SUPPLEMENTARY INFORMATION

Dual-catalytic structural isomerisation as a route to α-arylated ketones

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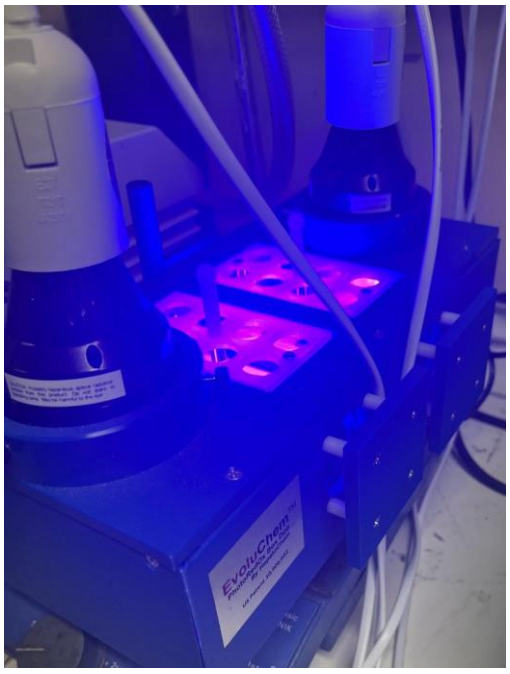
Unless otherwise stated, all reactions were performed with standard Schlenk techniques. All reagents and starting materials were purchased at reagent grade and used as received. Anhydrous solvents were dried using an Innovative Technology PS-MD-5 solvent purification system. Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F254 aluminum plates with unmodified silica and visualized either under UV light or stained with potassium permanganate, vanillin, *p*-anisaldehyde stain or cerium ammonium molybdate (Hanessian's stain). Column chromatography was performed with Merck silica gel 60 (35 – 70 mesh). Preparative TLC was performed using pre-coated TLC plates SIL G-50 UV250 (Layer: 0.50 mm silica gel 60 with fluorescent indicator UV_{250}); detection under UV light.

All ^{1}H, ^{13}C NMR and ^{19}F NMR spectra were recorded at ambient temperature on either Varian V-NMRS 600, Varian V-NMRS 400, Bruker AV-600 or Bruker AV-400 spectrometer. Chemical shifts (δ/ppm) were referenced to the residual solvent peak in ^{1}H (7.26 ppm for $CDCl_3$) and ^{13}C spectra (77.16 ppm for $CDCl_3$). Coupling constants (J) are given in Hz. Signals are described as br = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, p = quintet, h = sextet and m = multiplet.

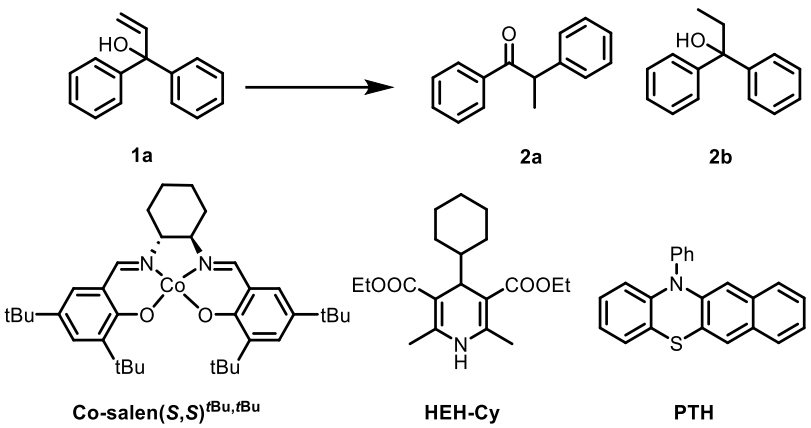
High-resolution mass spectrometry (HRMS) was performed using Thermo Scientific LTQ Orbitrap XL spectrometer. Infrared (IR) spectra were recorded on a Perkin Elmer Spektrum 100 FT-IR spectrometer Spectrum 100 spectrometer with an UATR Diamond/KRS-5 crystal with attenuated total reflectance (ATR) and signals reported as wavenumbers in reciprocal centimeters. HPLC was performed using a Chiralpak IG, (150 x 4.6) mm, 5µ, 97:3 n-hexane/EtOH at 0.5 mL/min flow rate.

All the photochemical reactions were carried out in an EvoluChem™ PhotoRedOxBox Duo equipped with two EvoluChem™ LED 405 PF lamps (λ_{max} = 405 nm, 18 W).



Picture 1. Photo of the set-up

1. Optimization of reaction conditions



Scheme 1. Reaction used for optimization of reaction conditions

The optimizations of the reaction conditions were carried out on 0.1 mmol scale, using **1a** as a starting material. The yields were determined using internal standard $CHBr_3$ or CH_2Br_2 (1.0 eq, 0.1 mmol).

The optimized conditions are as follows:

Allylic alcohol (1.0 eq, 0.1 mmol), photocatalyst (PTH) (1 mol%, 1 µmol, 0.32 mg), Co-salen(*S*,*S*)^{tBu,tBu} (3 mol%, 3 µmol, 1.81 mg), cyclohexane-Hantzsch ester (HEH-Cy) (0.8 eq, 0.08 mmol, 26.8 mg), benzene (0.03 M, 3.3 mL), co-solvent hexafluoro isopropanol (HFIP) (1 M, 9.5 eq, 0.1 mL), additive acetic acid (1.0 eq, 0.1 mmol, 5.72 µL). The reactions were performed under inert atmosphere and by irradiating reaction mixture with 405 nm light (18 W) for 17 h.

1.1. Control reactions

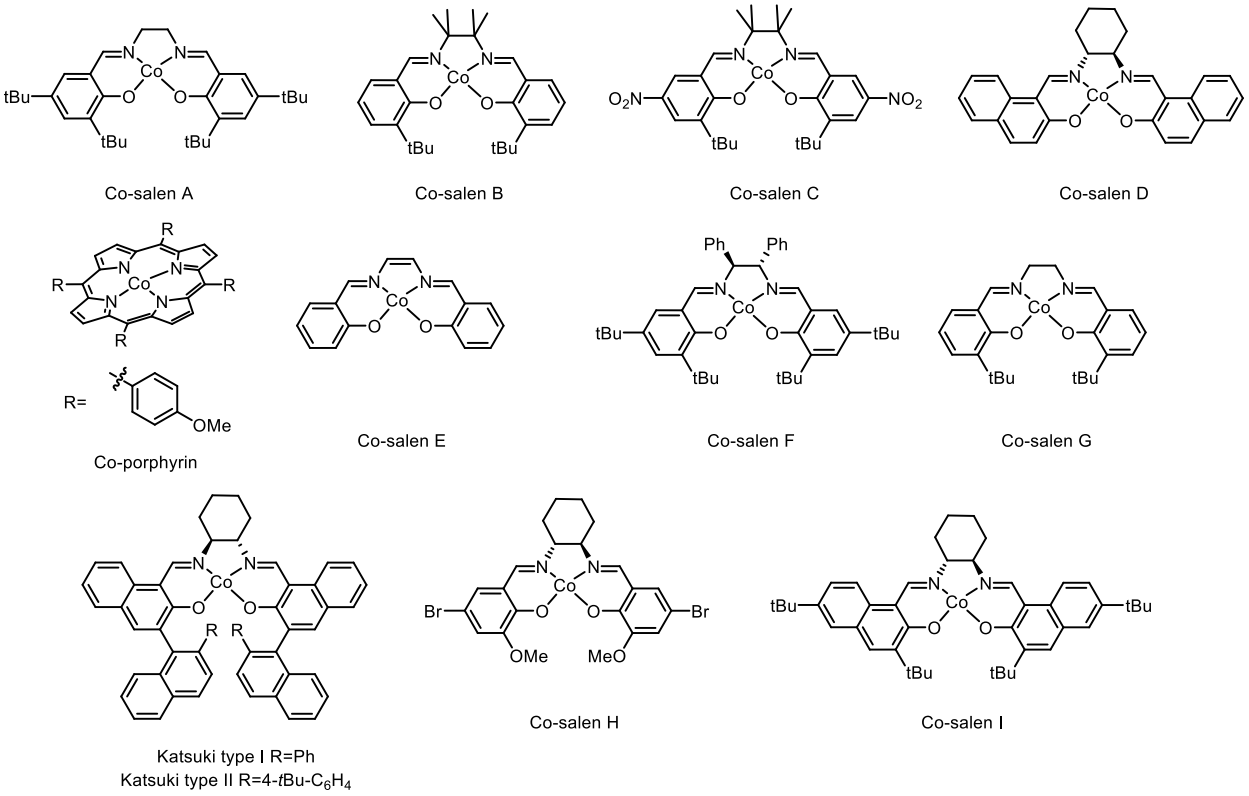
Entry	Variation	2a (%)	2b (%)	RSM (%)
1	None	75 (75)	20	0
2	w/o PTH	0	0	100
3	w/o Co	0	0	100
4	w/o HEH-Cy	0	0	97
5	w/o AcOH	33	20	40
6	w/o HFIP	40	14	36
7	w/o light	0	0	81
8	Under air	0	0	72

1.2. Modifications of photocatalyst

Entry	Photocatalyst (1 mol%) (Irradiation wavelength)	2a (%)	2b (%)	RSM (%)
1	4CzIPN (450 nm)	64	30	X
2	$Ir(pCF_3ppy)_3$ (405 nm)	76	22	X
3	MesAcr (450 nm)	59	11	25

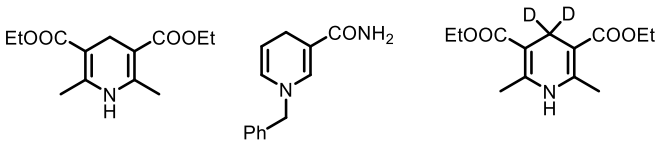
4	Ir(dtbbpy)(ppy)$_2$ (405 nm)	83	17	X

1.3. Modifications of Co-source



Entry	Co-source (3 mol%)	2a (%)	2b (%)	RSM (%)
1	A	0	0	85
2	B	38	16	28
3	C	55	25	0
4	D	31	0	46
5	Co-porphyrin	0	0	100
6	E	17	7	62
7	F	20	0	50
8	G	25	5	67
9	Katsuki I	0	0	83
10	Katsuki II	0	0	85
11	H	27	5	46
12	I	57	17	0

1.4. Modifications of Hantzsch ester



HEH BNAD HEH-D4
D incorporation >95%

Entry	Hantzsch ester or BNAD (0.8 eq)	2a (%)	2b (%)	RSM (%)
1	HEH	50	36	0
2	BNAD	16	0	84
3	HEH-D4	75	26	0

Loadings of HEH-Cy

Entry	HEH-Cy (x eq)	2a (%)	2b (%)	RSM (%)
1	0.2	0	0	100
2	0.6	62	15	20
3	1	62	21	0

1.5. Modifications of solvents

Entry	Solvent (0.03 M)	2a (%)	2b (%)	RSM (%)
1	Dioxane	42	17	27
2	THF	0	0	92
3	MeCN	0	0	96
4	Et_2O	61	24	5
5	DMF	26	17	36
6	DMSO	15	0	38
7	Acetone	57	0	29
8	DCM	0	0	55

1.6. Modifications of concentration

Entry	PhH [M]	2a (%)	2b (%)	RSM (%)
1	0.06	70	20	0
2	0.015	70	25	0

1.7. Modifications of co-solvents

Entry	Co-solvent (1M)	Dynamic viscosity [mPa*s] at 20°C	2a (Isolated yield) (%)	2b (%)	RSM (%)	*e.r* of 2a
1	HFIP	1.65	75 (75)	20	0	54:46
2	1-octanol	9.0	72 (60)	0	0	50:50
3	Cyclohexanone	2.2	58 (50)	42	0	50:50
4	Dimethoxyethane (glyme)	0.42	68 (57)	32	0	50:50

1.8. Modifications of additives

Unless otherwise stated, 1.0 eq of additive was used. Reactions were carried out in the absence of acetic acid.

Entry	Additive	2a (%)	2b (%)	RSM (%)
1	Pyridine	46	26	26
2	Piperidine	52	12	28
3	Piperidine (9.5 eq) (Piperidine: HFIP=1:1)	19	24	50
4	Triphenyl acetic acid	70	24	0
5	*p*-Fluorobenzoic acid	47	12	41

2. Substrate scope

Unless otherwise stated, the substrate scope was carried out on 0.18 mmol scale, under optimised reaction conditions. The ^{1}H NMR yield was determined by using 1 eq (0.18 mmol) of the internal standard ($CHBr_3$ or CH_2Br_2).

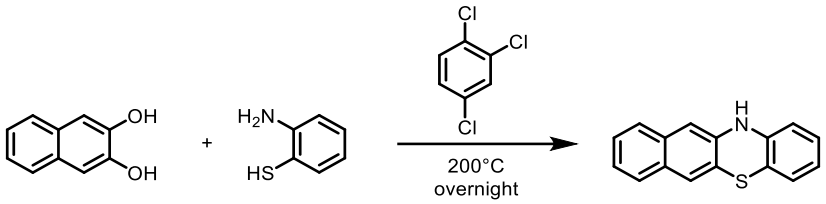
Entry	a (%)	b (%)	RSM (%)	Isolated yield of a (%)
2a[a]	75	20	0	75
2b[a]	76	8	0	67
2c	66	17	0	66
2d	70	0	0	54
2e	80	0	0	68
2f	75	23	0	51
2g	68	25	5	40
2h, 2h’	56	14	0	51
2i	60	0	0	59
2j	89	9	0	85
2k, 2k’	74	0	0	53
2l, 2l’[a]	70	0	0	70
2m	80	14	0	77
2n	63	25	0	61
2o	72	27	0	49
2p[a]	Not determined	0	0	82
2q[a]	44	11	0	44
2r	80	20	0	63
2s[a]	57	0	0	57
2t[a]	62	37	0	41
2u	83	0	0	61
2v, 2v’[a]	63	0	10	47

[a]0.1 mmol scale

3. General procedures

3.1. Preparation of PTH

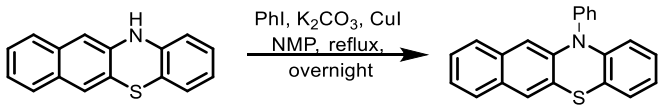
Step 1: Synthesis of benzo[*b*]phenothiazine



A mixture of 2,3-dihydroxynapthalene (1.0 eq, 50.0 mmol), 2-aminothiophenol (1.0 eq, 50.0 mmol) and 1,2,4-trichlorobenzene (25 mL) were placed in an oven-dried round-bottom flask and fitted with a magnetic stirrer. The round-bottom flask was placed in a sand bath, the reaction mixture was heated to 200°C and maintained at that temperature overnight. On cooling, the product crystallized from the reaction mixture. The crude was filtered by vacuum filtration. The crystals were washed with pentane, followed by washing with a minimum amount of hot ethanol. The product benzo[*b*]phenothiazine was obtained as yellow-green powder in 6% yield (800.3 mg, 3.21 mmol).

^{1}H NMR (600 MHz, DMSO) δ 8.96 (s, 1H), 7.59 – 7.54 (m, 2H), 7.49 (s, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.98 – 6.95 (m, 2H), 6.78 – 6.74 (m, 2H).
^{13}C NMR (151 MHz, DMSO) δ 140.6, 139.1, 133.3, 129.7, 127.5, 126.5, 126.2, 126.1, 125.9, 124.0, 123.5, 121.3, 119.9, 115.7, 114.6, 107.9.
These data are in agreement with those reported previously. [1]

Step 2: Synthesis of 12-Phenyl-12*H*-benzo[*b*]phenothiazine



A mixture of 12H-benzo[*b*]phenothiazine (1.0 eq, 3.21 mmol), iodobenzene (1.5 eq, 4.82 mmol), K_2CO_3 (1.5 eq, 4.82 mmol) and CuI (10 mol %, 0.321 mmol) in N-methylpyrrolidone (3.0 mL) was refluxed overnight. The mixture was cooled to room temperature, the resulting black viscous suspension was diluted with distilled water (15 mL). The crude was extracted with CH_2Cl_2 (3 x 15 mL), the combined organic layer was washed with brine (30 mL), dried with $MgSO_4$, and concentrated *in vacuo.* The crude product was purified by flash chromatography (SiO_2, Pentane/EtOAc, 95:5). It was isolated as a green solid with 41 % yield (430.7 mg, 1.32 mmol).

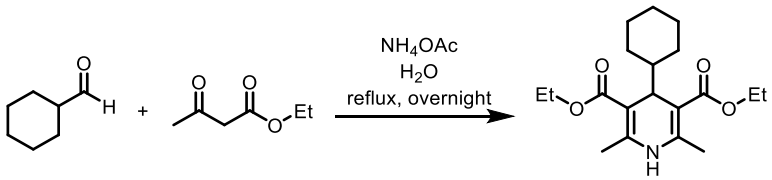
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.58 – 7.51 (m, 2H), 7.48 – 7.42 (m, 3H), 7.32 – 7.27 (m, 1H), 7.24 – 7.16 (m, 2H), 7.06 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.90 – 6.78 (m, 2H), 6.37 (s, 1H), 6.19 (dd, *J* = 8.1, 1.3 Hz, 1H)
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 141.9, 141.2, 133.2, 131.2, 130.2, 128.7, 126.9, 126.6, 126.3, 126.1, 124.5, 124.3, 122.3, 122.1, 119.5, 111.2.

These data are in agreement with those reported previously.[2]

Data for the photocatalyst: E_{ox}^{*}= - 1.97 V; E_{ox}= + 0.85 V. [3]

3.2. Preparation of Hantzsch esters

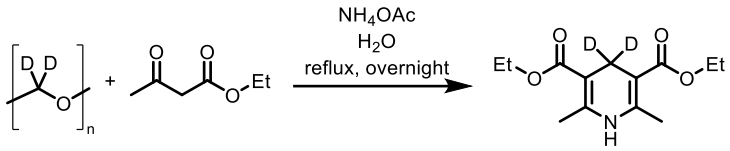
HEH-Cy (Diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate)



A mixture of cyclohexane carbaldehyde (1.0 eq, 10.0 mmol), ethyl acetoacetate (4.0 eq, 40.0 mmol), and ammonium acetate (2.0 eq, 20.0 mmol) in 20 mL of distilled water was vigorously stirred at refluxing temperature for 17 h. Then, the reaction mixture was allowed to cool down to room temperature. The crude reaction mixture was extracted three times with dichloromethane and the combined organic phase was washed with brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Then, the desired product was obtained by crystallization with ethanol. HEH-Cy is isolated as a yellow solid in 47% yield (1.59 g, 4.74 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.49 (s, 1H), 4.25 – 4.11 (m, 4H), 3.92 (d, *J* = 5.7 Hz, 1H), 2.30 (s, 6H), 1.65 (s, 2H), 1.55 – 1.48 (m, 2H), 1.30 (dt, *J* = 7.5, 6.7 Hz, 6H), 1.25 – 1.18 (m, 1H), 1.11 – 1.02 (m, 3H), 0.99 – 0.85 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 144.5, 102.2, 59.7, 45.9, 38.6, 29.0,26.9, 26.8, 19.6, 14.5.
HRMS (ESI): calculated for [$C_{19}H_{29}NO_4Na$]: 358.1989, found: 358.1986.
IR (neat): ν 3337, 2920, 1692, 1647, 1483, 1295, 1210, 1118, 1019, 1048, 741 cm^{-1}.

HEH-D4 (Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-4,4-d_2)

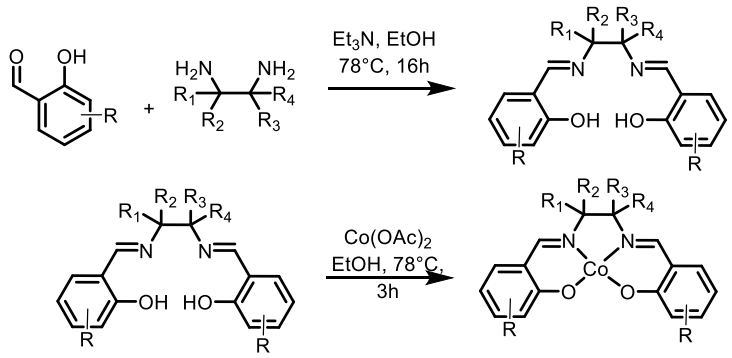


A mixture of paraformaldehyde-d2 (1.0 eq, 3.0 mmol), ethyl acetoacetate (4.0 eq, 12.0 mmol) and ammonium acetate (2.0 eq, 6.0 mmol) in 6 mL of distilled water was vigorously stirred at refluxing temperature for 17 h. Then, the reaction mixture was allowed to cool down to room temperature. The crude reaction mixture was extracted three times with dichloromethane and the organic phase was washed with brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The desired product was obtained on crystallization with ethanol. Isolated as a bright yellow solid in 53% yield (406 mg, 1.59 mmol). Deuterium incorporation: >95%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.09 (s, 1H), 4.17 (d, *J* = 7.1 Hz, 4H), 2.19 (s, 6H), 1.28 (d, *J* = 7.1 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 144.9, 99.6, 59.8, 19.4, 14.6.

These data agree with those reported previously. [4]

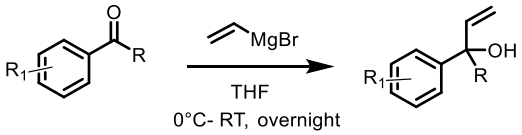
3.3. Preparation of Co-salens[1]



The aldehyde (2.0 eq, 6.0 mmol) and diamine (1.0 eq, 3.0 mmol) were placed in a round bottom flask and the atmosphere was exchanged with Argon. Dry ethanol (60 mL) and triethylamine (5.0 eq, 15.0 mmol) were added to the flask and the mixture was left to stir under reflux for 16 h. Then, water was added, and the yellow precipitate was washed with cold EtOH: H_2O (1:1) mixture. The formed ligand was dried and used in the next step without further purification.

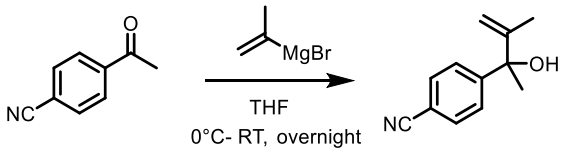
The crude salen ligand (1.0 eq) was suspended in dry ethanol (0.1 M) and it was refluxed under inert atmosphere. After 10 minutes, $Co(OAc)_2$ (2.0 eq) was added to the solution and the mixture was left stirring at reflux during 3h. Then, it was allowed to cool down to room temperature, and the red precipitate was filtered, washed with cold ethanol, and dried.

3.4. Preparation of starting materials



The ketone (1.0 eq, 3.0 mmol) was added to an oven-dried three-neck round-bottom flask. It was dissolved in anhydrous THF (10 mL), and the solution was allowed to stir at 0°C for 10 minutes. To the cold solution, vinyl magnesium bromide solution (1 M in THF, 2.0 eq, 6 mmol, 6 mL) was added dropwise and the reaction mixture was allowed to reach room temperature and left to stir overnight. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl. The crude mixture was extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with brine (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, Pentane/EtOAc).

3.5. Preparation of compound 1u



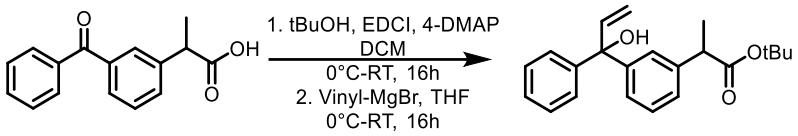
[1] Katsuki type Co-salen ligands were a donation from the group of Prof. Dr. Johannes M. Wahl (Johannes Gutenberg- Universität Mainz)

Mg turnings (2.0 eq, 6 mmol, 144 mg) were placed in Schlenk flask and the atmosphere was exchanged with argon. To this, I_2 (one crystal) was added, and the mixture was suspended in dry THF (6 mL). It was left to stir vigorously at room temperature until the color turned bright yellow. To this, 2-bromopropene was added (2.0 eq, 6 mmol, 0.54 mL). It was heated at 60°C for 1 h and left to cool down to room temperature before it was used in the next stage.

4-cyanoacetophenone (1.0 eq, 3 mmol, 435.5 mg) was put in another Schlenk flask and the atmosphere was exchanged with argon. The ketone was dissolved in dry THF (5 mL). To this flask, freshly prepared Grignard reagent was added dropwise at 0°C, and it was left to warm up to room temperature and left to stir overnight.

The reaction mixture was quenched with saturated aqueous solution of NH_4Cl. The crude mixture was extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with brine (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, Pentane/EtOAc). The compound was isolated as a white solid in 17% yield (96.9 mg, 0.52 mmol).

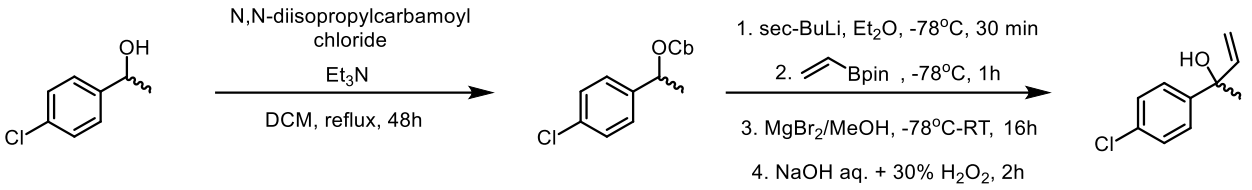
3.6. Preparation of compound 1v



Ketoprofen (1.0 eq, 4 mmol, 1.017 g), EDCI (1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide) (1.1 eq, 4.4 mmol, 832 mg) and 4-DMAP (4-dimethylamino pyridine) (0.5 eq, 2 mmol, 244.34 mg) were put in a round bottom flask and the atmosphere was exchanged with Argon. The mixture was dissolved in dry DCM (15 mL). Then, tert-butyl alcohol (1.13 eq, 4.52 mmol, 0.43 mL) was added at 0°C. The reaction mixture was allowed to warm up to room temperature and left to stir overnight. Then, the reaction was quenched with saturated aqueous solution of $NaHCO_3$, and it was extracted 3x with DCM. Combined organic layers were washed with brine, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure.

The obtained crude ester was used for the next step without purification. The obtained ester was put in round bottom flask, it was dissolved in dry THF (10 mL) under Argon atmosphere. The reaction mixture was cooled down to 0°C, and vinyl-MgBr (2.5 eq, 10 mmol, 10 mL) was added dropwise. The mixture was allowed to warm up to room temperature and left to stir overnight. Then, the reaction was quenched with saturated aqueous solution of NH_4Cl, it was extracted 3x with EtOAc, combined organic layers were washed with brine, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The product was purified by column chromatography using pentane: acetone as eluent (9:1). The compound was isolated as a white solid and the isolated yield over two steps is 31% (418.9 mg, 1.24 mmol).

3.7. General procedure for preparation of enantiomerically enriched compound



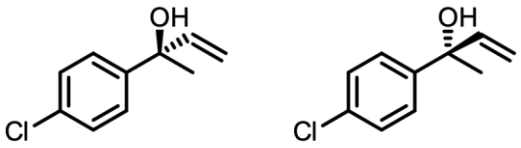
Step 1:

A solution containing enantiomerically enriched alcohol (1.0 eq), *N, N*-diisopropylcarbamoyl chloride (1.2 eq), and triethylamine (1.3 eq) in anhydrous dichloromethane (1.3 M) was refluxed for 48 h. Subsequently, the reaction mixture was poured into water and extracted with dichloromethane. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude product was used for further reactions.

Step 2:

s-Butyllithium (1.3 eq; 1.4 M solution in cyclohexane) was added dropwise to a stirred solution of carbamate (1.0 eq.) in anhydrous, degassed diethyl ether at -78°C under argon atmosphere. The resulting yellow, homogeneous solution was stirred for 30 minutes at -78°C. Neat vinylboronic acid pinacol ester (1.5 eq) was then added dropwise. The mixture was stirred for 1h at -78°C, and then magnesium bromide[2] (1.3 eq; 1.0 M solution in MeOH) was added dropwise. The reaction was stirred for an additional 15 minutes at -78°C, then it was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding a mixture of ice-cold 3.0 M aqueous sodium hydroxide (2 mL per 1 mmol of carbamate) and a cold 30% aqueous hydrogen peroxide solution (1.4 mL per 1 mmol of carbamate) and stirred at room temperature for 2 hours (pressure build-up is possible, these steps should be done with care). The reaction mixture was then partitioned between water and diethyl ether, and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to obtain the crude product. Purification was performed by flash column chromatography using pentane: EtOAc = 94:6.

Two enantiomers are prepared according to the above procedure: **1n-*R* ((*R*)-2-(4-chlorophenyl)but-3-en-2-ol)** and **1n-*S* ((*S*)-2-(4-chlorophenyl)but-3-en-2-ol).**

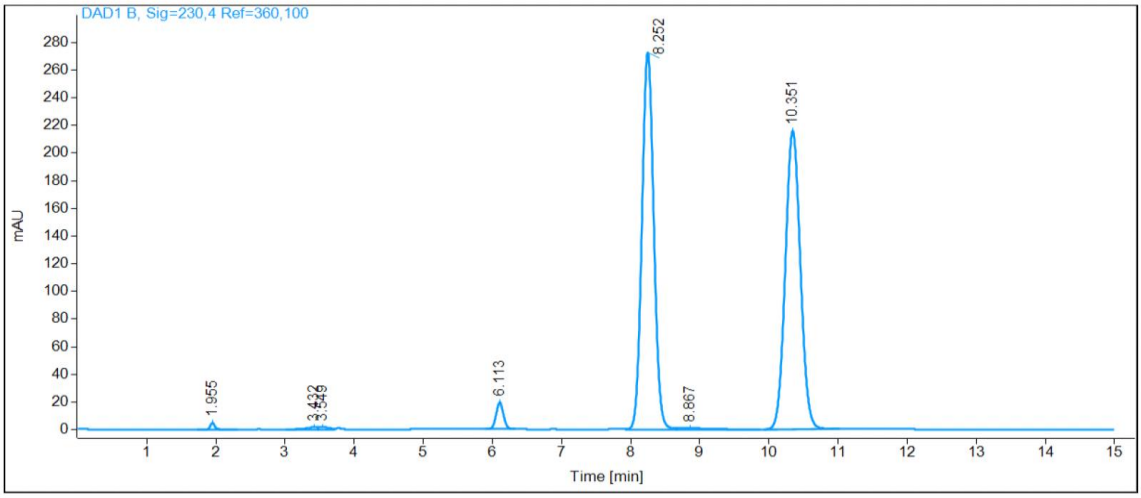


1n-*R* 1n-*S*

[2] After purchasing the magnesium bromide solid from a commercial vendor, it was necessary to dry it overnight under vacuum and at a high temperature to eliminate any moisture.

The enantiomeric ratio was determined by chiral high-performance liquid chromatography (HPLC) using the racemic product (**1n**) prepared according to the procedure described in section 3.4 as reference material.

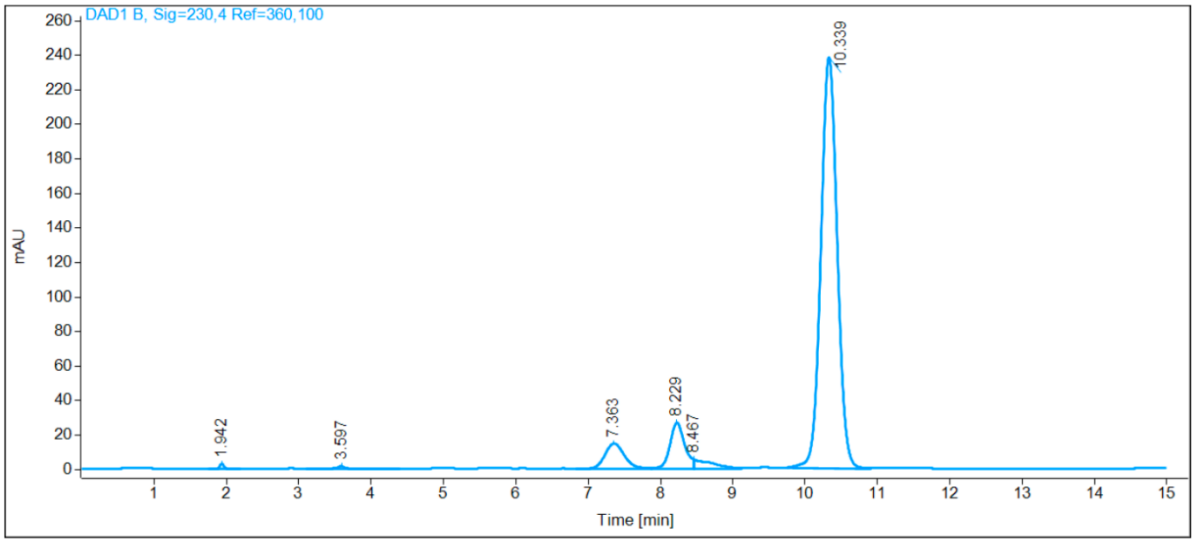
The chiral HPLC conditions were as follows: Chiralpak IG column, dimensions 150 x 4.6 mm, particle size 5µ, mobile phase 97:3 n-hexane/ethyl alcohol (EtOH) at a flow rate of 0.5 mL/min.



Name	NV RG 10-1 rac				
RT [min]	Type	Area%	Area	Height	Width [min]
1.96	BB	0.36	24.23	4.84	0.08
3.43	BV	0.27	18.21	1.55	0.17
3.55	VV	0.26	17.24	1.59	0.16
6.11	VB	2.25	151.48	19.62	0.12
8.25	VV	48.11	3241.28	272.77	0.19
8.87	VB	0.45	30.47	1.29	0.35
10.35	MM	48.31	3255.02	215.80	0.25
	Sum	100.00	6737.92		

1n-*R:* ((*R*)-2-(4-chlorophenyl)but-3-en-2-ol)

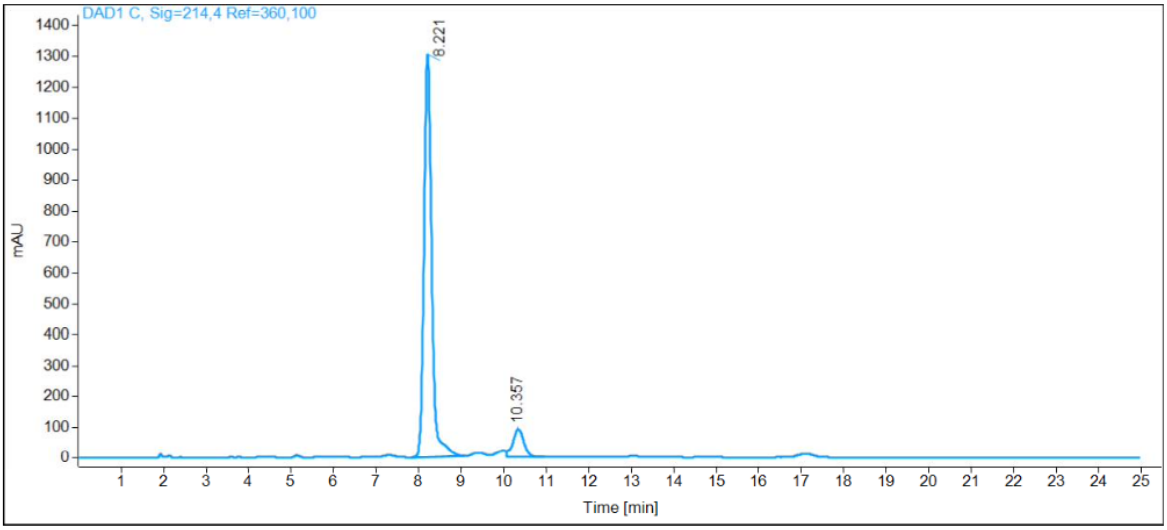
Reaction was performed on 2.00 mmol scale. The product appeared as a yellow oil (114.7 mg, 0.62 mmol, 31%). The retention times (t_R) for the (R)-enantiomer (major) and (S)-enantiomer (minor) were 10.34 min and 8.23 min, respectively, with an enantiomeric ratio (*e.r.*) of 91:9.



Name	NV 219				
RT [min]	Type	Area%	Area	Height	Width [min]
1.94	BB	0.26	11.92	2.95	0.06
3.60	BB	0.31	13.97	1.47	0.13
7.36	BV	6.04	272.71	14.63	0.29
8.23	MF	8.39	378.94	26.89	0.23
8.47	FM	2.07	93.40	5.28	0.29
10.34	MM	82.93	3745.95	238.71	0.26
	Sum	100.00	4516.88		

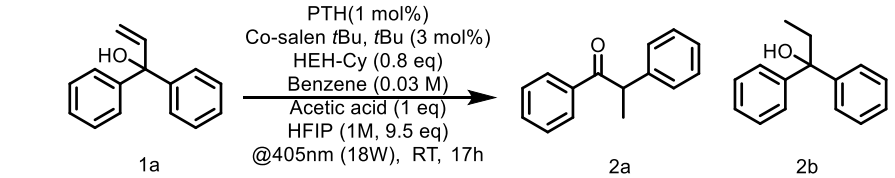
1n-*S*: (*S*)-2-(4-chlorophenyl)but-3-en-2-ol

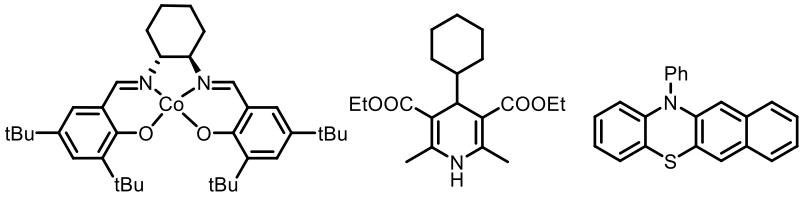
Reaction performed on 5.00 mmol scale. The product appeared as a colorless oil (229.6 mg, 1.25 mmol, 25%). The retention times (t_R) for the (S) – enantiomer (major) and (R) -enantiomer (minor) were 8.22 min and 10.36 min with an enantiomeric ratio (*e.r.*) of 9:91.



Name	NV249				
RT [min]	Type	Area%	Area	Height	Width [min]
2.14	VB	4.87	32.55	8.86	0.06
6.10	VB	4.01	26.85	2.51	0.16
8.22	BB	91.13	16571.68	1302.12	0.20
10.36	VB	8.87	1613.41	90.07	0.27
13.07	BB	29.83	199.57	10.30	0.30
	Sum	138.71	18444.06		

3.8. General procedure for aryl migration reactions (for compounds 2a-2v)





Co-salen (*S*, *S*) *t*Bu, *t*Bu HEH-Cy PTH

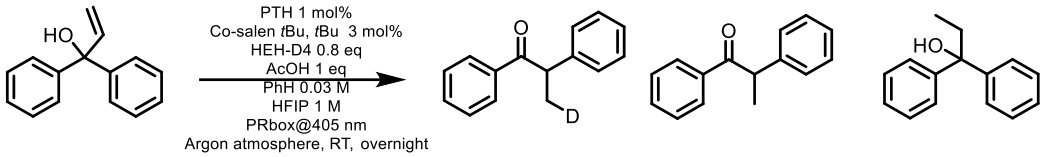
To an 8 mL vial, the starting material (1.0 eq, 0.18 mmol) was added, followed by the addition of Hantzsch ester cyclohexane (0.8 eq, 0.144 mmol, 48.3 mg), Co-salen(*S,S*)^{tBu,tBu} (3 mol %, 5.4 µmol, 3.26 mg), and photocatalyst PTH (1 mol %, 1.8 µmol, 0.6 mg). The vial was then sealed with a septum and purged with argon for 15 minutes. After this, anhydrous PhH (0.03 M, 6 mL) was added, followed by HFIP (1 M, 9.3 eq, 0.18 mL) and AcOH (1.0 eq, 0.18 mmol, 10.3 µL). The vial was subjected to irradiation using 405 nm lamp (18 W) for 17 h. After this time, the mixture was filtered through a silica plug, and the silica was washed with acetone (2 mL). The mixture was then concentrated *in vacuo.* The crude product was purified by preparative TLC.

3.9. Procedure for reaction on 1 mmol scale

To a Schlenk flask, the starting material **1a** (1.0 eq, 1 mmol, 210.3 mg) was added, followed by the addition of Hantzsch ester cyclohexane (0.8 eq, 0.8 mmol, 268.3 mg), Co-salen(*S,S*)$^{t\text{Bu},t\text{Bu}}$ (3 mol %, 0.03 mmol, 18.1 mg), and photocatalyst PTH (1 mol %, 0.1 mmol, 3.2 mg). The Schlenk flask was evacuated and purged with argon for 15 minutes. After this, anhydrous PhH (0.06 M, 17.8 mL) was added, followed by HFIP (1 M, 1 mL) and AcOH (1.0 eq, 1 mmol, 57.2 µL). The Schlenk flask was subjected to irradiation using two 405 nm lamps (18 W) for 48 h. After this time, the mixture was filtered through silica plug, and the silica was washed with acetone (20 mL). The crude mixture was then concentrated *in vacuo.* The crude product was purified by column chromatography (Pentane: Acetone = 98:2) and obtained as a white solid. The isolated yield of compound **2a** is 66% (138.6 mg, 0.66 mmol).

4. Mechanistic experiments

4.1. Reaction with HEH-D4

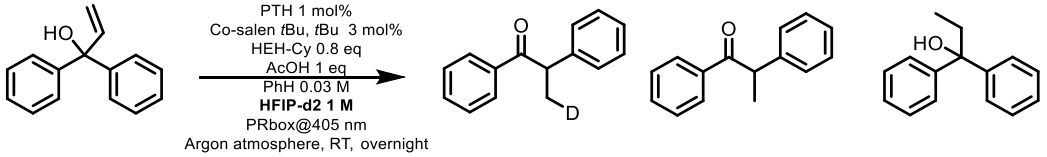


1a **2a-*d*** **2a** **2b**

To an 8 mL vial, the starting material (1.0 eq, 0.1 mmol, 21.03 mg) was added, followed by the addition of deuterated Hantzsch ester (HEH-D4) (0.8 eq, 0.08 mmol, 20.42 mg), Co-salen (*S,S*) *t*Bu, *t*Bu (3 mol %, 3 µmol, 1.81 mg), and photocatalyst PTH (1 mol %, 1 µmol, 0.32 mg). The vial was then sealed with a septum and purged with argon for 15 minutes. After this, anhydrous PhH (0.03 M, 3.3 mL) was added, followed by HFIP (1 M, 0.1 mL) and AcOH (1.0 eq, 0.1 mmol, 5.72 µL). The vial was subjected to irradiation using 405 nm lamp (18 W) for 17 h. After this time, the mixture was filtered through a silica plug, and the silica was washed with acetone (2 mL). The crude mixture was then concentrated *in vacuo.* ^{1}H NMR yield was determined by using 1.0 eq (0.1 mmol) of $CHBr_3$ as the internal standard. ^{2}D NMR is recorded in chloroform-*h*, using benzene-*d*6 as the internal standard.

Products **2a-*d*** and **2a** are obtained in 74% ^{1}H NMR yield. ^{1}H NMR yield of **2b** is 26%, and no starting material is observed. Based on ^{1}H NMR, there is 25% D incorporation.

Reaction with HFIP-d2



1a **2a-*d*** **2a** **2b**

To an 8 mL vial, the starting material (1.0 eq, 0.1 mmol, 21.03 mg) was added, followed by the addition of Hantzsch ester cyclohexane (0.8 eq, 0.08 mmol, 26.83 mg), Co-salen (*S,S*) *t*Bu, *t*Bu (3 mol %, 3 µmol, 1.81 mg), and photocatalyst PTH (1 mol %, 1 µmol, 0.32 mg). The vial was then sealed with a septum and purged with argon for 15 minutes. After this, anhydrous PhH (0.03 M, 3.3 mL) was added, followed by HFIP-d2 (1 M, 0.1 mL) and AcOH (1.0 eq, 0.1 mmol, 5.72 µL). The vial was subjected to irradiation using 405 nm lamp (18 W) for 17 h. After this time, the mixture was filtered through a silica plug, and the silica was washed with acetone (2 mL). The crude mixture was then concentrated *in vacuo.* ^{1}H NMR yield was determined by using 1.0 eq (0.1 mmol) of $CHBr_3$ as the internal standard. ^{2}D NMR is recorded in chloroform-*h*, using benzene-*d*6 as the internal standard. The crude product was purified by preparative TLC. The isolated yield is 52% (0.093 mmol, 19.6 mg).

Products **2a-*d*** and **2a** are obtained in 63% ^{1}H NMR yield. ^{1}H NMR yield of **2b** is 13%, and no starting material is observed. Based on ^{1}H NMR, there is 50% D incorporation.

4.2. UV-Vis spectra

The UV-Vis spectrum of PTH is recorded in benzene. λ_{max} abs= 371 nm.

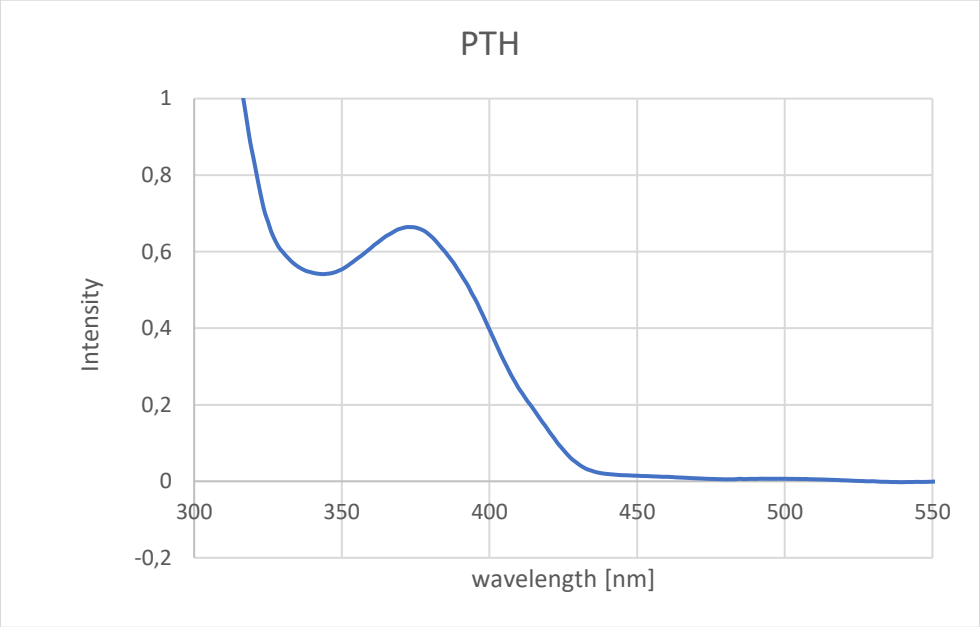


Figure 1. UV-VIS spectrum of PTH.

The UV-Vis spectrum of Co-salen(*S,S*)^{tBu,tBu} is recorded in benzene.

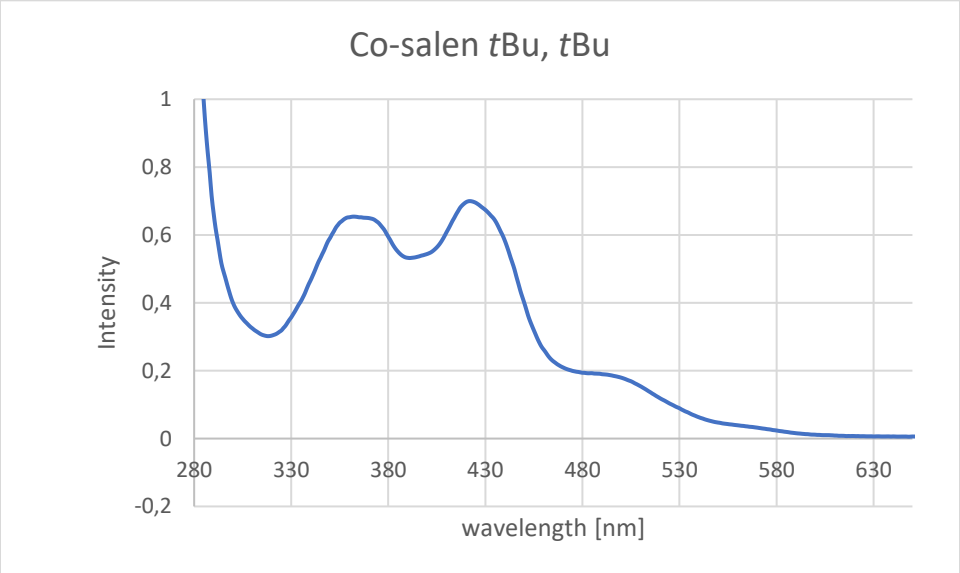


Figure 2. UV-VIS spectrum of Co-salen.

4.3. Fluorescence quenching experiment

Quenching of PTH with Co-salen.

To a standard solution of PTH (0.1 mM in benzene) were added HFIP (V(benzene): V(HFIP)=35, in the same ratio as in the optimized reaction conditions) and AcOH (V(benzene): V(AcOH)=612, the same ratio as in the optimized reaction conditions). To this solution, different amounts of standard solution of Co-salen (1 mM in benzene) were added to afford the final concentrations reported in table below. Then, fluorescence of the solutions was measured.

Excitation wavelength: 379 nm.

Excitation slit: 10 nm, emission slit: 10 nm.

Entry	[Co] (mM)
1	0
2	0.01
3	0.02
4	0.03
5	0.04
6	0.05
7	0.06
8	0.07

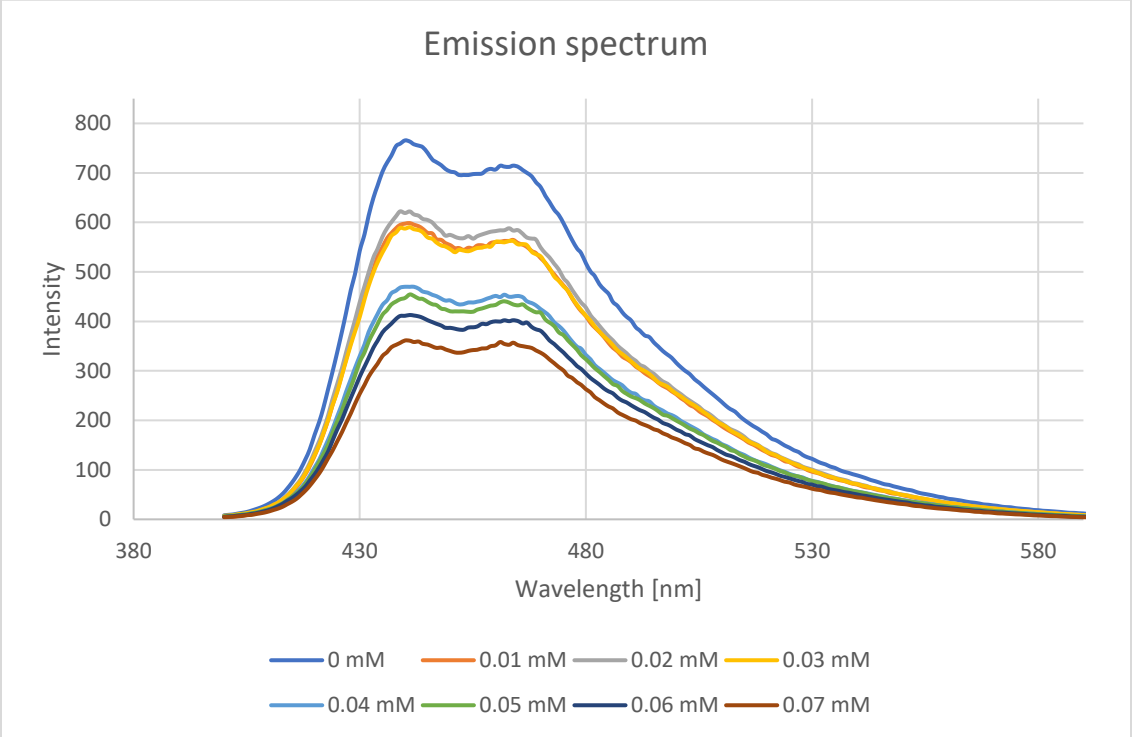


Figure 3. Emission spectrum of PTH with increasing concentrations of Co-salen.

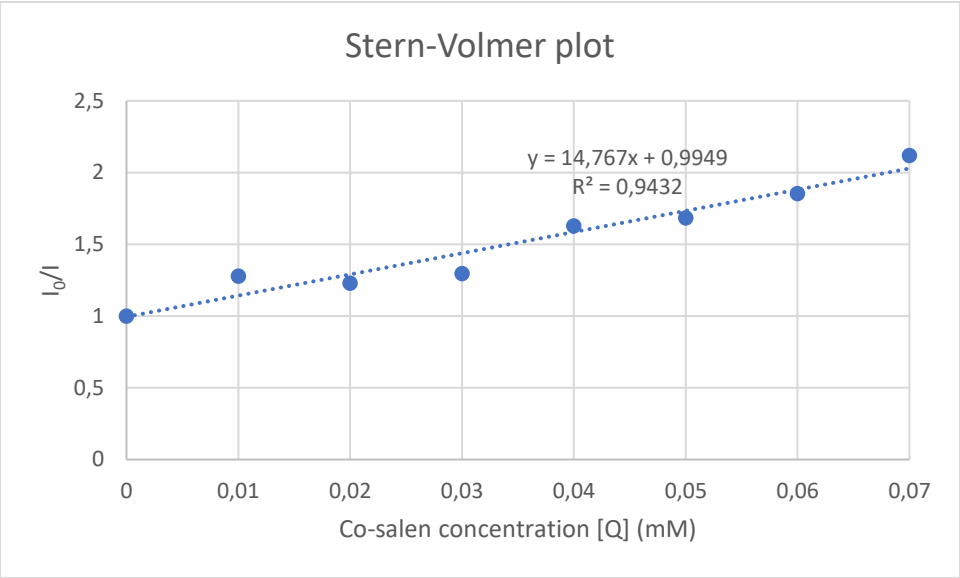


Figure 4. Stern-Volmer plot of PTH with increasing concentrations of Co-salen.

The Co-salen complex has absorption in the visible light region (in the emission region of the PTH). To consider the inner-filter effect of Co-salen, the quenching ratio I_0/I has been corrected using the following formula:[5]

$$\left(\frac{\mathrm{I0}}{\mathrm{I}}\right)\mathrm{corr} = \left(\frac{I0}{I}\right)\left(\frac{Abs(PTH)}{Abs(PTH)+Abs(Co-salen)}\right)\left(\frac{1-10\text{^}-(Abs(PTH)+Abs(Co-salen))}{1-10\text{^}-(Abs(PTH))}\right)$$

The correction was done based on the measured steady state emission intensity (I=426 nm) of the excited state of PTH.

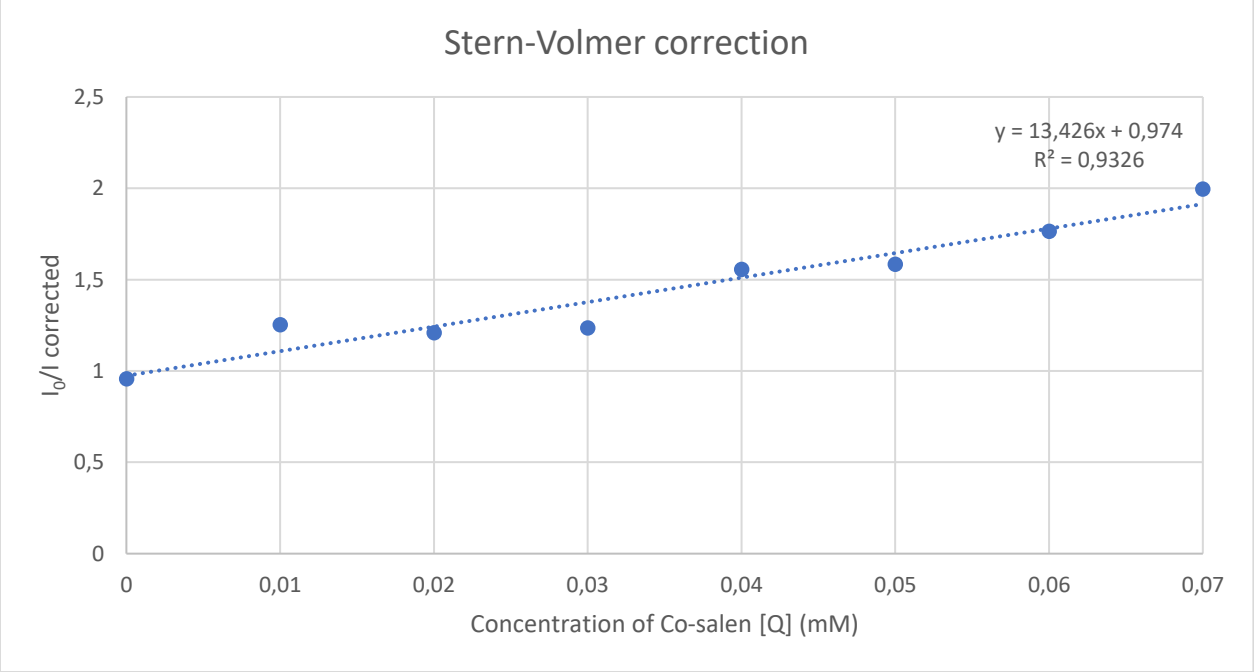
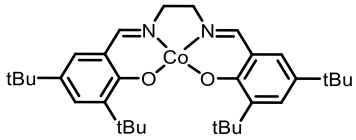


Figure 5. Corrected Stern-Volmer plot of PTH with increasing concentrations of Co-salen.

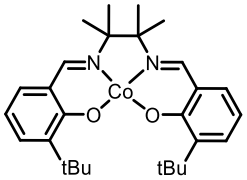
5. Characterization data

Co-salen A



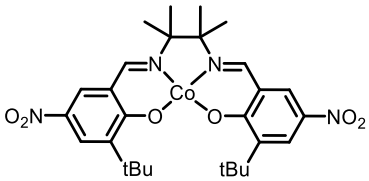
Prepared following procedure for Co-salen catalyst. Isolated as red solid in 51% yield (841 mg, 1.53 mmol).
HRMS (ESI): calculated for $[C_{32}H_{46}CoN_2O_2]$: 549.2886, found: 594.2882.

Co-salen B



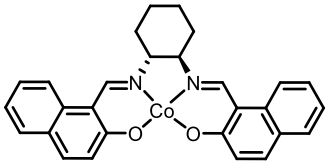
Prepared following procedure for Co-salen catalyst preparation. Isolated as red solid in 63% yield (933 mg, 1.89 mmol).
HRMS (APCI): calculated for $[C_{28}H_{39}CoN_2O_2]$: 494.2338, found: 494.2340.

Co-salen C



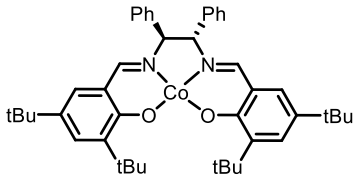
Prepared following procedure for Co-salen catalyst preparation. Isolated as red solid in 82% yield (1.43 g, 2.46 mmol).
HRMS (ESI): calculated for $[C_{28}H_{36}CoN_4O_6Na]$: 606.1859, found: 606.1843.

Co-salen D



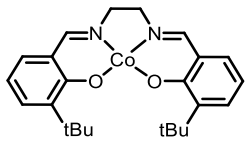
Prepared following procedure for Co-salen catalyst preparation using *R*, *R*- diamine. Isolated as red solid in 69% yield (992 g, 2.07 mmol).
HRMS (ESI): calculated for $[C_{28}H_{24}CoN_2O_2]$: 479.1164, found: 479.1159.

Co-salen F



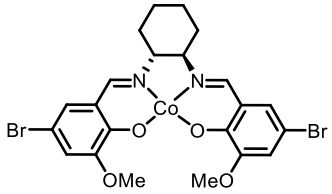
Prepared following procedure for Co-salen catalyst preparation using *S*, *S*- diamine. Isolated as red solid in 52% yield (1095 mg, 1.56 mmol).
HRMS (ESI): calculated for [$C_{44}H_{55}CoN_2O_2$]: 702.3590, found: 702.3567.

Co-salen G



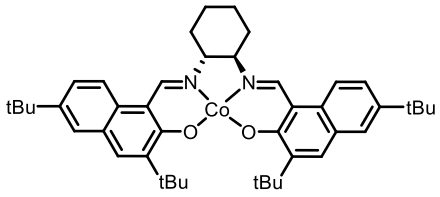
Prepared following procedure for Co-salen catalyst. Isolated as red solid in 26% yield (341.21 mg, 0.78 mmol).
HRMS (ESI): calculated for [$C_{24}H_{30}CoN_2O_2$]: 437.1634, found: 437.1626.

Co-salen H



Prepared following procedure for Co-salen catalyst preparation using *R*, *R*- diamine. Isolated as red solid in 52% yield (931.6 mg, 1.56 mmol).
HRMS (ESI): calculated for [$C_{22}H_{22}CoN_2O_4Br_2Na$]: 617.9170, found: 617.9176.

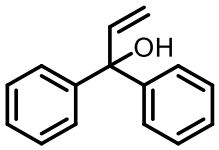
Co-salen I



Prepared following procedure for Co-salen catalyst preparation using *R*, *R*-diamine. Isolated as red solid in 20% yield (429.2 mg, 0.61 mmol).
HRMS (ESI): calculated for [$C_{44}H_{56}CoN_2O_2$]: 703.3654, found: 703.3668.

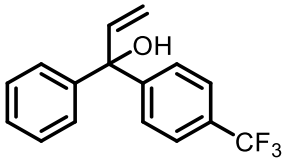
5.1. Starting materials

1a (1,1-diphenylprop-2-en-1-ol)



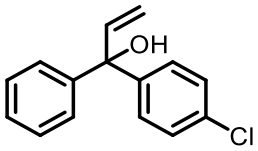
Isolated as a colorless oil in 63% yield (395 mg, 1.88 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 4H), 7.33 (dd, *J* = 8.5, 6.9 Hz, 4H), 7.29 – 7.26 (m, 2H), 6.55 – 6.48 (m, 1H), 5.35 – 5.32 (m, 1H), 5.31 (s, 1H), 2.28 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 143.7, 128.3, 127.4, 127.0, 79.5.
These data are in agreement with those reported previously. [6]

1b (1-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol)



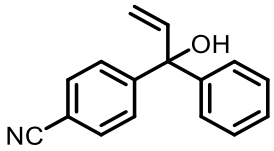
Isolated as a colorless oil in 71% yield (593.2 mg, 2.13 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.53 – 7.51 (m, 2H), 7.38 – 7.33 (m, 4H), 7.31 – 7.28 (m, 1H), 6.50 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.38 – 5.32 (m, 2H), 2.37 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 149.7, 145.3, 142.9, 129.8 (q, *J*= 32.2 Hz), 128.6, 127.9, 127.3, 127.0, 125.2 (q, *J*=3.7 Hz), 115.1, 79.3.
^{19}F NMR (470 MHz) δ - 62.3 (s)
These data are in accordance with those reported previously. [7]

1c (1-(4-chlorophenyl)-1-phenylprop-2-en-1-ol)



Isolated as a colorless oil in 67% yield (491.4 mg, 2 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 9H), 6.47 (dd, J = 16.8, 10.9 Hz, 1H), 5.32 (m, 2H), 2.26 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 144.2, 143.1, 133.2, 128.4, 128.3, 128.3, 127.6, 126.8, 114.5, 79.1.
These data are in accordance with those reported previously. [8]

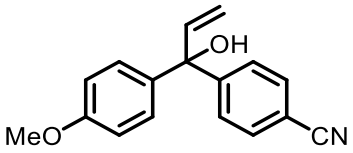
1d (4-(1-hydroxy-1-phenylallyl)benzonitrile)



Isolated as pale yellow solid in 96 % yield (678.8 mg, 2.88 mmol).

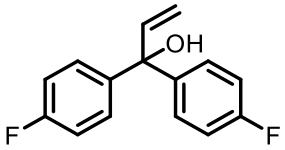
^{1}H NMR (600 MHz, CDCl3) δ 7.60 (d, 2H, J=7.8 Hz), 7.52(d, 2H, J = 8.2 Hz), 7.36-7.20 (m, 5H), 6.48 (m, 1H), 5.34 (m, 2H), 2.39 (s, 1H).
^{13}C NMR (151 MHz, CDCl3) δ 150.8, 144.8, 142.4, 132.2, 128.6, 128.5, 127.6, 126.9, 118.8, 115.4, 111.0, 79.2, 30.9
These data are in accordance with those reported previously. [9]

1e (4-(1-hydroxy-1-(4-methoxyphenyl)allyl)benzonitrile)



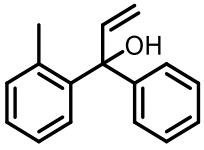
Isolated as a pale-yellow oil in is 29% yield (232 mg, 1.16 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.51 – 7.49 (m, 2H), 7.25 – 7.23 (m, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.44 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.35 (dd, *J* = 10.5, 1.0 Hz, 1H), 5.32 (dd, *J* = 17.1, 1.0 Hz, 1H), 3.80 (s, 3H), 2.27 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 151.1, 142.6, 137.1, 131.9, 128.3, 127.5, 118.9,115.0, 113.8, 110.9, 78.9, 55.3
HRMS (ESI) (m/z): calculated for [$C_{17}H_{15}NO_2Na$]: 288.0995, found 288.0996.
IR (neat): v 3463, 2229, 1606, 1507, 1247, 1175, 1031, 831 cm^{-1}.

1f (1,1-bis(4-fluorophenyl)prop-2-en-1-ol)



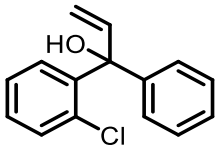
Isolated as a colorless oil in 78% yield (579 mg, 2.35 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 4H), 7.04 – 6.97 (m, 4H), 6.45 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.33 (dd, *J* = 10.5, 1.0 Hz, 1H), 5.28 (dd, *J* = 17.1, 1.0 Hz, 1H), 2.25 (s, 1H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -115.2 – -115.3 (m).
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.5 Hz), 143.4, 141.5 (d, *J* = 3.3 Hz), 128.8 (d, *J* = 8.0 Hz), 115.2 (d, *J* = 21.3 Hz), 114.6, 78.9.
These data are in agreement with those reported previously.[10]

1g (1-phenyl-1-(*o*-tolyl)prop-2-en-1-ol)



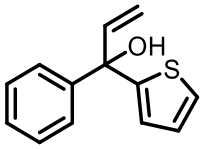
Isolated as colorless oil in 56% yield (380.3 mg, 1.69 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.31 – 7.29 (m, 4H), 7.25 – 7.19 (m, 3H), 7.14 – 7.12 (m, 1H), 6.53 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.33 – 5.20 (m, 2H), 2.23 (s, 1H), 2.03 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 143.8, 143.3, 137.5, 132.6, 128.3, 128.0, 127.6, 127.1, 126.4, 125.5, 80.1, 21.6.
These data are in accordance with those reported previously.[8]

1h (1-(2-chlorophenyl)-1-phenylprop-2-en-1-ol)



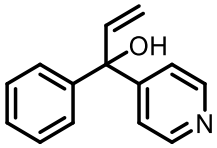
Isolated as a colorless oil in 58% yield (426.1 mg, 1.74 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, J =7.6, 1.5 Hz, 1H), 7.35 – 7.26 (m, 8H), 6.61 (dd, J = 17.0, 10.7 Hz, 1H), 5.36-5.32 (m, 2H), 3.22 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 142.5, 141.5, 132.7, 131.4, 129.3, 129.1, 128.4, 127.5, 126.9, 126.6, 115.2, 79.8.
These data are in accordance with those reported previously.[8]

1i (1-phenyl-1-(thiophen-2-yl)prop-2-en-1-ol)



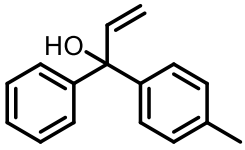
Isolated as yellow oil in 54% yield (353.4 mg, 1.63 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 – 7.29 (m, 1H), 7.27 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.88 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.40 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.32 (dd, *J* = 10.5, 1.0 Hz, 1H), 2.49 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 145.1, 143.2, 128.3, 127.7, 126.8, 126.4, 125.7, 125.7, 114.2, 77.6.
HRMS (MS quantitative): calculated for [$C_{13}H_{12}OS$]: 216.0604, found: 216.0603.
IR (neat): ν 3544, 3451, 1445, 1319, 1158, 990, 930, 836, 697cm^{-1}.

1j (1-phenyl-1-(pyridin-4-yl)prop-2-en-1-ol)



Isolated as brown crystals in 41% yield (259.5 mg, 1.23 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (m, 2H), 7.37-7.30 (m, 7H), 6.5 (dd, J = 10.8, 6.3 Hz, 1H), 5.37 (m, 2H), 2.62 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 149.9, 142.3, 128.7, 128.1, 127.0, 121.8, 116.2, 115.6, 79.0
These data are in accordance with those reported previously.[11]

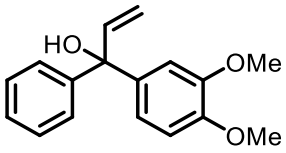
1k (1-phenyl-1-(*p*-tolyl)prop-2-en-1-ol)



Isolated as a colorless oil in 85% yield (572.4 mg, 2.55 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.31 (t, *J*= 7.7 Hz, 2H), 7.24 (m, 3H), 7.13 (m, 2H), 6.50 (dd, *J* = 10.5, 6.4 Hz, 1H), 5.30 (m, 2H), 2.33 (s, 3H), 2.24 (s, 1H).

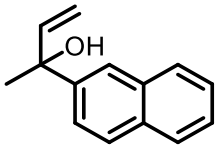
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 143.7, 142.9, 137.0, 128.9, 128.1, 113.8, 79.3, 21.0.
HRMS (ESI) (m/z) calculated for [$C_{16}H_{16}ONa$]: 247.1093, found 247.1088.
IR (neat): v 3555, 3459, 3025, 1508, 1446, 1406, 1323, 1168 **c**m^{-1}.

1l (1-(3,4-dimethoxyphenyl)-1-phenylprop-2-en-1-ol)



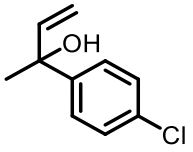
Isolated as a pale-yellow oil in 70% yield (570.6 mg, 2.11 mmol).
^{1}H NMR (600 MHz, CDCl3) δ 7.40 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.27 (m, 1H), 6.95 (d, J = 2.1 Hz, 1H), 6.86 (dd, J = 8.4, 2.1 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 6.48 (dd, J = 17.0, 10.6 Hz, 1H), 5.32 (dd, J = 9.5, 1.2 Hz, 1H), 5.31 – 5.29 (m, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.24 (s, 1H).
^{13}C NMR (151 MHz, CDCl3) δ 148.8, 148.4, 145.9, 143.8, 138.6, 128.3, 127.4, 127.0, 119.5, 114.0, 110.6, 79.4, 56.0, 56.0.
ESI: calculated for [C17H18O3Na]: 293.1149, found: 293.1148.
IR (neat): v 3498, 2933, 1592, 1509, 1446, 1232, 1162, 1026, 936, 759 cm^{-1}.

1m (2-(naphthalen-2-yl)but-3-en-2-ol)



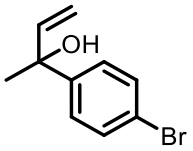
Isolated as a colorless oil in 51% yield (302 mg, 1.52 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.87 – 7.80 (m, 3H), 7.57 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.50 – 7.44 (m, 2H), 6.26 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.35 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.20 (dd, *J* = 10.6, 1.1 Hz, 1H), 1.98 (s, 1H), 1.76 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 143.9, 133.3, 132.6, 128.3, 128.1, 127.6, 126.2, 126.0, 124.2, 123.5, 75.1, 29.5.
These data are in accordance with those reported previously.[12]

1n (2-(4-chlorophenyl)but-3-en-2-ol)



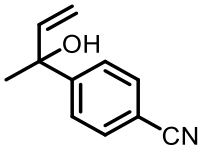
Isolated as colorless oil in 43% yield (235.6 mg, 1.29 mmol)**.**
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.32 – 7.28 (m, 2H), 6.13 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.32 – 5.25 (m, 1H), 5.19 – 5.14 (m, 1H), 1.87 (s, 1H), 1.63 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 144.6, 133.0, 128.5, 126.9, 113.0, 74.6, 29.5.
HRMS: calculated for [$C_{10}H_{11}OCl$]: 182.0493, found: 184.0492.
IR (neat): v 3387, 2980, 1488, 1404, 1367, 1092, 1010, 923, 826 cm^{-1}

1o (2-(4-bromophenyl)but-3-en-2-ol)



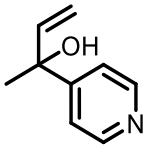
Isolated as colorless oil in 36% yield (245.6 mg, 1.08 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.8 Hz,2H), 7.35 (d, J = 8.8 Hz ,2H), 6.13 (dd, J = 10.9 Hz, 7.0 Hz ,1H), 5.30 (d, J=17.1, 1H), 5.16 (d, J= 10.6 Hz, 1H) ,1.89 (s, 1H), 1.63 (s, 3H)
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 144.5, 131.4, 127.3, 121.1, 113.0, 74.6, 29.5
HRMS (ESI) (m/z) calculated for [$C_{10}H_{11}OBr$]: 225.9988, found 225.9989.
IR (neat): ν 3391, 2979, 1485, 1396, 1365, 1076, 1005, 923 cm^{-1}.

1p (4-(2-hydroxybut-3-en-2-yl)benzonitrile)



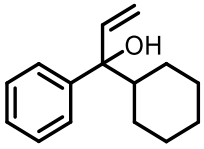
Isolated as a yellow oil in 48% yield (250 mg, 1.44 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.60 – 7.57 (m, 2H), 6.12 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.32 (dd, *J* = 17.3, 0.8 Hz, 1H), 5.21 (dd, *J* = 10.6, 0.8 Hz, 1H), 2.65 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 143.8, 132.2, 126.2, 119.0, 113.8, 111.0, 74.8, 29.5.
ESI: calculated for [$C_{11}H_{11}ONNa$]: 196.0733, found: 196.0727.
IR (neat): ν 3458, 2981, 2230, 1688, 1606, 1501, 1404, 1362, 1066, 996, 927, 838 cm^{-1}

1q (2-(pyridin-4-yl)but-3-en-2-ol)



Isolated as a white solid in 54% yield (240.6 mg, 1.61 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 – 8.51 (m, 2H), 7.44 – 7.35 (m, 2H), 6.12 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.32 (d, *J* = 17.3 Hz, 1H), 5.20 (dd, *J* = 10.6, 0.8 Hz, 1H), 1.64 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 149.9, 143.6, 120.4, 113.8, 74.3, 29.3.
These data are in accordance with those reported previously. [13]

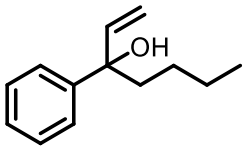
1r (1-cyclohexyl-1-phenylprop-2-en-1-ol)



Isolated as colorless oil in 52% yield (340 mg, 1.57 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.36 – 7.29 (m, 2H), 7.23 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.34 – 6.27 (m, 1H), 5.31 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.18 (dd, *J* = 10.8, 1.2 Hz, 1H), 1.78 – 1.73 (m, 3H), 1.72 – 1.67 (m, 1H), 1.63 (d, *J* = 12.9 Hz, 1H), 1.46 (d, *J* = 12.9 Hz, 1H), 1.24 – 1.06 (m, 3H), 1.05 – 0.97 (m, 2H).

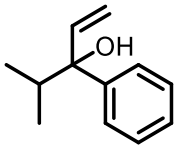
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 143.5, 128.2, 126.7, 125.6, 112.7, 79.3, 47.8, 27.3, 26.9, 26.8, 26.7, 26.6.
ESI: calculated for [$C_{15}H_{20}ONa$]: 239.1406, found: 239.1397.
IR (neat): ν 3477, 2928, 2853, 1741, 1447, 1261, 1078, 1013, 800, 700 cm^{-1}

1s (3-phenylhept-1-en-3-ol)



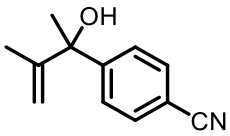
Isolated as a colorless oil in 74% yield (423 mg, 2.22 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.19 – 7.13 (m, 1H), 6.13 (ddd, *J* = 17.3, 10.7, 1.0 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.07 (dd, *J* = 10.7, 1.1 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.78 – 1.74 (m, 1H), 1.25 – 1.19 (m, 3H), 1.12 – 1.06 (m, 1H), 0.79 (t, *J* = 8.7 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 144.6, 128.3, 126.9, 125.5, 112.6, 77.1, 42.0, 25.9, 23.1, 14.2.
ESI: calculated for [$C_{13}H_{17}O$]: 189.1274, found: 189.1273.
IR (neat): ν 3457, 2953, 2866, 1448, 991, 919, 698 cm^{-1}

1t (4-methyl-3-phenylpent-1-en-3-ol)



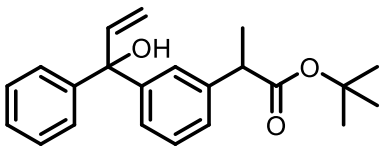
Isolated as a colorless oil in 90% yield (476.5 mg, 2.7 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.30 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.32 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.19 (dd, *J* = 10.8, 1.2 Hz, 1H), 2.23 – 2.15 (m, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 143.4, 128.2, 126.7, 125.6, 112.8, 79.4, 37.4, 17.2, 16.9.
HRMS (MS quantitative): calculated for [C_9H_9O]: 133.0648, found: 133.0645.
IR (neat): ν 3475, 2967, 2877, 2326, 2103, 1809, 1448, 1383, 1166, 983, 919, 759, 700 cm^{-1}

1u (4-(2-hydroxy-3-methylbut-3-en-2-yl)benzonitrile)



Isolated as a white solid in 17% yield (96.9 mg, 0.52 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 5.20 (s, 1H), 5.02 (s, 1H), 1.69 (s, 3H), 1.60 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.5, 149.2, 132.2, 126.3, 119.1, 112.1, 110.9, 29.1, 18.9.
ESI: calculated for [$C_{12}H_{13}ONNa$]: 210.0892, found: 210.0889.
IR (neat): ν 3471, 2966, 2231, 1689, 1604, 1403, 1365, 1260, 1097, 1016, 910 cm^{-1}.

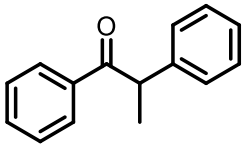
1v (*tert*-butyl 2-(3-(1-hydroxy-1-phenylallyl)phenyl)propanoate)



Isolated as a white solid in 31% yield (418.9 mg, 1.24 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 3H), 7.27 – 7.24 (m, 3H), 7.21 – 7.17 (m, 1H), 6.53 – 6.43 (m, 1H), 5.34 – 5.25 (m, 2H), 3.58 (q, *J* = 7.1 Hz, 1H), 2.30 (s, 1H), 1.41 (dd, *J* = 7.2, 1.4 Hz, 3H), 1.34 (d, *J* = 1.4 Hz, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 146.0, 145.9, 143.6, 141.3, 128.4, 128.3, 127.4, 127.0, 127.0, 126.4, 125.6, 125.5, 114.2, 80.6, 79.5, 46.7, 28.0, 18.5.
ESI: calculated for [$C_{22}H_{26}O_3Na$]: 361.1774, found: 361.1776.
IR (neat): ν 3439, 2978, 1705, 1368, 1149, 994, 925, 701 cm^{-1}.

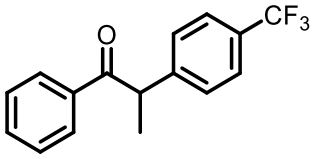
5.2. Products characterization data

2a (1,2-diphenylpropan-1-one)



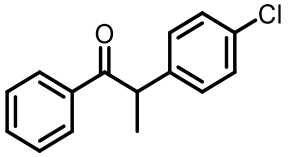
Reaction is carried out on 0.1 mmol scale. The isolated yield is 75% yield (15.8 mg, 0.075 mmol).
1H NMR (600 MHz, CDCl3) δ 7.97 – 7.92 (m, 2H), 7.47 (dd, J = 7.3, 1.3 Hz, 1H), 7.38 (d, J = 7.8 Hz, 2H), 7.31 – 7.27 (m, 4H), 7.22 – 7.18 (m, 1H), 4.69 (q, J = 6.9 Hz, 1H), 1.54 (d, J = 6.9 Hz, 3H).
13C NMR (151 MHz, $CDCl_3$) δ 200.5, 141.6, 136.6, 132.9, 129.1, 128.9, 128.6, 127.9, 127.0, 48.0, 19.6.
These data are in agreement with those reported previously. [14]

2b (1-phenyl-2-(4-(trifluoromethyl)phenyl)propan-1-one)



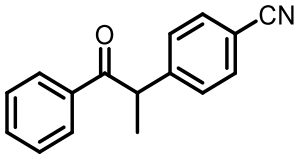
Reaction is carried out on 0.1 mmol scale. The isolated yield is 67% (18.8 mg, 0.067 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.44 – 7.38 (m, 4H), 4.77 (q, *J* = 6.9 Hz, 1H), 1.56 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.8, 145.5, 136.3, 133.3, 129.3 (d, *J* = 32.5 Hz), 128.9, 128.8, 128.3, 126.1 (q, *J* = 3.8 Hz), 124.2 (d, *J* = 280.6 Hz), 47.6, 19.6.
^{19}F NMR (565 MHz, $CDCl_3$) δ -62.55.
These data are in agreement with those reported previously. [15]

2c (2-(4-chlorophenyl)-1-phenylpropan-1-one)



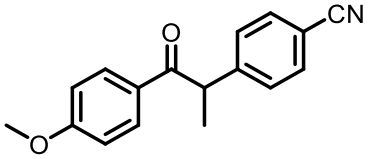
Reaction is carried out on 0.18 mmol scale. The isolated yield is 66% (29.2 mg, 0.12 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.22 (m, 4H), 4.68 (d, *J* = 7.1 Hz, 1H), 1.53 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.1, 139.9, 136.3, 133.1,132.9, 129.3, 129.2, 128.8, 128.7, 47.2, 19.5.
These data are in accordance with those reported previously. [16]

2d (4-(1-oxo-1-phenylpropan-2-yl)benzonitrile



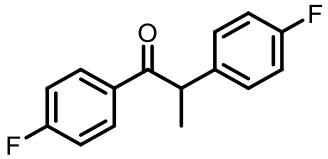
Reaction is carried out on 0.18 mmol scale. The isolated yield is 54% (22.8 mg, 0.097 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.44 – 7.39 (m, 4H), 4.76 (d, *J* = 6.9 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.4, 146.8, 136.1, 133.5, 132.9, 128.9, 128.8, 118.8, 111.1, 47.8, 19.4.
These data are in agreement with those reported previously. [17]

2e (4-(1-(4-methoxyphenyl)-1-oxopropan-2-yl)benzonitrile)



Reaction is carried out on 0.18 mmol scale. The isolated yield 68% (32.4 mg, 0.12 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.37 (m, 2H), 6.93 – 6.83 (m, 2H), 4.71 (d, *J* = 6.9 Hz, 1H), 3.83 (s, 3H), 1.53 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 163.8, 147.2, 132.8, 131.1, 129.0, 128.7, 118.8, 114.0, 111.0, 55.6, 47.4, 19.5.
IR (neat): ν 2965, 2228, 1673, 1599, 1507, 1256, 1169, 1018, 795 cm^{-1}.
HRMS (APCI): m/z calculated for [$C_{17}H_{16}NO_2$]: 266.1176, found: 266.1187.

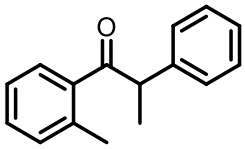
2f (1,2-bis(4-fluorophenyl)propan-1-one)



Reaction is carried out on 0.18 mmol scale. The isolated yield is 51% (22.4 mg, 0.09 mmol).

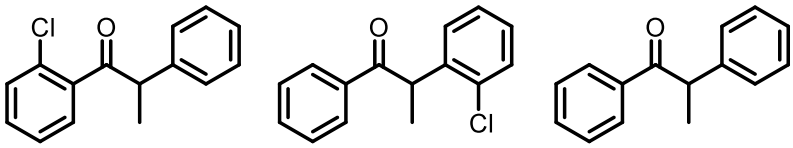
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.25 – 7.20 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 4.62 (q, *J* = 6.9 Hz, 1H), 1.51 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 165.7 (d, *J* = 254.9 Hz), 162.0 (d, *J* = 245.8 Hz), 137.1 (d, *J* = 3.1 Hz), 132.8 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 9.1 Hz), 129.4 (d, *J* = 7.9 Hz), 116.1 (d, *J* = 21.5 Hz), 115.8 (d, *J* = 21.9 Hz), 47.2, 19.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ -105.2 – -105.3 (m), -112.9 – -118.3 (m).
These data are in agreement with those reported previously. [18]

2g (2-phenyl-1-(o-tolyl)propan-1-one)



Reaction is carried out on 0.18 mmol scale. The isolated yield is 40% (16.3 mg, 0.072 mmol)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.17 (m, 8H), 4.55 (q, *J* = 6.9 Hz, 1H), 2.35 (s, 3H), 1.57 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 204.8, 140.6, 138.7, 138.0, 131.7, 130.8, 128.9, 128.1, 128.0, 127.1, 125.5, 50.9, 20.9, 18.7.
These data are in accordance with those reported previously. [19]

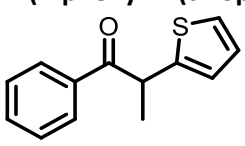
2h: 1-(2-chlorophenyl)-2-phenylpropan-1-one; 2h': 2-(2-chlorophenyl)-1-phenylpropan-1-one; 2a: 1,2-diphenylpropan-1-one)



2h 2h' 2a

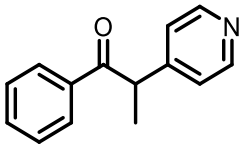
Reaction done on 0.18 mmol scale. The isolated yield is 51% (22.46 mg, 0.092 mmol) (2h: 2h':2a = 8.3:1:1)
2h: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 3H), 7.24 – 7.21 (m, 3H), 7.18 – 7.14 (m, 2H), 7.08 (dd, *J* = 7.4, 1.3 Hz, 1H), 4.52 (q, *J* = 6.3 Hz, 1H), 1.59 (d, *J* = 6.9 Hz, 3H).
2h'+2a (selected peaks): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 3H), 7.50 – 7.45 (m, 2H), 7.42 – 7.36 (m, 4H), 4.69 (q, *J* = 6.8 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 1H), 1.54 (d, *J* = 6.9 Hz, 3H), 1.50 (d, *J* = 6.8 Hz, 3H).
2h, 2h'+2a (selected peaks): **^{13}C NMR** (151 MHz, $CDCl_3$) δ 204.2, 139.9, 139.6, 133.1, 132.9, 131.2, 130.5, 130.3, 129.1, 128.9, 128.9, 128.7, 128.6, 128.4, 127.9, 127.6, 127.3, 127.0, 126.7, 52.3, 48.0, 44.3, 19.6, 17.9, 17.9.
These data are in accordance with those reported previously in the literature. [20]

2i (1-phenyl-2-(thiophen-2-yl)propan-1-one)



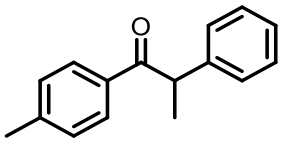
Reaction is carried out on 0.18 mmol scale. The isolated yield 59% (23 mg, 0.11 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.58 – 7.50 (m, 1H), 7.48 – 7.40 (m, 2H), 7.17 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.89 – 6.87 (m, 1H), 5.00 (d, *J* = 6.9 Hz, 1H), 1.62 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.2, 143.8, 136.2, 133.2, 128.9, 128.8, 127.1, 125.1, 124.7, 42.4, 20.3.
These data are in accordance with those reported previously. [21]

2j (1-phenyl-2-(pyridin-4-yl)propan-1-one)

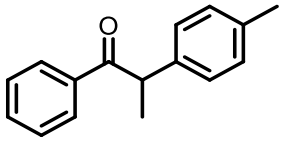


Reaction is carried out on 0.18 mmol scale. The isolated yield is 85% (32.3 mg, 0.153 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.9 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 3H), 7.22 (d, *J* = 5.8 Hz, 3H), 4.69 (q, *J* = 8.3 Hz, 1H), 1.54 (d, *J* = 7.3 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 199.2, 150.4, 150.3, 136.1, 133.5, 128.8, 128.8, 123.2, 47.2, 19.1.
These data are in accordance with those reported previously.[22]

2k (2-phenyl-1-(p-tolyl)propan-1-one) and 2k': 1-phenyl-2-(p-tolyl)propan-1-one)



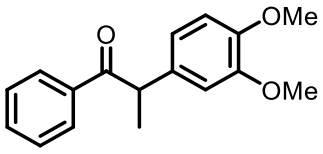
2k



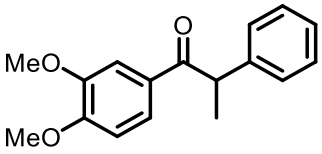
2k'

Reaction done on 0.18 mmol scale. The product is isolated as an inseparable 1:1 mixture of 2k and 2k' (21.4 mg, 0.095 mmol, 53%).
2k: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.30 – 7.27 (m, 4H), 7.19 – 7.13 (m, 3H), 4.70 – 4.60 (m, 1H), 2.35 (s, 3H), 1.54 – 1.49 (m, 3H).
2k': **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.49 – 7.45 (m, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.19 (m, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.86 – 4.34 (m, 1H), 2.28 (s, 3H), 1.54 – 1.48 (m, 3H).
2k+2k': **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.6, 200.1, 143.7, 141.9, 138.6, 136.7, 136.6, 134.1, 132.8, 129.8, 129.3, 129.1, 129.0,128.9, 128.6, 127.9, 126.9, 47.6, 21.7, 21.1, 19.6, 19.6.
These data are in accordance with those reported previously.[23, 24]

2l (2-(3,4-dimethoxyphenyl)-1-phenylpropan-1-one) and 2l' (1-(3,4-dimethoxyphenyl)-2-phenylpropan-1-one)



2l



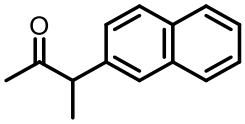
2l'

Reaction is carried out on 0.1 mmol scale. The product is isolated as an inseparable mixture of 2l and 2l' (18.9 mg, 0.07mmol, 70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.59 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.28 – 7.24 (m, 1H), 7.23 – 7.17 (m, 1H), 6.84 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.81 – 6.77 (m, 3H), 4.66 (q, *J* = 7.0 Hz, 1H), 4.62 (q, *J* = 7.1 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 1.53 (d, *J* = 3.3 Hz, 3H), 1.52 (d, *J* = 3.2 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.7, 199.0, 153.2, 149.5, 149.1, 148.2, 142.2, 136.8, 132.9, 129.1, 128.9, 128.6, 127.8, 127.0, 123.5, 120.3, 111.7, 111.3, 110.9, 110.1, 56.1, 56.1, 56.0, 56.0, 47.7, 47.6, 19.7, 19.6.

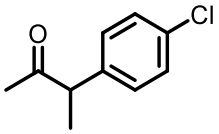
These data are in accordance with those reported previously. [25,26]

2m (3-(naphthalen-2-yl)butan-2-one)



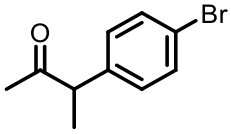
Reaction is carried out on 0.18 mmol scale. The isolated yield is 77% (27.7 mg, 0.14 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 3H), 7.71 – 7.68 (m, 1H), 7.52 – 7.45 (m, 2H), 7.33 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.92 (q, *J* = 6.9 Hz, 1H), 2.08 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 209.0, 138.2, 133.8, 132.7, 128.9, 127.8, 126.8, 126.5, 126.1, 126.0, 54.0, 28.6, 17.4.
These data are in accordance with those reported previously. [27]

2n (3-(4-chlorophenyl)butan-2-one)



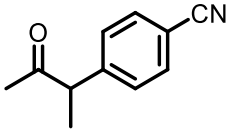
Reaction done on 0.18 mmol scale. The isolated yield 61% (20.2 mg, 0.11 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.17 – 7.13 (m, 2H), 3.72 (d, *J* = 7.0 Hz, 1H), 2.05 (s, 3H), 1.37 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 208.4, 139.2, 133.3, 129.3, 129.3, 53.2, 28.5, 17.4.
These data are in accordance with those reported previously. [28]

2o (3-(4-bromophenyl)butan-2-one)



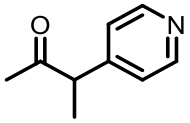
Reaction is carried out on 0.18 mmol scale. Isolated yield 49% (20.1 mg, 0.88 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 3.71 (q, J = 6.8 Hz, 1H), 2.05 (s, 3H), 1.37 (d, J = 6.7 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 208.3, 139.7, 132.2, 129.7, 121.3, 53.2, 28.3, 17.3.
These data are in accordance with those reported previously. [29]

2p (4-(3-oxobutan-2-yl)benzonitrile)



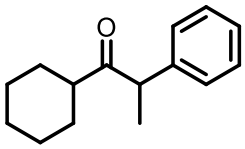
Reaction is carried out on 0.1 mmol scale. The isolated yield is 82% (14.3 mg, 0.082 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.39 – 7.31 (m, 2H), 3.82 (d, *J* = 7.0 Hz, 1H), 2.08 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 207.3, 145.9, 132.9, 128.8, 118.7, 111.4, 53.7, 28.8, 17.4.
HRMS (ESI): m/z calculated for [$C_{11}H_{12}ON$]: 174.0913, found: 174.0910.
IR (neat): ν 2962, 1715, 1258, 1014, 793 cm^{-1}.

2q (3-(pyridin-4-yl)butan-2-one)



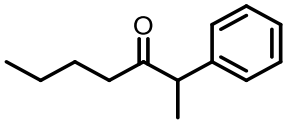
Reaction is carried out on 0.1 mmol scale, isolated yield 44% (6.6 mg, 0.044 mmol).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 2H), 7.18 (s, 2H), 3.75 (d, *J* = 7.1 Hz, 1H), 2.09 (s, 3H), 1.41 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 206.7, 151.3, 148.7, 123.9, 53.2, 28.8, 17.1.
HRMS (ESI): calculated for [$C_9H_{12}NO$]: 150.0913, found: 150.0910.
IR (neat): ν 2921, 2853, 2107, 1727, 1461, 1013, 800, 669 cm^{-1}.

2r (1-cyclohexyl-2-phenylpropan-1-one)



The reaction is carried out on a 0.18 mmol scale. The isolated yield is 63% yield (24.7 mg, 0.11 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.23 (m, 2H), 3.94 (q, *J* = 6.9 Hz, 1H), 2.48 – 2.40 (m, 1H), 1.89 – 1.84 (m, 1H), 1.80 – 1.75 (m, 1H), 1.71 – 1.66 (m, 1H), 1.66 – 1.61 (m, 1H), 1.51 – 1.46 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.32 – 1.10 (m, 4H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.0, 140.9, 128.9, 128.1, 127.1, 51.3, 49.6, 29.6, 28.4, 26.0, 25.9, 25.4, 18.3.
These data are in agreement with those reported previously.[30]

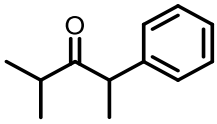
2s (2-phenylheptan-3-one)



Reaction is carried out on 0.1 mmol scale. The isolated yield is 57% (10.8 mg, 0.057 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 – 7.18 (m, 2H), 3.75 (q, *J* = 7.0 Hz, 1H), 2.36 – 2.32 (m, 2H), 1.51 – 1.43 (m, 2H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.22 – 1.13 (m, 2H), 0.81 (d, *J* = 7.4 Hz, 3H).

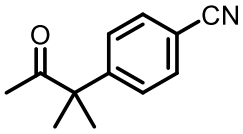
^{13}C NMR (151 MHz, $CDCl_3$) δ 211.2, 140.9, 129.0, 128.0, 127.2, 53.1, 40.9, 26.1, 22.3, 17.6, 13.9.
These data are in agreement with those reported previously in the literature.[31]

2t (2-methyl-4-phenylpentan-3-one)



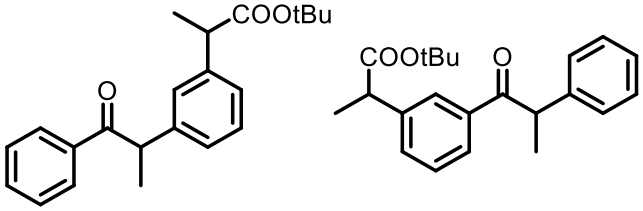
Reaction is carried out on 0.1 mmol scale, the isolated yield is 41% (7.3 mg, 0.041 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 3.92 (q, *J* = 7.0 Hz, 1H), 2.68 (d, *J* = 6.9 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.07 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.8, 140.9, 129.0, 128.1, 127.2, 51.3, 39.3, 19.4, 18.4, 18.3.
These data match those reported previously. [32]

2u (4-(2-methyl-3-oxobutan-2-yl)benzonitrile)



Reaction is carried out on 0.18 mmol scale. The isolated yield is 61% (20.6 mg, 0.11 mmol).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 1.94 (s, 3H), 1.50 (s, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 209.6, 149.6, 132.7, 127.0, 118.7, 111.1, 53.0, 25.8, 25.1.
IR (neat): ν 2296, 2925, 2228, 1709, 1606, 1606, 1466, 1357, 1257, 1091, 1019, 839, 797 cm^{-1}.
HRMS (ESI): m/z $[M+Na]^+$calculated for $[C_{12}H_{13}ONa]^+$: 210.0889, found: 210.0885.

2v (tert-butyl 2-(3-(1-oxo-1-phenylpropan-2-yl)phenyl)propanoate and 2v' (tert-butyl 2-(3-(2-phenylpropanoyl)phenyl)propanoate)



2v 2v'

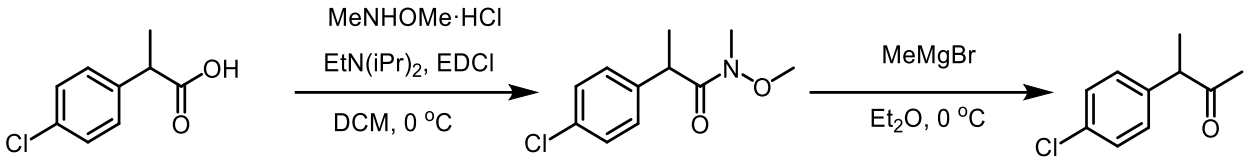
Reaction is carried out on 0.1 mmol scale. The product is isolated as an inseparable 1:1 mixture of 2v and 2v' (15.9 mg, 0.047 mmol, 47%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.89 (s, 1H), 7.83 – 7.79 (m, 1H), 7.48 – 7.44 (m, 1H), 7.42 (d, *J* = 6.5 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.32 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.28 (d, *J* = 4.2 Hz, 4H), 7.24 – 7.18 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 4.73 – 4.61 (m, 2H), 3.62 (q, *J* = 7.2 Hz, 1H), 3.56 (q, *J* = 7.2 Hz, 1H), 1.55 – 1.50 (m, 6H), 1.42 – 1.38 (m, 6H), 1.36 (d, *J* = 7.6 Hz, 9H), 1.32 (d, *J* = 7.6 Hz, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.4, 173.7, 173.5, 142.0, 141.8, 141.6, 136.8, 136.7, 132.9, 132.9, 132.1, 132.0, 129.2, 129.1, 128.9, 128.7, 128.6, 128.1, 128.0, 127.9, 127.1, 127.0, 126.4, 126.4, 126.1, 126.0, 80.9, 80.6, 48.1, 48.0, 46.6, 46.4, 28.1, 28.0, 19.7, 19.6, 18.6, 18.4.
HRMS (ESI): calculated for $[C_{22}H_{26}O_3Na]$: 361.1774, found: 361.1763.

IR (neat): ν 2977, 1725, 1683, 1597, 1451, 1368, 1232, 1148, 1065, 698 cm^{-1}

6. Investigation into stereospecificity

The enantiomeric ratio was determined by chiral high-performance liquid chromatography (HPLC) using the racemic product was prepared according to the procedure described in section 3.4 as reference material. The chiral HPLC conditions were as follows Chiralpak IG column, dimensions 150 x 4.6 mm, particle size 5µ, mobile phase 97:3 n-hexane/ethyl alcohol (EtOH) at a flow rate of 0.5 mL/min.

6.1 Preparation procedure of racemic reference compound 2n via Weinreb-Nahm amide.

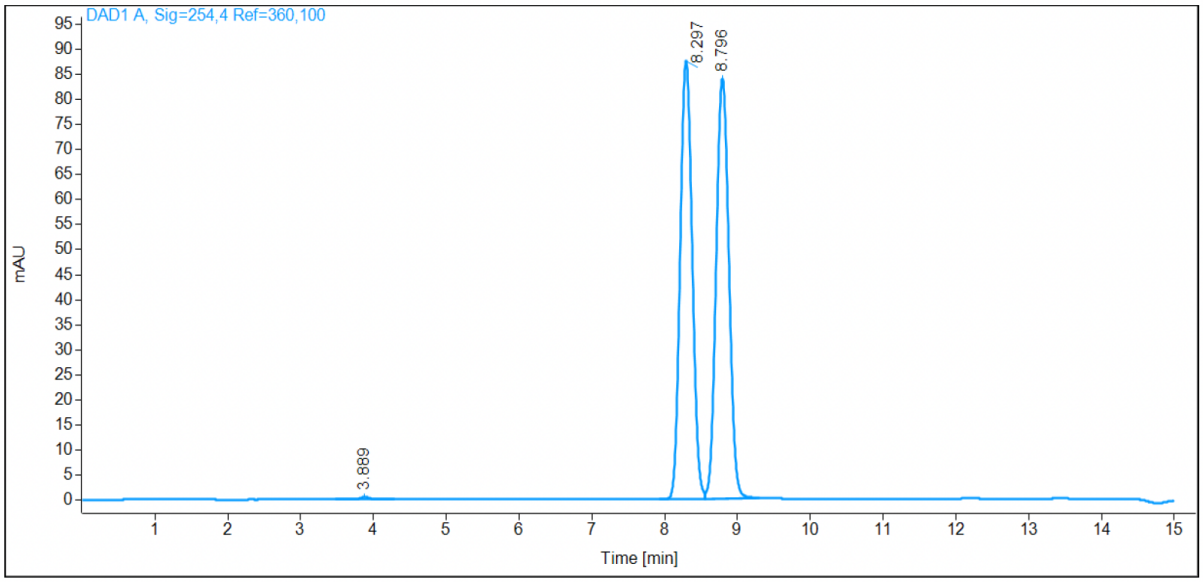


Step 1: Synthesis of 2-(4-chlorophenyl)-*N*-methoxy-*N*-methylpropanamide

To an ice-cooled solution of 2-(4-chlorophenyl)propanoic acid (1.0 eq. 10.0 mmol) in 70 mL of CH_2Cl_2, *N,O*-dimethylhydroxylamine hydrochloride (1.0 eq. 10.0 mmol, 0.975 g), diisopropylethylamine (1.0 eq., 10.0 mmol, 1.8 mL) were added. Then, a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (1.0 eq. 10.0 mmol, 1.96 g) in 20 mL of CH_2Cl_2 was added dropwise. After 1h at 0 °C, the mixture is washed with 1.0 M HCl. The organic layer collected, dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford Weinreb-Nahm amide, which was carried on to the next step without purification.

Step 2: Synthesis of 3-(4-chlorophenyl)butan-2-one

To an ice-cooled solution of crude Weinreb-Nahm amide in 50 mL of Et_2O, was added dropwise 3.0 M methyl magnesium bromide (3.0 eq., 30.0 mmol). A white precipitate quickly appeared. After 1 h, the reaction was quenched with aqueous solution of NH_4Cl. The organic layer was extracted with EtOAc. The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, Pentane/EtOAc = 5:95) to afford the colorless oil (1.03 g, 6.95 mmol, 70%).

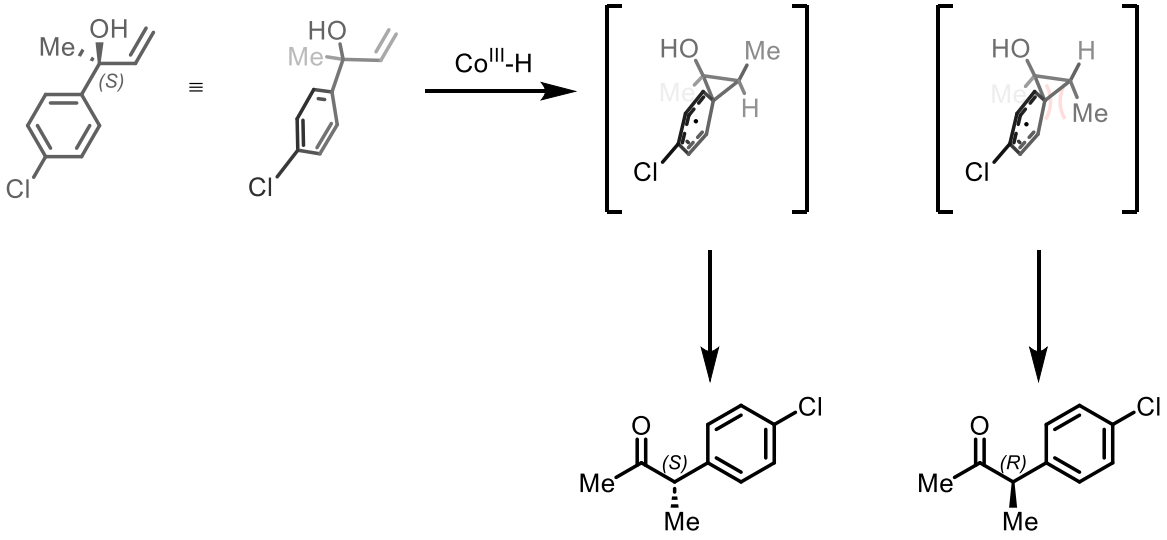


Name NV 231 rac

RT [min]	Type	Area%	Area	Height	Width [min]
3.89	BB	0.24	4.95	0.48	0.16
8.30	MF	49.41	1001.78	87.48	0.19
8.80	FM	50.34	1020.67	83.93	0.20
	Sum	100.00	2027.40		

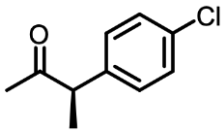
6.2 Stereospecificity - enantiomeric product analysis

Stereochemical model



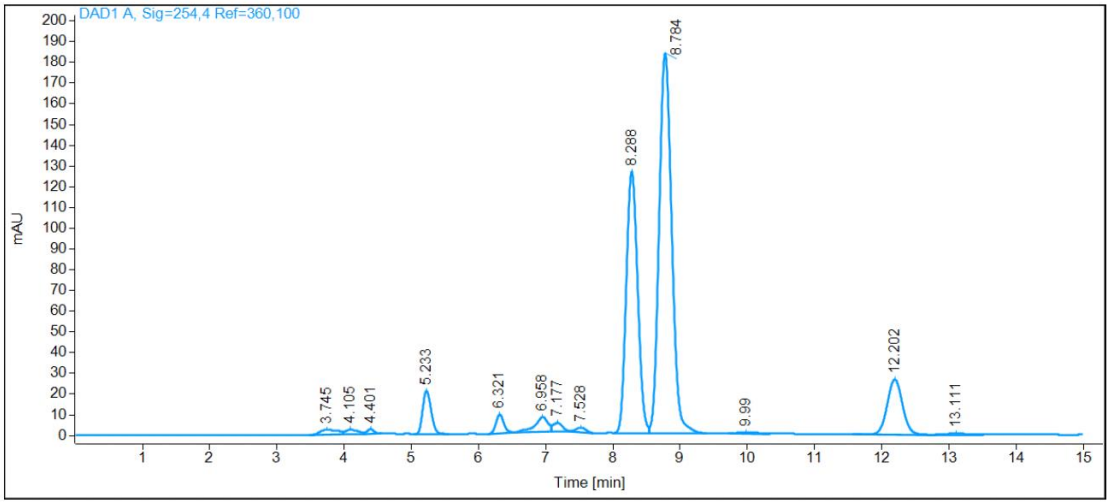
We hypothesize that the conformation during attack by the C-centered radical will influence the stereochemical outcome of these reactions. Cobalt coordination at the alcohol could also occur.

2n-*R* (*R*)-3-(4-chlorophenyl)butan-2-one



(*R*) – 1n in reaction with Co-(*S,S*)

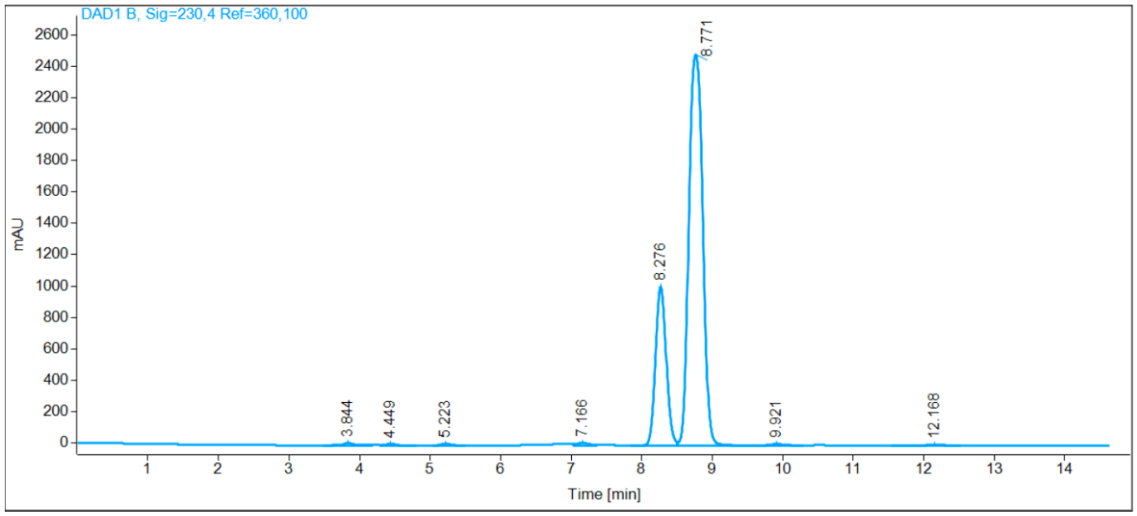
Reaction was carried out on 0.18 mmol scale. The product was isolated as a colorless oil (15.1 mg, 0.08 mmol, 46%). Purification done by column chromatography using pentane: acetone = 95:5.
The retention times (t_R) for the minor and major enantiomers were 8.29 min and 8.78 min with an enantiomeric ratio (*e.r.*) of 38:62.



Name	NV 223				
RT [min]	Type	Area%	Area	Height	Width [min]
3.74	BV	0.93	44.84	2.32	0.27
4.10	VV	0.63	30.35	2.41	0.17
4.40	VB	0.35	17.04	2.38	0.11
5.23	BV	3.77	181.50	20.76	0.14
6.32	BB	1.50	72.19	8.92	0.13
6.96	BV	1.96	94.58	7.10	0.19
7.18	VB	0.82	39.43	4.10	0.15
7.53	BB	0.45	21.81	2.21	0.16
8.29	BV	30.84	1486.21	126.03	0.19
8.78	VB	49.30	2376.21	183.23	0.20
9.99	BV	0.34	16.18	0.81	0.33
12.20	VB	8.75	421.48	26.67	0.24
13.11	BV	0.37	17.61	0.62	0.41
	Sum	100.00	4819.42		

(*R*) – 1n in reaction with Co-(*R,R*).

Reaction was carried out on 0.18 mmol scale. The product was isolated as a colorless oil (16.4 mg, 0.09 mmol, 50%). Purification done by column chromatography using pentane: acetone = 95:5.
The retention times (t_R) for the minor and major enantiomers were 8.28 min and 8.77 min with an enantiomeric ratio (*e.r.*) of 24:76.

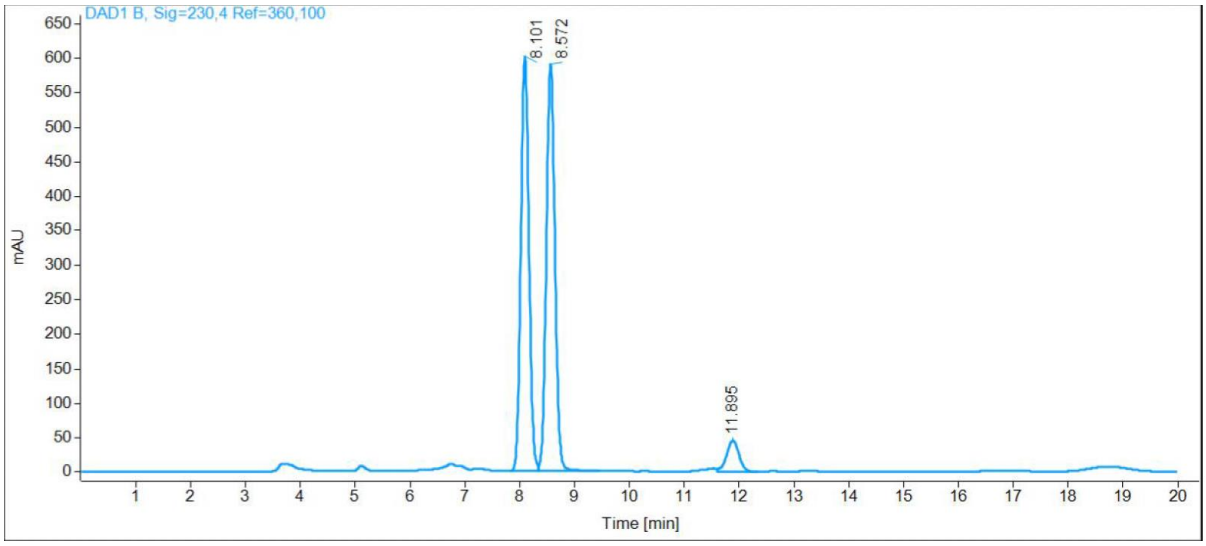


Name NV 234-S2

RT [min]	Type	Area%	Area	Height	Width [min]
3.84	BV	0.46	209.44	18.04	0.16
4.45	VB	0.23	103.61	13.01	0.12
5.22	VV	0.22	98.67	10.41	0.15
7.17	VV	0.47	215.86	15.76	0.20
8.28	BV	23.54	10734.43	1011.68	0.17
8.77	VV	74.54	33982.51	2489.69	0.22
9.92	VV	0.33	152.35	10.00	0.23
12.17	BV	0.21	94.80	5.47	0.27
	Sum	100.00	45591.66		

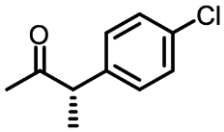
(*R*) – 1n in reaction with Co-salen C

Reaction was carried out on 0.18 mmol scale. The product isolated as a colorless oil (3.84 mg, 0.021 mmol, 12 %). Purification by column chromatography using pentane: acetone = 95:5.
The retention times (t_R) for the two enantiomers were 8.10 min and 8.57 min with an enantiomeric ratio (*e.r.*) of 49:51.



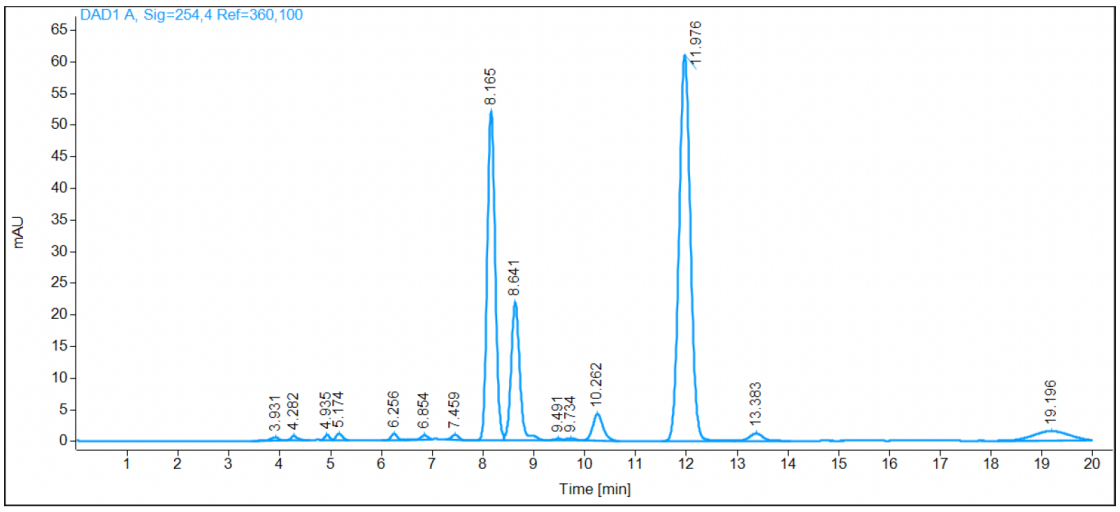
Name	NV 248				
RT [min]	Type	Area%	Area	Height	Width [min]
8.10	BV	46.22	6154.69	601.73	0.16
8.57	VB	48.41	6445.52	590.84	0.17
11.89	BV	67.30	2175.06	140.91	0.24
	Sum	161.92	14775.27		

2n-*S* (*S*)-3-(4-chlorophenyl)butan-2-one



(S)-1n in reaction with Co-(*R,R*).

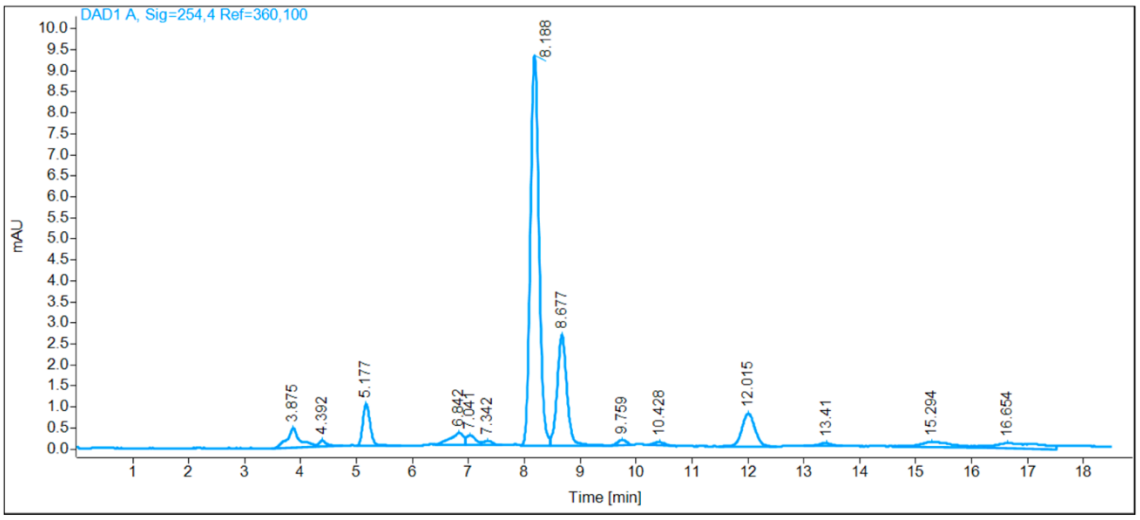
Reaction was carried out on 0.1 mmol scale. The product was isolated as a colorless oil (10.0 mg, 0.055 mmol, 55%). Purification by column chromatography using pentane: acetone = 95:5.
The retention times (t_R) for the major and minor enantiomers were 8.17 min and 8.64 min with an enantiomeric ratio (*e.r.*) of 69:31.



Name	NV 258				
RT [min]	Type	Area%	Area	Height	Width [min]
3.93	BV	0.36	7.06	0.53	0.18
4.28	VB	0.38	7.63	0.77	0.14
4.94	BV	0.27	5.35	0.83	0.10
5.17	VB	0.44	8.67	1.02	0.14
6.26	BB	0.41	8.20	1.02	0.13
6.85	BV	0.35	6.97	0.71	0.15
7.46	BB	0.39	7.72	0.82	0.15
8.17	BV	28.68	568.53	52.00	0.17
8.64	VB	13.00	257.82	21.76	0.18
9.49	BV	0.15	3.02	0.25	0.18
9.73	VV	0.24	4.84	0.37	0.20
10.26	VB	3.08	61.11	4.25	0.22
11.98	BV	47.47	941.11	61.00	0.24
13.38	VB	1.12	22.21	1.18	0.29
19.20	BBA	3.65	72.35	1.48	0.64
	Sum	100.00	1982.60		

(*S*)-1n in reaction with Co-(*S,S*).

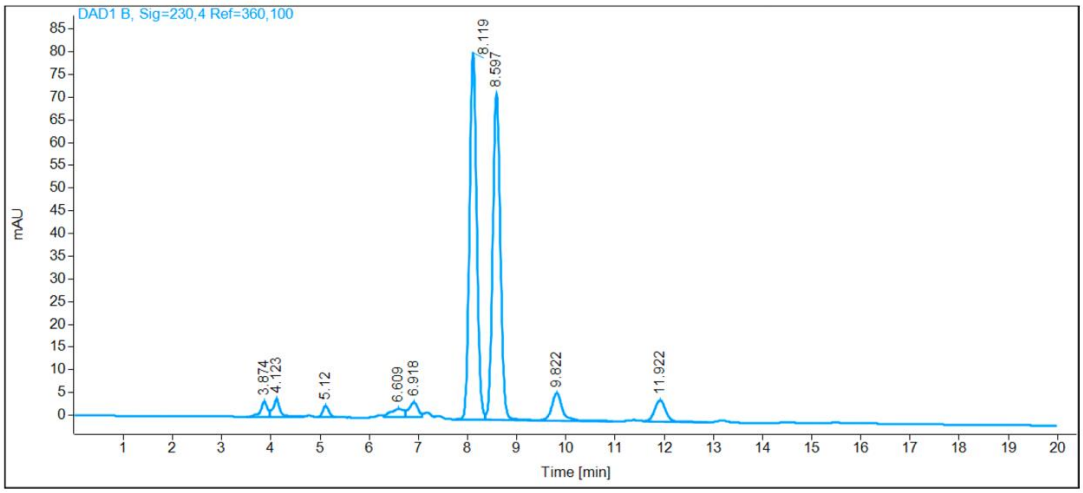
Reaction was carried out on 0.1 mmol scale. The product was isolated as a colorless oil (4.2 mg, 0.023 mmol, 23%). Purification by column chromatography using pentane: acetone = 95:5. The retention times (t_R) for the major and minor enantiomers were 8.18 min and 8.68 min with an enantiomeric ratio (*e.r.*) of 75:25.



Name	NV 265				
RT [min]	Type	Area%	Area	Height	Width [min]
3.87	BV	4.08	7.57	0.47	0.22
4.39	VB	0.87	1.62	0.15	0.16
5.18	BB	4.95	9.18	0.99	0.14
6.84	BV	2.44	4.53	0.28	0.22
7.04	VV	1.38	2.55	0.22	0.18
7.34	VB	0.60	1.11	0.09	0.18
8.19	BV	52.73	97.82	9.27	0.16
8.68	VB	17.31	32.12	2.63	0.19
9.76	BB	0.74	1.38	0.13	0.16
10.43	BB	0.60	1.11	0.08	0.17
12.01	BB	6.88	12.76	0.78	0.25
13.41	BB	0.65	1.21	0.07	0.23
15.29	MM	2.91	5.41	0.13	0.70
16.65	MM	3.85	7.15	0.13	0.95
	Sum	100.00	185.50		

(*S*)-1n with Fe(acac)$_3$

Reaction was carried out according to the literature[33]
Reaction was carried out on 0.1 mmol scale. The product was isolated as a pale red oil (2.4 mg, 0.013 mmol, 13%). Purification was done by column chromatography using pentane: acetone = 95:5. The retention times (t_R) for the two enantiomers were 8.12 min and 8.60 min with an enantiomeric ratio (*e.r.*) of 51:49.



Name NV 280 up

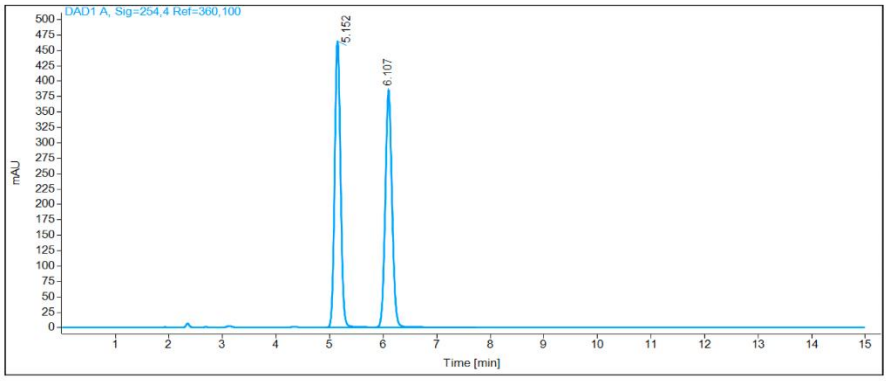
RT [min]	Type	Area%	Area	Height	Width [min]
3.87	BV	1.75	33.88	3.42	0.15
4.12	VV	2.11	40.87	3.97	0.14
5.12	BB	1.10	21.28	2.47	0.14
6.61	VV	1.82	35.17	1.89	0.25
6.92	VV	2.16	41.91	3.22	0.20
8.12	BV	42.37	820.67	80.81	0.16
8.60	VB	40.11	776.91	72.05	0.17
9.82	BB	4.60	89.12	6.05	0.22
11.92	VV	3.98	77.07	4.74	0.25
	Sum	100.00	1936.88		

6.3 Stereospecificity – product reactivity

The ketone product **2a** (1,2-diphenylpropan-1-one) was subjected to the optimised reaction conditions as described in section 3.8. The enantiomeric ratio of the ketone product was analysed by HPLC. The chiral HPLC conditions were as follows: Chiralpak IG column, dimensions 150 x 4.6 mm, particle size 5µ, mobile phase 97:3 n-hexane/ethyl alcohol (EtOH) at a flow rate of 1.0 mL/min with 26 bar starting pressure and 20 °C.

2a (1,2-diphenylpropan-1-one) in the reaction with Co-(S,S)

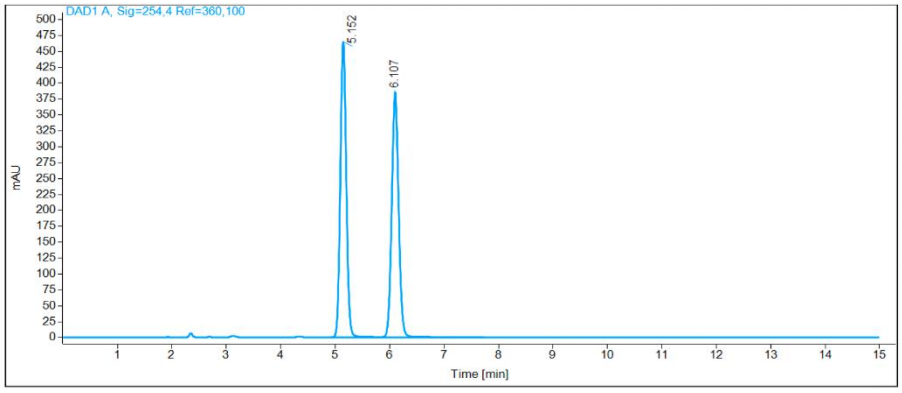
Reaction was carried out on 0.18 mmol scale. The ketone product recovered as a yellow oil (23.0 mg, 0.11 mmol, 62%). The retention times (t_R) for the two enantiomers were 5.15 min and 6.11 min with an enantiomeric ratio (e.r.) of 50:50.



Name	NV 210				
RT [min]	Type	Area%	Area	Height	Width [min]
5.15	VB	50.04	3511.86	464.94	0.12
6.11	BB	49.96	3506.30	385.13	0.14
	Sum	100.00	7018.16		

2a (1,2-diphenylpropan-1-one) in the reaction with Co-(R,R)

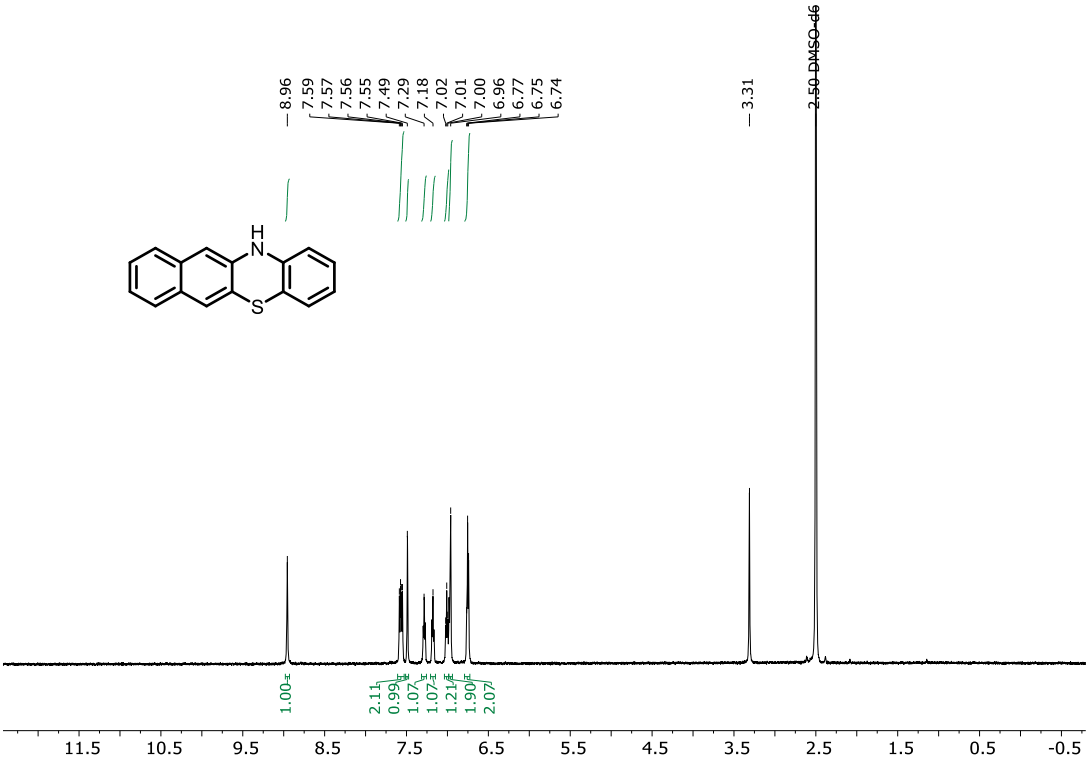
Reaction was carried out on 0.18 mmol scale. The ketone product recovered as a yellow oil (33.9 mg, 0.16 mmol, 90%). The retention times (t_R) for the two enantiomers were 5.14 min and 6.07 min with an enantiomeric ratio (e.r.) of 50:50.

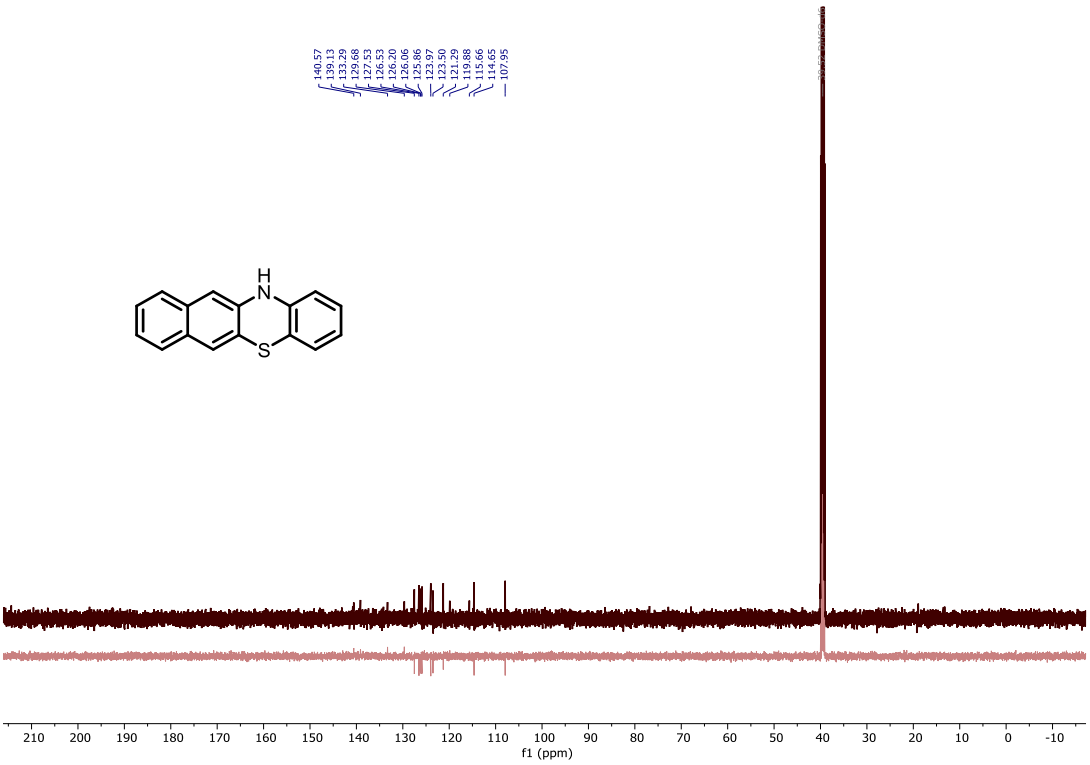


Name	NV 210				
RT [min]	Type	Area%	Area	Height	Width [min]
5.15	VB	50.04	3511.86	464.94	0.12
6.11	BB	49.96	3506.30	385.13	0.14
	Sum	100.00	7018.16		

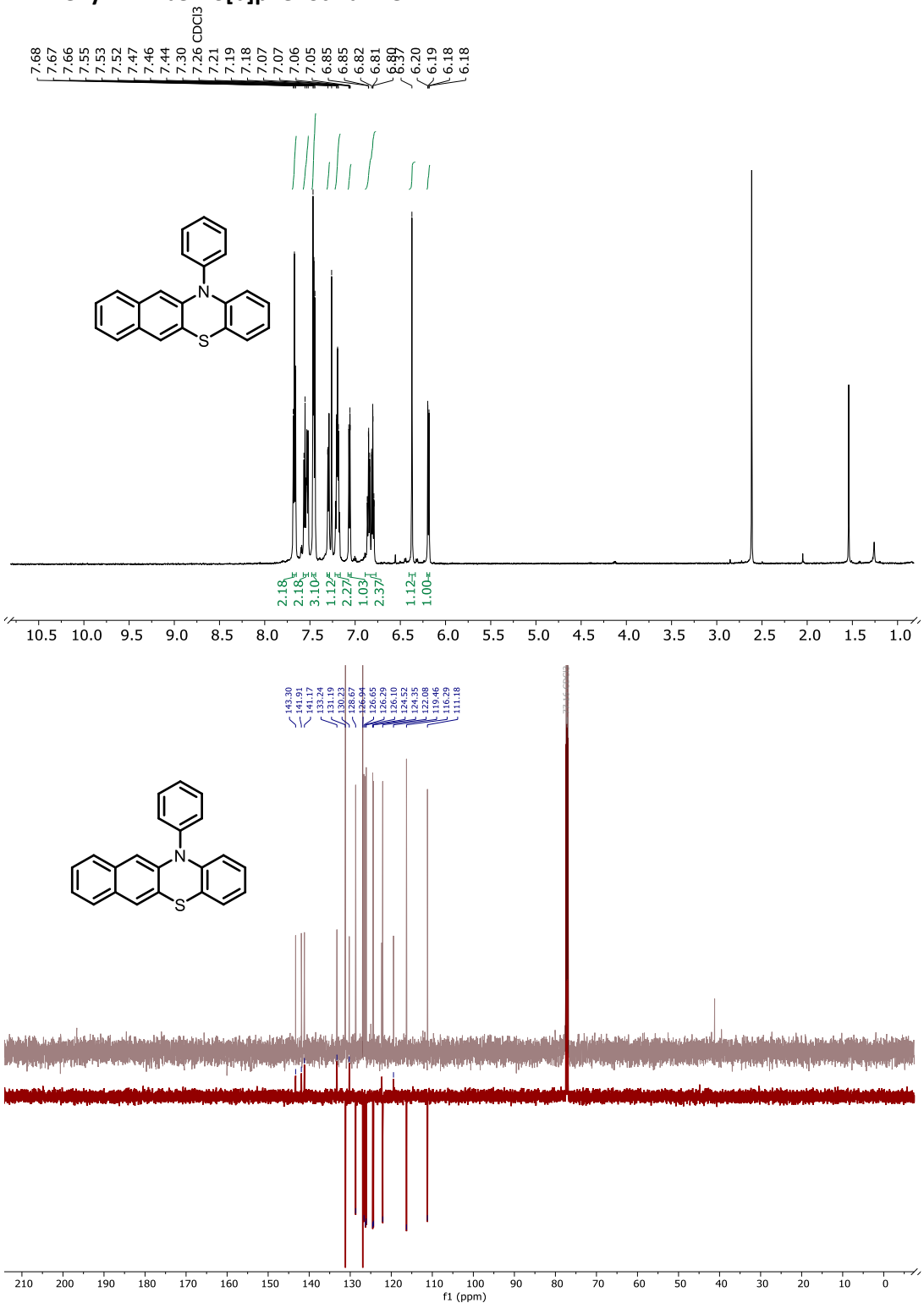
7. SPECTRA

Benzo[*b*]phenothiazine

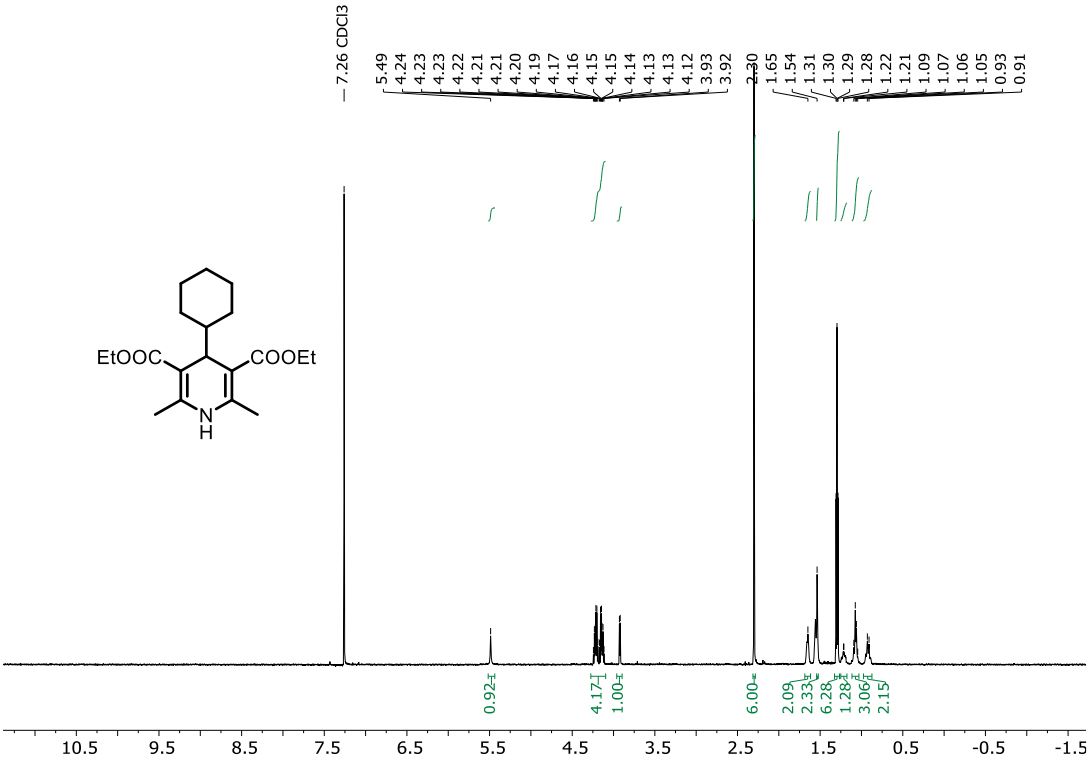


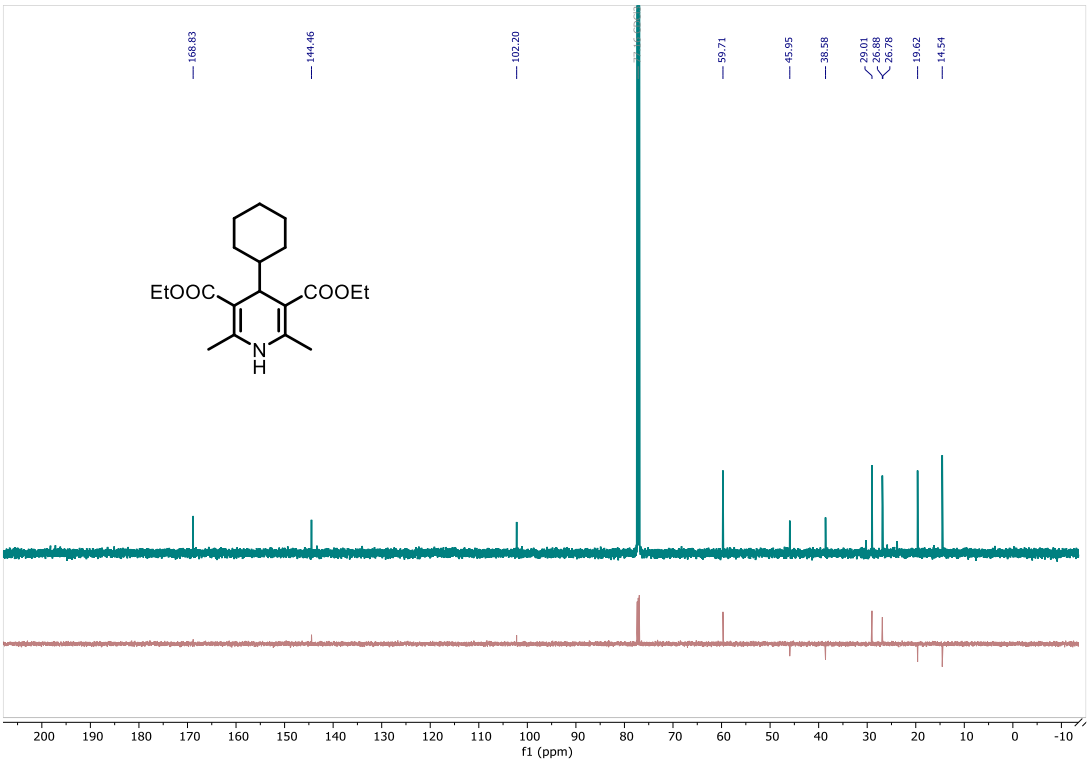


12-Phenyl-12H-benzo[*b*]phenothiazine

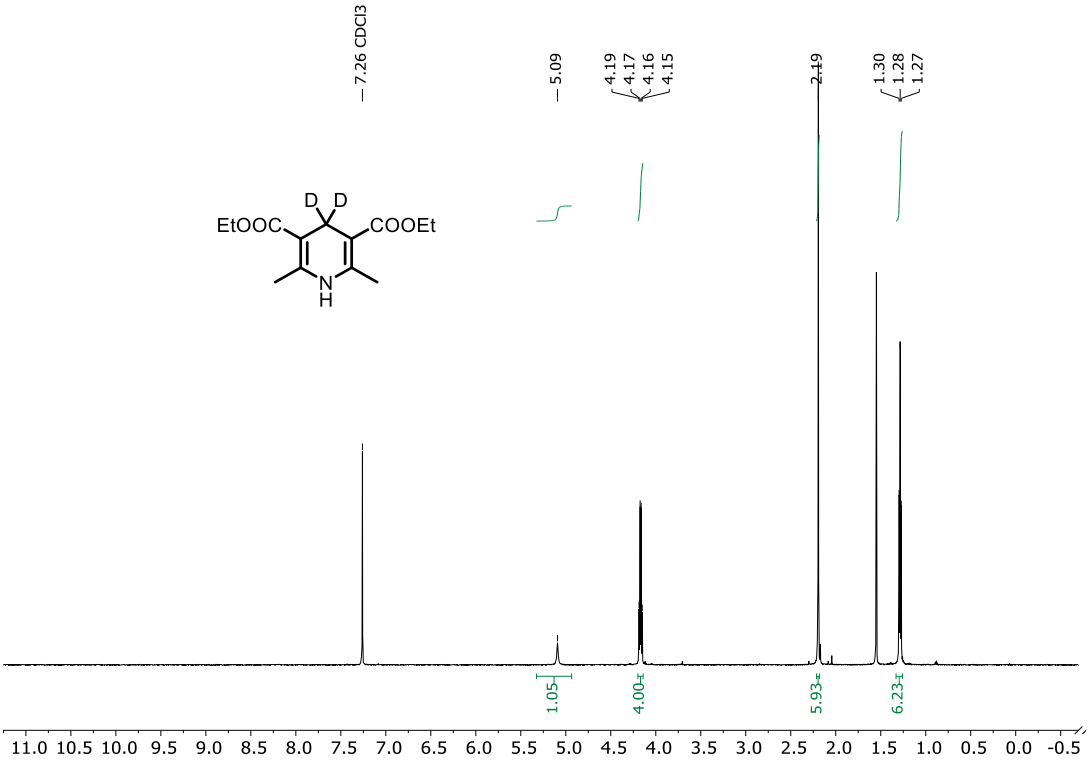


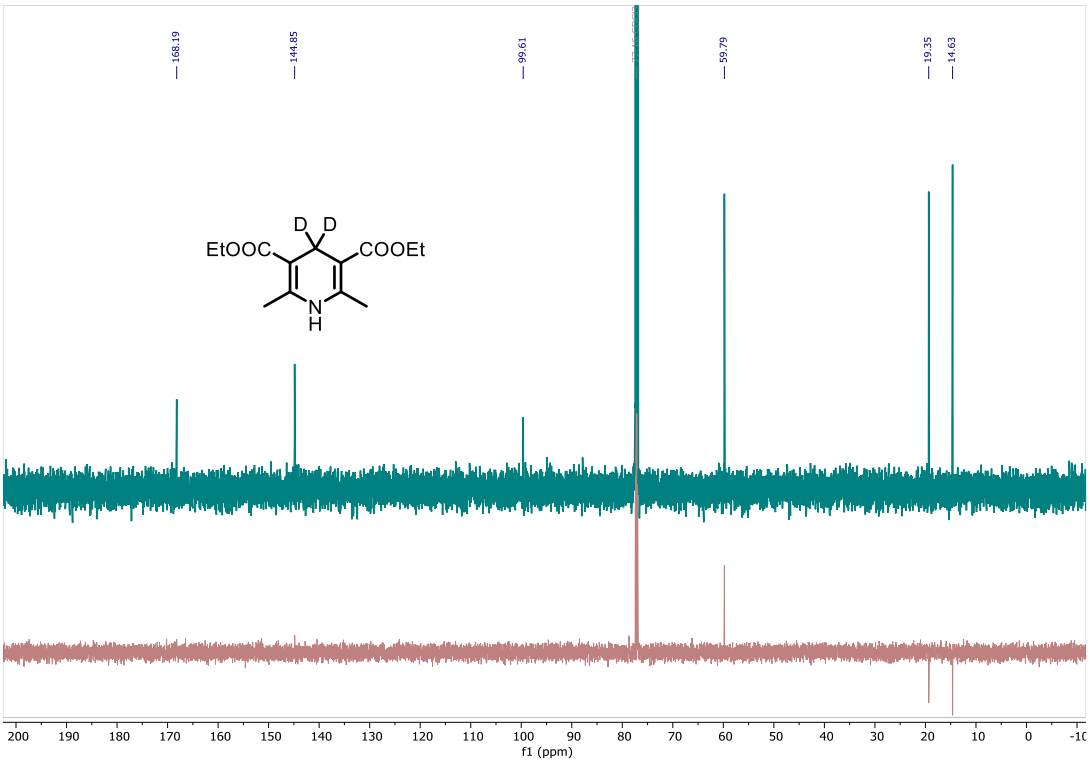
HEH-Cy (Diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate)



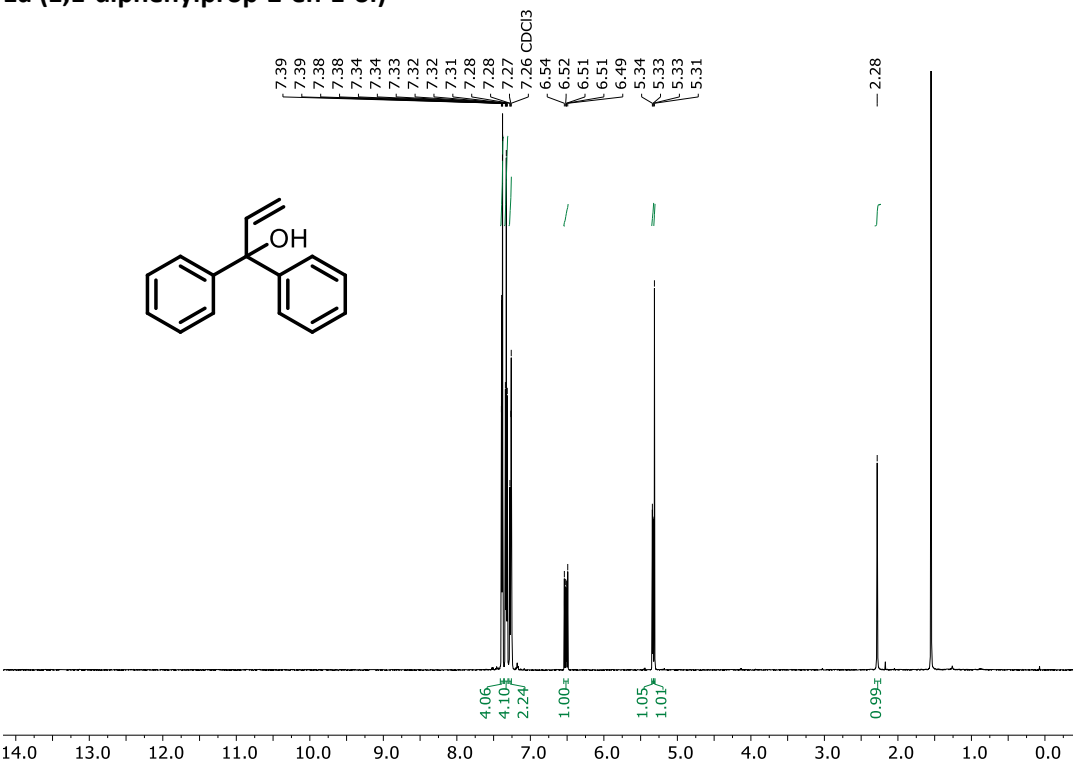


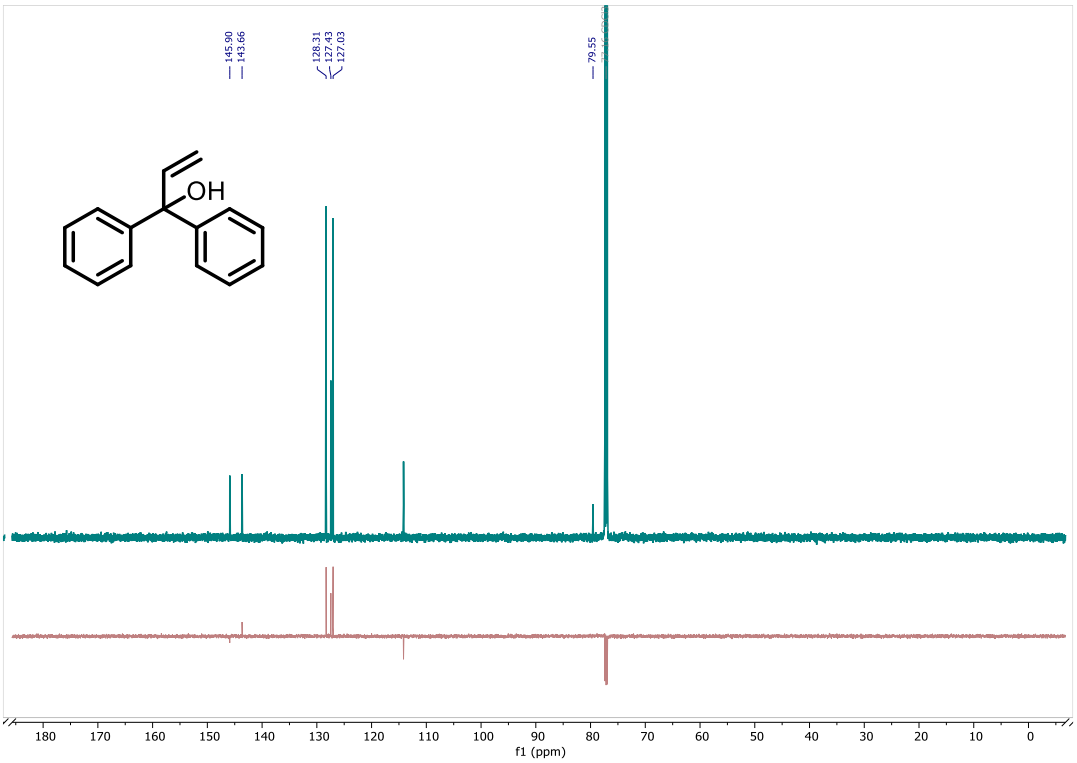
HEH-D4 (Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-4,4-d2)



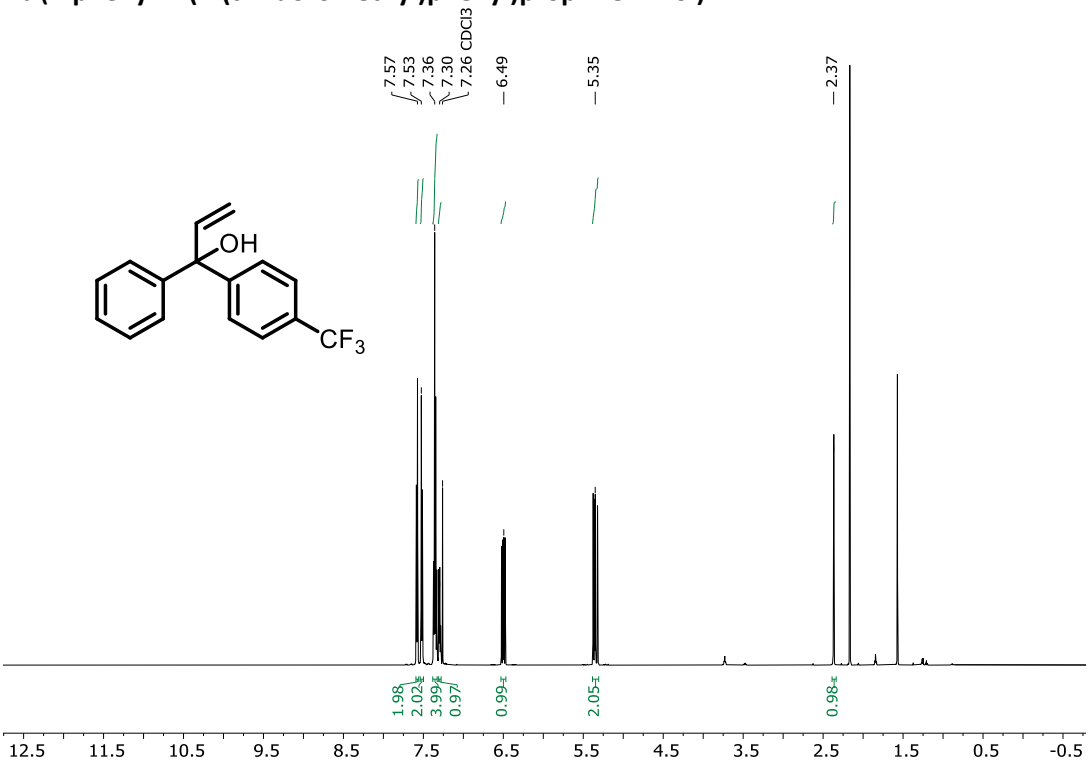


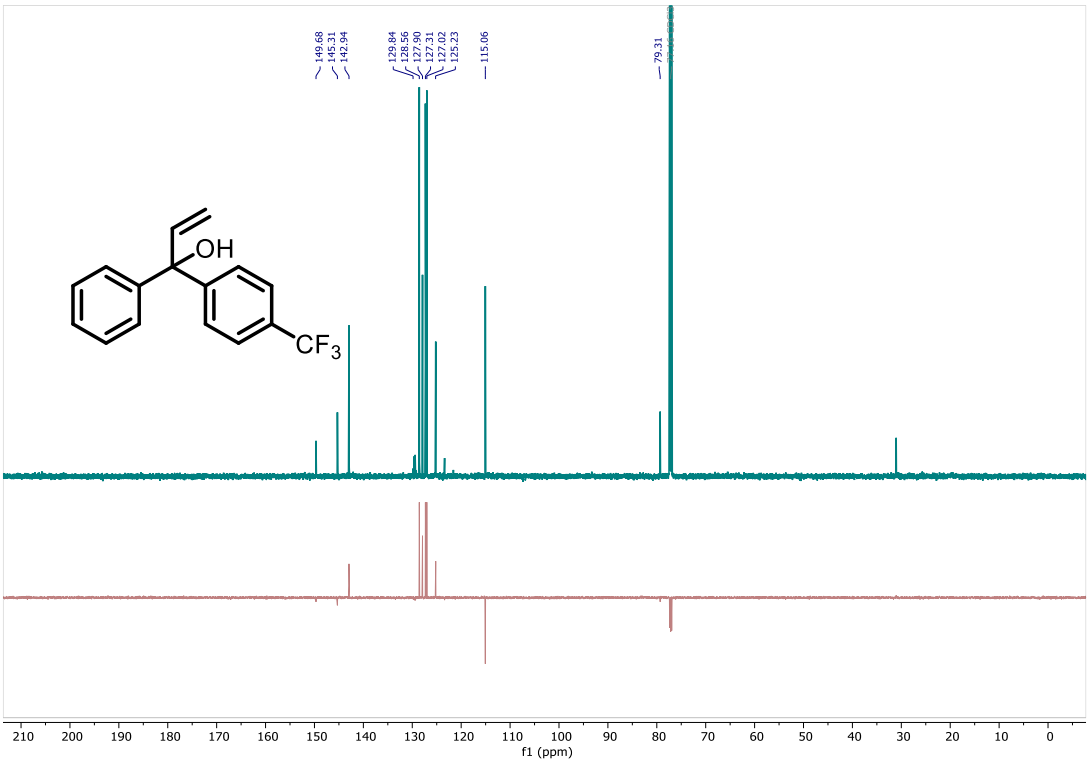
1a (1,1-diphenylprop-2-en-1-ol)

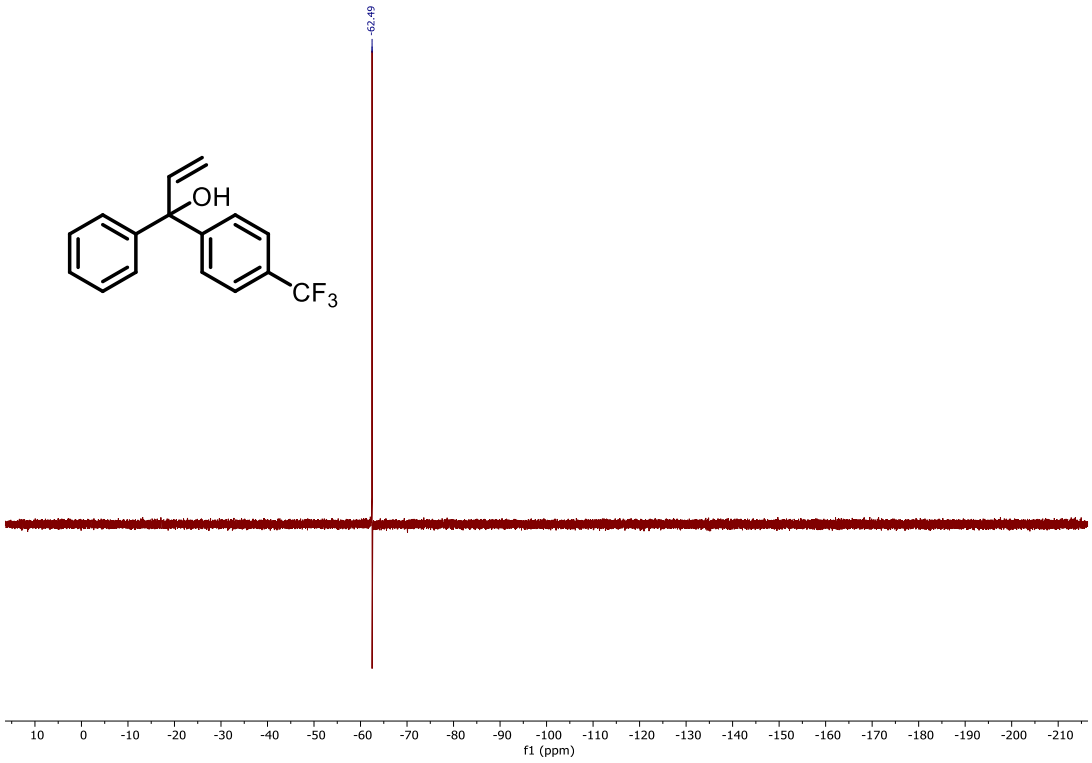




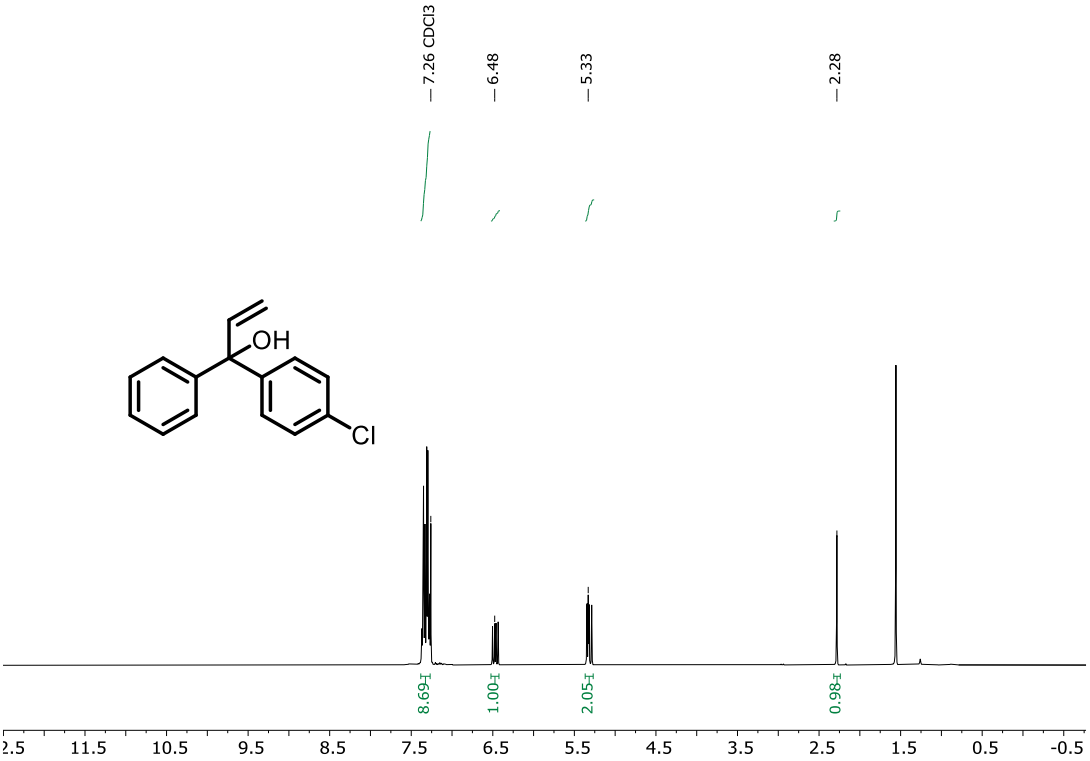
1b (1-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol)

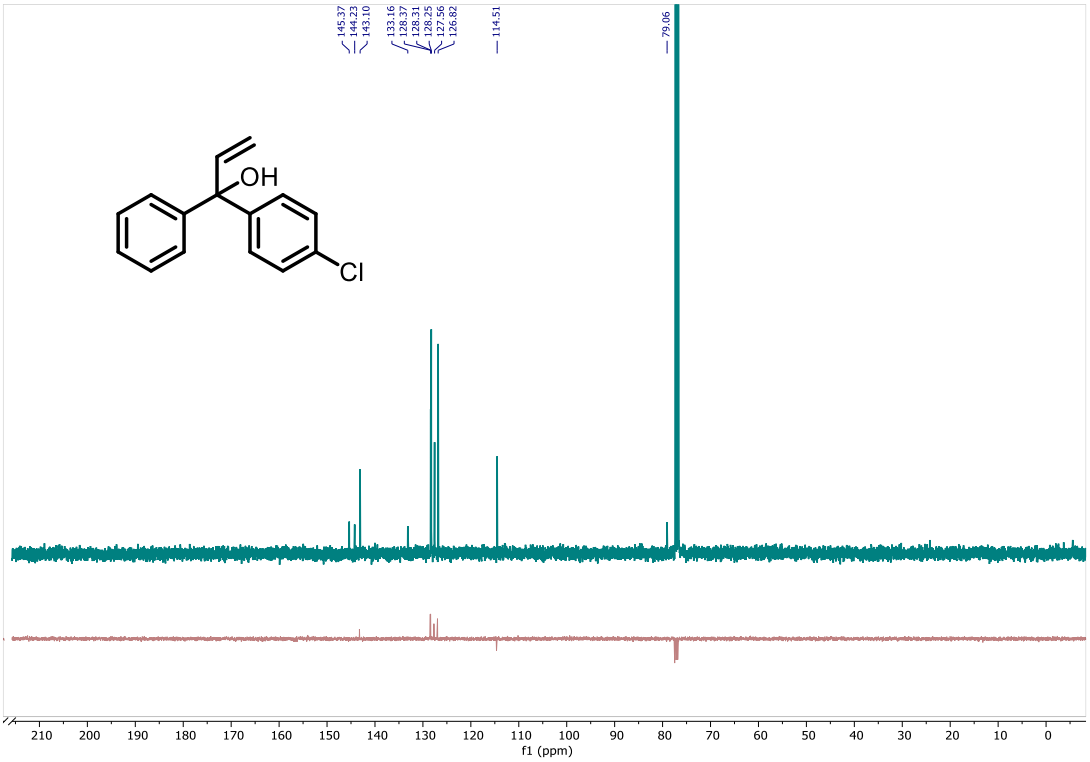




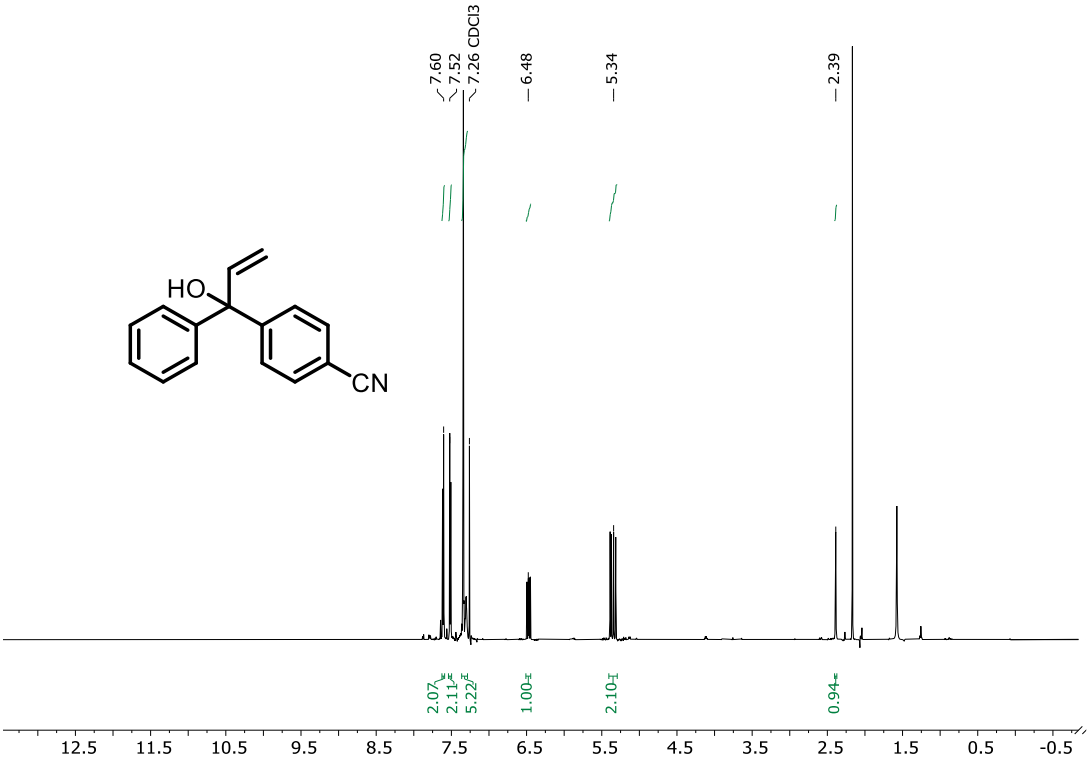

-62,49
OH
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

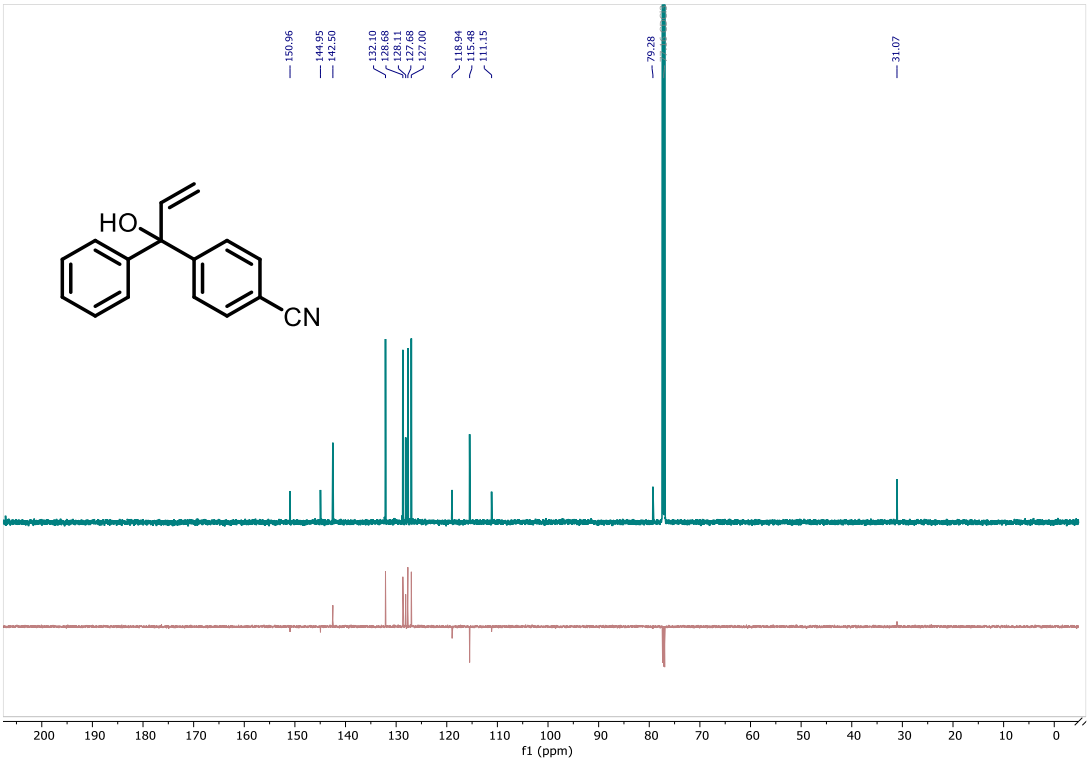
1c (1-(4-chlorophenyl)-1-phenylprop-2-en-1-ol)



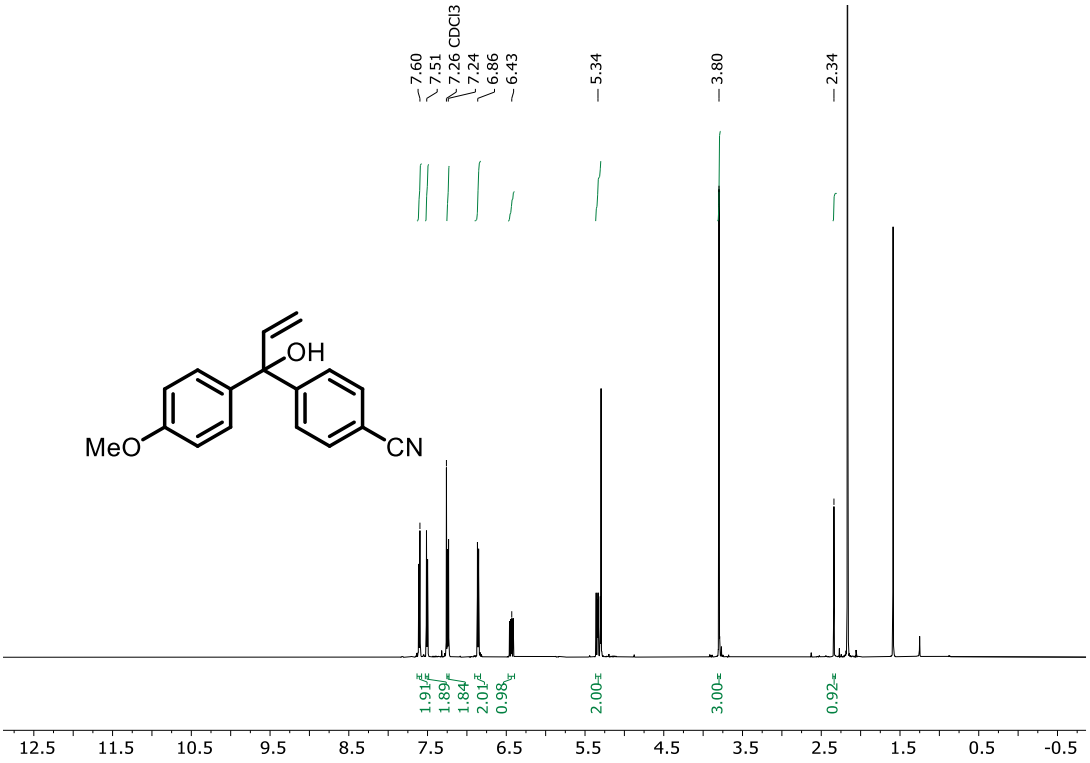


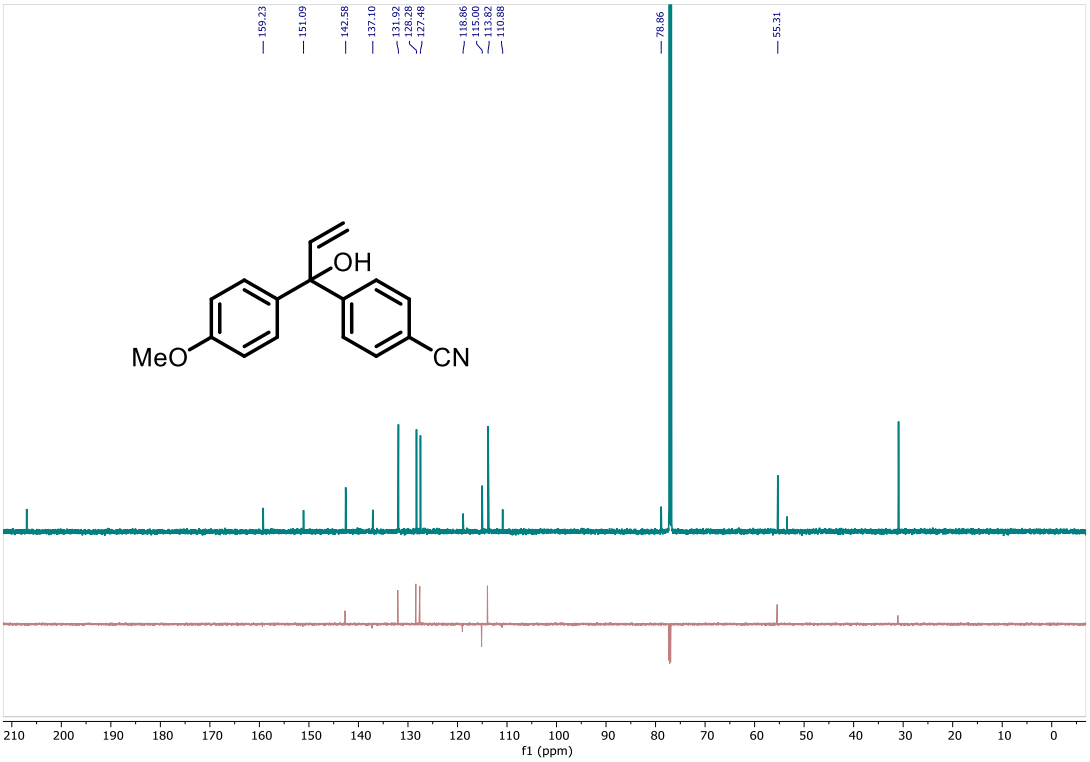
1d (4-(1-hydroxy-1-phenylallyl)benzonitrile)



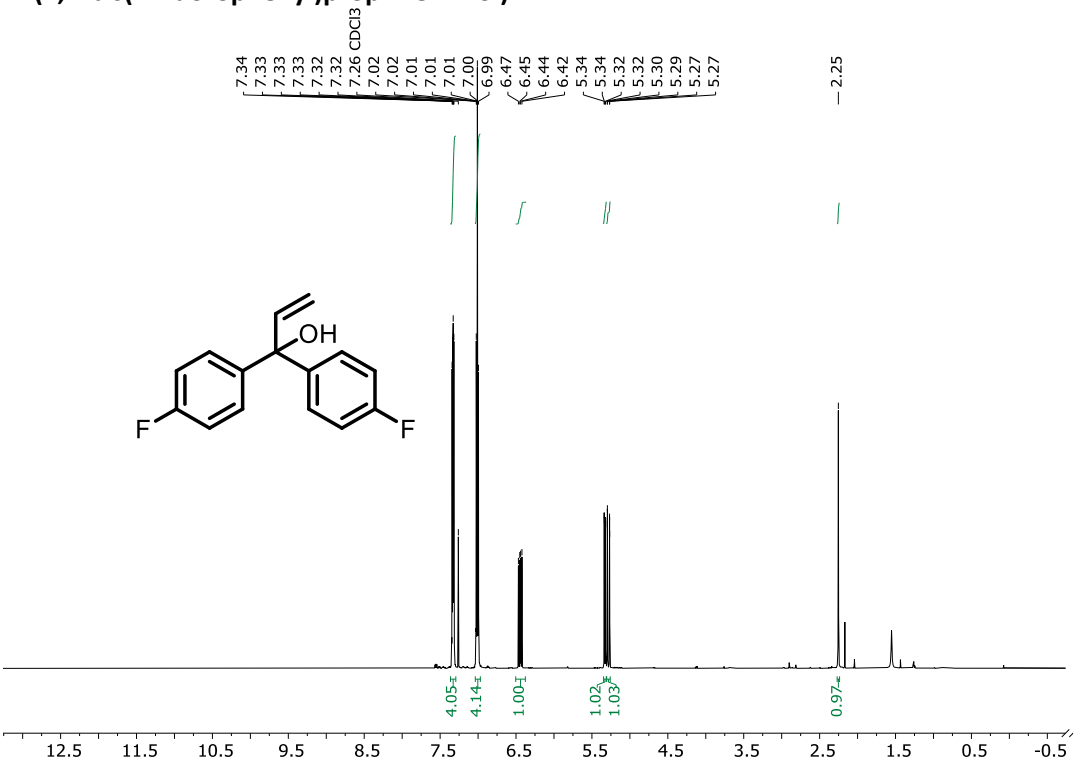


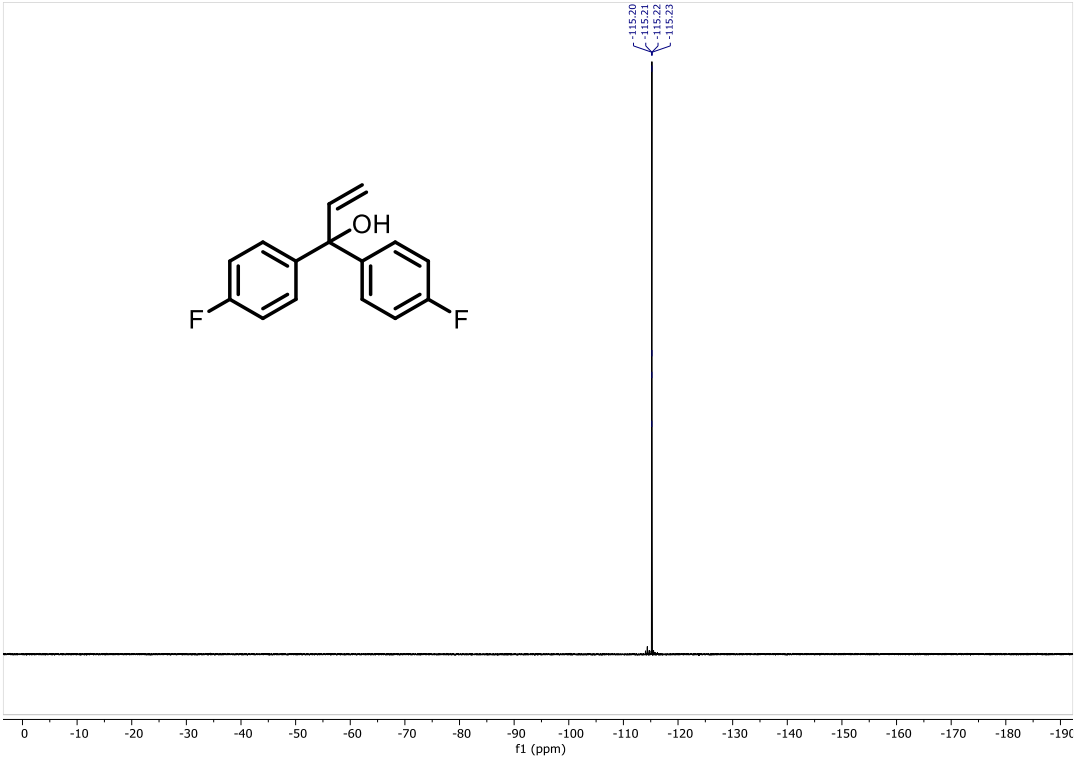
1e (4-(1-hydroxy-1-(4-methoxyphenyl)allyl)benzonitrile)

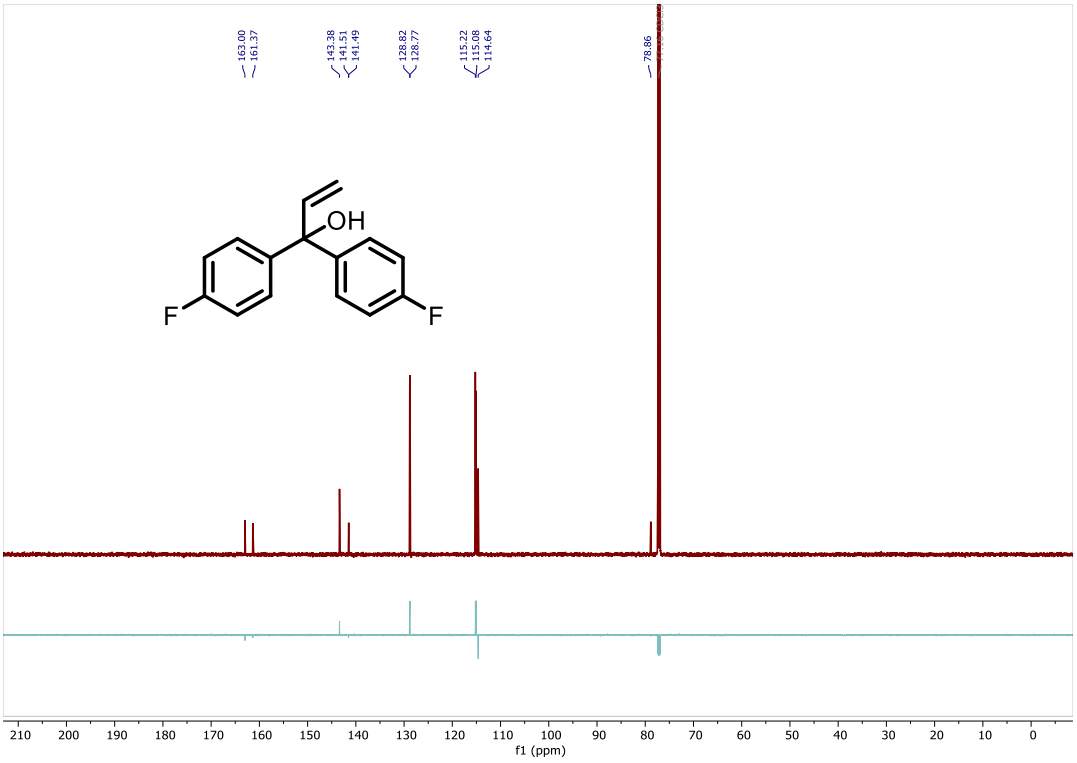




1f (1,1-bis(4-fluorophenyl)prop-2-en-1-ol)



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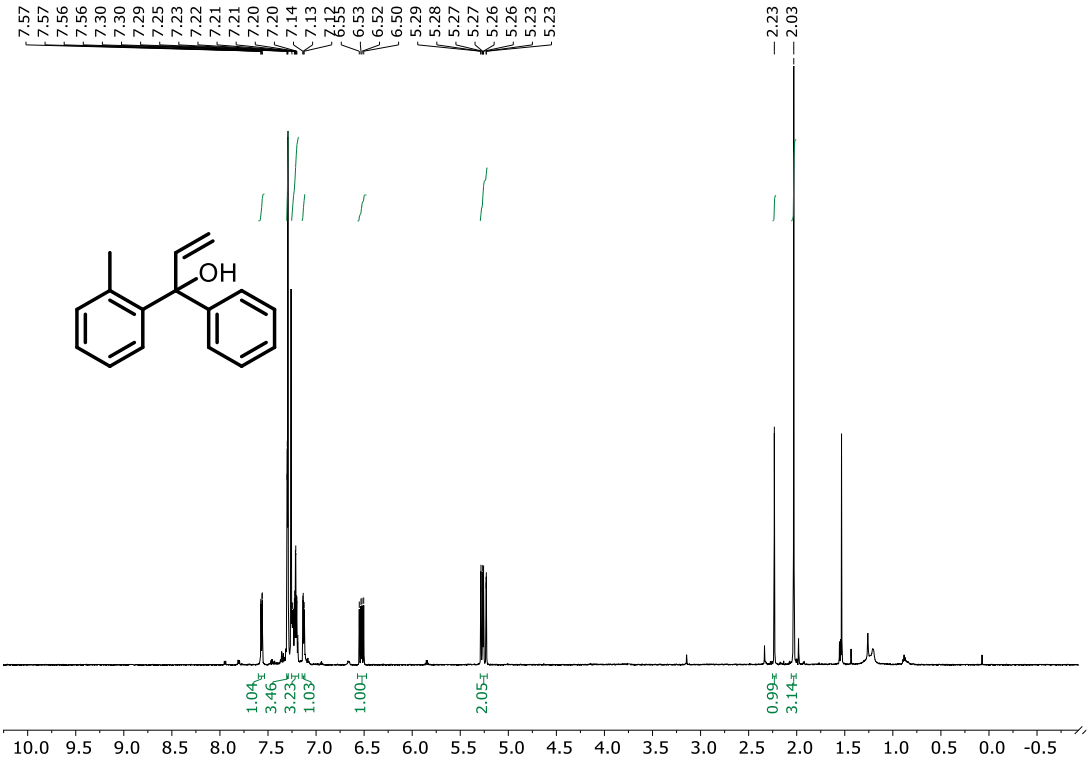
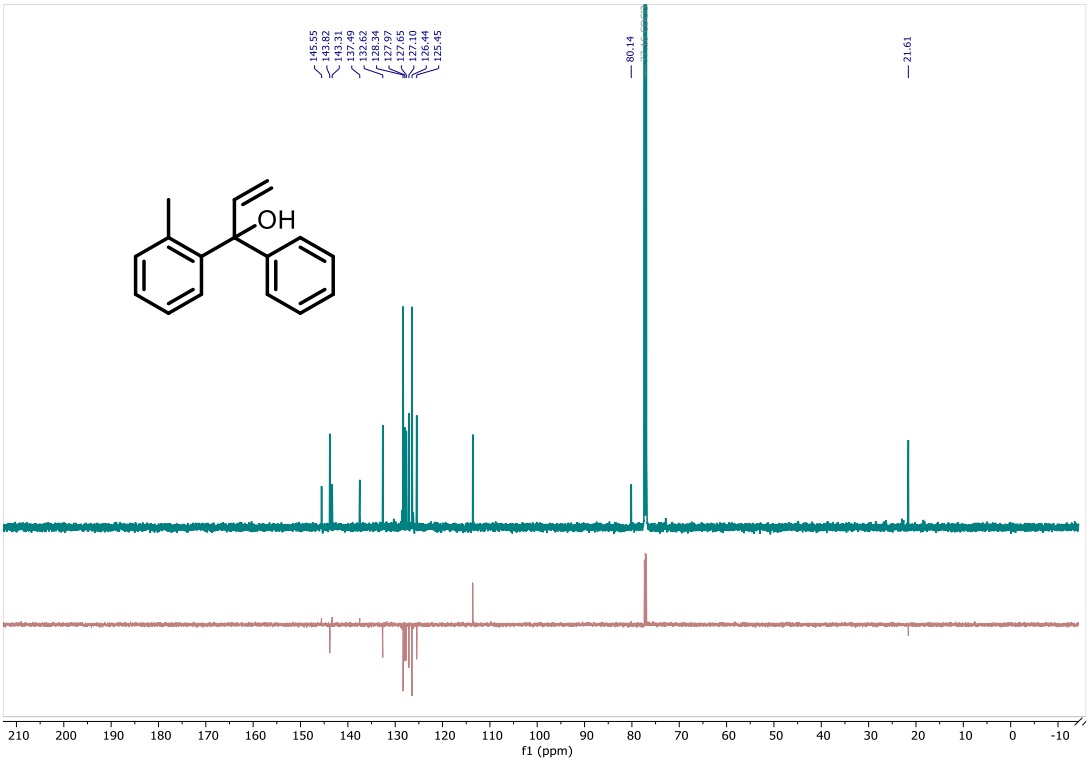
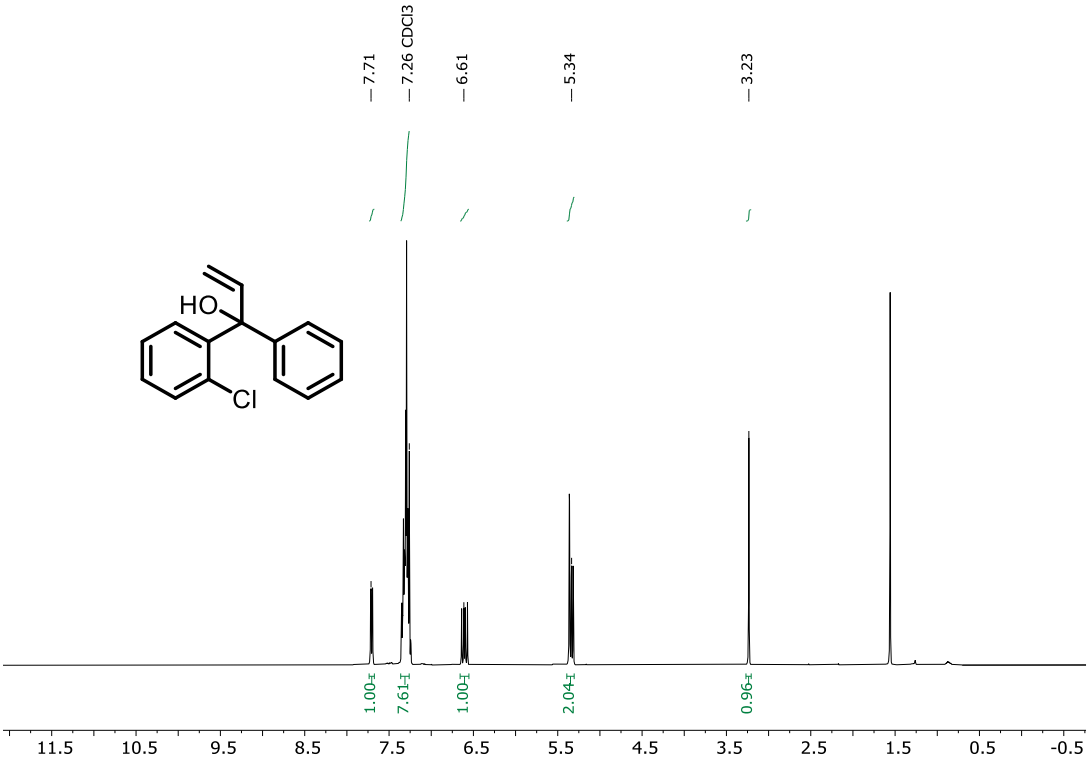
161.37
143.38
141.51
141.49
128.82
128.77
115.22
115.08
114.64
78.86
OH
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

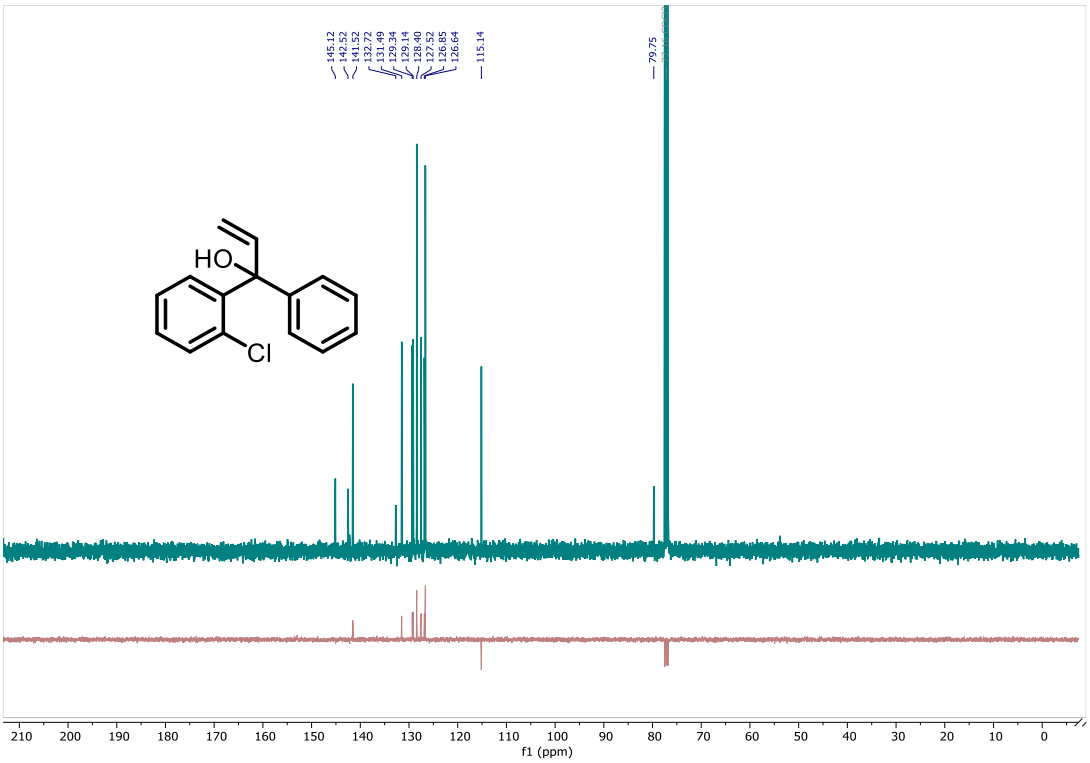
1g (1-phenyl-1-(o-tolyl)prop-2-en-1-ol)



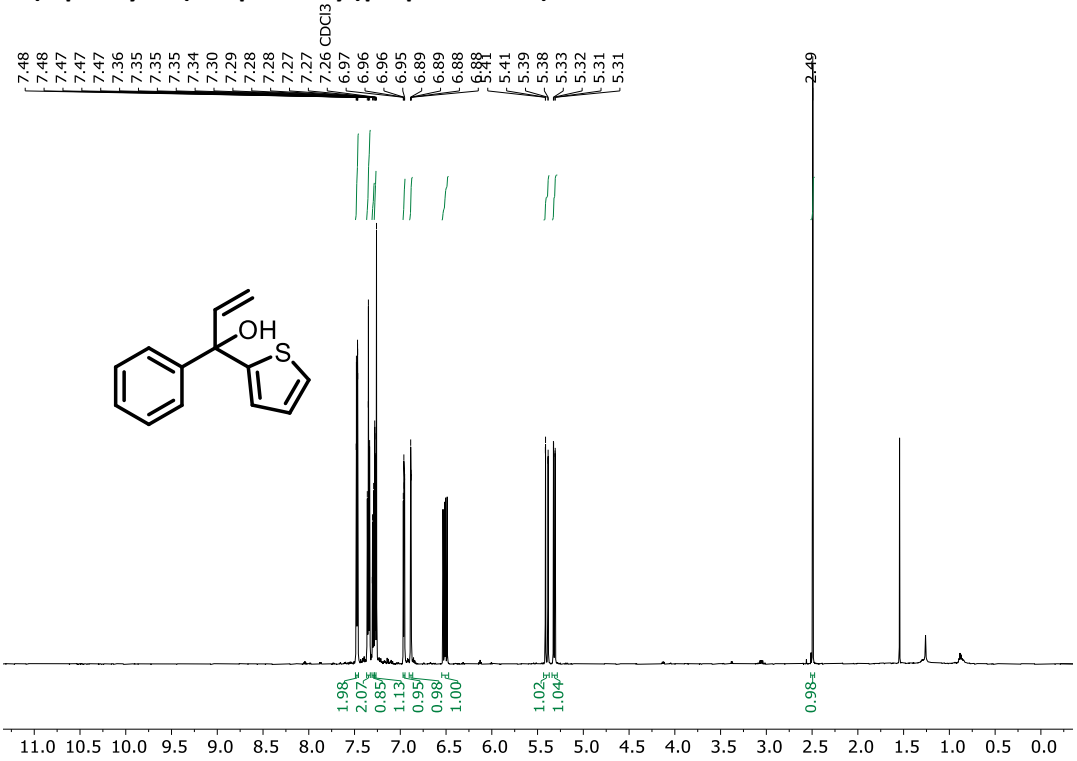


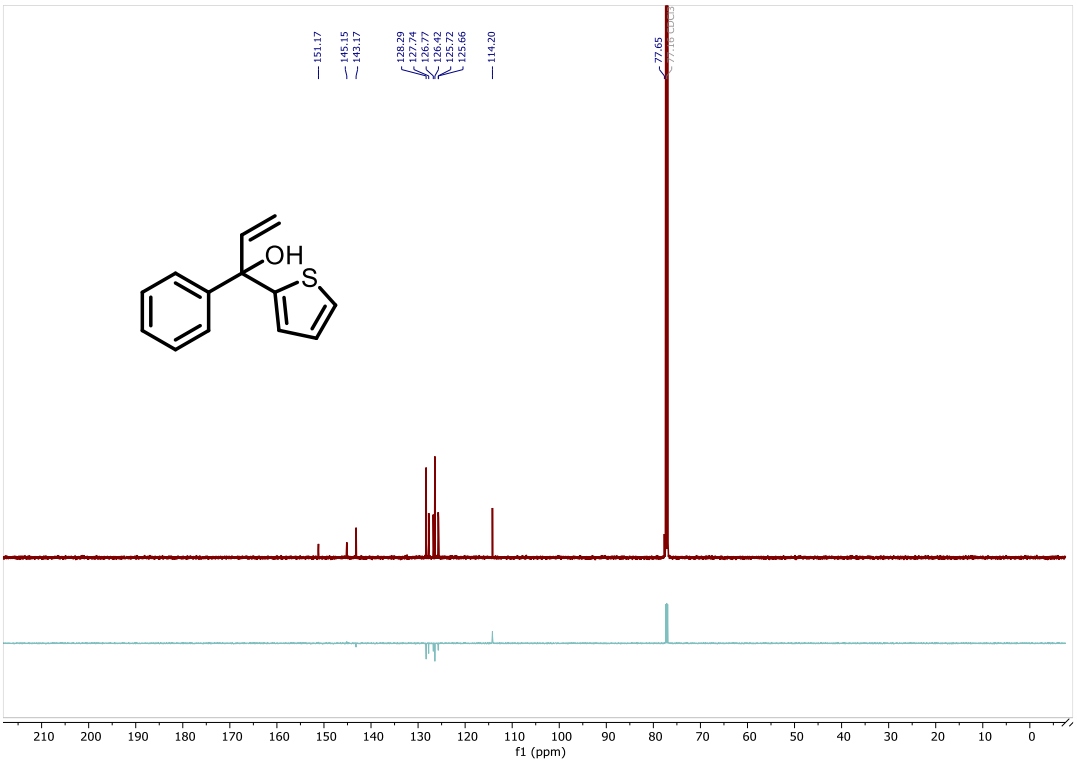
1h (1-(2-chlorophenyl)-1-phenylprop-2-en-1-ol)



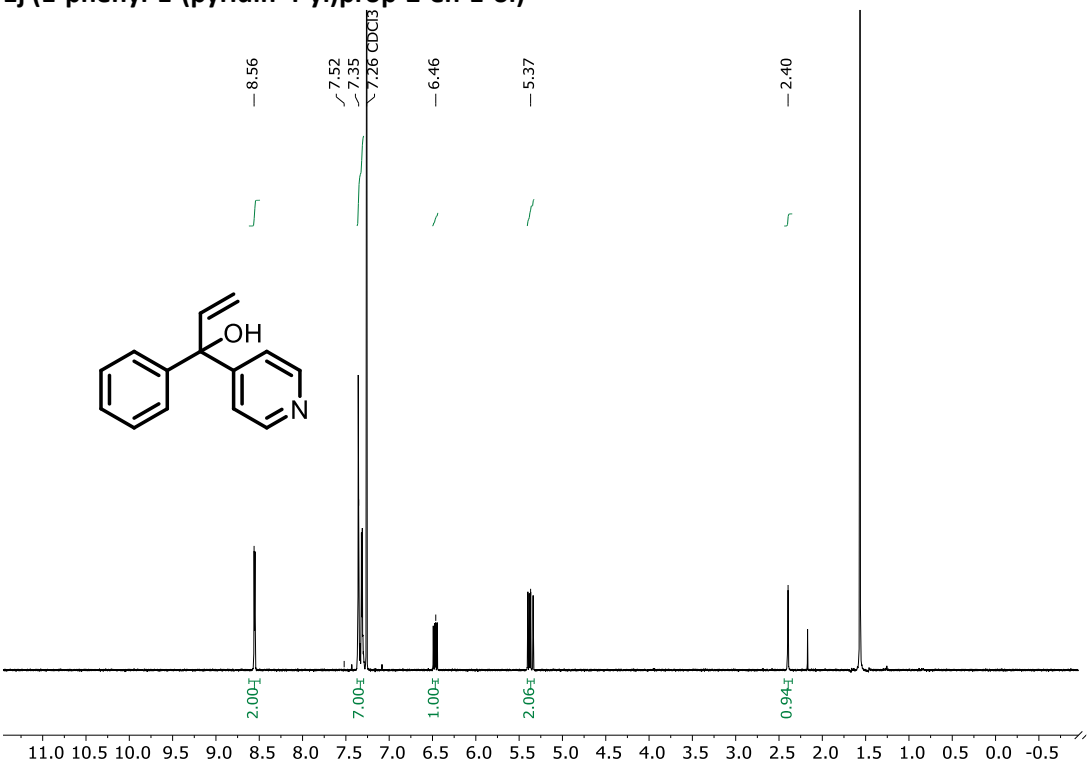


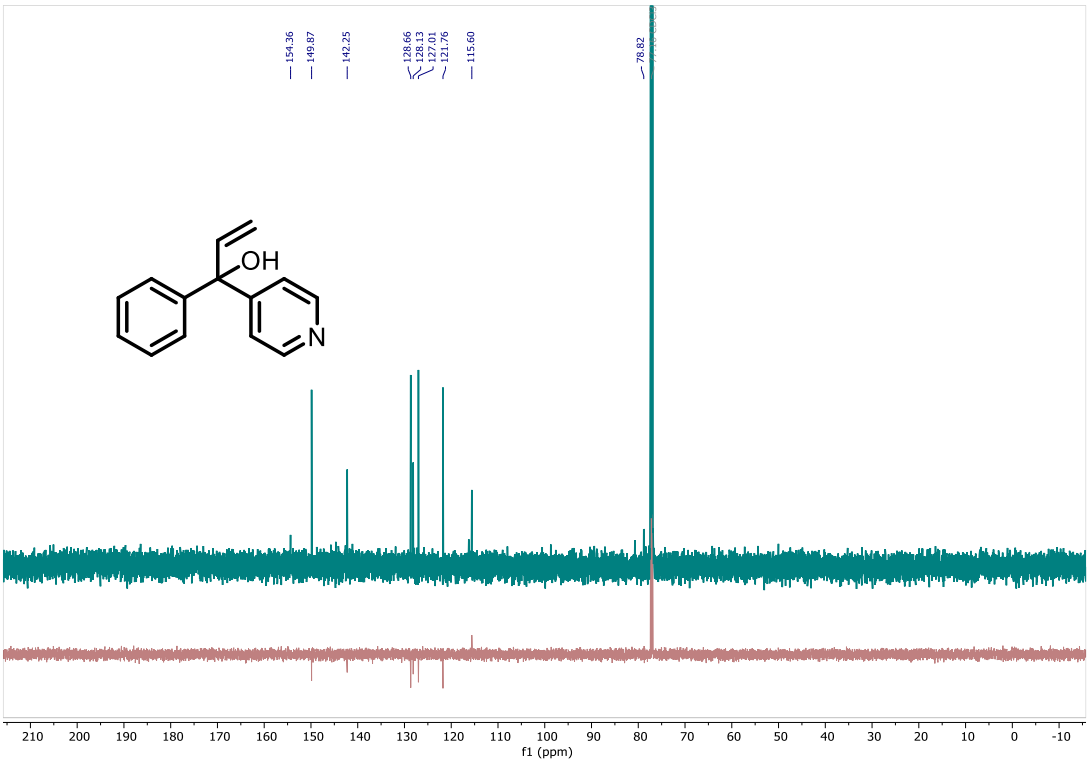
1i (1-phenyl-1-(thiophen-2-yl)prop-2-en-1-ol)



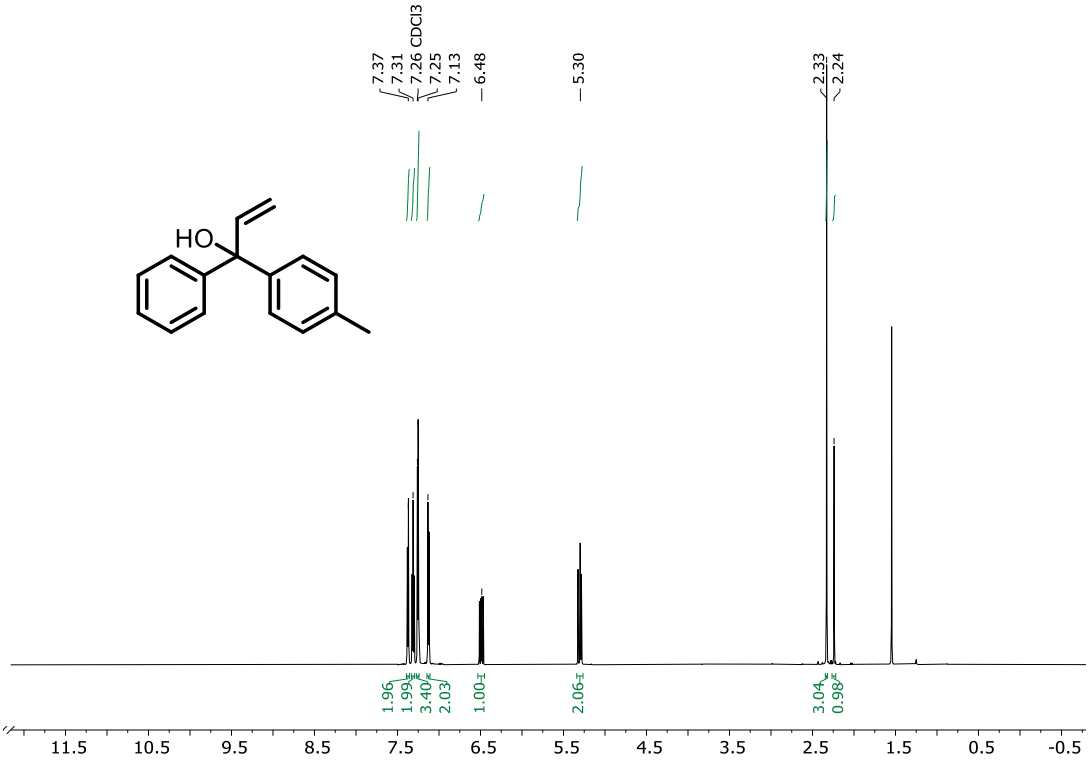


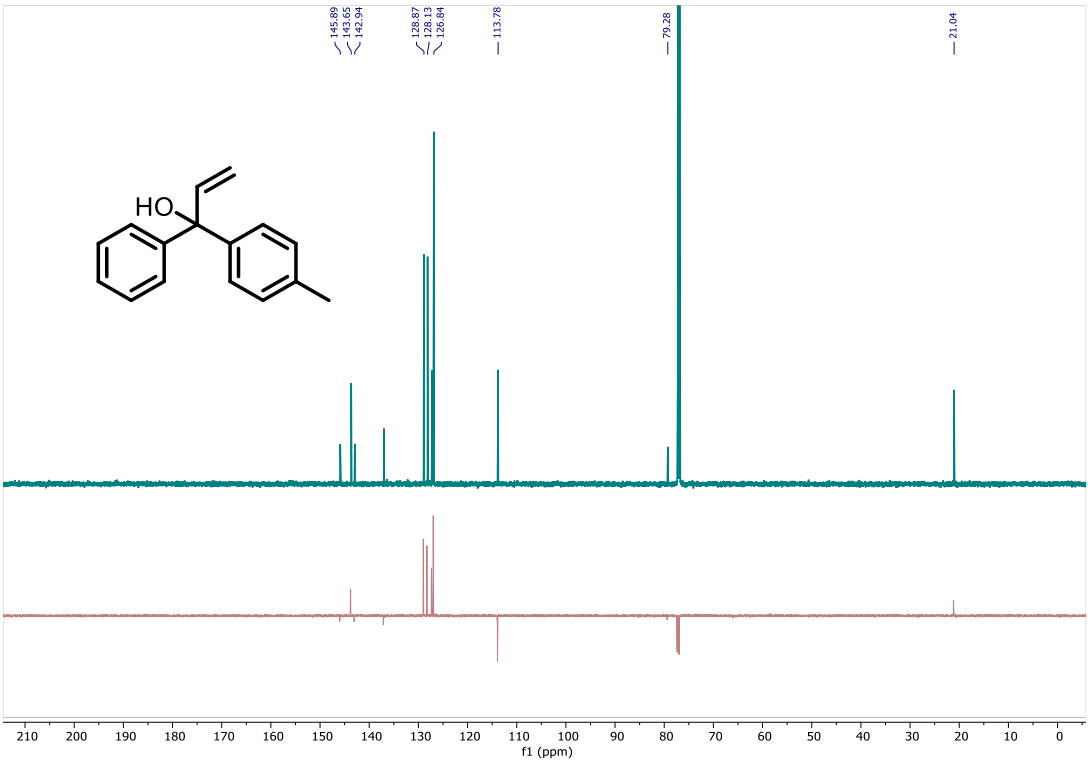
1j (1-phenyl-1-(pyridin-4-yl)prop-2-en-1-ol)



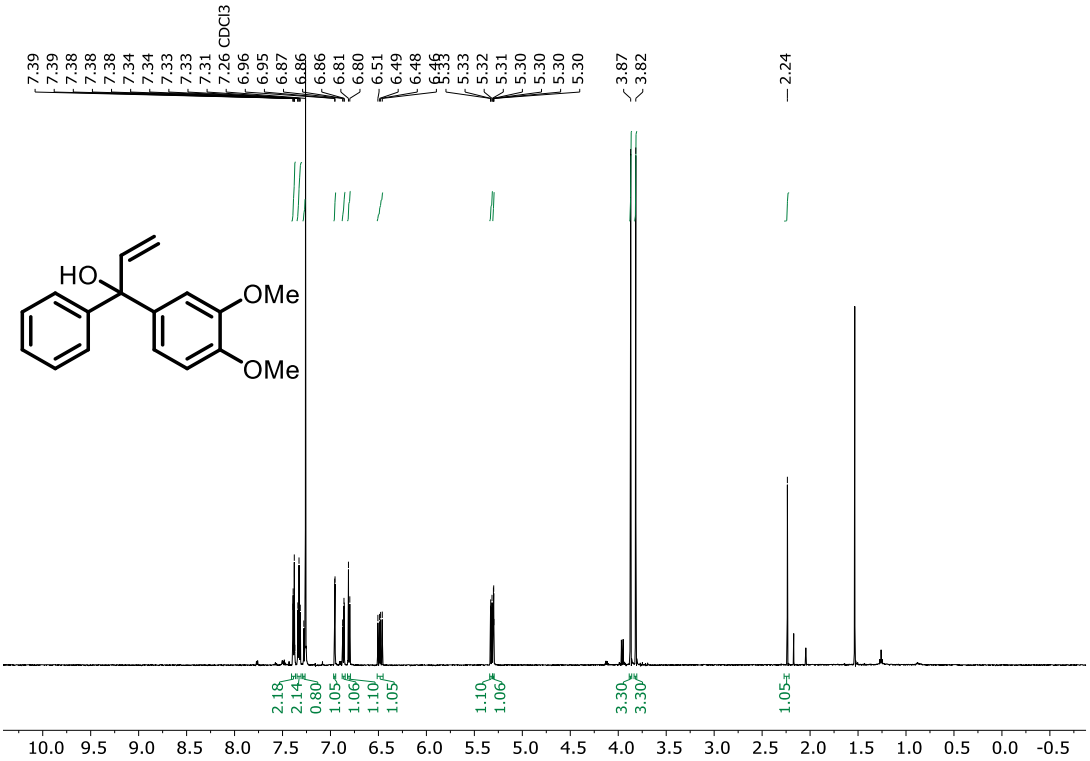


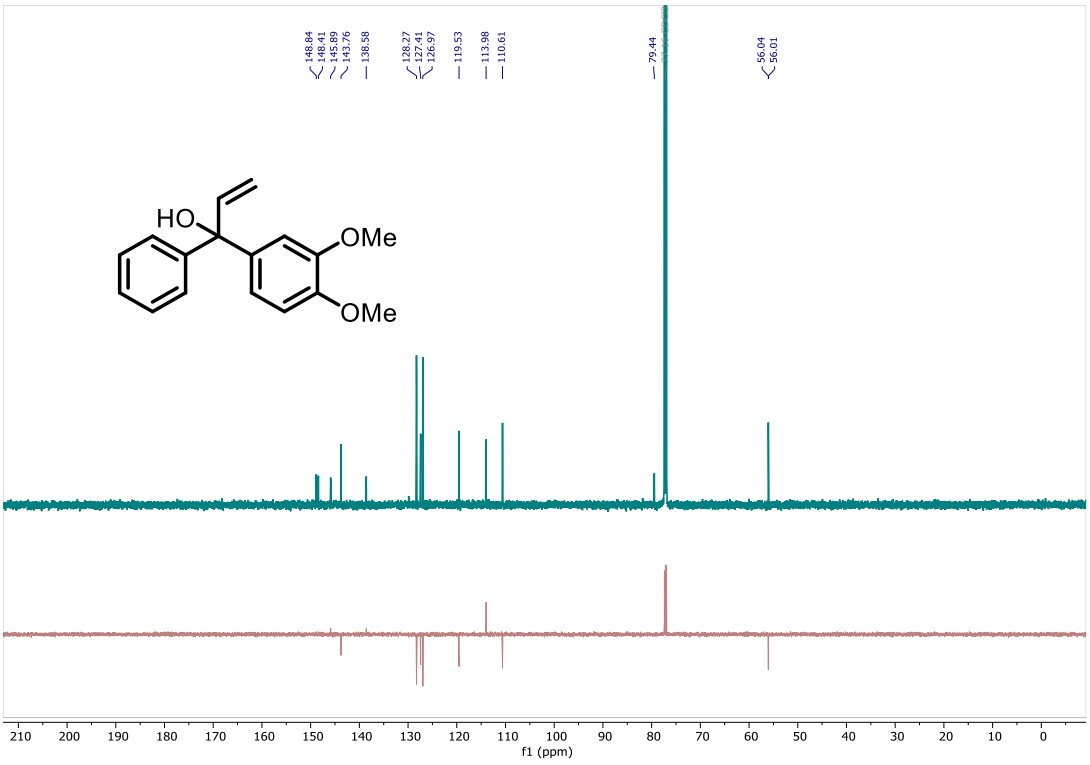
1k (1-phenyl-1-(p-tolyl)prop-2-en-1-ol)



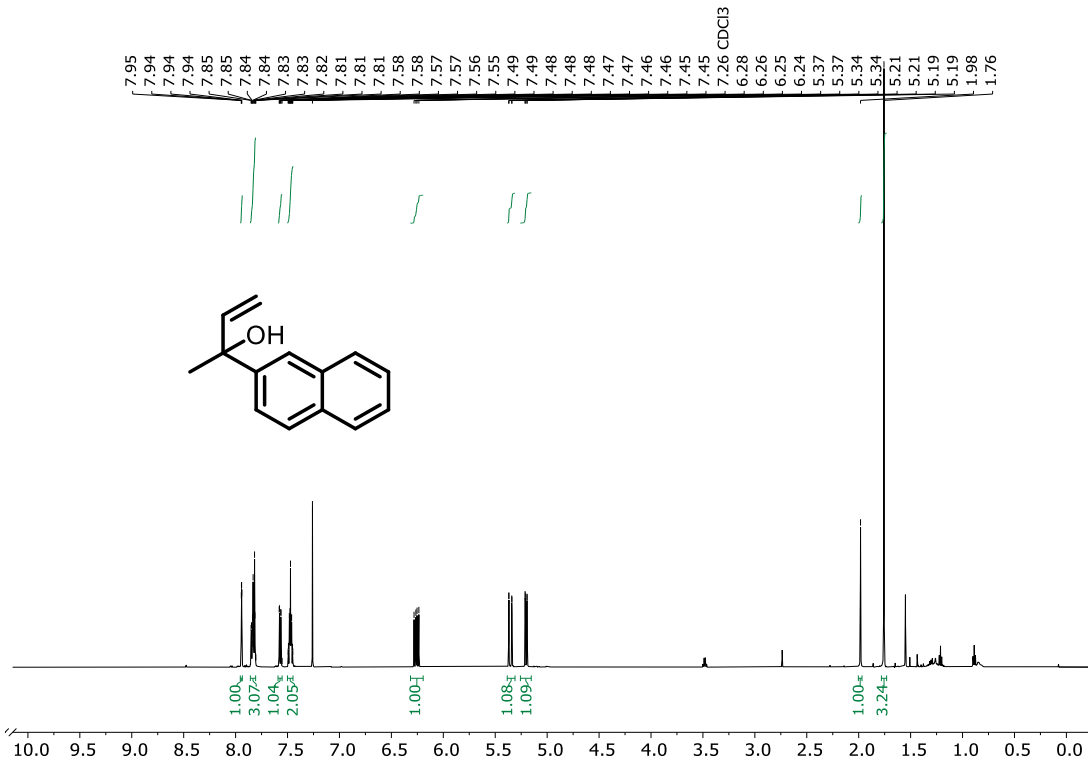


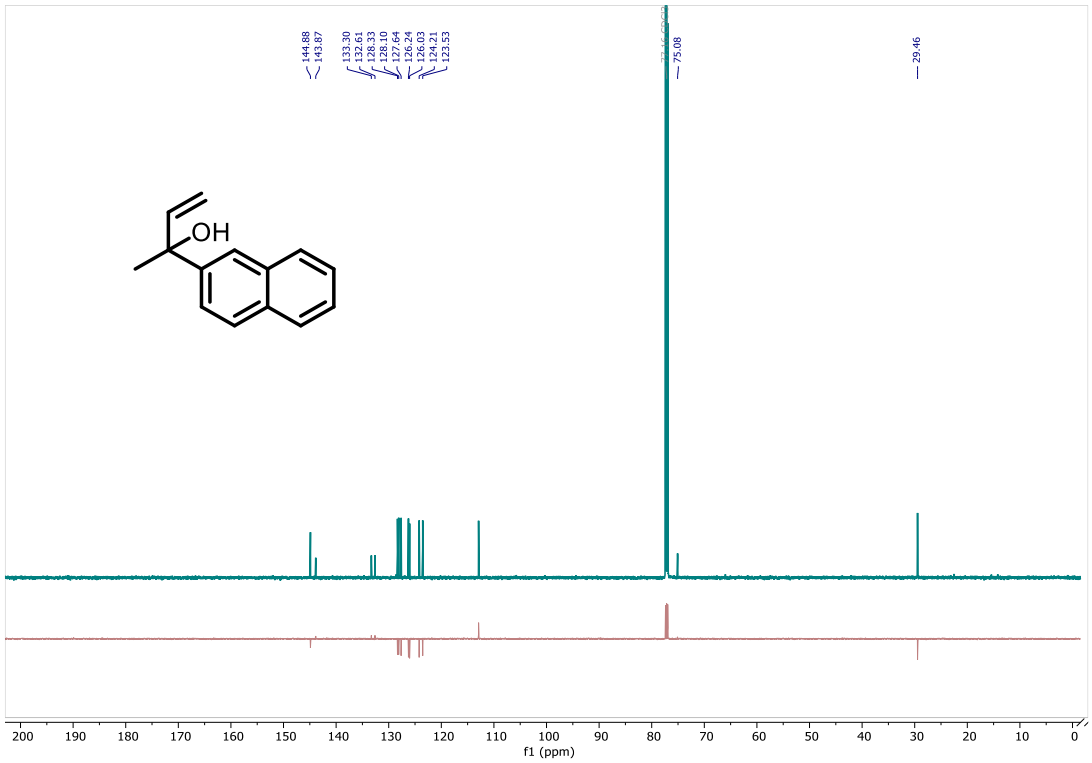
1l (1-(3,4-dimethoxyphenyl)-1-phenylprop-2-en-1-ol)



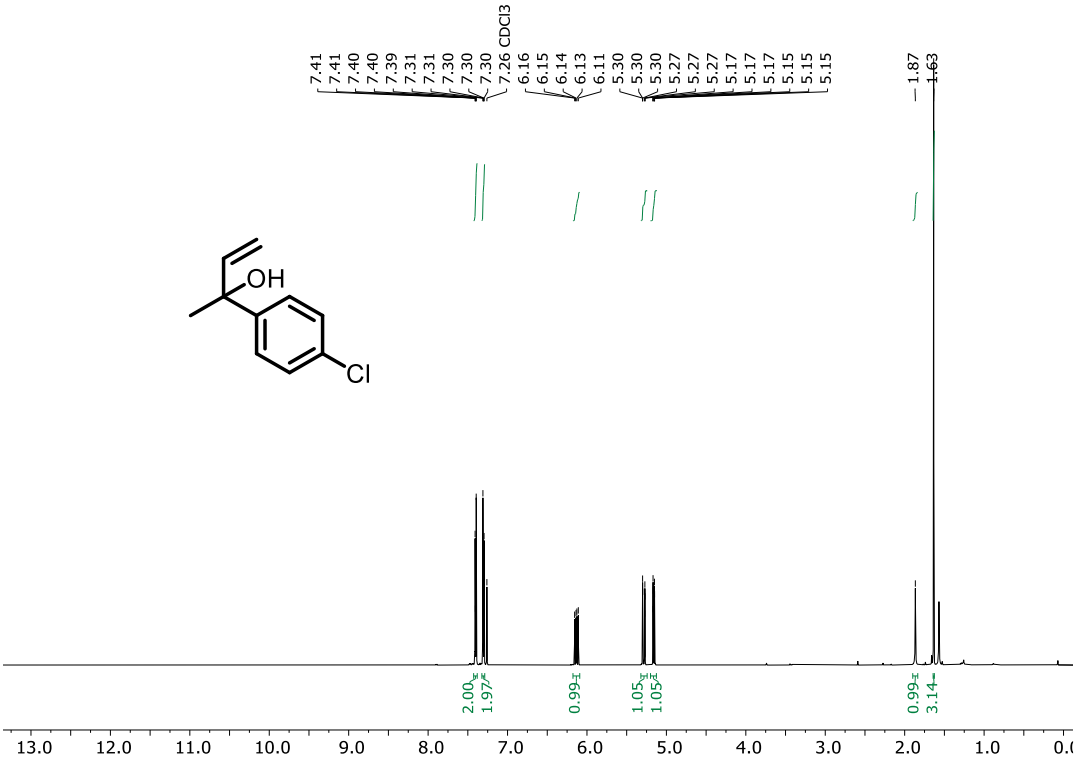


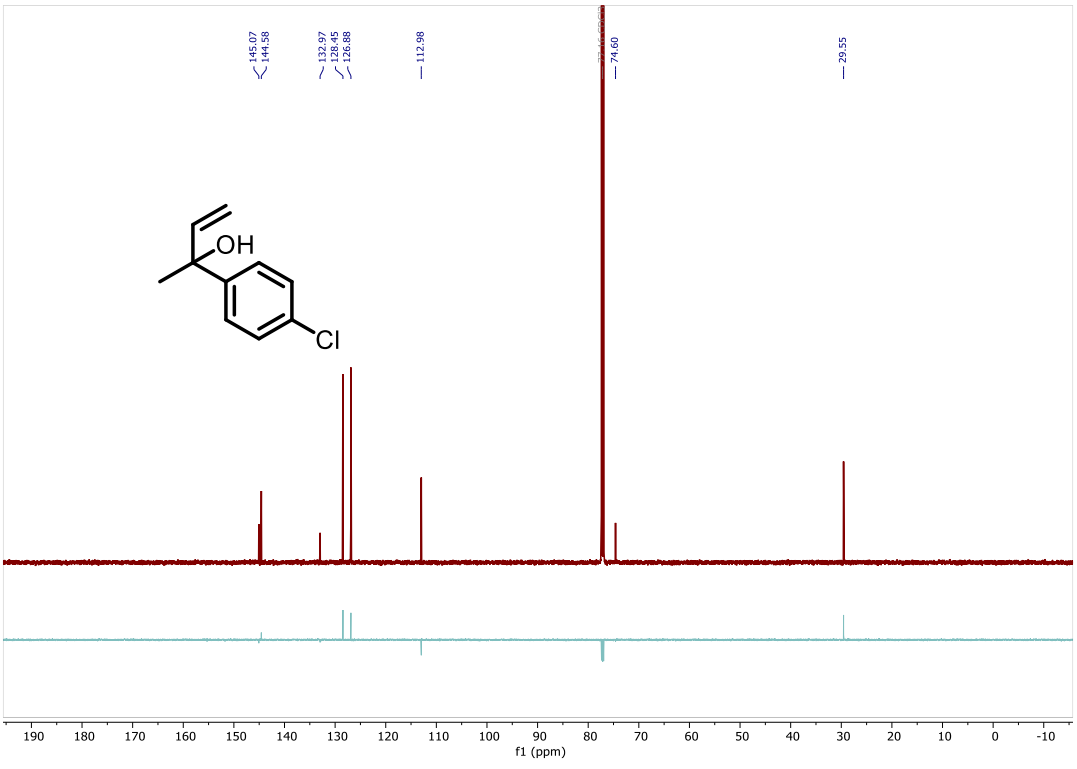
1m (2-(naphthalen-2-yl)but-3-en-2-ol)



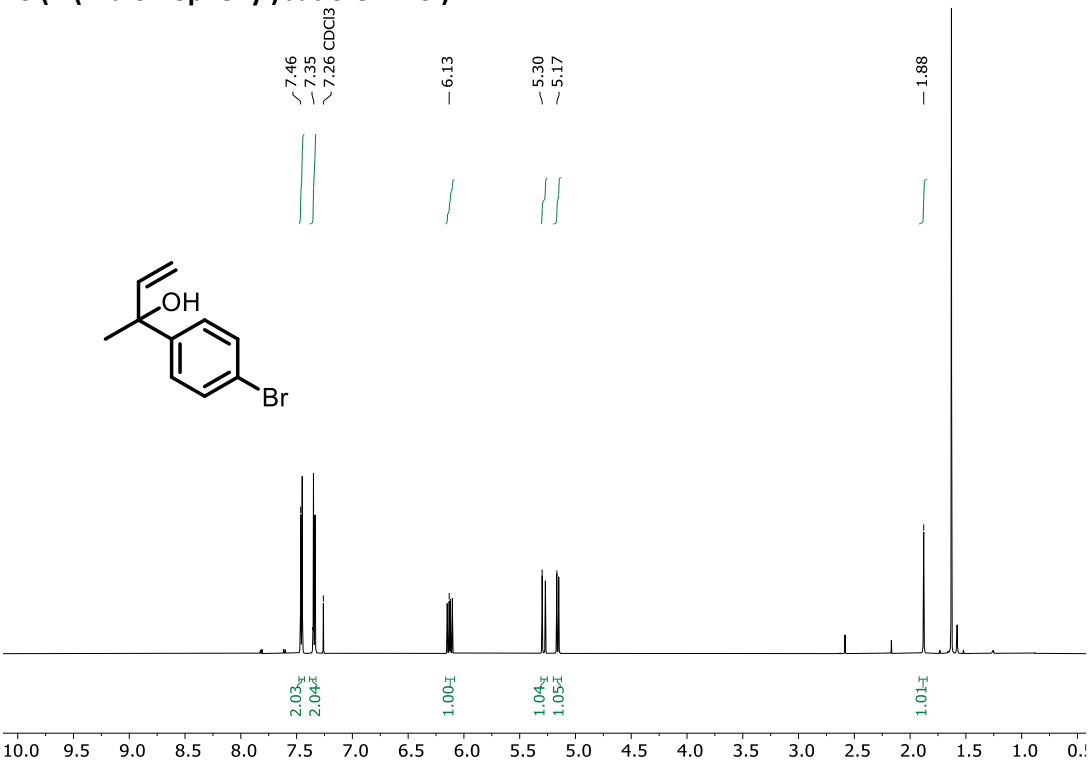


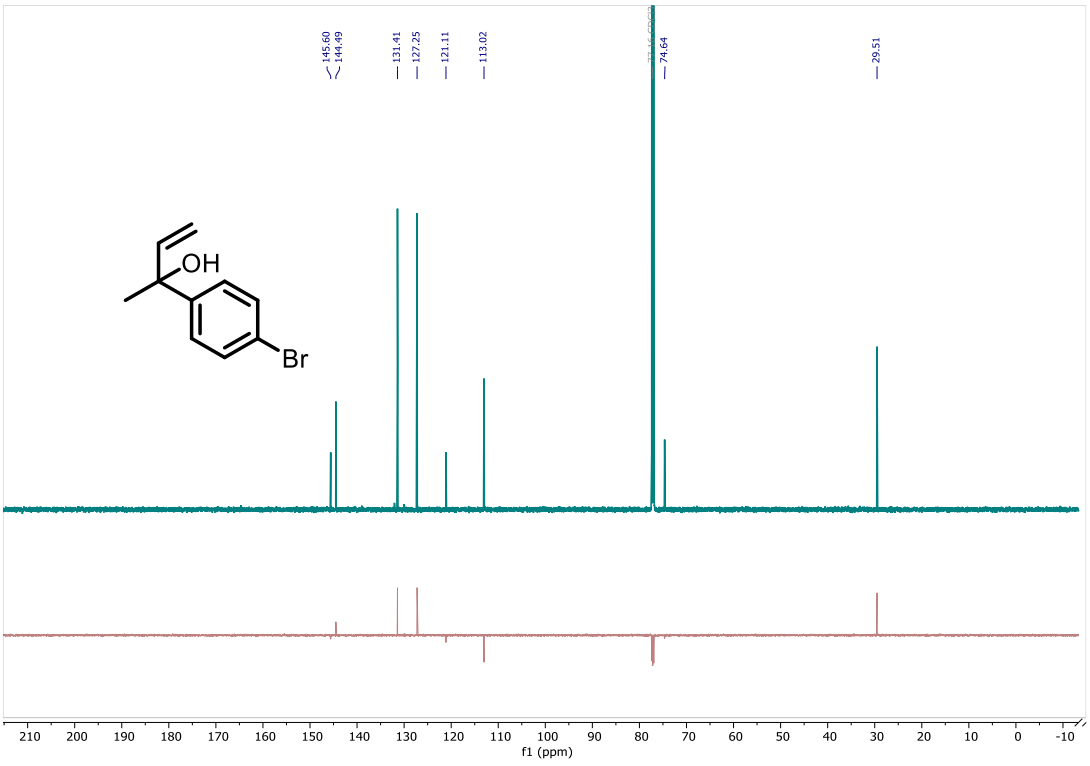
1n (2-(4-chlorophenyl)but-3-en-2-ol)



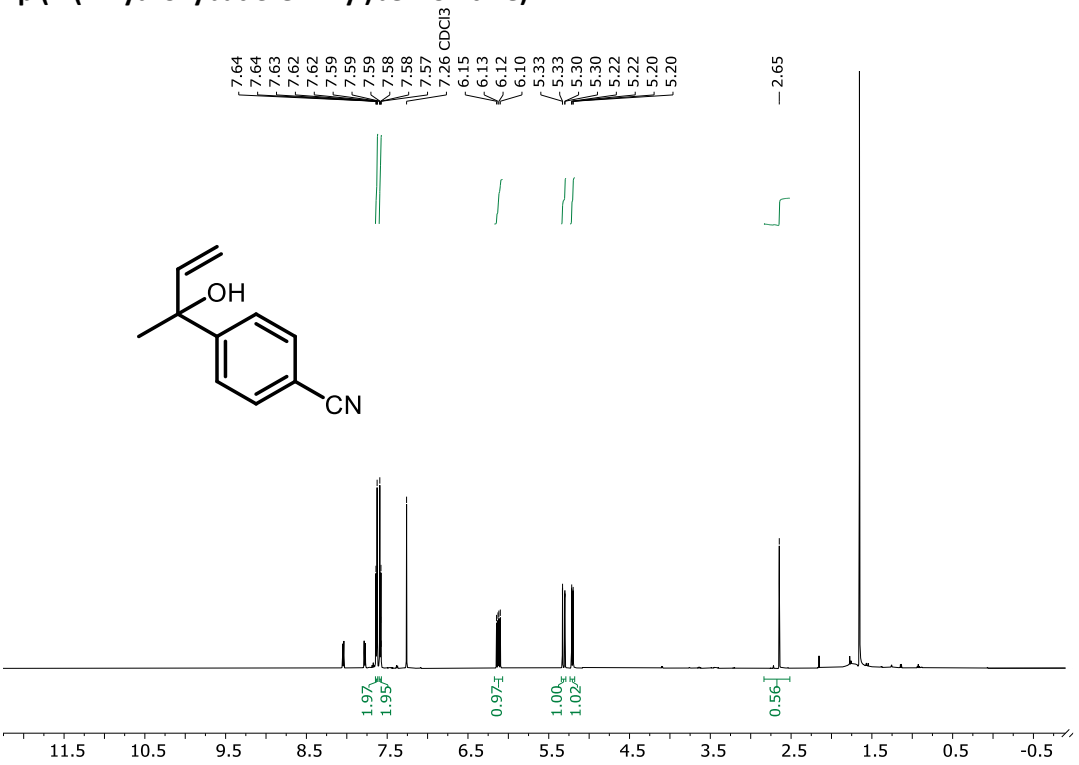


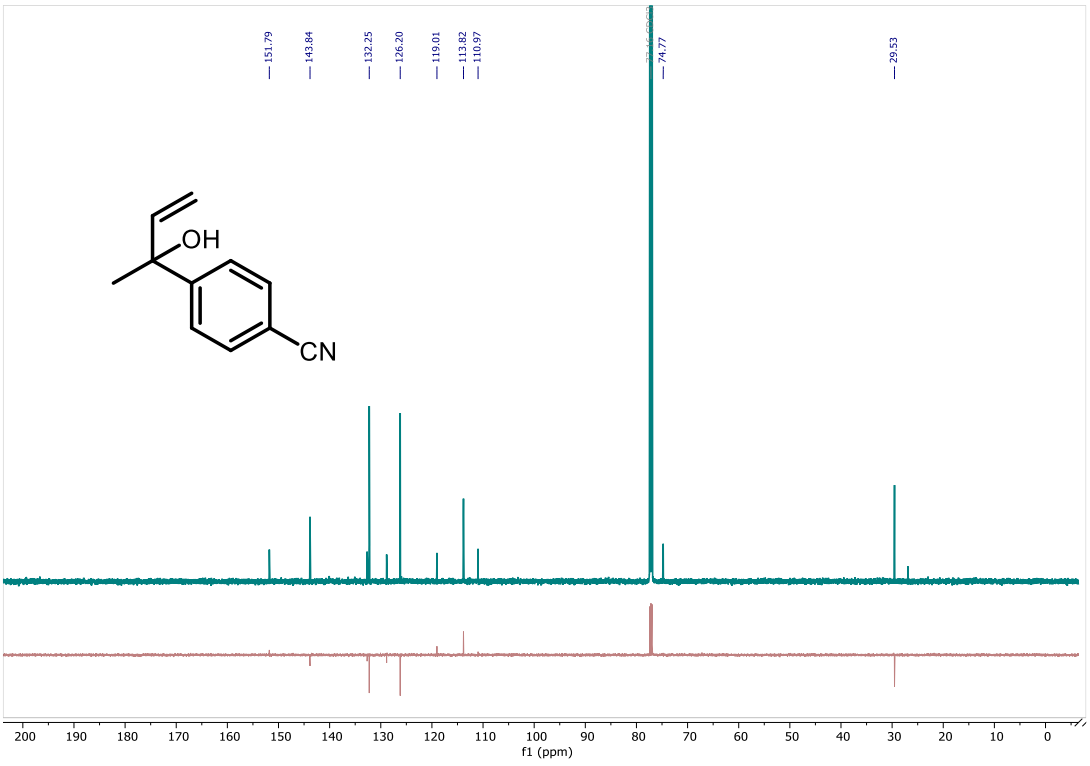
1o (2-(4-bromophenyl)but-3-en-2-ol)



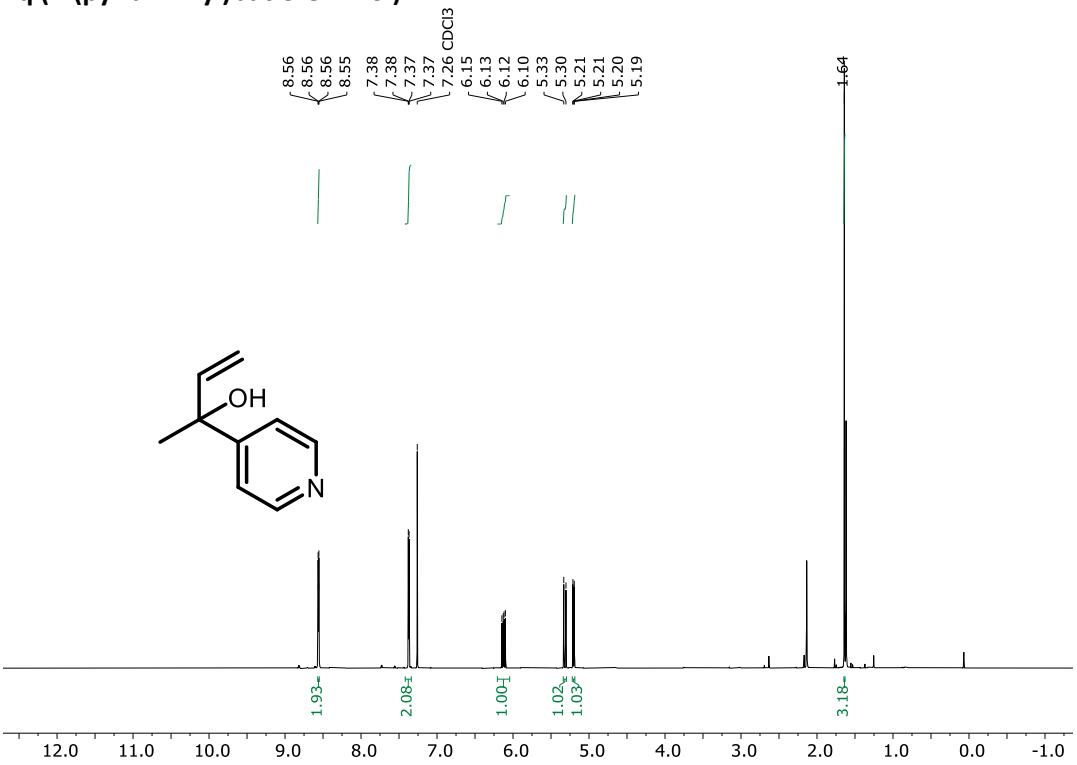


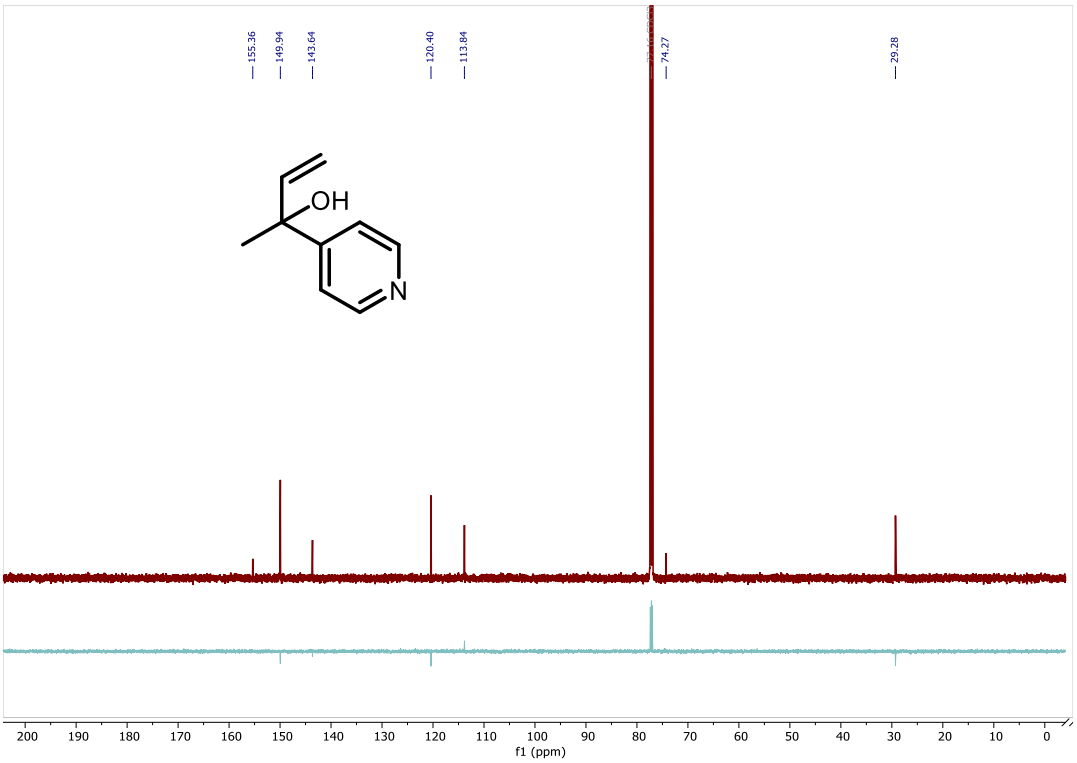
1p (4-(2-hydroxybut-3-en-2-yl)benzonitrile)



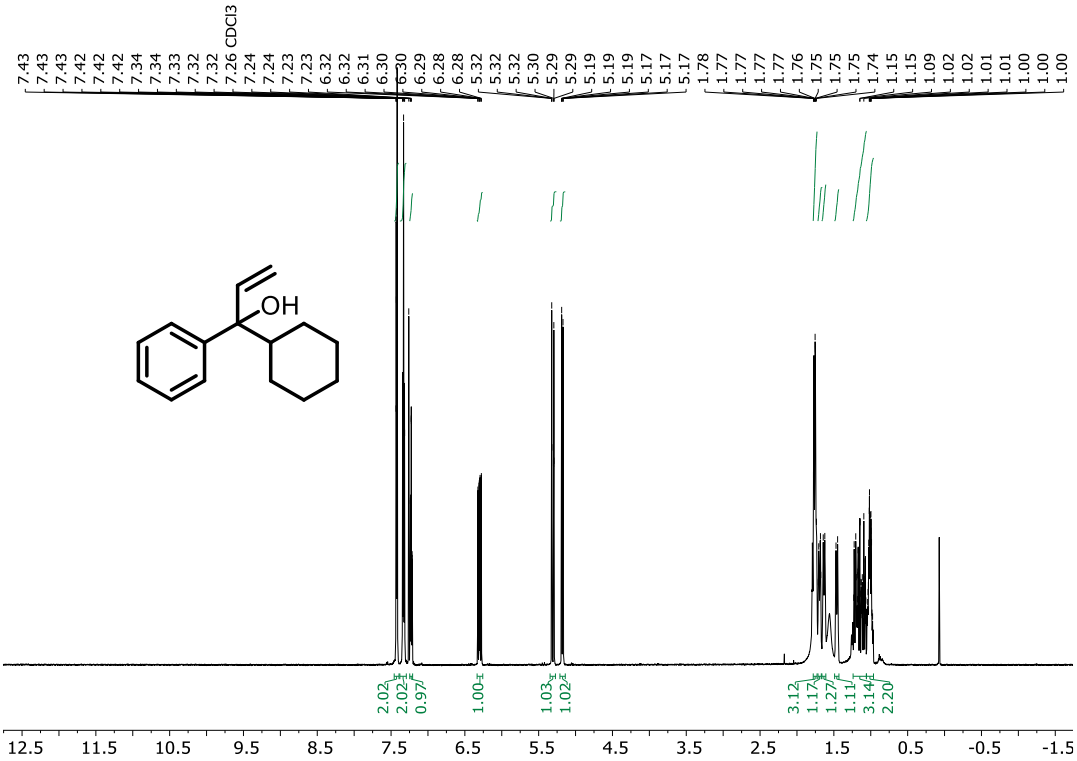


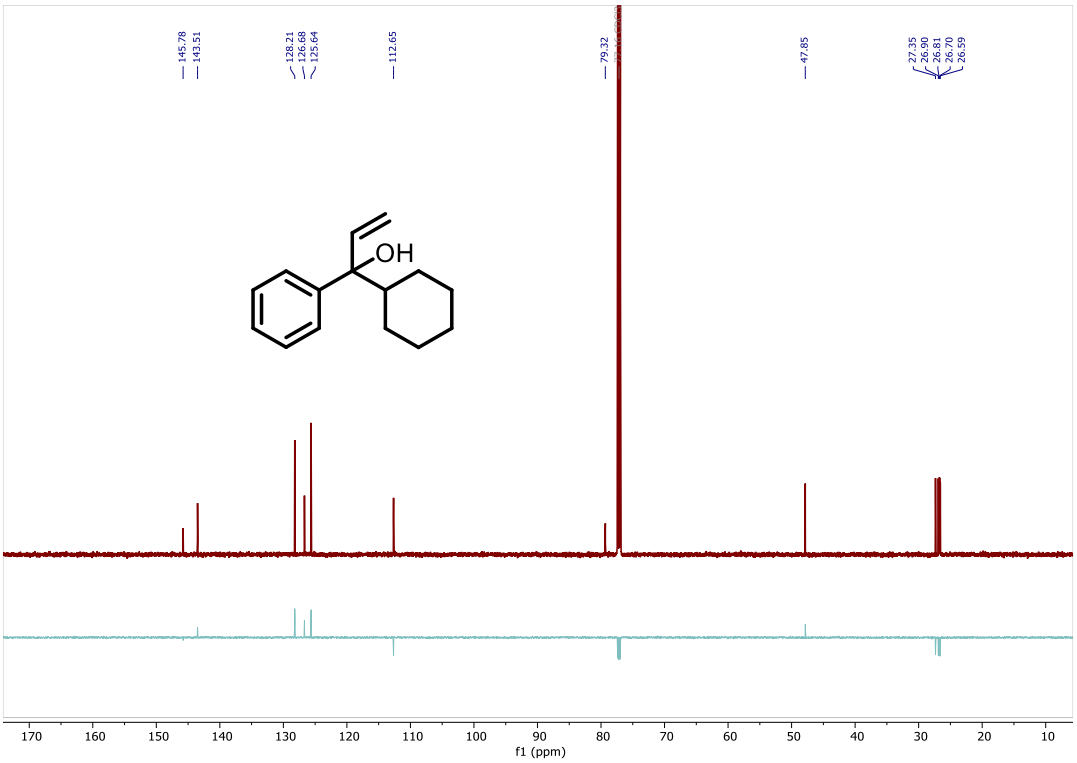
1q (2-(pyridin-4-yl)but-3-en-2-ol)



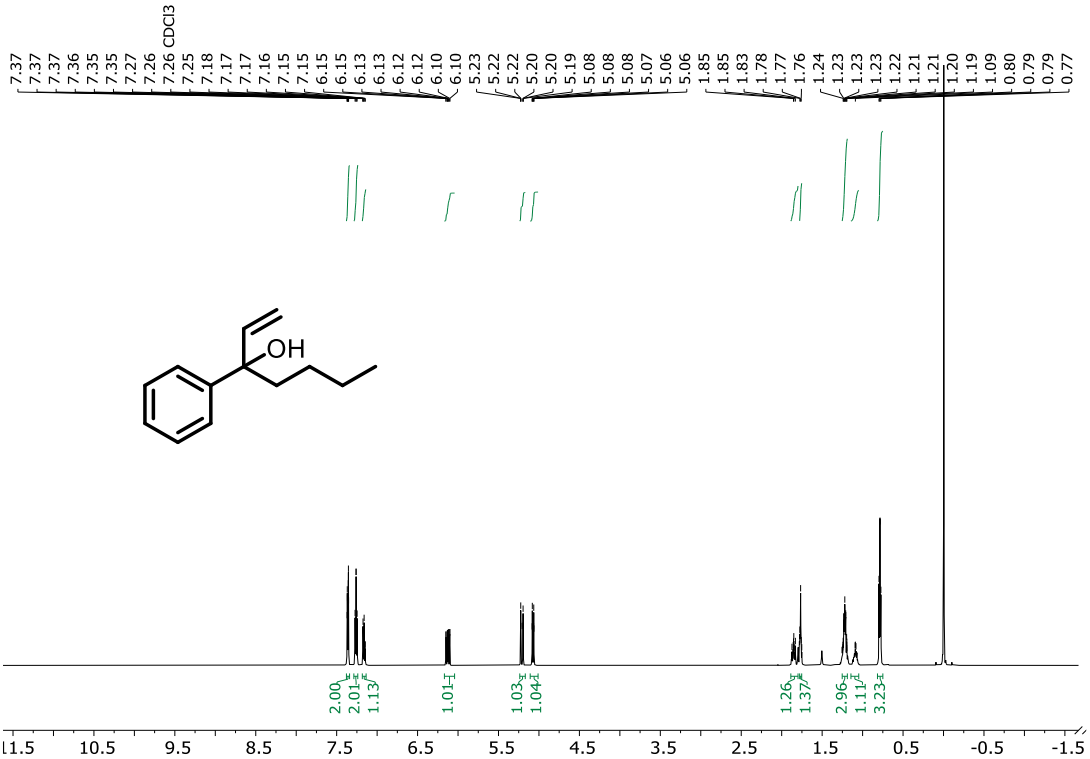


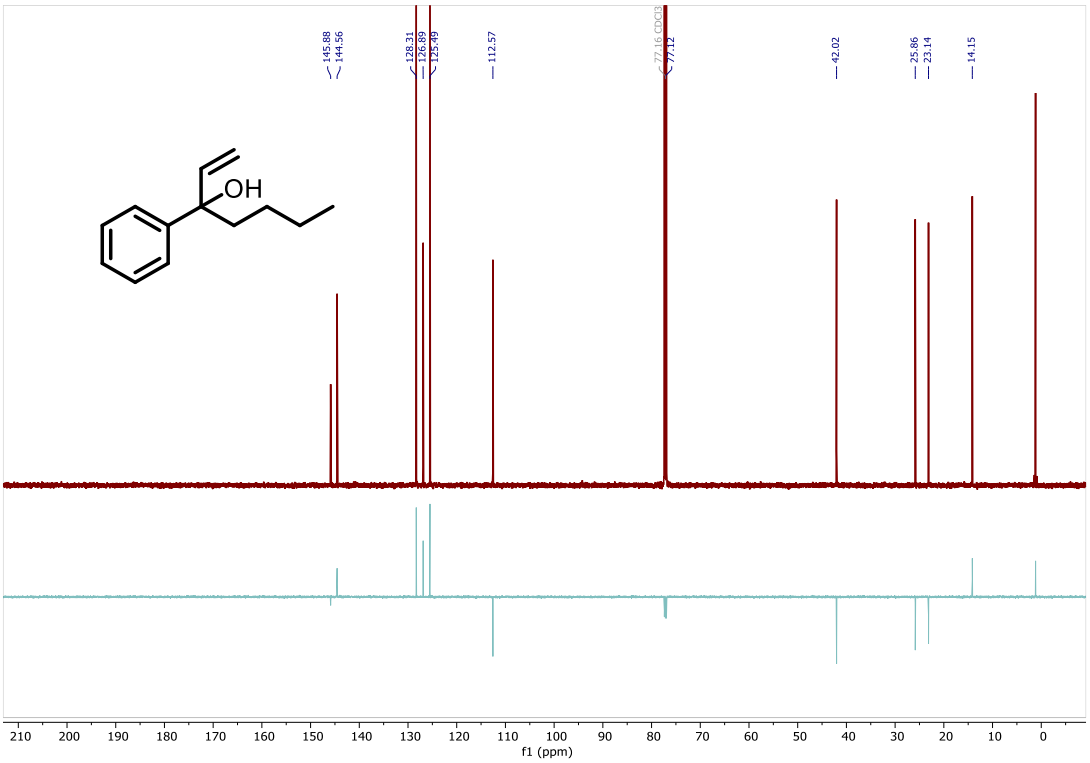
1r (1-cyclohexyl-1-phenylprop-2-en-1-ol)



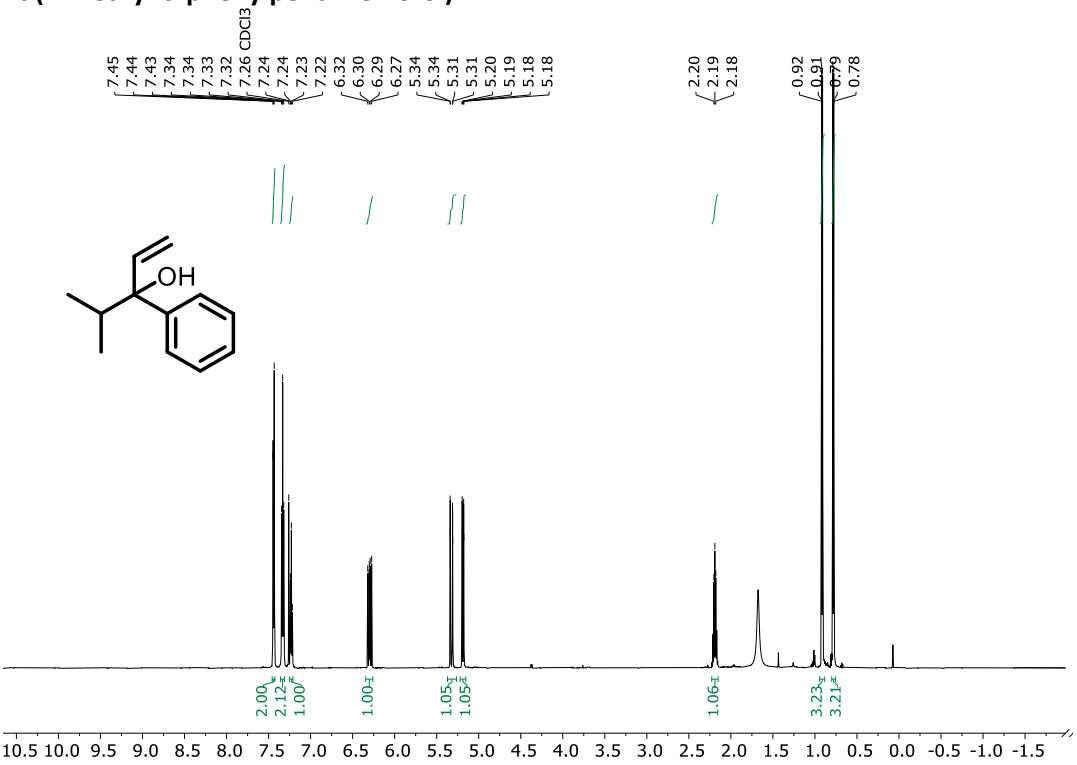


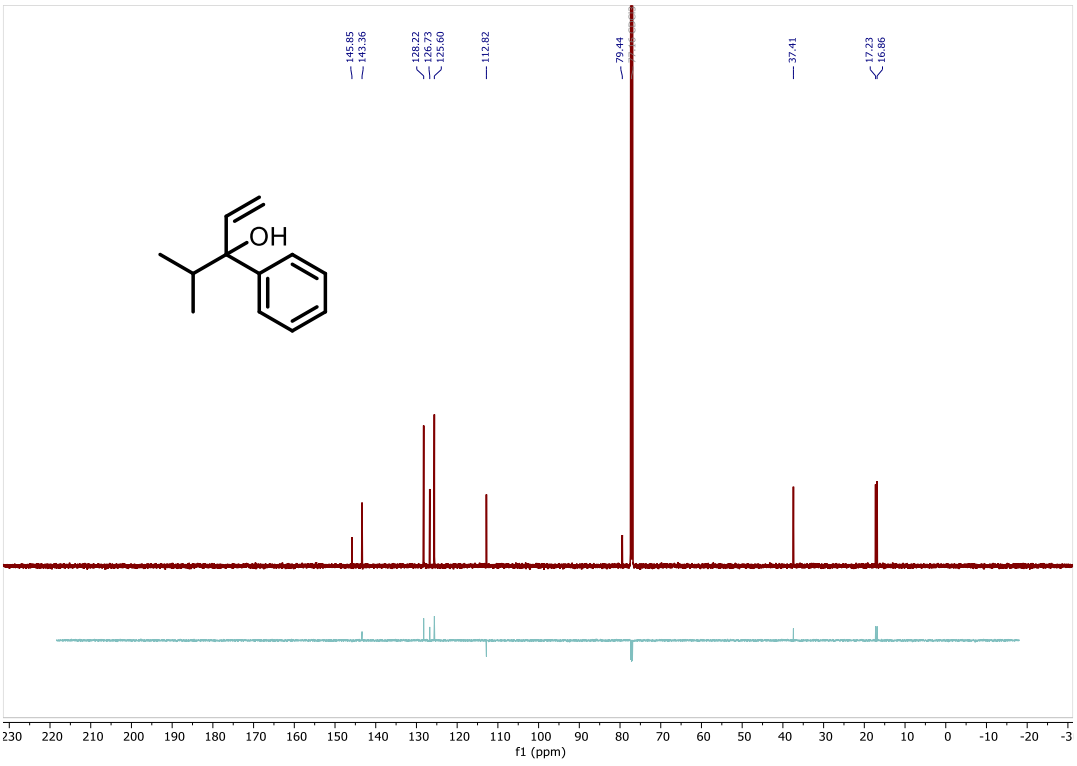
1s (3-phenylhept-1-en-3-ol)



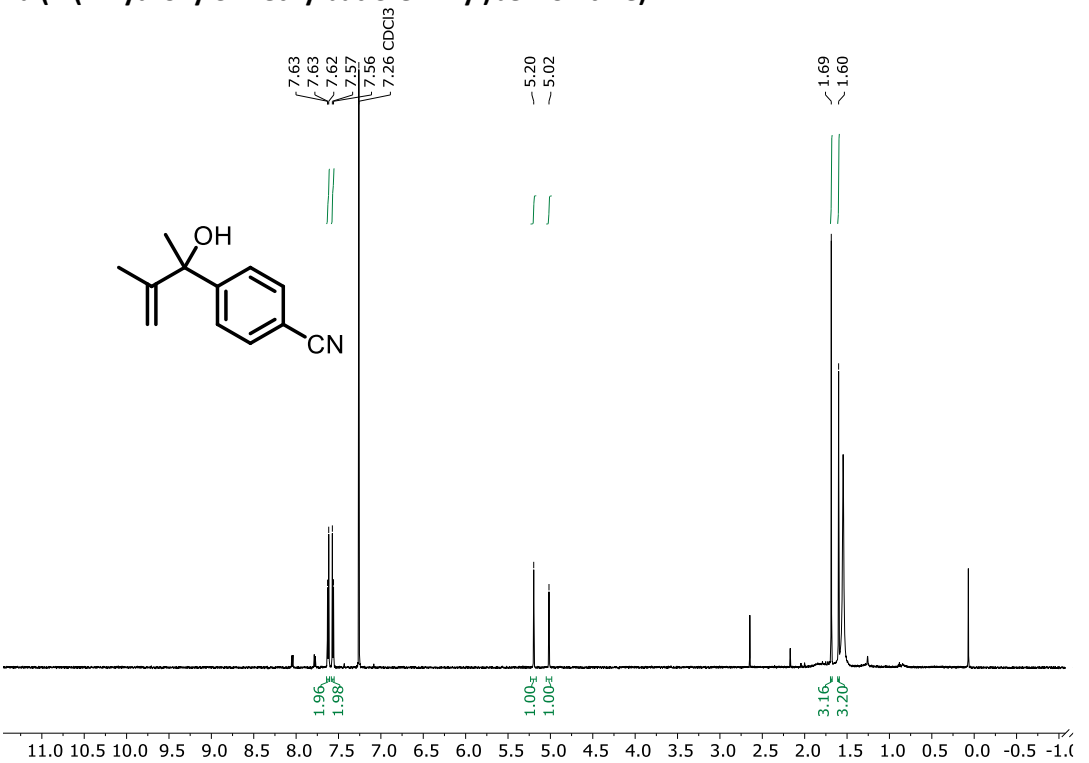


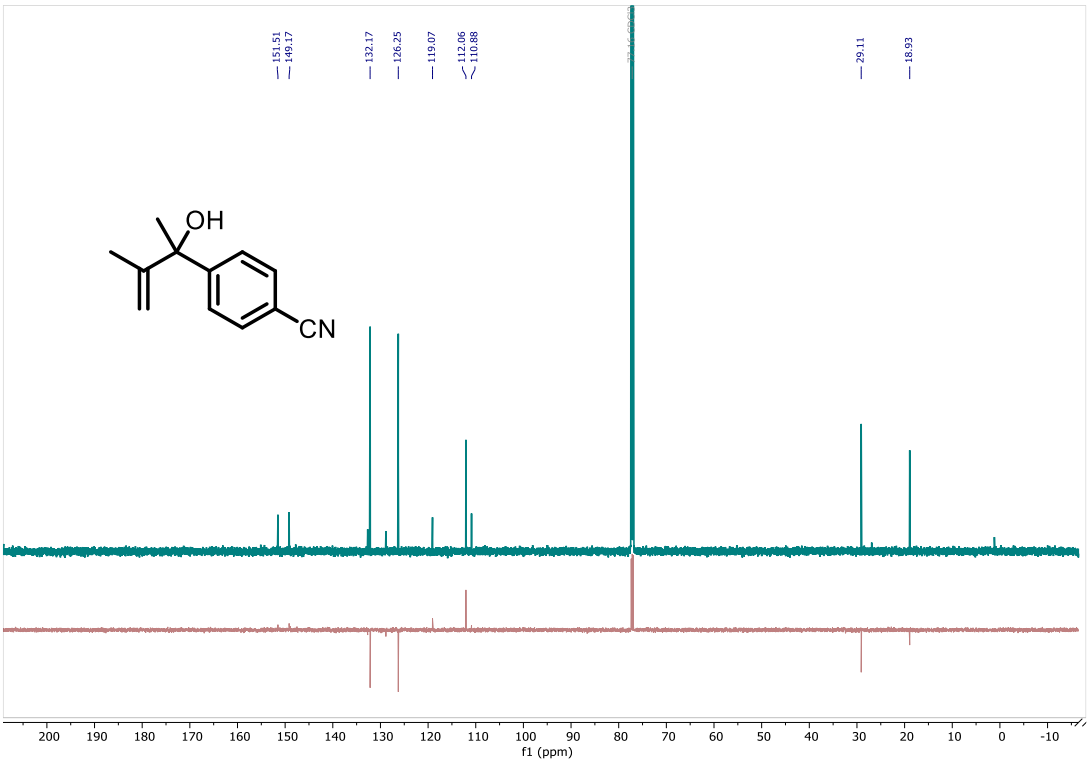
1t (4-methyl-3-phenylpent-1-en-3-ol)



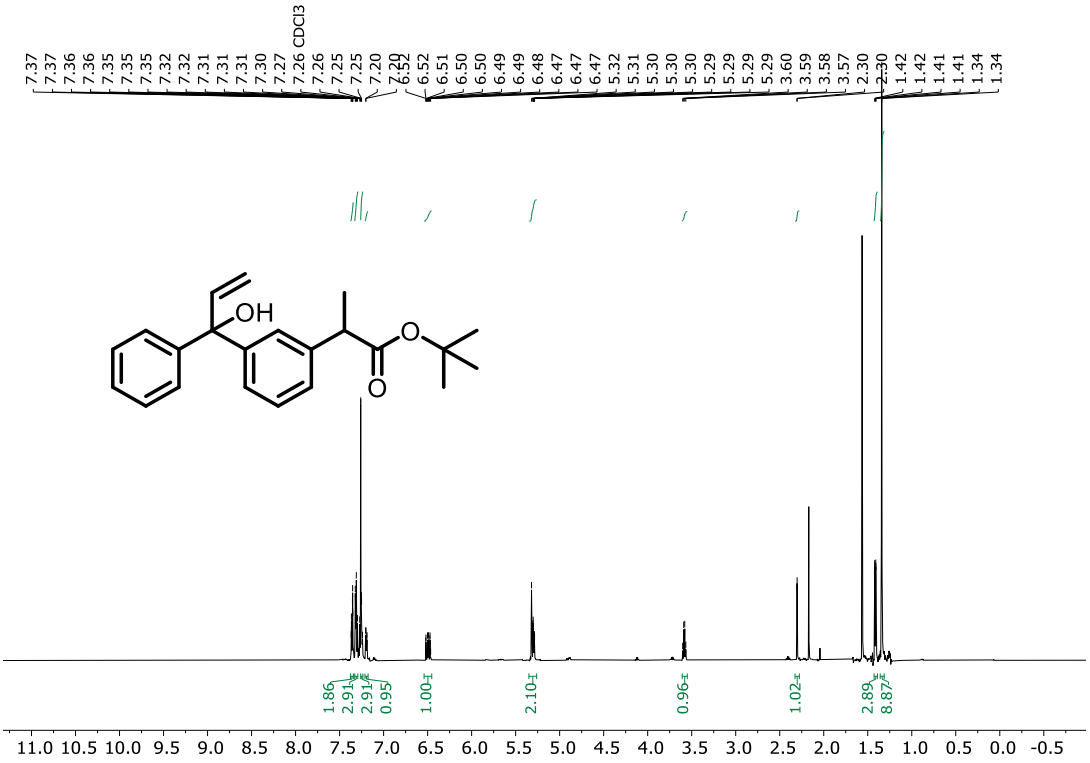


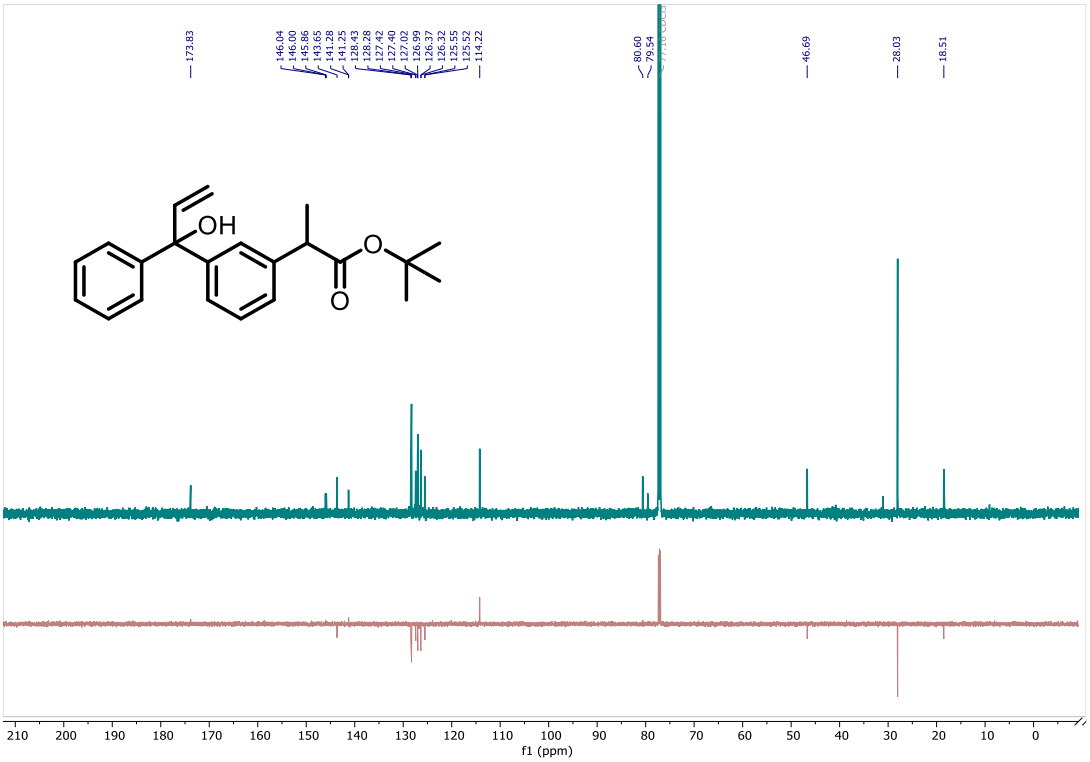
1u (4-(2-hydroxy-3-methylbut-3-en-2-yl)benzonitrile)



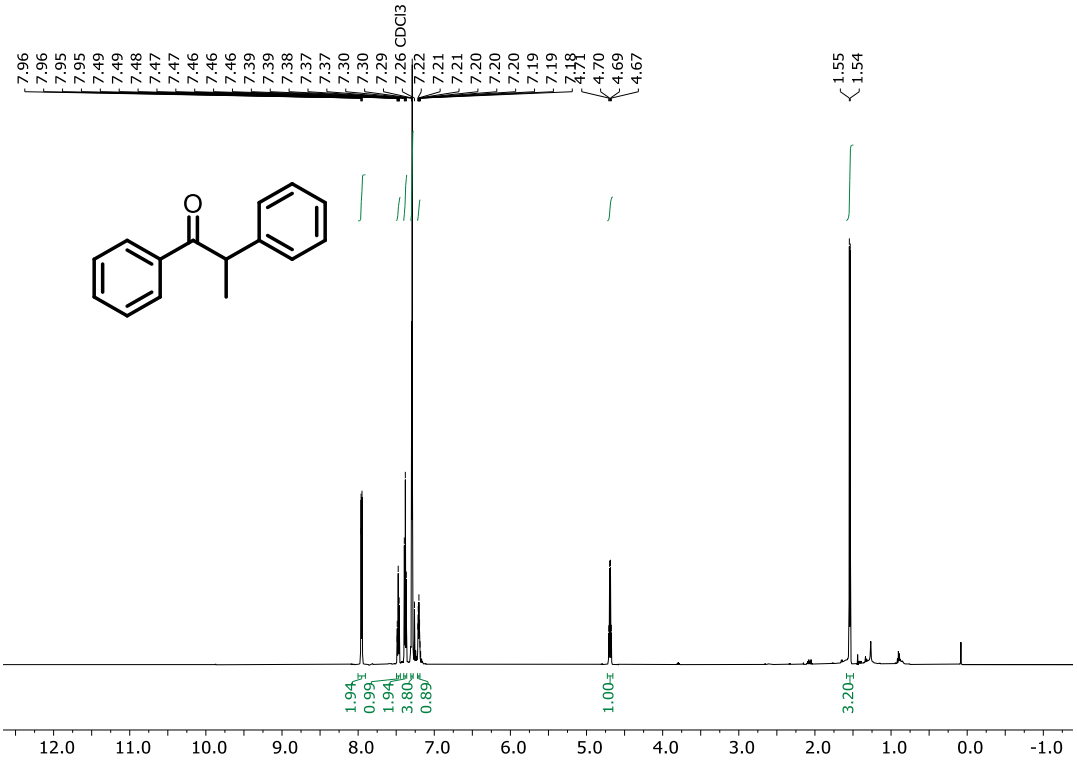


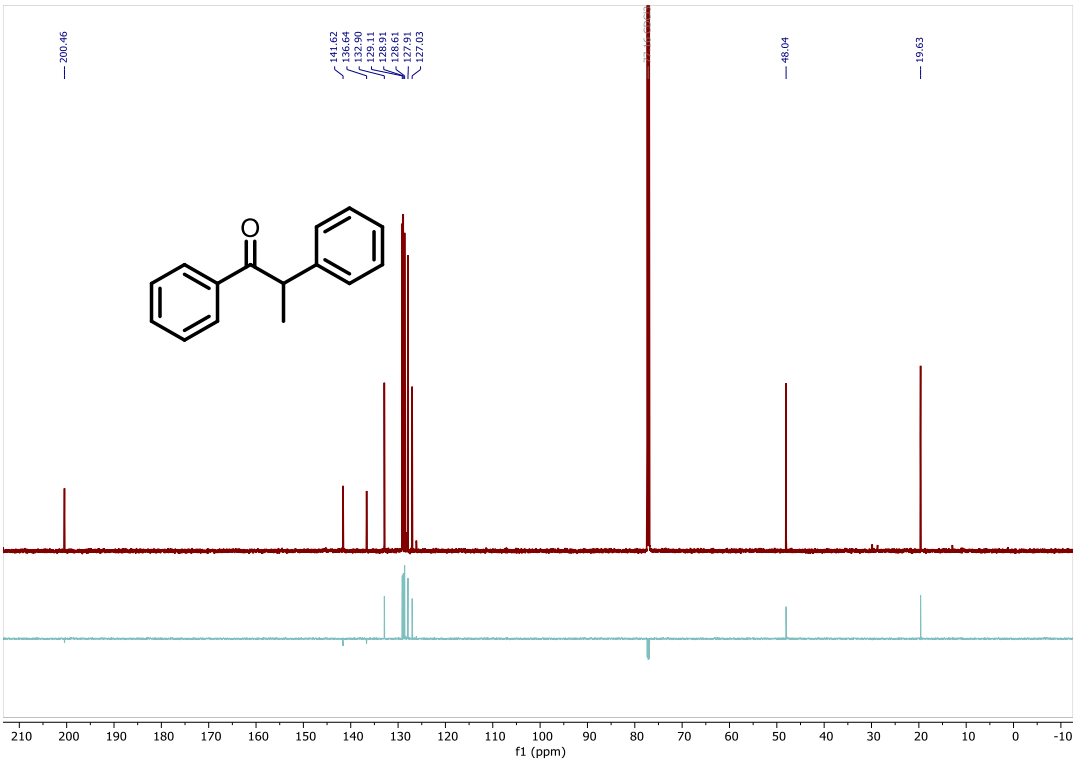
1v (*tert*-butyl 2-(3-(1-hydroxy-1-phenylallyl)phenyl)propanoate)



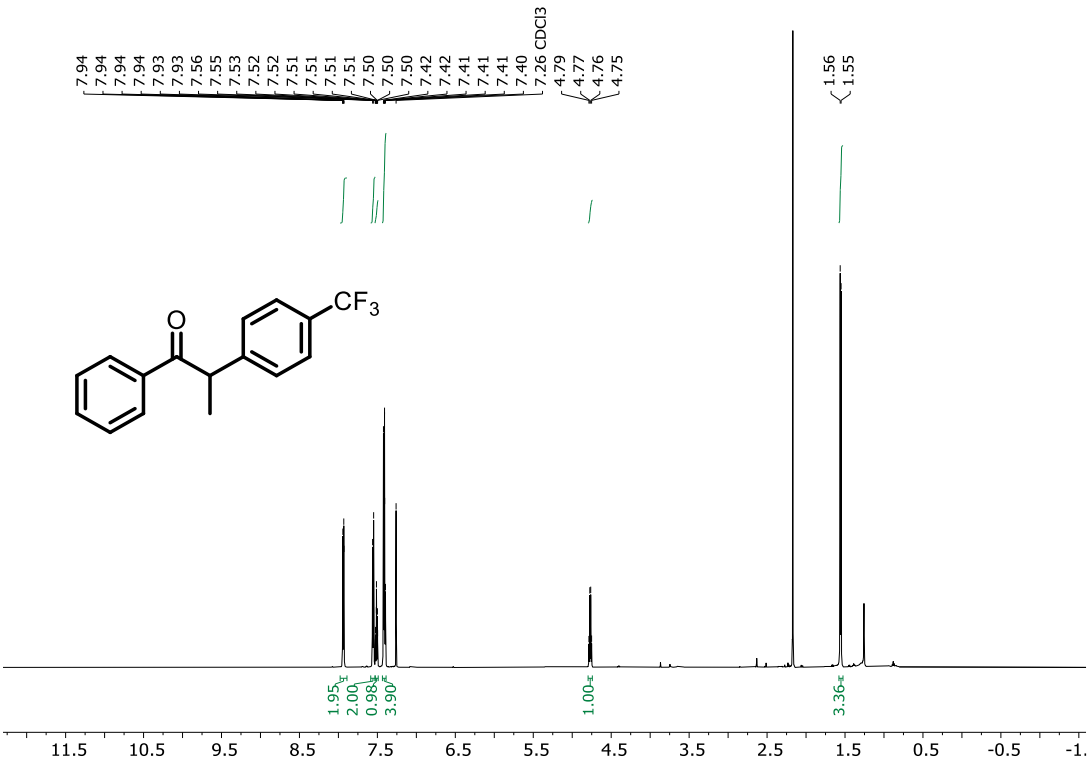


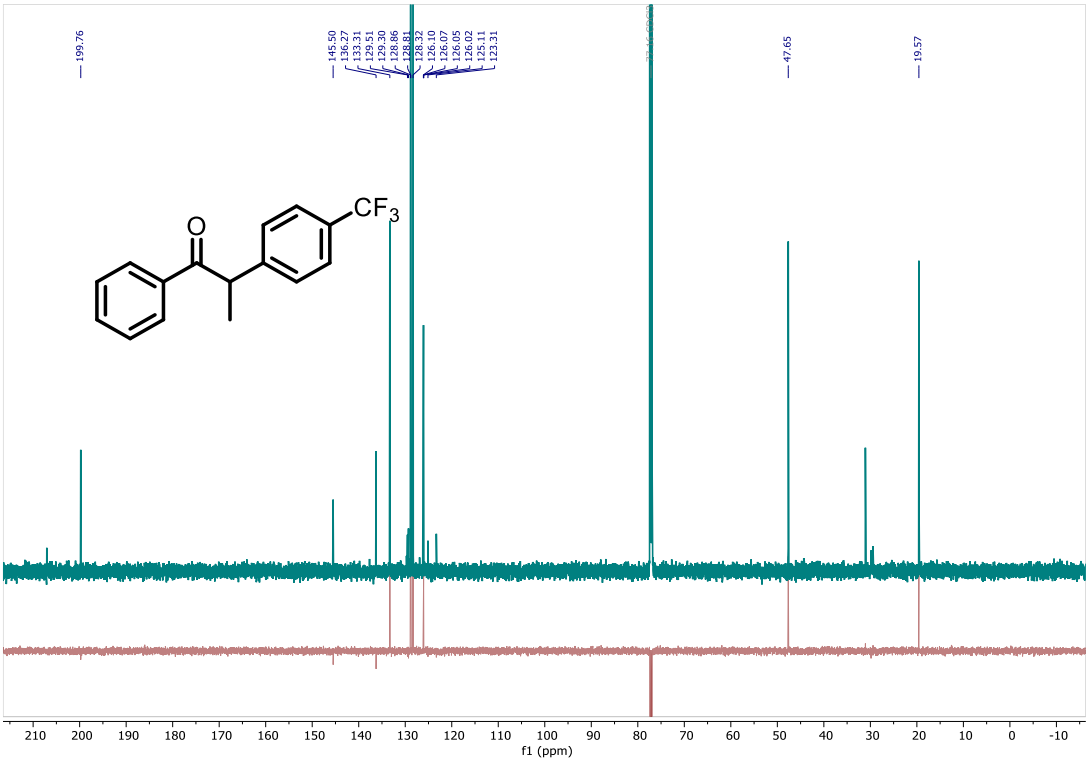
2a (1,2-diphenylpropan-1-one)

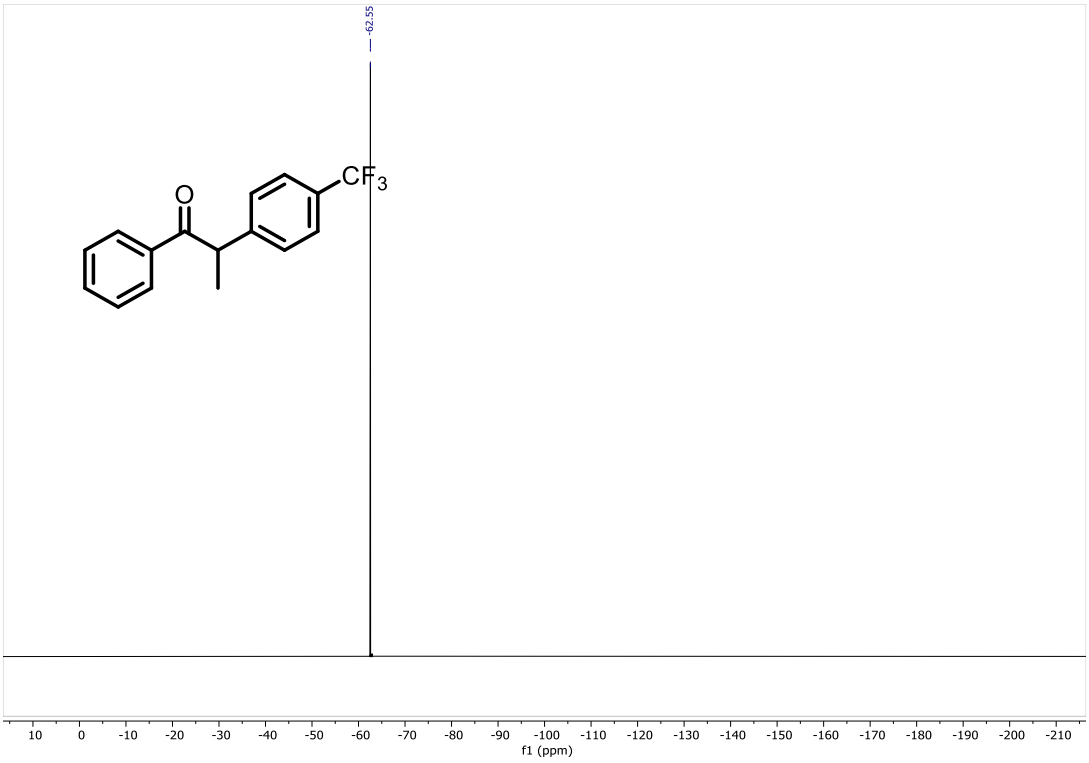




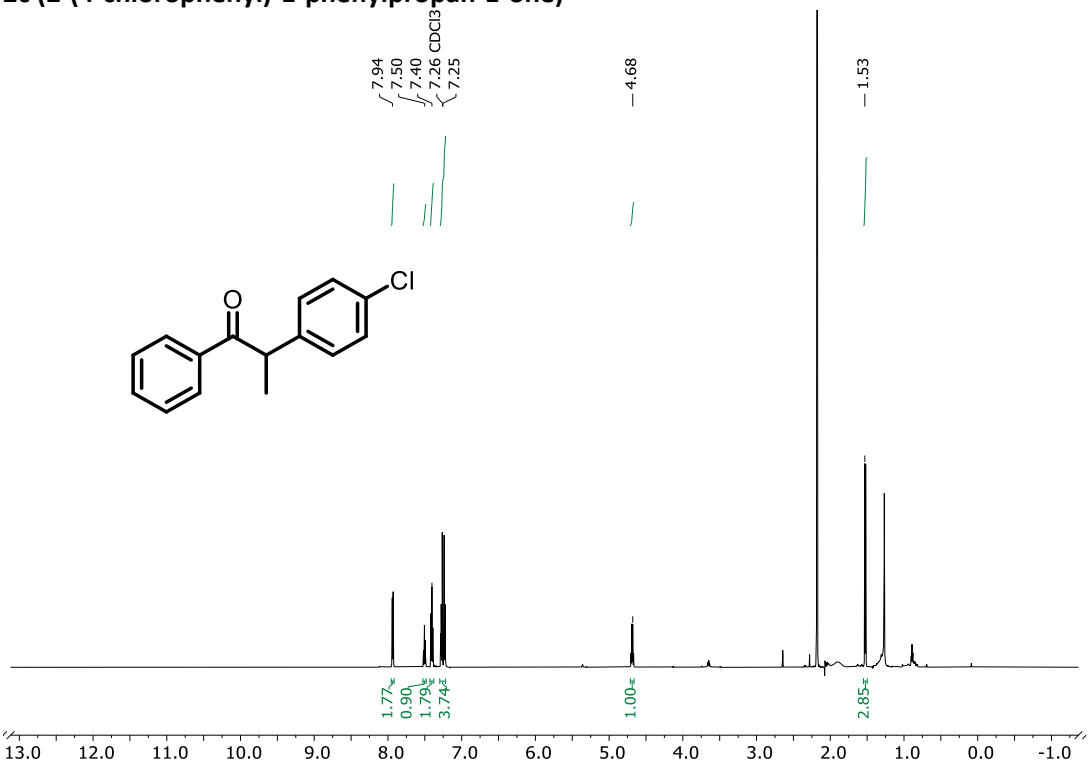
2b (1-phenyl-2-(4-(trifluoromethyl)phenyl)propan-1-one)

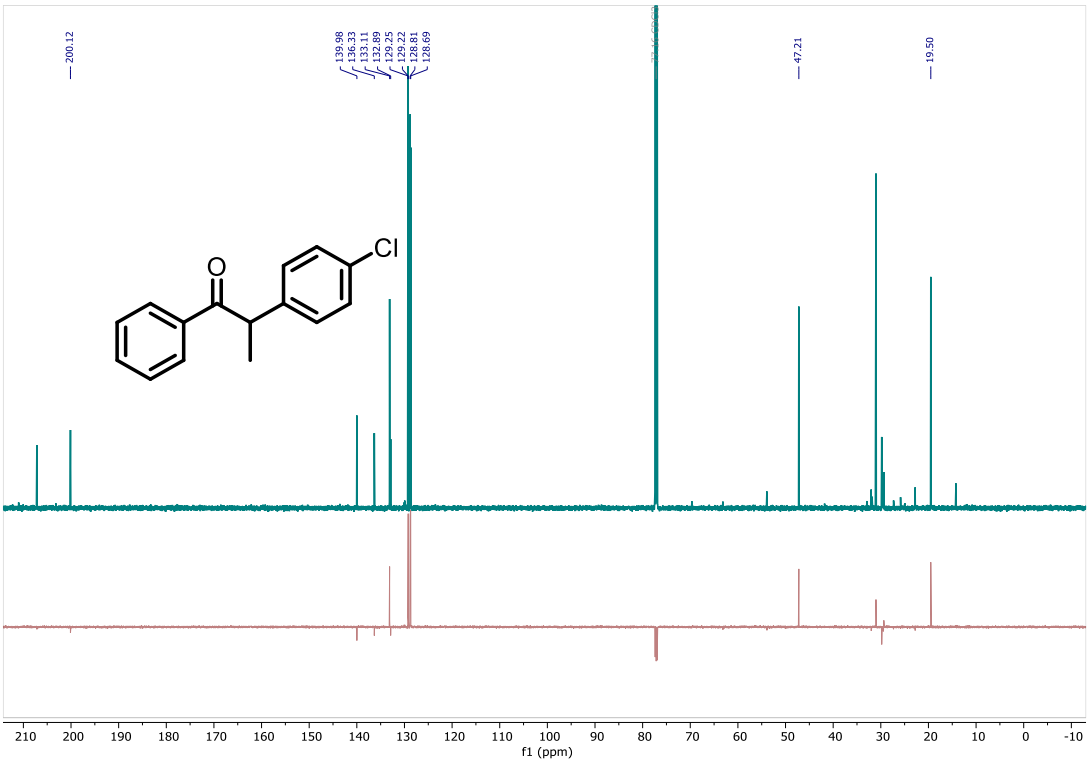




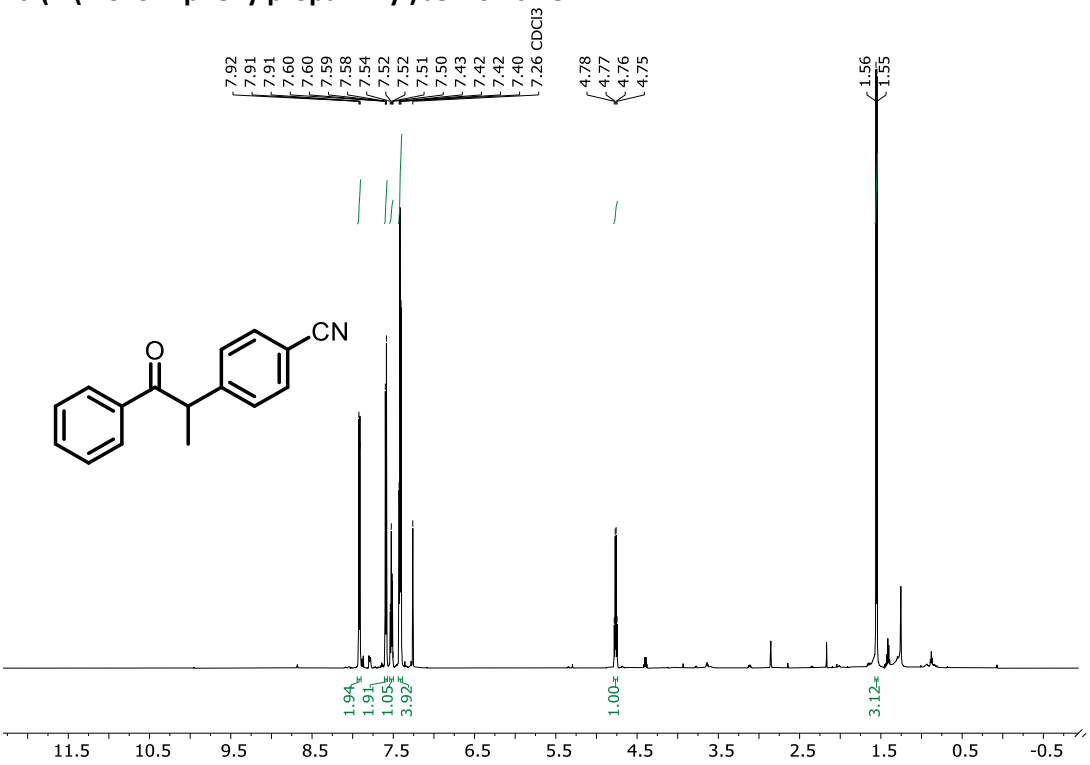

-62.55
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

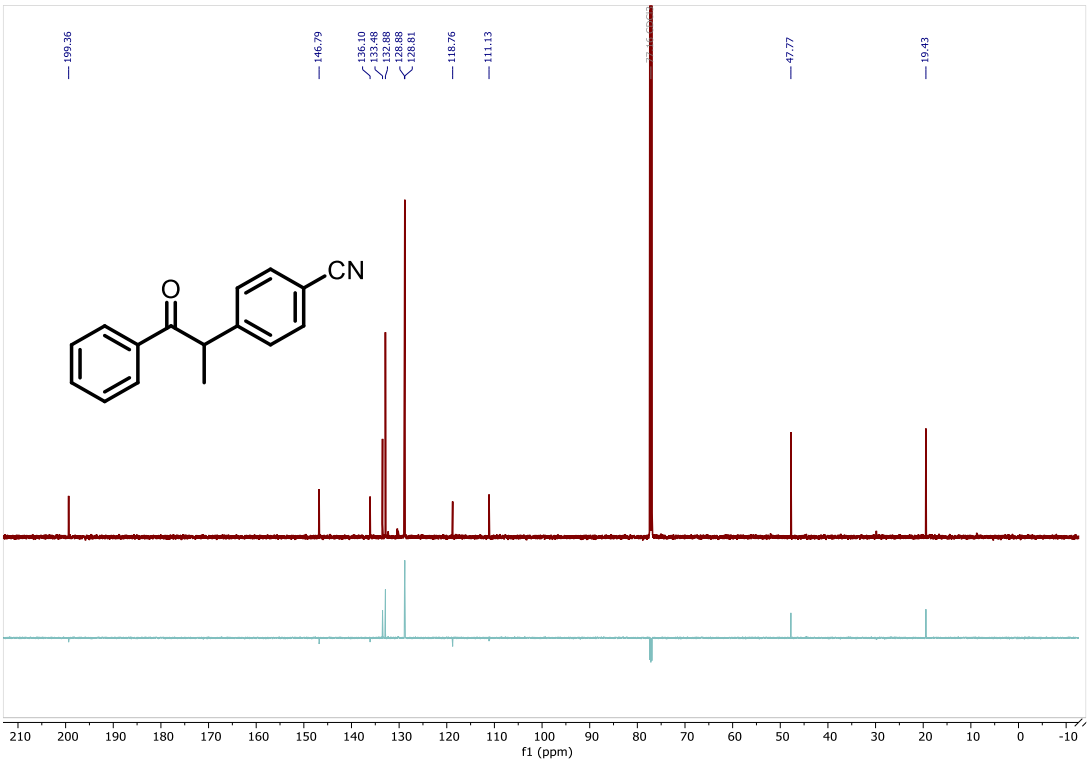
2c (2-(4-chlorophenyl)-1-phenylpropan-1-one)



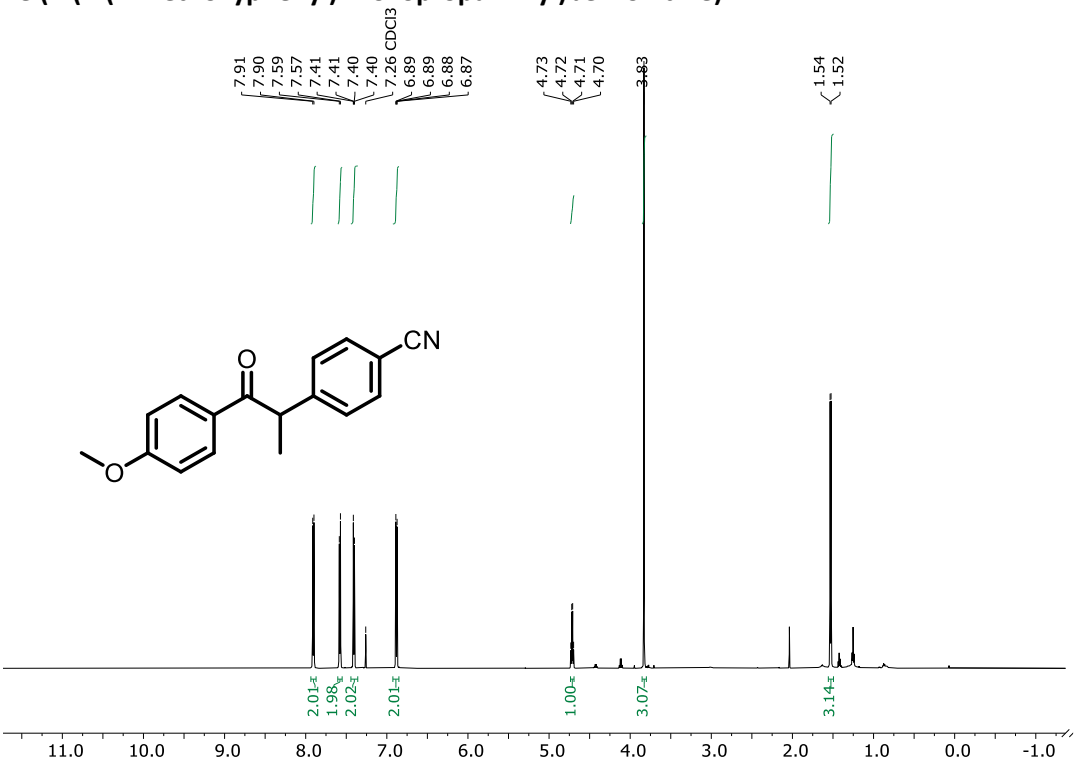


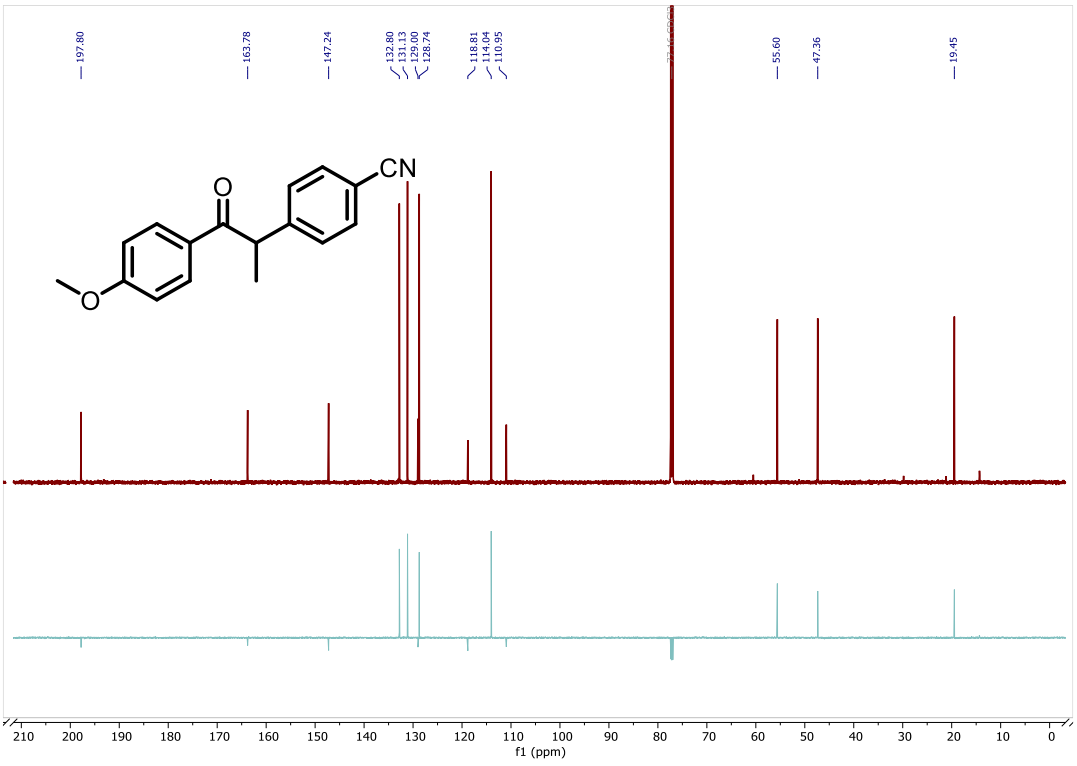
2d (4-(1-oxo-1-phenylpropan-2-yl)benzonitrile



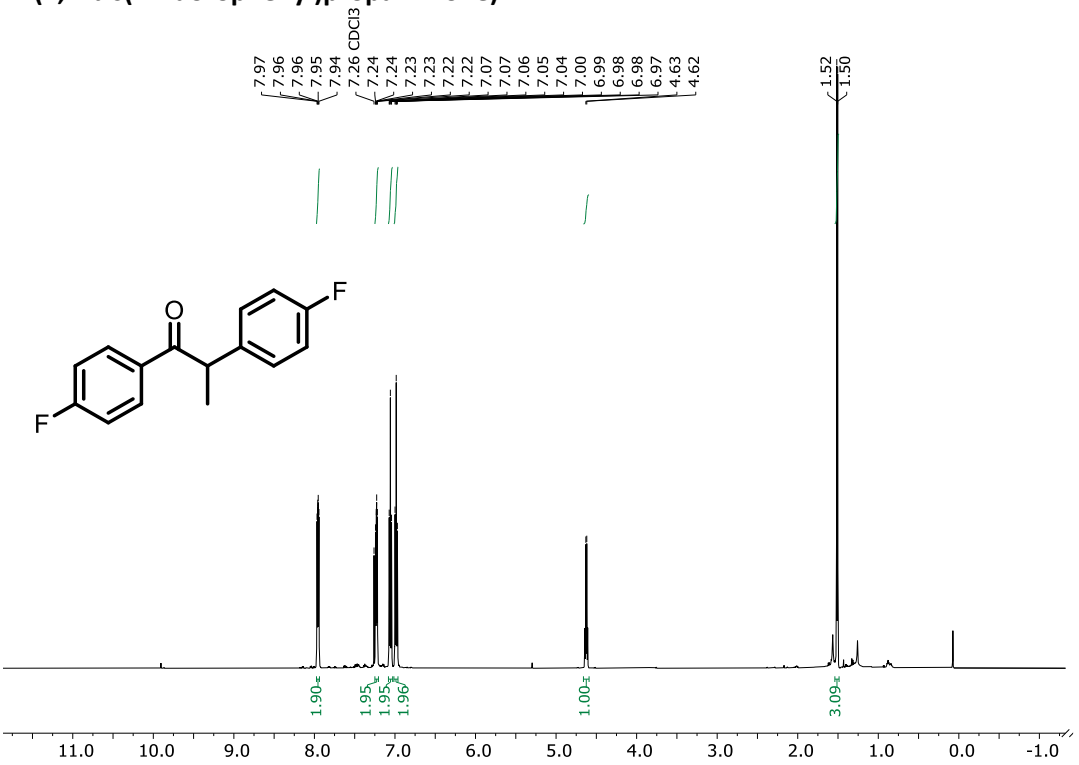


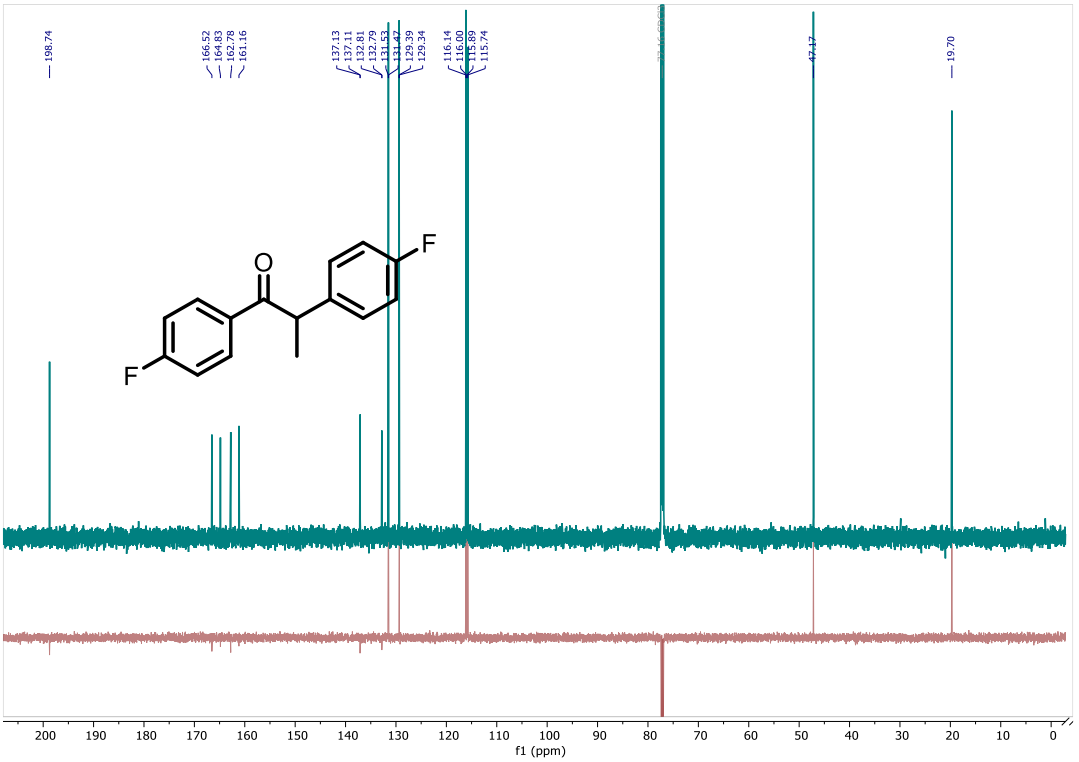
2e (4-(1-(4-methoxyphenyl)-1-oxopropan-2-yl)benzonitrile)

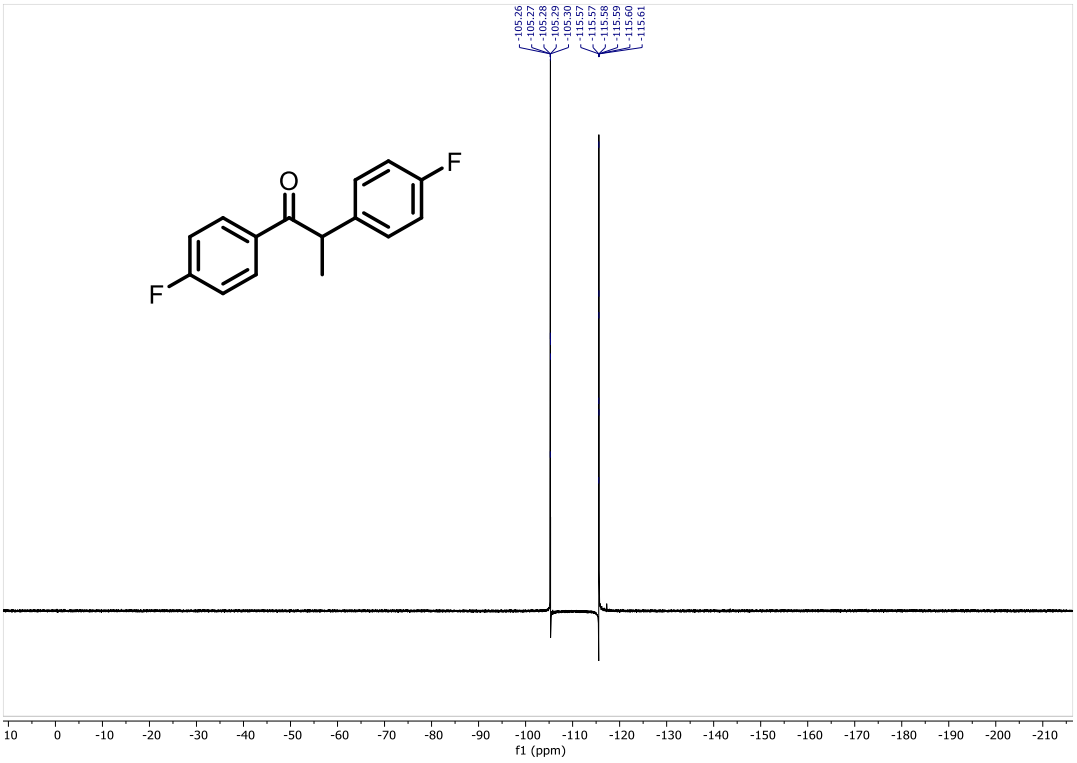




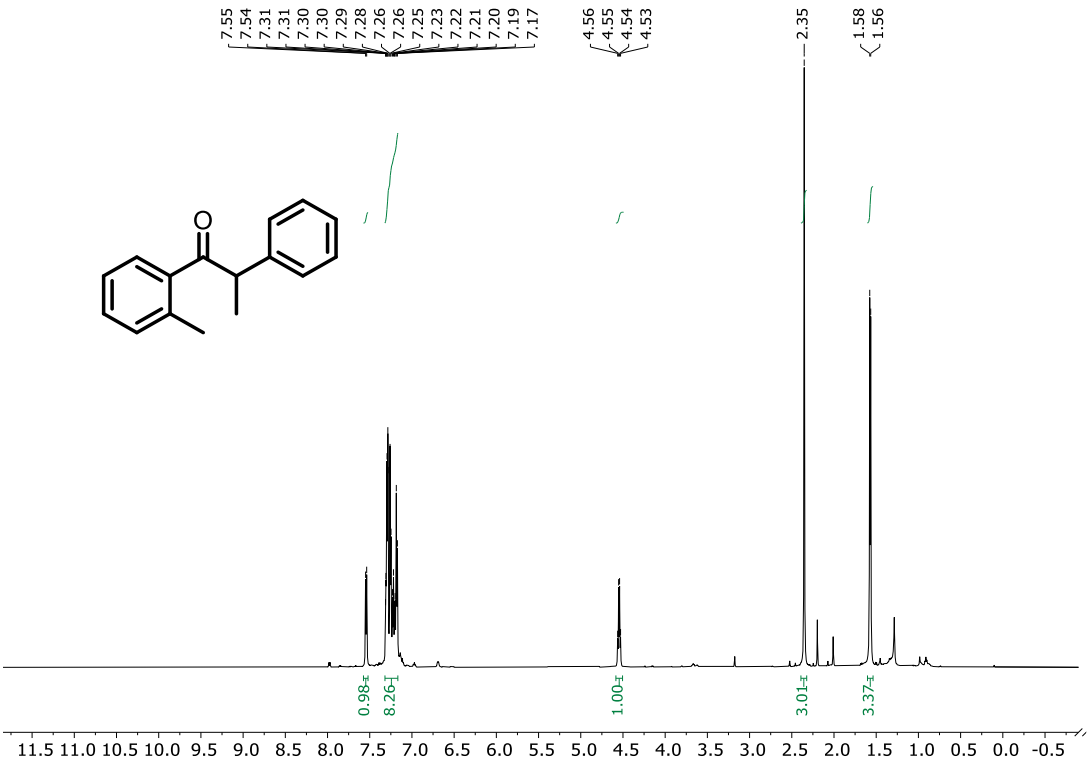
2f (1,2-bis(4-fluorophenyl)propan-1-one)

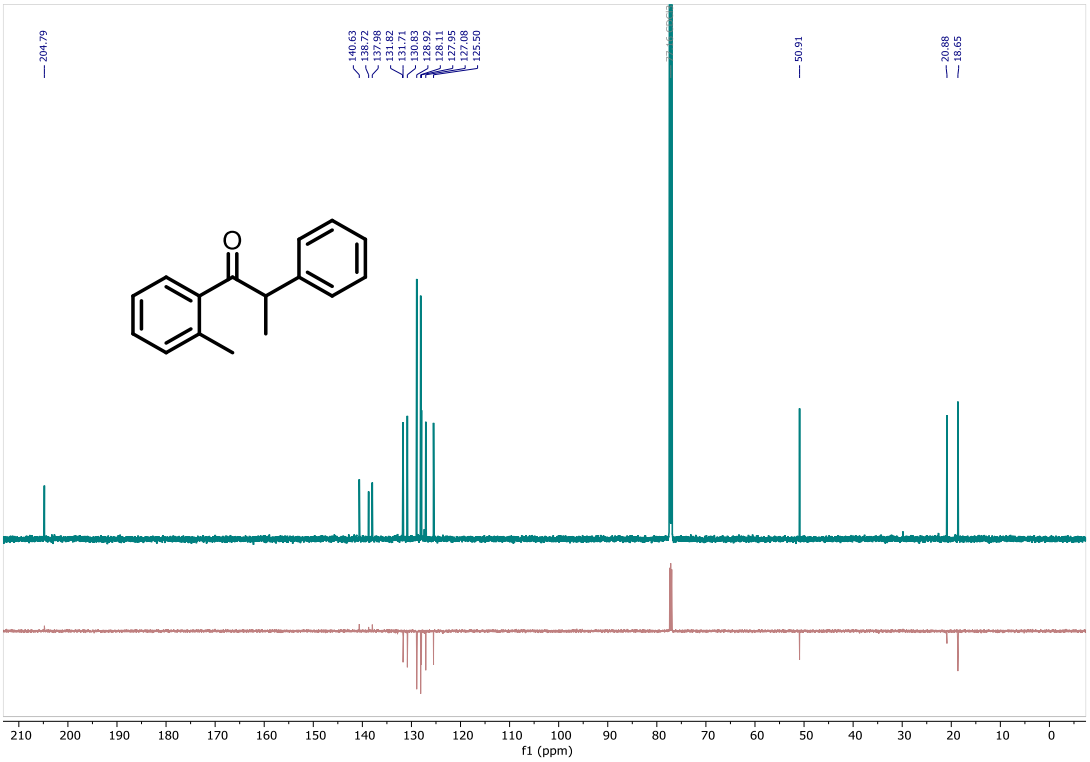




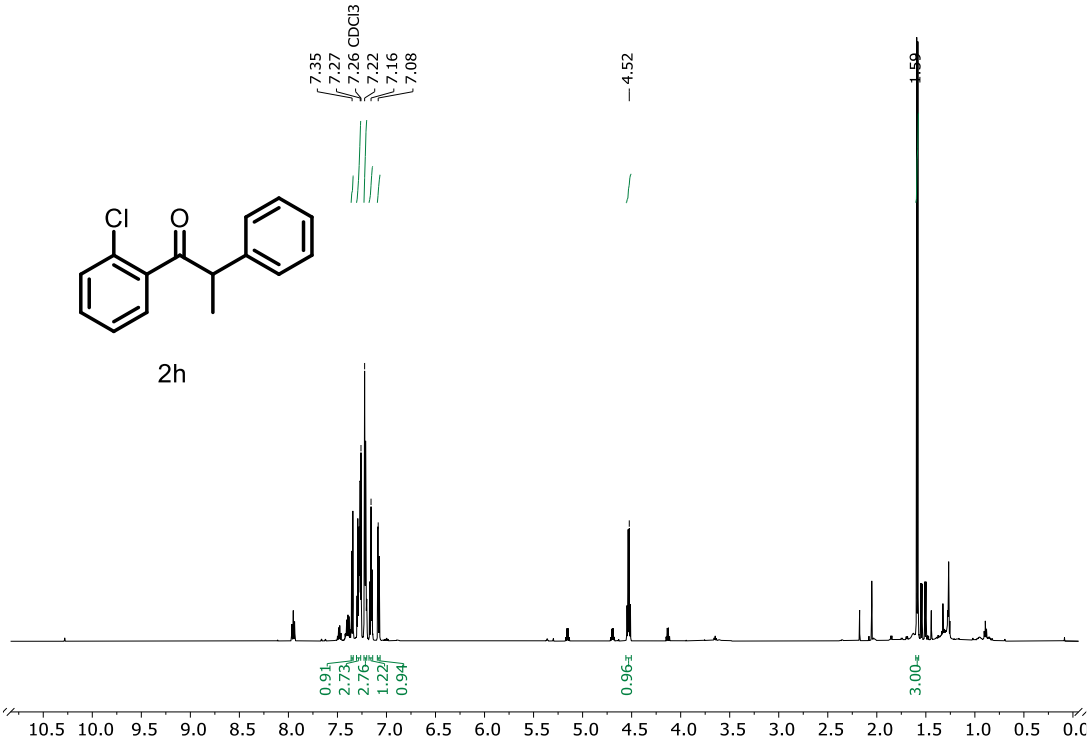

-105.26
-105.27
-105.28
-105.29
-105.30
-115.57
-115.57
-115.58
-115.59
-115.60
-115.61
O
F
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2g(2-phenyl-1-(o-tolyl)propan-1-one)

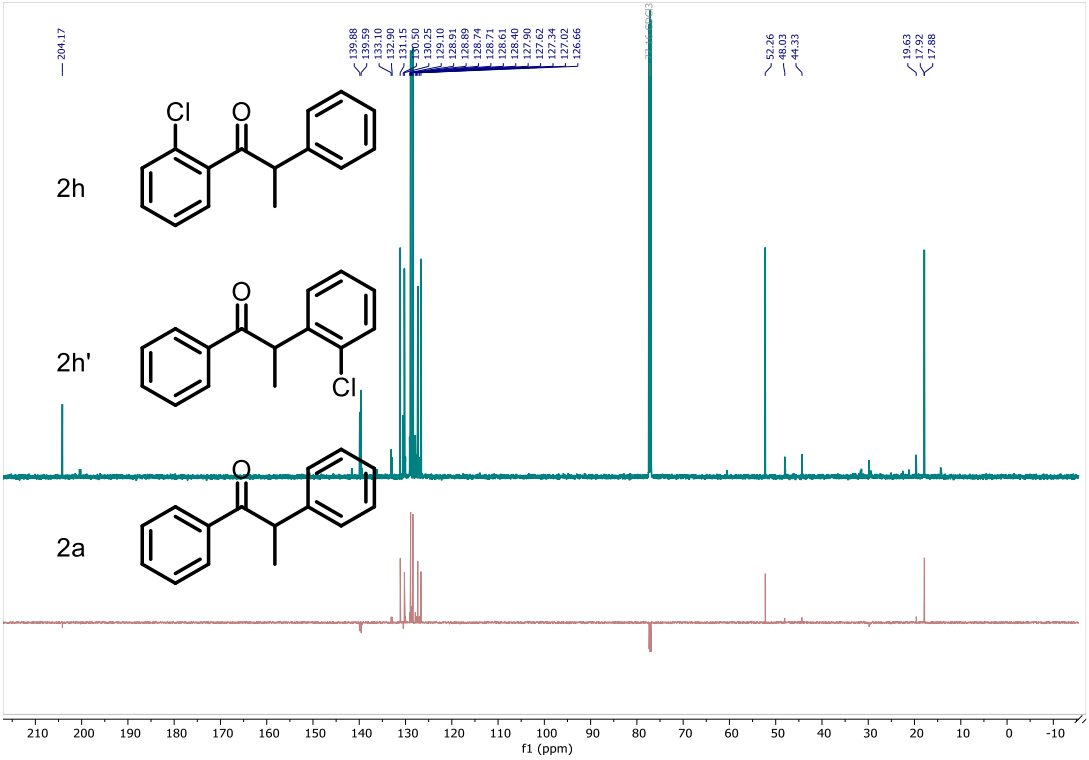




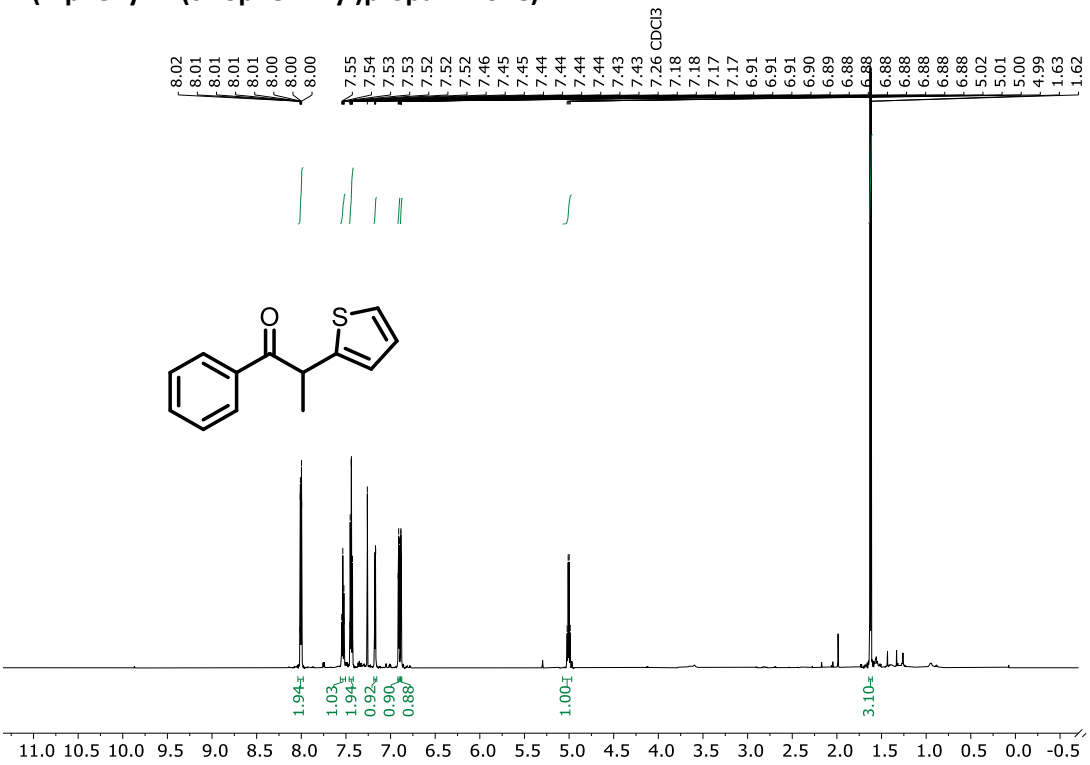
2h: (1-(2-chlorophenyl)-2-phenylpropan-1-one); 2h': 2-(2-chlorophenyl)-1-phenylpropan-1-one; 2a: 1,2-diphenylpropan-1-one)

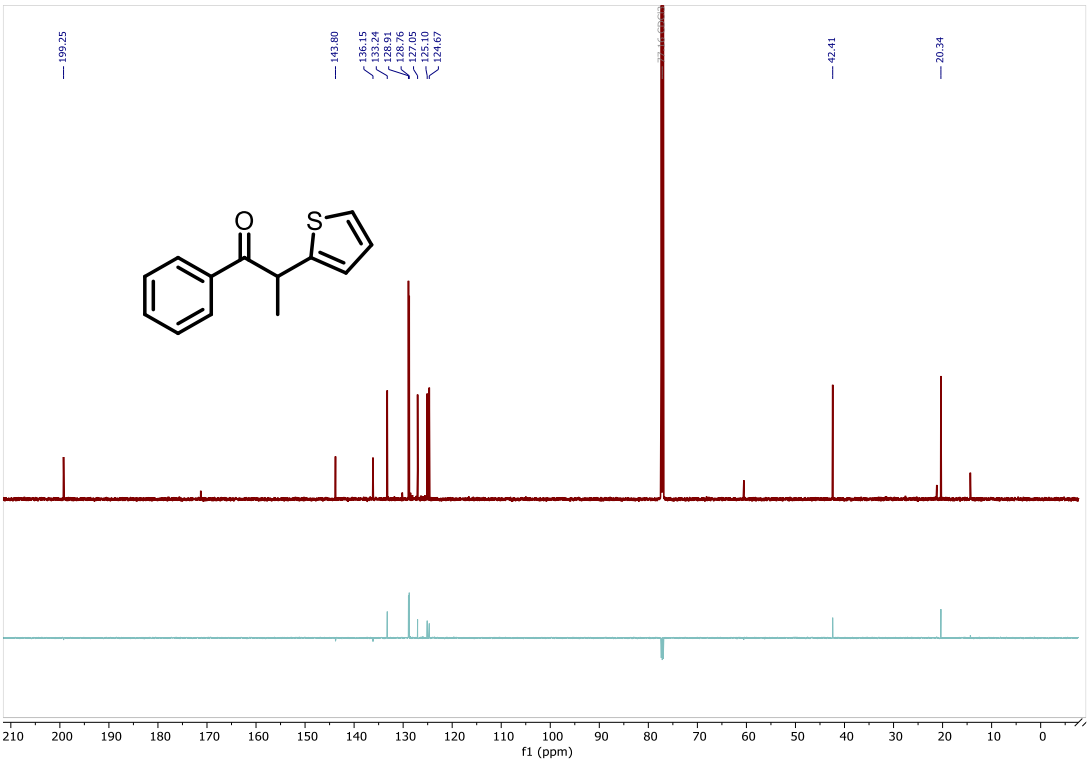


Compounds 2h'+2a, selected peaks

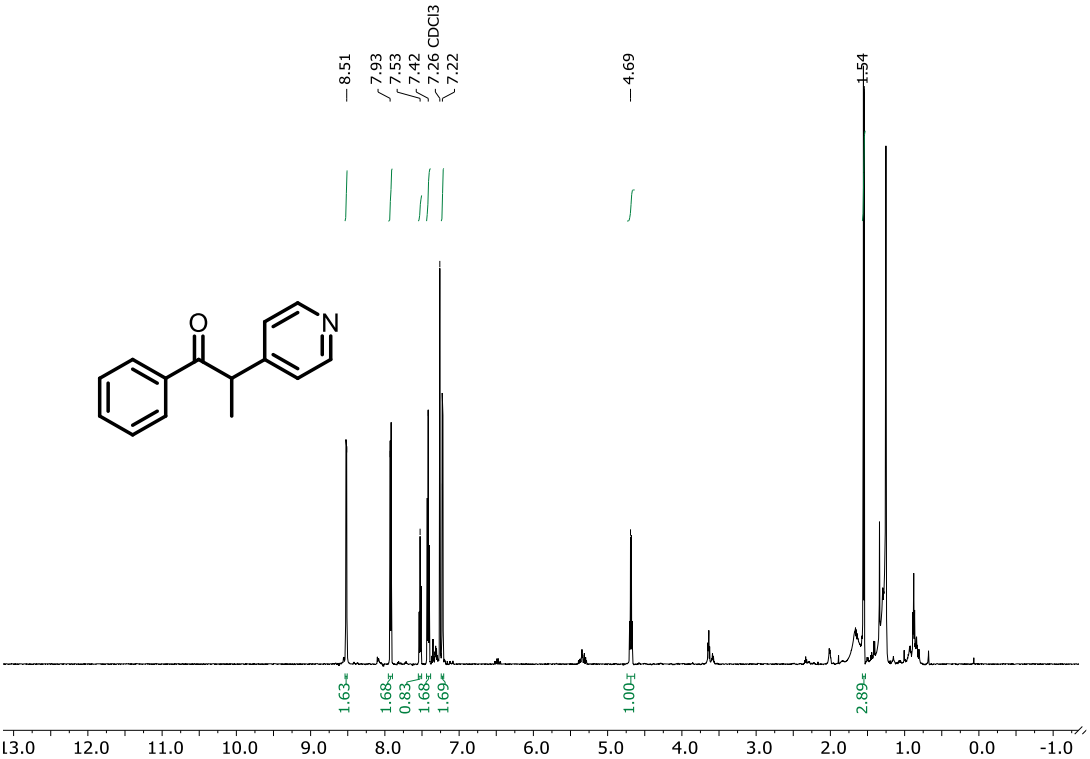

204.17
139.88
139.59
133.10
132.90
131.15
130.50
130.25
129.10
128.91
128.89
128.74
128.71
128.61
128.40
127.90
127.62
127.34
127.02
126.66
52.26
48.03
44.33
19.63
17.92
17.88
Cl
O
2h
O
2h'
Cl
O
2a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

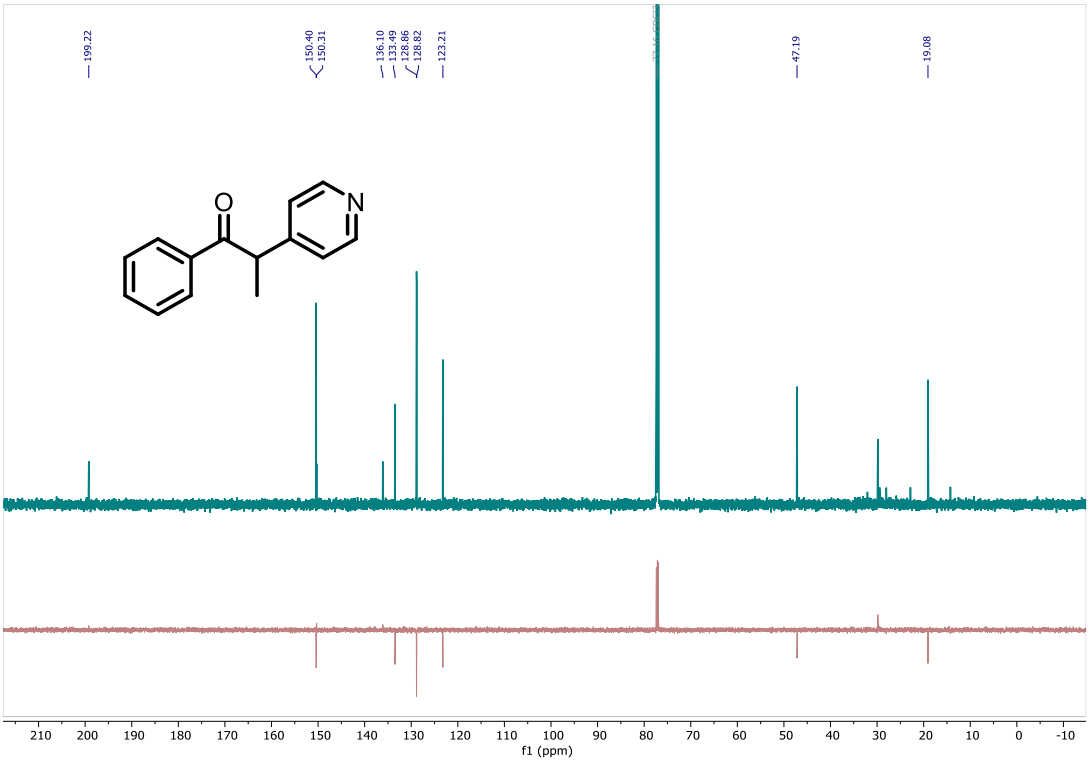
2i (1-phenyl-2-(thiophen-2-yl)propan-1-one)



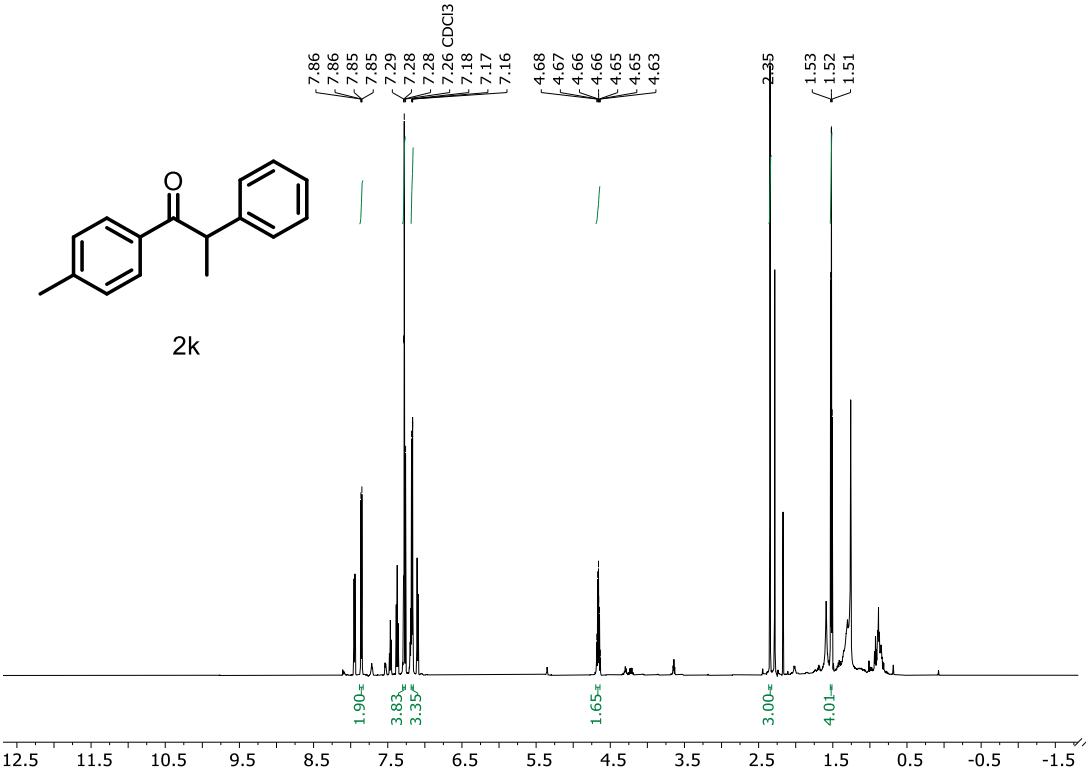


2j (1-phenyl-2-(pyridin-4-yl)propan-1-one)

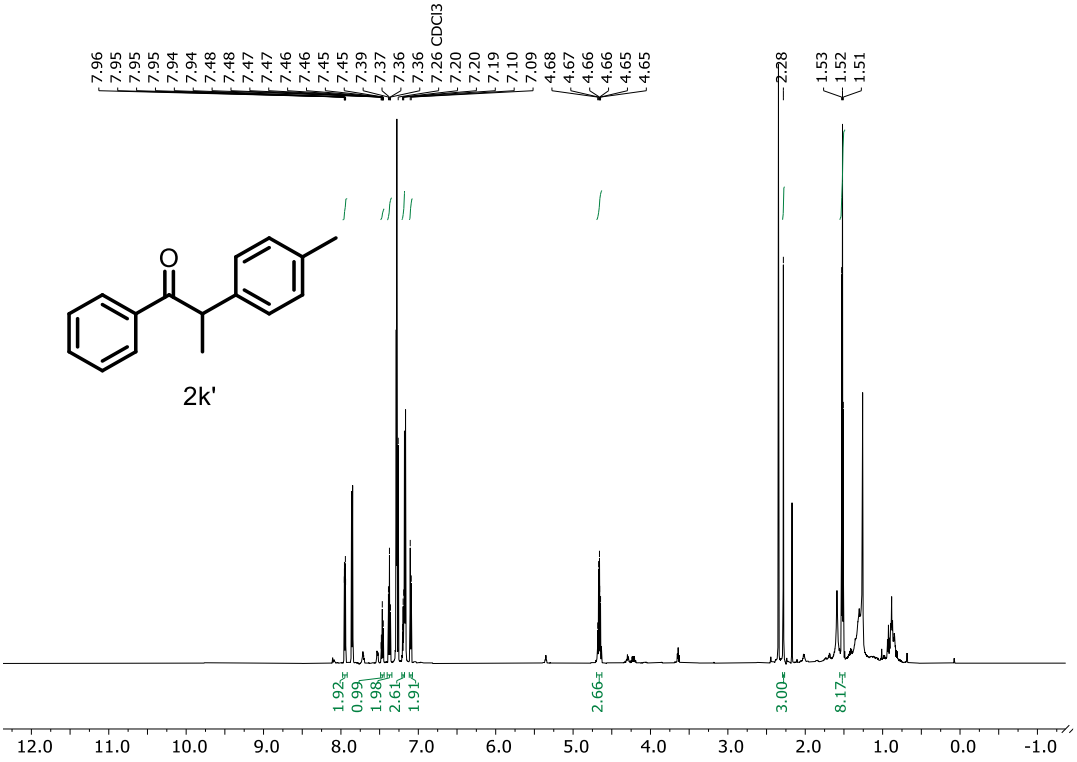


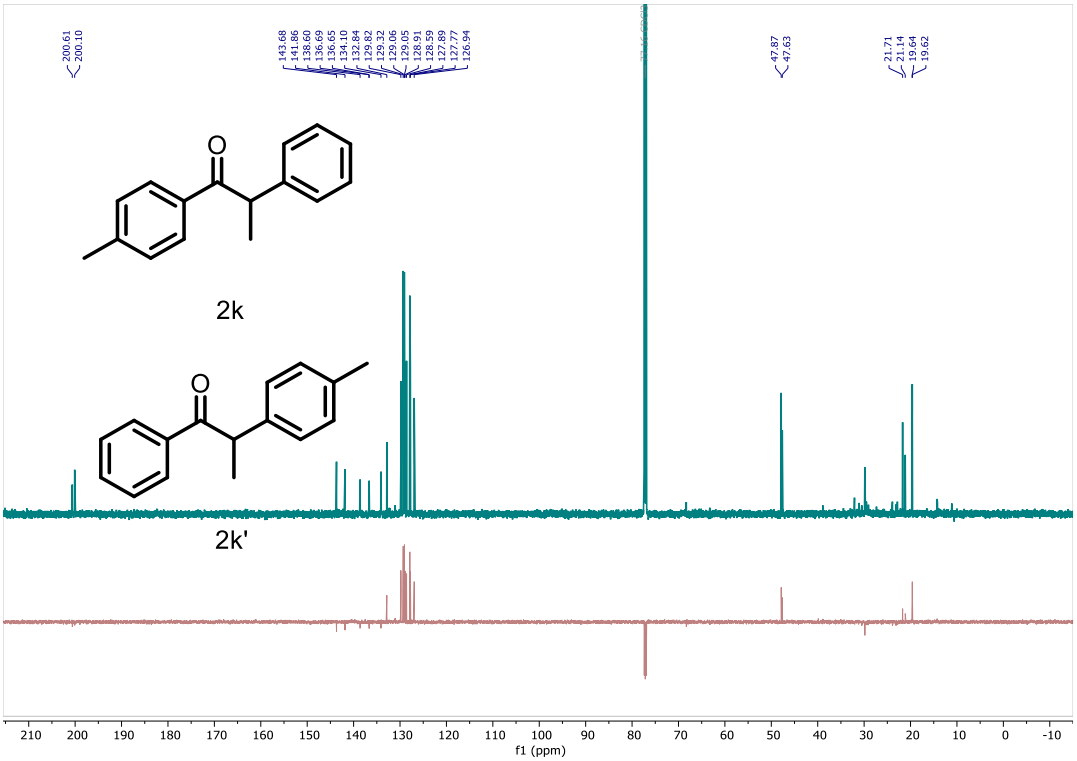


2k (2-phenyl-1-(p-tolyl)propan-1-one); 2k' (1-phenyl-2-(p-tolyl)propan-1-one)
Compound 2k (peaks at 4.63-4.68 and 1.51-1.53 belong to 2k+2k')

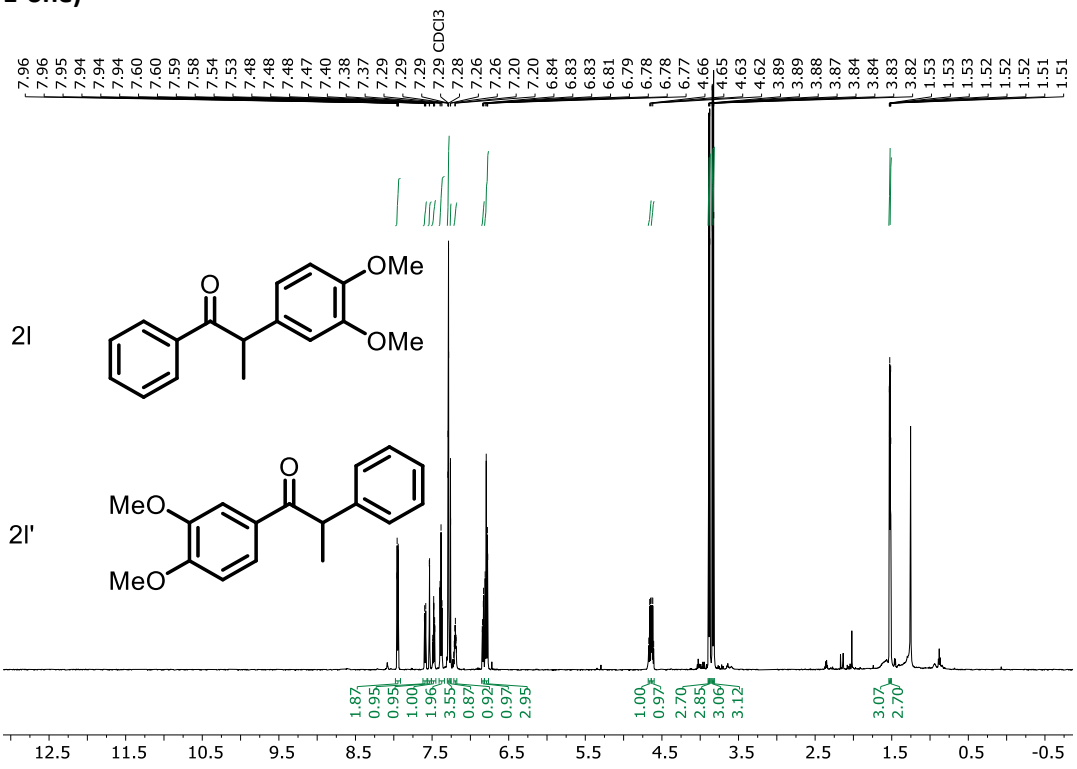


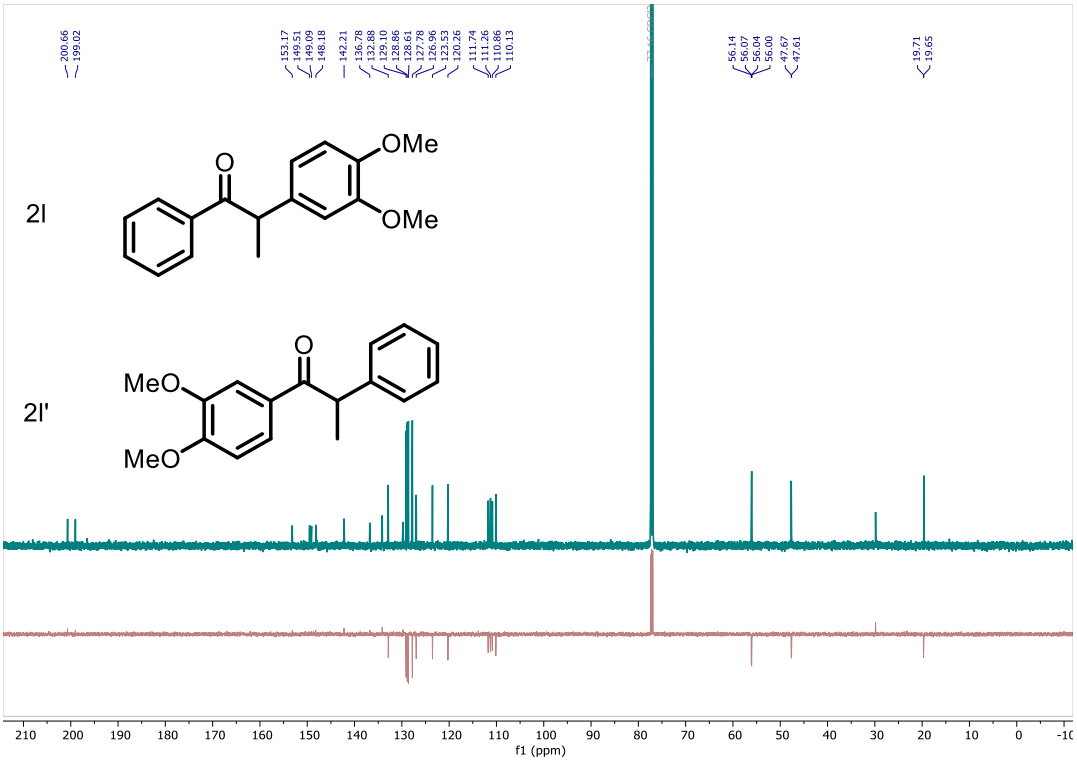
Compound 2k’ (peaks at 4.65-4.68 and 1.51-1.53 belong to 2k+2k’)



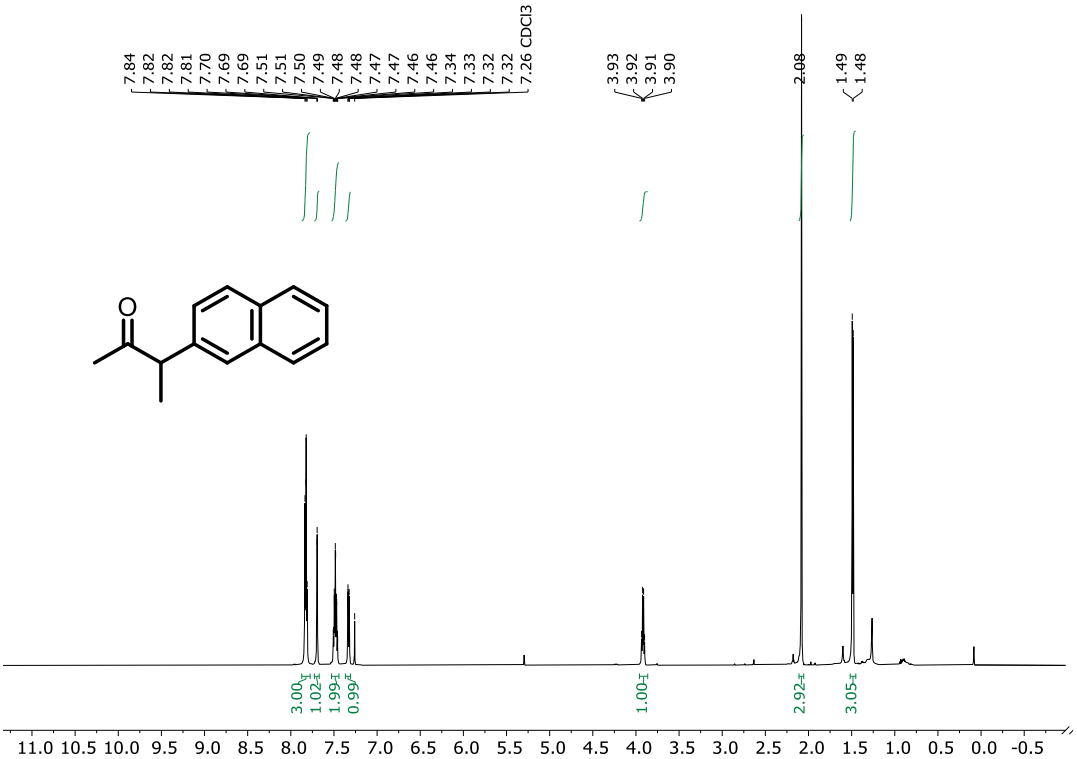


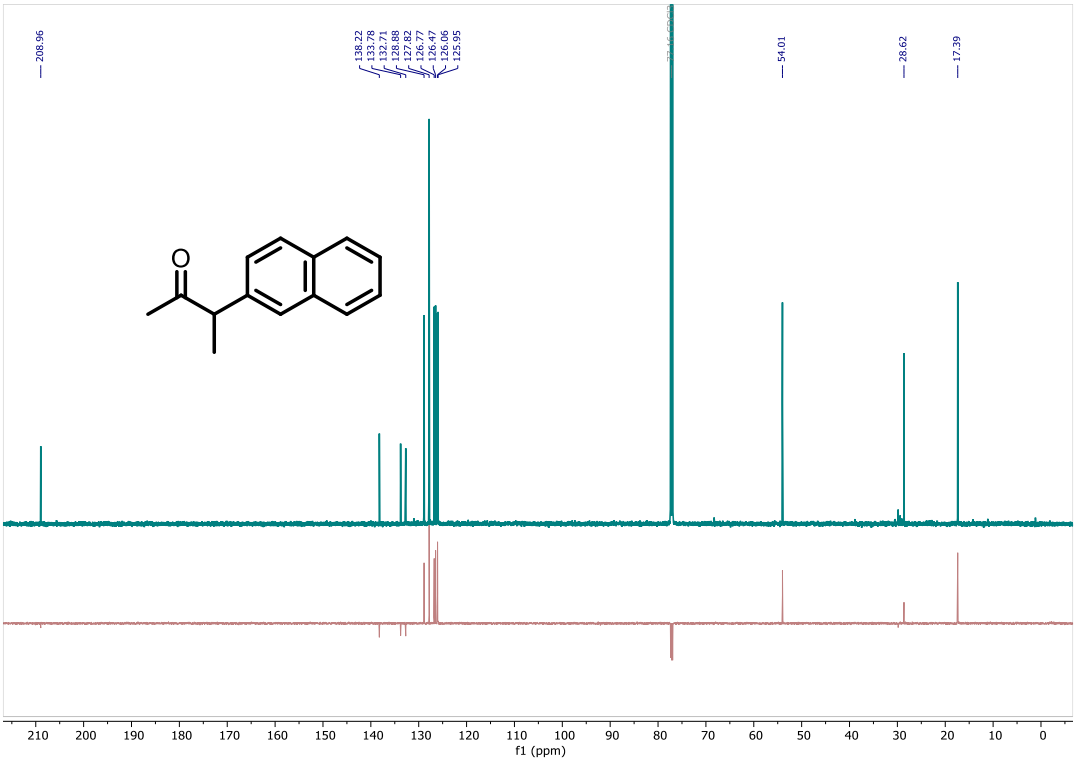
2l (2-(3,4-dimethoxyphenyl)-1-phenylpropan-1-one)) and 2l' (1-(3,4-dimethoxyphenyl)-2-phenylpropan-1-one)



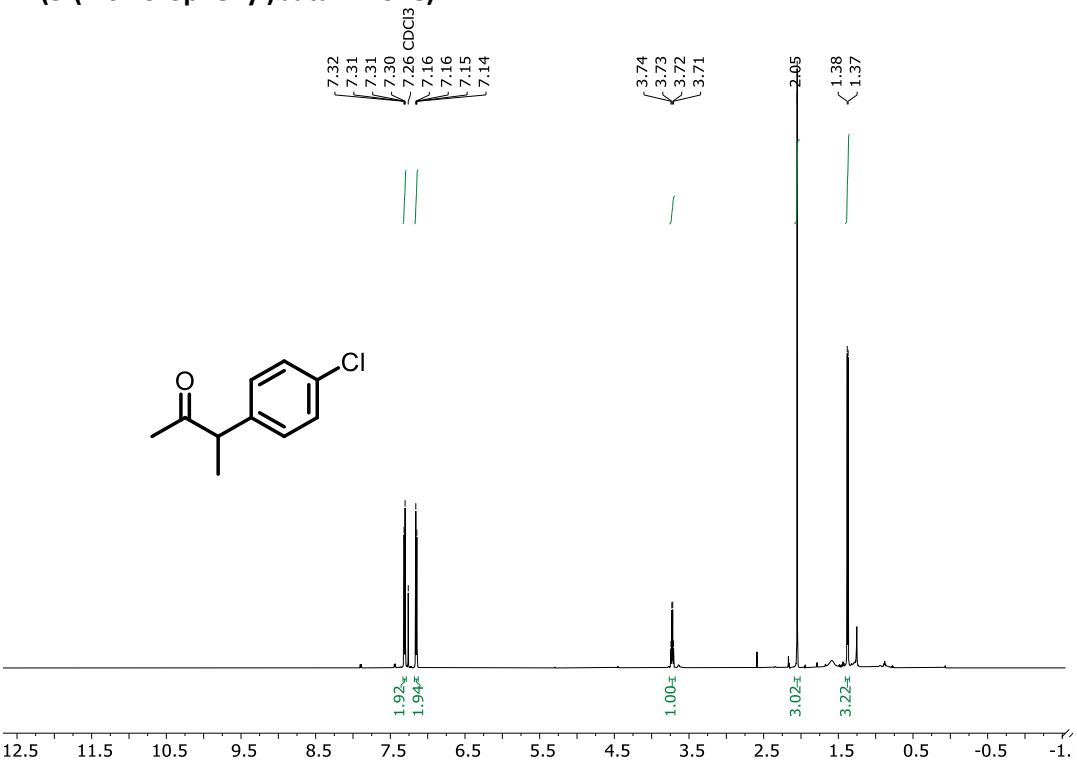


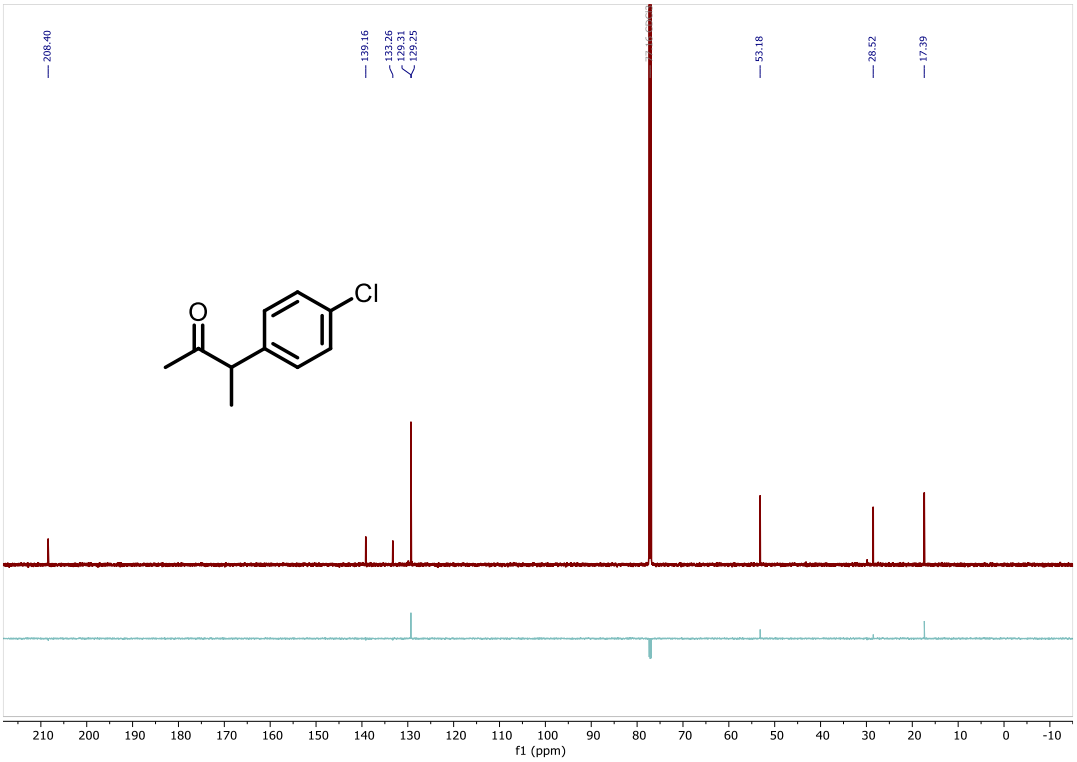
2m (3-(naphthalen-2-yl)butan-2-one)



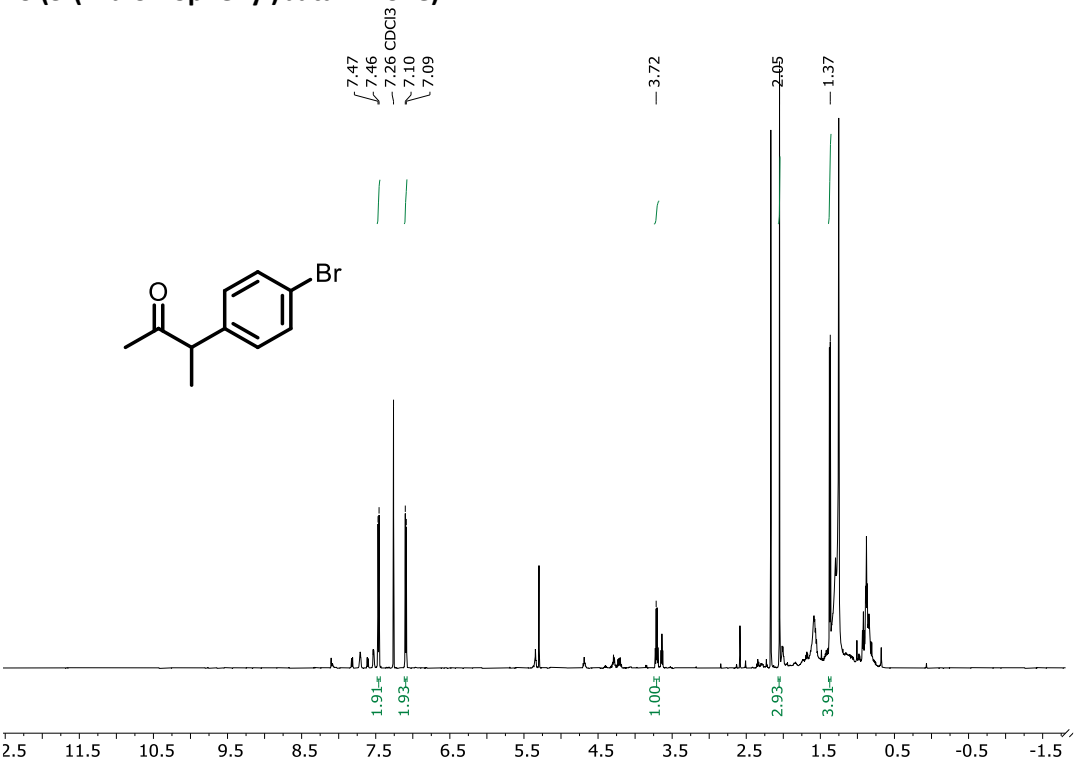


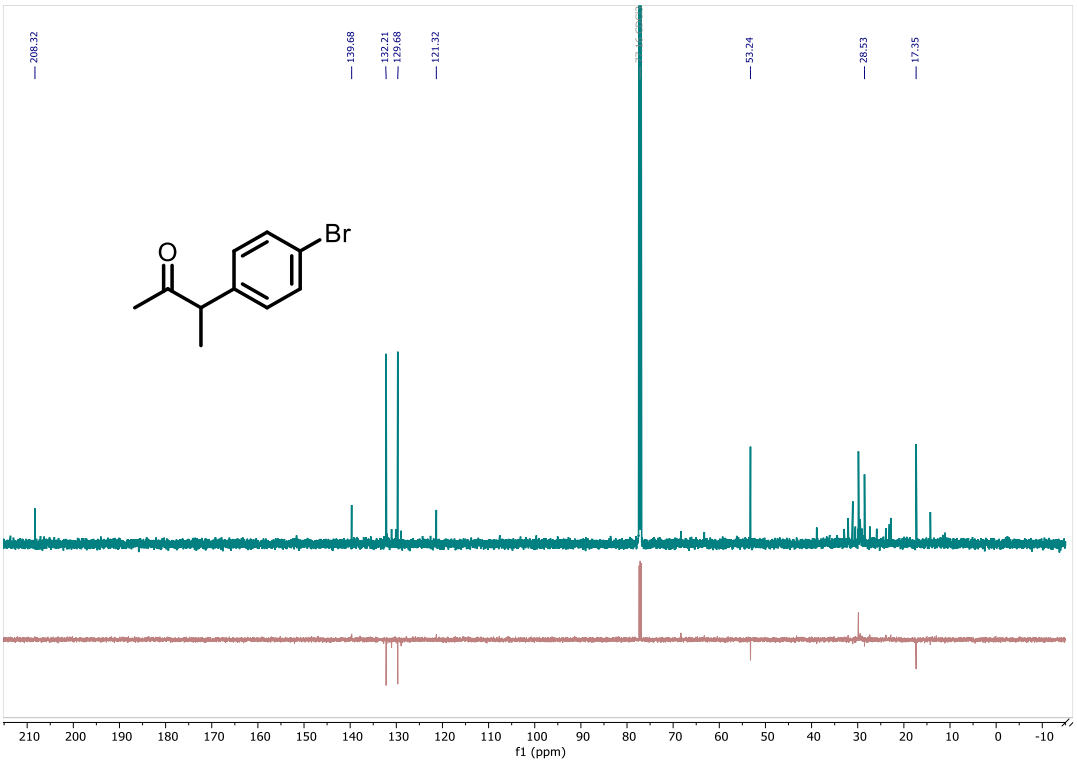
2n (3-(4-chlorophenyl)butan-2-one)



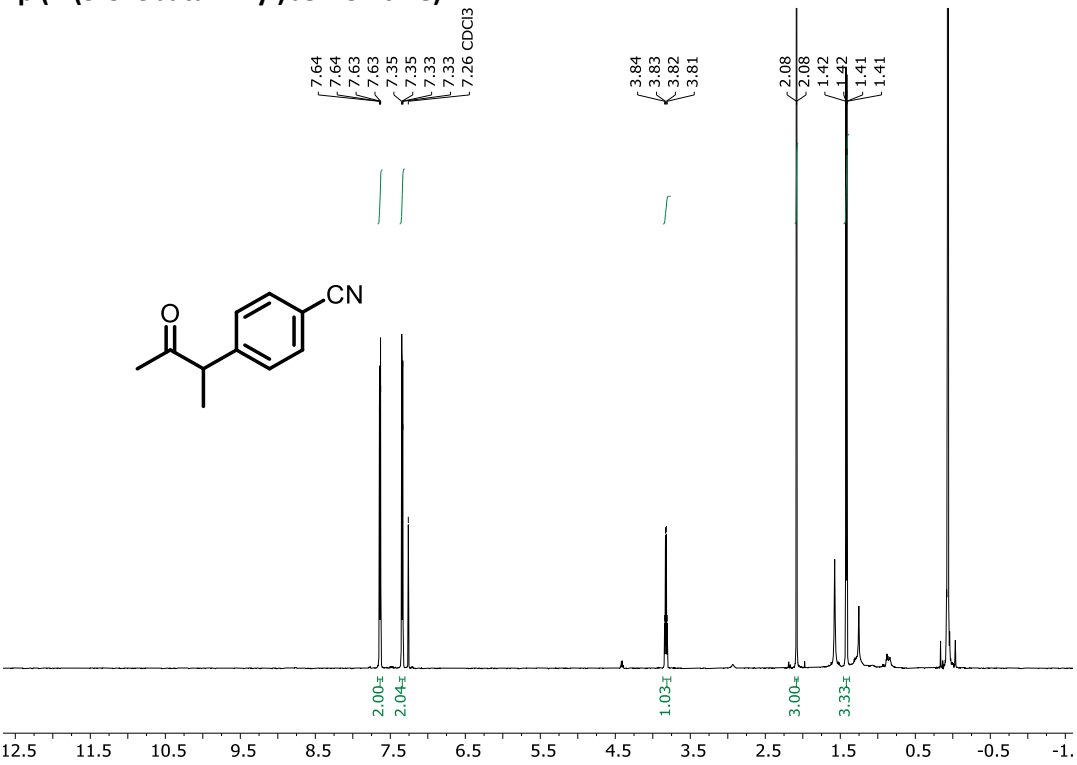


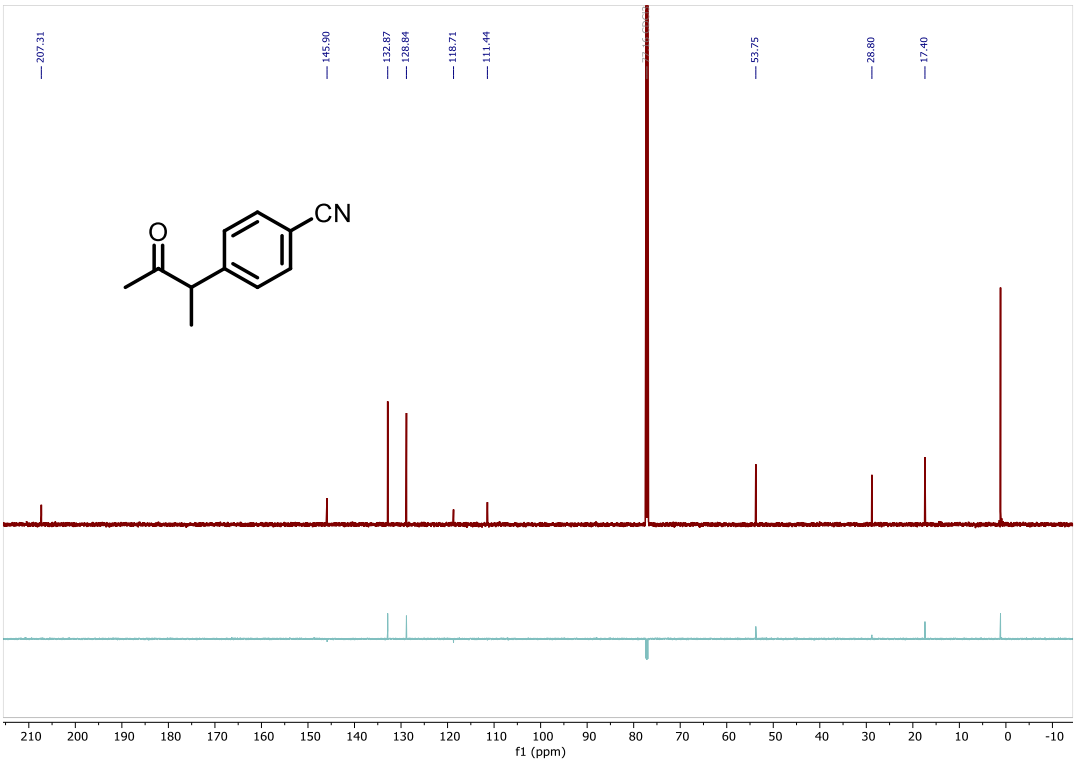
2o (3-(4-bromophenyl)butan-2-one)



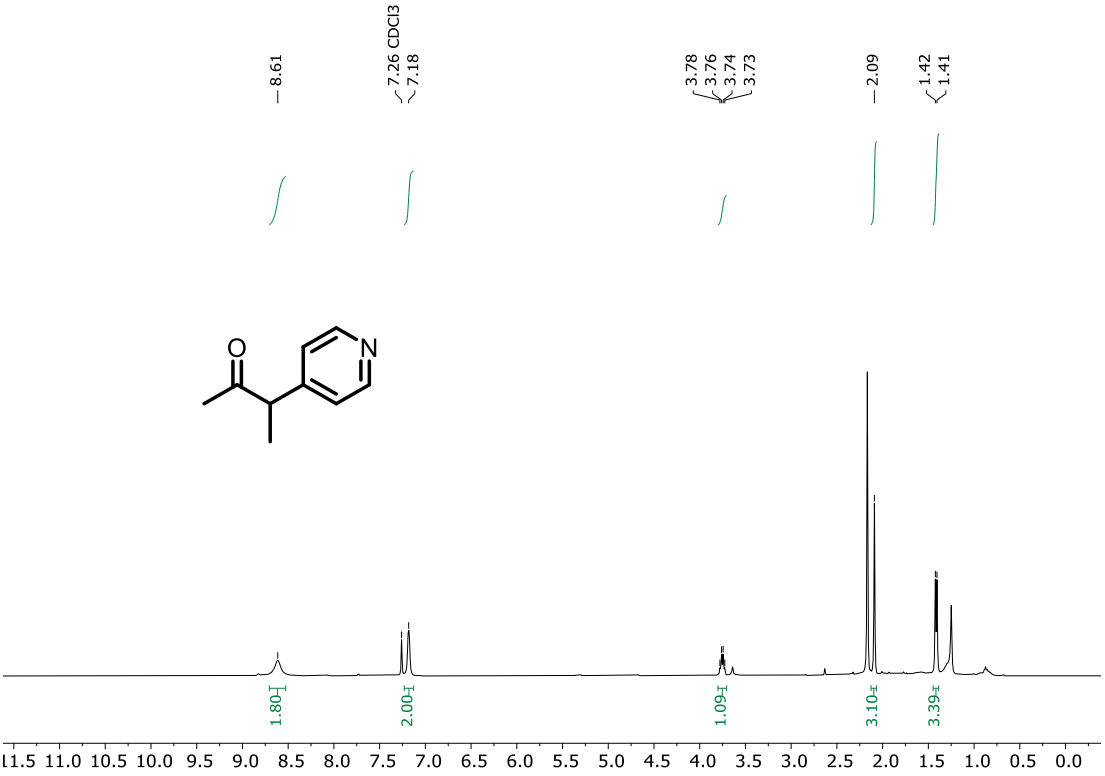


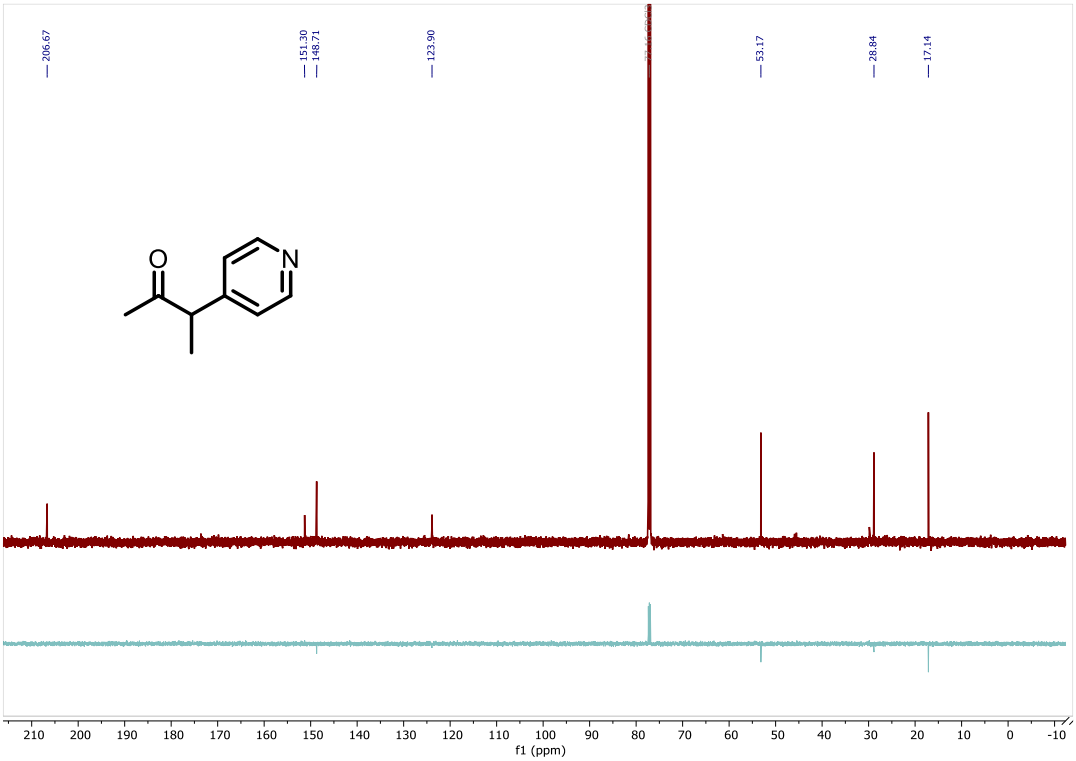
2p (4-(3-oxobutan-2-yl)benzonitrile)



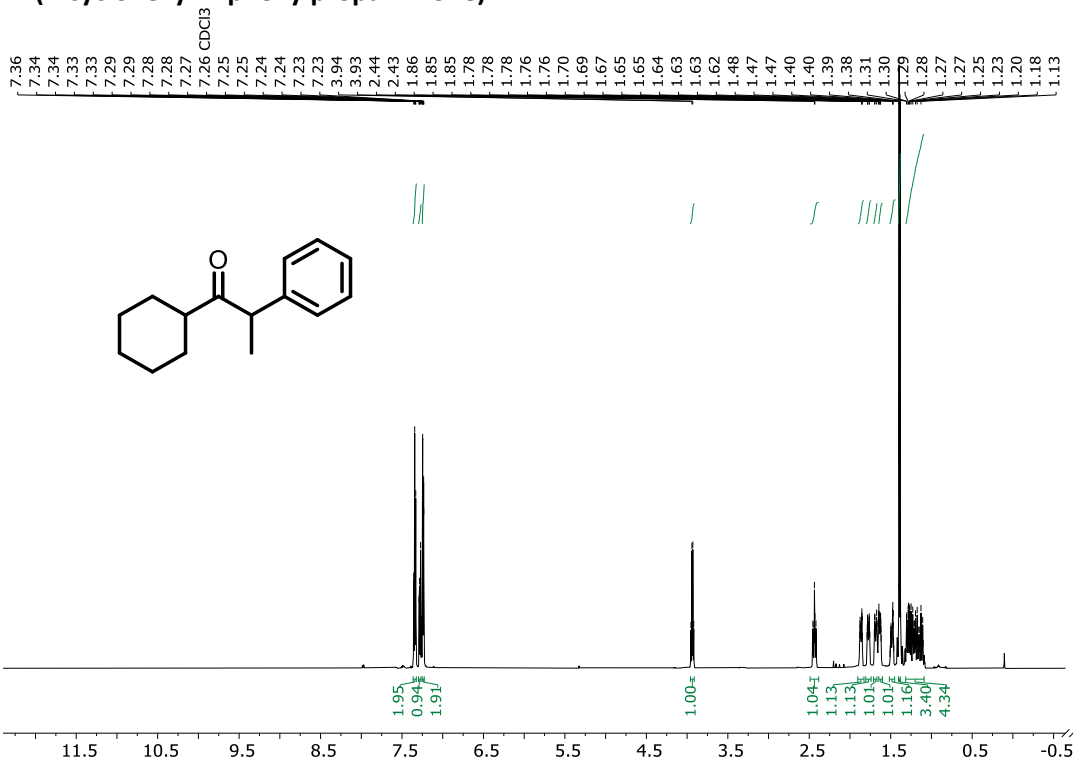


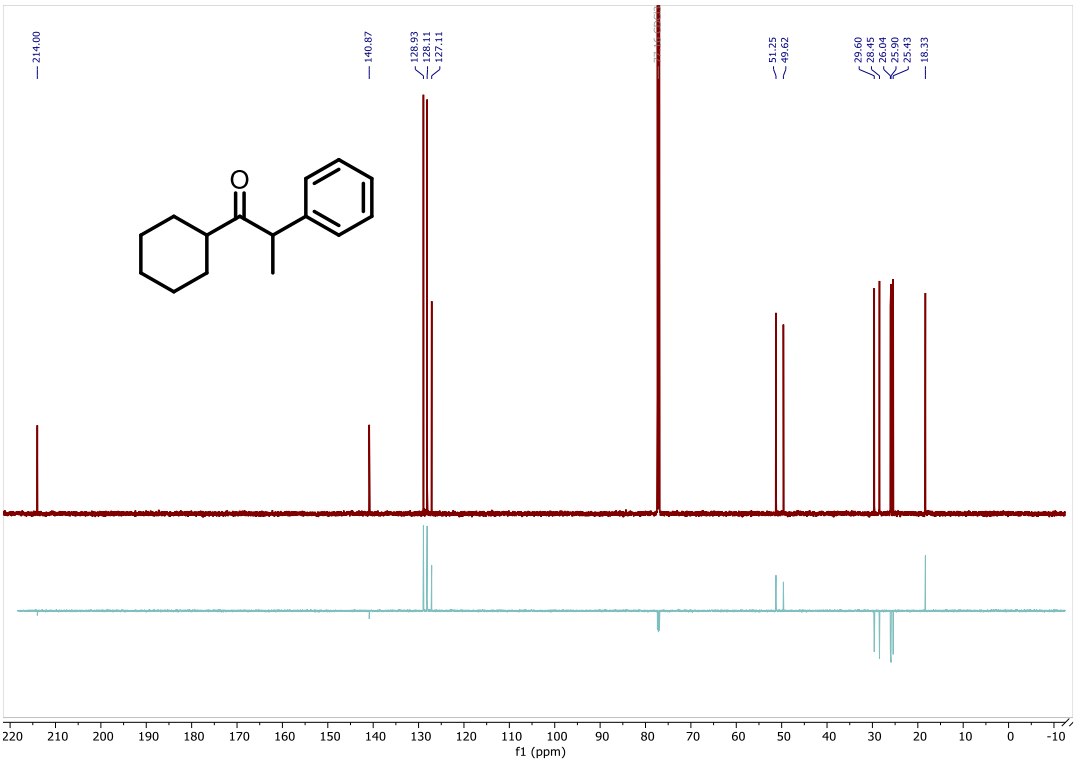
2q (3-(pyridin-4-yl)butan-2-one)



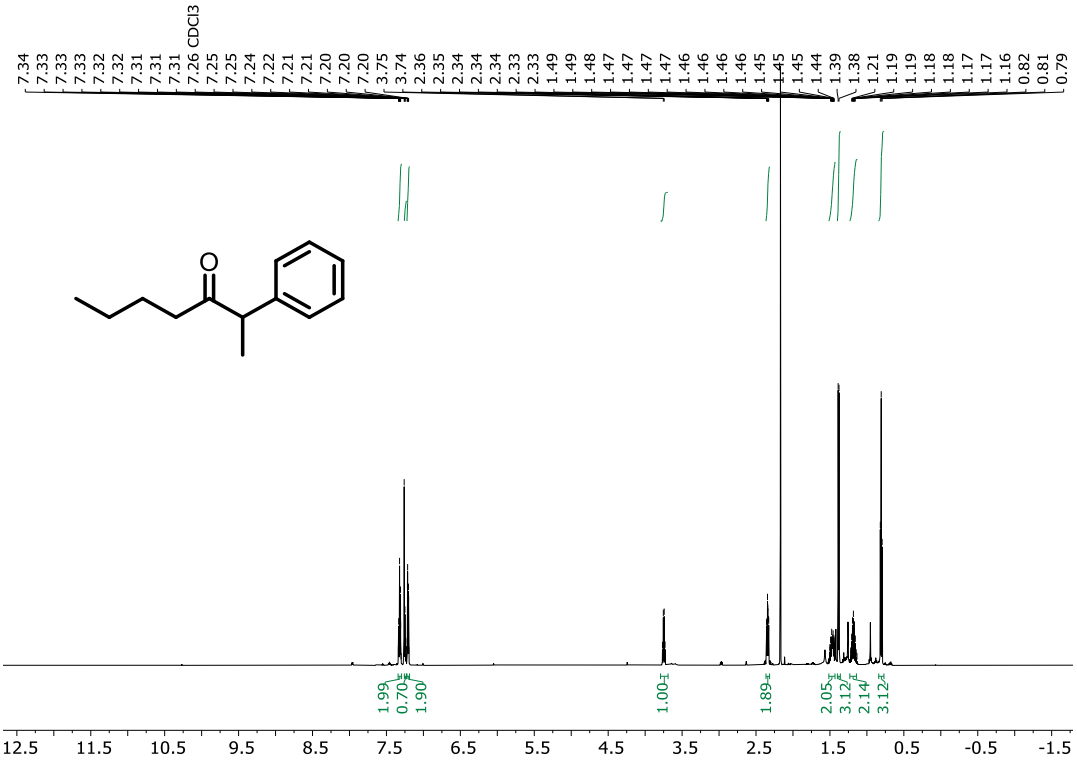


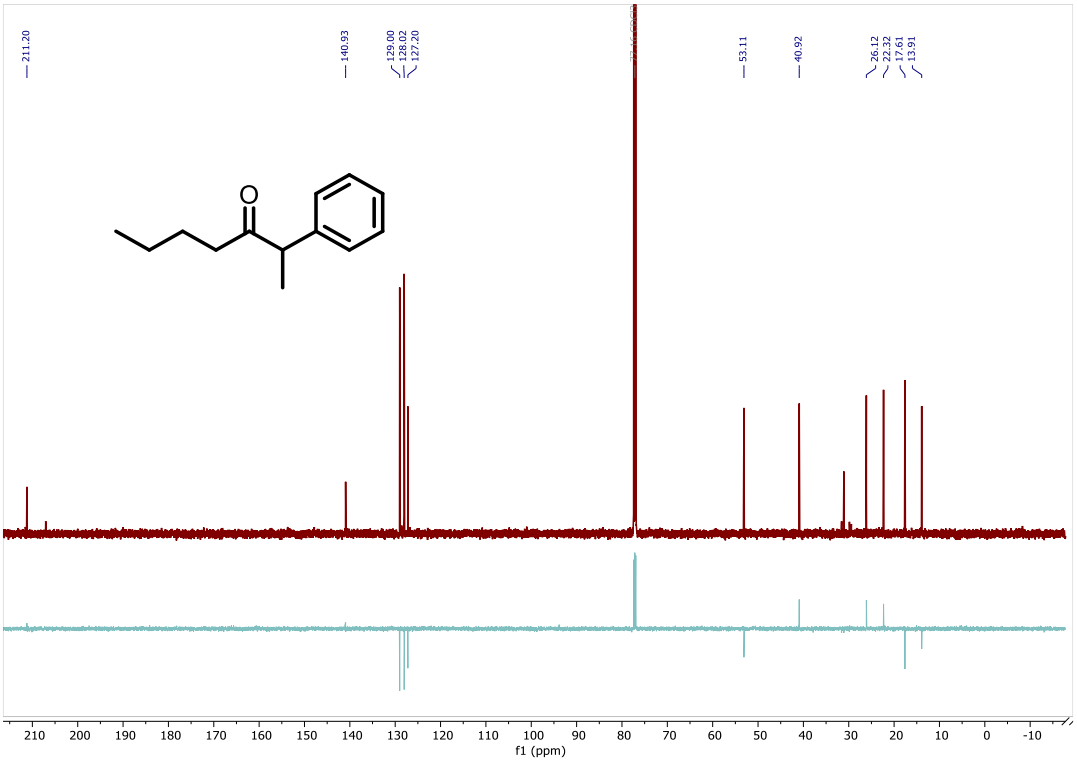
2r (1-cyclohexyl-2-phenylpropan-1-one)



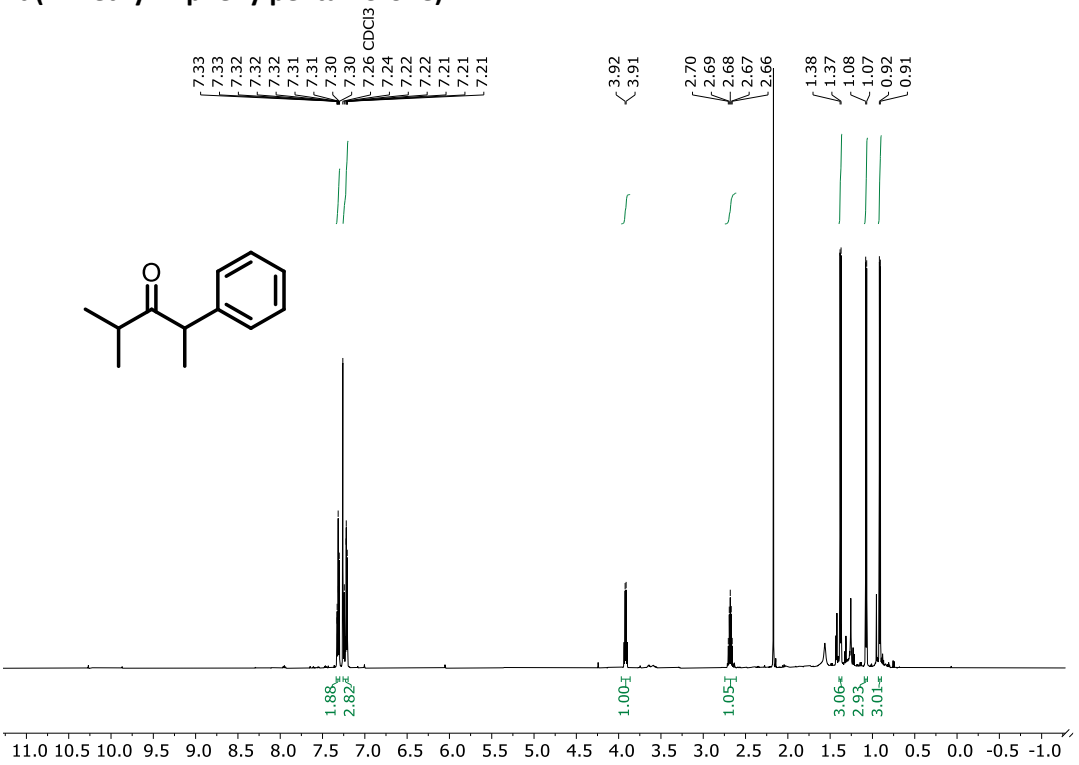


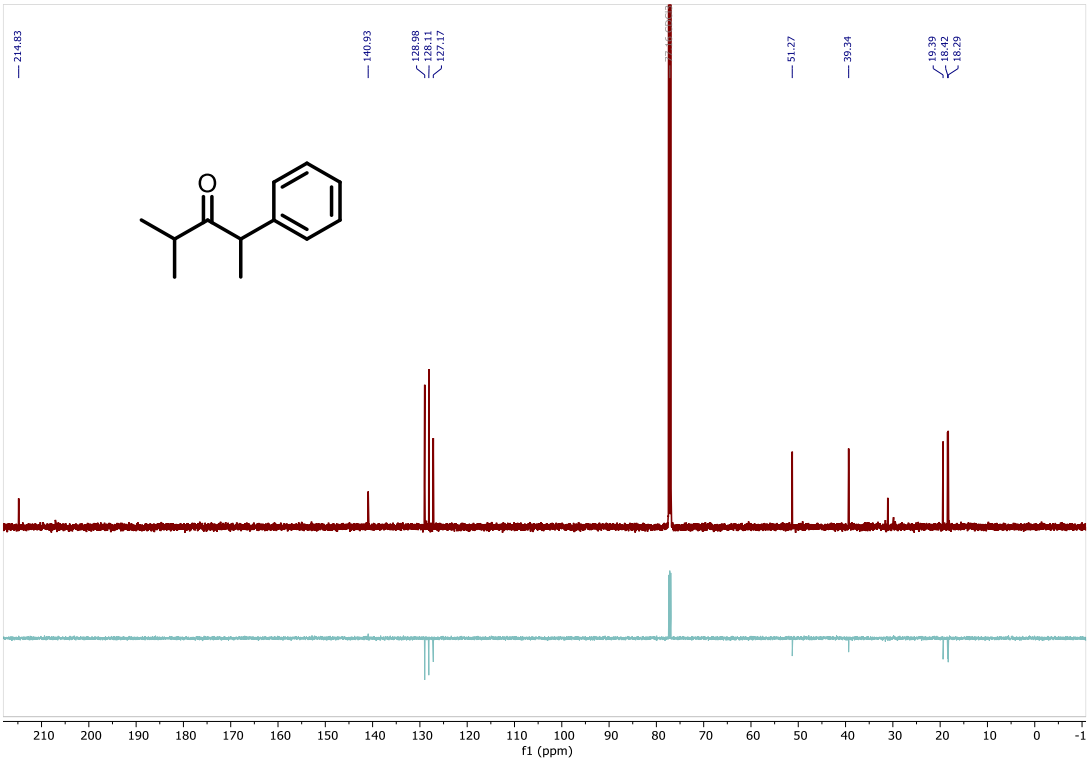
2s (2-phenylheptan-3-one)



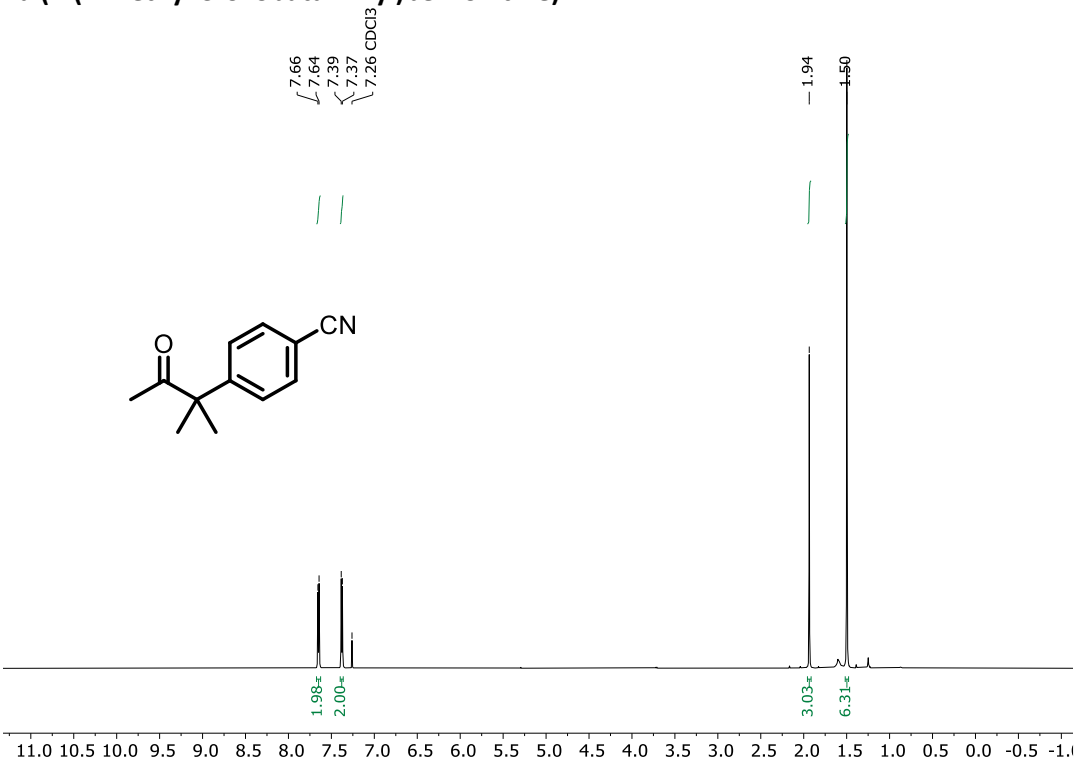


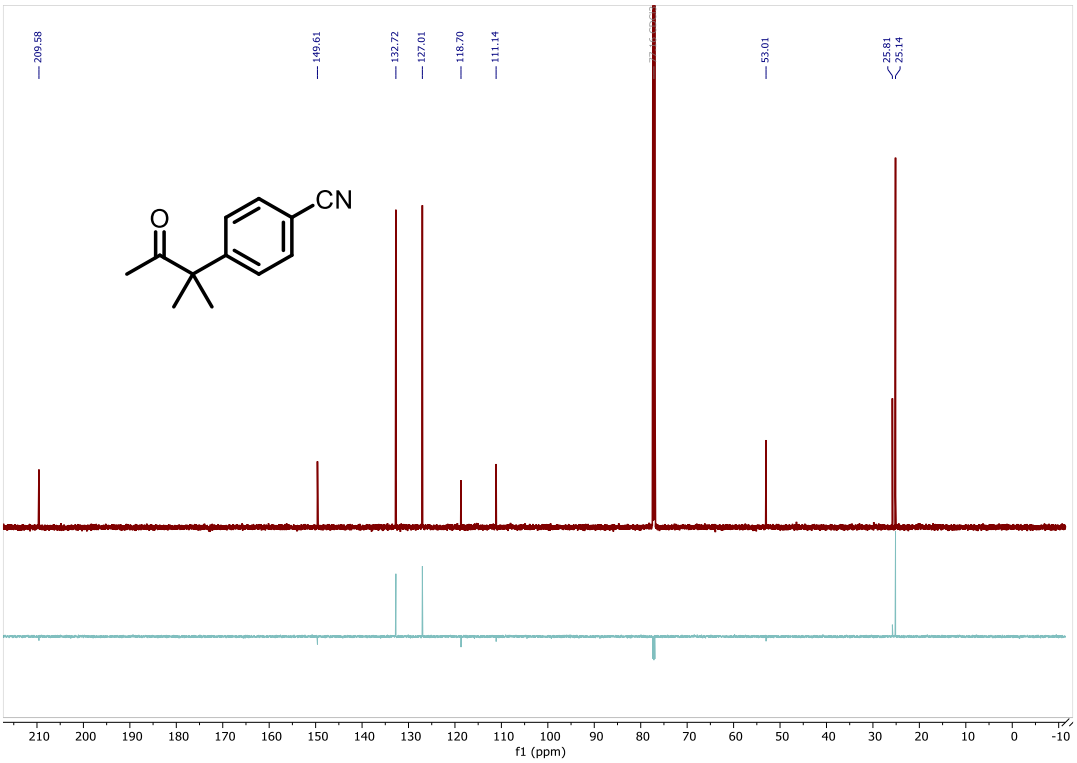
2t (2-methyl-4-phenylpentan-3-one)



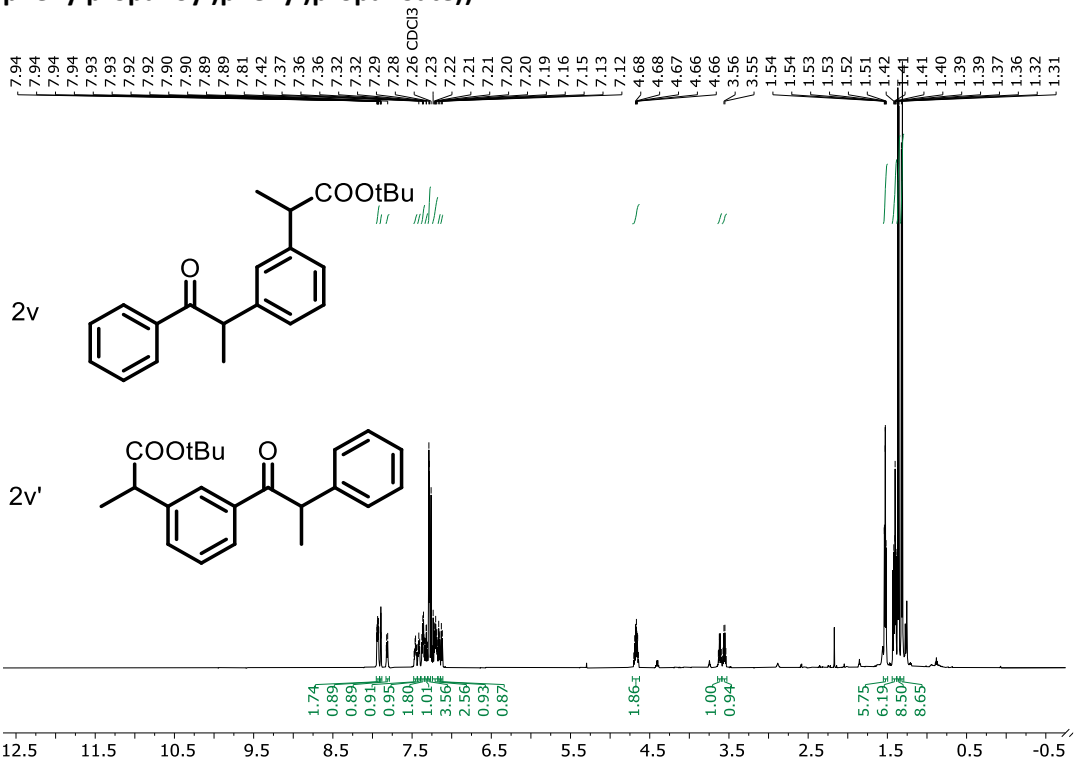


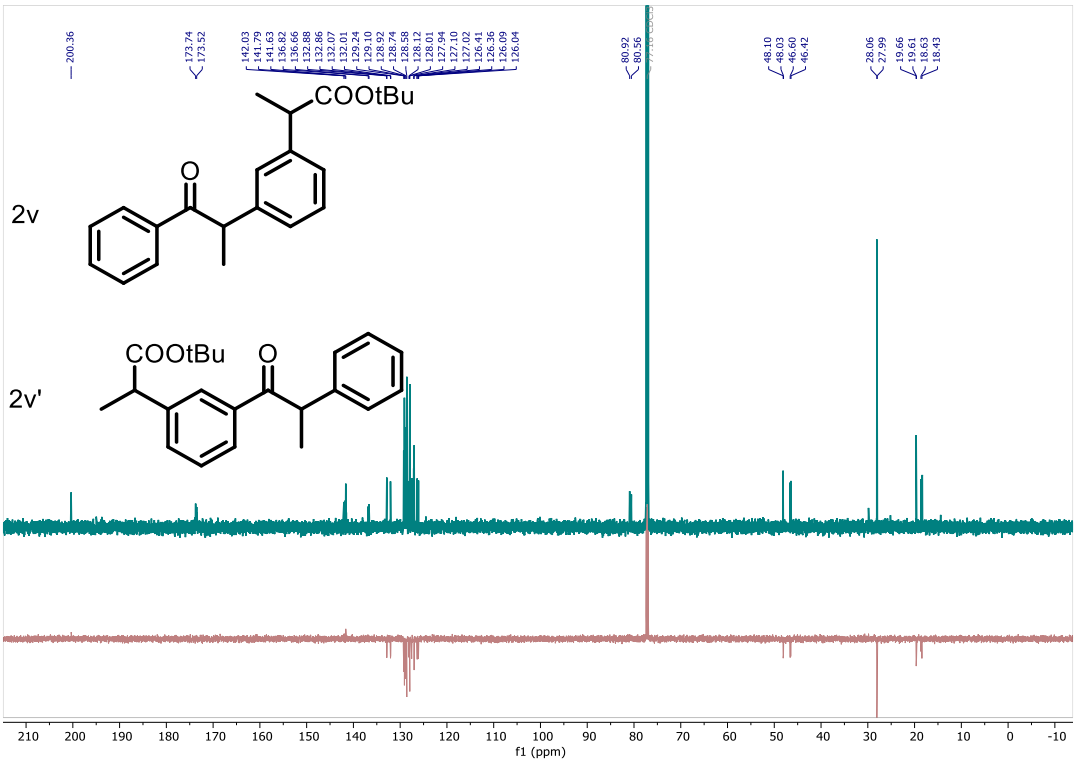
2u (4-(2-methyl-3-oxobutan-2-yl)benzonitrile)



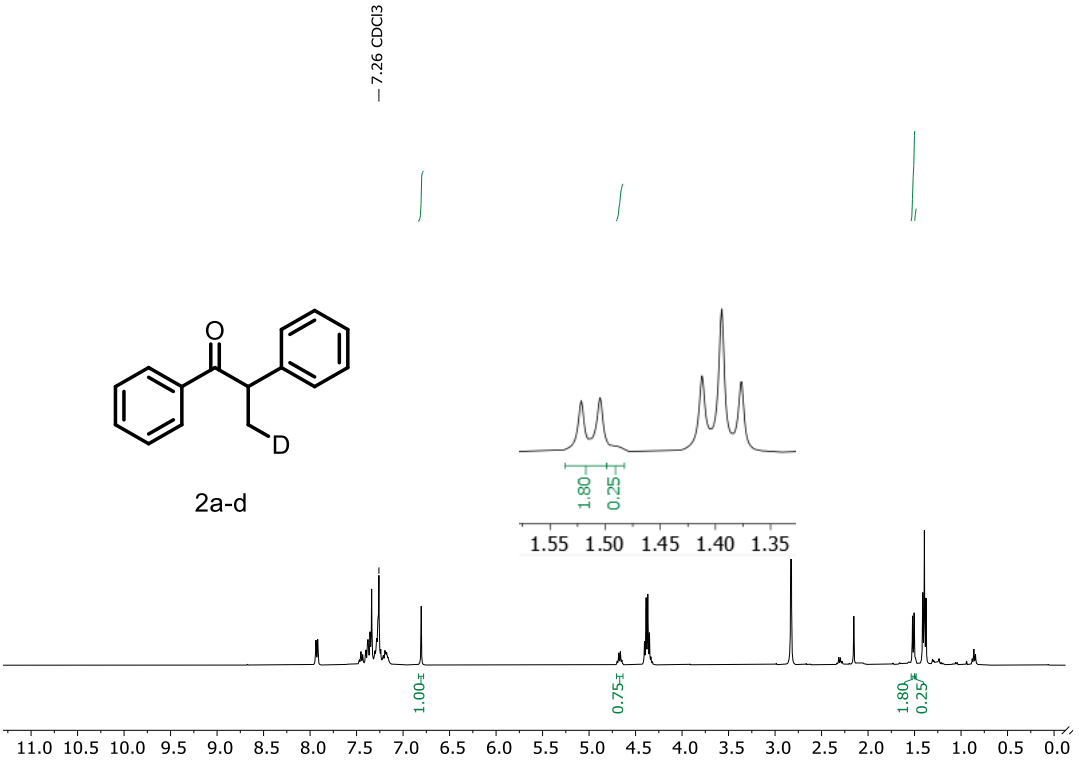


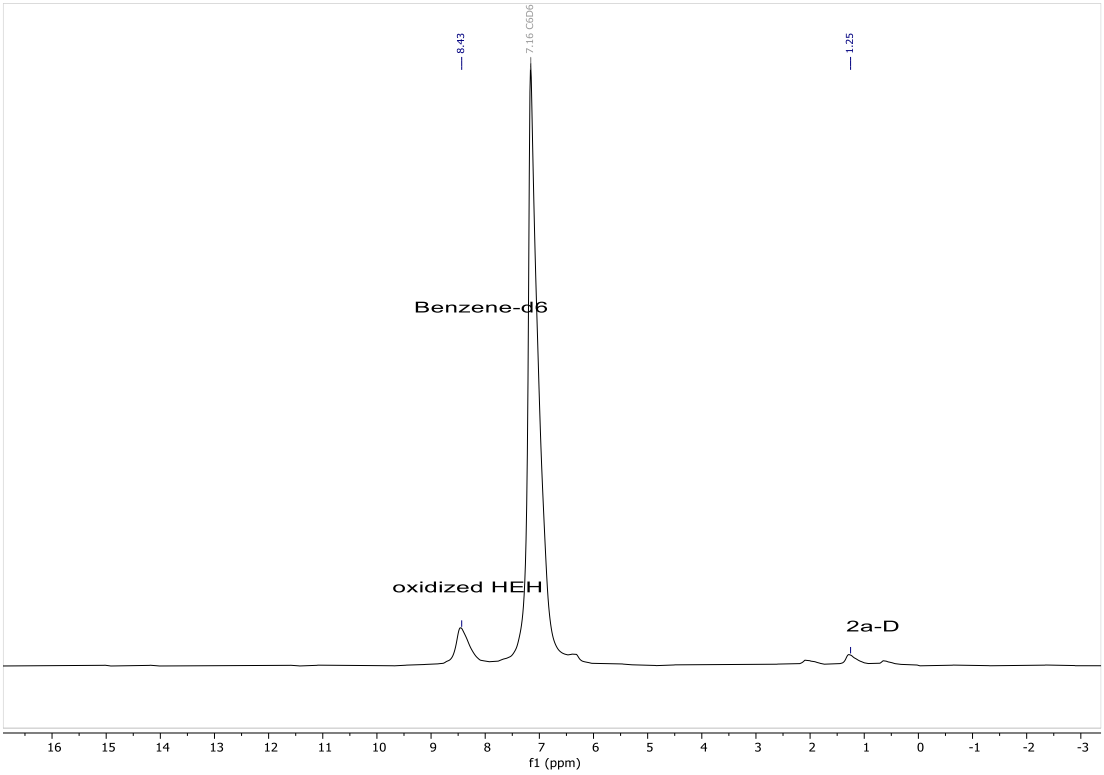
2v ((tert-butyl 2-(3-(1-oxo-1-phenylpropan-2-yl)phenyl)propanoate) and 2v' (tert-butyl 2-(3-(2-phenylpropanoyl)phenyl)propanoate))



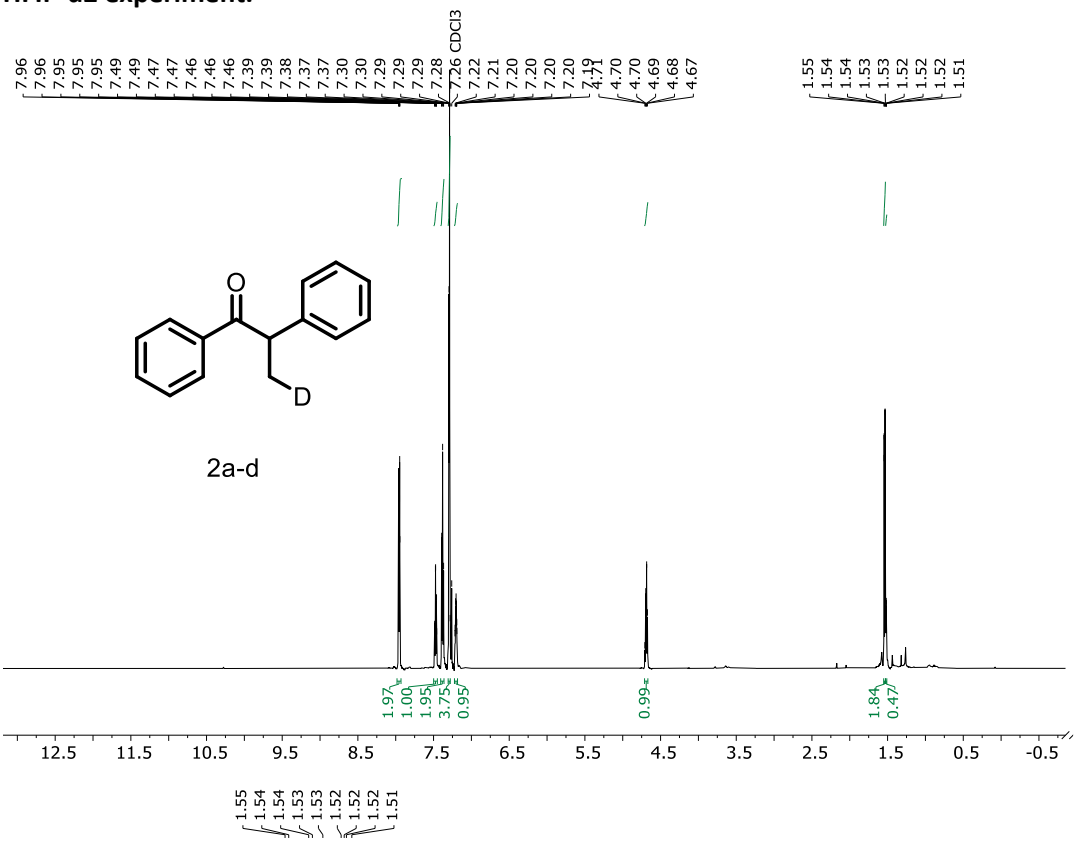


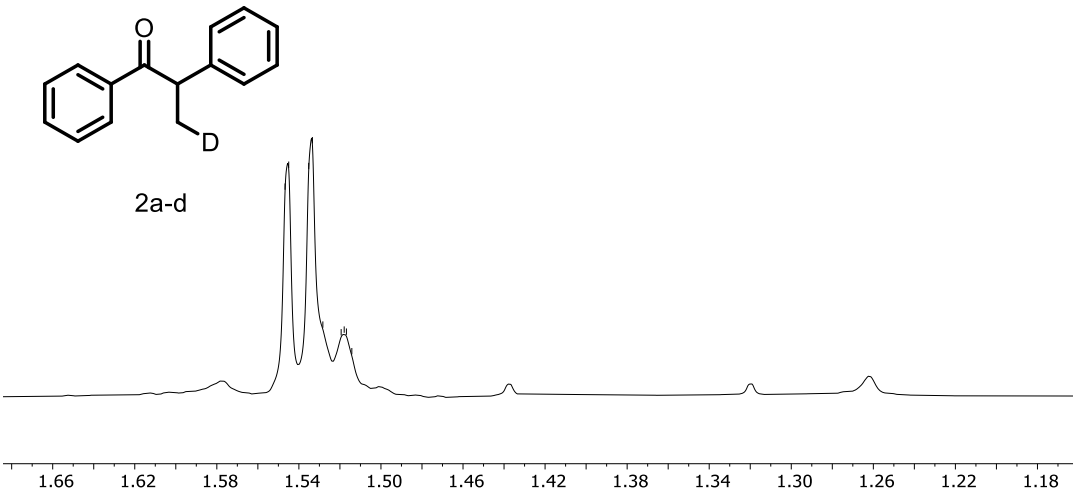
HEH-D4 experiment.

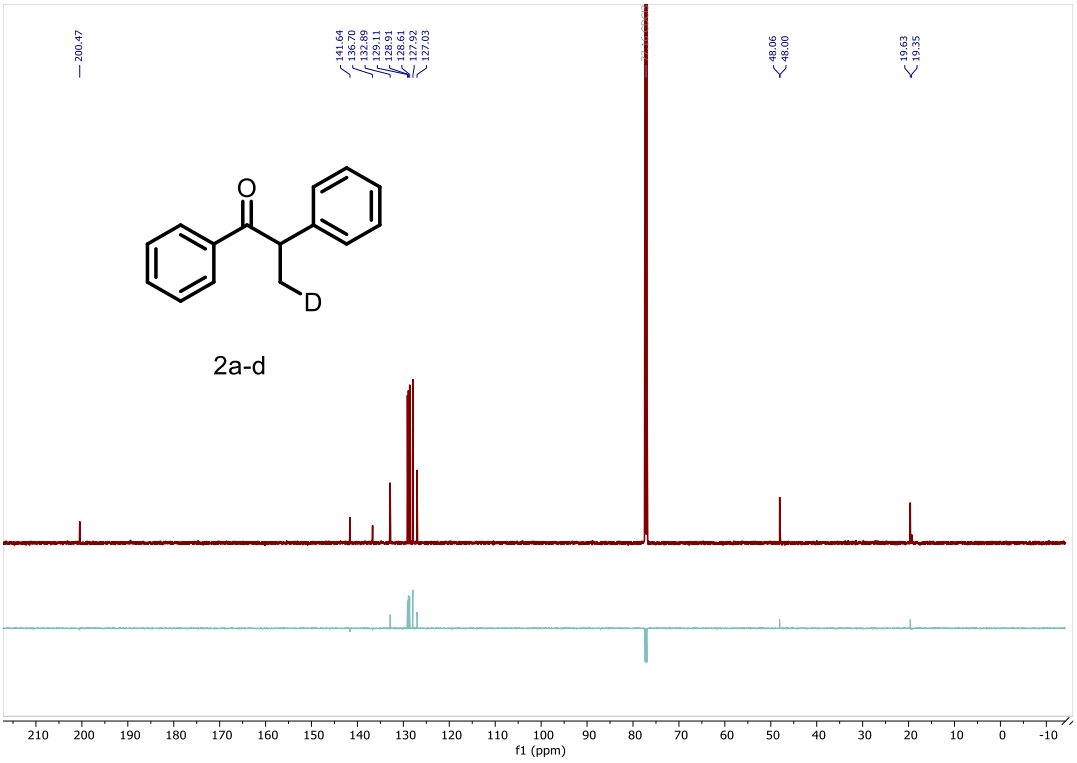


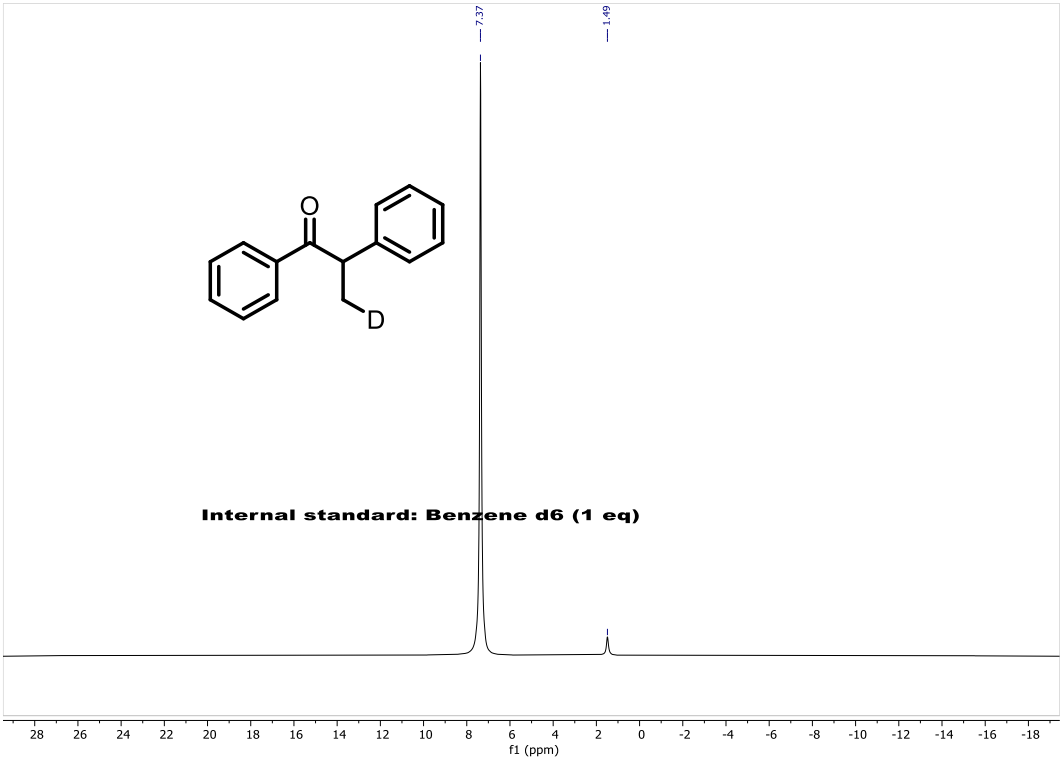


HFIP-d2 experiment.






200.47
141.64
136.70
132.89
129.11
128.91
128.61
127.92
127.03
48.06
48.00
19.63
19.35
O
D
2a-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.37
1.49
O
D
Internal standard: Benzene d6 (1 eq)
28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18
f1 (ppm)

8. References

(1) Bub, C. L.; Thönnißen, V.; Patureau, F. W. Benzophenothiazine and Its Cr(III)-Catalyzed Cross Dehydrogenative Couplings. *Org. Lett.* **2020**, *22* (23), 9196–9198. https://doi.org/10.1021/acs.orglett.0c03354.

(2) Zemtsov, A. A.; Lunkov, S. S.; Levin, V. V.; Dilman, A. D. Synthesis of Trifluoromethylated Dithiocarbamates via Photocatalyzed Substitution Reaction: Pentafluoropyridine as Activating Reagent. *Eur. J. Org. Chem.* **2021**, *2021* (6), 1007–1010. https://doi.org/10.1002/ejoc.202001572.

(3) Nagao, K.; Ohmiya, H. Carbocation Generation by Organophotoredox Catalysis. *Journal of Synthetic Organic Chemistry, Japan* **2021**, *79* (11), 1005–1012. https://doi.org/10.5059/yukigoseikyokaishi.79.1005.

(4) Li, H.; Liu, Y.; Chiba, S. Anti-Markovnikov Hydroarylation of Alkenes via Polysulfide Anion Photocatalysis. *Chem. Commun.* **2021**, *57* (51), 6264–6267. https://doi.org/10.1039/D1CC02185K.

(5) Nakagawa, M.; Matsuki, Y.; Nagao, K.; Ohmiya, H. A Triple Photoredox/Cobalt/Brønsted Acid Catalysis Enabling Markovnikov Hydroalkoxylation of Unactivated Alkenes. *J. Am. Chem. Soc.* **2022**, *144* (18), 7953–7959. https://doi.org/10.1021/jacs.2c00527.

(6) Kusy, R.; Grela, K. Ligand-Free (Z)-Selective Transfer Semihydrogenation of Alkynes Catalyzed by in Situ Generated Oxidizable Copper Nanoparticles. *Green Chem.* **2021**, *23* (15), 5494–5502. https://doi.org/10.1039/D1GC01206A.

(7) Liu, X.; Xiong, F.; Huang, X.; Xu, L.; Li, P.; Wu, X. Copper-Catalyzed Trifluoromethylation-Initiated Radical 1,2-Aryl Migration in α,α-Diaryl Allylic Alcohols. *Angew. Chem. Int. Ed.* **2013**, *52* (27), 6962–6966. https://doi.org/10.1002/anie.201302673.

(8) Huang, H.-L.; Yan, H.; Yang, C.; Xia, W. Visible Light-Mediated Arylalkylation of Allylic Alcohols through Concomitant 1,2-Aryl Migration. *Chem. Commun.* **2015**, *51* (23), 4910–4913. https://doi.org/10.1039/C4CC10321A.

(9) Liu, X.; Xiong, F.; Huang, X.; Xu, L.; Li, P.; Wu, X. Copper-Catalyzed Trifluoromethylation-Initiated Radical 1,2-Aryl Migration in α,α-Diaryl Allylic Alcohols. *Angewandte Chemie International Edition* **2013**, *52* (27), 6962–6966. https://doi.org/10.1002/anie.201302673.

(10) de Azevedo, O. D. C. C.; Elliott, P. I. P.; Gabbutt, C. D.; Heron, B. M.; Lord, K. J.; Pullen, C. Synthesis and Photochromism of Novel Pyridyl-Substituted Naphthopyrans. *J. Org. Chem.* **2020**, *85* (16), 10772–10796. https://doi.org/10.1021/acs.joc.0c01296.

(11) Wei, X.-J.; Noël, T. Visible-Light Photocatalytic Difluoroalkylation-Induced 1, 2-Heteroarene Migration of Allylic Alcohols in Batch and Flow. *J. Org. Chem.* **2018**, *83* (18), 11377–11384. https://doi.org/10.1021/acs.joc.8b01624.

(12) Isomura, M.; Petrone, D. A.; Carreira, E. M. Coordination-Induced Stereocontrol over Carbocations: Asymmetric Reductive Deoxygenation of Racemic Tertiary Alcohols. *J. Am. Chem. Soc.* **2019**, *141* (11), 4738–4748. https://doi.org/10.1021/jacs.9b00862.

(13) Wei, X.-J.; Noël, T. Visible-Light Photocatalytic Difluoroalkylation-Induced 1, 2-Heteroarene Migration of Allylic Alcohols in Batch and Flow. *J. Org. Chem.* **2018**, *83* (18), 11377–11384. https://doi.org/10.1021/acs.joc.8b01624.

(14) Pichette Drapeau, M.; Fabre, I.; Grimaud, L.; Ciofini, I.; Ollevier, T.; Taillefer, M. Transition-Metal-Free α-Arylation of Enolizable Aryl Ketones and Mechanistic Evidence for a Radical Process. *Angewandte Chemie International Edition* **2015**, *54* (36), 10587–10591. https://doi.org/10.1002/anie.201502332.

(15) Kim, J.; Jang, J.; Lee, Y.; Shin, K. Exogenous Ligand-Free NiH-Catalyzed Hydroacylation of Aryl Alkenes with Aroyl Fluorides. *Org. Lett.* **2022**, *24* (29), 5412–5416. https://doi.org/10.1021/acs.orglett.2c02110.

(16) Kim, J.; Jang, J.; Lee, Y.; Shin, K. Exogenous Ligand-Free NiH-Catalyzed Hydroacylation of Aryl Alkenes with Aroyl Fluorides. *Org. Lett.* **2022**, *24* (29), 5412–5416. https://doi.org/10.1021/acs.orglett.2c02110.

(17) Marelli, E.; Renault, Y.; Sharma, S. V.; Nolan, S. P.; Goss, R. J. M. Mild, Aqueous α-Arylation of Ketones: Towards New Diversification Tools for Halogenated Metabolites and Drug Molecules. *Chemistry – A European Journal* **2017**, *23* (16), 3832–3836. https://doi.org/10.1002/chem.201700680.
(18) Li, J.; Wang, Z.-X. Nickel-Catalyzed Transformation of Aryl 2-Pyridyl Ethers via Cleavage of the Carbon–Oxygen Bond: Synthesis of Mono-α-Arylated- Ketones. *Synthesis* **2018**, *50* (16), 3217–3223. https://doi.org/10.1055/s-0037-1609963.
(19) Cherney, A. H.; Reisman, S. E. Pd-Catalyzed Fukuyama Cross-Coupling of Secondary Organozinc Reagents for the Direct Synthesis of Unsymmetrical Ketones. *Tetrahedron* **2014**, *70* (20), 3259–3265. https://doi.org/10.1016/j.tet.2013.11.104.
(20) Deng, Z.; Chen, C.; Cui, S. Fe(III)-Mediated Isomerization of α,α-Diarylallylic Alcohols to Ketones via Radical 1,2-Aryl Migration. *RSC Adv.* **2016**, *6* (96), 93753–93755. https://doi.org/10.1039/C6RA20007A.
(21) Hong, Y.-T.; Barchuk, A.; Krische, M. J. Branch-Selective Intermolecular Hydroacylation: Hydrogen-Mediated Coupling of Anhydrides to Styrenes and Activated Olefins. *Angewandte Chemie International Edition* **2006**, *45* (41), 6885–6888. https://doi.org/10.1002/anie.200602377.
(22) Ueda, Y.; Iwai, T.; Sawamura, M. Nickel-Copper-Catalyzed Hydroacylation of Vinylarenes with Acyl Fluorides and Hydrosilanes. *Chem. Eur. J.* **2019**, *25* (40), 9410–9414. https://doi.org/10.1002/chem.201900822.
(23) Templ, J.; Schnürch, M. Selective α-Methylation of Aryl Ketones Using Quaternary Ammonium Salts as Solid Methylating Agents. *J. Org. Chem.* **2022**, *87* (6), 4305–4315. https://doi.org/10.1021/acs.joc.1c03158.
(24) Su, F.; Zou, J.; Lv, X.; Lu, F.; Long, Y.; Tang, K.; Li, B.; Chai, H.; Wu, X.; Chi, Y. R. Carbene-Catalyzed Intermolecular Dehydrogenative Coupling of Aldehydes with C(Sp^3)−H Bonds. *Angew Chem Int Ed* **2023**, *62* (23), e202303388. https://doi.org/10.1002/anie.202303388.
(25) Todorovic, N.; Awuah, E.; Albu, S.; Ozimok, C.; Capretta, A. Synthesis of Substituted Isoquinolines via Pd-Catalyzed Cross-Coupling Approaches. *Org. Lett.* **2011**, *13* (23), 6180–6183. https://doi.org/10.1021/ol202565j.
(26) Templ, J.; Schnürch, M. Selective α-Methylation of Aryl Ketones Using Quaternary Ammonium Salts as Solid Methylating Agents. *J. Org. Chem.* **2022**, *87* (6), 4305–4315. https://doi.org/10.1021/acs.joc.1c03158.
(27) Krasodomski, W.; Łuczyński, M. K.; Wilamowski, J.; Sepioł, J. J. Synthesis of Alkylphenanthrenes from Naphthylalkylidenemalonodinitriles. A Route to 1-Methyl-, 2-Methyl-, and 1,2-Dimethylphenanthrene. *Tetrahedron* **2003**, *59* (30), 5677–5683. https://doi.org/10.1016/S0040-4020(03)00884-6.
(28) Liu, C.; He, C.; Shi, W.; Chen, M.; Lei, A. Ni-Catalyzed Mild Arylation of α-Halocarbonyl Compounds with Arylboronic Acids. *Org. Lett.* **2007**, *9* (26), 5601–5604. https://doi.org/10.1021/ol702456z.
(29) Jana, S.; Clements, M. D.; Sharp, B. K.; Zheng, N. Fe(II)-Catalyzed Amination of Aromatic C−H Bonds via Ring Opening of 2 *H* -Azirines: Synthesis of 2,3-Disubstituted Indoles. *Org. Lett.* **2010**, *12* (17), 3736–3739. https://doi.org/10.1021/ol101130e.
(30) Yang, P.-F.; Shu, W. Direct Synthesis of Mono-α-Arylated Ketones from Alcohols and Olefins via Ni-Catalyzed Oxidative Cross-Coupling. *Org. Lett.* **2020**, *22* (15), 6203–6208. https://doi.org/10.1021/acs.orglett.0c02340.
(31) Wang, J.-L.; Li, H.-J.; Wang, H.-S.; Wu, Y.-C. Regioselective 1,2-Diol Rearrangement by Controlling the Loading of BF3·Et2O and Its Application to the Synthesis of Related Nor-Sesquiterene- and Sesquiterene-Type Marine Natural Products. *Org. Lett.* **2017**, *19* (14), 3811–3814. https://doi.org/10.1021/acs.orglett.7b01679.

(32) Xiao, L.-J.; Fu, X.-N.; Zhou, M.-J.; Xie, J.-H.; Wang, L.-X.; Xu, X.-F.; Zhou, Q.-L. Nickel-Catalyzed Hydroacylation of Styrenes with Simple Aldehydes: Reaction Development and Mechanistic Insights. *J. Am. Chem. Soc.* **2016**, *138* (9), 2957–2960. https://doi.org/10.1021/jacs.6b00024.
(33) Deng, Z.; Chen, C.; Cui, S. Fe(Iii)-Mediated Isomerization of α,α-Diarylallylic Alcohols to Ketones via Radical 1,2-Aryl Migration. *RSC Advances* **2016**, *6* (96), 93753–93755. https://doi.org/10.1039/C6RA20007A.