Dearomative Tandem Annulation to Access Chiral Indoline-Fused Bicycle[2.2.2]octanes using the Modularly Designed Organocatalysts

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Supporting Information

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1. General Information

General Procedures. All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under an atmosphere of argon if needed. Gas-tight syringes with stainless steel needles were used to transfer air- and moisture-sensitive liquids. All moisture and/or air sensitive solid compounds were manipulated inside normal desiccators. Flash column chromatography was performed over silica gel (40 – 45 μm, 300 – 400 mesh).

Analytical thin layer chromatography (TLC) was performed on silica gel $HSGF_{254}$ glass plates (purchased from Jiangyou silica gel development Co., Ltd, Yantai, China) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) or I_2 and to a solution of $KMnO_4$ (1 g of $KMnO_4$, 6 g of K_2CO_3 and 0.1 g of KOH in 100 mL of H_2O) or vanillin (2 g of vanillin and 4 mL of concentrated H_2SO_4 in 100 mL of EtOH) followed by heating.

Organic solutions were concentrated at 30 – 40 °C on rotary evaporators at ~80 mbar followed by drying on vacuum pump below 1 mbar. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Materials. Commercial reagents and solvents were obtained from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin and Energy Chemical and used as received with the following exceptions: THF and toluene were purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.[1] The 3-nitroindoles **1**[2] and *trans*-7-oxo-5-heptenals **2**[3] were prepared according to literature procedure.

Instrumentation.

- Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured on a JEOL JNM-ECZ600R/S1 spectrometer at ambient temperature for ^{1}H at 600 MHz. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using tetramethylsilane (TMS) as an internal standard or residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$) or DMSO-d_6: δ 2.50 (CD_2HSOCD_3)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, brs = broad singlet), coupling constant(s) (Hz), integration].
- Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra measured on a JEOL JNM-ECZ600R/S1 spectrometer at ambient temperature for ^{13}C at 151 MHz.. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon

resonances of the solvent (δ 77.00 ($CDCl_3$) or δ 39.52 (DMSO-d_6)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (C_q = fully substituted carbon)].

- High resolution mass spectra (HRMS) were performed on an Agilent 6230 time-of-flight (TOF) LC/MS instrument or a Waters SYNAPT G2 mass spectrometer by using an electrospray ionization (ESI) ionization source analyzed by quadrupole time-of-flight (Q-TOF). Melting points were determined on a SGW X-4 digital melting point apparatus and temperatures were not corrected.

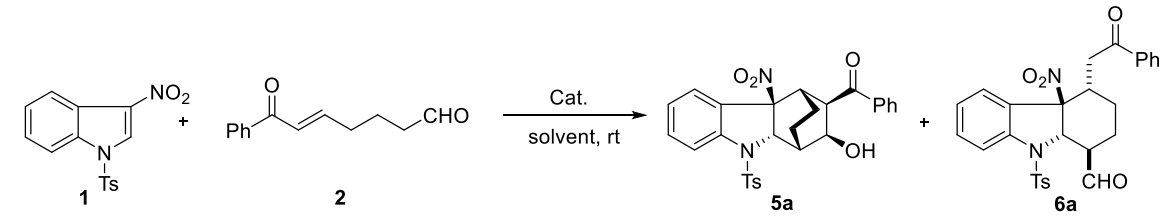
- Enantiomeric excess (ee) values were determined on an Agilent 1260 Infinity II chiral HPLC or Waters ACQUITY UPC² using Daicel CHIRALPAK® IC columns with 2-propanol and hexane or CO_2 as eluent.

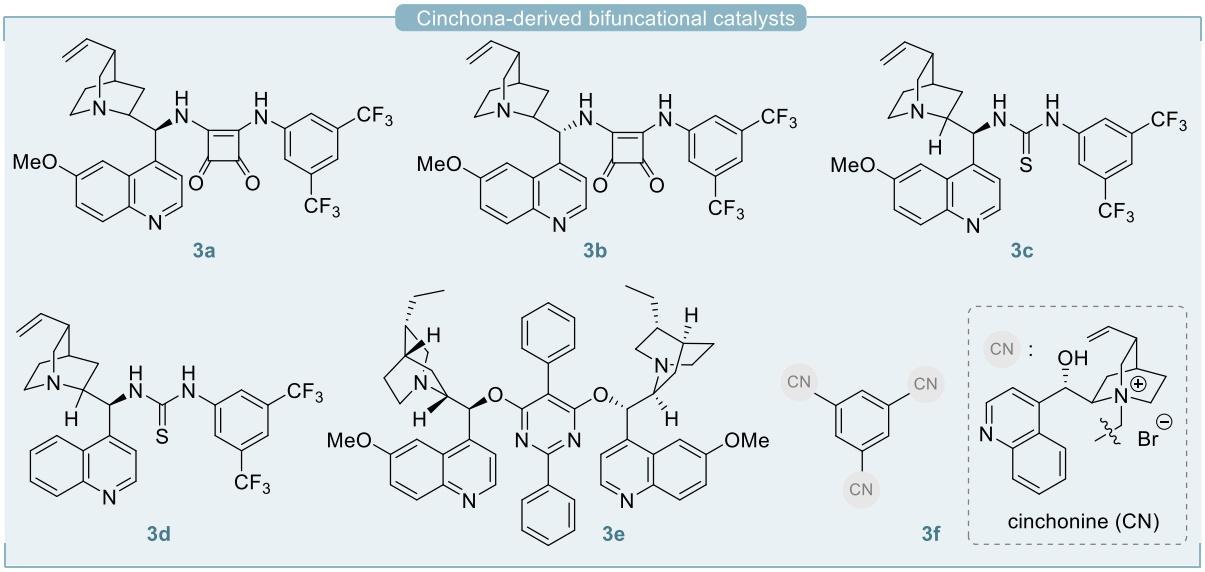
- Optical rotation was measured with a Rudolph Autopol IV automatic polarimeter at 20 °C using 100 mm cell of 2.5 mL capacity, and $[\alpha]_D^{20}$ values reported in degrees; concentration (c) is in 10 mg/mL.

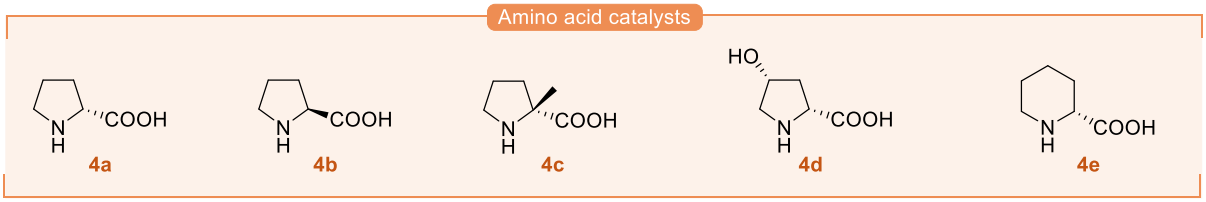
- Melting points were determined on an OptiMelt Automated Meling Point System using open glass capillaries and temperatures were not corrected, reported in degrees Celsius.

2. Optimization of Reaction Conditions.

Table S1. Optimization of the asymmetric dearomative tandem reactions.[a]



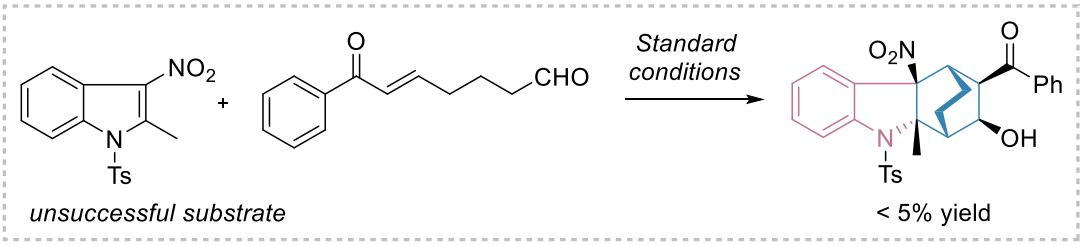




Entry	Cat.	Solvent	Temp. (°C)	**5a**/**6a**[b]	Yield of **6a** (%)[c]	Yield of **5a** (%)[d]	Ee (%)[e]
1	**3a**/**4a**	Tol	rt	75:25	24	71	87
2	**3a**/**4a**	DCM	rt	ND	<5	<5	ND
3	**3a**/**4a**	MeCN	rt	ND	<5	<5	ND
4	**3a**/**4a**	THF	rt	ND	<5	<5	ND
5	**3a**/**4a**	*i*Pr$_2$O	rt	ND	<5	<5	ND
6	**3a**/**4a**	Actone	rt	ND	<5	<5	ND
7	**3a**/**4a**	*p*-Xylene	rt	60:40	23	36	82
8	**3a**/**4a**	*o*-Xylene	rt	62:38	35	56	84
9	**3a**/**4a**	*m*-Xylene	rt	57:43	38	52	83
10	**3a**/**4a**	Mesitylene	rt	54:46	33	40	83
11	**3a**/**4a**	PhCl	rt	53:47	43	49	78
12	**3a**/**4a**	PhF	rt	55:45	34	41	75
13	**3a**	Tol	rt	ND	<5	<5	ND
14	**4a**	Tol	rt	ND	<5	<5	ND

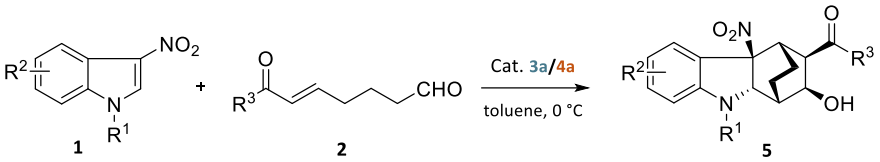
15	**3a**/**4b**	Tol	rt	ND	<5	<5	ND
16	**3b**/**4b**	Tol	rt	71:29	26	64	84
17	**3b**/**4a**	Tol	rt	ND	<5	<5	ND
18	**3c**/**4a**	Tol	rt	68:34	30	58	77
19	**3d**/**4a**	Tol	rt	70:30	28	65	76
20	**3e**/**4a**	Tol	rt	81:19	16	66	0
21[f]	**3f**/**4a**	Tol	rt	ND	<5	<5	ND
23	**3a**/**4c**	Tol	rt	ND	<5	<5	ND
24	**3a**/**4d**	Tol	rt	ND	<5	<5	ND
25	**3a**/**4e**	Tol	rt	ND	<5	<5	ND
26[g]	**3a**/**4a**	Tol	rt	74:26	15	41	80
27[h]	**3a**/**4a**	Tol	rt	71:29	10	23	82
28	**3a**/**4a**	Tol	60	ND	<5	<5	ND
29	**3a**/**4a**	Tol	0	88:12	11	80	98
30[i]	**3a**/**4a**	Tol	0	73:27	21	56	94
31[j]	**3a**/**4a**	Tol	0	ND	<5	<5	ND

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.15 mmol), **3** (0.02 mmol) and **4** (0.04 mmol) in solvent (1.0 mL). [b] The ratio of **5a** and **6a** was determined by crude ^{1}H NMR analysis. [c] Yield of **6a** were determined by ^{1}H NMR analysis of the crude reaction mixture with CH_2Br_2 as an internal standard. [d] Isolated yield of **5a**. [e] Determined by chiral-phase HPLC analysis of **5a**. [f] 0.2 mL of 20% K_2CO_3 (aq.) was added. [g] **3** (0.02 mmol) and **4** (0.02 mmol) were used. [h] **3** (0.02 mmol) and **4** (0.01 mmol) were used. [i] Concentration was increased to 0.2 M using 0.5 mL of Tol. [j] 4Å MS (80 mg) was added. NR: no reaction.



3. General Procedure for the Dearomative Tandem Annulations

3.1 General Procedure for the Asymmetric Dearomative Tandem Annulations to Synthesize Bridged-ring Indoline Products ***5***

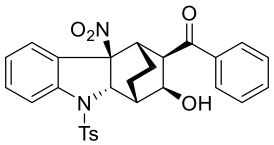


To a glass tube were added **3a** (0.02 mmol), **4a** (0.04 mmol) and **1** (0.1 mmol) in Tol (1.0 mL). After the mixture cooled to 0 ℃, **2** (0.15 mmol) was added and the resulting suspension stirred at 0 ℃ until complete conversion of 3-nitroindoles as indicated by TLC. Then the reaction mixture was purified by column chromatography on silica gel to afford the corresponding products **5**, which were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, HPLC, etc.

3.2 Gram-scale Synthesis of the Product ***5a***

To a glass tube were added **3a** (0.2 mmol), **4a** (0.4 mmol) and **1a** (2.0 mmol) in Tol (20 mL). After the mixture cooled to 0 ℃, **2a** (3.0 mmol) was added and the resulting suspension stirred at 0 ℃ until complete conversion of 3-nitroindoles as indicated by TLC. Then the reaction mixture was purified by column chromatography on silica gel to afford the product **5a** (674.2 mg) as white solid in 65% yield. The enantiomeric excess of the product was determined to be 98% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min).

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(phenyl)methanone 5a



Prepared according to the general procedure to afford **5a** (41.5 mg, m. p. = 197.8 – 201.1 °C) in 80% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the product was determined to be 98% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 18.12 min, tminor = 14.55 min; $[\alpha]_D^{20}$ = -160.3 (c = 0.10 in CH_2Cl_2)

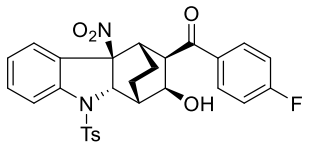
*NMR and HRMS data for the product **5a**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.49 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 4.2 Hz, 1H), 4.64 – 4.52 (m, 1H), 3.18 (d, *J* = 9.0 Hz, 1H), 3.15 – 3.12 (m, 1H), 2.95 – 2.81 (m, 2H), 2.37 (s, 3H), 2.24 – 2.18 (m, 1H), 2.16 – 2.10 (m, 1H), 1.47 (td, *J* = 12.6, 4.2 Hz, 1H), 1.36 – 1.31 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 198.9, 145.1, 143.0, 136.9, 133.5, 132.7, 132.5, 129.9, 129.0, 127.7, 127.6, 127.0, 125.1, 125.0, 116.1, 97.3, 66.0, 64.0, 44.1, 38.0, 36.6, 21.6, 15.9, 15.1.

HRMS (ESI-TOF) m/z: **$[M + H]^+$** calcd for $C_{28}H_{27}N_2O_6S^+$ 519.1584; found 519.1584.

(4-fluorophenyl)((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)methanone 5b



Prepared according to the general procedure to afford **5b** (33.8 mg, m. p. = 216.7 – 218.9 ºC) in 63% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 96% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 15.34 min, tminor = 10.50 min; $[\alpha]_D^{20}$ = -171.3 (c = 0.10 in CH_2Cl_2)

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

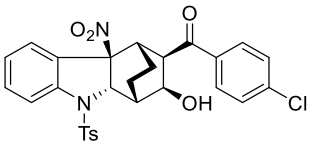
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 9.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 8.4 Hz, 2H), 5.34 (d, *J* = 4.2 Hz, 1H), 4.60 – 4.57 (m, 1H), 3.12 – 3.11 (m, 2H), 2.90 – 2.85 (m, 1H), 2.79 (d, *J* = 6.6 Hz, 1H), 2.37 (s, 3H), 2.22 – 2.12 (m, 2H), 1.49 – 1.45 (m, 1H), 1.36 – 1.31 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 197.1, 165.8 (C-F, $^1J_{C\text{-}F}$ = 255.9 Hz), 145.2, 143.0, 133.4 (C-F, $^4J_{C\text{-}F}$ = 2.9 Hz), 132.6, 132.5, 130.4 (C-F, $^3J_{C\text{-}F}$ = 10.1 Hz), 129.9, 127.6, 127.0, 125.1, 124.9, 116.1 (C-F, $^2J_{C\text{-}F}$ = 21.7 Hz), 116.1, 97.2, 66.0, 64.0, 44.1, 38.0, 36.6, 21.6, 15.8, 15.1.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -103.88 – -103.93 (m, 1F).

HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calcd for $C_{28}H_{25}FN_2O_6SNa^+$ 559.1310; found 559.1308.

(4-chlorophenyl)((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)methanone 5c



Prepared according to the general procedure to afford **5c** (35.9 mg, m. p. = 221.7 – 224.6 ºC) in 65% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 91% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 21.29 min, tminor = 15.88 min; $[\alpha]_D^{20}$ = -182.8 (c = 0.10 in CH_2Cl_2)

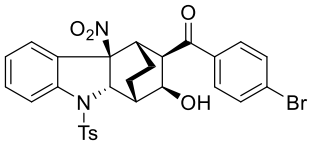
*NMR and HRMS data for the product **5c**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 4.2 Hz, 1H), 4.61 – 4.58 (m, 1H), 3.15 – 3.10 (m, 1H), 3.09 (d, *J* = 9.0 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.64 (d, *J* = 6.0 Hz, 1H), 2.37 (s, 3H), 2.22 – 2.13 (m, 2H), 1.49 – 1.45 (m, 1H), 1.38 – 1.32 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 197.4, 145.2, 143.0, 139.9, 135.4, 132.6, 132.5, 129.9, 129.3, 129.1, 127.7, 127.0, 125.1, 124.9, 116.1, 97.2, 66.0, 64.0, 44.3, 38.0, 36.5, 21.6, 15.8, 15.2.

HRMS (ESI-TOF) m/z: **[M + H]**$^+$ calcd for $C_{28}H_{26}{}^{35}ClN_2O_6S^+$ 553.1195, $C_{28}H_{26}{}^{37}ClN_2O_6S^+$ 555.1165; found 553.1202, 555.1171.

(4-bromophenyl)((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)methanone 5d



Prepared according to the general procedure to afford **5d** (36.4 mg, m. p. = 220.4 – 224.5 ºC) in 61% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 95% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 14.51 min, tminor = 11.76 min; $[\alpha]_D^{20}$ = -296.7 (c = 0.10 in CH_2Cl_2)

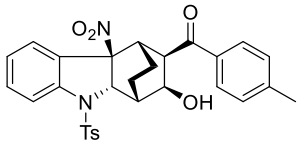
*NMR and HRMS data for the product **5d**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.46 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 3.6 Hz, 1H), 4.63 – 4.57 (m, 1H), 3.15 – 3.10 (m, 1H), 3.07 (d, *J* = 9.0 Hz, 1H), 2.90 – 2.86 (m, 1H), 2.66 (d, *J* = 5.4 Hz, 1H), 2.37 (s, 3H), 2.22 – 2.13 (m, 2H), 1.48 – 1.42 (m, 1H), 1.38 – 1.32 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 197.6, 145.2, 142.9, 135.8, 132.5, 132.2, 129.9, 129.2, 128.6, 127.6, 127.0, 125.1, 124.9, 116.1, 97.2, 65.9, 64.0, 44.3, 38.0, 36.5, 21.6, 15.8, 15.1.

HRMS (ESI-TOF) m/z: **[M + H]$^+$** calcd for $C_{28}H_{26}{}^{79}BrN_2O_6S^+$ 597.0689, $C_{28}H_{26}{}^{81}BrN_2O_6S^+$ 599.0669; found 597.0679, 599.0669.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(p-tolyl)methanone 5e



Prepared according to the general procedure to afford **5e** (34.6 mg, m. p. = 212.9 – 215.6 ºC) in 65% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 99% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 25.09 min, tminor = 20.11 min; $[\alpha]_D^{20}$ = -289.5 (c = 0.10 in CH_2Cl_2)

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

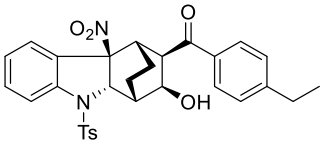
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 4.2 Hz, 1H), 4.55 – 4.52 (m, 1H), 3.19 (d, *J* = 9.0 Hz, 1H),

3.14 (d, *J* = 7.2 Hz, 1H), 3.12 – 3.09 (m, 1H), 2.87 – 2.85 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 2.24 – 2.18 (m, 1H), 2.12 – 2.07 (m, 1H), 1.50 – 1.45 (m, 1H), 1.34 – 1.28 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 198.8, 145.1, 144.7, 143.0, 134.3, 132.8, 132.5, 129.9, 129.7, 127.9, 127.6, 127.1, 125.0, 116.1, 97.4, 66.0, 64.0, 43.7, 38.1, 36.8, 21.6, 21.6, 15.9, 15.1.

HRMS (ESI-TOF) m/z: **[M + H]$^+$** calcd for $C_{29}H_{29}N_2O_6S^+$ 533.1741; found 533.1734.

(4-ethylphenyl)((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)methanone 5f



Prepared according to the general procedure to afford **5f** (34.4 mg, m. p. = 194.7 – 198.0 ºC) in 63% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 95% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 22.62 min, tminor = 18.40 min; $[\alpha]_D^{20}$ = -216.7 (c = 0.10 in CH_2Cl_2)

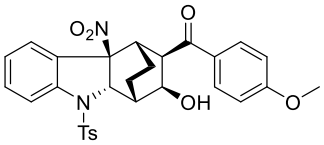
*NMR and HRMS data for the product **5f**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 8.4 Hz, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 4.2 Hz, 1H), 4.55 – 4.52 (m, 1H), 3.21 (d, *J* = 9.6 Hz, 1H), 3.18 (d, *J* = 7.2 Hz, 1H), 3.14 – 3.08 (m, 1H), 2.87 – 2.83 (m, 1H), 2.69 (q, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 2.26 – 2.19 (m, 1H), 2.13 – 2.07 (m, 1H), 1.53 – 1.42 (m, 1H), 1.36 – 1.28 (m, 1H), 1.24 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 198.8, 150.8, 145.0, 143.0, 134.4, 132.8, 132.5, 129.8, 128.5, 128.0, 127.6, 127.1, 125.0, 125.0, 116.1, 97.4, 66.0, 64.0, 43.7, 38.1, 36.8, 28.9, 21.6, 15.9, 15.1, 15.0.

HRMS (ESI-TOF) m/z: **[M + H]$^+$** calcd for $C_{30}H_{31}N_2O_6S^+$ 547.1897; found 547.1893.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(4-methoxyphenyl)methanone 5g



Prepared according to the general procedure to afford **5g** (34.0 mg, m. p. = 184.7 – 187.1 °C) in 62% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 94% by chiral HPLC analysis on Chiralpak IC column (40% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 14.68 min, tminor = 10.45 min; $[\alpha]_D^{20}$ = -163.0 (c = 0.10 in CH_2Cl_2)

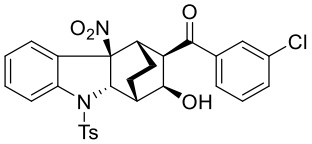
*NMR and HRMS data for the product **5g**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 5.34 (d, *J* = 3.6 Hz, 1H), 4.51 – 4.48 (m, 1H), 3.86 (s, 3H), 3.40 (d, *J* = 7.8 Hz, 1H), 3.21 (d, *J* = 9.0 Hz, 1H), 3.14 – 3.06 (m, 1H), 2.86 – 2.83 (m, 1H), 2.36 (s, 3H), 2.26 – 2.19 (m, 1H), 2.10 – 2.04 (m, 1H), 1.51 – 1.46 (m, 1H), 1.32 – 1.26 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 197.9, 163.9, 145.0, 143.1, 132.9, 132.5, 130.2, 129.9, 129.6, 127.6, 127.1, 125.0, 116.2, 114.2, 97.4, 66.0, 64.0, 55.6, 43.1, 38.2, 37.1, 21.6, 16.0, 15.1.

HRMS (ESI-TOF) m/z: **$[M + H]^+$** calcd for $C_{29}H_{29}N_2O_7S^+$ 549.1690; found 549.1695.

(3-chlorophenyl)((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)methanone 5h



Prepared according to the general procedure to afford **5h** (40.4 mg, m. p. = 192.4 – 195.9 °C) in 73% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 92% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 11.84 min, tminor = 10.32 min; $[\alpha]_D^{20}$ = -208.0 (c = 0.10 in CH_2Cl_2)

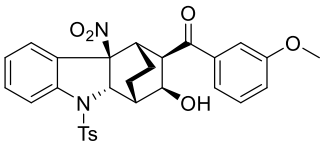
*NMR and HRMS data for the product **5h**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.64 (s, 1H), 7.52 – 7.47 (m, 4H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 4.2 Hz, 1H), 4.61 – 4.58 (m, 1H), 3.15 – 3.10 (m, 1H), 3.08 (d, *J* = 9.0 Hz, 1H), 2.88 – 2.86 (m, 1H), 2.74 (d, *J* = 6.6 Hz, 1H), 2.37 (s, 3H), 2.22 – 2.10 (m, 1H), 1.50 – 1.44 (m, 1H), 1.37 – 1.32 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 197.5, 145.2, 142.9, 138.6, 135.3, 133.3, 132.6, 130.2, 129.9, 127.9, 127.6, 126.9, 125.7, 125.2, 124.9, 116.2, 97.2, 65.9, 63.9, 44.3, 37.9, 36.5, 21.6, 15.8, 15.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calcd for $C_{28}H_{25}{}^{35}ClN_2O_6SNa^+$ 575.1014, $C_{28}H_{25}{}^{37}ClN_2O_6SNa^+$ 577.0985; found 577.0995.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(3-methoxyphenyl)methanone 5i



Prepared according to the general procedure to afford **5i** (39.5 mg, m. p. = 167.9 – 170.2 °C) in 72% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 99% by chiral HPLC analysis on Chiralpak IC column (30% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 11.82 min, tminor = 9.95 min; $[\alpha]_D^{20}$ = -188.3 (c = 0.10 in CH_2Cl_2)

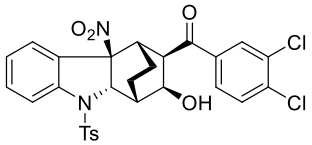
*NMR and HRMS data for the product **5i**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.13 (m, 2H), 7.09 (d, *J* = 8.4, 2.8 Hz, 1H), 5.34 (d, *J* = 3.6 Hz, 1H), 4.62 – 4.52 (m, 1H), 3.82 (s, 3H), 3.16 (d, *J* = 9.0 Hz, 1H), 3.14 – 3.11 (m, 1H), 2.92 (d, *J* = 6.0 Hz, 1H), 2.87 – 2.85 (m, 1H), 2.36 (s, 3H), 2.25 – 2.17 (m, 1H), 2.15 – 2.10 (m, 1H), 1.49 – 1.44 (m, 1H), 1.35 – 1.30 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 198.7, 160.1, 145.1, 143.0, 138.3, 132.7, 132.5, 130.0, 129.8, 127.6, 127.0, 125.1, 125.0, 120.0, 120.0, 116.1, 112.1, 97.3, 66.0, 64.0, 55.4, 44.2, 38.0, 36.6, 21.6, 15.9, 15.1.

HRMS (ESI-TOF) m/z: **[M + H]$^+$** calcd for $C_{29}H_{29}N_2O_7S^+$ 549.1690; found 549.1697.

(3,4-dichlorophenyl)((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-ethanocarbazol-3-yl)methanone 5j



Prepared according to the general procedure to afford **5j** (38.8 mg, m. p. = 211.5 – 214.6 ºC) in 66% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 91% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 11.26 min, tminor = 9.15 min; $[\alpha]_D^{20}$ = -92.0 (c = 0.10 in CH_2Cl_2)

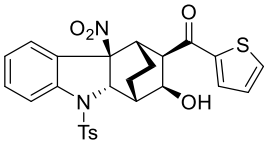
*NMR and HRMS data for the product **5j**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 7.2 Hz, 1H), 7.74 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.47 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 4.2 Hz, 1H), 4.66 – 4.56 (m, 1H), 3.13 – 3.08 (m, 1H), 3.02 (d, *J* = 9.0 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.61 (d, *J* = 4.8 Hz, 1H), 2.37 (s, 3H), 2.21 – 2.14 (m, 2H), 1.48 – 1.42 (m, 1H), 1.39 – 1.33 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 196.4, 145.2, 142.9, 137.9, 136.7, 133.6, 132.6, 132.5, 130.9, 129.9, 129.7, 127.6, 126.9, 126.6, 125.3, 124.9, 116.2, 97.1, 65.9, 63.9, 44.4, 37.9, 36.4, 21.6, 15.7, 15.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calcd for $C_{28}H_{24}{}^{35}Cl^{35}ClN_2O_6SNa^+$ 609.0624, $C_{28}H_{24}{}^{37}Cl^{35}ClN_2O_6SNa^+$ 611.0595, $C_{28}H_{24}{}^{37}Cl^{37}ClN_2O_6SNa^+$ 613.0565; found 609.0619, 611.0598, 613.0566.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(thiophen-2-yl)methanone 5k



Prepared according to the general procedure to afford **5k** (35.1 mg, m. p. = 188.1 – 191.4 ºC) in 67% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 99% by chiral HPLC analysis on Chiralpak IC column (25% 2-propanol/n-hexane, 1.0 mL/min), UV 220 nm, tmajor = 14.39 min, tminor = 15.95 min; $[\alpha]_D^{20}$ = -209.3 (c = 0.10 in CH_2Cl_2)

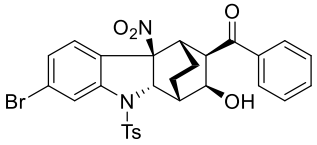
*NMR and HRMS data for the product **5k**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 4.2 Hz, 1H), 6.51 (d, *J* = 4.2 Hz, 1H), 5.32 (d, *J* = 4.2 Hz, 1H), 4.60 – 4.57 (m, 1H), 3.17 – 3.14 (m, 1H), 3.09 (d, *J* = 7.8 Hz, 1H), 3.04 (d, *J* = 9.0 Hz, 1H), 2.86 – 2.84 (m, 1H), 2.36 (s, 3H), 2.24 – 2.18 (m, 1H), 2.13 – 2.08 (m, 1H), 1.51 – 1.46 (m, 1H), 1.35 – 1.28 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.7, 152.6, 146.5, 145.0, 143.0, 132.9, 132.4, 129.8, 127.6, 126.9, 125.1, 125.0, 117.4, 116.1, 112.6, 97.3, 66.0, 63.7, 44.7, 38.1, 36.4, 21.6, 16.0, 15.1.

HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calcd for $C_{26}H_{24}N_2O_6S_2Na^+$ 547.0968; found 547.0966.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-7-bromo-2-hydroxy-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(phenyl)methanone 5l



Prepared according to the general procedure to afford **5l** (37.6 mg, m. p. = 199.6 – 202.3 ºC) in 63% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 86% by chiral HPLC analysis on Chiralpak IC column (15% 2-propanol/n-hexane, 1.0 mL/min), UV 220 nm, tmajor = 15.29 min, tminor = 9.77 min; $[\alpha]_D^{20}$ = -177.7 (c = 0.10 in CH_2Cl_2)

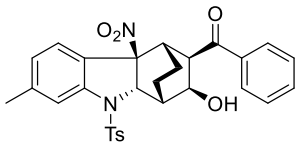
*NMR and HRMS data for the product **5l**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.04 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 5.32 (d, *J* = 4.2 Hz, 1H), 4.59 – 4.55 (m, 1H), 3.16 (d, *J* = 9.0 Hz, 1H), 3.13 – 3.09 (m, 1H), 2.88 – 2.86 (m, 1H), 2.80 – 2.70 (m, 1H), 2.40 (s, 3H), 2.23 – 2.12 (m, 2H), 1.47 – 1.42 (m, 1H), 1.34 – 1.28 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 198.4, 145.5, 144.1, 136.9, 133.6, 132.4, 130.1, 129.1, 128.3, 127.7, 127.6, 126.7, 126.2, 126.0, 119.1, 96.8, 66.4, 63.9, 44.3, 37.8, 36.4, 21.7, 15.8, 15.1.

HRMS (ESI-TOF) m/z: **$[M + H]^+$** calcd for $C_{28}H_{26}{}^{79}BrN_2O_6S^+$ 597.0689, $C_{28}H_{26}{}^{81}BrN_2O_6S^+$ 599.0669; found 597.0688, 599.0665.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-7-methyl-4a-nitro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(phenyl)methanone 5m



Prepared according to the general procedure to afford **5m** (42.6 mg, m. p. = 193.4 – 195.1 °C) in 80% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 97% by chiral HPLC analysis on Chiralpak IC column (30% 2-propanol/CO_2, 1.5 mL/min), UV 230 nm, tmajor = 8.09 min, tminor = 6.51 min; $[\alpha]_D^{20}$ = -256.8 (c = 0.10 in CH_2Cl_2)

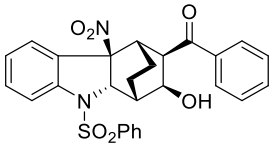
*NMR and HRMS data for the product **5m**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.73 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.69 (s, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.31 (d, *J* = 3.6 Hz, 1H), 4.60 – 4.49 (m, 1H), 3.23 (d, *J* = 9.0 Hz, 1H), 3.13 – 3.09 (m, 1H), 3.00 (d, *J* = 6.0 Hz, 1H), 2.85 – 2.83 (m, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 2.23 – 2.17 (m, 1H), 2.11 – 2.06 (m, 1H), 1.50 – 1.42 (m, 1H), 1.33 – 1.27 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 199.2, 145.0, 143.3, 143.2, 136.9, 133.5, 132.9, 129.8, 129.0, 127.8, 127.6, 126.1, 124.6, 124.3, 116.5, 97.3, 66.3, 64.0, 44.1, 38.2, 36.6, 22.0, 21.6, 15.9, 15.1.

HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calcd for $C_{29}H_{28}N_2O_6SNa^+$ 555.1560; found 555.1561.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-(phenylsulfonyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(phenyl)methanone 5n



Prepared according to the general procedure to afford **5n** (28.3 mg, m. p. = 209.7 – 212.1 ºC) in 56% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 96% by chiral HPLC analysis on Chiralpak IC column (30% 2-propanol/CO_2, 1.5 mL/min), UV 210 nm, tmajor = 7.57 min, tminor = 5.99 min; $[\alpha]_D^{20}$ = -102.7 (c = 0.10 in CH_2Cl_2)

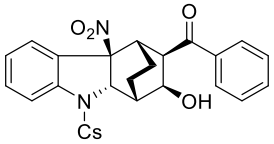
*NMR and HRMS data for the product **5n**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.89 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.17 (t, *J* = 7.8 Hz, 1H), 5.33 (d, *J* = 4.2 Hz, 1H), 4.60 – 4.56 (m, 1H), 3.20 (d, *J* = 9.6 Hz, 1H), 3.16 – 3.10 (m, 1H), 2.94 (s, 1H), 2.88 – 2.86 (m, 1H), 2.24 – 2.19 (m, 1H), 2.15 – 2.09 (m, 1H), 1.50 – 1.45 (m, 1H), 1.36 – 1.30 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 199.0, 142.9, 136.9, 135.7, 134.0, 133.6, 132.6, 129.3, 129.0, 127.7, 127.6, 127.1, 125.2, 125.0, 116.2, 97.3, 66.1, 64.0, 44.0, 38.1, 36.6, 15.9, 15.1.

HRMS (ESI-TOF) m/z: **[M + Na]**$^+$ calcd for $C_{27}H_{24}N_2O_6SNa^+$ 527.1247; found 527.1256.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-9-((4-chlorophenyl)sulfonyl)-2-hydroxy-4a-nitro-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(phenyl)methanone 5o



Prepared according to the general procedure to afford **5o** (31.8 mg, m. p. = 216.8 – 219.7 ºC) in 59% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 98% by

chiral HPLC analysis on Chiralpak IC column (25% 2-propanol/CO_2, 1.5 mL/min), UV 230 nm, tmajor = 7.34 min, tminor = 5.91 min; $[\alpha]_D^{20}$ = -220.0 (c = 0.10 in CH_2Cl_2)

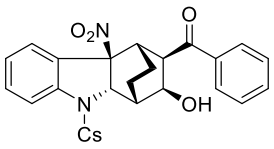
*NMR and HRMS data for the product **5o**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.48 – 7.39 (m, 4H), 7.19 (t, *J* = 7.8 Hz, 1H), 5.32 (d, *J* = 7.2 Hz, 1H), 4.54 – 4.49 (m, 1H), 3.21 (d, *J* = 10.2 Hz, 1H), 3.17 – 3.14 (m, 1H), 3.04 (d, *J* = 6.0 Hz, 1H), 2.87 – 2.80 (m, 1H), 2.25 – 2.20 (m, 1H), 2.15 – 2.09 (m, 1H), 1.50 – 1.45 (m, 1H), 1.36 – 1.30 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 199.0, 142.6, 140.8, 136.9, 134.2, 133.6, 132.7, 129.6, 129.0, 129.0, 127.8, 127.2, 125.5, 125.1, 116.1, 97.3, 66.3, 63.9, 43.9, 38.2, 36.6, 15.9, 15.1.

HRMS (ESI-TOF) m/z: **[M + Na]$^+$** calcd for $C_{27}H_{23}Cl^{35}N_2O_6SNa^+$ 561.0858, $C_{27}H_{23}Cl^{37}N_2O_6SNa^+$ 563.0828; found 561.0858, 563.0835.

((1*S*,2*S*,3*R*,4*S*,4a*R*,9a*S*)-2-hydroxy-4a-nitro-9-((4-nitrophenyl)sulfonyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-ethanocarbazol-3-yl)(phenyl)methanone 5p



Prepared according to the general procedure to afford **5p** (26.9 mg, m. p. = 208.9 – 210.6 ºC) in 49% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 98% by chiral HPLC analysis on Chiralpak IC column (25% 2-propanol/CO_2, 1.5 mL/min), UV 254 nm, tmajor = 12.58 min, tminor = 11.89 min; $[\alpha]_D^{20}$ = -195.0 (c = 0.10 in CH_2Cl_2)

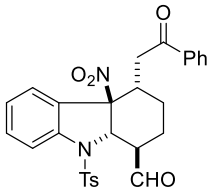
*NMR and HRMS data for the product **5p**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.30 (d, *J* = 9.0 Hz, 2H), 8.04 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 6.6 Hz, 1H), 5.29 (d, *J* = 4.2 Hz, 1H), 4.55 – 4.44 (m, 1H), 3.27 (d, *J* = 9.6 Hz, 1H), 3.23 (d, *J* = 7.8 Hz, 1H), 3.20 – 3.15 (m, 1H), 2.84 – 2.81 (m, 1H), 2.29 – 2.23 (m, 1H), 2.11 – 2.06 (m, 1H), 1.54 – 1.48 (m, 1H), 1.34 – 1.28 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 199.2, 150.8, 142.2, 141.3, 136.7, 133.8, 133.0, 129.1, 128.9, 127.8, 127.5, 126.0, 125.1, 124.4, 116.1, 97.2, 66.6, 63.7, 43.6, 38.5, 36.5, 16.0, 15.1.

HRMS (ESI-TOF) m/z: **[M + H]**$^+$ calcd for $C_{27}H_{24}N_3O_8S^+$ 550.1279; found 550.1277.

4a-nitro-4-(2-oxo-2-phenylethyl)-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole-1-carbaldehyde 6



Prepared according to the general procedure to afford **6** (5.6 mg, m. p. = 137.6 – 140.1 °C) in 11% yield as white solid.

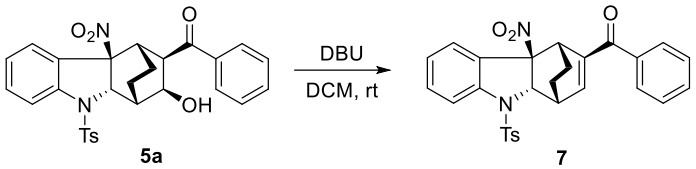
*NMR and HRMS data for the product **6**:*

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.08 (d, *J* = 2.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 5.38 (d, *J* = 8.4 Hz, 1H), 3.26 (dd, *J* = 16.8, 10.2 Hz, 1H), 3.20 – 3.16 (m, 1H), 3.12 (d, *J* = 18.0 Hz, 1H), 2.57 – 2.52 (m, 1H), 2.36 (s, 3H), 2.02 – 1.96 (m, 1H), 1.85 – 1.80 (m, 2H), 1.13 – 1.06 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 200.8, 195.8, 145.0, 142.6, 136.1, 134.5, 133.7, 132.4, 129.7, 128.8, 127.9, 127.1, 126.2, 125.3, 118.4, 100.7, 67.1, 54.2, 39.2, 38.1, 26.1, 21.8, 21.6.

HRMS (ESI-TOF) m/z: **[M + H]**$^+$ calcd for $C_{28}H_{27}N_2O_6S^+$ 519.1584; found 519.1593.

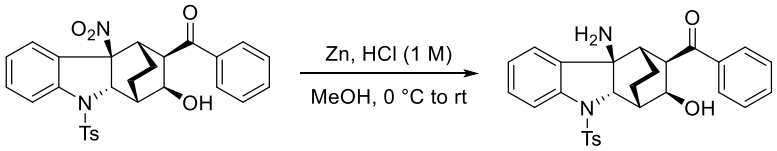
4. Synthetic Applications



5a **7**

(96% ee, 74% yield, > 19:1 dr)

The bridged-ring indoline product **5a** (0.1 mmol) was dissolved in DCM (1.0 mL). Subsequently, DBU (0.25 mmol) was added and the resulting suspension stirred at room temperature until complete conversion of **5a** as indicated by TLC. Then the reaction mixture was purified by column chromatography on silica gel to afford the corresponding product **7**, which were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, HPLC, etc.

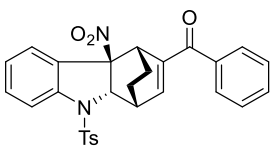


5a **8**

(97% ee, 70% yield, > 19:1 dr)

The bridged-ring indoline product **5a** (0.1 mmol) was dissolved in MeOH (2.5 mL). Subsequently, Zn powder (0.22 mmol) and HCl (1 mL, 1 M) was added at 0 °C. Then the reaction mixture stirred at room temperature until complete conversion of **5a** as indicated by TLC. $NaHCO_3$ (aq) was added until pH > 10, followed by the extraction with CH_2Cl_2. The combined organic layers were washed with brine, then dried over sodium sulfate and concentrated under reduced pressure. After removal of the solvent under reduced pressure, the resulting crude material was purified by column chromatography on silica gel to afford the corresponding product **8**, which were dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, HPLC.

((1*R*,4*S*,4a*R*,9a*S*)-4a-nitro-9-tosyl-4,4a,9,9a-tetrahydro-1*H*-1,4-ethanocarbazol-3-yl)(phenyl)methanone 7



Prepared according to the general procedure to afford **7** (37.0 mg, m. p. = 208.9 – 210.6 ºC) in 74% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 96% by chiral HPLC analysis on Chiralpak IC column (10% 2-propanol/n-hexane, 1.0 mL/min), UV 254 nm, tmajor = 17.83 min, tminor = 16.25 min; $[\alpha]_D^{20}$ = -401.3 (c = 0.10 in CH_2Cl_2)

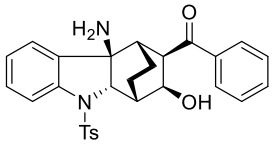
NMR and HRMS data for the product 7:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 6.6 Hz, 1H), 5.26 (d, *J* = 2.4 Hz, 1H), 4.55 – 4.50 (m, 1H), 3.71 – 3.67 (m, 1H), 2.36 (s, 3H), 1.93 – 1.87 (m, 1H), 1.72 – 1.66 (m, 1H), 1.52 – 1.43 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 192.5, 145.2, 145.0, 143.4, 141.7, 136.8, 133.1, 132.2, 131.6, 129.8, 128.7, 128.6, 128.2, 127.5, 125.6, 125.0, 115.5, 98.4, 67.6, 38.5, 38.0, 21.6, 21.4, 20.0.

HRMS (ESI-TOF) m/z: **$[M + H]^+$** calcd for $C_{28}H_{25}N_2O_5S^+$ 501.1479; found 501.1477.

((1*R*,4*S*,4a*R*,9a*S*)-4a-amino-9-tosyl-4,4a,9,9a-tetrahydro-1*H*-1,4-ethanocarbazol-3-yl)(phenyl)methanone 8



Prepared according to the general procedure to afford **8** (34.0 mg, m. p. = 99.3 – 102.9 ºC) in 70% yield as white solid. The diastereomeric ratio was determined to be >19:1 by crude ^{1}H NMR analysis. The enantiomeric excess of the major product was determined to be 97% by chiral HPLC analysis on Chiralpak IC column (30% 2-propanol/n-CO_2, 1.5 mL/min), UV 290 nm, tmajor = 19.00 min, tminor = 12.90 min; $[\alpha]_D^{20}$ = -81.6 (c = 0.10 in CH_2Cl_2)

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

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 4.74 (s, 1H), 4.60 – 4.53 (m, 1H), 4.16 (s, 1H), 3.88 (d, *J* = 4.2 Hz, 1H), 3.28 (d, *J* = 7.2 Hz, 1H), 3.19 (d, *J* = 9.0 Hz, 1H), 2.72 – 2.69 (m, 1H),

2.40 – 2.36 (m, 1H), 2.35 (s, 3H), 2.19 – 2.13 (m, 1H), 1.93 – 1.87 (m, 1H), 1.73 – 1.69 (m, 1H), 1.49 – 1.44 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 201.0, 144.4, 142.9, 137.2, 133.5, 133.2, 132.6, 130.1, 129.6, 128.8, 127.8, 127.5, 124.6, 124.2, 115.7, 70.3, 67.0, 65.4, 44.8, 38.1, 33.8, 21.5, 16.0, 15.4.

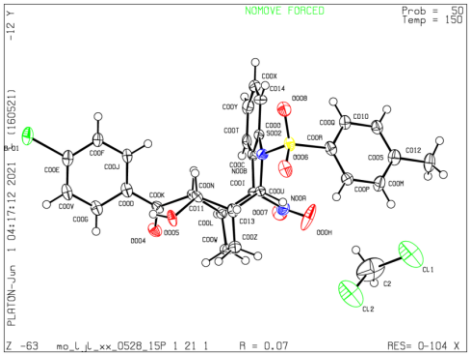
HRMS (ESI-TOF) m/z: **$[M + Na]^+$** calcd for $C_{28}H_{28}N_2O_4SNa^+$ 511.1662; found 511.1652.

5. Crystal Data and Structure Refinement for 5d

Crystal preparation and measurement

To a tube containing **5d** (20 mg) was added a 5:1 mixture of petroleum ether and dichloromethane (about 4 mL). Tube was sealed up and kept aside for 7 days at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the structure of **5d**. The data were collected by an Agilent Gemini equipped with a Mo radiation source (Kα = 0.71073 Å) at 150.0 K. CCDC 2108113 (**5d**) contains the supplementary crystallographic data for this paper.

Crystal Data (at 50% probability level)



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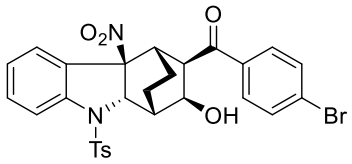


5d

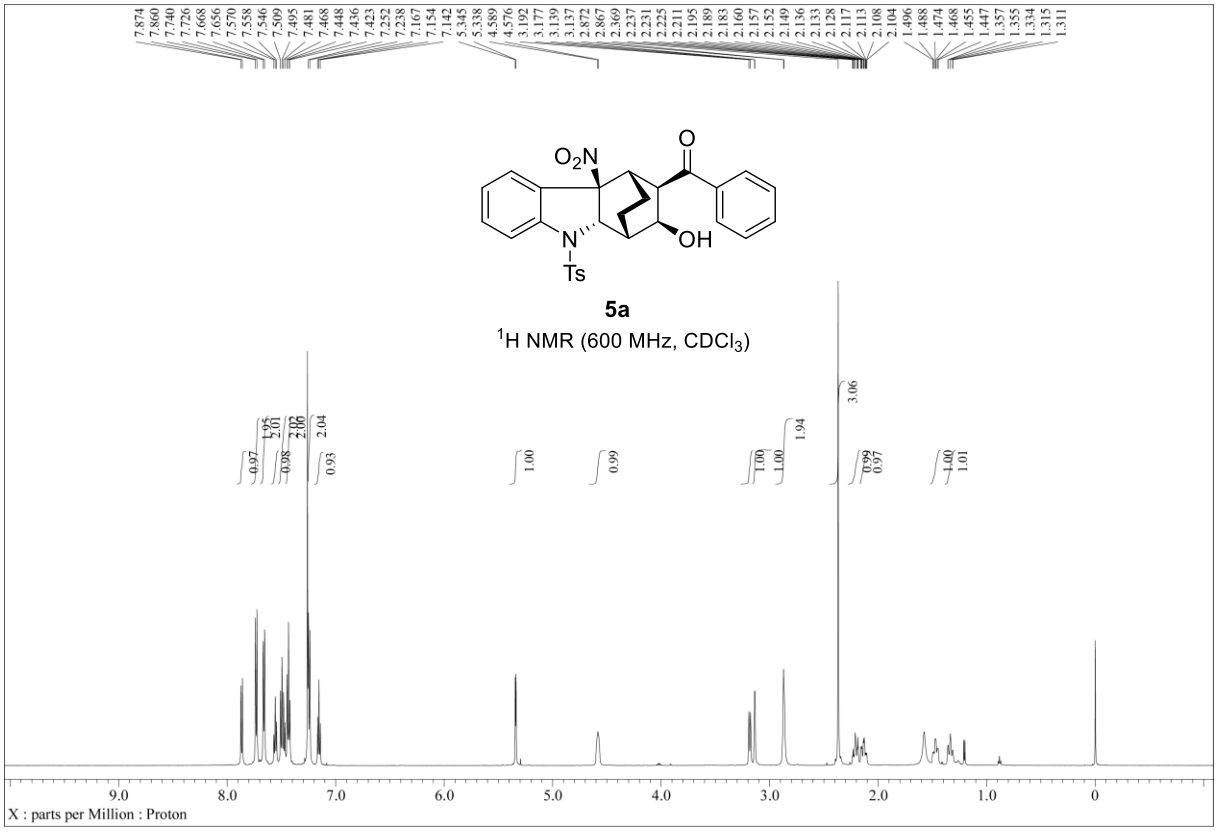
Identification code	**5d**
Empirical formula	$C_{29}H_{27}BrCl_2N_2O_6S$
Formula weight	682.39
Temperature/K	150.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.6602(3)
b/Å	13.1717(5)
c/Å	11.7135(4)
α/°	90
β/°	108.3090(10)
γ/°	90
Volume/Å^3	1414.99(8)
Z	2
ρ_{calc}g/cm^3	1.602
μ/mm^{-1}	1.763
F(000)	696.0
Crystal size/mm^3	0.38 × 0.19 × 0.17
Radiation	MoKα (λ = 0.71073)

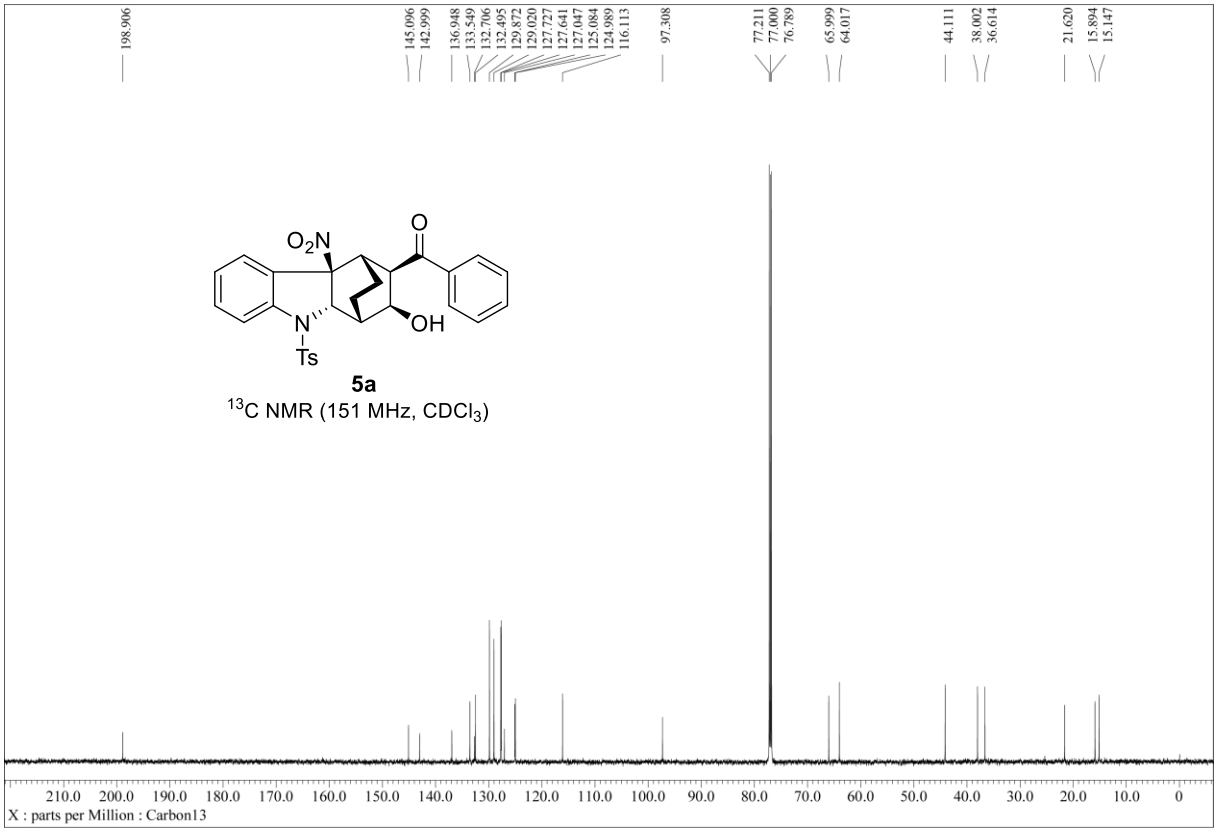
2Θ range for data collection/°	4.442 to 55.008
Index ranges	$-12 \leq h \leq 11$, $-17 \leq k \leq 17$, $-15 \leq l \leq 15$
Reflections collected	36907
Independent reflections	6450 [$R_{int} = 0.0515$, $R_{sigma} = 0.0501$]
Data/restraints/parameters	6450/1/366
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	$R_1 = 0.0654$, $wR_2 = 0.1788$
Final R indexes [all data]	$R_1 = 0.0761$, $wR_2 = 0.1870$
Largest diff. peak/hole / e $Å^{-3}$	1.70/-2.01
Flack parameter	0.015(4)

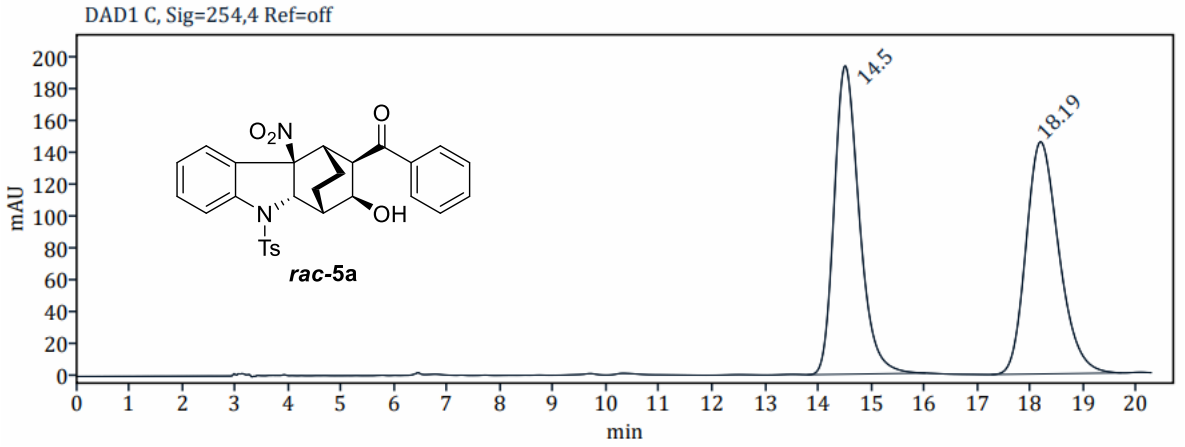
6. References and Notes

1. (a) E. Krell, Handbook of laboratory distillation, Elseriver Publishing Company, Amsterdam-London-New York. **1963**; (b) M. J. Rosengart, The technique of distillation and rectification in the laboratory, VEB Verlag Technik, Berlin. **1954**; (c) F. Stage, *Angew. Chem., Int. Ed*., **1947**, *19*, 175–183.
2. (a) M.-S. Mei, Y.-H. Wang, Q. Hu, Q.-H. Li, D.-Y. Shi, D. Gao, G. Ge, G.-Q. Lin and P. Tian, *Chem., Commun.,* 2020, **56**, 10718–10721; (b) Q. Wan, J.-H. Xie, C. Zheng, Y.-F. Yuan and S.-L. You, *Angew. Chem., Int. Ed*., 2021, **60**, 19730–19734.
3. (a) G. Black, F. Dinon, S. Fratucello, P. Murphy, M. Nielsen, H. Williams and N. Walshe, *Tetrahedron Lett.*, 1997, **38**, 8561–8564. (b) E. L. Richards, P. J. Murphy, F. Dinon, S. Fratucello, P. M. Browm, T. Gelbrich and M. B. Hursthouse, *Tetrahedron*, 2001, **57**, 7771–7784.

7. Copies of NMR Spectra







Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
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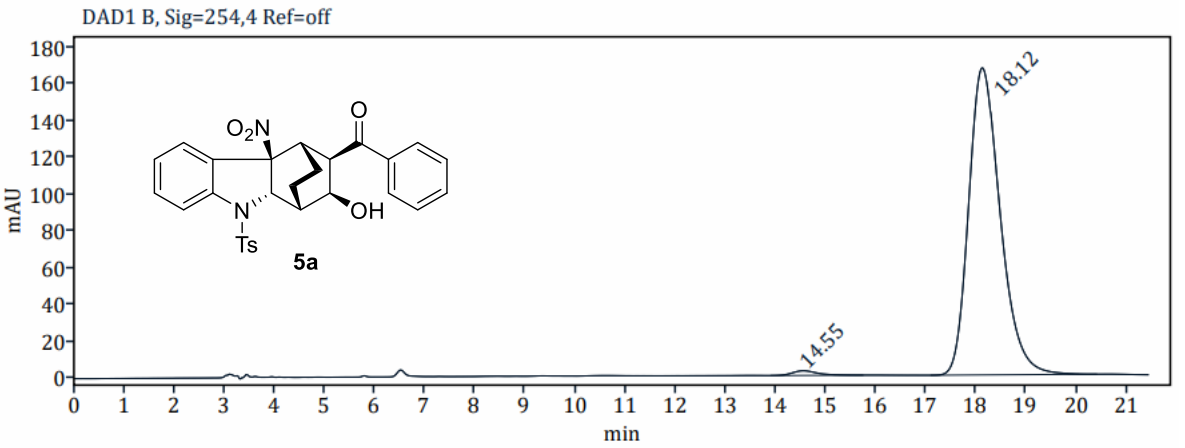
2	18.19	6272.837	145.2508	49.7240



Peak Analysis Report

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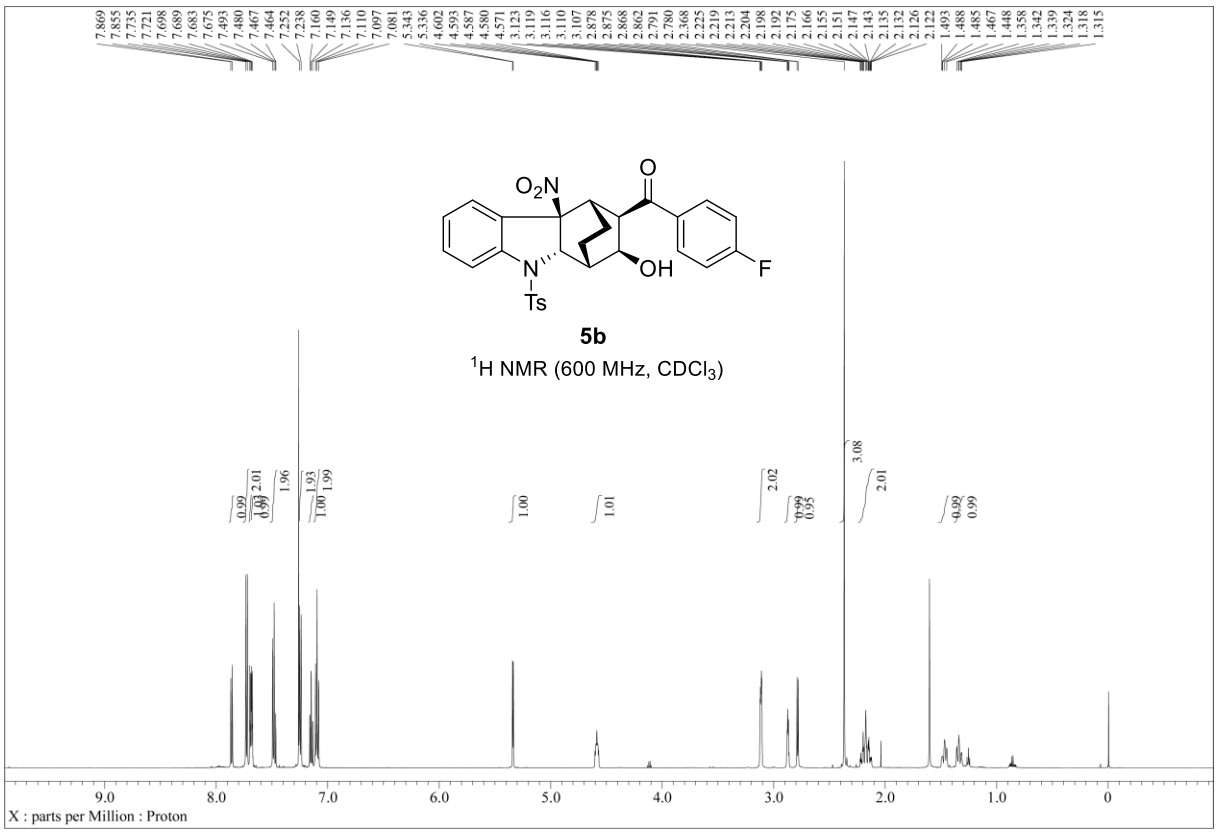
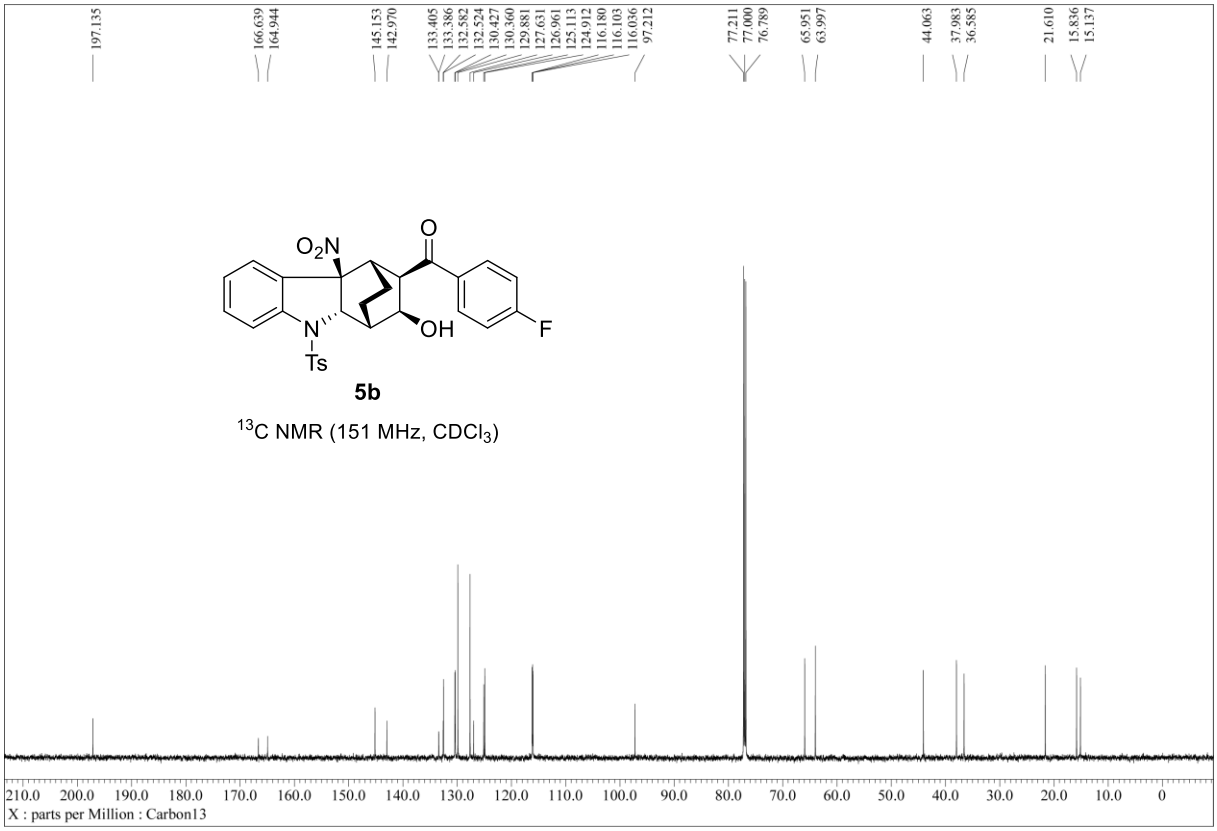


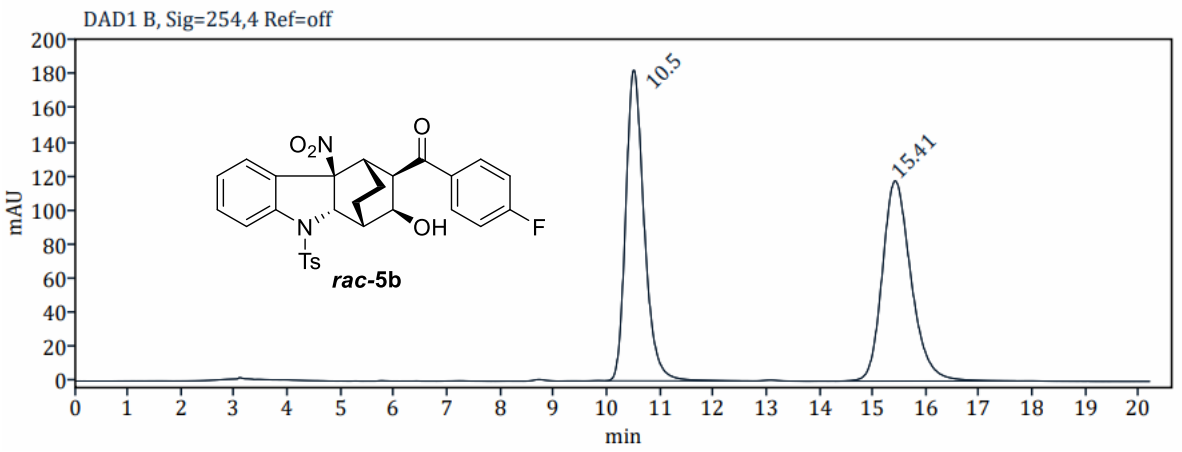
5b

^{1}H NMR (600 MHz, $CDCl_3$)



5b

^{13}C NMR (151 MHz, $CDCl_3$)



Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
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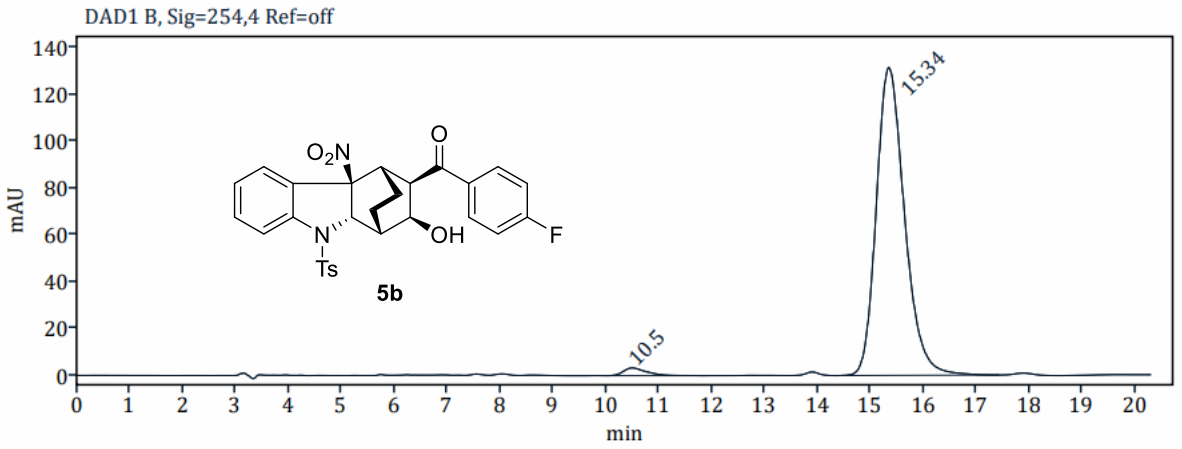

Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
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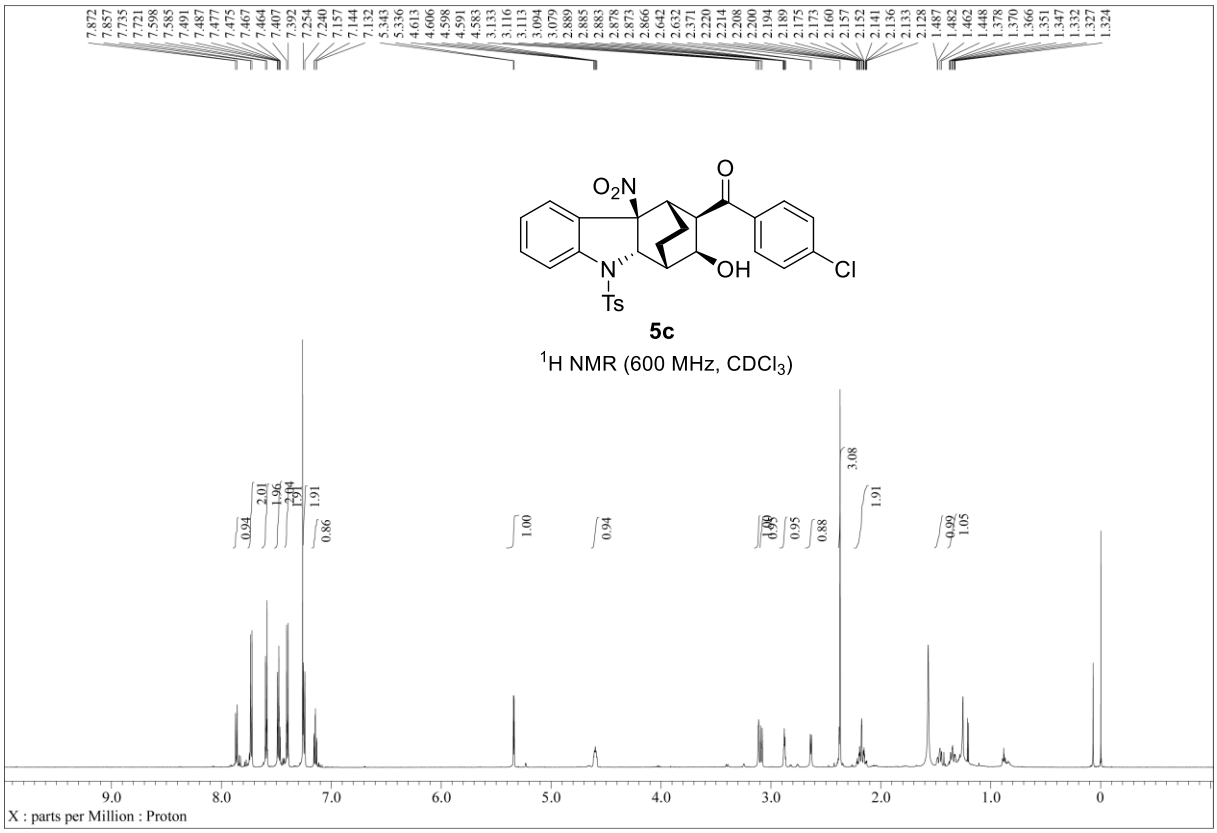
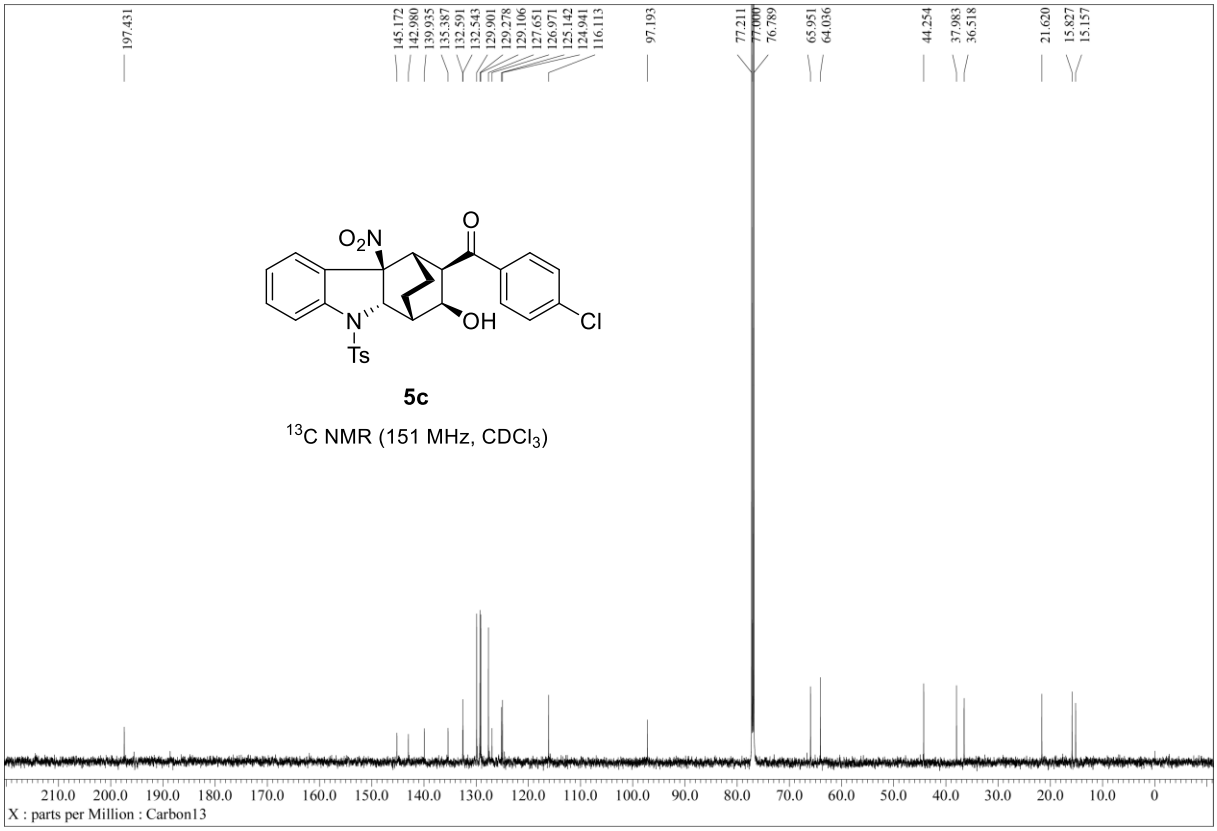


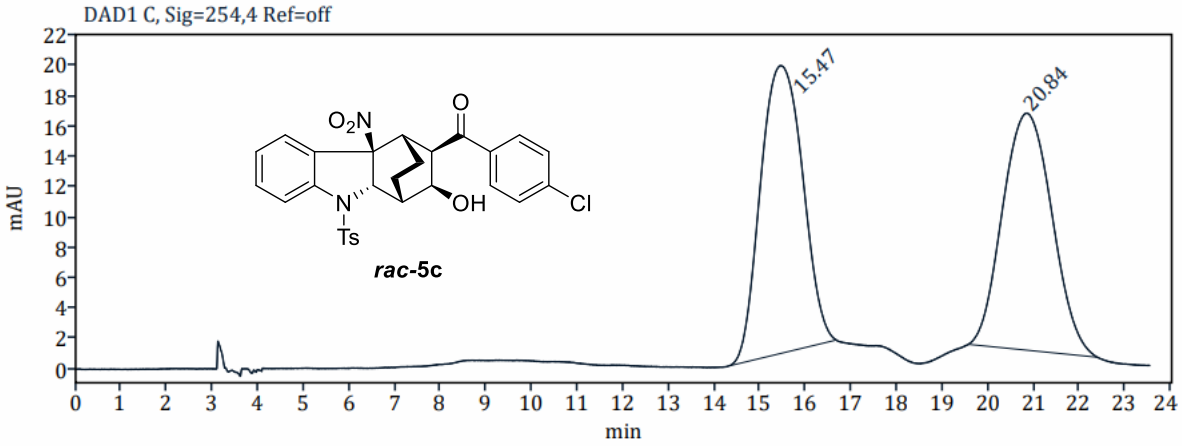
5c

^{1}H NMR (600 MHz, $CDCl_3$)



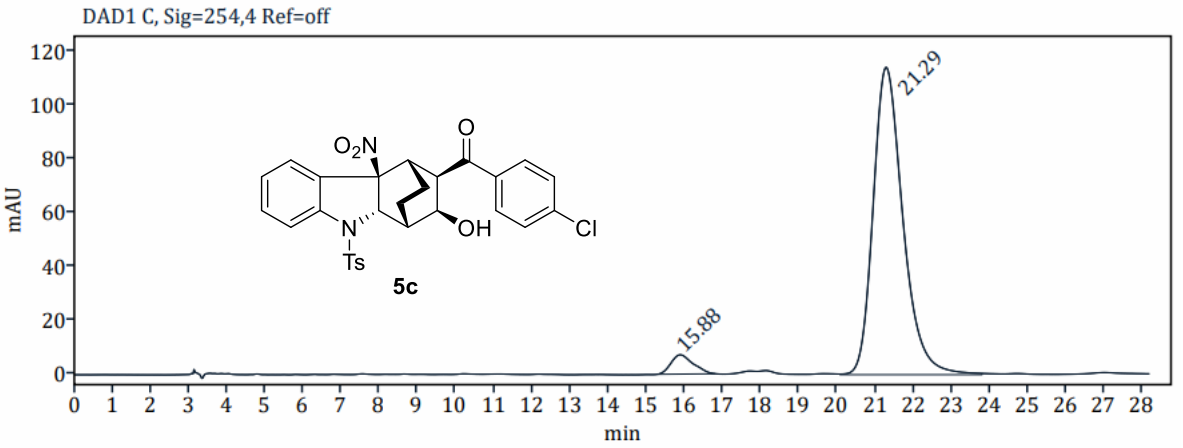
5c

^{13}C NMR (151 MHz, $CDCl_3$)



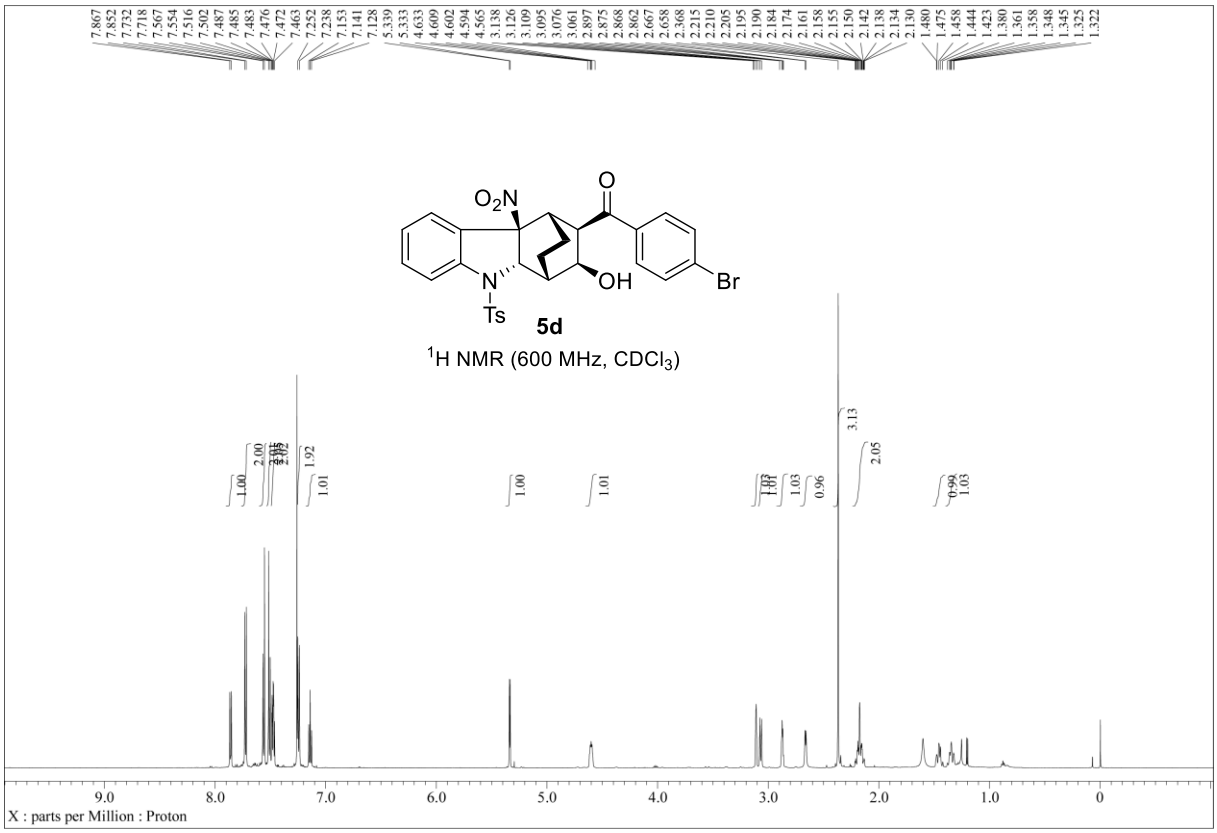
Peak Analysis Report

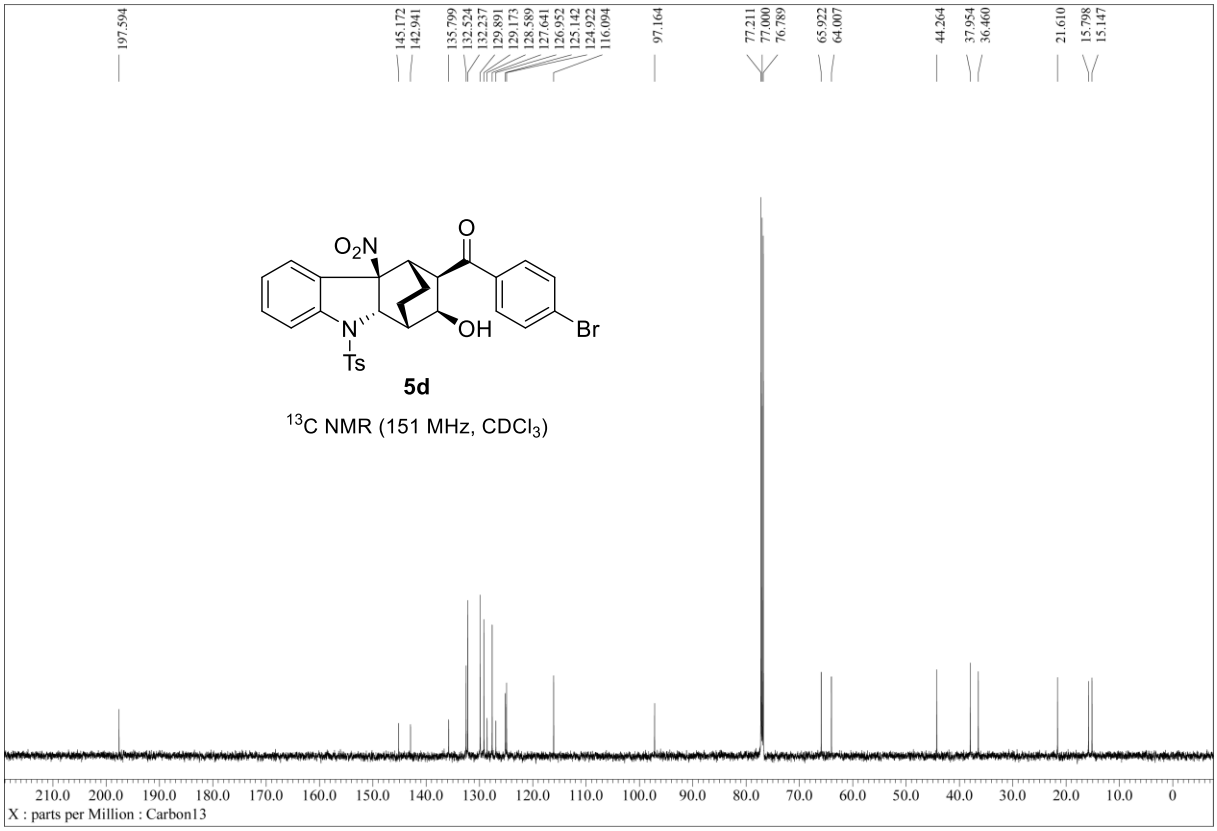
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	15.47	1223.549	18.9828	50.8944
2	20.84	1180.542	15.6480	49.1056

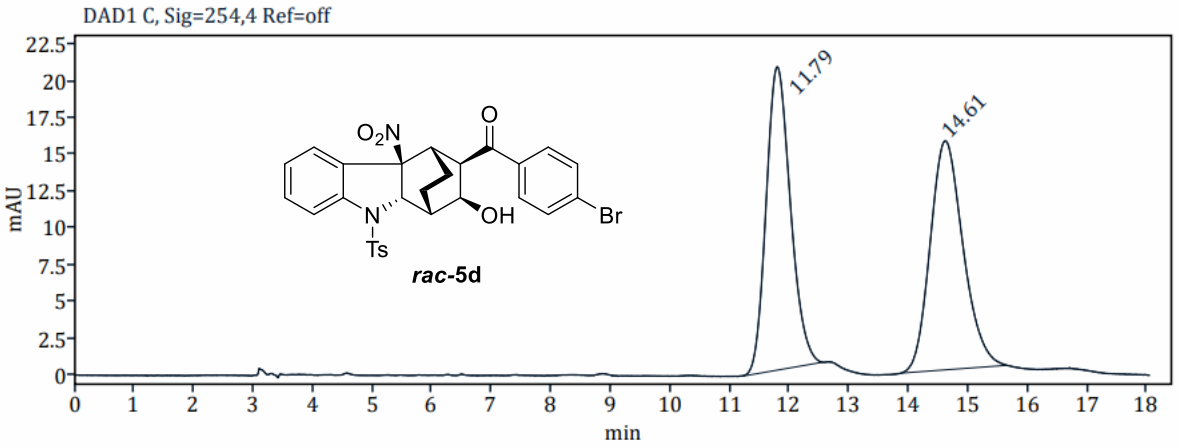


Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	15.88	289.067	7.1745	4.4645
2	21.29	6185.709	114.0182	95.5355

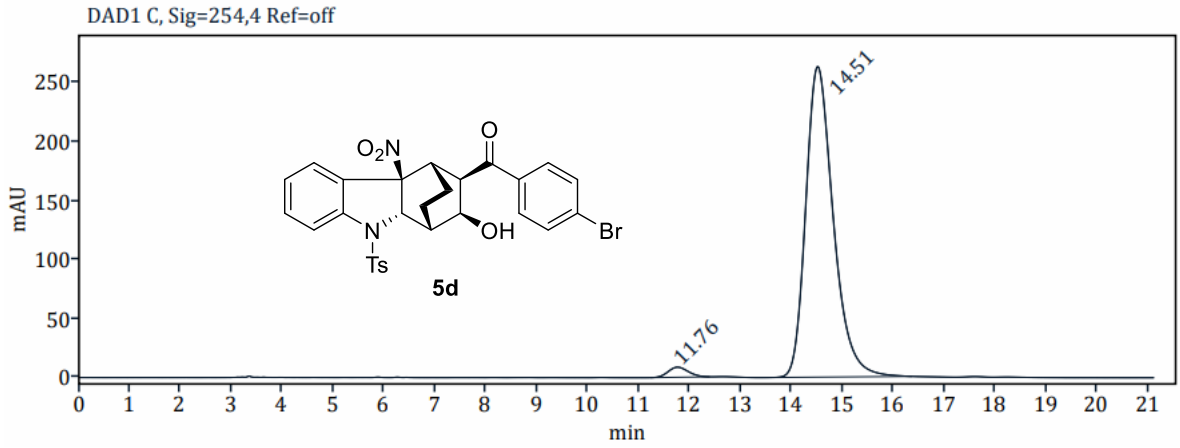

7.867 7.852 7.732 7.718 7.567 7.554 7.516 7.502 7.487 7.485 7.483 7.476 7.472 7.463 7.252 7.238 7.153 7.141 7.128 5.339 5.333 4.633 4.609 4.602 4.594 4.565 3.138 3.126 3.109 3.095 3.076 3.061 2.897 2.875 2.868 2.862 2.667 2.658 2.368 2.215 2.210 2.205 2.195 2.190 2.184 2.174 2.161 2.158 2.155 2.150 2.142 2.138 2.134 2.130 1.480 1.475 1.458 1.444 1.423 1.380 1.361 1.358 1.348 1.345 1.325 1.322
O2N
O
N
Ts
OH
Br
5d
1H NMR (600 MHz, CDCl3)
1.00 2.00 1.92 1.01 1.00 1.01 1.03 0.96 3.13 2.05 0.99 1.03
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton


197.594
145.172 142.941 135.799 132.524 132.237 129.891 129.173 128.589 127.641 126.952 125.142 124.922 116.094
97.164
77.211 77.000 76.789
65.922 64.007
44.264 37.954 36.460
21.610 15.798 15.147
O2N
O
N
Ts
OH
Br
5d
13C NMR (151 MHz, CDCl3)
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13



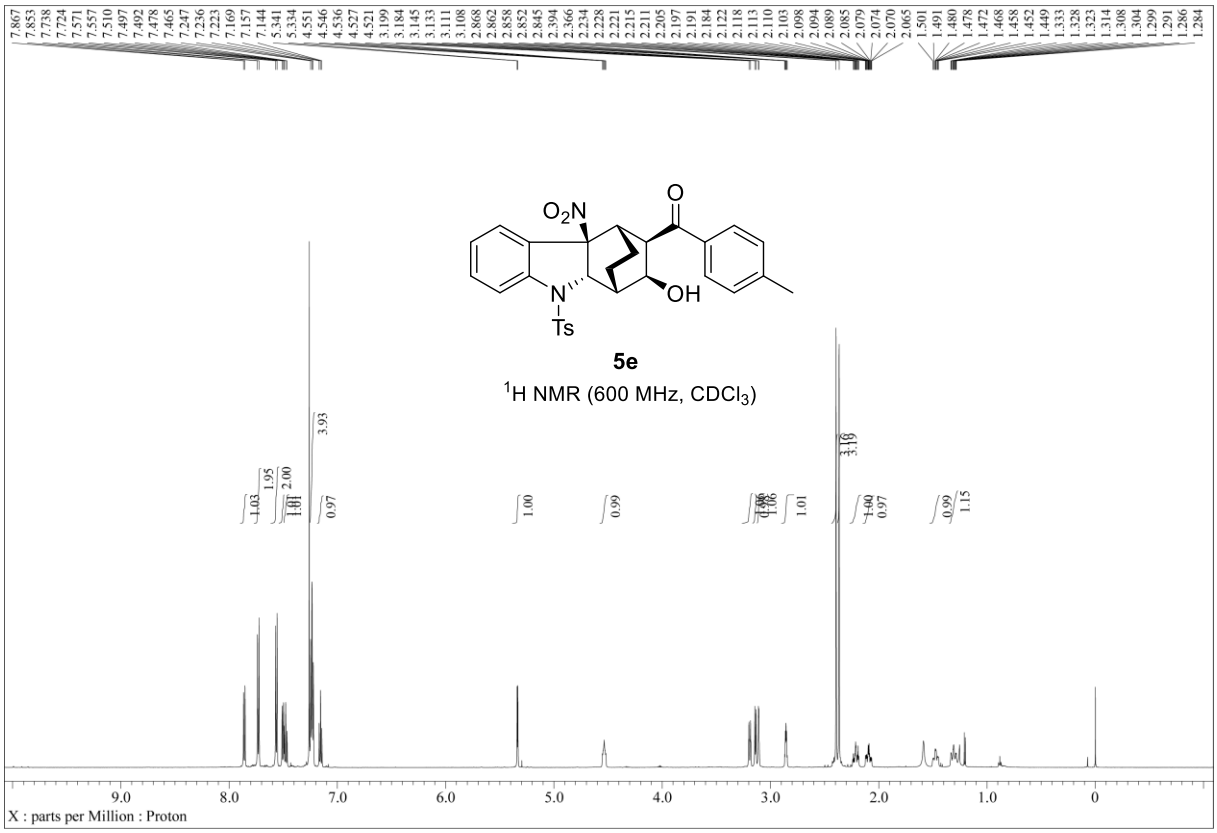
Peak Analysis Report

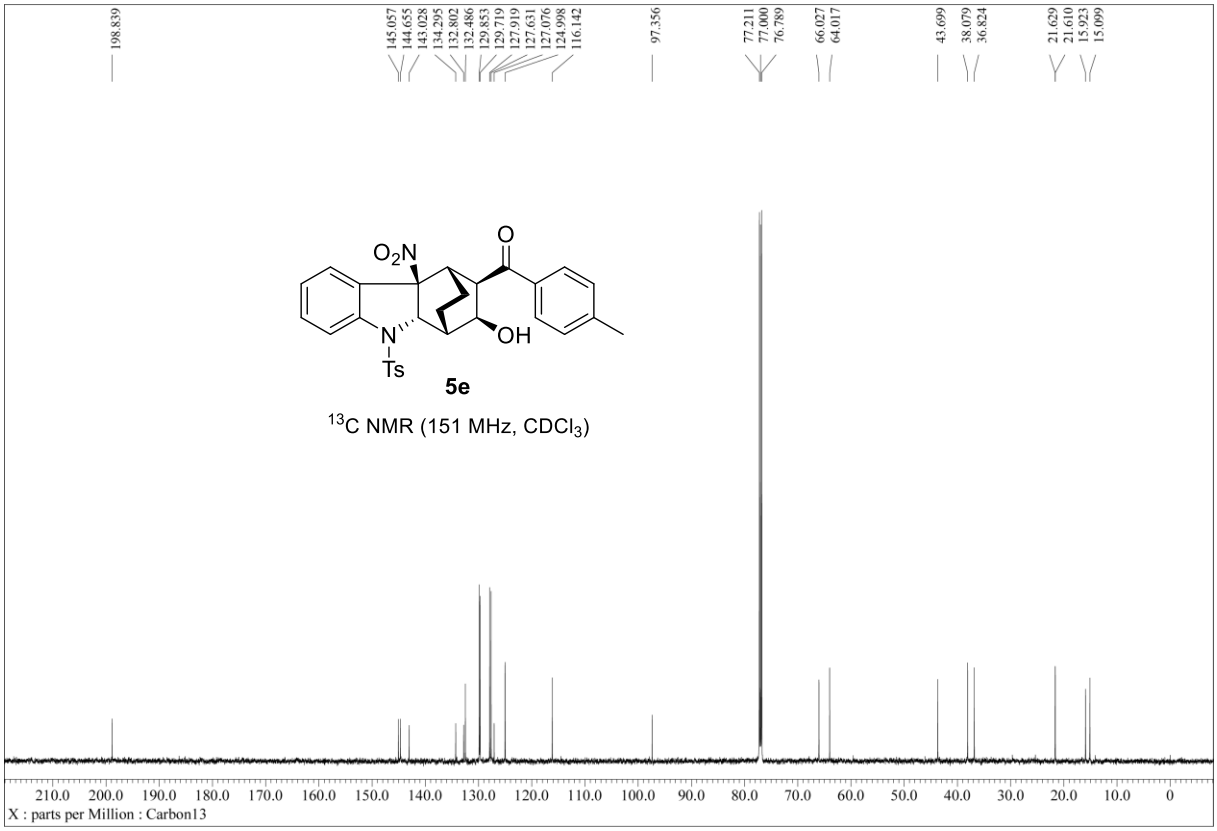
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	11.79	585.173	20.6531	49.4379
2	14.61	598.480	15.6018	50.5621

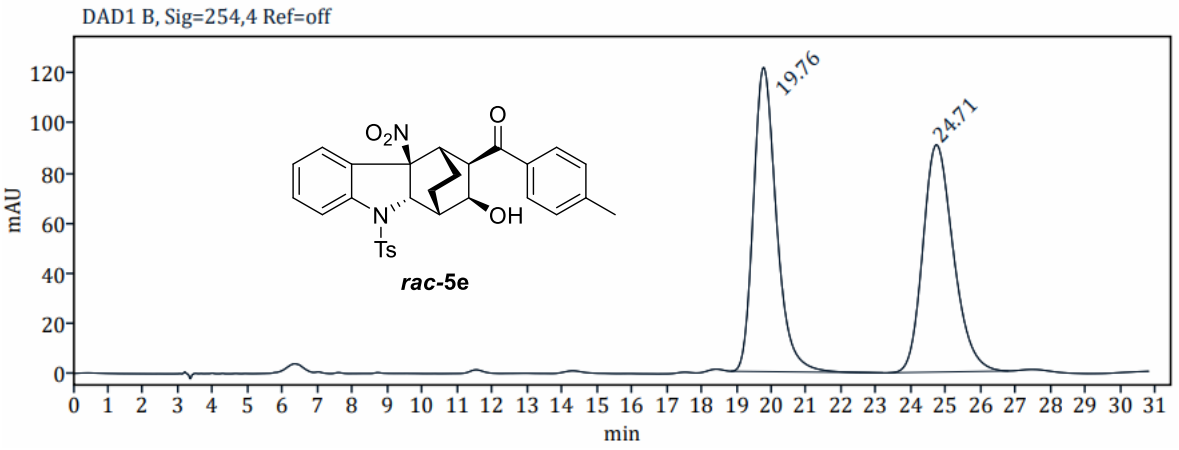


Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	11.76	236.481	8.5729	2.3275
2	14.51	9923.606	263.6922	97.6725

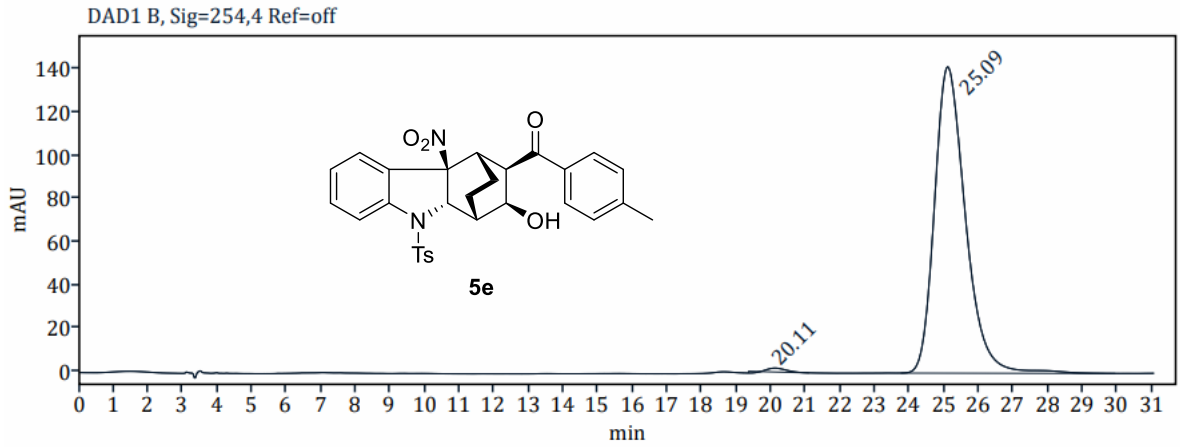

O2N
O
N
Ts
OH
5e
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


O2N
O
N
Ts
OH
5e
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



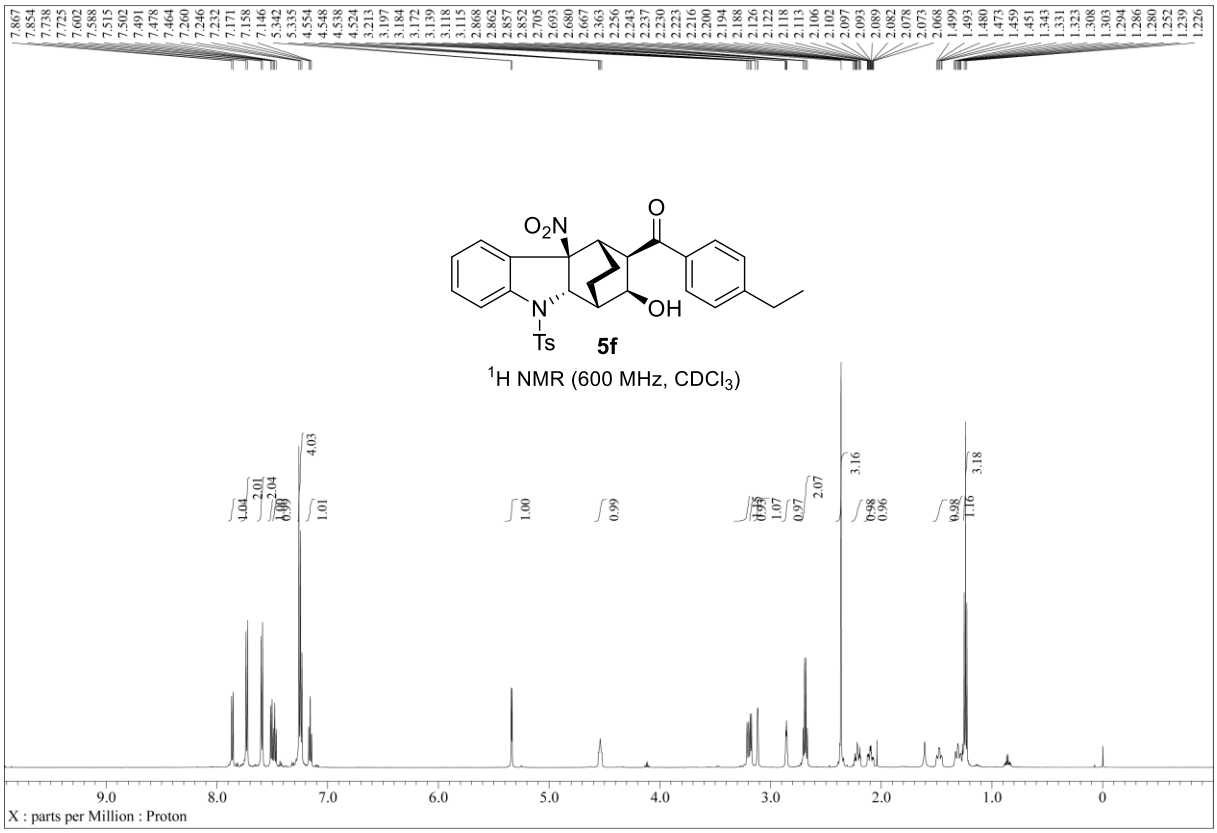
Peak Analysis Report

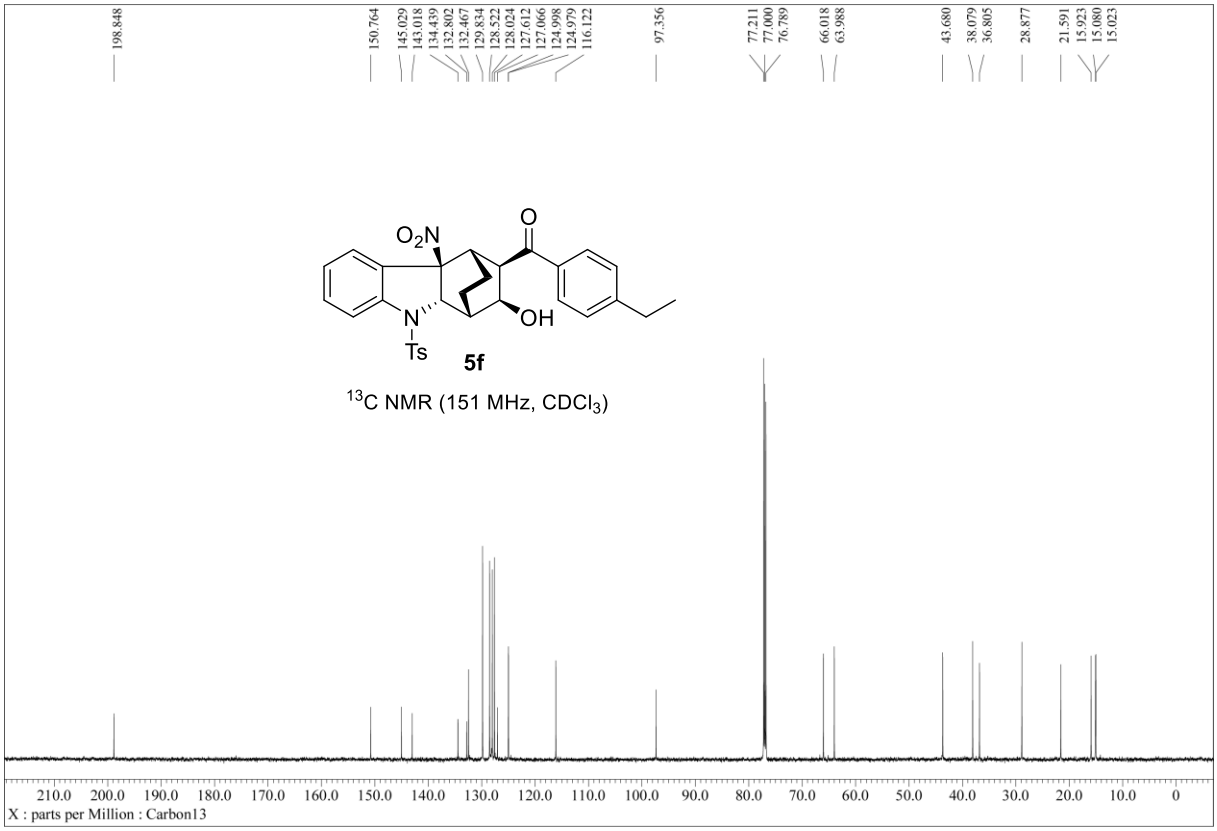
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	19.76	5584.543	121.7328	50.1779
2	24.71	5544.943	91.0214	49.8221

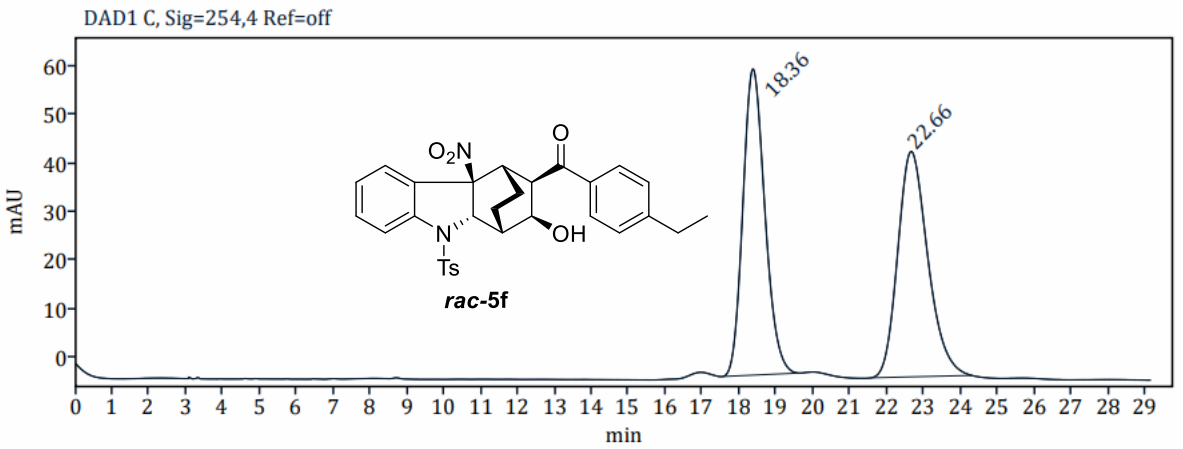


Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	20.11	65.915	1.7759	0.7402
2	25.09	8838.594	141.7842	99.2598

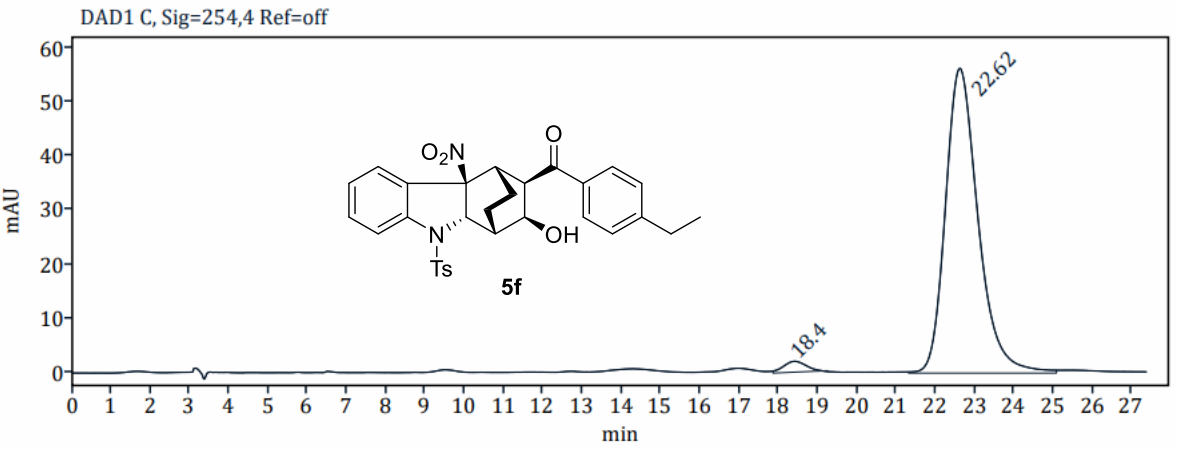

O2N
O
N
Ts
OH
5f
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


O2N
O
N
Ts
OH
5f
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



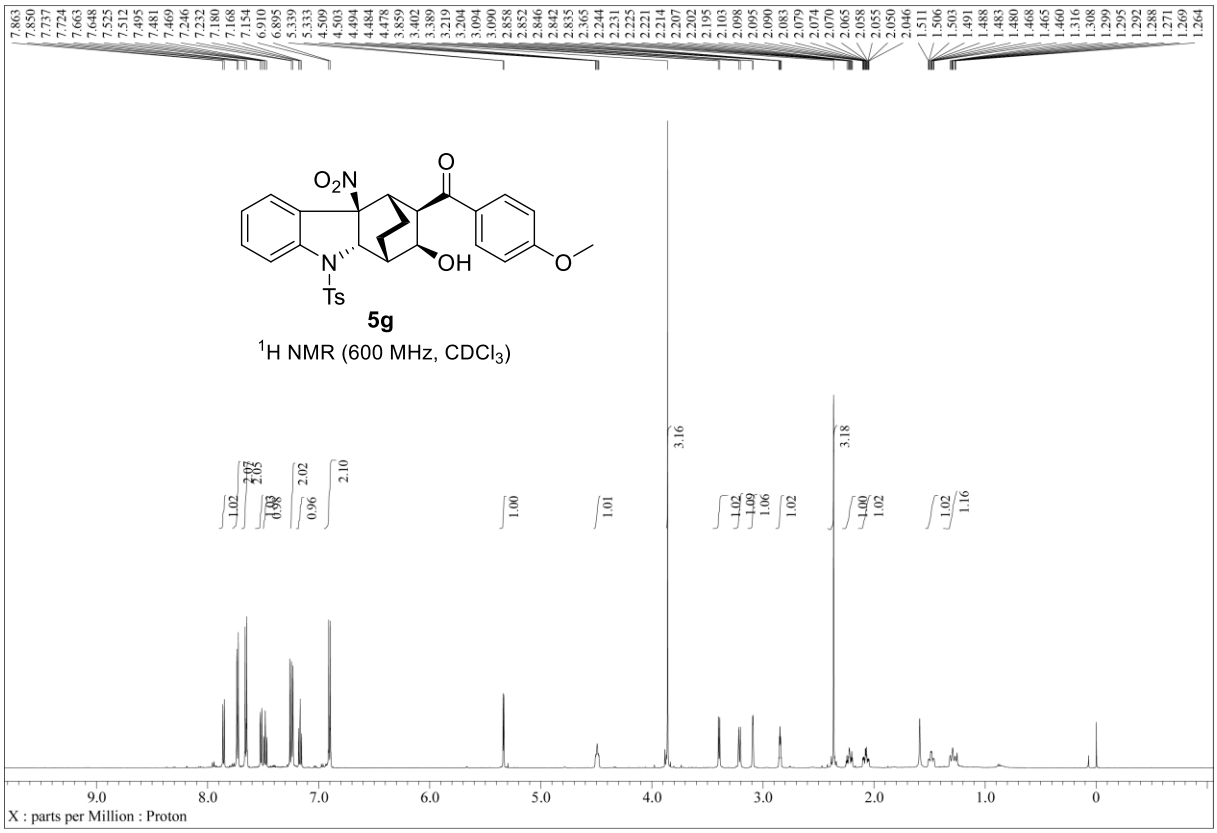
Peak Analysis Report

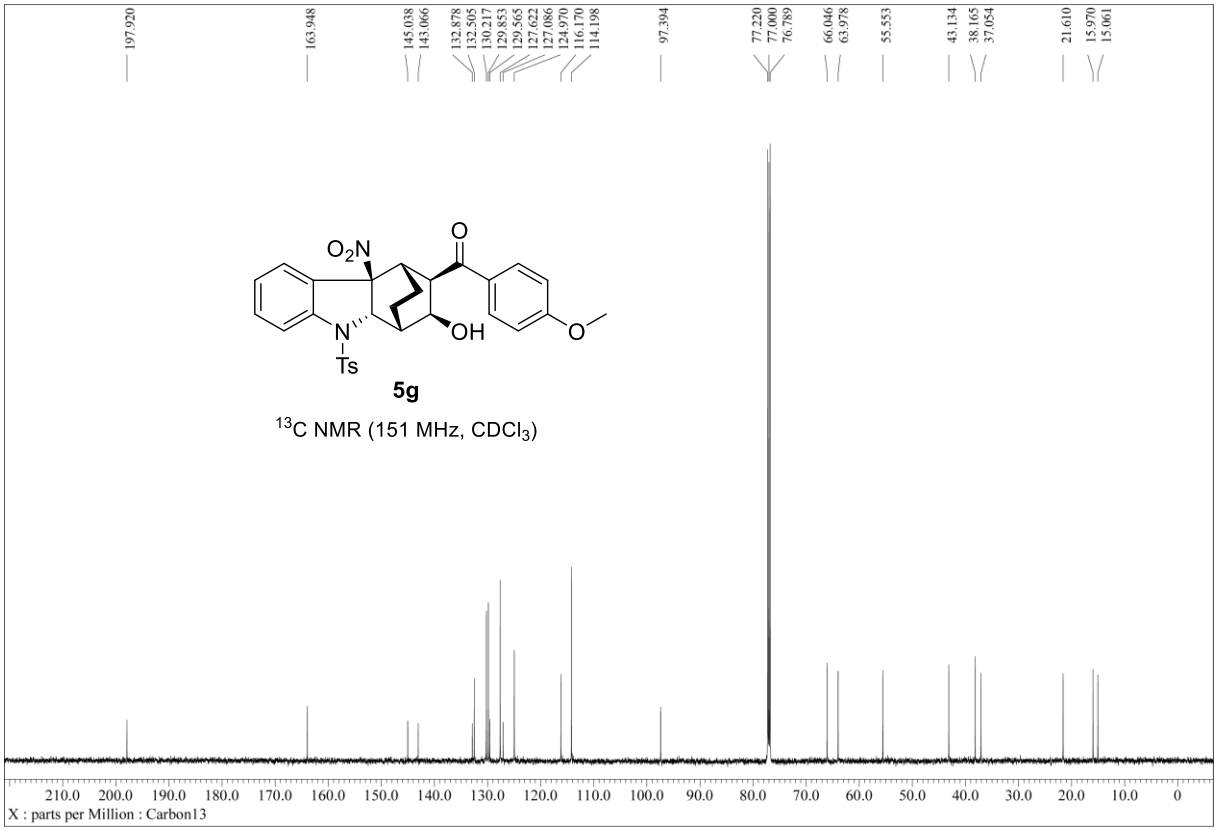
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	18.36	2616.212	63.1299	49.8068
2	22.66	2636.512	46.5077	50.1932

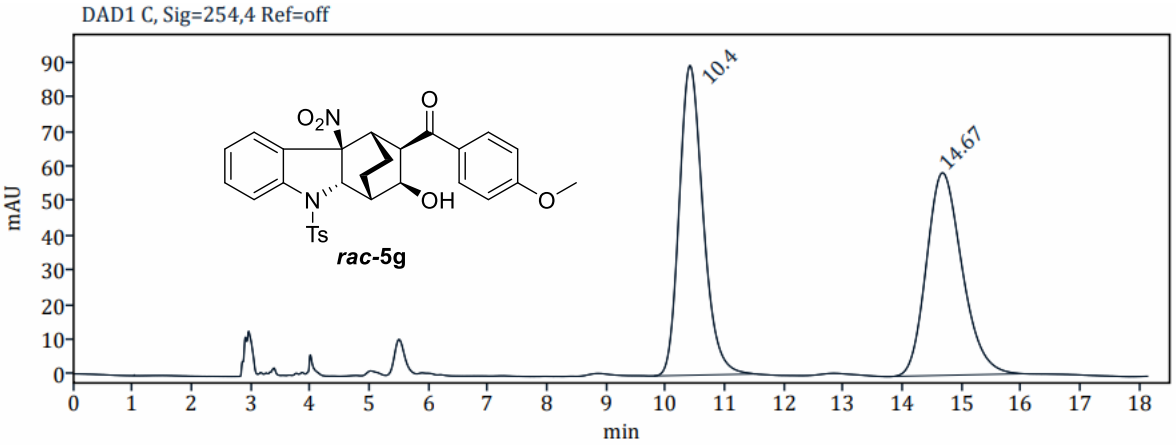


Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	18.40	80.613	2.0321	2.4112
2	22.62	3262.658	56.3014	97.5888

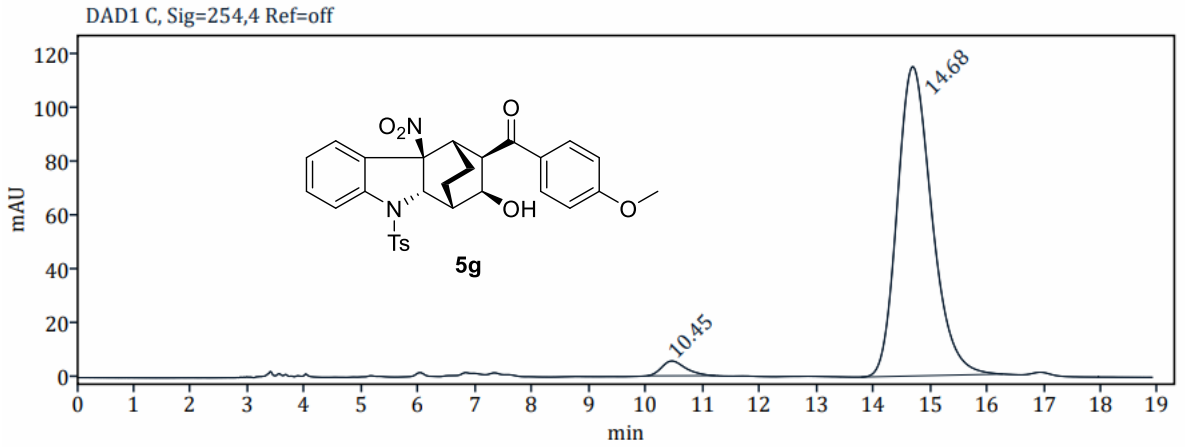

7.863 7.850 7.737 7.724 7.663 7.648 7.525 7.512 7.495 7.481 7.469 7.246 7.232 7.180 7.168 7.154 6.910 6.895 5.339 5.333 4.509 4.503 4.494 4.484 4.478 3.859 3.402 3.389 3.219 3.204 3.094 3.090 2.858 2.852 2.846 2.842 2.835 2.365 2.244 2.231 2.225 2.221 2.214 2.207 2.202 2.195 2.103 2.098 2.095 2.090 2.083 2.079 2.074 2.070 2.065 2.058 2.055 2.050 2.046 1.511 1.506 1.503 1.491 1.488 1.483 1.480 1.468 1.465 1.460 1.316 1.308 1.299 1.295 1.292 1.288 1.271 1.269 1.264
O2N
O
OH
O
N
Ts
5g
1H NMR (600 MHz, CDCl3)
3.16
3.18
1.02 2.07 2.05 1.03 0.98 0.96 2.02 2.10 1.00 1.01 1.02 1.09 1.06 1.02 1.00 1.02 1.02 1.16
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton


197.920 163.948 145.038 143.066 132.878 132.505 130.217 129.853 129.565 127.622 127.086 124.970 116.170 114.198 97.394 77.220 77.000 76.789 66.046 63.978 55.553 43.134 38.165 37.054 21.610 15.970 15.061
O2N
O
OH
O
N
Ts
5g
13C NMR (151 MHz, CDCl3)
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13



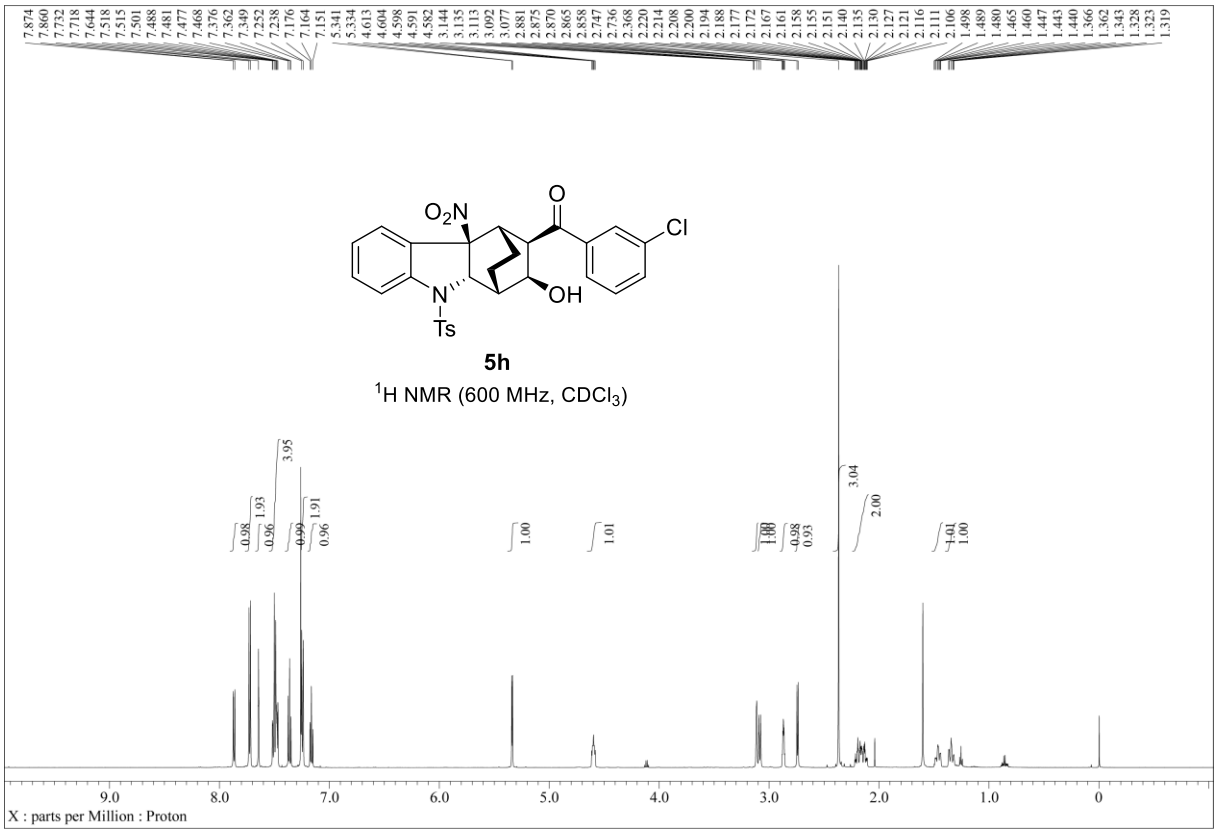
Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	10.40	2509.014	89.5259	50.5684
2	14.67	2452.612	58.5872	49.4316



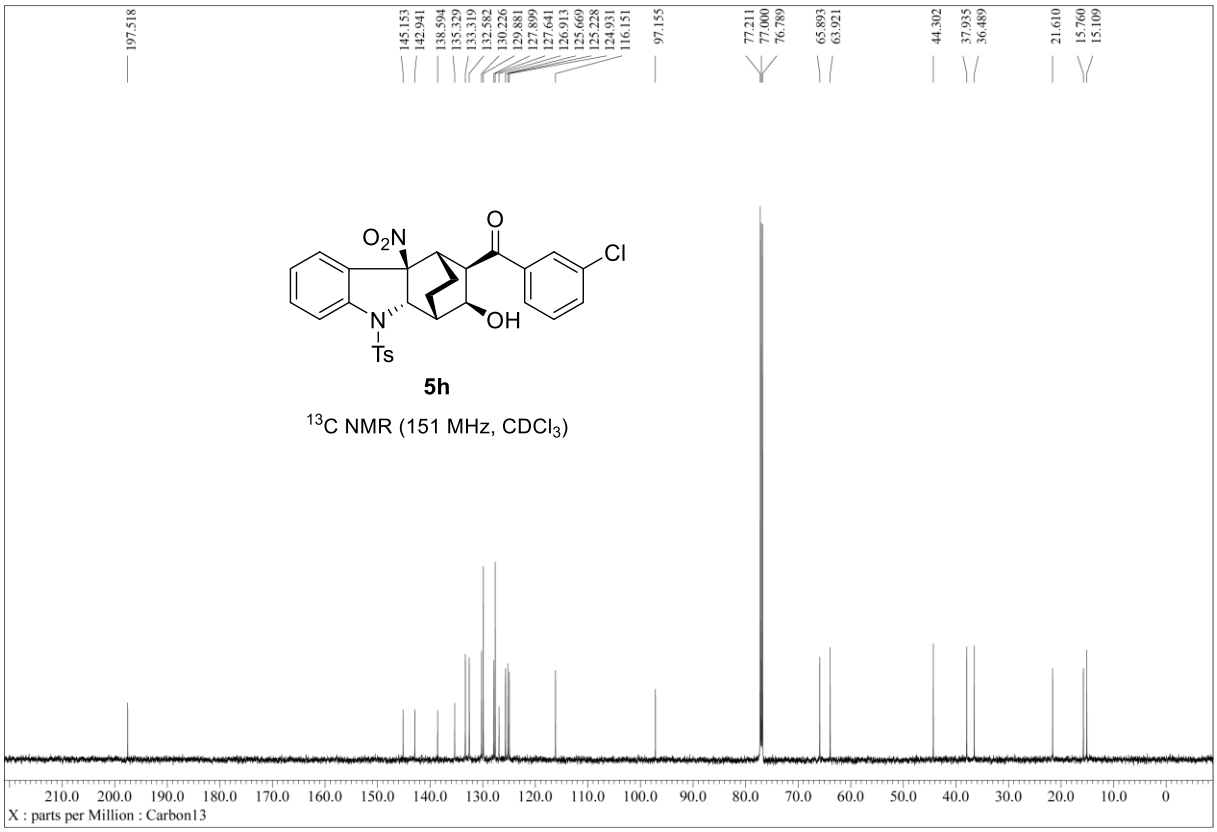
Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	10.45	162.510	5.5274	3.2268
2	14.68	4873.703	115.2774	96.7732



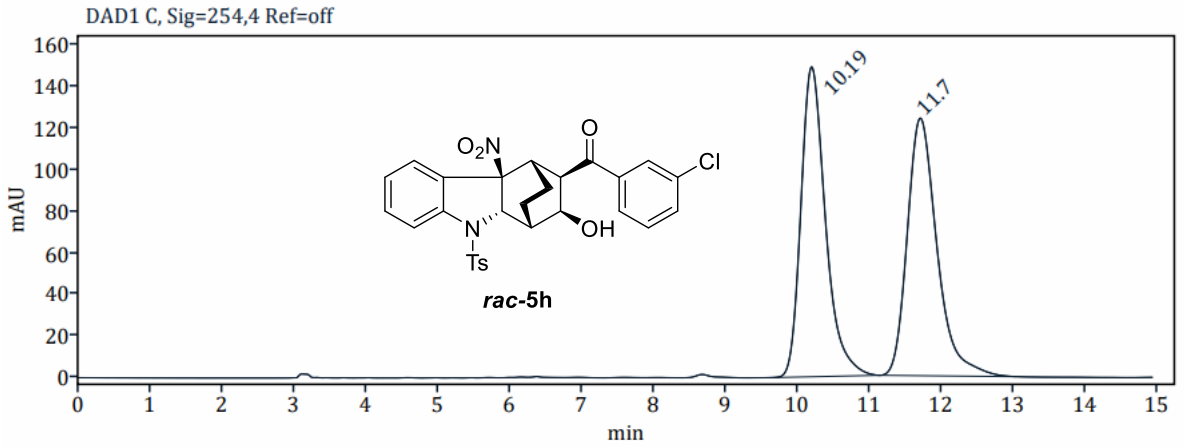
5h

^{1}H NMR (600 MHz, $CDCl_3$)



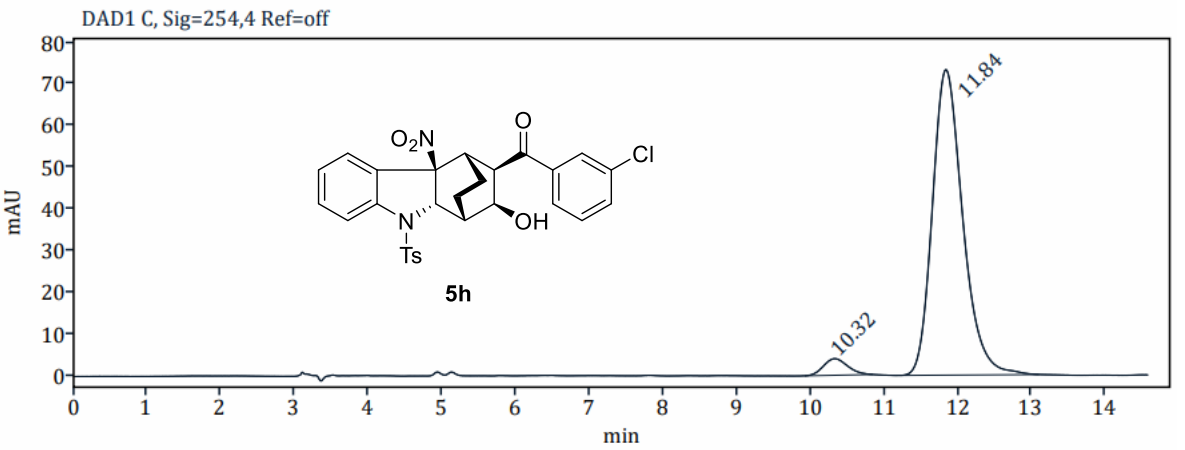
5h

^{13}C NMR (151 MHz, $CDCl_3$)



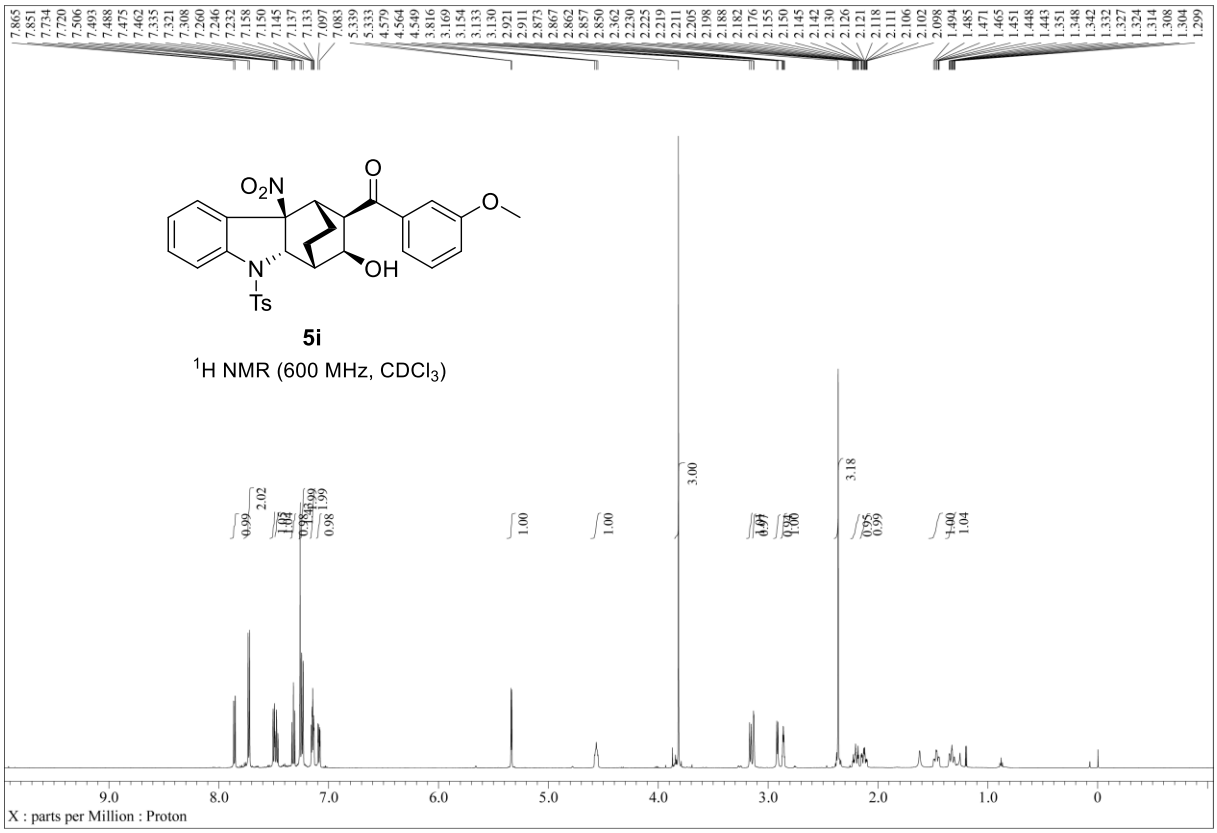
Peak Analysis Report

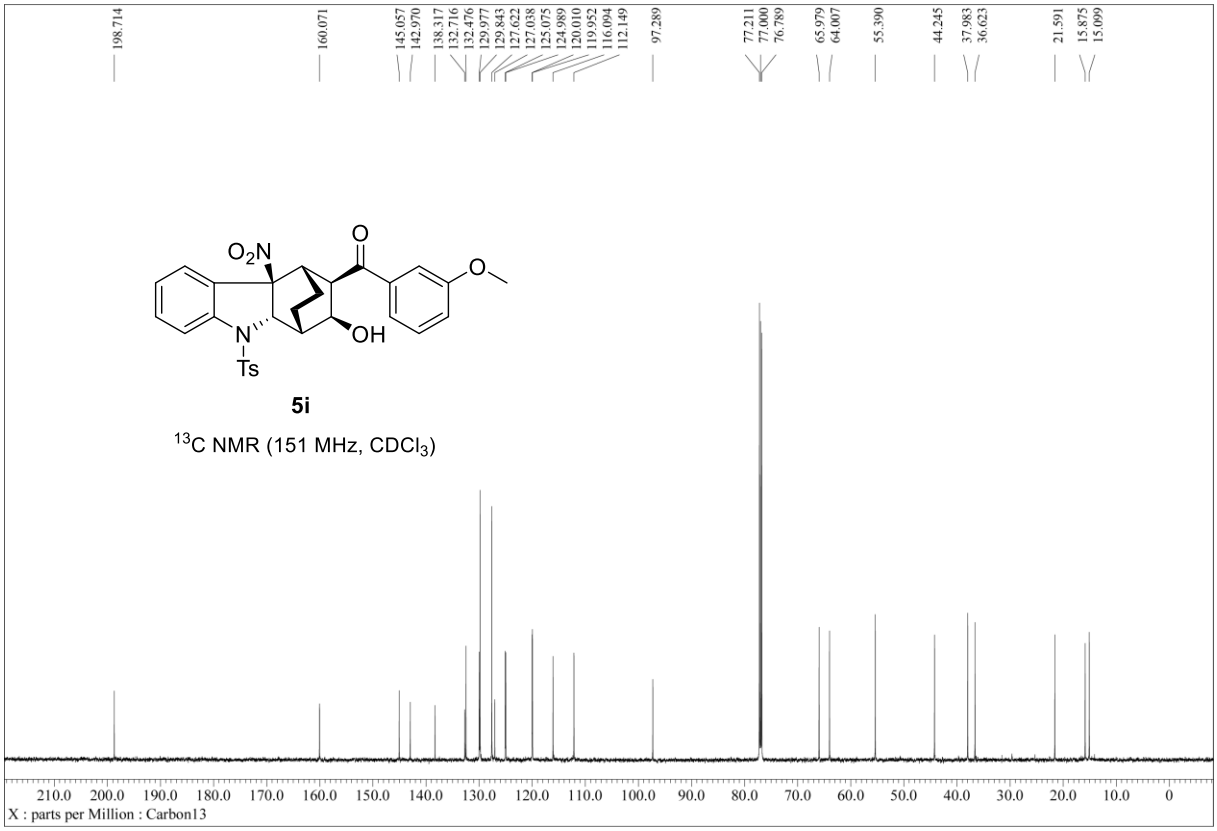
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	10.19	3538.387	149.1756	49.8607
2	11.70	3558.157	123.9943	50.1393

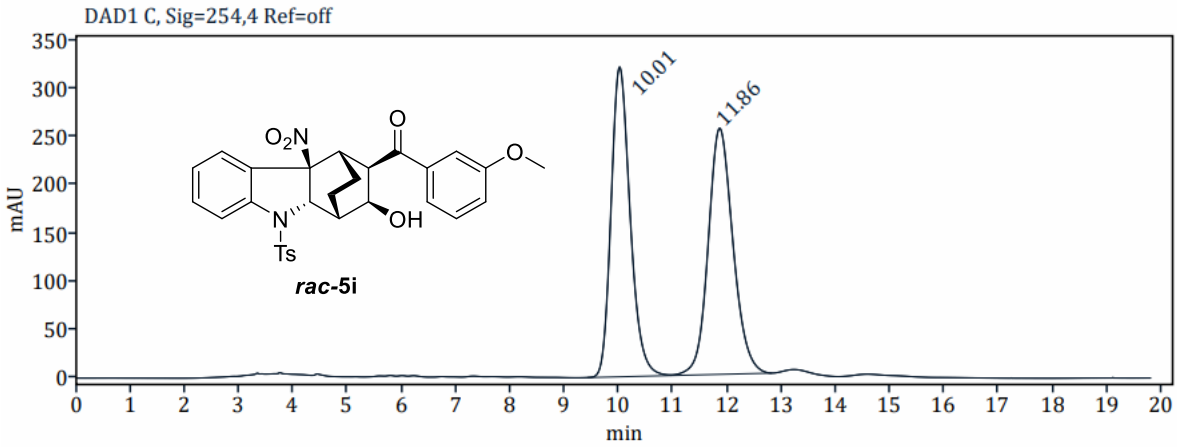


Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	10.32	90.701	3.9968	4.1468
2	11.84	2096.560	73.1662	95.8532

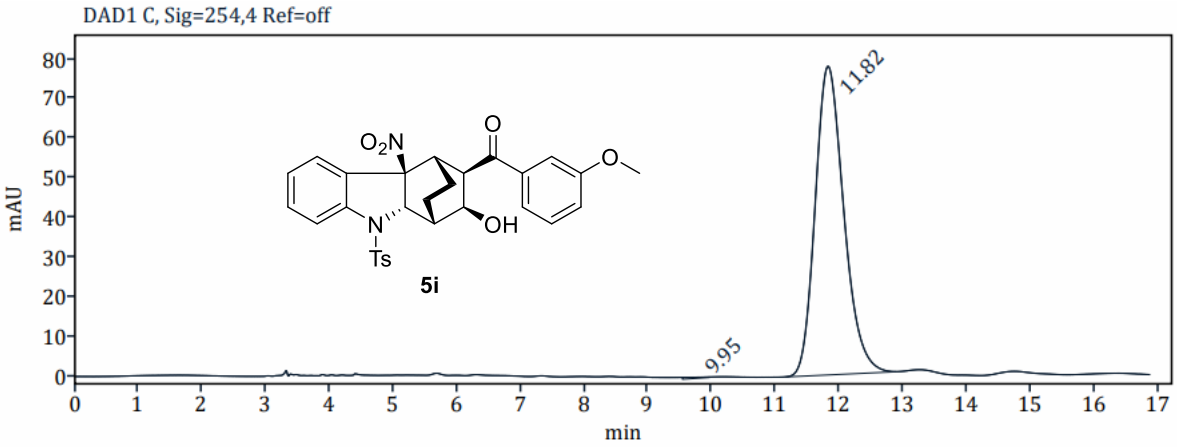

O2N
O
O
N
Ts
OH
5i
1H NMR (600 MHz, CDCl3)
3.00
3.18
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


198.714
160.071
145.057
142.970
138.317
132.716
132.476
129.977
129.843
127.622
127.038
125.075
124.989
120.010
119.952
116.094
112.149
97.289
77.211
77.000
76.789
65.979
64.007
55.390
44.245
37.983
36.623
21.591
15.875
15.099
O2N
O
O
N
Ts
OH
5i
13C NMR (151 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13



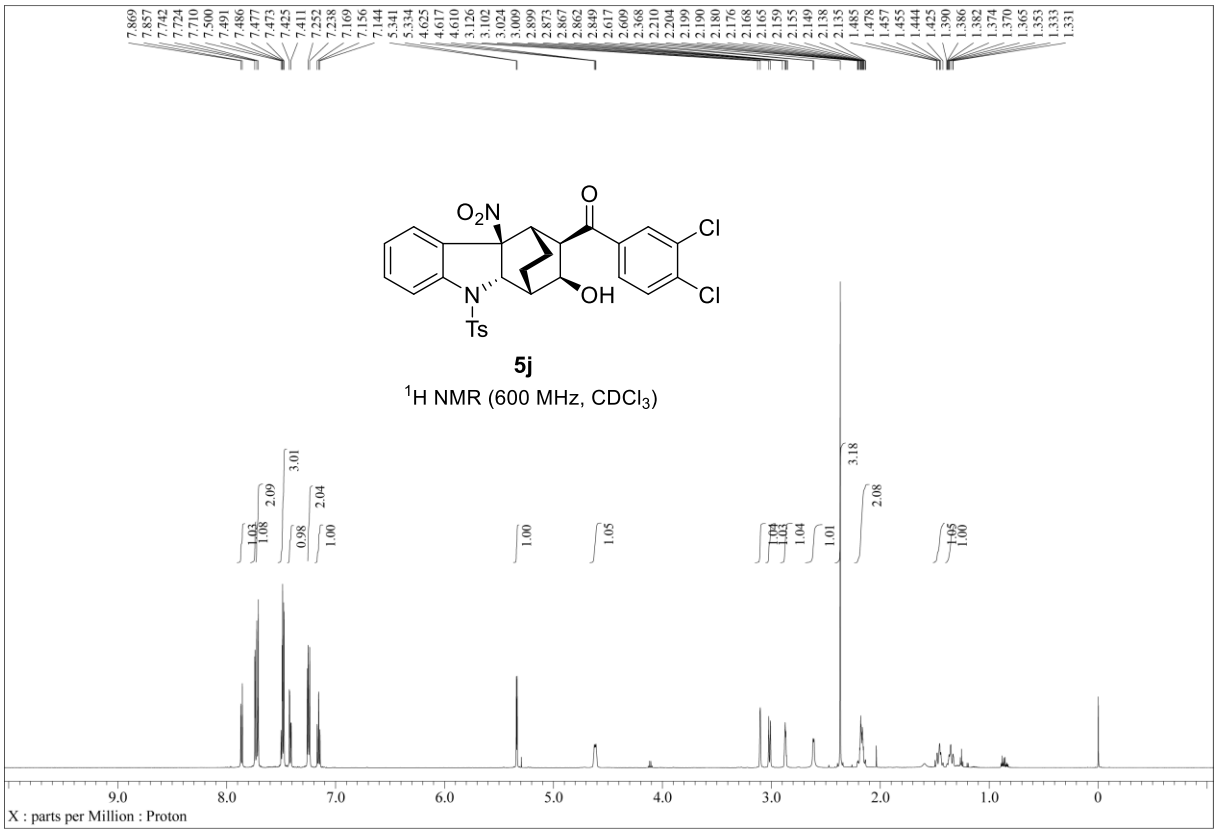
Peak Analysis Report

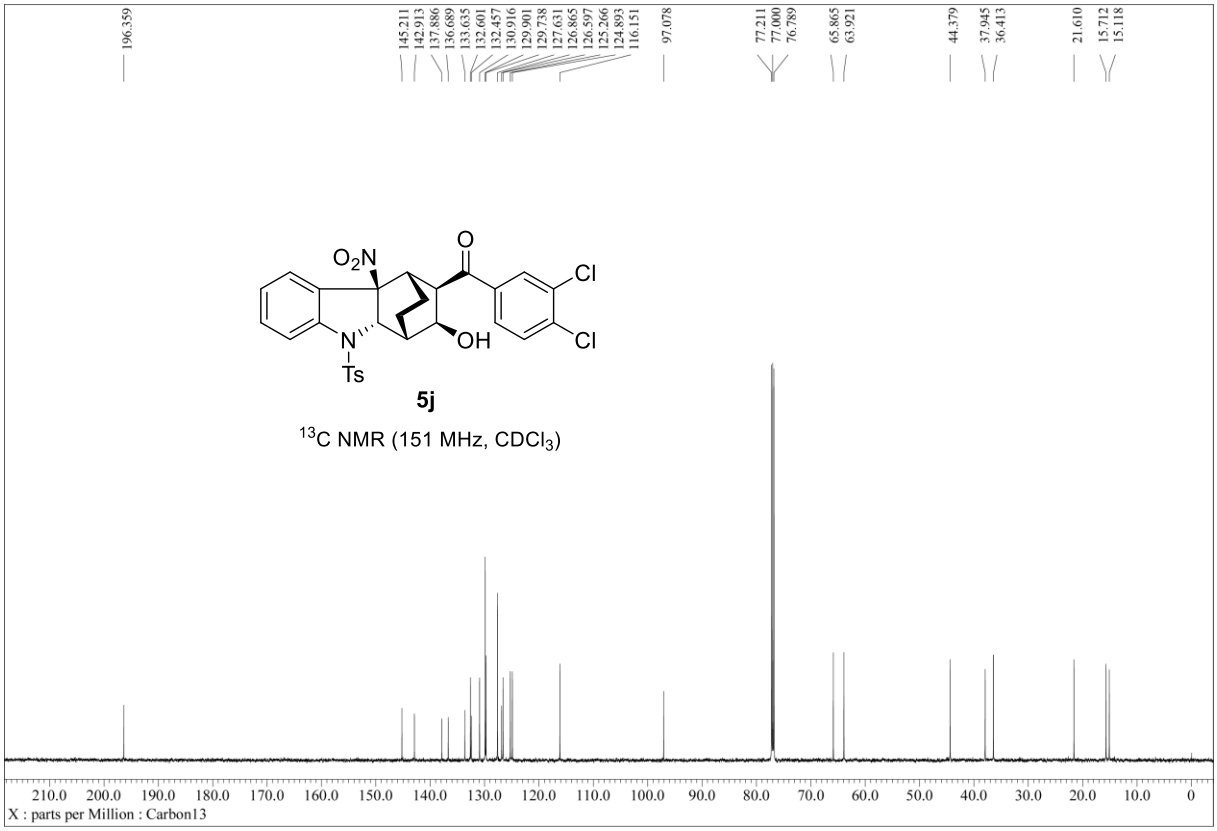
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	10.01	7858.137	321.3943	49.1882
2	11.86	8117.525	255.3147	50.8118

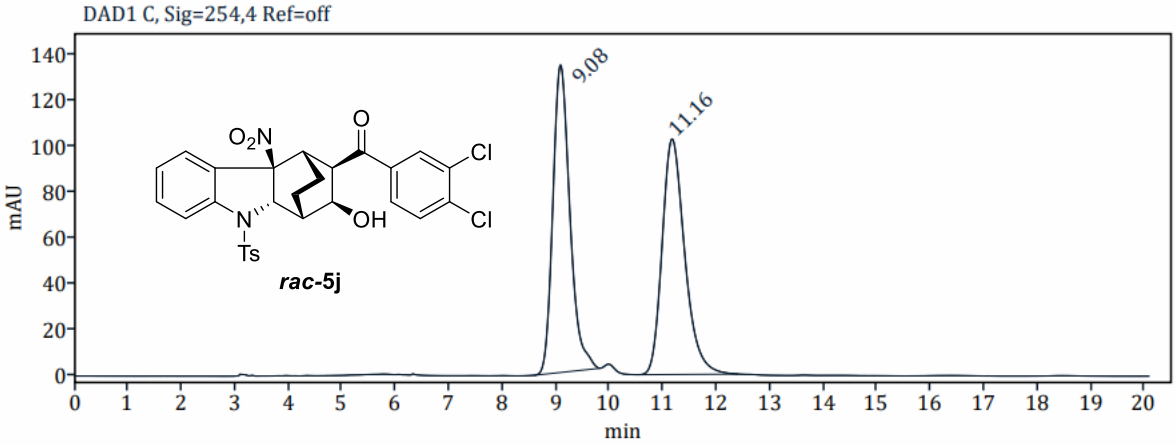


Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	9.95	7.329	0.1481	0.3005
2	11.82	2431.764	77.8186	99.6995

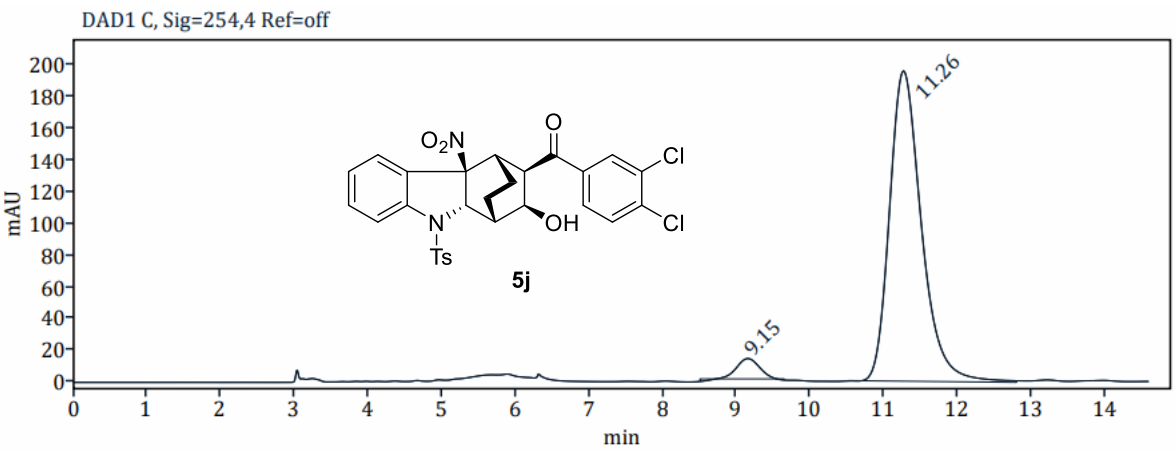

7.869 7.857 7.742 7.724 7.710 7.500 7.491 7.486 7.477 7.473 7.425 7.411 7.252 7.238 7.169 7.156 7.144 5.341 5.334 4.625 4.617 4.610 3.126 3.102 3.024 3.009 2.899 2.873 2.867 2.862 2.849 2.617 2.609 2.368 2.210 2.204 2.199 2.190 2.180 2.176 2.168 2.165 2.159 2.155 2.149 2.138 2.135 1.485 1.478 1.457 1.455 1.444 1.425 1.390 1.386 1.382 1.374 1.370 1.365 1.353 1.333 1.331
O2N
O
Cl
Cl
OH
N
Ts
5j
1H NMR (600 MHz, CDCl3)
1.03 1.08 2.09 3.01 0.98 2.04 1.00 1.00 1.05 1.04 1.03 1.04 1.01 3.18 2.08 1.05 1.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton


196.359
145.211 142.913 137.886 136.689 133.635 132.601 132.457 130.916 129.901 129.738 127.631 126.865 126.597 125.266 124.893 116.151
97.078
77.211 77.000 76.789
65.865 63.921
44.379
37.945 36.413
21.610
15.712 15.118
O2N
O
Cl
Cl
OH
N
Ts
5j
13C NMR (151 MHz, CDCl3)
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13



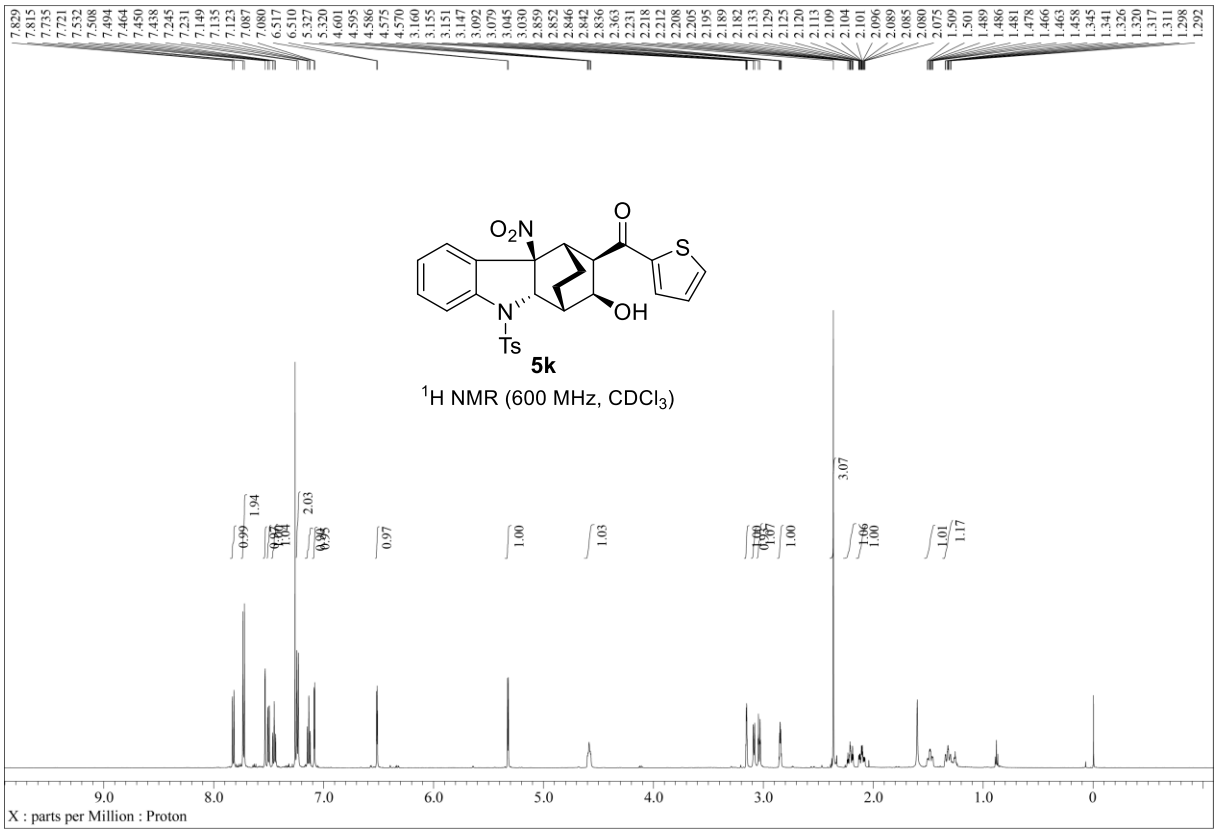
Peak Analysis Report

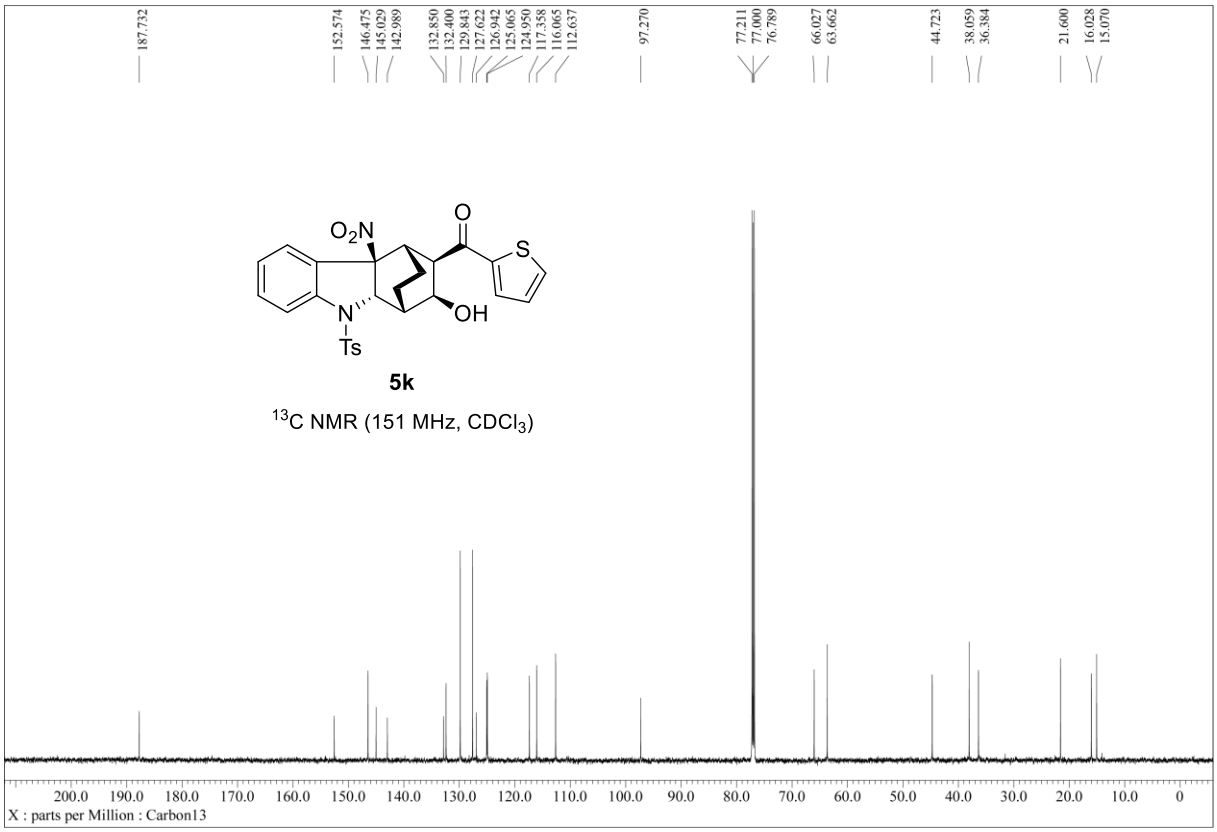
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	9.08	2983.310	134.4505	49.6491
2	11.16	3025.481	102.9560	50.3509

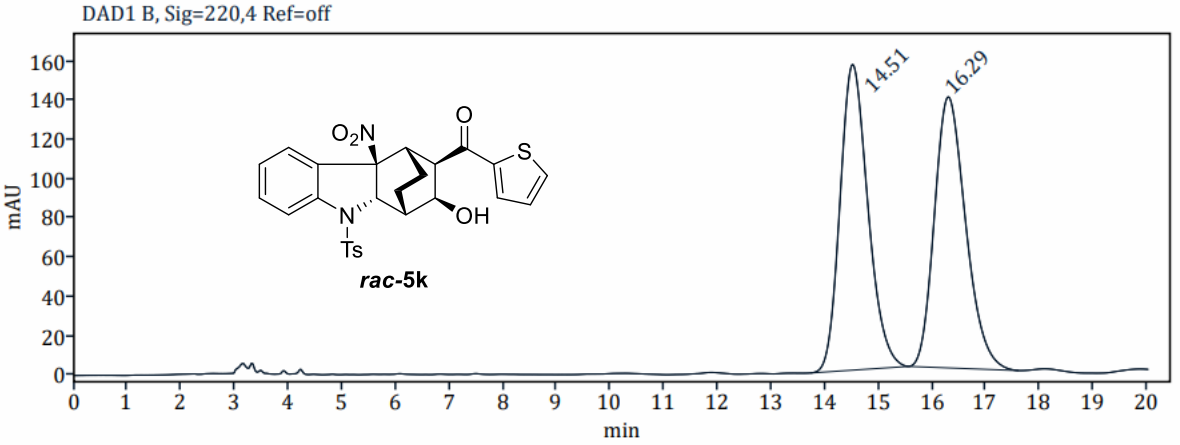


Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	9.15	278.061	12.8069	4.5220
2	11.26	5870.960	195.1780	95.4780

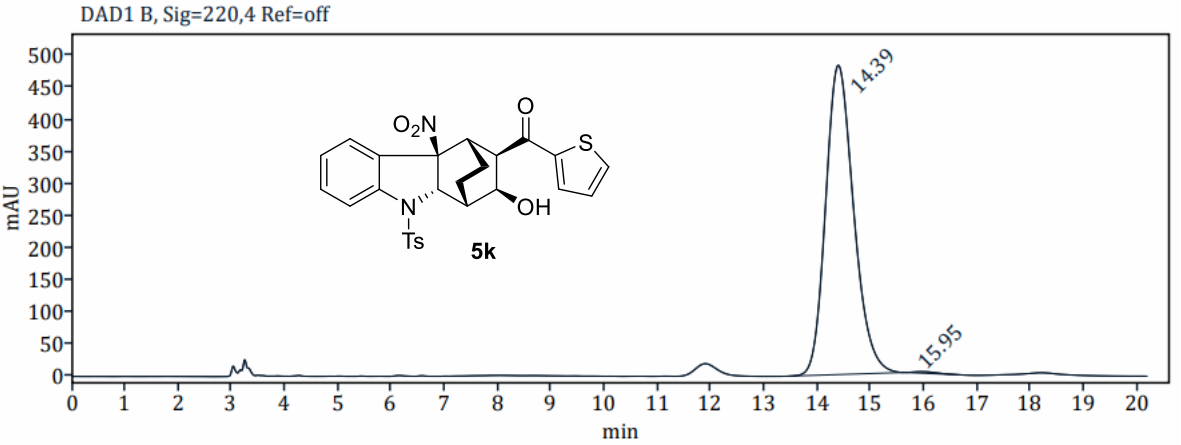

O2N
O
S
N
Ts
OH
5k
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


O2N
O
S
N
Ts
OH
5k
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



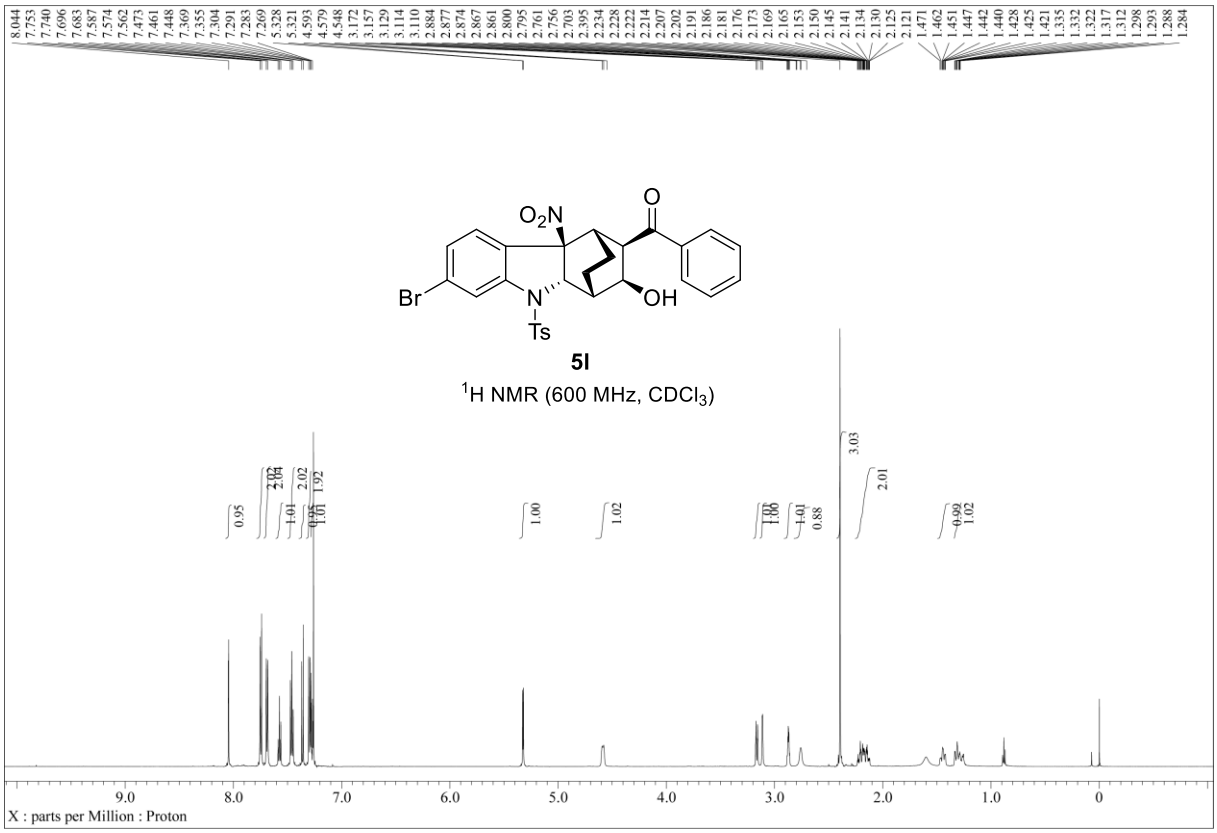
Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	14.51	5636.539	155.7686	50.1198
2	16.29	5609.599	138.1238	49.8802



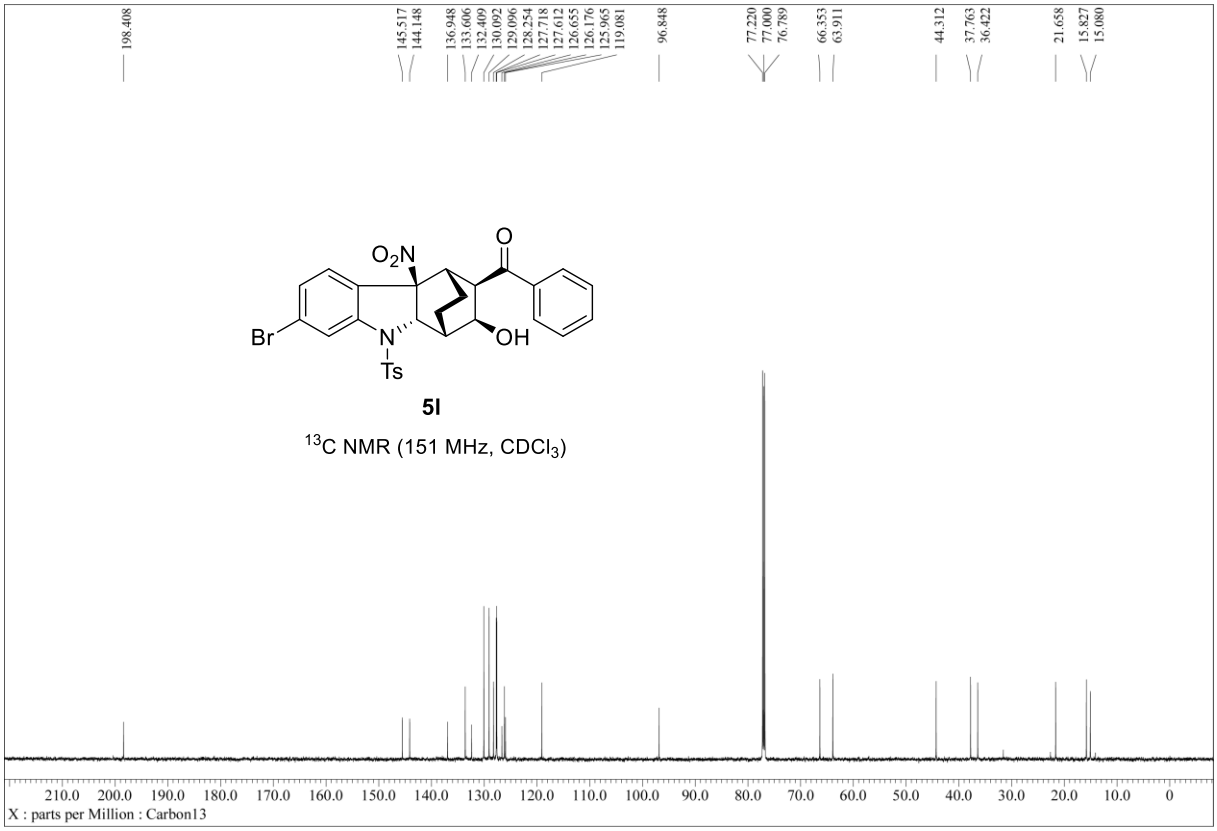
Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	14.39	17684.963	482.7234	99.5603
2	15.95	78.104	2.4308	0.4397



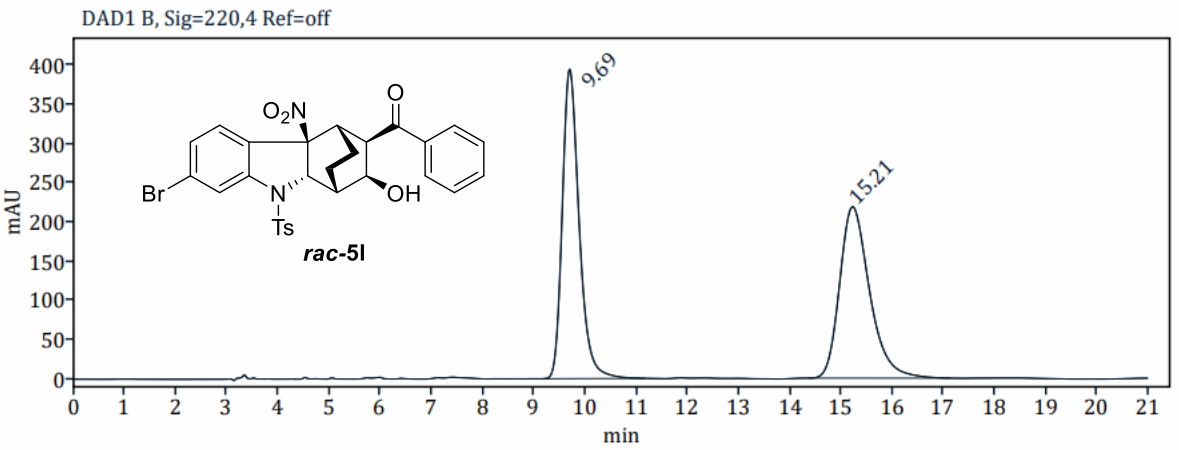
5l

^{1}H NMR (600 MHz, $CDCl_3$)



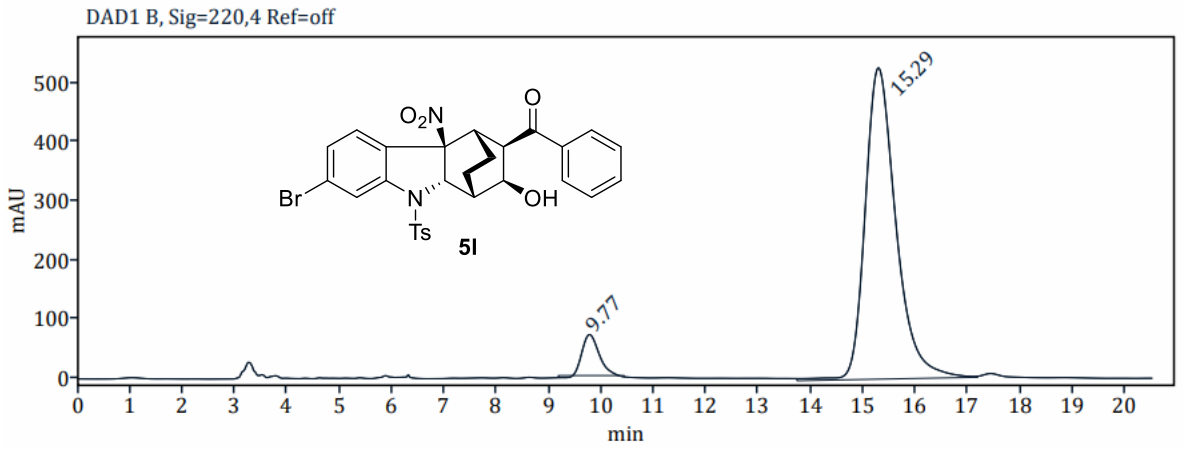
5l

^{13}C NMR (151 MHz, $CDCl_3$)



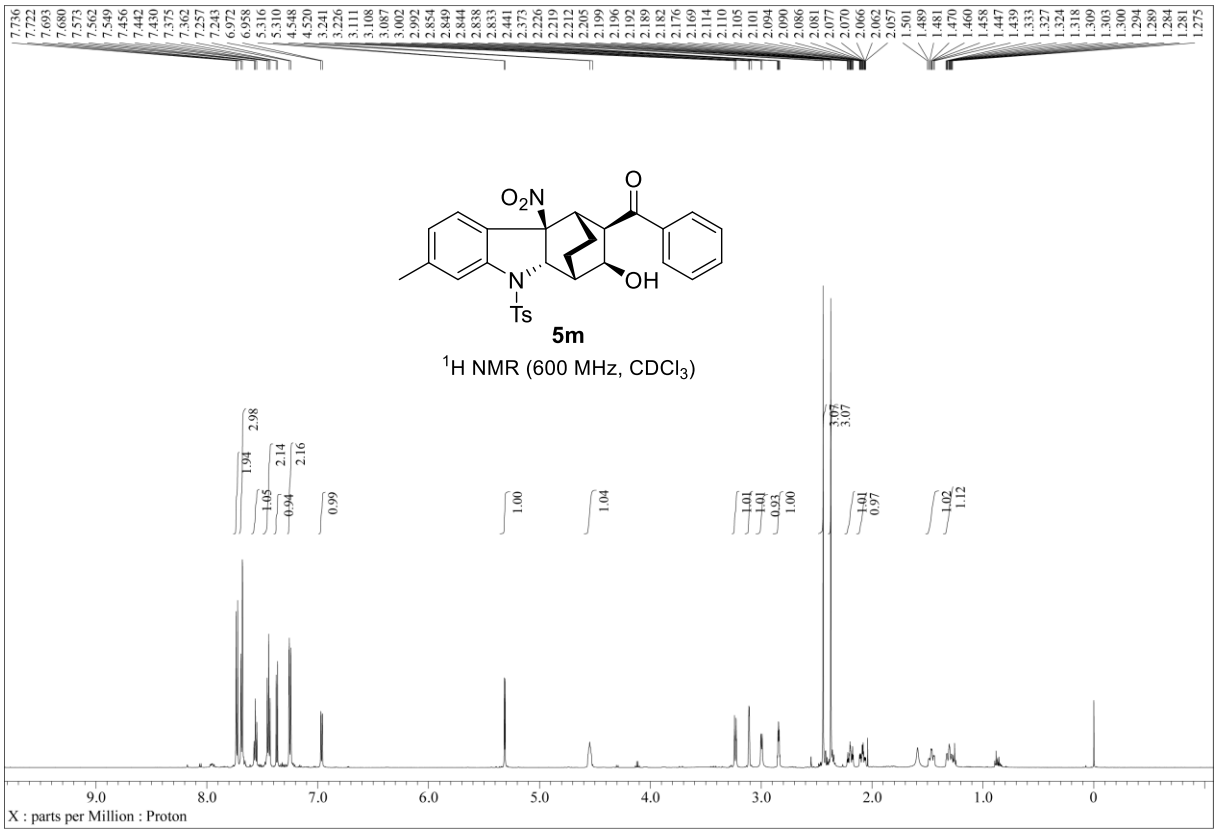
Peak Analysis Report

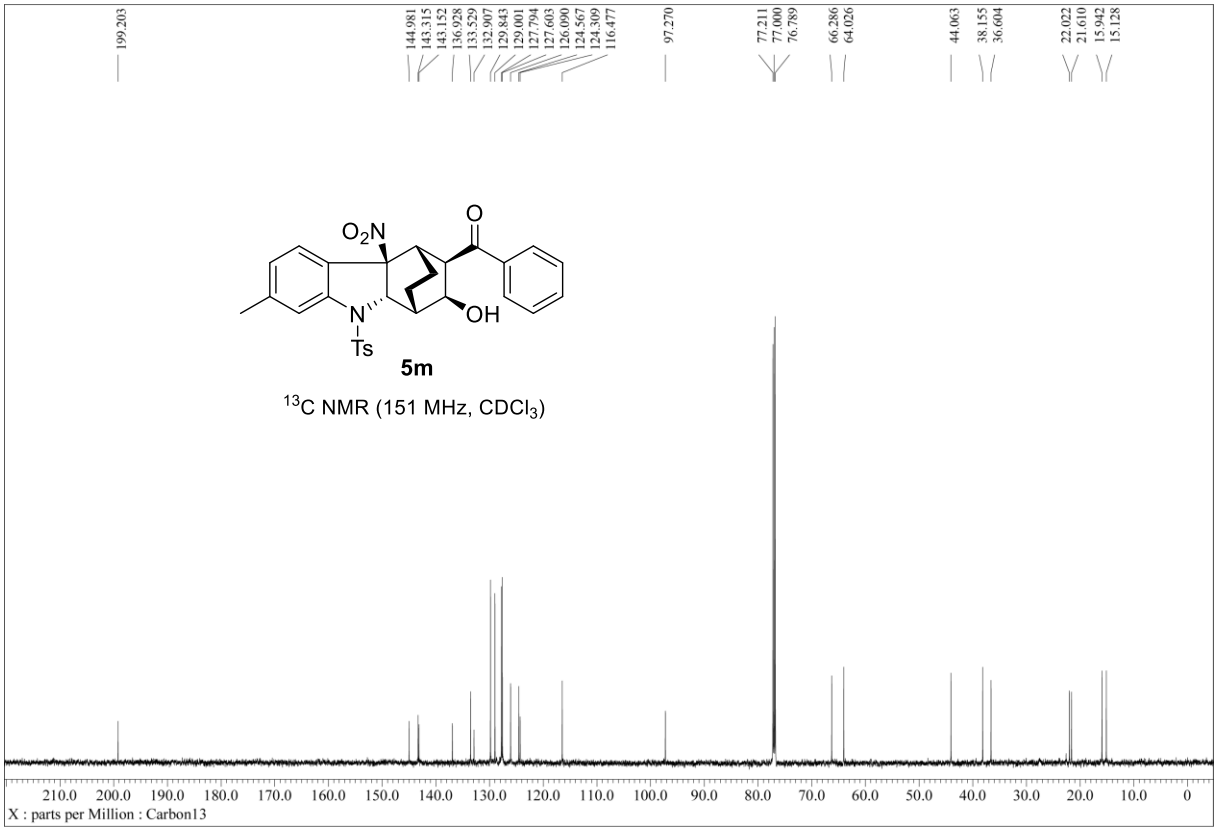
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	9.69	9022.183	394.3294	50.3623
2	15.21	8892.372	218.4385	49.6377

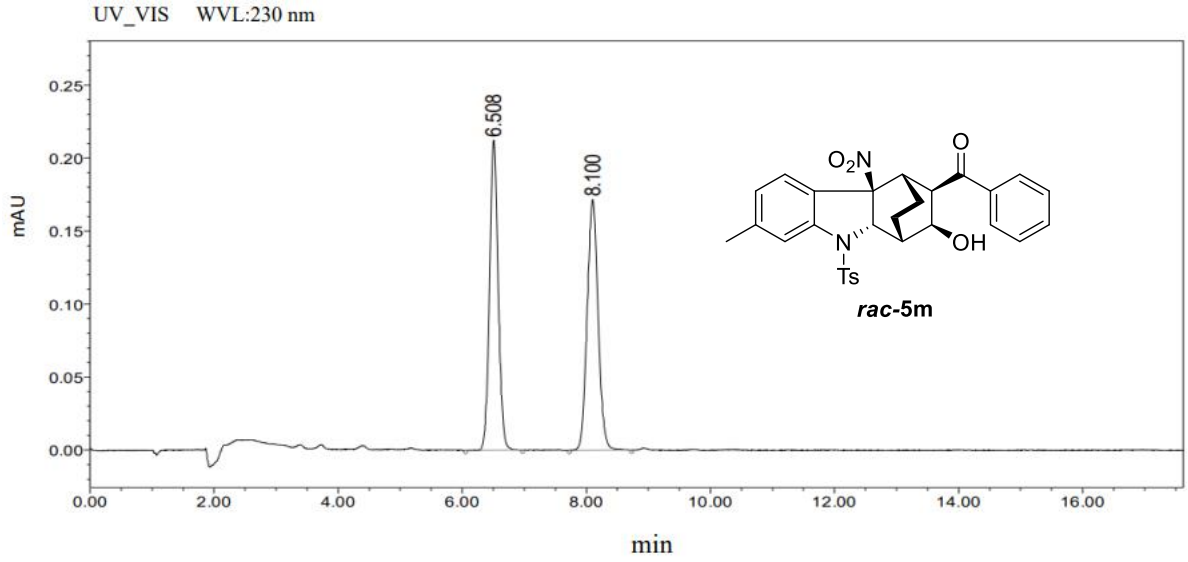


Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	9.77	1565.024	69.3534	6.7557
2	15.29	21601.080	527.6303	93.2443

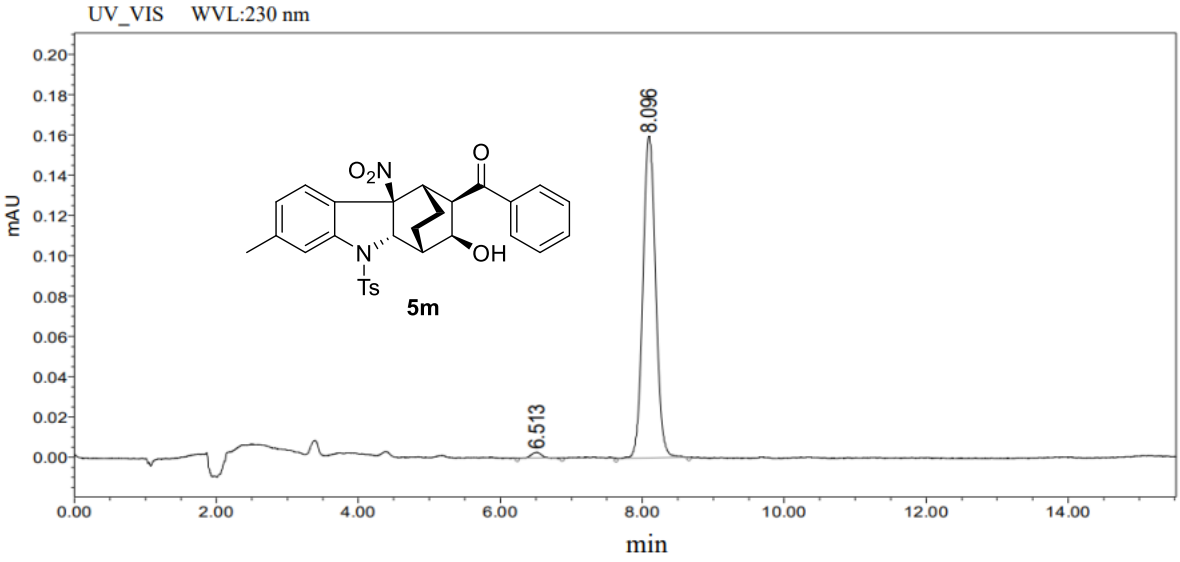

7.736 7.722 7.693 7.680 7.573 7.562 7.549 7.456 7.442 7.430 7.375 7.362 7.257 7.243 6.972 6.958 5.316 5.310 4.548 4.520 3.241 3.226 3.111 3.108 3.087 3.002 2.992 2.854 2.849 2.844 2.838 2.833 2.441 2.373 2.226 2.219 2.212 2.205 2.199 2.196 2.192 2.189 2.182 2.176 2.169 2.114 2.110 2.105 2.101 2.094 2.090 2.086 2.081 2.077 2.070 2.066 2.062 2.057 1.501 1.489 1.481 1.470 1.460 1.458 1.447 1.439 1.333 1.327 1.324 1.318 1.309 1.303 1.300 1.294 1.289 1.284 1.281 1.275
O2N
O
N
Ts
OH
5m
1H NMR (600 MHz, CDCl3)
2.98 1.94 2.14 2.16 1.05 0.94 0.99 1.00 1.04 1.01 1.01 0.93 1.00 3.07 3.07 1.01 0.97 1.02 1.12
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton


199.203 144.981 143.315 143.152 136.928 133.529 132.907 129.843 129.001 127.794 127.603 126.090 124.567 124.309 116.477 97.270 77.211 77.000 76.789 66.286 64.026 44.063 38.155 36.604 22.022 21.610 15.942 15.128
O2N
O
N
Ts
OH
5m
13C NMR (151 MHz, CDCl3)
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13



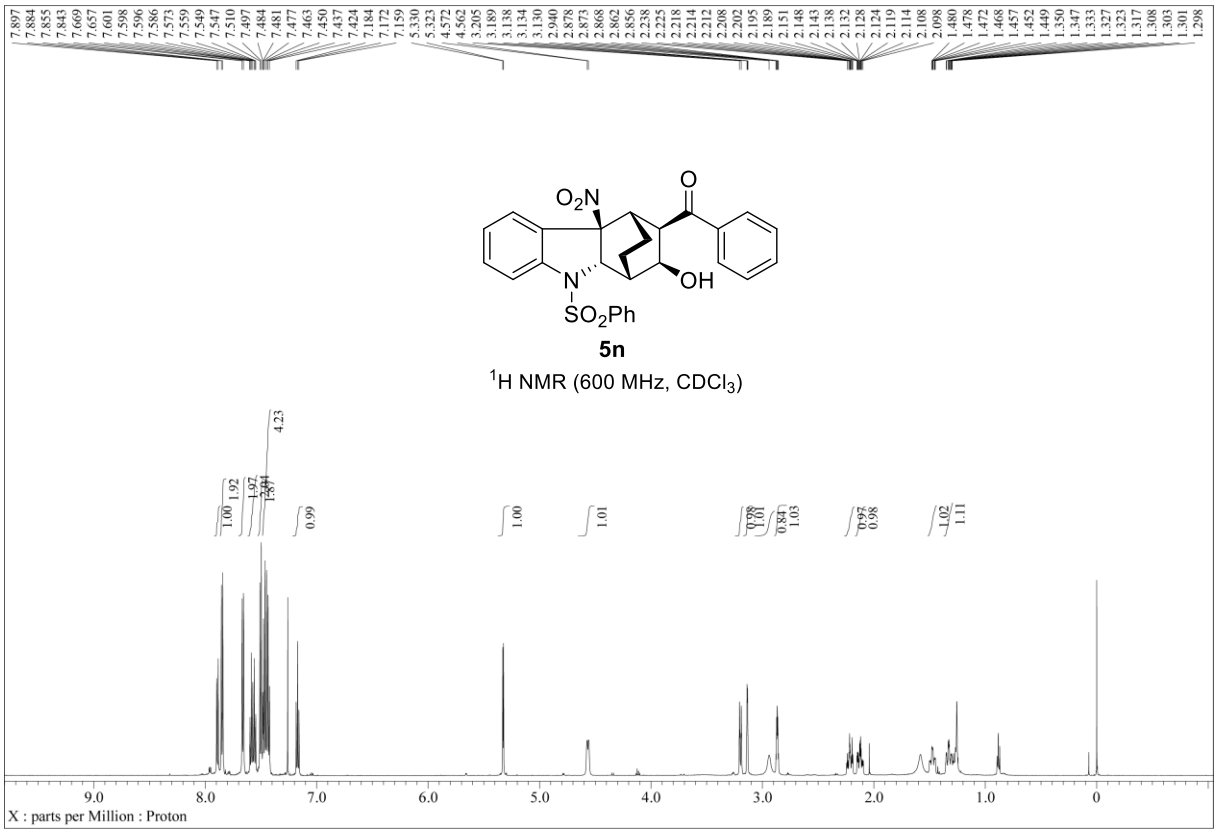
Peak Analysis Report

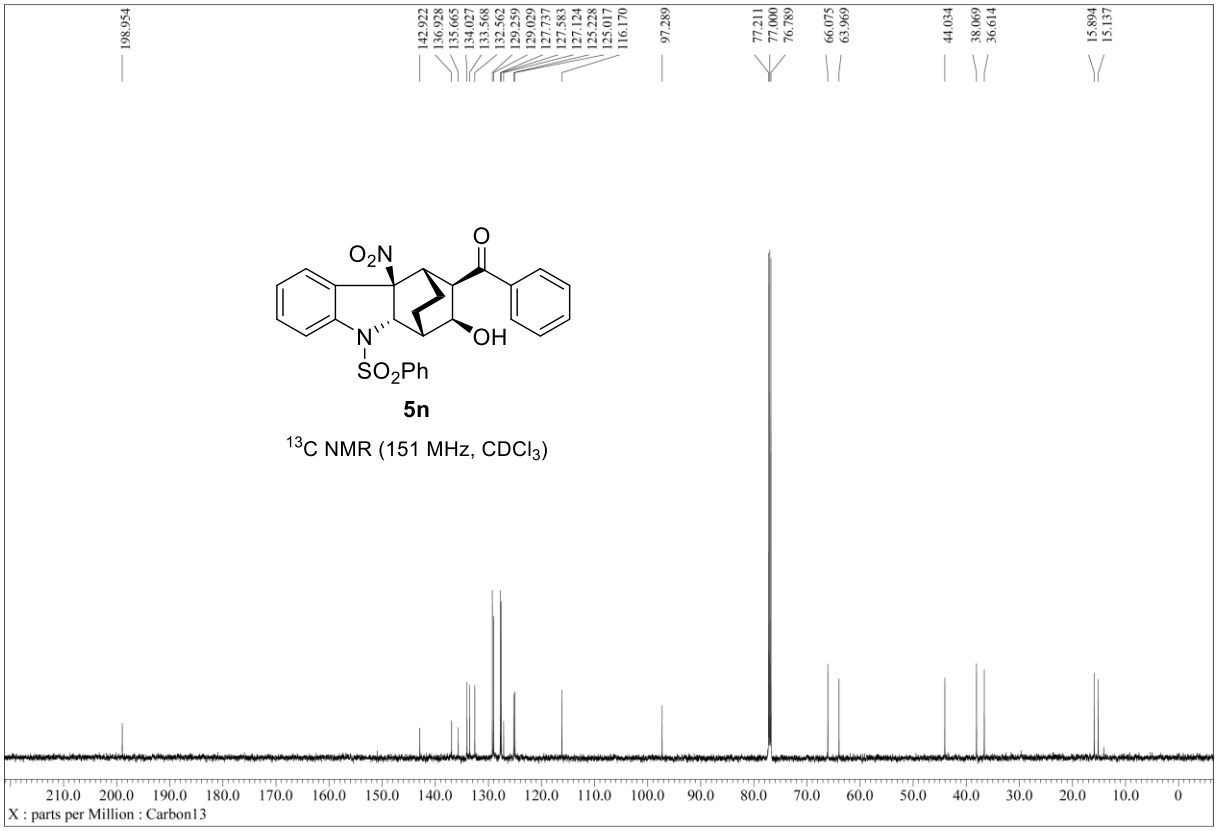
Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	6.508	2083763	212391	49.49
2	8.100	2118157	171599	50.41

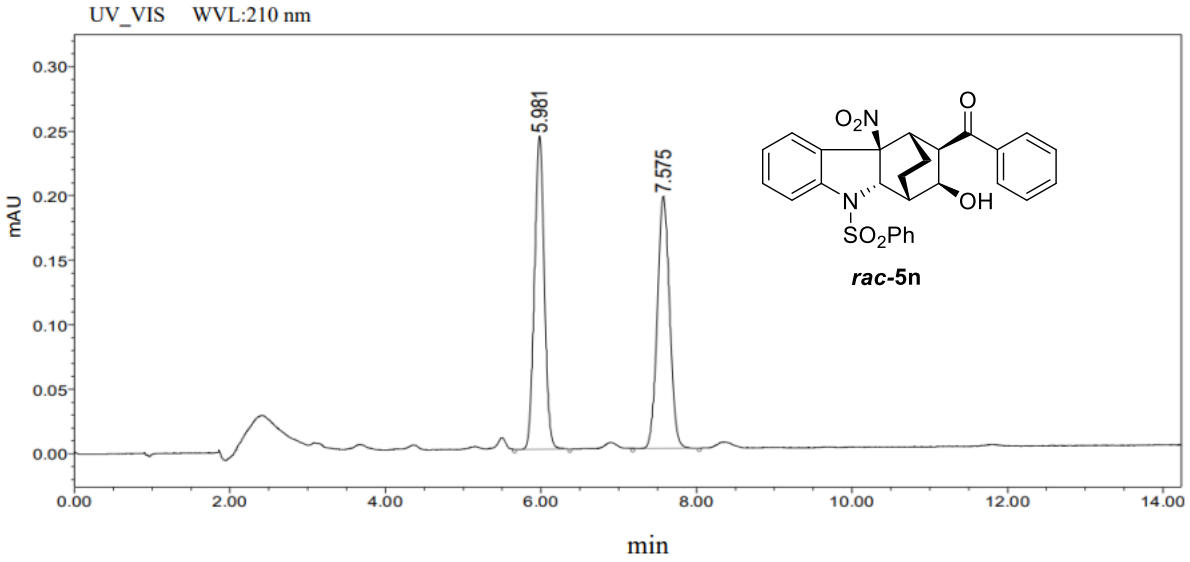


Peak Analysis Report

Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	6.513	27995	2814	1.39
2	8.096	1984273	159664	98.61

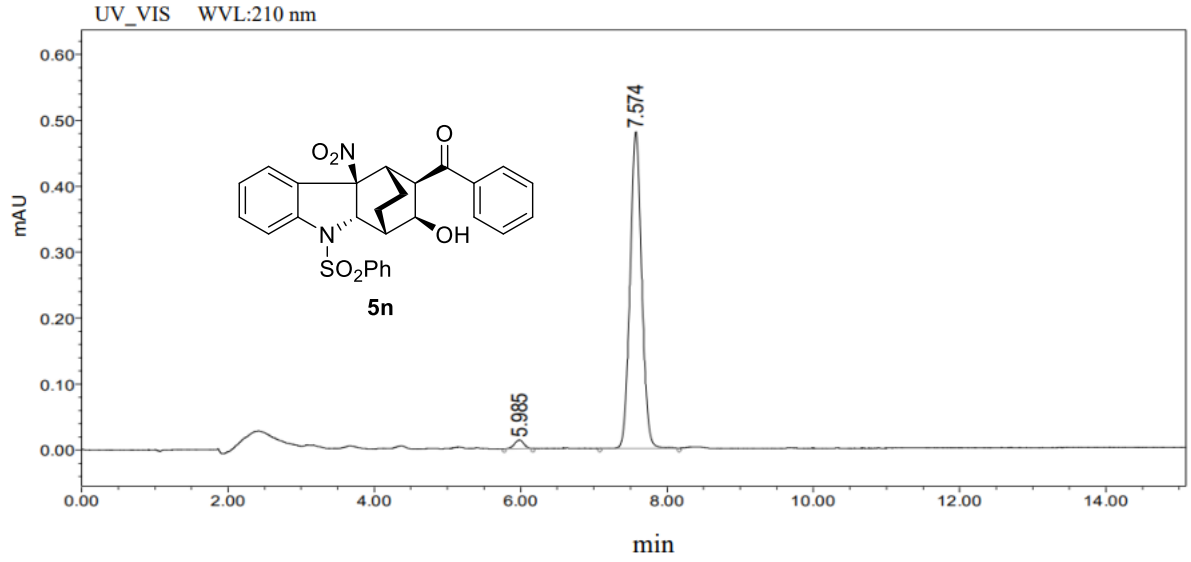

O2N
O
N
OH
SO2Ph
5n
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


O2N
O
N
OH
SO2Ph
5n
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



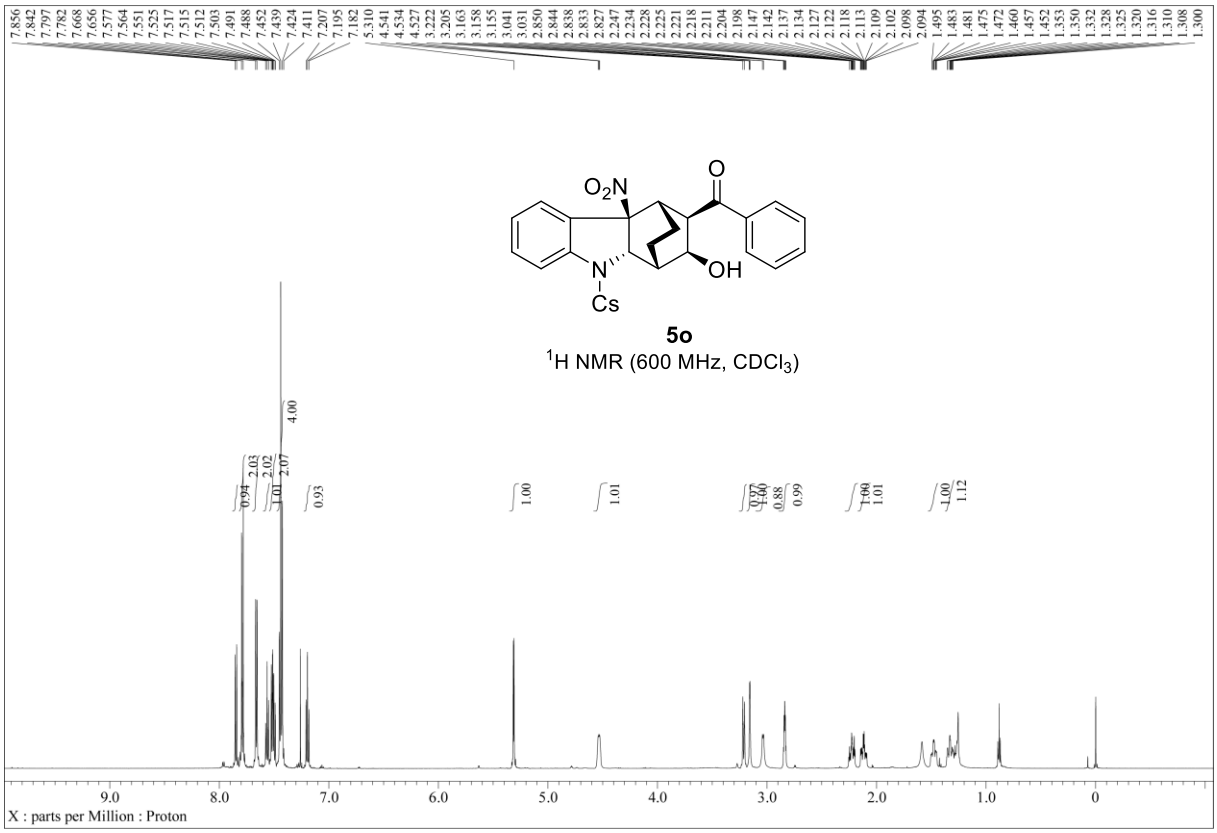
Peak Analysis Report

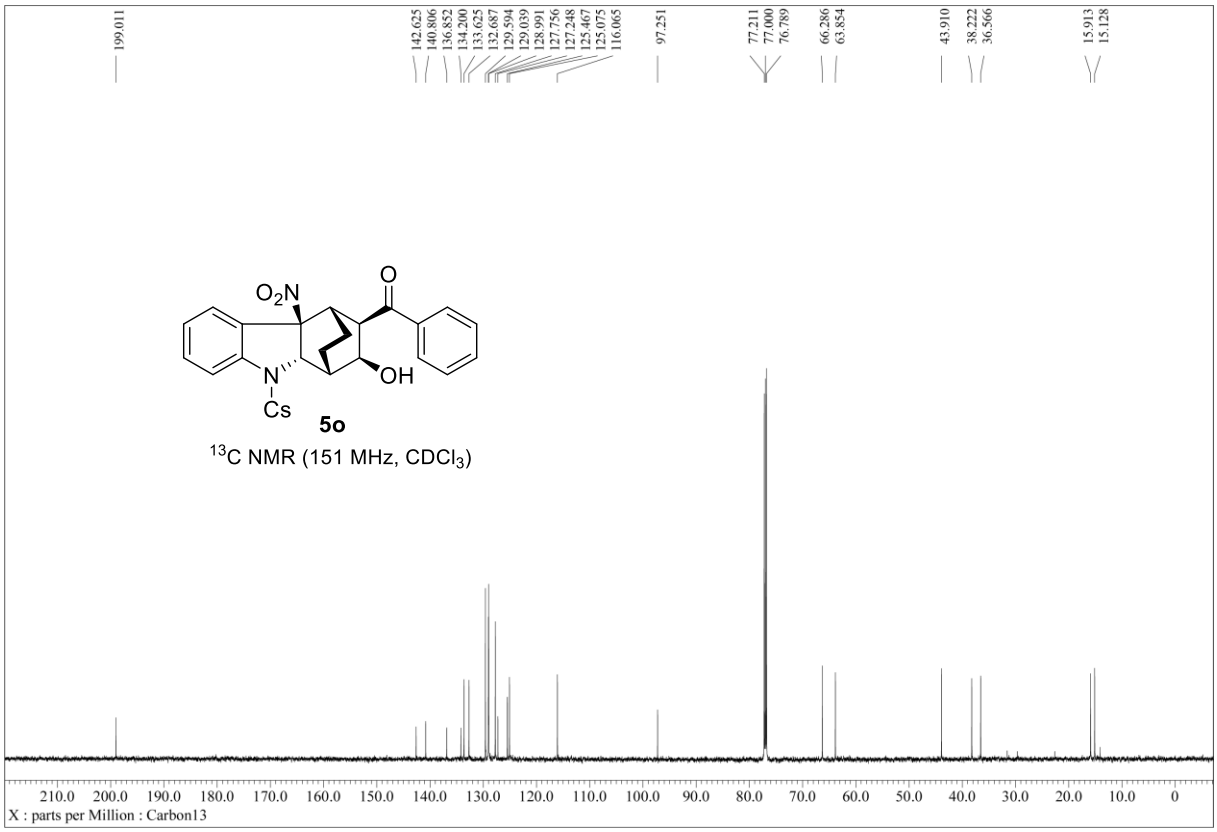
Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	5.981	2154099	242718	50.03
2	7.575	2151133	195339	49.97

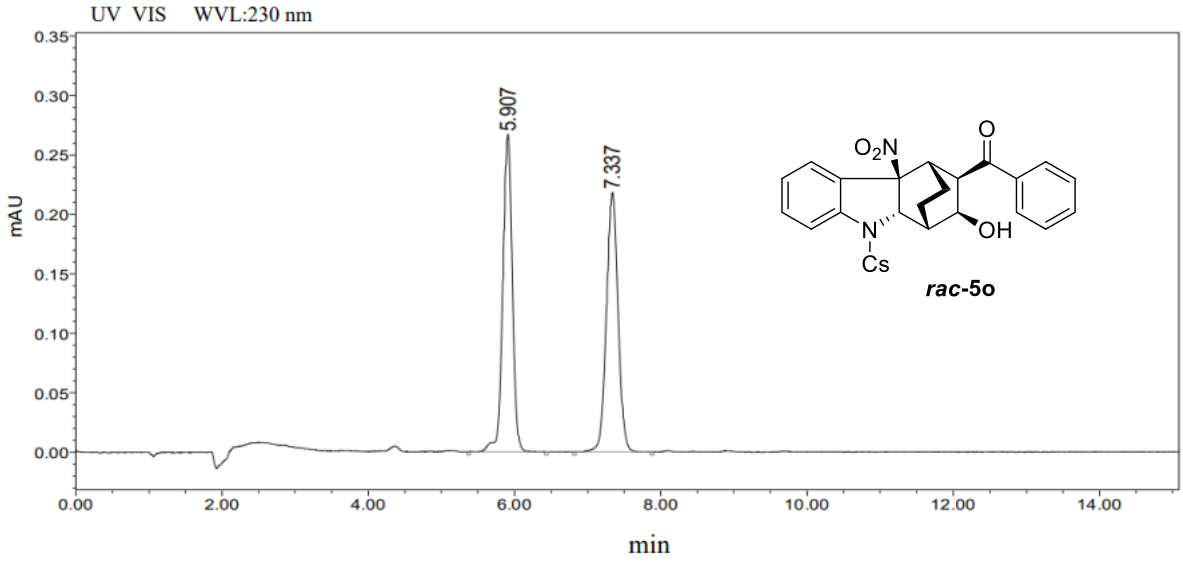


Peak Analysis Report

Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	5.985	112957	12901	2.07
2	7.574	5334519	480111	97.93

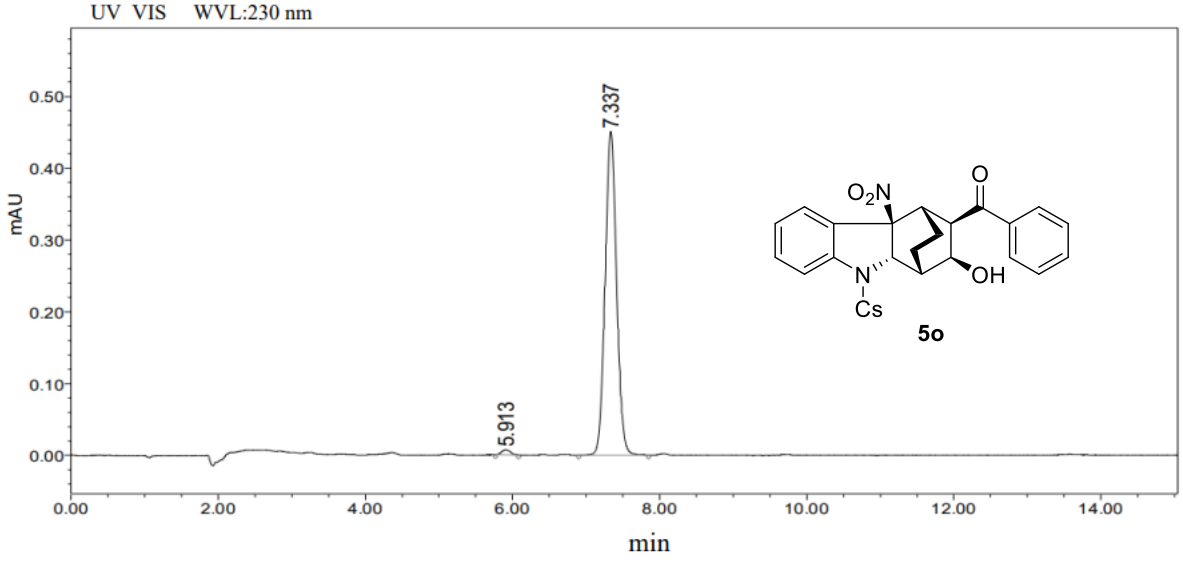

O2N
O
N
OH
Cs
5o
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton


O2N
O
N
OH
Cs
5o
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



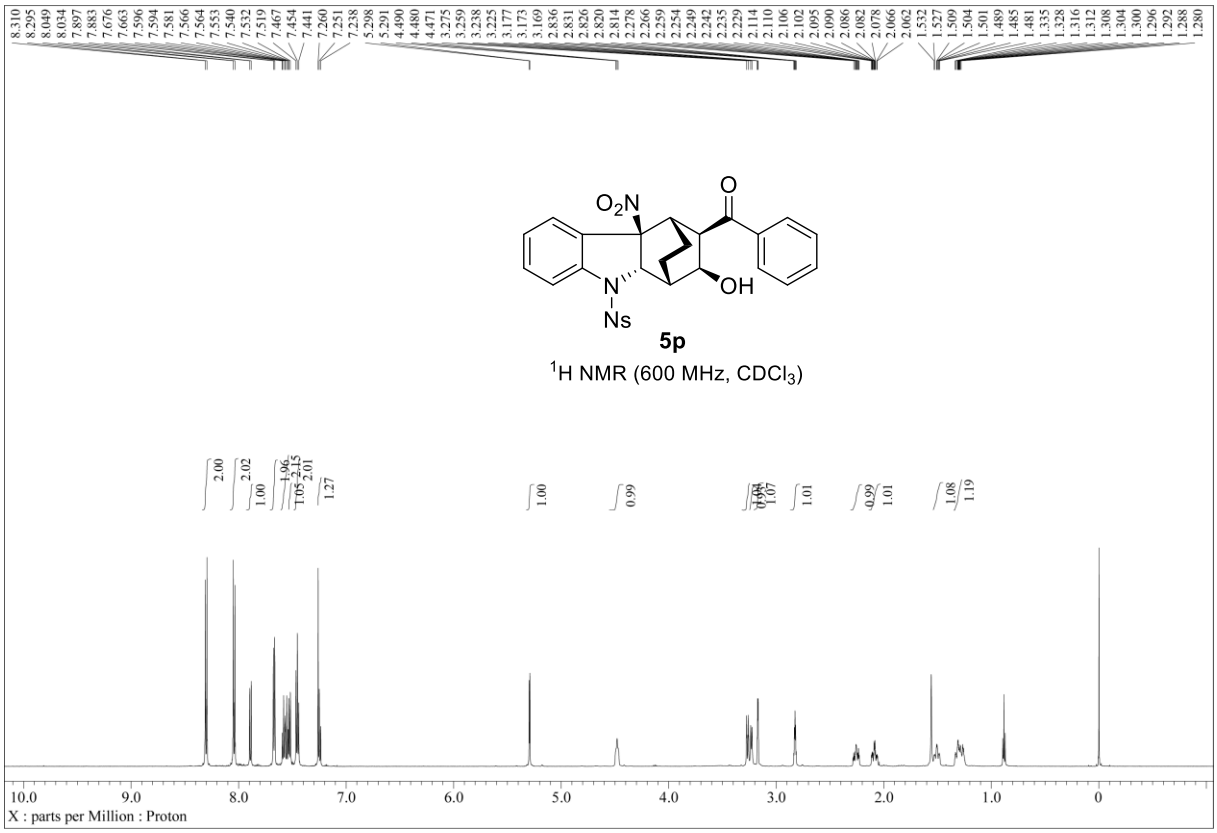
Peak Analysis Report

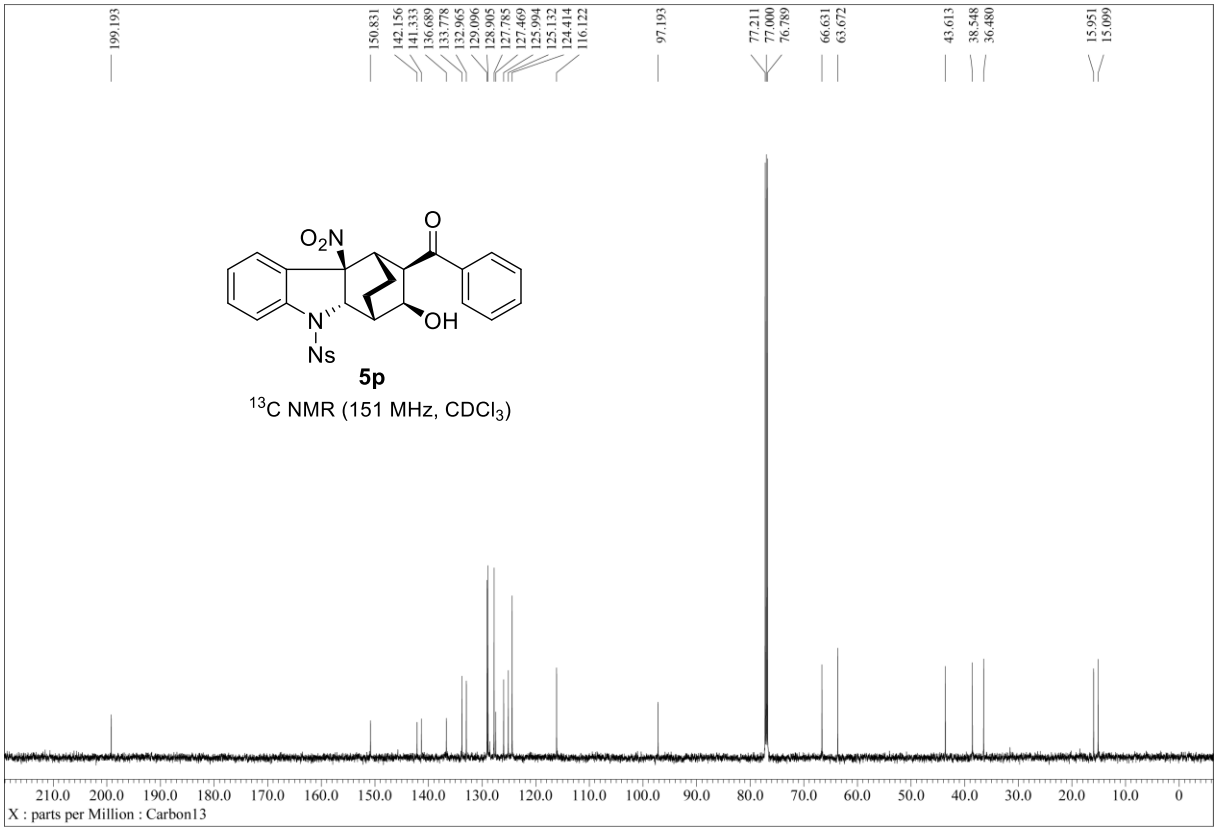
Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	5.907	2407478	266760	49.85
2	7.337	2421736	218203	50.15

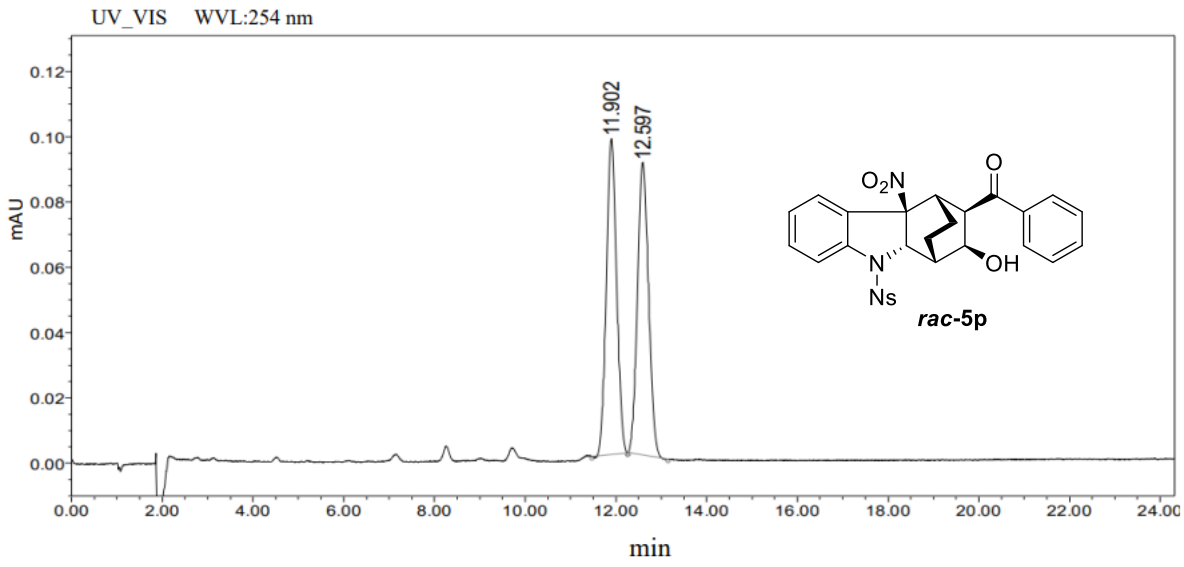


Peak Analysis Report

Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	5.913	56715	6914	1.15
2	7.337	4889894	450304	98.85

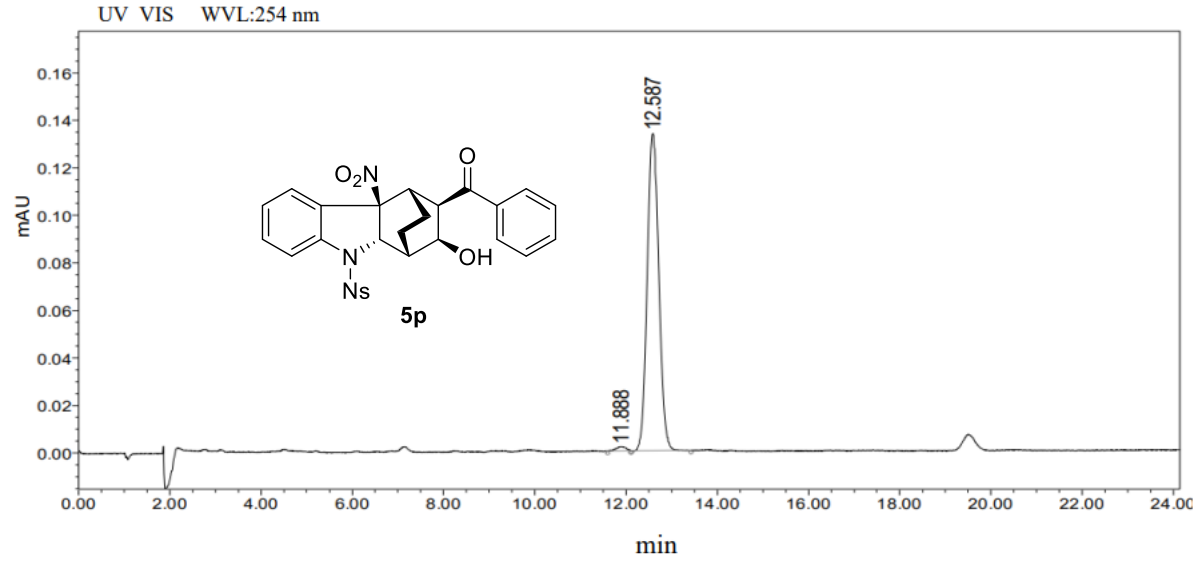

8.310 8.295 8.049 8.034 7.897 7.883 7.676 7.663 7.596 7.594 7.581 7.566 7.564 7.553 7.540 7.532 7.519 7.467 7.454 7.441 7.260 7.251 7.238 5.298 5.291 4.490 4.480 4.471 3.275 3.259 3.238 3.225 3.177 3.173 3.169 2.836 2.831 2.826 2.820 2.814 2.278 2.266 2.259 2.254 2.249 2.242 2.235 2.229 2.114 2.110 2.106 2.102 2.095 2.090 2.086 2.082 2.078 2.066 2.062 1.532 1.527 1.509 1.504 1.501 1.489 1.485 1.481 1.335 1.328 1.316 1.312 1.308 1.304 1.300 1.296 1.292 1.288 1.280
O2N
O
OH
N
Ns
5p
1H NMR (600 MHz, CDCl3)
2.00 2.02 1.00 1.96 2.15 1.05 2.01 1.27 1.00 0.99 1.07 1.01 0.99 1.01 1.08 1.19
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton


199.193 150.831 142.156 141.333 136.689 133.778 132.965 129.096 128.905 127.785 127.469 125.994 125.132 124.414 116.122 97.193 77.211 77.000 76.789 66.631 63.672 43.613 38.548 36.480 15.951 15.099
O2N
O
OH
N
Ns
5p
13C NMR (151 MHz, CDCl3)
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13



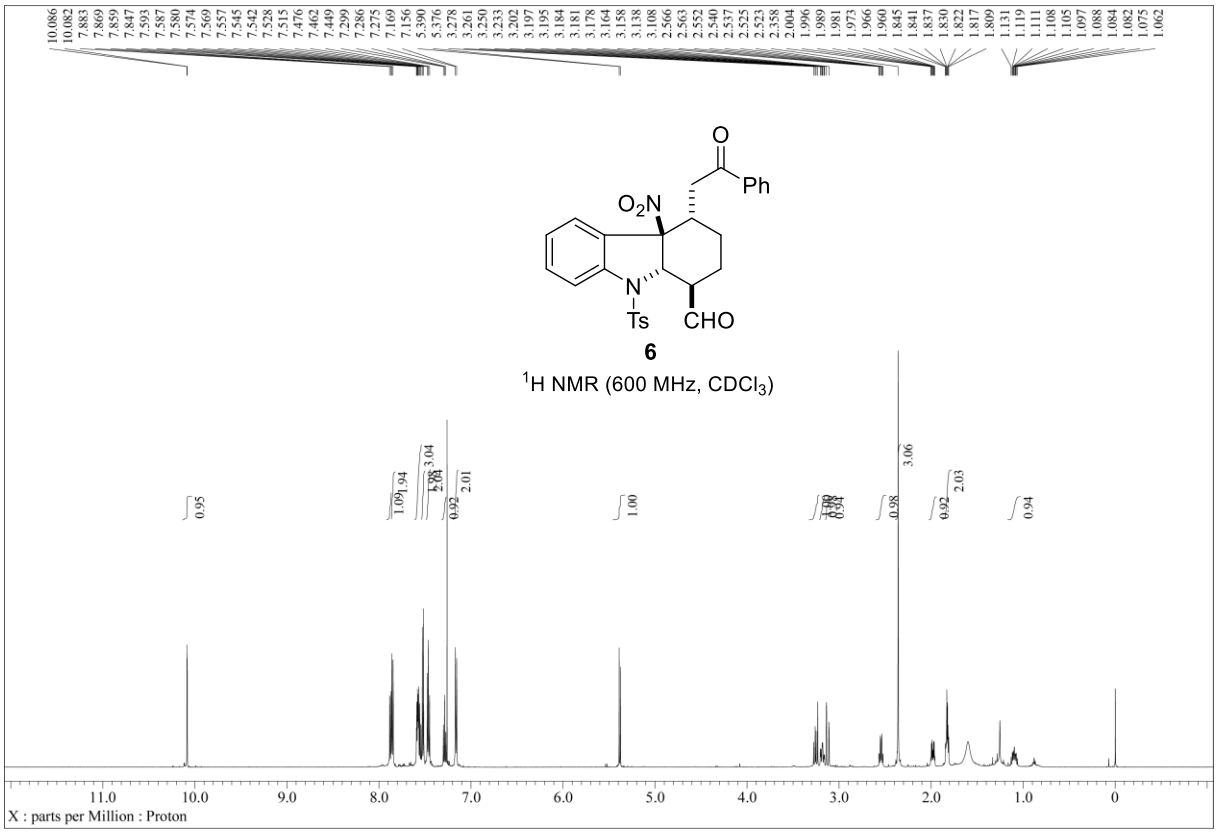
Peak Analysis Report

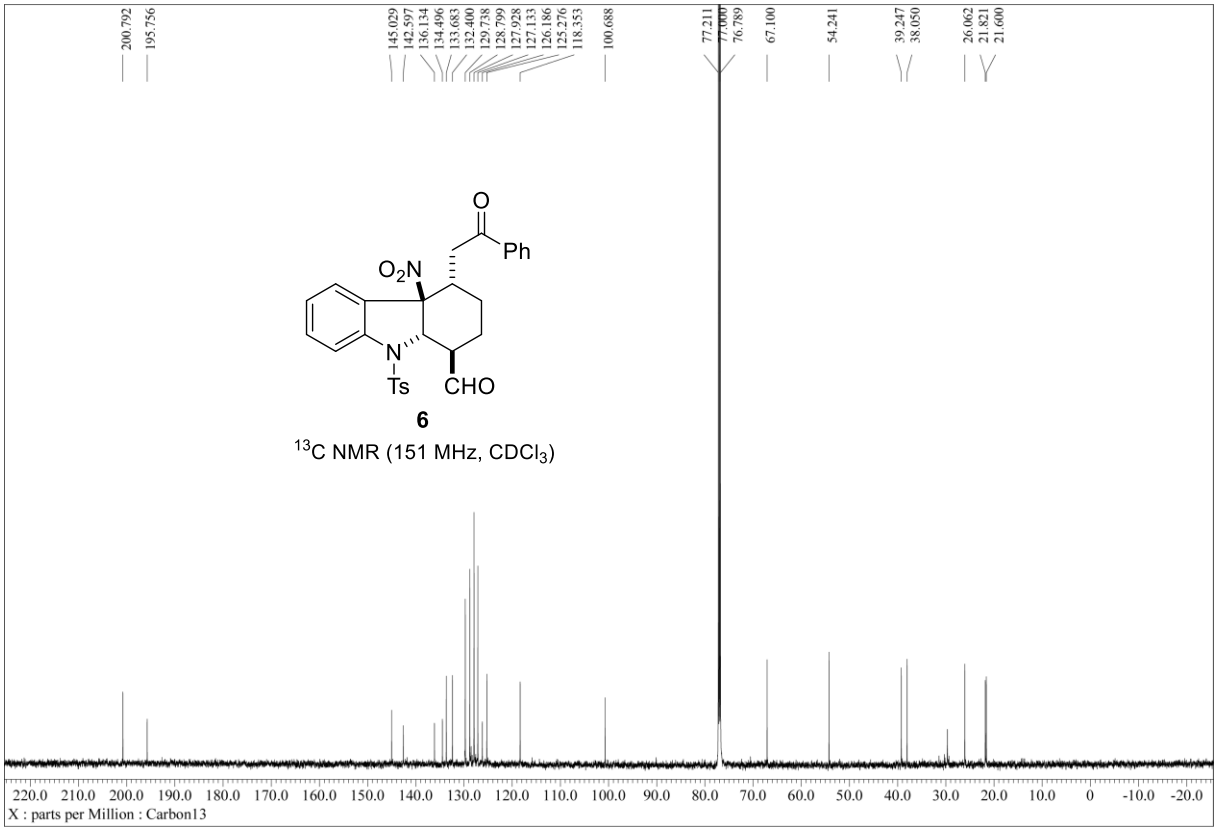
Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	11.902	1529278	96644	49.94
2	12.597	1533014	89542	50.06

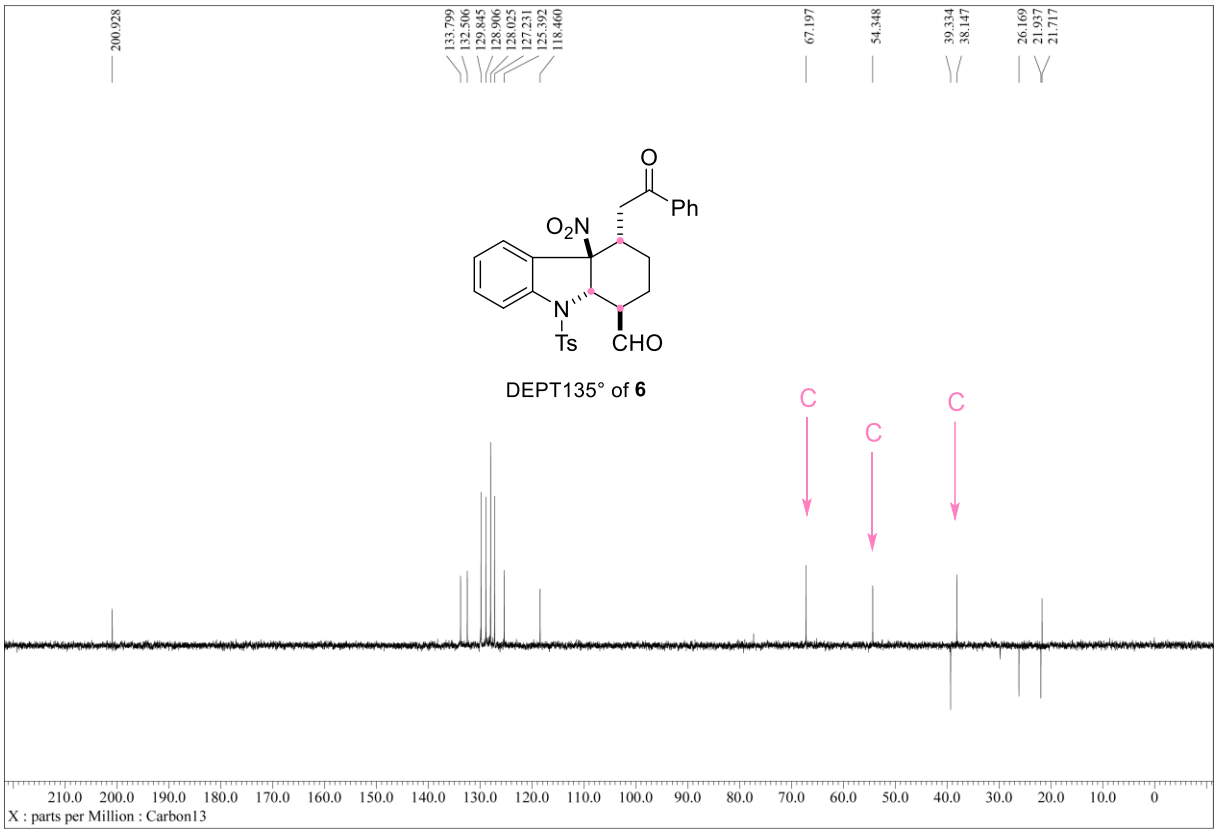


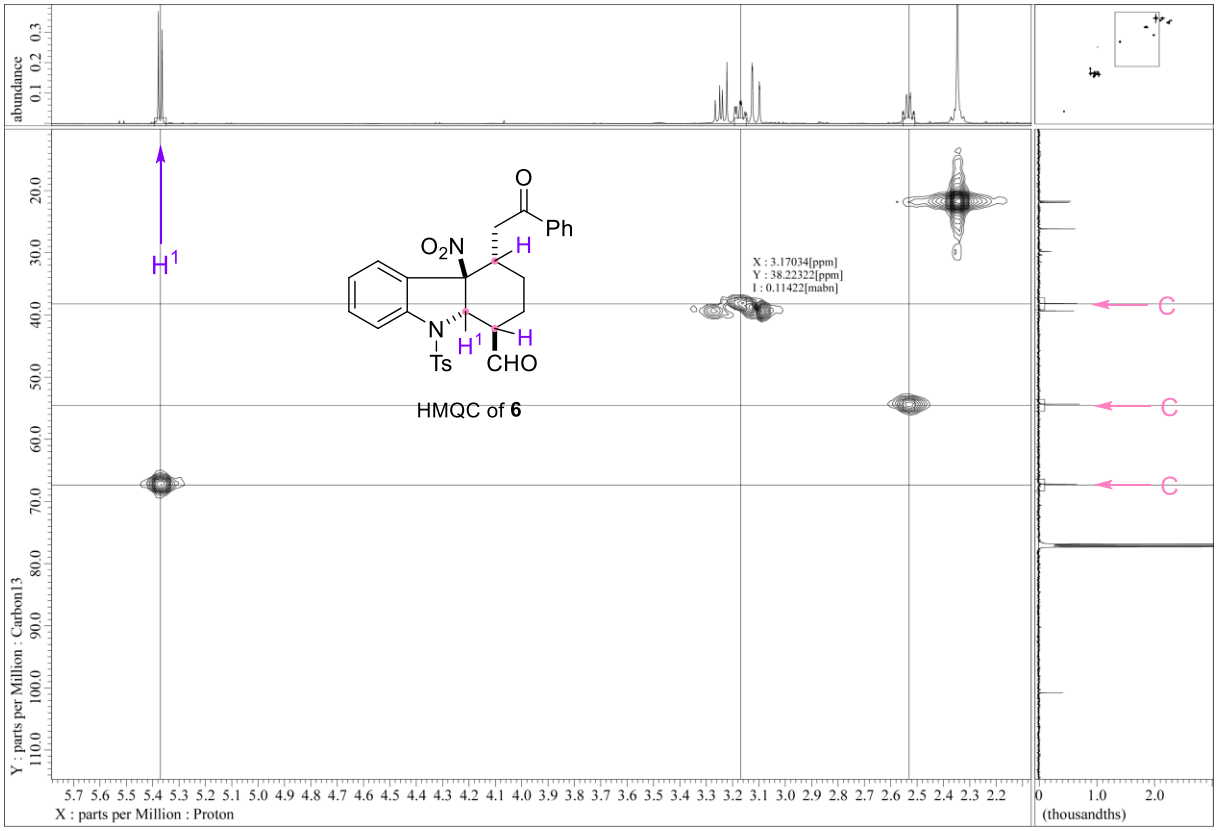
Peak Analysis Report

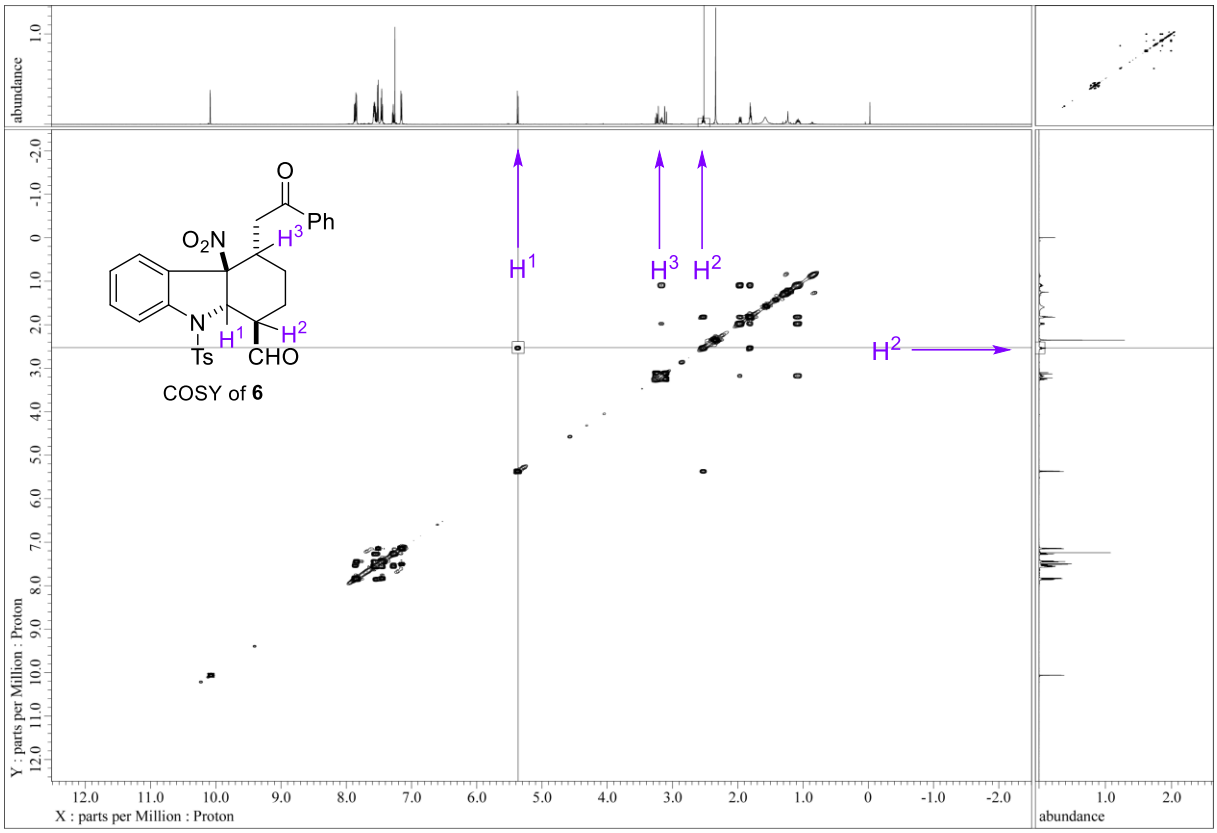
Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	11.888	26488	1813	1.11
2	12.587	2352535	133567	98.89

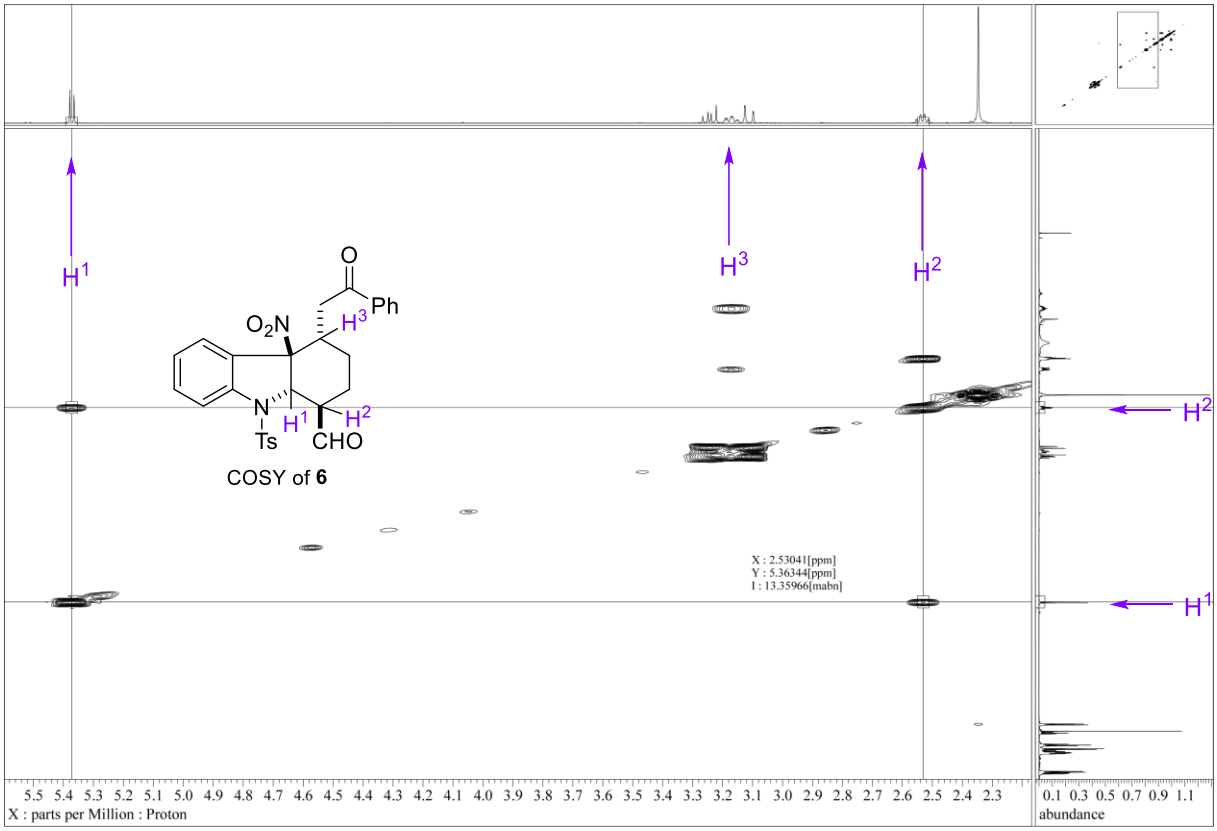

O
Ph
O2N
N
Ts
CHO
6
1H NMR (600 MHz, CDCl3)
X : parts per Million : Proton

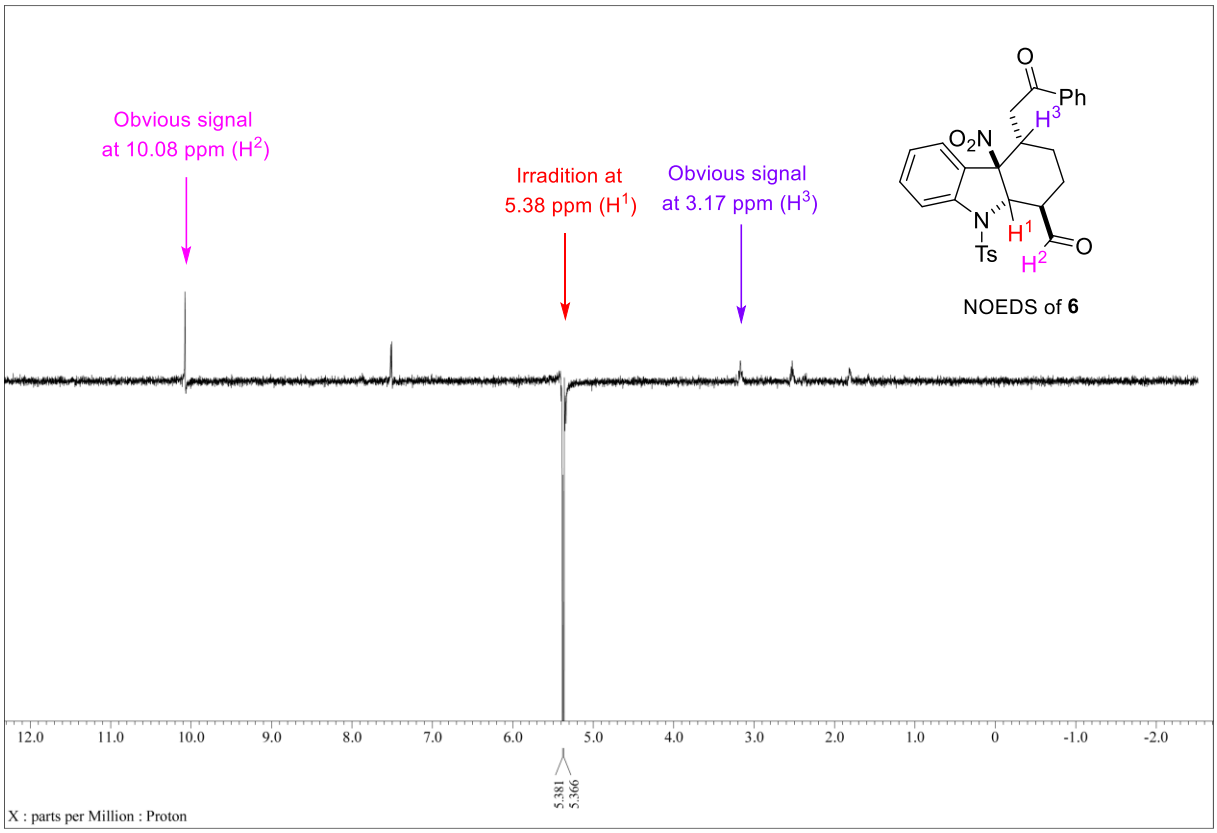

O
Ph
O2N
N
Ts
CHO
6
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13

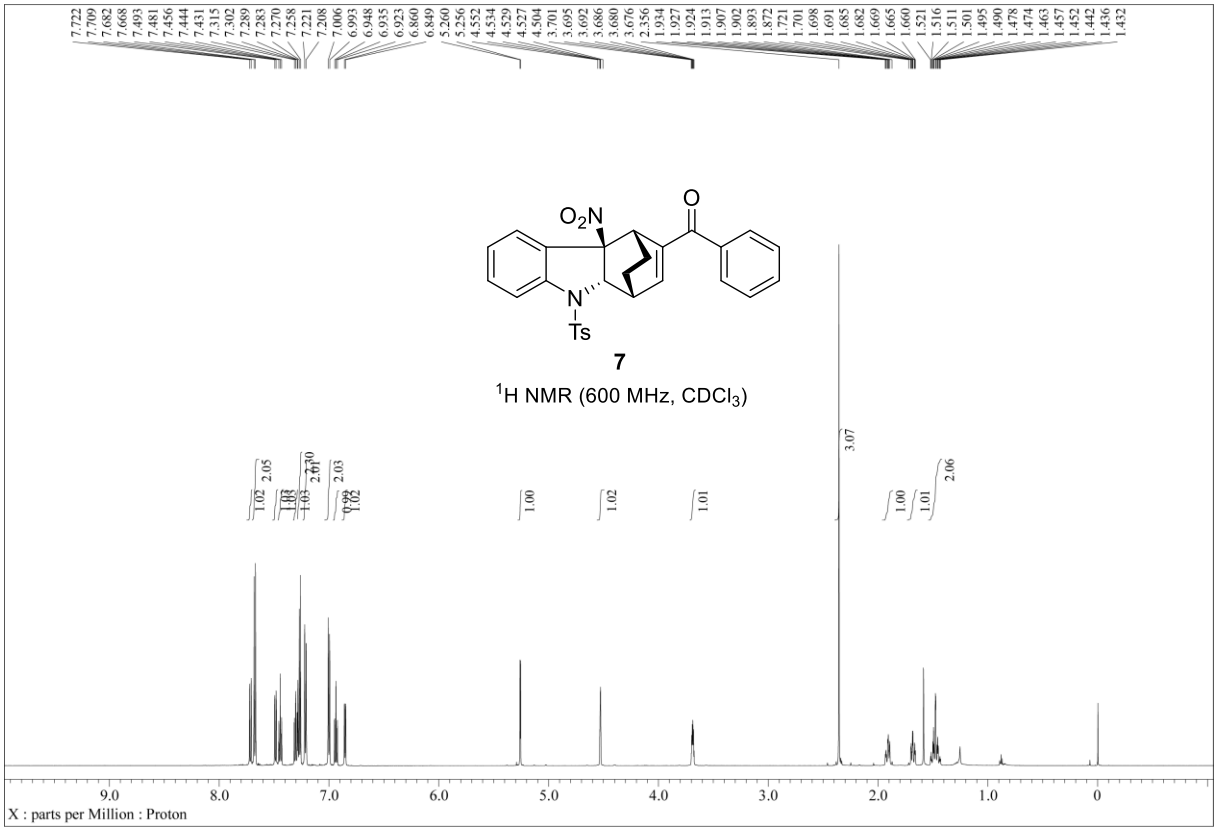

200.928
133.799
132.506
129.845
128.906
128.025
127.231
125.392
118.460
67.197
54.348
39.334
38.147
26.169
21.937
21.717
O
Ph
O2N
N
Ts
CHO
DEPT135° of 6
C
C
C
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13

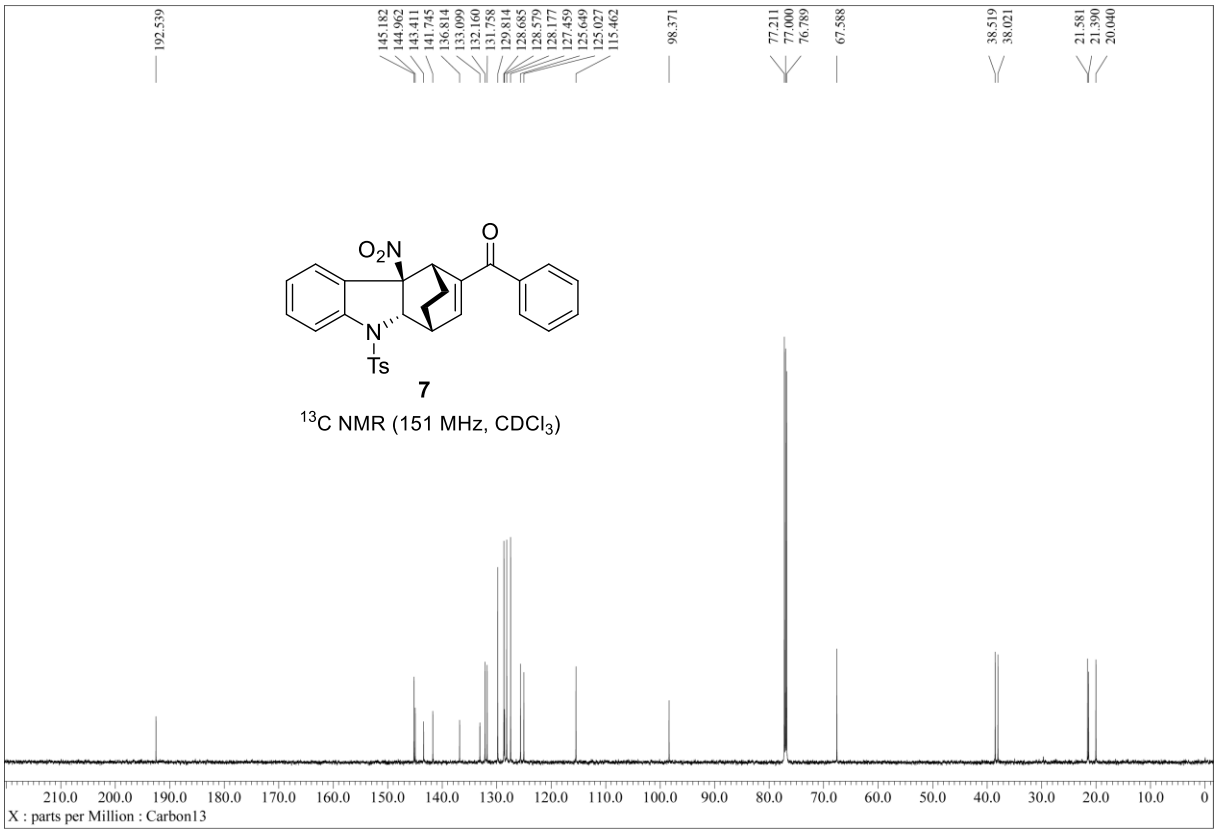

abundance
0.1 0.2 0.3
H1
O
Ph
O2N
H
N
H1
H
Ts
CHO
HMQC of 6
X : 3.17034[ppm]
Y : 38.22322[ppm]
I : 0.11422[mabn]
C
C
C
20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0
Y : parts per Million : Carbon13
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2
X : parts per Million : Proton
0 1.0 2.0
(thousandths)

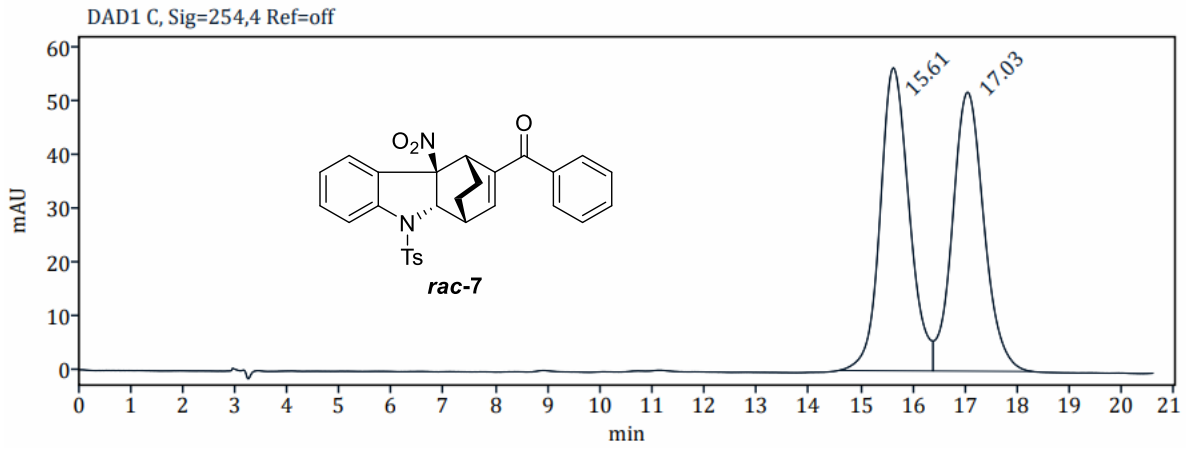

abundance
O
Ph
O2N
H3
N
H1
H2
Ts
CHO
COSY of 6
H1
H3
H2
H2
Y : parts per Million : Proton
X : parts per Million : Proton
abundance


H1
O
Ph
O2N
H3
N
H1
H2
Ts
CHO
COSY of 6
H3
H2
X : 2.53041[ppm]
Y : 5.36344[ppm]
I : 13.35966[mabn]
H2
H1
X : parts per Million : Proton
abundance


Obvious signal
at 10.08 ppm (H2)
Irradition at
5.38 ppm (H1)
Obvious signal
at 3.17 ppm (H3)
O
Ph
H3
O2N
N
Ts
H1
O
H2
NOEDS of 6
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
5.381
5.366
X : parts per Million : Proton

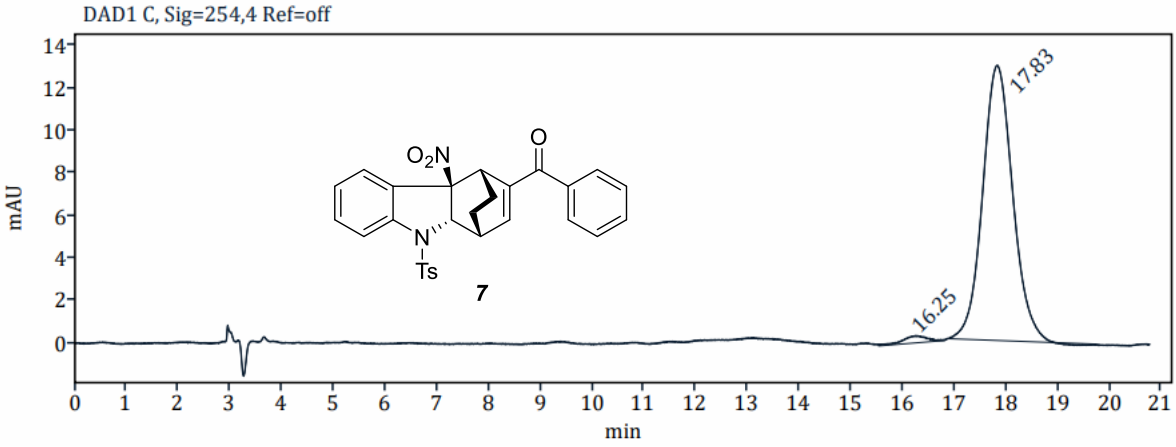

O2N
O
N
Ts
7
1H NMR (600 MHz, CDCl3)
3.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton





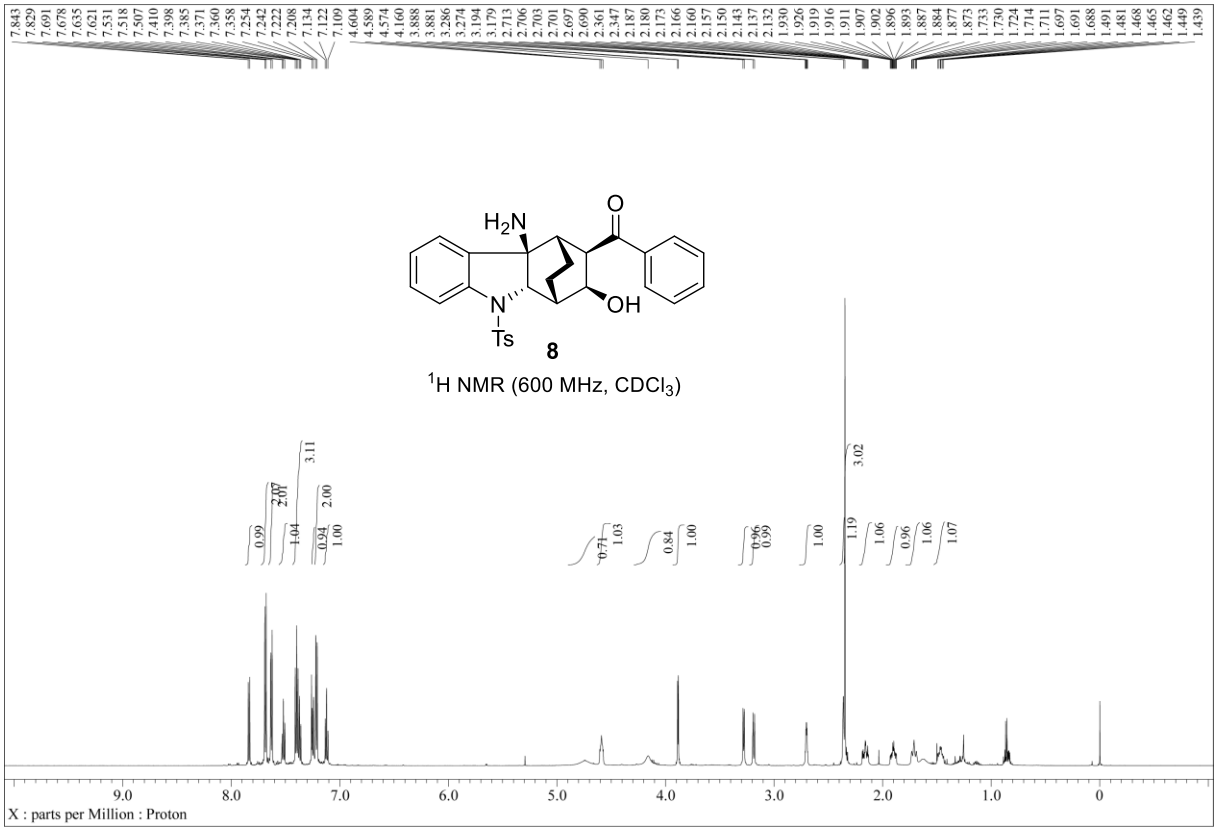
Peak Analysis Report

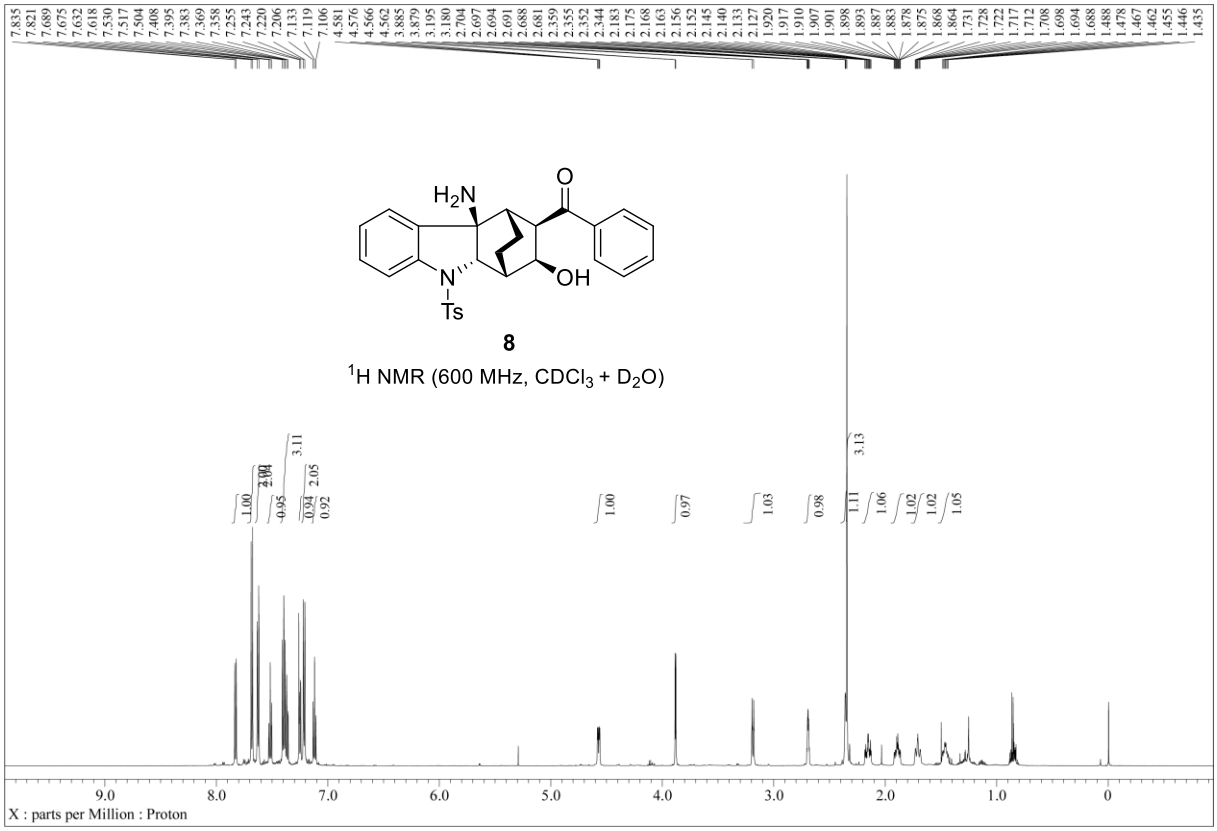
Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	15.61	2193.441	56.6290	50.0064
2	17.03	2192.879	52.1559	49.9936

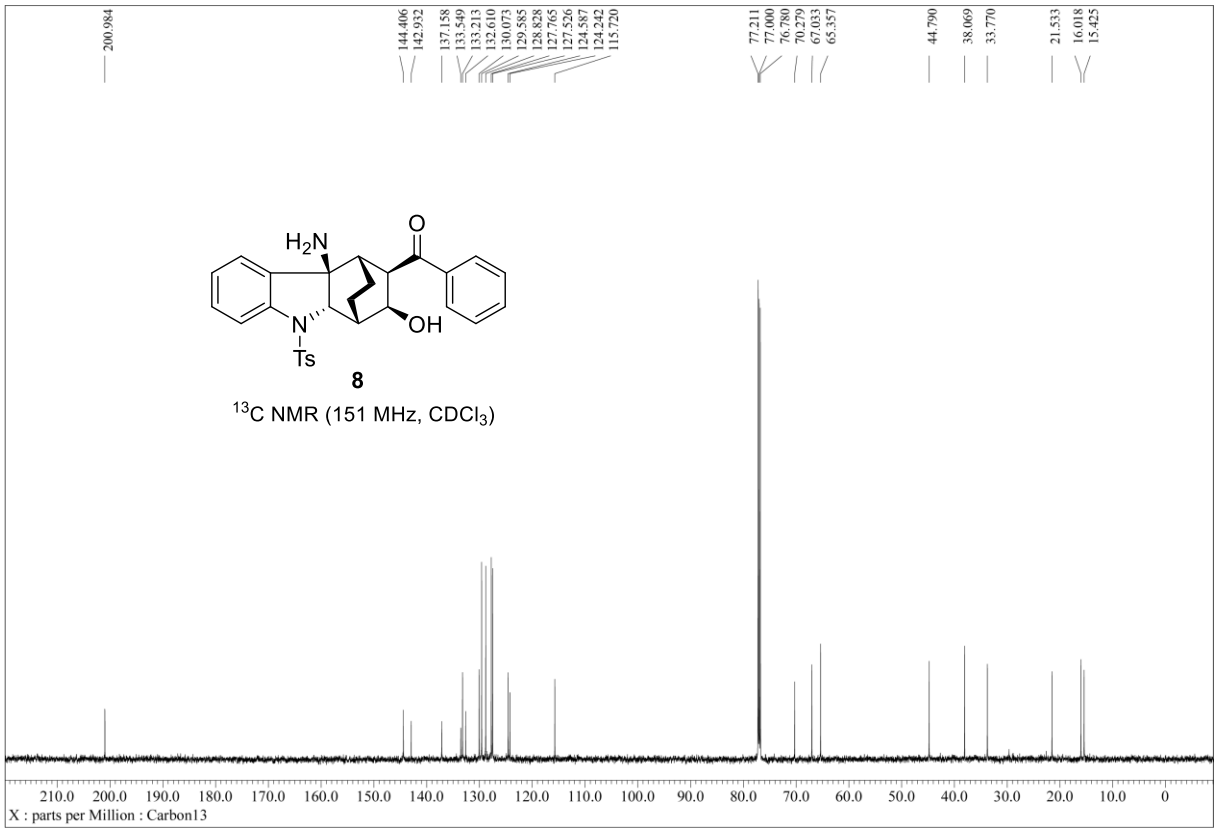


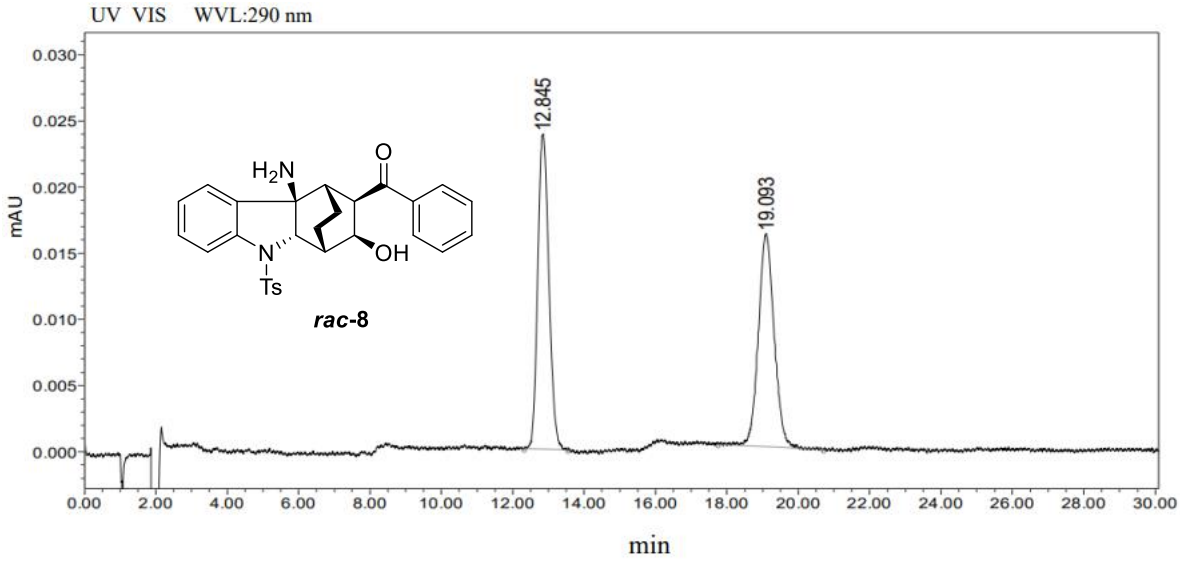
Peak Analysis Report

Peak #	Ret. Time [min]	Area [mAU*s]	Height [mAU]	Rel. Area [%]
1	16.25	11.141	0.3572	2.0755
2	17.83	525.645	12.9703	97.9245




H2N
O
N
Ts
OH
8
1H NMR (600 MHz, CDCl3 + D2O)
X : parts per Million : Proton

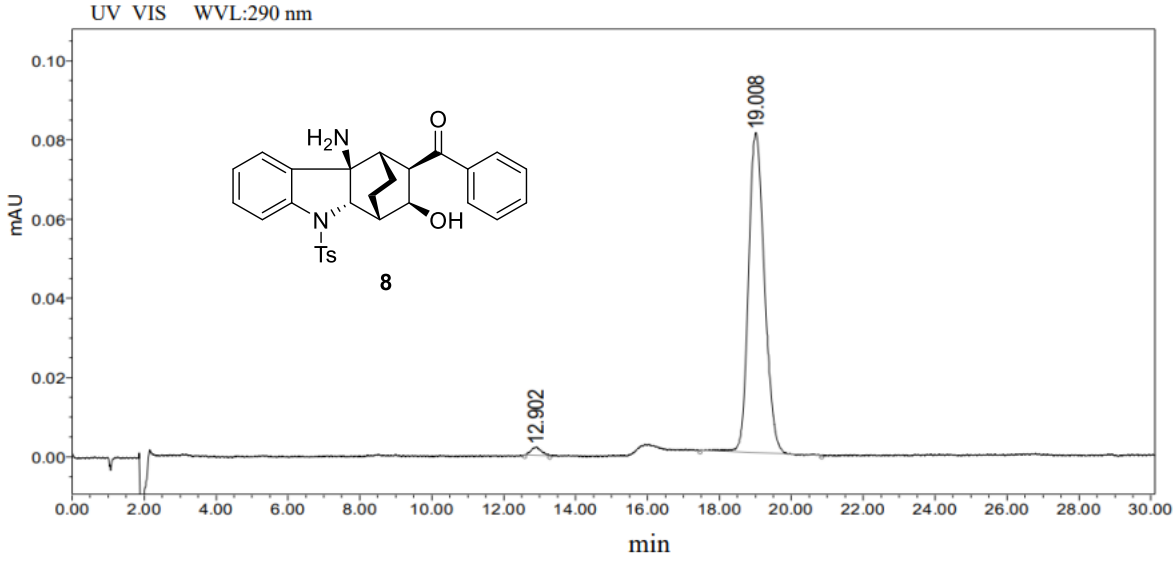

H2N
O
N
Ts
OH
8
13C NMR (151 MHz, CDCl3)
X : parts per Million : Carbon13



***rac*-8**

Peak Analysis Report

Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	12.845	509368	23785	50.47
2	19.093	499814	16093	49.53



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Peak Analysis Report

Peak #	Ret. Time [min]	Area [μV*sec]	Height [μV]	Rel. Area [%]
1	12.902	39108	1994	1.55
2	19.008	2494432	80717	98.45