Enantioselective Synthesis of Tricyclic β-Lactones by NHC-Catalyzed Desymmetrization of Cyclic 1,3-Diketones

Sayan Shee,[†] Subrata Mukherjee,[†] Rajesh G. Gonnade[‡] and Akkattu T. Biju*[,†]

[†] *Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, India*
[‡]*Centre for Materials Characterization, CSIR-National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune - 411008, India*

atbiju@iisc.ac.in

Supporting Information

1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 25 °C Corresponds to the room temperature of the lab when the experiments were carried out, and reactions at 50 °C have been performed using the pre-heated oil-bath maintained at 50 °C. Dry toluene was purchased from commercial sources and stored under argon over sodium wire and dry MeOH was purchased from commercial sources and stored under argon over 4Å molecular sieves. The 2-bromoenals were synthesized from the corresponding α,β-unsaturated aldehydes following the literature procedure.[1] The cyclopentane-1,3-dione derivative **2a, 2t** were synthesized by following the literature procedure.[2] The triazolium salt **4** was synthesized following the literature procedure.[3] Na_2CO_3 was dried by heating at 120 °C under vacuum and cooling under argon atmosphere. LiOAc was purchased from Aldrich and was used without further purification. 4Å molecular sieves were powdered and activated in furnace (300 °C) before use.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 400 and Bruker Ultrashield spectrometer in $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, ν-max in cm^{-1}. Optical rotations were measured on JASCO P-2000 polarimeter at 20 °C using 50 mm cell of 1mL capacity. HRMS (ESI) data were recorded on a Micromass Q-TOF Micro instrument. HPLC analysis was performed on Agilent Technologies 1260 Infinity with UV detector.

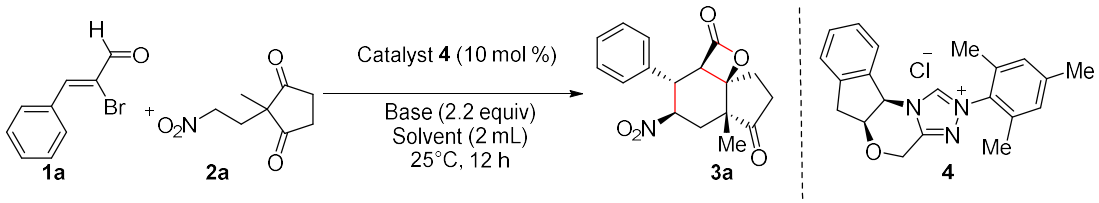
---

[1] (a) Allen, C. F. H.; Edens, *Jr.* C. O. *Org. Synth.* **1945**, *25,* 92. (b) Li, W.; Li, J.; Wan, Z.-K.; Wu, J.; Massefski, W. *Org. Lett.* **2007**, *9*, 4607.

[2] (a) Hayashi, Y.; Koshino, S.; Ojima, K.; Kwon, E. *Angew. Chem. Int. Ed.* **2017**, *56*, 11812. (b) Ramachary, D. B.; Kishor, M. *Org. Biomol. Chem.* **2008**, *6*, 4176.

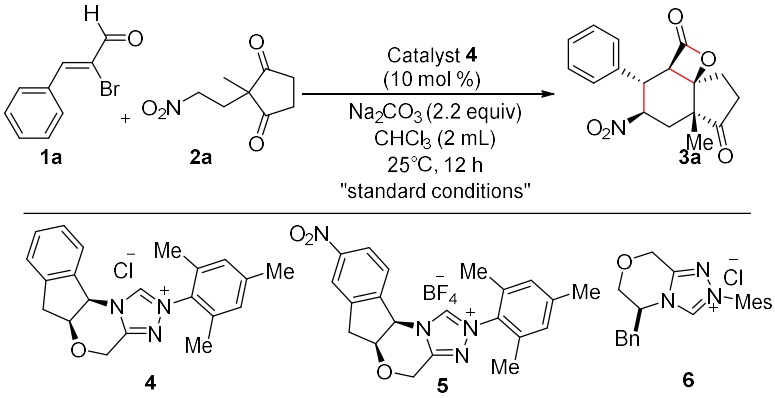
[3] Struble, J. R.; Bode, J. W. *Org. Synth*. **2010**, *87*, 362.

2. General Procedure for the Optimization of Reaction Conditions



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (0.0092 g, 0.025 mmol) and 2-methyl-2-(2-nitroethyl) cyclopentane-1,3-dione **2a** (0.25 mmol) and α-bromo cinnamaldehyde **1a** (0.25 mmol) were added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added solvent (2.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture base (0.55 mmol) was successively added and stirred for 12 h. After 12 h of stirring, the reaction is quenched and the reaction mixture is diluted with CH_2Cl_2 (2.0 mL) and filtered through a short pad of silica gel and eluted with ethyl acetate (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ^1H NMR using CH_2Br_2 (18 µL, 0.25 mmol) as the internal standard. The enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.

Optimization Studies

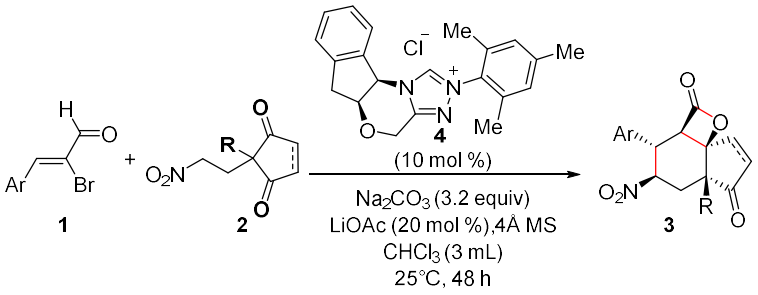


entry	variation of standard conditions[a]	yield (%)[b]	dr[c]	ee[d]
1	none	35	4:1	96
2	**5** instead of **4**	30	6:1	98
3	**6** instead of **4**	28	5:1	92
4	Cs_2CO_3 instead of Na_2CO_3	30	4:1	98

5	DIPEA instead of Na_2CO_3	17	2:1	96
6	K_3PO_4 instead of Na_2CO_3	33	4:1	98
7	Et_3N instead of Na_2CO_3	15	3:1	92
8	DMAP instead of Na_2CO_3	14	2:1	98
9	K_2CO_3 instead of Na_2CO_3	32	4:1	98
10	DBU instead of Na_2CO_3	<5	-	-
11	DABCO instead of Na_2CO_3	<5	-	-
12	DCM instead of $CHCl_3$	30	4:1	98
13	DME instead of $CHCl_3$	18	4:1	96
14	THF instead of $CHCl_3$	18	5:1	96
15	DCE instead of $CHCl_3$	30	3:1	96
16	1,4-dioxane instead of $CHCl_3$	14	3:1	98
17	CH_3CN instead of $CHCl_3$	19	4:1	98
18	toluene instead of $CHCl_3$	25	3:1	98
19	48 h instead of 12h	38	5:1	96
20	Slow addition of **1a**	14	2:1	98
21[e]	1.2 equiv of **1a**	40	5:1	96
22[f]	1.5 equiv of**1a**	49	5:1	96
23[g]	2 equiv of **1a**	54	5:1	96
24	1.5 equiv of **2a**	32	3:1	97
25	4 equiv of Na_2CO_3	43	4:1	98
26[g]	0°C instead of 25°C	44	4:1	96
27[g]	0°C to 25°C	50	10:1	96
28[g]	45°C instead of 25°C	14	2:1	92
29[g]	4 ml $CHCl_3$	52	4:1	96
30[g]	20 mol% LiOAc as additive	59	>20:1	>99
31[g]	50 mol% LiCl as additive	35	4:1	98
32[g]	20 mol% LiOAc & 4 Å MS as additive	61	>20:1	>99
33[g]	20 mol% NaOAc & 4 Å MS as additive	56	17:1	98
34[g]	20 mol% NH_4OAc & 4 Å MS as additive	52	17:1	98
35[g]	**20 mol % LiOAc, & 4 Å MS as additive**	**65**	**>20:1**	**>99**

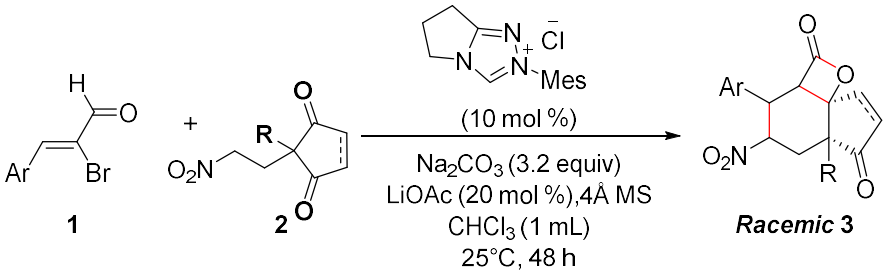
[a] **1a** (0.25 mmol), **2a** (0.25 mmol), **4** (10 mol %), Na_2CO_3 (2.2 equiv), $CHCl_3$ (2.0 mL), 25 °C, 12h. [b] The yields were determined by ^1H NMR analysis of crude product using CH_2Br_2 as internal standard. [c] Diastereomeric ratio was determined by ^1H NMR spectroscopy prior to purification. [d] Enantiomeric excess was determined by HPLC analysis on a chiral stationary phase. [e] Reaction time is 48 h and Na_2CO_3 (2.4 equiv). [f] Reaction time is 48 h and Na_2CO_3 (2.7 equiv). [g] Reaction time is 48 h and Na_2CO_3 (3.2 equiv) and reaction carried out using 2.0 equiv of **1a** and 3.0 ml solvent.

3. General Procedure for the Enantioselective Synthesis of Tricyclic β- Lactones

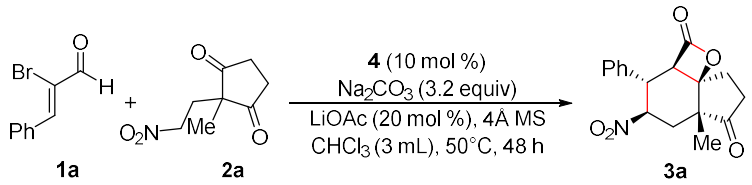


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (0.0092 g, 0.025 mmol) and cyclopentane-1,3-dione derivative **2** (0.25 mmol) and 2-bromoenal **1** (0.5 mmol), LiOAc (0.05 mmol), 4 Å molecular sieves (100 mg) were added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added $CHCl_3$ (3 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture Na_2CO_3 (0.8 mmol) was successively added and stirred for 48 h. After 48 h of stirring, the reaction is quenched and the solvent was evaporated, and the crude residue was purified by flash column chromatography on silica gel to afford the corresponding tricyclic β-lactone derivatives.

All the racemic compounds were synthesized using *N*-mesityl triazolium-derived carbene (10 mol %) under identical conditions.



Procedure for the 1.0 mmol scale synthesis of 3a



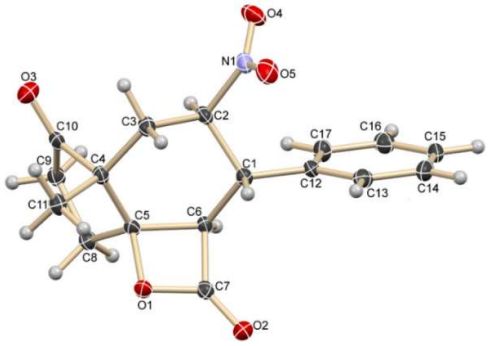
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (36.8 mg, 0.1 mmol) and cyclopentane-1,3-dione derivative **2a** (185.2 mg, 1.0 mmol) and 2-bromoenal **1a** (424 mg, 2.0 mmol), LiOAc (13.2 mg, 0.2 mmol), 4 Å molecular sieves (400 mg) were added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added $CHCl_3$ (12 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture, Na_2CO_3 (339 mg, 3.2 equiv) was successively added and stirred for 48 h. After 48 h of stirring, the reaction is quenched and the solvent was evaporated, and the crude residue was purified by flash column chromatography on silica gel (Pet. ether- Et-OAc: 80:20) to afford 5a-methyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3a** as a colorless solid (193 mg, 61% yield, >99% ee and >20:1 dr).

4. X-Ray Data of 3a

Compound **3a** has been crystallized from mixture of CH_2Cl_2-Pet.ether. The chromatographically pure **3a** was taken in a 5.0 mL vial and dissolved in minimum CH_2Cl_2. Then a few drops of Pet.ether was added slowly through the walls of the vial. Slow evaporation of the solvents provided good quality crystals of **3a**. X-ray intensity data measurements of compound **3a** was carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Cu micro-focus sealed tube diffraction source (CuK_α= 1.54178 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.1 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 40 frames. Data were collected with ωscan width of 0.5° at different settings of φ and $2\theta$with a frame time of 10 secs keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was

monitored by APEX3 program (Bruker, 2016).[4] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016).[4] Using APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008)[5] structure solution program, using direct methods. The model was refined with a version of ShelXL-2013 (Sheldrick, 2015)[6] using Least Squares minimization. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on its parent atoms. An *ORTEP* III[6] view of the compound was drawn with 50% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii. The absolute configuration was established by anomalous dispersion effect (Flack parameter, 0.05(3) in X-ray diffraction measurements carried out with Cu radiation. The single-crystal X-ray diffraction data analysis clearly established that the synthesize compound has *S, R*, *R, R* and *R* configurations at C1, C2, C4, C5 and C6 positions respectively.

Crystal data of **3a** $C_{17}H_{17}NO_5$, M = 315.31, colorless needle, 0.21 x 0.17 x 0.09 mm^3, monoclinic, chiral space group $P2_1$, a = 7.7612(2) Å, b = 10.9857(3) Å, c = 8.7485(2) Å, β= 92.1780(10)°, V = 745.38(3) $Å^3$, Z = 2, T = 100(2) K, $2\theta_{max}$= 149.124°, D_{calc} (g cm^{-3}) = 1.405, $F(000)$ = 332, μ (mm^{-1}) = 0.867, 31633 reflections collected, 2920 unique reflections (R_{int} = 0.0391, R_{sig} = 0.0187), 2918 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.867, T_{max} = 0.926, 210 refined parameters, number of restraints = 1, Good of Fit = S = 1.085, $R1$ = 0.0264, $wR2$ = 0.0682 (all data R = 0.0264, $wR2$ = 0.0682), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.234, $\Delta\rho_{min}$= -0.141 ($eÅ^{-3}$).

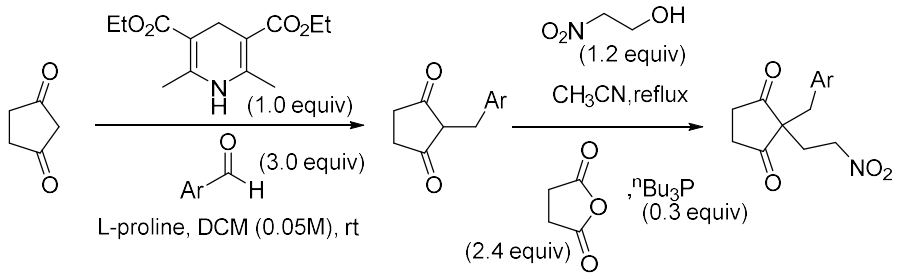


ORTEP representation of the X-ray structure of **3a** (thermal ellipsoids at 50% probability)

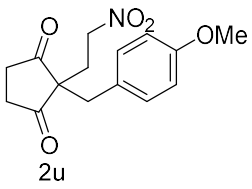
[4] Bruker (2016). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA
[5] Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112.
[6] Sheldrick, G. M. *Acta Crystallogr*. **2015**, *C71*, 3.

5. Synthesis and Characterization of Cyclopentane-1,3-dione Derivatives

Following a reported procedure,[2] 1,3-cyclopentanedione (1.0 equiv), Hantzsch ester (1 equiv), and the corresponding aldehyde (3.0 equiv) were added to CH_2Cl_2. To the suspension was added *L*-Proline (0.05 equiv) and the mixture stirred for the time indicated. The solvent was then removed under reduced pressure followed by purified by column chromatography to provide the cyclopentane-1,3-dione derivative bearing benzyl group at 2 position as a light brown solid. Next, 2-benzylcyclopentane-1,3-dione derivatives and 2-nitroethanol (1.2 equiv), succinic anhydride (2.4 equiv) and tributylphosphine (0.3 equiv) were added and the reaction mixture and heated under reflux for 2 hours. Water was added and heating continued for a further 0.5 hours. The reaction was allowed to cool, brine added and the solution extracted with EtOAc. The organic fractions were combined, washed with brine before drying over $MgSO_4$. Filtration and removal of the solvent under reduced pressure yielded the crude product which was subjected to silica gel column chromatography (EtOAc: Pet.ether) to provide the required cyclopentane-1,3-dione derivatives.



2-(4-Methoxybenzyl)-2-(2-nitroethyl)cyclopentane-1,3-dione (2u)

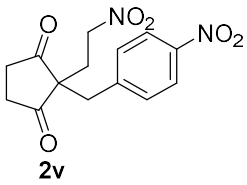


Following the general procedure, treatment of 2-(4-methoxybenzyl) cyclopentane-1,3-dione (0.6 g, 2.75 mmol) and 2-nitroethanol (0.35 g, 3.85 mmol) with succinic anhydride (0.66 g, 6.6 mmol), and tributylphosphine (0.4 ml, 0.82 mmol) in CH_3CN (6.0 mL) and stirring the reaction mixture under reflux for 2 h followed by flash column chromatography (Pet. ether-EtOAc: 80:20) afforded 2-(4-methoxybenzyl)-2-(2-nitroethyl)cyclopentane-1,3-dione **2u** as a yellow solid (515 mg, 64% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.32; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.95 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.40 (t, *J* = 8.7 Hz, 2H), 3.77 (s, 3H), 2.89 (s, 2H), 2.58 (dd, J_1 = 19.7

Hz, J_2 = 6.7 Hz, 2H), 2.39 (t, J = 6.8 Hz, 2H), 2.06 (dd, J_1 = 19.1 Hz, J_2 = 6.2 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 216.0, 159.3, 130.9, 125.6, 114.3, 70.9, 60.0, 55.3, 43.8, 36.3, 30.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{15}H_{17}NNaO_5$ 314.0999; found 314.1005. **FTIR (cm^{-1})** 3005, 2964, 2920, 1722, 1611, 1555, 1417, 1301, 1251, 962.

2-(4-Nitrobenzyl)-2-(2-nitroethyl)cyclopentane-1,3-dione (2v)

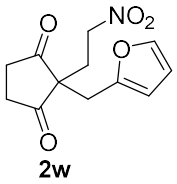


2v

Following the general procedure, treatment of 2-(4-nitrobenzyl) cyclopentane-1,3-dione (0.346 g, 1.48 mmol) and 2-nitroethanol (0.189 g, 2.07 mmol) with succinic anhydride (0.355 g, 3.5 mmol), and tributylphosphine (0.2 ml, 0.44 mmol) in CH_3CN (5.0 mL) and stirring the reaction mixture under reflux for 2 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded 2-(4-nitrobenzyl)-2-(2-nitroethyl)cyclopentane-1,3-dione **2v** as a yellow solid (302 mg, 70% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.15; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 4.44 (t, J = 6.8 Hz, 2H), 3.03 (s, 2H), 2.72 (dd, J_1 = 19.9 Hz, J_2 = 6.8 Hz, 2H), 2.41 (t, J = 6.8 Hz, 2H), 2.16 (dd, J_1 = 19.3 Hz, J_2 = 6.2 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 214.5, 147.7, 141.6, 131.1, 124.0, 70.5, 59.3, 42.1, 36.1, 30.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{14}H_{15}N_2O_6$ 307.0925; found 307.0927. **FTIR (cm^{-1})** 3080, 2971, 2926, 1723, 1603, 1556, 1418, 1349, 1108, 963.

2-(Furan-2-ylmethyl)-2-(2-nitroethyl)cyclopentane-1,3-dione (2w)



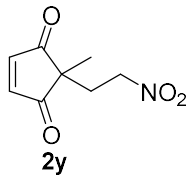
2w

Following the general procedure, treatment of 2-(furan-2-ylmethyl) cyclopentane-1,3-dione (0.402 g, 2.25 mmol) and 2-nitroethanol (0.287 g, 3.15 mmol) with succinic anhydride (0.542 g, 5.4 mmol), and tributylphosphine (0.3 ml, 0.6 mmol) in CH_3CN (5.0 mL) and stirring the reaction mixture under reflux for 2 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded 2-(furan-2-ylmethyl)-2-(2-nitroethyl)cyclopentane-1,3-dione **2w** as a yellow solid (472 mg, 72% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.34; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29-7.28 (m, 1H), 6.28-6.27 (m, 1H), 6.06 (d, J = 3.2 Hz, 1H), 4.40 (t, J = 6.9 Hz, 2H), 2.98 (s, 2H), 2.68 (dd, J_1 = 19.9 Hz, J_2 = 7.3 Hz, 2H), 2.43 (dd, J_1 = 18.5 Hz, J_2 = 5.9 Hz, 2H), 2.38 (t, J = 6.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 214.5, 148.3, 142.6, 111.0, 109.2, 70.7, 57.4, 35.7, 29.9. **HRMS (ESI)**

m/z: $[M+Na]^+$ calcd for $C_{12}H_{13}NNaO_5$ 274.0686; found 274.0691. **FTIR (cm^{-1})** 3156, 3123, 2924, 1724,1555, 1426, 1386, 1320, 1188, 919.

2-Methyl-2-(2-nitroethyl)cyclopent-4-ene-1,3-dione (2y)

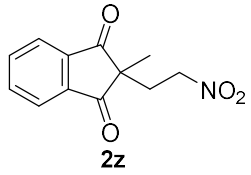


2y

Following the literature procedure, treatment of 2-methyl-2-(2-nitroethyl) cyclopentane-1,3-dione (0.2 g, 1.08 mmol) and $CuBr_2$ (0.53 g, 2.37 mmol) in MeOH (8.0 mL) and stirring the reaction mixture under reflux for 1 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded2-methyl-2-(2-nitroethyl)cyclopent-4-ene-1,3-dione **2y** as a yellow solid (165 mg, 84% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (s, 2H), 4.45-4.41 (m, 2H), 2.34-2.30 (m, 2H) 1.22 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 205.5, 147.8, 70.7, 47.7, 30.0, 18.7. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_8H_9NNaO_4$ 206.0424; found 206.0424. **FTIR (cm^{-1})** 3080, 2971, 2926, 1723, 1603, 1556, 1418, 1349, 1108, 963.

2-Methyl-2-(2-nitroethyl)-1*H*-indene-1,3(2*H*)-dione (2z)



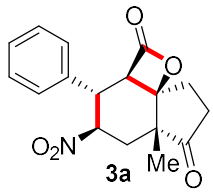
2z

Following the general procedure, treatment of 2-methyl-1*H*-indene-1,3(2*H*)-dione (0.2 g, 6.243 mmol) and and 2-nitroethanol (0.682 g, 7.492 mmol) with succinic anhydride (1.499 g, 14.983 mmol), and tributylphosphine (0.9 ml, 1.87 mmol) in CH_3CN (11.0 mL) and stirring the reaction mixture under reflux for 2 h followed by flash column chromatography (Pet. ether-EtOAc: 80:20) afforded 2-methyl-2-(2-nitroethyl)-1*H*-indene-1,3(2*H*)-dione **2z** as a white solid (1.08 g, 74% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.16; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01-7.98 (m, 2H), 7.93-7.89 (m, 2H), 4.49-4.45 (m, 2H), 2.50-2.46 (m, 2H) 1.34 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 202.2, 140.4, 136.5, 124.0, 71.0, 51.2, 30.7, 19.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{12}H_{11}NNaO_4$ 256.0580; found 256.0586. **FTIR (cm^{-1})** 3434, 2976, 2932, 1708, 1596, 1554, 1428, 1383, 1186, 984.

6. Synthesis and Characterization of Tricyclic β-Lactone Derivatives

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5*a*-Methyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete2,6 (2a*H*)-dione (3a)

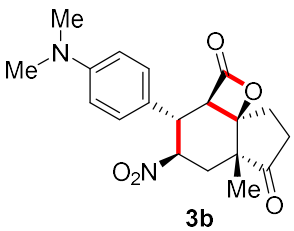


Following the general procedure, treatment of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded5a-methyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3a** as a colorless solid (50 mg, 63% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.30; ee = >99%, $[\alpha]_D^{25}$ = -217.0 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 14.4 min, *Minor*: 17.3 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 3H), 7.11 (d, *J* = 6.9 Hz, 2H), 4.40-4.36 (m, 1H), 3.77 (dd, J_1 = 11.9 Hz, J_2 = 6.8 Hz, 1H), 3.60 (d, *J* = 6.7 Hz, 1H), 2.90-2.82 (m, 1H), 2.73-2.62 (m, 2H), 2.38-2.28 (m, 2H), 2.15 (t, *J* = 12.9 Hz, 1H),1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.6, 167.7, 138.4, 129.7, 128.8, 127.5, 85.3, 83.0, 60.2, 50.6, 44.7, 36.0, 34.8, 30.6, 19.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}NNaO_5$ 338.0999; found 338.1004. **FTIR (cm^{-1})** 3453, 3070, 2921, 1831, 1747, 1554, 1456, 1375, 1251, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-(Dimethylamino)phenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3b)

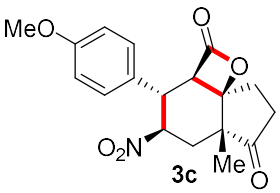


Following the general procedure, treatment of (*Z*)-2-bromo-3-(4-(dimethylamino)phenyl)acrylaldehyde **1b** (127 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-(dimethylamino)phenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno3a,4-b]oxete-2,6(2a*H*)-dione **3b** as a orange solid (36 mg, 40% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.34; ee =>99%, $[\alpha]_D^{25}$= -223.88 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 17.7 min, *Minor*: 29.8 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.63 Hz, 2H), 6.63 (d, *J* = 8.54 Hz, 2H), 4.33.4.27 (m, 1H), 3.65 (dd, J_1 = 11.59 Hz, J_2 = 6.9 Hz, 1H), 3.57 (d, *J* = 6.9 Hz, 1H), 2.91 (s, 6H), 2.88-2.80 (m, 1H), 2.68-2.64 (m, 2H), 2.37-2.29 (m, 2H), 2.13 (t, *J* = 12.98 Hz, 1H),1.24 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.9, 168.0, 150.5, 127.9, 125.4, 113.1, 85.8, 83.1, 60.6, 50.5, 44.1, 40.5, 36.0, 35.0, 30.7, 19.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{23}N_2O_5$ 359.1601; found 359.1598. **FTIR (cm^{-1})** 2923, 2805, 2327, 1830, 1747, 1555, 1522, 1371, 1220, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Methoxyphenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2a*H*)-dione (3c)

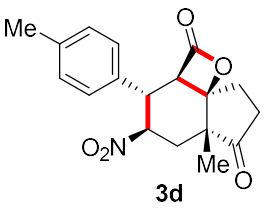


Following the general procedure, treatment of (*Z*)-2-bromo-3-(4-methoxyphenyl)acrylaldehyde **1c** (120.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3c** as a yellow solid (58 mg, 67% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.40; ee = >99%, $[\alpha]_D^{25}$= -164.32 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 18.2 min, *Minor*: 24.4 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.65 Hz, 2H), 6.84 (d, *J* = 8.58 Hz, 2H), 4.34-4.28 (m, 1H), 3.77 (s,3H), 3.70 (dd, J_1 = 11.86 Hz, J_2 = 6.96 Hz, 1H), 3.56 (d, *J* = 6.90 Hz, 1H) 2.88-2.81 (m, 1H), 2.70-2.62 (m, 2H), 2.38-2.27 (m, 2H), 2.14 (t, *J* = 13.12 Hz, 1H), 1.25 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.6, 167.6, 159.6, 130.0 128.2, 114.9, 85.5, 82.9, 60.3, 55.3, 50.4, 44.1, 35.8, 34.8, 30.5, 19.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{20}NO_6$ 346.1285; found 346.1286. **FTIR (cm^{-1})** 3469, 2978, 2924, 1836, 1745, 1553, 1458, 1376, 1257, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(*p*-tolyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3d)



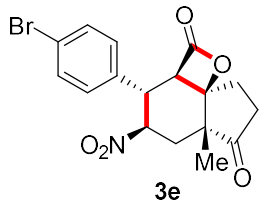
3d

Following the general procedure, treatment of (*Z*)-2-bromo-3-(p-tolyl)acrylaldehyde **1d** (112.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-methyl-4-nitro-3-(*p*-tolyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3d** as a white solid (54 mg, 65% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.37; ee = >99%, $[\alpha]_D^{25}$= -218.68 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 14.8 min, *Minor*: 18.7 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d,*J* = 7.8 Hz,2H), 6.99 (d, *J* = 8.0 Hz, 2H), 4.37-4.30 (m, 1H), 3.72 (dd, J_1 = 11.9 Hz, J_2 = 6.8 Hz, 1H), 3.57 (d, *J* = 6.8 Hz, 1H), 2.89-2.78 (m, 1H), 2.72-2.60 (m, 2H), 2.38-2.32 (m, 2H), 2.30 (s, 3H), 2.14 (t, *J* = 12.9 Hz, 1H),1.25 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.8, 167.8, 138.6, 135.3, 130.3, 127.1, 85.4, 83.0, 60.3, 50.5, 44.4, 36.0, 34.8, 30.6, 21.2, 19.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{19}H_{23}NNaO_6$ 384.1418; found 384.1425. **FTIR (cm^{-1})** 3024, 2922, 2327, 1834, 1745, 1554, 1456, 1375, 1249, 982.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Bromophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3e)



3e

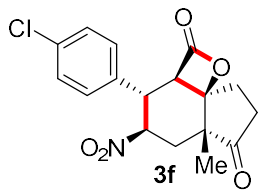
Following the general procedure, treatment of (*Z*)-2-bromo-3-(4-bromophenyl)acrylaldehyde**1e** (144.9 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-bromophenyl)-

5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3e** as a yellow solid (52 mg, 52% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.27; ee = 90%, $[\alpha]_D^{25}$= -92.12 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 20.4 min, *Minor*: 31.8 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.32 Hz,2H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.36-4.29 (m, 1H), 3.73 (dd, J_1 = 11.9 Hz, J_2 = 7.0 Hz, 1H), 3.51 (d, *J* = 7.1 Hz, 1H), 2.90-2.82 (m, 1H), 2.74-2.62 (m, 2H), 2.38-2.26 (m, 2H), 2.14 (t, *J* = 13.1 Hz, 1H), 1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.5, 167.4, 137.2, 132.9, 128.9, 122.9, 84.8, 83.0, 59.9, 50.5, 44.2, 35.9, 34.8, 30.6, 19.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{18}H_{20}BrNNaO_6$ 448.0366; found 448.0375. **FTIR (cm^{-1})** 3025, 2923, 1832, 1749, 1555, 1491, 1375, 1251, 1105, 981.

(2*aR*,3*S*,4*R*,5*aR*,8*aR*)-3-(4-Chlorophenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione (3f)



3f

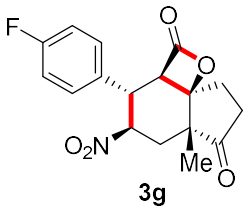
Following the general procedure, treatment of (*Z*)-2-bromo-3-(4-chlorophenyl)acrylaldehyde **1f** (122.7 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2*aR*,3*S*,4*R*,5*aR*,8*aR*)-3-(4-chlorophenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione **3f** as a colorless solid (49.8 mg, 57% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.25; ee = >99%, $[\alpha]_D^{25}$= -164.4 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 19.2 min, *Minor*: 29.2 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.36-4.29 (m, 1H), 3.75 (dd, J_1 = 12.0 Hz, J_2 = 7.0 Hz, 1H), 3.52 (d, *J* = 7.0 Hz, 1H), 2.90-2.82 (m, 1H), 2.74-2.62 (m, 2H), 2.38-2.26 (m, 2H), 2.14 (t, *J* = 13.0 Hz, 1H),1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.5, 167.4, 136.7, 134.8, 129.9, 128.6, 85.0, 83.0, 60.0, 50.5, 44.2, 35.9, 34.8, 30.6, 19.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using

MeOH) $C_{18}H_{20}ClNNaO_6$ 404.0871; found 404.0869. **FTIR (cm^{-1})** 3027, 2961, 2921, 1832, 1749, 1555, 1457, 1373, 1249, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Fluorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3g)



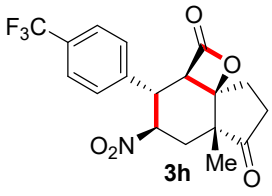
3g

Following the general procedure, treatment of (*Z*)-2-bromo-3-(4-fluorophenyl)acrylaldehyde **1g** (114.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-fluorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3g** as a white solid (48 mg, 58% yield).

***R**$_f$* (Pet. ether /EtOAc = 80/20): 0.26; ee = 99%, $[\alpha]_D^{25}$= -124.76 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 19.4 min, *Minor*: 27.1 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.08 (m, 2H), 7.05-7.01 (m, 2H), 4.36-4.29 (m, 1H), 3.75 (dd, J_1 = 11.98 Hz, J_2 = 6.95 Hz, 1H), 3.54 (d, J = 7.03 Hz, 1H), 2.90-2.82 (m, 1H), 2.74-2.62 (m, 2H), 2.38-2.27 (m, 2H), 2.14 (t, J = 12.76 Hz, 1H), 1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.6, 167.6, 162.6 (d, J = 248.5 Hz), 134.0 (d, J = 3.3 Hz), 129.0 (d, J = 8.2 Hz), 116.8 (d, J = 21.4 Hz), 85.2, 83.0, 60.1, 50.5, 44.2, 35.9, 34.8, 30.6, 19.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{18}H_{20}FNNaO_6$ 388.1167; found 388.1174. **FTIR (cm^{-1})** 3419, 2960, 2922, 1831, 1748, 1555, 1458, 1375, 1223, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(4-(trifluoromethyl)phenyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3h)



3h

Following the general procedure, treatment of (*Z*)-2-bromo-3-(4-(trifluoromethyl)phenyl)acrylaldehyde **1h** (139.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash

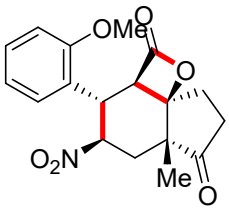
column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-methyl-4-nitro-3-(4-(trifluoromethyl)phenyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3h** as a colorless solid (44 mg, 46% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.30; ee = 86%, $[\alpha]_D^{25}$= -122.92 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 13.8 min, *Minor*: 21.6 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.29-7.27 (m, 2H), 4.43-4.37 (m, 1H), 3.85 (dd, J_1 = 11.9 Hz, J_2 = 6.9 Hz, 1H), 3.53 (d, *J* = 7.0 Hz, 1H), 2.91-2.83 (m, 1H), 2.77-2.63 (m, 2H), 2.38-2.30 (m, 2H), 2.16 (t, *J* = 12.9 Hz, 1H),1.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.5, 167.3, 142.2, 131.1 (q, *J*= 33.4 Hz), 127.8, 126.7 (q, *J*= 3.86 Hz), 123.7 (q, *J*= 272.3 Hz), 84.6, 83.0, 59.8, 50.6, 44.5, 35.8, 34.8, 30.6, 19.2. **HRMS (ESI)** m/z: $[M+K]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{19}H_{20}F_3KNO_6$ 454.0874; found 454.0870. **FTIR (cm^{-1})** 3453, 3070, 2921, 1831, 1747, 1554, 1456, 1375, 1251, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(2-Methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3i)

Following the general procedure, treatment of (*Z*)-2-bromo-3-(2-methoxyphenyl)acrylaldehyde**1i** (120.5 mg,0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4**(9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(2-methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3i** as a yellow solid (62 mg, 71% yield).



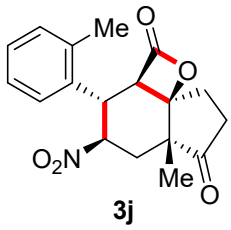
3i

R_f (Pet. ether /EtOAc = 80/20): 0.40; ee = >99%, $[\alpha]_D^{25}$= -127.68 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 11.8 min, *Minor*: 14.4 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 1H), 7.11-7.08 (m, 1H), 6.94-6.88 (m, 2H), 4.80-4.73 (m, 1H), 3.83 (s, 3H), 3.75 (d, *J* = 6.10 Hz,1H), 3.64 (dd, J_1 = 11.43, J_2 = 6.07 1H), 2.87-2.80 (m, 1H), 2.68-2.59 (m, 2H), 2.73-2.62 (m, 2H), 2.09 (t, *J* = 13.10 Hz, 1H), 1.25 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 214.1, 169.1, 156.2, 131.8, 130.4, 125.2, 121.8, 111.9, 83.3, 83.1, 58.6, 55.5, 50.5, 43.9, 35.5, 34.3, 30.4, 19.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{20}NO_6$

346.1285; found 346.1282. **FTIR (cm^{-1})** 2959, 2921,2844, 1832, 1749, 1555, 1460, 1375, 1246, 982.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(o-tolyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3j)

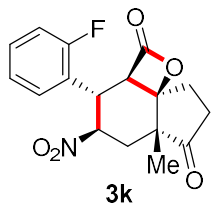


3j

Following the general procedure, treatment of (*Z*)-2-bromo-3-(o-tolyl)acrylaldehyde **1j** (112.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-methyl-4-nitro-3-(o-tolyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3j** as a colorless solid (54 mg, 65% yield).

***R**$_f$* (Pet. ether /EtOAc = 80/20): 0.35; ee = >99%, $[\alpha]_D^{25}$= -219.3 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 20.5 min, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20-7.15 (m, 3H), 6.91 (d, *J* = 6.9 Hz, 1H), 4.48-4.41 (m, 1H), 4.19-4.11 (m, 1H), 3.52 (d, *J* = 6.7 Hz, 1H), 2.89-2.81 (m, 1H), 2.74-2.59 (m, 2H), 2.41 (s, 3H), 2.38-2.30 (m, 2H), 2.17 (t, *J* = 12.9 Hz, 1H),1.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.8, 167.8, 134.6, 131.6, 128.3, 127.9, 127.4, 114.1, 85.38, 82.9, 61.0, 50.6, 39.6, 36.0, 35.0, 30.6, 19.6, 19.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) for $C_{19}H_{23}NKO_6$ 400.1157; found 400.1158. **FTIR (cm^{-1})** 3022, 2975, 2925, 1831, 1749, 1556, 1459, 1375, 1252, 982.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(2-Fluorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3k)

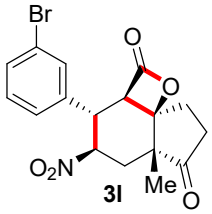


3k

Following the general procedure, treatment of (*Z*)-2-bromo-3-(2-fluorophenyl)acrylaldehyde **1k** (114.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL)

and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(2-fluorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno [3a,4-b]oxete-2,6(2a*H*)-dione **3k** as a white solid (35 mg, 45% yield). ***R**f* (Pet. ether /EtOAc = 80/20): 0.27; ee = >99%, $[\alpha]_D^{25}$= -115.80 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 11.3 min, *Minor*: 13.3 min,
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.333-7.30 (m, 1H), 7.19-7.16 (m, 1H), 7.11-7.05 (m, 2H), 4.52-4.46 (m, 1H), 3.77-3.72 (m, 2H), 2.85-2.78 (m, 1H), 2.72-2.64 (m, 2H), 2.53-2.37 (m, 2H), 2.09 (t, *J* = 13.3 Hz, 1H), 1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.8, 168.1, 160.5 (d, *J* = 243.9 Hz), 131.6 (d, *J* = 4.4 Hz), 131.0 (d, *J* = 8.9 Hz), 125.7 (d, *J* = 11.6 Hz), 125.4 (d, *J* = 3.3 Hz), 116.6 (d, *J* = 20.9 Hz), 84.3, 83.6, 58.9, 50.7, 41.7, 35.5, 34.2, 30.3, 19.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{18}H_{20}FNNaO_6$ 388.1167; found 388.1173. **FTIR (cm^{-1})** 2975, 2925, 1834, 1749, 1557, 1457, 1374, 1248, 983.

(2*aR*,3*S*,4*R*,5*aR*,8*aR*)-3-(3-Bromophenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione (3l)

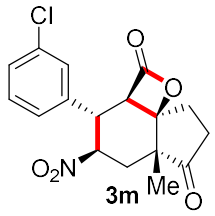


3l

Following the general procedure, treatment of (*Z*)-2-bromo-3-(3-bromophenyl)acrylaldehyde **2l** (144.9 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3-bromophenyl)-5*a*-methyl-4-nitrohexa hydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione **3l** as a white solid (50 mg, 51% yield).
***R**f* (Pet. ether /EtOAc = 80/20): 0.26; ee = >99%, $[\alpha]_D^{25}$= -159.48 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 13.9 min, *Minor*: 15.8 min,
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 2H), 7.06 (d, *J* = 7.8 Hz, 1H), 4.37-4.30 (m, 1H), 3.74 (dd, J_1 = 12.0 Hz, J_2 = 6.8 Hz, 1H), 3.54 (d, *J* = 6.8 Hz, 1H), 2.92-2.84 (m, 1H), 2.75-2.63 (m, 2H), 2.40.2.31 (m, 2H), 2.13 (t, *J* = 13.0 Hz, 1H),1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.4, 168.9, 140.5, 132.1, 131.3, 130.2, 126.1, 123.7, 84.8, 83.0, 59.9, 50.6, 44.3, 35.9, 34.8, 30.6, 19.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of

corresponding ring-opened product using MeOH) $C_{18}H_{20}BrNNaO_6$ 448.0366; found 448.0367. **FTIR (cm^{-1})** 3023, 2925, 1831, 1748, 1553, 1490, 1374, 1251, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3Chlorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3m)

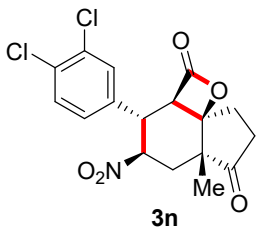


Following the general procedure, treatment of (*Z*)-2-bromo-3-(3-chlorophenyl)acrylaldehyde **1m** (122.7 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2*aR*,3*S*,4*R*,5*aR*,8*aR*)-3-(3-chlorophenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione **3m** as a white solid (38 mg, 44% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.24; ee = >99%, $[\alpha]_D^{25}$= -61.36 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 13.0 min, *Minor*: 14.9 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.28 (m, 2H), 7.10 (s, 1H), 7.03-7.00 (m, 1H), 4.37-4.30 (m, 1H), 3.75 (dd, J_1 = 11.9 Hz, J_2 = 6.9 Hz, 1H), 3.55 (d, J = 6.8 Hz, 1H), 2.92-2.84 (m, 1H), 2.75-2.63 (m, 2H), 2.40-2.28 (m, 2H), 2.14 (t, J = 13.0 Hz, 1H), 1.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.4, 167.3, 140.3, 135.6, 131.1, 129.1, 127.3, 125.6, 84.9, 83.0, 60.0, 50.6, 44.3, 35.9, 34.8, 30.6, 19.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{18}H_{20}ClNNaO_6$ 404.0871; found 404.0874. **FTIR (cm^{-1})** 3026, 2961, 2921, 1831, 1749, 1555, 1457, 1374, 1212, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3,4-Dichlorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3n)



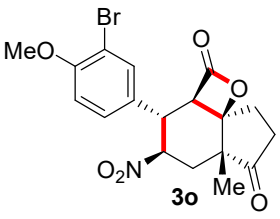
Following the general procedure, treatment of (*Z*)-2-bromo-3-(3,4-dichlorophenyl)acrylaldehyde **1n** (140.0 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in

$CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3,4-dichloro phenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3n** as a yellow solid (44 mg, 46% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.28; ee = >99%, $[\alpha]_D^{25}$= -101.56 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 14.6 min, *Minor*: 21.2 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 2.2 Hz, 1H), 7.00-6.98 (m, 1H) 4.36-4.29 (m, 1H), 3.73 (dd, J_1 = 12.0 Hz, J_2 = 7.1 Hz, 1H), 3.50 (d, *J* = 7.1 Hz, 1H), 2.91-2.83 (m, 1H), 2.76-2.63 (m, 2H), 2.39-2.30 (m, 2H), 2.13 (t, *J* = 13.1 Hz, 1H),1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.5, 167.3, 138.2, 133.8, 133.2, 131.7, 129.2, 126.7, 84.5, 83.0, 59.6, 50.5, 44.0, 35.8, 34.8, 30.6, 19.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{18}H_{19}Cl_2NNaO_6$ 438.0482; found 438.0486. **FTIR (cm^{-1})** 3026, 2978, 2926, 1832, 1749, 1556, 1470, 1375, 1251, 982.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3-Bromo-4-methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3o)



3o

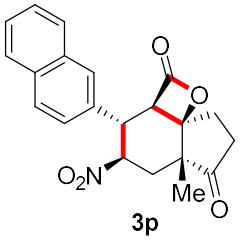
Following the general procedure, treatment of (*Z*)-2-bromo-3-(3-bromo-4-methoxyphenyl)acrylaldehyde **1o** (159.9 mg,0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3-bromo-4-methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3o** as a yellow solid (56.3 mg, 53% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.41; ee = >99%, $[\alpha]_D^{25}$= -168.35 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 21.6 min, *Minor*: 27.6 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.3 Hz, 1H), 7.05 (dd, J_1 = 8.5 Hz, J_2 = 2.3 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 4.33-4.26 (m, 1H), 3.85 (s, 3H), 3.66 (dd, J_1 = 11.9 Hz, J_2 = 7.0 Hz, 1H), 3.54 (d, *J* = 7.1 Hz, 1H) 2.89-2.81 (m, 1H), 2.72-2.62 (m, 2H), 2.40-2.29 (m, 2H), 2.12 (t, *J* = 12.9 Hz, 1H), 1.24 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.7, 167.6, 156.1, 131.6, 131.4,

128.1, 112.8, 111.4, 85.2, 83.1, 60.0, 54.1, 50.5, 43.9, 35.9, 34.9, 30.6, 19.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{19}H_{22}BrNNaO_7$ 478.0472; found 478.0475. **FTIR (cm^{-1})** 3469, 2976, 2923, 1834, 1745, 1552, 1457, 1375, 1255, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-3-(naphthalen-2-yl)-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3p)



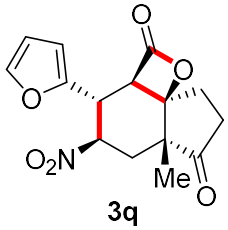
3p

Following the general procedure, treatment of (*Z*)-2-bromo-3-(naphthalen-2-yl)acrylaldehyde **1p** (130.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5*a*-methyl-3-(naphthalen-2-yl)-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione **3p** as a white solid (49 mg, 54% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.34; ee = 99%, $[\alpha]_D^{25}$= -171.92 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 18.8 min, *Minor*: 26.1 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.77 (m, 3H), 7.61 (s, 1H), 7.51-7.48 (m, 2H), 7.18 (d, J = 8.66 Hz, 1H), 4.54-4.48 (m, 1H), 3.94 (dd, J_1 = 11.9 Hz, J_2 = 6.9 Hz, 1H), 3.67 (d, J = 6.77 Hz, 1H), 2.90-2.82 (m, 1H), 2.76-2.63 (m, 2H), 2.43-2.32 (m, 2H), 2.20 (t, J = 12.89 Hz, 1H),1.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.8, 167.8, 135.3, 133.4, 133.1, 130.0, 128.1, 127.9, 127.1, 127.0, 126.9, 123.7, 85.1, 83.1, 60.0, 50.6, 44.9, 36.0, 34.8, 30.6, 19.3. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{22}H_{23}NNaO_6$ 420.1418; found 420.1423. **FTIR (cm^{-1})** 3023, 2977, 2925, 1832, 1749, 1556, 1456, 1376, 1281, 982.

(2a*R*,3*R*,4*R*,5a*R*,8a*R*)-3-(Furan-2-yl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3q)



3q

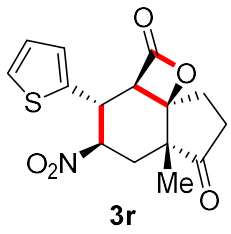
Following the general procedure, treatment of (*Z*)-2-bromo-3-(furan-2-yl)acrylaldehyde **1q** (100.5 mg, 0.5 mmol) and 2-methyl-2-(2-

nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*R*,4*R*,5a*R*,8a*R*)-3-(furan-2-yl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3q** as a white solid (40 mg, 52% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.37; ee = 96%, $[\alpha]_D^{25}$= -199.52 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IC, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 19.4 min, *Minor*: 23.8 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 6.29-6.27 (m, 1H), 6.20 (d, *J* = 3.34 Hz, 1H), 4.39-4.33 (m, 1H), 3.97 (dd, J_1 = 11.1 Hz, J_2 = 5.3 Hz, 1H), 3.82 (d, *J* = 5.31 Hz, 1H), 2.86-2.73 (m, 1H), 2.67-2.63 (m, 2H), 2.41-2.37 (m, 2H), 2.09 (t, *J* = 13.04 Hz, 1H), 1.24 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.5, 167.5, 149.7, 143.4, 111.0, 109.0, 83.5, 83.0, 56.6, 50.4, 37.2, 36.0, 33.6, 30.4, 19.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{15}H_{15}NNaO_6$ 328.0792; found 328.0786. **FTIR (cm^{-1})** 3120, 3067, 2923, 1831, 1750, 1557, 1453, 1338, 1246, 987.

(2a*R*,3*R*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(thiophen-2-yl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3r)



3r

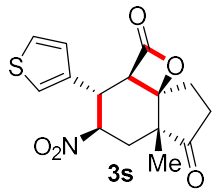
Following the general procedure, treatment of (*Z*)-2-bromo-3-(thiophen-2-yl)acrylaldehyde **1r** (108.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*R*,4*R*,5a*R*,8a*R*)-5a-methyl-4-nitro-3-(thiophen-2-yl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3r** as a white solid (37 mg, 45% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.26; ee = 98%, $[\alpha]_D^{25}$= -221.08 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 22.2 min, *Minor*: 26.9 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.24 (m, 1H), 6.92-6.90 (m, 2H), 4.34-4.37 (m, 1H), 4.16 (dd, J_1 = 11.66 Hz, J_2 = 6.17 Hz, 1H), 3.71 (d, *J* = 6.02 Hz, 1H), 2.89-2.81 (m, 1H), 2.70-2.61 (m, 2H), 2.40-2.31 (m, 2H), 2.12 (t, *J* = 13.10 Hz, 1H), 1.25 (s, 3H). **^{13}C NMR (100 MHz,**

$CDCl_3$) δ 213.4, 167.2, 141.4, 127.8, 126.8, 126.0, 86.4, 83.2, 60.7, 50.4, 39.6, 36.0, 34.5, 30.5, 19.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{16}H_{19}NNaO_6S$ 376.0825; found 376.0830. **FTIR (cm^{-1})** 3451, 2978, 2924, 1831, 1748, 1556, 1457, 1375, 1124, 981.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(thiophen-3-yl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3s)



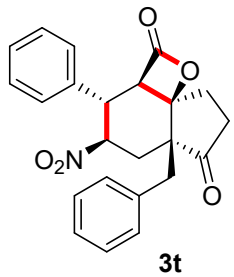
3s

Following the general procedure, treatment of (*Z*)-2-bromo-3-(thiophen-3-yl)acrylaldehyde **1s** (108.5 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2a** (46.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-methyl-4-nitro-3-(thiophen-3-yl)hexahydro-2*H*-indeno [3a,4-b]oxete-2,6(2a*H*)-dione **3s** as a colorless solid (33 mg, 42% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.25; ee = 98%, $[\alpha]_D^{25}$= -167.76 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IC, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 20.8 min, *Minor*: 22.7 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 1H), 7.10 (s, 1H), 6.89 (d, *J* = 5.1 Hz, 1H), 4.40-4.34 (m, 1H), 3.94 (dd, J_1 = 11.9 Hz, J_2 = 6.6 Hz, 1H), 3.55 (d, *J* = 6.7 Hz, 1H), 2.90-2.79 (m, 1H), 2.71-2.60 (m, 2H), 2.36-2.22 (m, 2H), 2.12 (t, *J* = 12.8 Hz, 1H), 1.25 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.6, 167.7, 138.7, 128.3, 125.2, 122.8, 85.0, 83.0, 59.7, 50.4, 39.8, 35.9, 34.9, 30.6, 19.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{16}H_{19}NNaO_6S$ 376.0825; found 376.0830. **FTIR (cm^{-1})** 3106, 2977, 2923, 1831, 1749, 1556, 1458, 1375, 1209, 982.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Benzyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3t)



3t

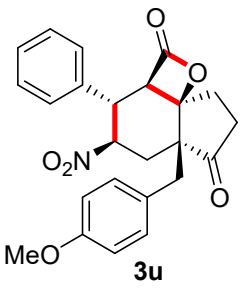
Following the general procedure, treatment of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol) and 2-benzyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2t** (65.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3

mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 50 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-benzyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3t** as a white solid (37 mg, 38% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.25; ee = >99%, $[\alpha]_D^{25}$= -232.96 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 11.6 min, *Minor*: 16.1 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 6H), 7.16-7.10 (m, 4H), 4.37-4.30 (m, 1H), 3.78 (dd, J_1 = 12.0 Hz, J_2 = 6.9 Hz, 1H), 3.57 (d, J = 6.9 Hz, 1H), 3.09 (d, J = 13.5 Hz, 1H), 2.98 (d, J = 13.5 Hz, 1H), 2.71 (dd, J_1 = 13.4 Hz, J_2 = 2.9 Hz, 1H), 2.46-2.38 (m, 1H), 2.25-2.13 (m, 2H), 2.10-1.97 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 214.2, 167.9, 138.2, 134.2, 130.7, 129.7, 128.7, 127.9, 127.2, 126.7, 85.2, 83.4, 62.2, 55.6, 44.7, 40.9, 36.8, 35.1, 31.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{24}H_{25}NNaO_6$ 446.1574; found 446.1581. **FTIR (cm^{-1})** 3065,3031, 2922, 1825, 1747, 1557, 1495, 1375, 1210, 989.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-(4-Methoxybenzyl)-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3u)



3u

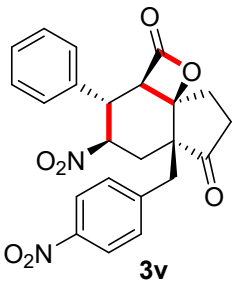
Following the general procedure, treatment of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol) and 2-(4-methoxybenzyl)-2-(2-nitroethyl)cyclopentane-1,3-dione **2u** (72.8 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 50 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5*a*-(4-methoxybenzyl)-4-nitro-3-phenylhexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2a*H*)-dione **3u** as a white solid (42 mg, 40% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.36; ee = >99%, $[\alpha]_D^{25}$= -112.24 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 15.4 min, *Minor*: 21.4 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 3H), 7.11-7.05 (m, 4H), 6.08 (d, J = 8.6 Hz, 2H) 4.36-4.29 (m, 1H), 3.88-3.74 (m, 4H), 3.57 (d, J = 6.8 Hz, 1H), 3.05 (d, J = 13.8 Hz, 1H), 2.93 (d, J = 13.6 Hz, 1H), 2.69 (dd, J_1 = 13.4 Hz, J_2 = 2.7 Hz, 1H), 2.45-2.38 (m, 1H), 2.25-2.14 (m,

2H), 2.10-1.99 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 214.5, 168.0, 159.3, 138.3, 131.8, 129.7, 128.7, 127.2, 126.0, 114.1, 85.2, 83.5, 62.2, 55.7, 55.4, 44.7, 40.3, 36.9, 35.2, 31.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{25}H_{27}NNaO_7$ 476.1680; found 476.1685. **FTIR (cm^{-1})** 3067, 3031, 2917, 1832, 1746, 1512, 1449, 1374, 1251, 988.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-4-Nitro-5a-(4-nitrobenzyl)-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3v)



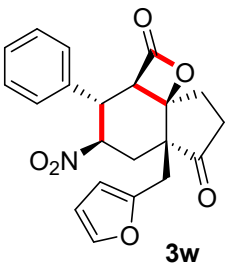
3v

Following the general procedure, treatment of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol) and 2-(4-nitrobenzyl)-2-(2-nitroethyl)cyclopentane-1,3-dione **2v** (76.5 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 50 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-4-nitro-5a-(4-nitrobenzyl)-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6 (2a*H*)-dione **3v** as a white solid (56 mg, 51% yield).

***R*$_f$**(Pet. ether /EtOAc = 80/20): 0.2; ee = >99%, $[\alpha]_D^{25}$= -149.6 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*:32.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.34-7.29 (m, 5H),7.12-7.10 (m, 2H), 4.36-4.29 (m, 1H), 3.78 (dd, J_1 = 11.9 Hz, J_2 = 6.9 Hz, 1H), 3.64 (d, J = 7.1 Hz, 1H), 3.17 (d, J = 13.4 Hz, 1H), 3.08 (d, J = 13.4 Hz, 1H),2.67 (dd, J_1 = 13.3 Hz, J_2 = 2.8 Hz, 1H), 2.55-2.48 (m, 1H), 2.35-2.19 (m, 3H), 2.07-1.98 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** 213.5, 167.3, 147.7, 141.8, 137.9, 131.8, 129.8, 128.9, 127.1, 123.9, 84.9, 82.9, 62.2, 55.3, 44.6, 40.1, 36.7, 35.0, 31.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{24}H_{24}N_2NaO_8$ 491.1425; found 491.1430. **FTIR (cm^{-1})** 3029, 2925, 1833, 1748, 1557, 1521, 1377, 1347, 1211 989.

(2a*R*,3*S*,4*R*,5a*S*,8a*R*)-5a-(Furan-2-ylmethyl)-4-nitro-3-phenylhexahydro-2*H*indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3w)

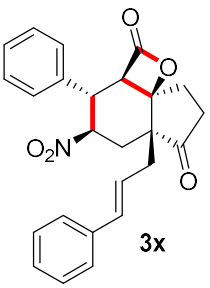


Following the general procedure, treatment of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol) and 2-(furan-2-ylmethyl)-2-(2-nitroethyl)cyclopentane-1,3-dione **2w** (62.8 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 50 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded(2a*R*,3*S*,4*R*,5a*S*,8a*R*)-5a-(furan-2-ylmethyl)-4-nitro-3-phenylhexahydro-2*H* indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3w** as a white solid (38 mg, 40% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.26; ee = 98%, $[\alpha]_D^{25}$= -176.96 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 14.4 min, *Minor*: 19.4 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 4H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.32 (s, 1H), 6.17-6.16 (m, 1H), 4.37-4.31 (m, 1H), 3.76 (dd, J_1 = 12.0 Hz, J_2 = 6.9 Hz, 1H), 3.59 (d, *J* = 6.7 Hz, 1H), 3.11 (d, *J* = 14.6 Hz, 1H), 3.03 (d, *J* = 14.6 Hz, 1H), 2.75-2.65 (m, 2H), 2.28-2.16 (m, 3H), 2.07-1.97 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** 213.1, 167.8, 148.6, 142.4, 138.2, 129.7, 128.8, 127.2, 111.0, 110.1, 85.1, 82.9, 61.8, 53.9, 44.7, 36.6, 34.7, 33.3, 31.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for (mass of corresponding ring-opened product using MeOH) $C_{22}H_{24}NO_7$ 414.1547; found 414.1552. **FTIR (cm^{-1})** 3479, 3120, 2923, 1831, 1750, 1557, 1453, 1375, 1211, 987.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Cinnamyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3x)



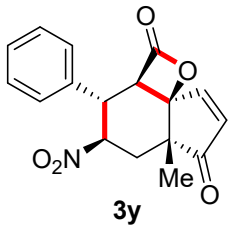
Following the general procedure, treatment of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol) and 2-cinnamyl-2-(2-nitroethyl)cyclopentane-1,3-dione **2x** (71.8 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 50 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-cinnamyl-

4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **(3x)** as a white solid (47 mg, 45% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.32; ee = >99%, $[\alpha]_D^{25}$= -240.96 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak OD-H, 85:15 Hexane / IPA, 1.0 mL/min) *Major*: 24.0 min, *Minor*: 48.1 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 8H), 7.12 (d, *J* = 7.0 Hz, 2H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.13-6.03 (m, 1H), 4.41-4.34 (m, 1H), 3.77 (dd, J_1 = 11.9 Hz, J_2 = 6.8 Hz, 1H), 3.63 (d, *J* = 6.9 Hz, 1H), 2.79-2.72 (m, 3H), 2.63-2.60 (m, 2H), 2.37-2.32 (m, 2H), 2.15 (t, *J* = 12.9 Hz, 1H) . **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.36, 167.67, 138.28, 136.41, 135.89, 129.72, 128.82, 128.46, 128.14, 127.17, 126.52, 121.40, 85.32, 83.21, 61.55, 54.46, 44.63, 37.43, 36.40, 34.12, 31.51. **HRMS (ESI**) calculated $[M+Na]^+$ calcd for $C_{25}H_{23}NNaO_5$ 440.1468; found 440.1476. **FTIR (cm^{-1})** 3063,3033, 2925, 1827, 1745, 1555, 1493, 1374, 1211, 989.

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-phenyl-3,4,5,5a-tetrahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3y)



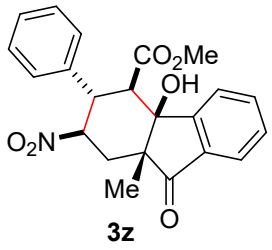
3y

Following the general procedure, treatment of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)cyclopent-4-ene-1,3-dione **2y** (45.79 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by flash column chromatography (Pet. ether- EtOAc: 80:20) afforded (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-methyl-4-nitro-3-phenyl-3,4,5,5a-tetrahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione **3y** as a white solid (47 mg, 60% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.28; ee = >99%, $[\alpha]_D^{25}$= -370.40 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 17.1 min, *Minor*: 25.1 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 5.78 Hz,1H), 7.33-7.28 (m, 3H), 7.09 (d, *J* = 6.96 Hz, 2H), 6.53 (d, *J* = 5.9 Hz, 1H), 4.37-4.31 (m, 1H), 3.92 (d, *J* = 7.33 Hz, 1H), 3.80 (dd, J_1 = 11.62 Hz, J_2 = 7.31 Hz, 1H), 2.91-2.87 (m, 1H), 2.23 (t, *J* = 13.27 Hz, 1H), 1.34 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 204.4, 166.6, 158.4, 137.7, 135.1, 129.7, 128.8, 127.3, 85.07, 81.9, 60.0, 49.8, 44.8, 35.0, 22.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}NNaO_5$ 336.0842; found 336.0840. **FTIR (cm^{-1})** 3068, 3029, 2924, 1836, 1725, 1554, 1454, 1340, 1109, 910.

Methyl (2*R*,3*S*,4*R*,4*aS*,9*aR*)-4*a*-hydroxy-9*a*-methyl-2-nitro-9-oxo-3-phenyl-2,3,4,4*a*,9,9*a*-hexahydro-1*H*-fluorene-4-carboxylate (3z)



3z

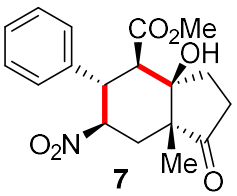
Following the general procedure, treatment of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol) and 2-methyl-2-(2-nitroethyl)-1*H*-indene-1,3(2*H*)-dione **2z** (58.3 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), and Na_2CO_3 (84.7 mg, 0.8 mmol), LiOAc (3.3 mg, 0.05 mmol), and activated powdered 4Å MS (100 mg) in $CHCl_3$ (3.0 mL) and stirring the reaction mixture at 25 °C for 48 h followed by treatment of 1.0 mL of Et_3N in methanol (1.0 mL) and stirred at 30 °C for 24 h under argon atmosphere. Evaporation of the solvent followed by silica gel flash column chromatography afforded methyl (2*R*,3*S*,4*R*,4*aS*,9*aR*)-4*a*-hydroxy-9*a*-methyl-2-nitro-9-oxo-3-phenyl-2,3,4,4*a*,9,9*a*-hexahydro-1*H*-fluorene-4-carboxylate **3z** as a white solid (54 mg, 55% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.45; ee = >99%, $[\alpha]_D^{25}$= -131.72 (c 0.1, $CHCl_3$). **HPLC** (ChiralpakIA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 11.5 min, *Major*: 17.5 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.1 Hz, 1H), 7.6 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.24-7.20 (m, 3H), 7.09-7.07 (m, 2H), 5.60 (s, 1H), 4.87-4.80 (m, 1H), 3.79 (t, *J* =11.9 Hz, 1H), 3.14 (s, 3H), 3.02 (dd, J_1 = 13.6 Hz, J_2 = 4.6 Hz, 1H), 2.44-2.36 (m, 2H), 1.22 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 203.0, 173.5, 154.8, 135.1, 135.0, 132.8, 129.6, 128.9, 128.5, 128.0, 124.8, 122.8, 86.9, 58.8, 57.5, 52.2, 45.3, 33.2, 24.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{22}H_{21}NNaO_6$ 418.1261; found 418.1267. **FTIR (cm^{-1})** 3433, 3032, 2929, 1713, 1747, 1554, 1440, 1377, 1219, 966.

7. Functionalization of Tricyclic β-Lactones

Methyl (3a*R*,4*R*,5*S*,6*R*,7a*R*)-3a-hydroxy-7a-methyl-6-nitro-1-oxo-5-phenyloctahydro-1*H*-indene-4-carboxylate (7)



7

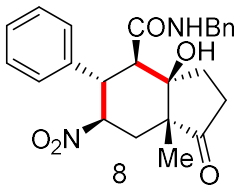
An oven-dried round-bottomed flask was charged with (2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5*a*-methyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3*a*,4-*b*]oxete2,6(2a*H*)-dione **(3a)**(63.1 mg, 0.2 mmol) and 1.0 mL of Et_3N in methanol (1.0 mL). The reaction mixture was stirred at 30 °C for 24 h under argon atmosphere. Evaporation of the solvent followed by silica gel flash column

chromatography afforded methyl(3a*R*,4*R*,5*S*,6*R*,7a*R*)-3a-hydroxy-7a-methyl-6-nitro-1-oxo-5-phenyloctahydro-1*H*-indene-4-carboxylate **7**as a yellow solid (65 mg, 94% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.45; ee = >99%, $[\alpha]_D^{25}$= -77.44 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 15.5 min, *Minor*: 21.4 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 2H), 4.72-4.64 (m, 1H), 4.50 (s, 1H), 3.70 (t, *J* = 11.9 Hz, 1H), 3.29 (s, 3H), 2.72-2.60 (m, 2H), 2.47 (d, *J* = 12.3 Hz,1H), 2.39-2.16 (m, 3H), 1.88-1.82 (m,1H), 1.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 215.2, 173.3, 135.6, 128.9, 128.5, 127.9, 86.4, 76.4, 54.2, 53.0, 52.3, 44.8, 34.2, 32.8, 30.8, 19.1. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{18}H_{21}NNaO_6$ 370.1261; found 370.1268. **FTIR (cm^{-1})** 3471, 3032, 2925, 1831, 1745, 1554, 1439, 1376, 1285, 1071, 942.

(3a*R*,4*R*,5*S*,6*R*,7a*R*)-*N*-Benzyl-3a-hydroxy-7a-methyl-6-nitro-1-oxo-5-phenyloctahydro-1*H*-indene-4-carboxamide (8)

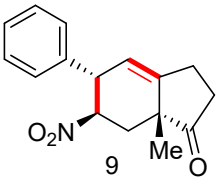


To a dry Schlenk tube containing compound **(**2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5*a*-methyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete2,6(2a*H*)-dion**e (3a)** (40.0 mg, 0.125 mmol) in THF (2.0 mL) was added benzylamine (28.0 µL, 0.25 mmol) at room temperature. The resulting mixture was allowed to stir 48 h. Then thesolution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (2:1) to afford the (3a*R*,4*R*,5*S*,6*R*,7a*R*)-*N*-benzyl-3a-hydroxy-7a-methyl-6-nitro-1-oxo-5-phenyloctahydro-1*H*-indene-4-carboxamide (**8**) as a yellow solid (44.3 mg, 84% yield).

***R**f* (Pet. ether /EtOAc = 80/20): 0.52; ee = >99%, $[\alpha]_D^{25}$= -118.0 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 80:20 Hexane / IPA, 1.0 mL/min) *Major*: 8.7 min, *Minor*: 11.5 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.13 (m, 6H), 7.06 (d, *J* = 6.9 Hz, 2H), 6.59 (d, *J* = 7.1 Hz, 2H), 6.15 (s, 1H), 5.77 (t, *J* = 4.9 Hz, 1H), 4.73-4.66 (m, 1H), 4.07 (dd, J_1 = 14.6 Hz, J_2 = 6.2 Hz, 1H), 3.94 (dd, J_1 = 14.8 Hz, J_2 = 4.6 Hz, 1H), 3.78 (t, *J* = 11.8 Hz, 1H), 2.72-2.51 (m, 2H), 2.26-2.13 (m, 3H), 2.05 (d, *J* = 11.9 Hz,1H), 1.96-1.90 (m, 1H), 1.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 216.1, 171.7, 136.5, 136.3, 129.3, 128.8, 128.5, 127.8, 127.7, 127.6, 86.5, 76.8, 54.2, 53.2, 44.8, 43.7, 34.2, 32.7, 30.7, 19.1. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{24}H_{27}N_2O_5$ 423.1914; found 423.1918. **FTIR (cm^{-1})** 3329, 3031, 2927, 1743, 1632, 1554, 1457, 1374, 1220, 1084, 947.

(5*S*,6*R*,7a*R*)-7a-Methyl-6-nitro-5-phenyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-one (9)



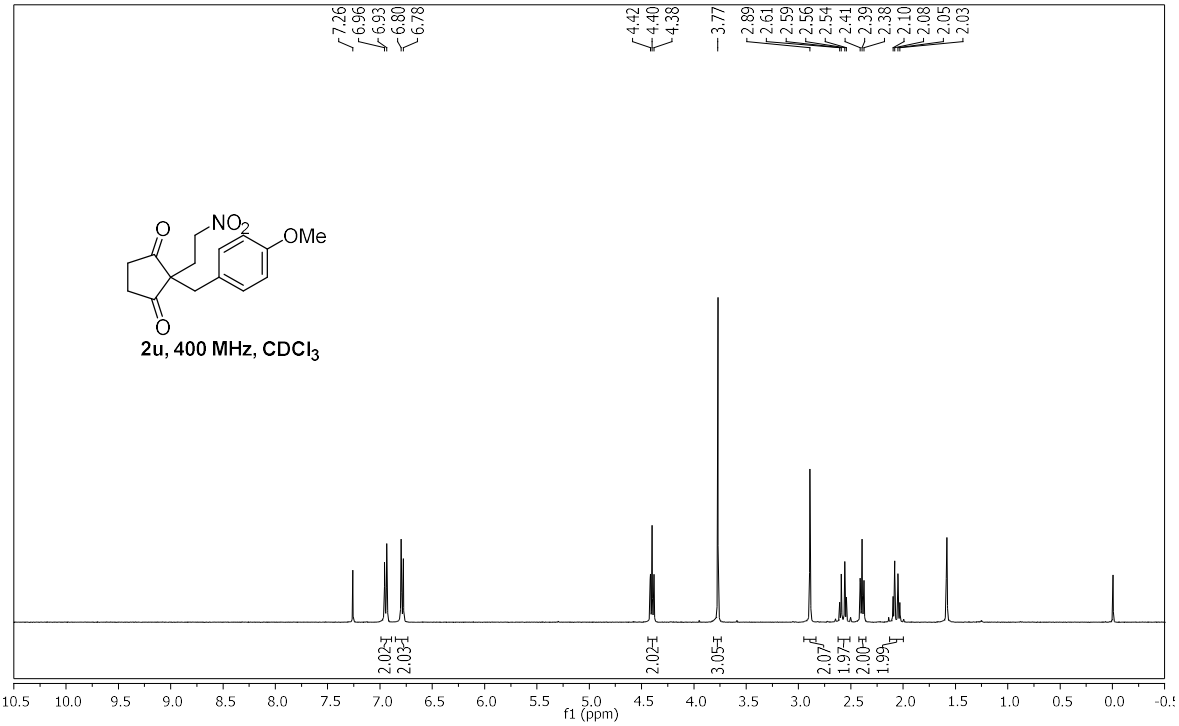
An oven-dried round-bottomed flask was charged with (2a*R*,3*S*,4*R*, 5a*R*,8a*R*)-5*a*-methyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3*a*,4-*b*]oxete2,6 (2a*H*)-dione (**3a)** (40.0 mg, 0.125 mmol) and 200 mg of silica in toluene (2.0 mL). The reaction mixture was heated at 60 °C for 6 h under argon atmosphere. Upon consumption of the starting material (**3a**) (TLC), the crude reaction mixture was passed through Celite and concentrated under reduced pressure to get a sufficiently pure (5*S*,6*R*,7*aR*)-7*a*-methyl-6-nitro-5-phenyl-2,3,5,6,7,7*a*-hexahydro-1*H*-inden-1-one (**9**) as a yellow solid (29 mg, 87% yield).

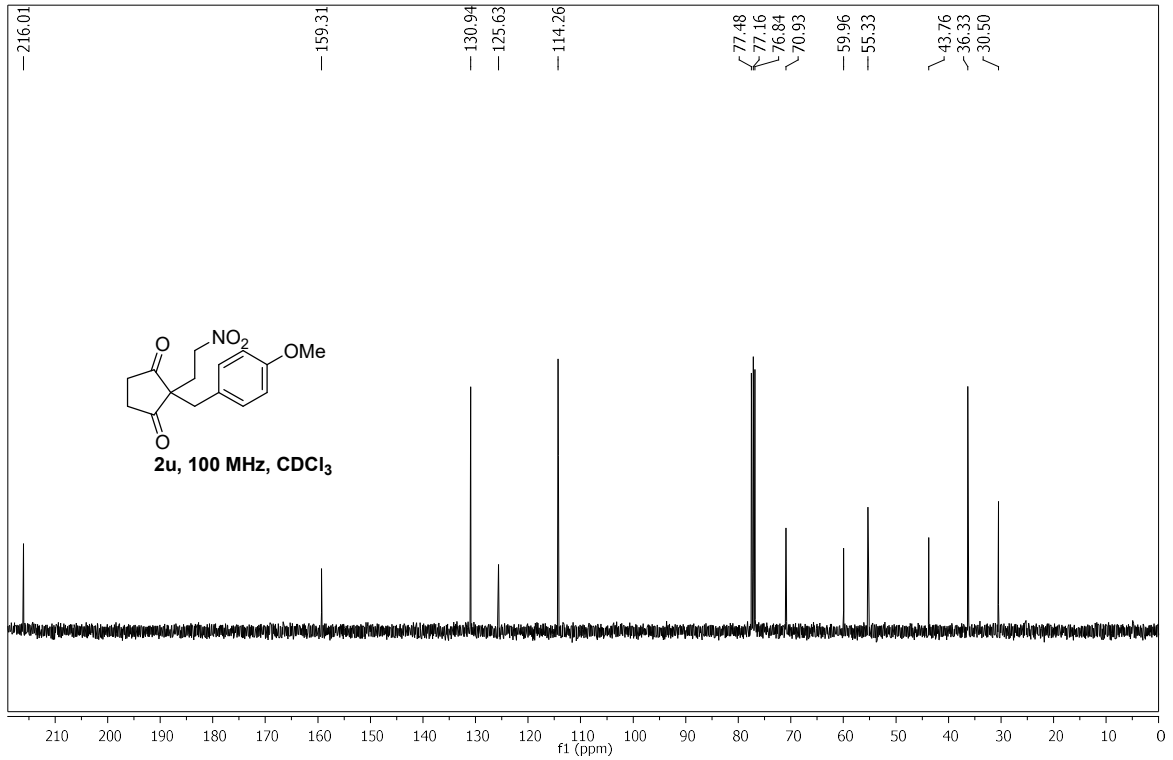
***R**f* (Pet. ether /EtOAc = 80/20): 0.15; ee = >99%, $[\alpha]_D^{25}$= -501.72 (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Major*: 7.4 min, *Minor*: 8.2 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 3H), 7.14-7.12 (m, 2H), 5.68-5.67 (m, 1H), 4.40-4.34 (m, 1H), 4.07-4.04 (m, 1H), 2.86-2.80 (m,1H), 2.76-2.61 (m, 3H), 2.39-2.29 (m, 2H), 1.23 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 215.0, 143.1, 140.9, 140.2, 129.1, 128.0, 122.2, 88.0, 48.8, 44.6, 36.3, 32.6, 26.0, 23.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{16}H_{17}NNaO_3$ 294.1101; found 294.1107. **FTIR (cm^{-1})** 3031, 2970, 2927, 2851, 1745, 1549, 1453, 1373, 1260, 1059, 973.

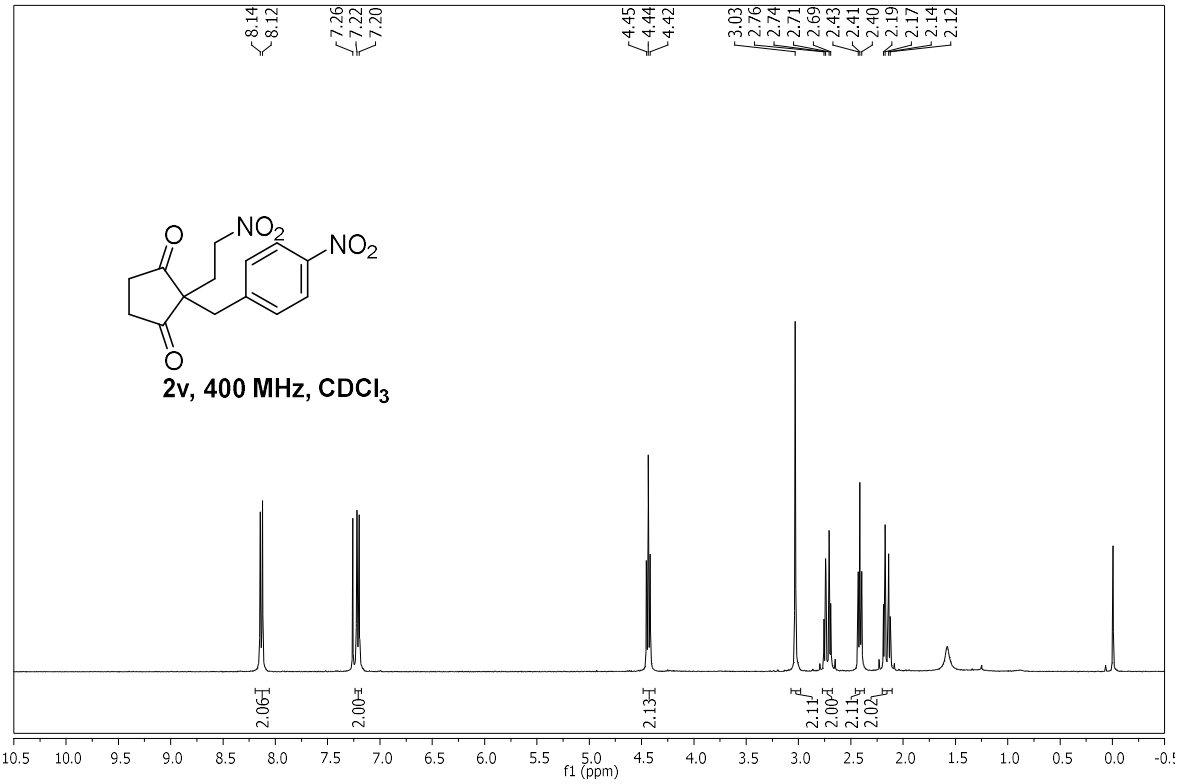
8. ^{1}H and ^{13}C NMR Spectra of Cyclopentane-1,3-dione Derivatives

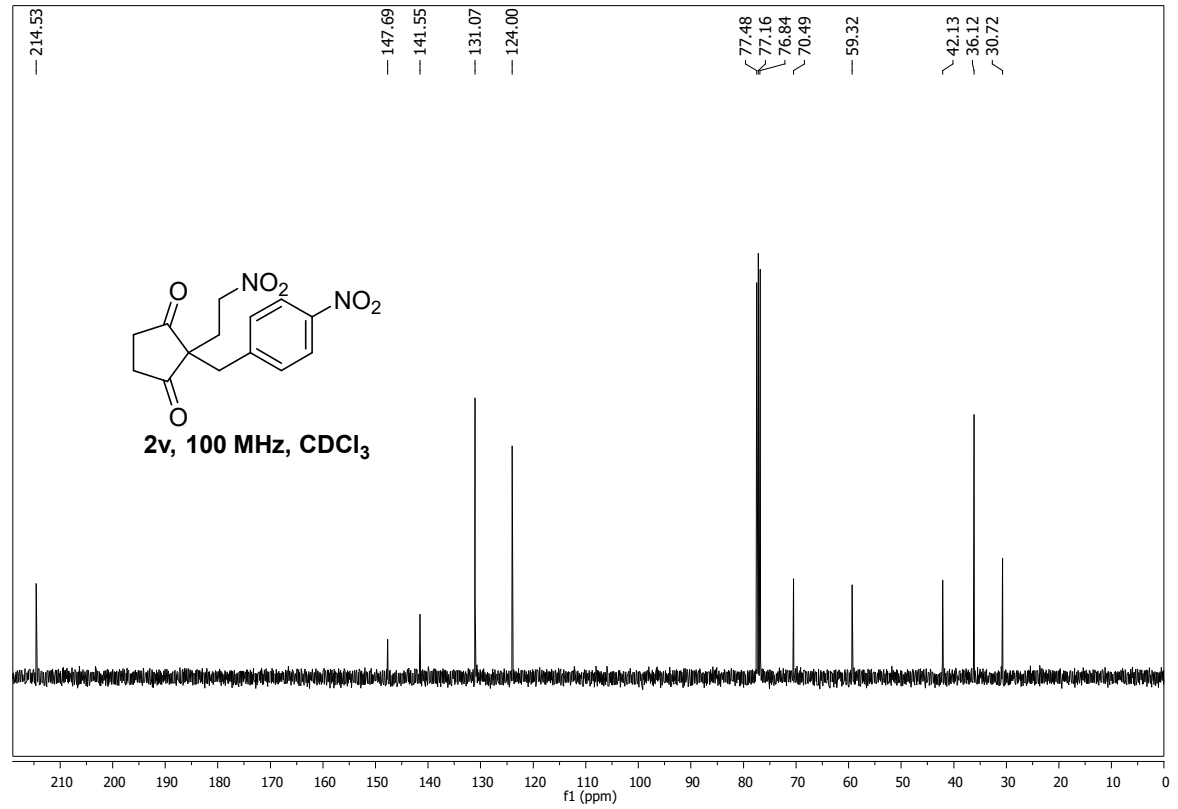
2-(4-Methoxybenzyl)-2-(2-nitroethyl)cyclopentane-1,3-dione (2u)



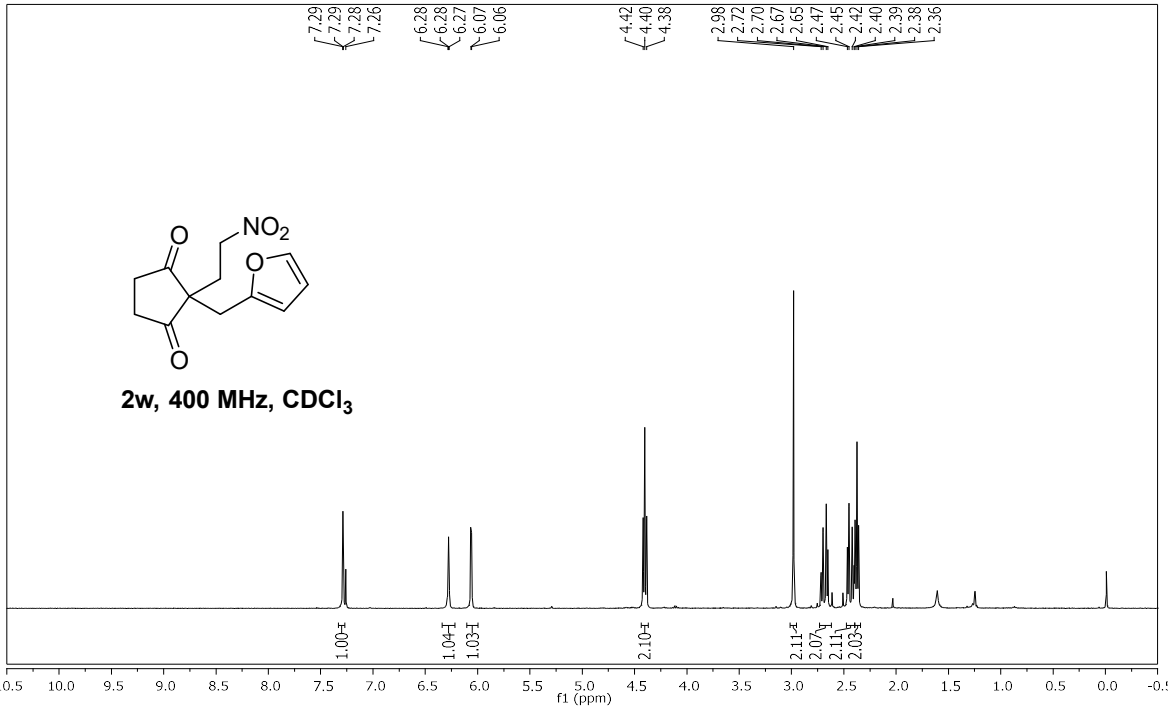


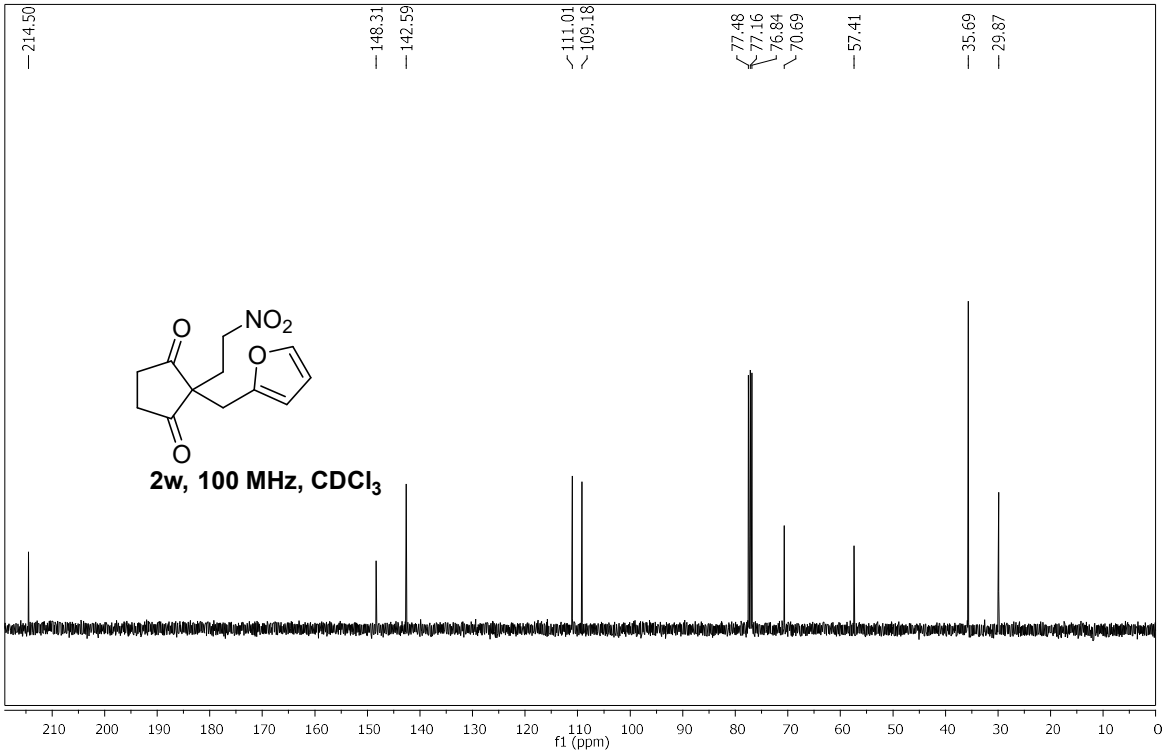
2-(4-Nitrobenzyl)-2-(2-nitroethyl)cyclopentane-1,3-dione (2v)



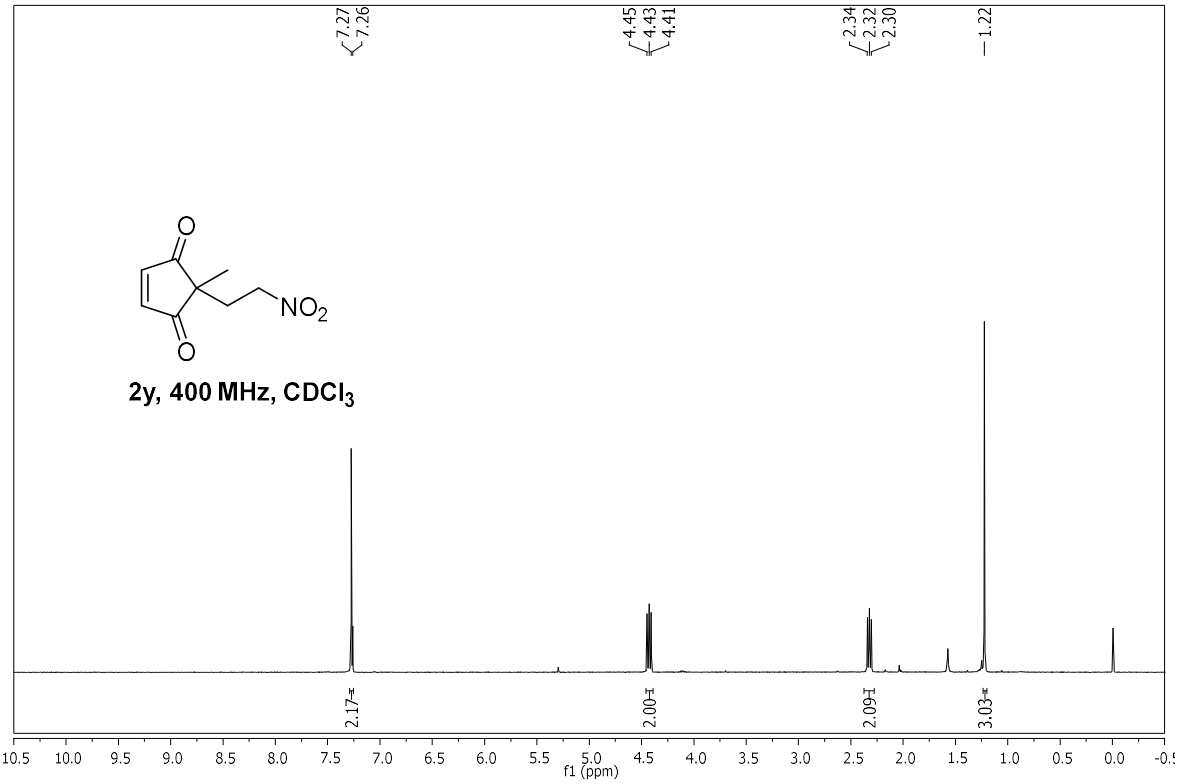


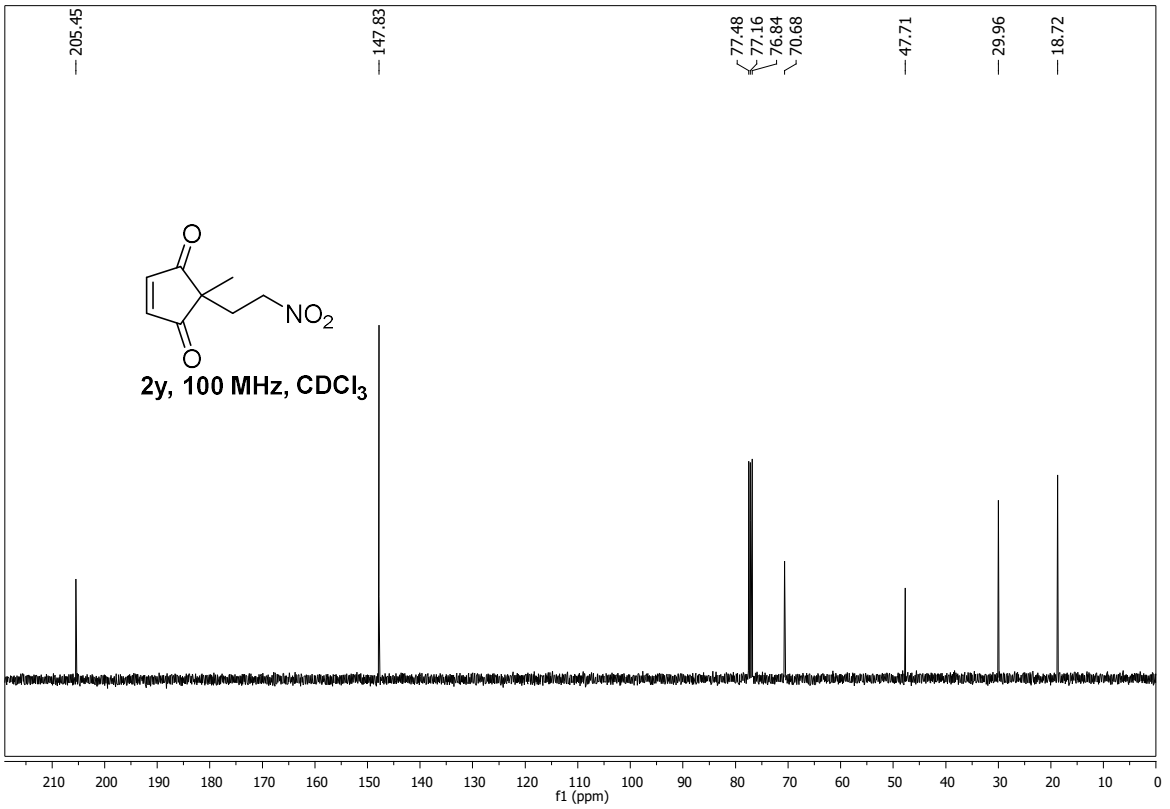
2-(Furan-2-ylmethyl)-2-(2-nitroethyl)cyclopentane-1,3-dione (2w)



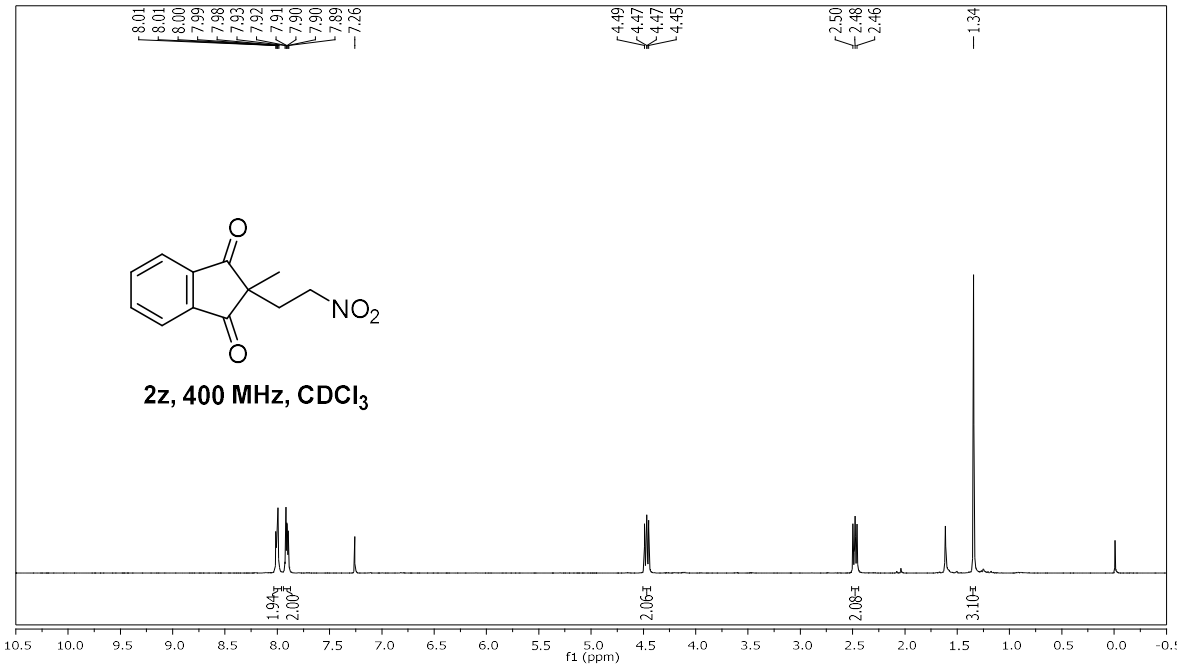


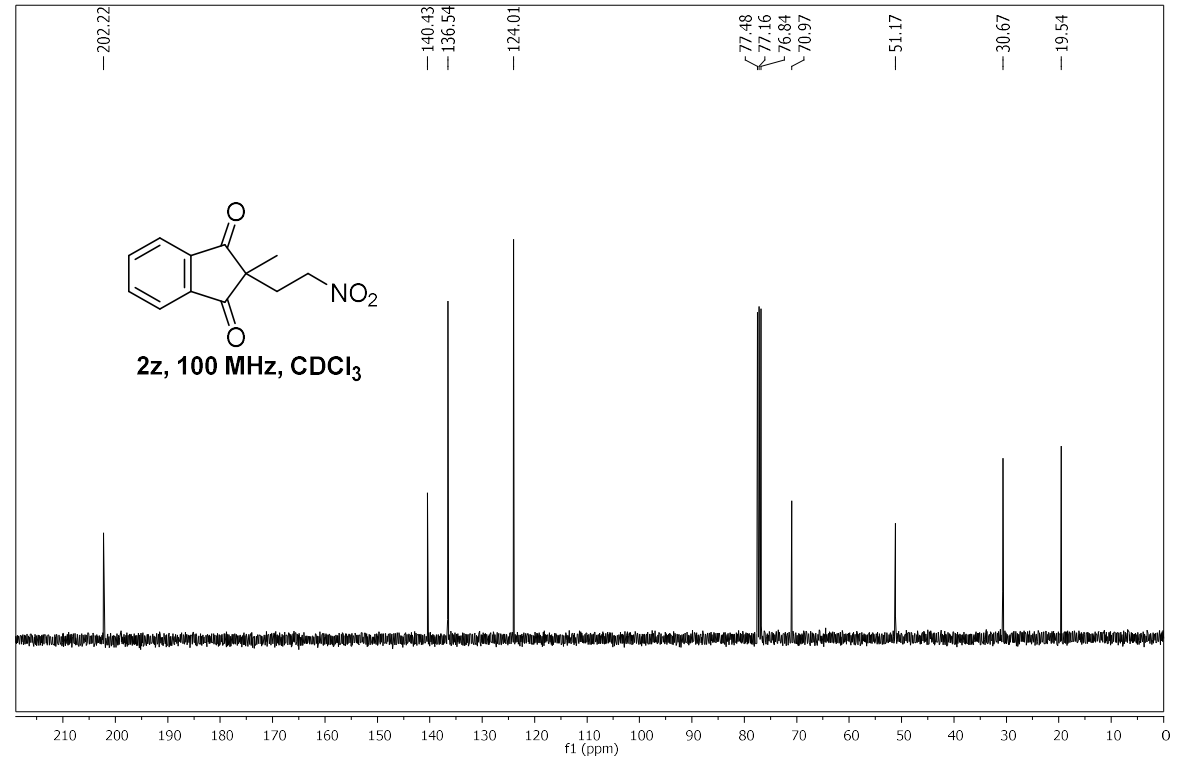
2-Methyl-2-(2-nitroethyl)cyclopent-4-ene-1,3-dione (2y)





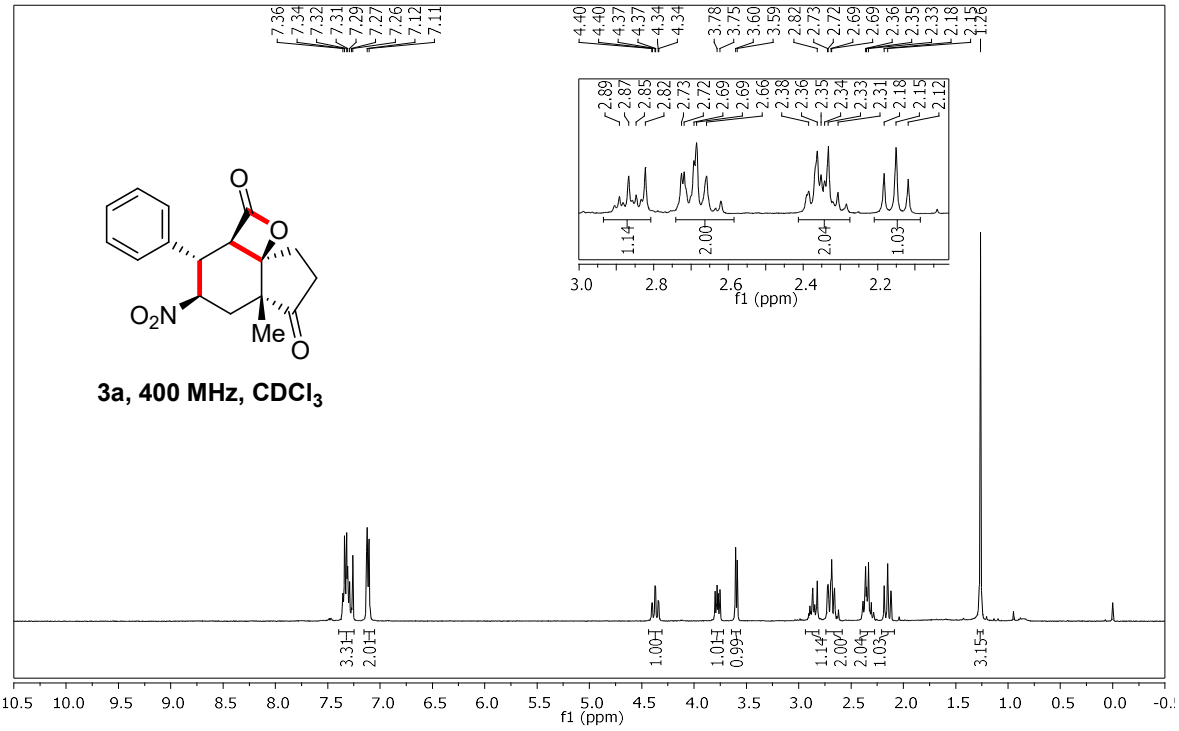
2-Methyl-2-(2-nitroethyl)-1*H*-indene-1,3(2*H*)-dione (2z)

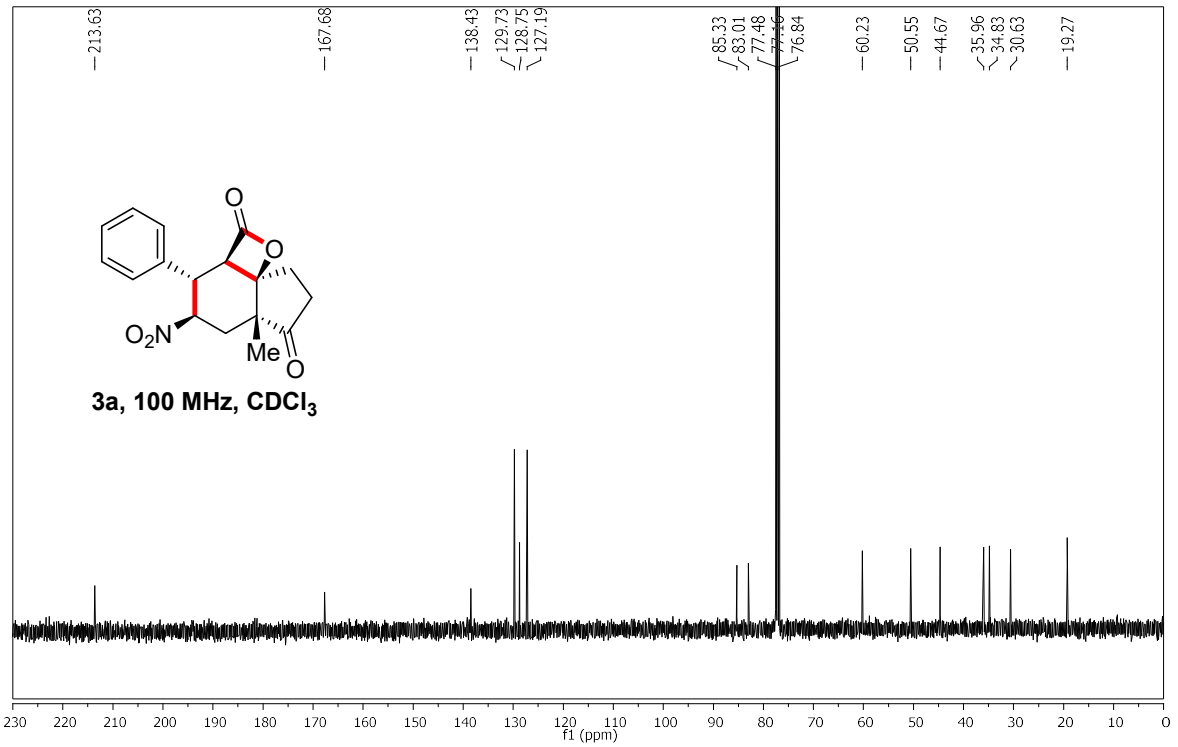




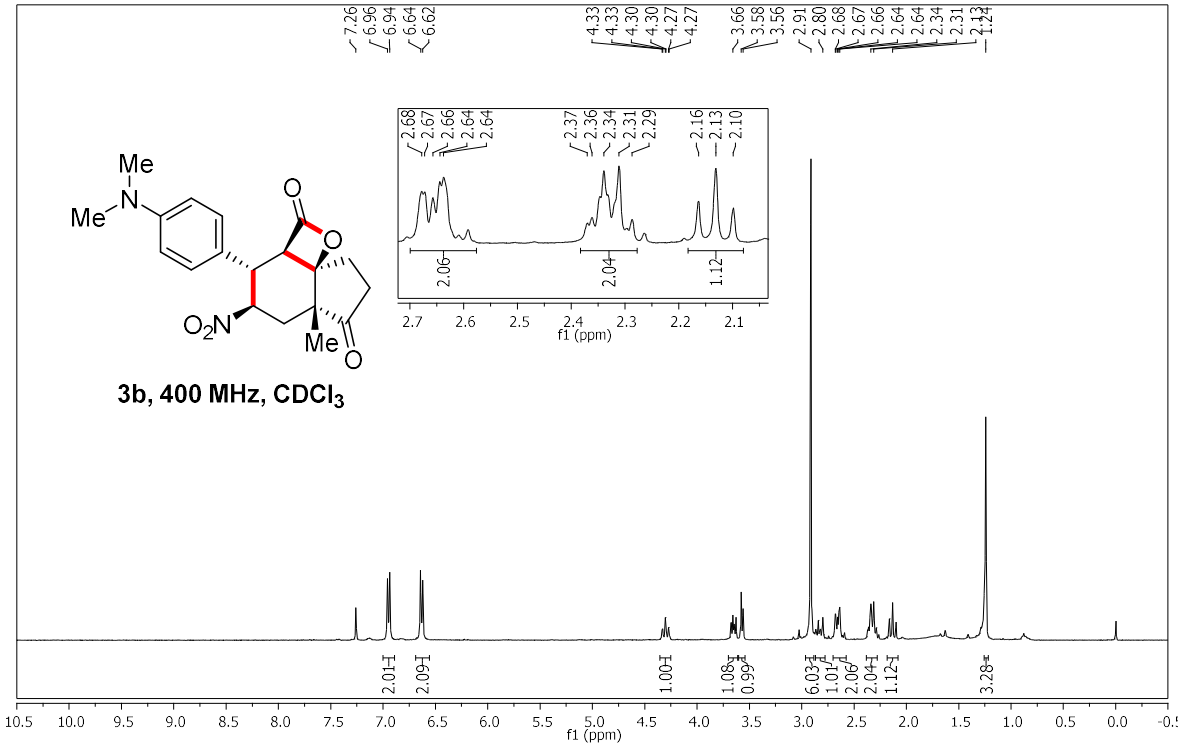
9. ^{1}H and ^{13}C NMR Spectra of Tricyclic β-Lactone Derivatives

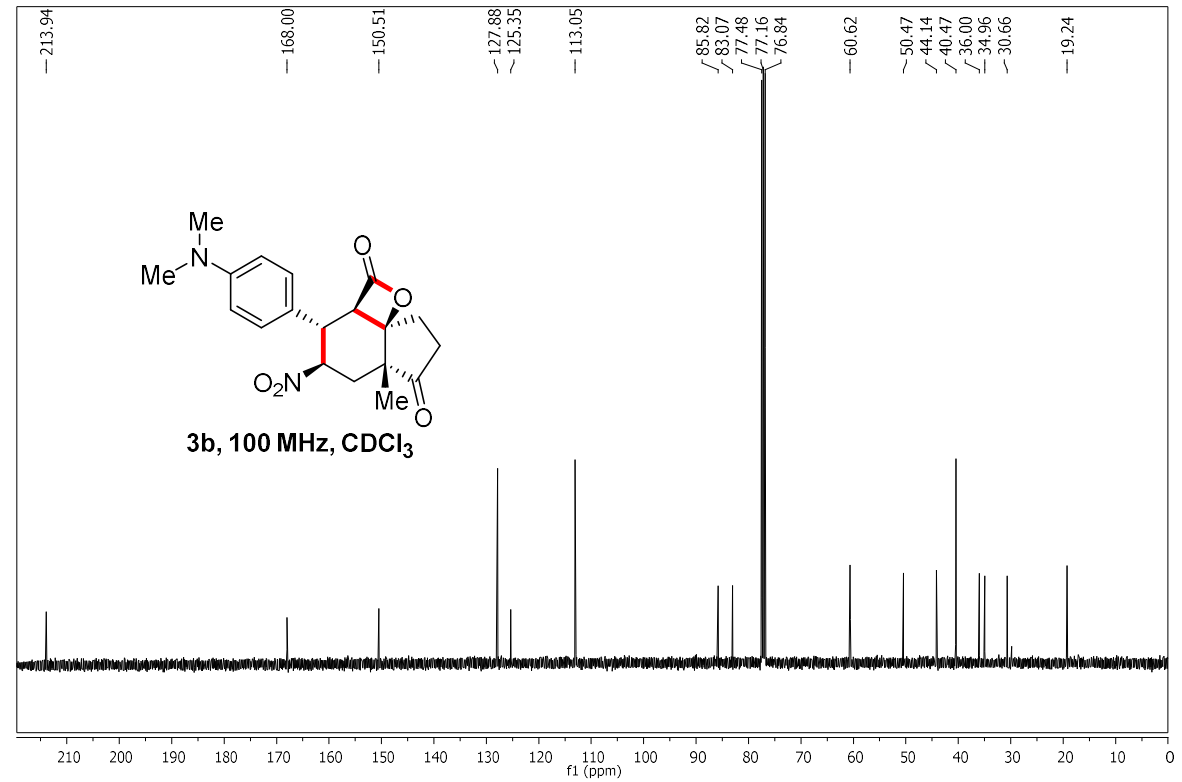
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5*a*-Methyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete2,6(2a*H*)-dione (3a)



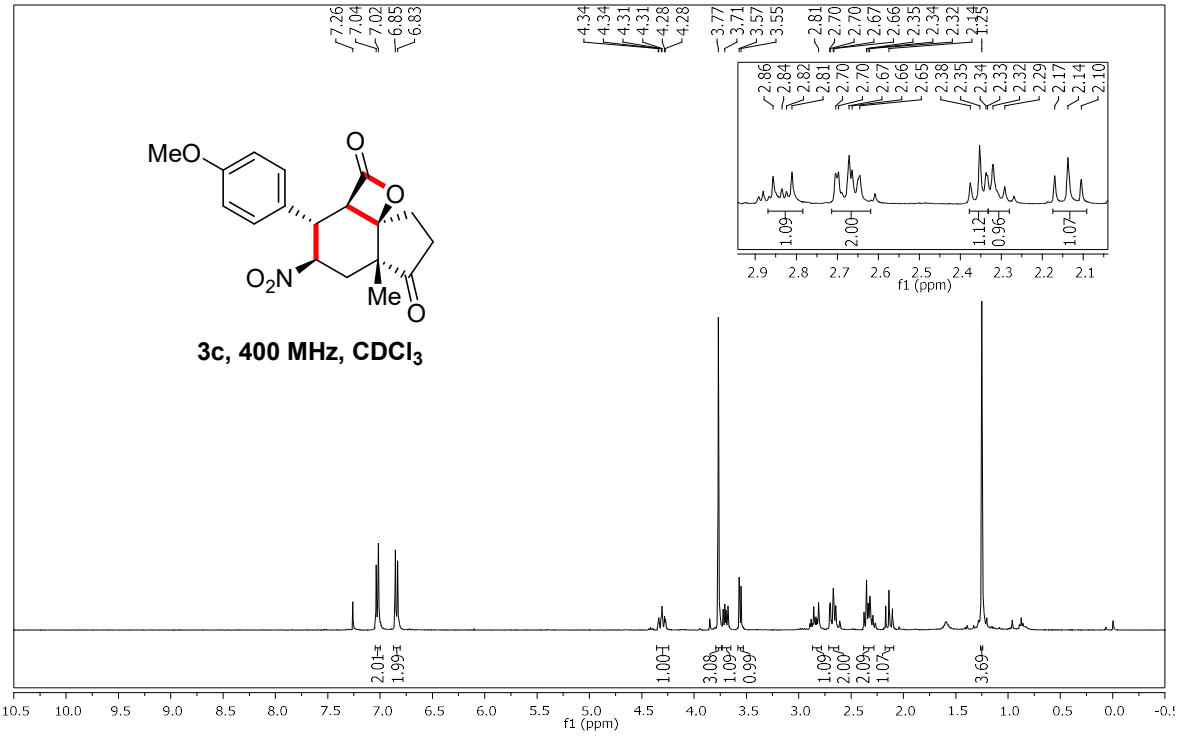


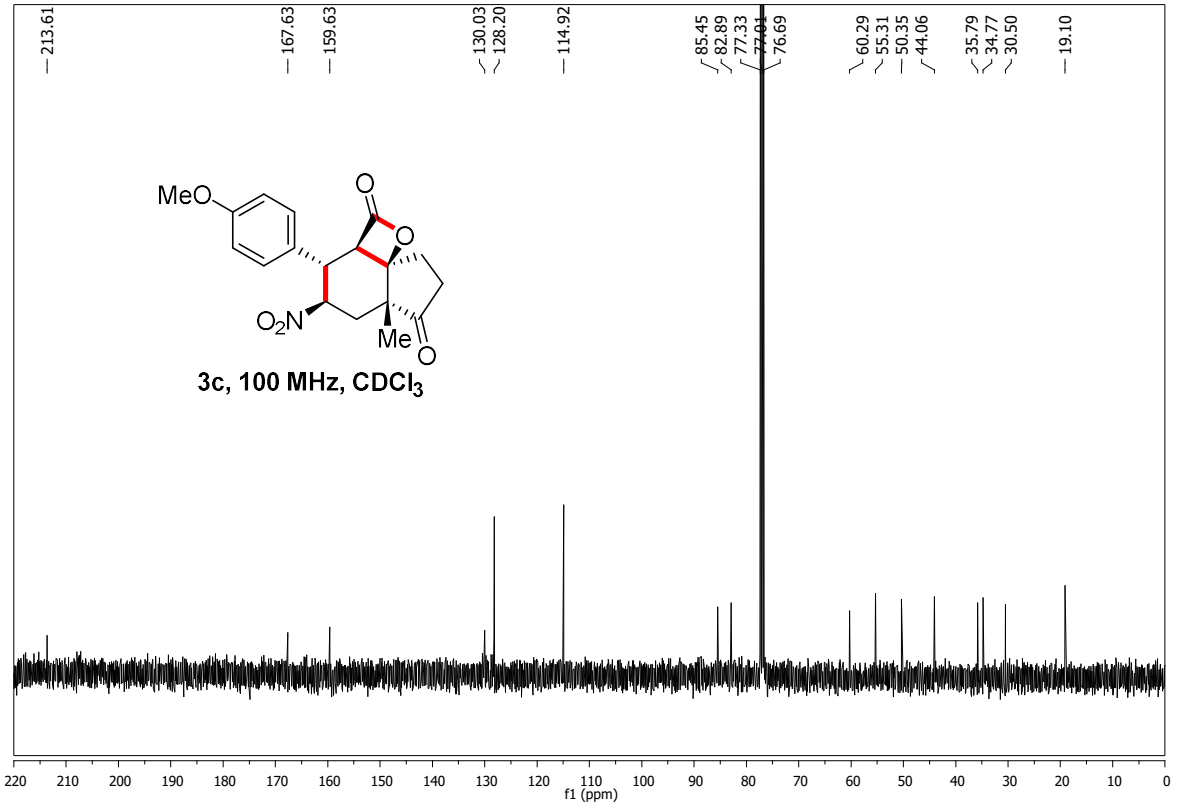
2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-(Dimethylamino)phenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3b)



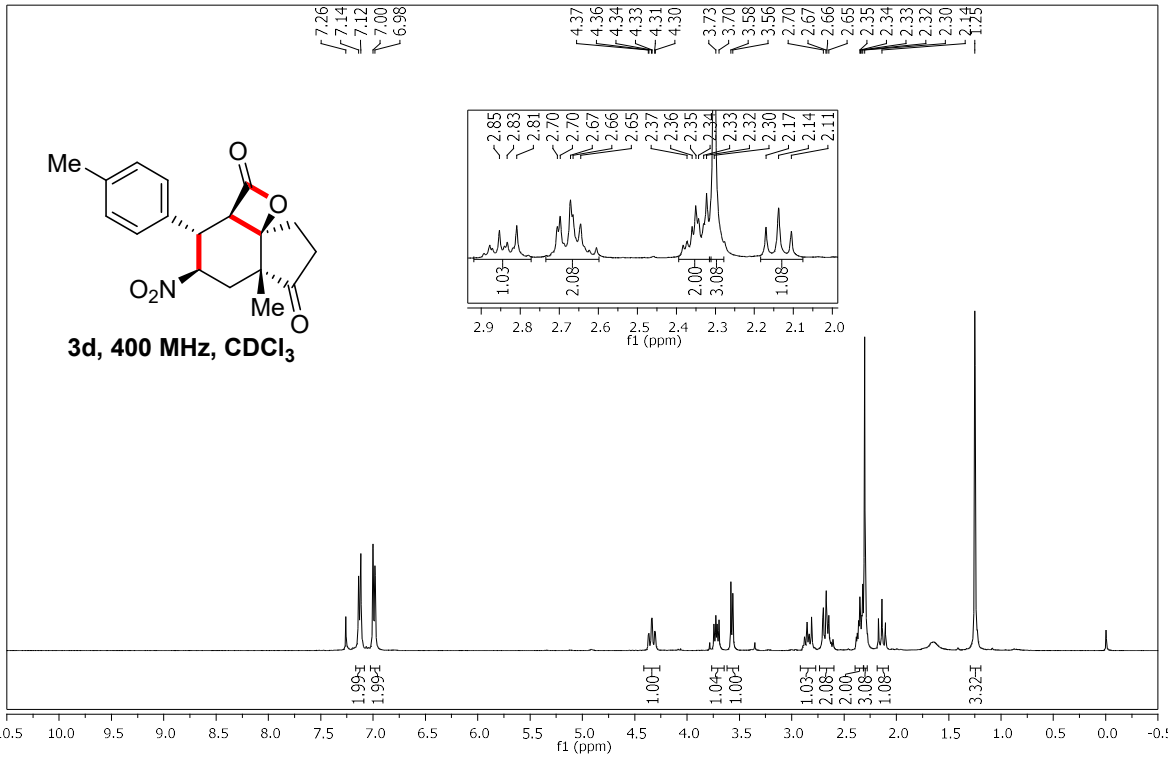


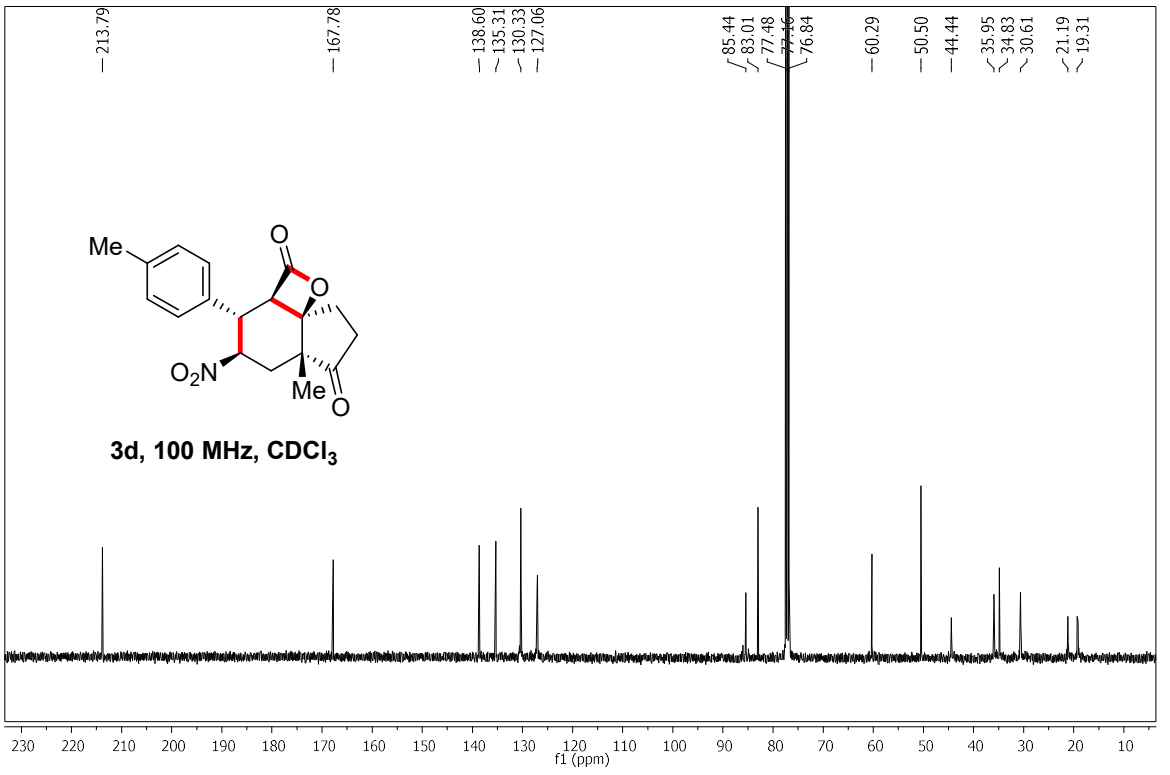
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3c)



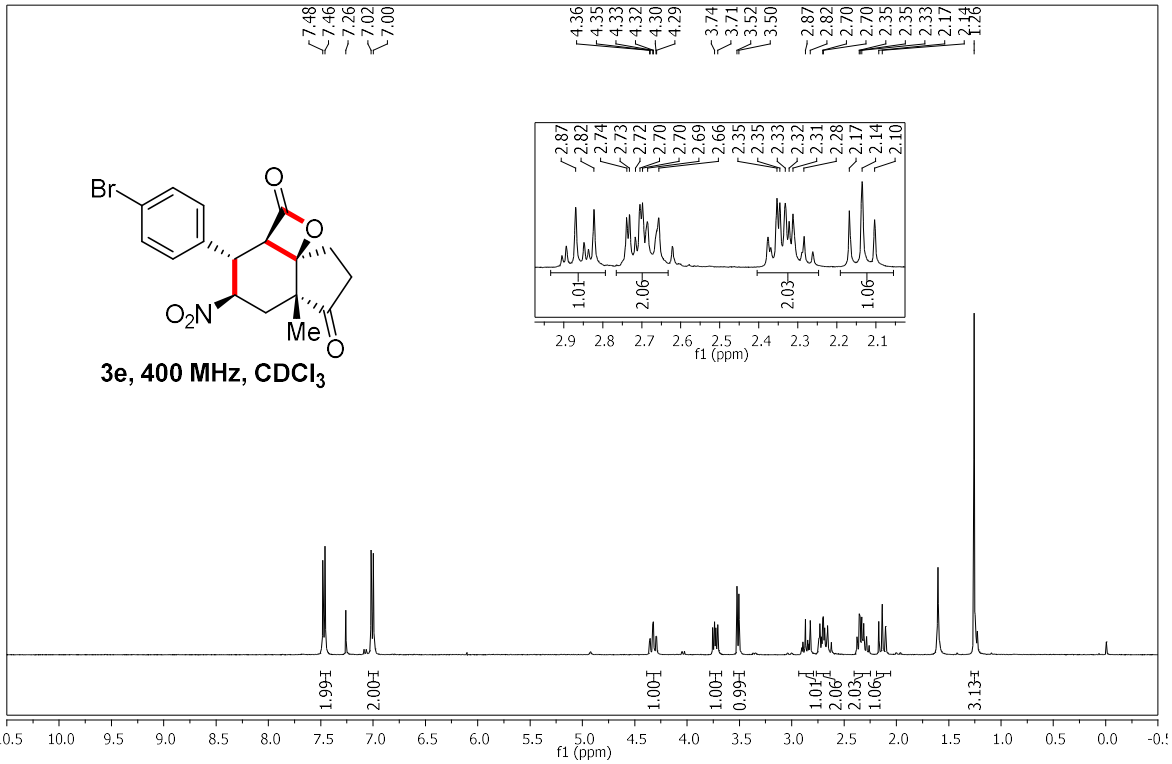


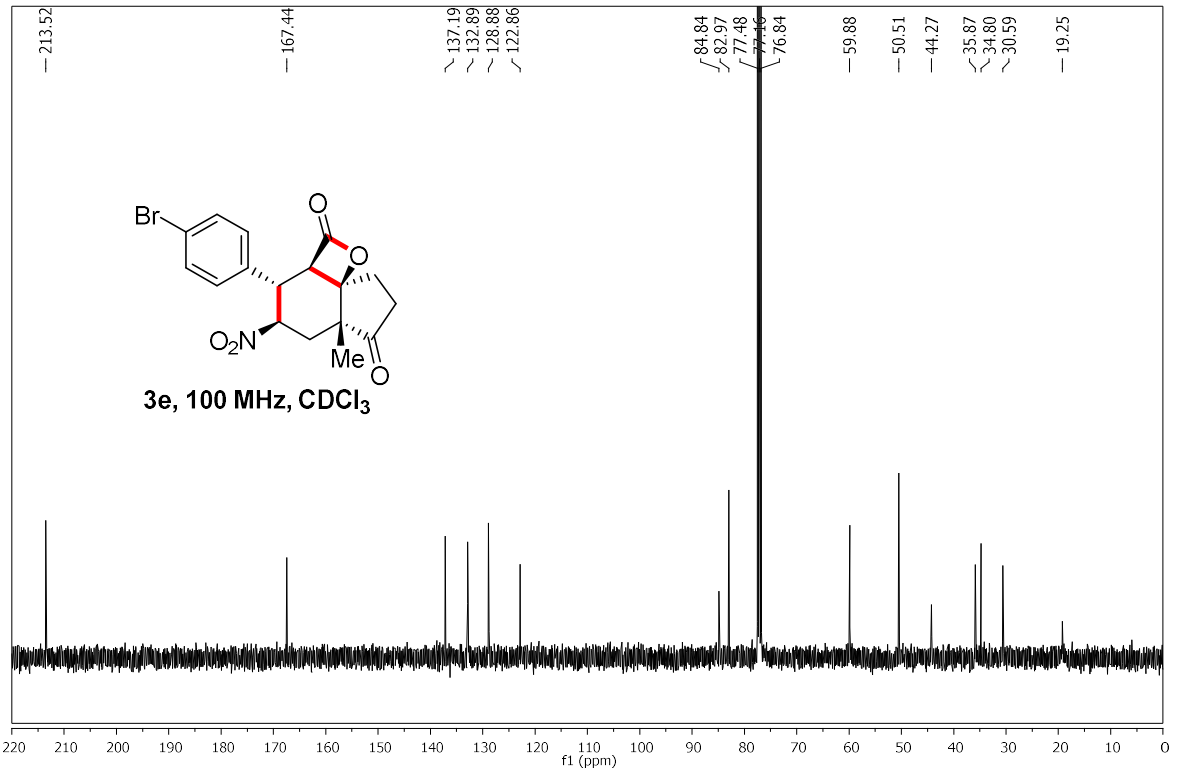
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(p-tolyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3d)



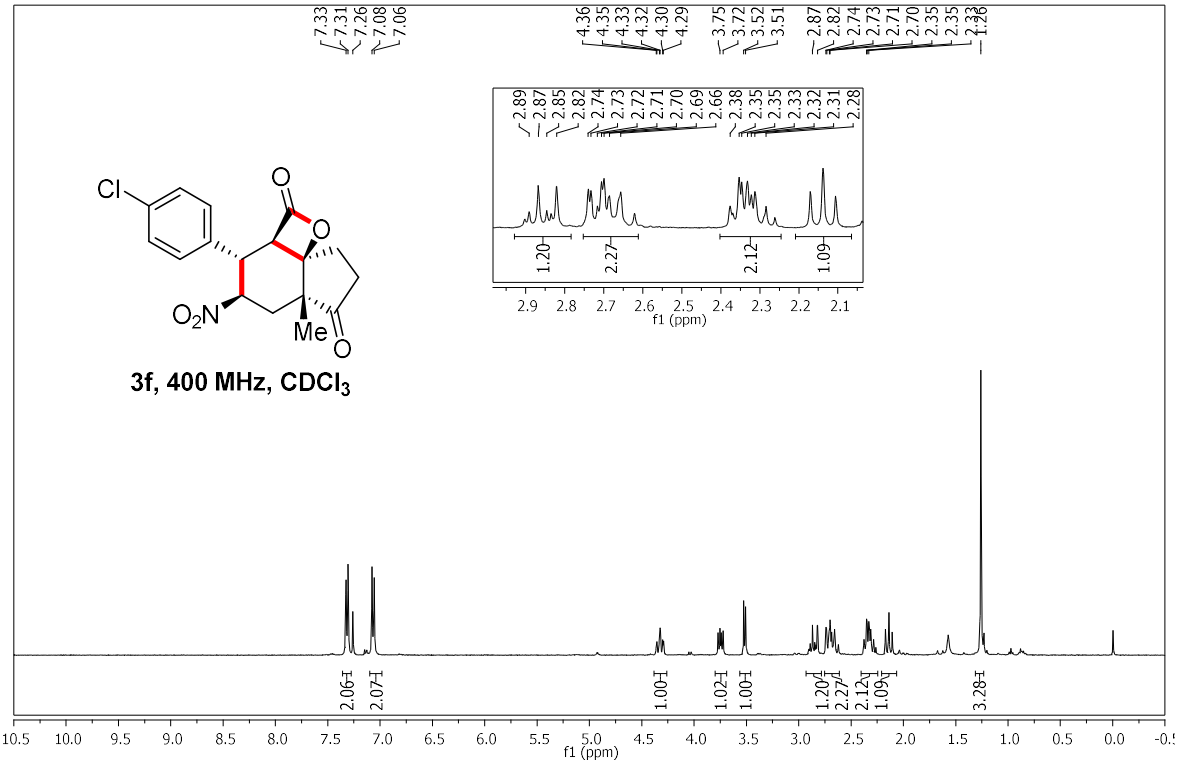


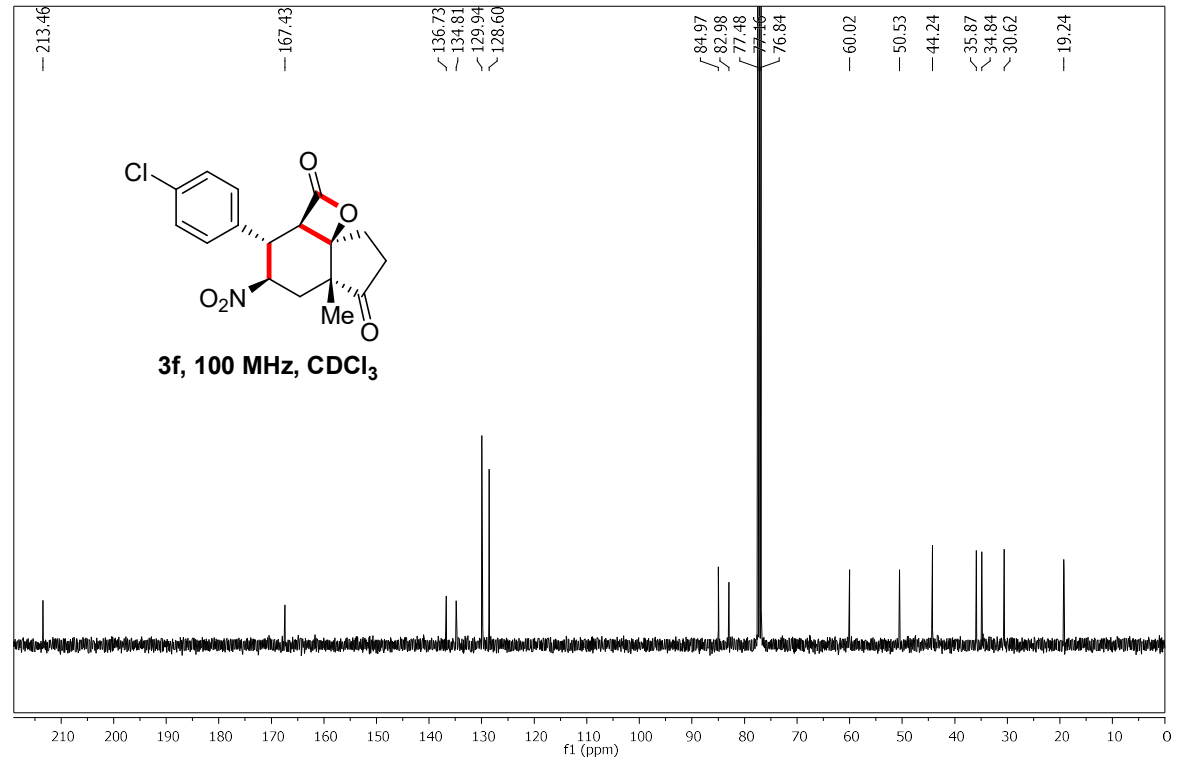
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Bromophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3e)



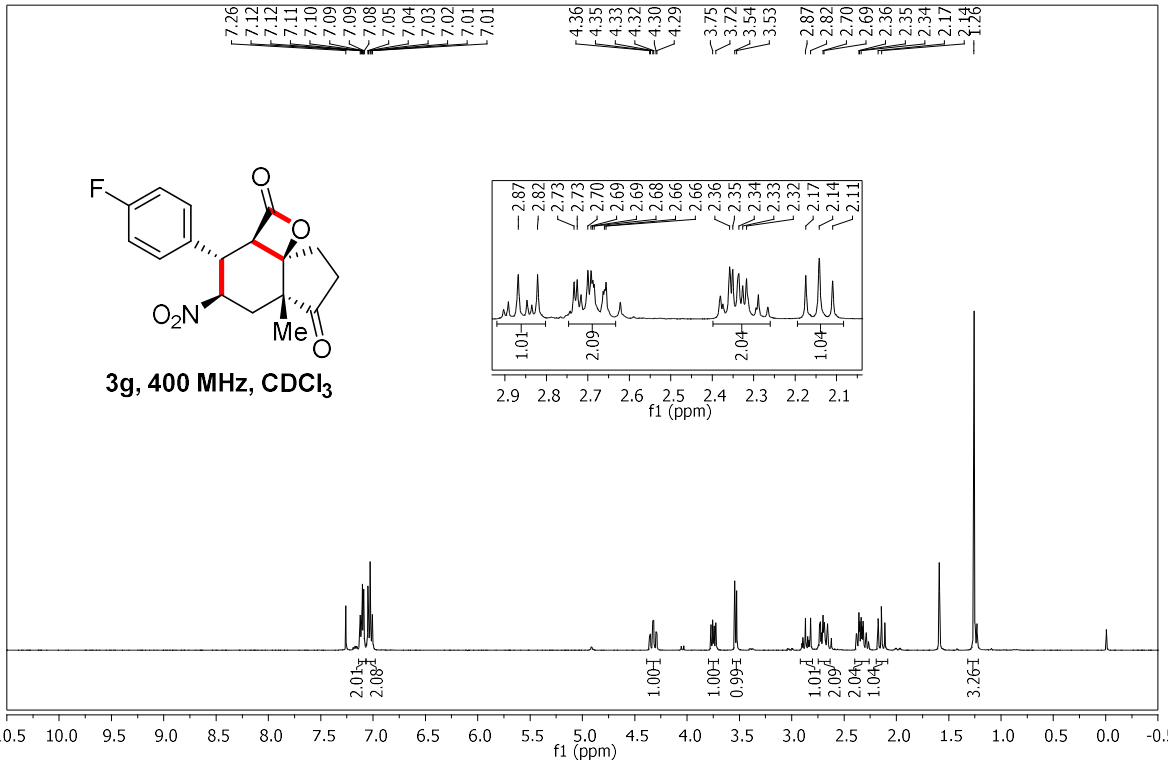


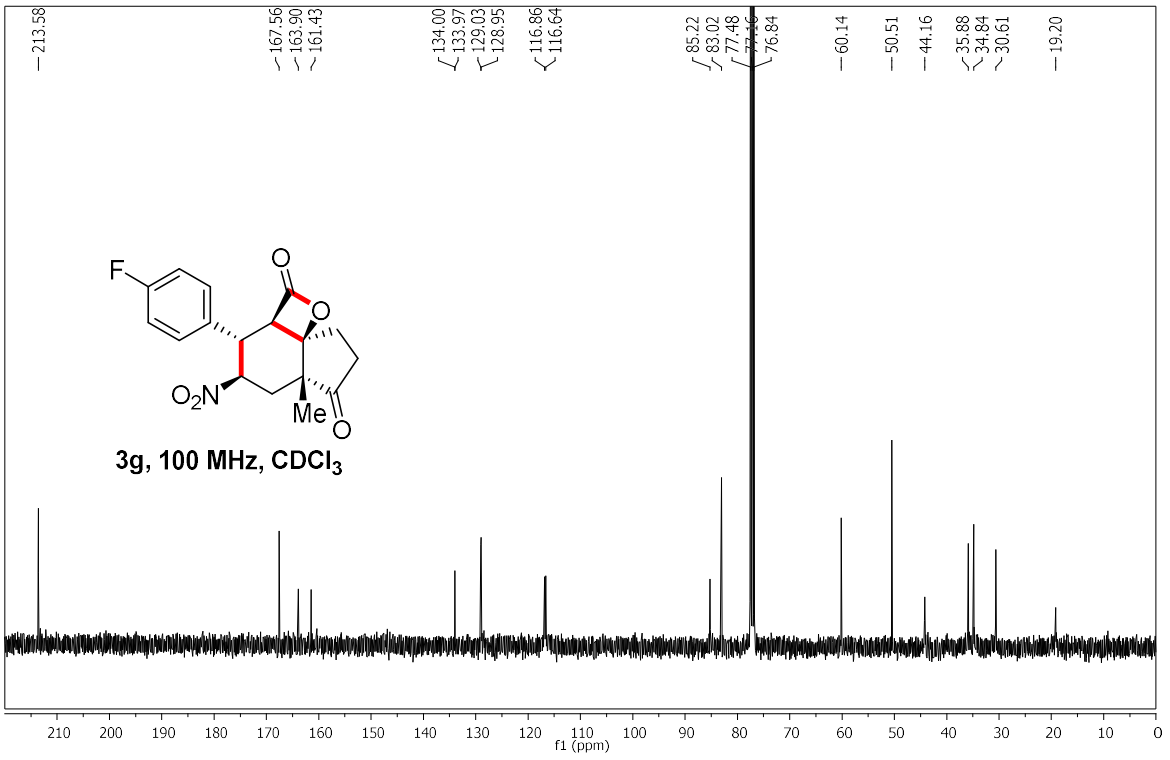
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Chlorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-b]oxete-2,6(2a*H*)-dione (3f)



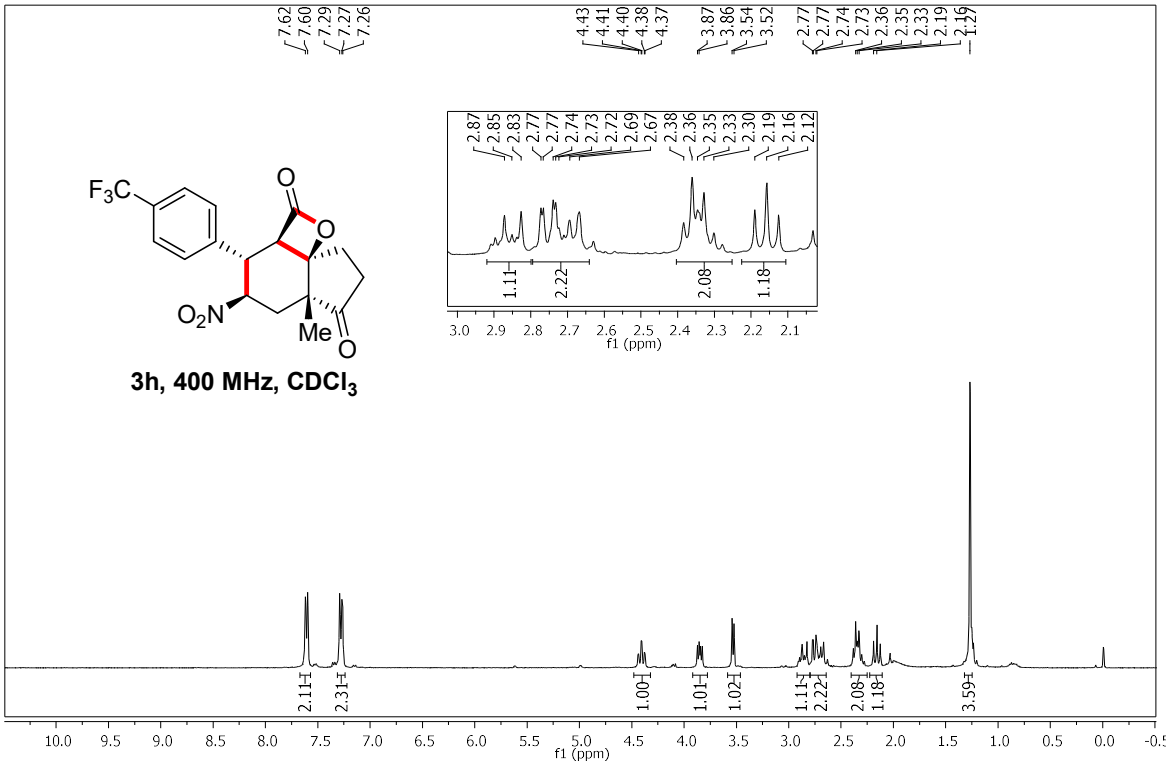


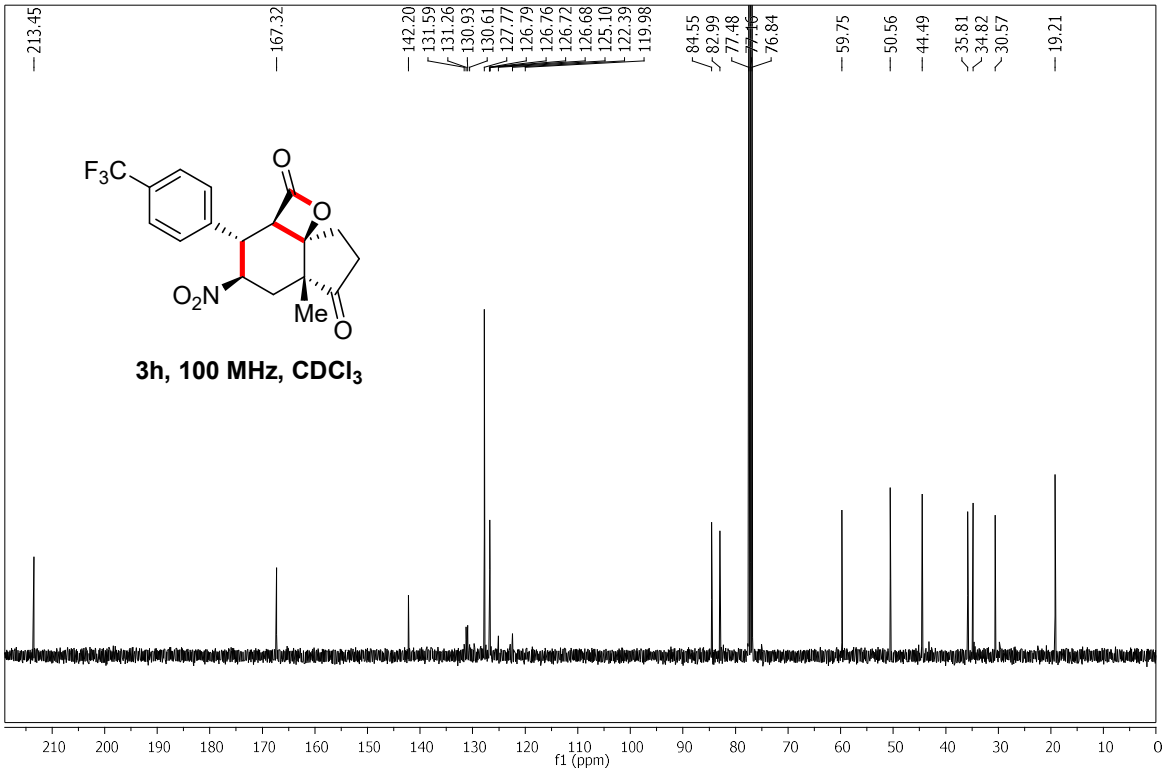
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Fluorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3g)



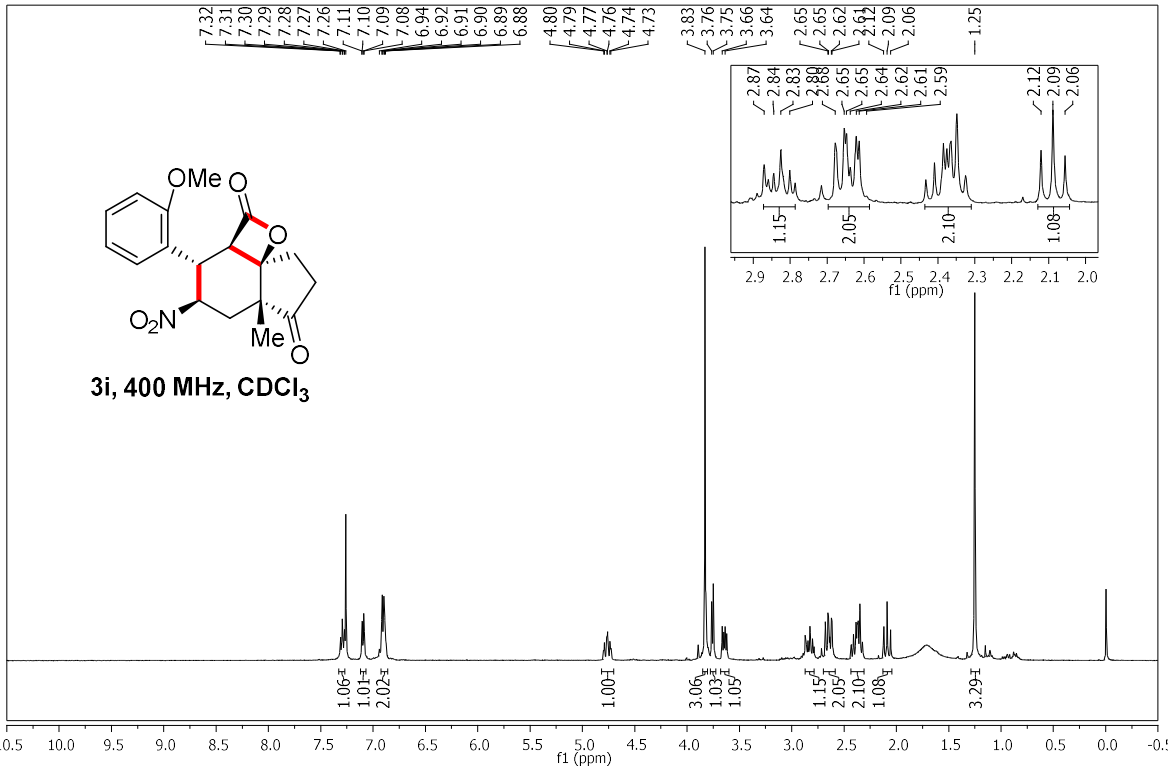


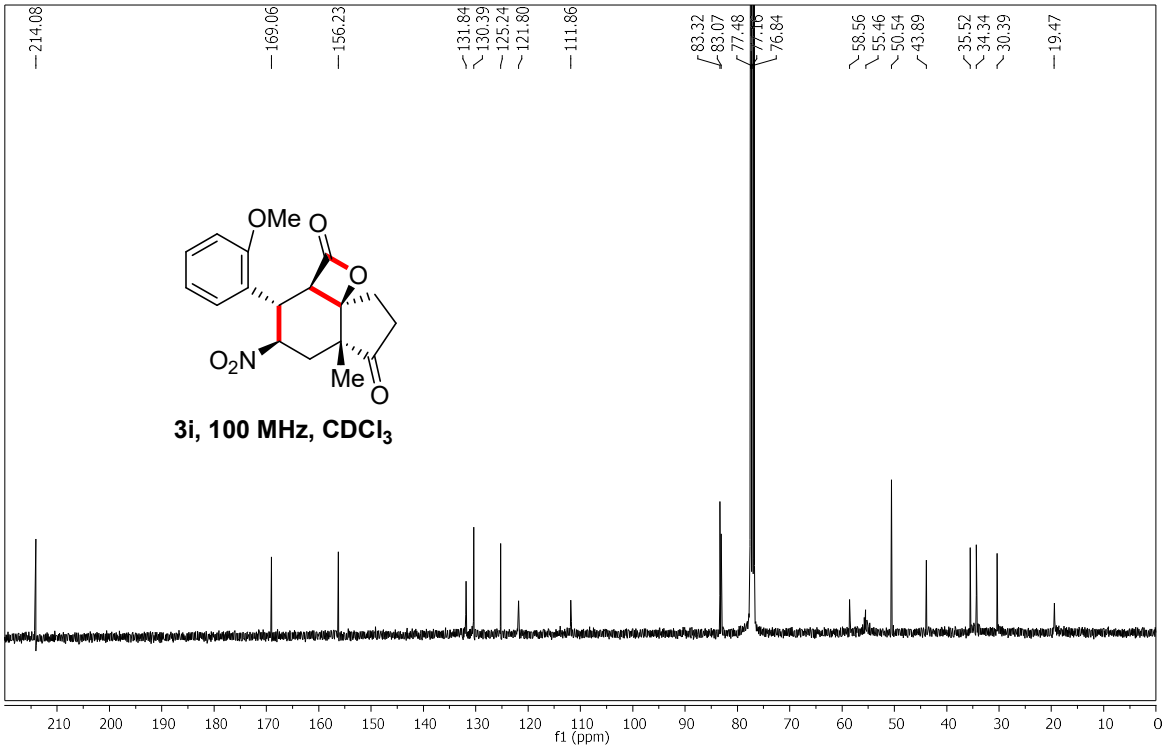
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(4-(trifluoromethyl)phenyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3h)



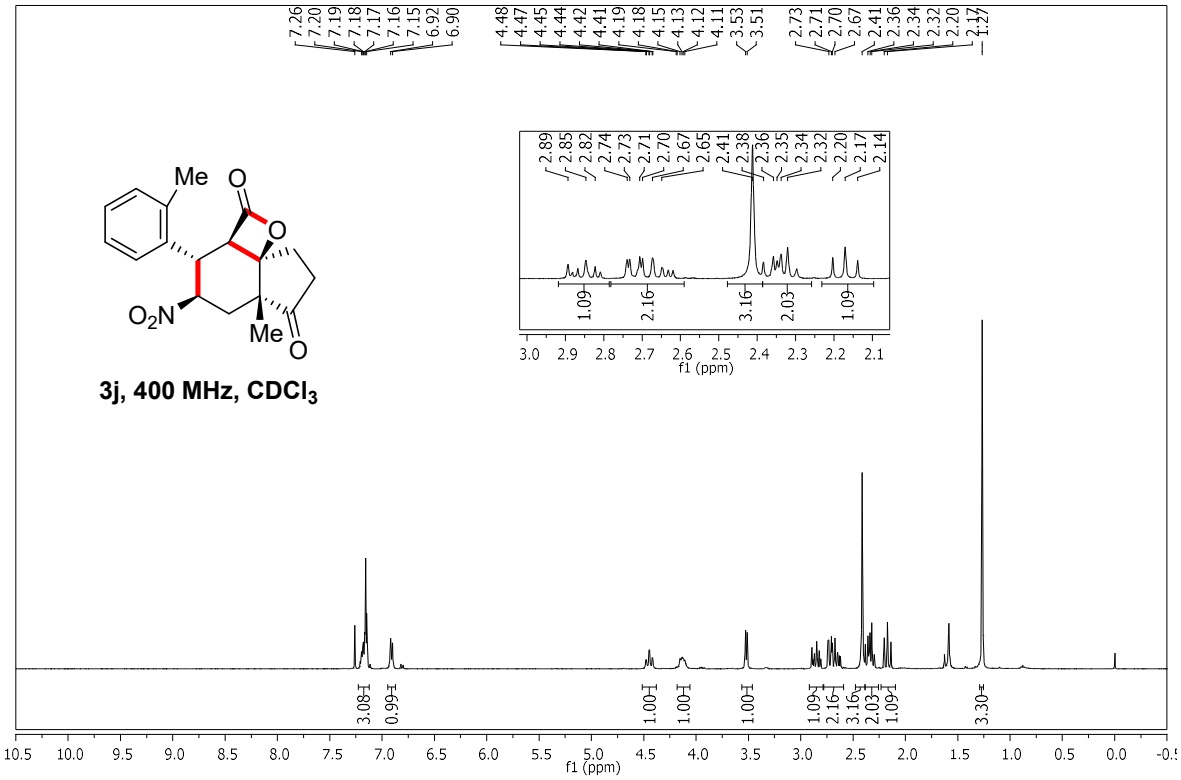


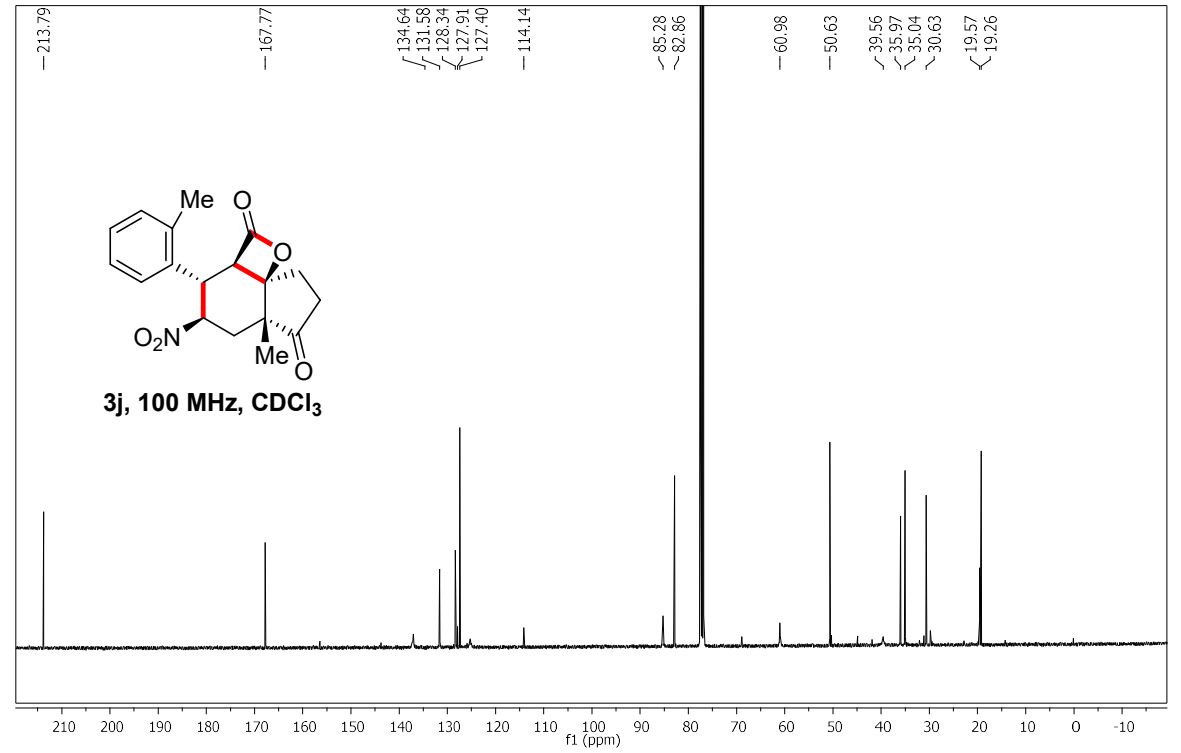
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(2-Methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3i)



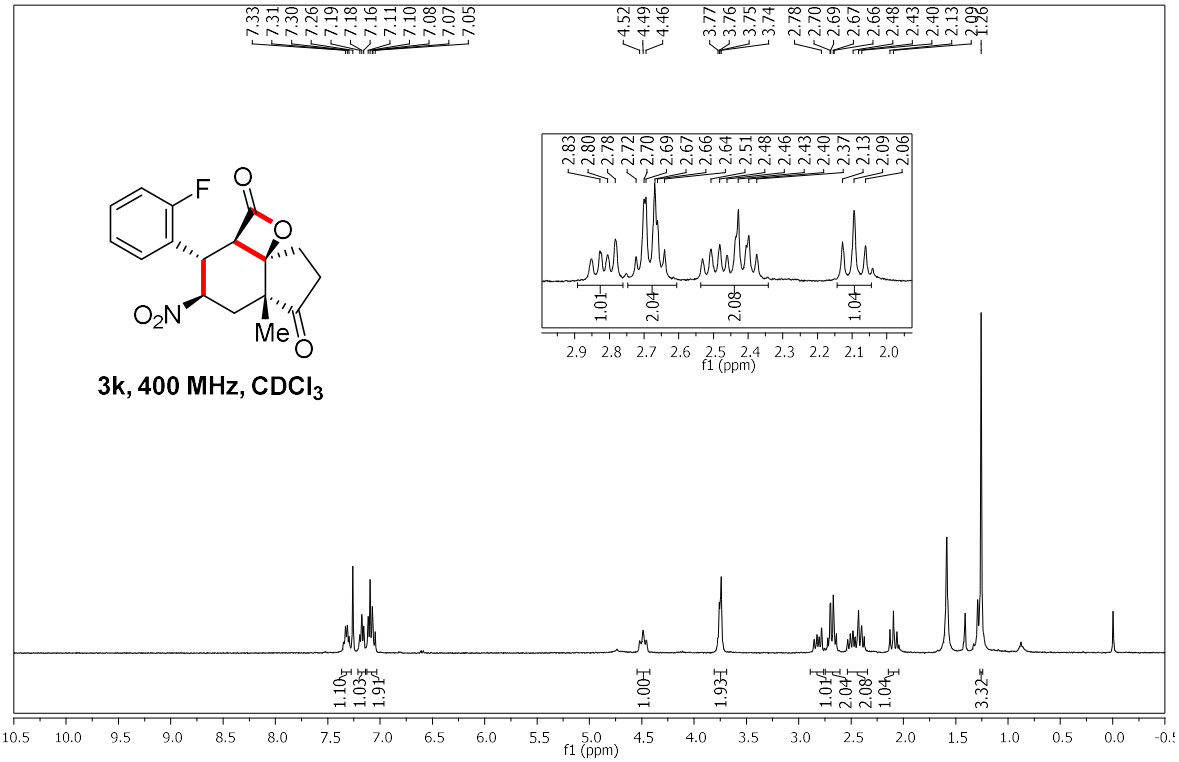


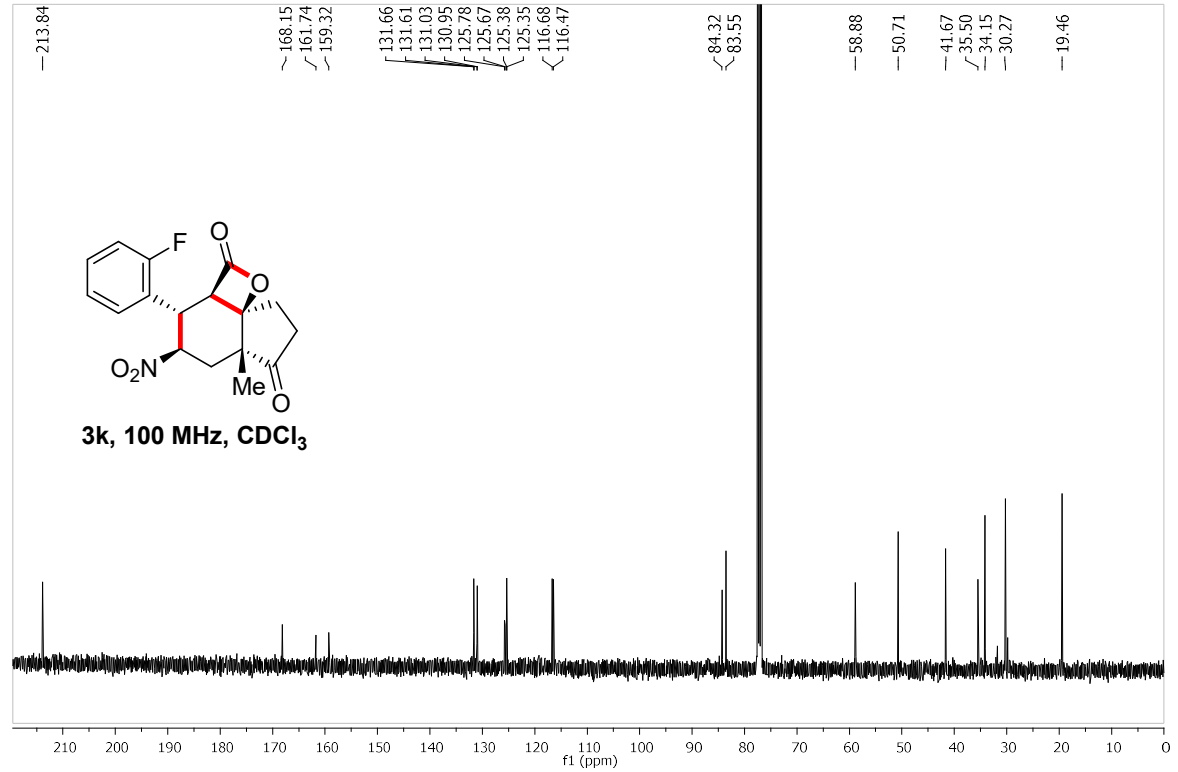
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(o-tolyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3j)



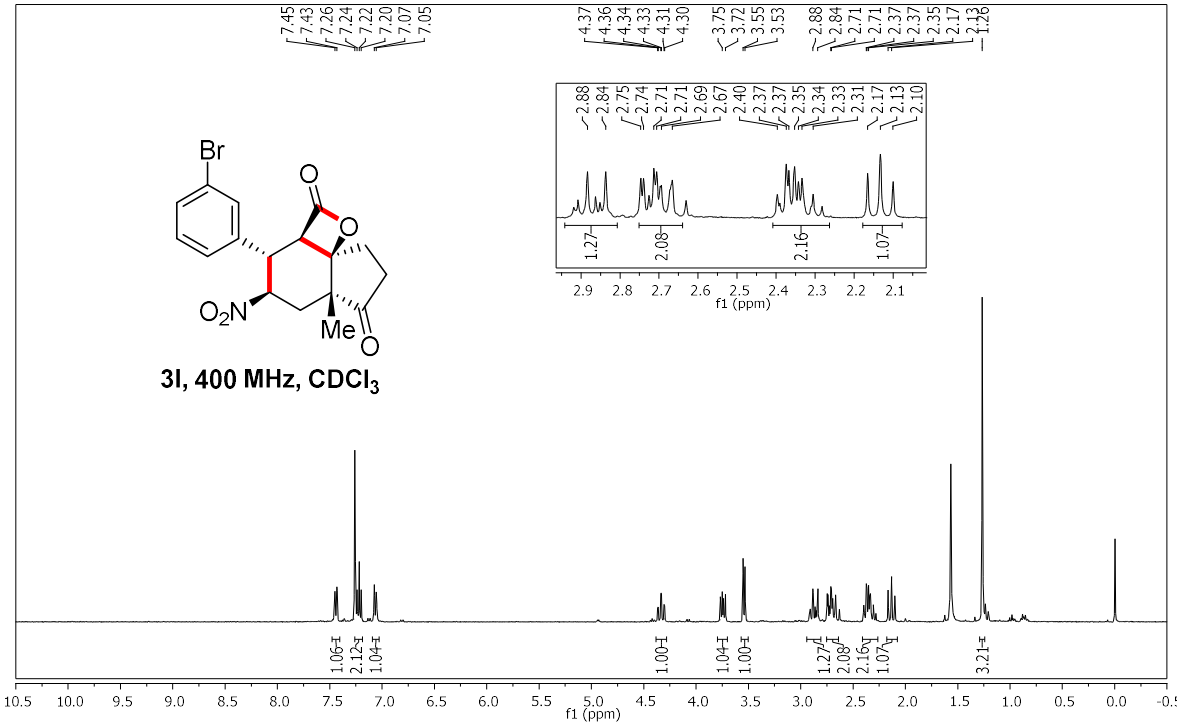


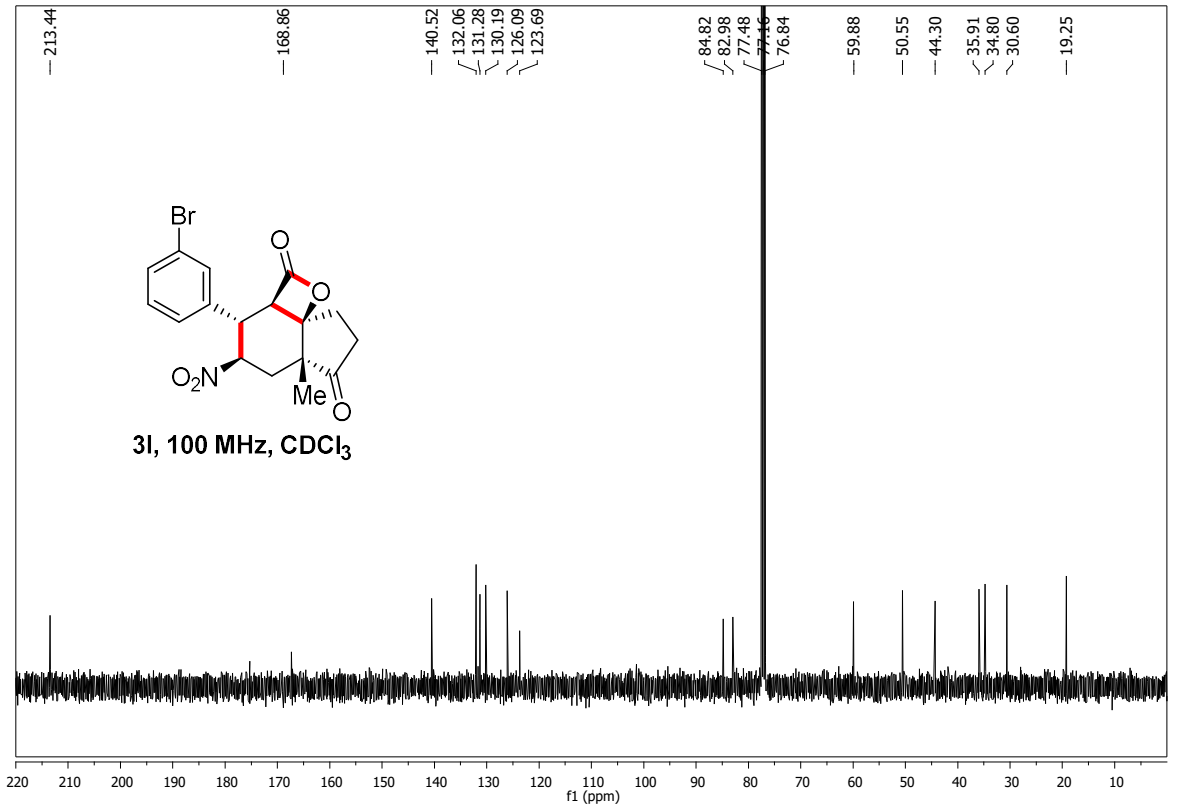
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(2-Fluorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3k)



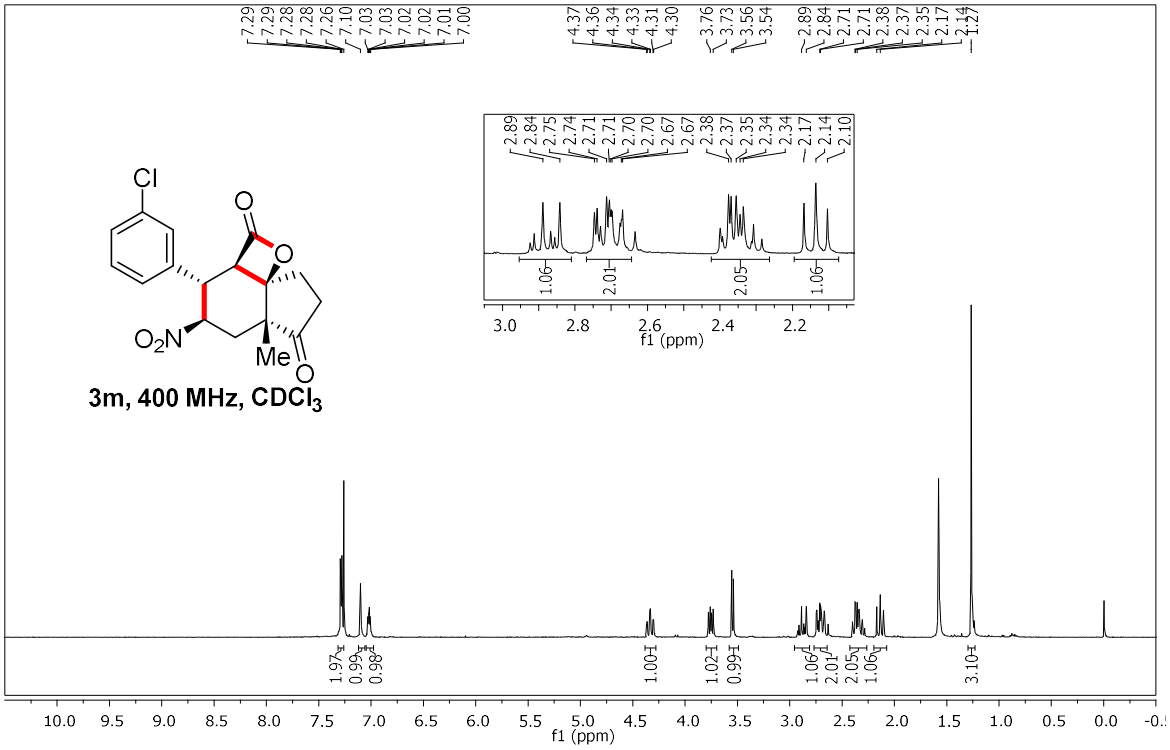


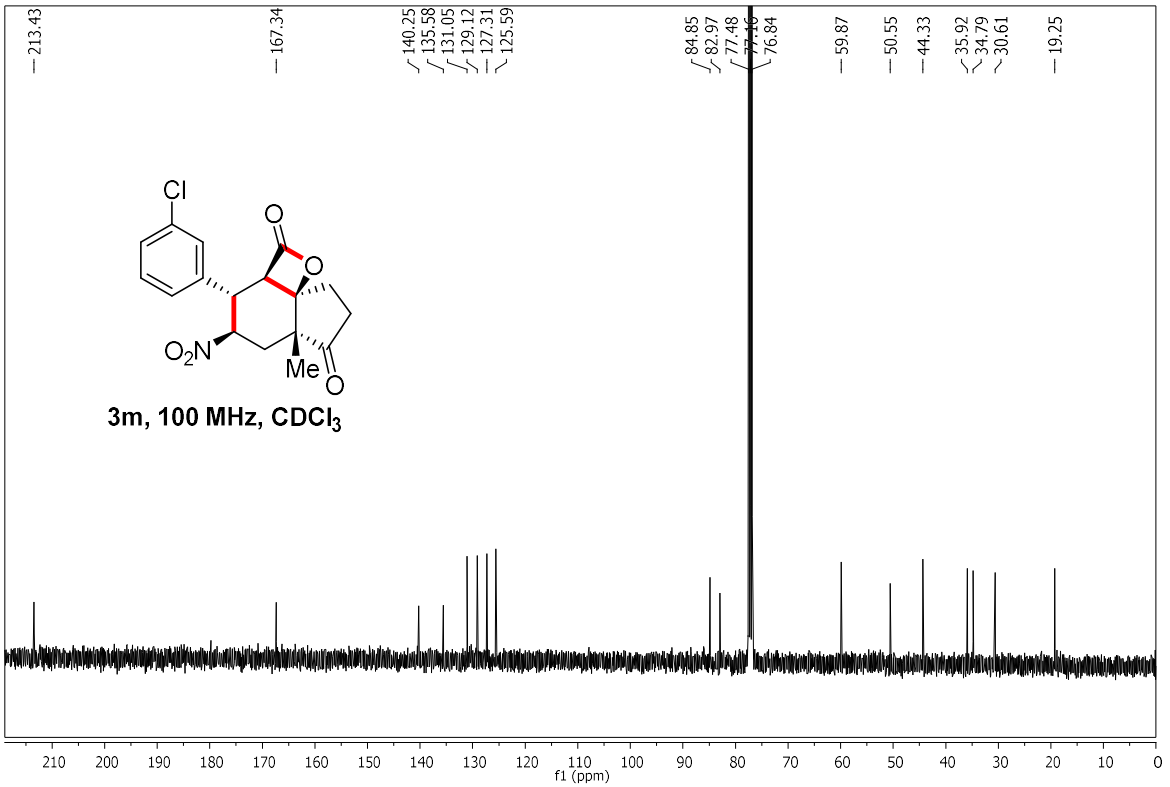
(2*aR*,3*S*,4*R*,5*aR*,8*aR*)-3-(3-Bromophenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione (3l)



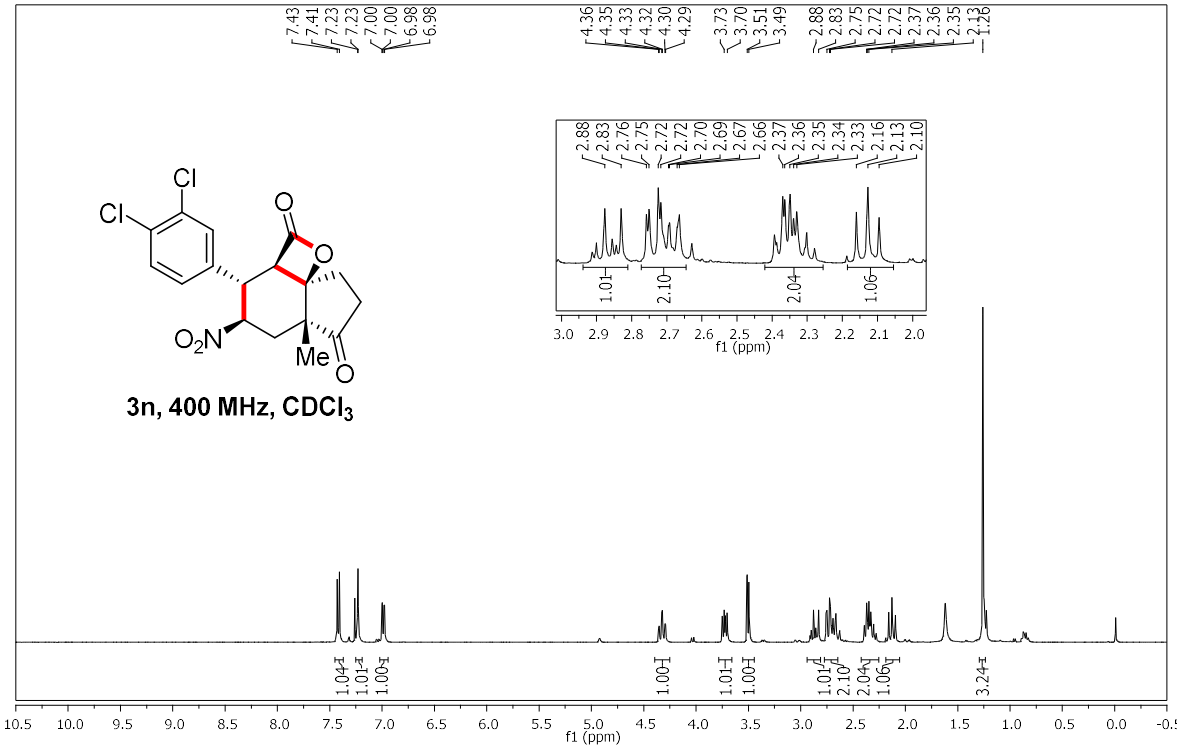


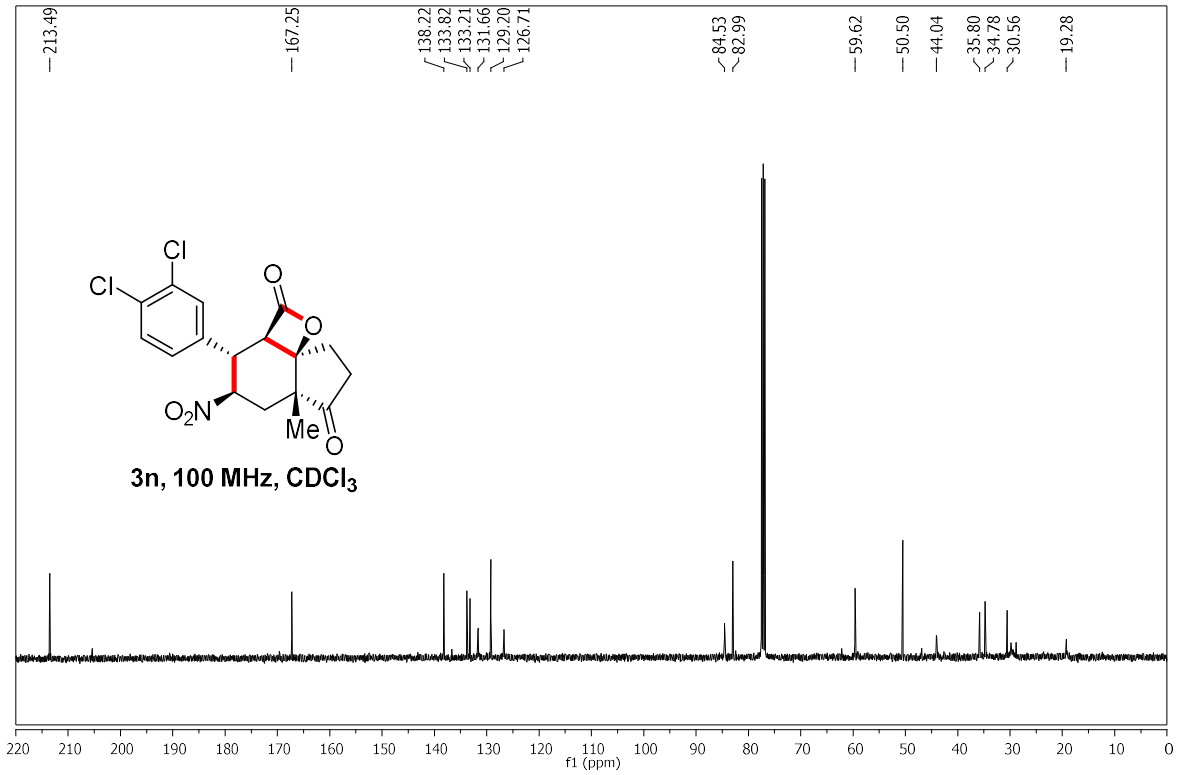
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3Chlorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3m)



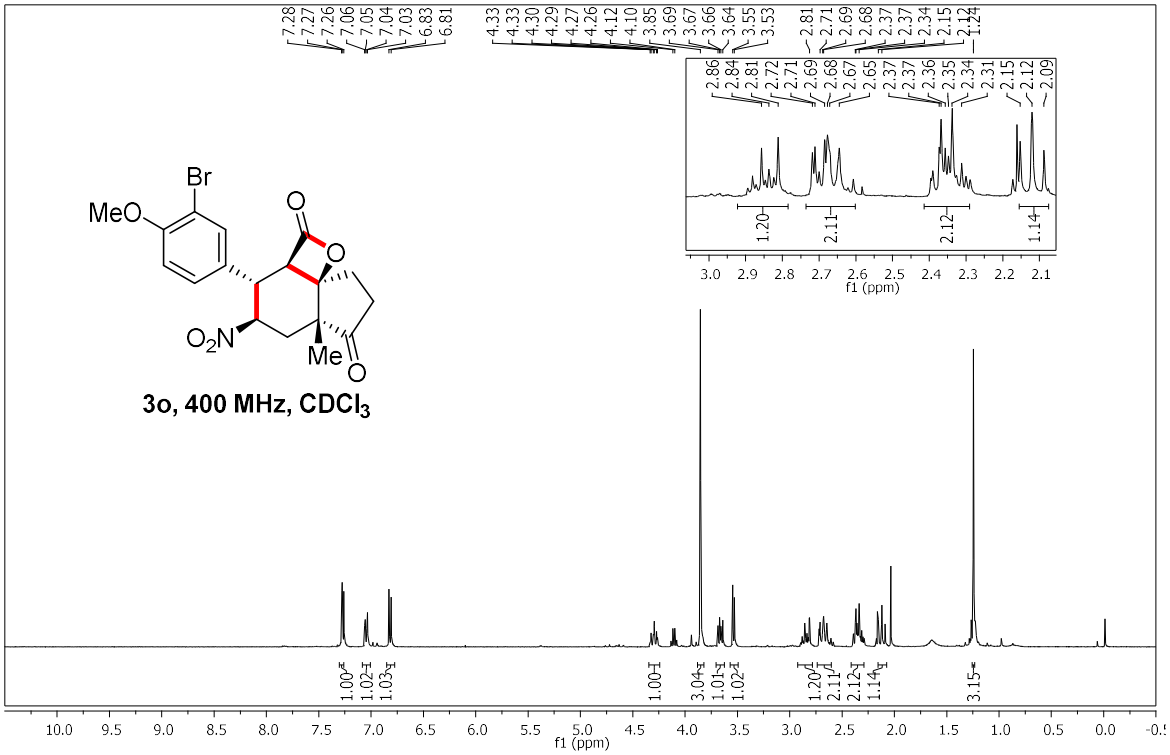


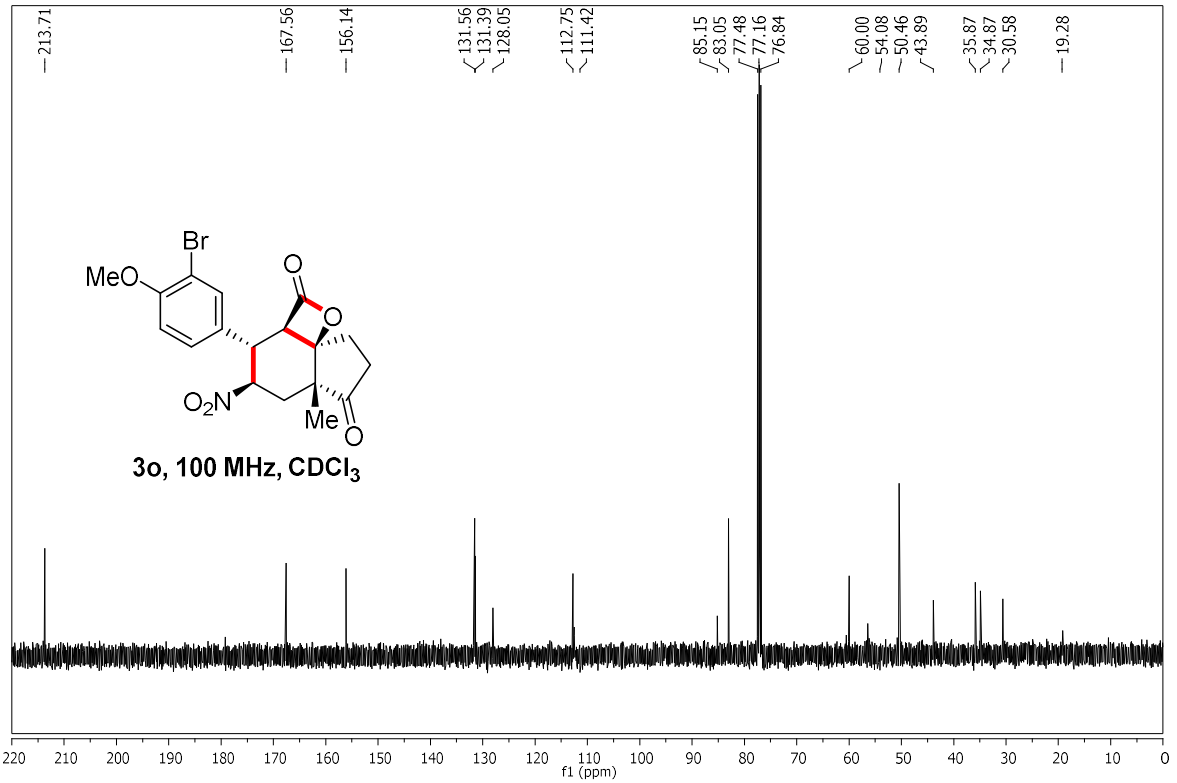
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3,4-Dichlorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3n)



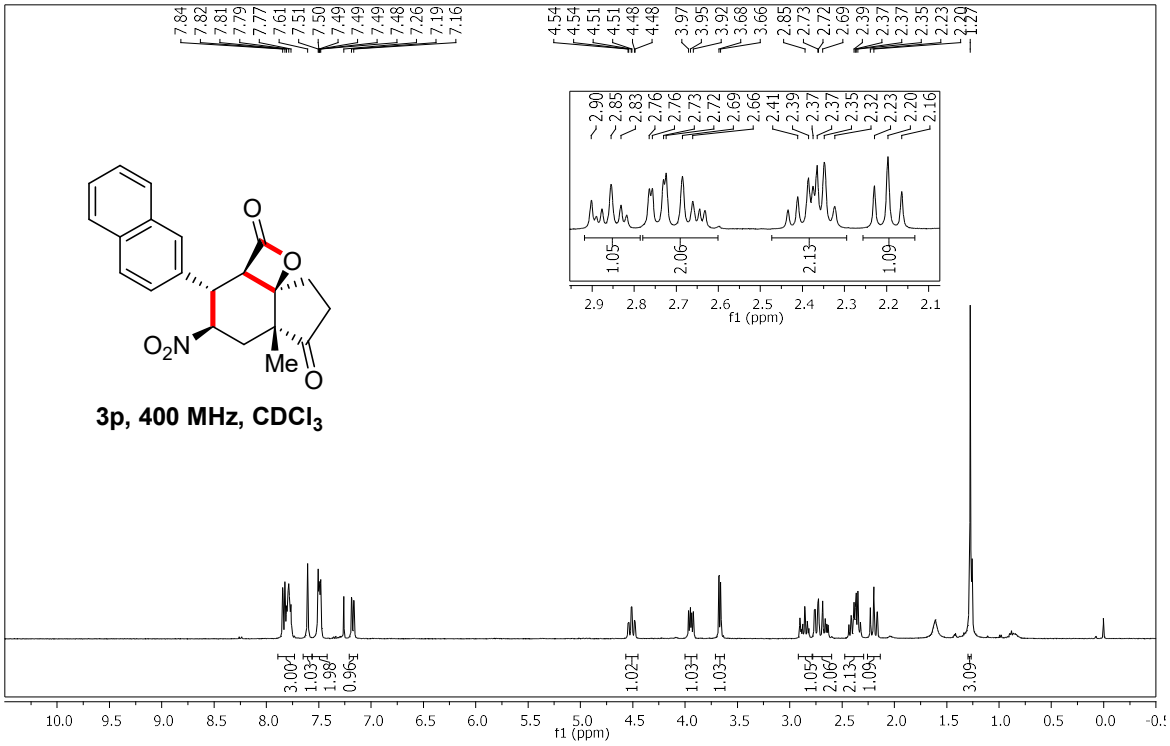


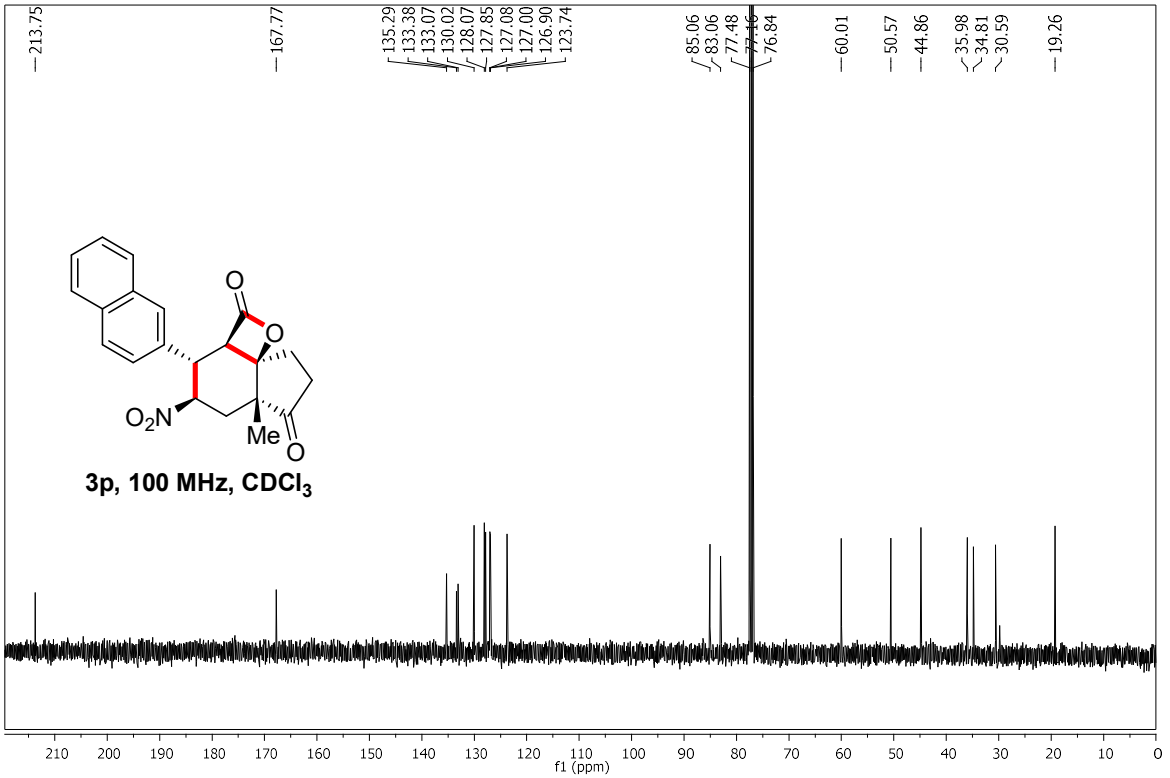
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3-Bromo-4-methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3o)



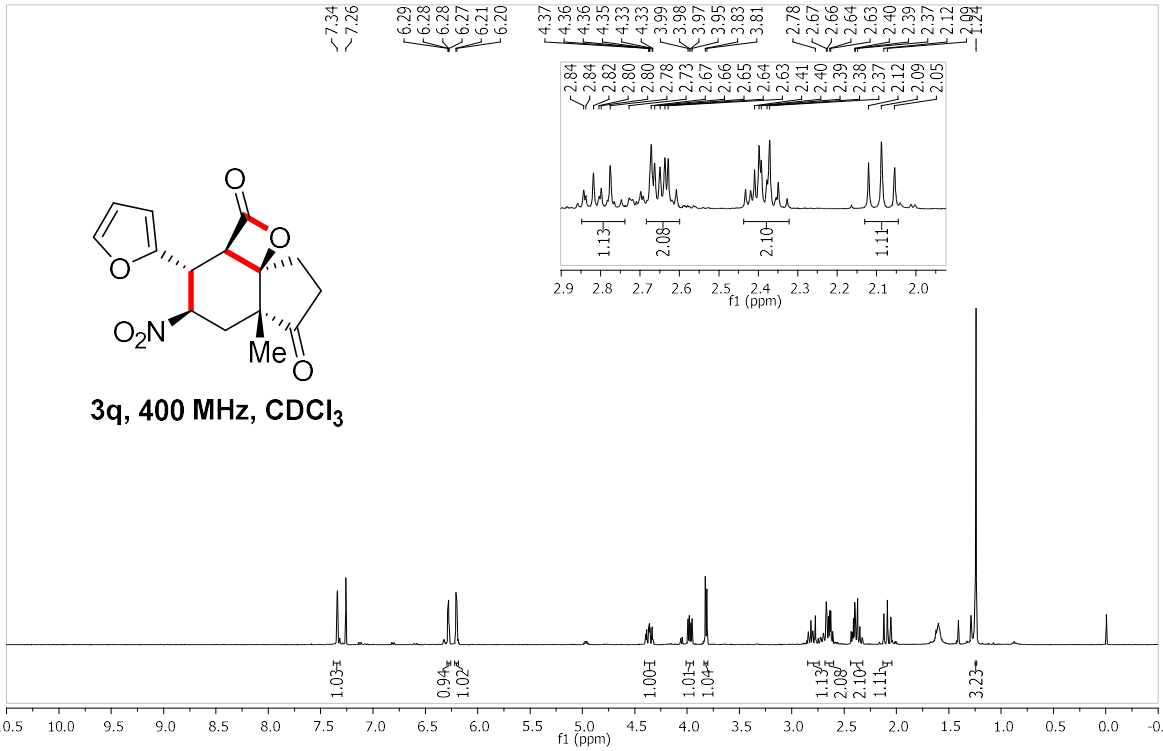


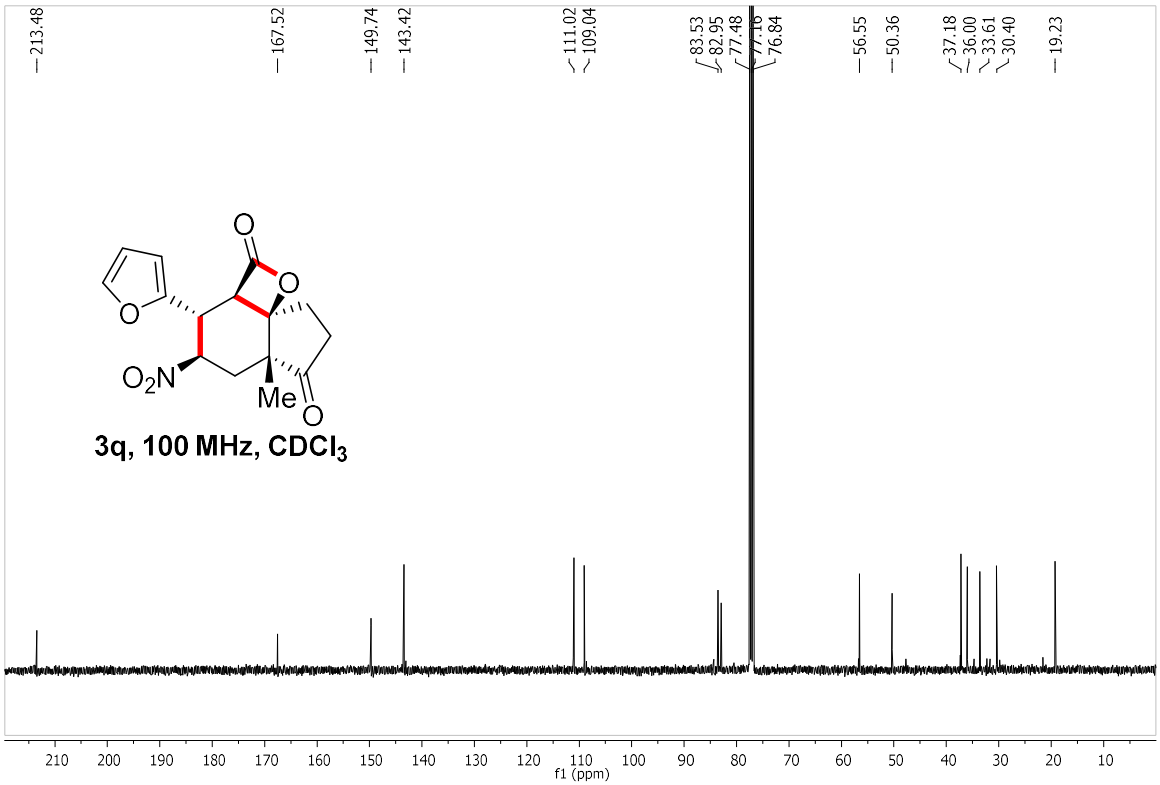
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-3-(naphthalen-2-yl)-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3p)



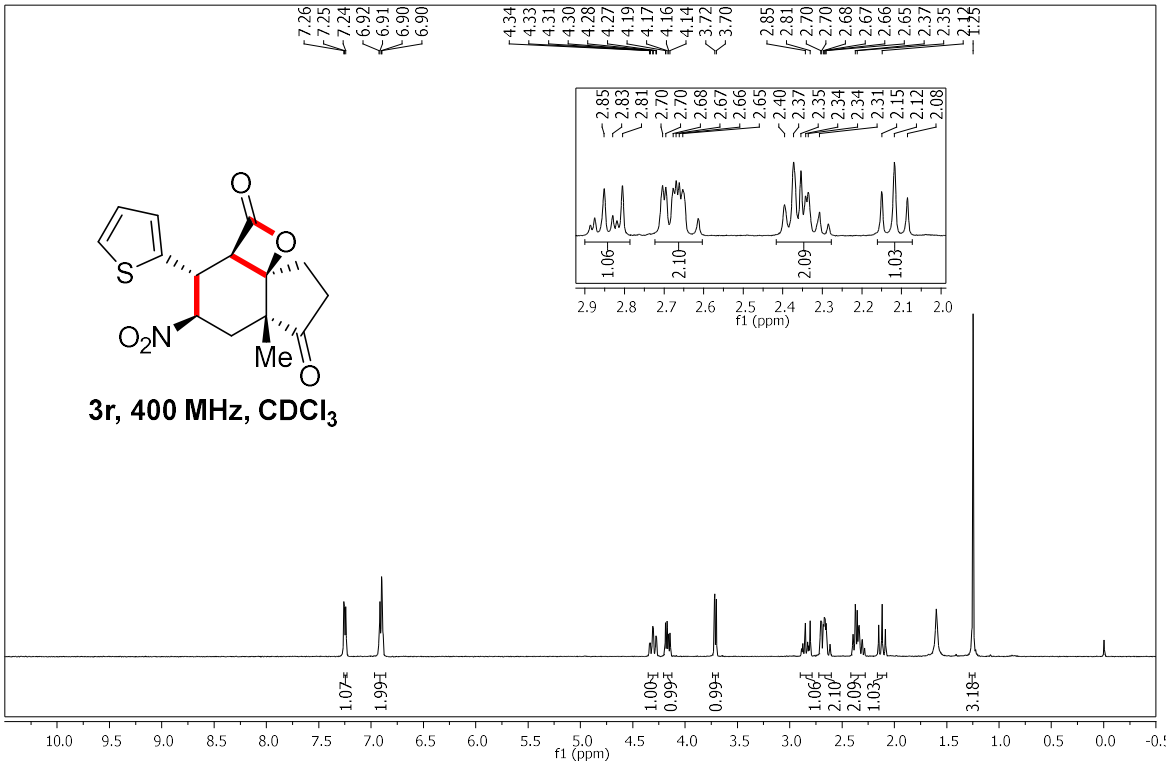


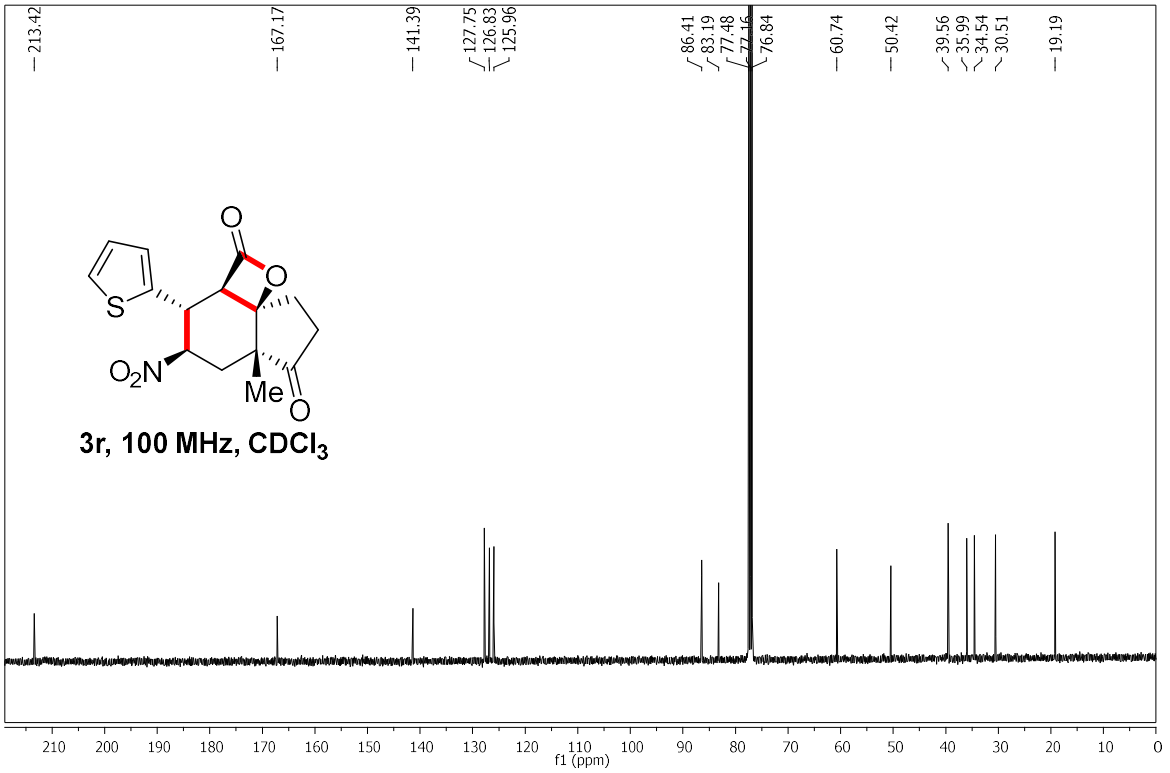
(2a*R*,3*R*,4*R*,5a*R*,8a*R*)-3-(Furan-2-yl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3q)



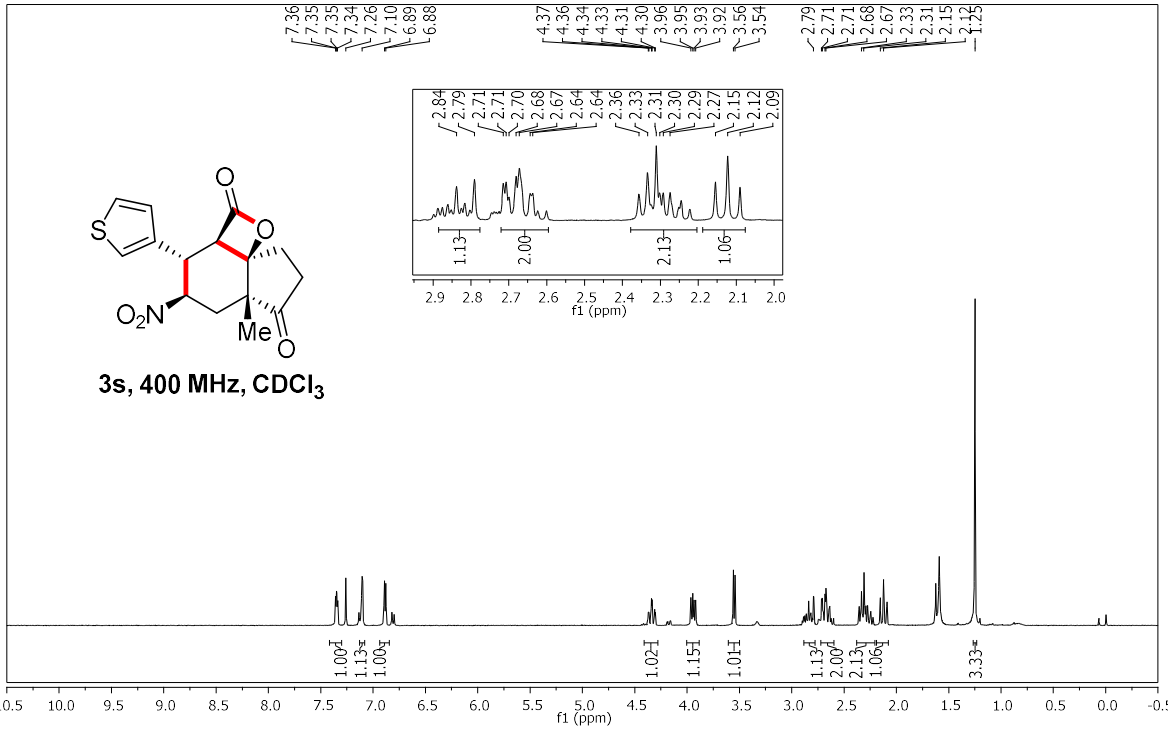


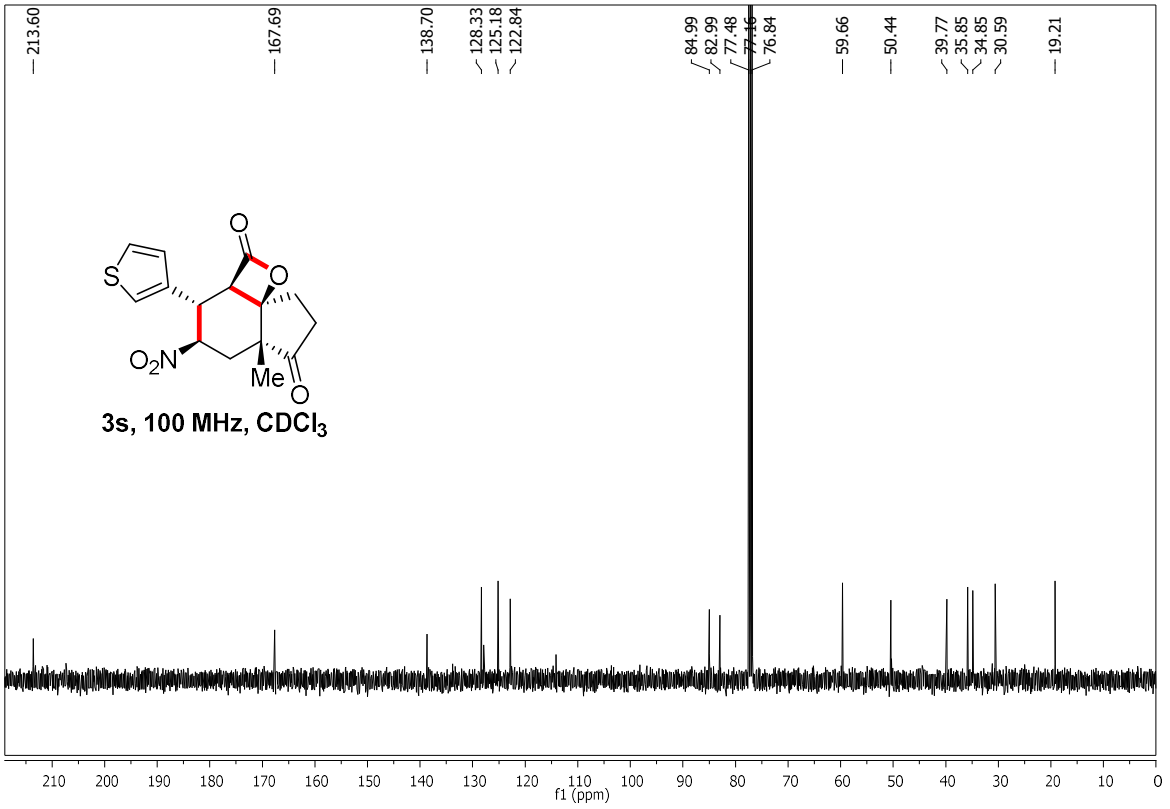
(2a*R*,3*R*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(thiophen-2-yl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3r)



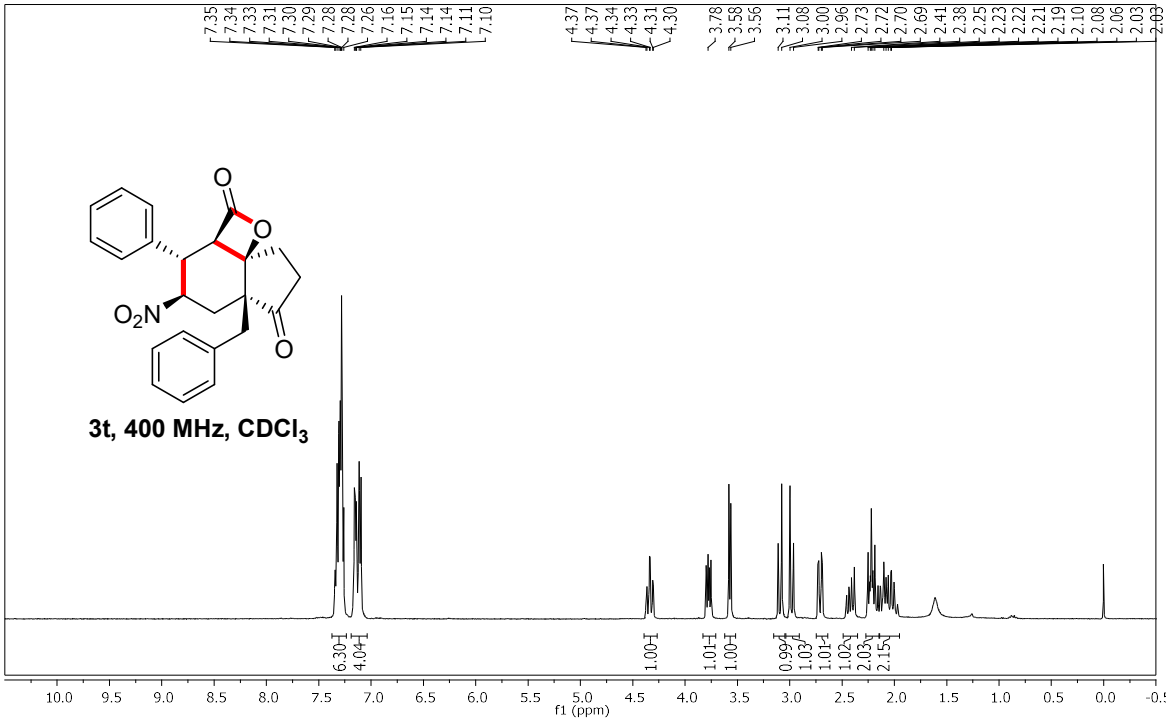


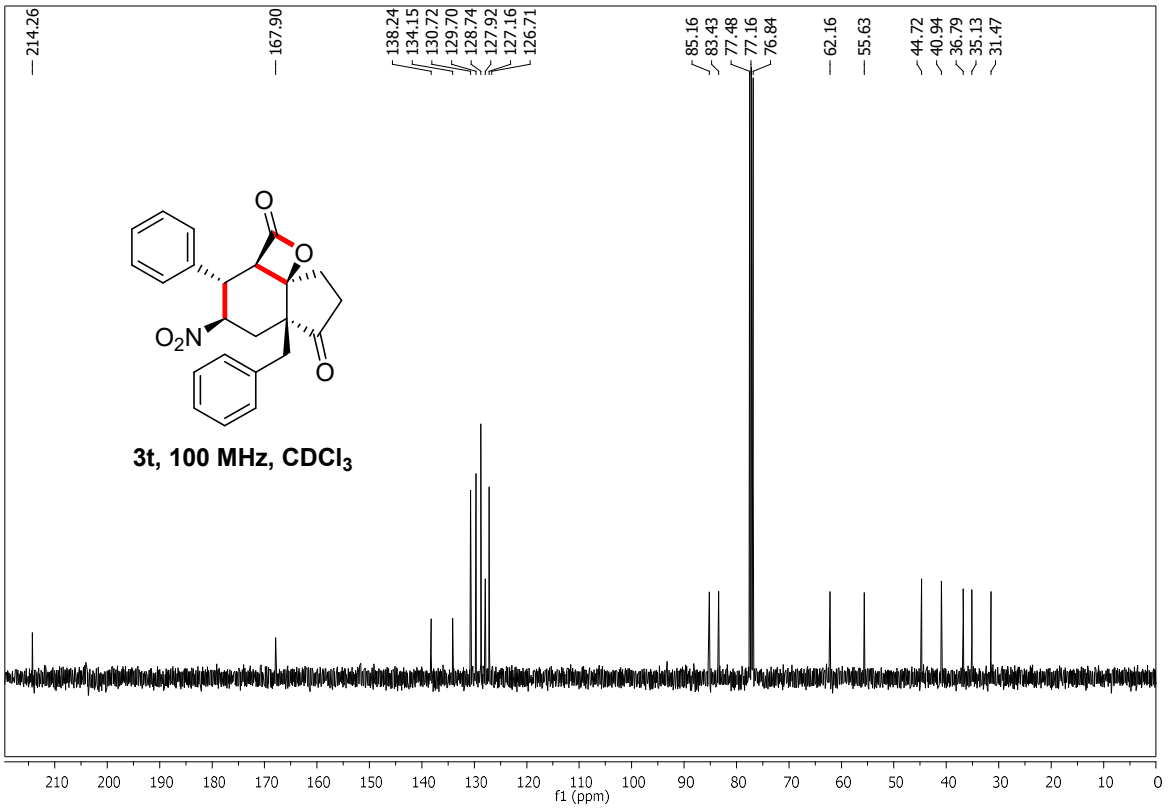
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(thiophen-3-yl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3s)



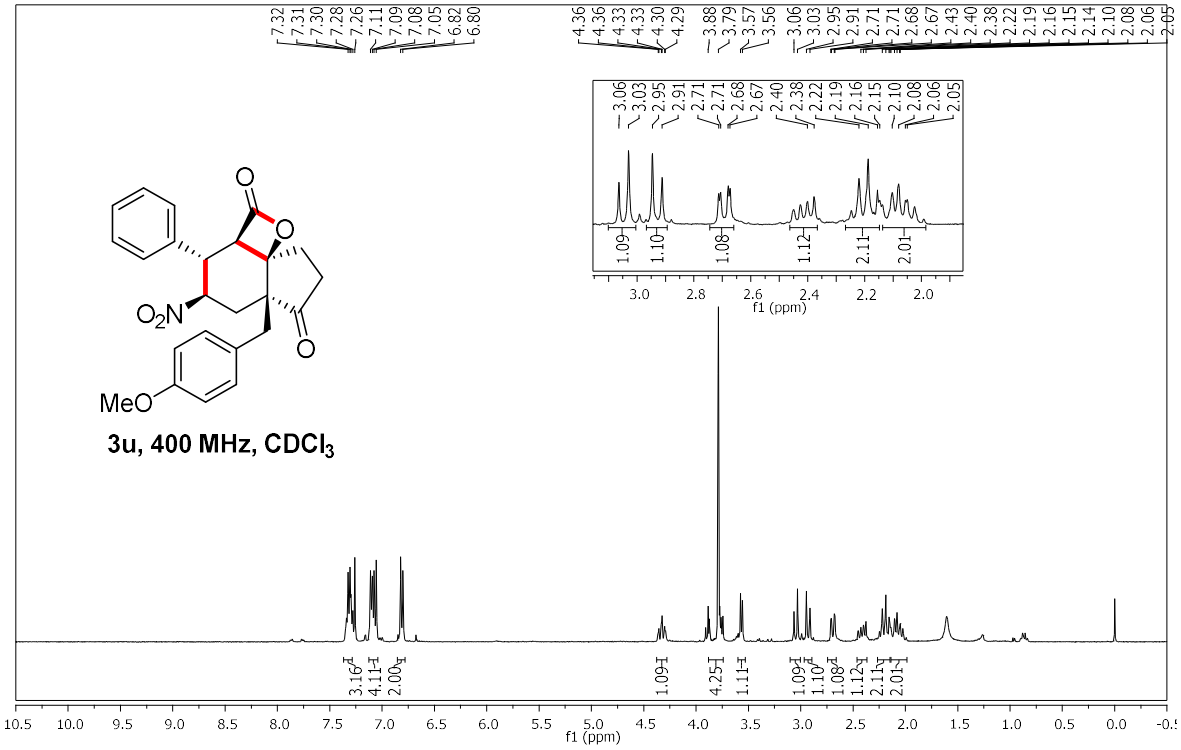


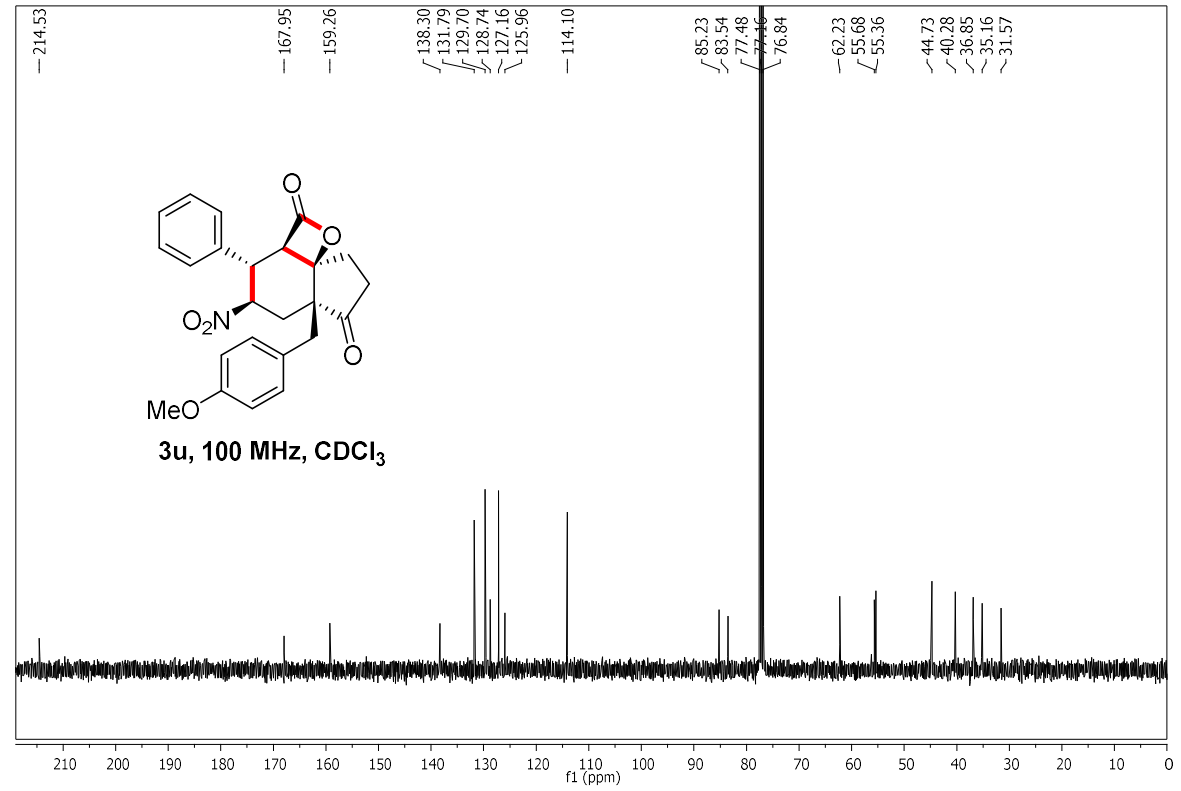
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Benzyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3t)



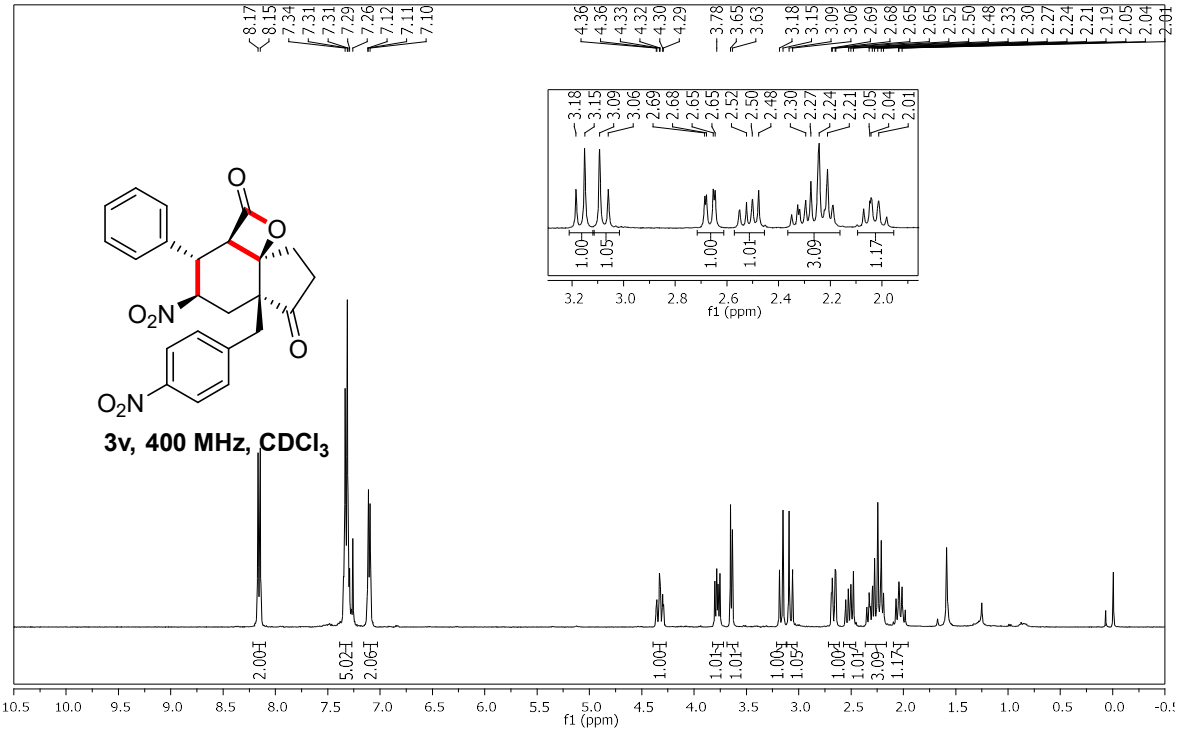


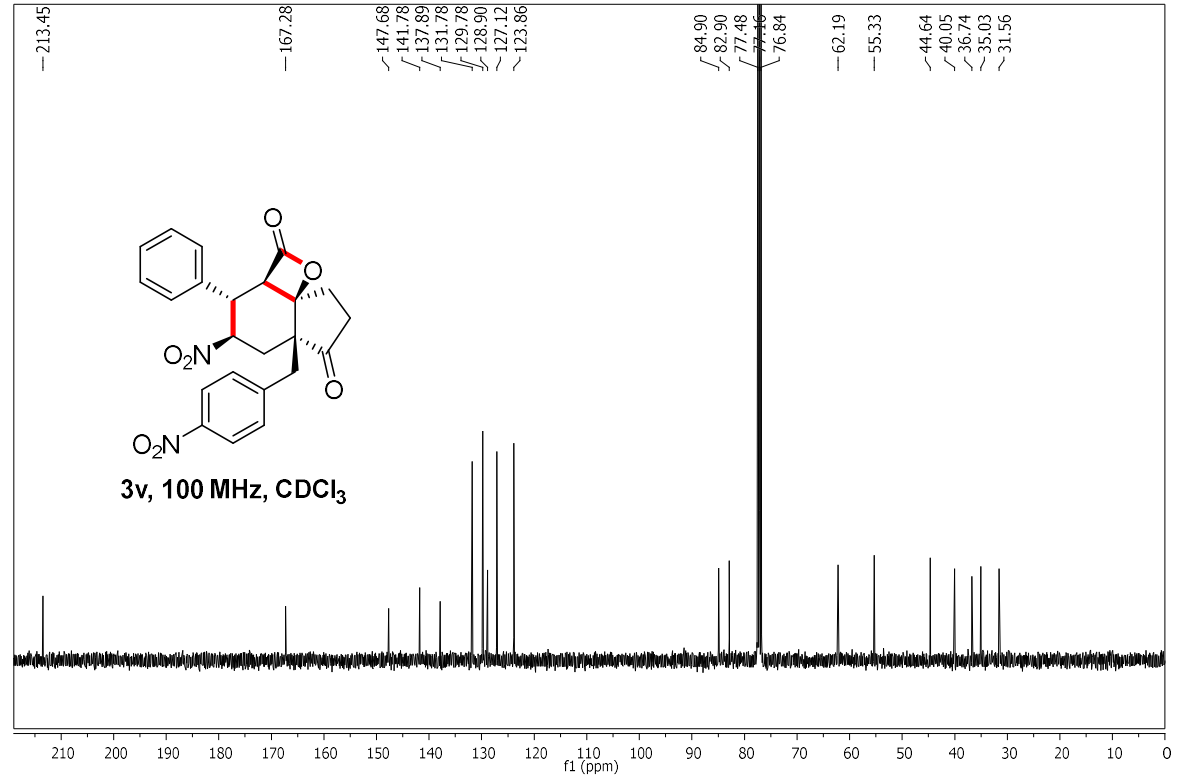
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-(4-Methoxybenzyl)-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3u)



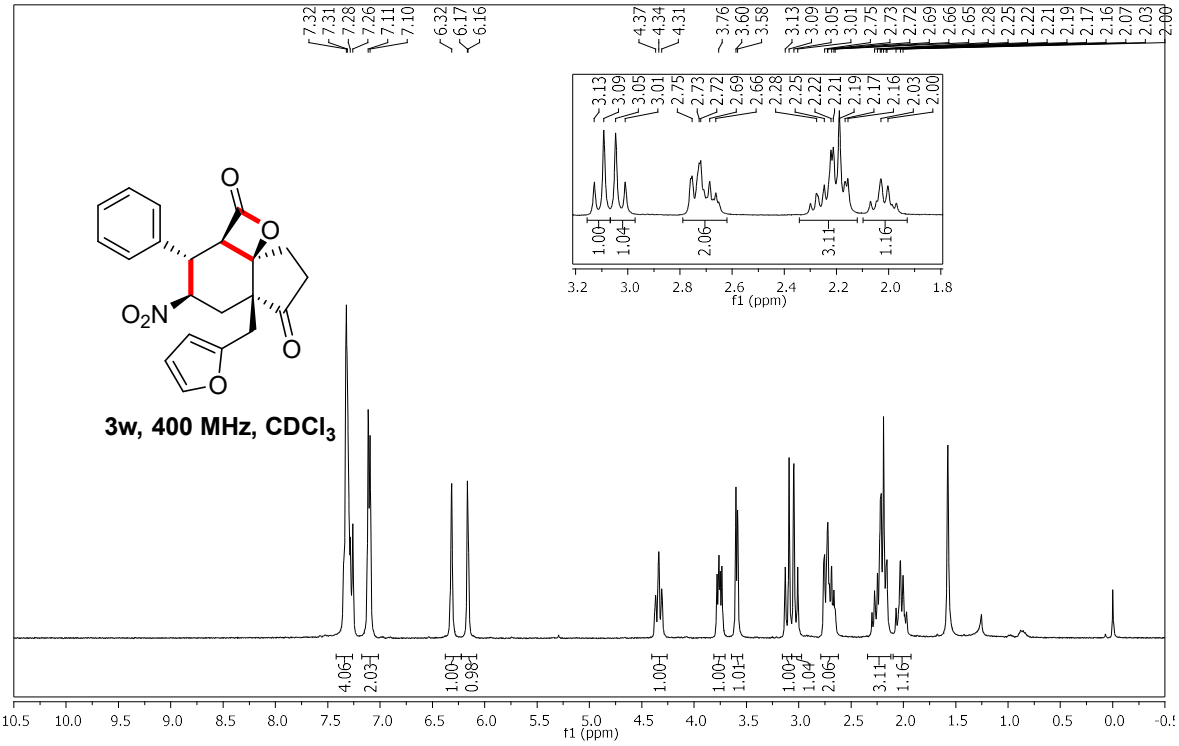


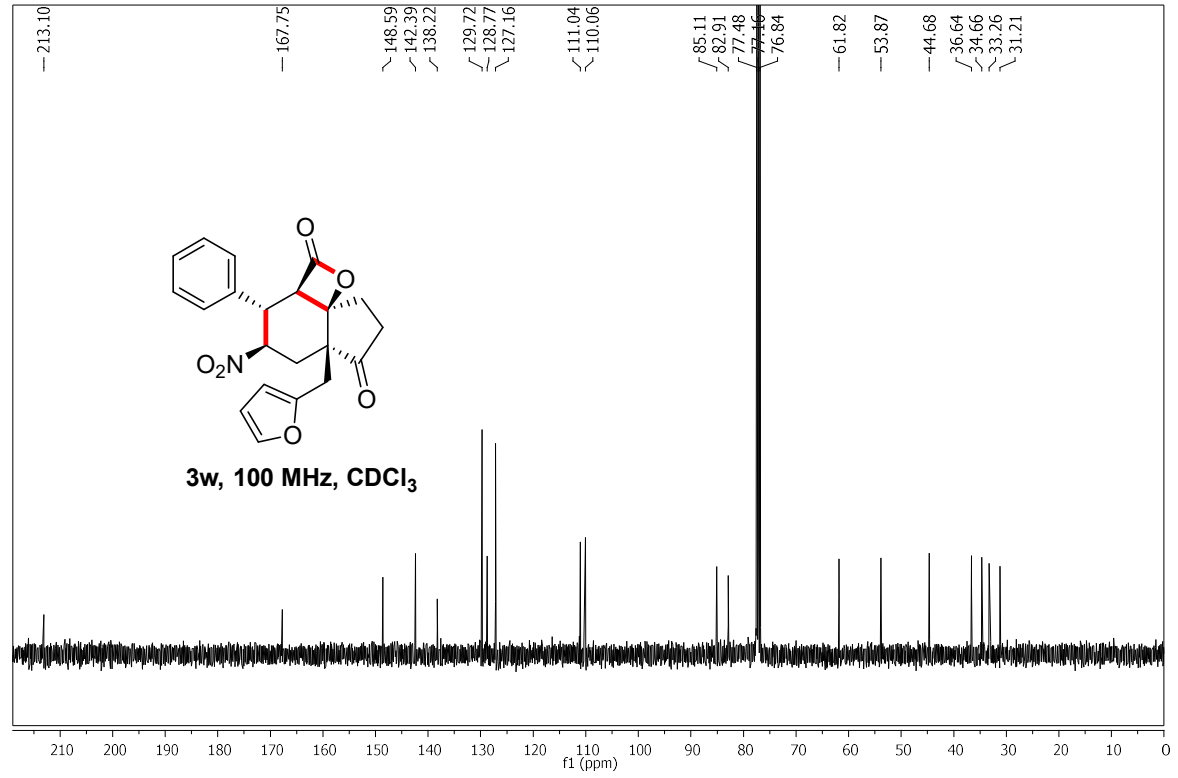
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-4-Nitro-5a-(4-nitrobenzyl)-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3v)



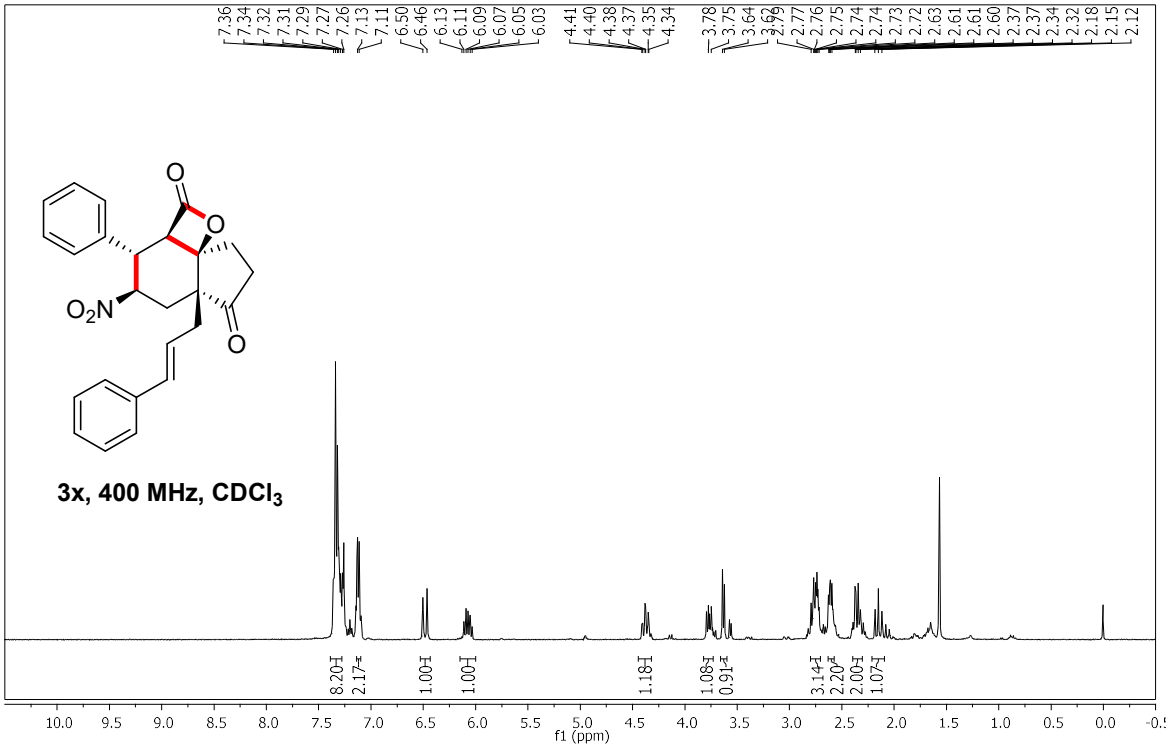


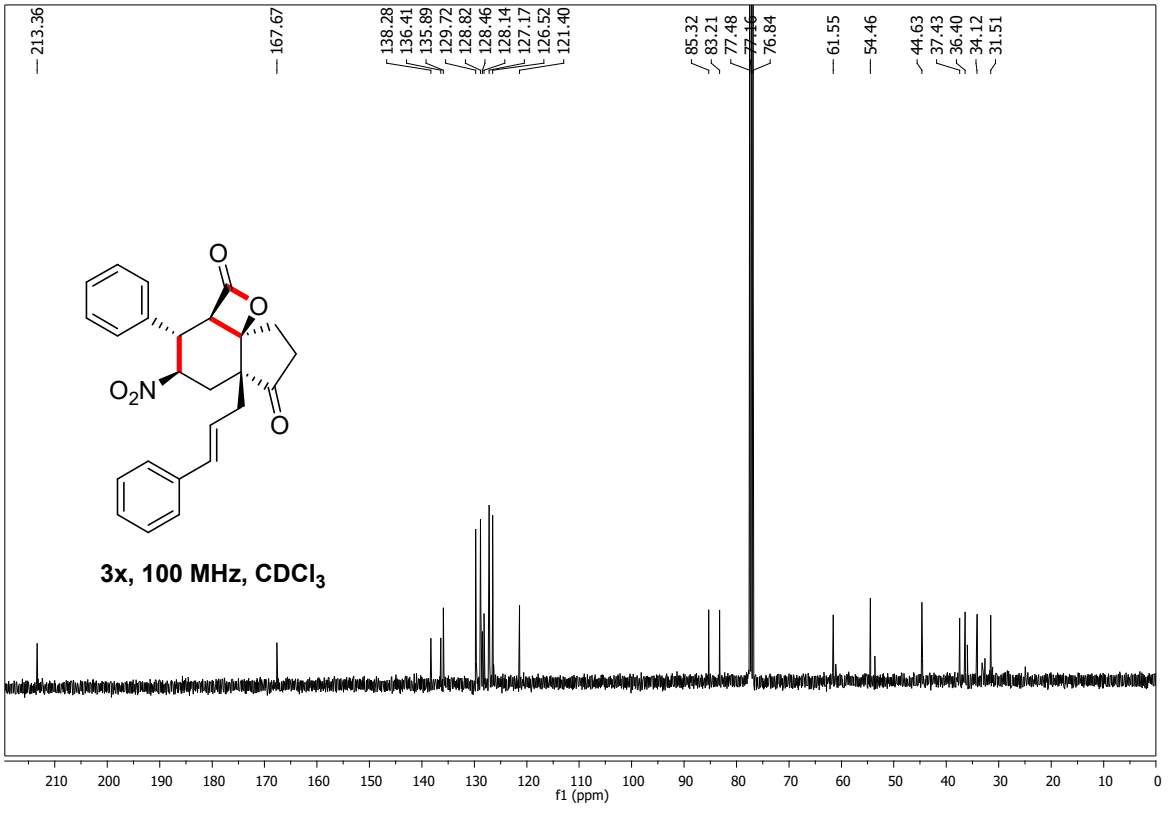
(2a*R*,3*S*,4*R*,5a*S*,8a*R*)-5a-(Furan-2-ylmethyl)-4-nitro-3-phenylhexahydro-2*H*indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3w)



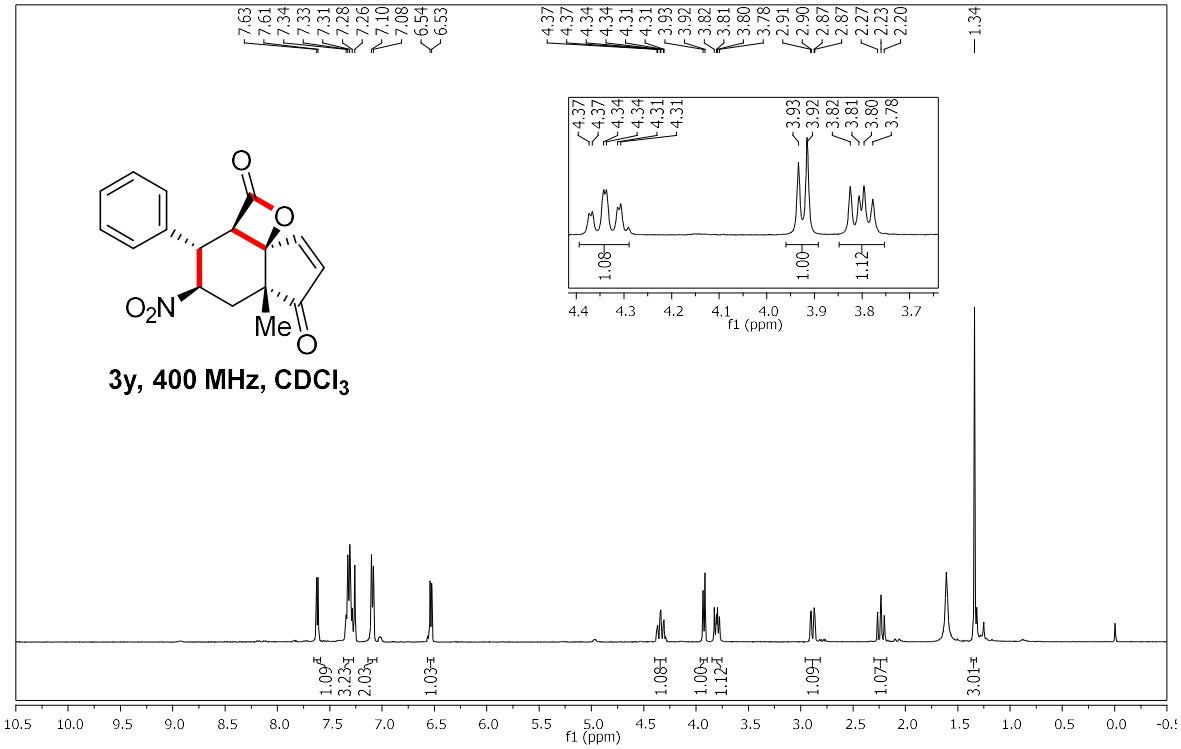


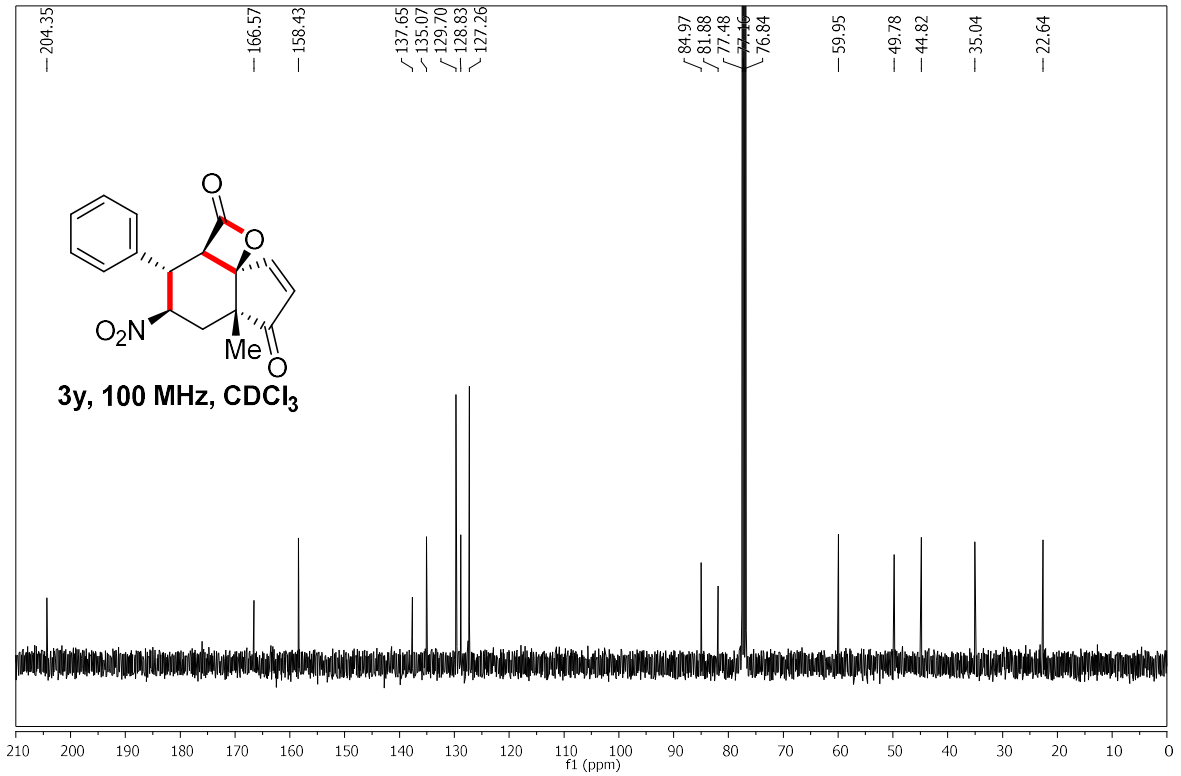
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Cinnamyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3x)



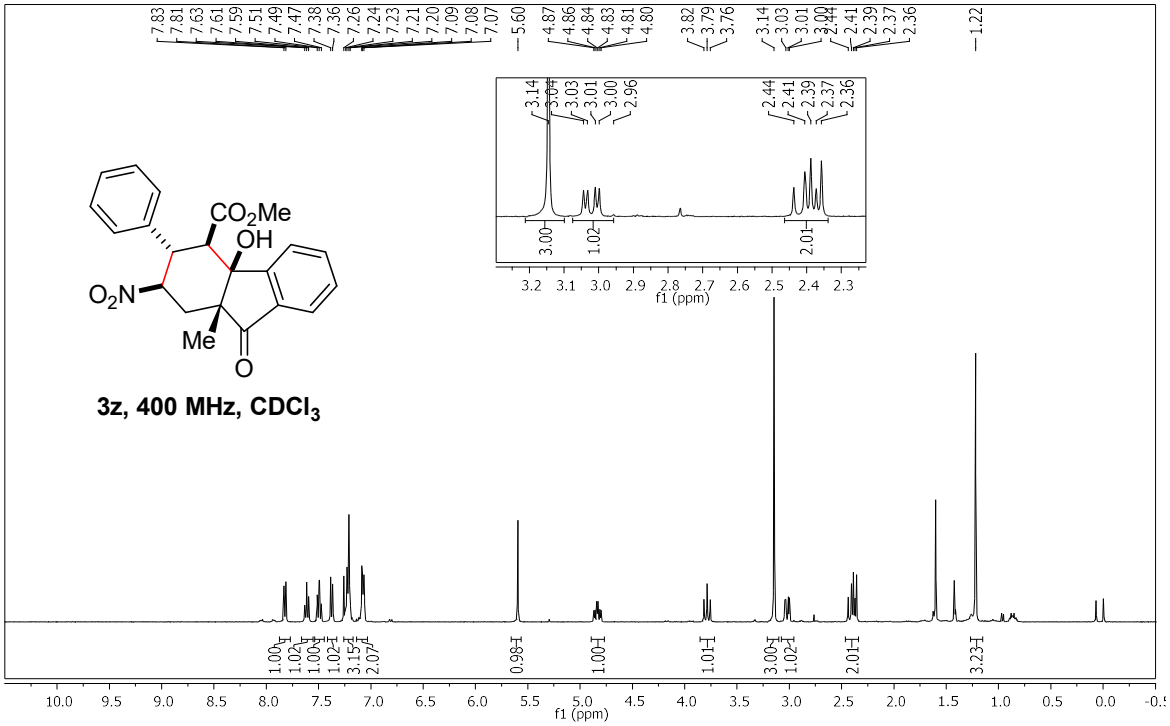


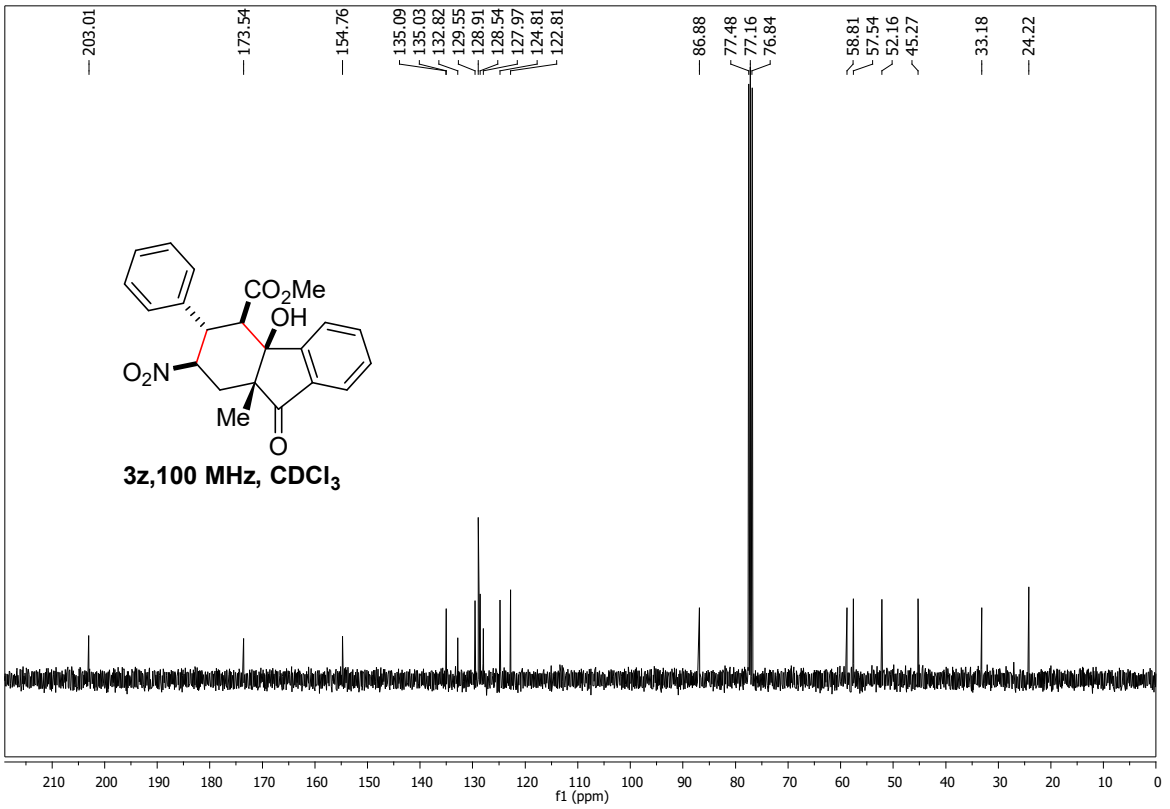
(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-phenyl-3,4,5,5a-tetrahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3y)



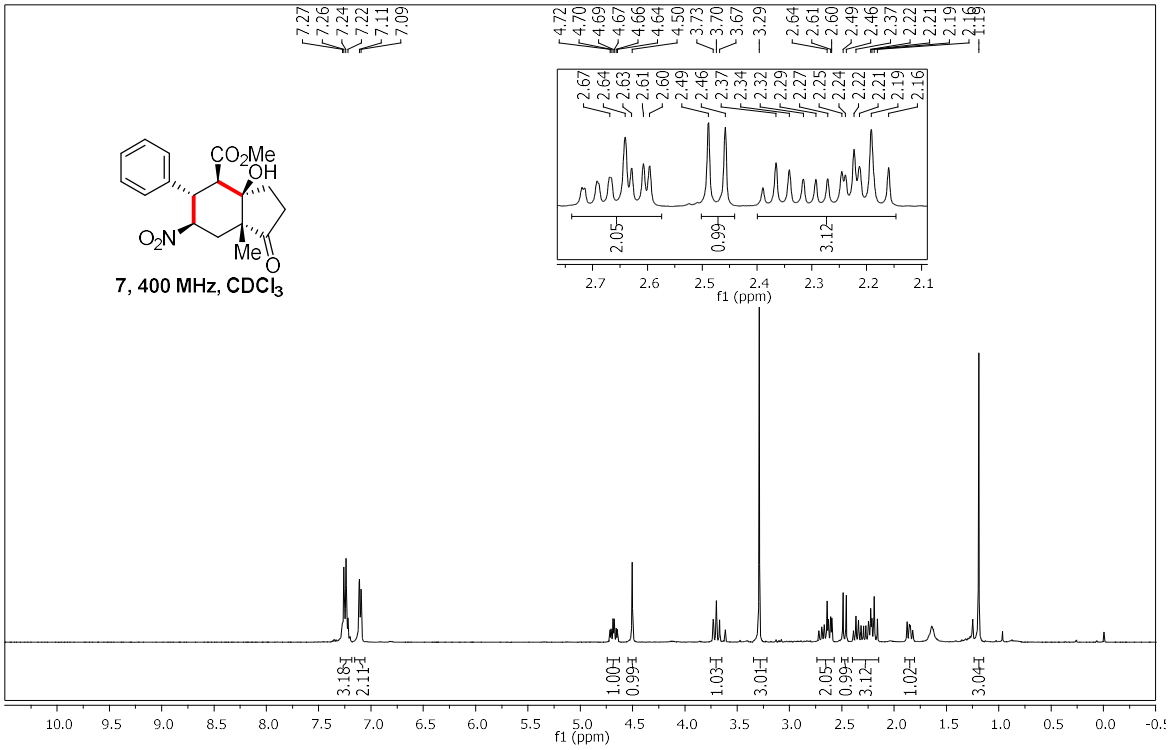


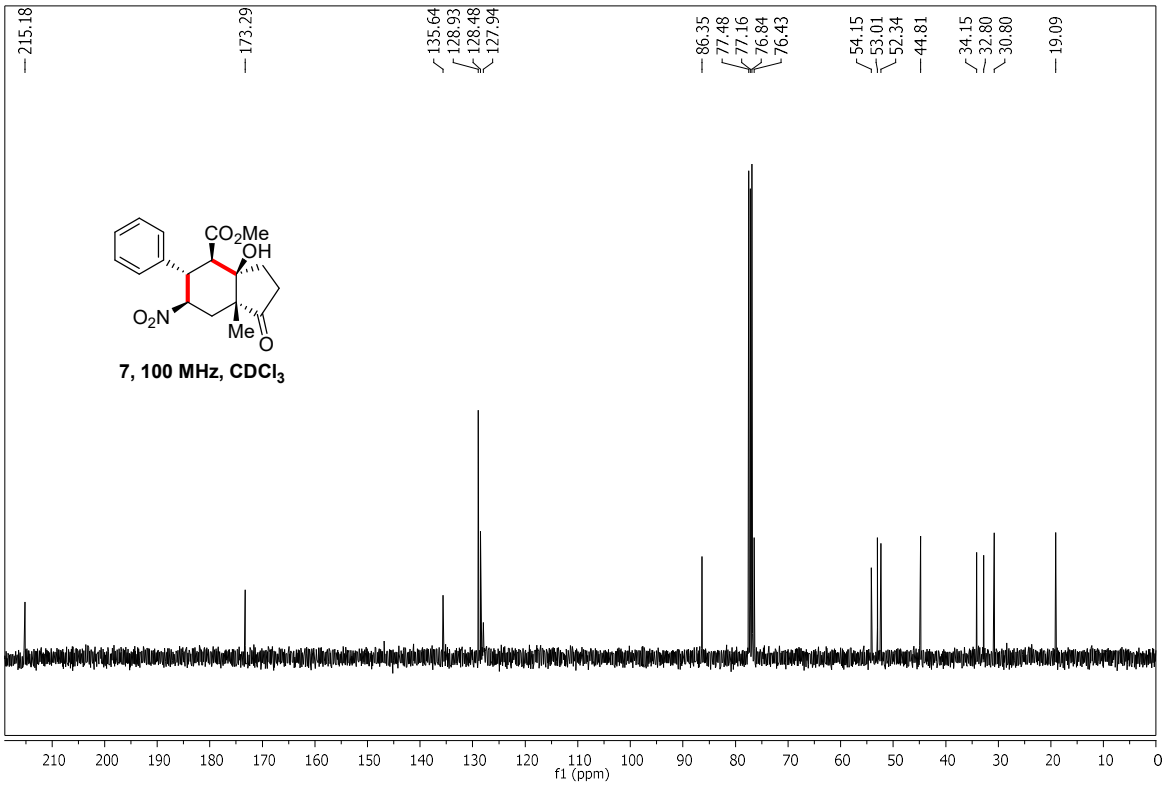
Methyl (2*R*,3*S*,4*R*,4a*S*,9a*R*)-4a-hydroxy-9a-methyl-2-nitro-9-oxo-3-phenyl-2,3,4,4a,9,9a-hexahydro-1*H*-fluorene-4-carboxylate (3z)



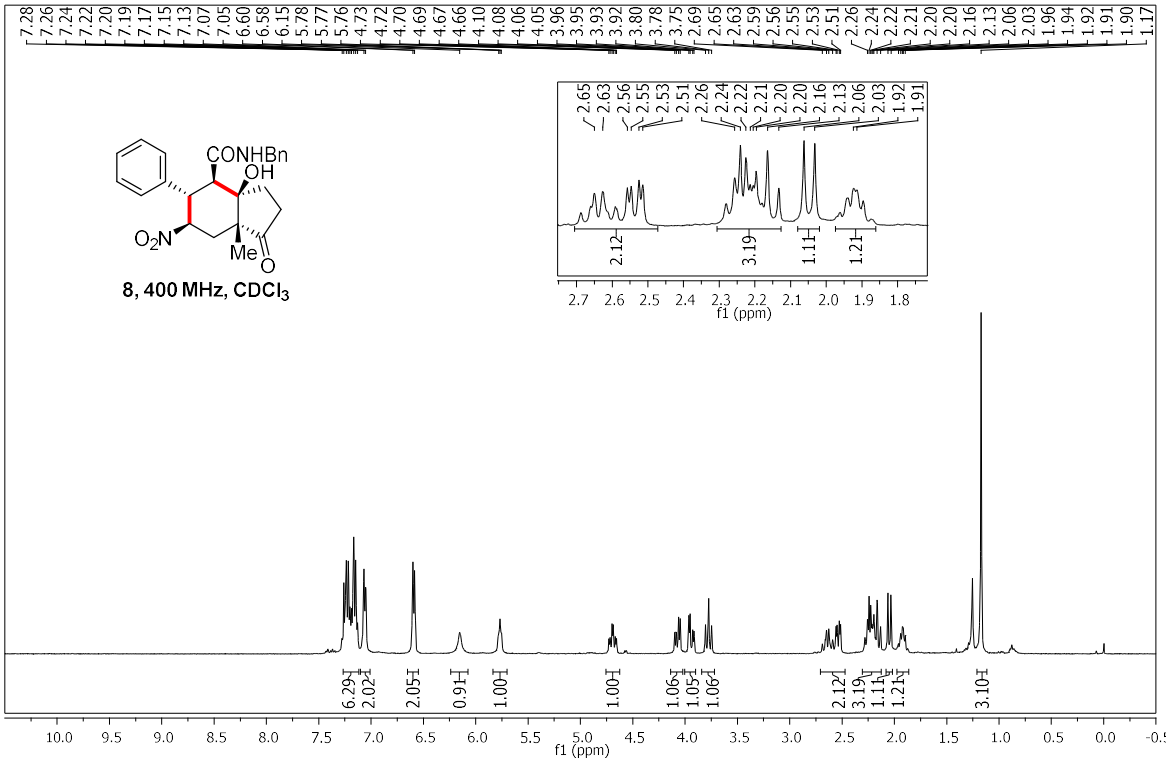


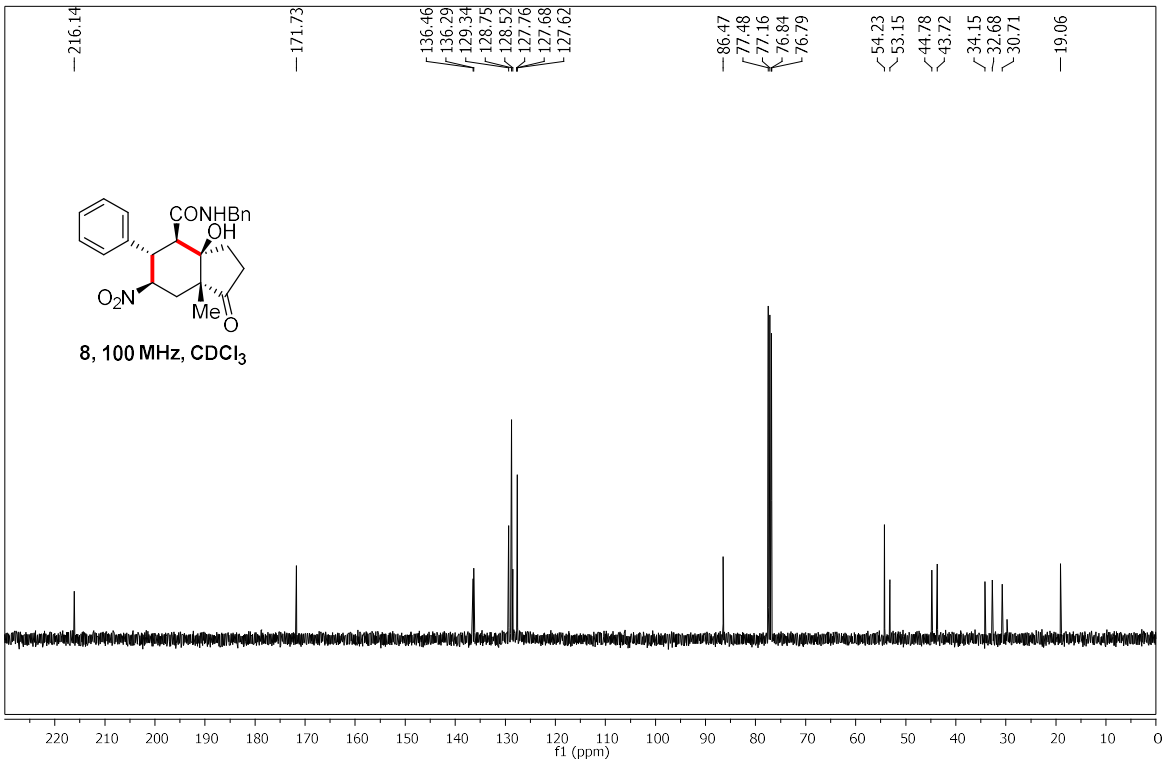
Methyl (3a*R*,4*R*,5*S*,6*R*,7a*R*)-3a-hydroxy-7a-methyl-6-nitro-1-oxo-5-phenyloctahydro-1*H*-indene-4-carboxylate (7)



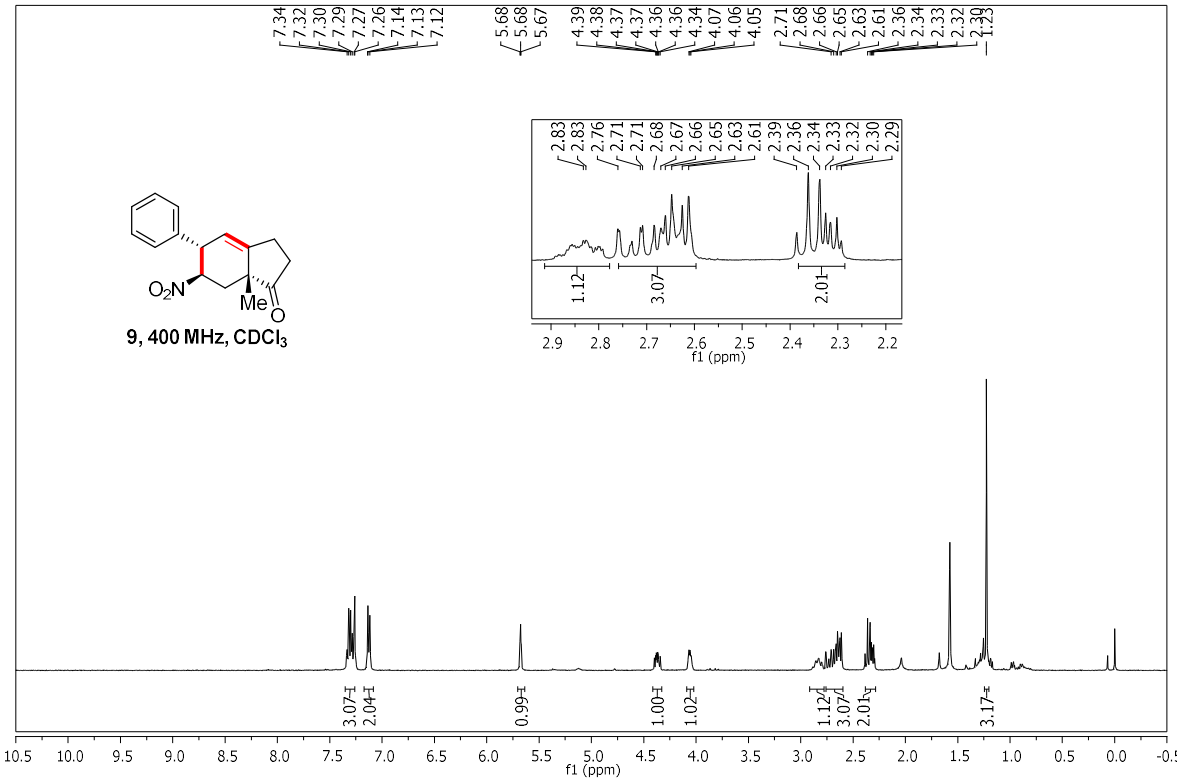


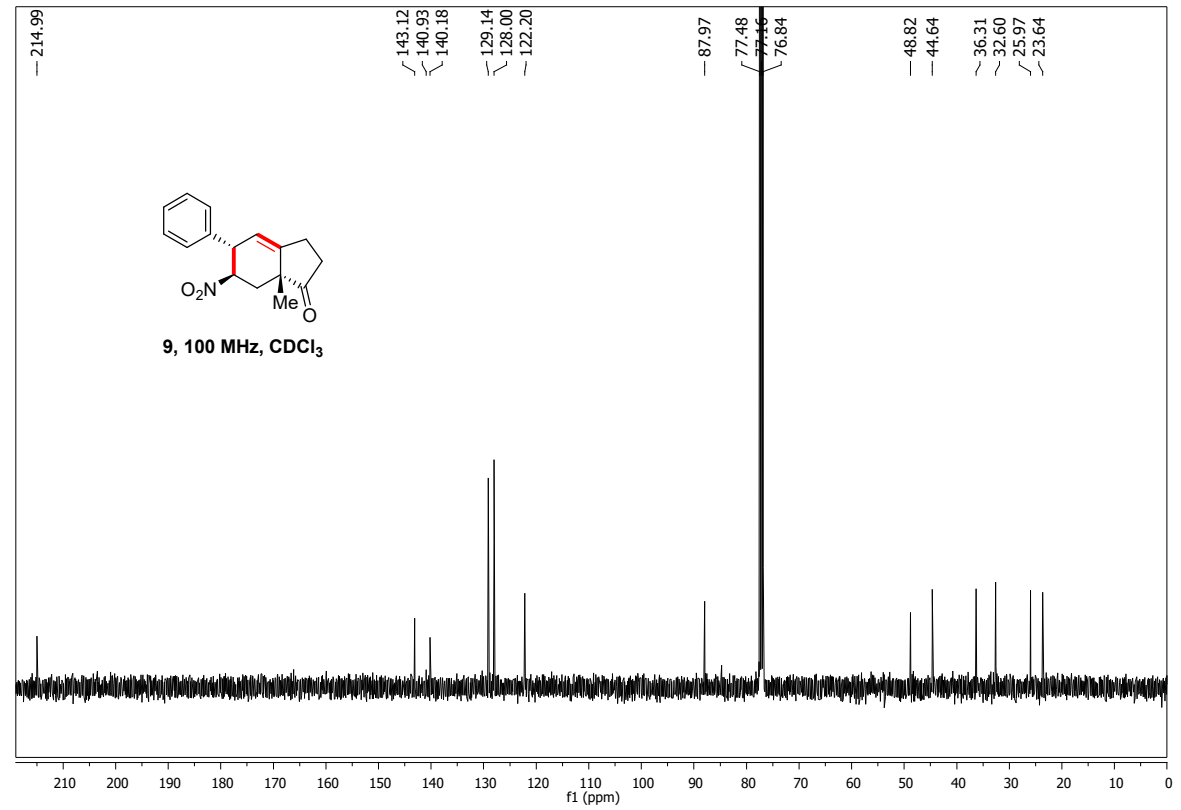
(3a*R*,4*R*,5*S*,6*R*,7a*R*)-*N*-Benzyl-3a-hydroxy-7a-methyl-6-nitro-1-oxo-5-phenyloctahydro-1*H*-indene-4-carboxamide (8)





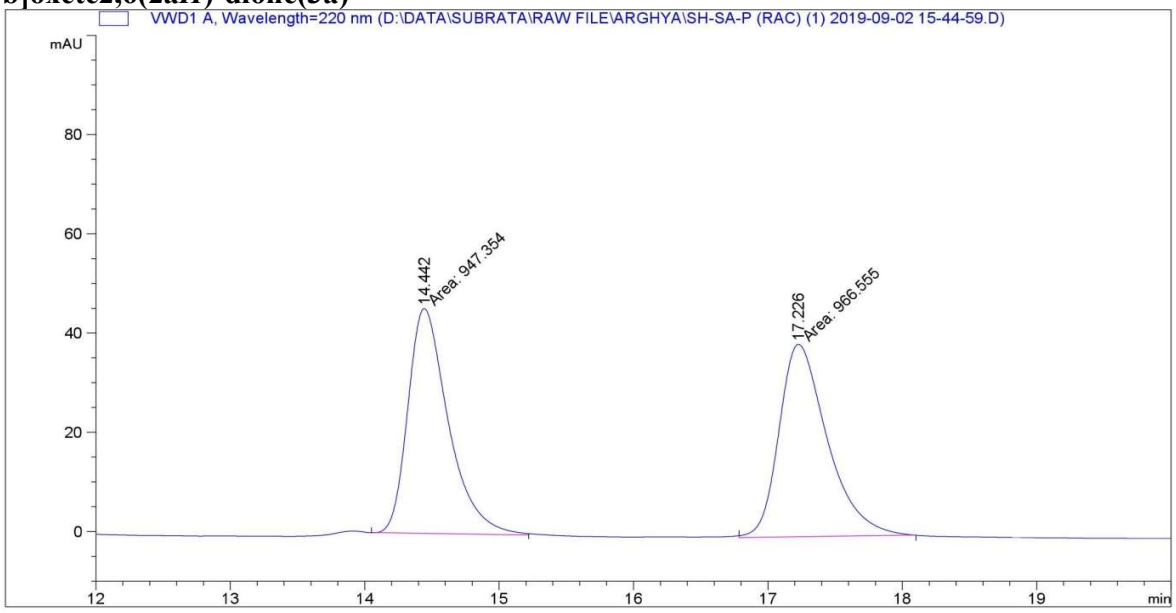
(5*S*,6*R*,7a*R*)-7a-Methyl-6-nitro-5-phenyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-one (9)



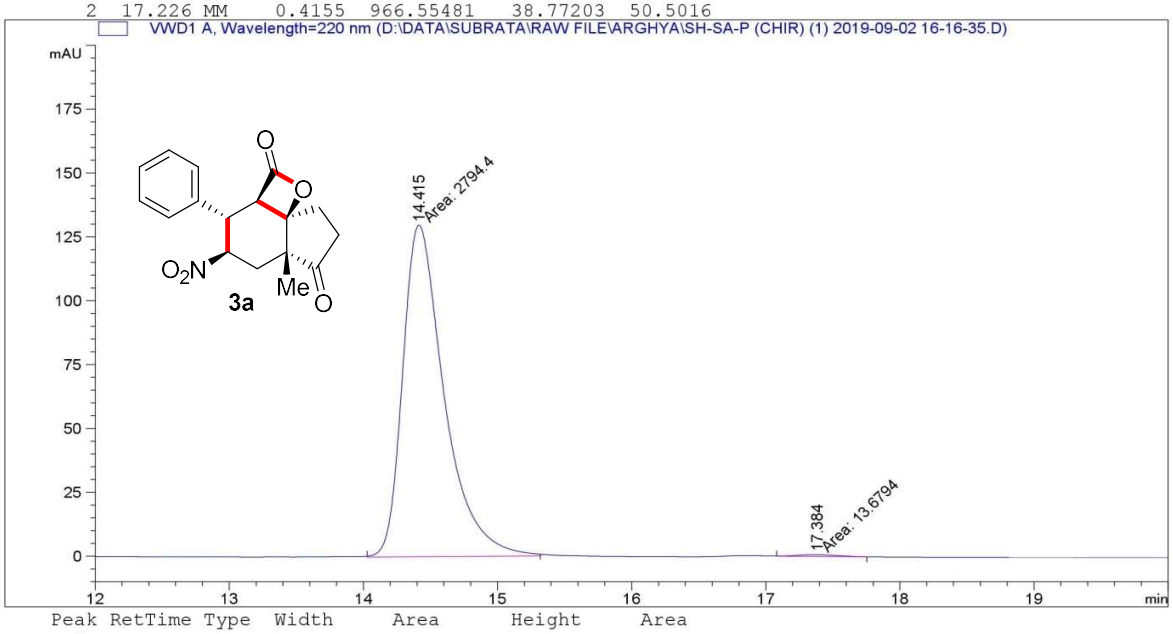


10. HPLC data of Tricyclic β-Lactone Derivatives

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete2,6(2a*H*)-dione(3a)



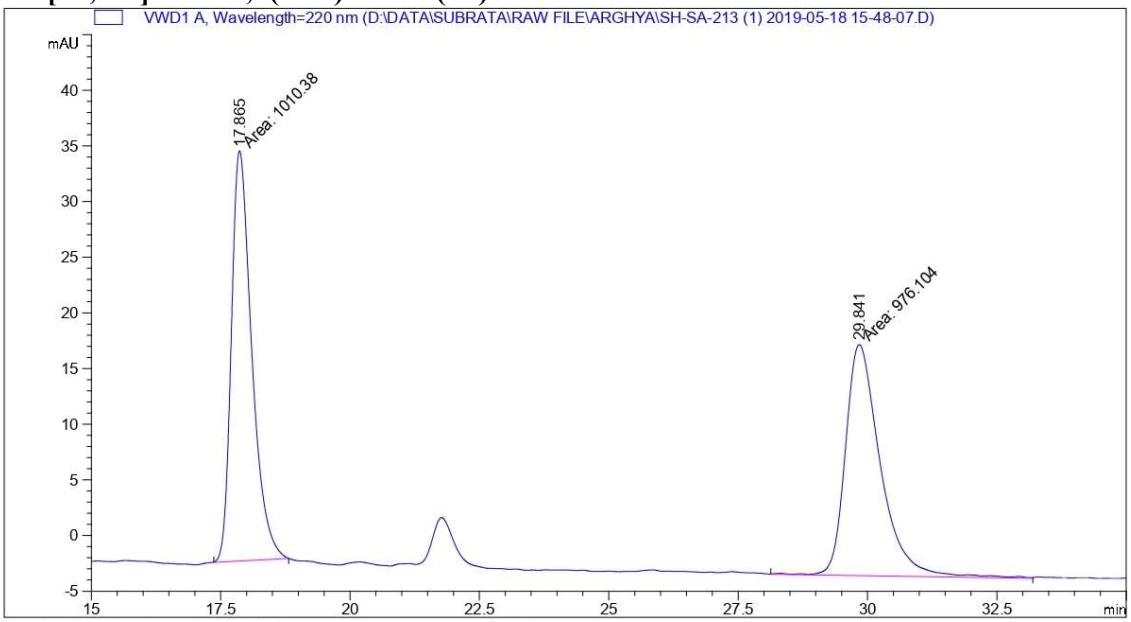
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.442	MM	0.3485	947.35413	45.30332	49.4984
2	17.226	MM	0.4155	966.55481	38.77203	50.5016



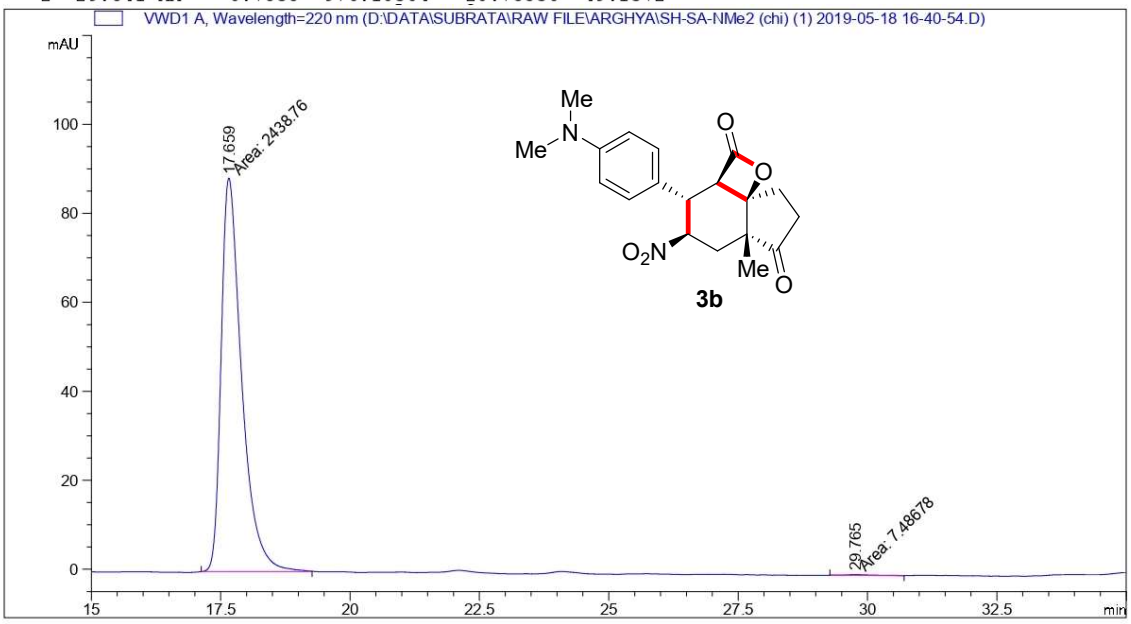
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.415	MM	0.3588	2794.39917	129.81471	99.5129
2	17.384	MM	0.3516	13.67940	6.48353e-1	0.4871

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-(Dimethylamino)phenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3b)



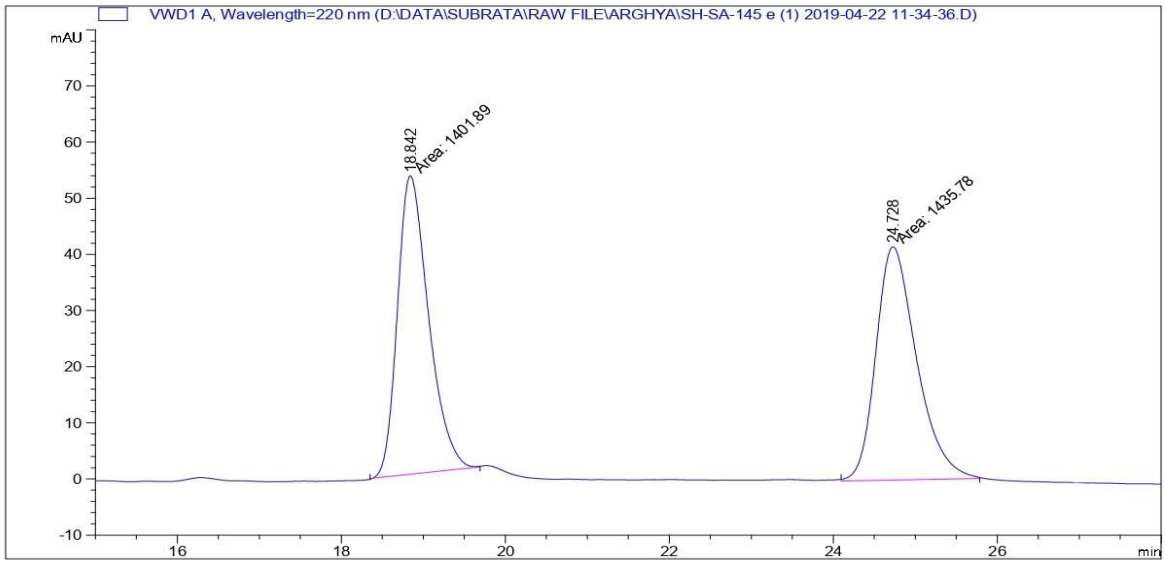
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.865	MM	0.4569	1010.38275	36.85571	50.8628
2	29.841	MM	0.7838	976.10364	20.75536	49.1372



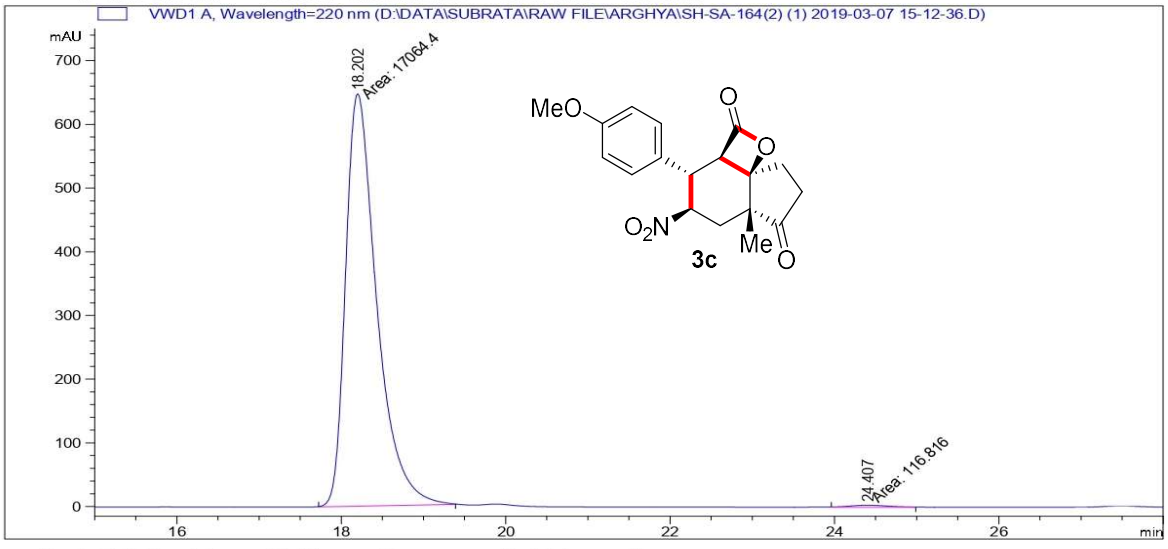
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.659	MM	0.4597	2438.76270	88.42683	99.6939
2	29.765	MM	0.7436	7.48678	1.67801e-1	0.3061

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Methoxyphenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2a*H*)-dione (3c)



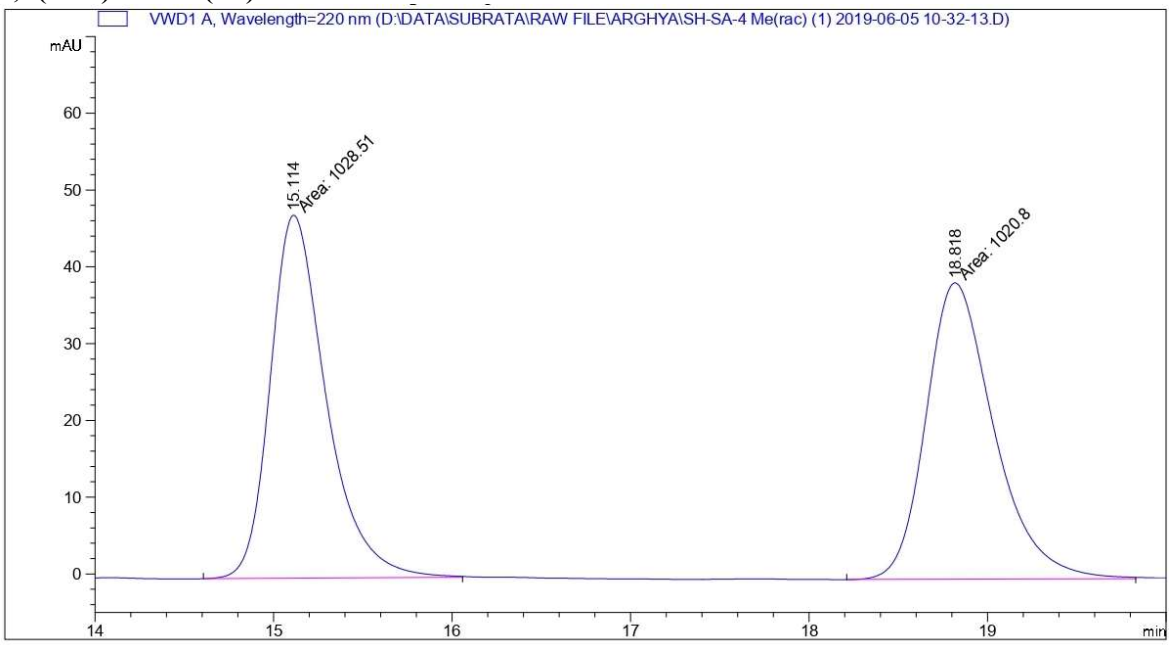
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.842	MM	0.4395	1401.89331	53.16604	49.4028
2	24.728	MM	0.5757	1435.78430	41.56287	50.5972



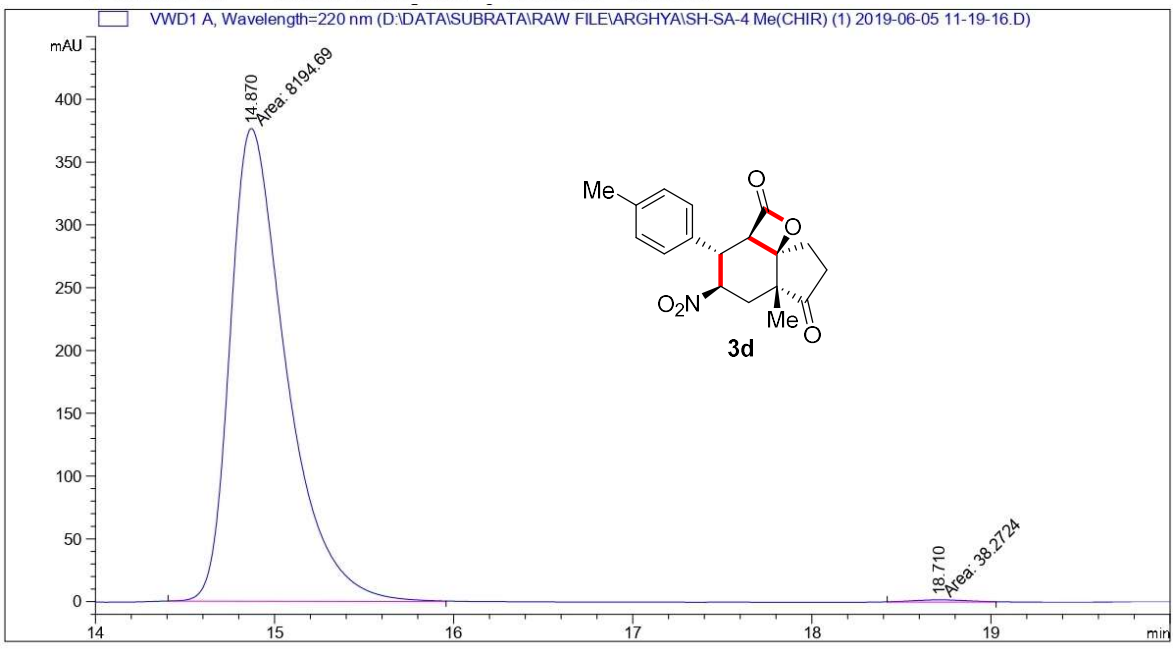
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.202	MM	0.4394	1.70644e4	647.23926	99.3201
2	24.407	MM	0.5739	116.81639	3.39218	0.6799

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(p-tolyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3d)



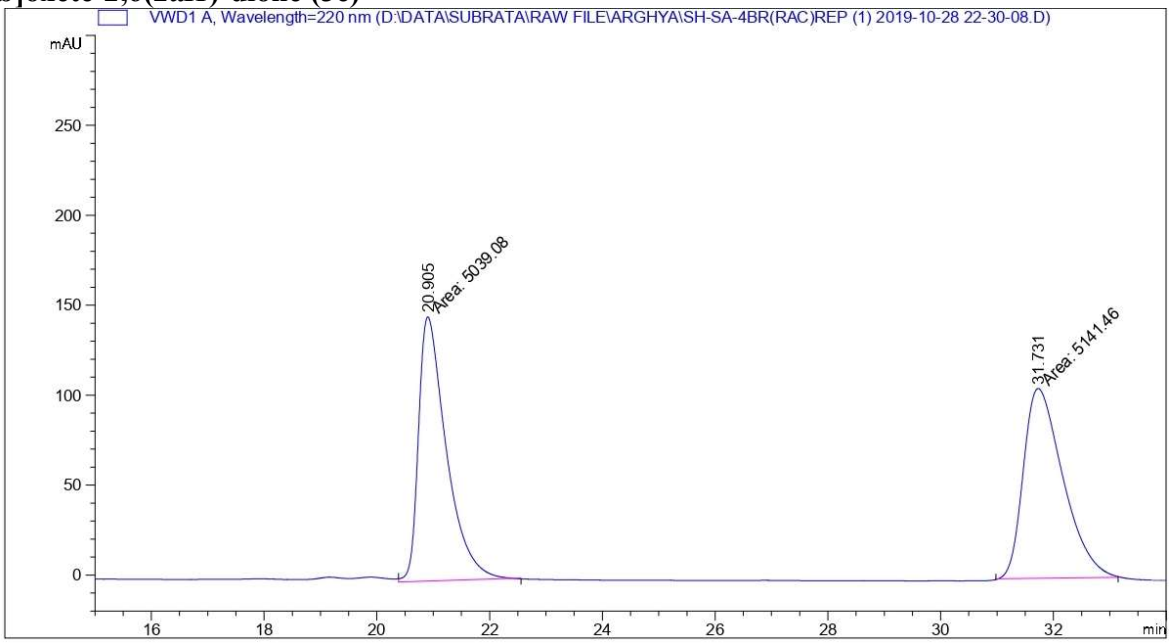
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.114	MM	0.3626	1028.51489	47.26968	50.1881
2	18.818	MM	0.4409	1020.80377	38.58947	49.8119



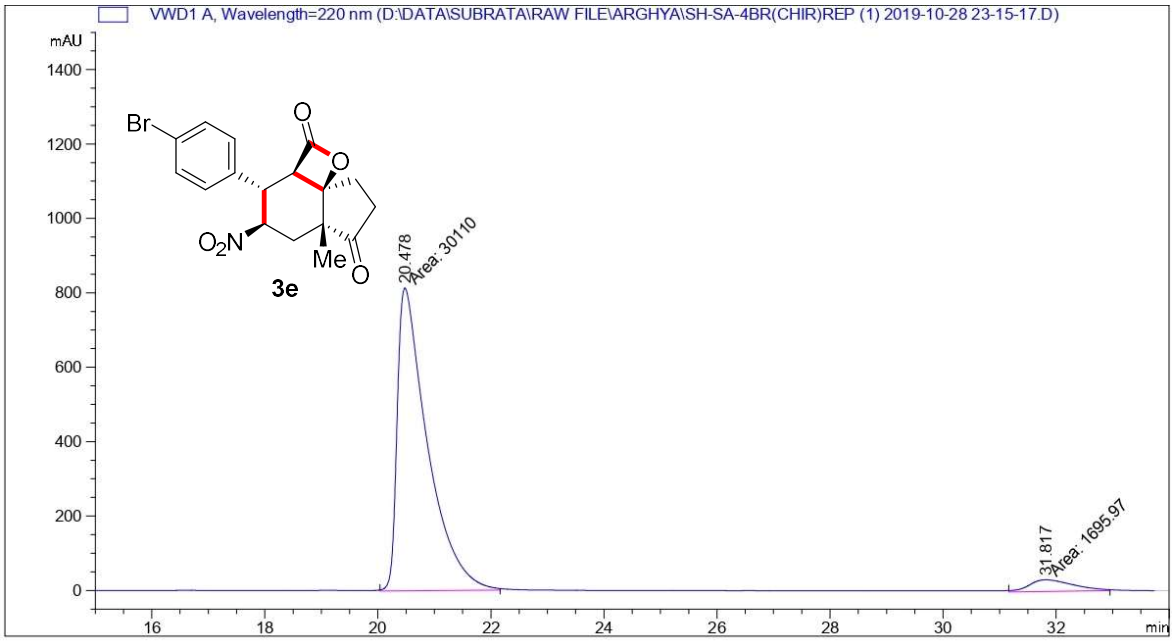
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.870	MM	0.3628	8194.69141	376.42502	99.5351
2	18.710	MM	0.3648	38.27245	1.74864	0.4649

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Bromophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3e)



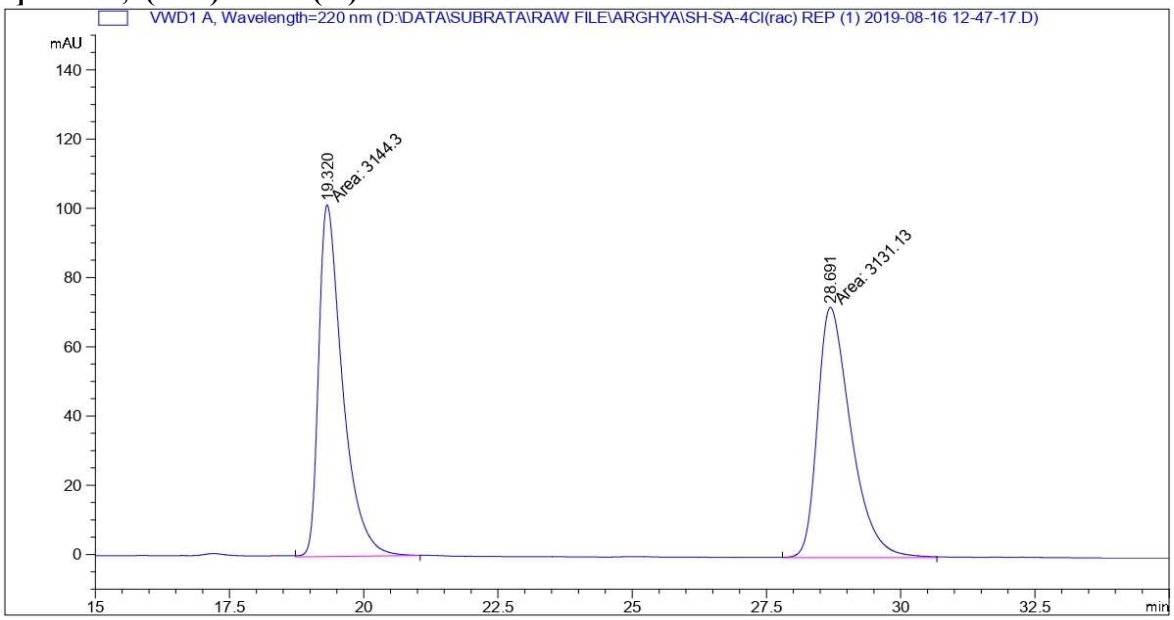
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.905	MM	0.5719	5039.08252	146.85559	49.4972
2	31.731	MM	0.8125	5141.45703	105.46387	50.5028



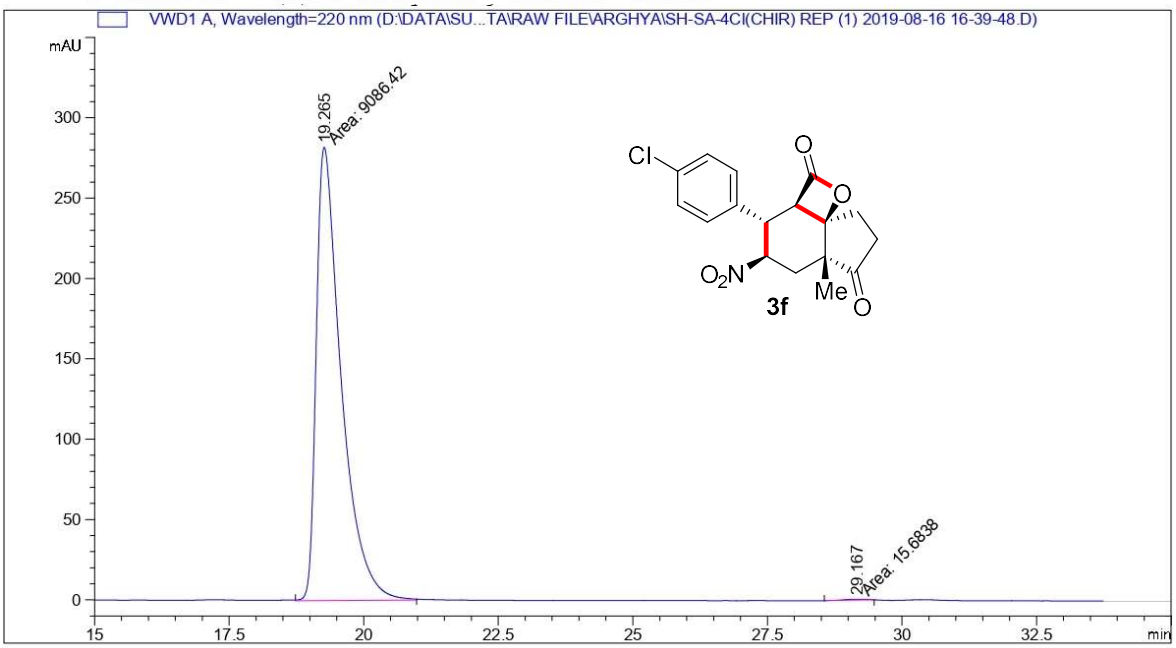
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.478	MM	0.6169	3.01100e4	813.46704	94.6678
2	31.817	MM	0.9010	1695.96948	31.37029	5.3322

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2*aR*,3*S*,4*R*,5*aR*,8*aR*)-3-(4-Chlorophenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione (3f)



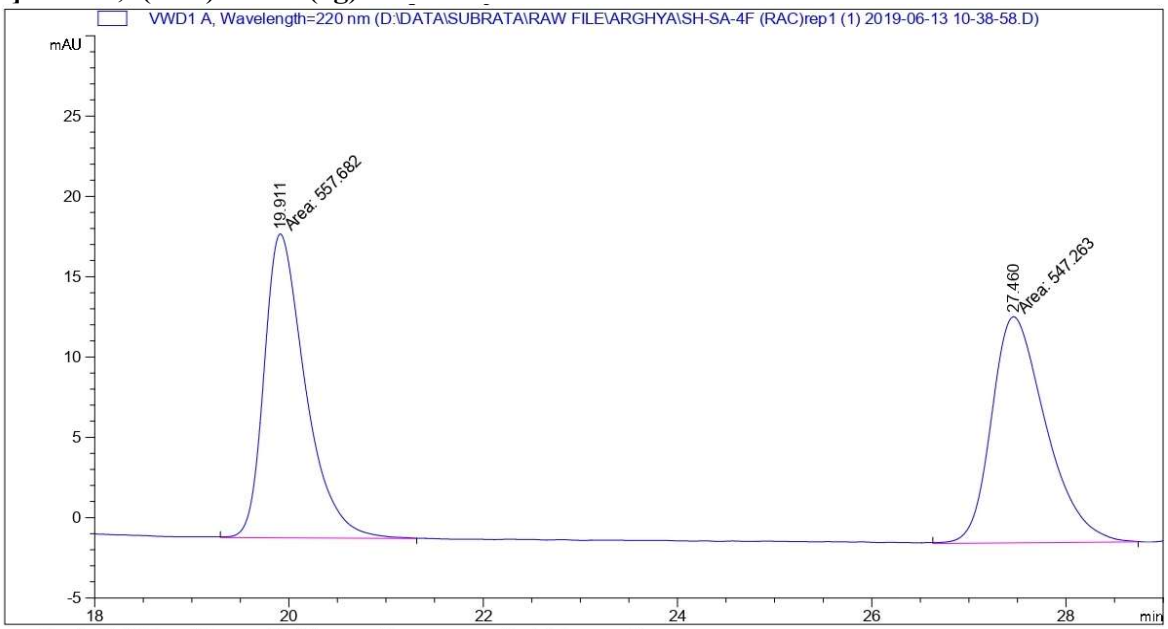
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.320	MM	0.5160	3144.30469	101.56245	50.1050
2	28.691	MM	0.7218	3131.12891	72.29446	49.8950



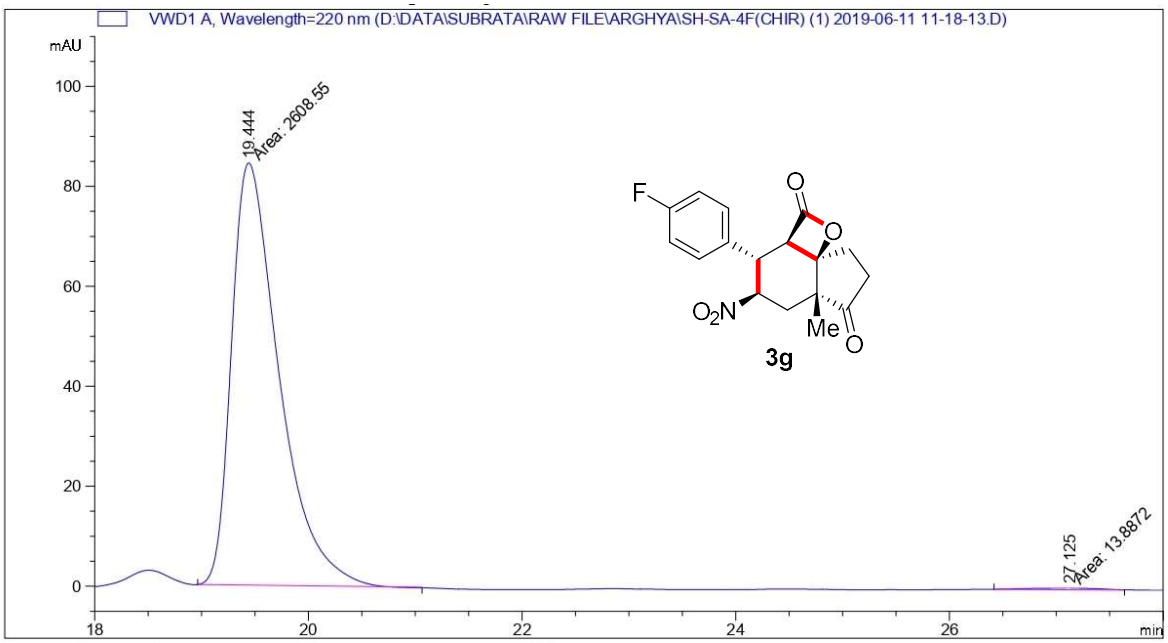
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.265	MM	0.5369	9086.42188	282.05655	99.8277
2	29.167	MM	0.4628	15.68375	5.64871e-1	0.1723

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(4-Fluorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3g)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.911	MM	0.4914	557.68225	18.91395	50.4715
2	27.460	MM	0.6481	547.26288	14.07326	49.5285

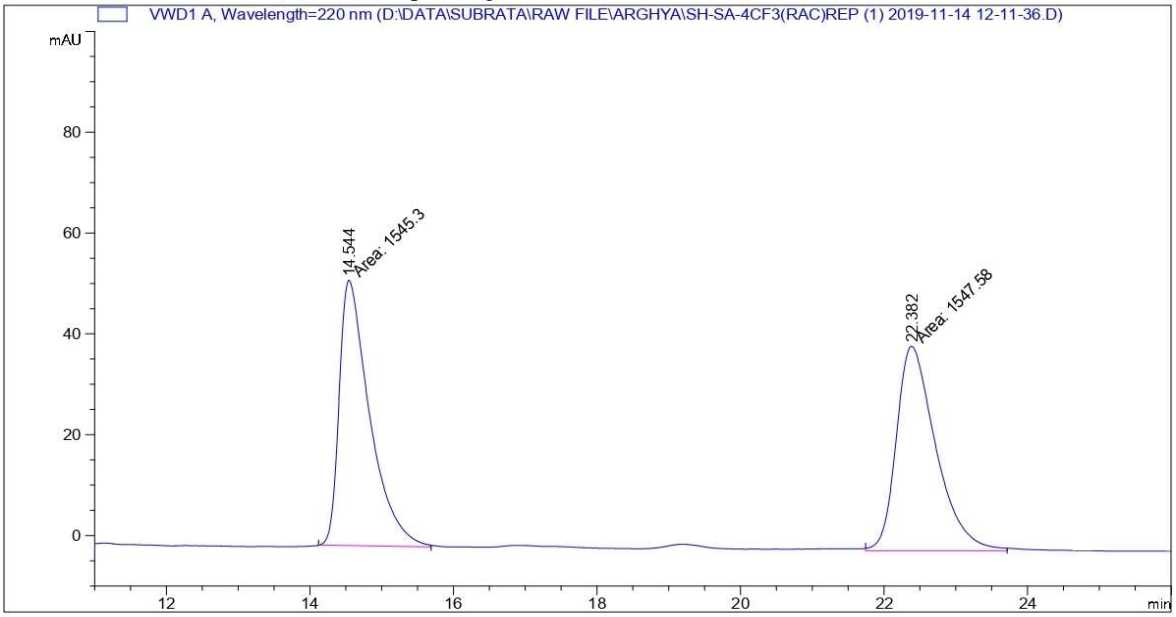


3g

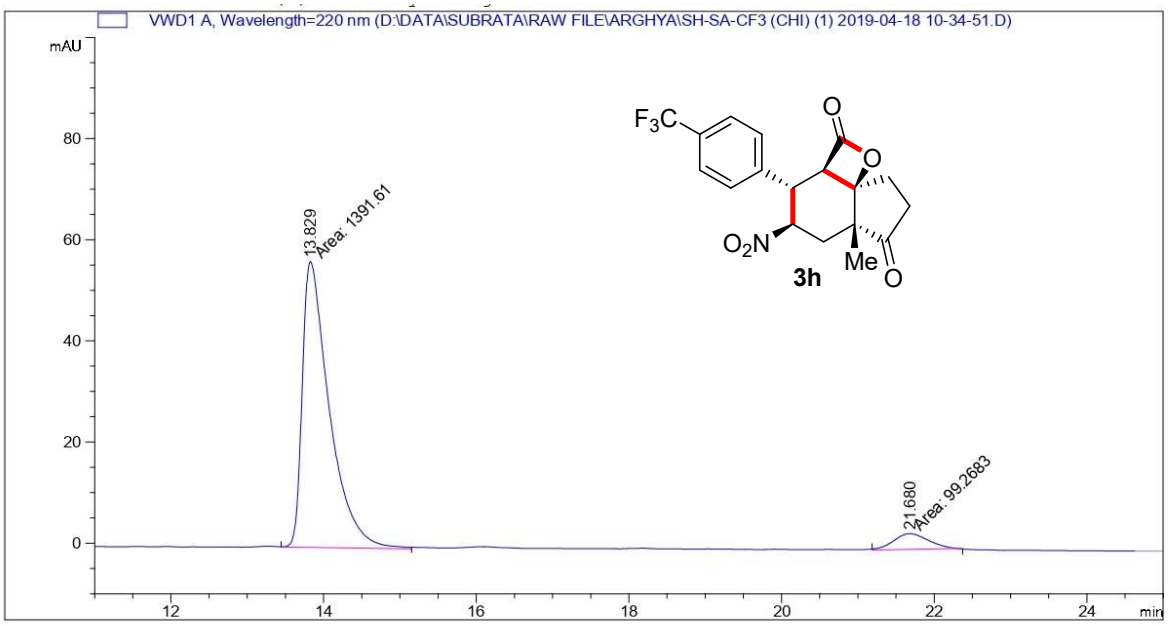
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.444	MM	0.5148	2608.55054	84.45856	99.4704
2	27.125	MM	0.6826	13.88718	3.39088e-1	0.5296

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(4-trifluoromethyl)-phenylhexahydro-2*H*-indeno[3a,4-b]oxete2,6(2a*H*)-dione (3h)



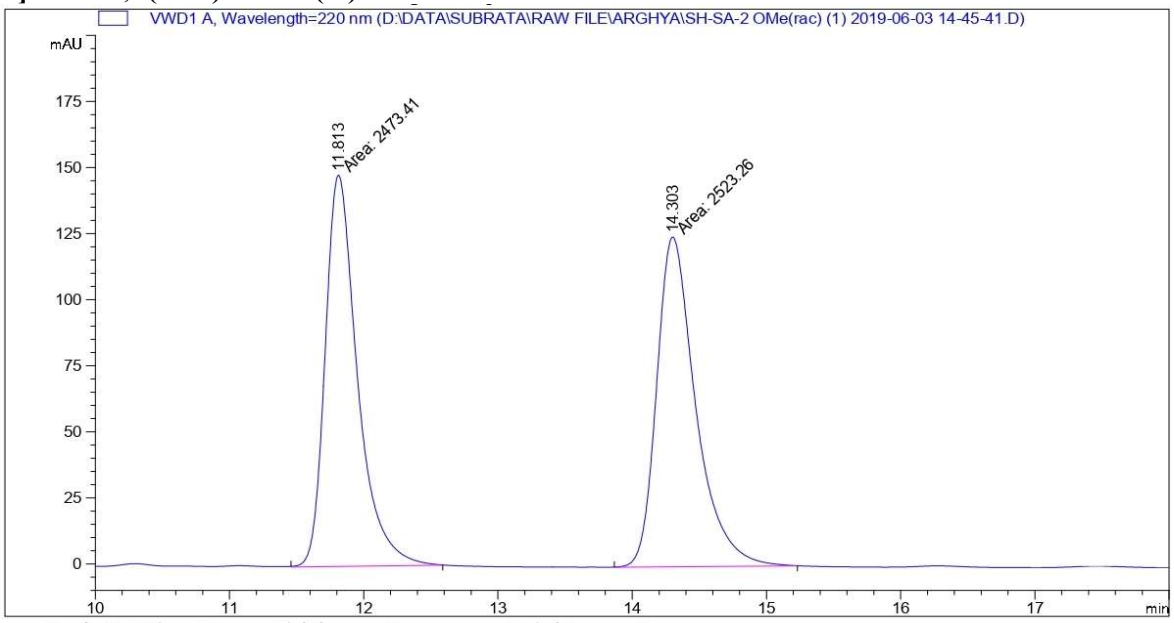
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.544	MM	0.4896	1545.30066	52.60073	49.9632
2	22.382	MM	0.6366	1547.57825	40.51761	50.0368



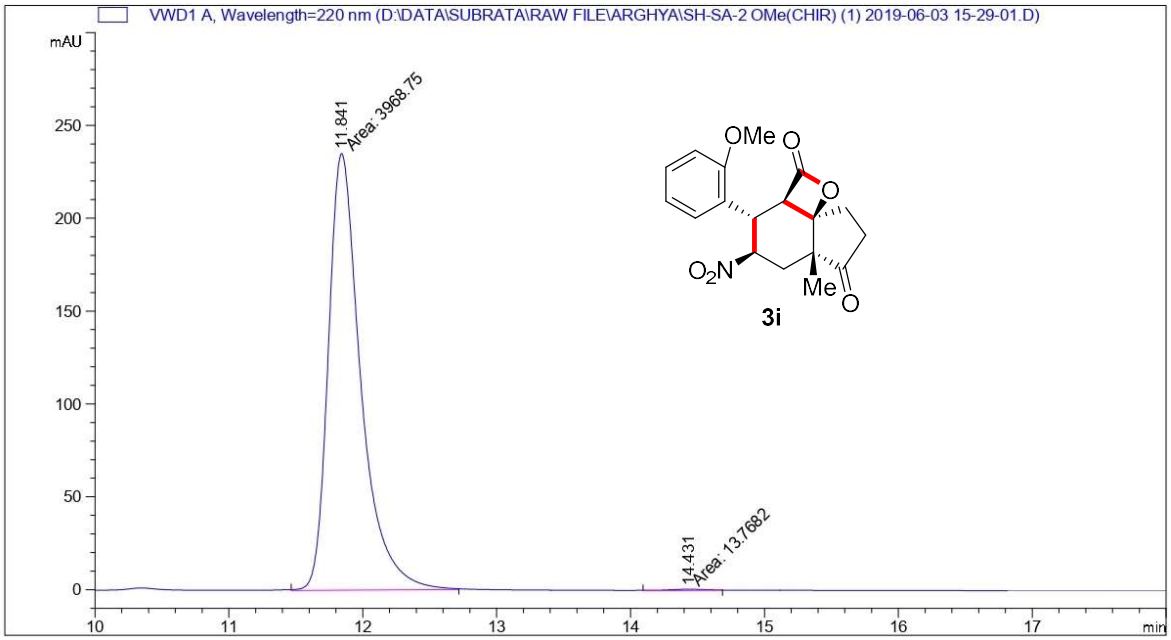
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.829	MM	0.4102	1391.60620	56.53920	93.3416
2	21.680	MM	0.5302	99.26832	3.12046	6.6584

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(2-Methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3i)



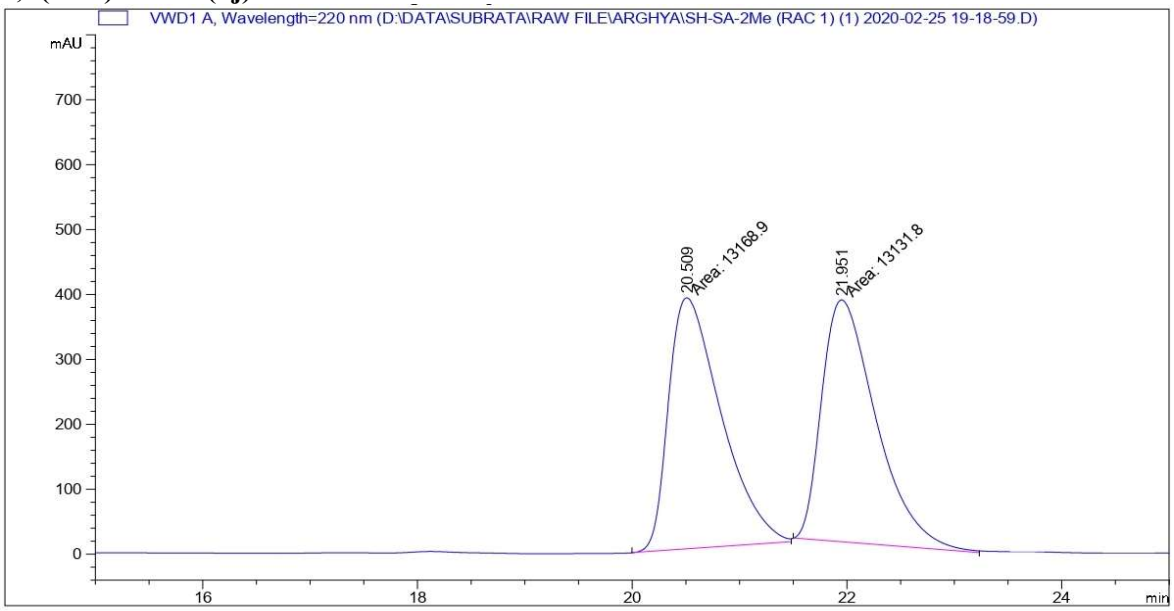
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.813	MM	0.2784	2473.40674	148.06802	49.5011
2	14.303	MM	0.3370	2523.26489	124.80038	50.4989



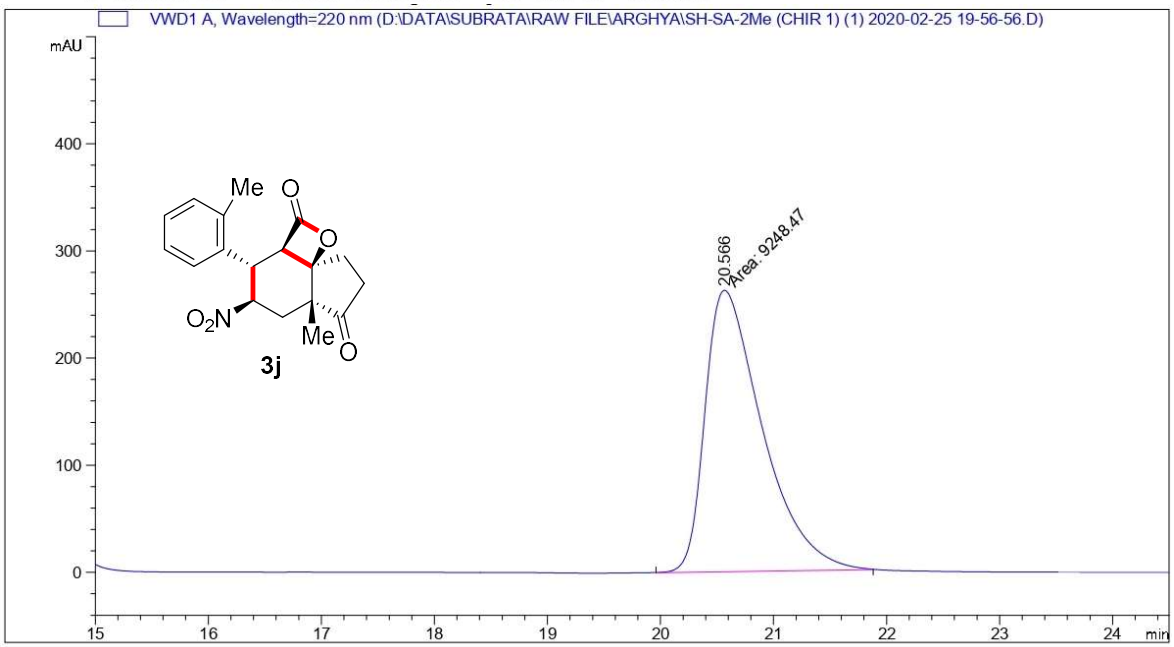
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.841	MM	0.2814	3968.74634	235.08987	99.6543
2	14.431	MM	0.3574	13.76818	6.42070e-1	0.3457

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(o-tolyl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3j)



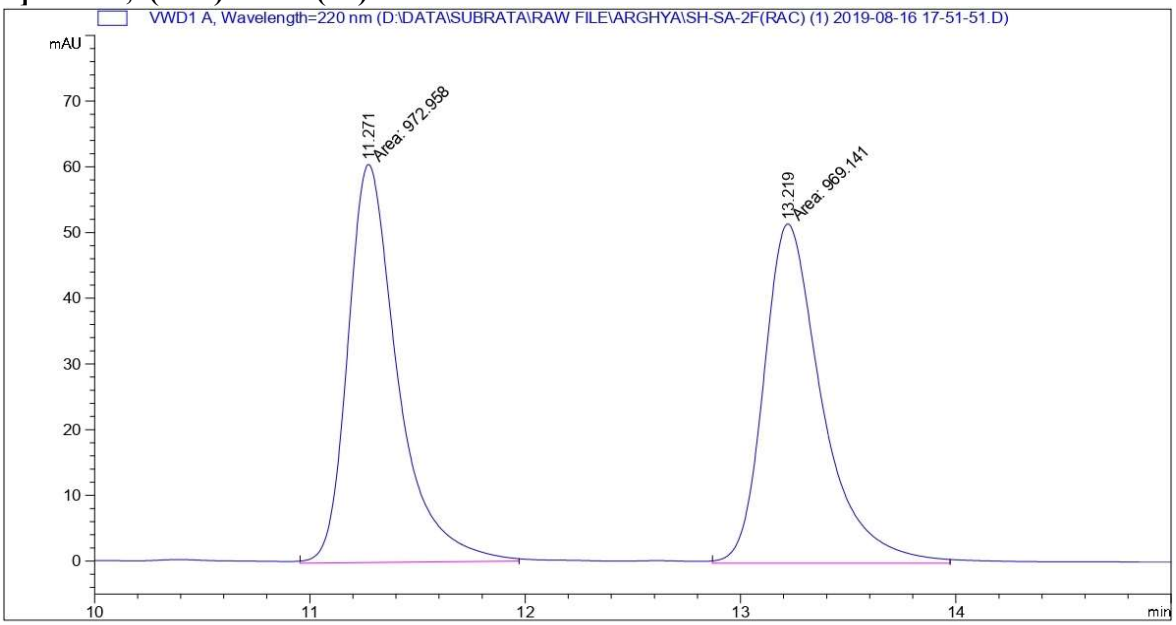
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.509	MM	0.5676	1.31689e4	386.68896	50.0706
2	21.951	MM	0.5876	1.31318e4	372.47964	49.9294



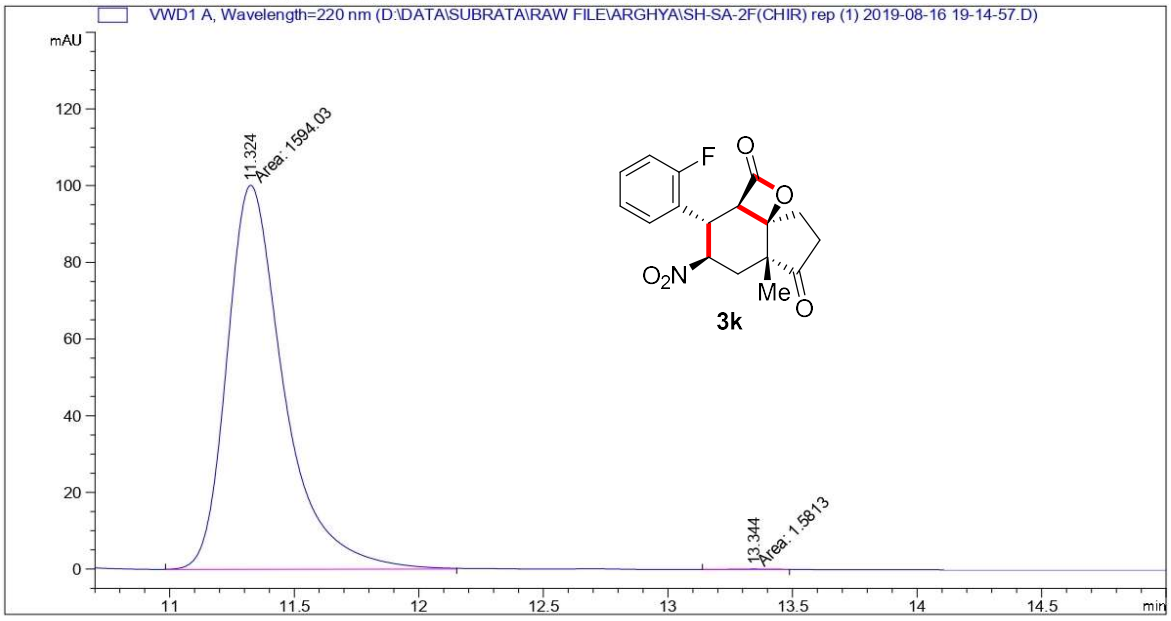
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.566	MM	0.5869	9248.46680	262.64459	100.0000

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(2-Fluorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3k)



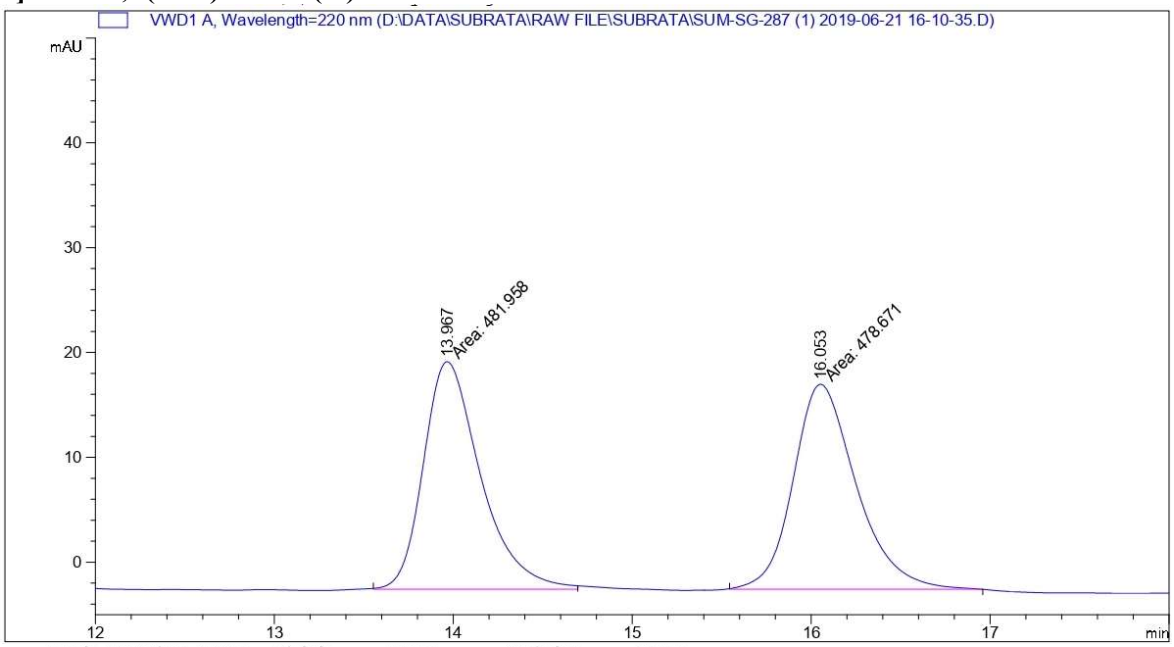
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.271	MM	0.2677	972.95819	60.57100	50.0983
2	13.219	MM	0.3129	969.14050	51.61535	49.9017



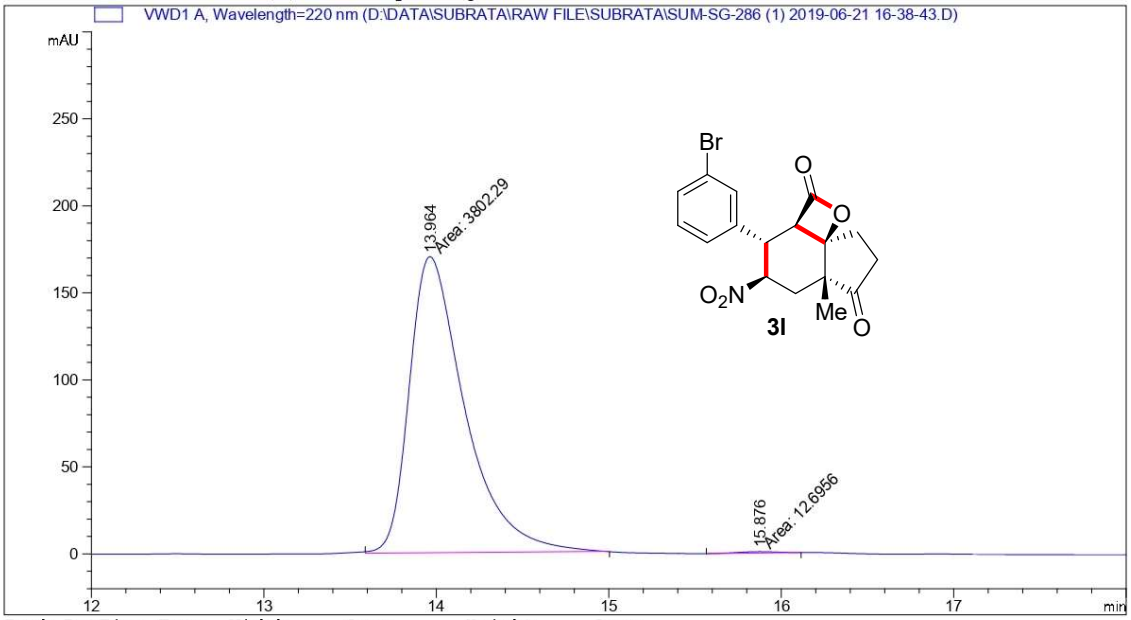
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.324	MM	0.2653	1594.03430	100.15165	99.9009
2	13.344	MM	0.2122	1.58130	1.24215e-1	0.0991

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2*aR*,3*S*,4*R*,5*aR*,8*aR*)-3-(3-Bromophenyl)-5*a*-methyl-4-nitrohexahydro-2*H*-indeno[3*a*,4-*b*]oxete-2,6(2*aH*)-dione (3l)



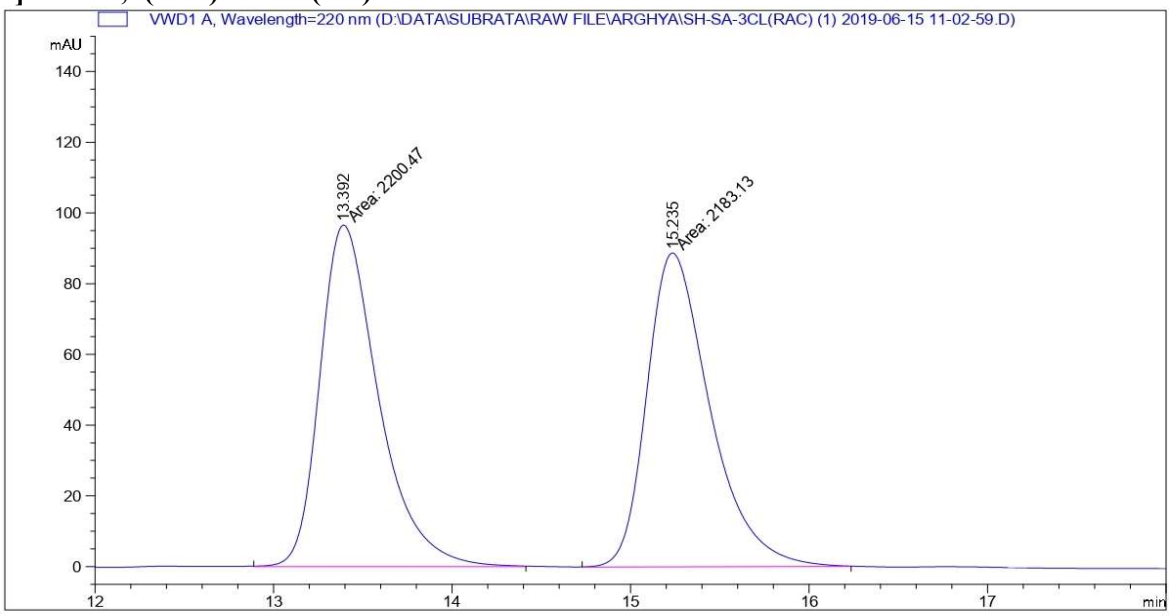
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.967	MM	0.3702	481.95840	21.69776	50.1711
2	16.053	MM	0.4081	478.67059	19.54736	49.8289



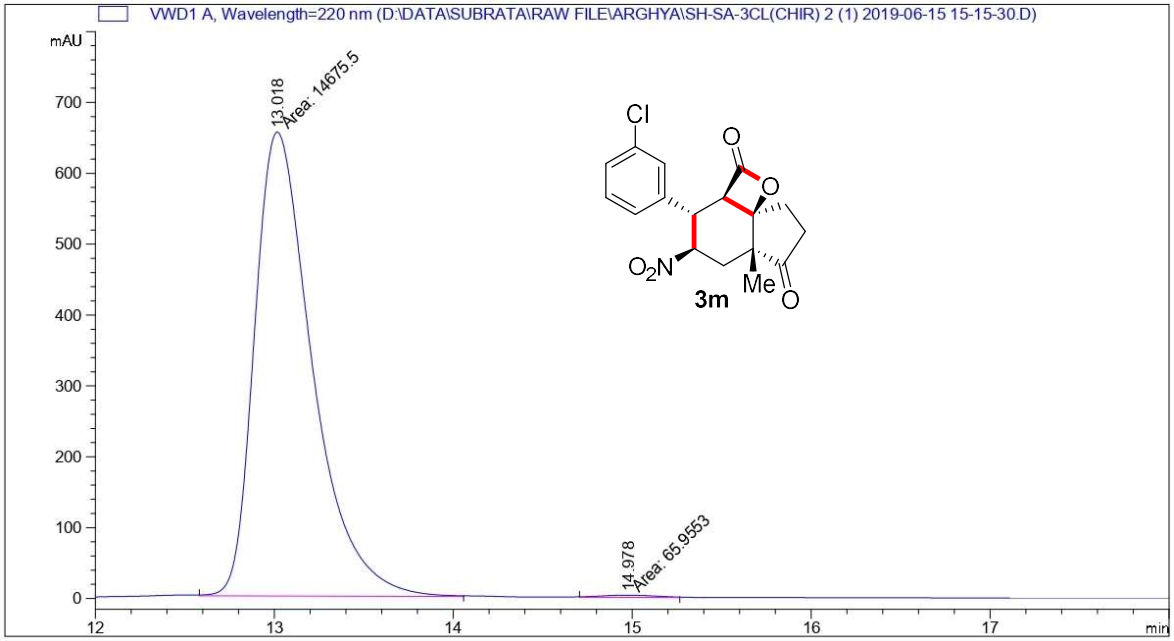
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.964	MM	0.3725	3802.29150	170.11305	99.6672
2	15.876	MM	0.2740	12.69561	7.72301e-1	0.3328

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3 Chlorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3m)



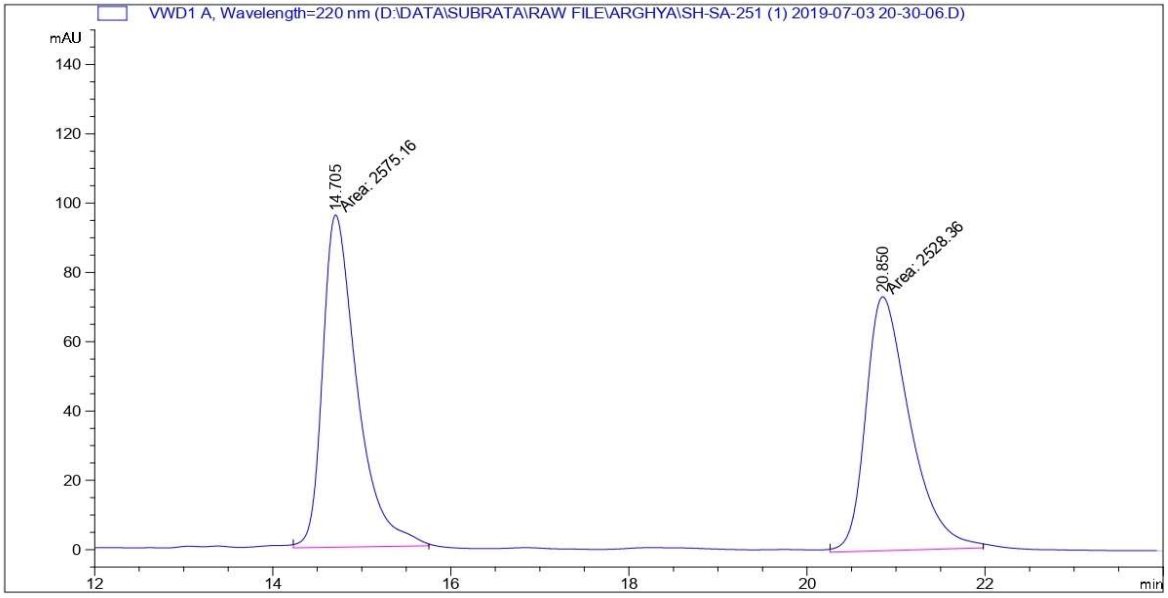
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.392	MM	0.3797	2200.47217	96.59611	50.1978
2	15.235	MM	0.4099	2183.13330	88.76357	49.8022



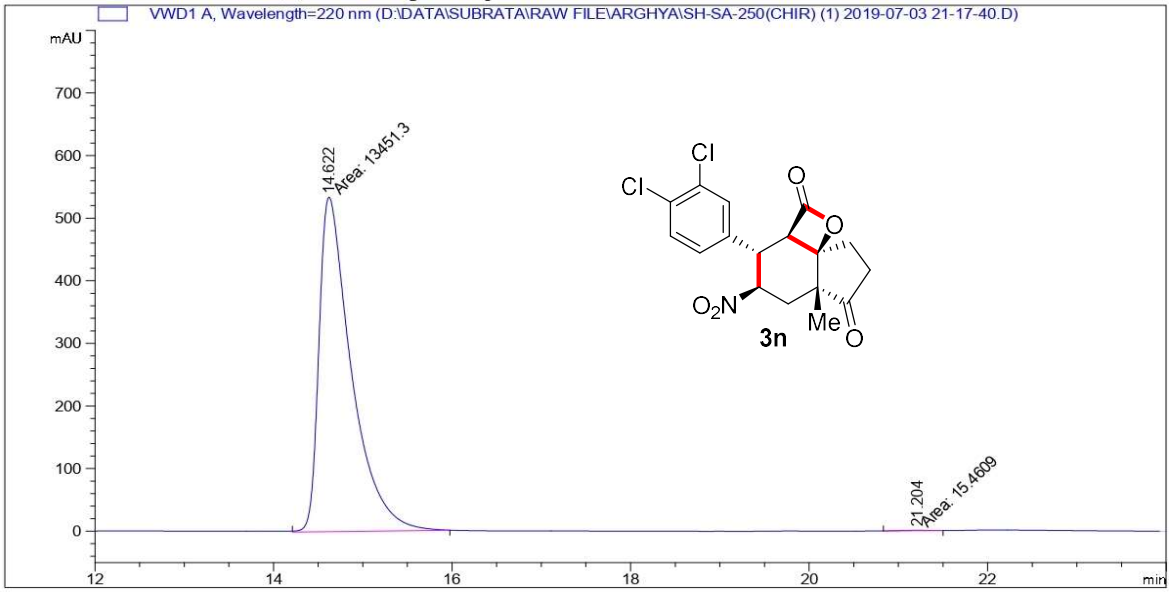
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.018	MM	0.3737	1.46755e4	654.56738	99.5526
2	14.978	MM	0.3572	65.95528	3.07727	0.4474

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3,4-Dichlorophenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3n)



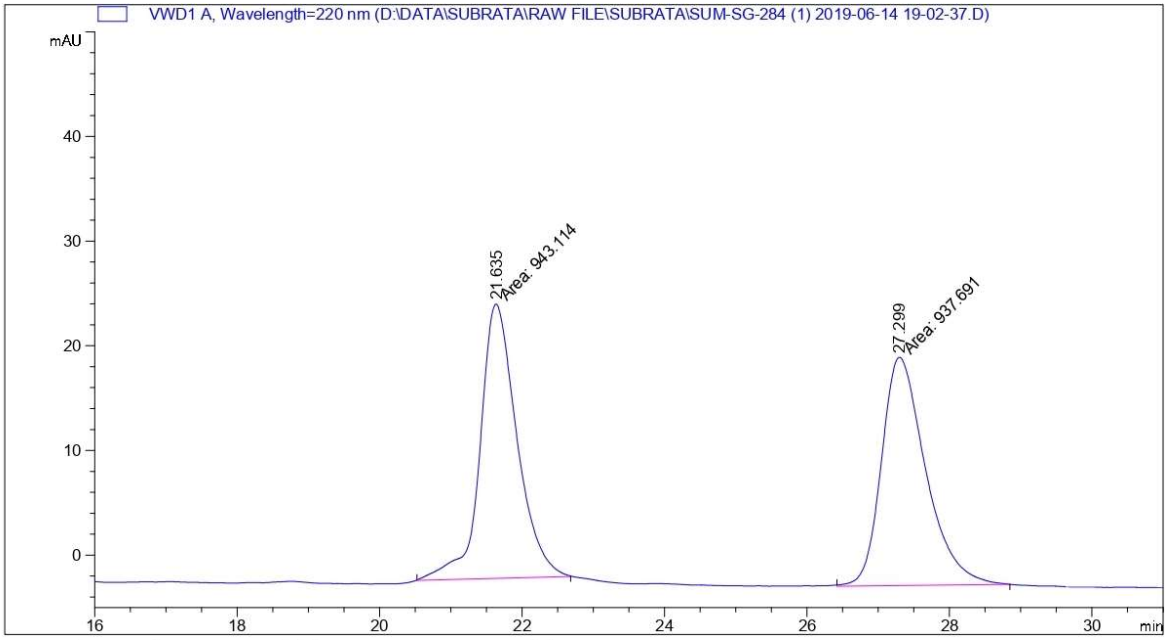
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.705	MM	0.4475	2575.16260	95.90157	50.4585
2	20.850	MM	0.5750	2528.36255	73.28782	49.5415



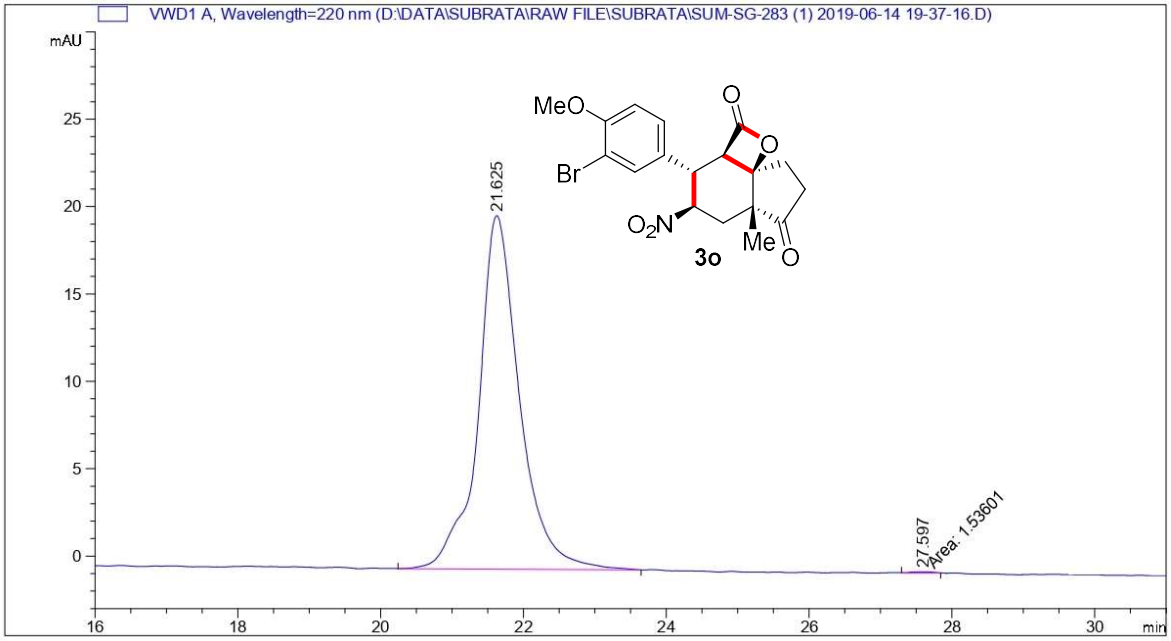
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.622	MM	0.4196	1.34513e4	534.33258	99.8852
2	21.204	MM	0.3789	15.46085	6.80081e-1	0.1148

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-3-(3-Bromo-4-methoxyphenyl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3o)



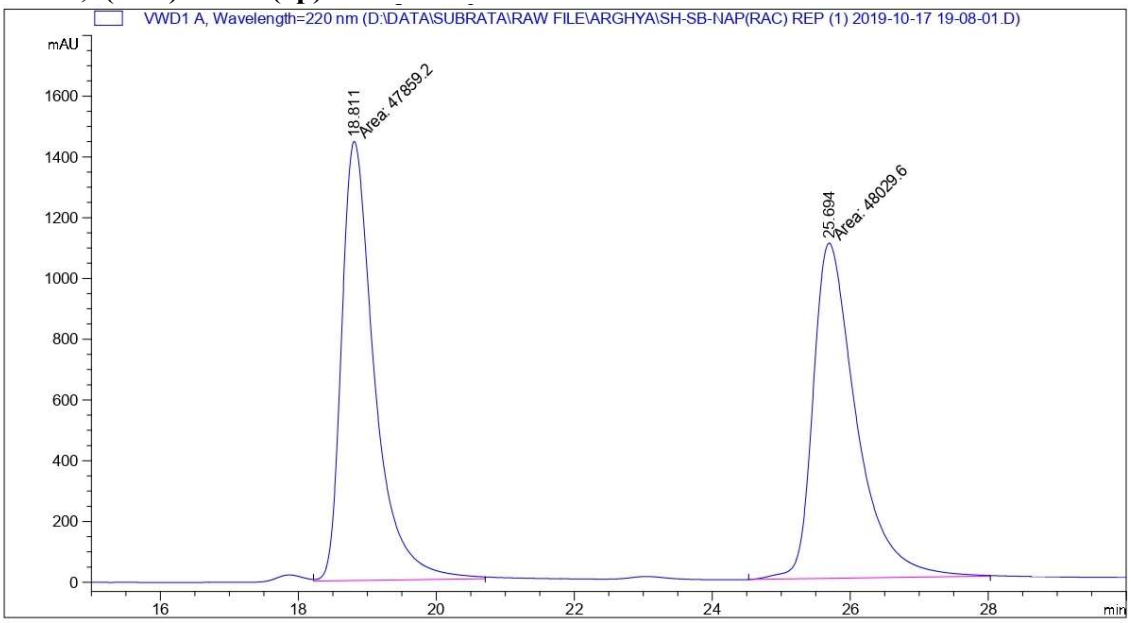
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.635	MM	0.5999	943.11407	26.20073	50.1442
2	27.299	MM	0.7170	937.69110	21.79679	49.8558



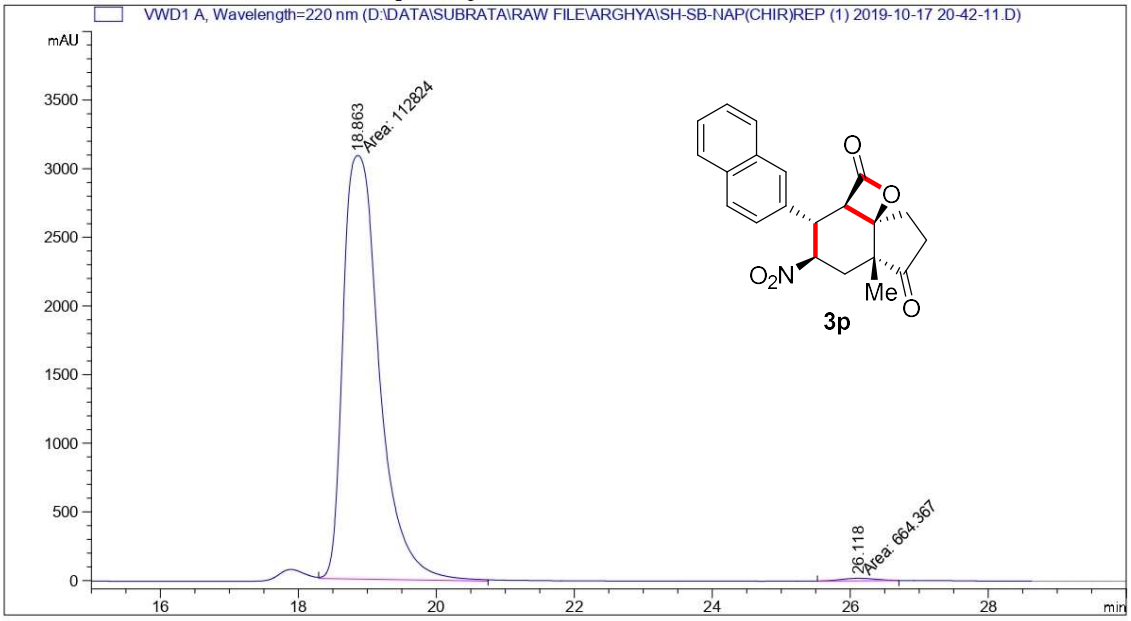
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.625	BB	0.5882	811.44281	20.21967	99.8111
2	27.597	MM	0.3574	1.53601	7.16242e-2	0.1889

Sample Info : CHIRALPAK IA, 10%IPA-Hexane, 1.0 mL/min, 254 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-3-(naphthalen-2-yl)-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3p)



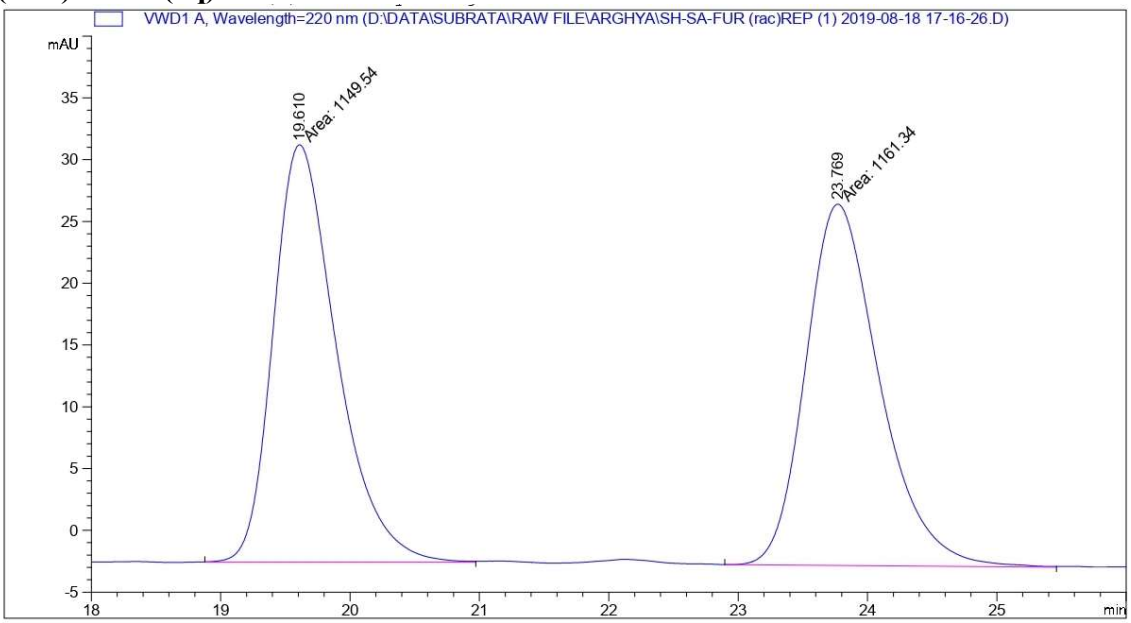
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.811	MM	0.5518	4.78592e4	1445.47668	49.9111
2	25.694	MM	0.7254	4.80296e4	1103.45667	50.0889



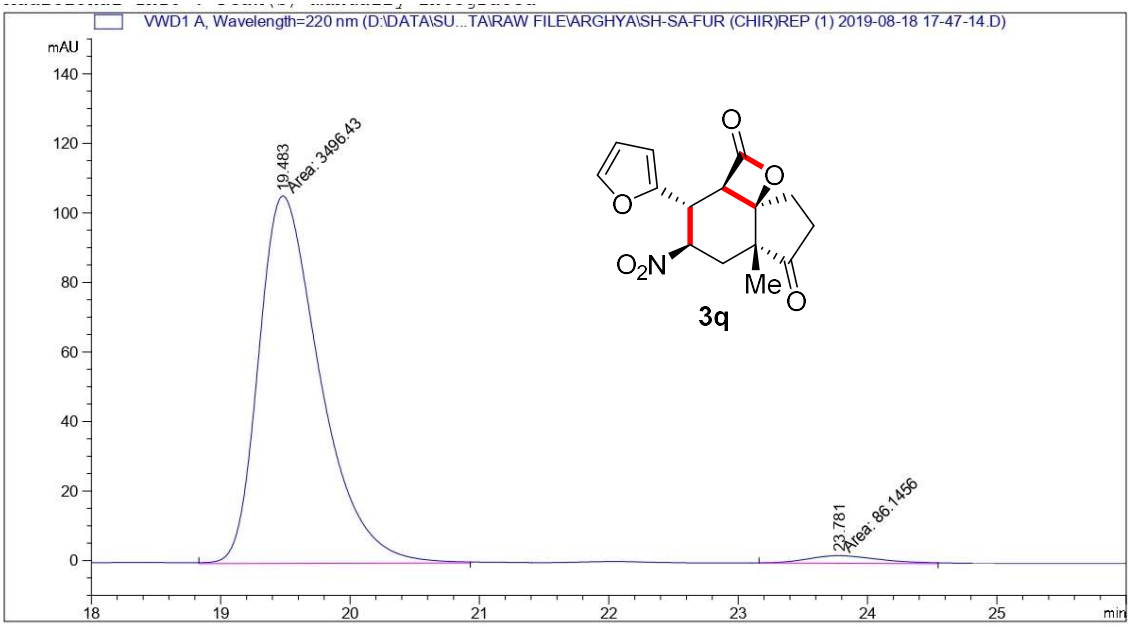
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.863	MM	0.6095	1.12824e5	3085.27612	99.4146
2	26.118	MM	0.5924	664.36725	18.69024	0.5854

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*R*,4*R*,5a*R*,8a*R*)-3-(Furan-2-yl)-5a-methyl-4-nitrohexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3q)



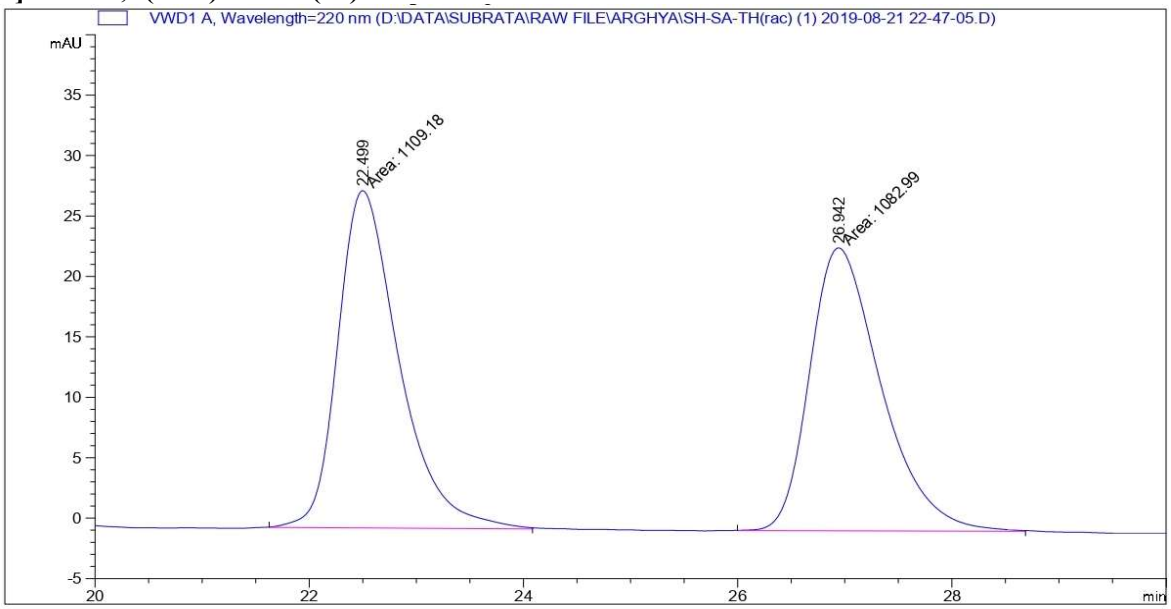
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.610	MM	0.5673	1149.53882	33.77121	49.7447
2	23.769	MM	0.6619	1161.33765	29.24184	50.2553



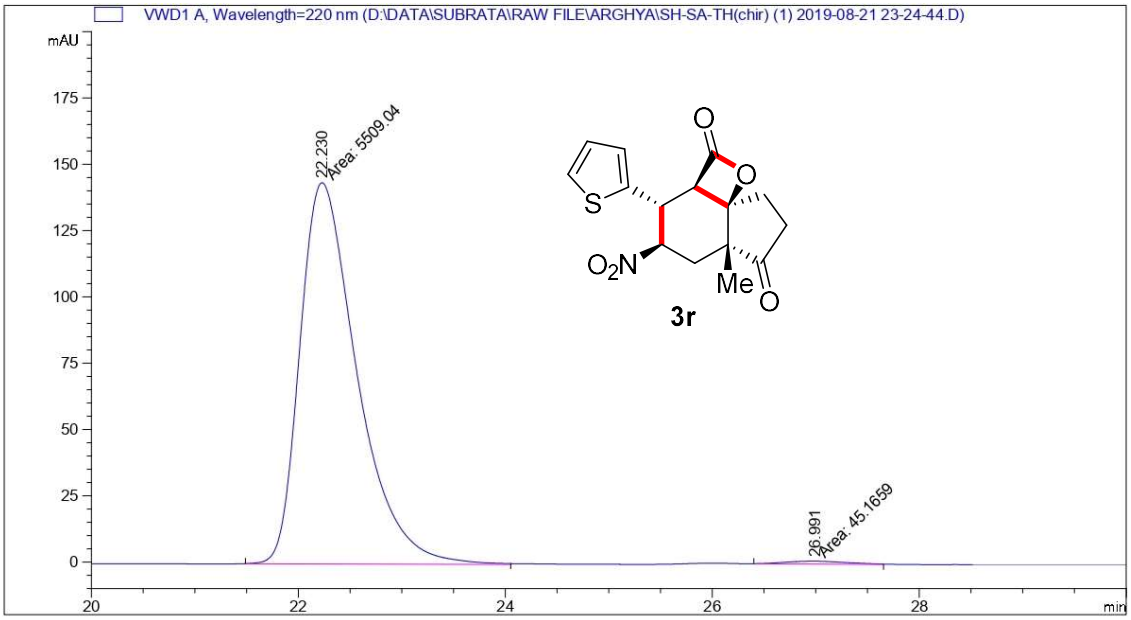
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.483	MM	0.5512	3496.42749	105.71329	97.5954
2	23.781	MM	0.6492	86.14558	2.21153	2.4046

Sample Info : CHIRALPAK IC, 10% IPA-HEXANE, 1 mL -min, 220 nm

(2a*R*,3*R*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(thiophen-2-yl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3r)



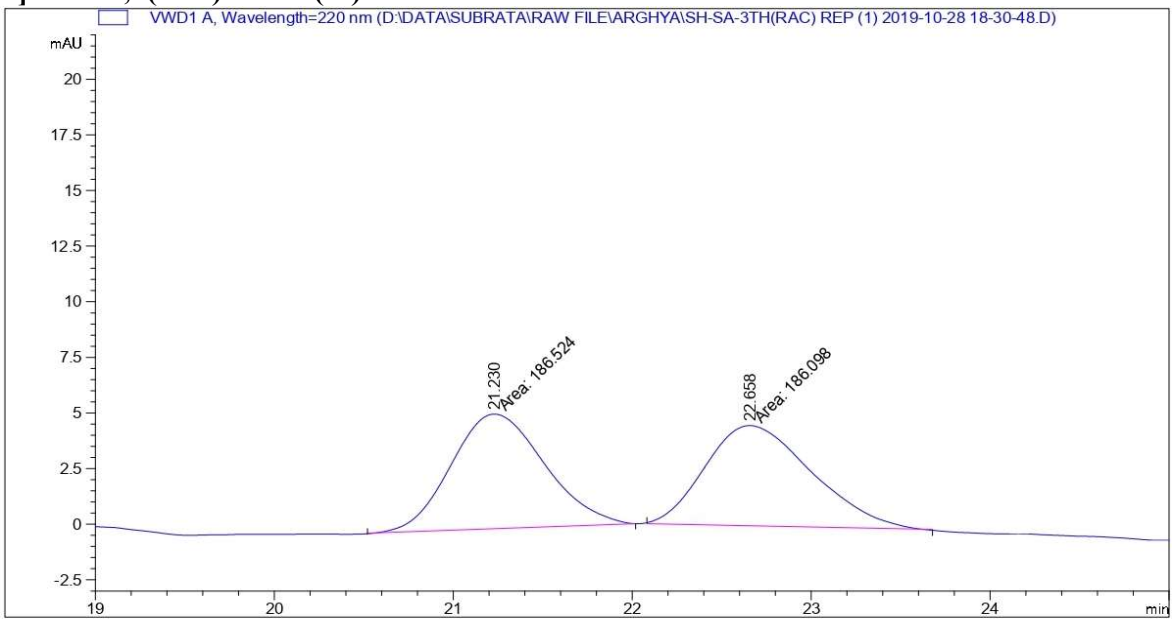
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.499	MM	0.6625	1109.17676	27.90394	50.5974
2	26.942	MM	0.7713	1082.98657	23.40303	49.4026



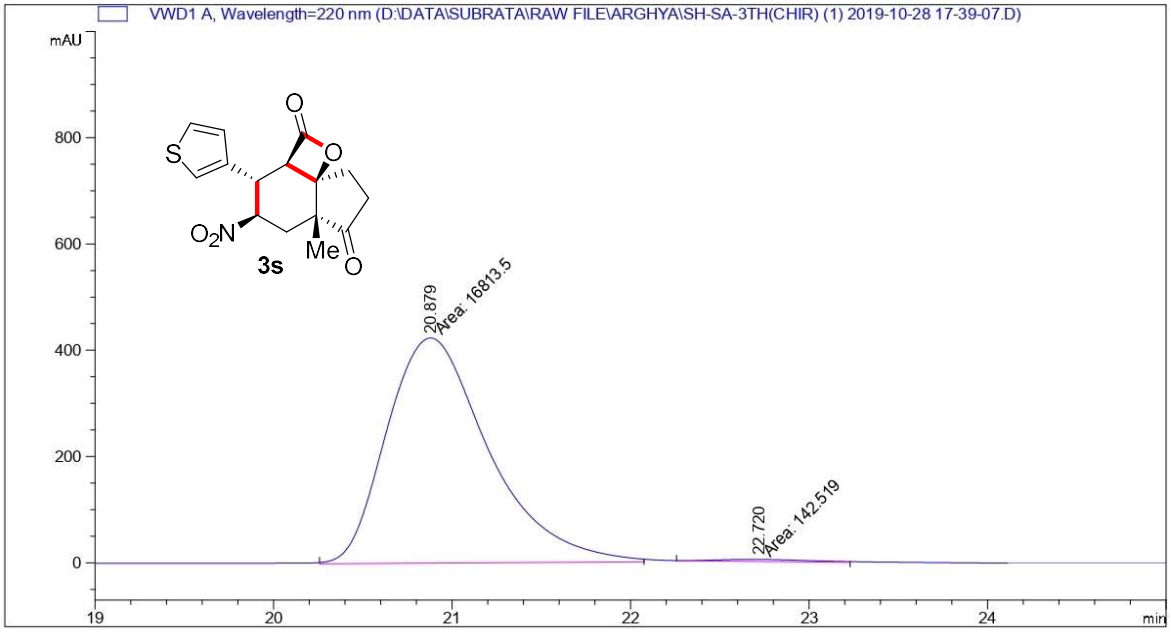
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.230	MM	0.6388	5509.04248	143.73544	99.1868
2	26.991	MM	0.6967	45.16589	1.08052	0.8132

Sample Info : CHIRALPAK IC, 10% IPA-HEXANE, 1 mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-(thiophen-3-yl)hexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3s)



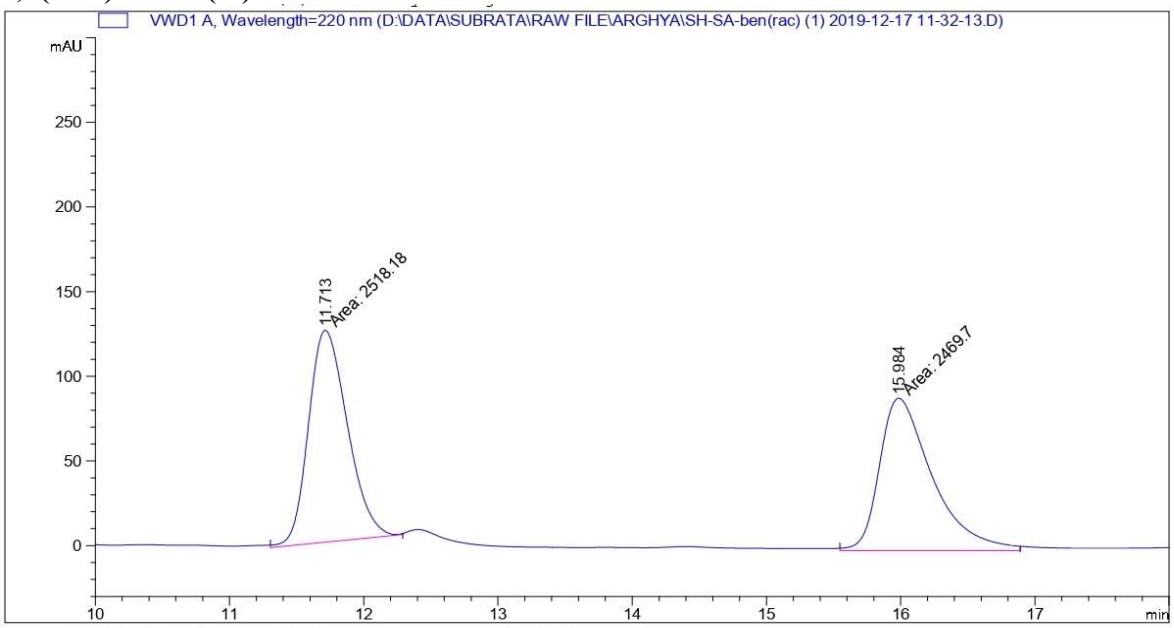
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.230	MM	0.6035	186.52415	5.15078	50.0571
2	22.658	MM	0.6885	186.09833	4.50500	49.9429



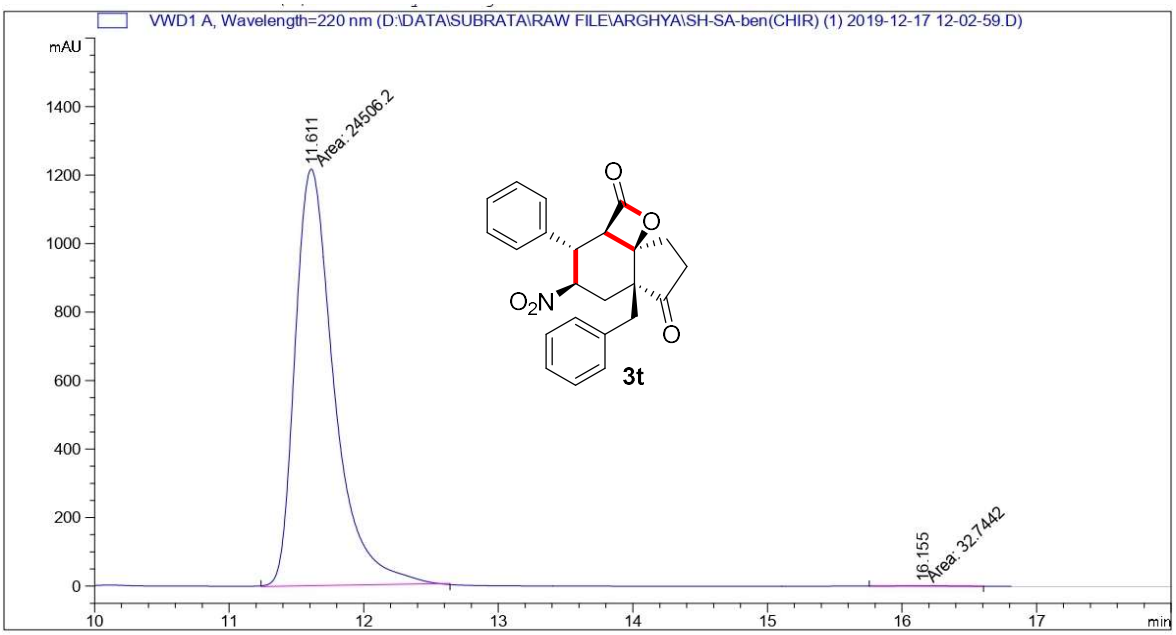
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.879	MM	0.6617	1.68135e4	423.51276	99.1595
2	22.720	MM	0.5989	142.51880	3.96580	0.8405

Sample Info : CHIRALPAK IC, 10 %IPA-HEXANE, 1 mL -min, 254nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Benzyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3t)



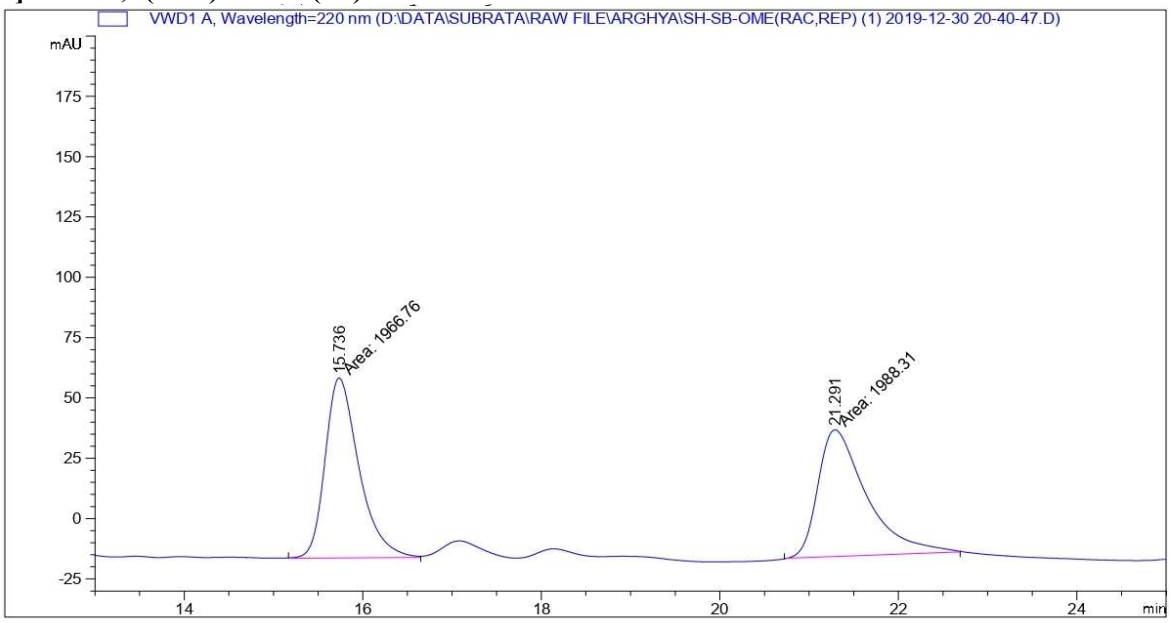
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.713	MM	0.3355	2518.17627	125.10009	50.4859
2	15.984	MM	0.4571	2469.70166	90.05299	49.5141



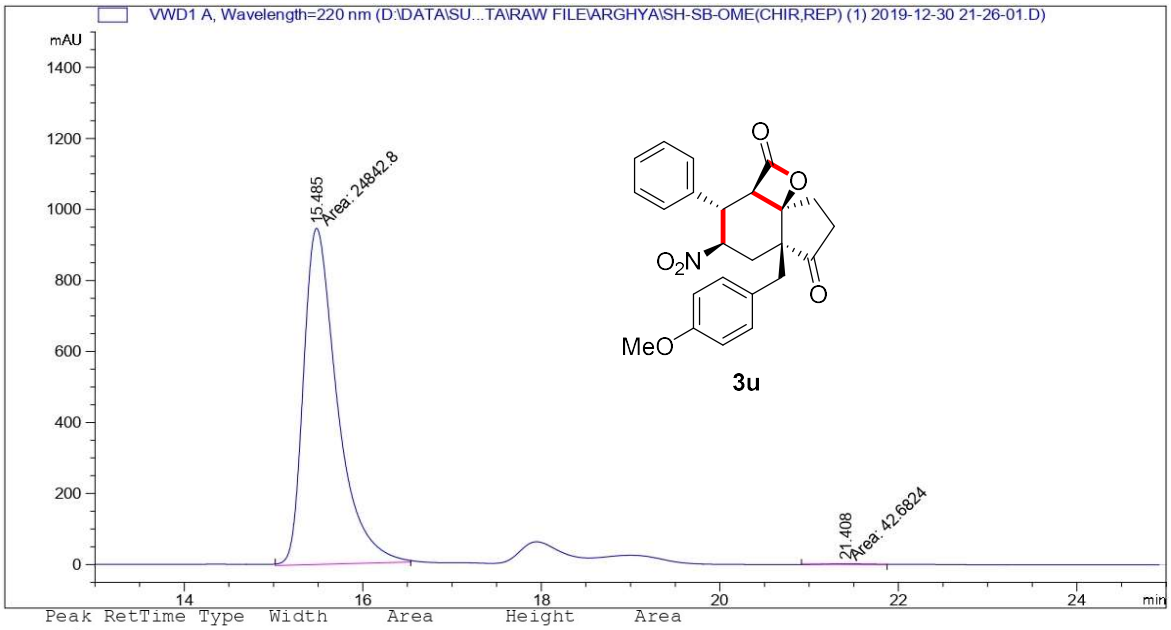
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.611	MM	0.3359	2.45062e4	1215.97314	99.8666
2	16.155	MM	0.4023	32.74419	1.35649	0.1334

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-(4-Methoxybenzyl)-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3u)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.736	MM	0.4395	1966.76172	74.58603	49.7276
2	21.291	MM	0.6310	1988.30933	52.52089	50.2724

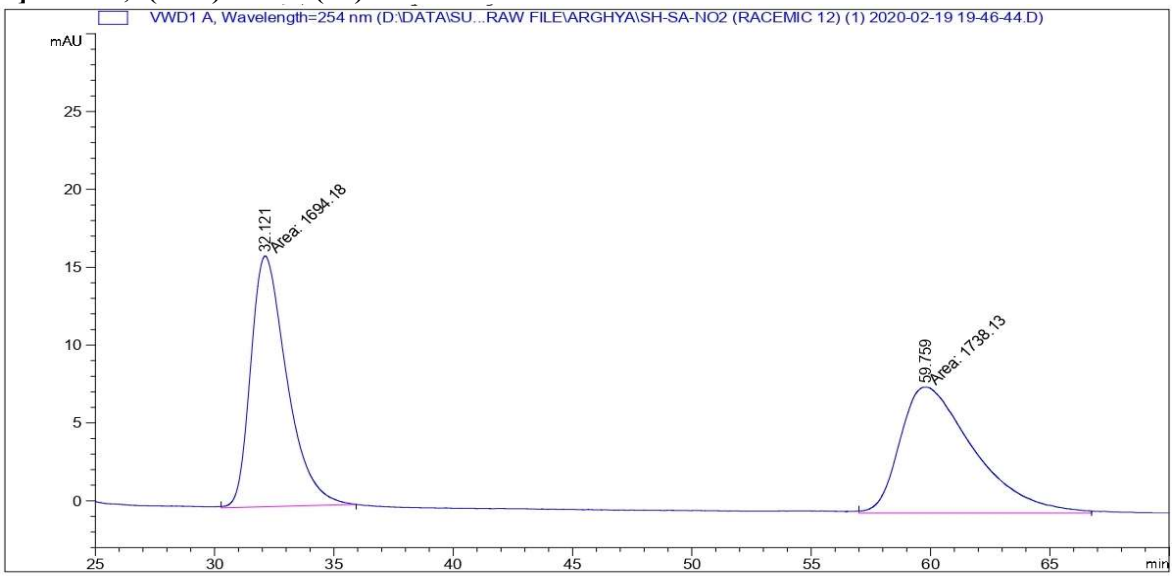


3u

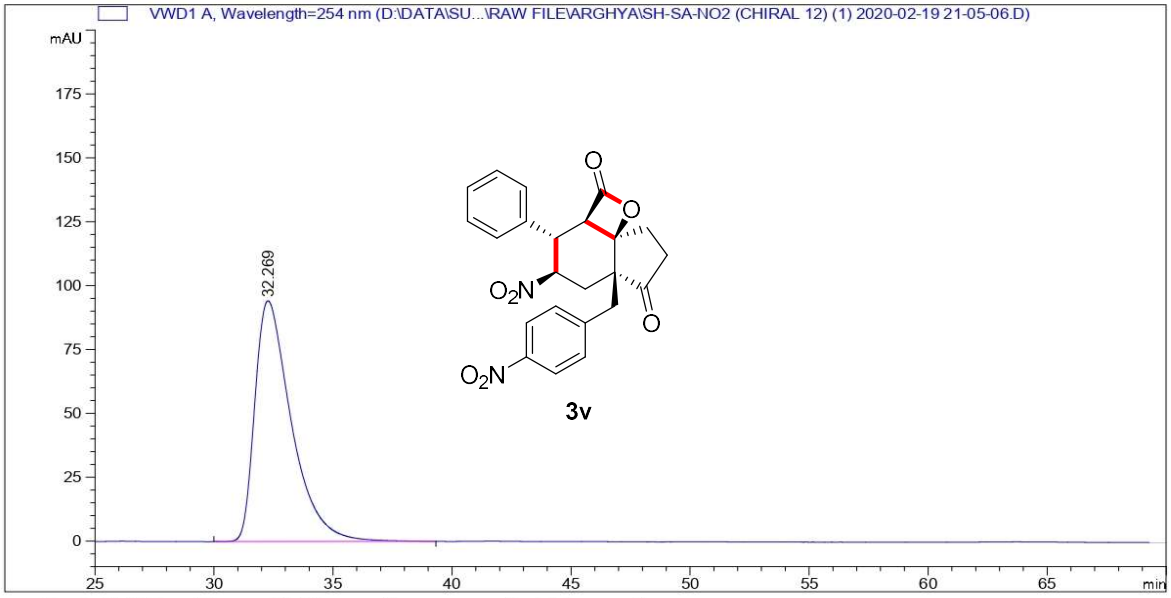
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.485	MM	0.4373	2.48428e4	946.86902	99.8285
2	21.408	MM	0.4684	42.68240	1.51882	0.1715

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-4-Nitro-5a-(4-nitrobenzyl)-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3v)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.121	MM	1.7535	1694.18030	16.10247	49.3598
2	59.759	MM	3.5845	1738.13013	8.08181	50.6402

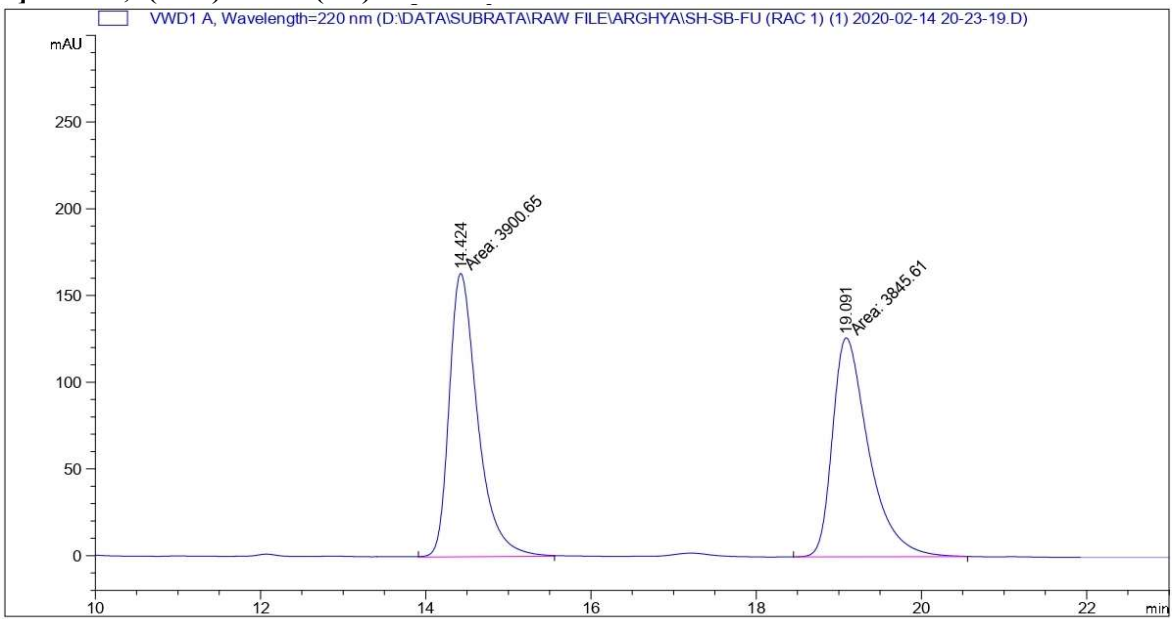


3v

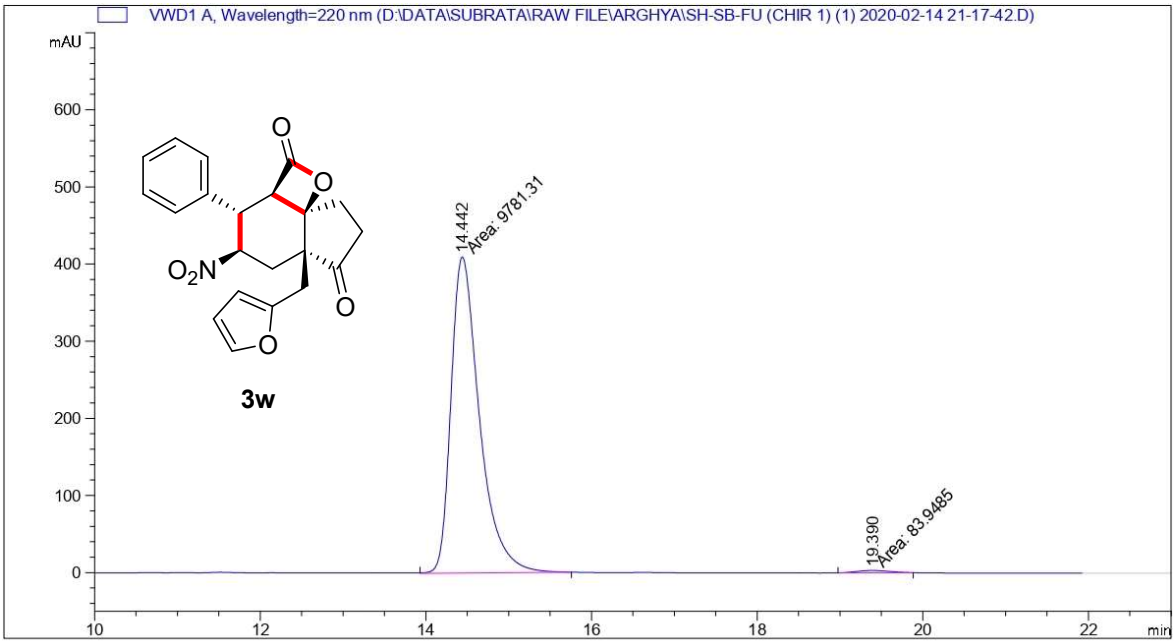
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.269	BB	1.5562	1.00514e4	94.24731	100.0000

Sample Info : CHIRALPAK OD-H, 20 % IPA-HEXANE, 1 mL -min, 254 nm

(2a*R*,3*S*,4*R*,5a*S*,8a*R*)-5a-(Furan-2-ylmethyl)-4-nitro-3-phenylhexahydro-2*H*indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3w)



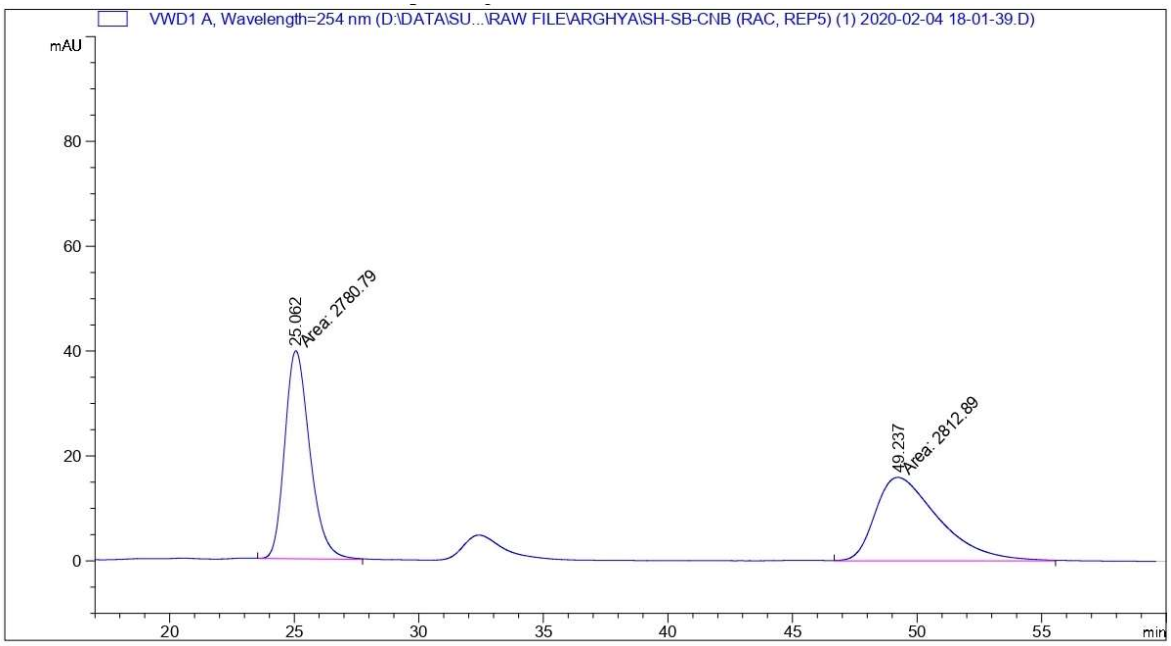
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.424	MM	0.3980	3900.65308	163.33611	50.3553
2	19.091	MM	0.5075	3845.60889	126.28579	49.6447



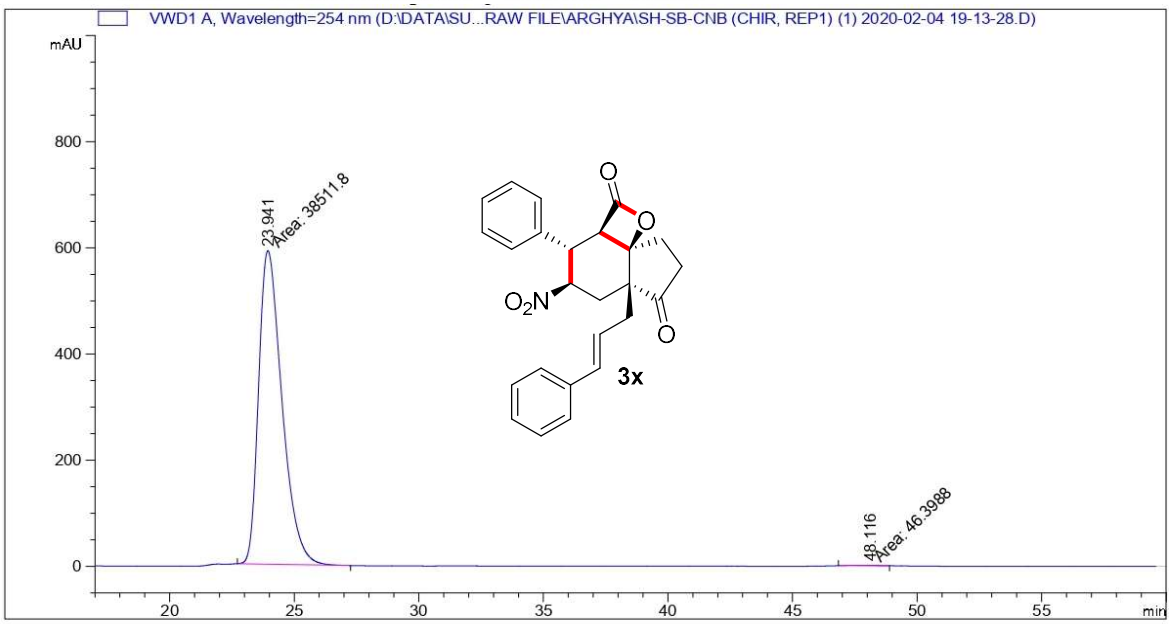
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.442	MM	0.3979	9781.30664	409.75076	99.1490
2	19.390	MM	0.4623	83.94849	3.02621	0.8510

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Cinnamyl-4-nitro-3-phenylhexahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3x)



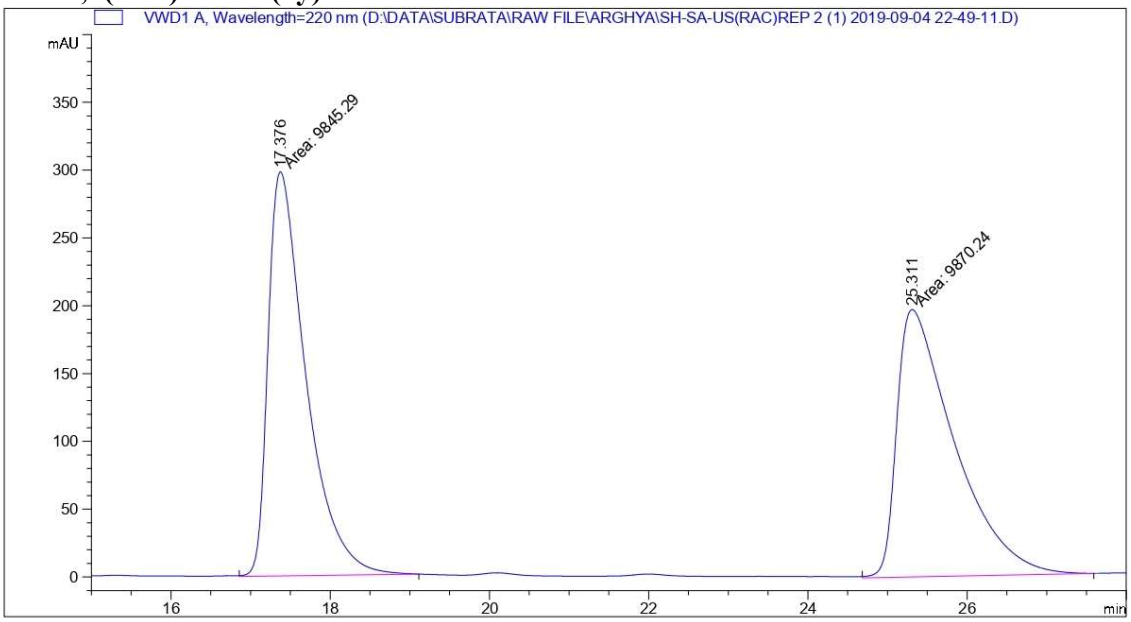
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.062	MM	1.1679	2780.78735	39.68352	49.7130
2	49.237	MM	2.9426	2812.89136	15.93214	50.2870



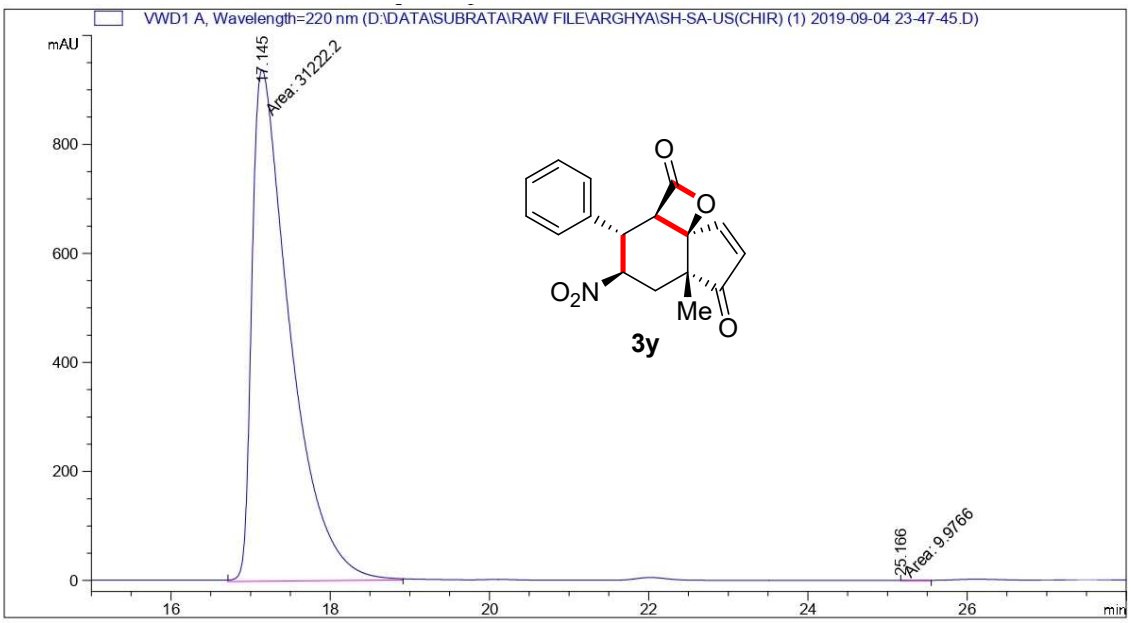
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.941	MM	1.0862	3.85118e4	590.91553	99.8797
2	48.116	MM	1.2905	46.39884	5.99256e-1	0.1203

Sample Info : CHIRALPAK OD-H, 15 % IPA-HEXANE, 1 mL -min, 254 nm

(2a*R*,3*S*,4*R*,5a*R*,8a*R*)-5a-Methyl-4-nitro-3-phenyl-3,4,5,5a-tetrahydro-2*H*-indeno[3a,4-b]oxete-2,6(2a*H*)-dione (3y)



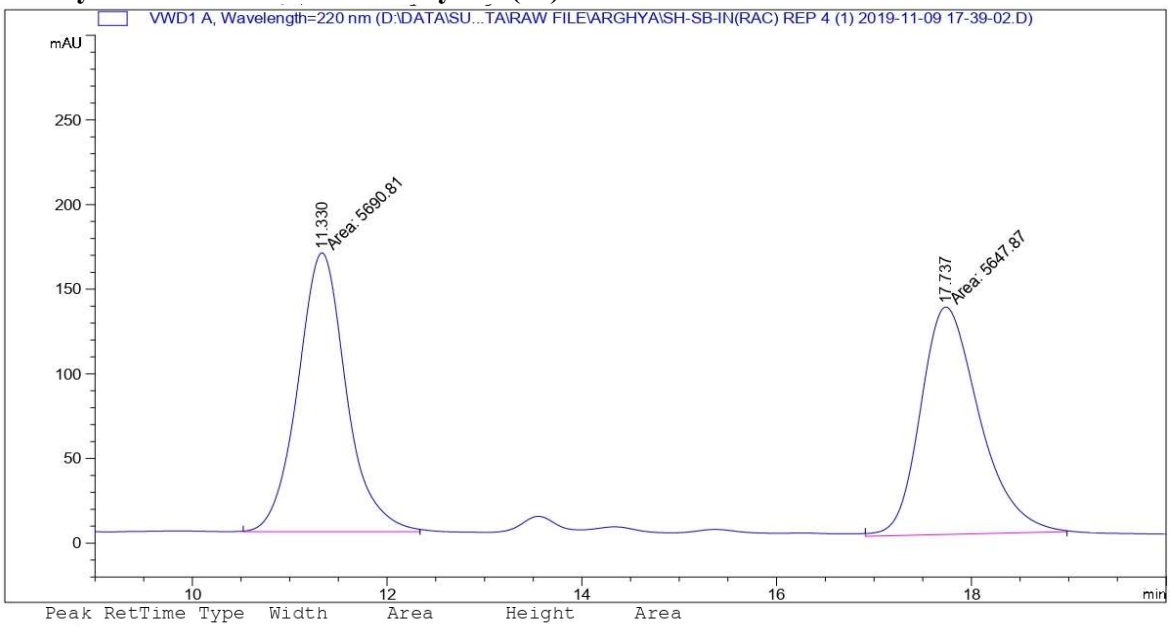
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.376	MM	0.5507	9845.29004	297.95111	49.9367
2	25.311	MM	0.8346	9870.24121	197.11281	50.0633



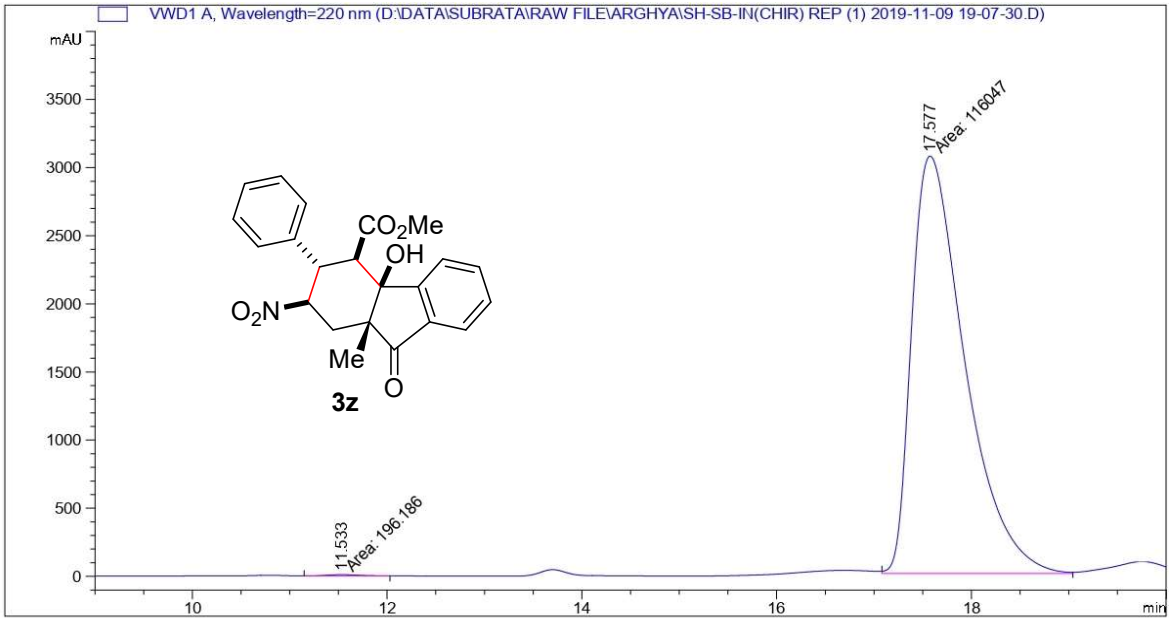
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.145	MM	0.5546	3.12222e4	938.19769	99.9681
2	25.166	MM	0.2827	9.97660	5.88077e-1	0.0319

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

Methyl (2*R*,3*S*,4*R*,4*aS*,9*aR*)-4*a*-hydroxy-9*a*-methyl-2-nitro-9-oxo-3-phenyl-2,3,4,4*a*,9,9*a*-hexahydro-1*H*-fluorene-4-carboxylate (3z)



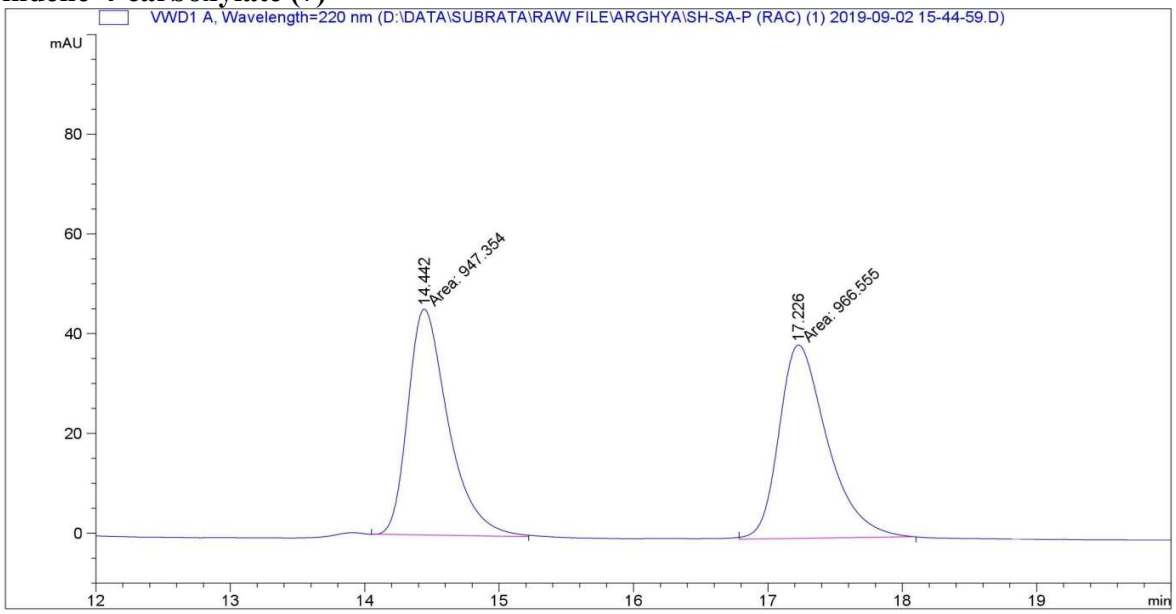
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.330	MM	0.5760	5690.81152	164.65791	50.1894
2	17.737	MM	0.7007	5647.87061	134.34683	49.8106



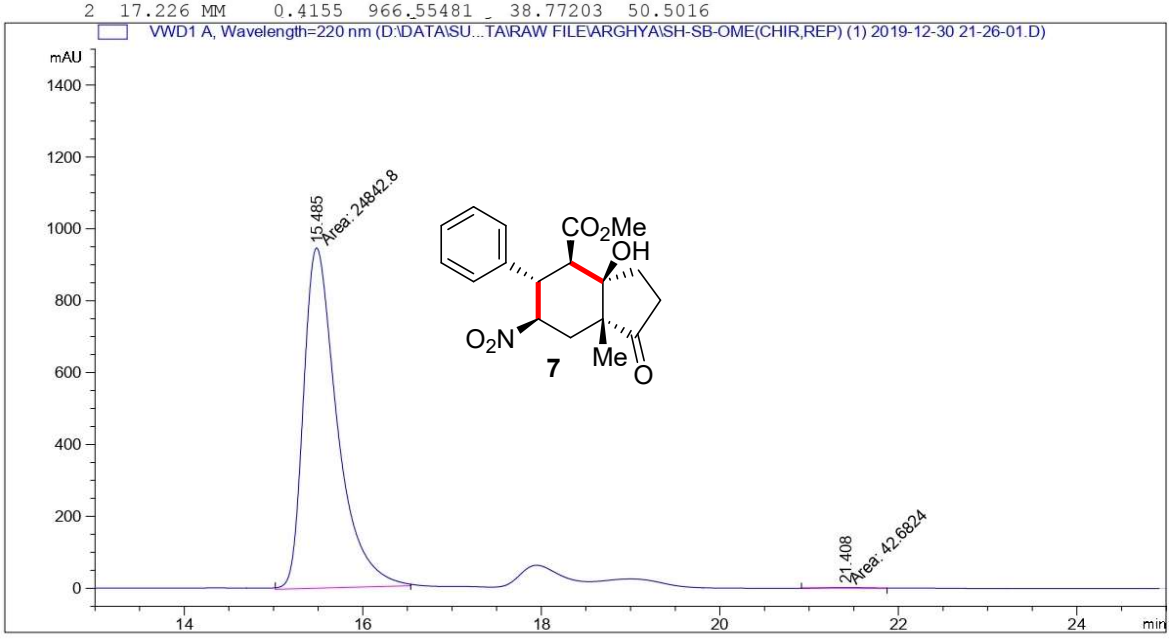
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.533	MM	0.3727	196.18636	8.77224	0.1688
2	17.577	MM	0.6315	1.16047e5	3062.49756	99.8312

Sample Info : CHIRALPAK IC, 10 %IPA-HEXANE, 1.0 mL -min, 220nm

Methyl(3a*R*,4*R*,5*S*,6*R*,7a*R*)-3a-hydroxy-7a-methyl-6-nitro-1-oxo-5-phenyloctahydro-1*H*-indene-4-carboxylate (7)



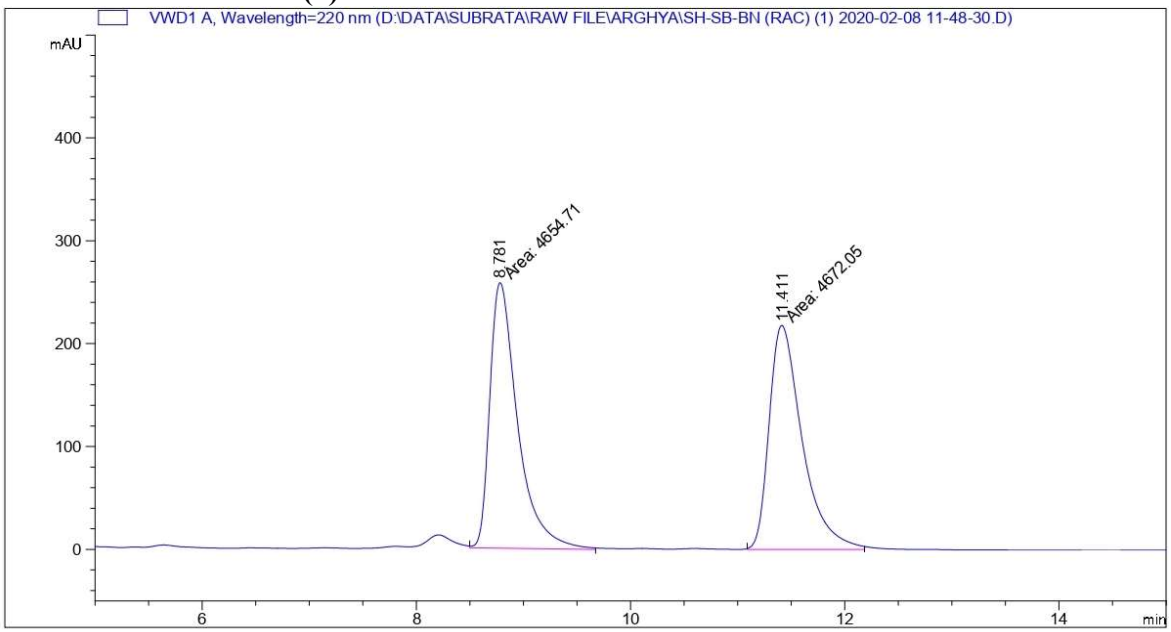
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.442	MM	0.3485	947.35413	45.30332	49.4984
2	17.226	MM	0.4155	966.55481	38.77203	50.5016



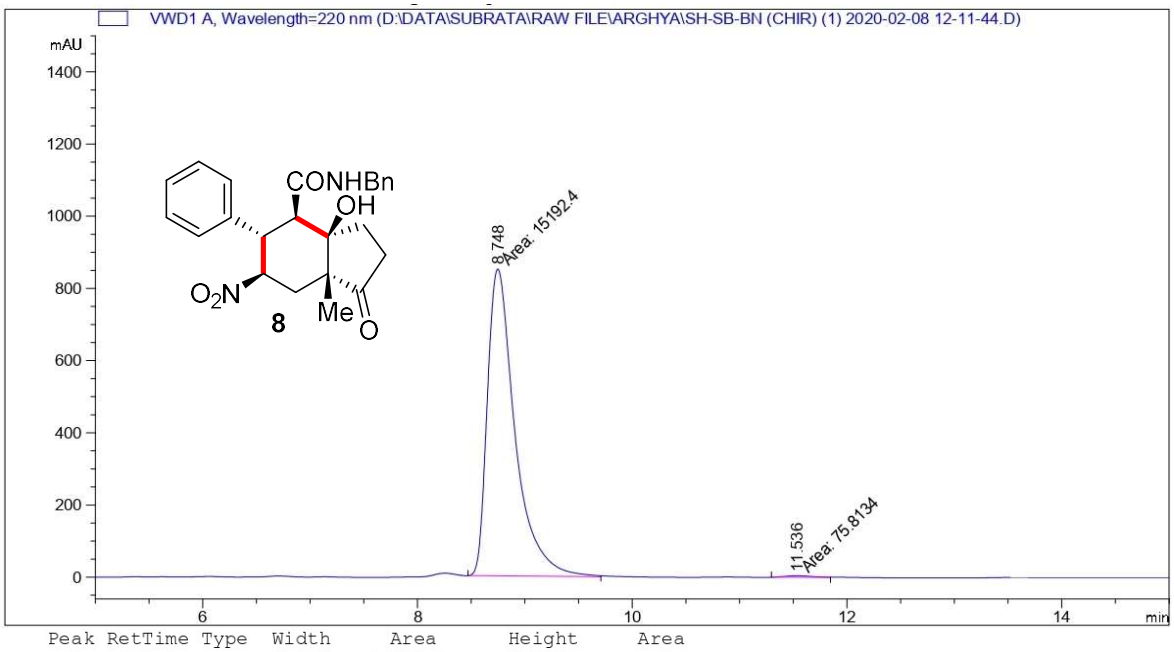
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.485	MM	0.4373	2.48428e4	946.86902	99.8285
2	21.408	MM	0.4684	42.68240	1.51882	0.1715

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm

(3a*R*,4*R*,5*S*,6*R*,7a*R*)-N-Benzyl-3a-hydroxy-7a-methyl-6-nitro-1-oxo-5-phenyloctahydro-1*H*-indene-4-carboxamide (8)



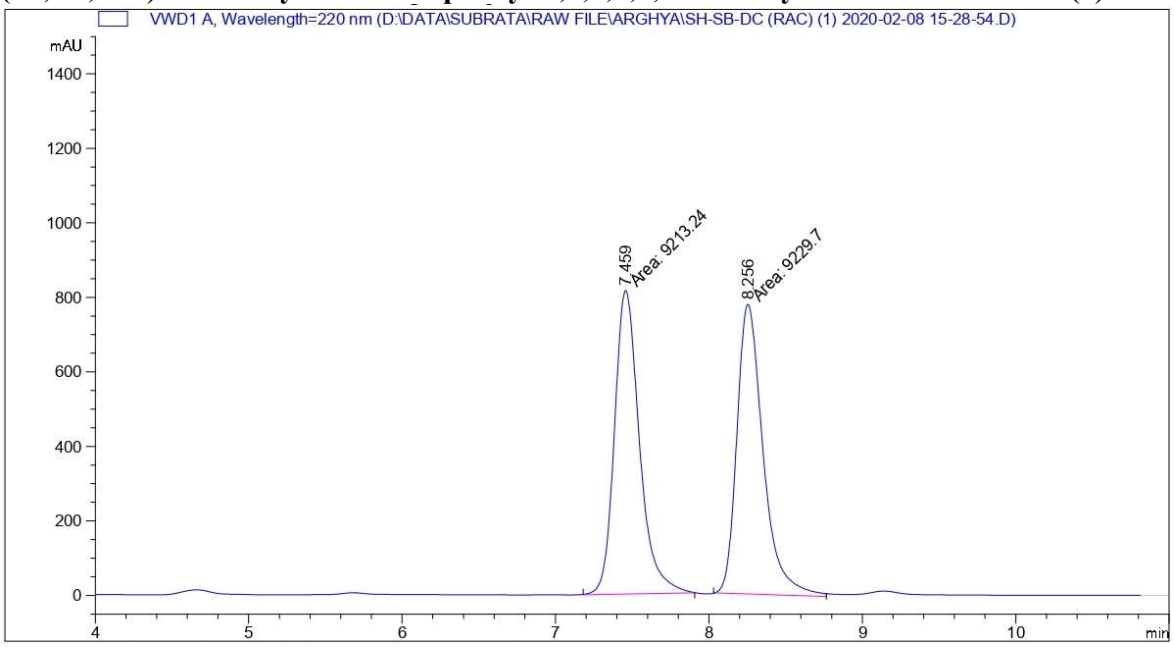
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.781	MM	0.3006	4654.70605	258.08517	49.9070
2	11.411	MM	0.3574	4672.05420	217.89012	50.0930



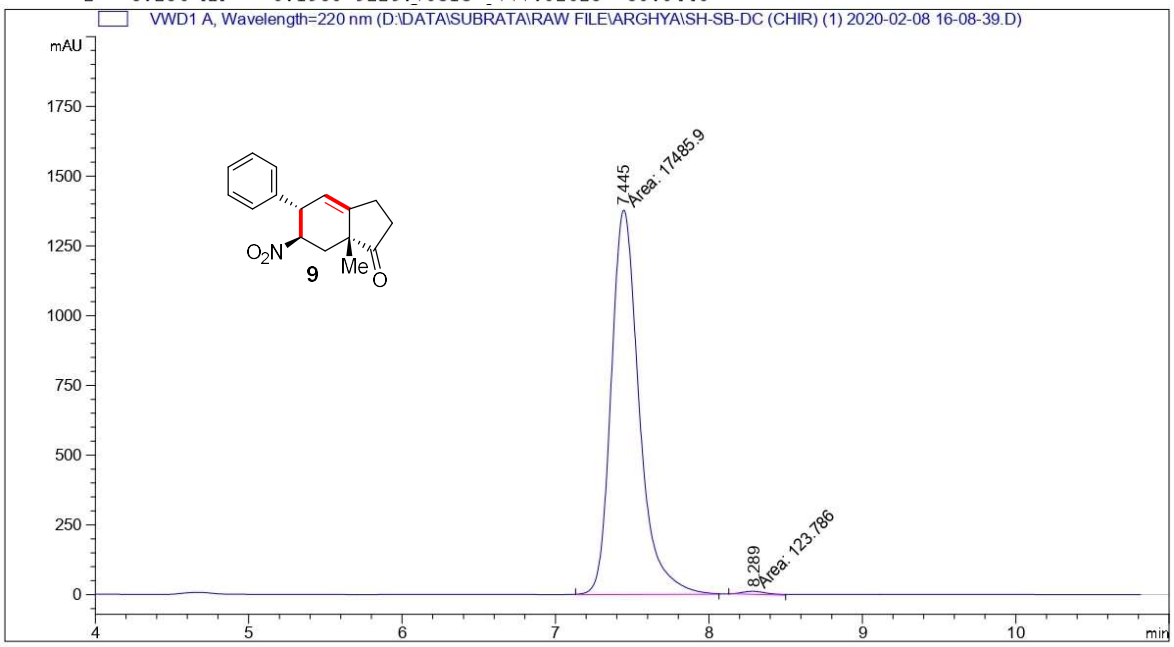
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.748	MM	0.2978	1.51924e4	850.38239	99.5035
2	11.536	MM	0.2952	75.81345	4.28015	0.4965

Sample Info : CHIRALPAK IA, 20 % IPA-HEXANE, 1 mL -min, 220 nm

(5*S*,6*R*,7a*R*)-7a-Methyl-6-nitro-5-phenyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-one (9)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.459	MM	0.1884	9213.23535	814.87262	49.9554
2	8.256	MM	0.1980	9229.70313	777.02625	50.0446



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.445	MM	0.2116	1.74859e4	1377.50806	99.2971
2	8.289	MM	0.1898	123.78584	10.87072	0.7029

Sample Info : CHIRALPAK IA, 10% IPA-HEXANE, 1.0mL -min, 220 nm