

ELECTRONIC SUPPORTING INFORMATION

Visible photons for the nucleophilic ring opening of epoxides.

Beatrice Bernardoni,^a Lorenzo Di Terlizzi,^{a,*} Eirini M. Galathri,^b Christoforos G. Kokotos,^b Maurizio Fagnoni,^{a,*} Stefano Protti^a

^a *PhotoGreen Lab, Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy. E-mail: lorenzo.diterlizzi01@universitadipavia.it, maurizio.fagnoni@unipv.it*

^b *Laboratory of Organic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Athens 15771, Greece.*

TABLE OF CONTENTS

1. General information.	p. S2
2. Experimental details.	p. S6
3. Mechanistic investigation.	p. S30
4. Process Mass Intensity (PMI).	p. S31
5. References.	p. S33
6. ¹H and ¹³{¹H}C NMR spectra of compounds 3-59.	p. S37

1. General information.

All the chemicals employed in the present investigation are commercially available and have been purchased in the highest purity grade available. Arylazo sulfones **1a,b** (Figure S1) were previously synthesized and fully characterized by our research groups.^{S1, S2} Epoxides **2a-f**, **2i** (Figure S1) were commercially available and were used without any further purifications, epoxide **2g**^{S3} and **2h**^{S4} were prepared following known procedures. Analytical thin layer chromatography (TLC) plates (silica gel 60 F254) were visualized either with an UV lamp (254 nm), or treatment with the properly chosen stain. Flash column chromatography was carried out by using 40-63 μm particle sized silica gel with air pressure. NMR experiments were carried out in the deuterated solvent of choice. ^1H and ^{13}C NMR spectra were recorded on a 300 or 75 MHz spectrometer, respectively.

GC-MS analyses were carried out using a Thermo Scientific DSQII single quadrupole GC-MS system. A Restek Rtx-5MS (30 m \times 0.25 mm \times 0.25 μm) capillary column was used for the separation of analytes with helium as a carrier gas at 1 mL/min. The injection in the GC system was performed in split mode, and the injector temperature was 250 $^\circ\text{C}$. The GC oven temperature was held at 60 $^\circ\text{C}$ for 2 min, increased to 220 $^\circ\text{C}$ by a temperature ramp of 5 $^\circ\text{C min}^{-1}$, and held for 10 min. The transfer line temperature was 250 $^\circ\text{C}$, and the ion source temperature was 250 $^\circ\text{C}$. High resolution mass spectra were determined on an AEI MS-9 using electrospray ionization (ESI) and a time-of-flight (TOF). Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent as the internal reference. The following abbreviations are used for the multiplicities: s: singlet; d: doublet; t: triplet; q: quadruplet; quint: quintuplet; hept: heptaplet; m: multiplet or overlap of non-equivalent resonances; br s: broad singlet; app: apparent; rot: rotamer. Coupling constants (J) are reported in Hertz (Hz). Photochemical experiments have been carried out in 3 mL pyrex vials. A 40W Kessil lamp (emission centered at 427 nm) has been employed as the light source in an EvoluChemTM PhotoRedox monobox equipped with a fan as the cooling system (Figure S3). The reaction course has been monitored by means of TLC and GC-FID analyses.

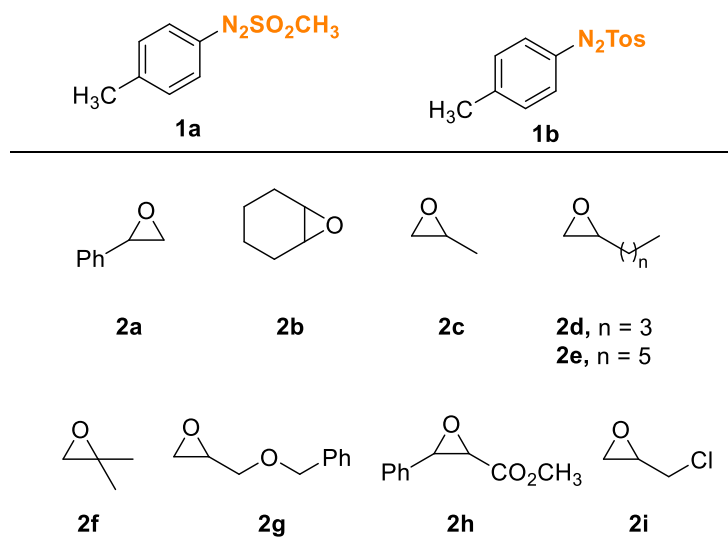


Figure S1. Arylazo sulfones **1a,b** and epoxides **2a-i** employed in the present work.

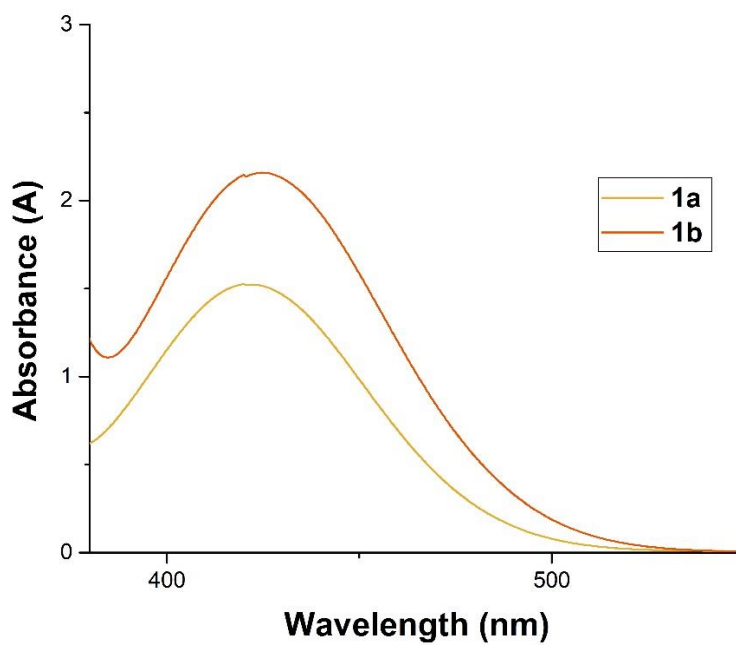
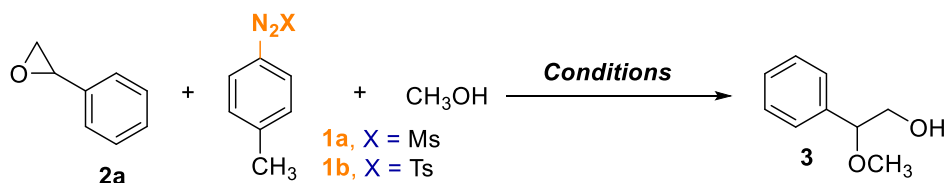


Figure S2. Visible portion of the UV-Vis spectra of **1a,b** (10^{-2} M) in acetonitrile.

Table S1. Optimization for the PAG catalyzed ring-opening of **2a**.

Entry	Conditions	Yield
1	2a (1 mmol, 1M), 1a (10 mol%), CH ₃ OH (10 mmol, 10 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	99%
2	2a (1 mmol, 1M), 1a (10 mol%), CH ₃ OH (5 mmol, 5 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	46%
3	2a (1 mmol, 1M), 1a (10 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	13%
4	2a (1 mmol, 1M), 1a (5 mol%), CH ₃ OH (10 mmol, 10 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	99%
5	2a (1 mmol, 1M), 1a (5 mol%), CH ₃ OH (5 mmol, 5 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	99%
6	2a (1 mmol, 1M), 1a (10 mol%), CH ₃ OH (5 mmol, 5 equiv.), CH ₃ CN, hv 427 nm, oxygen atmosphere	99%
7	2a (1 mmol, 1M), 1a (2.5 mol%), CH ₃ OH (5 mmol, 5 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	36%
8	2a (1 mmol, 1M), 1a (2.5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	14%
9	2a (1 mmol, 2M), 1a (2.5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	42%
10	2a (1 mmol), 1a (2.5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), neat, hv 427 nm, air equilibrated	99%
11	2a (1 mmol), 1a (5 mol%), CH ₃ OH (5 mmol, 5 equiv.), CH ₃ CN, hv 427 nm, oxygen atmosphere	99%
12	2a (1 mmol), 1a (5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), CH ₃ CN, hv 427 nm, oxygen atmosphere	99%
13	2a (1 mmol), 1a (2.5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), CH ₃ CN, hv 427 nm, oxygen atmosphere	99%
14	2a (1 mmol), 1b (5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), CH ₃ CN, hv 427 nm, oxygen atmosphere	99%
15	2a (1 mmol), 1b (5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), CH ₃ CN, hv 427 nm, air equilibrated	99%

Table S1 (continued)

16	2a (1 mmol), 1a (5 mol%), CH ₃ OH (5 mmol, 5 equiv.), CH ₂ Cl ₂ , hv 427 nm, air equilibrated	99%
17	2a (1 mmol, 2M), 1a (5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), DMC, hv 427 nm, air equilibrated	99%
18	2a (1 mmol, 2M), 1a (5 mol%), CH ₃ OH (2.5 mmol, 2.5equiv.), AcOEt, hv 427 nm, air equilibrated	99%
19	2a (1 mmol, 2M), 1a (5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), DMC, hv 440 nm, air equilibrated	99%
20	2a (1 mmol, 2M), 1a (5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), DMC, hv 456 nm, air equilibrated	99%
21	2a (1 mmol, 2M), 1a (5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), NaHCO ₃ (0.15 mmol, 0.15 equiv.), neat, hv 427 nm, air equilibrated	0%
22	2a (1 mmol, 2M), 1a (5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), Pyridine (0.15 mmol, 0.15 equiv.), neat, hv 427 nm, air equilibrated	0%
23	2a (1 mmol), CH ₃ OH (10 mmol, 10 equiv.), CH ₂ Cl ₂ , hv 427 nm, air equilibrated	0%
24	2a (1 mmol, 2M), MSA (0.5 mol%), CH ₃ OH (2.5 mmol, 2.5 equiv.), DMC, air equilibrated	24%

2. Experimental details

General procedure for the synthesis of compounds 3-56. An epoxide **2a-i** (0.5-1 mmol, 1-2 M, 1.0 equiv.) and the chosen nucleophilic partner (2.5 equiv.) were mixed together in a flame-dried vial. Then, arylazo sulfone **1a** (5 mol%) was then added and the obtained mixture was irradiated under vigorous stirring with a 427 nm KESSIL Lamp for 16 h (Figure S3). In selected cases, the reaction was performed in DMC or in a DMC:water 1:1 mixture. The crude product was isolated by means of column chromatography (stationary phase: 40-63 μm particle sized silica gel, eluant: cyclohexane-ethyl acetate mixture). In some cases, the work-up consists in the addition of MgSO_4 , removal of the desiccant and the solvent that allows to obtain a product of sufficient purity.

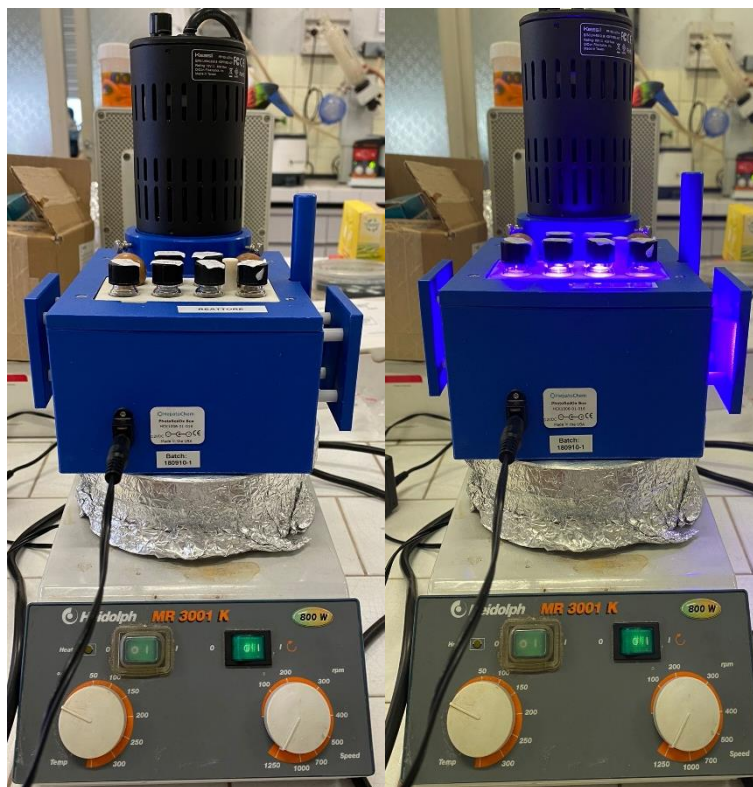


Figure S3. Photochemical set-up employed for the visible-light epoxides ring opening: EvoluChemTM PhotoRedox monobox equipped with a fan as the cooling system placed upon a stirring plate with a 427 nm emission centred KESSIL lamp. Lamp off (left), lamp on (right).

General procedure for the large-scale ring-opening reaction. In a flame-dried glass vessel, the selected epoxide **2a-e** (5 mmol, 2.5 M, 1.0 equiv.) and the nucleophile (12.5 mmol, 2.5 equiv.) were dissolved in DMC/water 1:1 to reach a final volume of 5 mL. Arylazo sulfone **1a** (0.25 mmol, 5 mol%) was added and the so formed mixture was irradiated under vigorous stirring with a 427 nm KESSIL Lamp (Figure S4). After 16 h the completion of the reaction was checked both by GC-FID analysis and by TLC. The isolated pure products were obtained after chromatographic column separation (silica gel as stationary phase and cyclohexane-ethyl acetate mixtures as eluants) or by simple work-up (vide supra). Compounds **15**, **17**, **33**, **36**, **37**, **39** and **43** have been then isolated in >99% yield by adopting this approach.

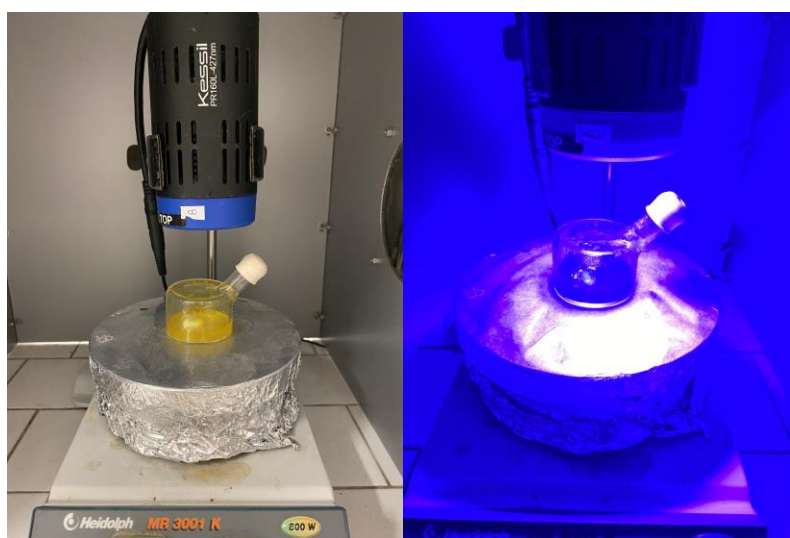
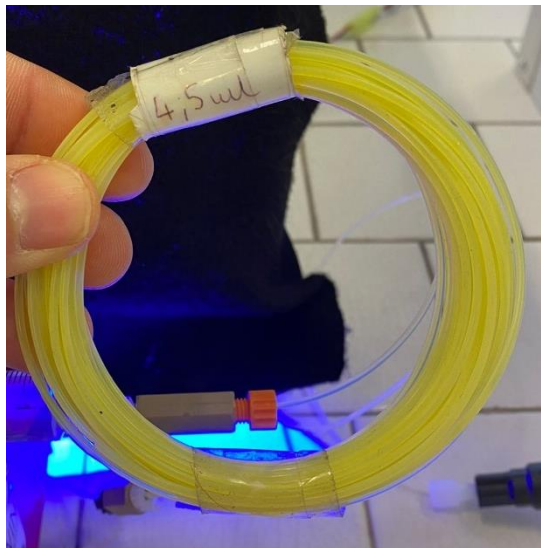


Figure S4. Photochemical apparatus for the large-scale visible-light induced epoxide ring-opening. Lamp off (left), lamp on (right).

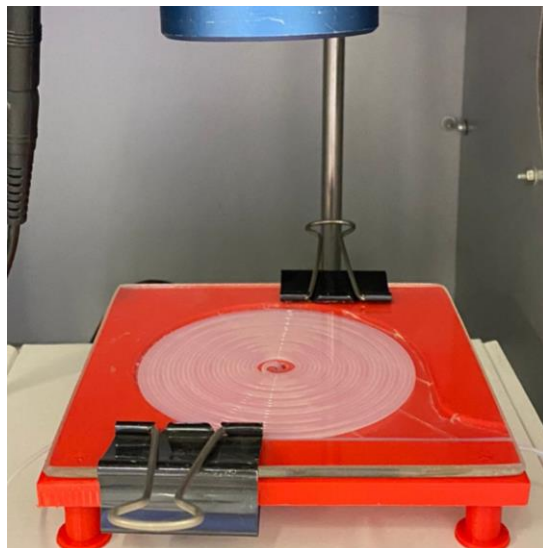
Procedure for the ring-opening reaction under flow conditions. In an Erlenmeyer flask, a solution containing 20 mmol of the chosen epoxide **2b** or **2c** (5 M, 1 equiv.), 198.0 mg of **1a** (1 mmol, 5 mol%) and 4.0 mL of DMC/water 1:1 was charged into a coiled tubing reservoir (PTFE, internal diameter: 1 mm; Figure S5a). The reaction mixture was then flown through the channels of the reactor Figure S5b by means of a syringe pump (Figure S5c) using a flow rate of $50 \mu\text{L} \cdot \text{min}^{-1}$ upon irradiation with a LED lamp (Kessil PR-160L, 40 W, emission centred at 427 nm; see a representative picture of the experimental setup in Figure S6). A fan cooling was applied to keep temperature below $30 \text{ }^\circ\text{C}$. The progress of the reaction was monitored by GC-FID and, upon completion, after 6 h the crude mixture was poured into a round bottom flask and the solvent removed via rotary evaporation. The product thus obtained were isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of

the solvent under vacuum. By adopting this approach, compounds **33** and **36** have been isolated both in >99% yield.

a)



b)



c)

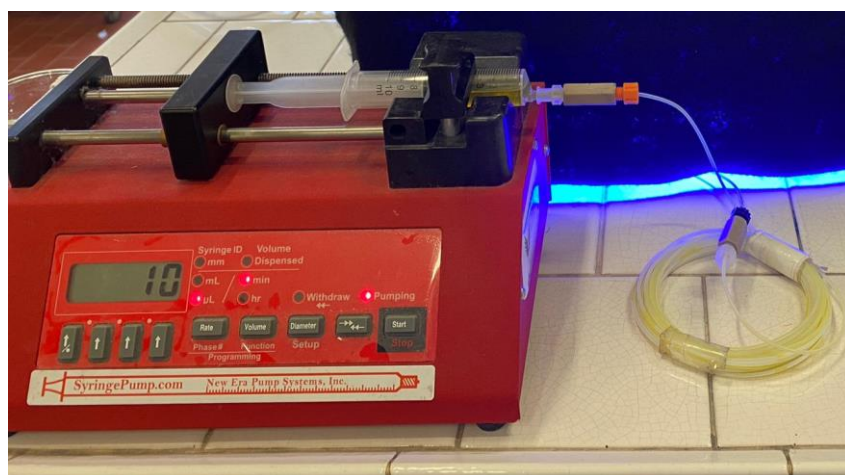
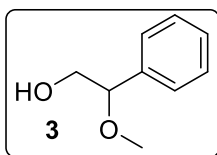


Figure S5. Flow set-up. a) coiled tubing reservoir with the reaction mixture. b) photochemical reactor c) syringe-pump employed.



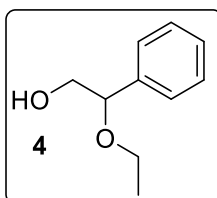
Figure S6. Overall view of the flow set-up employed for this protocol, a box equipped with a fan inside, a syringe-pump that pushed the solution from the coiled tube reservoir to the channel of the reactor where the mixture was irradiated by a 427 nm emission centred KESSIL lamp. The photolyzed solution is recovered in an Erlenmeyer flask.

Synthesis of compounds 3-56.



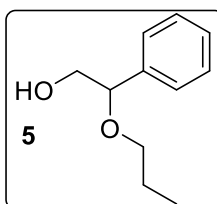
2-Methoxy-2-phenylethan-1-ol (3). Starting from 113 μL of **2a** (1 mmol), 100 μL of MeOH (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **3** (152.0 mg, 1 mmol, >99% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). Spectroscopic data were in accordance with the literature.^{S5}

3. ^1H NMR (CDCl_3 , 300 MHz) δ 7.34–7.17 (m, 5H), 4.26 (dd, $J = 8.3, 3.7$ Hz, 1H), 3.66–3.48 (m, 2H), 3.24 (s, 3H), 3.16 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 138.4, 128.4, 128.0, 126.8, 84.8, 67.2, 56.8.



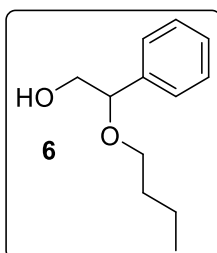
2-Ethoxy-1-phenylethan-1-ol (4). Starting from 113 μL of **2a** (1 mmol), 142 μL of EtOH (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **4** (166.0 mg, 1 mmol, >99% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). Spectroscopic data were in accordance with the literature.^{S5}

4. ^1H NMR (CDCl_3 , 300 MHz) δ 7.53–7.17 (m, 5H), 4.44 (dd, $J = 8.3, 4.0$ Hz, 1H), 3.74–3.57 (m, 2H), 3.55–3.37 (m, 2H), 2.87–2.68 (m, 1H), 1.24 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 139.1, 128.5, 128.0, 126.8, 82.9, 67.4, 64.6, 15.4.



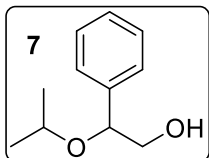
2-Phenyl-2-propoxyethan-1-ol (5). Starting from 113 μL of **2a** (1 mmol), 186 μL of propanol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **5** (126.0 mg, 0.7 mmol, 70% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). Spectroscopic data were in accordance with the literature.^{S5}

5. ^1H NMR (CDCl_3 , 300 MHz) δ 7.45–7.25 (m, 5H), 4.43 (dd, $J = 8.3, 4.1$ Hz, 1H), 3.78–3.53 (m, 2H), 3.49–3.25 (m, 2H), 2.56 (s, 1H), 1.65 (sextet, $J = 7.4$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 139.0, 128.4, 127.9, 126.7, 82.8, 70.8, 67.4, 22.9, 10.5.



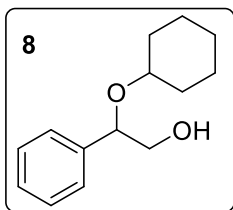
2-Butoxy-2-phenylethan-1-ol (6). Starting from 113 μL of **2a** (1 mmol), 228 μL of 1-butanol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **6** (170.8 mg, 0.88 mmol, 88% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). Spectroscopic data were in accordance with the literature.^{S6}

6. ^1H NMR (300 MHz, CDCl_3) δ 7.38–7.14 (m, 5H), 4.34 (dd, $J = 8.3, 4.0$ Hz, 1H), 3.67–3.44 (m, 2H), 3.43–3.19 (m, 2H), 2.55 (s, 1H), 1.61–1.19 (m, 4H), 0.84 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 139.0, 128.4, 127.9, 126.7, 82.9, 68.9, 67.3, 31.8, 19.2, 13.8.



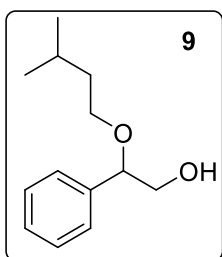
2-Isopropoxy-2-phenylethan-1-ol (7). Starting from 113 μL of **2a** (1 mmol), 191 μL of isopropyl alcohol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **7** (138.6 mg, 0.77 mmol, 77% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). Spectroscopic data were in accordance with the literature.^{S5}

7. ^1H NMR (CDCl_3 , 300 MHz) δ 7.39–7.29 (m, 5H), 4.56 (dd, $J = 7.8, 4.7$ Hz, 1H), 3.69–3.56 (m, 3H), 2.47 (s, 1H), 1.23 (d, $J = 6.0$ Hz, 3H), 1.16 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 140.2, 128.9, 128.4, 127.3, 80.5, 70.1, 68.0, 24.0, 21.9.



2-(Cyclohexyloxy)-2-phenylethan-1-ol (8). Starting from 113 μL of **2a** (1 mmol), 260 μL of cyclohexanol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **8** (191.0 mg (0.87 mmol, 87% yield, yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 95:5). Spectroscopic data were in accordance with the literature.^{S5}

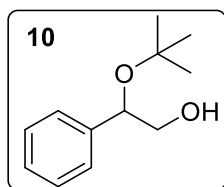
8 ^1H NMR (300 MHz, CDCl_3) δ 7.45–7.26 (m, 5H), 4.61 (dd, $J = 7.8, 4.7$ Hz, 1H), 3.71–3.53 (m, 2H), 3.31 (tt, $J = 9.4, 3.8$ Hz, 1H), 2.60 (s, 1H), 2.11–1.96 (m, 1H), 1.85–1.66 (m, 3H), 1.52 (s, 1H), 1.43–1.30 (m, 2H), 1.21 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 139.8, 128.3, 127.7, 126.7, 79.6, 75.5, 67.4, 33.5, 31.5, 25.6, 24.1, 23.9.



2-(Isopentyloxy)-2-phenylethan-1-ol (9). Starting from 113 μL of **2a** (1 mmol), 272 μL of isoamyl alcohol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **9** (158.1 mg (0.76 mmol, 76% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1).

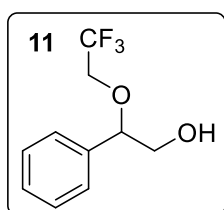
9. ^1H NMR (300 MHz, CDCl_3) δ 7.52–7.21 (m, 5H), 4.42 (dd, $J = 8.3, 4.1$ Hz, 1H), 3.74–3.62 (m, 2H), 3.44 (d, $J = 22.6$ Hz, 2H), 2.59 (s, 1H), 1.81–1.65 (m, 1H), 1.58–1.39 (m, 2H), 0.91 (dd, $J = 12.3, 6.6$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 139.0, 128.4, 127.9, 126.7, 82.9, 67.5, 67.3, 38.6, 24.9, 22.7, 22.3.

HRMS (ESI-TOF) m/z : calcd. for $\text{C}_{13}\text{H}_{21}\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 209.1543, found: 209.1547.



2-(*tert*-Butoxy)-2-phenylethan-1-ol (10). Starting from 113 μL of **2a** (1 mmol), 239 μL of *tert*-butanol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **10** (124.2 mg, 0.64 mmol, 64% yield, colourless oil that crystallized upon storage in the fridge) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). Spectroscopic data were in accordance with the literature.^{S5}

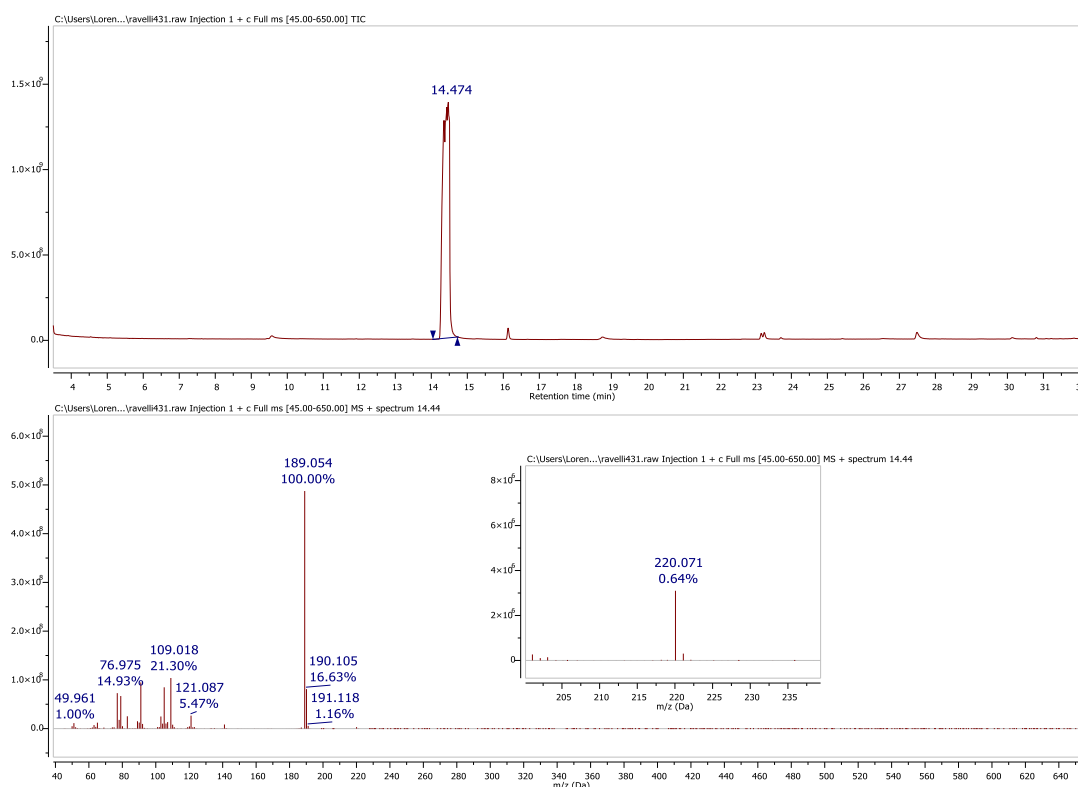
10. ^1H NMR (300 MHz, CDCl_3) δ 7.44–7.07 (m, 5H), 4.56 (dd, $J = 8.0, 4.6$ Hz, 1H), 3.45 (t, $J = 5.8$ Hz, 2H), 2.30 (s, 1H), 1.12 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 142.2, 128.1, 127.2, 126.3, 75.1, 74.8, 67.8, 28.7.



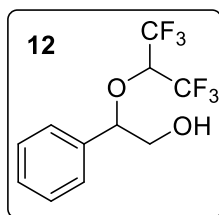
2-Phenyl-2-(2,2,2-trifluoroethoxy)ethan-1-ol (11). Starting from 113 μL of **2a** (1 mmol), 166.5 μL of 2,2,2-trifluoroethanol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **11** (178.5 mg, 0.81 mmol, 81% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). Spectroscopic data were in accordance with the literature.^{S7}

NMR analyses pointed out the presence of 1-phenyl-2-(2,2,2-trifluoroethoxy)ethan-2-ol (< 5%) as a minor regioisomer not visible by GC-MS analysis (see below).

11. ^1H NMR (300 MHz, CDCl_3) δ 7.58–7.05 (m, 5H), 4.82–4.37 (m, 1H), 4.08–3.45 (m, 4H), 2.52 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 136.6, 128.8, 128.4, 126.8, 123.8 (q, $J = 278.6$ Hz), 84.5, 67.3 (d, $J = 7.5$ Hz), 66.1 (q, $J = 34.3$ Hz).



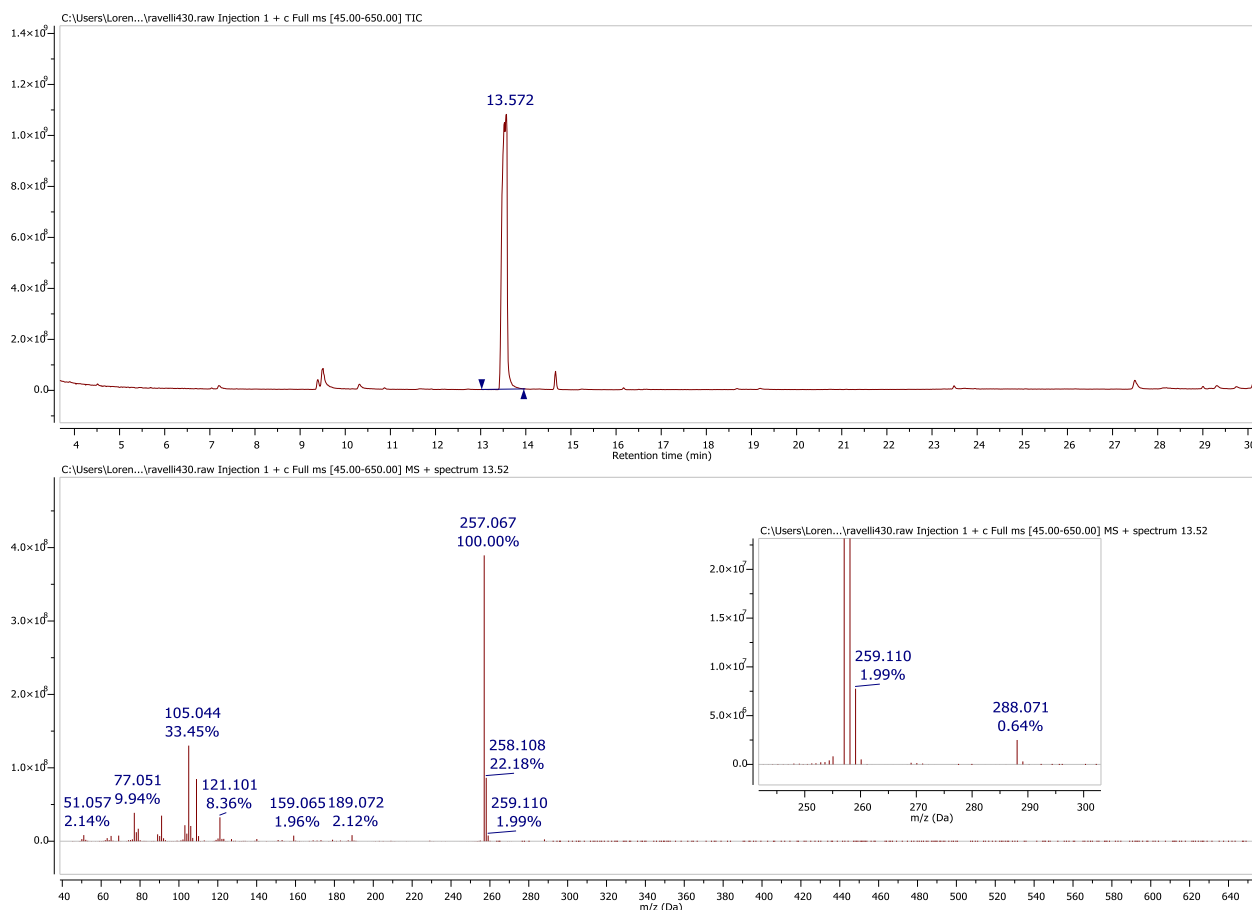
GC-MS trace of the crude reaction mixture (Up). GC-MS analysis of product **11** (Down).



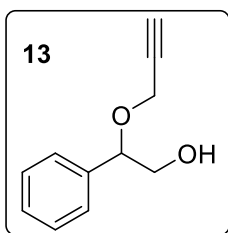
2-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-2-phenylethan-1-ol (12).

Starting from 113 μL of **2a** (1 mmol), 258 μL of 1,1,1,3,3,3-hexafluoro-2-propanol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **12** (88.2 mg, 0.38 mmol, 38% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 8:2). Spectroscopic data were in accordance with the literature.^{S8} NMR analyses pointed out the presence of 1-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2-phenylethan-2-ol as a minor regioisomer (< 5%) not visible by GC-MS analysis (see below).

12. ^1H NMR (300 MHz, CDCl_3) δ 7.48–7.25 (m, 5H), 4.89 (dd, $J = 8.2, 3.6$ Hz, 1H), 4.33–4.08 (m, 1H), 3.97 (dd, $J = 12.3, 8.2$ Hz, 1H), 3.73 (dd, $J = 12.3, 3.6$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 129.5, 128.8, 128.7, 127.6, 121.39 (q, $J = 283.5$ Hz), 86.0, 73.8–71.9 (m), 66.6.



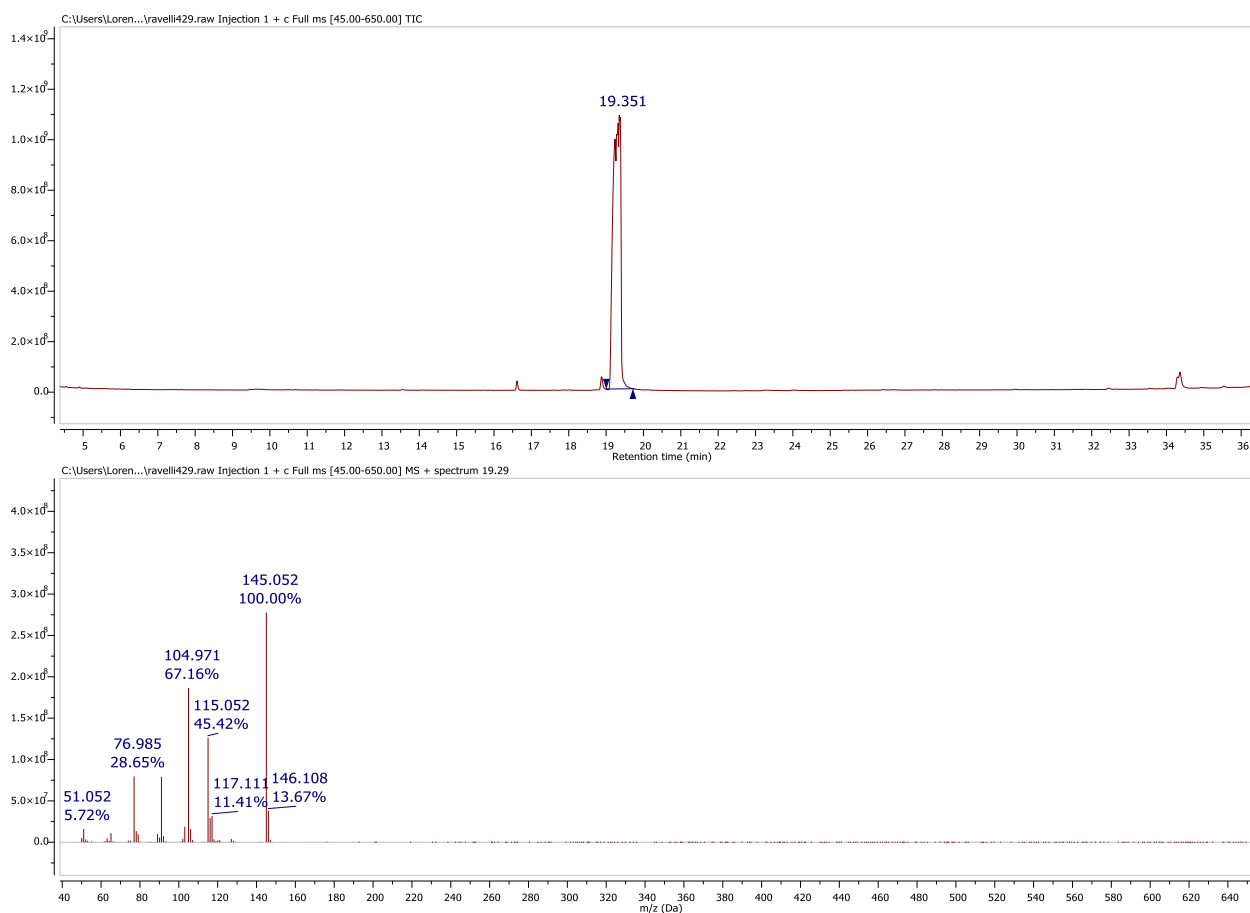
GC-MS trace of the crude reaction mixture (Up). GC-MS analysis of product **12** (Down).



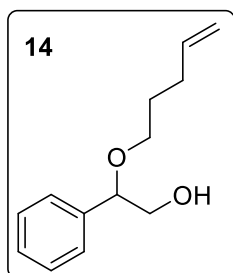
2-Phenyl-2-(prop-2-yn-1-yloxy)ethan-1-ol (13). Starting from 113 μL of **2a** (1 mmol), 145 μL of propargyl alcohol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **13** (143.4 mg, 0.81 mmol, 81% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). Spectroscopic data were in accordance with the literature.^{S9} NMR

analyses pointed out the presence of 1-phenyl-2-(prop-2-yn-1-yloxy)ethan-2-ol (< 5%) as a minor regioisomer not visible by GC-MS analysis (see below).

13. ^1H NMR (CDCl_3 , 300 MHz) δ 7.39–7.31 (m, 5H), 4.70 (dd, $J = 8.3, 3.8$ Hz, 1H), 4.22 (dd, $J = 15.7, 2.5$ Hz, 1H), 3.98 (dd, $J = 15.7, 2.4$ Hz, 1H), 3.88–3.63 (m, 2H), 2.90–2.63 (m, 1H), 2.47 (t, $J = 2.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 137.4, 128.5, 128.3, 127.0, 81.7, 79.5, 74.7, 66.9, 55.9.



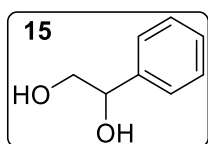
GC-MS trace of the crude reaction mixture (Up). GC-MS analysis of product **13** (Down).



2-(Pent-4-en-1-yloxy)-2-phenylethan-1-ol (14). Starting from 113 μL of **2a** (1 mmol), 256 μL of pent-4-en-1-ol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **14** (138.8 mg, 0.67 mmol, 67% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1).

14. ^1H NMR (300 MHz, CDCl_3) δ 7.64–7.07 (m, 5H), 5.82 (ddt, $J = 16.9, 10.2, 6.6$ Hz, 1H), 5.20–4.81 (m, 2H), 4.42 (dd, $J = 8.3, 4.0$ Hz, 1H), 3.84–3.20 (m, 4H), 2.64 (d, $J = 7.3$ Hz, 1H), 2.33–1.96 (m, 2H), 1.97–1.43 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 138.9, 138.1, 128.4, 127.9, 126.7, 114.7, 82.9, 68.5, 67.3, 30.3, 28.9.

HRMS (ESI-TOF) m/z : calcd. for $\text{C}_{13}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 229.1204, found: 229.1202.

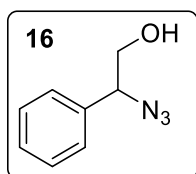


1-Phenylethane-1,2-diol (15). Starting from 113 μL of **2a** (1 mmol), 387 μL of a solution DMC:water (1:1) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **15** (138.0 mg, 1.0 mmol, >99% yield) was isolated by flash column chromatography

(eluent Cyclohexane-Ethyl acetate 7:3). The same reaction was performed on a larger scale employing 565 μL of **2a** (5 mmol), 49.5 mg of **1a** (0.25 mmol, 5 mol%) in 1.9 mL of a DMC:water (1:1) solution. Product **15** (690 mg, 5.0 mmol, >99% yield) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S10}

15. ^1H NMR (300 MHz, CDCl_3) δ 7.35–7.26 (m, 5H), 4.76 (dd, $J = 8.3, 3.5$ Hz, 1H), 4.44 (s, 1H), 4.10 (s, 1H), 3.73–3.55 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 140.5, 128.3, 127.7, 126.0, 74.6, 67.9.

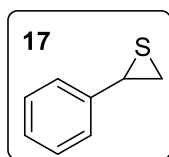
m. p. = 62.4–63.0 (lit.^{S11} = 61.3–64.2)



2-Azido-2-phenylethan-1-ol (16). Starting from 113 μL of **2a** (1 mmol), 130 mg of sodium azide (2.5 mmol, 2.5 equiv.), 9.9 mg of **1a** (0.05 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **16** (140.2 mg, 0.86 mmol, 86% yield, pale yellow oil) was isolated by flash column chromatography

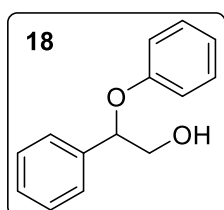
(eluent Cyclohexane-Ethyl acetate 7:3). The same reaction was performed on a larger scale employing 565 μL of **2a** (5 mmol), 650 mg of sodium azide (12.5 mmol, 2.5 equiv.) and 49.5 mg of **1a** (0.25 mmol, 5 mol%) dissolved in 500 μL of a DMC:H₂O (1:1) solution. Product **16** (815 mg, 5.0 mmol, >99% yield) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S12}

16. ^1H NMR (CDCl_3 , 300 MHz) δ 7.44–7.32 (m, 5H), 4.67 (t, J = 6.4 Hz, 1H), 3.74 (d, J = 6.4 Hz, 2H), 2.58 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 136.8, 129.4, 129.2, 127.6, 68.3, 66.9.



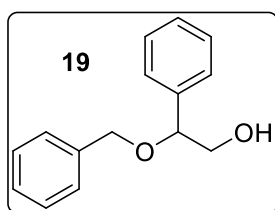
2-Phenylthiirane (17). Starting from 113 μL of **2a** (1 mmol), 240.0 mg of KSCN (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%) dissolved in 100 μL of a DMC: H_2O (1:1) solution. Product **17** (116.3 mg, 0.85 mmol, 85% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane). The same reaction was performed on a larger scale employing 565 μL of **2a** (5 mmol), 1.2 g of potassium thiocyanate (12.5 mmol, 2.5 equiv.), 49.5 mg of **1a** (0.25 mmol, 5 mol%) dissolved in 500 μL of a DMC: H_2O (1:1) solution. Product **17** (680 mg, 5.0 mmol, >99% yield) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S13}

17. ^1H NMR (300 MHz, CDCl_3) δ 7.64–7.01 (m, 5H), 3.93 (dd, J = 6.6, 5.6 Hz, 1H), 2.90 (dd, J = 6.6, 1.5 Hz, 1H), 2.69 (dd, J = 5.6, 1.5 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 139.0, 128.5, 127.6, 126.7, 36.1, 27.3.



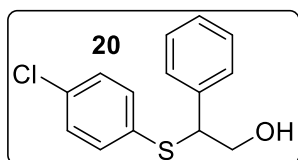
2-Phenoxy-2-phenylethan-1-ol (18). Starting from 113 μL of **2a** (1 mmol), 235 mg of phenol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **18** (64.8 mg, 0.32 mmol, 32% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 8:2). Spectroscopic data were in accordance with the literature.^{S14}

18. ^1H NMR (300 MHz, CDCl_3) δ 7.42–7.03 (m, 7H), 6.97–6.64 (m, 3H), 5.31–5.11 (m, 1H), 3.86–3.75 (m, 2H), 2.23 (bs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 157.7, 137.7, 129.3, 128.7, 128.1, 126.2, 121.1, 115.8, 81.0, 67.5.



2-(Benzyloxy)-2-phenylethan-1-ol (19). Starting from 113 μL of **2a** (1 mmol), 260 μL of benzyl alcohol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). Product **19** (228.0 mg, 1.0 mmol, >99% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 95:5). Spectroscopic data were in accordance with the literature.^{S15}

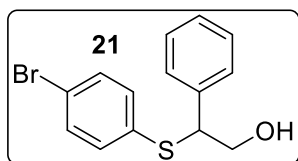
19. ^1H NMR (300 MHz, CDCl_3) δ 7.45–7.35 (m, 10H), 4.69 (s, 1H), 4.64–4.52 (m, 2H), 4.38 (d, J = 11.5 Hz, 1H), 3.83–3.61 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 138.9, 137.9, 128.6, 128.4, 128.2, 127.9, 127.8, 127.0, 82.3, 70.7, 67.3.



2-((4-Chlorophenyl)thio)-2-phenylethan-1-ol (20). Starting from 56.5 μL of **2a** (0.5 mmol), 178.6 mg of 4-chlorothiophenol (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **20** (97.7 mg, 0.37 mmol,

74% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 8:2). Spectroscopic data were in accordance with the literature.^{S16}

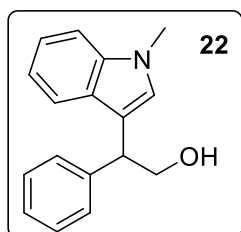
20. ^1H NMR (300 MHz, CDCl_3) δ 7.50–6.87 (m, 9H), 4.21 (t, J = 6.9 Hz, 1H), 3.89–3.76 (m, 2H), 2.29 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 138.6, 133.8, 133.7, 132.2, 129.0, 128.7, 128.0, 127.8, 65.1, 56.1.



2-((4-Bromophenyl)thio)-2-phenylethan-1-ol (21). Starting from 56.5 μL of **2a** (0.5 mmol), 178.6 mg of 4-chlorothiophenol (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **21** (78.5 mg, 0.37 mmol,

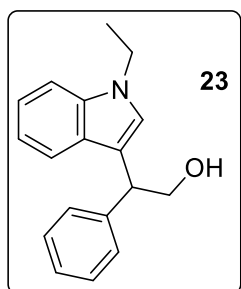
51% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 8:2). Spectroscopic data were in accordance with the literature.^{S17}

21. ^1H NMR (300 MHz, CDCl_3) δ 7.42–7.28 (m, 7H), 7.25–7.13 (m, 2H), 4.34–4.28 (m, 1H), 3.99–3.86 (m, 2H), 2.03 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 138.4, 133.9, 132.8, 131.9, 128.70, 127.9, 127.9, 121.7, 65.1, 56.1.



2-(1-Methyl-1H-indol-3-yl)-2-phenylethan-1-ol (22). Starting from 56.5 μL of **2a** (0.5 mmol), 156 μL of 1-methylindole (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **22** (99.8 mg, 0.39 mmol, 78% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3). Spectroscopic data were in accordance with the literature.^{S18}

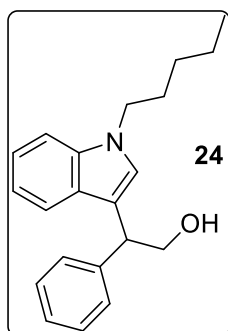
22. ^1H NMR (300 MHz, CDCl_3) δ 7.51 (dt, J = 8.0, 1.0 Hz, 1H), 7.41–7.32 (m, 5H), 7.31–7.22 (m, 2H), 7.13–7.04 (m, 1H), 6.99 (d, J = 1.0 Hz, 1H), 4.52 (t, J = 6.8 Hz, 1H), 4.32–4.15 (m, 2H), 3.79 (s, 3H), 1.72 (bs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 141.8, 137.1, 128.5, 128.2, 127.4, 126.6, 126.6, 121.8, 119.4, 119.0, 114.4, 109.2, 66.4, 45.5, 32.7.



2-(1-Ethyl-1H-indol-3-yl)-2-phenylethan-1-ol (23). Starting from 56.5 μL of **2a** (0.5 mmol), 181 μL of 1-ethylindole (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **23** (95.4 mg, 0.36 mmol, 72% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3).

23. ^1H NMR (300 MHz, CDCl_3) δ 7.55 (dt, $J = 8.0, 1.0$ Hz, 1H), 7.45–7.36 (m, 5H), 7.32–7.26 (m, 2H), 7.16–7.07 (m, 2H), 4.56 (t, $J = 6.8$ Hz, 1H), 4.31–4.16 (m, 4H), 1.81 (s, 1H), 1.53 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 141.9, 136.2, 128.5, 128.3, 127.6, 126.6, 124.9, 121.7, 119.5, 118.9, 114.5, 109.3, 66.5, 45.6, 40.9, 15.4.

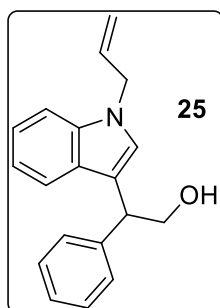
HRMS (ESI-TOF) m/z : calcd. for $\text{C}_{18}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: 266.1547, found: 266.1539.



2-(1-Pentyl-1H-indol-3-yl)-2-phenylethan-1-ol (24). Starting from 56.5 μL of **2a** (0.5 mmol), 170 μL of 1-pentylindole (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **24** (120.0 mg, 0.39 mmol, 80% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3).

24. ^1H NMR (300 MHz, CDCl_3) δ 7.50 (d, $J = 7.9$ Hz, 1H), 7.41–7.33 (m, 5H), 7.29–7.22 (m, 2H), 7.13–7.03 (m, 2H), 4.53 (t, $J = 6.8$ Hz, 1H), 4.32–4.18 (m, 2H), 4.12 (t, $J = 7.2$ Hz, 2H), 1.88 (p, $J = 7.3$ Hz, 2H), 1.69 (s, 1H), 1.42–1.36 (m, 4H), 0.98–0.91 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 141.8, 136.5, 128.5, 128.2, 127.5, 126.6, 125.6, 121.6, 119.4, 118.8, 114.2, 109.4, 66.4, 46.3, 45.5, 29.9, 29.1, 22.2, 13.9.

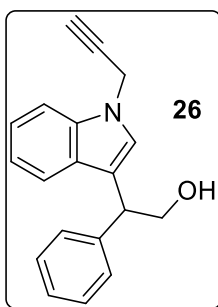
HRMS (ESI-TOF) m/z : calcd. for $\text{C}_{21}\text{H}_{26}\text{NO}$ $[\text{M}+\text{H}]^+$: 308.2016, found: 308.2020.



2-(1-Allyl-1H-indol-3-yl)-2-phenylethan-1-ol (25). Starting from 56.5 μL of **2a** (0.5 mmol), 190 μL of 1-allylindole (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **25** (77.6 mg, 0.28 mmol, 56% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3).

25. ^1H NMR (300 MHz, CDCl_3) δ 7.39 (d, $J = 7.9$ Hz, 1H), 7.31–7.21 (m, 5H), 7.20–7.09 (m, 3H), 6.97 (d, $J = 5.3$ Hz, 1H), 5.92 (dtt, $J = 16.8, 11.1, 5.2$ Hz, 1H), 5.16–5.02 (m, 2H), 4.80–4.58 (m, 2H), 4.42 (t, $J = 6.8$ Hz, 1H), 4.32–4.02 (m, 2H), 1.51 (bs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 141.6, 136.6, 133.4, 128.5, 128.2, 127.6, 126.6, 121.8, 119.4, 119.1, 117.3, 114.7, 109.6, 66.4, 48.7, 45.5.

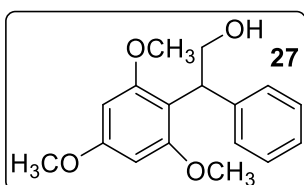
HRMS (ESI-TOF) m/z : calcd. for $\text{C}_{19}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: 278.1547, found: 278.1537.



2-(1-Propargyl-1H-indol-3-yl)-2-phenylethan-1-ol (26). Starting from 56.5 μL of **2a** (0.5 mmol), 194 μL of 1-propargylindole (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **26** (74.3 mg, 0.27 mmol, 54% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3).

26. ^1H NMR (300 MHz, CDCl_3) δ 7.61 (d, $J = 7.9$ Hz, 1H), 7.55–7.37 (m, 7H), 7.28–7.17 (m, 2H), 4.96 (d, $J = 2.7$ Hz, 2H), 4.62 (t, $J = 6.7$ Hz, 1H), 4.40–4.26 (m, 2H), 2.54 (q, $J = 2.7$ Hz, 1H), 1.97 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 141.6, 136.3, 128.6, 128.3, 127.9, 126.7, 125.0, 122.2, 119.6, 115.6, 109.4, 77.8, 73.6, 66.4, 45.6, 35.7.

HRMS (ESI-TOF) m/z : calcd. for $\text{C}_{19}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: 276.1390, found: 276.1386.

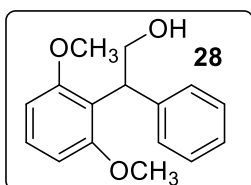


2-Phenyl-2-(2,4,6-trimethoxyphenyl)ethan-1-ol (27). Starting from 56.5 μL of **2a** (0.5 mmol), 210 mg of 1,3,5-trimethoxybenzene (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%) in 500 μL of DMC. Product **27** (126.7 mg, 0.44 mmol, 88% yield, colourless solid) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3). Spectroscopic data

were in accordance with the literature.^{S8}

27. ^1H NMR (300 MHz, CDCl_3) δ 7.27–7.15 (m, 4H), 7.12–7.03 (m, 1H), 6.09 (s, 2H), 4.75 (t, $J = 7.3$ Hz, 1H), 4.23 (d, $J = 7.3$ Hz, 2H), 3.74 (s, 3H), 3.67 (s, 6H), 1.74 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 160.0, 159.4, 142.4, 128.0, 127.9, 125.6, 110.5, 91.2, 64.8, 55.7, 55.2, 43.2.

$m. p.$ = 80.3–80.9 $^\circ\text{C}$ (lit.^{S8} = 80.0–81.0)

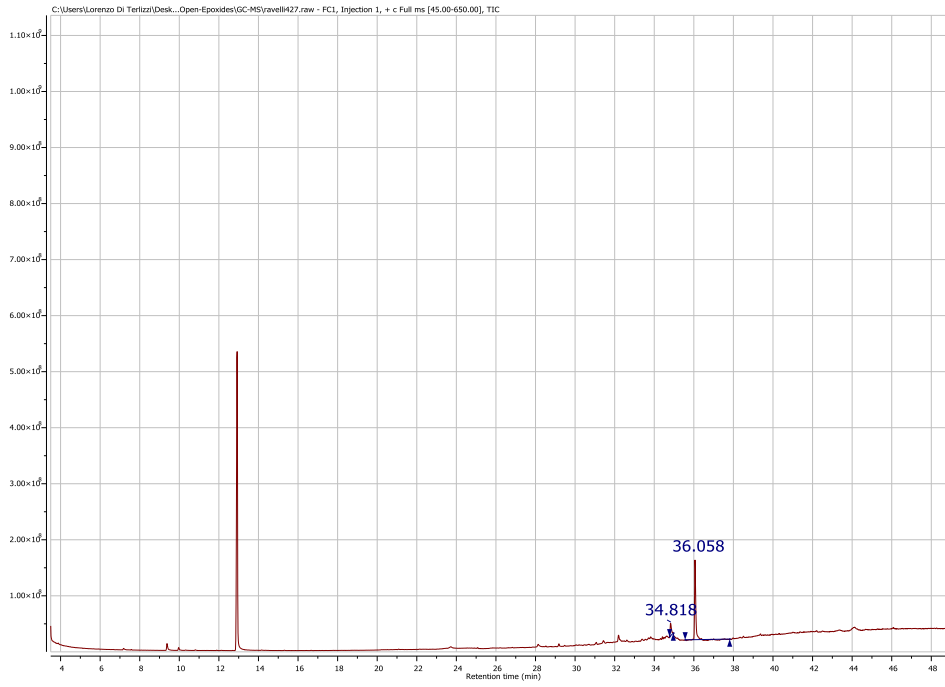


2-(2,6-Dimethoxyphenyl)-2-phenylethan-1-ol (28). Starting from 56.5 μL of **2a** (0.5 mmol), 163 μL of 1,3-dimethoxybenzene (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **28** (100.6 mg, 0.39 mmol, 78% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 8:2). Traces of another isomer (<5%) was detected by NMR analysis. GC-

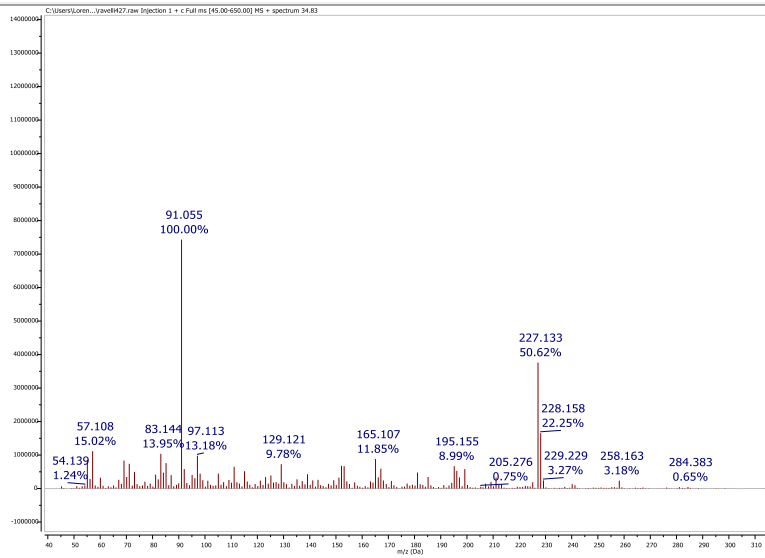
MS analysis of the crude mixture showed that the byproduct has the same molecular weight of **28** (see below).

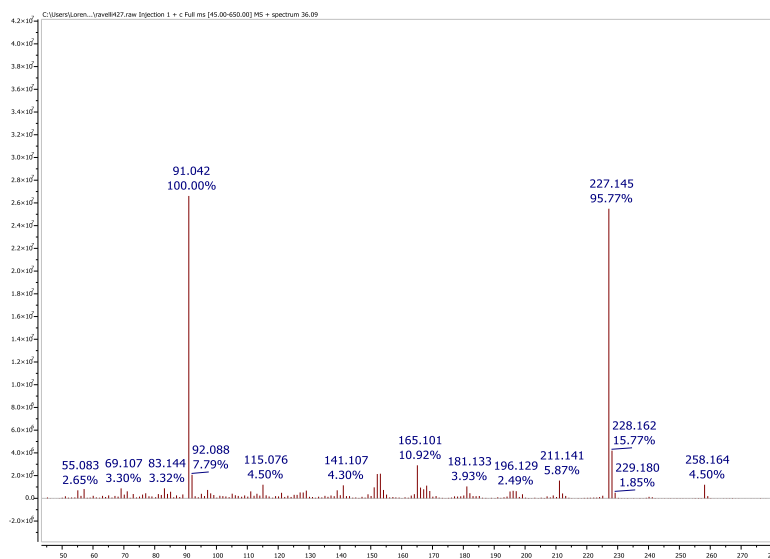
28. ^1H NMR (300 MHz, CDCl_3) δ 7.36–7.26 (m, 5H), 7.13–7.07 (m, 1H), 6.51 (s, 2H), 4.61 (t, $J = 7.2$ Hz, 1H), 4.15 (dd, $J = 7.2, 1.3$ Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 1.83 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 159.5, 158.3, 141.7, 128.6, 128.4, 126.3, 122.2, 104.1, 98.8, 65.3, 55.4, 55.2, 45.9.

HRMS (ESI-TOF) m/z : calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 259.1354, found: 281.1153

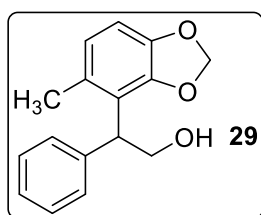


RT	Scan	Type	Height	Area	Total Height %	Total Area %	Start time	
1	36.1	2229	BB	141536598	9865949	92.71	96.13	35.9
2	34.8	2144	BB	11132817	397694	7.29	3.87	34.7



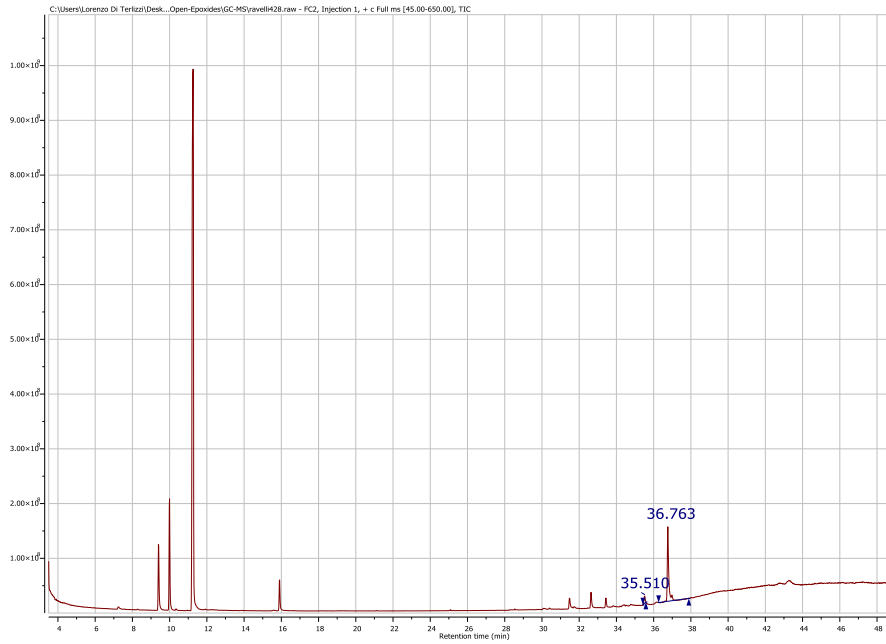


GC-MS trace of the crude reaction mixture (Up). GC-MS analysis of product **28** (retention time 36.0 min, middle) and its regioisomer (retention time 34.8 min, down).

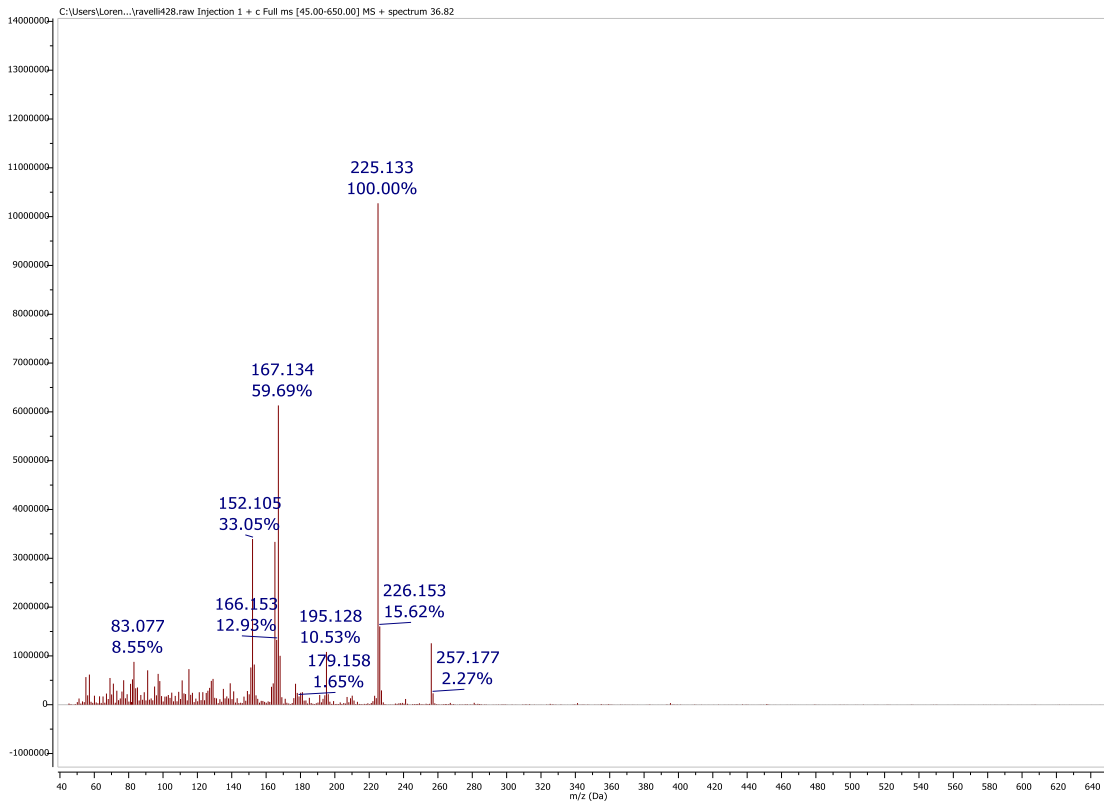


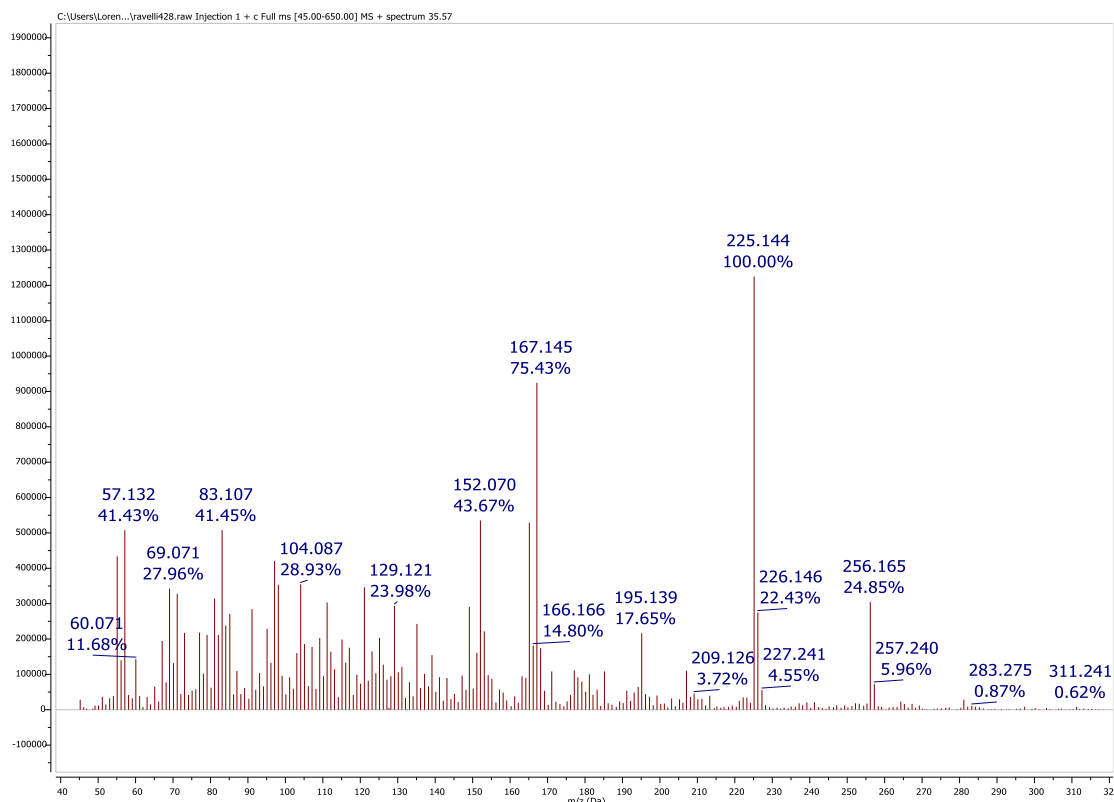
2-(2,6-Dimethoxyphenyl)-2-phenylethan-1-ol (29). Starting from 56.5 μL of **2a** (0.5 mmol), 150 μL of 5-methylbenzo[*d*][1,3]dioxole (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **29** (76.8 mg, 0.30 mmol, 60% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 8:2). Traces of a minor regioisomer (<2%) were detected by NMR analysis. GC-MS analysis of the crude mixture showed that the byproduct has the same molecular weight of **29** (see below).

29. ^1H NMR (300 MHz, CDCl_3) δ 7.32–7.23 (m, 5H), 6.86 (s, 1H), 6.69 (s, 1H), 5.93 (s, 2H), 4.35 (t, $J = 7.1$ Hz, 1H), 4.11 (dd, $J = 7.1, 1.4$ Hz, 2H), 2.22 (s, 3H), 1.66 (s, 1H). ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 145.9, 145.8, 141.0, 132.1, 130.2, 128.6, 128.2, 126.6, 110.9, 107.1, 100.7, 65.9, 49.0, 19.7. HRMS (ESI-TOF) m/z : calcd. for $\text{C}_{16}\text{H}_{17}\text{O}_3$ $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$: 239.1078, found: 239.1065.

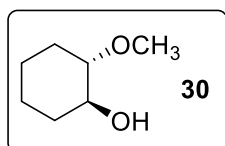


RT	Scan	Type	Height	Area	Total Height %	Total Area %	Start time	
1	36.8	2276	BB	136904609	18038800	91.95	95.70	35.8
2	35.5	2190	BB	11988467	811090	8.05	4.30	35.4





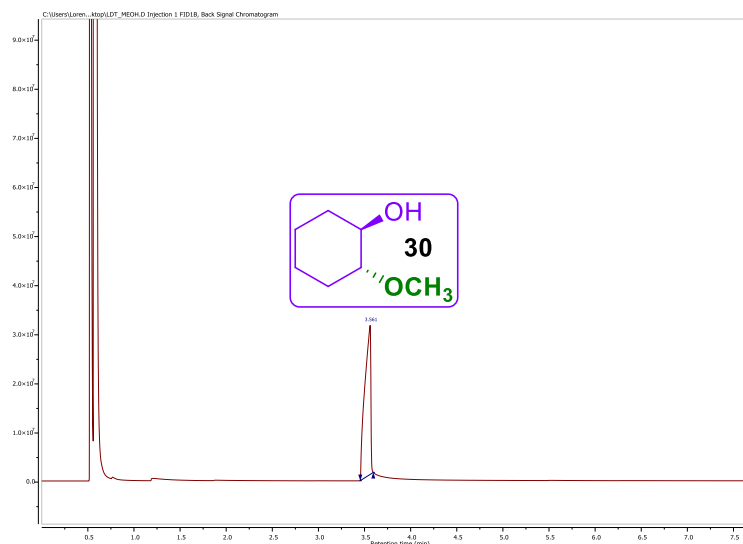
GC-MS trace of the crude reaction mixture (Up). GC-MS analysis of product **29** (retention time 36.8 min, middle) and its regioisomer (retention time 35.5 min, down).



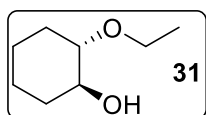
2-Methoxycyclohexan-1-ol (30). Starting from 50.0 μL of **2b** (0.5 mmol), 55 μL of methanol (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%).

Product **30** (65.5 mg, 0.5 mmol, >99% yield, colourless oil, *trans* isomer) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1) as the only diastereoisomer (see also the chromatogram of the crude mixture below). Spectroscopic data were in accordance with the literature.^{S19}

30. ^1H NMR (300 MHz, CDCl_3) δ 3.33–3.25 (m, 5H), 2.82 (ddd, $J = 10.4, 8.5, 4.3$ Hz, 1H), 2.09–1.93 (m, 1H), 1.93–1.80 (m, 1H), 1.67–1.49 (m, 2H), 1.21–0.92 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 84.7, 73.3, 56.1, 32.0, 28.2, 23.9, 23.7.



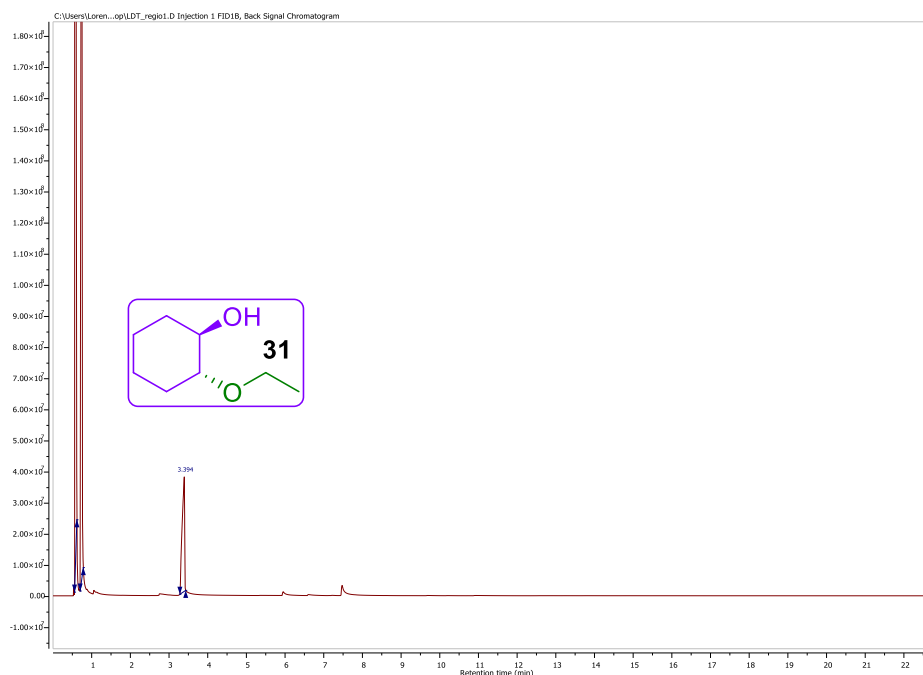
GC-MS trace of the crude reaction mixture.



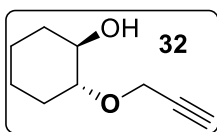
2-Methoxycyclohexan-1-ol (31). Starting from 50.0 μL of **2b** (0.5 mmol), 73 μL of ethanol (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%).

Product **31** (72.1 mg, 0.5 mmol, >99% yield, colourless oil, *trans* isomer) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1) as the only diastereoisomer (see also the chromatogram of the crude mixture below). Spectroscopic data were in accordance with the literature.^{S19}

31. ¹H NMR (300 MHz, CDCl₃) δ 4.35–4.31 (m, 2H), 3.67 (dq, $J = 9.3, 7.0$ Hz, 1H), 3.45–3.31 (m, 2H), 3.12–2.84 (m, 1H), 2.12–1.83 (m, 2H), 1.67–1.63 (m, 2H), 1.26–1.17 (m, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 83.2, 73.5, 63.9, 31.9, 29.1, 24.2, 23.8, 15.5.



GC-MS trace of the crude reaction mixture.

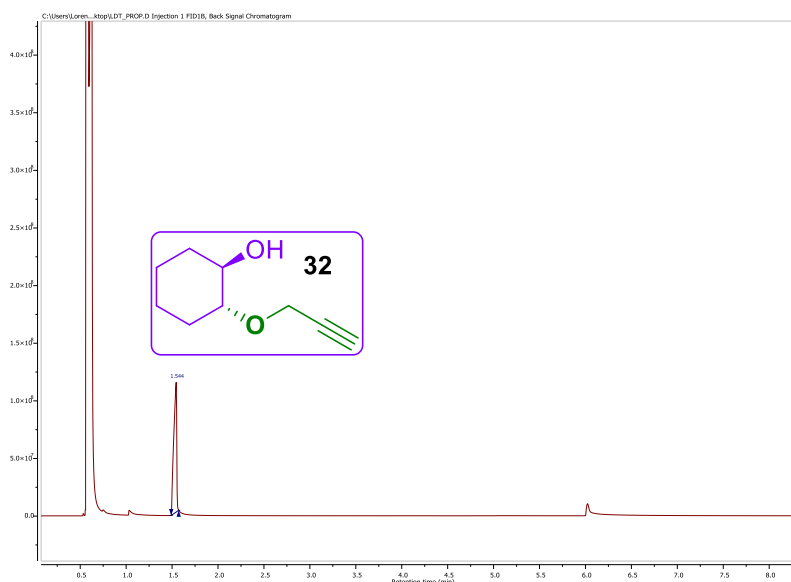


2-(Prop-2-yn-1-yloxy)cyclohexan-1-ol (32). Starting from 50 μL of **2b** (0.5 mmol), 73 μL of propargyl alcohol (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Product **32** (75.4 mg, 0.5 mmol, >99% yield, pale yellow

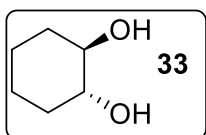
oil, *trans* isomer) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1) as the only diastereoisomer (see also the chromatogram of the crude mixture below).

32. ^1H NMR (CDCl_3 , 300 MHz) δ 4.30 (dd, $J = 15.8, 2.4$ Hz, 1H), 4.19 (dd, $J = 15.9, 2.4$ Hz, 1H), 3.44 (ddd, $J = 10.3, 8.4, 4.6$ Hz, 1H), 3.25 (ddd, $J = 10.3, 8.5, 4.4$ Hz, 1H), 2.79 (s, 1H), 2.45 (t, $J = 2.4$ Hz, 1H), 2.18–1.91 (m, 2H), 1.71 (tt, $J = 8.6, 2.6$ Hz, 2H), 1.31–1.13 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 82.9, 80.2, 74.2, 73.4, 56.0, 32.0, 28.8, 24.0, 23.7.

HRMS (ESI-TOF) m/z : calcd. for $\text{C}_9\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 155.1074, found: 155.1078.



GC-MS trace of the crude reaction mixture.



Cyclohexane-1,2-diol (33). Starting from 50.0 μL of **2b** (0.5 mmol), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC: H_2O (1:1) solution. Product **33** (58.8 mg, 0.5 mmol, >99% yield, colorless solid, *trans* isomer) was isolated in

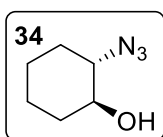
satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum.

The same reaction was performed on a larger scale employing 500 μL of **2b** (5 mmol), 49.5 mg of **1a** (0.25 mmol, 5 mol%) dissolved in 1.0 mL of a DMC:water (1:1) solution. Product **33** (588 mg, 5.0 mmol, >99% yield) was isolated as above. The same reaction was performed in flow employing 2.0 mL of **2b** (20 mmol), 198 mg of **1a** (1 mmol, 5 mol%) and 4 mL of a DMC:water (1:1) solution. Product **33** (2.32 g, 20 mmol, >99% yield) was collected in the Erlenmeyer flask after 6 h of

irradiation and obtained as a pure solid after the removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S20}

33. ¹H NMR (300 MHz, CDCl₃) δ 4.27 (s, 2H), 3.34–3.25 (m, 2H), 1.97–1.87 (m, 2H), 1.70–1.61 (m, 2H), 1.21 (t, *J* = 6.4 Hz, 4H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 75.4, 32.8, 24.2.

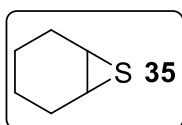
m. p. = 100–103 °C (lit.^{S21} 102–103 °C).



2-Azidocyclohexan-1-ol (34). Starting from 100 μL of **2b** (1 mmol), 162.5 mg of sodium azide (2.5 mmol, 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution.

Product **34** (141.5 mg, 1.0 mmol, >99% yield, colorless solid, *trans* isomer) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S22}

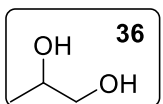
34. ¹H NMR (300 MHz, CDCl₃) δ 3.51–3.29 (m, 1H), 3.25–2.97 (m, 1H), 2.64 (s, 1H), 2.11–1.91 (m, 2H), 1.74 (dd, *J* = 6.2, 3.1 Hz, 2H), 1.28 (d, *J* = 1.3 Hz, 4H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 73.4, 67.0, 32.9, 29.7, 24.1, 23.7.



7-Thiabicyclo[4.1.0]heptane (35). Starting from 50.0 μL of **2b** (0.5 mmol), 120 mg of KSCN (1.25 mmol 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **35** (57.0 mg, 0.5 mmol, 99% yield,

colourless oil) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S23}

35. ¹H NMR (300 MHz, CDCl₃) δ 3.27–3.14 (m, 2H), 2.16 (td, *J* = 5.4, 4.5, 2.4 Hz, 4H), 1.60–1.49 (m, 2H), 1.24 (s, 2H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 36.9, 25.7, 19.3.

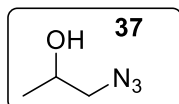


Propylene glycol (36). Starting from 17.7 μL of **2c** (0.5 mmol), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **36** (38.0

mg, 0.5 mmol, 99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. The same reaction was performed on a larger scale employing 177 μL of **2c** (5 mmol), 49.5 mg of **1a** (0.25 mmol, 5 mol%) dissolved in 1.0 mL of a DMC:H₂O (1:1) solution. Product **36** (380 mg, 5.0 mmol, >99% yield) was isolated as above.

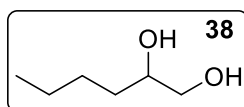
The same reaction was performed in flow employing 708 μL of **2c** (20 mmol), 198 mg of **1a** (1 mmol, 5 mol%) dissolved in 4.0 mL of a DMC:H₂O (1:1) solution. Product **36** (1.52 g, 20 mmol, >99% yield) was collected in the Erlenmeyer flask after 6 h of irradiation and obtained as a pure solid after the removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S24}

36. ^1H NMR (300 MHz, CDCl_3) δ 4.68–4.37 (m, 2H), 3.86–3.64 (m, 1H), 3.46 (ddd, $J = 11.4, 5.9, 3.1$ Hz, 1H), 3.27 (ddd, $J = 11.4, 7.7, 5.2$ Hz, 1H), 1.03 (d, $J = 6.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 68.1, 67.5, 18.5.



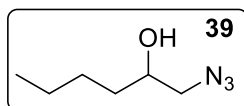
1-Azidopropan-2-ol (37). Starting from 17.7 μL of **2c** (0.5 mmol), 81.2 mg of sodium azide (1.25 mmol, 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **37** (50.5 mg, 0.5 mmol, >99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. The same reaction was performed on a larger scale employing 177 μL of **2c** (5 mmol), 813 mg of sodium azide (12.5 mmol, 2.5 equiv.), 49.5 mg of **1a** (0.25 mmol, 5 mol%) dissolved in 1.0 mL of a DMC:H₂O (1:1) solution. Product **37** (505 mg, 5.0 mmol, >99% yield) was isolated as above. Spectroscopic data were in accordance with the literature.^{S25}

37. ^1H NMR (300 MHz, CDCl_3) δ 3.87 (dtd, $J = 7.1, 6.3, 3.8$ Hz, 1H), 3.34–3.03 (m, 2H), 2.91 (bs, 1H), 1.12 (d, $J = 6.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 66.3, 57.8, 19.8.



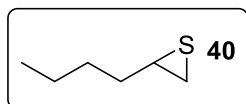
Hexane-1,2-diol (38). Starting from 61.7 μL of **2d** (0.5 mmol), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **38** (59.0 mg, 0.5 mmol, 99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S11}

38. ^1H NMR (300 MHz, CDCl_3) δ 4.04 (s, 2H), 3.69–3.41 (m, 2H), 3.28 (dd, $J = 11.3, 7.9$ Hz, 1H), 1.37–1.13 (m, 6H), 0.79 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 72.2, 66.6, 32.6, 27.7, 22.6, 13.9.



1-Azidohexan-2-ol (39). Starting from 61.7 μL of **2d** (0.5 mmol), 81.2 mg of sodium azide (1.25 mmol, 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **39** (70.2 mg, 0.5 mmol, >99% yield, pale yellow oil) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. The same reaction was performed on a larger scale employing 617 μL of **2d** (5 mmol), 813 mg of sodium azide (12.5 mmol, 2.5 equiv.), 49.5 mg of **1a** (0.25 mmol, 5 mol%) dissolved in 1 mL of a DMC:H₂O (1:1) solution. Product **39** (715 mg, 5.0 mmol, >99% yield) was isolated as above. Spectroscopic data were in accordance with the literature.^{S26}

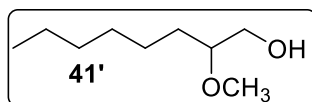
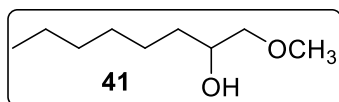
39. ^1H NMR (300 MHz, CDCl_3) δ 3.79–3.73 (m, 1H), 3.38 (dd, $J = 12.4, 3.4$ Hz, 1H), 3.25 (dd, $J = 12.4, 7.3$ Hz, 1H), 2.25 (bs, 1H), 1.53–1.32 (m, 6H), 0.92 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 70.7, 57.0, 33.9, 27.5, 22.5, 13.8.



2-Butylthiirane (40). Starting from 61.7 μL of **2d** (0.5 mmol), 120 mg of KSCN (1.25 mmol 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved

in 100 μL of a DMC:H₂O (1:1) solution. Product **40** (58.0 mg, 0.5 mmol, >99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S23}

40. ^1H NMR (300 MHz, CDCl_3) δ 2.89 (q, $J = 6.1$ Hz, 1H), 2.50 (d, $J = 6.3$ Hz, 1H), 2.15 (d, $J = 5.7$ Hz, 1H), 1.52–1.34 (m, 6H), 0.93 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 36.2, 35.9, 31.4, 25.8, 22.2, 13.9.

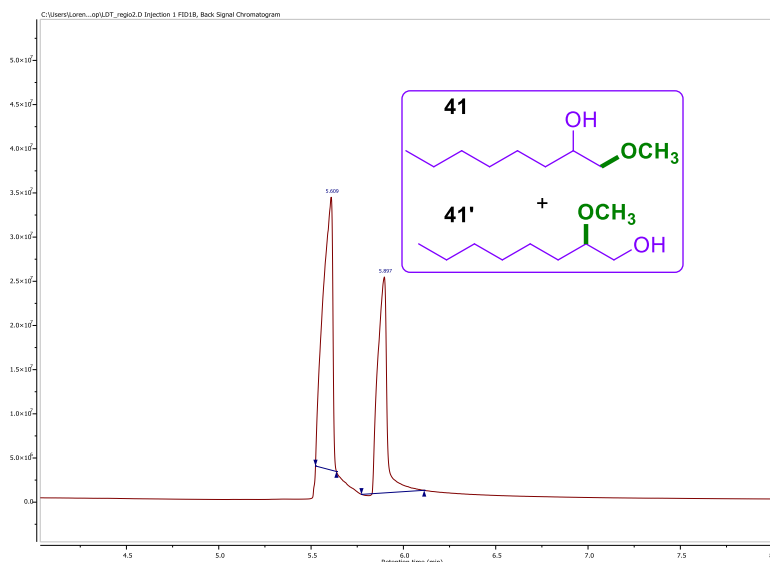


Ring opening of 1,2-epoxyoctane 2e with methanol. Compound **41** and **41'** were

obtained starting from 76.0 μL of **2e** (0.5 mmol), 55 μL of methanol (1.25 mmol, 2.5 equiv.) and 4.9 mg of **1a** (0.025 mmol, 5 mol%). Compounds **41** (40.1 mg, 0.25 mmol, 50% yield) and **41'** (34.4 mg, 0.22 mmol, 43% yield) were isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1) both as colourless oils (see the chromatogram of the crude mixture below). The same reaction performed with 64.0 μL of **2e** (0.5 mmol), 55 μL of methanol (1.25 mmol, 2.5 equiv.) and 6.9 mg of **1b** (0.025 mmol, 5 mol%) afforded **41** and **41'** respectively in 70% and 30% yield as determined by GC analysis. Spectroscopic data for **41** and **41'** were in accordance with the literature.^{S27}

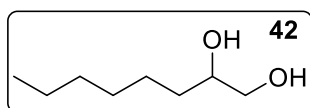
41. ^1H NMR (300 MHz, CDCl_3) δ 3.81–3.76 (m, 1H), 3.44–3.40 (m, 4H), 3.25 (dd, $J = 9.5, 7.9$ Hz, 1H), 2.32 (s, 1H), 1.47–1.40 (m, 2H), 1.34–1.30 (m, 8H), 0.95–0.85 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 79.0, 70.2, 58.9, 33.0, 31.6, 29.2, 25.4, 22.5, 13.9.

41'. ^1H NMR (300 MHz, CDCl_3) δ 3.76–3.66 (m, 1H), 3.53–3.46 (m, 1H), 3.42 (s, 3H), 3.33–3.23 (m, 1H), 1.99 (s, 1H), 1.62–1.38 (m, 2H), 1.33–1.29 (m, 8H), 0.95–0.85 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 81.5, 63.9, 56.9, 31.6, 30.2, 29.4, 25.2, 22.5, 13.9.



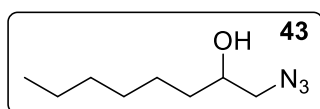
RT	Scan	Type	Height	Area	Total Height %	Total Area %	Start time	
1	5.90	7010	BB	24442789	1436482	44.17	42.84	5.77
2	5.61	6667	BB	30897300	1917021	55.83	57.16	5.52

GC-MS trace of the crude reaction mixture.



Octane-1,2-diol (42). Starting from 76.0 μL of **2e** (0.5 mmol), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **42** (73.0 mg, 0.5 mmol, >99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S11}

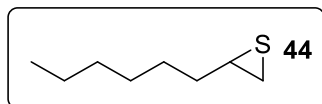
42. ¹H NMR (300 MHz, CDCl₃) δ 3.97 (s, 2H), 3.71–3.52 (m, 2H), 3.37 (dd, $J = 11.3, 7.8$ Hz, 1H), 1.49–1.18 (m, 10H), 0.97–0.73 (m, 3H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 72.2, 66.6, 32.9, 31.7, 29.3, 25.5, 22.5, 13.9.



2-Azido-octan-1-ol (43). Starting from 76.0 μL of **2e** (0.5 mmol), 81.2 mg of sodium azide (1.25 mmol, 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **43** (85.2 mg, 0.5 mmol, >99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. The same reaction was performed on a larger scale employing 760 μL of **2e** (5 mmol), 813 mg of sodium azide (12.5 mmol, 2.5 equiv.), 49.5 mg of **1a** (0.25 mmol, 5 mol%) dissolved in 400 μL of a DMC:H₂O (1:1) solution. Product **43** (850 mg, 5.0 mmol, >99% yield) was isolated as above.

43. ^1H NMR (300 MHz, CDCl_3) δ 3.82–3.74 (m, 1H), 3.40 (dd, $J = 12.4, 3.4$ Hz, 1H), 3.27 (dd, $J = 12.4, 7.4$ Hz, 1H), 1.90 (bs, 1H), 1.53–1.45 (m, 2H), 1.35–1.29 (m, 8H), 0.95–0.86 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 70.8, 57.0, 34.2, 31.6, 29.1, 25.3, 22.5, 14.0.

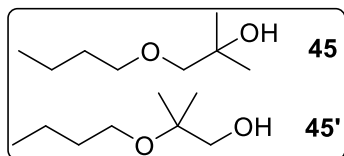
HRMS (ESI-TOF) m/z : calcd. for $\text{C}_8\text{H}_{19}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 172.1452, found: 172.1448.



2-Hexylthiirane (44). Starting from 76.0 μL of **2e** (0.5 mmol), 120 mg of KSCN (1.25 mmol 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%)

dissolved in 100 μL of a DMC: H_2O (1:1) solution. Product **44** (72.0 mg, 0.5 mmol, >99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S23}

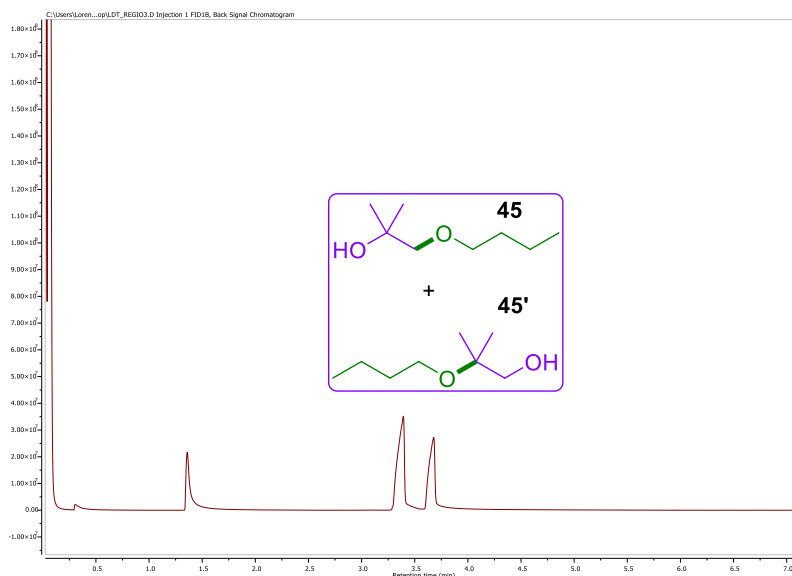
44. ^1H NMR (300 MHz, CDCl_3) δ 2.89 (q, $J = 6.2$ Hz, 1H), 2.50 (d, $J = 6.3$ Hz, 1H), 2.15 (d, $J = 5.7$ Hz, 1H), 1.54–1.48 (m, 2H), 1.36–1.27 (m, 8H), 0.89 (t, $J = 6.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 36.5, 36.0, 31.6, 29.2, 28.8, 25.8, 22.5, 14.0.



Ring opening of isobutene oxide 2f with n-butanol. Starting from 88.0 μL of **2f** (1.0 mmol), 228 μL of butanol (2.5 mmol, 2.5 equiv.) and 9.9 mg of **1a** (0.05 mmol, 5 mol%). The two regioisomers **45**^{S28} and

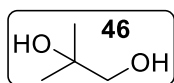
45'^{S29} (146.0 mg, 1.0 mmol, >99% yield in a 1:1 ratio, see the chromatogram below) were isolated as an inseparable mixture by treatment with MgSO_4 , filtration and removal of the solvent under vacuum.

^1H NMR (300 MHz, CDCl_3 of the mixture) δ 3.64–3.29 (m, 3H + 3H), 3.24 (s, 1H + 1H), 2.19 (s, 1H), 1.70–1.43 (m, 2H + 2H), 1.42–1.28 (m, 2H + 2H), 1.21–1.14 (m, 13H), 0.98–0.90 (m, 3H + 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 of the mixture) δ 74.9, 74.7, 68.9, 67.4, 61.4, 32.3, 22.5, 22.0, 19.3, 19.2, 13.8.



	RT	Scan	Type	Height	Area	Total Height %	Total Area %	Start time
1	3.68	4939	BB	26789039	1784046	47.16	51.76	3.56
2	3.39	4600	BB	30011677	1662510	52.84	48.24	3.31

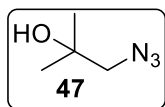
GC-MS trace of the crude reaction mixture.



2-Methylpropane-1,2-diol (46). Starting from 88.0 μL of **2f** (1.0 mmol), 9.9 mg of **1a** (0.05 mmol, 5 mol%) dissolved in 200 μL of a DMC:H₂O (1:1) solution. Product

46 (90.0 mg, 1.0 mmol, >99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S30}

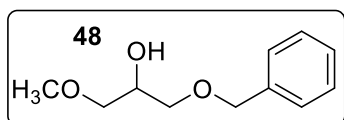
46. ¹H NMR (300 MHz, CDCl₃) δ 3.90 (s, 2H), 3.38 (s, 2H), 1.17 (s, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 71.2, 70.6, 25.5.



1-Azido-2-methylpropan-2-ol (47). Starting from 88.0 μL of **2f** (1.0 mmol), 164.2 mg of sodium azide (2.5 mmol, 2.5 equiv.), 9.9 mg of **1a** (0.05 mmol, 5 mol%)

dissolved in 200 μL of a DMC:H₂O (1:1) solution. Product **47** (115.0 mg, 1.0 mmol, >99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S31}

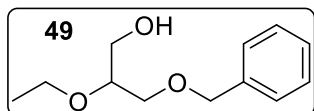
47. ¹H NMR (300 MHz, CDCl₃) δ 3.26 (s, 2H), 2.01 (s, 1H), 1.26 (s, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 70.8, 62.0, 26.7.



1-(Benzyloxy)-3-methoxypropan-1-ol (48). Starting from 77.0 μL of **2g** (0.5 mmol), 51 μL of MeOH and 4.9 mg of **1a** (0.025 mmol, 5

mol%). Product **48** (98.0 mg, 0.5 mmol, >99% yield, pale yellow oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 9:1). (Spectroscopic data were in accordance with the literature.^{S32}

48. ¹H NMR (300 MHz, CDCl₃) δ 7.47–7.20 (m, 5H), 4.58 (s, 2H), 4.16–3.87 (m, 1H), 3.55 (dd, *J* = 7.5, 5.5 Hz, 2H), 3.47 (t, *J* = 5.3 Hz, 2H), 3.40 (s, 3H), 2.54 (s, 1H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 137.9, 128.3, 127.7, 127.6, 73.7, 73.4, 71.2, 69.4, 59.1.



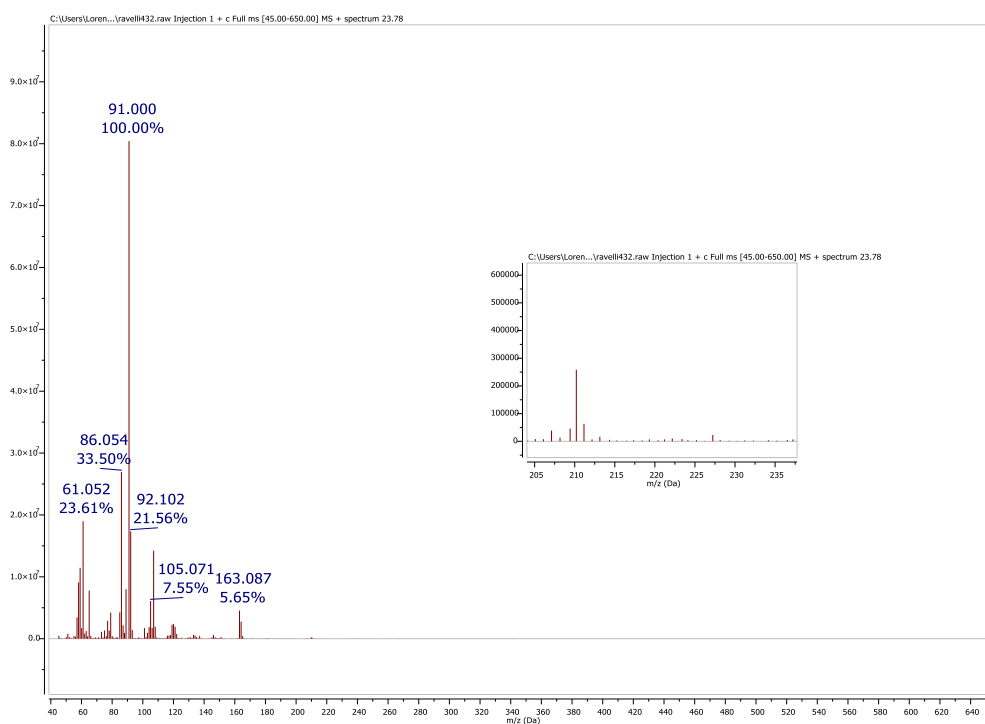
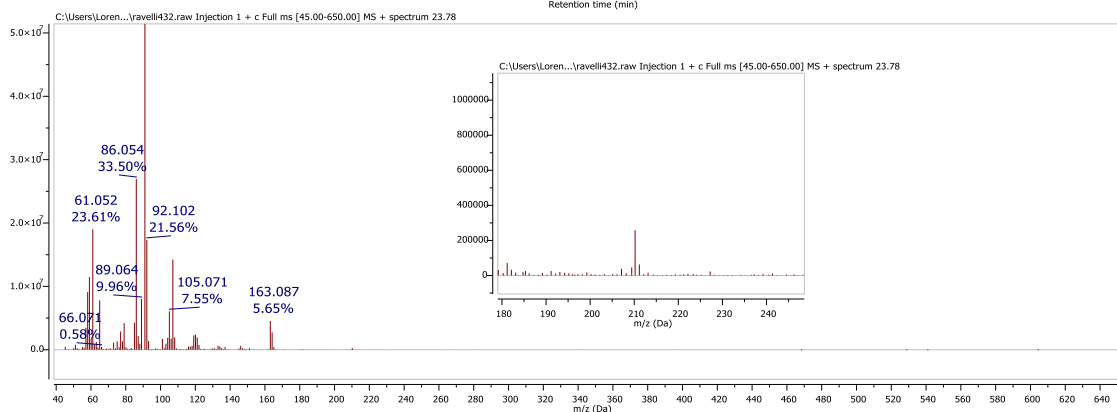
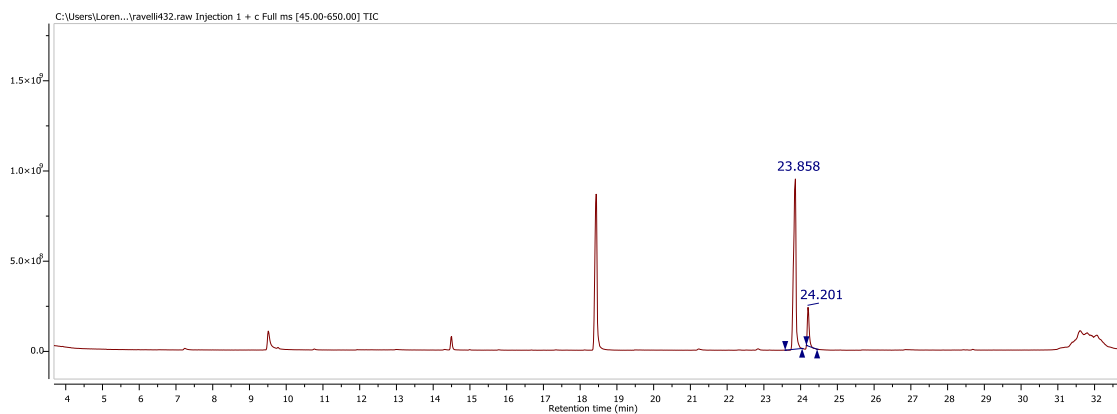
1-(Benzyloxy)-3-ethoxypropan-2-ol (49). Starting from 77.0 μL of **2g** (0.5 mmol), 73 μL of EtOH and 4.9 mg of **1a** (0.025 mmol, 5 mol%).

Product **49** (105.1 mg, 0.5 mmol, >99% yield, pale yellow oil) was isolated by flash column chromatography). NMR analyses pointed out the presence of 2-(benzyloxy)-3-ethoxypropan-1-ol as the minor regioisomer (<5%). GC-MS analysis of the crude mixture showed that the byproduct has the same molecular weight of **49** (see below).

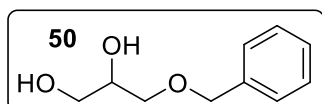
49. ¹H NMR (300 MHz, CDCl₃) δ 7.41–7.34 (m, 5H), 4.58 (s, 2H), 4.20–3.89 (m, 1H), 3.59–3.47 (m, 6H), 2.65 (s, 1H), 1.22 (t, *J* = 7.0 Hz, 3H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 137.9, 128.3, 127.6, 127.5, 73.3, 71.5, 71.3, 69.4, 66.7, 15.0.

HRMS (ESI-TOF) *m/z*: calcd. for C₁₂H₁₈O₃Na [M+Na]⁺: 233.1154, found: 233.1144.

	RT	Scan	Type	Height	Area	Total Height %	Total Area %	Start time
1	24.2	1418	BB	157286291	6411399	14.26	7.93	24.1
2	23.9	1394	BB	945969855	74435040	85.74	92.07	23.7



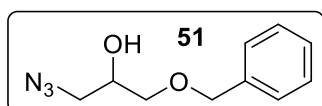
GC-MS trace of the crude reaction mixture (Up). GC-MS analysis of product **49** (retention time 23.8 min, middle) and its regioisomer (retention time 24.2 min, down).



3-(Benzyloxy)propane-1,2-diol (50). Starting from 77.0 μL of **2g** (0.5 mmol), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **50** (91.0 mg, 0.5 mmol, >99% yield, colourless oil) was isolated

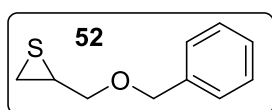
in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S33}

50. ¹H NMR (300 MHz, CDCl₃) δ 7.55–7.12 (m, 5H), 4.56 (s, 2H), 3.90 (td, *J* = 5.9, 2.9 Hz, 1H), 3.75–3.61 (m, 2H), 3.60–3.51 (m, 2H), 2.70 (s, 2H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 137.6, 128.4, 127.8, 127.7, 73.5, 71.7, 70.6, 63.9.



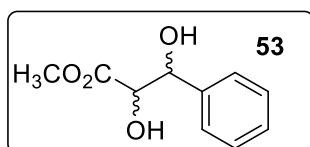
1-Azido-3-(benzyloxy)propan-2-ol (51). Starting from 77.0 μL of **2g** (0.5 mmol), 81.2 mg of sodium azide (1.25 mmol, 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **51** (98.0 mg, 0.46 mmol, 91% yield, pale yellow oil) was isolated by flash column chromatography (eluant Cyclohexane-Ethyl acetate 7:3). Spectroscopic data were in accordance with the literature.^{S34}

51. ¹H NMR (300 MHz, CDCl₃) δ 7.43–7.30 (m, 5H), 4.58 (d, *J* = 2.5 Hz, 2H), 3.99 (q, *J* = 4.9 Hz, 1H), 3.59–3.52 (m, 3H), 3.40 (dd, *J* = 5.5, 2.0 Hz, 1H), 2.57 (s, 1H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 137.5, 128.4, 127.7, 127.7, 73.5, 71.2, 69.6, 53.4.



2-((Benzyloxy)methyl)thiirane (52). Starting from 77.0 μL of **2g** (0.5 mmol), 120 mg of KSCN (1.25 mmol 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **52** (91.0 mg, 0.5 mmol, >99% yield, colourless oil) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S35}

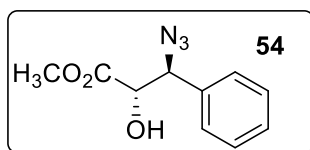
52. ¹H NMR (300 MHz, CDCl₃) δ 7.70–7.11 (m, 5H), 4.62 (s, 1H), 3.72 (dd, *J* = 10.6, 5.7 Hz, 1H), 3.52 (dd, *J* = 10.6, 6.7 Hz, 1H), 3.14 (ddd, *J* = 12.1, 6.7, 5.7 Hz, 1H), 2.55 (dt, *J* = 6.2, 1.3 Hz, 1H), 2.24 (dd, *J* = 5.3, 1.3 Hz, 1H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 137.8, 128.4, 127.7, 127.7, 74.6, 73.0, 32.1, 23.7.



Methyl 2,3-dihydroxy-3-phenylpropanoate (53). Starting from 178 μL of **2h** (1 mmol), 9.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 200 μL of a DMC:H₂O (1:1) solution. Product **53** (99.9 mg, 0.51 mmol, 51% yield) was isolated as a 1:1 mixture of diastereomers by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3). Spectroscopic data were in accordance with the literature.^{S36}

53. ¹H NMR (300 MHz, CDCl₃, of the mixture) δ 7.47–7.29 (m, 5H + 5H), 5.03 (t, *J* = 3.5 Hz, 1H + 1H), 4.51 (d, *J* = 4.3 Hz, 1H), 4.38 (d, *J* = 3.0 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.11 (bs, 2H + 2H).

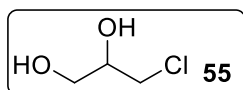
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , of the mixture) δ 173.1, 172.3, 139.8, 138.5, 129.4, 128.4, 128.2, 128.1, 128.0, 126.2, 126.1, 120.0, 74.9, 74.7, 52.8, 52.3.



Methyl 3-azido-2-hydroxy-3-phenylpropanoate (54). Starting from 178 μL of **2h** (1 mmol), 162.4 mg of sodium azide (2.5 mmol, 2.5 equiv.), 9.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 200 μL of a DMC:H₂O

(1:1) solution. Product **54** (41.9 mg, 0.19 mmol, 19% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3) as the *trans* isomer. Spectroscopic data were in accordance with the literature.^{S36}

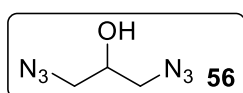
54. ^1H NMR (300 MHz, CDCl_3) δ 7.41–7.32 (m, 5H), 4.88 (d, $J = 4.0$ Hz, 1H), 4.72–4.13 (m, 1H), 3.72 (s, 3H), 2.93 (d, $J = 6.1$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 171.7, 134.2, 128.8, 128.6, 127.6, 73.7, 67.2, 52.6.



3-Chloropropane-1,2-diol (55). Starting from 39.0 μL of **2i** (0.5 mmol), 4.9 mg of **1a** (0.025 mmol, 5 mol%) dissolved in 100 μL of a DMC:H₂O (1:1)

solution. Product **55** (55.0 mg, 0.5 mmol, >99% yield, pale yellow oil) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S37}

55. ^1H NMR (300 MHz, CDCl_3) δ 3.91 (td, $J = 5.7, 3.7$ Hz, 1H), 3.77–3.72 (m, 1H), 3.68–3.55 (m, 3H), 3.28 (bs, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 71.7, 63.6, 45.7.

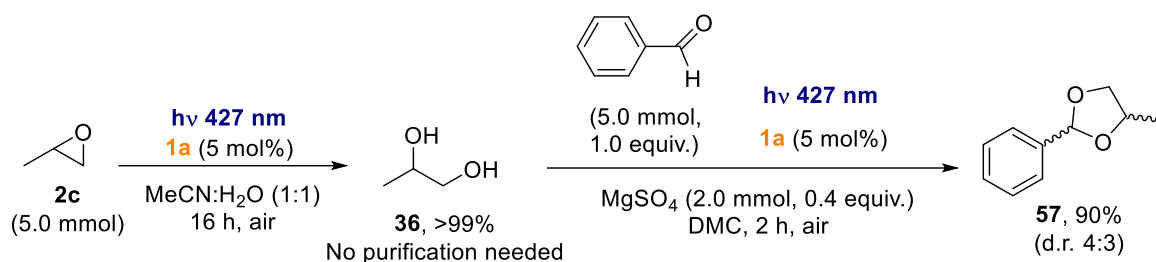


1,3-Diazidopropan-2-ol (56). Starting from 39.0 μL of **2i** (0.5 mmol), 81.2 mg of sodium azide (1.25 mmol, 2.5 equiv.), 4.9 mg of **1a** (0.025 mmol, 5 mol%)

dissolved in 100 μL of a DMC:H₂O (1:1) solution. Product **56** (71.0 mg, 0.5 mmol, >99% yield, pale yellow oil) was isolated in satisfying purity by treatment with MgSO_4 , filtration and removal of the solvent under vacuum. Spectroscopic data were in accordance with the literature.^{S38}

56. ^1H NMR (300 MHz, CDCl_3) δ 5.85 (bs, 1H), 4.03–3.82 (m, 1H), 3.45–3.31 (m, 4H), 3.27 (bs, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 69.5, 53.8.

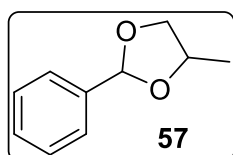
Post transformations.



Scheme S1. Telescopic synthesis of a 2-phenyl-4-methyl-1,3-dioxolane.

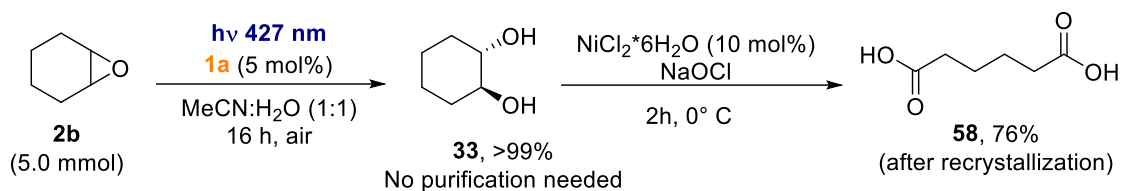
Telescopic synthesis of 2-phenyl-4-methyl-1,3-dioxolane 57 (Scheme S1). Propylene glycol **36** was prepared by irradiation of a solution of 88.5 μ L of **2c** (5 mmol), 49.9 mg of **1a** (0.025 mmol, 5 mol%) in 1 mL of a MeCN:H₂O (1:1). Product **36** (380.0 mg, 5.0 mmol, 99% yield) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum.

Diol **36** was mixed with 510 μ L of benzaldehyde (5 mmol, 1 equiv.), 240 mg of MgSO₄ (2 mmol, 0.4 equiv.) and 49.5 mg of **1a** (0.025 mmol, 5 mol%) in 8 mL of dimethyl carbonate and irradiated for 2 h under vigorous stirring.^{S39} The photolyzed mixture was concentrated under vacuum. Product **57** (738 mg, 4.5 mmol, 90% yield, colourless oil) was isolated by flash column chromatography (eluent Cyclohexane-Ethyl acetate 7:3) as a mixture of diastereoisomers in a (4:3) ratio. Spectroscopic data for **57** were in accordance with literature.^{S40}



4-Methyl-2-phenyl-1,3-dioxolane (**57**).

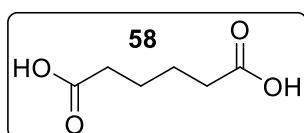
57 ¹H NMR (300 MHz, CDCl₃, of the mixture) δ 7.61–7.56 (m, 4H minor), 7.48–7.41 (m, 5H major), 6.04 (s, 1H minor), 5.88 (s, 1H major), 4.45–4.22 (m, 3H minor + major), 4.13 (dd, J = 7.5, 6.5 Hz, 1H minor), 3.61 (dt, J = 18.5, 7.5 Hz, 2H minor + major), 1.43 (d, J = 6.1 Hz, 3H major), 1.38 (d, J = 6.1 Hz, 3H minor). ¹³C {¹H} NMR (75 MHz, CDCl₃, of the mixture) δ 138.7, 138.1, 129.2, 129.0, 128.3, 126.6, 126.3, 104.0, 103.0, 73.3, 72.2, 71.9, 71.3, 18.5, 18.3.



Scheme S2. Telescopic synthesis of adipic acid.

Telescopic synthesis of adipic acid 58 (Scheme S2). 1,2-Cyclohexandiol **33** was synthesized by irradiation of a solution of 500 μL of **2b** (5 mmol), 49.5 mg of **1a** (0.025 mmol, 5 mol%) in 1 mL of a MeCN:H₂O (1:1). Product **33** (510.0 mg, 5 mmol, 99% yield) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum.

Diol **33** was dissolved in 1 mL of a DMC/water 1:1 mixture. To the so formed mixture, 36 mg of NiCl₂ hexahydrate were added and the mixture was cooled to 0 °C under vigorous stirring. Finally, 30 mL of bleach (5% aqueous sodium hypochlorite solution) were poured into the mixture while maintaining a vigorous stirring.^{S41} After 2 h the resulting solution was acidified with 2 M HCl and extracted with ether, dried over MgSO₄, concentrated under vacuum affording the crude product that was recrystallized from water yielding 555 mg of **58** (76% yield) as a white solid. Spectroscopic data were in accordance with the literature.^{S41}

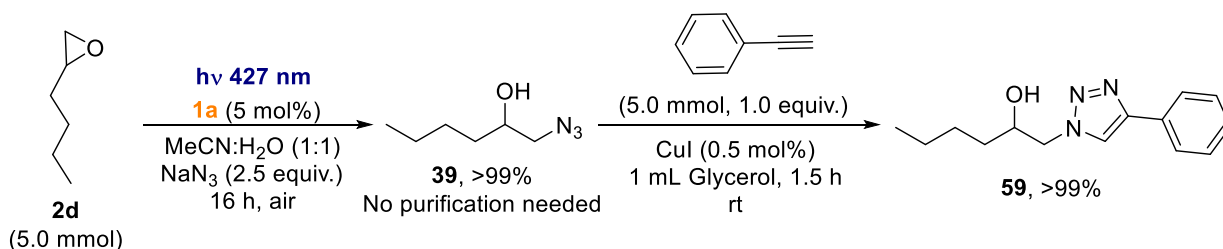


Adipic acid (58).^{S41}

58. ¹H NMR (300 MHz, DMSO-*d*₆) δ 11.81 (s, 2H), 2.24–2.10 (m, 4H), 1.54–1.40 (m, 4H). ¹³C{¹H} NMR (75 MHz, DMSO-*d*₆) δ 174.3, 33.3,

24.0.

m. p. (water) = 152–153 °C (lit.^{S39} = 153–154 °C).

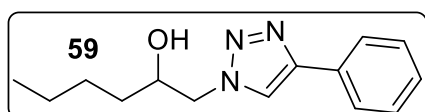


Scheme S3. Telescopic synthesis of substituted triazole **59**.

Telescopic synthesis of triazole 59 (Scheme S3). Compound **39** was synthesized by irradiation of a solution of 617 μL of **2d** (5 mmol), 813 mg of sodium azide (12.5 mmol, 2.5 equiv.), 49.5 mg of **1a**

(0.025 mmol, 5 mol%) in 400 μL of MeCN:H₂O (1:1. Product **39** (715 mg, 5 mmol, 99% yield) was isolated in satisfying purity by treatment with MgSO₄, filtration and removal of the solvent under vacuum.

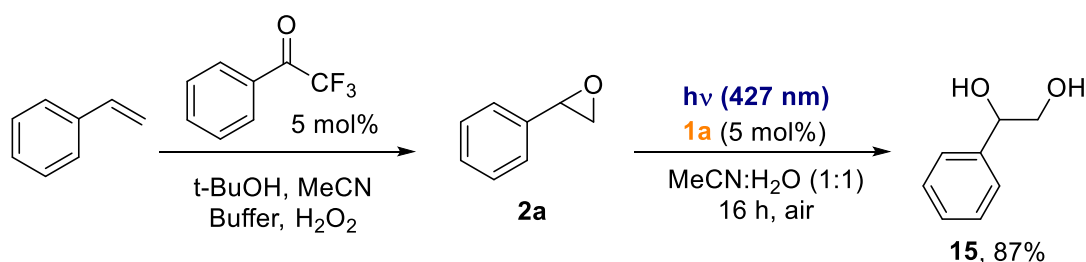
To the azido alcohol **39** obtained, 1 mL of glycerol, 548 μL of phenylacetylene and 4.8 mg of CuI were added. The so-formed mixture was stirred for 90 min at room temperature, quenched with 5 mL of H₂O, extracted with diethyl ether, dried over MgSO₄, filtrated and concentrated under vacuum. Product **59** (1.25 g, 5 mmol, >99% yield, colourless solid) was isolated by flash column chromatography (eluant Cyclohexane-Ethyl acetate 7:3). Spectroscopic data were in accordance with the literature.^{S42}



1-(4-Phenyl-1H-1,2,3-triazol-1-yl)hexan-2-ol (59).

59. ¹H NMR (300 MHz, CDCl₃) δ 7.81 (s, 1H), 7.68 (dd, J = 8.2, 1.5 Hz, 2H), 7.44–7.26 (m, 3H), 4.56–4.41 (m, 1H), 4.21 (dt, J = 16.8, 5.6 Hz, 2H), 3.74 (s, 1H), 1.69–1.35 (m, 6H), 0.94 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 147.1, 130.2, 128.7, 127.9, 125.4, 121.1, 70.3, 56.3, 34.1, 27.5, 22.4, 13.9.

m. p. = 92–93 °C (lit.^{S43} = 92–94 °C).



Scheme S4. Telescopic synthesis of diol **15**.

Telescopic synthesis of diol 15 (Scheme S4). Styrene (104 mg, 1.00 mmol) was placed in a round-bottom flask, followed by 2,2,2-trifluoro-1-phenylethanone (9.0 mg, 0.05 mmol). *tert*-butyl alcohol (1 mL), aqueous buffer solution (1 mL, 0.6 M K₂CO₃, 4 \times 10⁻⁴ M EDTA), acetonitrile (0.8 mL) and 30% aqueous H₂O₂ (1.8 mL) were added consecutively. The reaction mixture was allowed to stir for 2 h at room temperature. Then, the reaction mixture was diluted with H₂O (6 mL) and extracted with CHCl₃ (3 \times 6 mL). The combined organic layers were washed with H₂O (2 \times 6 mL), dried over anhydrous Na₂SO₄ and the solvent was removed *in vacuo*. (100% yield).^{S44} The resulting crude mixture was placed in a glass vial, followed by arylazo sulfones **1a** (9.9 mg, 0.05 mmol, 5 mol%) and acetonitrile:water (1:1, 0.5 mL). The vial was left stirring under blue LED bulb irradiation (427 nm) for 16 h. Product **15** (120 mg, 0.87 mmol, 87% yield, colourless solid) was isolated by flash column chromatography (eluant Cyclohexane-Ethyl acetate 7:3).

3. Mechanistic investigation.

Kinetic analyses. In a flame-dried vial, epoxide **2a** (113 μL , 1 mmol, 2 M, 1.0 equiv.) and methanol (100 μL , 2.5 mmol, 2.5 equiv.) were dissolved in DMC (500 μL as the final volume). Arylazo sulfone **1a** (0.05 mmol, 5 mol%) was then added and the so formed mixture was irradiated under vigorous stirring with a 40W 427 nm KESSIL Lamp. The irradiations were monitored at 15', 30', 60', 120', 180', 240', 480', 960' and each mixture was diluted 1:20 with a solution of DMC containing the standard (cyclododecane, 0.1 M) and analysed by GC-FID (Figure S7).

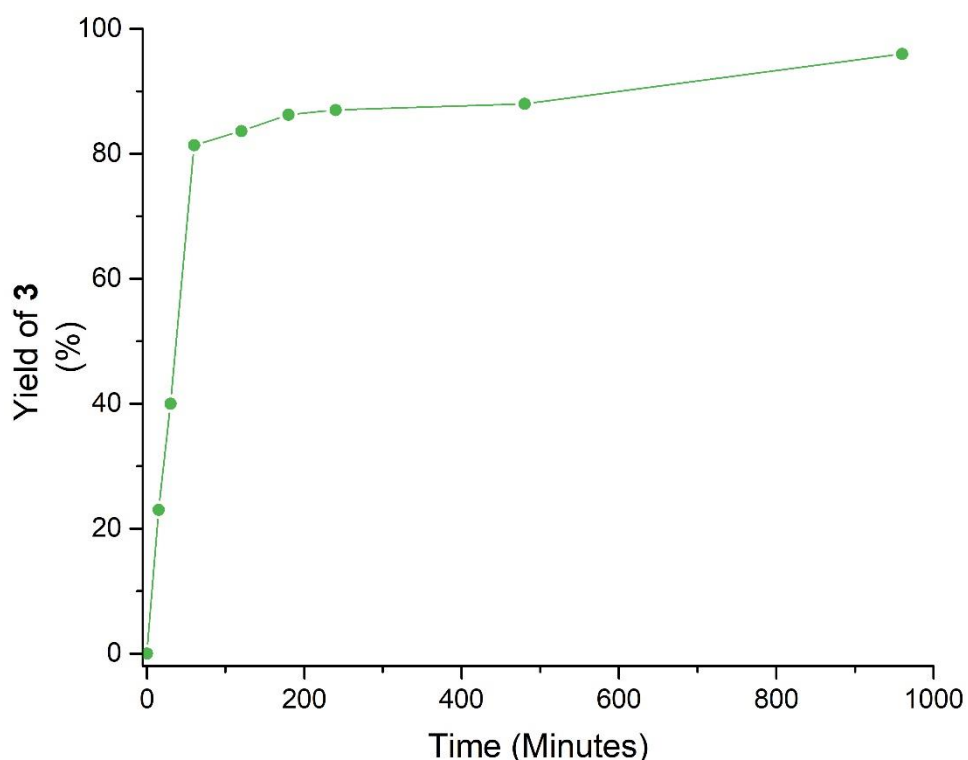
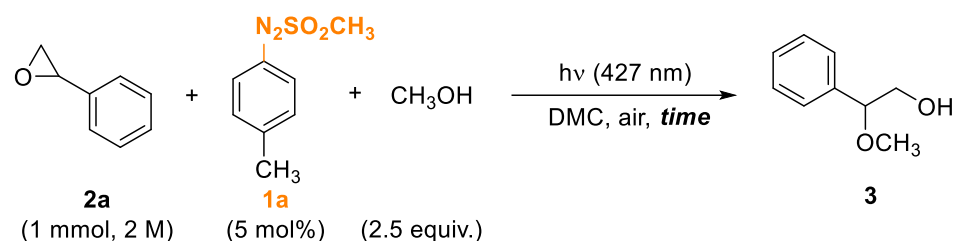
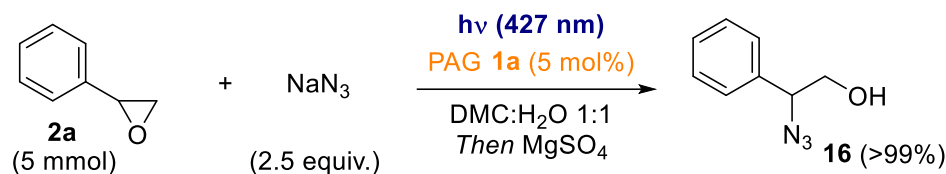


Figure S7. Kinetic studies on the reaction of the ring opening of styrene oxide **2a**. In the plot the yield of formation of the product **3** is reported.

4. Process Mass Intensity (PMI).

The Process Mass Intensity metric was calculated for selected reactions herein reported.

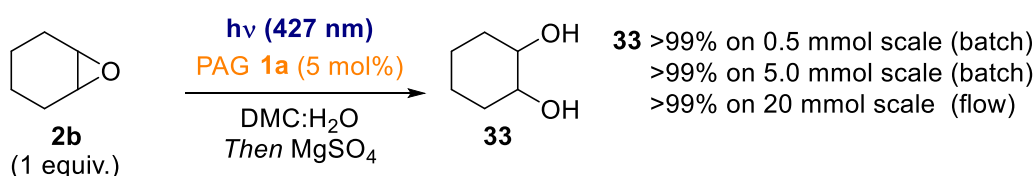
Synthesis of 2-Azido-2-phenylethan-1-ol (16).



Scheme S5. Synthesis of 16.

$$\text{PMI} = \frac{\text{Mass}_{2a} + \text{Mass}_{\text{NaN}_3} + \text{Mass}_{\text{H}_2\text{O}} + \text{Mass}_{\text{DMC}} + \text{Mass}_{\text{PAG}} + \text{Mass}_{\text{MgSO}_4}}{\text{Mass}_{16}}$$
$$\frac{601 \text{ mg} + 650 \text{ mg} + 250 \text{ mg} + 268 \text{ mg} + 49.5 \text{ mg} + 500 \text{ mg}}{815 \text{ mg}}$$

Measured PMI = 2.84 Kg/Kg



Scheme S6. Synthesis of 33 on different conditions.

$$\text{PMI}_{(0.5 \text{ mmol scale})} = \frac{\text{Mass}_{2b} + \text{Mass}_{\text{H}_2\text{O}} + \text{Mass}_{\text{DMC}} + \text{Mass}_{\text{PAG}} + \text{Mass}_{\text{MgSO}_4}}{\text{Mass}_{33}}$$
$$\frac{49.1 \text{ mg} + 50.0 \text{ mg} + 53.5 \text{ mg} + 4.90 \text{ mg} + 50.0 \text{ mg}}{58.8 \text{ mg}}$$

$$\text{Measured PMI} = 3.53 \text{ Kg/Kg}$$

$$\text{PMI}_{(5.0 \text{ mmol scale})} = \frac{\text{Mass}_{2b} + \text{Mass}_{\text{H}_2\text{O}} + \text{Mass}_{\text{DMC}} + \text{Mass}_{\text{PAG}} + \text{Mass}_{\text{MgSO}_4}}{\text{Mass}_{33}}$$
$$\frac{491 \text{ mg} + 500 \text{ mg} + 535 \text{ mg} + 49.0 \text{ mg} + 500 \text{ mg}}{588 \text{ mg}}$$

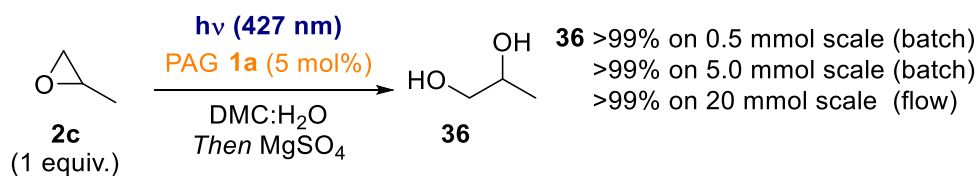
$$\text{Measured PMI} = 3.53 \text{ Kg/Kg}$$

$$\text{PMI}_{(20 \text{ mmol scale flow})}$$

$$\frac{Mass_{2b} + Mass_{H_2O} + Mass_{DMC} + Mass_{PAG} + Mass_{MgSO_4}}{Mass_{33}}$$

$$\frac{1963\text{ mg} + 200\text{ mg} + 963\text{ mg} + 198\text{ mg} + 1000\text{ mg}}{2320\text{ mg}}$$

$$\text{Measured PMI} = 1.86\text{ Kg/Kg}$$



Scheme S7. Synthesis of **36** on different conditions.

$$PMI_{(0.5\text{ mmol scale})}$$

$$\frac{Mass_{2c} + Mass_{H_2O} + Mass_{DMC} + Mass_{PAG} + Mass_{MgSO_4}}{Mass_{36}}$$

$$\frac{15.1\text{ mg} + 50.0\text{ mg} + 53.5\text{ mg} + 4.90\text{ mg} + 50.0\text{ mg}}{38.0\text{ mg}}$$

$$\text{Measured PMI} = 4.56\text{ Kg/Kg}$$

$$PMI_{(5.0\text{ mmol scale})}$$

$$\frac{Mass_{2c} + Mass_{H_2O} + Mass_{DMC} + Mass_{PAG} + Mass_{MgSO_4}}{Mass_{36}}$$

$$\frac{151\text{ mg} + 500\text{ mg} + 535\text{ mg} + 49.0\text{ mg} + 500\text{ mg}}{380\text{ mg}}$$

$$\text{Measured PMI} = 4.56\text{ Kg/Kg}$$

$$PMI_{(20\text{ mmol scale flow})}$$

$$\frac{Mass_{2b} + Mass_{H_2O} + Mass_{DMC} + Mass_{PAG} + Mass_{MgSO_4}}{Mass_{33}}$$

$$\frac{608\text{ mg} + 200\text{ mg} + 963\text{ mg} + 198\text{ mg} + 1000\text{ mg}}{1520\text{ mg}}$$

$$\text{Measured PMI} = 1.95\text{ Kg/Kg}$$

5. References.

- S1 L. Di Terlizzi, A. Martinelli, D. Merli, S. Protti and M. Fagnoni, Arylazo Sulfones as Nonionic Visible-Light Photoacid Generators. *J. Org. Chem.* 2023, **88**, 6313–6321.
- S2 C. Lian, G. Yue, J. Mao, D. Liu, Y. Ding, Z. Liu, D. Qiu, X. Zhao, K. Lu, M. Fagnoni and S. Protti, Visible-Light-Driven Synthesis of Arylstannanes from Arylazo Sulfones. *Org. Lett.* 2019, **21**, 5187–5191.
- S3 M. L. Jamieson, P. A. Hume, D. P. Furkert and M. A. Brimble, Divergent Reactivity via Cobalt Catalysis: An Epoxide Olefination. *Org. Lett.* 2016, **18**, 468–471.
- S4 G. Moyna, H. J. Williams and A. I. Scott. An Improved Procedure for the Epoxidation of Methyl Cinnamate Derivatives and Production of Acid Sensitive Epoxides. *Synth. Commun.* 1995, **26**, 2235–2239.
- S5 X.-L. Shi, B. Sun, Q. Hu, Y. Chen and P. Duan, Fiber-supported Fe(III) complex catalyst in spinning basket reactor for cleaner ring-opening of epoxides with alcohols, *Green Chem.* 2019, **21**, 3573–3582.
- S6 G. Kumar, G. Kumar and R. Gupta, Lanthanide-based coordination polymers as promising heterogeneous catalysts for ring opening reactions, *RSC Adv.* 2016, **6**, 21352–21361.
- S7 M. Westermaier and H. Mayr, Regio- and Stereoselective Ring-Opening Reactions of Epoxides with Indoles and Pyrroles in 2,2,2-Trifluoroethanol, *Chem. Eur. J.* 2008, **14**, 1638–1647.
- S8 G.-X. Li and J. Qu, Friedel–Crafts alkylation of arenes with epoxides promoted by fluorinated alcohols or water, *Chem. Commun.* 2010, **46**, 2653–2655.
- S9 K. Tanemura and T. Suzuki, Aniline-terephthalaldehyde resin p-toluenesulfonate (ATRTP) as a highly efficient and reusable catalyst for alcoholysis, hydrolysis, and acetolysis of epoxides, *Synth. Commun.* 2016, **46**, 1781–1789.
- S10 P. V. Ramachandran, A. A. Alawaed and H. J. Hamann, A Safer Reduction of Carboxylic Acids with Titanium Catalysis, *Org. Lett.* 2022, **24**, 8481–8486.
- S11 B.J. Deadman, S. Gian, V. Eng Yee Lee, L. A. Adrio, K. Hellgardt and K. K. Hii, On-demand, in situ, generation of ammonium peroxydisulfate (peroxymonosulfate) for the dihydroxylation of alkenes to vicinal diols. *Green Chem.* 2022, **24**, 5570–5578.
- S12 R. O. Torres-Ochoa, A. Leclair, Q. Wang and J. Zhu, Iron-Catalysed Remote C(sp³)@H Azidation of O-Acyl Oximes and N-Acyloxy Imidates Enabled by 1,5-Hydrogen Atom Transfer of Iminyl and Imidate Radicals: Synthesis of *g*-Azido Ketones and *b*-Azido Alcohols, *Chem. Eur. J.* 2019, **25**, 9477–9484.

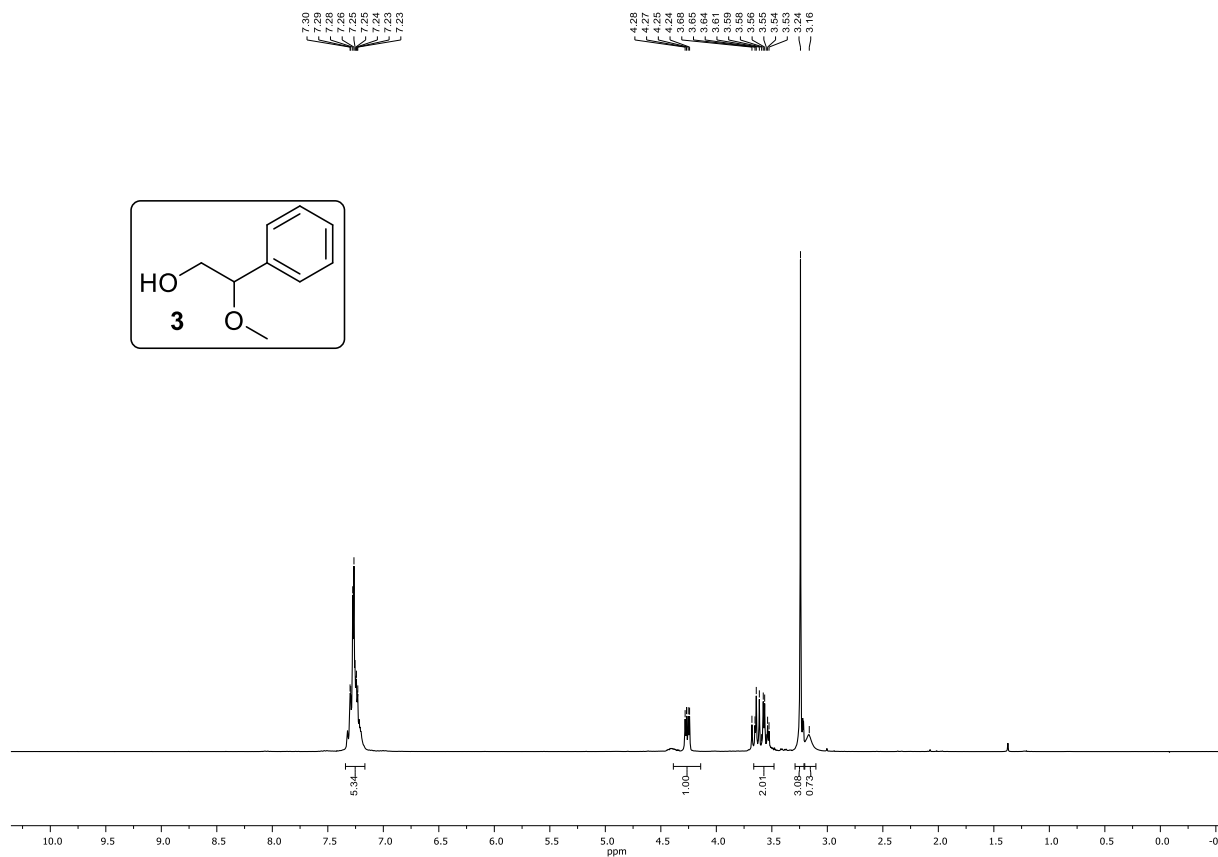
- S13 B. Li, P. Ni, H. Huang, F. Xiao and G.-J. Deng, Three-Component Thieno[2,3-b]indole Synthesis from Indoles, Alkenes or Alkynes and Sulfur Powder under Metal-Free Conditions, *Adv. Synth. Catal.* 2017, **359**, 4300–4304.
- S14 K. Huang, H. Wang, V. Stepanenko, M. De Jesus, C. Torruellas, W. Correa and M. Ortiz-Marciales, Chiral Epoxides via Borane Reduction of 2-Haloketones Catalyzed by Spiroborate Ester: Application to the Synthesis of Optically Pure 1,2-Hydroxy Ethers and 1,2-Azido Alcohols, *J. Org. Chem.* 2011, **76**, 1883–1886.
- S15 Z.-X. Zhang, B.-H. Zhu, P.-X. Xie, J.-Q. Tang, X.-L. Li, C. Zhu, Y.-W. Yin and L.-W. Ye, Facile synthesis of α -alkoxyl amides via scandium-catalyzed oxidative reaction between ynamides and alcohols. *RSC Adv.* 2018, **8**, 18308–18315.
- S16 R. Ma, J. Feng, K. Zhang, B. Zhanga and D. Du, Photoredox β -thiol- α -carbonylation of enones accompanied by unexpected Csp²-C(CO) bond cleavage. *Org. Biomol. Chem.* 2020, **18**, 7549–7553.
- S17 B. Movassagh, M. Navidi, One-pot synthesis of β -hydroxysulfides from styrenes and disulfides using the Zn/AlCl₃ system. *Tetrahedron Lett.* 2008, **49**, 6712–6714.
- S18 A. Tyagi, J. Khan, N. Yadav, R. Mahato and C. K. Hazra, Catalyst-Switchable Divergent Synthesis of Bis(indolyl)alkanes and 3-Alkylated Indoles from Styrene Oxides, *J. Org. Chem.* 2022, **87**, 10229–10240.
- S19 J. Chen, J. Jia and T. Tu, Fiber-supported Fe(III) complex catalyst in spinning basket reactor for cleaner ring-opening of epoxides with alcohols. *Green Chem.* 2019, **21**, 3573–3582.
- S20 B. J. Deadman, S. Gian, V. Eng Yee Lee, L. A. Adrio, K. Hellgardt and K. K. Hii, On-demand, in situ, generation of ammonium caroate (peroxymonosulfate) for the dihydroxylation of alkenes to vicinal diols. *Green Chem.* 2022, **24**, 5570–5578.
- S21 D. D. Roberts, Neighboring hydroxyl group effect in solvolysis reactions of common ring p-toluenesulfonates. *J. Org. Chem.* 1968, **33**, 118–123.
- S22 I. A. Andreev, M. A. Boichenko, N. K. Ratmanova, O. A. Ivanova, I. I. Levina, V. N. Khrustalev, I. A. Sedov, I. V. Trushkov, 4-(Dimethylamino)Pyridinium Azide in Protic Ionic Liquid Media as a Stable Equivalent of Hydrazoic Acid. *Adv. Synth. Catal.* 2022, **364**, 2403–2415.
- S23 T.-J. Yue, M.-C. Zhang, G.-G. Gu, L.-Y. Wang, W.-M. Ren and X.-B. Lu, Precise Synthesis of Poly(thioester)s with Diverse Structures by Copolymerization of Cyclic Thioanhydrides and Episulfides Mediated by Organic Ammonium Salts. *Angew. Chem. Int. Ed.* 2019, **58**, 618–623.

- S24 B. F. S. Nunes, M. C. Oliveira and A. C. Fernandes, Dioxomolybdenum complex as an efficient and cheap catalyst for the reductive depolymerization of plastic waste into value-added compounds and fuels. *Green Chem.* 2020, **22**, 2419–2425.
- S25 Y.-F. Chen, C.-H. Wu, L.-H. Chen, H.-W. Lee, J.-C. Lee, T.-K. Yeh, J.-Y. Chang, M.-C. Chou, H.-L. Wu, Y.-P. Lai, J.-S. Song, K.-C. Yeh, C.-T. Chen, C.-J. Lee, K.-S. Shia, M.-R. Shen, Discovery of Potential Neuroprotective Agents against Paclitaxel-Induced Peripheral Neuropathy. *J. Med. Chem.* 2022, **65**, 4767–4782.
- S26 G. Sabitha, R. S. Babu, M. Rajkumar and J. S. Yadav, Cerium(III) Chloride Promoted Highly Regioselective Ring Opening of Epoxides and Aziridines Using NaN₃ in Acetonitrile: A Facile Synthesis of 1,2-Azidoalcohols and 1,2-Azidoamines. *Org. Lett.* 2002, **4**, 343–345.
- S27 J. Barluenga, H. Vázquez-Villa, A. Ballesteros and J. M. González, Copper(II) Tetrafluoroborate Catalyzed Ring-Opening Reaction of Epoxides with Alcohols at Room Temperature. *Org. Lett.* 2002, **4**, 2817–2819.
- S28 E. Taeger, E. Kahlert and H. Walter, Über die Einwirkung von Metallen auf α -Halogenäther. III. Die Reaktion von Carbonylverbindungen mit grignardierten α -Chloräthern. *J. Prakt. Chem.* 1965, **28**, 13–20.
- S29 P. Petrow, *J. Appl. Chem-USSR* 1955, **28**, 556–558.
- S30 J. J. Rojas, E. Torrisi, M. A. J. Dubois, R. Hossain, A. J. P. White, G. Zappia, J. J. Mousseau, C. Choi and J. A. Bull, Oxetan-3-ols as 1,2-bis-Electrophiles in a Brønsted-Acid-Catalyzed Synthesis of 1,4-Dioxanes. *Org. Lett.* 2022, **24**, 2365–2370.
- S31 M. N. S. Rad, S. Behrouz, M. Behrouz, A. Sami, M. Mardkhoshnood, A. Zarenezhad and E. Zarenezhad, design, synthesis and biological evaluation of novel 1,2,3-triazolyl β -hydroxy alkyl/carbazole hybrid molecules. *Mol. Divers.* 2016, **20**, 705–718.
- S32 K. Jeyakumar and D. K. Chand, Ring-Opening Reactions of Epoxides Catalyzed by Molybdenum(VI) -Dichloride Dioxide. *Synthesis*, 2008, **5**, 807–819.
- S33 X.-M. Chen, X.-S. Ning and Y.-B. Kang, Aerobic Acetoxyhydroxylation of Alkenes Co-catalyzed by Organic Nitrite and Palladium. *Org. Lett.* 2016, **18**, 5368–5371.
- S34 L. He, M. Wanunu, H.-S. Byun and R. Bittman, Regioselective and Stereospecific Azidation of 1,2- and 1,3-Diols by Azidotrimethylsilane via a Mitsunobu Reaction. *J. Org. Chem.* 1999, **64**, 6049–6055.
- S35 J. Donga and J. Xu, Facile synthesis of thietanes via ring expansion of thiiranes. *Org. Biomol. Chem.* 2017, **15**, 836–844.
- S36 S. Hüttel, G. Testolin, J. Herrmann, T. Planke, F. Gille, M. Moreno, M. Stadler, M. Brönstrup, A. Kirschning and R. Müller, Discovery and Total Synthesis of Natural Cystobactamid

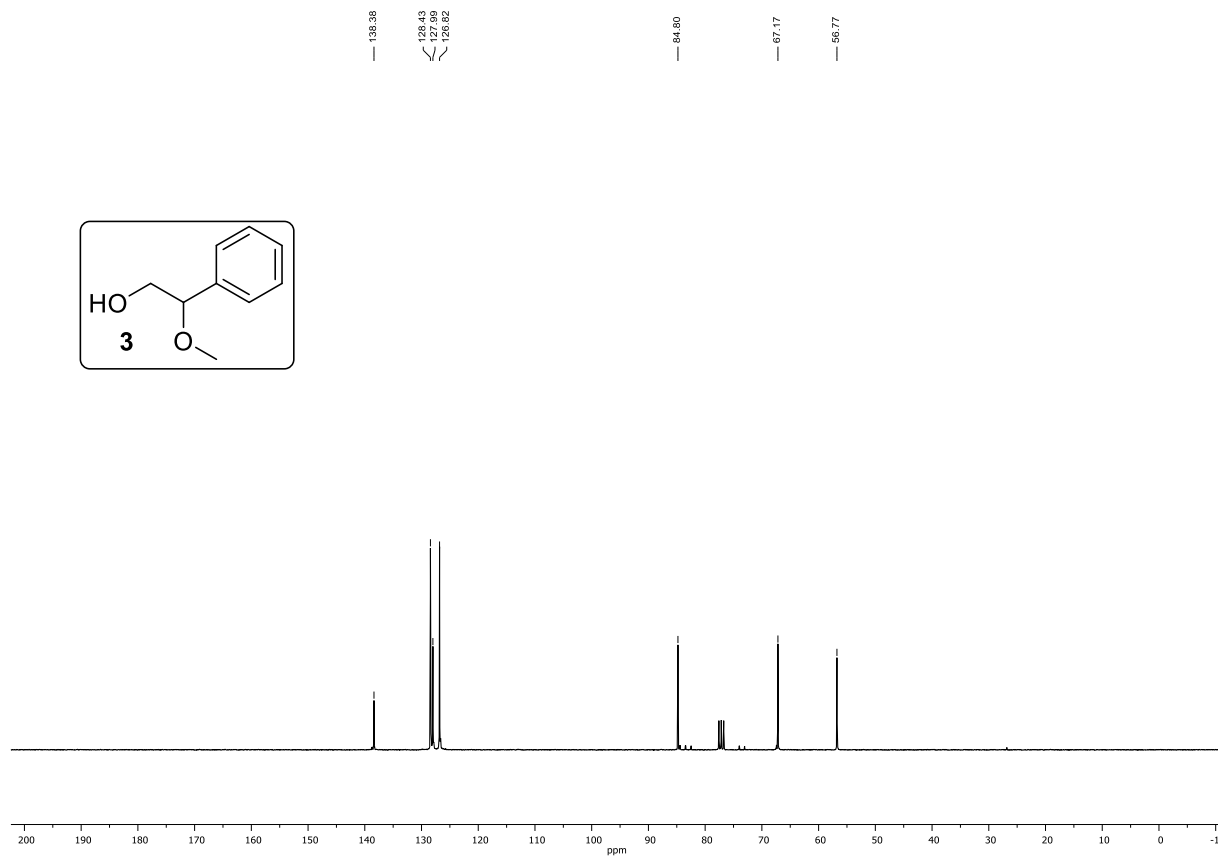
- Derivatives with Superior Activity against Gram-Negative Pathogens. *Angew. Chem. Int. Ed.* 2017, **56**, 12760–12764.
- S37 D. Giomi, M. Malavolti, O. Piccolo, A. Salvini and A. Brandia, A convenient method for producing mono- and dichlorohydrins from glycerol. *RSC Adv.* 2014, **4**, 46319–46326.
- S38 D. Kumari, S. G. Anjitha, C. S. Pant, M. Patil, H. Singha and S. Banerjee, Synthetic approach to novel azido esters and their utility as energetic plasticizers. *RSC Adv.* 2014, **4**, 39924–39933.
- S39 L. Di Terlizzi, E. M. Galathri, S. Protti, C. G. Kokotos and M. Fagnoni, A General Metal-Free Protocol for the Visible-Light-Driven Protection of Carbonyls. *ChemSusChem*, 2023, **16**, e202201998.
- S40 L.-J. Liu, Q.-J. Luan, J. Lu, D.-M. Lv, W.-Z. Duan, X. Wang and S.-W. Gong, 8-Hydroxy-2-methylquinoline-modified H₄SiW₁₂O₄₀: a reusable heterogeneous catalyst for acetal/ketal formation. *RSC Adv.* 2018, **8**, 26180–26187.
- S41 J. M. Grill, J. W. Ogle and S. A. Miller, An Efficient and Practical System for the Catalytic Oxidation of Alcohols, Aldehydes, and α,β -Unsaturated Carboxylic Acids. *J. Org. Chem.* 2006, **71**, 9291–9296.
- S42 C. Vidal and J. García-Álvarez, Glycerol: a biorenewable solvent for base-free Cu(I)-catalyzed 1,3-dipolar cycloaddition of azides with terminal and 1-iodoalkynes. Highly efficient transformations and catalyst recycling. *Green Chem.* 2014, **16**, 3515–3521.
- S43 R. Eisavi and A. Karimia, CoFe₂O₄/Cu(OH)₂ magnetic nanocomposite: an efficient and reusable heterogeneous catalyst for one-pot synthesis of β -hydroxy-1,4-disubstituted-1,2,3-triazoles from epoxides. *RSC Adv.* 2019, **9**, 29873–29887.
- S44 A. Tsoukaki, E. Skolia, I. Triandafillidi and C. G. Kokotos, Organocatalytic Synthesis of Thiiranes from Alkenes. *Eur. J. Org. Chem.* 2022, e202200463.

6. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compounds 3-59.

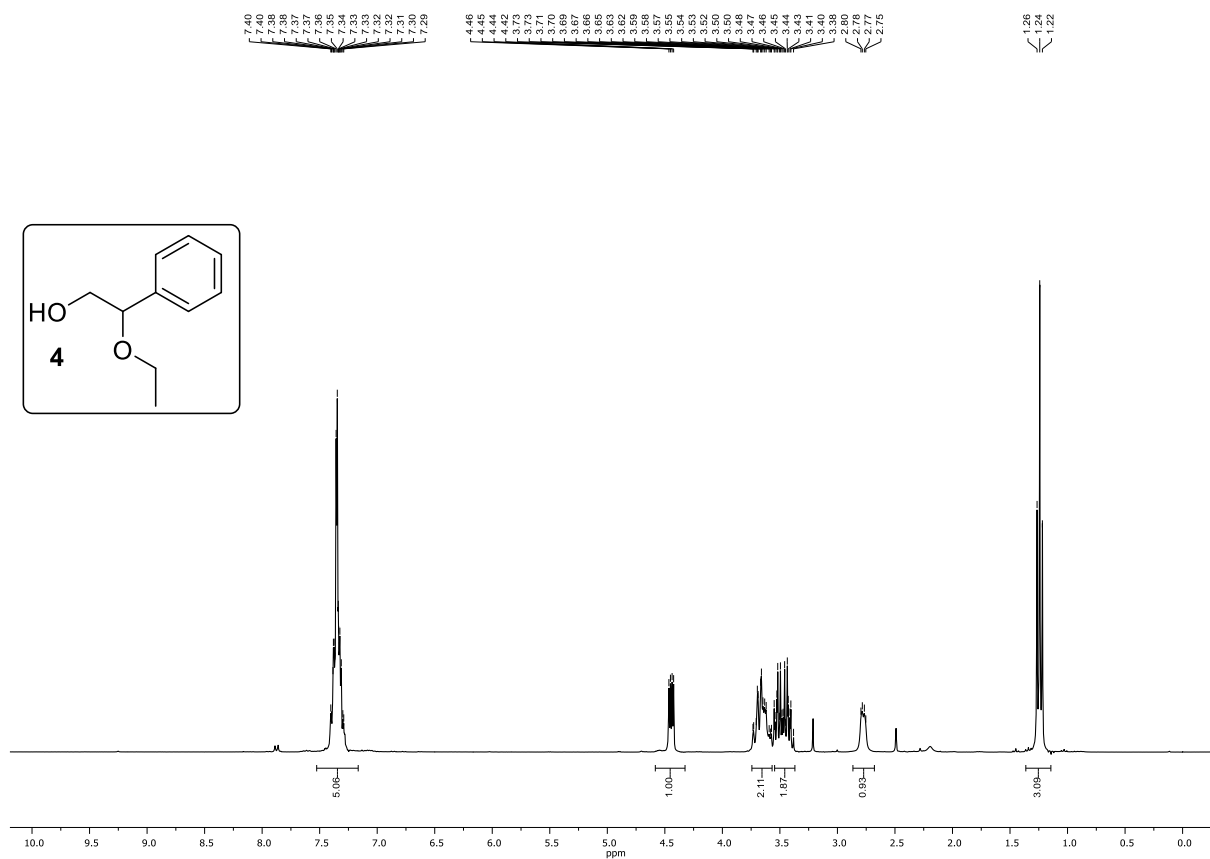
^1H NMR (CDCl_3 , 300 MHz)



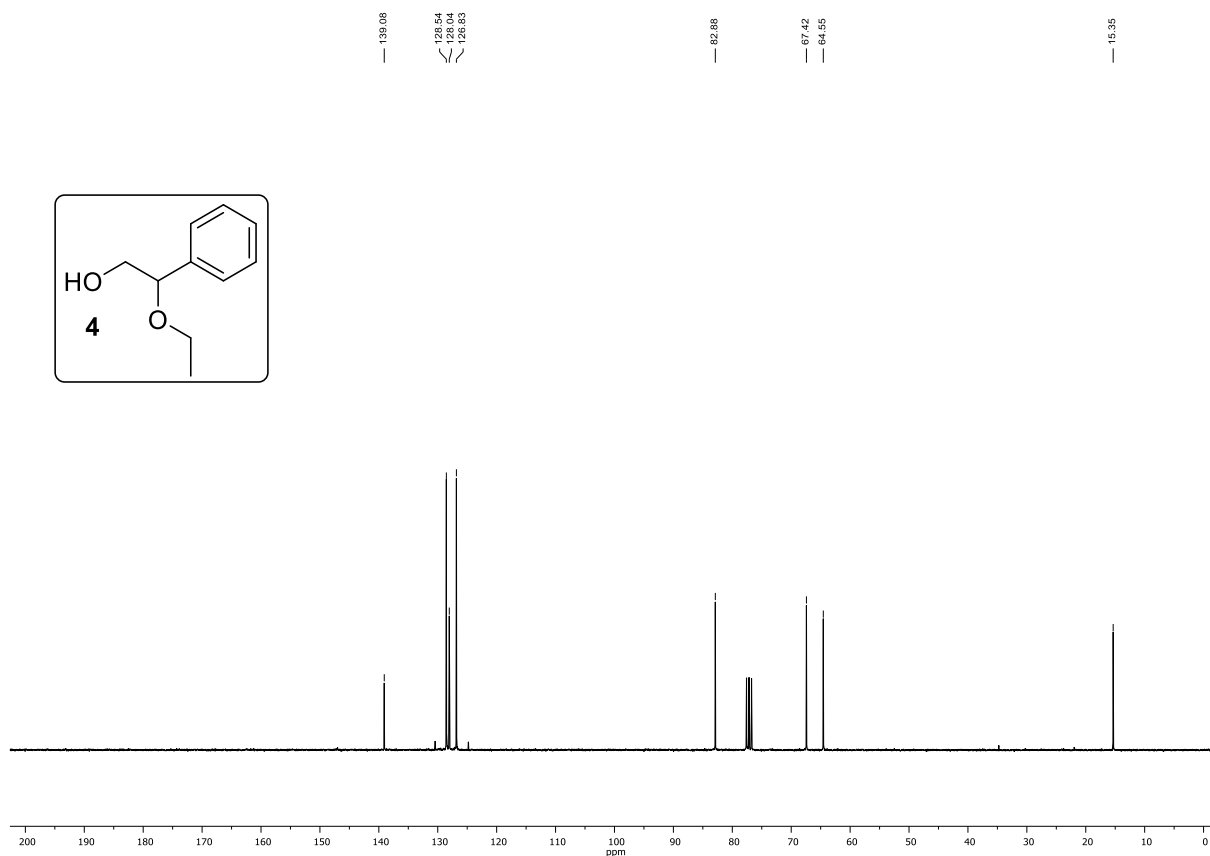
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



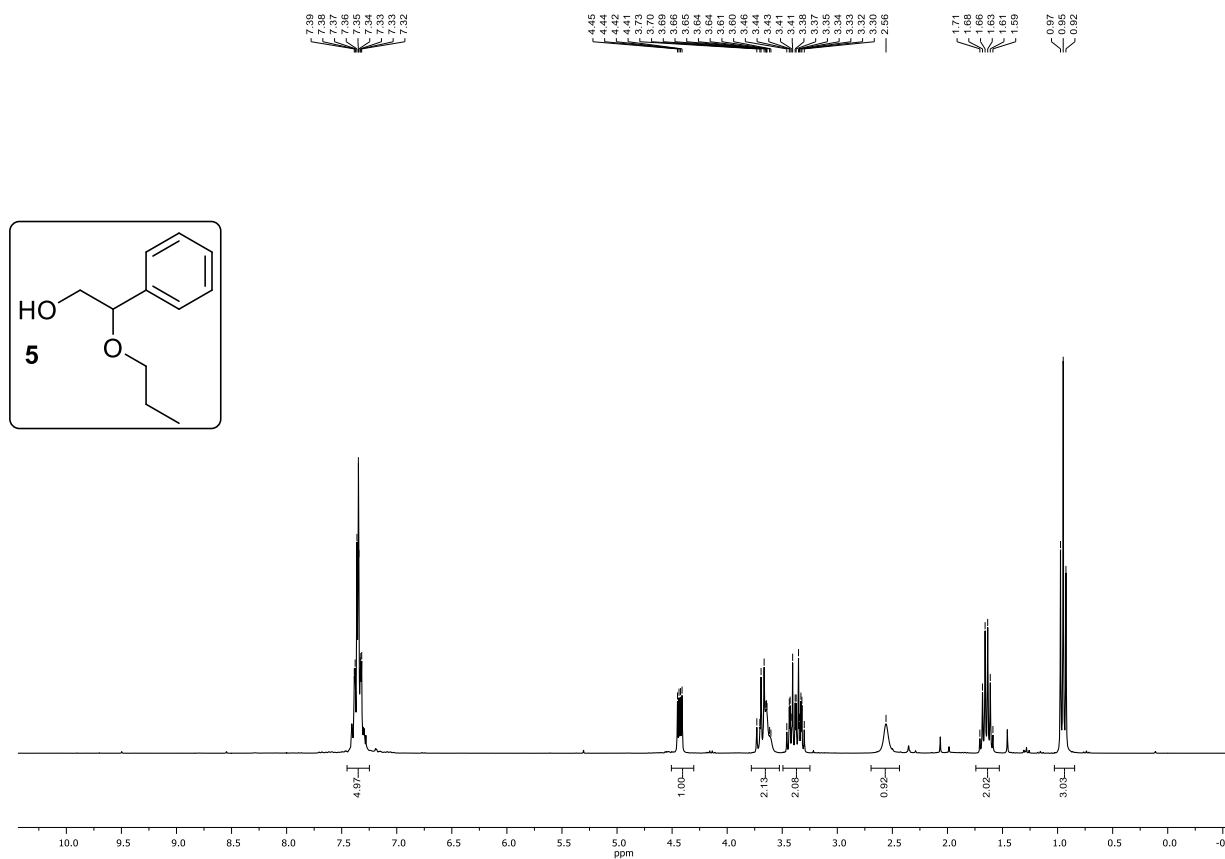
^1H NMR (CDCl_3 , 300 MHz)



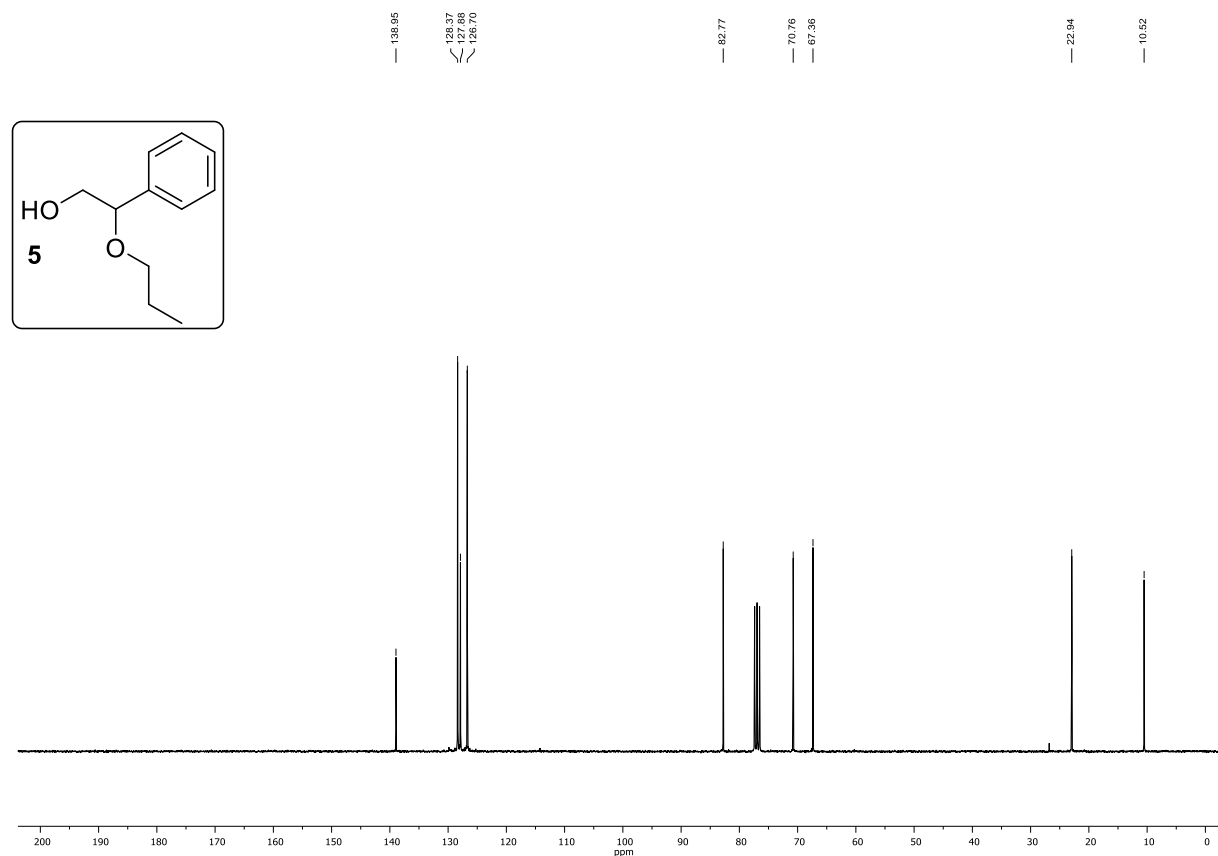
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



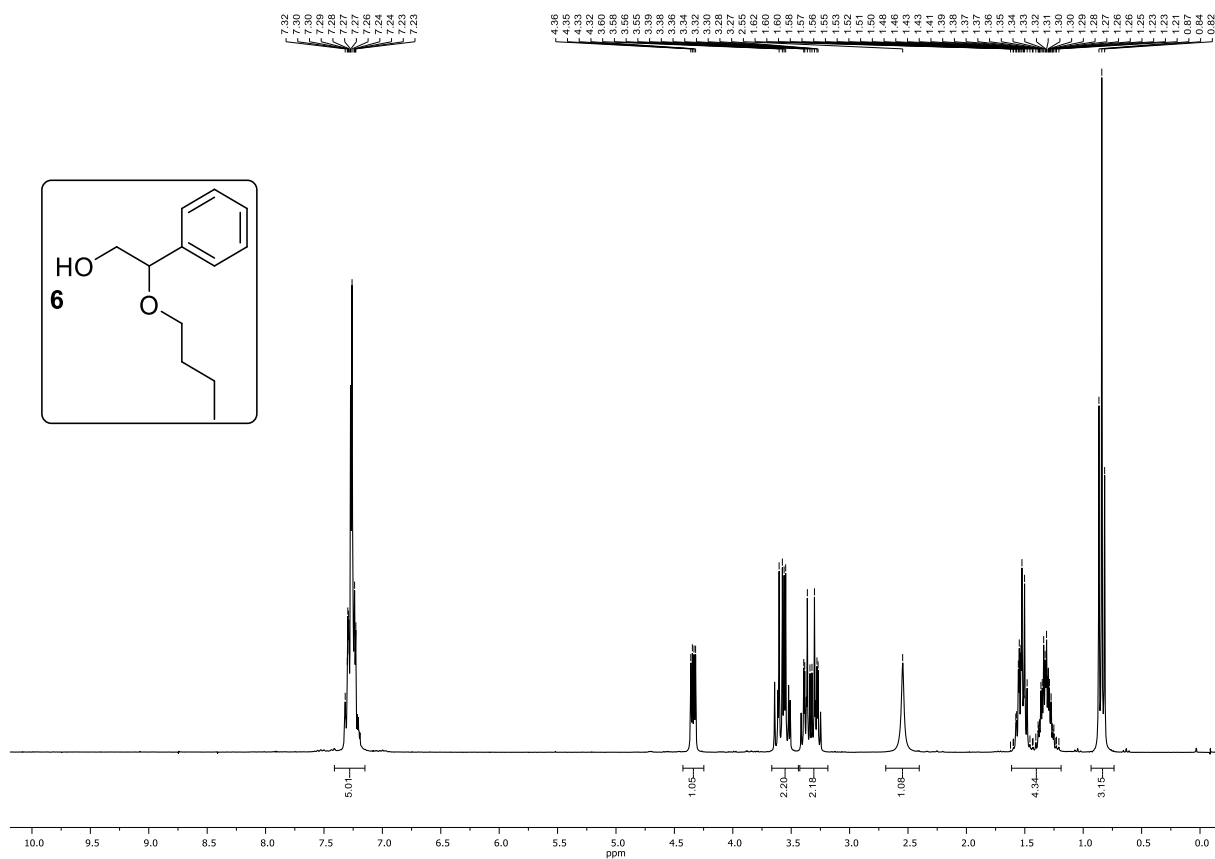
^1H NMR (CDCl_3 , 300 MHz)



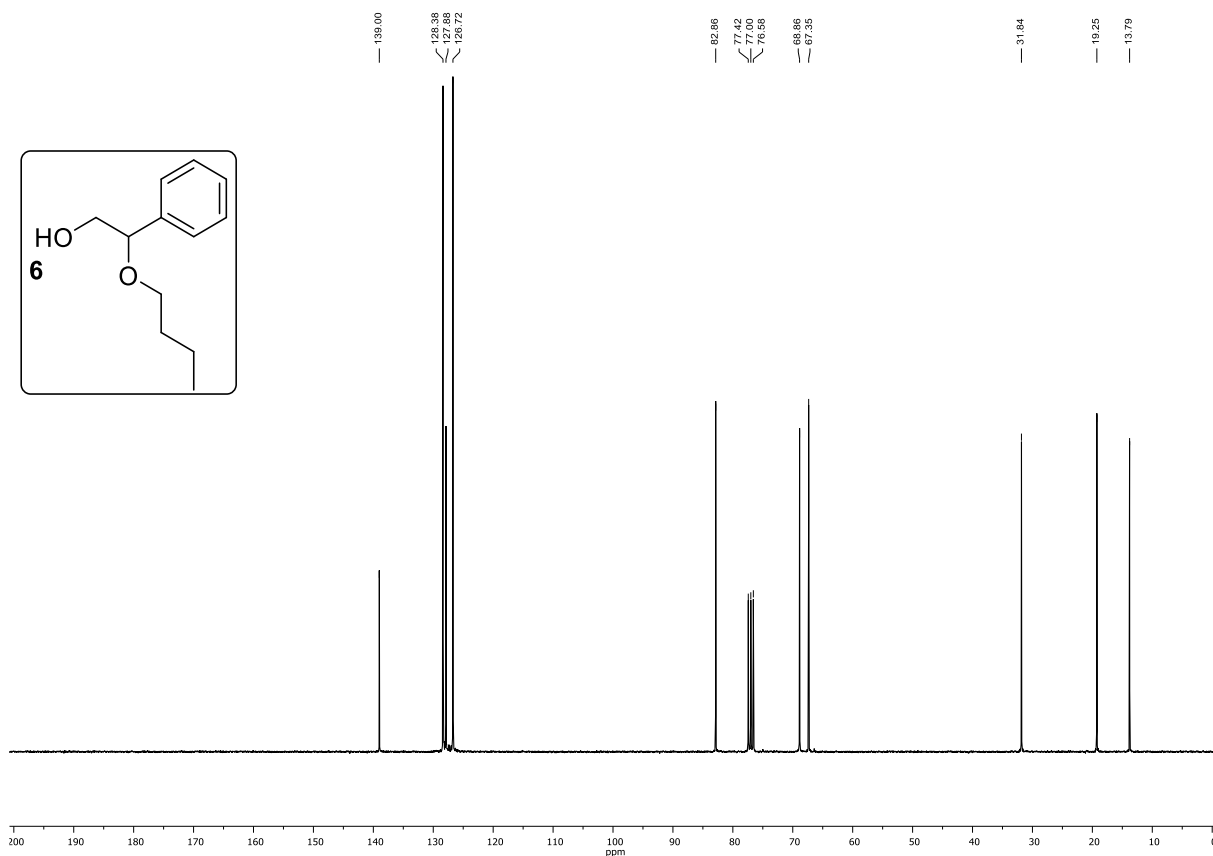
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)



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



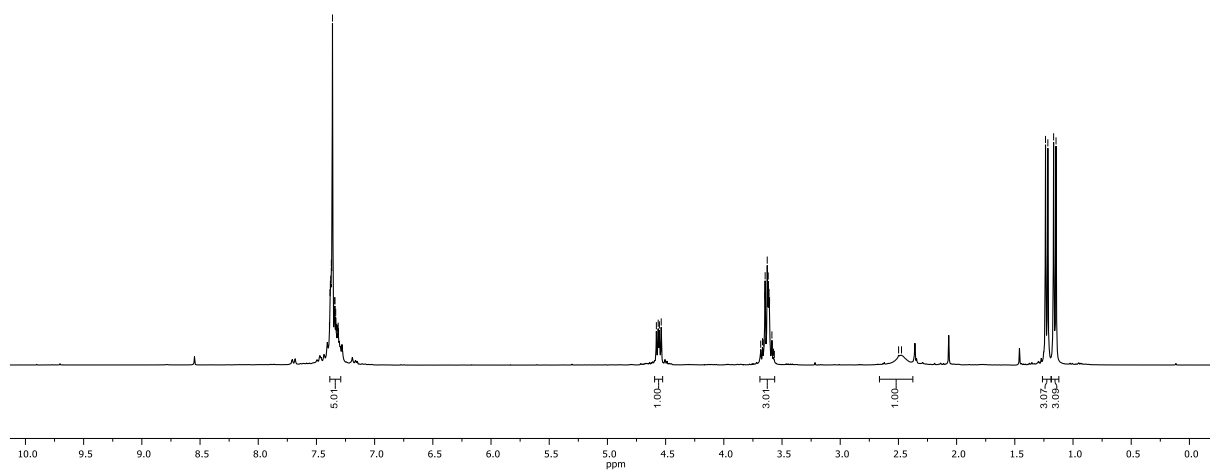
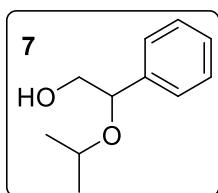
^1H NMR (CDCl_3 , 300 MHz)

7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.31

4.58
4.56
4.54
3.68
3.67
3.65
3.65
3.64
3.63
3.61
3.59
3.57

2.50
2.47

1.24
1.17
1.15



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

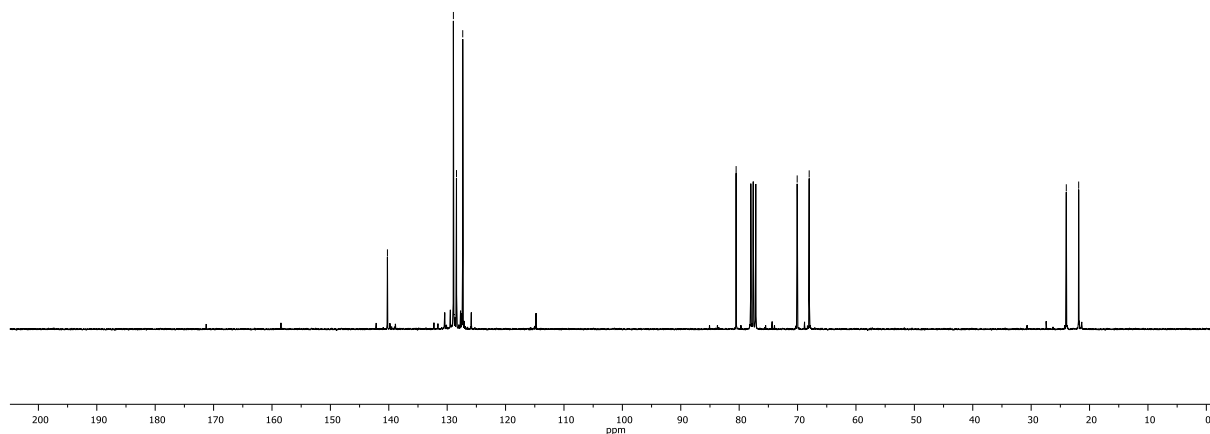
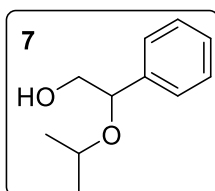
140.23

128.94
127.94

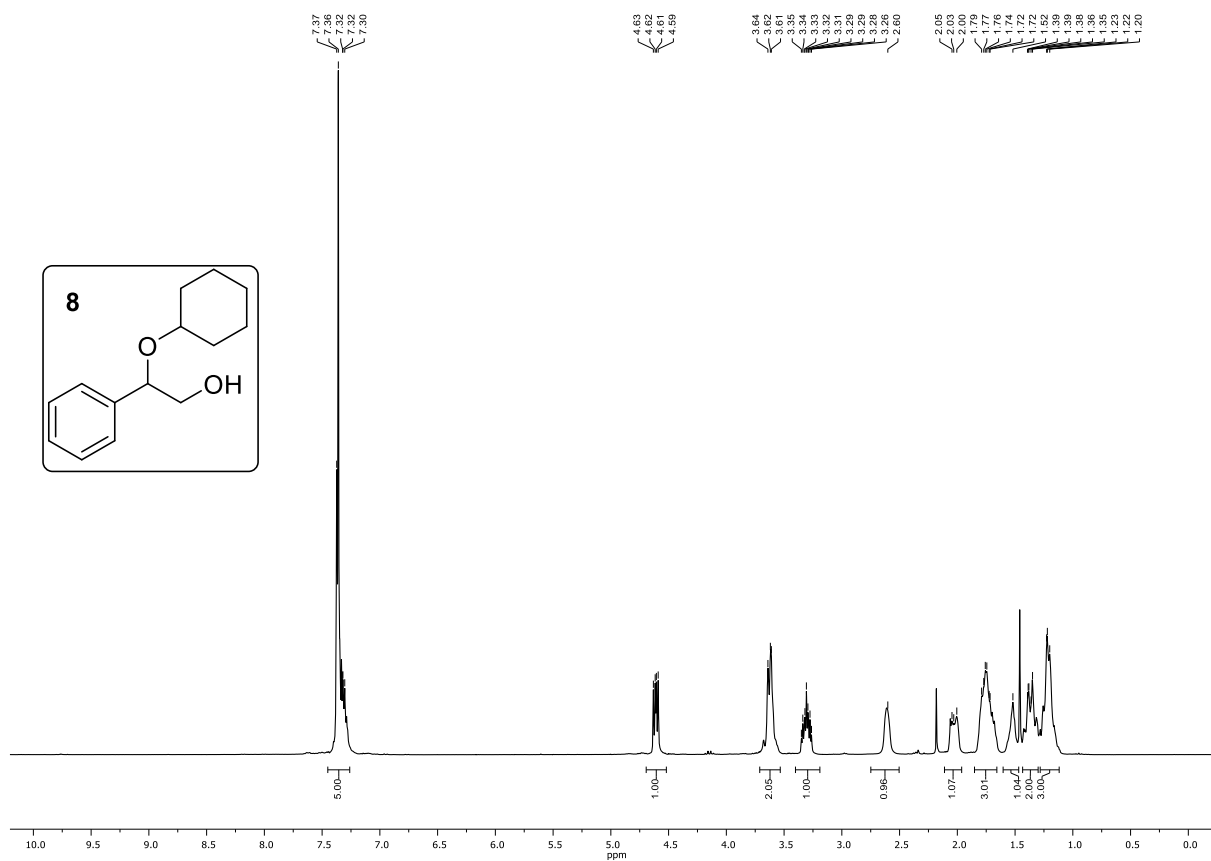
80.52

70.07
68.01

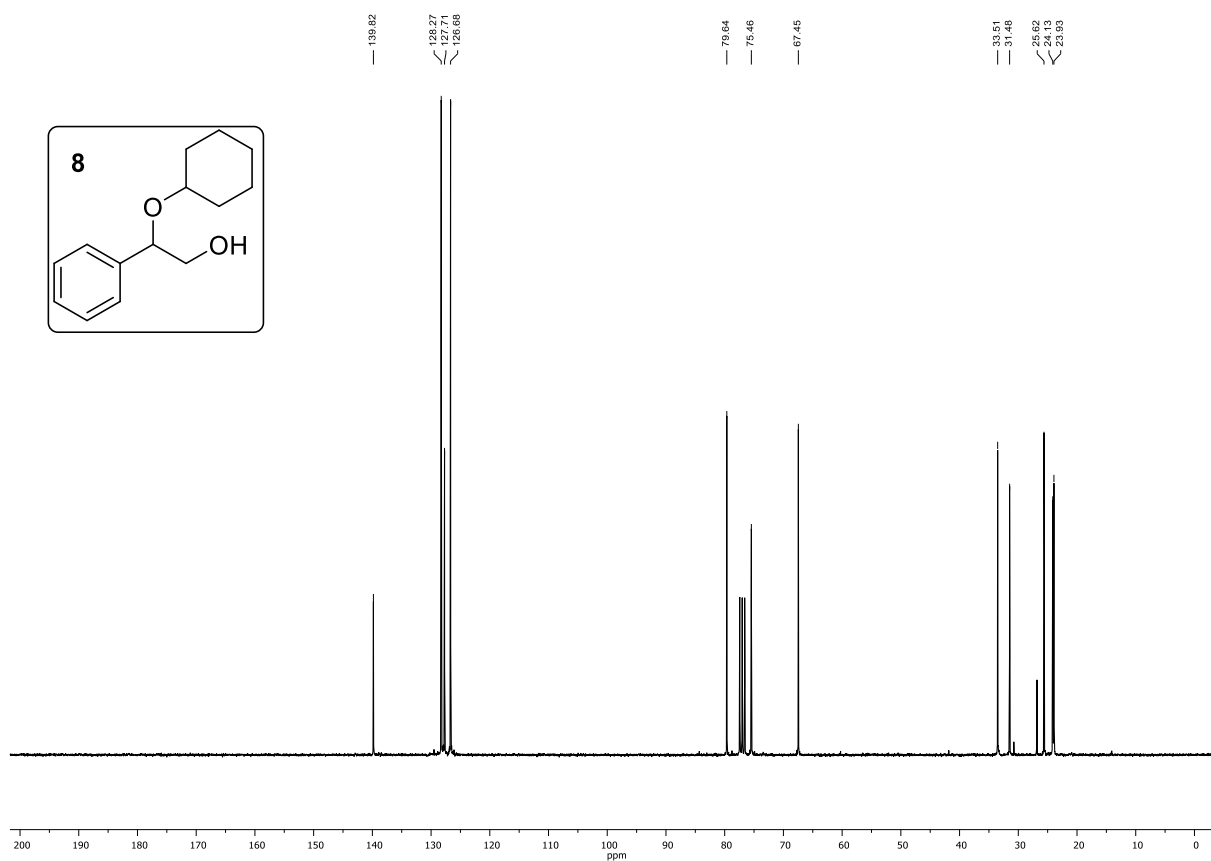
23.88
21.86



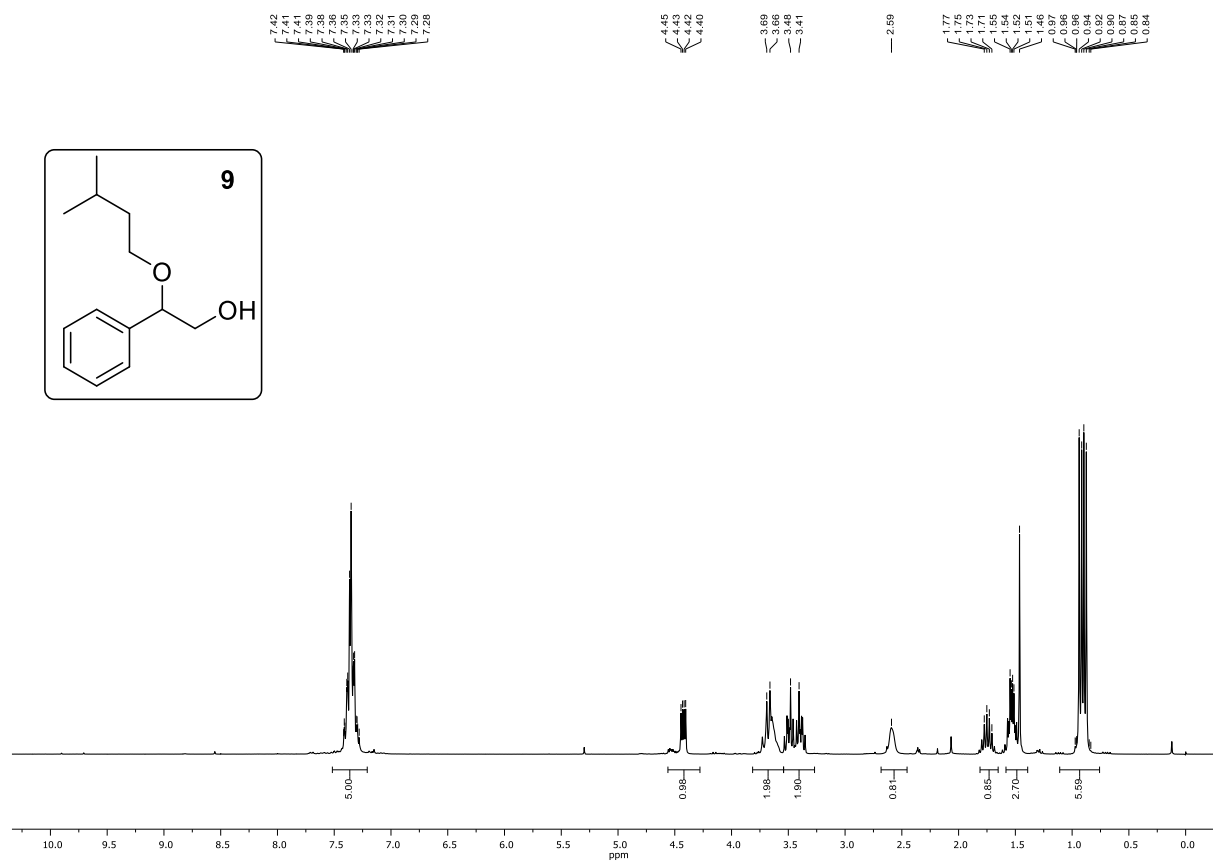
^1H NMR (CDCl_3 , 300 MHz)



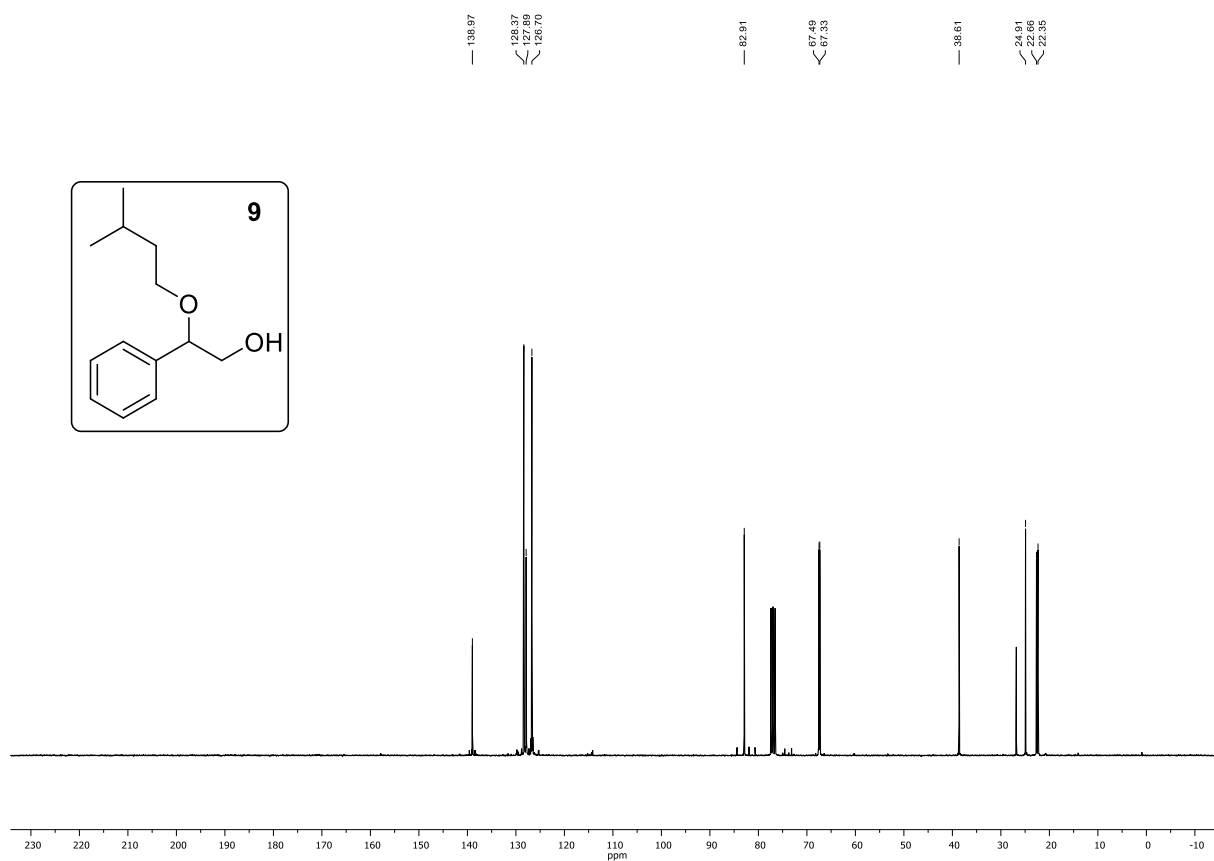
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



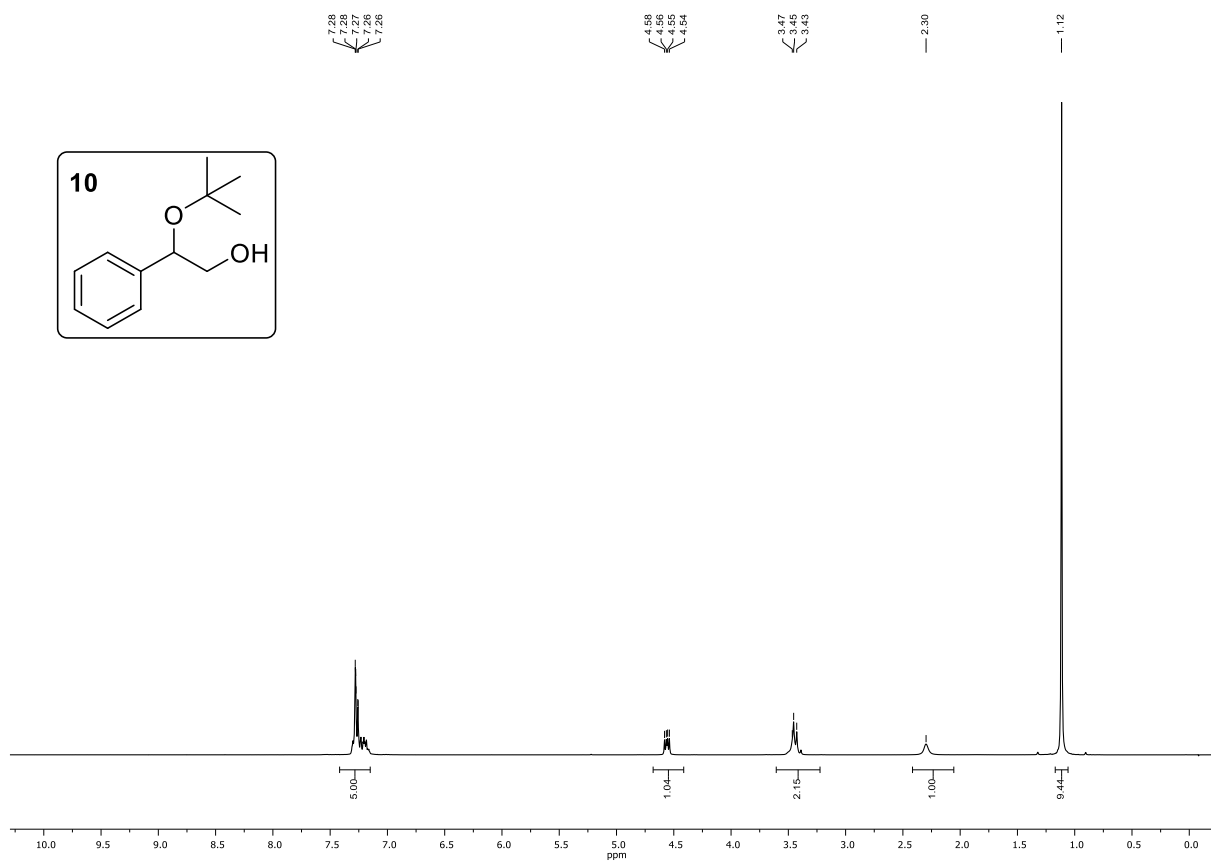
^1H NMR (CDCl_3 , 300 MHz)



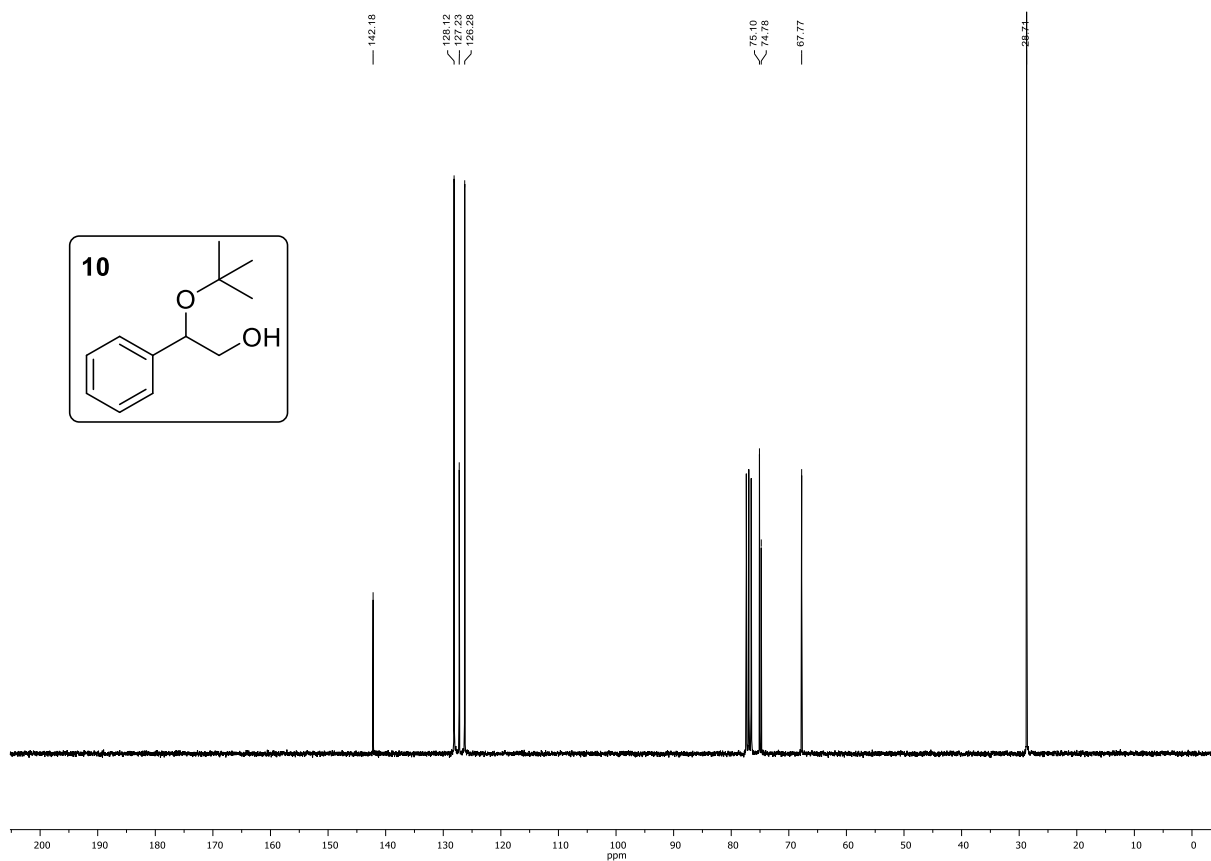
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



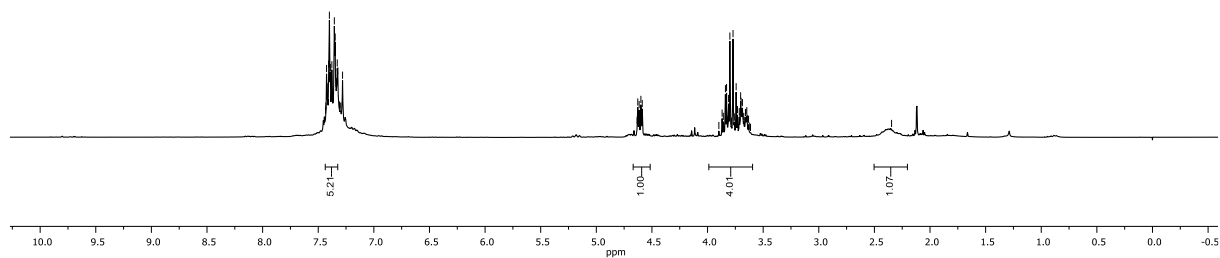
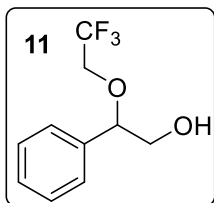
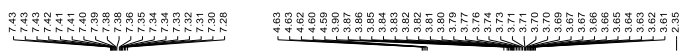
^1H NMR (CDCl_3 , 300 MHz)



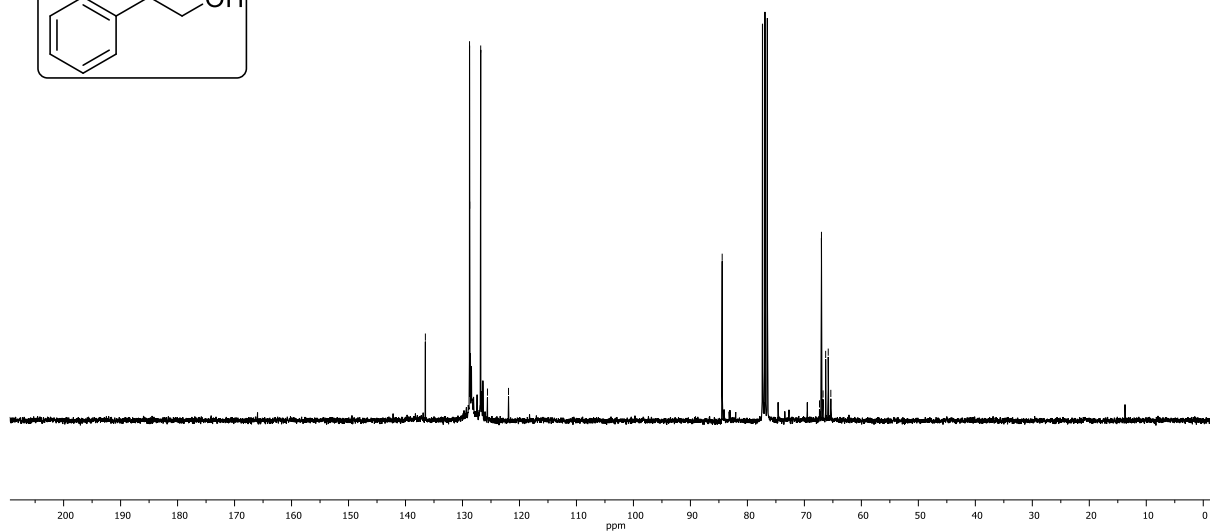
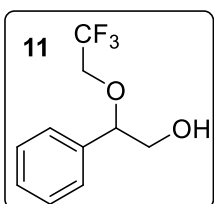
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



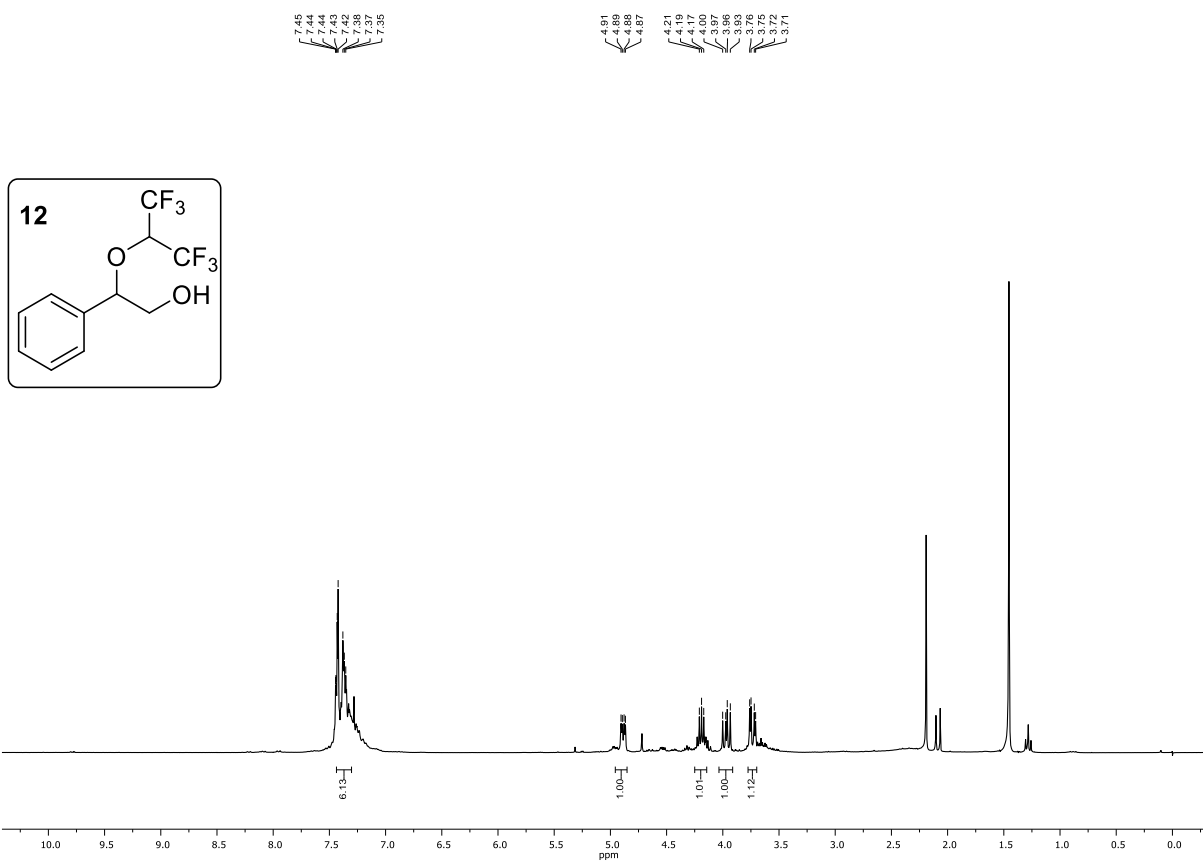
^1H NMR (CDCl_3 , 300 MHz)



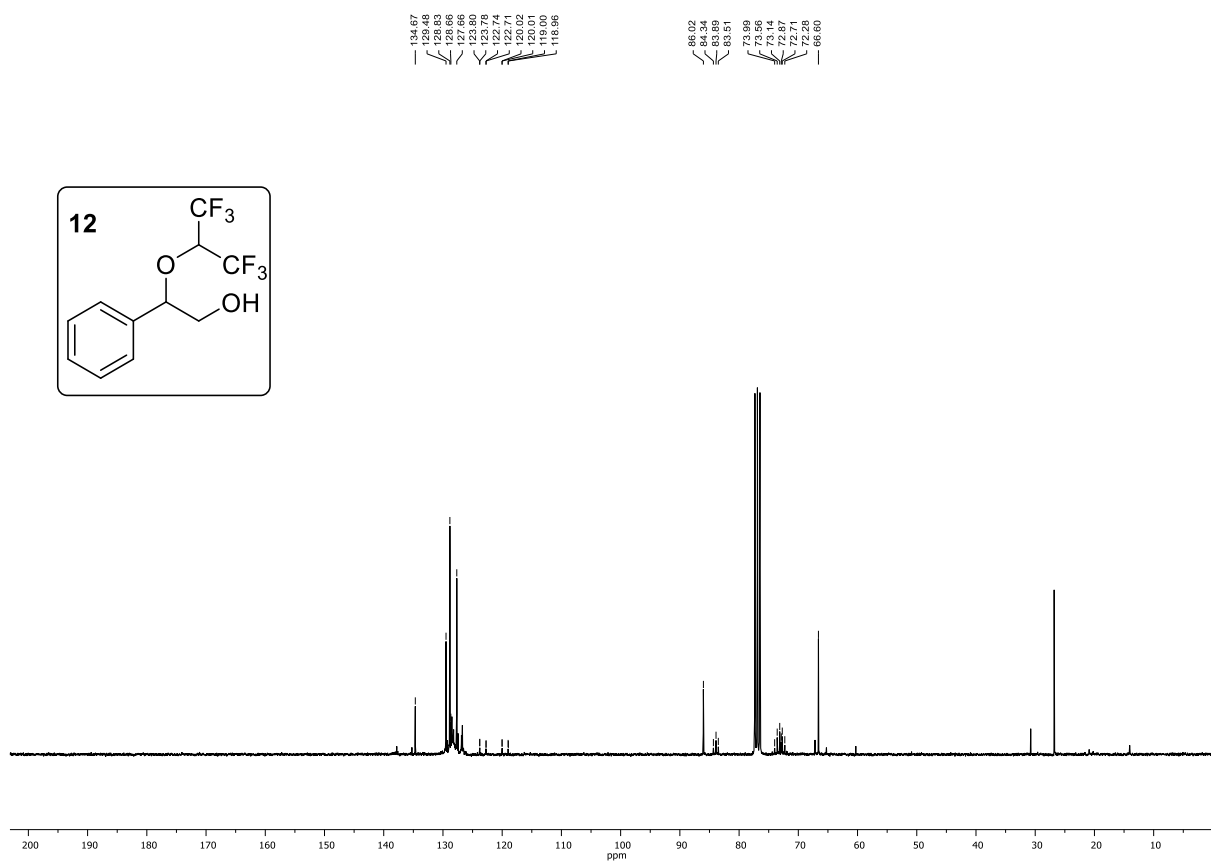
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



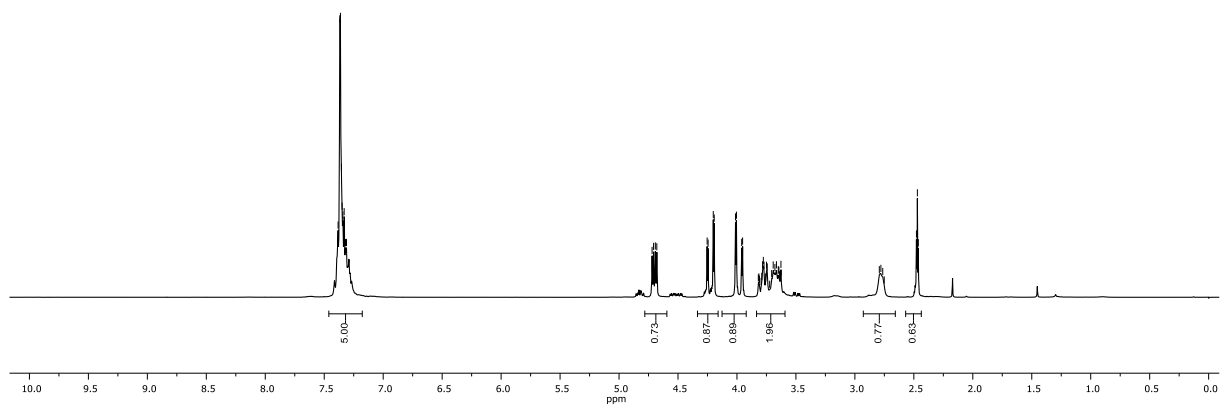
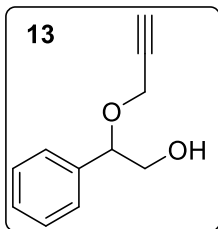
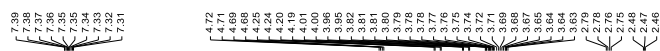
^1H NMR (CDCl_3 , 300 MHz)



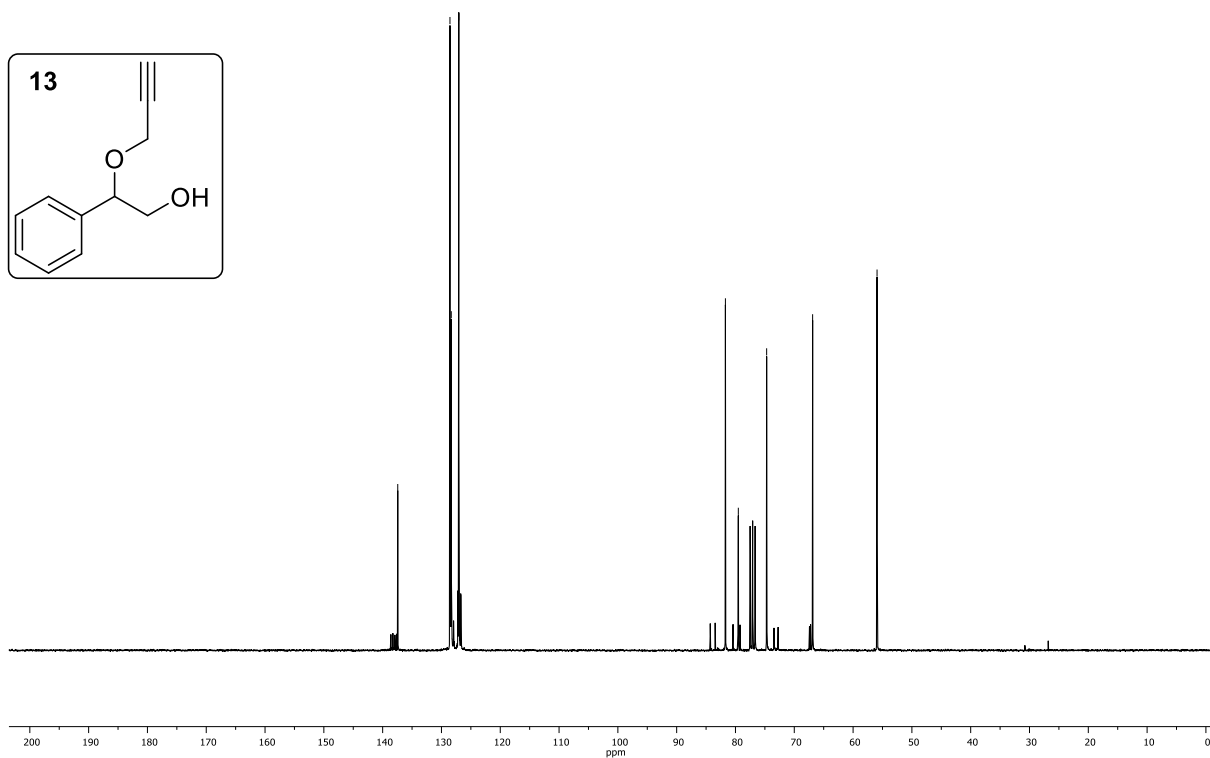
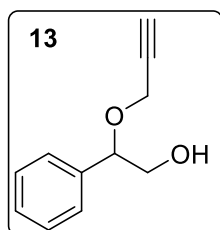
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



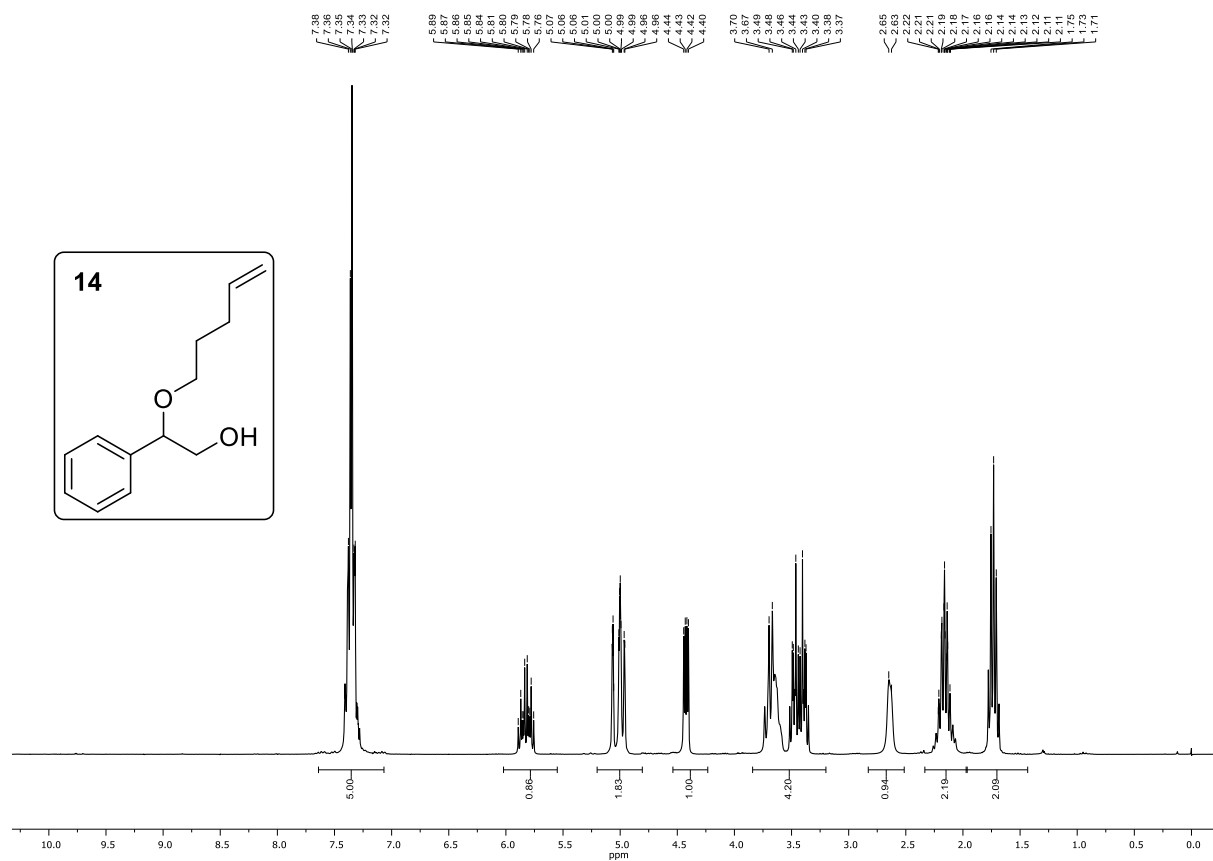
^1H NMR (CDCl_3 , 300 MHz)



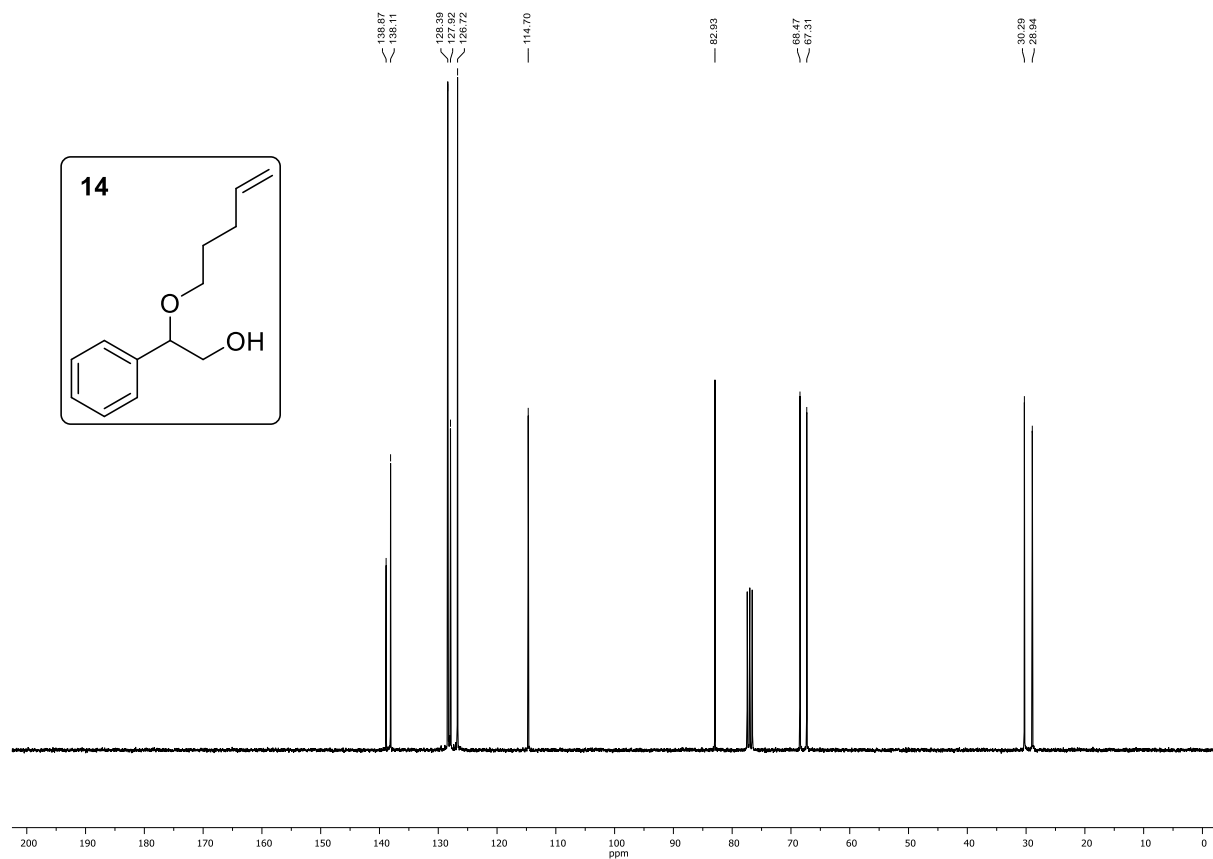
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



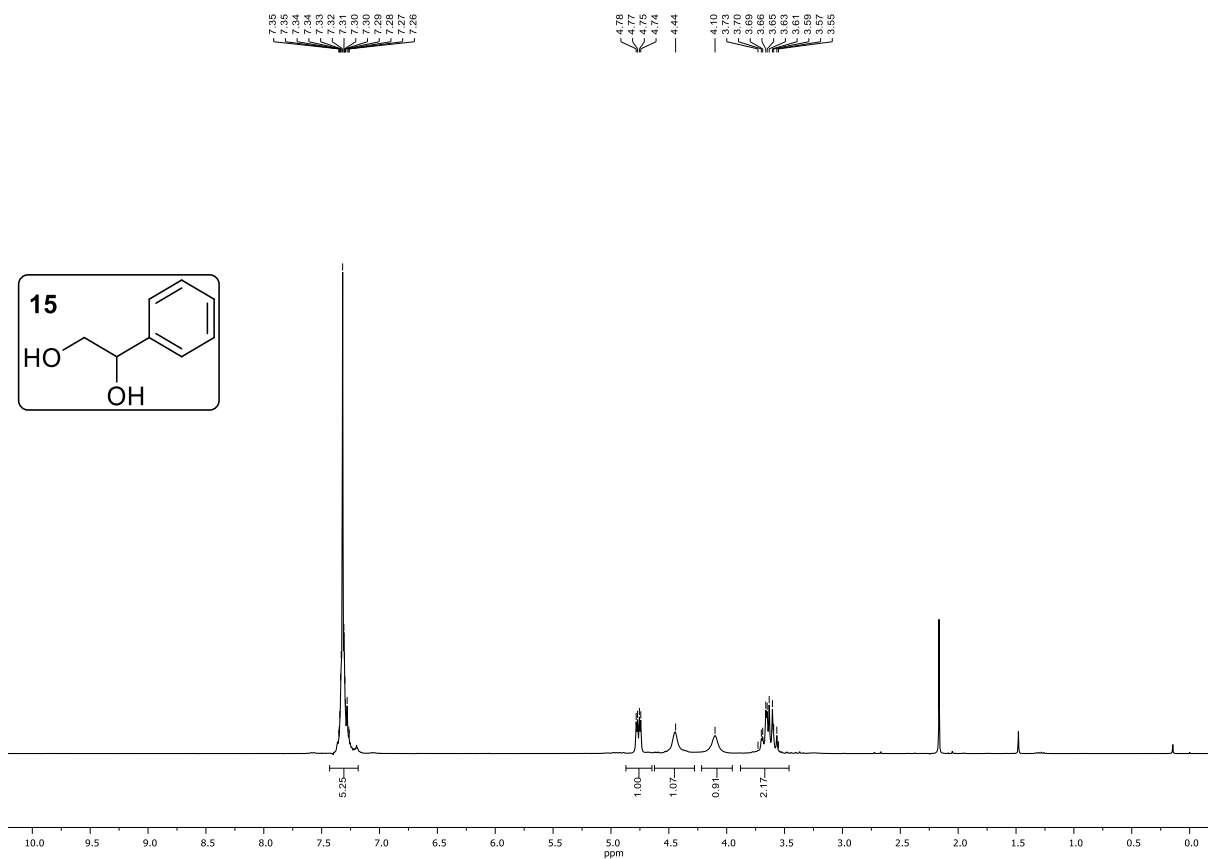
^1H NMR (CDCl_3 , 300 MHz)



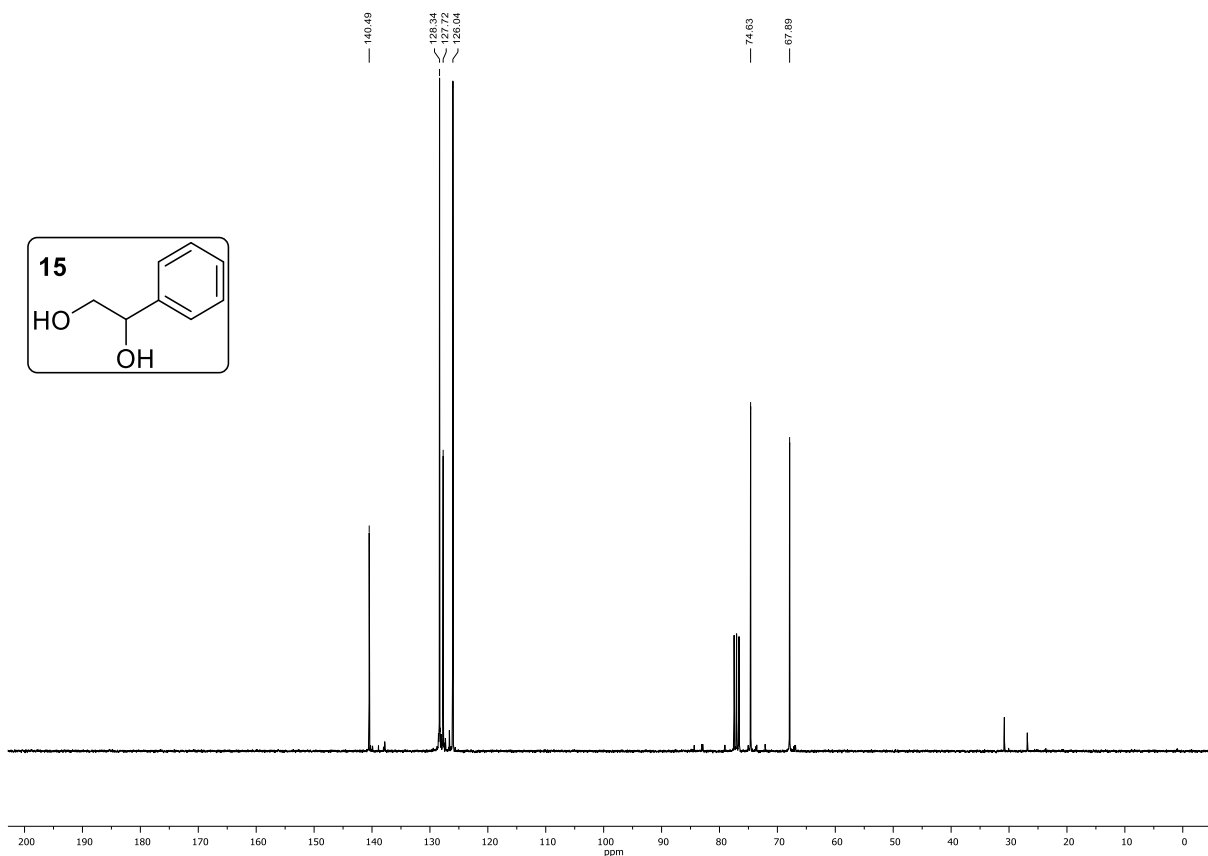
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)



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



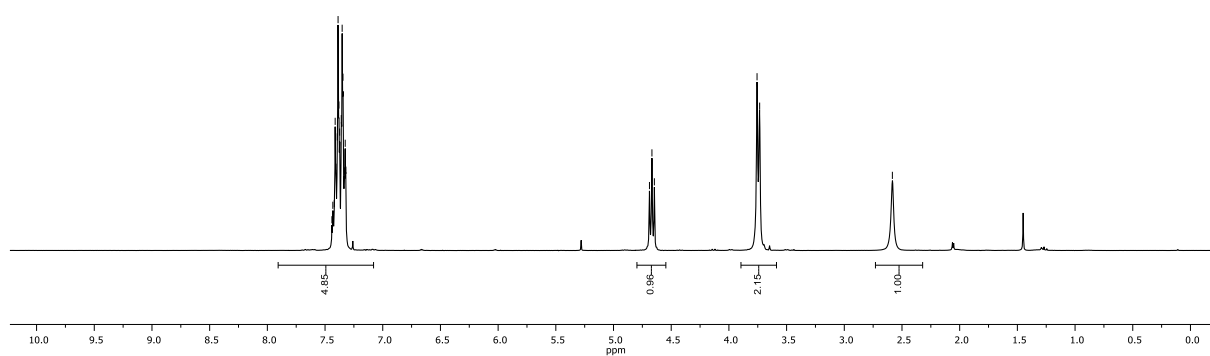
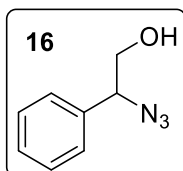
^1H NMR (CDCl_3 , 300 MHz)

7.44
7.43
7.42
7.41
7.39
7.37
7.36
7.35
7.33
7.32

4.69
4.67
4.65

3.76
3.73

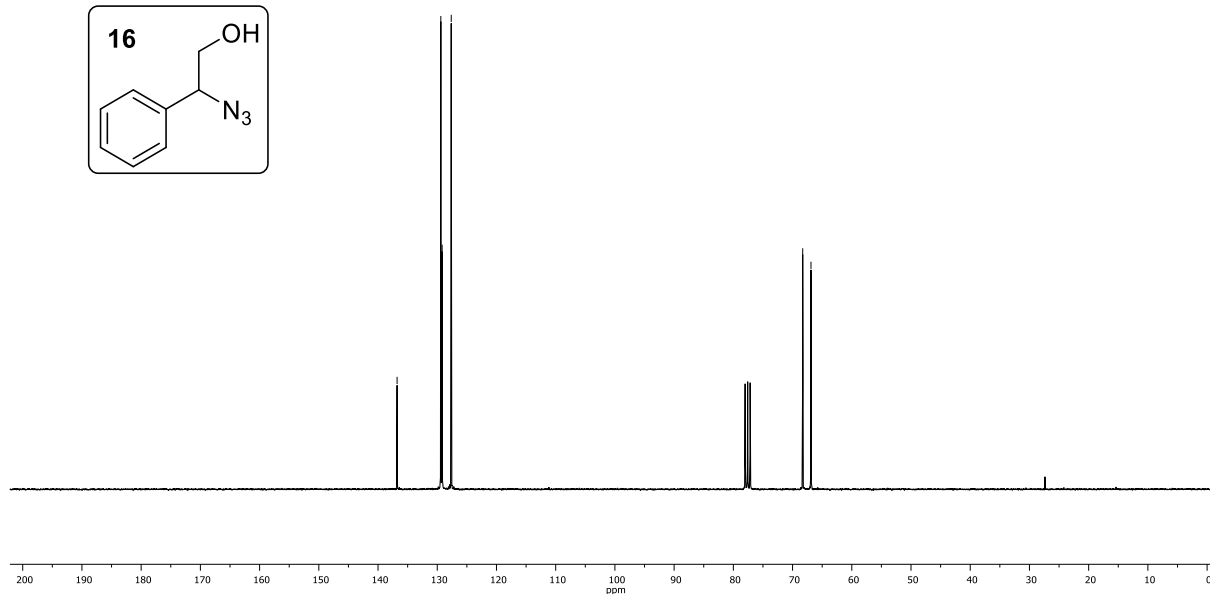
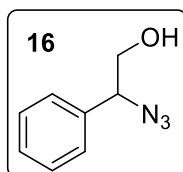
2.59



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

136.78
128.40
125.17
127.64

68.29
66.89

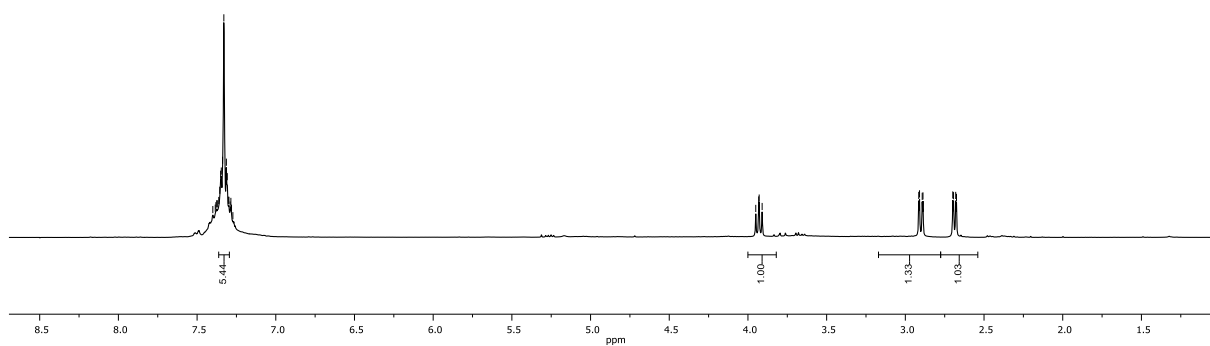
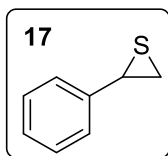


^1H NMR (CDCl_3 , 300 MHz)

7.40
7.38
7.36
7.35
7.34
7.33
7.31
7.30
7.29
7.28
7.27

3.95
3.93
3.91

2.91
2.89
2.70
2.69
2.67



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

139.05

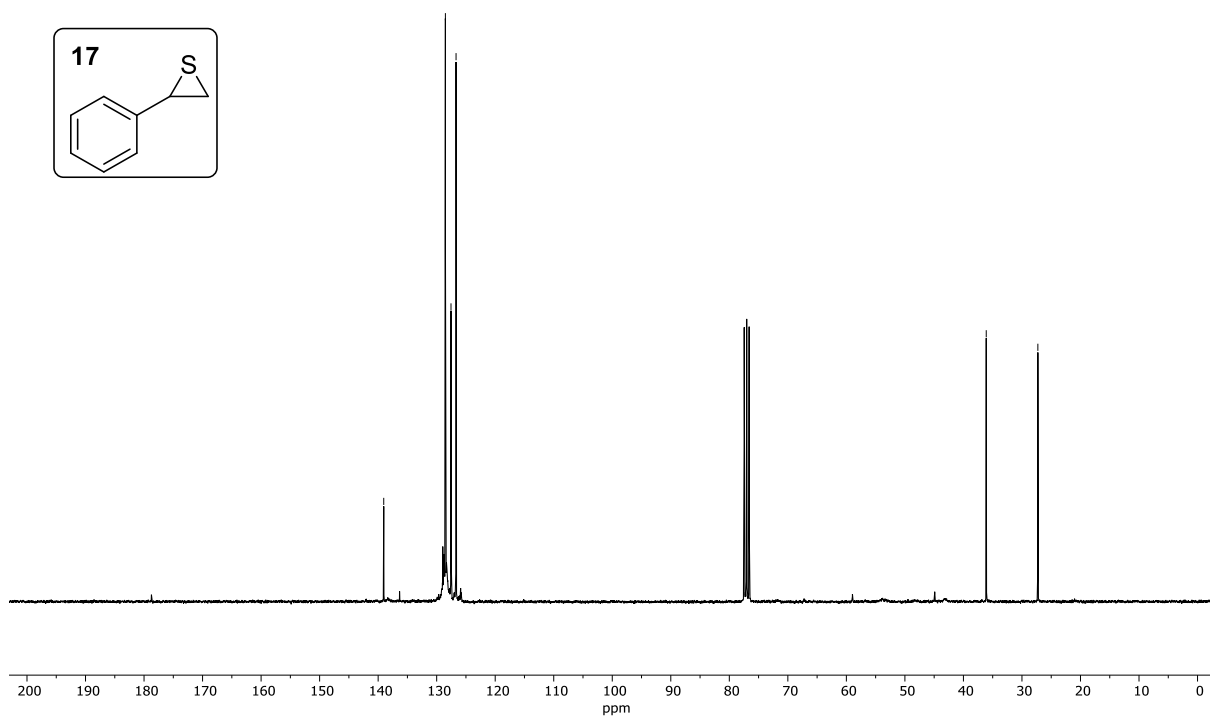
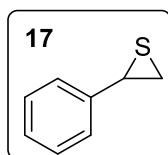
128.51

127.55

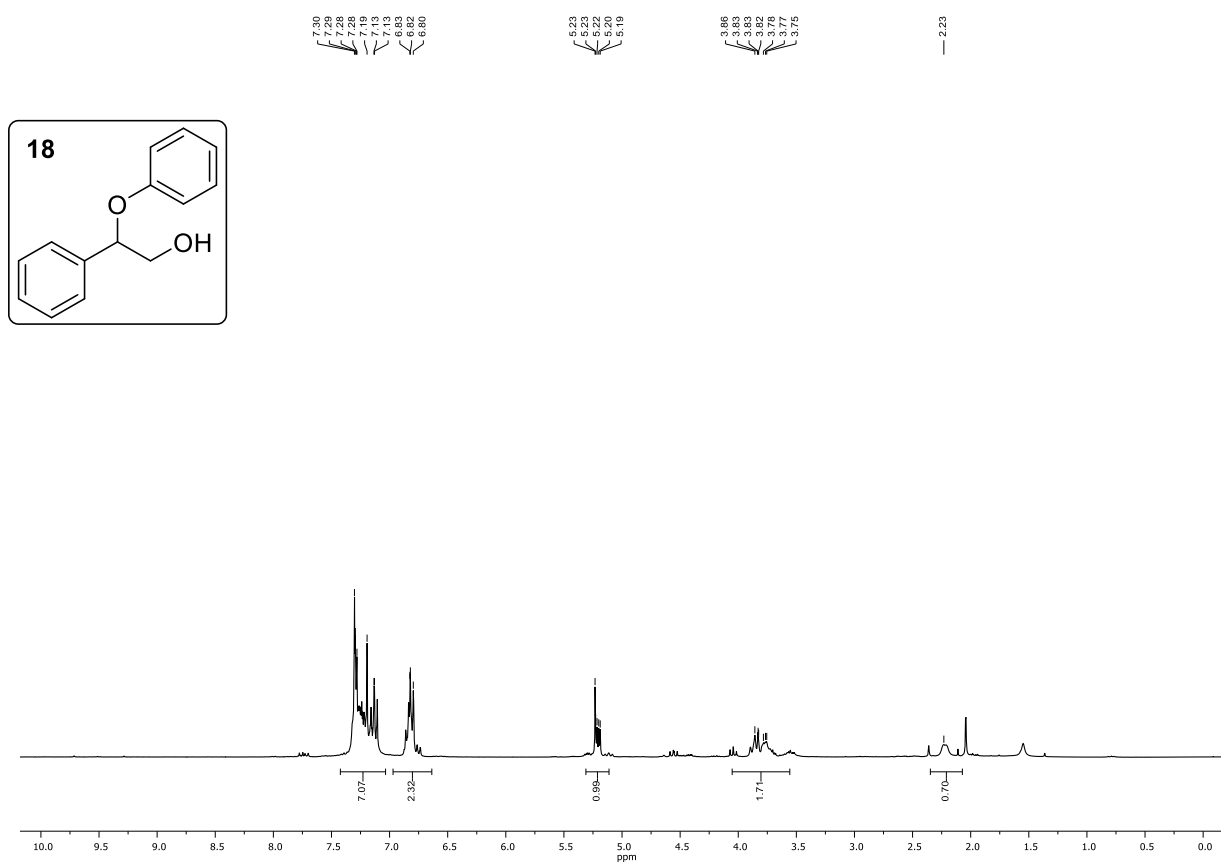
126.69

36.10

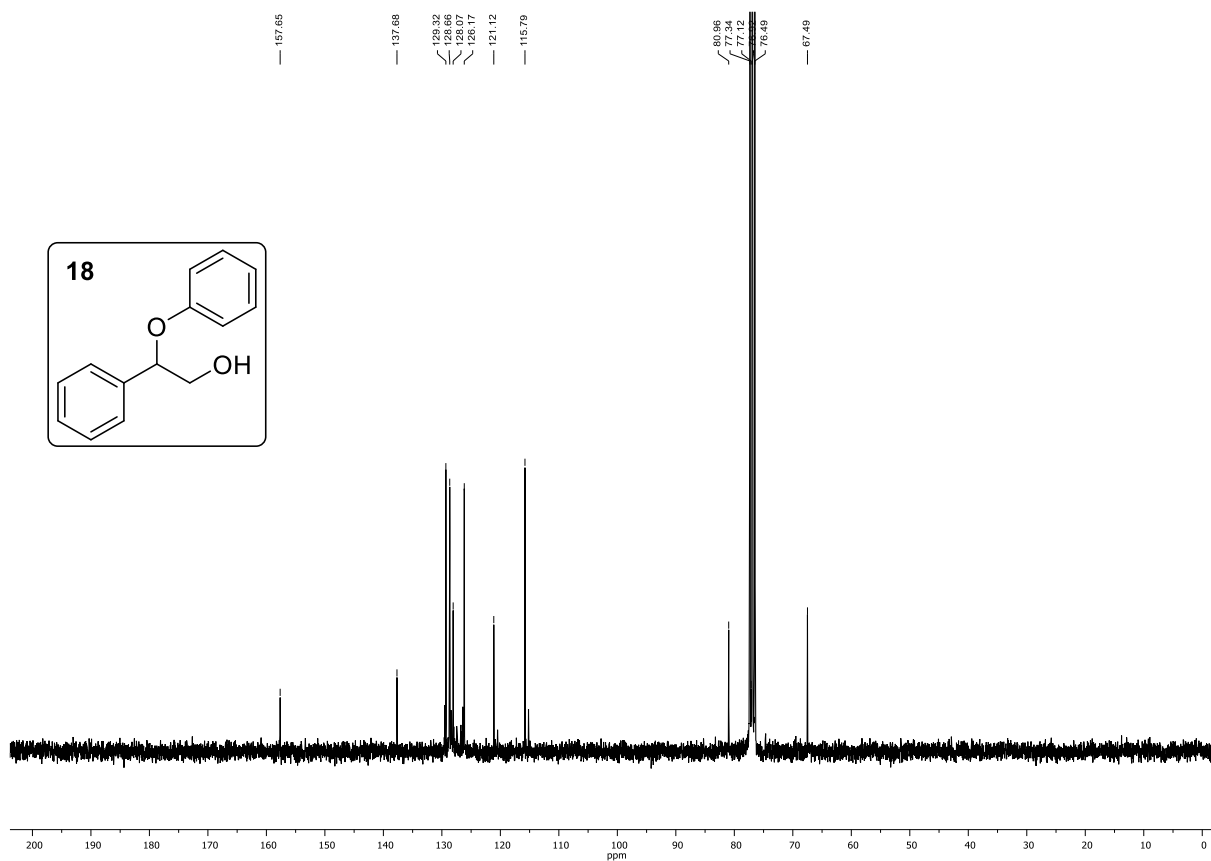
27.28



^1H NMR (CDCl_3 , 300 MHz)



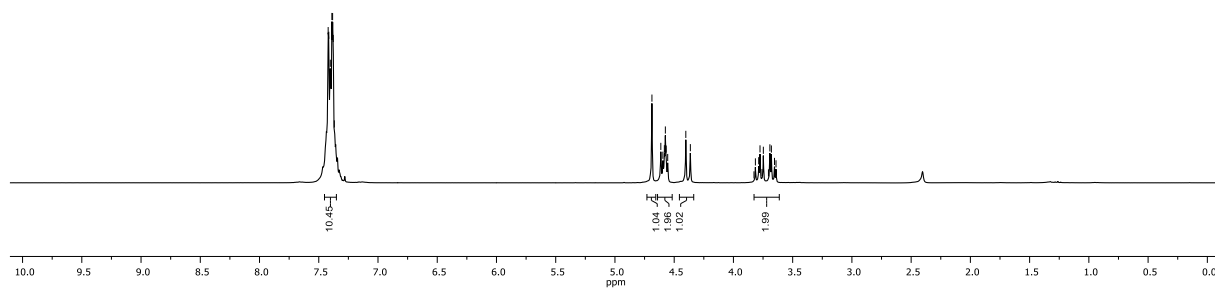
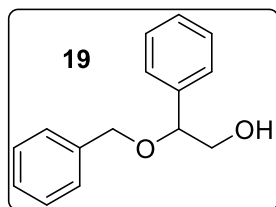
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)

7.42
7.40
7.39
7.38
7.37

4.69
4.61
4.59
4.57
4.55
4.40
4.36
3.85
3.79
3.78
3.75
3.70
3.69
3.65
3.64



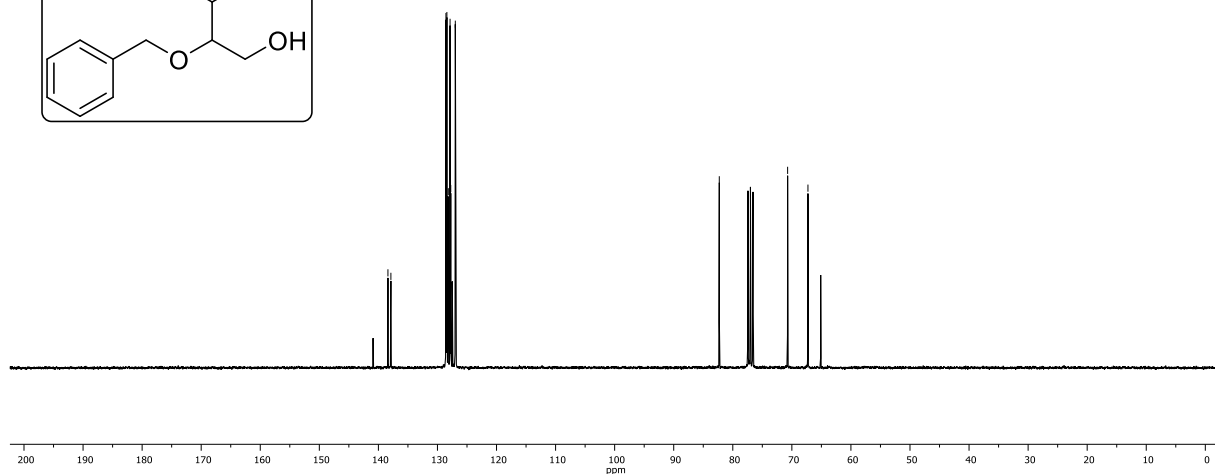
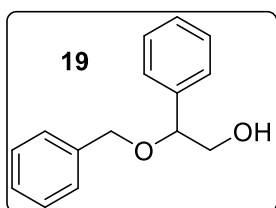
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)

138.38
137.86
128.96
128.40
128.17
127.75
126.98

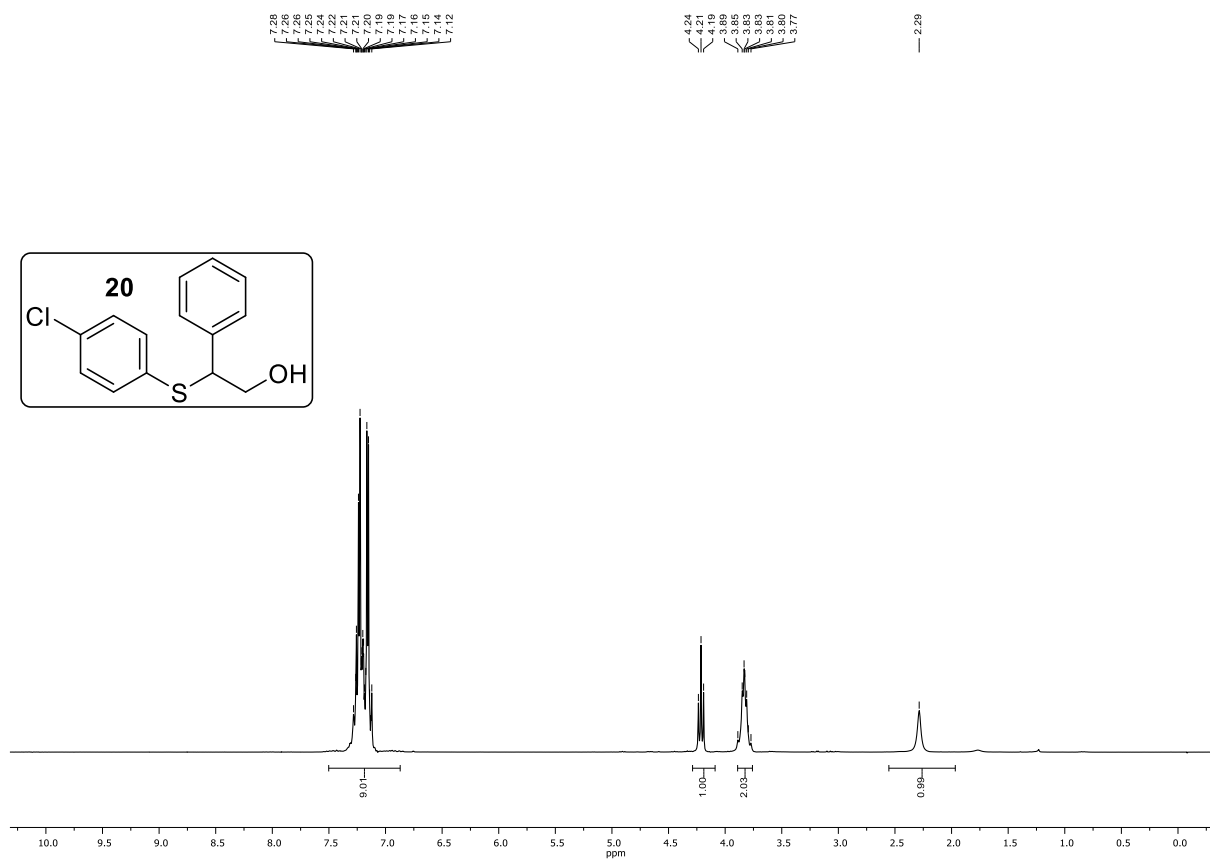
82.29

70.72

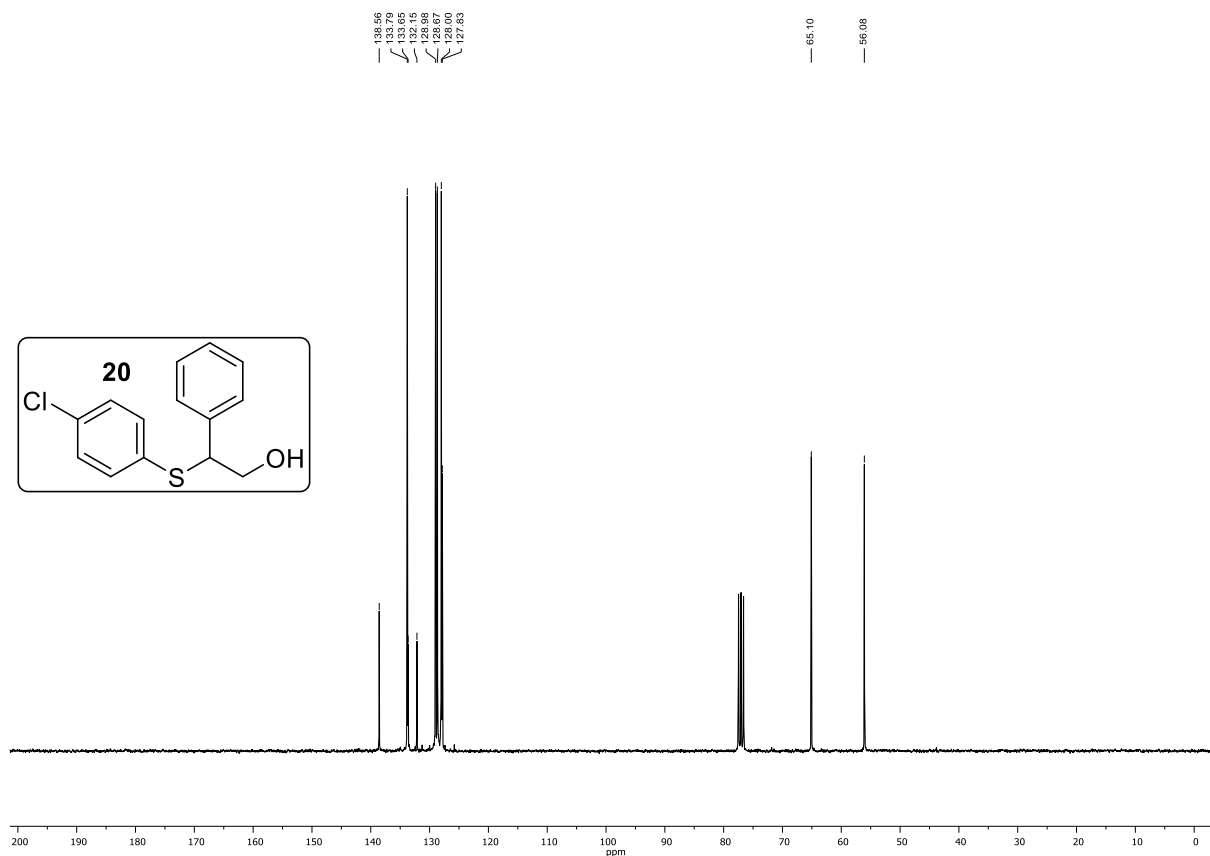
67.27



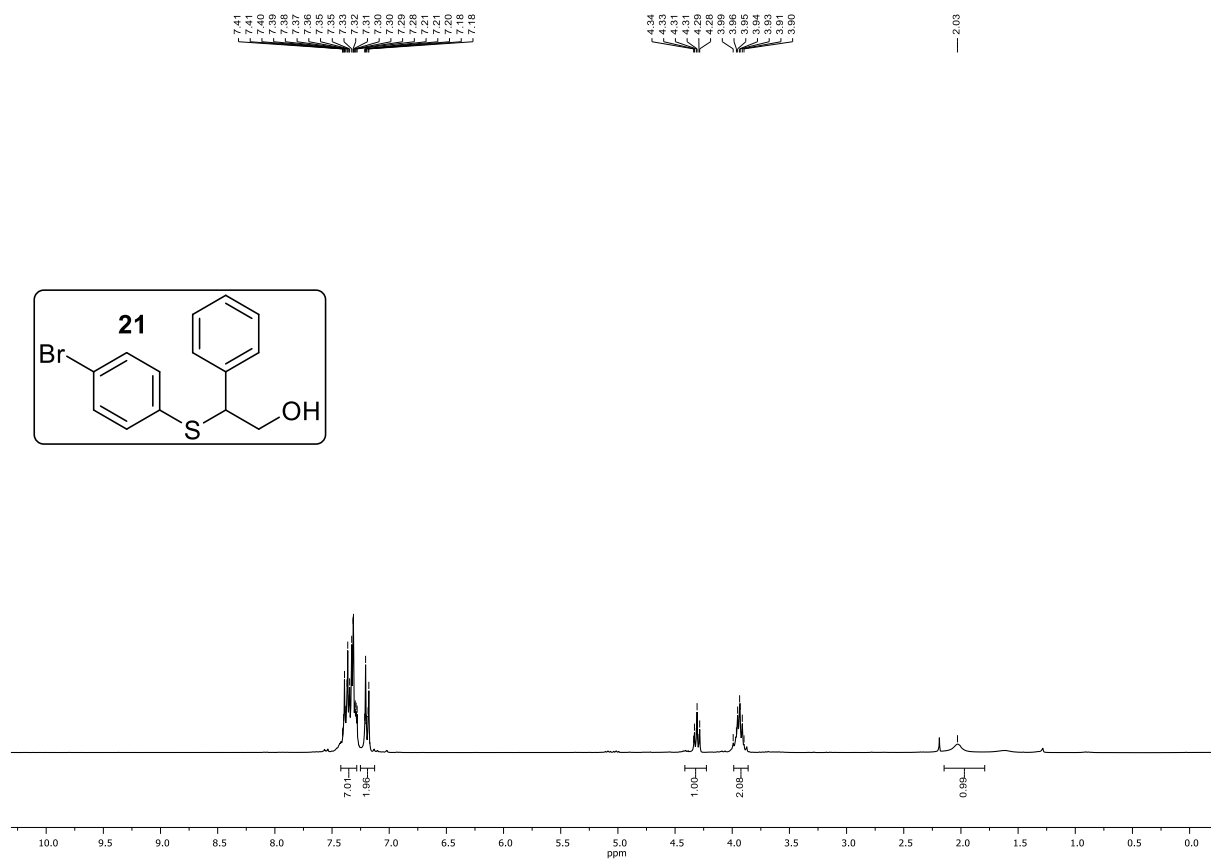
^1H NMR (CDCl_3 , 300 MHz)



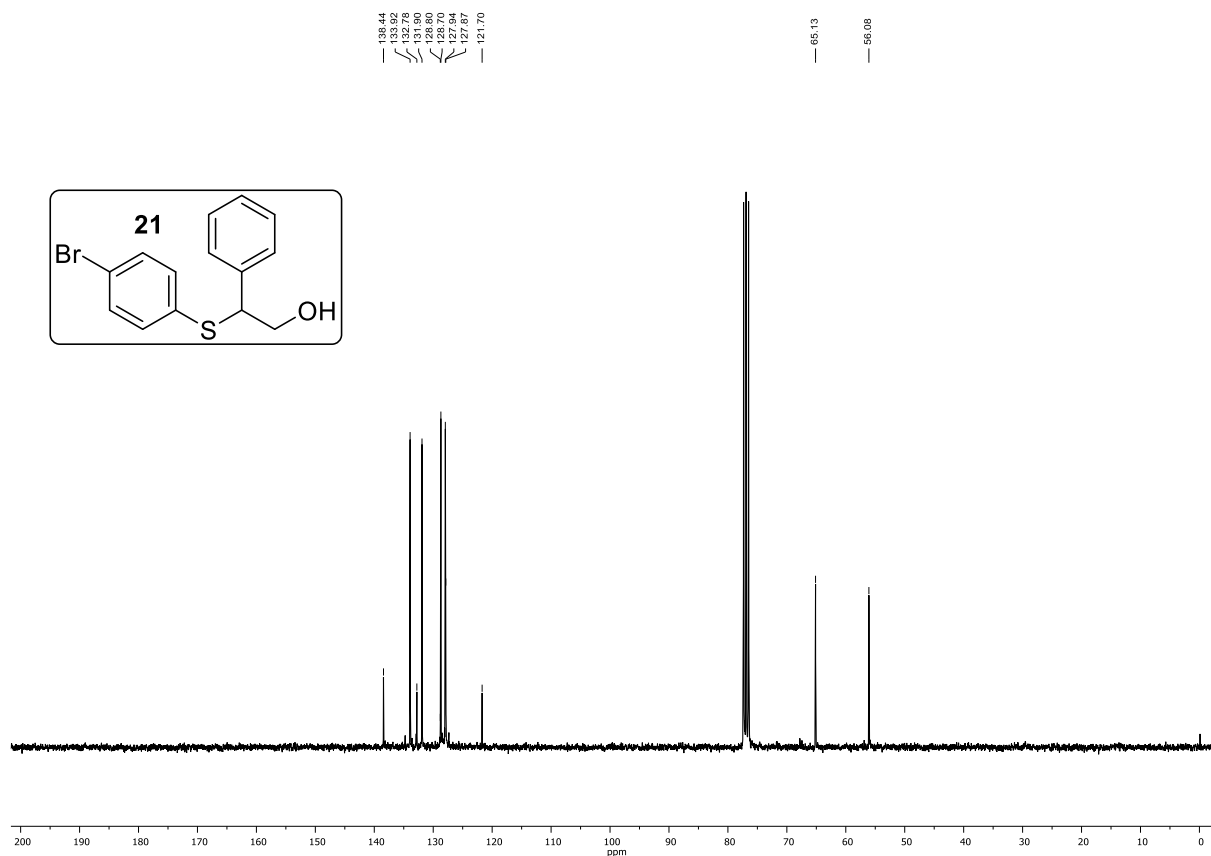
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



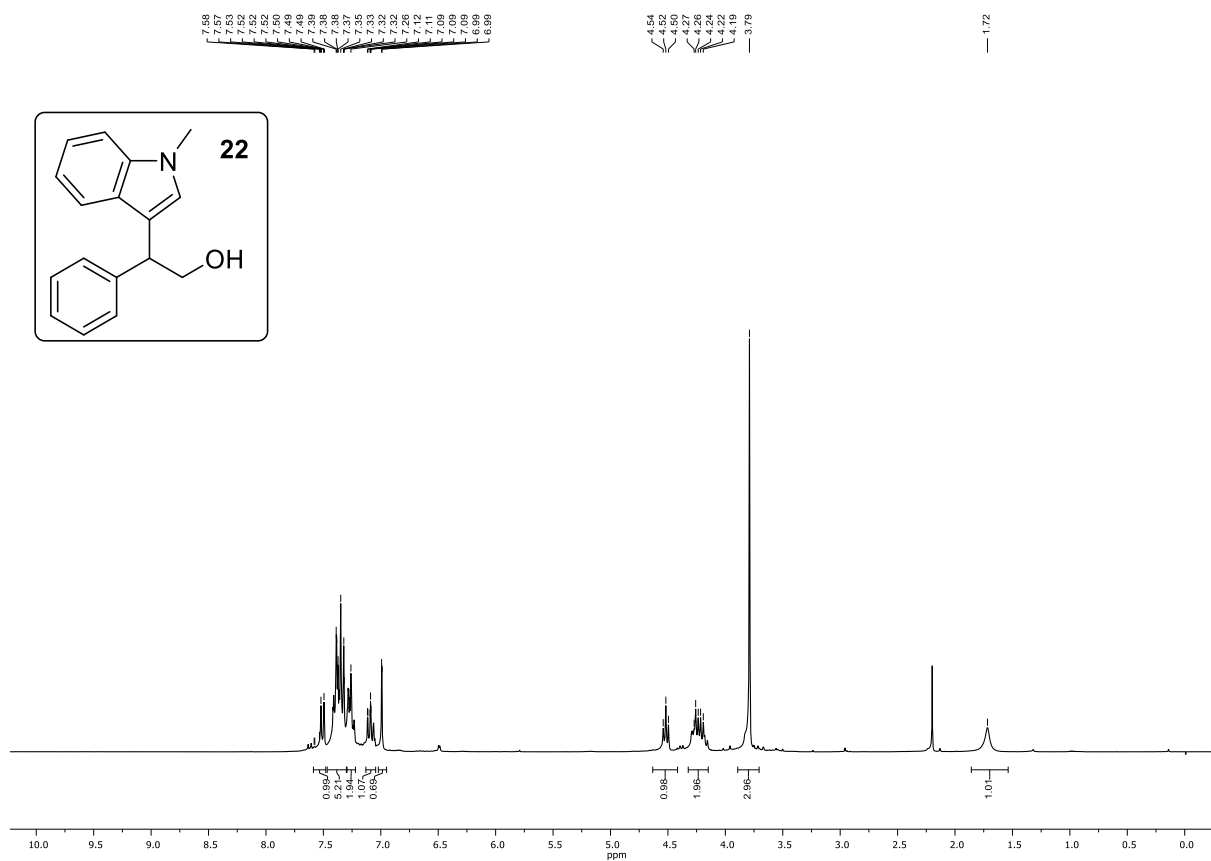
^1H NMR (CDCl_3 , 300 MHz)



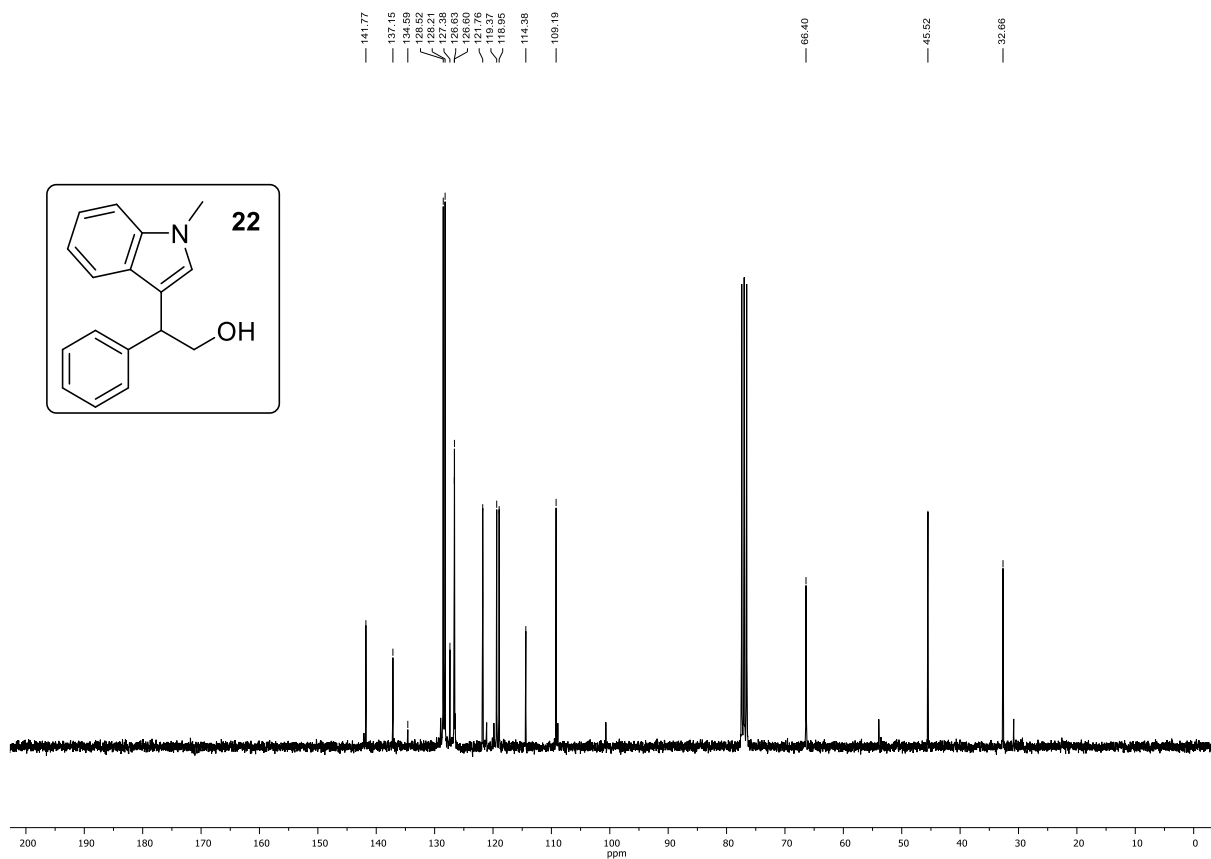
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



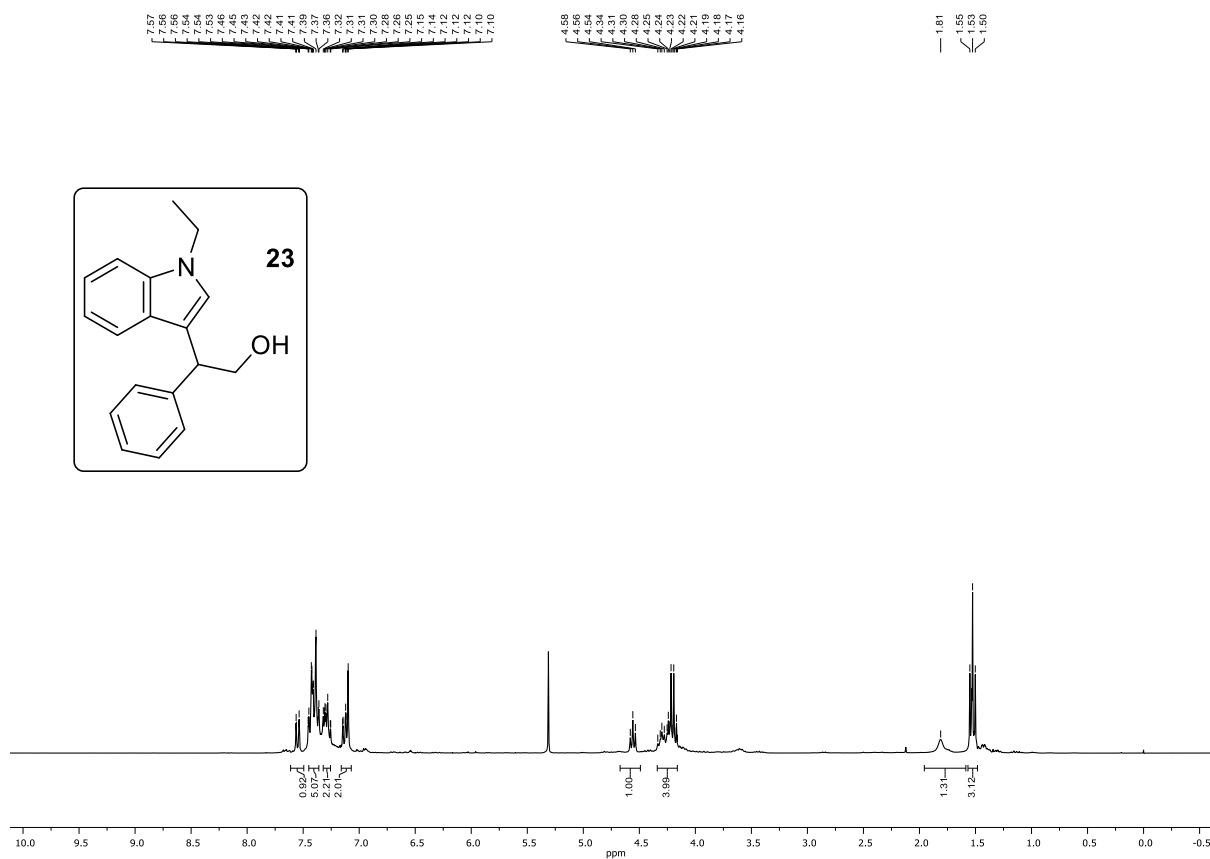
^1H NMR (CDCl_3 , 300 MHz)



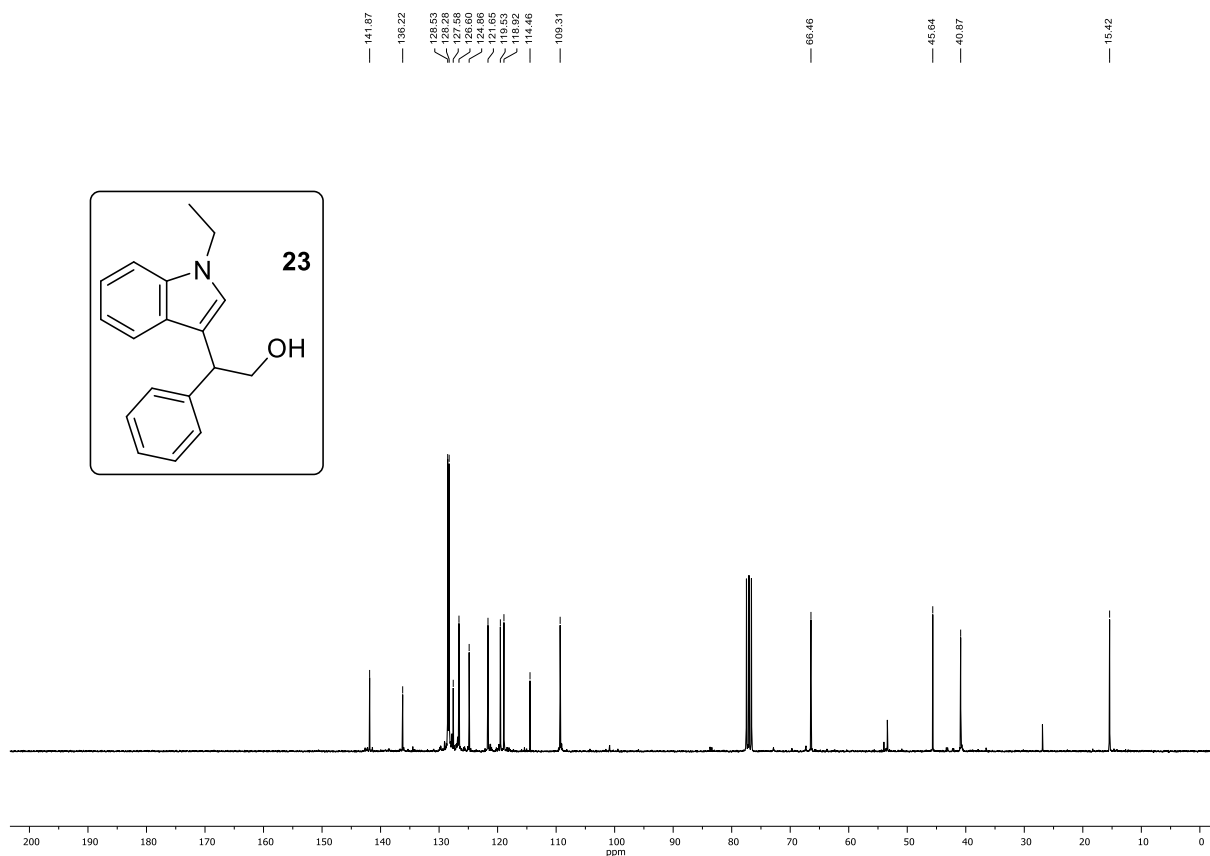
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



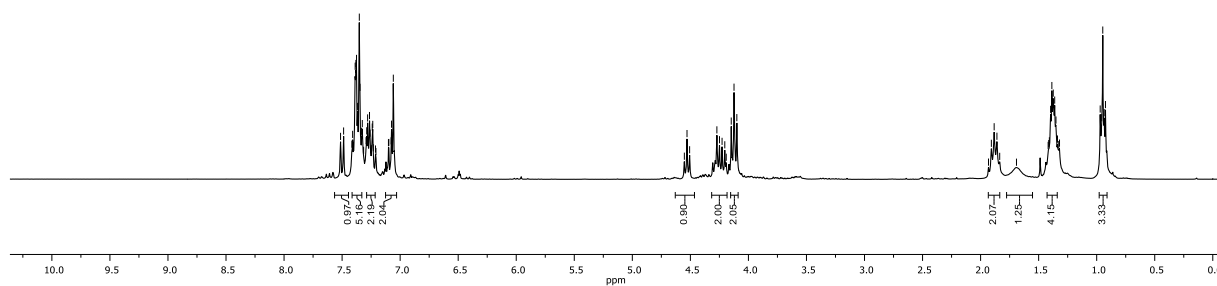
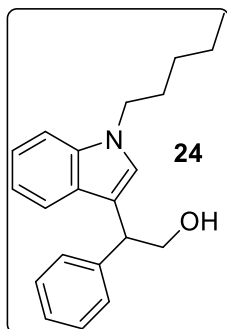
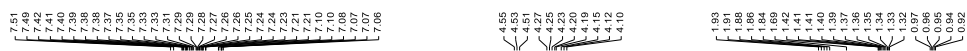
^1H NMR (CDCl_3 , 300 MHz)



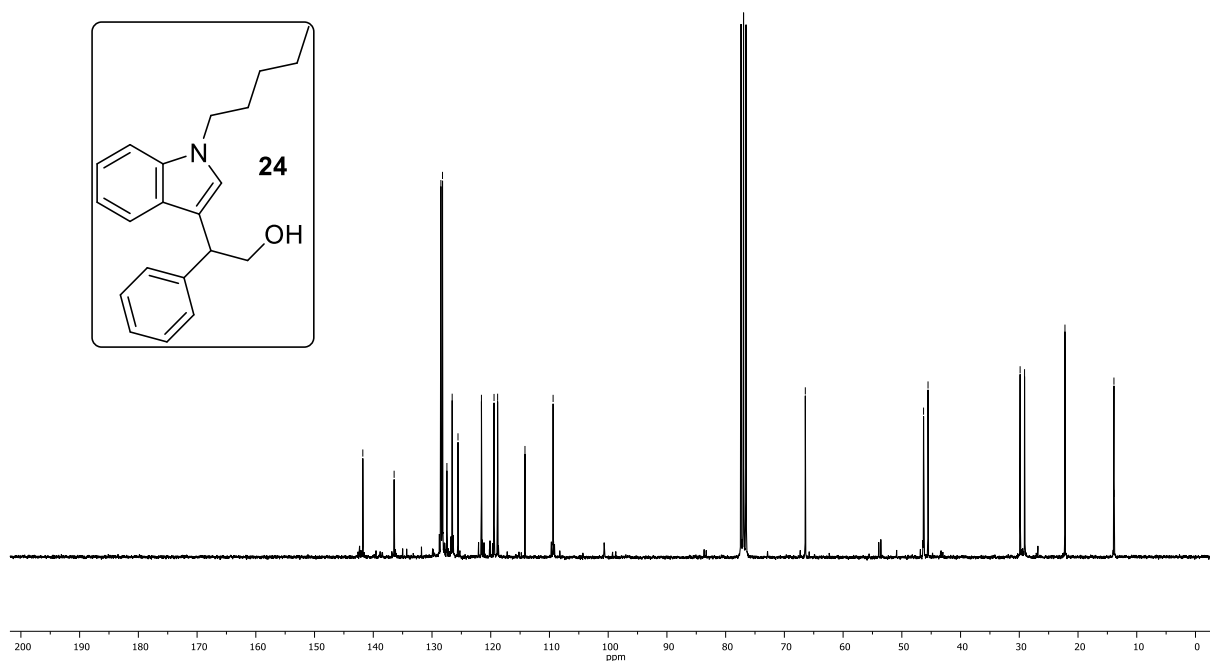
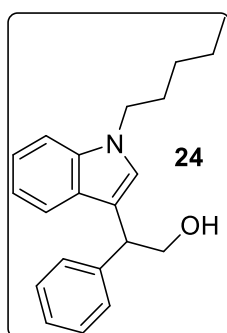
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



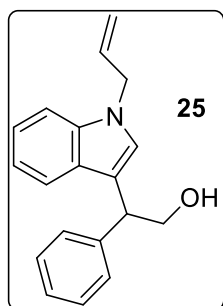
^1H NMR (CDCl_3 , 300 MHz)



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

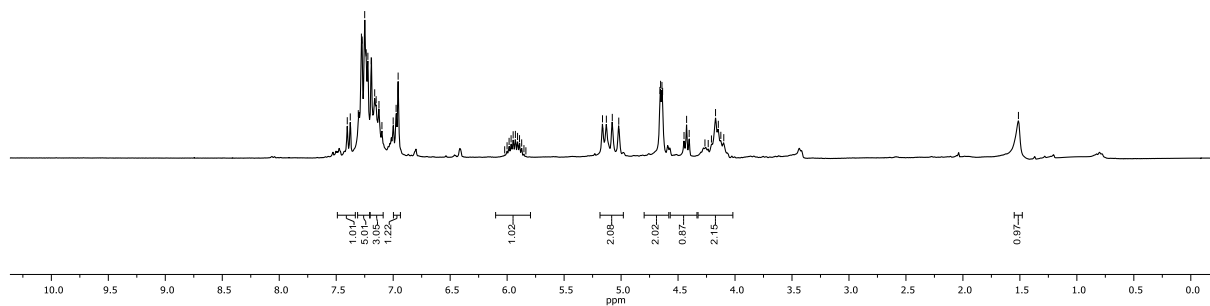


^1H NMR (CDCl_3 , 300 MHz)

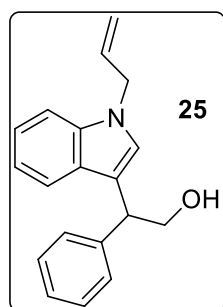


7.40
7.31
7.28
7.27
7.24
7.22
7.19
7.18
7.15
7.12
7.10
7.00
6.97
6.96
6.95
6.98
6.97
6.97
6.93
6.91
6.89
6.88
6.85
6.84
5.16
5.13
5.12
5.09
4.66
4.65
4.64
4.45
4.42
4.26
4.24
4.21
4.15
4.12
4.10

1.51



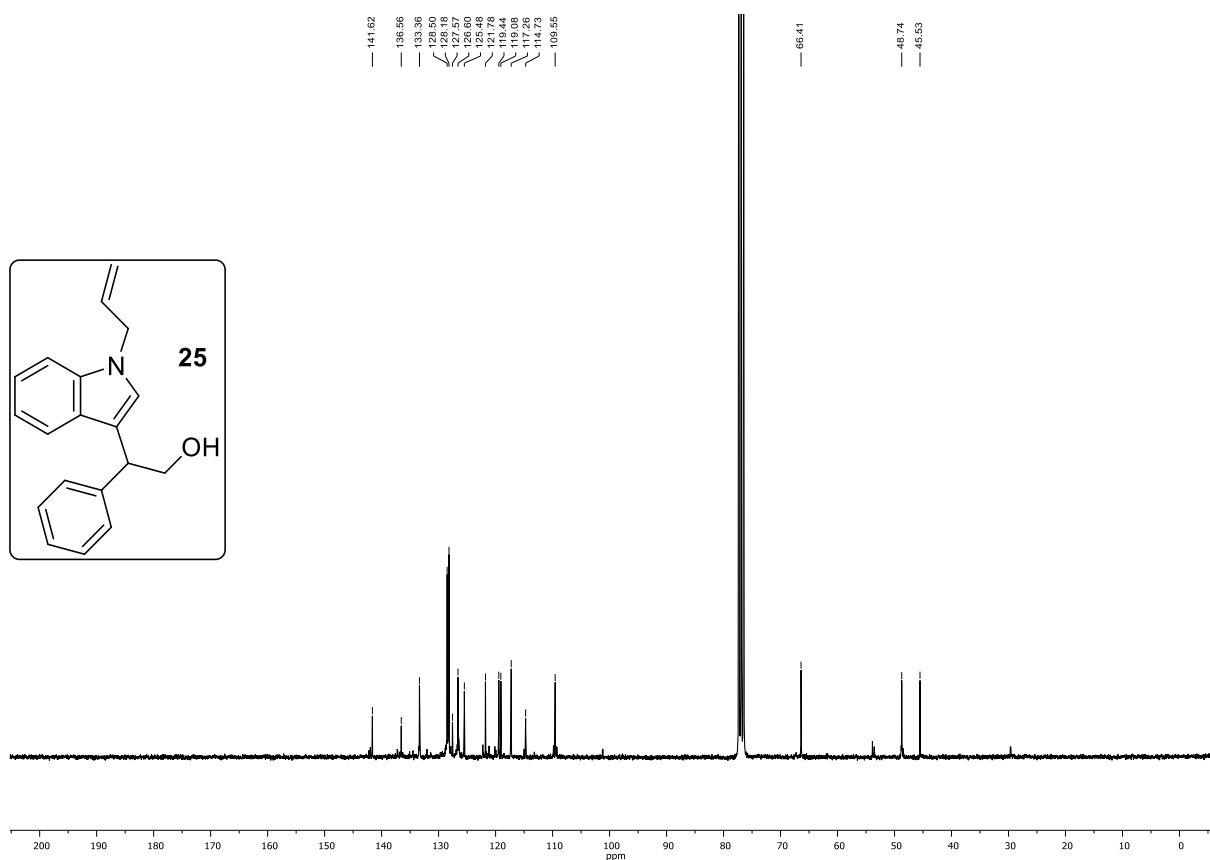
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



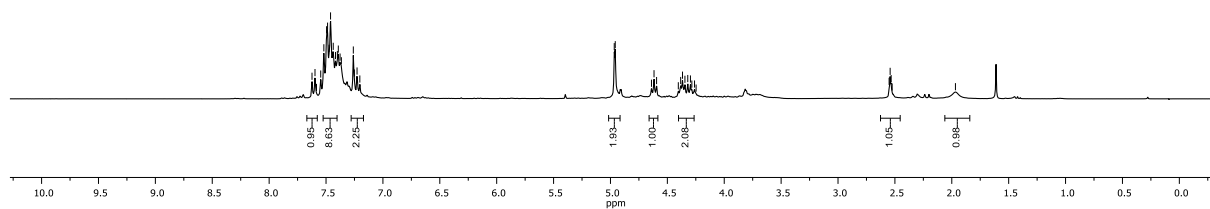
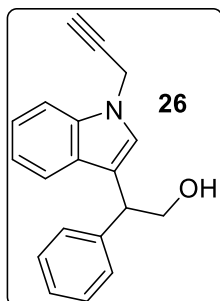
141.62
136.56
133.36
128.50
128.19
126.60
125.48
121.78
119.08
117.28
114.73
109.55

66.41

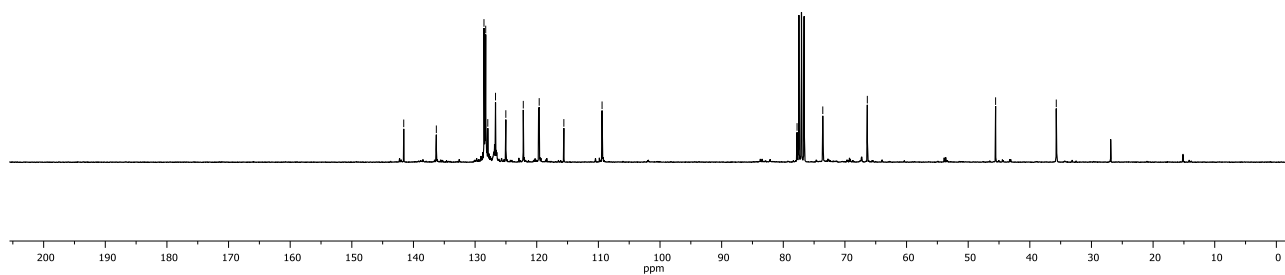
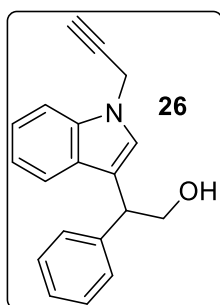
48.74
45.53



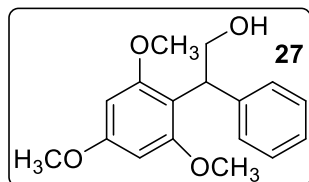
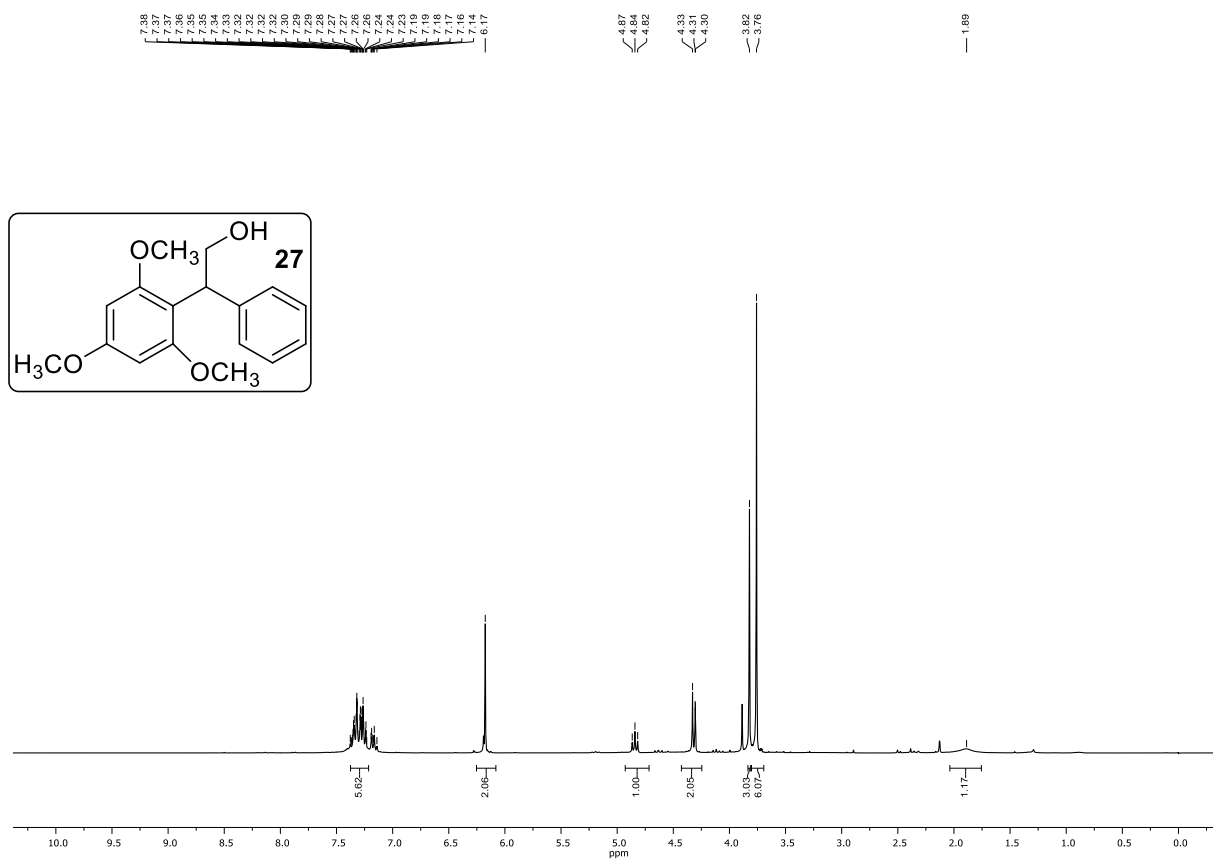
^1H NMR (CDCl_3 , 300 MHz)



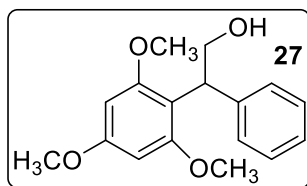
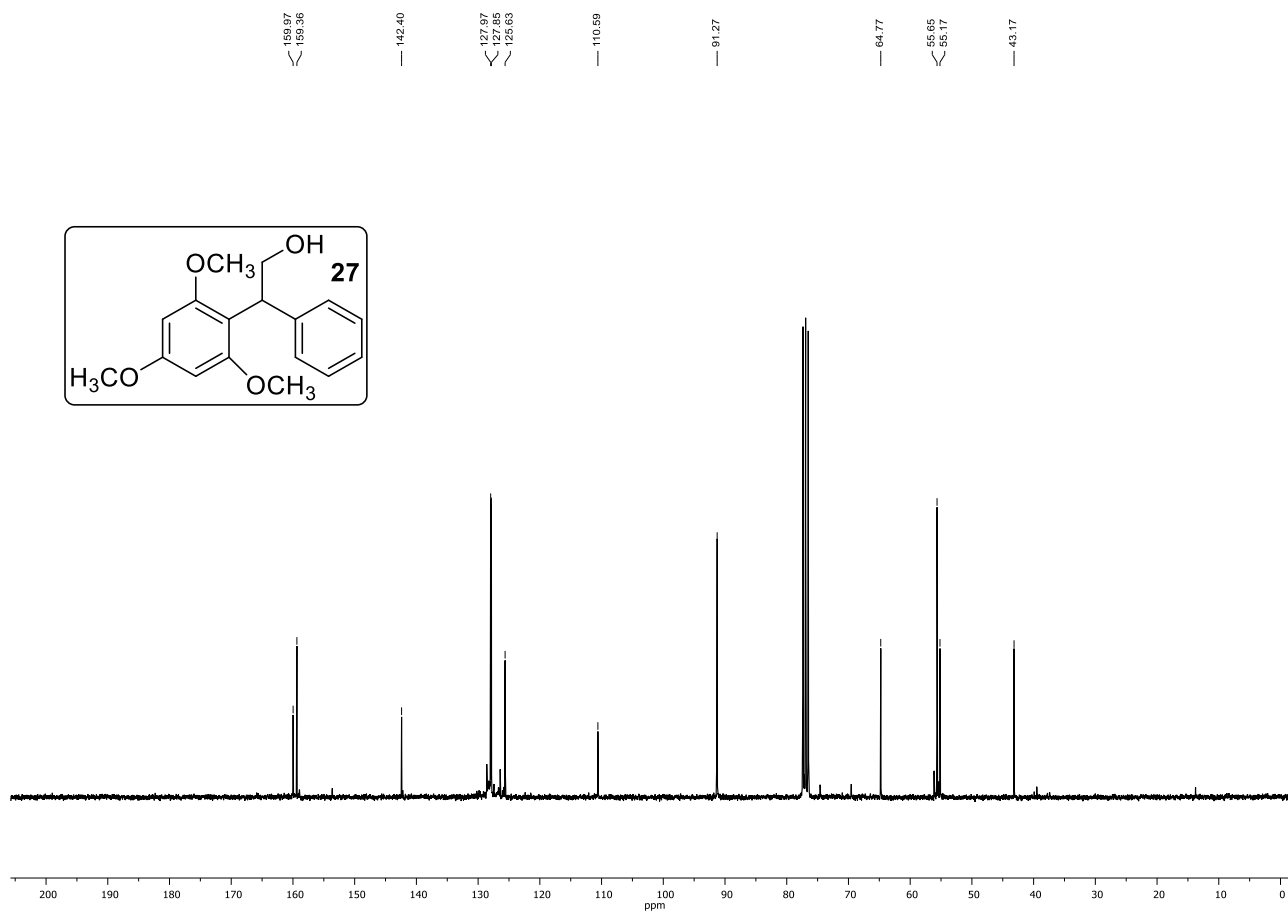
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



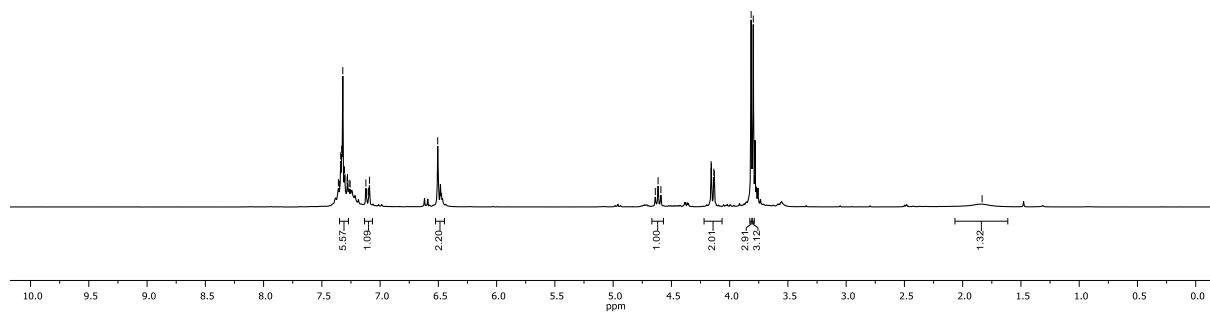
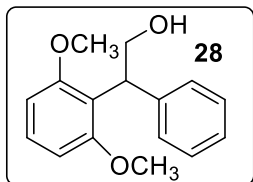
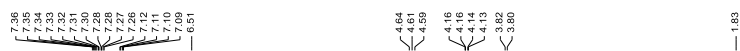
^1H NMR (CDCl_3 , 300 MHz)



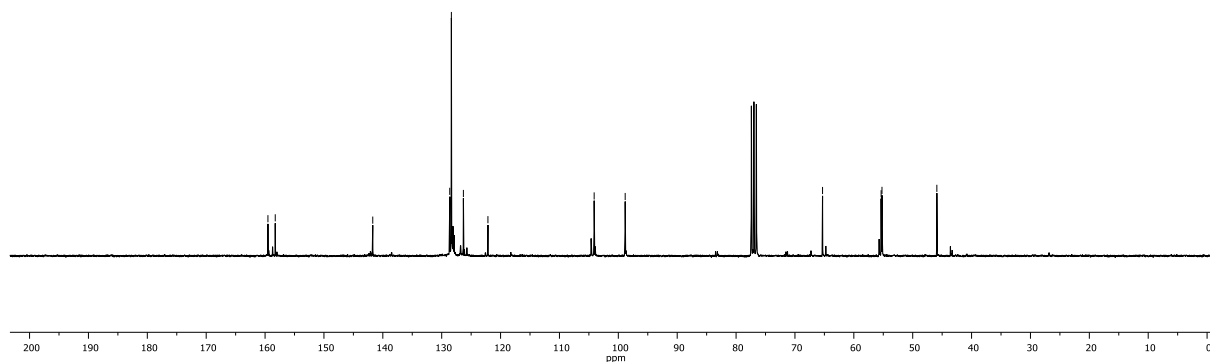
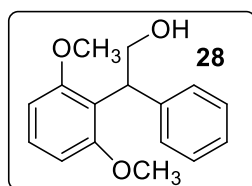
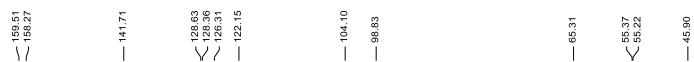
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



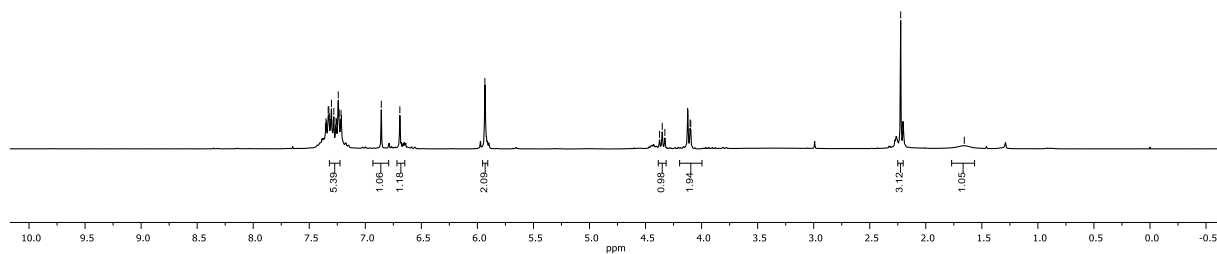
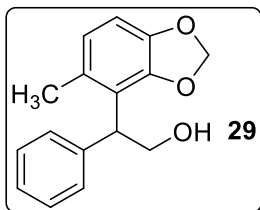
^1H NMR (CDCl_3 , 300 MHz)



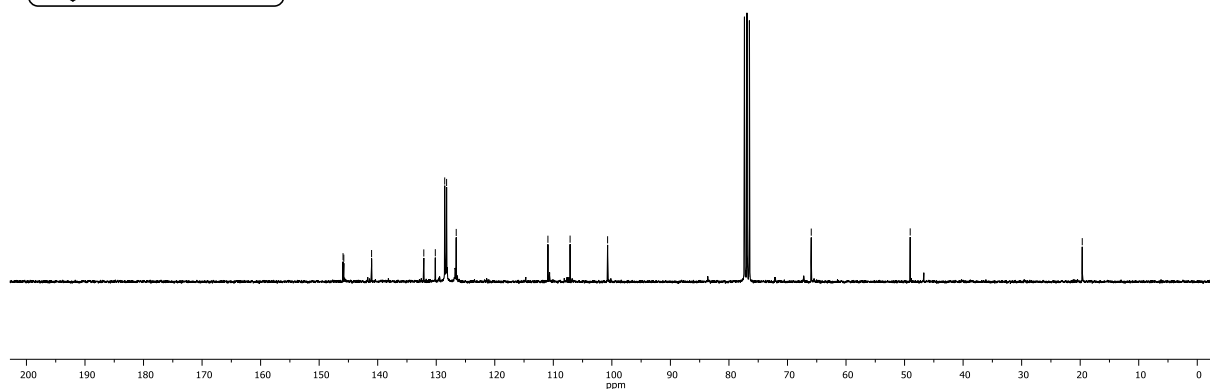
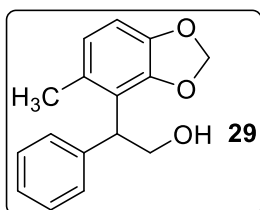
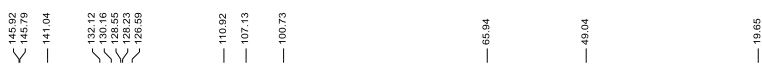
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



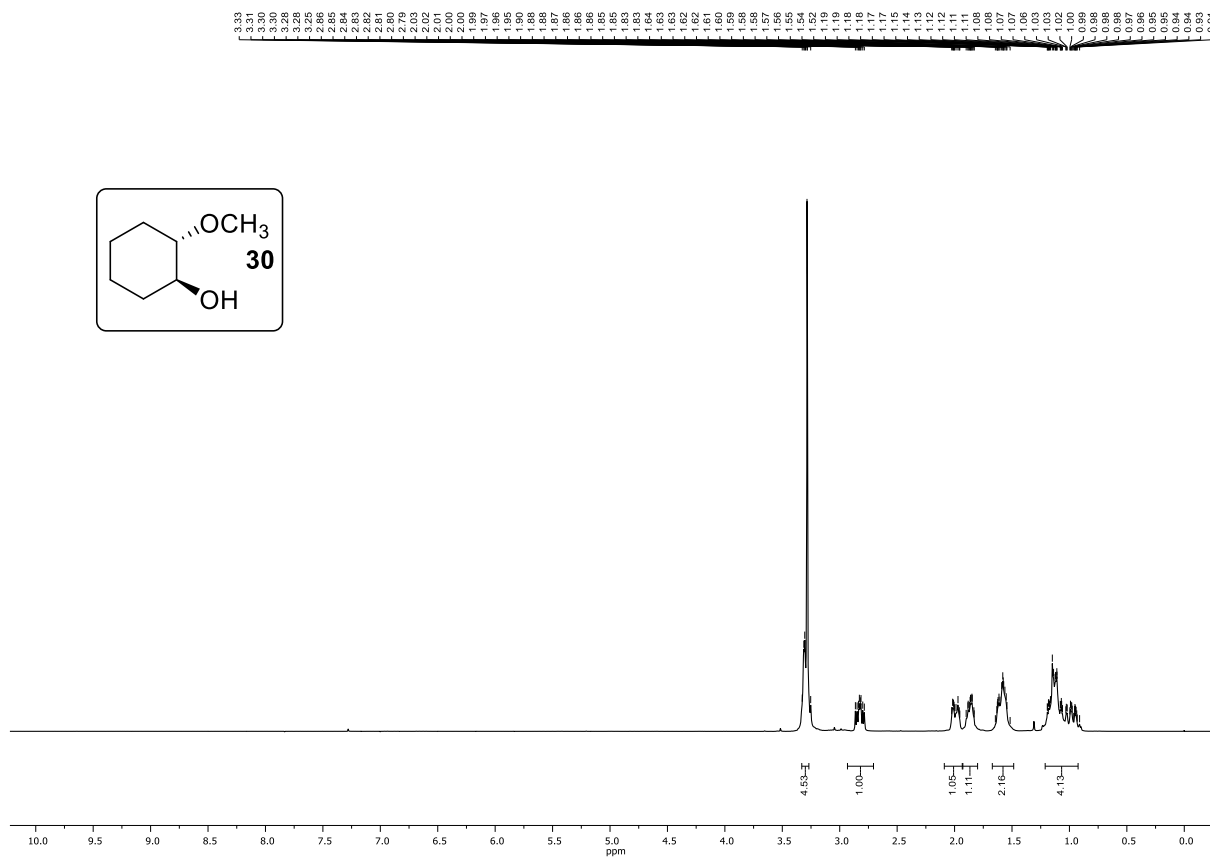
^1H NMR (CDCl_3 , 300 MHz)



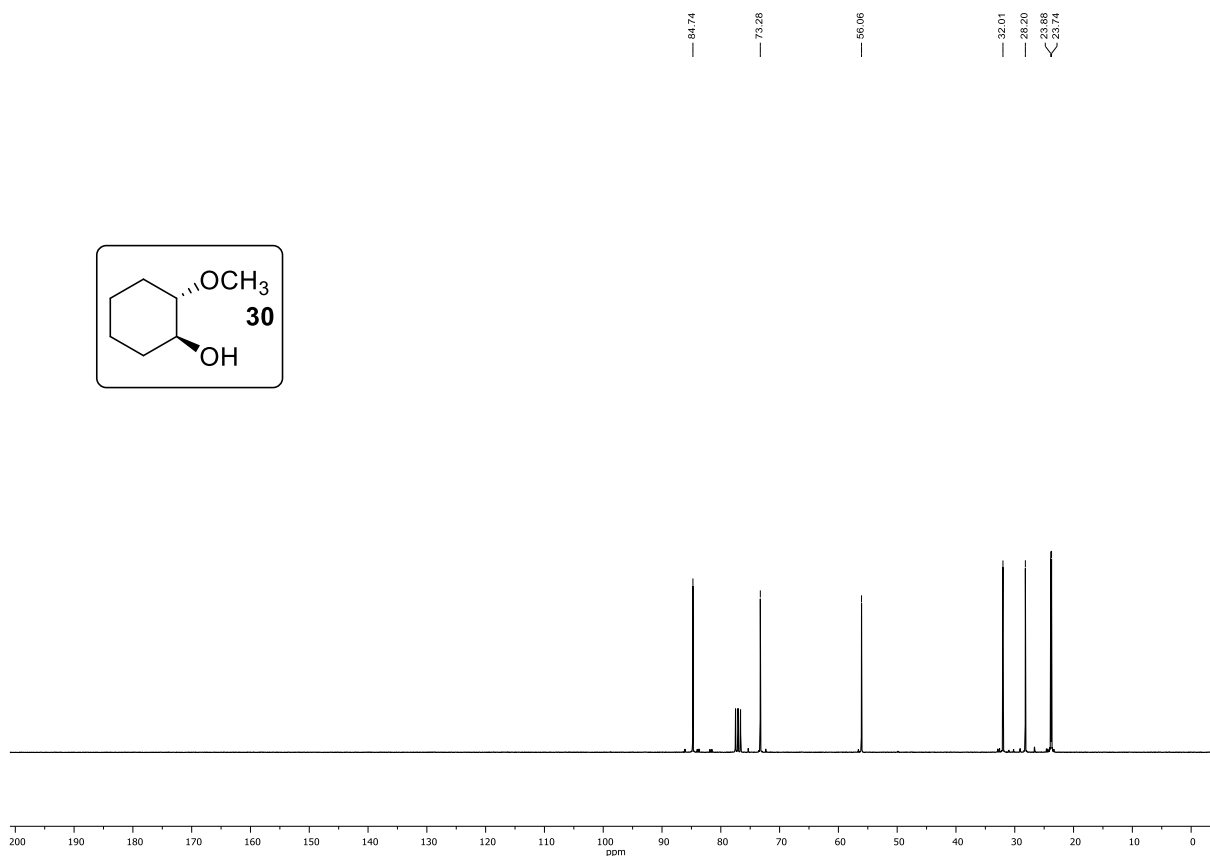
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



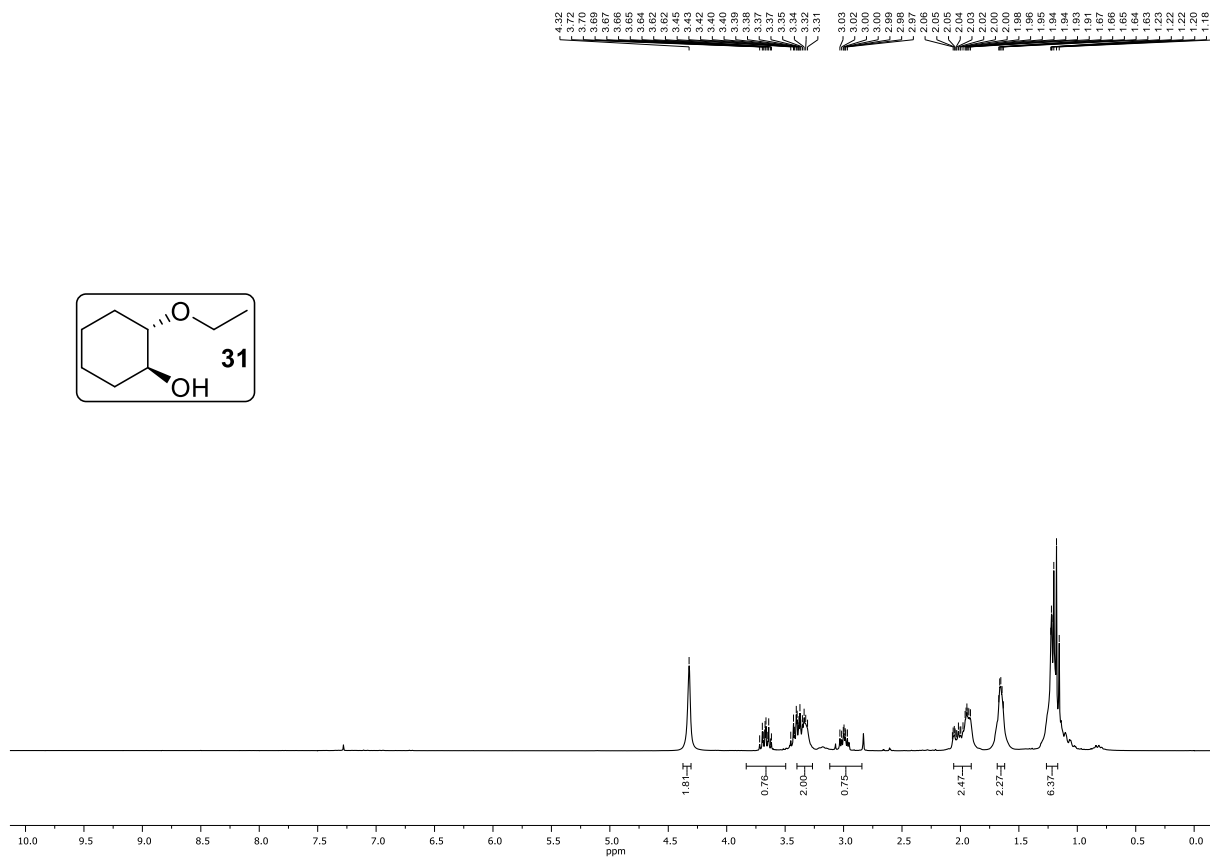
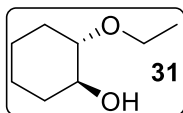
^1H NMR (CDCl_3 , 300 MHz)



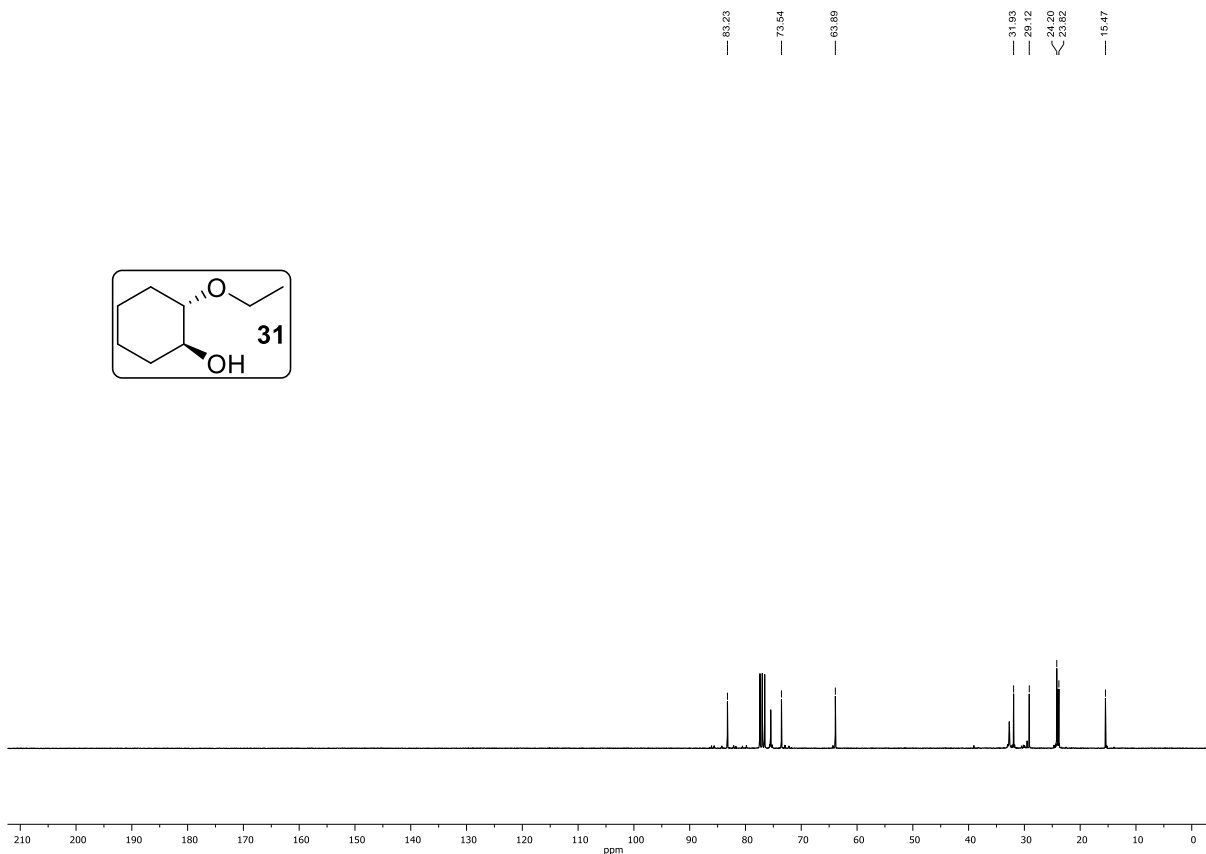
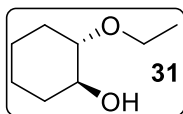
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



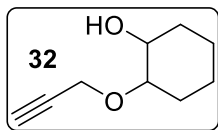
^1H NMR (CDCl_3 , 300 MHz)



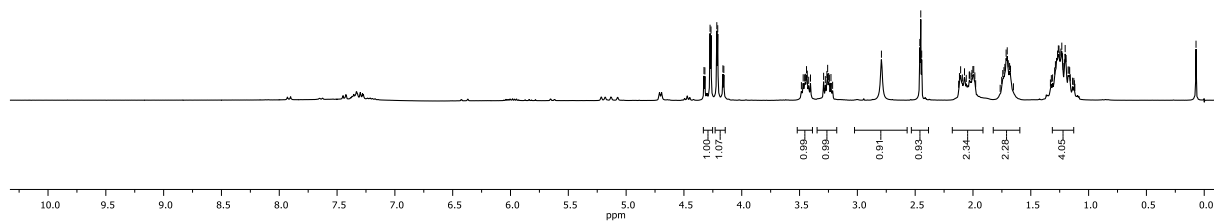
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



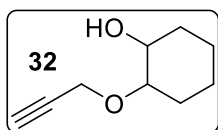
^1H NMR (CDCl_3 , 300 MHz)



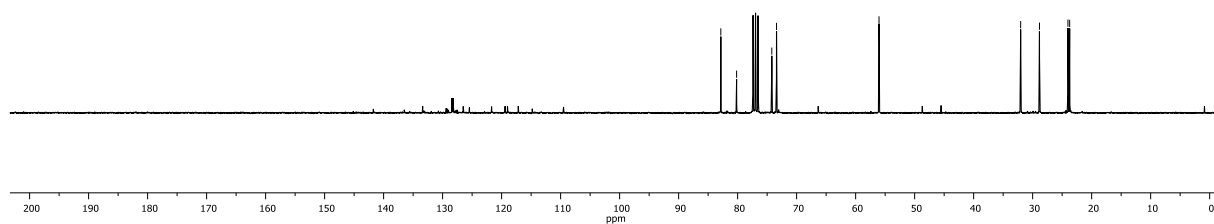
4.33
4.32
4.27
4.22
4.21
4.16
4.15
3.47
3.47
3.46
3.44
3.44
3.41
3.29
3.28
3.28
3.26
3.25
3.24
3.24
3.21
3.21
2.79
2.46
2.46
2.44
2.44
2.12
2.12
2.11
2.09
2.09
2.05
2.05
2.02
2.02
2.00
2.00
1.99
1.98
1.76
1.75
1.74
1.74
1.72
1.71
1.70
1.69
1.68
1.68
1.35
1.32
1.31
1.29
1.29
1.27
1.26
1.25
1.25
1.24
1.23
1.22
1.22
1.21
1.20
1.19
1.18
1.18
1.17
1.16
1.16
1.14
1.13
1.12
1.12
0.07



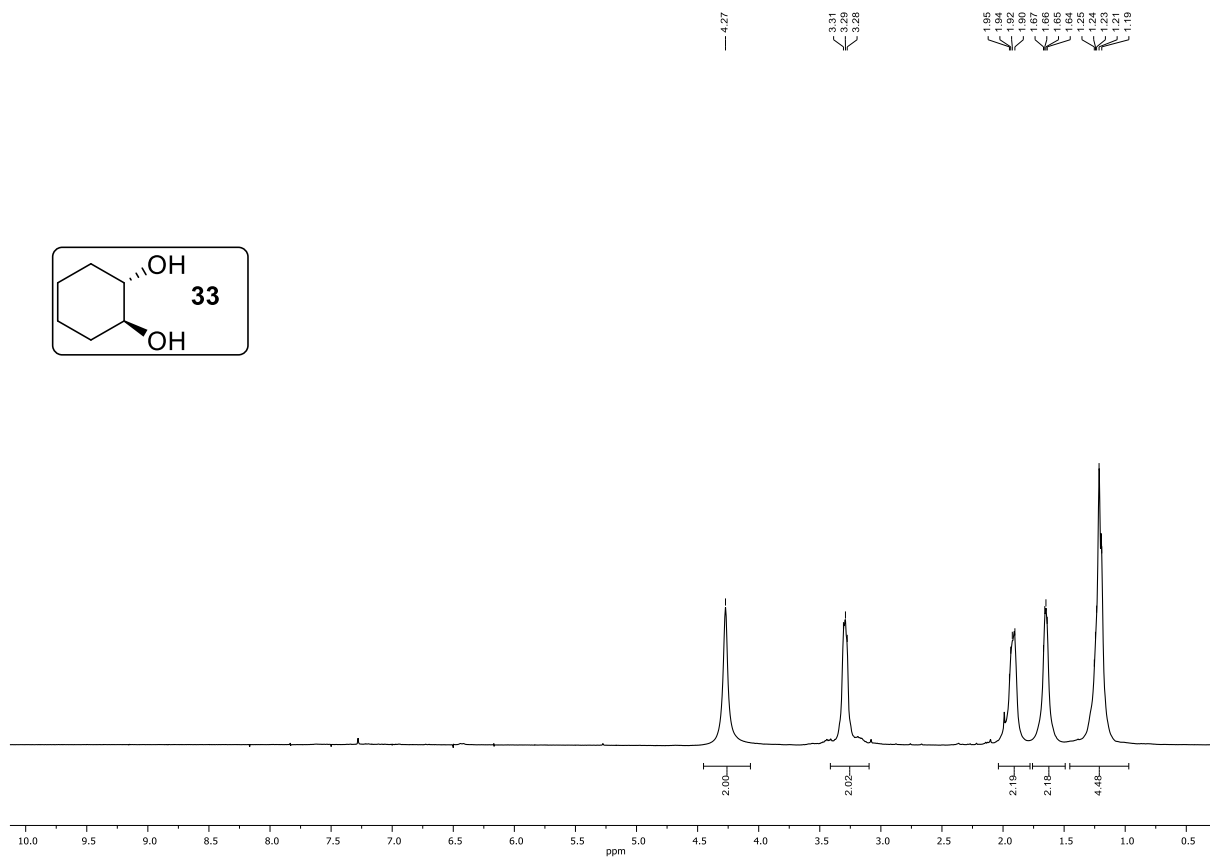
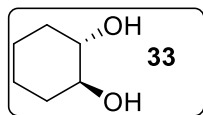
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



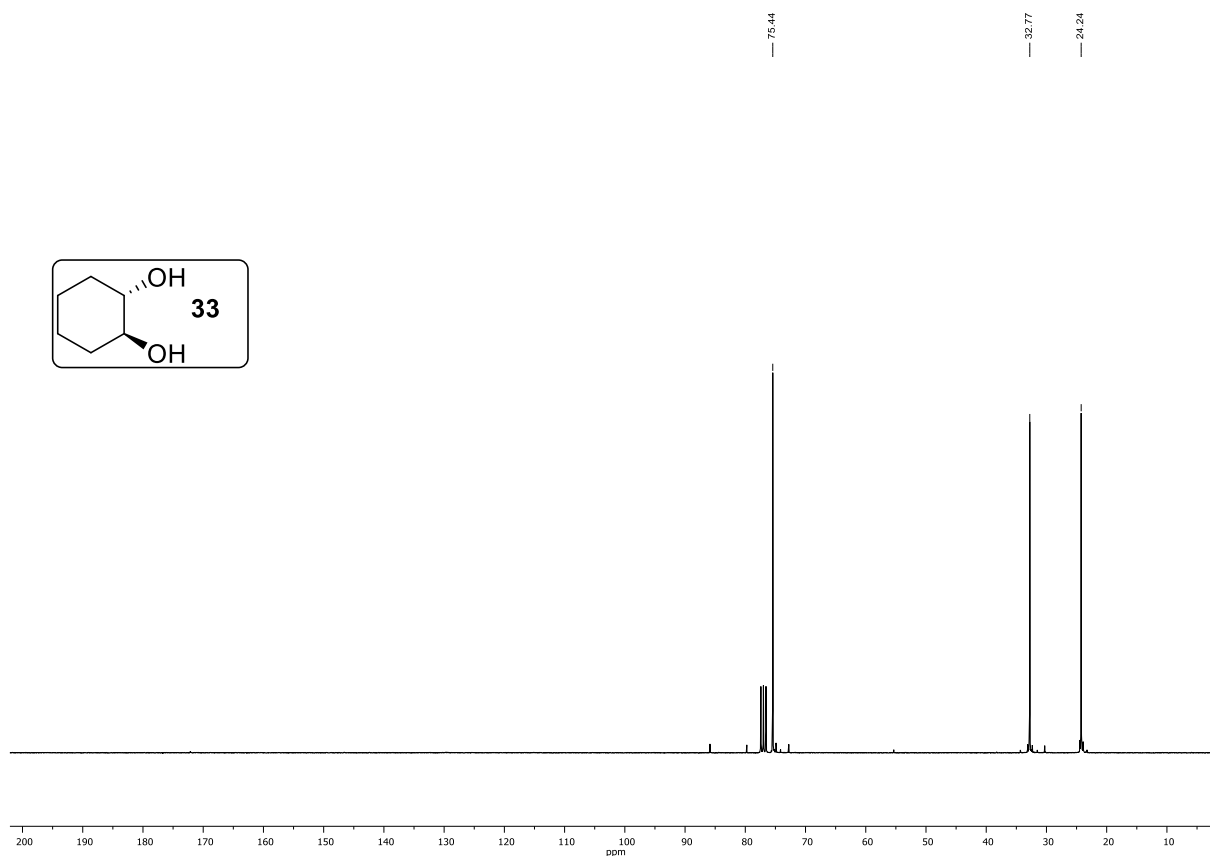
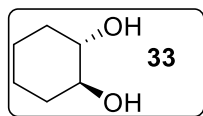
82.85
80.17
74.21
73.41
56.04
32.03
28.84
24.02
23.79



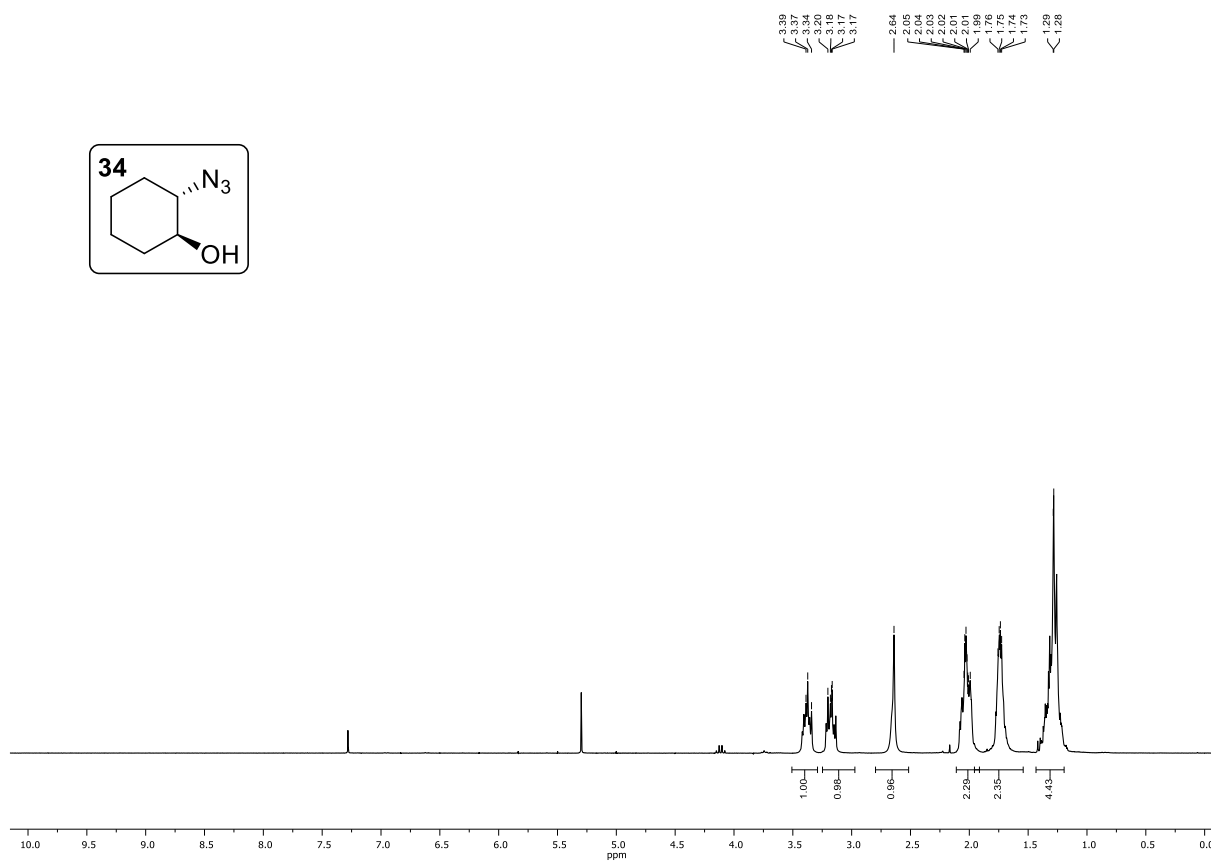
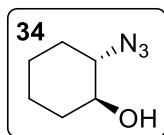
^1H NMR (CDCl_3 , 300 MHz)



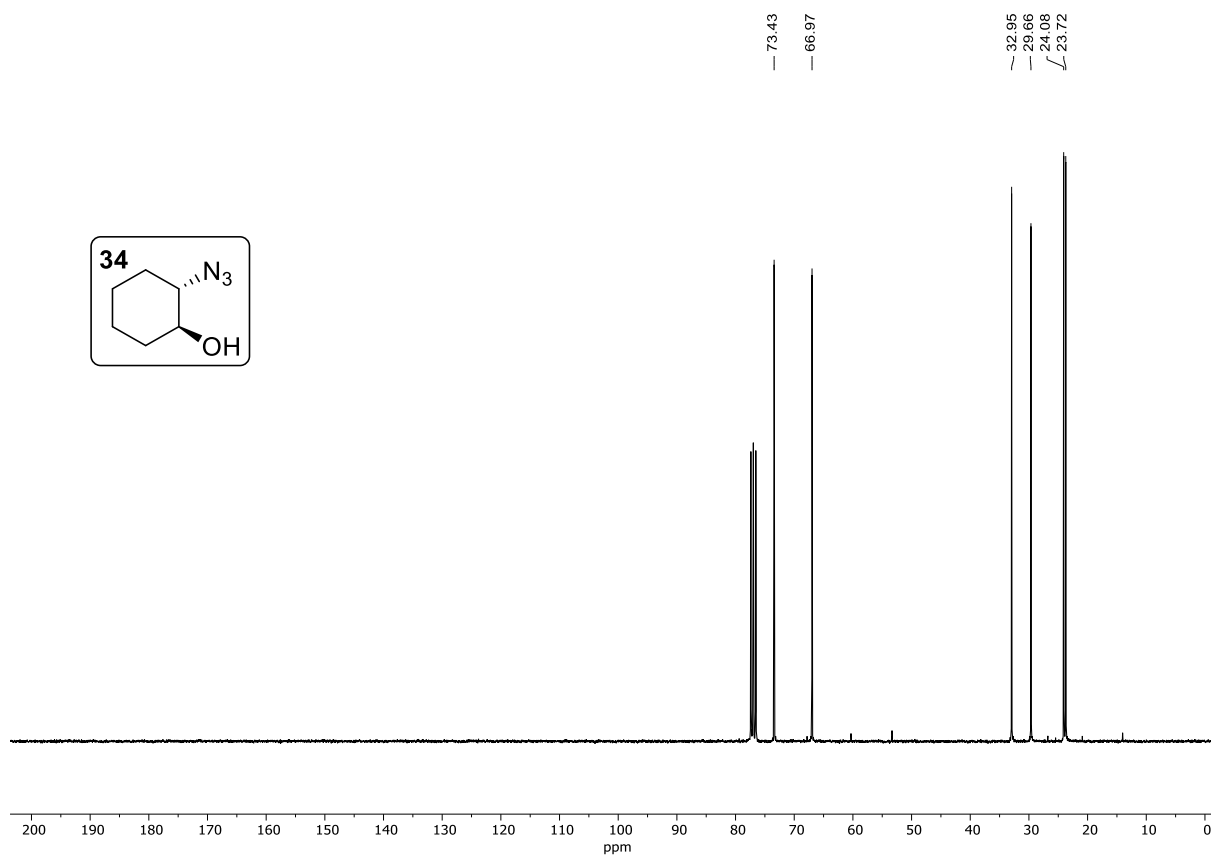
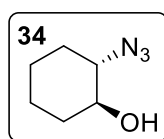
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



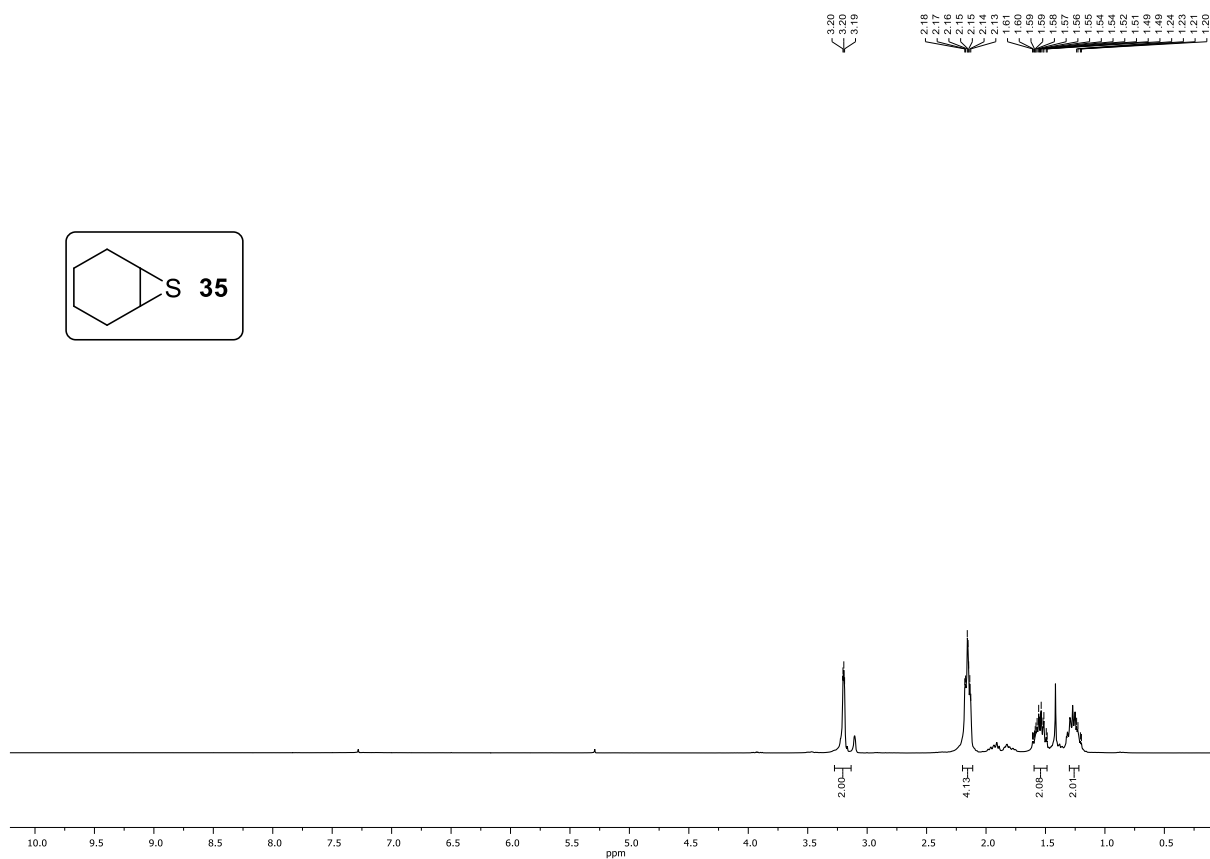
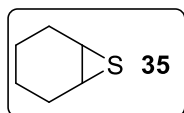
^1H NMR (CDCl_3 , 300 MHz)



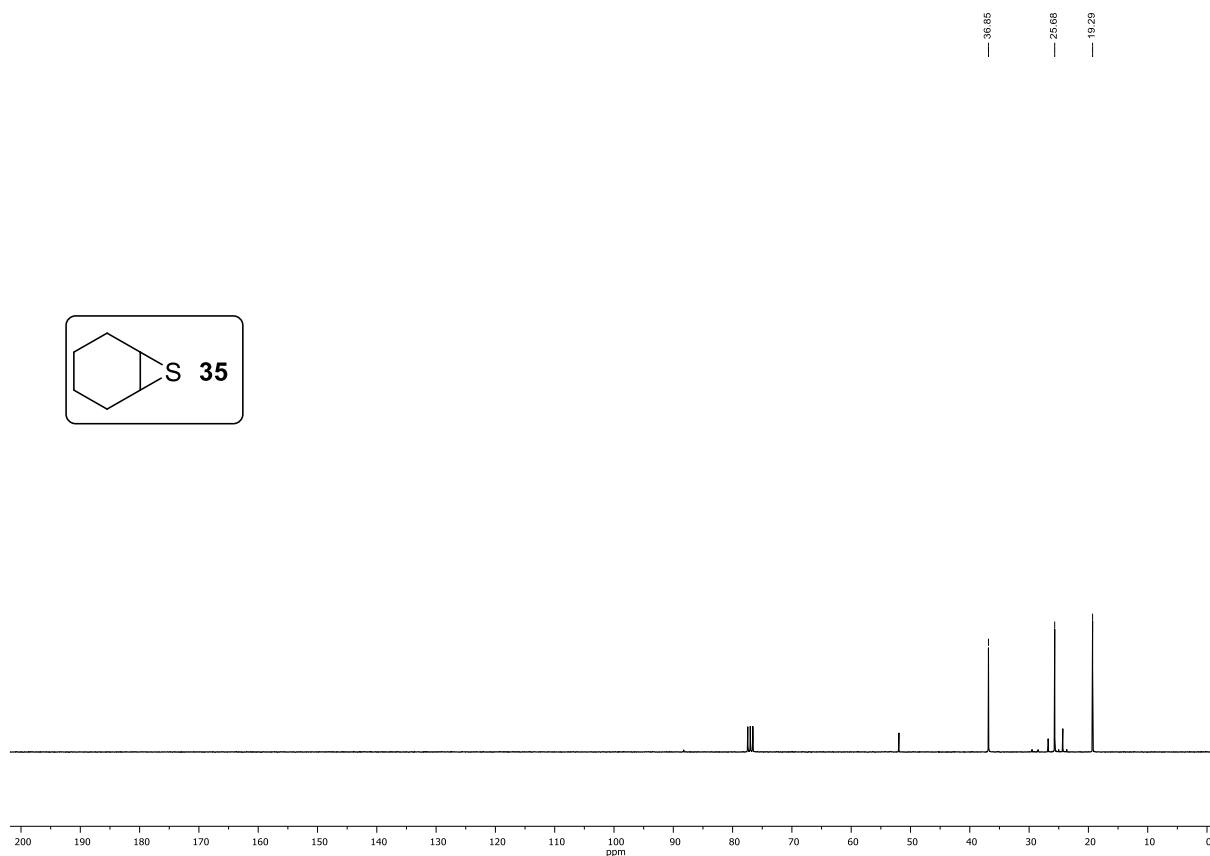
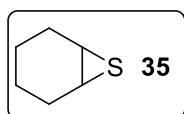
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



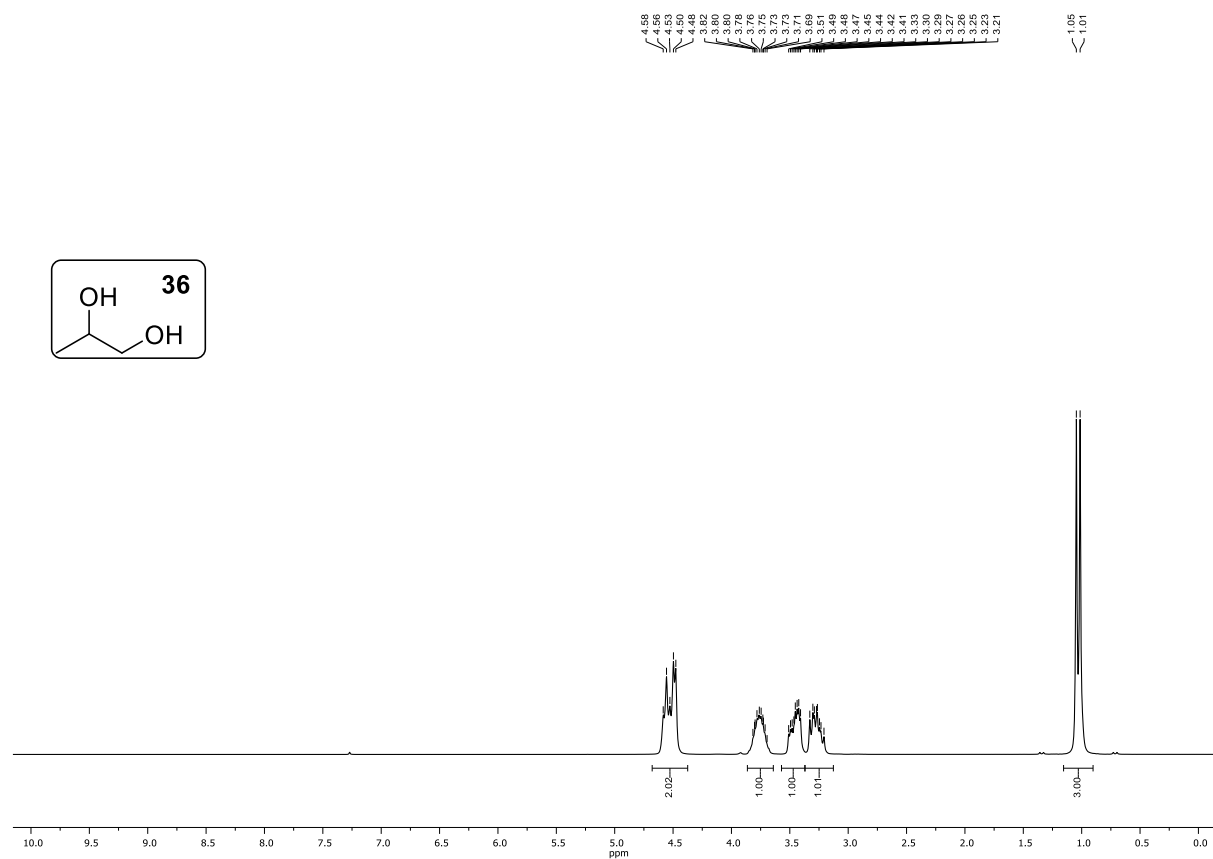
^1H NMR (CDCl_3 , 300 MHz)



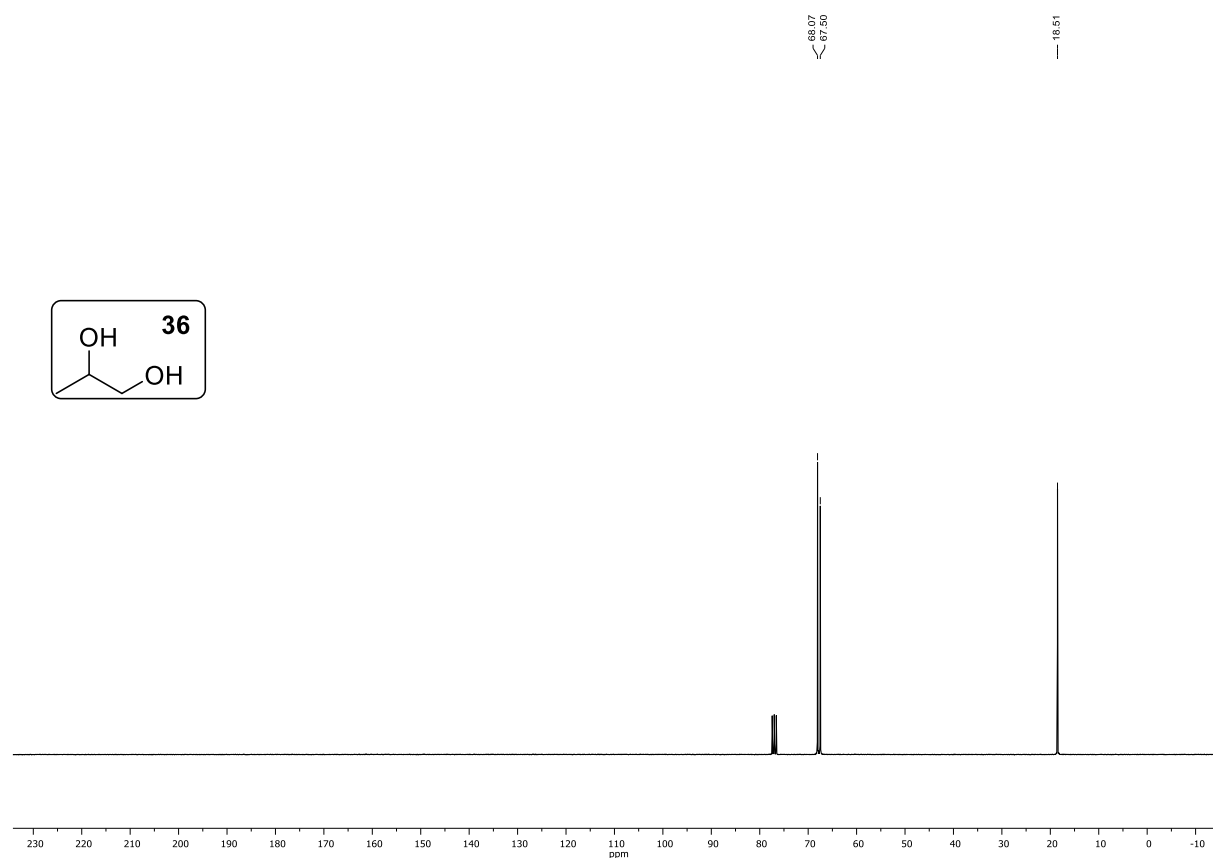
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)



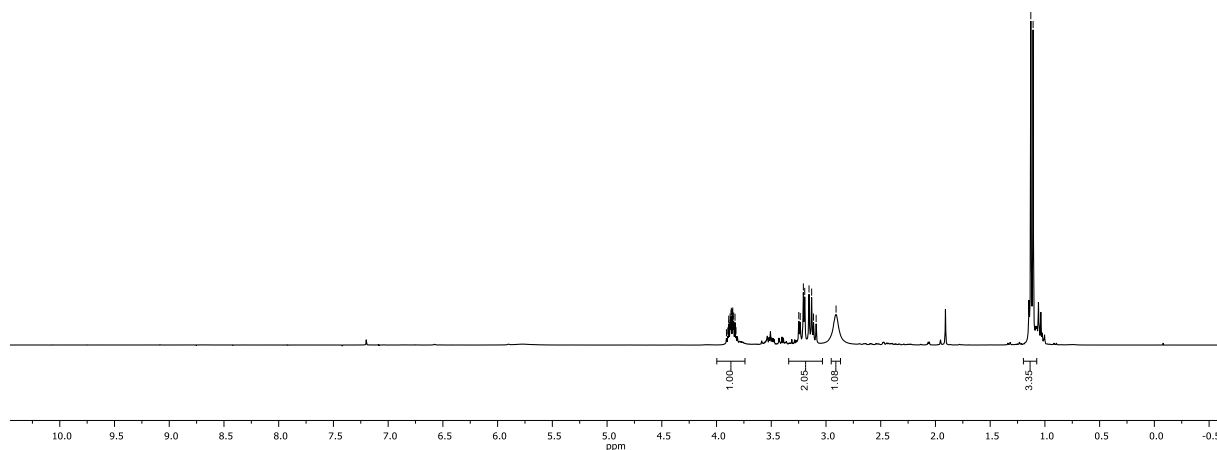
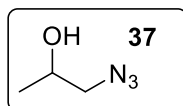
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)

3.91
3.89
3.88
3.88
3.87
3.86
3.85
3.84
3.83
3.82
3.24
3.21
3.19
3.13
3.11
2.99
2.91

1.13
1.11

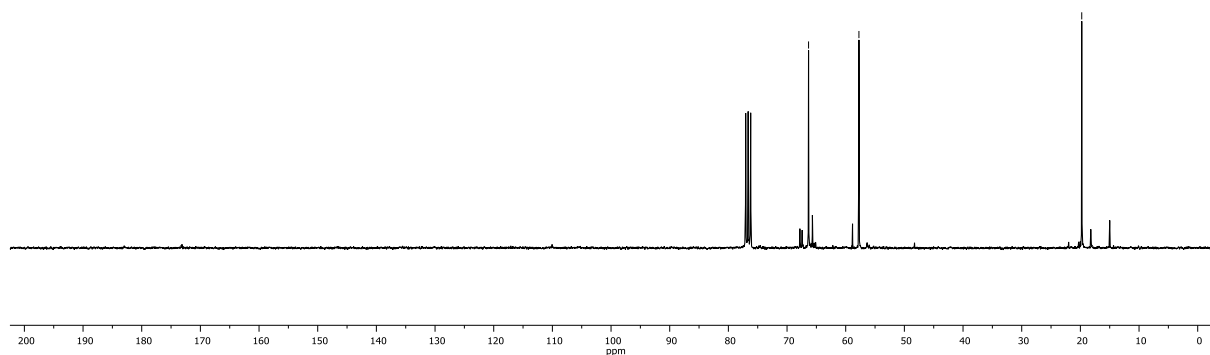
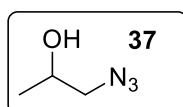


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)

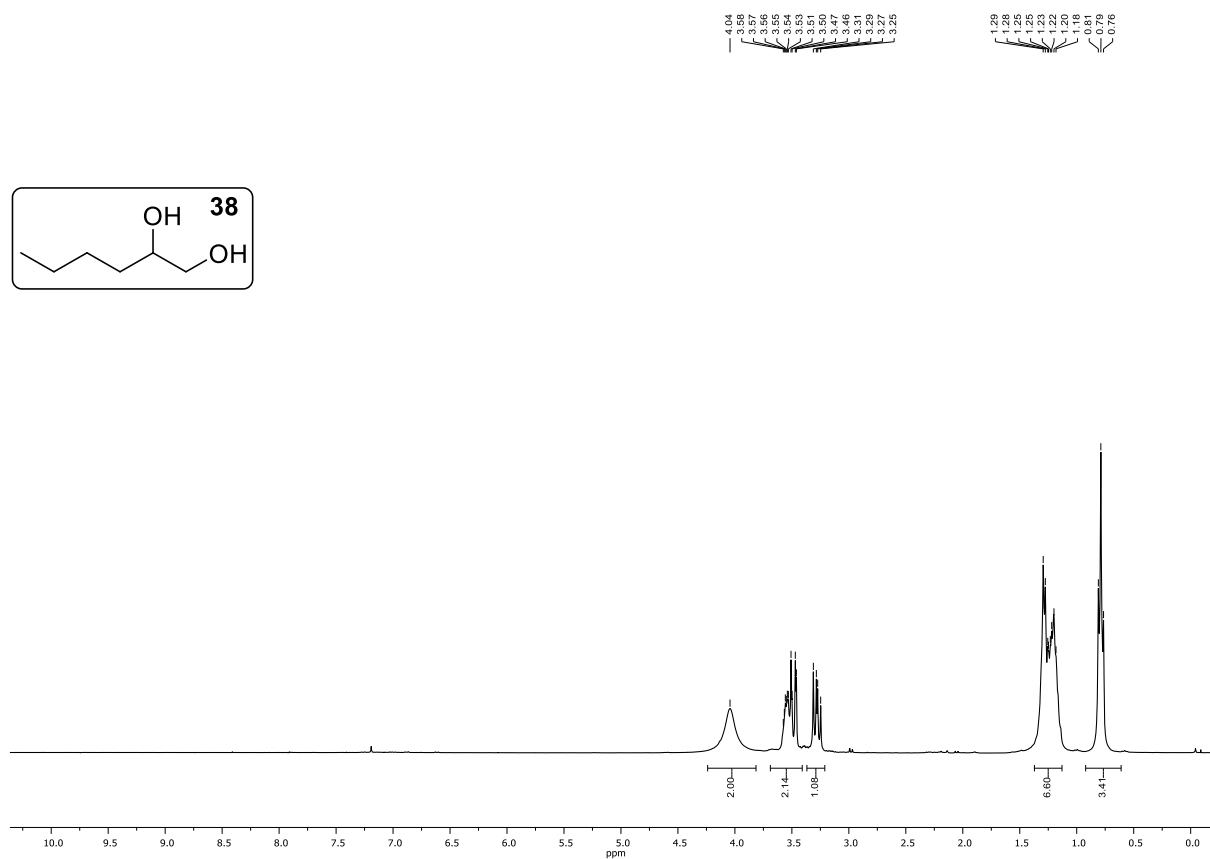
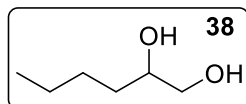
66.33

57.75

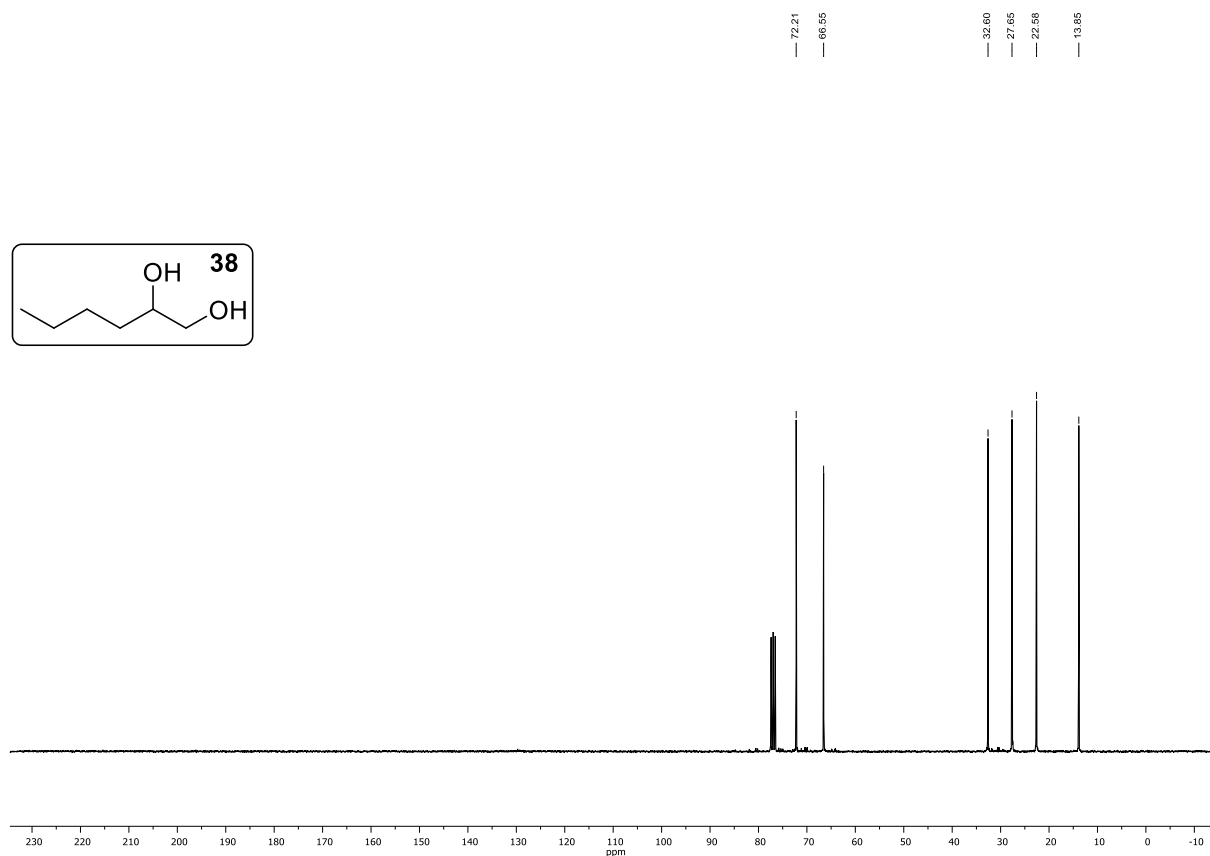
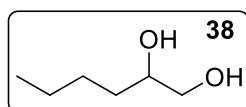
19.77



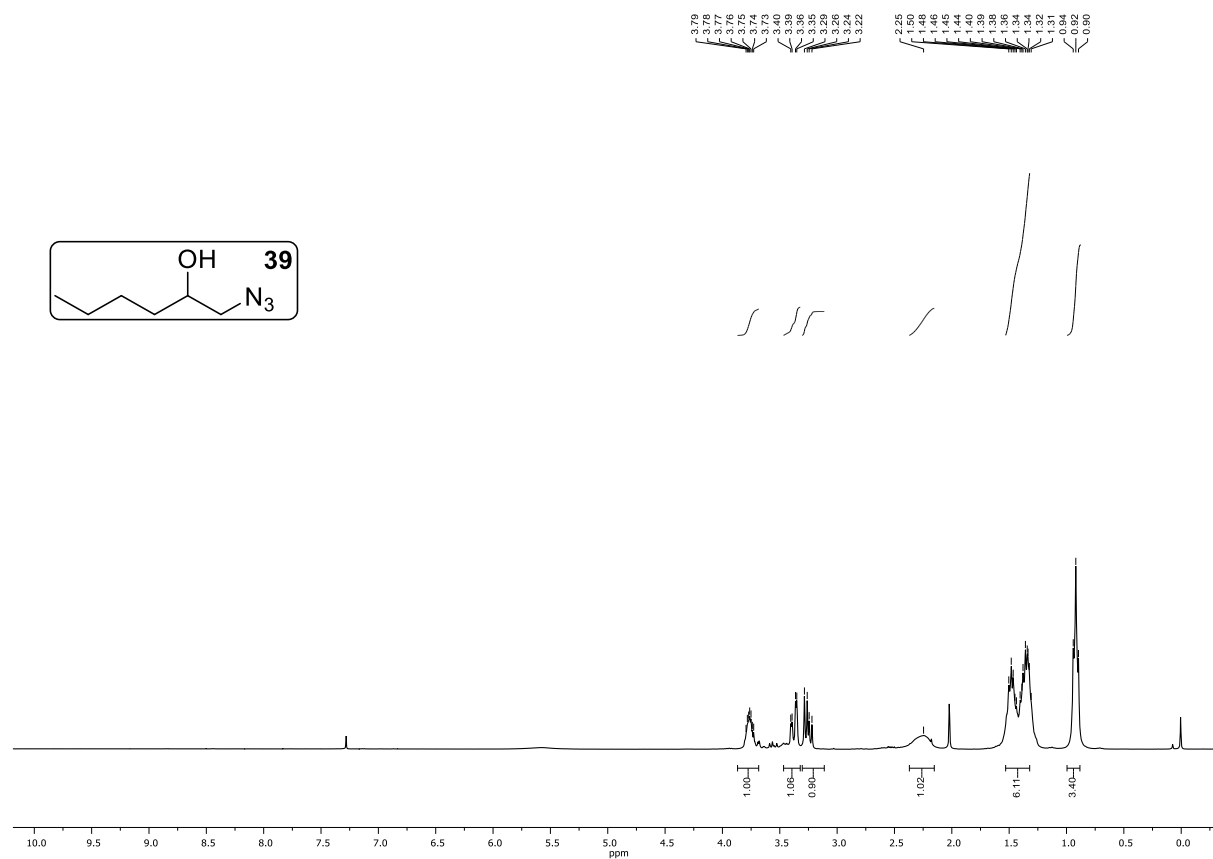
^1H NMR (CDCl_3 , 300 MHz)



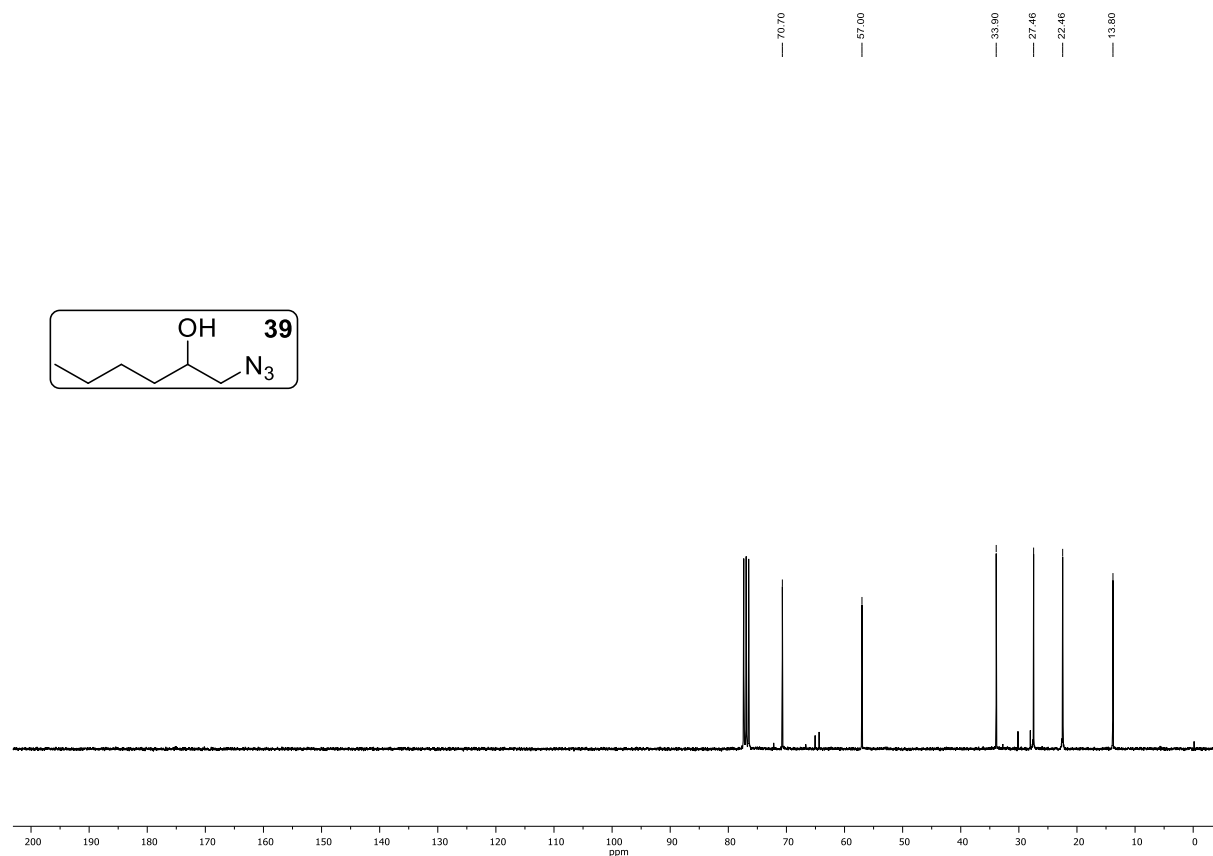
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)

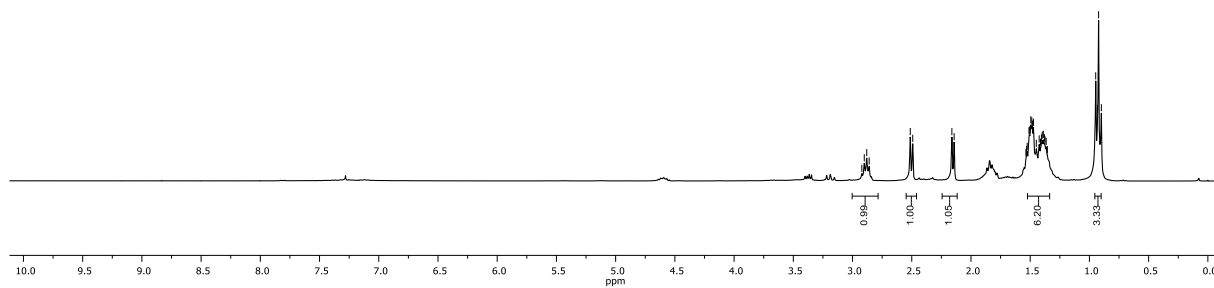
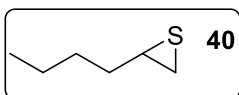


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



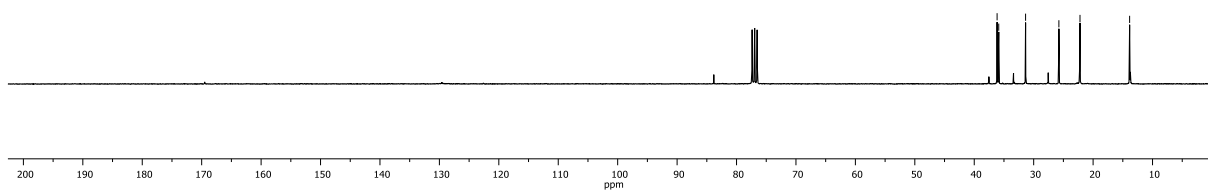
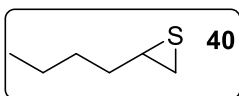
^1H NMR (CDCl_3 , 300 MHz)

2.82
2.88
2.86
2.51
2.49
2.16
2.14
1.53
1.53
1.51
1.49
1.48
1.48
1.45
1.42
1.41
1.40
1.39
1.37
1.37
0.95
0.92
0 en

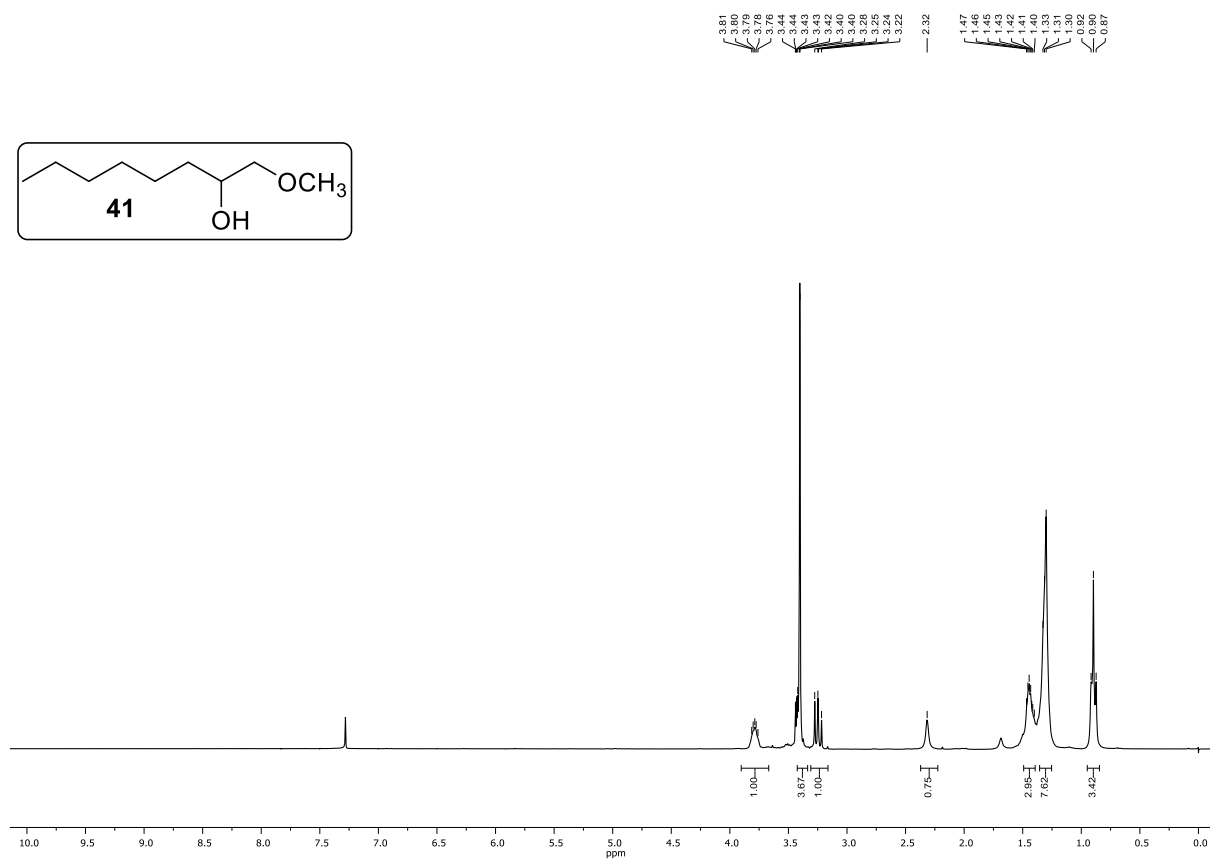
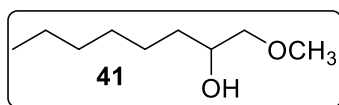


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)

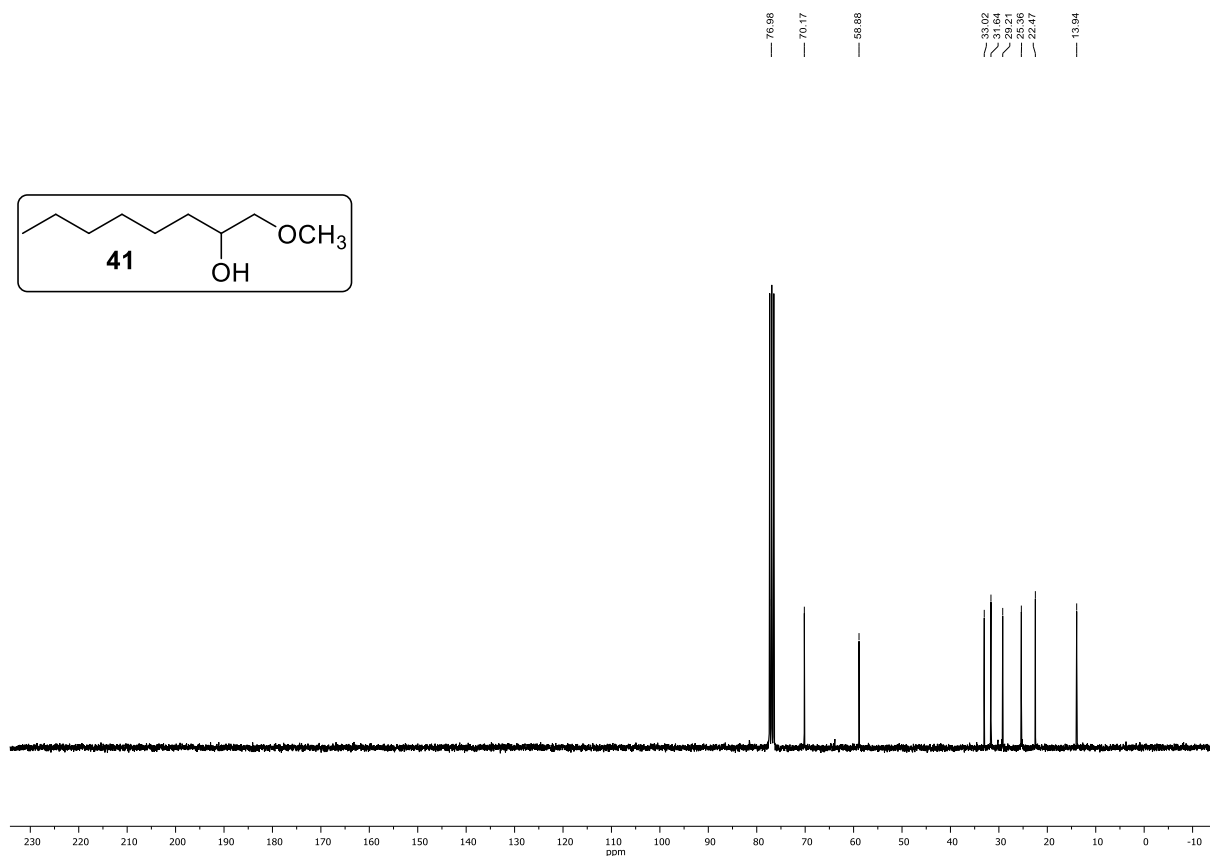
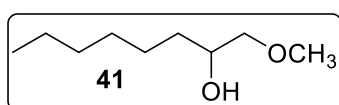
36.15
35.88
31.36
25.76
22.20
13.85



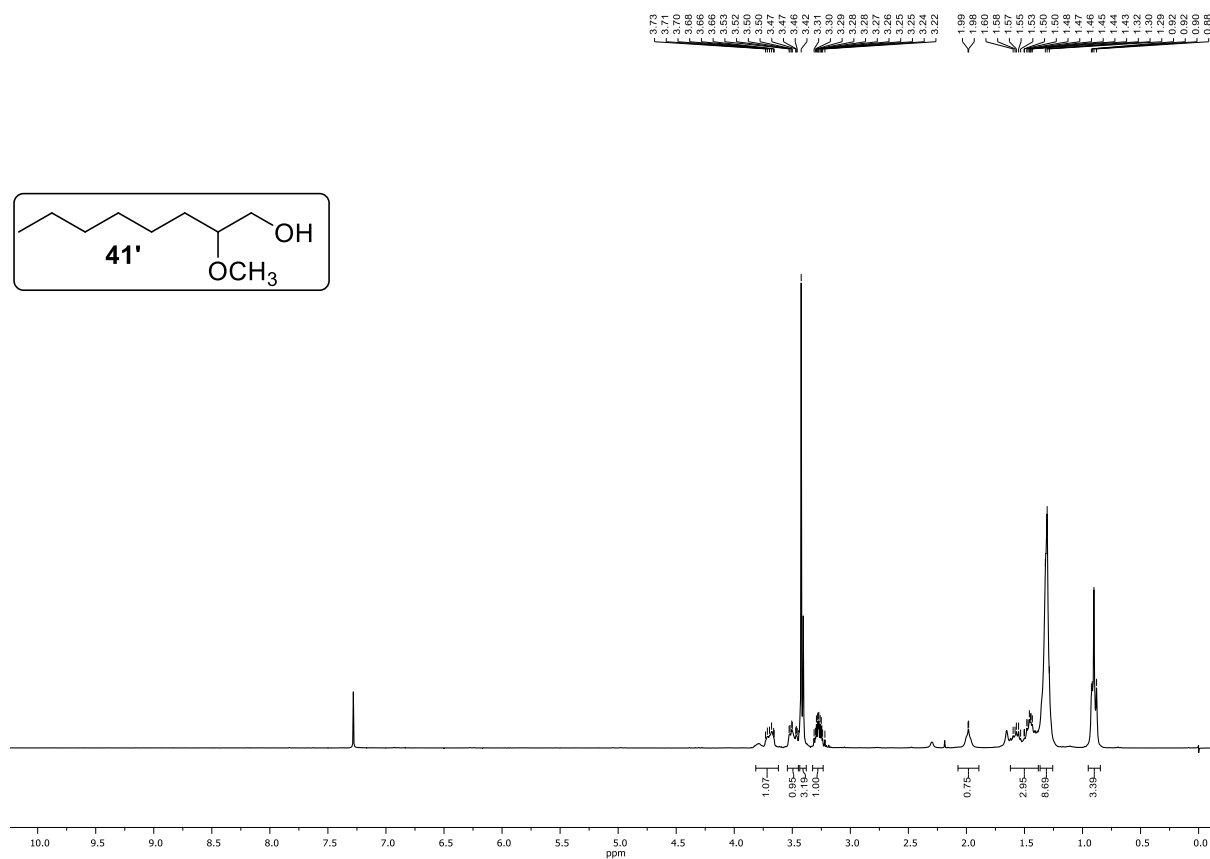
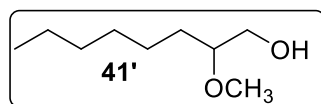
^1H NMR (CDCl_3 , 300 MHz)



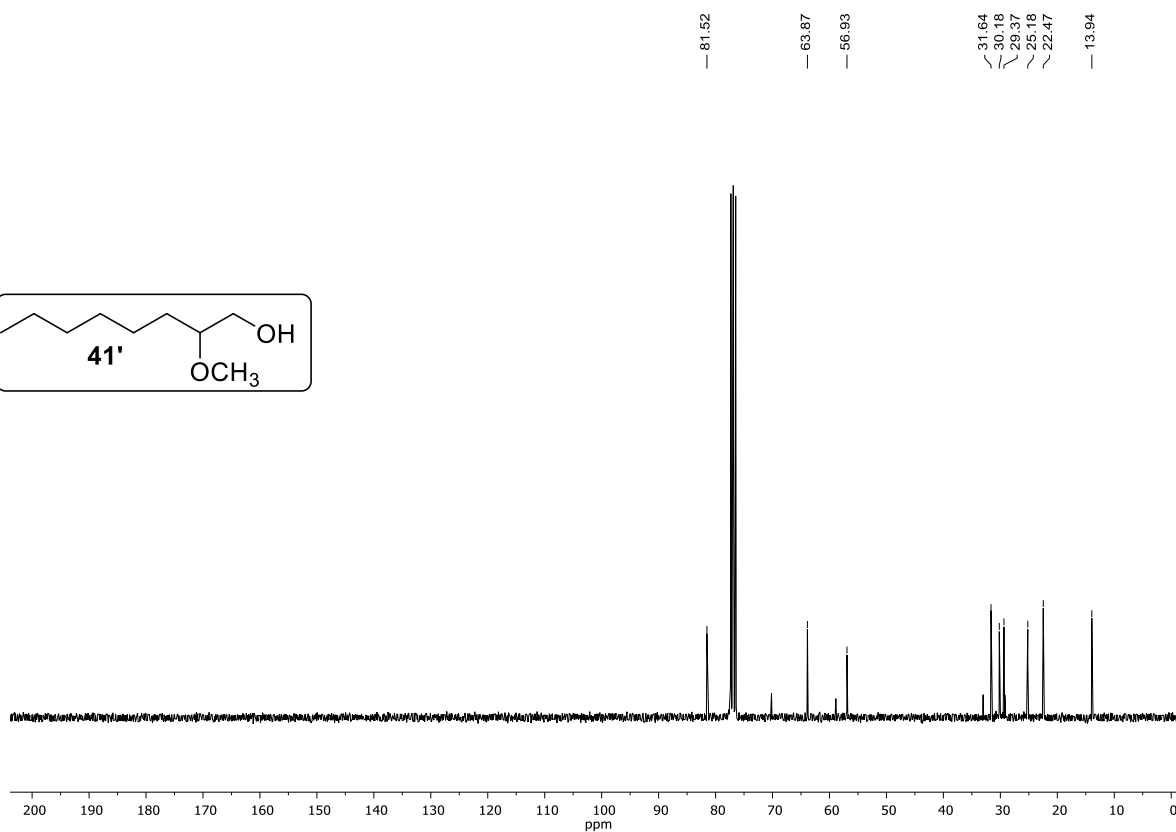
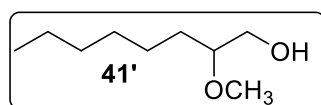
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



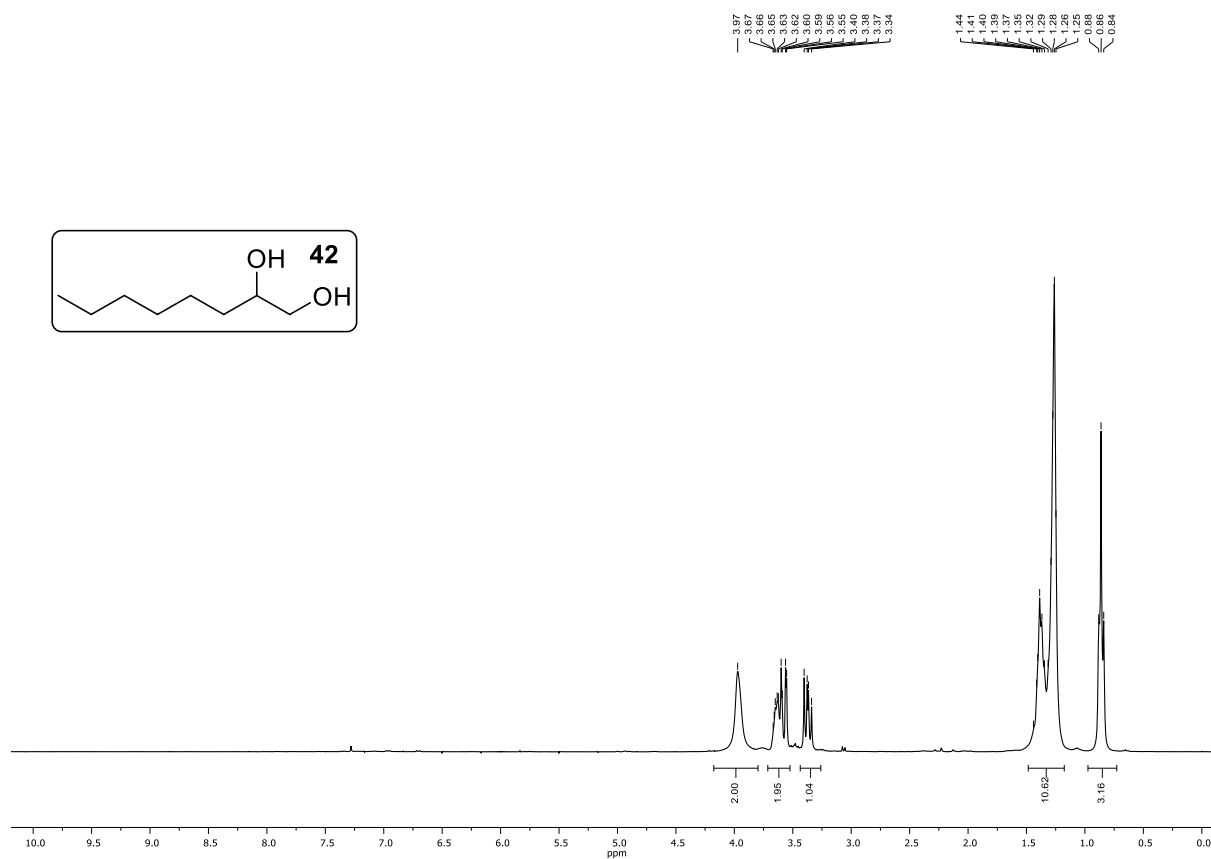
^1H NMR (CDCl_3 , 300 MHz)



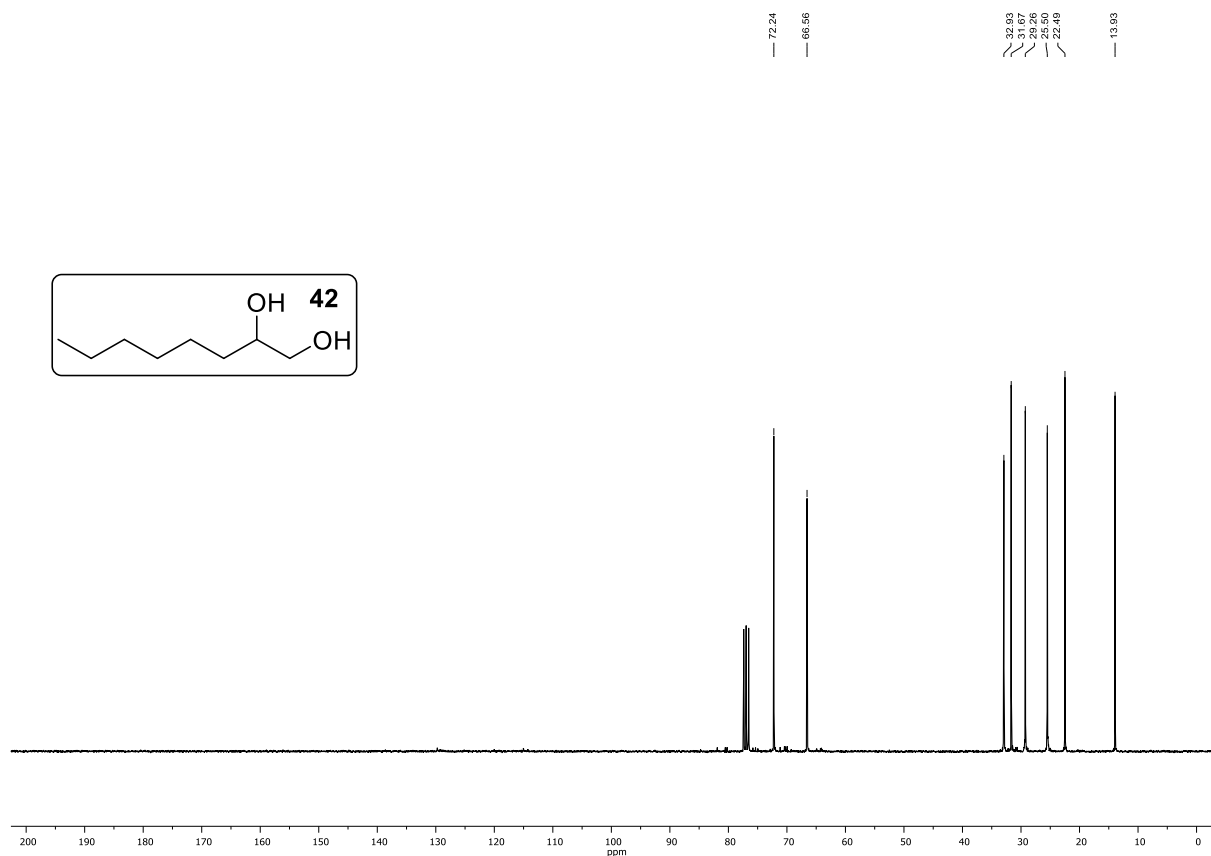
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



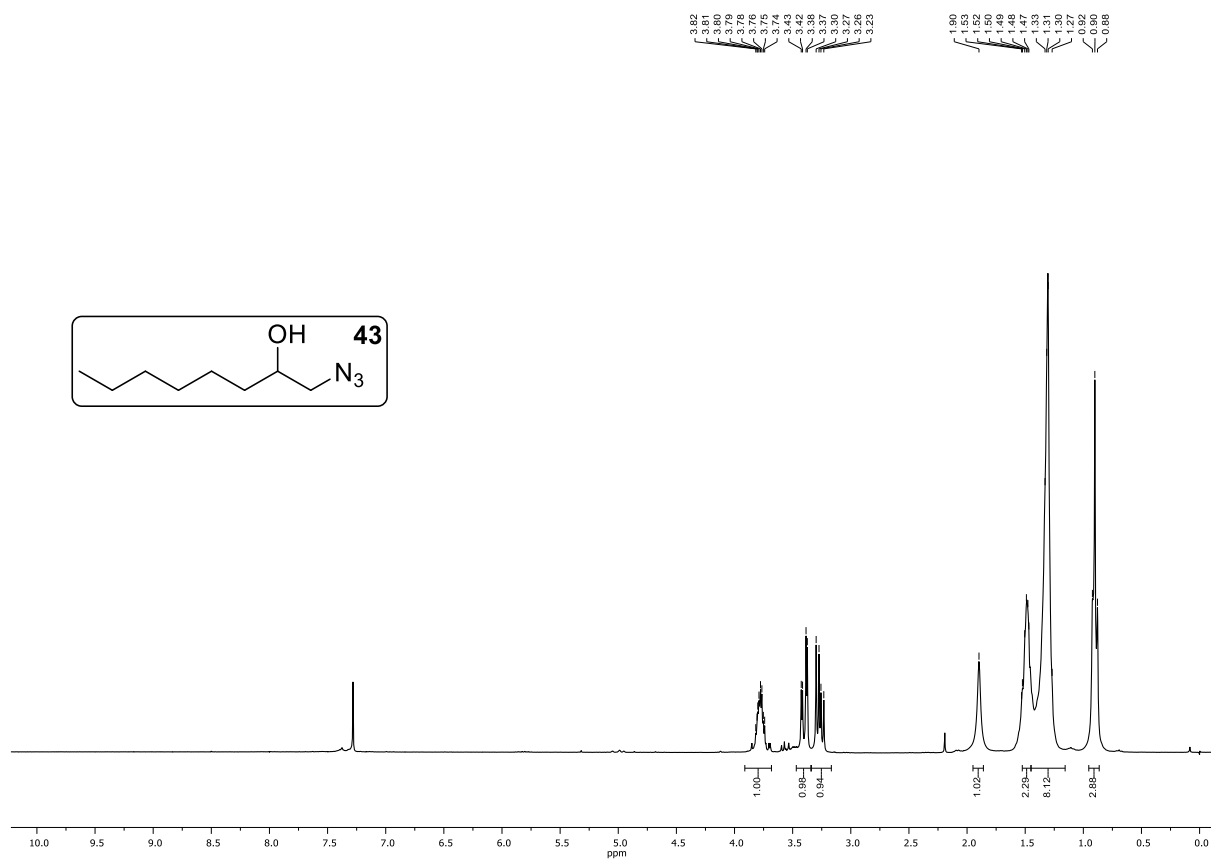
^1H NMR (CDCl_3 , 300 MHz)



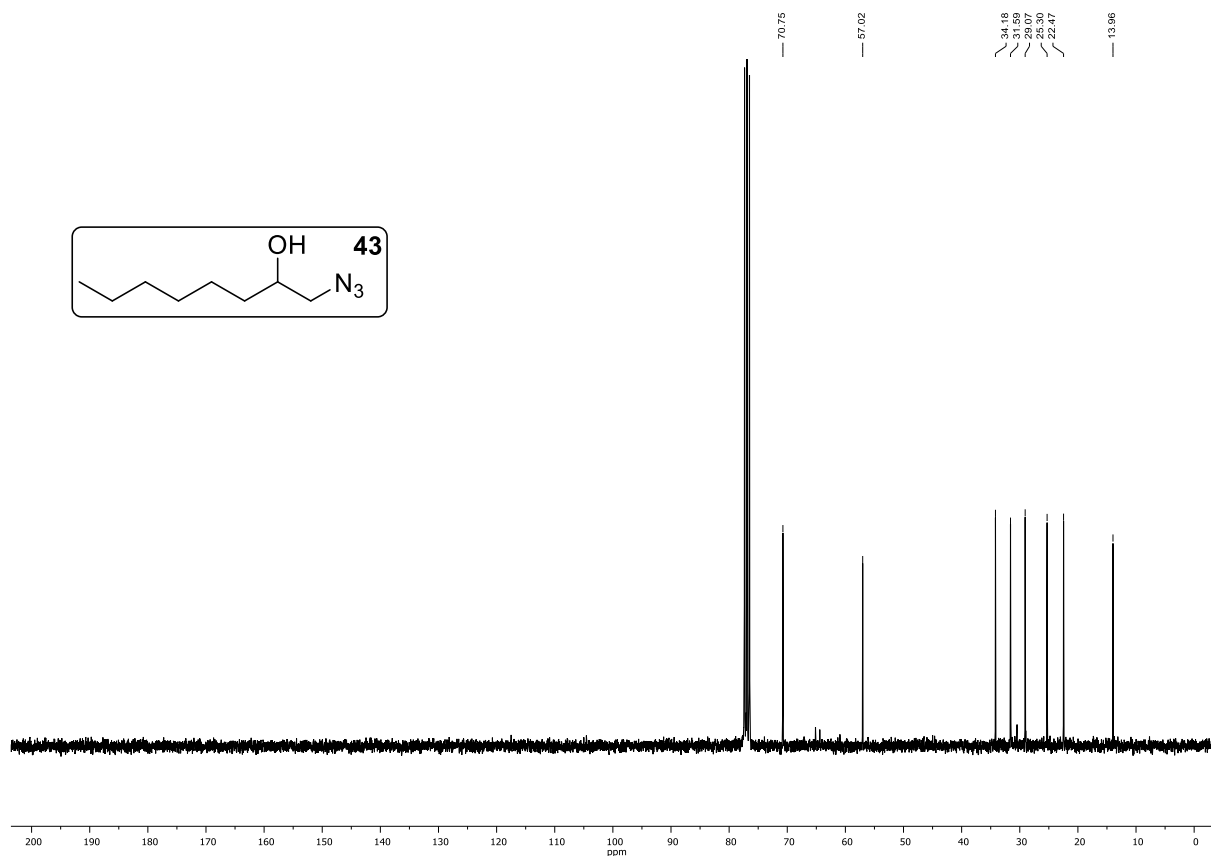
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



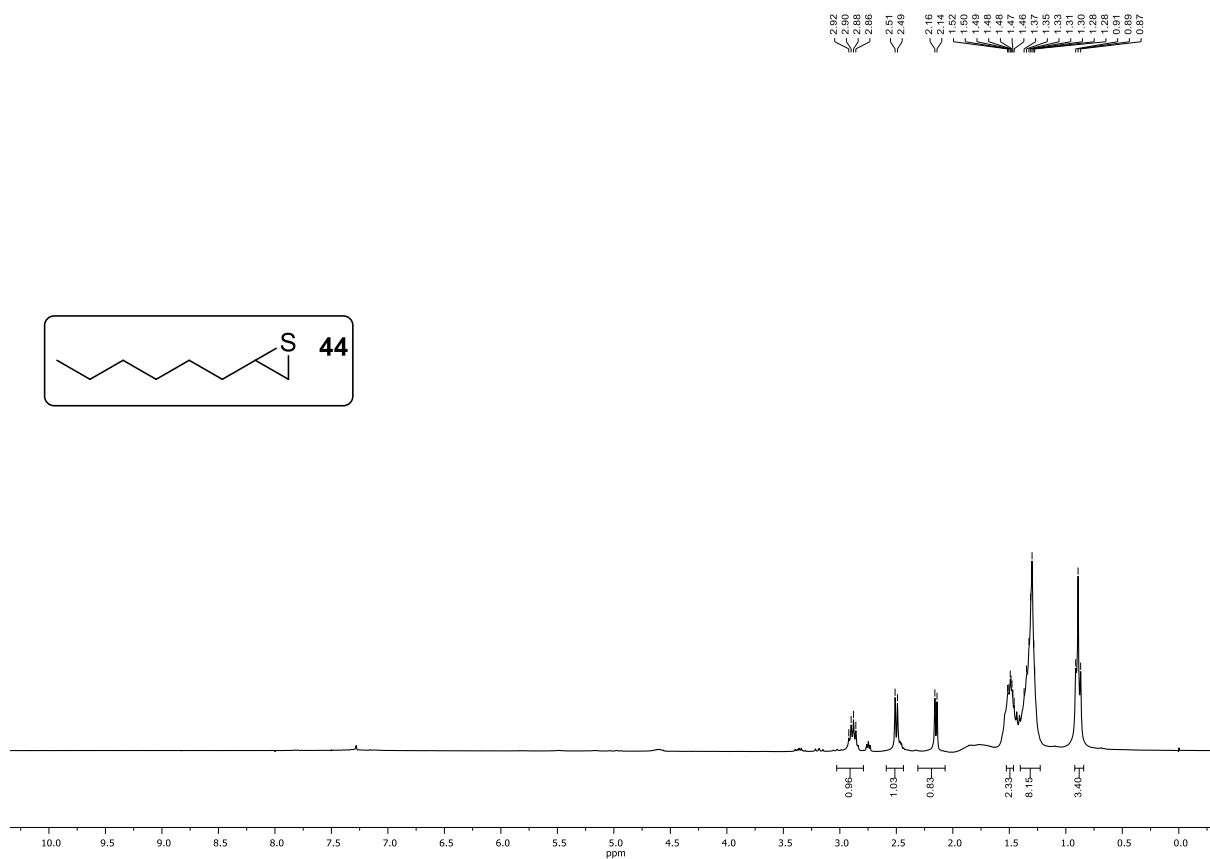
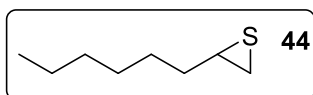
^1H NMR (CDCl_3 , 300 MHz)



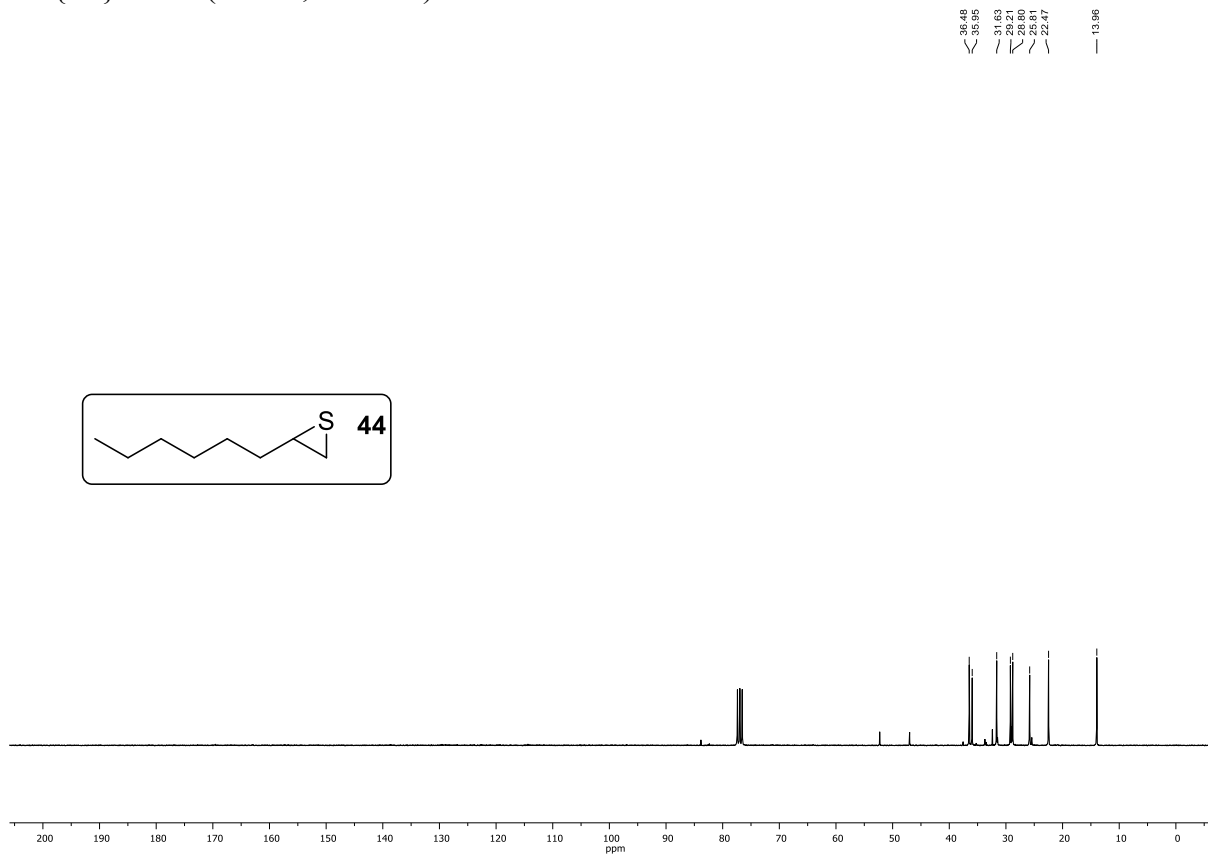
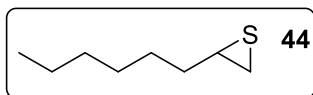
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)

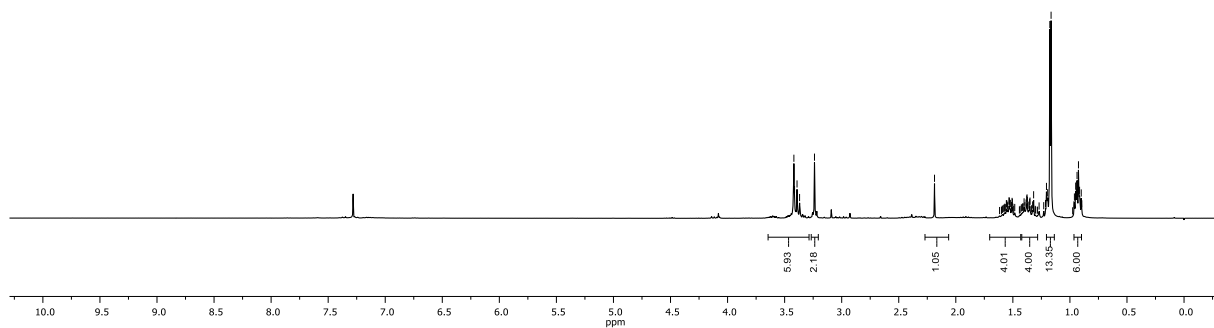
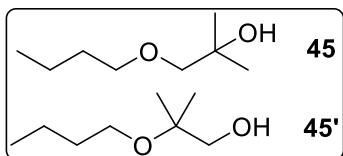


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



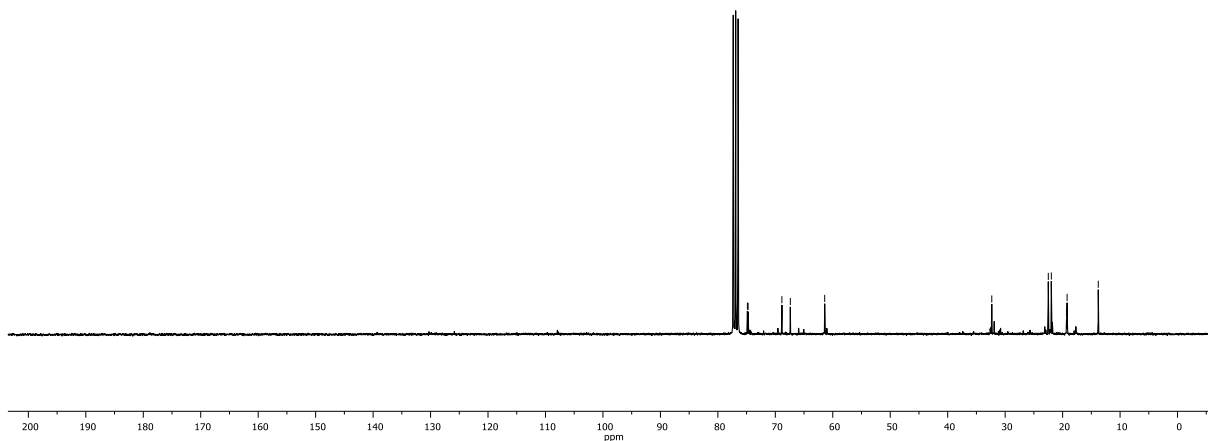
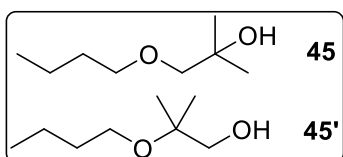
^1H NMR (CDCl_3 , 300 MHz)

3.42
3.41
3.40
3.37
3.24
3.24
3.19
1.66
1.59
1.59
1.58
1.57
1.56
1.55
1.55
1.53
1.53
1.51
1.50
1.49
1.49
1.44
1.44
1.43
1.42
1.41
1.41
1.39
1.38
1.38
1.37
1.35
1.35
1.34
1.32
1.30
1.30
1.27
1.23
1.23
1.21
1.20
1.18
1.18
0.98
0.98
0.94
0.94
0.93
0.92
0.90

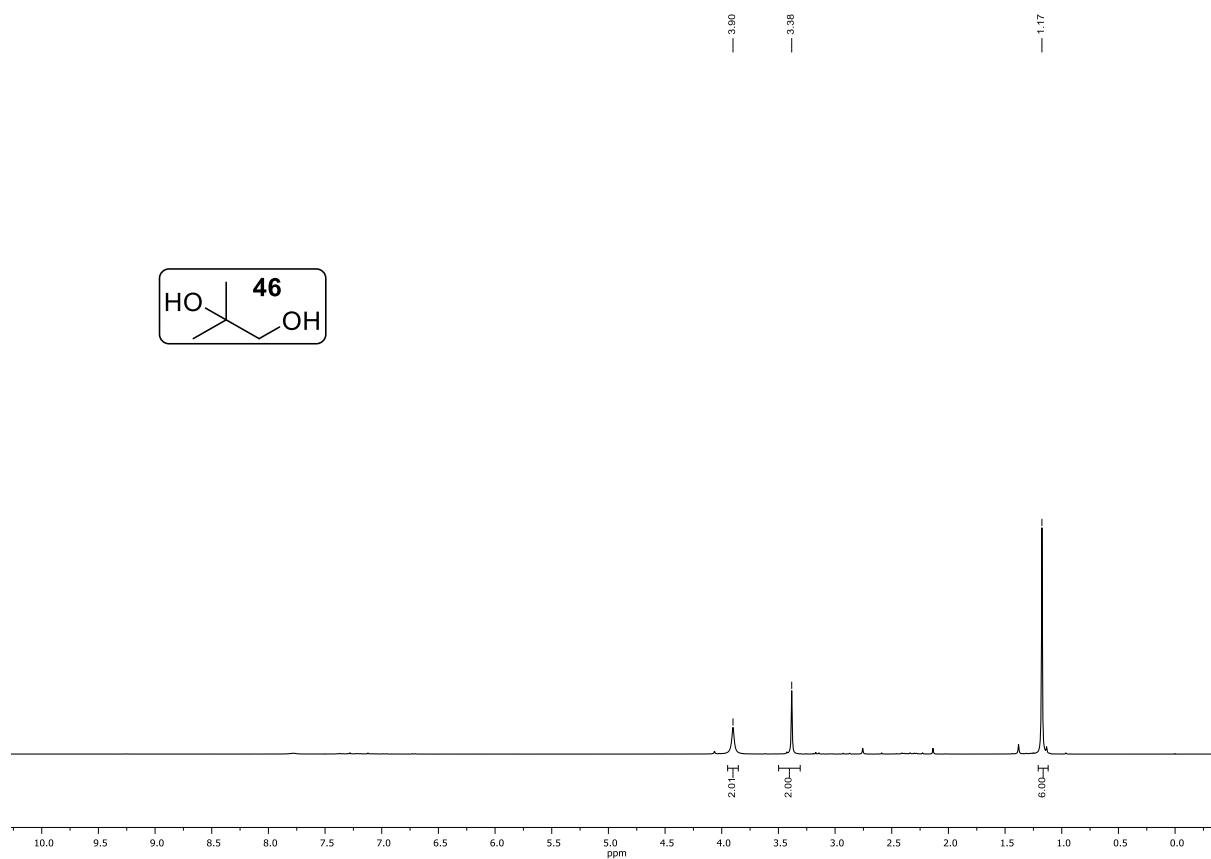


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)

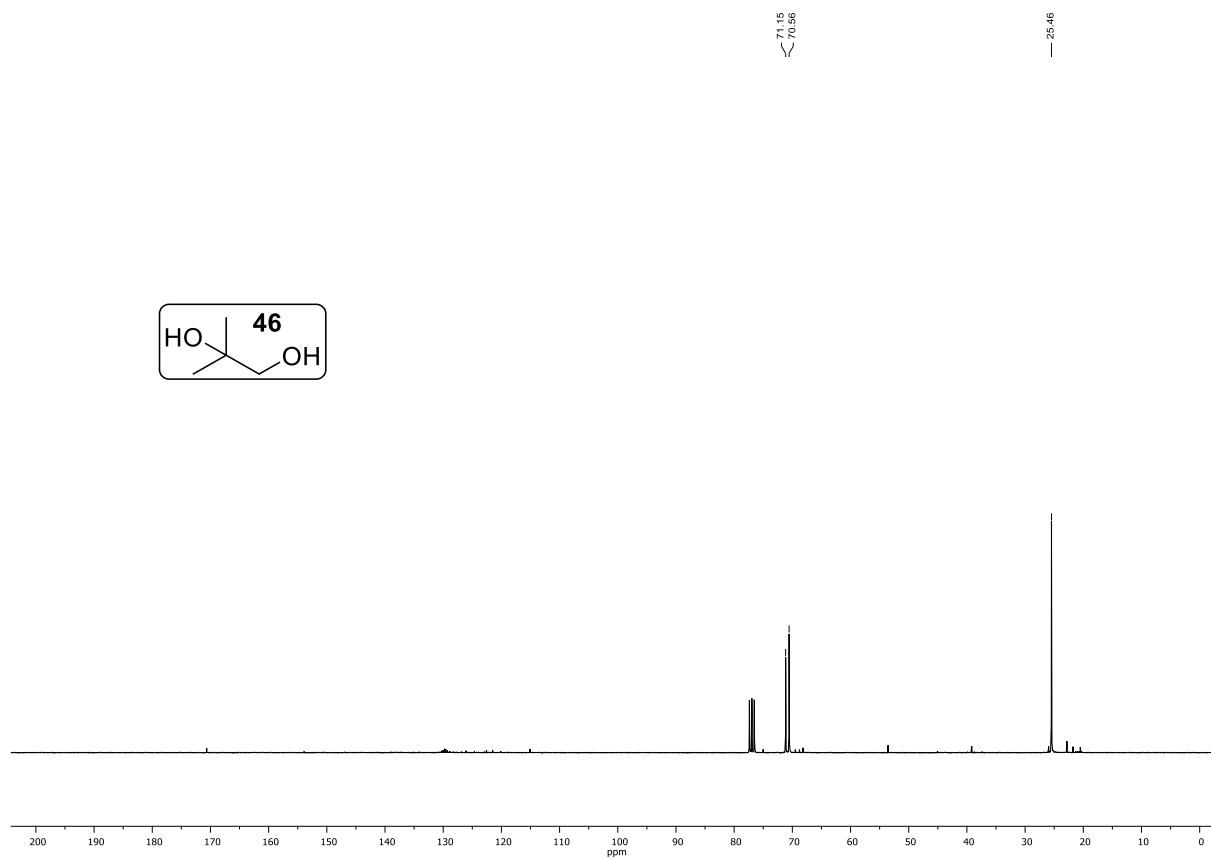
74.88
74.74
68.86
67.39
61.41
32.33
22.49
21.97
19.32
19.22
13.80



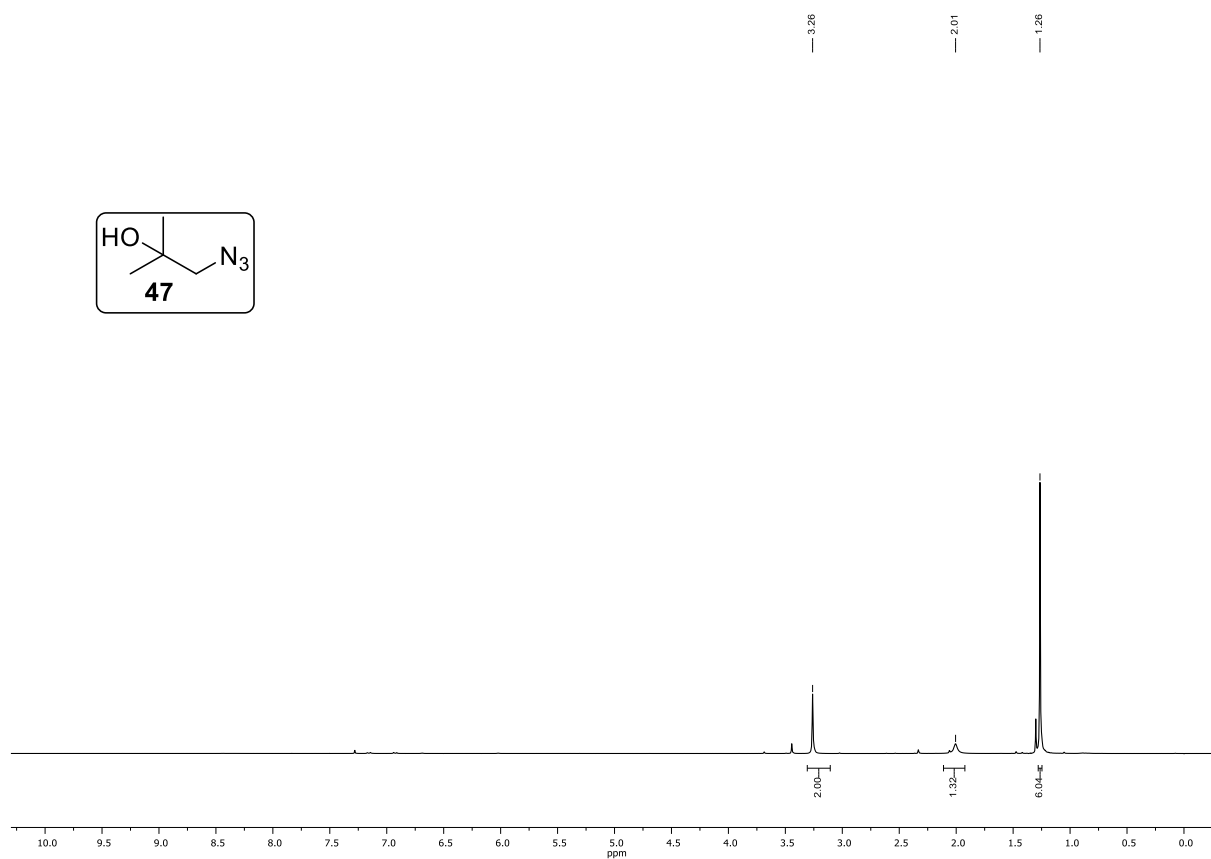
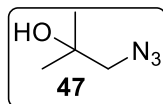
^1H NMR (CDCl_3 , 300 MHz)



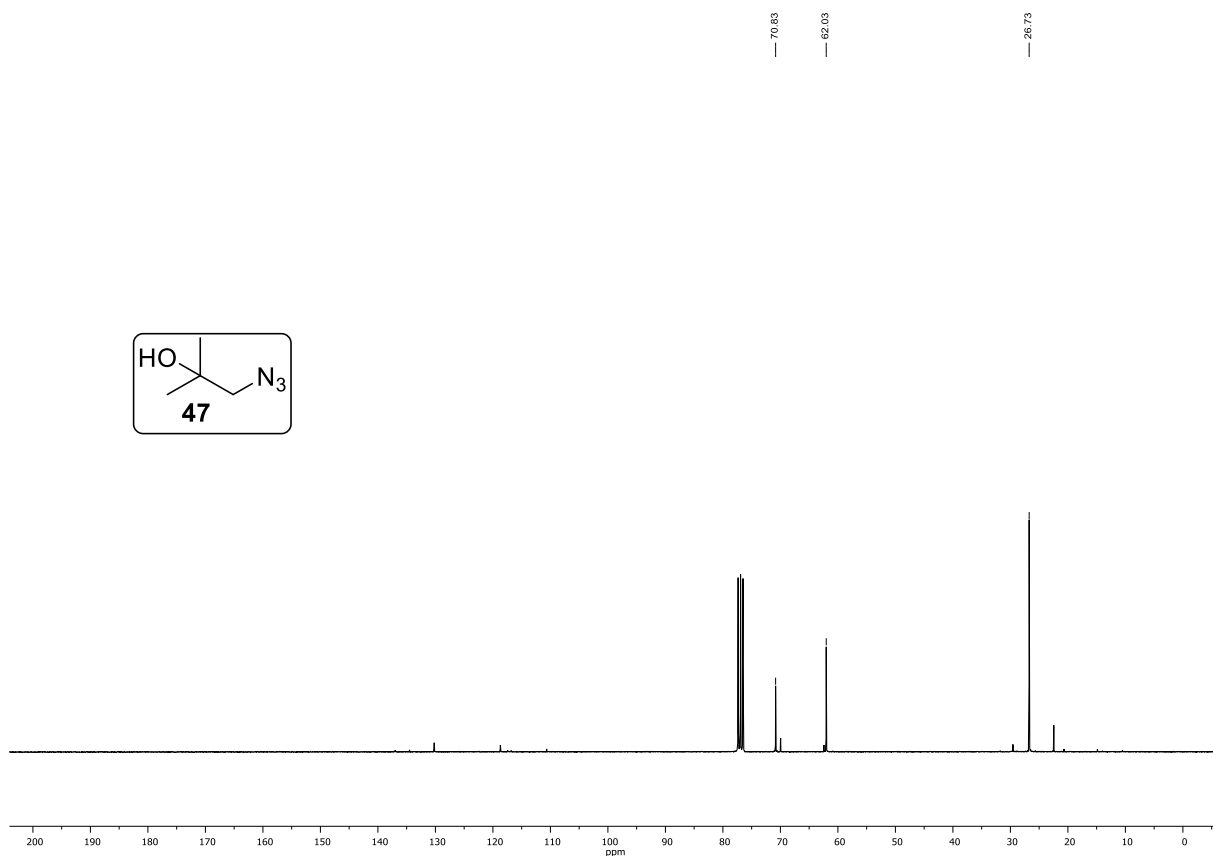
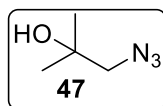
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



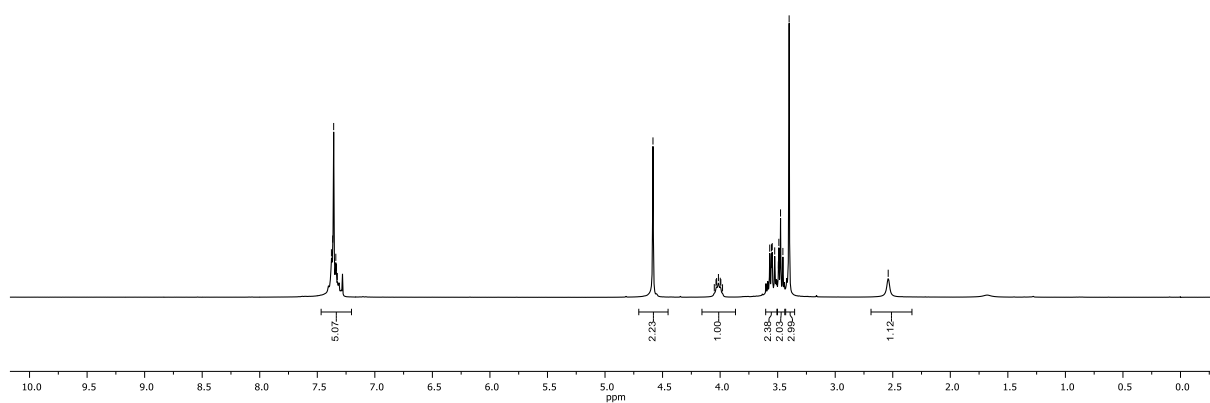
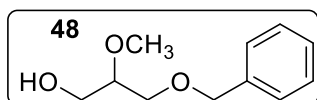
^1H NMR (CDCl_3 , 300 MHz)



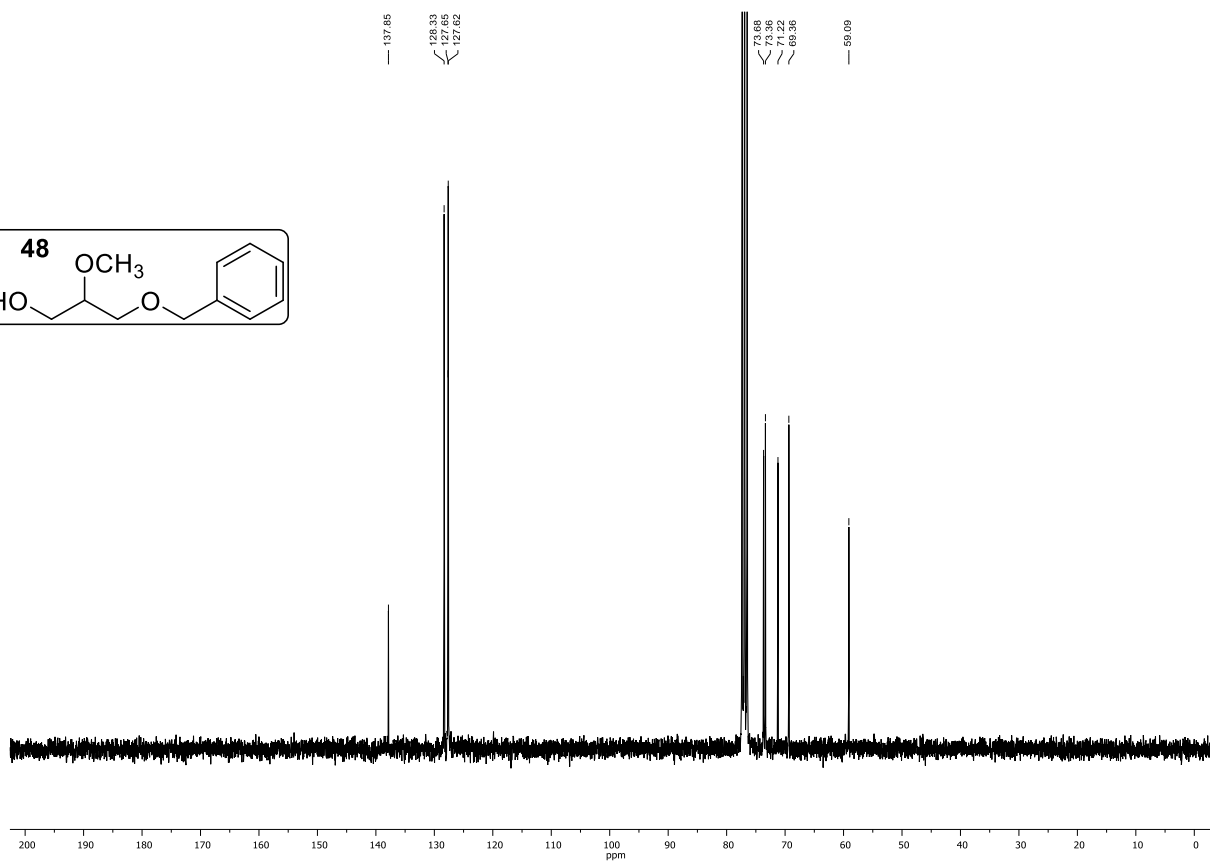
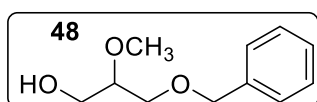
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



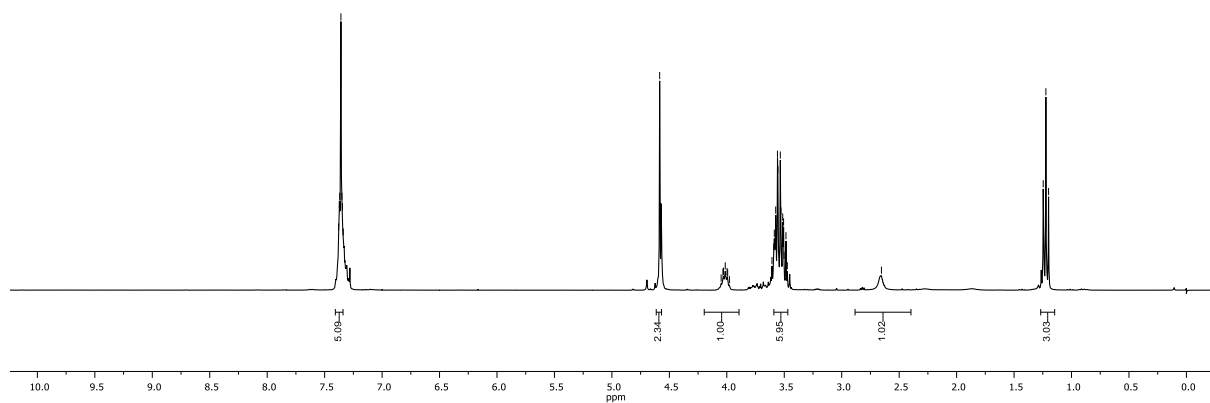
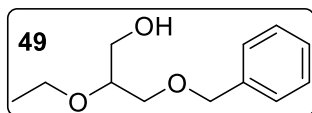
^1H NMR (CDCl_3 , 300 MHz)



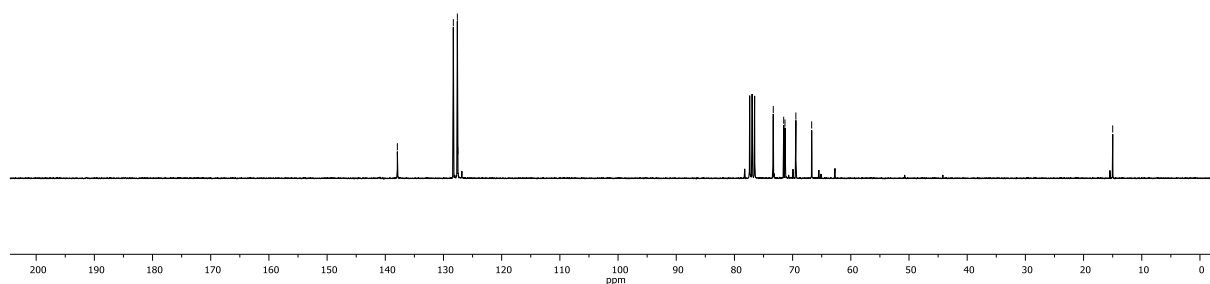
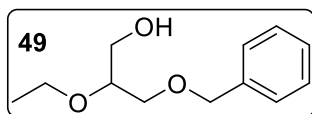
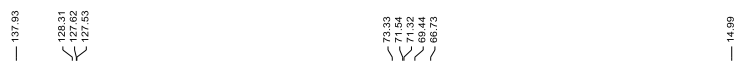
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



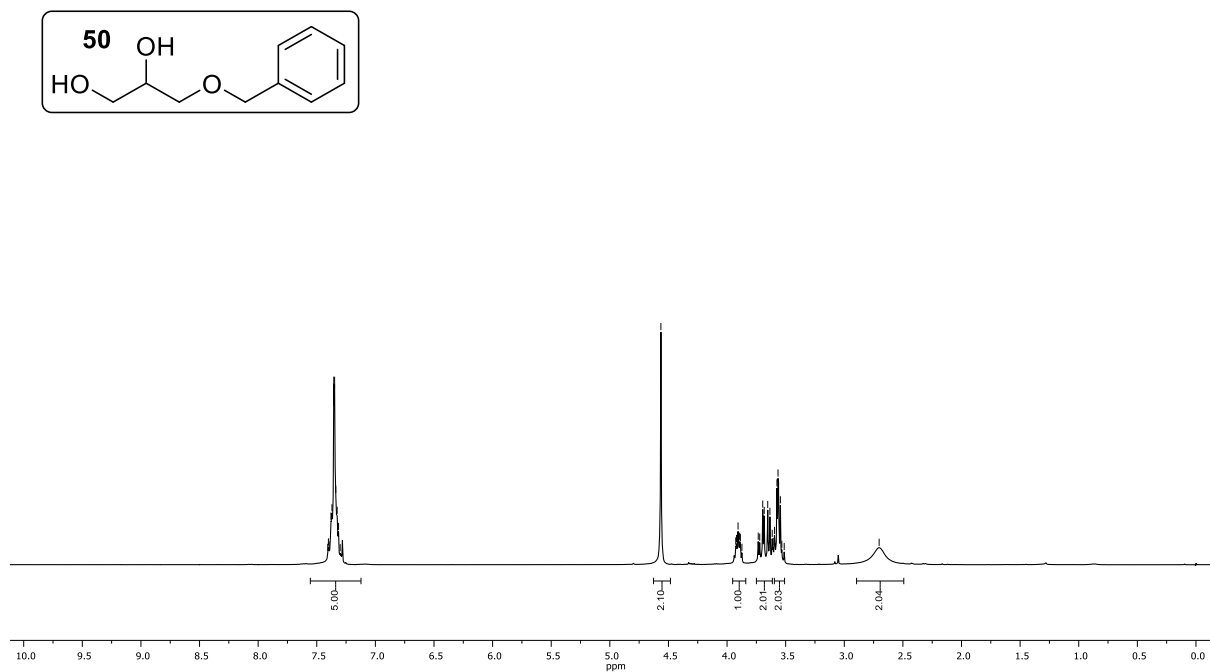
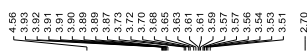
^1H NMR (CDCl_3 , 300 MHz)



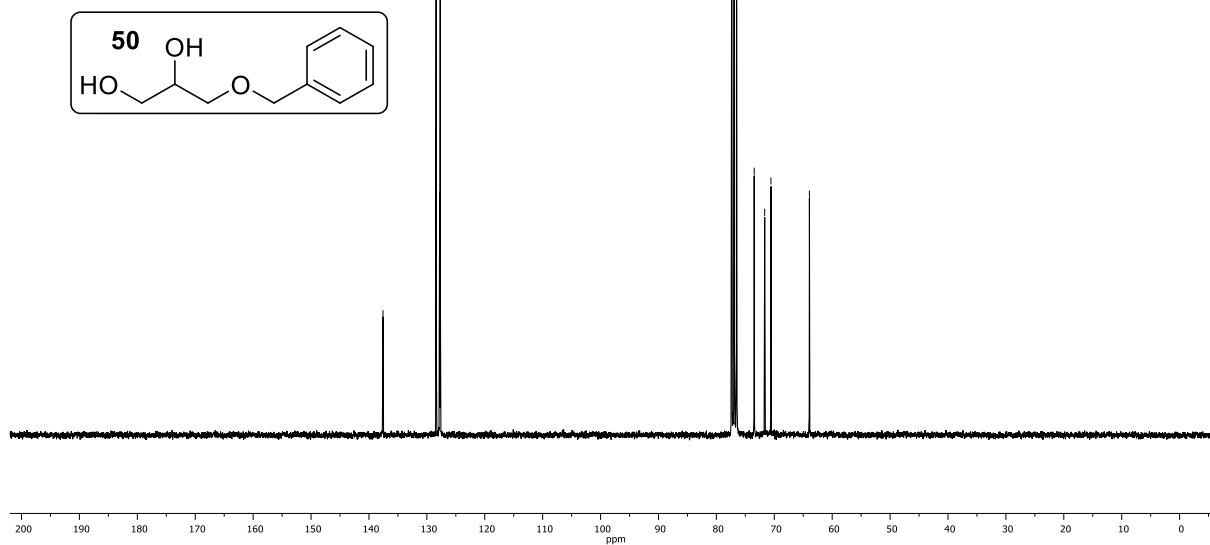
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



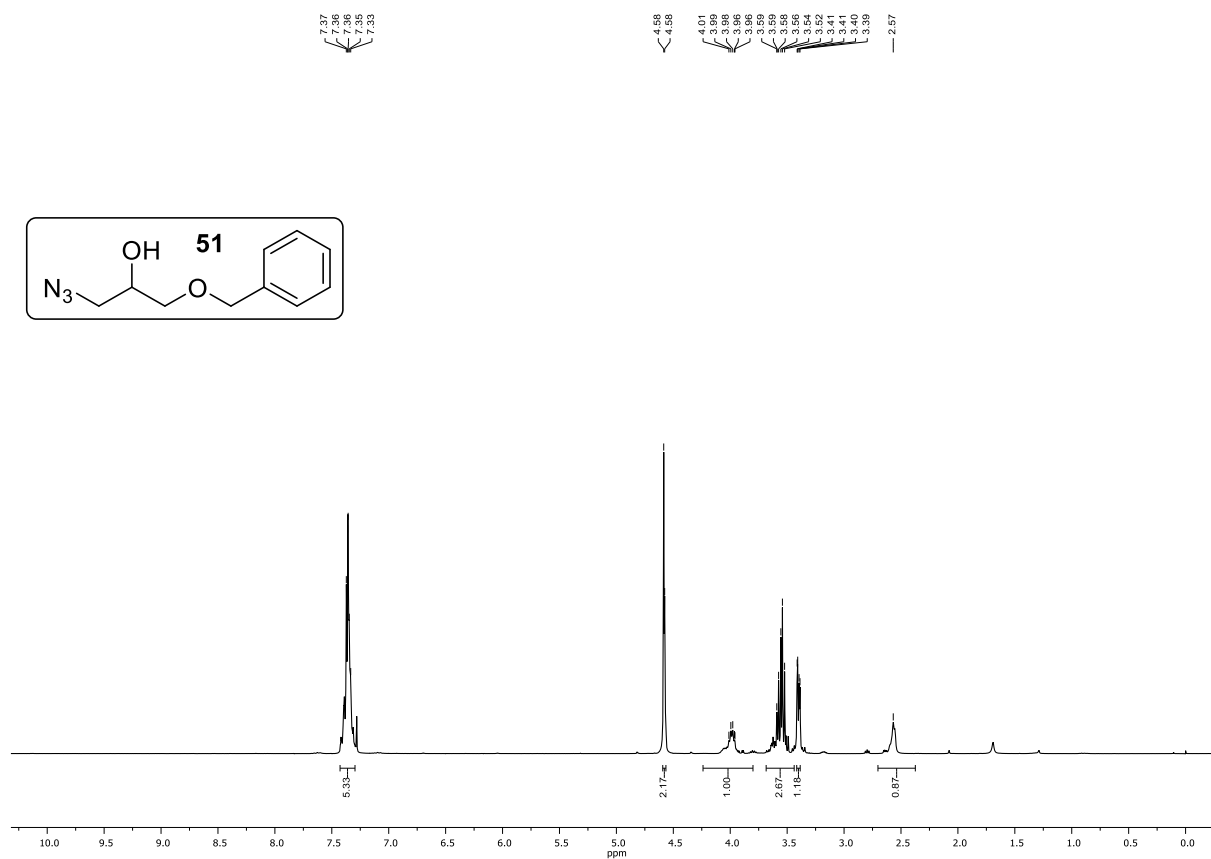
^1H NMR (CDCl_3 , 300 MHz)



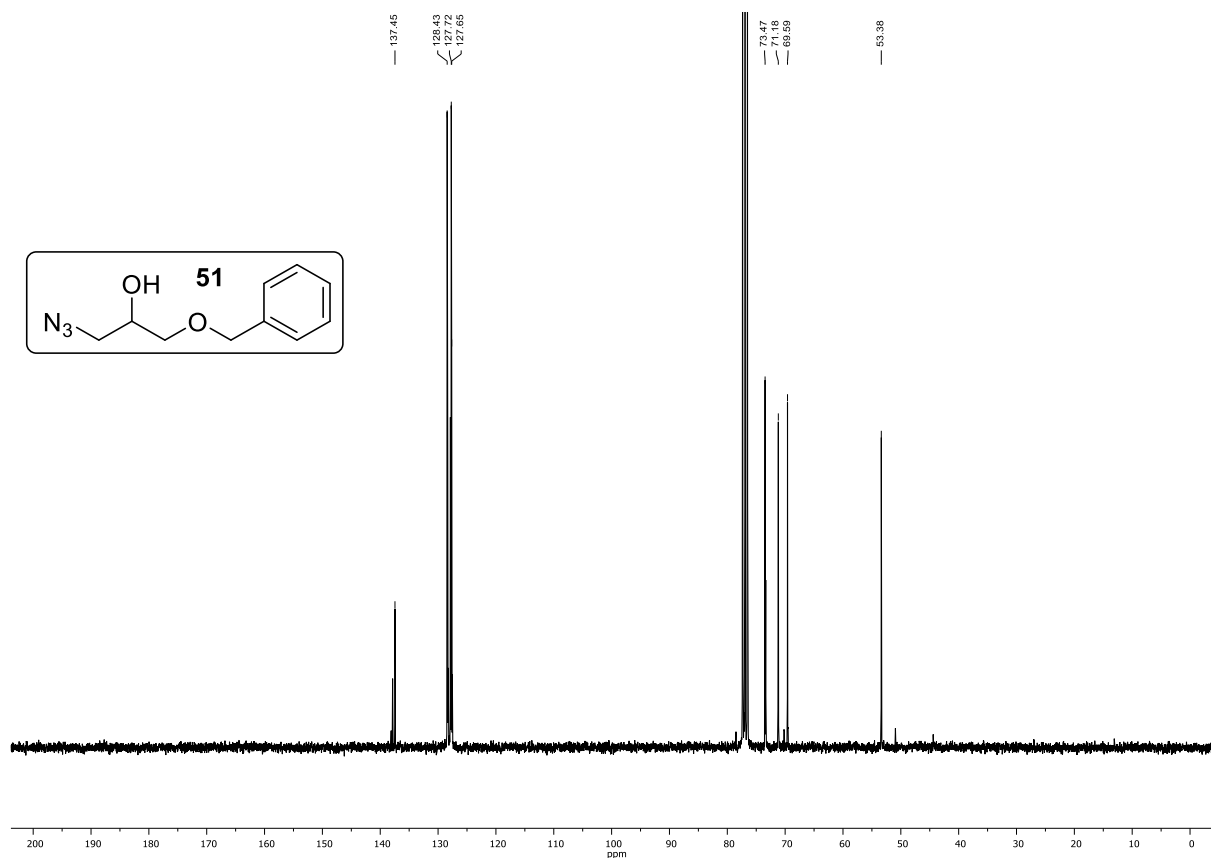
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)



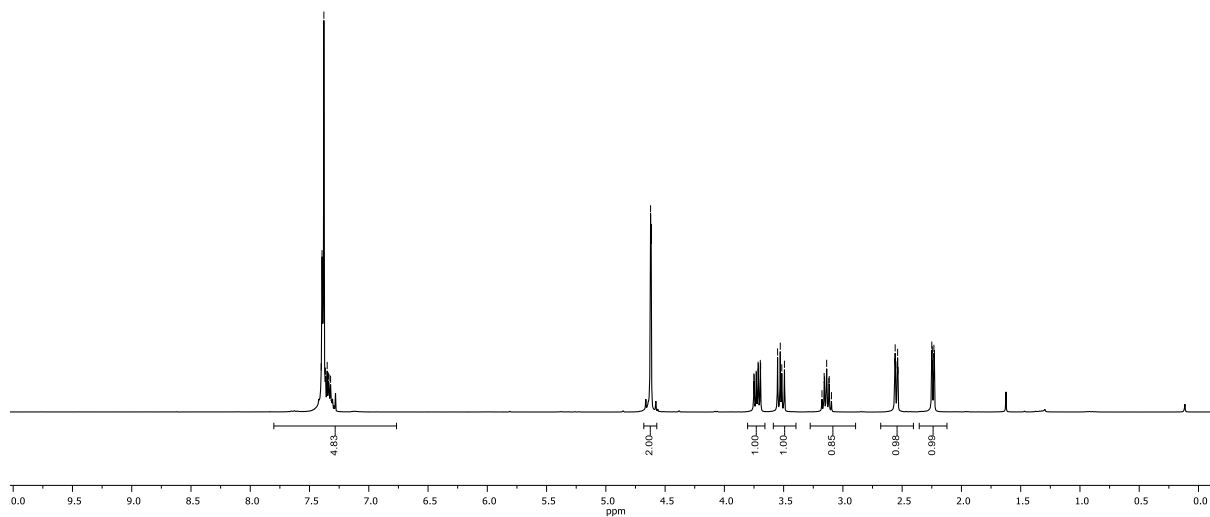
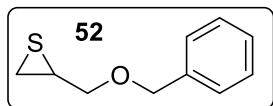
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)

7.40
7.39
7.38
7.36
7.35
7.34
7.32

4.82
3.75
3.75
3.75
3.72
3.72
3.70
3.69
3.55
3.52
3.49
3.18
3.14
3.12
3.12
3.10
2.56
2.56
2.54
2.54
2.25
2.25
2.23

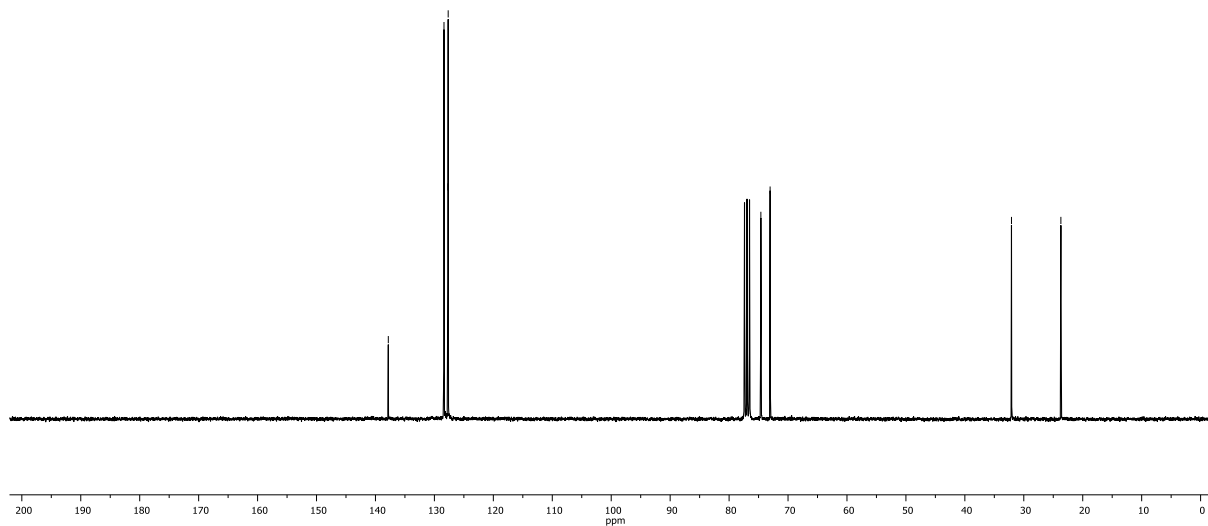
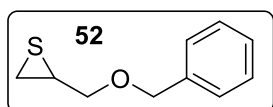


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)

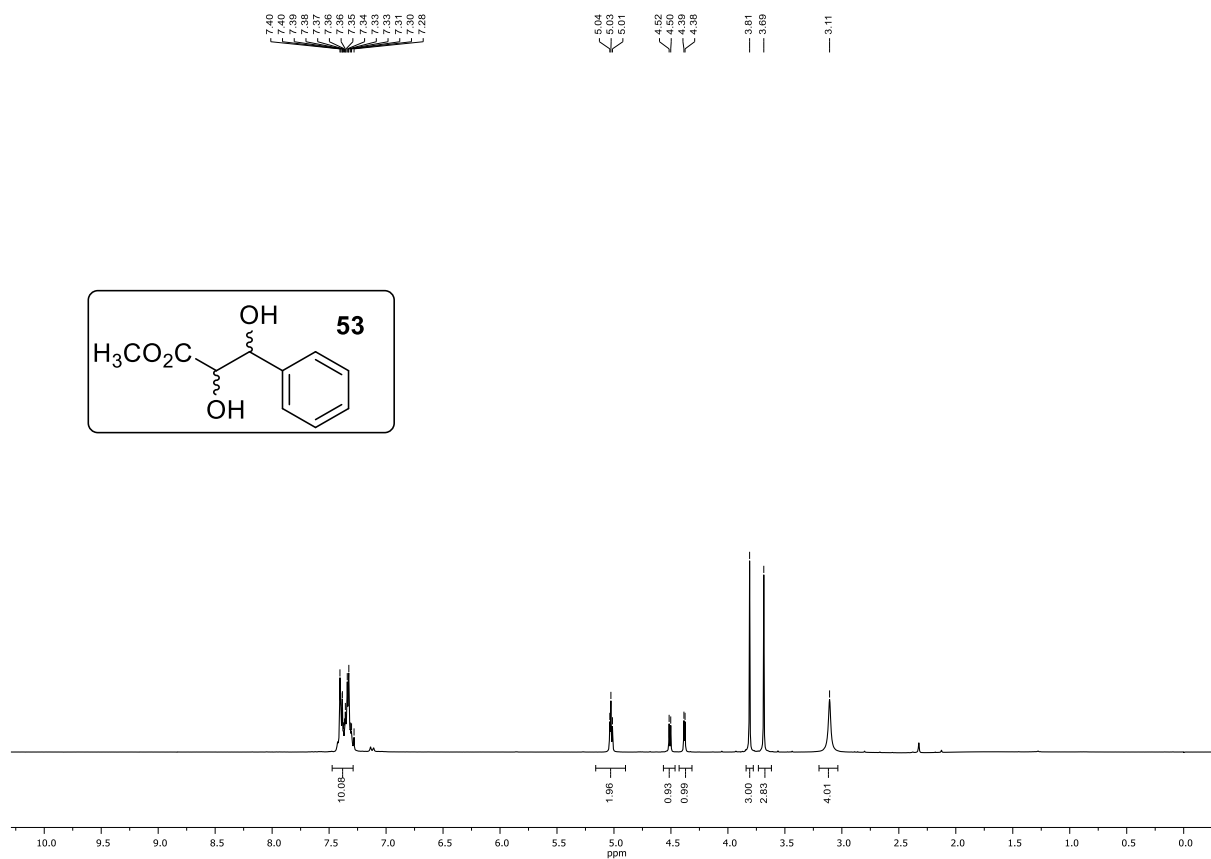
137.82
128.37
127.06

74.61
73.04

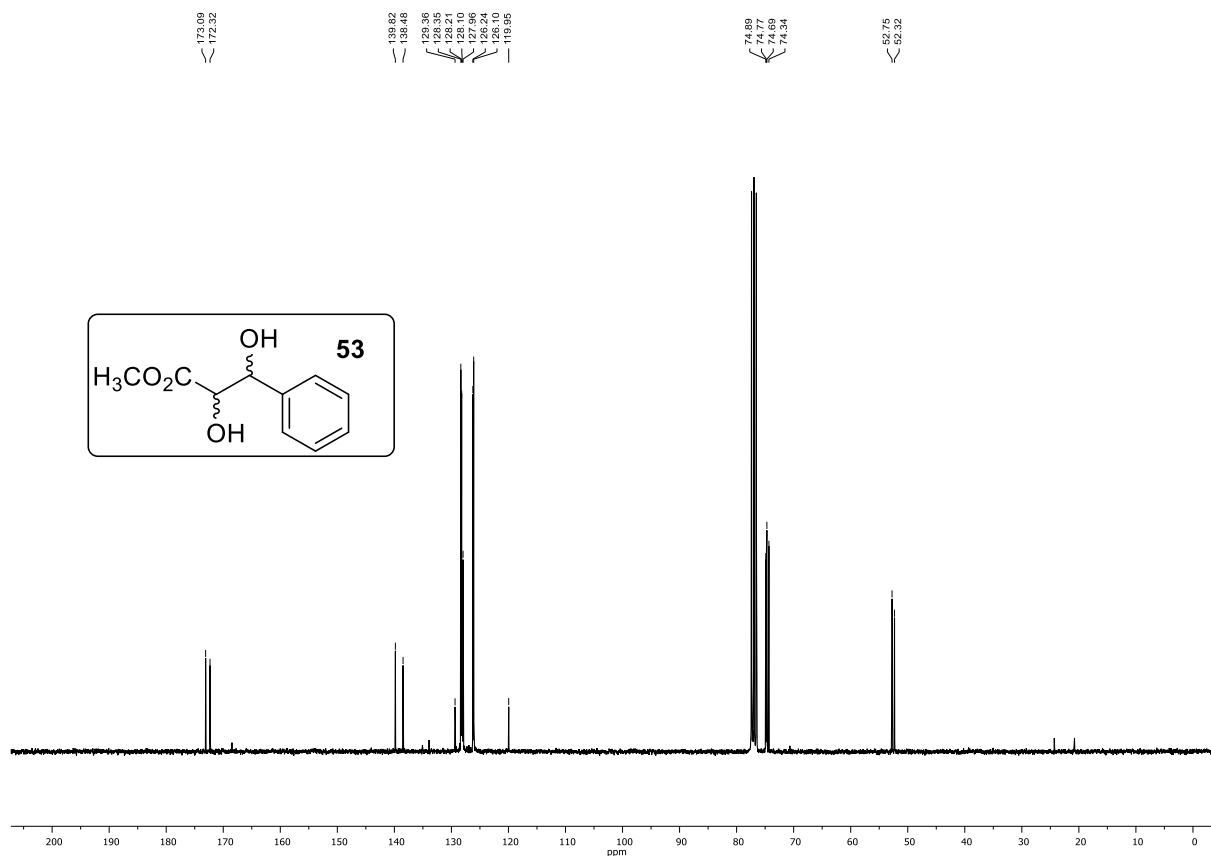
32.09
23.71



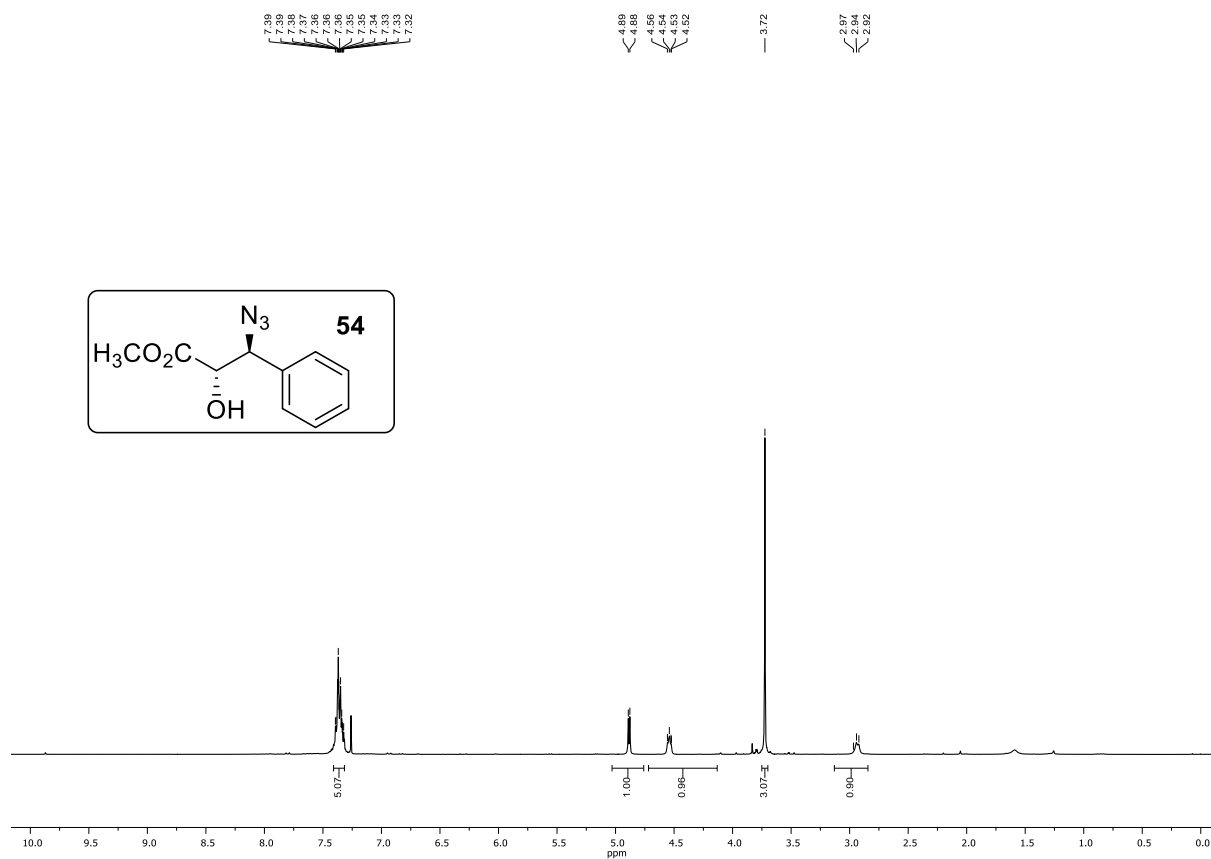
^1H NMR (CDCl_3 , 300 MHz)



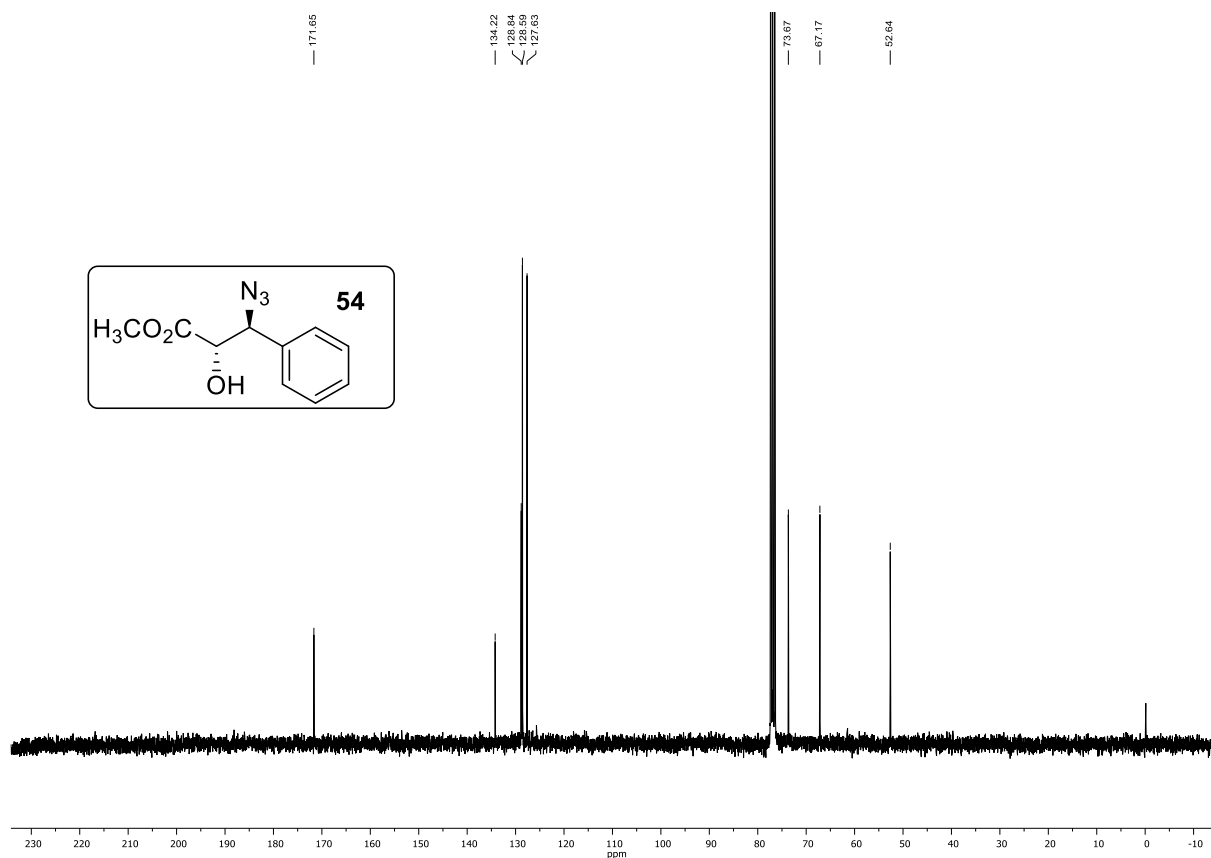
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)

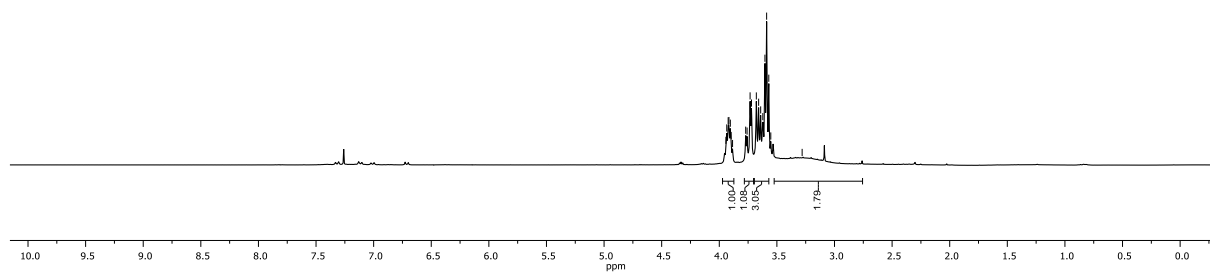
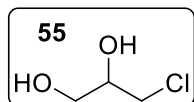


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)



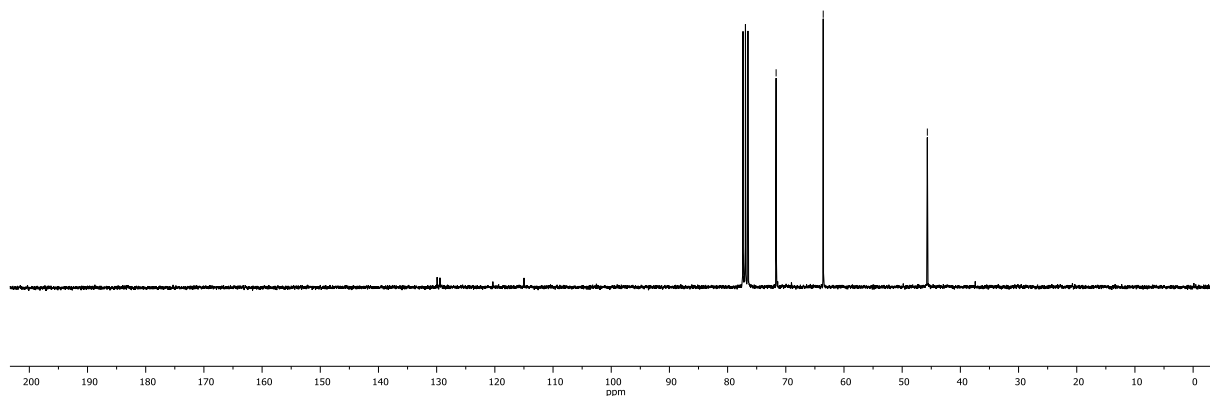
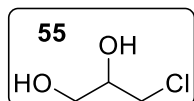
^1H NMR (CDCl_3 , 300 MHz)

3.94
3.94
3.92
3.92
3.90
3.90
3.89
3.89
3.76
3.73
3.62
3.62
3.66
3.64
3.65
3.59
3.57
3.28



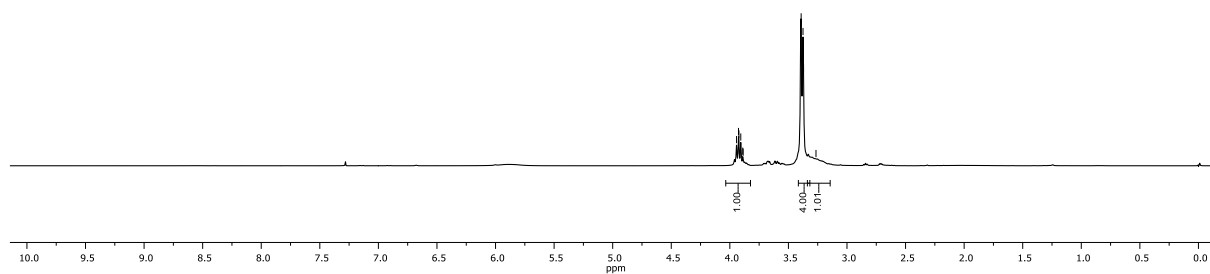
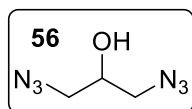
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)

71.66
63.57
45.68



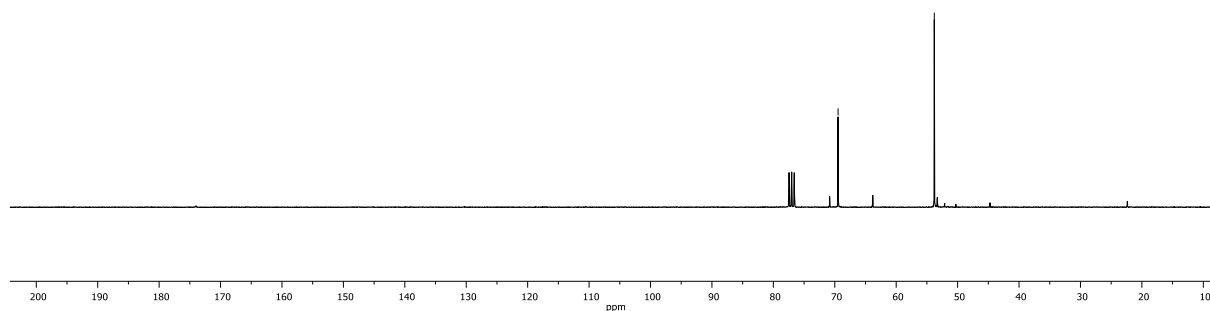
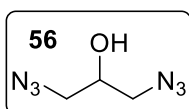
^1H NMR (CDCl_3 , 300 MHz)

3.94
3.93
3.92
3.91
3.89
3.40
3.39
3.38
3.37
3.26

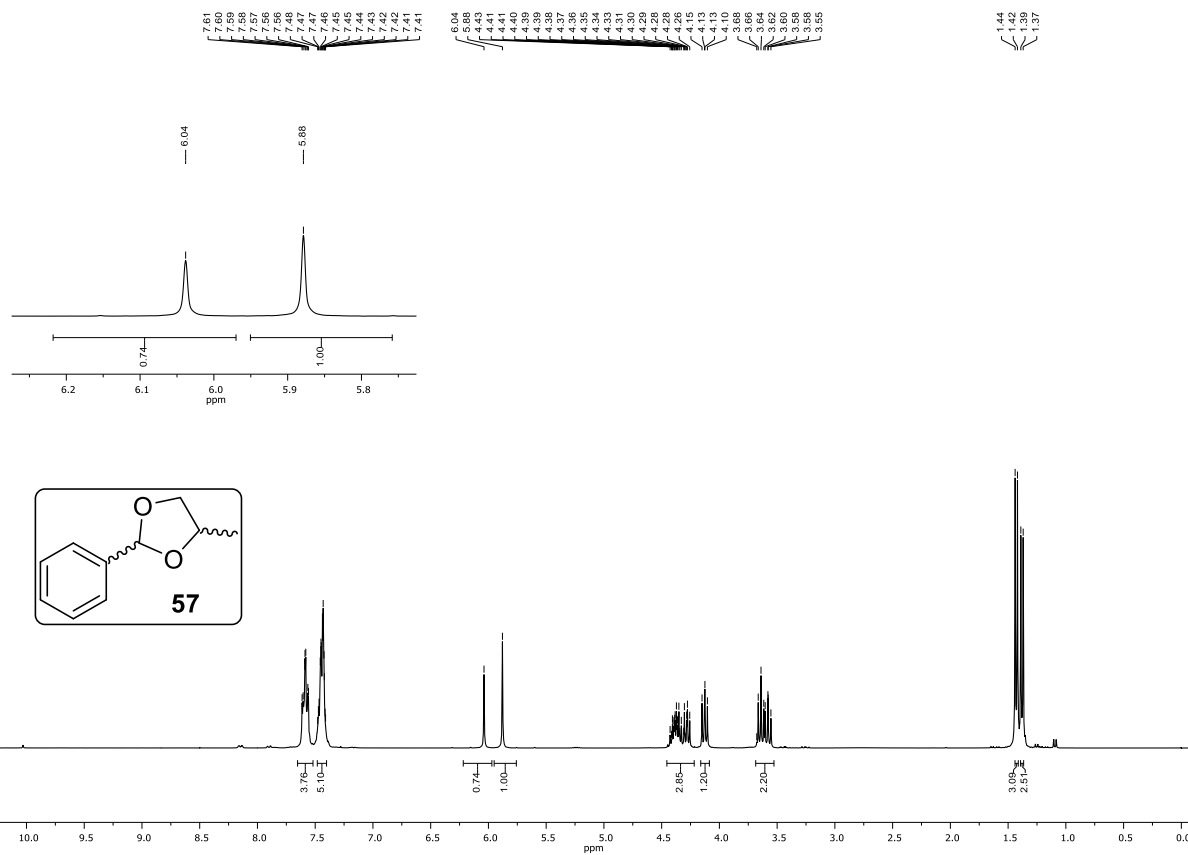


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz)

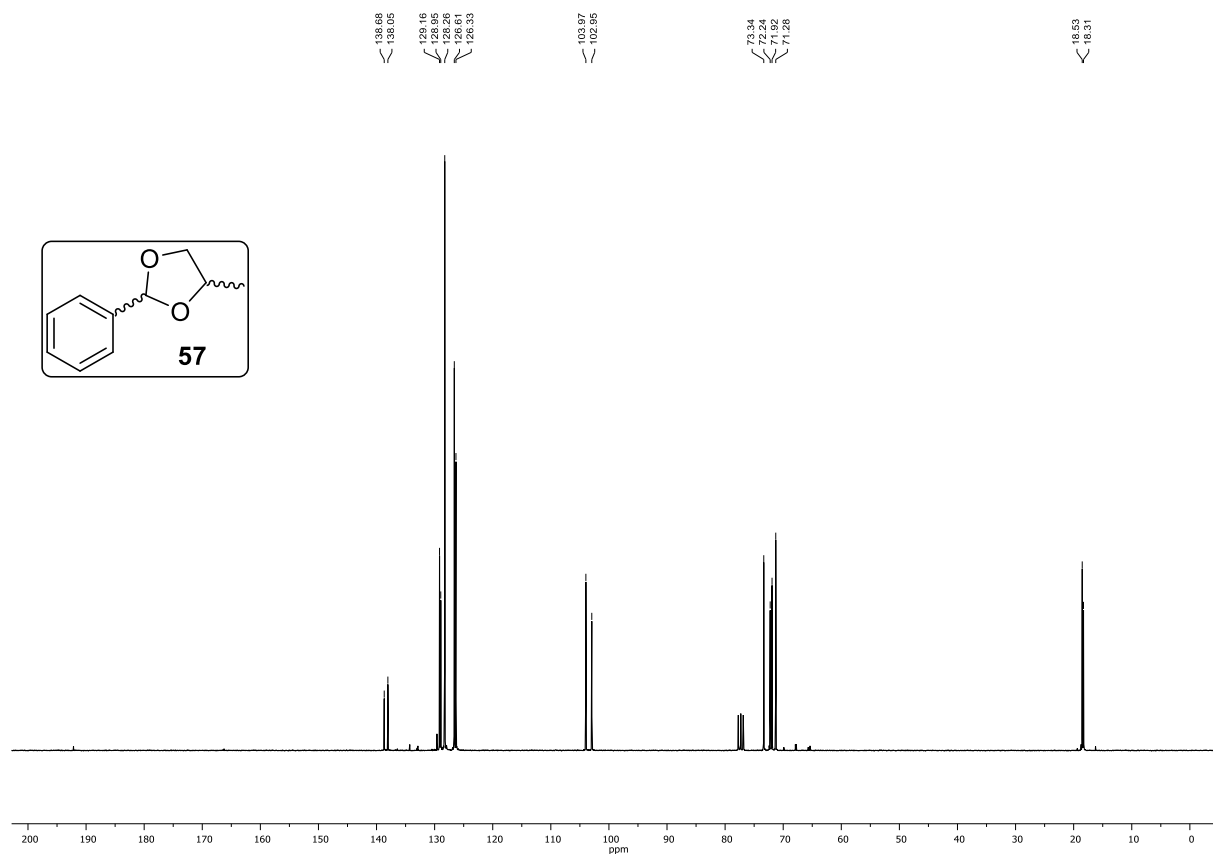
69.46
53.79



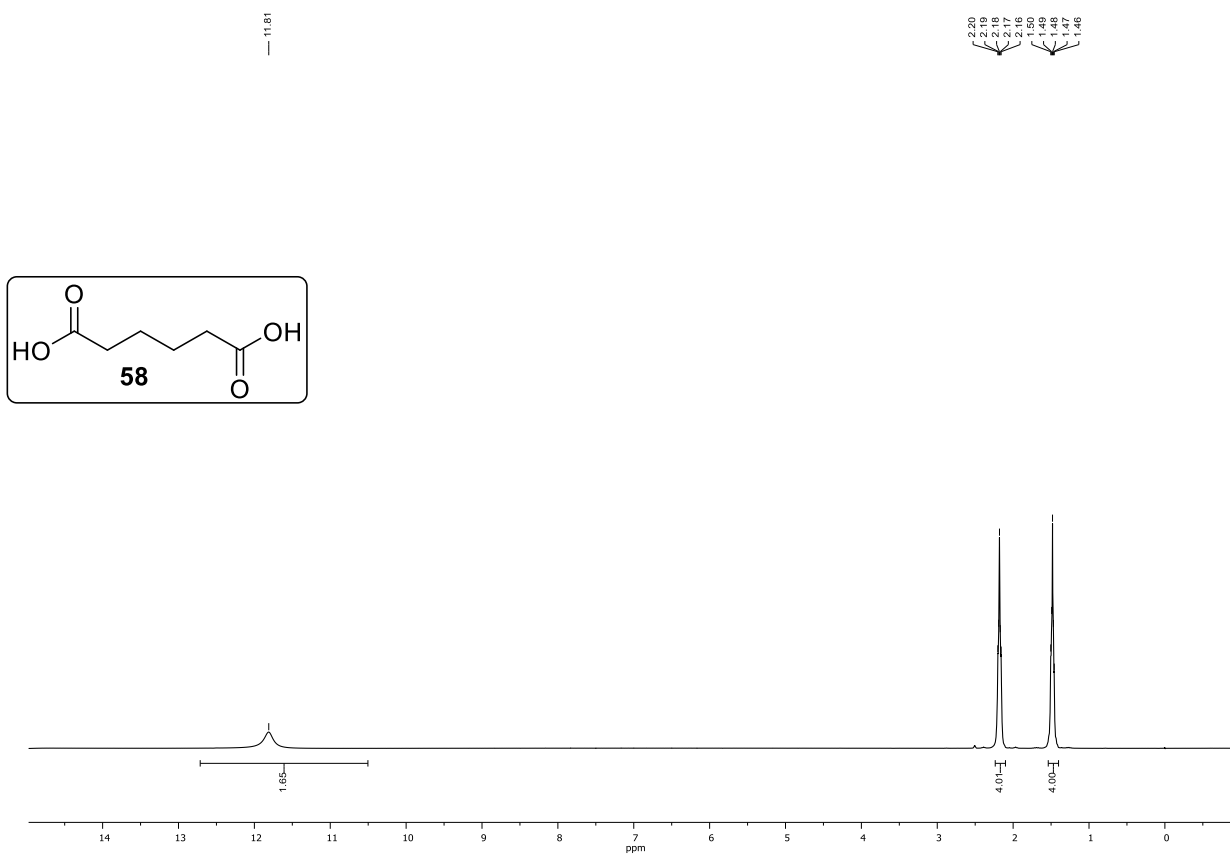
$^1\text{H NMR (CDCl}_3, 300\text{ MHz)}$



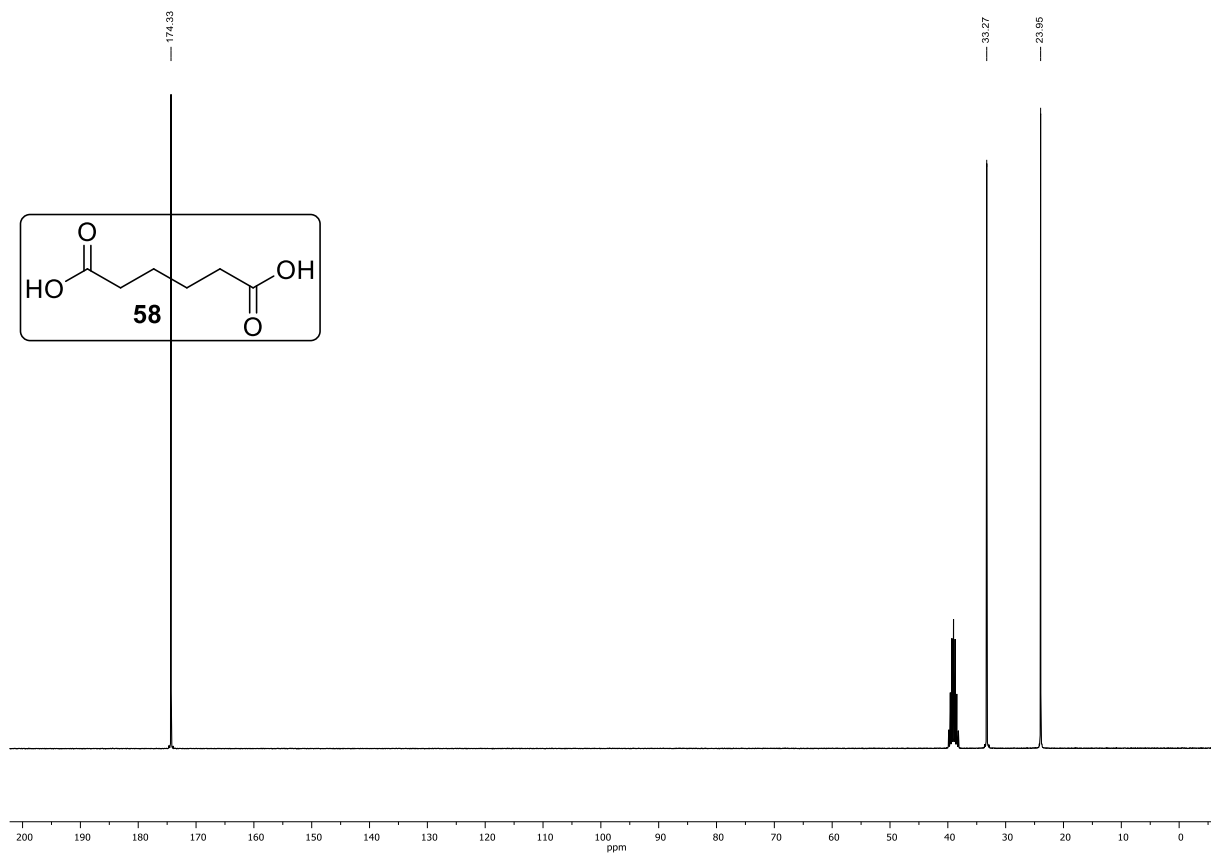
$^{13}\text{C}\{^1\text{H}\} \text{NMR (CDCl}_3, 75\text{ MHz)}$



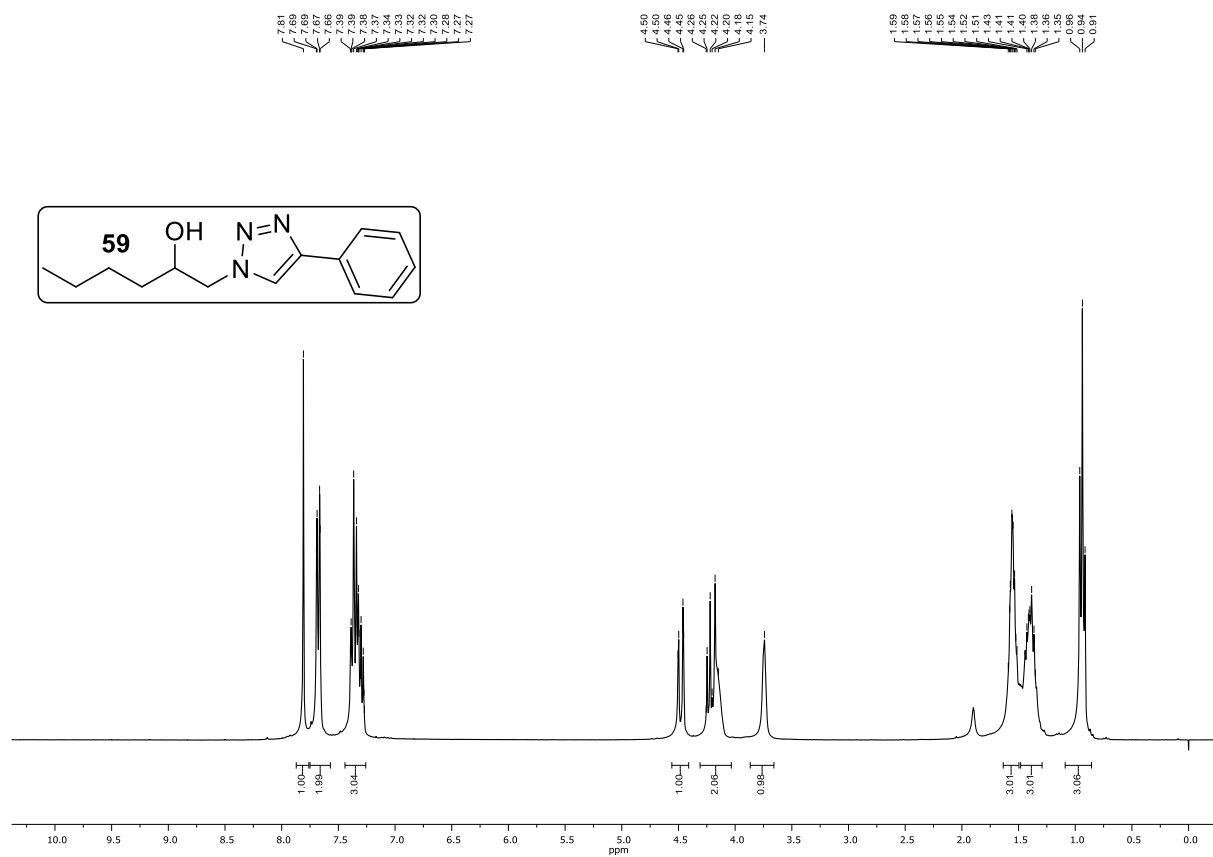
^1H NMR (DMSO- d_6 , 300 MHz)



$^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 75 MHz)



^1H NMR (CDCl_3 , 300 MHz)



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

