

--- Electronic Supplementary Information---

Asymmetric alkene-alkene reductive cross-coupling reaction via visible-light photoredox/cobalt dual catalysis

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1. General Information

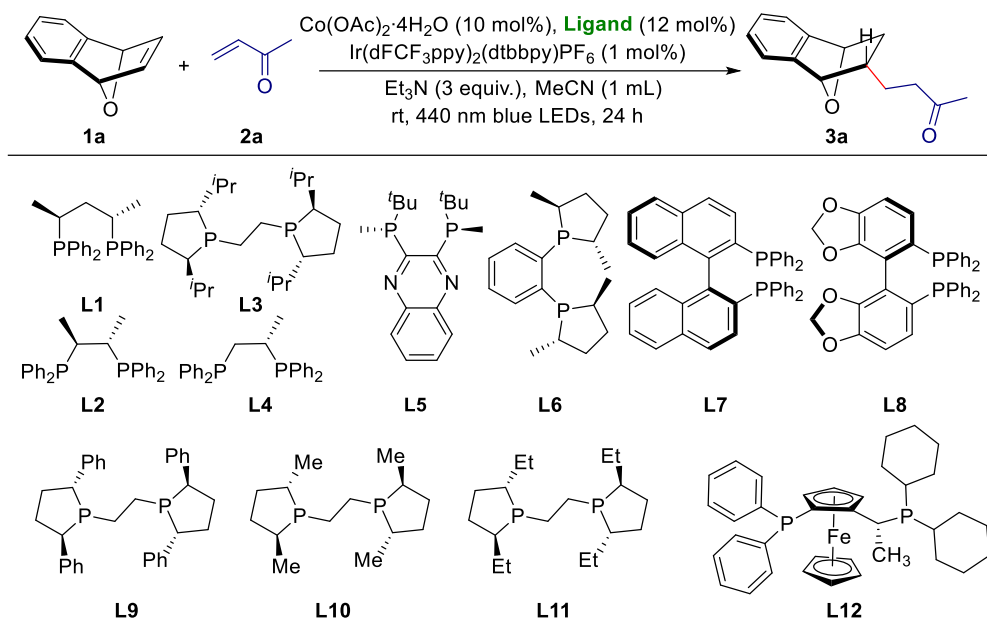
All the reactions were performed in oven-dried glassware under an argon or nitrogen atmosphere using standard Schlenk techniques. Reaction temperatures are reported as the bath temperature surrounding the vessel unless otherwise stated. Non-halogenated solvents were dried over calcium hydride. All the solvents were degassed with argon and stored over activated molecular sieves (4 Å).

Analytics: ^1H , ^{13}C , and ^{19}F NMR spectra have been recorded on Bruker (^1H : 500 MHz, ^{13}C { ^1H }: 126 MHz, ^{19}F { ^1H }: 470 MHz) and JEOL (^1H : 400 MHz, ^{13}C { ^1H }: 101 MHz, ^{19}F { ^1H }: 376 MHz) and were referenced to the resonances of the solvent used. Multiplicities have been indicated as: br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet) or m (multiplet). Coupling constants (J) are reported in Hertz (Hz). FT-IR spectra were recorded by Bruker Optics ALPHA II spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer. HPLC was recorded on Waters HPLC with Photodiode Array Detector. Optical rotations were recorded using a 100 mm cell on Anton Paar Polarimeter (MCP 100) and are reported as follows: $[\alpha]_D^{25}$ (c in g per 1 mL solvent). For thin-layer chromatography (TLC) analysis, Merck pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used, and visualization was accomplished by UV light (254 nm), I_2 , KMnO_4 , and cerium molybdate.

Chemicals: Commercially available chemicals were bought from Sigma–Aldrich, Alfa–Aesar, Avra Synthesis, BLD Pharma, and TCI and used without further purification. Dry solvents were prepared according to the standard procedure and degassed by freeze–pump–thaw cycles prior to use. No attempts were made to optimize yields for substrate, catalyst, and ligand.

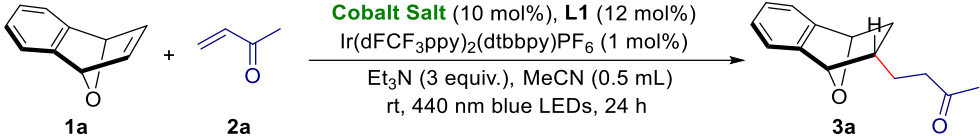
2. Optimization of the Reaction Conditions:

Table S1. The Effect of the Chiral Ligands^a



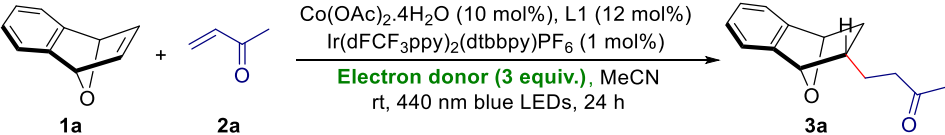
Entry	Ligand	Yield of 3a (%)	Enantiomeric ratio	Diastereomeric ratio
1	L1	94	96:4	>99:1
2	L2	39	90:10	>99:1
3	L3	43	17.2:82.8	>99:1
4	L4	trace	---	---
5	L5	trace	---	---
6	L6	trace	---	---
7	L7	27	71.7:28.3	>99:1
8	L8	31	49.5:50.5	>99:1
9	L9	<10	---	---
10	L10	trace	---	---
11	L11	trace	---	---
12	L12	<10	---	---

^aReaction Conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), Ir(dFCF₃ppy)₂(dtbbpy)PF₆ (1 mol%), Co(OAc)₂·4H₂O (10 mol%), Ligand (12 mol%), NEt₃ (0.3 mmol), Blue LED (440 nm) in MeCN (1 ml) at room temperature under Ar. Yields and diastereomeric ratios are determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. Enantiomeric ratios are checked by the chiral HPLC stationary phase column.

Table S2. The Effect of the Cobalt Salts^a


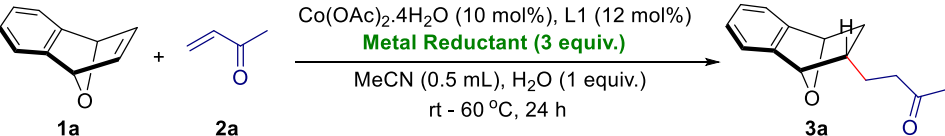
Entry	Cobalt salt	Yield of 3a (%)	Enantiomeric ratio	Diastereomeric ratio
1	CoCl ₂	65	95:5	>99:1
2	Co(OAc)₂·4H₂O	94	96:4	>99:1
3	CoBr ₂	17	80:20	>99:1
4	Co(acac) ₂	87	96:4	>99:1

^aReaction Conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), Ir(dFCF₃ppy)₂(dtbbpy)PF₆ (1 mol%), Cobalt salt (10 mol%), **L1** (12 mol%), NEt₃ (0.3 mmol), Blue LED (440 nm) in MeCN (1 mL) at room temperature under Ar. Yields and diastereomeric ratios are determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. Enantiomeric ratios are checked by the chiral HPLC stationary phase column.

Table S3. The Effect of Electron Donors^a


Entry	Electron donor	Yield of 3a (%)	Enantiomeric ratio	diastereotiomeric ratio
1	DIPEA	57	95.3:4.7	>99:1
2	Et₃N	94	96:4	>99:1
3	Hantzsch ester	59	95.4:4.6	>99:1

^aReaction Conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), Ir(dFCF₃ppy)₂(dtbbpy)PF₆ (1 mol%), Co(OAc)₂·4H₂O (10 mol%), **L1** (12 mol%), Electron donor (0.3 mmol), Blue LED (440 nm) in MeCN (1 mL) at room temperature under Ar. Yields and diastereomeric ratios are determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. Enantiomeric ratios are checked by the chiral HPLC stationary phase column. DIPEA= Diisopropylethylamine.

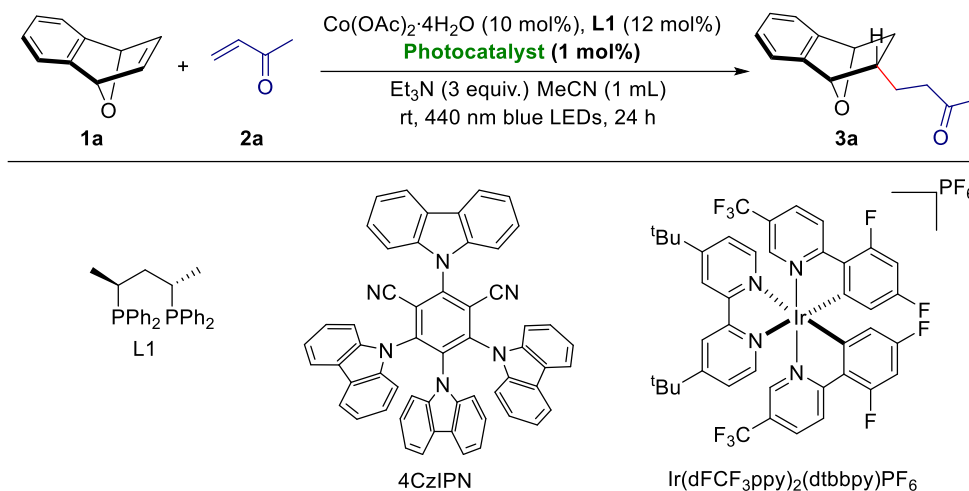
Table S4. Thermal reactions in the presence of metallic reductants^a


Entry	Metal Reductant	Yield of 3a (%)	Enantiomeric ratio	diastereotiomeric ratio
1	Zn dust	25	96:4	>99:1
2	In powder	20	96:4	>99:1
3	Mn flakes	<5	-	-

^aReaction Conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), Metal reductant (0.3 mmol) Co(OAc)₂·4H₂O (10 mol%), **L1** (12 mol%), in MeCN (0.5 mL) at rt to 60 °C under Ar. Yields and diastereomeric ratios are determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene

as an internal standard. Enantiomeric ratios are checked by the chiral HPLC stationary phase column.

Table S5. The Effect of the Photocatalysts and Wavelengths of Light^a



Entry	Photocatalyst	Wavelength	Yield of 3a (%)	Enantiomeric ratio	Diastereomeric ratio
1	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	440 nm	94	96:4	>99:1
2	4CzIPN	440 nm	90	95:5	>99:1
3 ^{b,d}	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	440 nm	67	96:4	>99:1
4 ^{c,d}	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	440 nm	54	95.5:4.5	>99:1
5 ^{b,d}	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	427 nm	48	95.5:4.5	>99:1
6 ^{b,d}	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	456 nm	48	95.5:4.5	>99:1

^aReaction Conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (1 mol%), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (10 mol%), **L1** (12 mol%), NEt_3 (0.3 mmol), Kessil Blue LED (25 intensity) in MeCN (1 mL) at room temperature under Ar. Yields and diastereomeric ratios are determined by ¹HNMR analysis using 1,3,5-trimethoxy benzene as an internal standard. Enantiomeric ratios are checked by the chiral HPLC stationary phase column. ^b10 mol% $\text{Et}_3\text{N} \cdot \text{HOTf}$. ^c50 intensity. ^d**2a** (0.3 mmol)

Table S6. The Effect of Solvent and Equivalency of **2a^a**

Reaction scheme showing the conversion of **1a** and **2a** to **3a** under the following conditions: $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (10 mol%), **L1** (12 mol%), $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (1 mol%), Et_3N (3 equiv.), Solvent (1 mL), rt, 440 nm blue LEDs, 24 h.

Entry	Solvent	2a (x equiv)	Yield of 3a (%)	Enantiomeric ratio	diastereomeric ratio
1	MeCN	5	94	96:4	>99:1
2 ^b	MeCN	3	61	95.5:4.5	>99:1
3 ^b	DMSO	3	50	96:4	>99:1
4 ^b	Toluene	3	7	--	--
5 ^b	THF	3	20	--	--
6 ^b	CH_2Cl_2	3	18	--	--
7 ^b	MeCN	4	72	95.5:4.5	>99:1

^aReaction Conditions: **1a** (0.1 mmol), **2a** (0.3-0.5 mmol), $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (1 mol%), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (10 mol%), **L1** (12 mol%), NEt_3 (0.3 mmol), Blue LED (440 nm) in Solvent

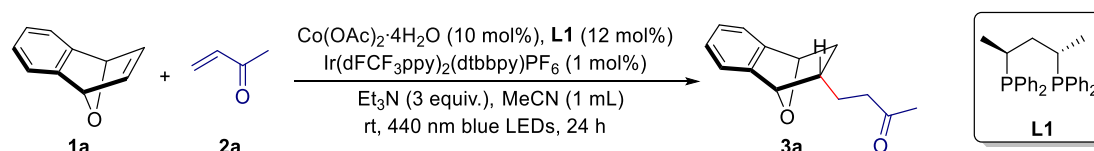
at room temperature under Ar. Yields and diastereomeric ratios are determined by ¹HNMR analysis of crude mixture using 1,3,5-trimethoxybenzene as an internal standard. Enantiomeric ratios are checked by the chiral HPLC stationary phase column. ^bH₂O (1 equiv.) is added as a proton source.

Table S7. Control Experiment^a

Entry	Deviation	Yield of 3a (%)	Enantiomeric ratio	Diastereomeric ratio
1	None	94	96:4	>99:1
2	no photocatalyst	trace	---	---
3	no Co Salt/Ligand	trace	---	---
4	no Et ₃ N	trace	---	---
5	no Light	trace	---	---

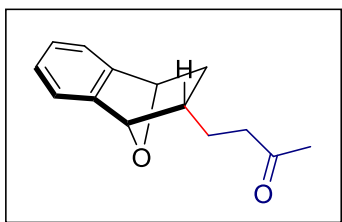
^aReaction Conditions: **1a** (0.05 mmol), **2a** (0.25 mmol), Ir(dFCF₃ppy)₂(dtbbpy)PF₆ (1 mol%), Co(OAc)₂·4H₂O (10 mol%), **L1** (12 mol%), NEt₃ (0.3 mmol), Blue LED (440 nm) in 0.5 mL MeCN at room temperature under Ar. Yields and diastereomeric ratios are determined by ¹HNMR analysis using 1,3,5-trimethoxy benzene as an internal standard. Enantiomeric ratios are checked by the chiral HPLC stationary phase column.

3. General Procedure for the Asymmetric Reductive Coupling of Oxabenzonorbornadiene (**1a**) and Methyl Vinyl Ketone (**2a**) via Visible Light Photoredox-Cobalt dual catalysis



In an argon-filled glove box, a 15 mL reaction tube was charged with Co(OAc)₂·4H₂O (2 mg; 10 mol%) and (*S,S*)-**L1** (5.6 mg; 12 mol%) in 1 mL dry MeCN. The mixture was stirred for 10 minutes. Then Ir(dFCF₃ppy)₂(dtbbpy)PF₆ (1 mg; 1 mol%), triethyl amine (41 μL; 0.3 mmol), **1a** (14.4 mg, 0.1 mmol) and **2a** (43 μL; 0.5 mmol) were sequentially added into the tube. The tube was sealed and removed from the glove box. Then the reaction tube was stirred for 24 h under irradiation with 440 nm Kessil blue LEDs at room temperature. After 24 h, the mixture was filtered through the small pad of silica gel with additional ethyl acetate and concentrated in a vacuum. Yields and diastereomeric ratio were determined by crude ¹HNMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane as eluent to afford the desired reductive coupling product. The enantiomeric ratio was checked by the chiral HPLC stationary phase column.

4. Characterization Data:



4-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)butan-2-one (3a)

Colorless oil. Yield = 90%; 15.9 mg. er = 96:4, dr = >99:1

R_f 0.2 (15 % EtOAc in Hexane)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.24 – 7.19 (m, 2H), 7.14 – 7.11 (m, 2H), 5.36 (d, J = 4.4 Hz, 1H), 5.03 (s, 1H), 2.53 (t, J = 7.4 Hz, 2H), 2.16 (s, 3H), 1.99 – 1.92 (m, 1H), 1.81 – 1.74 (m, 1H), 1.72 – 1.67 (m, 1H), 1.64 – 1.60 (m, 2H).

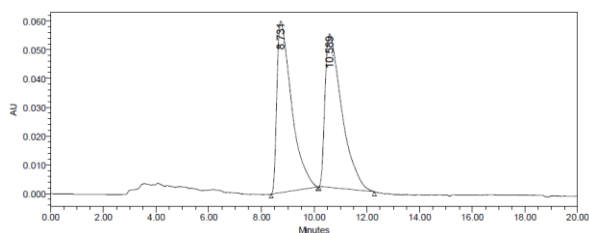
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.8 (s, C=O), 146.2 (s, Ar), 145.9 (s, Ar), 126.9 (d, ArH), 119.2 (d, ArH), 83.3 (d, CH), 79.7 (d, CH), 42.3 (t, CH_2), 40.3 (q, CH_3), 34.8 (d, CH), 30.3 (t, CH_2), 29.2 (t, CH_2).

IR (ATR/ ν cm^{-1}): 2941, 2868, 1709, 1456.

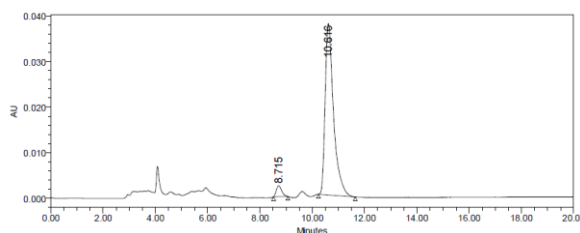
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ Calculated for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Na}^+$: 239.1043, found 239.1037.

$[\alpha]_D^{25} = +35^\circ$ (c = 0.001 in CHCl_3)

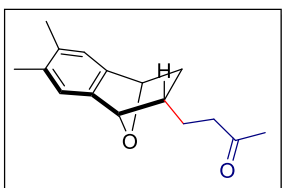
HPLC : Daicel CHIRALPAK OD-H; hexane: i PrOH = 85:15; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. t_R = 10.616 min (major) and 8.715 min (minor). Enantiomeric ratio = 96:4.



	RT	Area	% Area	Height
1	8.731	2305311	49.51	59503
2	10.589	2350640	50.49	53248



	RT	Area	% Area	Height
1	8.715	33803	3.92	2364
2	10.616	829131	96.08	37533



4-((1S,2S,4R)-6,7-dimethyl-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)butan-2-one (3b):

Colorless oil. Yield = 79%; 19.3 mg. er = 93.7:6.3, dr = >99:1

R_f 0.3 (10 % EtOAc in Hexane)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.01 (s, 1H), 6.99 (s, 1H), 5.29 (d, J = 4.3 Hz, 1H), 4.96 (s, 1H), 2.51 (t, J = 7.6 Hz, 2H), 2.23 (s, 6H), 2.15 (s, 3H), 1.97-1.90 (m, 1H), 1.79-1.72 (m, 1H), 1.69 – 1.63 (m, 1H), 1.61-1.57 (m, 2H).

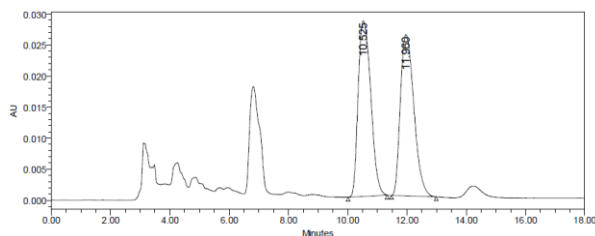
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.4, 143.6, 143.4, 134.3, 120.1, 120.1, 82.7, 79.1, 41.9, 40.2, 34.8, 29.8, 28.8, 19.8.

IR (ATR/v cm^{-1}): 2928, 2863, 1714, 1454.

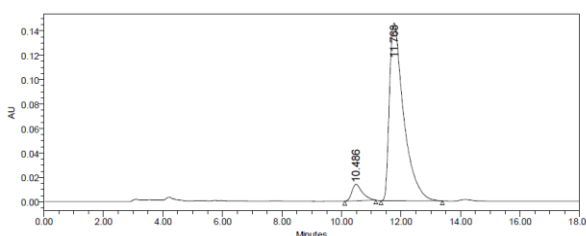
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{Na}^+$: 267.1356, found 267.1358.

$[\alpha]_D^{25} = +41^\circ$ ($c = 0.001$ in CHCl_3).

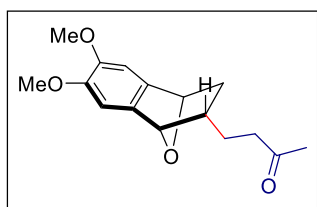
HPLC Data: Daicel CHIRALPAK OD-H; hexane: i PrOH = 90:10; detection wavelength = 279.4 nm; flow rate = 1.0 mL/min. $t_R = 11.768$ min (major) and 10.486 min (minor), Enantiomeric ratio = 93.7:6.3.



	RT	Area	% Area	Height
1	10.525	831778	50.16	28230
2	11.960	826511	49.84	25947



	RT	Area	% Area	Height
1	10.486	327502	6.35	13526
2	11.768	4829779	93.65	145345



4-((1S,2S,4R)-6,7-dimethoxy-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)butan-2-one (3c):

White solid. Yield = 80%; 22.1 mg. er = 96:4, dr = >99:1

R_f 0.2 (25 % EtOAc in Hexane)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.85 (s, 1H), 6.82 (s, 1H), 5.30 (d, $J = 4.5$ Hz, 1H), 4.97 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.51 (t, $J = 7.4$ Hz, 2H), 2.15 (s, 3H), 1.97 – 1.90 (m, 1H), 1.78–1.71 (m, 1H), 1.67 – 1.61 (m, 1H), 1.57 – 1.54 (m, 2H).

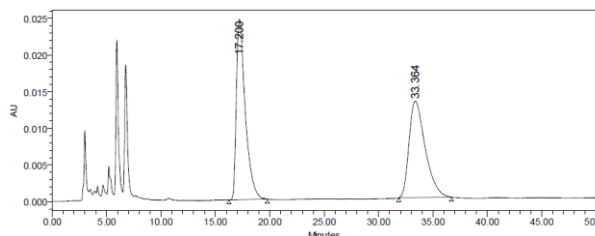
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.8, 148.2, 138.5, 138.3, 104.4, 104.3, 83.6, 80.0, 56.7, 42.4, 40.7, 35.3, 30.3, 29.3.

IR (ATR/v cm^{-1}): 2925, 2855, 1711, 1464, 1264.

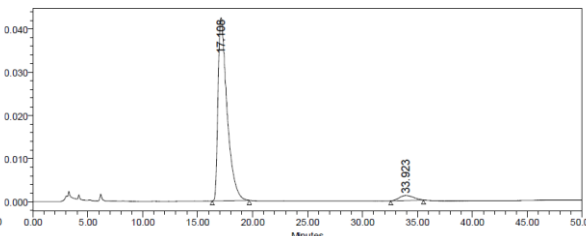
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{20}\text{O}_4\text{Na}^+$: 299.1254, found 299.1254.

$[\alpha]_D^{25} = +25^\circ$ ($c = 0.001$ in CHCl_3)

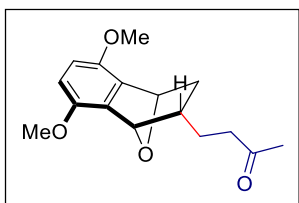
HPLC Data: Daicel CHIRALPAK OD-H; hexane: i PrOH = 70:30; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. $t_R = 17.108$ min (major) and 33.923 min (minor). Enantiomeric ratio = 96:4.



	RT	Area	% Area	Height
1	17.200	1421146	51.15	24618
2	33.364	1357246	48.85	13150



	RT	Area	% Area	Height
1	17.108	2456305	96.05	42429
2	33.923	101013	3.95	1157



4-((1S,2S,4R)-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)butan-2-one (3d):

White solid. Yield = 92%; 25.4 mg. er = 97.6:2.4, dr = >99:1

R_f 0.2 (20 % EtOAc in Hexane)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.62 (s, 2H), 5.52 (d, $J = 4.9$ Hz, 1H), 5.19 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H) 2.53 (t, $J = 7.6$ Hz, 2H), 2.16 (s, 3H), 1.96 – 1.89 (m, 1H), 1.81 – 1.74 (m, 1H), 1.72 – 1.67 (m, 1H), 1.66 – 1.62 (m, 1H), 1.58 – 1.54 (m, 1H).

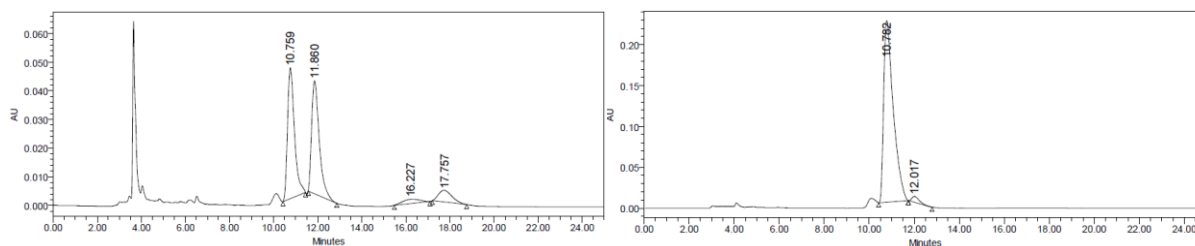
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.9, 147.0, 146.9, 135.4, 135.1, 111.6, 81.1, 56.5, 42.3, 39.9, 34.4, 30.4, 29.2.

IR (ATR/ ν cm^{-1}): 2933, 2845, 1709, 1498.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{20}\text{O}_4\text{Na}^+$: 299.1254, found 299.1253.

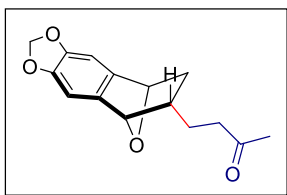
$[\alpha]_D^{25} = +37^\circ$ ($c = 0.001$ in CHCl_3)

HPLC Data: Daicel CHIRALPAK OD-H; hexane: i PrOH = 85:15; detection wavelength = 286.6 nm; flow rate = 1.0 mL/min. $t_R = 10.782$ min (major) and 12.017 min (minor), Enantiomeric ratio = 97.6:2.4.



	RT	Area	% Area	Height
1	10.759	990732	45.27	45666
2	11.860	942358	43.06	39391
3	16.227	78768	3.60	1484
4	17.757	176832	8.08	4087

	RT	Area	% Area	Height
1	10.782	6587423	97.57	221780
2	12.017	163727	2.43	7267



4-((5S,6S,8R)-5,6,7,8-tetrahydro-5,8-epoxynaphtho[2,3-d][1,3]dioxol-6-yl)butan-2-one (3e):

White solid. Yield = 77%; 20.0 mg. er = 95:5, dr = >99:1

R_f 0.2 (20 % EtOAc in Hexane)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.72 (d, $J = 9.8$ Hz, 2H), 5.93 (s, 1H), 5.90 (s, 1H), 5.26 (d, $J = 4.1$ Hz, 1H), 4.93 (s, 1H), 2.50 (t, $J = 7.5$ Hz, 2H), 2.15 (s, 3H), 1.95-1.88 (m, 1H), 1.78-1.70 (m, 1H), 1.66-1.60 (m, 1H), 1.56 – 1.54 (m, 2H).

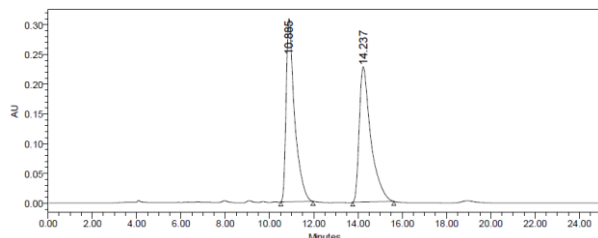
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.5, 146.3, 139.6, 139.4, 101.4, 101.4, 101.2, 83.1, 42.1, 40.3, 34.8, 30.0, 28.9.

IR (ATR/ ν cm^{-1}): 2936, 2868, 1708, 1620, 1467.

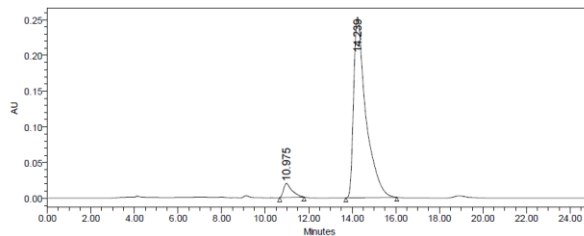
HRMS (ESI-TOF): m/z $[M+Na]^+$ calculated for $C_{15}H_{16}O_4Na^+$: 283.0941, found 283.0954.

$[\alpha]_D^{25} = +35^\circ$ ($c = 0.001$ in $CHCl_3$).

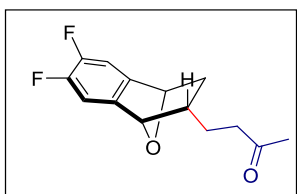
HPLC Data: Daicel CHIRALPAK OD-H; hexane: *i*PrOH = 80:20; detection wavelength = 294.9 nm; flow rate = 1.0 mL/min. $t_R = 14.239$ min (major) and 10.975 min (minor), Enantiomeric ratio = 95:5.



	RT	Area	% Area	Height
1	10.885	8190681	49.85	307429
2	14.237	8240955	50.15	227004



	RT	Area	% Area	Height
1	10.975	523533	5.04	19610
2	14.239	9865208	94.96	252805



4-((1S,2S,4R)-6,7-difluoro-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)butan-2-one (3f):

Yellow oil. Yield = 69%; 17.40 mg. er = 94.4:5.6, dr = >99:1

R_f 0.3 (12 % EtOAc in Hexane)

1H NMR (500 MHz, $CDCl_3$) δ 7.06 – 7.00 (m, 2H), 5.31 (t, $J = 2.7$ Hz, 1H), 4.99 (s, 1H), 2.51 (t, $J = 7.4$ Hz, 2H), 2.15 (s, 3H), 1.97-1.89 (m, 1H), 1.79-1.72 (m, 1H), 1.70 – 1.64 (m, 1H), 1.59 – 1.57 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.1, 149.0 (dd, $^1J_{C-F} = 248.2$ Hz, $^2J_{C-F} = 15.1$ Hz), 148.9 (dd, $^1J_{C-F} = 248.2$ Hz, $^2J_{C-F} = 15.1$ Hz), 141.5 (dd, $^2J_{C-F} = 32.2$, $^3J_{C-F} = 3.7$ Hz), 141.4 (dd, $^2J_{C-F} = 32.2$, $^3J_{C-F} = 3.7$ Hz), 108.8 (overlap), 108.7 (overlap), 82.5, 79.0, 41.6, 39.7, 34.2, 29.9, 28.4.

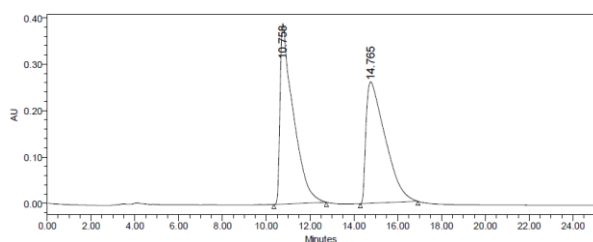
^{19}F NMR (471 MHz, $CDCl_3$) δ -140.04 – -140.21 (m).

IR (ATR/ ν cm^{-1}): 2933, 2871, 1714, 1615, 1477.

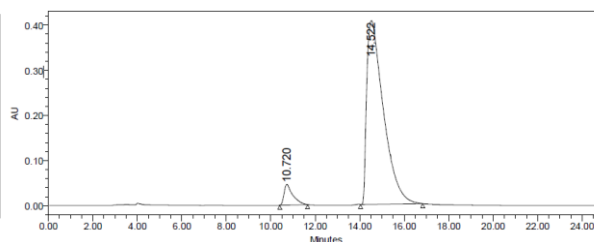
HRMS (ESI-TOF): m/z $[M+Na]^+$ calculated for $C_{14}H_{14}F_2O_2 Na^+$: 275.0854, found 275.0852.

$[\alpha]_D^{25} = +34^\circ$ ($c = 0.001$ in $CHCl_3$).

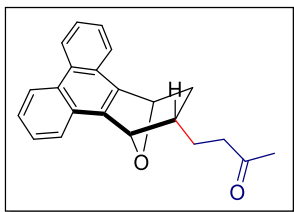
HPLC Data: Daicel CHIRALPAK OD-H; hexane: *i*PrOH = 90:10; detection wavelength = 272.3 nm; flow rate = 1.0 mL/min. $t_R = 14.522$ min (major) and 10.720 min (minor), Enantiomeric ratio = 94.4:5.6.



	RT	Area	% Area	Height
1	10.758	16317990	50.63	389423
2	14.765	15910908	49.37	261689



	RT	Area	% Area	Height
1	10.720	1249566	5.56	45967
2	14.522	21206383	94.44	407376



4-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxytriphenylen-2-yl)butan-2-one (3g):

White solid. Yield = 86%; 27.2 mg. er = 94:6, dr = >99:1

R_f 0.3 (15 % EtOAc in Hexane)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.74 – 8.72 (m, 2H), 7.91 – 7.88 (m, 2H), 7.67 – 7.62 (m, 4H), 5.97 (d, $J = 4.6$ Hz, 1H), 5.66 (s, 1H), 2.60 (t, $J = 7.6$ Hz, 2H), 2.18 (s, 3H), 2.13 – 2.05 (m, 1H), 1.97 – 1.90 (m, 1H), 1.78 – 1.74 (m, 1H), 1.71 – 1.65 (m, 2H).

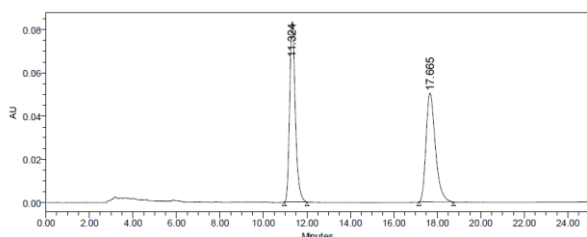
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.3, 140.6, 140.2, 130.0, 126.8, 126.7, 126.0, 125.7, 125.6, 124.0, 123.9, 123.5, 123.5, 82.2, 78.7, 42.1, 40.2, 34.6, 29.8, 28.8.

IR (ATR/ ν cm^{-1}): 2930, 2863, 1711, 1516.

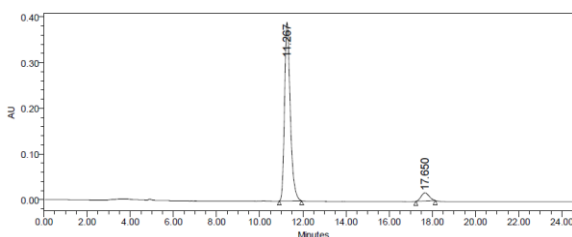
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2\text{Na}^+$: 339.1356, found 339.1365.

$[\alpha]_D^{25} = +29^\circ$ ($c = 0.001$ in CHCl_3)

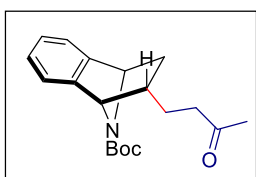
HPLC Data: Daicel CHIRALPAK AD-H; hexane: i PrOH = 50:50; detection wavelength = 358.1 nm; flow rate = 1.0 mL/min. $t_R = 11.267$ min (major) and 17.651 min (minor), Enantiomeric ratio = 94:6



RT	Area	% Area	Height
1 11.324	1506292	50.17	83330
2 17.665	1496379	49.83	50339



RT	Area	% Area	Height
1 11.267	7207861	94.01	391044
2 17.650	459368	5.99	17812



tert-butyl(1S,2S,4R)-2-(3-oxobutyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3h):

White solid. Yield = 72%; 22.7 mg. er = 95.4:4.6, dr = >99:1

R_f 0.3 (10 % EtOAc in Hexane).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.22 – 7.20 (m, 2H), 7.11 – 7.06 (m, 2H), 5.08 (bs, 1H), 4.82 (s, 1H), 2.52 (t, $J = 7.5$ Hz, 2H), 2.15 (s, 3H), 1.93 – 1.87 (m, 1H), 1.77 – 1.74 (m, 1H), 1.65 – 1.59 (m, 3H), 1.36 (s, 9H).

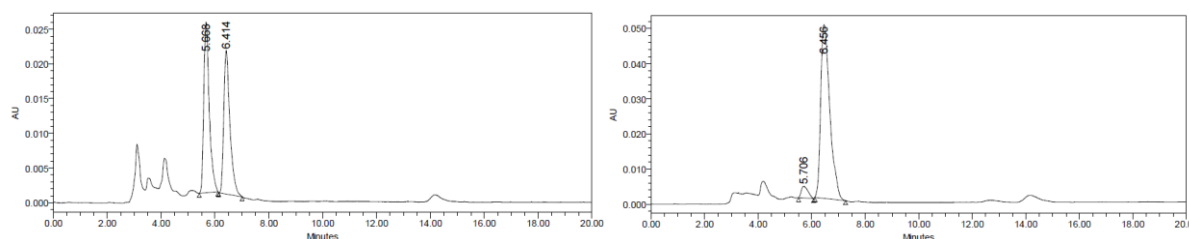
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.3 (s, C=O), 145.3 (s, C=O), 126.3 (d, ArH), 119.7 (s, Ar), 80.0 (d, CH), 61.3 (s, C), 42.0 (t, CH_2), 29.9 (q, $\text{CH}_3 + \text{t}$, CH_2 , overlapped), 28.8 (t, CH_2), 28.2 (q, CH_3). One (d, CH) is not visible.

IR (ATR/ ν cm^{-1}): 2941, 2869, 1686, 1714.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{19}\text{H}_{25}\text{NO}_3\text{Na}^+$: 338.1727, found 338.1722.

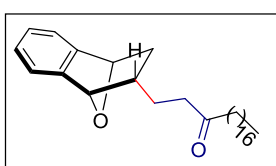
$[\alpha]_D^{25} = +37^\circ$ ($c = 0.001$ in CHCl_3)

HPLC Data: Daicel CHIRALPAK OD-H; hexane: *i*PrOH = 90:10; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. t_R = 6.456 min (major) and 5.706 min (minor), Enantiomeric ratio = 95.4:4.6.



	RT	Area	% Area	Height
1	5.668	352756	51.89	24583
2	6.414	327089	48.11	20677

	RT	Area	% Area	Height
1	5.706	56505	4.63	3258
2	6.456	1163071	95.37	49342



**1-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)icosan-3-one-methane (1/1)
(3i):**

White solid. Yield = 95%; 42 mg. er = 94.1:5.9, dr = >99:1

R_f 0.3 (5 % EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.23 – 7.19 (m, 2H), 7.15 – 7.11 (m, 2H), 5.35 (d, J = 4.3 Hz, 1H), 5.02 (s, 1H), 2.49 (t, J = 7.5 Hz, 2H), 2.40 (t, J = 7.4 Hz, 2H), 1.99 – 1.92 (m, 1H), 1.80 – 1.73 (m, 1H), 1.71 – 1.66 (m, 1H), 1.61 – 1.55 (m, 3H), 1.25 (bs, 29H), 0.88 (t, J = 6.8 Hz, 3H).

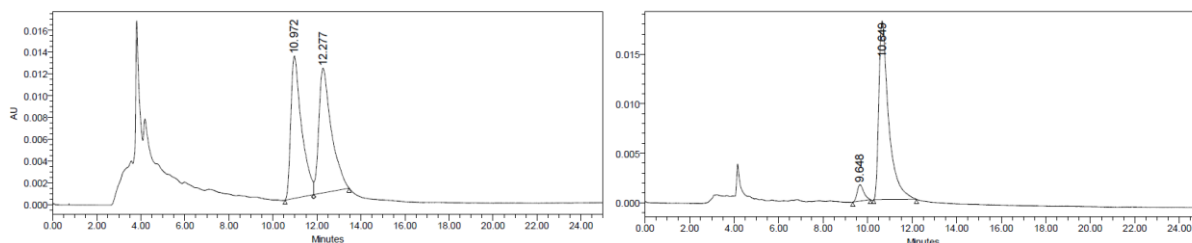
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 211.2, 146.2, 146.0, 126.9, 119.2, 83.3, 79.8, 43.3, 41.4, 40.4, 34.9, 32.3, 30.1, 30.0, 29.9, 29.8, 29.8, 29.7, 29.3, 24.3, 23.1, 14.5.

IR (ATR/ ν cm^{-1}): 2917, 2855, 1703, 1456.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{30}\text{H}_{48}\text{O}_2\text{Na}^+$: 463.3547, found 463.3553.

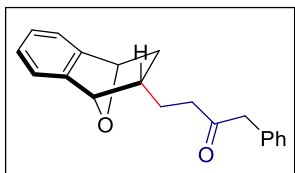
$[\alpha]_D^{25} = +29^\circ$ (c = 0.001 in CHCl_3)

HPLC Data: Daicel CHIRALPAK OD-H; hexane: *i*PrOH = 98:2; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. t_R = 10.649 min (major) and 9.648 min (minor), Enantiomeric ratio = 94.1:5.9.



	RT	Area	% Area	Height
1	10.972	441458	49.36	13037
2	12.277	452925	50.64	11434

	RT	Area	% Area	Height
1	9.648	34092	5.86	1669
2	10.649	548152	94.14	18012



1-phenyl-4-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)butan-2-one (3j):¹

Colorless oil. Yield = 56%; 16.4 mg. er = 95.8:4.2, dr = >99:1

R_f 0.3 (10 % EtOAc in Hexane).

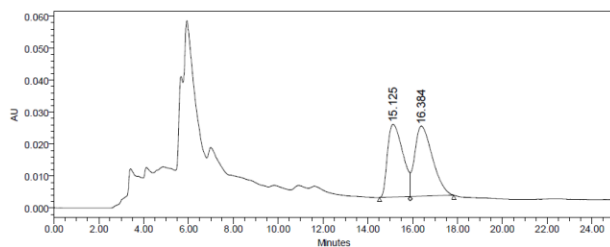
¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.32 (m, 2H), 7.28 – 7.27 (m, 1H), 7.21 – 7.16 (m, 4H), 7.13 – 7.11 (m, 2H), 5.32 (d, J = 4.0 Hz, 1H), 4.95 (s, 1H), 3.70 (s, 2H), 2.55 (t, J = 6.8 Hz, 2H), 1.96 – 1.89 (m, 1H), 1.79 – 1.72 (m, 1H), 1.66 – 1.61 (m, 1H), 1.54 – 1.52 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 208.2, 146.2, 145.9, 134.6, 129.8, 129.2, 127.5, 126.9, 119.2, 83.2, 79.7, 50.6, 40.4, 40.2, 34.8, 29.1.

IR (ATR/v cm⁻¹): 2925, 2855, 1714, 1498, 1456.

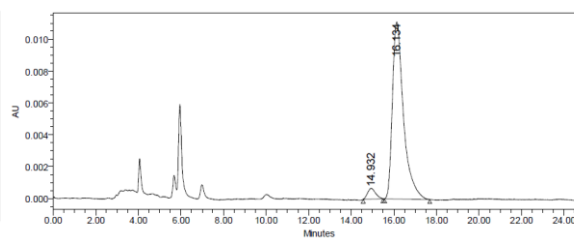
HRMS (ESI-TOF): m/z [M+Na]⁺ calculated for C₂₀H₂₀O₂ Na⁺: 315.1356, found 315.1361.

[α]_D²⁵ = +25° (c = 0.001 in CHCl₃).

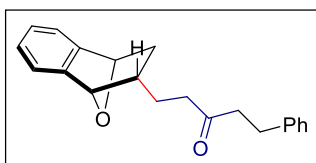
HPLC Data: Daicel CHIRALPAK OD-H; hexane: iPrOH = 85:15; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. *t*_R = 16.134 min (major) and 14.932 min (minor), Enantiomeric ratio = 95.8:4.2.



	RT	Area	% Area	Height
1	15.125	1081351	47.17	22816
2	16.384	1211156	52.83	21968



	RT	Area	% Area	Height
1	14.932	17374	4.19	682
2	16.134	397547	95.81	11096



1-phenyl-5-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl) pentan-3-one (3k):¹

Colourless oil. Yield = 61%; 18.7 mg. er = 94:6, dr = >99:1

R_f 0.3 (10 % EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.28 (s, 1H), 7.25 (s, 1H), 7.22 – 7.16 (m, 5H), 7.15 – 7.11 (m, 2H), 5.34 (d, J = 4.4 Hz, 1H), 4.99 (s, 1H), 2.90 (t, J = 7.6 Hz, 2H), 2.75 (t, J = 7.1 Hz, 2H), 2.47 (t, J = 7.4 Hz, 2H), 1.96 – 1.91 (m, 1H), 1.79 – 1.72 (m, 1H), 1.68 – 1.62 (m, 1H), 1.59 – 1.55 (m, 2H).

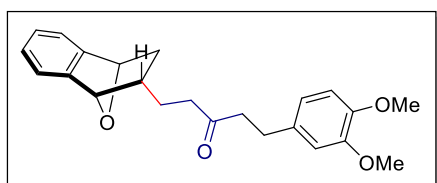
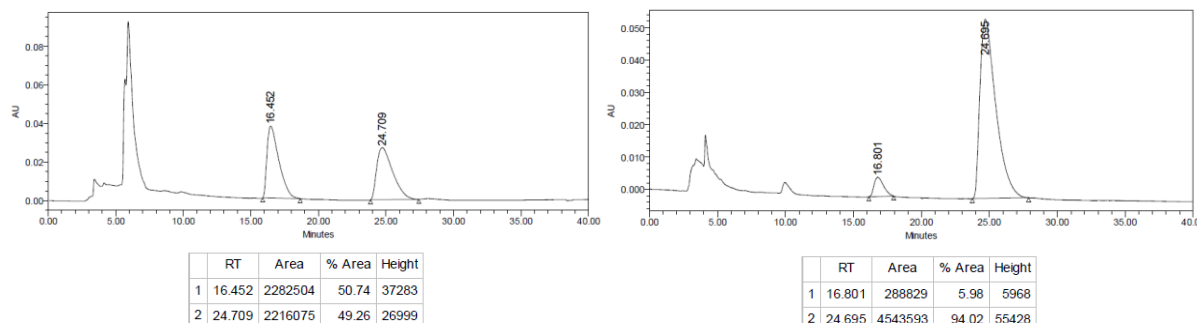
¹³C NMR (126 MHz, CDCl₃) δ 210.0, 146.2, 145.9, 141.4, 128.9, 128.7, 126.9, 126.5, 119.3, 83.3, 79.7, 44.7, 41.7, 40.3, 34.8, 30.2, 29.2.

IR (ATR/v cm⁻¹): 2938, 2920, 1698, 1498, 1384.

HRMS (ESI-TOF): m/z $[M+Na]^+$ calculated for $C_{21}H_{22}O_2Na^+$: 329.1512, found 329.1512.

$[\alpha]_D^{25} = +18^\circ$ ($c = 0.001$ in $CHCl_3$)

HPLC Data: Daicel CHIRALPAK OD-H; hexane: *i*PrOH = 85:15; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. $t_R = 24.695$ min (major) and 16.801 min (minor), Enantiomeric ratio = 94:6.



1-(3,4-dimethoxyphenyl)-5-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)pentan-3-one (3l):

Colorless oil. Yield = 75%; 27.5 mg. er = 94.1:5.9, dr = >99:1

R_f 0.3 (20 % EtOAc in Hexane)

1H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 2H), 7.15 – 7.12 (m, 2H), 6.78-6.76 (m, 1H), 6.71 – 6.70 (m, 2H), 5.34 (d, $J = 4.1$ Hz, 1H), 5.00 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.86 – 6.70 (m, 2H), 2.74 – 2.71 (m, 2H), 2.47 (t, $J = 7.5$ Hz, 2H), 1.98 – 1.91 (m, 1H), 1.79 – 1.72 (m, 1H), 1.68 – 1.63 (m, 2H), 1.59 – 1.56 (m, 1H).

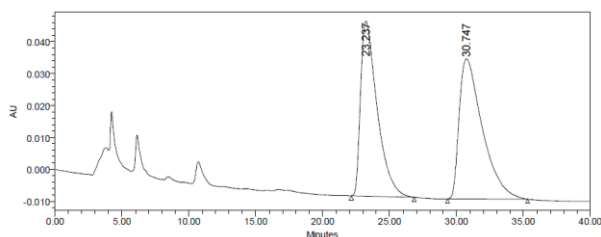
^{13}C NMR (126 MHz, $CDCl_3$) δ 209.9, 149.1, 147.6, 145.9, 145.7, 133.8, 126.7, 120.2, 119.0, 111.9, 111.5, 83.0, 79.5, 56.0, 55.9, 44.7, 41.4, 40.0, 34.5, 29.6, 28.9.

IR (ATR/ ν cm^{-1}): 2928, 2855, 1711, 1589, 1511.

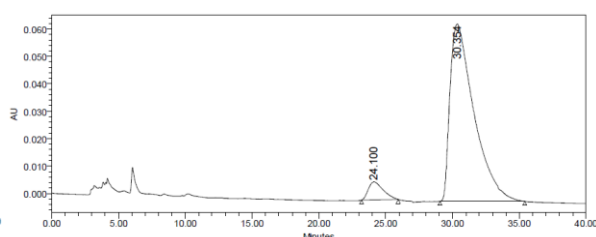
HRMS (ESI-TOF): m/z $[M+Na]^+$ calculated for $C_{23}H_{26}O_4Na^+$: 389.1723, found 389.1720.

$[\alpha]_D^{25} = +21^\circ$ ($c = 0.001$ in $CHCl_3$)

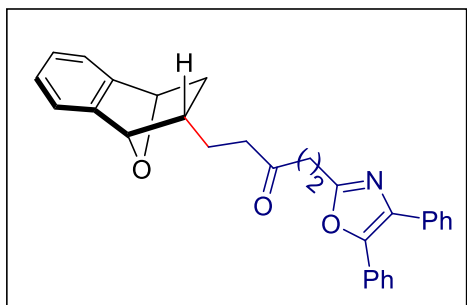
HPLC Data: Daicel CHIRALPAK OD-H; hexane: *i*PrOH = 70:30; detection wavelength = 280.6 nm; flow rate = 1.0 mL/min. $t_R = 30.35$ min (major) and 24.10 min (minor), Enantiomeric ratio = 94.1:5.9.



	RT	Area	% Area	Height
1	23.237	4725622	47.25	54851
2	30.747	5274735	52.75	43914



	RT	Area	% Area	Height
1	24.100	507868	5.92	6561
2	30.354	8074474	94.08	64760



1-(4,5-diphenyloxazol-2-yl)-5-((1*S*,2*S*,4*R*)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)pentan-3-one (3m):

Colorless oil. Yield = 54%; 24.2 mg. er = 94:6, dr = >99:1

R_f 0.2 (20% EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.60 (d, $J = 7.3$ Hz, 2H), 7.55 (d, $J = 7.6$ Hz, 2H), 7.36 – 7.31 (m, 6H), 7.20 (d, $J = 4.6$ Hz, 2H), 7.13 – 7.10 (m, 2H), 5.35 (d, $J = 3.7$ Hz, 1H), 5.03 (s, 1H), 3.14 (t, $J = 6.9$ Hz, 2H), 3.04 (t, $J = 7.5$ Hz, 2H), 2.62 (t, $J = 7.5$ Hz, 2H), 2.06 – 1.99 (m, 1H), 1.87 – 1.80 (m, 1H), 1.74 – 1.69 (m, 1H), 1.60 (d, $J = 9.2$ Hz, 2H).

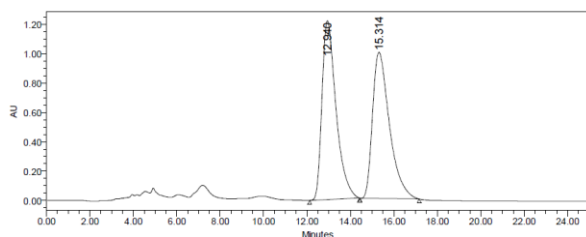
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.4, 162.4, 145.9, 145.7, 145.5, 135.2, 132.6, 129.1, 128.8, 128.7, 128.6, 128.2, 128.0, 126.6, 126.6, 126.6, 119.0, 118.9, 83.0, 79.5, 41.3, 40.0, 39.1, 34.5, 29.0, 22.3.

IR (ATR/ ν cm^{-1}): 2912, 2855, 1714, 1579, 1446.

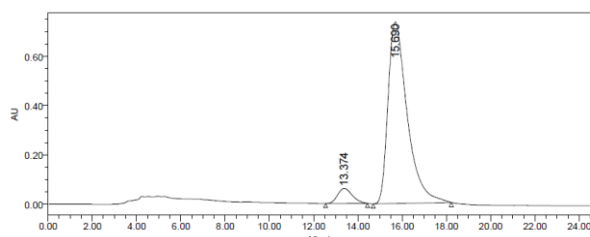
HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{28}\text{NO}_3^+$: 450.2064, found 450.2061.

$[\alpha]_D^{25} = +27^\circ$ ($c = 0.001$ in CHCl_3).

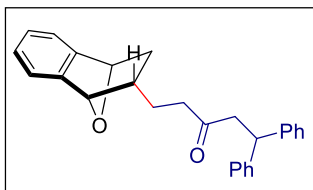
HPLC Data: Daicel CHIRALPAK OD-H; hexane: i PrOH = 60:40; detection wavelength = 288.9 nm; flow rate = 1.0 mL/min. $t_R = 15.690$ min (major) and 13.374 min (minor), enantiomeric ratio = 94:6.



	RT	Area	% Area	Height
1	12.940	54757462	50.40	1219149
2	15.314	53894453	49.60	996864



	RT	Area	% Area	Height
1	13.374	2819579	5.98	61342
2	15.690	44306469	94.02	735184



1,1-diphenyl-4-((1*S*,2*S*,4*R*)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)butan-2-one (3n):

Colorless oil. Yield = 92%; 35.0 mg. er = 94:6, dr = >99:1

R_f 0.3 (10% EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.26 (m, 2H), 7.25 – 7.21 (m, 5H), 7.20 – 7.16 (m, 4H), 7.15 – 7.11 (m, 3H), 5.31 (d, *J* = 4.3 Hz, 1H), 4.92 (s, 1H), 4.60 (t, *J* = 7.6 Hz, 1H), 3.17 (d, *J* = 7.3 Hz, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.89 – 1.82 (m, 1H), 1.69– 1.64 (m, 1H), 1.56 – 1.52 (m, 1H), 1.49 (d, *J* = 7.8 Hz, 2H).

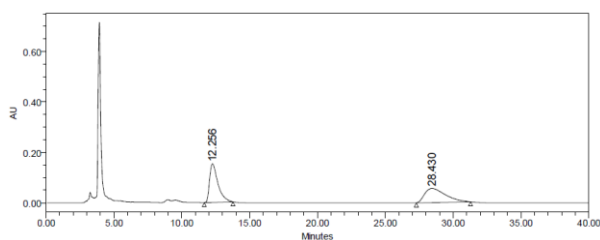
¹³C NMR (126 MHz, CDCl₃) δ 208.8, 145.9, 145.6, 144.0, 128.7, 127.8, 126.6, 119.0, 118.9, 83.0, 79.4, 49.0, 46.2, 42.0, 39.8, 34.4, 28.6.

IR (ATR/v cm⁻¹): 2933, 2855, 1711, 1493, 1451.

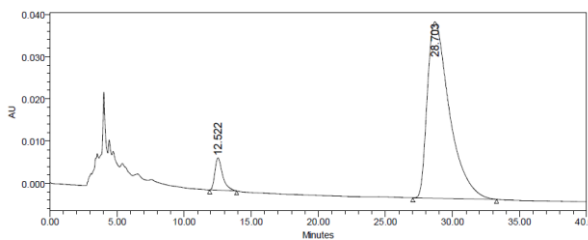
HRMS (ESI-TOF): *m/z* [M+Na]⁺ calculated for C₂₇H₂₆O₂ Na⁺: 405.1825, found 405.1823.

[α]_D²⁵ = +20° (*c* = 0.001 in CHCl₃).

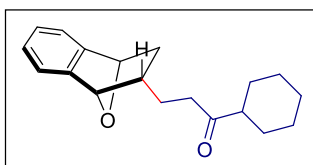
HPLC Data: Daicel CHIRALPAK OD-H; hexane: *i*PrOH = 50:50; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. *t_R* = 28.703 min (major) and 12.522 min (minor), enantiomeric ratio = 94:6.



	RT	Area	% Area	Height
1	12.256	6535309	52.33	152849
2	28.430	5954039	47.67	55820



	RT	Area	% Area	Height
1	12.522	303562	5.98	7687
2	28.703	4773118	94.02	41768



1-cyclohexyl-3-((1*S*,2*S*,4*R*)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)propan-1-one (3o):

Colorless oil. Yield = 73%; 21 mg. er = 94.1:5.9, dr = >99:1

R_f 0.4 (5% EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.23 – 7.18 (m, 2H), 7.15 – 7.11 (m, 2H), 5.35 (d, *J* = 5.3 Hz, 1H), 5.03 (s, 1H), 2.53 (t, *J* = 7.4 Hz, 2H), 2.39 – 2.31 (m, 1H), 1.98 – 1.91 (m, 1H), 1.86 – 1.74 (m, 5H), 1.69 – 1.64 (m, 2H), 1.61 – 1.59 (m, 1H), 1.36 – 1.18 (m, 6H).

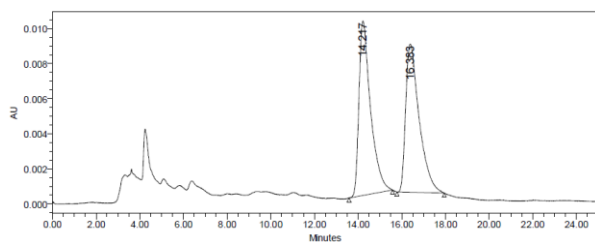
^{13}C NMR (126 MHz, CDCl_3) δ 213.8, 146.0, 145.8, 126.6, 119.0, 83.1, 79.5, 51.1, 40.1, 38.9, 34.6, 28.9, 28.7, 26.0, 25.8.

IR (ATR/ ν cm^{-1}): 2925, 2855, 1706, 1456.

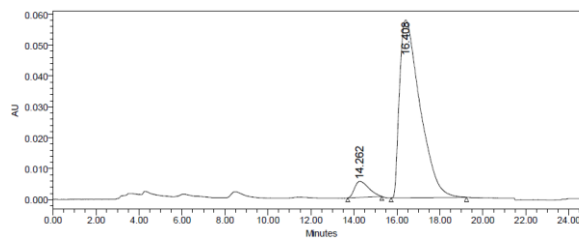
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{Na}^+$: 307.1669, found 307.1682.

$[\alpha]_D^{25} = +37^\circ$ ($c = 0.001$ in CHCl_3).

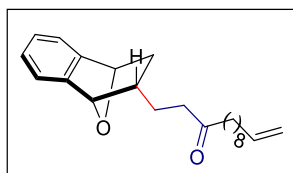
HPLC Data: Daicel CHIRALPAK OD-H; hexane: $i\text{PrOH} = 98:2$; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. $t_R = 16.174$ min (major) and 14.193 min (minor), Enantiomeric ratio = 94.1:5.9.



	RT	Area	% Area	Height
1	14.217	371889	50.27	9954
2	16.383	367825	49.73	8482



	RT	Area	% Area	Height
1	14.262	237314	5.90	5199
2	16.408	3786743	94.10	57532



1-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)tridec-12-en-3-one (3p):

Colorless oil. Yield = 62%; 21.2 mg. er = 94.9:5.1, dr = >99:1

R_f 0.5 (5% EtOAc in Hexane);

^1H NMR (500 MHz, CDCl_3) δ 7.23 – 7.19 (m, 2H), 7.14 – 7.12 (m, 2H), 5.86 – 5.76 (m, 1H), 5.36 (d, $J = 3.8$ Hz, 1H), 5.02 (s, 1H), 5.01 – 4.91 (m, 2H), 2.49 (t, $J = 7.4$ Hz, 2H), 2.42 – 2.38 (m, 2H), 2.06 – 2.00 (m, 2H), 1.99 – 1.91 (m, 1H), 1.80 – 1.72 (m, 1H), 1.71 – 1.66 (m, 1H), 1.62 – 1.60 (m, 2H), 1.58 – 1.53 (m, 2H), 1.39 – 1.33 (m, 2H), 1.29 – 1.27 (m, 8H).

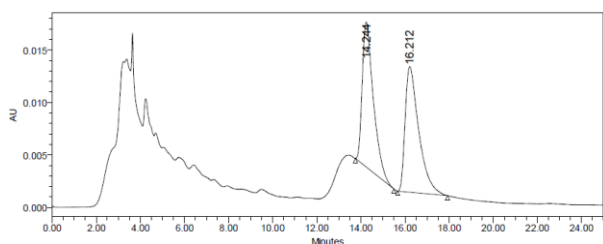
^{13}C NMR (126 MHz, CDCl_3) δ 211.2, 146.2, 146.0, 139.6, 126.9, 119.2, 114.5, 83.3, 79.8, 43.3, 41.3, 40.4, 34.8, 34.2, 29.7, 29.7, 29.6, 29.4, 29.2, 24.3.

IR (ATR/ ν cm^{-1}): 2923, 2853, 1709, 1460.

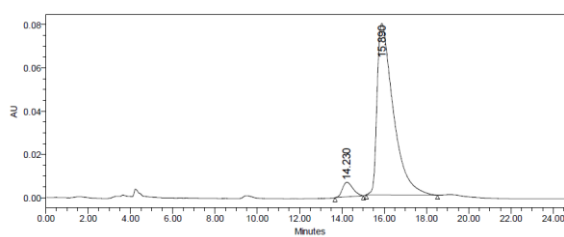
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{23}\text{H}_{32}\text{O}_2\text{Na}^+$: 363.2295, found 363.2318.

$[\alpha]_D^{25} = +23^\circ$ ($c = 0.001$ in CHCl_3).

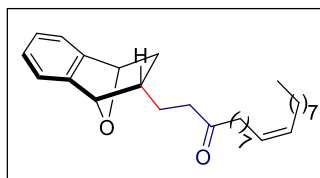
HPLC Data: Daicel CHIRALPAK OD-H; hexane: $i\text{PrOH} = 98:2$; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. $t_R = 15.890$ min (major) and 14.230 min (minor), Enantiomeric ratio = 94.9:5.1.



	RT	Area	% Area	Height
1	14.244	487185	48.81	13815
2	16.212	510907	51.19	11977



	RT	Area	% Area	Height
1	14.230	228559	5.14	6750
2	15.890	4215099	94.86	79162



(Z)-1-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)icos-11-en-3-one-methane (1/1) (3q):

Colorless oil. Yield = 68%; 29.8 mg. er = 89:11, dr = >99:1

R_f 0.4 (5 % EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.23 – 7.19 (m, 2H), 7.15 – 7.12 (m, 2H), 5.39 – 5.31 (m, 3H), 5.02 (s, 1H), 2.49 (t, $J = 7.5$ Hz, 2H), 2.40 (t, $J = 7.5$ Hz, 2H), 2.03 – 1.99 (m, 4H), 1.97 – 1.91 (m, 1H), 1.80 – 1.73 (m, 1H), 1.71 – 1.66 (m, 1H), 1.61 – 1.58 (m, 4H), 1.35 – 1.26 (m, 20H), 0.88 (t, $J = 6.7$ Hz, 3H).

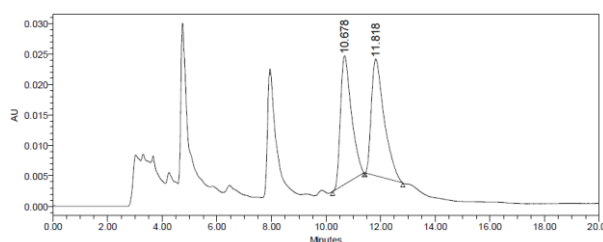
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 211.0, 146.0, 145.8, 130.2, 129.9, 126.7, 119.0, 83.1, 79.5, 43.1, 41.1, 40.2, 34.6, 32.1, 30.0, 29.9, 29.7, 29.5, 29.4, 29.9, 29.1, 27.4, 27.4, 24.1, 22.9, 14.3.

IR (ATR/ ν cm^{-1}): 2936, 2868, 1709, 1460.

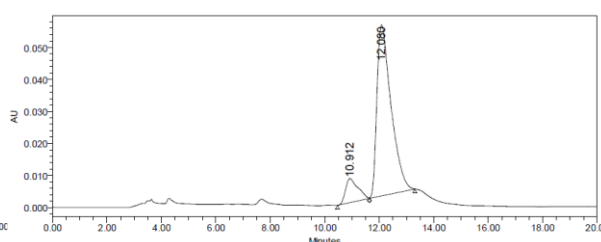
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{30}\text{H}_{46}\text{NO}_2\text{Na}^+$: 461.3390, found 461.3403.

$[\alpha]_D^{25} = +21^\circ$ ($c = 0.001$ in CHCl_3).

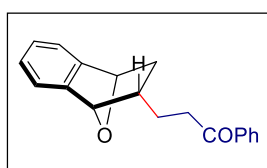
HPLC Data: Daicel CHIRALPAK OD-H; hexane: i PrOH = 98:2; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. $t_R = 12.080$ min (major) and 10.912 min (minor), Enantiomeric ratio = 89:11.



	RT	Area	% Area	Height
1	10.678	582779	48.33	21077
2	11.818	623138	51.67	19110



	RT	Area	% Area	Height
1	10.912	237308	10.98	7533
2	12.080	1922998	89.02	53414



1-phenyl-3-((1S,2S,4R)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)propan-1-one (3r):¹

Colorless oil. Yield = 50%; 13.9 mg. er = 96.1:3.9, dr = >99:1

R_f 0.4 (8% EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.14 – 7.12 (m, 2H), 5.38 (t, *J* = 2.7 Hz, 1H), 5.09 (s, 1H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.18 – 2.10 (m, 1H), 1.98 – 1.91 (m, 1H), 1.83 – 1.78 (m, 1H), 1.67 – 1.65 (m, 2H).

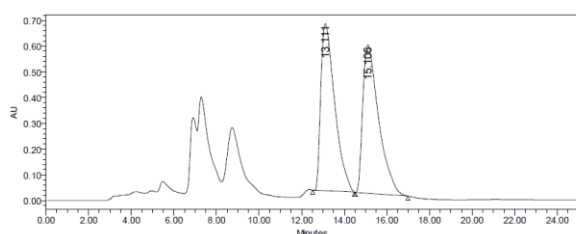
¹³C NMR (126 MHz, CDCl₃) δ 200.0, 146.0, 145.7, 137.1, 133.2, 128.8, 128.2, 126.6, 119.0, 118.9, 83.1, 79.5, 40.2, 36.9, 34.7, 29.6.

IR (ATR/v cm⁻¹): 2956, 2923, 2852, 1740, 1680, 1459.

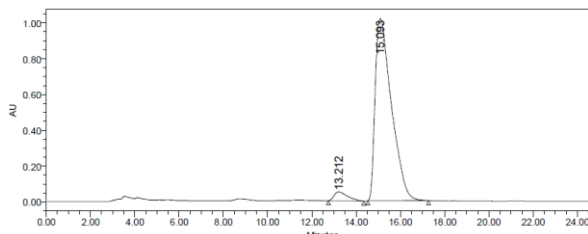
HRMS (ESI-TOF): *m/z* [M+Na]⁺ calculated for C₁₉H₁₈O₂Na⁺: 301.1199, found 301.1204.

[α]_D²⁵ = +16° (c = 0.001 in CHCl₃)

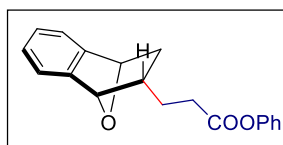
HPLC Data: Daicel CHIRALPAK OD-H; hexane: *i*PrOH = 90:10; detection wavelength = 239.1 nm; flow rate = 1.0 mL/min. *t_R* = 15.093 min (major) and 13.211 min (minor), Enantiomeric ratio = 96.1:3.9.



	RT	Area	% Area	Height
1	13.111	29460245	49.62	649048
2	15.106	29914646	50.38	575379



	RT	Area	% Area	Height
1	13.212	2117960	3.91	49835
2	15.093	52074969	96.09	1020316



phenyl 3-((1*S*,2*S*,4*R*)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)propanoate (3s):

Colorless oil. Yield = 56%; 16.5 mg. er = 82.5:17.5, dr = >99:1

R_f 0.3 (5% EtOAc in Hexane)

¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.35 (m, 2H), 7.25 – 7.21 (m, 3H), 7.17 – 7.14 (m, 2H), 7.08 – 7.05 (m, 2H), 5.40 (d, *J* = 3.7 Hz, 1H), 5.11 (s, 1H), 2.73 – 2.62 (m, 2H), 2.19 – 2.12 (m, 1H), 2.01 – 1.94 (m, 1H), 1.86 – 1.80 (m, 1H), 1.70 – 1.68 (m, 2H).

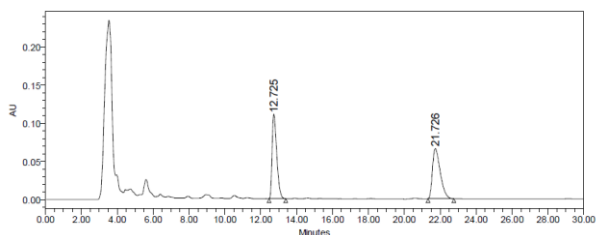
¹³C NMR (126 MHz, CDCl₃) δ 172.0, 150.9, 146.0, 145.7, 129.6, 126.8, 126.0, 121.7, 119.1, 83.0, 79.6, 40.2, 34.7, 33.1, 30.2.

IR (ATR/v cm⁻¹): 2920, 2852, 1753, 1589, 1488, 1191.

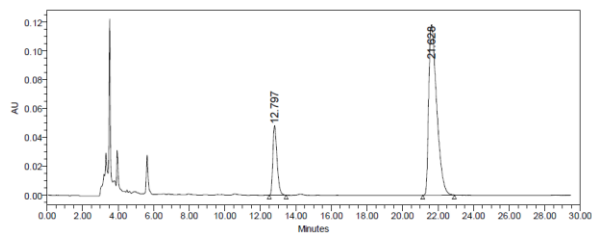
HRMS (ESI-TOF): *m/z* [M+Na]⁺ calculated for C₁₉H₁₈O₃Na⁺: 317.1148, found 317.1154.

[α]_D²⁵ = +24° (c = 0.001 in CHCl₃).

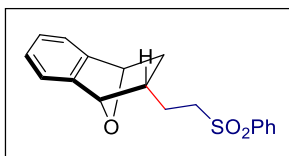
HPLC Data: Daicel CHIRALPAK IC-3; hexane: *i*PrOH = 70:30; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. *t_R* = 21.628 min (major) and 12.797 min (minor), enantiomeric ratio = 82.5:17.5.



	RT	Area	% Area	Height
1	12.725	1988683	50.09	110456
2	21.726	1981355	49.91	65650



	RT	Area	% Area	Height
1	12.797	783858	17.53	48040
2	21.628	3688134	82.47	118347



(1S,2S,4R)-2-(2-(phenylsulfonyl)ethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3t):

Colorless oil. Yield = 65%; 20.5 mg. er = 96:4, dr = >99:1

R_f 0.2 (20% EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.94 – 7.92 (m, 2H), 7.69 – 7.65 (m, 1H), 7.61 – 7.56 (m, 2H), 7.21 – 7.18 (m, 2H), 7.15 – 7.12 (m, 2H), 5.34 (d, $J = 4.9$ Hz, 1H), 4.98 (s, 1H), 3.17 (dd, $J = 8.7, 7.5$ Hz, 2H), 2.13 – 2.04 (m, 1H), 1.96 – 1.88 (m, 1H), 1.84 – 1.78 (m, 1H), 1.64 – 1.60 (m, 1H), 1.56 – 1.51 (m, 1H).

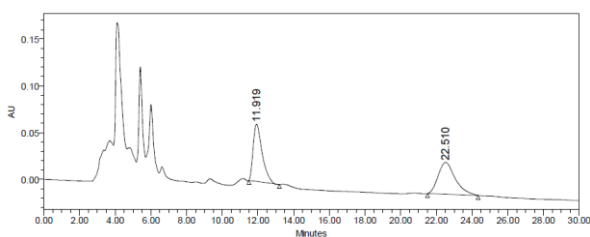
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 145.5, 144.9, 139.0, 133.9, 129.4, 128.1, 126.7, 119.0, 82.6, 79.3, 54.8, 39.3, 34.2, 27.7.

IR (ATR/ ν cm^{-1}): 2928, 1735, 1459, 1443, 1306, 1145.

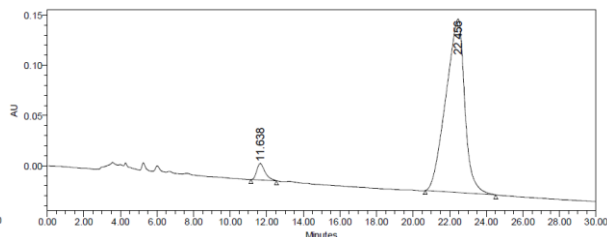
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{18}\text{SO}_3\text{Na}^+$: 337.0869, found 337.0881.

$[\alpha]_D^{25} = +36^\circ$ (c = 0.001 in CHCl_3).

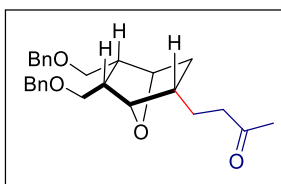
HPLC Data: Daicel CHIRALPAK OD-H; hexane: i PrOH = 60:40; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. $t_R = 22.456$ min (major) and 11.638 min (minor), enantiomeric ratio = 96:4.



	RT	Area	% Area	Height
1	11.919	2188623	49.07	61848
2	22.510	2271591	50.93	34184



	RT	Area	% Area	Height
1	11.638	517209	4.01	16315
2	22.456	12366357	95.99	172628



4-((1S,2S,4R,5R,6S)-5,6-bis((benzyloxy)methyl)-7-oxabicyclo[2.2.1]heptan-2-yl)butan-2-one (5):

Yellowish-dense liquid. Yield = 58%; 23.7 mg. er = 97.9:2.1, dr = >99:1

R_f 0.3 (20% EtOAc in Hexane).

¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.26 (m, 6H), 4.50 – 4.42 (m, 5H), 4.11 (s, 1H), 3.44 – 3.41 (m, 2H), 3.34 – 3.31 (m, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.14 – 2.11 (m, 5H), 1.75 – 1.66 (m, 3H), 1.53 – 1.43 (m, 1H), 1.31 – 1.25 (m, 1H).

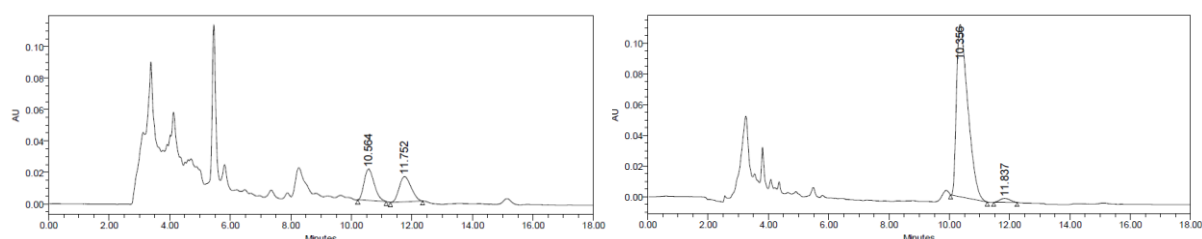
¹³C NMR (126 MHz, CDCl₃) δ 208.8 (s, C=O), 138.4 (s, Ar), 128.6 (d, ArH), 127.9 (d, ArH), 127.7 (d, ArH), 83.2 (d, CH), 79.6 (d, CH), 73.4 (t, CH₂), 69.1 (t, CH₂), 69.0 (t, CH₂), 46.0 (q, CH₃), 45.9 (d, CH), 42.1 (t, CH₂), 41.6 (d, CH), 37.0 (t, CH₂), 30.0 (d, CH), 29.3 (t, CH₂).

IR (ATR/v cm⁻¹): 2930, 2865, 1740, 1719, 1451, 1368.

HRMS (ESI-TOF): *m/z* [M+Na]⁺ calculated for C₂₆H₃₂O₄Na⁺: 431.2193, found 431.2209.

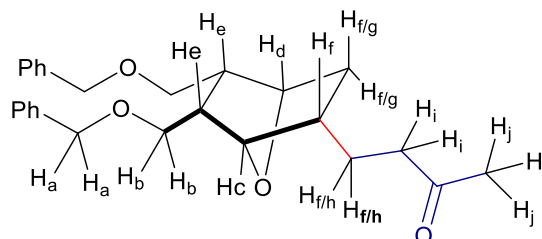
[α]_D²⁵ = -12° (c = 0.001 in CHCl₃).

HPLC Data: Daicel CHIRALPAK OJ-H; hexane: *i*PrOH = 50:50; detection wavelength = 258.0 nm; flow rate = 1.0 mL/min. *t_R* = 11.837 min (major) and 10.356 min (minor), Enantiomeric ratio = 97.9:2.1.



RT	Area	% Area	Height	
1	10.564	461994	51.54	19952
2	11.752	434464	48.46	15986

RT	Area	% Area	Height	
1	10.356	2923414	97.89	112088
2	11.837	62990	2.11	2604



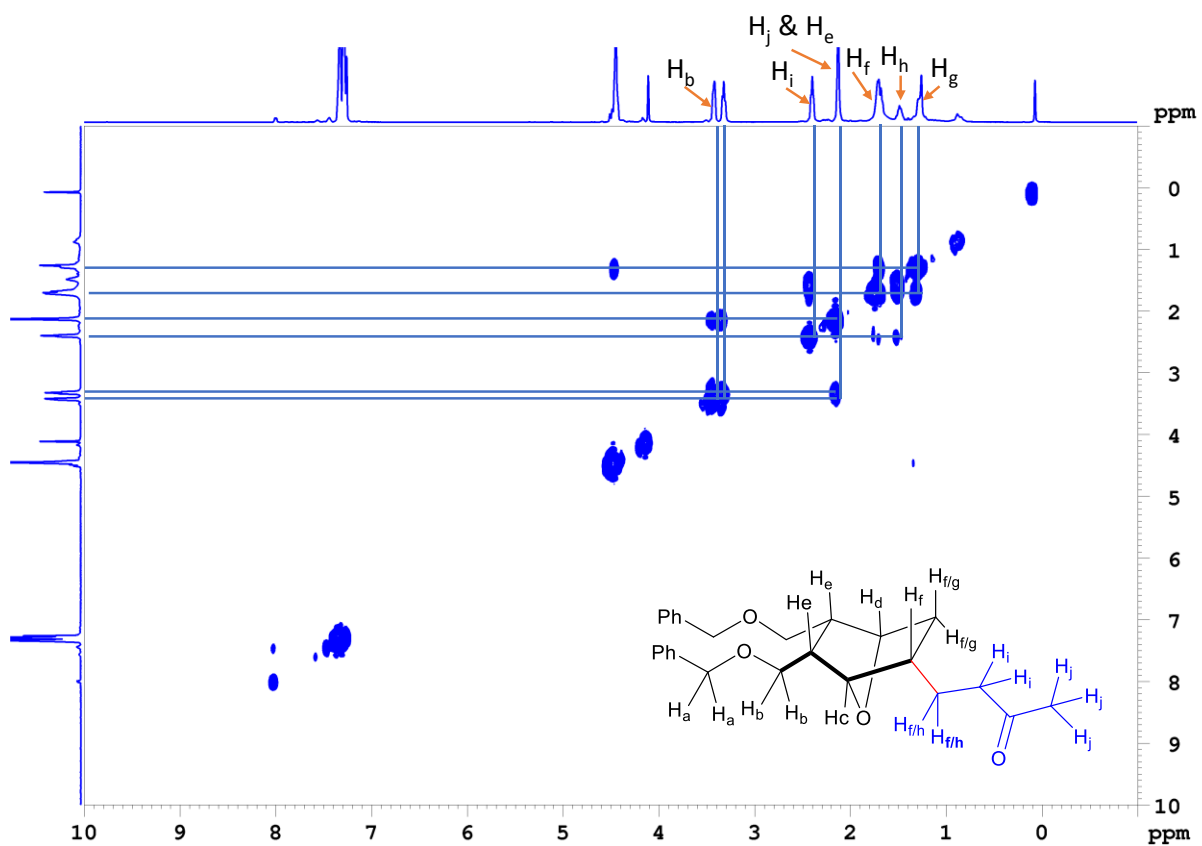


Figure S1. COSY for the adduct 5 in CDCl₃

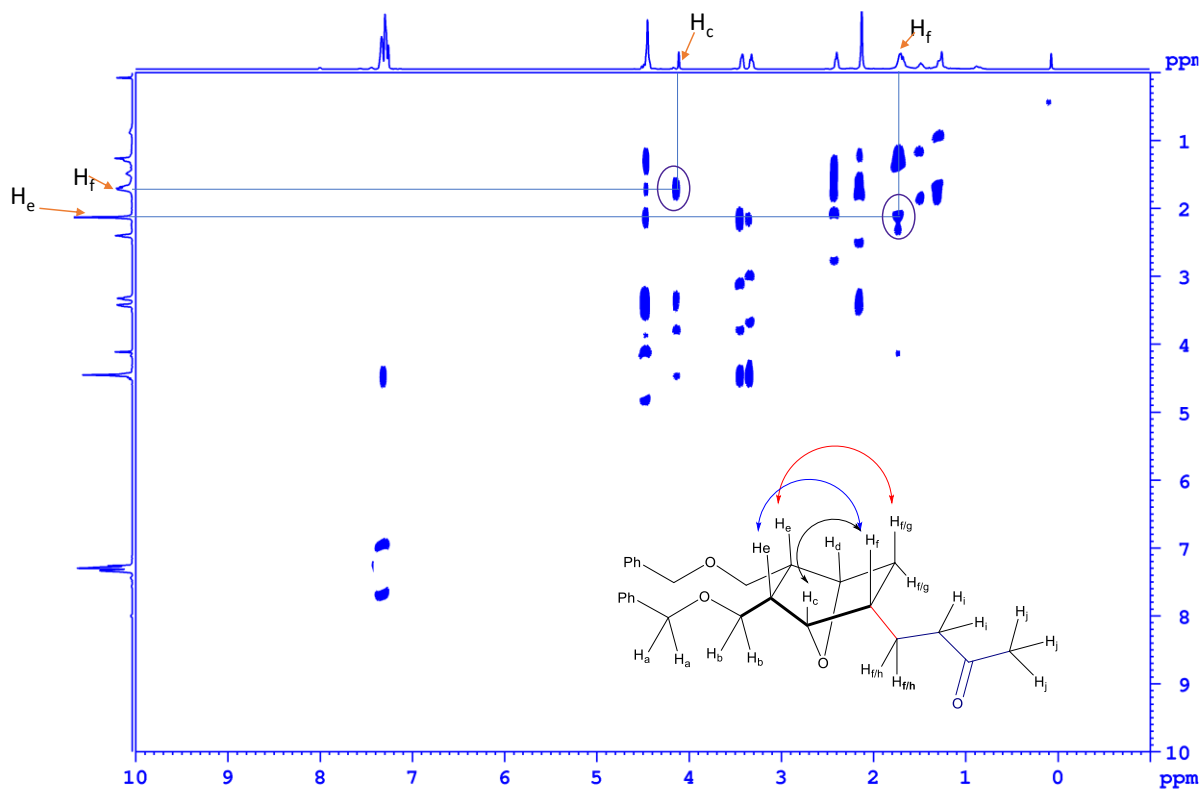


Figure S2. NOESY for the adduct 5 in CDCl₃

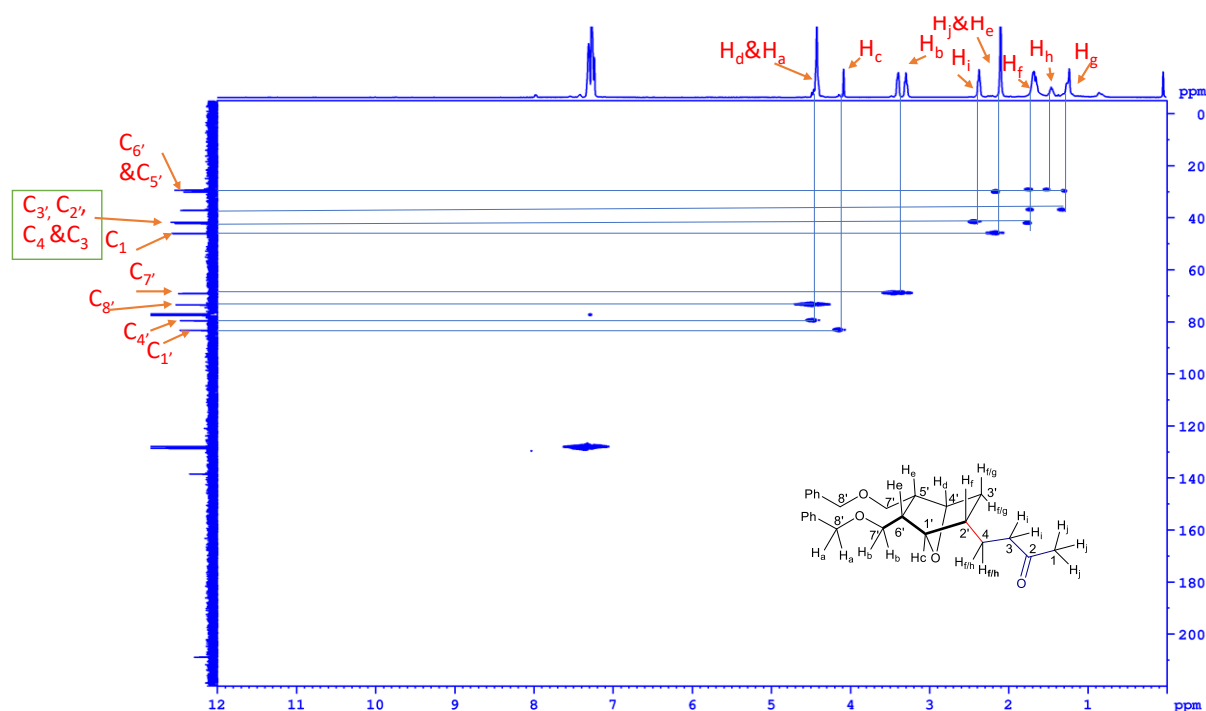
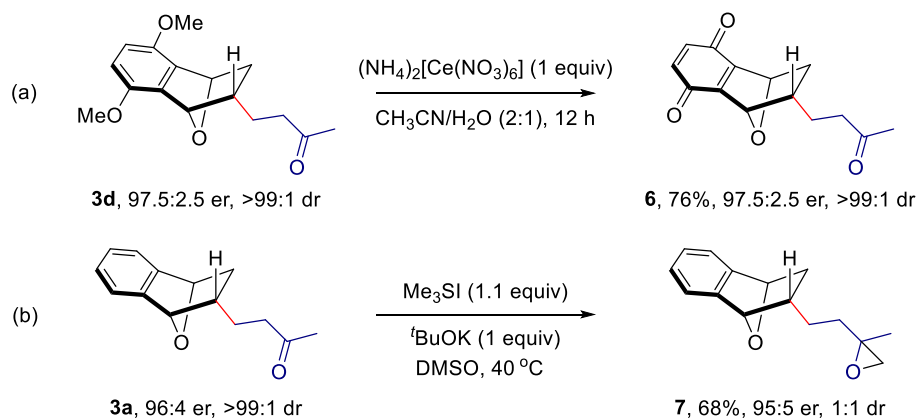


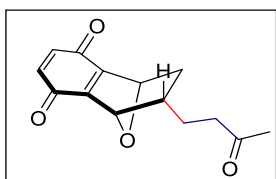
Figure S3. HSQC for the adduct **5** in CDCl_3

5. Derivatization of the Asymmetric Products



a) CAN Oxidation of **3d**:

To the solution of **3d** (0.05 mmol; 13.8 mg) in MeCN-water (0.75 mL, 2:1), CAN (0.15 mmol; 83 mg) was added at 0 °C. The reaction mixture was allowed to stir at 24 °C for 12 h. The reaction mixture was quenched by saturated aq. NaHCO_3 and extracted by ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated. The crude mixture was purified by flash column chromatography to yield **6**.²



(1*S*,2*S*,4*R*)-2-(3-oxobutyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene-5,8-dione (6):

Yellowish Solid. Yield = 76%; 19.0 mg. er = 97.8:2.2, dr = >99:1

R_f 0.3 (20 % EtOAc in Hexane)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.61 (s, 2H), 5.40 (d, $J = 0.9$ Hz, 1H), 5.08 (s, 1H), 2.54 (t, $J = 7.4$ Hz, 2H), 2.16 (s, 3H), 1.91 – 1.77 (m, 3H), 1.72 – 1.68 (m, 1H), 1.64 – 1.61 (m, 1H).

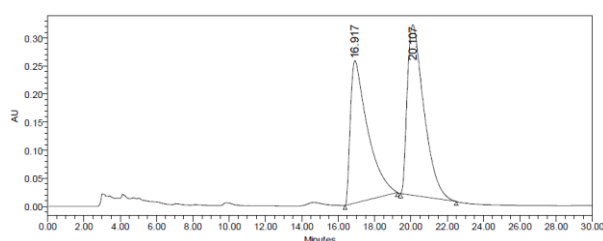
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 207.9, 183.2, 183.1, 150.9, 150.7, 136.4, 136.3, 80.7, 41.8, 38.0, 32.1, 30.2, 28.1.

IR (ATR/ ν cm^{-1}): 2954, 2920, 2855, 1703, 1680, 1456, 1376.

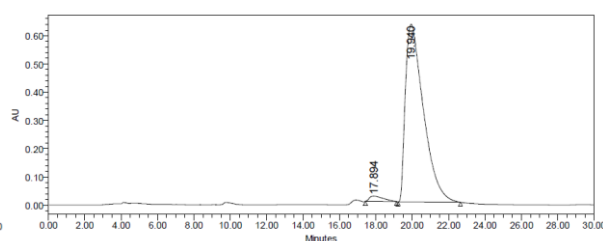
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{14}\text{O}_4\text{Na}^+$: 269.0784, found 269.0789.

$[\alpha]_D^{25} = -1^\circ$ ($c = 0.001$ in CHCl_3).

HPLC Data: Daicel CHIRALPAK OD-H; hexane: i PrOH = 85:15; detection wavelength = 252.1 nm; flow rate = 1.0 mL/min. $t_R = 19.940$ min (major) and 17.894 min (minor), enantiomeric ratio = 97.8:2.2.



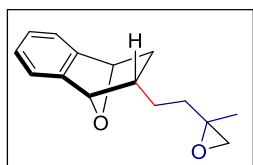
	RT	Area	% Area	Height
1	16.917	16793367	46.44	253737
2	20.107	19364601	53.56	303403



	RT	Area	% Area	Height
1	17.894	985598	2.23	18418
2	19.940	43279438	97.77	628533

b) Epoxidation of 3a:

To a solution of t BuOK (1 equiv., 112 mg) in DMSO at room temperature, trimethyl sulphonium iodide (1.1 equiv., 121mg) was added and stirred for 30 minutes. Then a solution of **3a** (0.5 mmol, 108 mg) in DMSO was added and stirred overnight. After the completion of the reaction, it was quenched with water and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel with hexane and ethyl acetate mixture as eluent to afford the desired epoxidation product **7**.³



(1*S*,2*S*,4*R*)-2-(2-(2-methyloxiran-2-yl)ethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (7):

Colourless oil. Yield = 68%; 15.7 mg. er = 95:5, dr = 1:1

R_f 0.3 (5% EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.24 – 7.20 (m, 4H), 7.18 – 7.10 (m, 4H), 5.36 (s, 1H), 5.35 (s, 1H), 5.04 (s, 1H), 5.02 (s, 1H), 2.63 – 2.61 (m, 2H), 2.59 (d, $J = 4.8$ Hz, 2H), 1.84 – 1.73 (m, 2H), 1.70 – 1.64 (m, 4H), 1.63 – 1.55 (m, 8H), 1.34 (s, 3H), 1.33 (s, 3H).

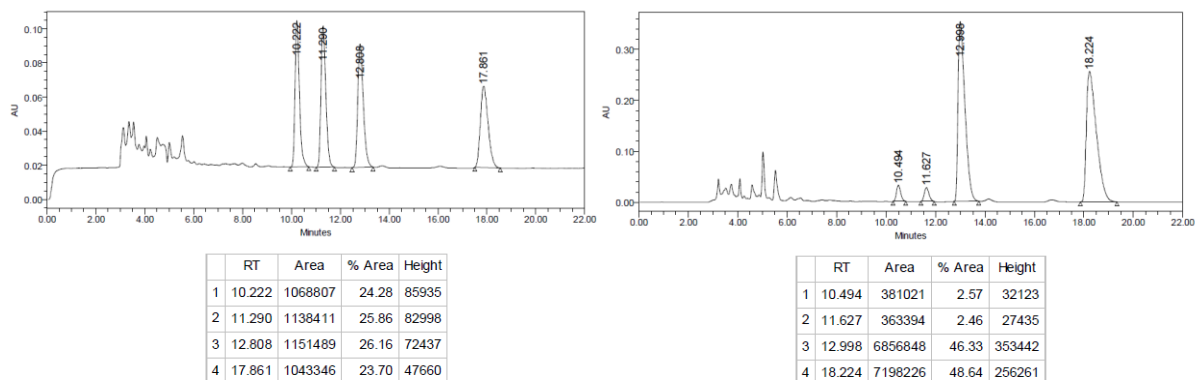
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 145.9, 145.8, 126.6, 126.6, 118.9, 118.9, 118.9, 83.6, 83.0, 79.5, 56.9, 56.9, 54.0, 40.7, 40.6, 35.4, 35.4, 34.8, 30.6, 21.1, 21.0.

IR (ATR/ ν cm^{-1}): 2923, 2858, 1727, 1462.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{14}\text{O}_4\text{Na}^+$: 253.1199, found 253.1210.

$[\alpha]_D^{25} = +38^\circ$ ($c = 0.001$ in CHCl_3).

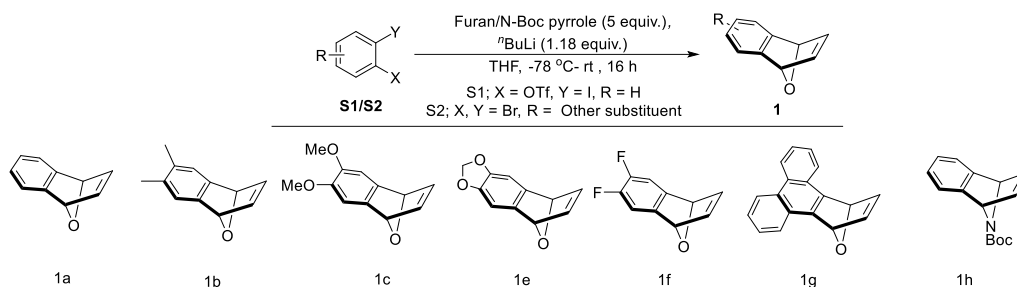
HPLC Data: Daicel CHIRALPAK IC-3; hexane: i PrOH = 60:40; detection wavelength = 264.0 nm; flow rate = 1.0 mL/min. $t_R = 18.224$ min, 12.998 min (major) and 10.494 min, 11.627 min (minor), enantiomeric ratio = 95:5, diastereomeric ratio = 1:1.



6. Synthesis of the starting materials:

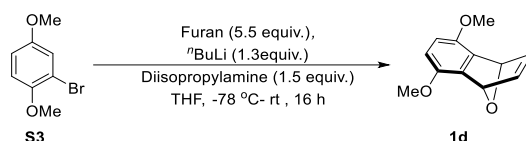
6A. General procedure for the synthesis of Bicyclic alkene

A.



A 100 mL Schlenk tube equipped with a magnetic stir bar and **S1** or **S2** (3 mmol) was kept under vacuum for 10 minutes and purged with Ar by three times. Then furan (5 equiv., 1.2 mL) in THF/ Et_2O (20 mL) was added, and the mixture was cooled to -78°C . n BuLi (1.5 mL, 2 M in hexanes, 1.05 mmol) was added to the mixture dropwise, maintaining the reaction temperature. The reaction was stirred for 2 hours at -78°C and then warmed to rt. After 16 h, the reaction mixture was quenched by the sat. NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted three times with DCM/ Et_2O . The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , concentrated, and purified by column chromatography (EtOAc/hexane) on silica gel to yield the targeted starting material.⁴

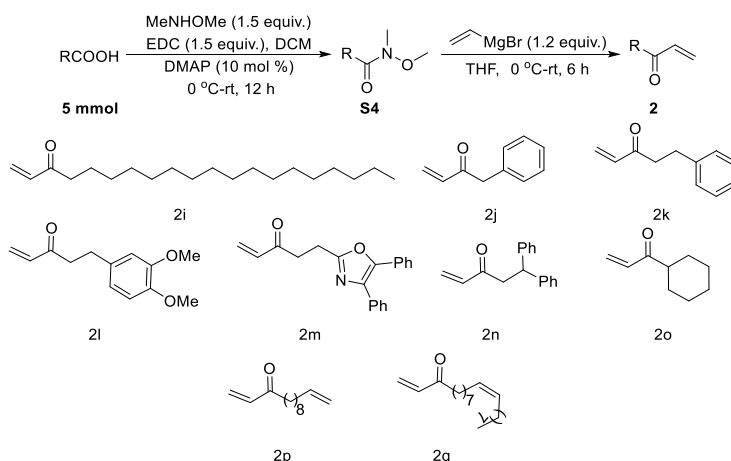
B.



A 100 mL Schlenk tube equipped with a magnetic stir bar was kept under vacuum for 10 minutes and purged with Ar. Then diisopropylamine (1.5 equiv., 0.5 mL) in THF (4 mL) was added, and the solution was cooled to -78 °C. *n*BuLi (1.4 mL, 1.9 M in hexanes, 2.6 mmol) was added to the mixture dropwise. It was kept at -78 °C for 15 minutes. Then furan (5.5 equiv., 0.8 mL) was added dropwise. After 5 min, **S3** (2 mmol) in 1 mL THF was added to the mixture. The reaction was stirred for 2 hours at -78 °C and then warmed to rt. After 16 h, the reaction mixture was quenched by the sat. NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted three times with DCM/Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, concentrated, and purified by column chromatography (EtOAc/hexane) on silica gel to yield the targeted starting material.⁵

6B. General procedure for the synthesis of α,β -unsaturated ketone:

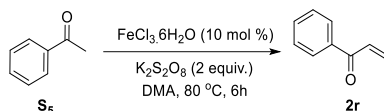
A.



Carboxylic acid (5 mmol) and 4-dimethylaminopyridine (10 mol%) were dissolved in CH₂Cl₂ (12.5 mL), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (1.5 equiv.) was added portion wise. The reaction mixture was stirred for 1h at rt. N,O-dimethyl hydroxylamine (1.5 equiv.) was added, and the mixture was stirred for 16 h at rt. After the completion of the reaction, water was added, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with saturated aq. NaHCO₃ and saturated aq. NaCl solutions, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica, providing the desired Weinreb amide.⁶ To the stirring solution of **S4** (4 mmol) in 6 mL anhydrous THF at <0 °C (ice-NaCl bath), a solution of vinyl magnesium bromide (1.2 equiv., 4.8 mmol, 1M in THF) was added dropwise. The resulting mixture was stirred at 0°C for 1h (white solid formed), then at rt for 4 h (the solid dissolved). The reaction was monitored by checking the TLC. After the completion of the reaction, saturated aq. NH₄Cl solution was added, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with saturated aq. NaCl and saturated

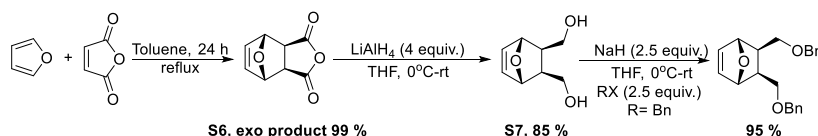
aq. NaCl solution, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica, providing the desired α,β -unsaturated ketone.⁷

B.



S5 (1 mmol), FeCl₃·6H₂O (27 mg, 0.1 mmol), K₂S₂O₈ (540 mg, 2.0 mmol), and DMA (4.0 mL) were sequentially added to a 15 mL tube under air. The tube was sealed and stirred at 80 °C for 6 h. Upon completion (monitored by TLC), the resulting mixture was diluted with Et₂O (15 mL) and washed with brine (10 mL × 3). The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (230-400 mesh) using hexane-EtOAc as eluent to yield the desired product **2r**.⁸

6C.

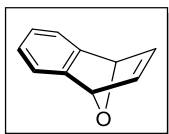


Maleic anhydride (5 mmol) and furan (1.5 equiv., 7.5 mmol) were dissolved in 10 mL of toluene. The resulting mixture was heated to reflux for 24 h. A white precipitate was formed. The reaction was cooled to rt. The solid was filtered with a Büchner funnel and washed with ether. After recrystallization from hexane-EtOAc, crystals were collected. Exo-cycloadduct **S6** (822 mg, 95%) was gained as a white powder and used without further purification.

S6 (4.95 mmol) was dissolved in dry THF (10 mL) and kept at 0 °C. Then LiAlH₄ (4 equiv.) was added to the solution slowly under an argon atmosphere. The reaction was warmed to room temperature and stirred for 7 h. After the completion of the reaction, the reaction mixture was quenched by the saturated aq. NH₄Cl solution, and extracted with EtOAc. Combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified via flash chromatography on silica gel (230-400 mesh) using hexane-EtOAc as eluent to yield the desired product **S7** (658 mg, 85%).

NaH (2.5 equiv.) was taken in a 50 mL RB with a magnetic stir bar and kept in a vacuum for 10 min. Then a solution of **S7** (1 equiv., 1.0 mmol) in dry THF was added slowly at 0 °C. A benzyl bromide (2.5 equiv., 2.5 mmol) was added after 30 minutes and kept at room temperature under an argon atmosphere overnight. After the completion of the reaction, it was quenched by the addition of water (5 mL), extracted with ether, dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified via flash chromatography on silica gel (230-400 mesh) by using hexane-EtOAc as eluent to yield the desired product **4** (320 mg, 95%).⁹

7. Characterization data of starting materials:



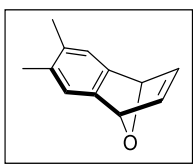
1,4-dihydro-1,4-epoxynaphthalene (1a): The above-targeted compound was prepared by following procedure **6A.A** from **S1**.^{4a}

Colorless solid. Yield = 87 %; 376 mg.

R_f 0.4 (5 % EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.27– 7.25 (m, 2H), 7.03 (t, J = 1.1 Hz, 2H), 6.99 – 6.97 (m, 2H), 5.72 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 149.1, 143.1, 125.1, 120.4, 82.4.



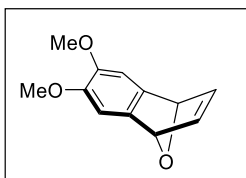
6,7-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (1b): The above-targeted compound was prepared by following procedure **6A.A** from **S2b**.^{4b}

White solid. Yield = 84 %; 432 mg.

R_f 0.5 (3 % EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.06 (s, 2H), 7.00 (s, 2H), 5.66 (s, 2H), 2.20 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 146.8, 143.2, 132.7, 122.3, 82.4, 19.9.



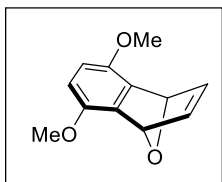
6,7-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene (1c): The above-targeted compound was prepared by following procedure **6A.A** from **S2c**.^{4b}

White solid. Yield = 63 %; 386 mg.

R_f 0.3 (15 % EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.04 (s, 2H), 6.96 (s, 2H), 5.67 (s, 2H), 3.84 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 145.9, 143.4, 141.8, 106.9, 82.6, 56.5.

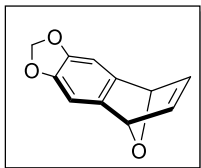


5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene (1d): The above-targeted compound was prepared by following procedure **6A.B** from **S3**.⁵

White solid. Yield = 86 %; 527 mg.

R_f 0.3 (15% EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.07 (s, 2H), 6.54 (s, 2H), 5.93 (s, 2H), 3.79 (s, 6H).
¹³C NMR (126 MHz, CDCl₃) δ 148.1, 143.0, 137.7, 111.9, 80.5, 56.6.



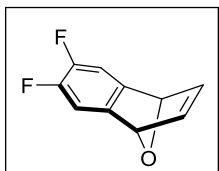
5,8-dihydro-5,8-epoxynaphtho[2,3-d][1,3]dioxole (1e): The above-targeted compound was prepared by following procedure **6A.A** from **S2e**.^{4b}

Yield = 90 %; 508 mg.

R_f 0.3 (5% EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.04 (s, 2H), 6.83 (s, 2H), 5.93 (s, 1H), 5.89 (s, 1H), 5.64 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 144.6, 143.6, 143.5, 104.1, 101.4, 82.7.



6,7-difluoro-1,4-dihydro-1,4-epoxynaphthalene (1f): The above-targeted compound was prepared by following procedure **6A.A** from **S2f**.^{4d}

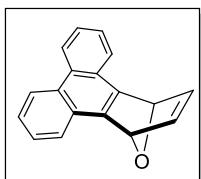
Yellow liquid. Yield = 62 %; 335 mg.

R_f 0.6 (15% EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 7.07 (t, *J*_{F-H} = 7.7 Hz, 2H), 7.03 (s, 2H), 5.69 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 147.5 (dd, ¹*J*_{F-C} = 248.22, ²*J*_{F-C} = 15.12 Hz), 145.3 (t, ³*J*_{F-C} = 5.04 Hz), 143.2, 110.9–110.0 (m), 82.3.

¹⁹F NMR (471 MHz, CDCl₃) δ -142.30.



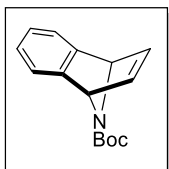
1,4-dihydro-1,4-epoxytriphenylene (1g): The above-targeted compound was prepared by following procedure **6A.A** from **S2g**.^{4c}

White solid. Yield = 75 %; 550 mg.

R_f 0.2 (5% EtOAc in Hexane);

¹H NMR (500 MHz, CDCl₃) δ 8.74 (d, *J* = 9.8 Hz, 2H), 7.95 (d, *J* = 9.5 Hz, 2H), 7.64 (d, *J* = 6.1 Hz, 4H), 7.29 (s, 2H), 6.40 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 147.0, 144.1, 127.3, 126.8, 126.0, 123.6, 123.2, 103.2, 82.2.



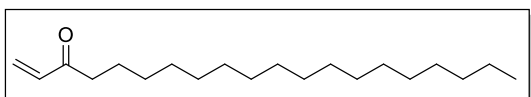
Tert-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (1h): The above-targeted compound was prepared by following procedure **6A.A** from **S1h**.^{4a}

Yellowish solid. Yield = 75 %; 547 mg.

R_f 0.3 (5% EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.26 (s, 2H), 6.99 – 6.93 (m, 4H), 5.48 (s, 2H), 1.38 (s, 9H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.3, 148.5, 125.1, 121.1, 80.7, 66.3, 28.3.



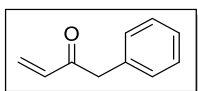
Icos-1-en-3-one (2i): The above-targeted compound was prepared by following procedure **6B.A** from **S4i**.⁶⁻⁷

White solid. Yield (50 %; 590 mg)

R_f 0.3 (2% EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.35 (dd, $J = 17.7, 10.5$ Hz, 1H), 6.21 (d, $J = 17.7$ Hz, 1H), 5.81 (d, $J = 11.9$ Hz, 1H), 2.57 (t, $J = 7.4$ Hz, 2H), 1.64 – 1.58 (m, 2H), 1.55 (s, 2H), 1.25 (s, 26H), 0.88 (t, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 201.3, 136.8, 127.9, 39.9, 32.1, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 24.2, 22.8, 14.3.

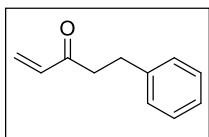


1-phenylbut-3-en-2-one (2j): The targeted compound was prepared by following procedure **6B.A** from **S4**.⁶⁻⁷

Colorless liquid. Yield (40 %; 234 mg).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.33 (ddd, $J = 7.5, 6.3, 1.4$ Hz, 2H), 7.29 – 7.25 (m, 1H), 7.23 – 7.20 (m, 2H), 6.41 (dd, $J = 17.5, 10.4$ Hz, 1H), 6.31 (dd, $J = 17.6, 1.3$ Hz, 1H), 5.83 (dd, $J = 10.4, 1.4$ Hz, 1H), 3.88 (s, 2H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 197.9, 135.7, 134.2, 129.6, 129.2, 128.9, 127.1, 47.3.



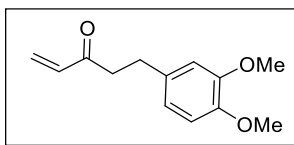
5-phenylpent-1-en-3-one (2k): The targeted compound was prepared by following procedure **6B.A** from **S4k**.⁶⁻⁷

Colorless liquid. Yield = 61 %, 385 mg.

R_f 0.3 (2% EtOAc in Hexane)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.21 – 7.18 (m, 3H), 6.39 – 6.33 (m, 1H), 6.24 – 6.19 (m, 1H), 5.83 (d, $J = 10.7$ Hz, 1H), 2.99 – 2.90 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 199.9, 141.2, 136.7, 128.7, 128.5, 128.3, 126.3, 41.4, 30.0.

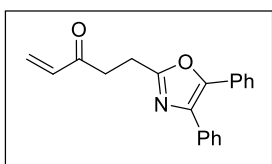


5-(3,4-dimethoxyphenyl)pent-1-en-3-one (2l): The above-targeted compound was prepared by following procedure **6B.A** from **S4l**.⁶⁻⁷

Colourless liquid. Yield = 55 %, 485 mg.

R_f 0.2 (5% EtOAc in Hexane);

^1H NMR (500 MHz, CDCl_3) δ 6.80 – 6.78 (m, 1H), 6.73 (s, 2H), 6.43 – 6.30 (m, 1H), 6.23 – 6.19 (m, 1H), 5.83 (dd, J = 10.7, 2.6 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.90 (bs, 4H).



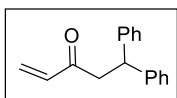
5-(4,5-diphenyloxazol-2-yl)pent-1-en-3-one (2m): The above-targeted compound was prepared by following procedure **6B.A** from **S4m**.⁶⁻⁷

Colourless liquid. Yield = 51 %, 619 mg.

R_f 0.3 (10% EtOAc in Hexane);

^1H NMR (500 MHz, CDCl_3) δ 7.66 – 7.60 (m, 2H), 7.59 – 7.53 (m, 2H), 7.38 – 7.29 (m, 6H), 6.46 – 6.41 (m, 1H), 6.34 – 6.31 (m, 1H), 5.91 (dd, J = 10.5, 1.1 Hz, 1H), 3.24 – 3.18 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 198.4, 162.4, 145.4, 136.3, 135.1, 133.8, 129.0, 128.8, 128.7, 128.6, 128.5, 128.1, 128.0, 126.5, 36.7, 22.0.



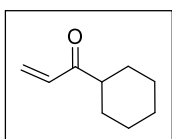
5,5-diphenylpent-1-en-3-one (2n): The above-targeted compound was prepared by following procedure **6B.A** from **S4n**.⁶⁻⁷

Colourless liquid. Yield = 65 %, 615 mg.

R_f 0.3 (3% EtOAc in Hexane);

^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.25 (m, 8H), 7.24 – 7.19 (m, 2H), 6.39 – 6.34 (m, 1H), 6.24 (dd, J = 17.7, 1.1 Hz, 1H), 5.82 (dd, J = 10.6, 1.1 Hz, 1H), 4.73 (t, J = 7.5 Hz, 1H), 3.39 (d, J = 7.5 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 198.5, 143.9, 136.5, 128.5, 128.3, 127.9, 127.8, 126.4, 45.9, 45.6.



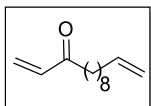
1-cyclohexylprop-2-en-1-one (2o): The above-targeted compound was prepared by following procedure **6B.A** from **S4o**.⁶⁻⁷

Colourless liquid. Yield = 58 %, 321 mg.

R_f 0.3 (2% EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.44 – 6.37 (m, 1H), 6.23 (dd, $J = 17.5, 1.5$ Hz, 1H), 5.72 (dd, $J = 10.5, 1.5$ Hz, 1H), 2.63 – 2.56 (m, 1H), 1.83 – 1.76 (m, 4H), 1.67 (d, $J = 12.4$ Hz, 1H), 1.40 – 1.19 (m, 5H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 203.5, 135.1, 127.8, 48.3, 28.6, 26.0, 25.8.



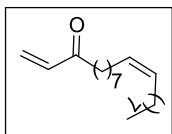
trideca-1,12-dien-3-one (2p): The above-targeted compound was prepared by following procedure **6B.A** from **S4p**.⁶⁻⁷

Colourless liquid. Yield = 52 %, 405 mg.

R_f 0.5 (3% EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.34 (m, 1H), 6.20 (d, $J = 17.7$ Hz, 1H), 5.85 – 5.74 (m, 2H), 5.02 – 4.88 (m, 2H), 2.56 (t, $J = 7.5$ Hz, 2H), 2.05 – 2.00 (m, 2H), 1.63 – 1.59 (m, 2H), 1.39 – 1.35 (m, 2H), 1.28 (s, 8H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 201.2, 139.3, 136.7, 127.9, 114.3, 39.8, 33.9, 29.5, 29.4, 29.3, 29.2, 29.0, 24.1.



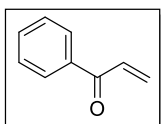
(Z)-icosa-1,11-dien-3-one (2q): The above-targeted compound was prepared by following procedure **6B.A** from **S4q**.⁶⁻⁷

Colourless liquid. Yield = 63 %, 737 mg.

R_f 0.5 (2% EtOAc in Hexane);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.39 – 6.31 (m, 1H), 6.20 (d, $J = 17.5$ Hz, 1H), 5.80 (d, $J = 10.7$ Hz, 1H), 5.38 – 5.32 (m, 2H), 2.57 (t, $J = 7.5$ Hz, 2H), 2.02 – 2.00 (m, 4H), 1.65 – 1.59 (m, 2H), 1.33 – 1.24 (m, 20H), 0.88 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 201.2, 136.8, 130.1, 129.9, 127.9, 39.8, 32.1, 29.9, 29.8, 29.7, 29.5, 29.4, 29.3, 27.4, 27.3, 24.2, 22.8, 14.2.

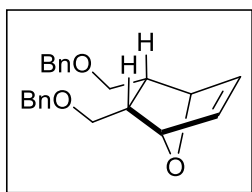


1-phenylprop-2-en-1-one (2r): The above-targeted compound was prepared by following procedure **6B.B** from **S4r**.⁸

Colourless liquid. Yield = 70 %, 93 mg.

R_f 0.4 (4% EtOAc in Hexane).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.96 – 7.90 (m, 2H), 7.57 – 7.53 (m, 1H), 7.48 – 7.43 (m, 2H), 7.14 (dd, J = 17.0, 10.6 Hz, 1H), 6.45 – 6.40 (m, 1H), 5.93 – 5.88 (m, 1H).
 $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 191.0, 137.3, 133.0, 132.5, 130.1, 128.7, 128.6.



(5S,6R)-5,6-bis((benzyloxy)methyl)-7-oxabicyclo[2.2.1]hept-2-ene (4): The above-targeted compound was prepared by following procedure **6C** from **S7**.⁹

Colourless liquid. Yield = 95 %; 320.00 mg.

R_f 0.3 (5% EtOAc in Hexane).

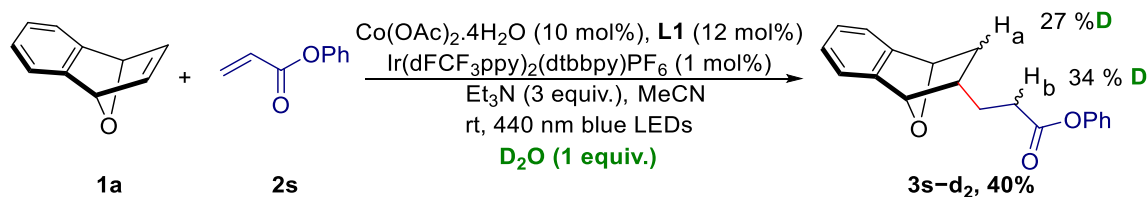
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.38 – 7.28 (m, 10H), 6.36 (s, 2H), 4.89 (s, 2H), 4.55 – 4.47 (m, 4H), 3.62 – 3.57 (m, 2H), 3.42 – 3.57 (m, 2H), 1.98 (t, J = 6.3 Hz, 2H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.4, 135.7, 128.6, 127.9, 127.8, 80.9, 73.5, 70.0, 40.2.

8. Control Experiments and Mechanistic Studies:

8.1 Deuterium Scrambling Experiments

a)



In an argon-filled glove box, a 15 mL reaction tube was charged with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2 mg; 10 mol%) and (*S,S*)-L1 (5.6 mg; 12 mol%) in 1 mL dry acetonitrile. The mixture was stirred for 10 minutes. Then $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (1 mg; 1 mol%), triethyl amine (41 μL ; 3 equiv.), **1a** (14.4 mg, 0.1 mmol) and **2a** (43 μL ; 5 equiv.) were sequentially added into the tube. The tube was sealed and removed from the glove box. Then D_2O (1.8 μL ; 1 equiv.) was added into the tube. The tube was sealed and removed from the glove box. Then the reaction tube was stirred for 24 hours under irradiation with 440 nm blue LEDs at room temperature. After completion of the reaction, the mixture was filtered through the small pad of silica gel with additional ethyl acetate and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with hexane and Ethyl acetate as eluent to afford the desired reductive coupling product **3s-d₂**. Deuterium incorporation was observed at 27% and 34% at 'a' and 'b' positions, respectively.

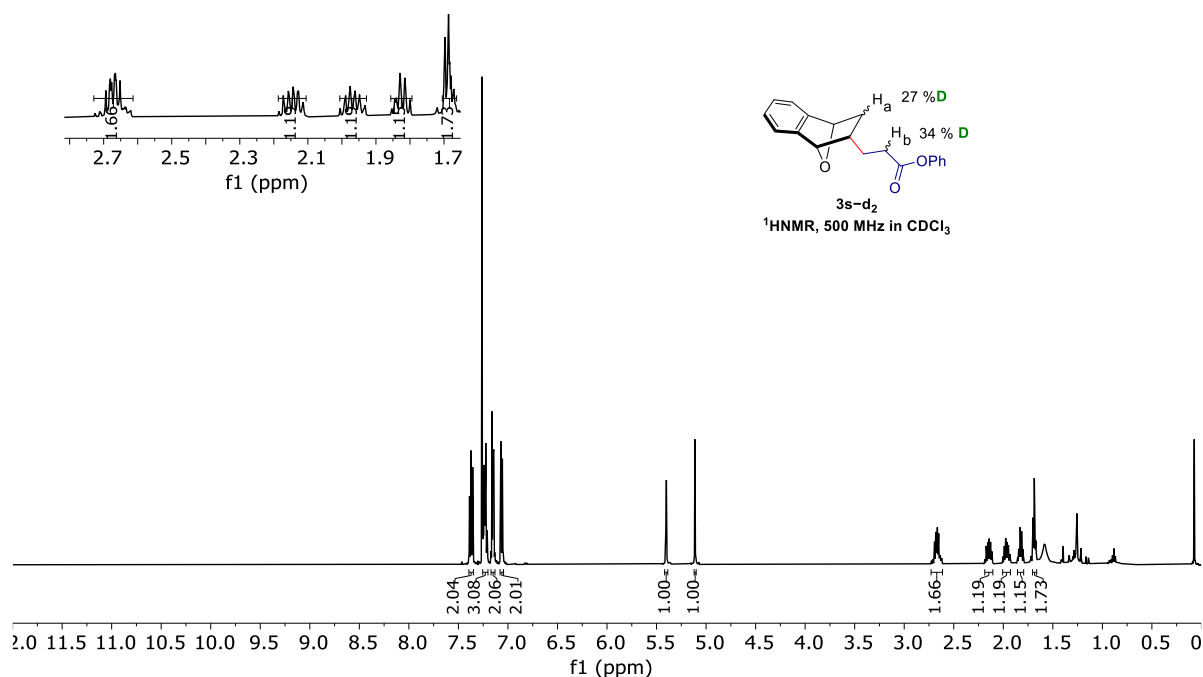
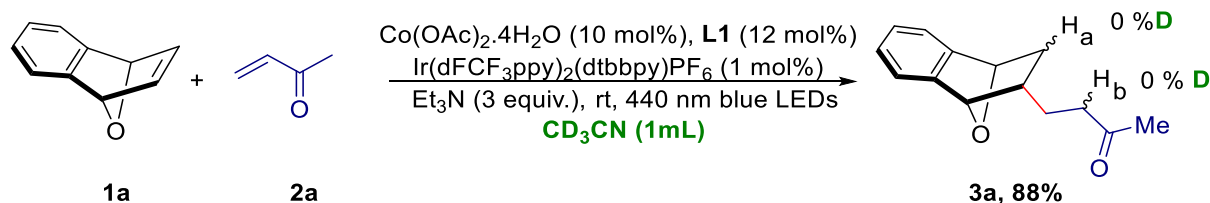


Figure S4. ^1H NMR of **3s-d₂** indicated 27% and 34% D incorporations at ‘a’ and ‘b’ positions, respectively.

b)



In an argon-filled glove box, a 15 mL reaction tube was charged with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2 mg; 10 mol%) and (*S,S*)-L1 (5.6 mg; 12 mol%) in 1 mL CD_3CN . The mixture was stirred for 10 minutes. Then $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (1 mg; 1 mol%), triethyl amine (41 μL ; 3 equiv.), **1a** (14.4 mg, 0.1 mmol) and **2a** (43 μL ; 5 equiv.) were sequentially added into the tube. The tube was sealed and removed from the glove box. Then the reaction tube was stirred for 24 hours under irradiation with 440 nm blue LEDs at room temperature. After completion of the reaction, the mixture was filtered through the small pad of silica gel with additional ethyl acetate and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with Hexane and Ethyl acetate as eluent to afford the desired reductive coupling product. Deuterium incorporation was not observed at ‘a’ and ‘b’ positions.

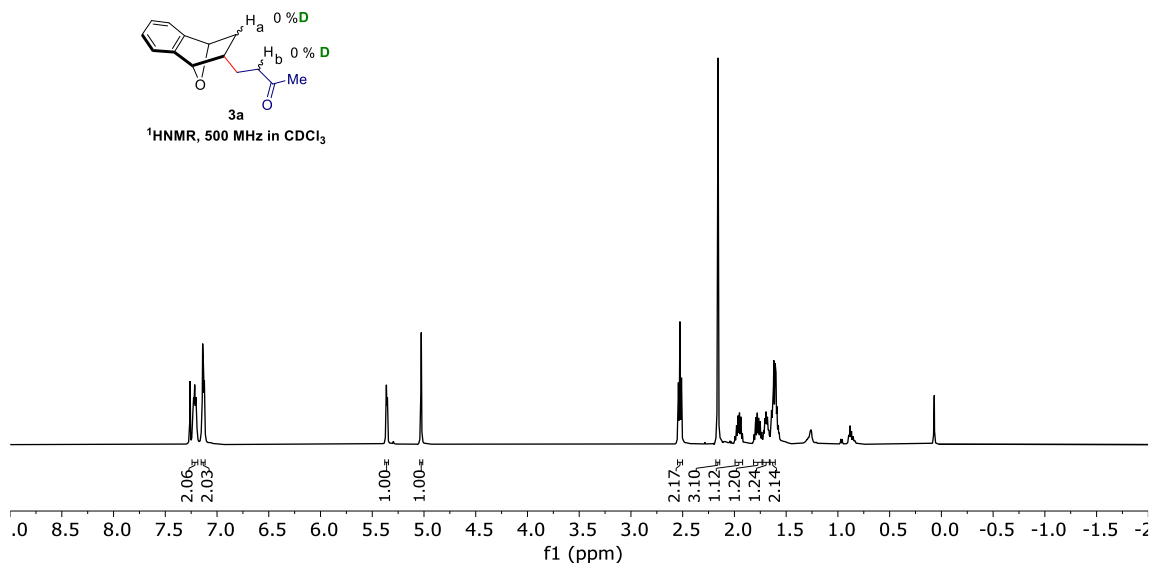
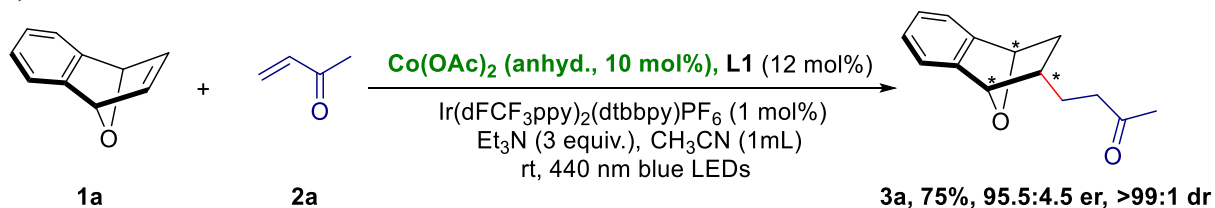


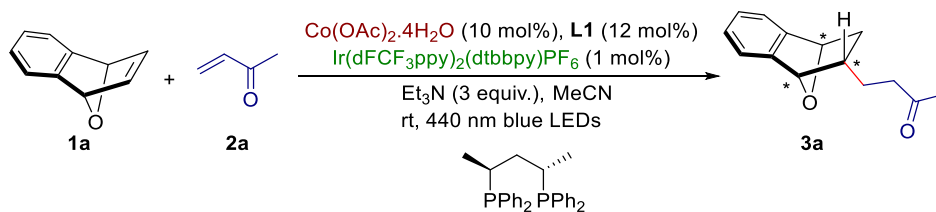
Figure S5. ^1H NMR of **3a** indicated 0% D incorporations at ‘a’ and ‘b’ positions.

c)



In a argon-filled glove box, a 15 mL reaction tube was charged with Co(OAc)_2 (anhyd.) (1.7 mg; 10 mol%) and (*S,S*)-L1 (5.6 mg; 12 mol%) in 1 mL dry acetonitrile. The mixture was stirred for 10 minutes. Then $\text{Ir(dFCF}_3\text{ppy)}_2\text{(dtbbpy)PF}_6$ (1 mg; 1 mol%), triethyl amine (41 μL ; 3 equiv.), **1a** (14.4 mg, 0.1 mmol) and **2a** (43 μL ; 5 equiv.) were sequentially added into the tube. The tube was sealed and removed from the glove box. Then the reaction tube was stirred for 24 hours under irradiation with 440 nm blue LEDs at room temperature. After completion of the reaction, the mixture was filtered through the small pad of silica gel with additional ethyl acetate and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with Hexane and Ethyl acetate as eluent to afford the desired reductive coupling product **3a** in 75% yield, 95.5:4.5 er and >99:1 dr.

8.2 Light on-off experiment:



In an argon-filled glove box, a 15 mL reaction tube was charged with $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ (2 mg; 10 mol%) and (*S,S*)-L1 (5.6 mg; 12 mol%) in 1 mL dry acetonitrile. The mixture was stirred for 10 minutes. Then $\text{Ir(dFCF}_3\text{ppy)}_2\text{(dtbbpy)PF}_6$ (1 mg; 1 mol%), triethyl amine (41 μL ; 3 equiv.),

1a (14.4 mg, 0.1 mmol) and **2a** (43 μ L; 5 equiv.) were sequentially added into the tube. The tube was sealed and removed from the glove box. Then the reaction tube was placed in light and dark for every alternative 20 min up to 2 hours. After every 20 min interval, the aliquot was taken out by a needle under the Ar atmosphere and quenched with water, the organic part was taken in EtOAc, and Gas chromatography was carried out. The yields were determined using 1,3,5-trimethoxy benzene as an internal standard.

Table S8:

Entry	time (min)	Light source	GC yield (%)
1	0	--	0
2	20	on	39
3	40	off	39
4	60	on	62.7
5	80	off	62.8
6	100	on	65.2
7	120	off	65.5

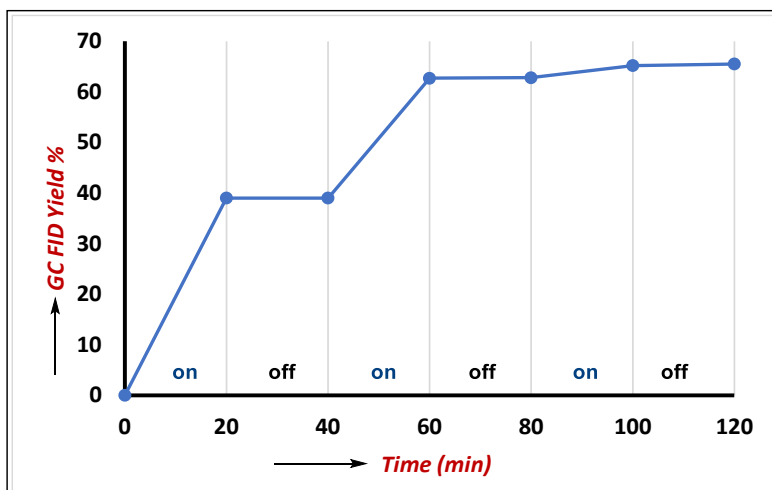


Figure S6. Reaction profile with the light on/off over time.

8.3 Stern-Vollmer fluorescence quenching studies

Rates of quenching (k_q) were determined using Stern–Vollmer kinetics (eq. 1).

$$\frac{I_0}{I} = k_q \tau_0 [\text{Quencher}] + 1 \dots\dots (1)$$

Where I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher, and τ_0 is the lifetime of the photocatalyst (2300 ns for $[\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6]$ in acetonitrile).

Stern-Vollmer fluorescence quenching studies were carried out using a 10^{-8} M solution of $[\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6]$ in acetonitrile and variable concentrations of triethyl amine (Et_3N). The samples were prepared in 3.5 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with Parafilm inside an argon-filled glove bag. The solutions were irradiated at 440nm, and the luminescence was measured at 472nm.

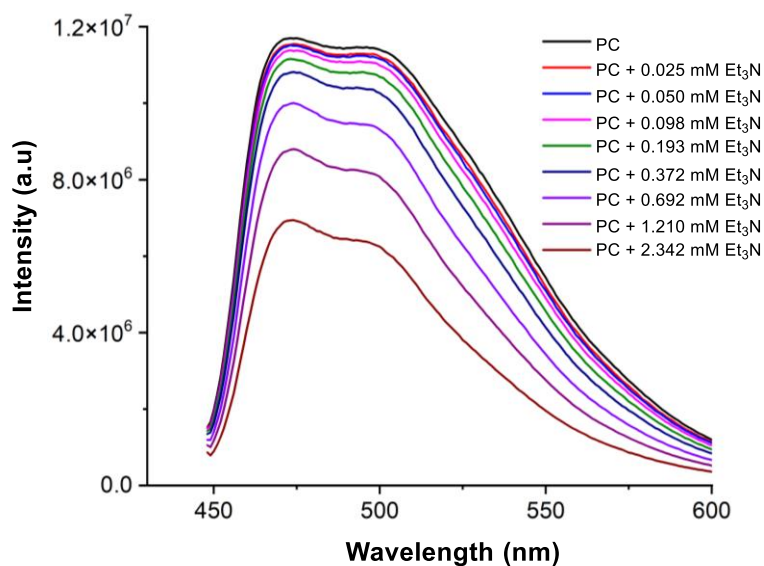


Figure S7a. Stern–Volmer Luminescence quenching experiment of $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ with NEt_3 in MeCN. The emission intensity of $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ solution is strongly affected by the gradual increase of the amount of NEt_3 .

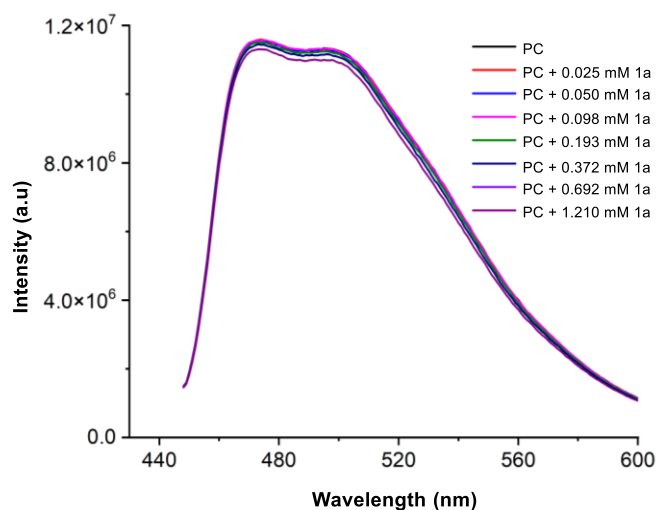


Figure S7b. Stern–Volmer Luminescence quenching experiment of $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ with **1a** in MeCN. The emission intensity of $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ solution was unaffected by the gradual increase of the amount of **1a**.

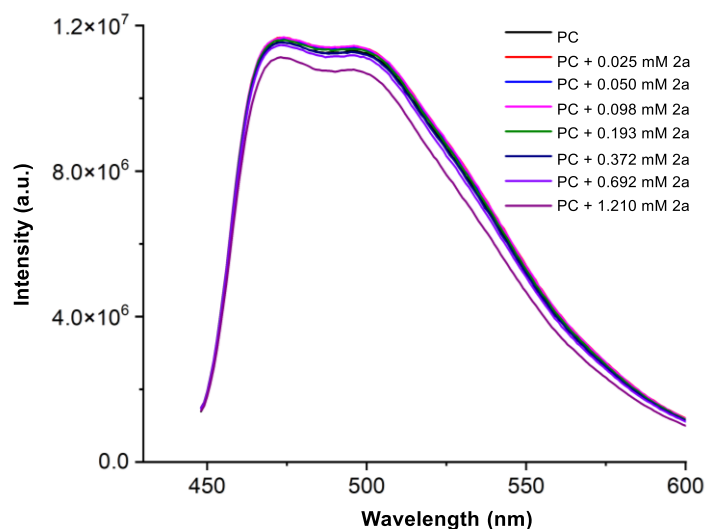


Figure S7c. Stern–Volmer Luminescence quenching experiment of Ir(dFCF₃ppy)₂(dtbbpy)PF₆ with **2a** in MeCN. The emission intensity of Ir(dFCF₃ppy)₂(dtbbpy)PF₆ solution was unaffected by the gradual increase of the amount of **2a**.

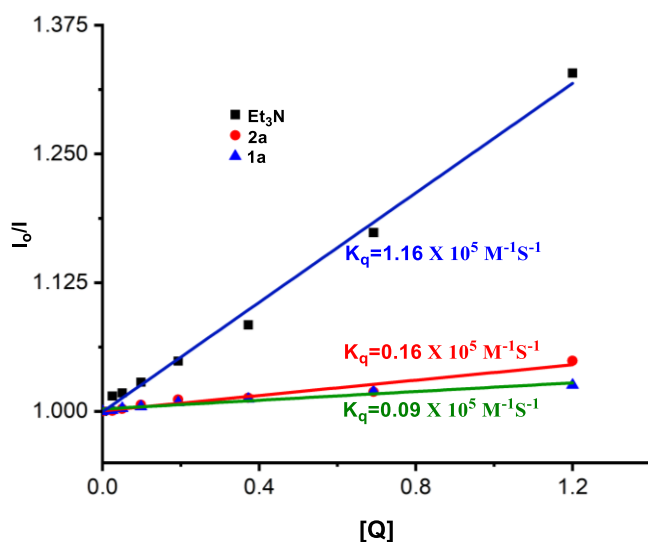


Figure S7d. Stern–Volmer Linear plot of Ir(dFCF₃ppy)₂(dtbbpy)PF₆ at a variable concentration of Et₃N, **1a** and **2a**.

A linear Stern-Volmer plot was obtained at the variable concentration of Et₃N. From the plot $k_q = 1.16 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ was obtained.

A similar experiment was repeated against variable concentrations of oxabicyclic alkene. Relatively no quenching was observed, and a linear Stern-Volmer plot was drawn with $k_q = 0.091 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

A similar experiment was repeated against variable concentrations of methyl vinyl ketone. No quenching was observed, and a linear Stern-Volmer plot was drawn with $k_q = 0.16 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

8.4 Cyclic Voltammetry:

Glassy Carbon, Platinum (Pt) wire, Ag/AgCl (aqueous, saturated KCl) electrodes were used as the working, counter, and reference electrodes, respectively. Cyclic Voltammetry was carried out in CHI-660 potentiostat workstation at a rate of 0.1 V/s in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Ag/AgCl electrode was standardized using ferrocene. To convert the potentials from Ag/AgCl (non-aqueous) to SCE, the potential for ferrocene was measured under the above conditions in CH₃CN, and 0.450 V was added from the measured values. The whole solution was degassed with nitrogen bubbling to remove the dissolved oxygen. The Co(OAc)₂·4H₂O·(S,S)-bdpp complex was formed in situ by adding Co(OAc)₂·4H₂O (0.01 mmol) and (S,S)-bdpp (0.012 mmol) into acetonitrile (3 mL). The solutions were stirred for 2 h in Ar filled glove box. As shown in Figure S7, the first reduction peak [$E_{1/2}(\text{Co(II)/Co(I)}) = -0.87 \text{ V vs SCE}$ in MeCN] of the red-coloured cyclic voltammogram is corresponding to the Co(II)/Co(I) couple of Co(OAc)₂·4H₂O·(S,S)-bdpp complex. Based on the earlier literature, the reduction potential of Ir(dFCF₃ppy)₂(dtbbpy)PF₆ [$E_{1/2}(\text{Ir(III)/Ir(II)}) = -1.37 \text{ V vs SCE}$ in MeCN] is -1.37 V vs SCE in MeCN. The reduced Ir(II) spontaneously undergoes a single electron transfer (SET) to reduce the diphosphine coordinated Co(II) complex [$E_{1/2}(\text{Ir(III)/Ir(II)}) = -1.37 \text{ V}$, $E_{1/2}(\text{Co(II)/Co(I)}) = -0.87 \text{ V vs SCE}$ in MeCN] and regenerates Ir(III) and produces the low valent Co(I) complex.

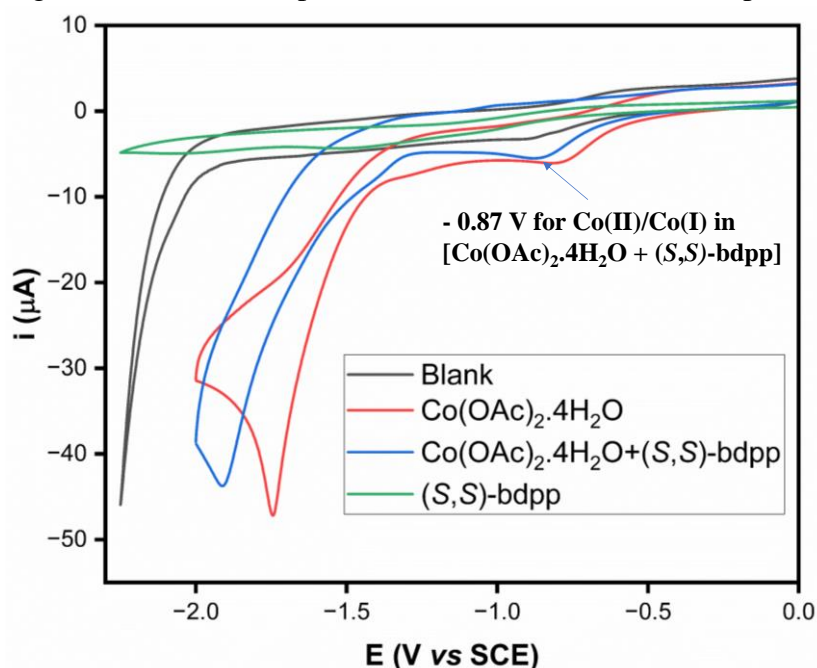
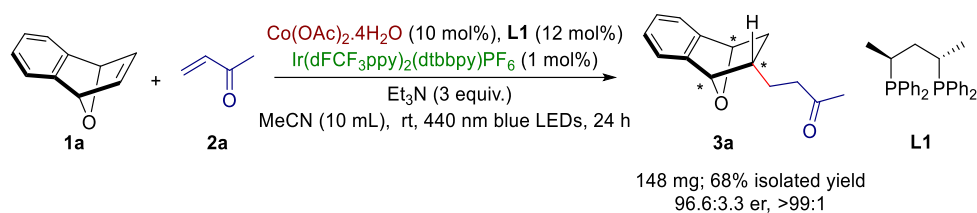


Figure S8. Reductive Cyclic Voltammogram of blank, Co(OAc)₂·4H₂O, (S,S)-bdpp ligand and the Co(OAc)₂·4H₂O in presence of (S,S)-bdpp in MeCN.

9. Scale-up experiment:



In an argon-filled glove box, a 50 mL Schenk RB was charged with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (20 mg; 10 mol%) and (*S,S*)-L1 (53 mg; 12 mol%) in 10 mL dry acetonitrile. The mixture was stirred for 10 min. Then $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (10 mg; 1 mol%), triethyl amine (418 μL ; 3 equiv.), **1a** (144.17 mg, 1 mmol) and **2a** (416 μL ; 5 equiv.) were sequentially added into the RB. The RB was sealed and removed from the glove box. Then the reaction vessel was stirred for 24 h under irradiation with 440 nm blue LEDs at room temperature. After completion of the reaction, the mixture was filtered through the small pad of silica gel with additional ethyl acetate and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with Hexane and Ethyl acetate as eluent to afford the desired reductive coupling product. Then, the enantiomeric ratio was checked by the chiral HPLC stationary phase column.

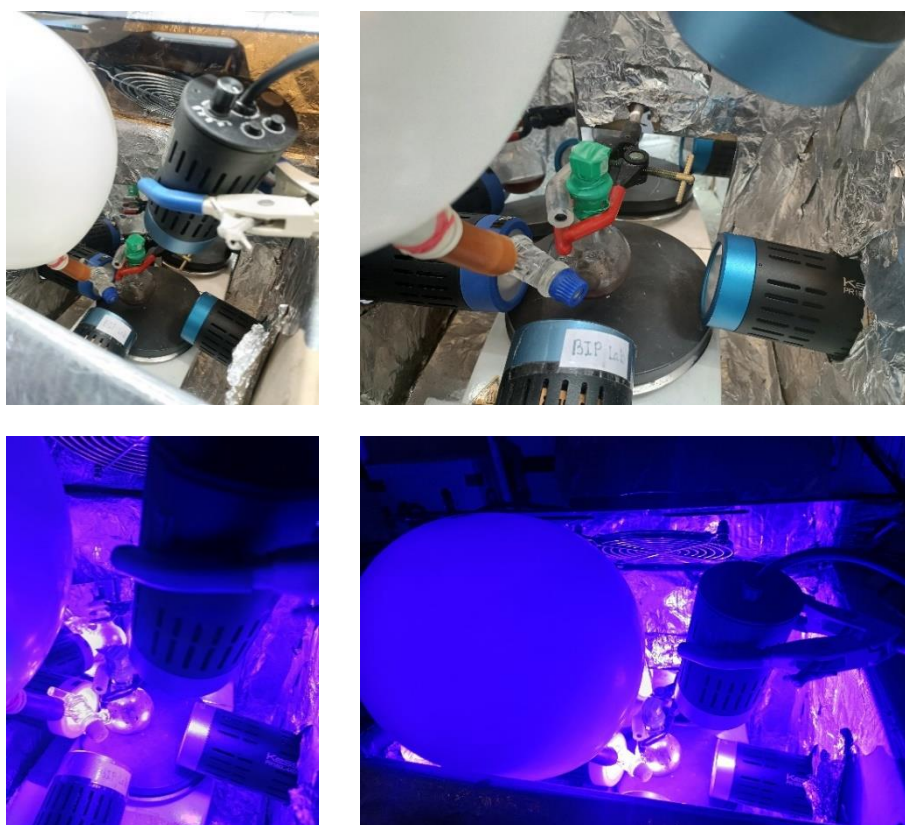
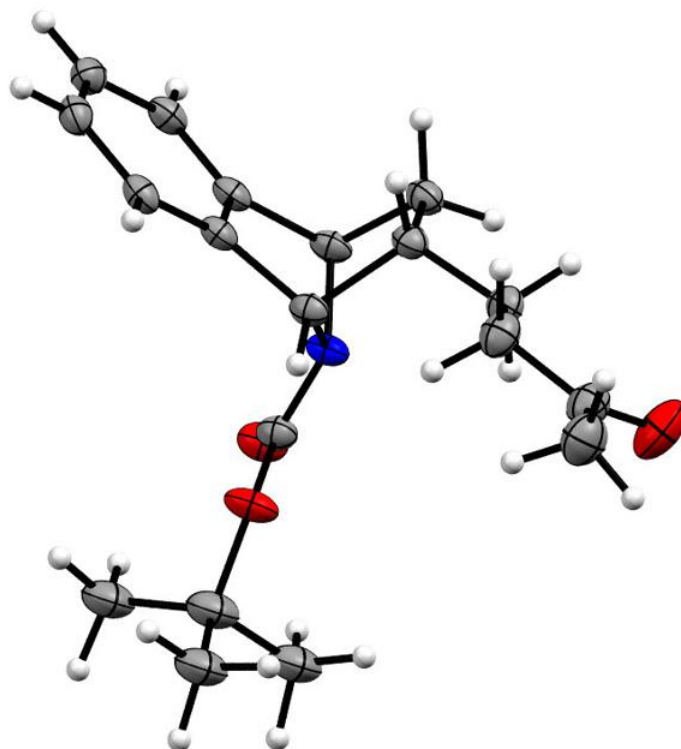


Figure S8: Reaction set-up for the scale-up reaction.

10. Crystal Data of 3h:



CCDC: 2268782.

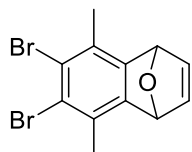
Figure S9: Molecular structure for compound **3h**. Crystallization procedure: 10.0 mg solid compound was taken in a glass vial and dissolved in 0.5 mL hexane. It was kept in another glass vial containing 0.5 mL pentane and was capped tightly. It was allowed for slow diffusion at 1 °C. Its melting point is in range 61-63 °C.

Table S9: Crystal data and structure refinement for 3h_auto.

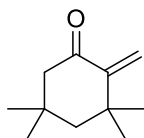
Identification code	“3h”auto
Empirical formula	C ₁₉ H ₂₅ NO ₃
Formula weight	315.40
Temperature/K	100.3(9)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.13080(10)
b/Å	11.62940(10)
c/Å	25.4879(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1817.22(4)
Z	4
ρ _{calc} /cm ³	1.153
μ/mm ⁻¹	0.618

F(000)	680.0
Crystal size/mm ³	0.5 × 0.05 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.936 to 135.98
Index ranges	-7 ≤ h ≤ 7, -13 ≤ k ≤ 13, -30 ≤ l ≤ 30
Reflections collected	21967
Independent reflections	3309 [R _{int} = 0.0683, R _{sigma} = 0.0304]
Data/restraints/parameters	3309/0/194
Goodness-of-fit on F ²	1.022
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0424, wR ₂ = 0.1044
Final R indexes [all data]	R ₁ = 0.0437, wR ₂ = 0.1055
Largest diff. peak/hole / e Å ⁻³	0.28/-0.48
Flack parameter	-0.04(11)

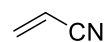
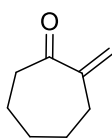
11. Unsuccessful Substates:



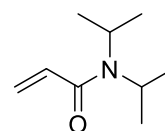
Debrominated pdt



mostly ring opening pdt



10 % pdt
and the er is n.d

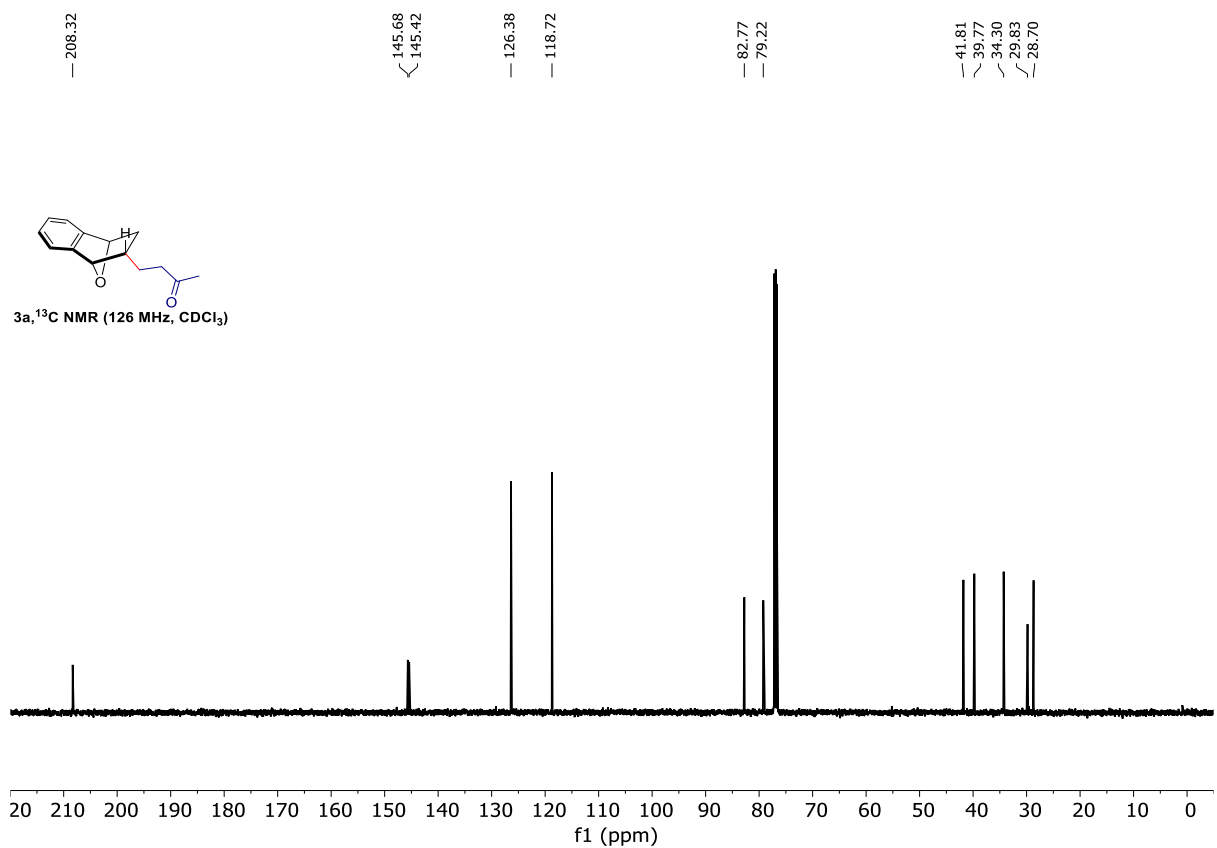
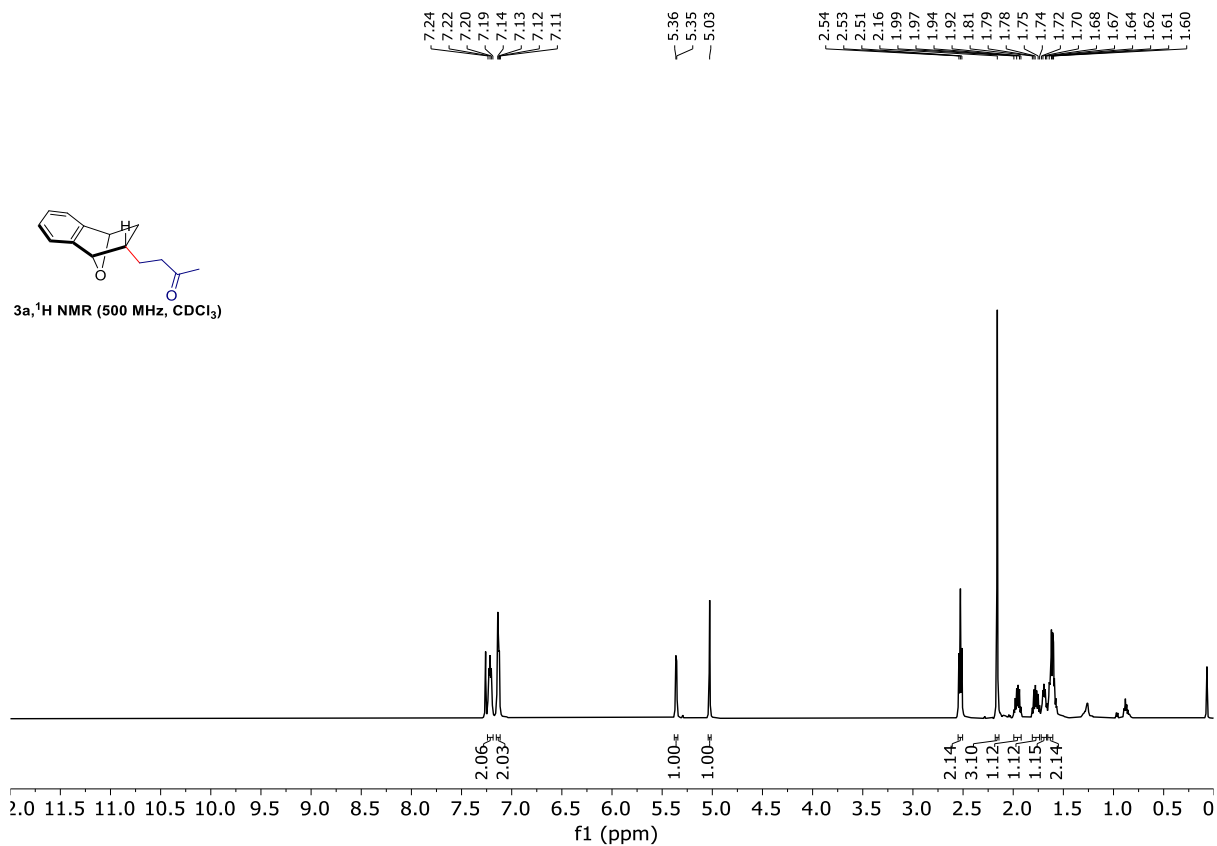


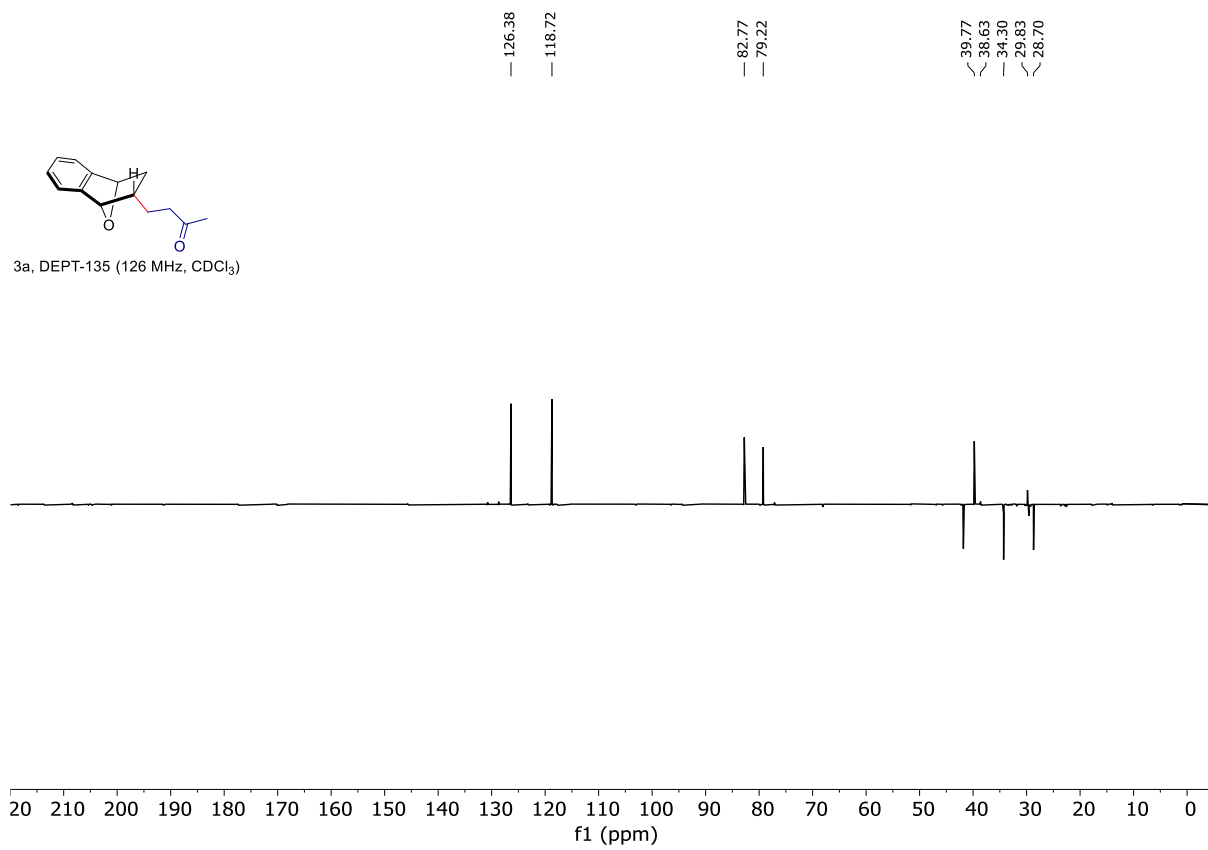
no pdt formation

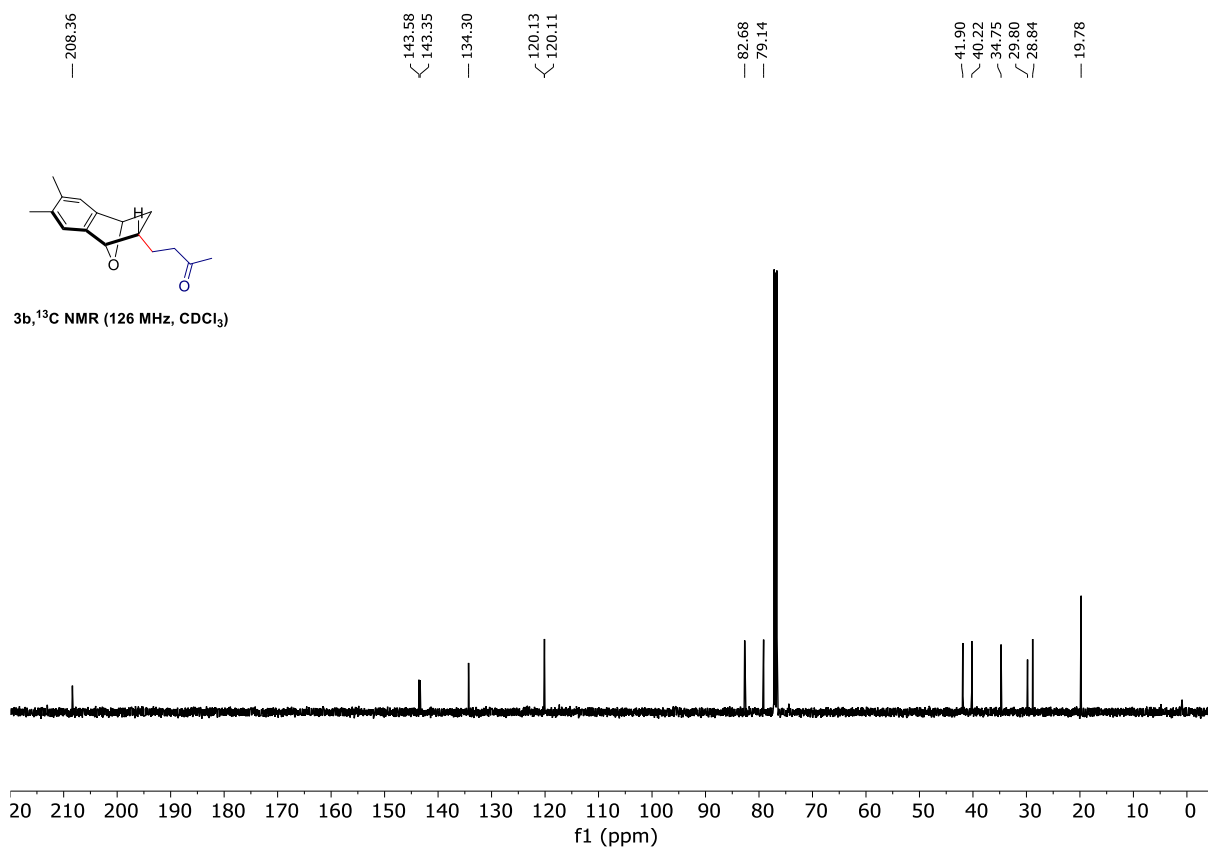
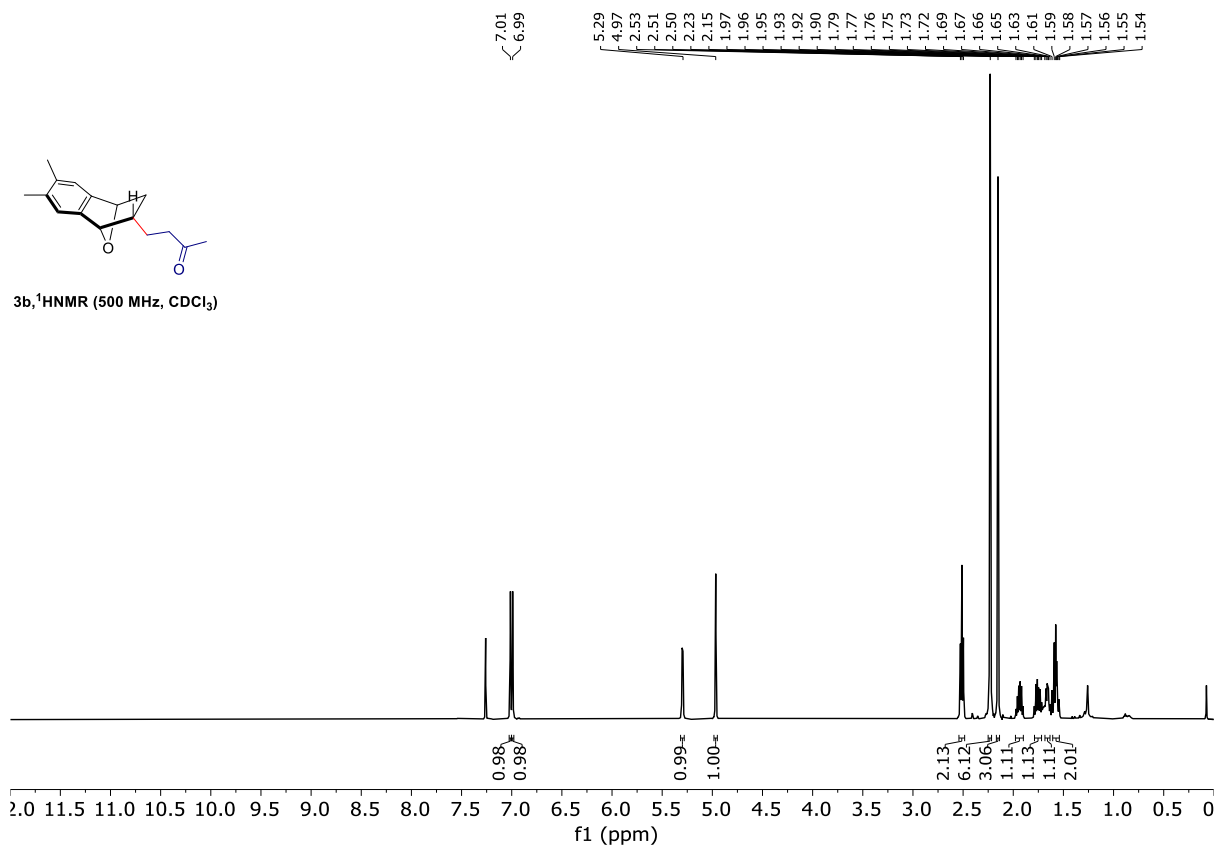
12. Reference:

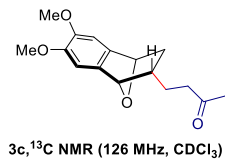
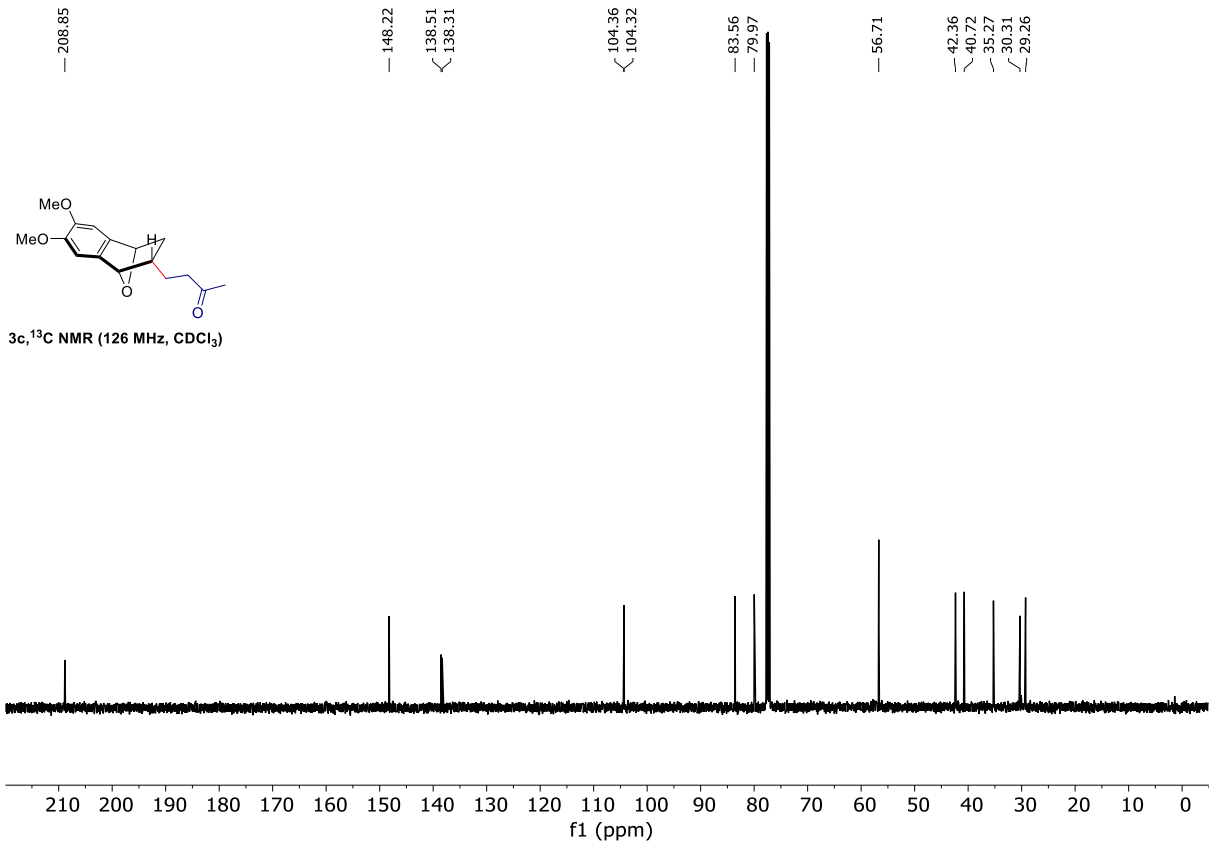
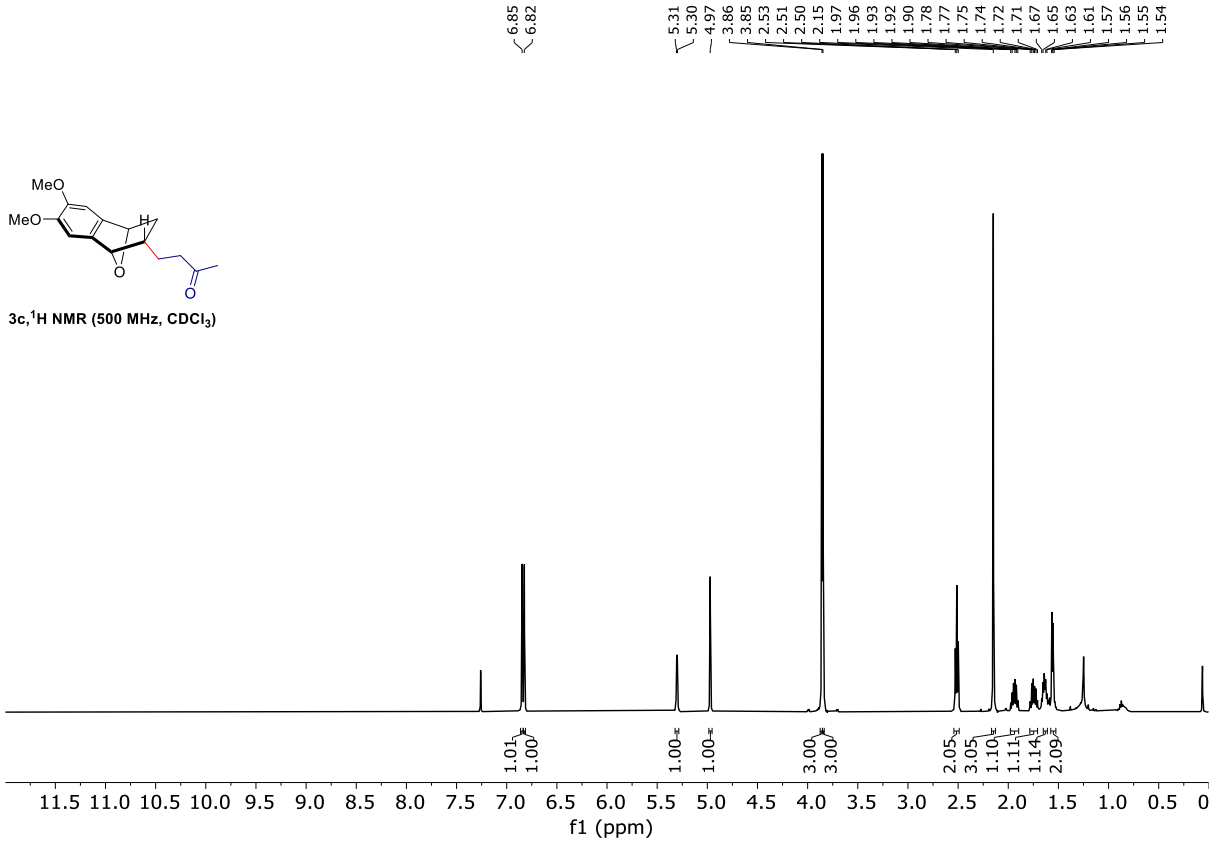
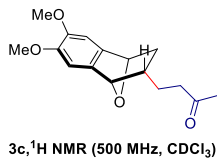
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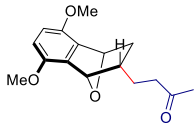
13. Copies of NMR Spectra



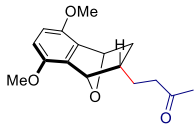
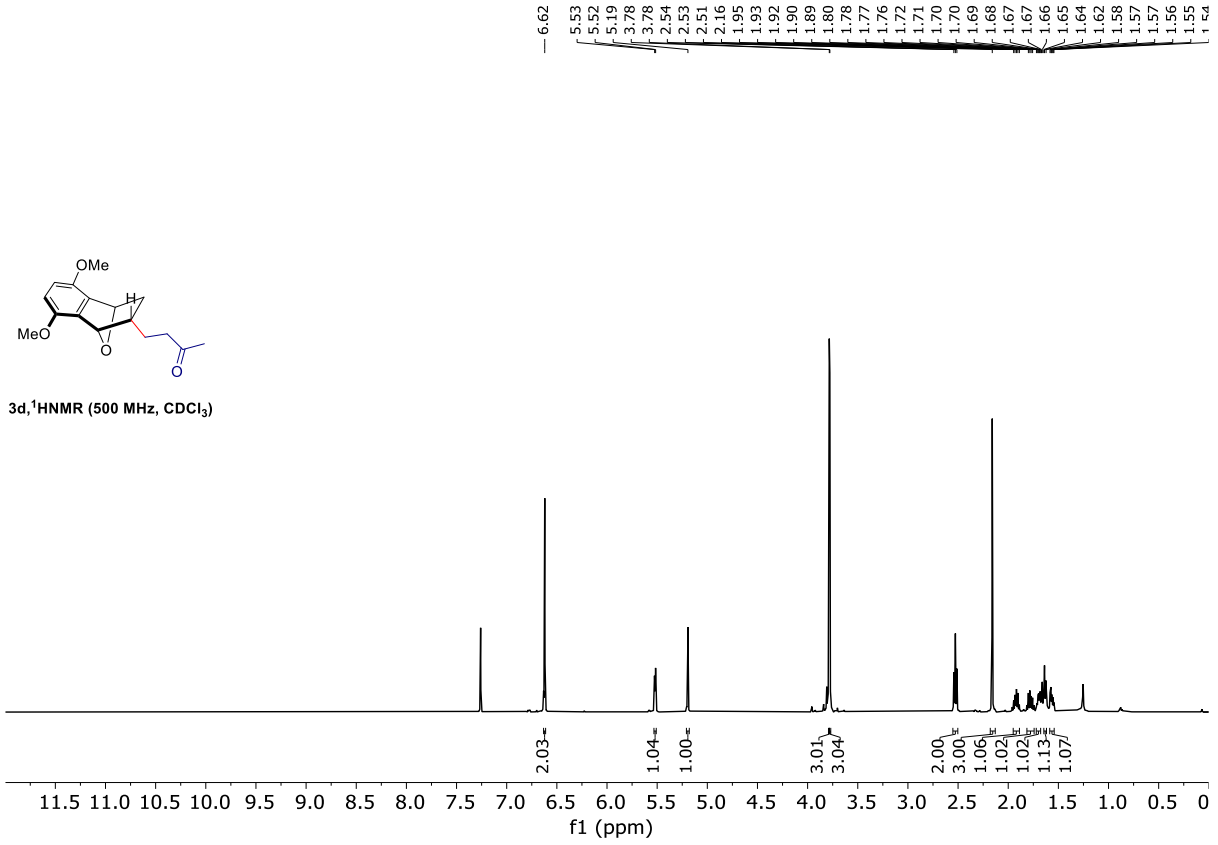




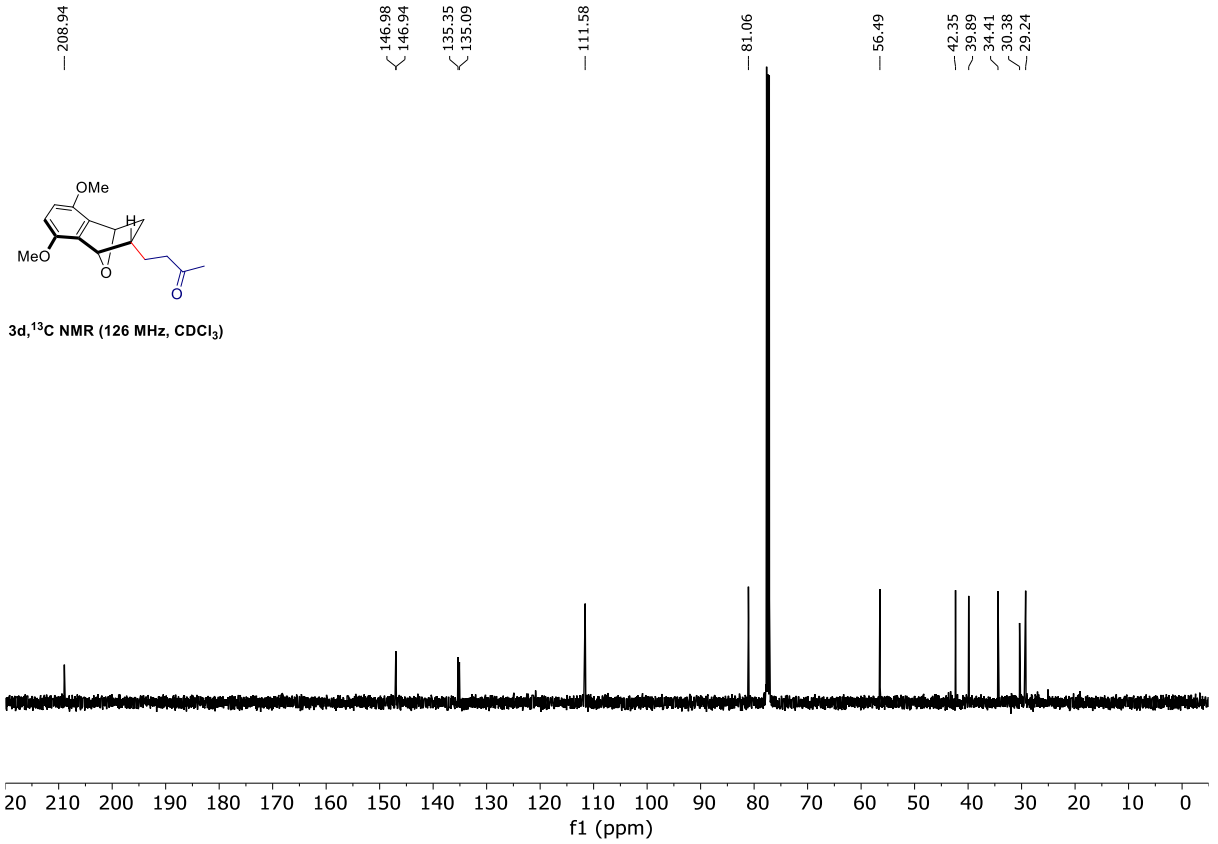


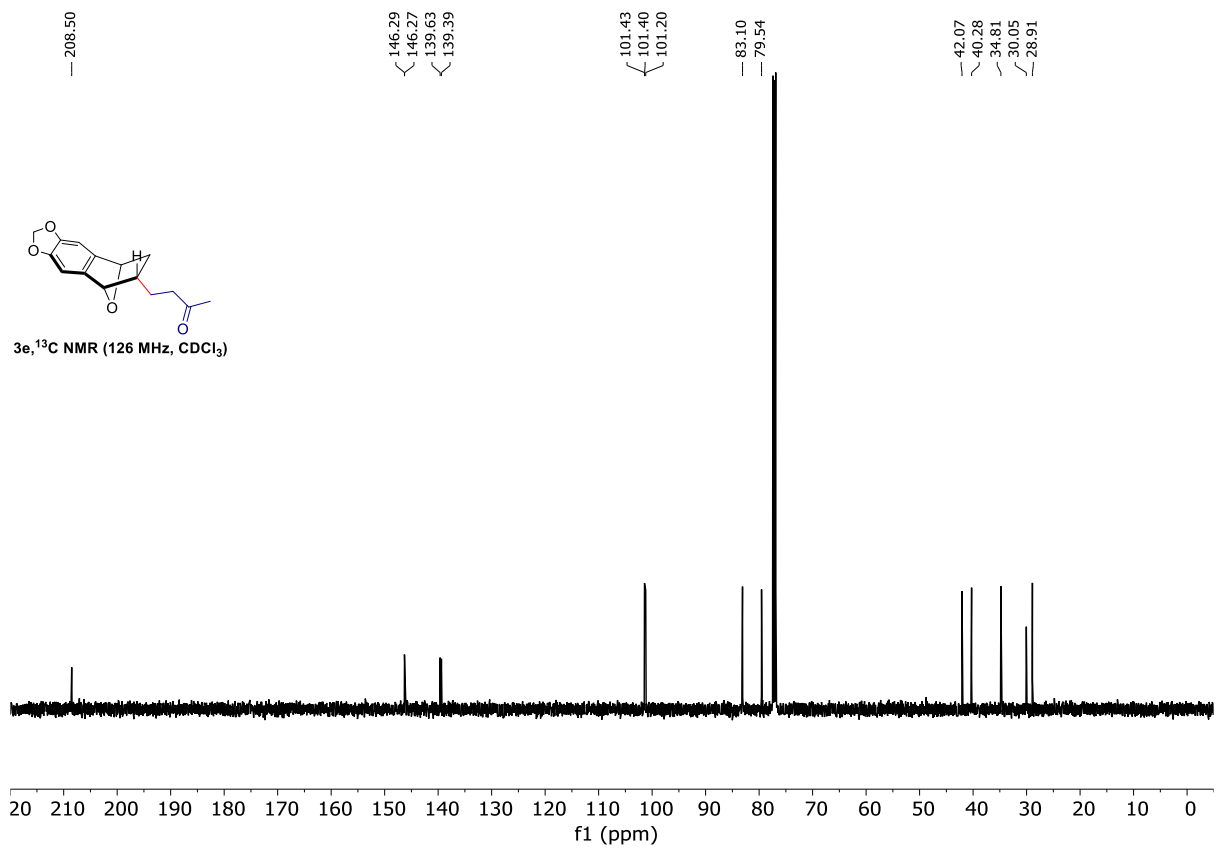
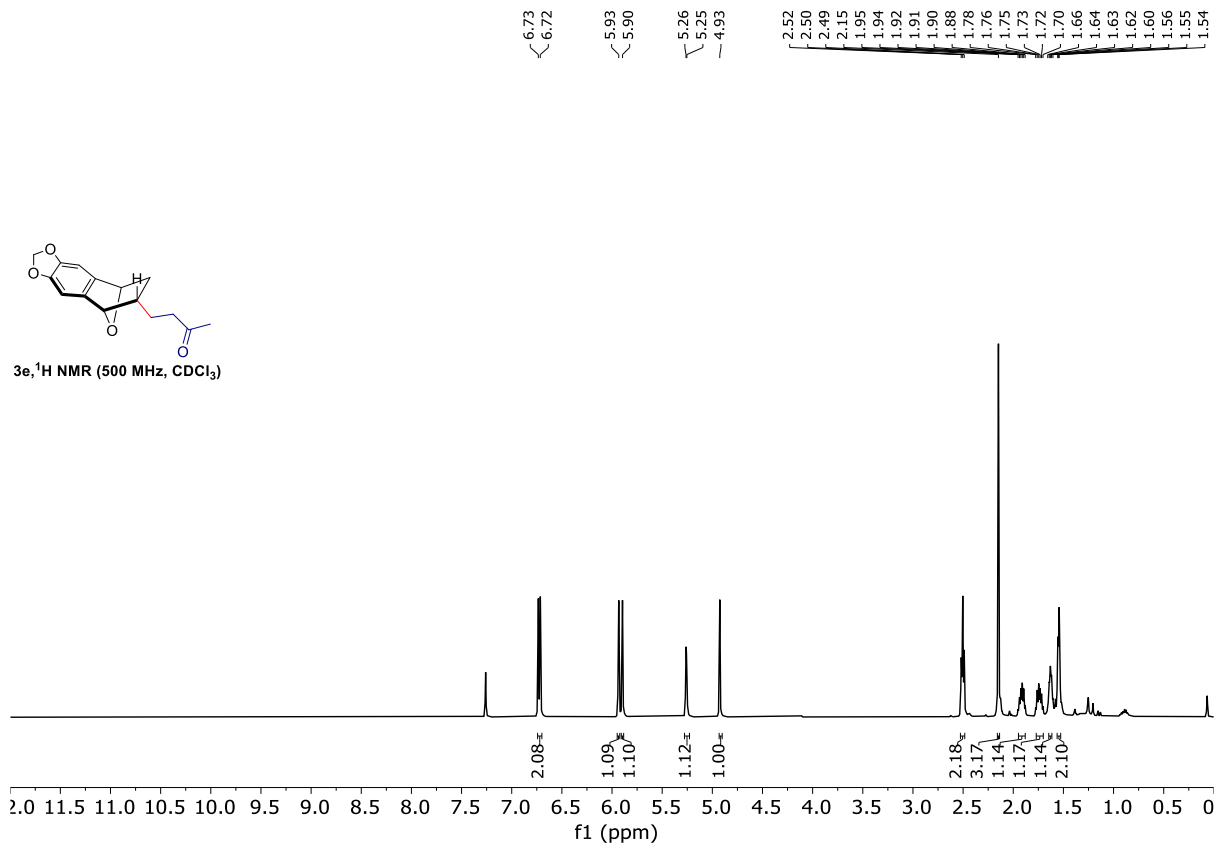


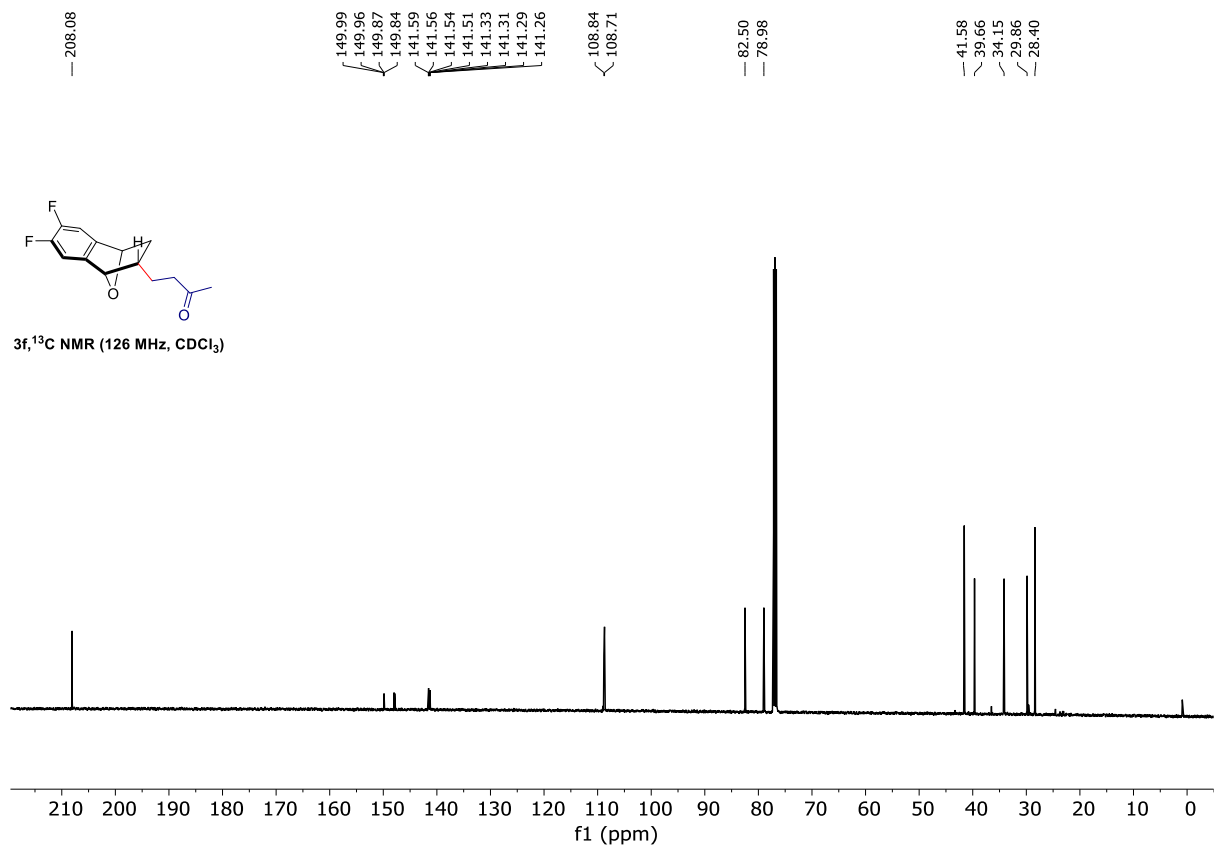
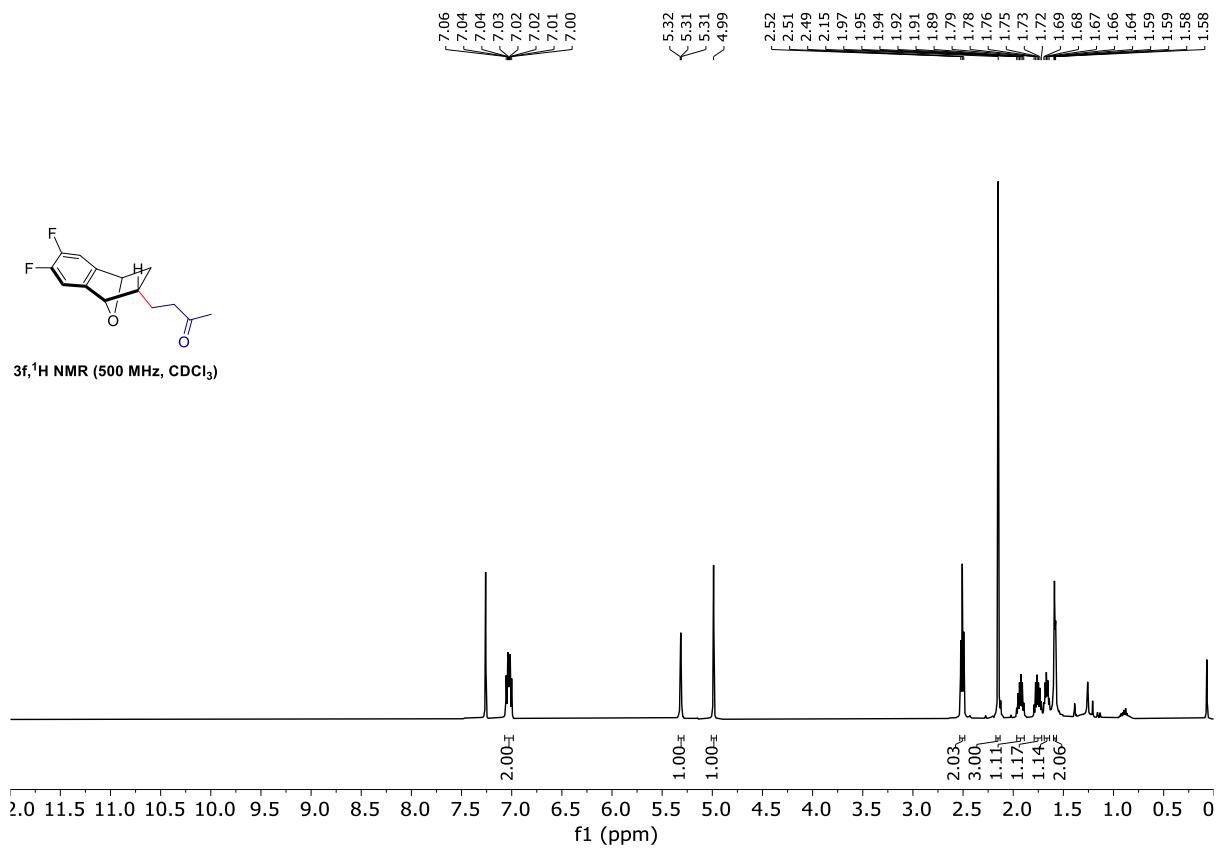
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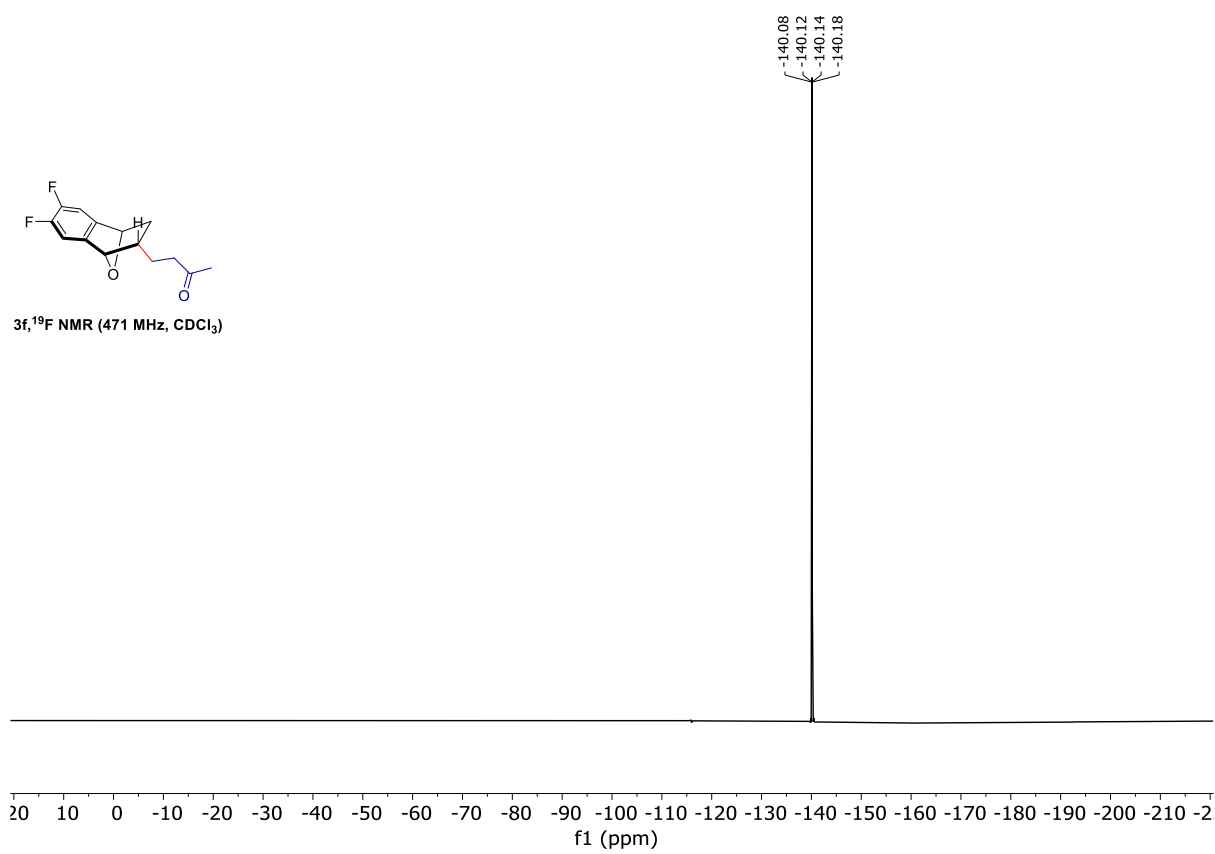
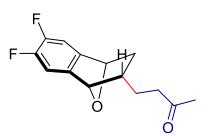


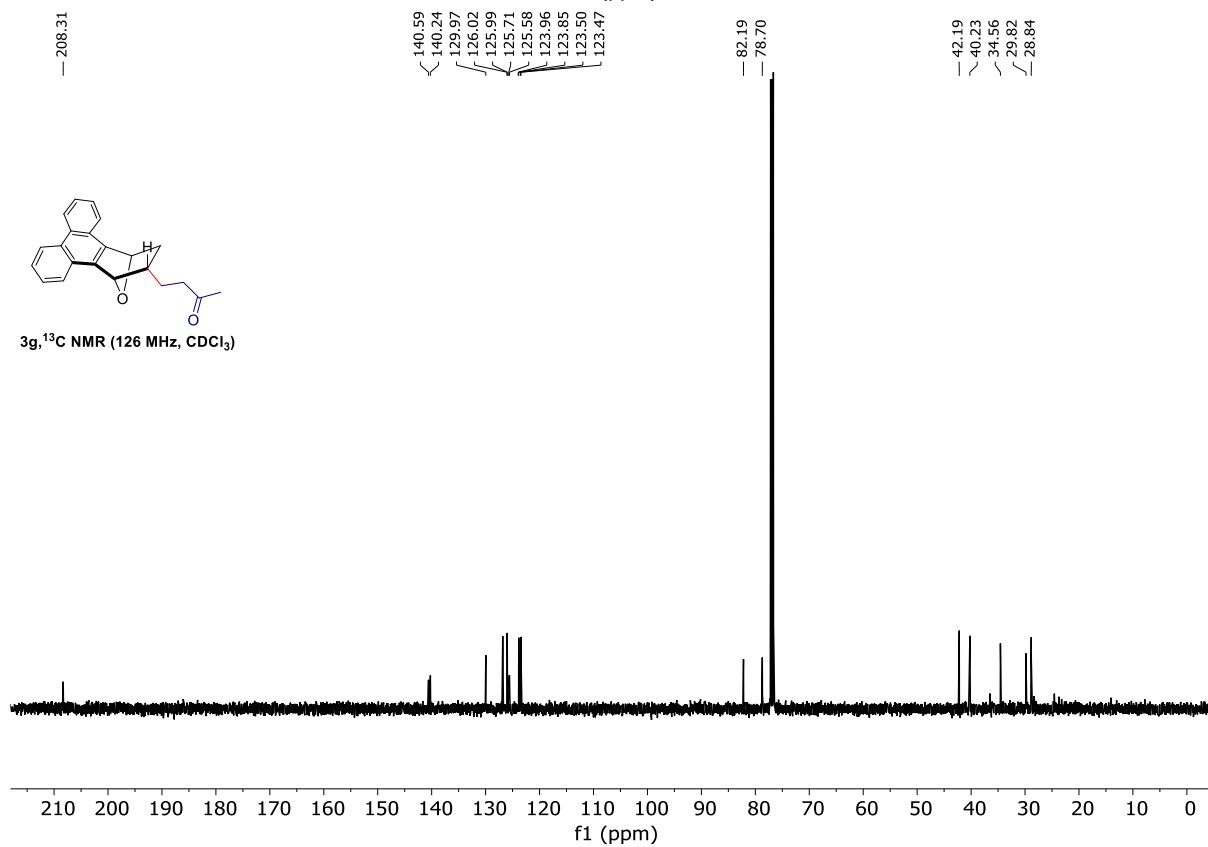
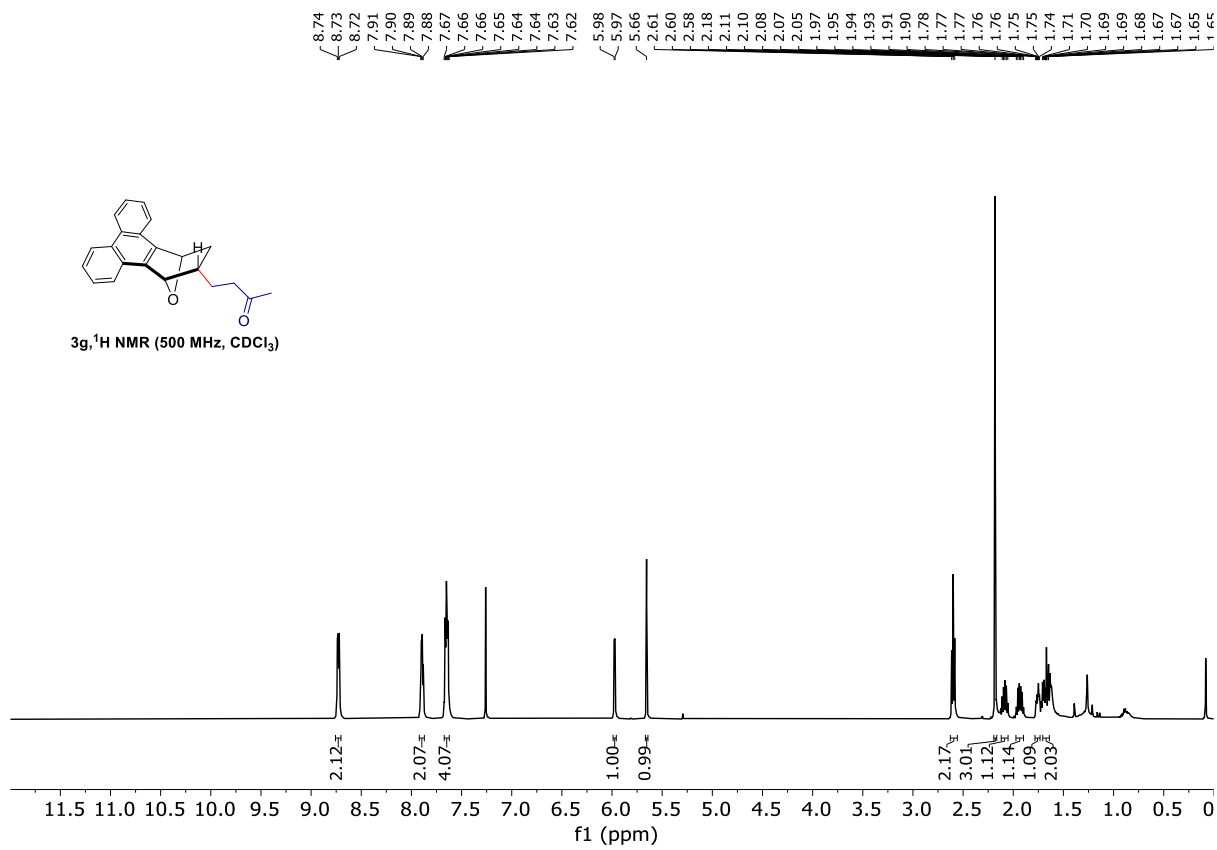
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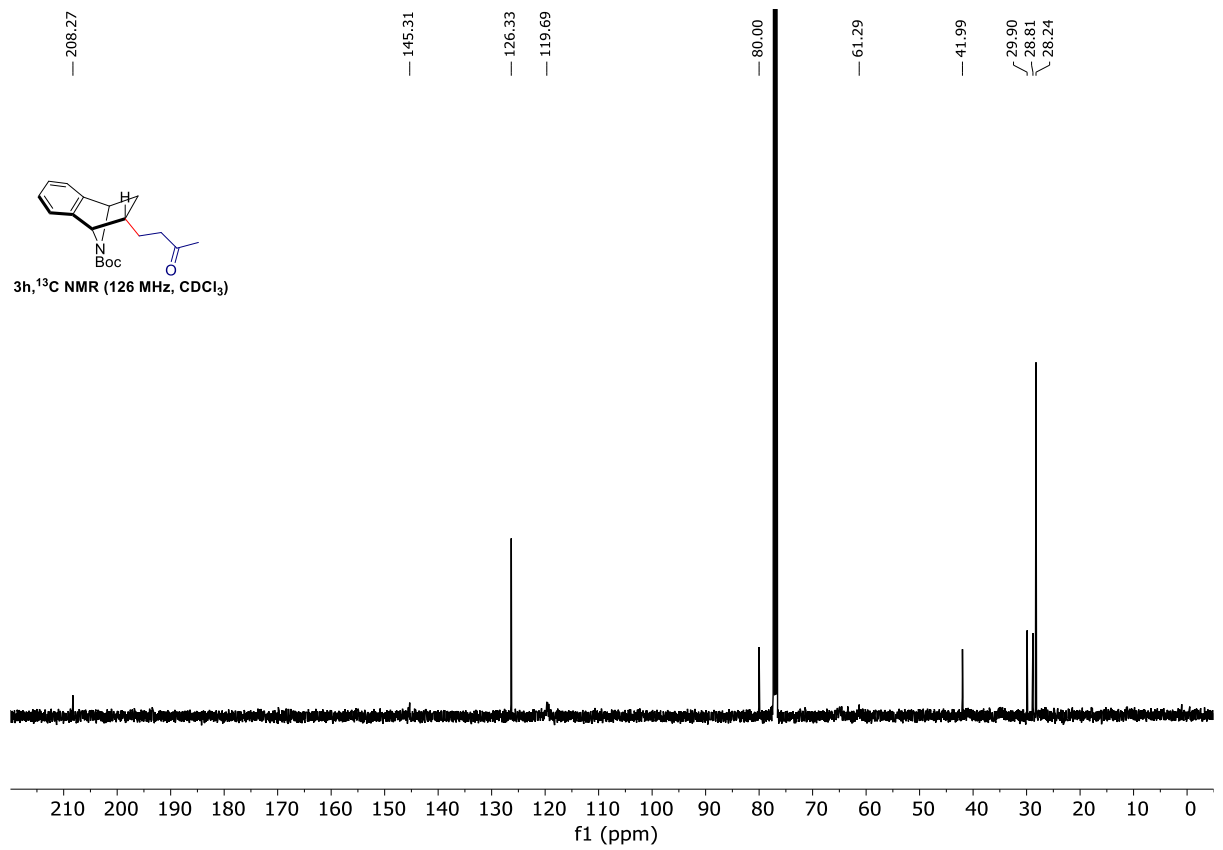
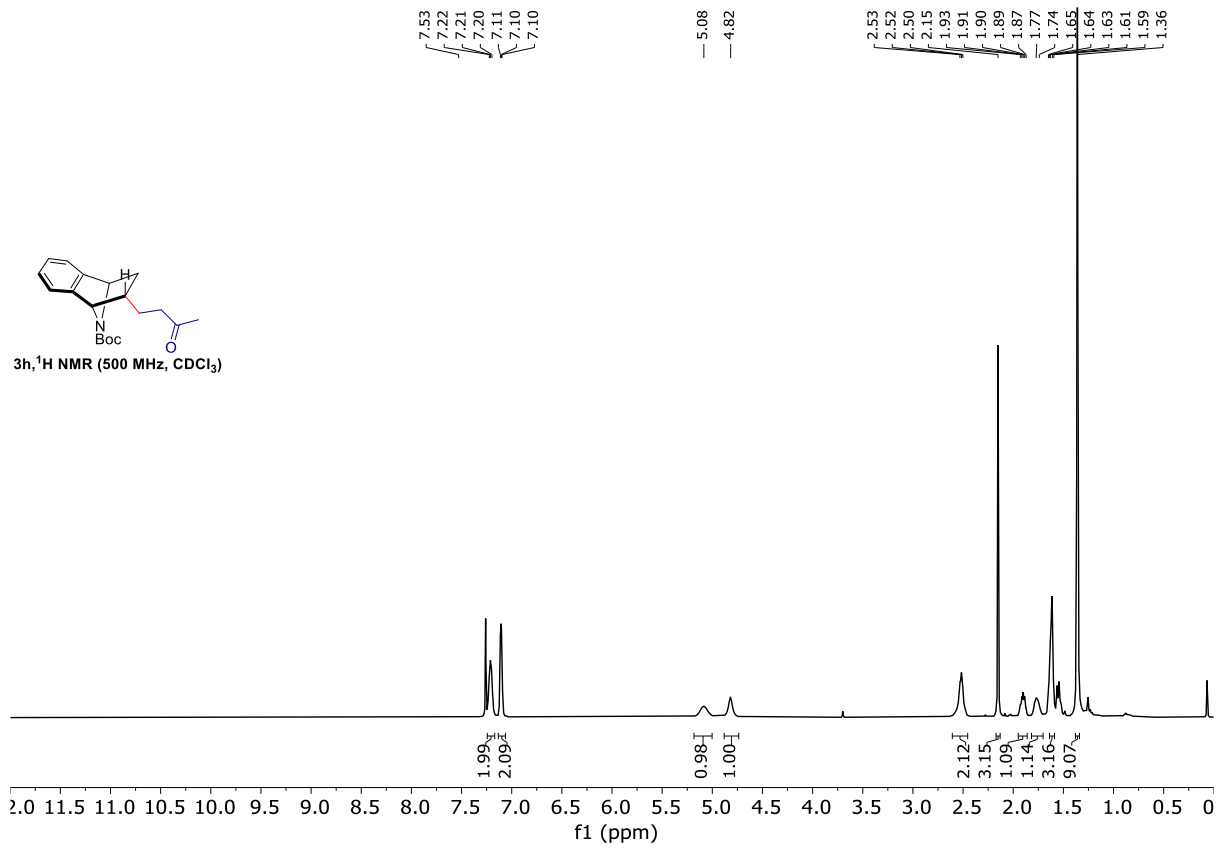


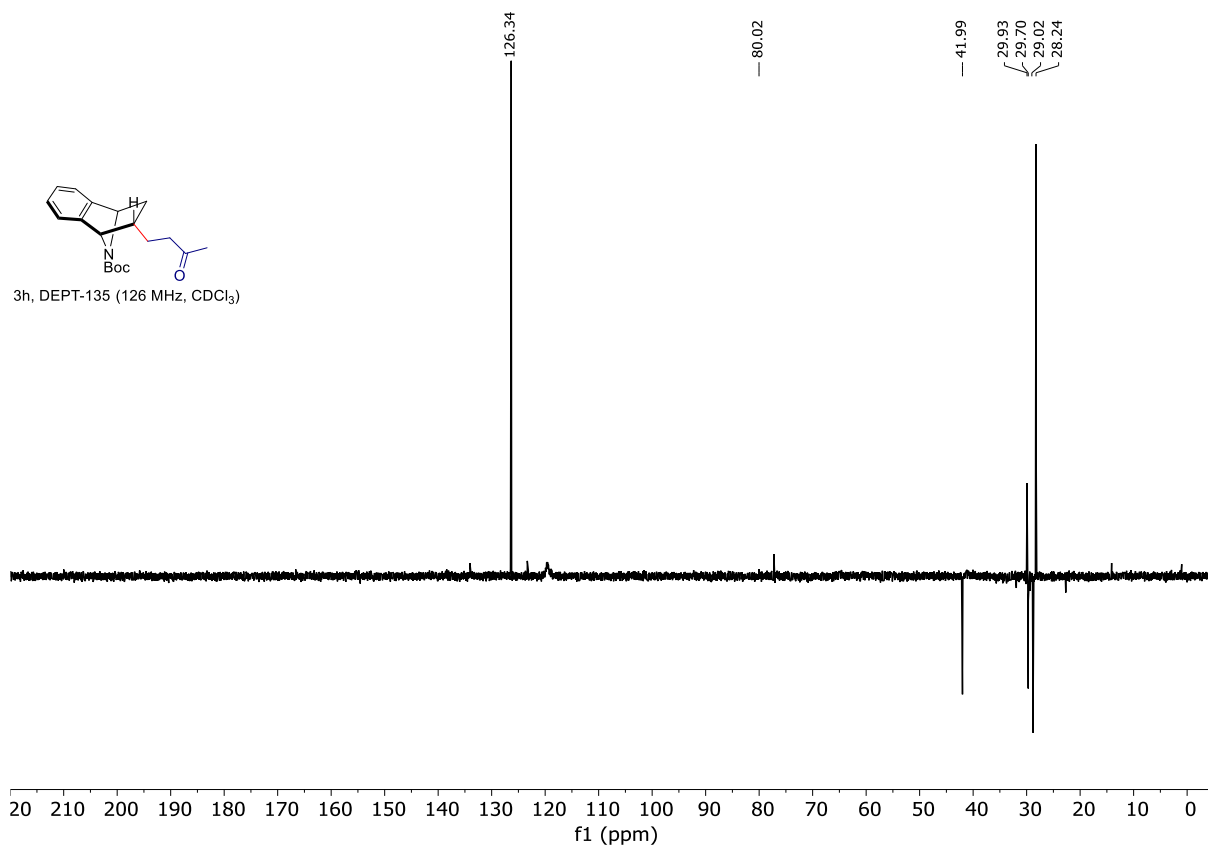


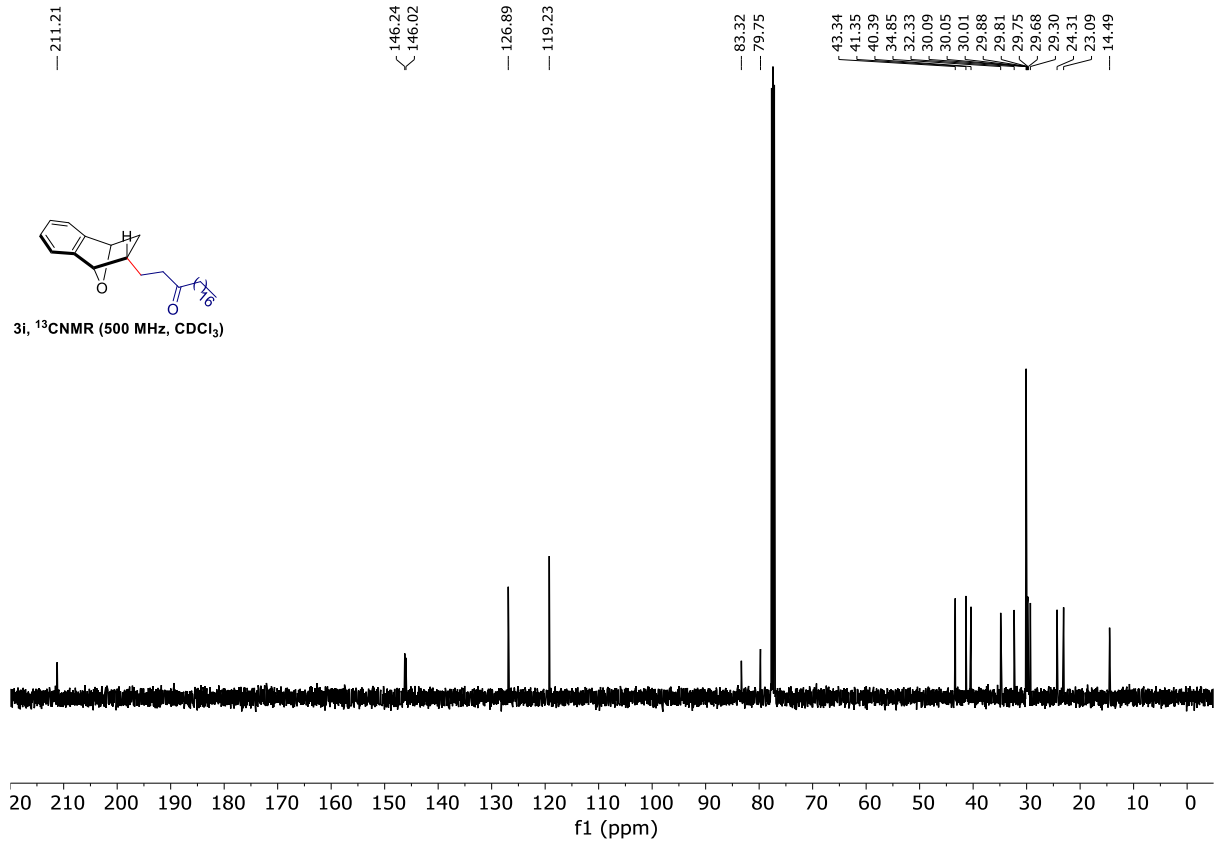
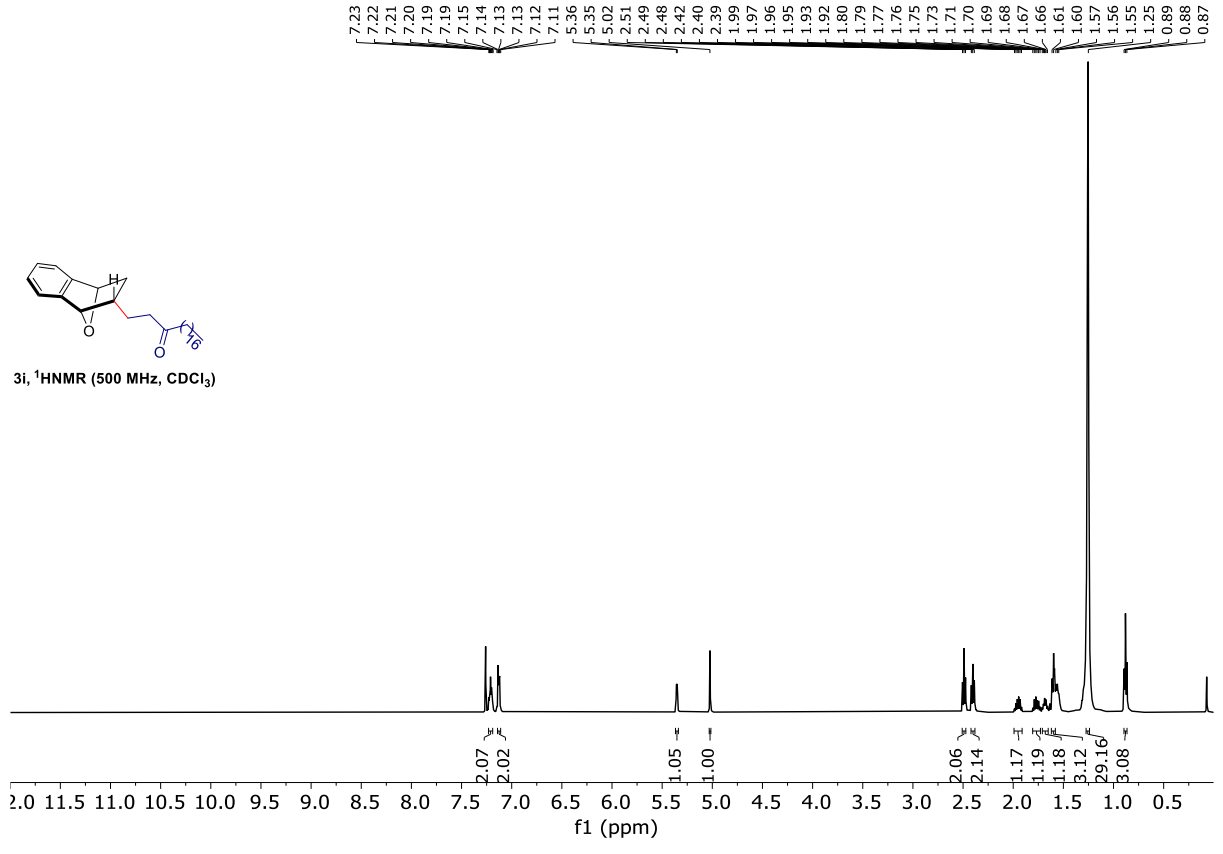


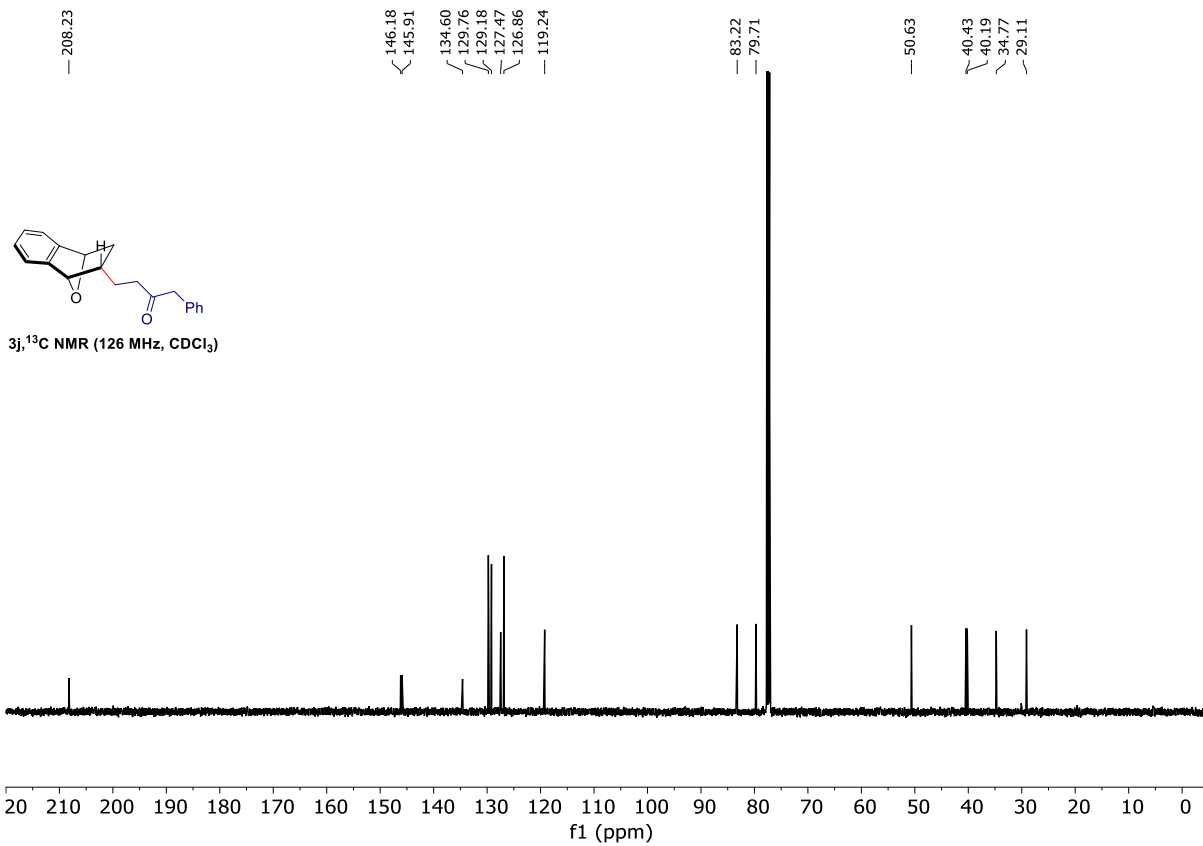
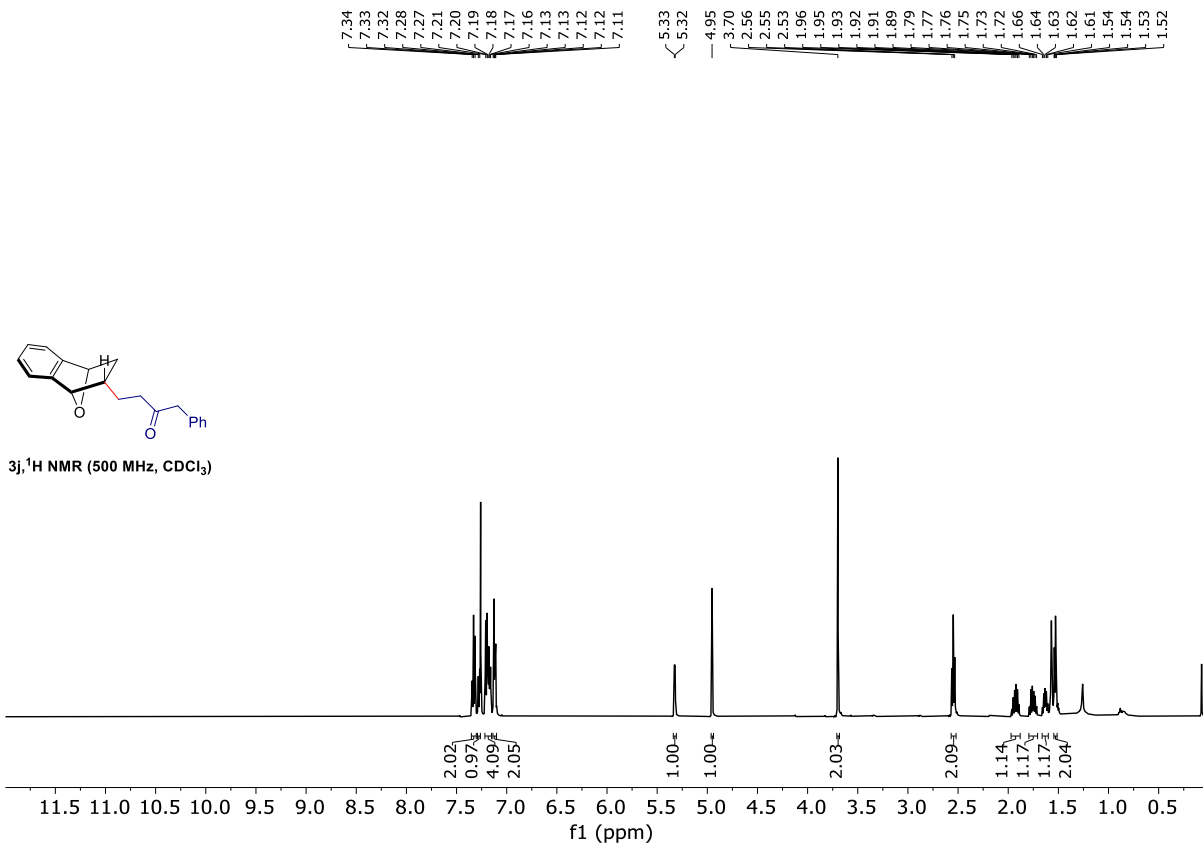


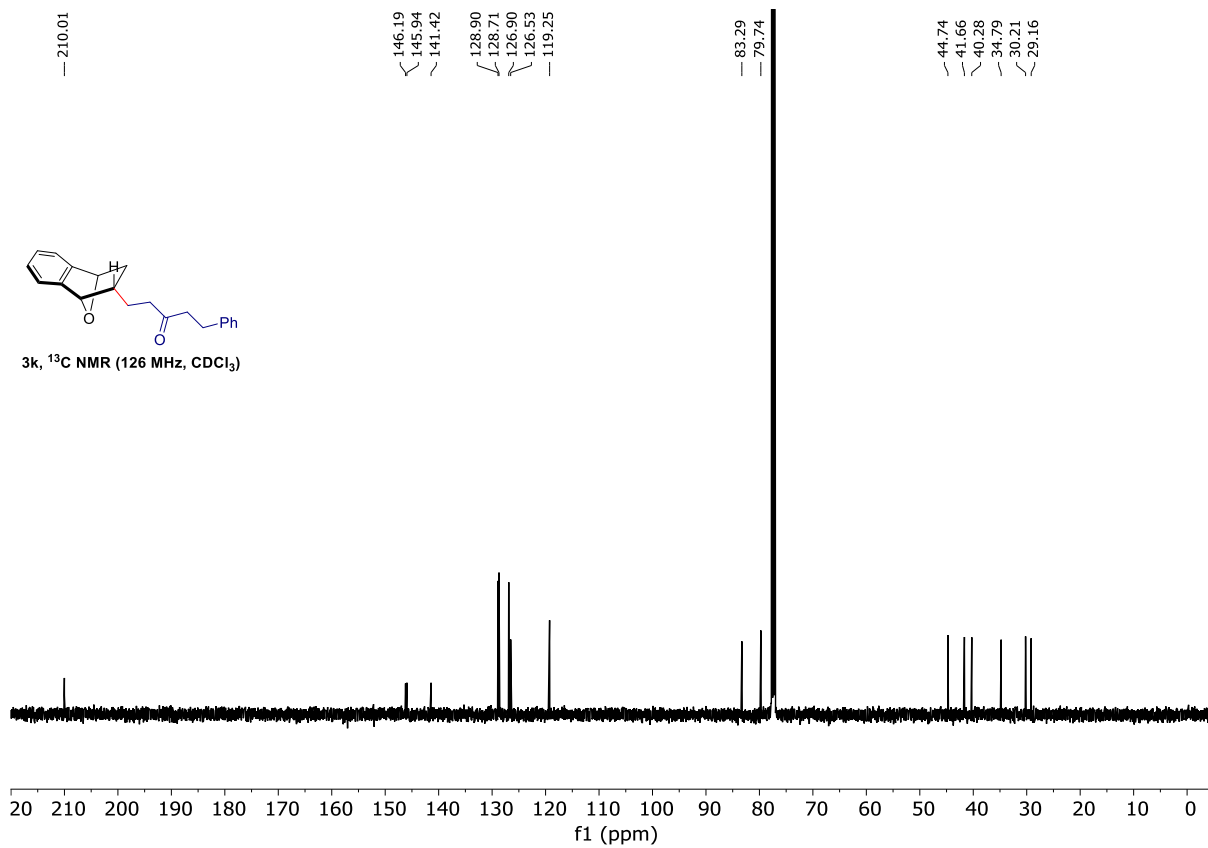
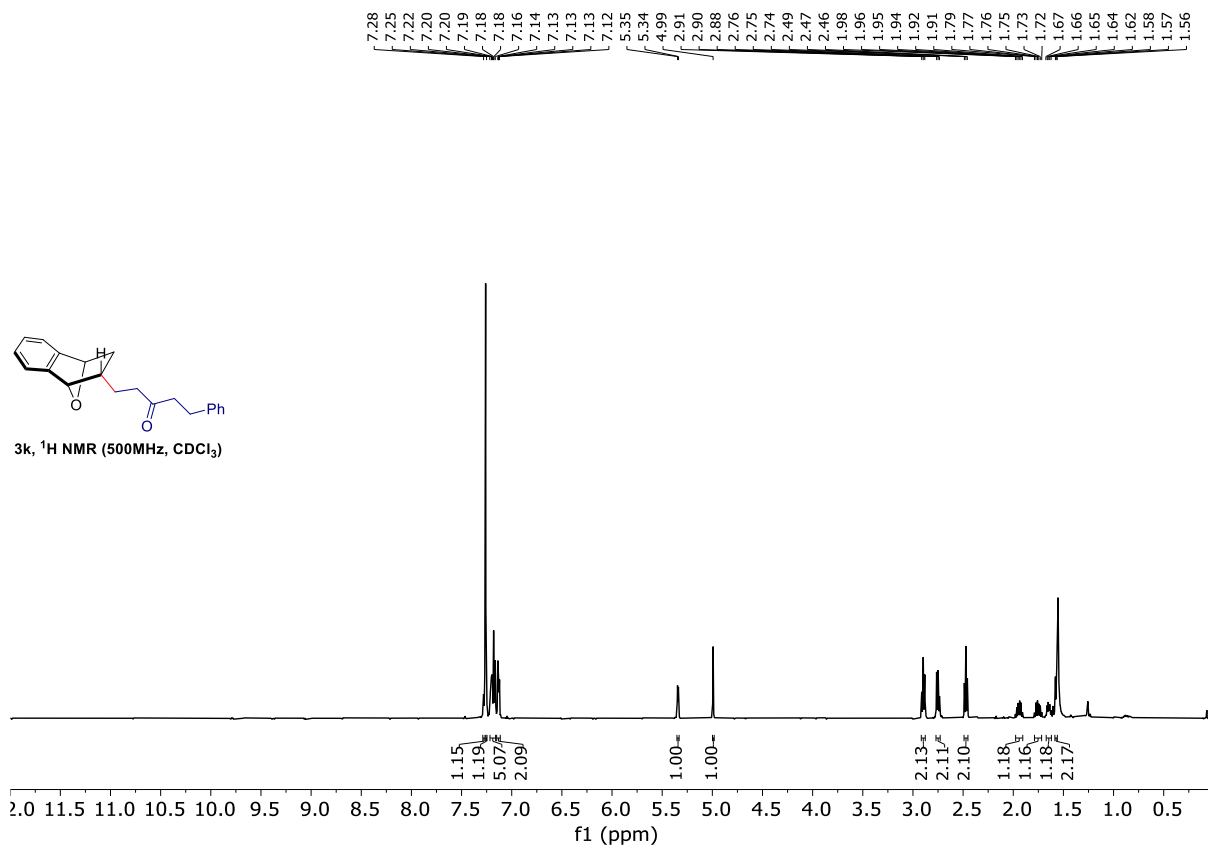


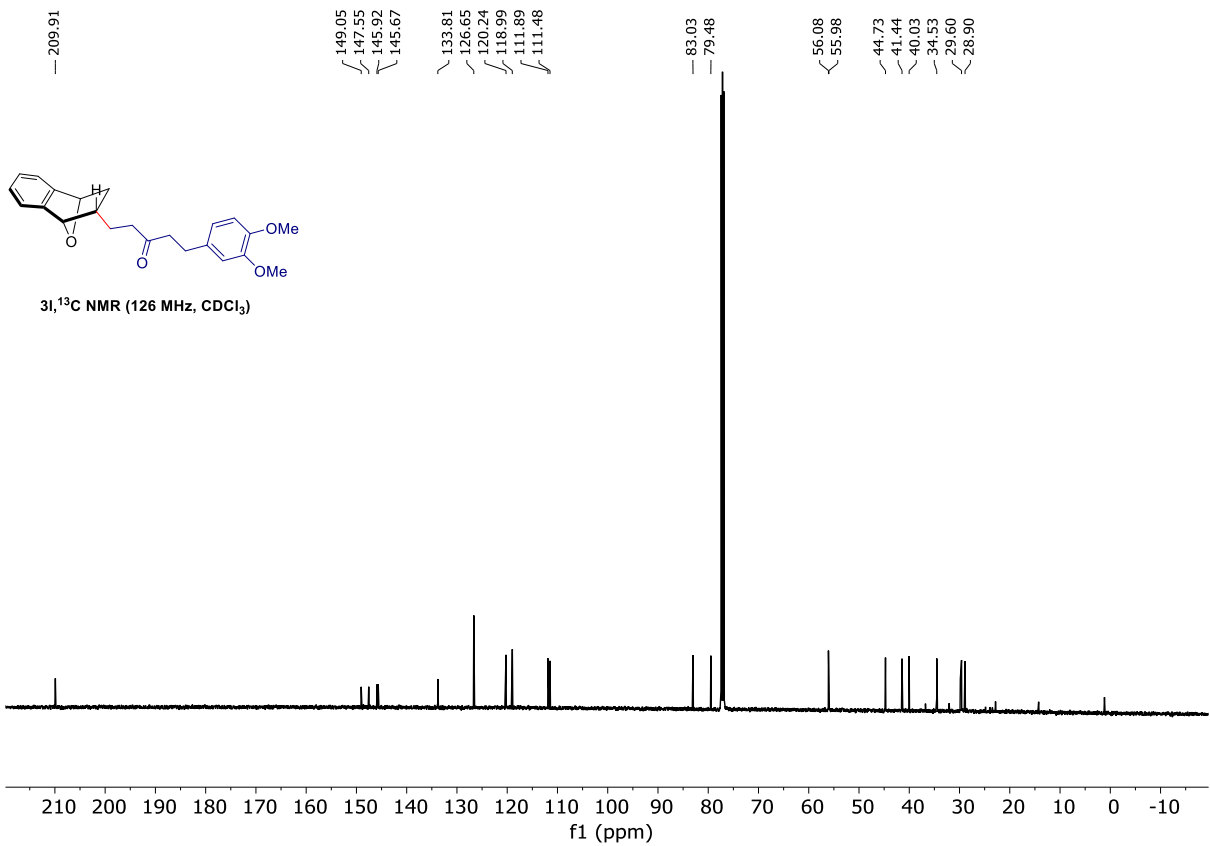
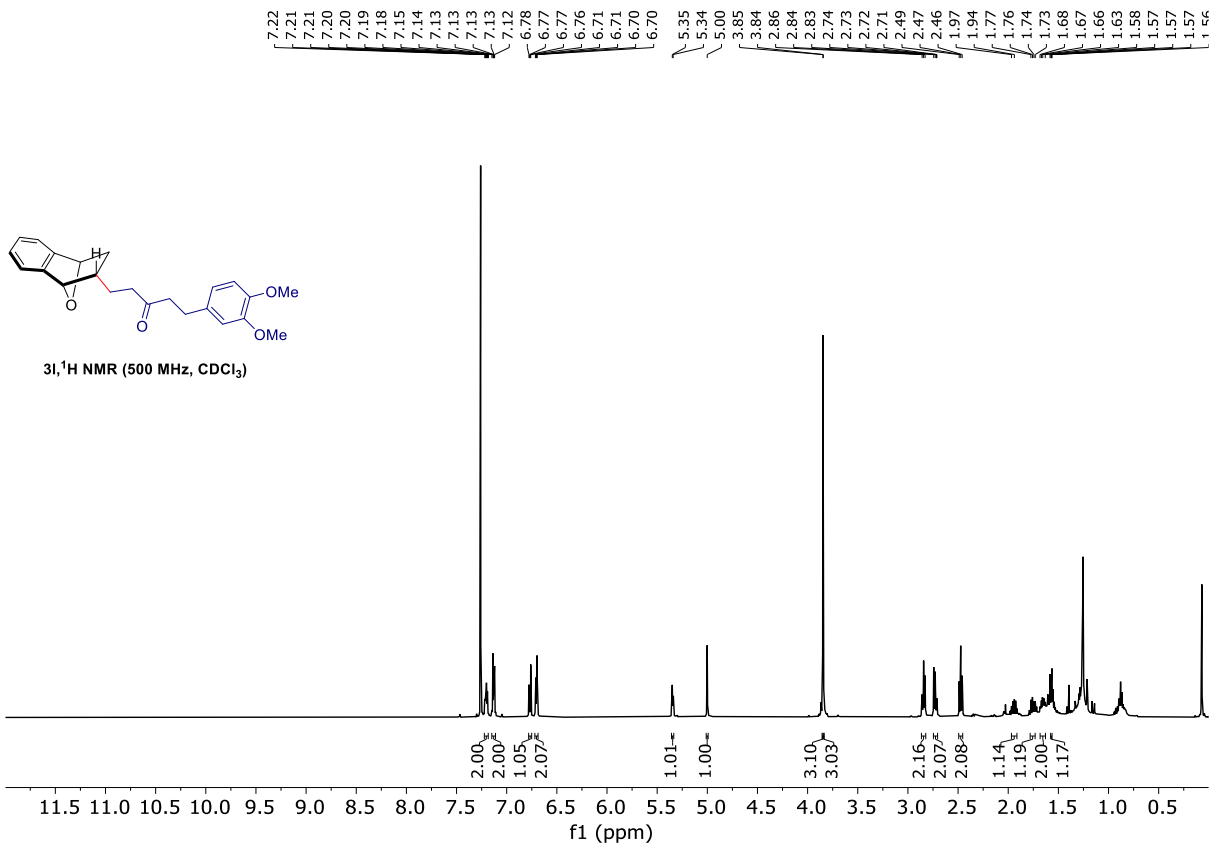


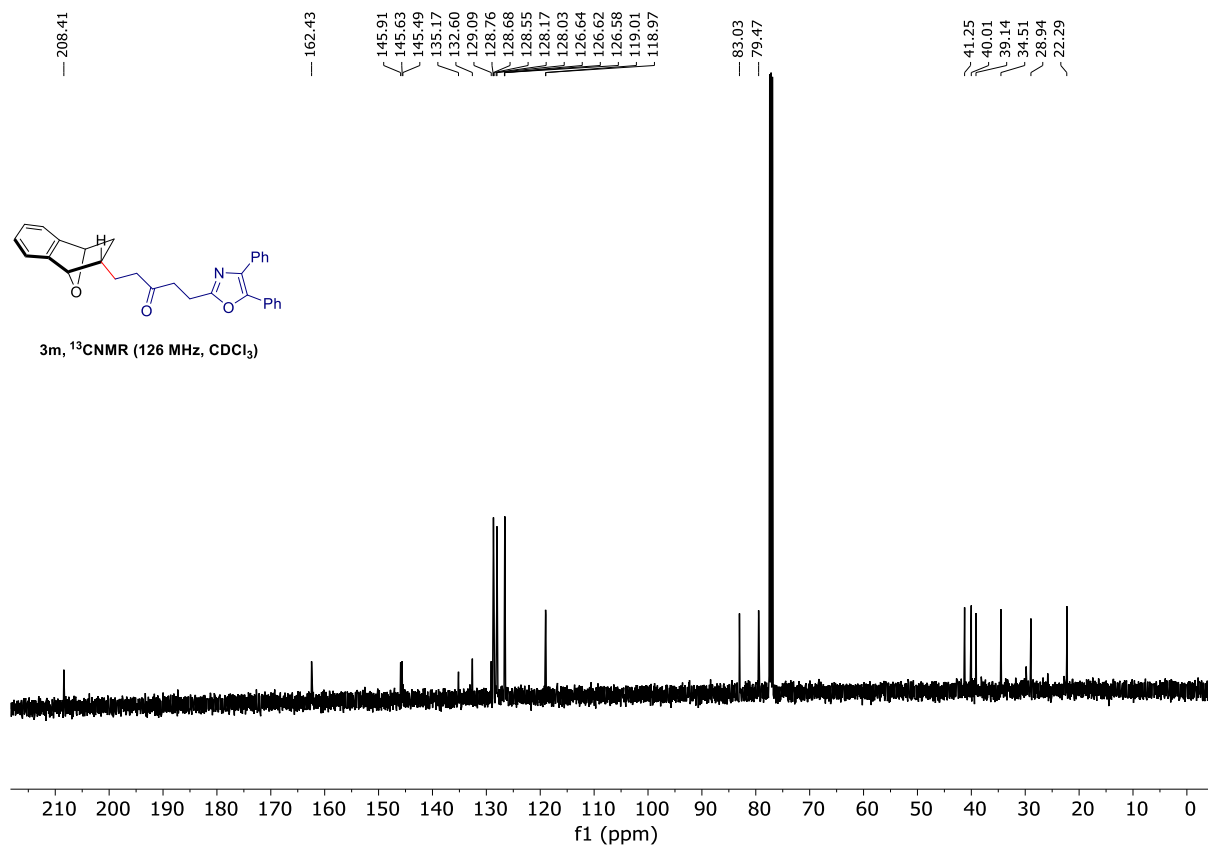
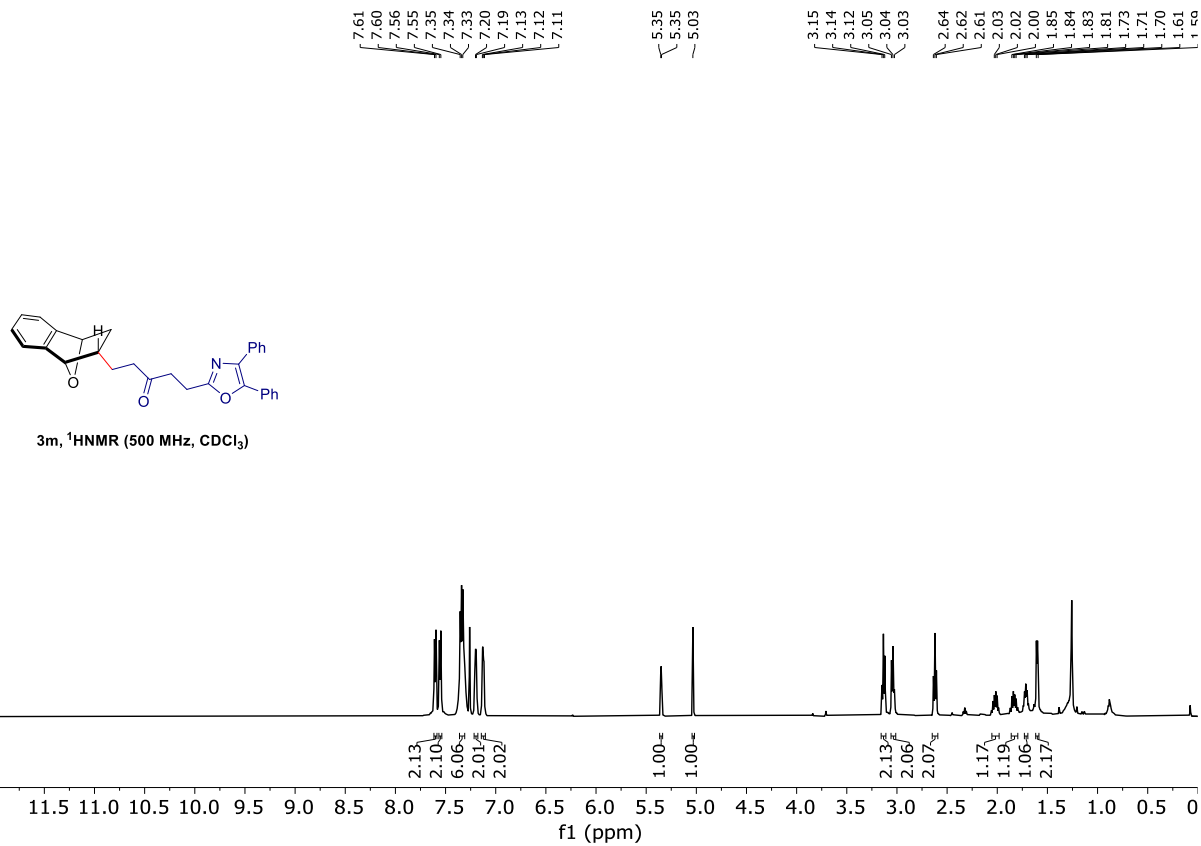


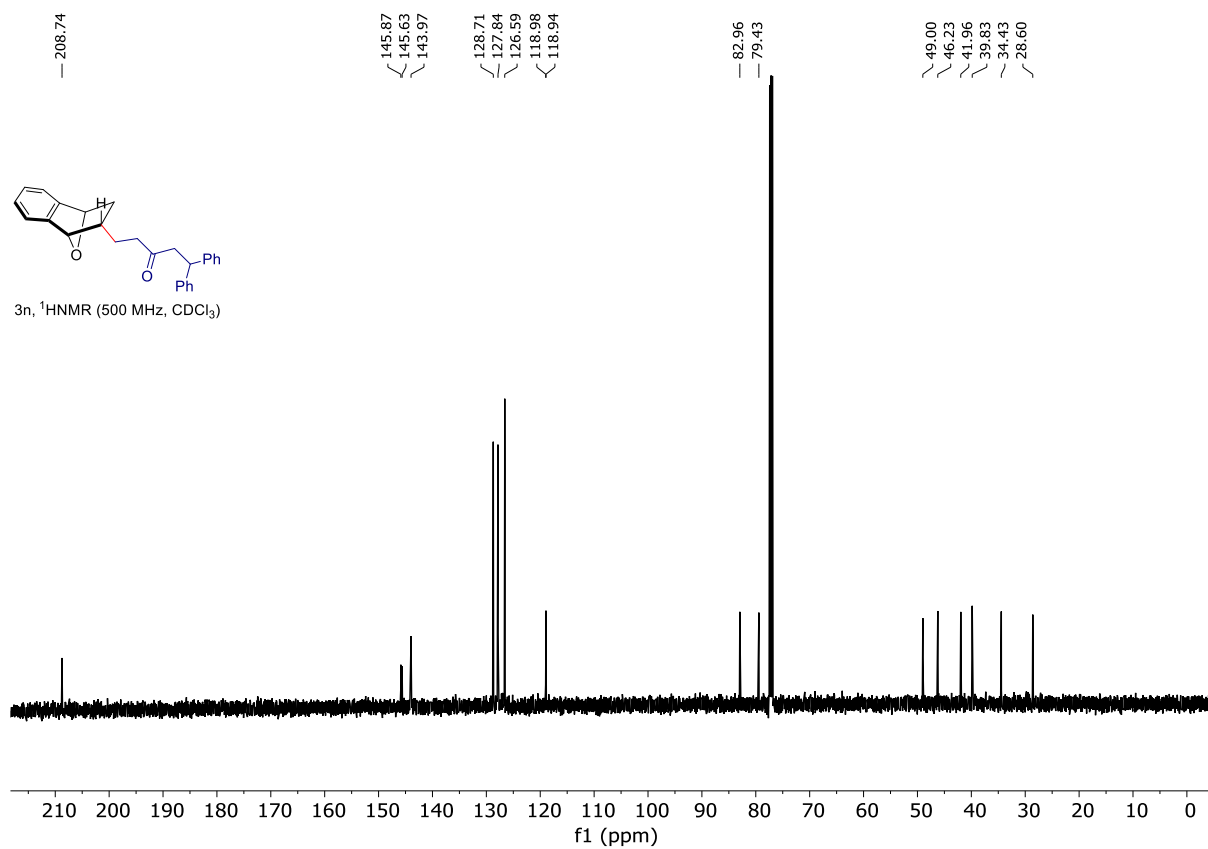
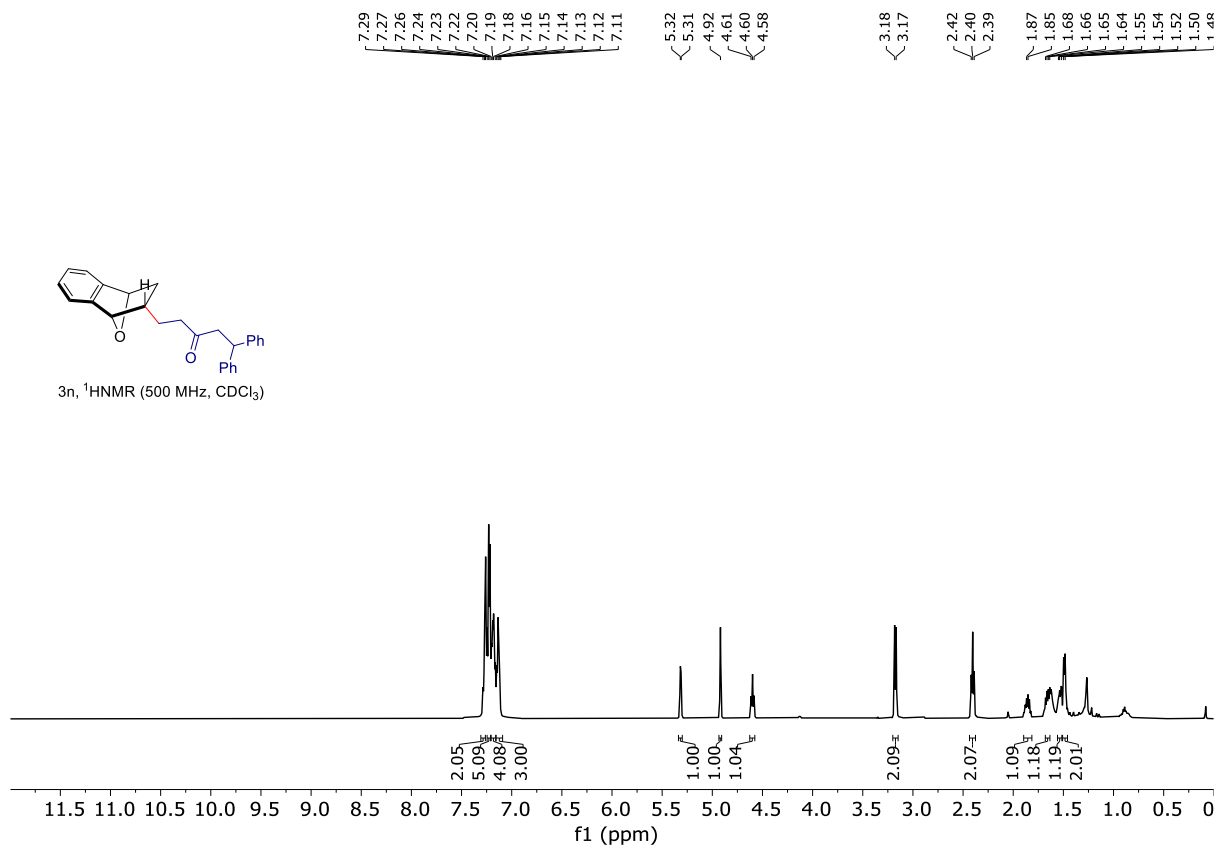
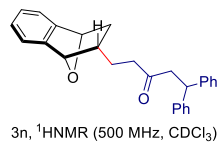


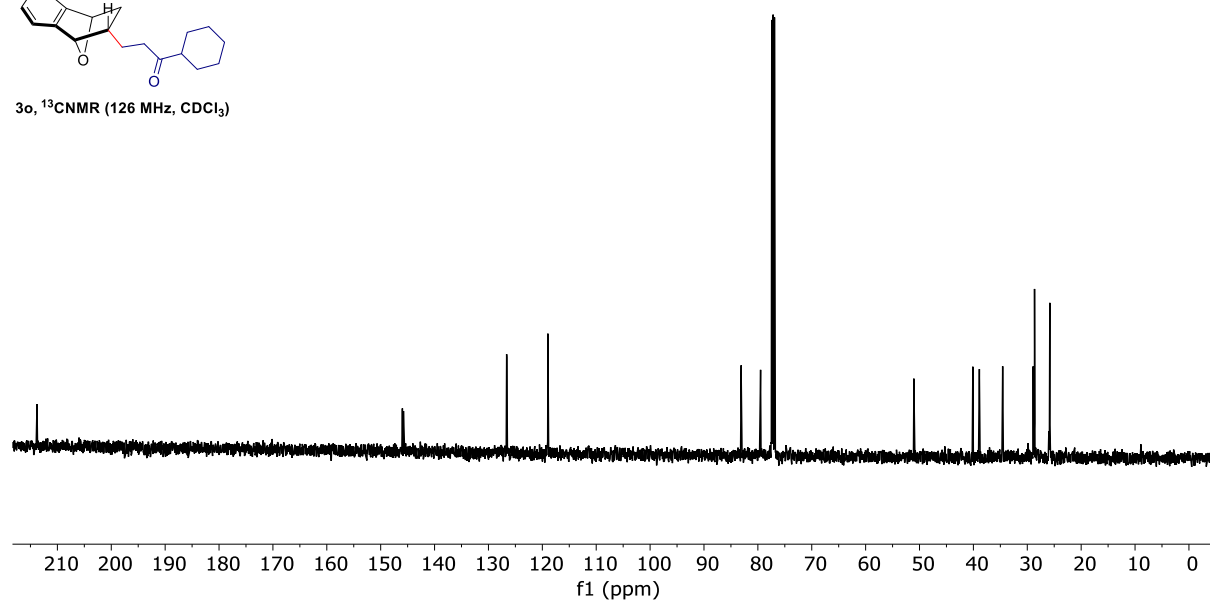
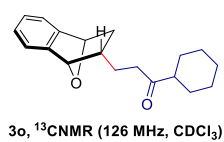
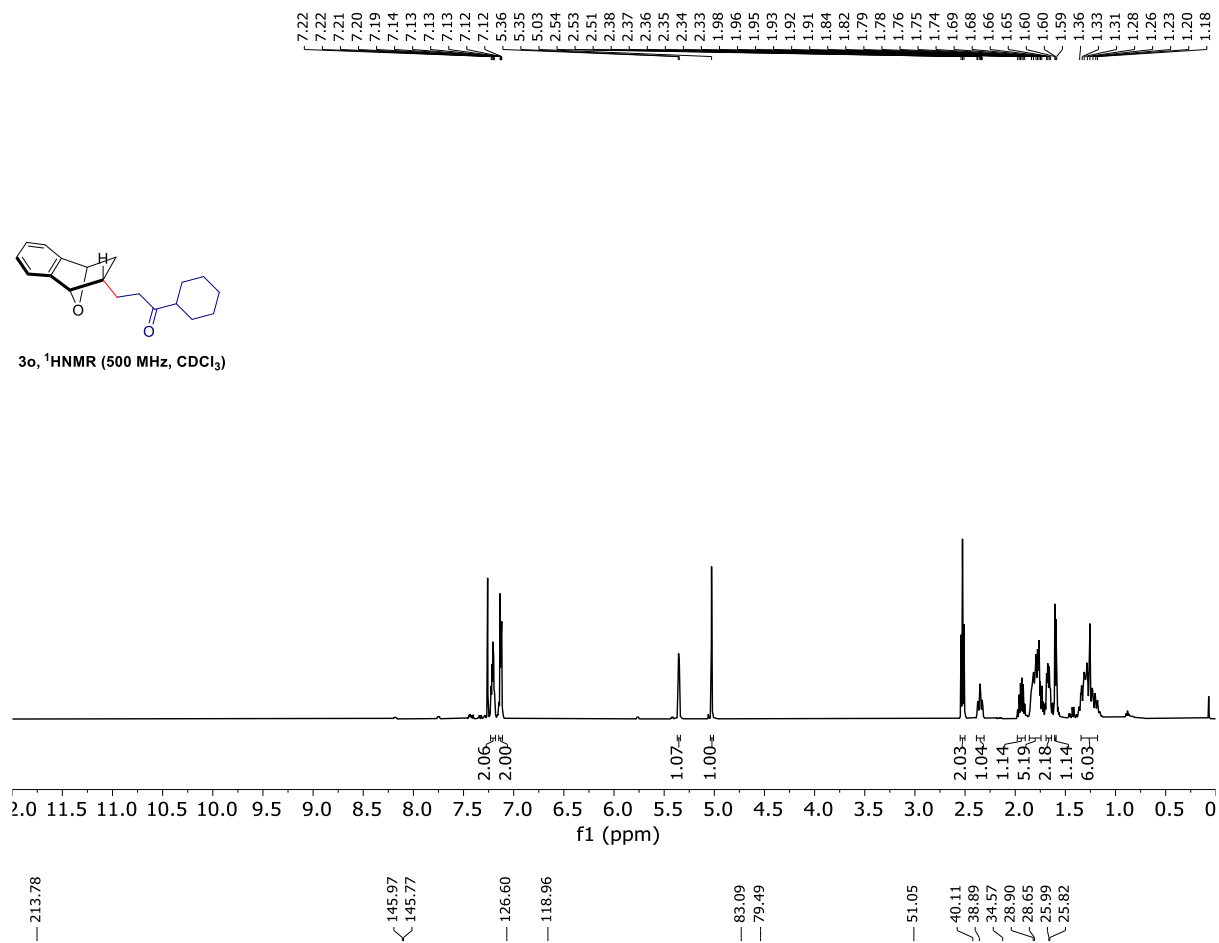
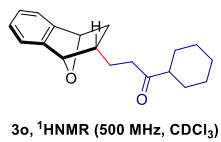




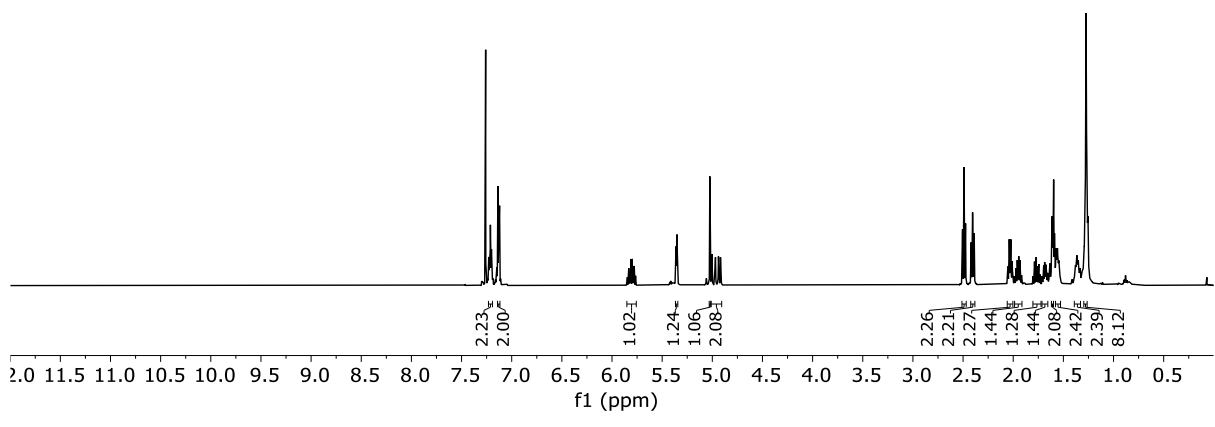
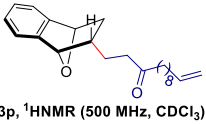




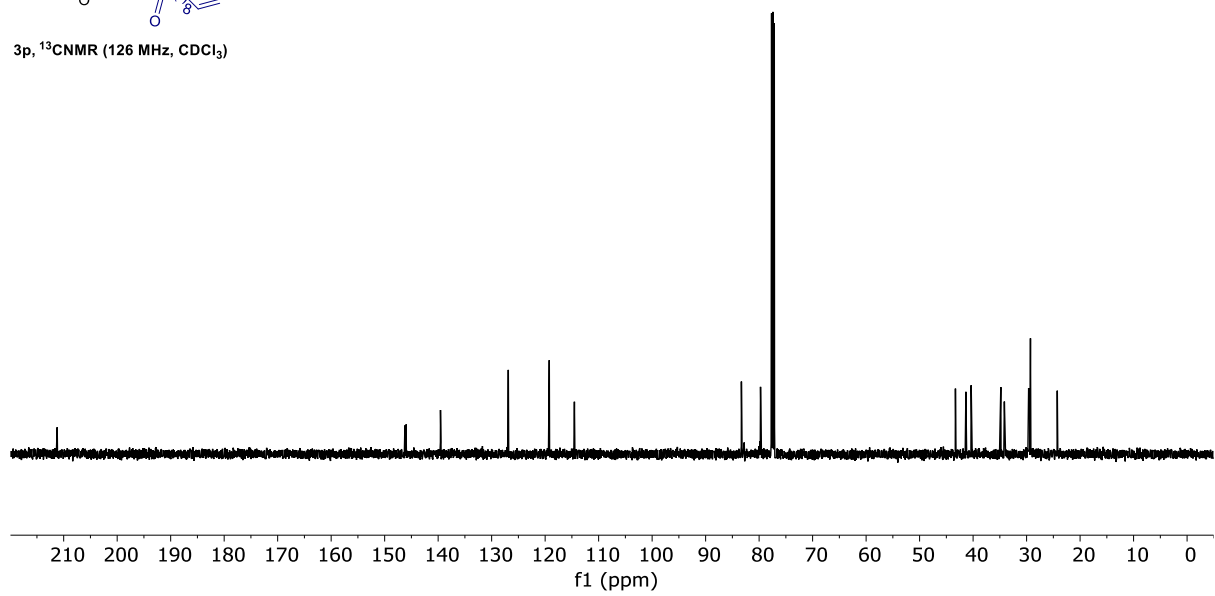
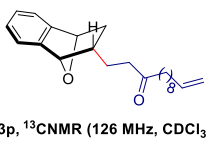


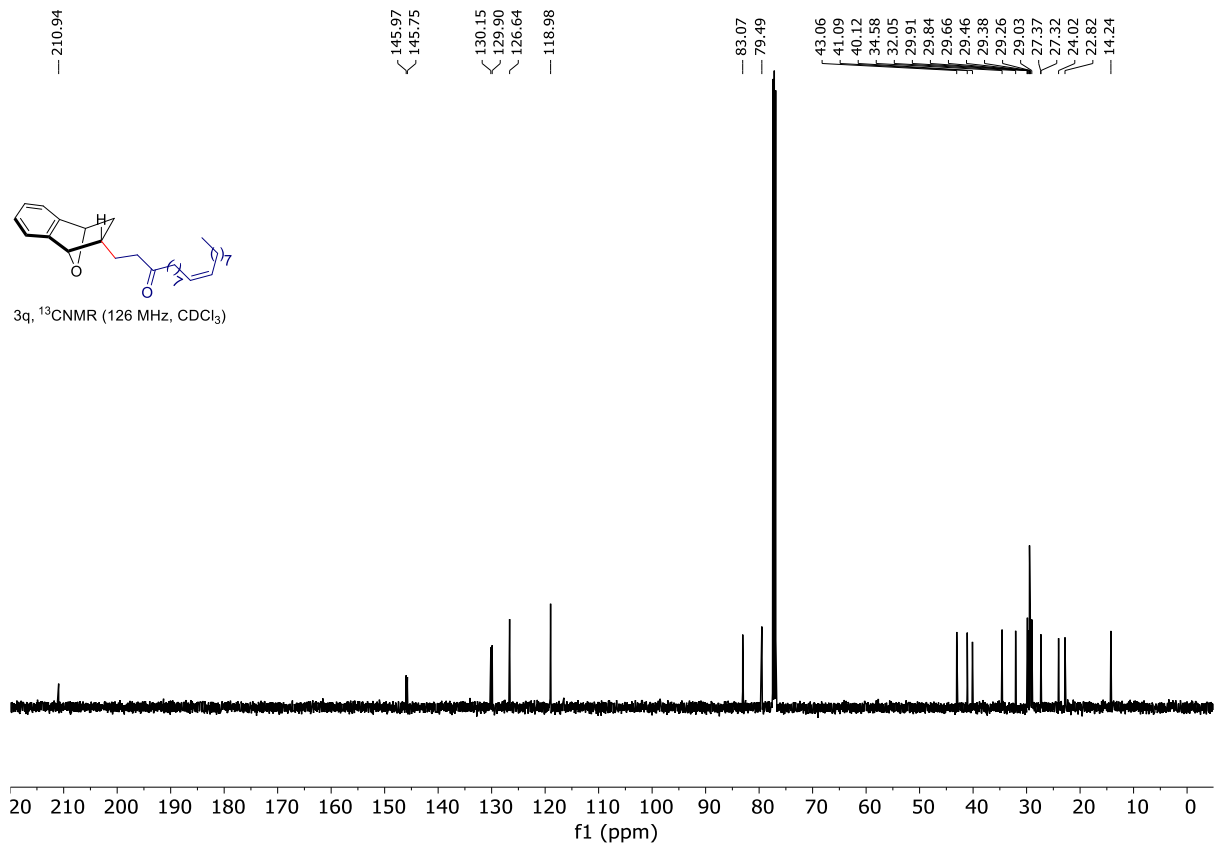
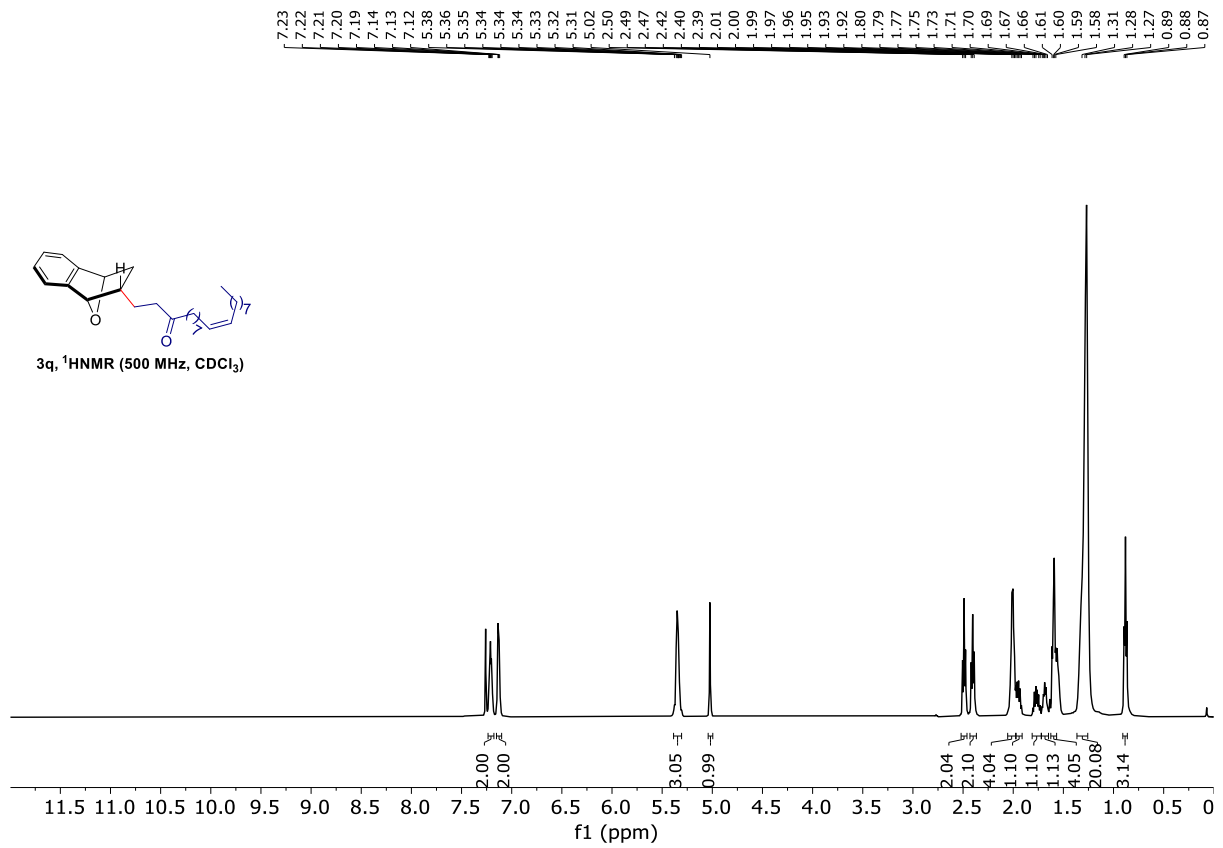


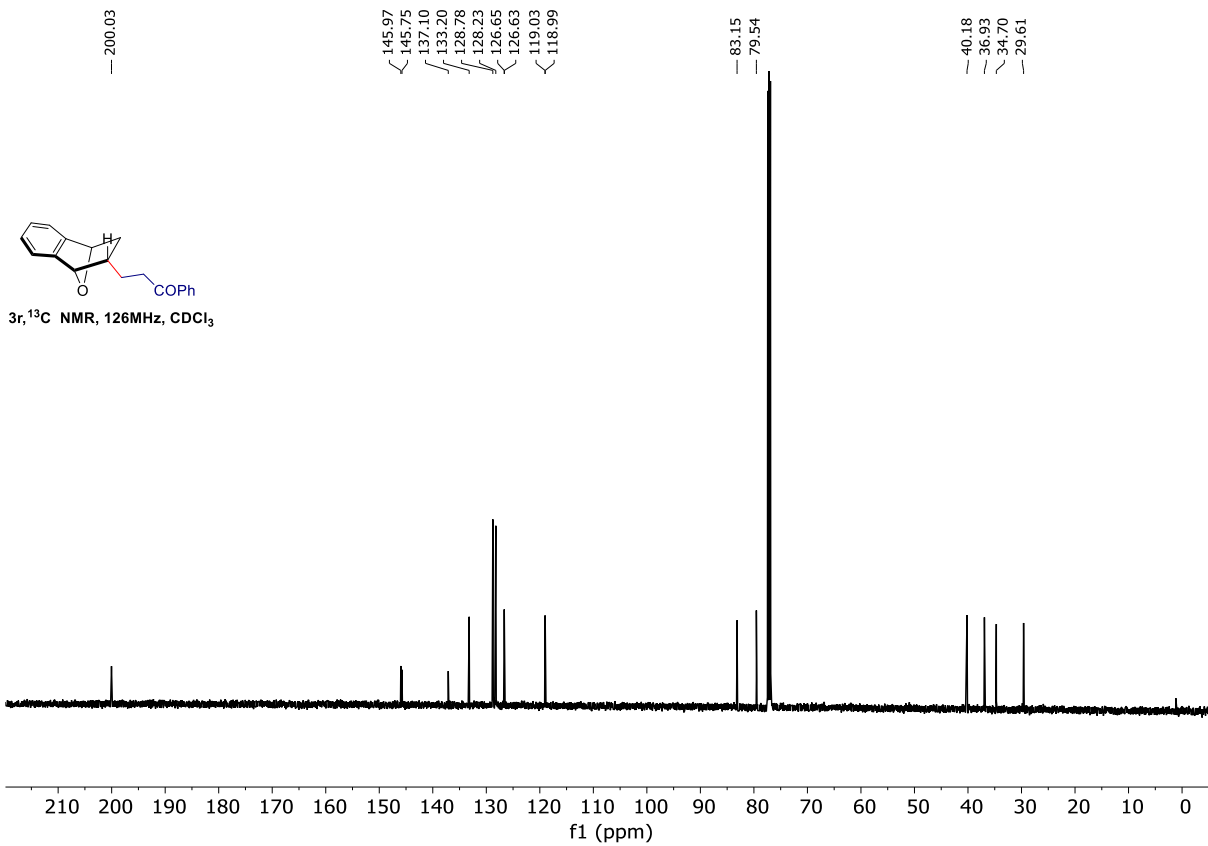
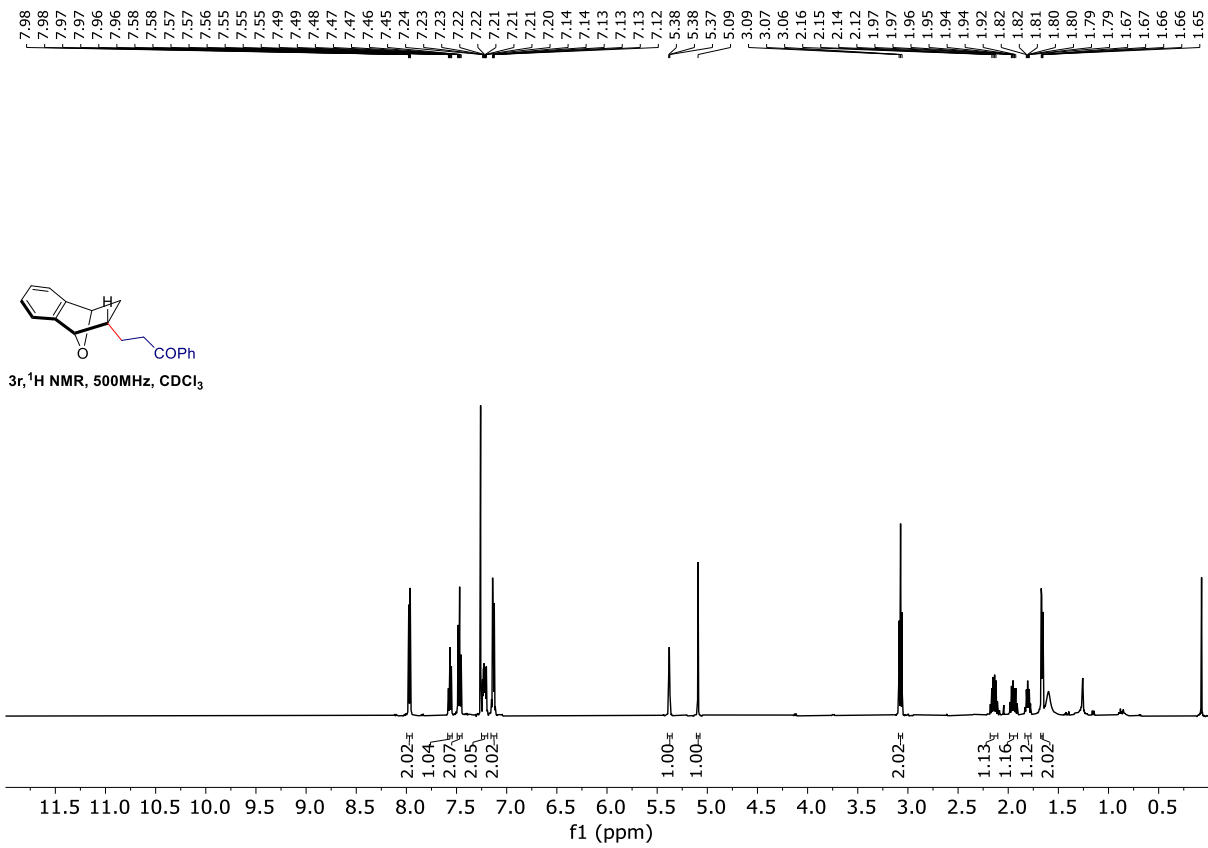
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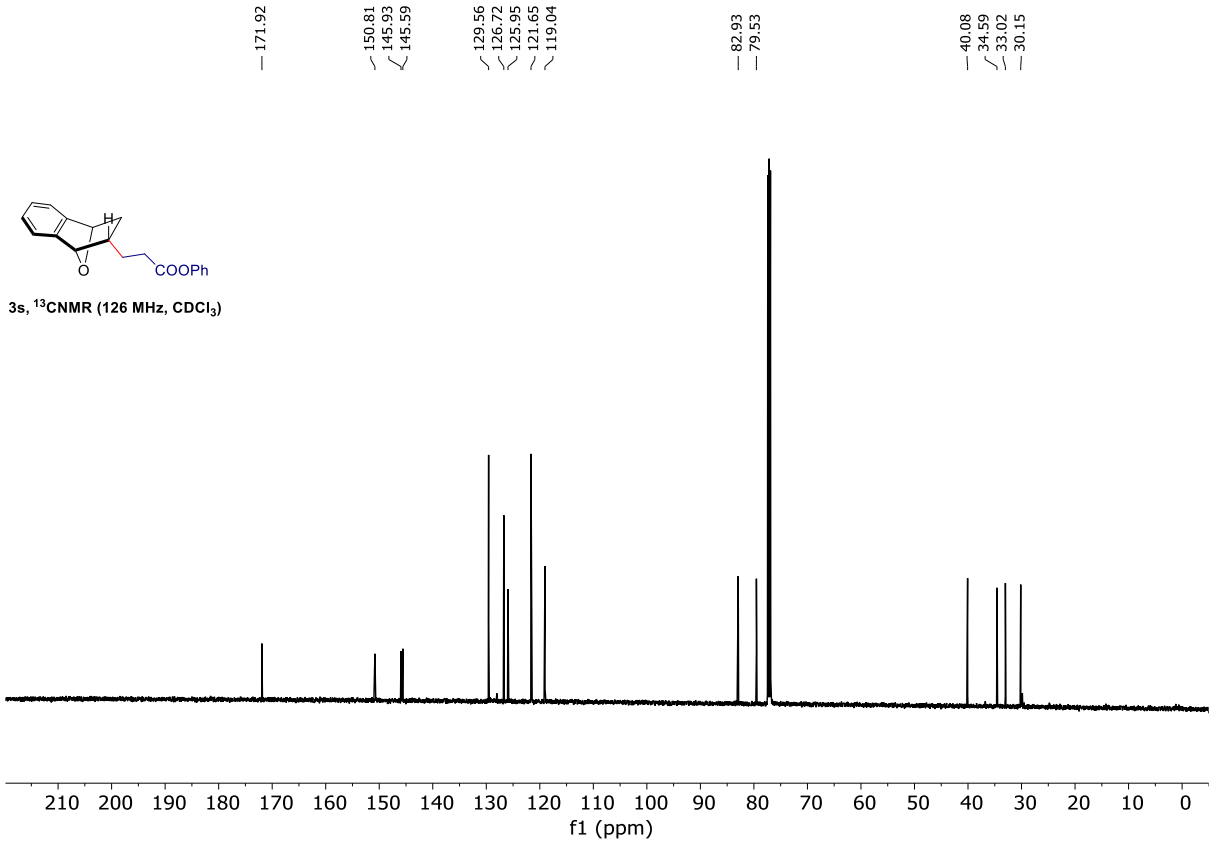
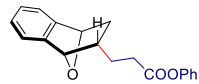
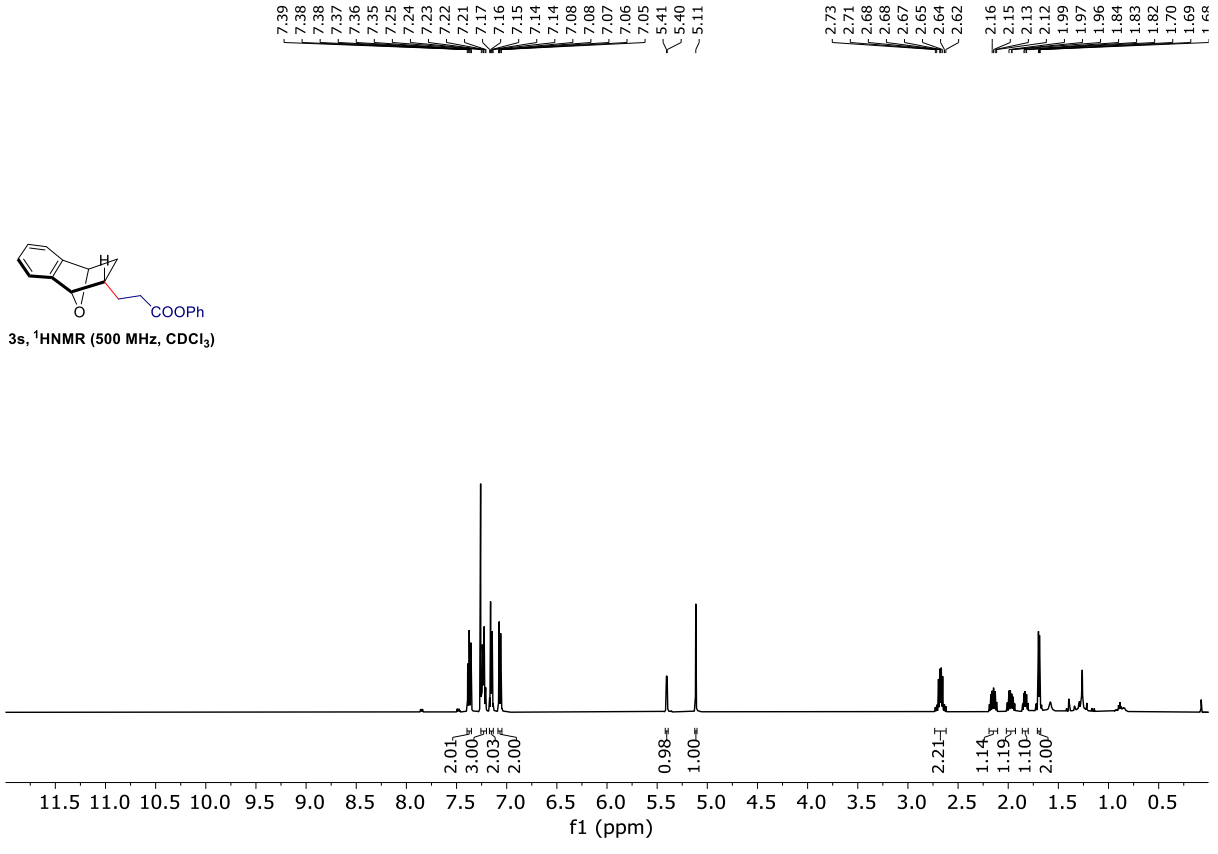
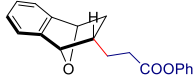


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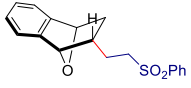




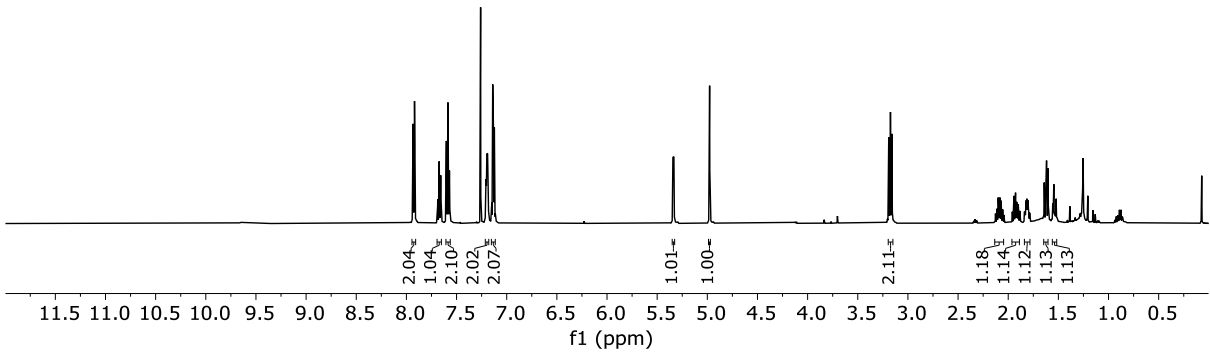




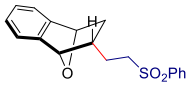
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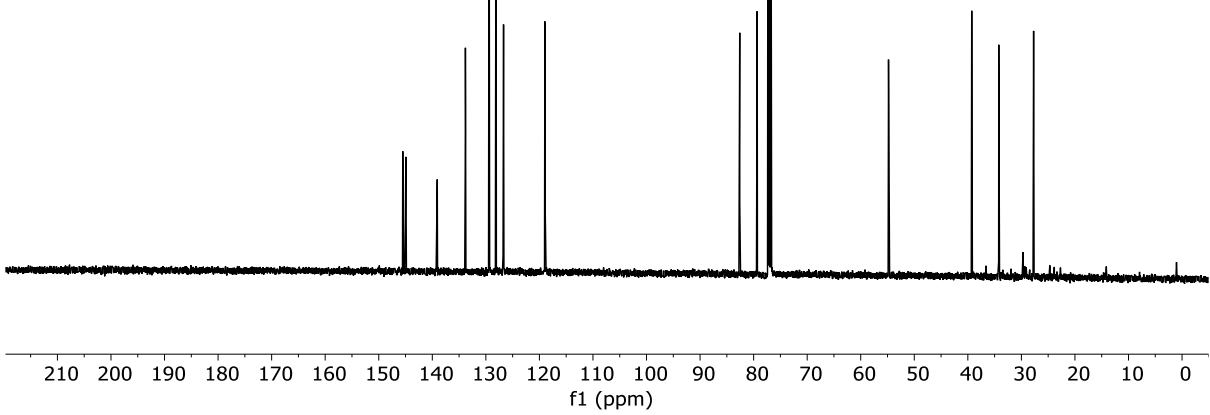
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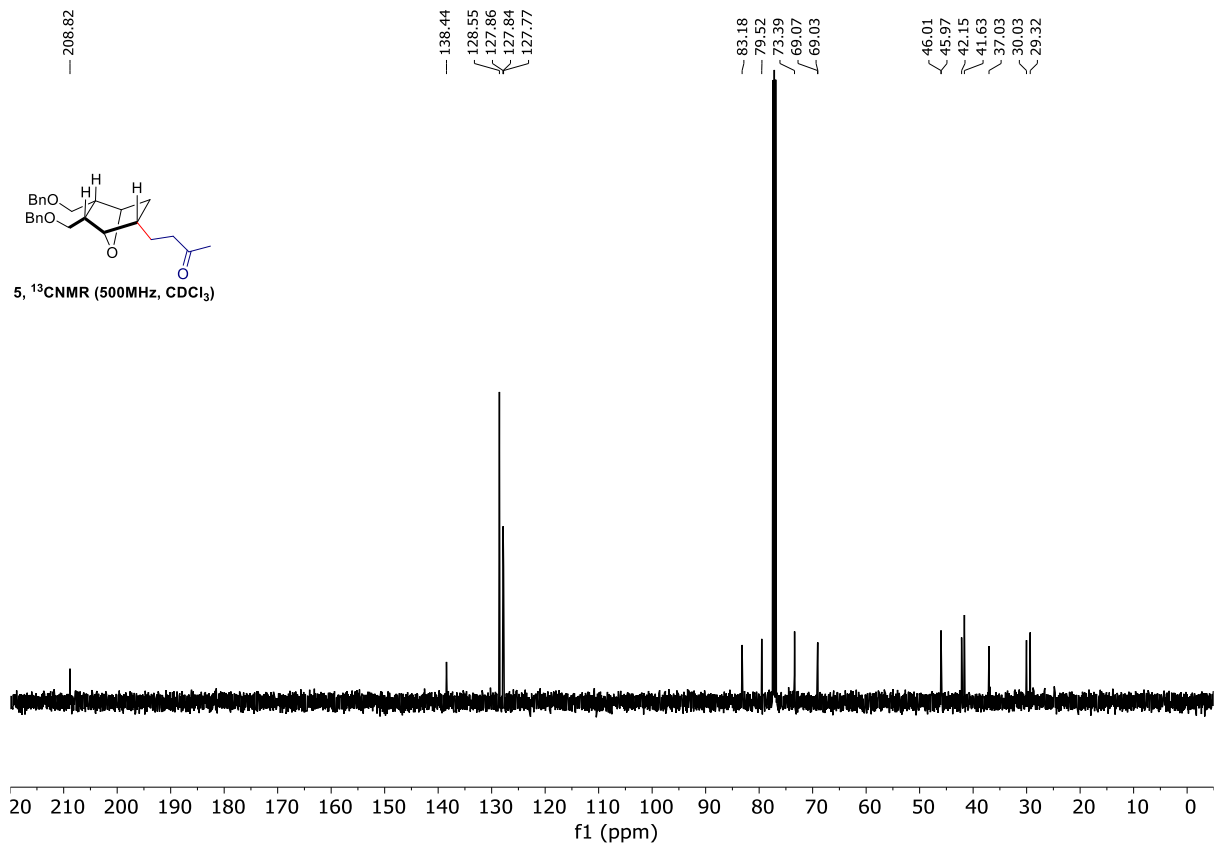
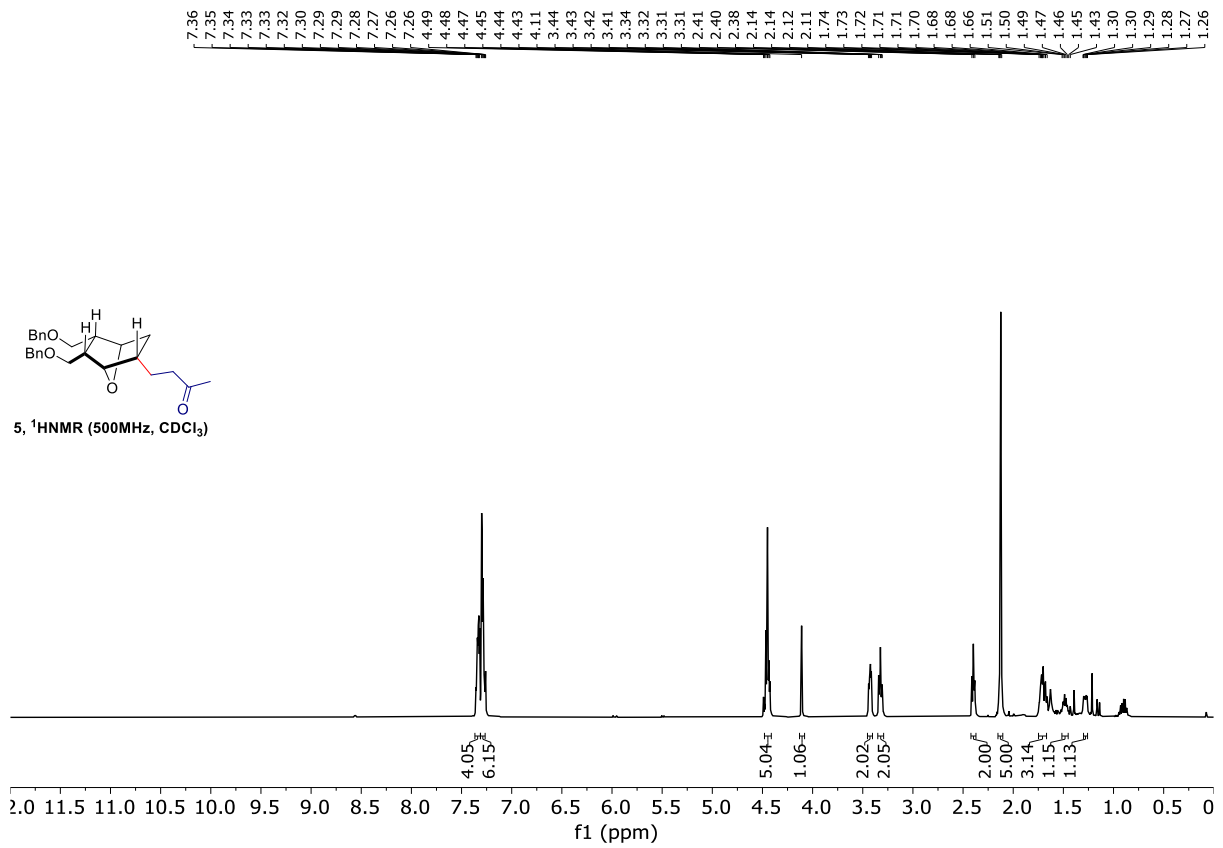


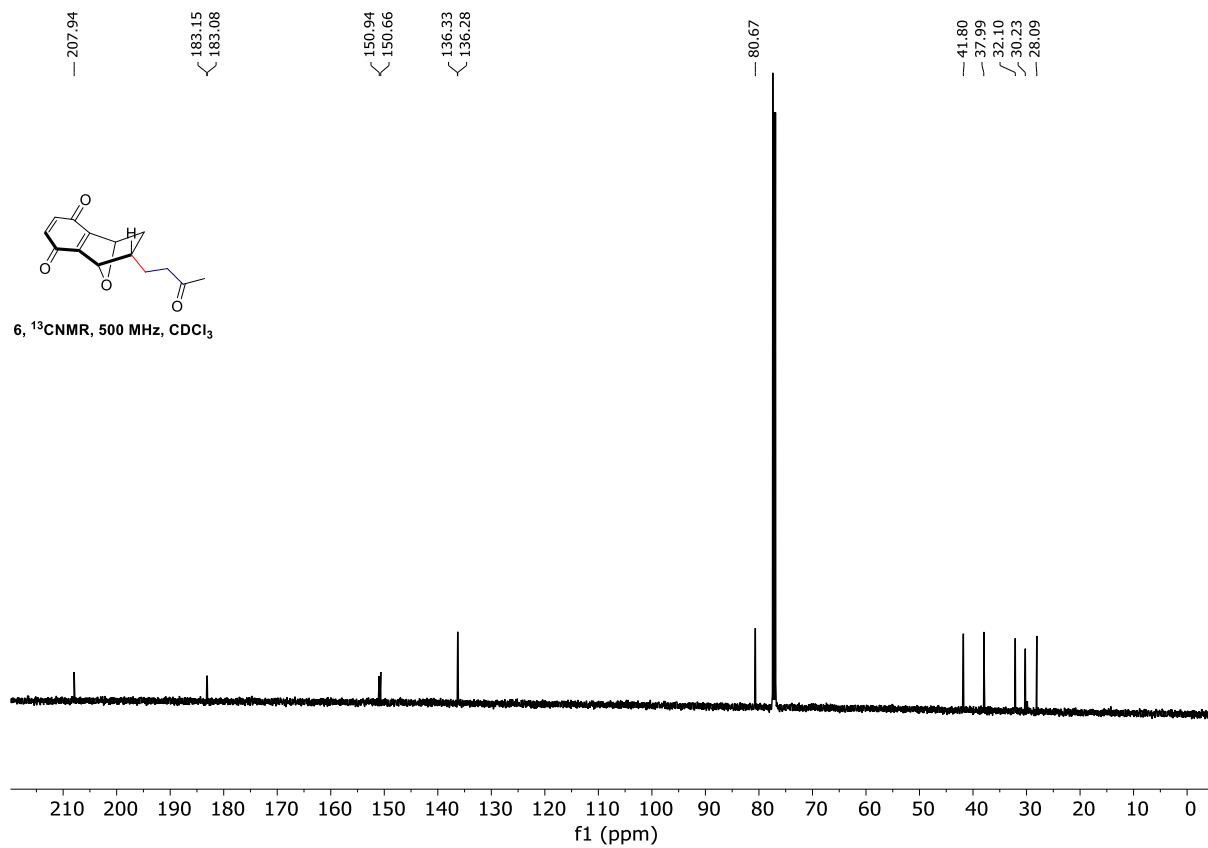
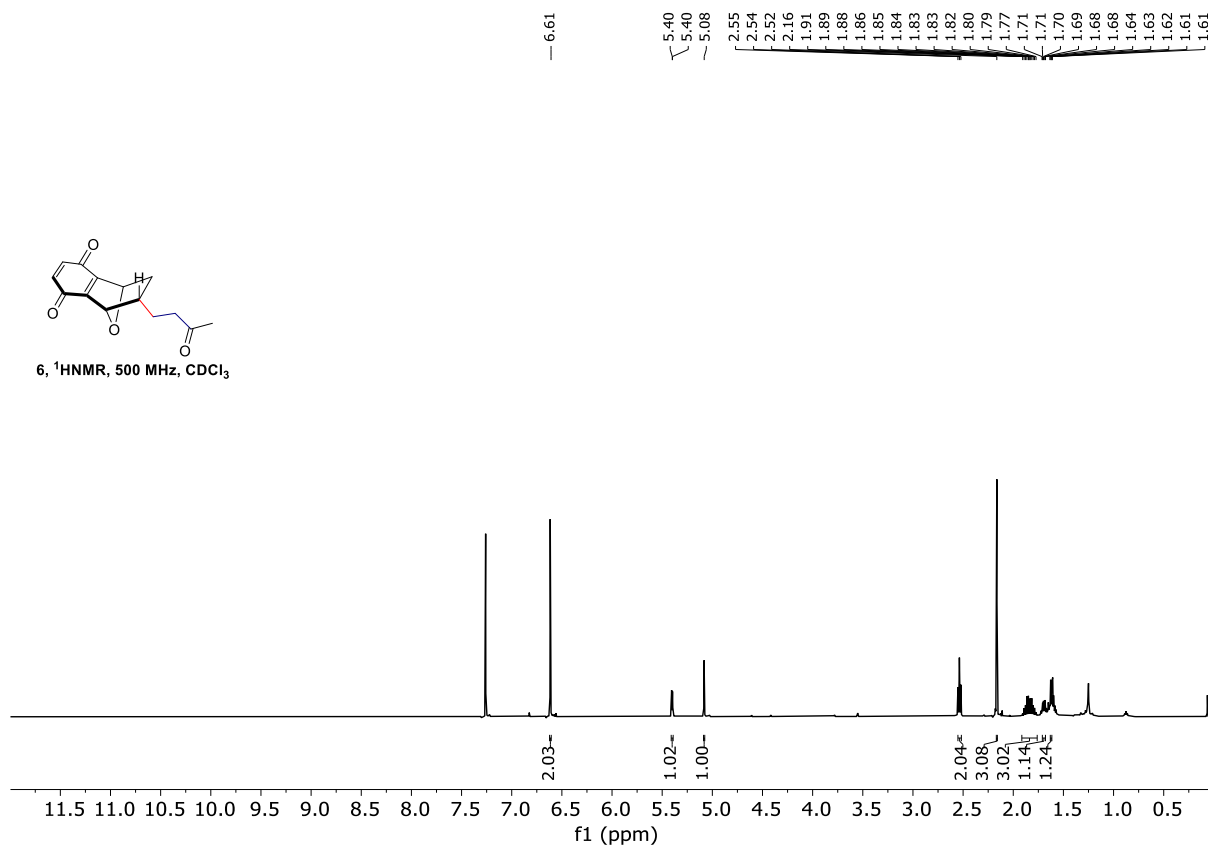
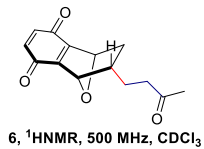
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79.33
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34.23
27.72

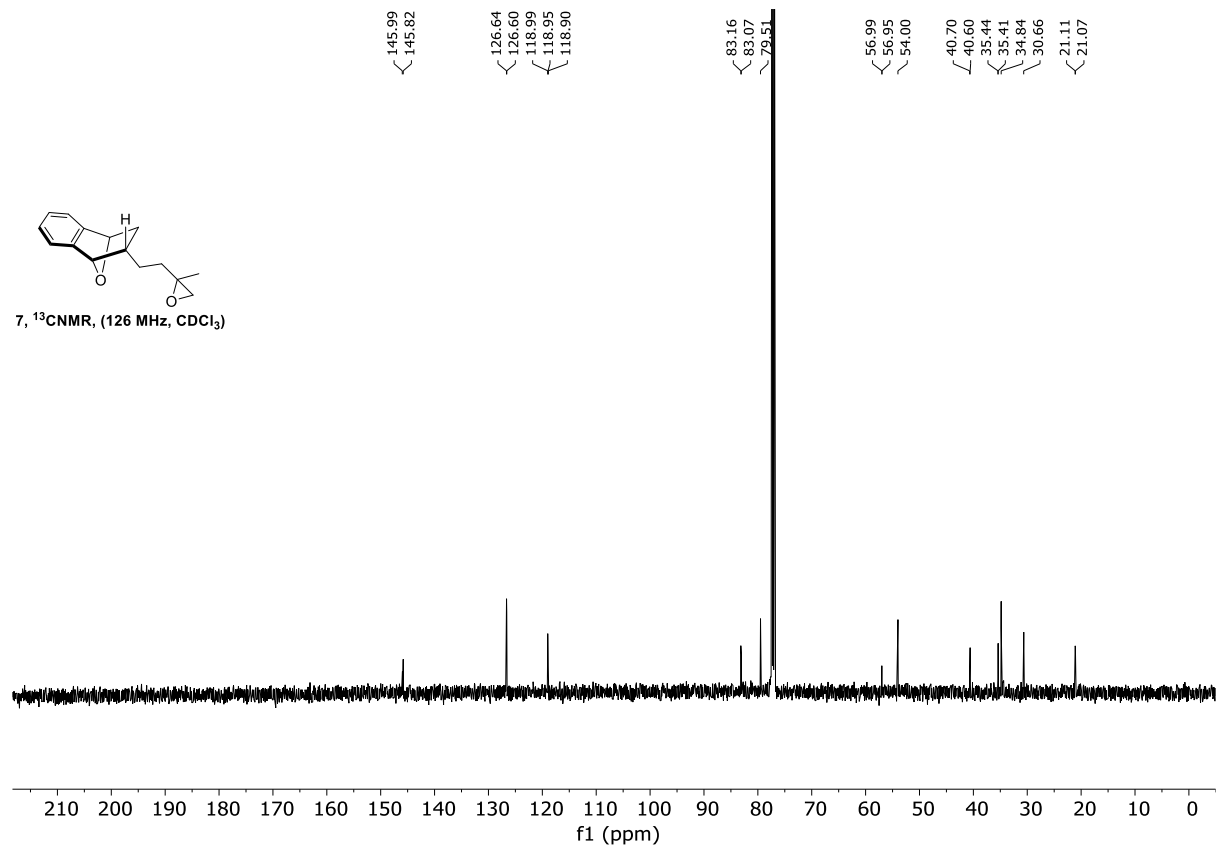
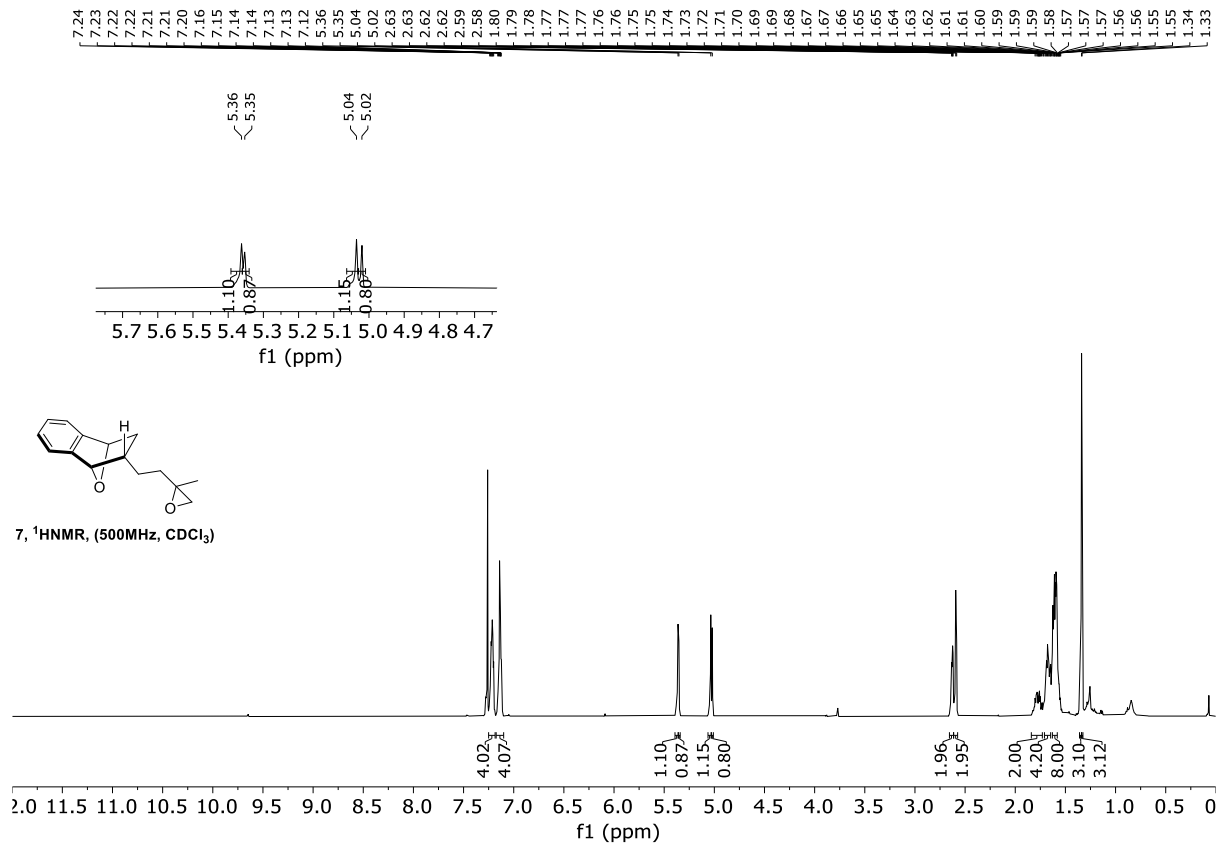


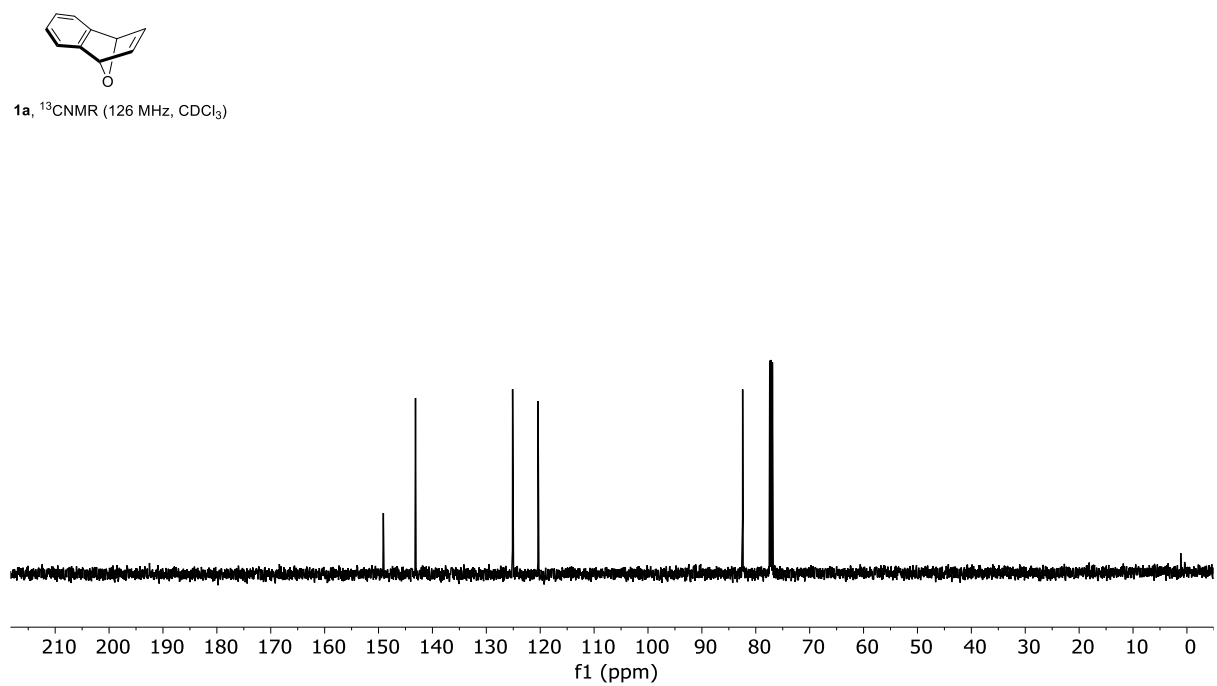
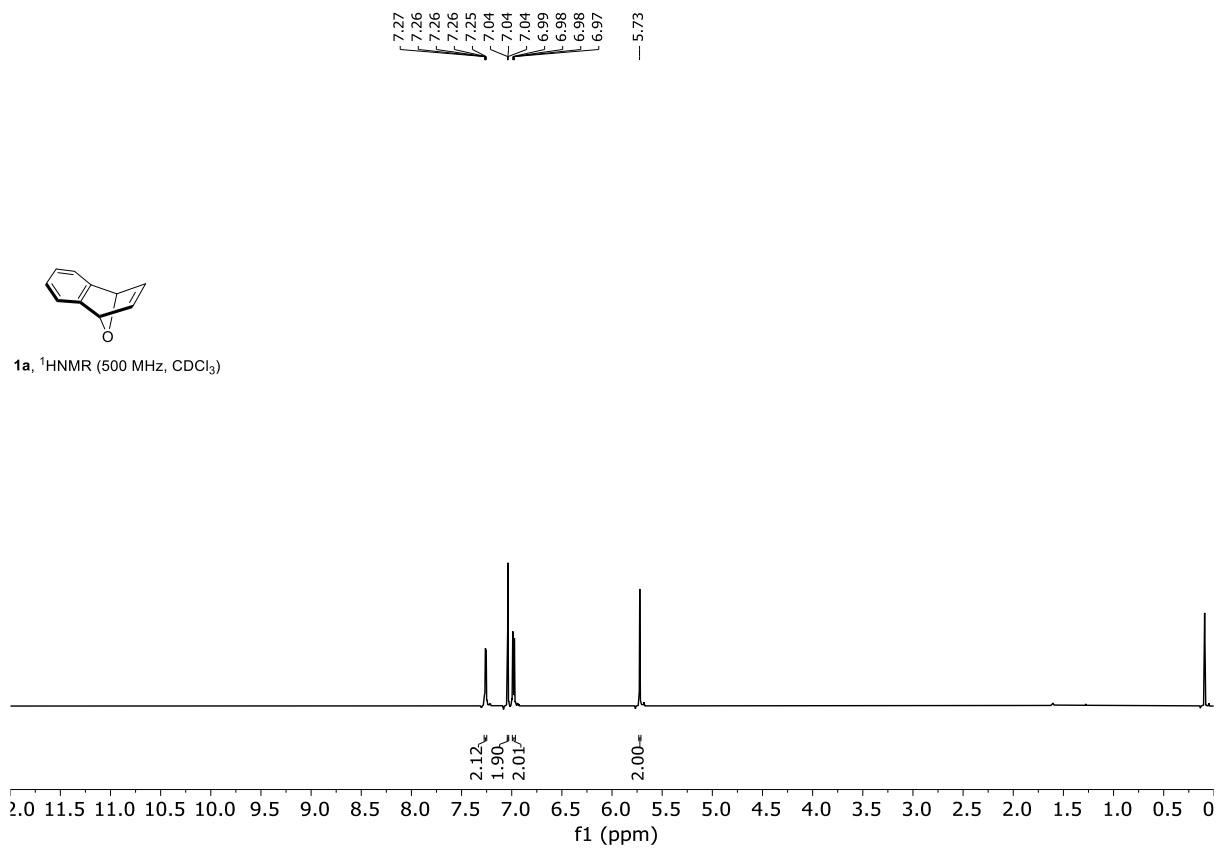
3t, ¹³CNMR (126 MHz, CDCl₃)

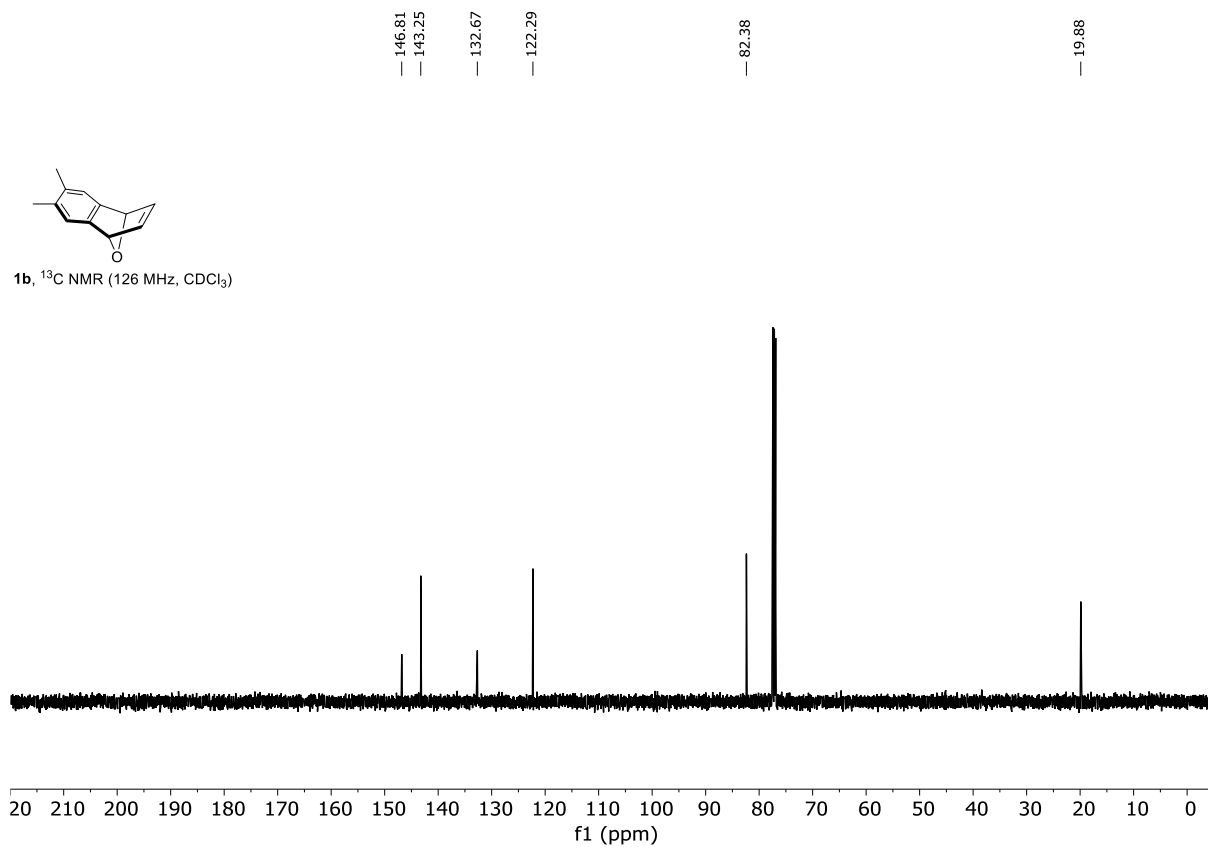
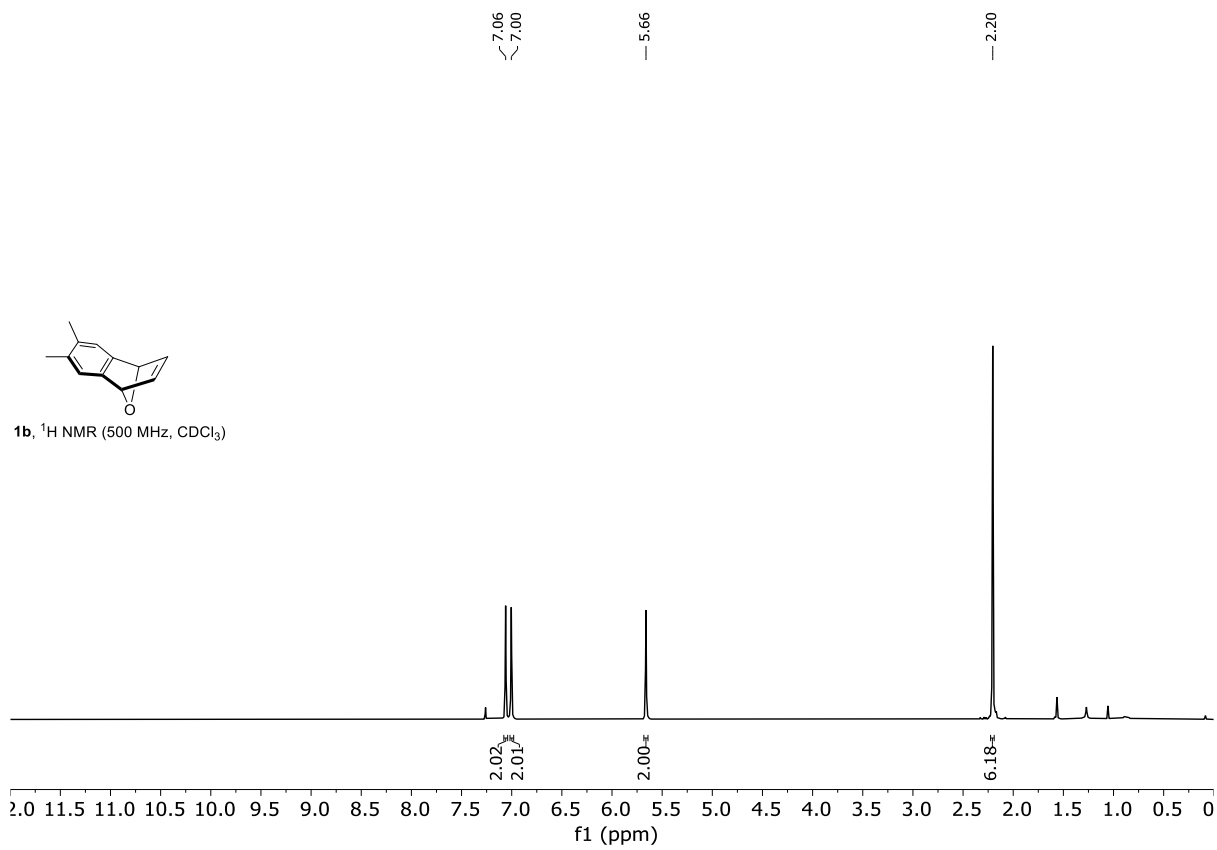


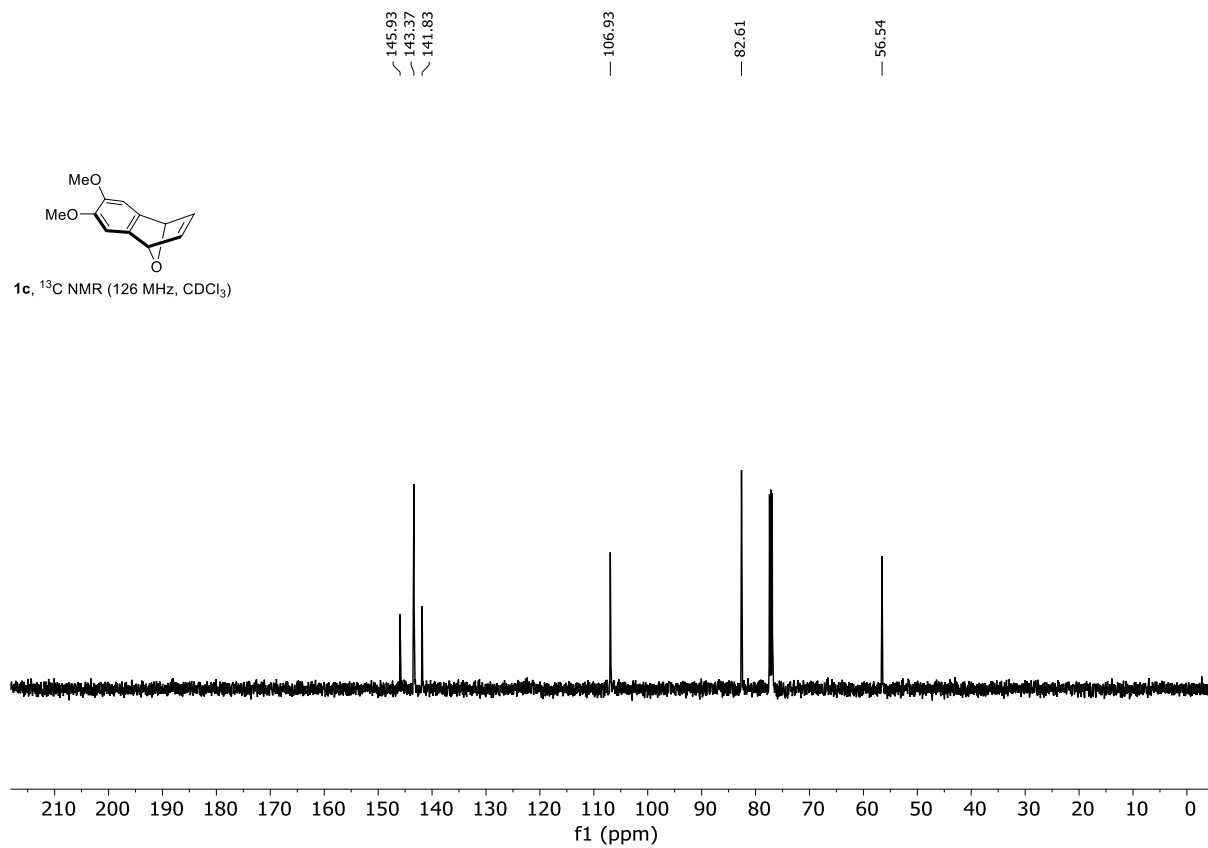
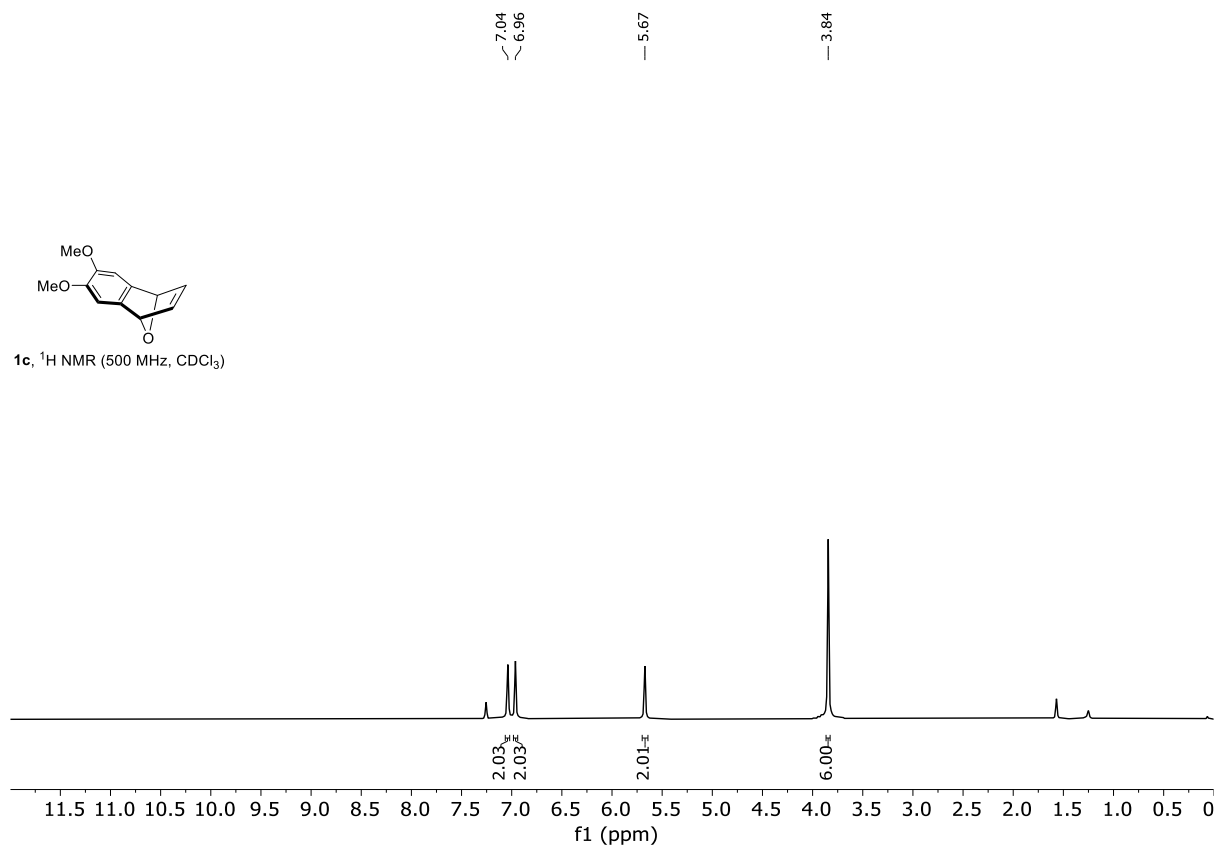


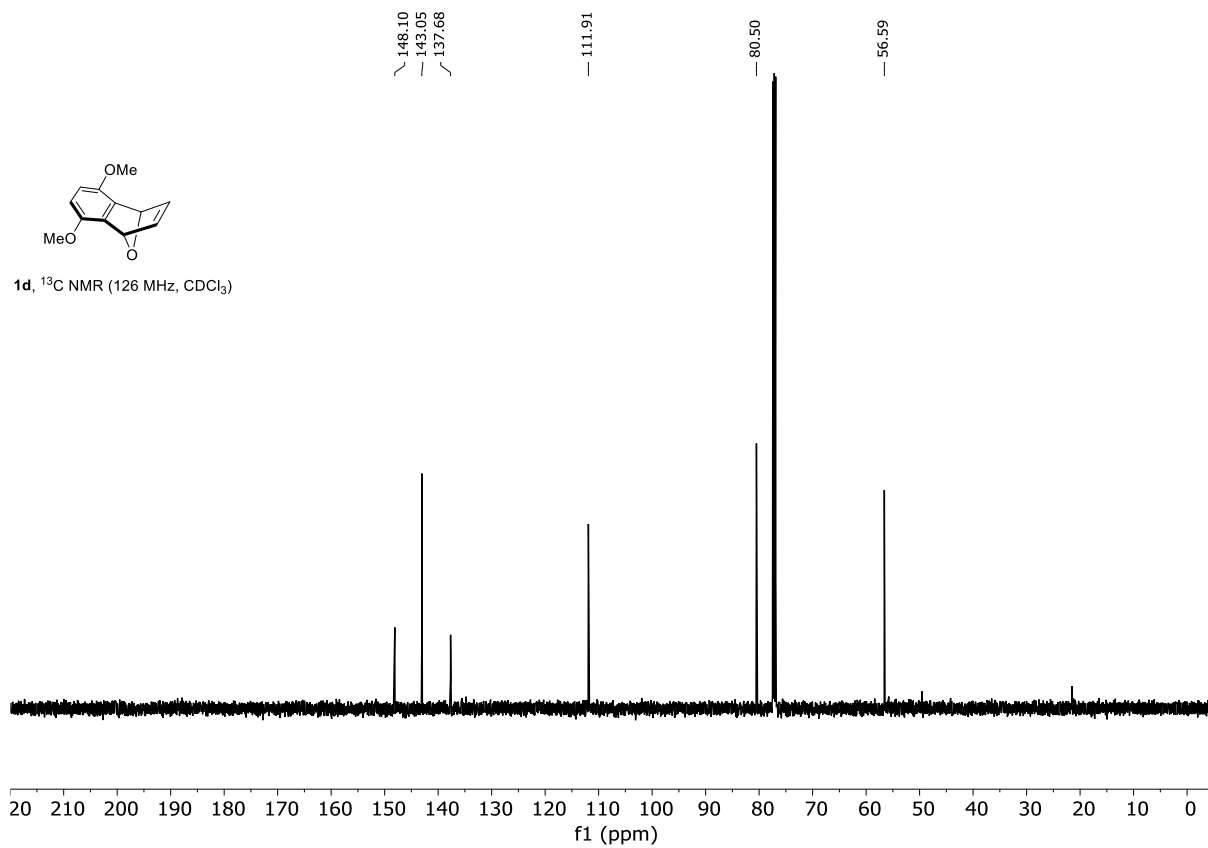
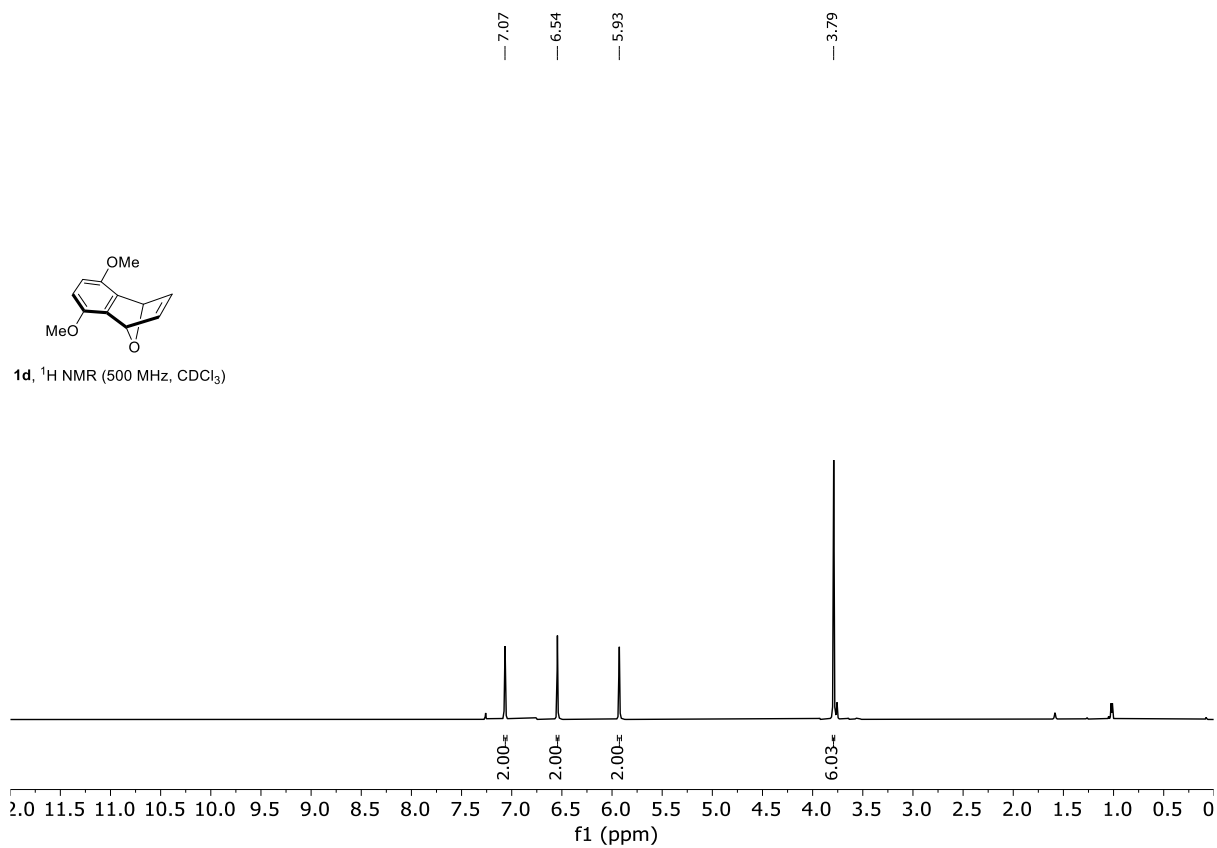


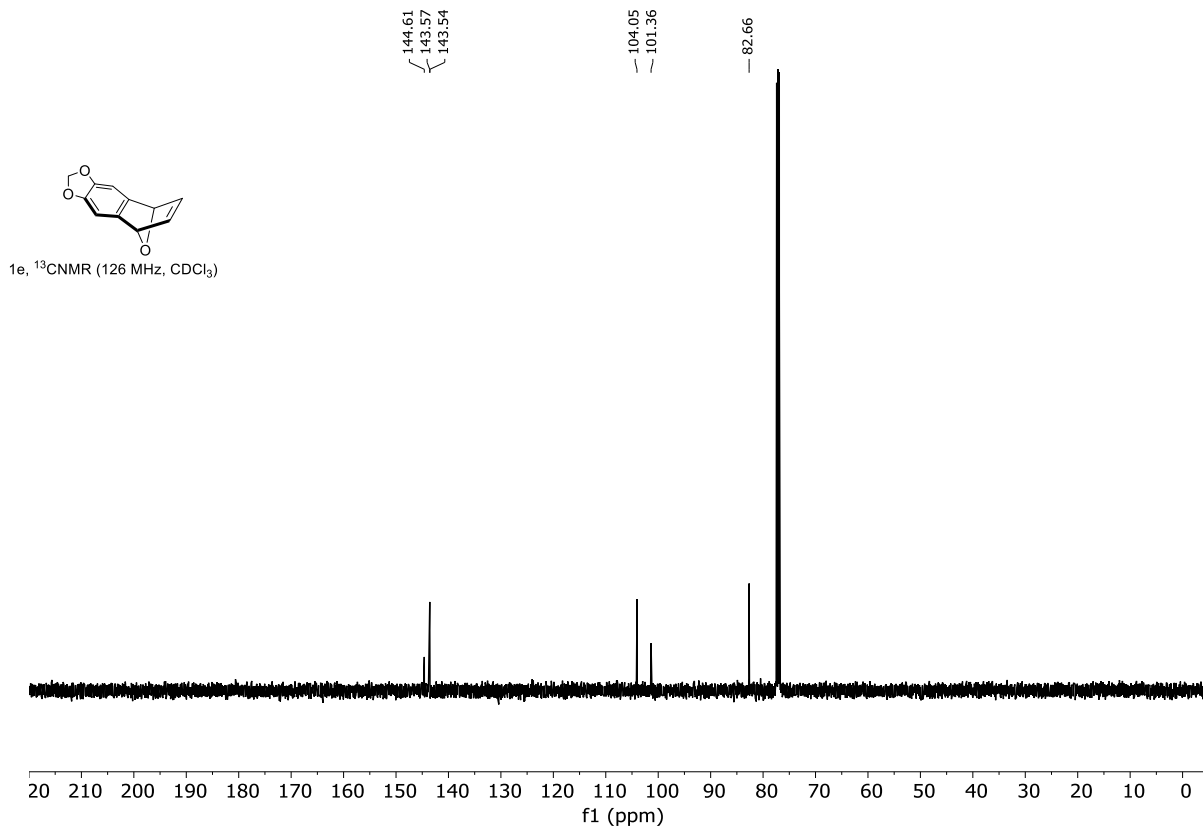
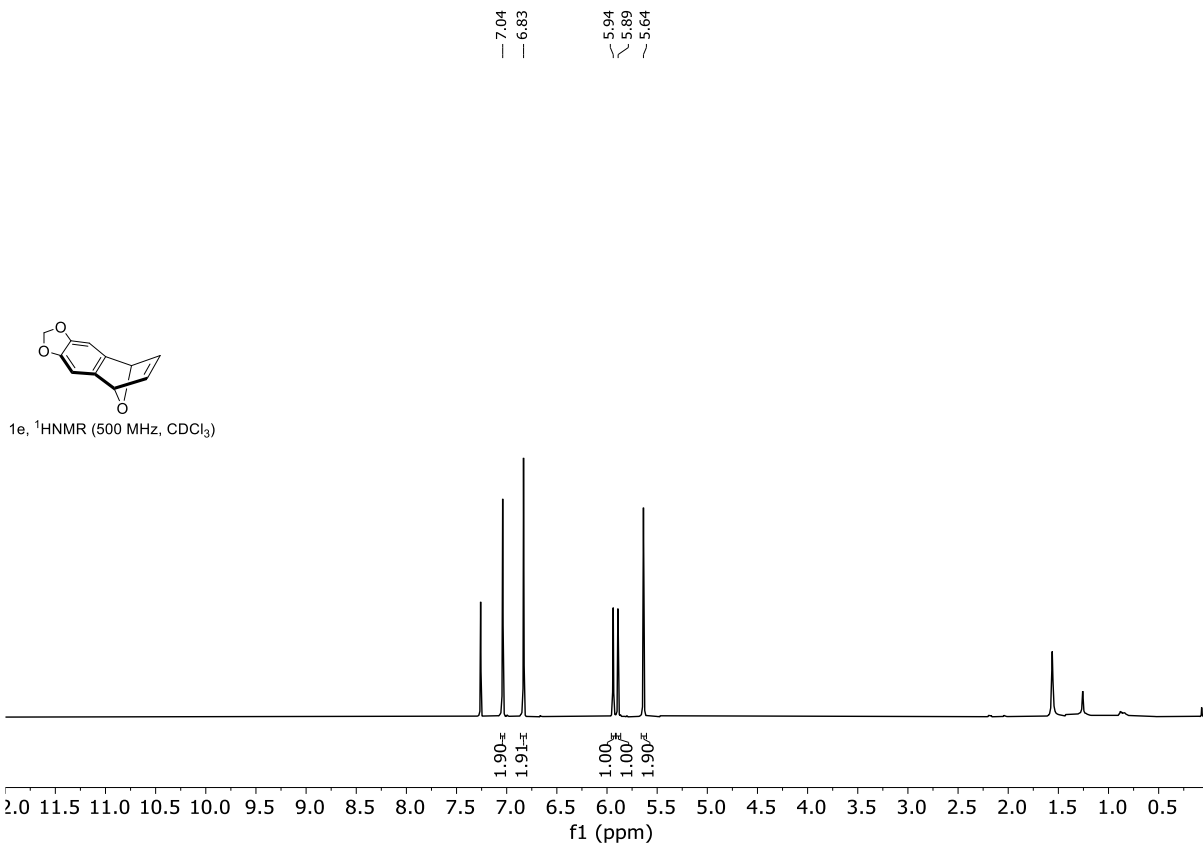


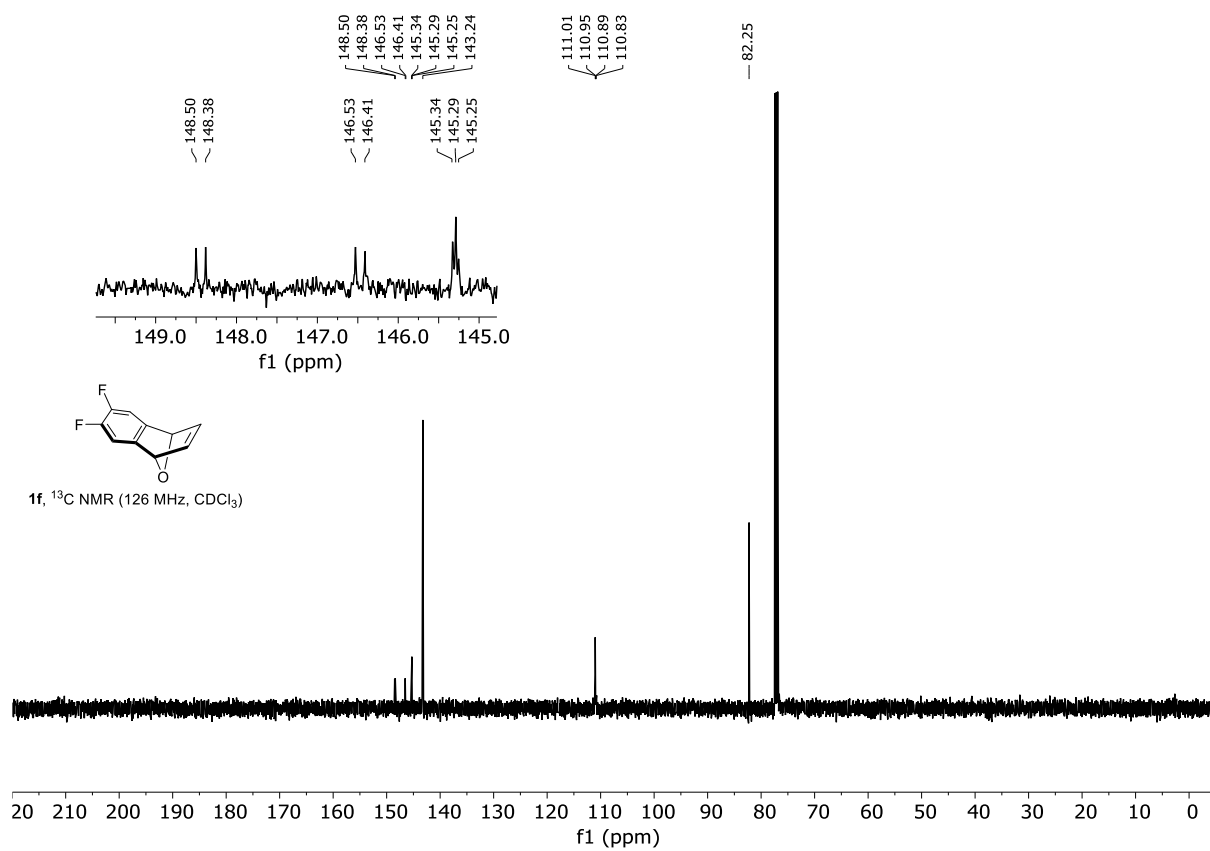
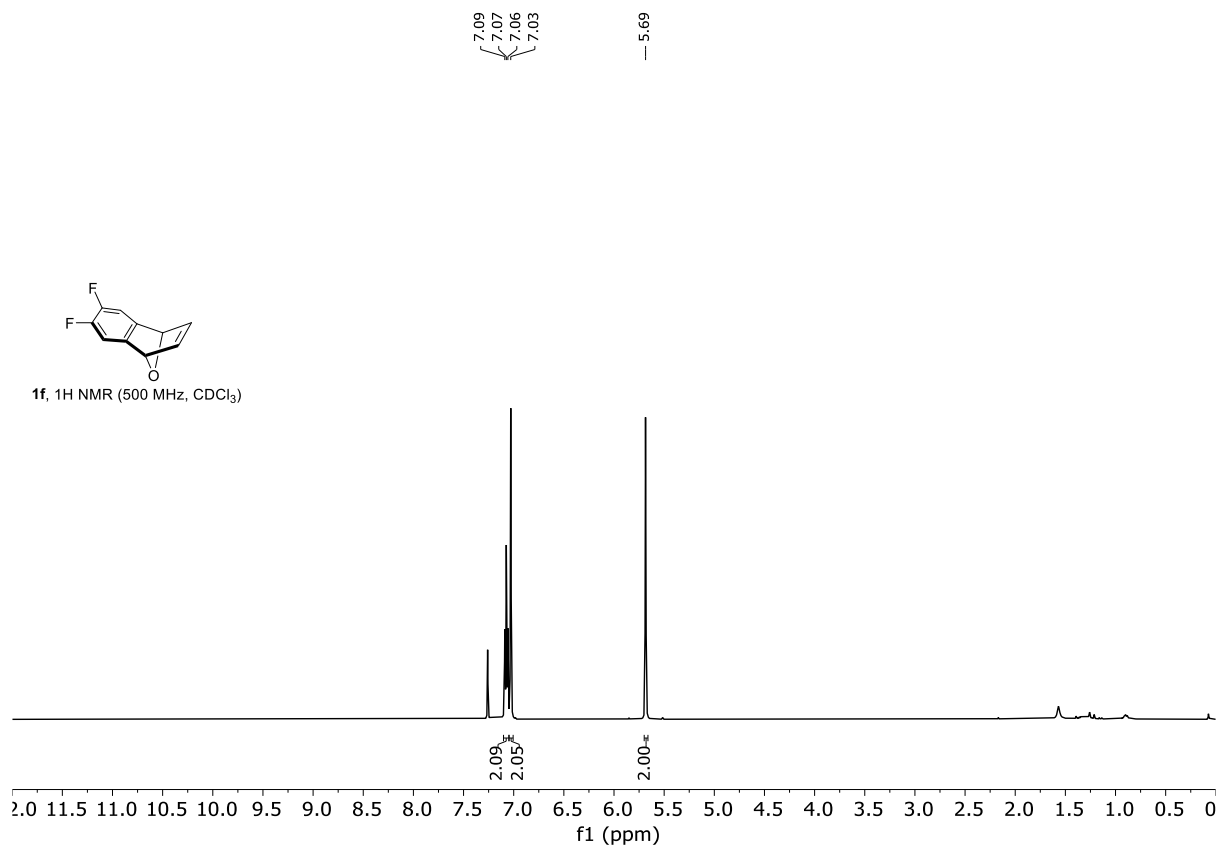


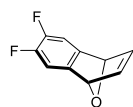




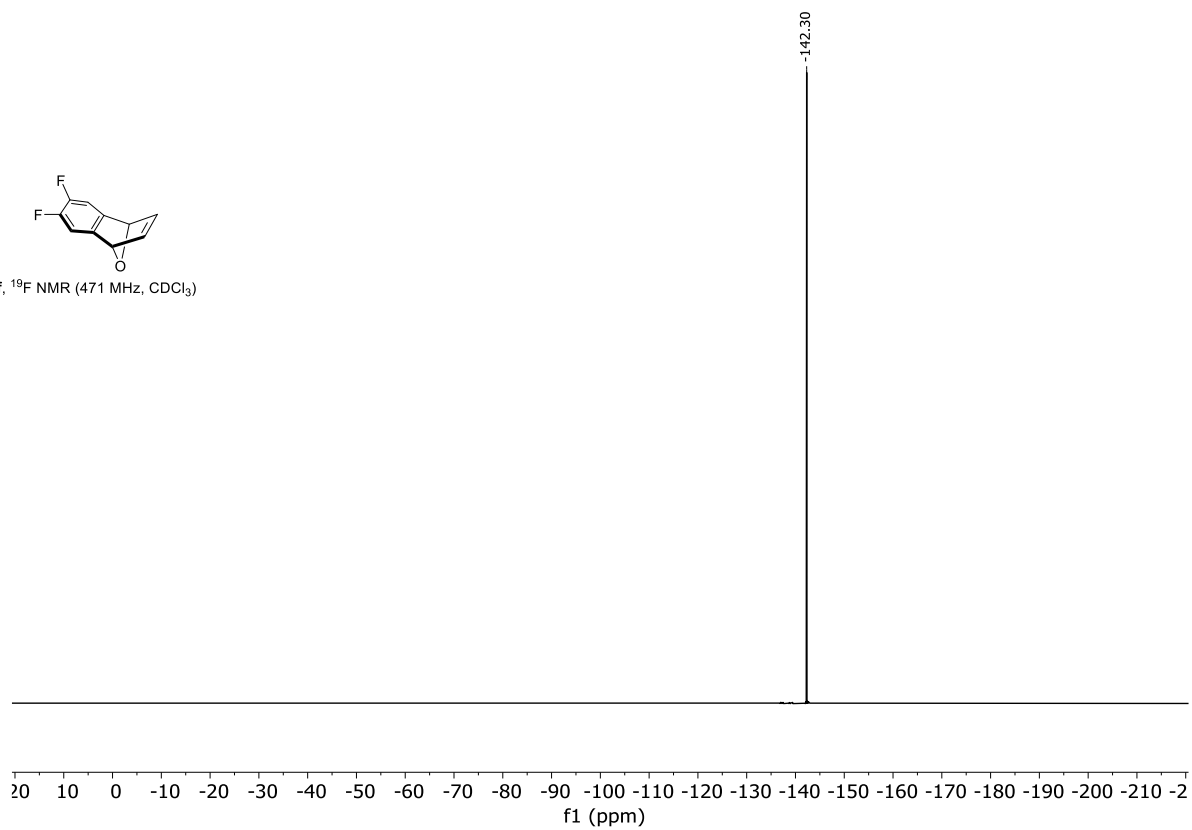


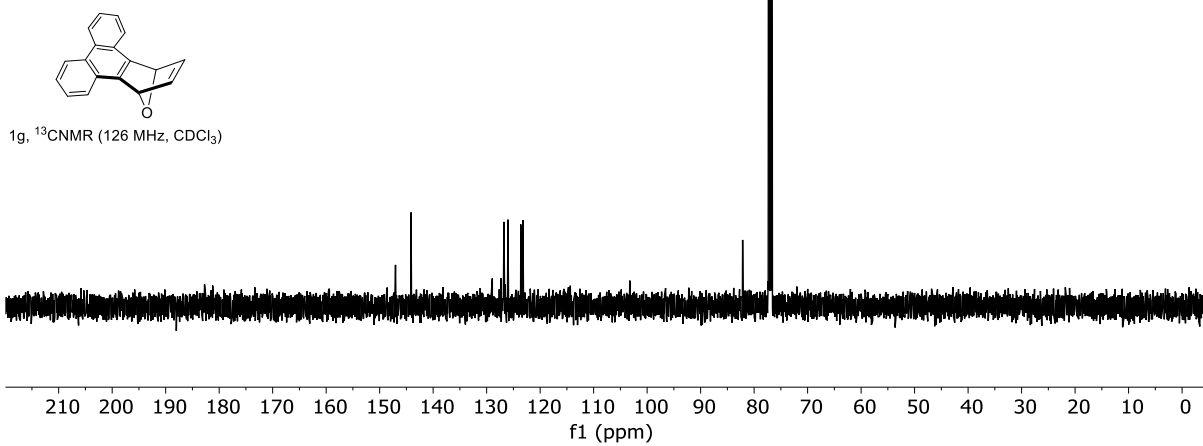
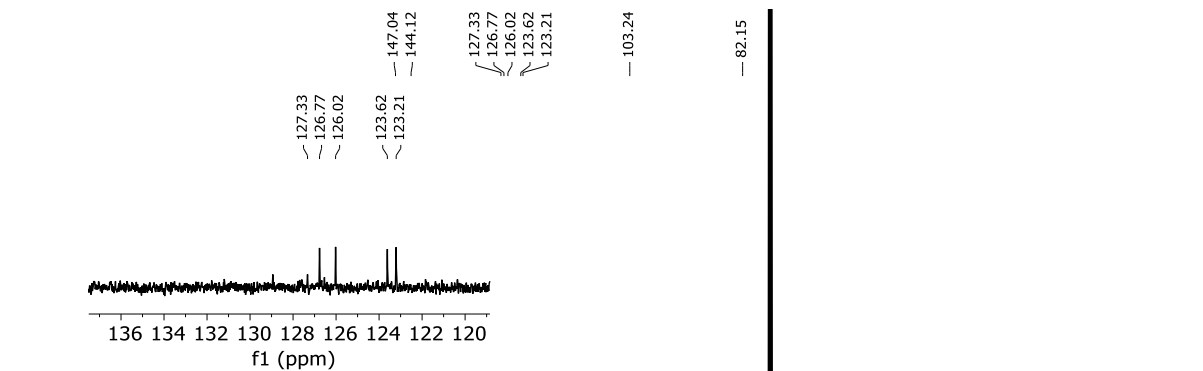
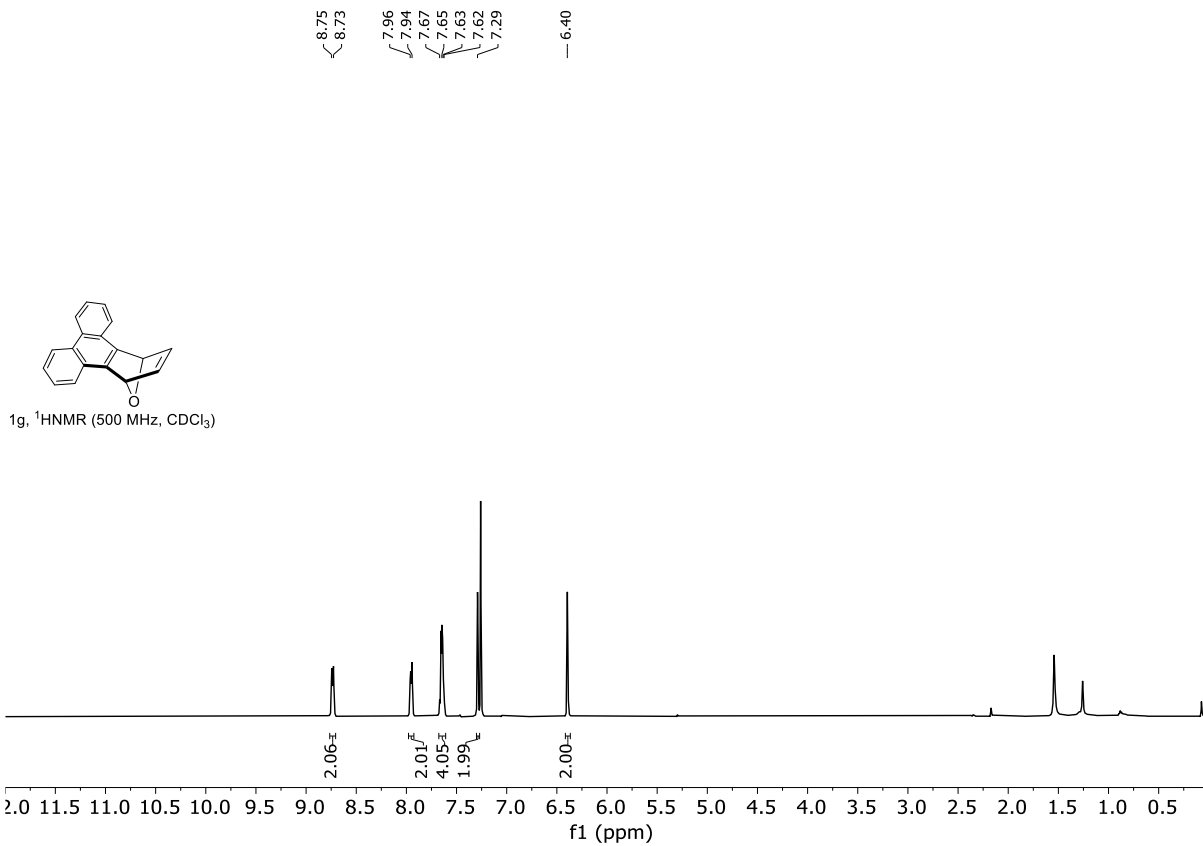


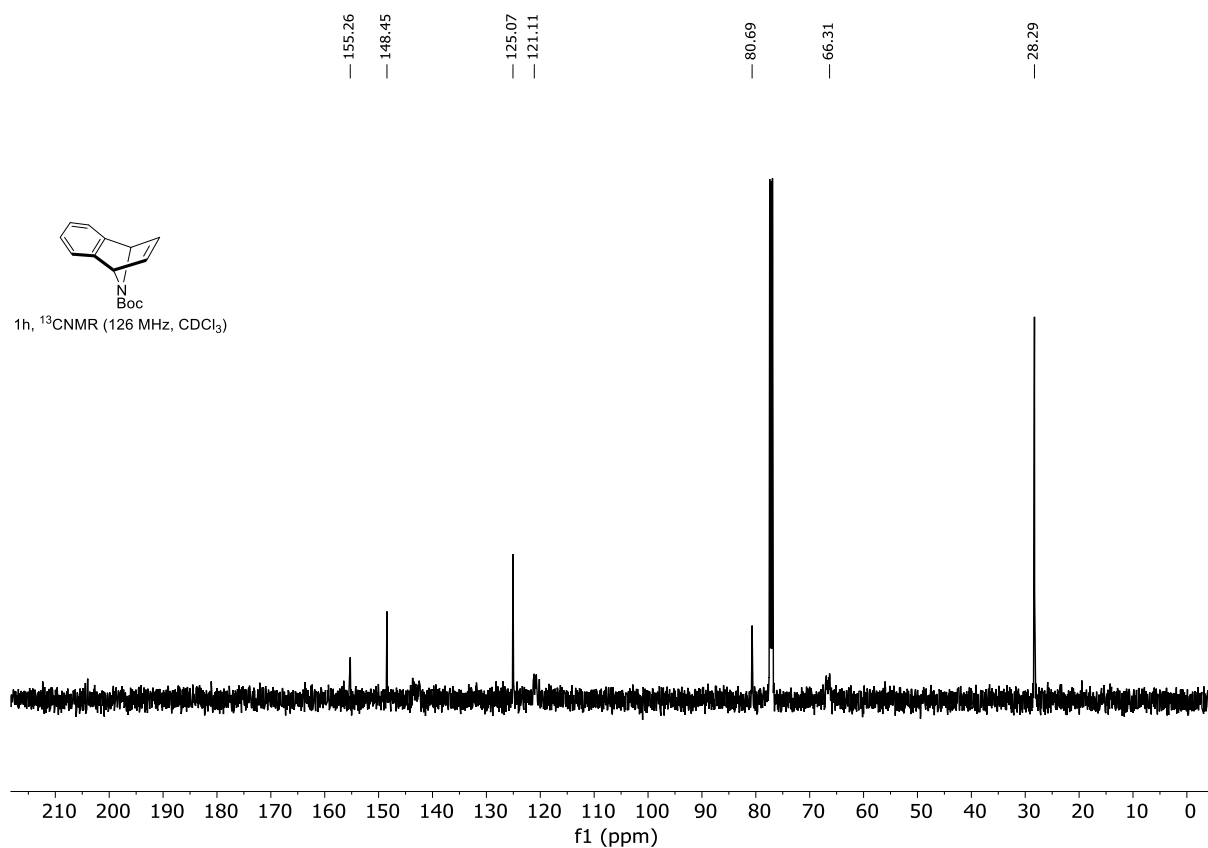
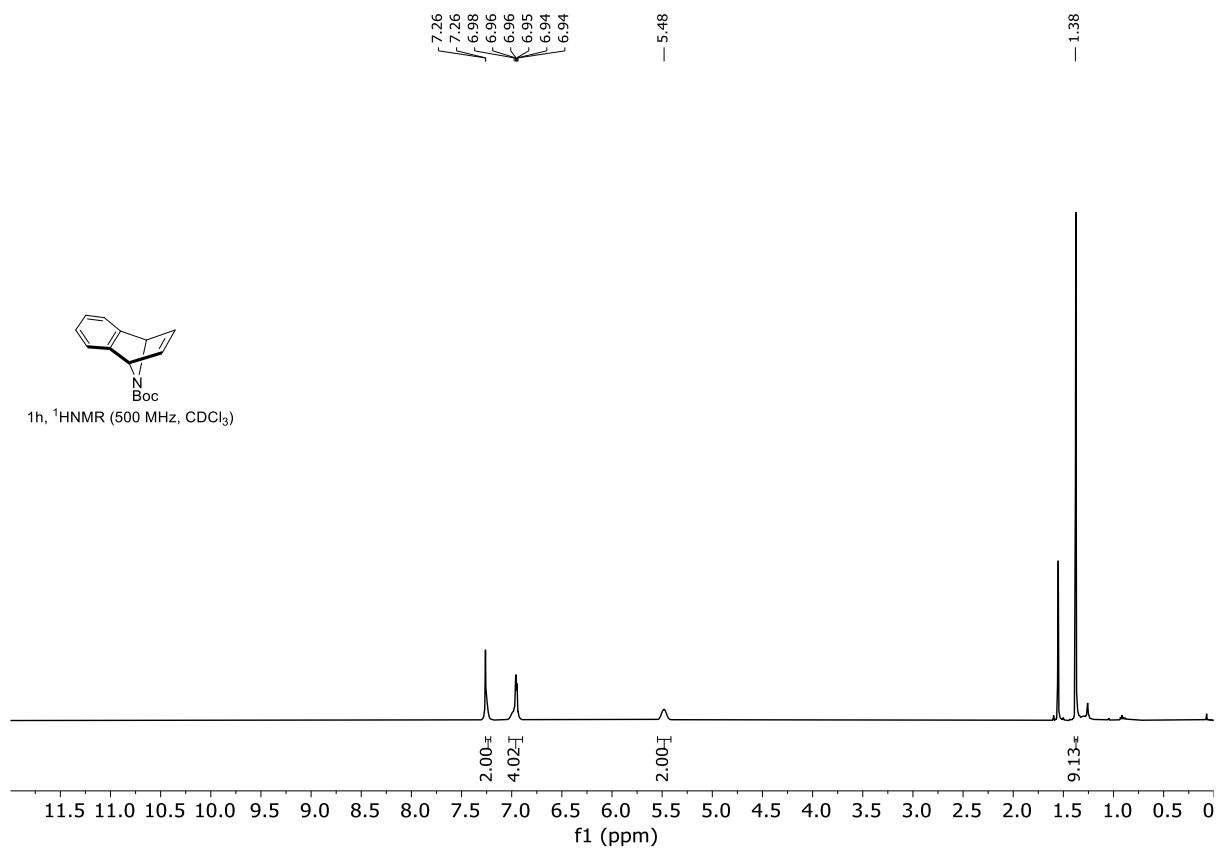


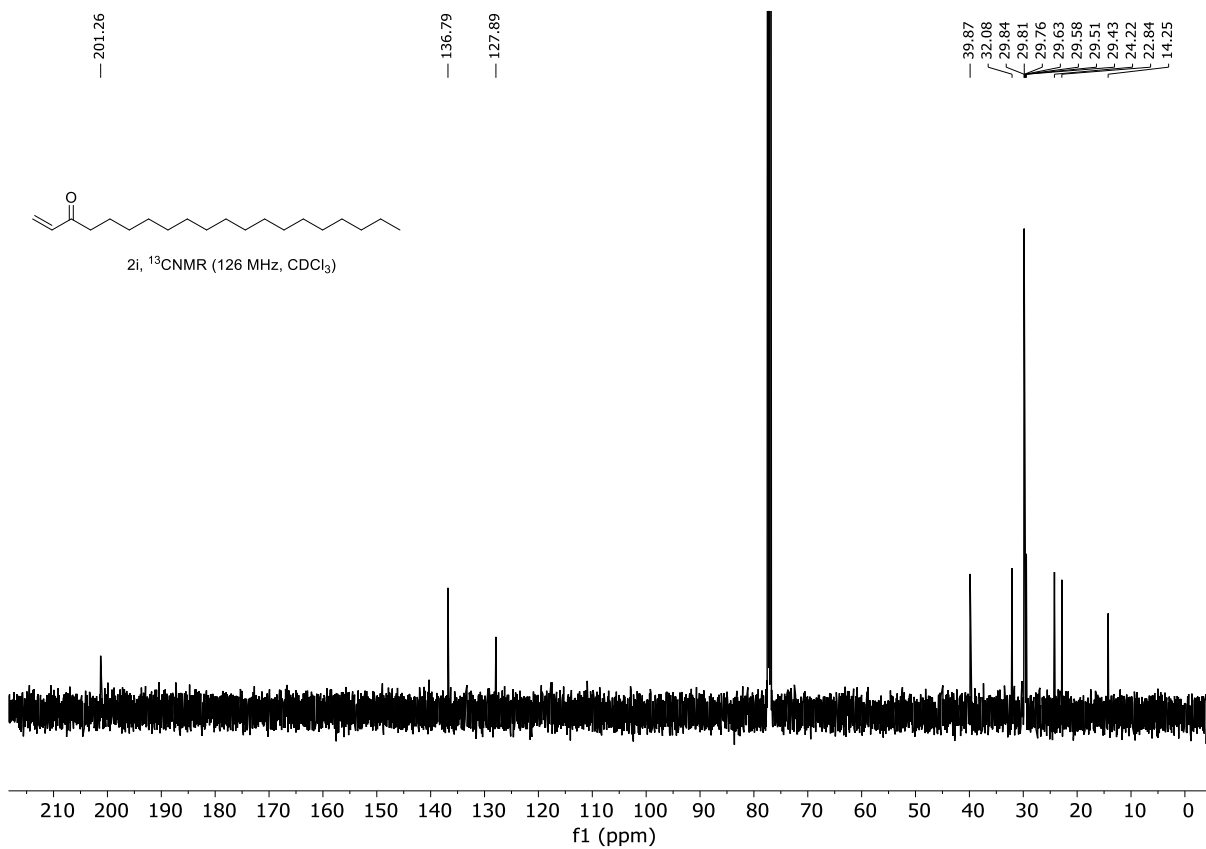
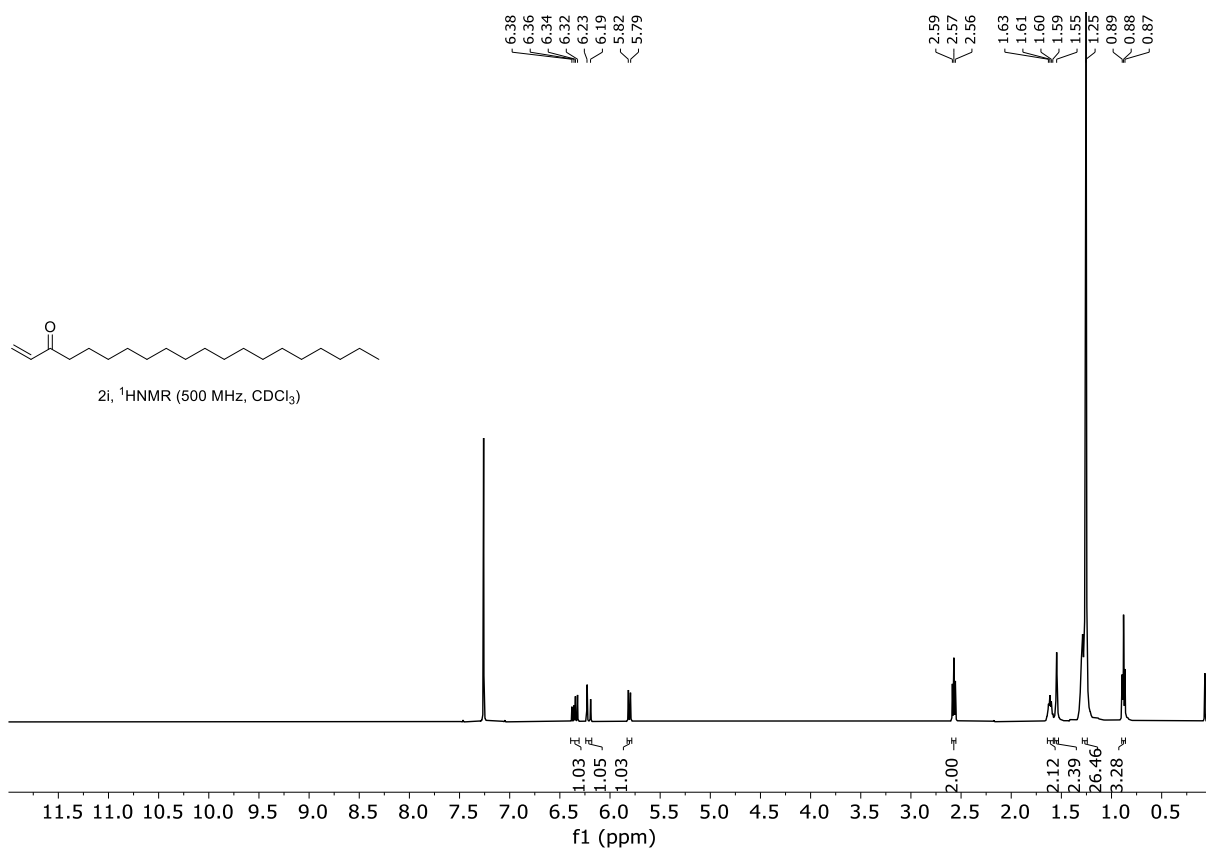


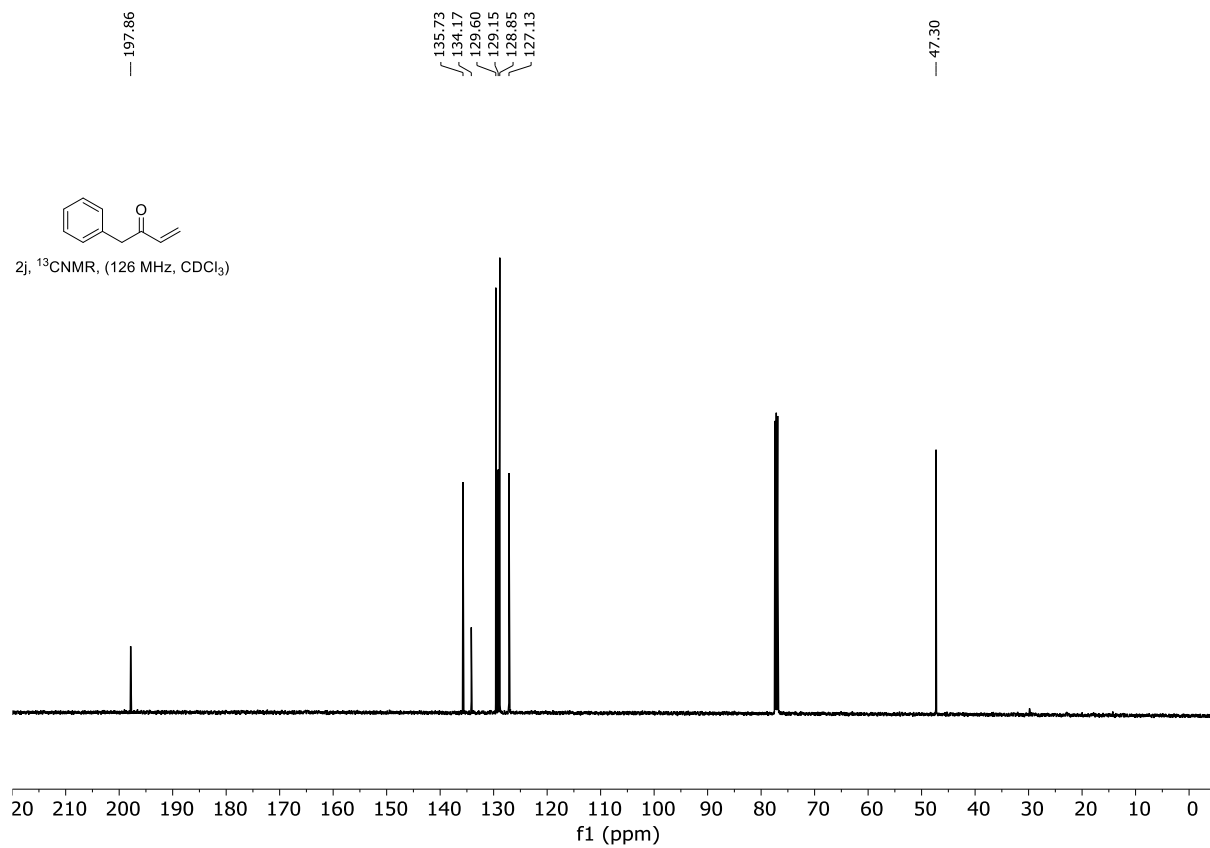
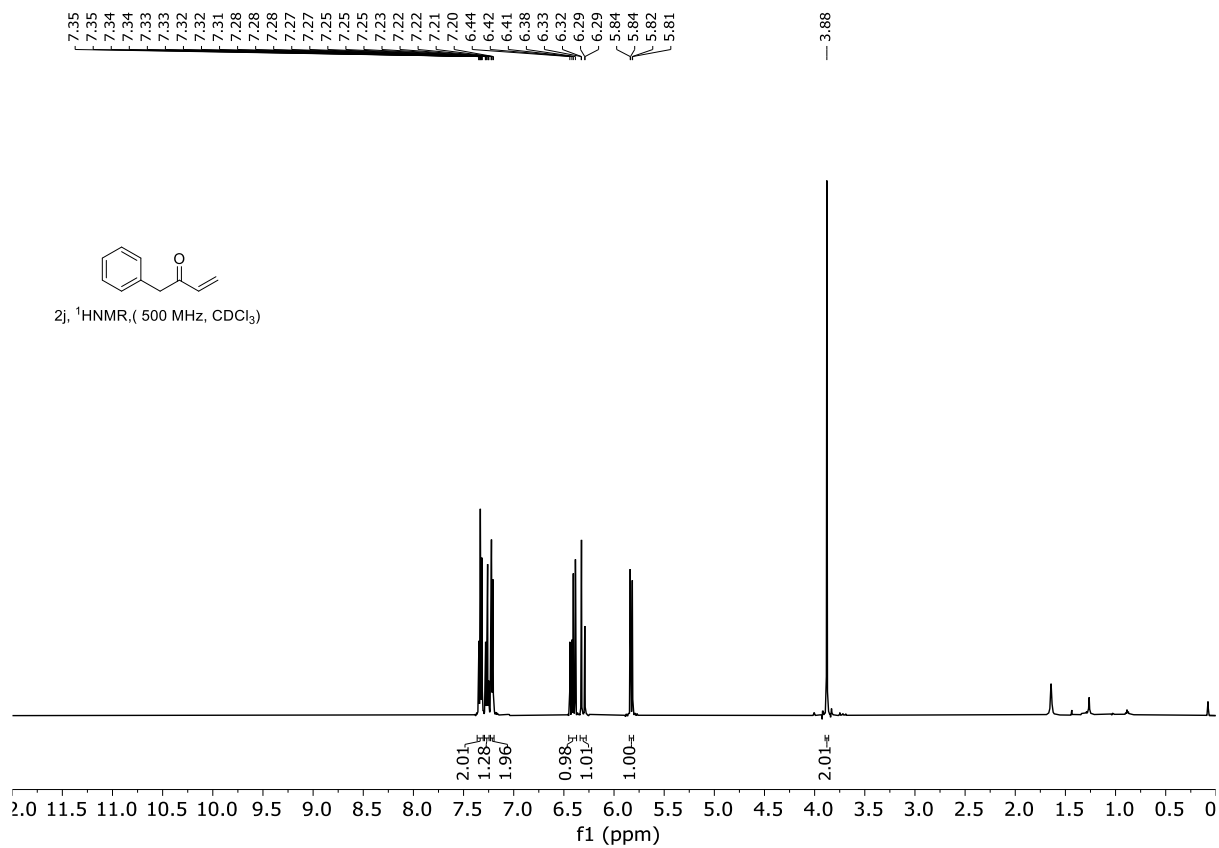
1f, ^{19}F NMR (471 MHz, CDCl_3)

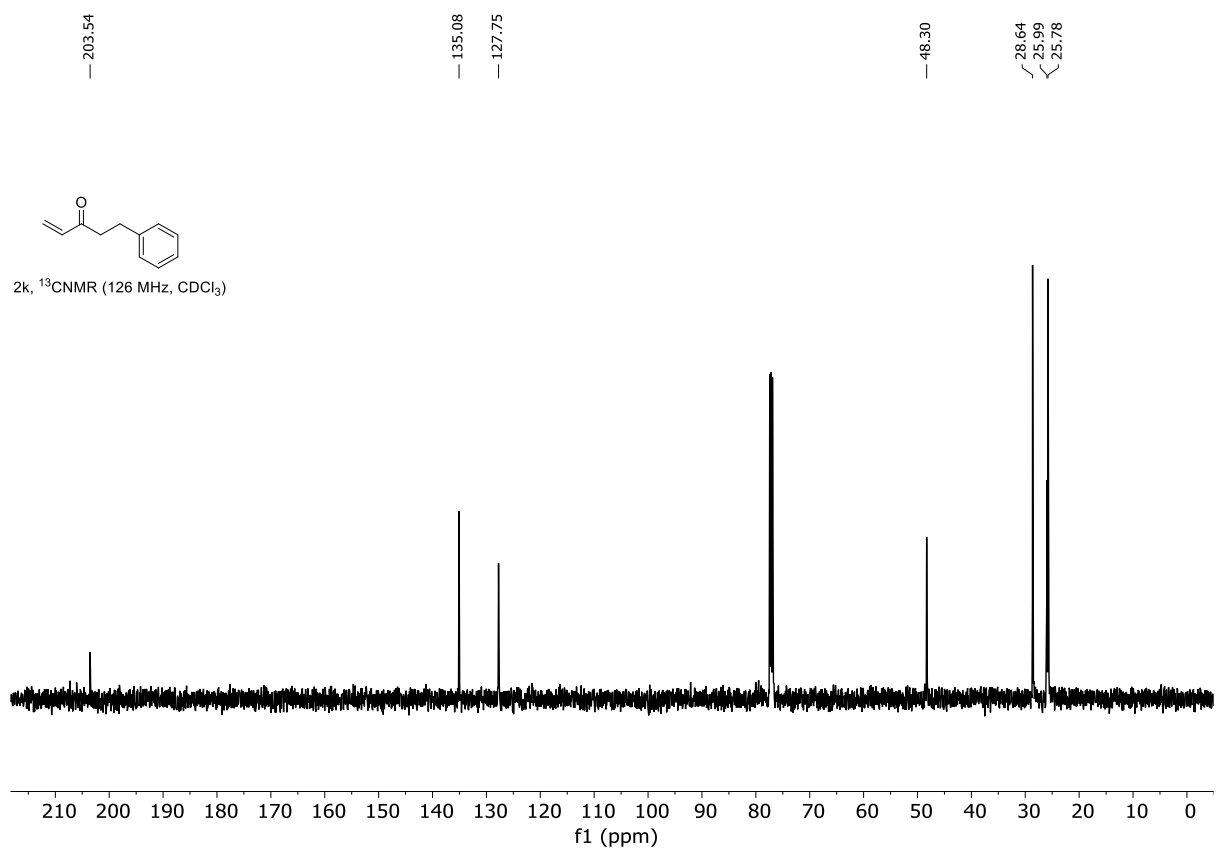
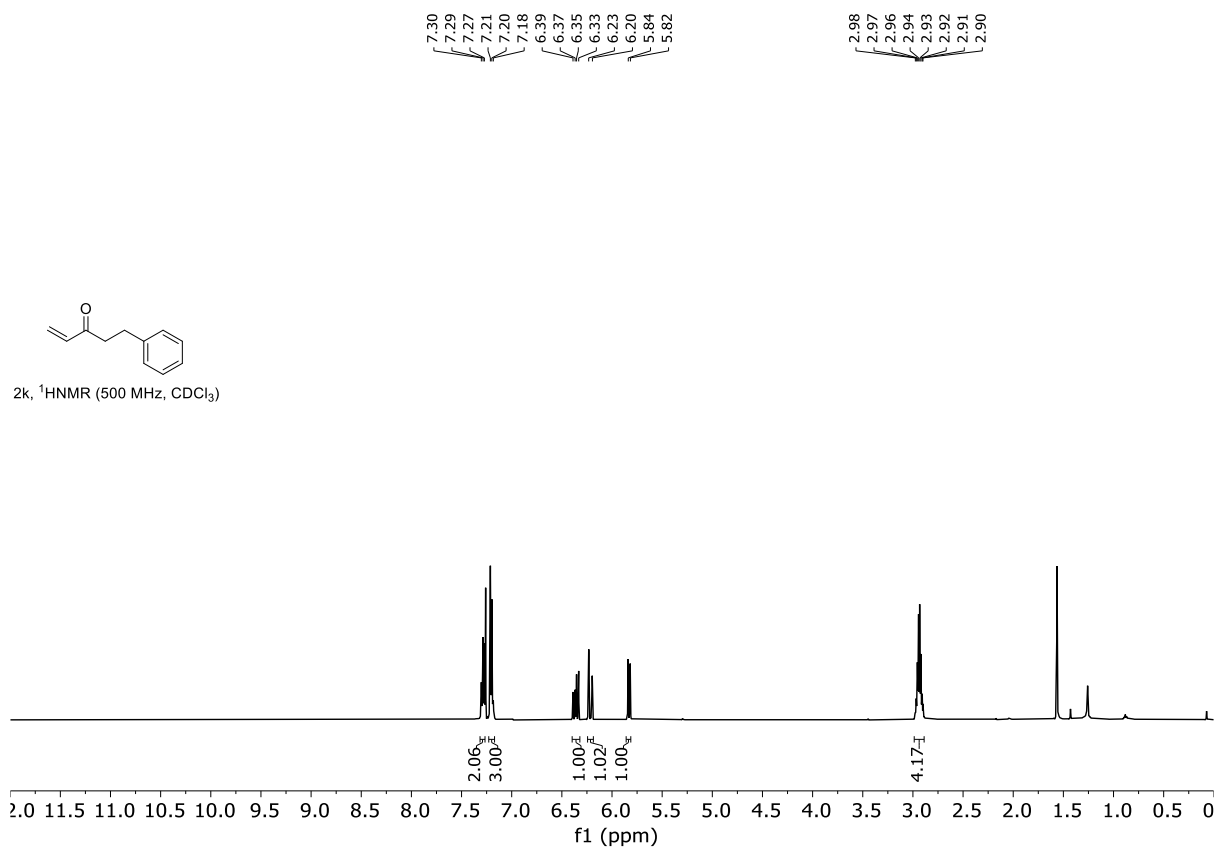


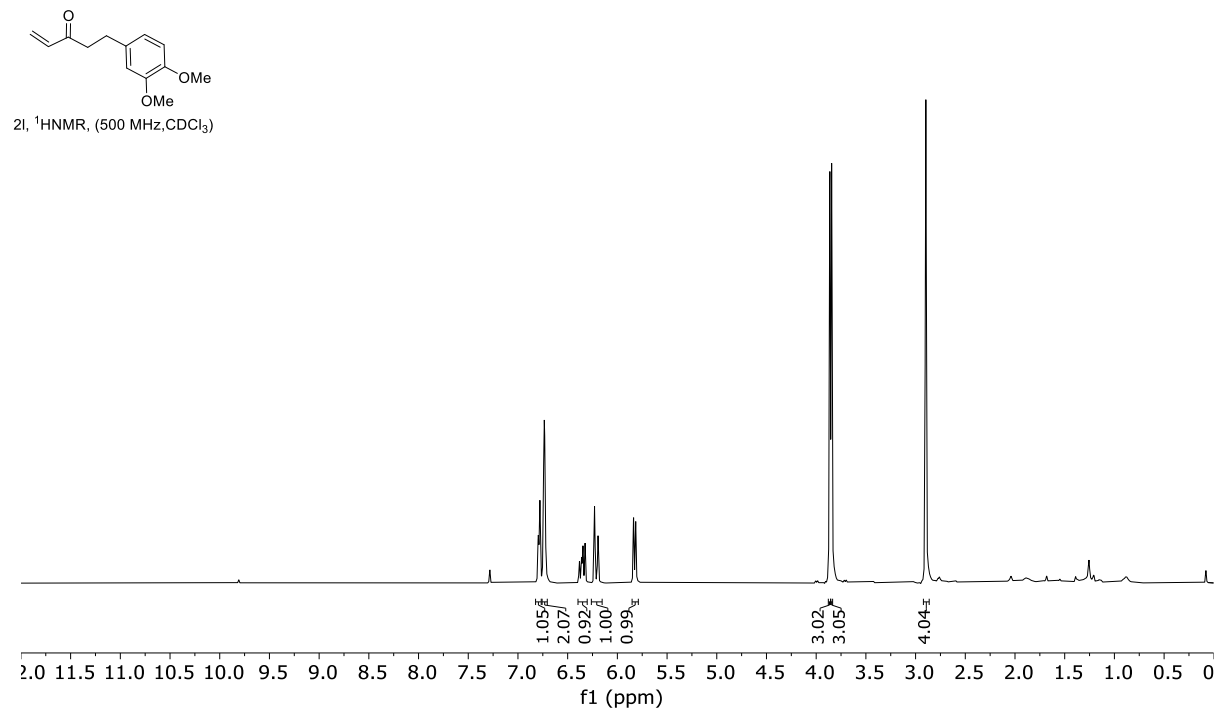




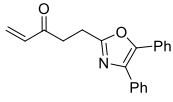




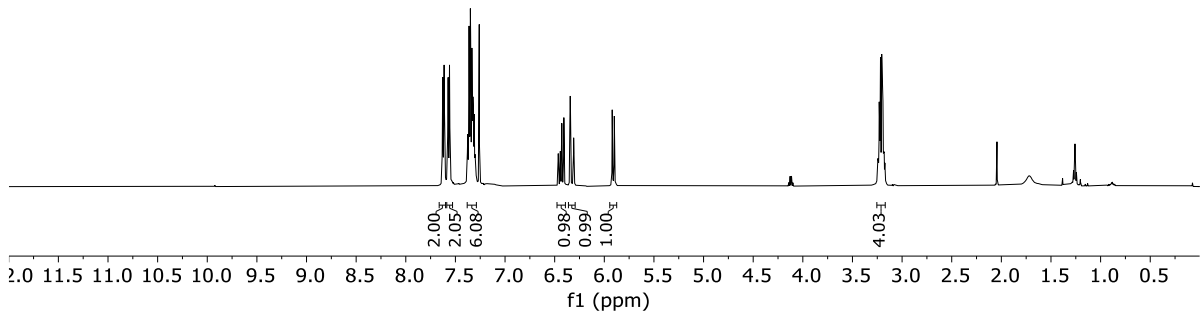




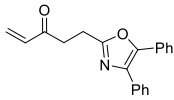
7.63
7.63
7.61
7.61
7.58
7.57
7.56
7.56
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
6.44
6.44
6.41
6.41
6.34
6.34
6.31
6.31
5.82
5.82
5.90
5.90
3.24
3.24
3.23
3.23
3.23
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3.20
3.20
3.19
3.19
3.18
3.18



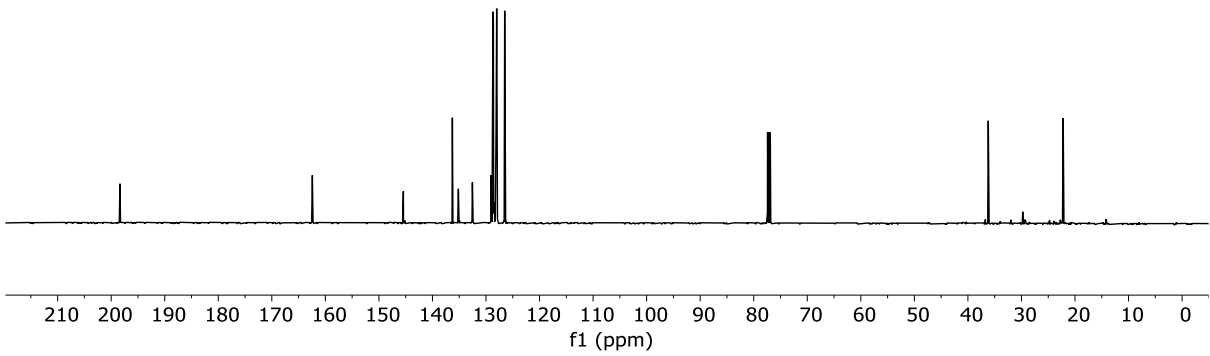
2m, ¹H NMR (500 MHz, CDCl₃)

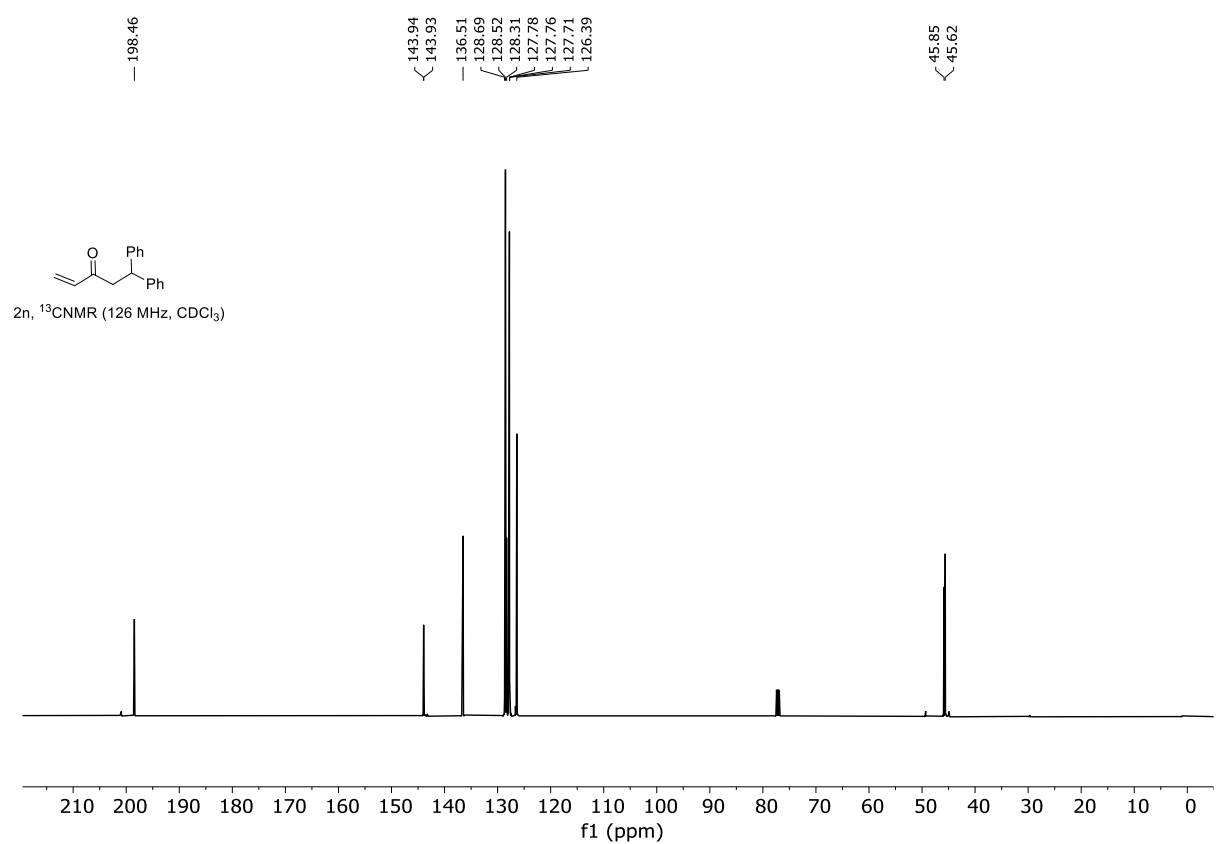
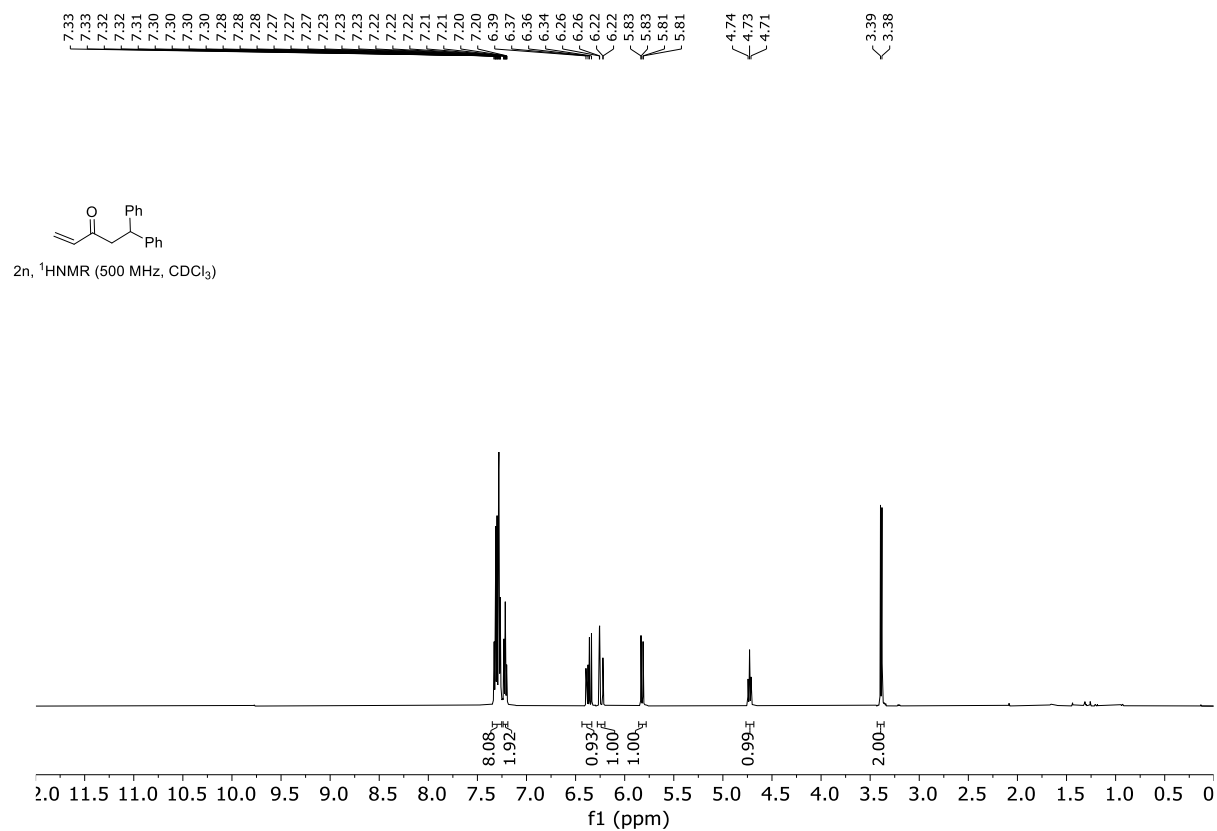


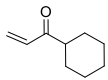
198.36
162.43
145.43
136.28
135.16
132.54
129.04
128.82
128.70
128.62
128.49
128.12
128.01
126.51
36.19
22.21



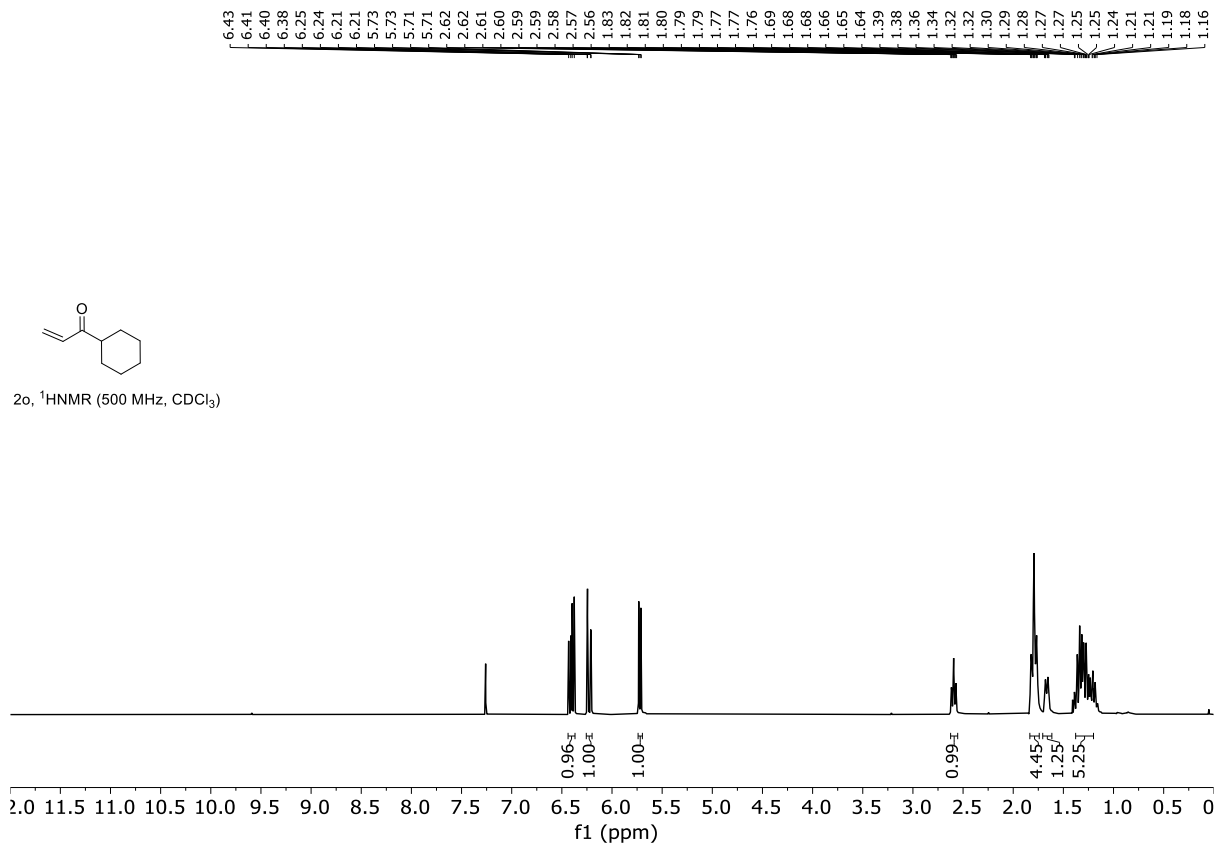
2m, ¹³C NMR (126 MHz, CDCl₃)







2o, ¹HNMR (500 MHz, CDCl₃)



— 203.54

— 135.08

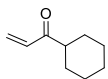
— 127.75

— 48.30

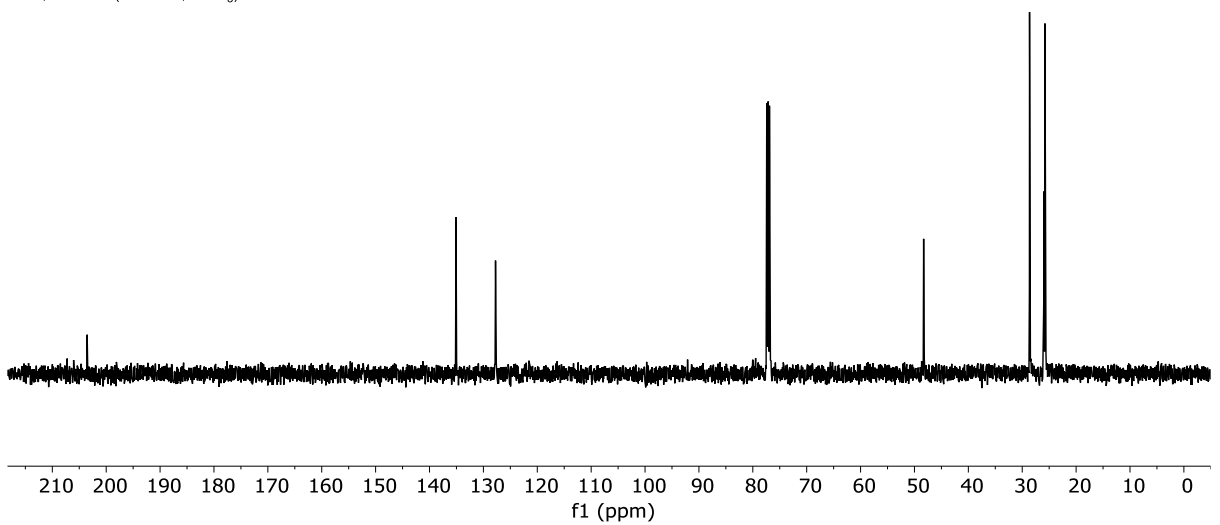
— 28.64

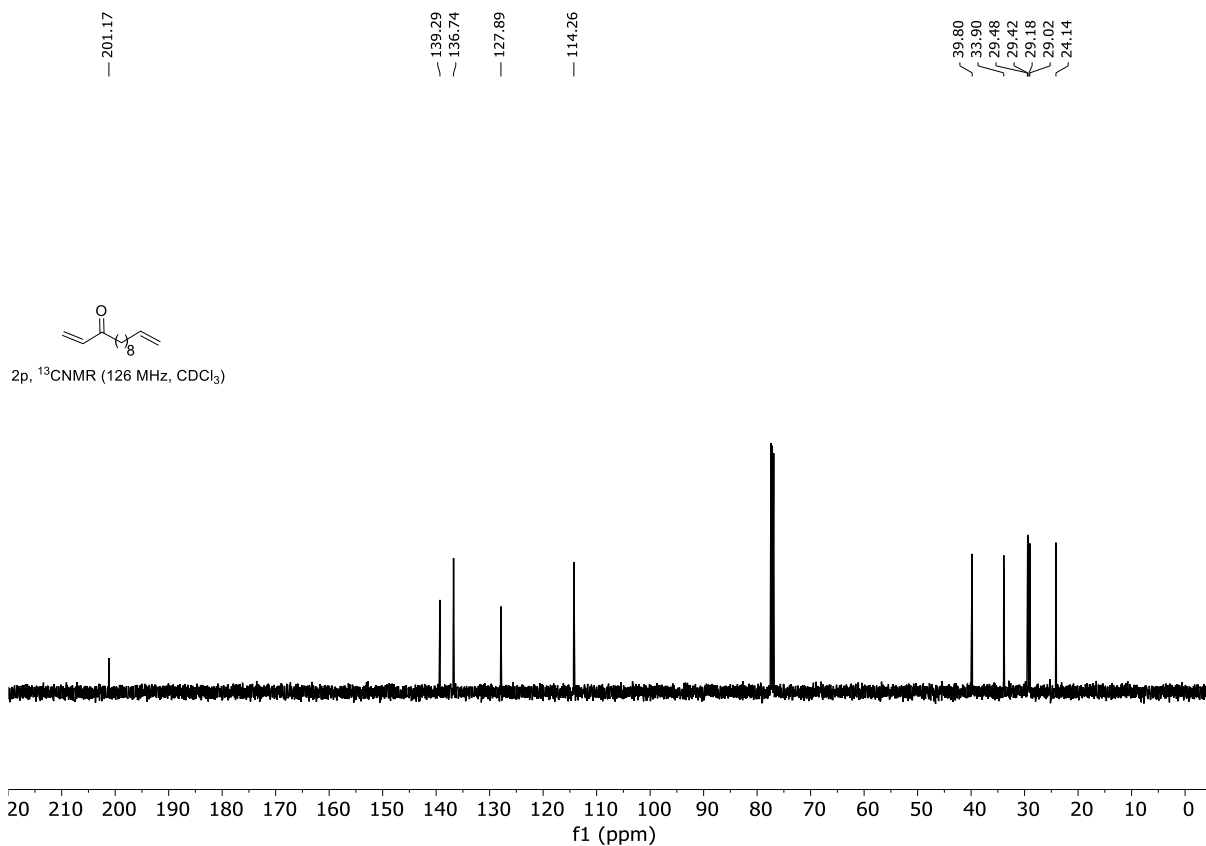
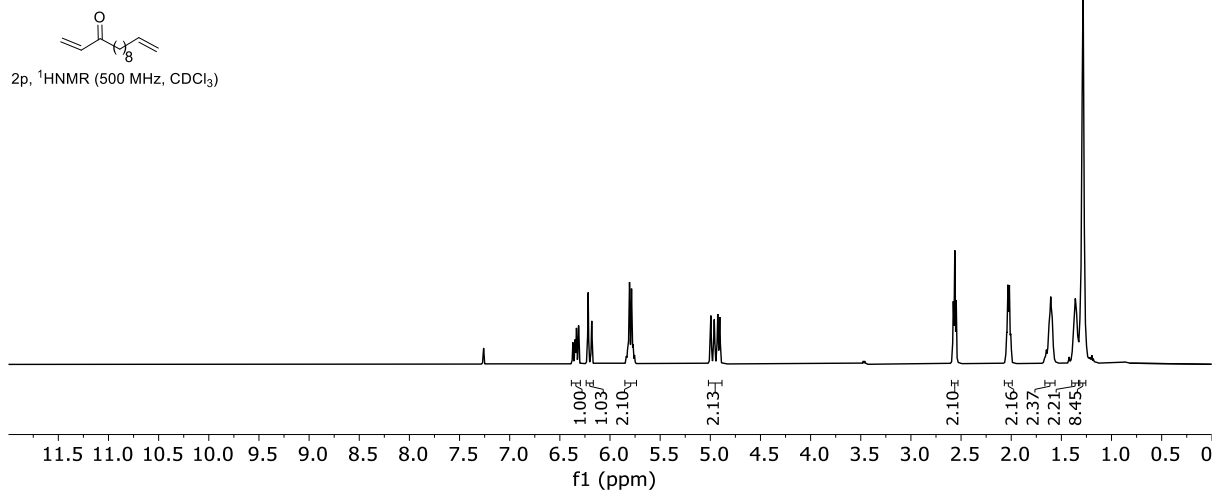
— 25.99

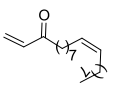
— 25.78

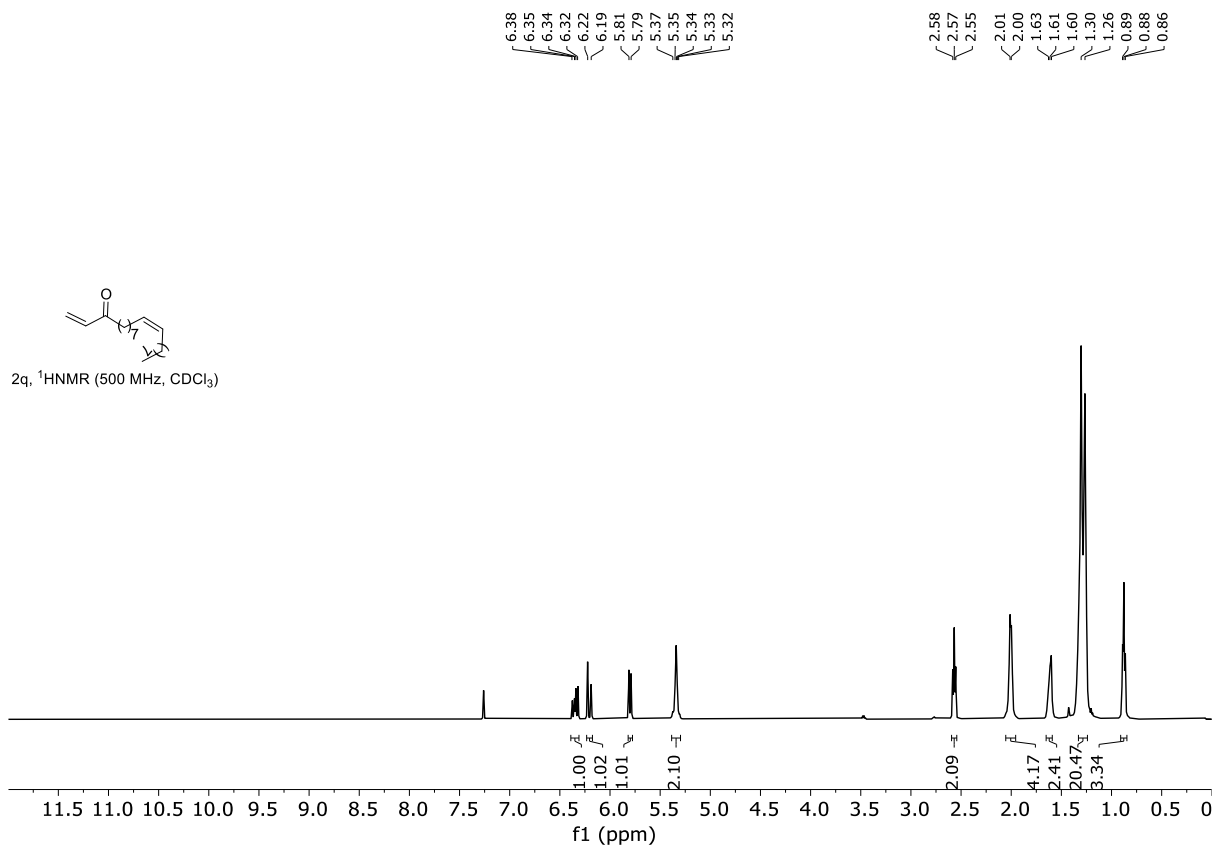


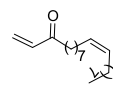
2o, ¹³CNMR (126 MHz, CDCl₃)






 2q, ¹HNMR (500 MHz, CDCl₃)




 2q, ¹³CNMR (126 MHz, CDCl₃)

