Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Organocatalytic Enantioselective Desymmetrization of Enal-Tethered Cyclohexane-1,3-diones

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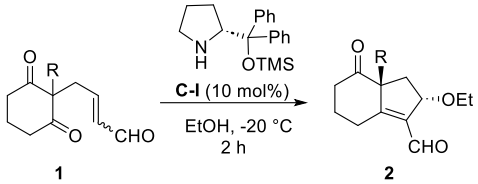
I. General details:

Unless otherwise noted, all reagents were used as received from commercial suppliers. TMS-Prolinol catalysts were purchased from Sigma-Aldrich and used without further purification. All reactions were performed under a nitrogen atmosphere and in flame-dried or oven-dried glassware with magnetic stirring. Unless otherwise noted, all solvents were purchased from Merk, Finar, or Spectrochem, and used without further purification. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), iodine treatment, or using *p*-anisaldehyde stain or *β*-naphthol stain. Column chromatography was carried out using silica gel (60-120 mesh & 100-200 mesh) packed in glass columns. NMR spectra were recorded at 300, 400, 500 MHz (H) and 75, 100, 125 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm) as internal standard, and coupling constants (*J*) are given in Hz.The following abbreviations were used to designate the multiplicities: s = singlet; d = doublet; t = triplet; q= quartet; dd = doublet of doublet; dt = doublet of triplet; dq = doublet of quartet; m = multiplet; br.s = broad singlet; qd = quartet of doublet. HRMS were recorded using ESI-TOF techniques**.** Enantiomeric ratio (*er*) values were determined by chiral HPLC of the purified product with hexane and *i*-PrOH as solvents and diastereomer ratio (*dr*) values were determined by ^{1}H NMR analysis. All chiral compound's optical rotation was measured on a Horiba SEPA-300.

II. Experimental Procedures and Analytical Data

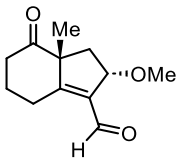
IIa. Experimental procedures and analytical data of products:

General Procedure for organocatalytic enantioselective desymmetrization:

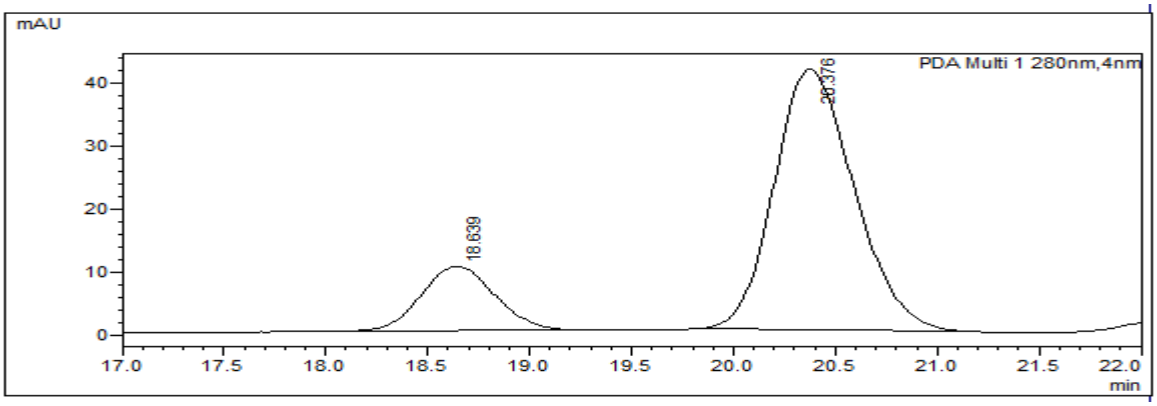


To a stirred solution of enal-tethered cyclohexane 1,3-dione **1** (0.3 mmol) in EtOH (1.5 mL, 0.2 M) at -20 ^{o}C was added Jørgensen-Hayashi catalyst **C-I** (10.2 mg, 0.03 mmol, 10 mol%) under nitrogen atmosphere. The reaction was allowed to stir at the same temperature until complete consumption of starting material (monitored by TLC). Afterward, the solvent was evaporated under reduced pressure at 40-45^{o}C (rotary evaporator water bath) and the crude residue was directly purified by column chromatography on silica gel (EtOAc in Hexane) to give the desired product **2**with from 5:1 to >20:1 ratio of diastereoselectivity (*dr*). [**Note:** For racemic products, Piperidine catalyst (10 mol%) was used at room temperature and followed the same procedure as above]. The enantiomeric excess was determined by chiral HPLC analysis. Here, diastereoselectivity (*dr*) was measured from ^{1}H NMR analysis of crude product and reported the NMR data for major isomer of product **2**.

(2S,7aR)-2-Methoxy-7a-methyl-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2a):



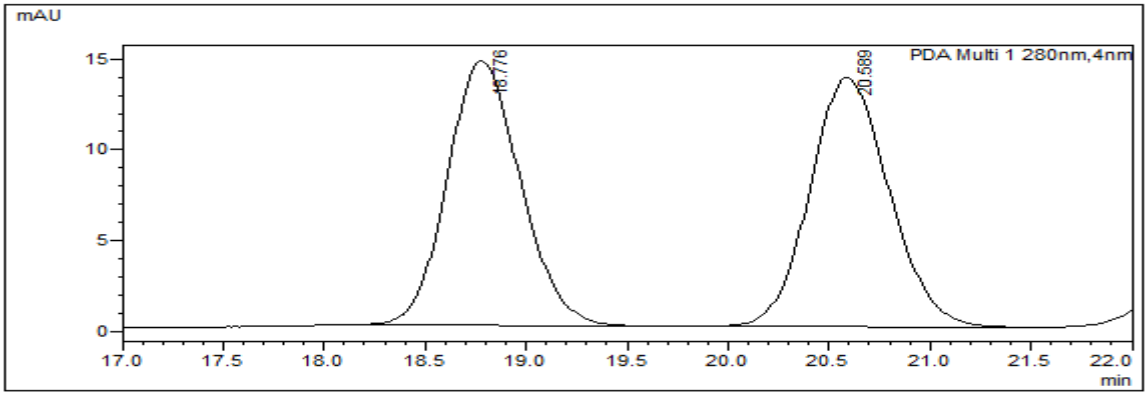
Prepared according to the general procedure as described above in 82% yield (51 mg; *dr* = >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 4.72 (ddd, *J* = 7.5, 5.2, 2.6 Hz, 1H), 3.42 – 3.39 (m, 1H), 3.37 (d, *J* = 0.8 Hz, 3H), 2.70 (ddd, *J* = 15.4, 13.6, 6.1 Hz, 1H), 2.55 – 2.45 (m, 2H), 2.41 (dd, *J* = 14.0, 5.1 Hz, 1H), 2.29 – 2.18 (m, 1H), 2.08 (dd, *J* = 14.1, 7.3 Hz, 1H), 1.81 – 1.67 (m, 1H), 1.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 188.5, 166.8, 135.6, 81.3, 62.3, 57.0, 38.1, 37.5, 26.4, 24.1, 23.0; HRMS (ESI) calcd for $C_{12}H_{17}O_3$ $[M+H]^+$: 209.1178; found: 209.1226; $[\alpha]^{20}_D$ = -125.22° (*c* 1.0, $CHCl_3$); 85:15*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 280 nm, Flow rate = 1 mL/min, Retention times: 18.64 min (minor), 20.37 min (major).



<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	18.639	207841	9498	15.001	18.459
2	20.376	1177659	41956	84.999	81.541
Total		1385500	51453	100.000	100.000

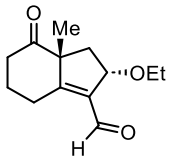


<Peak Table>

PDA Ch1 280nm

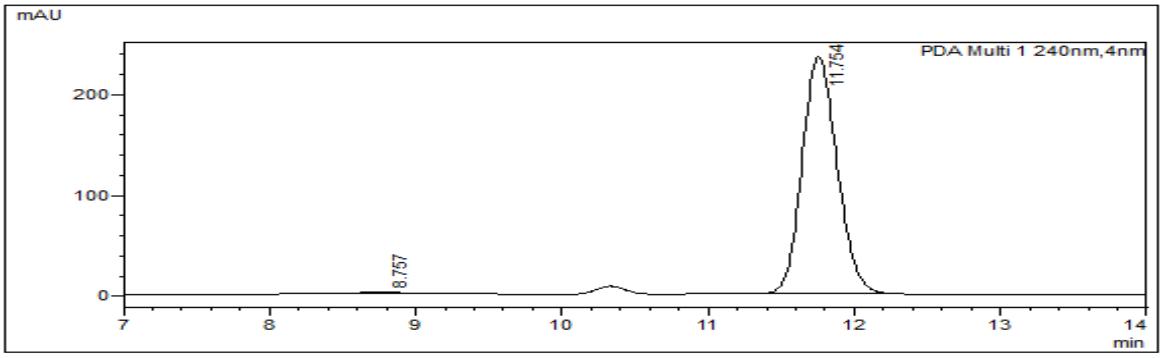
Peak#	Ret. Time	Area	Height	Area%	Height%
1	18.776	367629	14570	49.537	51.453
2	20.589	374508	13747	50.463	48.547
Total		742137	28317	100.000	100.000

(2*S*,7a*R*)2-Ethoxy-7a-methyl-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2b):



Prepared according to the general procedure as described above in 94% yield (62 mg;*dr* = 10:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.5) to afford yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 4.79 (ddd, *J* = 8.0, 5.5, 2.7 Hz, 1H), 3.59 (q, *J* = 7.0 Hz, 2H), 3.39 (dt, *J* = 14.7, 4.3 Hz, 1H), 2.69 (ddd, *J* = 15.5, 13.3, 6.1 Hz, 1H), 2.54 – 2.47 (m, 1H), 2.47 – 2.41 (m, 1H), 2.38 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.27 – 2.17 (m, 1H), 2.13 (dd, *J* = 14.0, 7.3 Hz, 1H), 1.82 – 1.66

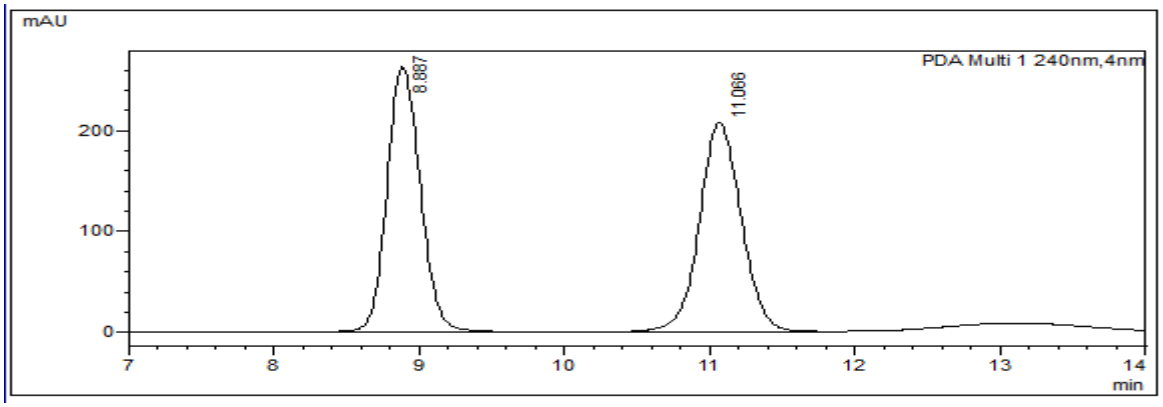
(m, 1H), 1.35 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 188.8, 166.1, 135.7, 79.8, 65.2, 62.1, 39.2, 37.5, 26.4, 23.9, 22.9, 15.7; HRMS (ESI) calcd for $C_{13}H_{19}O_3$ $[M+H]^+$: 223.1328; found: 223.1320; $[\alpha]^{20}_D$ = -137.20° (*c* 1.0, $CHCl_3$); 99:1*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 80:20,detected at 240 nm, Flow rate = 1 mL/min, Retention times: 8.75 min (minor), 11.75 min (major).



<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.757	52116	1194	1.317	0.505
2	11.754	3903953	235268	98.683	99.495
Total		3956069	236462	100.000	100.000

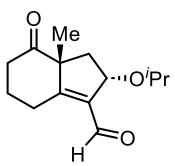


<Peak Table>

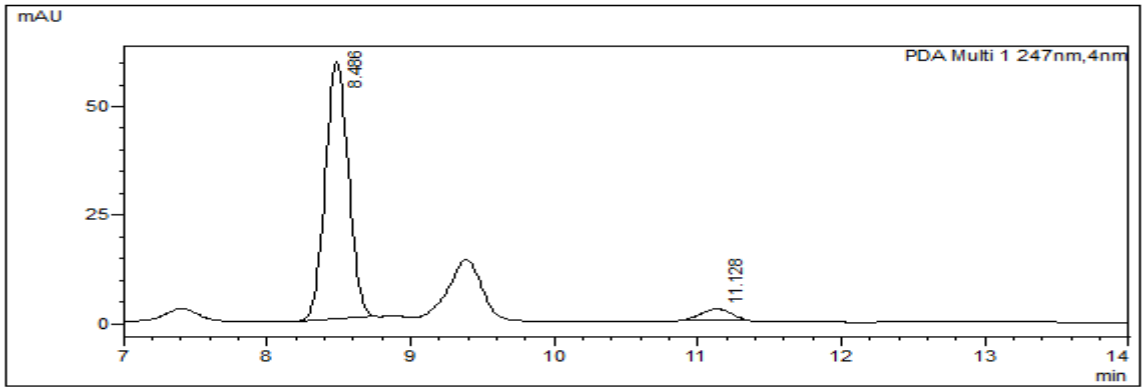
PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.887	4192839	263403	49.958	55.883
2	11.066	4199831	207940	50.042	44.117
Total		8392670	471343	100.000	100.000

(2S,7aR)-2-Isopropoxy-7a-methyl-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2c):



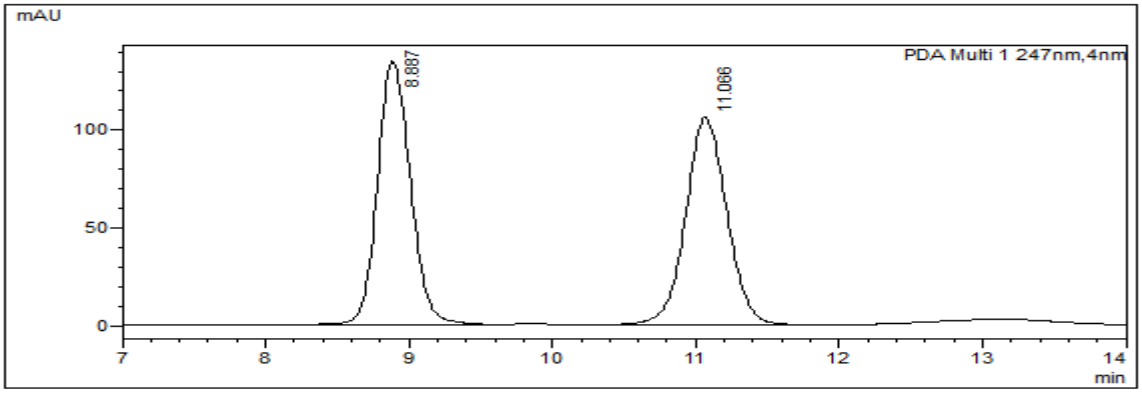
Prepared according to the general procedure as described above in 52% yield (36 mg; *dr* = >20:1). It was purified by flash chromatography (20% EtOAc/hexane; R_f = 0.5) to afford yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 4.85 – 4.77 (m, 1H), 3.90 – 3.78 (m, 1H), 3.38 (d, *J* = 14.7 Hz, 1H), 2.74 – 2.62 (m, 1H), 2.54 – 2.39 (m, 2H), 2.33 (dd, *J* = 13.9, 5.7 Hz, 1H), 2.23 – 2.11 (m, 2H), 1.85 – 1.70 (m, 1H), 1.34 (s, 3H), 1.17 (d, *J* = 6.0 Hz, 3H), 1.16 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.9, 188.8, 165.4, 136.1, 78.2, 72.1, 61.9, 40.7, 37.6, 26.4, 23.8, 23.3, 22.9, 22.4; HRMS (ESI) calcd for $C_{14}H_{20}O_3$ [M]·: 236.1412; found: 236.1413; $[\alpha]^{20}_D$ = -110.30° (*c* 1.0, $CHCl_3$); 95:5*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 247 nm, Flow rate = 1 mL/min, Retention times: 8.48 min (major), 11.12 min (minor).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.486	664557	59254	94.987	95.963
2	11.128	35072	2493	5.013	4.037
Total		699630	61747	100.000	100.000

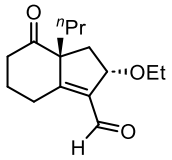


<Peak Table>

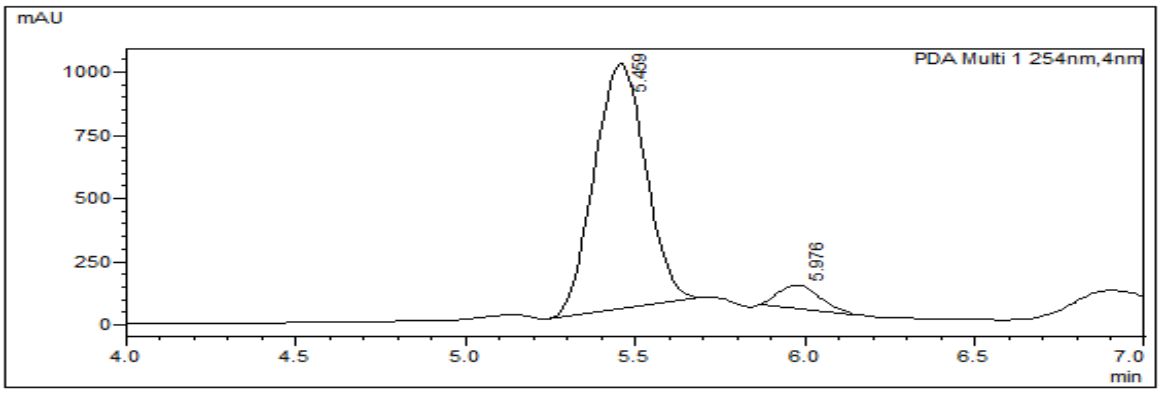
PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.887	2153812	134881	50.404	56.007
2	11.066	2119308	105947	49.596	43.993
Total		4273120	240828	100.000	100.000

(2*S*,7a*R*)2-Ethoxy-7-oxo-7a-propyl-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2d):



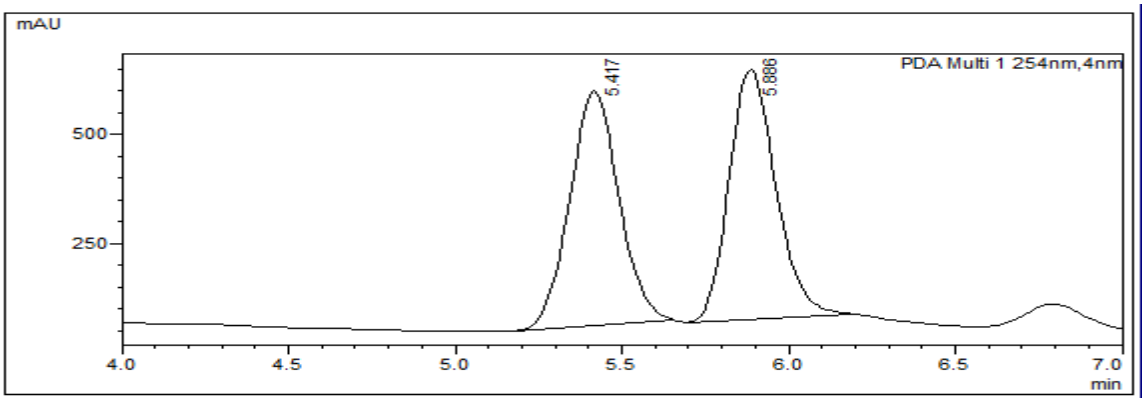
Prepared according to the general procedure as described above in 76% yield (57 mg; *dr* = 18:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.4) to afford yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 4.75 (ddd, *J* = 7.7, 5.3, 2.7 Hz, 1H), 3.58 (qd, *J* = 7.0, 1.6 Hz, 2H), 3.39 (dt, *J* = 14.5, 4.1 Hz, 1H), 2.67 (ddd, *J* = 15.2, 13.5, 6.2 Hz, 1H), 2.50 – 2.40 (m, 2H), 2.35 (dd, *J* = 14.3, 5.3 Hz, 1H), 2.26 – 2.11 (m, 2H),1.81 – 1.67 (m, 2H), 1.55 – 1.47 (m, 1H), 1.35 – 1.21 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.13 – 1.03 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 187.9, 168.5, 136.3, 79.1, 68.3, 65.5, 41.0, 38.1, 34.5, 24.4, 23.2, 18.4, 15.7, 14.5; HRMS (ESI) calcd for $C_{15}H_{23}O_3$ $[M+H]^+$: 251.1641; found: 251.1634; $[\alpha]^{20}_D$ = +87.60° (*c* 1.0, $CHCl_3$); 93:7% *er*; Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 5.45 min (major), 5.97 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	5.459	10319502	968758	92.982	91.158
2	5.976	778895	93966	7.018	8.842
Total		11098397	1062725	100.000	100.000

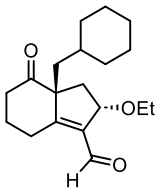


<Peak Table>

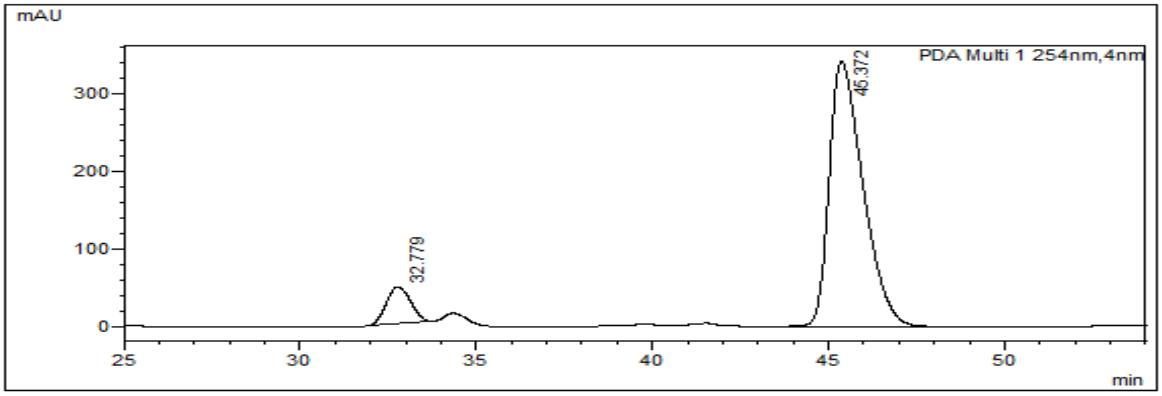
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	5.417	5520956	539871	49.754	48.546
2	5.886	5575543	572203	50.246	51.454
Total		11096499	1112073	100.000	100.000

(2*S*,7a*R*) 7a-(Cyclohexylmethyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2e):



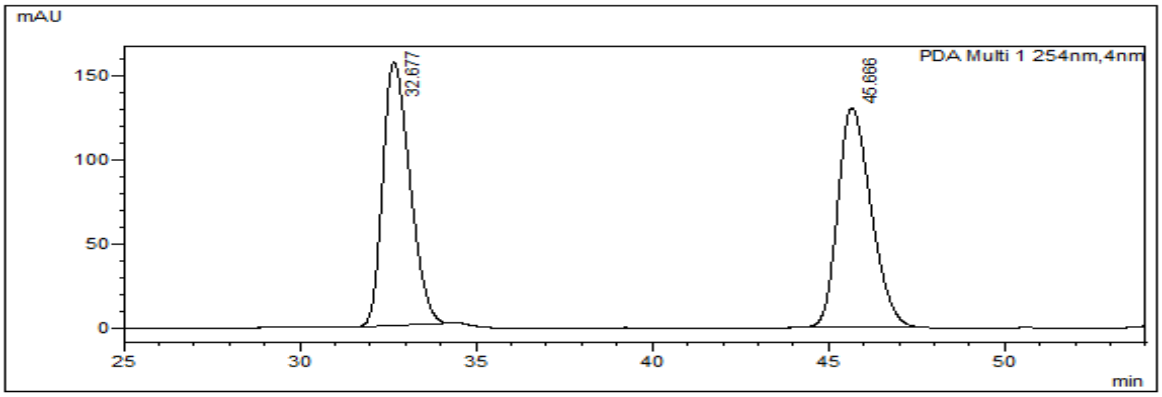
Prepared according to the general procedure as described above in 72% yield (65 mg; *dr* = >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.5) to afford colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 4.75 (ddd, *J* = 7.6, 5.1, 2.6 Hz, 1H), 3.62 – 3.53 (m, 2H), 3.37 (dt, *J* = 14.5, 2.7 Hz, 1H), 2.70 (ddd, *J* = 14.8, 13.7, 6.2 Hz, 1H), 2.55 – 2.43 (m, 2H), 2.40 (dd, *J* = 14.3, 5.1 Hz, 1H), 2.24 – 2.15 (m, 1H),2.18 (dd, J = 14.3, 7.5 Hz, 1H),1.80 (dd, J = 14.0, 5.3 Hz, 1H), 1.72 (ddd, J = 13.4, 11.2, 6.7 Hz, 1H), 1.66 – 1.52 (m, 5H), 1.34 (dd, *J* = 14.1, 6.0 Hz, 1H), 1.30 – 1.20 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.14 – 1.00 (m, 2H), 0.97 – 0.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 188.6, 166.3, 136.0, 80.1, 67.3, 65.1, 46.1, 38.2, 36.2, 35.0, 34.8, 34.7, 26.3 (2C), 26.1, 24.7, 23.2, 15.7; HRMS (ESI) calcd for $C_{19}H_{29}O_3$ $[M+H]^+$: 305.2111; found: 305.2110; $[\alpha]^{20}_D$ = -127.79° (*c* 1.0, $CHCl_3$); 91:9*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 98:02, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 32.77 min (minor), 45.37 min (major).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	32.779	2266247	47407	9.071	12.218
2	45.372	22718224	340589	90.929	87.782
Total		24984471	387996	100.000	100.000

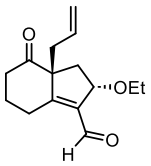


<Peak Table>

PDA Ch1 254nm

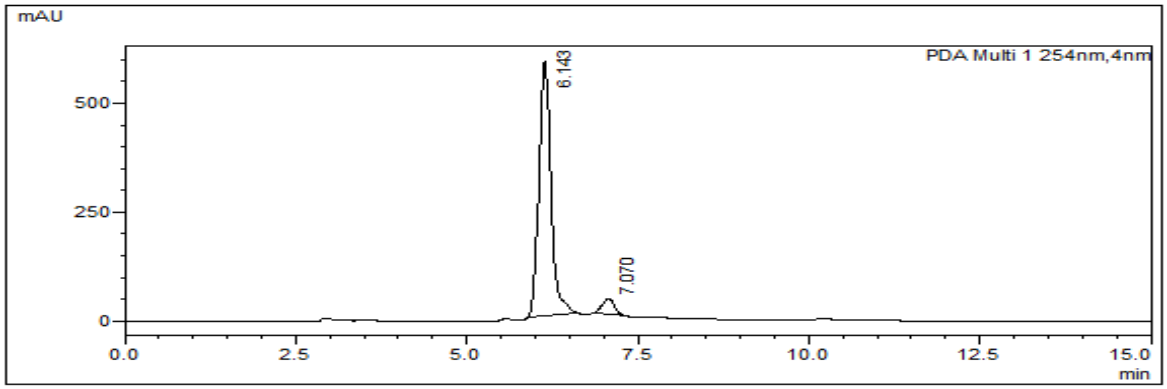
Peak#	Ret. Time	Area	Height	Area%	Height%
1	32.677	8358339	155933	49.695	54.601
2	45.666	8460942	129655	50.305	45.399
Total		16819280	285588	100.000	100.000

(2*S*,7a*R*)-7a-Allyl-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2f):



Prepared according to the general procedure as described above in 78% yield (58 mg; *dr* = >5:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford yellow liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 5.59 – 5.44 (m, 1H), 5.17 – 5.08 (m, 1H), 4.74 – 4.67 (m, 1H), 3.58 (qd, *J* = 7.0, 1.0 Hz, 2H), 3.42 (dt, *J* = 14.7, 2.6 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.53 – 2.36 (m, 5H), 2.35 – 2.19 (m, 3H), 1.85 – 1.66 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

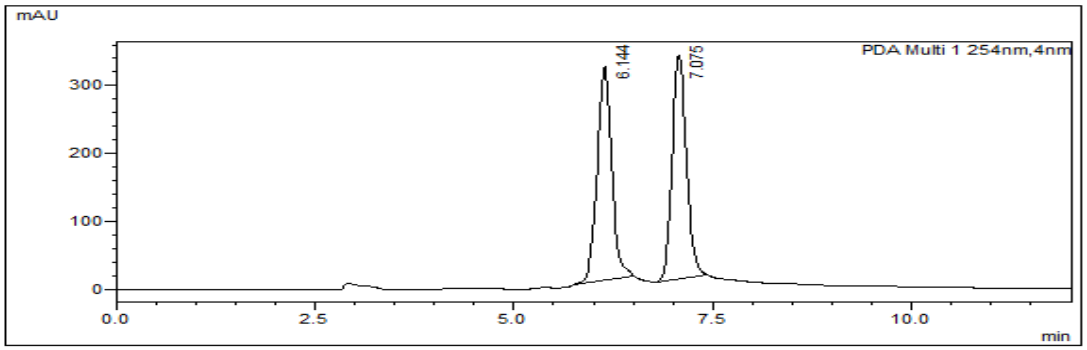
209.3, 188.5, 164.2, 136.8, 131.3, 119.9, 80.1, 66.8, 65.3, 42.4, 37.9, 36.1, 24.0, 23.0, 15.7; HRMS (ESI) calcdfor $C_{15}H_{21}O_3$ $[M+H]^+$: 249.1485; found: 249.1493; $[\alpha]^{20}_D$ = +61.00° (*c* 1.0, $CHCl_3$); 97:3*er*; Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 6.14 min (major), 7.07 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.143	7241744	585854	96.729	95.754
2	7.070	244910	25981	3.271	4.246
Total		7486654	611835	100.000	100.000

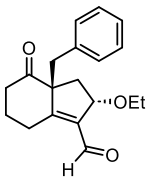


<Peak Table>

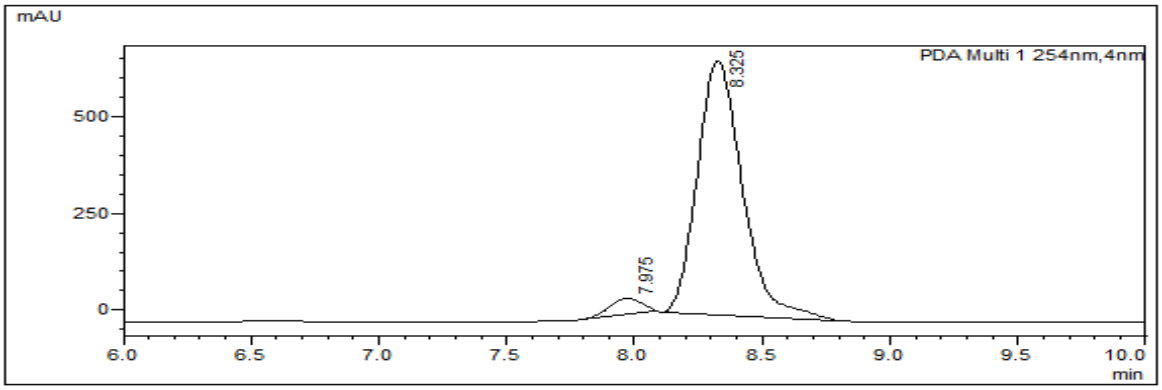
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.144	4033603	314394	49.579	48.855
2	7.075	4102059	329132	50.421	51.145
Total		8135662	643526	100.000	100.000

(2*S*,7a*R*)-7a-Benzyl-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2g):



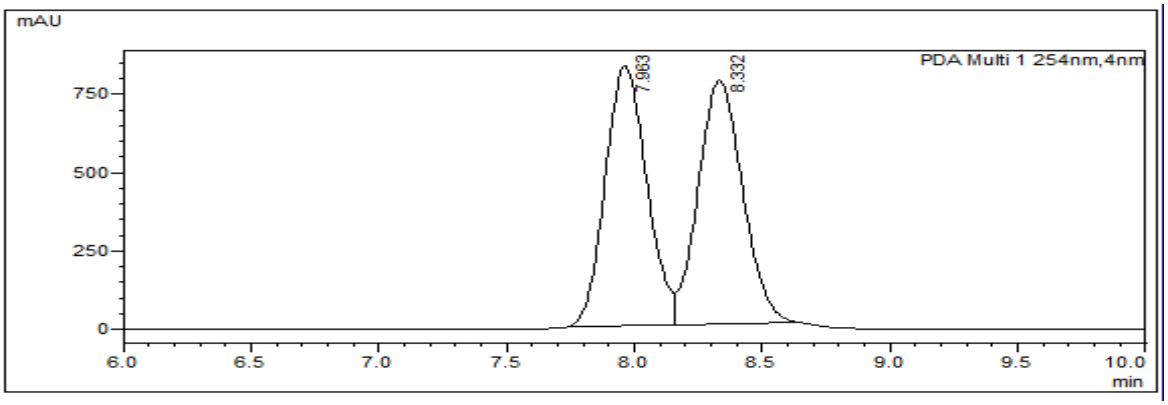
Prepared according to the general procedure as described above in 88% yield (78 mg; *dr*= >5:1). It was purified by column chromatography (30% EtOAc/hexane; R_f = 0.5) to afford brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.26 – 7.23 (m, 3H), 7.02 – 6.98 (m, 2H), 3.78 (td, J = 6.9, 2.8 Hz, 1H), 3.56 – 3.49 (m, 1H), 3.45 – 3.35 (m, 2H), 3.06 (d, *J* = 13.3 Hz, 1H), 2.86 (d, *J* = 13.3 Hz, 1H), 2.78 (ddd, *J* = 15.5, 10.2, 4.7 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.54 (dt, *J* = 15.5, 3.8 Hz, 1H), 2.35 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.31 – 2.22 (m, 1H), 2.14 (dd, *J* = 14.0, 6.2 Hz, 1H), 1.82 (ddt, *J* = 26.2, 13.2, 4.4 Hz, 1H), 1.08 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 188.7, 162.8, 138.0, 135.2, 130.1, 128.5, 127.6, 79.7, 67.4, 65.2, 43.5, 38.4, 36.8, 24.0, 23.5, 15.6; HRMS (ESI) calcd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1641; found: 299.1634; $[\alpha]^{20}_D$= -73.43°(*c*1.0, $CHCl_3$); 96:4 *er*; Chiral HPLC analysis of the product: DaicelChiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 70:30, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 7.97 min (minor), 8.32 min (major).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.975	370640	41426	4.437	5.959
2	8.325	7982312	653727	95.563	94.041
Total		8352952	695153	100.000	100.000

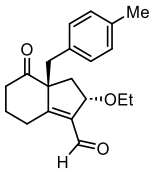


<Peak Table>

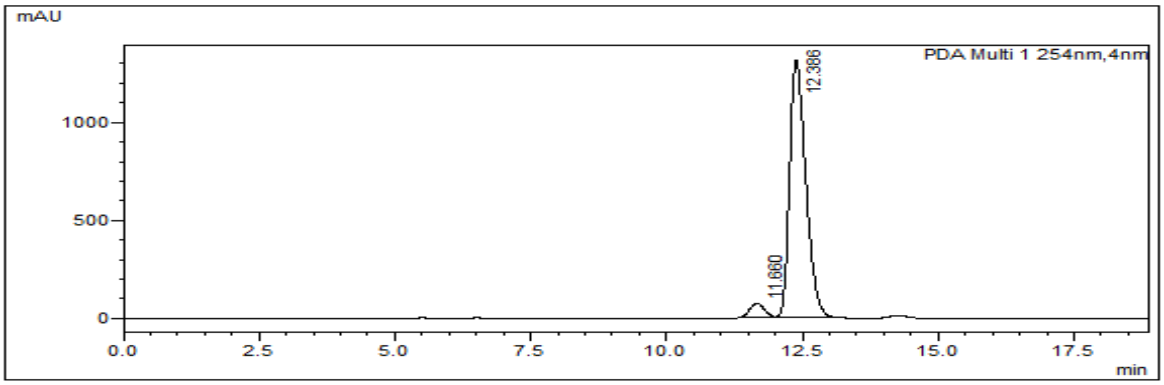
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.963	9436081	829354	50.061	51.525
2	8.332	9413034	780260	49.939	48.475
Total		18849114	1609614	100.000	100.000

(2*S*,7a*R*)-2-Ethoxy-7a-(4-methylbenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2h):



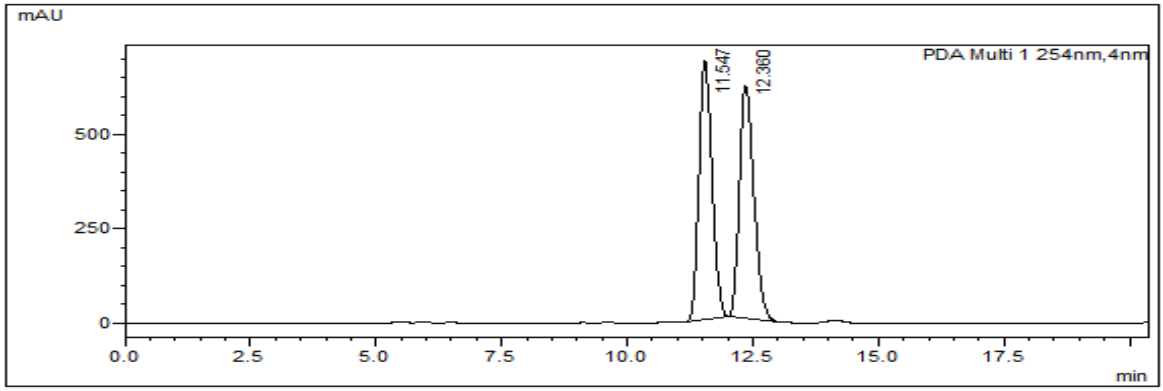
Prepared according to the general procedure as described above in 80% yield (74 mg; *dr* = >20:1). It was purified by column chromatography (40% EtOAc/hexane; R_f = 0.4) to afford colourless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 3.85 (td, *J* = 7.0, 2.8 Hz, 1H), 3.51 (dt, *J* = 16.6, 4.0 Hz, 1H), 3.41 (tdd, *J* = 9.1, 7.0, 2.1 Hz, 2H), 3.02 (d, *J* = 13.3 Hz, 1H), 2.83 (d, *J* = 13.3 Hz, 1H), 2.78 (ddd, *J* = 15.5, 13.2, 6.0 Hz, 1H), 2.63 (dddd, *J* = 15.3, 12.7, 5.4, 2.9 Hz, 1H), 2.53 (dt, *J* = 15.5, 3.2 Hz, 1H), 2.34 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.31 (s, 3H), 2.29 – 2.21 (m, 1H), 2.13 (dd, *J* = 14.0, 6.2 Hz, 1H), 1.81 (ddt, *J* = 26.3, 13.2, 4.4 Hz, 1H), 1.09 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 188.7, 163.2, 137.9, 137.3, 132.0, 129.9, 129.2, 79.8, 67.6, 65.1, 43.2, 38.4, 36.7, 24.0, 23.5, 21.2, 15.6; HRMS (ESI) calcd for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798; found: 313.1792; $[\alpha]^{20}_D$ = -23.39° (*c* 1.0, $CHCl_3$); 96:4*er*; Chiral HPLC analysis of the product: Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 11.66 min (minor), 12.38 min(major).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.660	1273753	72038	4.486	5.217
2	12.386	27119496	1308764	95.514	94.783
Total		28393249	1380802	100.000	100.000

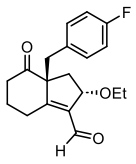


<Peak Table>

PDA Ch1 254nm

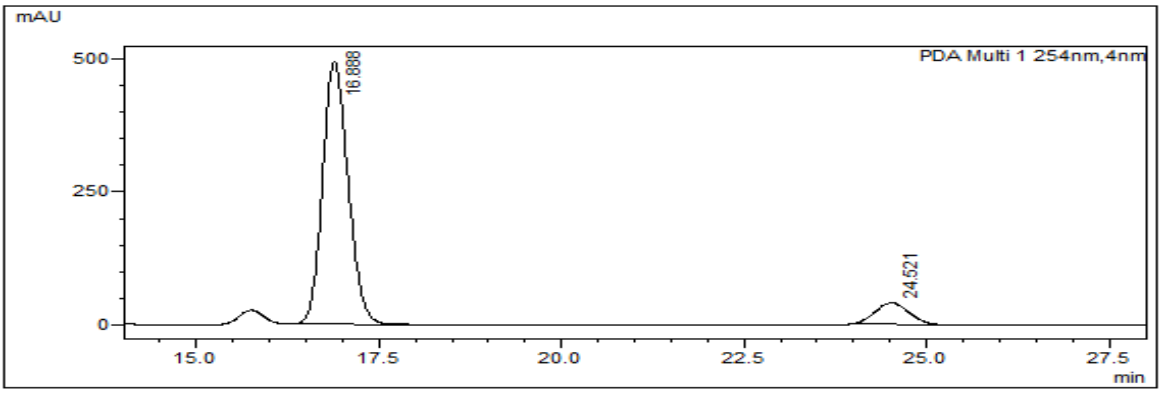
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.547	12497808	685877	50.319	52.681
2	12.360	12339592	616061	49.681	47.319
Total		24837399	1301938	100.000	100.000

(2*S*,7a*R*)-2-Ehoxy-7a-(4-fluorobenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2i):



Prepared according to the general procedure as described above in 71% yield (67 mg; *dr* = >20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f= 0.3) to afford yellow liquid;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.00 – 6.91 (m, 4H), 3.84 (td, *J* = 6.9, 2.9 Hz, 1H), 3.53 (dt, *J* = 13.7, 3.1 Hz, 1H), 3.48 – 3.37 (m, 2H), 3.02 (d, *J* = 13.5 Hz, 1H), 2.85 (d, *J* = 13.5 Hz, 1H), 2.76 (ddd, *J* = 15.5, 13.2, 6.0 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.57 – 2.52 (m, 1H), 2.30 (dd, *J* = 14.1, 7.2 Hz, 1H),

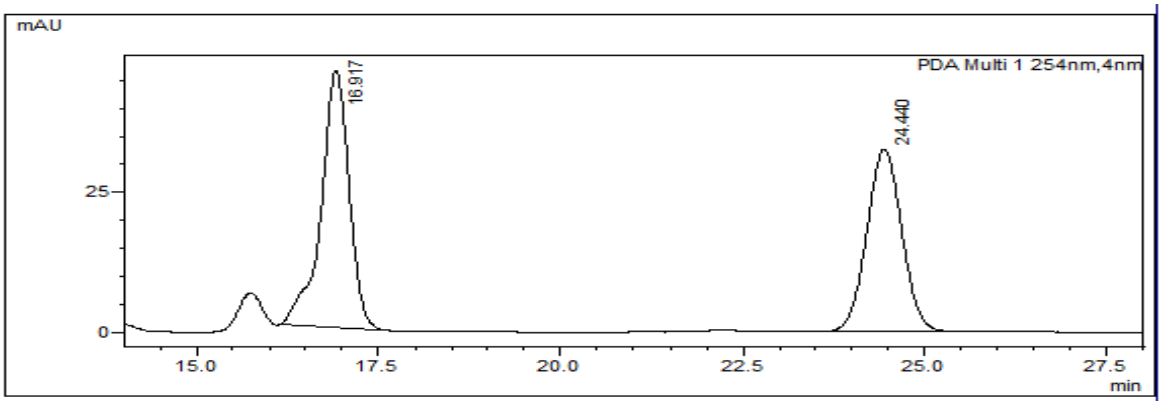
2.28 – 2.23 (m, 1H), 2.15 (dd, *J* = 14.1, 6.2 Hz, 1H), 1.83 (ddt, *J* = 26.3, 13.2, 4.4 Hz, 1H)), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 187.9, 168.4, 162.19 (d, J_{CF} = 247.23 Hz), 137.1, 132.2 (d, J_{CF} = 2.7 Hz), 131.5(d, J_{CF} = 7.42 Hz), 115.5 (d, J_{CF} = 21.33 Hz), 78.7, 68.7, 65.6, 44.1, 38.9, 34.7, 24.4, 23.7, 15.7;^{19}F NMR (471 MHz, $CDCl_3$) δ -113.21.HRMS (ESI)calcd for $C_{19}H_{22}O_3F$ $[M+H]^+$: 317.1547; found: 317.1552; $[\alpha]^{20}_D$ = +62.09° (*c*1.0, $CHCl_3$); 91:9*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 90:10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 16.88 min (major), 24.52 min(minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.888	12000018	492343	91.383	92.873
2	24.521	1131562	37780	8.617	7.127
Total		13131580	530123	100.000	100.000

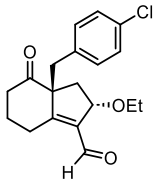


<Peak Table>

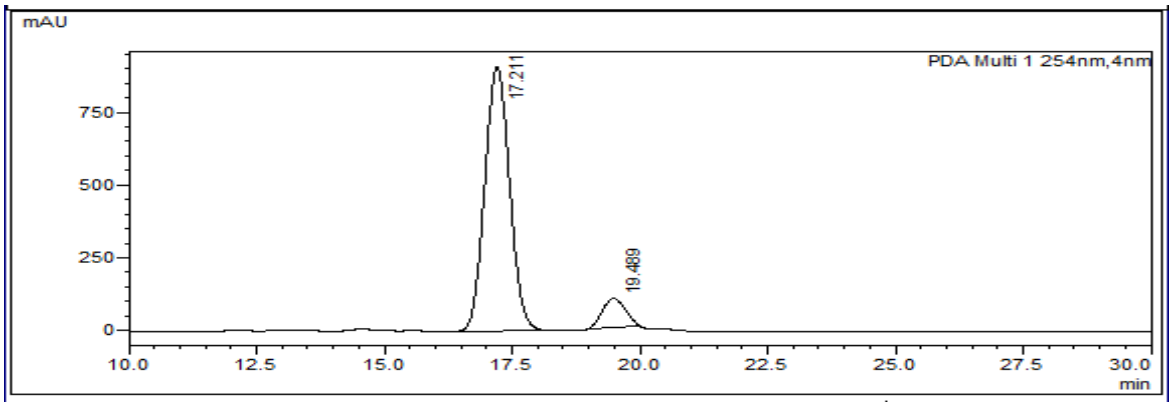
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.917	1104225	44343	50.471	57.679
2	24.440	1083618	32536	49.529	42.321
Total		2187843	76879	100.000	100.000

(2*S*,7a*R*)-7a-(4-Chlorobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2j):



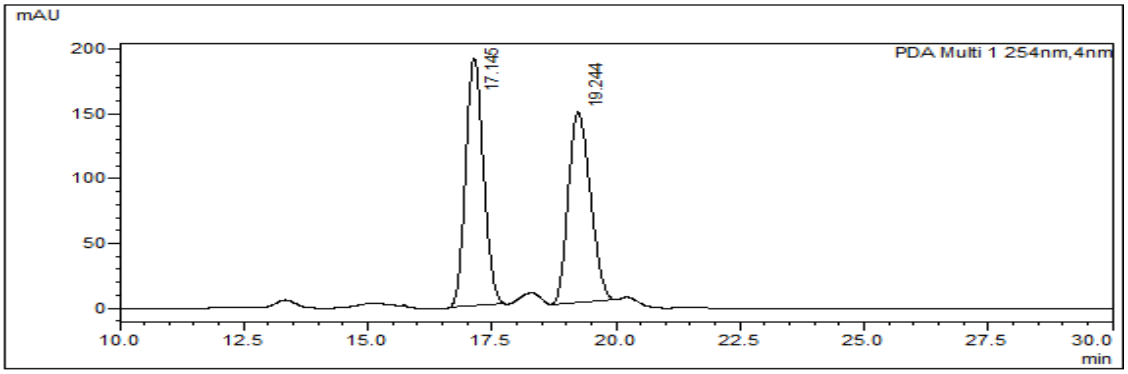
Prepared according to the general procedure as described above in 77% yield (76 mg; *dr* = >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford colourless liquid;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 3.90 (td, *J* = 6.9, 2.7 Hz, 1H), 3.54 (dt, *J* = 14.7, 3.7 Hz, 1H), 3.49 – 3.37 (m, 2H), 3.01 (d, *J* = 13.4 Hz, 1H), 2.86 (d, *J* = 13.5 Hz, 1H), 2.76 (ddd, *J* = 15.4, 13.2, 5.9 Hz, 1H), 2.65 – 2.58 (m, 1H), 2.58 – 2.51 (m, 1H), 2.29 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.26 – 2.22 (m, 1H), 2.16 (dd, *J* = 14.2, 6.1 Hz, 1H), 1.82 (tdd, *J* = 17.3, 8.8, 4.2 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 188.9, 162.3, 137.9, 133.8, 133.7, 131.3, 128.7, 79.8, 67.3, 65.2, 42.7, 38.3, 36.7, 24.0, 23.5, 15.6;HRMS (ESI) calcd for $C_{19}H_{22}O_3Cl$ $[M+H]^+$: 333.1252; found: 333.1263; $[\alpha]^{20}_D$ = +17.33° (*c* 1.0, $CHCl_3$); 93:7*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5µ column; hexane/2-propanol = 90:10, detected at 254 nm, Flow rate = 1mL/min, Retention times: 17.21 min (major), 19.48 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.211	30694502	906895	92.912	91.483
2	19.489	2341462	84432	7.088	8.517
Total		33035963	991327	100.000	100.000

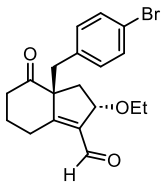


<Peak Table>

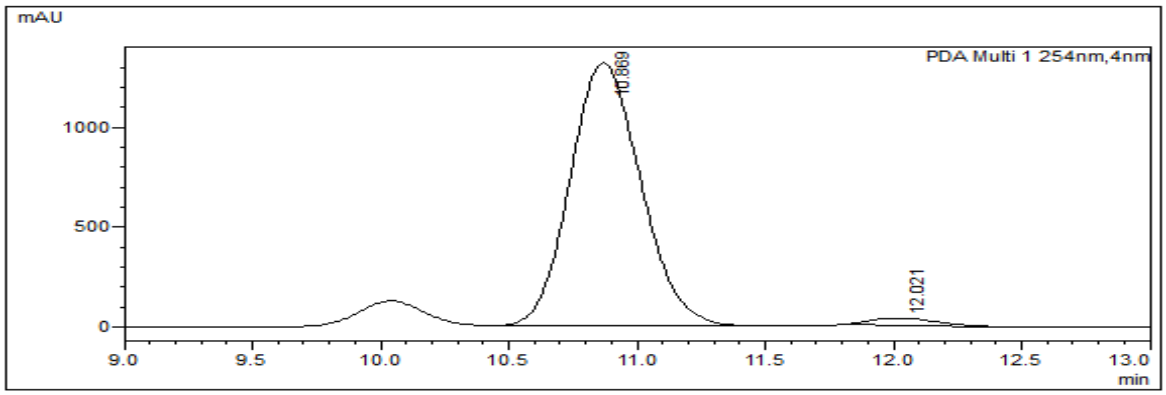
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.145	4750826	190721	50.417	56.199
2	19.244	4672206	148645	49.583	43.801
Total		9423032	339366	100.000	100.000

(2*S*,7a*R*)-7a-(4-Bromobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2k):



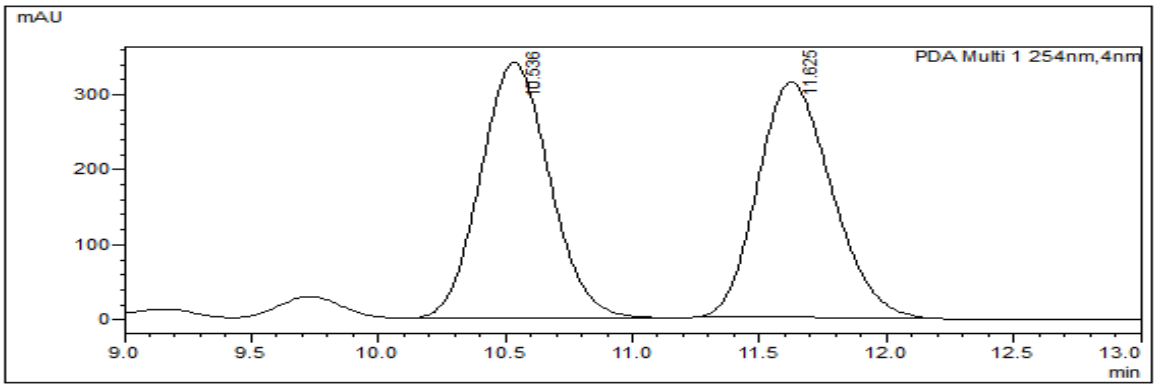
Prepared according to the general procedure as described above in 81% yield (91mg; *dr* = >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford colourless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.91 (td, *J* = 7.0, 2.8 Hz, 1H), 3.54 (dt, *J* = 6.3, 3.7 Hz, 1H), 3.43 (dddd, *J* = 16.1, 9.1, 7.0, 2.1 Hz, 2H), 2.99 (d, *J* = 13.4 Hz, 1H), 2.84 (d, *J* = 13.4 Hz, 1H), 2.76 (ddd, *J* = 15.5, 13.1, 6.0 Hz, 1H), 2.62 (ddd, *J* = 12.2, 5.3, 2.8 Hz, 1H), 2.54 (dt, *J* = 8.8, 4.0 Hz, 1H), 2.28 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.26 – 2.21 (m, 1H), 2.16 (dd, *J* = 14.2, 6.1 Hz, 1H), 1.82 (dddd, *J* = 22.0, 13.2, 9.0, 4.5 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 187.8, 168.2, 137.2, 135.4, 131.7, 131.3, 121.5, 78.7, 68.5, 65.6, 44.3, 38.9, 34.6, 24.4, 23.7, 15.7; HRMS (ESI) calcd for $C_{19}H_{22}O_3Br$ $[M+H]^+$: 377.0746; found: 377.0750; $[\alpha]^{20}_D$ = -26.19° (*c* 1.0, $CHCl_3$); 98:2*er*, Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5µ column; hexane/2-propanol = 90:10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 10.86 min (major), 12.02 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.869	25211989	1317765	97.532	97.295
2	12.021	638009	36630	2.468	2.705
Total		25849998	1354395	100.000	100.000

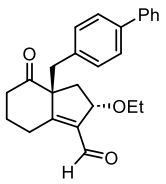


<Peak Table>

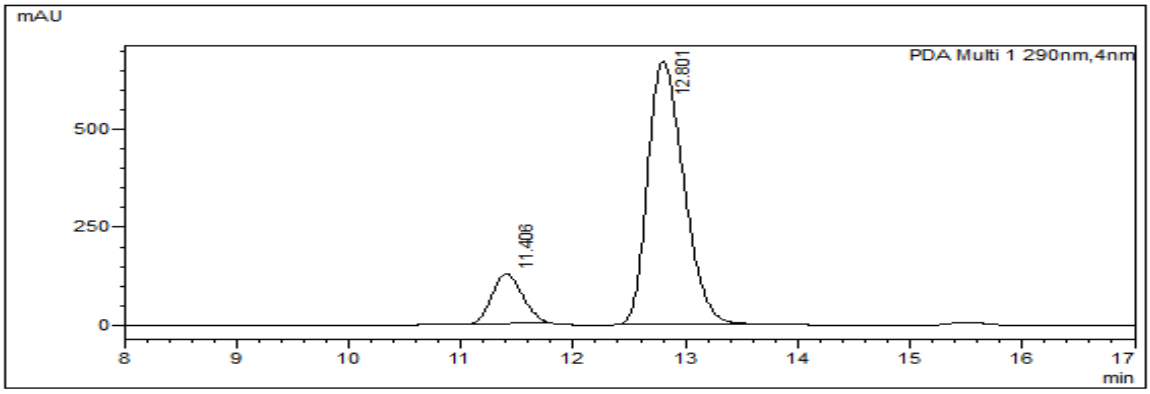
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.536	6424947	340644	50.268	52.110
2	11.625	6356404	313062	49.732	47.890
Total		12781350	653706	100.000	100.000

(2*S*,7a*R*)-7a-([1,1'-Biphenyl]-4-ylmethyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2l):



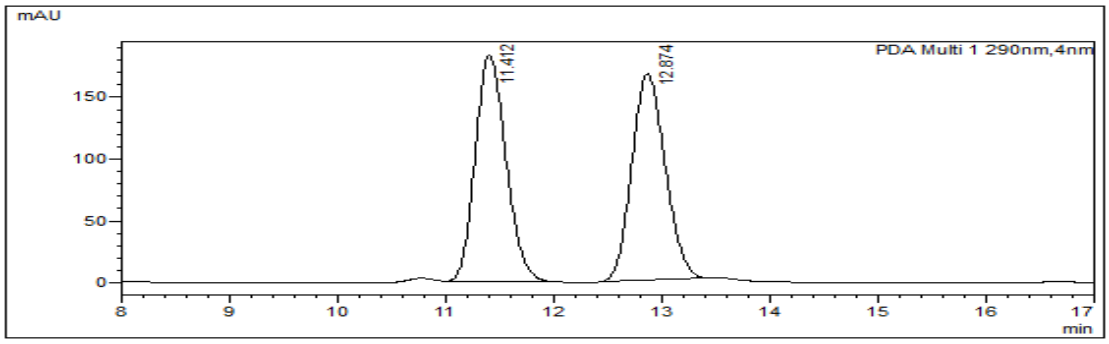
Prepared according to the general procedure as described above in 70% yield (78 mg; *dr* = >20:1). It was purified by flash chromatography (50% EtOAc/hexane; R_f = 0.3) to afford colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.57 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.93 (td, *J* = 7.0, 2.8 Hz, 1H), 3.55 (dt, *J* = 14.9, 2.9 Hz, 1H), 3.50 – 3.35 (m, 2H), 3.09 (d, *J* = 13.3 Hz, 1H), 2.93 (d, *J* = 13.3 Hz, 1H), 2.81 (ddd, *J* = 15.4, 13.2, 6.0 Hz, 1H), 2.67 (dddd, J = 15.4, 12.3, 5.2, 2.7 Hz, 1H)), 2.56 (dt, *J* = 15.4, 3.2 Hz, 1H), 2.39 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.33 – 2.23 (m, 1H), 2.18 (dd, *J* = 14.1, 6.1 Hz, 1H), 1.84 (dddd, J = 22.0, 13.2, 8.9, 4.5 Hz, 1H), 1.09 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.1, 188.7, 162.8, 140.5, 140.4, 137.9, 134.3, 130.5, 129.0, 127.6, 127.1, 127.1, 79.8, 67.5, 65.2, 43.2, 38.4, 36.8, 24.1, 23.6, 15.6; HRMS (ESI) calcd for $C_{25}H_{27}O_3N$ $[M+H]^+$: 375.1954; found: 375.1947; $[\alpha]^{20}_D$ = -6.99° (*c* 1.0, $CHCl_3$); 91:9*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5µ column; hexane/2-propanol = 90:10, detected at 290 nm, Flow rate = 1 mL/min, Retention times: 11.40 min (minor), 12.80 min (major).



<Peak Table>

PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.406	1521547	98478	9.269	12.798
2	12.801	14894219	671023	90.731	87.202
Total		16415766	769501	100.000	100.000

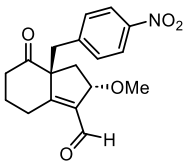


<Peak Table>

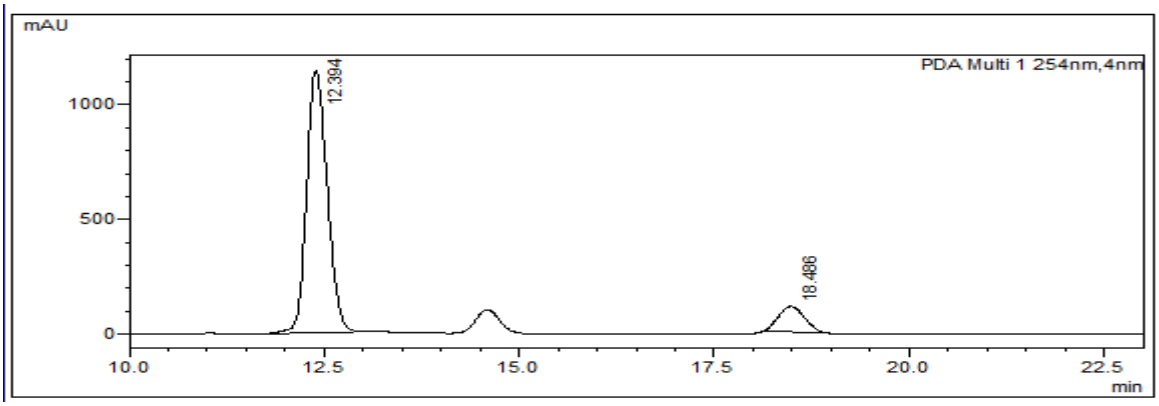
PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.412	3611368	182784	50.179	52.283
2	12.874	3585663	166822	49.821	47.717
Total		7197030	349606	100.000	100.000

(2*S*,7a*R*)-2-Methoxy-7a-(4-nitrobenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2m):



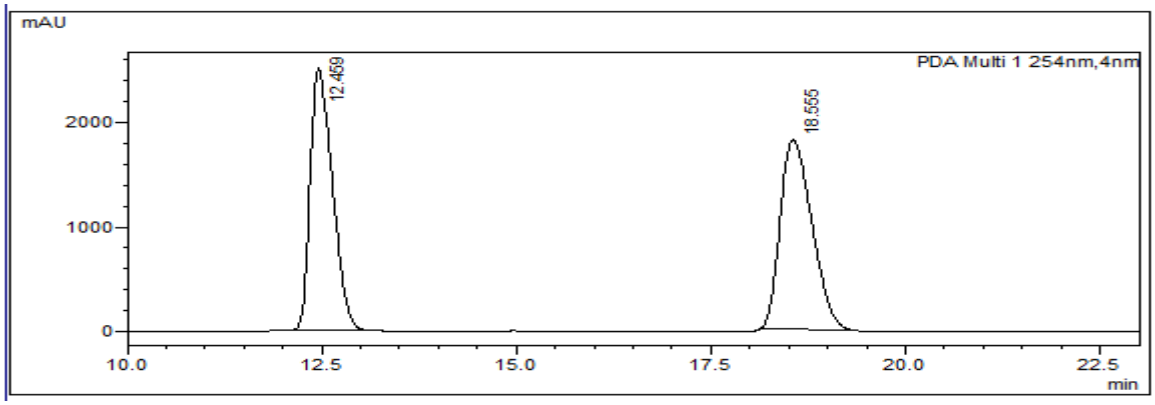
Prepared according to the general procedure as described above in 66% yield (67 mg; *dr* = 7:1). It was purified by flash chromatography (50% EtOAc/hexane; R_f = 0.3) to afford red liquid;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 3.96 (td, *J* = 6.9, 2.8 Hz, 1H), 3.58 (dt, *J* = 14.8, 3.1 Hz, 1H), 3.49 – 3.37 (m, 2H), 3.10 (d, *J* = 13.4 Hz, 1H), 3.04 (d, *J* = 13.4 Hz, 1H), 2.78 (ddd, *J* = 15.5, 13.1, 6.0 Hz, 1H), 2.66 – 2.56 (m, 2H), 2.33 – 2.21 (m, 1H),2.24 (ddd, *J* = 20.3, 14.3, 6.6 Hz, 2H),1.85 (ddt, *J* = 26.5, 13.1, 4.5 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.1, 188.6, 161.6, 147.4, 142.5, 138.0, 130.9, 123.7, 79.7, 67.0, 65.4, 42.9, 38.3, 36.5, 24.0, 23.5, 15.6; HRMS (ESI) calcd for $C_{19}H_{20}O_5N$ $[M-H]^+$: 342.1336; found: 342.1339; $[\alpha]^{20}_D$ = -73.30° (*c* 1.0, $CHCl_3$); 89:11*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 12.39 min (major), 18.48 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.394	21095539	1145248	89.199	91.226
2	18.486	2554360	110150	10.801	8.774
Total		23649899	1255398	100.000	100.000

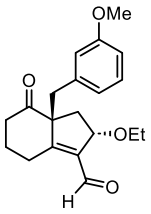


<Peak Table>

PDA Ch1 254nm

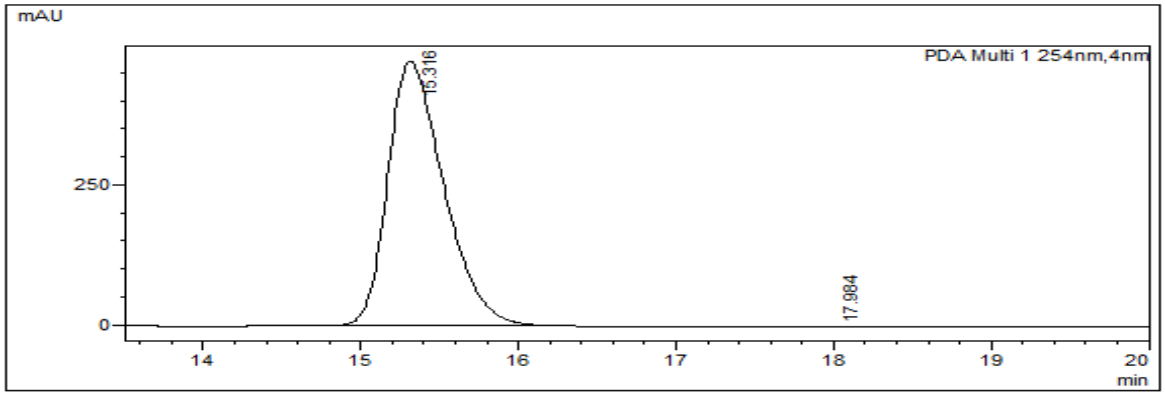
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.459	50073819	2513895	49.205	58.074
2	18.555	51692391	1814904	50.795	41.926
Total		101766210	4328799	100.000	100.000

(2*S*,7a*R*)-2-Ethoxy-7a-(3-methoxybenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2n):



Prepared according to the general procedure as described above in 78% yield (76 mg; *dr* = >20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.4) to afford colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 1.9 Hz, 1H), 3.92 (td, *J* = 6.8, 2.8 Hz, 1H), 3.75 (s, 3H), 3.52 (dt, *J* =

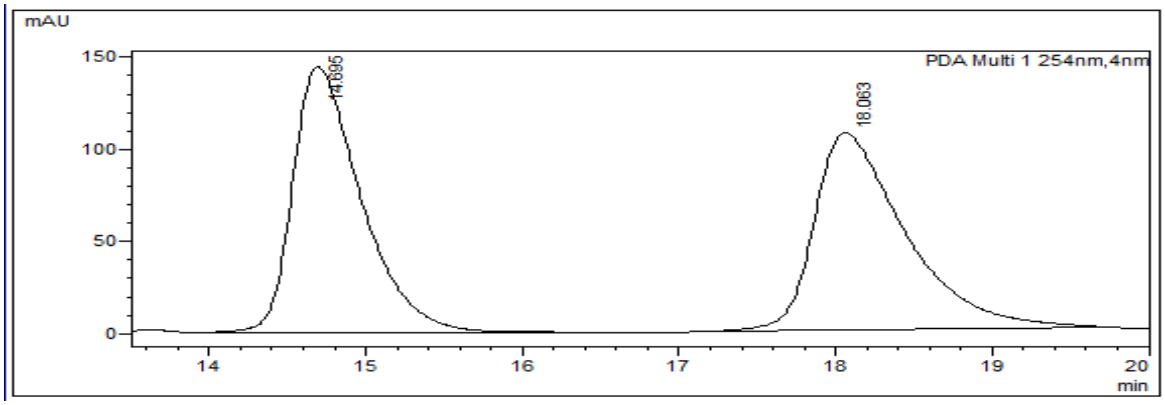
14.7, 3.7 Hz, 1H), 3.47 – 3.38 (m, 2H), 3.03 (d, *J* = 13.3 Hz, 1H), 2.84 (d, *J* = 13.3 Hz, 1H), 2.78 (ddd, *J* = 15.5, 13.2, 6.1 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.54 (dt, *J* = 15.5, 3.2 Hz, 1H), 2.36 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.30 – 2.21 (m, 1H), 2.15 (dd, *J* = 14.2, 6.1 Hz, 1H)), 1.82 (tdd, J = 17.6, 8.9, 4.4 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.1, 188.7, 162.9, 159.5, 138.0, 136.7, 129.5, 122.5, 116.2, 112.6, 79.8, 67.4, 65.2, 55.4, 43.5, 38.4, 36.8, 24.0, 23.5, 15.6;HRMS (ESI) calcd for $C_{20}H_{24}O_4Na$ $[M+Na]^+$: 351.1566 found: 351.1555; $[\alpha]^{20}_D$ = -25.50° (*c*1.0, $CHCl_3$); >99:1*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X 4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 15.31 min (major), 17.98 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.316	11668212	471236	99.680	99.840
2	17.984	37460	755	0.320	0.160
Total		11705672	471991	100.000	100.000

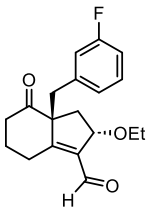


<Peak Table>

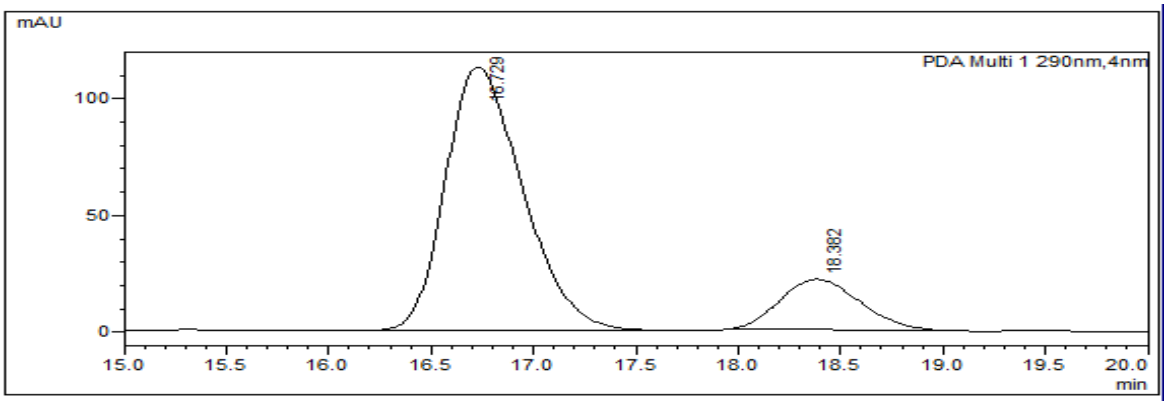
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.695	4420731	144588	50.285	57.466
2	18.063	4370622	107017	49.715	42.534
Total		8791353	251605	100.000	100.000

(2*S*,7a*R*)-2-Ethoxy-7a-(3-fluorobenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2o):



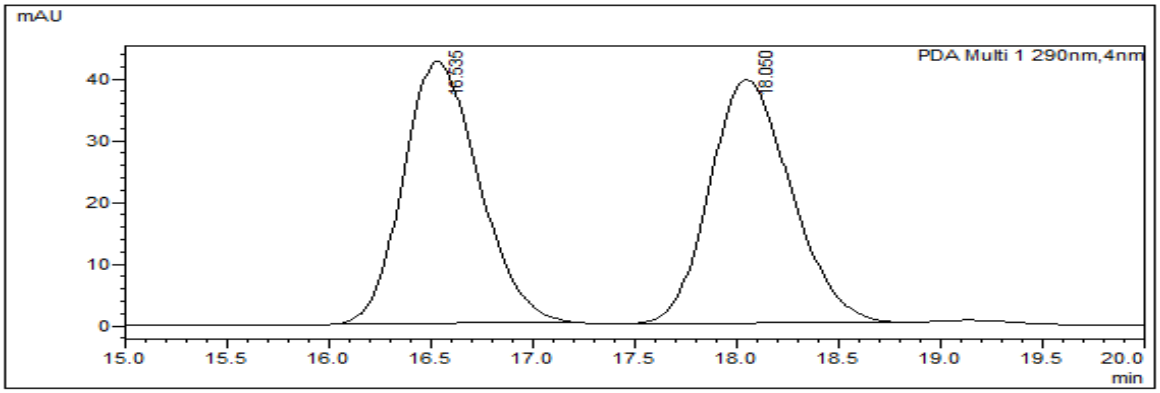
Prepared according to the general procedure as described above in 70% yield (66 mg; *dr*= >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford red liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.23 (td, *J* = 8.0, 6.0 Hz, 1H), 6.96 (tdd, *J* = 8.5, 2.5, 0.6 Hz, 1H)), 6.78 (d, *J* = 7.7 Hz, 1H), 6.73 (dt, *J* = 9.6, 1.9 Hz, 1H), 3.92 (td, *J* = 7.0, 2.8 Hz, 1H), 3.53 (dt, *J* = 14.8, 3.1 Hz, 1H), 3.49 – 3.38 (m, 2H), 3.03 (d, *J* = 13.4 Hz, 1H), 2.88 (d, *J* = 13.4 Hz, 1H), 2.77 (ddd, *J* = 15.5, 13.2, 6.0 Hz, 1H), 2.66 – 2.58 (m, 1H), 2.55 (dt, *J* = 15.6, 4.2 Hz,1H), 2.32 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.26 (dddd, *J* = 11.8, 8.9, 5.9, 3.1 Hz, 1H), 2.17 (dd, *J* = 14.2, 6.1 Hz, 1H), 1.83 (ddt, *J* = 26.3, 13.2, 4.4 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.7, 188.6, 162.6 (d, J_{CF} = 248.08 Hz), 162.4,138.0, 137.7(d, J_{CF} = 7.38 Hz), 129.96 (d, J_{CF} = 8.2 Hz), 125.75 (d, J_{CF} = 2.2 Hz), 117.0 (d, J_{CF} = 21.18 Hz), 114.59 (d, J_{CF} = 29.21 Hz), 79.7, 67.2, 65.3, 43.0, 38.3, 36.6, 24.0, 23.5, 15.6.;^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7; HRMS (ESI) calcd for $C_{19}H_{22}O_3F$ $[M+H]^+$: 317.1547; found: 317.1542; $[\alpha]^{20}_D$ = +47.80° (*c* 1.0, $CHCl_3$); 91:9*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 90:10, detected at 290 nm, Flow rate = 1 mL/min, Retention times: 16.72 min (major), 18.38 min (minor).



<Peak Table>

PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.729	2966201	112569	91.036	88.596
2	18.382	292058	14490	8.964	11.404
Total		3258259	127059	100.000	100.000

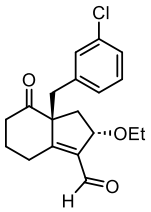


<Peak Table>

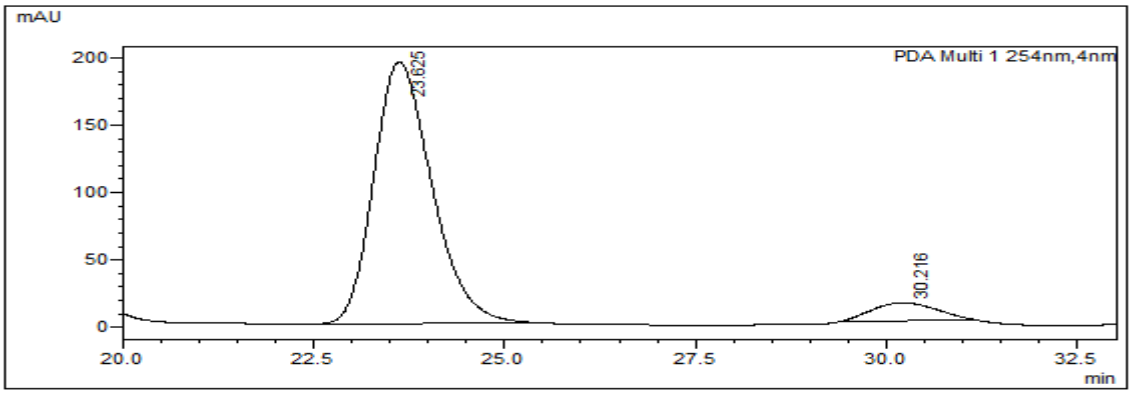
PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.535	1103006	42544	50.158	51.923
2	18.050	1096036	39392	49.842	48.077
Total		2199041	81936	100.000	100.000

(2*S*,7a*R*)-7a-(3-Chlorobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2p):



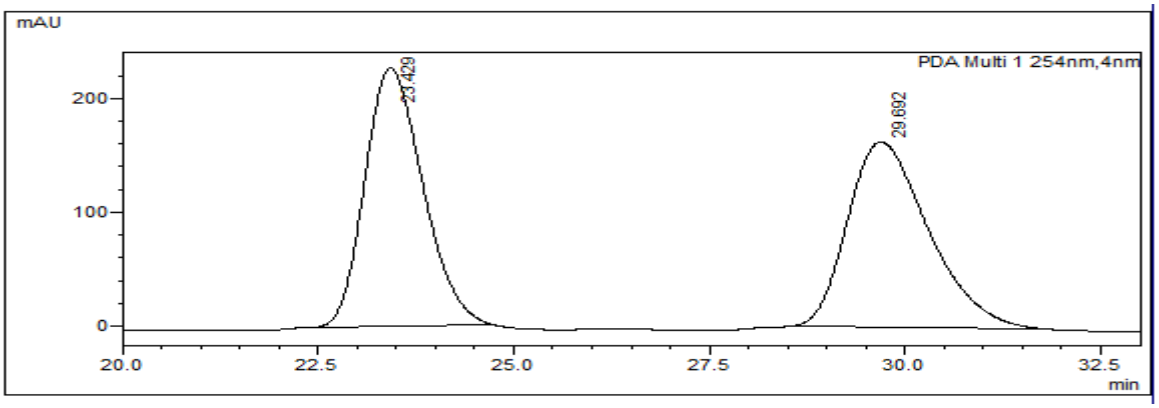
Prepared according to the general procedure as described above in 71% yield (70 mg; *dr* = >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.23 (t, *J* = 1.5 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 1.7 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 3.92 (td, *J* = 7.0, 2.8 Hz, 1H), 3.53 (dt, *J* = 14.8, 3.2 Hz, 1H), 3.48 – 3.39 (m, 2H), 3.00 (d, *J* = 13.4 Hz, 1H), 2.86 (d, *J* = 13.4 Hz, 1H), 2.76 (ddd, *J* = 15.5, 13.1, 6.0 Hz, 1H), 2.66 – 2.58 (m, 1H), 2.55 (dt, *J* = 6.6, 4.0 Hz, 1H), 2.30 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.26 – 2.21 (m, 1H), 2.17 (dd, *J* = 14.2, 6.1 Hz, 1H), 1.86 (ddt, J = 26.2, 13.0, 4.5 Hz, 1H)), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.7, 188.5, 162.4, 138.0, 137.3, 134.3, 130.1, 129.7, 128.1, 127.8, 79.7, 67.2, 65.3, 42.9, 38.3, 36.6, 24.0, 23.5, 15.5; HRMS (ESI) calcd for $C_{19}H_{22}O_3Cl$ $[M+H]^+$: 333.1252; found: 333.1243; $[\alpha]^{20}_D$ = -26.60° (*c* 1.0, $CHCl_3$); 93:7*er*; Chiral HPLC analysis of the product: Daicel Chiralpak IC 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 23.62 min (major), 30.21 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	23.625	10258262	193997	92.643	93.439
2	30.216	814646	13621	7.357	6.561
Total		11072908	207618	100.000	100.000

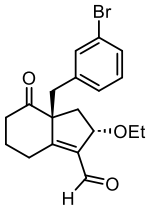


<Peak Table>

PDA Ch1 254nm

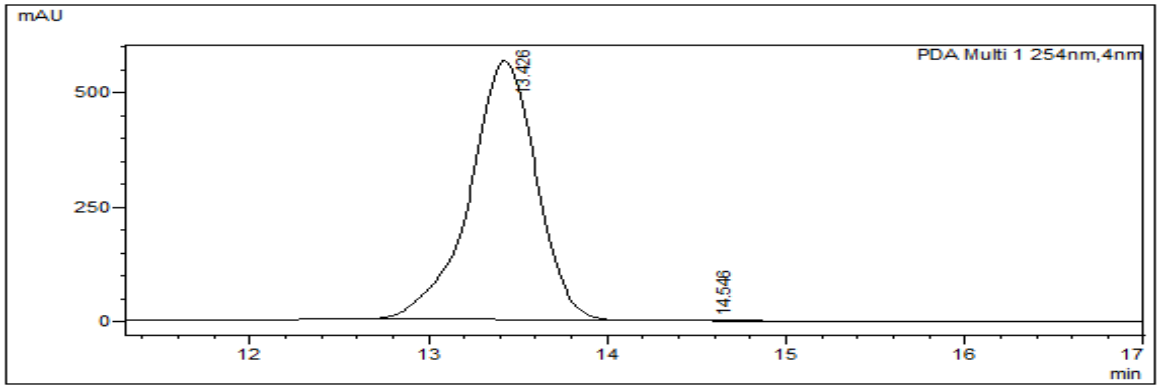
Peak#	Ret. Time	Area	Height	Area%	Height%
1	23.429	11689697	227057	50.134	58.289
2	29.692	11627119	162477	49.866	41.711
Total		23316816	389534	100.000	100.000

(2*S*,7a*R*)-7a-(3-Bromobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2q):



Prepared according to the general procedure as described above in 75% yield (84 mg; *dr* = >20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.5) to afford colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.40 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.17 (t, *J* = 1.7 Hz, 1H),

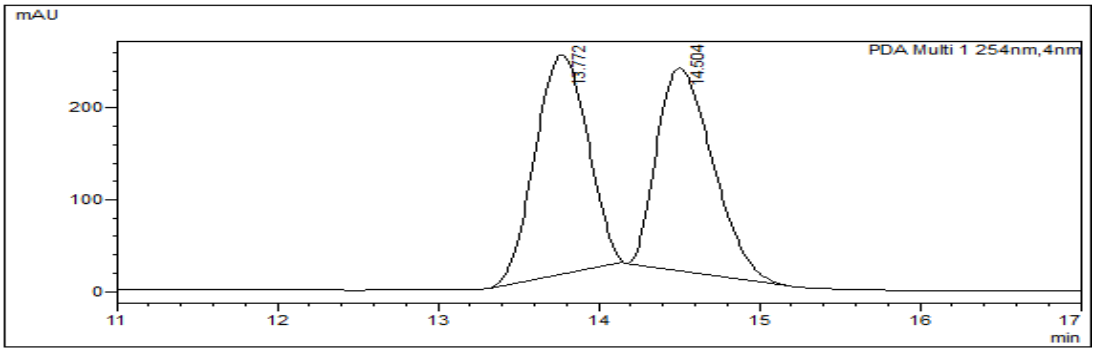
7.13 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 3.89 (td, *J* = 7.0, 2.9 Hz, 1H), 3.53 (dt, *J* = 14.8, 3.1 Hz, 1H), 3.49 – 3.38 (m, 2H), 2.99 (d, *J* = 13.4 Hz, 1H), 2.85 (d, *J* = 13.4 Hz, 1H), 2.76 (ddd, *J* = 15.5, 13.1, 6.0 Hz, 1H), 2.64 – 2.59 (m, 1H), 2.55 (dt, *J* = 8.6, 3.7 Hz, 1H), 2.29 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.27 – 2.22 (m, 1H), 2.17 (dd, *J* = 14.2, 6.1 Hz, 1H), 1.88 – 1.77 (m, 1H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.7, 188.5, 162.3, 138.1, 137.5, 133.1, 130.7, 130.0, 128.6, 122.5, 79.7, 67.2, 65.2, 42.8, 38.3, 36.6, 24.0, 23.5, 15.5; HRMS (ESI) calcd for $C_{19}H_{22}O_3NBr$ $[M+H]^+$: 377.0746; found: 377.0751; $[\alpha]^{20}_D$ = -24.00° (*c* 1.0, $CHCl_3$); >99:1*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5μ column; hexane/2-propanol = 90:10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 13.42 min (major), 14.54 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.426	14680946	566644	99.540	99.552
2	14.546	67879	2551	0.460	0.448
Total		14748825	569195	100.000	100.000

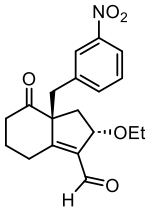


<Peak Table>

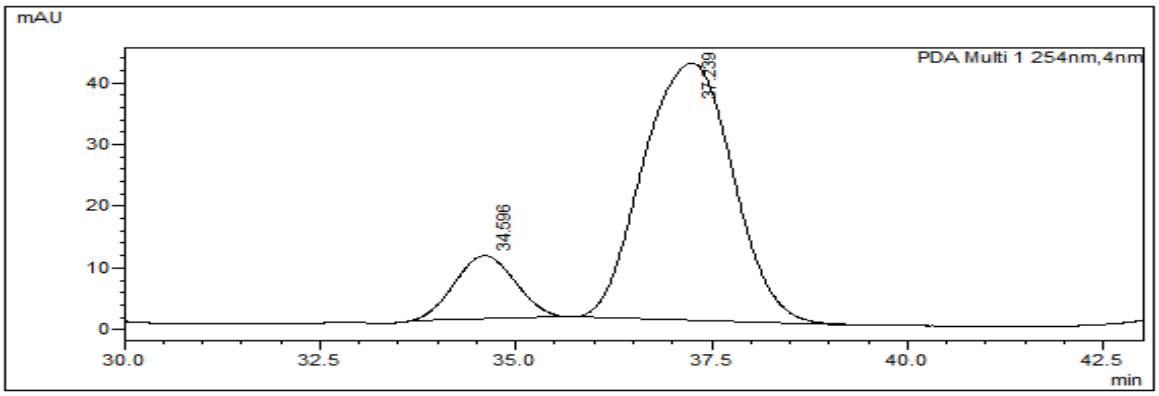
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.772	5452842	238604	50.410	51.926
2	14.504	5364092	220900	49.590	48.074
Total		10816934	459504	100.000	100.000

(2*S*,7a*R*)-2-Ethoxy-7a-(3-nitrobenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2r):



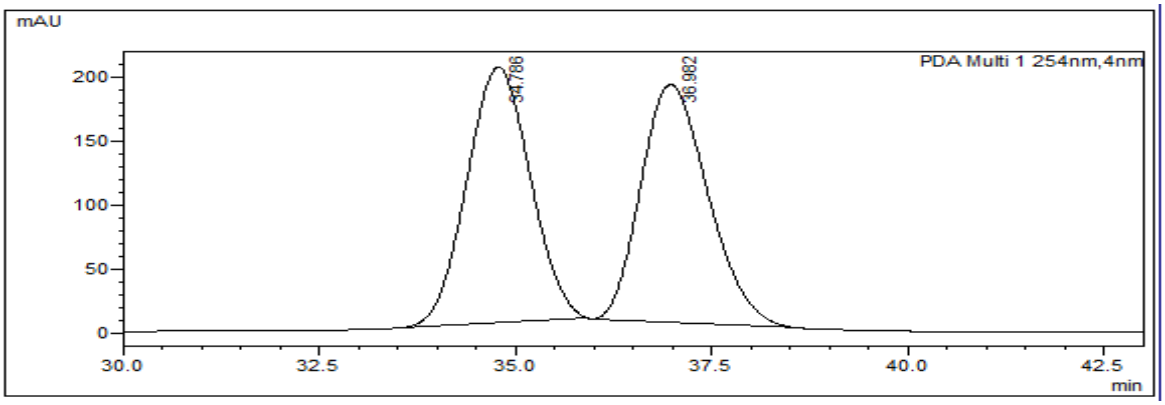
Prepared according to the general procedure as described above in 62% yield (63 mg; *dr* = >20:1). It was purified by flash chromatography (50% EtOAc/hexane; R_f = 0.3) to afford yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.14 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 7.91 (t, *J* = 1.9 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 3.94 (td, *J* = 6.7, 2.8 Hz, 1H), 3.57 (dt, *J* = 14.9, 3.2 Hz, 1H), 3.43 (qq, *J* = 9.1, 7.0 Hz, 2H), 3.08 (q, *J* = 13.6 Hz, 2H), 2.80 (ddd, *J* = 15.6, 13.1, 6.0 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.60 (dt, *J* = 15.8, 3.1 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.25 (qd, *J* = 14.4, 6.6 Hz, 2H), 1.86 (ddt, *J* = 26.3, 13.2, 4.5 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 188.3, 162.0, 148.2, 138.2, 137.3, 135.9, 129.5, 124.8, 122.7, 79.6, 67.1, 65.4, 42.7, 38.3, 36.3, 24.1, 23.4, 15.5; HRMS (ESI) calcd for $C_{19}H_{22}O_5N$ $[M+H]^+$: 344.1492; found: 344.1496; $[\alpha]^{20}_D$ = -3.20° (*c* 1.0, $CHCl_3$); 86:14*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5µ column; hexane/2-propanol = 90:10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 34.59 min (minor), 37.23 min (major).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	34.596	554398	10253	14.271	19.721
2	37.239	3330323	41736	85.729	80.279
Total		3884721	51988	100.000	100.000

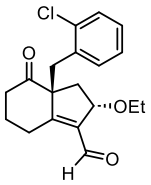


<Peak Table>

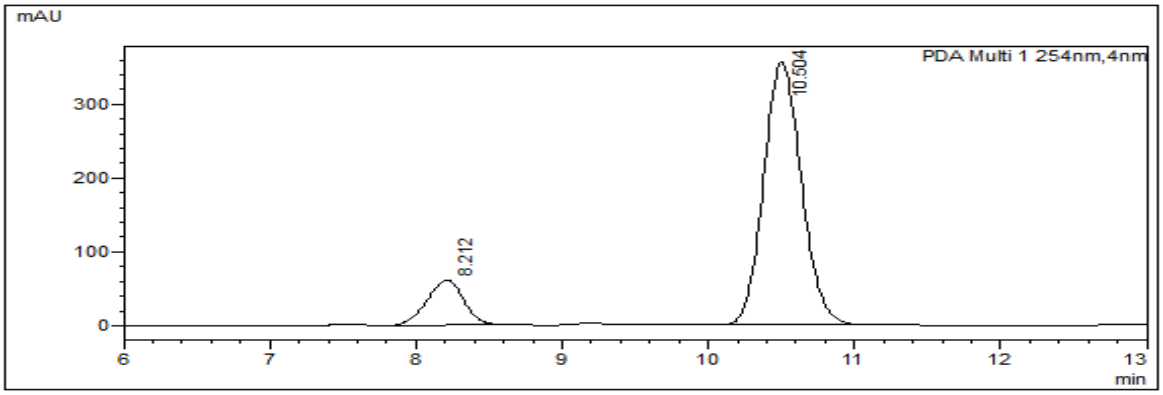
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	34.786	11268378	199923	50.388	51.800
2	36.982	11094868	186027	49.612	48.200
Total		22363247	385950	100.000	100.000

(2*S*,7a*R*)-7a-(2-Chlorobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2s):



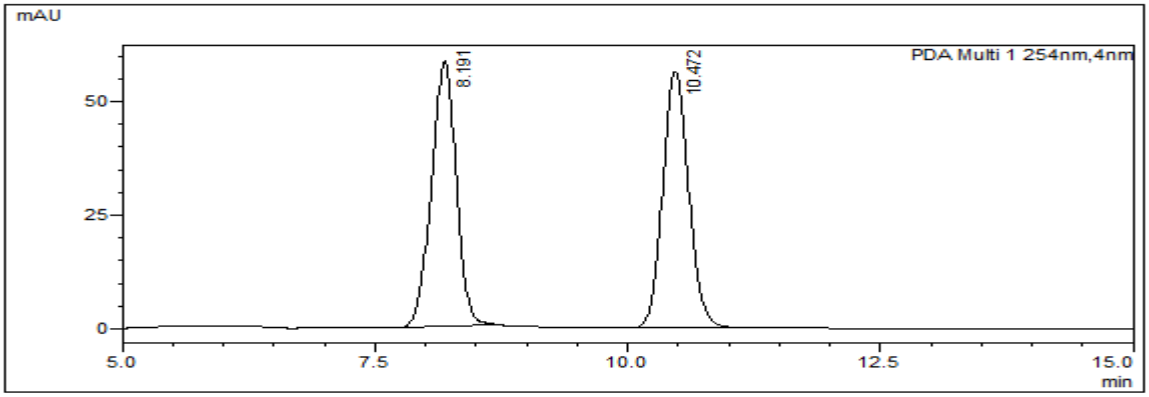
Prepared according to the general procedure as described above in 82% yield (81 mg; *dr* = >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.5) to afford colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.36 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.18 (dtd, *J* = 16.8, 7.4, 1.6 Hz, 2H), 6.98 (dd, *J* = 7.4, 1.8 Hz, 1H), 4.09 (td, *J* = 6.8, 2.9 Hz, 1H), 3.53 – 3.42 (m, 3H), 3.22 (d, *J* = 13.7 Hz, 1H), 3.09 (d, *J* = 13.8 Hz, 1H), 2.79 (ddd, *J* = 15.4, 13.1, 5.9 Hz, 1H), 2.66 (dddd, *J* = 15.3, 12.6, 5.3, 3.0 Hz, 1H), 2.55 (dt, *J* = 15.4, 3.3 Hz, 1H), 2.42 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.29 – 2.19 (m, 1H), 2.06 (dd, *J* = 14.1, 6.5 Hz, 1H), 1.87 – 1.73 (m, 1H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 188.7, 163.4, 137.8, 135.0, 133.6, 131.9, 130.1, 129.0, 126.8, 80.0, 66.8, 65.2, 39.7, 38.6, 36.5, 24.0, 23.8, 15.6; HRMS (ESI) calcd for $C_{19}H_{22}O_3Cl$ $[M+H]^+$: 333.1252; found: 333.1266; $[\alpha]^{20}_D$ = -68.92° (*c* 1.0, $CHCl_3$); 91:9*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5µ column; hexane/2-propanol = 90:10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 8.21 (minor), 10.50 min (major).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.212	651781	46661	9.230	11.584
2	10.504	6409914	356158	90.770	88.416
Total		7061695	402820	100.000	100.000

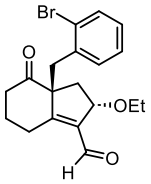


<Peak Table>

PDA Ch1 254nm

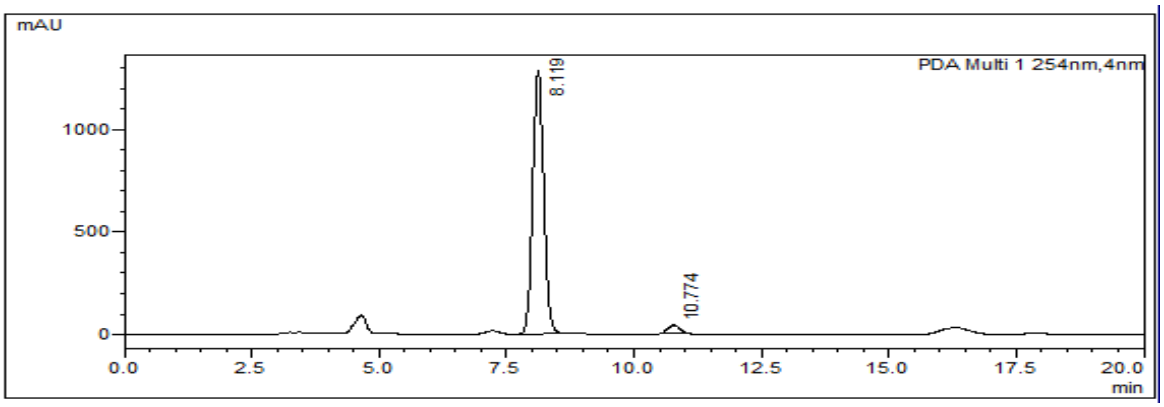
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.191	991847	58271	49.785	50.863
2	10.472	1000396	56292	50.215	49.137
Total		1992243	114563	100.000	100.000

(2*S*,7a*R*)-7a-(2-Bromobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2t):



Prepared according to the general procedure as described above in 86% yield (97 mg; *dr* = 11:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.88 (s, 1H), 7.56 (d, *J*=8.0, 1H), 7.26 (d, *J*=0.9, 1H), 7.20 (t, *J*=7.5, 1H), 7.12 (t, *J*=7.6, 1H), 6.96 (d, *J*=7.6, 1H), 4.17 (td, *J*=6.6, 2.7, 1H), 3.55 – 3.43 (m, 3H), 3.29 (d, *J*=13.9,

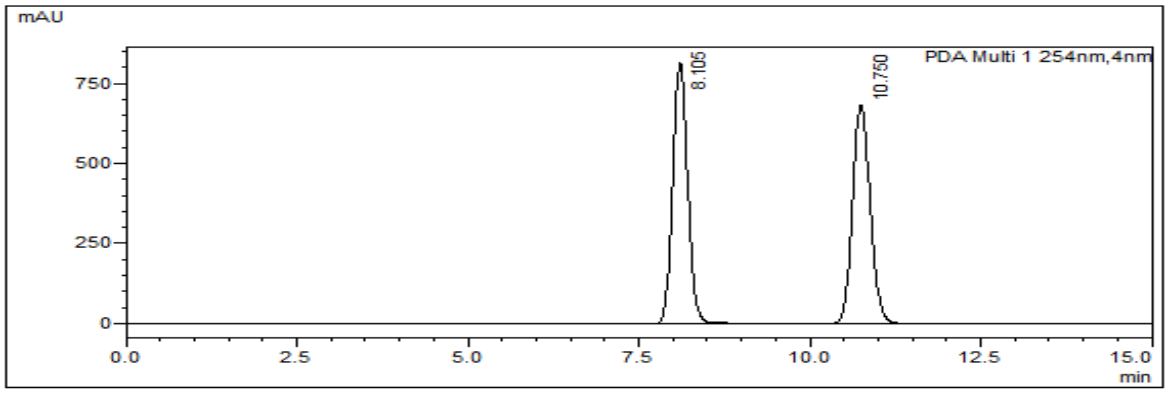
1H), 3.11 (d, *J*=13.9, 1H), 2.79 (ddd, *J*=14.9, 13.6, 5.9, 1H), 2.71 – 2.60 (m, 1H), 2.60 – 2.52 (m, 1H), 2.43 (dd, *J*=14.1, 7.1, 1H), 2.29 – 2.19 (m, 1H), 2.08 (dd, *J*=14.1, 6.4, 1H), 1.87 – 1.74 (m, 1H), 1.12 (t, *J*=7.0, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 188.8, 163.3, 137.8, 135.4, 133.5, 131.6, 129.2, 127.4, 126.0, 80.1, 66.9, 65.3, 42.1, 38.7, 36.4, 24.0, 23.8, 15.6; HRMS(ESI) calcd for $C_{19}H_{22}O_3Br$ $[M+H]^+$: 377.0746; found: 377.0751; $[\alpha]^{20}_D$ = +48.50° (*c* 1.0, $CHCl_3$); 97:3*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5μ column; hexane/2-propanol = 90:10, detected at 254 nm, Flow rate = 1 mL/min, Retention time: 8.11 min (major), 10.77 min(minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.119	19189186	1283651	96.569	96.853
2	10.774	681671	41711	3.431	3.147
Total		19870857	1325362	100.000	100.000

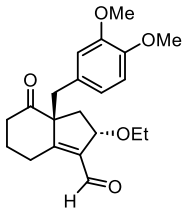


<Peak Table>

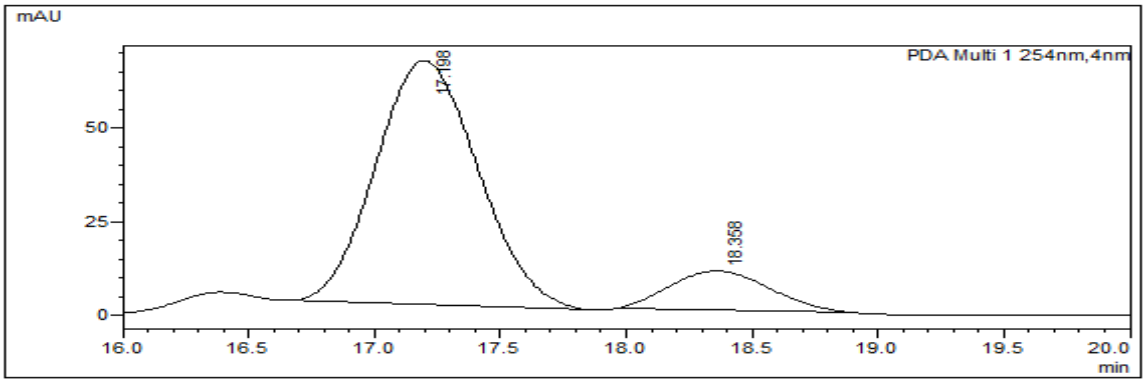
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.105	12412304	816438	50.200	54.397
2	10.750	12313202	684455	49.800	45.603
Total		24725506	1500893	100.000	100.000

(2*S*,7a*R*)-7a-(3,4-Dimethoxybenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2u):



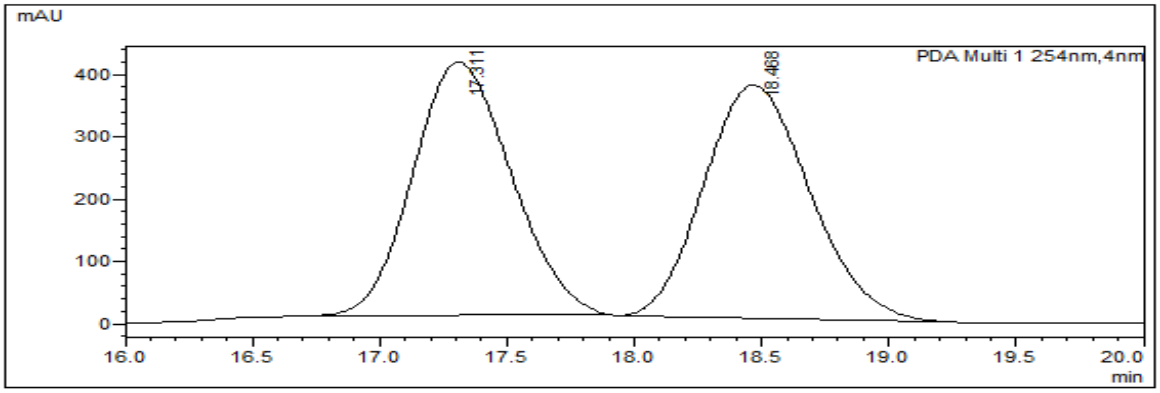
Prepared according to the general procedure as described above in 76% yield (81mg; *dr*= 14:1). It was purified by flash chromatography (50% EtOAc/hexane; R_f = 0.3) to afford yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.56 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.49 (d, *J* = 1.9 Hz, 1H), 3.89 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.54 (dt, *J* = 6.4, 3.6 Hz, 1H), 3.49 – 3.35 (m, 2H), 3.04 (d, *J* = 13.5 Hz, 1H), 2.80 (d, *J* = 13.4 Hz, 1H), 2.77 – 2.69 (m, 1H), 2.67 – 2.57 (m, 1H), 2.53 (dt, *J* = 15.6, 3.4 Hz, 1H), 2.35 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.14 (dd, *J* = 13.9, 6.1 Hz, 1H), 1.90 – 1.73 (m, 1H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 188.9, 162.7, 148.7, 148.6, 137.8, 127.6, 122.5, 113.3, 111.1, 79.9, 67.5, 65.1, 56.1, 56.0, 43.3, 38.4, 37.0, 23.9, 23.6, 15.6; HRMS (ESI) calcd for $C_{21}H_{27}O_5$ $[M+H]^+$: 359.1853; found: 359.1847; $[\alpha]^{20}_D$ = -40.66° (*c* 1.0, $CHCl_3$); 90:10*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5µ column; hexane/2-propanol = 92:08, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 17.19 min (major), 18.35 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.198	1820446	64945	89.769	88.146
2	18.358	207480	8734	10.231	11.854
Total		2027926	73679	100.000	100.000

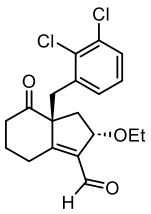


<Peak Table>

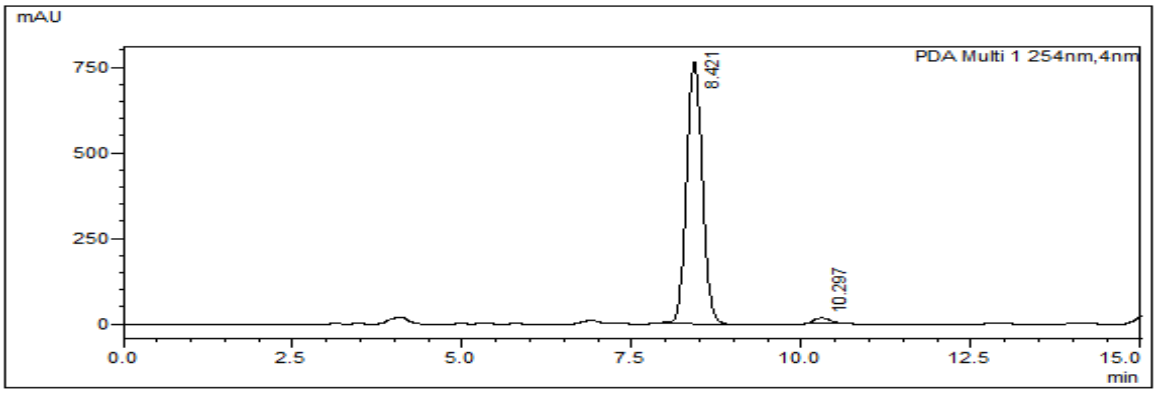
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.311	10926119	407111	50.410	52.180
2	18.468	10748341	373093	49.590	47.820
Total		21674460	780203	100.000	100.000

(2*S*,7a*R*)-7a-(2,3-Dichlorobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2v):



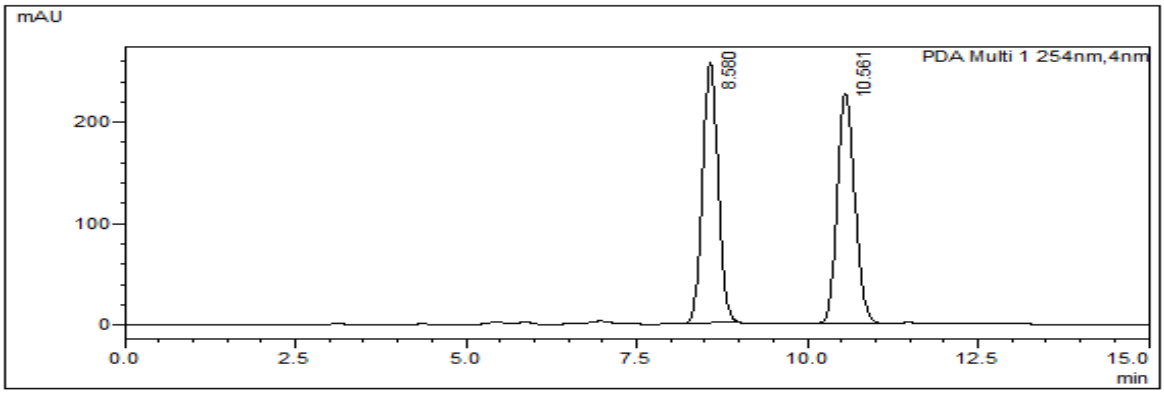
Prepared according to the general procedure as described above in 85% yield (93mg; *dr*= >20:1, with inseparableimpurities). It was purified by flash chromatography (50% EtOAc/hexane; R_f = 0.4) to afford colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.39 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.89 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.23 (td, *J* = 6.7, 2.9 Hz, 1H), 3.55 – 3.44 (m, 3H), 3.31 (d, *J* = 14.0 Hz, 1H), 3.12 (d, *J* = 14.0 Hz, 1H), 2.78 (ddd, *J* = 15.4, 13.0, 6.0 Hz, 1H), 2.68 – 2.60 (m, 1H), 2.59 – 2.53 (m, 1H), 2.35 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.31 – 2.18 (m, 1H), 2.10 (dd, *J* = 14.2, 6.4 Hz, 1H), 1.81 (ddt, *J* = 26.1, 13.1, 4.4 Hz, 1H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.8, 187.9, 167.9, 137.5, 137.1, 133.7, 133.2, 130.8, 129.6, 127.1, 78.9, 67.8, 65.7, 42.2, 39.3, 35.4, 24.1, 23.9, 15.6; HRMS (ESI) calcd for $C_{19}H_{21}O_3Cl_2$ $[M+H]^+$: 367.0862; found: 367.0859; $[\alpha]^{20}_D$ = -81.65° (*c* 1.0, $CHCl_3$); 98:2*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5µ column; hexane/2-propanol = 90:10, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 8.42 min (major), 10.29 min (minor).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.421	12417949	765351	97.983	97.955
2	10.297	255603	15982	2.017	2.045
Total		12673552	781333	100.000	100.000

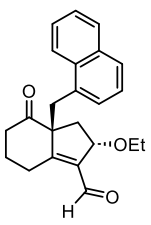


<Peak Table>

PDA Ch1 254nm

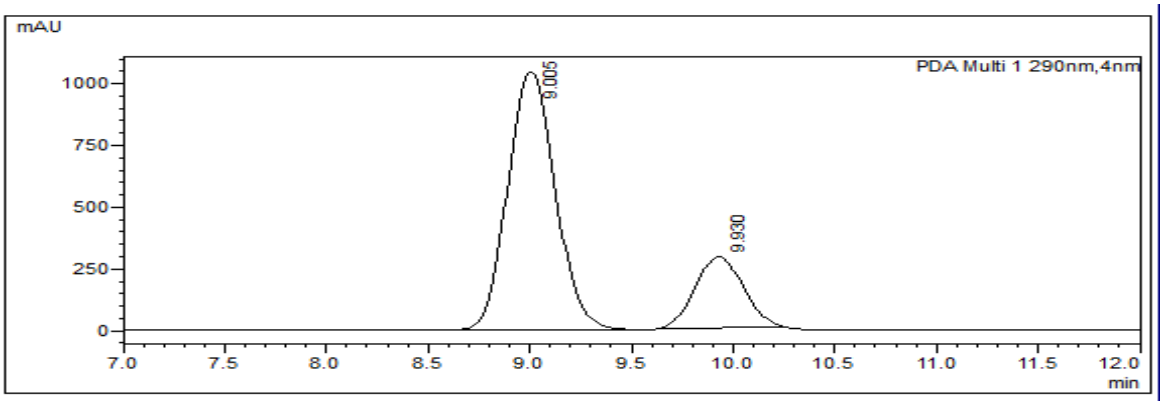
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.580	4070035	257172	50.095	53.274
2	10.561	4054650	225563	49.905	46.726
Total		8124685	482735	100.000	100.000

(2*S*,7a*R*)-2-Ethoxy-7a-(naphthalen-1-ylmethyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2w):



Prepared according to the general procedure as described above in 72% yield (75 mg; *dr* = >20:1). It was purified by flash chromatography (50% EtOAc/hexane; R_f = 0.3) to afford yellow liquid;^{1}H NMR

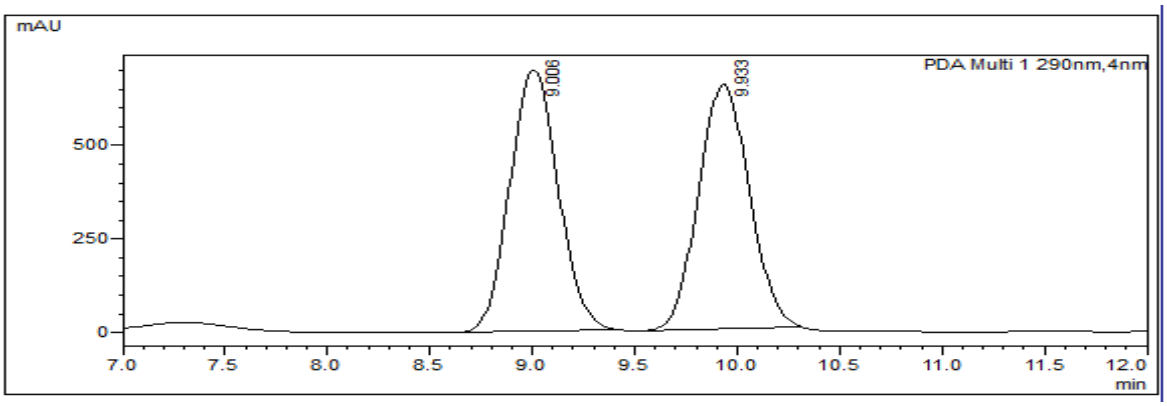
(400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.21 – 8.17 (m, 1H), 7.86 – 7.83 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.38 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.18 (dd, *J* = 7.1, 0.8 Hz, 1H), 4.63 (dd, *J* = 5.0, 2.0 Hz, 1H), 3.95 (d, *J* = 14.2 Hz, 1H), 3.70 (d, *J* = 14.2 Hz, 1H), 3.66 – 3.55 (m, 2H), 3.24 (dt, *J* = 14.6, 3.0 Hz, 1H), 2.59 – 2.43 (m, 2H), 2.18 – 2.15 (m, 2H), 2.09 (ddd, *J* = 14.6, 12.9, 5.3 Hz, 1H), 2.03 – 1.94 (m, 1H), 1.57 – 1.41 (m, 1H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.2, 187.9, 169.1, 137.8, 134.1, 133.4, 132.9, 128.9, 128.2, 128.0, 126.2, 125.9, 125.3, 124.5, 78.8, 69.1, 65.9, 42.0, 40.0, 37.0, 24.2, 23.7, 15.7; HRMS:(ESI) calcd for $C_{23}H_{25}O_3[M+H]^+$: 349.1798; found: 349.1791; $[\alpha]^{20}_D$ = +45.50° (*c* 1.0, $CHCl_3$); 83:17*er*; Chiral HPLC analysis of the product: Daicel Chiralpak AD-H 250X4.6 mm 5μ column; hexane/2-propanol = 90:10, detected at 290 nm, Flow rate = 1 mL/min, Retention times: 9.00 min (major), 9.93 min (minor).



<Peak Table>

PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.005	16937764	1042415	82.889	80.948
2	9.930	3496579	245351	17.111	19.052
Total		20434342	1287766	100.000	100.000

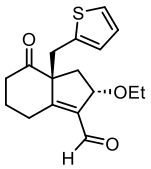


<Peak Table>

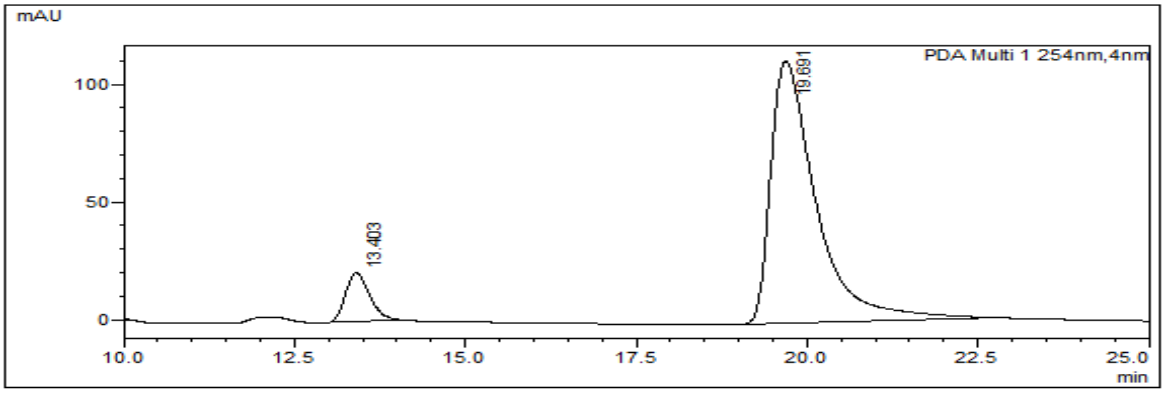
PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.006	11495496	696312	50.457	51.615
2	9.933	11287181	652744	49.543	48.385
Total		22782677	1349055	100.000	100.000

(2*S*,7a*R*)-2-Ethoxy-7-oxo-7a-(thiophen-2-ylmethyl)-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2x):



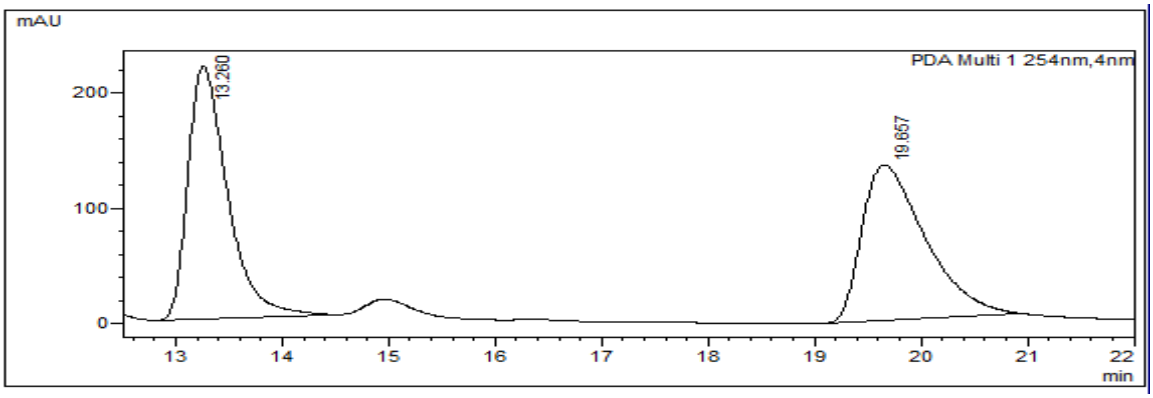
Prepared according to the general procedure as described above in 84% yield (76 mg; *dr* = >20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.3) to afford red liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.17 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.92 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.75 (d, *J* = 2.7 Hz, 1H), 4.14 (ddd, *J* = 7.4, 5.7, 2.8 Hz, 1H), 3.54 – 3.43 (m, 3H), 3.25 (d, *J* = 14.5 Hz, 1H), 3.15 (d, *J* = 14.5 Hz, 1H), 2.76 (ddd, *J* = 15.5, 13.1, 6.1 Hz, 1H), 2.65 – 2.58 (m, 1H), 2.54 (dt, *J* = 15.2, 3.8 Hz, 1H), 2.39 (dd, *J* = 14.3, 7.3 Hz, 1H),2.30 (dd, *J* = 14.3, 5.6 Hz, 1H), 2.31 – 2.22 (m, 1H), 1.90 – 1.76 (m, 1H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 188.5, 162.6, 138.2, 136.4, 127.7, 127.0, 125.4, 80.0, 67.8, 65.3, 38.2, 37.8, 36.8, 24.0, 23.3, 15.6; HRMS (ESI) calcd for $C_{17}H_{21}O_3S$ $[M+H]^+$: 305.1205; found: 305.1216; $[\alpha]^{20}_D$ = -18.09° (*c* 1.0, $CHCl_3$); 91:9*er*; Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 254nm, Flow rate = 1 mL/min, Retention times: 13.40 min (minor), 19.69 min (major).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.403	511536	20684	8.972	15.647
2	19.691	5190222	111508	91.028	84.353
Total		5701758	132192	100.000	100.000

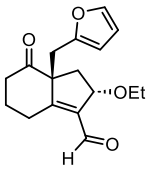


<Peak Table>

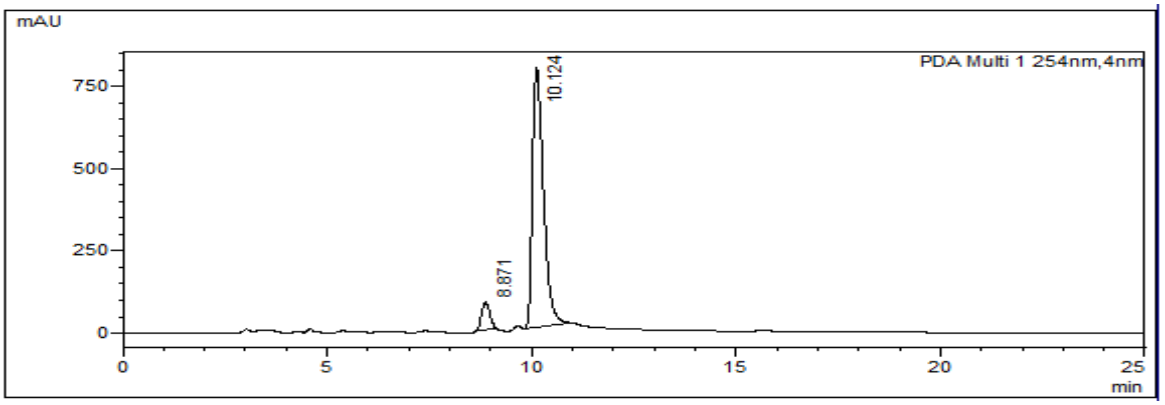
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.260	5652903	219248	50.419	61.948
2	19.657	5558929	134676	49.581	38.052
Total		11211832	353924	100.000	100.000

(2*S*,7a*R*)-2-Ethoxy-7a-(furan-2-ylmethyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde(2y):



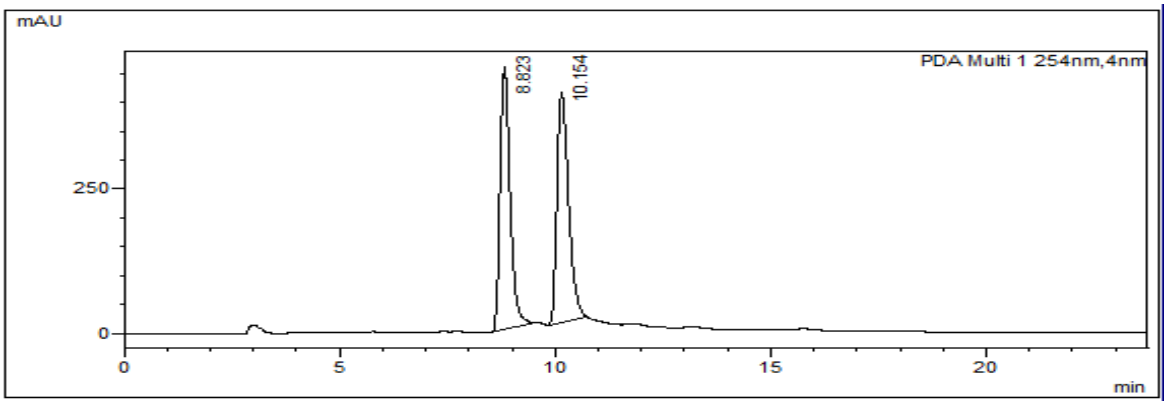
Prepared according to the general procedure as described above in 82% yield (70 mg; *dr* = >20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.3) to red liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.28 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.27 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.05 (d, *J* = 3.6 Hz, 1H), 4.33 (ddd, *J* = 7.4, 5.7, 2.8 Hz, 1H), 3.57 – 3.48 (m, 2H), 3.45 (dt, *J* = 6.2, 3.7 Hz, 1H), 3.02 (s, 2H), 2.76 (ddd, *J* = 15.5, 13.2, 6.1 Hz, 1H), 2.64 – 2.57 (m, 1H), 2.52 (dt, *J* = 15.5, 4.0 Hz, 1H), 2.39 (dd, *J* = 14.2, 7.3 Hz, 1H), 2.29 (dd, *J* = 14.3, 5.6 Hz, 1H), 2.25 – 2.20 (m, 1H), 1.79 (ddt, *J* = 26.2, 13.2, 4.5 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.2, 188.5, 163.4, 149.8, 142.5, 137.4, 110.7, 108.9, 79.8, 66.8, 65.2, 38.1, 36.9, 36.5, 24.0, 23.2, 15.6; HRMS (ESI) calcd for $C_{17}H_{21}O_4$ $[M+H]^+$: 289.1434; found: 289.1425; $[\alpha]^{20}_D$ = +12.62° (*c* 0.5, $CHCl_3$); 94:6 *er*; Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5µ column; hexane/2-propanol = 80:20, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 8.87 min (minor), 10.12 min (major).



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.871	926721	74391	5.883	8.599
2	10.124	14826207	790681	94.117	91.401
Total		15752928	865072	100.000	100.000



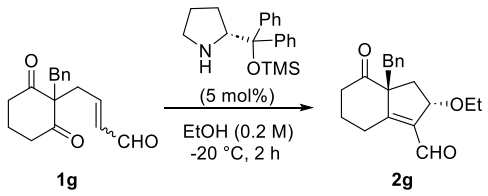
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.823	7305066	453432	49.613	53.318
2	10.154	7418895	396992	50.387	46.682
Total		14723961	850424	100.000	100.000

IIb. One mmol-Scale reaction and Synthetic utility

IIba. One-mmol Scale reaction:

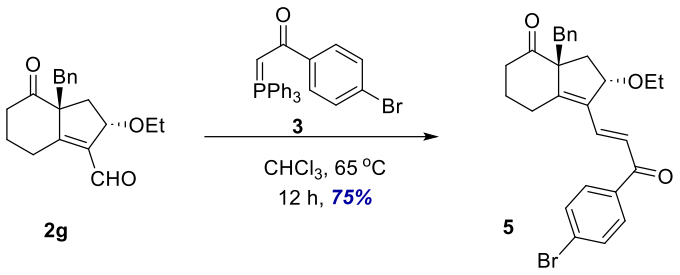


To a stirred solution of enal-tethered Cyclohexane 1,3-dione **1g** (270 mg, 1.0 mmol) in EtOH (5 mL, 0.2 M) at -20 ^{o}C was added Jørgensen-Hayashi catalyst **C-I** (16 mg, 0.05 mmol, 5 mol%) under nitrogen atmosphere. The reaction was allowed to stir at the same temperature until complete

consumption of starting material (monitored by TLC). Afterward, the solvent was evaporated under reduced pressure and the crude residue was directly purified by column chromatography on silica gel (EtOAc in Hexane) to give the desired product**2g** in 82% yield (244 mg); $[\alpha]_{20}^{D}$ = -85.91° (*c* 1.0, $CHCl_3$); 96:4 *er*.

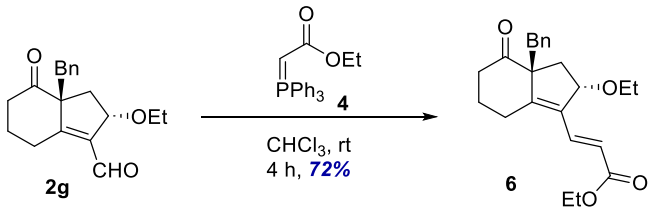
IIbb. Synthetic utility:

(2*S*,3a*R*)-3a-Benzyl-1-((*Z*)-3-(4-bromophenyl)-3-oxoprop-1-en-1-yl)-2-ethoxy-2,3,3a,5,6,7-hexahydro-4*H*-inden-4-one (5):



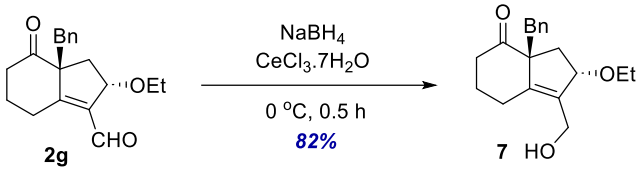
The solution of aldehyde **2g** (60 mg, 0.2 mmol, 1 equiv) in CH_2Cl_2 (4 mL, 0.05 M) was added 4-bromo phenyl phosphorene**3** (138 mg, 0.30 mmol, 1.5 equiv) in one portion at room temperature under a nitrogen atmosphere. The reaction mixture was stirred at 65 °C using preheated oil bath for 12h and then concentrated in vacuo. The crude reaction mixture was purified by flash column chromatography (20% EtOAc/hexane; R_f = 0.4) to give dienone**5** in 75% yields (72 mg, *dr* = >20:1) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 15.3 Hz, 1H)), 7.60 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.21 (m, 3H), 7.13 (d, *J* = 15.3 Hz, 1H), 6.99 (dd, *J* = 6.5, 2.9 Hz, 2H), 3.73 (td, *J* = 6.8, 2.6 Hz, 1H), 3.44 (dq, *J* = 9.0, 7.0 Hz, 1H), 3.25 (dq, *J* = 9.1, 7.0 Hz, 1H), 3.12 – 3.05 (m, 2H), 2.85 – 2.74 (m, 2H), 2.65 – 2.56 (m, 1H), 2.53 (dt, *J* = 15.2, 3.0 Hz, 1H), 2.36 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.30 – 2.23 (m, 1H), 2.19 (dd, *J* = 13.8, 6.7 Hz, 1H), 1.75 (dt, *J* = 26.2, 13.2, 4.4 Hz, 1H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.0, 189.9, 155.0, 137.2, 135.8, 135.7, 135.3, 132.0, 130.1, 130.0, 128.3, 127.9, 127.3, 123.0, 80.9, 66.8, 63.1, 43.3, 38.5, 35.8, 24.7, 23.8, 15.7; HRMS (ESI) calcd for $C_{27}H_{27}O_3BrNa$ $[M+Na]^+$: 501.1035; found: 501.1048; $[\alpha]^{20}_D$ = -101.99° (*c* 1.0, $CHCl_3$).

Ethyl (*E*)-3-((2*S*,7a*R*)-7a-benzyl-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-inden-3-yl)acrylate(6):



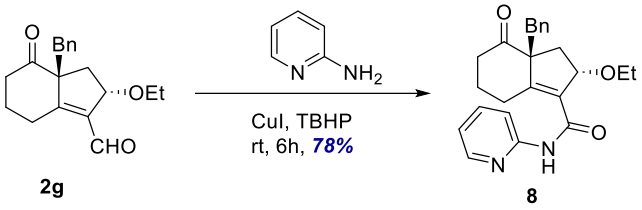
The solution of aldehyde **2g** (60 mg, 0.2 mmol, 1 equiv) in CH_2Cl_2 (3 mL, 0.1 M) was added desired phosphorene (105 mg, 0.30 mmol, 1.5 equiv) in one portion at room temperature under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2h and then concentrated in vacuo. The crude reaction mixture was purified by flash column chromatography (20% EtOAc/hexane; R_f = 0.5) to give bicyclic ester **6** in 72% yield (53 mg, *dr* = >20:1) as an yellow oil;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 15.8 Hz, 1H), 7.24 – 7.19 (m, 3H), 6.99 – 6.95 (m, 2H), 5.97 (d, *J* = 15.7 Hz, 1H), 4.27 – 4.12 (m, 2H), 3.60 (td, *J* = 6.7, 2.7 Hz, 1H), 3.37 (dq, *J* = 9.0, 7.0 Hz, 1H), 3.19 (dq, *J* = 9.0, 7.0 Hz, 1H), 3.06 (d, *J* = 13.2 Hz, 1H), 3.00 (dt, *J* = 14.5, 2.9 Hz, 1H), 2.77 (d, *J* = 13.2 Hz, 1H), 2.76 (ddd, *J* = 19.5, 11.3, 3.9 Hz, 1H)), 2.60 – 2.53 (m, 1H), 2.50 (dt, *J* = 15.3, 4.3 Hz, 1H), 2.31 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.12 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.74 (dt, *J* = 26.4, 13.2, 4.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 167.8, 152.3, 135.7, 135.5, 134.9, 130.1, 128.3, 127.3, 120.0, 80.8, 66.5, 63.4, 60.5, 43.2, 38.6, 35.9, 24.7, 23.6, 15.5, 14.5; HRMS (ESI) calcdfor $C_{23}H_{28}O_4Na$ $[M+Na]^+$: 391.1885; found: 391.1889; $[\alpha]^{20}_D$ = -17.00° (*c*1.0, $CHCl_3$).

(2*S*,3a*R*)-3a-Benzyl-2-ethoxy-1-(hydroxymethyl)-2,3,3a,5,6,7-hexahydro-4*H*-inden-4-one (7):



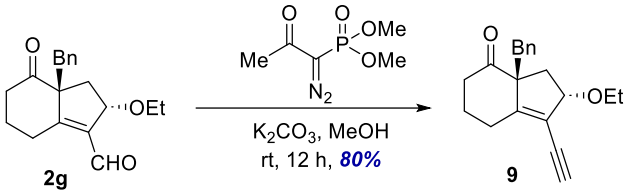
To a solution of**2g**(60 mg, 0.2 mmol, 1 equiv) and$CeCl_3 \cdot 7H_2O$ (112 mg, 1.5 equiv) in 3 mL of MeOH was added$NaBH_4$(11 mg, 1.5 equiv) over a period of 5 min. The reactionmixture was stirred for 30 min at room temperature, quenched withH_2O (5 mL), extracted with ethyl acetate (3×5 mL), dried overNa_2SO_4, concentrated under vacuo, and then purified byflashchromatography (30% EtOAc in hexanes;R_f= 0.3) to afford a colour less oil (49 mg, 82% yield*dr* = >20:1);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 3H), 7.04 – 6.98 (m, 2H), 4.22 (d, *J* = 12.4 Hz, 1H), 3.99 (d, *J* = 12.4 Hz, 1H), 3.50 – 3.38 (m, 2H), 3.19 (dq, *J* = 9.1, 7.0 Hz, 1H), 2.99 (d, *J* = 13.2 Hz, 1H), 2.79 – 2.70 (m, 3H), 2.47 (dt, *J* = 15.2, 3.1 Hz, 1H), 2.43 – 2.33 (m, 2H), 2.28 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.22 – 2.11 (m, 1H), 2.02 (dd, *J* = 13.5, 6.7 Hz, 1H), 1.79 (dt, *J* = 26.4, 13.2, 4.4 Hz, 1H), 1.08 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.4, 142.2, 136.7, 136.1, 130.2, 128.1, 127.2, 84.2, 65.9, 64.6, 58.4, 42.5, 38.6, 36.9, 25.2, 22.8, 15.5; HRMS (ESI) calcd for $C_{19}H_{24}O_3Na$ $[M+Na]^+$: 323.1623; found: 323.1631; $[\alpha]^{20}_D$ = +15.83 ° (*c* 1.0, $CHCl_3$).

(2*S*,7a*R*)-7a-Benzyl-2-ethoxy-7-oxo-N-(pyridin-2-yl)-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carboxamide(8):



A sealable reaction tube equipped with a magnetic stirrer bar was charged with aldehyde **2g** (60 mg, 0.2 mmol), amines (22 mg, 1.2 equiv, 0.2 mmol), CuI (5 mg, 0.05 equiv, 0.03 mmol), tert-butyl hydroperoxide (TBHP, 36 mg, 2 equiv, 0.4 mmol), water (1 mL). The reaction vessel was carried out at room temperature. After stirring the mixture for 6 h, it was diluted with ethyl acetate, washed with water and brine, dried with Mg_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the corresponding product in 78% yield (61 mg; *dr* = >20:1). It was purified by flash chromatography (10%EtOAc/hexane; R_f = 0.4) to afford a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.32 (dd, *J* = 58.4, 6.2 Hz, 2H), 7.80 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.25 (m, 3H), 7.11 – 7.02 (m, 3H), 3.89 (dt, *J* = 15.5, 3.4 Hz, 1H), 3.86 – 3.78 (m, 1H), 3.63 – 3.53 (m, 1H), 3.52 – 3.43 (m, 1H), 3.10 (d, *J* = 13.3 Hz, 1H), 2.86 (d, *J* = 13.2 Hz, 1H), 2.79 (dd, *J* = 18.6, 11.1, 4.2 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.52 (dt, *J* = 15.3, 3.6 Hz, 1H), 2.40 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.27 – 2.20 (m, 1H), 2.17 (dd, *J* = 13.7, 6.6 Hz, 1H), 1.80 (ddt, *J* = 26.0, 13.0, 4.5 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 163.5, 160.2, 151.1, 135.3, 130.6, 130.3, 130.0, 128.6, 128.4, 127.5, 119.6, 115.1, 80.8, 66.2, 64.5, 43.4, 38.5, 36.7, 24.6, 24.2, 15.4; HRMS (ESI) calcd for $C_{24}H_{27}O_3N_2$ $[M+H]^+$: 391.2016; found: 391.2029; $[\alpha]^{20}_D$ = +11.00 ° (*c* 1.0, $CHCl_3$).

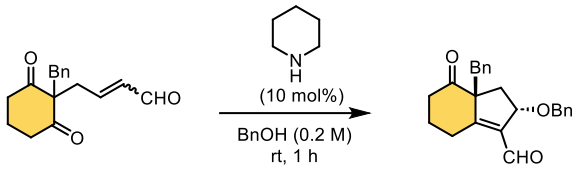
(2*S*,3a*R*)-3a-Benzyl-2-ethoxy-1-ethynyl-2,3,3a,5,6,7-hexahydro-4*H*-inden-4-one (9):



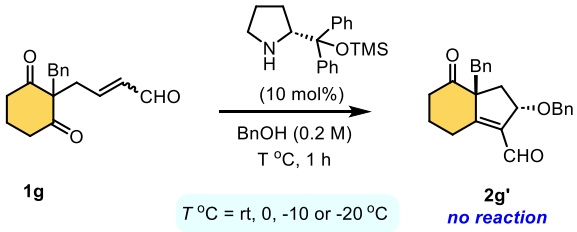
To a solution of **2g** (60 mg, 0.2 mmol) and dimethyldiazomethylphosphonate (Ohira-Bestmann reagent) (46 mg, 1.25 equiv, 0.25 mmol) in dry methanol (2mL), was added potassium carbonate (41 mg, 1.5 equiv, 0.3mmol) at 0 °C under argon atmosphere. The mixture was stirred at 0°C for 30 min and room temperature for 12h. After addition of EtOAc (5 mL) and aqueous saturated ammonium chloride (2 mL), the organic layer was separated, and the aqueous layer was extracted with EtOAc (5

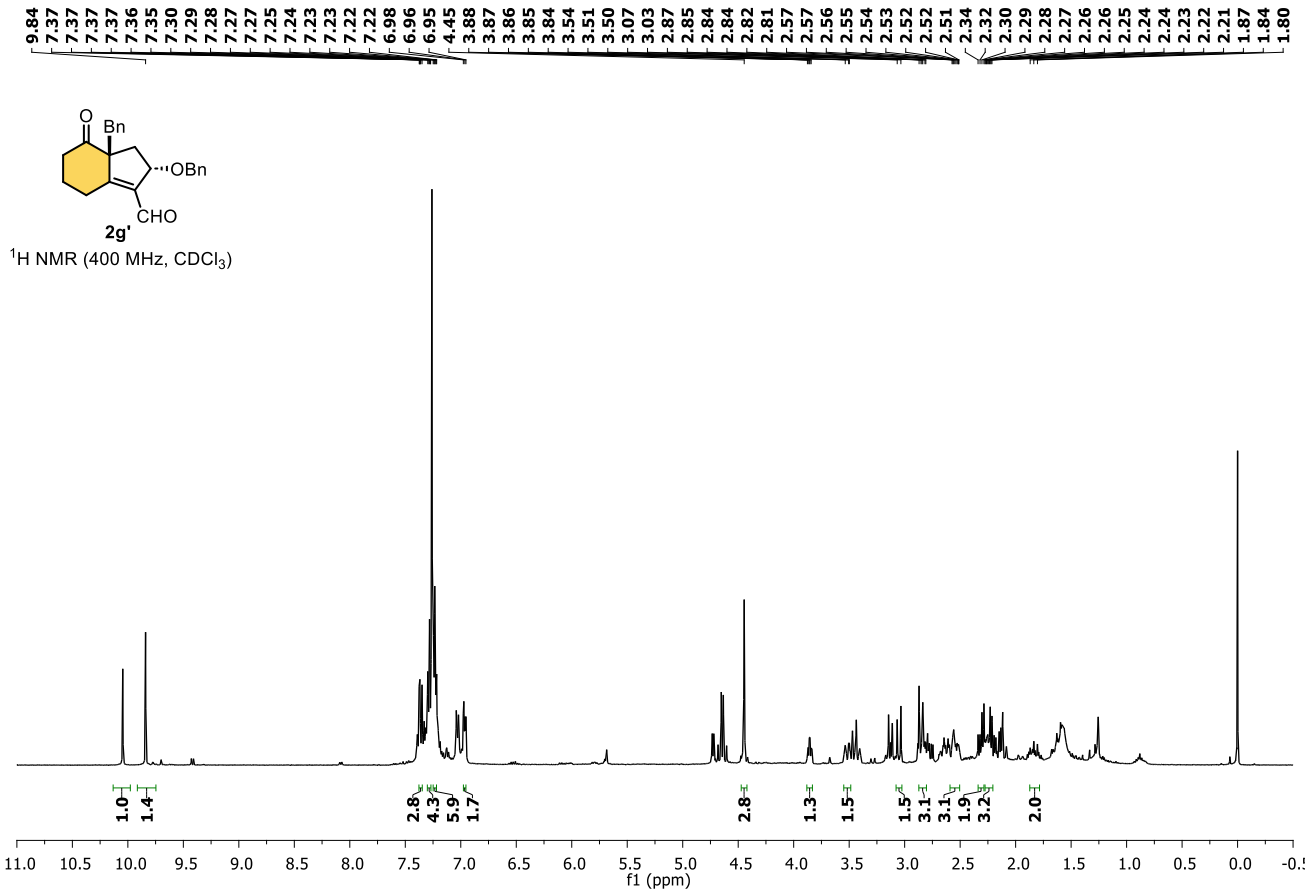
mL x 2). The combined organic layers were dried, concentrated. Flash column chromatography of crude reaction mixture on silica gel (20% EtOAc/hexane; R_f = 0.6) to afford desired alkyne **9** in 80% yield (47 mg, *dr* = >20:1) as a brown solid; mp = 80–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 3H), 7.05 – 7.02 (m, 2H), 3.48 – 3.33 (m, 3H), 3.12 (br.s, 1H), 3.03 (d, *J* = 13.2 Hz, 1H), 2.97 (dt, *J* = 14.5, 4.3 Hz, 1H), 2.77 (d, *J* = 13.2 Hz, 1H), 2.70 (ddd, *J* = 19.4, 11.4, 3.9 Hz, 1H), 2.56 – 2.41 (m, 2H), 2.28 (dd, *J* = 13.7, 7.1 Hz, 1H), 2.22 – 2.10 (m, 1H), 2.06 (dd, *J* = 13.7, 7.0 Hz, 1H),1.76 (tdd, *J* = 17.8, 8.9, 4.5 Hz, 1H), 1.09 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 154.4, 135.8, 130.2, 128.3, 127.3, 121.9, 82.5, 82.1, 78.4, 65.7, 64.6, 42.8, 38.5, 37.2, 24.7, 24.5, 15.5; HRMS (ESI) calcd for $C_{20}H_{22}O_2Na$ $[M+Na]^+$: 317.1512; found: 317.1517; $[\alpha]^{20}_D$ = -40.57° (*c* 1.0, $CHCl_3$).

IIbc. Standard reaction with 1g in BnOH solvent:

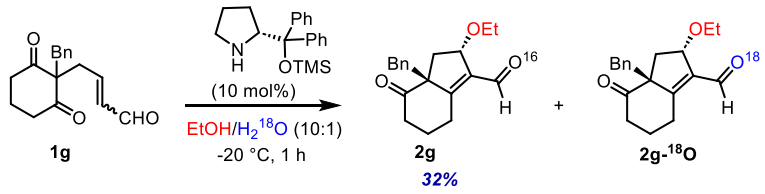


To a stirred solution of enal-tethered cyclohexane 1,3-dione **1g** (0.3 mmol) in BnOH (1.5 mL, 0.2 M) at room temperature was added piperidine (10.2 mg, 0.03 mmol, 10 mol%) under nitrogen atmosphere. The reaction was allowed to stir at the same temperature until complete consumption of starting material (monitored by TLC). Afterward, the solvent was evaporated under reduced pressure at 40-45^{o}C (rotary evaporator water bath) and the crude residue was directly purified by column chromatography on silica gel (EtOAc in Hexane) to give the desired product **2g'** in >10% yield with 1:1.4 ratio of diastereoselectivity (*dr*). However, asymmetric reaction with Jørgensen-Hayashi catalyst **C-I** at various temperatures failed to give the desired product and most of the starting material was recovered.





IIc. Labeling Experiments.



Major peak at m/z = 321.1424 for product 2g was detected in HRMS analysis

To a stirred solution of enal-tethered cyclohexane 1,3-dione **1g** (30 mg,0.1 mmol) in EtOH (1.0 mL, 0.1 M) and $H_2{}^{18}O$ (0.1 mL) at -20 ^oC was added Jørgensen-Hayashi catalyst **C-I** (3.6 mg, 0.01 mmol, 10 mol%) under nitrogen atmosphere. The reaction was allowed to stir at the same temperature until complete consumption of starting material (monitored by TLC). Afterward, the solvent was concentrated under reduced pressure and residue was directly subjected to flash column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired product **2g** in 32% yield (10 mg). No ^{18}O incorporation was detected in HRMS analysis.

Elemental Composition Report

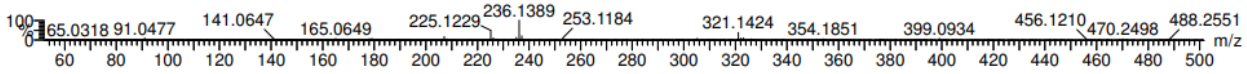
Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
291 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-23 N: 0-1 O: 0-4 Na: 0-1 S: 0-1 Br: 0-1 I: 0-2

17-Oct-2023
17OCT2023_CRB_A_298_1 18 (0.341) AM2 (Ar,12000.0,0.00,0.00); Cm (15:21-(24:30+6:11))

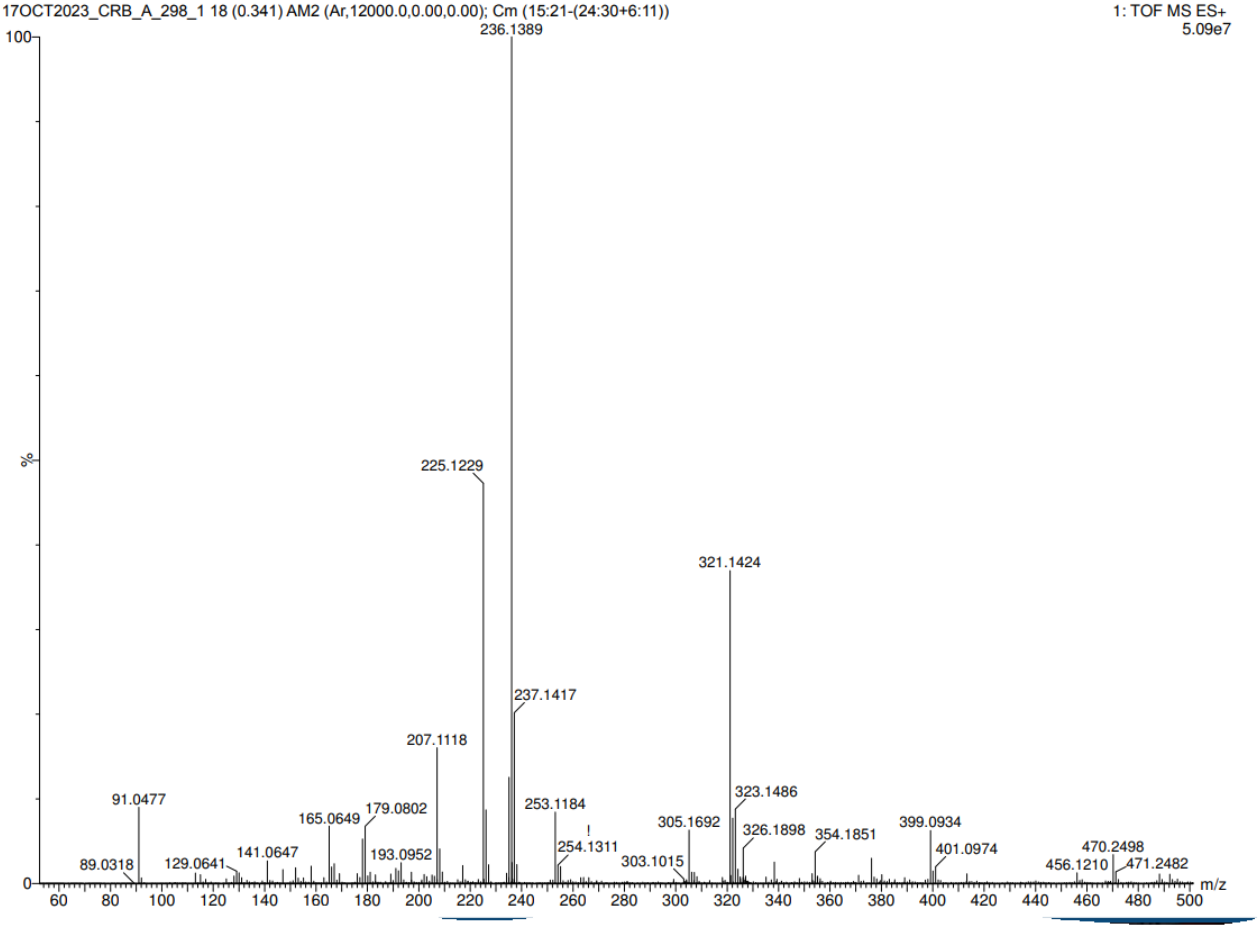
1: TOF MS ES+
5.09e+007



Minimum:				-1.5				
Maximum:		5.0	15.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
321.1424	321.1467	-4.3	-13.4	8.5	511.7	n/a	n/a	C19 H22 O3 Na

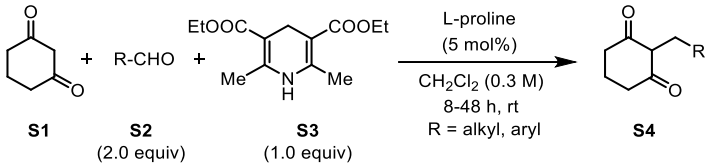
17-Oct-2023
17OCT2023_CRB_A_298_1 18 (0.341) AM2 (Ar,12000.0,0.00,0.00); Cm (15:21-(24:30+6:11))

1: TOF MS ES+
5.09e7

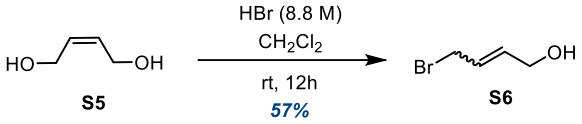


IId. General procedure for the synthesis of enal-tethered cyclohexane 1,3-diones 1 & analytical data:

IIda. Synthesis and analytical data of substrate 1:

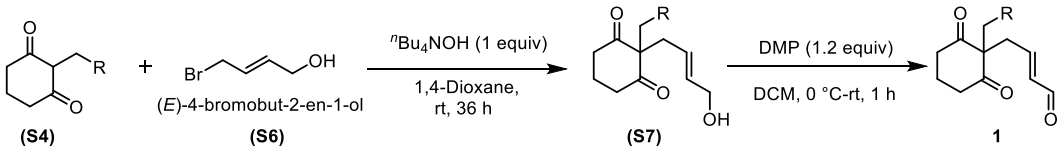


2-substituted 1,3-cyclohexadienones**S 4**were prepared using to Ramachary reductive coupling protocol.[1]



To a CH_2Cl_2 (300 mL) solution of (*Z*)-2-buten-1,4-diol (**S5**) (44.0 g, 41.2 mL, 0.5 mol) at 0 °C was added hydrobromic acid (HBr, 8.8M, 142 mL, 1.25 mol) over 20 min. The resulting mixture was then allowed to react at room temperature for 12 h and the reaction mixture slowly becoming into dark grey colour. The reaction was quenched by adding brine solution (300 mL) and extracted with CH_2Cl_2 (6 × 300 mL). The combined organic extracts were dried over $MgSO_4$, filtrated, and the solvent was removed with a rotary evaporator (30 °C, 300 mbar). The residue was purified by flash column chromatography (silica gel, CH_2Cl_2) to afford the bromo allyl alcohol**S6** (42.8 g, 57%, *E/Z* = 9:1) as a grey liquid.[2]

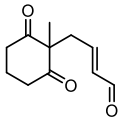
General procedure:



To a solution of 2-methylcyclohexane-l,3-dione(**S4**), (630 mg, 5.0 mmol, 1.0 equiv) and aqueous Bu_4NOH (40% in H_2O, 3.3 mL, 1 equiv) was added a solution of substituent (E)-4-bromobut-2-en-1-ol (6.0 mmol, 1.2 equiv) in dioxane (5 mL). The solution was stirred for 36 h. The solution was neutralized with 10% aqueous HCl. The two liquid layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried with Na_2SO4, and the solvent was evaporated. The residue was purified by column chromatography on silica gel to give the correspondingdesired enol-tethered cyclohexane 1,3-dione **S7**product.[3]

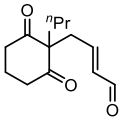
To a stirred solution of allyl alcohol **S7** (5.0 mmol) in 25 mL of CH_2Cl_2 was added Dess Martin Periodinane (3.18 g; 7.5 mmol, 1.5 equiv) in portion wise at 0 ^oC. The resulting reaction mixture was stirred at room temperature for 1h. Then the reaction mixture was diluted with water (15 mL) and extracted with CH_2Cl_2 (25 mL × 3). The combined organic solvent was washed with $NaHCO_3$ (25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography (EtOAc/hexane) to give the desired enal-tethered cyclohexane 1,3-diones **1** in good yields and the *Z/E* ratio of all substrates varies from 1:1 to >20:1.[4]

4-(1-Methyl-2,6-dioxocyclohexyl)but-2-enal (1a):



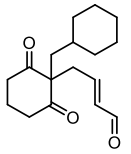
Prepared according to the general procedure as described above in 68% yield (660 mg, *E/Z* =10:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.3) to afford a colourless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, *J* = 7.9 Hz, 1H), 6.61 (dt, *J* = 15.4, 7.7 Hz, 1H), 6.05 (ddd, *J* = 15.6, 7.8, 1.0 Hz, 1H), 2.80 – 2.70 (m, 4H), 2.61 – 2.52 (m, 2H), 2.04 (tt, J = 12.0, 5.9 Hz, 1H), 1.81 (dtd, J = 19.8, 10.0, 5.0 Hz, 1H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 193.7, 152.9, 135.8, 65.0, 37.8, 36.7, 23.3, 17.5; HRMS (ESI) calcd for $C_{11}H_{15}O_3$ $[M+H]^+$: 195.1015; found: 195.1019.

4-(2,6-Dioxo-1-propylcyclohexyl)but-2-enal (1d):



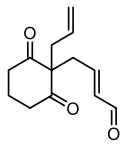
Prepared according to the general procedure as described above in 64% yield (710 mg, *E/Z* = 9:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.3) to afford a yellow liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 7.9 Hz, 1H), 6.62 (dt, *J* = 15.5, 7.3 Hz, 1H), 6.09 (ddt, *J* = 15.6, 7.9, 1.2 Hz, 1H), 2.79 (dd, *J* = 7.3, 1.2 Hz, 2H), 2.77 – 2.70 (m, 2H), 2.57 (dt, *J* = 10.3, 5.4 Hz, 2H), 2.14 – 2.04 (m, 1H), 1.80 – 1.74 (m, 3H), 1.23 – 1.15 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 193.8, 153.5, 135.9, 69.6, 40.1, 38.7, 34.8, 17.9, 17.4, 14.3;HRMS (ESI) calcd for $C_{13}H_{19}O_3$ $[M+H]^+$: 223.1328; found: 223.1330.

4-(1-(Cyclohexylmethyl)-2,6-dioxocyclohexyl)but-2-enal (1e):



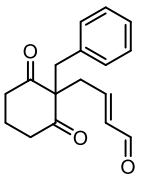
Prepared according to the general procedure as described above in 71% yield (979 mg, *E/Z* =12:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.5) to afford a colourless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 7.9 Hz, 1H), 6.58 (dt, *J* = 15.6, 7.8 Hz, 1H), 6.07 (ddd, *J* = 15.6, 7.8, 1.1 Hz, 1H), 2.83 – 2.74 (m, 4H), 2.54 (dt, *J* = 16.2, 5.3 Hz, 2H), 2.14 – 2.04 (m, 1H), 1.83 – 1.75 (m, 1H), 1.73 (d, *J* = 5.6 Hz, 2H), 1.62 (d, *J* = 14.1 Hz, 2H), 1.52 (d, *J* = 12.9 Hz, 2H), 1.36 – 1.25 (m, 1H), 1.23 – 1.03 (m, 4H), 0.93 – 0.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 193.8, 153.5, 135.8, 69.2, 45.5, 38.7, 35.7, 34.7, 34.1, 26.2, 25.9, 17.5; HRMS (ESI) calcd for $C_{17}H_{25}O_3$ $[M+H]^+$: 277.1798; found: 277.1791.

4-(1-Allyl-2,6-dioxocyclohexyl)but-2-enal (1f):



Prepared according to the general procedure as described above in 62% yield (682 mg, E/Z =10:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.4) to afford a colourless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 7.8 Hz, 1H), 6.56 (dt, *J* = 15.6, 7.3 Hz, 1H), 6.03 (ddt, *J* = 15.6, 7.9, 1.2 Hz, 1H), 5.50 (ddt, *J* = 17.5, 10.2, 7.4 Hz, 1H), 5.12 – 5.02 (m, 2H), 2.73 (dd, *J* = 7.3, 1.2 Hz, 2H), 2.66 (ddd, *J* = 16.4, 10.7, 5.6 Hz, 2H), 2.56 (dt, *J* = 10.8, 5.4 Hz, 2H), 2.50 (d, *J* = 7.4 Hz, 2H), 2.10 – 2.00 (m, 1H), 1.81 – 1.69 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 193.6, 152.9, 135.9, 130.8, 120.5, 68.7, 41.9, 38.8, 35.3, 17.0; HRMS (ESI) calcd for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1172; found: 221.1175.

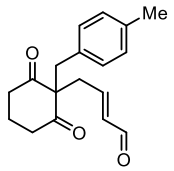
4-(1-Benzyl-2,6-dioxocyclohexyl)but-2-enal (1g):



Prepared according to the general procedure as described above in 80% yield (1.08 g, *E/Z*=>20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.5) to afford colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.20 (m, 3H), 6.97 (dd, *J* = 7.4, 2.0 Hz,

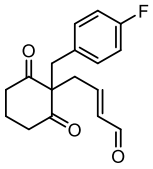
2H), 6.51 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.05 (ddt, *J* = 15.5, 7.7, 1.0 Hz, 1H), 3.10 (s, 2H), 2.84 (dd, *J* = 7.6, 1.0 Hz, 2H), 2.41 (ddd, *J* = 17.1, 7.1, 4.7 Hz, 2H), 2.21 (ddd, *J* = 17.1, 9.7, 5.2 Hz, 2H), 1.58 (ddq, *J* = 19.1, 9.6, 4.7 Hz, 1H), 1.41 (dtt, *J* = 14.1, 7.1, 5.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.5, 193.4, 151.6, 136.1, 135.2, 129.9, 128.8, 127.7, 69.0, 45.4, 40.5, 38.6, 15.9; HRMS (ESI) calcd for $C_{17}H_{19}O_3$ $[M+H]^+$: 271.1328; found: 271.1324.

4-(1-(4-Methylbenzyl)-2,6-dioxocyclohexyl)but-2-enal (1h):



Prepared according to the general procedure as described above in 72% yield (1.02 g, E/Z= 2:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.4) to afford a yellow liquid;^{1}H NMR (500 MHz, $CDCl_3$,) for mixture of isomers: δ 9.96 (d, *J* = 7.9 Hz, 0.3H), 9.35 (d, *J* = 7.8 Hz, 0.7H), 7.02 (d, *J* = 7.1 Hz, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.50 (dt, *J* = 15.4, 7.6 Hz, 0.7H), 6.21 (dt, *J* = 10.7, 8.6 Hz, 0.3H), 6.02 (ddd, *J* = 15.5, 7.8, 0.7 Hz, 0.7H), 5.89 – 5.84 (m, 0.3H), 3.09 (d, *J* = 8.5 Hz, 0.6H), 3.05 (d, *J* = 9.5 Hz, 2 H), 2.81 (d, *J* = 7.5 Hz, 1.4H), 2.45 – 2.34 (m, 2H), 2.26 (s, 3H), 2.25 – 2.14 (m, 2H), 1.62 – 1.51 (m, 1H), 1.50 – 1.38 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.9, 210.5, 193.5, 191.2, 151.9, 145.3, 137.4, 136.0, 132.3, 131.9, 129.7, 129.7, 129.5, 129.5, 69.2, 69.1, 45.6, 45.2, 40.6, 40.4, 38.3, 34.1, 21.1, 16.0, 15.8; HRMS (ESI) calcd for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485; found: 285.1481.

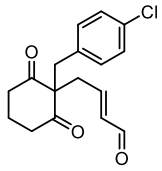
4-(1-(4-Fluorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1i):



Prepared according to the general procedure as described above in 70% yield (1.0 g, *E/Z* =>20:1). It was purified by flash chromatography (20% EtOAc/hexane; R_f = 0.4) to afford a colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 7.7 Hz, 1H), 6.97 – 6.90 (m, 4H), 6.50 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.05 (ddt, *J* = 15.6, 7.7, 1.2 Hz, 1H), 3.08 (s, 2H), 2.81 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.43 (ddd, *J* = 17.1, 7.4, 4.8 Hz, 2H), 2.23 (ddd, *J* = 17.2, 9.3, 5.2 Hz, 2H), 1.63 (ddq, *J* = 18.9, 9.5, 4.8 Hz, 1H), 1.43 (dtt, *J* = 10.4, 7.4, 5.2 Hz, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 193.3, 162.3(d, J_{CF} = 250.82 Hz), 151.1, 136.2, 131.6(d, J_{CF} = 7.87 Hz), 131.1(d, J_{CF} = 3.54 Hz), 115.7 (d, J_{CF} = 21.40 Hz), 68.9,

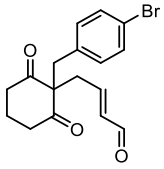
43.9, 40.4, 38.9, 15.9;^{19}F NMR (471 MHz, $CDCl_3$) δ -112.10. HRMS (ESI) calcd for $C_{17}H_{18}O_3F$ $[M+H]^+$: 289.1234; found: 289.1229.

4-(1-(4-Chlorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1j):



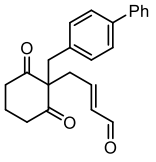
Prepared according to the general procedure as described above in 73% yield (1.1 g, E/Z=>20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford a colourless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.52 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.07 (ddd, *J* = 15.6, 7.7, 1.0 Hz, 1H), 3.09 (s, 2H), 2.82 (dd, *J* = 7.6, 1.0 Hz, 2H), 2.45 (ddd, *J* = 17.1, 7.4, 4.8 Hz, 2H), 2.24 (ddd, *J* = 17.2, 9.3, 5.2 Hz, 2H), 1.65 (ddq, *J* = 18.9, 9.4, 4.8 Hz, 1H), 1.46 (dtt, *J* = 10.5, 7.4, 5.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 193.2, 150.9, 136.3, 133.9, 133.7, 131.4, 129.0, 68.8, 44.0, 40.5, 39.0, 16.0; HRMS (ESI) calcd for $C_{17}H_{18}O_3Cl$ $[M+H]^+$: 305.0939; found: 305.0951.

4-(1-(4-Bromobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1k):



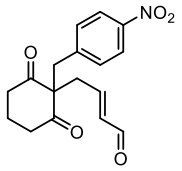
Prepared according to the general procedure as described above in 76% yield (1.1 g, *E/Z* = 4:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.5) to afford a colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (d, *J* = 7.8 Hz, 0.2H), 9.39 (d, *J* = 7.7 Hz, 0.8H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.50 (dt, *J* = 15.2, 7.6 Hz, 0.8 H), 6.22 (dt, *J* = 11.2, 8.1 Hz, 0.2H), 6.04 (ddd, *J* = 16.6, 8.2, 1.7 Hz, 0.8H), 5.91 (ddd, *J* = 11.2, 7.8, 1.3 Hz, 0.2H), 3.12 – 3.00 (m, 2.2H), 2.79 (d, J = 7.6 Hz, 1.8H),2.43 (ddt, *J* = 14.7, 12.2, 6.1 Hz, 2H), 2.28 – 2.18 (m, 2H), 1.64 (ddq, *J* = 18.7, 9.3, 4.6 Hz, 1H), 1.50 – 1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 210.1, 193.2, 190.9, 150.9, 144.5, 136.2, 134.3, 132.5, 131.9, 131.8, 131.6, 131.6, 121.7, 68.6, 68.6, 44.3, 43.7, 40.6, 40.3, 38.9, 34.6, 15.9, 15.8; HRMS (ESI) calcd for $C_{17}H_{18}O_3Br$ $[M+H]^+$: 349.0433; found: 349.0438.

4-(1-([1,1'-Biphenyl]-4-ylmethyl)-2,6-dioxocyclohexyl)but-2-enal (1l):



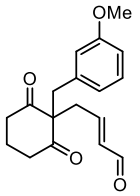
Prepared according to the general procedure as described above in 65% yield (1.1 g, *E/Z* = >20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.4 to afford a colourless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.54 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.07 (ddt, *J* = 15.6, 7.8, 0.9 Hz, 1H), 3.15 (s, 2H), 2.87 (dd, *J* = 7.6, 1.0 Hz, 2H), 2.45 (ddd, *J* = 17.0, 7.0, 4.8 Hz, 2H), 2.29 (ddd, *J* = 17.0, 9.6, 5.3 Hz, 2H), 1.61 (ddq, *J* = 19.1, 9.6, 4.8 Hz, 1H), 1.49 (dtt, *J* = 14.1, 7.0, 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 193.3, 151.6, 140.3, 140.2, 136.1, 134.2, 130.3, 128.9, 127.5, 127.3, 126.9, 69.0, 44.8, 40.4, 38.5, 16.0; HRMS (ESI) calcd for $C_{23}H_{23}O_3$ $[M+H]^+$: 347.1641; found: 347.1645.

4-(1-(4-Nitrobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1m):



Prepared according to the general procedure as described above in 56% yield (882mg, *E/Z*=>20:1). It was purified by flash chromatography (50% EtOAc/hexane; R_f = 0.4) to afford a yellow liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, *J* = 7.7 Hz, 1H), 8.07 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.17 (d, *J* = 7.3 Hz, 2H), 6.52 (dt, *J* = 15.5, 7.6 Hz, 1H), 6.06 (dddd, *J* = 15.6, 7.7, 2.4, 1.3 Hz, 1H), 3.21 (s, 2H), 2.80 (d, *J* = 7.6 Hz, 2H), 2.50 (ddd, *J* = 17.1, 8.0, 5.0 Hz, 2H), 2.29 (ddd, *J* = 17.2, 8.6, 5.1 Hz, 2H), 1.82 – 1.68 (m, 1H), 1.45 (dtt, *J* = 13.3, 8.2, 5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 193.0, 149.9, 147.3, 143.3, 136.5, 131.1, 123.8, 68.6, 42.5, 40.1, 39.5, 16.0; HRMS (ESI) calcd for $C_{17}H_{16}O_5N$ $[M-H]^+$: 314.1023; found: 314.1038.

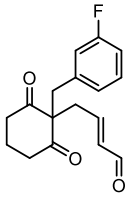
4-(1-(3-Methoxybenzyl)-2,6-dioxocyclohexyl)but-2-enal (1n):



Prepared according to the general procedure as described above in 48% yield (806 mg, *E/Z*= 8:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.4) to afford a colourless liquid;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H)), 6.74 (ddd, *J* = 8.3, 2.5, 0.7 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.50 (t, *J* = 6.5 Hz, 1H), 6.21 (dt, *J* = 11.2, 8.5 Hz, 1H), 5.88 (ddt, *J* = 10.6, 8.2, 1.3 Hz, 1H), 3.72 (s, 3H), 3.11 (dd, *J* = 8.5, 1.1 Hz, 2H), 3.07 (s, 2H), 2.38 (ddd, *J* = 17.2, 7.1, 4.6 Hz, 2H), 2.18 (ddd, *J* = 17.1, 9.7, 5.2 Hz, 2H), 1.57 (dtt, *J* = 14.3, 9.5, 4.6 Hz, 1H),

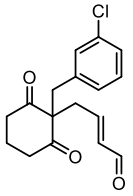
1.40 (qdd, *J* = 11.6, 6.1, 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.9, 191.1, 159.8, 145.0, 136.7, 132.4, 129.9, 122.1, 115.5, 113.1, 68.8, 55.3, 45.9, 40.74, 3.48, 15.7; HRMS (ESI) calcd for $C_{18}H_{21}O_4$ $[M+H]^+$: 301.1434; found: 301.1428.

4-(1-(3-Fluorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1o):



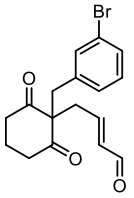
Prepared according to the general procedure as described above in 59% yield (993 mg, *E/Z* =20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.4) to afford a yellow liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.94 (tdd, *J* = 8.5, 2.6, 0.7 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.74 – 6.70 (dt, *J* = 9.6, 1.9 Hz, 1H), 6.52 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.08 (ddt, *J* = 15.6, 7.7, 1.1 Hz, 1H), 3.11 (s, 2H), 2.84 (dd, *J* = 7.6, 1.1 Hz, 2H), 2.45 (ddd, *J* = 17.2, 7.5, 4.8 Hz, 2H), 2.26 (ddd, *J* = 17.2, 9.2, 5.2 Hz, 2H), 1.66 (dtt, *J* = 14.1, 9.4, 4.8 Hz, 1H), 1.45 (dtt, *J* = 14.2, 7.5, 5.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 193.3, 162.8 (d, J_{CF} = 246.19 Hz),150.9, 137.7 (d, J_{CF} = 6.96 Hz), 136.4, 130.4(d, J_{CF} = 8.27 Hz), 125.76 (d, J_{CF} = 2.4 Hz), 117.0(d, J_{CF} = 21.35 Hz), 114.7(d, J_{CF} = 20.65 Hz), 68.7, 44.3, 40.5, 39.2, 16.0.^{19}F NMR (471 MHz, $CDCl_3$) δ -112.1; HRMS (ESI) calcd for $C_{17}H_{18}FO_3$ $[M+H]^+$: 289.1234; found: 289.1229.

4-(1-(3-Chlorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1p):



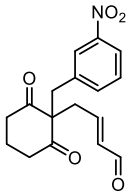
Prepared according to the general procedure as described above in 68% yield (1.0 g, *E/Z*=>20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.4) to afford a colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, *J* = 7.8 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.91 (s, 1H), 6.81 (dd, *J* = 5.0, 1.6 Hz, 1H), 6.46 (dt, *J* = 15.4, 7.6 Hz, 1H), 5.98 (ddd, *J* = 15.6, 7.8, 1.1 Hz, 1H), 3.01 (s, 2H), 2.75 (d, *J* = 7.6 Hz, 2H), 2.40 (ddd, *J* = 16.9, 7.2, 5.0 Hz, 2H), 2.23 (ddd, *J* = 17.1, 9.2, 5.2 Hz, 2H), 1.60 (ddt, *J* = 18.8, 9.4, 4.6 Hz, 1H), 1.42 (tdd, *J* = 12.7, 7.3, 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.8, 193.1, 150.9, 137.3, 136.1, 134.3, 129.9, 129.8, 128.1, 127.7, 68.5, 43.6, 40.1, 38.7, 15.9; HRMS (ESI) calcd for $C_{17}H_{18}O_3Cl$ $[M+H]^+$: 305.0939; found: 305.0932.

4-(1-(3-Bromobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1q):



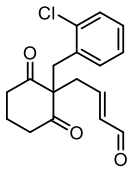
Prepared according to the general procedure as described above in 74% yield (1.2 g, *E/Z* = >20:1). It was purified by flash chromatography (40% EtOAc/hexane; R_f = 0.5) to afford a colourless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, *J* = 7.7 Hz, 1H), 7.37 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.17 – 7.14 (m, 1H),7.12 (d, *J* = 7.9 Hz, 1H), 6.92 (dt, *J* = 7.9, 1.4 Hz, 1H), 6.52 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.07 (ddt, *J* = 15.6, 7.7, 1.2 Hz, 1H), 3.07 (s, 2H), 2.83 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.46 (ddd, *J* = 17.2, 7.5, 4.8 Hz, 2H), 2.26 (ddd, *J* = 17.2, 9.3, 5.2 Hz, 2H), 1.66 (dtt, *J* = 14.1, 9.5, 4.8 Hz, 1H), 1.47 (dtt, *J* = 14.2, 7.5, 5.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.1, 193.3, 150.9, 137.7, 136.4, 132.9, 130.9, 130.4, 128.7, 122.9, 68.7, 44.1, 40.5, 39.1, 16.0;HRMS (ESI) calcd for $C_{17}H_{18}O_3Br[M+H]^+$: 349.0433; found: 349.0428.

4-(1-(3-Nitrobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1r):



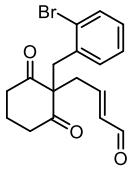
Prepared according to the general procedure as described above in 52% yield (819 mg, E/Z=20:1). It was purified by flash chromatography (50% EtOAc/hexane; R_f = 0.3) to afford a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, *J* = 7.7 Hz, 1H), 8.06 (ddd, *J* = 8.2, 2.1, 1.0 Hz, 1H), 7.85 (t, *J* = 1.8 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 6.53 (dt, *J* = 15.3, 7.6 Hz, 1H), 6.06 (dd, *J* = 15.6, 7.7 Hz, 1H), 3.22 (s, 2H), 2.80 (d, *J* = 7.6 Hz, 2H), 2.53 (ddd, *J* = 17.1, 8.1, 5.0 Hz, 2H), 2.36 (ddd, *J* = 17.1, 8.6, 5.1 Hz, 2H), 1.76 (tdd, *J* = 13.6, 8.7, 5.0 Hz, 1H), 1.51 (dtt, *J* = 18.6, 8.1, 5.1 Hz, 1H));^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 193.1, 150.0, 148.4, 137.7, 136.6, 136.4, 129.7, 124.9, 122.7, 68.7, 42.2, 40.0, 39.1, 16.2; HRMS (ESI) calcd for $C_{17}H_{16}O_5N[M-H]^-$: 314.1023; found: 314.1030.

4-(1-(2-Chlorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1s):



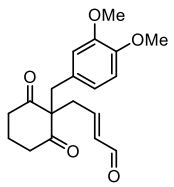
Prepared according to the general procedure as described above in 66% yield (1.0 mg, *E/Z* = >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.4) to afford a colourless liquid;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.06 (dd, *J* = 7.1, 2.2 Hz, 1H), 6.47 (dt, *J* = 15.5, 7.4 Hz, 1H), 6.06 (ddt, *J* = 15.6, 7.8, 1.2 Hz, 1H), 3.27 (s, 2H), 2.90 (dd, *J* = 7.4, 1.2 Hz, 2H), 2.61 – 2.49 (m, 4H), 1.94 – 1.85 (m, 1H), 1.73 – 1.63 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 193.6, 152.4, 136.4, 135.0, 132.8, 132.5, 130.2, 129.4, 127.1, 68.9, 41.6, 40.0, 36.5, 16.7;HRMS (ESI) calcd for $C_{17}H_{18}O_3Cl$ $[M+H]^+$: 305.0952; found: 305.0939.

4-(1-(2-bromobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1t):



Prepared according to the general procedure as described above in 69% yield (1.2 g, E/Z = >20:1). It was purified by flash chromatography (30% EtOAc/hexane; R_f = 0.5) to afford a colourless liquid;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (d, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.20 (td, *J* = 7.5, 1.3 Hz, 1H), 7.09 (td, *J* = 7.7, 1.7 Hz, 1H), 7.01 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.44 (dt, *J* = 15.5, 7.4 Hz, 1H), 6.00 (dd, *J* = 15.7, 7.8 Hz, 1H), 3.27 (s, 2H), 2.86 (dd, *J* = 7.4, 1.0 Hz, 2H), 2.60 – 2.47 (m, 4H), 1.91 – 1.82 (m, 1H), 1.66 (tdd, *J* = 15.0, 10.0, 5.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.9, 193.5, 152.4, 136.2, 134.5, 133.5, 132.1, 129.4, 127.6, 125.6, 68.9, 43.4, 39.9, 36.3, 16.6; HRMS (ESI) calcd for $C_{17}H_{18}O_3Br$ $[M+H]^+$: 349.0438; found: 349.0438.

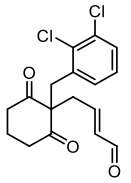
4-(1-(3,4-Dimethoxybenzyl)-2,6-dioxocyclohexyl)but-2-enal (1u):



Prepared according to the general procedure as described above in 58% yield (957 mg, E/Z = >20:1). It was purified by flash chromatography (20% EtOAc/hexane; R_f = 0.3) to afford a colourless liquid;^{1}H

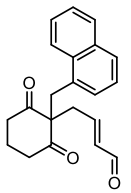
NMR (400 MHz, $CDCl_3$) δ 9.96 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.51 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 6.21 (dt, *J* = 11.2, 8.5 Hz, 1H), 5.88 (ddt, *J* = 11.1, 8.0, 1.2 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.10 (dd, *J* = 8.5, 1.1 Hz, 2H), 3.06 (s, 2H), 2.37 (ddd, *J* = 17.2, 7.2, 4.6 Hz, 2H), 2.14 (ddd, *J* = 17.2, 9.6, 5.1 Hz, 2H), 1.56 (ddq, *J* = 18.9, 9.4, 4.6 Hz, 1H), 1.36 (dtt, *J* = 10.3, 7.2, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.4, 191.1, 148.9, 148.4, 144.9, 132.4, 127.6, 122.0, 112.8, 111.2, 68.9, 56.0, 55.9, 45.8, 40.9, 34.7, 15.7; HRMS (ESI) calcd for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540; found: 331.1531.

4-(1-(2,3-Dichlorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1v):



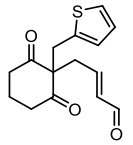
Prepared according to the general procedure as described above in 54% yield (912 mg, E/Z =20:1). It was purified by flash chromatography (20% EtOAc/hexane; R_f = 0.3) to afford a colourless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 10.02 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.98 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.16 (dt, *J* = 11.2, 8.2 Hz, 1H), 5.87 (dd, *J* = 11.2, 7.9 Hz, 1H), 3.32 (s, 2H), 3.15 (d, *J* = 8.2 Hz, 2H), 2.56 – 2.52 (m, 4H), 1.95 – 1.83 (m, 1H), 1.72 (td, *J* = 14.7, 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.8, 193.5, 151.9, 136.4, 135.2, 134.0, 133.4, 130.4, 130.1, 127.3, 68.6, 41.8, 39.9, 36.6, 16.6; HRMS (ESI) calcd for $C_{17}H_{17}O_3Cl_2$ $[M+H]^+$: 339.0549; found: 339.0557.

4-(1-(Naphthalen-1-ylmethyl)-2,6-dioxocyclohexyl)but-2-enal (1w):



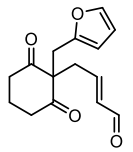
Prepared according to the general procedure as described above in 60% yield (960 mg, E/Z = 20:1). It was purified by flash chromatography (20% EtOAc/hexane; R_f = 0.2) to afford a colourless liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 9.37 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.36 (d, *J* = 8.0, 7.2 Hz, 1H), 7.16 (d, *J* = 6.5 Hz, 1H), 6.49 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.07 (dd, *J* = 15.6, 7.8 Hz, 1H), 3.59 (s, 2H), 3.03 (dd, *J* = 7.6, 0.9 Hz, 2H), 2.30 (ddd, *J* = 17.0, 6.4, 4.5 Hz, 2H), 1.83 (ddd, *J* = 21.8, 10.4, 5.2 Hz, 2H), 1.45 – 1.35 (m, 1H), 1.28 – 1.18 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.0, 193.5, 151.9, 136.3, 133.9, 131.9, 131.7, 128.9, 128.8, 128.7, 126.7, 126.1, 125.3, 123.8, 69.1, 42.3, 40.7, 38.8, 15.7; HRMS (ESI) calcd for $C_{21}H_{24}O_3N$ $[M+NH_4]^+$: 338.1750; found: 338.1754.

4-(2,6-dioxo-1-(Thiophen-2-ylmethyl)cyclohexyl)but-2-enal (1x):



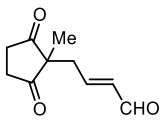
Prepared according to the general procedure as described above in 63% yield (869 mg, E/Z =20:1). It was purified by flash chromatography (20% EtOAc/hexane; R_f = 0.3) to afford a orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 5.1 Hz, 1H), 6.85 (t, *J* = 4.3 Hz, 1H), 6.67 (d, *J* = 3.3 Hz, 1H), 6.53 (dt, *J* = 15.5, 7.6 Hz, 1H), 6.04 (ddd, *J* = 15.6, 7.7, 0.8 Hz, 1H), 3.31 (s, 2H), 2.78 (d, *J* = 7.6 Hz, 2H), 2.50 – 2.33 (m, 4H), 1.76 – 1.64 (m, 1H), 1.56 – 1.44 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 193.2, 150.8, 136.8, 136.1, 127.9, 127.1, 125.2, 68.8, 40.1, 38.9, 37.5, 16.0; HRMS (ESI) calcd for $C_{15}H_{17}O_3S$ $[M+H]^+$: 277.0892; found: 277.0906.

4-(1-(Furan-2-ylmethyl)-2,6-dioxocyclohexyl)but-2-enal (1y):



Prepared according to the general procedure as described above in 55% yield (791 mg, E/Z =17:1). It was purified by flash chromatography (20% EtOAc/hexane; R_f = 0.3) to afford a orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.55 (dt, *J* = 15.4, 7.7 Hz, 1H), 6.24 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.08 – 5.99 (m, 2H), 3.13 (s, 2H), 2.79 (dd, *J* = 7.5, 1.2 Hz, 2H), 2.55 – 2.44 (m, 4H), 1.71 (qd, *J* = 6.9, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.2, 193.4, 151.6, 149.4, 142.2, 136.1, 110.8, 108.9, 67.4, 39.4, 37.6, 36.5, 16.5; HRMS (ESI) calcd for $C_{15}H_{17}O_4$ $[M+H]^+$: 261.1121; found: 261.1125.

4-(1-methyl-2,5-dioxocyclopentyl)but-2-enal (1z):



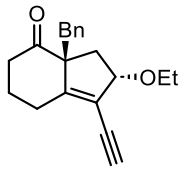
Prepared according to the general procedure as described above in 50% yield (450 mg, E/Z =17:1). It was purified by flash chromatography (60% EtOAc/hexane; R_f = 0.3) to afford a orange liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.38 (d, *J*=7.8, 1H), 6.62 (dd, *J*=15.4, 7.7, 1H), 6.01 (ddt, *J*=15.6, 7.8, 1.3, 1H), 2.88 – 2.80 (m, 2H), 2.72 – 2.63 (m, 2H), 2.53 (dd, *J*=7.6, 1.3, 2H), 1.13 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 214.7, 193.3, 150.5, 136.2, 56.0, 36.3, 35.0, 19.9.HRMS (ESI) calcd for $C_{10}H_{13}O_3$ $[M+H]^+$: 181.0865; found: 181.0870.

III. References:

1. (a) D. B. Ramachary, M. Kishor, *Org. Biomol. Chem.*, 2008, **6**, 4176.
2. X.-W. Li, A. Ear, L. Roger, Dr. N. Riache, A. Deville, B. Nay. *Chem. Eur. J.* 2013,**19**, 16389 – 16393.
3. C. Zhu, D. Wang, Y. Zhao, W. Sun,and Z. Shi, *J. Am. Chem. Soc*. 2017, **139**, 16486.
4. S. B. Thopate, L. R. Magham, S. Dinda, R. Chegondi, *Org. Lett.* **2023**, *25*, 1072.

IV. X-Ray crystallographic data

X-ray crystallographic data for compound 9:



The purified compound **9** was dissolved in a mixed solvent of dichloromethane/*n*-hexane (1:3), and placed in a dark cabinet for slowly evaporation. Colorless crystals were collected after few days for X-ray analysis.

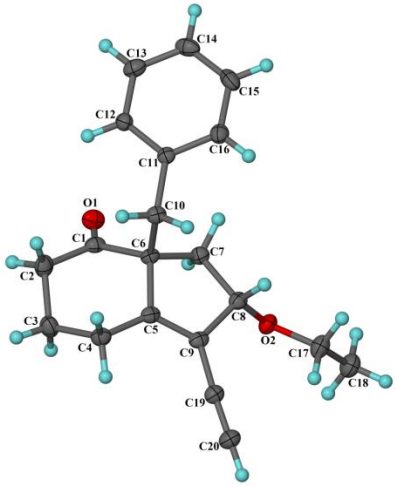


Figure caption: ORTEP diagram of compound **9** (KB690) compound with the atom-numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

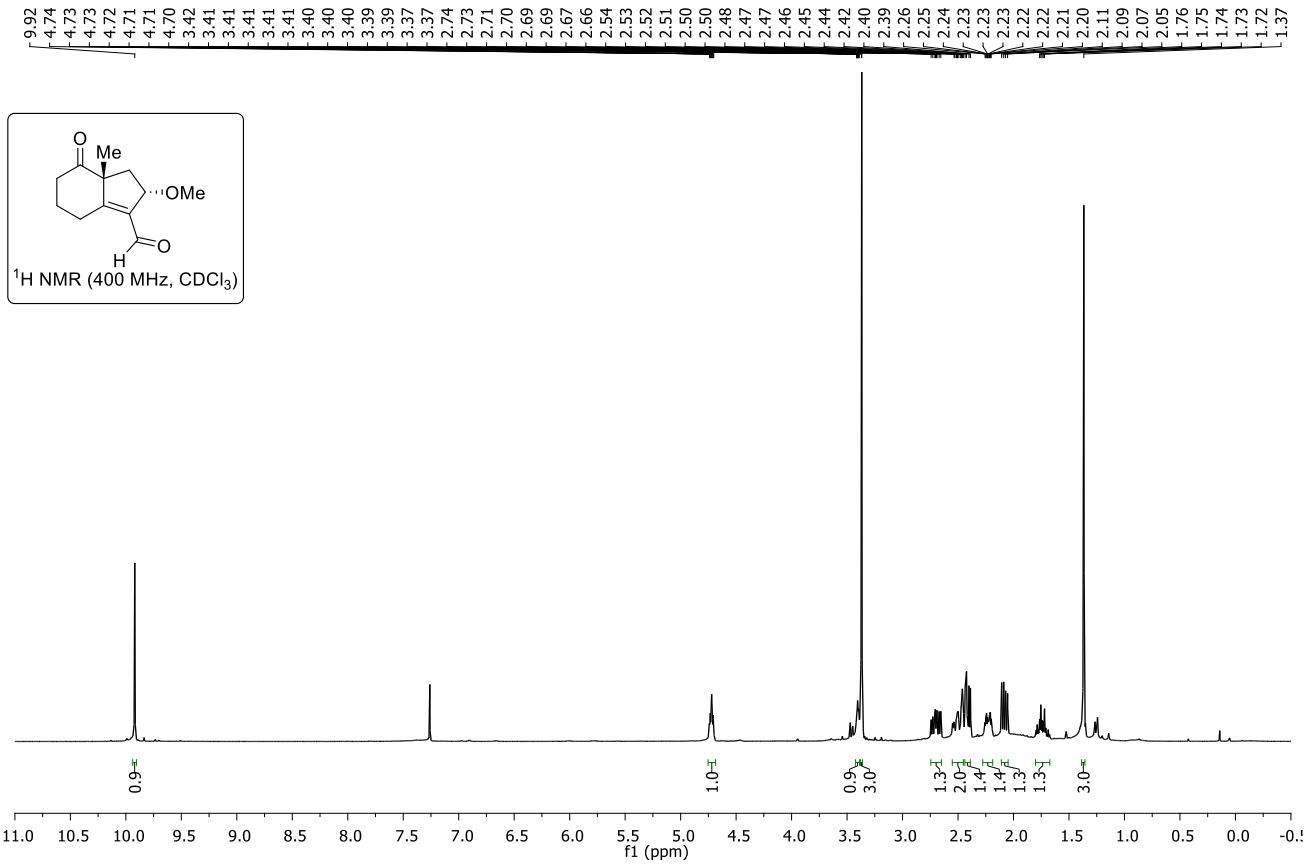
Crystal data for compound 9: $C_{20}H_{22}O_2$, M = 294.37, Monoclinic, space group $P2_1$(No.4), a =8.546(4)Å, b =6.518(3)Å, c = 15.600(8)Å, α = 90°, β = 105.428(9)°, γ = 90°, V = 837.6(7)Å^3, Z = 2, D_c = 1.167 g/cm^3, F_{000} = 316, Bruker D8 QUEST PHOTON-III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 60º, μ= 0.074 mm^{-1}, 17575 reflections collected, 5101 unique (R_{int} = 0.0555), 200 parameters, *R1* = 0.0440, *wR2* =0.0899, *R* indices based on 3824 reflections with I > 2σ(I) (refinement on F^2), Flack parameter = 0.3(5), Final *GooF* = 1.051, largest difference hole and peak = -0.183 and 0.236 e.Å^{-3}. **CCDC deposition number 2296090** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

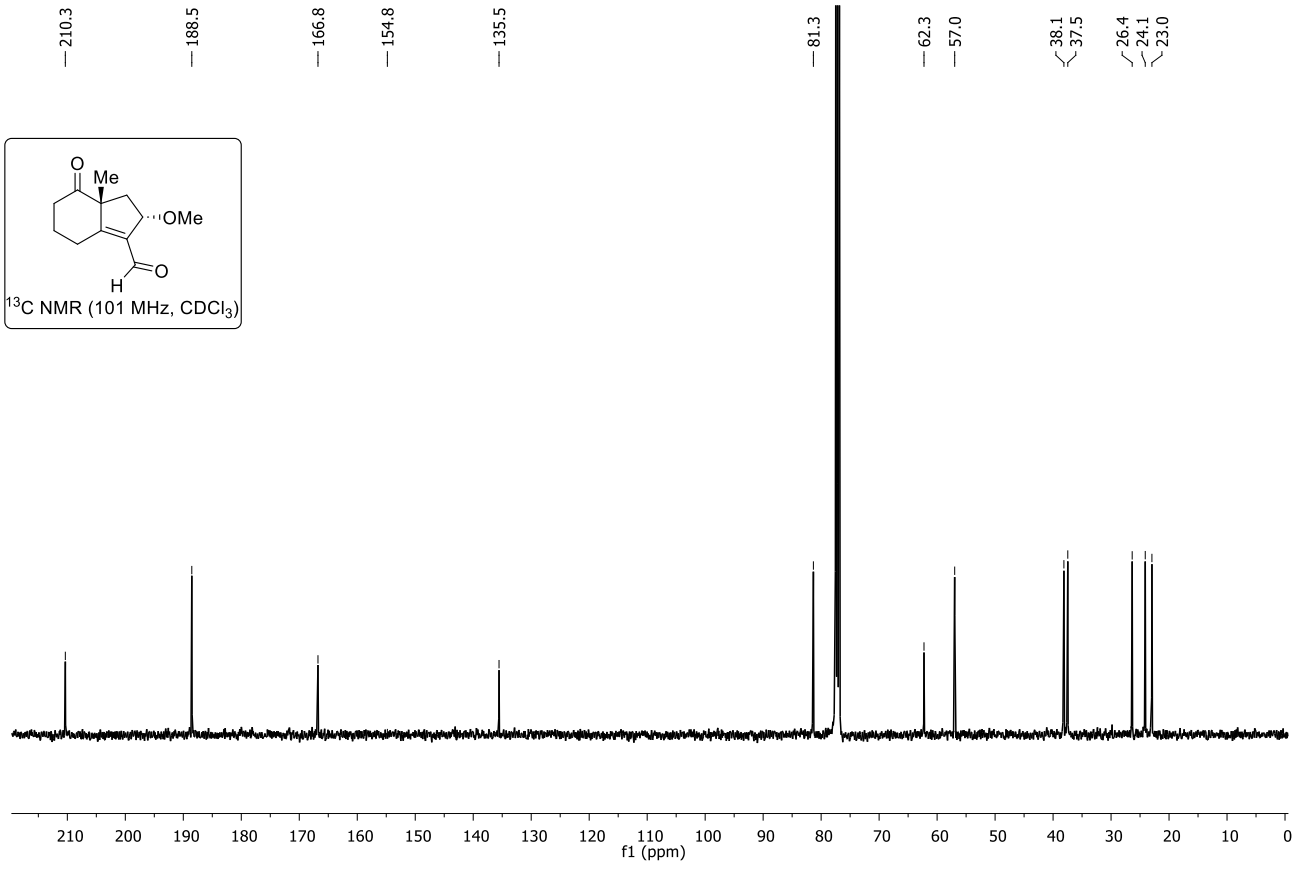
Data collection and Structure solution details: Single crystal X-ray data were collected at room temperature on a Bruker D8 QUEST equipped with a four-circle kappa diffractometer and PHOTON-III C7 HPAD detector. An Iμs microfocus Mo source (λ=0.71073Å) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omega scans were used to collect the necessary data. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97 and refinement was carried out by full-matrix least-squares technique using SHELXL-2019/2.[1-4] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with U_{iso}(H) = 1.2U_{eq} (C) or 1.5U_{eq} for methyl atoms.**CCDC deposition number 2296090** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. G. M. Sheldrick, *ActaCrystallogr.,* 2015, **C71**, 3-8.
3. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Cryst.*, 2011, **44**, 1281-1284.
4. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.

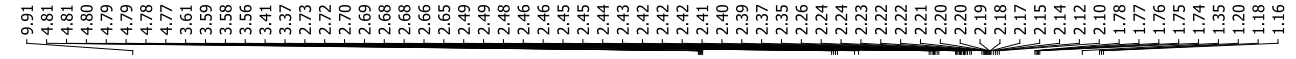
V. ^{1}H &^{13}C NMR Spectra

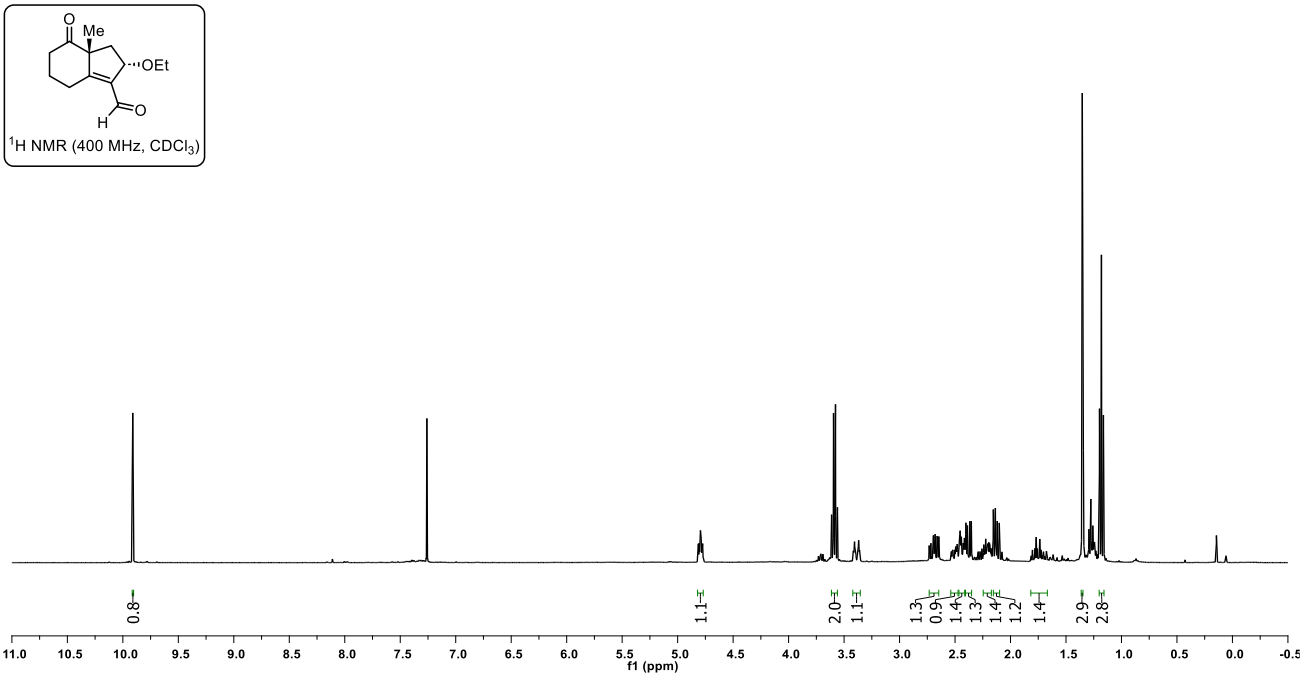
(2*S*,7a*R*)-2-Methoxy-7a-methyl-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2a):

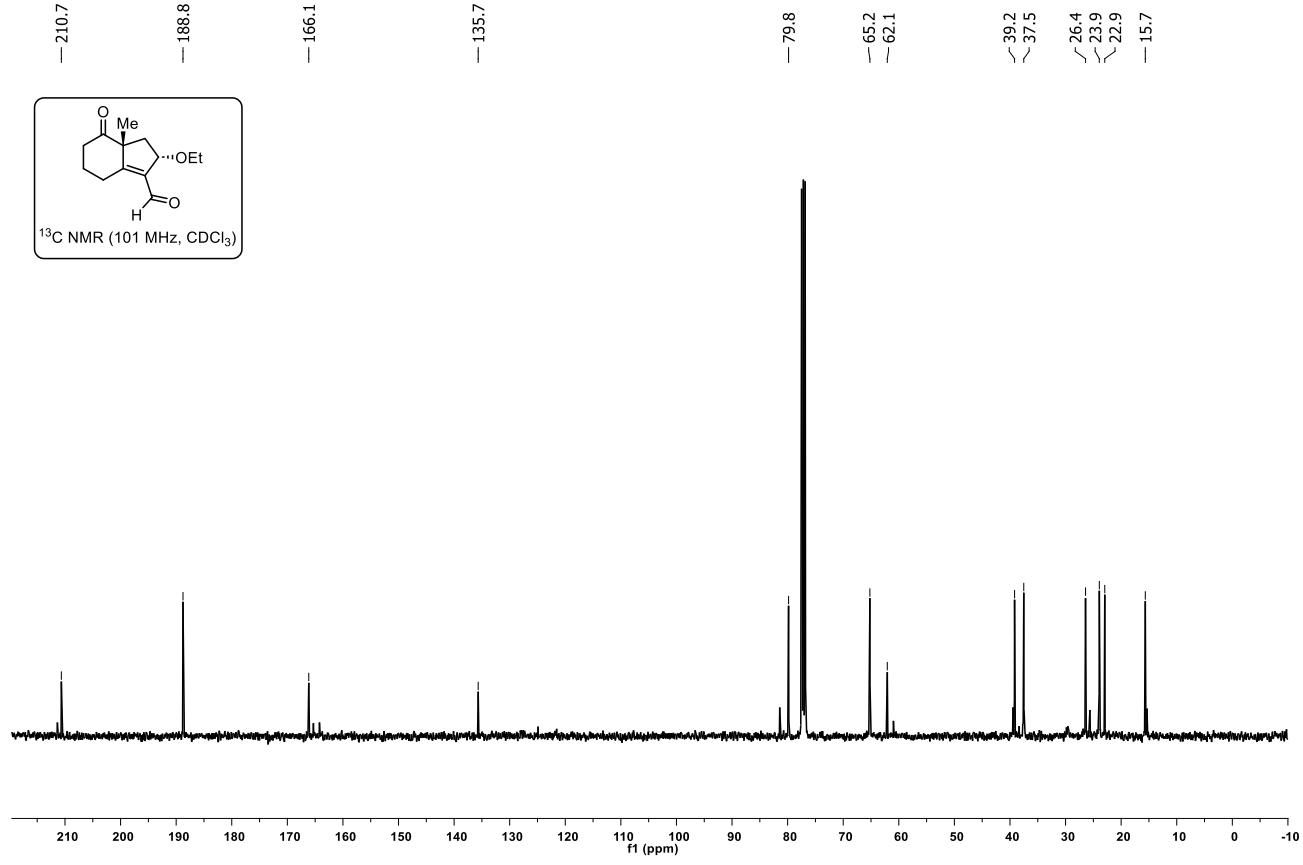




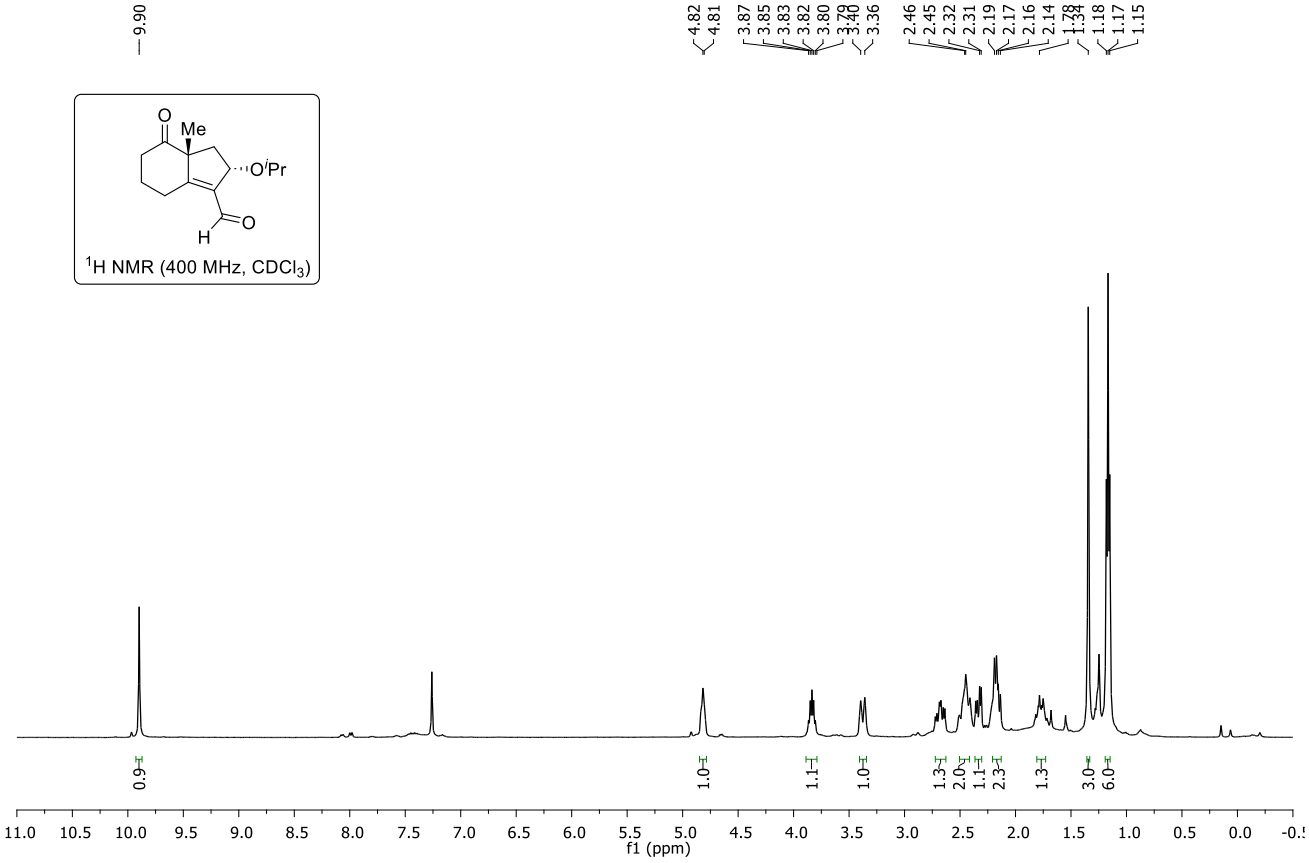
(2S,7aR)-2-Ethoxy-7a-methyl-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2b):

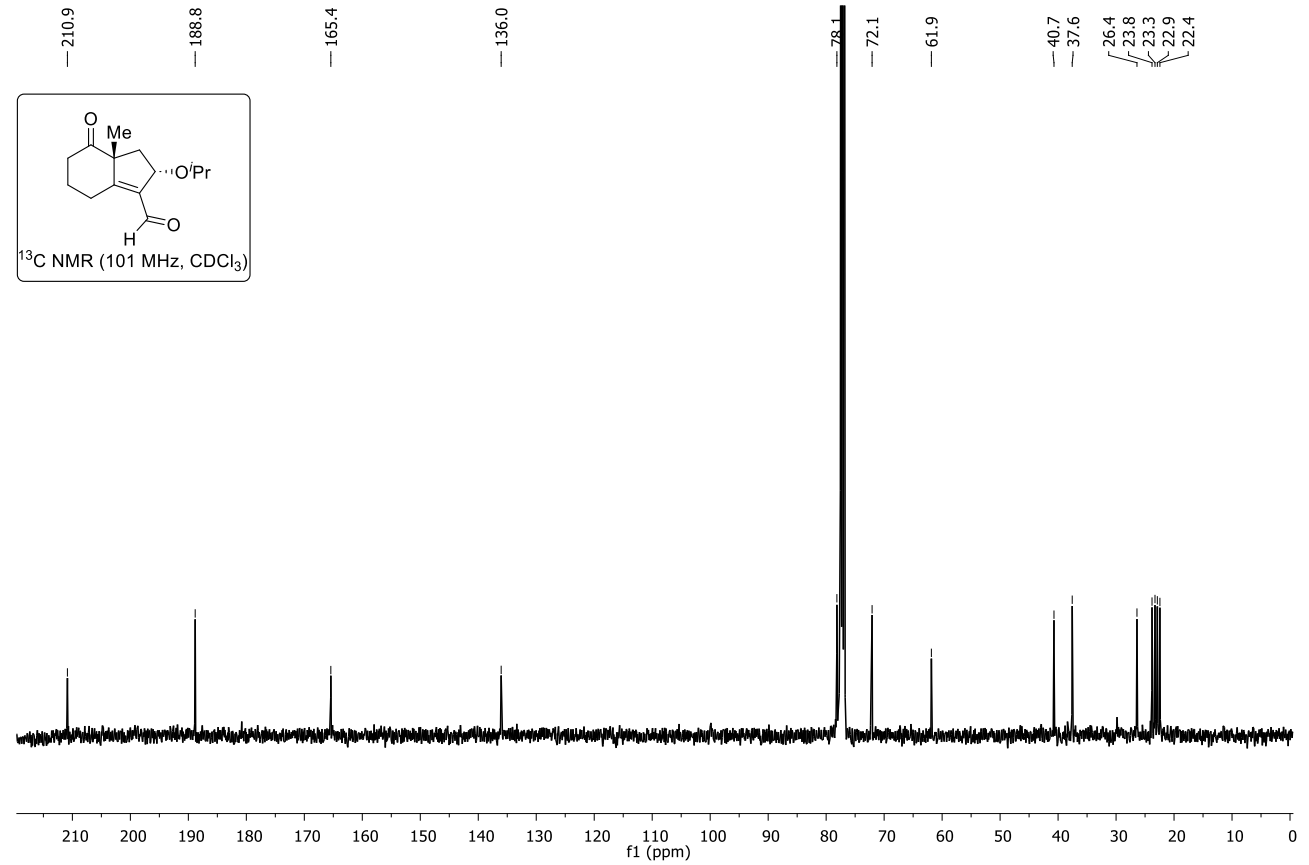




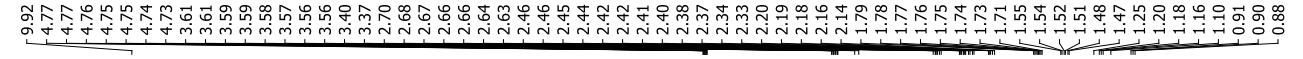


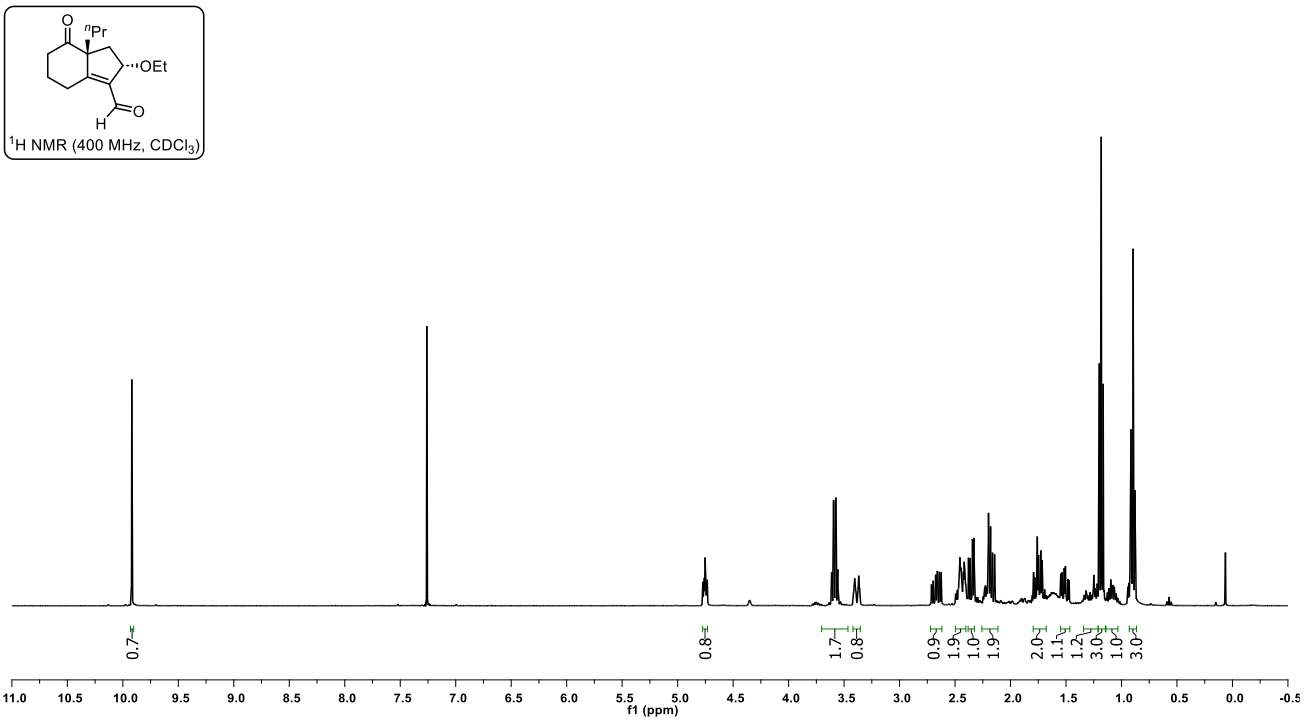
(2S,7aR)-2-Isopropoxy-7a-methyl-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2c):

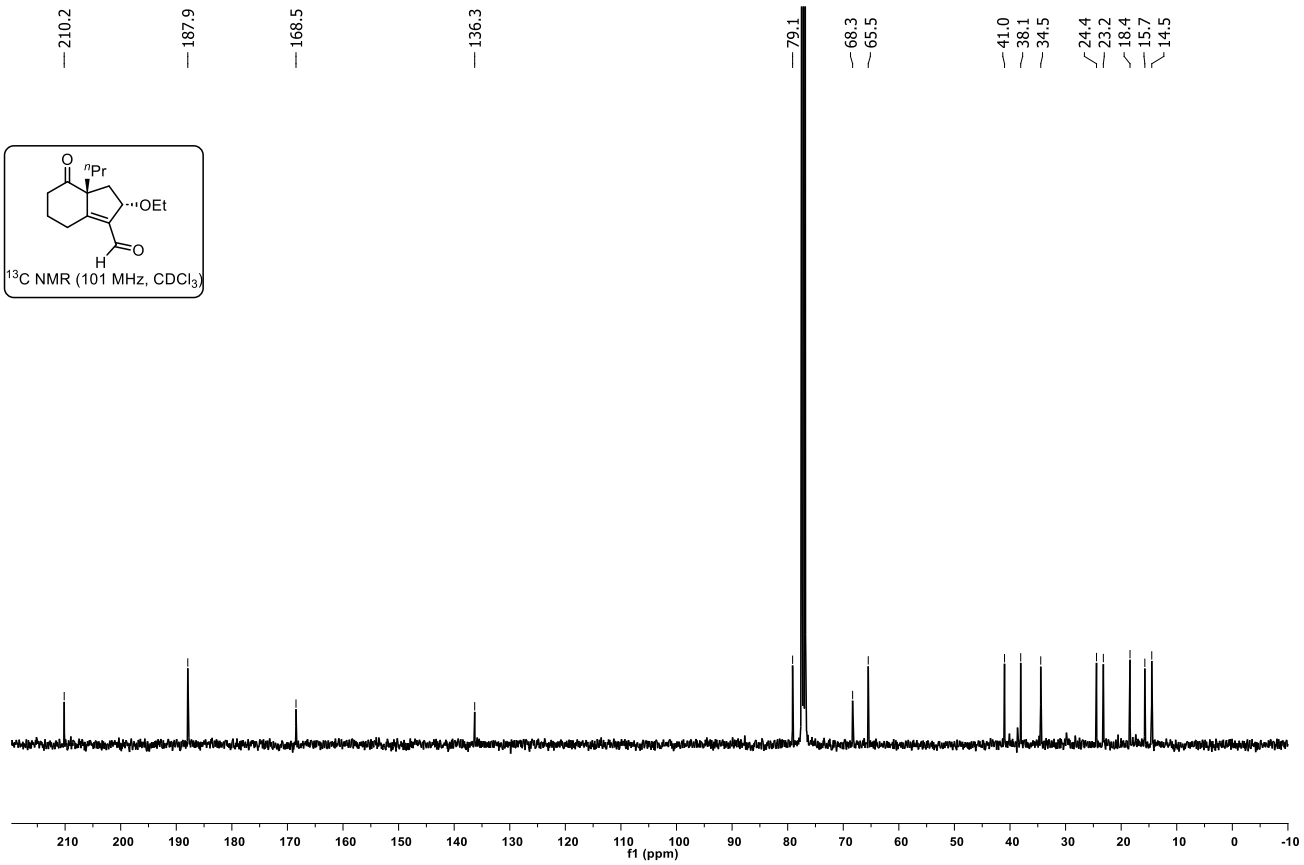




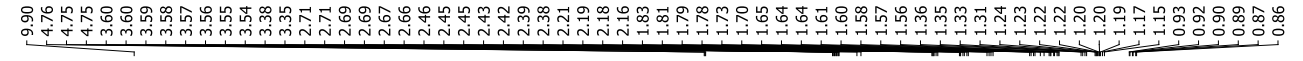
(2*S*,7a*R*)2-Ethoxy-7-oxo-7a-propyl-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2d):

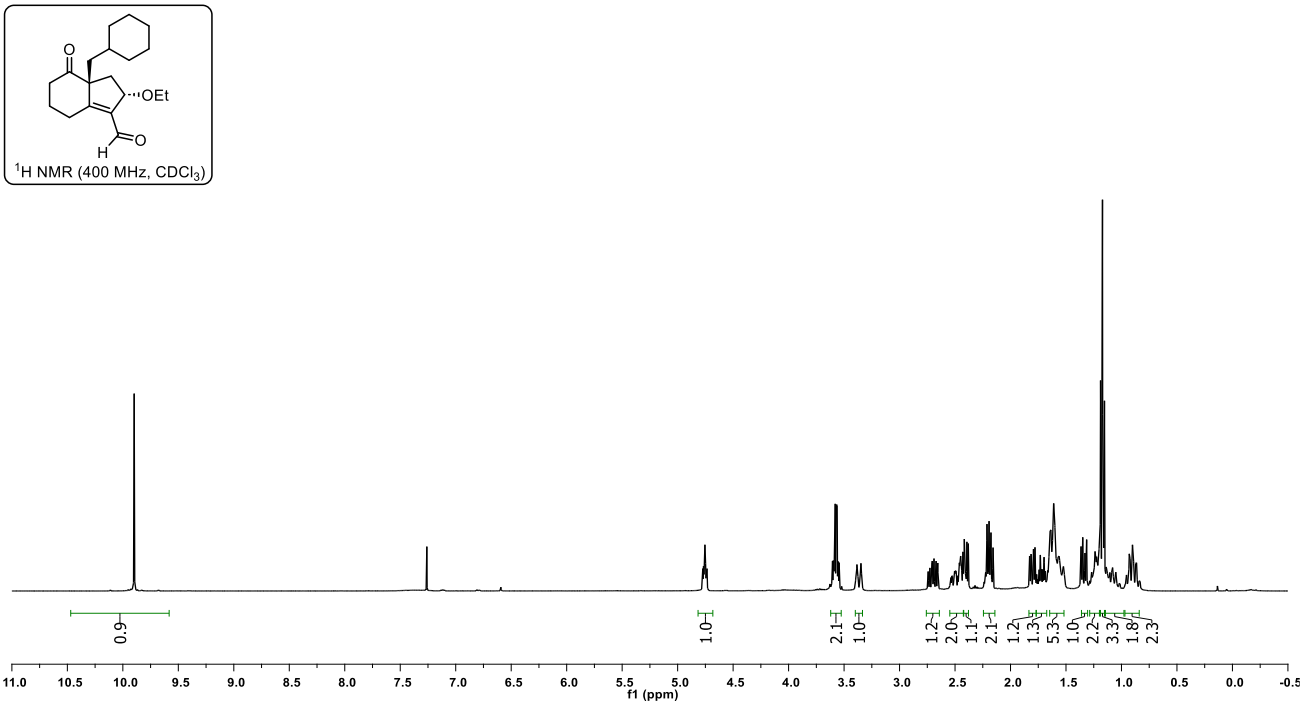


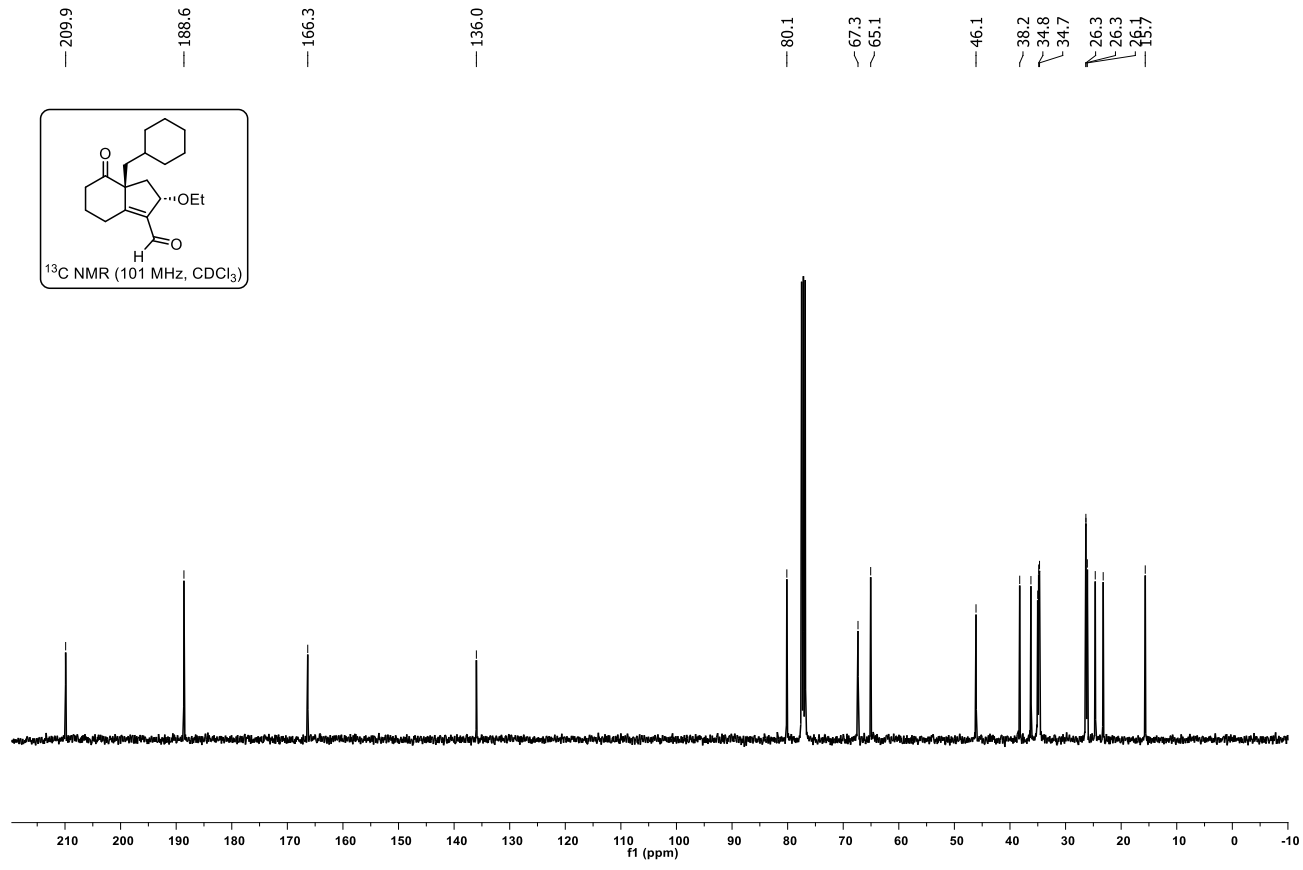




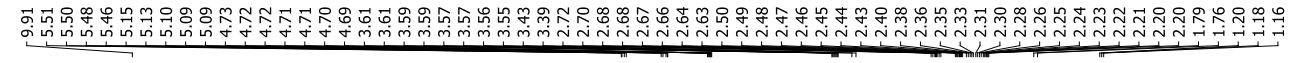
(2*S*,7a*R*) 7a-(Cyclohexylmethyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2e):

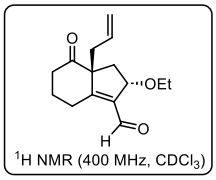


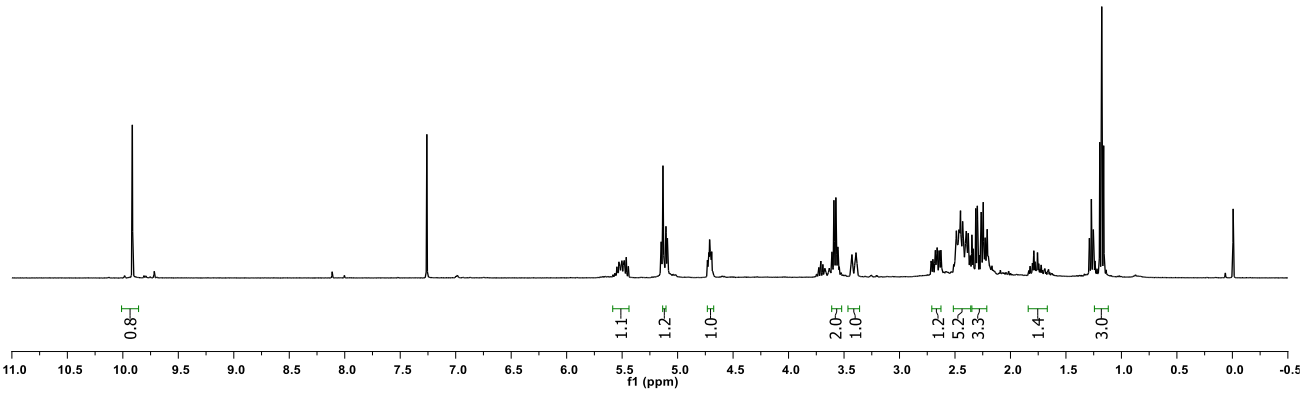


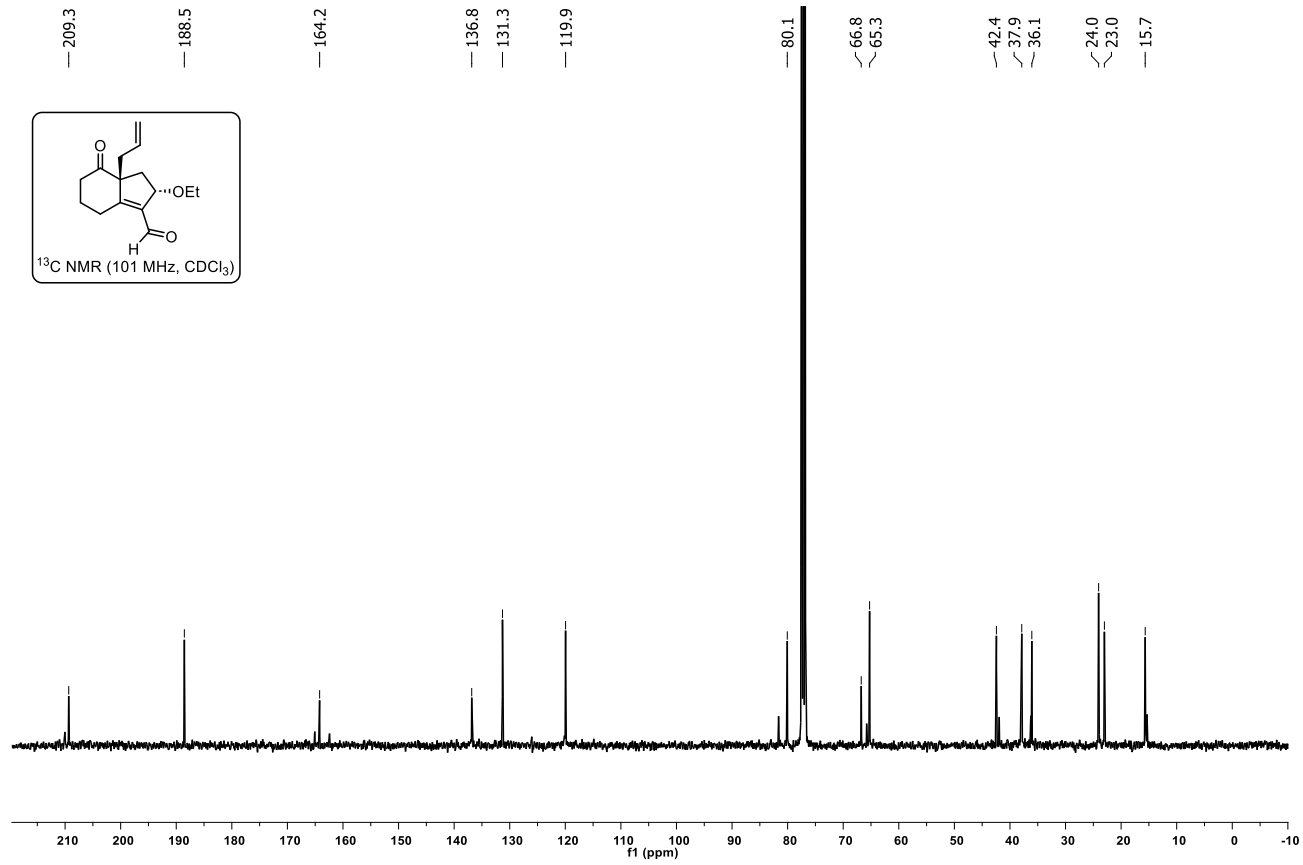


(2*S*,7a*R*)-7a-Allyl-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2f):

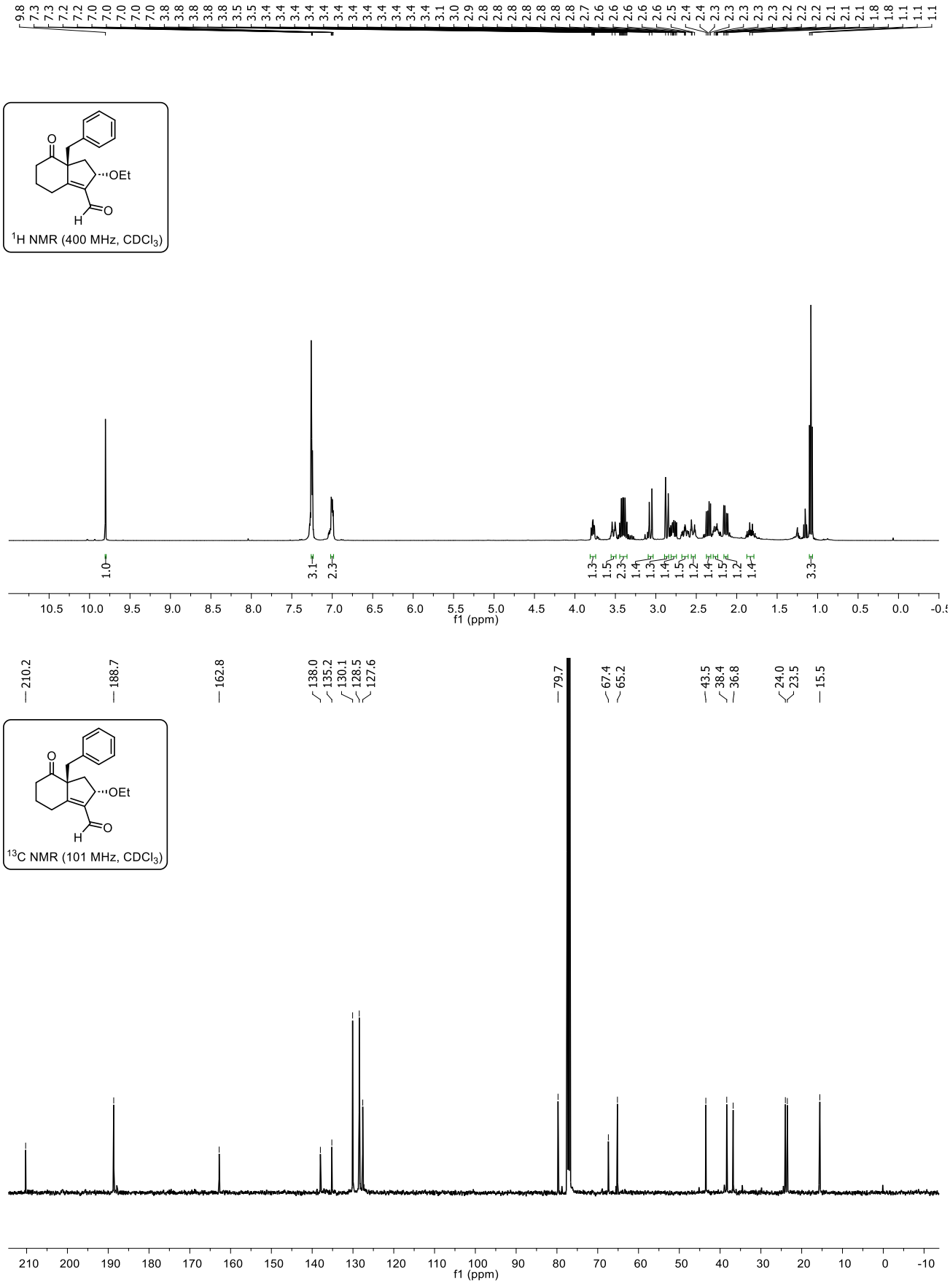




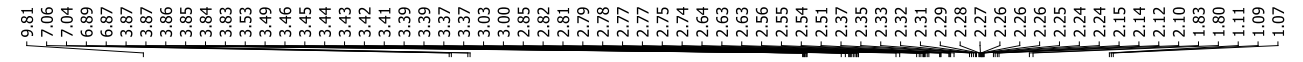


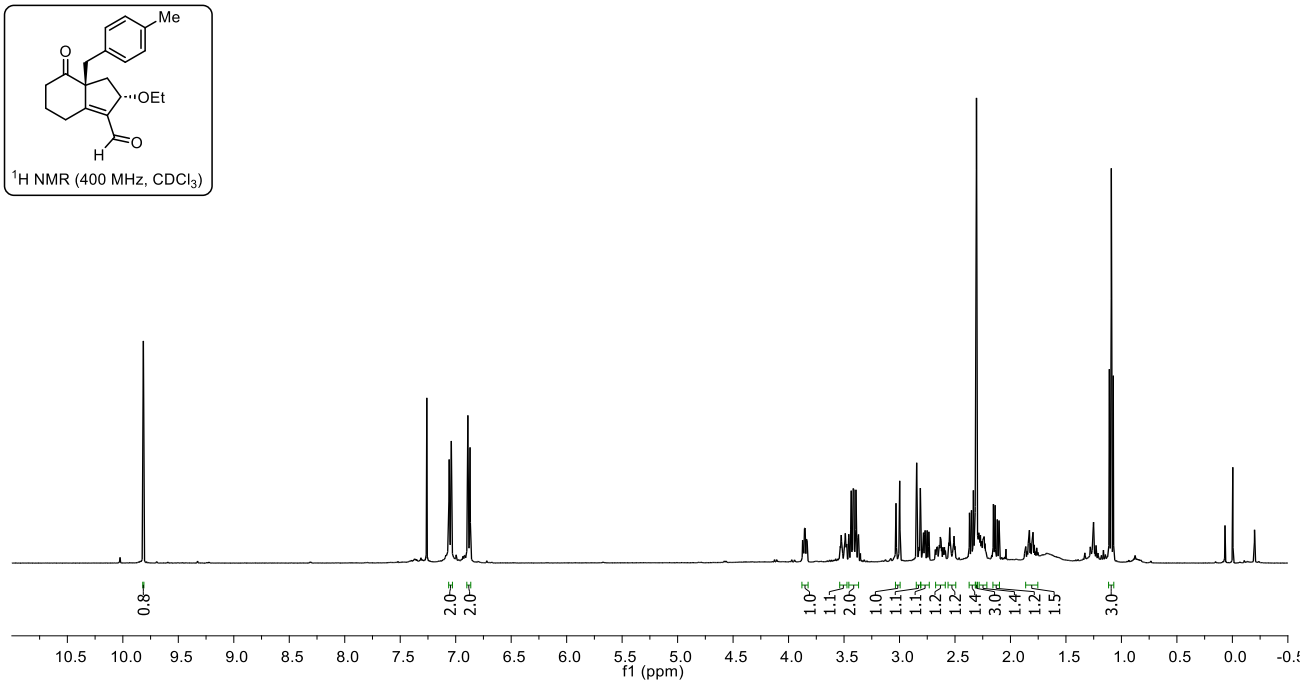


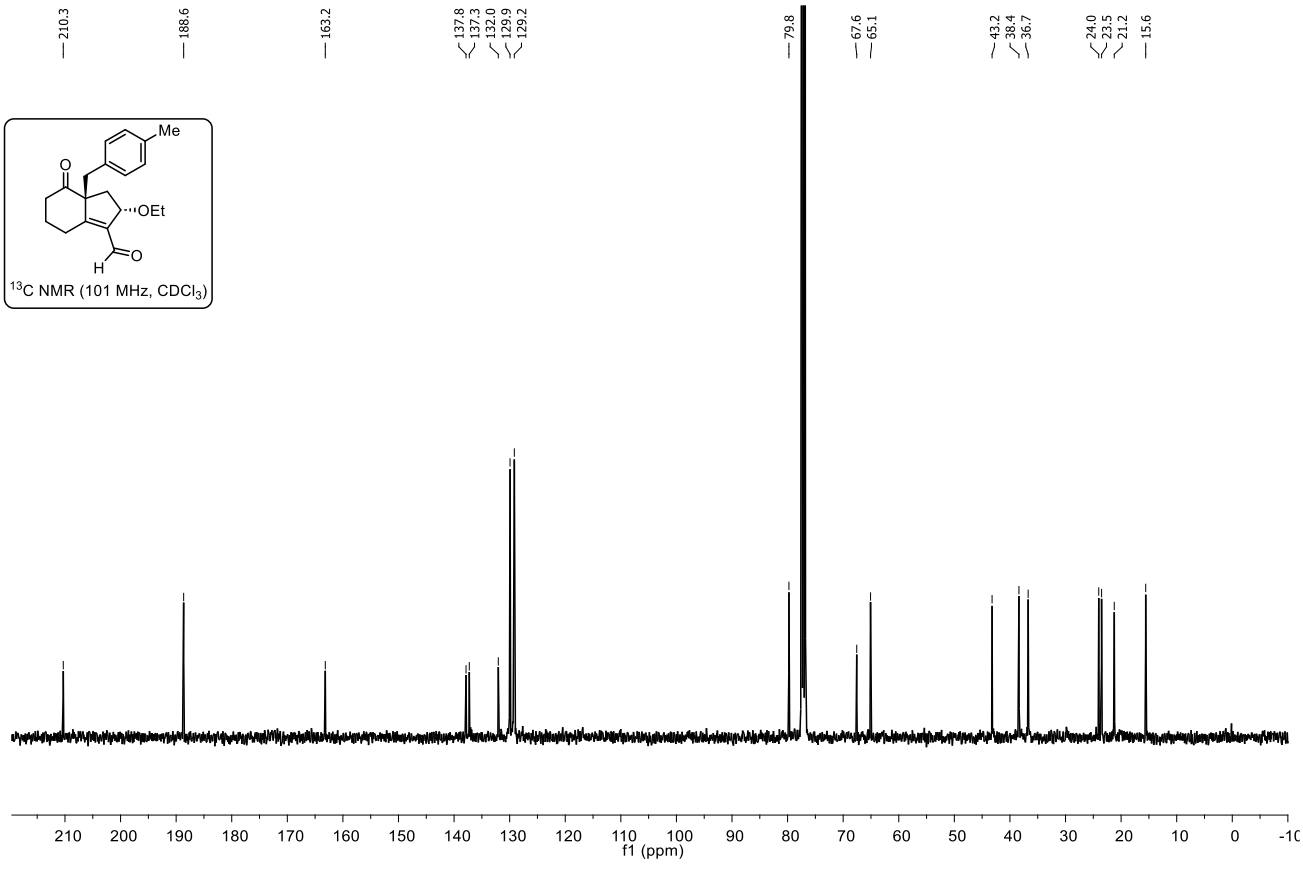
(2*S*,7a*R*)-7a-Benzyl-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2g):



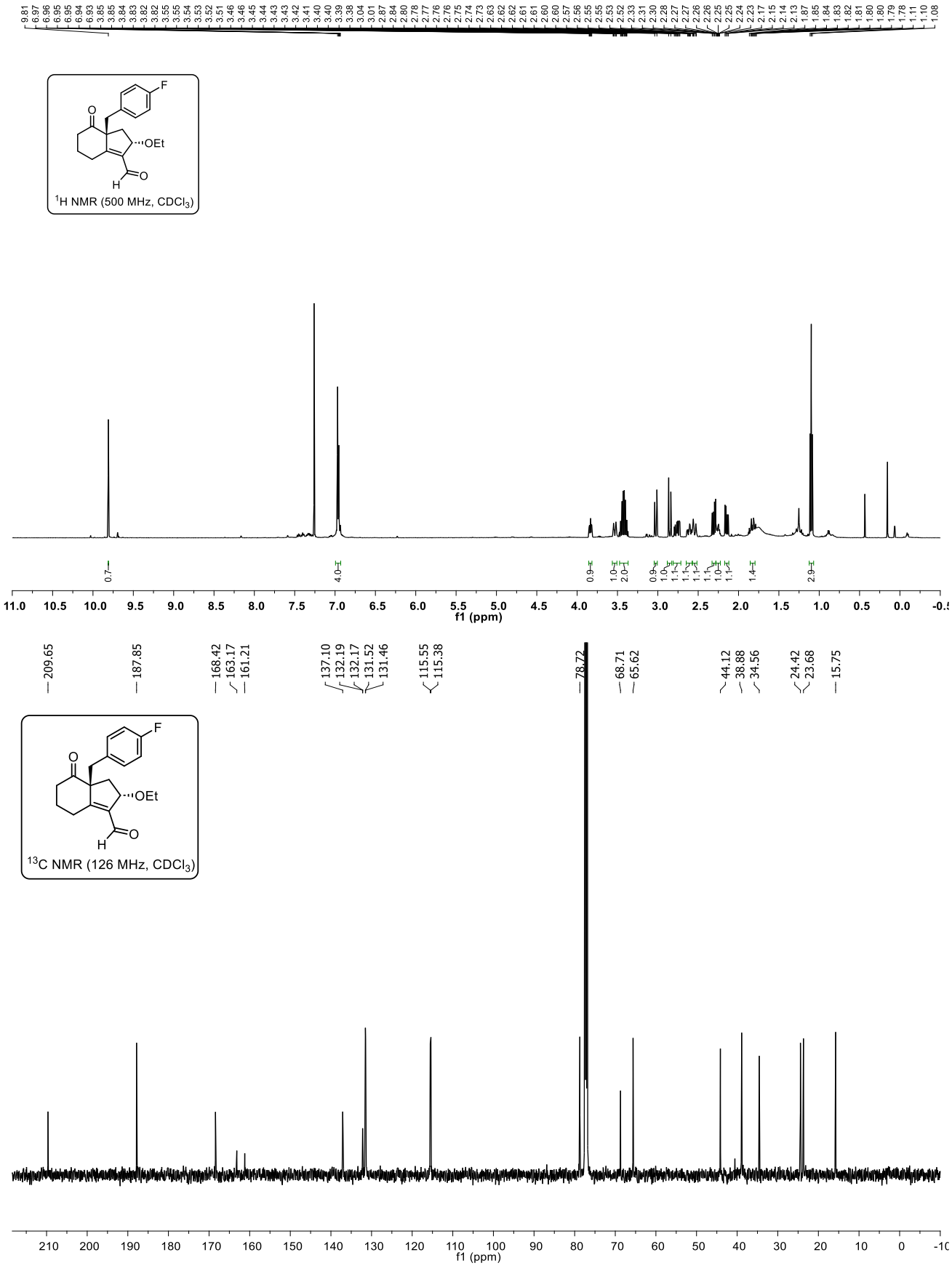
(2*S*,7a*R*)-2-Ethoxy-7a-(4-methylbenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2h):

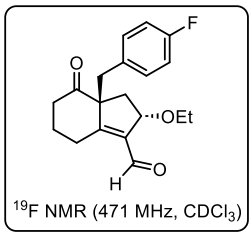






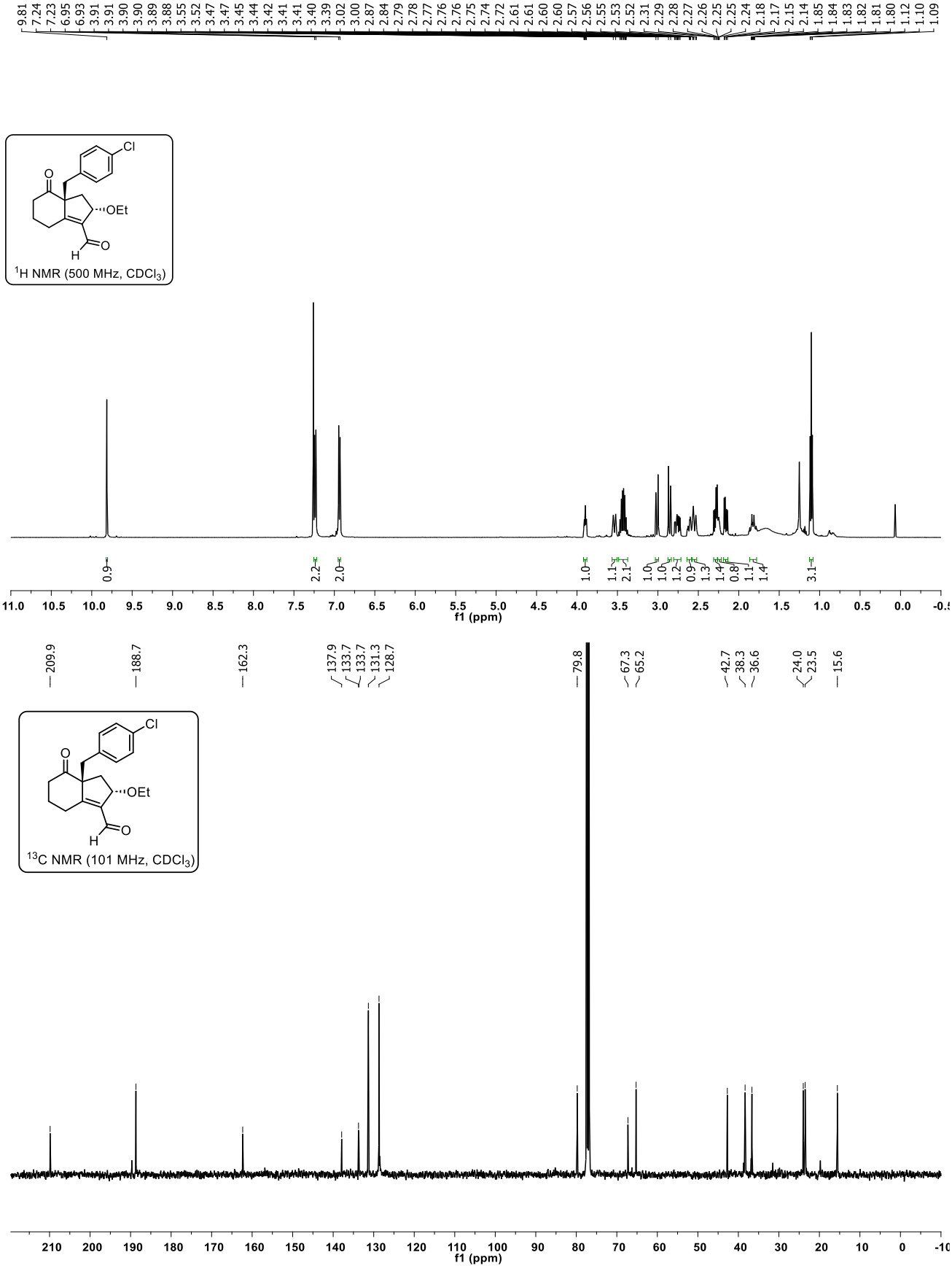
(2*S*,7a*R*)-2-Ehoxy-7a-(4-fluorobenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2i):



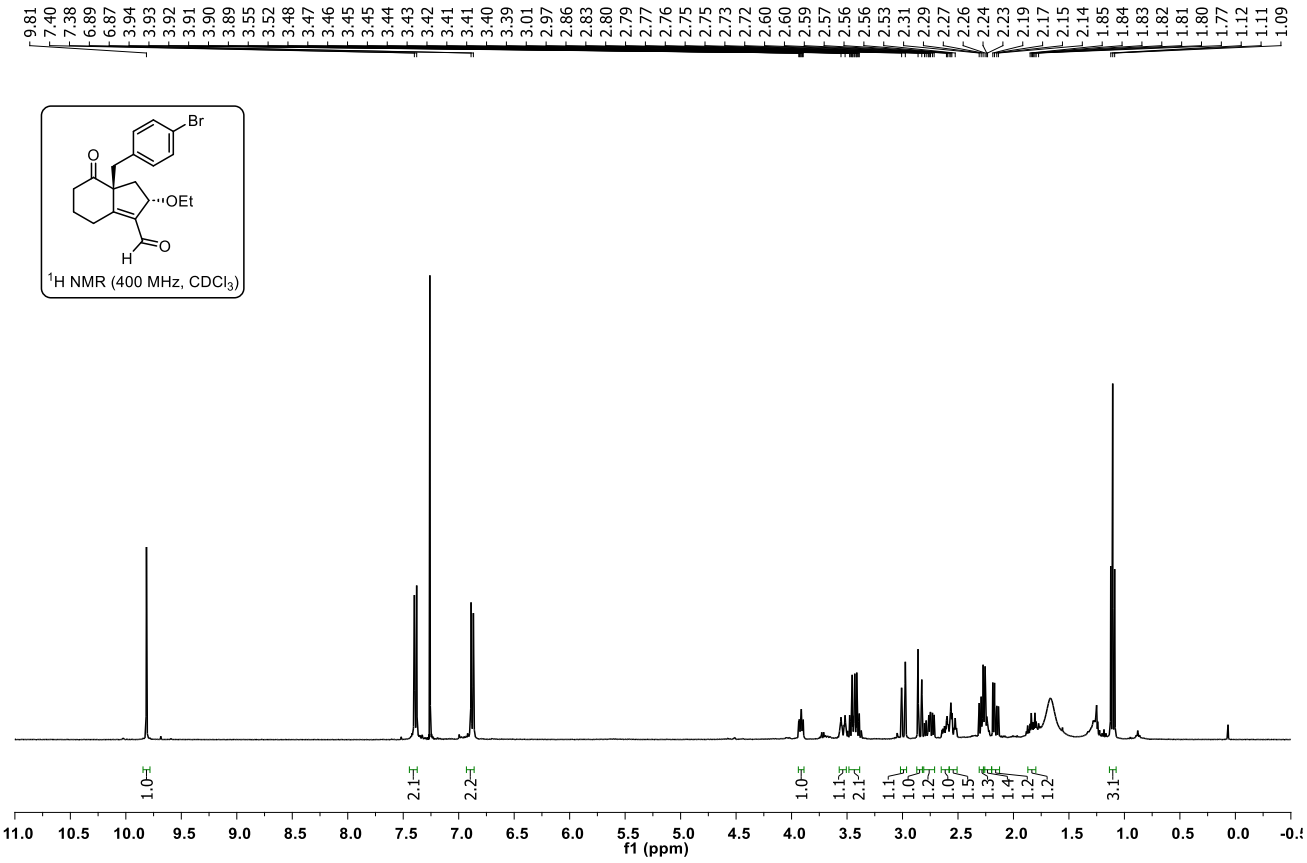


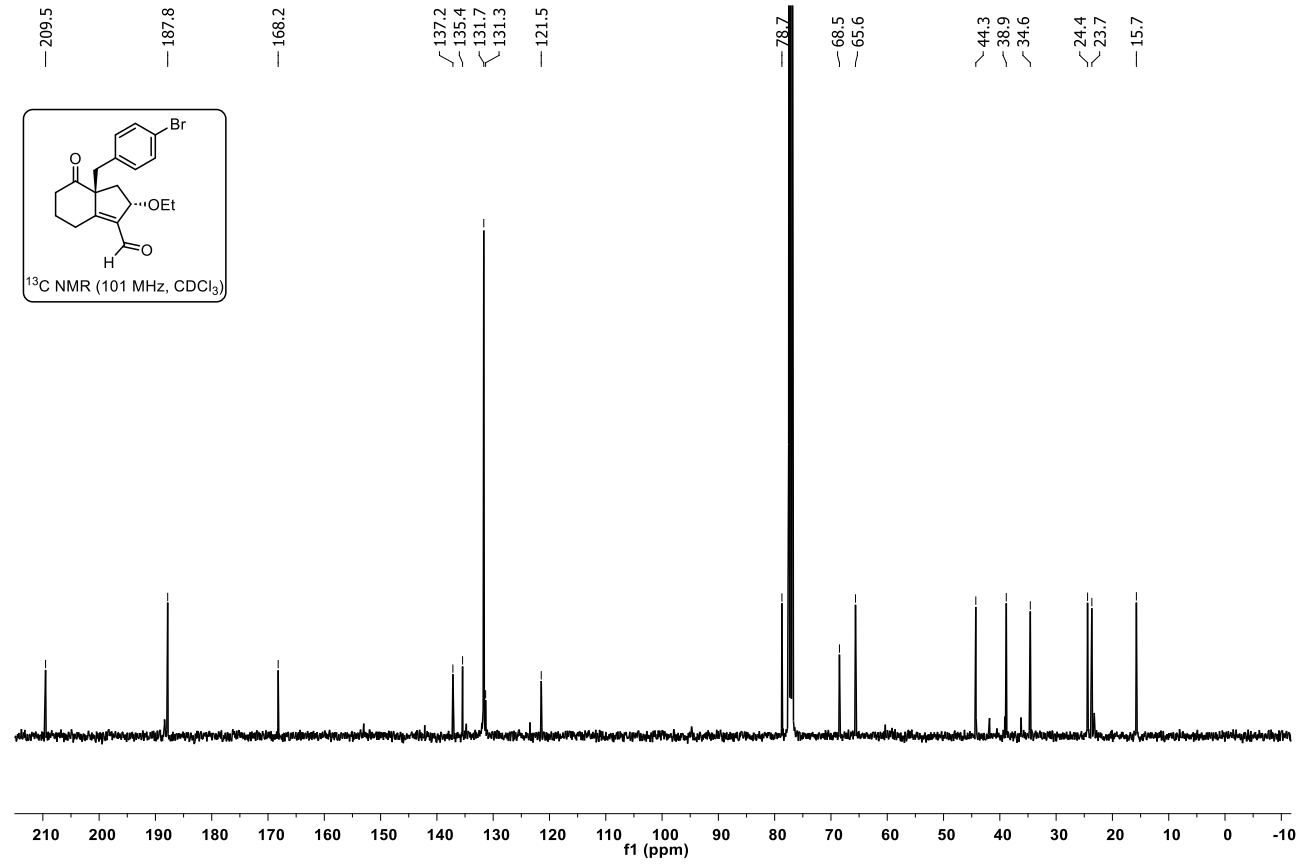
^{19}F NMR (471 MHz, $CDCl_3$)

(2*S*,7a*R*)-7a-(4-Chlorobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2j):

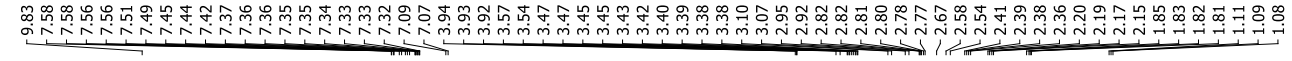


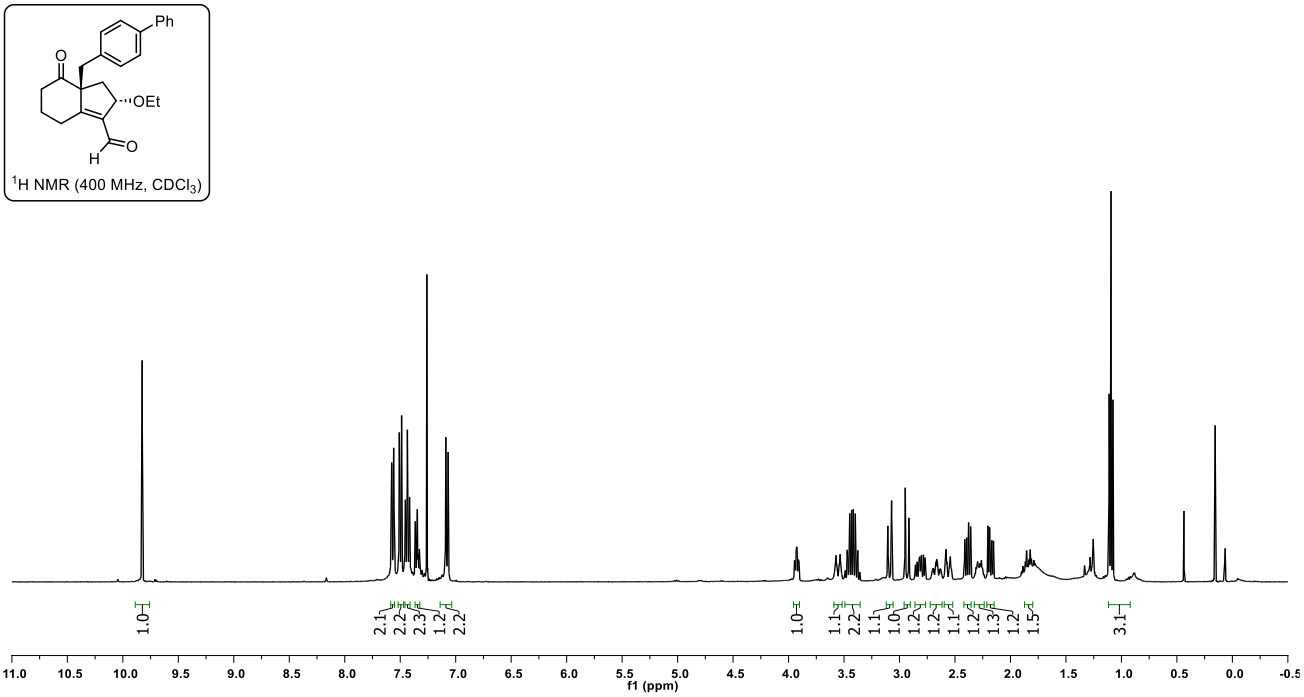
(2*S*,7a*R*)-7a-(4-Bromobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2k):

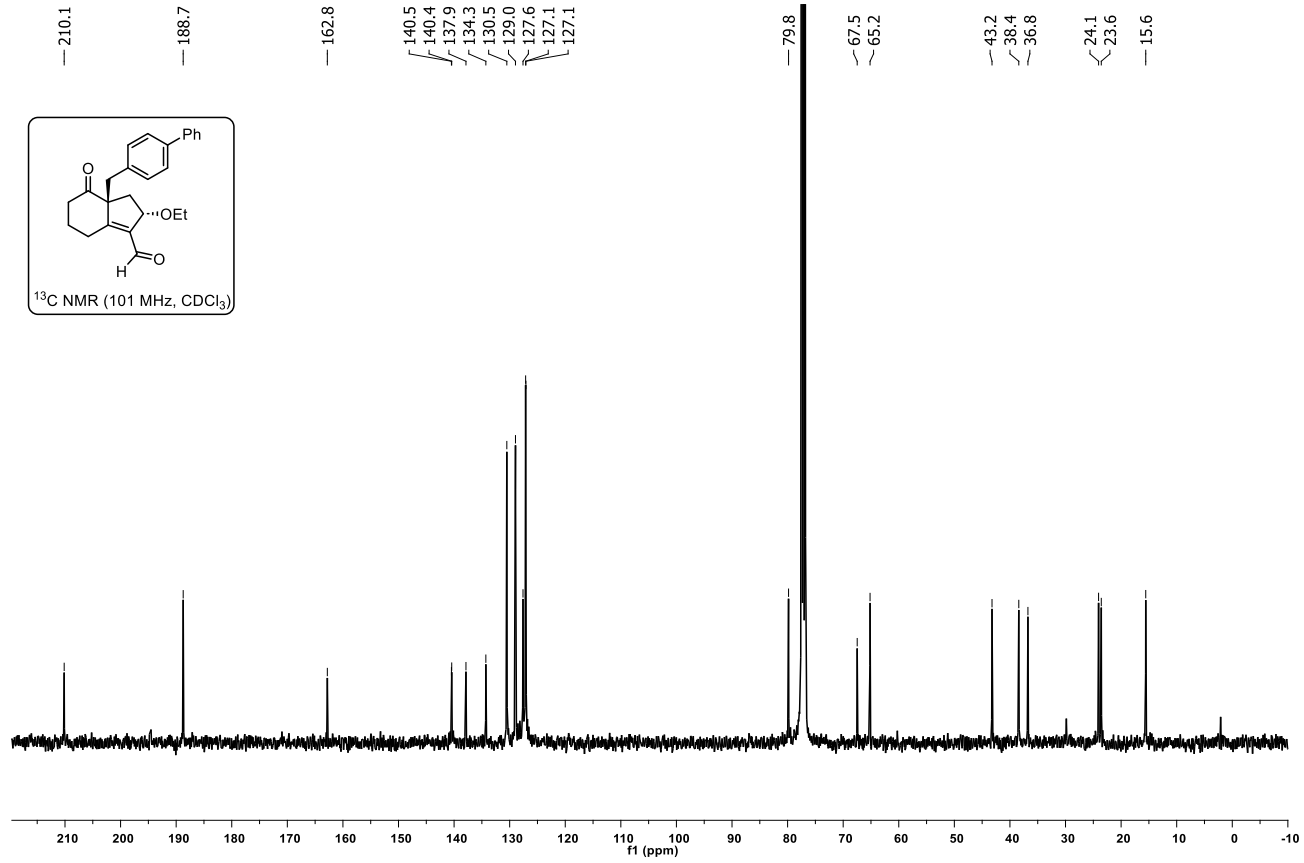




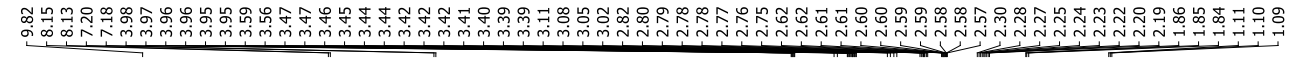
(2*S*,7a*R*)-7a-([1,1'-Biphenyl]-4-ylmethyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2l):

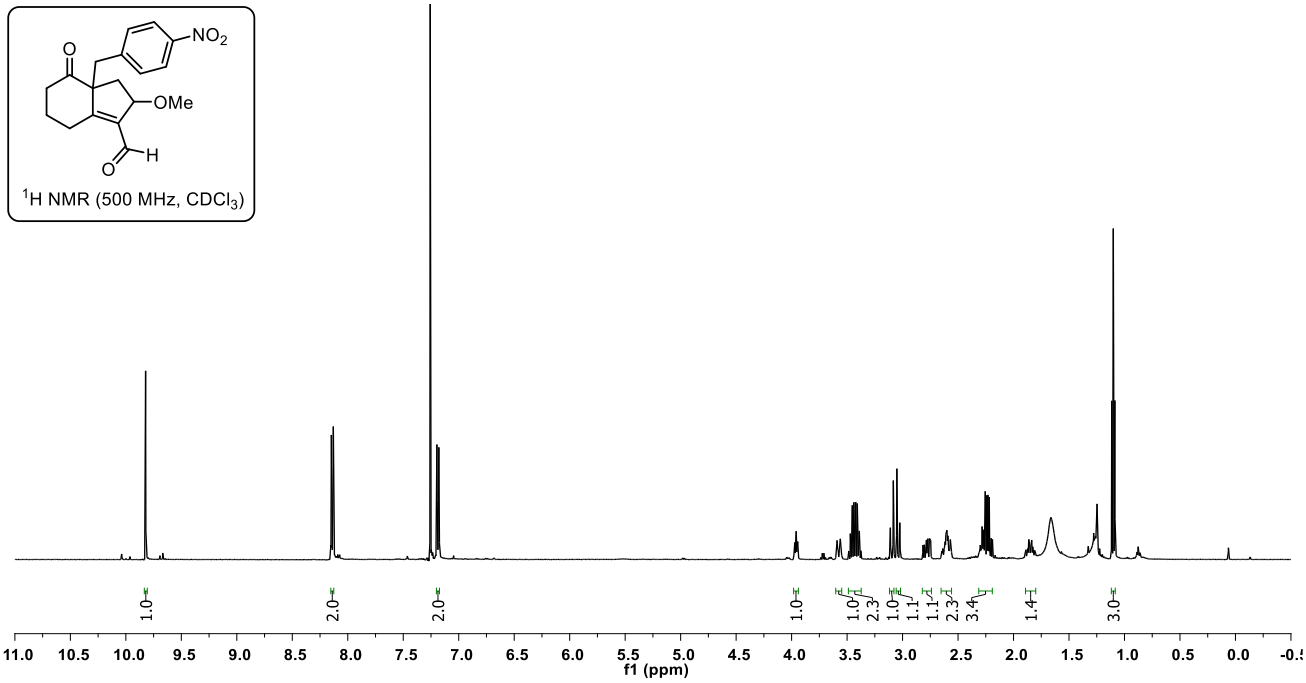


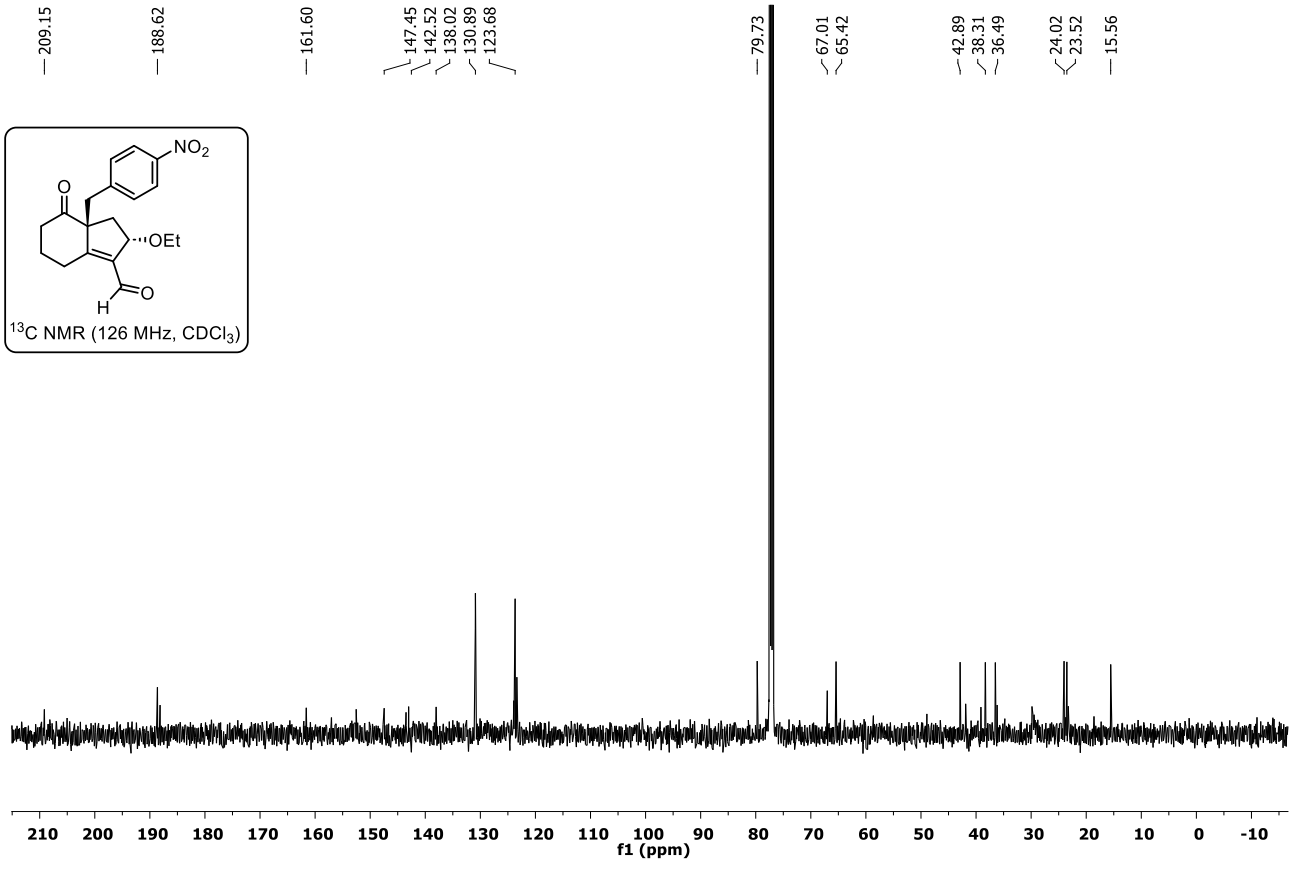




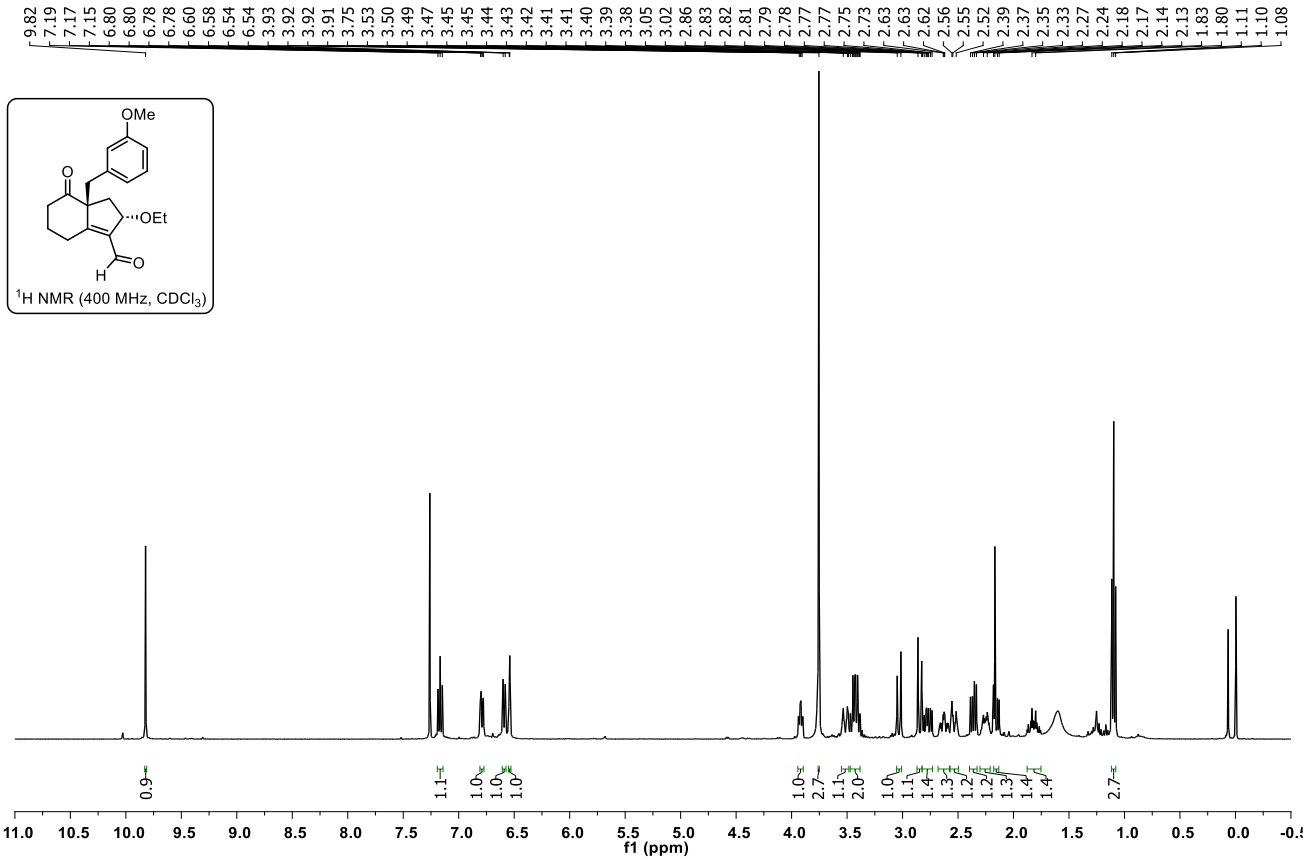
(2*S*,7a*R*)-2-Methoxy-7a-(4-nitrobenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2m):

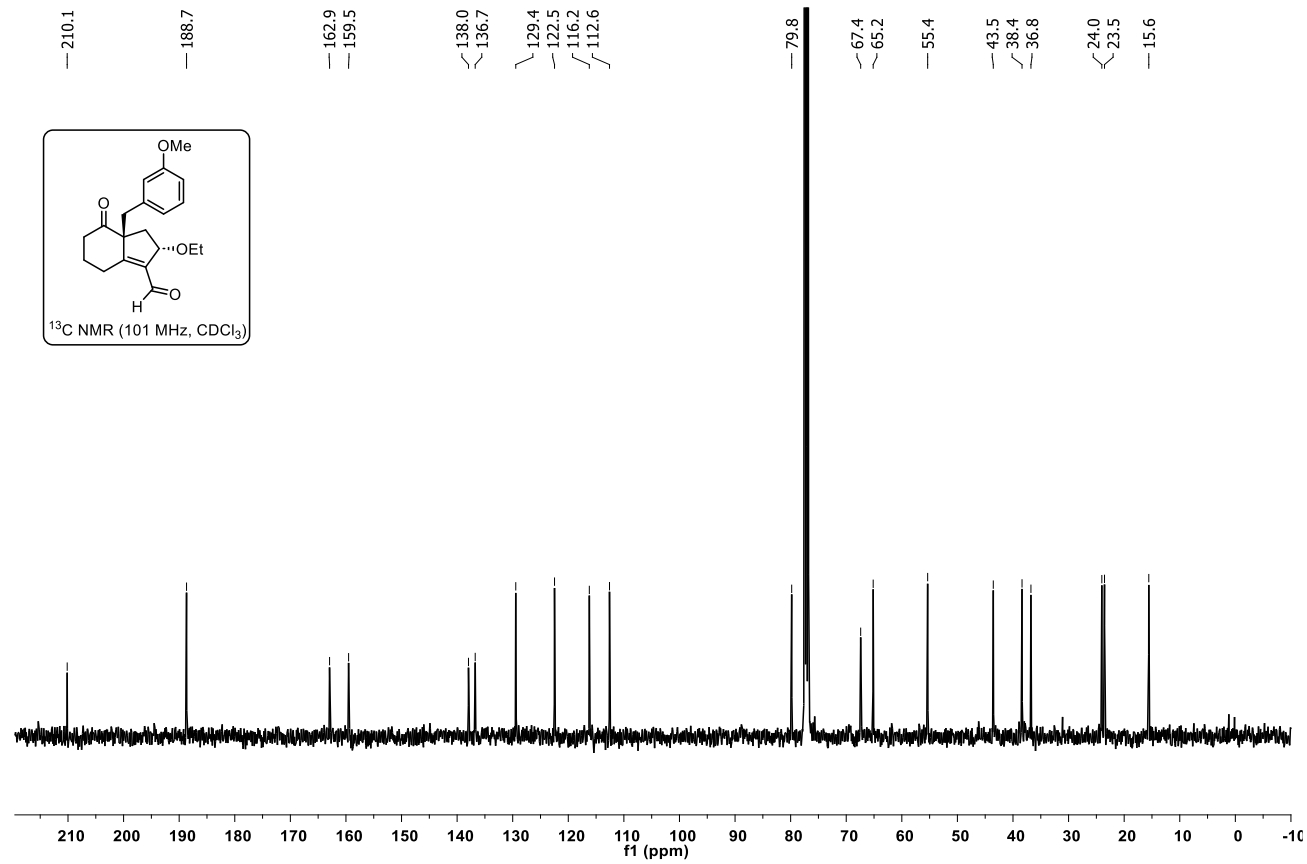




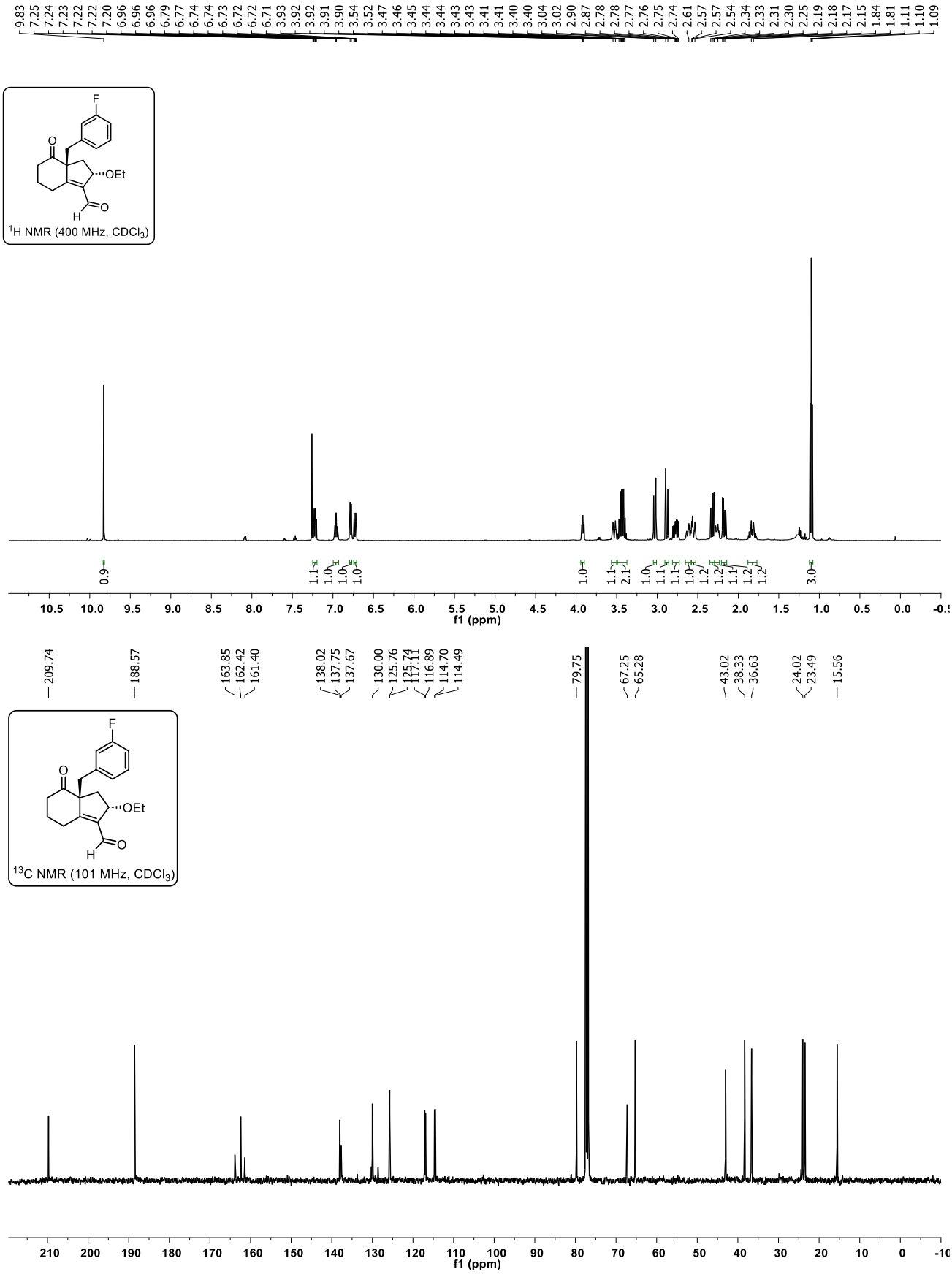


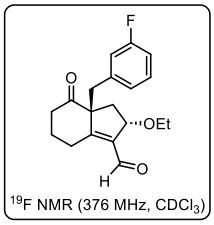
(2*S*,7a*R*)-2-Ethoxy-7a-(3-methoxybenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2n):





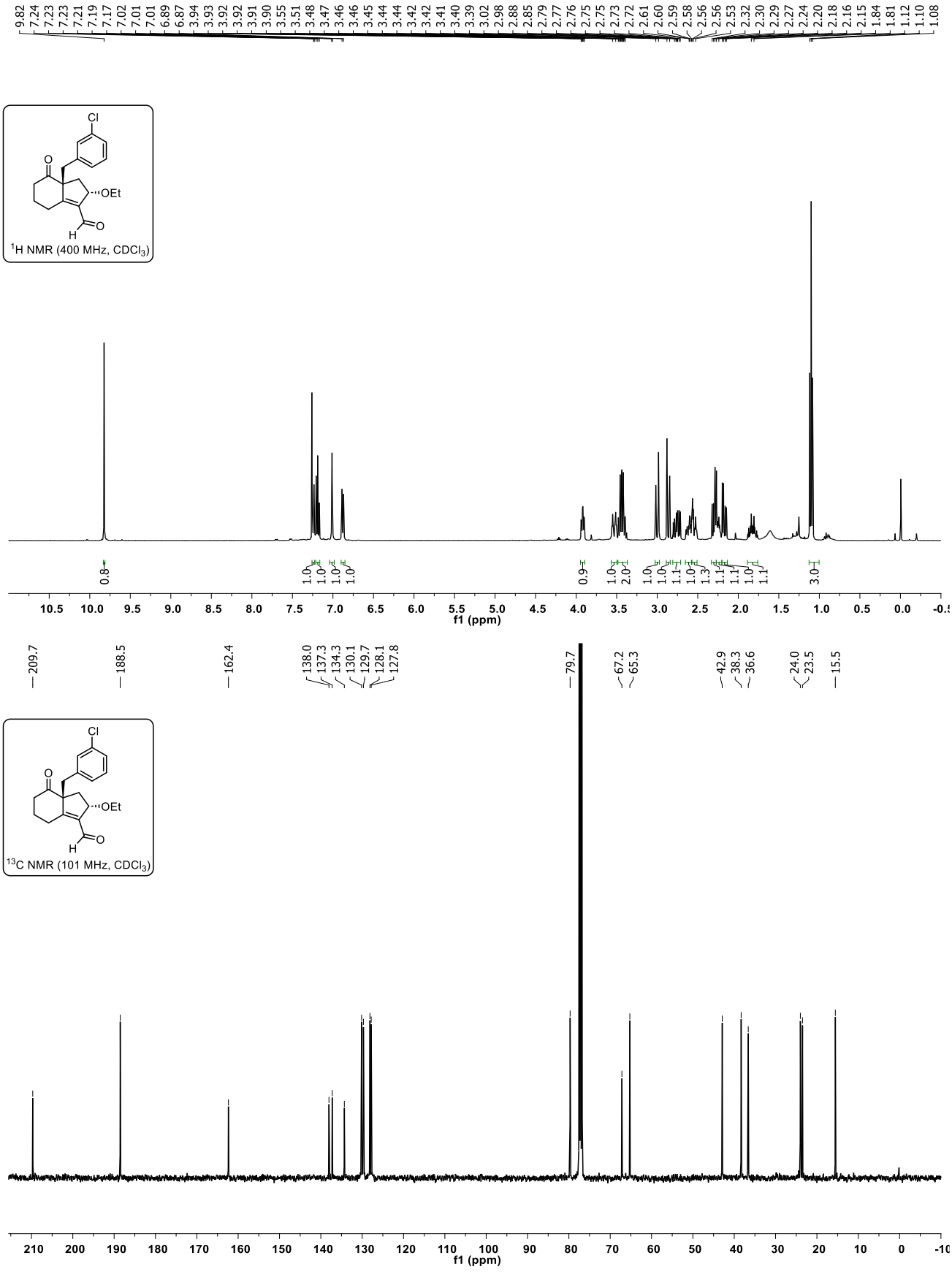
(2*S*,7a*R*)-2-Ethoxy-7a-(3-fluorobenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2o):



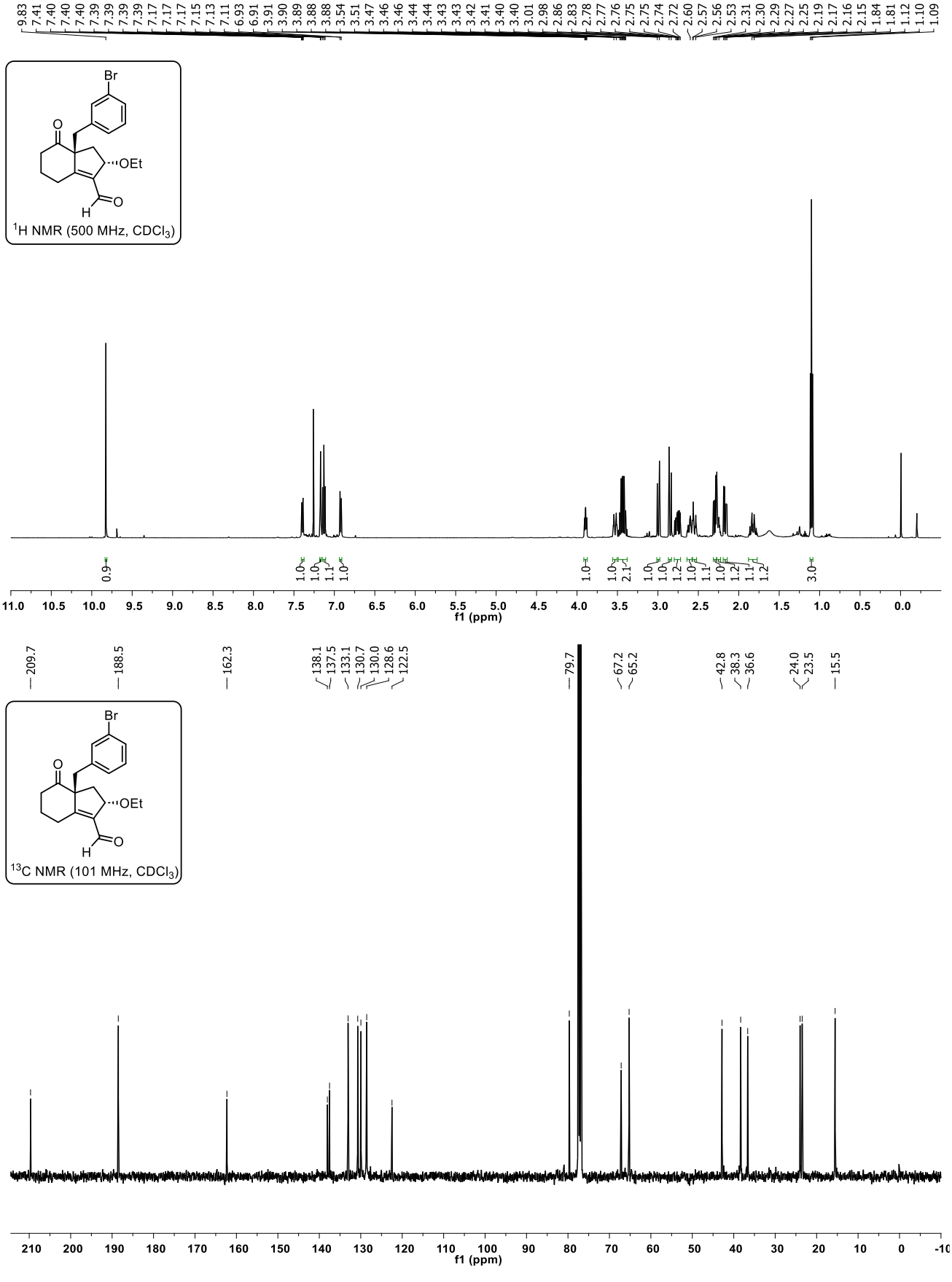


^{19}F NMR (376 MHz, $CDCl_3$)

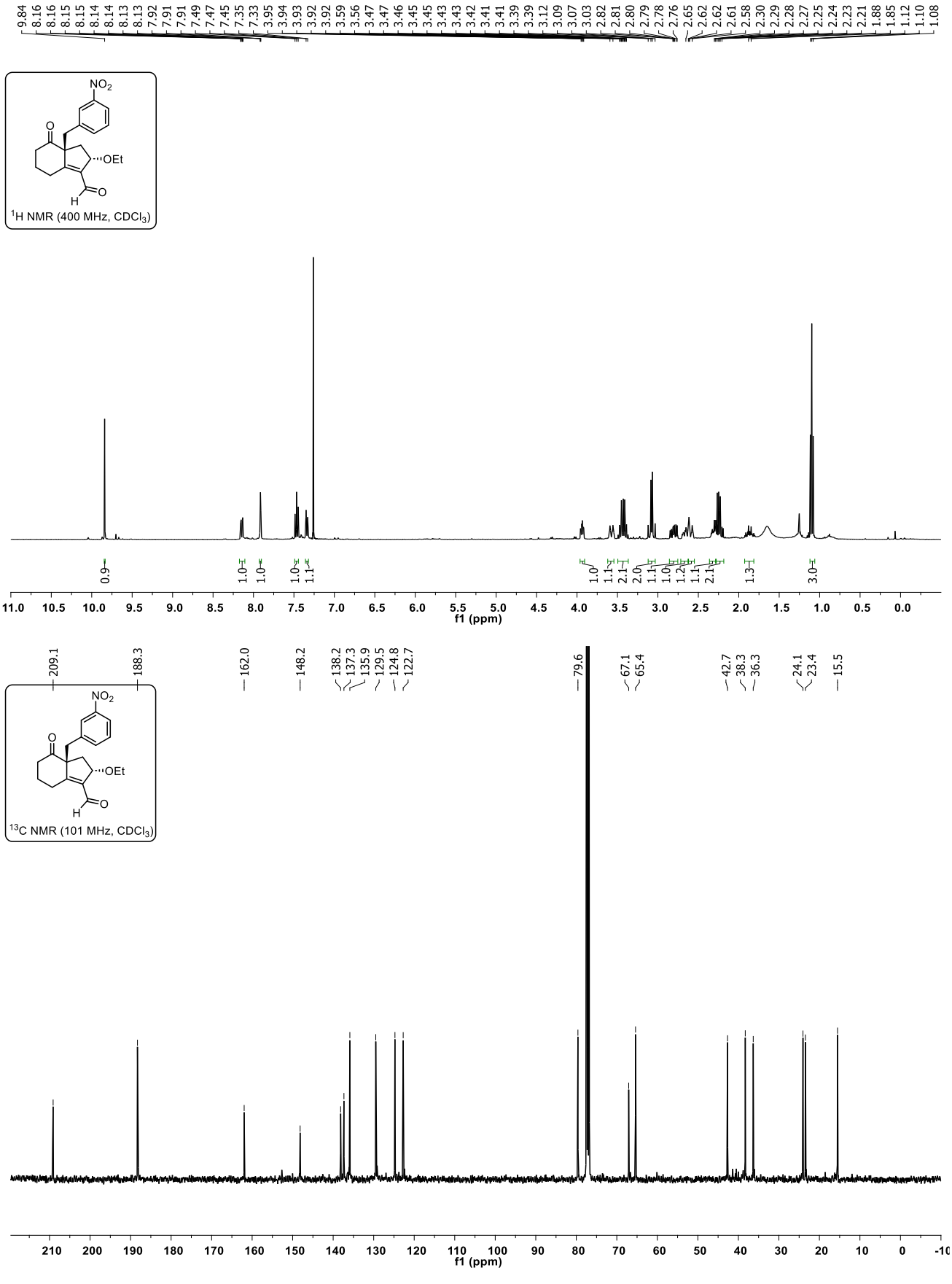
(2*S*,7a*R*)-7a-(3-Chlorobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2p):



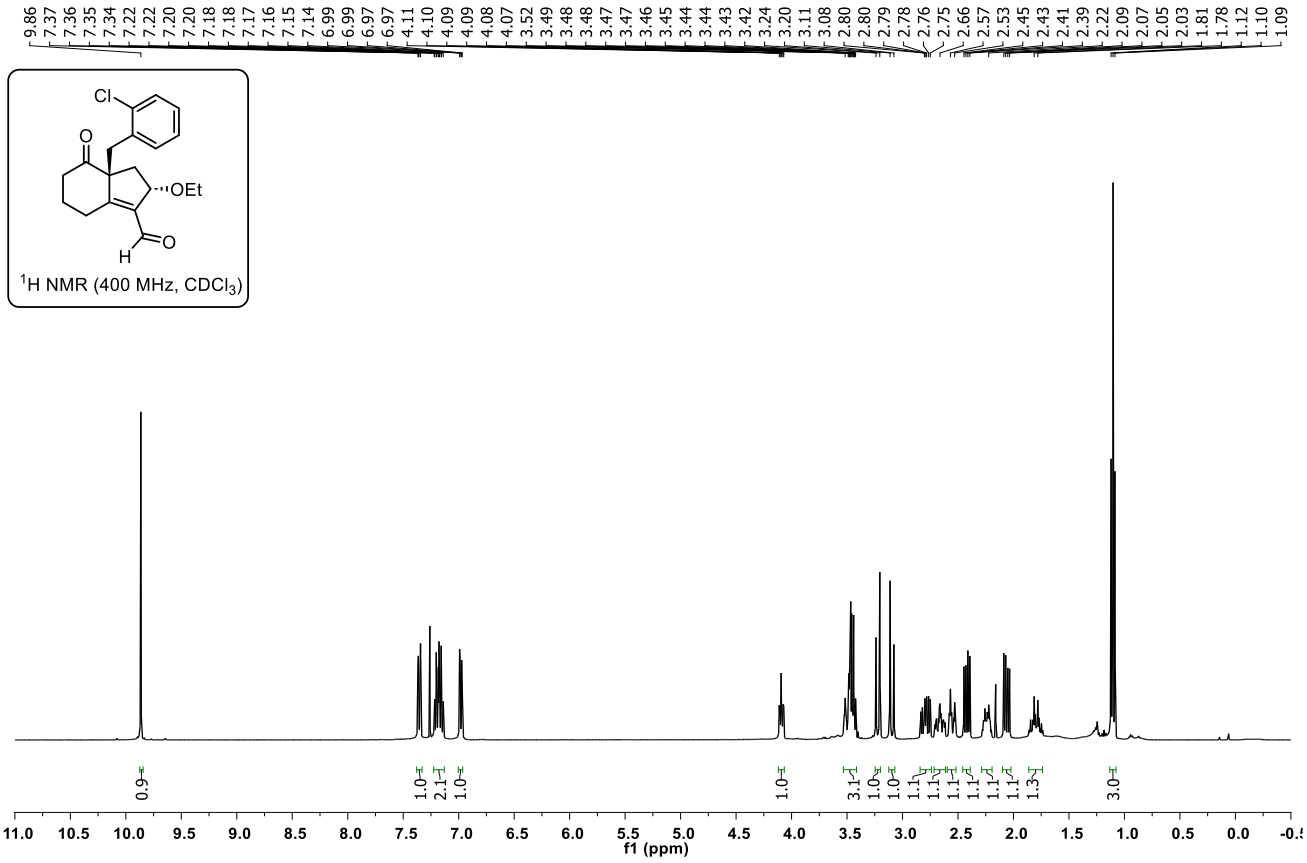
(2*S*,7a*R*)-7a-(3-Bromobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2q):

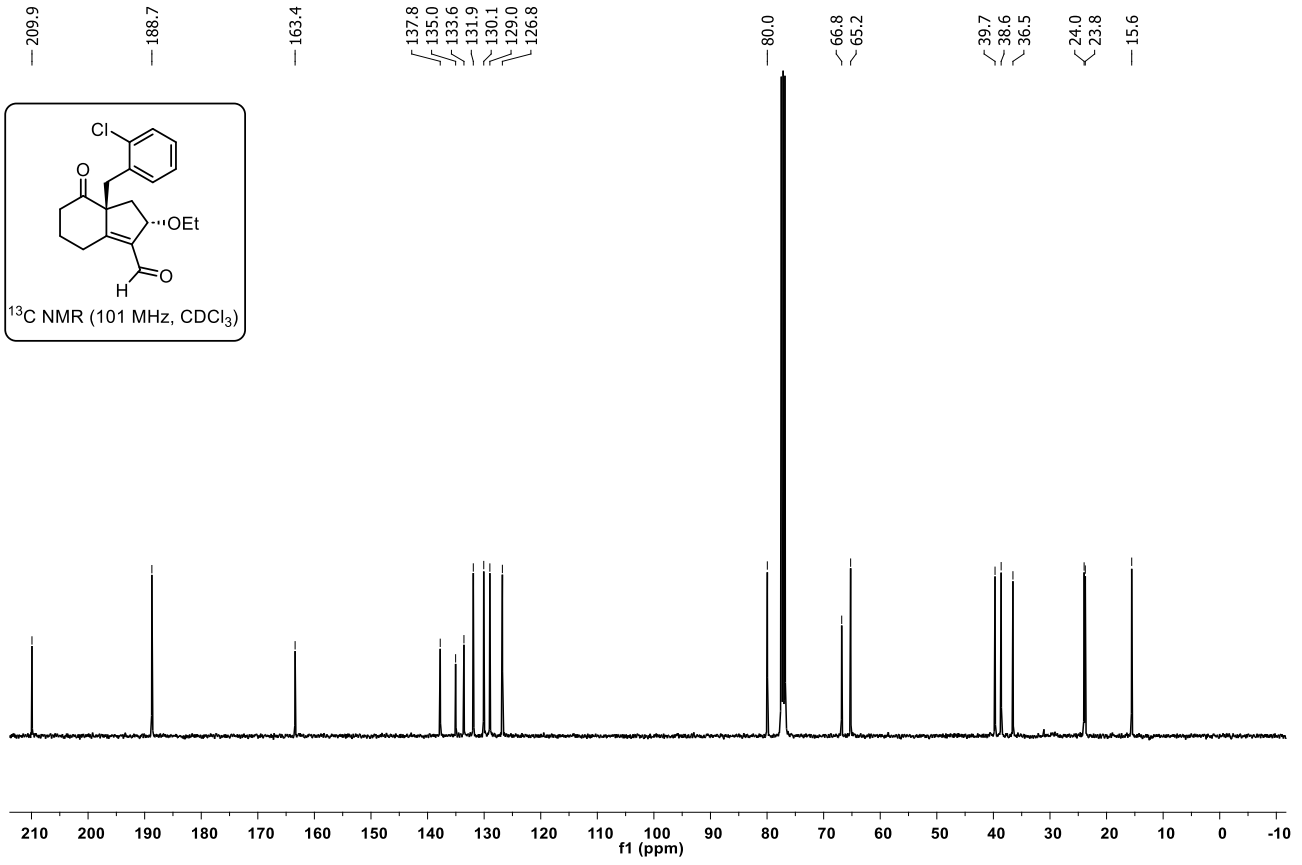


(2*S*,7a*R*)-2-Ethoxy-7a-(3-nitrobenzyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2r):

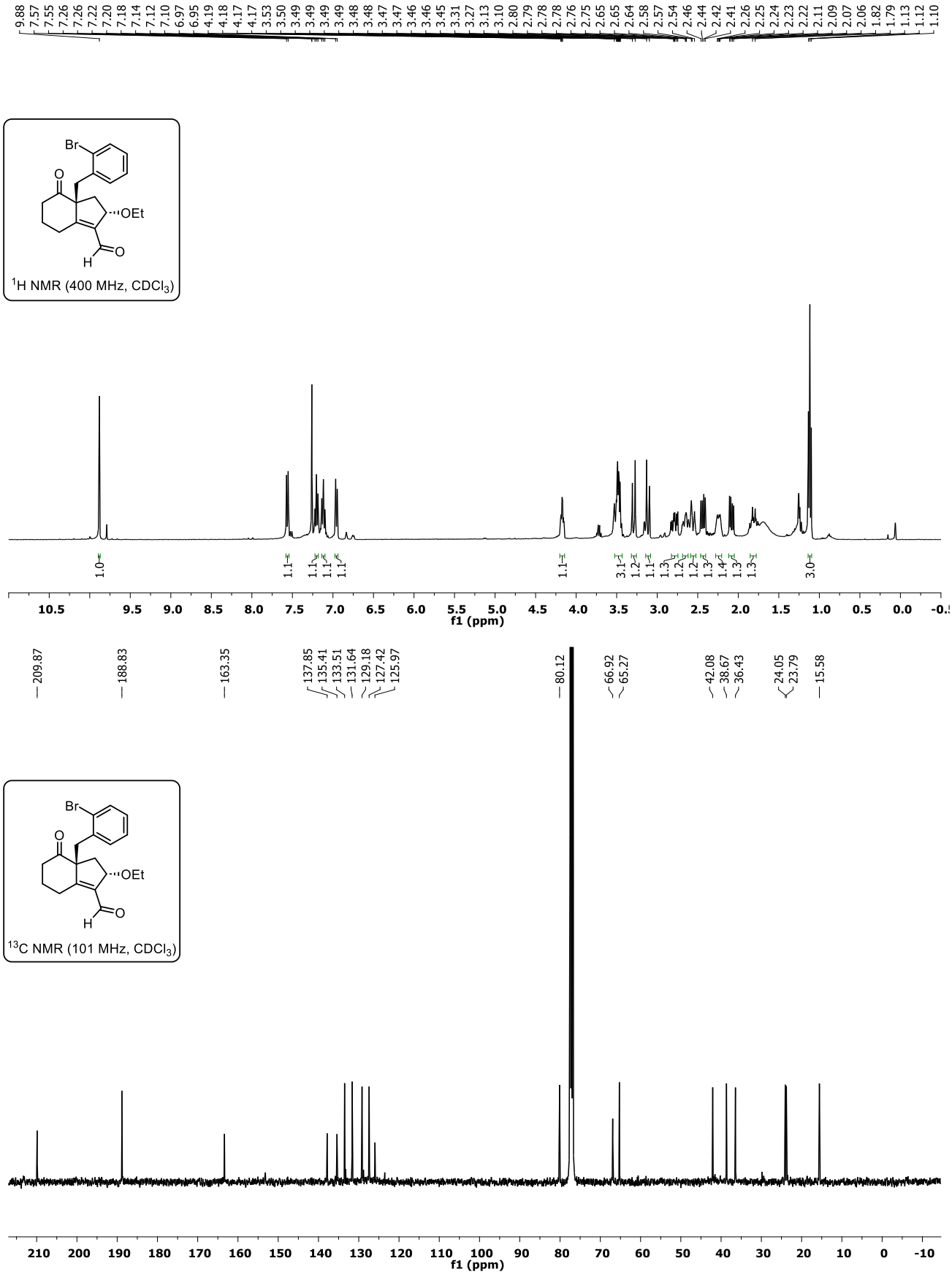


(2*S*,7a*R*)-7a-(2-Chlorobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2s):

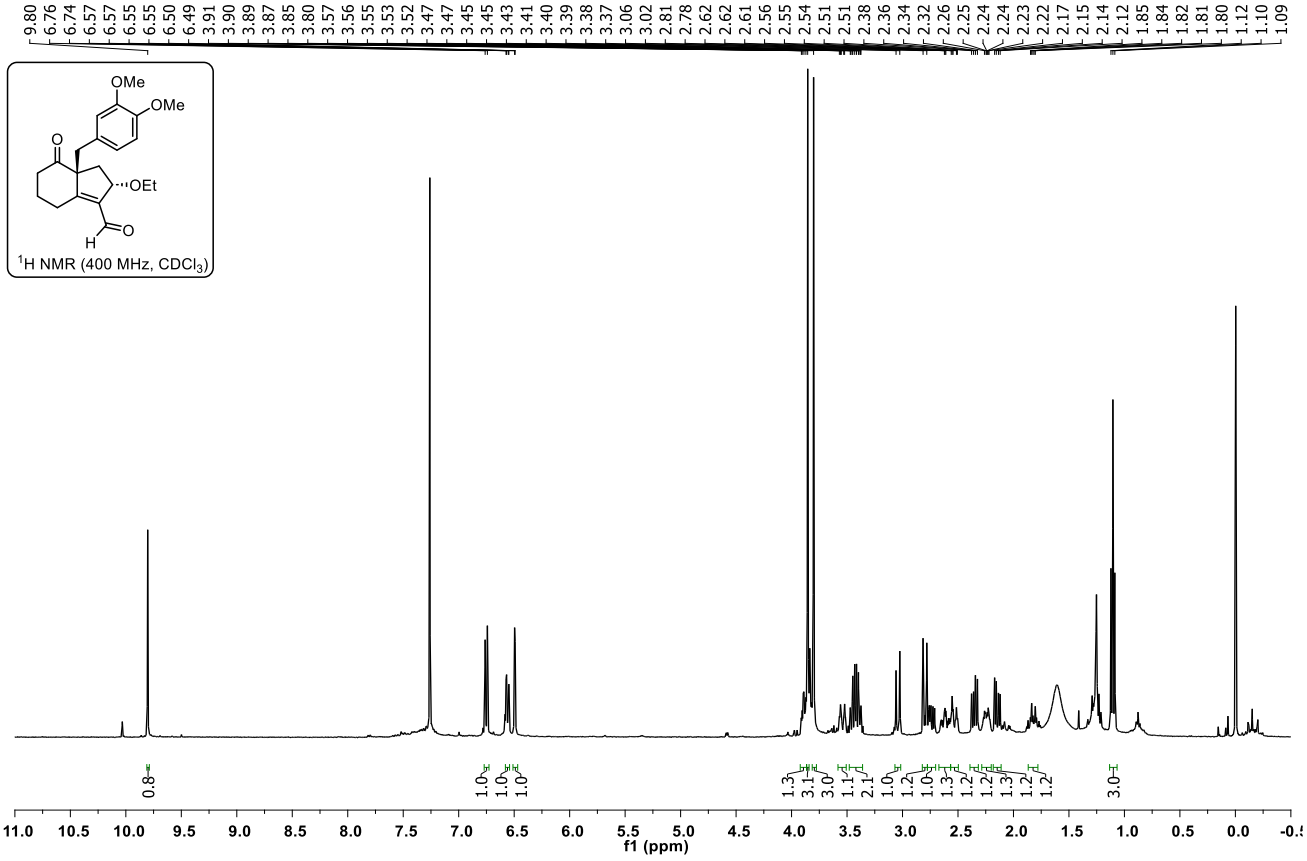


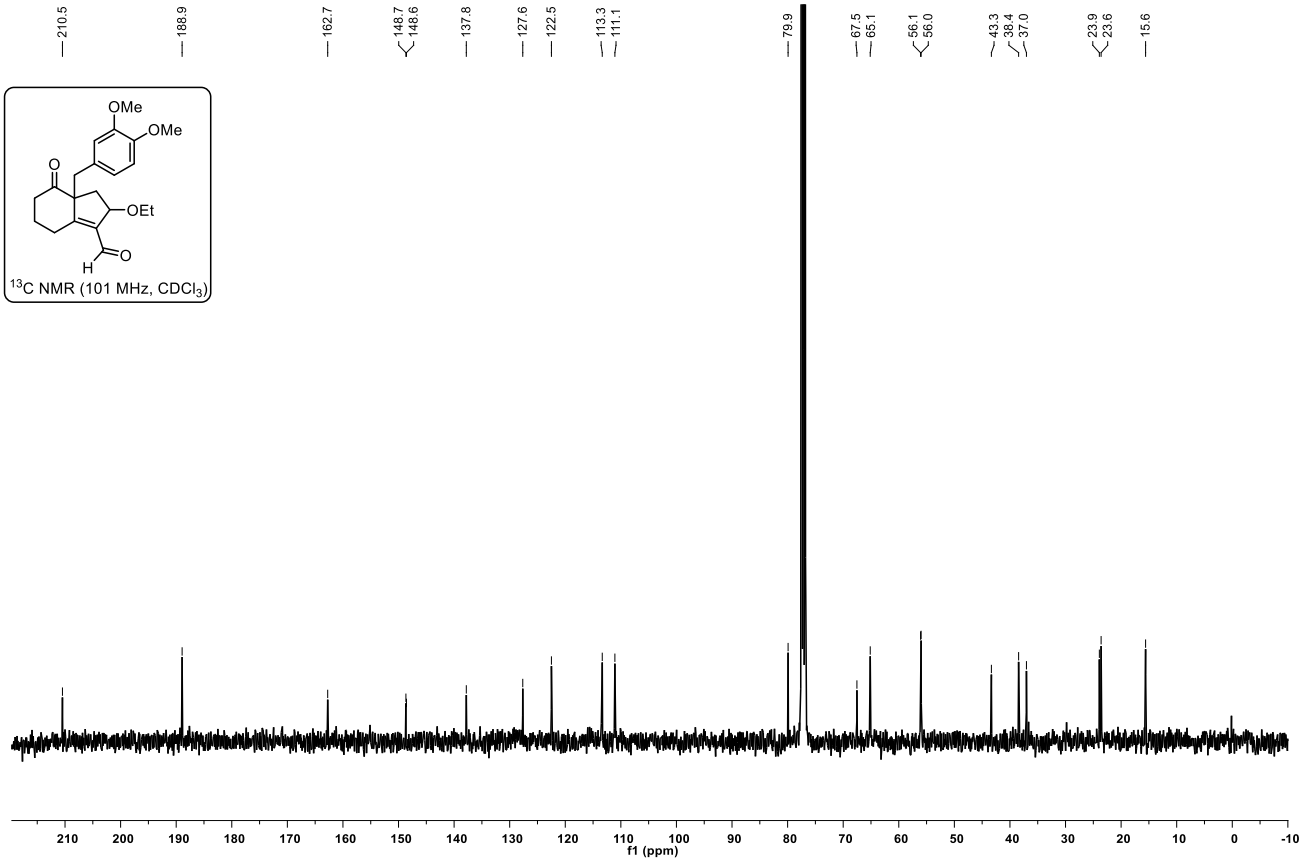


(2*S*,7a*R*)-7a-(2-Bromobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2t):

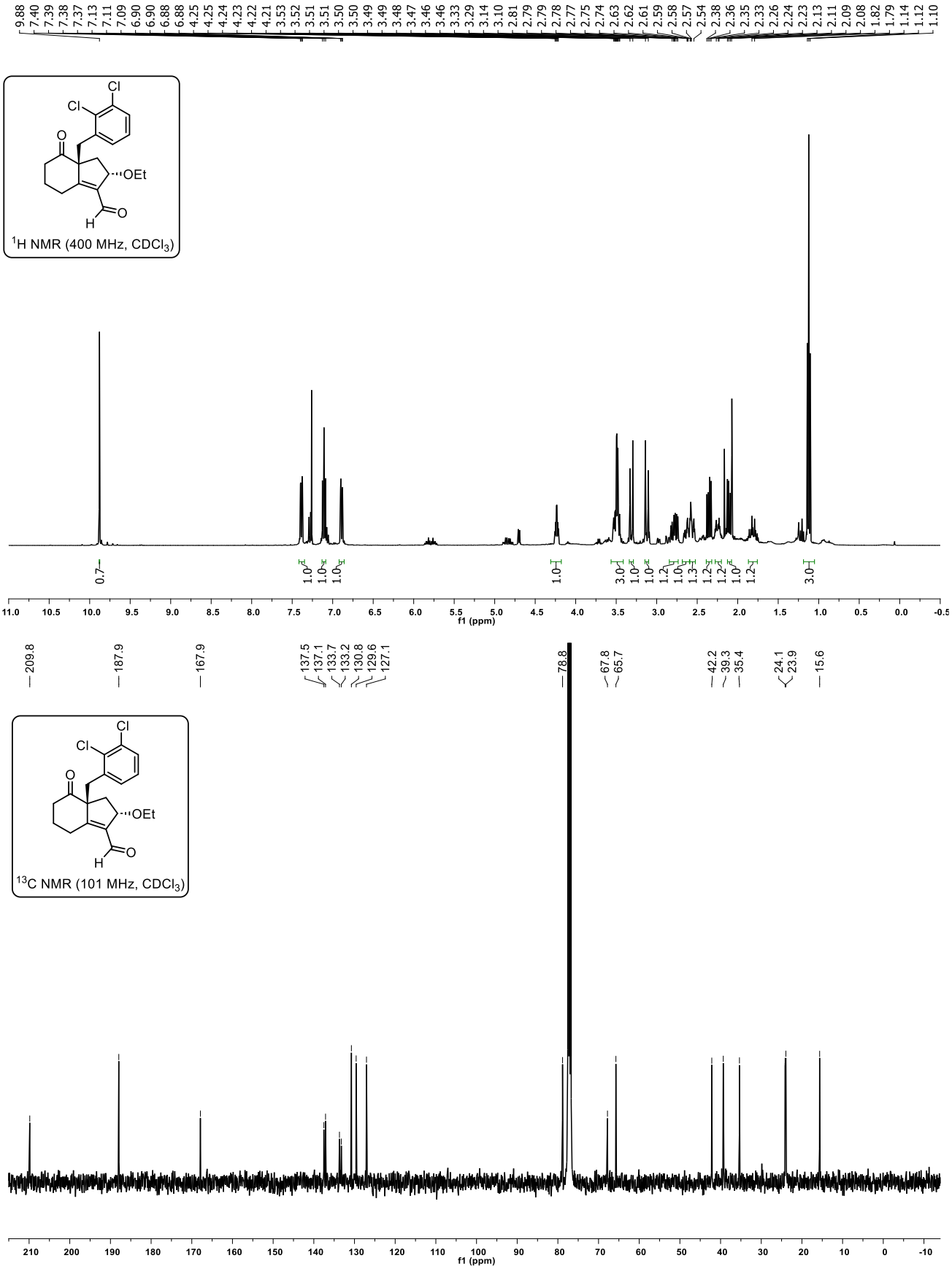


(2*S*,7a*R*)-7a-(3,4-Dimethoxybenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2u):

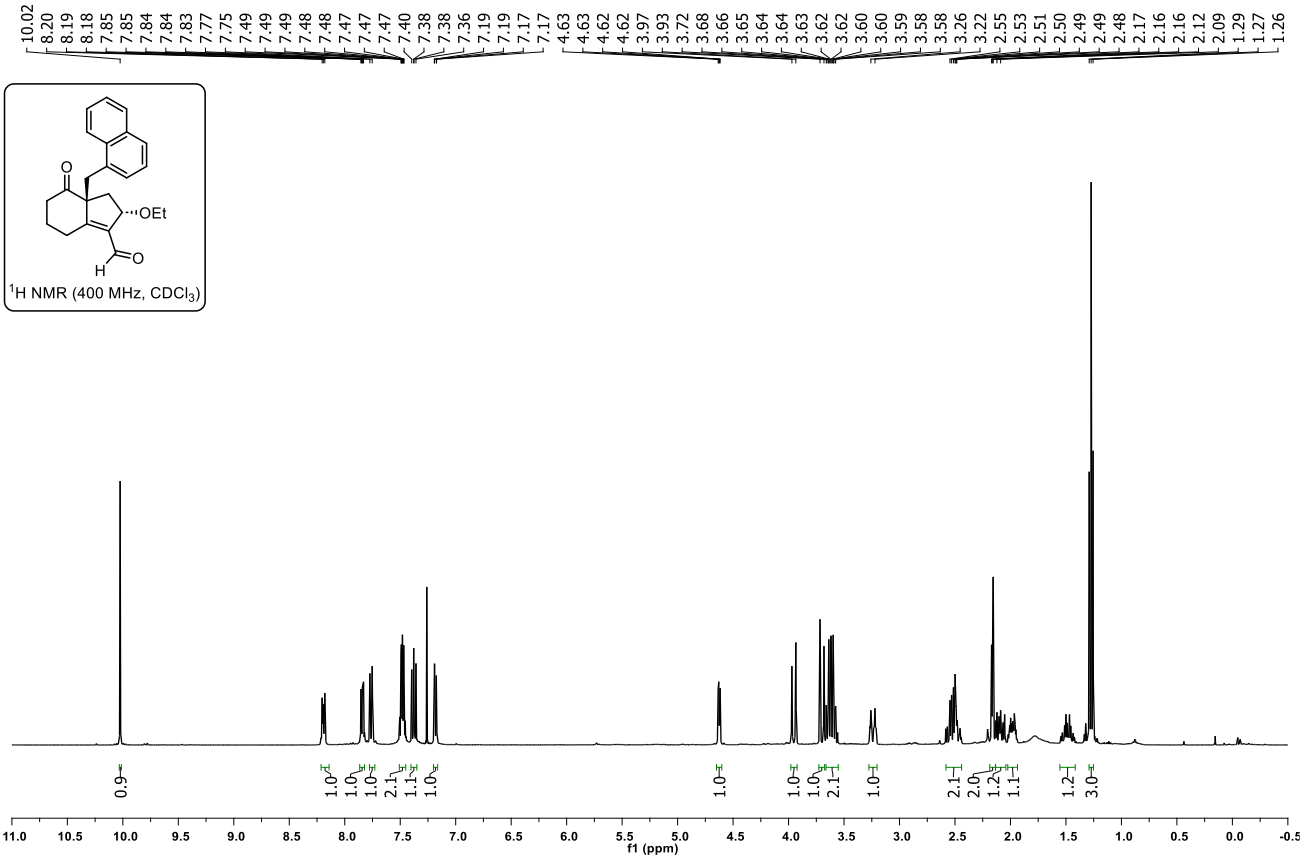


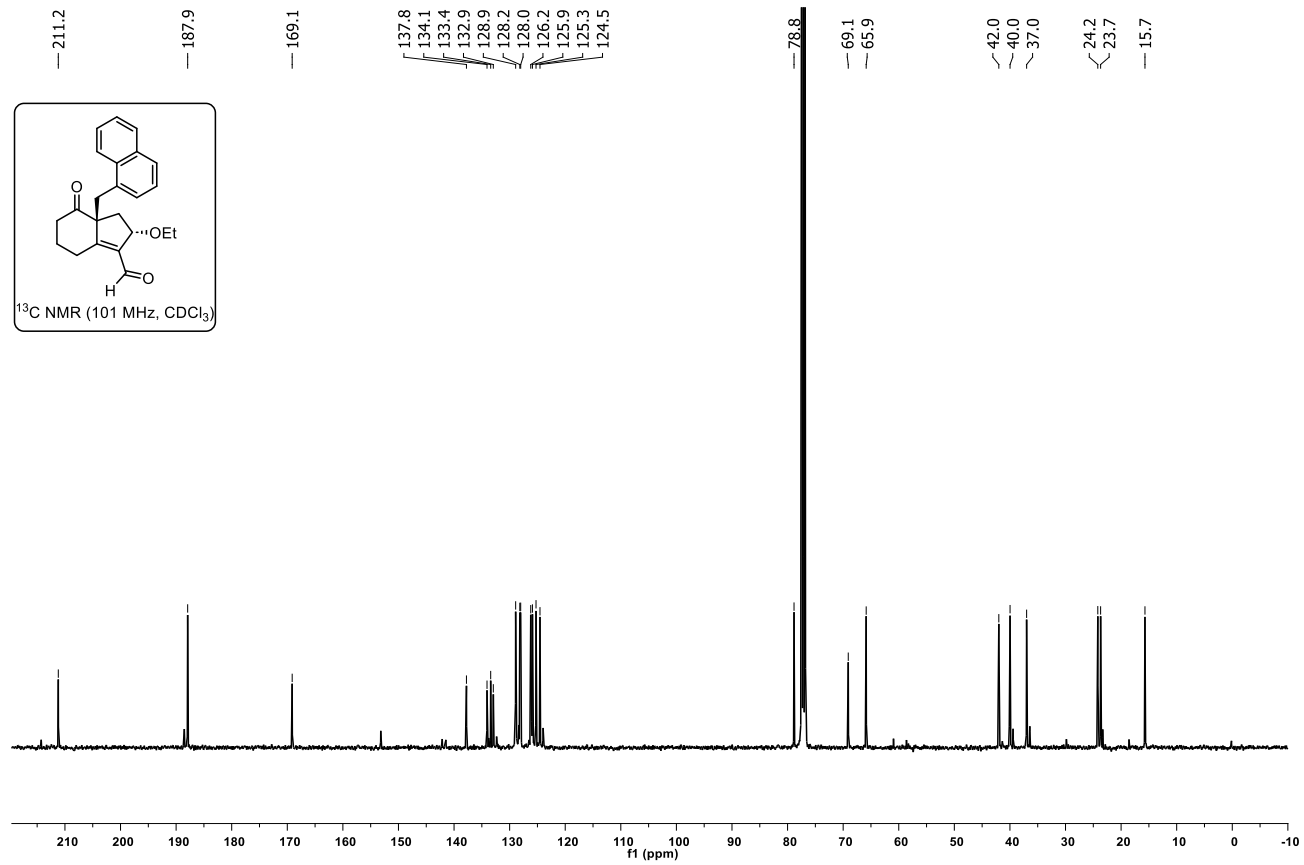


(2*S*,7a*R*)-7a-(2,3-Dichlorobenzyl)-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2v):

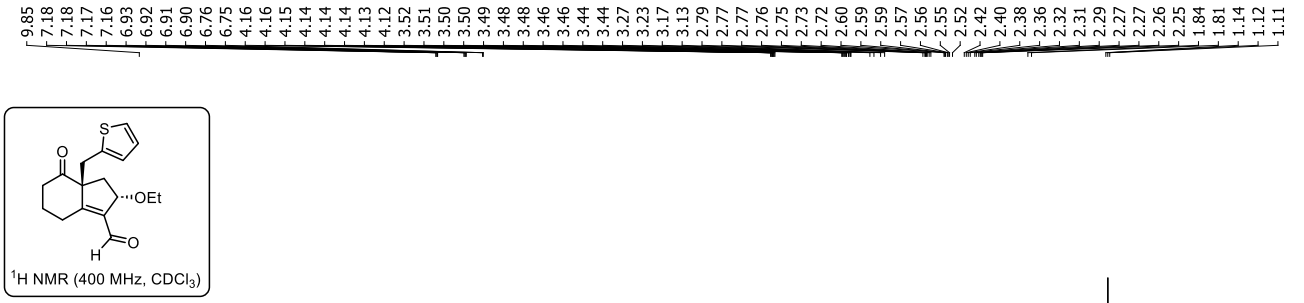


(2*S*,7a*R*)-2-Ethoxy-7a-(naphthalen-1-ylmethyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2w):

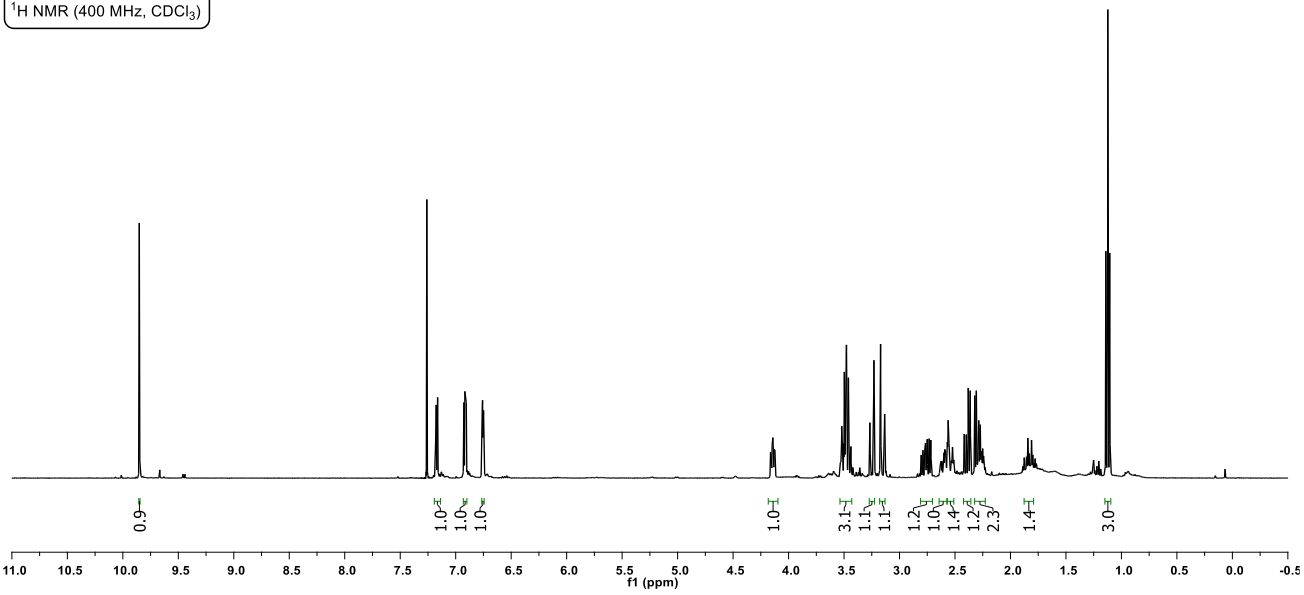


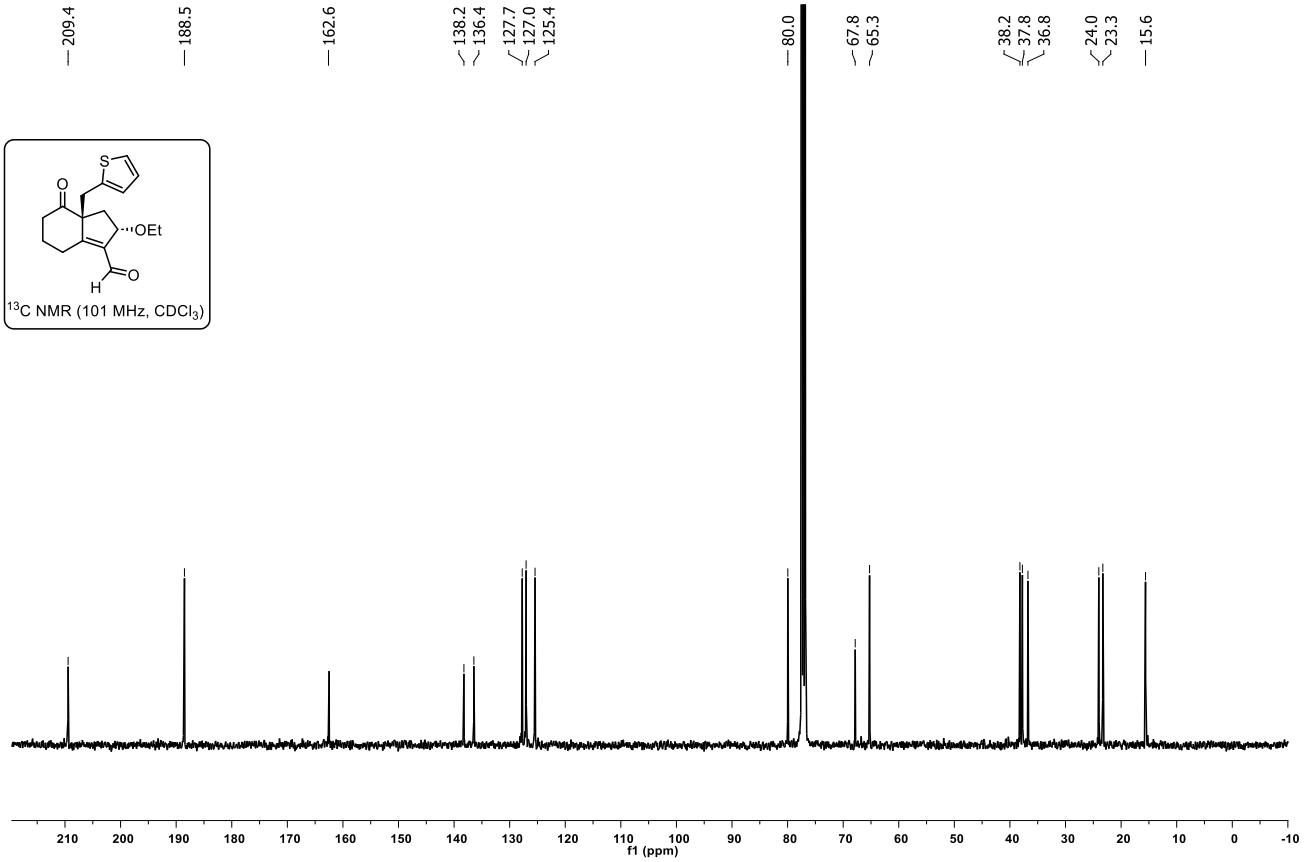


(2*S*,7a*R*)-2-Ethoxy-7-oxo-7a-(thiophen-2-ylmethyl)-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2x):



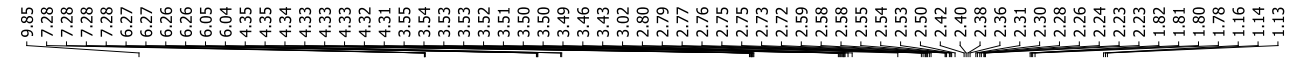
^{1}H NMR (400 MHz, $CDCl_3$)

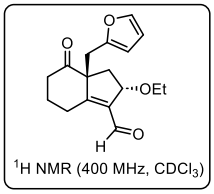


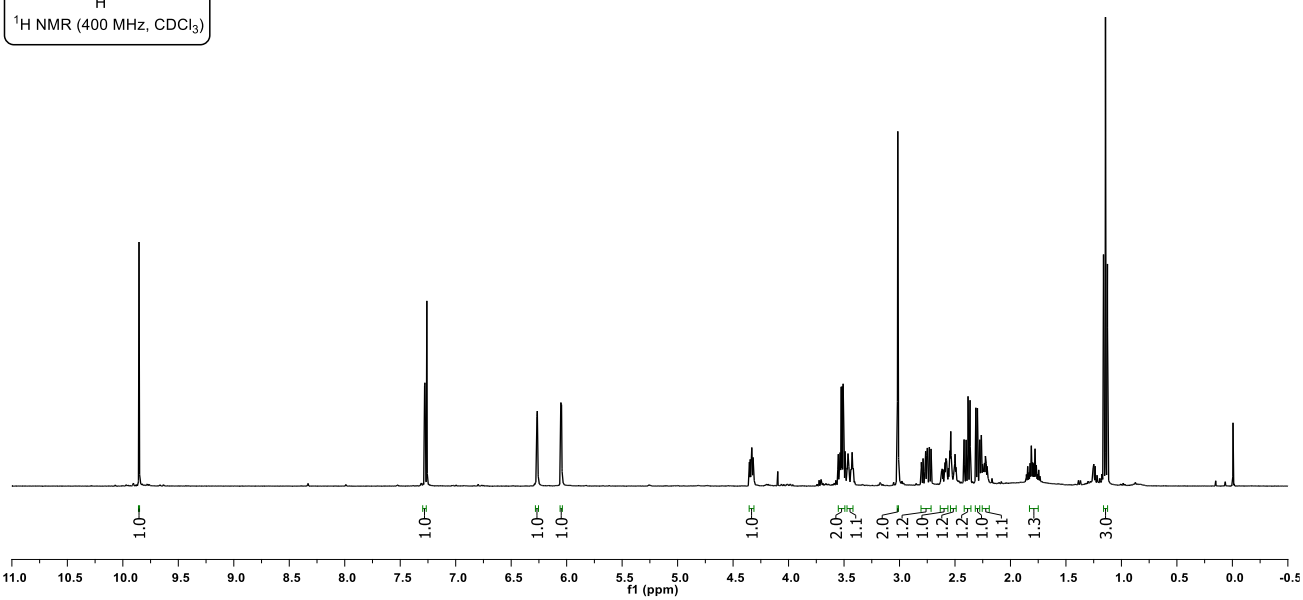


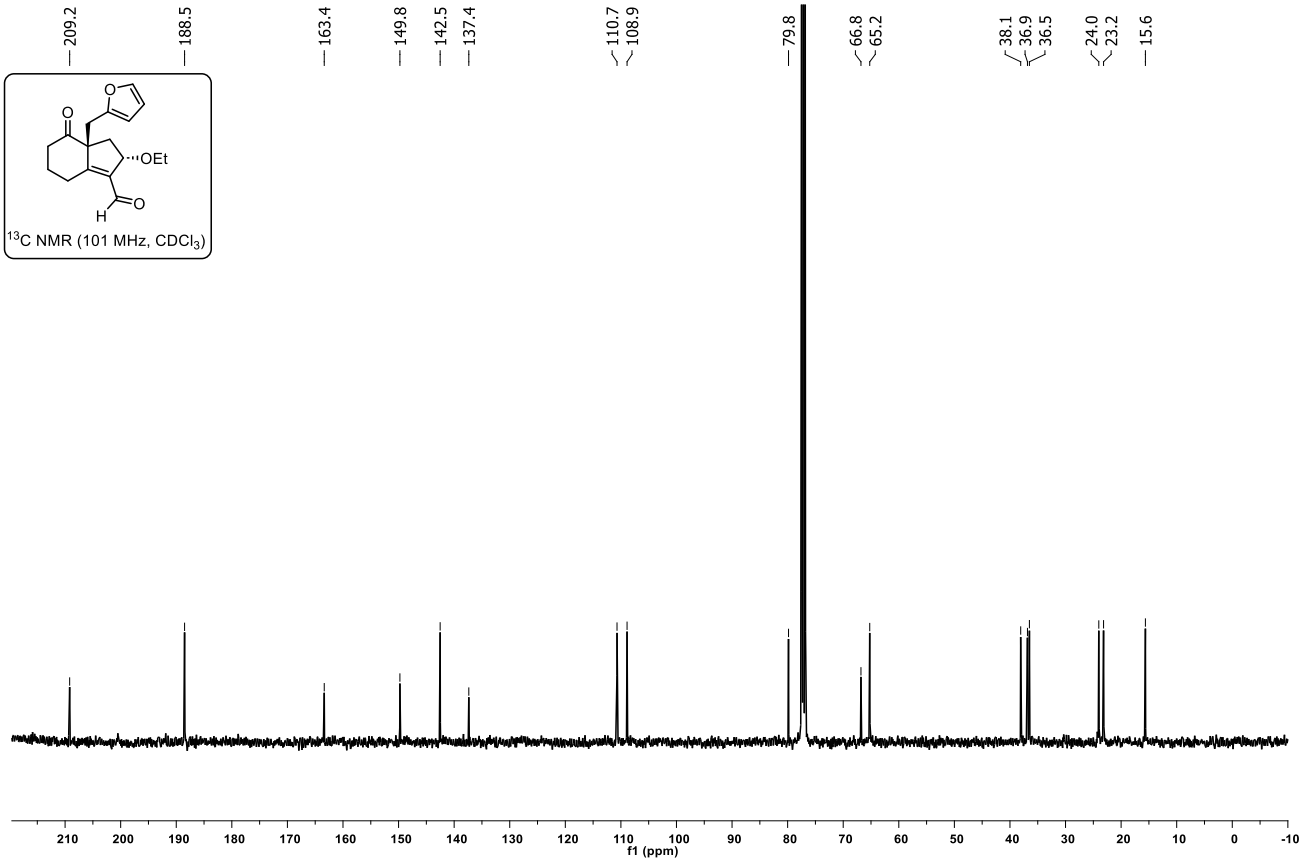
^{13}C NMR (101 MHz, $CDCl_3$)

(2*S*,7a*R*)-2-Ethoxy-7a-(furan-2-ylmethyl)-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carbaldehyde (2y):

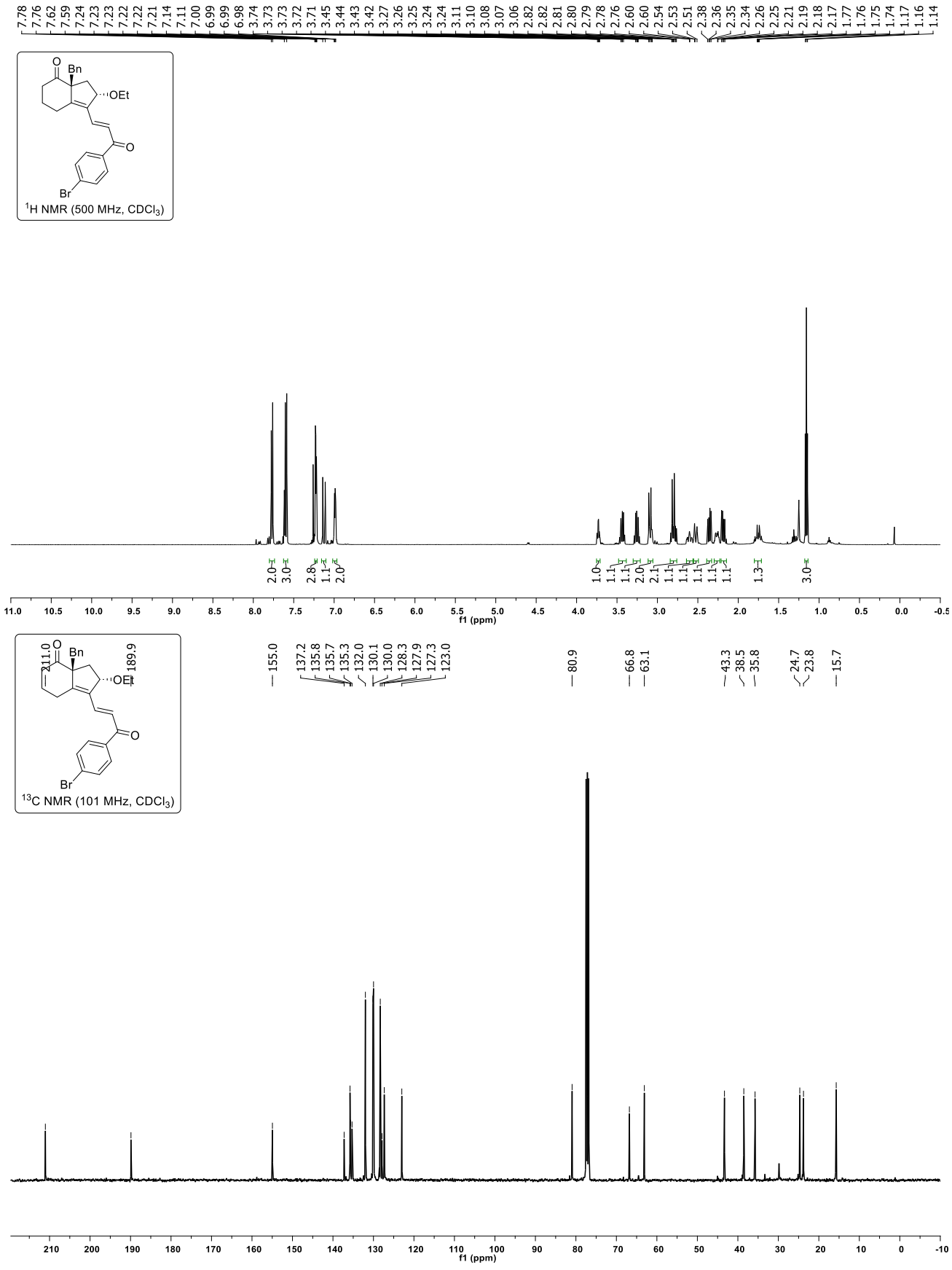




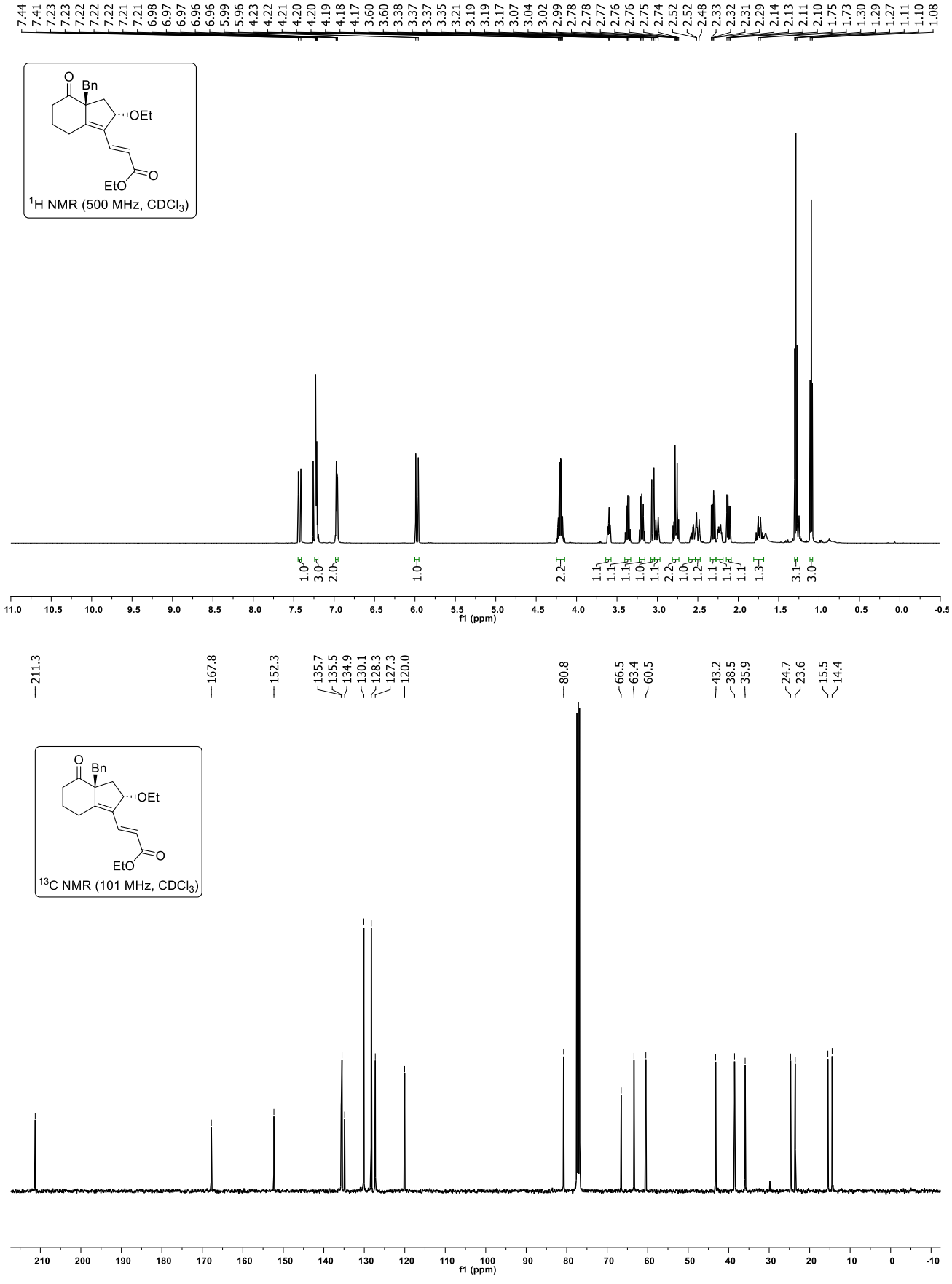




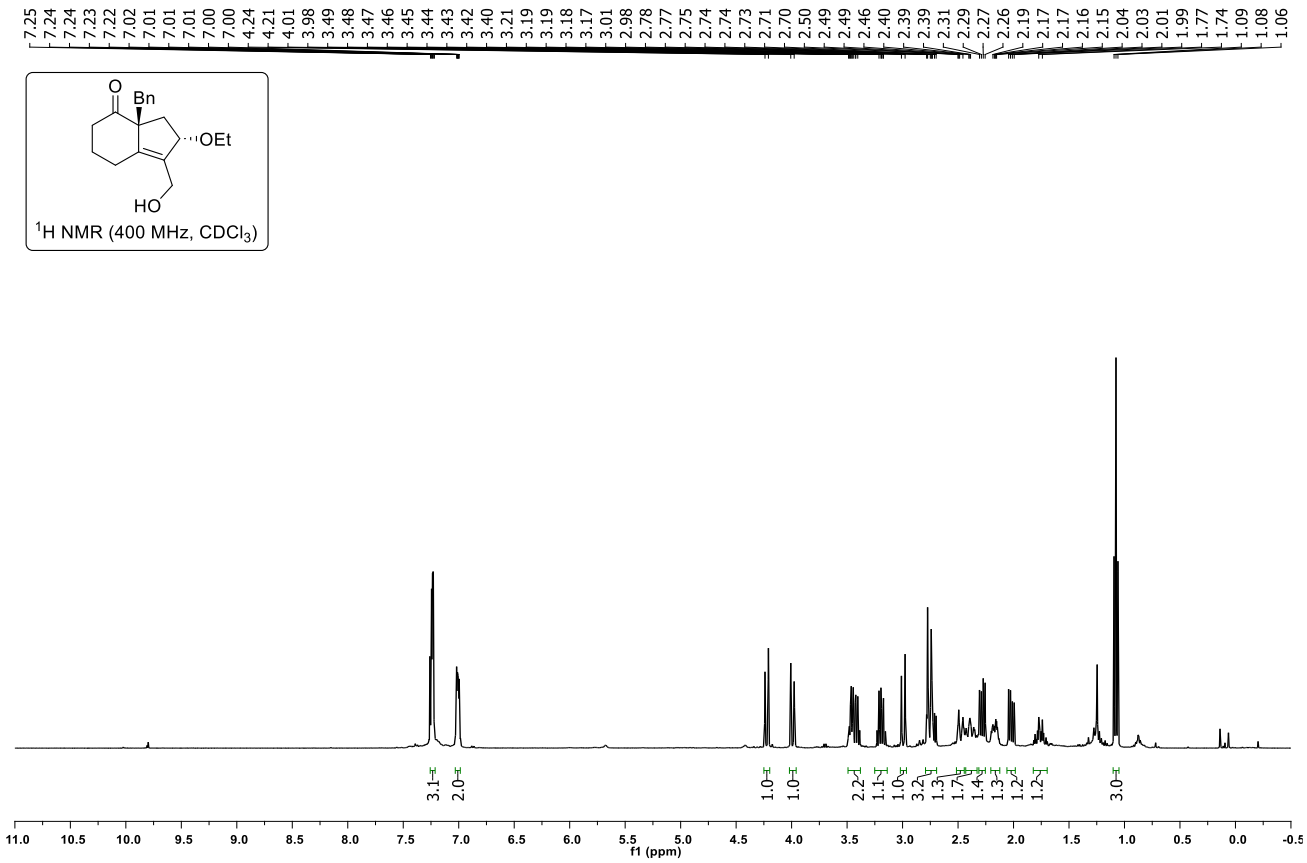
(2*S*,3a*R*)-3a-Benzyl-1-((*Z*)-3-(4-bromophenyl)-3-oxoprop-1-en-1-yl)-2-ethoxy-2,3,3a,5,6,7-hexahydro-4*H*-inden-4-one (5):

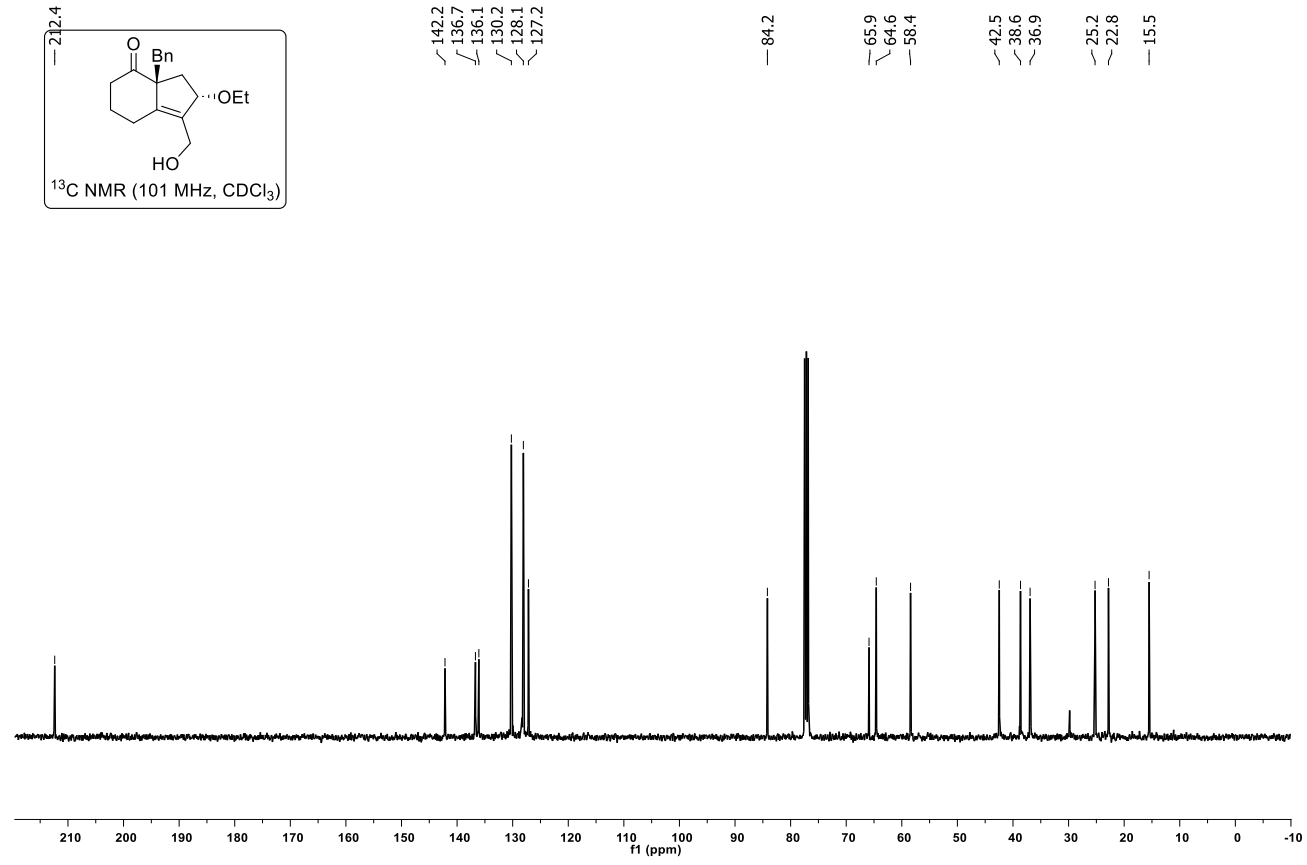


Ethyl (*E*)-3-((2*S*,7a*R*)-7a-benzyl-2-ethoxy-7-oxo-2,4,5,6,7,7a-hexahydro-1*H*-inden-3-yl)acrylate(6):

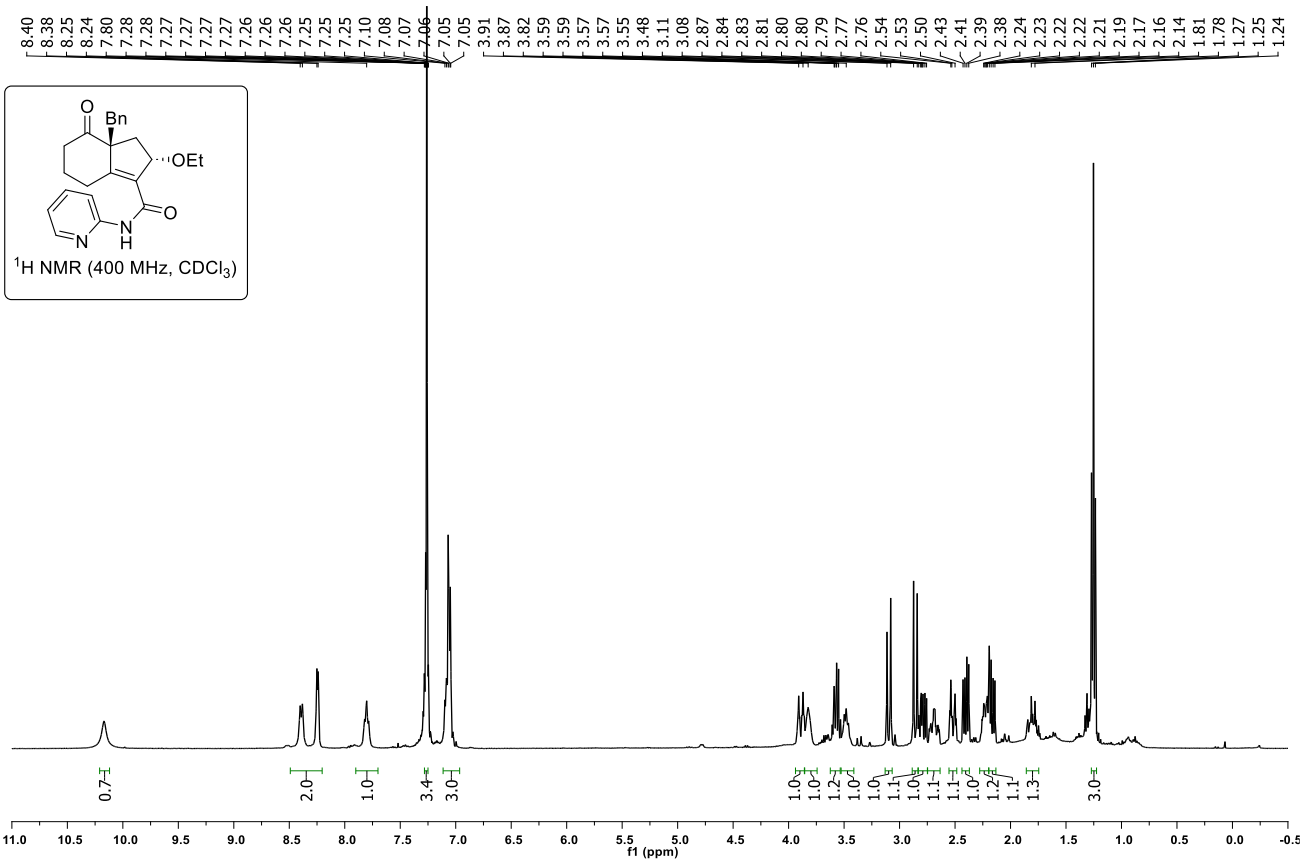


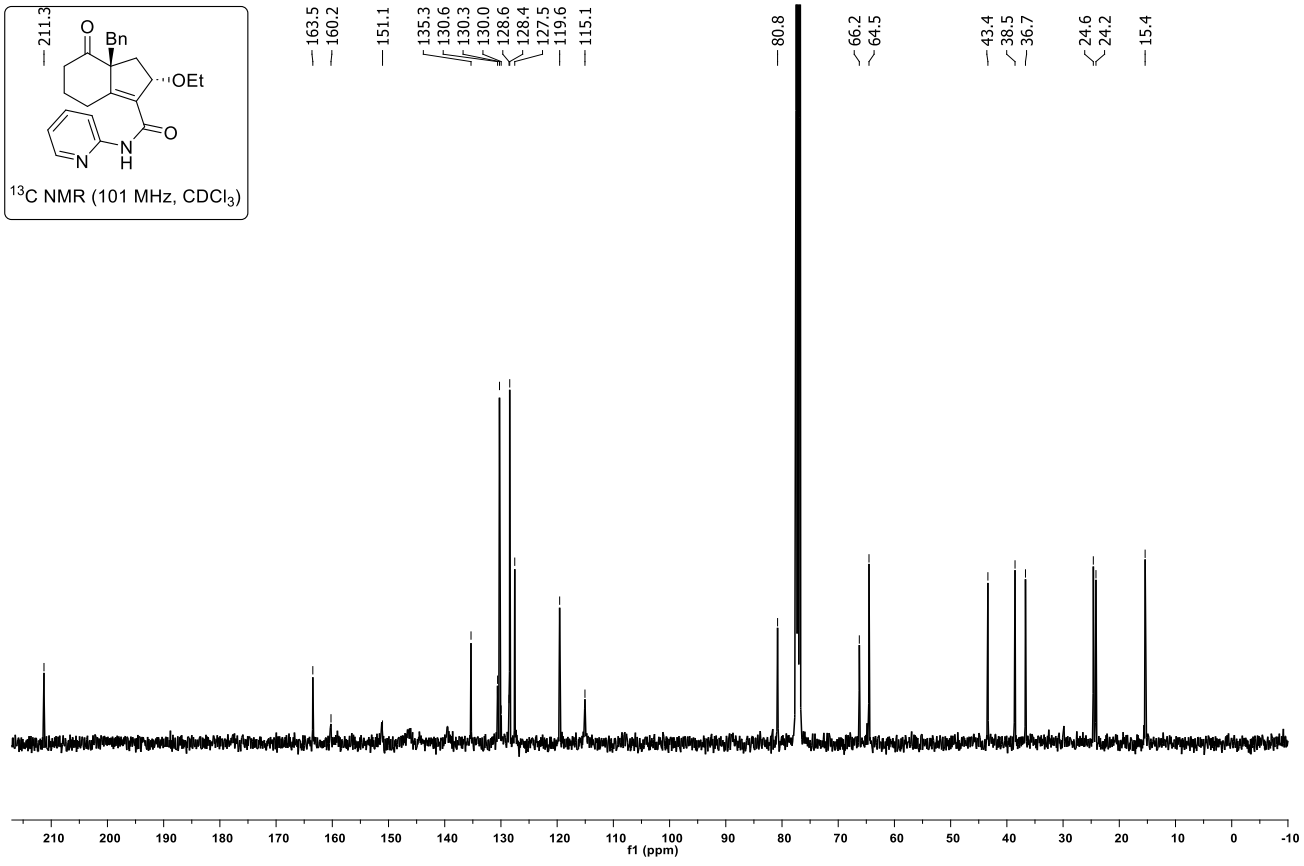
(2*S*,3a*R*)-3a-Benzyl-2-ethoxy-1-(hydroxymethyl)-2,3,3a,5,6,7-hexahydro-4*H*-inden-4-one (7):



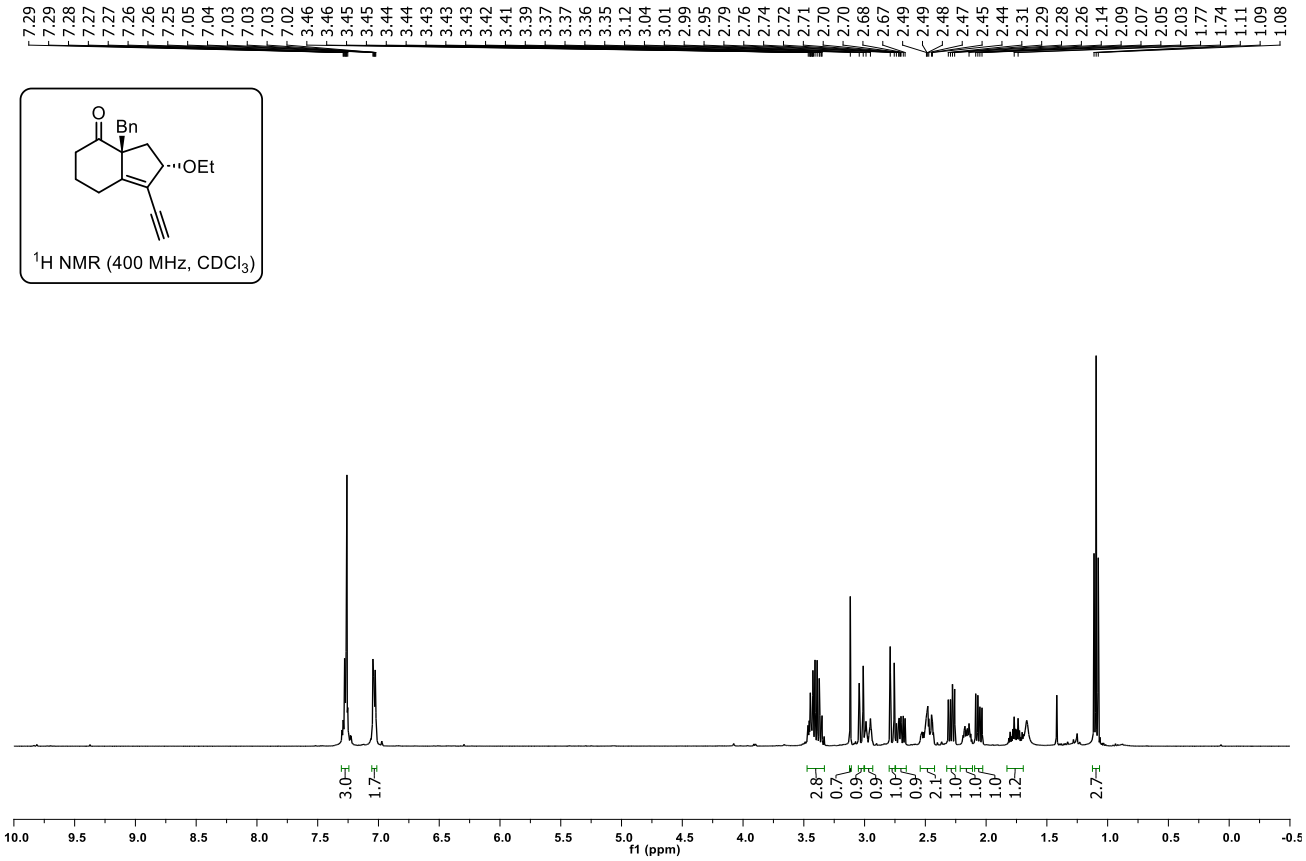


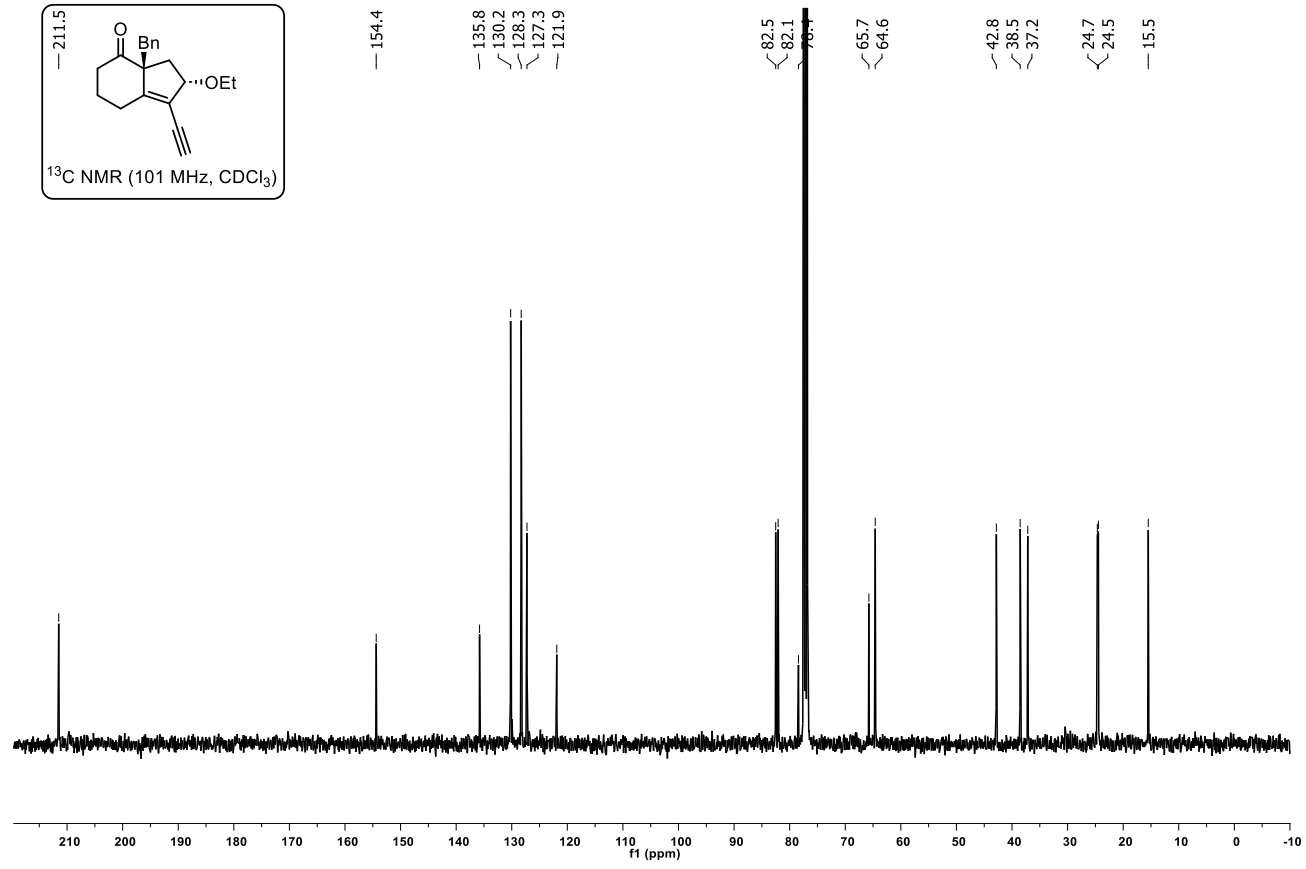
(2*S*,7a*R*)-7a-Benzyl-2-ethoxy-7-oxo-N-(pyridin-2-yl)-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carboxamide(8):



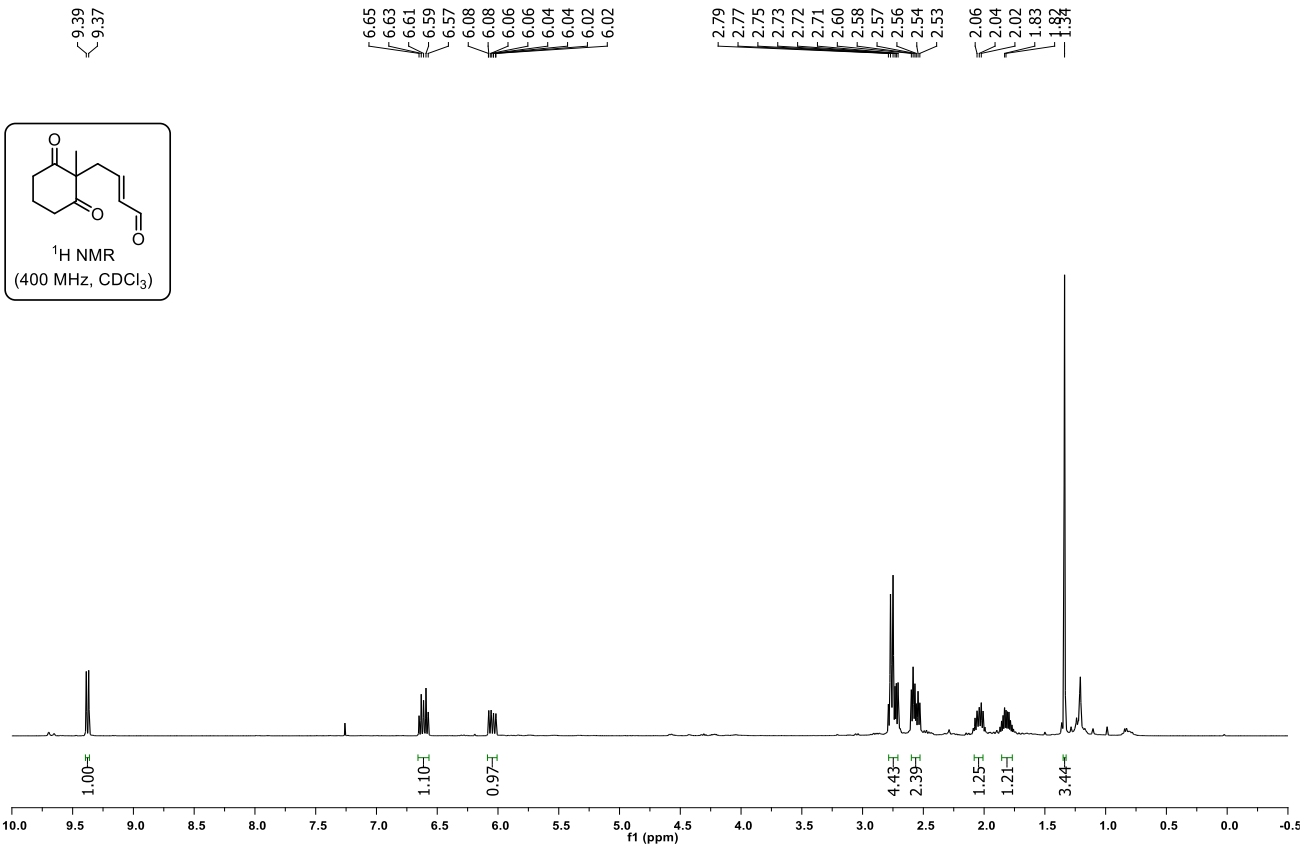


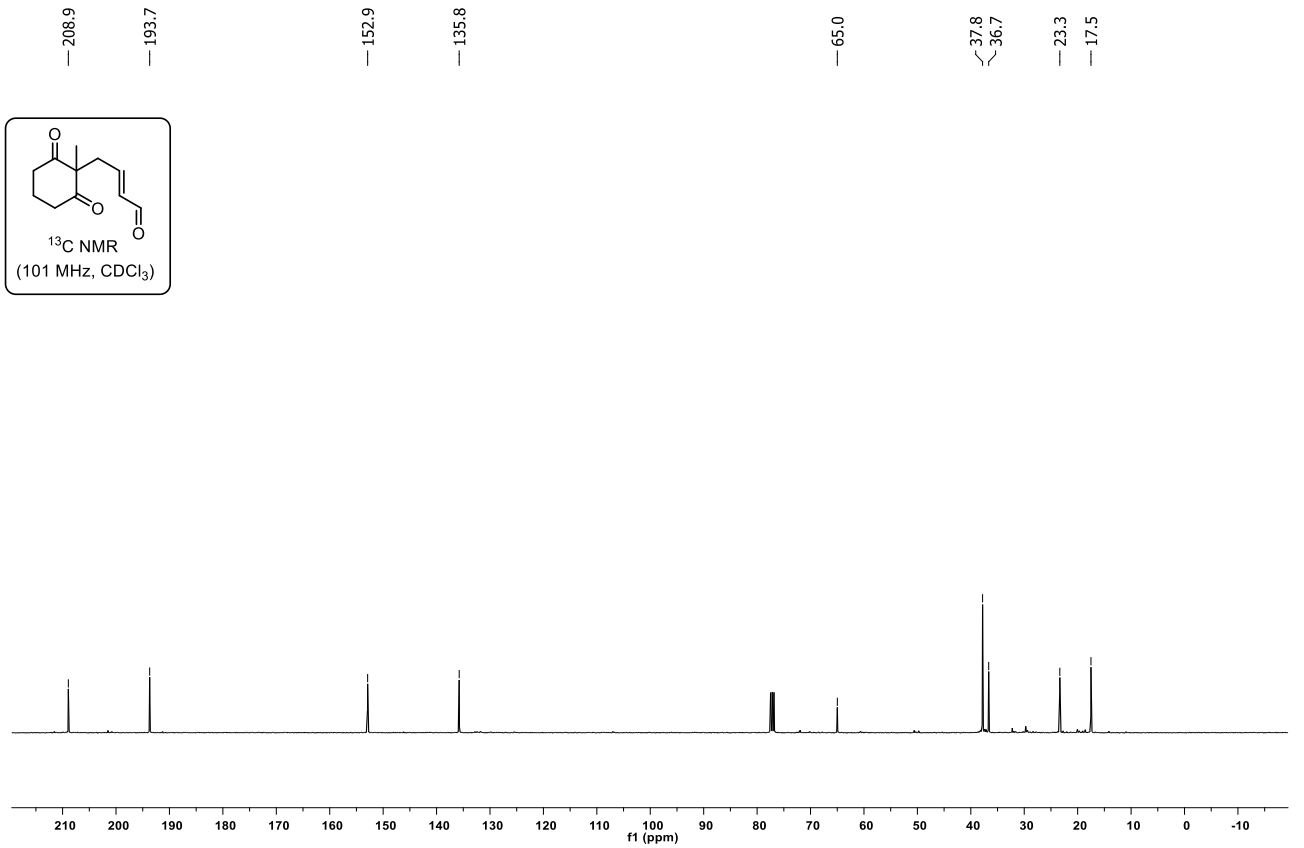
(2*S*,3a*R*)-3a-Benzyl-2-ethoxy-1-ethynyl-2,3,3a,5,6,7-hexahydro-4*H*-inden-4-one (9):



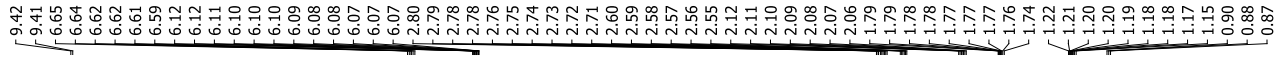


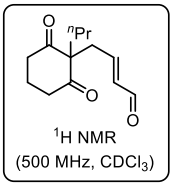
4-(1-Methyl-2,6-dioxocyclohexyl)but-2-enal (1):

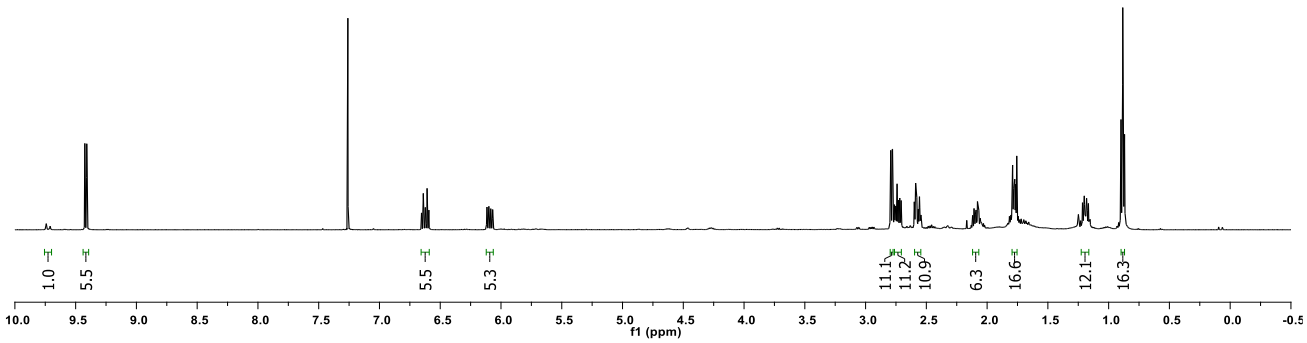


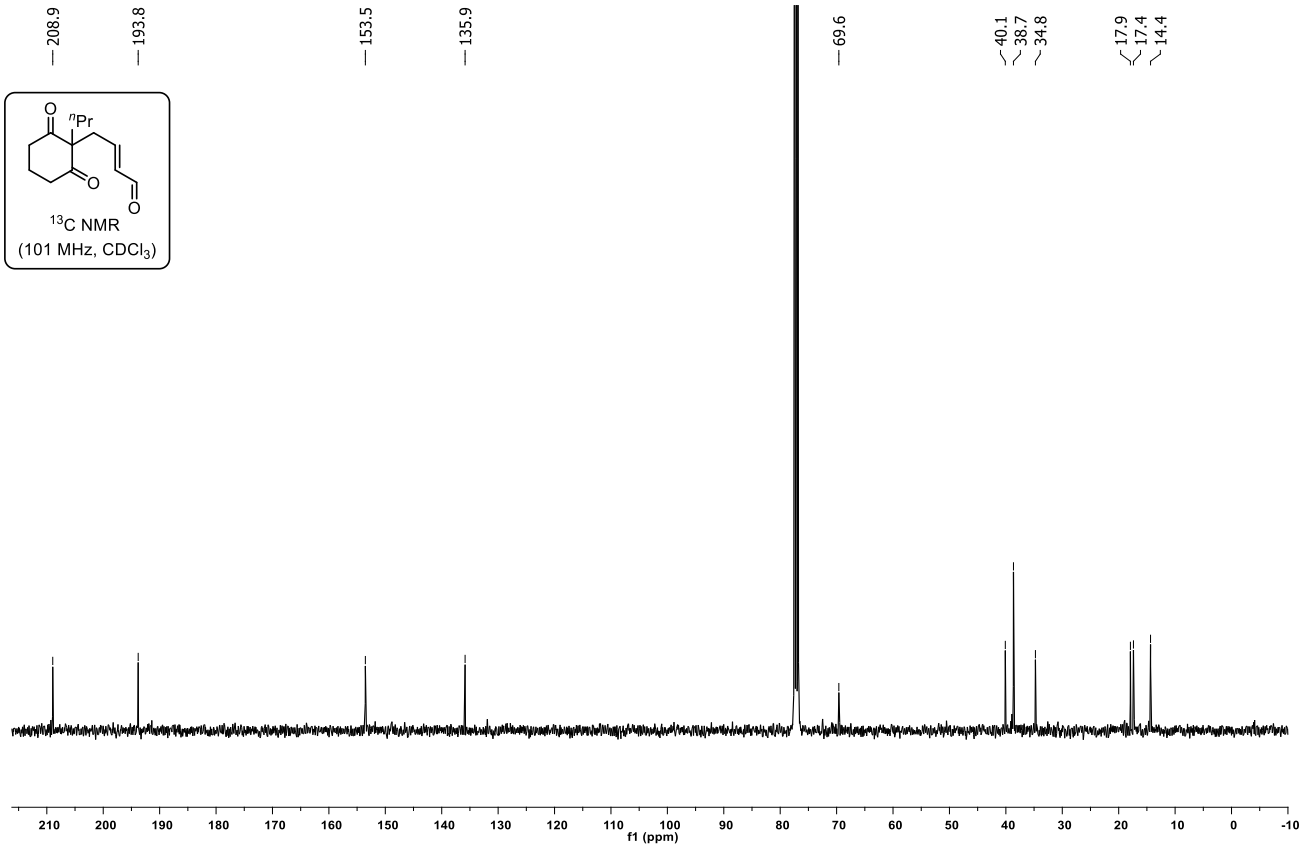


4-(2,6-Dioxo-1-propylcyclohexyl)but-2-enal (1d):

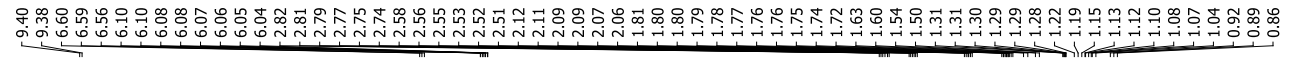


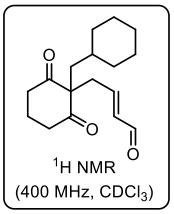


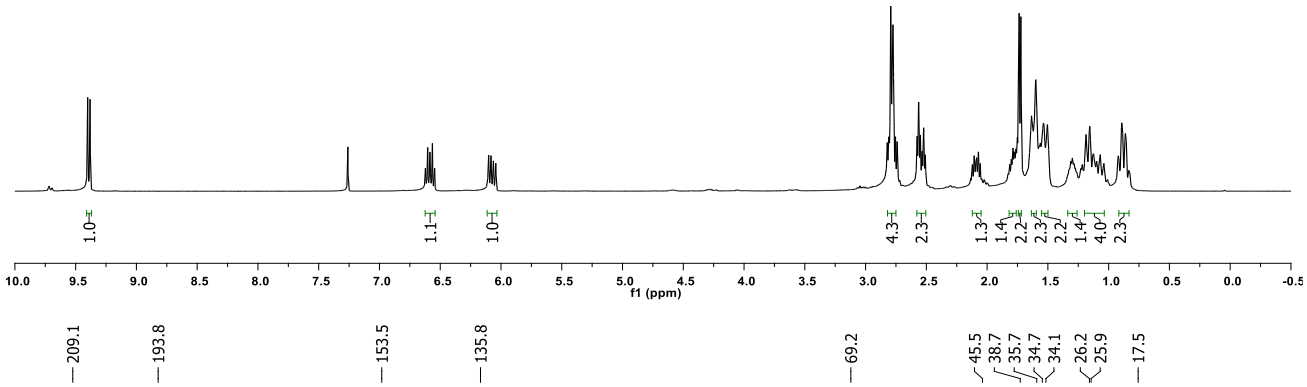


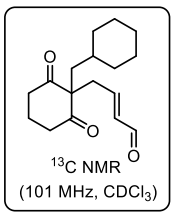


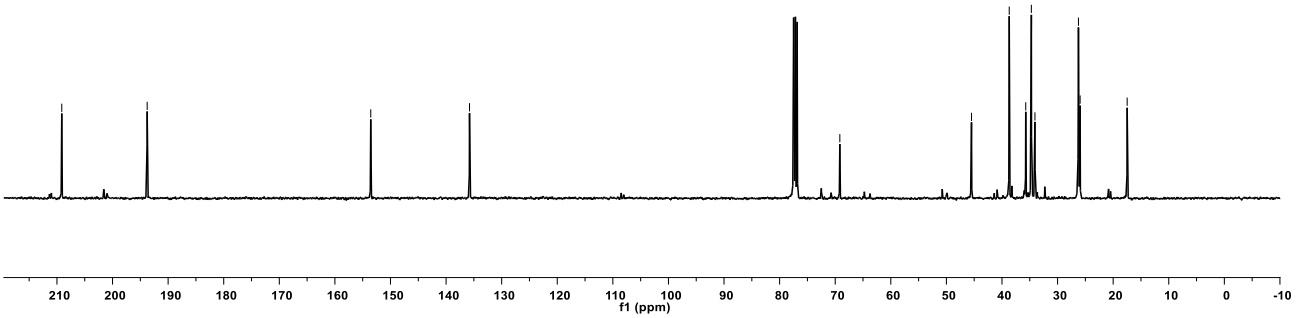
4-(1-(Cyclohexylmethyl)-2,6-dioxocyclohexyl)but-2-enal (1e):



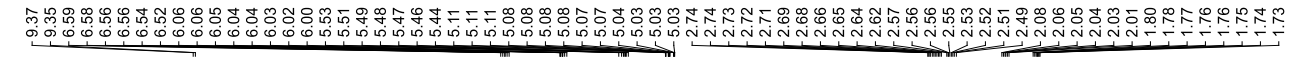


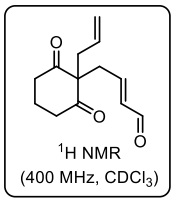


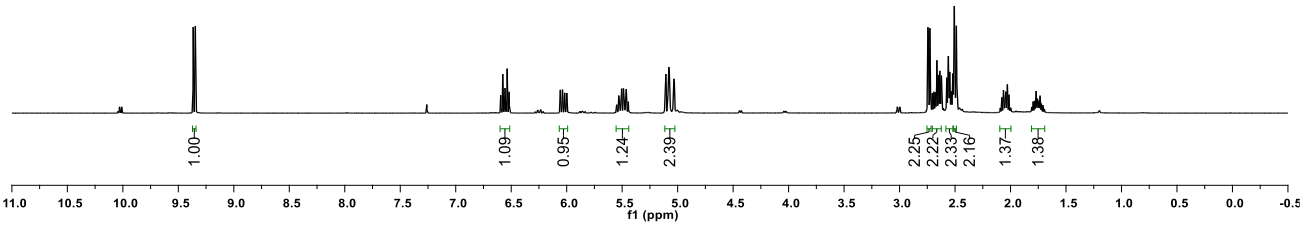


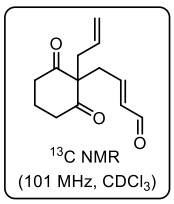


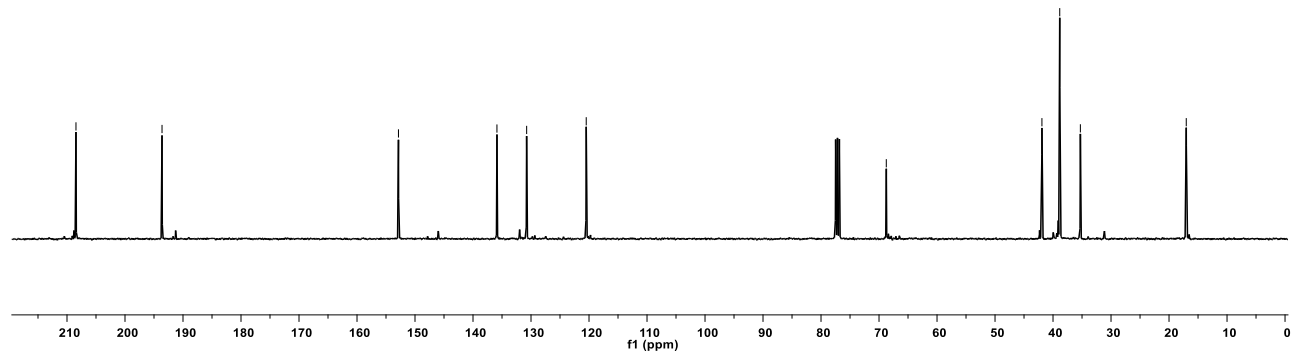
4-(1-Allyl-2,6-dioxocyclohexyl)but-2-enal (1f):



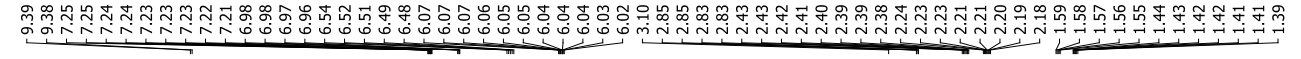


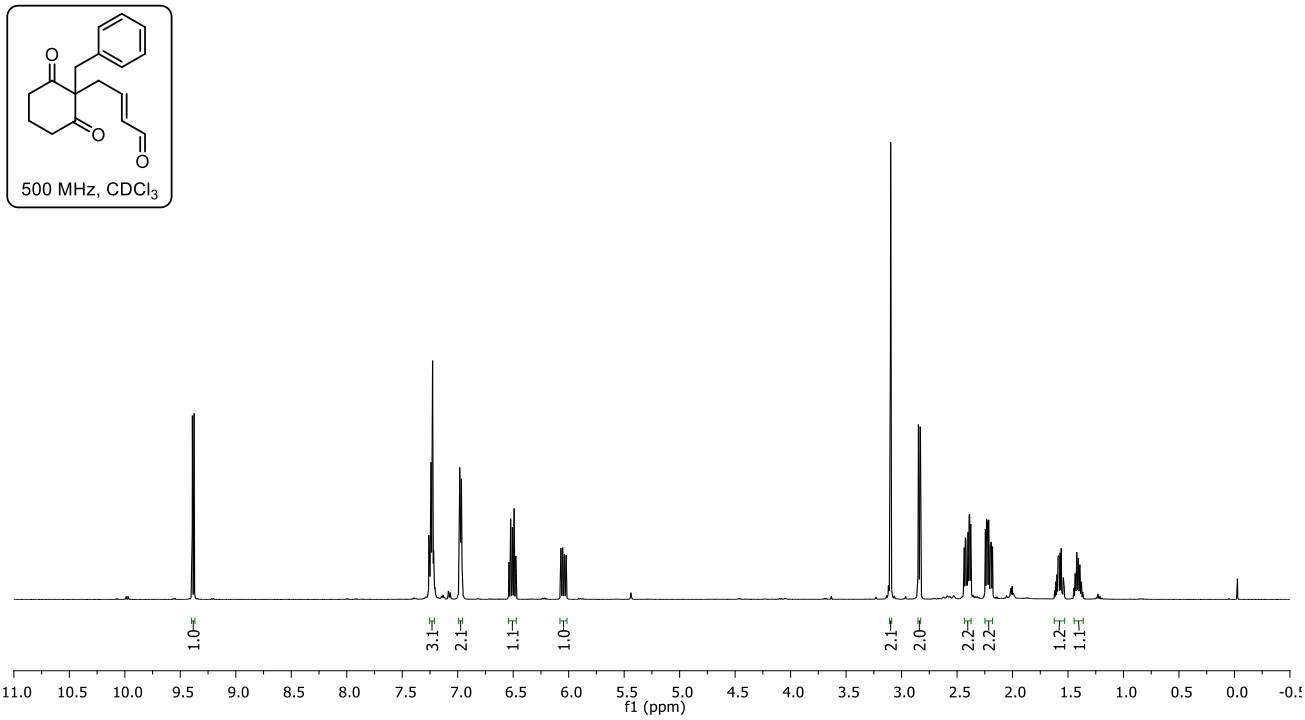


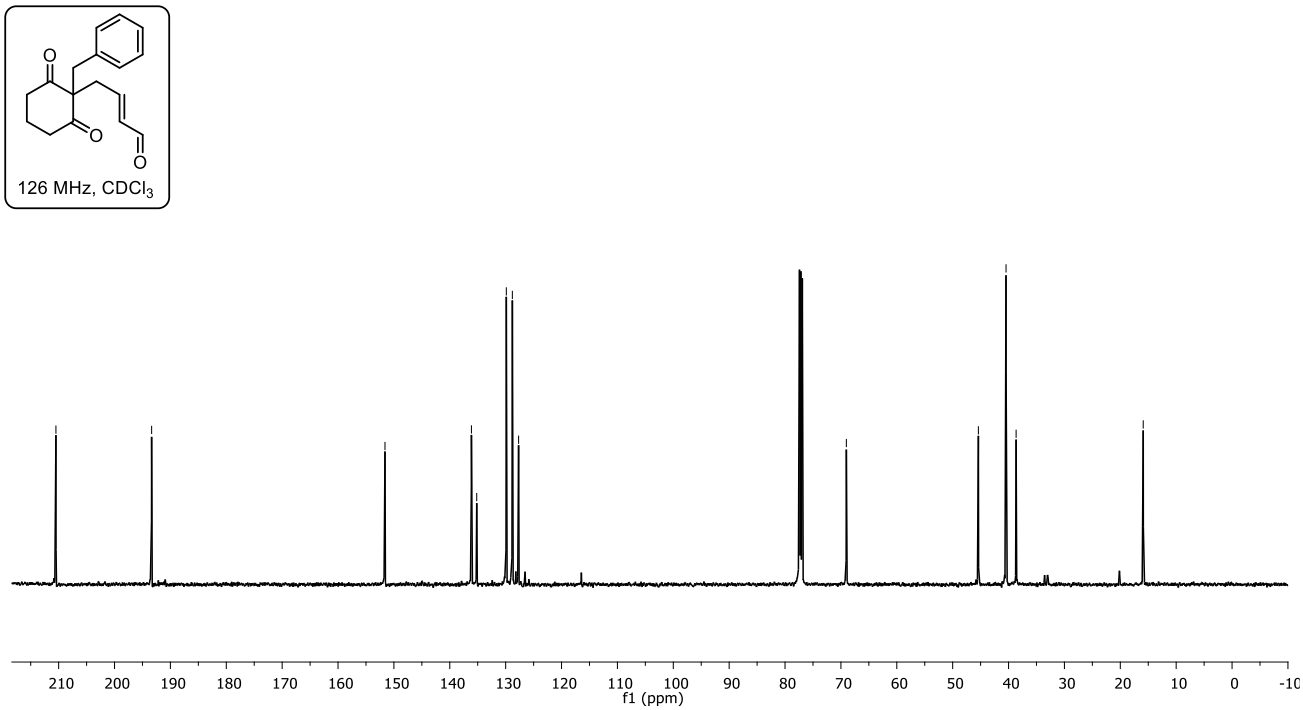




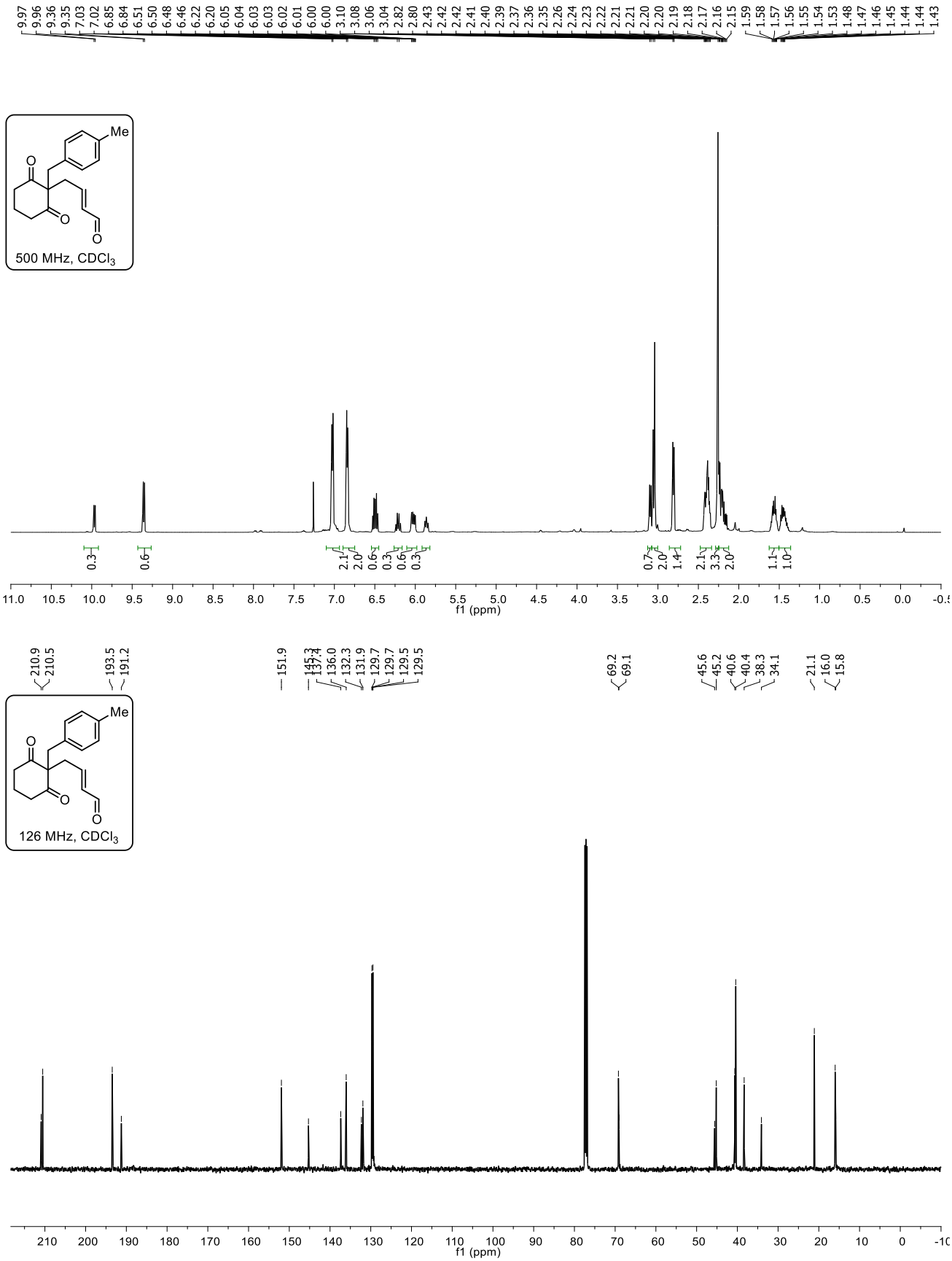
4-(1-Benzyl-2,6-dioxocyclohexyl)but-2-enal(1g):



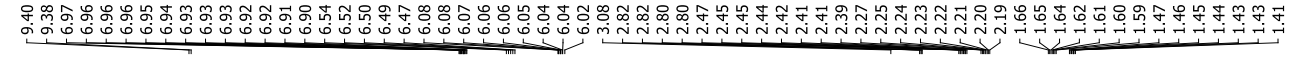


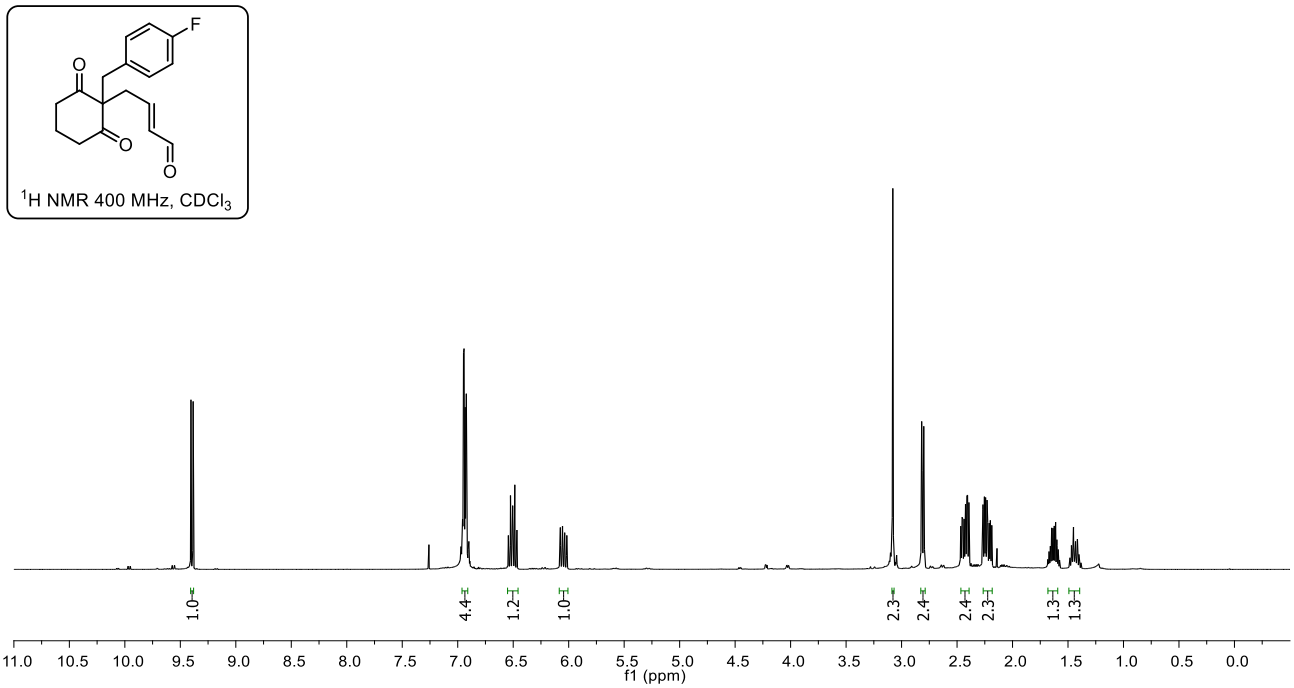


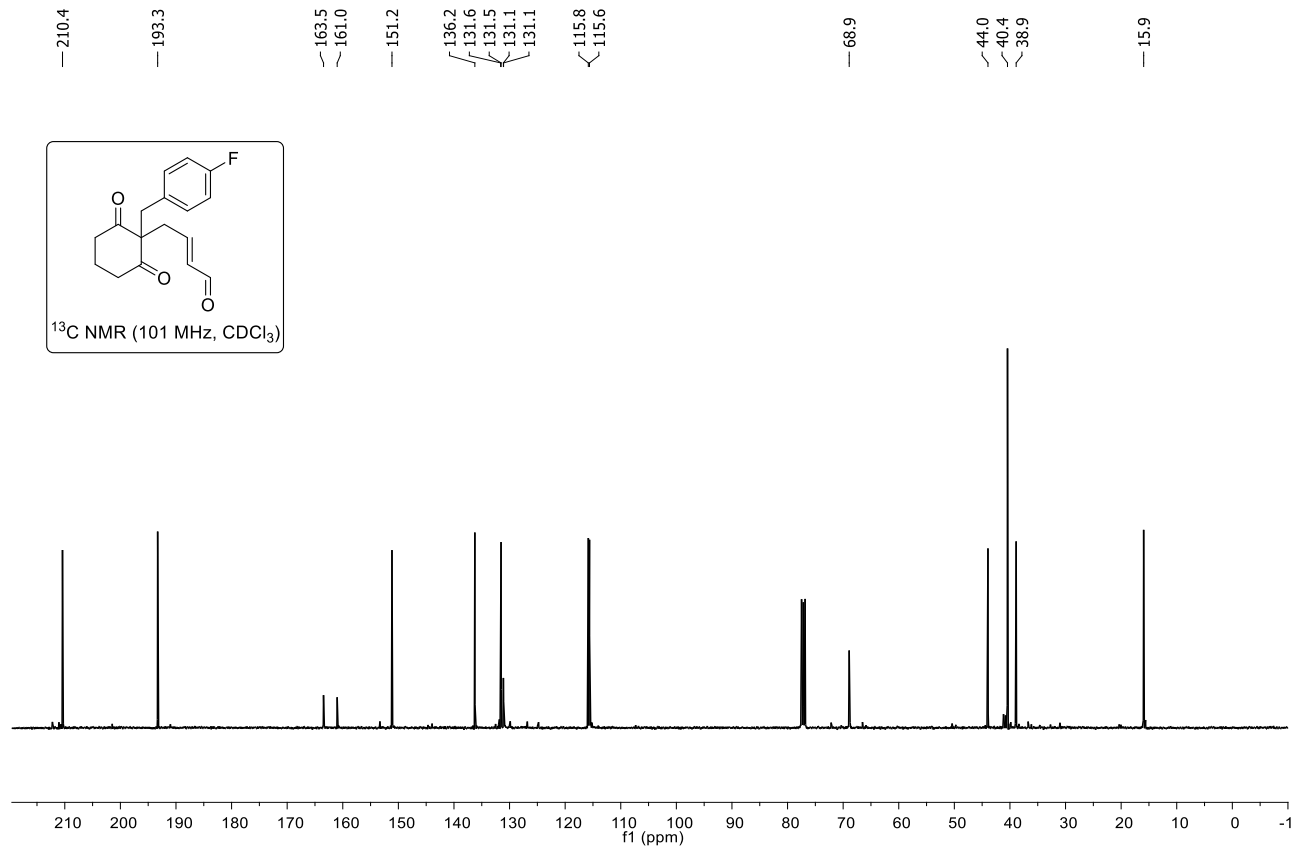
4-(1-(4-Methylbenzyl)-2,6-dioxocyclohexyl)but-2-enal (1h):

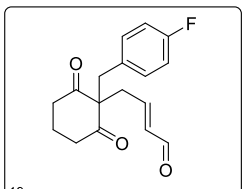


4-(1-(4-Fluorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1i):



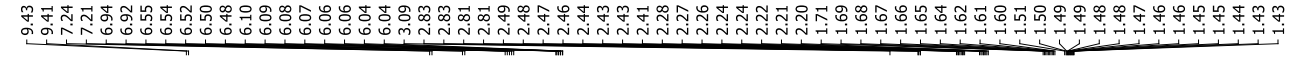


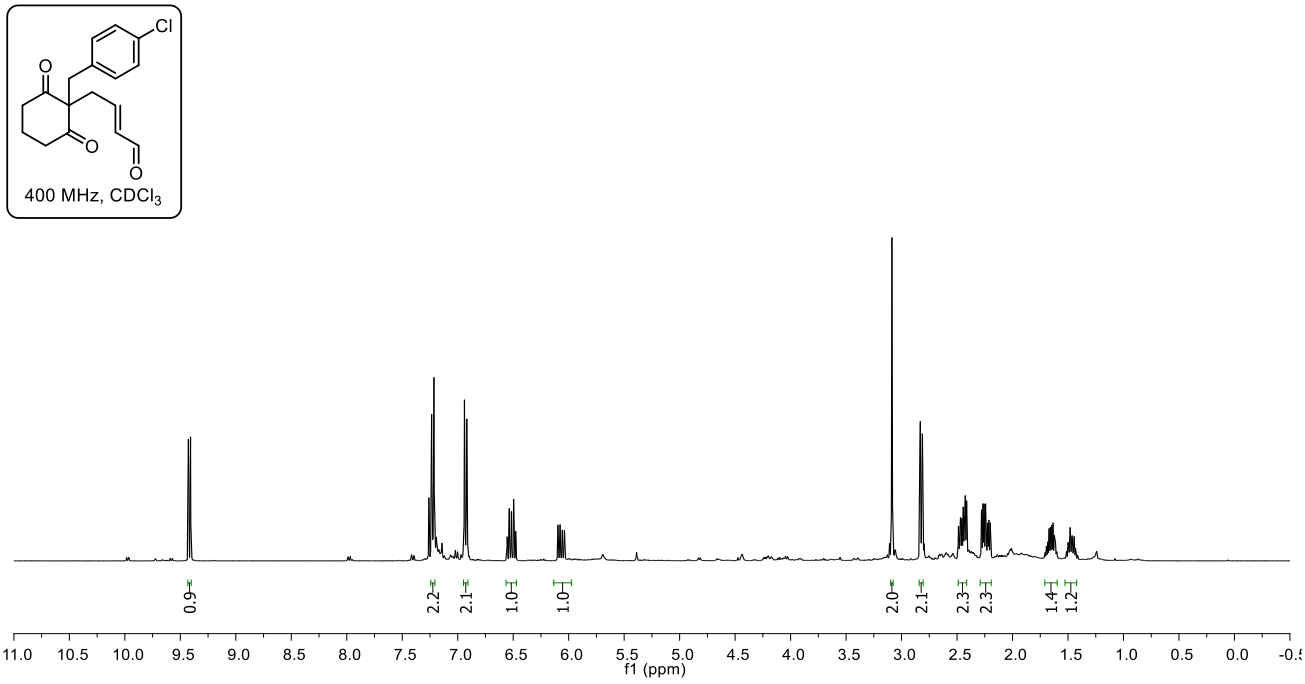


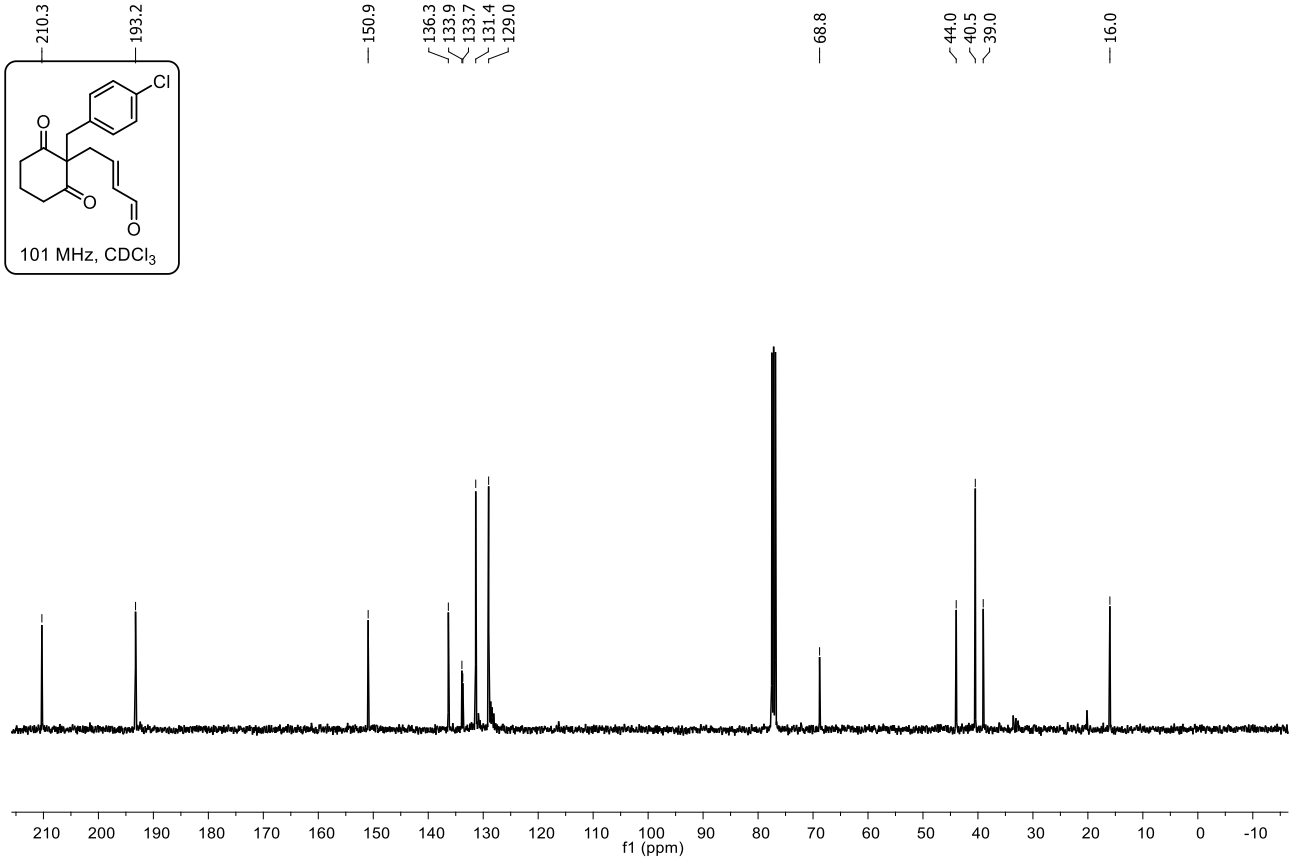


^{19}F NMR (471 MHz, $CDCl_3$)

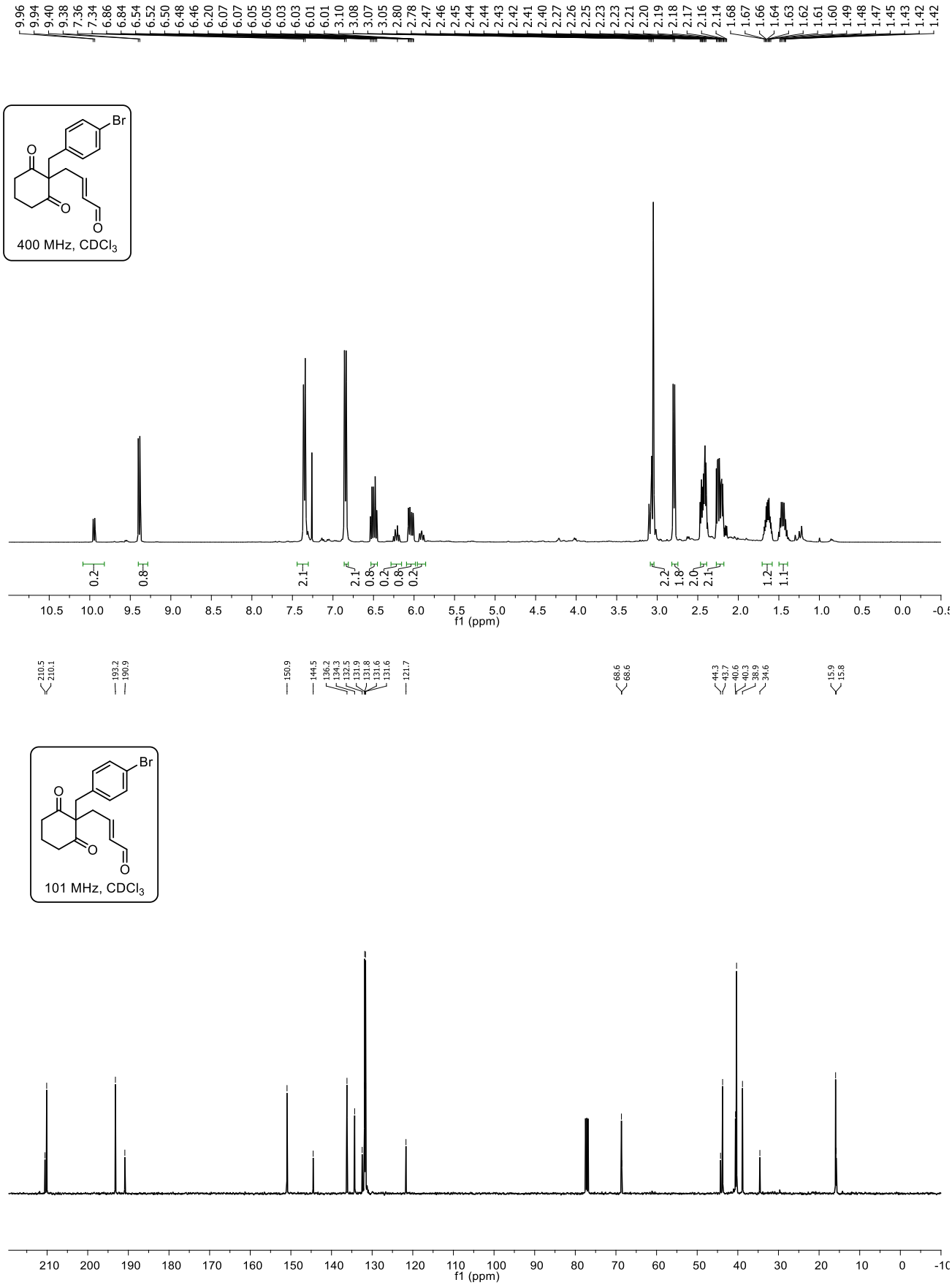
4-(1-(4-Chlorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1j):



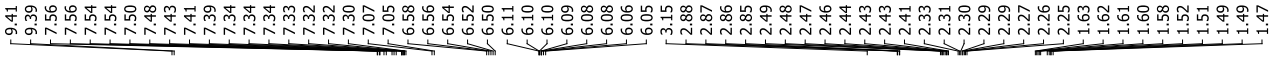


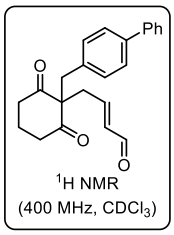


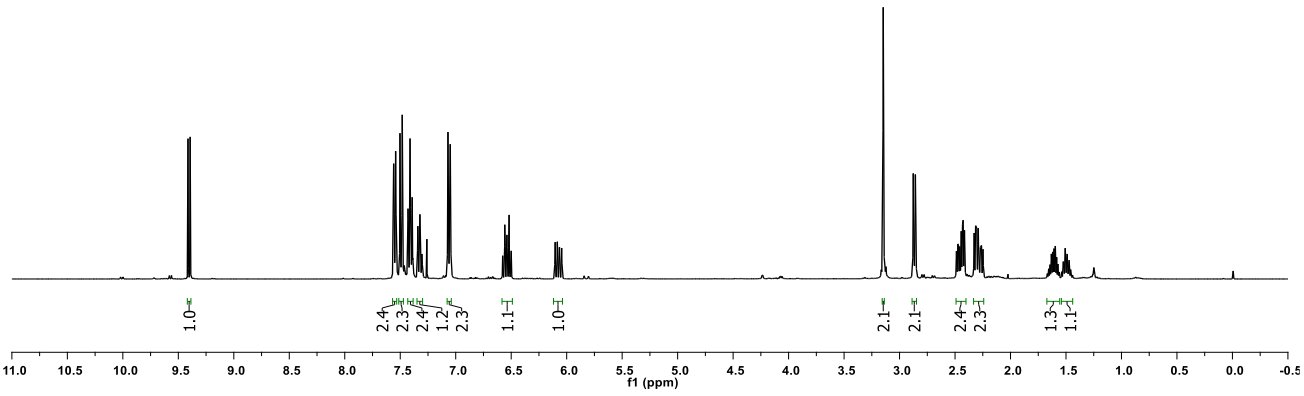
4-(1-(4-Bromobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1k):

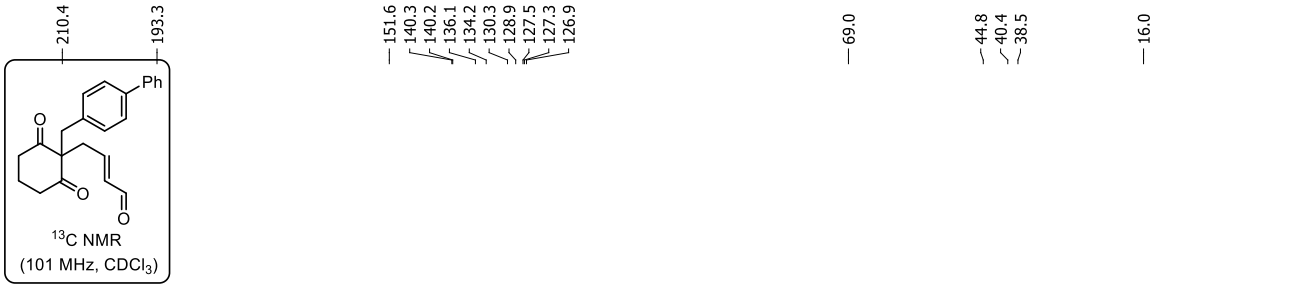


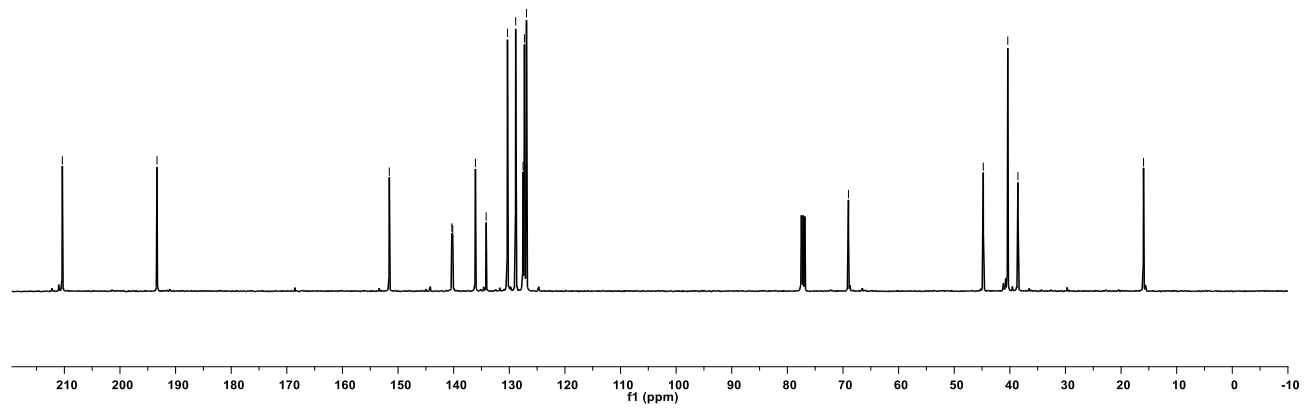
4-(1-([1,1'-Biphenyl]-4-ylmethyl)-2,6-dioxocyclohexyl)but-2-enal (1l):



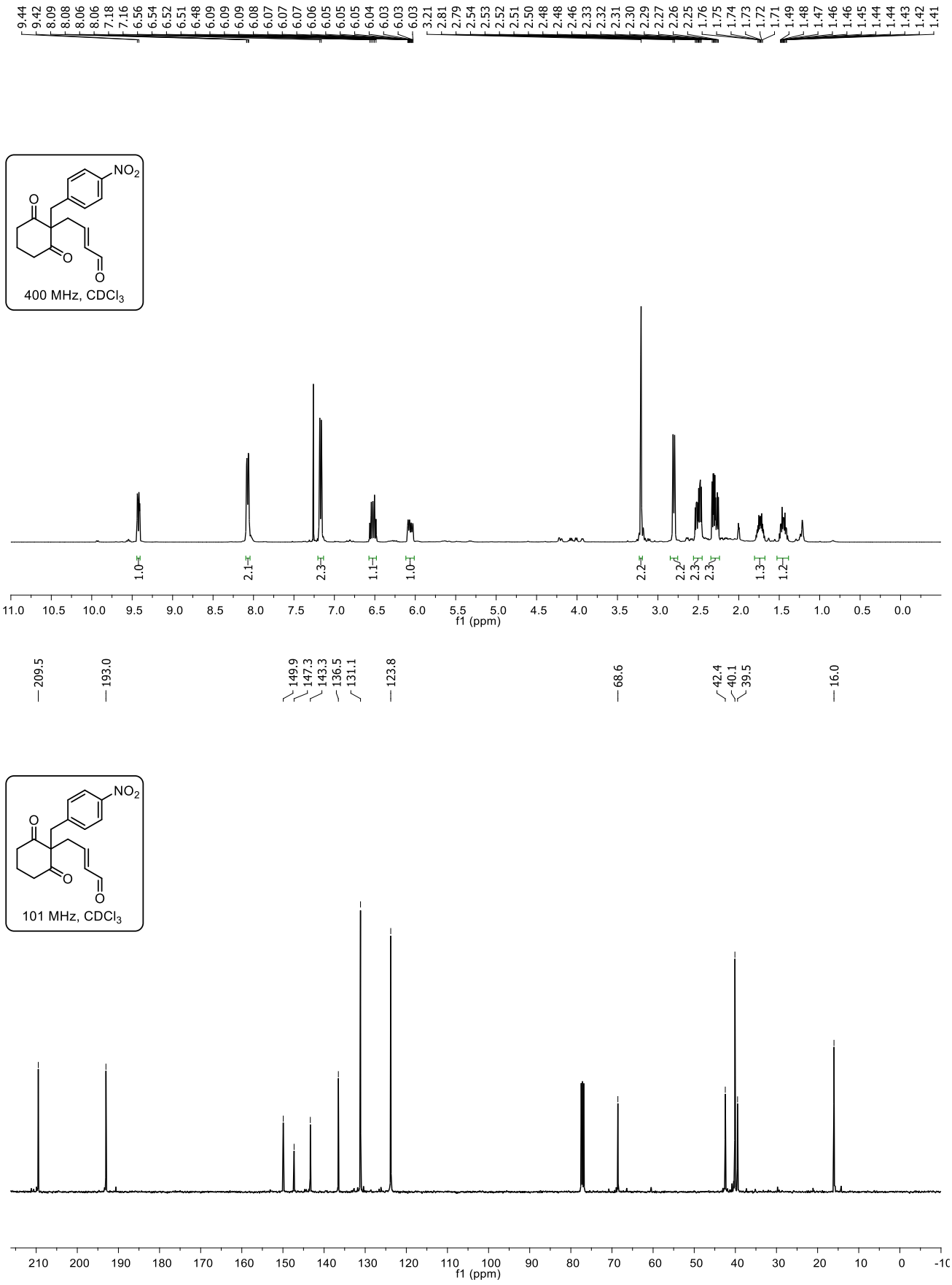




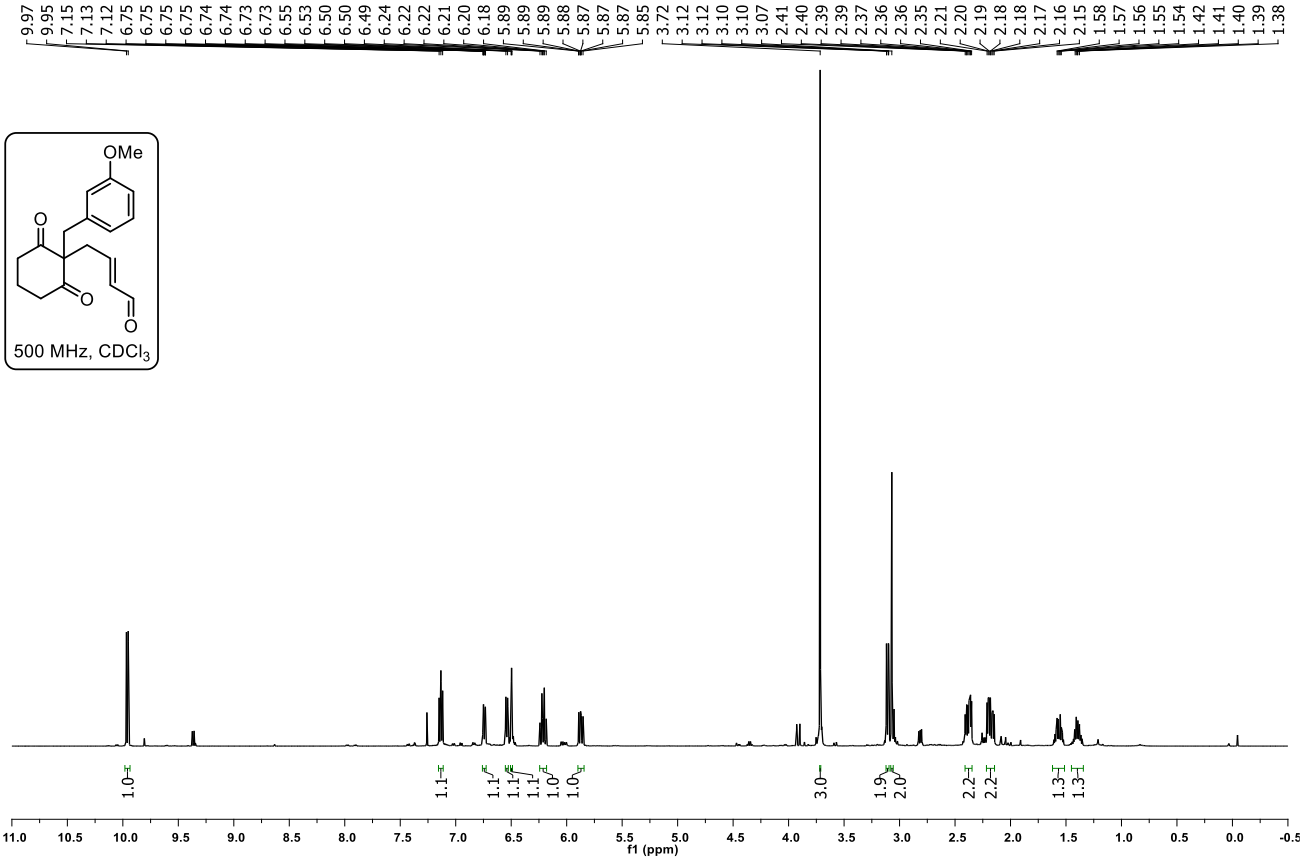


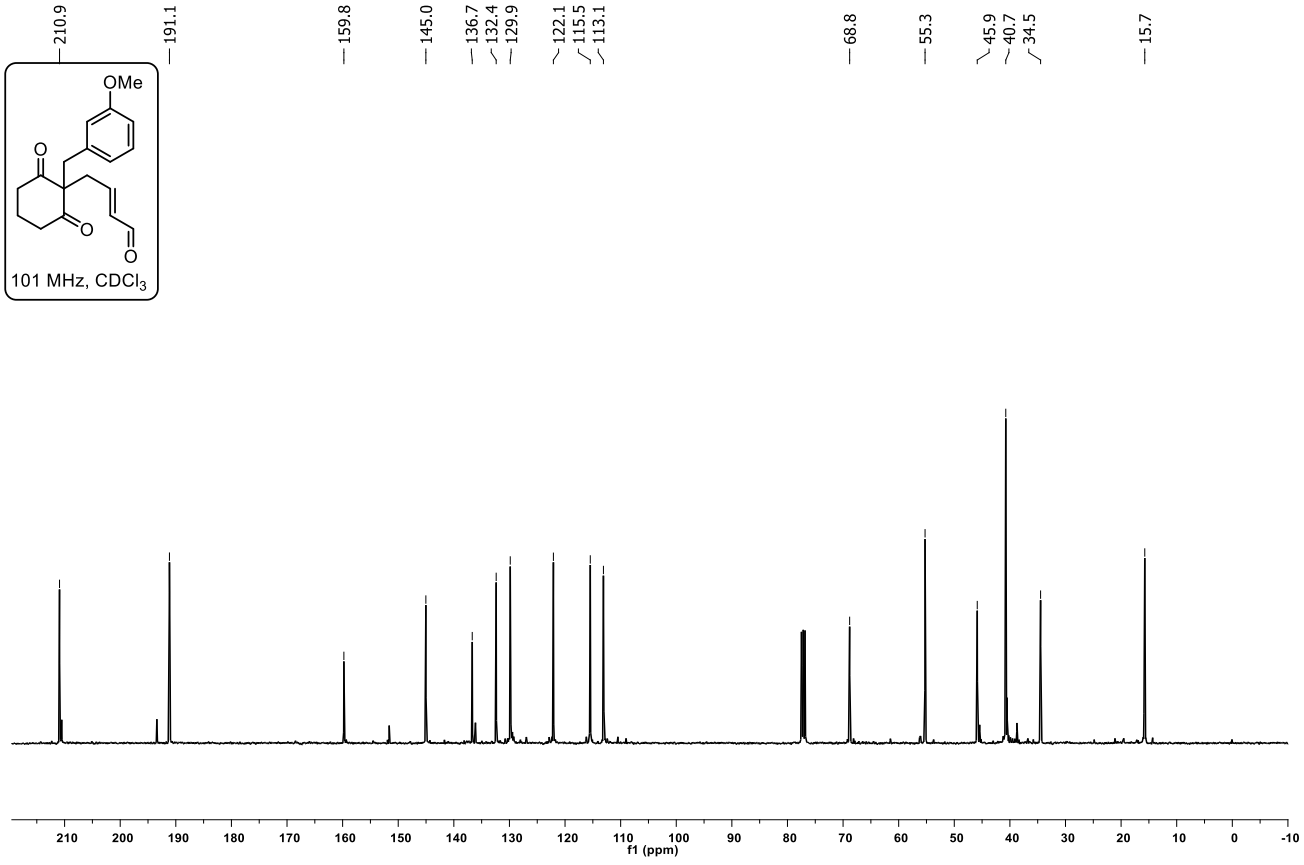


4-(1-(4-Nitrobenzyl)-2,6-dioxocyclohexyl)but-2-enal(1m):

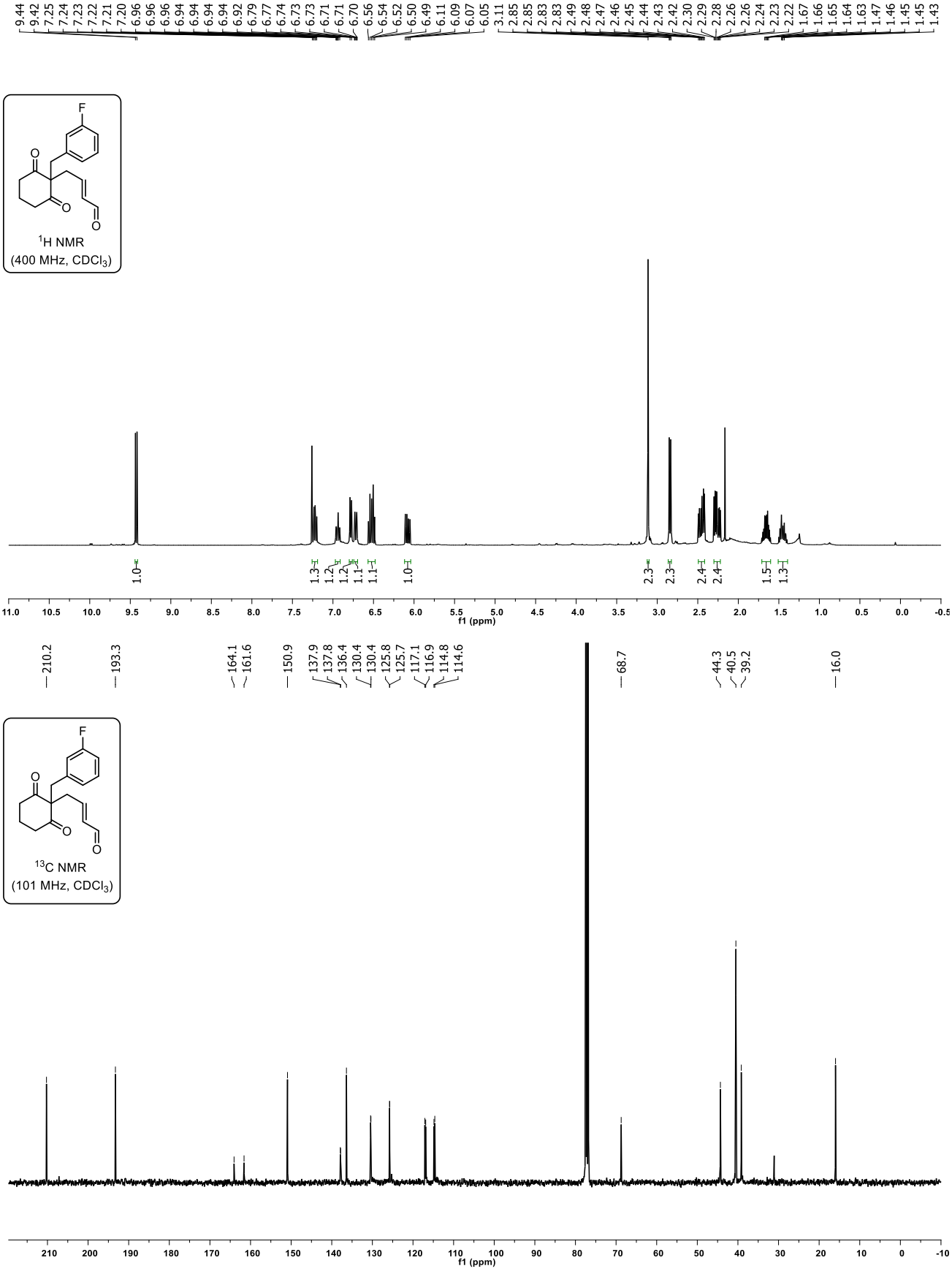


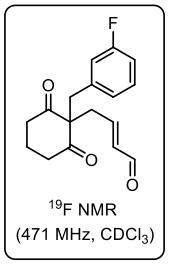
4-(1-(3-Methoxybenzyl)-2,6-dioxocyclohexyl)but-2-enal (1n):





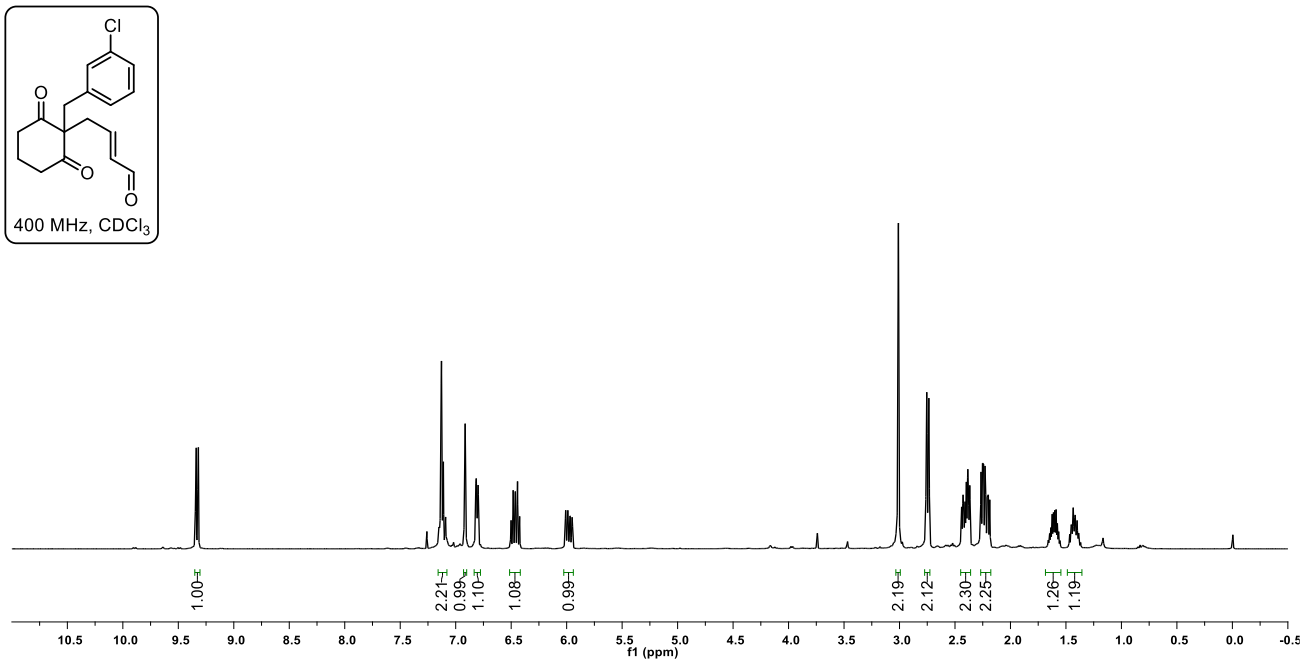
4-(1-(3-Fluorobenzyl)-2,6-dioxocyclohexyl)but-2-enal(1o):

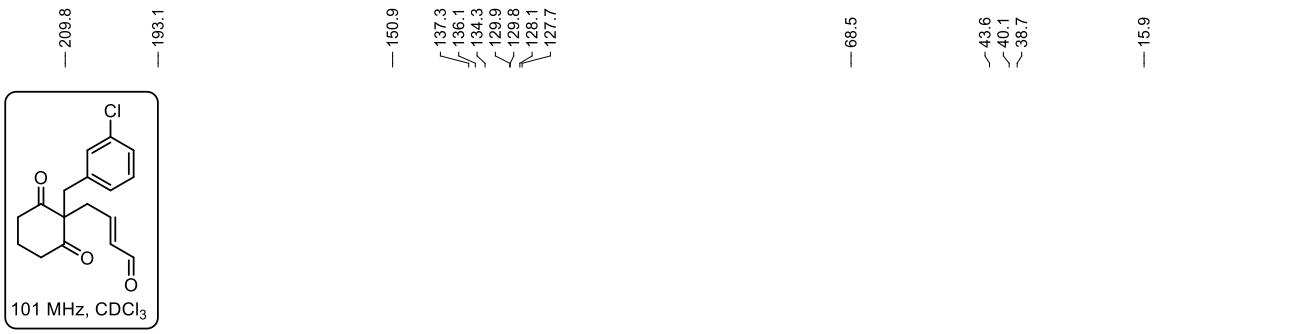




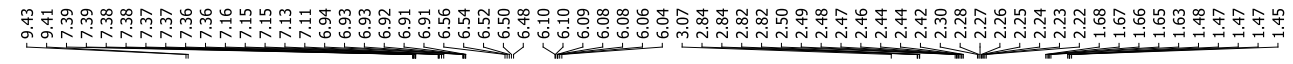
^{19}F NMR
(471 MHz, $CDCl_3$)

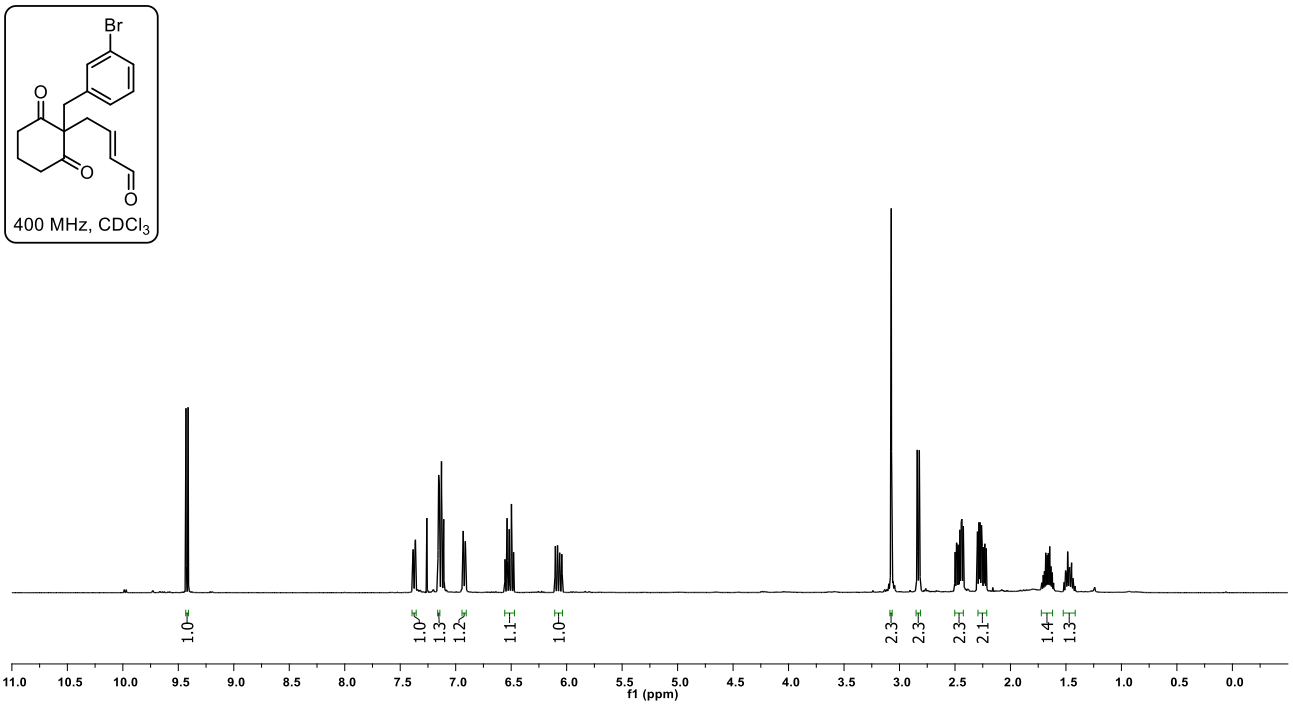
4-(1-(3-Chlorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1p):

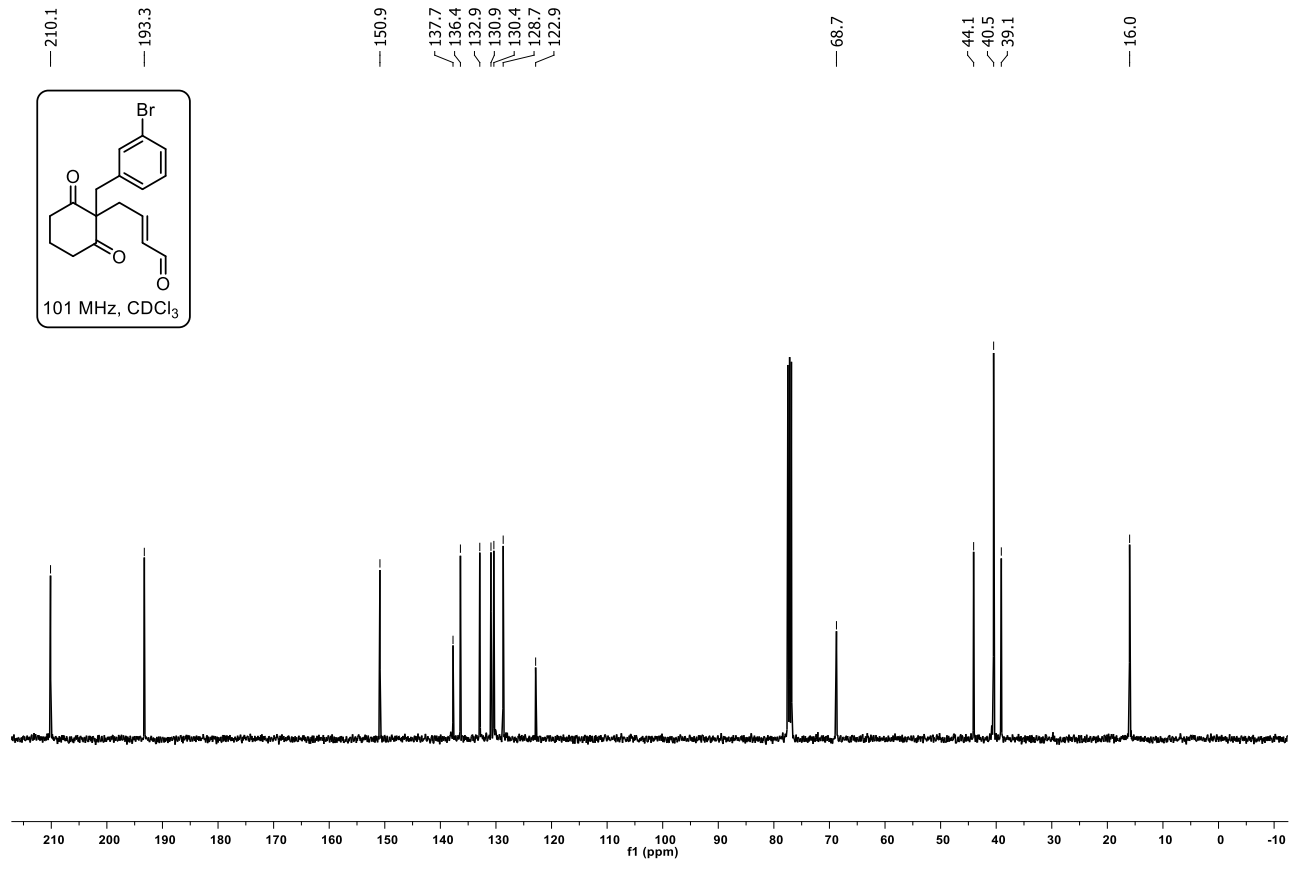




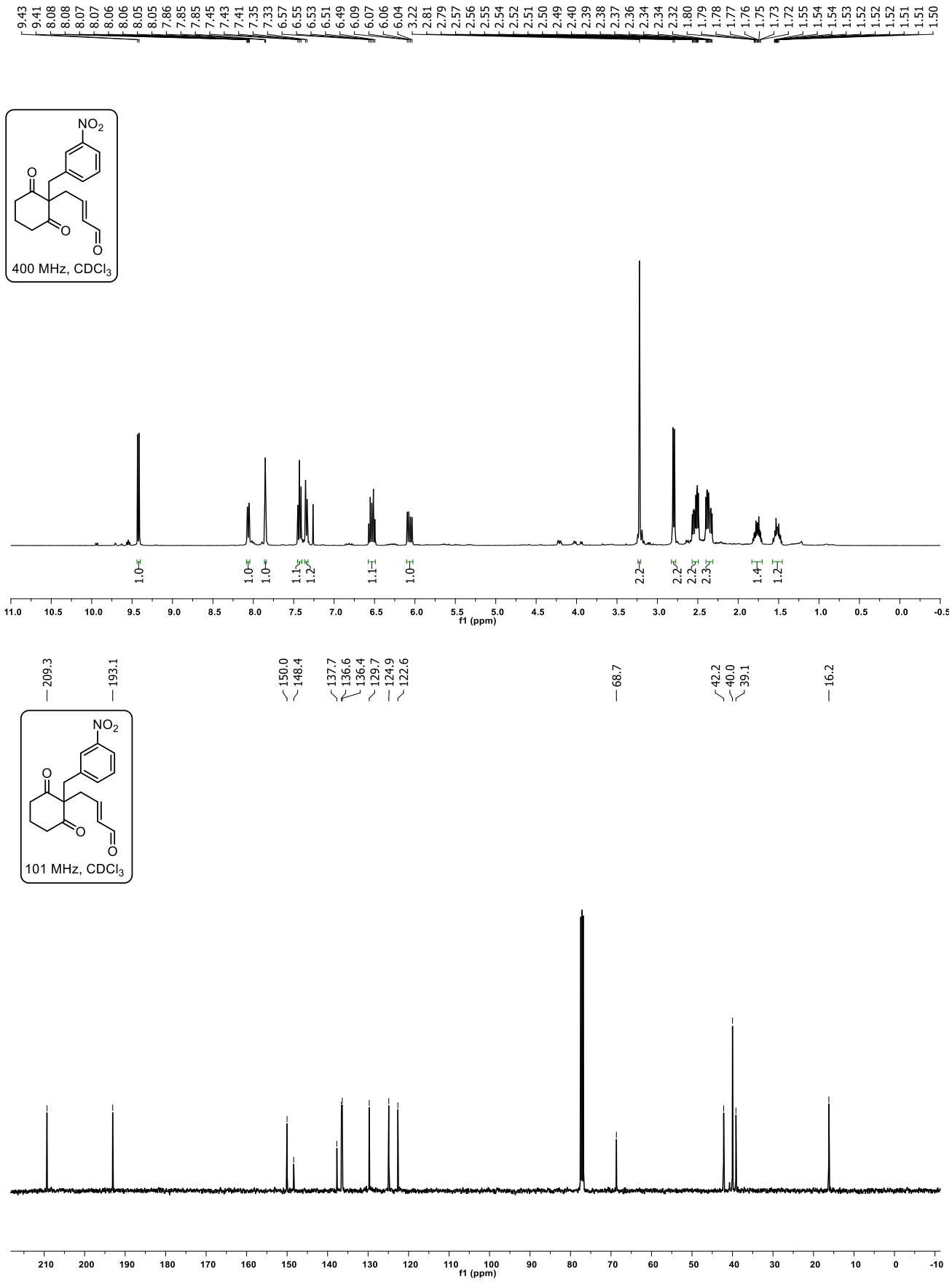
4-(1-(3-Bromobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1q):



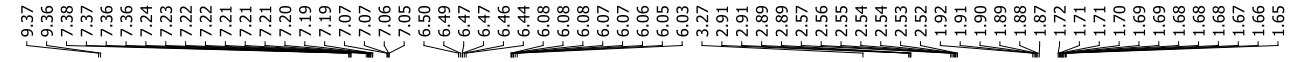


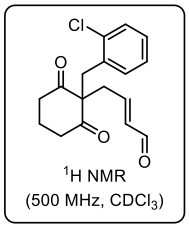


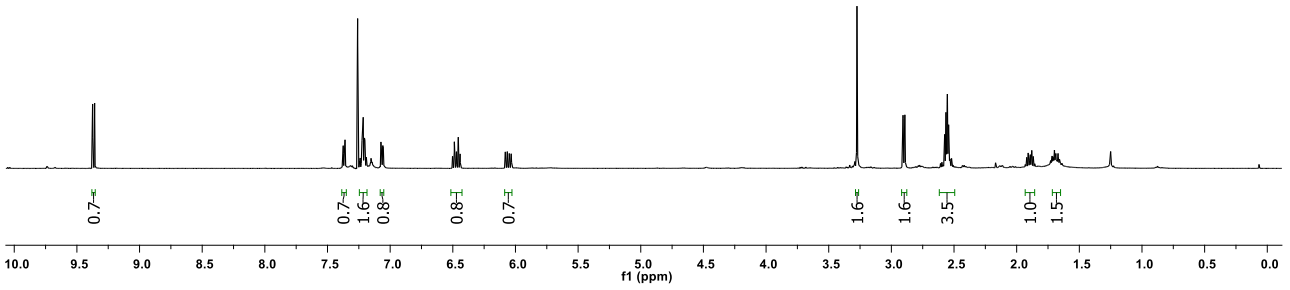
4-(1-(3-Nitrobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1j):

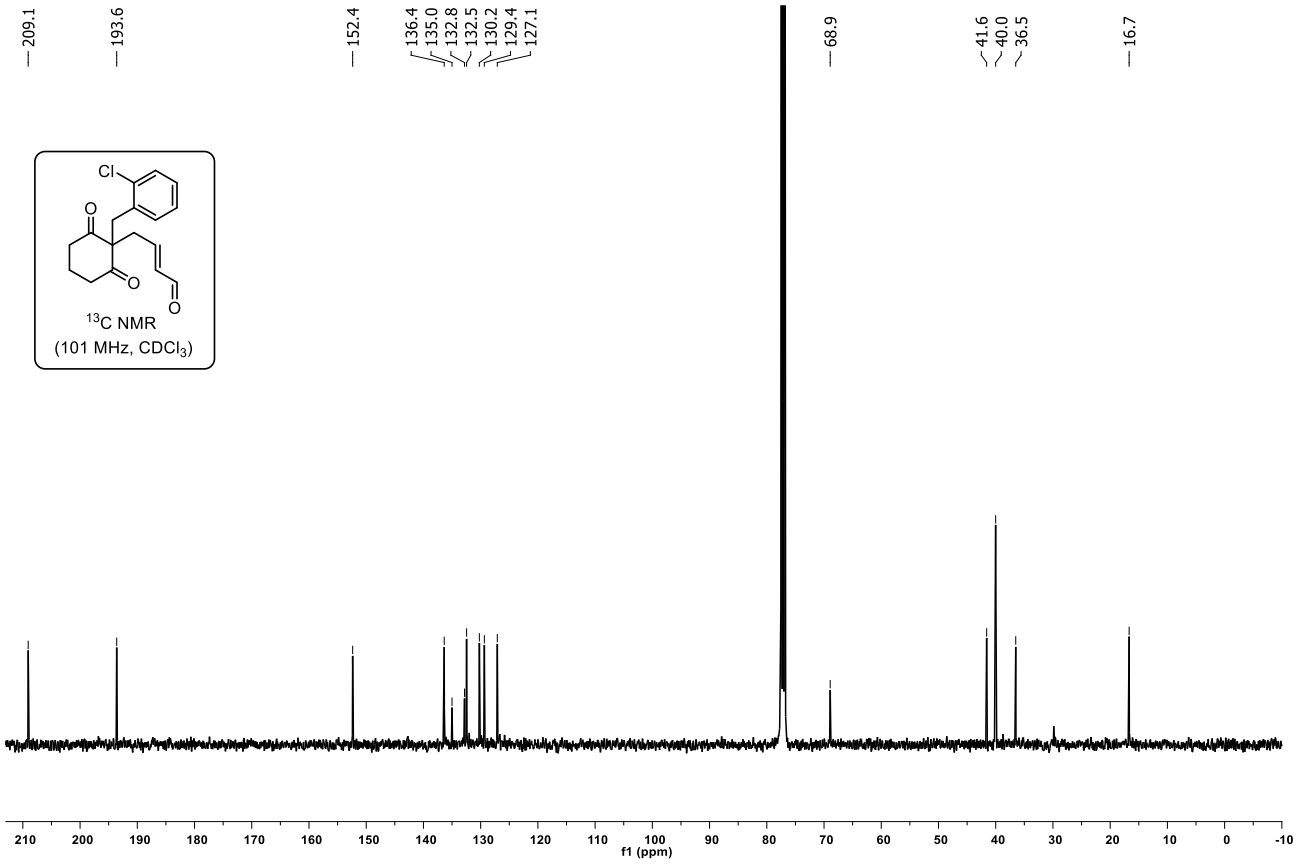


4-(1-(2-Chlorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1s):

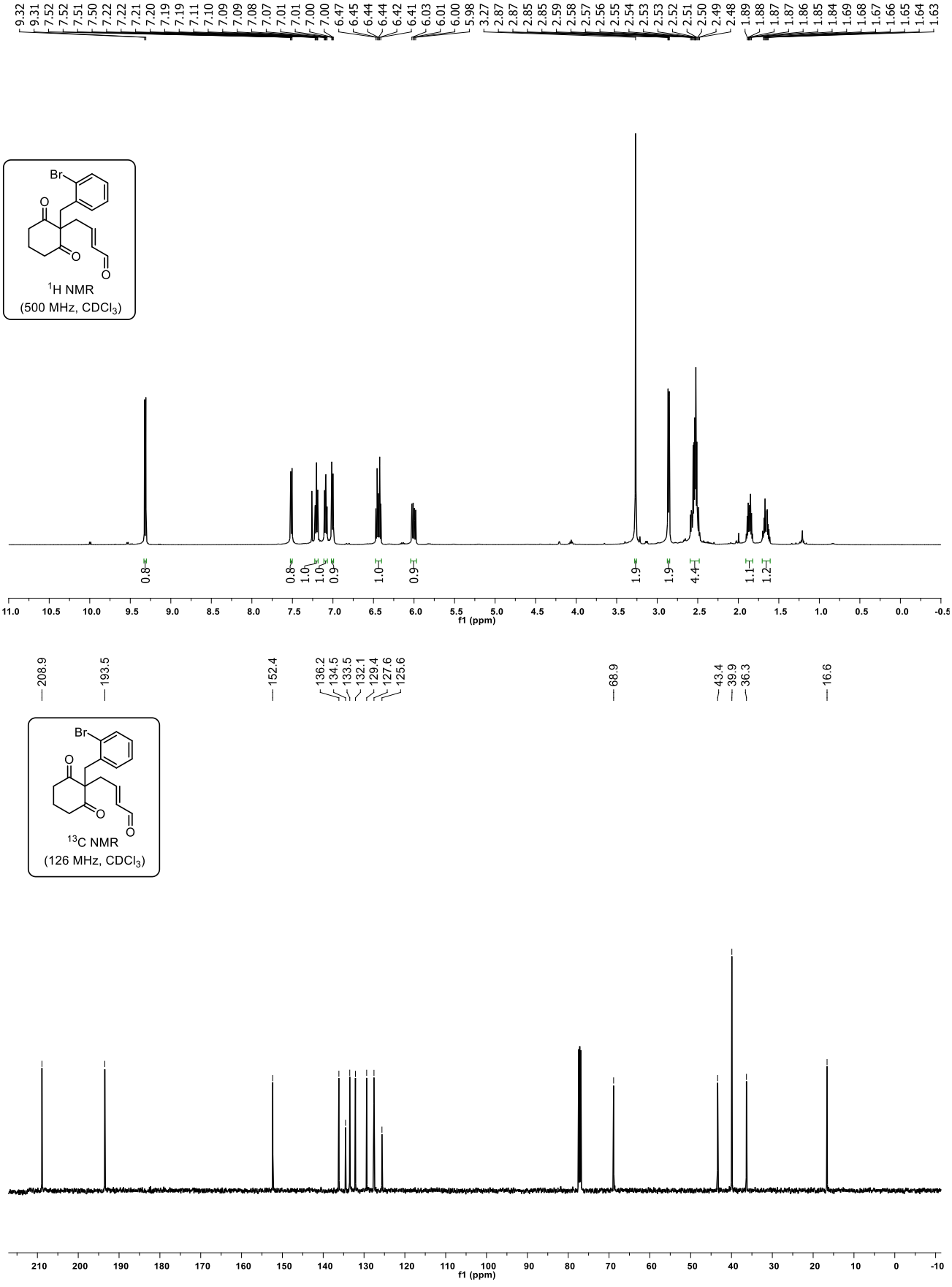




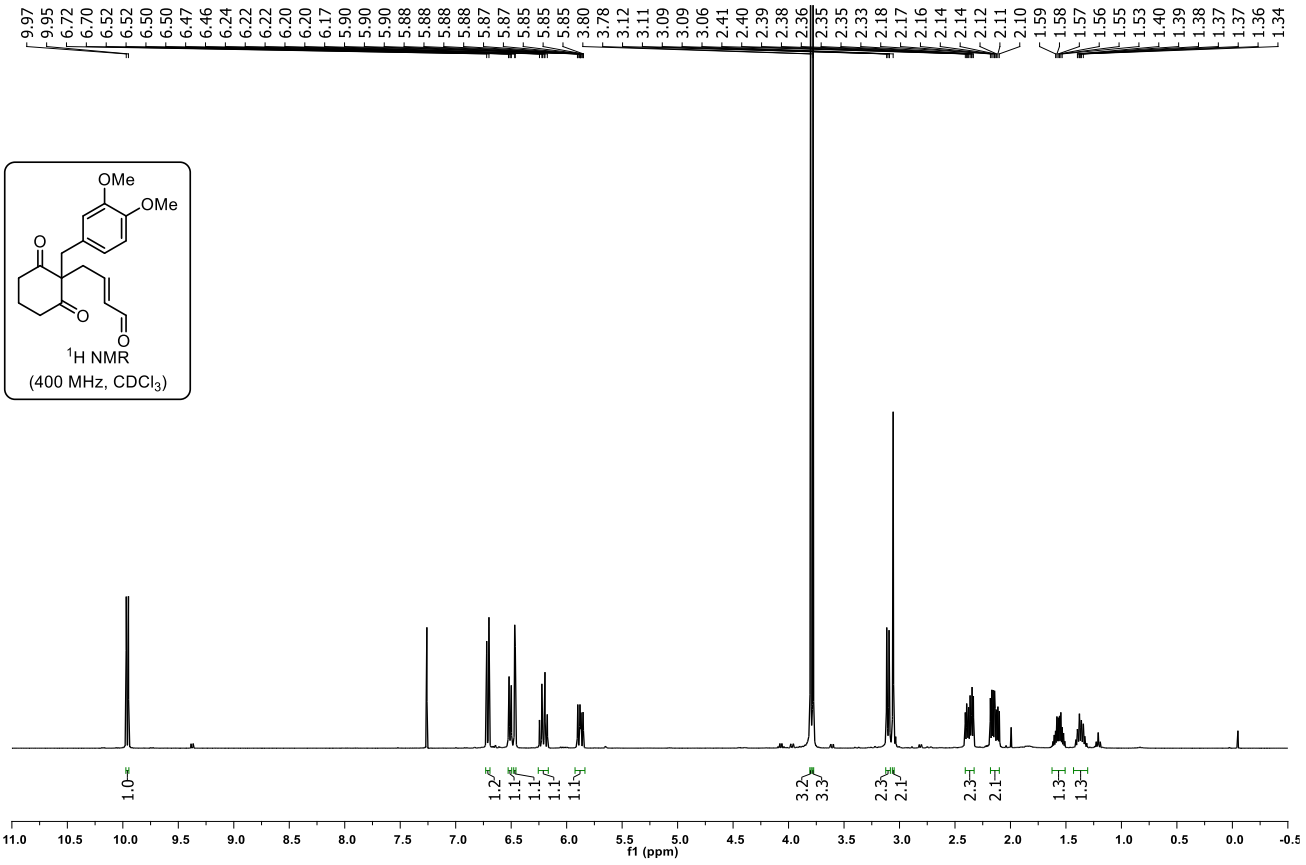


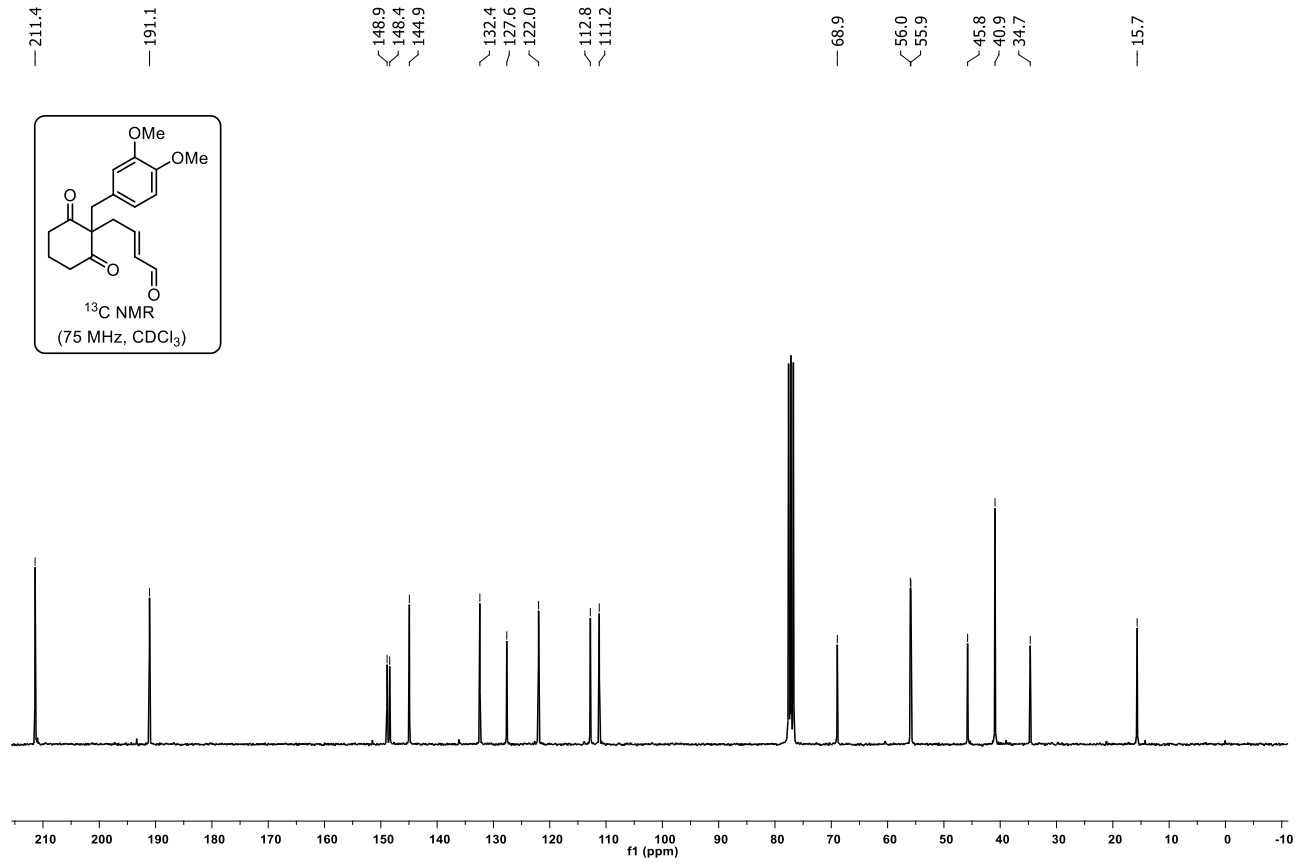


4-(1-(2-bromobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1t):

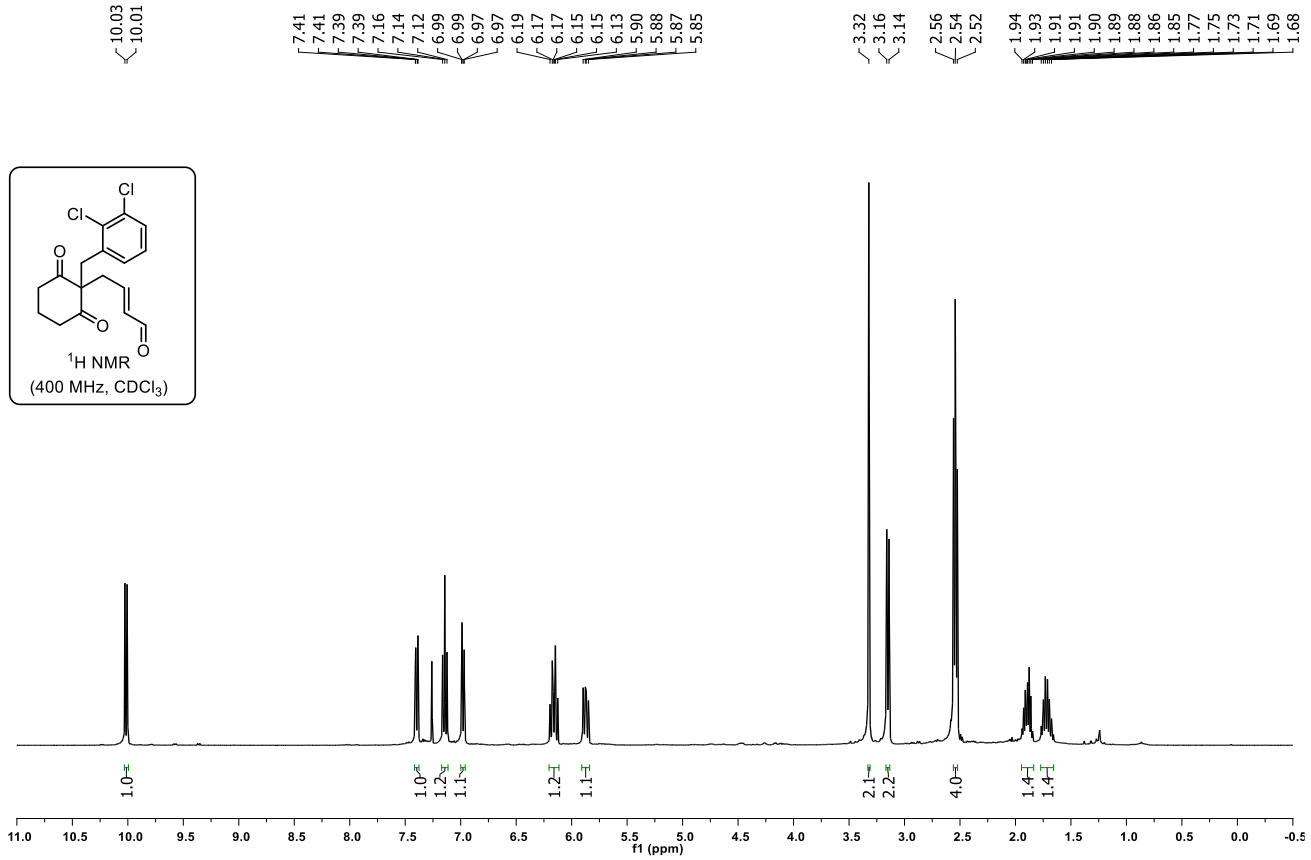


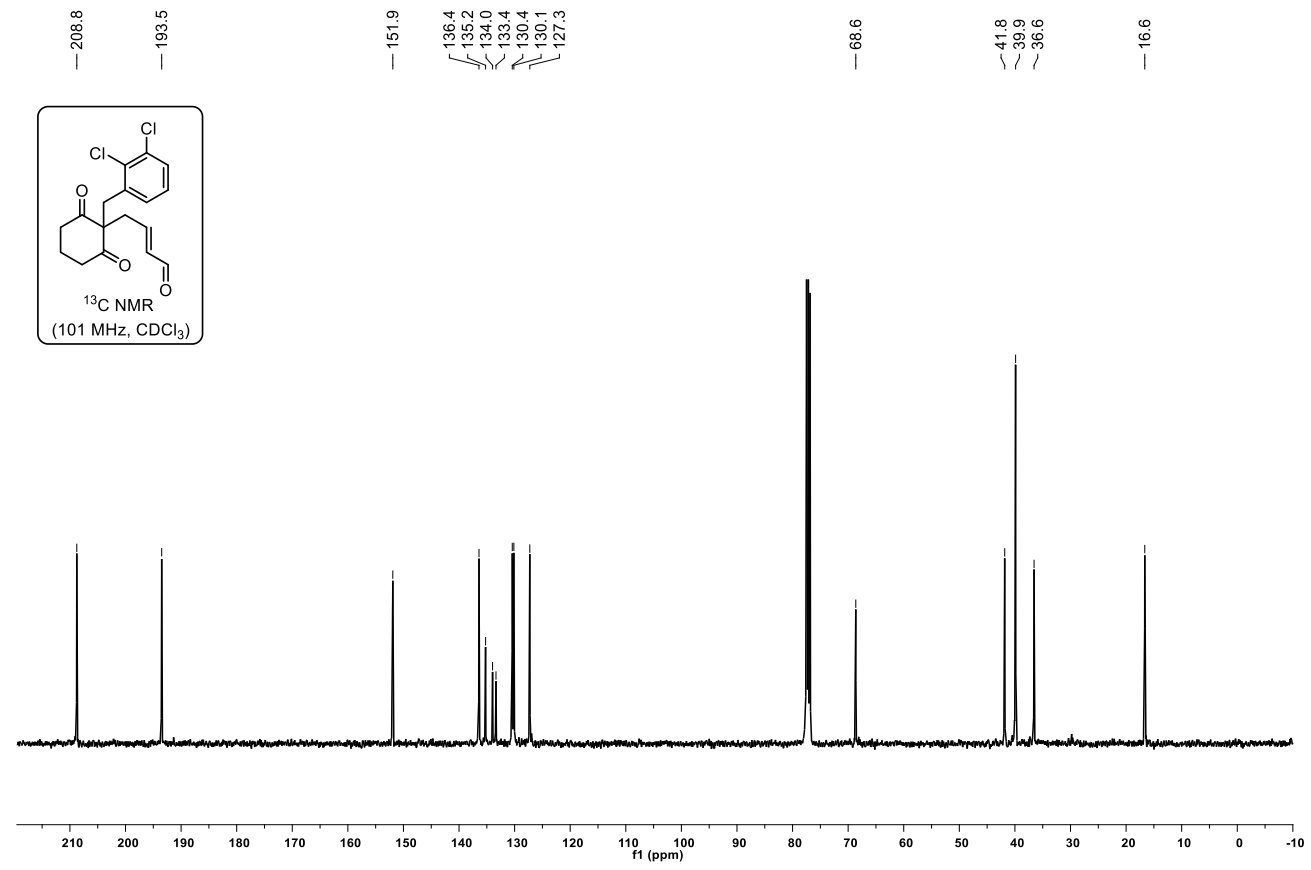
4-(1-(3,4-Dimethoxybenzyl)-2,6-dioxocyclohexyl)but-2-enal (1u):



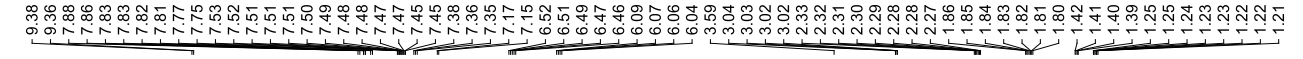


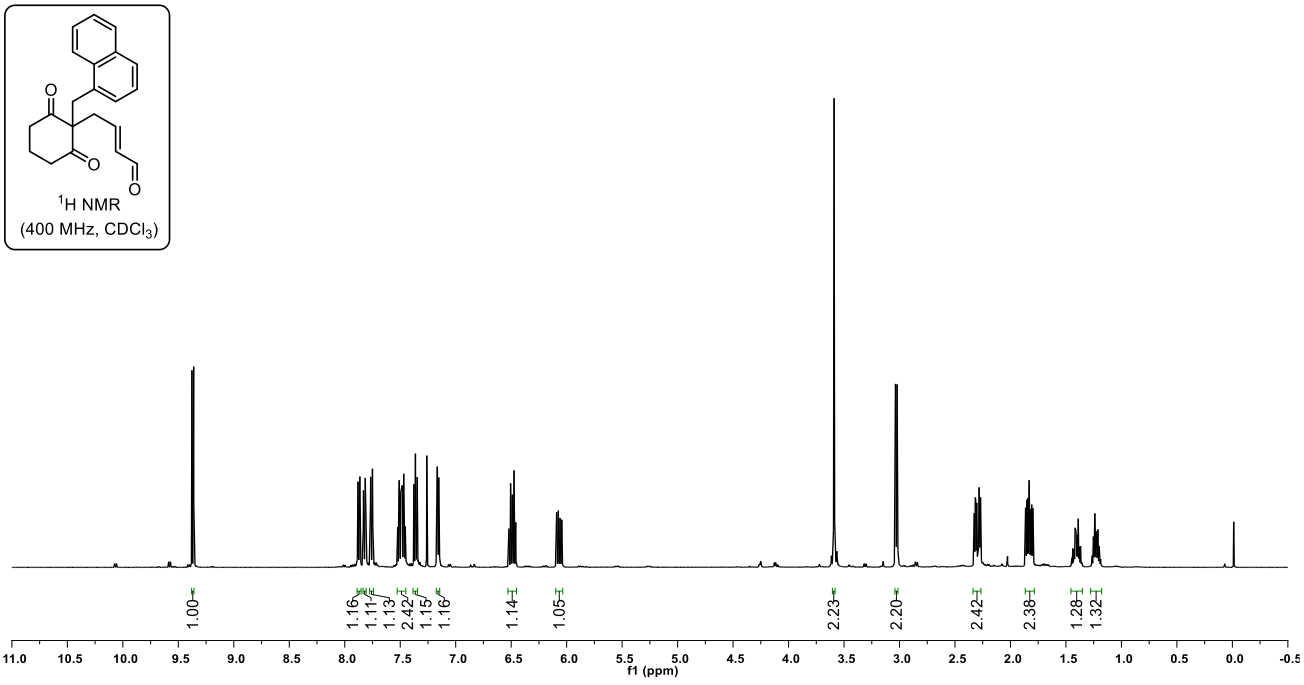
4-(1-(2,3-Dichlorobenzyl)-2,6-dioxocyclohexyl)but-2-enal (1v):

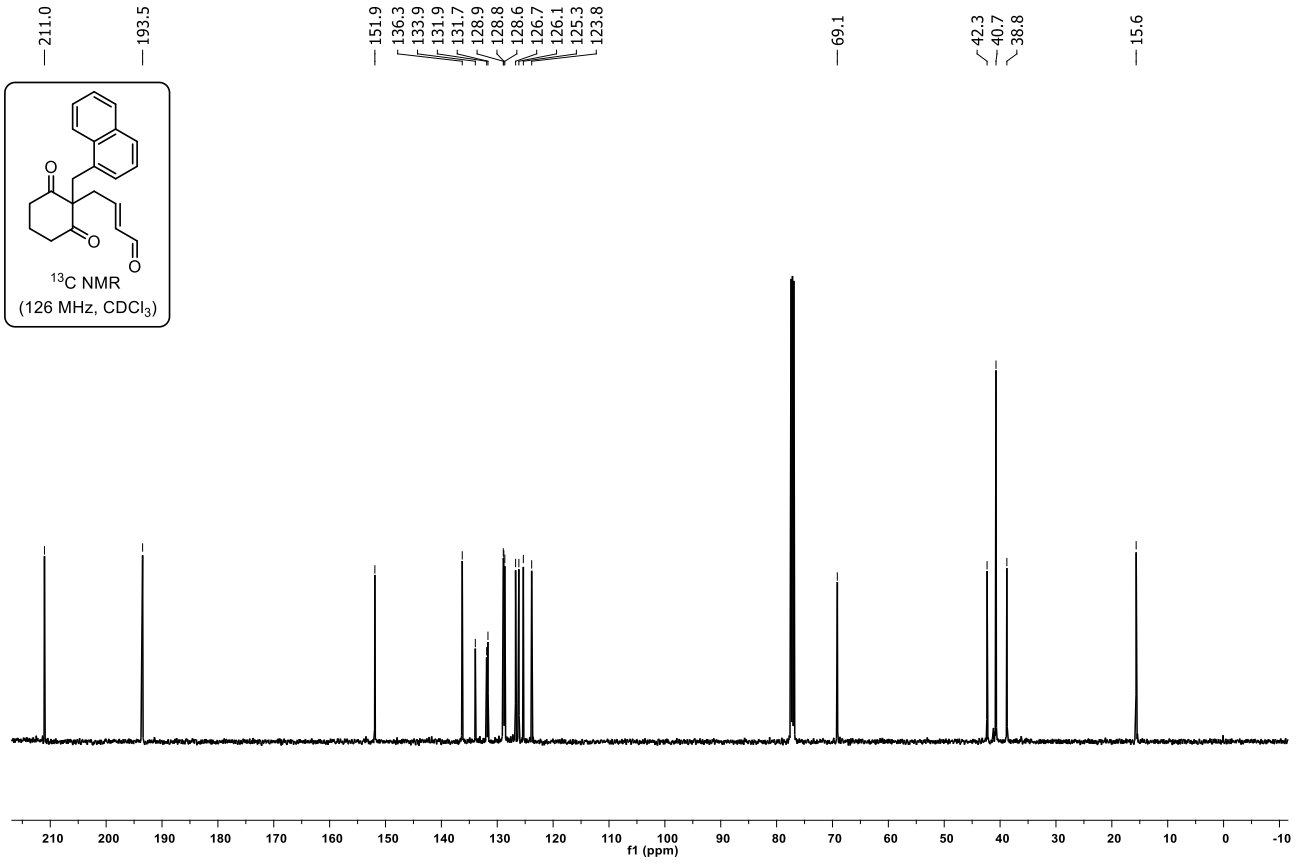




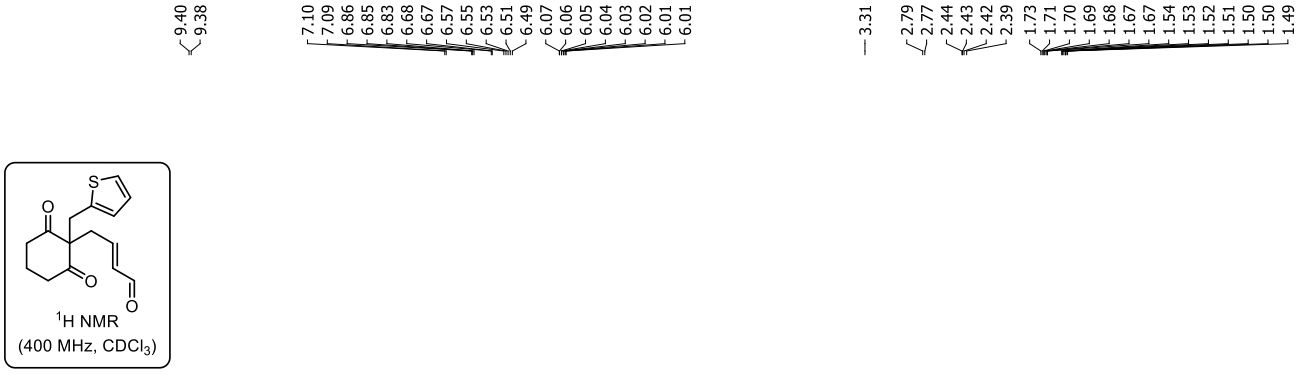
4-(1-(Naphthalen-1-ylmethyl)-2,6-dioxocyclohexyl)but-2-enal (1w):

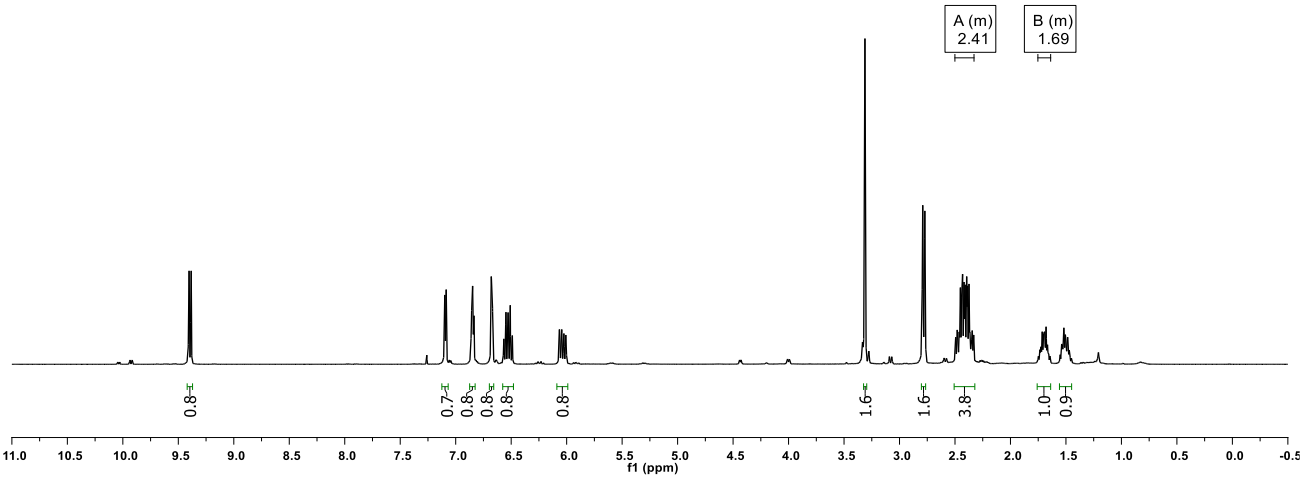


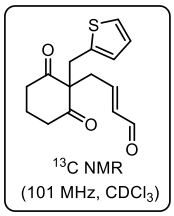


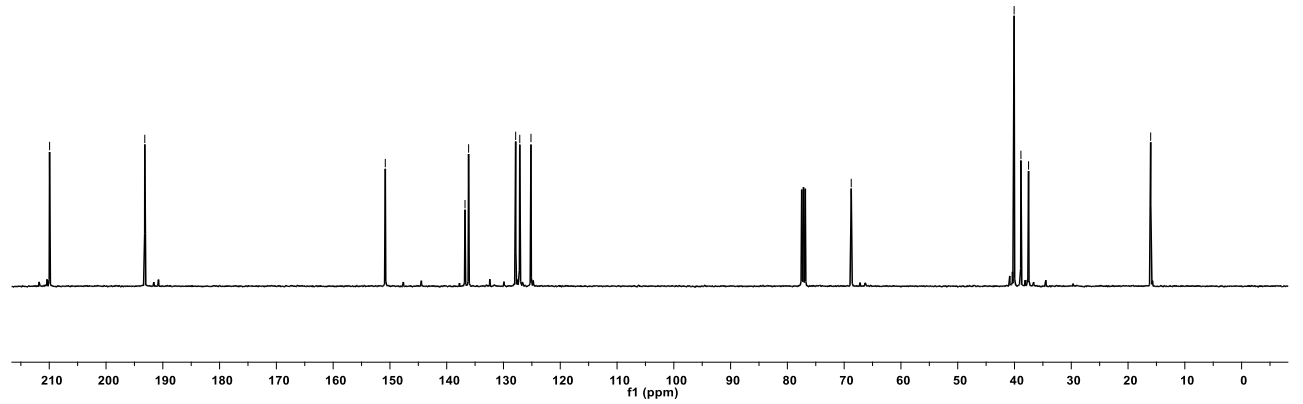


4-(2,6-dioxo-1-(Thiophen-2-ylmethyl)cyclohexyl)but-2-enal (1x):

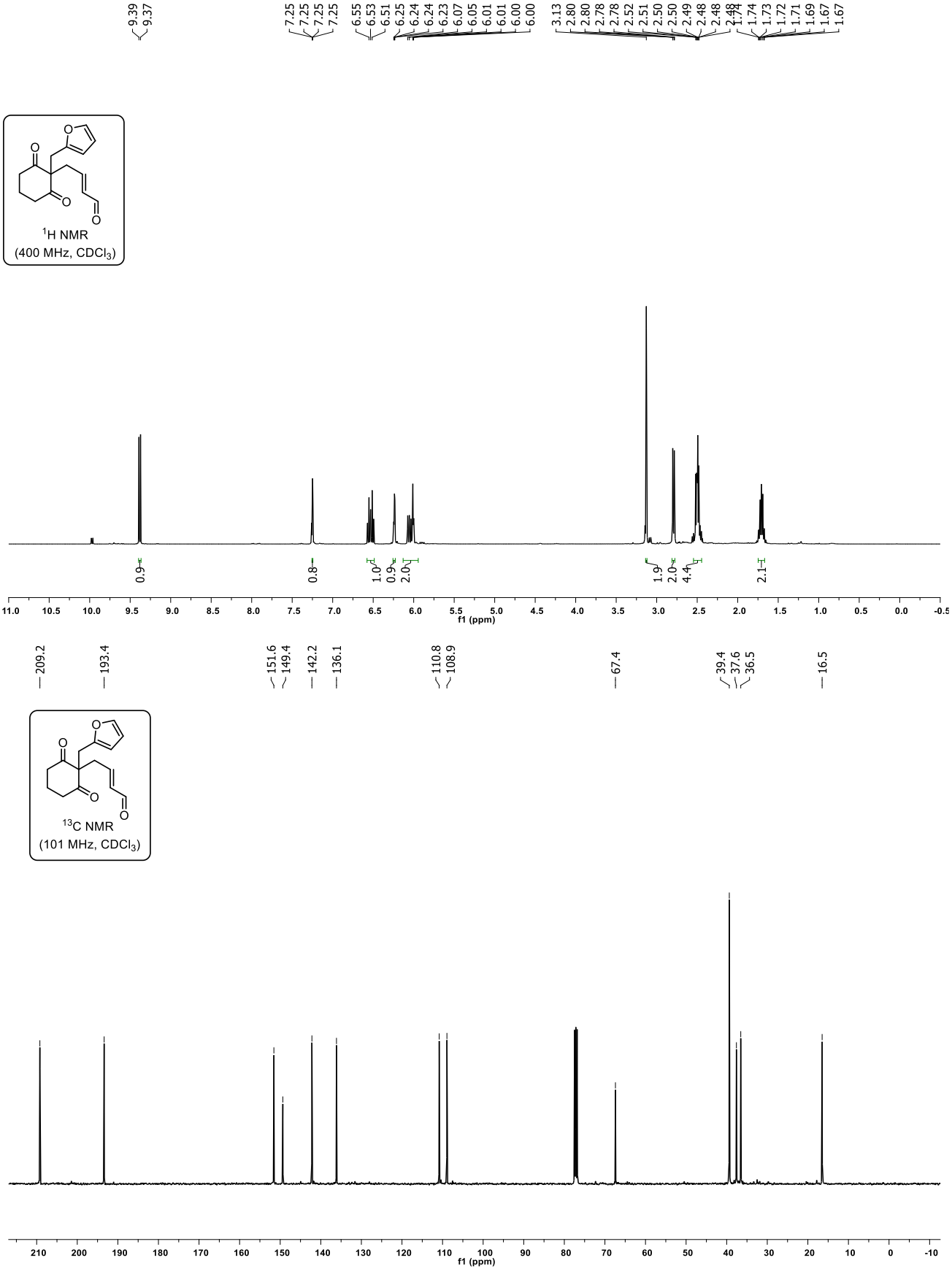








4-(1-(Furan-2-ylmethyl)-2,6-dioxocyclohexyl)but-2-enal (1y):



4-(1-methyl-2,5-dioxocyclopentyl)but-2-enal (1z):