Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

From Oximes to Tertiary Alcohols in Water, at Room Temperature in Air: Hybrid One-pot Tandem Assembly of Enzymatic Deoximation and RLi/RMgX Reagents

Davide Arnodo,[a,b] Marina Ramos-Martín,[a] Luciana Cicco,[a,c] Vito Capriati,[c] Nicolás Ríos-Lombardía,[d] Javier González-Sabín,[,d] Alejandro Presa Soto,[*,a] and Joaquín García-Álvarez.[*,a]*

[a] Laboratorio de Química Sintética Sostenible (QuimSinSos), Departamento de Química Orgánica e Inorgánica (IUQOEM), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Química, Universidad de Oviedo. C/Julián Clavería 8, 33006, Oviedo (Spain)

[b] Dipartimento di Chimica–Università degli Study di Torino, Via P. Giuria 7, 10125 Torino, Italy.

[c] Dipartimento di Farmacia–Scienze del Farmaco, Università di Bari "Aldo Moro", Consorzio C.I.N.M.P.I.S., Via E. Orabona 4, I-70125 Bari, Italy.

[d] EntreChem SL, Vivero Ciencias de la Salud. Santo Domingo de Guzmán, Oviedo, 33011, Spain.

e-mail: jgsabin@entrechem.com; presaalejandro@uniovi.es; garciajoaquin@uniovi.es

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Abbreviations list

AZADO	2-azaadamantane-*N*-oxyl
BnMgCl	benzylmagnesium chloride
n-BuLi	*normal*-butyllithium
s-BuLi	*sec*-butyllithium
t-BuLi	*tert*-butyllithium
$CDCl_3$	deuterated chloroform
$CHCl_3$	chloroform
CPME	cyclopentyl methyl ether
DCM	dichloromethane
Et_2O	diethyl ether
EtOAc	ethyl acetate
GC-FID	gas chromatography-flame ionization detector
CH_3CN	acetonitrile
MeLi	methyllithium
NMR	nuclear magnetic resonance
PhLi	phenyllithium
R_f	retention factor
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
THF	tetrahydrofuran
TLC	thin layer chromatography
UV	ultraviolet

Experimental Details

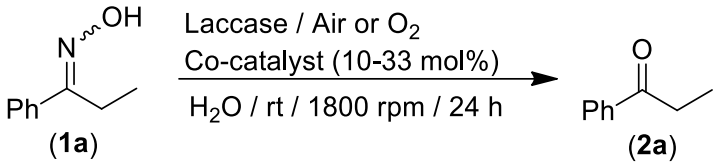
Materials and methods. All reagents were obtained from commercial suppliers and used without further purification. Laccase from *Trametes Versicolor* or *Rhus Vernicifera*, TEMPO and AZADO were purchased from Sigma Aldrich. Organometallic reagents were purchased from Sigma Aldrich: i) 2.5 M solution of *n*-BuLi in hexanes; ii) 1.6 M solution of MeLi in Et_2O; iii) 1.4 M solution of *s*-BuLi in cyclohexane; iv) 1.7 M solution of *t*-BuLi in pentane; v) 1.9 M solution of PhLi in dibutyl ether; vi) 2.0 M solution of BnMgCl in THF; vii) 1.0 M solution of 2-thienyllithium in THF/hexanes; viii) 1.0 M solution of allylmagnesium bromide in Et_2O. Concentrations of all organolithium reagents were determined by titration with L-menthol,[1] and for the Grignard reagents titration against iodine was employed.[2] All the rest of reagents and solvents were of the highest quality available. Ketoximes **1a**-**j** were synthesized according to the procedure reported in the literature.[3] Reactions were monitored by GC-FID analysis or by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminum plates (60 Merck F_{254}) with UV light (254 nm) or *p*-anisaldehyde indicator[4] as visualizing agents. R_f values refer to TLC carried out on silica gel plates. Chromatographic separations were carried out under pressure on silica gel (40-63 μm, 230-400 mesh) using flash-column techniques. Full characterization data, including copies of ^1H and $^{13}C\{^1H\}$ NMR spectra, have been presented for the known compounds.

Instrumentation. ^1H NMR (600 MHz) and $^{13}C\{^1H\}$ (150 MHz) NMR spectra were recorded on a Jeol ECZR600 spectrometer at room temperature. ^1H NMR (300 MHz) and $^{13}C\{^1H\}$ (75 MHz) NMR spectra were recorded on a Bruker DPX-300 spectrometer at room temperature. Calibration was made on the signal of the residual solvent (^1H $CHCl_3$: 7.26 ppm; $^{13}C\{^1H\}$ $CDCl_3$: 77.16 ppm). Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (*J*) in Hertz (Hz). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Gas chromatography (GC) analyses were performed on an Agilent Technologies 7820A chromatographic system equipped with a HP-5 (30 m x 0.32 mm x 0.25 μm) column. Melting points were determined on a Stuart Scientific SMP3 melting point apparatus.

Deoximation of propiophenone oxime **1a** into ketone **2a** promoted by the system laccase/TEMPO/O_2 in aqueous media at room temperature after 24 hours

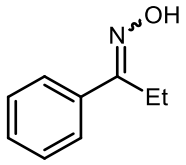
All reactions were performed at room temperature. In an 8 mL vial equipped with a magnetic stirrer Laccase and co-catalyst (eq.) were added to a 0.73 mmol (109 mg) suspension of propiophenone oxime **1a** in water (1 mL) and the mixture was stirred under the selected atmosphere for 24 h. Then, the reaction mixture was extracted with dichloromethane (3 x 5 mL), the organic layers were combined, washed with brine (1 x 5 mL), dried with Na_2SO_4 and the solvent removed *in vacuo*. Conversion of **1a** into propiophenone **2a** was determined by GC-FID analysis of the crude reaction mixtures (presented in Figures S8-S17). A sample of **1a** was synthesized according to the procedure reported in the literature[3] and used as reference for GC-FID analyses (^{1}H and ^{13}C{^{1}H} NMR presented in Figure S1 and S2, GC-FID presented in Figure S5). A sample of commercial **2a** (Sigma-Aldrich 99%) was analyzed and used as reference for GC-FID analyses of the reaction crudes (^{1}H and ^{13}C{^{1}H} NMR presented in Figure S3 and S4, GC-FID presented in Figure S6).

Table S1. Deoximation of propiophenone oxime **1a** into ketone **2a** promoted by the system laccase/TEMPO/O_2 in aqueous media at room temperature after 24 hours.[a]

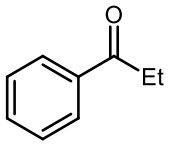


Entry	Laccase[b,c]	Co-catalyst	Oxidant	Conversion[d] (%)
1	*T. Versicolor*	TEMPO (33 mol%)	Air	47[e]
2	*T. Versicolor*	TEMPO (33 mol%)	Air	84
3	*T. Versicolor*	TEMPO (10 mol%)	Air	40
4	*T. Versicolor*	TEMPO (33 mol%)	O_2	>99
5	*Rhus Vernicifera*	TEMPO (33 mol%)	O_2	1
6	$CuCl_2 \cdot 2H_2O$/TMEDA	TEMPO (33 mol%)	O_2	1
7	*T. Versicolor*	AZADO (33 mol%)	O_2	>99
8	*T. Versicolor*	TEMPO (33 mol%)	O_2	>99[f]
9	-	TEMPO (33 mol%)	O_2	0
10	*T. Versicolor*	-	O_2	2

[a] General conditions: 24 h of reaction at room temperature and at 1800 rpm, using 0.73 mmol of **1a** in 1 mL of water. [b] 280 mg of *T. Versicolor* (0.5 U/mg); 2.8 mg of *Rhus Vernicifera* (50 U/mg) were employed [c] U/mg = Units of activity per mg of enzyme. [d] Determined by GC-FID, no significant amount of by-products was detected [110 ºC; 4 min; 10 °C/min; 220 °C; 2 min]. [e] Stirring speed 800 rpm. [f] 100 μL of CH_3CN were added as co-solvent.



1-phenylpropan-1-one oxime (1a): white solid (R_f = 0.23 hexane/EtOAc 8/2 v/v), mp 50.2−51.6 °C (hexane). Mixture of *E* and *Z* stereoisomers (*E*/*Z* = 10/1). ^{1}H NMR (300 MHz, $CDCl_3$, mixture of *E* and *Z* stereoisomers): δ 7.88 (br s, 2H, *E* + *Z*), 7.68-7.51 (m, 4H, *E* + *Z*), 7.50-7.28 (m, 6H, *E* + *Z*), 2.84 (q, *J* = 7.6 Hz, 2H, *E*), 2.63 (q, *J* = 7.4 Hz, 2H, *Z*), 1.19 (t, *J* = 7.6 Hz, 3H, *E*) superimposed to 1.12 (t, *J* = 7.6 Hz, 3H, *Z*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, mixture of *E* and *Z* stereoisomers): δ 160.9 (*E*), 159.7 (*Z*), 135.7 (*E*), 133.7 (*Z*), 129.3 (*E*), 129.0 (*Z*), 128.7 (*E*), 128.4 (*Z*), 127.9 (*Z*), 126.4 (*E*), 29.1 (*Z*), 19.9 (*E*), 11.3 (*Z*), 11.0 (*E*).[5]



1-phenylpropan-1-one (2a): colorless liquid (R_f = 0.25 hexane/Et_2O 9/1 v/v). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H) superimposed to 7.46 (t, *J* = 7.3 Hz, 2H), 3.01 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.9, 137.1, 133.0, 128.7, 128.1, 31.9, 8.4.[6]

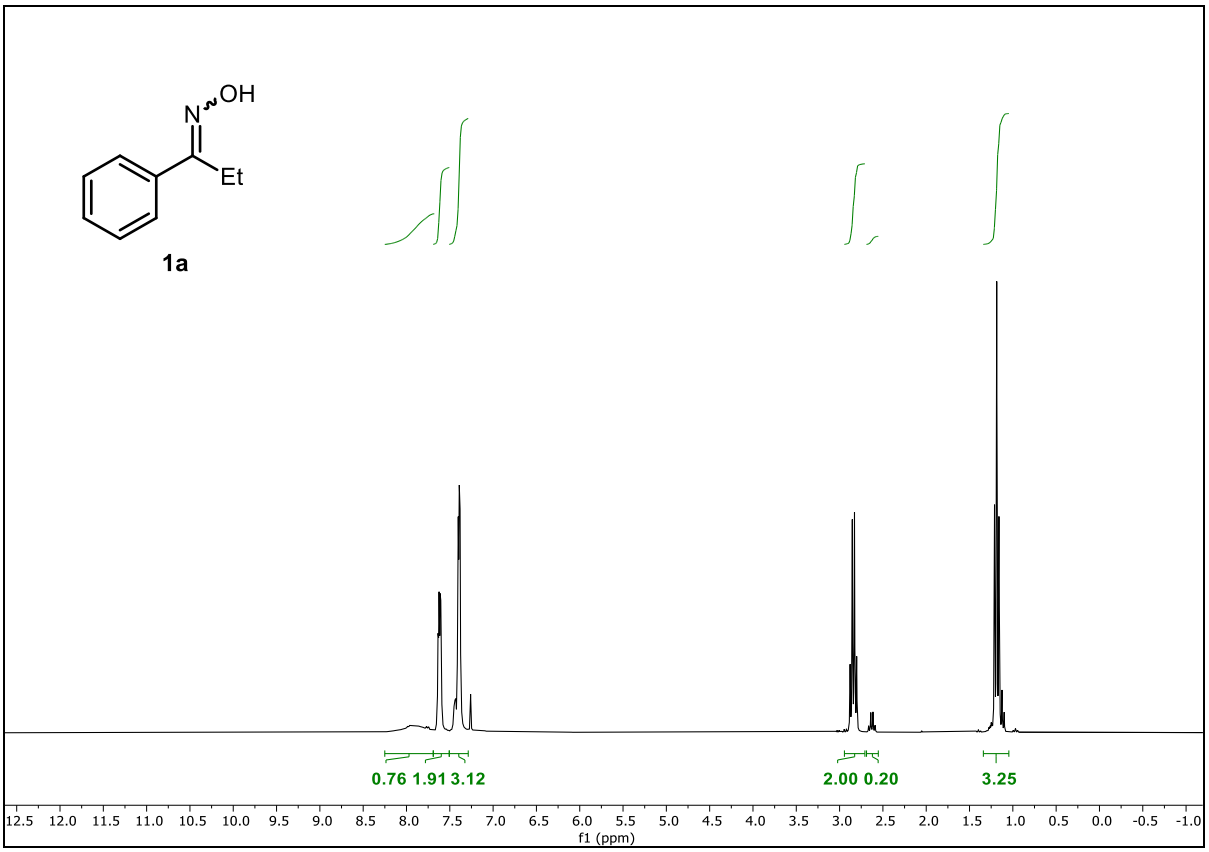


Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of propiophenone oxime **1a**.

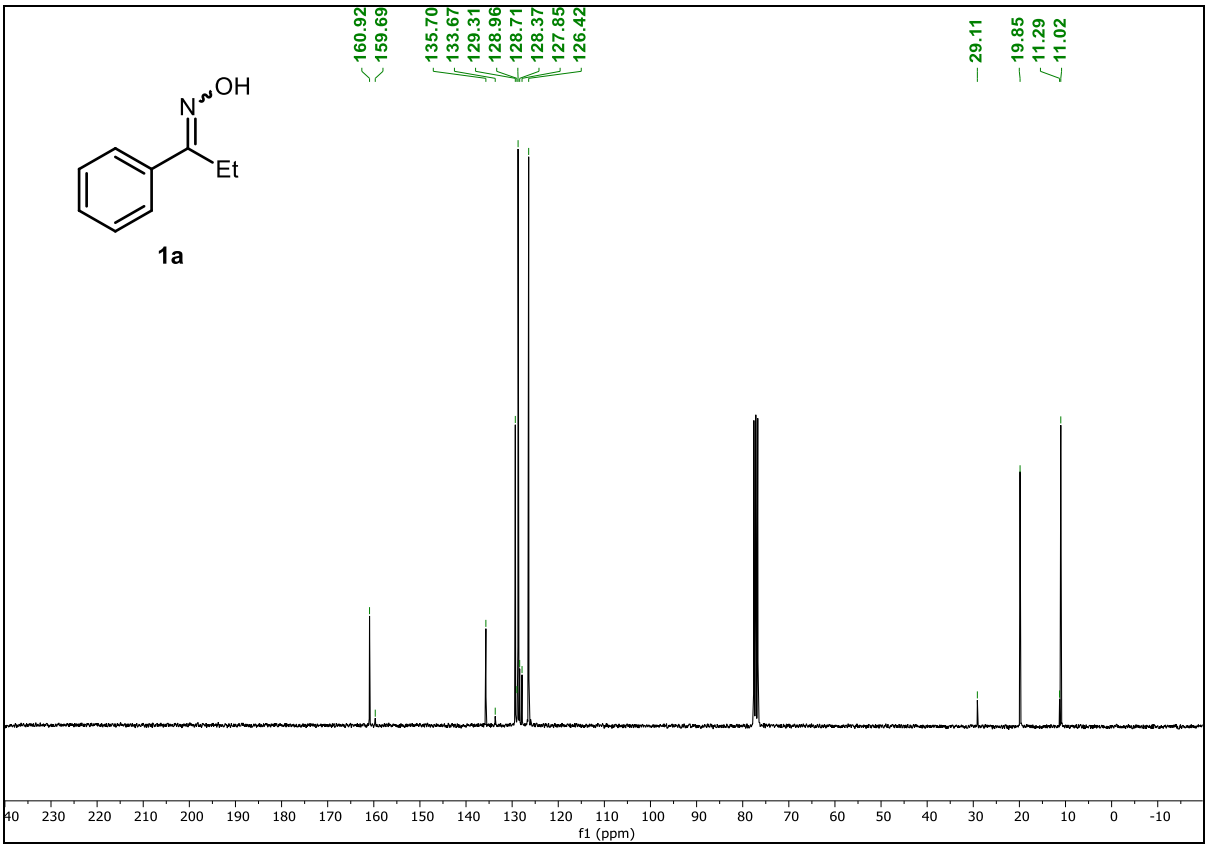


Figure S2. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectrum of propiophenone oxime **1a**.

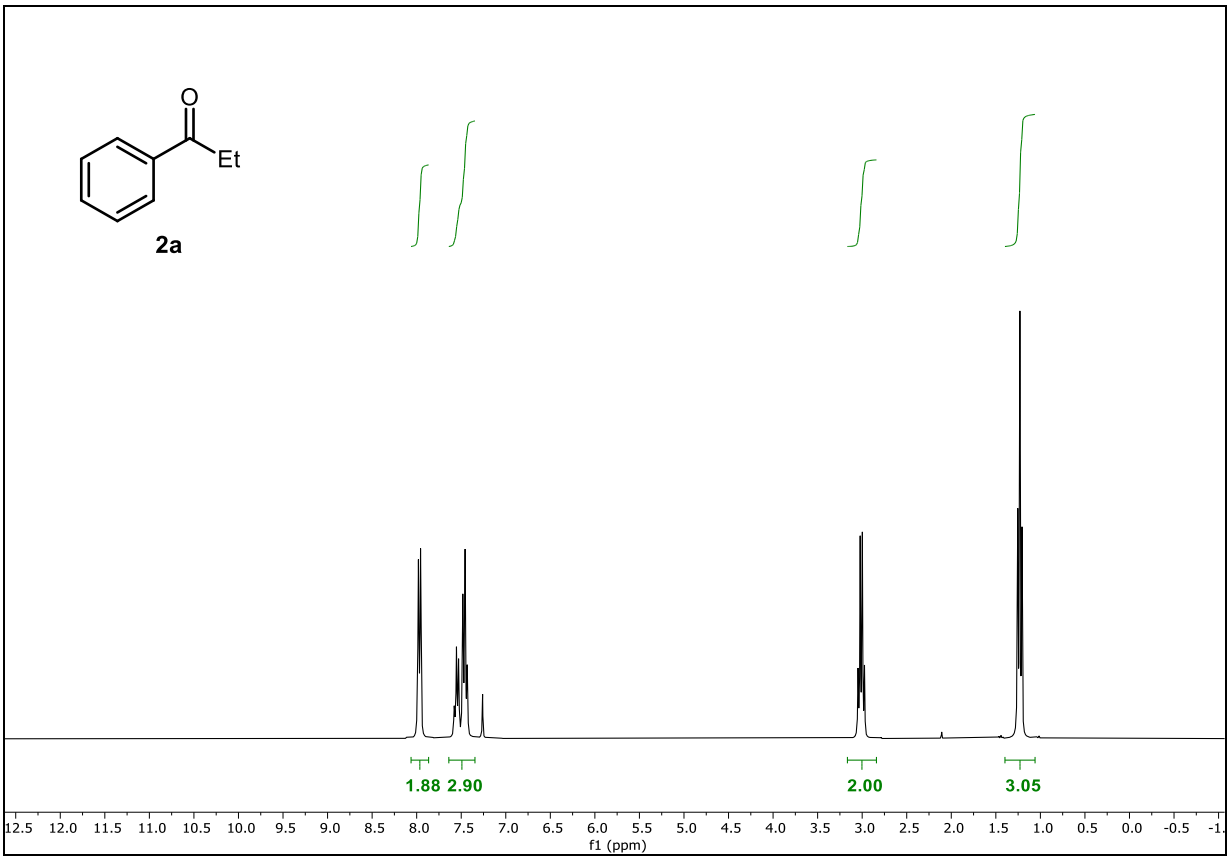


Figure S3. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of propiophenone **2a**.

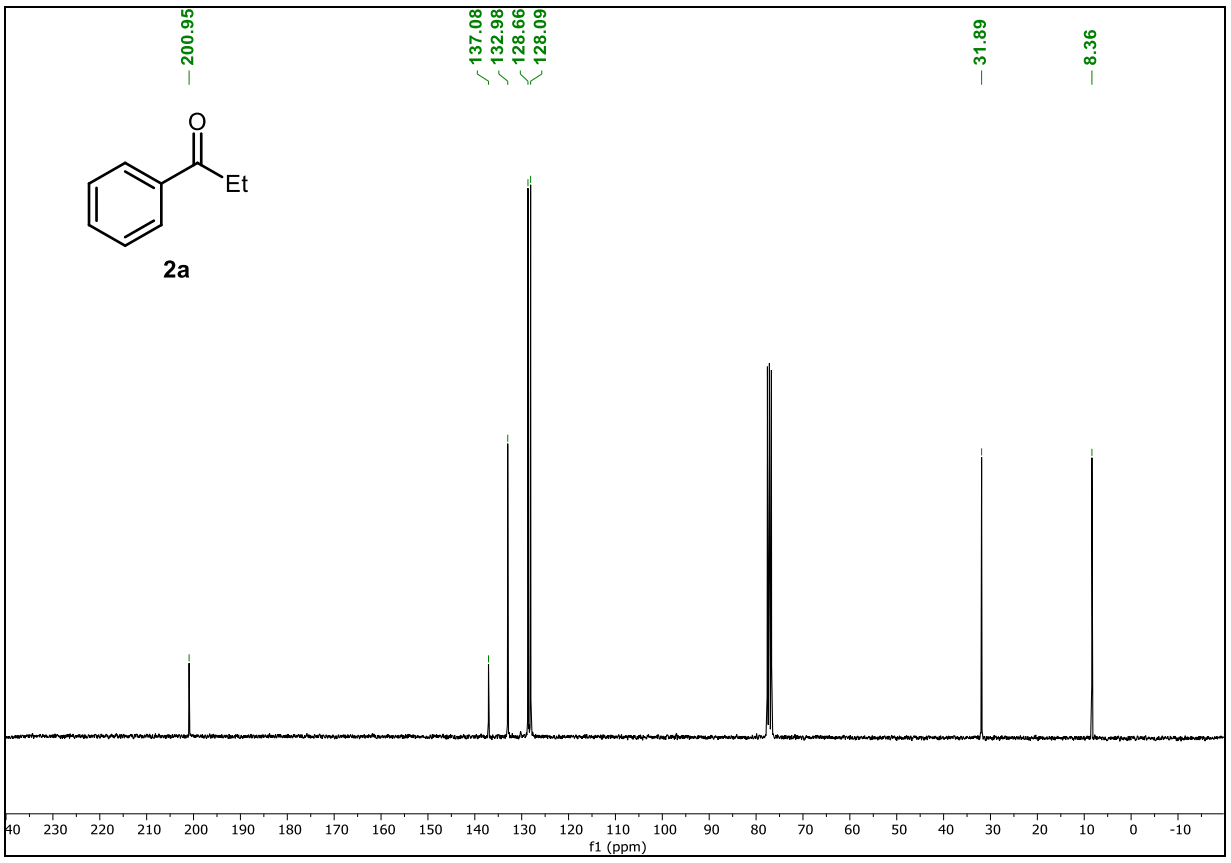


Figure S4. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectrum of propiophenone **2a**.

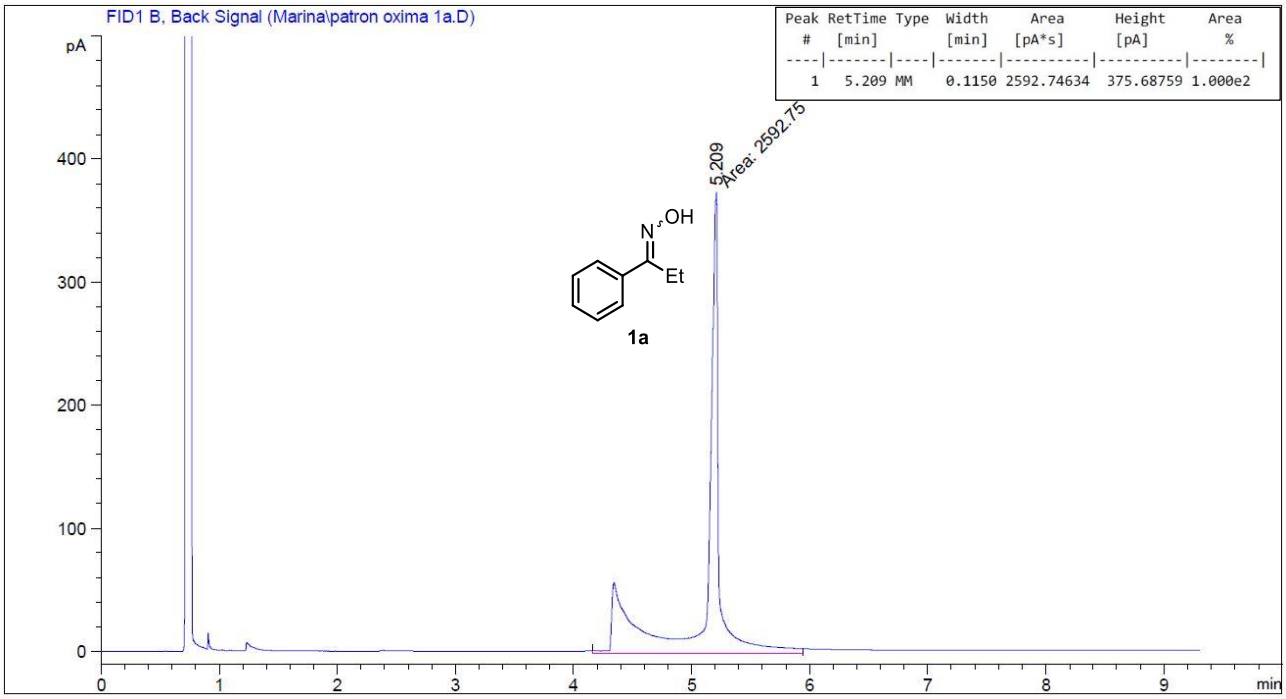


Figure S5. GC-FID chromatogram of propiophenone oxime (**1a**).

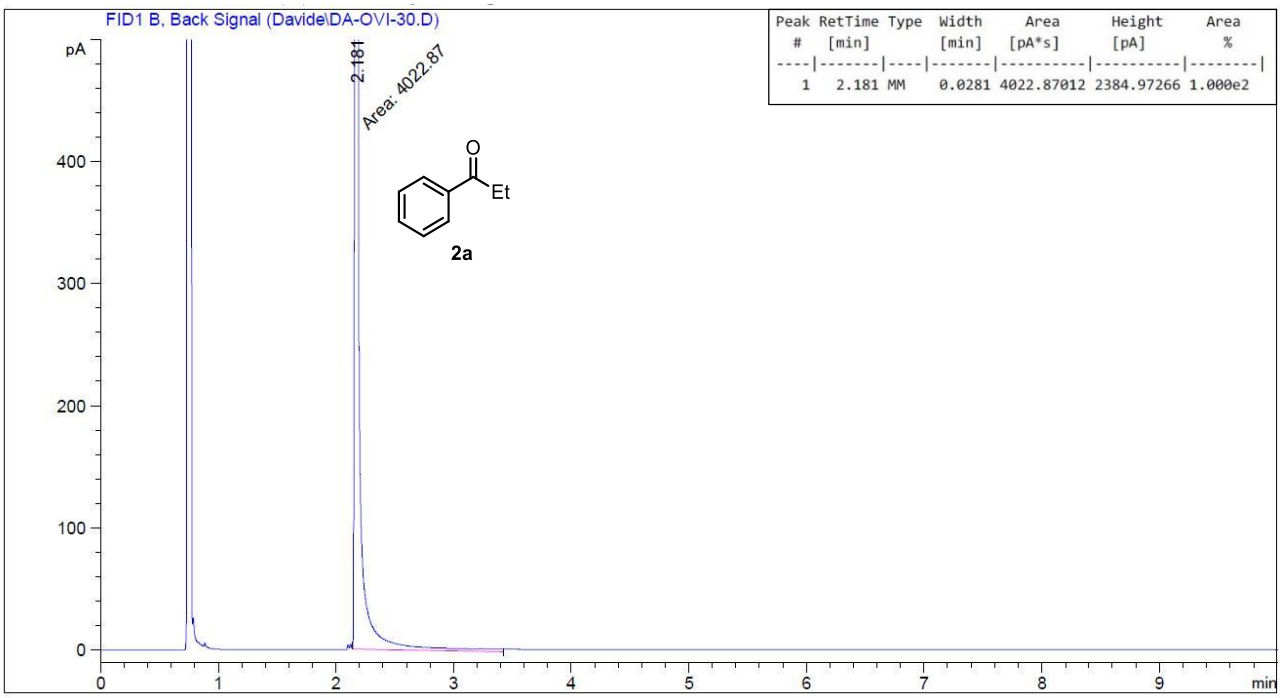
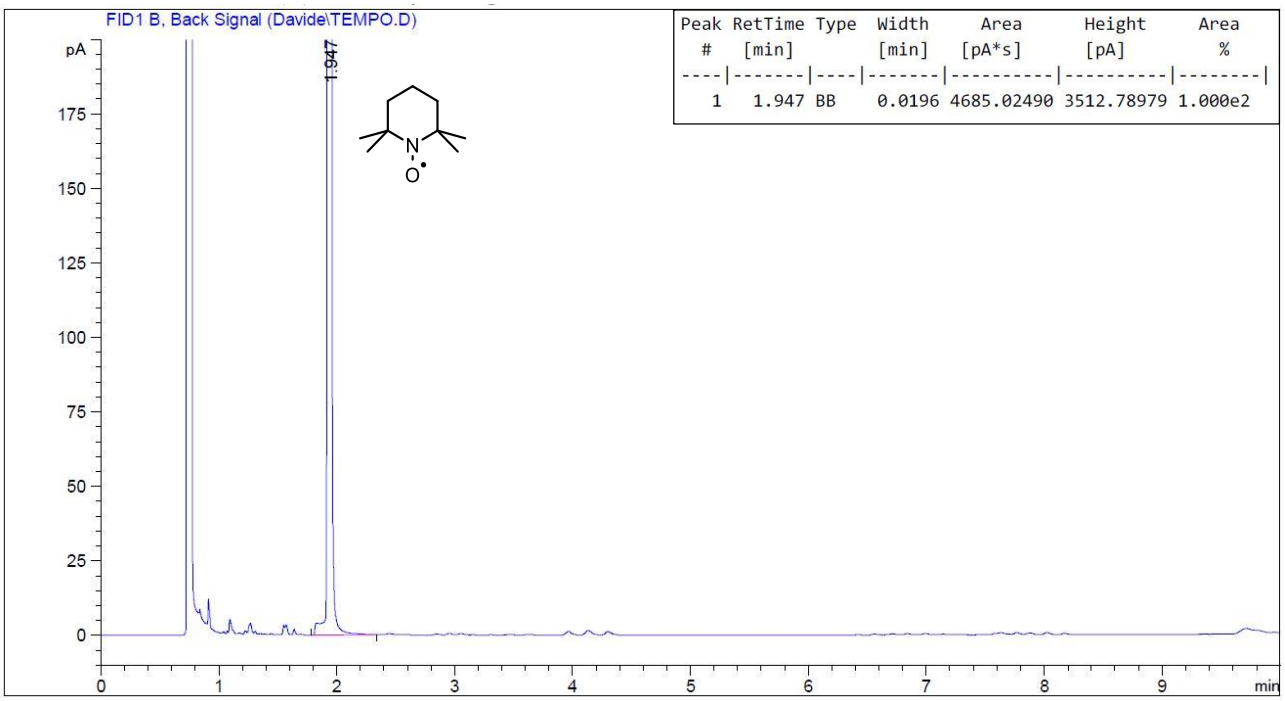
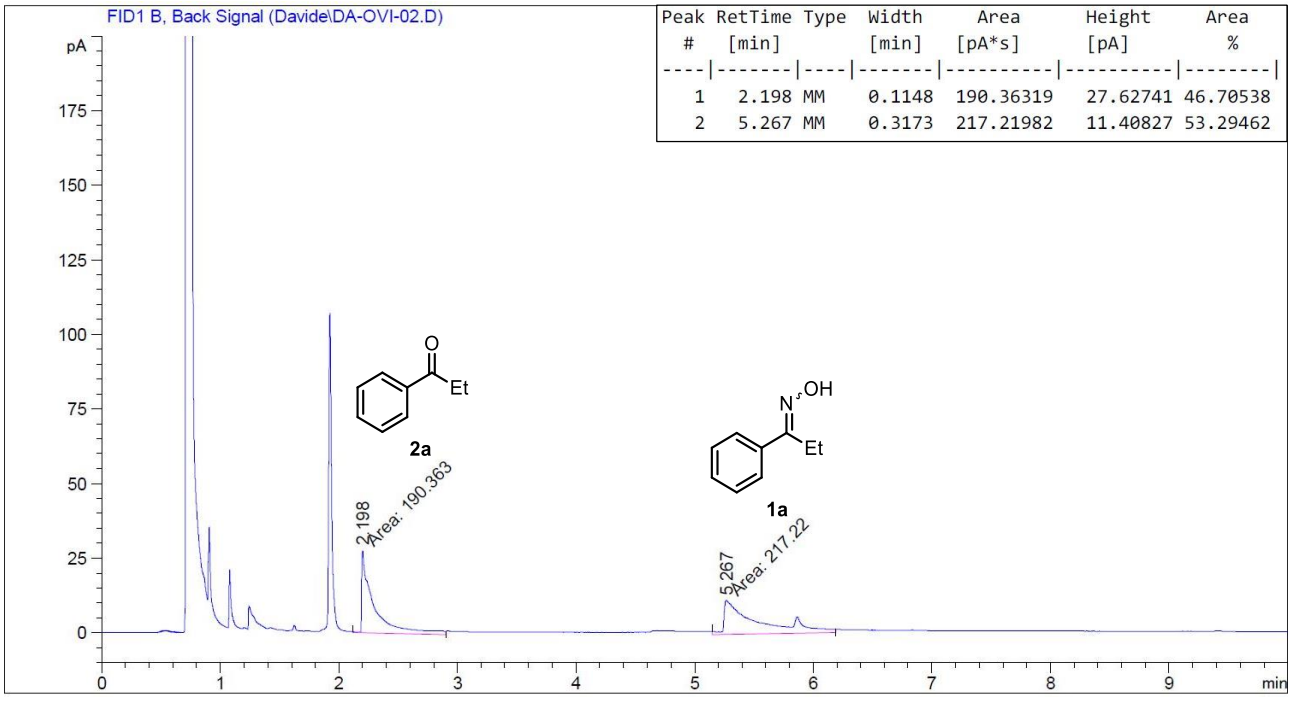


Figure S6. GC-FID chromatogram of propiophenone (**2a**).



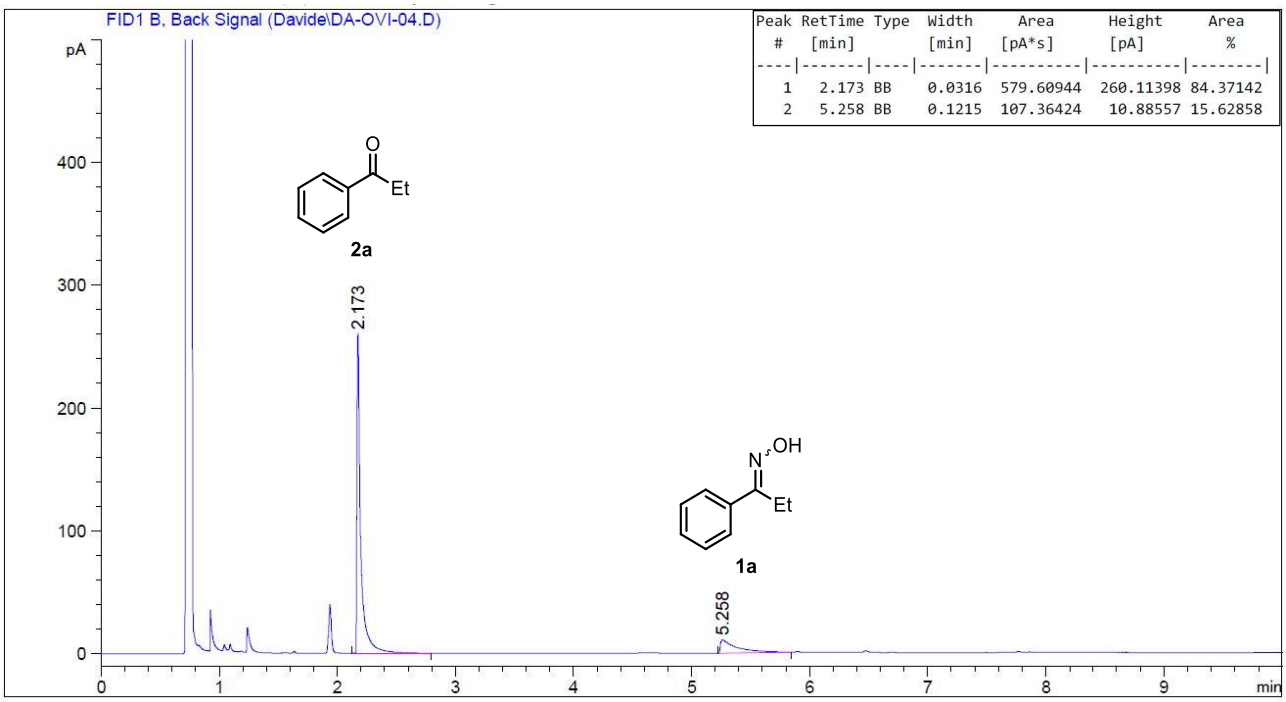
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.947	BB	0.0196	4685.02490	3512.78979	1.000e2

Figure S7. GC-FID chromatogram of TEMPO.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.198	MM	0.1148	190.36319	27.62741	46.70538
2	5.267	MM	0.3173	217.21982	11.40827	53.29462

Figure S8. Table S1, entry 1: GC-FID chromatogram of the reaction crude.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.173	BB	0.0316	579.60944	260.11398	84.37142
2	5.258	BB	0.1215	107.36424	10.88557	15.62858

Figure S9. Table S1, entry 2: GC-FID chromatogram of the reaction crude.

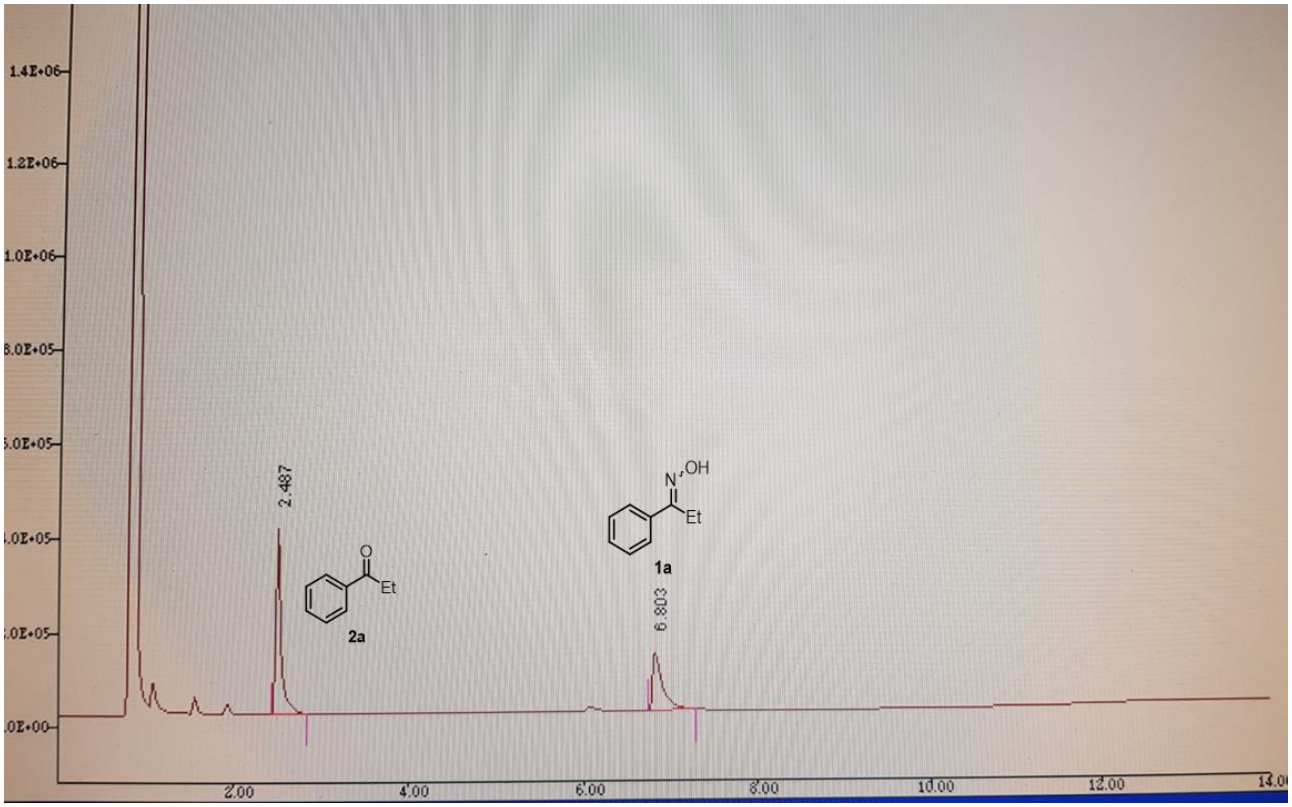


Figure S10. Table S1, entry 3: GC-FID chromatogram of the reaction crude.

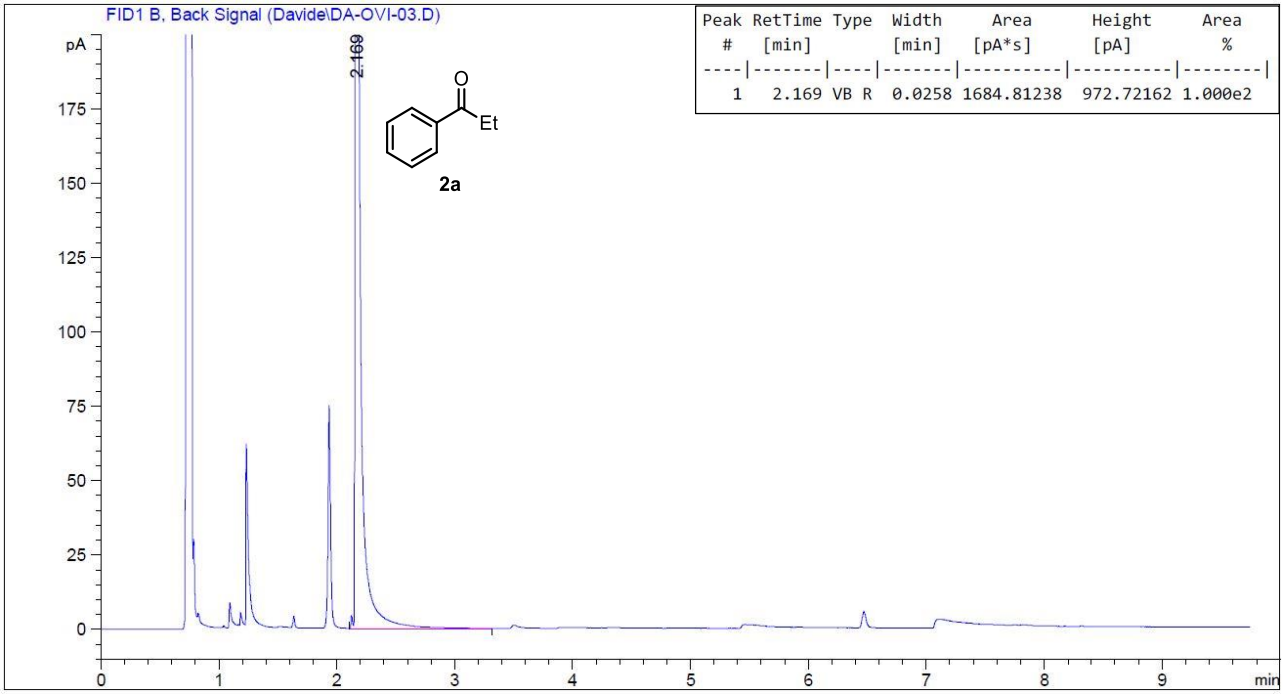


Figure S11. Table S1, entry 4: GC-FID chromatogram of the reaction crude.

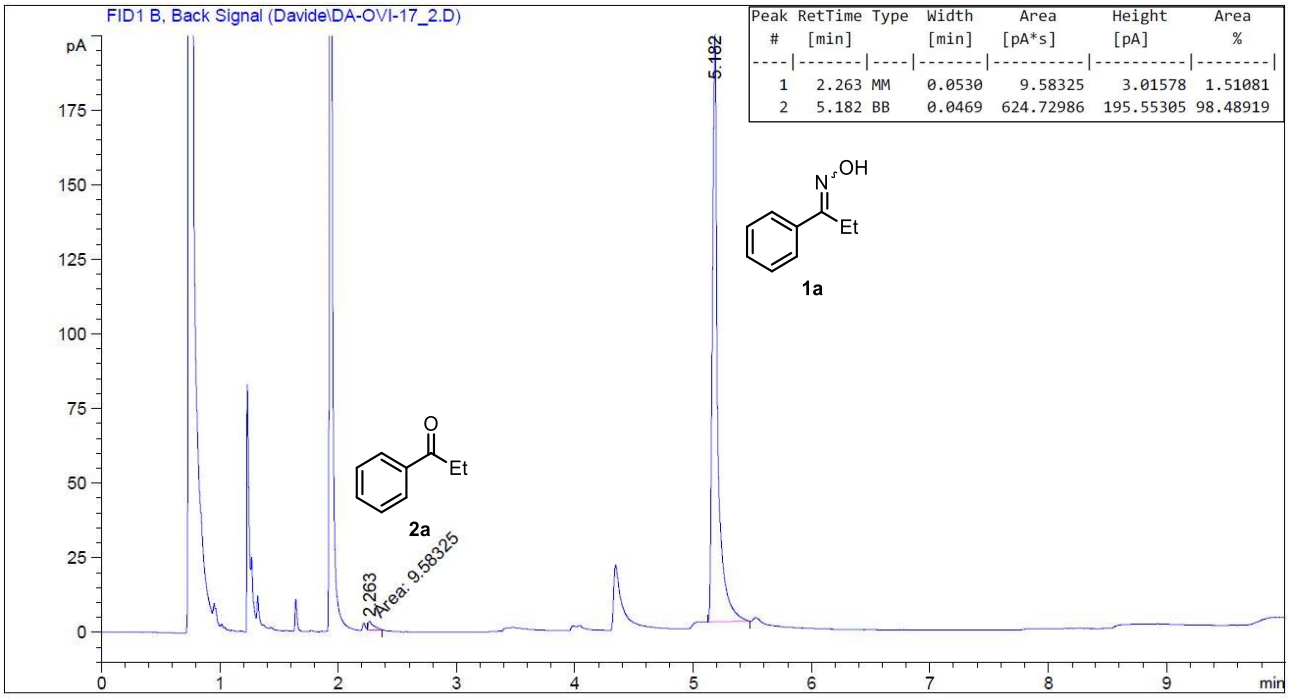
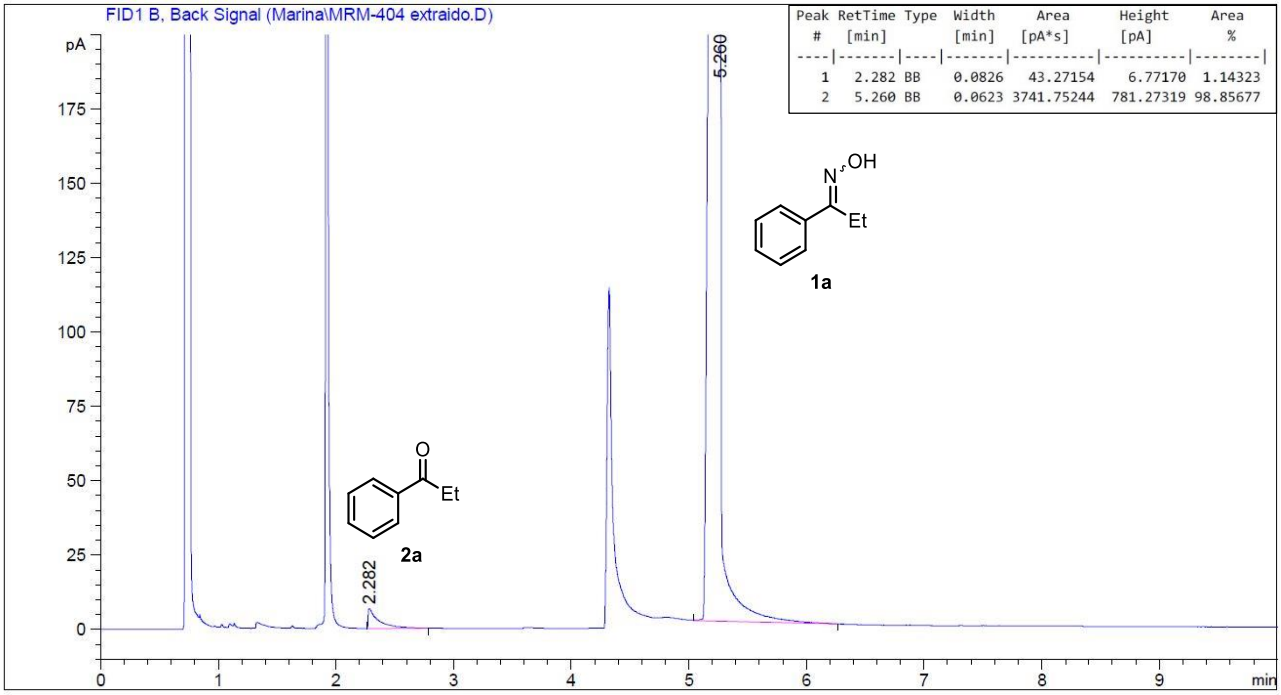
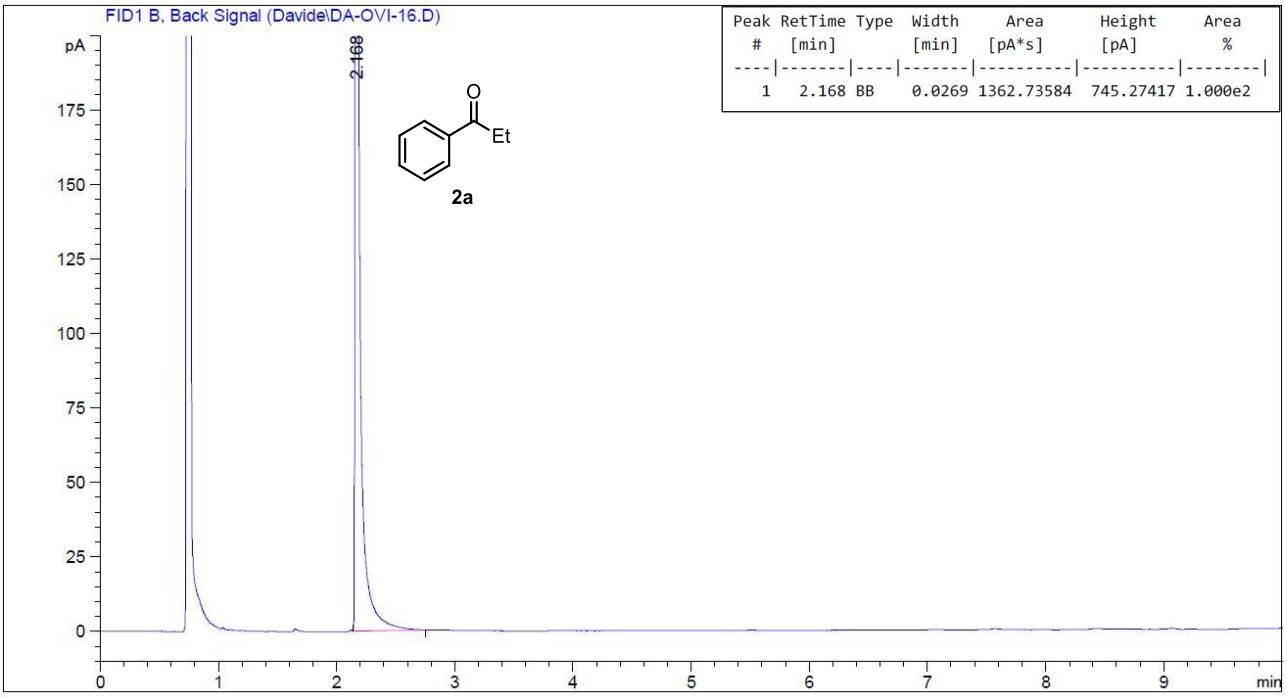


Figure S12. Table S1, entry 5: GC-FID chromatogram of the reaction crude.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.282	BB	0.0826	43.27154	6.77170	1.14323
2	5.260	BB	0.0623	3741.75244	781.27319	98.85677

Figure S13. Table S1, entry 6: GC-FID chromatogram of the reaction crude.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.168	BB	0.0269	1362.73584	745.27417	1.000e2

Figure S14. Table S1, entry 7: GC-FID chromatogram of the reaction crude.

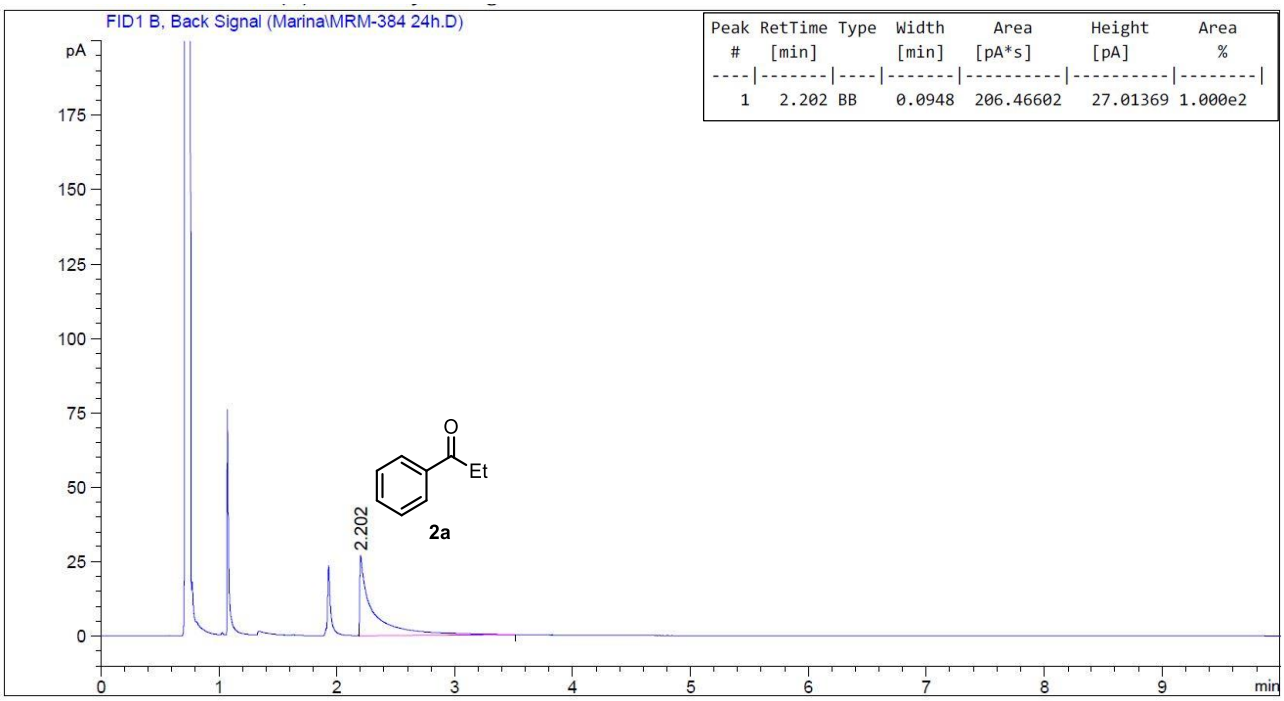


Figure S15. Table S1, entry 8: GC-FID chromatogram of the reaction crude.

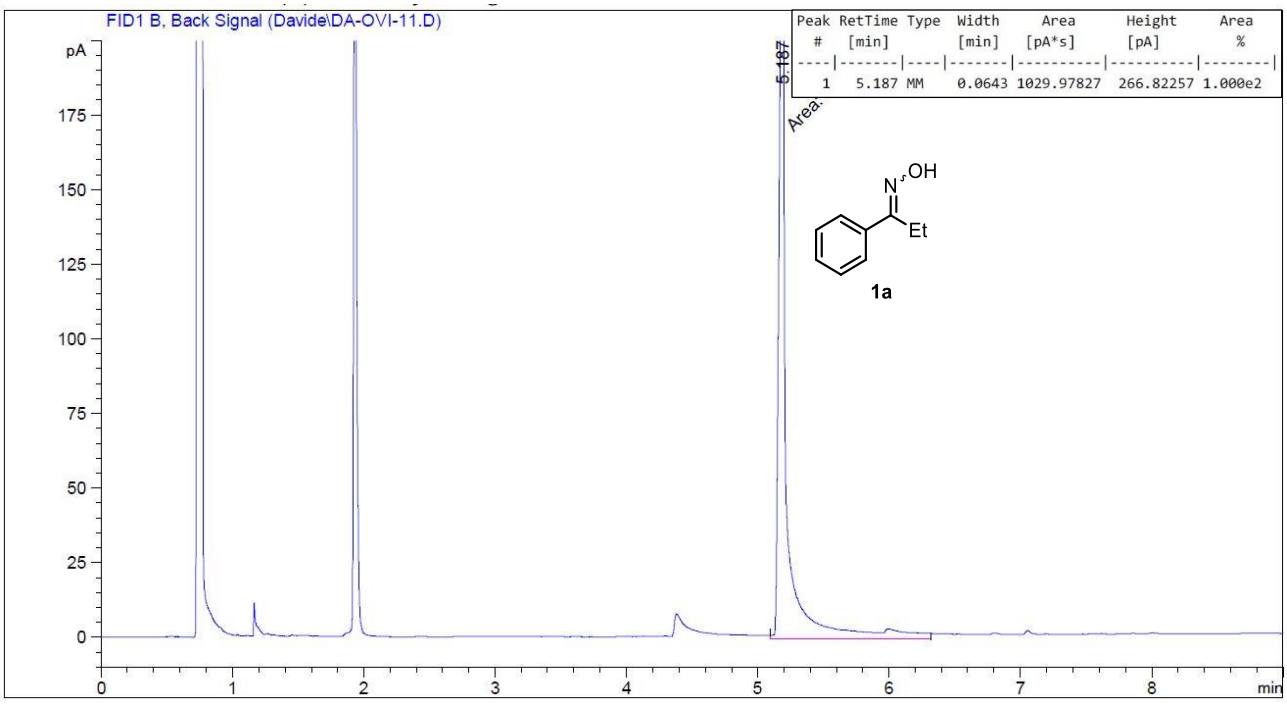


Figure S16. Table S1, entry 9: GC-FID chromatogram of the reaction crude.

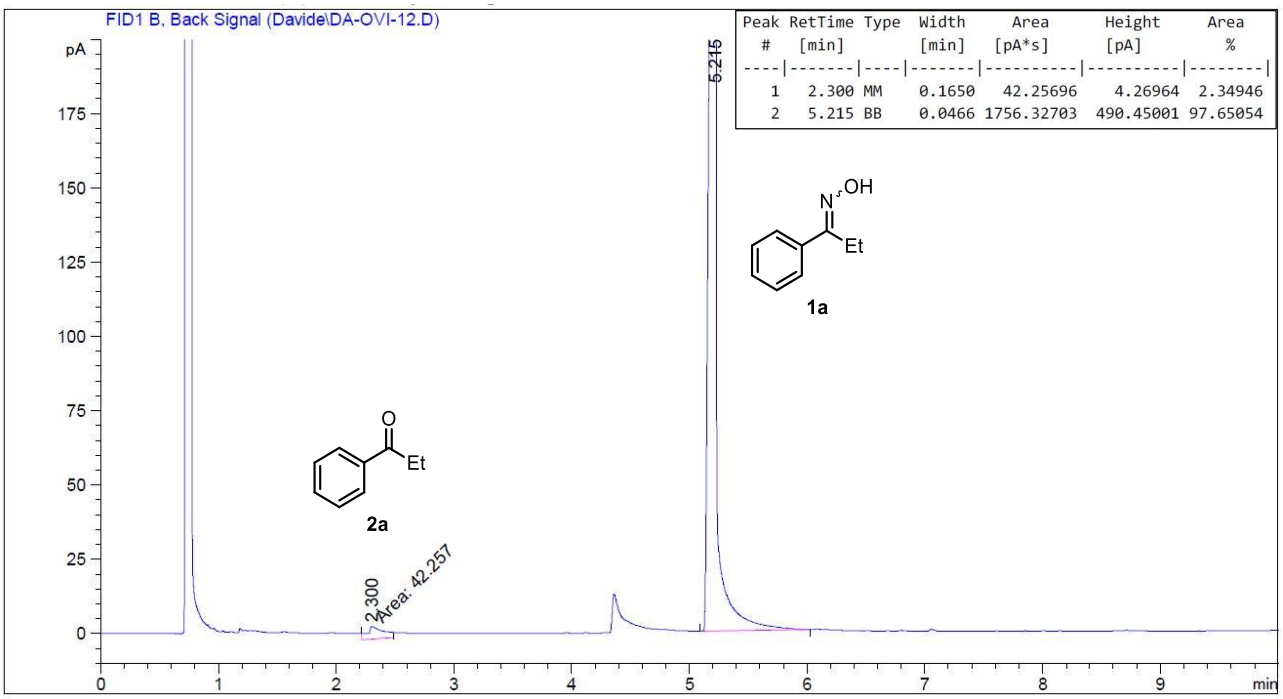
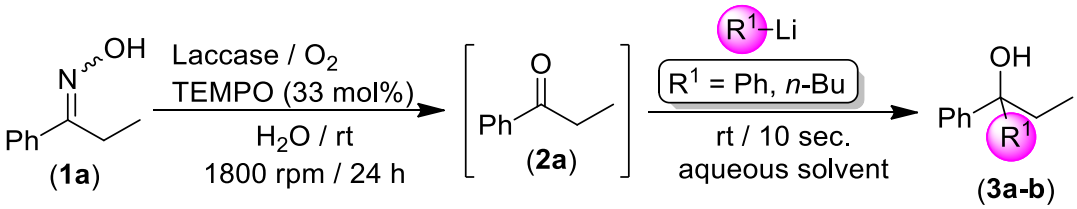


Figure S17. Table S1, entry 10: GC-FID chromatogram of the reaction crude.

Hybrid one-pot tandem transformation of ketoxime **1a** into tertiary alcohols **3a-b** promoted by combination of the laccase/TEMPO/O_2 system with the chemoselective addition of RLi reagents (R = Ph or *n*-Bu) in aqueous media, at room temperature and in the presence of air

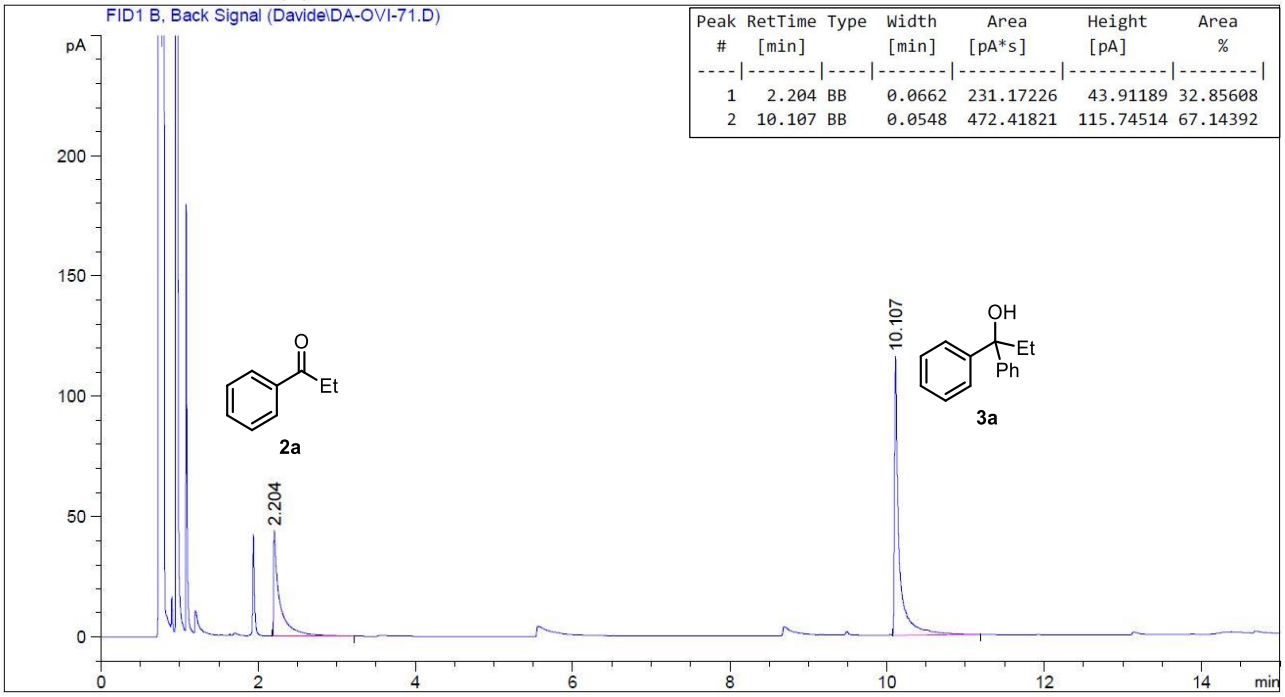
T. versicolor laccase (280 mg, 0.5 U/mg) and TEMPO (38 mg, 33 mol%) were added to a 0.73 mmol (109 mg) suspension of propiophenone oxime **1a** in water (1 mL) and the mixture was stirred vigorously (1800 rpm) in an 8 mL vial under oxygen atmosphere for 24 h. Once the biodeoximation reaction was completed (GC-FID analysis, 24 h), 1 mL of ethereal co-solvent was added to form a biphasic reaction medium (apart from Table S2, entry 1). Next, the corresponding organolithium reagent (RLi, selected equivalents) was rapidly spreaded over the reaction mixture at room temperature, under air. After 10 s, a saturated solution of NH_4Cl_{aq} (2.5 mL) was added, and the mixture was extracted with dichloromethane (3 x 5 mL). The combined organic phases were washed with brine (1 x 5 mL), dried over anhydrous Na_2SO_4, and the solvents were removed *in vacuo*. Conversion of **1a** into tertiary alchols **3a-b** was determined by GC-FID analysis of the crude reaction mixtures (presented in Figures S18-S24). The crude products obtained with the optimized conditions (Table S2, entry 2 for **3a**; Table S2, entry 6 for **3b**) were purified by flash column chromatography and characterized by ^1H and $^{13}C\{^1H\}$ NMR.

Table S2. Hybrid one-pot tandem transformation of ketoxime **1a** into tertiary alcohols **3a-b** promoted by combination of the laccase/TEMPO/O_2 system with the chemoselective addition of RLi reagents (R = Ph or n-Bu) in aqueous media, at room temperature and in the presence of air.[a]



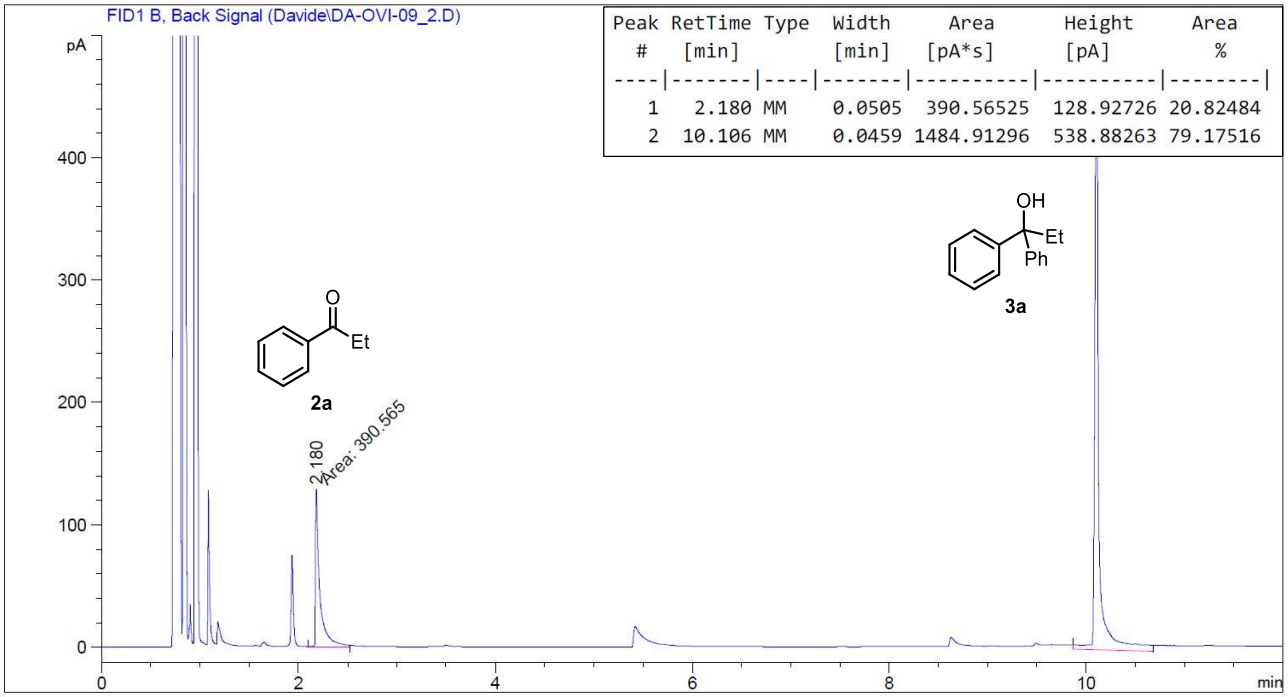
Entry	R^1-Li	Equiv.	Solvent	Product	Conversion [b] (%)
1	PhLi	3.0	H_2O	**3a**	67
2	PhLi	3.0	H_2O/CPME	**3a**	79
3	PhLi	2.0	H_2O/CPME	**3a**	60
4	PhLi	3.0	H_2O/2-MeTHF	**3a**	65
5	*n*-BuLi	2.0	H_2O/CPME	**3b**	28
6	*n*-BuLi	3.0	H_2O/CPME	**3b**	62
7	*n*-BuLi	3.0	H_2O/2-MeTHF	**3b**	37

[a] General conditions: 24 h of reaction at room temperature and at 1800 rpm; Laccase from *T. Versicolor* (0.5 U/mg, 280 mg) per 0.73 mmol of **1a**, 0.33 eq. TEMPO in 1 mL of water were used. Then 1 mL of the co-solvent and the RLi reagent [R = Ph (1.9 M in *n*-Bu_2O) or *n*-Bu (2.5 M in hexanes)] were added without any isolation/purification. [b] Determined by GC-FID, no significant amount of by-products was detected [110 ºC; 4 min; 10 °C/min; 220 °C; 2 min].



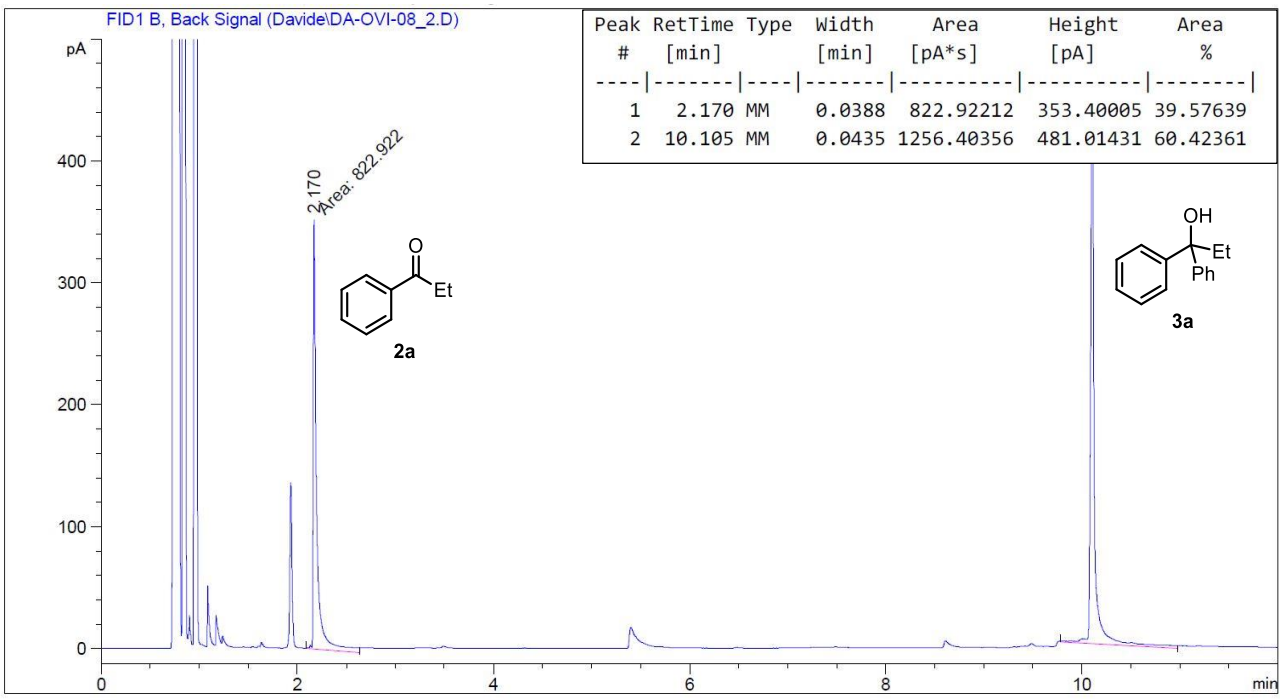
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.204	BB	0.0662	231.17226	43.91189	32.85608
2	10.107	BB	0.0548	472.41821	115.74514	67.14392

Figure S18. Table S2, entry 1: GC-FID chromatogram of the reaction crude.



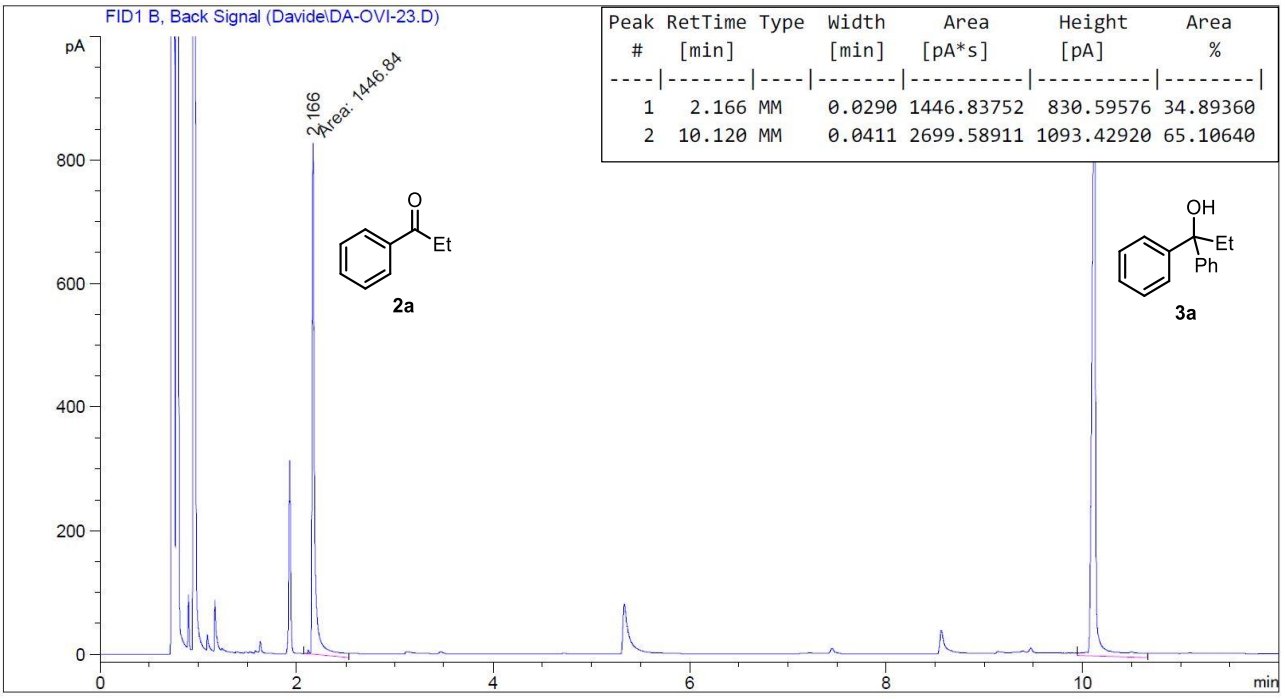
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.180	MM	0.0505	390.56525	128.92726	20.82484
2	10.106	MM	0.0459	1484.91296	538.88263	79.17516

Figure S19. Table S2, entry 2: GC-FID chromatogram of the reaction crude.



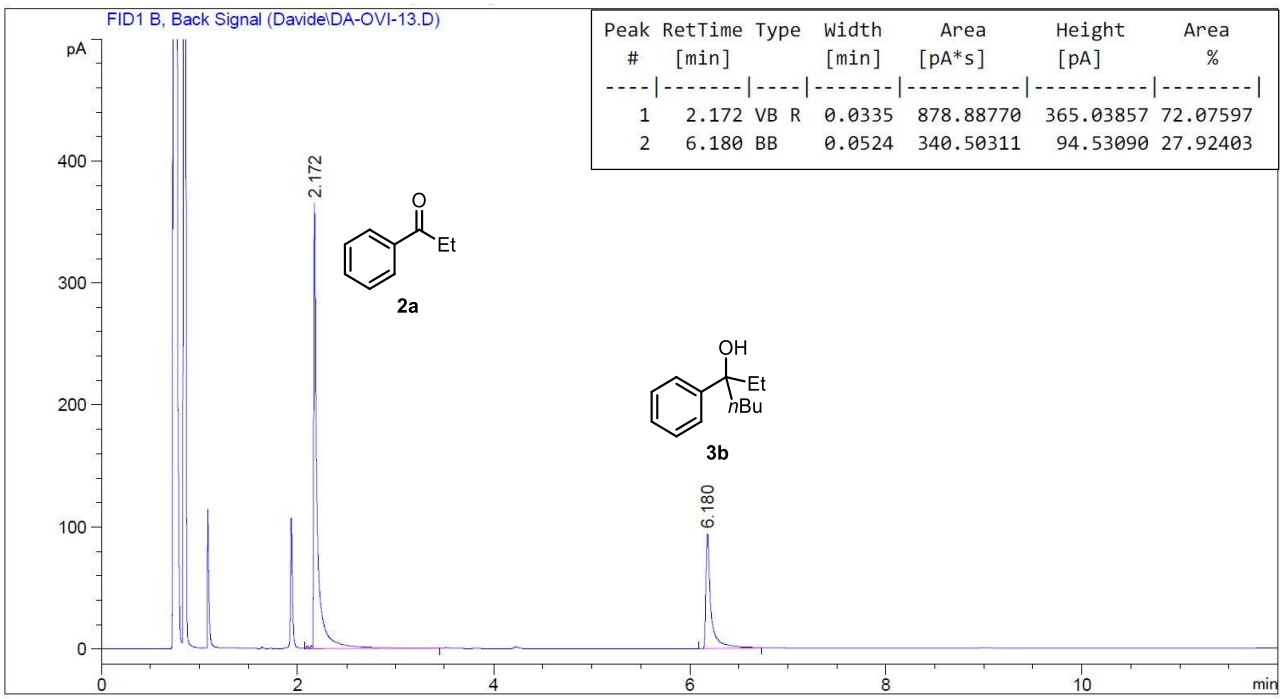
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.170	MM	0.0388	822.92212	353.40005	39.57639
2	10.105	MM	0.0435	1256.40356	481.01431	60.42361

Figure S20. Table S2, entry 3: GC-FID chromatogram of the reaction crude.



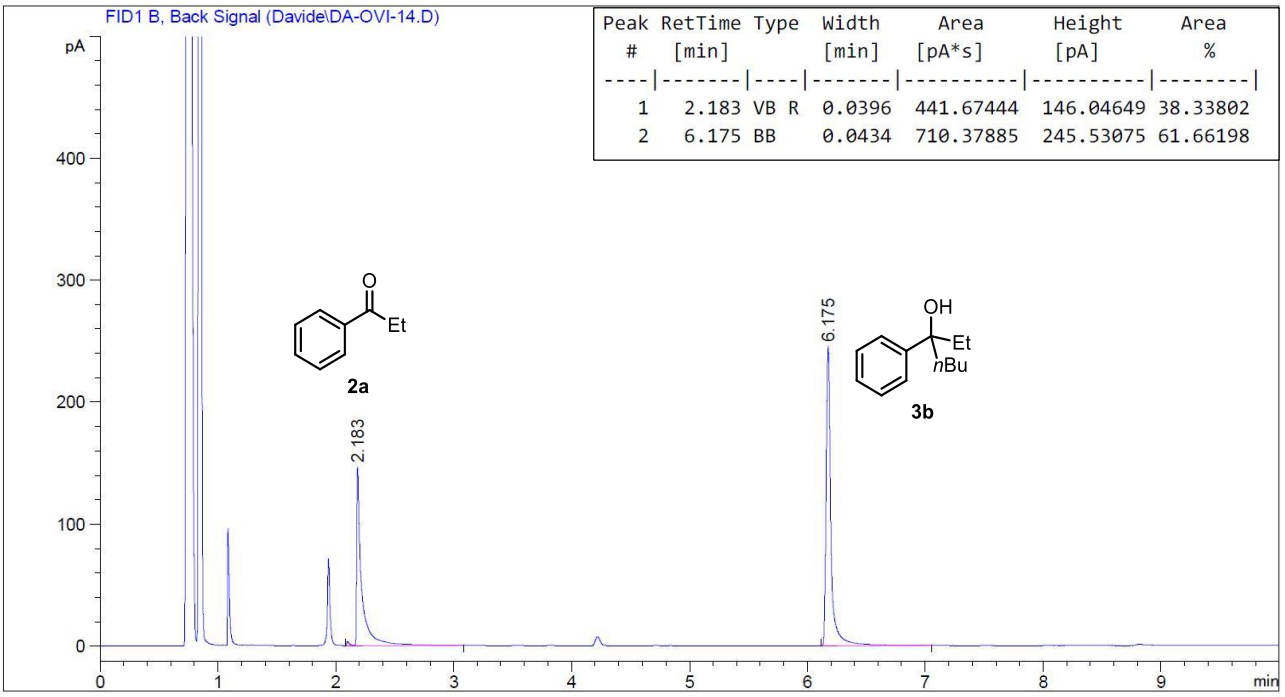
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.166	MM	0.0290	1446.83752	830.59576	34.89360
2	10.120	MM	0.0411	2699.58911	1093.42920	65.10640

Figure S21. Table S2, entry 4: GC-FID chromatogram of the reaction crude.



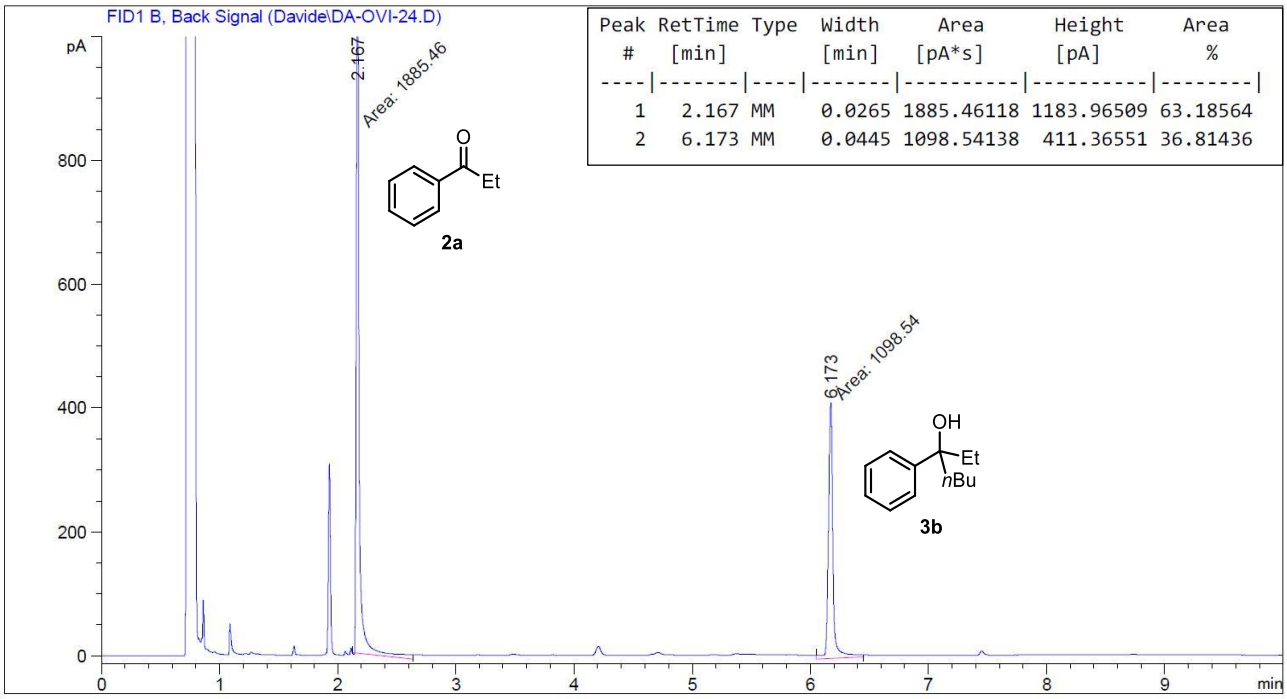
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.172	VB R	0.0335	878.88770	365.03857	72.07597
2	6.180	BB	0.0524	340.50311	94.53090	27.92403

Figure S22. Table S2, entry 5: GC-FID chromatogram of the reaction crude.



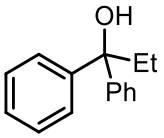
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.183	VB R	0.0396	441.67444	146.04649	38.33802
2	6.175	BB	0.0434	710.37885	245.53075	61.66198

Figure S23. Table S2, entry 6: GC-FID chromatogram of the reaction crude.

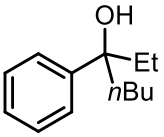


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.167	MM	0.0265	1885.46118	1183.96509	63.18564
2	6.173	MM	0.0445	1098.54138	411.36551	36.81436

Figure S24. Table S2, entry 7: GC-FID chromatogram of the reaction crude.



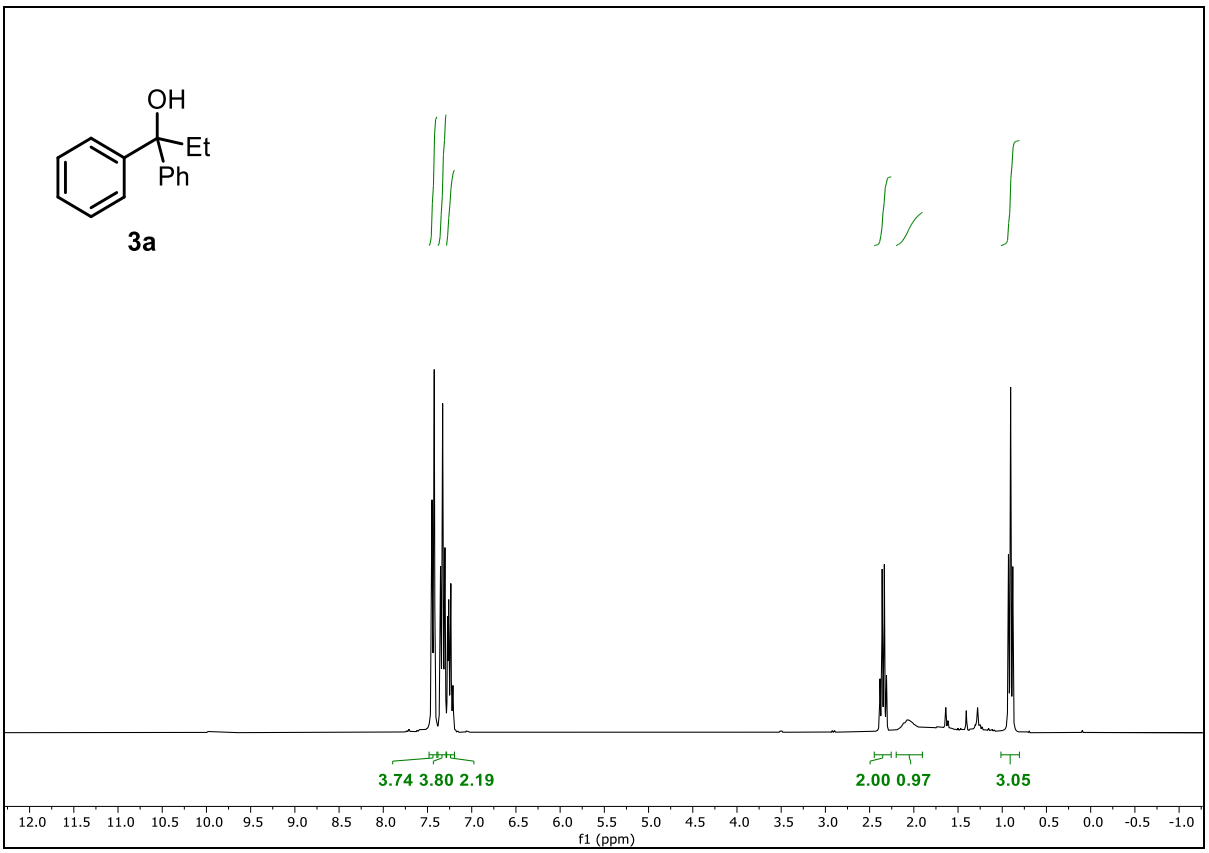
1,1-diphenylpropan-1-ol (3a): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3a** as a white solid (70%, R_f = 0.19 hexane/Et_2O 9/1 v/v), mp 93.2−94.6 °C (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.28-7.18 (m, 2H), 2.35 (q, *J* = 7.3 Hz, 2H), 2.06 (br s, 1H), 0.91 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 147.0, 128.2, 126.9, 126.2, 78.6, 34.6, 8.2.[7]



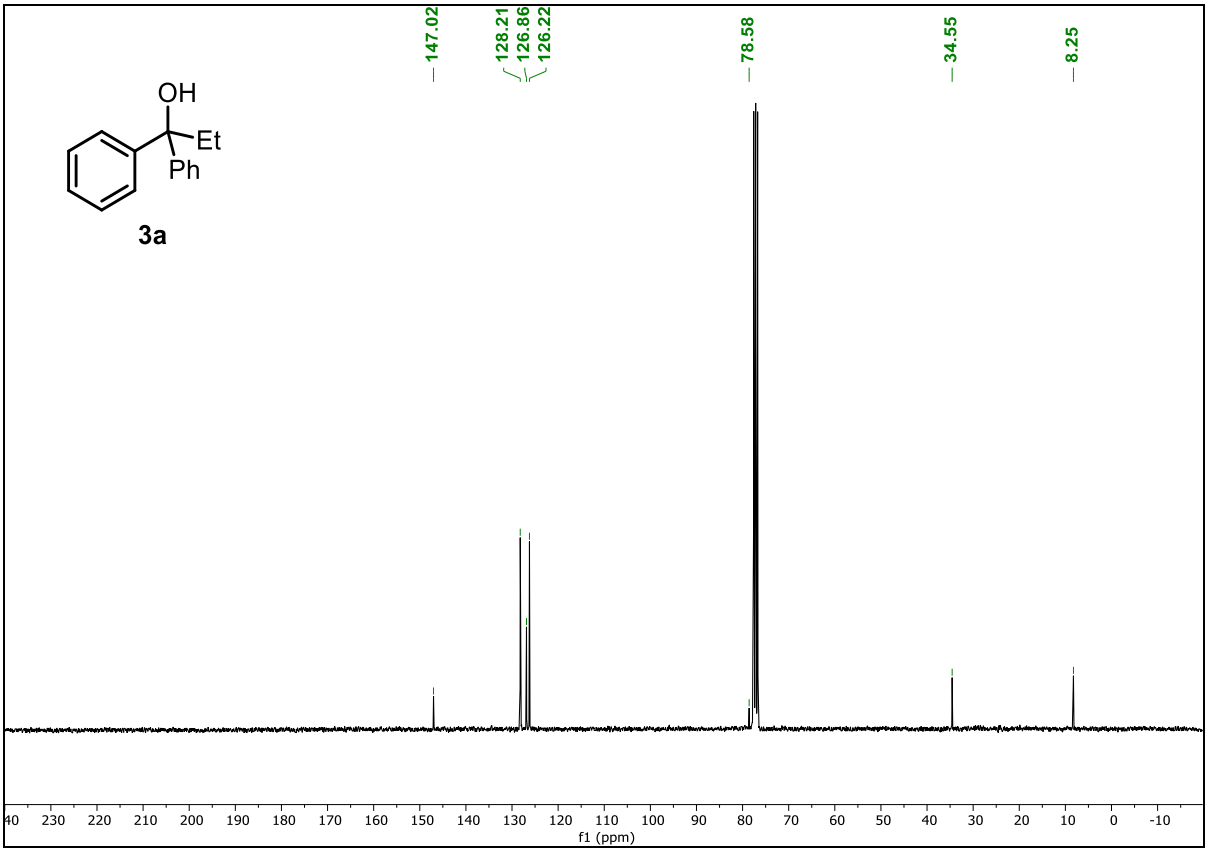
3-phenylheptan-3-ol (3b): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3b** as a colorless oil (57%, R_f = 0.29 hexane/Et_2O 9/1 v/v). ^1H NMR (300 MHz, $CDCl_3$): δ 7.48-7.34 (m, 4H), 7.33-7.23 (m, 1H), 2.02-1.76 (m, 4H), 1.67 (br s, 1H), 1.40-1.22 (m, 3H), 1.18-1.00 (m, 1H), 0.90 (t, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.7, 127.6, 125.8, 124.9, 41.9, 35.0, 25.2, 22.7, 13.6, 7.4.[7]

1,1-diphenylpropan-1-ol (3a)

^{1}H NMR (300 MHz, $CDCl_3$)

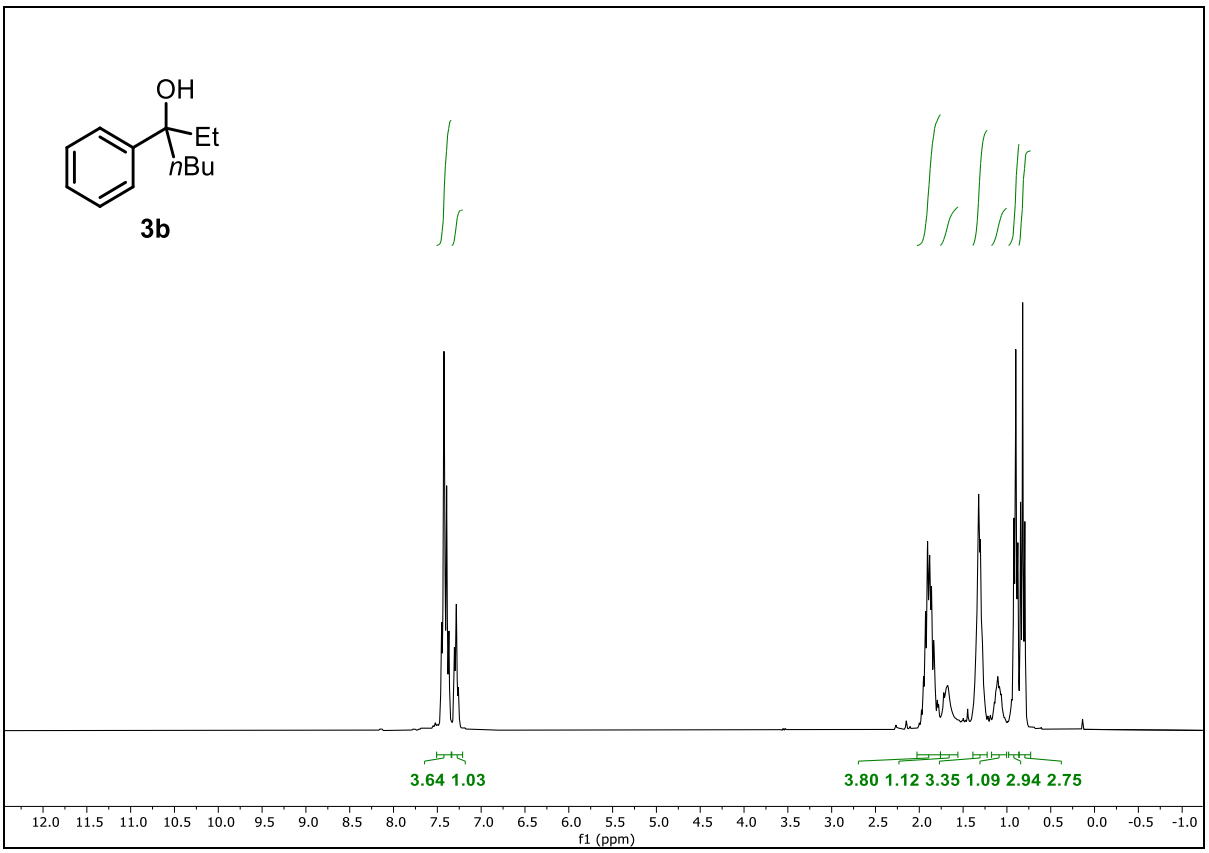


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

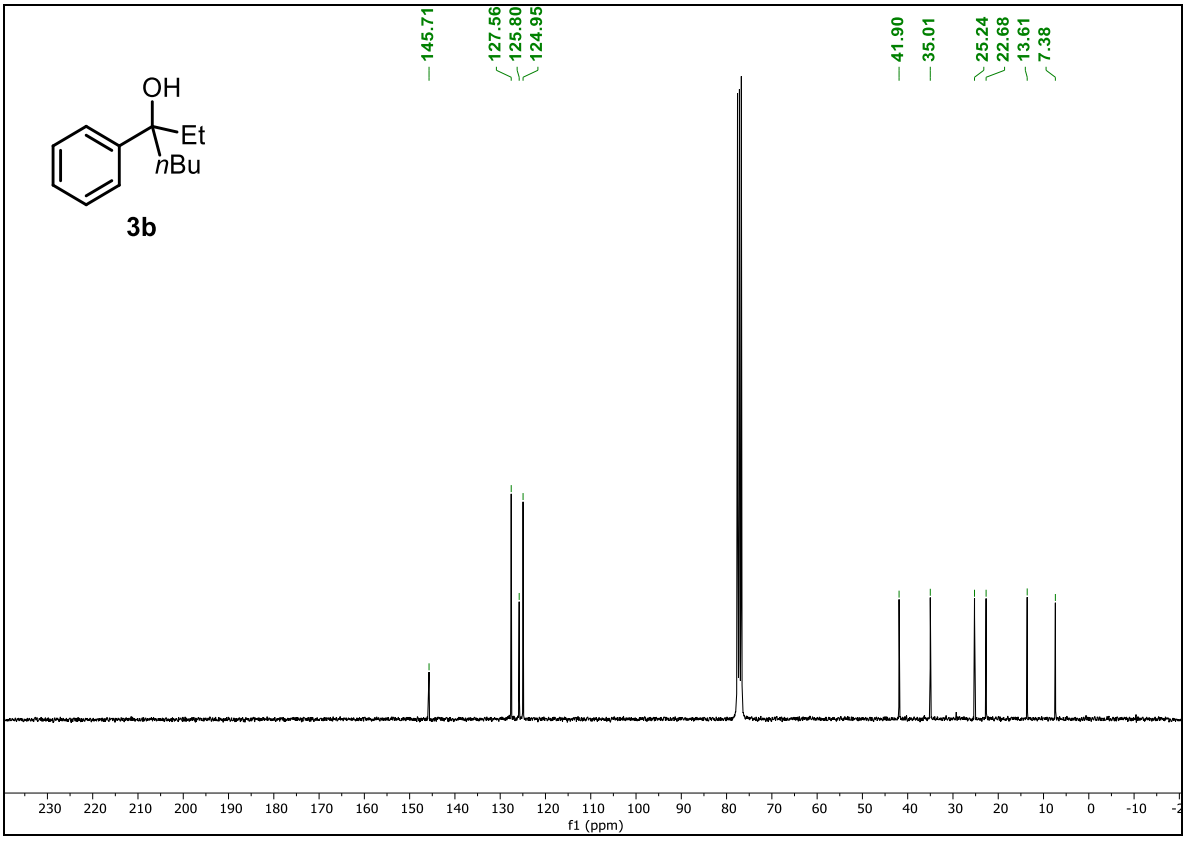


3-phenylheptan-3-ol (3b)

^{1}H NMR (300 MHz, $CDCl_3$)



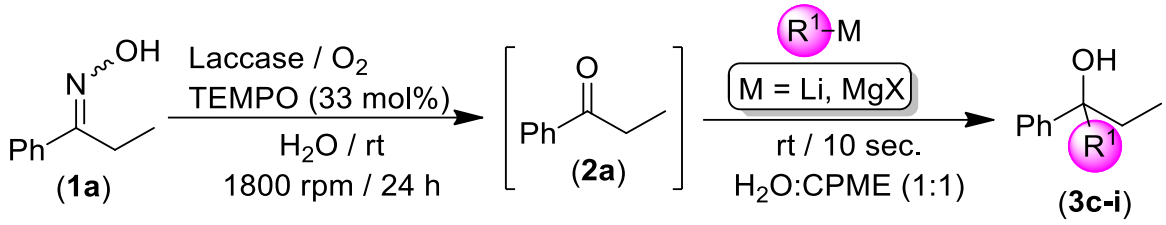
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



Hybrid one-pot tandem transformation of ketoxime **1a** into tertiary alcohols **3c-i** promoted by combination of the laccase/TEMPO/O_2 system with the chemoselective addition of RLi/RMgX in aqueous media, at room temperature and in the presence of air

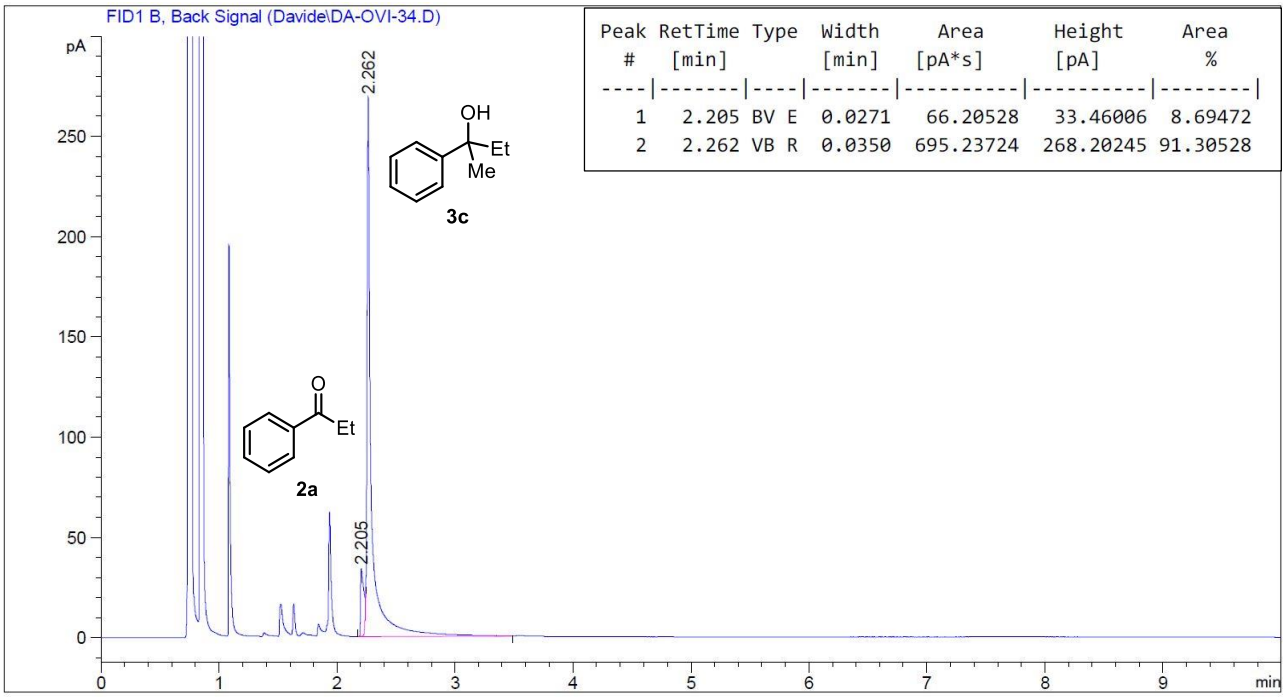
T. versicolor laccase (280 mg, 0.5 U/mg) and TEMPO (38 mg, 33 mol%) were added to a 0.73 mmol (109 mg) suspension of propiophenone oxime **1a** in water (1 mL) and the mixture was stirred vigorously (1800 rpm) in an 8 mL vial under oxygen atmosphere for 24 h. Once the biodeoximation reaction was completed (GC-FID analysis, 24 h), 1 mL of CPME was added as co-solvent to form a biphasic reaction medium. Next, the corresponding organolithium (RLi, 3.0 eq) or Grignard (RMgX, 3.0 eq) reagent was rapidly spreaded over the reaction mixture at room temperature, under air. After 10 s, a saturated solution of NH_4Cl_{aq} (2.5 mL) (2.5 mL) was added, and the mixture was extracted with dichloromethane (3 x 5 mL). The combined organic phases were washed with brine (1 x 5 mL), dried over anhydrous Na_2SO_4, and the solvents were removed *in vacuo*. Conversion of **1a** into tertiary alchols **3c-i** was determined by GC-FID analysis of the crude reaction mixtures (presented in Figures S25-S31). The crude products were purified by flash column chromatography and characterized by ^1H and $^{13}C\{^1H\}$ NMR.

Table S3. Hybrid one-pot tandem transformation of ketoxime **1a** into tertiary alcohols **3c-i** promoted by combination of the laccase/TEMPO/O_2 system with the chemoselective addition of RLi/RMgX in aqueous media, at room temperature and in the presence of air.[a]



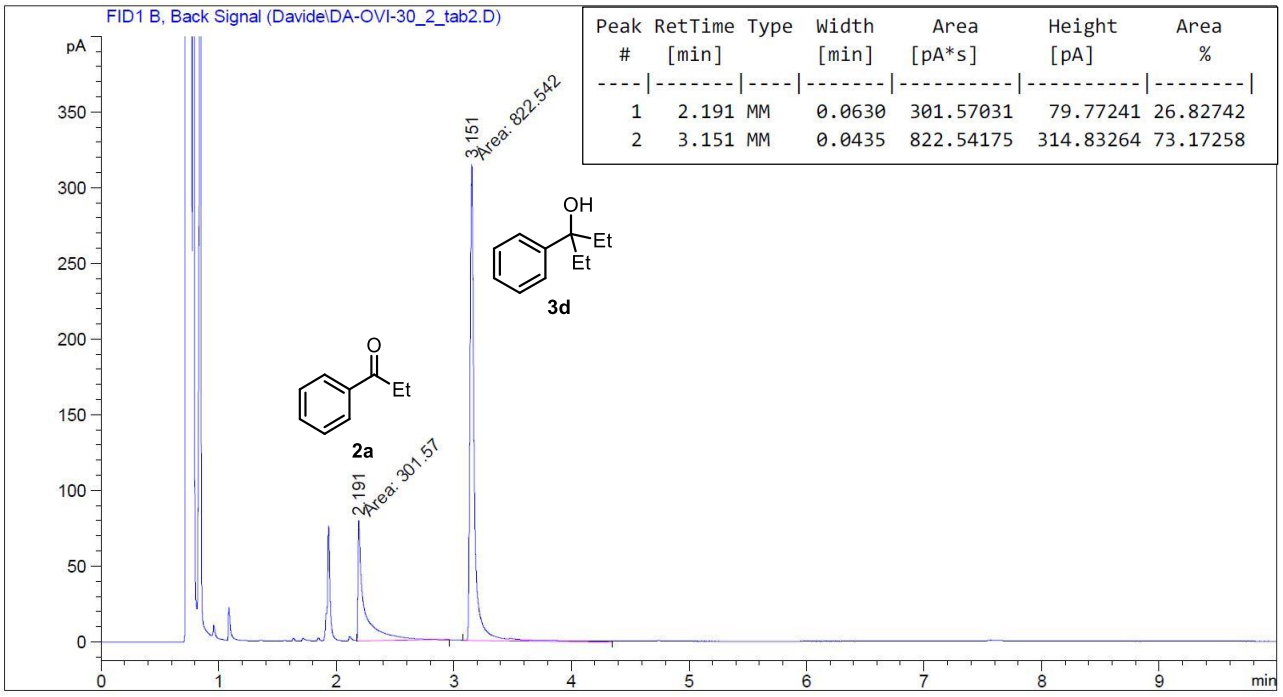
Entry	R^1-M [b] (3.0 eq)	Product	Conversion [c] (%)	Yield [d] (%)
1	MeLi	**3c**	91	82
2	EtLi	**3d**	73	66
3	*s*-BuLi	**3e**	69	64
4	*t*-BuLi	**3f**	53	40
5	2-ThienLi	**3g**	55	46
6	AllylMgBr	**3h**	62	50
7	BenzylMgCl	**3i**	46	33

[a] General conditions: 24 h of reaction at room temperature and at 1800 rpm; Laccase from *T. Versicolor* (0.5 U/mg, 280 mg) per 0.73 mmol of **1a**, 0.33 eq. TEMPO in 1 mL of water were used. [b] Then 1 mL of CPME and the RLi [R = Me (1.6 M in Et_2O); Et (0.5 M in benzene/cyclohexane); *s*-Bu (1.4 M in cyclohexane); *t*-Bu (1.7 M in pentane); 2-thienyl (1.0 M in THF/hexanes)] or RMgX [R = allyl (1.0 M in Et_2O); benzyl (2.0 M in THF)] reagents were added without any isolation/purification. [c] Determined by GC-FID, no significant amount of by-products was detected [110 ºC; 4 min; 10 °C/min; 220 °C; 2 min]. [d] Isolated yield.



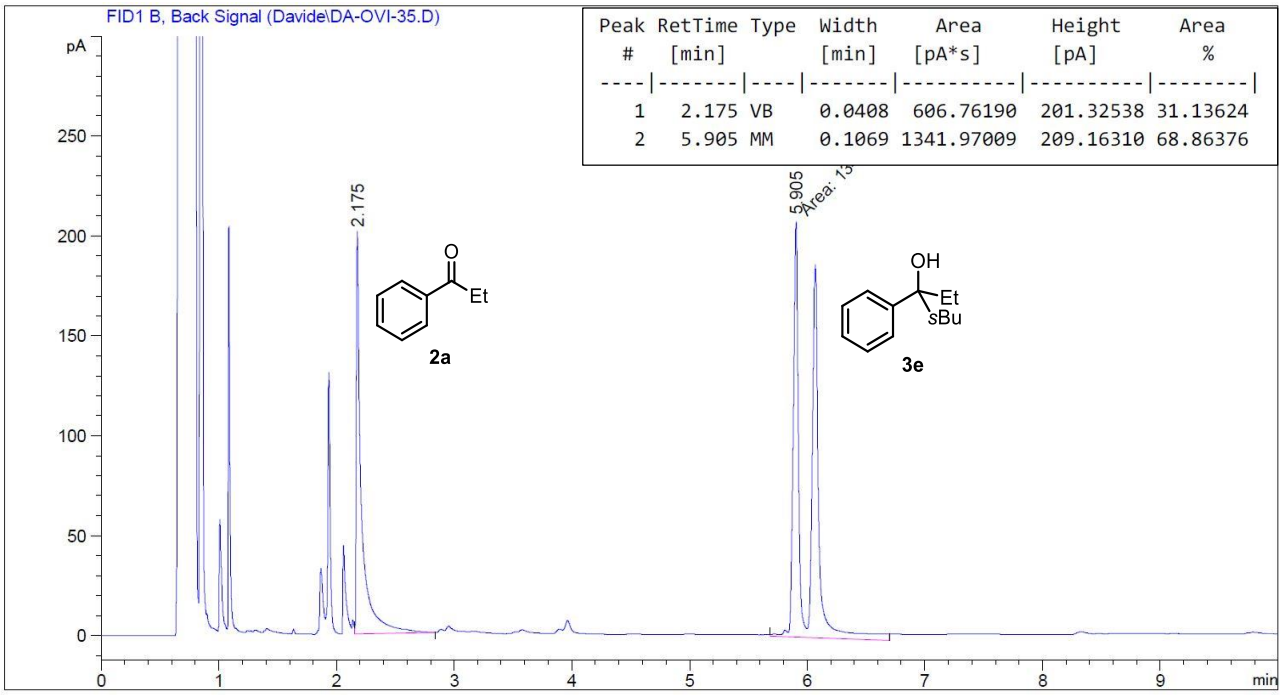
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.205	BV E	0.0271	66.20528	33.46006	8.69472
2	2.262	VB R	0.0350	695.23724	268.20245	91.30528

Figure S25. Table S3, entry 1 (R-M: MeLi): GC-FID chromatogram of the reaction crude.



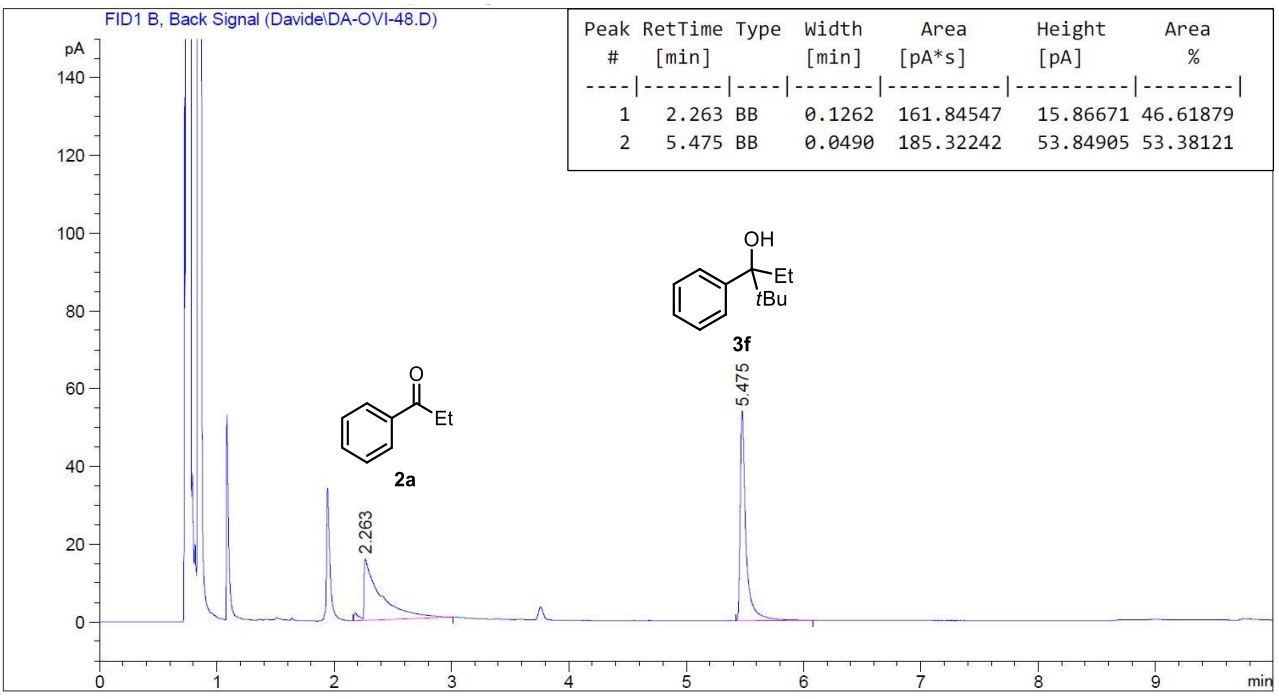
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.191	MM	0.0630	301.57031	79.77241	26.82742
2	3.151	MM	0.0435	822.54175	314.83264	73.17258

Figure S26. Table S3, entry 2 (R-M: EtLi): GC-FID chromatogram of the reaction crude.



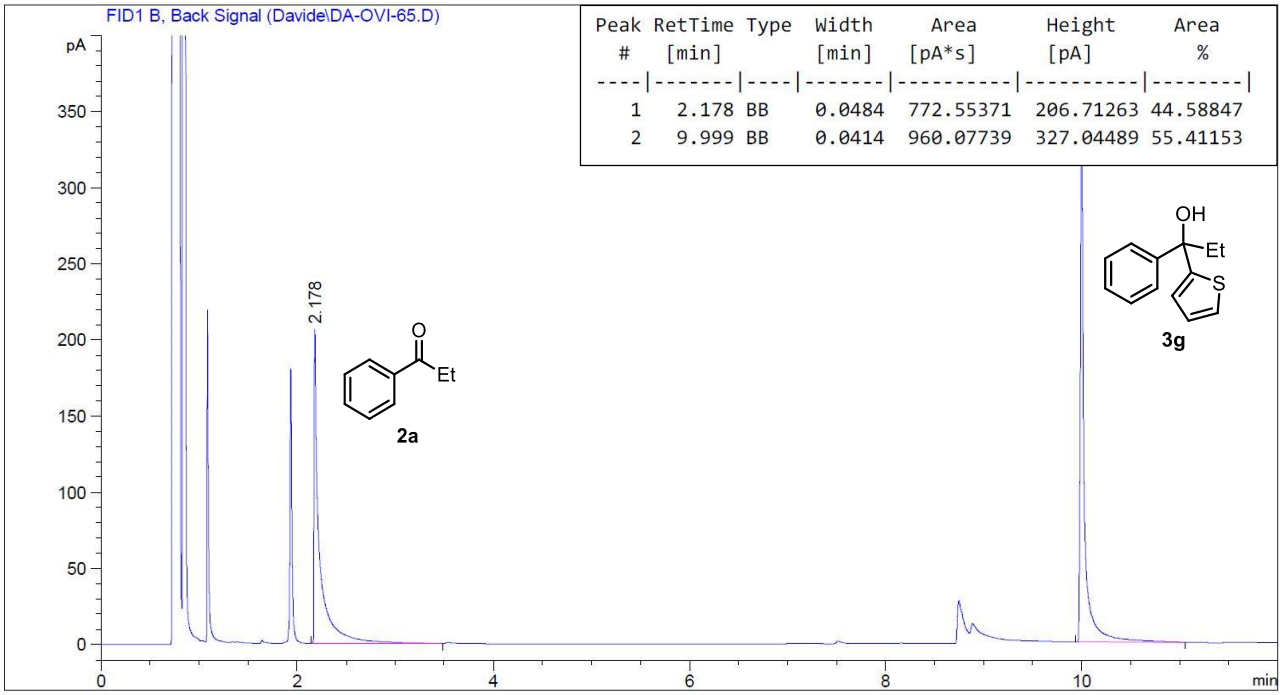
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.175	VB	0.0408	606.76190	201.32538	31.13624
2	5.905	MM	0.1069	1341.97009	209.16310	68.86376

Figure S27. Table S3, entry 3 (R-M: *s*-BuLi): GC-FID chromatogram of the reaction crude.



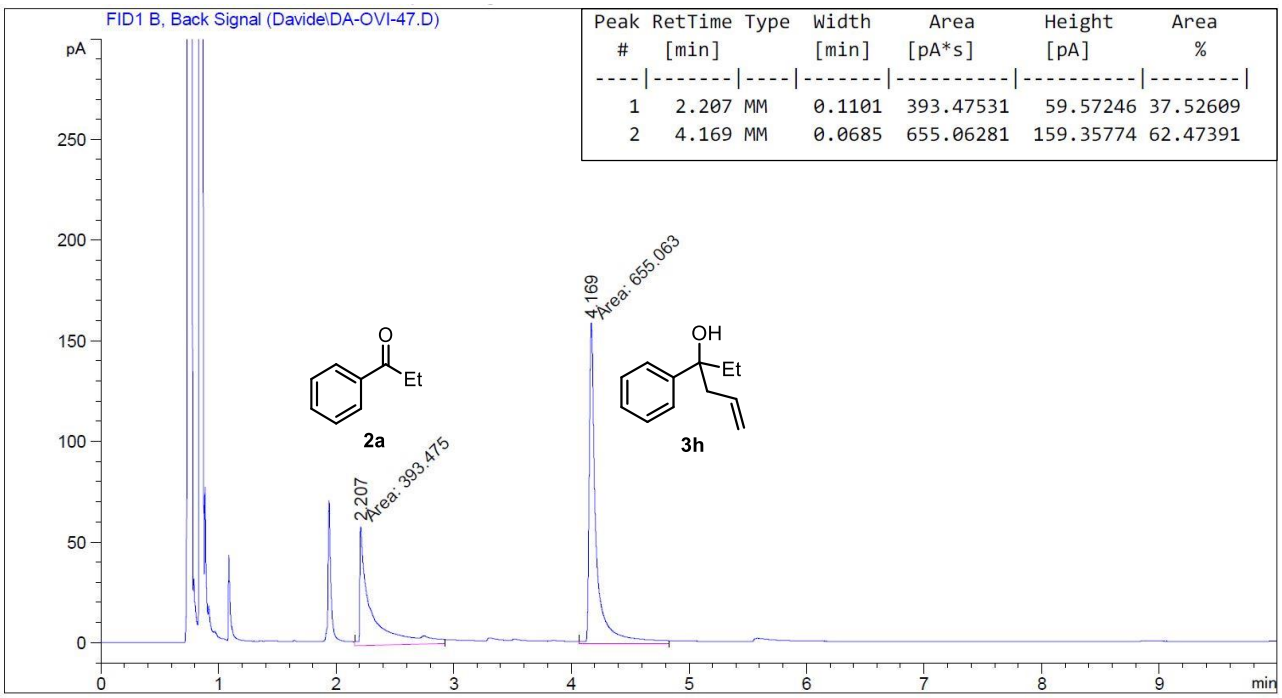
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.263	BB	0.1262	161.84547	15.86671	46.61879
2	5.475	BB	0.0490	185.32242	53.84905	53.38121

Figure S28. Table S3, entry 4 (R-M: *t*-BuLi): GC-FID chromatogram of the reaction crude.



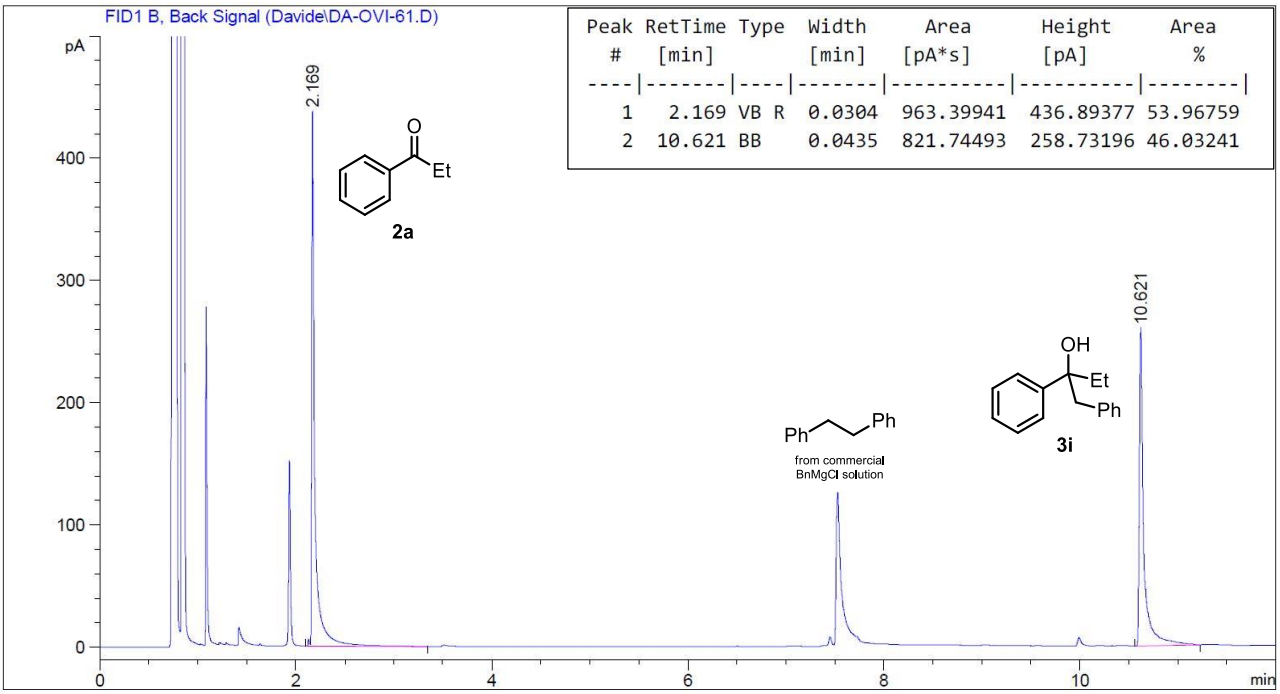
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.178	BB	0.0484	772.55371	206.71263	44.58847
2	9.999	BB	0.0414	960.07739	327.04489	55.41153

Figure S29. Table S3, entry 5 (R-M: 2-ThienLi): GC-FID chromatogram of the reaction crude.



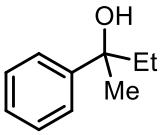
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.207	MM	0.1101	393.47531	59.57246	37.52609
2	4.169	MM	0.0685	655.06281	159.35774	62.47391

Figure S30. Table S3, entry 6 (R-M: AllylMgBr): GC-FID chromatogram of the reaction crude.

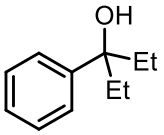


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.169	VB R	0.0304	963.39941	436.89377	53.96759
2	10.621	BB	0.0435	821.74493	258.73196	46.03241

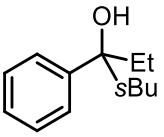
Figure S31. Table S3, entry 7 (R-M: BnMgCl): GC-FID chromatogram of the reaction crude.



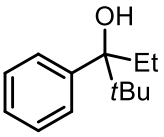
2-phenylbutan-2-ol (3c): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3c** as a colorless oil (82%, R_f = 0.16 hexane/Et_2O 9/1 v/v). ^1H NMR (300 MHz, $CDCl_3$): δ 7.51-7.42 (m, 2H), 7.41-7.32 (m, 2H), 7.30-7.22 (m, 1H), 1.87 (qd, *J* = 7.3, 3.8 Hz, 2H), 1.77 (br s, 1H), 1.58 (s, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 147.9, 128.2, 126.6, 125.0, 75.1, 36.8, 29.8, 8.4.[7]



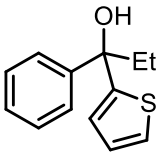
3-phenylpentan-3-ol (3d): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3d** as a colorless oil (66%, R_f = 0.22 hexane/Et_2O 9/1 v/v). ^1H NMR (300 MHz, $CDCl_3$): δ 7.47-7.32 (m, 4H), 7.30-7.20 (m, 1H), 2.00-1.77 (m, 4H), 1.69 (br s, 1H), 0.80 (t, *J* = 7.4 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.7, 127.9, 126.2, 125.4, 77.3, 34.9, 7.7.[8]



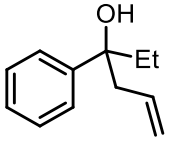
4-methyl-3-phenylhexan-3-ol (3e): flash column chromatography (hexane/Et_2O 95/5 v/v) gave product **3e** as a colorless oil (64%, R_f = 0.21 hexane/Et_2O 95/5 v/v). Mixture of diastereomers (d_r = 1:1). ^1H NMR (300 MHz, $CDCl_3$, mixture of diastereoisomers): δ 7.46-7.31 (m, 8H), 7.30-7.20 (m, 2H), 1.95 (dq, *J* = 14.4, 7.4 Hz, 4H), 1.86-1.68 (m, 2H), 1.59 (br s, 2H), 1.44-1.23 (m, 2H), 1.05-0.64 (m, 18H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, mixture of diastereoisomers): δ 144.7, 144.4, 127.0, 126.9, 125.3, 125.2, 125.1, 79.1, 78.9, 44.0, 43.8, 31.3, 31.0, 23.3, 22.4, 12.9, 11.9, 11.8, 7.1.[7]



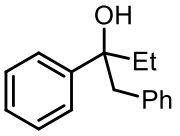
2,2-dimethyl-3-phenylpentan-3-ol (3f): flash column chromatography (hexane/Et_2O 95/5 v/v) gave product **3f** as a colorless oil (40%, R_f = 0.26 hexane/Et_2O 95/5 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.33-7.28 (m, 2H), 7.24-7.19 (m, 1H), 2.23 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.87 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.68 (s, 1H), 0.91 (s, 9H), 0.68 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 143.0, 127.9, 127.2, 126.3, 81.4, 38.5, 27.0, 26.0, 8.3.[9]



1-phenyl-1-(thiophen-2-yl)propan-1-ol (3g): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3g** as a pale yellow oil (46%, R_f = 0.23 hexane/Et_2O 9/1 v/v). ^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.42-7.21 (m, 4H), 7.00-6.89 (m, 2H), 2.38 (q, *J* = 7.5 Hz, 2H) superimposed to 2.33 (s, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 153.2, 145.7, 128.2, 127.2, 126.7, 125.9, 124.8, 124.1, 77.5, 36.5, 8.4.[10]



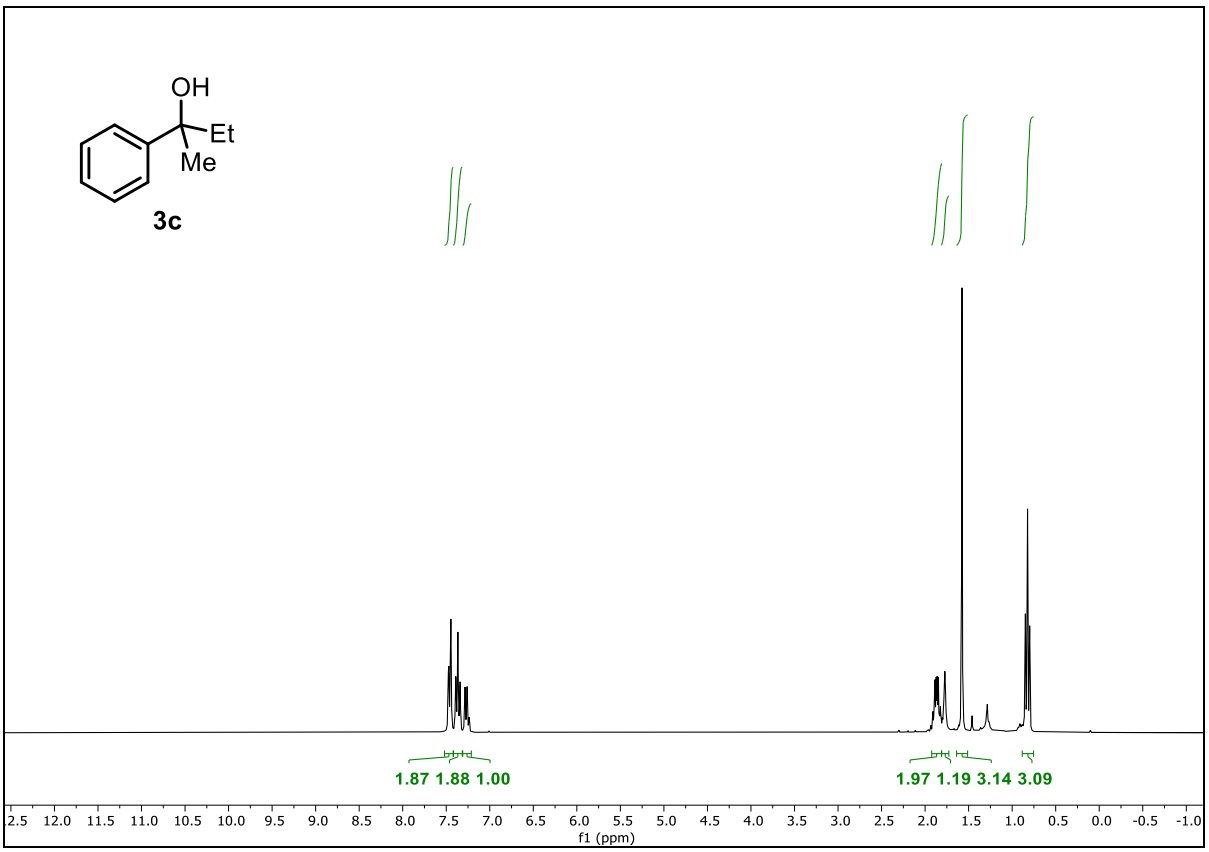
3-phenylhex-5-en-3-ol (3h): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3h** as a colorless oil (50%, R_f = 0.23 hexane/Et_2O 9/1 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.1 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.27-7.22 (m, 1H), 5.65-5.53 (m, 1H), 5.19-5.07 (m, 2H), 2.74 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.52 (dd, *J* = 13.8, 8.6 Hz, 1H), 1.99 (br s, 1H), 1.92-1.80 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 145.3, 133.2, 127.6, 126.0, 125.0, 119.1, 75.5, 46.5, 34.8, 7.4.[11]



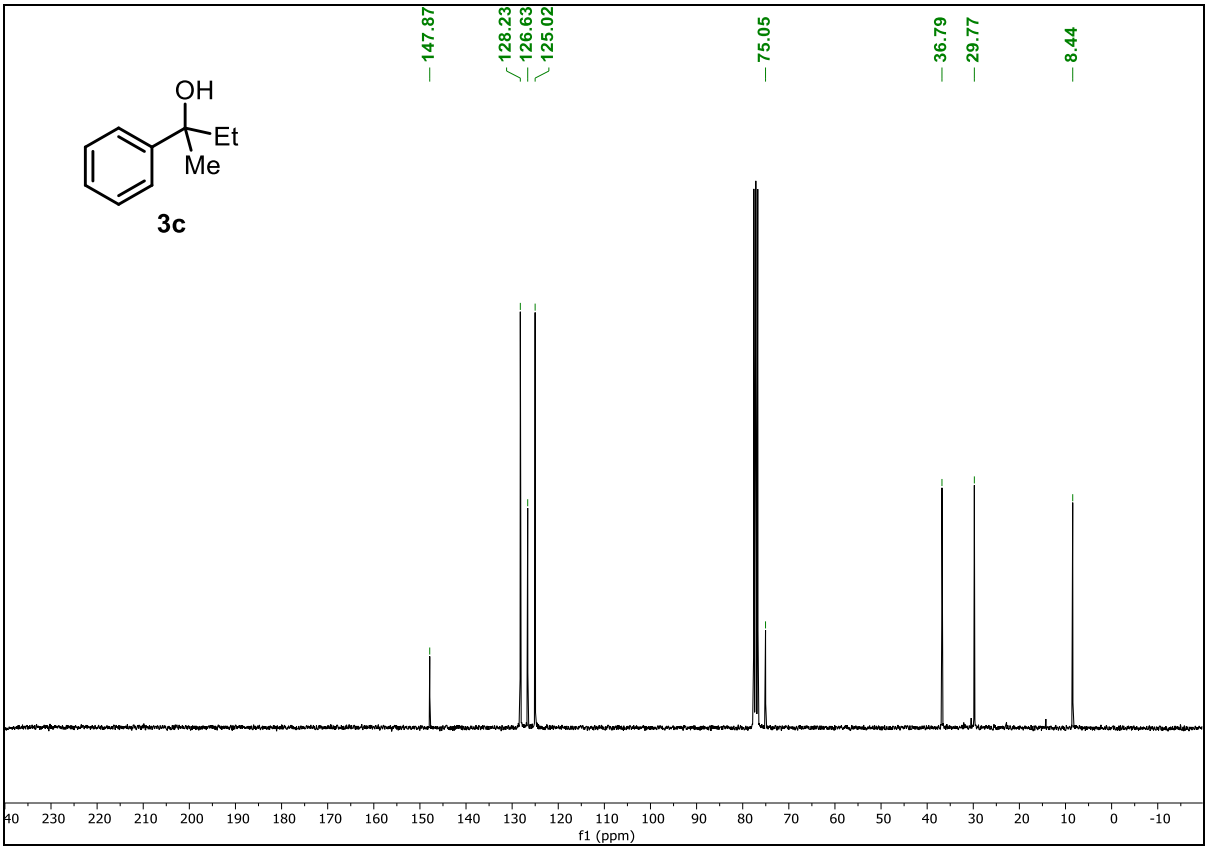
1,2-diphenylbutan-2-ol (3i): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3i** as a colorless oil (33%, R_f = 0.25 hexane/Et_2O 9/1 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.37-7.31 (m, 4H), 7.27-7.23 (m, 1H), 7.22-7.19 (m, 3H), 7.00-6.95 (m, 2H), 3.18 (d, *J* = 13.4 Hz, 1H), 3.08 (d, *J* = 13.3 Hz, 1H), 2.01 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.85 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.76 (br s, 1H), 0.79 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 145.1, 136.1, 130.3, 127.7, 127.6, 126.3, 126.1, 125.2, 76.6, 49.1, 34.1, 7.5.[12]

2-phenylbutan-2-ol (3c)

^{1}H NMR (300 MHz, $CDCl_3$)

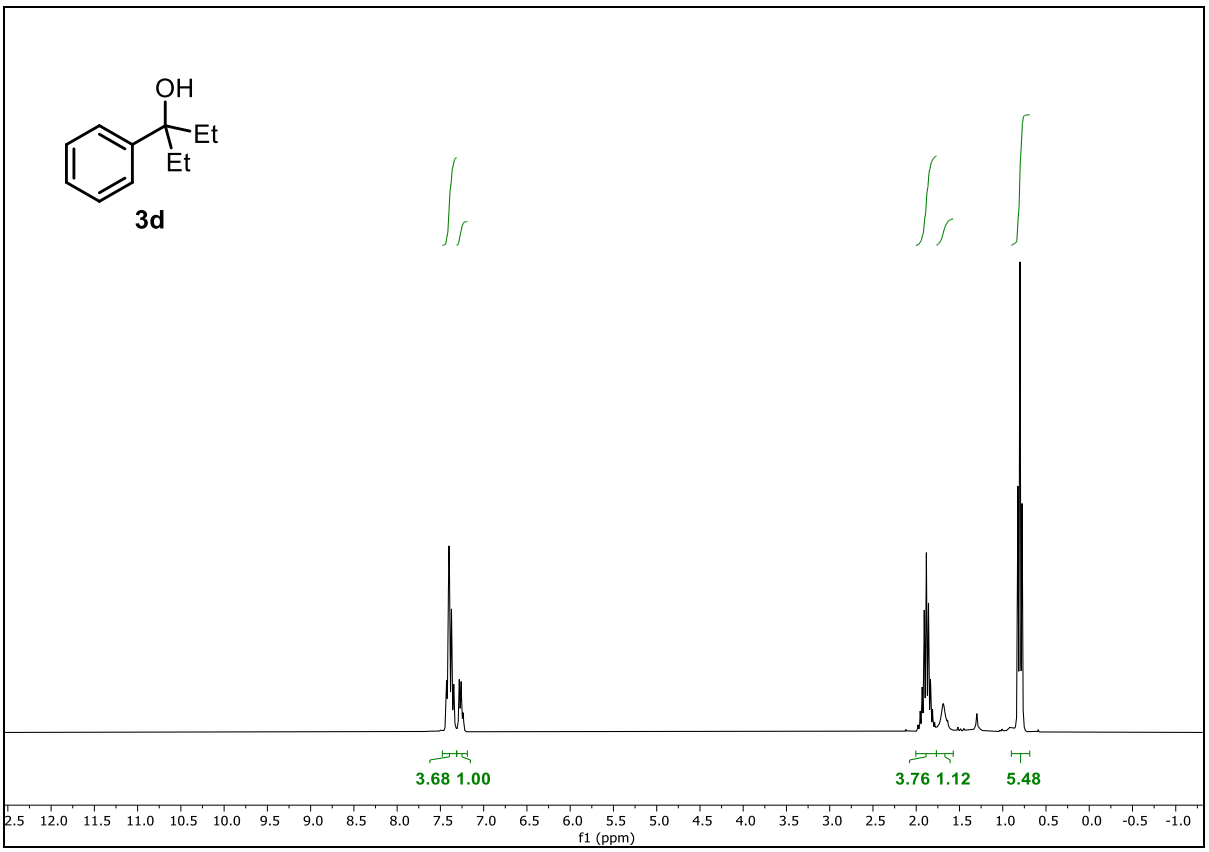


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

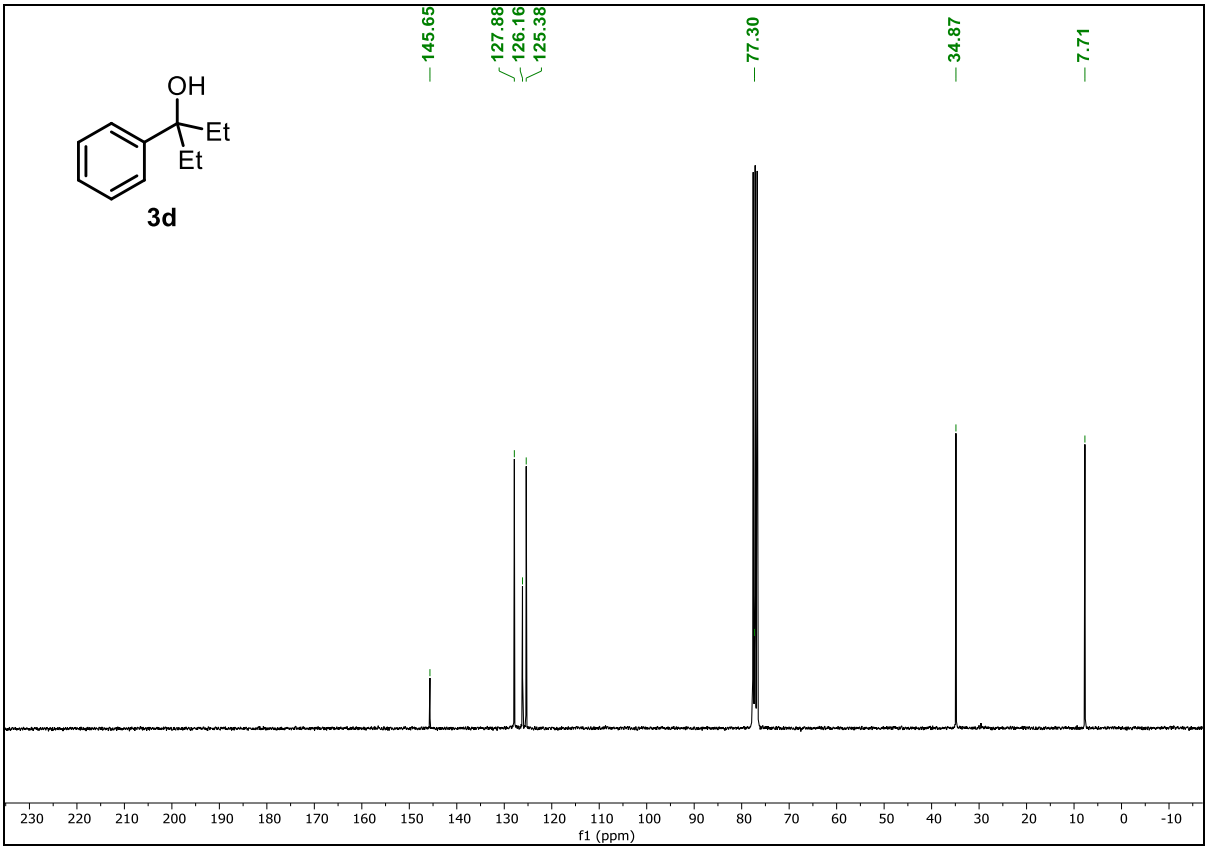


3-phenylpentan-3-ol (3d)

^{1}H NMR (300 MHz, $CDCl_3$)

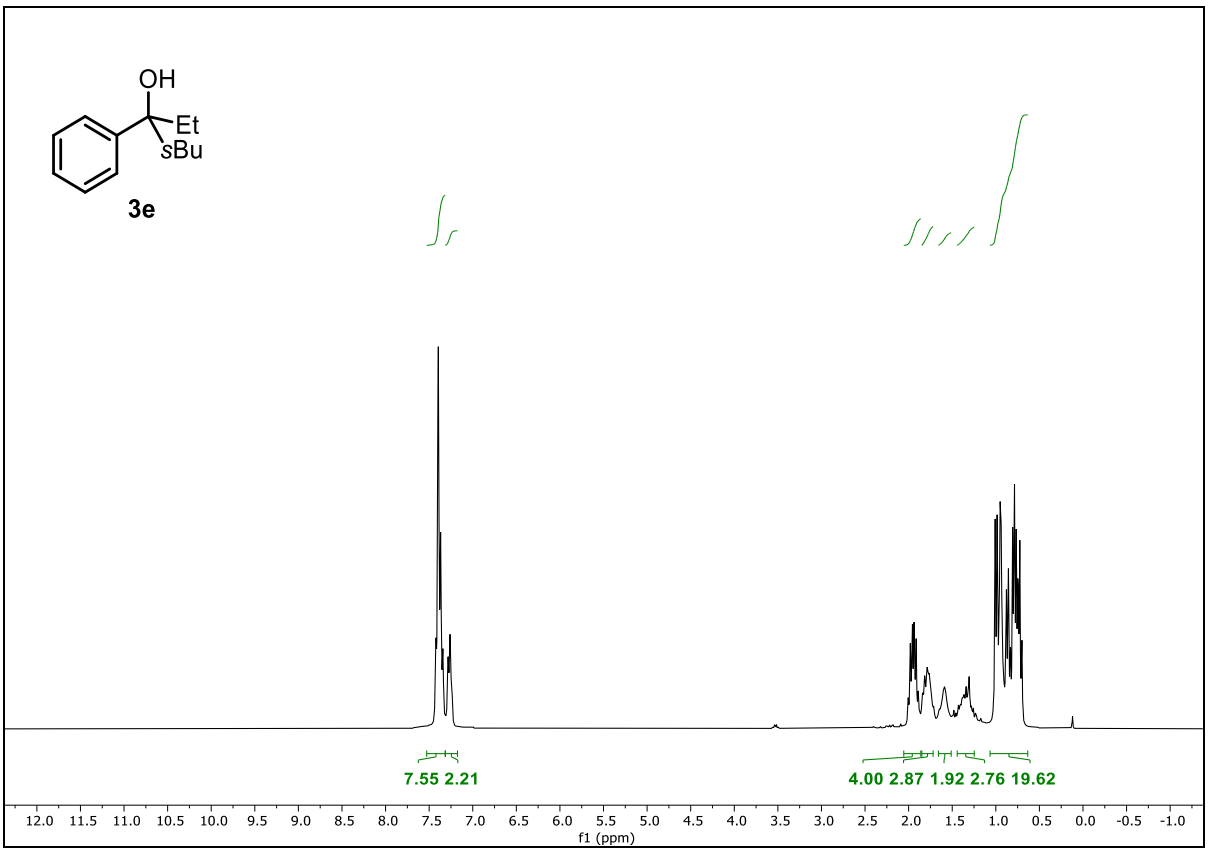


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

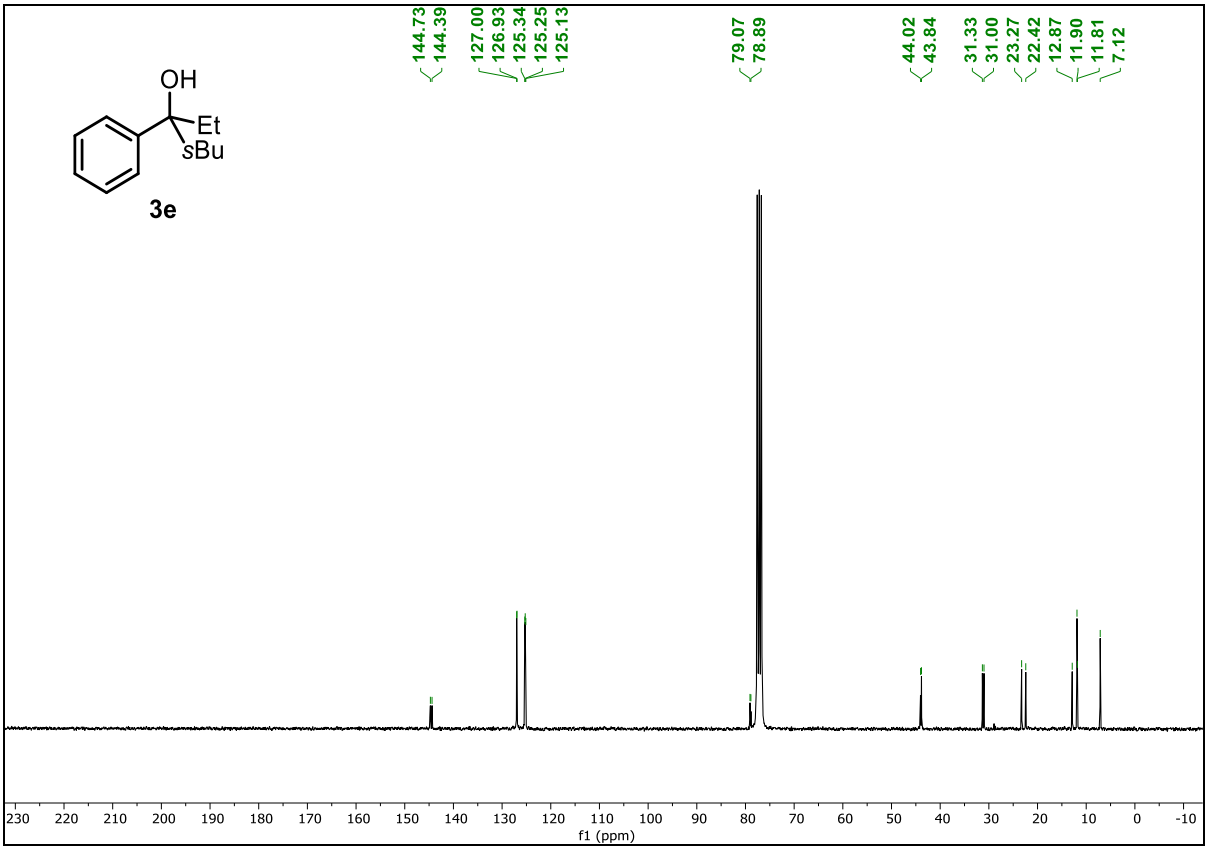


4-methyl-3-phenylhexan-3-ol (3e)

^{1}H NMR (300 MHz, $CDCl_3$)

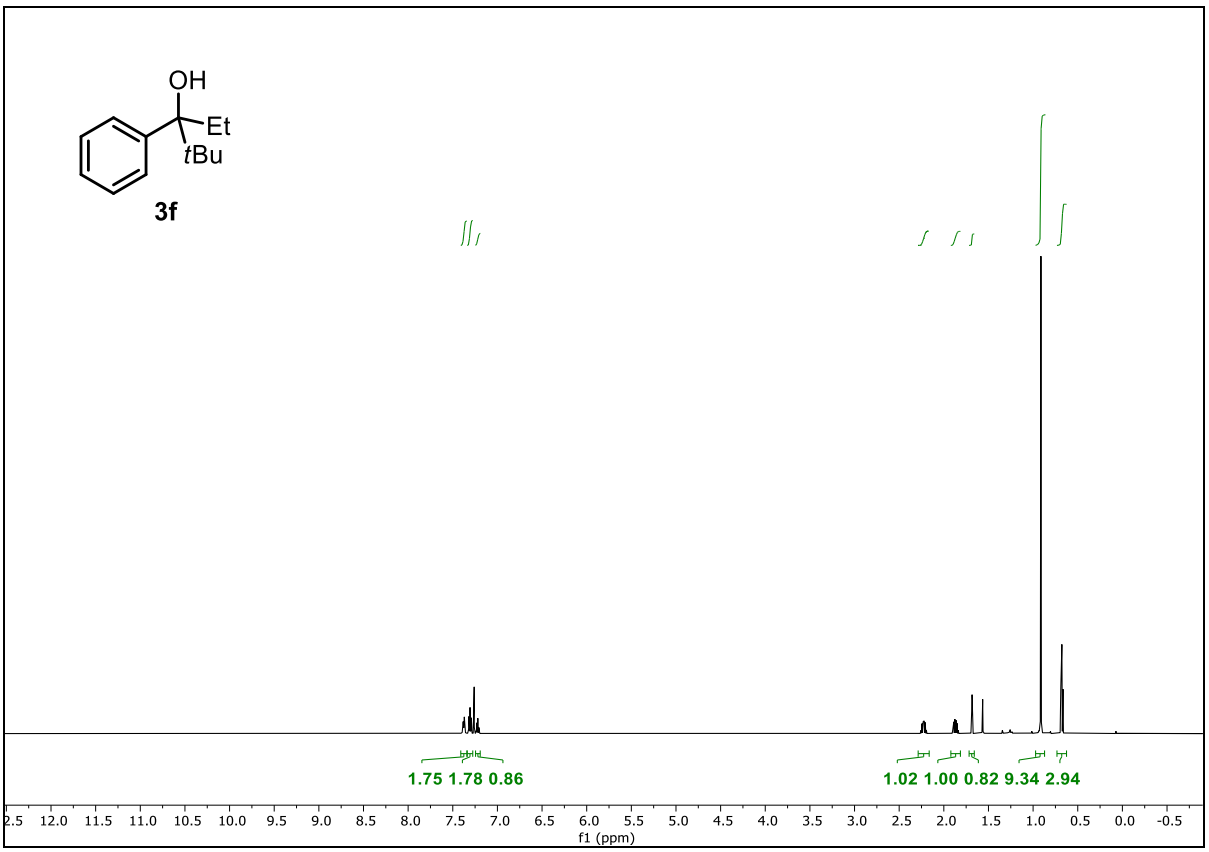


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

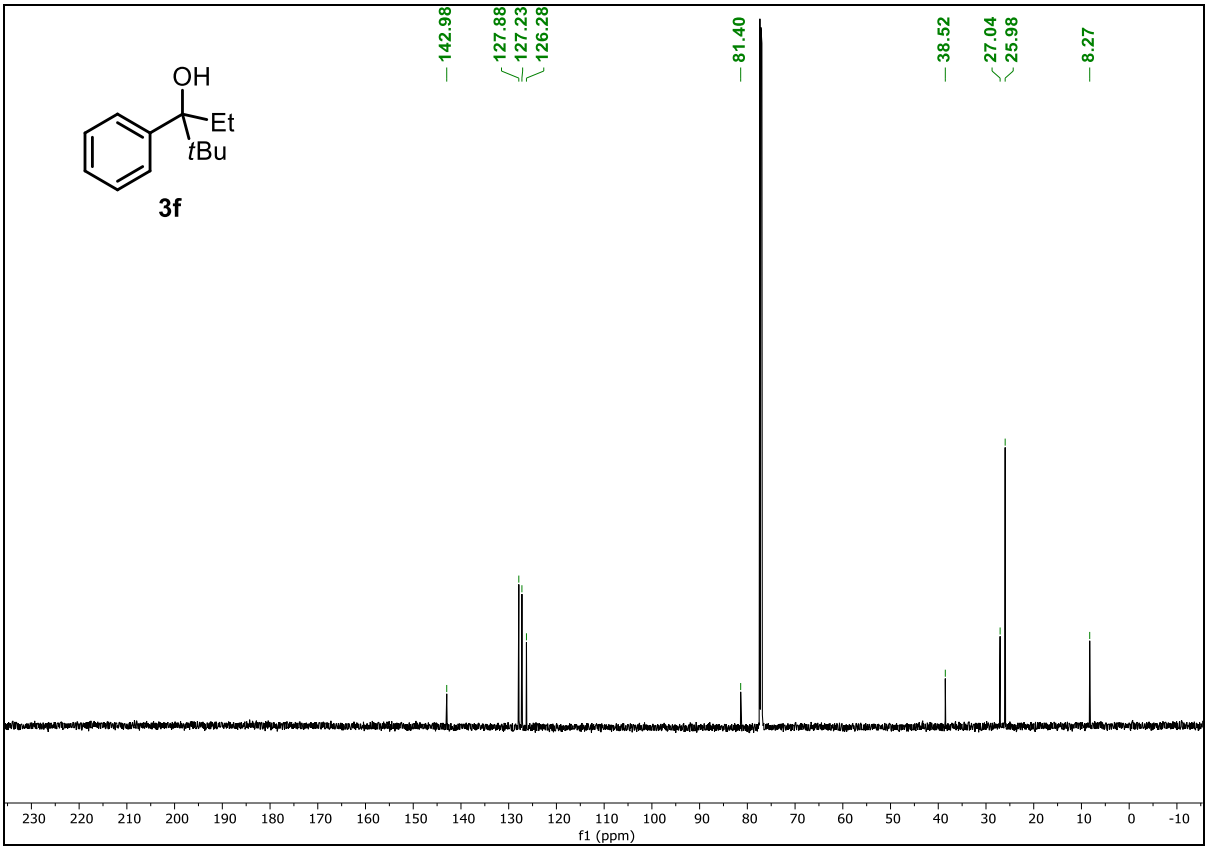


2,2-dimethyl-3-phenylpentan-3-ol (3f)

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

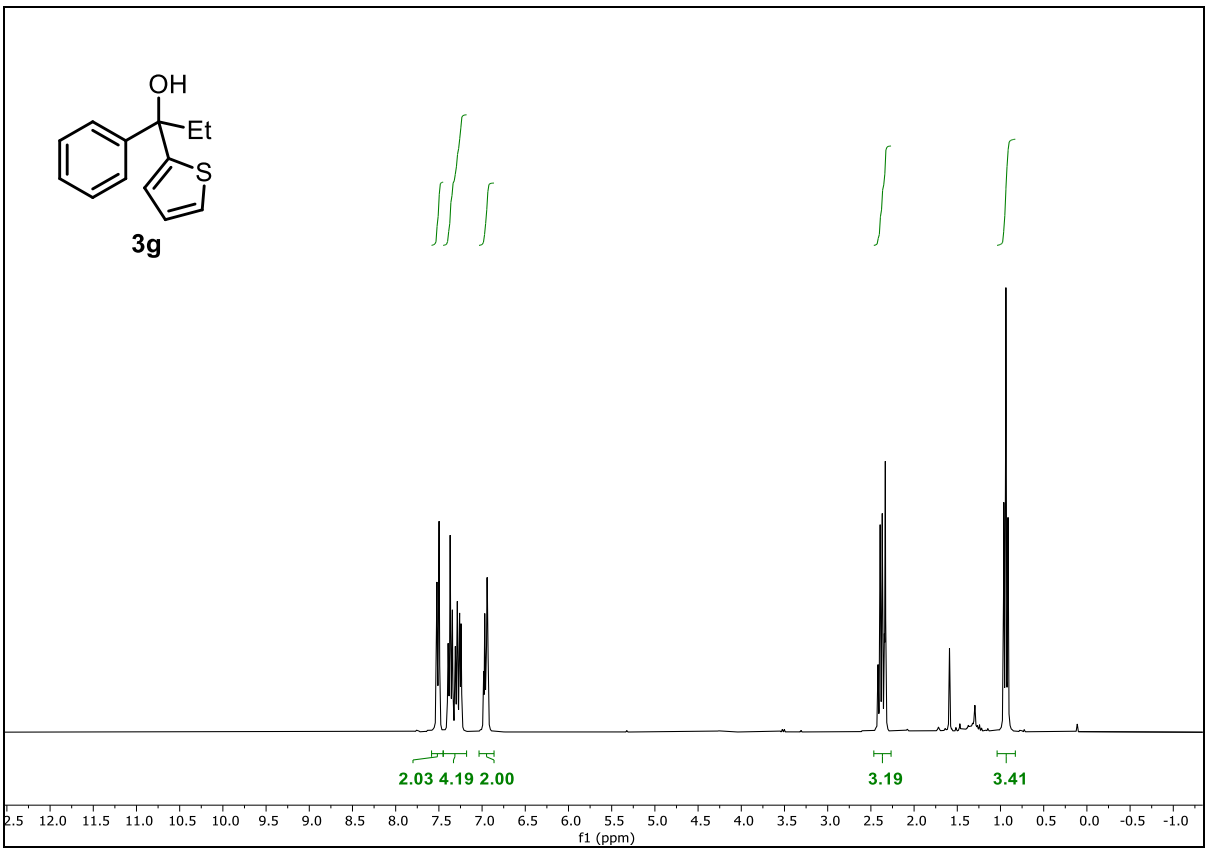


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

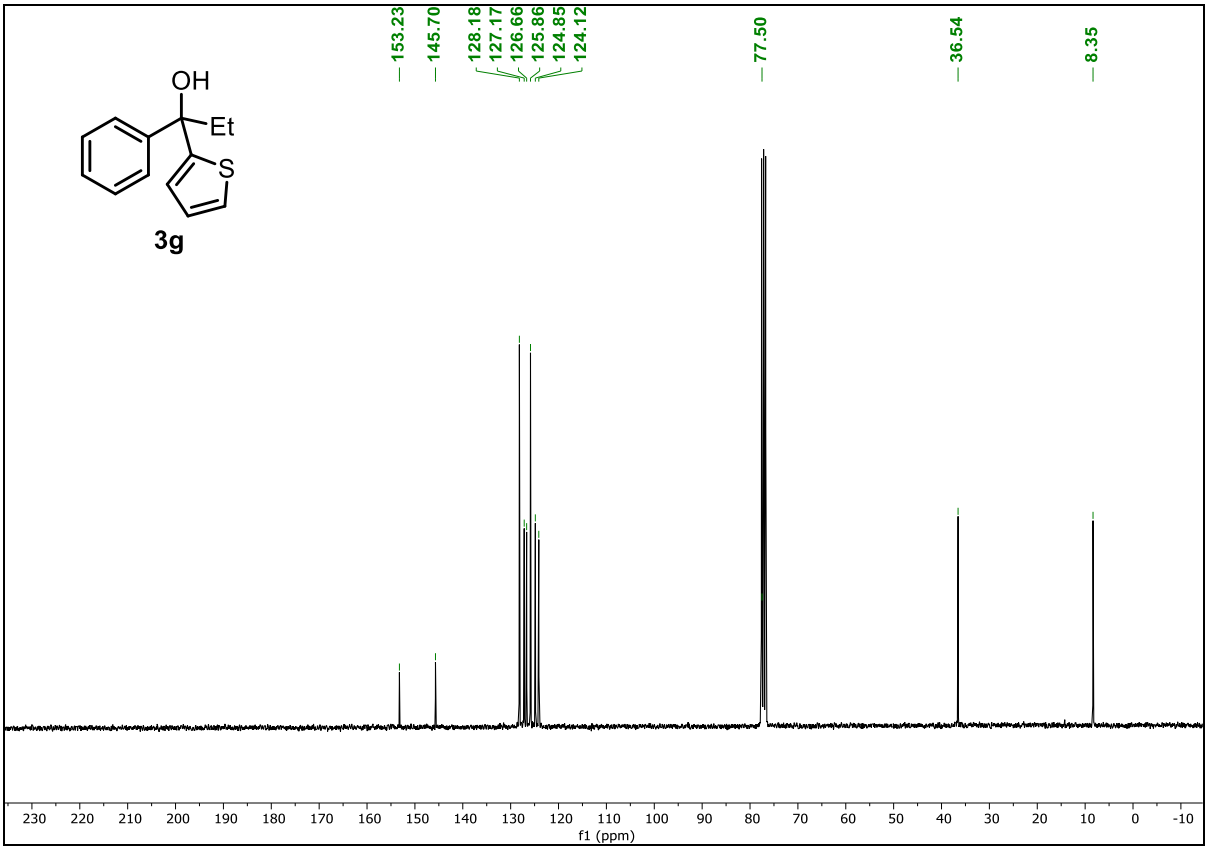


1-phenyl-1-(thiophen-2-yl)propan-1-ol (3g)

^{1}H NMR (300 MHz, $CDCl_3$)

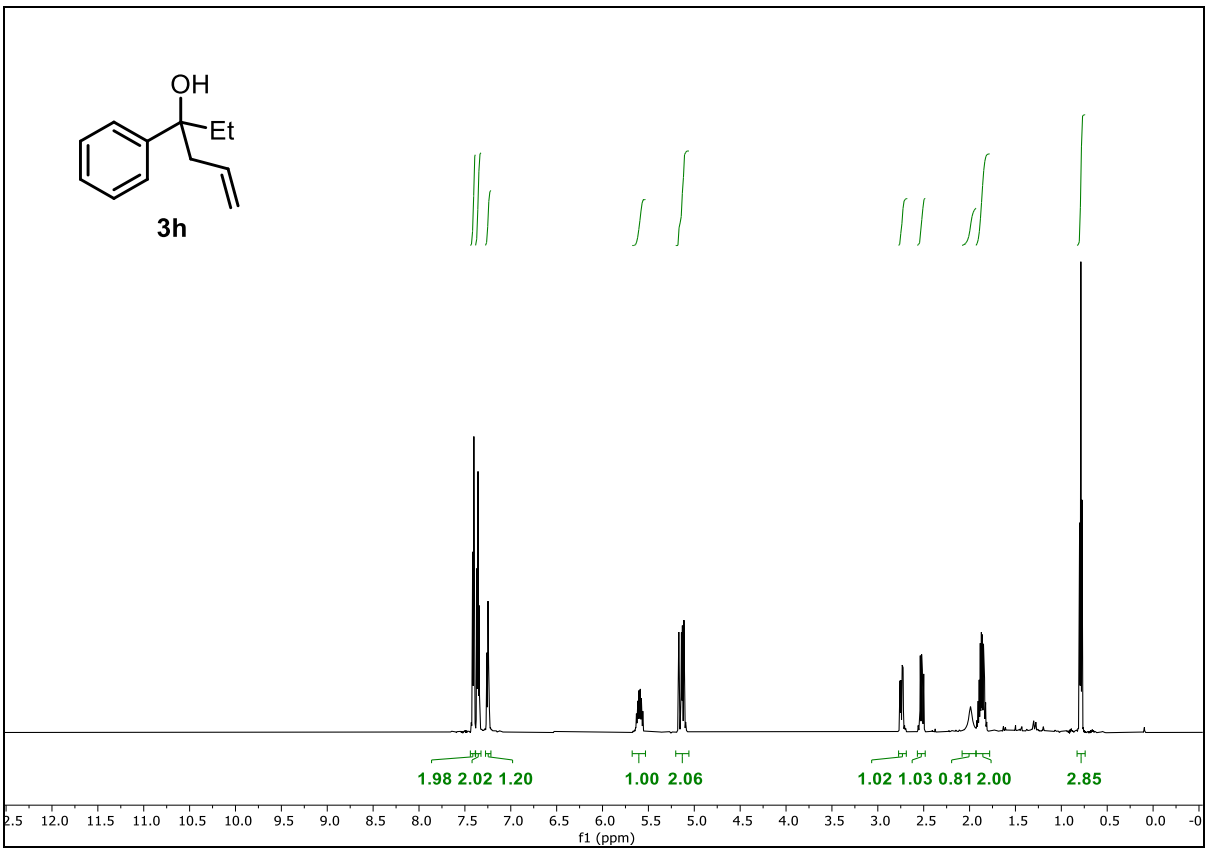


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

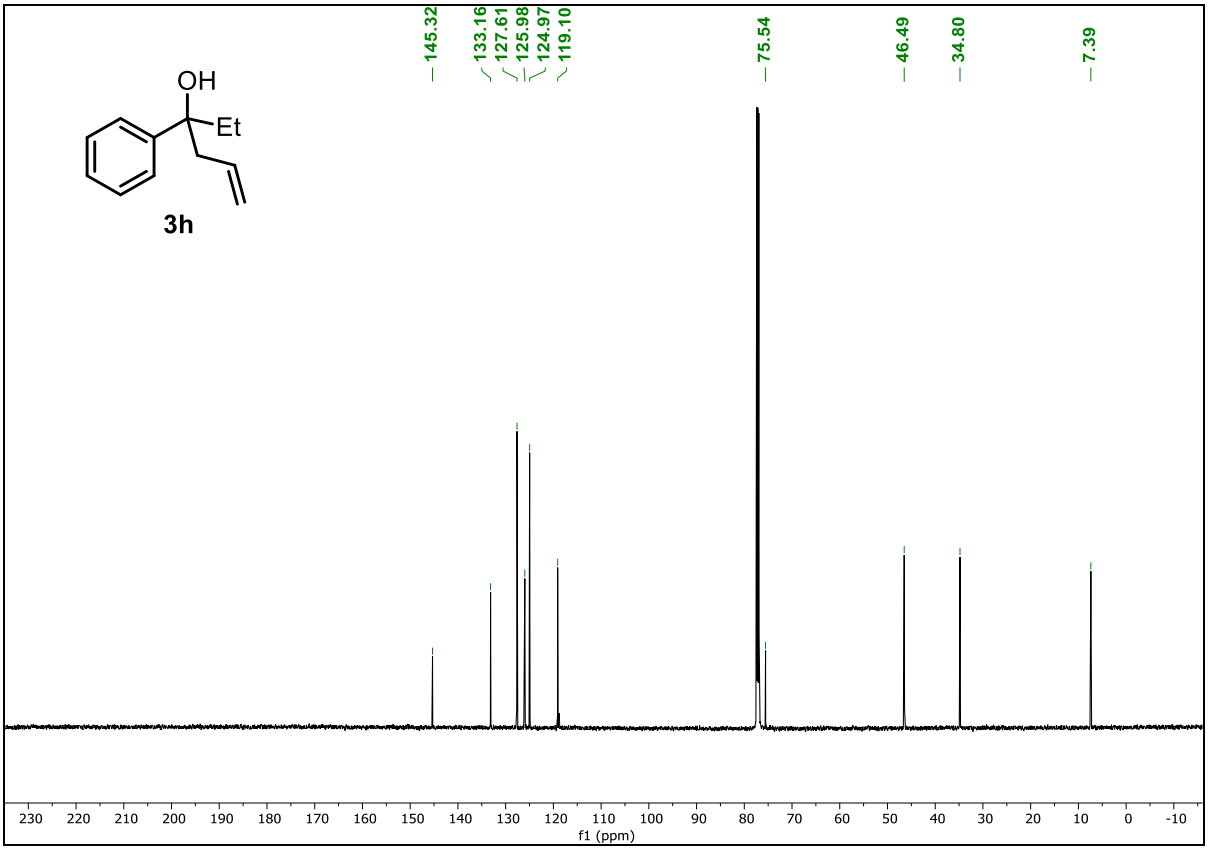


3-phenylhex-5-en-3-ol (3h)

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

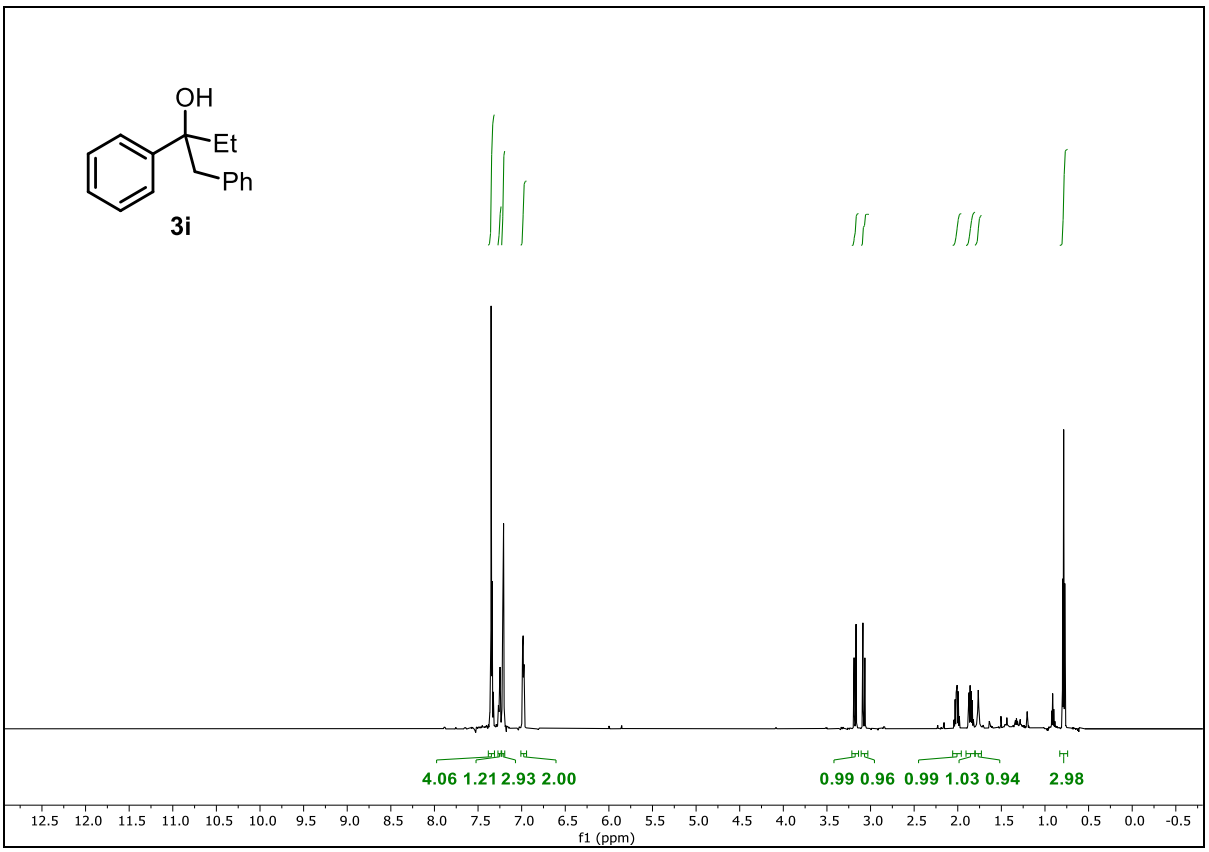


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

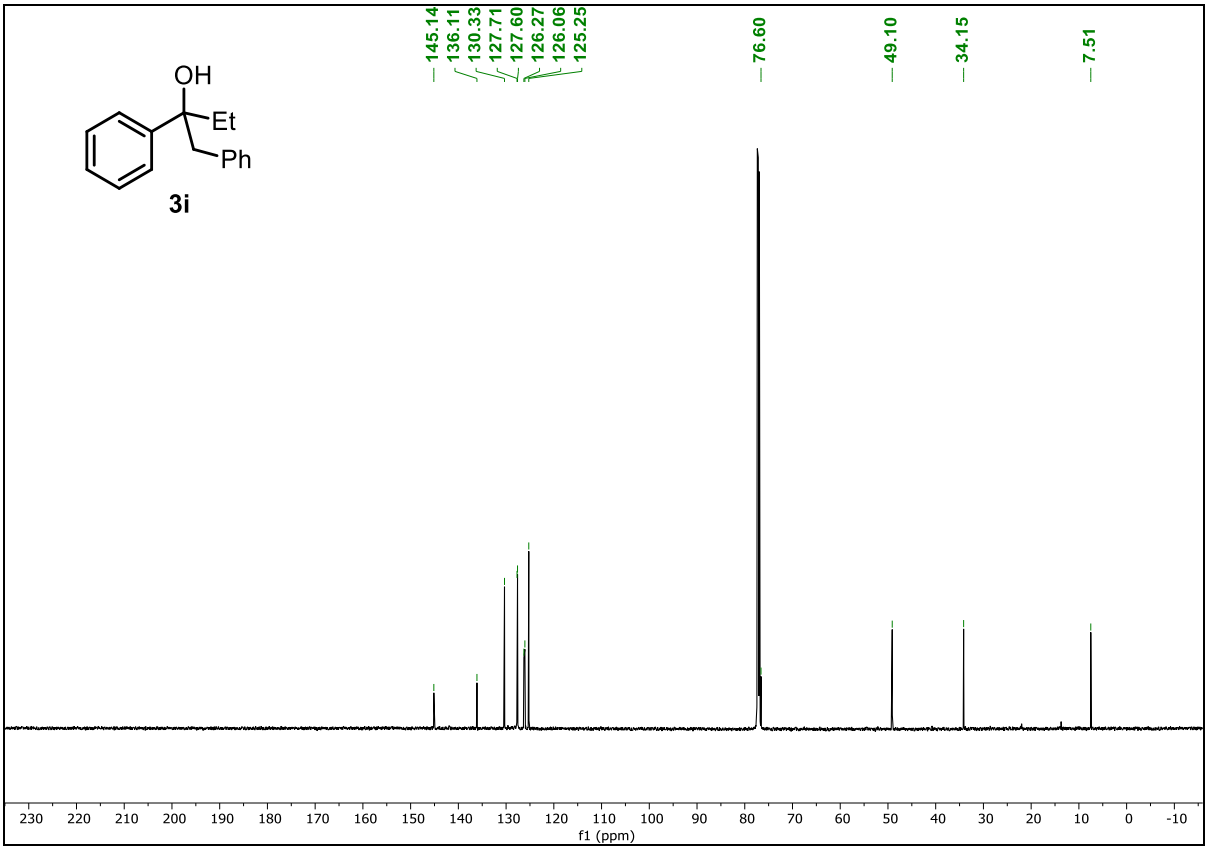


1,2-diphenylbutan-2-ol (3i)

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



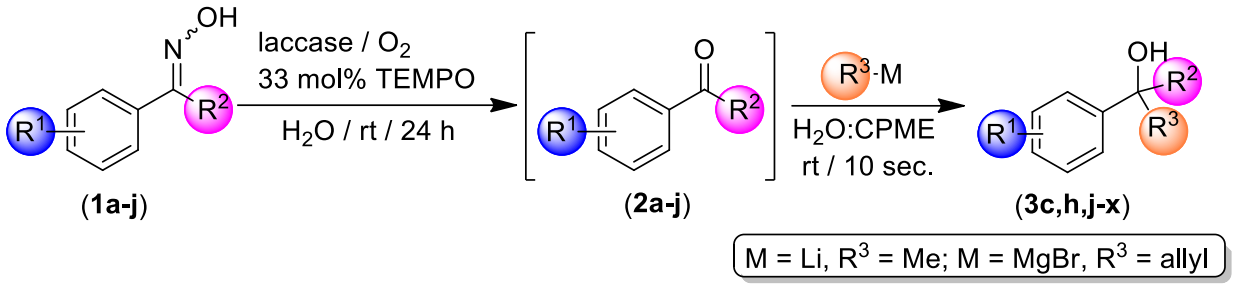
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)



Hybrid one-pot tandem transformation of ketoximes **1a-j** into tertiary alcohols **3c**,**h**,**j-x** promoted by combination of the laccase/TEMPO/O_2 system with the chemoselective addition of MeLi/AllylMgBr in aqueous media, at room temperature and in the presence of air

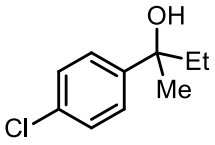
T. versicolor laccase (280 mg, 0.5 U/mg) and TEMPO (38 mg, 33 mol%) were added to a 0.73 mmol (109 mg) suspension of the corresponding ketoxime **1a-j** in water (1 mL) and the mixture was stirred vigorously (1200 rpm) in an 8 mL vial under oxygen atmosphere for 24 h. Then 1 mL of CPME was added as co-solvent to form a biphasic reaction medium. Next, MeLi (3.0 eq, 1.6 M in Et_2O) or AllylMgBr (3.0 eq, 1.0 M in Et_2O) was rapidly spreaded over the reaction mixture at room temperature, under air. After 3 s, a saturated solution of NH_4Cl_{aq} (2.5 mL) was added, and the mixture was extracted with dichloromethane (3 x 5 mL). The combined organic phases were washed with brine (1 x 5 mL), dried over anhydrous Na_2SO_4, and the solvents were removed *in vacuo*. The crude tertiary alcohols **3c**,**h**,**j-x** products obtained were purified by flash column chromatography and characterized by ^1H and $^{13}C\{^1H\}$ NMR.

Table S4. Hybrid one-pot tandem transformation of ketoximes **1a-i** into tertiary alcohols **3c**,**h**,**j-x** promoted by combination of the laccase/TEMPO/O_2 system with the chemoselective addition of MeLi/AllylMgBr in aqueous media, at room temperature and in the presence of air.[a]

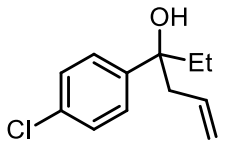


Entry	R^1	R^2	R^3-M	Product	Yield[b] (%)
1	H (**1a**)	Et	MeLi	**3c**	82
2	H (**1a**)	Et	AllylMgBr	**3h**	50
3	*p*-Cl (**1b**)	Et	MeLi	**3j**	83
4	*p*-Cl (**1b**)	Et	AllylMgBr	**3k**	58
5	*p*-OMe (**1c**)	Et	MeLi	**3l**	72
6	*p*-OMe (**1c**)	Et	AllylMgBr	**3m**	52
7	*p*-Me (**1d**)	Et	MeLi	**3n**	54
8	*p*-Me (**1d**)	Et	AllylMgBr	**3o**	36
9	H (**1e**)	Me	MeLi	**3p**	74
10	H (**1e**)	Me	AllylMgBr	**3q**	43
11	*p*-Cl (**1f**)	Me	MeLi	**3r**	78
12	*m*-Cl (**1g**)	Me	MeLi	**3s**	29
13	*o*-Cl (**1h**)	Me	MeLi	**3t**	11
14	*p*-Cl (**1f**)	Me	AllylMgBr	**3u**	16
13	*m*-OMe (**1i**)	Me	MeLi	**3v**	40
14	*m*-OMe (**1i**)	Me	AllylMgBr	**3w**	28
15	*p*-OMe (**1i**)	Me	MeLi	**3x**	88

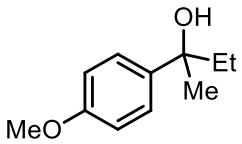
[a] General conditions: 24 h of reaction at room temperature and at 1800 rpm; Laccase from *T. Versicolor* (0.5 U/mg, 280 mg) per 0.73 mmol of **1a-i**, 0.33 eq. TEMPO in 1 mL of water were used. Then 1 mL of CPME and MeLi (3.0 eq, 1.6 M in Et_2O) or AllylMgBr (3.0 eq, 1.0 M in Et_2O) reagents were added without any isolation/purification. [b] Isolated yield.



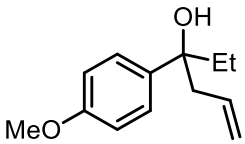
2-(4-chlorophenyl)butan-2-ol (3j): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3j** as a colorless oil (83%, R_f = 0.21 hexane/Et_2O 9/1 v/v). ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.6 Hz, 2H) superimposed to 7.30 (d, *J* = 8.6 Hz, 2H), 1.90-1.75 (m, 2H) superimposed to 1.72 (br s, 1H), 1.54 (s, 3H), 0.80 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 146.2, 132.2, 128.1, 126.4, 74.6, 36.6, 29.7, 8.2.[13]



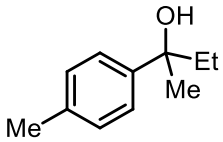
3-(4-chlorophenyl)hex-5-en-3-ol (3k): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3k** as a colorless oil (58%, R_f = 0.20 hexane/Et_2O 9/1 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.7 Hz, 2H) superimposed to 7.37 (d, *J* = 8.7 Hz, 2H), 5.70-5.56 (m, 1H), 5.25-5.14 (m, 2H), 2.75 (dd, *J* = 13.8, 5.9 Hz, 1H), 2.55 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.00-1.81 (m, 3H), 0.83 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 143.2, 132.0, 131.1, 127.0, 125.9, 118.8, 74.6, 45.8, 34.1, 6.6.[14]



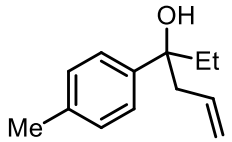
2-(4-methoxyphenyl)butan-2-ol (3l): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3l** as a colorless oil (72%, R_f = 0.19 hexane/Et_2O 9/1 v/v). ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 1.82 (qd, *J* = 7.3, 2.4 Hz, 2H), 1.70 (br s, 1H), 1.53 (s, 3H), 0.79 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 158.3, 140.0, 126.2, 113.5, 74.7, 55.3, 36.8, 29.7, 8.5.[15]



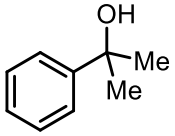
3-(4-methoxyphenyl)hex-5-en-3-ol (3m): flash column chromatography (hexane/EtOAc 95/5 v/v) gave product **3m** as a colorless oil (35%, Rf = 0.11 hexane/EtOAc 95/5 v/v). ^1H NMR (300 MHz, CDCl3): δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.68-5.54 (m, 1H), 5.19-5.08 (m, 2H), 3.83 (s, 3H), 2.72 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.49 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.90-1.77 (m, 2H), 1.61 (br s, 1H), 0.78 (t, *J* = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl3): δ 158.1, 137.9, 133.8, 126.6, 119.4, 113.3, 75.8, 55.2, 46.9, 35.3, 7.9.[16]



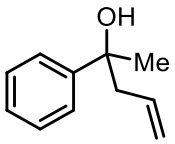
2-(*p*-tolyl)butan-2-ol (3n): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3n** as a colorless oil (54%, R_f = 0.18 hexane/Et_2O 9/1 v/v). ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H), 1.83 (qd, *J* = 7.2, 3.2 Hz, 2H), 1.69 (br s, 1H), 1.54 (s, 3H), 0.80 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.0, 136.2, 128.9, 125.0, 74.9, 36.8, 29.8, 21.1, 8.5.[14]



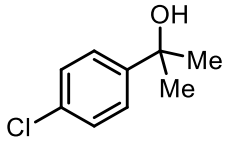
3-(*p*-tolyl)hex-5-en-3-ol (3o): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3o** as a colorless oil (36%, R_f = 0.24 hexane/Et_2O 9/1 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.29-7.24 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.66-5.51 (m, 1H), 5.17-5.04 (m, 2H), 2.74-2.64 (m, 1H), 2.53-2.44 (m, 1H), 2.34 (s, 3H), 1.97 (br s, 1H), 1.89-1.76 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 142.9, 136.0, 133.9, 128.9, 125.5, 119.5, 76.0, 47.0, 35.4, 21.1, 8.0.[17]



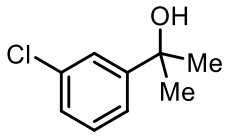
2-phenylpropan-2-ol (3p): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3p** as a colorless oil (74%, R_f = 0.21 hexane/Et_2O 9/1 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.51-7.48 (m, 2H), 7.37-7.32 (m, 2H), 7.27-7.23 (m, 1H), 1.79 (br s, 1H), 1.60 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 149.2, 128.4, 126.8, 124.5, 72.7, 31.9.[18]



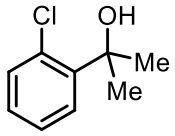
2-phenylpent-4-en-2-ol (3q): flash column chromatography (hexane/Et_2O 9/1 v/v) gave product **3q** as a colorless oil (43%, R_f = 0.25 hexane/Et_2O 9/1 v/v). ^1H NMR (600 MHz, $CDCl_3$): δ 7.47-7.42 (m, 2H), 7.37-7.32 (m, 2H), 7.27-7.22 (m, 1H), 5.63 (dddd, *J* = 16.9, 10.3, 8.3, 6.4 Hz, 1H), 5.17-5.08 (m, 2H), 2.69 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.51 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.06 (br s, 1H), 1.56 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 147.7, 133.8, 128.3, 126.7, 124.9, 119.6, 73.7, 48.6, 30.0.[19]



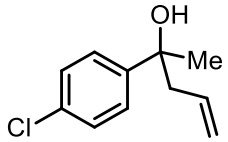
2-(4-chlorophenyl)propan-2-ol (3r): flash column chromatography (hexane/EtOAc 9/1 v/v) gave product **3r** as a colorless oil (78%, R_f = 0.25 hexane/EtOAc 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 1.56 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 147.7, 132.5, 128.3, 125.9, 72.2, 31.8.[15]



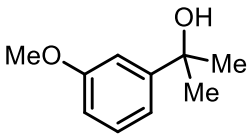
2-(3-chlorophenyl)propan-2-ol (3s): flash column chromatography (hexane/EtOAc 9/1 v/v) gave product **3s** as a colorless oil (29%, R_f = 0.25 hexane/EtOAc 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (t, *J* = 1.6 Hz, 20 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 1.57 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 151.4, 134.9, 129.4, 126.7, 124.9, 122.7, 72.2, 31.6.[15]



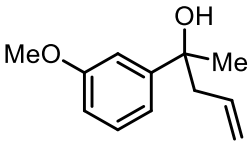
2-(2-chlorophenyl)propan-2-ol (3t): flash column chromatography (hexane/EtOAc 9/1 v/v) gave product **3t** as a colorless oil (11%, R_f = 0.25 hexane/EtOAc 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 2.68 (brs, 1H), 1.76 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 144.8, 131.3, 131.2, 128.1, 126.8, 72.9, 29.3.[15]



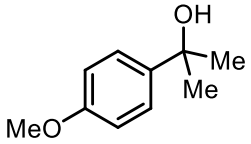
2-(4-chlorophenyl)pent-4-en-2-ol (3u): flash column chromatography (hexane/EtOAc 8/2 v/v) gave product **3u** as a pale yellow oil (16%, R_f = 0.26 hexane/EtOAc 8/2 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40–7.34 (m, 2H), 7.32–7.27 (m, 2H), 5.62–5.58 (m, 1H), 5.18–5.08 (m, 2H), 2.63 (dt, *J* = 18.6, 9.3 Hz, 1H), 2.48 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.23–2.08 (m, 1H), 1.52 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 146.2, 133.3, 132.2, 128.3, 126.3, 119.8, 73.5, 48.5, 30.1.[20]



2-(3-methoxyphenyl)propan-2-ol (3v): flash column chromatography (hexane/EtOAc 8/2 v/v) gave product **3v** as a colorless oil (40%, R_f = 0.21 hexane/EtOAc 8/2 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 2H), 6.80 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.82 (s, 3H), 1.58 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 159.6, 150.9, 129.2, 116.8, 111.8, 110.6, 72.4, 55.2, 31.6.[15]



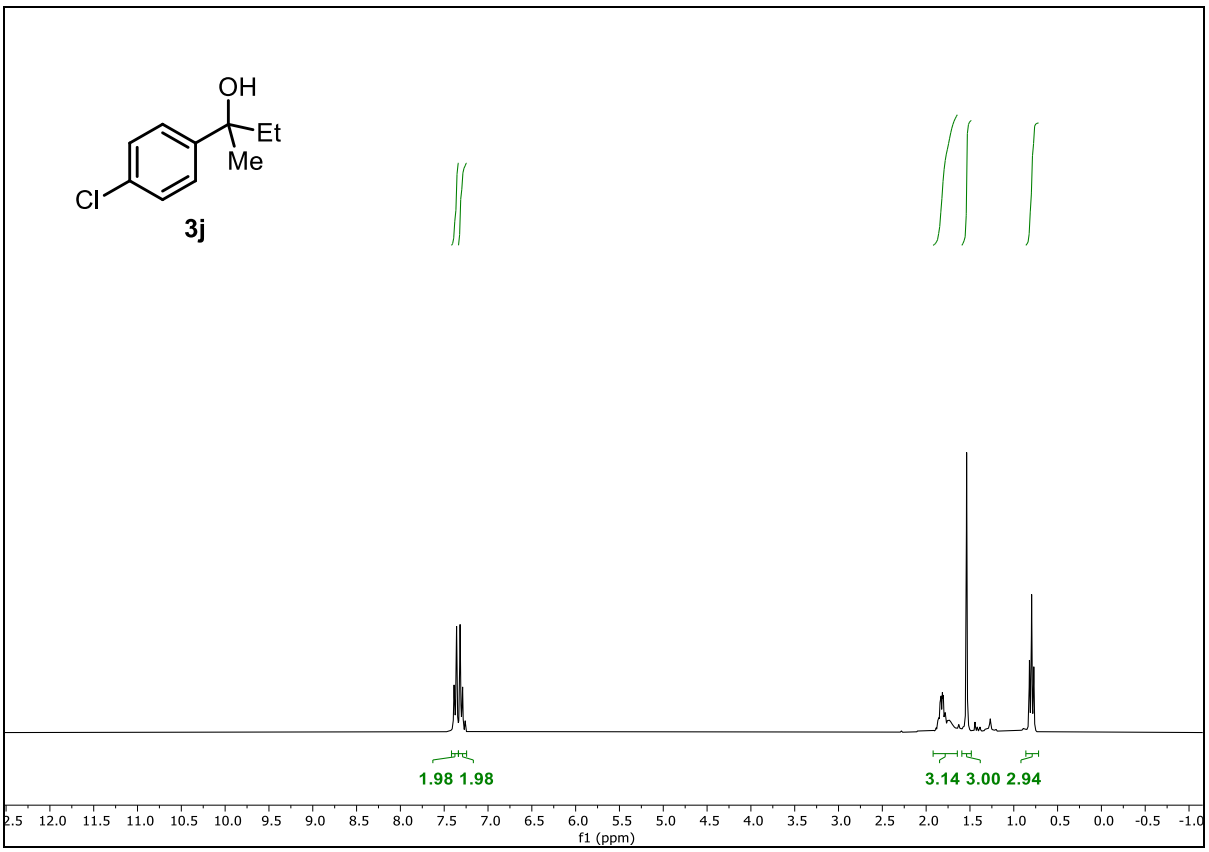
2-(3-methoxy-phenyl)-pent-4-en-2-ol (3w): flash column chromatography (hexane/EtOAc 8/2 v/v) gave product **3w** as a colorless oil (28%, R_f = 0.21 hexane/EtOAc 8/2 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 4.0 Hz, 1H), 5.67–5.57 (m, 1H), 5.16–5.11 (m, 2H), 3.83 (s, 3H), 2.69 (q, *J* = 6.8 Hz, 1H), 2.48 (q, *J* = 6.8 Hz, 1H), 2.05 (s, br, 1H), 1.53 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 159.9, 149.5, 133.6, 129.1, 119.6, 117.2, 111.7, 110.5, 73.5, 55.3, 48.4, 29.9.[20]



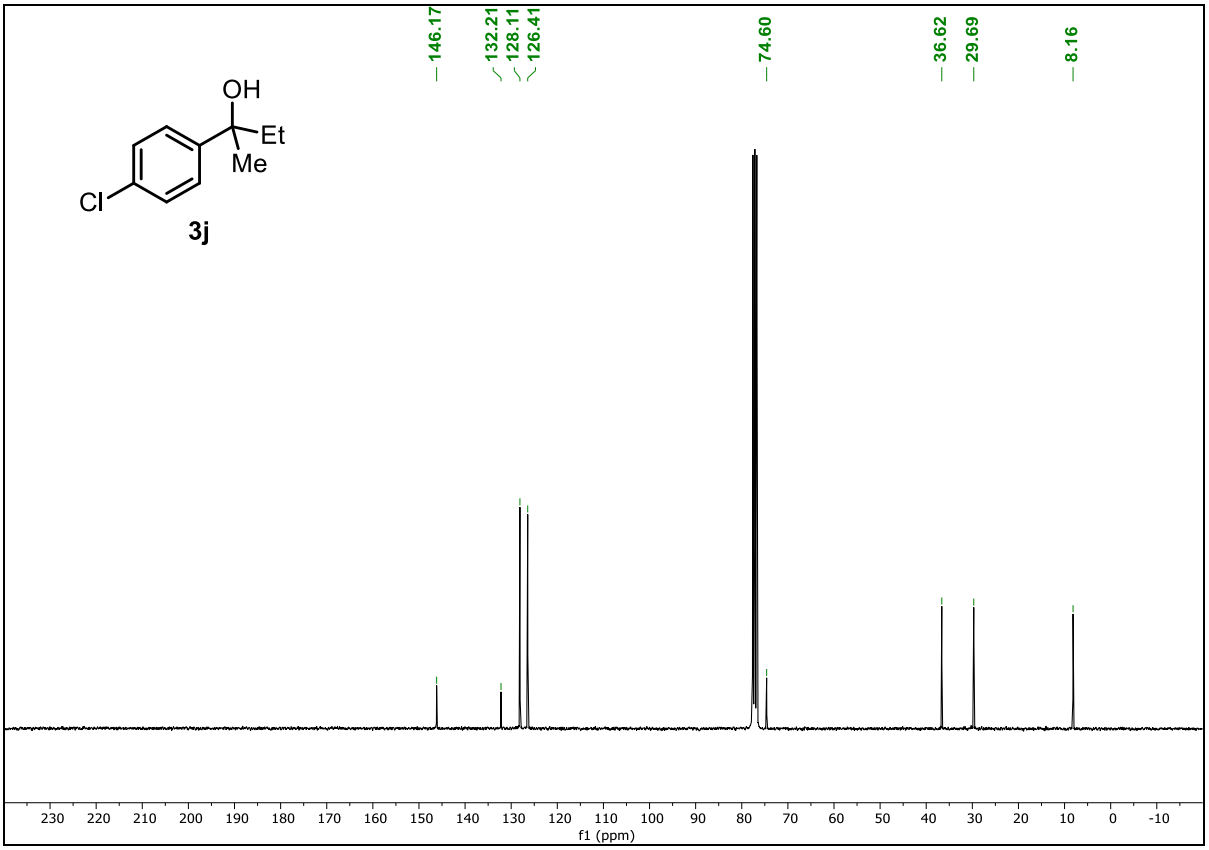
2-(4-Methoxyphenyl)propan-2-ol (3x): colorless oil (88%, R_f = 0.26 hexane/AcOEt 8/2 v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 6.0 Hz, 2H), 6.87 (d, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 1.56 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): 154.4, 137.4, 121.6, 109.5, 68.2, 51.3, 27.9, 27.8.[8]

2-(4-chlorophenyl)butan-2-ol (3j)

^{1}H NMR (300 MHz, $CDCl_3$)

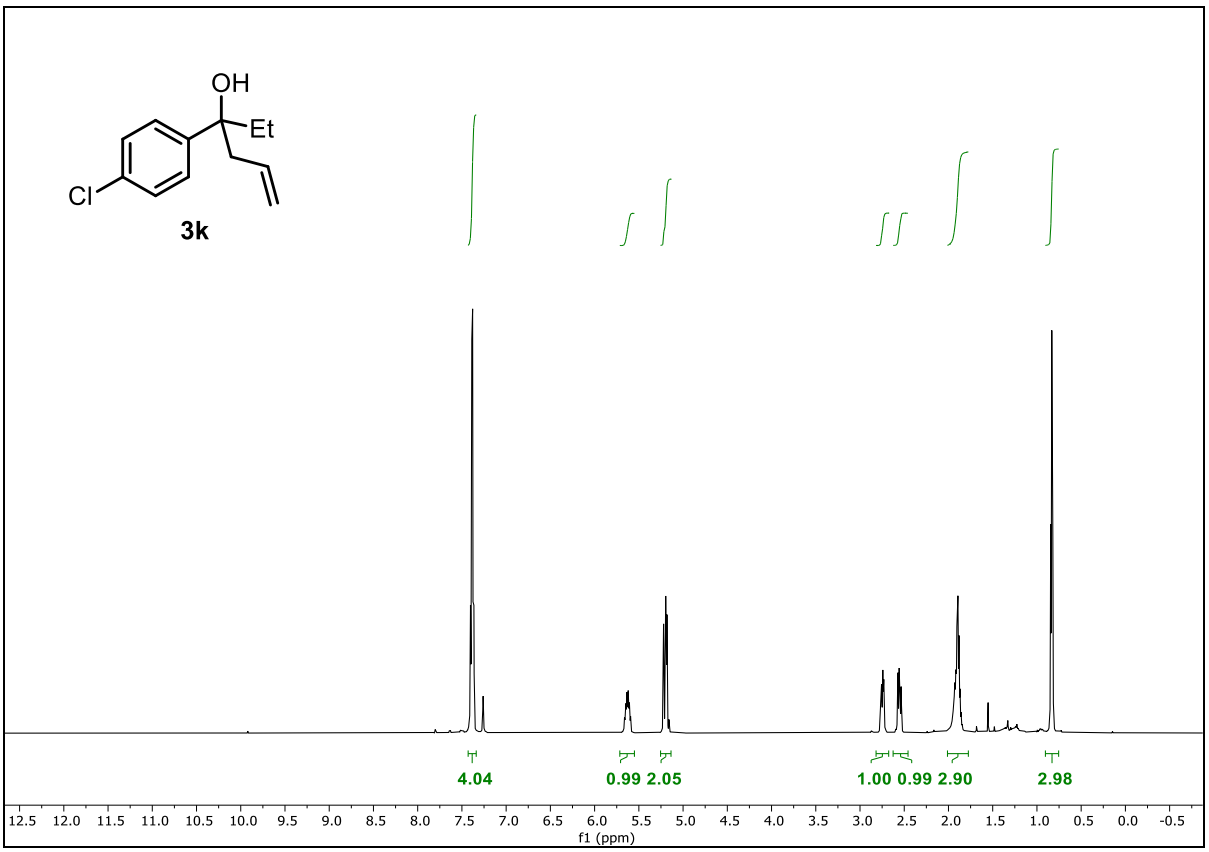


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

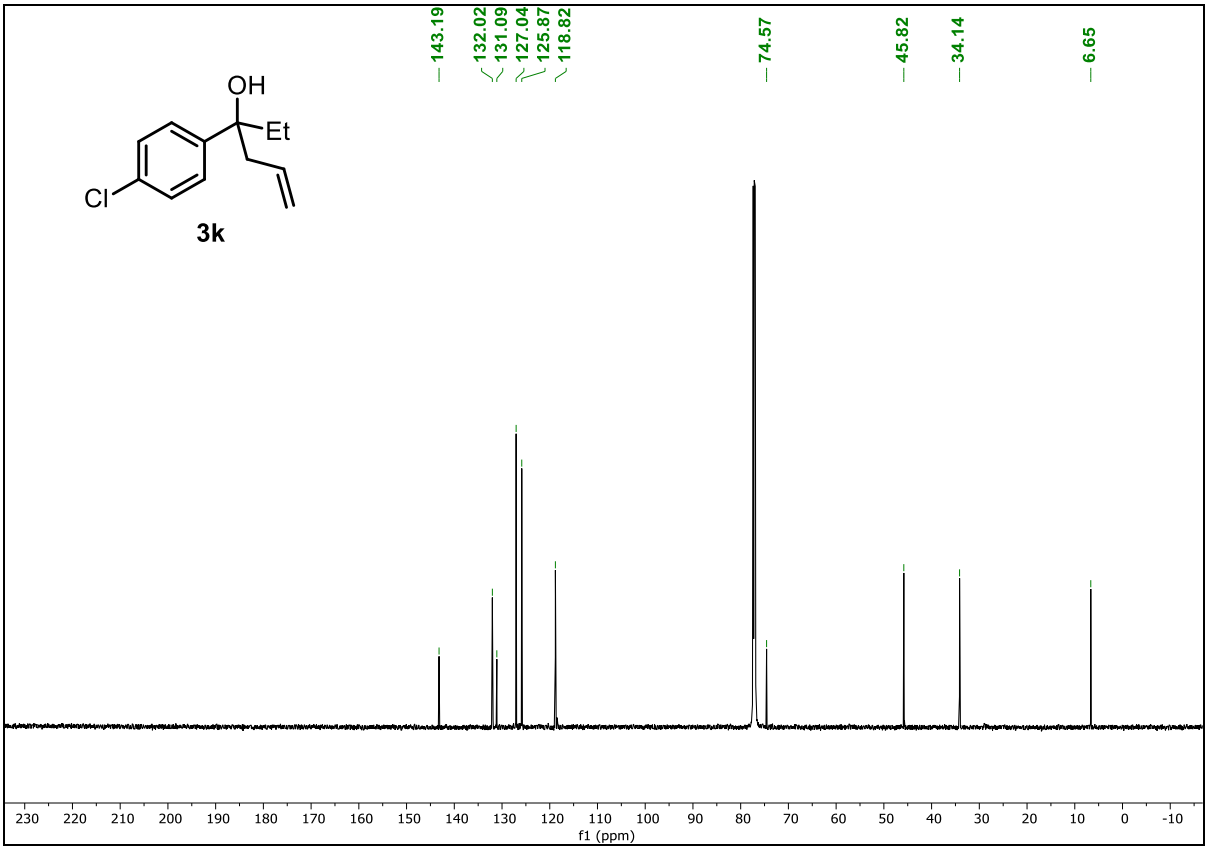


3-(4-chlorophenyl)hex-5-en-3-ol (3k)

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

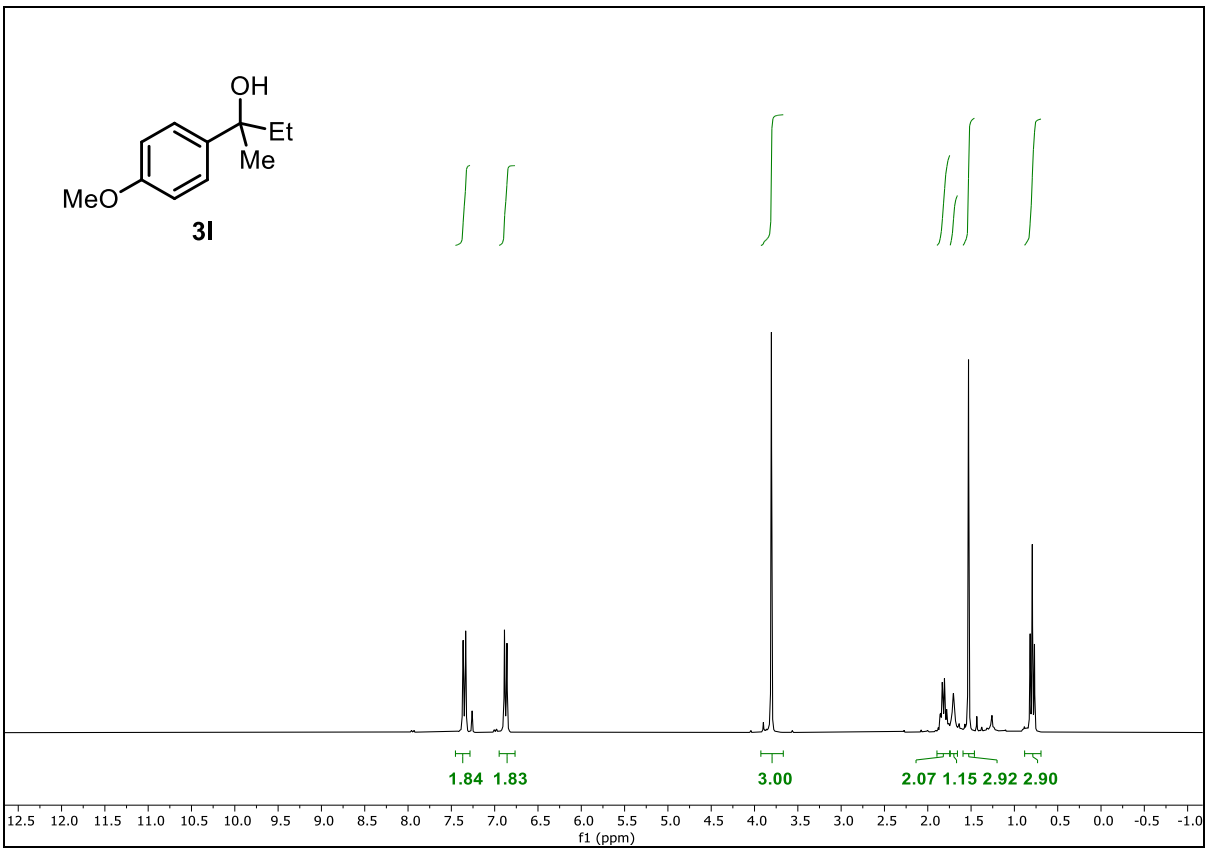


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

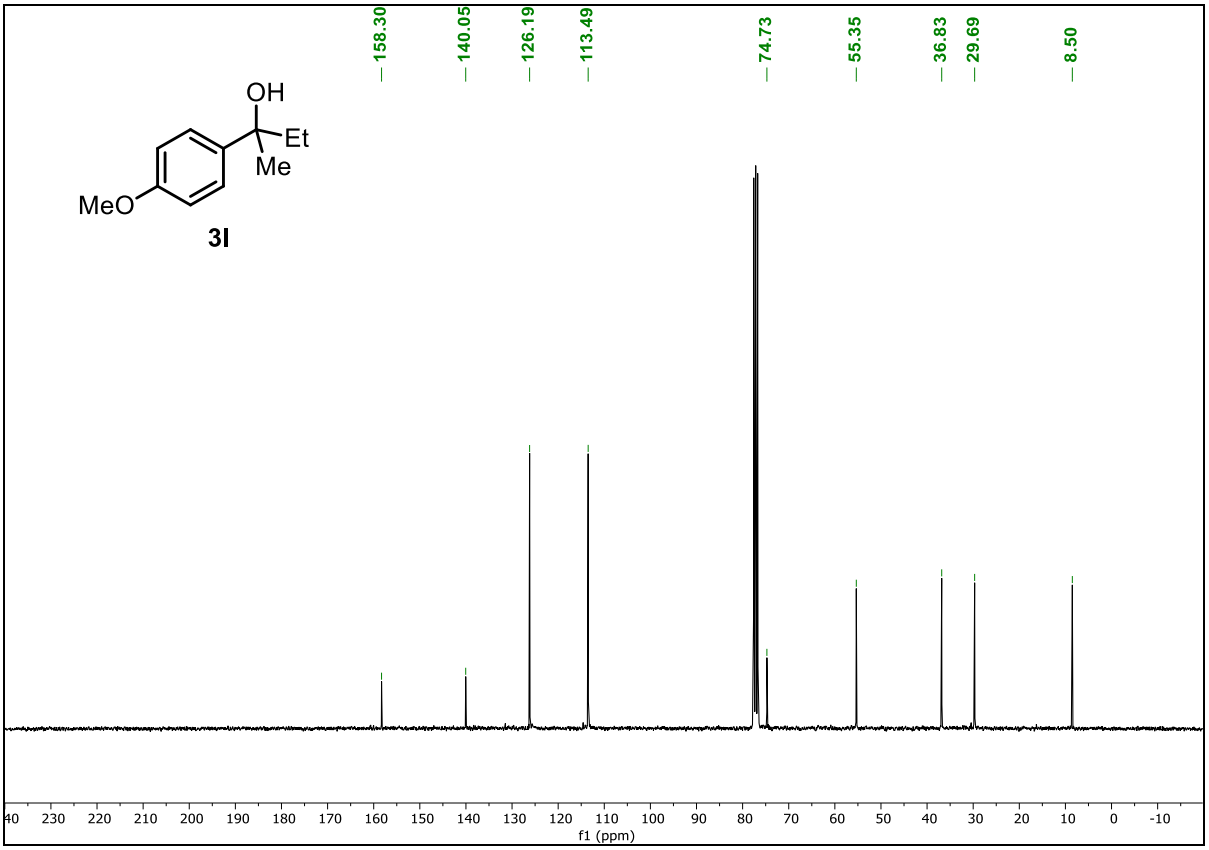


2-(4-methoxyphenyl)butan-2-ol (3l)

^{1}H NMR (300 MHz, $CDCl_3$)

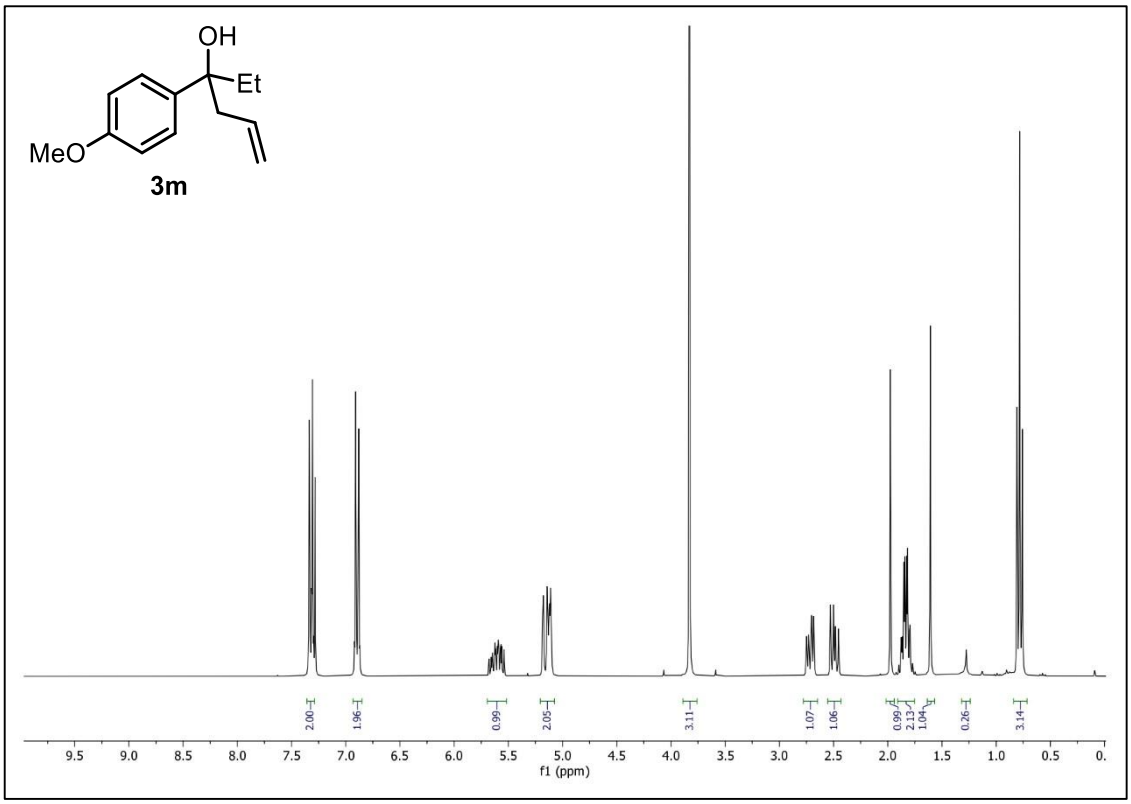


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

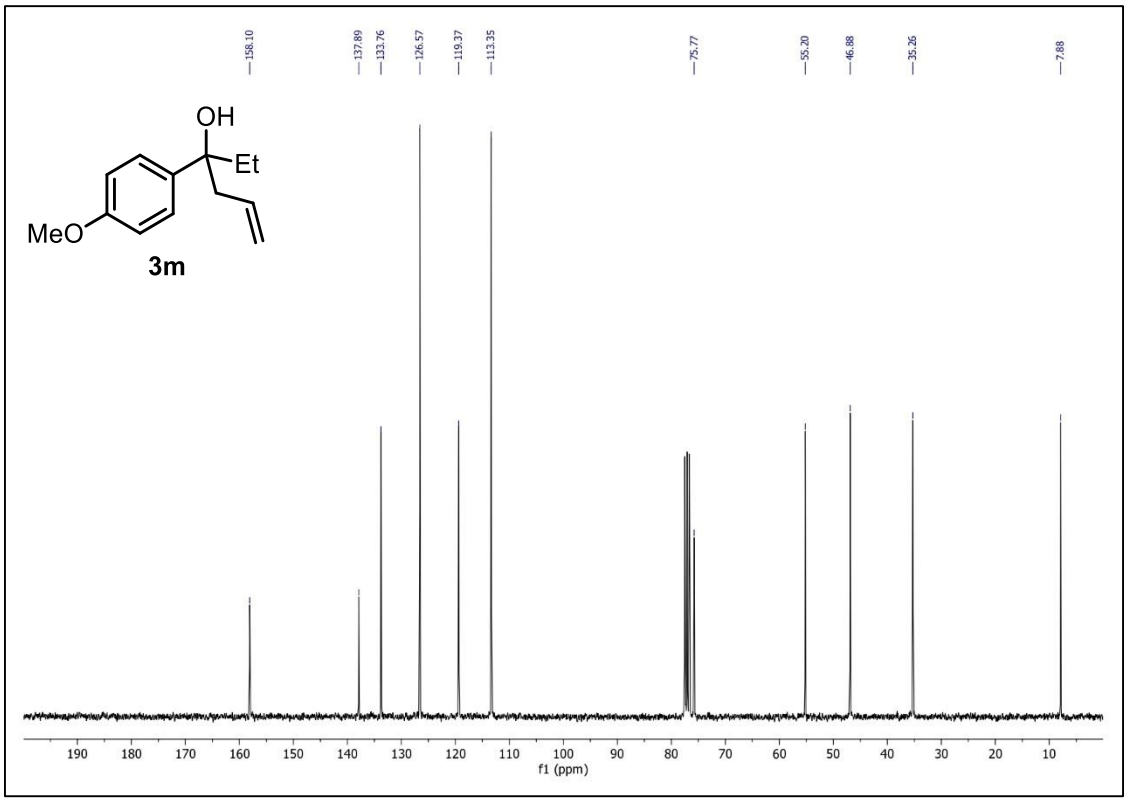


3-(4-methoxyphenyl)hex-5-en-3-ol (3m)

^{1}H NMR (300 MHz, $CDCl_3$)

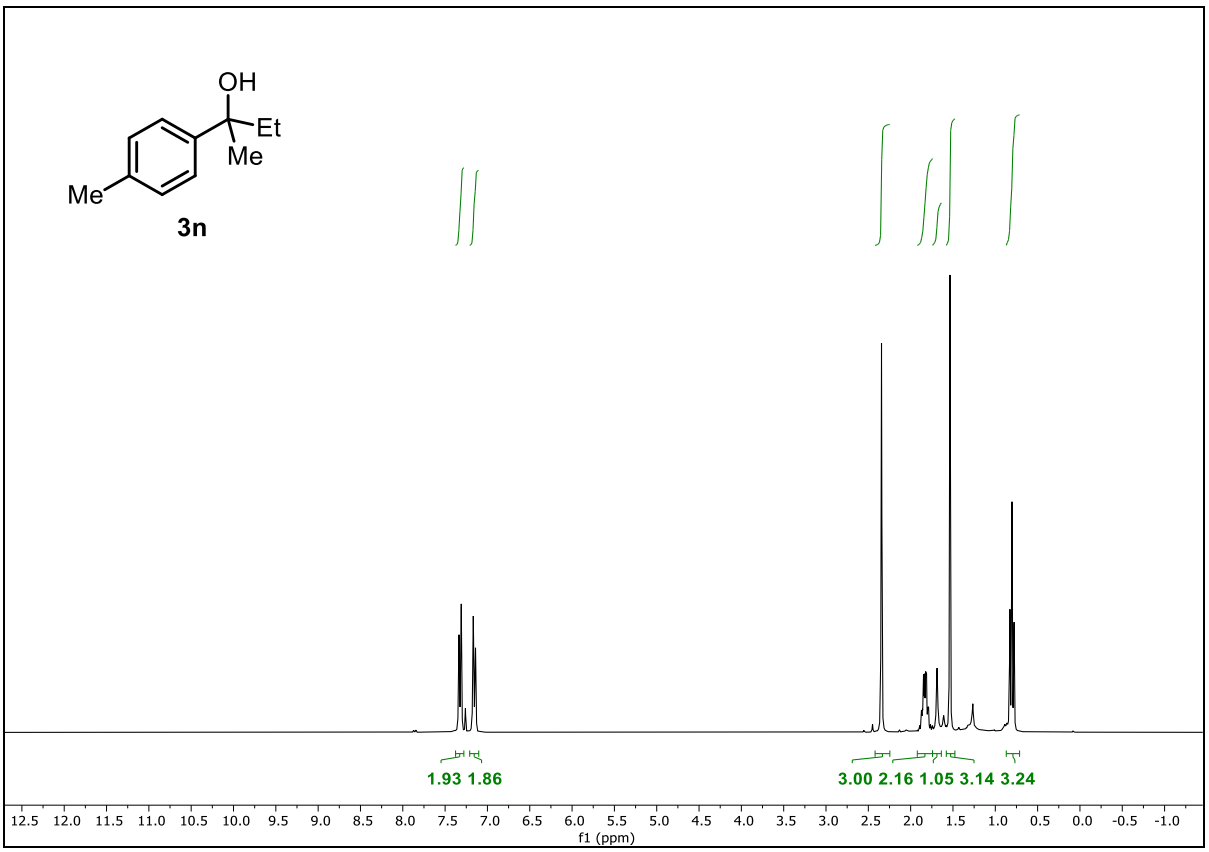


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

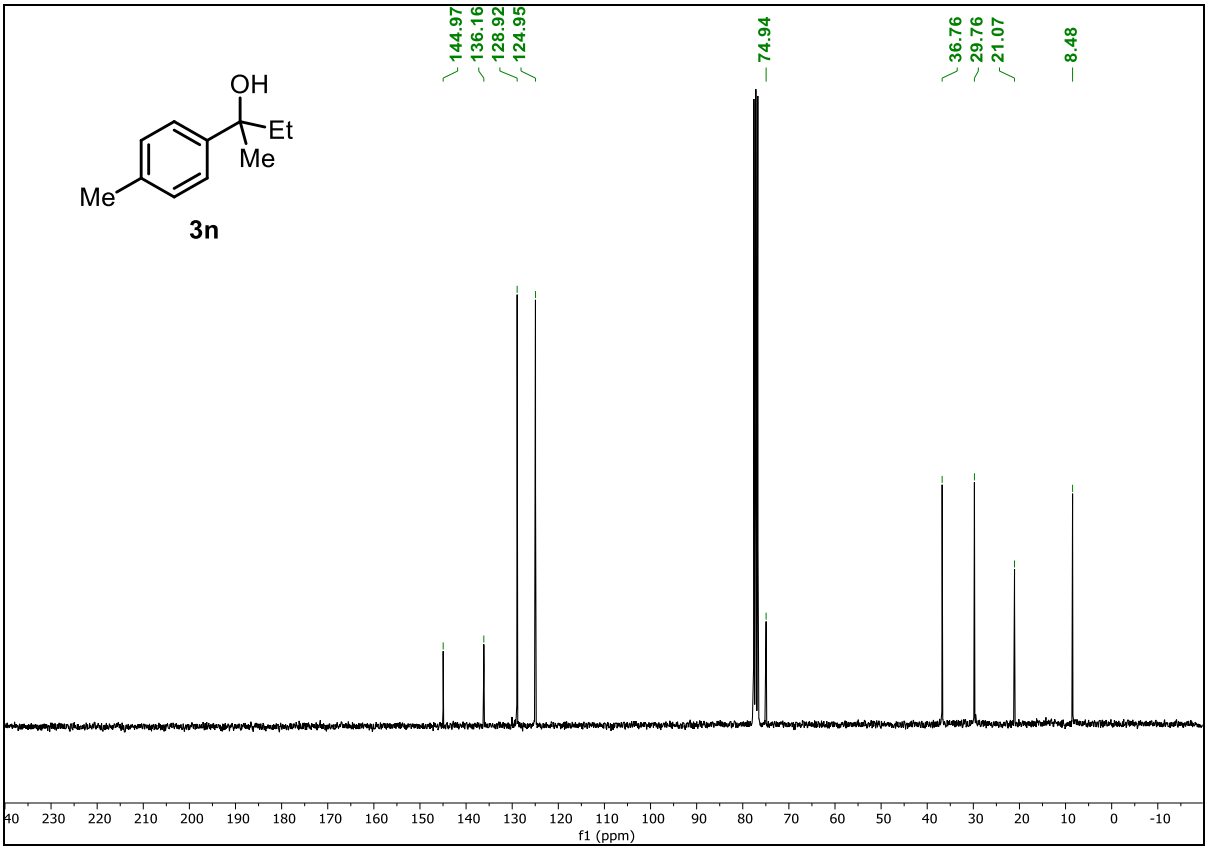


2-(*p*-tolyl)butan-2-ol (3n)

^{1}H NMR (300 MHz, $CDCl_3$)

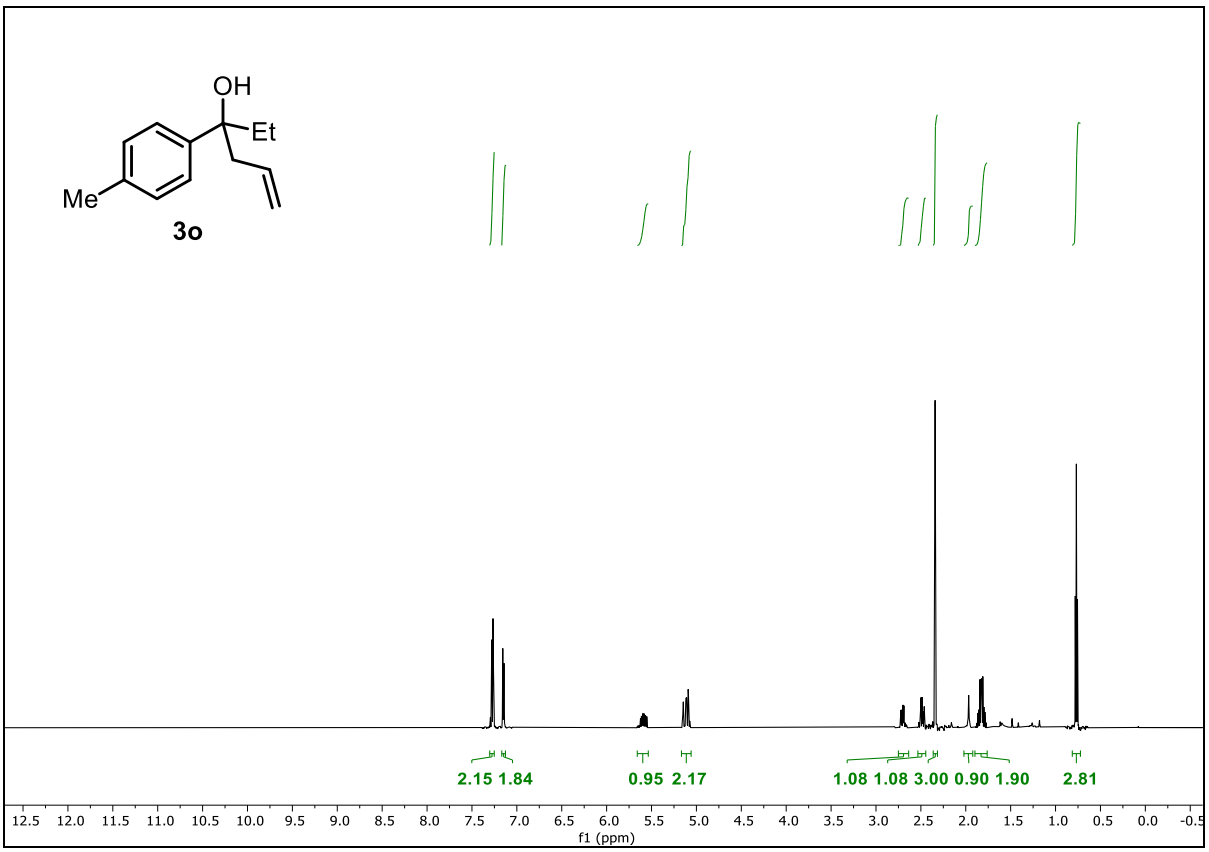


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

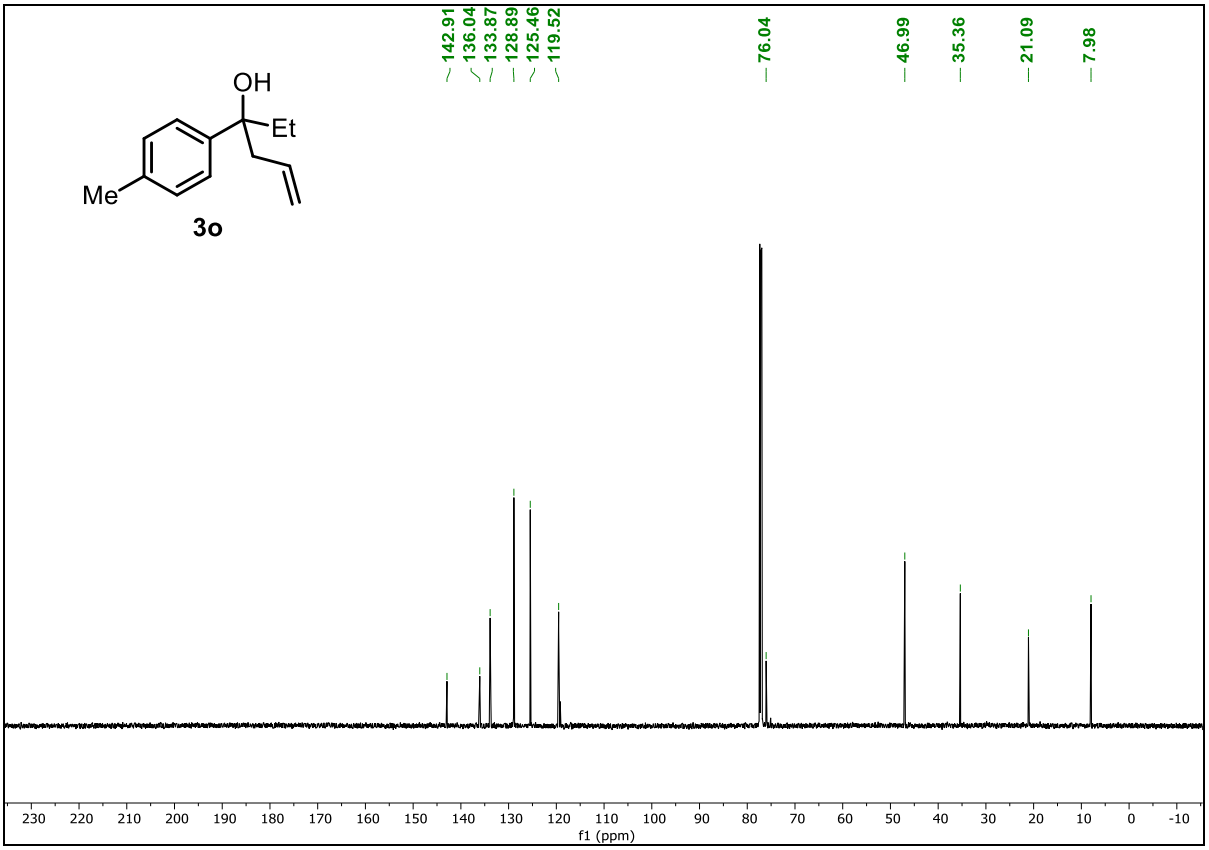


3-(*p*-tolyl)hex-5-en-3-ol (3o)

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

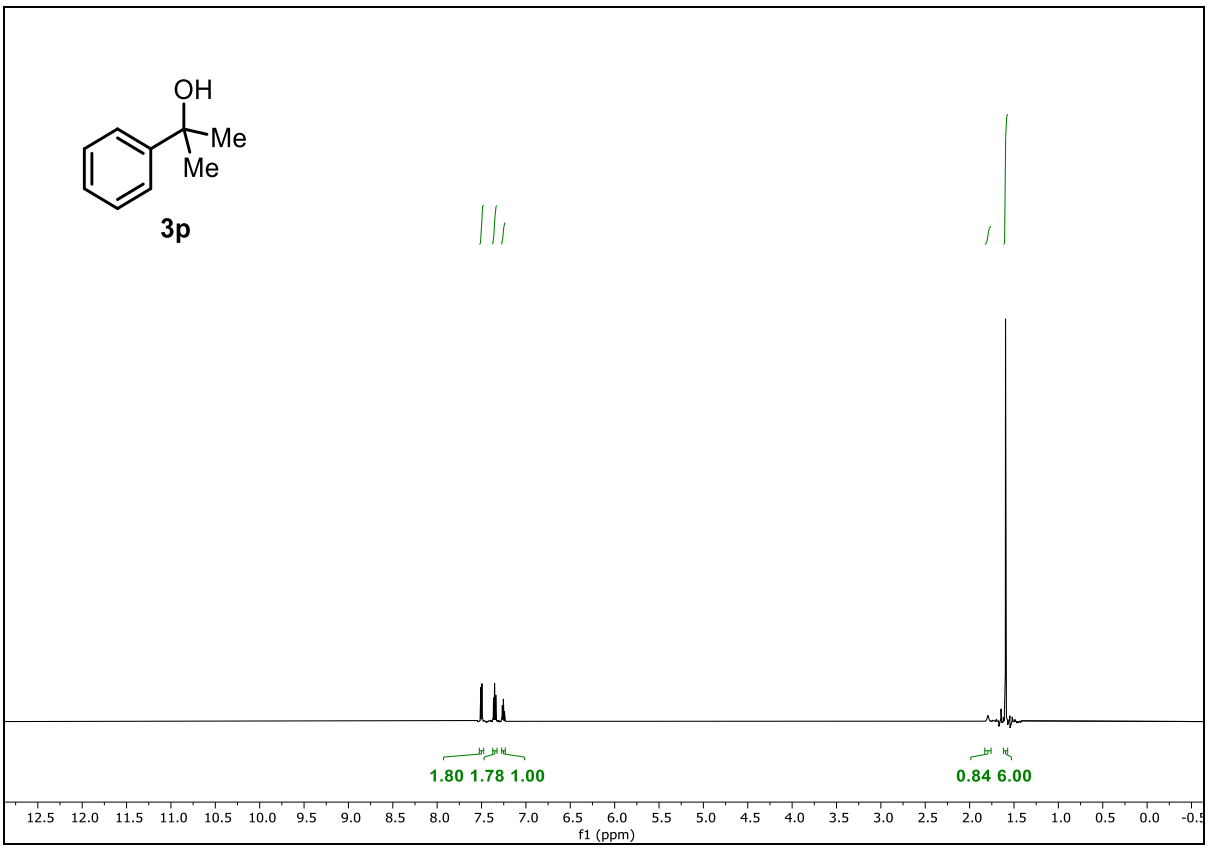


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

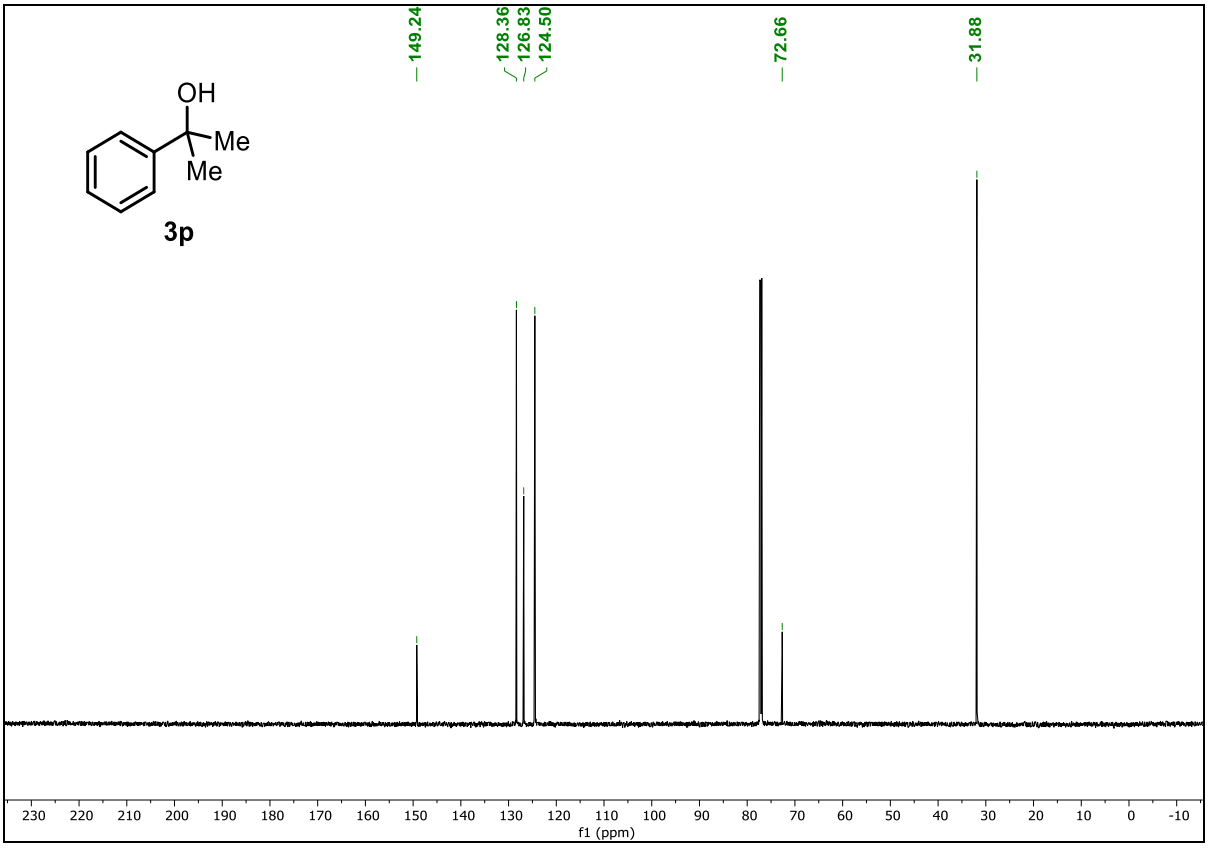


2-phenylpropan-2-ol (3p)

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

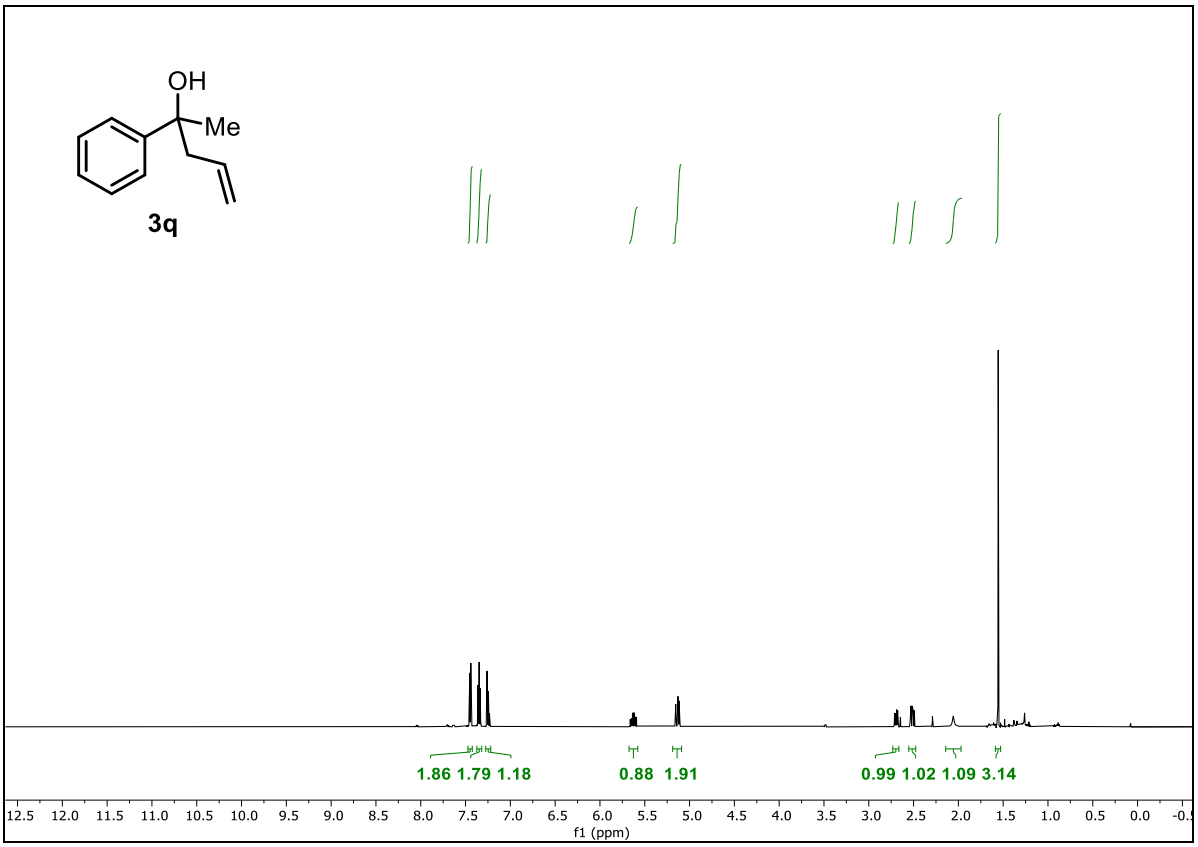


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

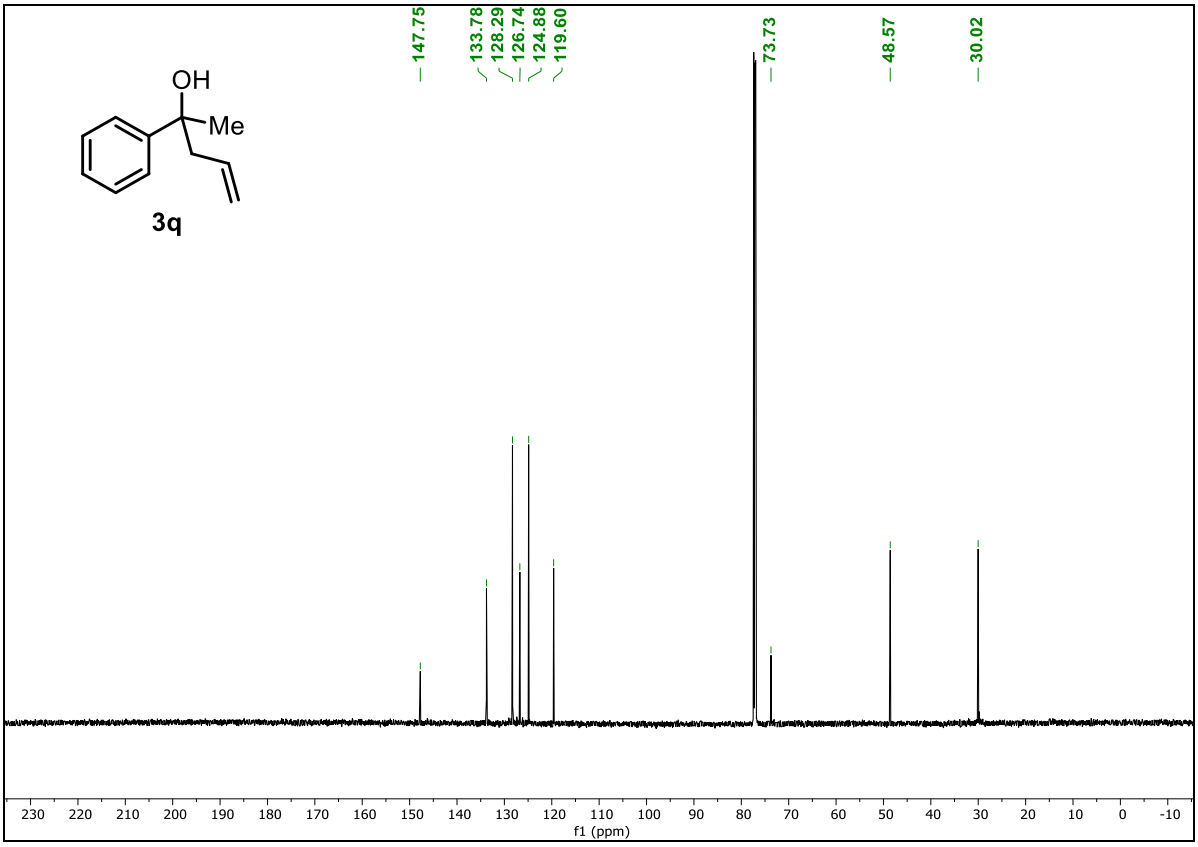


2-phenylpent-4-en-2-ol (3q)

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

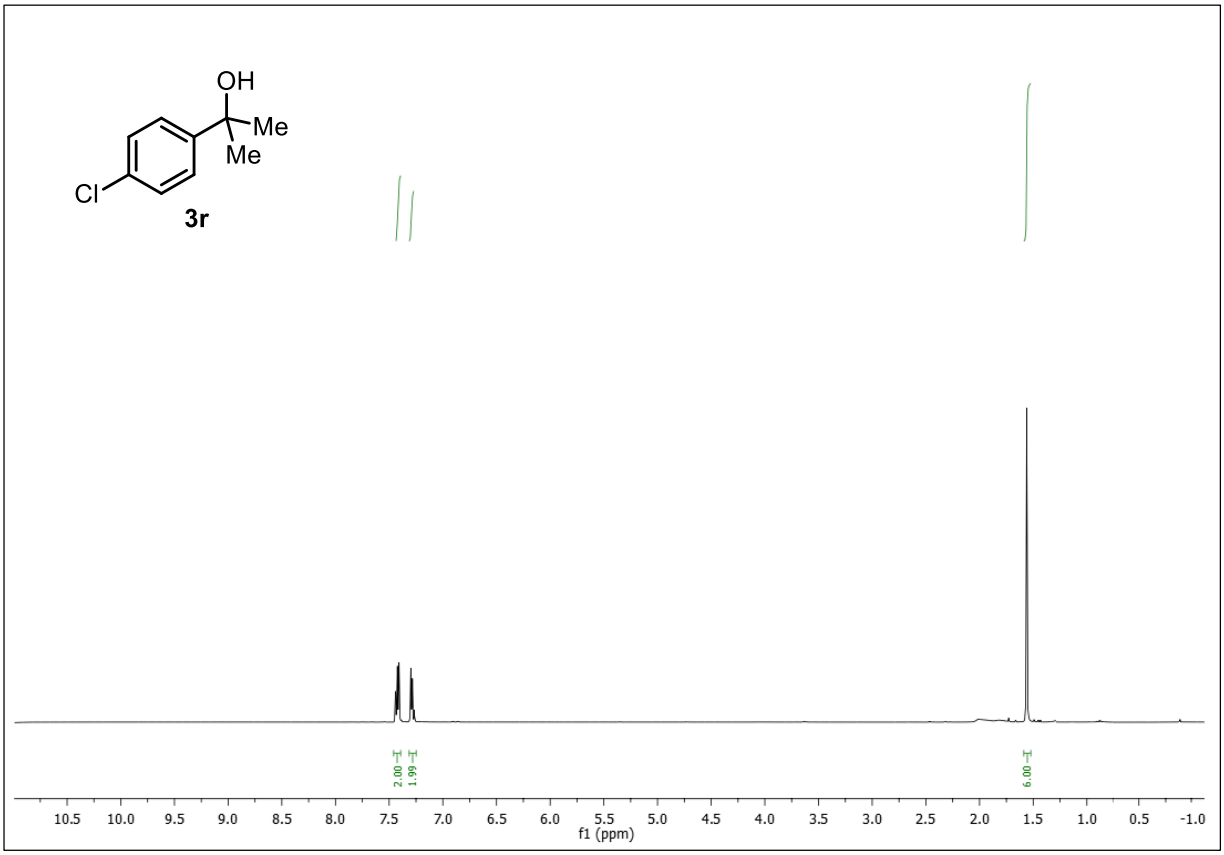


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

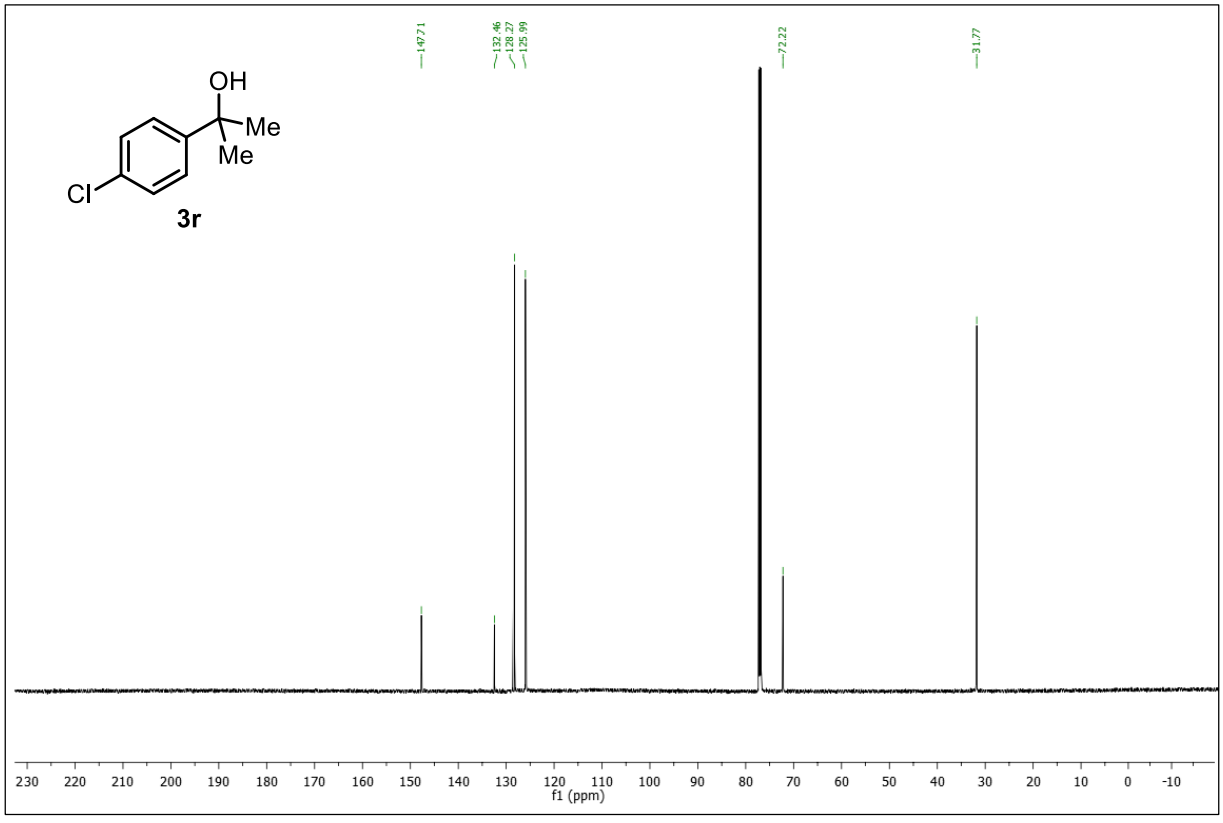


2-(4-chlorophenyl)propan-2-ol (3r)

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

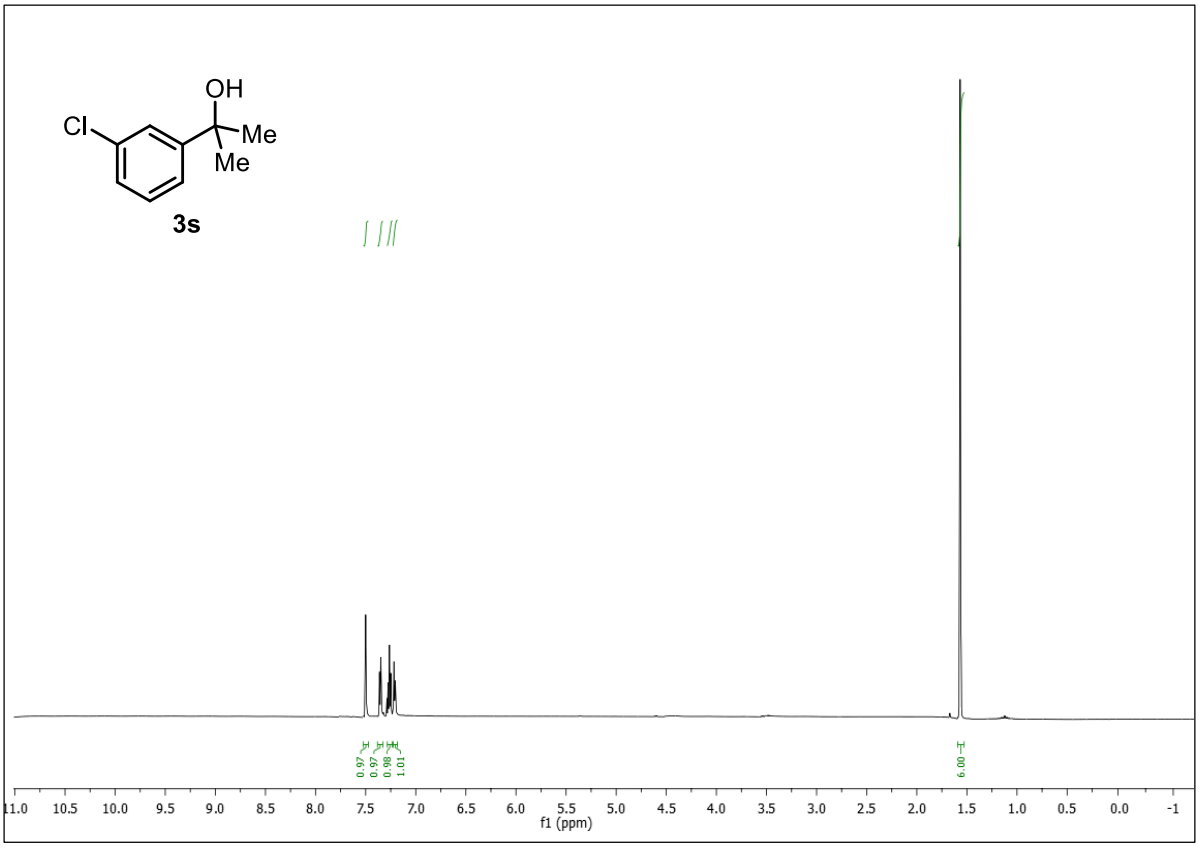


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

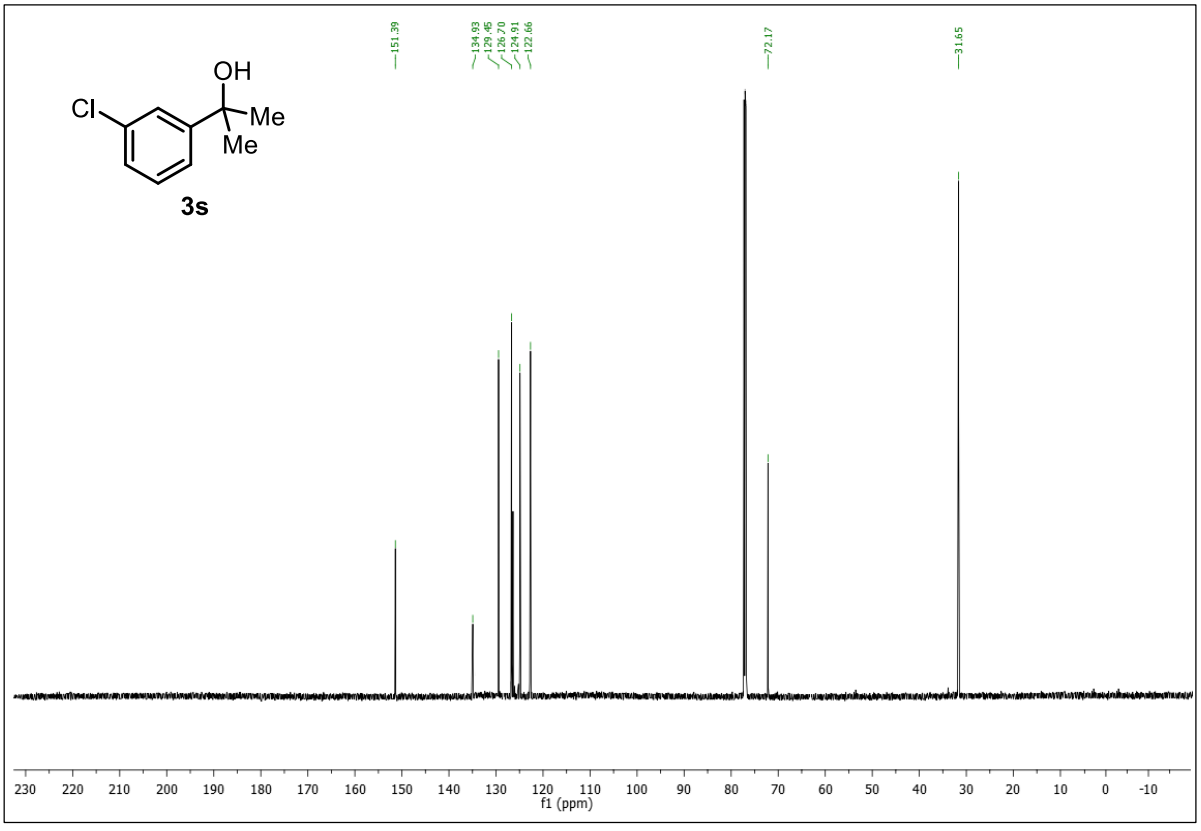


2-(3-chlorophenyl)propan-2-ol (3s)

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

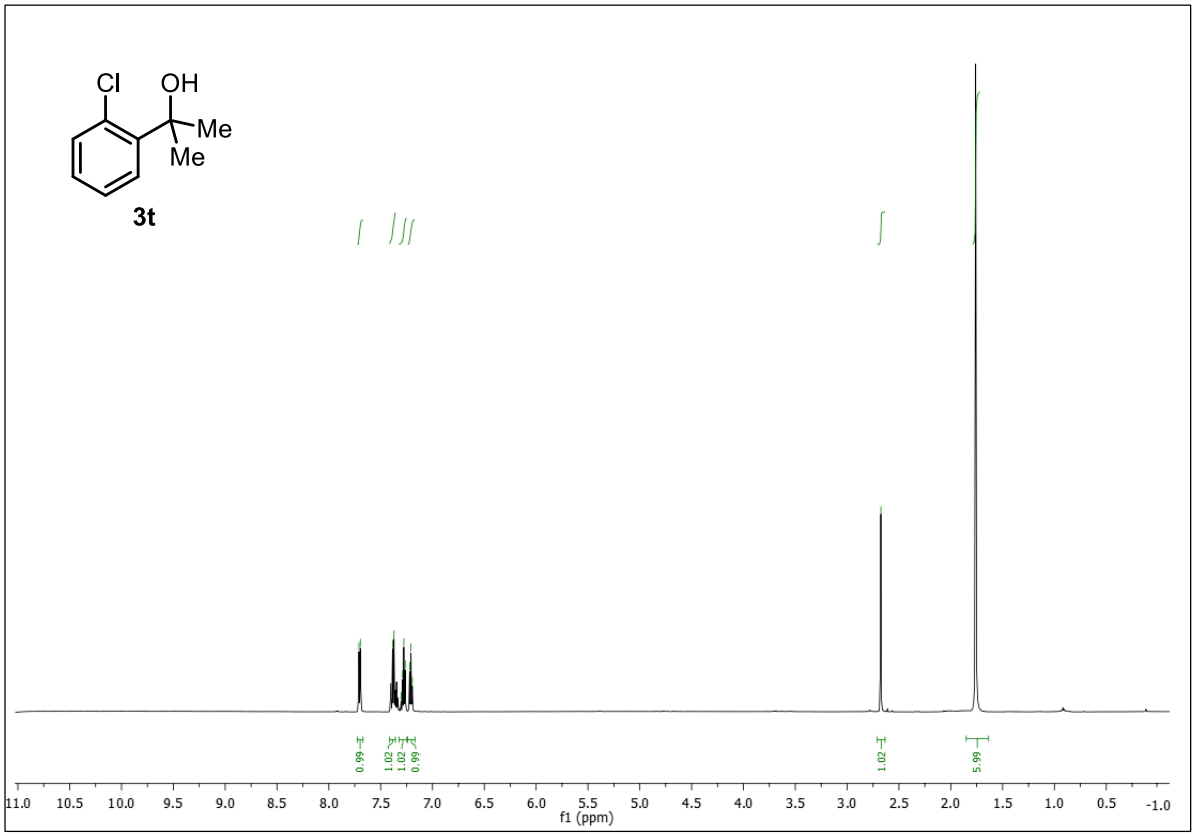


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

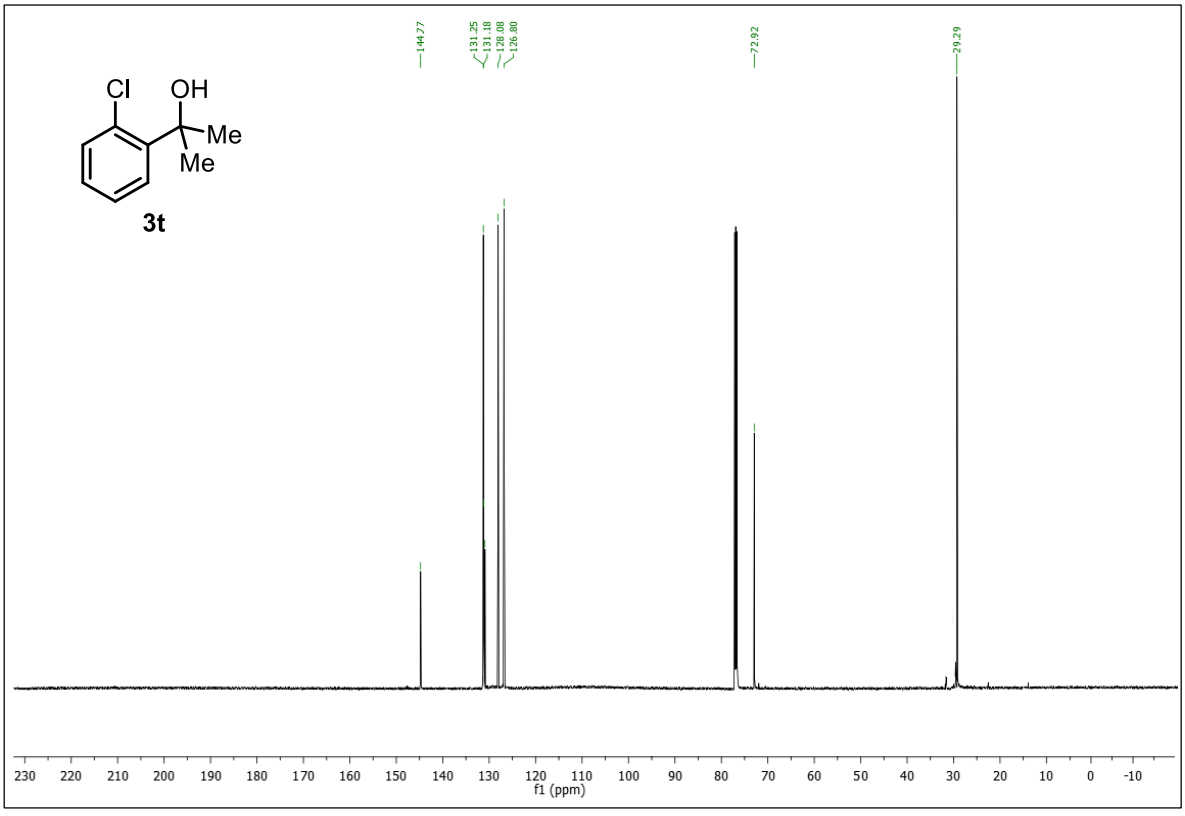


2-(2-chlorophenyl)propan-2-ol (3t)

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

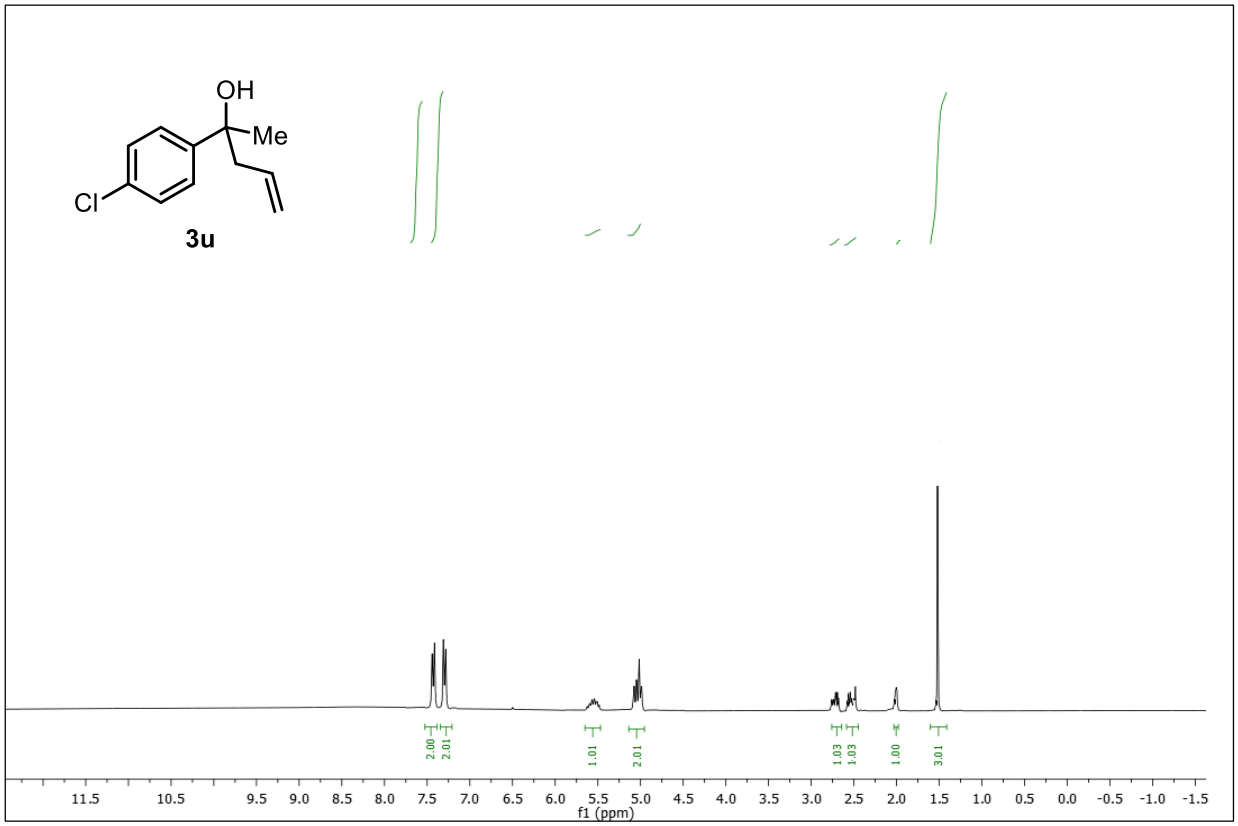


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

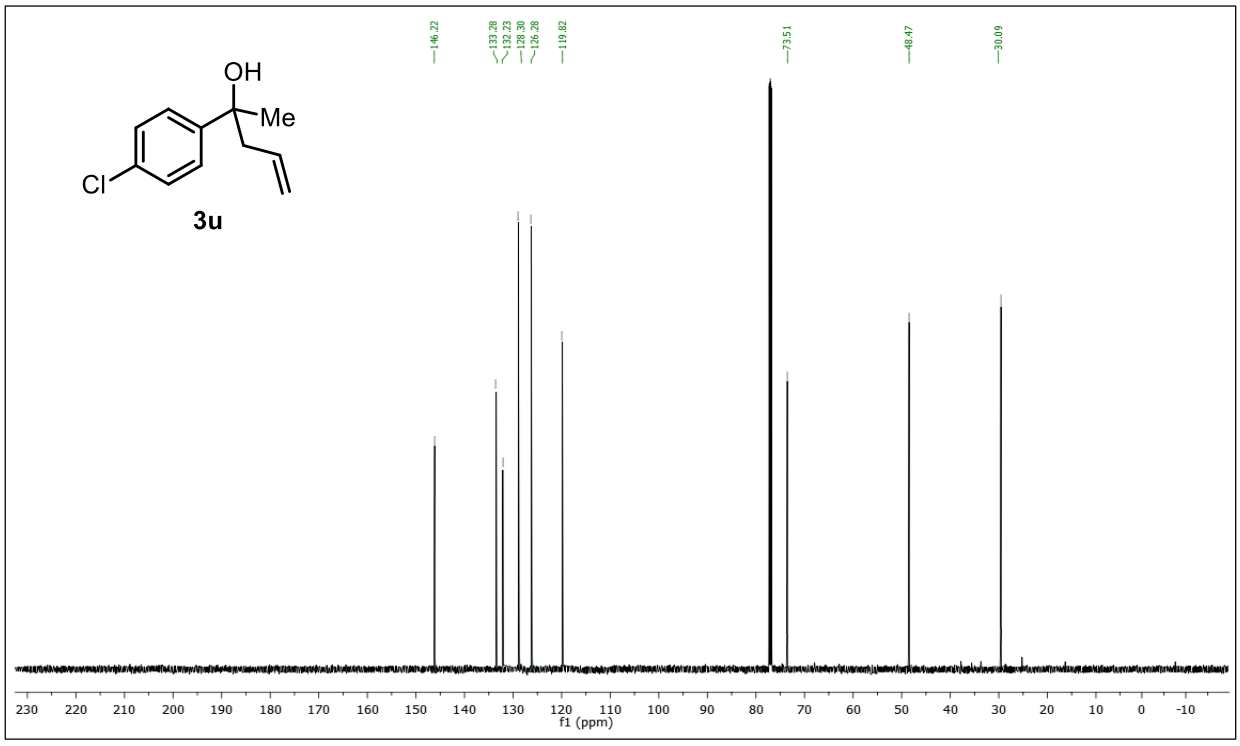


2-(4-chlorophenyl)pent-4-en-2-ol (3u)

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

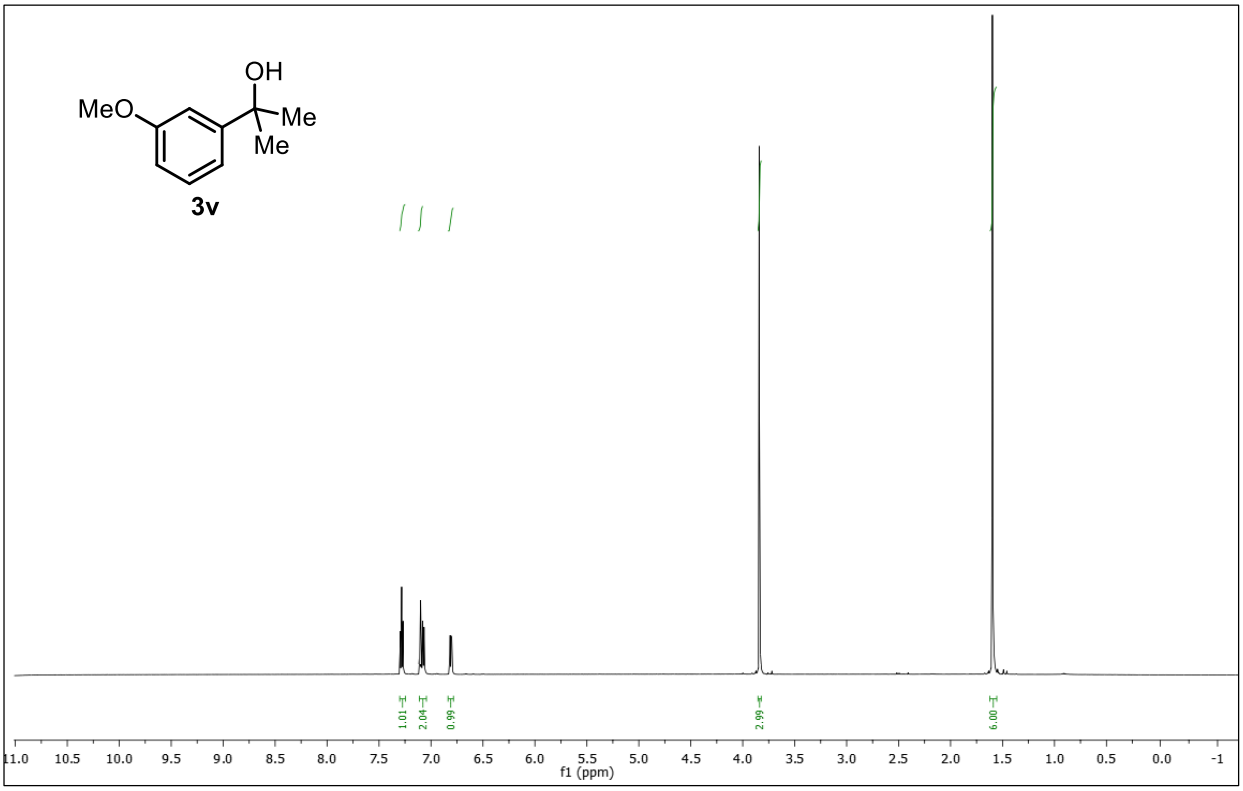


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

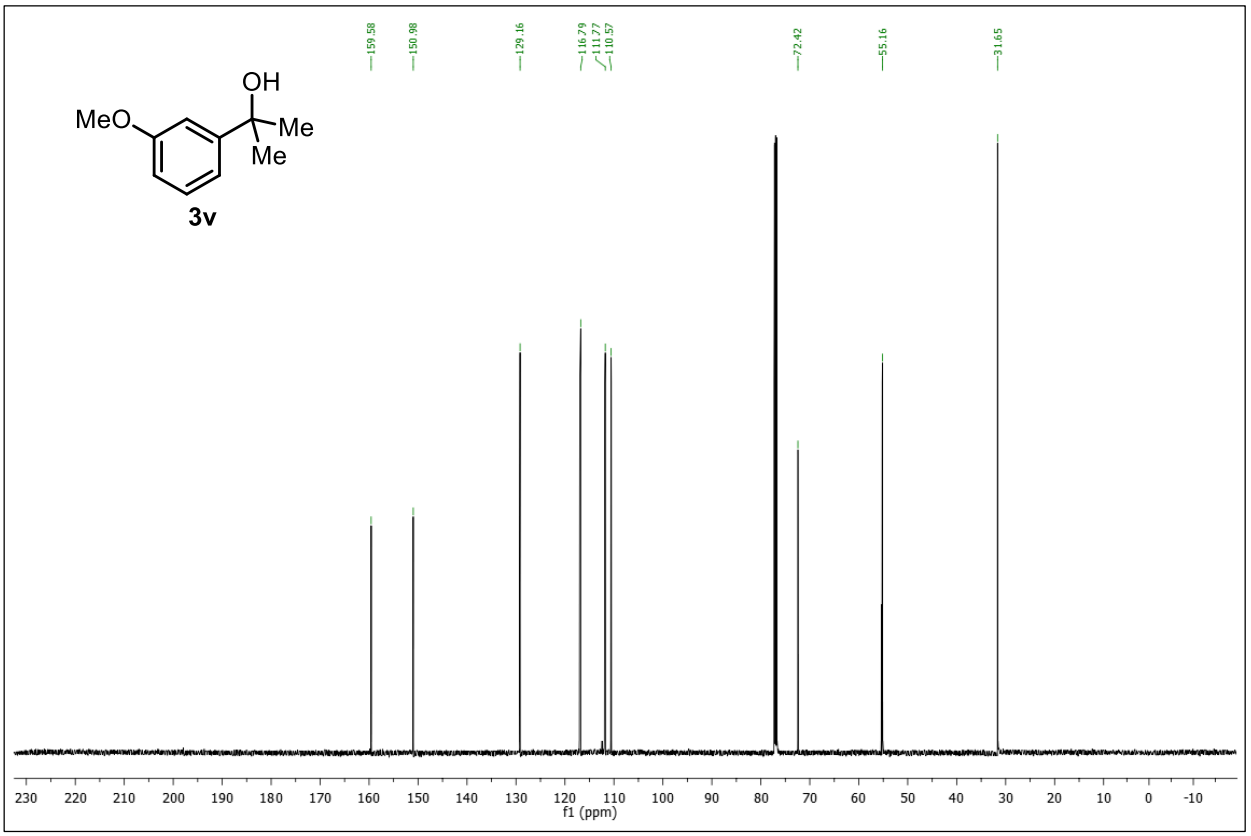


2-(3-methoxyphenyl)propan-2-ol (3v)

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

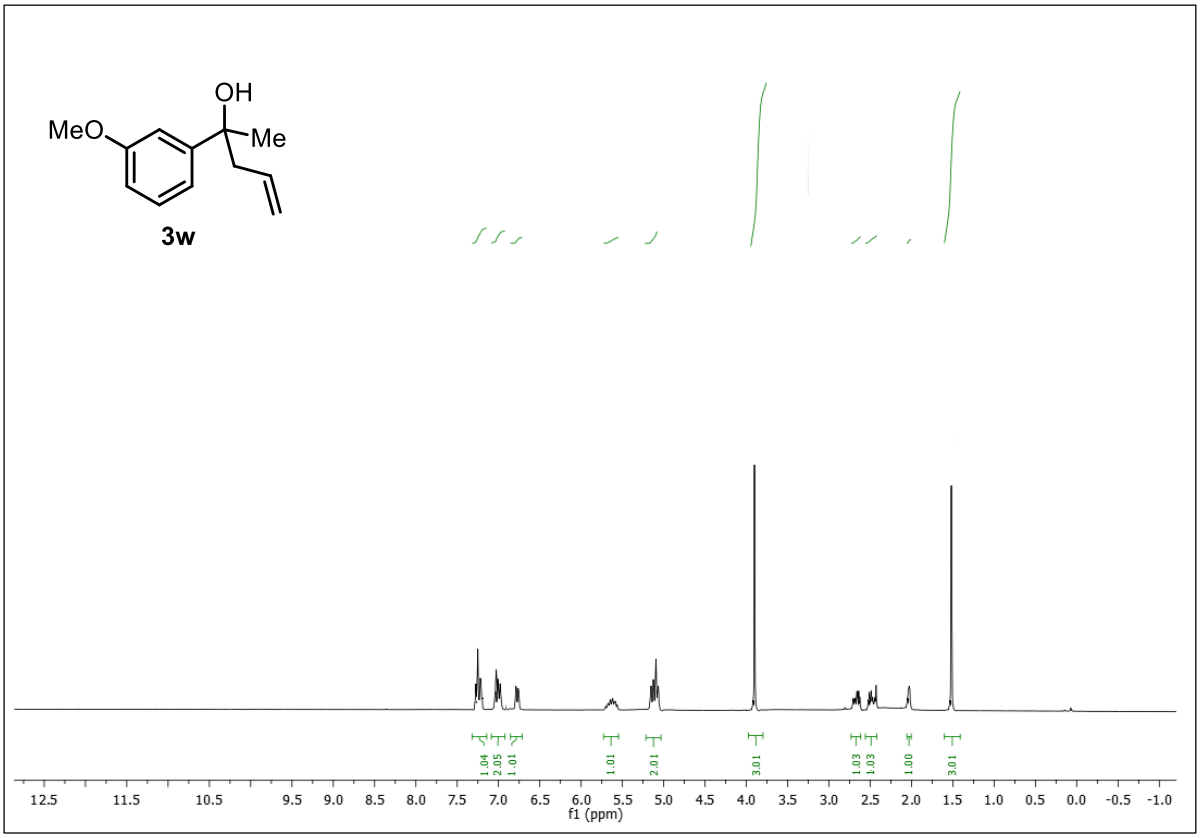


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

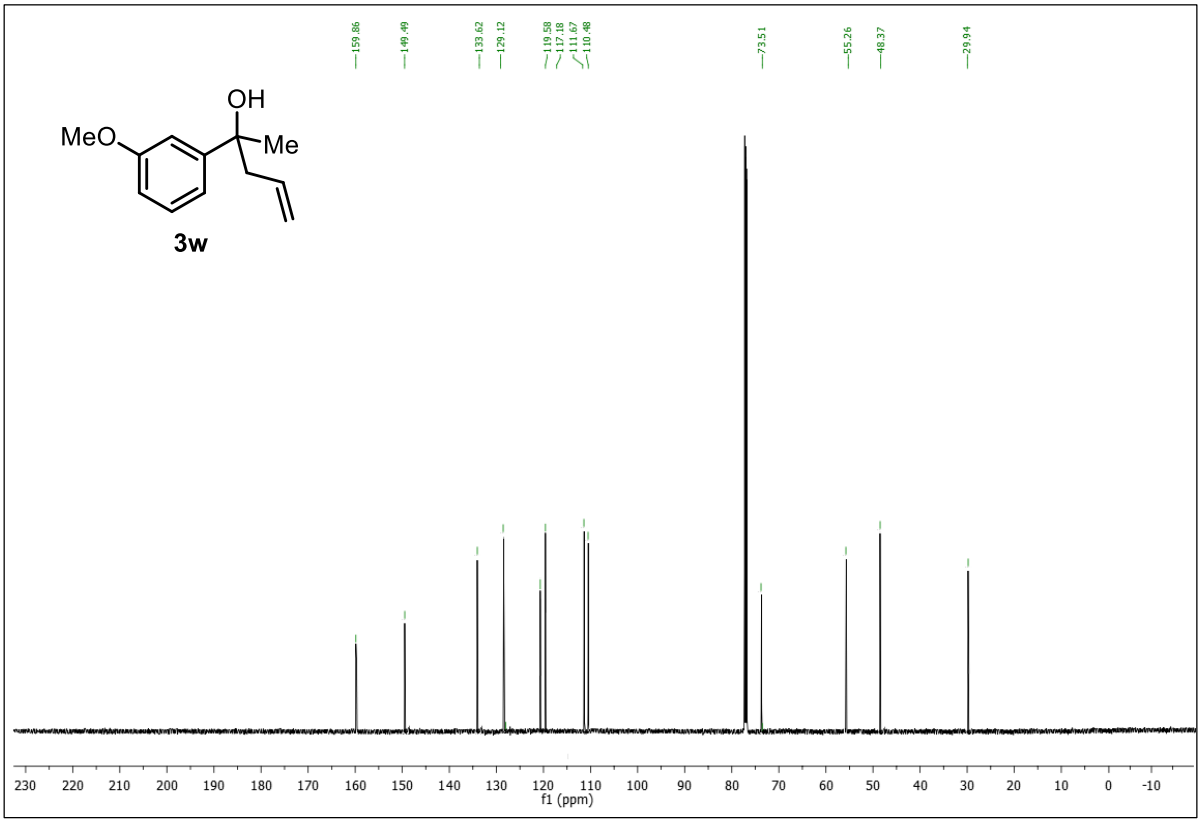


2-(3-methoxy-phenyl)-pent-4-en-2-ol (3w)

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

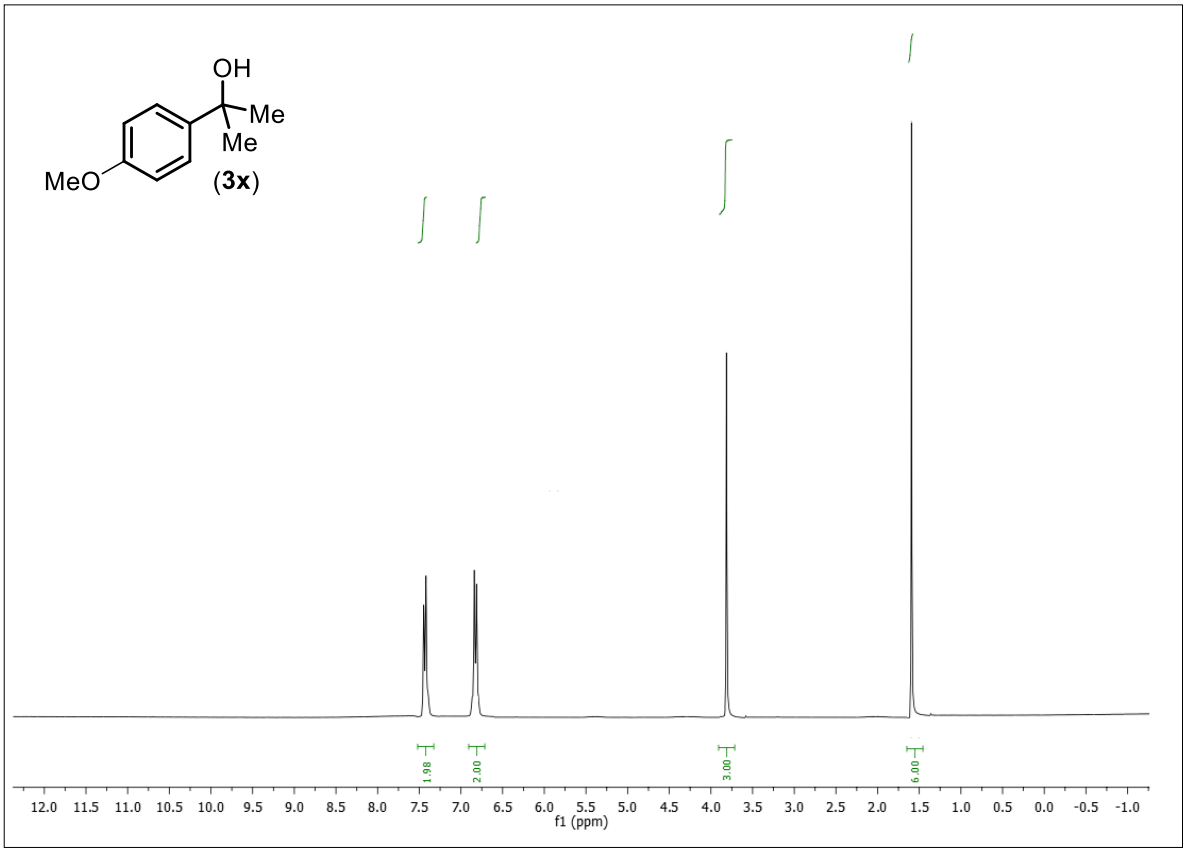


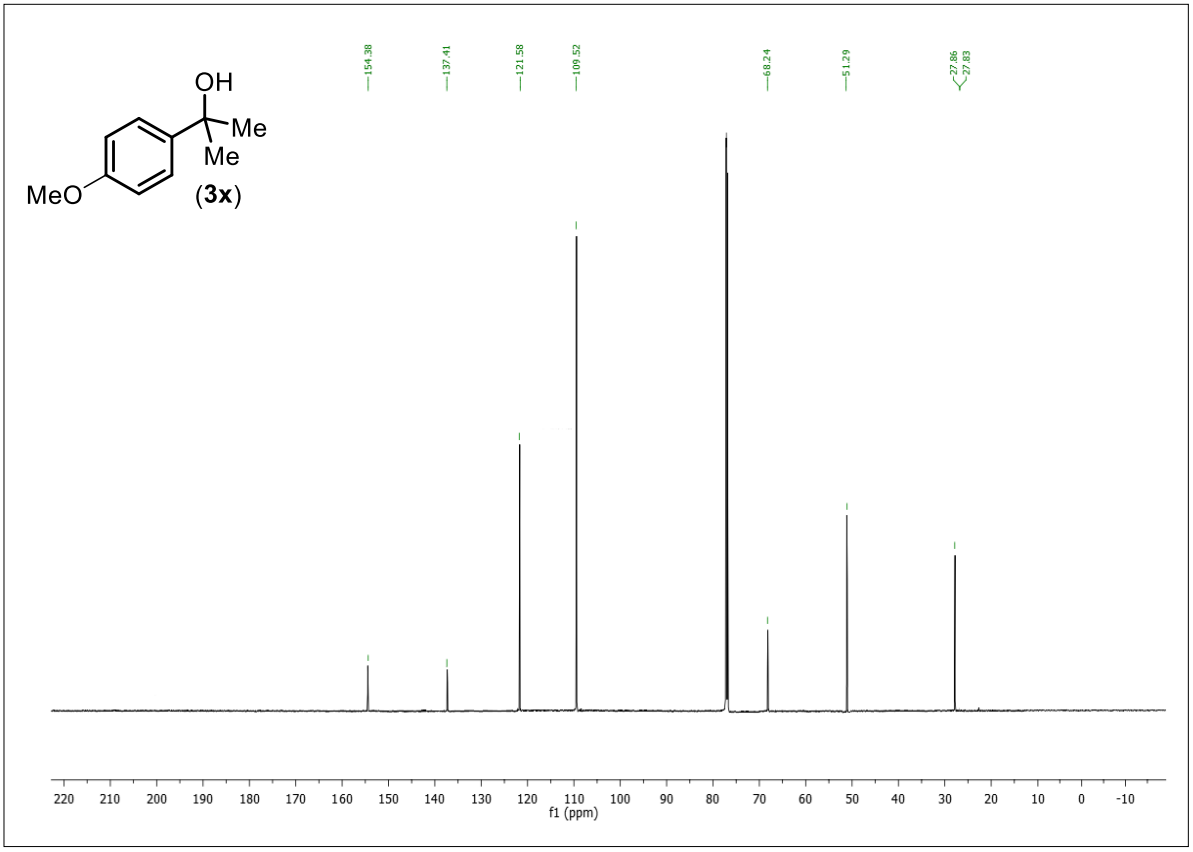
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)



2-(4-methoxyphenyl)propan-2-ol (3x)

^{1}H NMR (300 MHz, $CDCl_3$)





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