.6, 38.4, 36.4, 28.7, 26.1, 22.0, 21.6. HRMS (ESI-TOF) calcd for $C_{31}H_{31}NO_2Na$ ([M+Na$^+$]) = 472.2247, Found 472.2246.



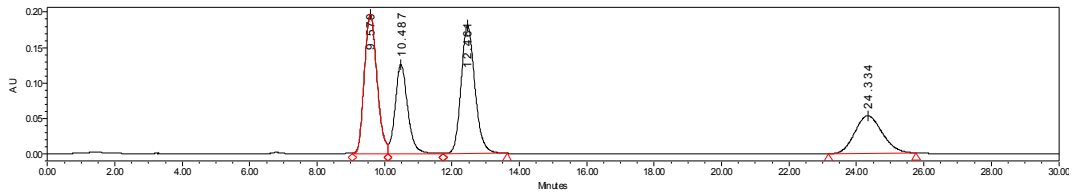


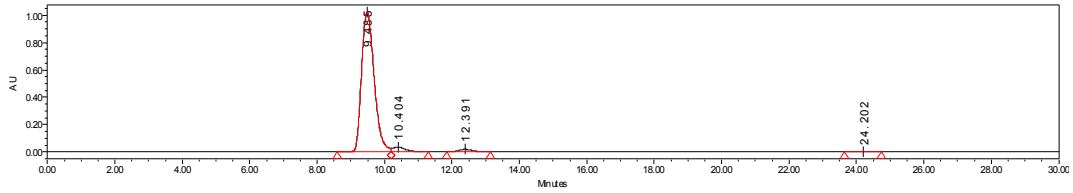
	Retention Time	Area	% Area
1	19.419	306429	1.93
2	21.321	67199	0.42
3	30.610	15280920	96.21
4	50.578	228576	1.44

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-3-(4-Methoxyphenyl)-3-oxo-1-phenylpropyl)-4-methylcyclohexylidene)indolin-2-one (3pa)



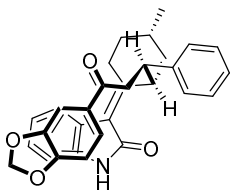
yield 45.0 mg, 96%; pale yellow solid; 96% ee, 96/4 dr; $[\alpha]_D^{22}$ = + 110.6 (c = 0.65 in CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 9.58 min, t_2 = 10.49 min, t_3 = 12.46 min, t_4 = 24.33 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.66 – 7.61 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.98 – 6.92 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.62 – 6.54 (m, 2H), 5.25 (dd, *J* = 11.2, 3.2 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.69 (s, 3H), 3.40 – 3.27 (m, 2H), 3.20 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.73 (td, *J* = 14.0, 4.8 Hz, 1H), 2.19 – 2.04 (m, 2H), 1.46 (dd, *J* = 13.6, 1.8 Hz, 1H), 1.26 – 1.17 (m, 1H), 1.08 (td, *J* = 13.6, 4.8 Hz, 1H), 0.78 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 170.5, 166.8, 163.0, 144.5, 139.5, 130.2, 130.2, 128.7, 128.5, 127.9, 126.5, 124.3, 124.0, 123.5, 121.8, 113.2, 109.3, 55.4, 43.6, 42.6, 41.6, 38.4, 36.5, 28.7, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{31}H_{31}NO_3Na$ ([M+Na^+]) = 488.2196, Found 488.2198.



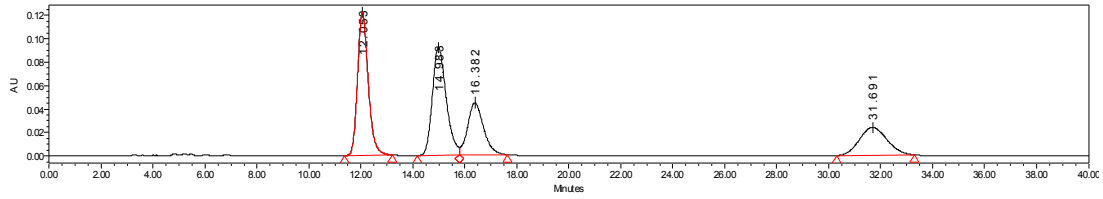


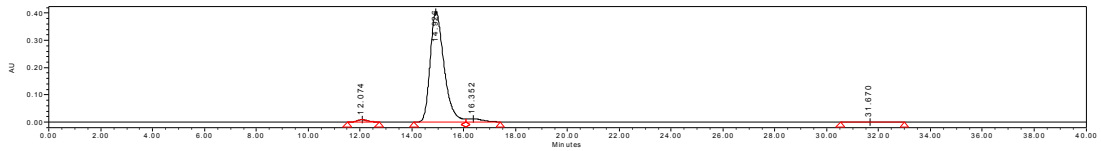
	Retention Time	Area	% Area
1	9.485	26525652	94.80
2	10.404	910180	3.25
3	12.391	491971	1.76
4	24.202	51968	0.19

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-3-oxo-1-phenylpropyl)-4-methylcyclohexylidene)indolin-2-one (3qa)



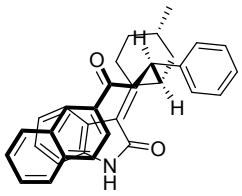
yield 39.2 mg, 82%; pale yellow solid; 97% ee, 96/4 dr; $[\alpha]_D^{22}$ = + 109.9 (c = 0.81 in CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 12.05 min, t_2 = 14.98 min, t_3 = 16.38 min, t_4 = 31.69 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.52 (dd, *J* = 13.2, 8.0 Hz, 3H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.29 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.17 – 7.10 (m, 2H), 6.95 (td, *J* = 7.6, 0.8 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 5.87 – 5.77 (m, 2H), 5.26 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.04 – 3.91 (m, 1H), 3.42 (dd, *J* = 16.8, 6.8 Hz, 1H), 3.34 – 3.23 (m, 1H), 3.05 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.70 (td, *J* = 14.0, 4.8 Hz, 1H), 2.21 – 2.00 (m, 2H), 1.50 – 1.42 (m, 1H), 1.27 – 1.15 (m, 1H), 1.08 (td, *J* = 13.6, 4.8 Hz, 1H), 0.78 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 170.7, 166.6, 151.3, 147.7, 144.5, 139.5, 132.0, 128.7, 128.4, 127.9, 126.6, 124.4, 124.2, 123.9, 123.8, 121.8, 109.3, 107.7, 107.4, 101.6, 44.0, 42.7, 41.6, 38.3, 36.4, 28.8, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{31}H_{29}NO_4Na$ ([M+Na^+]) = 502.1989, Found 502.1992.



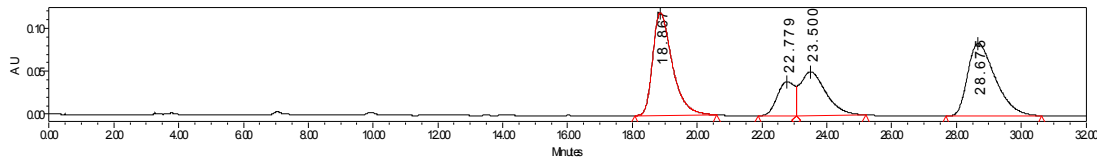


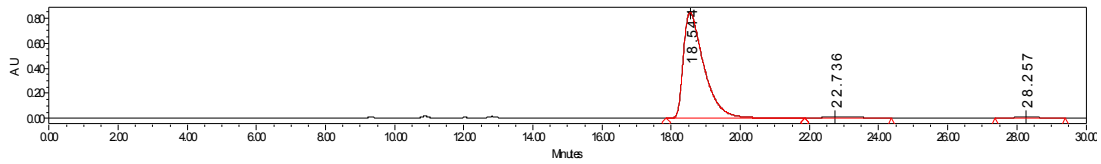
	Retention Time	Area	% Area
1	12.074	243742	1.54
2	14.926	15082563	95.08
3	16.352	479136	3.02
4	31.670	58134	0.37

(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*)-3-(naphthalen-2-yl)-3-oxo-1-phenylpropyl)cyclohexylidene)indolin-2-one (3ra)



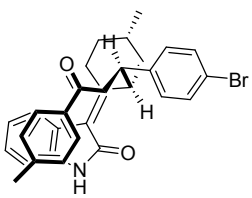
yield 41.8 mg, 86%; pale yellow solid; 97% ee, 98/2 dr; $[\alpha]_D^{19}$ = + 125.0 (c = 0.61 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 18.87 min, t_2 = 22.78 min, t_3 = 23.50 min, t_4 = 28.68 min; 1H NMR (400 MHz, CDCl3) δ 8.55 (s, 1H), 8.14 (s, 1H), 7.71 – 7.60 (m, 3H), 7.59 – 7.49 (m, 4H), 7.46 – 7.41 (m, 1H), 7.40 – 7.33 (m, 3H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.97 (td, *J* = 7.6, 0.8 Hz, 1H), 6.89 (td, *J* = 7.6, 1.2 Hz, 1H), 6.51 (dd, *J* = 7.6, 0.4 Hz, 1H), 5.32 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.11 – 4.01 (m, 1H), 3.64 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.38 – 3.30 (m, 1H), 3.27 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.77 (td, *J* = 14.0, 5.2 Hz, 1H), 2.21 – 2.05 (m, 2H), 1.49 (dd, *J* = 14.0, 2.4 Hz, 1H), 1.30 – 1.17 (m, 1H), 1.10 (td, *J* = 13.6, 4.8 Hz, 1H), 0.80 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 170.6, 166.5, 144.5, 139.3, 135.2, 134.4, 132.3, 129.6, 129.5, 128.8, 128.4, 128.1, 128.0, 127.9, 127.6, 126.6, 126.4, 124.2, 123.8, 123.7, 123.7, 121.7, 109.2, 43.9, 43.1, 41.6, 38.4, 36.4, 28.8, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{34}H_{31}NO_2Na$ ([M+Na^+]) = 508.2247, Found 508.2254.





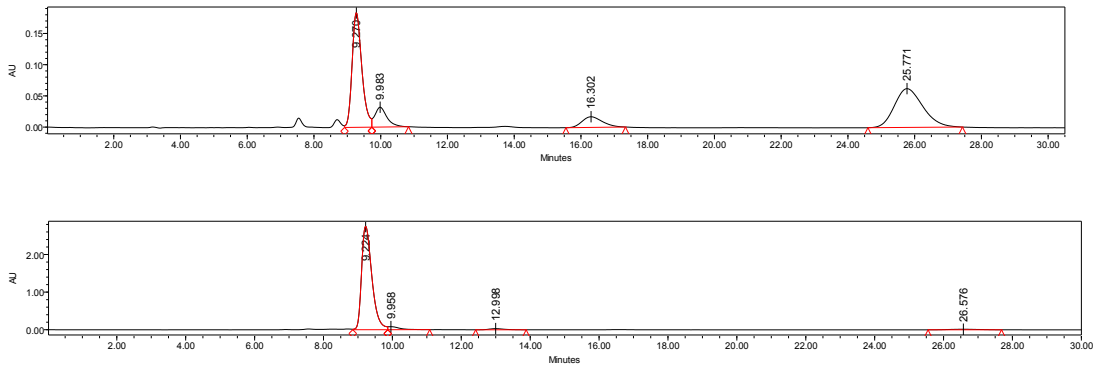
	Retention Time	Area	% Area
1	18.544	34847780	96.13
2	22.736	847493	2.34
3	28.257	557282	1.54

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-1-(4-Bromophenyl)-3-oxo-3-(p-tolyl)propyl)-4-methylcyclohexylidene)indolin-2-one (3sa)



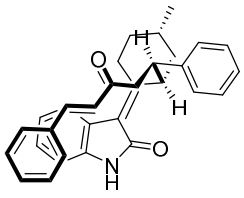
yield 43.5 mg, 83%; pale yellow solid; 97% ee, 95/5 dr; $[\alpha]_D^{19}$ =

+ 94.9 (c = 0.68 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 9.22 min, t_2 = 9.96 min, t_3 = 13.00 min, t_4 = 26.58 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.56 (dd, *J* = 8.4, 2.1 Hz, 3H), 7.41 (dd, *J* = 26.0, 8.4 Hz, 4H), 7.15 (td, *J* = 7.6, 0.8 Hz, 1H), 7.01 – 6.92 (m, 3H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.21 (dd, *J* = 11.2, 3.2 Hz, 1H), 4.03 – 3.87 (m, 1H), 3.39 – 3.18 (m, 3H), 2.66 (td, *J* = 14.0, 4.8 Hz, 1H), 2.23 (s, 3H), 2.14 – 2.00 (m, 2H), 1.44 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.35 – 1.17 (m, 1H), 1.09 (td, *J* = 13.6, 4.8 Hz, 1H), 0.79 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 170.5, 165.9, 143.5, 143.5, 139.5, 134.5, 131.8, 130.2, 128.9, 128.1, 128.0, 124.3, 123.8, 123.6, 121.9, 120.3, 109.4, 42.8, 42.6, 41.3, 38.3, 36.4, 28.6, 26.1, 22.0, 21.6. HRMS (ESI-TOF) calcd for $C_{31}H_{30}{}^{78.9183}BrNO_2Na$ ([M+Na$^+$]) = 550.1352, Found 550.1349. HRMS (ESI-TOF) calcd for $C_{31}H_{30}{}^{80.9163}BrNO_2Na$ ([M+Na$^+$]) = 552.1332, Found 552.1337.



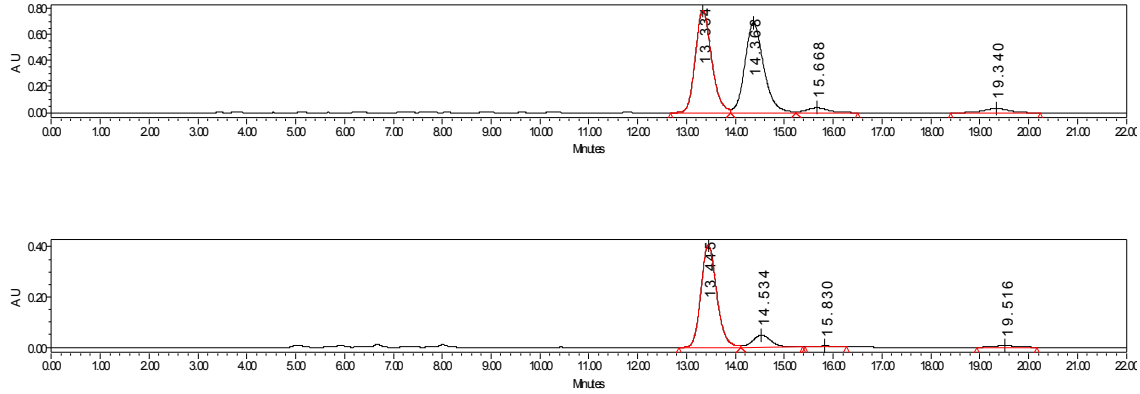
	Retention Time	Area	% Area
1	9.224	57210733	94.06
2	9.958	1874798	3.08
3	12.998	873181	1.44
4	26.576	863214	1.42

(*Z*)-3-((2*S*,4*S*)-4-Methyl-2-((*R*,*E*)-3-oxo-1,5-diphenylpent-4-en-1-yl)cyclohexylidene)indolin-2-one (3ta)



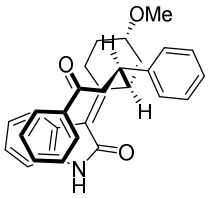
yield 22.3 mg, 48%; pale yellow solid; 76% ee, 97/3 dr; $[\alpha]_D{}^{19}$ = + 75.7 (c = 0.42 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm)

retention time: t_1 = 13.33 min, t_2 = 14.37 min, t_3 = 15.67 min, t_4 = 19.34 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.13 (m, 7H), 7.11 – 7.06 (m, 1H), 6.97 (td, *J* = 7.6, 0.8 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.30 (d, *J* = 16.4 Hz, 1H), 5.29 – 5.18 (m, 1H), 3.93 – 3.80 (m, 1H), 3.33 (d, *J* = 14.4 Hz, 1H), 3.10 (dd, *J* = 16.4, 6.4 Hz, 1H), 2.89 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.71 (td, *J* = 14.0, 4.8 Hz, 1H), 2.16 – 2.02 (m, 2H), 1.51 – 1.41 (m, 1H), 1.25 – 1.16 (m, 1H), 1.08 (td, *J* = 13.2, 4.8 Hz, 1H), 0.78 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 170.5, 166.7, 144.2, 142.1, 139.4, 134.6, 130.2, 128.8, 128.7, 128.4, 128.2, 128.1, 126.7, 126.6, 124.3, 124.0, 123.6, 121.9, 109.5, 45.5, 44.0, 41.5, 38.3, 36.4, 28.7, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{32}H_{31}NO_2Na$ ([M+Na^+]) = 484.2247, Found 484.2256.



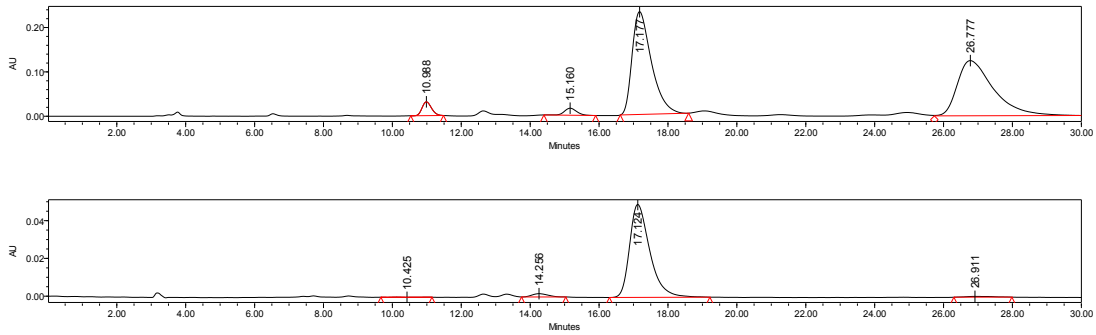
	Retention Time	Area	% Area
1	13.445	9082757	85.66
2	14.534	1247545	11.77
3	15.830	86048	0.81
4	19.516	186462	1.76

(*Z*)-3-((2*S*,4*S*)-4-Methoxy-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3ab)



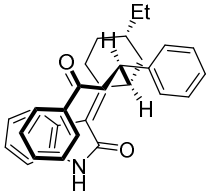
yield 39.0 mg, 86%; pale yellow solid; 98% ee, 97/3 dr; $[\alpha]_D^{19}$ = + 93.0 (c = 0.44 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 10.61 min, t_2 = 14.50 min, t_3 = 15.68 min, t_4 = 24.57 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.66 – 7.59 (m, 2H), 7.56 –

7.49 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.20 (m, 2H), 7.16 – 7.09 (m, 3H), 6.95 (td, *J* = 8.0, 1.2 Hz, 1H), 6.72 – 6.64 (m, 1H), 5.34 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.93 – 3.76 (m, 2H), 3.54 (dd, *J* = 17.0, 6.6 Hz, 1H), 3.42 – 3.34 (m, 1H), 3.23 (s, 3H), 3.14 (dd, *J* = 17.2, 6.4 Hz, 1H), 2.76 (td, *J* = 14.4, 5.2 Hz, 1H), 2.45 – 2.36 (m, 1H), 1.87 – 1.79 (m, 1H), 1.51 – 1.42 (m, 1H), 1.28 – 1.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 170.1, 163.2, 143.9, 139.4, 136.8, 132.6, 128.9, 128.3, 128.1, 127.9, 126.9, 124.5, 124.2, 123.6, 121.9, 109.4, 73.5, 56.0, 43.9, 43.1, 41.0, 33.9, 32.6, 27.2. HRMS (ESI-TOF) calcd for $C_{30}H_{29}NO_3Na$ ([M+Na$^+$]) = 474.2040, Found 474.2040.



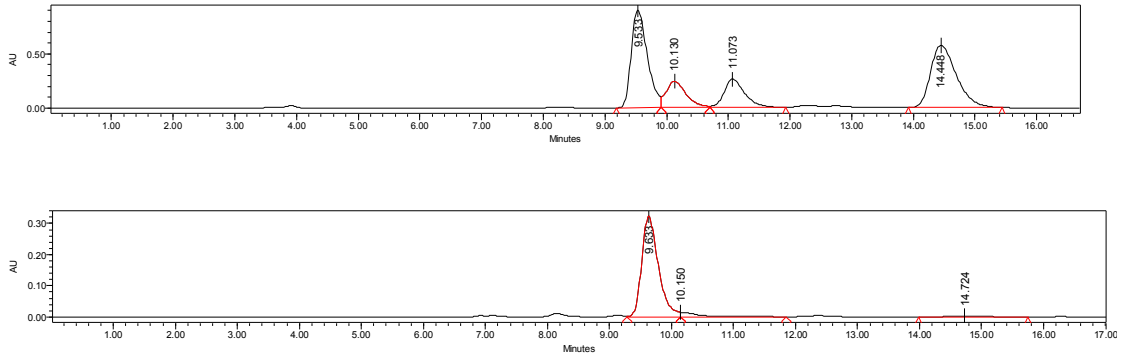
	Retention Time	Area	% Area
1	10.425	2374	0.11
2	14.256	55004	2.64
3	17.124	2005038	96.12
4	26.911	23658	1.13

(*Z*)-3-((2*S*,4*S*)-4-Ethyl-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3ac)



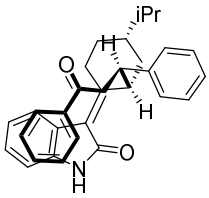
yield 42.5 mg, 95%; pale yellow solid; 96% ee, 95/5 dr; $[\alpha]_D^{22}$ = + 99.8 (c = 0.90 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 9.53 min, t_2 = 10.13 min, t_3 = 11.07 min, t_4 = 14.45 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.72 – 7.62 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.19 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 3H), 6.96 (td, *J* = 7.6, 0.8 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.26 (dd, *J* = 11.2, 2.8 Hz, 1H), 4.06 – 3.86 (m, 1H), 3.44 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.40 – 3.33 (m, 1H), 3.30 (dd, *J* = 17.0, 7.4 Hz, 1H), 2.72 (td, *J* = 14.0, 5.2 Hz, 1H), 2.15 (d, *J* =

11.6 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.58 – 1.49 (m, 1H), 1.32 – 1.12 (m, 2H), 1.10 – 0.99 (m, 2H), 0.78 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 170.8, 167.0, 144.2, 139.6, 137.0, 132.5, 128.7, 128.5, 128.1, 128.0, 127.9, 126.6, 124.3, 123.9, 123.5, 121.8, 109.5, 43.5, 43.0, 41.6, 36.0, 34.2, 32.7, 29.3, 28.7, 11.5. HRMS (ESI-TOF) calcd for $C_{31}H_{31}NO_2Na$ ([M+Na^+]) = 472.2247, Found 472.2251.



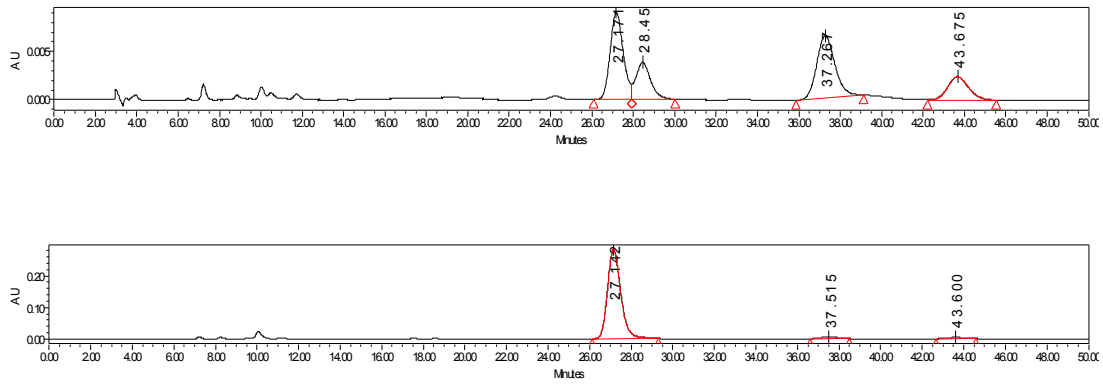
	Retention Time	Area	% Area
1	9.633	6025631	93.39
2	10.150	310387	4.81
3	14.724	115972	1.80

(*Z*)-3-((2*S*,4*S*)-4-Isopropyl-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3ad)



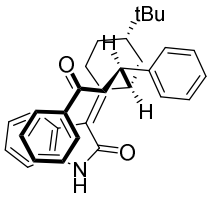
yield 41.3 mg, 89%; pale yellow solid; 95% ee, 98/2 dr; $[\alpha]_D^{19}$ = + 96.8 (c = 0.69 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 27.17 min, t_2 = 28.45 min, t_3 = 37.27 min, t_4 = 43.68 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.30 – 7.16 (m, 2H), 7.15 – 7.08 (m, 3H), 6.95 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 5.25 (d, J = 10.4 Hz, 1H), 4.04 – 3.91 (m, 1H), 3.48 – 3.22 (m, 3H), 2.76 – 2.62 (m, 1H), 2.10 (d, J = 11.6 Hz, 1H), 1.89 – 1.74 (m, 1H), 1.49 (d, J = 13.6 Hz, 1H), 1.32 – 1.23 (m, 2H), 1.15 – 1.05 (m, 1H), 0.78 (d, J = 5.2 Hz, 3H), 0.70 (d, J = 5.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 170.6, 167.0, 144.2, 139.5, 137.1, 132.5, 128.7, 128.5, 128.1, 128.0, 127.9, 126.6, 124.3, 123.9, 123.3, 121.8, 109.5, 43.4, 42.9, 41.6, 37.0,

33.1, 32.4, 31.6, 28.8, 20.0, 19.6. HRMS (ESI-TOF) calcd for $C_{32}H_{33}NO_2Na$ ([M+Na$^+$]) = 486.2404, Found 486.2401.

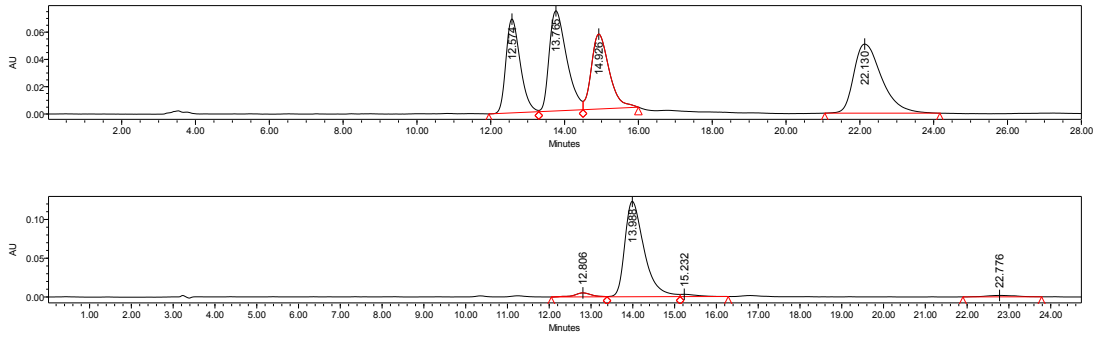


	Retention Time	Area	% Area
1	27.142	12604621	95.58
2	37.515	339896	2.58
3	43.600	243646	1.85

(*Z*)-3-((2*S*,4*S*)-4-(Tert-butyl)-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3ae)

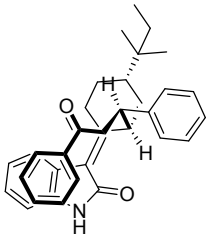


yield 42.4 mg, 89%; pale yellow solid; 96% ee, 95/5 dr; $[\alpha]_D^{22}$ = + 89.6 (c = 0.89 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 12.81 min, t_2 = 13.99 min, t_3 = 15.23 min, t_4 = 22.78 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.68 – 7.62 (m, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.23 – 7.17 (m, 1H), 7.19 – 7.18 (m, 3H), 6.95 (td, *J* = 7.6, 0.8 Hz, 1H), 6.80 – 6.74 (m, 1H), 5.40 – 5.16 (m, 1H), 4.05 – 3.91 (m, 1H), 3.44 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.41 – 3.34 (m, 1H), 3.28 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.70 (td, *J* = 13.6, 4.8 Hz, 1H), 2.19 – 2.09 (m, 1H), 1.83 – 1.74 (m, 1H), 1.51 (dd, *J* = 13.6, 2.4 Hz, 1H), 1.39 – 1.26 (m, 1H), 1.16 (td, *J* = 13.6, 4.8 Hz, 1H), 0.73 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 169.7, 166.0, 143.1, 138.6, 136.0, 131.5, 127.6, 127.1, 127.0, 126.9, 125.7, 123.3, 122.9, 122.2, 120.8, 108.5, 42.4, 41.9, 40.6, 39.6, 31.4, 30.0, 28.2, 28.1, 26.3. HRMS (ESI-TOF) calcd for $C_{33}H_{35}NO_2Na$ ([M+Na$^+$]) = 500.2560, Found 500.2564.

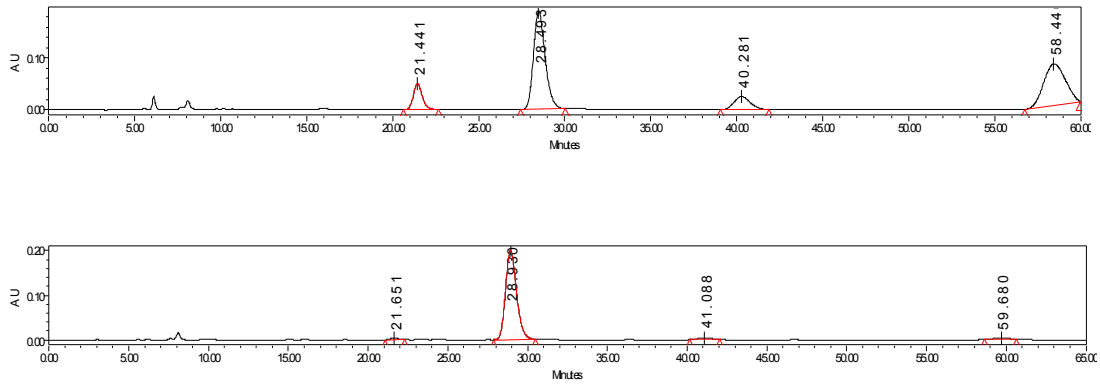


	Retention Time	Area	% Area
1	12.806	145910	3.43
2	13.988	3939120	92.57
3	15.232	80435	1.89
4	22.776	89996	2.11

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-3-Oxo-1,3-diphenylpropyl)-4-(tert-pentyl)cyclohexylidene)indolin-2-one (3af)

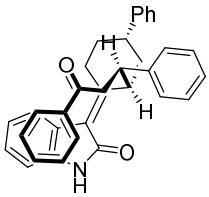


yield 44.7 mg, 91%; pale yellow solid; 96% ee, 96/4 dr; $[\alpha]_D^{19}$ = + 87.9 (c = 0.85 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 21.44 min, t_2 = 28.49 min, t_3 = 40.28 min, t_4 = 58.44 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.67 – 7.63 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.18 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 3H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.40 – 5.19 (m, 1H), 4.06 – 3.96 (m, 1H), 3.50 – 3.34 (m, 2H), 3.28 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.71 (td, *J* = 14.0, 4.8 Hz, 1H), 2.14 – 2.06 (m, 1H), 1.95 – 1.85 (m, 1H), 1.53 – 1.46 (m, 1H), 1.41 – 1.01 (m, 4H), 0.79 (t, *J* = 7.2 Hz, 3H), 0.68 (s, 3H), 0.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 170.7, 167.1, 144.1, 139.6, 137.0, 132.5, 128.6, 128.1, 128.0, 127.9, 126.7, 124.2, 123.9, 123.1, 121.8, 109.5, 43.5, 43.1, 41.6, 38.3, 34.7, 32.3, 30.7, 29.1, 28.8, 23.9, 23.8, 8.4. HRMS (ESI-TOF) calcd for $C_{34}H_{37}NO_2Na$ ([M+Na^+]) = 514.2717, Found 514.2718.

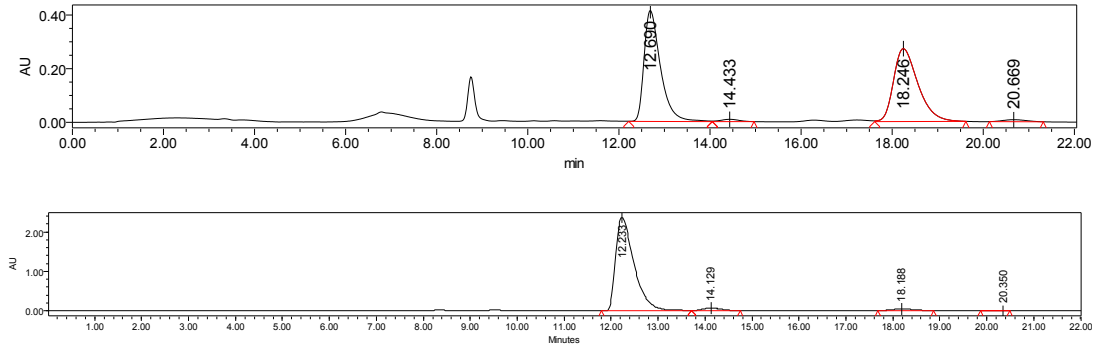


	Retention Time	Area	% Area
1	21.651	140066	1.38
2	28.930	9558191	94.28
3	41.088	248295	2.45
4	59.680	191168	1.89

(*Z*)-3-((2*S*,4*S*)-2-((*R*)-3-Oxo-1,3-diphenylpropyl)-4-phenylcyclohexylidene)indolin-2-one (3ag)

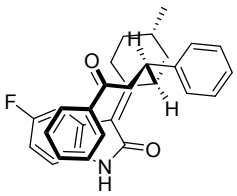


yield 46.2 mg, 93%; pale yellow solid; 95% ee, 97/3 dr; $[\alpha]_D^{17}$ = + 62.5 (c = 0.75 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 12.44 min, t_2 = 14.20 min, t_3 = 18.24 min, t_4 = 20.47 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.73 – 7.65 (m, 2H), 7.64 – 7.54 (m, 3H), 7.37 – 7.28 (m, 3H), 7.25 – 7.10 (m, 9H), 6.98 (td, *J* = 7.6, 0.8 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 5.49 – 5.31 (m, 1H), 4.25 – 4.11 (m, 1H), 3.58 – 3.43 (m, 2H), 3.39 – 3.23 (m, 2H), 2.92 (td, *J* = 14.0, 5.2 Hz, 1H), 2.30 (d, *J* = 11.2 Hz, 1H), 1.82 (qd, *J* = 12.8, 3.8 Hz, 1H), 1.70 – 1.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 170.4, 165.1, 145.7, 144.0, 139.5, 137.0, 132.6, 128.9, 128.5, 128.4, 128.2, 128.2, 127.9, 126.8, 126.8, 126.3, 124.4, 123.9, 123.8, 121.9, 109.5, 43.4, 43.1, 41.6, 37.5, 34.8, 28.8. HRMS (ESI-TOF) calcd for $C_{35}H_{32}NO_2$ ([M+H$^+$]) = 498.2428, Found 498.2433.

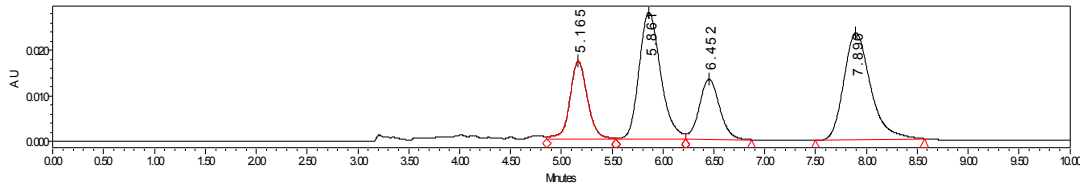


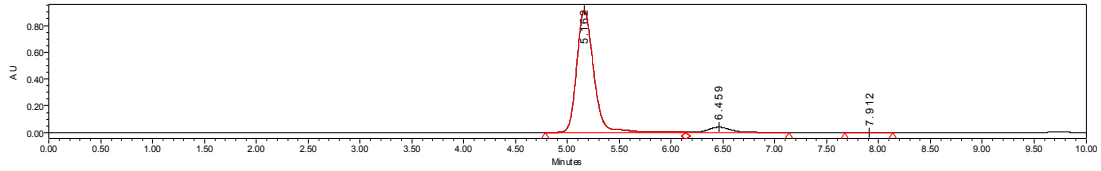
	Retention Time	Area	% Area
1	12.233	64726521	94.77
2	14.129	2008287	2.94
3	18.188	1562861	2.29
4	20.350	856	0.00

(*Z*)-5-Fluoro-3-((2*S*,4*S*)-4-methyl-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3ah)



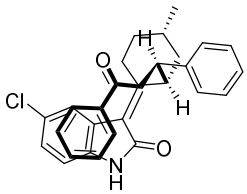
yield 29.8 mg, 66%; pale yellow solid; 89% ee, 99/1 dr; $[\alpha]_D^{22}$ = + 90.3 (c = 0.61 in CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 5.17 min, t_2 = 5.86 min, t_3 = 6.45 min, t_4 = 7.90 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.69 – 7.63 (m, 2H), 7.53 – 7.46 (m, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.25 – 7.21 (m, 1H), 7.19 – 7.12 (m, 2H), 6.84 (td, *J* = 8.8, 2.4 Hz, 1H), 6.64 (dd, *J* = 8.4, 4.8 Hz, 1H), 5.24 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.06 – 3.94 (m, 1H), 3.47 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.17 (dd, *J* = 16.8, 6.4 Hz, 2H), 2.74 (td, *J* = 14.0, 4.8 Hz, 1H), 2.17 – 2.10 (m, 2H), 1.47 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.25 – 1.16 (m, 1H), 1.08 (td, *J* = 13.6, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 170.6, 168.6, 159.7, 157.4, 144.2, 136.9, 135.4, 132.6, 128.8, 128.4, 128.2, 127.9, 126.7, 124.8, 124.7, 123.5, 114.3, 114.1, 112.1, 111.8, 109.6, 109.5, 43.7, 43.1, 41.8, 38.3, 36.4, 28.8, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}FNO_2Na$ ([M+Na^+]) = 476.1996, Found 476.1996.



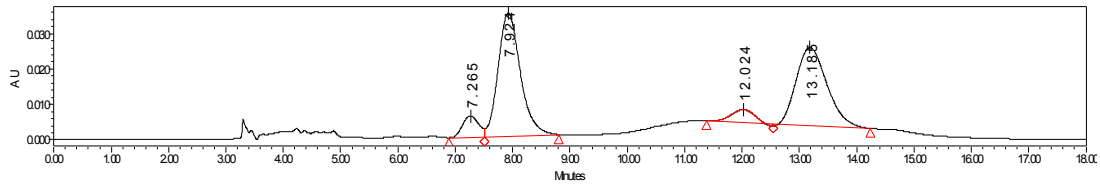


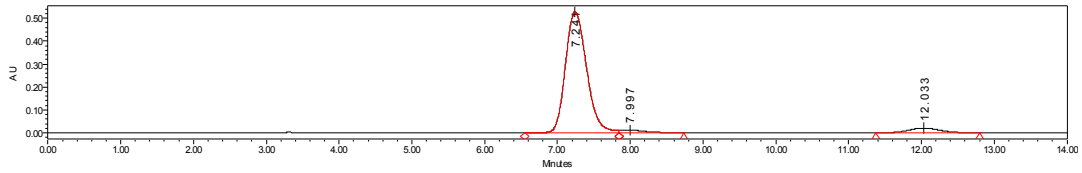
	Retention Time	Area	% Area
1	5.162	10316191	94.37
2	6.459	606764	5.55
3	7.912	9211	0.08

(*Z*)-5-Chloro-3-((2*S*,4*S*)-4-methyl-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3ai)



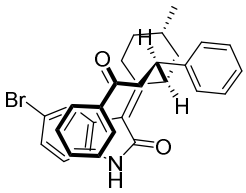
yield 31.1 mg, 66%; pale yellow solid; 89% ee, 98/2 dr; $[\alpha]_D^{22}$ = + 112.1 (c = 0.60 in CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH = 95/5, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 7.26 min, t_2 = 7.92 min, t_3 = 12.02 min, t_4 = 13.19 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.69 – 7.62 (m, 2H), 7.53 – 7.45 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.20 (m, 2H), 7.19 – 7.12 (m, 2H), 7.09 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.21 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.04 – 3.87 (m, 1H), 3.47 (dd, *J* = 17.0, 6.6 Hz, 1H), 3.22 – 3.08 (m, 2H), 2.74 (td, *J* = 14.0, 4.8 Hz, 1H), 2.18 – 2.06 (m, 2H), 1.46 (dd, *J* = 13.8, 1.8 Hz, 1H), 1.30 – 1.14 (m, 1H), 1.07 (td, *J* = 13.2, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 170.2, 169.0, 144.2, 137.8, 136.9, 132.6, 128.8, 128.4, 128.2, 127.9, 127.6, 127.0, 126.7, 125.2, 124.5, 123.0, 110.1, 43.8, 43.1, 41.8, 38.3, 36.4, 29.0, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{34.9689}ClNO_2Na$ ([M+Na$^+$]) = 492.1701, Found 492.1695. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{36.9659}ClNO_2Na$ ([M+Na$^+$]) = 494.1671, Found 494.1680.



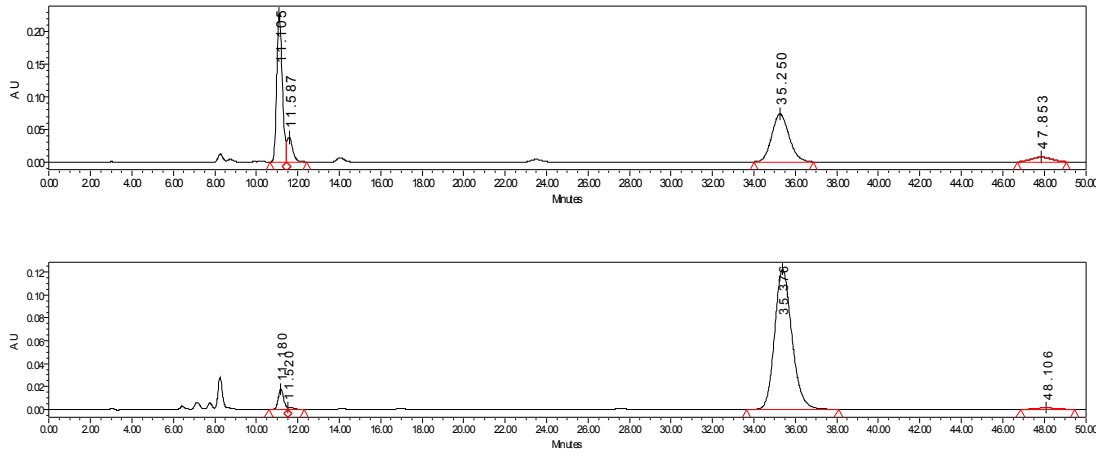


	Retention Time	Area	% Area
1	7.241	10659988	92.36
2	7.997	262679	2.28
3	12.033	619189	5.36

(*Z*)-5-Bromo-3-((2*S*,4*S*)-4-methyl-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3aj)

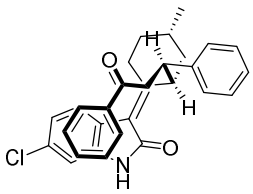


yield 34.9 mg, 68%; pale yellow solid; 91% ee, 98/2 dr; $[\alpha]_D^{19}$ = + 109.8 (c = 0.62 in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 11.18 min, t_2 = 11.52 min, t_3 = 35.38 min, t_4 = 48.11 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.70 – 7.59 (m, 3H), 7.53 – 7.45 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.26 – 7.20 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 5.21 (dd, *J* = 11.2, 3.2 Hz, 1H), 4.04 – 3.92 (m, 1H), 3.48 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.21 – 3.02 (m, 2H), 2.75 (td, *J* = 14.0, 4.8 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.47 (dd, *J* = 13.2, 2.0 Hz, 1H), 1.28 – 1.16 (m, 1H), 1.07 (td, *J* = 13.6, 4.8 Hz, 1H), 0.79 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 170.1, 169.0, 144.2, 138.2, 136.9, 132.6, 130.5, 128.8, 128.4, 128.2, 127.9, 127.2, 126.7, 125.6, 122.9, 114.4, 110.7, 43.8, 43.1, 41.8, 38.3, 36.4, 29.1, 26.0, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{78.9183}BrNO_2Na$ ([M+Na$^+$]) = 536.1196, Found 536.1196. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{80.9163}BrNO_2Na$ ([M+Na$^+$]) = 538.1175, Found 538.1177.



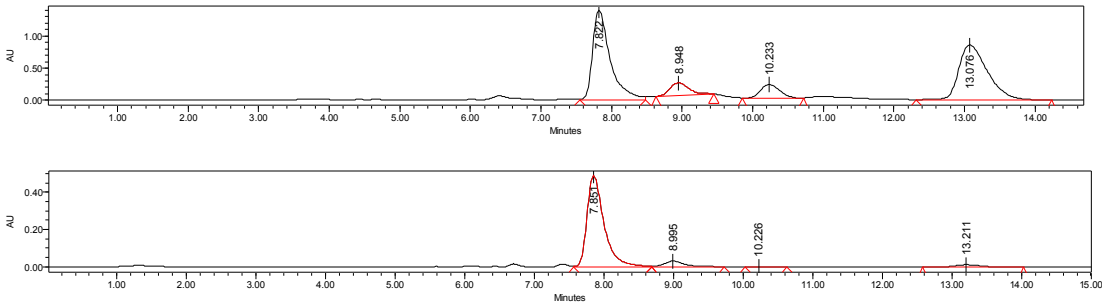
	Retention Time	Area	% Area
1	11.180	320130	4.27
2	11.520	27765	0.37
3	35.376	7063257	94.18
4	48.106	88681	1.18

(*Z*)-6-Chloro-3-((2*S*,4*S*)-4-methyl-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3ak)



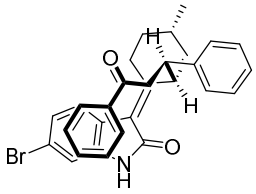
yield 38.5 mg, 82%; pale yellow solid; 92% ee, 91/9 dr; $[\alpha]_D^{22}$ = + 92.3 (c = 0.74 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 7.85 min, t_2 = 9.00 min, t_3 = 10.23 min, t_4 = 13.21 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.67 – 7.61 (m, 2H), 7.52 – 7.43 (m, 3H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.26 – 7.21 (m, 1H), 7.19 – 7.13 (m, 2H), 6.92 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 5.21 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.05 – 3.93 (m, 1H), 3.47 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.24 – 3.11 (m, 2H), 2.74 (td, *J* = 14.0, 4.8 Hz, 1H), 2.17 – 2.05 (m, 2H), 1.48 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.28 – 1.15 (m, 1H), 1.08 (td, *J* = 13.6, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 170.6, 167.7, 144.2, 140.4, 136.9, 133.4, 132.6, 128.8, 128.3, 128.2, 127.9, 126.7, 125.1, 122.8, 122.3, 121.7, 109.9, 43.8, 43.1, 41.8, 38.3, 36.3, 29.1, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{34.9689}ClNO_2Na$ ([M+Na^+]) = 492.1701, Found 492.1695. HRMS (ESI-TOF) calcd for

$C_{30}H_{28}{}^{36.9659}ClNO_2Na$ ([M+Na$^+$]) = 494.1671, Found 494.1675.

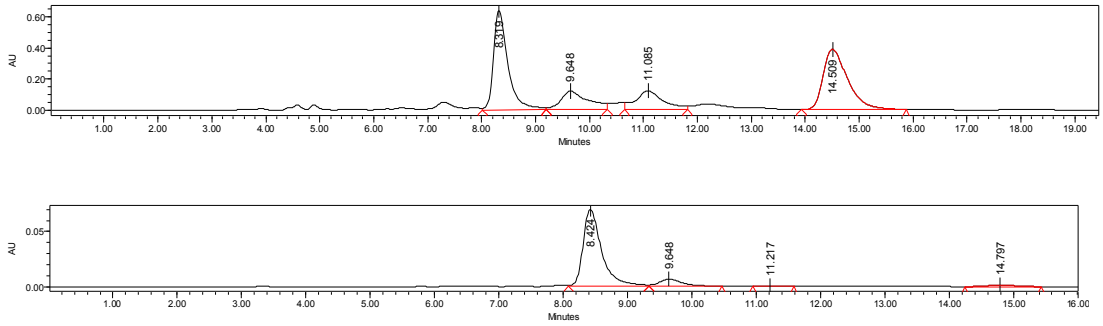


	Retention Time	Area	% Area
1	7.851	8485762	87.27
2	8.995	794635	8.17
3	10.226	75962	0.78
4	13.211	367035	3.77

(*Z*)-6-Bromo-3-((2*S*,4*S*)-4-methyl-2-((*R*)-3-oxo-1,3-diphenylpropyl)cyclohexylidene)indolin-2-one (3al)



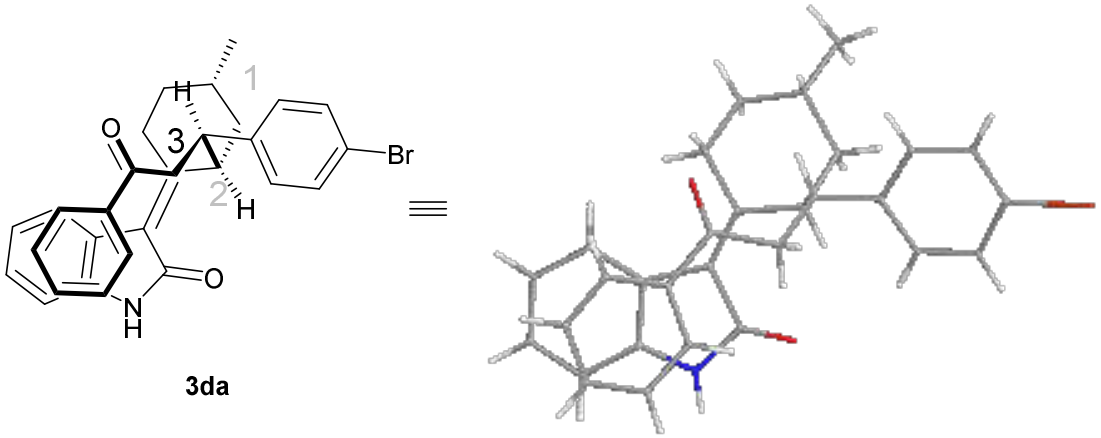
yield 38.7 mg, 75%; pale yellow solid; 94% ee, 90/10 dr; $[\alpha]_D^{22}$ = + 88.2 (c = 0.78 in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, low rate 1.0 mL/min, λ = 254 nm) retention time: t_1 = 8.42 min, t_2 = 9.65 min, t_3 = 11.22 min, t_4 = 14.80 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.71 – 7.60 (m, 2H), 7.54 – 7.45 (m, 2H), 7.41 – 7.35 (m, 3H), 7.34 – 7.29 (m, 1H), 7.28 – 7.20 (m, 1H), 7.19 – 7.12 (m, 2H), 7.08 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 5.21 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.05 – 3.87 (m, 1H), 3.47 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.25 – 3.11 (m, 2H), 2.73 (td, *J* = 14.0, 5.2 Hz, 1H), 2.18 – 2.04 (m, 2H), 1.48 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.27 – 1.16 (m, 1H), 1.09 (td, *J* = 13.8, 4.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 170.5, 168.1, 144.2, 140.6, 136.9, 132.6, 128.8, 128.3, 128.2, 127.9, 126.8, 125.4, 124.6, 122.9, 122.8, 121.3, 112.8, 43.8, 43.1, 41.8, 38.2, 36.3, 29.1, 26.1, 22.0. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{78.9183}BrNO_2Na$ ([M+Na$^+$]) = 536.1196, Found 536.1199. HRMS (ESI-TOF) calcd for $C_{30}H_{28}{}^{80.9163}BrNO_2Na$ ([M+Na$^+$]) = 538.1175, Found 538.1183.



	Retention Time	Area	% Area
1	8.424	1416119	87.15
2	9.648	158682	9.77
3	11.217	5866	0.36
4	14.797	44221	2.72

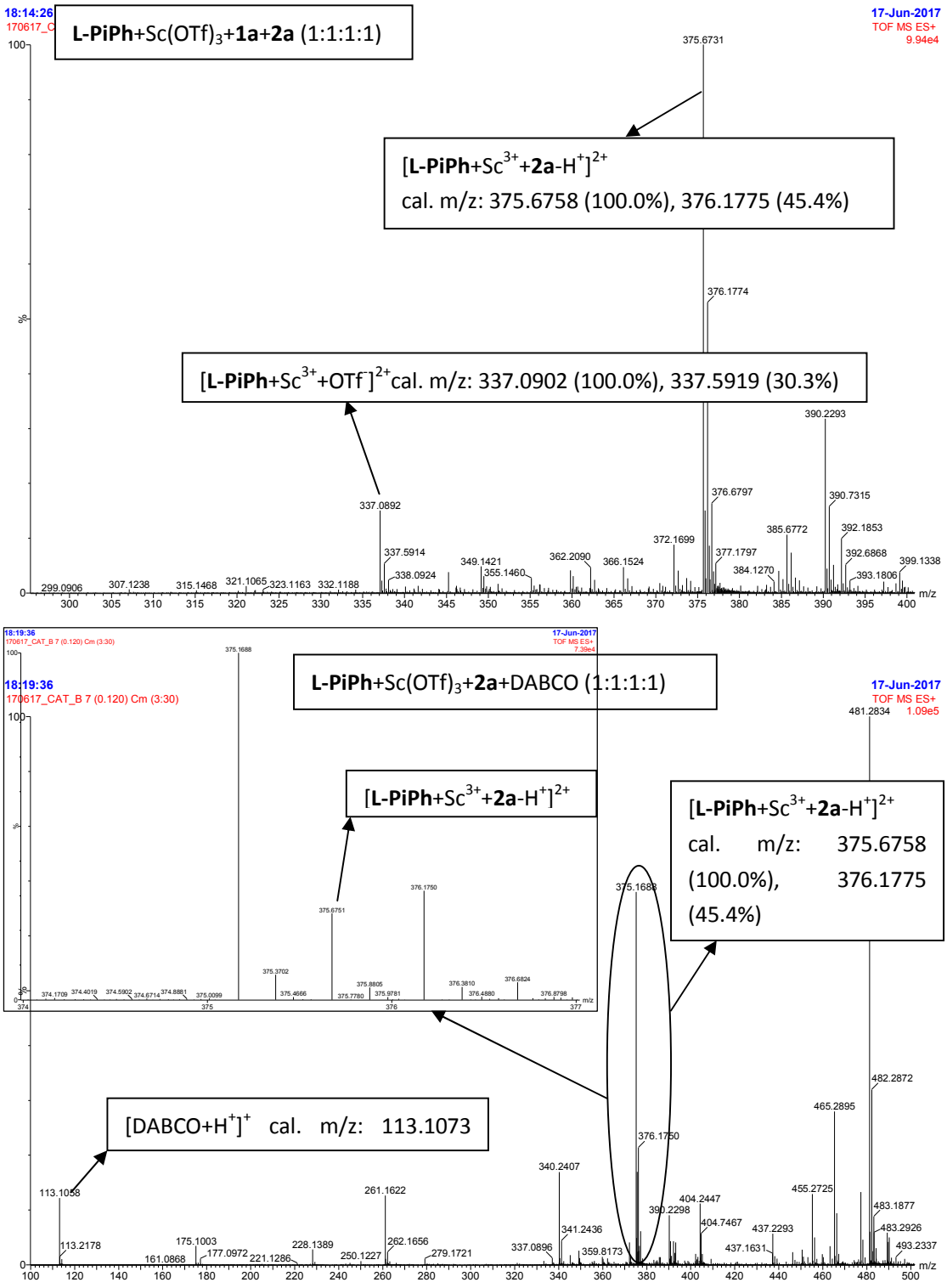
(I) The X-ray data for 3da

The cycloadduct **3da** was recrystallized from EtOAc and Pet. CCDC-1536145 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./data_request/cif.



3da

(J) HRMS analysis

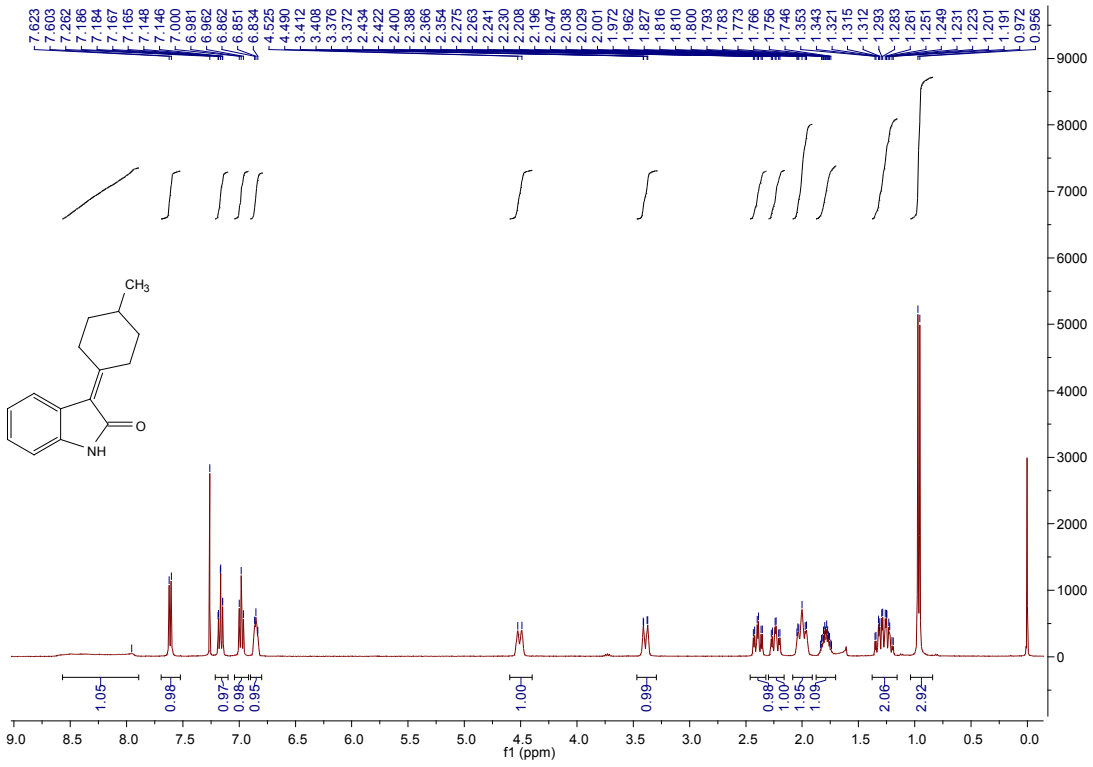


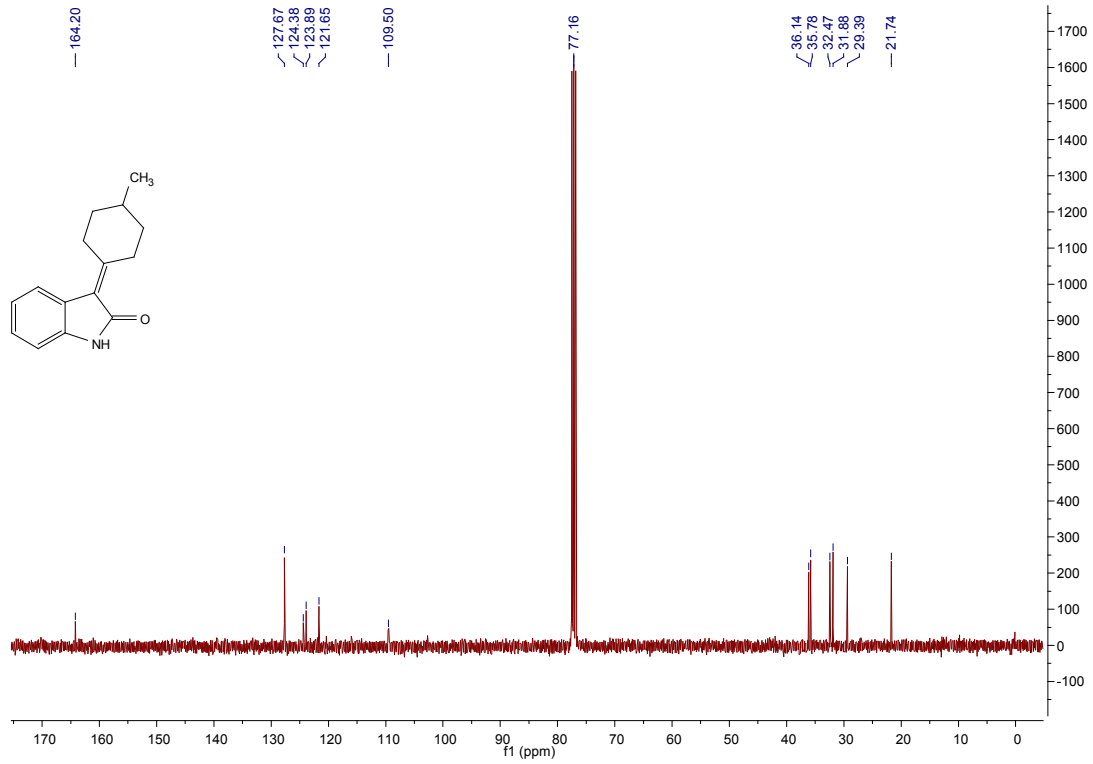
(K) References

1. (a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett.*, 2005, 2445. (b) X. H. Liu, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2011, **44**, 574. (c) X. H. Liu, L. L. Lin and X. M. Feng, *Org. Chem. Front.*, 2014, **1**, 298.

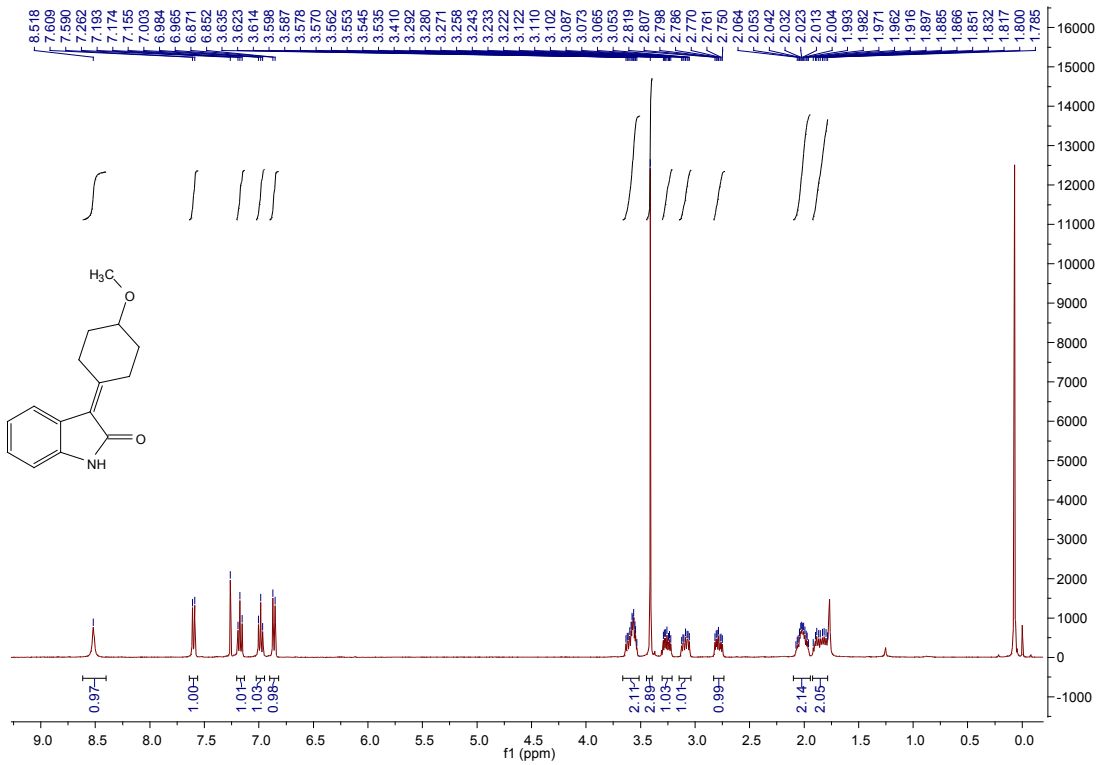
(L) Copies of NMR spectra

2a





2b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3.623
3.614
3.598
3.587
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3.280
3.271
3.258
3.243
3.233
3.222
3.122
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3.102
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3.073
3.065
3.053
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2.807
2.798
2.786
2.770
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2.750
2.064
2.053
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2.032
2.023
2.013
2.004
1.993
1.982
1.971
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1.916
1.897
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1.851
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1.817
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1.785
H3C
O
O
NH
0.97
1.00
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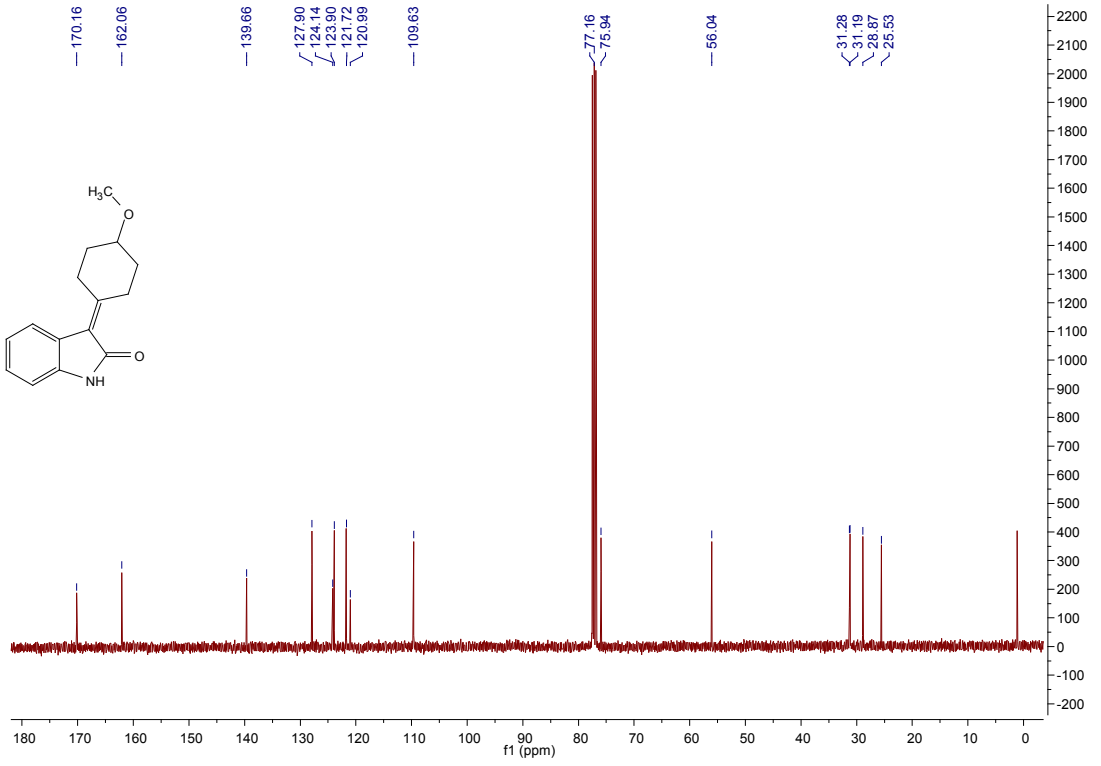
0.98
2.11
2.89
1.03
1.01
0.99
2.14
2.05
f1 (ppm)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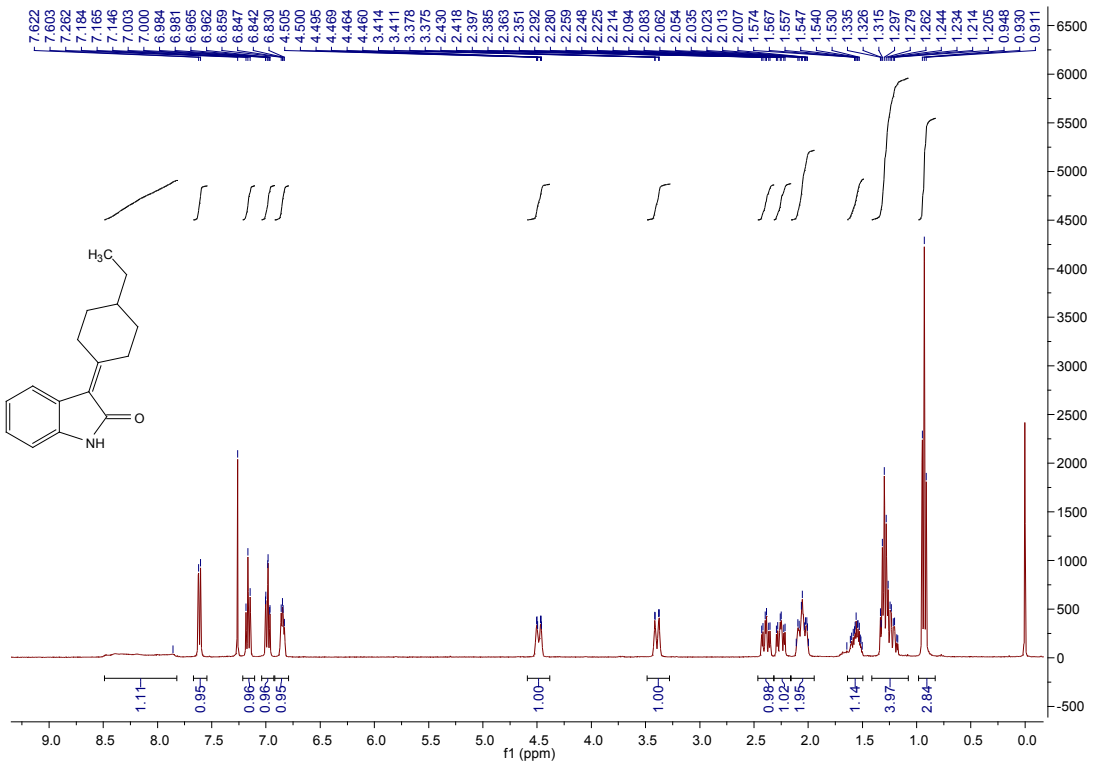
28.87
25.53
H3C
O
O
NH
f1 (ppm)

2c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O
NH
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0.98
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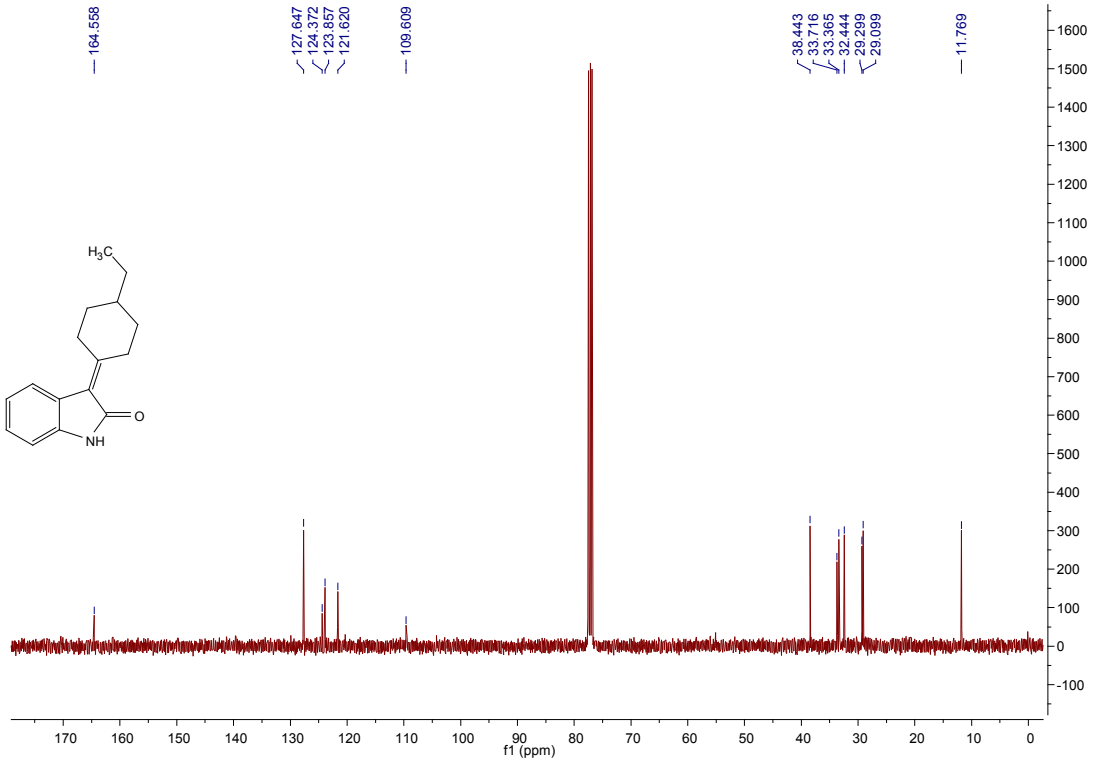
f1 (ppm)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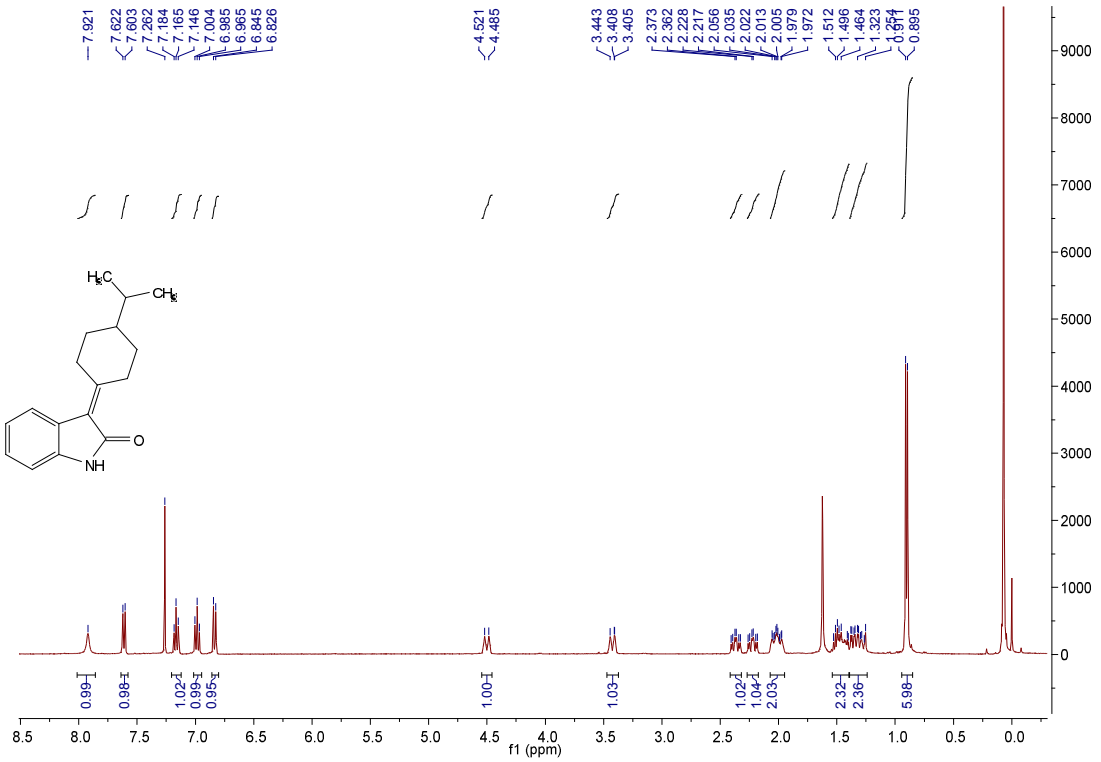
O
NH
f1 (ppm)

2d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0.99
0.95
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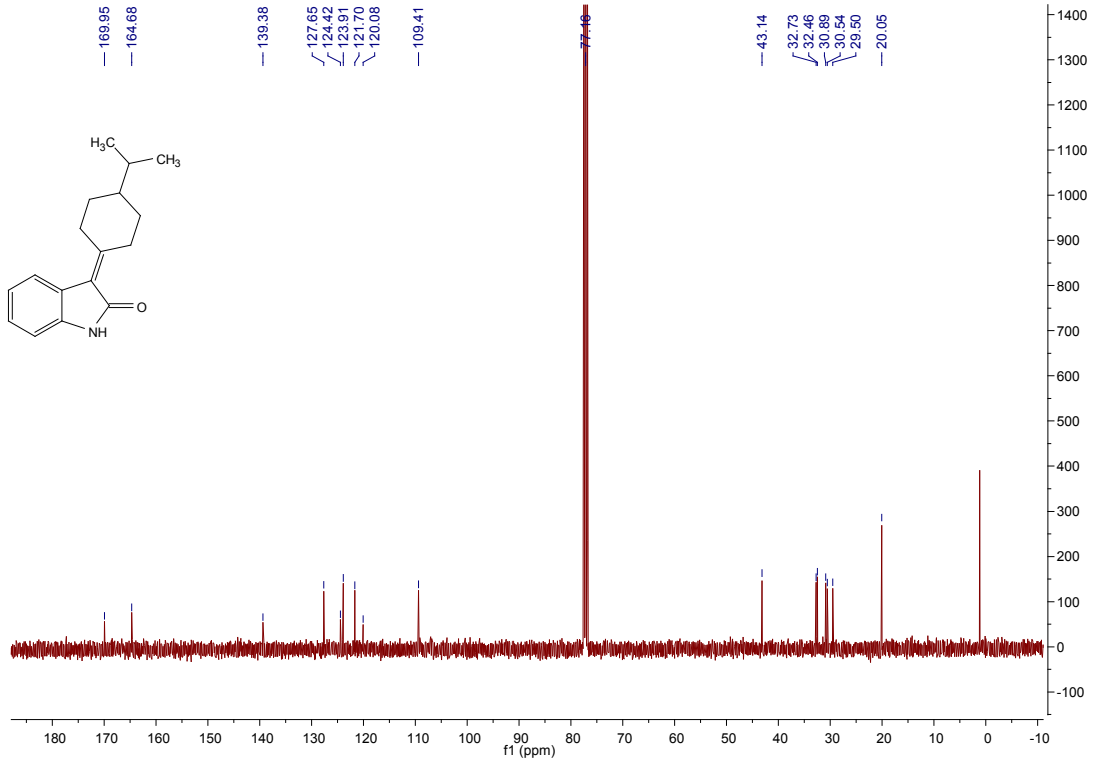
1.03
1.02
1.04
2.03
2.32
2.36
5.98
f1 (ppm)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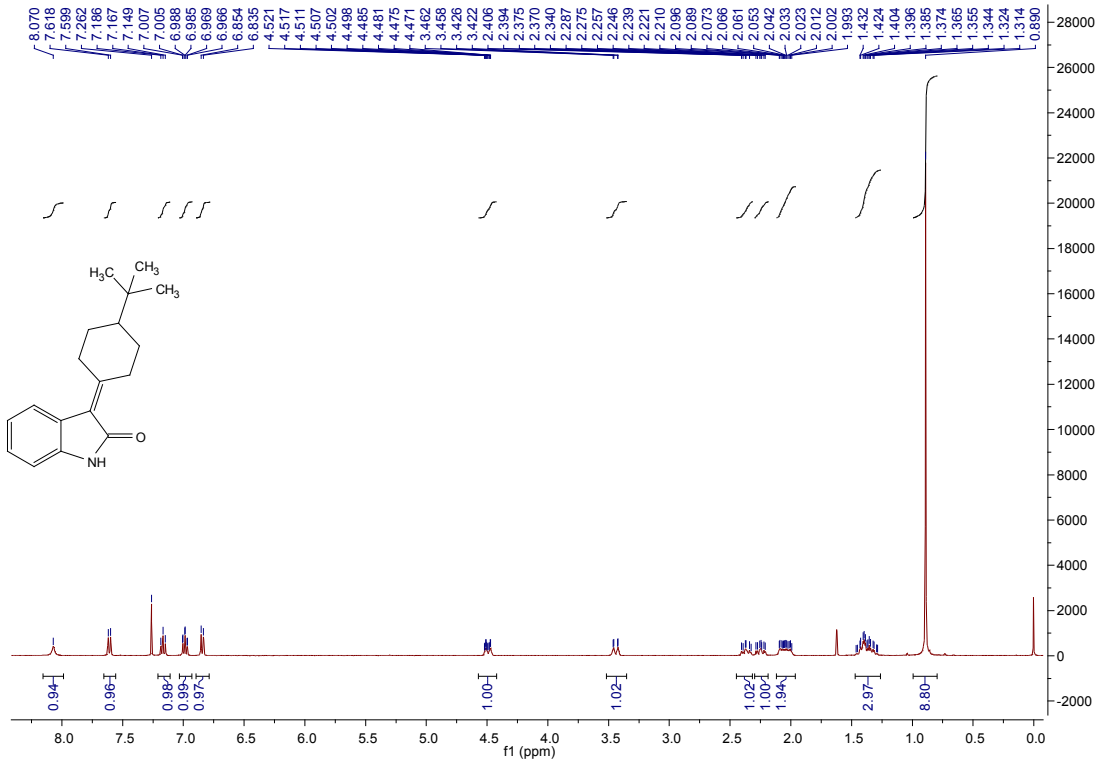
164.68
139.38
127.65
124.42
123.91
121.70
120.08
109.41
77.16
43.14
32.73
32.46
30.89
30.54
29.50
20.05
H3C
CH3
O
NH
f1 (ppm)

2e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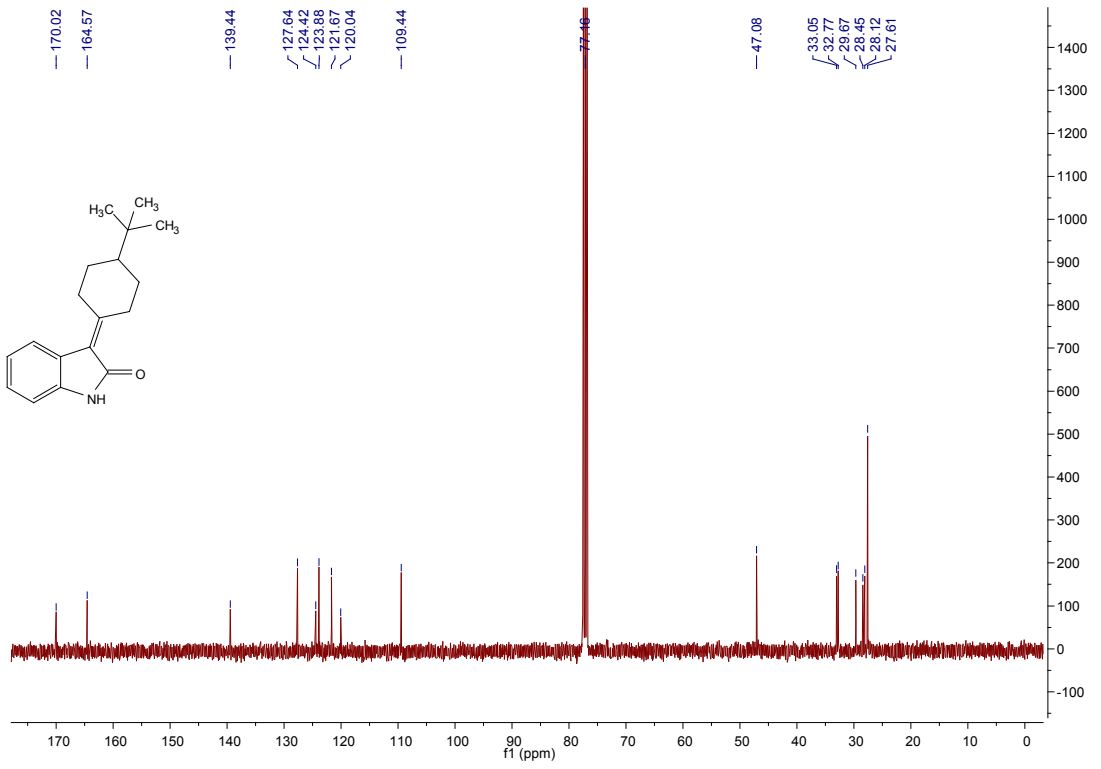
7.599
7.282
7.166
7.167
7.149
7.007
7.005
6.988
6.985
6.969
6.966
6.854
6.835
4.521
4.517
4.511
4.507
4.502
4.498
4.485
4.481
4.475
4.471
3.462
3.458
3.426
3.422
2.406
2.394
2.375
2.370
2.340
2.287
2.275
2.257
2.246
2.239
2.221
2.210
2.096
2.089
2.073
2.066
2.061
2.053
2.042
2.033
2.023
2.012
2.002
1.993
1.432
1.424
1.404
1.396
1.385
1.374
1.365
1.355
1.344
1.324
1.314
0.890
H3C
CH3
CH3
O
NH
0.94
0.96
0.98
0.99
0.97
1.00
1.02
1.02
1.00
1.94
2.97
8.80
f1 (ppm)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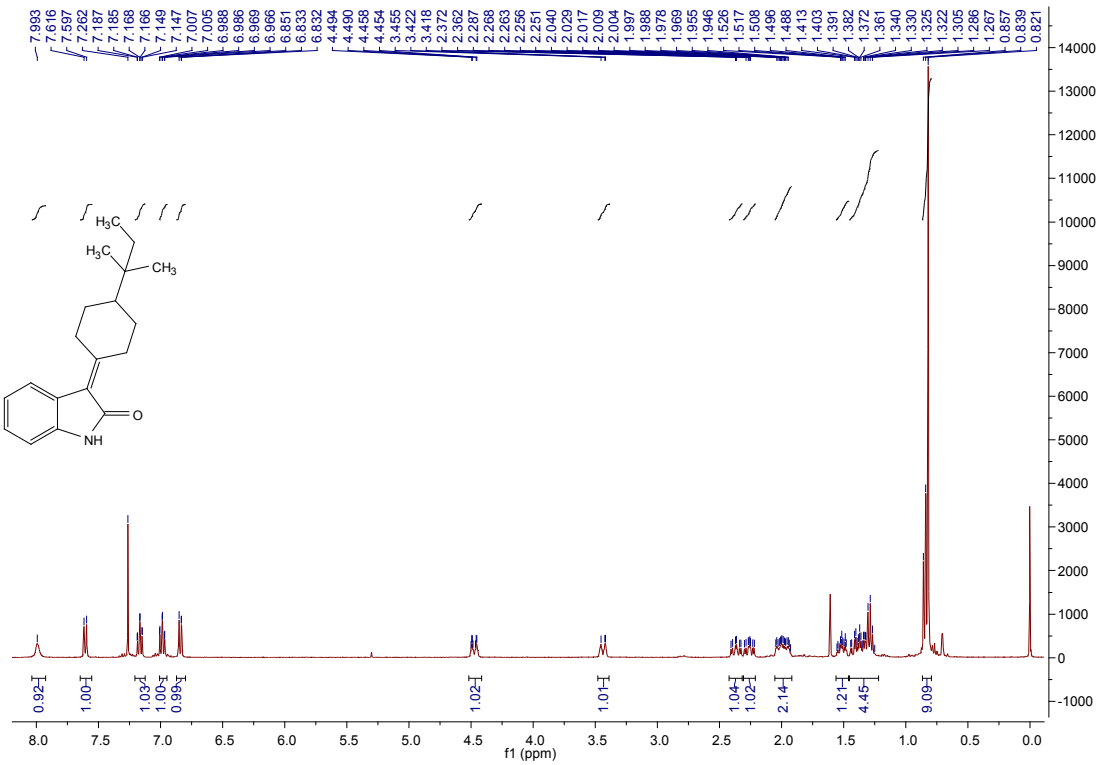
164.57
139.44
127.64
124.42
123.88
121.67
120.04
109.44
77.48
47.08
33.05
32.77
29.67
28.45
28.12
27.61
H3C
CH3
CH3
O
NH
f1 (ppm)

2f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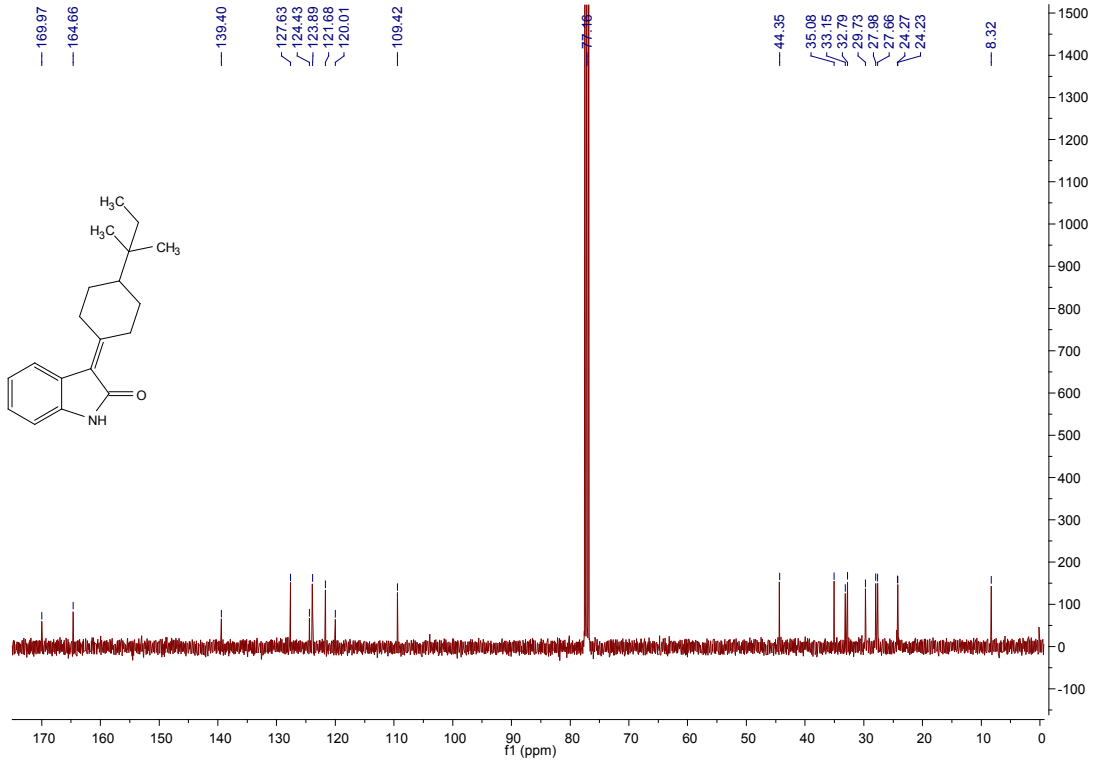
7.616
7.597
7.262
7.187
7.185
7.168
7.166
7.149
7.147
7.007
7.005
6.988
6.986
6.969
6.966
6.851
6.833
6.832
4.494
4.490
4.458
4.454
3.455
3.422
3.418
2.372
2.362
2.287
2.268
2.263
2.236
2.251
2.040
2.029
2.017
2.009
2.004
1.997
1.988
1.978
1.969
1.955
1.946
1.526
1.517
1.508
1.496
1.488
1.413
1.403
1.391
1.382
1.372
1.361
1.340
1.330
1.325
1.322
1.305
1.286
1.267
0.857
0.839
0.821
H3C
H3C
CH3
O
NH
0.92
1.00
1.03
1.00
0.99
1.02
1.01
1.04
1.02
2.14
1.21
4.45
9.09
f1 (ppm)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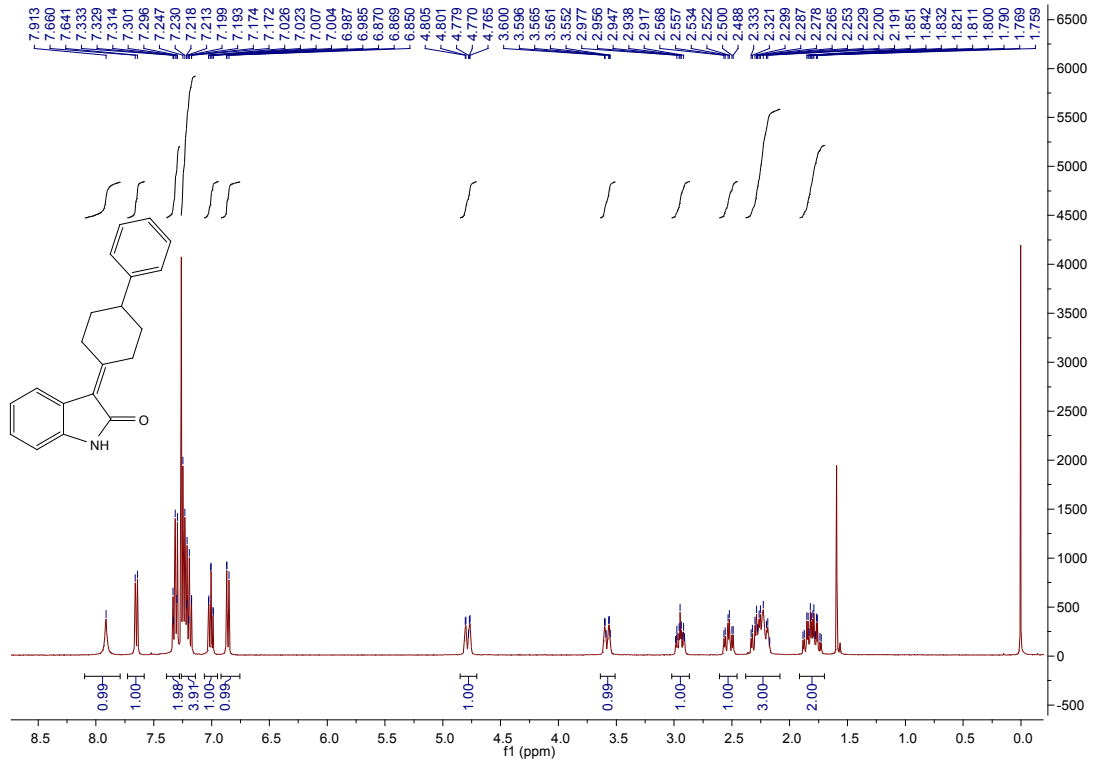
164.66
139.40
127.63
124.43
123.89
121.68
120.01
109.42
77.16
44.35
35.08
33.15
32.79
29.73
27.98
27.66
24.27
24.23
8.32
H3C
H3C
CH3
O
NH
f1 (ppm)

2g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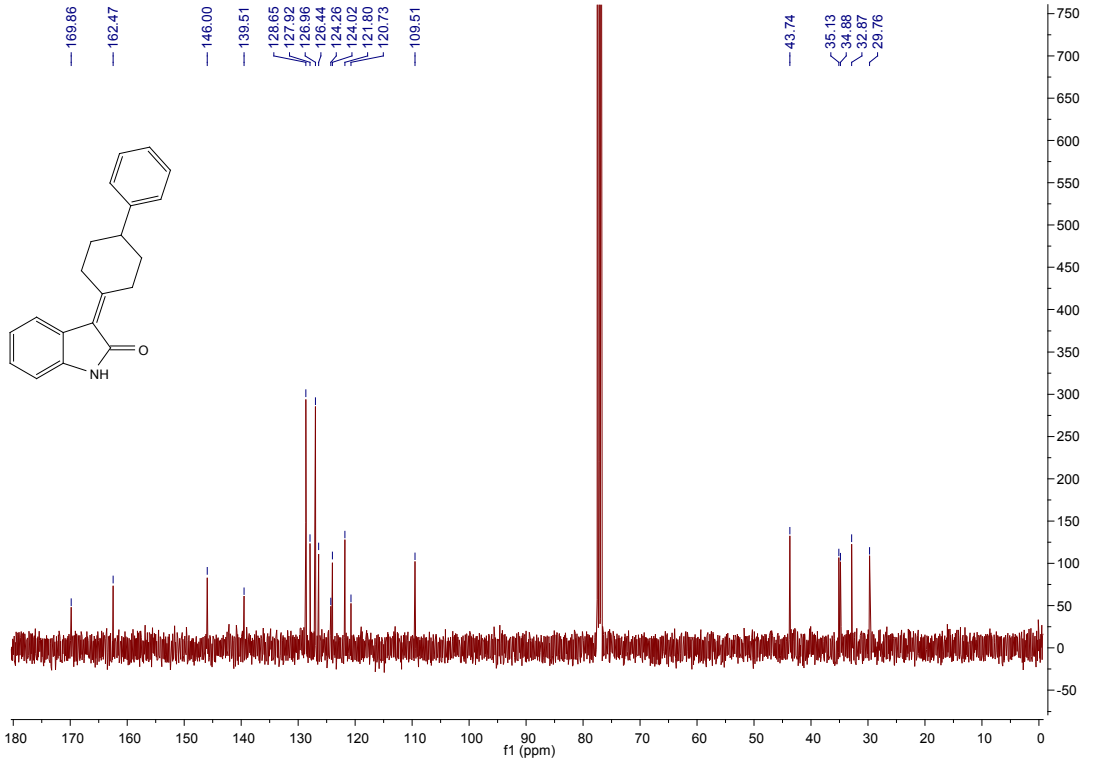
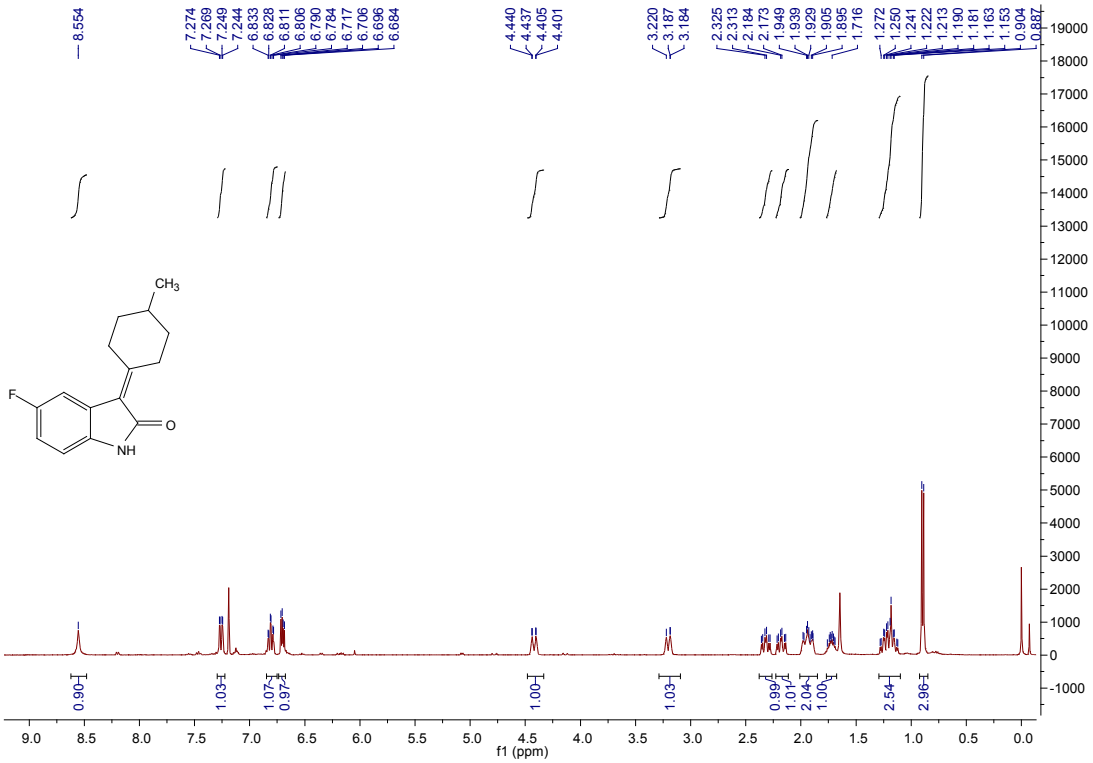
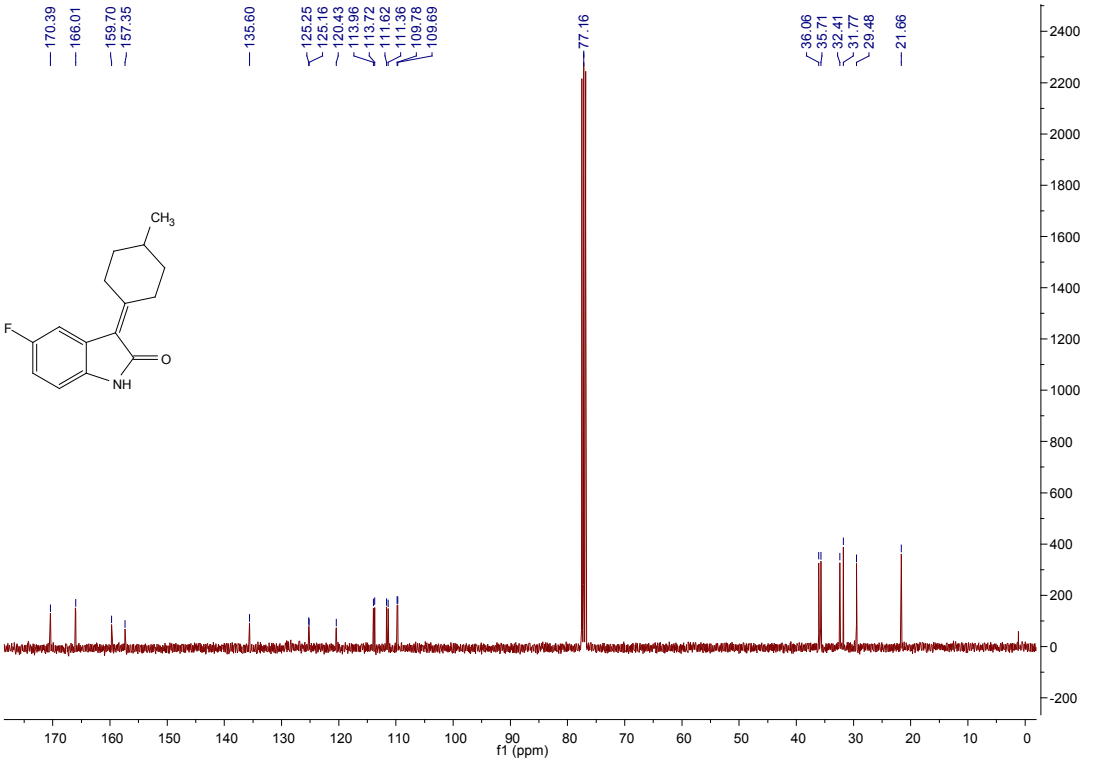
7.660
7.641
7.333
7.329
7.314
7.301
7.296
7.247
7.230
7.218
7.213
7.199
7.193
7.174
7.172
7.026
7.023
7.007
7.004
6.987
6.985
6.870
6.869
6.850
4.805
4.801
4.779
4.770
4.765
3.600
3.596
3.565
3.561
3.552
2.977
2.956
2.947
2.938
2.917
2.568
2.557
2.534
2.522
2.500
2.488
2.333
2.321
2.299
2.287
2.278
2.265
2.253
2.229
2.200
2.191
1.851
1.842
1.832
1.821
1.811
1.800
1.790
1.769
1.759
NH
O
0.99
1.00
1.98
3.91
1.00
0.99
1.00
0.99
1.00
1.00
3.00
2.00
f1 (ppm)

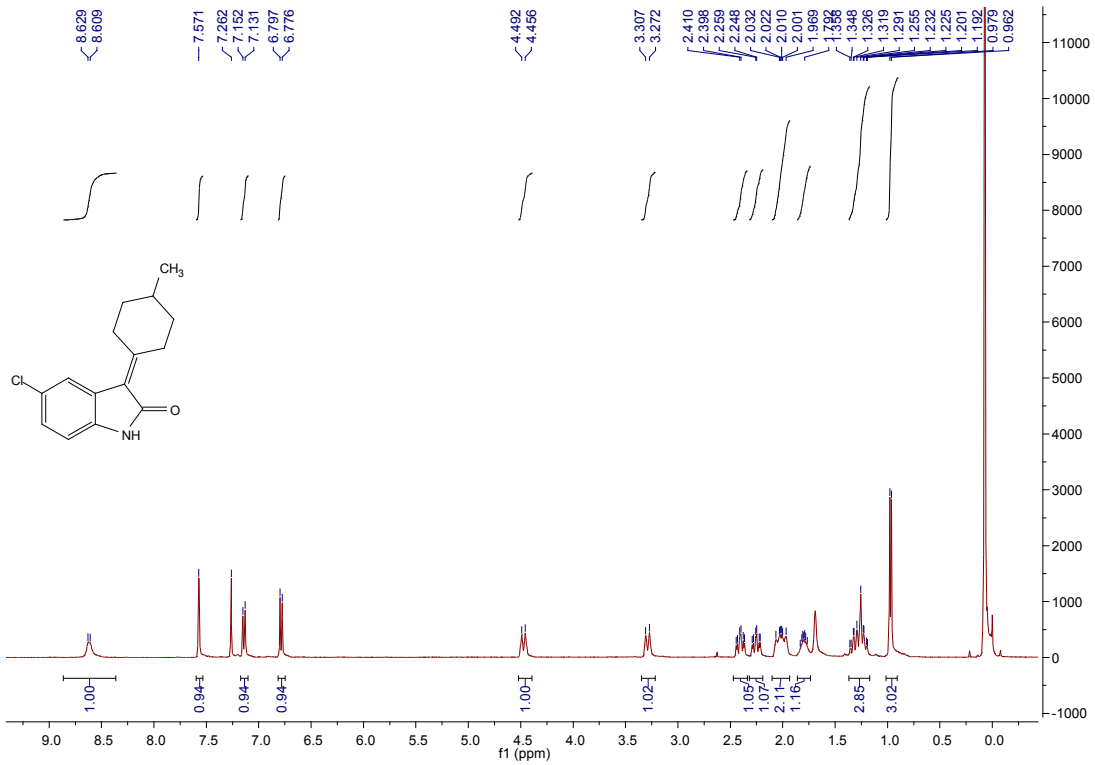

169.86
162.47
146.00
139.51
128.65
127.92
126.96
126.44
124.26
124.02
121.80
120.73
109.51
43.74
35.13
34.88
32.87
29.76
NH
O
f1 (ppm)

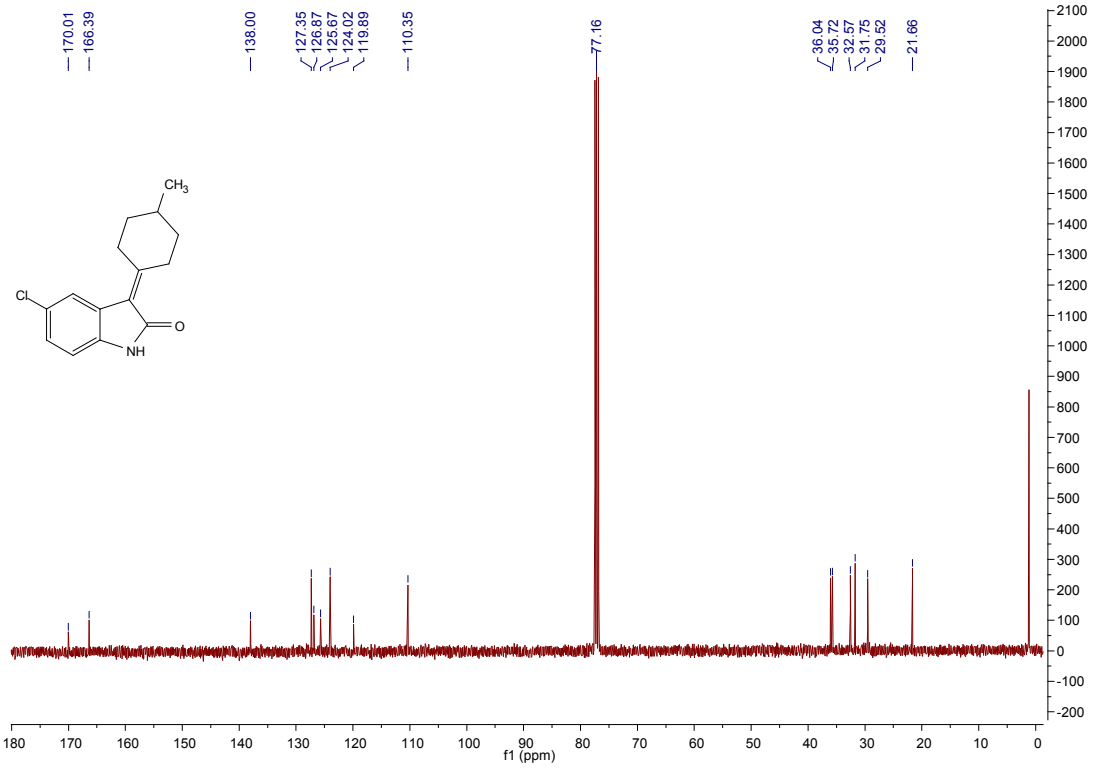
2h


8.554
7.274
7.269
7.249
7.244
6.833
6.828
6.811
6.806
6.790
6.784
6.717
6.706
6.696
6.684
4.440
4.437
4.405
4.401
3.220
3.187
3.184
2.325
2.313
2.184
2.173
1.949
1.939
1.929
1.905
1.895
1.716
1.272
1.250
1.241
1.222
1.213
1.190
1.181
1.163
1.153
0.904
0.887
CH3
F
O
NH
0.90
1.03
1.07
0.97
1.00
1.03
0.99
1.01
2.04
1.00
2.54
2.96
f1 (ppm)

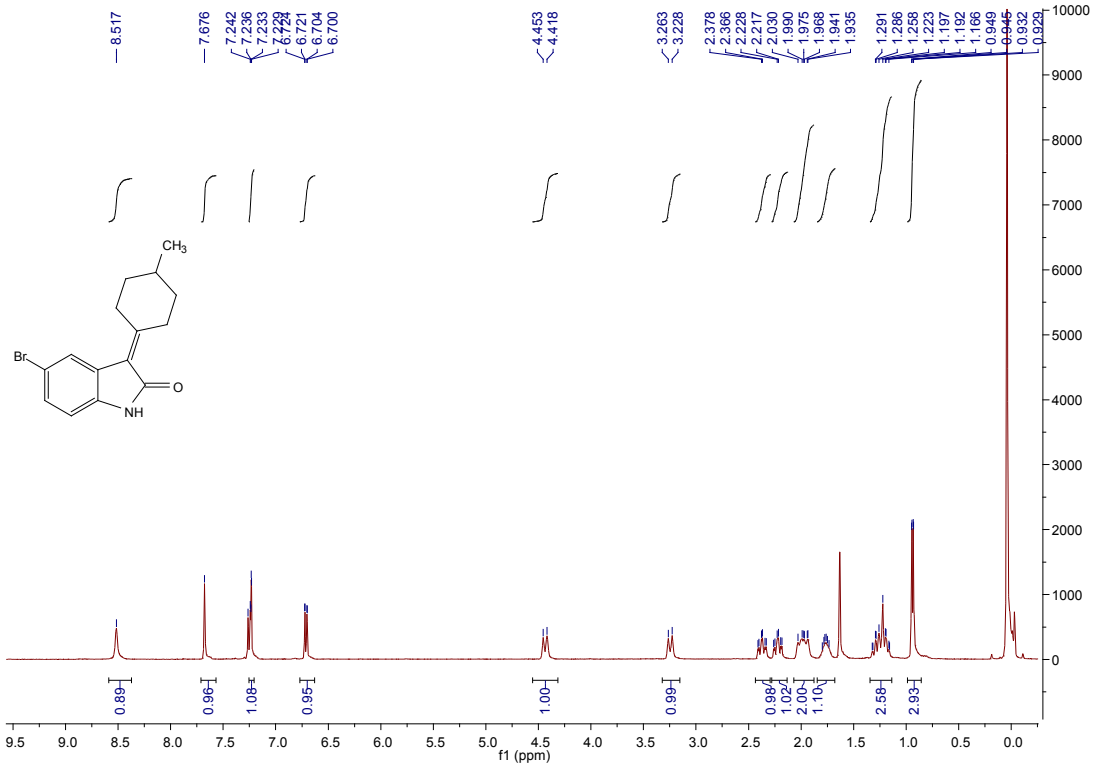

170.39
166.01
159.70
157.35
135.60
125.25
125.16
120.43
113.96
113.72
111.62
111.36
109.78
109.69
77.16
36.06
35.71
32.41
31.77
29.48
21.66
CH3
F
O
NH
f1 (ppm)

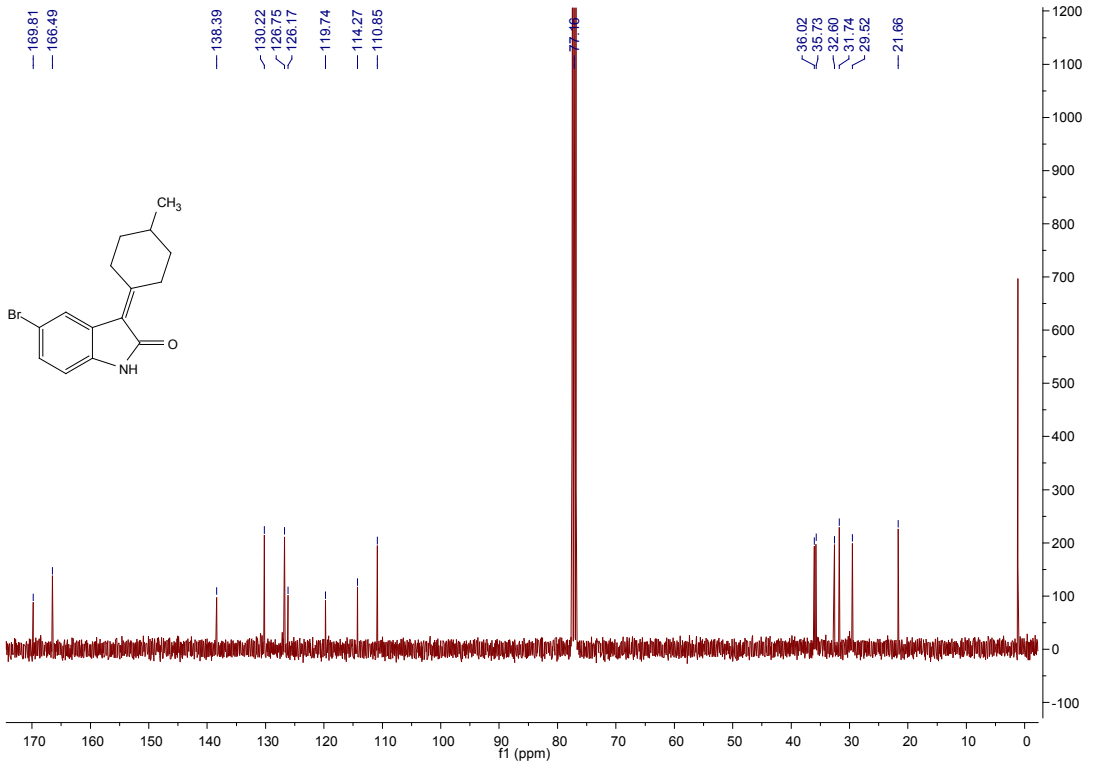
2i


8.629
8.609
7.571
7.262
7.152
7.131
6.797
6.776
4.492
4.456
3.307
3.272
2.410
2.398
2.259
2.248
2.032
2.022
2.010
2.001
1.969
1.348
1.326
1.319
1.291
1.255
1.232
1.225
1.201
1.192
0.979
0.962
CH3
Cl
O
NH
1.00
0.94
0.94
0.94
1.00
1.02
1.05
1.07
2.11
1.16
2.86
3.02
f1 (ppm)

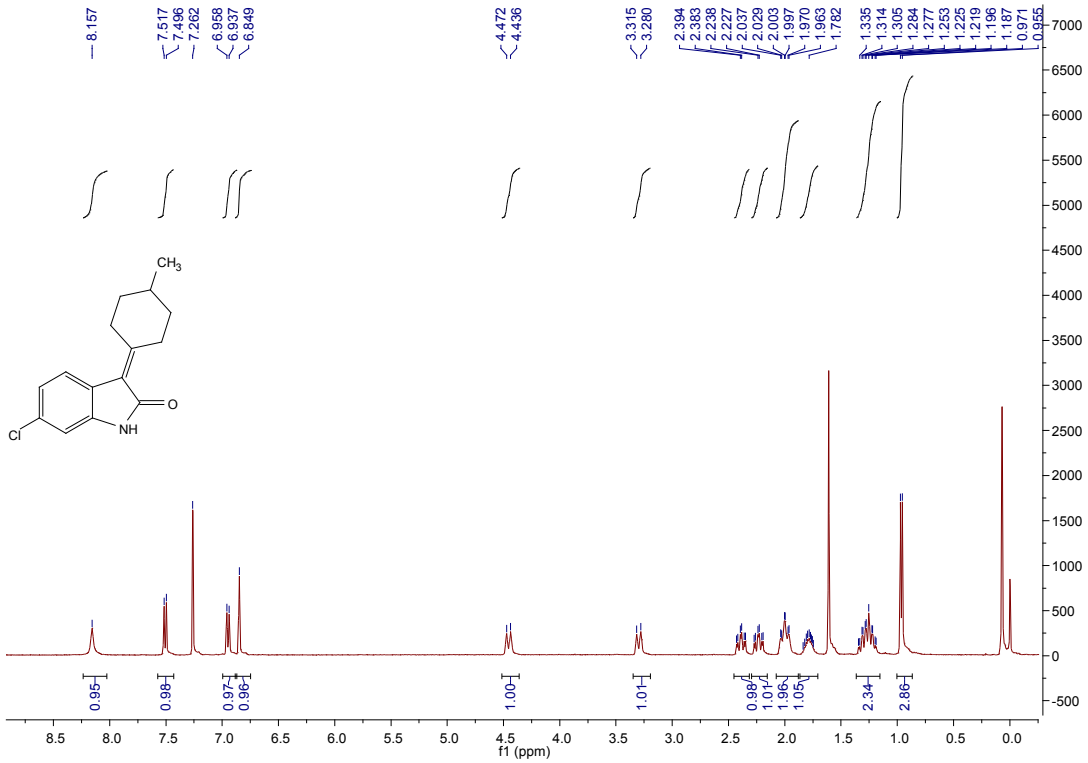

170.01
166.39
138.00
127.35
126.87
125.67
124.02
119.89
110.35
77.16
36.04
35.72
32.57
31.75
29.52
21.86
CH3
Cl
O
NH
f1 (ppm)

2j


8.517
7.676
7.242
7.236
7.233
6.721
6.704
6.700
4.453
4.418
3.263
3.228
2.378
2.366
2.228
2.217
2.030
1.990
1.975
1.968
1.941
1.935
1.291
1.286
1.258
1.223
1.197
1.192
1.166
0.949
0.932
0.929
CH3
Br
O
NH
0.89
0.96
1.08
0.95
1.00
0.99
0.98
1.02
2.00
1.10
2.58
2.93
f1 (ppm)


169.81
166.49
138.39
130.22
126.75
126.17
119.74
114.27
110.85
77.16
36.02
35.73
32.60
31.74
29.52
21.66
CH3
Br
O
NH
f1 (ppm)

2k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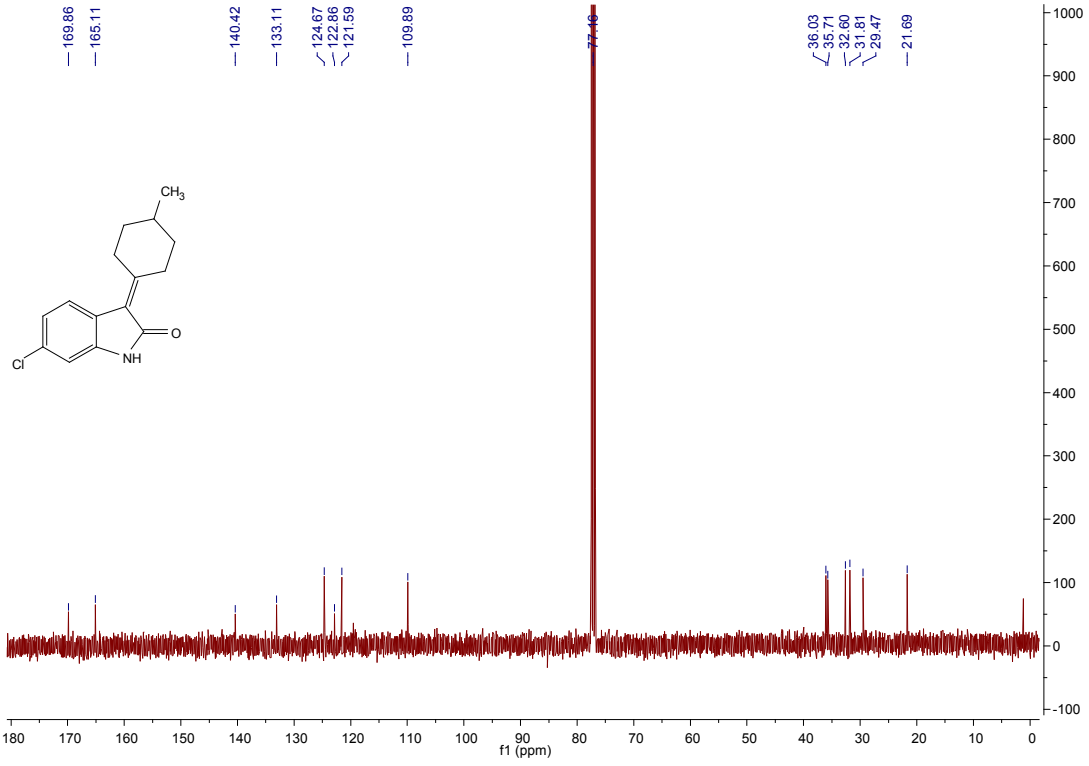
7.517
7.496
7.262
6.958
6.937
6.849
4.472
4.436
3.315
3.280
2.394
2.383
2.238
2.227
2.037
2.029
2.003
1.997
1.970
1.963
1.782
1.335
1.314
1.305
1.284
1.277
1.253
1.225
1.219
1.196
1.187
0.971
0.955
CH3
O
NH
Cl
0.95
0.98
0.97
0.96
1.00
1.01
0.98
1.01
1.96
1.05
2.34
2.86
f1 (ppm)


169.86
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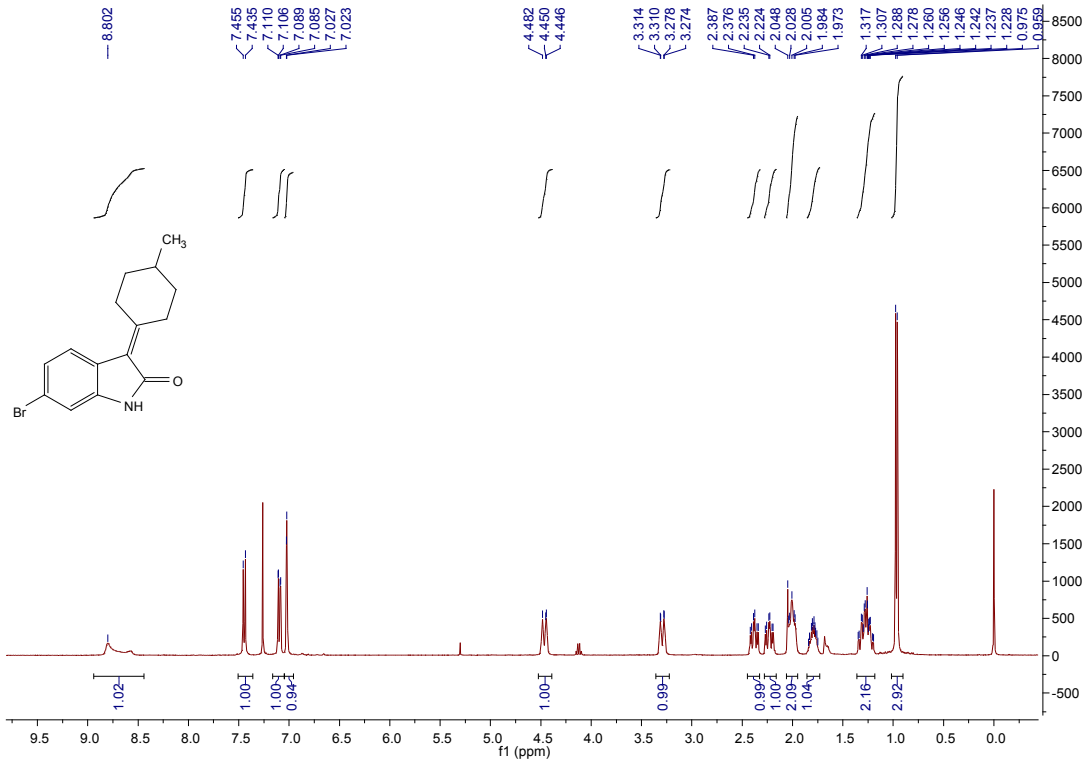
140.42
133.11
124.67
122.86
121.59
109.89
77.16
36.03
35.71
32.60
31.81
29.47
21.69
CH3
O
NH
Cl
f1 (ppm)

2l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7.435
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7.106
7.089
7.085
7.027
7.023
4.482
4.450
4.446
3.314
3.310
3.278
3.274
2.387
2.376
2.235
2.224
2.048
2.028
2.005
1.984
1.973
1.317
1.307
1.288
1.278
1.260
1.256
1.246
1.242
1.237
1.228
0.975
0.959
CH3
O
NH
Br
1.02
1.00
1.00
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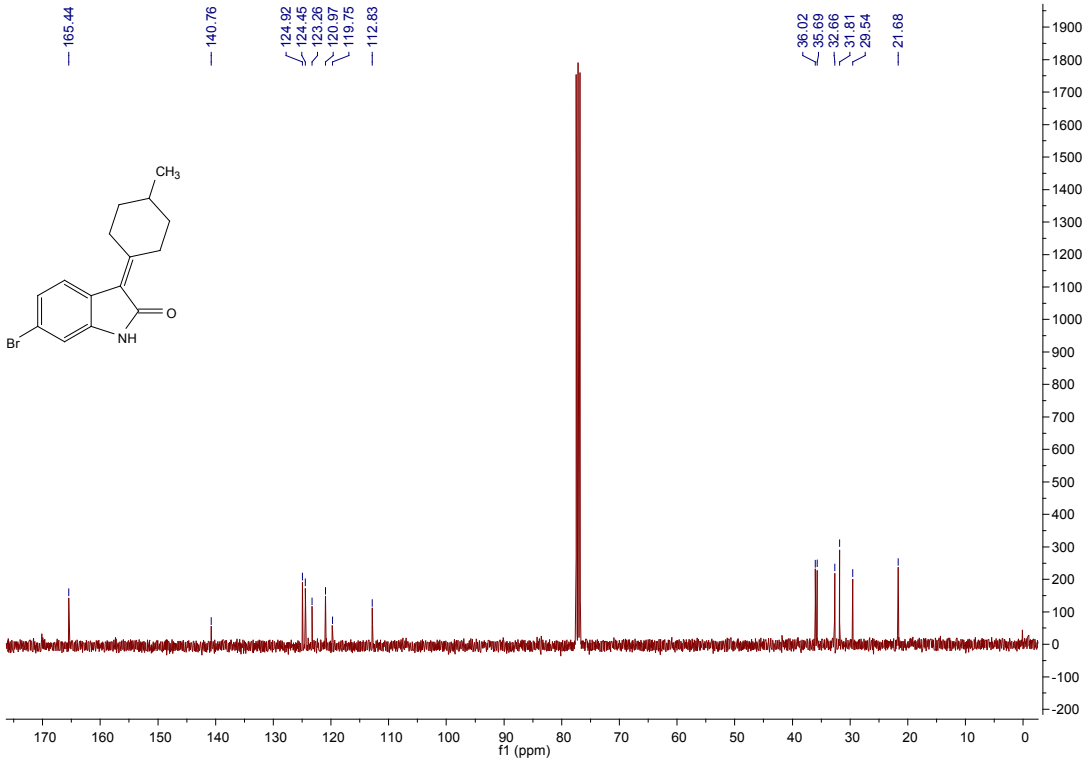
1.00
0.99
0.99
1.00
2.09
1.04
2.16
2.92
f1 (ppm)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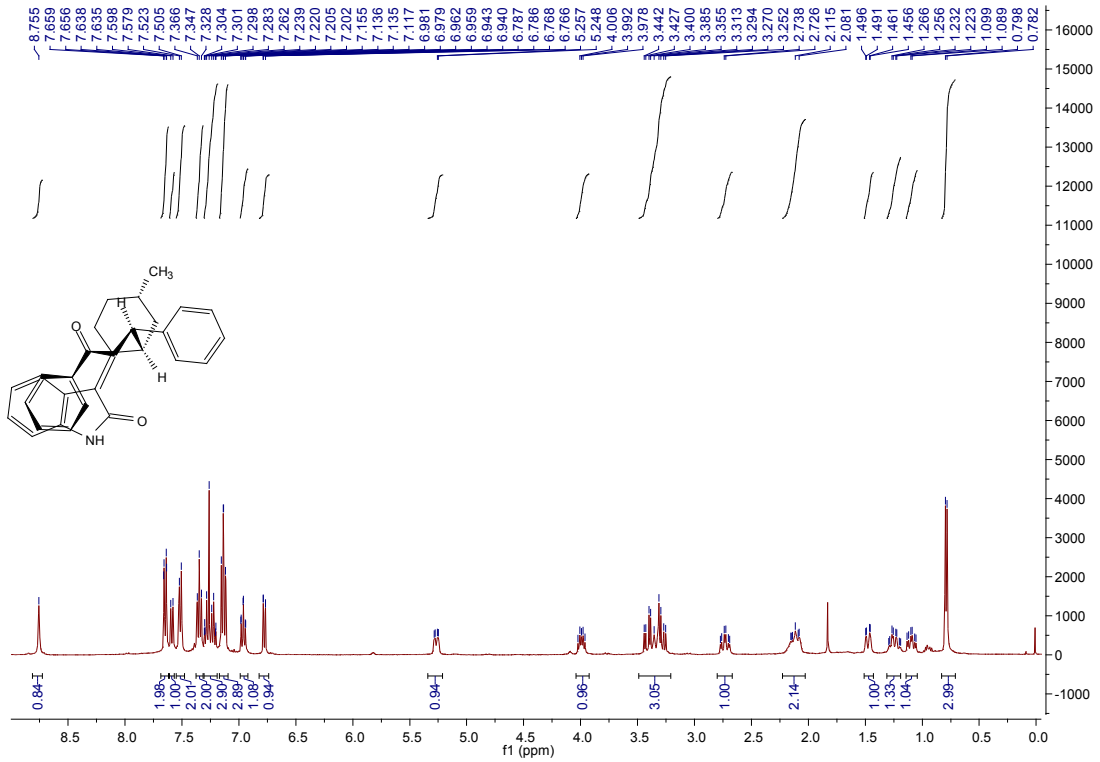
124.45
123.26
120.97
119.75
112.83
36.02
35.69
32.86
31.81
29.54
21.68
CH3
O
NH
Br
f1 (ppm)

3aa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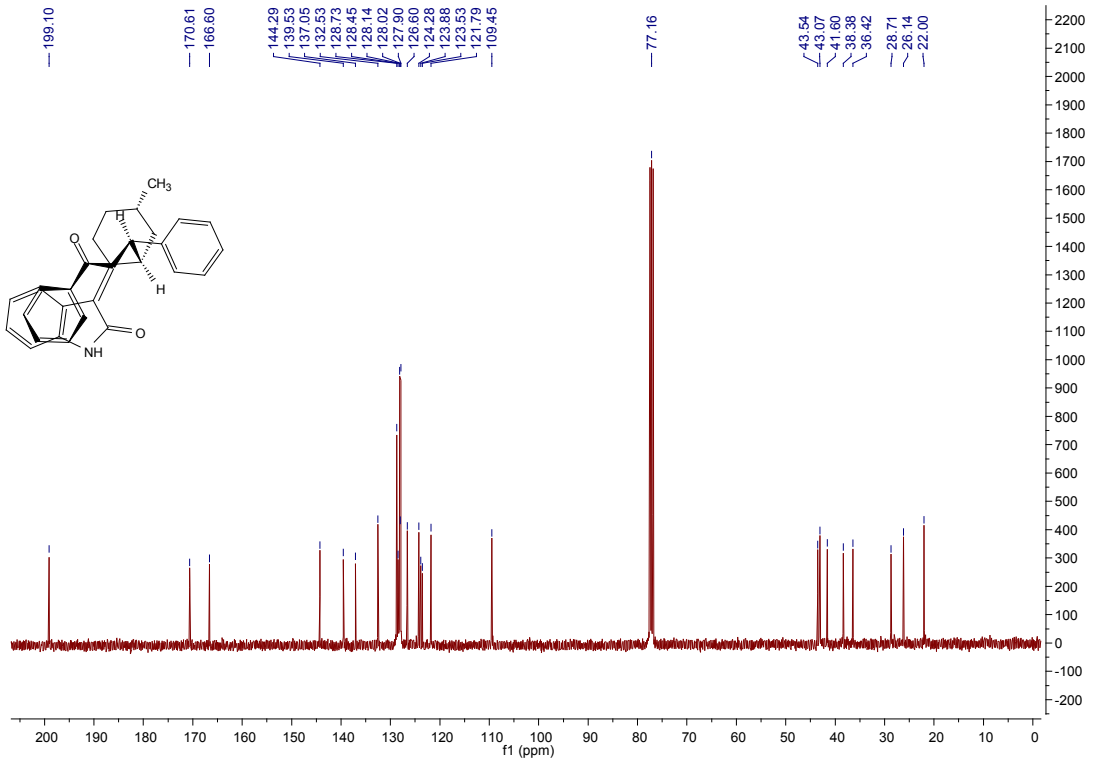
7.523
7.505
7.366
7.347
7.328
7.304
7.301
7.298
7.283
7.262
7.239
7.220
7.205
7.202
7.155
7.136
7.135
7.117
6.981
6.979
6.962
6.959
6.943
6.940
6.787
6.786
6.768
6.766
5.257
5.248
4.006
3.992
3.978
3.442
3.427
3.400
3.385
3.355
3.313
3.294
3.270
3.252
2.738
2.726
2.115
2.081
1.496
1.491
1.461
1.456
1.266
1.256
1.232
1.223
1.099
1.089
0.798
0.782
CH3
H
O
H
O
NH
0.84
1.98
1.00
2.01
2.00
2.90
2.89
1.08
0.94
0.94
0.96
3.05
1.00
2.14
1.00
1.33
1.04
2.99
f1 (ppm)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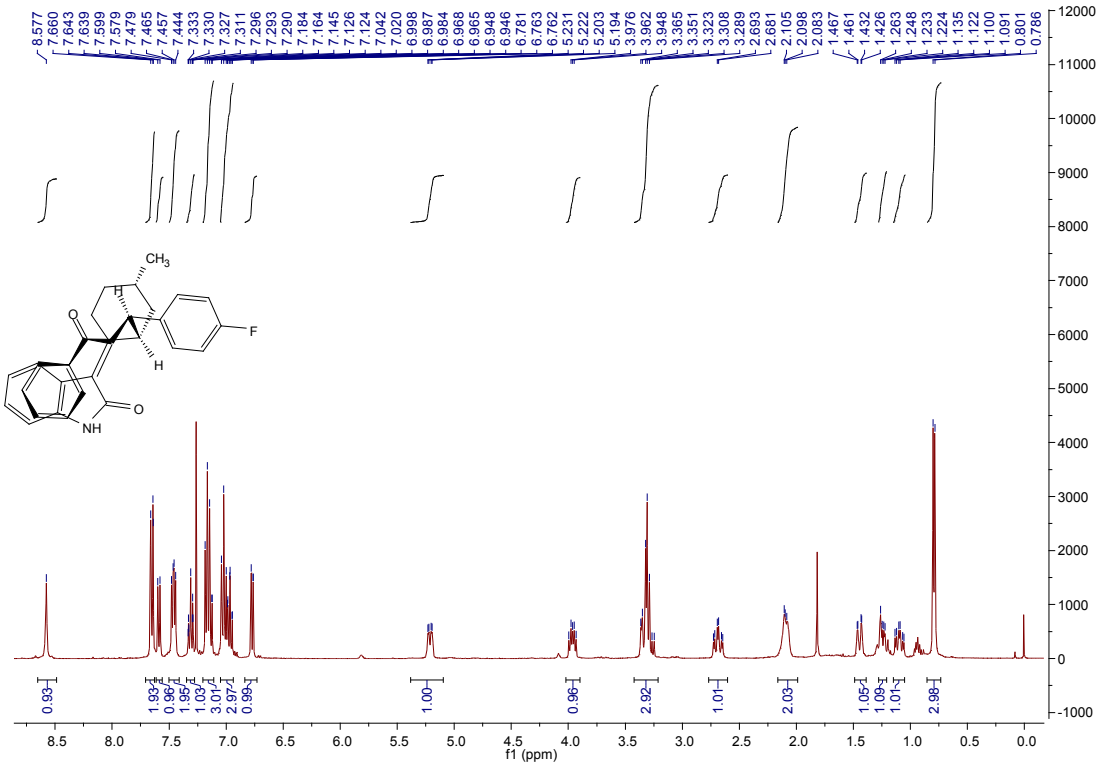
170.61
166.60
144.29
139.53
137.05
132.53
128.73
128.45
128.14
128.02
127.90
126.60
124.28
123.88
123.53
121.79
109.45
77.16
43.54
43.07
41.60
38.38
36.42
28.71
26.14
22.00
CH3
H
O
H
O
NH
f1 (ppm)

3ba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7.639
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7.465
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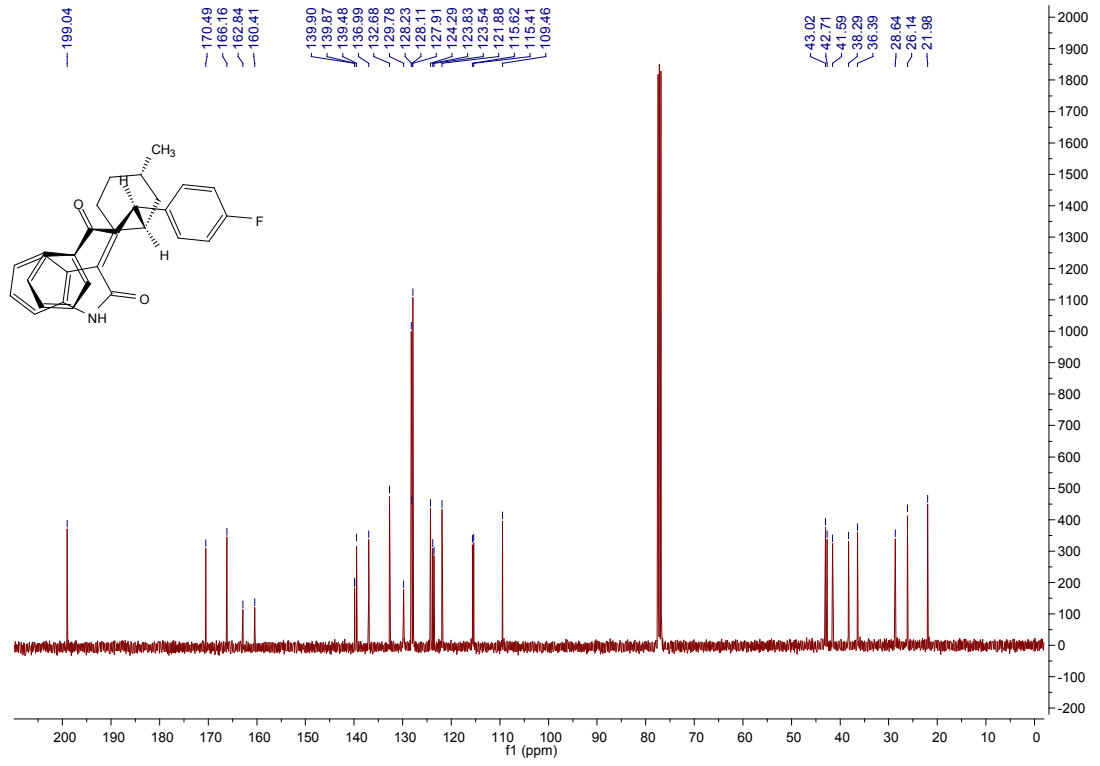
7.444
7.333
7.330
7.327
7.311
7.296
7.293
7.290
7.184
7.164
7.145
7.126
7.124
7.042
7.020
6.998
6.987
6.984
6.968
6.965
6.948
6.946
6.781
6.763
6.762
5.231
5.222
5.203
5.194
3.976
3.962
3.948
3.365
3.351
3.323
3.308
3.289
2.693
2.681
2.105
2.098
2.083
1.467
1.461
1.432
1.426
1.263
1.248
1.233
1.224
1.135
1.122
1.100
1.091
0.801
0.786
CH3
H
O
F
H
O
NH
0.93
1.93
0.96
1.95
1.03
3.01
2.97
0.99
1.00
0.96
2.92
1.01
2.03
1.05
1.09
1.01
2.98
f1 (ppm)


199.04
170.49
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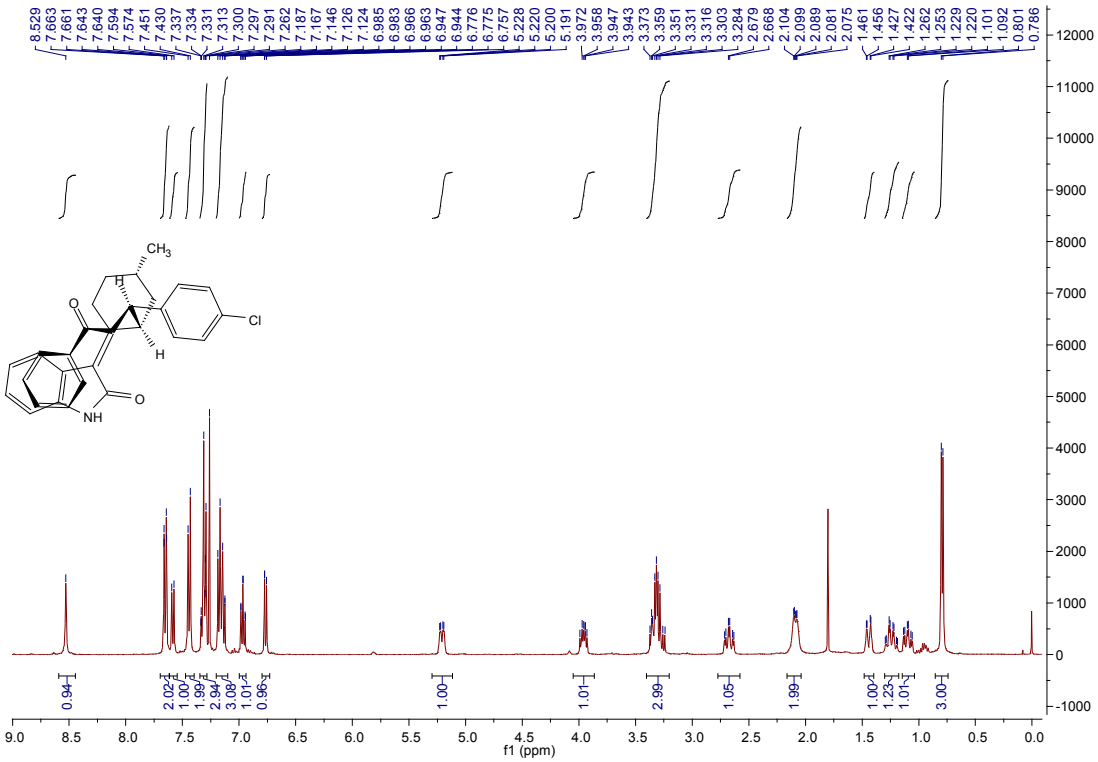
162.84
160.41
139.90
139.87
139.48
136.99
132.68
129.78
128.23
128.11
127.91
124.29
123.83
123.54
121.88
115.62
115.41
109.46
43.02
42.71
41.59
38.29
36.39
28.64
26.14
21.98
CH3
H
O
F
H
O
NH
f1 (ppm)

3ca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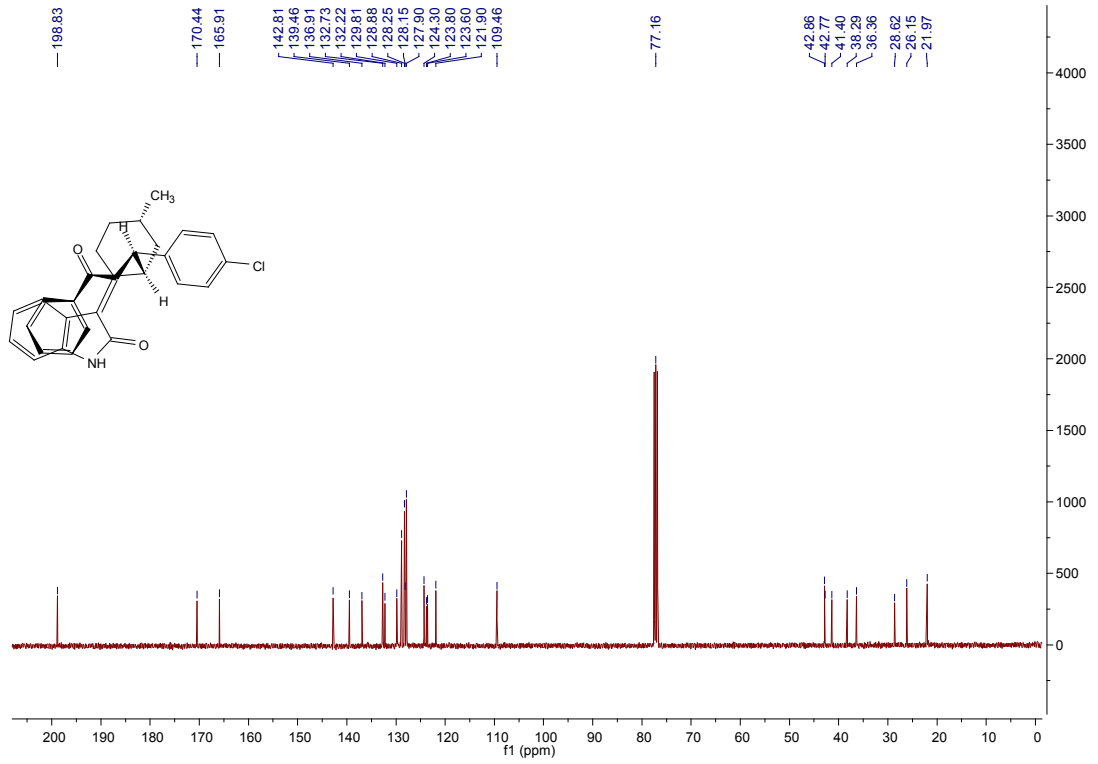
7.334
7.331
7.313
7.300
7.297
7.291
7.262
7.187
7.167
7.146
7.126
7.124
6.985
6.983
6.966
6.963
6.947
6.944
6.776
6.775
6.757
5.228
5.220
5.200
5.191
3.972
3.958
3.947
3.943
3.373
3.359
3.351
3.331
3.316
3.303
3.284
2.679
2.668
2.104
2.099
2.089
2.081
2.075
1.461
1.456
1.427
1.422
1.262
1.253
1.229
1.220
1.101
1.092
0.801
0.786
CH3
H
O
Cl
H
O
NH
0.94
2.02
1.00
1.99
2.94
3.08
1.01
0.96
1.00
1.01
2.99
1.05
1.99
1.00
1.23
1.01
3.00
f1 (ppm)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136.91
132.73
132.22
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128.25
128.15
127.90
124.30
123.80
123.60
121.90
109.46
77.16
42.86
42.77
41.40
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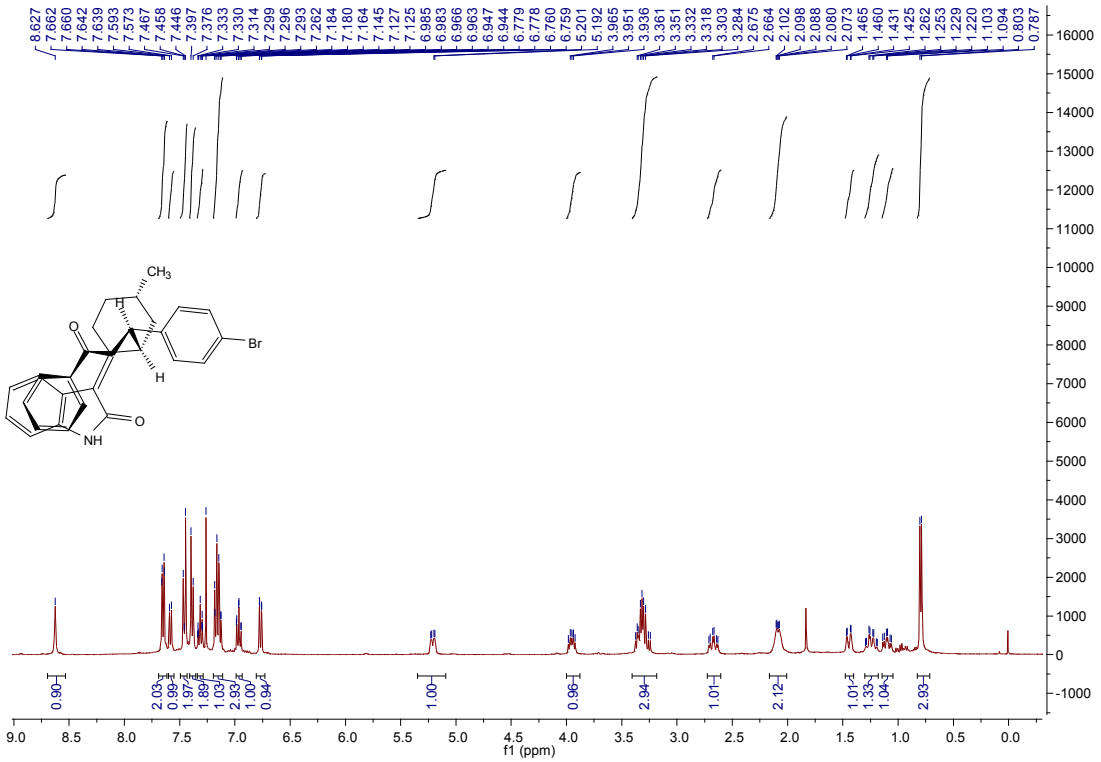
36.36
28.62
26.15
21.97
CH3
H
O
Cl
H
O
NH
f1 (ppm)

3da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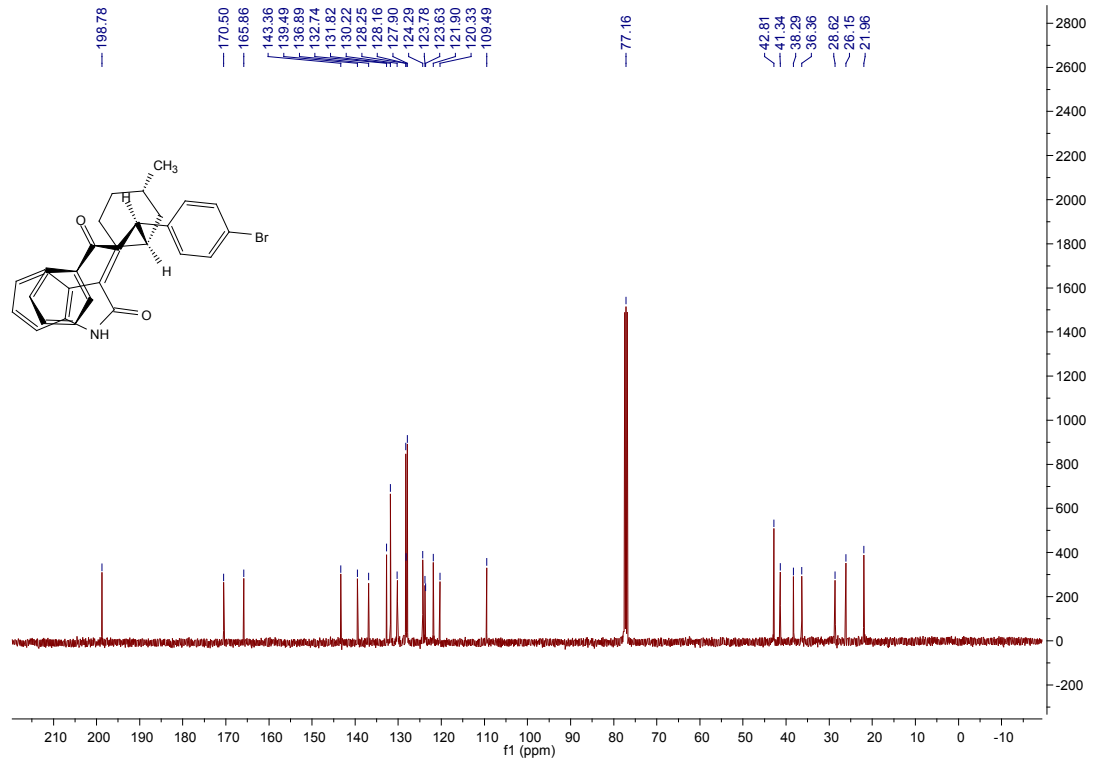
7.376
7.333
7.330
7.314
7.299
7.296
7.293
7.262
7.184
7.180
7.164
7.145
7.127
7.125
6.985
6.983
6.966
6.963
6.947
6.944
6.779
6.778
6.760
6.759
5.201
5.192
3.965
3.951
3.936
3.361
3.351
3.332
3.318
3.303
3.284
2.675
2.664
2.102
2.098
2.088
2.080
2.073
1.465
1.460
1.431
1.425
1.262
1.253
1.229
1.220
1.103
1.094
0.803
0.787
CH3
H
O
Br
H
O
NH
0.90
2.03
0.99
1.97
1.89
1.03
2.93
1.00
0.94
1.00
0.96
2.94
1.01
2.12
1.01
1.33
1.04
2.93
f1 (ppm)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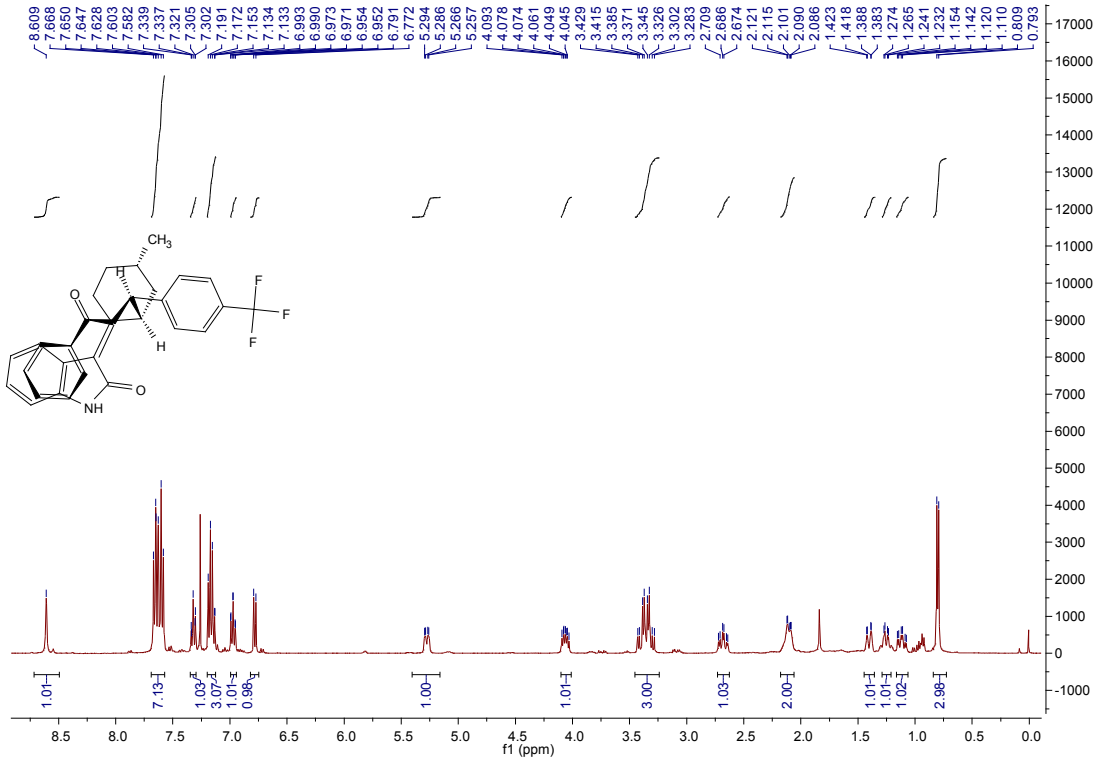
132.74
131.82
130.22
128.25
128.16
127.90
124.29
123.78
123.63
121.90
120.33
109.49
77.16
42.81
41.34
38.29
36.36
28.62
26.15
21.96
CH3
H
O
Br
H
O
NH
f1 (ppm)

3ea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7.603
7.582
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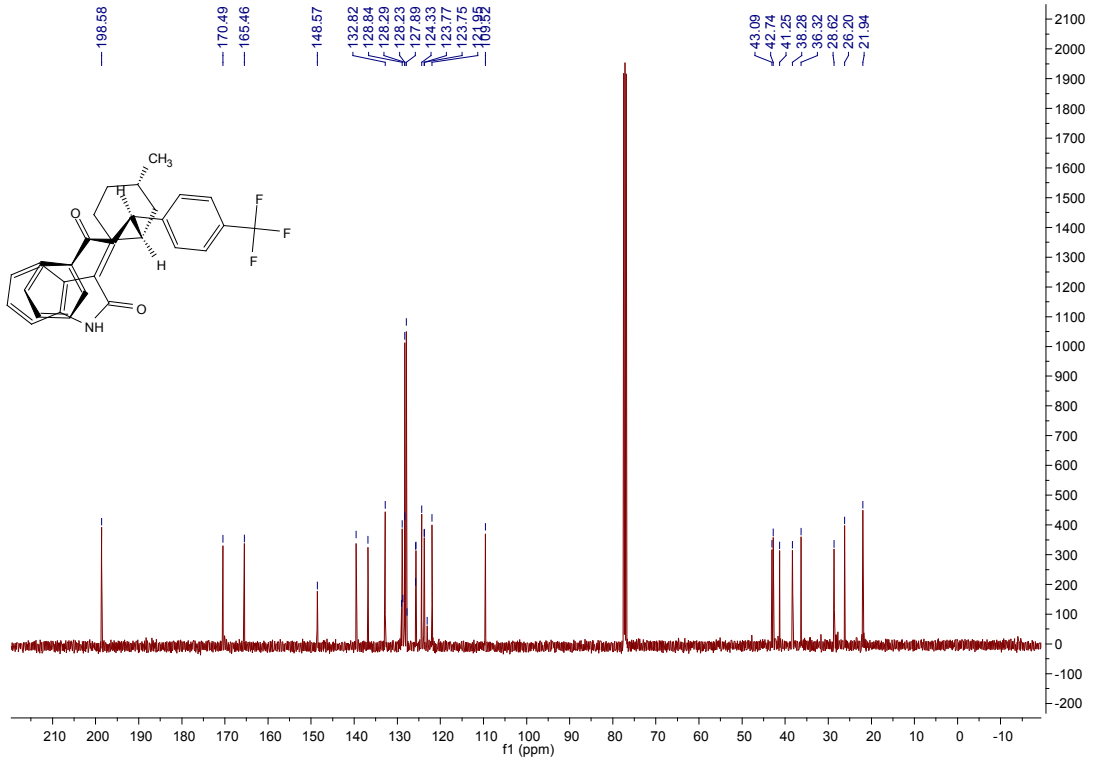
7.337
7.321
7.305
7.302
7.191
7.172
7.153
7.134
7.133
6.993
6.990
6.973
6.971
6.954
6.952
6.791
6.772
5.294
5.286
5.266
5.257
4.093
4.078
4.074
4.061
4.049
4.045
3.429
3.415
3.385
3.371
3.345
3.326
3.302
3.283
2.709
2.686
2.674
2.121
2.115
2.101
2.090
2.086
1.423
1.418
1.388
1.383
1.274
1.265
1.241
1.232
1.154
1.142
1.120
1.110
0.809
0.793
CH3
H
O
F
F
F
H
O
NH
1.01
7.13
1.03
3.07
1.01
0.98
1.00
1.01
3.00
1.03
2.00
1.01
1.01
1.02
2.98
f1 (ppm)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128.23
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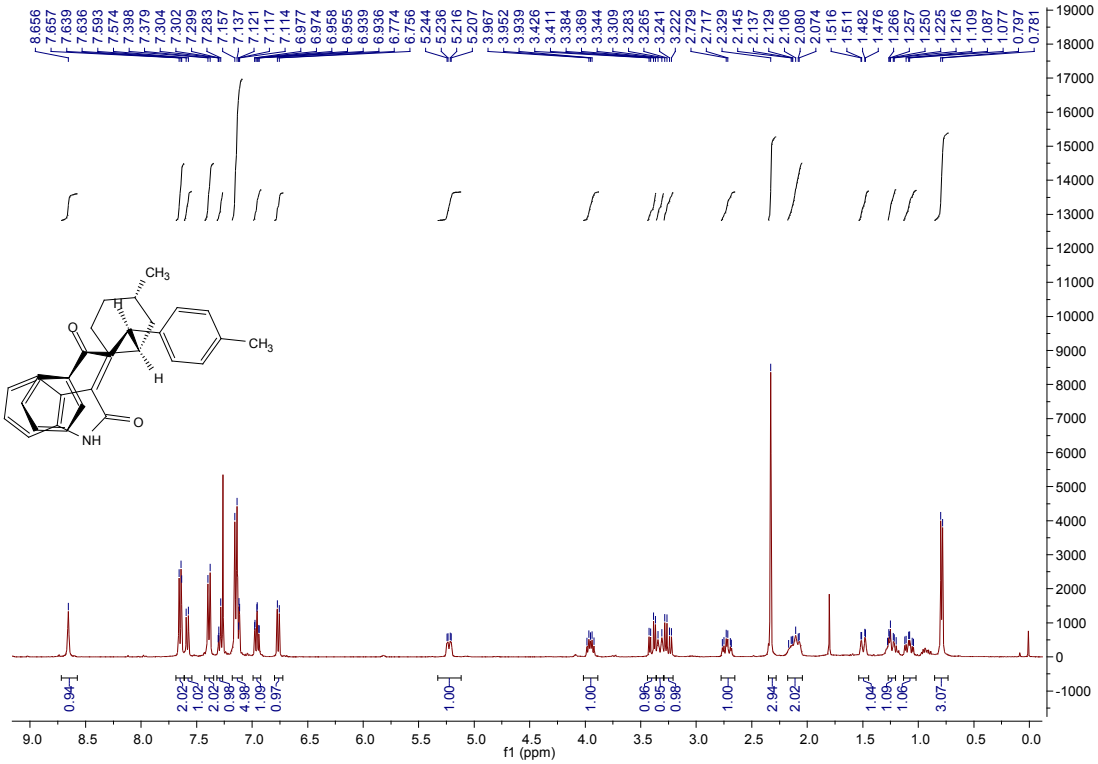
124.33
123.77
123.75
43.09
42.74
41.25
38.28
36.32
28.62
26.20
21.94
CH3
H
O
F
F
F
H
O
NH
f1 (ppm)

3fa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7.639
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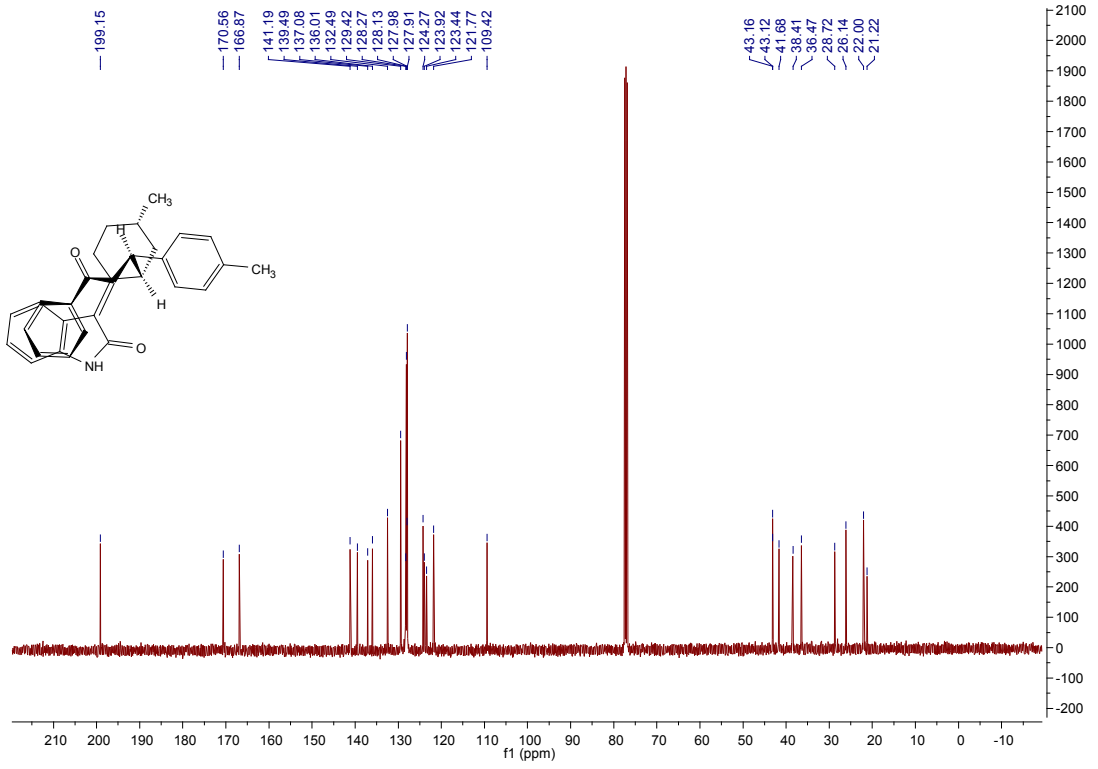
7.574
7.398
7.379
7.304
7.302
7.299
7.283
7.157
7.137
7.121
7.117
7.114
6.977
6.974
6.958
6.955
6.939
6.936
6.774
6.756
5.244
5.236
5.216
5.207
3.967
3.952
3.939
3.426
3.411
3.384
3.369
3.344
3.309
3.283
3.265
3.241
3.222
2.729
2.717
2.329
2.145
2.137
2.129
2.106
2.080
2.074
1.516
1.511
1.482
1.476
1.266
1.257
1.250
1.225
1.216
1.109
1.087
1.077
0.797
0.781
CH3
H
O
CH3
H
O
NH
0.94
2.02
1.02
2.02
0.98
4.98
1.09
0.97
1.00
1.00
0.96
0.95
0.98
1.00
2.94
2.02
1.04
1.09
1.06
3.07
f1 (ppm)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137.08
136.01
132.49
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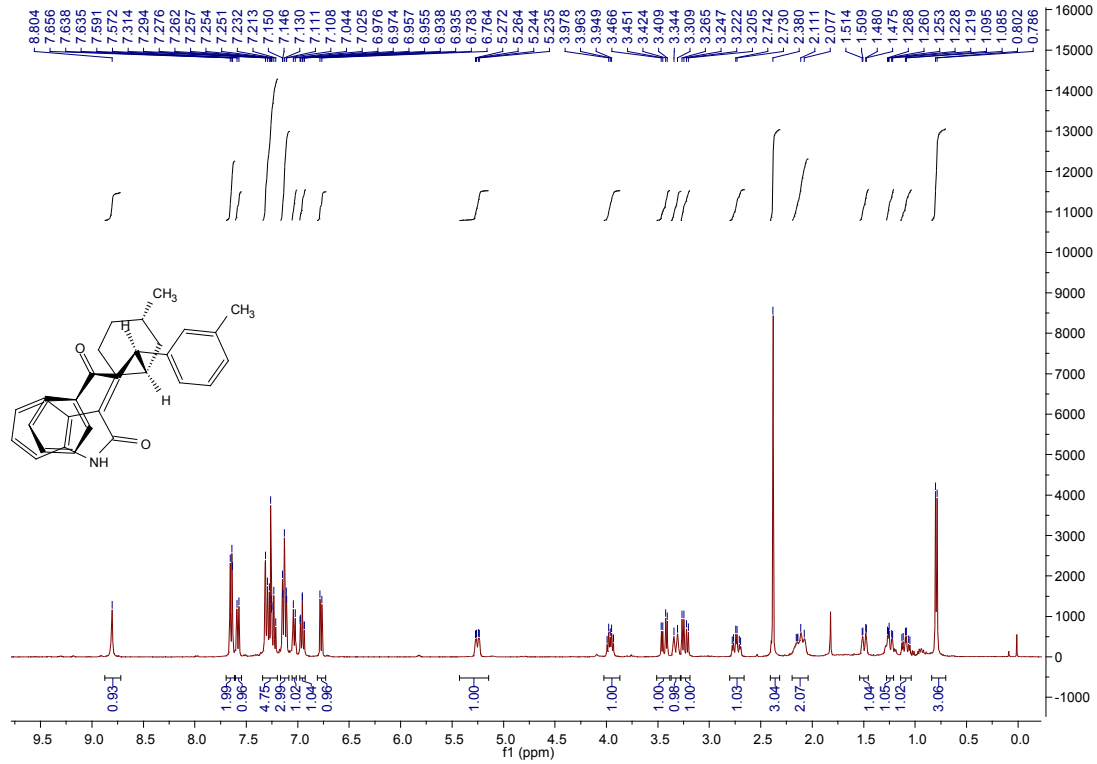
128.27
128.13
127.98
127.91
124.27
123.92
123.44
121.77
109.42
43.16
43.12
41.68
38.41
36.47
28.72
26.14
22.00
21.22
CH3
H
O
CH3
H
O
NH
f1 (ppm)

3ga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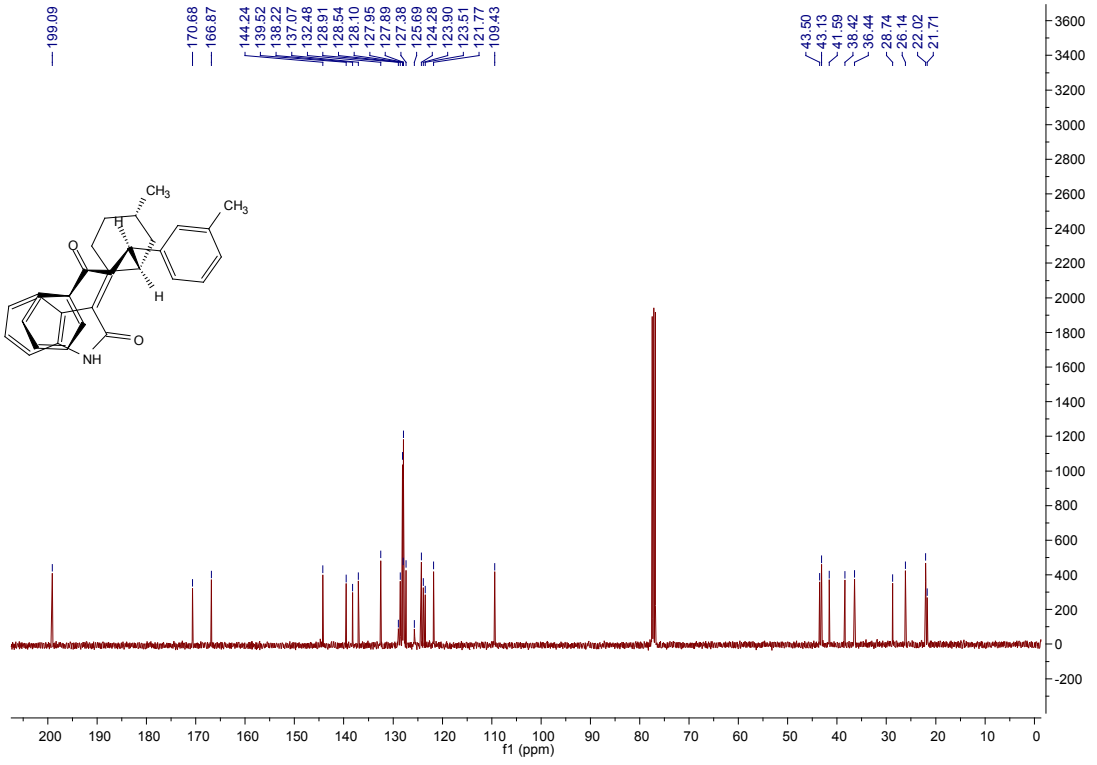
7.294
7.276
7.262
7.257
7.254
7.251
7.232
7.213
7.150
7.146
7.130
7.111
7.108
7.044
7.025
6.976
6.974
6.957
6.955
6.938
6.935
6.783
6.764
5.272
5.264
5.244
5.235
3.978
3.963
3.949
3.466
3.451
3.424
3.409
3.344
3.309
3.265
3.247
3.222
3.205
2.742
2.730
2.380
2.111
2.077
1.514
1.509
1.480
1.475
1.268
1.260
1.253
1.228
1.219
1.095
1.085
0.802
0.786
CH3
CH3
H
O
H
O
NH
0.93
1.99
0.96
4.75
2.99
1.02
1.04
0.96
1.00
1.00
1.00
0.98
1.00
1.03
3.04
2.07
1.04
1.05
1.02
3.06
f1 (ppm)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132.48
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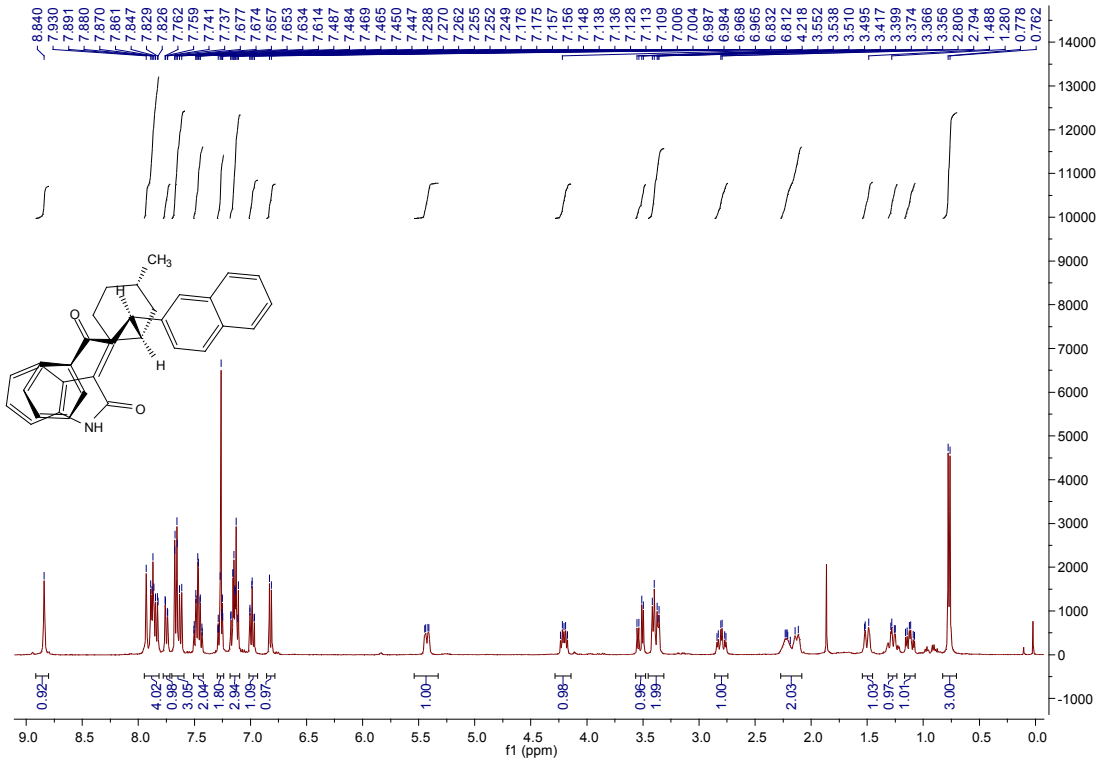
128.54
128.10
127.95
127.89
127.38
125.69
124.28
123.90
123.51
121.77
109.43
43.50
43.13
41.59
38.42
36.44
28.74
26.14
22.02
21.71
CH3
CH3
H
O
H
O
NH
f1 (ppm)

3ha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7.741
7.737
7.677
7.674
7.657
7.653
7.634
7.614
7.487
7.484
7.469
7.465
7.450
7.447
7.288
7.270
7.262
7.255
7.252
7.249
7.176
7.175
7.157
7.156
7.148
7.138
7.136
7.128
7.113
7.109
7.006
7.004
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6.968
6.965
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6.812
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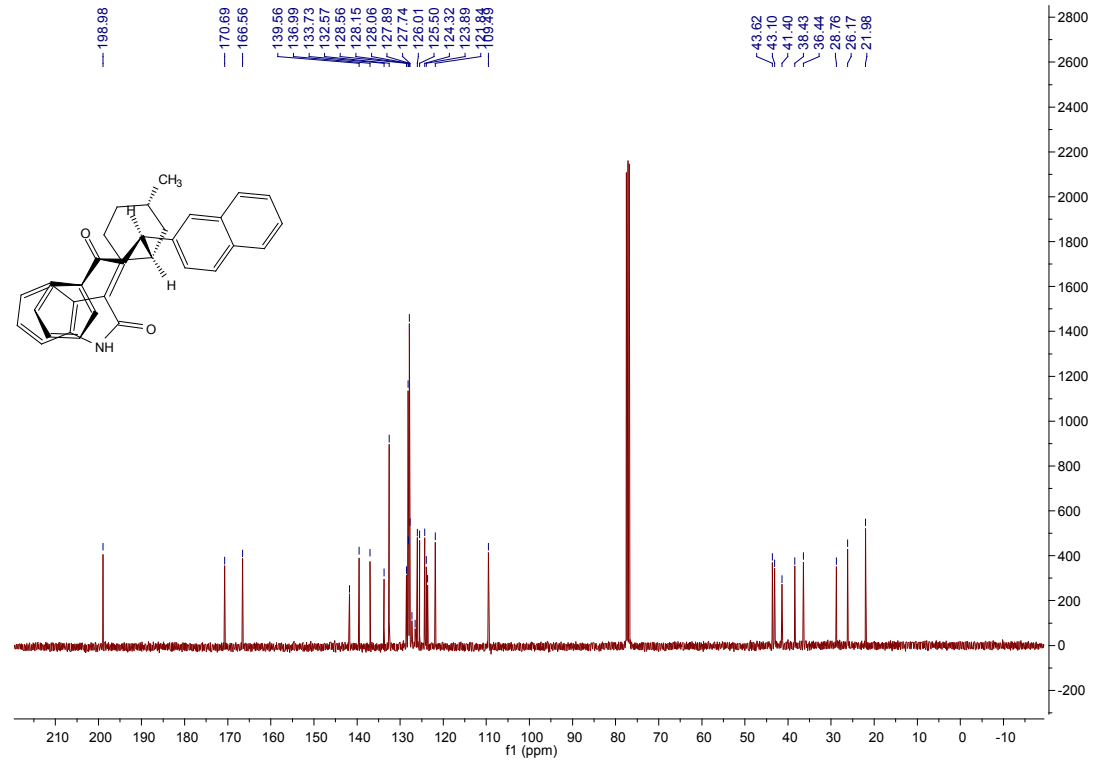
3.552
3.538
3.510
3.495
3.417
3.399
3.374
3.366
3.356
2.806
2.794
1.488
1.280
0.778
0.762
CH3
H
O
H
O
NH
0.92
4.02
0.98
3.05
2.04
1.80
2.94
1.09
0.97
1.00
0.98
0.96
1.99
1.00
2.03
1.03
0.97
1.01
3.00
f1 (ppm)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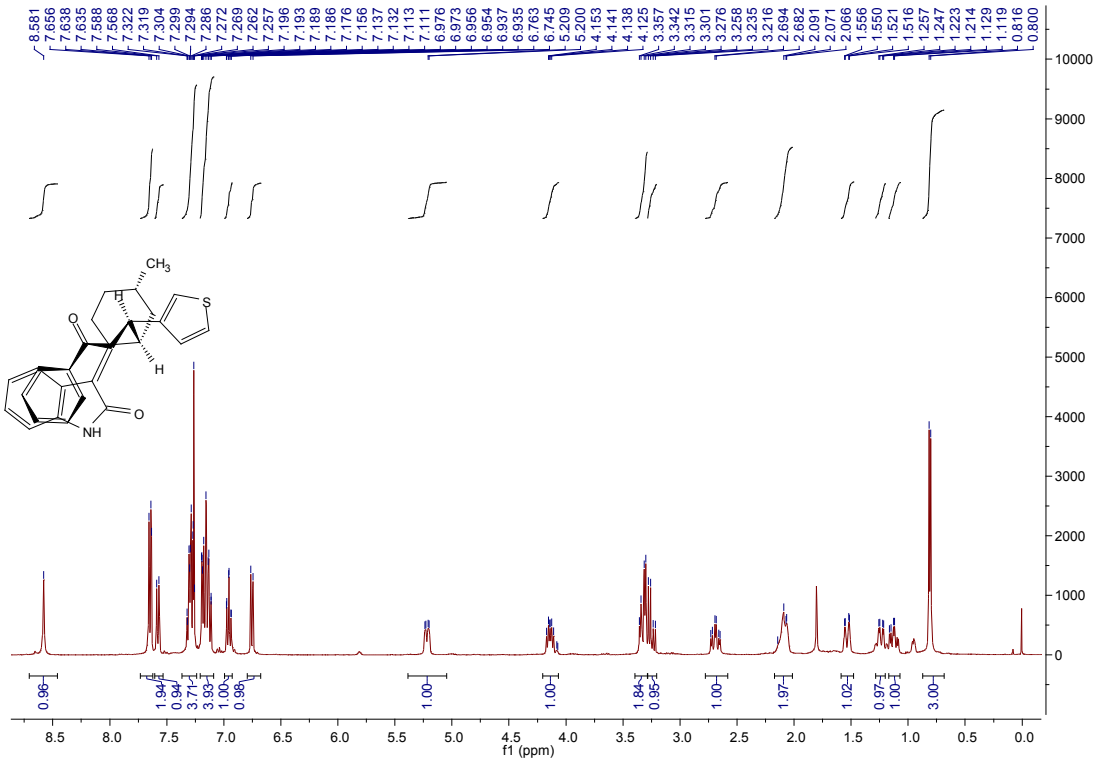
132.57
128.56
128.15
128.06
127.89
127.74
126.01
125.50
124.32
123.89
43.62
43.10
41.40
38.43
36.44
28.76
26.17
21.98
CH3
H
O
H
O
NH
f1 (ppm)

3ia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7.272
7.269
7.262
7.257
7.196
7.193
7.189
7.186
7.176
7.156
7.137
7.132
7.113
7.111
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6.973
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6.954
6.937
6.935
6.763
6.745
5.209
5.200
4.153
4.141
4.138
4.125
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3.301
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3.258
3.235
3.216
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2.682
2.091
2.071
2.066
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1.550
1.521
1.516
1.257
1.247
1.223
1.214
1.129
1.119
0.816
0.800
CH3
H
S
O
H
O
NH
0.96
1.94
0.94
3.71
3.93
1.00
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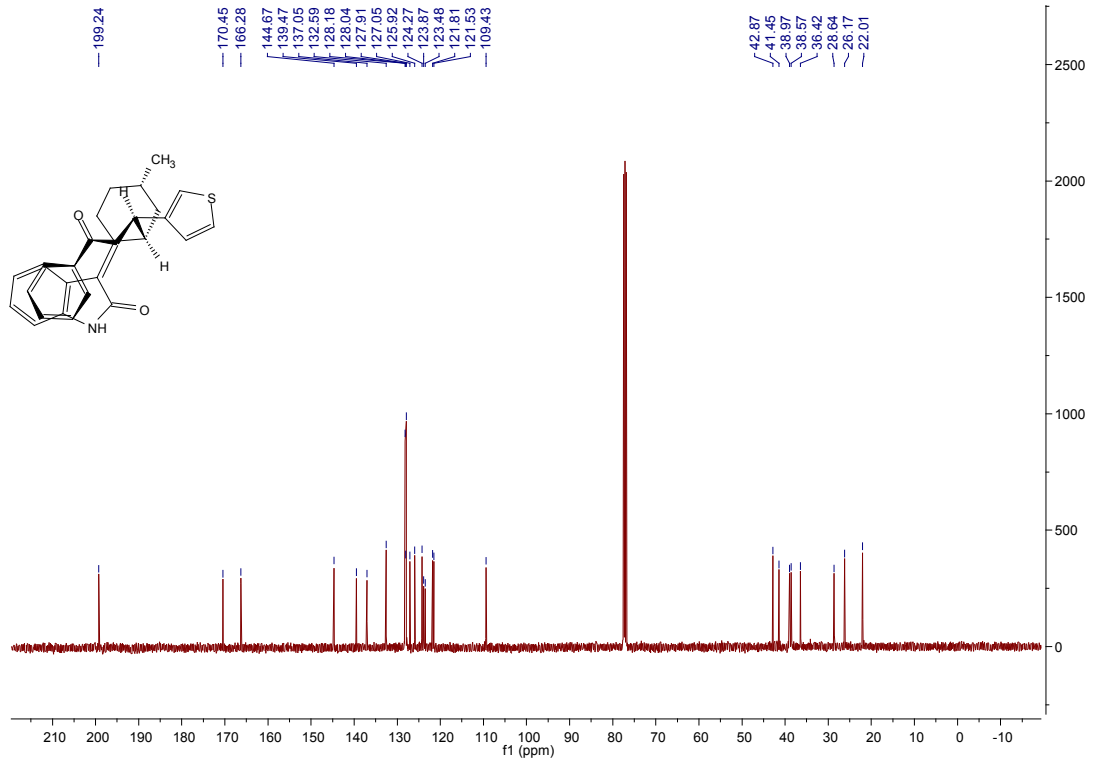
1.00
1.97
1.02
0.97
1.00
3.00
f1 (ppm)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127.91
127.05
125.92
124.27
123.87
123.48
121.81
121.53
109.43
42.87
41.45
38.97
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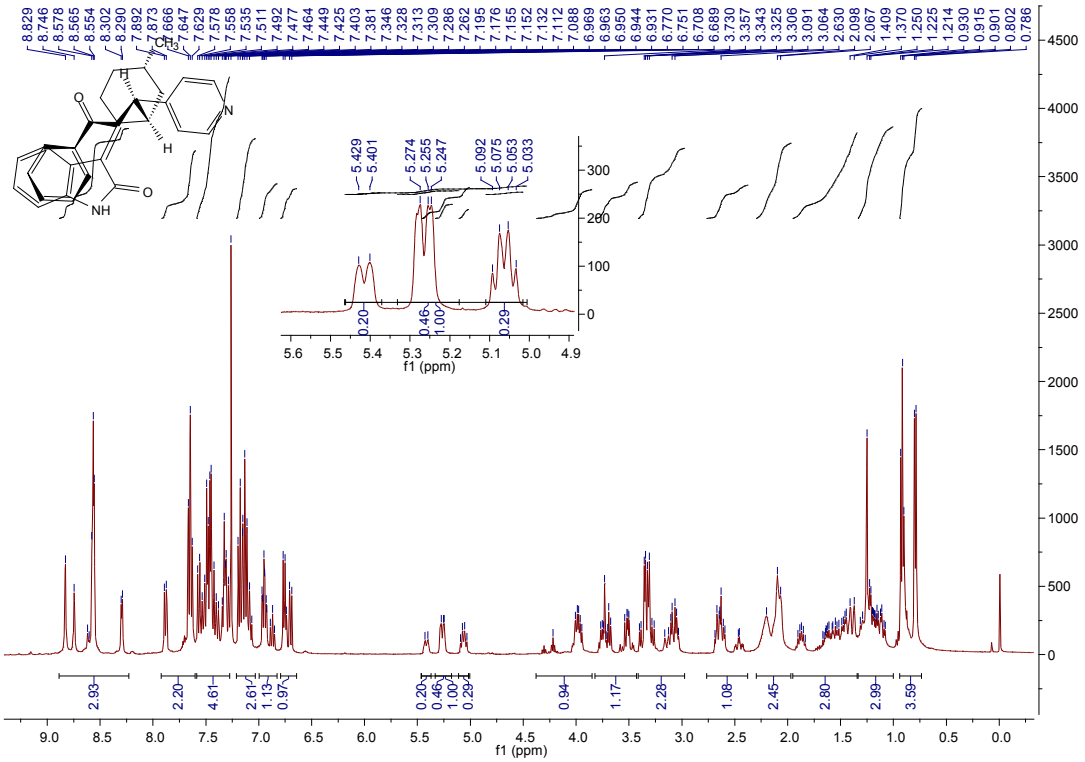
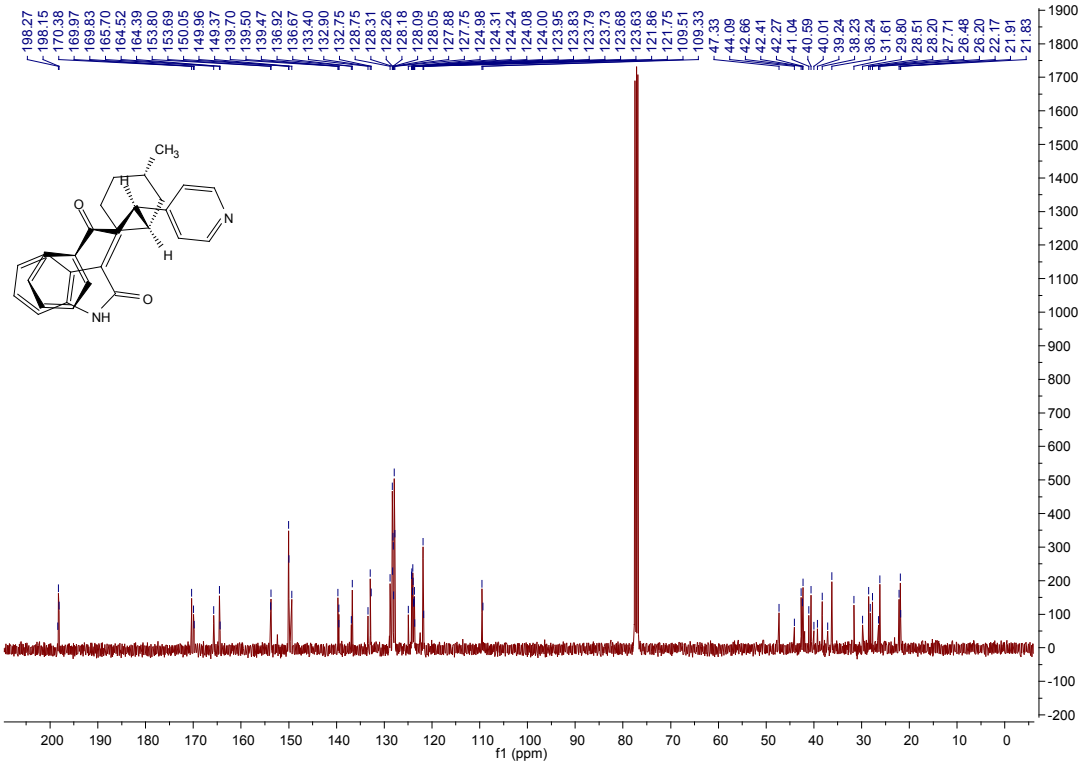
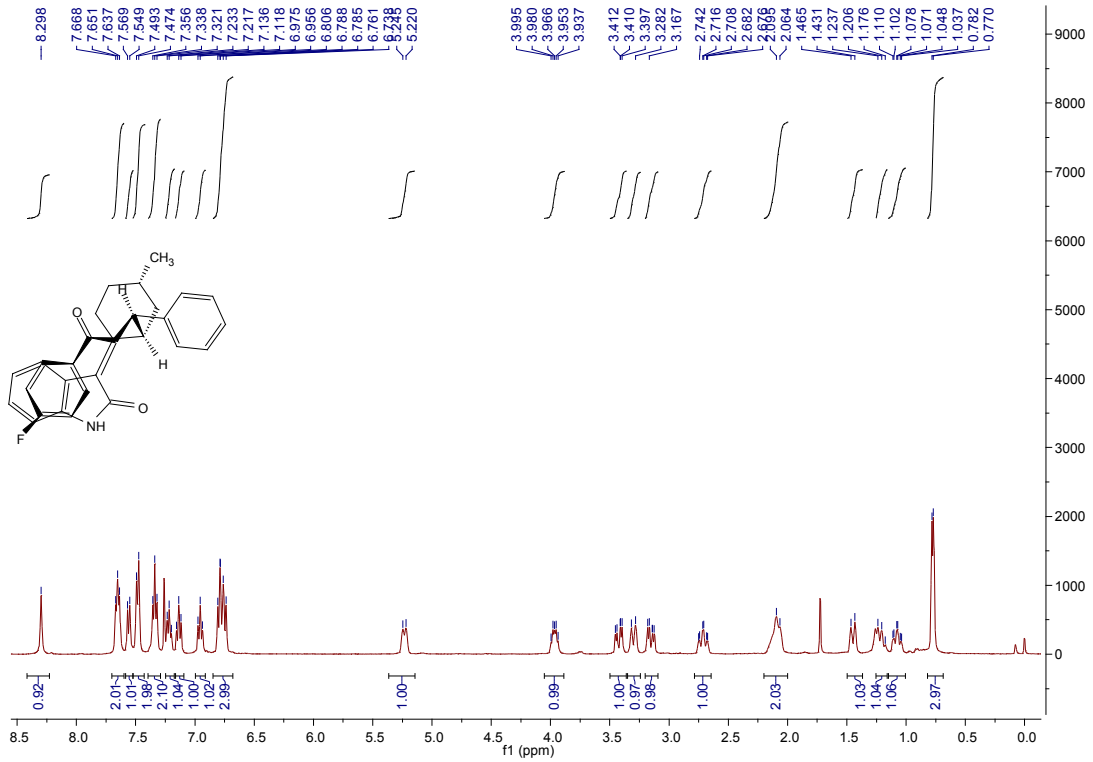
26.17
22.01
CH3
H
S
O
H
O
NH
f1 (ppm)

3ja





3ka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7.217
7.136
7.118
6.975
6.956
6.806
6.788
6.785
6.761
6.738
6.235
5.220
3.995
3.980
3.966
3.953
3.937
3.412
3.410
3.397
3.282
3.167
2.742
2.716
2.708
2.682
2.095
2.064
1.465
1.431
1.237
1.206
1.176
1.110
1.102
1.078
1.071
1.048
1.037
0.782
0.770
CH3
H
O
H
O
NH
F
0.92
2.01
1.01
1.98
2.10
1.04
1.00
1.02
2.99
1.00
0.99
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0.97
0.98
1.00
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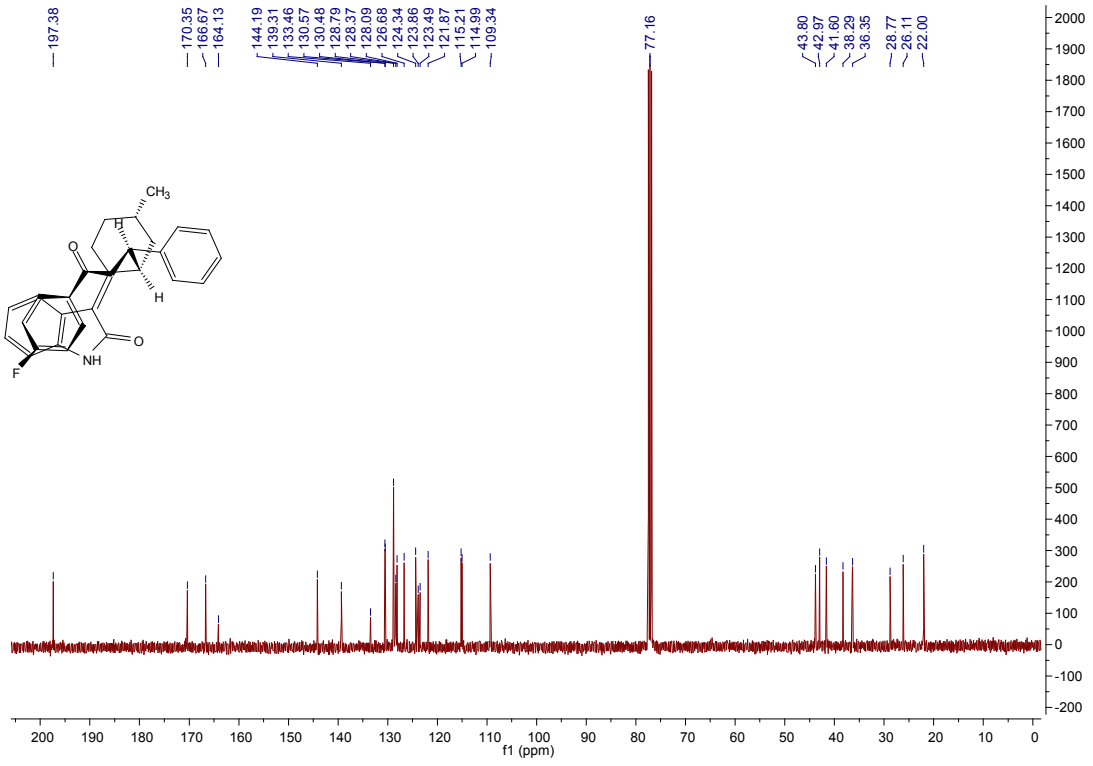
1.03
1.04
1.06
2.97
f1 (ppm)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130.57
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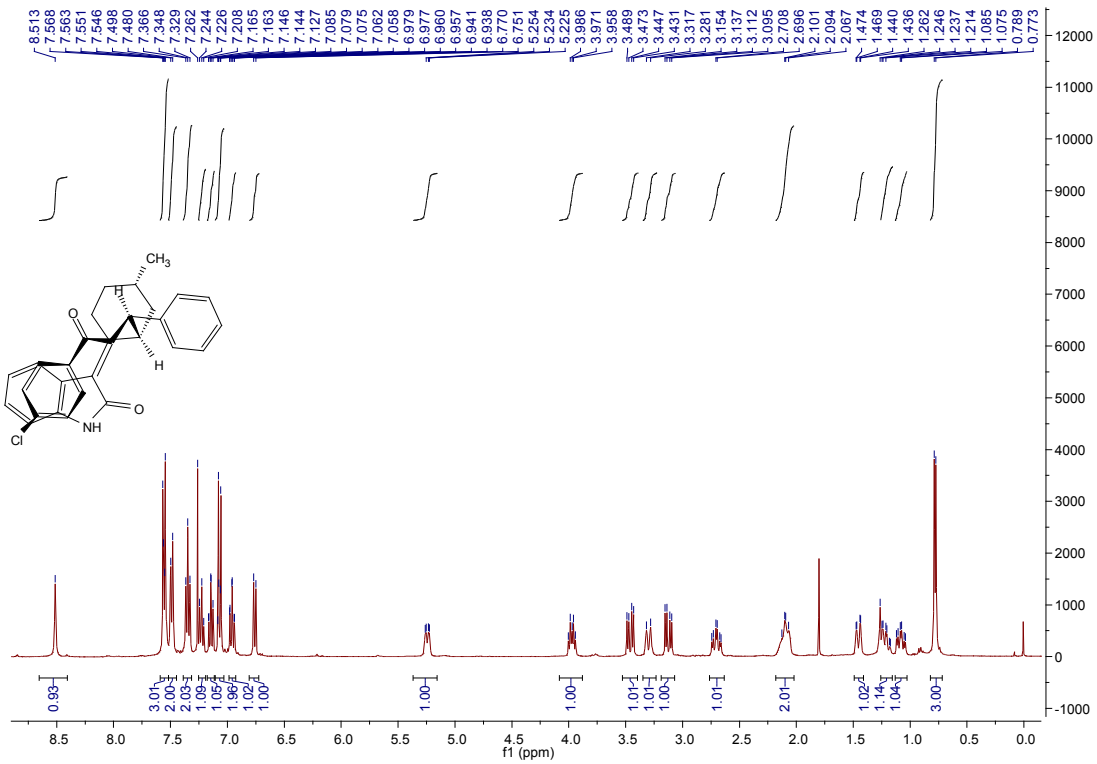
128.79
128.37
128.09
126.68
124.34
123.86
123.49
121.87
115.21
114.99
109.34
77.16
43.80
42.97
41.60
38.29
36.35
28.77
26.11
22.00
CH3
H
O
H
O
NH
F
f1 (ppm)

3la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7.262
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7.226
7.208
7.165
7.163
7.146
7.144
7.127
7.085
7.079
7.075
7.062
7.058
6.979
6.977
6.960
6.957
6.941
6.938
6.770
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5.234
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3.986
3.971
3.958
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3.431
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3.095
2.708
2.696
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2.067
1.474
1.469
1.440
1.436
1.262
1.246
1.237
1.214
1.085
1.075
0.789
0.773
CH3
H
O
H
O
NH
Cl
0.93
3.01
2.00
2.03
1.09
1.05
1.96
1.02
1.00
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1.01
1.00
1.01
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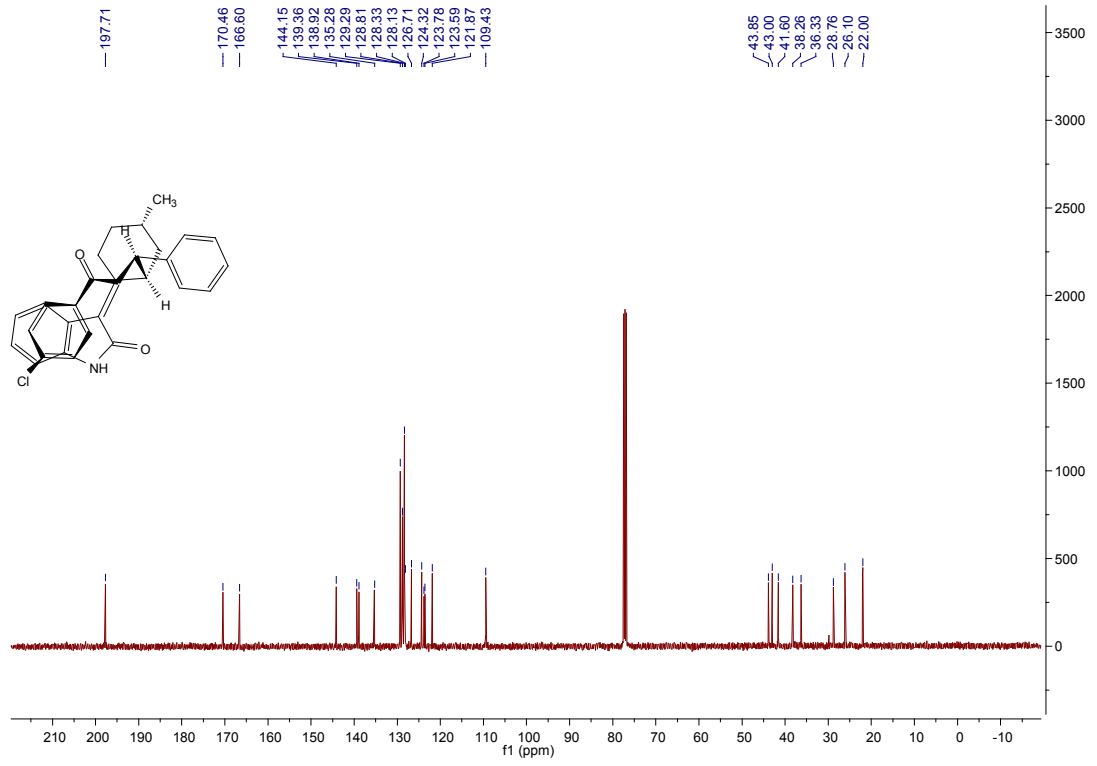
1.02
1.14
1.04
3.00
f1 (ppm)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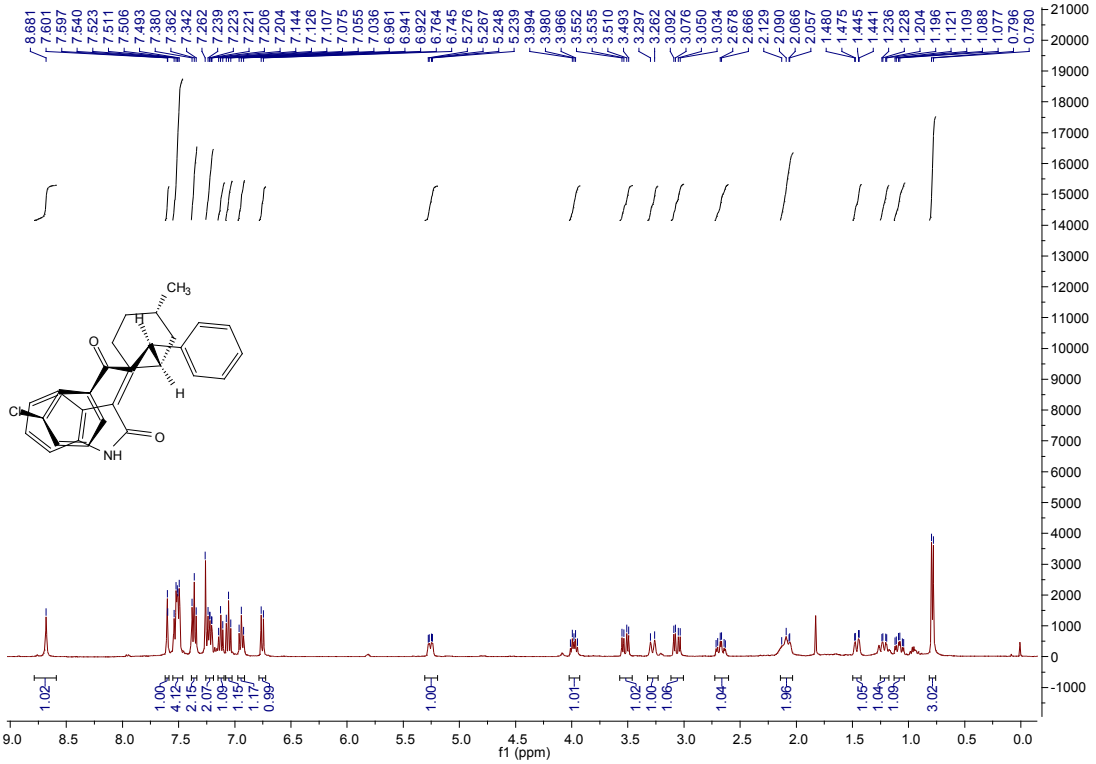
129.29
128.81
128.33
128.13
126.71
124.32
123.78
123.59
121.87
109.43
43.85
43.00
41.60
38.26
36.33
28.76
26.10
22.00
CH3
H
O
H
O
NH
Cl
f1 (ppm)

3ma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7.239
7.223
7.221
7.206
7.204
7.144
7.126
7.107
7.075
7.055
7.036
6.961
6.941
6.922
6.764
6.745
5.276
5.267
5.248
5.239
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3.980
3.966
3.552
3.535
3.510
3.493
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3.262
3.092
3.076
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3.034
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2.066
2.057
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1.475
1.445
1.441
1.236
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1.204
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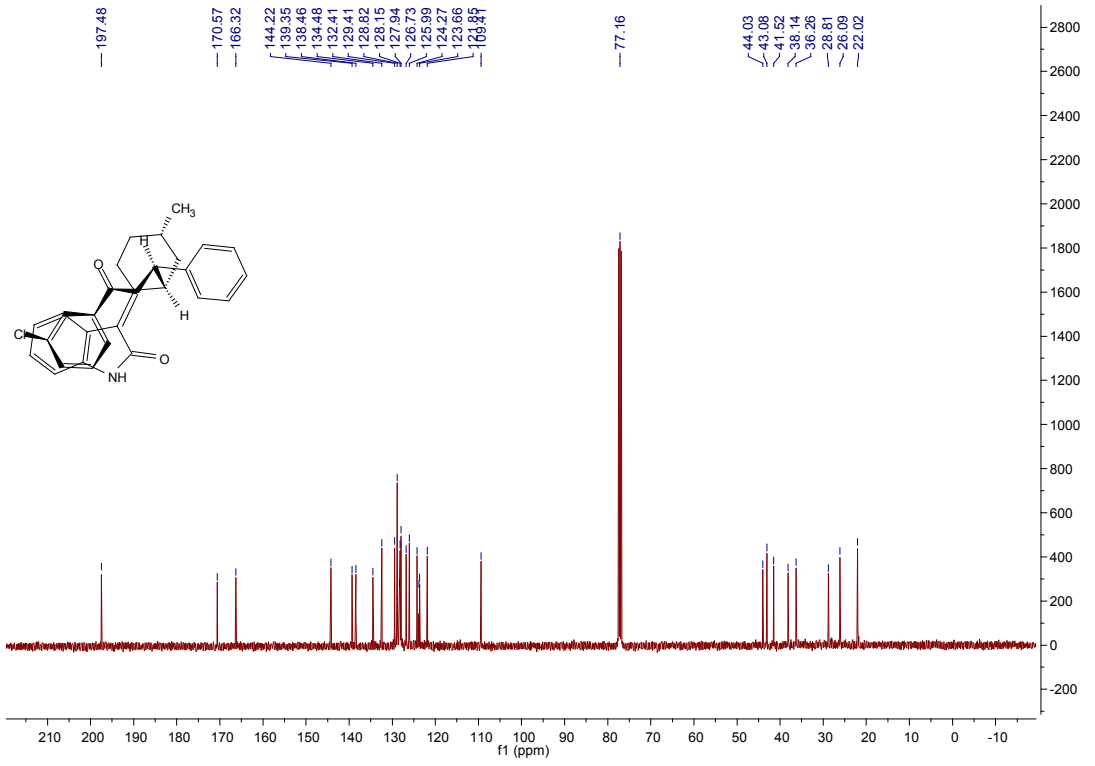
1.121
1.109
1.088
1.077
0.796
0.780
CH3
H
O
H
Cl
O
NH
1.02
1.00
4.12
2.15
2.07
1.09
1.15
1.17
0.99
1.00
1.01
1.02
1.00
1.06
1.04
1.96
1.05
1.04
1.09
3.02
f1 (ppm)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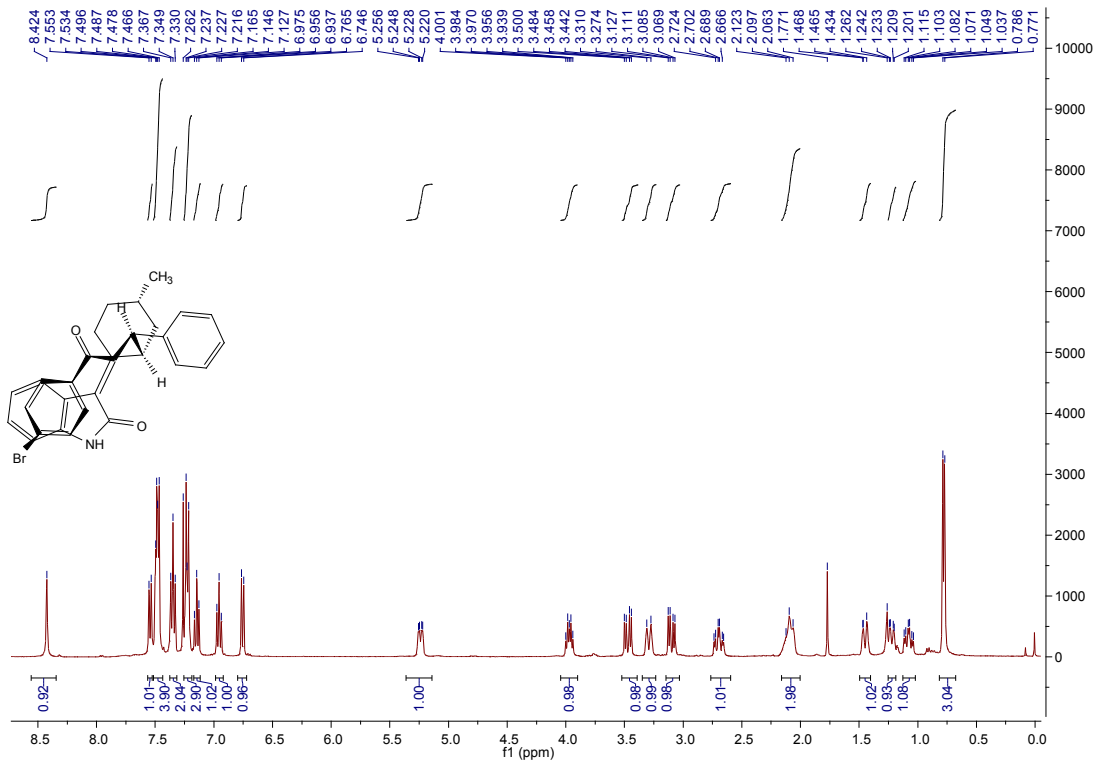
134.48
132.41
129.41
128.82
128.15
127.94
126.73
125.99
124.27
123.66
77.16
44.03
43.08
41.52
38.14
36.26
28.81
26.09
22.02
CH3
H
O
H
Cl
O
NH
f1 (ppm)

3na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7.237
7.227
7.216
7.165
7.146
7.127
6.975
6.956
6.937
6.765
6.746
5.256
5.248
5.228
5.220
4.001
3.984
3.970
3.956
3.939
3.500
3.484
3.458
3.442
3.310
3.274
3.127
3.111
3.085
3.069
2.724
2.702
2.689
2.666
2.123
2.097
2.063
1.771
1.468
1.465
1.434
1.262
1.242
1.233
1.209
1.201
1.115
1.103
1.082
1.071
1.049
1.037
0.786
0.771
CH3
H
O
H
O
NH
Br
0.92
1.01
3.90
2.04
2.90
1.02
1.00
0.96
1.00
0.98
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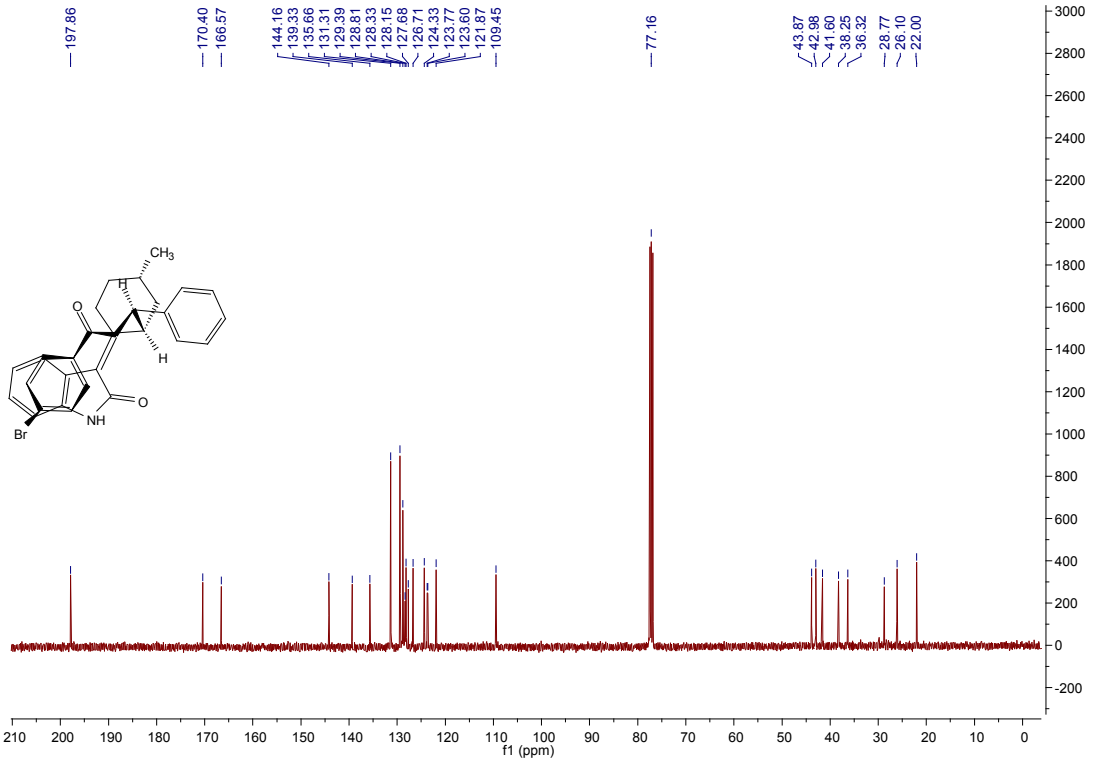
0.99
0.98
1.01
1.98
1.02
0.93
1.08
3.04
f1 (ppm)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129.39
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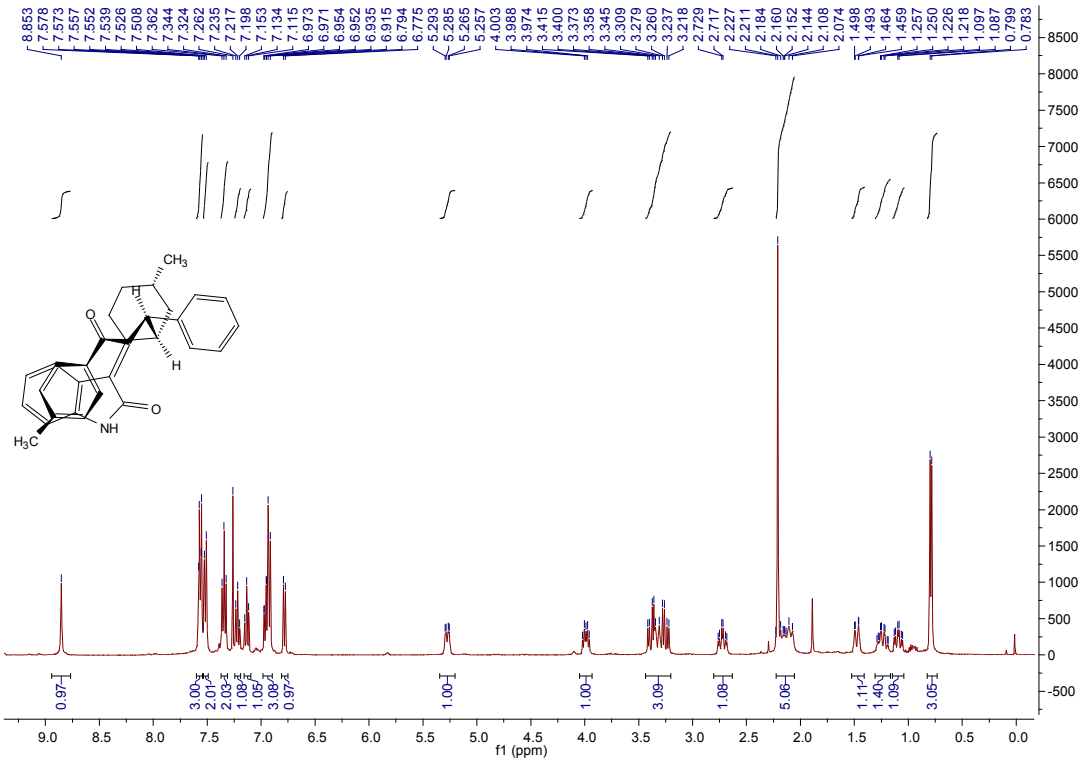
124.33
123.77
123.60
121.87
109.45
77.16
43.87
42.98
41.60
38.25
36.32
28.77
26.10
22.00
CH3
H
O
H
O
NH
Br
f1 (ppm)

3oa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7.324
7.262
7.235
7.217
7.198
7.153
7.134
7.115
6.973
6.971
6.954
6.952
6.935
6.915
6.794
6.775
5.293
5.285
5.265
5.257
4.003
3.988
3.974
3.415
3.400
3.373
3.358
3.345
3.309
3.279
3.260
3.237
3.218
2.729
2.717
2.227
2.211
2.184
2.160
2.152
2.144
2.108
2.074
1.498
1.493
1.464
1.459
1.257
1.250
1.226
1.218
1.097
1.087
0.799
0.783
CH3
H
O
H
O
NH
H3C
0.97
3.00
2.01
2.03
1.08
1.05
3.08
0.97
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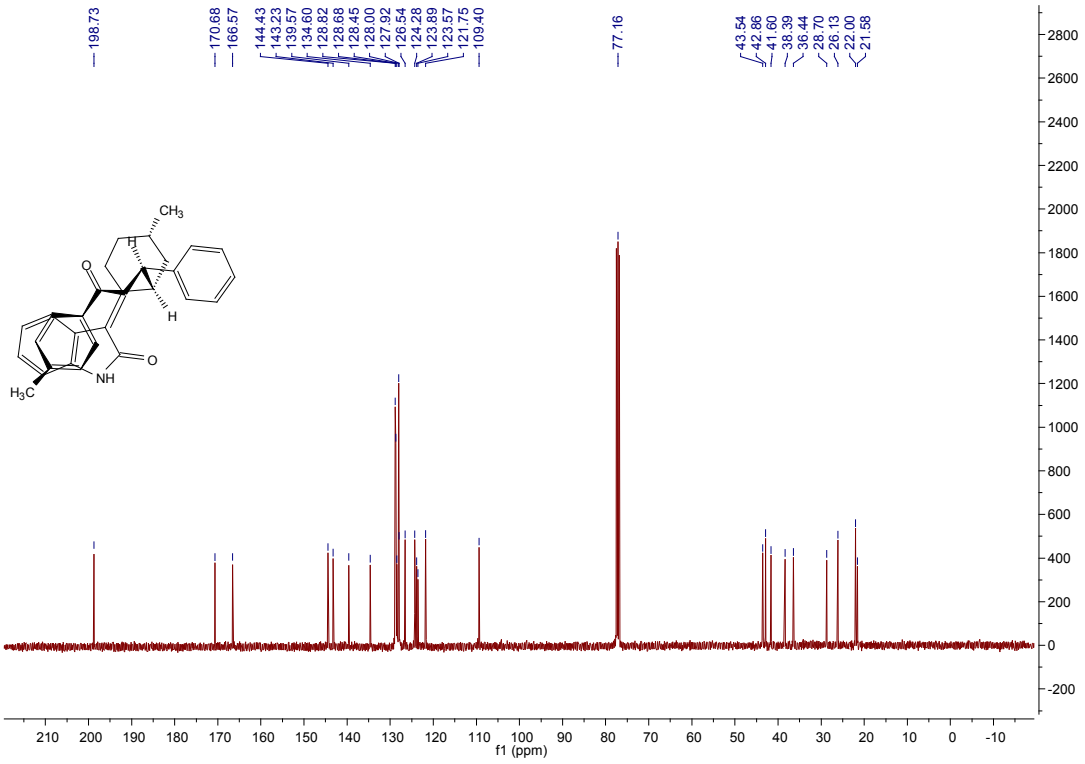
1.00
3.09
1.08
5.06
1.11
1.40
1.09
3.05
f1 (ppm)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127.92
126.54
124.28
123.89
123.57
121.75
109.40
77.16
43.54
42.86
41.60
38.39
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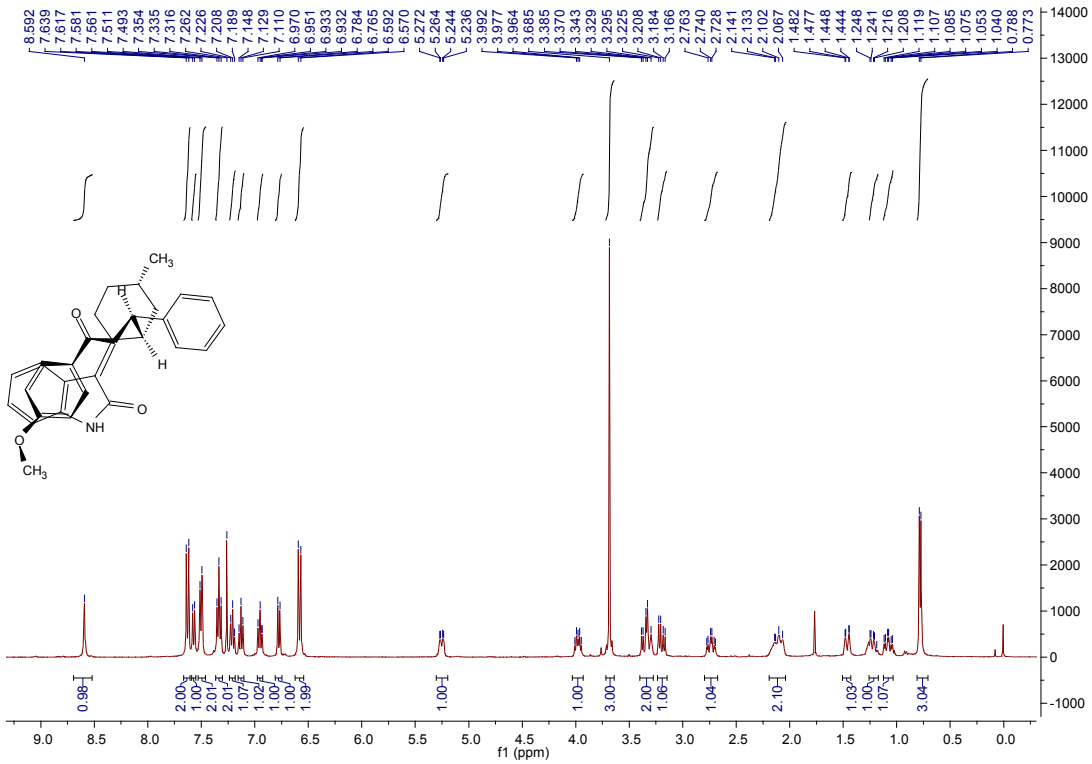
26.13
22.00
21.58
CH3
H
O
H
O
NH
H3C
f1 (ppm)

3pa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7.354
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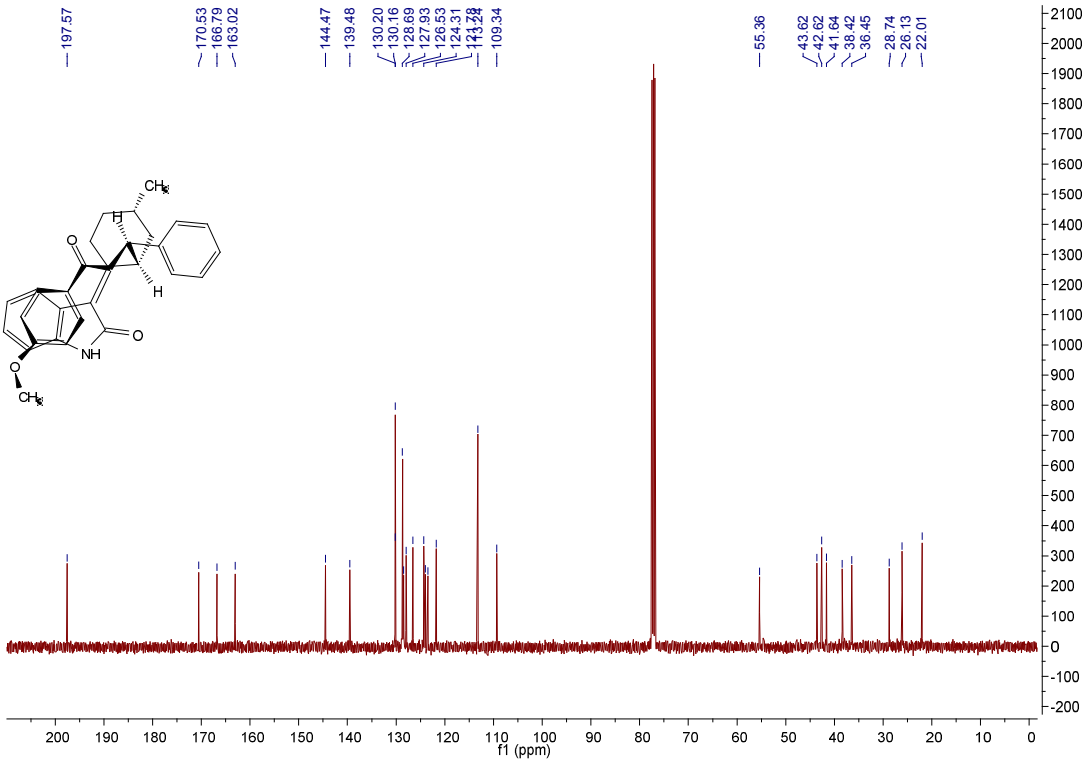
7.262
7.226
7.208
7.189
7.148
7.129
7.110
6.970
6.951
6.933
6.932
6.784
6.765
6.592
6.570
5.272
5.264
5.244
5.236
3.992
3.977
3.964
3.685
3.385
3.370
3.343
3.329
3.295
3.225
3.208
3.184
3.166
2.763
2.740
2.728
2.141
2.133
2.102
2.067
1.482
1.477
1.448
1.444
1.248
1.241
1.216
1.208
1.119
1.107
1.085
1.075
1.053
1.040
0.788
0.773
CH3
H
O
H
O
NH
O
CH3
0.98
2.00
1.00
2.01
2.01
1.07
1.02
1.00
1.00
1.99
1.00
1.00
3.00
2.00
1.06
1.04
2.10
1.03
1.00
1.07
3.04
f1 (ppm)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130.20
130.16
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127.93
126.53
124.31
109.34
55.36
43.62
42.62
41.64
38.42
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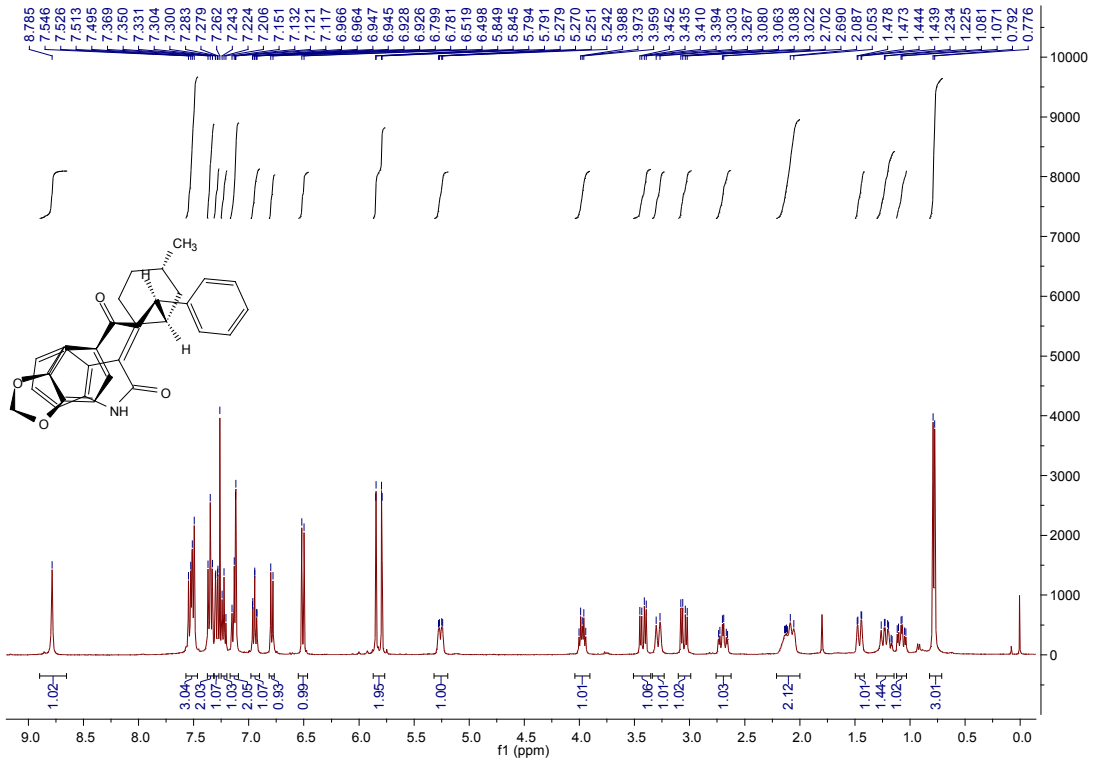
26.13
22.01
CH3
H
O
H
O
NH
O
CH3
f1 (ppm)

3qa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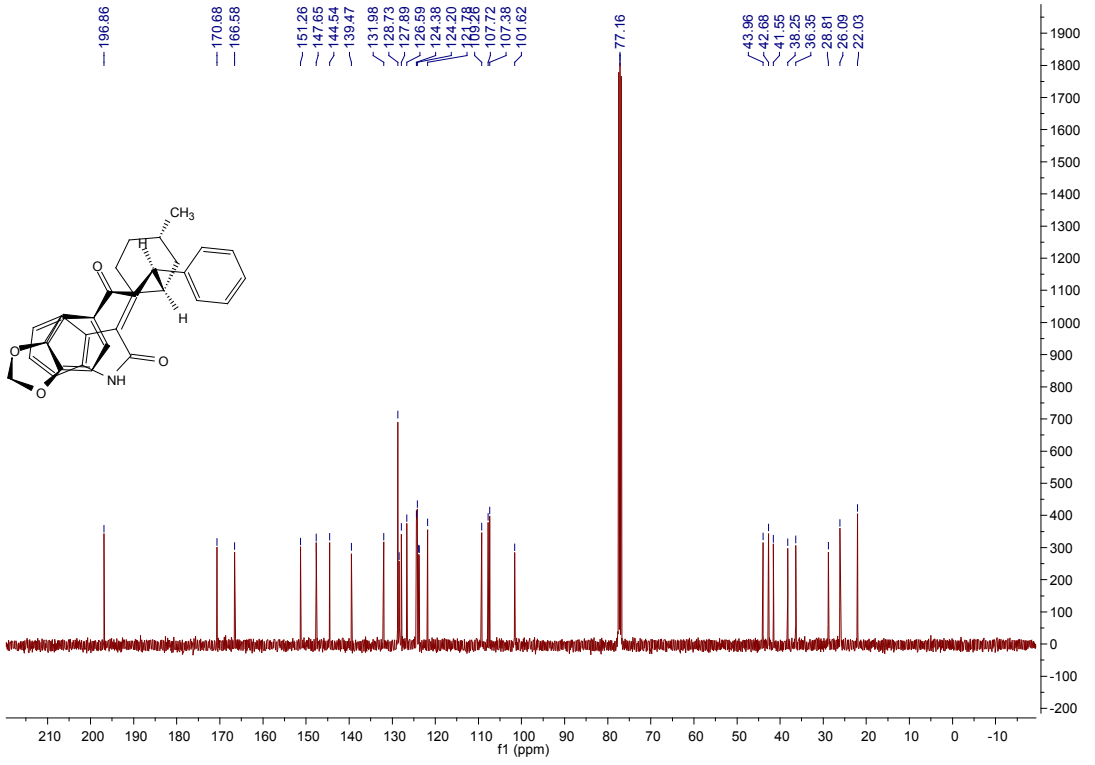
7.331
7.304
7.300
7.283
7.279
7.262
7.243
7.224
7.206
7.151
7.132
7.121
7.117
6.966
6.964
6.947
6.945
6.928
6.926
6.799
6.781
6.519
6.498
5.849
5.845
5.794
5.791
5.279
5.270
5.251
5.242
3.988
3.973
3.959
3.452
3.435
3.410
3.394
3.303
3.267
3.080
3.063
3.038
3.022
2.702
2.690
2.087
2.053
1.478
1.473
1.444
1.439
1.234
1.225
1.081
1.071
0.792
0.776
CH3
H
O
H
O
O
NH
O
1.02
3.04
2.03
1.07
1.03
2.05
1.07
0.93
0.99
1.95
1.00
1.01
1.06
1.01
1.02
1.03
2.12
1.01
1.44
1.02
3.01
f1 (ppm)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127.89
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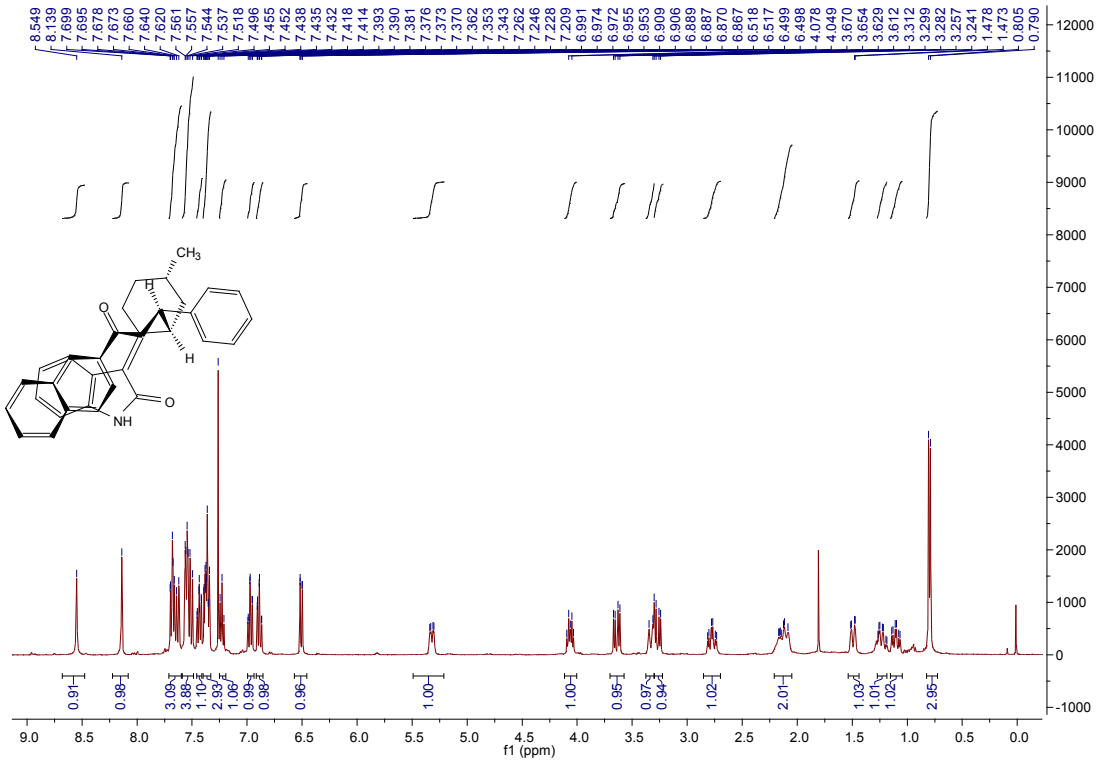
124.20
107.72
107.38
101.62
77.16
43.96
42.88
41.55
38.25
36.35
28.81
26.09
22.03
CH3
H
O
H
O
O
NH
O
f1 (ppm)

3ra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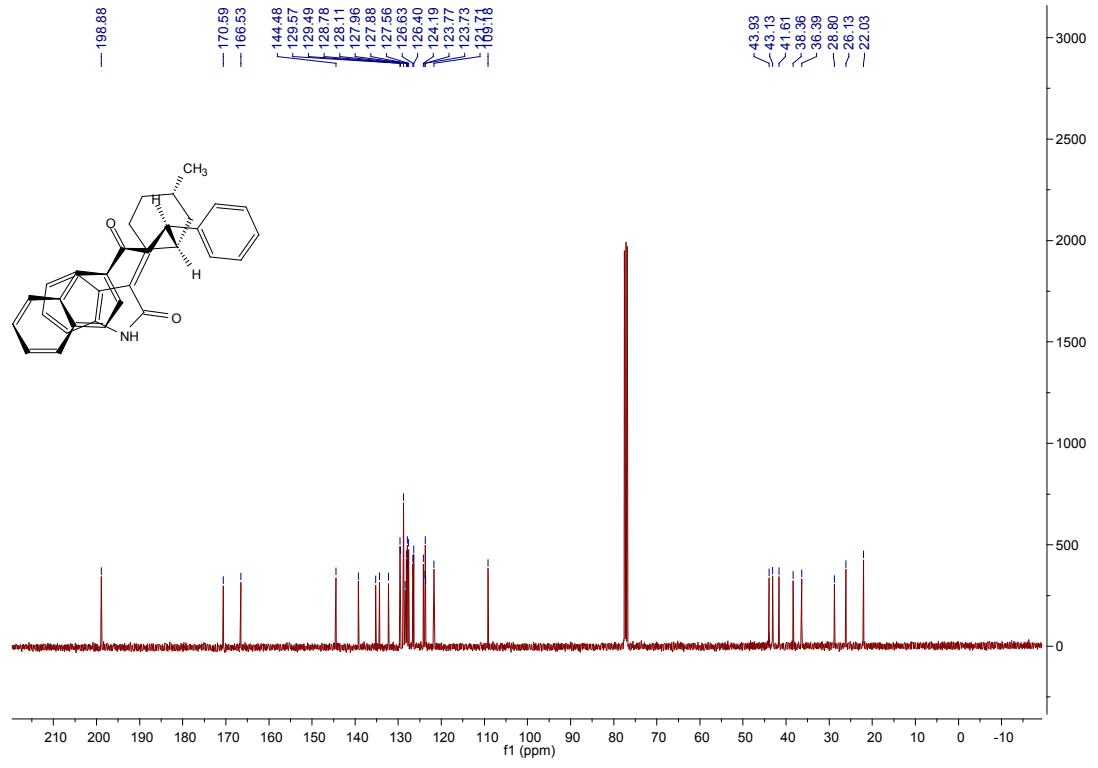
7.640
7.620
7.561
7.557
7.544
7.537
7.518
7.496
7.455
7.452
7.438
7.435
7.432
7.418
7.414
7.393
7.390
7.381
7.376
7.373
7.370
7.362
7.353
7.343
7.262
7.246
7.228
7.209
6.991
6.974
6.972
6.955
6.953
6.909
6.906
6.889
6.887
6.870
6.867
6.518
6.517
6.499
6.498
4.078
4.049
3.670
3.654
3.629
3.612
3.312
3.299
3.282
3.257
3.241
1.478
1.473
0.805
0.790
CH3
H
O
H
O
NH
0.91
0.98
3.09
3.88
1.10
2.93
1.06
0.99
0.98
0.96
1.00
1.00
0.95
0.97
0.94
1.02
2.01
1.03
1.01
1.02
2.95
f1 (ppm)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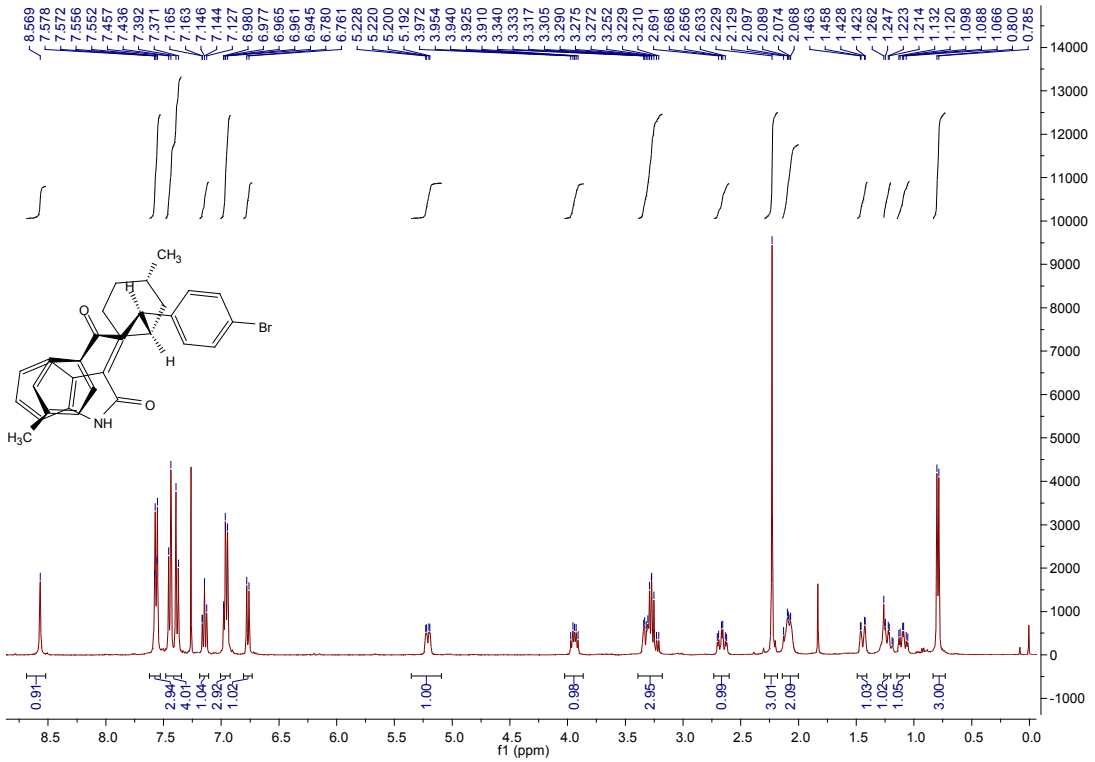
127.88
127.56
126.63
126.40
124.19
123.77
123.73
43.93
43.13
41.61
38.36
36.39
28.80
26.13
22.03
CH3
H
O
H
O
NH
f1 (ppm)

3sa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7.144
7.127
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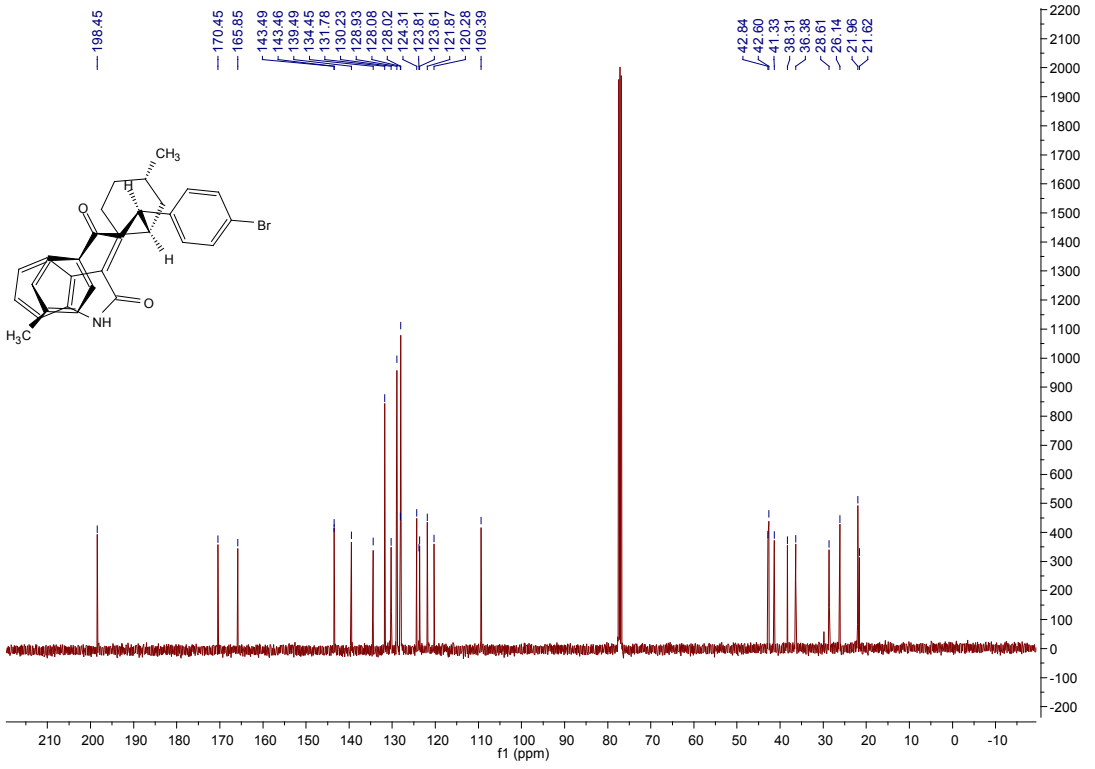
6.977
6.965
6.961
6.945
6.780
6.761
5.228
5.220
5.200
5.192
3.972
3.954
3.940
3.925
3.910
3.340
3.333
3.317
3.305
3.290
3.275
3.272
3.252
3.229
3.210
2.691
2.668
2.656
2.633
2.229
2.129
2.097
2.089
2.074
2.068
1.463
1.458
1.428
1.423
1.262
1.247
1.223
1.214
1.132
1.120
1.098
1.088
1.066
0.800
0.785
CH3
H
O
Br
H
O
NH
H3C
0.91
2.94
4.01
1.04
2.92
1.02
1.00
0.98
2.95
0.99
3.01
2.09
1.03
1.02
1.05
3.00
f1 (ppm)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131.78
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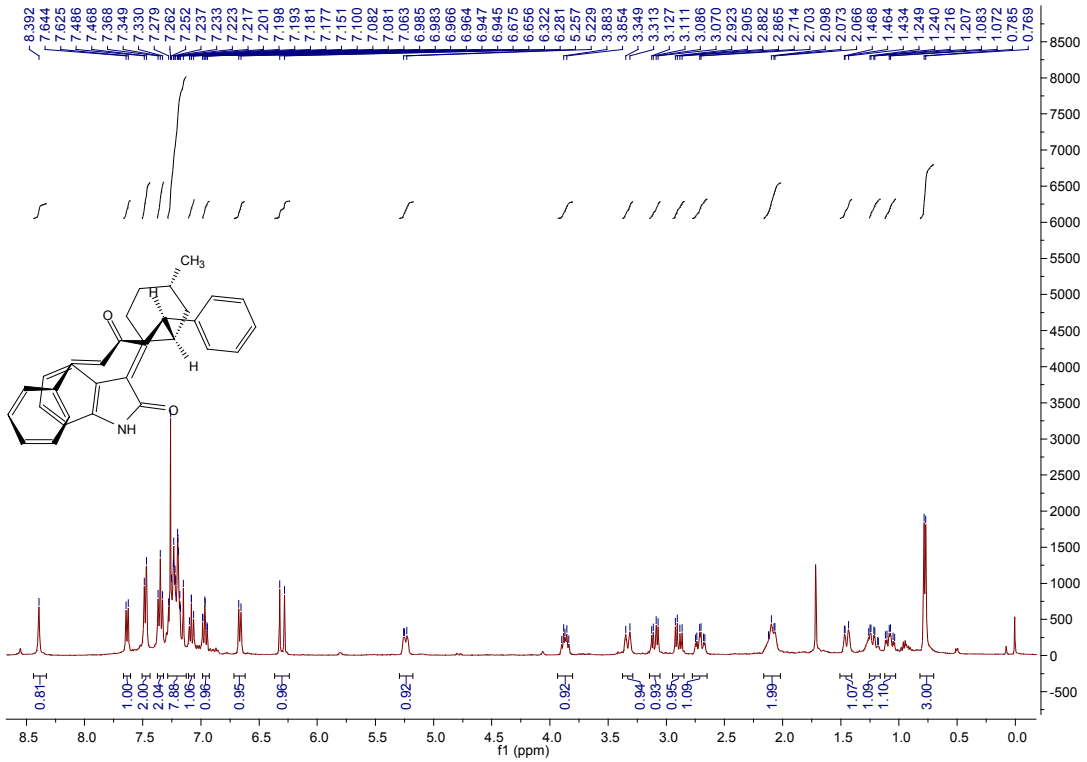
128.93
128.08
128.02
124.31
123.81
123.61
121.87
120.28
109.39
42.84
42.60
41.33
38.31
36.38
28.61
26.14
21.96
21.62
CH3
H
O
Br
H
O
NH
H3C
f1 (ppm)

3ta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7.262
7.252
7.237
7.233
7.223
7.217
7.201
7.198
7.193
7.181
7.177
7.151
7.100
7.082
7.081
7.063
6.985
6.983
6.966
6.964
6.947
6.945
6.675
6.656
6.322
6.281
5.257
5.229
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3.854
3.349
3.313
3.127
3.111
3.086
3.070
2.923
2.905
2.882
2.865
2.714
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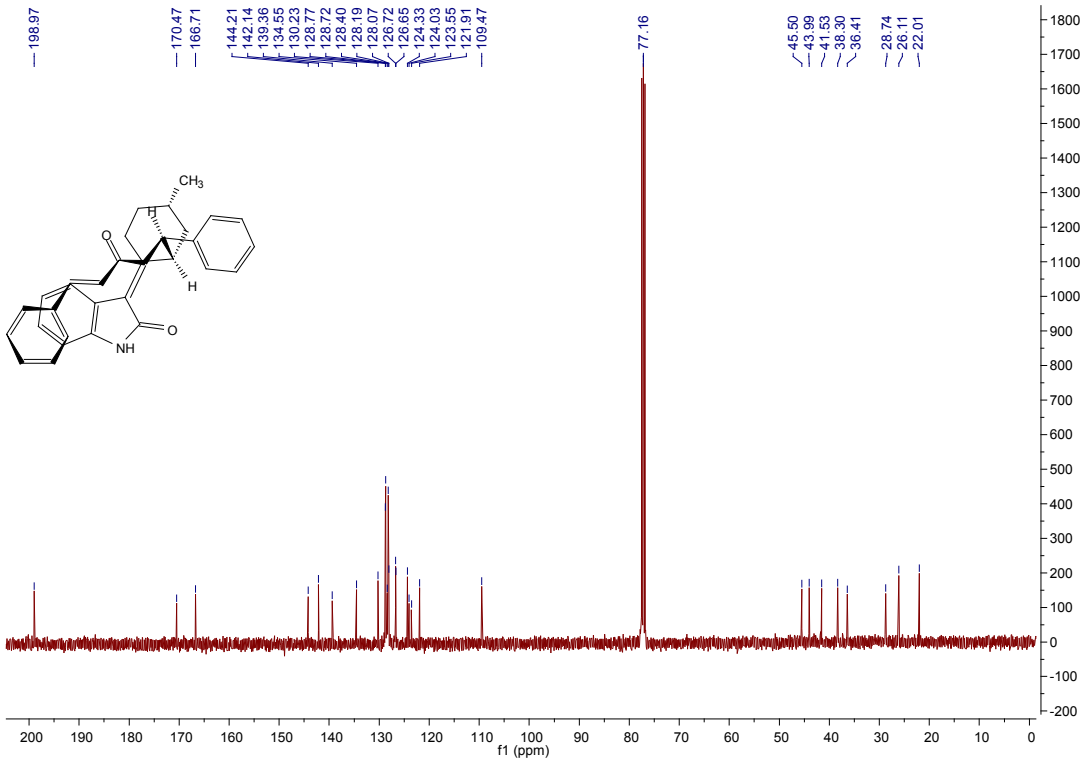
2.098
2.073
2.066
1.468
1.464
1.434
1.249
1.240
1.216
1.207
1.083
1.072
0.785
0.769
CH3
H
O
H
O
NH
0.81
1.00
2.00
2.04
7.88
1.06
0.98
0.95
0.96
0.92
0.92
0.94
0.93
0.95
1.09
1.99
1.07
1.09
1.10
3.00
f1 (ppm)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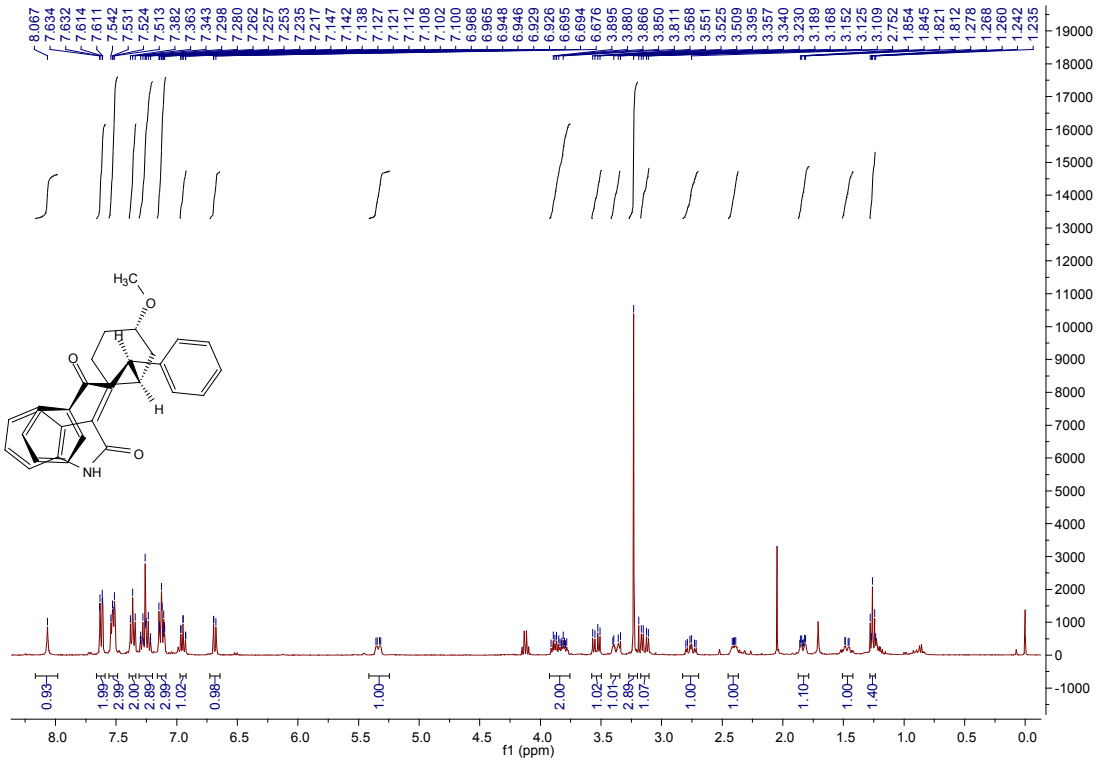
128.72
128.40
128.19
128.07
126.72
126.65
124.33
124.03
123.55
121.91
109.47
77.16
45.50
43.99
41.53
38.30
36.41
28.74
26.11
22.01
CH3
H
O
H
O
NH
f1 (ppm)

3ab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7.382
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7.343
7.298
7.280
7.262
7.257
7.253
7.235
7.217
7.147
7.142
7.138
7.127
7.121
7.112
7.108
7.102
7.100
6.968
6.965
6.948
6.946
6.929
6.926
6.695
6.694
6.676
3.895
3.880
3.866
3.850
3.811
3.568
3.551
3.525
3.509
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3.357
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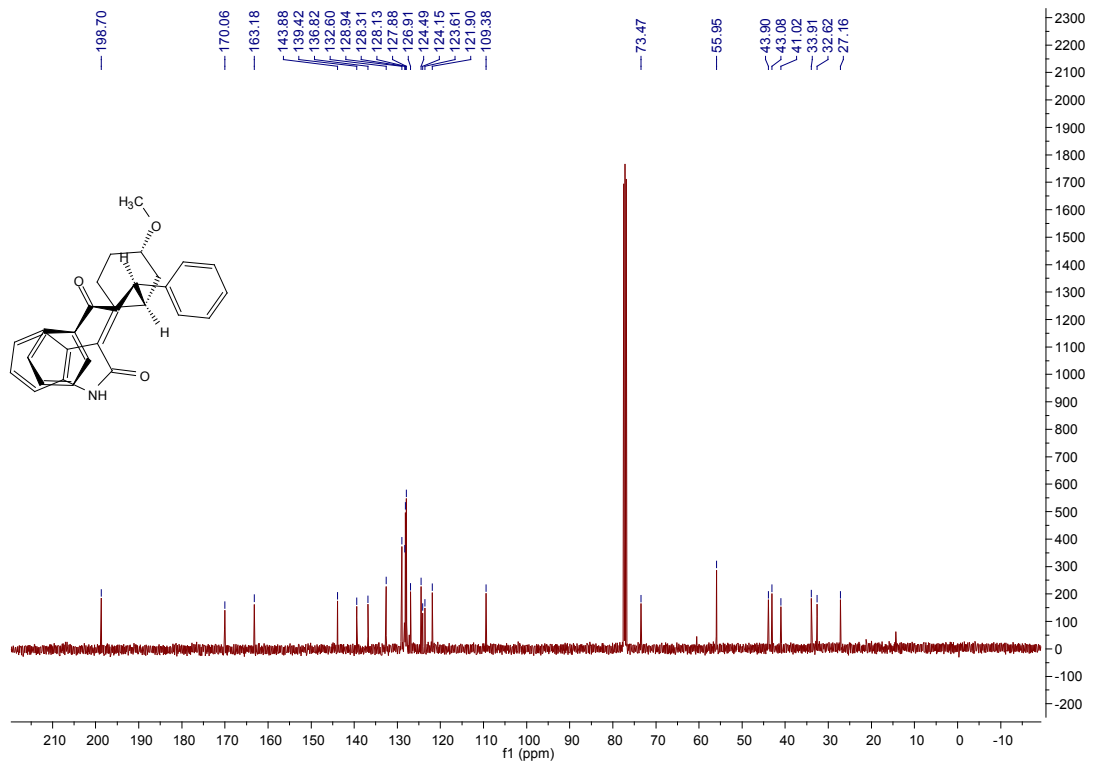
3.230
3.189
3.168
3.152
3.125
3.109
2.752
1.854
1.845
1.821
1.812
1.278
1.268
1.260
1.242
1.235
H3C
O
H
O
H
O
NH
0.93
1.99
2.99
2.00
2.89
2.99
1.02
0.98
1.00
2.00
1.02
1.01
2.89
1.07
1.00
1.00
1.10
1.00
1.40
f1 (ppm)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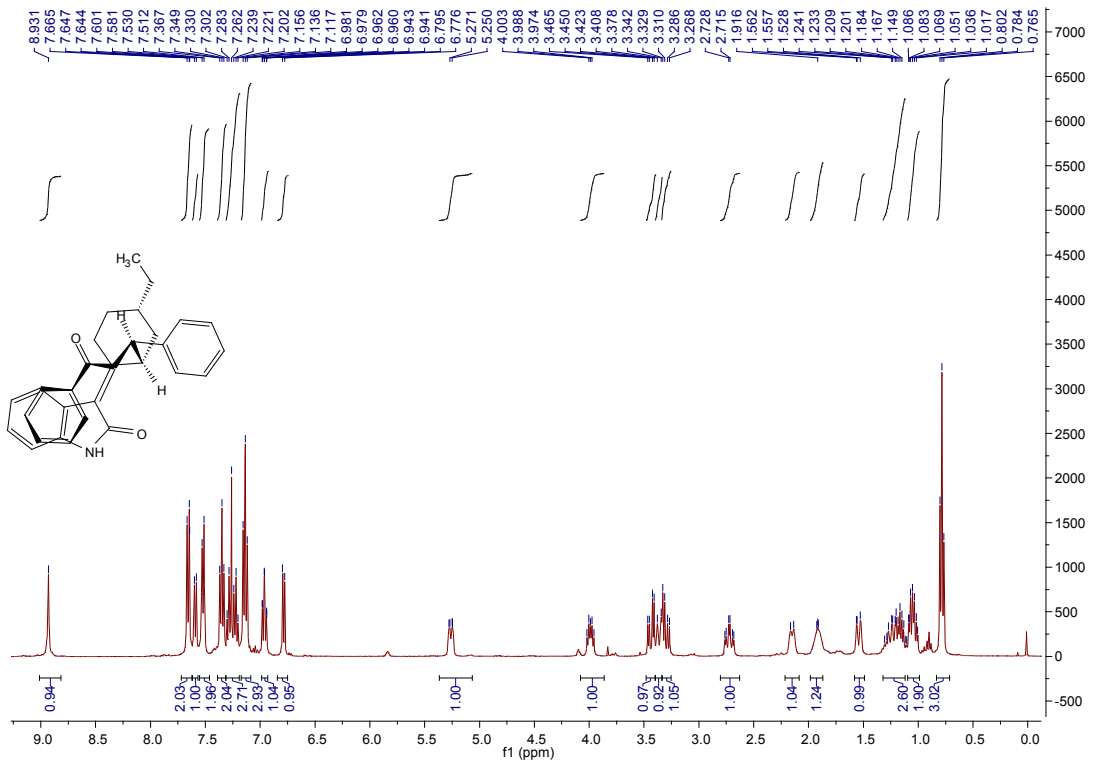
139.42
136.82
132.60
128.94
128.31
128.13
127.88
126.91
124.49
124.15
123.61
121.90
109.38
73.47
55.95
43.90
43.08
41.02
33.91
32.62
27.16
H3C
O
H
O
H
O
NH
f1 (ppm)

3ac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7.283
7.262
7.239
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7.202
7.156
7.136
7.117
6.981
6.979
6.962
6.960
6.943
6.941
6.795
6.776
5.271
5.250
4.003
3.998
3.974
3.465
3.450
3.423
3.408
3.378
3.342
3.329
3.310
3.286
3.268
2.728
2.715
1.916
1.562
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1.149
1.086
1.083
1.069
1.051
1.036
1.017
0.802
0.784
0.765
H3C
H
O
H
O
NH
0.94
2.03
1.00
1.96
2.04
2.71
2.93
1.04
0.95
1.00
1.00
0.97
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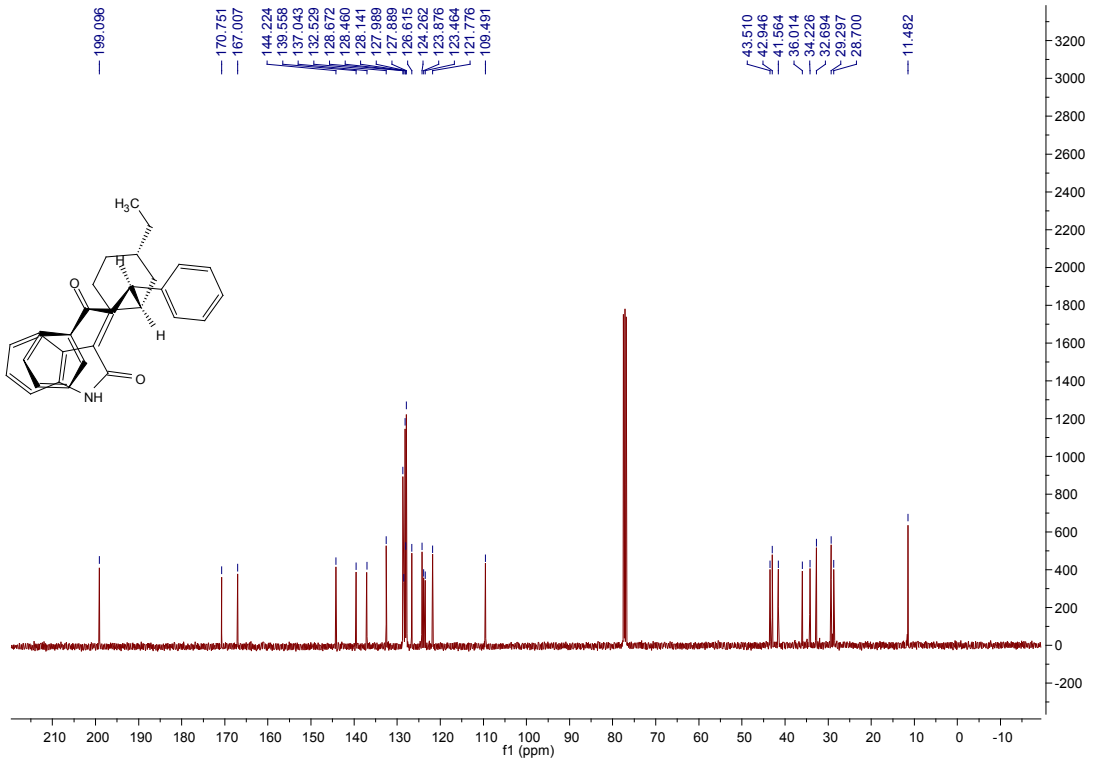
1.05
1.00
1.04
1.24
0.99
2.60
1.90
3.02
f1 (ppm)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124.262
123.876
123.464
121.776
109.491
43.510
42.946
41.564
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28.700
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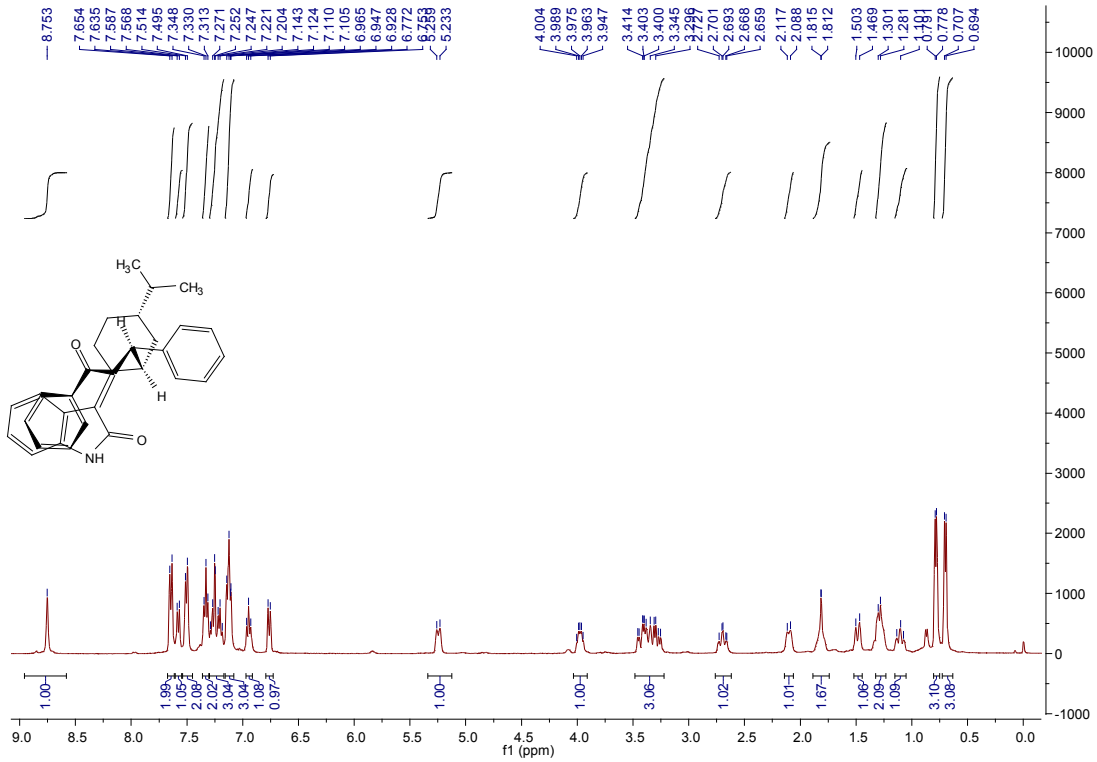
H
O
H
O
NH
f1 (ppm)

3ad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7.221
7.204
7.143
7.124
7.110
7.105
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6.947
6.928
6.772
5.233
4.004
3.989
3.975
3.963
3.947
3.414
3.403
3.400
3.345
2.701
2.693
2.668
2.659
2.117
2.088
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1.812
1.503
1.469
1.301
1.281
1.101
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0.707
0.694
H3C
CH3
H
O
H
O
NH
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2.08
2.02
3.04
1.08
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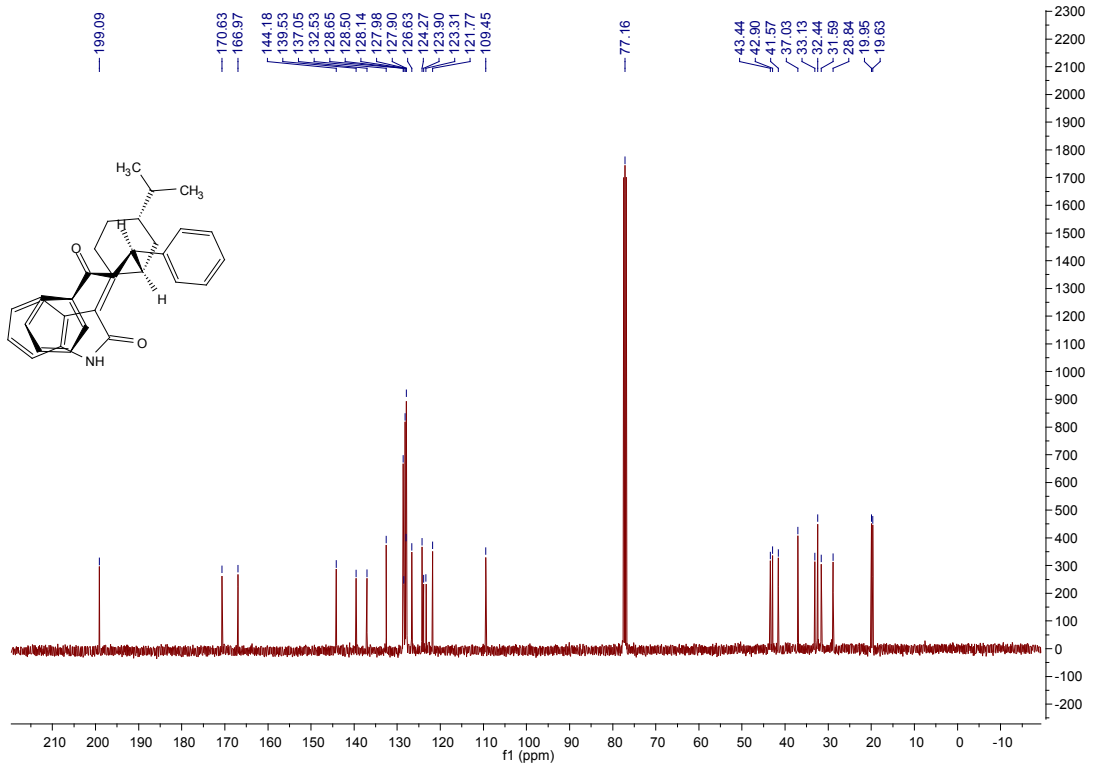
f1 (ppm)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123.90
123.31
121.77
109.45
77.16
43.44
42.90
41.57
37.03
33.13
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19.95
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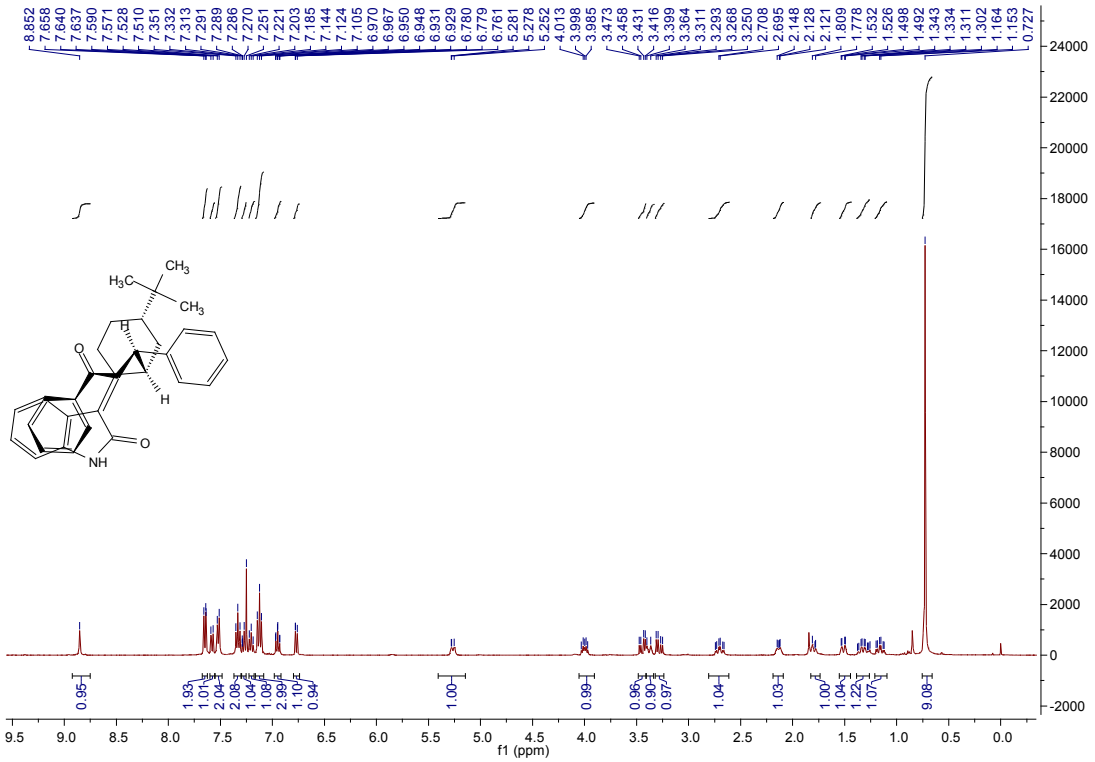
H3C
CH3
H
O
H
O
NH
f1 (ppm)

3ae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7.270
7.251
7.221
7.203
7.185
7.144
7.124
7.105
6.970
6.967
6.950
6.948
6.931
6.929
6.780
6.779
6.761
5.281
5.278
5.252
4.013
3.998
3.985
3.473
3.458
3.431
3.416
3.399
3.364
3.311
3.293
3.268
3.250
2.708
2.695
2.148
2.128
2.121
1.809
1.778
1.532
1.526
1.498
1.492
1.343
1.334
1.311
1.302
1.164
1.153
0.727
CH3
H3C
CH3
H
O
H
O
NH
0.95
1.93
1.01
2.04
2.08
1.04
1.08
2.99
1.10
0.94
1.00
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1.03
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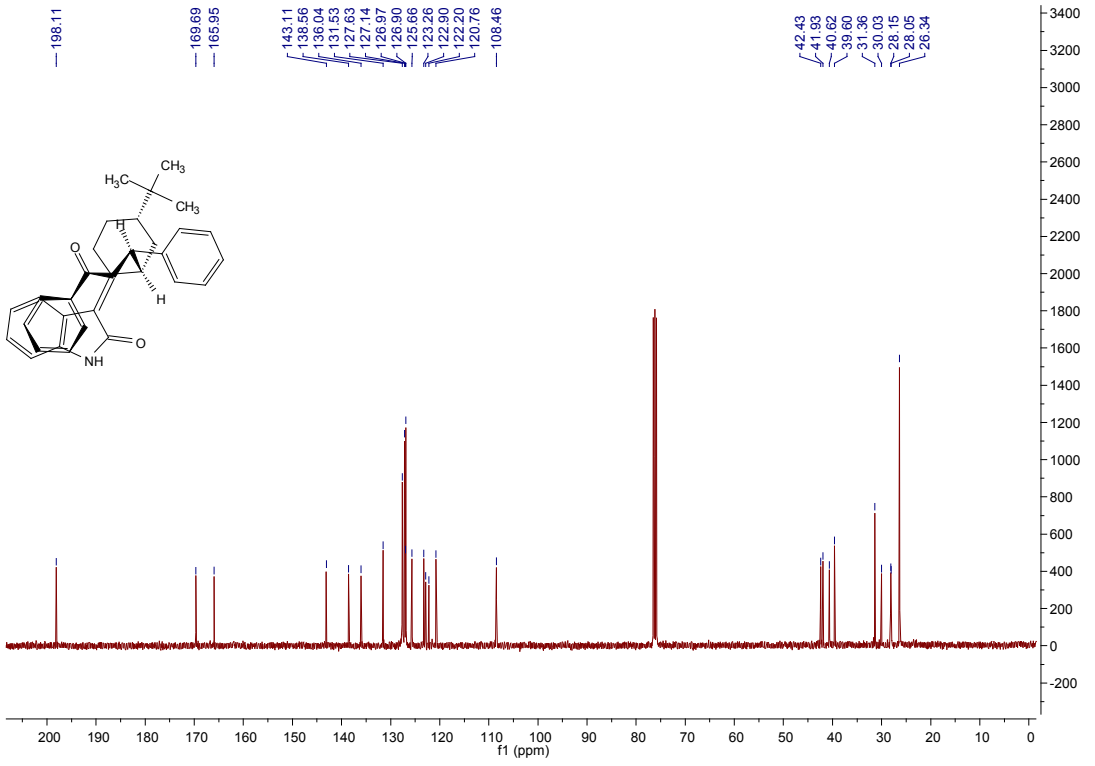
1.07
9.08
f1 (ppm)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123.26
122.90
122.20
120.76
108.46
42.43
41.93
40.62
39.60
31.36
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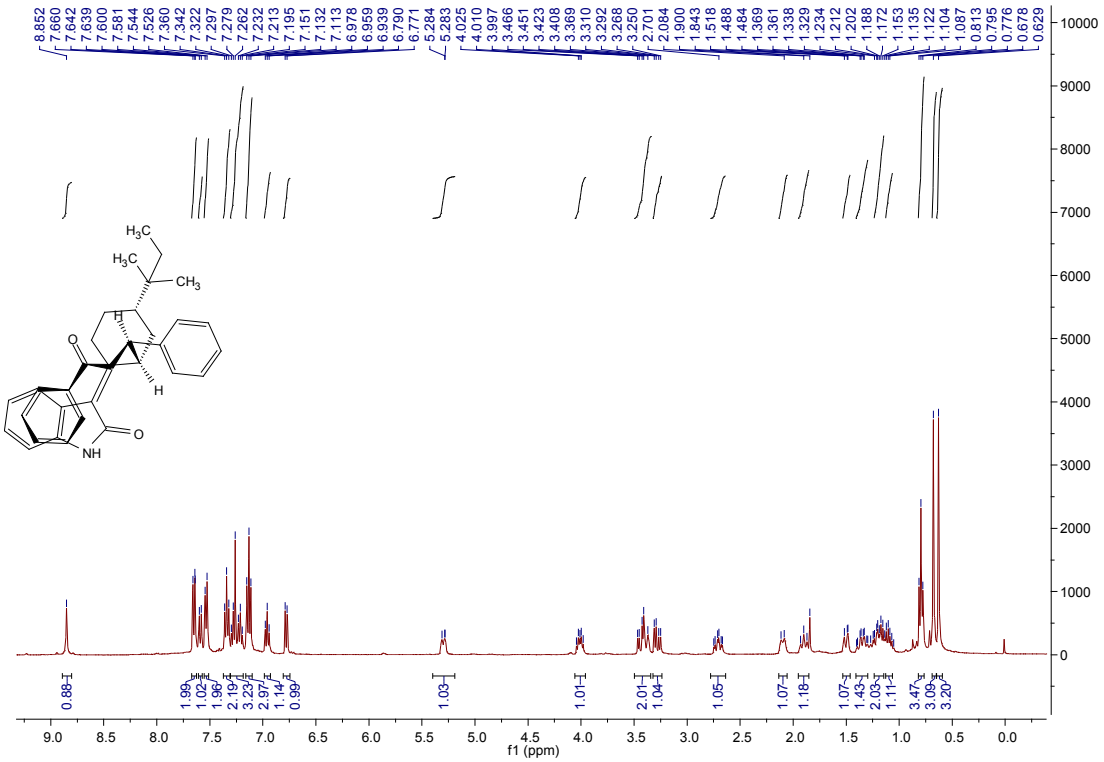
28.05
26.34
CH3
H3C
CH3
H
O
H
O
NH
f1 (ppm)

3af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7.526
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7.279
7.262
7.232
7.213
7.195
7.151
7.132
7.113
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6.939
6.790
6.771
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5.283
4.025
4.010
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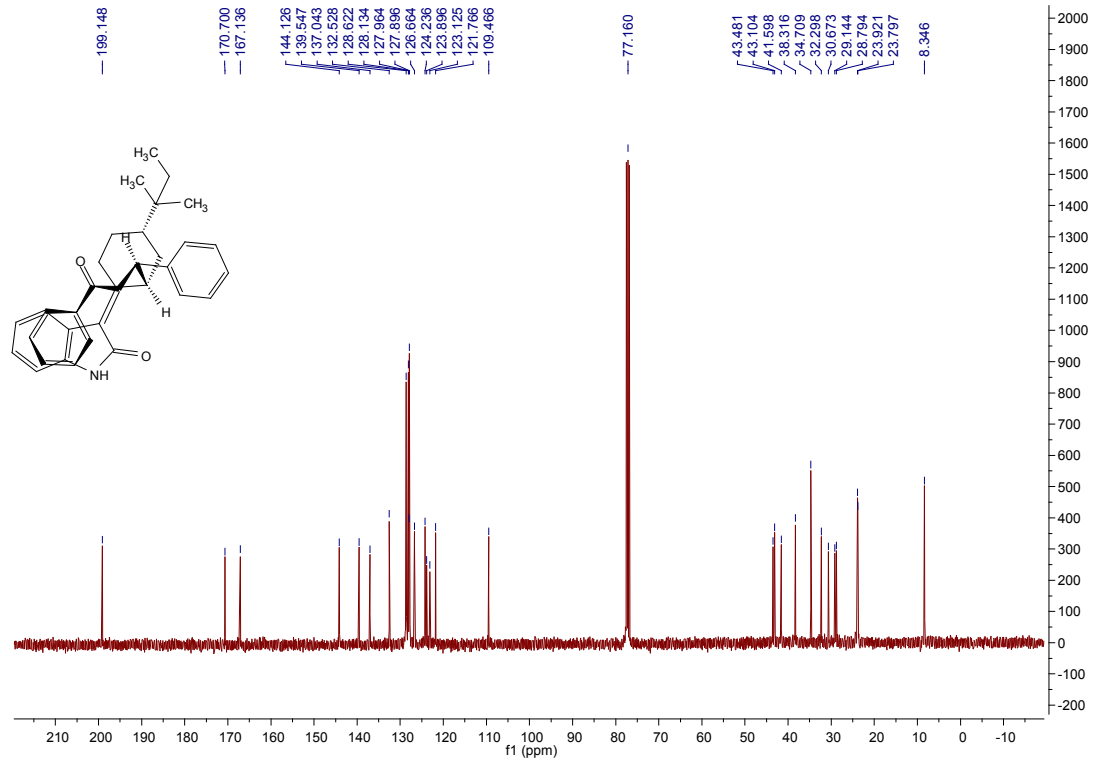
3.466
3.451
3.423
3.408
3.369
3.310
3.292
3.268
3.250
2.701
2.084
1.900
1.843
1.518
1.488
1.484
1.369
1.361
1.338
1.329
1.234
1.212
1.202
1.188
1.172
1.153
1.135
1.122
1.104
1.087
0.813
0.795
0.776
0.678
0.629
H3C
H3C
CH3
H
O
H
O
NH
0.88
1.99
1.02
1.96
2.19
3.23
2.97
1.14
0.99
1.03
1.01
2.01
1.04
1.05
1.07
1.18
1.07
1.43
2.03
1.11
3.47
3.09
3.20
f1 (ppm)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124.236
123.896
123.125
121.766
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77.160
43.481
43.104
41.598
38.316
34.709
32.298
30.673
29.144
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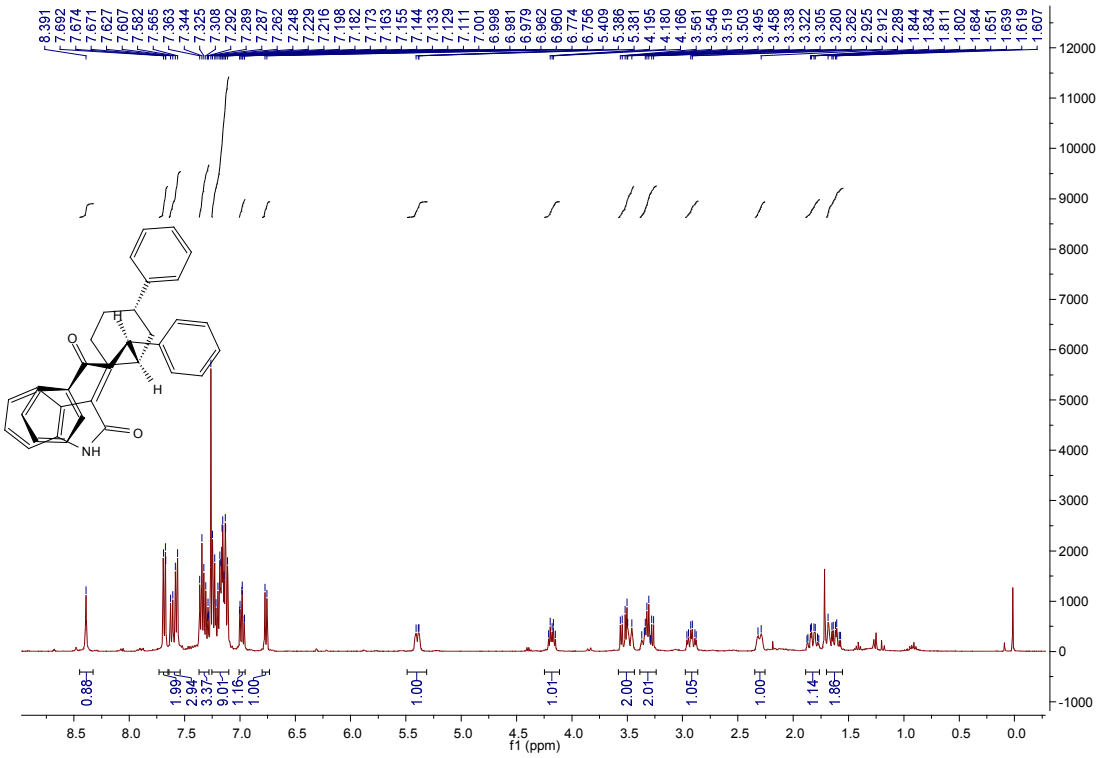
8.346
H3C
H3C
CH3
H
O
H
O
NH
f1 (ppm)

3ag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7.287
7.262
7.248
7.229
7.216
7.198
7.182
7.173
7.163
7.155
7.144
7.133
7.129
7.111
7.001
6.998
6.981
6.979
6.962
6.960
6.774
6.756
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5.386
5.381
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4.180
4.166
3.561
3.546
3.519
3.503
3.495
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3.338
3.322
3.305
3.280
3.262
2.925
2.912
2.289
1.844
1.834
1.811
1.802
1.684
1.651
1.639
1.619
1.607
O
H
H
O
NH
0.88
1.99
2.94
3.37
9.01
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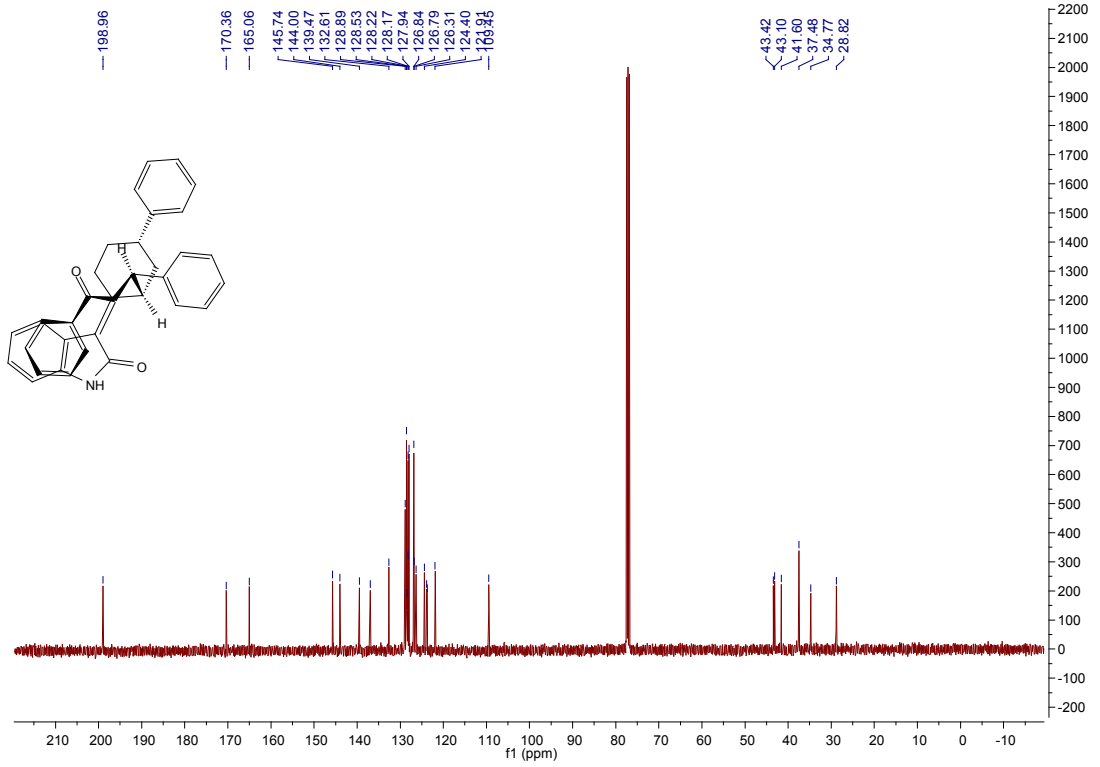
1.00
1.01
2.00
2.01
1.05
1.00
1.14
1.86
f1 (ppm)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126.84
126.79
126.31
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41.60
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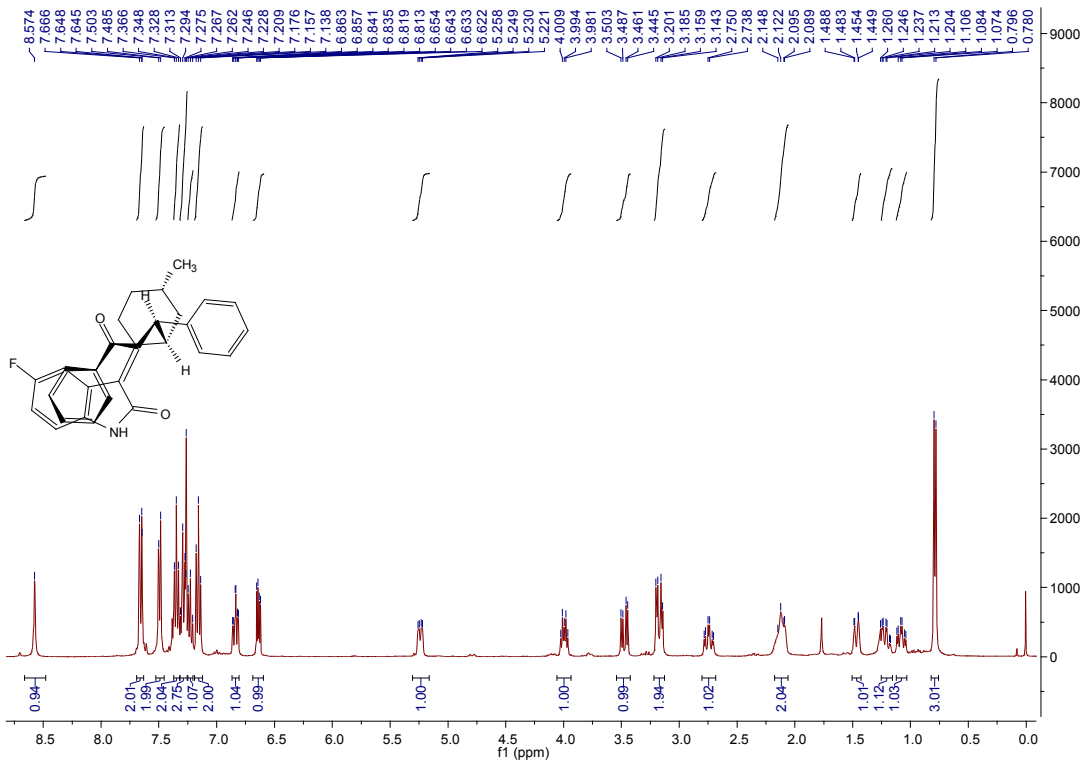
34.77
28.82
O
H
H
O
NH
f1 (ppm)

3ah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7.262
7.246
7.228
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7.157
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6.857
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6.835
6.819
6.813
6.654
6.643
6.633
6.622
5.258
5.249
5.230
5.221
4.009
3.994
3.981
3.503
3.487
3.461
3.445
3.201
3.185
3.159
3.143
2.750
2.738
2.148
2.122
2.095
2.089
1.488
1.483
1.454
1.449
1.260
1.246
1.237
1.213
1.204
1.106
1.084
1.074
0.796
0.780
CH3
H
O
F
H
O
NH
0.94
2.01
1.99
2.04
2.75
1.07
2.00
1.04
0.99
1.00
1.00
0.99
1.94
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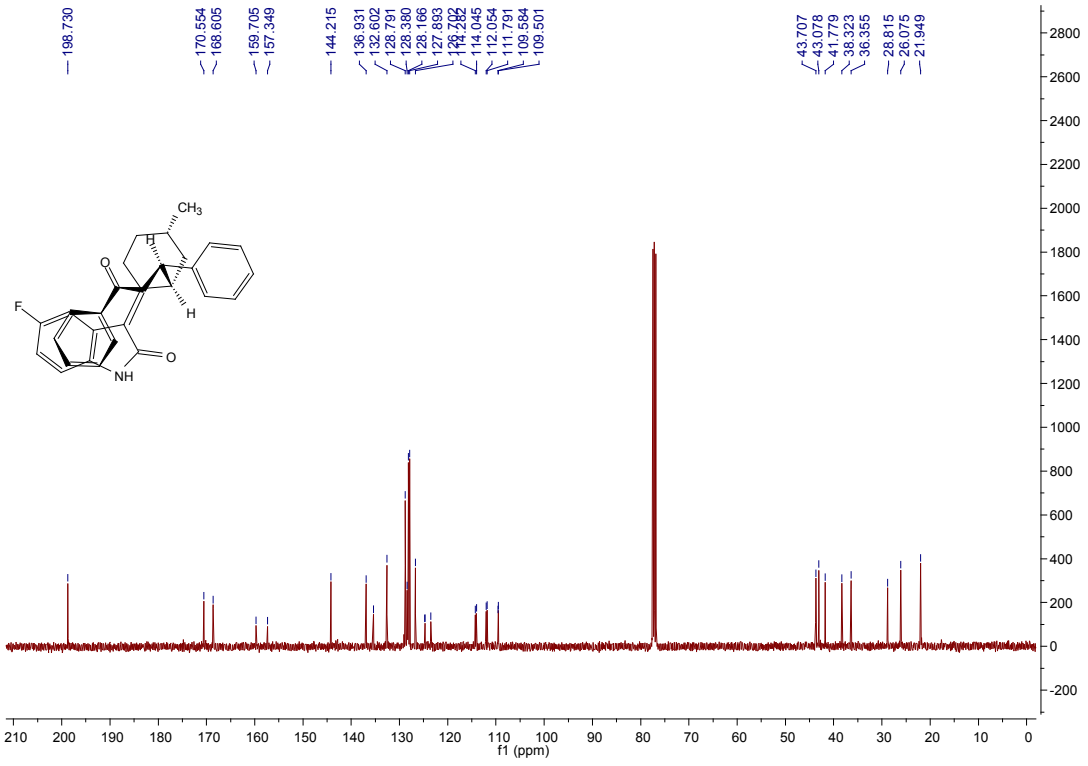
2.04
1.01
1.12
1.03
3.01
f1 (ppm)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114.045
112.054
111.791
109.584
109.501
43.707
43.078
41.779
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CH3
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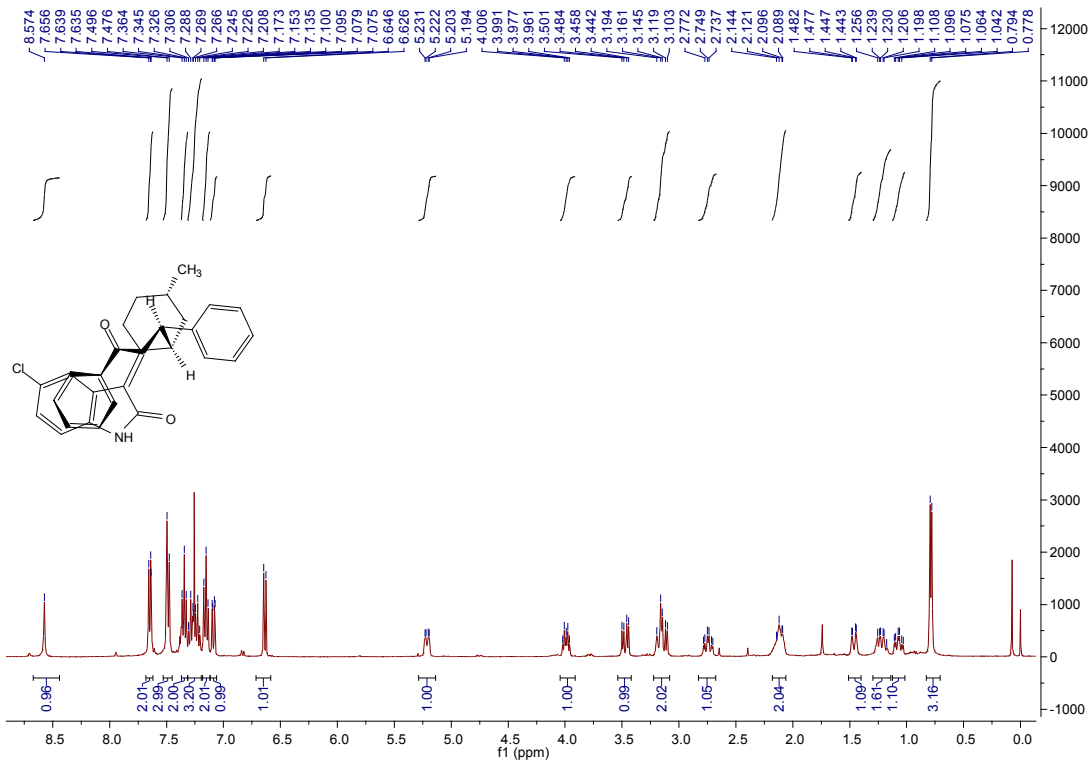
O
F
H
O
NH
f1 (ppm)

3ai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7.245
7.226
7.208
7.173
7.153
7.135
7.100
7.095
7.079
7.075
6.646
6.626
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5.203
5.194
4.006
3.991
3.977
3.961
3.501
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3.458
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3.119
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2.772
2.749
2.737
2.144
2.121
2.096
2.089
1.482
1.477
1.447
1.443
1.256
1.239
1.230
1.206
1.198
1.108
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1.075
1.064
1.042
0.794
0.778
CH3
H
O
Cl
H
O
NH
0.96
2.01
2.99
2.00
3.20
2.01
0.99
1.01
1.00
1.00
0.99
2.02
1.05
2.04
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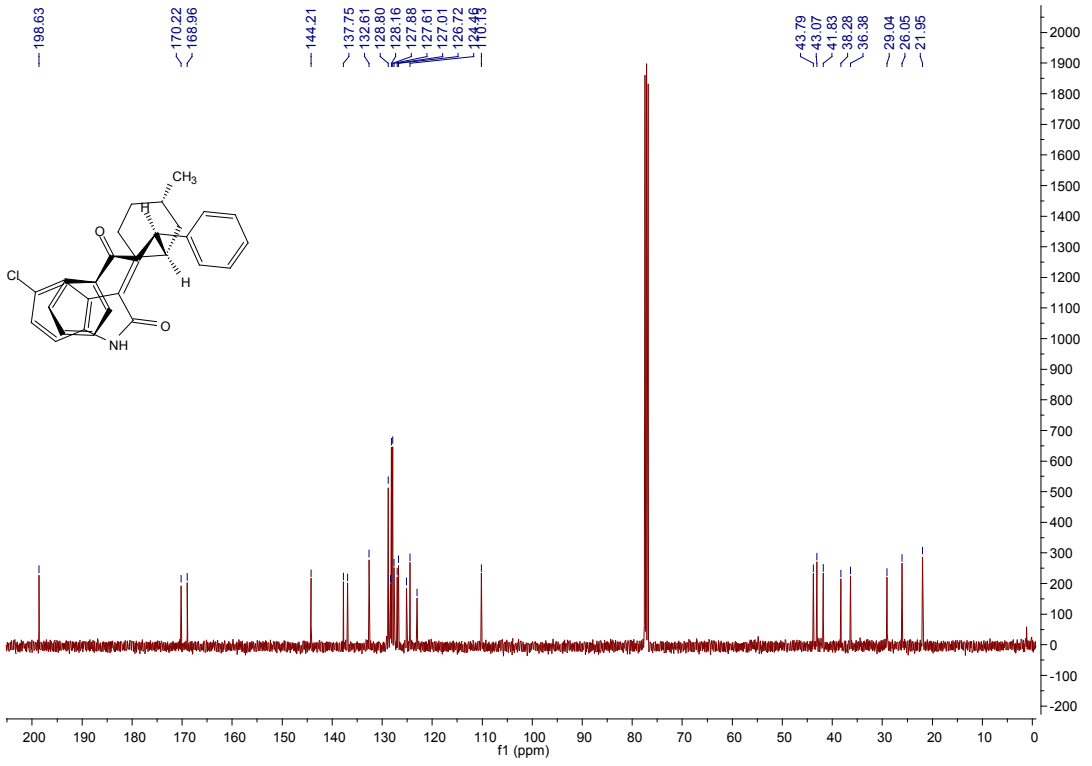
1.61
1.10
3.16
f1 (ppm)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127.01
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110.13
43.79
43.07
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29.04
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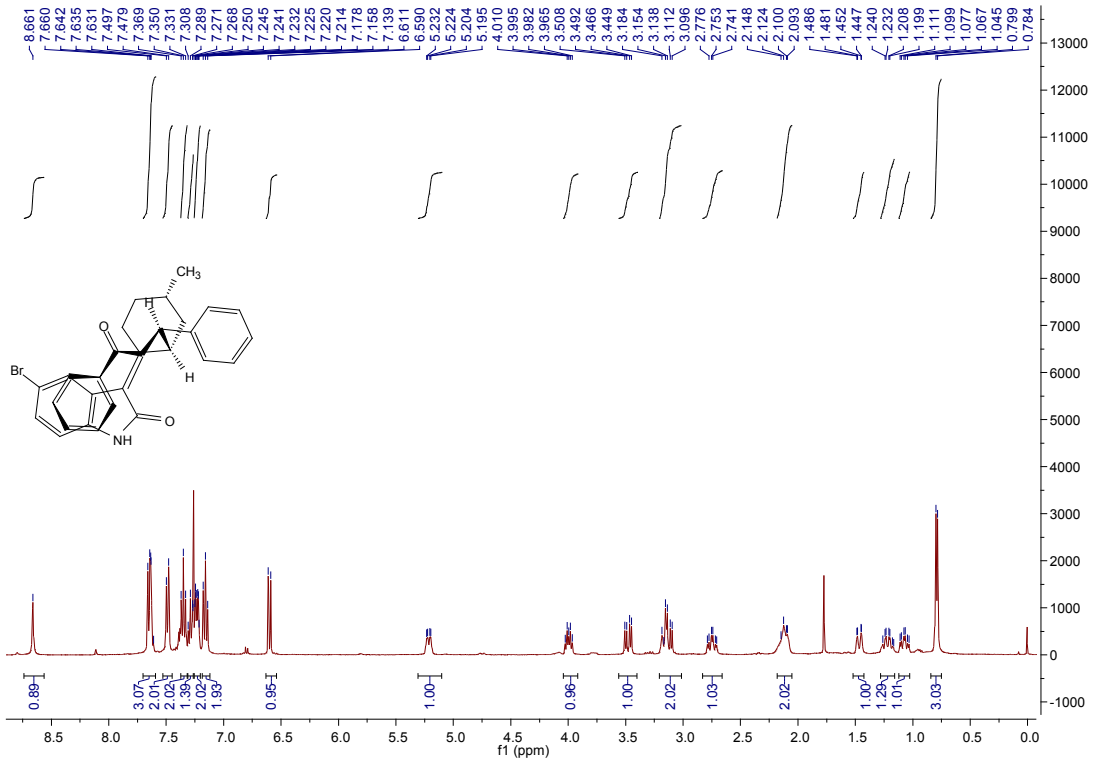
CH3
H
O
Cl
H
O
NH
f1 (ppm)

3aj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7.250
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7.241
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6.611
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5.224
5.204
5.195
4.010
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CH3
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O
Br
H
O
NH
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3.07
2.01
2.02
1.39
2.02
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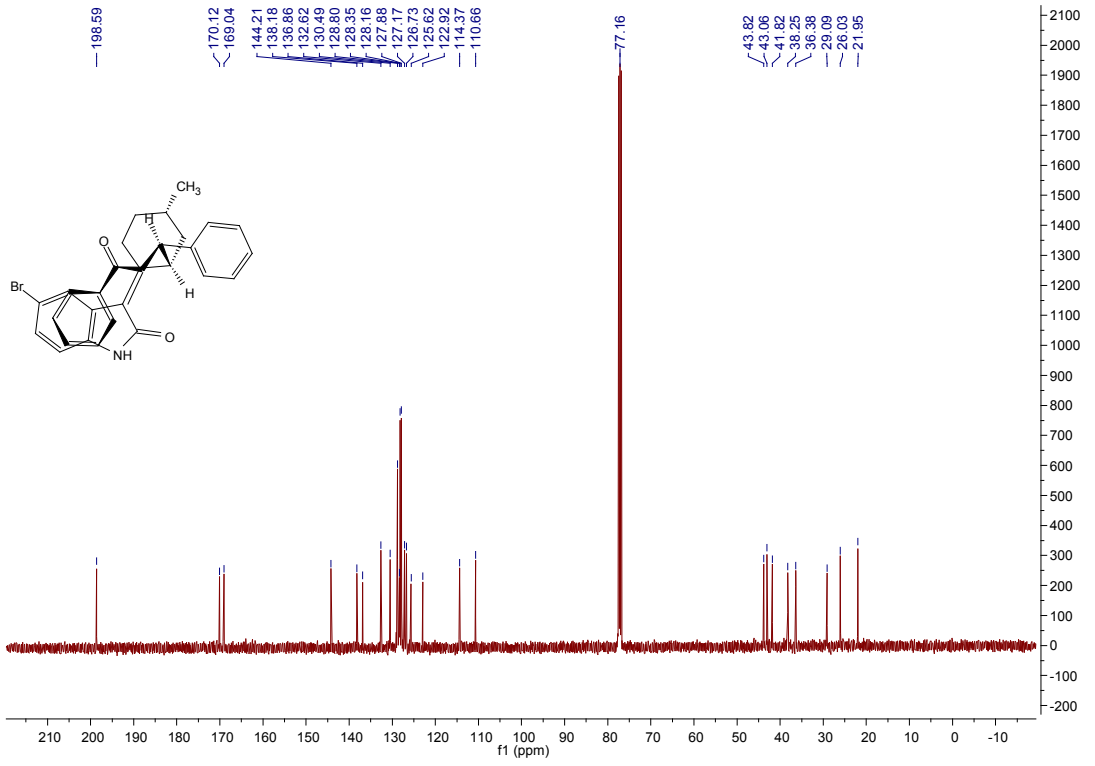
1.29
1.01
3.03
f1 (ppm)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127.17
126.73
125.62
122.92
114.37
110.66
77.16
43.82
43.06
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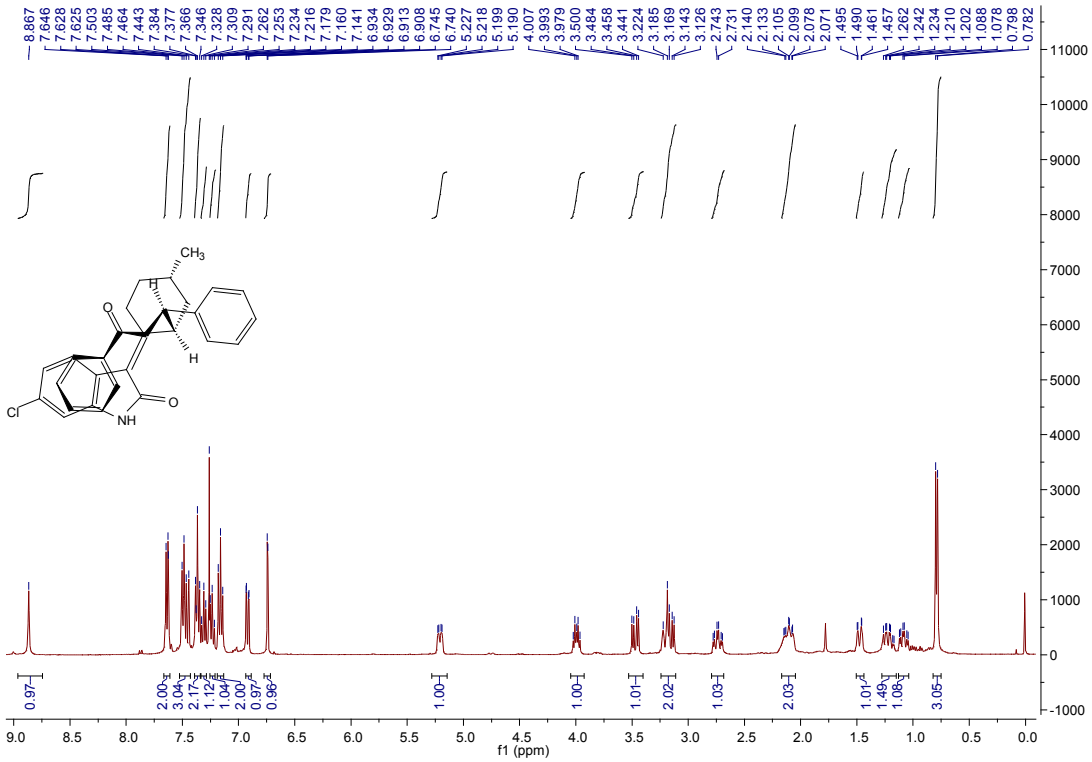
29.09
26.03
21.95
CH3
H
O
Br
H
O
NH
f1 (ppm)

3ak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7.291
7.262
7.253
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7.141
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5.218
5.199
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1.078
0.798
0.782
CH3
H
O
H
O
Cl
NH
0.97
2.00
3.04
2.17
1.12
1.04
2.00
0.97
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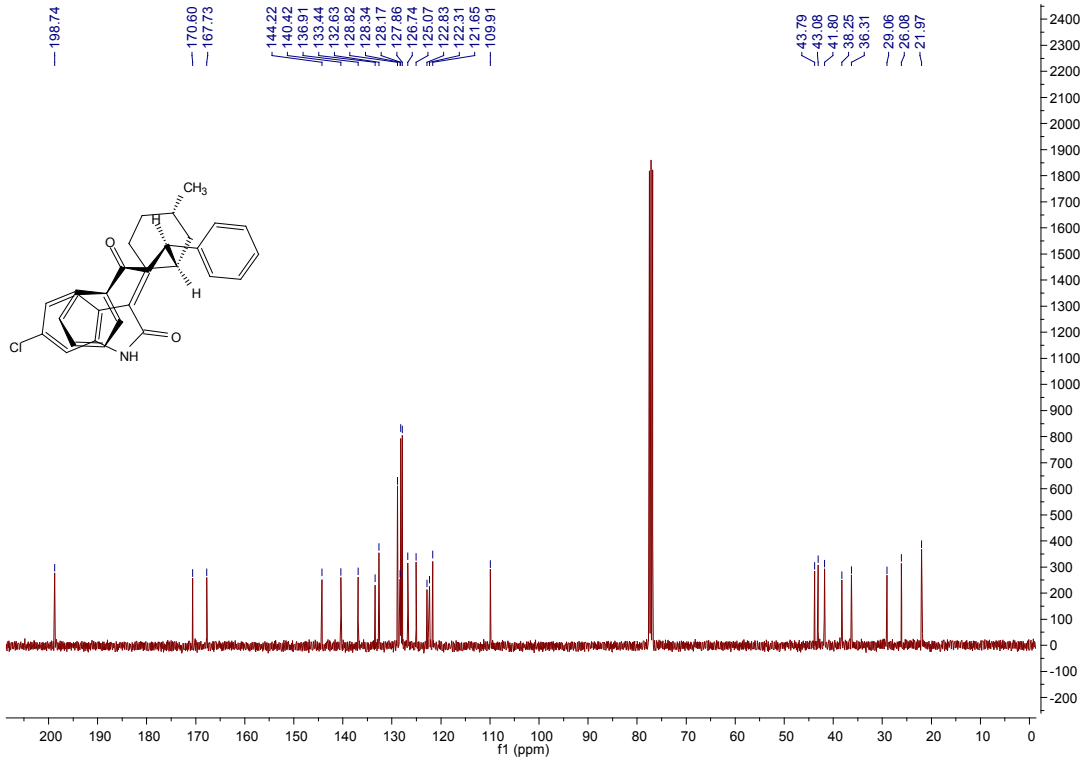
3.05
f1 (ppm)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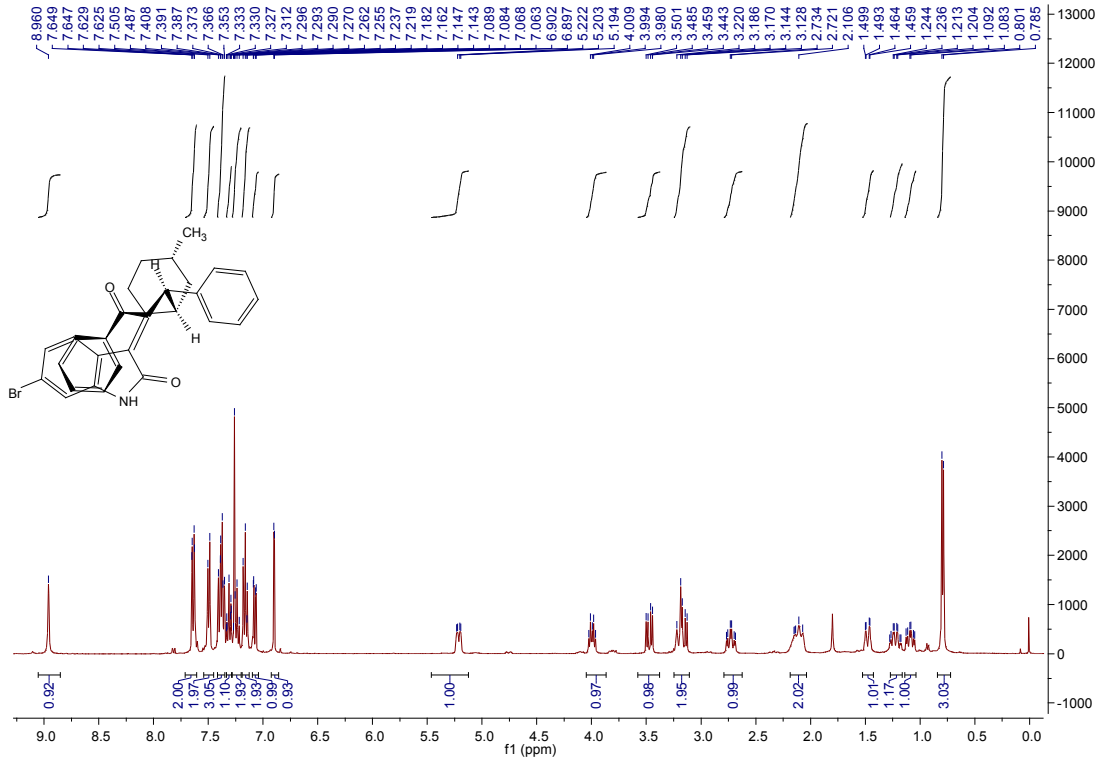
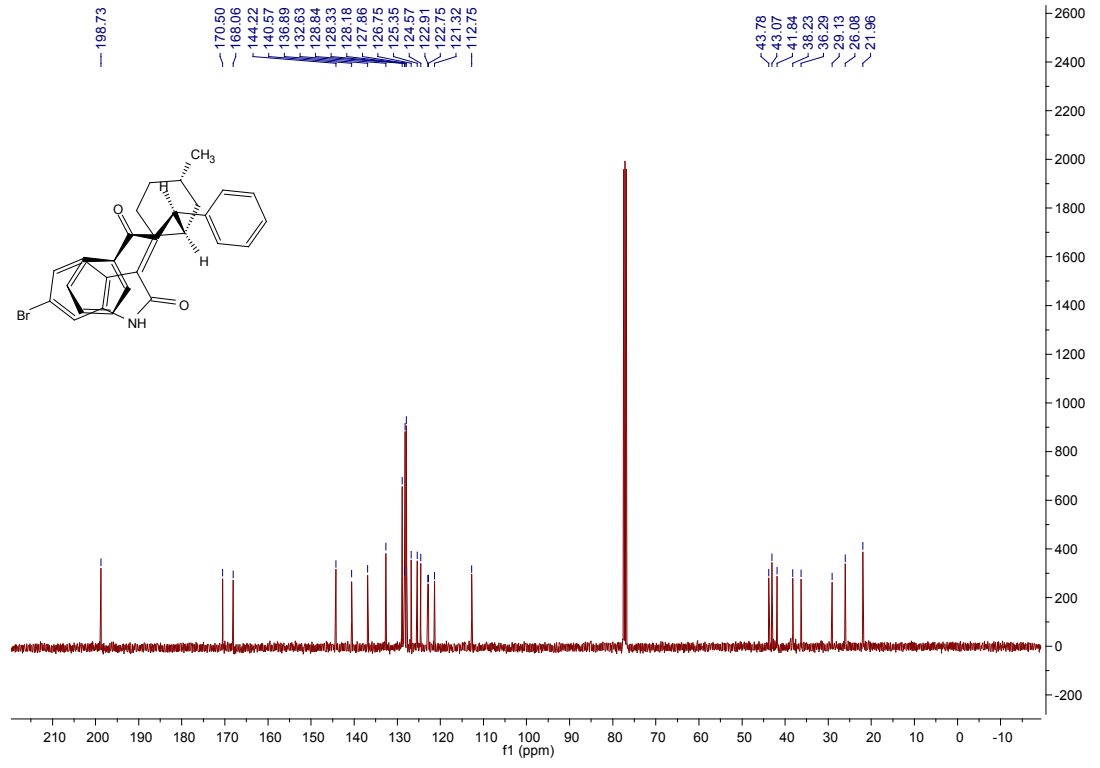
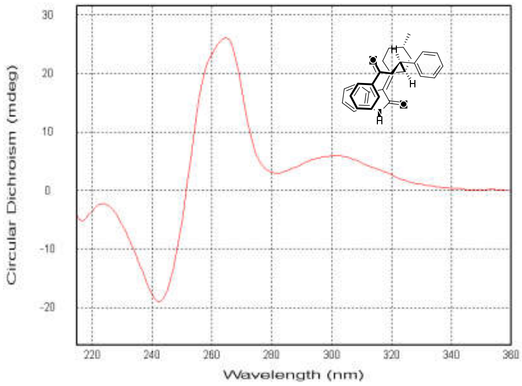
125.07
122.83
122.31
121.65
109.91
43.79
43.08
41.80
38.25
36.31
29.06
26.08
21.97
CH3
H
O
H
O
Cl
NH
f1 (ppm)

3al





(M) Copies of CD spectra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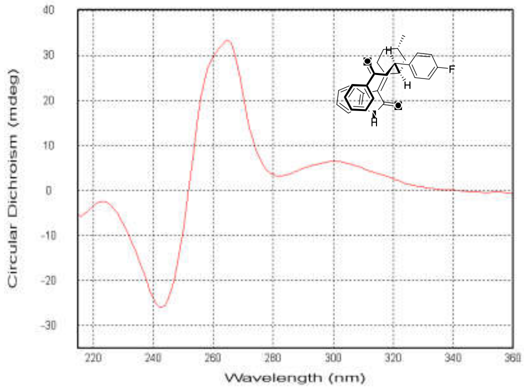
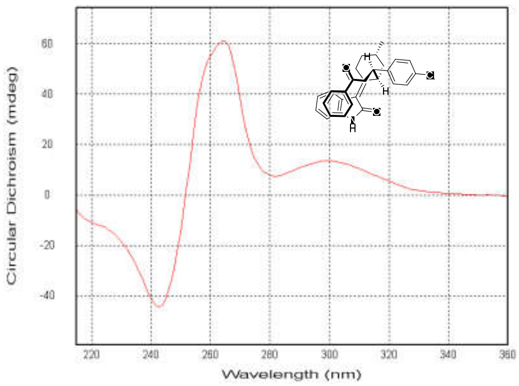
20
10
0
-10
-20
220 240 260 280 300 320 340 360
Wavelength (nm)


Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
220 240 260 280 300 320 340 360
Wavelength (nm)
F


Circular Dichroism (mdeg)
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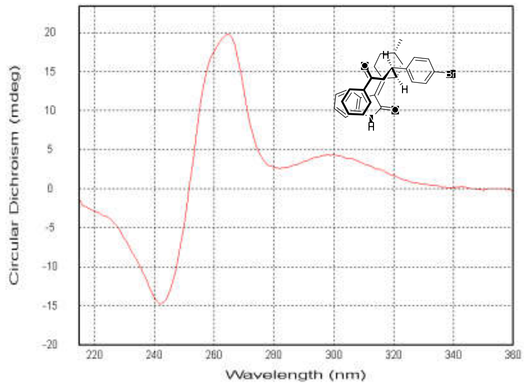
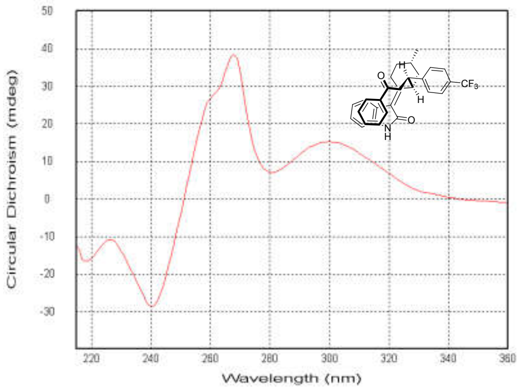
40
20
0
-20
-40
220 240 260 280 300 320 340 360
Wavelength (nm)


Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
-20
220 240 260 280 300 320 340 360
Wavelength (nm)


Circular Dichroism (mdeg)
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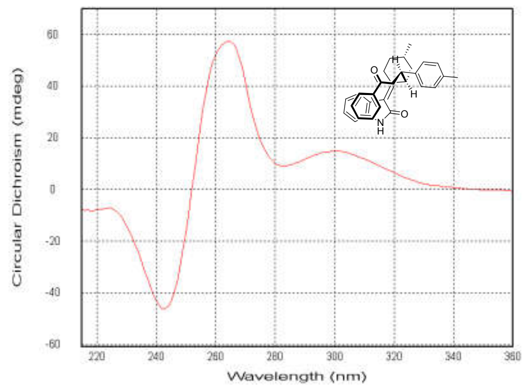
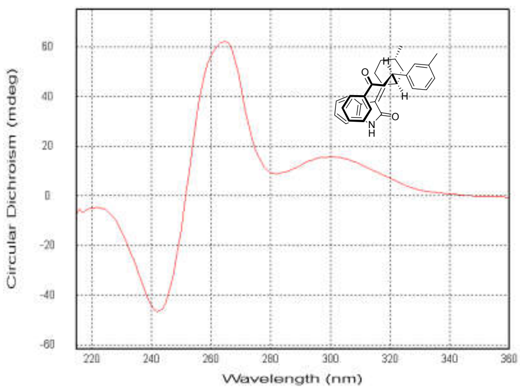
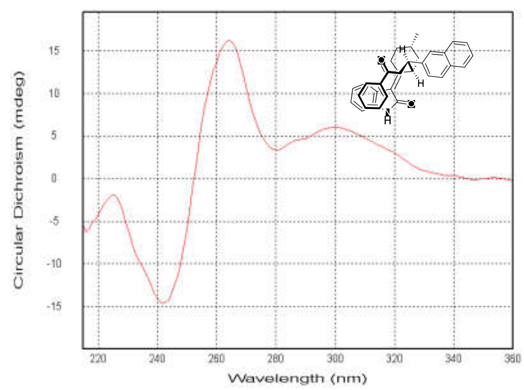
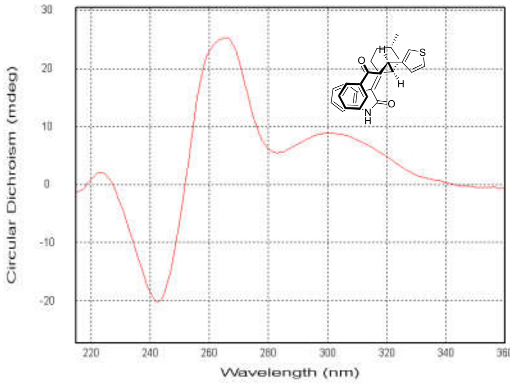
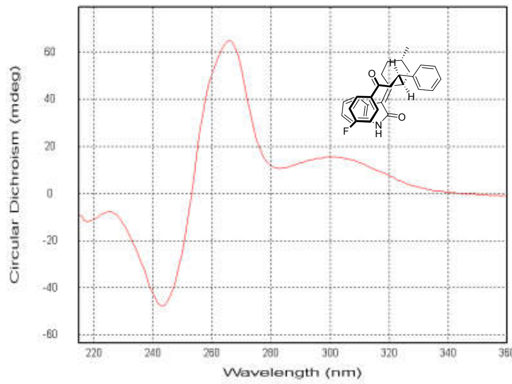
40
30
20
10
0
-10
-20
-30
220 240 260 280 300 320 340 360
Wavelength (nm)
CF3
NH
O

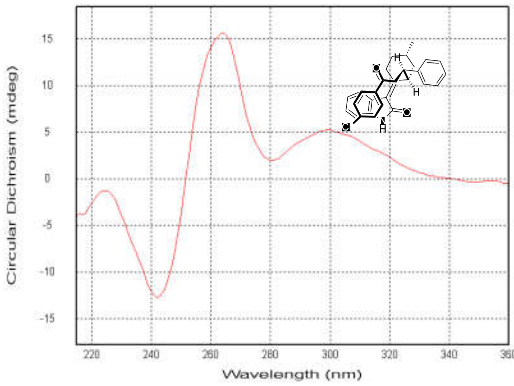

Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
220 240 260 280 300 320 340 360
Wavelength (nm)

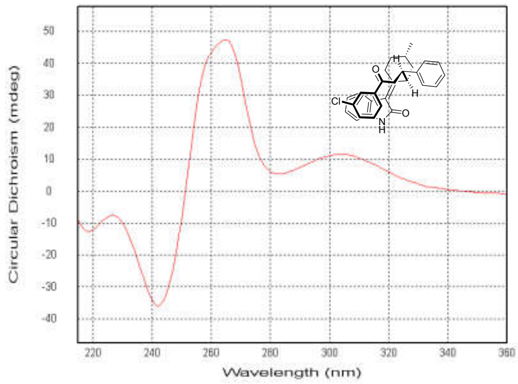

Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
220 240 260 280 300 320 340 360
Wavelength (nm)
NH

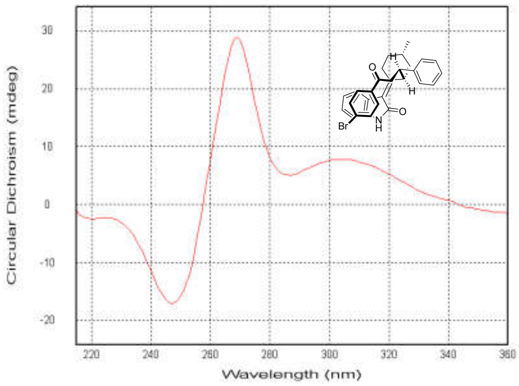

Circular Dichroism (mdeg)
15
10
5
0
-5
-10
-15
220 240 260 280 300 320 340 360
Wavelength (nm)

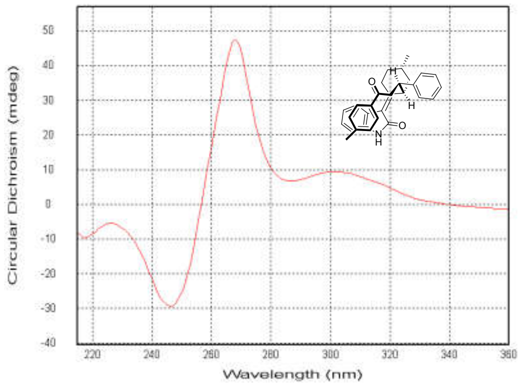

Circular Dichroism (mdeg)
Wavelength (nm)

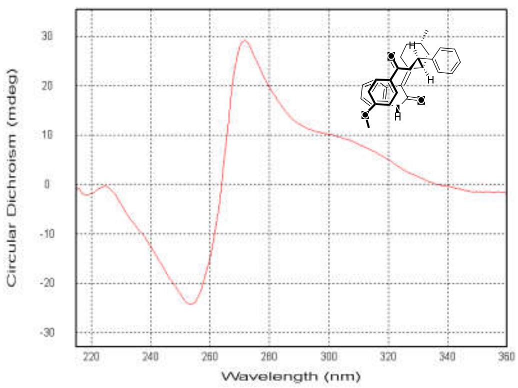

Circular Dichroism (mdeg)
Wavelength (nm)
F

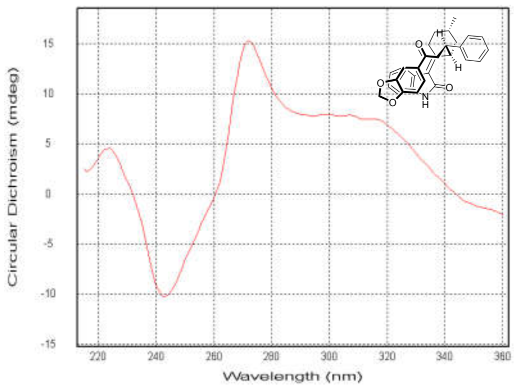

Circular Dichroism (mdeg)
Wavelength (nm)

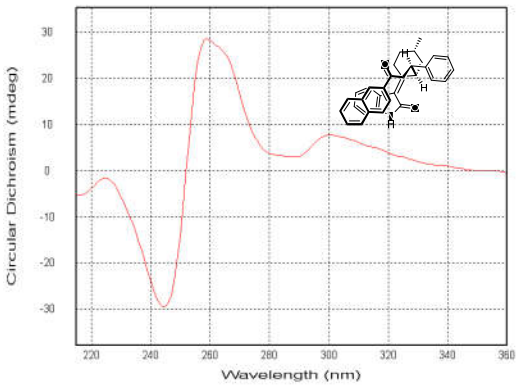

Circular Dichroism (mdeg)
Wavelength (nm)
Cl

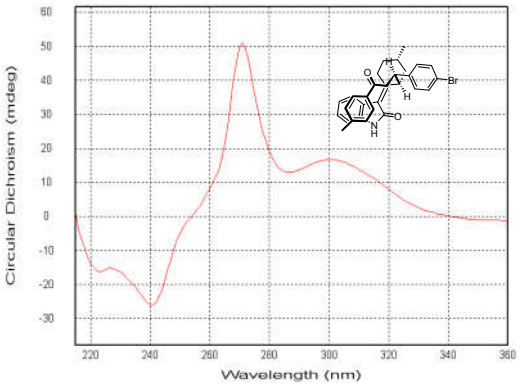

Circular Dichroism (mdeg)
Wavelength (nm)
Br

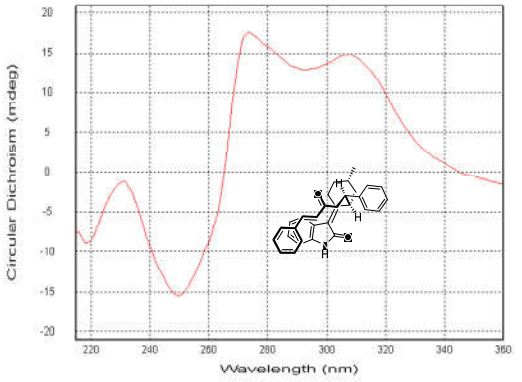

Circular Dichroism (mdeg)
Wavelength (nm)

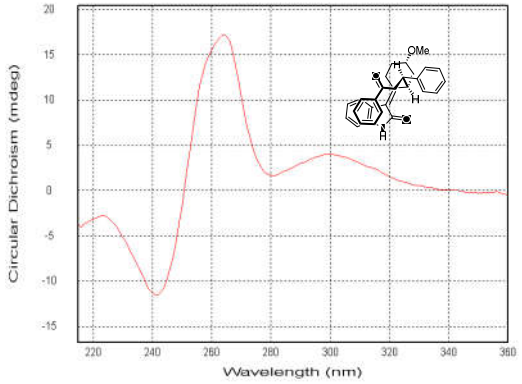

Circular Dichroism (mdeg)
Wavelength (nm)

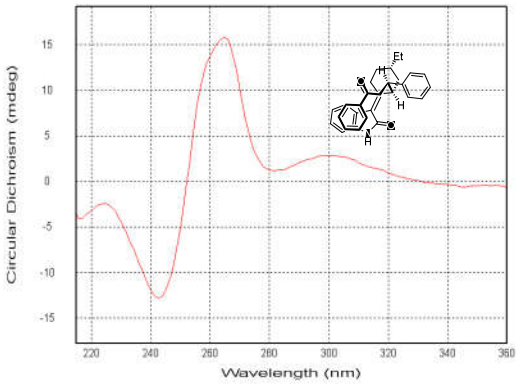

Circular Dichroism (mdeg)
Wavelength (nm)

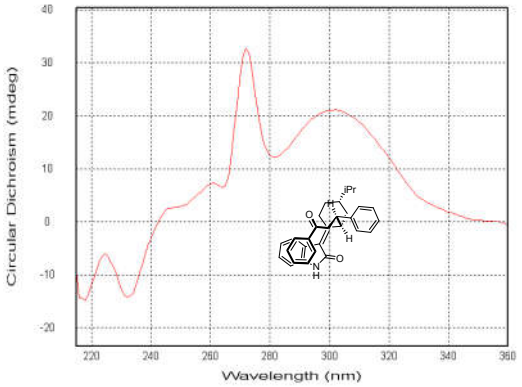

Circular Dichroism (mdeg)
Wavelength (nm)

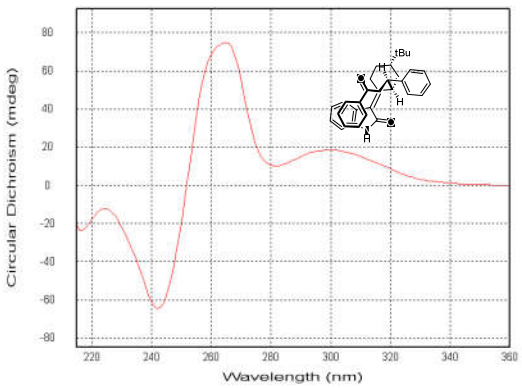

Br
Circular Dichroism (mdeg)
Wavelength (nm)

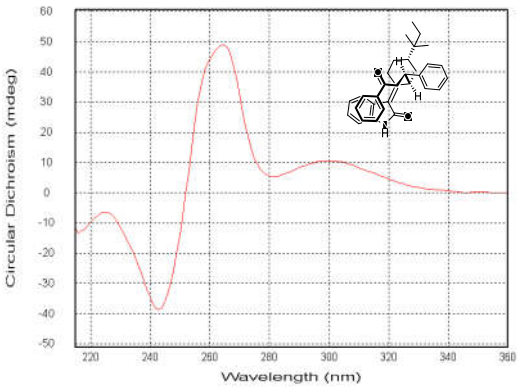

Circular Dichroism (mdeg)
Wavelength (nm)

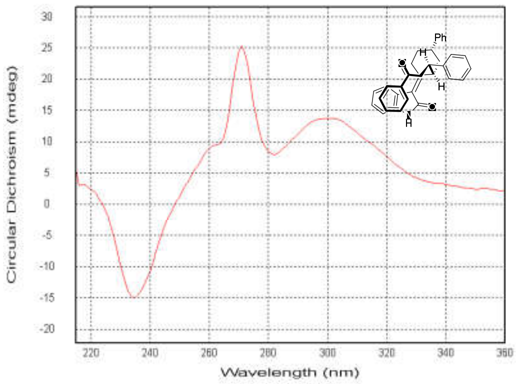

OMe
Circular Dichroism (mdeg)
Wavelength (nm)

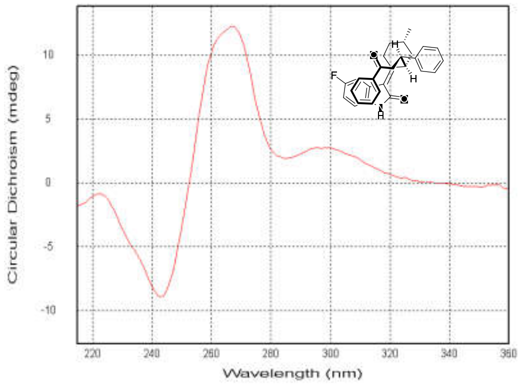

Et
Circular Dichroism (mdeg)
Wavelength (nm)

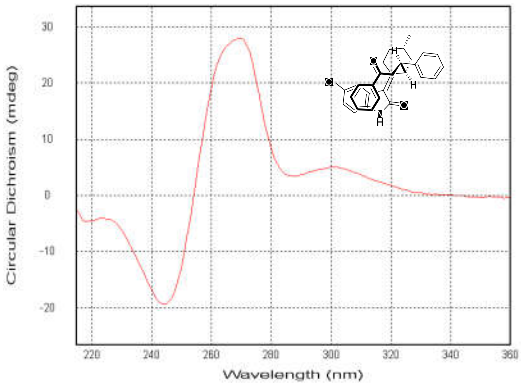

iPr
Circular Dichroism (mdeg)
Wavelength (nm)

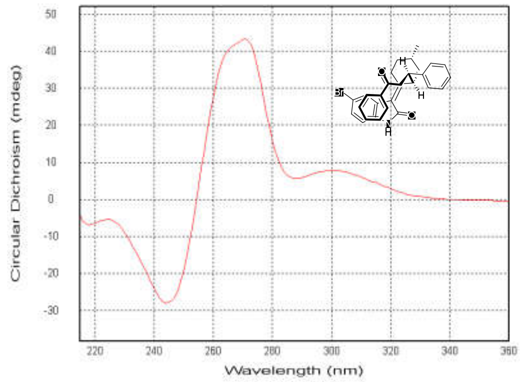

tBu
Circular Dichroism (mdeg)
Wavelength (nm)

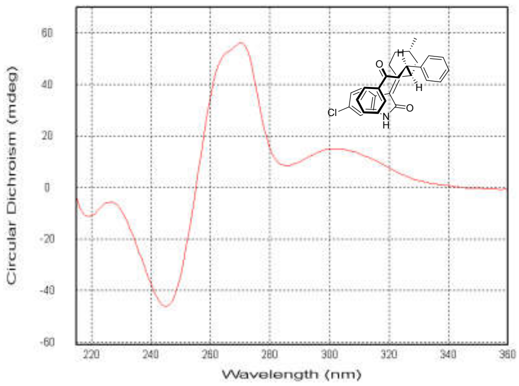

Circular Dichroism (mdeg)
Wavelength (nm)

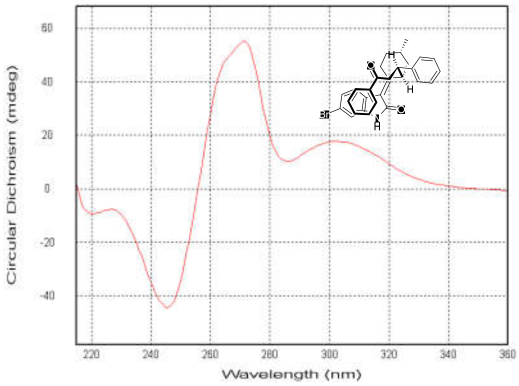

Circular Dichroism (mdeg)
Wavelength (nm)
30 25 20 15 10 5 0 -5 -10 -15 -20
220 240 260 280 300 320 340 360
Ph
H
H
N
H


Circular Dichroism (mdeg)
Wavelength (nm)
10 5 0 -5 -10
220 240 260 280 300 320 340 360
F
H
H
N
H


Circular Dichroism (mdeg)
Wavelength (nm)
30 20 10 0 -10 -20
220 240 260 280 300 320 340 360
H
H
N
H


Circular Dichroism (mdeg)
Wavelength (nm)
50 40 30 20 10 0 -10 -20 -30
220 240 260 280 300 320 340 360
Br
H
H
N
H


Circular Dichroism (mdeg)
Wavelength (nm)
60 40 20 0 -20 -40 -60
220 240 260 280 300 320 340 360
Cl
H
H
NH
O


Circular Dichroism (mdeg)
Wavelength (nm)
60 40 20 0 -20 -40
220 240 260 280 300 320 340 360
Br
H
H
N
H