Supporting Information

Sustainable Palladium-Catalyzed Tsuji-Trost Reactions Enabled by Aqueous Micellar Catalysis

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1. General Information

All commercial reagents were used without further purification unless otherwise noted. Organic solvents specified as "dry" and/or "degassed" such as THF, toluene, and DCM were taken from a solvent purification system (Innovative Technology, Inc.). All other solvents were used as received, such as EtOAc, Et_2O, hexanes, MeOH unless otherwise noted, purchased in 20 L drums from Fisher Scientific. TPGS-750-M was synthesized according to a literature procedure,[1] but can also be purchased from Sigma-Aldrich (now Millipore-Sigma), catalog number 763896. Thin layer chromatography (TLC) was performed using silica gel 60 F_{254} plates (Merck, 0.25 mm thickness) and analyzed by UV lamp (254 nm) and stains as noted. Silica gel column chromatography was conducted in glass columns with compressed air using SiliaFlash® F60 40-63 μm silica gel purchased from Silicycle. Argon used for inert gas/vacuum manifold was industrial grade purchased from Praxair, and passed through a column of anhydrous $CaSO_4$ (Drierite brand) before entering the manifold. The pump attached to the argon/vacuum manifold, used to evacuate reaction vessels and remove solvent from purified products was a Welch® 1400 DuoSeal® vacuum pump. Reactions were stirred and heated using IKA® Labortechnik brand stirring hotplates with temperature control probe. Vial-scale reactions were conducted in 1 dram (3.7 mL) screwcap glass vials (VWR #66011-041) capped with 14/20 rubber septa (VWR #89097-554), and stirred with 1/2" x 1/8" Teflon® coated magnetic stir bars (VWR #58947-140) with the ends clipped using scissors to fit inside the vial to allow them to spin without becoming stuck. Vial-scale reactions specified as heated (e.g., 45 °C) were placed in a Chemglass® (#CG-1991-04) aluminum block reactor in either of the two inner rings of holes, but never in the outermost ring, to ensure efficient stirring. The aluminum block reactor was placed on top of the previously mentioned stirring hotplate, with temperature probe, and the reactions stirred vigorously (i.e., 800-1200 rpm) to maintain efficient mixing. Glassware specified as "oven-dried" was dried for at least 4 h in an oven at 100 °C before use. ^{1}H and ^{13}C NMR spectra were taken using either 400 MHz Agilent® Technologies, 500 MHz Varian Unity Inova® or 600 MHz Varian Unity Inova® spectrometers, with either $CDCl_3$, CD_3OD, or DMSO-d_6 as noted. ^{1}H NMR spectra were referenced to 7.26 ppm ($CDCl_3$), 3.31 ppm (CD_3OD), or 2.50 ppm (DMSO-d_6). ^{13}C NMR spectra were referenced to 77.16 ppm ($CDCl_3$), 49.00 ppm (CD_3OD), or 29.84 ppm (DMSO-d_6). NMR spectra was processed using MestReNova software version 14.0.0-23239. Exact mass measurements were taken on a Waters GCT Premier high-resolution Time-of-flight mass spectrometer, with ionization method as noted.

[1] Lipshutz, B. H.; Ghorai, S.; Abela, A. R.; Moser, R.; Nishikata, T.; Duplais, C.; Krasovskiy, A.; Gaston, R. D.; Gadwood, R. C., TPGS-750-M: A Second-Generation Amphiphile for Metal-Catalyzed Cross-Couplings in Water at Room Temperature. *J. Org. Chem.* **2011**, *76*, 4379–4391.

2. General procedures for Tsuji-Trost reactions in water

2.1 Reaction vessel considerations

Catalyst stock solutions as well as reaction trials were conducted in 1-dram (3.7 mL) screw-top vials capped with a 14/20 rubber septum (see Figure 1a-b; see General Information above for supplier and part number). They are convenient for these reactions for several reasons. Multiple trials can be conducted at the same time because these vials fit in an aluminum block reactor. The flat bottom allows for vigorous stirring (whereas conical tubes and culture tubes do not seem to stir as

efficiently), and the small amount of headspace prevents excessive evaporation of low-boiling reagents like triethylamine, methyl formate, ammonia, etc., which can be a problem with larger vials and culture tubes frequently used for methodology studies. The use of larger vessels can be problematic in cases where solids or viscous reaction mixtures are present due to the tendency for material to be trapped on the glass, above the water line. In addition, reaction progress can be easily monitored without opening the vial by removing a small amount (~2-3 μ L) of reaction mixture for analysis by TLC or other means, without exposing the reaction to oxygen (which is a problem when using screw-caps). Disposable ½" x 1/8" stir bars are inexpensive and available in packs of 100, however, they are slightly too long to lay flat in a 1-dram vial (c), and frequently wedge/lodge in the vial, halting stirring. To remedy this, a small amount of material can be trimmed from the ends using scissors, so they lay flat in the vial (d). Only a small amount of material should be removed (d) to avoid exposing metal. Note: only small diameter needles should be used to add reagents or remove aliquots of reaction mixture, as large diameter needles tend to "core" the septum, potentially allowing oxygen to enter the reaction mixture.

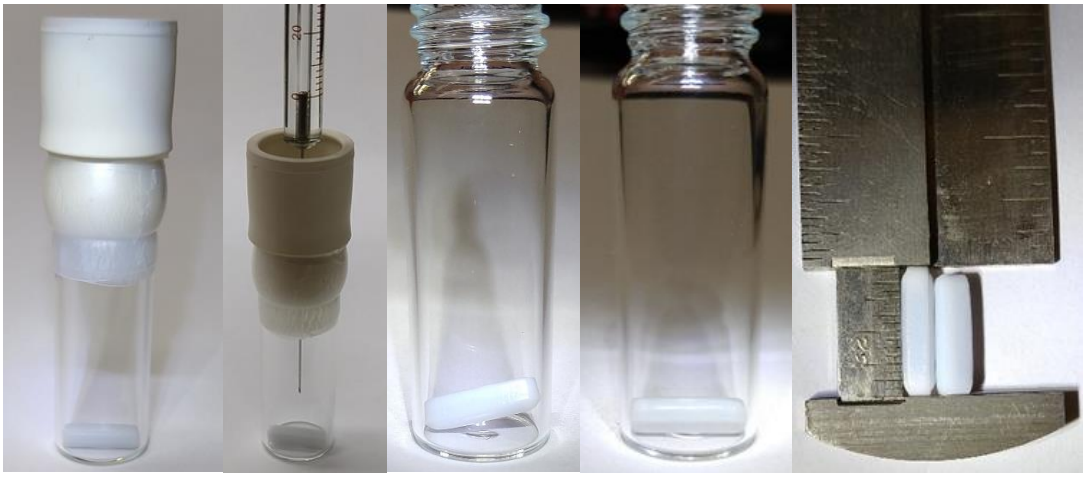


Figure 1: (a) reaction vial with stir bar and capped with a septum, (b) microliter syringe used to add liquid reagents, (c) ½" x 1/8" stir bar as received in vial, (d) ½" x 1/8" in vial after trimming the ends (e) untrimmed stir bar on left, trimmed stir bar on right.

2.2 Catalyst stock solution preparation

Due to the difficulty in accurately weighing sub-milligram quantities of Pd catalyst needed for "ppm" level catalyst loadings, it was necessary to prepare a catalyst stock solution. The preferred solvent for this stock solution was found to be toluene; other solvents such as THF, acetone, MeOH, and EtOAc were tested but were found to give inferior results. In addition, it is preferred to fully ligate the palladium prior to adding it to the reaction mixture, as quick and full ligation is difficult to achieve in the aqueous reaction medium, especially in the presence of substrates such as amines, sulfonamides, *N*-heterocycles, etc., which may interfere with in-situ ligation in the reaction medium. In addition, use of pre-ligated palladium, (e.g., PdDPEphosCl_2) was found to give inferior results to a freshly prepared stock solution made from [Pd(allyl)Cl]$_2$ and DPEphos. A 1-dram (~4 mL) scintillation vial with magnetic stir bar was oven dried (minimum 4 h at 100 ^{o}C). The vial was removed from the oven and capped with a 14/20 septum (see Figure 1 above) and attached to an

argon Schlenk manifold via a 22G (0.7 mm) diameter needle and vacuum was applied until the vial had cooled to rt, then the vial was backfilled with dry argon. The vial was opened and quickly added was $[Pd(allyl)Cl]_2$ (9.14 mg, 0.025 mmol) and DPEphos (26.9 mg, 0.050 mmol) and the vial was then capped with a 14/20 septum. Note: $[Pd(allyl)Cl]_2$ was typically weighed on a microgram balance to ensure as close to intended mass of Pd, due to difficulty in weighing small (mg) amounts of Pd on some balances, this stock solution may be scaled. We recommend keeping the same concentrations of reagents and toluene. The vial was re-attached to the Schlenk manifold and evacuated and backfilled with argon 3x. To the vial was added through the septum via syringe 2000 μL of dry, degassed toluene taken from a solvent purification system, with the vial still attached to the Schlenk line. The vial was stirred vigorously at rt, removing the needle and shaking the vial occasionally to rinse any material stuck above the liquid line. A fine yellow precipitate of ligated palladium formed and the vial is allowed to stir for a minimum of 10 min, but no more than 1 h before use. 20 μL of this stock solution is equivalent to 0.1 mol % Pd (1000 ppm) for a 0.5 mmol scale reaction. When transferring stock solution to a reaction mixture, it is necessary to continually stir the stock solution to prevent settling of the yellow suspension, and transfer the stock solution quickly to prevent it from settling in the microliter syringe used to transfer it. Note: some catalyst stock solutions (prepared under various concentrations during optimization) changed from a fine yellow suspension to a black color with material adhering to the glass, particularly if the stock solution is allowed to stir for >1 h. It was unclear if this was indicative of decomposition due to the presence of water, oxygen, or due to stock solution concentration. Test reactions using this blackened solution/material showed usable catalytic activity, but in the interest of utmost care, these solutions were not used for any important trials. Extensive testing, however, of the effect of this phenomenon was not conducted. Most stock solutions prepared according to the above procedure remained a fine yellow suspension even after standing overnight, suggesting that the shelf life of this stock solution is likely at least 24 h, but extensive shelf life testing was not conducted.

2.3 General procedure for intermolecular reactions

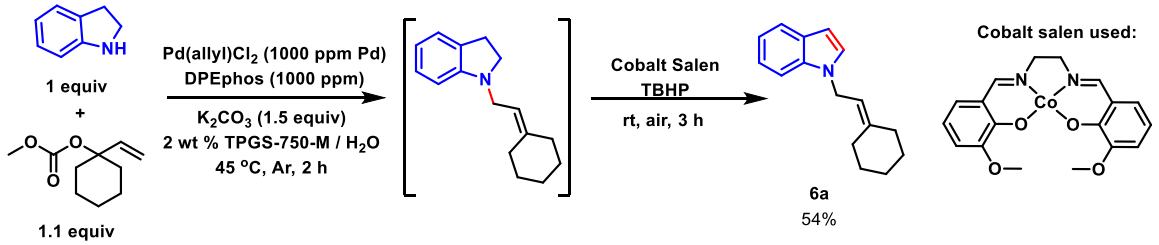
To a 1-dram (~4 mL) scintillation vial was added all solids (including solid starting materials and base, but not catalyst except in cases where >0.25 mol % Pd was used, in which case Pd and ligand were added as a solid at this point), then a Teflon coated magnetic stir bar (trimmed to fit vial, see Figure 1 (a)) and the vial capped with a 14/20 septum (see Figure 1). This was done with no special precautions against moisture or oxygen. The vial was attached to an argon manifold/Schlenk line via a 22G / 0.7 mm diameter needle. Vacuum was applied to the vial, and backfilled with argon (industrial grade), making no special attempt to prevent reagents from being sprayed around the inside of the vial during backfilling. The evacuation/backfill was repeated 3x, with several seconds of vacuum and refill allowed during each cycle to fully purge the vial. The argon needle was removed from the vial. Via syringe, was added through the septum a degassed 2 wt % TPGS-750-M / H_2O solution (0.5 mL), taking care to prevent introducing air/oxygen during the transfer. The vial was placed in an aluminum block reactor heated to 50 ^{o}C (to maintain an internal temperature of 45 ^{o}C) and stirred vigorously (~800-1000 rpm). Next, liquid reagents were added via syringe (i.e., allylic carbonate, Et_3N, methyl formate) in no particular order (Note: Et_3N and methyl formate were degassed by sparging ~2-3 mL portions with industrial grade argon for ~5-10 min before use). Lastly was added catalyst stock solution via syringe (20 uL for 0.1 mol % / 1000 ppm Pd) typically using a 50 uL or 100 uL microliter syringe with Teflon plunger to avoid introducing air (Note: many microliter syringes tend to leak air, the syringe used was selected because it does not leak), see above catalyst stock solution procedure for catalyst stock solution preparation.

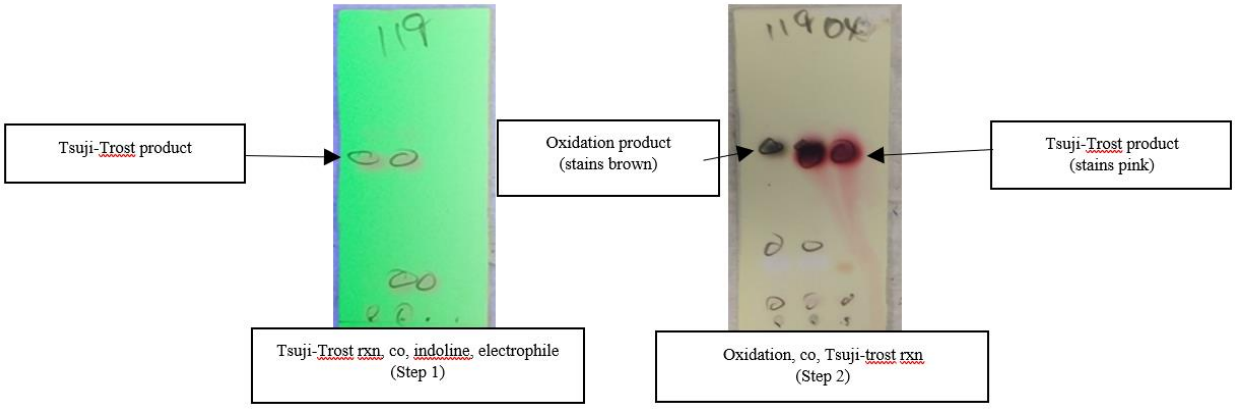
Note: While most reactions can be run at relatively high concentration (i.e., 0.5 mL of surfactant for a 0.5 mmol scale reaction), some particularly high molecular weight or crystalline substrates/products exhibit poor solubility at this concentration, and benefit from a more dilute reaction mixture (e.g., 1.0 mL surfactant solution rather than 0.5 mL). Reaction concentrations from 0.25 to 1.0 M (relative to limiting coupling partner to surfactant solution) were screened, no significant difference was seen, thus a more concentrated reaction mixture contributes to a lower E Factor. In addition, while significant oiling out/precipitate formation may occur when using K_2CO_3 as base, the use of triethylamine as base produces a much more uniform/homogeneous appearing reaction mixture.

2.4 General procedure for intramolecular reactions

The same catalyst stock solution and reaction conditions were used. However, the intramolecular reactions benefit from a lower reaction concentration to decrease byproduct formation. Therefore, a reaction concentration of 0.33 to 0.4 M (relative to surfactant solution, i.e., 1.25 mL surfactant solution for a 0.5 mmol scale trial for a concentration of 0.4 M) was typically used. Reactions run at 1.0 M as in intermolecular trials resulted in significantly decreased yields. In addition, Et_3N is the preferred base for intramolecular reactions as it decreases oiling out / precipitate formation which was associated with decreased yields and increased by-products when K_2CO_3 was used as base.

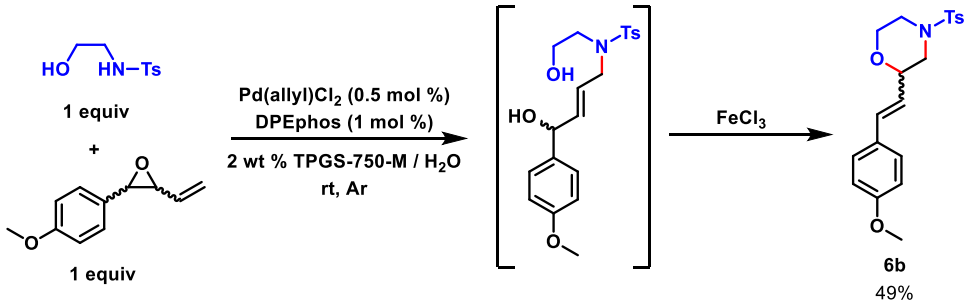
2.5 Procedures for 2-step-1 pot reactions





To a 1-dram (~4 mL) scintillation vial with magnetic stir bar was added K_2CO_3 (103.7 mg, 0.75 mmol, 1.5 equiv), with no special precautions against air or moisture. The vial was capped with a 14/20 septum, and attached to an argon Schlenk line via a 22G / 0.7mm diameter needle, and the vial was evacuated and back filled with argon 3x, then the needle removed. Via syringe was added 1.0 mL

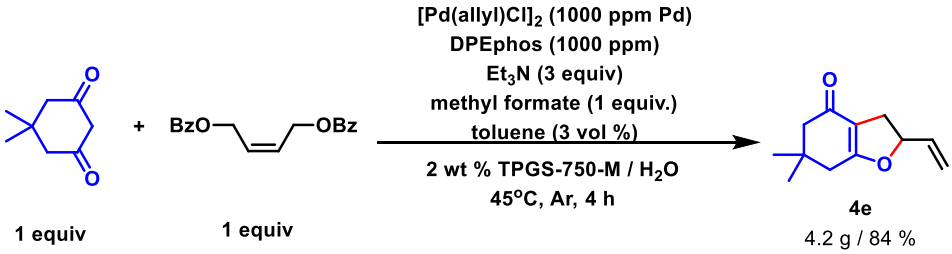
of degassed 2 wt % TPGS-750-M / H_2O solution and stirred briefly. Next, via microliter syringe was added indoline (59.6 mg, 0.5 mmol, 56.2 uL, 1 equiv) then allylic carbonate (101.3 mg, 0.55 mmol, 99.3 uL, 1.1 equiv) and the vial placed in an aluminum block reactor heated to 50 °C to maintain an internal temperature of 45 °C, and stirred vigorously (~800-1000 rpm). Catalyst stock solution (as prepared above) was added via microliter syringe (20 uL, 0.0005 mmol Pd, 0.1 mol %). After 2 h, an aliquot of the reaction mixture (~2-4 uL) was removed via microliter syringe and diluted Et_2O (~50 uL), rinsing the syringe into a test tube. The test tube was swirled and the organic layer used for TLC analysis using 7:93 (Et_2O/hexanes) which showed full consumption of indoline starting material. The vial was removed from the block reactor, allowed to cool to rt, uncapped and cobalt salen (9.6 mg, 0.025 mmol, 5 mol %) was added, and the vial re-capped (Note: surfactant solution may make the septum slippery, and may need to be wiped dry to prevent the septum from popping off of the vial), taking no precautions against air, and a 22G / 0.7 mm vent needle was placed through the septum to vent any pressure which might develop. Via microliter syringe was added TBHP (70% aqueous solution) (~260 uL, ~2.0 mmol, ~4 equiv) and the vial placed on a hot plate at rt and stirred vigorously for 3 h, upon which time the *N*-allylic indoline had been consumed, giving a new spot slightly higher (*N*-allyl indoline stains pink with Seebach's magic stain, *N*-allylic indole stains brown with this stain), Note: amounts of TBHP and cobalt catalyst were not optimized. To determine reaction completion it was necessary to filter an aliquot through a pipette with a small amount of silica in order to resolve *N*-allylic indoline from the *N*-allylic indole product due to extremely close R_f values. Alternatively, the conversion can be monitored by GC-MS. Note: this oxidation/dehydrogenation must not be allowed to proceed for longer than necessary, as reactions allowed to run overnight produced very little product and large amounts of black tar material. Upon reaction completion (~3 h), the vial was uncapped and extracted with EtOAc, 3 x 1.5 mL. The organic phase was dried over anhydrous Na_2SO_4 and adsorbed onto Celite. Silica gel column chromatography was conducted using hexanes, then 2 : 98 (Et_2O / hexanes) then 5 : 95 (Et_2O / hexanes) to give 61 mg (54%) of 1-(2-cyclohexylideneethyl)-1H-indole as a light yellow oil. See Sections 5 and 6 for characterization data and spectra.

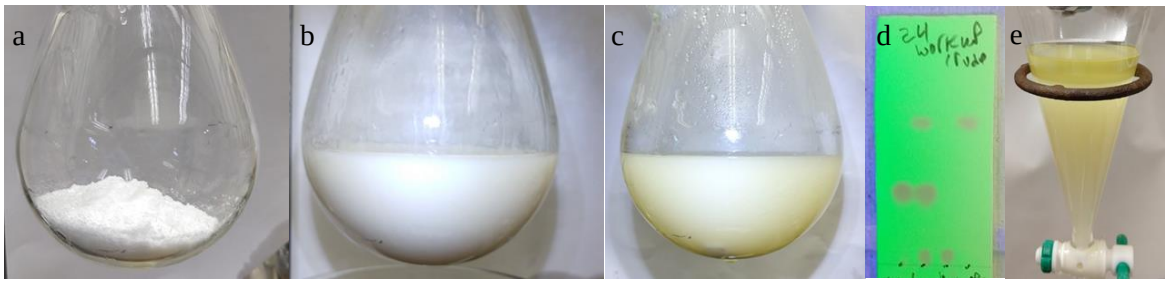


To a 1-dram (~4 mL) vial with magnetic stir bar was added $[Pd(allyl)Cl]_2$ (0.92 mg, 0.005 mmol, 0.5 mol %), DPEphos (2.7 mg, 0.005 mmol, 1.0 mol %), *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (107.6 mg, 0.5 mmol, 1.0 equiv), and the was vial capped with a 14/20 septum. The vial was attached to an argon Schlenk line via a 22G / 0.7 mm diameter needle and the vial evacuated and backfilled with argon 3x. Via syringe was added 1.0 mL of degassed 2 wt % TPGS-750-M / H_2O solution and the vial placed in aluminum block reactor at 45 °C. With stirring was added 2-(4-methoxyphenyl)-3-vinyloxirane (88.1 mg, 0.5 mmol, 83.4 uL, 1.0 equiv) via microliter syringe. The reaction was stirred for 3 days, upon which time the vinyl epoxide had been consumed,

producing the diol intermediate and a small amount of the vinyl morpholine product. The vial was removed from the reactor and opened. $FeCl_3 \bullet 6H_2O$ (20 mg, 0.074 mmol, 0.15 equiv) was added, the vial capped with a screw cap and placed back in the block reactor at 45 °C. The reaction was stirred for 5 h upon which time the diol intermediate was deemed consumed by TLC, diol intermediate R_f = 0.30 and vinyl morpholine product R_f = 0.80 with 75:25 (EtOAc/hexanes). The reaction was extracted with EtOAc, the organic phase dried with anhydrous Na_2SO_4, and the crude product adsorbed onto Celite. The product was purified via column chromatography with hexanes then 30/70 (EtOAc/hexanes) to give 2-(4-methoxystyryl)-4-tosylmorpholine as a pale yellow oil (91 mg / 49%). (Note: this sequence was also attempted using Et_3N as base (as per the usual general coupling procedures above), and was found to give additional byproducts and poor conversion of the diol to the vinyl morpholine. Methyl formate was screened as an additive and also failed to improve results. A water stable Lewis acid $Yb(OTf)_3$ was also screened in lieu of $FeCl_3 \bullet 6H_2O$ and it failed to produce a significant amount of the desired product, but did increase the number and amount of unidentified impurities.) See Sections 5 and 6 for characterization data and spectra.

2.6 Procedure for scaled-up reaction



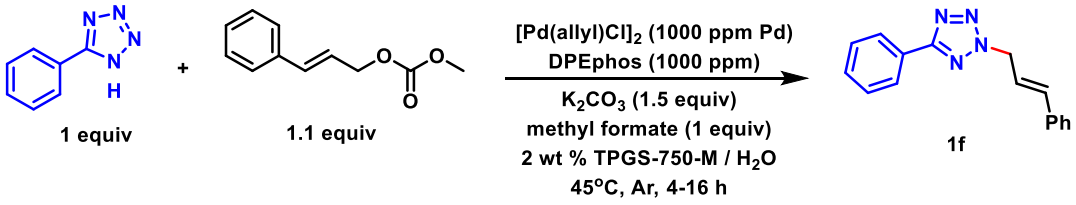


Multi-gram scale reaction: (a) solid reagents in 200 mL flask; (b) reaction mixture at start; (c) reaction upon completion (d) TLC from left to right: reaction mixture, co-spot, dimedone, (Z)-but-2-ene-1,4-diyl dibenzoate; (e) extraction.

To a 200 mL Schlenk flask with 24/40 neck was added a large oval magnetic stir bar (Note: the reaction requires vigorous stirring, so the largest possible stir bar should be used). Next, (Z)-but-2-ene-1,4-diyl dibenzoate (7.704 g, 26.0 mmol, 1.0 equiv) and dimedone (3.645 g, 26.0 mmol, 1 equiv) were added and the flask capped with 24/40 rubber septum. The flask was attached to an argon Schlenk manifold via the valve on the flask. The flask was evacuated/backfilled with argon 4x. Next, 60 mL of degassed 2 wt % TPGS-750-M / H_2O solution was added via syringe and the reaction placed in an oil bath at 50 °C to maintain an internal temperature of 45 °C and stirred vigorously. Via syringe,

degassed Et_3N (7.89 g, 78 mmol, 10.87 mL, 3 equiv) was added (Note: Et_3N degassed by sparging with argon for ~20 min, then evacuating/backfilling the flask 3x). Next, catalyst stock solution was added and the reaction stirred vigorously for 4 h, upon which time the reaction was deemed complete by TLC using 40:60 (EtOAc/hexanes). Catalyst stock solution was prepared by the following procedure: To an oven dried 1 dram (~4 mL) vial with magnetic stir bar, cooled under vacuum, was added $[Pd(allyl)Cl]_2$ (4.76 mg, 0.013 mmol, 0.1 mol % Pd) and DPEphos (14.0 mg, 0.026 mmol, 0.1 mol %) and the vial capped with a 14/20 rubber septum. The vial was attached to an argon Schlenk manifold via a 22G/0.7mm diameter needle and evacuated/backfilled with argon 3x. Dry, degassed toluene (2.0 mL) was added to the vial via syringe, and the stock solution stirred vigorously for 15 min, producing a fine yellow precipitate. The stock solution was transferred via syringe, under argon to the reaction flask. An additional 0.4 mL of toluene was added to the stock solution vial and used to rinse the walls of the vial and syringe, and transferred to the reaction flask. Upon reaction completion, the contents of the flask were poured into a 250 mL round bottom flask, rinsing with EtOAc, and the flask placed on a rotary evaporator to remove Et_3N (Note: extraction of the reaction mixture without removing Et_3N tends to produce a strong emulsion). The aqueous phase was extracted with EtOAc 3x (or until extracts contain no more product). The organic phase was dried over anhydrous Na_2SO_4, and the solvent removed via rotary evaporator. The crude product was purified by silica gel column chromatography using hexanes, then 20:80 (EtOAc/hexanes), then 30:70 (EtOAc/hexanes) to give 6,6-dimethyl-2-vinyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one, 4.21 g (84%). See Sections 5 and 6 for characterization data and spectra.

2.7 Procedure for recycle studies



	Reaction	Recycle 1	Recycle 2	Recycle 3
Yield	**86%**	**79%**	**81%**	**82%**
E Factor (organic)	**0.5**	**0.5**	**0.5**	**0.5**
E Factor (aqueous)	**9**	**7**	**7**	**9**

Reagent added	Reaction	Recycle 1	Recycle 2	Recycle 3
5-phenyl-1H-tetrazole	0.5 mmol	0.5 mmol	0.5 mmol	0.5 mmol
cinnamyl methyl carbonate	0.55 mmol	0.55 mmol	0.55 mmol	0.55 mmol
catalyst solution	1000 ppm Pd	1000 ppm Pd	1000 ppm Pd	1000 ppm Pd
K_2CO_3	0.75 mmol	0.75 mmol	0.75 mmol	0.75 mmol
methyl formate	0.5 mmol	0.5 mmol	0.5 mmol	0.5 mmol
2 wt % TPGS-750-M / H_2O	0.5 mL	+ 0.2 mL	+ 0.2 mL	+ 0.25 mL
water used to rinse product	0.5 mL	0.5 mL	0.5 mL	0.75 mL
product mass isolated	113 mg	103 mg	106 mg	107 mg
organic solvents used	47.3 mg	47.3 mg	47.3 mg	47.3 mg
aqueous used	1000 mg	700 mg	700 mg	1000 mg
E Factor (organic)	0.4	0.5	0.5	0.5
E Factor (water)	8.8	6.8	6.6	9.3

To a 1-dram (~4 mL) vial with magnetic stir bar was added 5-phenyl-1-H-tetrazole (73.1 mg, 0.5 mmol, 1.0 equiv) and K_2CO_3 (103.7 mg, 0.75 mmol, 1.5 equiv) and the vial was capped with a 14/20 rubber septum. The vial was attached to an argon Schlenk line via a 22G / 0.7mm needle and evacuated/backfilled with argon 3x. Via syringe was added 0.5 mL of degassed 2 wt % TPGS-750-M / H_2O solution and the vial placed in an aluminum block reactor at 50 ^oC to maintain an internal temperature of 45 ^oC, and stirred vigorously. Via syringe was added cinnamyl methyl carbonate (105.7 mg, 0.55 mmol, 1.1 equiv) and methyl formate (30 uL, 0.5 mmol). Next, via microliter syringe was added catalyst stock solution 20 uL (see section 2.2 for preparation). The reaction was stirred overnight (17 h) before removing from the block reactor. Upon cooling the reaction, the product solidified as a fine powder. The vial was opened and liquid was removed via pipette and placed in a second 1-dram vial (~0.3 mL recovered). An additional 0.2 mL of 2 wt % TPGS-750-M / H_2O solution was added to the vial to bring the total volume to 0.5 mL. To the vial was added 5-phenyl-1-H-tetrazole (73.1 mg, 0.5 mmol, 1.0 equiv) and K_2CO_3 (103.7 mg, 0.75 mmol, 1.5 equiv) and the vial was capped with a 14/20 rubber septum. The vial was attached to an argon Schlenk line via a 22G / 0.7 mm needle and evacuated/backfilled with argon 3x, vigorously shaking the reaction mixture in between evacuation/backfill cycles. Next, via microliter syringe was added catalyst stock solution 20 uL (see section 2.2 for preparation). The vial was placed in an aluminum block reactor at 45 ^oC and stirred for 4 h, upon which time the reaction was deemed complete by TLC. The vial was removed from the block reactor and cooled to rt while stirring, the product solidified as a fine powder. The vial was opened and the liquid removed via pipette and placed in a new vial (0.3 mL). This recycle procedure was repeated for a total of 3 recycles. Upon the 3rd recycle, the solution had become very viscous and the K_2CO_3 was not fully soluble, suggesting that 3x recycles was the extent of practical reuse of the reaction medium.

To the vials containing product was added 0.5 mL of DI water and the vials placed in an aluminum block reactor at 60 ^oC and stirred for 1 h. Upon cooling, the liquid was removed via pipette, leaving the product in the vial, and the product dried under vacuum.

See Section 5 and 6 for characterization data and spectra

2.8 Surfactant solution preparation and storage considerations

2 wt % TPGS-750-M / H_2O solution was typically prepared on a 100 mL scale, but this procedure can be scaled as necessary (see Figure 2 below). TPGS-750-M wax was melted by placing the vial/container in a hot water bath at 70-80 ^oC until fully melted. A 250 mL 14/20 necked round bottom flask (with no precautions against air or moisture) was placed horizontally on a top loading balance, and tared. Using a 1 mL syringe without needle, melted TPGS-750-M (2.0 g) was added to the flask, such that it forms a pool on the side of the flask (Figure 2A). The flask was removed from the balance and placed on ice until the TPGS-750-M fully solidified (Figure 2B). The flask was placed on a top loading balance and HPLC grade water was added such that the total mass of TPGS-750-M and water was 100 g, taking no special precautions against oxygen. A stir bar was added to the flask, and capped with a 14/20 septum. The flask was suspended above a magnetic stir plate at a 60^o angle, such that the TPGS-750-M remained above the water line. A long needle attached to an argon Schlenk manifold was placed through the septum, to the bottom of the flask and a vent needle inserted through the septum. The flask was stirred while argon was sparged through the water for ~2 h (Figure 2C), or in the event that the solution began to foam significantly, the sparging was stopped before 2 h. The flask was then rotated such that the TPGS-750-M was below the water line (Figure 2D), the vent needle removed, and stirred until fully dissolved (~4-14 h). Vacuum was applied to the flask and backfilled with argon 3x. This solution was stored attached to an argon manifold. Typically, surfactant solutions were stored for no more that 3-4 months and discarded if discolored (e.g., if yellow or milky in appearance).

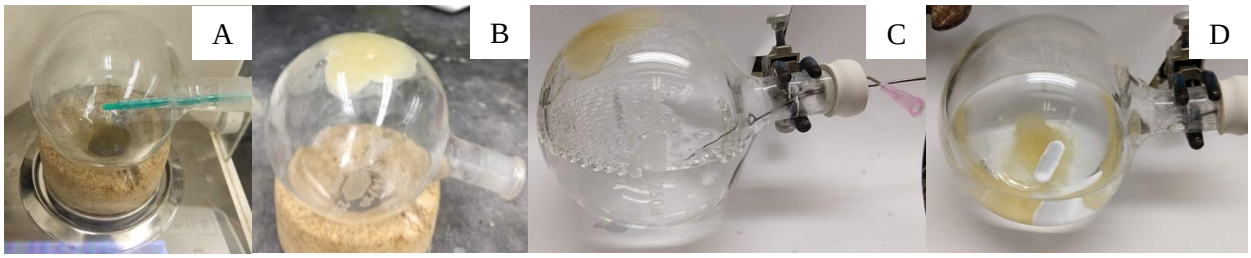


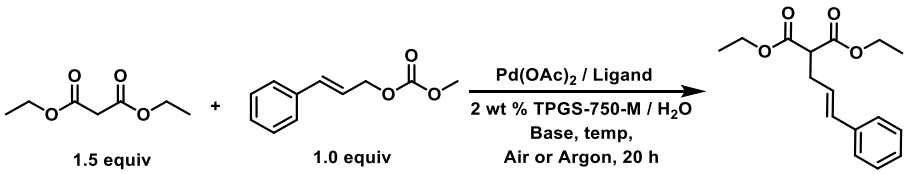
Figure 2: Preparation of a 2 wt % TPGS-750-M / H_2O. (A) adding melted TPGS-750-M to flask, (B) TPGS-750-M solidified after cooling, (C) sparging the water with argon while keeping TPGS-750-M wax above water line, (D) flask rotated after sparging, ready to be stirred to dissolve.

Note: TPGS-750-M solutions tend to foam vigorously if gas is introduced to the prepared solution (e.g., through sparging or gas-evolving reactions). Because of this, it is difficult to sparge prepared solutions. If the solution has been exposed to air, or is suspected to contain significant amounts of oxygen, vacuum can be applied to the flask and backfilled with argon, repeating several cycles, removing the flask from the manifold and shaking vigorously between vacuum/backfill cycles. While this is not as effective as degassing methods such as freeze-pump-thaw or prolonged sparging, this has been found to be a sufficient amount of degassing to enable even very sensitive “ppm” Pd catalyzed reactions.

3. Optimization and substrate scope development studies

3.1 Screening and optimization of reaction conditions

Table 1: Initial screening studies for the reaction of diethyl malonate with cinnamyl-OCO_2Me at ppm Pd loadings

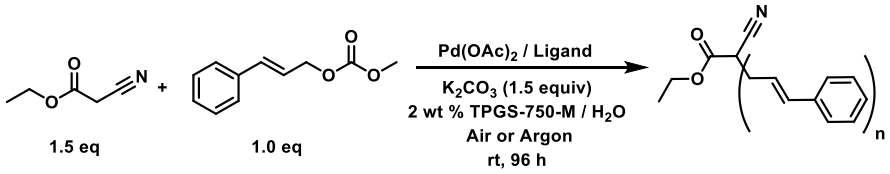


entry	Pd (mol %)	Ligand	Temp	Air/Argon	Catalyst Stock solution solvent	Base	Base equiv	Result[a]
1	0.2	SPhos	rt	Air	THF[b]	Et_3N	1.5	Trace conversion
2	0.2	SPhos	rt	Air	THF[b]	K_2CO_3	1.5	Trace conversion
3	0.2	PPh_3	rt	Air	THF[b]	Et_3N	1.5	Trace conversion
4	0.2	PPh_3	rt	Air	THF[b]	K_2CO_3	1.5	Trace conversion
5	0.1	SPhos	rt	Air	THF[b]	Et_3N	1.5	No conversion
6	0.1	SPhos	rt	Air	THF[b]	K_2CO_3	1.5	No conversion
7	0.1	PPh_3	rt	Air	THF[b]	Et_3N	1.5	No conversion
8	0.1	PPh_3	rt	Air	THF[b]	K_2CO_3	1.5	No conversion
9	0.2	PPh_3	rt	Argon	THF[b]	Et_3N	1.5	Trace conversion[f]
10	0.2	PPh_3	rt	Argon	THF[b]	K_2CO_3	1.5	~50% conversion
11	0.1	PPh_3	rt	Argon	THF[b]	Et_3N	1.5	>50% conversion
12	0.1	PPh_3	rt	Argon	THF[b]	K_2CO_3	1.5	~50% conversion
13	0.05	PPh_3	rt	Argon	THF[b]	Et_3N	1.5	No conversion
14	0.025	PPh_3	rt	Argon	THF[b]	Et_3N	1.5	No conversion
15	0.0125	PPh_3	rt	Argon	THF[b]	Et_3N	1.5	No conversion
16	0.05	SPhos	rt	Argon	THF[b]	Et_3N	1.5	Trace conversion
17	0.025	SPhos	rt	Argon	THF[b]	Et_3N	1.5	Trace conversion
18	0.0125	SPhos	rt	Argon	THF[b]	Et_3N	1.5	No conversion
19	0.05	PPh_3	45°C	Argon	THF[b]	Et_3N	1.5	Trace conversion
20	0.025	PPh_3	45°C	Argon	THF[b]	Et_3N	1.5	No conversion
21	0.0125	PPh_3	45°C	Argon	THF[b]	Et_3N	1.5	No conversion
22	0.05	SPhos	45°C	Argon	THF[b]	Et_3N	1.5	Trace conversion
23	0.025	SPhos	45°C	Argon	THF[b]	Et_3N	1.5	Trace conversion
24	0.0125	SPhos	45°C	Argon	THF[b]	Et_3N	1.5	No conversion
25	0.1	SPhos	rt	Air	Toluene	Et_3N	1.5	Trace conversion
26	0.1	SPhos	rt	Argon	Toluene	Et_3N	1.5	>50% conversion
27	0.1	SPhos	rt	Air	DCM	Et_3N	1.5	Trace conversion
28	0.1	SPhos	rt	Argon	DCM	Et_3N	1.5	~50% conversion
29	0.1	SPhos	rt	Air	THF	Et_3N	1.5	Trace conversion
30	0.1	SPhos	rt	Argon	THF	Et_3N	1.5	~50% conversion
31	0.1	SPhos	rt	Air	Toluene[c]	Et_3N	1.5	Trace conversion
32	0.1	SPhos	rt	Argon	Toluene[c]	Et_3N	1.5	>50% conversion
33	0.1	SPhos	rt	Air	DCM[c]	Et_3N	1.5	Trace conversion
34	0.1	SPhos	rt	Argon	DCM[c]	Et_3N	1.5	~50% conversion
35	0.1	SPhos	rt	Air	THF[c]	Et_3N	1.5	Trace conversion
36	0.1	SPhos	rt	Argon	THF[c]	Et_3N	1.5	~50% conversion
37	**0.1**	**PPh_3**	**rt**	**Argon**	**Toluene[d]**	**Et_3N**	**1.5**	**Full conversion**
38	**0.1**	**PPh_3**	**rt**	**Argon**	**Toluene[d]**	**Et_3N**	**3.0**	**Full conversion**
39	**0.1**	**PPh_3**	**rt**	**Argon**	**Toluene[d]**	**K_2CO_3**	**1.5**	**Full conversion**
40	**0.1**	**PPh_3**	**rt**	**Argon**	**Toluene[d]**	**K_2CO_3**	**3.0**	**Full conversion**
41	0.1	DPEPhos[e]	rt	Argon	**Toluene[d]**	Et_3N	1.5	<50% conversion
42	0.1	DPEPhos[e]	rt	Argon	Toluene[d]	Et_3N	3.0	<50% conversion

43	0.1	DPEPhos[e]	rt	Argon	Toluene[d]	K_2CO_3	1.5	<50% conversion
44	0.1	DPEPhos[e]	rt	Argon	Toluene[d]	K_2CO_3	3.0	<50% conversion
45	0.1	SPhos	rt	Argon	Toluene[d]	Et_3N	1.5	~50% conversion
46	0.1	SPhos	rt	Argon	Toluene[d]	Et_3N	3.0	~50% conversion
47	0.1	SPhos	rt	Argon	Toluene[d]	K_2CO_3	1.5	~50% conversion
48	0.1	SPhos	rt	Argon	Toluene[d]	K_2CO_3	3.0	~50% conversion

[a]Conversion estimated by TLC visualized using UV light.
[b]Very dilute catalyst stock solution, which required addition of 10% of total reaction volume. This later was found to be detrimental to the reaction conversion.
[c]Catalyst stock solution solvent removed via vacuum before adding surfactant solution.
[d]Et_3N added to catalyst stock solution as an activator. (all subsequent catalyst stock solutions using ligand/$Pd(OAc)_2$ were prepared this way).
[e]$Pd(OAc)_2$ is not an optimal Pd source for DPEphos, these trials mistakenly suggest that DPEphos is not an appropriate ligand for this reaction.
[f]This trial was suspected of being exposed to air.

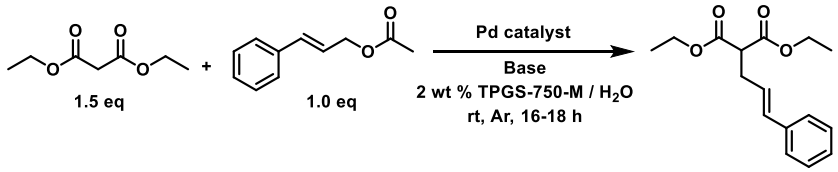
Table 2: Applying optimized conditions to a different nucleophile



Entry	Pd (mol %)	Ligand	Air/Argon	Catalyst stock solution solvent	Base	Base equiv	Result[a]
1	0.1	PPh_3	Argon	Toluene	K_2CO_3	1.5	Trace conversion
2	1.0	PPh_3	Argon	Toluene	K_2CO_3	1.5	~50% conversion
3	0.1	SPhos	Argon	Toluene	K_2CO_3	1.5	No conversion
4	**1.0**	**SPhos**	**Argon**	Toluene	**K_2CO_3**	**1.5**	**>50% conversion**
5	1.0	PPh_3	Air	Toluene	K_2CO_3	1.5	Trace conversion
6	1.0	Sphos	Air	Toluene	K_2CO_3	1.5	Trace conversion

[a]Conversion estimated by TLC visualized using UV light.

Table 3: Initial screening studies for the reaction of diethyl malonate with cinnamyl-OAc

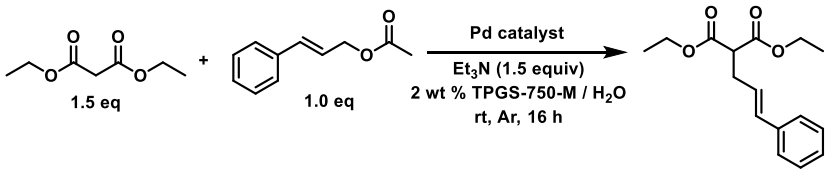


entry	Pd (%)	Pd source/Ligand	Catalyst stock solution Solvent	Added toluene as co-solvent	Base	Base equiv	Temp	Rxn conc. (M)	Result[a]
1	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	K_2CO_3	1.5	rt	0.5	~50% conversion
2	0.2	$Pd(OAc)_2/PPh_3$	Toluene	none	K_2CO_3	1.5	rt	0.5	~50% conversion
3	0.5	$Pd(OAc)_2/PPh_3$	Toluene	none	K_2CO_3	1.5	rt	0.5	~50% conversion
4	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	K_2CO_3	1.5	rt	0.25	~50% conversion
5	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	K_2CO_3	1.5	rt	0.5	~50% conversion
6	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	K_2CO_3	1.5	rt	1.0	~50% conversion
7	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	Et_3N	1.5	rt	0.25	~50% conversion
8	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	Et_3N	1.5	rt	0.5	~50% conversion
9	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	Et_3N	1.5	rt	1.0	~50% conversion
10	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	K_2CO_3	1.5	rt	1.0	<50% conversion
11	0.1	$Pd(OAc)_2/PPh_3$	Toluene	10 vol %	K_2CO_3	1.5	rt	1.0	<50% conversion
12	0.1	$Pd(OAc)_2/PPh_3$	Toluene	20 vol %	K_2CO_3	1.5	rt	1.0	<50% conversion
13	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	Et_3N	1.5	rt	1.0	~50% conversion
14	0.1	$Pd(OAc)_2/PPh_3$	Toluene	10 vol %	Et_3N	1.5	rt	1.0	~50% conversion
15	0.1	$Pd(OAc)_2/PPh_3$	Toluene	20 vol %	Et_3N	1.5	rt	1.0	<50% conversion
16[c]	0.1	$Pd(PPh_3)Cl_2$	THF	none	Et_3N	1.5	rt	1.0	~50% conversion
17[c]	0.1	$Pd(PPh_3)Cl_2$	THF	none	Et_3N	3.0	rt	1.0	<50% conversion
18[c]	0.1	$Pd(OAc)_2/PPh_3$	DCM	none	Et_3N	1.5	rt	1.0	<50% conversion
19[c]	0.1	$Pd(OAc)_2/PPh_3$	DCM	none	$Et_3N + K_2CO_3$	1.5 + 3.0	rt	1.0	<50% conversion
20[c]	0.1	$Pd(PPh_3)Cl_2$	THF	none	Et_3N	1.5	rt	1.0	~50% conversion
21[c]	0.1	$Pd(PPh_3)Cl_2$	THF	none	$Et_3N + K_2CO_3$	1.5 + 3.0	rt	1.0	<50% conversion
22[c]	0.1	$Pd(OAc)_2/PPh_3$	DCM	none	Et_3N	1.5	rt	1.0	<50% conversion
23[c]	0.1	$Pd(OAc)_2/PPh_3$	DCM	none	$Et_3N + K_2CO_3$	1.5 + 3.0	rt	1.0	<50% conversion
24[c]	0.5	$Pd(OAc)_2/PPh_3$	DCM[b]	none	Et_3N	1.5	rt	1.0	<50% conversion
25[c]	0.5	$Pd(PPh_3)Cl_2$	THF[b]	none	Et_3N	1.5	rt	1.0	~50% conversion
26	0.1	$Pd(OAc)_2$/Sphos	Toluene	none	Et_3N	1.5	rt	1.0	~50% conversion
27	**0.25**	**$Pd(OAc)_2$/Sphos**	**Toluene**	**none**	**Et_3N**	**1.5**	**rt**	**1.0**	**Full conversion**
28	0.5	$Pd(OAc)_2$/Sphos	Toluene	none	Et_3N	1.5	rt	1.0	Full conversion
29	1.0	$Pd(OAc)_2$/Sphos	Toluene	none	Et_3N	1.5	rt	1.0	Full conversion
30	0.5	$Pd(PPh_3)_4$	Toluene	none	Et_3N	1.5	rt	1.0	~50% conversion
31	1.0	$Pd(PPh_3)_4$	Toluene	none	Et_3N	1.5	rt	1.0	~50% conversion
32	0.1	$Pd(OAc)_2$/Sphos	Toluene	none	Et_3N	1.5	45°C	1.0	~50% conversion
33	**0.2**	**$Pd(OAc)_2$/Sphos**	**Toluene**	none	**Et_3N**	**1.5**	**45°C**	**1.0**	**Full conversion**
34	0.1	$Pd(OAc)_2/PPh_3$	Toluene	none	Et_3N	1.5	45°C	1.0	~50% conversion

35	0.2	$Pd(OAc)_2/PPh_3$	Toluene	none	Et_3N	1.5	45°C	1.0	~50% conversion
36	0.5	$Pd(OAc)_2/PPh_3$	Toluene	none	Et_3N	1.5	45°C	1.0	~50% conversion

[a]Conversion estimated by TLC visualized using UV light.
[b]Catalyst stock solution solvent removed via vacuum before adding surfactant solution.
[c]Trials have strange combinations of base due to a mistake in setting up trials.

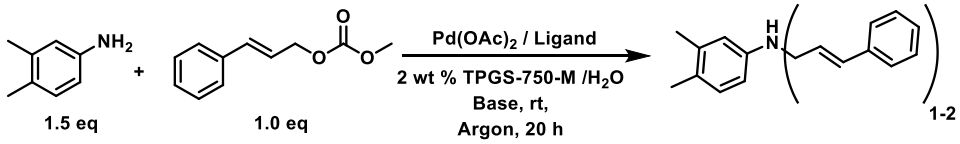
Table 4: Testing for possible oxygen penetration into reaction vessel during reaction



Trial	Pd (mol %)	Pd source/Ligand	Protection against oxygen	Result[a]
1[b]	0.1	$Pd(OAc)_2$/Sphos	Reaction in vial capped with phenolic cap	~50% conversion
2[b]	0.1	$Pd(OAc)_2$/Sphos	Reaction in vial capped with phenolic cap	~50% conversion
3[b]	0.1	$Pd(OAc)_2$/Sphos	Reaction in vial capped with Teflon lined cap	~50% conversion
4[b]	0.1	$Pd(OAc)_2$/Sphos	Reaction in vial capped with Teflon lined cap	~50% conversion
5[b]	0.1	$Pd(OAc)_2$/Sphos	Reaction in vial capped with rubber septum	~50% conversion
6[b]	0.1	$Pd(OAc)_2$/Sphos	Reaction in vial capped with rubber septum	~50% conversion
7[c]	0.1	$Pd(OAc)_2$/Sphos	Reaction in vial capped with septum, and vial placed in jar purged with argon	<50% conversion
8[c,d]	0.1	$Pd(OAc)_2$/Sphos	Reaction in vial capped with septum, and vial placed in jar purged with argon	<50% conversion

[a]Conversion estimated by TLC visualized using UV light.
[b]It was discovered that trials run in an aluminum block reactor on a hotplate were heated to 26-28°C due to the heat generated from the motor, possibly causing better conversion due to the temperature increase.
[c]These trials were run in a jar on top of a hot plate. The lab temperature at the time was 21-23°C, possibly causing lower conversion that the reactions run in a block reactor.
[d]Trial stopped stirring sometime overnight.

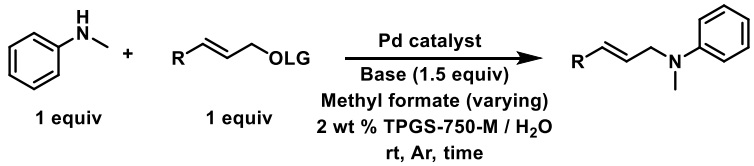
Table 5: Initial screening studies for an allylic amination



Trial	Pd (mol %)	Ligand	Catalyst stock soln. solvent	Base	Base eq.	Result[a]
1	0.1	PPh_3	Toluene	Et_3N	1.5	Full conversion
2	0.1	PPh_3	Toluene	Et_3N	3.0	Full conversion
3	**0.1**	**PPh_3**	**Toluene**	**K_2CO_3**	**1.5**	**Full conversion**
4	0.1	PPh_3	Toluene	K_2CO_3	3.0	Full conversion
5	0.1	DPEPhos[b]	Toluene	Et_3N	1.5	Full conversion
6	0.1	DPEPhos[b]	Toluene	Et_3N	3.0	>50% conversion
7	0.1	DPEPhos[b]	Toluene	K_2CO_3	1.5	>50% conversion
8	0.1	DPEPhos[b]	Toluene	K_2CO_3	3.0	>50% conversion
9	0.1	SPhos	Toluene	Et_3N	1.5	Full conversion
10	0.1	SPhos	Toluene	Et_3N	3.0	Full conversion
11	0.1	SPhos	Toluene	K_2CO_3	1.5	>50% conversion
12	0.1	SPhos	Toluene	K_2CO_3	3.0	Full conversion

[a]Conversion estimated by TLC visualized using UV light.
[b]$Pd(OAc)_2$ is not an optimal Pd source for DPEphos, these trials mistakenly suggest that DPEphos is not an appropriate ligand for this reaction.

Table 6: Screening Pd loading and conditions for allylic amination of *N*-methylaniline with various allylic substrates

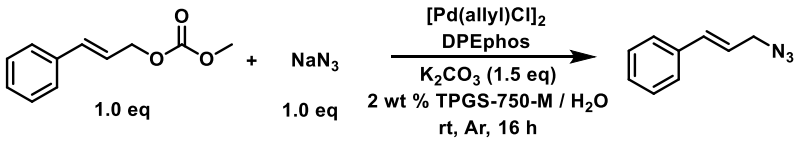


entry	Electrophile	Pd loading (mol %)	Catalyst	Methyl formate (equiv)	Base	Stock soln. solvent	Rxn time (h)	Result[a]
1	Cinnamyl-OAc	0.025	$Pd(OAc)_2/PPh_3$	none	Et_3N	Toluene	20	Trace conversion
2	Cinnamyl-OAc	0.05	$Pd(OAc)_2/PPh_3$	none	Et_3N	Toluene	20	Trace conversion
3	Cinnamyl-OAc	0.1	$Pd(OAc)_2/PPh_3$	none	Et_3N	Toluene	20	Trace conversion
4	Cinnamyl-OAc	0.2	$Pd(OAc)_2/PPh_3$	none	Et_3N	Toluene	20	<50% conversion
5	Cinnamyl-OCO_2Me	0.025	$Pd(OAc)_2/PPh_3$	none	Et_3N	Toluene	20	Trace conversion
6	Cinnamyl-OCO_2Me	0.05	$Pd(OAc)_2/PPh_3$	none	Et_3N	Toluene	20	Trace conversion
7	Cinnamyl-OCO_2Me	0.1	$Pd(OAc)_2/PPh_3$	none	Et_3N	Toluene	20	<50% conversion
8	Cinnamyl-OCO_2Me	0.2	$Pd(OAc)_2/PPh_3$	none	Et_3N	Toluene	20	~50% conversion
9	Cinnamyl-OAc	0.4	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	1.5	Full conversion
10	Cinnamyl-OAc	0.2	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	1.5	Full conversion
11	Cinnamyl-OAc	0.1	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	1.5	Full conversion
12	Cinnamyl-OAc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	1.5	Full conversion
13	Allyl alcohol	0.1	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	18	~50% conversion
14	Allyl alcohol	0.05	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	18	<50% conversion
15	Allyl acetate	0.1	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	18	Full conversion
16	Allyl acetate	0.05	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	18	>50% conversion
17	Allyl-OCO_2Me	0.1	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	18	Full conversion
18	Allyl-OCO_2Me	0.05	$[Pd(allyl)Cl]_2$/DPEphos	4	K_2CO_3	Toluene	18	Full conversion
19	Cinnnamyl-OAc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	3	K_2CO_3	Toluene	48	Full conversion

20	Cinnnamyl-OAc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	2	K_2CO_3	Toluene	48	Full conversion
21	Cinnnamyl-OAc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	1	K_2CO_3	Toluene	48	Full conversion
22	Cinnnamyl-OAc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	Full conversion
23	Cinnamyl-OCO_2Me	0.05	$[Pd(allyl)Cl]_2$/DPEphos	3	K_2CO_3	Toluene	48	Full conversion
24	Cinnamyl-OCO_2Me	0.05	$[Pd(allyl)Cl]_2$/DPEphos	2	K_2CO_3	Toluene	48	Full conversion
25	Cinnamyl-OCO_2Me	0.05	$[Pd(allyl)Cl]_2$/DPEphos	1	K_2CO_3	Toluene	48	Full conversion
26	Cinnamyl-OCO_2Me	0.05	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	Full conversion
27	Allyl-OBoc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	3	K_2CO_3	Toluene	48	Full conversion
28	Allyl-OBoc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	2	K_2CO_3	Toluene	48	Full conversion
29	Allyl-OBoc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	1	K_2CO_3	Toluene	48	Full conversion
30	Allyl-OBoc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	Full conversion
31	Cinnnamyl-OAc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	Full conversion
32	Cinnnamyl-OAc	0.025	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	~50% conversion
33	Cinnamyl-OAc	0.01	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	~50% conversion
34	Cinnamyl-OCO_2Me	0.05	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	Full conversion
35	**Cinnamyl-OCO_2Me**	**0.025**	**$[Pd(allyl)Cl]_2$/DPEphos**	**0.5**	**K_2CO_3**	**Toluene**	**48**	**Full conversion**
36	Cinnamyl-OCO_2Me	0.01	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	>50% conversion
37	Cinnamyl-OBoc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	Full conversion
38	Cinnnamyl-OBoc	0.025	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	~50% conversion
39	Cinnnamyl-OBoc	0.01	$[Pd(allyl)Cl]_2$/DPEphos	0.5	K_2CO_3	Toluene	48	<50% conversion
40	Cinnamyl-OAc	0.05	$[Pd(allyl)Cl]_2$/DPEphos	0	K_2CO_3	Toluene	48	Full conversion

[a]Conversion estimated by TLC visualized using UV light.

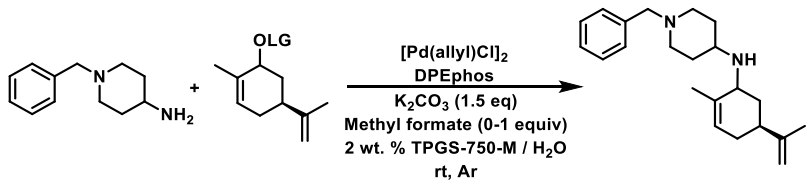
Table 7: Testing optimized amination conditions



Trial	Pd loading (mol %)	Result[a]
1	0.4	Full conversion
2	**0.2**	**Full conversion**
3	0.1	>50% conversion
4	0.05	~50% conversion

[a]Conversion estimated by TLC visualized using UV light.

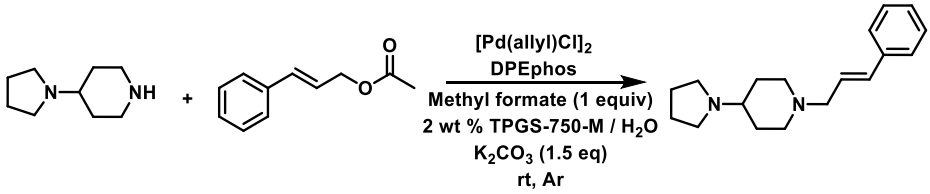
Table 8: Testing optimized amination conditions on a difficult electrophile



Entry	LG	Pd loading (mol %)	Methyl formate (equiv)	Result[a]
1	**Acetate**	**0.2 mol %**	**1**	**>50% conversion**
2	Acetate	0.2 mol %	0	<50% conversion
3	Alcohol	0.2 mol %	1	Trace conversion
4	Alcohol	0.2 mol %	0	No conversion
5	Acetate	0.1 mol %	1	Trace conversion
6	Acetate	0.1 mol %	0	No conversion

[a]Conversion estimated by TLC visualized using UV light.

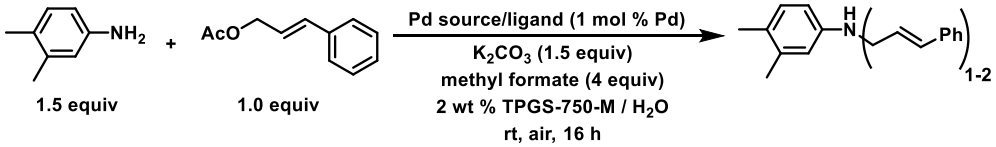
Table 9: Testing optimized allylic amination conditions



Entry	Pd loading (mol %)	Result[a]
1	0.4	~50% conversion
2	0.2	<50% conversion
3	0.1	Trace conversion
4	0.05	Trace conversion

[a]Conversion estimated by TLC visualized using UV light.

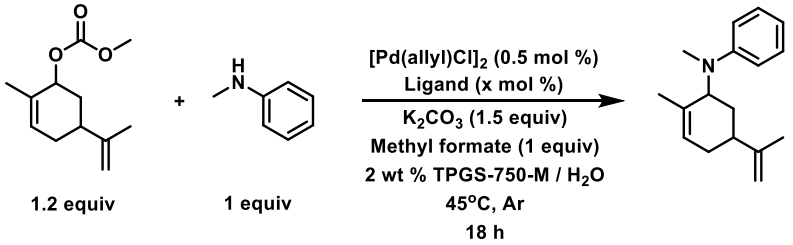
Table 10: Screening additional palladium sources and ligands



Entry	Pd catalyst	Conversion (%)[a]
1	**[Pd(allyl)Cl]$_2$/DPEphos**	**94**
2	[Pd(cinnamyl)Cl]$_2$/DPEphos	84
3	Pd(MeCN)$_2$Cl$_2$/DPEphos	91
4	Pd(OAc)$_2$/DPEphos	80
5	PdCl$_2$/DPEphos	78
6	Pd$_2$(dba)$_3$/DPEphos	69
7	Pd(DPEphos)Cl$_2$	86
8	Pd(DPPF)Cl$_2$	71
9	Pd(Xantphos)Cl$_2$	80
10	Pd(PPh$_3$)$_2$Cl$_2$	86

[a]Conversion determined by GC-MS.

Table 11: Screening additional ligands for allylic amination of a difficult electrophile

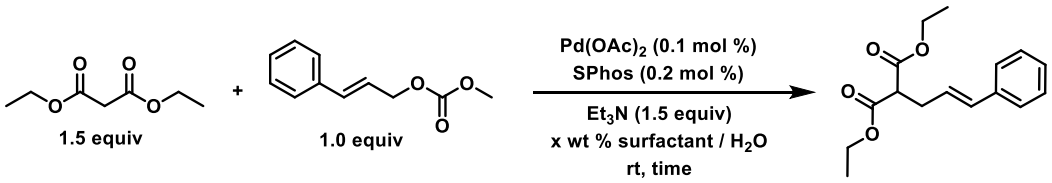


Entry	Ligand	Result[a]
1	**DPEphos (1 mol %)**	**Full conversion (75% isolated)**
2	DPPF (1 mol %)	~50% conversion
3	TDAPP (4 mol %)	<50% conversion
4	$P(OPPh)_3$ (4 mol %)	No conversion
5	**Xantphos (1 mol %)**	**Full conversion (73% isolated)**
6	DTBPF (1 mol %)	~50% conversion
7	PPh_3 (4 mol %)	>50% conversion

TDAPP = tris(4-(dimethylamino)phenyl) phosphite

[a]Conversion estimated by TLC visualized using UV light, isolated yield is of chromatographically purified product

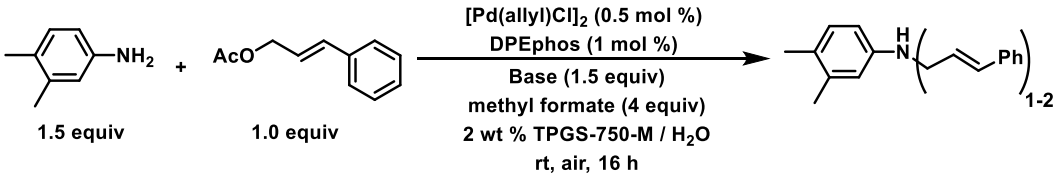
Table 12: Surfactant screening



Entry	Surfactant	Surfactant wt %	Conversion[a]
1	TPGS-750-M	1	60
2	**TPGS-750-M**	**2**	**75**
3	TPGS-750-M	3	55
4	SPGS-550-M	3	64
5	Triton X-100	2	50
6	Brij-30	2	40

[a]Conversion determined by GC-MS.

Table 13: Base screening

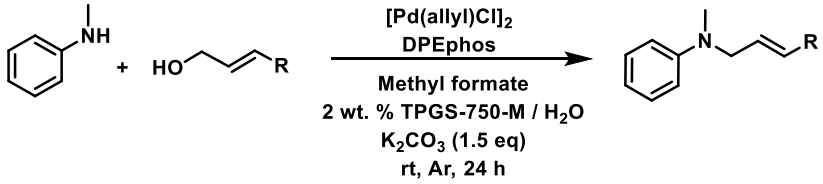


Entry	Base	Conversion (%)[a]
1	Et_3N	71
2	**K_2CO_3**	**94**
3	Na_2CO_3	89
4	Cs_2CO_3	90
5	K_3PO_4	87

6	NaOAc	73
7	KOAc	75
8	KOH	70
9	NaOH	76
10	LiOH	68

[a]Conversion determined by GC-MS.

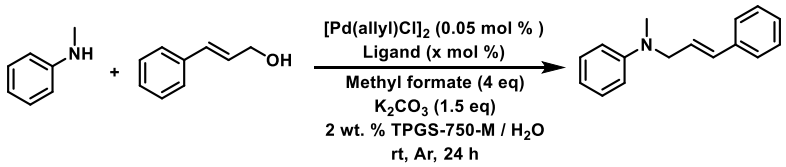
Table 14: Initial screening of conditions for amination of allylic alcohols at ppm Pd loadings



entry	Electrophile	Pd loading (%)	Temp	Methyl formate (equiv)	Rxn time (h)	Result[a]
1	Allyl alcohol	0.1	rt	4	24	~50% conversion
2	Octene-3-ol	0.1	rt	4	24	No conversion
3	Allyl alcohol	0.2	rt	4	24	~50% conversion
4	Octene-3-ol	0.2	rt	4	24	Trace conversion
5	Allyl alcohol	0.1	45°C	4	24	~50% conversion
6	Octene-3-ol	0.1	45°C	4	24	Trace conversion
7	**Allyl alcohol**	**0.2**	**45°C**	**4**	**24**	**>50% conversion**
8	**Octene-3-ol**	**0.2**	**45°C**	**4**	**24**	**~50% conversion**
9	Allyl alcohol	0.1	rt	0	24	Trace conversion
10	Octene-3-ol	0.1	rt	0	24	No conversion

[a]Conversion estimated by TLC visualized using UV light.

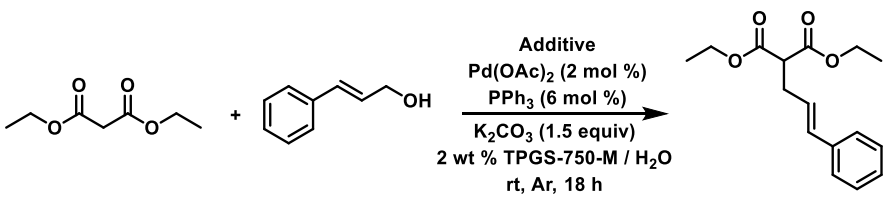
Table 15: Screening phosphite ligands against DPEphos for reaction of *N*-methylaniline with cinnamyl alcohol



entry	Ligand	Ligand mol %	Result[a]
1	**DPEPhos**	**0.1**	**~50% conversion**
2	**P(OPPh)$_3$**	**0.4**	**~50% conversion**
3	P(O-isooctyl)$_3$	0.4	Trace conversion
4	P(O-2,4-ditertbutylphenyl)$_3$	0.4	No conversion

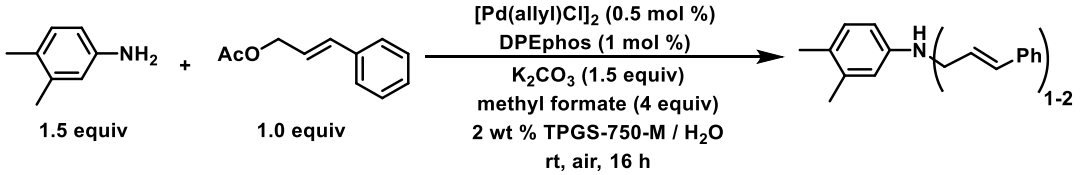
[a]Conversion estimated by TLC visualized using UV light.

Table 16: Screening additives for use with carbon nucleophiles + an allylic alcohol



entry	Additive	Result
1	None	No conversion
2	Methyl formate (3 equiv)	No conversion
3	Methyl OBBD (0.3 equiv)	No conversion

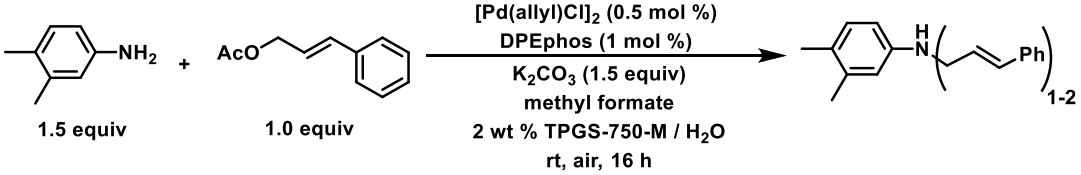
Table 17: Screening added THF as co-solvent



Entry	Added co-solvent	Conversion (%)[a]
1	**None**	**94**
2	10% THF by vol.	87
3	20% THF by vol.	82

[a]Conversion determined by GC-MS.

Table 18: Screening equivalents of methyl formate

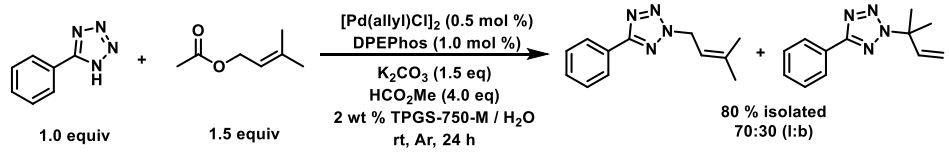


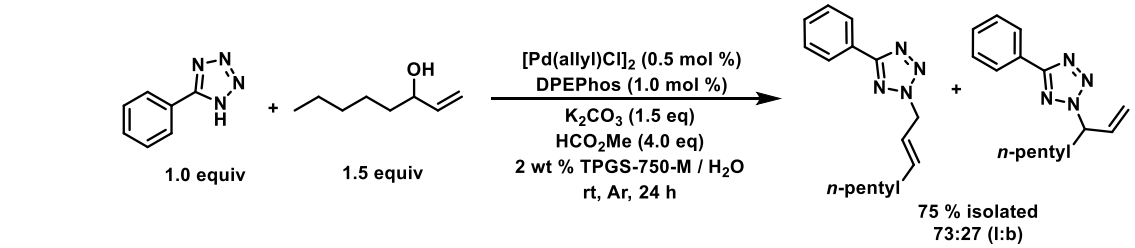
Entry	Methyl formate (equiv)	Conversion (%)[a]
1	none	89
2	**2**	**94**
3	4	94

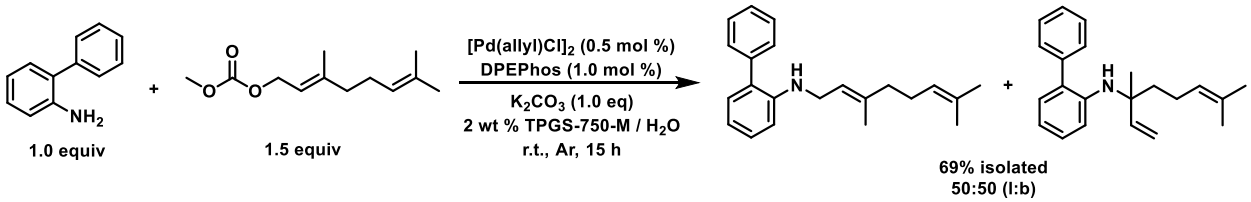
[a]Conversion determined by GC-MS.

3.2 Problematic substrates

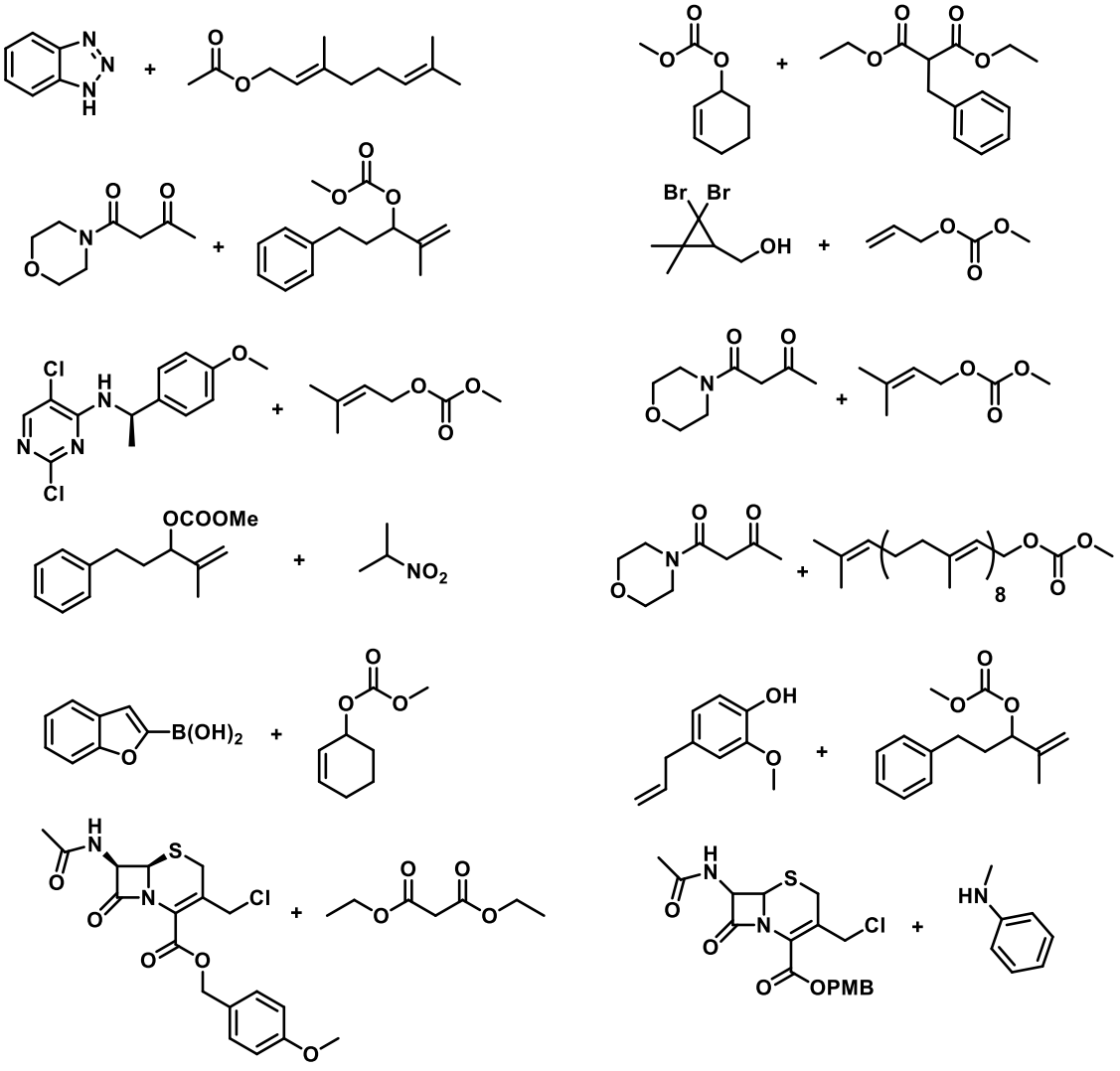
Selected substrates which gave mixtures of linear:branched products:



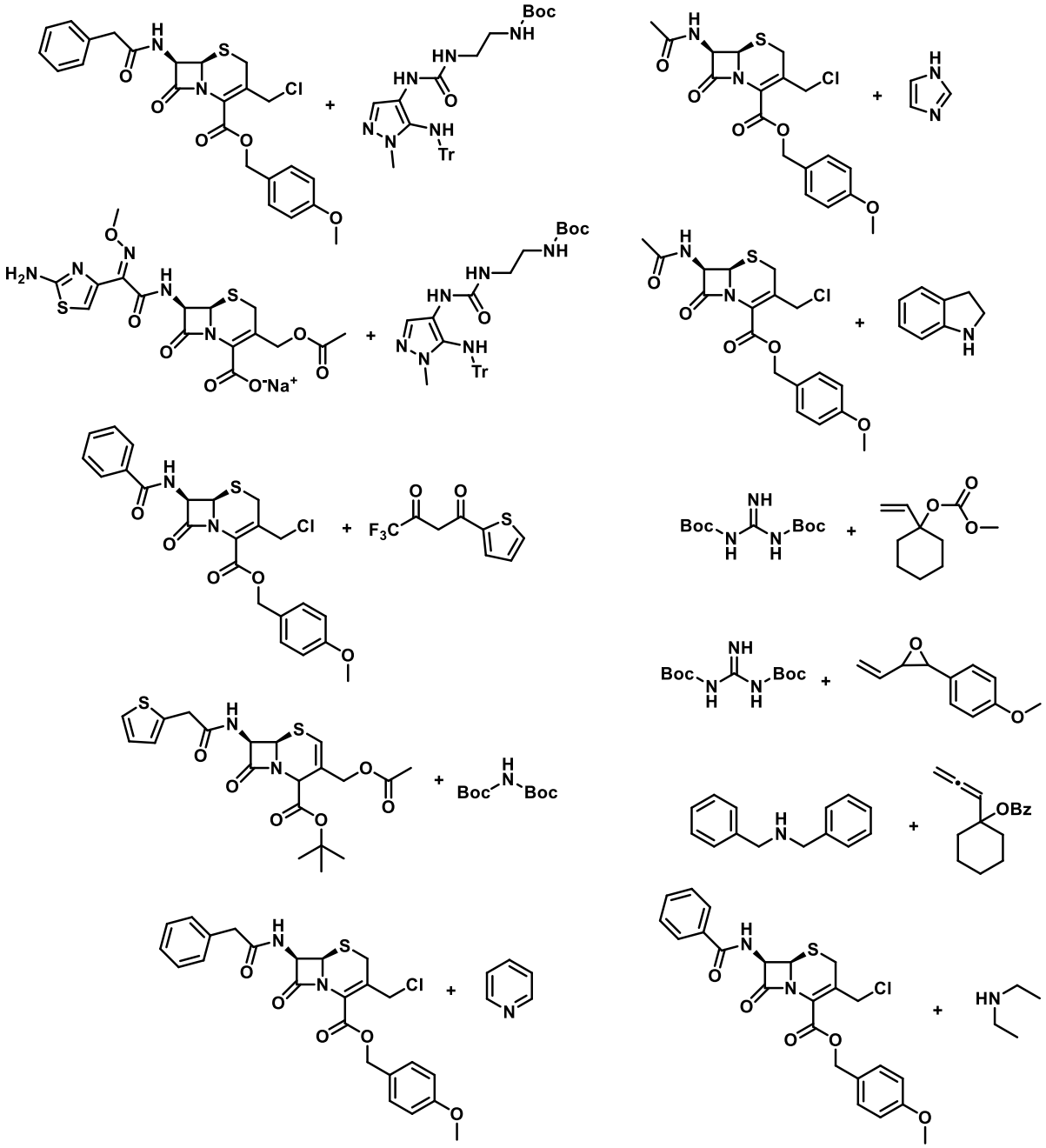

[Pd(allyl)Cl]2 (0.5 mol %)
DPEPhos (1.0 mol %)
K2CO3 (1.5 eq)
HCO2Me (4.0 eq)
2 wt % TPGS-750-M / H2O
rt, Ar, 24 h
1.0 equiv
1.5 equiv
n-pentyl
n-pentyl
75 % isolated
73:27 (l:b)


[Pd(allyl)Cl]2 (0.5 mol %)
DPEPhos (1.0 mol %)
K2CO3 (1.0 eq)
2 wt % TPGS-750-M / H2O
r.t., Ar, 15 h
1.0 equiv
1.5 equiv
69% isolated
50:50 (l:b)

Selected substrates which gave insufficient conversion at ppm Pd levels:

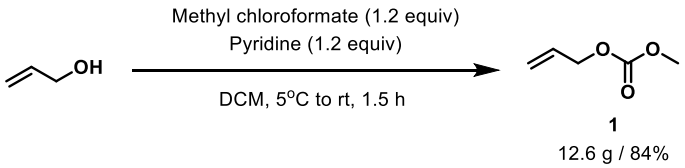


Selected substrates which gave decomposition and/or inseparable mixtures of products:



4. Synthesis of starting materials

Allyl methyl carbonate

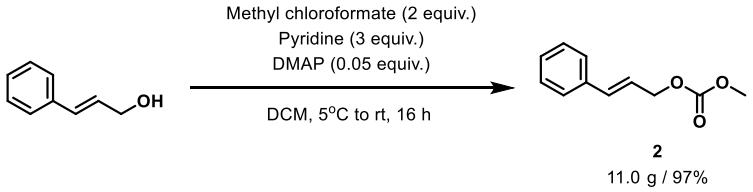


A 24/40 oven dried 500 mL round bottom flask with stir bar was capped with a septum and cooled under vacuum and backfilled with argon. To the flask was added 300 mL of dry DCM, allyl alcohol (10.0 g, 11.7 mL, 172 mmol, 1.0 equiv) and pyridine (16.3 g, 16.6 mL, 1.2 equiv). The flask was placed in an ice bath and stirred for 10 min before dropwise addition of methyl chloroformate (16.3 g, 13.3 mL, 172 mmol, 1.0 equiv.). The flask was stirred for 10 min before removing from the ice bath and allowed to warm to rt, ~1 h. An aliquot was removed and showed some allyl alcohol remaining. Additional methyl chloroformate (3.25 g, 2.7 mL, 34.4 mmol, 0.2 equiv) was added and the mixture was allowed to stir for an additional 30 min, at which time the reaction was deemed complete by NMR. The organic layer was washed with 1 M HCl (3 x 150 mL) then brine, then dried over anhydrous Na_2SO_4, and the bulk of the solvent removed via rotary evaporator. The crude product was purified by vacuum distillation (bp 83-87 °C at 97-100 torr) to give 12.6 g (84%) of allyl methyl carbonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 – 5.83 (m, 1H), 5.32 (ddq, *J* = 17.2, 2.9, 1.5 Hz, 1H), 5.23 (ddq, *J* = 10.4, 3.1, 1.3 Hz, 1H), 4.60 (d, *J* = 5.8 Hz, 2H), 3.76 (d, *J* = 2.1 Hz, 3H).

^{13}C NMR ($CDCl_3$,101 MHz): δ 155.7, 131.6, 118.9, 68.5, 54.8.

Spectra matched those previously reported: Mutlu, H.; Ruiz, J.; Solleder, S. C.; Meier, M. A. R. *Green Chem.* **2012**, *14*, 1728–1735.



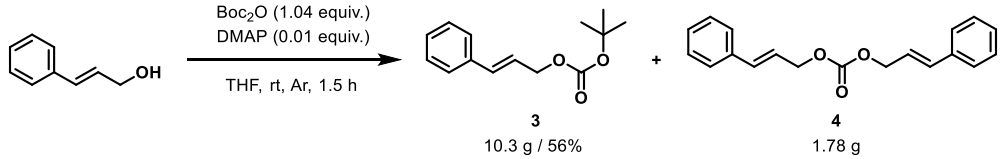
An oven dried 300 mL round bottom flask with stir bar was capped with a septum and cooled under vacuum and backfilled with argon. To the flask was added DCM (150 mL), freshly distilled cinnamyl alcohol (7.68 g, 57.2 mmol, 1.0 equiv), pyridine (13.6 g, 13.8 mL, 171 mmol, 3 equiv) and DMAP (350 mg, 2.6 mmol, 0.05 equiv). The flask was placed in an ice bath and stirred for 10 min before dropwise addition of methyl chloroformate (10.9 g, 115 mmol, 8.9 mL, 2 equiv) The flask was stirred for an additional 15 min before removing from the ice bath and allowed to warm to rt. The flask was stirred overnight (16 h) at rt, at which time the reaction was deemed complete by TLC (R_f 0.50 with 25:75 EtOAc:hexanes), staining with vanillin. The organic phase was washed with 2 M HCl (2 x 200 mL), then brine, and dried over anhydrous Na_2SO_4. The solvent was removed via rotary evaporator and

the crude product dissolved in EtOAc and filtered through silica and the solvent removed via rotary evaporator. The product was dried under vacuum to afford cinnamyl methyl carbonate (11.0 g, 97%) as a colorless oil which crystallized into white needles upon refrigeration.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.25 (m, 1H), 6.69 (dt, *J* = 15.8, 1.4 Hz, 1H), 6.30 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.80 (dd, *J* = 6.5, 1.4 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.8, 136.1, 134.9, 128.7, 128.3, 126.8, 122.5, 68.5, 54.9.

Spectra matched those previously reported: Su, Y.; Jiao, N. *Org. Lett.* **2009**, *11*, 2980–2983.



A 24/40 oven dried 300 mL round bottom flask with stir bar was capped with a septum and cooled under vacuum and backfilled with argon. Boc anhydride was melted in a water bath at ~60-70 °C and added via pipette to the reaction flask. The flask was capped with a septum and evacuated/backfilled with argon 1x. Via cannula was added dry THF (100 mL), and with stirring, via syringe was added freshly distilled, warm cinnamyl alcohol (10 g, 75 mmol, 1.0 equiv). The flask was opened and DMAP (91 mg, 0.75 mmol, 0.01 equiv.) was added, and the flask capped with septum, and the flask stirred at rt. Effervescence began soon after, at which time the reaction flask was placed in a room temperature water bath in case of exotherm. After stirring at rt for 1.5 h, the reaction was deemed complete by TLC (R_f 0.5 with 15:85 Et_2O:hexanes), staining with vanillin. The solvent was removed via rotary evaporator and the crude product dissolved in Et_2O and washed with 2 M HCl (2 x 50 mL), then brine, and dried over anhydrous Na_2SO_4 and the solvent removed via rotary evaporator. The crude product was distilled under vacuum (bp 130 °C at 1 torr) in collecting three fractions. Cinnamyl *t*-butyl carbonate was obtained as a viscous colorless oil (10.26 g, 56%), and dicinnamyl carbonate was obtained as a white solid from the distillation flask (1.78 g).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.24 (m, 1H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.32 (dtd, *J* = 15.9, 6.4, 0.9 Hz, 1H), 4.74 (dd, *J* = 6.4, 1.2 Hz, 2H), 1.53 (s, 9H).

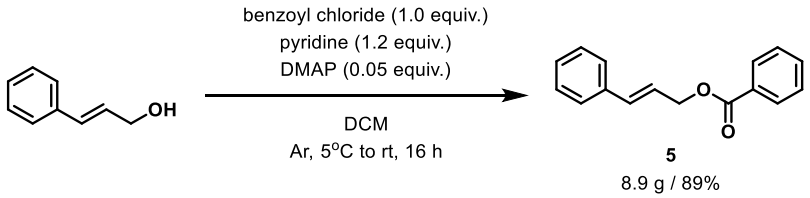
^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.5, 136.3, 134.5, 128.7, 128.2, 126.8, 123.0, 82.3, 67.6, 27.9.

di-cinnamyl carbonate:

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 – 7.40 (m, 4H), 7.39 – 7.33 (m, 4H), 7.33 – 7.27 (m, 2H), 6.74 (dt, *J* = 16.0, 1.4 Hz, 2H), 6.35 (dt, *J* = 15.9, 6.4 Hz, 2H), 4.85 (dd, *J* = 6.5, 1.4 Hz, 4H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.0, 136.1, 134.9, 128.7, 128.3, 126.8, 122.5, 68.5.

Spectra matched those previously reported: Trost, B. M.; Luan, X. *J. Am. Chem. Soc.* **2011**, *133*, 1706–1709.

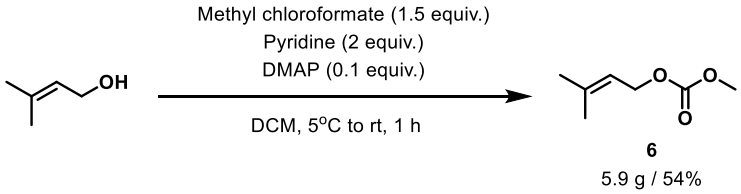


A 500 mL oven dried round bottom flask with stir bar was capped with a septum and cooled under vacuum and backfilled with argon. To the flask was added 170 mL of dry DCM, freshly distilled cinnamyl alcohol (5.63 g, 42.0 mmol, 1.0 equiv), pyridine (4.0 g, 50.4 mmol, 4.1 mL, 1.2 equiv.) and DMAP (256 mg, 2.1 mmol, 0.05 equiv). The flask was placed in an ice bath and stirred for 10 min before dropwise addition of benzoyl chloride (5.90 g, 42.0 mmol, 4.87 mL, 1.0 equiv). The flask was stirred for 10 min before removing from the ice bath and allowed to warm to rt. The flask was stirred overnight (16 h), upon which time the reaction was deemed complete by TLC (R_f = 0.70 with 20:80 Et_2O/hexanes). The reaction mixture was washed with 1 M HCl (2 x 100 mL), then brine, and dried over anhydrous Na_2SO_4 and the solvent removed via rotary evaporator. The product was dissolved in Et_2O and filtered through a plug of silica, eluting with 20:80 Et_2O/hexanes, the solvent removed via rotary evaporator and the product dried under vacuum to give cinnamyl benzoate as a viscous colorless oil (8.9 g / 89%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16 – 8.08 (m, 2H), 7.63 – 7.55 (m, 1H), 7.47 (dd, *J* = 16.4, 8.1 Hz, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 1H), 6.78 (d, *J* = 15.9 Hz, 1H), 6.44 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.02 (dd, *J* = 6.3, 1.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 166.4, 136.3, 134.3, 133.0, 130.3, 129.7, 128.7, 128.4, 128.1, 126.7, 123.3, 65.6.

Spectra matched those previously reported: Chun, S.; Chung, Y. K. *Org. Lett.* **2017**, *19*, 3787–3790.

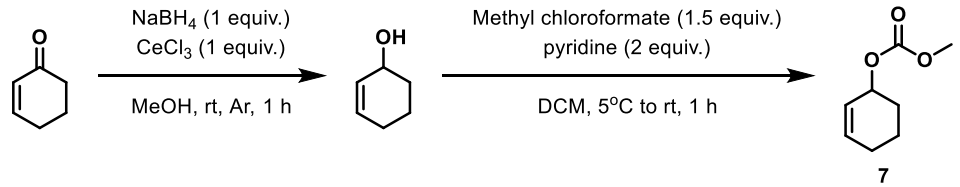


A 300 mL oven dried round bottom flask with stir bar was capped with a septum and cooled under vacuum and backfilled with argon. To the flask was added dry DCM (150 mL), then freshly distilled 3-methyl-2-buten-1-ol (6.46 g, 75 mmol, 7.6 mL, 1.0 equiv), pyridine (11.9 g, 150 mmol, 12.1 mL, 2 equiv.) and DMAP (900 mg, 7.5 mmol, 0.1 equiv). The flask was placed in an ice bath and stirred for 10 min before dropwise addition of methyl chloroformate (10.6 g, 112.5 mmol, 8.7 mL, 1.5 equiv). The flask was stirred for 10 min before removing from the ice bath and allowing to stir for 45 min while warming to rt. The reaction mixture was washed with 2 M HCl (3 x 100 mL), then brine, then dried over anhydrous $MgSO_4$, and the solvent removed via rotary evaporator. The crude product was purified by distillation (bp 110-120 °C at 100 torr) to give methyl (3-methylbut-2-en-1-yl) carbonate as a colorless oil (5.85 g / 54%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.23 (dddd, *J* = 7.3, 5.8, 2.9, 1.4 Hz, 1H), 4.47 (d, *J* = 7.3 Hz, 2H), 3.61 (s, 3H), 1.66 – 1.53 (m, 6H).

^{13}C NMR ($CDCl_3$,126 MHz): δ 155.6, 139.4, 118.1, 64.3, 64.3, 54.2, 54.2, 25.4, 25.4, 17.6, 17.6.

Spectra matched those previously reported: Schlatzer, T.; Kriegesmann, J.; Schröder, H.; Trobe, M.; Lembacher-Fadum, C.; Santner, S.; Kravchuk, A. V.; Becker, C. F. W.; Breinbauer, R. *J. Am. Chem. Soc.* **2019**, *141*, 14931–14937.



7

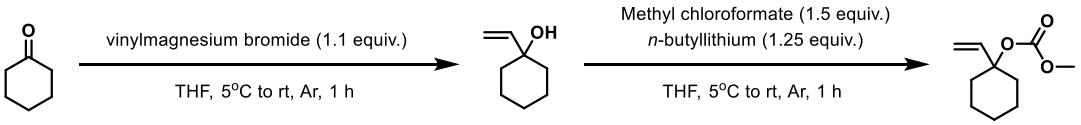
4.5 g / 58%

To a 100 mL round bottom flask with stir bar was added 25 mL MeOH (dried over anhydrous Na_2SO_4, then briefly dried over molecular sieves), cyclohexen-1-one (4.90 g, 50.9 mmol, 1.0 equiv) and cerium(III) chloride (12.55 g, 50.9 mmol, 1.0 equiv), and the mixture was stirred for 10 min. Next, $NaBH_4$ was added portion wise over ~20 min, and the reaction mixture stirred at rt for 1 h, with small portions of MeOH added to rinse the sides of the flask periodically. The reaction was deemed complete by TLC (R_f = 0.35 with 30:70 Et_2O/hexanes) staining with vanillin. The reaction mixture was poured into 100 mL of water and extracted with Et_2O, the organic layer was separated and dried over anhydrous $MgSO_4$. Note: the reaction with methyl chloroformate was attempted in this Et_2O solution, but only a small amount of conversion was seen, whether this was due to the choice of solvent or residual methanol and or water is unclear. This failed reaction mixture was washed with HCl, then brine, dried over anhydrous $MgSO_4$ and the solvent removed via rotary evaporation to give crude product, taking care not to distill off the product. The crude product was transferred to a dry 250 mL round bottom flask with stir bar. To the flask was added 150 mL of dry DCM and pyridine (7.91 g, 100 mmol, 8.1 mL, 2 equiv). The flask was placed in an ice bath and stirred for 10 min before dropwise addition of methyl chloroformate (7.08 g, 75 mmol, 5.8 mL, 1.5 equiv). The flask was removed from the ice bath and stirred for 20 min, upon which time the reaction was deemed complete by TLC (R_f 0.60 with 30:70 EtOAc/hexanes), staining with vanillin. The reaction mixture was washed with 2 M HCl (2 x 100 mL), then brine, and dried over anhydrous Na_2SO_4, and the solvent removed via rotary evaporator. The crude product was purified by Kugelrohr distillation to give cyclohex-2-en-1-yl methyl carbonate as a colorless oil (4.5 g / 58%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.90 – 5.83 (m, 1H), 5.67 (ddt, *J* = 10.1, 4.2, 2.2 Hz, 1H), 5.01 (dt, *J* = 5.3, 1.7 Hz, 1H), 3.66 (s, 3H), 2.04 – 1.94 (m, 1H), 1.94 – 1.84 (m, 1H), 1.79 (dddd, *J* = 13.4, 8.3, 5.8, 2.5 Hz, 1H), 1.75 – 1.59 (m, 2H), 1.59 – 1.47 (m, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.5, 133.4, 125.0, 71.9, 54.5, 28.3, 24.9, 18.6.

Spectra matched those previously reported: Hatano, M.; Kamiya, S.; Ishihara, K. *Chem. Commun.* **2012**, *48*, 9465–9467.



8

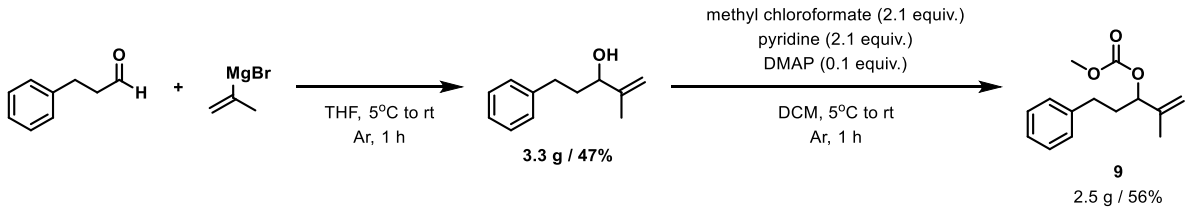
5.8 g / 63%

An oven dried 250 mL round bottom flask with stir bar was capped with a septum and cooled under vacuum and backfilled with argon. To the flask was added 100 mL of dry THF and freshly distilled cyclohexanone (4.90 g, 50 mmol, 5.17 mL, 1.0 equiv). Note: this reaction was attempted with an "old" bottle of cyclohexanone, and significant amounts of byproducts/decomposition products were noted, therefore we recommend distillation of any "old" samples of cyclohexanone prior to conducting this procedure. The flask was placed in an ice bath and stirred for 15 min before dropwise addition of a 1 M solution of vinylmagnesium bromide (55 mmol, 55 mL, 1.1 equiv). After stirring for 1 h, an aliquot was removed and the reaction deemed complete by TLC (R_f 0.20 with 7:93 EtOAc/hexanes). Note: we previously attempted to react this magnesium alkoxide with methyl chloroformate as a 2-step, 1-pot reaction (to avoid working up the alcohol intermediate); this gave a mixture of products and was not successful. The reaction was quenched by the addition of water, and the resulting precipitate removed via filtration, rinsing the precipitate with Et_2O. The filtrate was concentrated by rotary evaporation, placed in a separatory funnel with brine solution and Et_2O and shaken vigorously. The Et_2O layer was dried over anhydrous $MgSO_4$ and filtered through a short plug of silica, and the solvent removed via rotary evaporation in a 250 mL round bottom flask (Note: removal of protic compounds is very important in this step, *n*-butyllithium will quench upon contact of water or unwanted alcohols. Drying with anhydrous $MgSO_4$, then filtration through silica is a simple removal of water, but not rigorous or complete). To this flask was added dry THF (100 mL), and a stir bar, and the flask placed in an ice bath. After stirring for 10 min, a 2.5 M solution *n*-butyllithium in hexanes (62.5 mmol, 25 mL, 1.25 equiv) was added. An aliquot was removed and reacted with *o*-phenanthroline in dry THF which failed to show full lithiation. An additional 5 mL of 2.5 M *n*-butyllithium was added to the reaction flask, and another aliquot removed, which reacted with *o*-phenanthroline to give a deep red color, indicating active alkyl lithium remaining in solution. Next, methyl chloroformate (7.09 g, 75 mmol, 5.8 mL, 1.5 equiv) was added dropwise to the reaction flask. After stirring for 30 min, some allylic alcohol remained in the reaction mixture. An additional ~1 mL of methyl chloroformate was added to the reaction flask, and stirred for an additional 10 min, at which time the reaction was deemed complete via TLC (R_f = 0.60 with 7:93 EtOAc/hexanes). The reaction mixture was quenched with saturated NH_4Cl solution and the bulk of the solvent removed via rotary evaporation. The crude material was taken up in Et_2O and washed with saturated NH_4Cl, then brine, and dried over anhydrous Na_2SO_4. The solvent was removed via rotary evaporation and the product purified by column chromatography with 5:95 Et_2O/hexanes to give methyl (1-vinylcyclohexyl) carbonate as a colorless oil (5.8 g / 63%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.01 (ddq, *J* = 17.0, 11.0, 1.7 Hz, 1H), 5.21 – 5.09 (m, 2H), 3.64 (d, *J* = 2.8 Hz, 3H), 2.12 (dt, *J* = 8.0, 4.2 Hz, 2H), 1.59 – 1.44 (m, 7H), 1.30 – 1.18 (m, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.8, 153.7, 141.1, 114.7, 114.6, 83.0, 83.0, 53.9, 53.9, 34.6, 34.6, 25.2, 21.8, 21.7.

Spectra matched those previously reported: Sun, M.; Chen, J.-F.; Chen, S.; Li, C. *Org. Lett.* **2019**, *21*, 1278–1282.

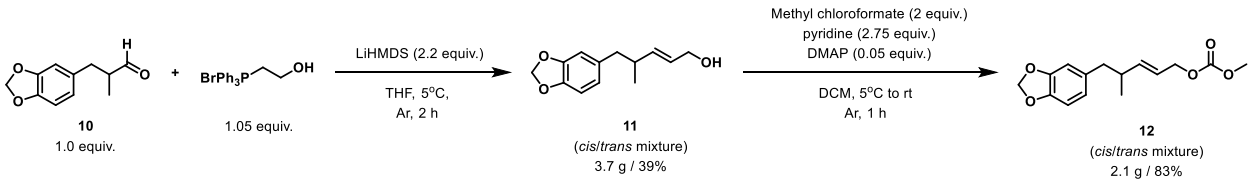


A 250 mL oven dried round bottom flask with stir bar was capped with a septum, cooled under vacuum, and backfilled with argon. To the flask was added 50 mL of dry THF and hydrocinnamaldehyde (5.37 g, 40 mmol, 5.27 mL, 1.0 equiv) and the flask placed in an ice bath. After stirring for 10 min, via dropwise addition was added a 0.5 M isopropenylmagnesium bromide in THF (50 mmol, 100 mL, 1.25 equiv). After stirring for 30 min, the reaction was deemed complete by TLC (R_f = 0.40 with 30:70 Et_2O/hexanes) staining with $KMnO_4$ and vanillin. The reaction was quenched with saturated NH_4Cl and extracted with Et_2O. The organic phase was washed with brine and dried over anhydrous $MgSO_4$ and the solvent removed via rotary evaporation. The crude product showed multiple products, visualized by vanillin and $KMnO_4$ stain. The crude product was purified by Kugelrohr distillation to give 2-methyl-5-phenylpent-1-en-3-ol as a colorless oil (3.3 g / 47%). To a dry 250 mL round bottom flask with stir bar was added 2-methyl-5-phenylpent-1-en-3-ol (3.3 g, 18.7 mmol, 1.0 equiv), pyridine (3.16 g, 40 mol, 3.2 mL, 2.1 equiv) and DMAP (220 mg, 1.8 mmol, 0.1 equiv.). The flask was placed in an ice bath and stirred for 10 min before dropwise addition of methyl chloroformate (3.77 g, 40 mmol, 3.09 mL, 2.1 equiv). The flask was removed from the ice bath after 10 min and allowed to warm to rt. After 1 h, the reaction was incomplete by TLC, an additional aliquot of methyl chloroformate (3.77 g, 40 mmol, 3.09 mL, 2.1 equiv) and pyridine (3.16 g, 40 mol, 3.2 mL, 2.1 equiv) were added to the reaction and stirred an additional 30 min, at which time the reaction was deemed complete by TLC (R_f 0.8 with 30:70 Et_2O/hexanes) staining with vanillin and $KMnO_4$. The organic phase was washed with 2 M HCl, then brine, and dried over anhydrous Na_2SO_4 and the solvent removed via rotary evaporation. The crude product was purified by column chromatography with hexanes then 7:1 Et_2O/hexanes to give methyl (2-methyl-5-phenylpent-1-en-3-yl) carbonate as a colorless oil (2.5 g / 56%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32 – 7.26 (m, 2H), 7.22 – 7.13 (m, 3H), 5.07 – 4.94 (m, 3H), 3.79 (s, 3H), 2.72 – 2.58 (m, 2H), 2.10 – 1.91 (m, 2H), 1.76 (dd, *J* = 1.5, 0.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.4, 142.6, 141.3, 128.6, 128.5, 126.2, 113.9, 81.2, 54.8, 34.5, 31.7, 17.9.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{14}H_{18}O_3Na$ 257.1154; found 257.1154.



An oven dried 24/40 500 mL round bottom flask with stir bar was capped with a septum and cooled under vacuum and backfilled with argon. To the flask was added 100 mL of dry THF and (2-hydroxyethyl)-triphenylphosphonium bromide (17.45 g, 45 mmol, 1.05 equiv) and the flask placed in an ice bath for 10 min. In a separate dry flask, a solution of LiHMDS (15.8 g, 94.5 mmol, 2.2 equiv) was prepared in dry THF (20 mL). The LiHMDS solution was added to the Wittig salt dropwise over 10 min and the flask stirred for 1 h. To the reaction flask was added dropwise freshly distilled 2-methyl-3-(3,4-methylenedioxyphenyl)-propanal (8.22 g, 42.75 mmol, 1.0 equiv) (Note: this aldehyde is also known as helional, or ocean propanal in suppliers of perfuming ingredients) and the reaction was stirred for 2 h. The reaction was deemed complete by TLC (R_f 0.25 with 20:80 EtOAc/hexanes), staining with vanillin and $KMnO_4$, which also showed multiple other byproducts/impurities. The reaction was quenched with saturated NH_4Cl, and the resulting mixture filtered through Celite, rinsing the filter cake with Et_2O. The solvent was removed from the filtrate via rotary evaporation and the crude product taken up in Et_2O, and the organic phase washed with saturated NH_4Cl, then brine, and dried over anhydrous Na_2SO_4. The organic phase was filtered through a short plug of silica, eluting with 50:50 EtOAc/hexanes, and the solvent removed via rotary evaporator. NMR of this product showed a highly impure mixture, so the product was further purified via column chromatography with 20:80 EtOAc/hexanes to 40:60 EtOAc/hexanes. 5-(benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-ol was obtained as a colorless oil (3.7 g / 39%).

An oven dried 100 mL round bottom flask with stir bar was capped with a septum, cooled under vacuum and backfilled with argon. To the flask was added dry DCM (45 mL), 5-(benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-ol (2.0 g, 9.08 mmol, 1.0 equiv), pyridine (1.98 g, 2.0 mL, 2.75 mL), and DMAP (53.4 mg, 53 mg, 0.05 equiv), the flask was placed in an ice bath and stirred for 10 min. Via syringe with dropwise addition was added methyl chloroformate (1.72 g, 18.2 mmol, 1.4 mL, 2.0 equiv) and the reaction stirred for 5 min before removing the flask from the ice bath and allowing to warm to rt. The reaction was stirred for 30 min, at which time the reaction was deemed complete by TLC (R_f = 0.50 with 20:80 EtOAc/hexanes), staining with vanillin. The reaction mixture was washed with 1 M HCl (3 x 50 mL), then brine, and the organic phase dried over anhydrous Na_2SO_4, and the solvent removed via rotary evaporator. The crude product was purified via column chromatography with hexanes then 15:85 EtOAc/hexanes to give 5-(benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl methyl carbonate as a colorless oil (2.1 g / 83%).

Aldehyde (helional)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.69 (d, *J* = 1.6 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 1.8 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.91 (s, 2H), 2.98 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.52 (dd, *J* = 13.7, 8.1 Hz, 1H), 1.07 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 204.5, 204.4, 147.8, 146.2, 132.6, 122.0, 109.4, 108.3, 101.0, 48.3, 36.5, 13.2.

Alcohol intermediate

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.71 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 1H), 6.57 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (d, *J* = 0.7 Hz, 2H), 5.68 – 5.26 (m, 2H), 4.09 – 3.82 (m, 2H), 2.62 – 2.33 (m, 3H), 1.00 (dd, *J* = 18.0, 6.5 Hz, 3H).

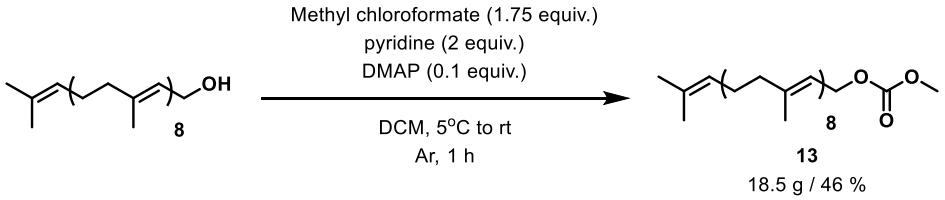
^{13}C NMR ($CDCl_3$, 126 MHz): δ 147.4, 145.6, 138.0, 137.8, 134.4, 127.7, 127.6, 122.0, 121.9, 109.6, 109.5, 107.9, 107.9, 100.8, 100.7, 63.8, 58.6, 43.5, 43.1, 38.1, 34.7, 21.1, 19.5.

Methyl carbonate product

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.70 (d, *J* = 7.9 Hz, 1H), 6.65 – 6.59 (m, 1H), 6.56 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (d, *J* = 1.6 Hz, 2H), 5.79 – 5.43 (m, 2H), 4.58 – 4.33 (m, 2H), 3.76 (d, *J* = 10.9 Hz, 3H), 2.65 – 2.34 (m, 3H), 0.99 (dd, *J* = 11.4, 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.7, 147.5, 145.8, 141.9, 140.6, 134.2, 122.2, 122.1, 122.1, 122.0, 109.7, 109.6, 108.1, 108.0, 100.8, 68.7, 63.8, 54.8, 43.3, 42.9, 38.3, 34.9, 20.7, 19.3.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{15}H_{18}O_5Na$ 301.1052; found 301.1054.

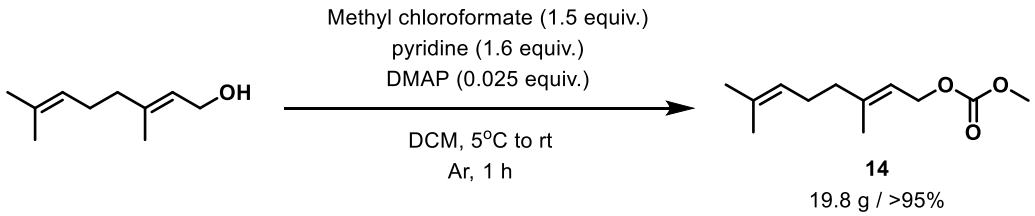


An oven dried 24/40 250 mL round bottom flask with stir bar was capped with a septum and cooled under vacuum and backfilled with argon. To the flask was added solanesol (~95% purity) (25.2 g, 40 mmol, 1.0 equiv.), dry DCM (100 mL) and the flask stirred for 20 min to dissolve. The flask was cooled in an ice bath and to the flask was added pyridine (6.32 g, 80 mmol, 6.43 mL, 2.0 equiv) and DMAP (488 mg, 4.0 mmol, 0.1 equiv). After stirring for 10 min, methyl chloroformate (6.62 g, 70 mmol, 5.4 mL, 1.75 equiv) was added dropwise via syringe. The flask was stirred 10 min before removing from the ice bath and stirring for 1 h, allowing to warm to rt. The reaction was deemed complete via TLC (R_f 0.60 with 30:70 Et_2O/hexanes) staining with $KMnO_4$. The reaction mixture was washed with 2 M HCl (3 x 50 mL), then brine, and the organic layer dried over anhydrous Na_2SO_4 and the solvent removed via rotary evaporator. The crude product was purified by column chromatography with hexanes then 10:90 Et_2O/hexanes to give solanesyl methyl carbonate as a white solid (18.46 g / 46%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.41 – 5.35 (m, 1H), 5.16 – 5.07 (m, 8H), 4.65 (d, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 2.08 (q, *J* = 7.1 Hz, 18H), 1.98 (dd, *J* = 9.2, 5.9 Hz, 14H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.5 Hz, 3H), 1.60 (d, *J* = 1.7 Hz, 24H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.9, 143.1, 135.5, 134.9, 134.9, 134.8, 134.8, 134.8, 134.8, 131.1, 124.4, 124.3, 124.3, 124.3, 124.2, 123.5, 117.8, 64.7, 54.5, 39.8, 39.7, 39.7, 39.7, 39.5, 29.7, 26.8, 26.7, 26.7, 26.7, 26.2, 25.7, 17.7, 16.5, 16.0, 16.0, 16.0.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{47}H_{76}O_3Na$ 711.5692; found 711.5695.

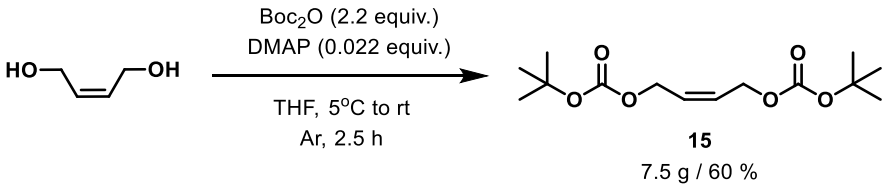


An oven dried 500 mL round bottom flask with stir bar was capped with a septum, cooled under vacuum, and backfilled with argon. To the flask was added dry DCM (250 mL), freshly distilled geraniol (14.53 g, 94.2 mmol, 16.3 mL, 1.0 equiv), pyridine (11.9 g, 150 mmol, 12.1 mL, 1.6 equiv) and DMAP (287 mg, 2.35 mmol, 0.025 equiv). The flask was placed in an ice bath and stirred for 15 min before adding methyl chloroformate (13.4 g, 141 mmol, 10.9 mL, 1.5 equiv) dropwise via syringe. The reaction was stirred for 10 min before removing from the ice bath and allowing to warm to rt. After stirring for 1 h, the reaction was deemed complete by TLC (R_f = 0.60 with 20:80 Et_2O/hexanes), staining with vanillin and $KMnO_4$. The reaction mixture was washed with 2 M HCl (3 x 100 mL), then brine, and the organic phase dried over anhydrous Na_2SO_4 and the solvent removed via rotary evaporation. The product was dissolved in Et_2O and filtered through a 6" x 1.5" column of silica, eluting with 10:90 EtOAc/hexanes. The solvent was removed via rotary evaporator and the product dried under vacuum to give (*E*)-3,7-dimethylocta-2,6-dien-1-yl methyl carbonate as a colorless oil (19.8 g / >95%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.38 – 5.29 (m, 1H), 5.03 (tt, *J* = 5.2, 2.5 Hz, 1H), 4.60 (d, *J* = 7.3 Hz, 2H), 3.72 (s, 3H), 2.09 – 1.97 (m, 4H), 1.67 (d, *J* = 1.8 Hz, 3H), 1.63 (d, *J* = 2.3 Hz, 3H), 1.55 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.9, 143.1, 131.8, 123.7, 117.8, 64.6, 54.6, 39.5, 26.2, 25.6, 17.6, 16.4.

Spectra matched those previously reported: Schlatzer, T.; Kriegesmann, J.; Schröder, H.; Trobe, M.; Lembacher-Fadum, C.; Santner, S.; Kravchuk, A. V.; Becker, C. F. W.; Breinbauer, R. *J. Am. Chem. Soc.* **2019**, *141*, 14931–14937.

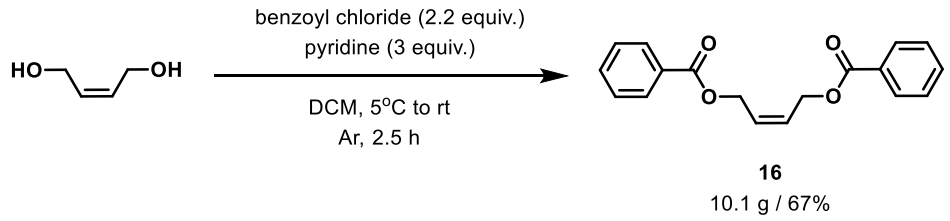


A 250 mL round bottom flask with stir bar was capped with a septum cooled under vacuum, and backfilled with argon. To the flask was added Boc_2O (20.8 g, 95.4 mmol, 2.2 equiv) and dry THF (75 mL). The flask was placed in an ice bath and stirred for 10 min before adding DMAP (117 mg, 0.954 mmol, 0.022 equiv), and (*Z*)-but-2-ene-1,4-diol (3.82 g, 43.4 mmol, 1.0 equiv) dropwise via syringe over ~10 min. The reaction mixture was stirred for 15 min before removing from the ice bath and allowing to warm to rt. After stirring for 2.5 h, the reaction was deemed complete by TLC (R_f = 0.70 with 20:80 EtOAc/hexanes), staining with vanillin and $KMnO_4$. The reaction mixture was washed with 1 M HCl, then 1 M KOH, then brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed via rotary evaporator. The crude product was purified by column chromatography with hexanes then 10:90 Et_2O/hexanes to give (*Z*)-but-2-ene-1,4-diyl di-*t*-butyl bis(carbonate) as a colorless oil (7.5 g / 60%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.76 (ddd, *J* = 5.2, 4.0, 1.2 Hz, 2H), 4.68 – 4.60 (m, 4H), 1.46 (s, 18H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.3, 128.1, 82.4, 62.4, 27.8.

Spectra matched those previously reported: Hassan, A.; Zbieg, J. R.; Krische, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3493–3496.

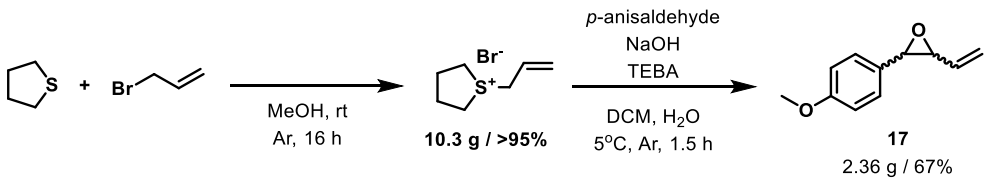


An oven dried 250 mL round bottom flask with stir bar was capped with a septum, cooled under vacuum and backfilled with argon. To the flask was added dry DCM (150 mL), cis-2-butenediol (4.47 g, 50.7 mmol, 1.0 equiv) and pyridine (11.87 g, 150 mmol, 12.1 mL, 3.0 equiv). The flask was placed in an ice bath and stirred for 15 min before dropwise addition of benzoyl chloride (15.7 g, 111.5 mmol, 13.0 mL, 2.2 equiv). The reaction was stirred for 10 min before removing the flask from the ice bath and allowing it to warm to rt. After stirring for 2.5 h, the reaction was deemed complete by TLC (R_f = 0.60 with 1:3 EtOAc/hexanes), showing full consumption of the diol and some benzoyl chloride remaining. To the flask was added ~2 mL of *N,N*-dimethylethanolamine, and the reaction stirred for an additional 10 min, at which point TLC showed disappearance of benzoyl chloride. The reaction mixture was washed with 2 M HCl (3 x 100 mL), then brine, and the organic phase dried over anhydrous Na_2SO_4 and the solvent removed via rotary evaporator. The crude product was recrystallized from hot hexanes to give (*Z*)-but-2-ene-1,4-diyl dibenzoate as flaky white crystals (10.1 g / 67%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11 – 8.02 (m, 4H), 7.58 – 7.52 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 4H), 5.99 – 5.90 (m, 2H), 5.01 (d, *J* = 4.5 Hz, 4H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 166.3, 133.1, 130.0, 129.7, 128.4, 128.4, 60.6.

Spectra matched those previously reported: Belger, C.; Neisius, N. M.; Plietker, B. *Chem. Eur. J.* **2010**, *16*, 12214–12220.



To a 50 mL round bottom flask with stir bar was added 15 mL of MeOH (dried over anhydrous Na_2SO_4 and briefly dried over molecular sieves). Via syringe was added allyl bromide (6.05 g, 50 mmol, 4.32

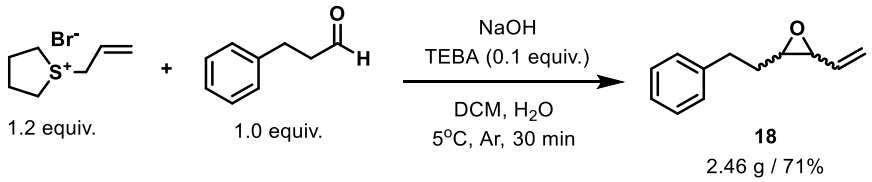
mL, 1.0 equiv) and tetrahydrothiophene (5.3 g, 5.3 mL, 60 mmol, 1.2 equiv) and the reaction mixture stirred overnight at rt. The solvent was removed via rotary evaporator and the product dried under vacuum to give 1-allyl-tetrahydrothiophenium bromide as an off white solid (10.3 g / >95%). (note: tetrahydrothiophene has an extremely unpleasant and strong odor, the waste should be segregated and stored in a fume hood until disposal.)

A 250 mL round bottom flask with a large stir bar (Note: the reaction mixture becomes viscous, efficient stirring is very important) was placed in an ice bath and 40 mL of DCM was added with no special precautions against air or moisture. With stirring, was added sequentially benzyltriethylammonium chloride (453 mg, 1.99 mmol, 0.1 equiv), 1-allyl-tetrahydrothiophenium bromide (5.0 g, 23.9 mmol, 1.20 equiv), and *p*-anisaldehyde (2.71 g, 19.9 mmol, 2.42 mL, 1.0 equiv). The flask was capped with a septum and briefly evacuated/backfilled with argon 3x, taking care not to evaporate a significant amount of DCM, then a vent needle was placed through the septum of the flask. In a 100 mL beaker with a stir bar, 31 mL of a 10 M NaOH solution was prepared, and this solution cooled in an ice bath with stirring. Once cold, this NaOH solution was added to the reaction flask over ~5 min while vigorously stirring the reaction flask. After stirring the reaction for 1.5 h, the reaction was deemed complete by TLC (R_f = 0.70 with 3:7 EtOAc/hexanes) staining with $KMnO_4$. While keeping the reaction flask in the ice bath in case of exotherm and with vigorous stirring, the reaction mixture was diluted with water (100 mL). The reaction mixture was then poured into a separatory funnel and extracted with DCM, the organic phase washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed via rotary evaporator and the crude product purified by column chromatography with hexanes then 10:90 EtOAc/hexanes. Note: it is helpful to pack the column with EtOAc and then hexanes, as packing the column with only hexanes caused some decomposition of the vinyl epoxide product during chromatography. 2-(4-Methoxyphenyl)-3-vinyloxirane was obtained as pale yellow oil (2.36 g / 67%), this material should be stored in the freezer as it slowly decomposes over time, becoming a darker yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 – 7.17 (m, 4H), 6.89 (dd, *J* = 8.9, 2.3 Hz, 4H), 5.73 (ddd, *J* = 17.6, 10.4, 7.4 Hz, 1H), 5.58 – 5.48 (m, 2H), 5.48 – 5.38 (m, 1H), 5.38 – 5.23 (m, 2H), 4.19 (d, *J* = 4.2 Hz, 1H), 3.79 (d, *J* = 0.5 Hz, 6H), 3.72 (d, *J* = 2.0 Hz, 1H), 3.62 (dd, *J* = 8.1, 4.2 Hz, 1H), 3.36 (dd, *J* = 7.4, 2.0 Hz, 1H). (Mixture of diastereomers).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.7, 159.2, 135.3, 132.3, 129.0, 127.6, 127.1, 126.8, 121.7, 119.3, 114.0, 113.6, 62.7, 60.1, 59.9, 58.6, 55.3, 55.2. (mixture of diastereomers).

Spectra matched those previously reported: Aubineau, T.; Cossy, J. *Org. Lett.* **2018**, *20*, 7419–7423.



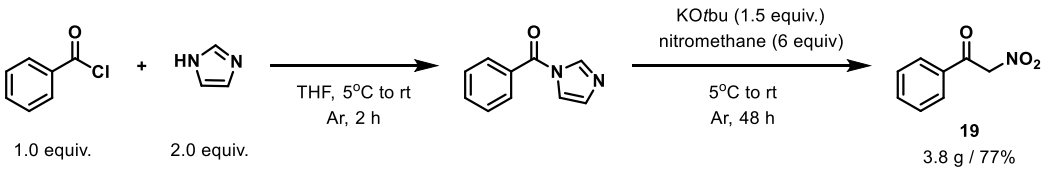
A 250 mL round bottom flask with a large stir bar (Note: the reaction mixture becomes viscous, efficient stirring is very important) was placed in an ice bath and 40 mL of DCM was added with no

special precautions against air or moisture. With stirring, was added sequentially benzyltriethylammonium chloride (455 mg, 2.0 mmol, 0.1 equiv), 1-allyl-tetrahydrothiophenium bromide (5.0 g, 23.9 mmol, 1.20 equiv), and hydrocinnamaldehyde (2.68 g, 20.0 mmol, 2.66 mL, 1.0 equiv). The flask was capped with a septum and briefly evacuated/backfilled with argon 3x, taking care not to evaporate a significant amount of DCM, then a vent needle was placed through the septum of the flask. In 100 mL beaker with stir bar, 31 mL of a 10 M NaOH solution was prepared, and this solution cooled in an ice bath with stirring. Once cold, this NaOH solution was added to the reaction flask over ~5 min while vigorously stirring the reaction flask. After stirring the reaction for 1.5 h, the reaction was deemed complete by TLC (R_f = 0.70 with 3:7 E_2O/hexanes) staining with vanillin and $KMnO_4$. While keeping the reaction flask in the ice bath in case of exotherm and with vigorous stirring, the reaction mixture was diluted with water (100 mL). The reaction mixture was then poured into a separatory funnel and extracted with DCM, the organic phase washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed via rotary evaporator and the crude product purified by column chromatography with hexanes then 10:90 EtOAc/hexanes. Note: it is helpful to pack the column with EtOAc and then hexanes, as packing the column with only hexanes caused some decomposition of the vinyl epoxide product during chromatography. 2-Phenethyl-3-vinyloxirane was obtained as colorless oil (2.46 g / 71%), this material should be stored in the freezer as it slowly decomposes over time.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.38 – 7.31 (m, 2H), 7.28 – 7.22 (m, 3H), 5.67 (dddd, *J* = 65.2, 17.6, 10.4, 7.3 Hz, 1H), 5.54 – 5.25 (m, 2H), 3.48 – 3.14 (m, 1H), 3.11 (dd, *J* = 7.5, 2.1 Hz, 1H), 2.93 – 2.83 (m, 2H), 2.79 (dt, *J* = 13.8, 7.7 Hz, 1H), 2.02 – 1.82 (m, 2H) (mixture of diastereomers).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 141.2, 135.7, 132.4, 128.5, 128.5, 128.4, 128.4, 126.1, 120.3, 119.0, 59.7, 58.9, 58.1, 57.2, 33.8, 32.5, 32.2, 29.6 (mixture of diastereomers).

Spectra matched those previously reported: Aubineau, T.; Cossy, J. *Org. Lett.* **2018**, *20*, 7419–7423.



An oven dried 250 mL round bottom flask with stir bar was capped with a septum, cooled under vacuum and backfilled with argon. To the flask was added dry THF (100 mL) and imidazole (4.10 g, 60 mmol, 2.0 equiv.). The flask was placed in an ice bath and stirred for 10 min before dropwise addition of benzoyl chloride (4.22 g, 30 mmol, 3.5 mL, 1.0 equiv). The flask was removed from the ice bath and stirred for 2 h before filtering the reaction mixture, rinsing with Et_2O. The solvent was removed from the filtrate to give (1H-imidazol-1-yl)(phenyl)methanone as an oil.

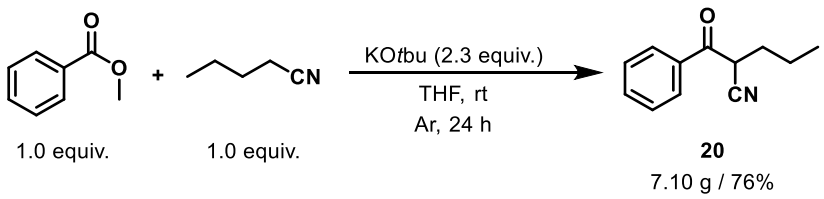
A 250 mL oven dried round bottom flask with stir bar was brought into an argon filled glove box and to it was added KO-*t*-Bu (5.05 g, 45 mmol, 1.5 equiv). The flask was removed from the glovebox and to the flask was added dry THF (60 mL) and the flask placed in an ice bath. After stirring for 10 min, via syringe was added nitromethane (10.9 g, 180 mmol, 9.8 mL, 6 equiv), the reaction became very viscous and an additional 15 mL of THF was added. The flask was removed from the ice bath and

stirred for 1 h while allowing to warm to rt. The flask was placed back in the ice bath and stirred for 10 min before adding (1H-imidazol-1-yl)(phenyl)methanone from the previous step as a solution in THF (50 mL). After 30 min, the flask was removed from the ice bath and allowed to stir for 48 h, upon which time the reaction was deemed complete by TLC (R_f = 0.60 with 50:50 EtOAc/hexanes). The crude product was isolated by filtration, the filter cake rinsed with DCM. The filter cake was dissolved in water, acidified with HCl and extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4 and filtered through a short plug of silica gel. The solvent was removed via rotary evaporation and the product dried under vacuum to give 2-nitro-1-phenylethan-1-one as a white solid crystalline solid (3.8 g / 77%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90 – 7.84 (m, 2H), 7.72 – 7.65 (m, 1H), 7.58 – 7.50 (m, 2H), 5.91 (s, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 186.0, 135.2, 133.5, 129.4, 128.4, 81.5.

Spectra matched those previously reported: Nguyen, H. H.; Kurth, M. J. *Org. Lett.* **2013**, *15*, 362–365.

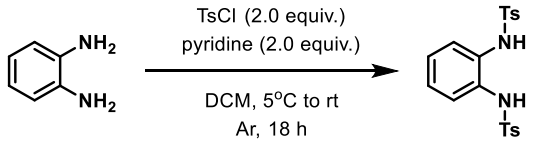


An oven dried 500 mL round bottom flask with a large stir bar was capped with a septum, cooled under vacuum and backfilled with argon. The flask was brought into an argon filled glovebox and KO-*t*-Bu (13.0 g, 116 mmol, 2.3 equiv) was added to the flask and the flask capped with a septum and removed from the glovebox. To the flask was added dry THF (175 mL) and stirred for 5 min before addition of valeronitrile (4.16 g, 50 mmol, 1.0 equiv). The flask was stirred for 10 min at rt before dropwise addition of methyl benzoate (7.49 g, 50 mmol, 1.0 equiv) dropwise via syringe. The reaction was stirred for 24 h at rt upon which time the reaction was deemed complete by TLC (R_f = 0.60 with 20:80 EtOAc/hexanes). The reaction mixture was poured into 1 M HCl (250 mL) and extracted with Et_2O. The organic phase was washed with brine, dried with anhydrous Na_2SO_4 and the solvent removed via rotary evaporator. The crude product was purified by column chromatography with 20:80 EtOAc/hexanes to give 2-benzoylpentanenitrile as a pale yellow oil (9.36 g / 76%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 – 7.90 (m, 2H), 7.61 (td, *J* = 7.4, 1.4 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 4.40 (dd, *J* = 8.1, 6.1 Hz, 1H), 2.00 – 1.88 (m, 2H), 1.66 – 1.46 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 191.1, 134.4, 133.9, 129.1, 128.7, 117.5, 39.9, 31.9, 20.4, 13.4.

Spectra matched those previously reported: Wang, X.; Studer, A. *J. Am. Chem. Soc.* **2016**, *138*, 2977–2980.



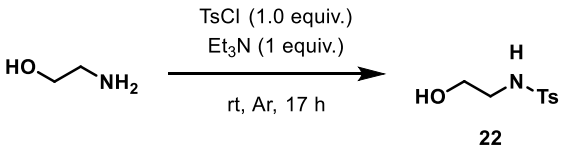
21
6.4 g / 64%

An oven dried 250 mL round bottom flask with stir bar was capped with a septum, cooled under vacuum and backfilled with argon. To the flask was added dry DCM (150 mL), *o*-phenylenediamine (2.59 g, 24.0 mmol, 1.0 equiv) and pyridine (3.80 g, 48.0 mmol, 2 equiv), and the flask placed in an ice bath. The flask was stirred for 15 min before addition of tosyl chloride (9.15 g, 48.0 g, 2 equiv) portion wise over 10 min. The flask was stirred for 15 min before removing from the ice bath, and allowed to warm to rt and stirred overnight (18 h). The reaction mixture was reduced to ~75 mL total volume via rotary evaporation, then diluted with water. After stirring for ~10 min the crude product precipitated as a paste, which was recovered via vacuum filtration, the filter cake rinsed with hexanes and dried under vacuum. The crude product was purified by recrystallization from hot EtOH (~200 mL) to give *N,N'*-(1,2-phenylene)bis(4-methylbenzenesulfonamide) as light purple needles (6.4 g / 64%).

^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.28 (s, 2H), 7.65 – 7.55 (m, 4H), 7.33 (d, *J* = 8.1 Hz, 4H), 7.04 – 6.93 (m, 4H), 2.34 (s, 6H).

^{13}C NMR (DMSO-d_6,126 MHz): δ 143.7, 136.1, 129.7, 129.7, 126.9, 125.9, 123.4, 21.0.

Spectra matched those previously reported: Ramadoss, V.; Alonso-Castro, A. J.; Campos-Xolalpa, N.; Ortiz-Alvarado, R.; Yahuaca-Juárez, B.; Solorio-Alvarado, C. R. *RSC Adv.* **2018**, *8*, 30761–30776.



22
4.4 g / 68%

A 100 mL round bottom flask with stir bar was capped with a septum, cooled under vacuum and backfilled with argon. To the flask was added DCM (50 mL), freshly distilled ethanolamine (1.83 g, 30 mmol, 1.0 equiv) and with stirring was added tosyl chloride (5.72 g, 30 mmol, 1.0 equiv), then Et_3N (3.03 g, 30 mmol, 4.2 mL, 1.0 equiv). The reaction was stirred at rt for 17 h, upon which time the reaction was deemed complete by TLC (R_f = 0.50 with EtOAc). The organic layer was washed with water, then 2 M HCl, then brine, the organic phase dried over anhydrous $MgSO_4$ and the solvent removed via rotary evaporation. Due to the presence of some residual ethanolamine, the crude product was taken up in EtOAc and filtered through a short plug of silica, eluting with 50:50 EtOAc/hexanes. The solvent was removed via rotary evaporation and the product dried under vacuum to give *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide as a white solid (4.4 g / 68 %).

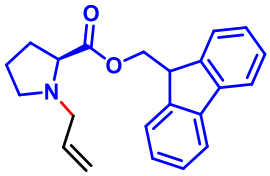
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 5.67 (s, 1H), 3.65 (q, *J* = 4.6 Hz, 2H), 3.03 (p, *J* = 6.8, 5.7 Hz, 3H), 2.40 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 143.67, 136.65, 129.88, 127.19, 61.32, 45.32, 21.60.

Spectra matched those previously reported: Aubineau, T.; Cossy, J. *Org. Lett.* **2018**, *20*, 7419–7423.

5. Substrate Scope

(9H-Fluoren-9-yl)methyl allyl-L-prolinate (1a)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: (9H-fluoren-9-yl)methyl L-prolinate trifluoroacetate (100.0 mg, 0.25 mmol, 1.0 equiv), allyl acetate (36.0 mg, 0.36 mmol, 38.8 μL, 1.5 equiv), K_2CO_3 (69 mg, 0.5 mmol, 2.0 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 2000 ppm Pd (40 μL of stock solution from Section 2.1). The desired compound was obtained as a colorless oil (62.5 mg / 75%).

TLC: R_f = 0.30 with 20:80 EtOAc/hexanes, UV active, stains with $KMnO_4$.

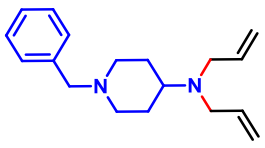
Flash Column chromatography: hexanes then 20:80 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.61 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.40 (td, *J* = 7.5, 1.0 Hz, 2H), 7.32 (tdd, *J* = 7.4, 2.2, 1.2 Hz, 2H), 5.94 – 5.84 (m, 1H), 5.15 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.07 (ddt, *J* = 10.1, 2.1, 1.1 Hz, 1H), 4.55 – 4.44 (m, 2H), 4.22 (t, *J* = 6.7 Hz, 1H), 3.27 (ddt, *J* = 13.2, 6.3, 1.4 Hz, 1H), 3.23 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.10 – 3.03 (m, 2H), 2.40 (dt, *J* = 9.2, 8.0 Hz, 1H), 2.09 (tt, *J* = 7.9, 3.9 Hz, 1H), 1.89 – 1.81 (m, 2H), 1.81 – 1.73 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 143.8, 143.7, 141.4, 141.3, 135.4, 127.7, 127.1, 127.1, 127.0, 125.0, 120.0, 117.3, 66.0, 64.9, 57.4, 53.2, 46.9, 29.4, 23.1.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{23}H_{23}NO_2$ 334.1807; found 334.1801.

N,N-Diallyl-1-benzylpiperidin-4-amine (1b)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: 4-amino-1-benzylpiperidine (95.2 mg, 0.5 mmol, 102.0 μL, 1.0 equiv), allyl acetate (110.0

mg 1.1 mmol, 118.5 μL, 2.2 equiv.), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv.), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a pale yellow oil which blackens upon exposure to air (117.6 mg / 87%).

TLC: R_f = 0.30 with 10:90 MeOH/DCM, faintly UV active, stains with I_2 and $KMnO_4$.

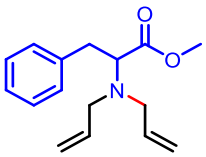
Flash Column chromatography: DCM then 10:90 MeOH/DCM.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (d, *J* = 4.4 Hz, 4H), 7.27 – 7.21 (m, 1H), 5.83 (ddt, *J* = 16.6, 10.1, 6.3 Hz, 2H), 5.15 (dq, *J* = 17.2, 1.7 Hz, 2H), 5.08 (dq, *J* = 10.1, 1.4 Hz, 2H), 3.48 (s, 2H), 3.14 (dt, *J* = 6.3, 1.5 Hz, 4H), 2.93 (dt, *J* = 11.3, 2.1 Hz, 2H), 2.56 (tt, *J* = 11.6, 3.9 Hz, 1H), 1.94 (td, *J* = 11.8, 2.5 Hz, 2H), 1.73 – 1.65 (m, 2H), 1.58 (qd, *J* = 12.1, 3.8 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 138.5, 137.3, 129.2, 128.2, 127.0, 116.5, 63.1, 57.6, 53.5, 53.0, 28.2.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{18}H_{27}N_2$ 271.2174; found 271.2173.

Methyl diallylphenylalaninate (1c)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: phenylalanine methyl ester hydrochloride (100.0 mg, 0.46 mmol, 1.0 equiv), allyl acetate (69.0 mg, 0.69 mmol, 74.4 μL, 1.5 equiv), K_2CO_3 (127.1 mg, 0.92 mmol, 2.0 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 2000 ppm Pd (40 μL of stock solution from Section 2.1). The desired compound was obtained as a colorless oil (62.6 mg / 70% using allyl acetate as limiting reagent).

TLC: R_f = 0.50 with 10:90 EtOAc/hexanes, UV active, stains with $KMnO_4$.

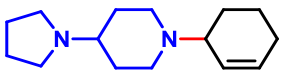
Flash Column chromatography: hexanes then 10:90 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28 – 7.22 (m, 2H), 7.21 – 7.12 (m, 3H), 5.68 (dddd, *J* = 17.3, 10.1, 7.3, 5.1 Hz, 2H), 5.14 (dq, *J* = 17.2, 1.7 Hz, 2H), 5.07 (dq, *J* = 10.2, 1.5 Hz, 2H), 3.71 (dd, *J* = 8.1, 7.1 Hz, 1H), 3.62 (s, 3H), 3.37 (ddt, *J* = 14.5, 5.1, 1.8 Hz, 2H), 3.12 – 3.07 (m, 2H), 3.07 – 2.86 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 138.6, 136.4, 136.4, 136.4, 129.4, 128.3, 126.3, 117.3, 117.3, 63.9, 53.7, 53.6, 51.2, 51.2, 35.8.

Spectra matched that previously reported: Yang, Q.; Xiao, W.-J.; Yu, Z. *Org. Lett.* **2005**, *7*, 871–874.

1-(Cyclohex-2-en-1-yl)-4-(pyrrolidin-1-yl)piperidine (1d)



The titled compound was obtained according to the procedure in section 2.2 using the following quantities: 4-(1-pyrrolidinyl)piperidine (77.1 mg, 0.5 mmol, 1.0 equiv), cyclohex-2-en-1-yl methyl carbonate (93.7 mg 0.6 mmol, 88.6 μL, 1.2 equiv), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv), methyl formate (30.0 mg, 0.5 mmol, 31 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a white semi-solid (93.5 mg / 80%).

TLC: R_f = 0.50 with 20:80 MeOH/DCM w/ a drop of Et_3N, stains with I_2 and $KMnO_4$.

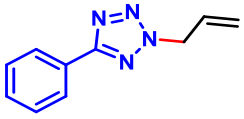
Flash Column chromatography: DCM then 10:90 MeOH/DCM then 15:83:2 MeOH/DCM/Et_3N.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.68 (dt, *J* = 10.1, 3.2 Hz, 1H), 5.58 – 5.48 (m, 1H), 3.18 – 3.08 (m, 1H), 2.81 – 2.70 (m, 2H), 2.54 (td, *J* = 6.3, 5.2, 2.6 Hz, 4H), 2.29 (td, *J* = 11.6, 2.6 Hz, 1H), 2.16 (td, *J* = 11.6, 2.5 Hz, 1H), 2.01 (ddd, *J* = 10.8, 6.9, 3.8 Hz, 1H), 1.83 (dddd, *J* = 25.2, 12.2, 5.7, 2.9 Hz, 4H), 1.75 – 1.62 (m, 6H), 1.56 – 1.36 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 129.7, 129.6, 62.0, 60.2, 51.0, 48.6, 46.5, 31.1, 31.1, 25.2, 23.2, 22.6, 21.5.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{15}H_{27}N_2$ 235.2174; found 235.2172.

2-Allyl-5-phenyl-2H-tetrazole (1e)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: 5-phenyl-1-H-tetrazole (73.1 mg, 0.5 mmol, 1.0 equiv), allyl methyl carbonate (63.9 mg 0.55 mmol, 62.5 μL, 1.1 equiv), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a colorless oil (89 mg / 96%).

TLC: R_f = 0.50 with 30:70 Et_2O/hexanes, UV active.

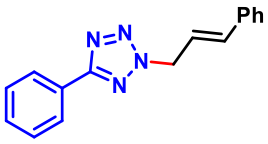
Flash Column chromatography: 20:80 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14 (ddp, *J* = 6.8, 2.8, 1.3 Hz, 2H), 7.46 (dddd, *J* = 7.0, 5.6, 4.6, 1.3 Hz, 3H), 6.19 – 6.04 (m, 1H), 5.39 (dq, *J* = 3.1, 1.4 Hz, 1H), 5.37 (dq, *J* = 7.3, 1.3 Hz, 1H), 5.23 (ddq, *J* = 5.7, 2.9, 1.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 130.4, 130.0, 128.9, 127.4, 126.9, 120.9, 55.4.

Spectra matched that previously reported: Jia, Y.-H.; Yang, K.-X.; Chen, S.-L.; Huang, M.-H. *J. Phys. Chem. A* **2018**, *122*, 8–15.

2-Cinnamyl-5-phenyl-2H-tetrazole (1f)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: 5-phenyl-1-H-tetrazole (73.1 mg, 0.5 mmol, 1.0 equiv), cinnamyl methyl carbonate (105.7 mg 0.55 mmol, 95.3 μ L, 1.1 equiv), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μ L of stock solution from Section 2.1). The desired compound was obtained as a white solid (mp = 65°C) (113.2 mg / 86%).

TLC: R_f = 0.25 with 10:90 Et_2O/hexanes, UV active.

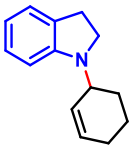
Flash Column chromatography: 10:90 Et_2O/hexanes. Alternatively, the reaction mixture can be filtered and the filter cake recrystallized from hot EtOAc and flooded with hexanes to give white needles.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.25 – 8.17 (m, 2H), 7.55 – 7.46 (m, 3H), 7.45 – 7.39 (m, 2H), 7.39 – 7.27 (m, 3H), 6.78 (dt, *J* = 15.8, 1.4 Hz, 1H), 6.47 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.42 (dt, *J* = 6.7, 1.9 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.4, 136.1, 135.5, 130.4, 128.9, 128.8, 128.6, 127.5, 126.9, 126.9, 126.9, 120.7, 55.2.

HRMS (ESI-TOF) *m/z*: $[M + Na + CH_3OH]^+$ calculated for $C_{17}H_{18}N_4ONa$ 317.1378; found 213.1376.

1-(cyclohex-2-en-1-yl)indoline (1g)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: indoline (59.6 mg, 0.5 mmol, 56.2 μ L, 1.0 equiv), cyclohex-2-en-1-yl methyl carbonate (93.7 mg 0.6 mmol, 88.6 μ L, 1.2 equiv.), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv.), methyl formate (30.0 mg, 0.5 mmol, 31 μ L, 1.0 equiv.), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μ L of stock solution from section 2.1). The desired compound was obtained as a colorless oil which blackens upon exposure to air (93 mg / 93%).

TLC: R_f = 0.60 with 20:80 Et_2O/hexanes, UV active, stains with Seebach's magic stain.

Flash Column chromatography: hexanes then 10:90 Et_2O/hexanes.

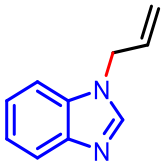
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.17 – 7.05 (m, 2H), 6.69 (td, *J* = 7.3, 1.0 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.02 – 5.91 (m, 1H), 5.71 (ddt, *J* = 10.1, 3.3, 2.2 Hz, 1H), 4.24 (dq, *J* = 6.3, 2.9 Hz, 1H), 3.50 – 3.35

(m, 2H), 3.06 – 2.96 (m, 2H), 2.12 (dtt, *J* = 8.7, 3.3, 1.8 Hz, 2H), 2.04 – 1.87 (m, 2H), 1.80 – 1.68 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 151.3, 130.8, 130.5, 128.7, 127.2, 124.5, 117.1, 107.5, 52.1, 48.1, 28.4, 25.2, 24.9, 21.8.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{14}H_{18}N$ 200.1439; found 200.1435.

1-Allyl-1H-benzo[d]imidazole (1h)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: benzimidazole (59.1 mg, 0.5 mmol, 1.0 equiv), allyl methyl carbonate (63.8 mg 0.55 mmol, 62.5 μL, 1.1 equiv), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv.), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a colorless oil (72.8 mg / 92%).

TLC: R_f = 0.50 with EtOAc, UV active, stains with $KMnO_4$.

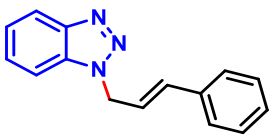
Flash Column chromatography: 50:50 EtOAc/hexanes then EtOAc.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89 (s, 1H), 7.82 (dt, *J* = 6.7, 2.9 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.32 – 7.25 (m, 2H), 5.99 (ddt, *J* = 17.2, 10.6, 5.5 Hz, 1H), 5.28 (dq, *J* = 10.3, 1.4 Hz, 1H), 5.18 (dq, *J* = 17.0, 1.5 Hz, 1H), 4.75 (dt, *J* = 5.6, 1.7 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 143.9, 143.0, 133.9, 132.0, 123.0, 122.2, 120.4, 118.7, 110.0, 47.4.

Spectra matched those previously reported: Şahin, N.; Özdemir, N.; Gürbüz, N.; Özdemir, İ. *Appl. Organomet. Chem.* **2019**, *33*, e4704.

1-Cinnamyl-1H-benzo[d][1,2,3]triazole (1i)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: benzotriazole (59.6 mg, 0.5 mmol, 1.0 equiv), cinnamyl methyl carbonate (105.7 mg 0.55 mmol, 95.3 μL, 1.1 equiv), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv.), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained

as a light yellow solid (57.2 mg / 50%,), isolated from the same trial as 2-cinnamyl-2H-benzo[d][1,2,3]triazole, see below, combined yield of >95%).

TLC: R_f = 0.20 with 30:70 Et_2O/hexanes, UV active.

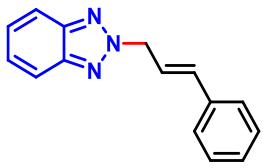
Flash Column chromatography: 10:90 Et_2O/hexanes then 50:50 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.13 – 8.06 (m, 1H), 7.61 – 7.54 (m, 1H), 7.50 – 7.43 (m, 1H), 7.41 – 7.23 (m, 6H), 6.68 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.44 – 6.35 (m, 1H), 5.44 (dd, *J* = 6.3, 1.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 146.3, 135.6, 134.5, 133.0, 128.7, 128.4, 127.4, 126.7, 124.0, 122.2, 120.1, 109.8, 50.6.

Spectra matched those previously reported: Gann, A. W.; Amoroso, J. W.; Einck, V. J.; Rice, W. P.; Chambers, J. J.; Schnarr, N. A. *Org. Lett.* **2014**, *16*, 2003–2005.

2-Cinnamyl-2H-benzo[d][1,2,3]triazole (1i)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: benzotriazole (59.6 mg, 0.5 mmol, 1.0 equiv), cinnamyl methyl carbonate (105.7 mg 0.55 mmol, 95.3 μL, 1.1 equiv), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a light yellow solid (58.5 mg / 50%,), isolated from the same trial as 1-cinnamyl-1H-benzo[d][1,2,3]triazole, see above, combined yield of >95%).

TLC: R_f = 0.50 with 30:70 Et_2O/hexanes, UV active.

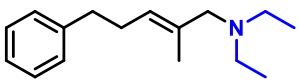
Flash Column chromatography: 10:90 Et_2O/hexanes then 50:50 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91 (dtd, *J* = 6.5, 3.1, 1.4 Hz, 2H), 7.41 (td, *J* = 6.5, 2.3 Hz, 4H), 7.35 – 7.24 (m, 3H), 6.79 (dd, *J* = 16.1, 1.6 Hz, 1H), 6.56 (dt, *J* = 15.7, 6.7 Hz, 1H), 5.51 (dd, *J* = 6.8, 1.5 Hz, 2H).

^{13}C NMR ($CDCl_3$,126 MHz): δ 144.7, 135.9, 135.5, 128.8, 128.5, 127.0, 126.6, 122.1, 118.2, 58.8.

Spectra matched those previously reported: Serra-Muns, A.; Pleixats, R. *J. Organomet. Chem.* **2010**, *695*, 1231–1236.

***(E)*-*N*,*N*-Diethyl-2-methyl-5-phenylpent-2-en-1-amine (1j)**



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: diethylamine (54.6 mg, 0.75 mmol, 77.5 μL, 1.36 equiv), methyl (2-methyl-5-phenylpent-1-en-3-yl) carbonate (117.2 mg 0.55 mmol, 113 μL, 1.0 equiv), K_2CO_3 (138.2 mg, 1.0 mmol, 1.82 equiv.), 2 wt % TPGS-750-M / H_2O (0.5 mL), 910 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a colorless oil (91.7 mg / 72%).

TLC: R_f = 0.30 with 30:70 Et_2O/hexanes (streaks), stains with I_2 and $KMnO_4$.

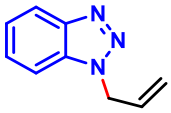
Flash Column chromatography: 30:70 Et_2O/hexanes then 50:50 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28 (dt, *J* = 7.5, 6.1 Hz, 2H), 7.20 (dt, *J* = 8.2, 2.0 Hz, 3H), 5.35 (ddt, *J* = 7.2, 5.8, 1.3 Hz, 1H), 2.88 (d, *J* = 1.2 Hz, 2H), 2.69 (dd, *J* = 8.6, 6.8 Hz, 2H), 2.43 (q, *J* = 7.1 Hz, 4H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.60 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR ($CDCl_3$,126 MHz): δ 142.4, 134.6, 128.6, 128.3, 126.3, 125.8, 62.2, 46.6, 36.1, 29.9, 15.1, 11.7.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{16}H_{26}N$ 232.2065; found 232.2065.

1-Allyl-1H-benzo[d][1,2,3]triazole (1k)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: benzotriazole (59.6 mg, 0.5 mmol, 1.0 equiv), allyl methyl carbonate (63.9 mg 0.55 mmol, 62.5 μL, 1.1 equiv), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a pale yellow oil (46.2 mg / 58%), isolated from the same trial as 2-allyl-2H-benzo[d][1,2,3]triazole, see below, combined yield of >95%).

TLC: R_f = 0.20 with 30:70 Et_2O/hexanes, UV active.

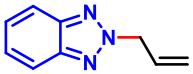
Flash Column chromatography: 10:90 Et_2O/hexanes then 50:50 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.04 (ddt, *J* = 8.3, 2.8, 1.4 Hz, 1H), 7.50 (dq, *J* = 8.3, 1.1 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.37 – 7.31 (m, 1H), 6.09 – 5.98 (m, 1H), 5.30 (ddd, *J* = 10.3, 2.5, 1.3 Hz, 1H), 5.28 – 5.21 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 133.0, 131.3, 127.4, 124.0, 120.1, 119.3, 109.8, 50.9.

Spectra matched those previously reported: Yan, W.; Liao, T.; Tuguldur, O.; Zhong, C.; Petersen, J. L.; Shi, X. *Chem. Asian J.* **2011**, *6*, 2720–2724.

2-Allyl-2H-benzo[d][1,2,3]triazole (1k)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: benzotriazole (59.6 mg, 0.5 mmol, 1.0 equiv), allyl methyl carbonate (63.9 mg 0.55 mmol, 62.5 μL, 1.1 equiv.), K_2CO_3 (104 mg, 0.75 mmol, 1.5 equiv.), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a pale yellow oil (31.0 mg / 39%), isolated from the same trial as 1-allyl-1H-benzo[d][1,2,3]triazole, see above, combined yield of >95%).

TLC: R_f = 0.50 with 30:70 Et_2O/hexanes, UV active.

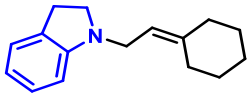
Flash Column chromatography: 10:90 Et_2O/hexanes then 50:50 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.45 – 7.33 (m, 2H), 6.20 (ddt, *J* = 16.6, 10.1, 6.3 Hz, 1H), 5.43 – 5.36 (m, 2H), 5.33 (dt, *J* = 6.3, 1.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 144.6, 131.2, 126.5, 120.3, 118.1, 59.1.

Spectra matched those previously reported: Yan, W.; Liao, T.; Tuguldur, O.; Zhong, C.; Petersen, J. L.; Shi, X. *Chem. Asian J* **2011**, *6*, 2720–2724.

1-(2-Cyclohexylideneethyl)indoline (1l)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: indoline (59.6 mg, 0.5 mmol, 56.2 μL, 1.0 equiv), methyl (1-vinylcyclohexyl) carbonate (110.5 mg 0.6 mmol, 108.3 μL, 1.2 equiv), K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv.), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a colorless oil (98.5 mg / 87%,).

TLC: R_f = 0.70 with 10:90 Et_2O/hexanes, UV active, stains with Seebach's magic stain and $KMnO_4$.

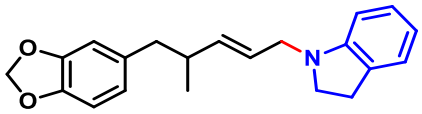
Flash Column chromatography: hexanes then 4:96 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.19 – 7.05 (m, 2H), 6.70 (td, *J* = 7.3, 0.9 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 5.31 (td, *J* = 7.0, 3.5 Hz, 1H), 3.76 (d, *J* = 7.0 Hz, 2H), 3.36 (t, *J* = 8.2 Hz, 2H), 2.98 (t, *J* = 8.2 Hz, 2H), 2.29 (t, *J* = 5.5 Hz, 2H), 2.18 (t, *J* = 5.4 Hz, 2H), 1.66 – 1.57 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 143.5, 130.5, 127.3, 124.4, 117.6, 116.7, 107.5, 53.0, 45.7, 37.3, 29.0, 28.7, 28.6, 27.8, 26.9.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{16}H_{22}N$ 228.1752; found 228.1751.

(*E*)-1-(5-(Benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl)indoline (1m)



The titled compound was obtained according to the procedure in section 2.2 using the following quantities: indoline (11.9 mg, 0.1 mmol, 11.2 μL, 1.0 equiv), 5-(benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl methyl carbonate (27.8 mg 0.1 mmol, 24.0 μL, 1.0 equiv), Et_3N (30.3 mg, 0.3 mmol, 3.0 equiv., 2 wt % TPGS-750-M / H_2O (0.2 mL), 1000 ppm Pd (10 μL of stock solution from section 2.1, but prepared 0.4x as concentrated). The desired compound was obtained as a colorless oil which blackens upon exposure to air (29.0 mg / 90%).

TLC: R_f = 0.70 with 20:80 Et_2O/hexanes, UV active, stains with I_2 and $KMnO_4$.

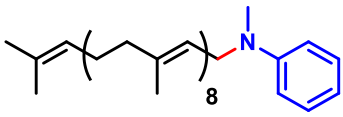
Flash Column chromatography: hexanes then 10:90 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.10 – 7.02 (m, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 – 6.62 (m, 2H), 6.57 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.92 (s, 2H), 5.61 (ddt, *J* = 15.5, 7.4, 1.4 Hz, 1H), 5.48 – 5.39 (m, 1H), 3.71 – 3.55 (m, 2H), 3.21 (td, *J* = 8.4, 3.4 Hz, 2H), 2.92 (t, *J* = 8.2 Hz, 2H), 2.60 – 2.46 (m, 2H), 2.42 (p, *J* = 6.9 Hz, 1H), 1.00 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 147.5, 145.7, 139.0, 134.7, 130.5, 127.3, 124.5, 124.5, 122.1, 117.7, 109.7, 108.0, 107.5, 100.8, 53.1, 51.4, 43.4, 38.7, 28.6, 20.1.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{24}NO_2$ 322.1807; found 322.1810.

N-Methyl-*N*-((2E,6E,10E,14E,18E,22E,26E,30E)-3,7,11,15,19,23,27,31,35-nonamethylhexatriaconta-2,6,10,14,18,22,26,30,34-nonaen-1-yl)aniline (1n)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: *N*-methylaniline (53.6 mg, 0.5 mmol, 54.1 μL, 1.0 equiv), solanesyl methyl carbonate (344.6 mg, 0.5 mmol, 1.0 equiv), Et_3N (151.6 mg, 1.5 mmol, 209 μL, 3.0 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL), $[Pd(allyl)Cl]_2$ (0.92 mg, 0.0025 mmol, 0.5 mol %), DPEphos (2.7 mg, 0.005 mmol, 1 mol %). The desired compound was obtained as a white solid (mp 42 °C) (310 mg / 86%).

TLC: R_f = 0.70 with 10:90 Et_2O/hexanes, UV active, stains with I_2 and $KMnO_4$.

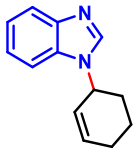
Flash Column chromatography: hexanes then 4:96 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 – 7.27 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 5.32 (td, *J* = 6.4, 1.7 Hz, 1H), 5.26 – 5.16 (m, 8H), 3.98 (d, *J* = 6.3 Hz, 2H), 2.97 (s, 3H), 2.17 (dq, *J* = 16.4, 7.6 Hz, 18H), 2.09 (dd, *J* = 9.5, 5.7 Hz, 15H), 1.82 – 1.76 (m, 6H), 1.69 (d, *J* = 8.5 Hz, 25H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 138.1, 135.2, 134.9, 134.9, 134.9, 134.9, 134.9, 131.2, 129.1, 124.6, 124.4, 124.4, 124.4, 124.3, 124.0, 121.1, 116.6, 113.1, 50.6, 39.9, 39.8, 39.8, 39.7, 37.9, 29.8, 26.9, 26.8, 26.8, 26.5, 25.8, 17.8, 16.3, 16.1, 16.1, 16.1.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{52}H_{82}N$ 720.6447; found 720.6461.

1-(Cyclohex-2-en-1-yl)-1H-benzo[d]imidazole (1o)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: benzimidazole (29.5 mg, 0.25 mmol, 1.0 equiv), cyclohex-2-en-1-yl methyl carbonate (46.8 mg, 0.3 mmol, 44.3 μL, 1.2 equiv), K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv), methyl formate (49 mg, 0.8 mmol, 50 μL, 3.2 equiv.), 2 wt % TPGS-750-M / H_2O (0.25 mL), $[Pd(allyl)Cl]_2$ (0.46 mg, 0.00125 mmol, 1 mol % Pd), DPEphos (1.35 mg, 0.0025 mmol, 1 mol %). The desired compound was obtained as a colorless oil (45.2 mg / 91%).

TLC: R_f = 0.50 with EtOAc UV active, stains with I_2 and $KMnO_4$.

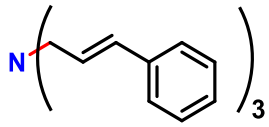
Flash Column chromatography: 25:75 EtOAc/hexanes then 40:60 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (s, 1H), 7.84 – 7.78 (m, 1H), 7.48 – 7.40 (m, 1H), 7.31 – 7.26 (m, 2H), 6.21 (dtd, *J* = 9.8, 3.8, 2.0 Hz, 1H), 5.86 (dq, *J* = 9.9, 2.5 Hz, 1H), 5.01 (dp, *J* = 5.7, 2.8 Hz, 1H), 2.30 – 1.93 (m, 5H), 1.72 (tdd, *J* = 6.3, 4.9, 2.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 142.2, 133.9, 133.4, 124.9, 122.7, 122.2, 120.6, 110.3, 51.2, 29.6, 24.9, 19.4.

Spectra matched those previously reported: Meng, X.; Li, X.; Chen, W.; Zhang, Y.; Wang, W.; Chen, J.; Song, J.; Feng, H.; Feng, B. *J. Hetero. Chem.* **2014**, *51*, 349–356.

(*E*)-Tricinnamylamine (1p)



The titled compound was obtained according to the procedure in section 2.2 using the following quantities: conc. ammonium hydroxide (175 mg, 5.0 mmol, 600 μL, 5 equiv), cinnamyl methyl carbonate (192.1 mg, 1.0 mmol, 173.2 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL), $[Pd(allyl)Cl]_2$ (1.83 mg, 0.005 mmol, 0.5 mol %), DPEphos (5.4 mg, 0.01 mmol, 1 mol %). The desired compound was obtained as a white crystalline solid (mp 88-89 °C) (109.8 mg / 90.1%).

TLC: R_f 0.50 with 25:75 EtOAc/hexanes, UV active, stains with $KMnO_4$.

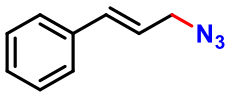
Flash column chromatography: hexanes then 15:85 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (d, *J* = 7.6 Hz, 6H), 7.38 (t, *J* = 7.5 Hz, 6H), 7.34 – 7.27 (m, 3H), 6.63 (d, *J* = 15.8 Hz, 3H), 6.40 (dt, *J* = 15.8, 6.7 Hz, 3H), 3.42 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 133.0, 128.7, 127.5, 127.3, 126.4, 56.2.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{27}H_{28}N$ 366.2222; found 366.2224.

(E)-(3-azidoprop-1-en-1-yl)benzene (1q)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: sodium azide (71.5 mg, 1.1 mmol, 1.1 equiv), cinnamyl methyl carbonate (192.1 mg, 1.0 mmol, 173.2 μL, 1.0 equiv) K_2CO_3 (207.3 mg, 1.5 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL),2000 ppm Pd (40 μL of stock solution from Section 2.1). The desired compound was obtained as a colorless oil (143.9 mg / 90.4%).

TLC: R_f 0.60 with 10:90 Et_2O/hexanes, UV active, stains with vanillin and $KMnO_4$.

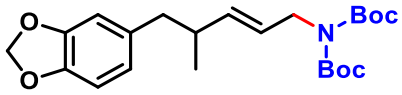
Flash column chromatography: hexanes then 3:97 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 – 7.41 (m, 2H), 7.41 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 6.68 (dt, *J* = 15.6, 1.5 Hz, 1H), 6.27 (dt, *J* = 15.7, 6.6 Hz, 1H), 3.96 (dd, *J* = 6.6, 1.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 134.6, 128.7, 128.3, 126.7, 122.5, 53.1.

Spectra matched those previously reported: Barragan, E.; Bugarin, A. *J. Org. Chem.* **2017**, *82*, 1499-1506.

(*E*)-5-(Benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-(di-*tert*-butyl iminodicarboxylate) (1r)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: di-*tert*-butyl iminodicarboxylate (23.9 mg, 0.11 mmol, 1.1 equiv), 5-(benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl methyl carbonate (27.8 mg 0.1 mmol, 24.0 μL, 1.0 equiv), K_2CO_3 (20.7 mg, 0.15 mmol, 1.5 equiv), methyl formate (6.0 mg, 0.1 mmol, 6.1 μL, 1.0 equiv) 2 wt % TPGS-750-M / H_2O (0.2 mL), 2500 ppm Pd (25 μL of stock solution prepared from $[Pd(allyl)Cl]_2$ (4.57 mg) and DPEphos (13.5 mg) in 2500 μL of toluene). The desired compound was obtained as a colorless viscous oil (35.0 mg / 84%).

TLC: R_f 0.50 with 20:80 Et_2O/hexanes, UV active, stains with $KMnO_4$.

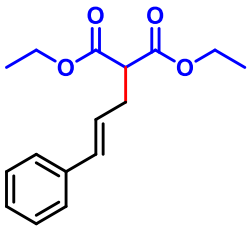
Flash column chromatography: hexanes, then 10:90 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.70 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 1.7 Hz, 1H), 6.56 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.90 (s, 2H), 5.56 (ddt, *J* = 15.3, 6.8, 1.2 Hz, 1H), 5.40 (dtd, *J* = 15.4, 6.1, 1.0 Hz, 1H), 4.08 (dd, *J* = 6.1, 1.3 Hz, 2H), 2.62 – 2.54 (m, 1H), 2.42 – 2.31 (m, 2H), 1.49 (s, 18H), 0.94 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 147.5, 145.7, 138.7, 134.5, 123.9, 122.1, 109.6, 108.0, 100.8, 82.2, 48.1, 43.2, 38.3, 28.2, 19.7.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{23}H_{33}NO_6Na$ 442.2206; found 442.2205.

Diethyl 2-cinnamylmalonate (2a)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: diethyl malonate (44.1 mg, 0.275 mmol, 42.0 μL, 1.1 equiv), cinnamyl methyl carbonate (48.1 mg 0.25 mmol, 43.3 μL, 1.0 equiv), K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (0.25 mL), 1000 ppm Pd (20 μL of stock solution prepared from $Pd(OAc)_2$ (2.81 mg) and PPh_3 (13.1 mg) in 1.0 mL toluene with 7.0 μL Et_3N. The desired compound was obtained as a colorless oil (55 mg / 80%).

TLC: R_f = 0.25 with 5:95 Et_2O/hexanes, UV active, stains with $KMnO_4$.

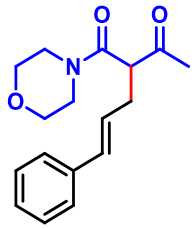
Flash column chromatography: hexanes then 10:90 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32 (dt, *J* = 14.9, 7.4 Hz, 4H), 7.23 (td, *J* = 6.8, 1.6 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.7, 7.2 Hz, 1H), 4.22 (qq, *J* = 6.8, 3.7 Hz, 4H), 3.50 (t, *J* = 7.5 Hz, 1H), 2.82 (td, *J* = 7.3, 1.4 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 137.2, 132.9, 128.6, 127.5, 126.3, 125.8, 61.6, 52.2, 32.4, 14.3.

Spectra matched those previously reported: Huang, X.; Fulton, B.; White, K.; Bugarin, A. *Org. Lett.* **2015**, *17*, 2594–2597.

2-Cinnamyl-1-morpholinobutane-1,3-dione (2b)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: 1-morpholinobutane-1,3-dione (47.1 mg, 0.275 mmol, 1.1 equiv), cinnamyl methyl carbonate (48.1 mg 0.25 mmol, 43.3 μL, 1.0 equiv), K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (0.25 mL), 1000 ppm Pd (20 μL of stock solution prepared from $Pd(OAc)_2$ (2.81 mg) and PPh_3 (13.1 mg) in 1.0 mL toluene with 7.0 μL Et_3N. The desired compound was obtained as a colorless oil (48 mg / 67%). **TLC:** R_f = 0.50 with EtOAc, UV active, stains with $KMnO_4$.

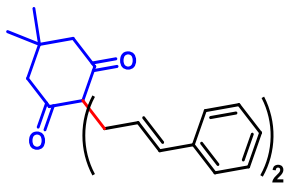
Flash Column chromatography: 10:90 EtOAc/hexanes, then 30:70 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 – 7.26 (m, 4H), 7.22 (tdd, *J* = 7.0, 5.0, 2.8 Hz, 1H), 6.47 (dd, *J* = 15.8, 1.5 Hz, 1H), 6.12 (dtd, *J* = 15.7, 7.2, 1.6 Hz, 1H), 3.77 – 3.46 (m, 9H), 2.91 – 2.73 (m, 2H), 2.20 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.1, 167.1, 136.9, 132.8, 128.6, 127.6, 126.2, 125.9, 66.9, 66.7, 57.9, 46.5, 42.7, 32.5, 27.2.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{17}H_{22}NO_3$ 288.1600; found 288.1607.

2,2-Dicinnamyl-5,5-dimethylcyclohexane-1,3-dione (2c)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: dimedone (70.1 mg, 0.5 mmol, 1.0 equiv), cinnamyl methyl carbonate (105.7 mg, 0.55 mmol, 95.3 μL, 1.1 equiv), K_2CO_3 (103.7 mg, 0.75 mmol, 1.5 equiv.), methyl formate (30.0 mg, 0.5 mmol, 30.6 μL, 1.0 equiv.), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a pale yellow oil (98.8 mg / 96%, using cinnamyl methyl carbonate as limiting reagent).

TLC: R_f = 0.40 with 50:50 Et_2O/hexanes, UV active, stains with $KMnO_4$.

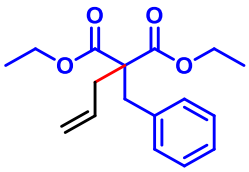
Flash column chromatography: hexanes then 40:60 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 – 7.26 (m, 8H), 7.24 – 7.18 (m, 2H), 6.45 (d, *J* = 15.7 Hz, 2H), 6.03 (dt, *J* = 15.4, 7.5 Hz, 2H), 2.72 (dd, *J* = 7.5, 1.3 Hz, 4H), 2.58 (s, 4H), 0.96 (s, 6H).

^{13}C NMR ($CDCl_3$**)** δ 209.0, 137.0, 134.5, 128.5, 127.5, 126.3, 123.9, 68.5, 52.3, 38.4, 30.7, 28.7.

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{26}H_{28}O_2Na$ 395.1987; found 395.1986.

Diethyl 2-allyl-2-benzylmalonate (2d)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: diethyl benzylmalonate (100 mg, 0.40 mmol, 94.0 μL, 1.0 equiv), allyl acetate (60.1 mg, 0.60 mmol, 64.7 μL, 1.5 equiv), K_2CO_3 (55.3 mg, 0.40 mmol, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (0.4 mL), 2000 ppm Pd (40 μL of stock solution from Section 2.1). The desired compound was obtained as a pale yellow oil (87.4 mg / 75%).

TLC: R_f = 0.30 with 10:90 EtOAc/hexanes, UV active, stains with $KMnO_4$.

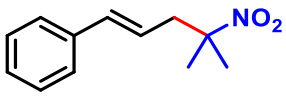
Flash column chromatography: hexanes then 10:90 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 – 7.22 (m, 3H), 7.16 – 7.10 (m, 2H), 5.85 – 5.73 (m, 1H), 5.18 (q, *J* = 1.2 Hz, 1H), 5.16 (dq, *J* = 3.9, 1.4 Hz, 1H), 4.26 – 4.11 (m, 4H), 3.26 (s, 2H), 2.58 (dt, *J* = 7.3, 1.3 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 136.2, 132.8, 130.1, 128.3, 127.0, 119.3, 119.3, 61.4, 58.9, 38.2, 36.6, 14.2.

Spectra matched those previously reported: Shimizu, A.; Hirata, G.; Onodera, G.; Kimura, M. *Adv. Syn. Cat.* **2018**, *360*, 1954–1960.

(*E*)-(4-Methyl-4-nitropent-1-en-1-yl)benzene (2e)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: 2-nitropropane (44.6 mg, 0.5 mmol, 45.4 μL, 1.0 equiv), *t*-butyl cinnamyl carbonate (128.9 mg, 0.55 mmol, 125.8 μL, 1.1 equiv), Et_3N (151.8 mg, 1.5 mmol, 209.2 μL, 3.0 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a colorless oil (72 mg / 70%).

TLC: R_f = 0.50 with plate run 1/8th of the way with Et_2O, dried and then run the rest of the way with hexanes (product difficult to separate from the electrophile starting material). UV active.

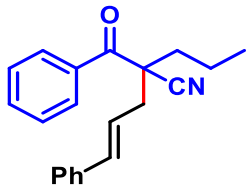
Flash column chromatography: hexanes then 5:95 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.08 (dt, *J* = 15.4, 7.5 Hz, 1H), 2.81 (dd, *J* = 7.5, 1.3 Hz, 2H), 1.65 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.67, 135.29, 128.61, 127.78, 126.36, 122.41, 88.09, 44.25, 27.82, 25.65.

Spectra matches those previously reported: Wade, P. A.; Morrow, S. D.; Hardinger, S. A. *J. Org. Chem.* **1982**, *47*, 365–367.

(*E*)-2-Benzoyl-5-phenyl-2-propylpent-4-enenitrile (2f)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: 2-benzoylpentanenitrile (93.6 mg, 0.5 mmol, 1.0 equiv), cinnamyl methyl carbonate (119.2 mg, 0.50 mmol, 107.5 μL, 1.0 equiv), K_2CO_3 (103.7 mg, 0.75 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL), $[Pd(allyl)Cl]_2$ (1.8 mg, 0.005 mmol, 1 mol %), DPEphos (5.4 mg, 0.01 mmol, 2 mol %). The desired compound was obtained as a pale yellow oil (151.7 mg / >95%).

TLC: R_f = 0.30 with 10:90 EtOAc/hexanes. UV active, stains with $KMnO_4$.

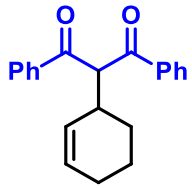
Flash column chromatography: hexanes then 10:90 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.12 – 8.07 (m, 2H), 7.62 – 7.57 (m, 1H), 7.52 – 7.46 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.58 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.23 (ddd, *J* = 15.4, 7.9, 7.1 Hz, 1H), 2.95 (dddd, *J* = 150.6, 13.9, 7.5, 1.3 Hz, 2H), 2.08 (dddd, *J* = 163.1, 13.6, 12.1, 4.7 Hz, 2H), 1.64 – 1.47 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 136.5, 135.8, 135.7, 133.5, 129.0, 128.6, 128.6, 127.9, 126.5, 122.1, 121.2, 52.2, 40.9, 39.3, 18.7, 14.0.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{21}H_{21}NONa$ 326.1521; found 326.1531.

2-(Cyclohex-2-en-1-yl)-1,3-diphenylpropane-1,3-dione (2g)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities for the racemic product: 1,3-diphenylpropane-1,3-dione (112.2 mg, 0.50 mmol, 1.0 equiv), cyclohex-2-en-1-yl methyl carbonate (78 mg, 0.50 mmol, 1.0 equiv), K_2CO_3 (173 mg, 1.25 mmol, 2.5 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL), $[Pd(allyl)Cl]_2$ (0.52 mg, 0.0028 mmol Pd, 0.57 mol % Pd), DPEphos (1.7 mg, 0.0032 mmol, 0.63 mol %). The desired compound was obtained as a pale yellow oil. (125.8 mg / 83%).

The titled compound was obtained according to the procedure in Section 2.2 using the following quantities for the asymmetric example: 1,3-diphenylpropane-1,3-dione (112.2 mg, 0.50 mmol, 1.0 equiv), cyclohex-2-en-1-yl methyl carbonate (78 mg, 0.50 mmol, 1.0 equiv), K_2CO_3 (173 mg, 1.25 mmol, 2.5 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL), $[Pd(allyl)Cl]_2$ (0.54 mg, 0.0030 mmol Pd, 0.60 mol % Pd), (*S*,*S*)-DACH-naphthyl Trost Ligand (2.8 mg, 0.0035 mmol, 0.7 mol %). The desired compound was obtained as a pale yellow oil. (132.2 mg / 87%).

TLC: R_f = 0.40 with 10:90 Et_2O/hexanes. UV active, stains with $KMnO_4$.

Flash column chromatography: hexanes then 10:90 Et_2O/hexanes.

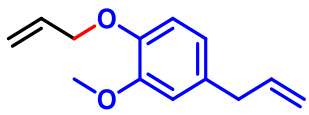
HPLC column conditions: 99:1 hexanes/isopropanol, using Chiral PAK ADH column.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99 (ddd, *J* = 8.6, 3.6, 1.4 Hz, 4H), 7.59 – 7.47 (m, 2H), 7.42 (td, *J* = 7.8, 1.6 Hz, 4H), 5.72 (ddt, *J* = 9.8, 3.6, 1.9 Hz, 1H), 5.51 (dd, *J* = 10.2, 2.5 Hz, 1H), 5.30 (d, *J* = 10.0 Hz, 1H), 3.49 (dtd, *J* = 10.5, 5.3, 2.6 Hz, 1H), 2.00 (tq, *J* = 5.9, 2.8 Hz, 2H), 1.81 – 1.67 (m, 2H), 1.58 (dddd, *J* = 13.1, 8.1, 6.0, 3.6 Hz, 1H), 1.38 (dddd, *J* = 12.4, 10.0, 8.0, 2.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.3, 194.9, 137.2, 137.0, 133.6, 133.5, 129.4, 128.9, 128.8, 128.8, 128.8, 128.6, 62.3, 37.3, 27.4, 25.1, 21.2.

Spectral data matched those previously reported: Zotto, C. D.; Michaux, J.; Zarate-Ruiz, A.; Gayon, E.; Virieux, D.; Campagne, J.-M.; Terrasson, V.; Pieters, G.; Gaucher, A.; Prim, D. *J. Organomet. Chem.* **2011**, *696*, 296–304.

4-Allyl-1-(allyloxy)-2-methoxybenzene (3a)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: eugenol (82.1 mg, 0.5 mmol, 77.5 μL, 1.0 equiv), allyl acetate (55.1 mg, 0.55 mmol, 59.3

μL, 1.1 equiv), K_2CO_3 (103.7 mg, 0.75 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a colorless oil (78.6 mg / 77%).

TLC: R_f = 0.80 with 20:80 EtOAc/hexanes. UV active, stains with $KMnO_4$

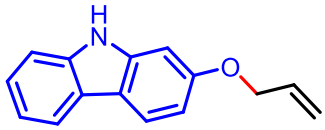
Flash column chromatography: hexanes then 5:95 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.82 (d, *J* = 8.1 Hz, 1H), 6.76 – 6.68 (m, 2H), 6.08 (ddt, *J* = 17.3, 10.7, 5.4 Hz, 1H), 5.96 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.45 – 5.36 (m, 1H), 5.27 (dq, *J* = 10.5, 1.4 Hz, 1H), 5.13 – 5.04 (m, 2H), 4.59 (dt, *J* = 5.4, 1.6 Hz, 2H), 3.86 (s, 3H), 3.34 (d, *J* = 6.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 146.4, 137.7, 133.6, 133.1, 120.4, 117.8, 115.7, 113.7, 112.3, 70.1, 55.9, 39.9.

Spectra matched those previously reported: Llevot, A.; Monney, B.; Sehlinger, A.; Behrens, S.; Meier, M. a. R. *Chem. Commun.* **2017**, *53*, 5175–5178.

2-(Allyloxy)-9H-carbazole (3b)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: 2-hydroxycarbazole (100 mg, 0.54 mmol, 1.0 equiv), allyl acetate (81.1 mg, 0.81 mmol, 87.4 μL, 1.5 equiv), K_2CO_3 (74.6 mg, 0.54 mmol, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 2000 ppm Pd (40 μL of stock solution from Section 2.1). The desired compound was obtained as a yellow solid (mp = 180 ^{o}C), (53.1 mg / 44%).

TLC: R_f = 0.30 with 20:80 EtOAc/hexanes. UV active, stains with $KMnO_4$

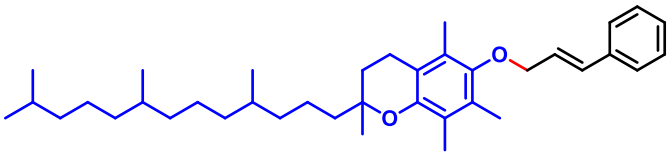
Flash column chromatography: hexanes then 20:80 EtOAc/hexanes.

^{1}H NMR (DMSO, 600 MHz): δ 11.20 – 11.06 (m, 1H), 7.99 (ddt, *J* = 24.0, 17.1, 7.8 Hz, 2H), 7.52 – 7.40 (m, 1H), 7.40 – 7.25 (m, 1H), 7.21 – 7.09 (m, 1H), 7.09 – 6.96 (m, 1H), 6.89 – 6.75 (m, 1H), 6.21 – 6.04 (m, 1H), 5.55 – 5.40 (m, 1H), 5.38 – 5.23 (m, 1H), 4.74 – 4.56 (m, 2H).

^{13}C NMR (151 MHz, DMSO) δ 157.8, 141.4, 140.2, 134.4, 124.6, 123.1, 121.3, 119.7, 119.0, 117.7, 116.8, 111.0, 108.6, 95.9, 95.9, 68.9.

Spectra matched those previously reported: Chattopadhyay, S. K.; Ghosh, D.; Mondal, P.; Ghosh, S. K. *Synthesis* **2012**, 44, 2448-2454.

6-(Cinnamyloxy)-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chromane (3c)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: ∝-tocopherol (racemic synthetic vitamin E) (215.4 mg, 0.5 mmol, 1.0 equiv) (added as though it were a solid due to the high viscosity), cinnamyl benzoate (143.0 mg 0.6 mmol, 129.5 μ L, 1.2 equiv), K_2CO_3 (103.7 mg, 0.75 mmol, 1.5 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μ L, 1.0 equiv) 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μ L of stock solution from Section 2.1). The desired compound was obtained as a pale yellow viscous oil (225.0 mg / 82%).

TLC: R_f = 0.40 with 5:95 Et_2O/hexanes, UV active.

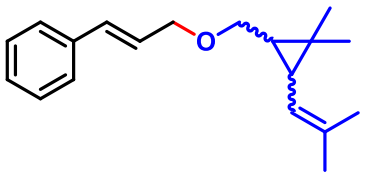
Flash column chromatography: hexanes, then 4:96 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 15.8 Hz, 1H), 6.55 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.43 (dd, *J* = 5.8, 1.5 Hz, 2H), 2.65 (t, *J* = 6.8 Hz, 2H), 2.29 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H), 1.93 – 1.79 (m, 2H), 1.62 (ddt, *J* = 19.7, 13.3, 6.9 Hz, 3H), 1.57 – 1.26 (m, 17H), 1.25 – 1.10 (m, 7H), 0.94 (dd, *J* = 9.9, 6.4 Hz, 13H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 147.9, 136.9, 132.0, 128.6, 128.0, 127.7, 126.6, 126.0, 125.8, 122.9, 117.6, 74.9, 74.8, 73.6, 40.2, 40.1, 39.5, 37.7, 37.7, 37.6, 37.6, 37.5, 37.5, 37.5, 37.4, 37.4, 32.9, 32.9, 32.8, 32.8, 31.4, 31.3, 28.1, 24.9, 24.9, 24.5, 24.0, 22.8, 22.7, 21.1, 20.8, 19.9, 19.8, 19.8, 19.7, 19.7, 13.0, 12.2, 11.9.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{38}H_{58}O_2Na$ 569.4335; found 569.4335.

(*E*)-(3-((2,2-Dimethyl-3-(2-methylprop-1-en-1-yl)cyclopropyl)methoxy)prop-1-en-1-yl)benzene (3d)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: chrysanthemyl alcohol, mixture of *cis* and *trans* (77.1 mg, 0.5 mmol, 86.9 μ L, 1.0 equiv), cinnamyl benzoate (131.1 mg, 0.55 mmol, 118.7 μ L, 1.1 equiv), K_2CO_3 (103.7 mg, 0.75 mmol, 1.5 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), $[Pd(allyl)Cl]_2$ (1.83 mg, 0.005 mmol, 1 mol %), DPEphos (5.4 mg, 0.01 mmol, 2 mol %). The desired compound was obtained as a colorless oil (114.7 mg / 85%).

TLC: R_f = 0.70 with 10:90 Et_2O/hexanes, UV active, stains with $KMnO_4$.

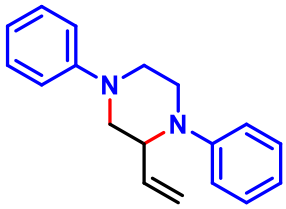
Flash column chromatography: hexanes then 3:97 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (dt, *J* = 8.1, 1.6 Hz, 2H), 7.33 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.28 – 7.23 (m, 1H), 6.63 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.95 (ddt, *J* = 9.6, 6.6, 1.4 Hz, 1H), 4.17 (ddd, *J* = 7.9, 6.2, 1.6 Hz, 2H), 3.62 (ddd, *J* = 71.1, 10.5, 6.4 Hz, 1H), 3.47 (ddd, *J* = 14.2, 10.5, 8.1 Hz, 1H), 1.80 – 1.69 (m, 6H), 1.18 (d, *J* = 1.9 Hz, 3H), 1.17 – 1.13 (m, 1H), 1.11 (s, 2H), 1.06 (s, 1H), 0.88 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.91, 133.05, 132.12, 132.09, 128.60, 127.63, 127.62, 126.77, 126.73, 126.53, 123.70, 119.38, 71.19, 71.01, 70.72, 67.72, 32.45, 28.85, 28.80, 28.22, 26.16, 25.82, 25.72, 22.68, 22.31, 21.58, 20.29, 18.59, 18.36, 15.62.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{26}ONa$ 293.1881; found 293.1881.

1,4-Diphenyl-2-vinylpiperazine (4a)



The titled compound was obtained according to the procedure in Section 2.2/2.3 using the following quantities: 1,2-dianilinoethane (106.2 mg, 0.5 mmol, 1.0 equiv), (*Z*)-but-2-ene-1,4-diyl di-*t*-butyl bis(carbonate) (144.17 mg 0.5 mmol, 139.7 μL, 1.0 equiv), Et_3N (151.7 mg, 1.5 mmol, 209.0 μL, 3.0 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (1.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a white crystalline solid (116.6 mg / 88%).

TLC: R_f = 0.70 with 20:80 Et_2O/hexanes, UV active, stains with $KMnO_4$.

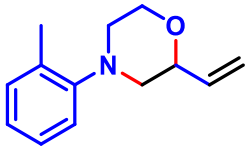
Flash column chromatography: hexanes, then 10:90 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 (qd, *J* = 7.0, 1.9 Hz, 4H), 7.12 – 7.03 (m, 4H), 7.00 (tt, *J* = 7.3, 1.1 Hz, 2H), 6.09 (ddd, *J* = 17.2, 10.5, 6.6 Hz, 1H), 5.38 – 5.24 (m, 2H), 4.45 – 4.33 (m, 1H), 3.69 – 3.60 (m, 2H), 3.57 – 3.44 (m, 3H), 3.36 – 3.23 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 150.2, 136.4, 129.2, 129.1, 119.9, 119.6, 117.6, 117.3, 115.9, 59.1, 54.2, 48.8, 45.9.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{21}N_2$ 265.1705; found 265.1709.

4-(*o*-Tolyl)-2-vinylmorpholine (4b)



The titled compound was obtained according to the procedure in Section 2.2/2.3 using the following quantities: 2-(*o*-tolylamino)ethan-1-ol (75.6 mg, 0.5 mmol, 1.0 equiv) (added as though it were a solid due to the high viscosity), (*Z*)-but-2-ene-1,4-diyl di-*t*-butyl bis(carbonate) (144.17 mg 0.5 mmol, 139.7 μL, 1.0 equiv), Et_3N (151.7 mg, 1.5 mmol, 209.0 μL, 3.0 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (1.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a colorless oil (70.4 mg / 74%).

TLC: R_f = 0.80 with 20:80 Et_2O/hexanes, UV active, stains with $KMnO_4$.

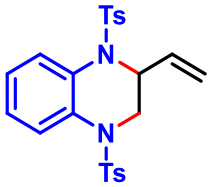
Flash column chromatography: hexanes, then 7:93 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27 – 7.18 (m, 2H), 7.04 (td, *J* = 7.9, 7.2, 1.4 Hz, 2H), 5.91 (ddd, *J* = 17.1, 10.6, 5.6 Hz, 1H), 5.40 (dt, *J* = 17.4, 1.6 Hz, 1H), 5.24 (dt, *J* = 10.7, 1.4 Hz, 1H), 4.23 (dddd, *J* = 9.9, 5.6, 2.6, 1.3 Hz, 1H), 4.05 (ddd, *J* = 11.1, 3.0, 1.9 Hz, 1H), 3.91 (td, *J* = 10.8, 3.0 Hz, 1H), 3.08 – 2.93 (m, 2H), 2.93 – 2.85 (m, 1H), 2.66 (dd, *J* = 11.6, 9.9 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 136.3, 132.7, 131.2, 126.7, 123.6, 119.2, 116.6, 76.9, 56.8, 51.7, 17.9.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{13}H_{18}NO$ 204.1388; found 204.1383.

1,4-Ditosyl-2-vinyl-1,2,3,4-tetrahydroquinoxaline (4c)



The titled compound was obtained according to the procedure in Section 2.2/2.3 using the following quantities: *N*,*N*'-(1,2-phenylene)bis(4-methylbenzenesulfonamide) (208.2 mg, 0.5 mmol, 1.0 equiv), (*Z*)-but-2-ene-1,4-diyl di-*t*-butyl bis(carbonate) (144.17 mg 0.5 mmol, 139.7 μL, 1.0 equiv), Et_3N (151.7 mg, 1.5 mmol, 209.0 μL, 3.0 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (1.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a white solid (218 mg / 93%).

TLC: R_f = 0.50 with 1:3 EtOAc/hexanes, UV active, stains with $KMnO_4$.

Flash column chromatography: hexanes, then 15:85 EtOAc/hexanes.

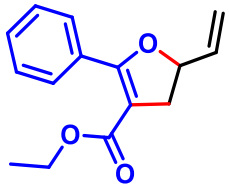
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 – 7.75 (m, 1H), 7.55 (dd, *J* = 9.2, 3.0 Hz, 3H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.20 (dd, *J* = 13.9, 8.0 Hz, 4H), 7.06 – 6.98 (m, 2H), 5.62 (ddd, *J* = 17.3, 10.4, 4.8 Hz, 1H), 5.33 – 5.23

(m, 1H), 5.10 (dd, *J* = 10.6, 1.8 Hz, 1H), 5.06 (dq, *J* = 4.2, 2.2 Hz, 1H), 4.06 (dd, *J* = 12.8, 4.0 Hz, 1H), 3.27 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.38 (d, *J* = 3.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2, 144.2, 136.4, 135.6, 133.4, 130.6, 129.9, 129.8, 127.2, 127.0, 126.0, 125.9, 125.7, 123.7, 119.5, 118.7, 55.7, 47.8, 21.6, 21.5.

Spectra matched those previously reported: Massacret, M.; Lhoste, P.; Sinou, D. *Euro. J. Org. Chem.* **1999**, *1999*, 129–134.

Ethyl 2-phenyl-5-vinyl-4,5-dihydrofuran-3-carboxylate (4d)



The titled compound was obtained according to the procedure in Section 2.2/2.3 using the following quantities: freshly distilled ethyl benzoylacetate (96.1 mg, 0.5 mmol, 86.6 μL, 1.0 equiv), (*Z*)-but-2-ene-1,4-diyl dibenzoate (148.1 mg 0.5 mmol, 1.0 equiv), Et_3N (101.1 mg, 1.0 mmol, 139 μL, 2.0 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (2.0 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a pale yellow oil (71 mg / 58%).

TLC: R_f = 0.50 with 20:80 Et_2O/hexanes, UV active, stains red with vanillin.

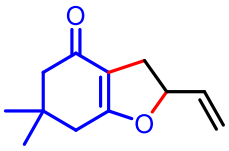
Flash Column chromatography: hexanes, then 5:95 Et_2O/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84 – 7.76 (m, 2H), 7.45 – 7.35 (m, 3H), 6.03 (ddd, *J* = 17.0, 10.4, 6.5 Hz, 1H), 5.42 – 5.22 (m, 2H), 5.22 – 5.13 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.31 (dd, *J* = 15.0, 10.5 Hz, 1H), 2.93 (dd, *J* = 15.0, 8.2 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 164.7, 137.0, 130.4, 130.1, 129.4, 127.7, 116.9, 102.2, 82.0, 59.8, 37.5, 14.3.

Spectra matched those previously reported: Wang, Y.; Zhang, W.-Y.; You, S.-L. *J. Am. Chem. Soc.* **2019**, *141*, 2228–2232.

6,6-Dimethyl-2-vinyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (4e)



The titled compound was obtained according to the procedure in Section 2.2/2.3 using the following quantities: dimedone (70.1 mg, 0.5 mmol, 1.0 equiv), (*Z*)-but-2-ene-1,4-diyl dibenzoate (148.1 mg 0.5 mmol, 1.0 equiv), Et_3N (151.7 mg, 1.5 mmol, 209 μL, 3.0 equiv), methyl formate (30.0 mg, 0.5 mmol,

30.6 μ L, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (1.5 mL), 1000 ppm Pd (20 μ L of stock solution from section 2.1). The desired compound was obtained as a pale yellow oil (76.1 mg / 79%). See scale-up example for large scale trial procedure and purification.

TLC: R_f = 0.30 with 40:60 EtOAc/ hexanes, UV active, stains with $KMnO_4$.

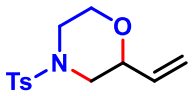
Flash column chromatography: 10:90 EtOAc/hexanes, then 30:70 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.87 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.28 – 5.10 (m, 3H), 3.00 – 2.91 (m, 1H), 2.59 – 2.51 (m, 1H), 2.24 (t, *J* = 1.9 Hz, 2H), 2.16 (s, 2H), 1.04 (d, *J* = 4.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 175.9, 136.3, 117.1, 111.3, 85.8, 50.9, 37.7, 34.0, 31.6, 28.7, 28.6.

Spectra match those previously reported: Tanimori, S.; Kato, Y.; Kirihata, M. *Synthesis* **2006**, 5, 865 – 869.

4-*N*-Tosyl-2-vinylmorpholine (4f)



The titled compound was obtained according to the procedure in Section 2.2/2.3 using the following quantities: *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (107.6 mg, 0.5 mmol, 1.0 equiv), (*Z*)-but-2-ene-1,4-diyl di-*t*-butyl bis(carbonate) (144.2 mg 0.5 mmol, 139.7 μ L, 1.0 equiv), Et_3N (151.7 mg, 1.5 mmol, 209 μ L, 3.0 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μ L, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (1.2 mL), 1000 ppm Pd (20 μ L of stock solution from section 2.1). The desired compound was obtained as a white solid (99.2 mg / 74%). Using the same ratio of reagents, but with (*Z*)-but-2-ene-1,4-diyl dibenzoate as electrophile gave this compound (89.0 mg / 67%).

TLC: R_f = 0.50, running the plate 1/8th of the way with 10:90 MeOH/DCM, drying, then running the plate all the way with 25:75 EtOAc/hexanes (this separates baseline material from the very polar nucleophile). UV active, stains with $KMnO_4$.

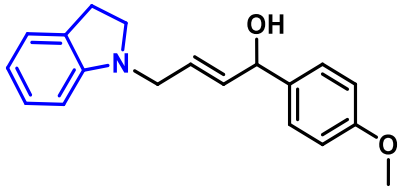
Flash column chromatography: hexanes then 20:80 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 – 7.58 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.70 (ddd, *J* = 17.4, 10.7, 5.4 Hz, 1H), 5.31 (dt, *J* = 17.4, 1.4 Hz, 1H), 5.19 (dt, *J* = 10.7, 1.4 Hz, 1H), 4.03 (dddt, *J* = 8.2, 5.4, 2.6, 1.3 Hz, 1H), 3.93 (ddd, *J* = 11.7, 3.4, 1.6 Hz, 1H), 3.69 (td, *J* = 11.5, 2.7 Hz, 1H), 3.54 (ddt, *J* = 39.4, 11.4, 2.2 Hz, 2H), 2.42 (s, 3H), 2.41 – 2.36 (m, 1H), 2.10 (dd, *J* = 11.4, 10.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.04, 134.75, 132.15, 129.85, 127.90, 117.74, 75.71, 65.76, 50.05, 45.43, 21.60.

Spectra matched those previously reported: Bandini, M.; Monari, M.; Romaniello, A.; Tragni, M. *Chem. Euro. J.* **2010**, *16*, 14272–14277.

(*E*)-4-(Indolin-1-yl)-1-(4-methoxyphenyl)but-2-en-1-ol (5a)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: indoline (59.6 mg, 0.5 mmol, 56.2 μL, 1.0 equiv), 2-(4-methoxyphenyl)-3-vinyloxirane (105.7 mg, 0.6 mmol, 100.1 μL, 1.2 equiv), K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a pale yellow oil which darkens upon exposure to air (139.0 mg / 94%). Note: compound is unstable and decomposes in <30 days.

TLC: R_f = 0.50 with 50:50 EtOAc/hexanes, UV active, stains with vanillin and Seebach's magic stain and $KMnO_4$.

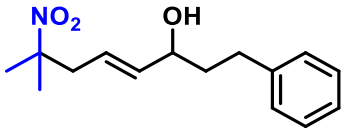
Flash column chromatography: 25:75 EtOAc/hexanes then 50:50 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34 – 7.27 (m, 2H), 7.15 – 7.06 (m, 2H), 6.96 – 6.88 (m, 2H), 6.71 (td, *J* = 7.3, 0.9 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 6.00 – 5.82 (m, 2H), 5.18 (d, *J* = 6.0 Hz, 1H), 3.83 (s, 3H), 3.78 – 3.71 (m, 2H), 3.41 – 3.28 (m, 2H), 2.98 (t, *J* = 8.3 Hz, 2H), 2.37 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 152.1, 135.5, 135.3, 130.3, 127.6, 127.4, 127.3, 127.3, 126.7, 124.5, 117.9, 114.1, 114.0, 107.5, 74.1, 55.3, 53.3, 50.9, 28.6.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{19}H_{22}NO_2$ 296.1650; found 296.1654.

(*E*)-7-Methyl-7-nitro-1-phenyloct-4-en-3-ol (5b)



The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: 2-nitropropane (44.6 mg, 0.5 mmol, 45.4 μL, 1.0 equiv), 2-phenethyl-3-vinyloxirane (95.83 mg, 0.55 mmol, 97.2 μL, 1.1 equiv), Et_3N (151.8 mg, 1.5 mmol, 3.0 equiv), methyl formate (30.0 mg, 0.5 mmol, 30.6 μL, 1.0 equiv), 2 wt % TPGS-750-M / H_2O (0.5 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a colorless oil (89.0 mg / 68%). Note: compound is unstable and decomposes in <30 days.

TLC: R_f = 0.25 with 25:75 EtOAc/hexanes, UV active, stains blue with vanillin, and also stains with Seebach's magic stain and $KMnO_4$.

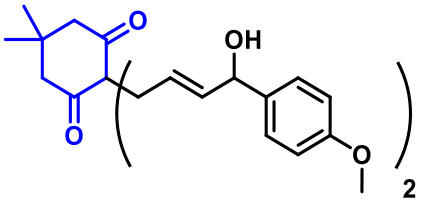
Flash column chromatography: hexanes then 20:80 EtOAc/hexanes.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 5.69 – 5.62 (m, 1H), 5.61 – 5.51 (m, 1H), 4.11 (q, *J* = 6.4 Hz, 1H), 2.70 (tdt, *J* = 13.8, 9.2, 6.7 Hz, 2H), 2.62 (d, *J* = 7.2 Hz, 2H), 2.03 – 1.93 (m, 1H), 1.91 – 1.76 (m, 2H), 1.59 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 138.9, 128.5, 128.5, 128.4, 128.4, 128.4, 125.9, 123.6, 88.0, 71.6, 43.5, 38.7, 31.6, 25.6, 25.5.

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{15}H_{21}NO_3Na$ 286.1419; found 286.1417.

2,2-bis((*E*)-4-Hydroxy-4-(4-methoxyphenyl)but-2-en-1-yl)-5,5-dimethylcyclohexane-1,3-dione (5c)



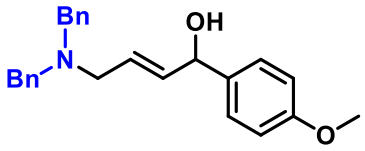
The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: dimedone (70.1 mg, 0.5 mmol, 1.0 equiv), 2-(4-methoxyphenyl)-3-vinyloxirane (88.1 mg, 0.50 mmol, 83.4 μL, 1.0 equiv), Et_3N (152 mg, 1.5 mmol, 210 μL, 3.0 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL), 1000 ppm Pd (20 μL of stock solution from Section 2.1). The desired compound was obtained as a pale yellow oil (119.7 mg / 97%, using the electrophile as limiting reagent).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.21 – 7.15 (m, 4H), 6.85 – 6.80 (m, 4H), 5.67 (dd, *J* = 15.3, 6.4 Hz, 2H), 5.52 – 5.43 (m, 2H), 5.00 (d, *J* = 6.3 Hz, 2H), 3.76 (s, 6H), 2.65 – 2.53 (m, 2H), 2.44 (td, *J* = 8.5, 7.9, 2.7 Hz, 8H), 0.86 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.07, 208.97, 208.86, 159.05, 137.62, 135.17, 135.16, 127.60, 127.59, 124.85, 124.81, 113.89, 113.86, 74.14, 68.17, 68.14, 55.32, 51.99, 37.21, 37.18, 30.74, 28.69.

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{30}H_{36}O_6Na$ 515.2410; found 515.2408.

(*E*)-4-(Dibenzylamino)-1-(4-methoxyphenyl)but-2-en-1-ol (5d)



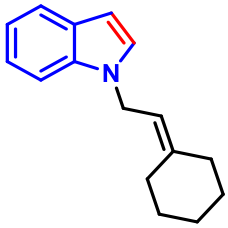
The titled compound was obtained according to the procedure in Section 2.2 using the following quantities: dibenzylamine (98.6 mg, 0.5 mmol, 96.1 μL, 1.0 equiv), 2-(4-methoxyphenyl)-3-vinyloxirane (88.1 mg, 0.5 mmol, 83.4 μL, 1.0 equiv), Et_3N (101.1 mg, 1.0 mmol, 126.5 μL, 2.0 equiv), 2 wt % TPGS-750-M / H_2O (1.0 mL), 1000 ppm Pd (20 μL of stock solution from section 2.1). The desired compound was obtained as a pale yellow oil (274.4 mg / 74%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 – 7.43 (m, 4H), 7.42 – 7.35 (m, 5H), 7.35 – 7.29 (m, 4H), 6.96 – 6.90 (m, 2H), 5.89 (q, *J* = 2.4 Hz, 2H), 5.20 – 5.16 (m, 1H), 3.84 (s, 3H), 3.66 (s, 4H), 3.16 (q, *J* = 1.8 Hz, 2H), 2.23 (s, 1H), 2.10 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.07, 139.64, 135.49, 135.37, 128.85, 128.66, 128.25, 127.58, 126.90, 113.91, 74.21, 58.13, 55.28, 55.19.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{25}H_{27}NO_2H$ 374.2120; found 374.2124.

1-(2-Cyclohexylideneethyl)-1H-indole (6a)



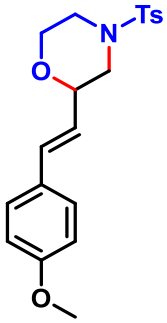
See Section 2.4 for experimental details.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.50 (d, *J* = 3.1 Hz, 1H), 5.35 (t, *J* = 7.1 Hz, 1H), 4.72 (d, *J* = 7.0 Hz, 2H), 2.36 (s, 2H), 2.14 (s, 2H), 1.67 – 1.57 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 136.1, 128.9, 127.4, 121.4, 121.0, 119.3, 116.6, 109.6, 101.0, 43.4, 37.1, 29.1, 28.5, 27.9, 26.8.

HRMS (CI-TOF) *m/z*: $[M]^+$ calculated for $C_{16}H_{19}N$ 225.1517; found 225.1525.

(*E*)-2-(4-Methoxystyryl)-4-tosylmorpholine (6b)



See Section 2.4 for experimental details.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 – 7.61 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 2H), 6.86 – 6.80 (m, 2H), 6.59 (dd, *J* = 16.1, 1.2 Hz, 1H), 5.90 (dd, *J* = 16.0, 6.1 Hz, 1H), 4.21 – 4.15 (m, 1H), 3.97 (ddd, *J* = 11.6, 3.6, 1.6 Hz, 1H), 3.78 (s, 3H), 3.77 – 3.72 (m, 1H), 3.65 (dt, *J* = 11.5, 2.3 Hz, 1H), 3.54 (dq, *J* = 11.6, 2.2 Hz, 1H), 2.47 – 2.39 (m, 4H), 2.20 (dd, *J* = 11.5, 10.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 144.0, 132.4, 132.2, 129.8, 128.9, 127.9, 127.8, 123.3, 114.1, 75.8, 65.8, 55.3, 50.5, 45.4, 21.6.

Spectra matched those previously reported: Aubineau, T.; Cossy, J. *Org. Lett.* **2018**, *20*, 7419–7423.

6. NMR Spectra

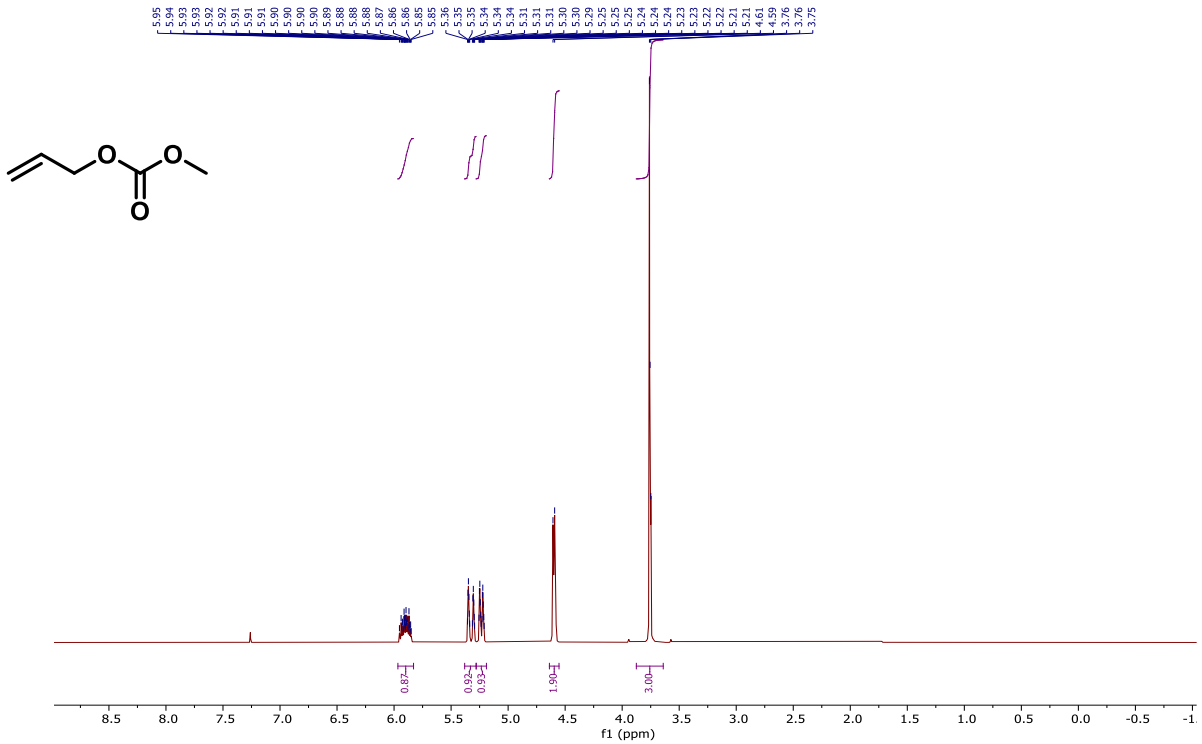


Figure 3: ^{1}H NMR (400 MHz, $CDCl_3$) of allyl methyl carbonate (**1**)

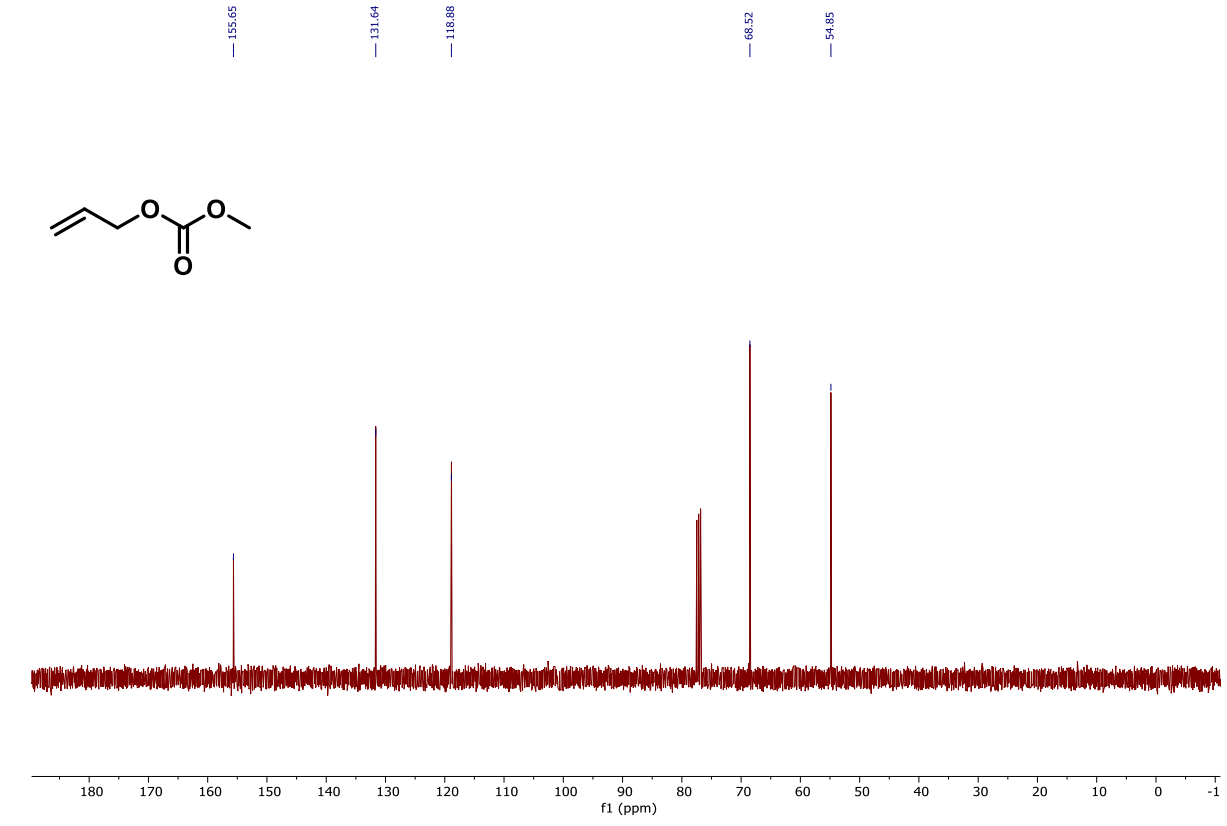


Figure 4: ^{13}C NMR (101 MHz, $CDCl_3$) of allyl methyl carbonate (**1**)

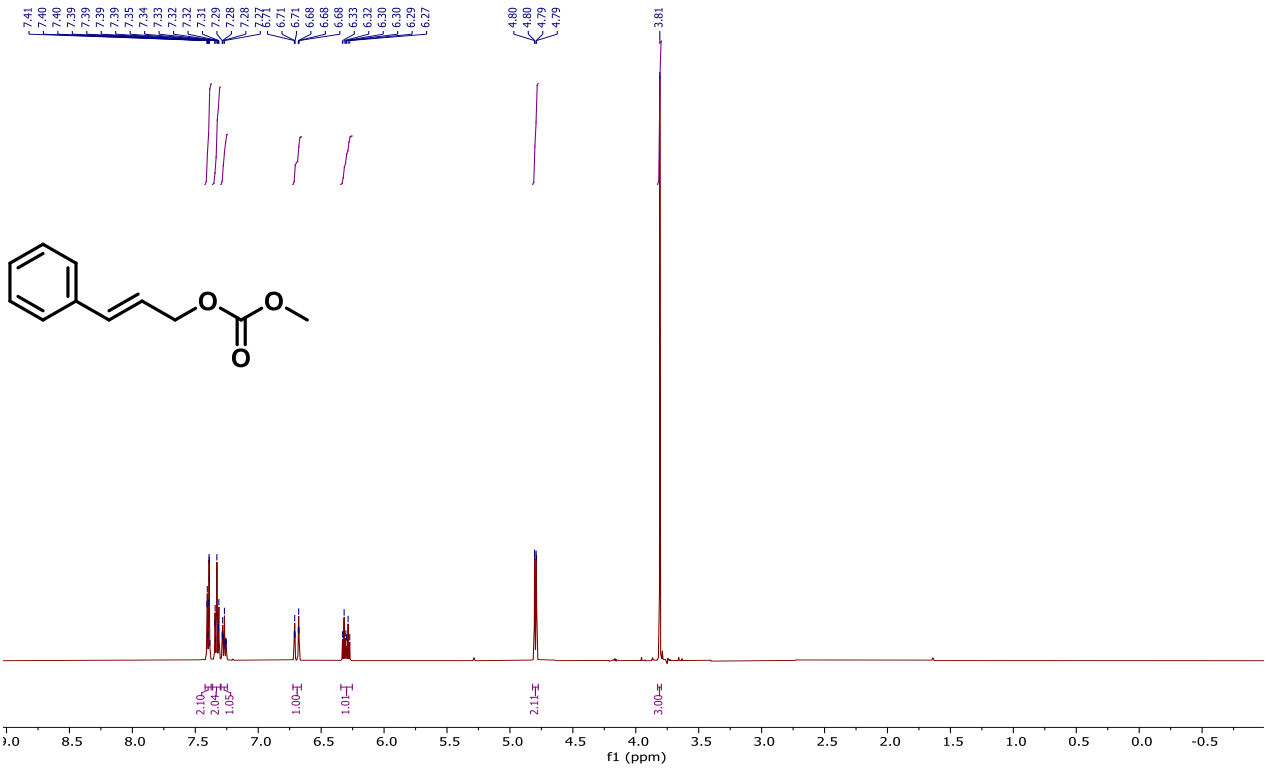


Figure 5: ^{1}H NMR (500 MHz, $CDCl_3$) of cinnamyl methyl carbonate (**2**)

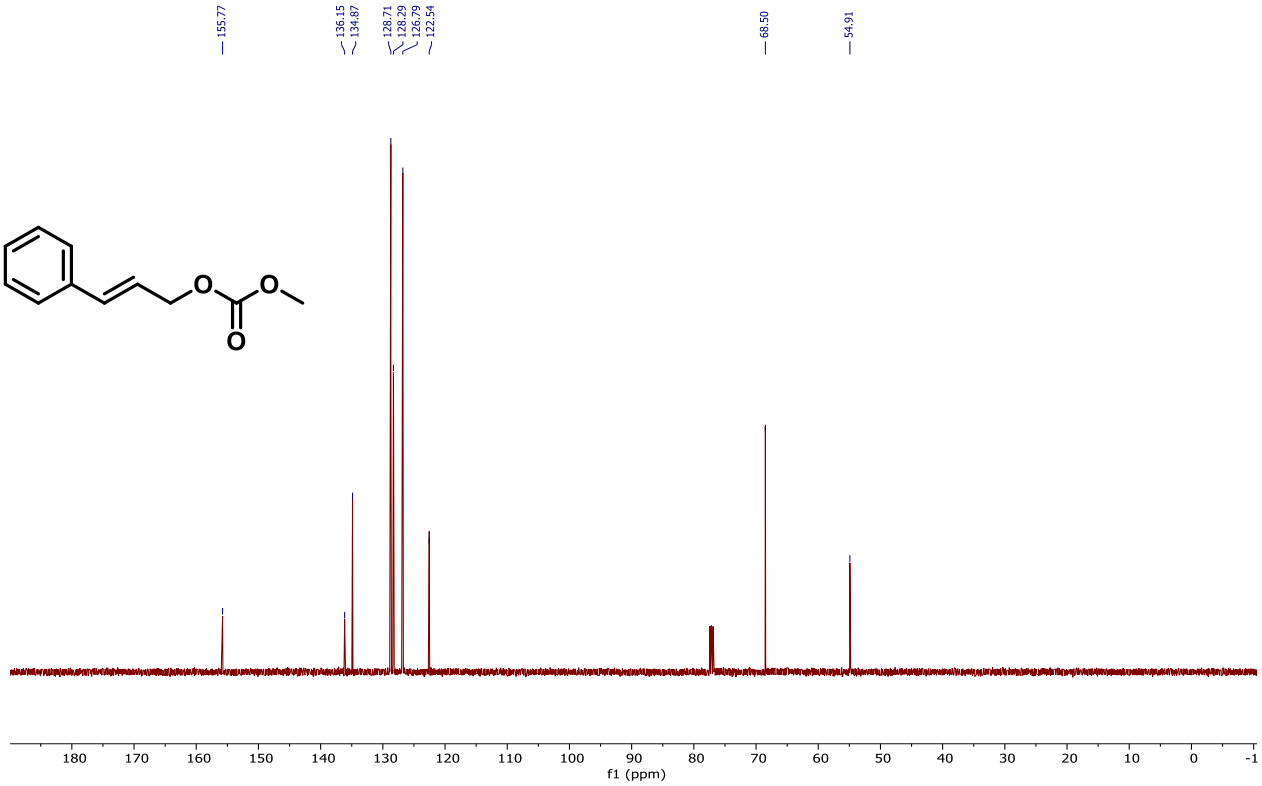


Figure 6: ^{1}H NMR (500 MHz, $CDCl_3$) of cinnamyl methyl carbonate (**2**)

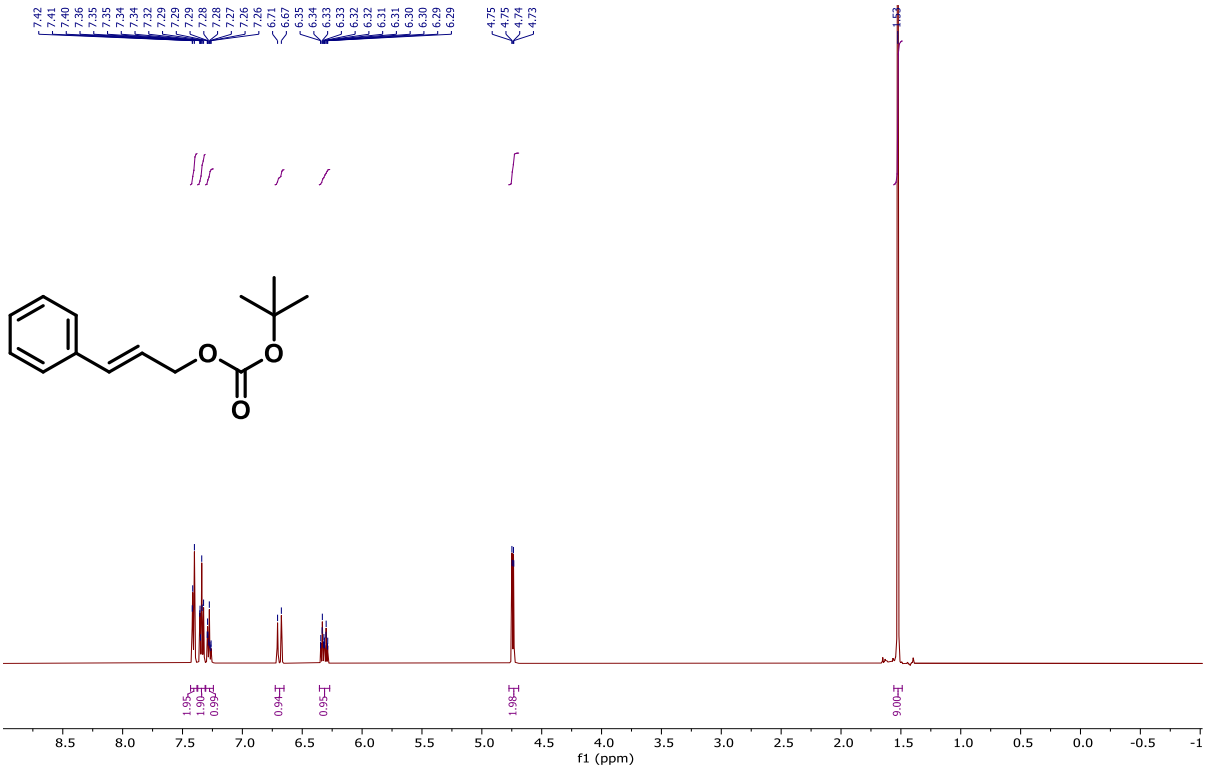


Figure 7: ^{1}H NMR (500 MHz, $CDCl_3$) of Cinnamyl *t*-butyl carbonate (**3**)

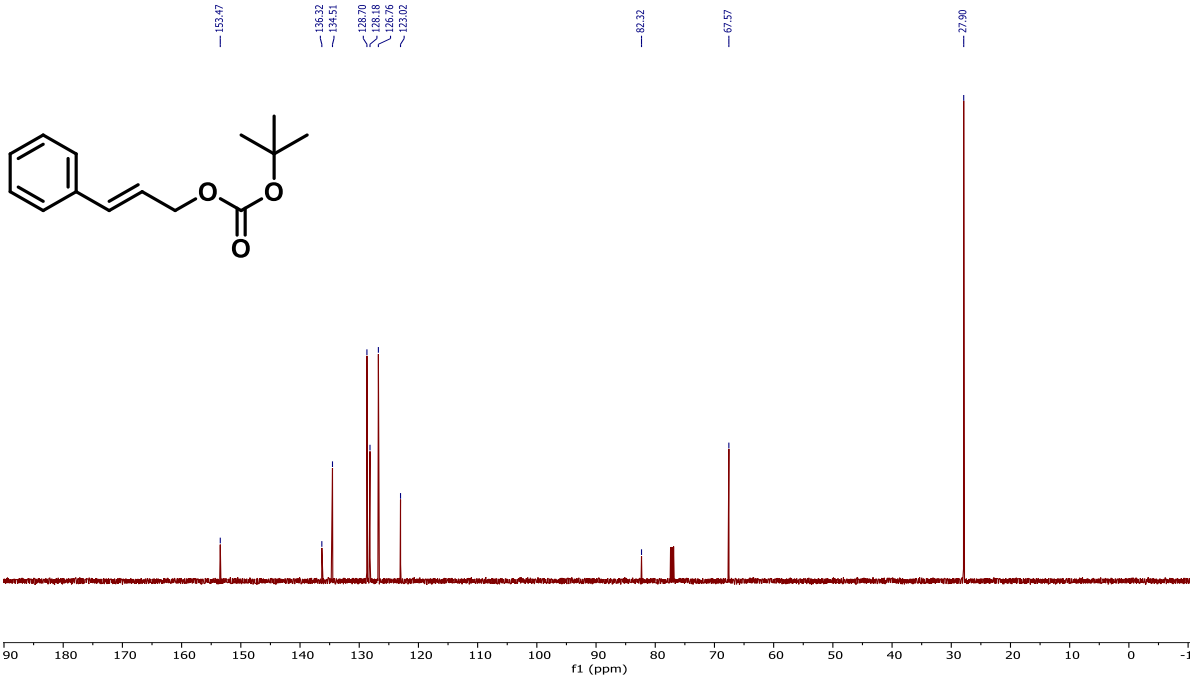


Figure 8: ^{13}C NMR (126 MHz, $CDCl_3$) of Cinnamyl *t*-butyl carbonate (**3**)

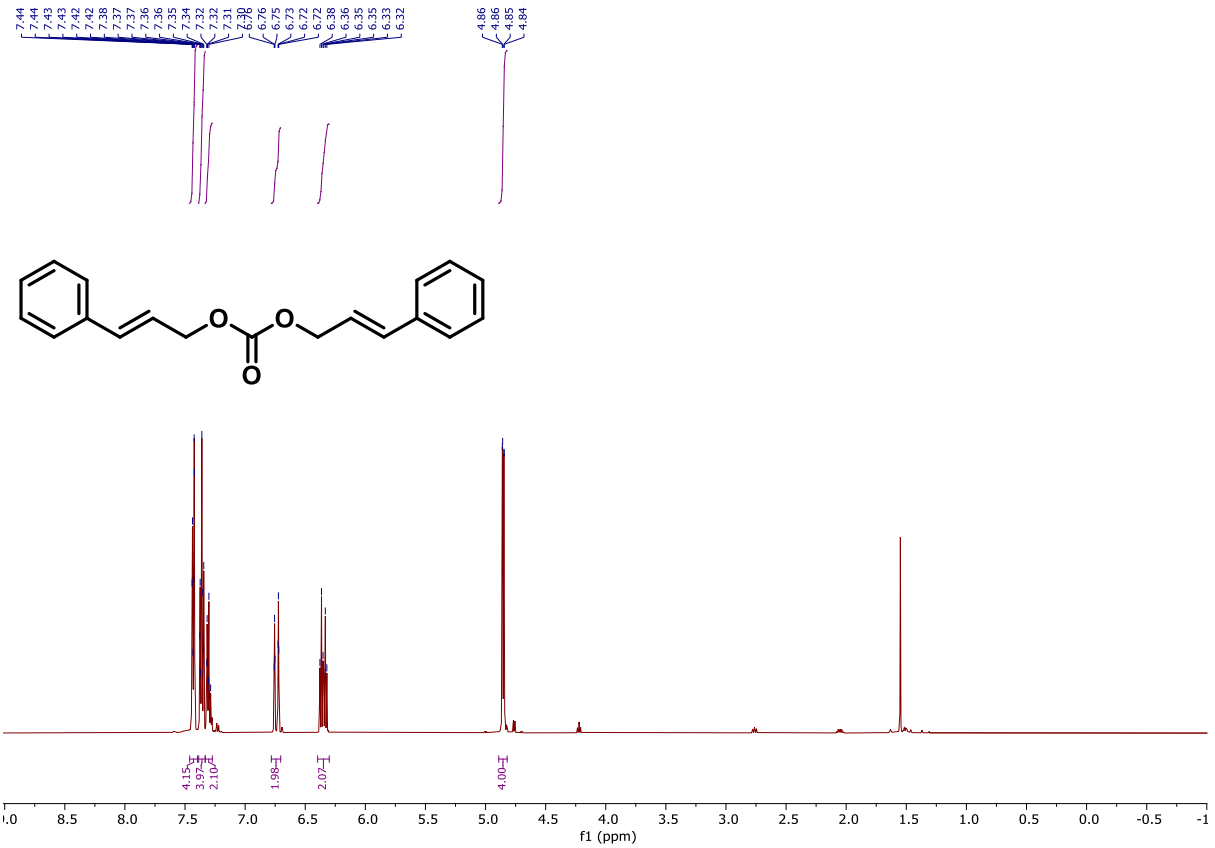


Figure 9: ^{1}H NMR (500 MHz, $CDCl_3$) of dicinnamyl carbonate (**4**)

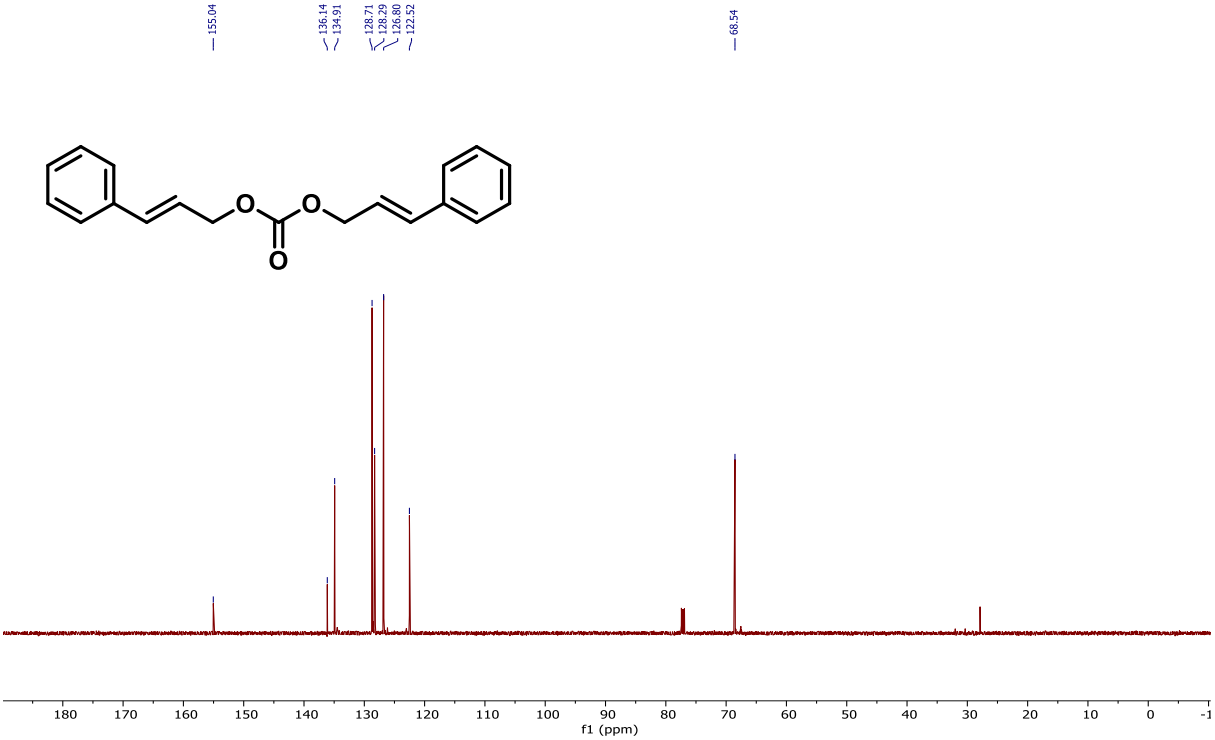


Figure 10: ^{13}C NMR (126 MHz, $CDCl_3$) of dicinnamyl carbonate (**4**)

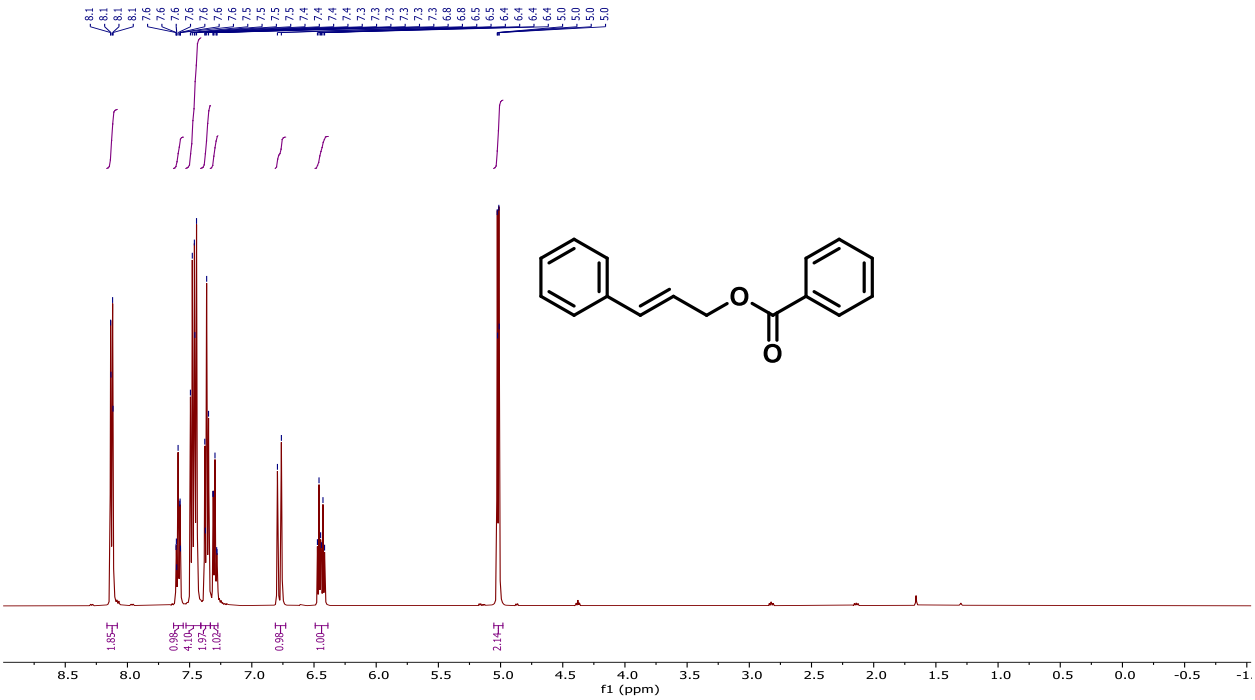


Figure 11: ^{1}H NMR (500 MHz, $CDCl_3$) of cinnamyl benzoate (**5**)

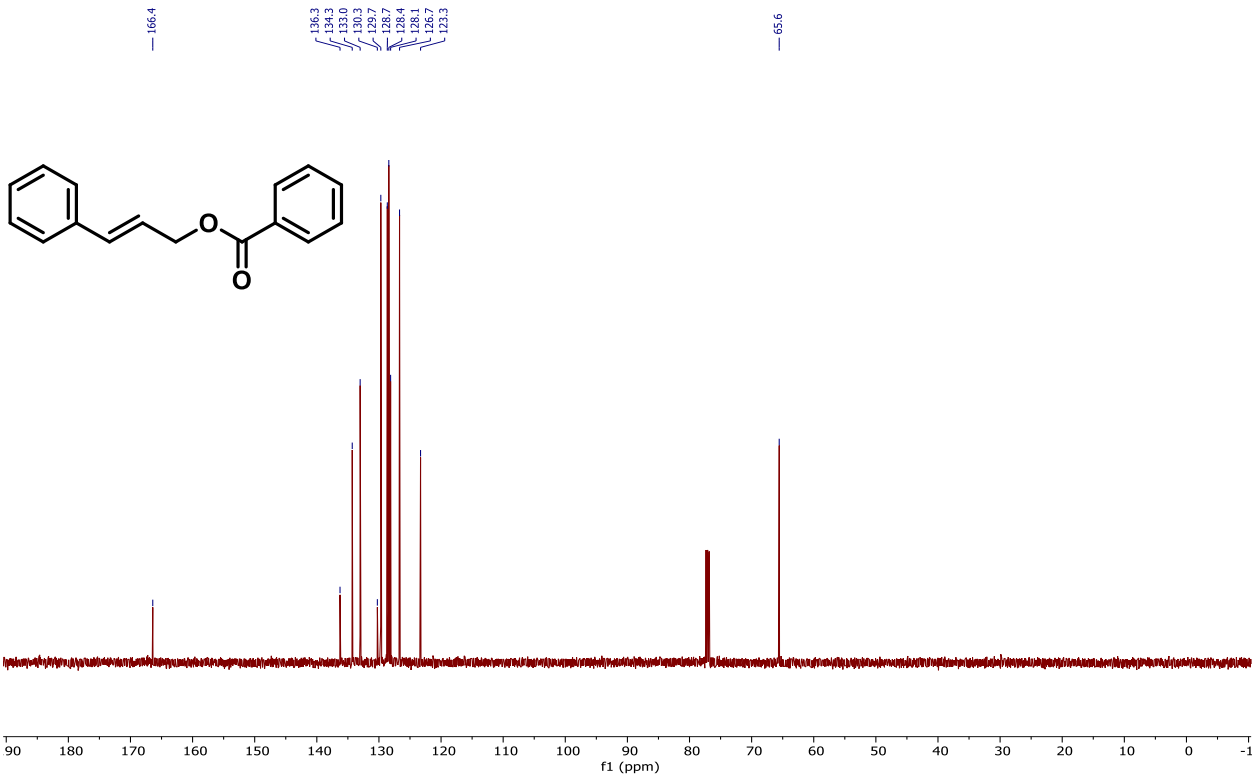


Figure 12: ^{13}C NMR (126 MHz, $CDCl_3$) of cinnamyl benzoate (**5**)

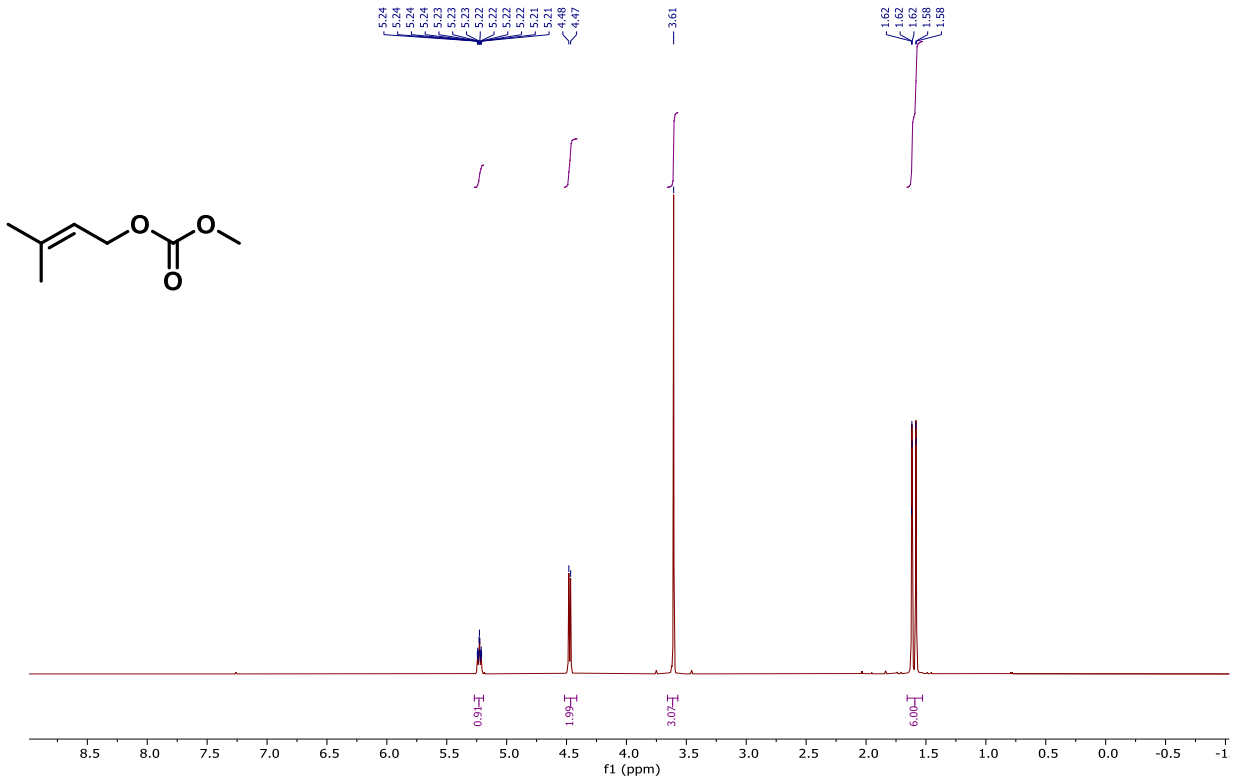


Figure 13: ^{1}H NMR (500 MHz, $CDCl_3$) of methyl (3-methylbut-2-en-1-yl) carbonate (**6**)

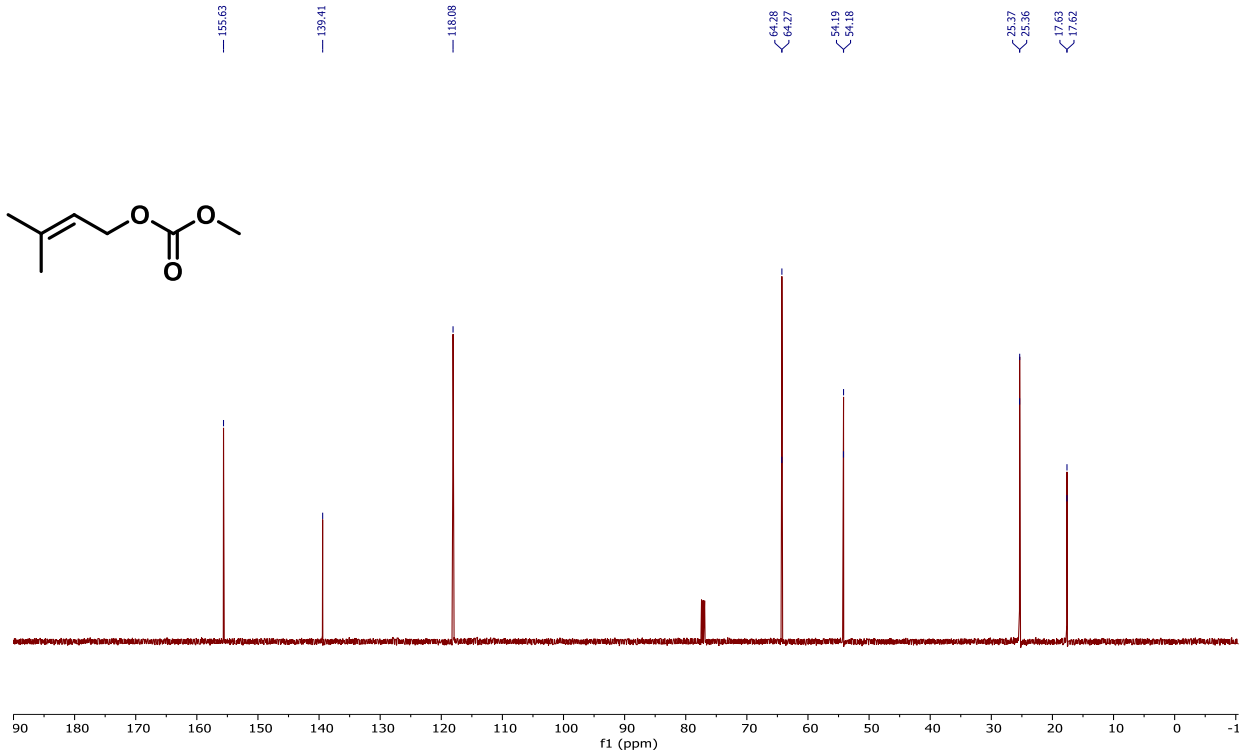


Figure 14: ^{13}C NMR (126 MHz, $CDCl_3$) of methyl (3-methylbut-2-en-1-yl) carbonate (**6**)

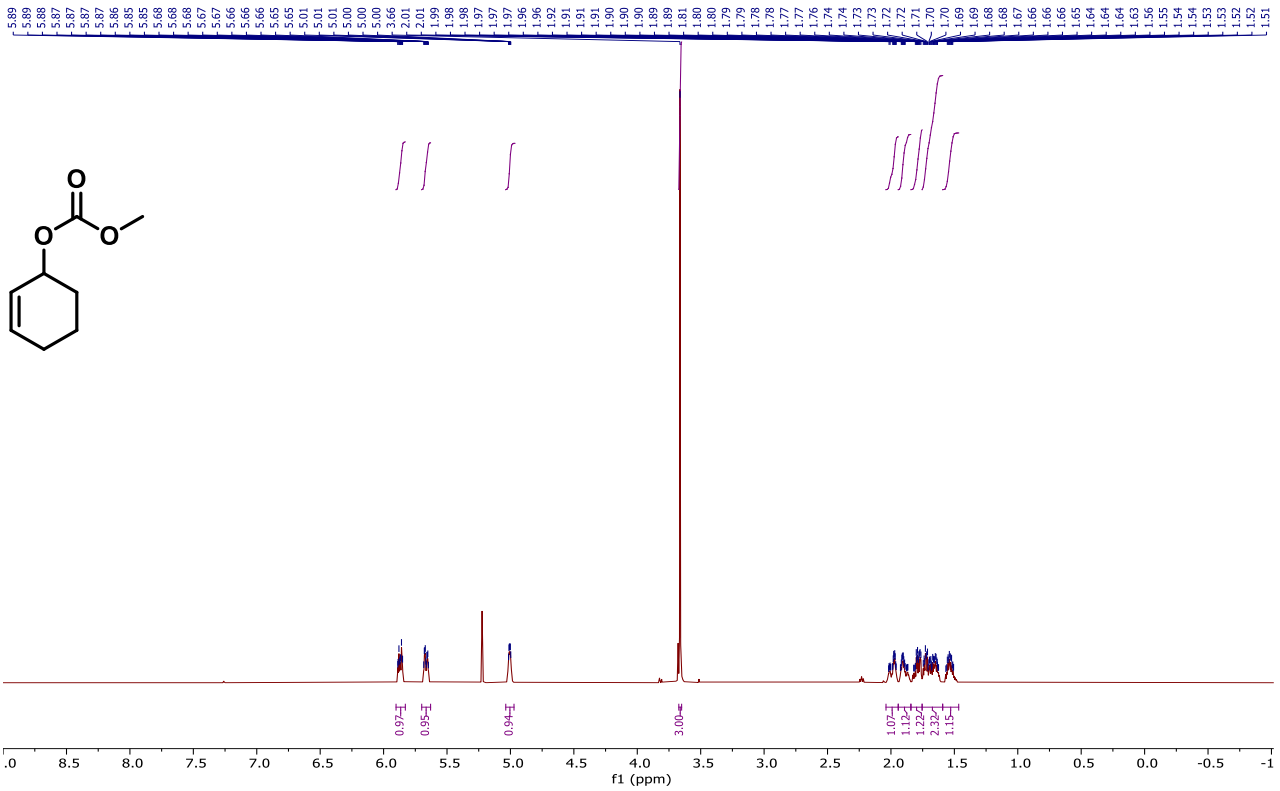


Figure 15: ^{1}H NMR (500 MHz, $CDCl_3$) of cyclohex-2-en-1-yl methyl carbonate (**7**)

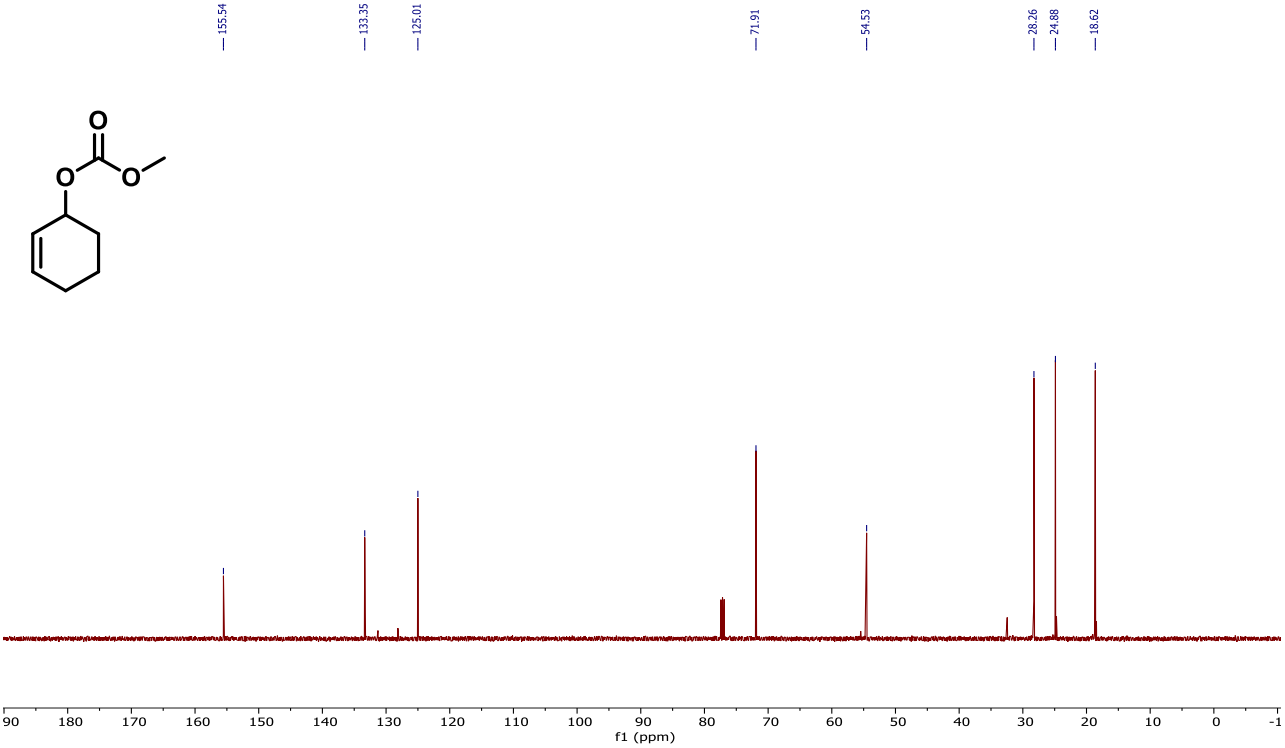


Figure 16: ^{13}C NMR (126 MHz, $CDCl_3$) of cyclohex-2-en-1-yl methyl carbonate (**7**)

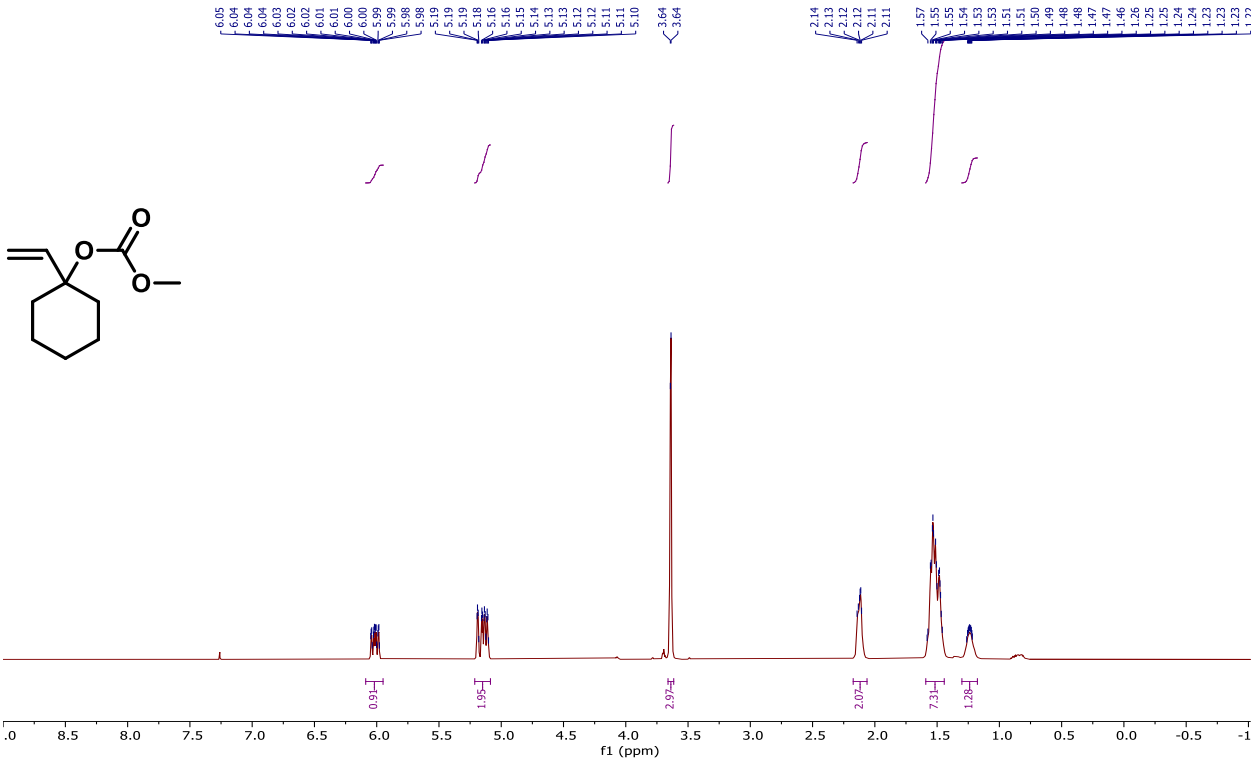


Figure 17: ^{1}H NMR (500 MHz, $CDCl_3$) of methyl (1-vinylcyclohexyl) carbonate (**8**)

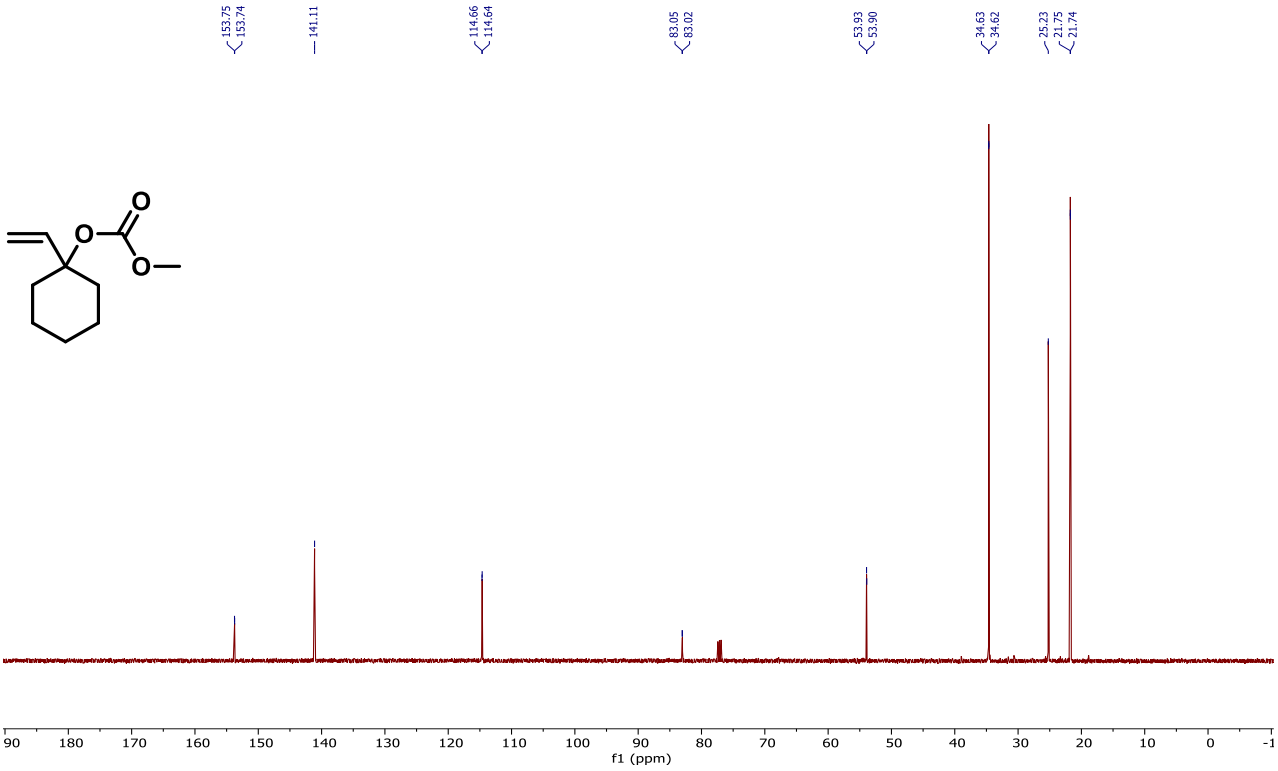


Figure 18: ^{13}C NMR (126 MHz, $CDCl_3$) of methyl (1-vinylcyclohexyl) carbonate (**8**)

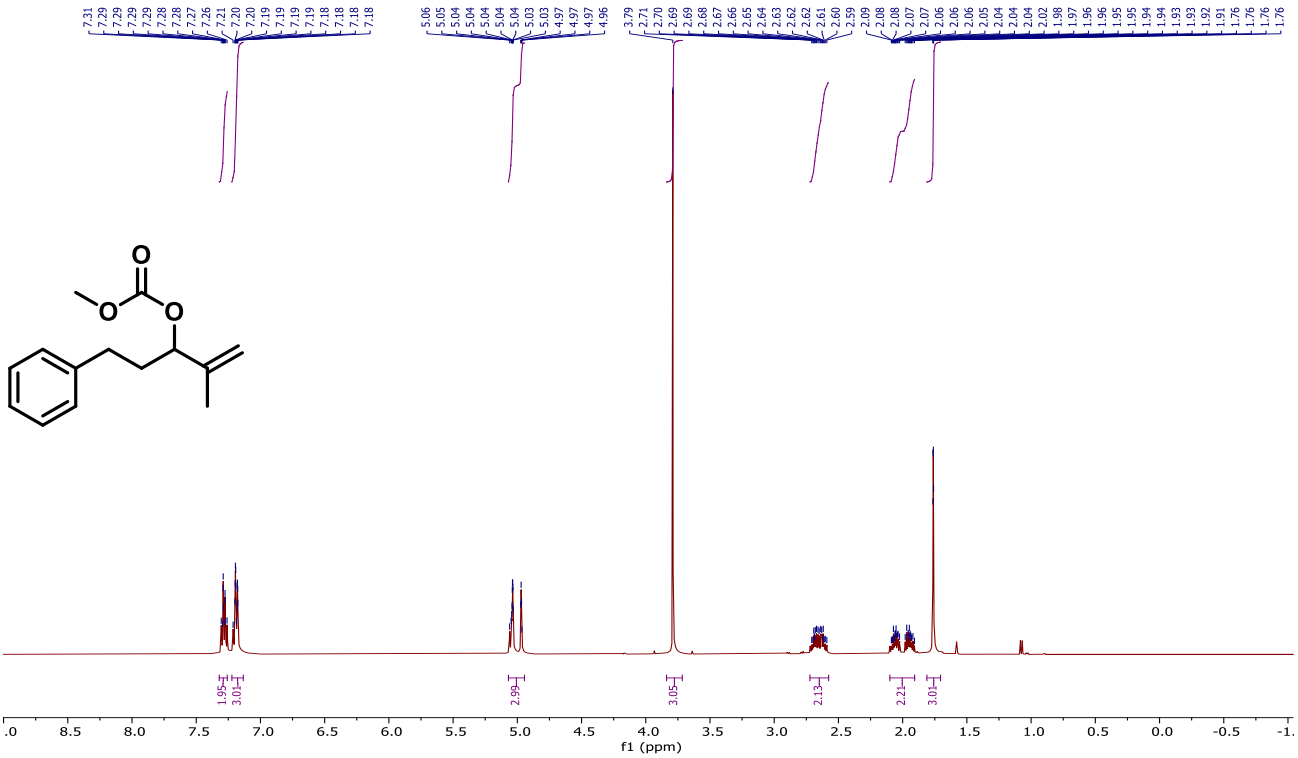


Figure 19: ^{1}H NMR (500 MHz, $CDCl_3$) of methyl (2-methyl-5-phenylpent-1-en-3-yl) carbonate (**9**)

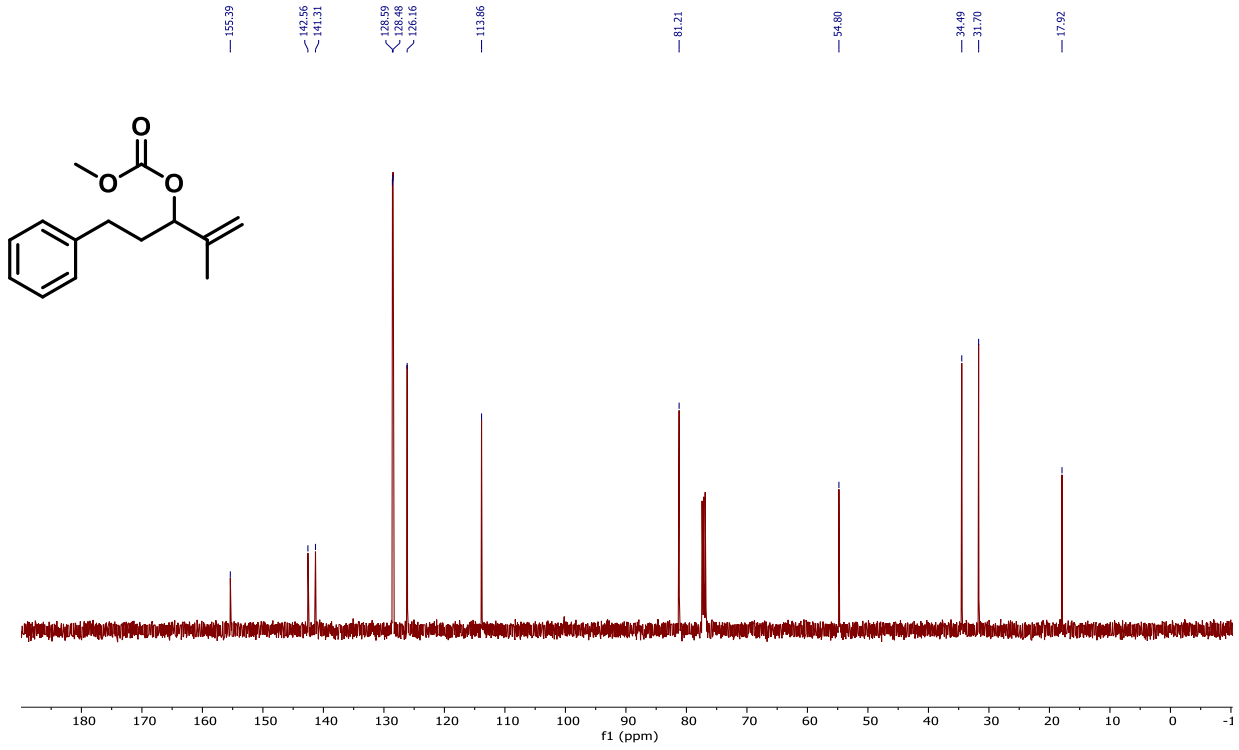


Figure 20: ^{13}C NMR (126 MHz, $CDCl_3$) of methyl (2-methyl-5-phenylpent-1-en-3-yl) carbonate (**9**)

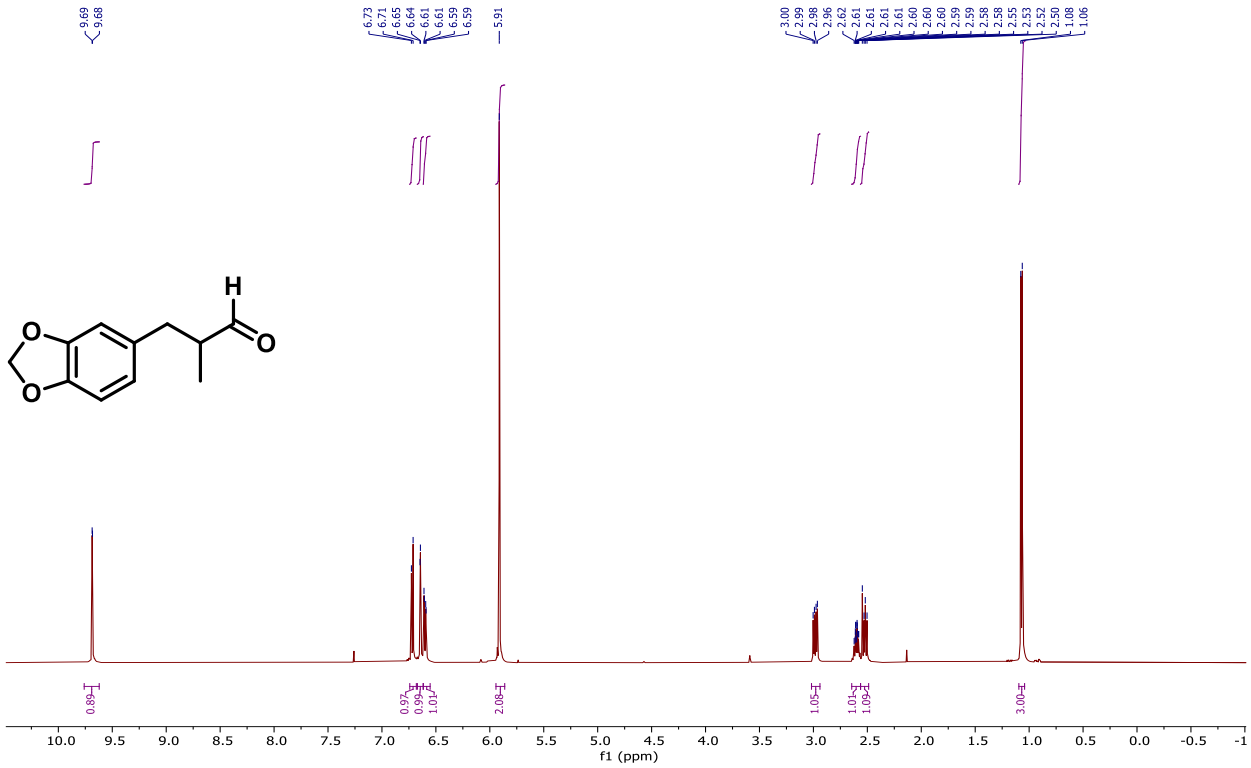


Figure 21: ^{1}H NMR (500 MHz, $CDCl_3$) of helional (**10**)

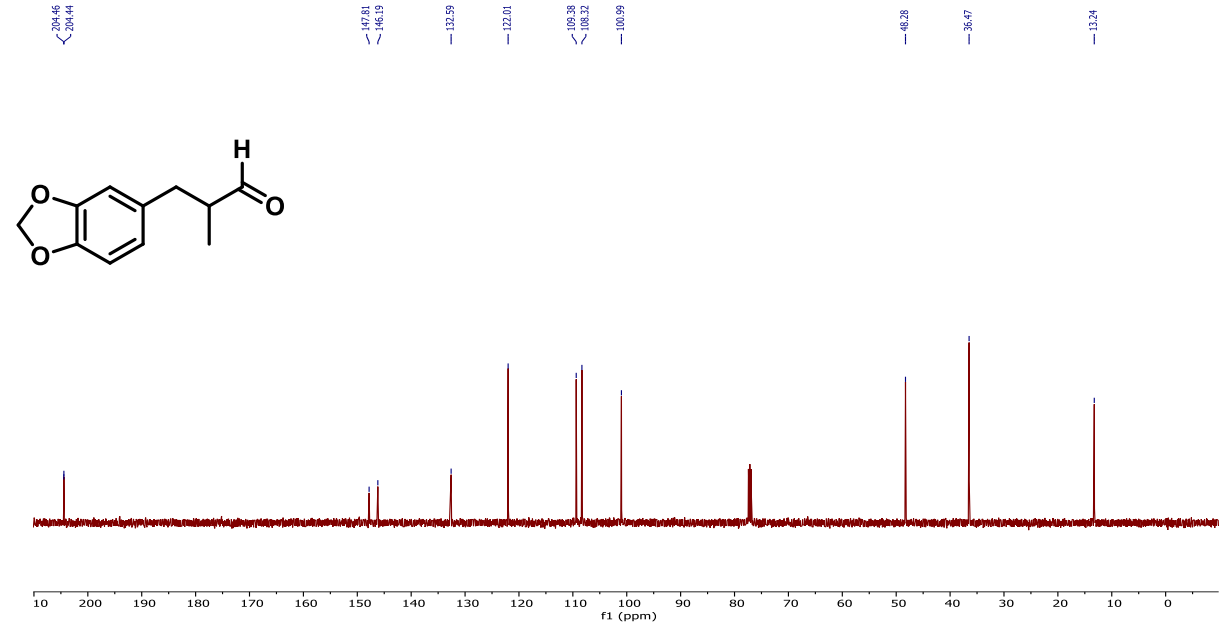


Figure 22: ^{1}H NMR (500 MHz, $CDCl_3$) of helional (**10**)

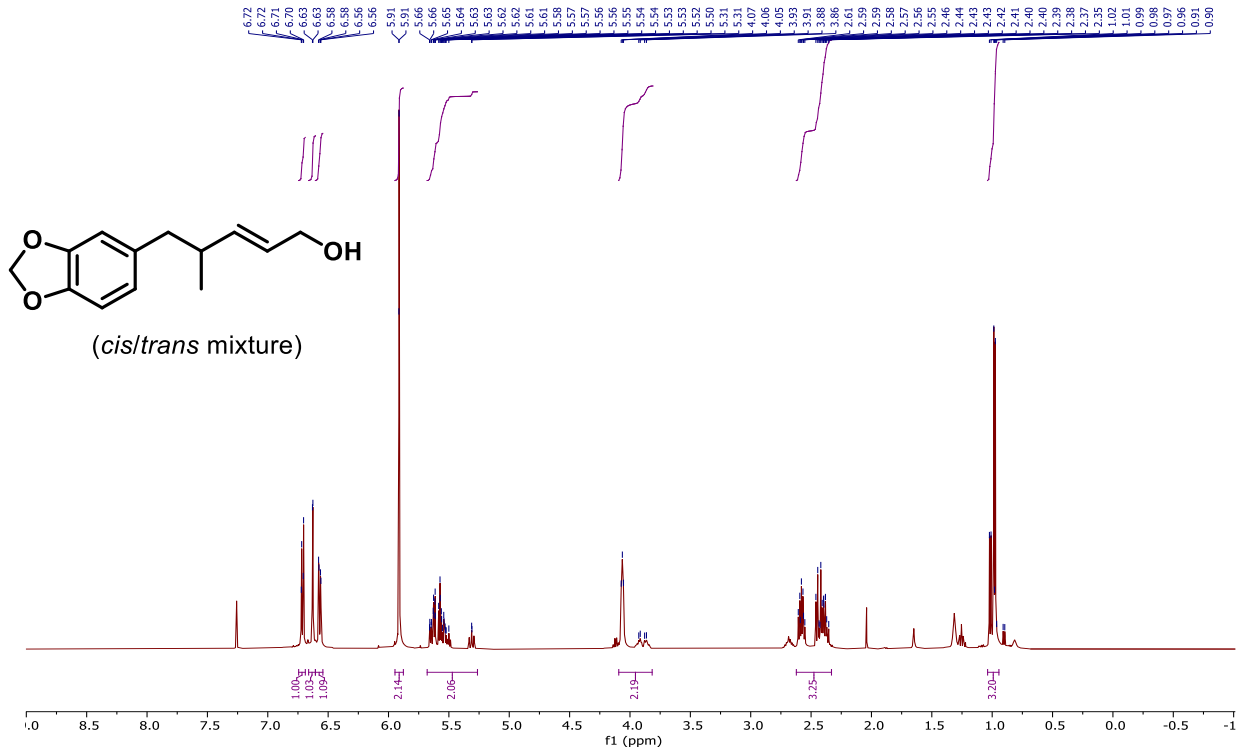


Figure 23: ^{1}H NMR (500 MHz, $CDCl_3$) of alcohol intermediate (**11**)

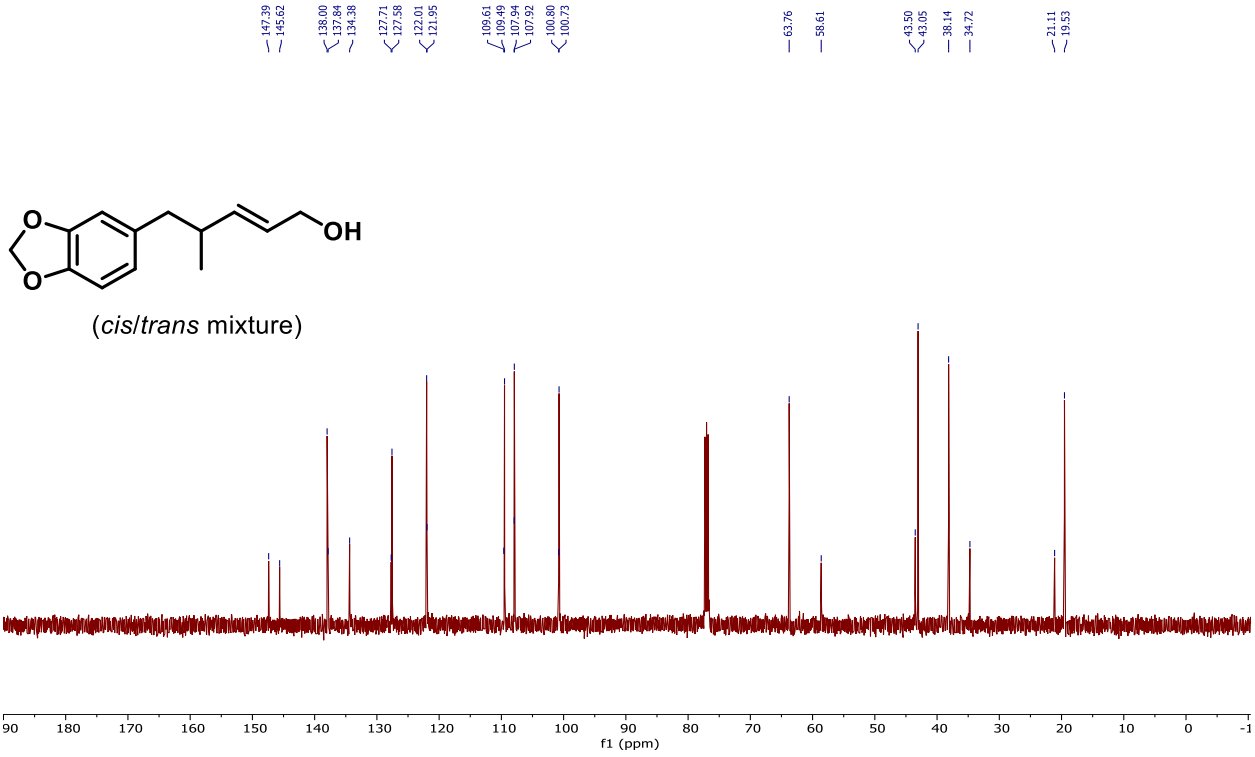


Figure 24: ^{13}C NMR (126 MHz, $CDCl_3$) of alcohol intermediate (**11**)

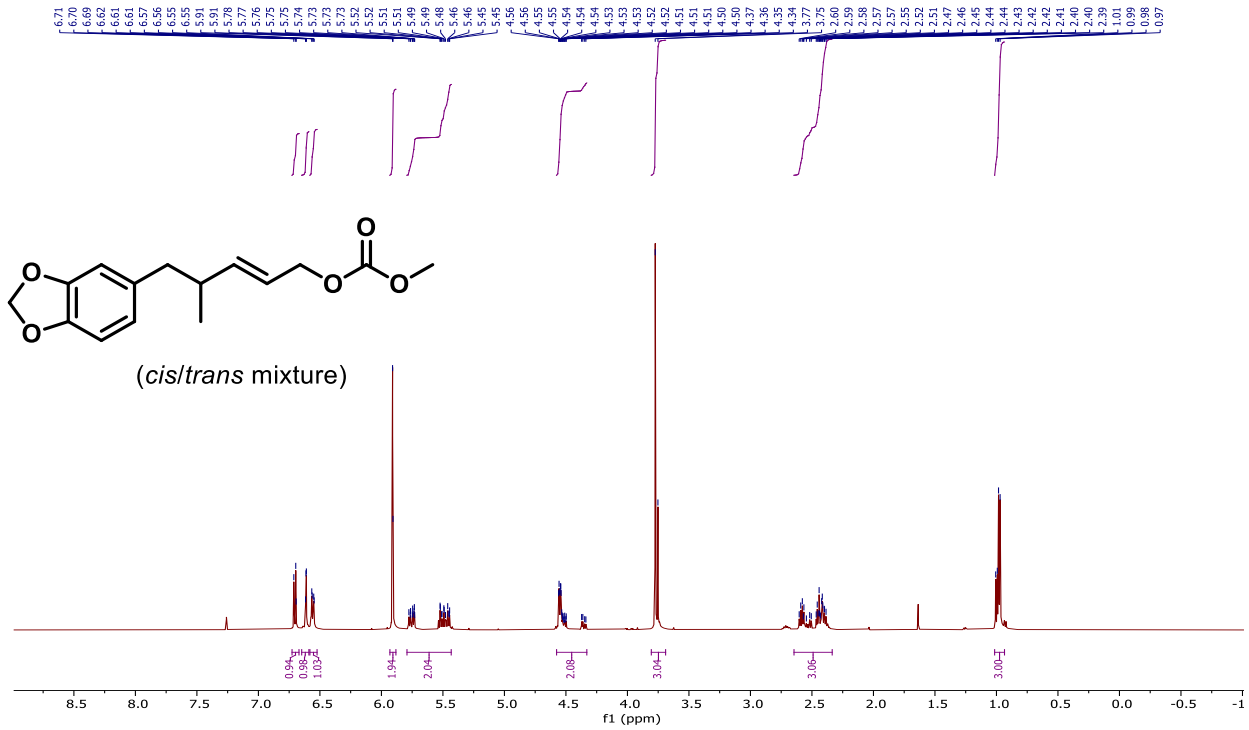


Figure 25: ^{1}H NMR (500 MHz, $CDCl_3$) of 5-(benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl methyl carbonate (**12**)

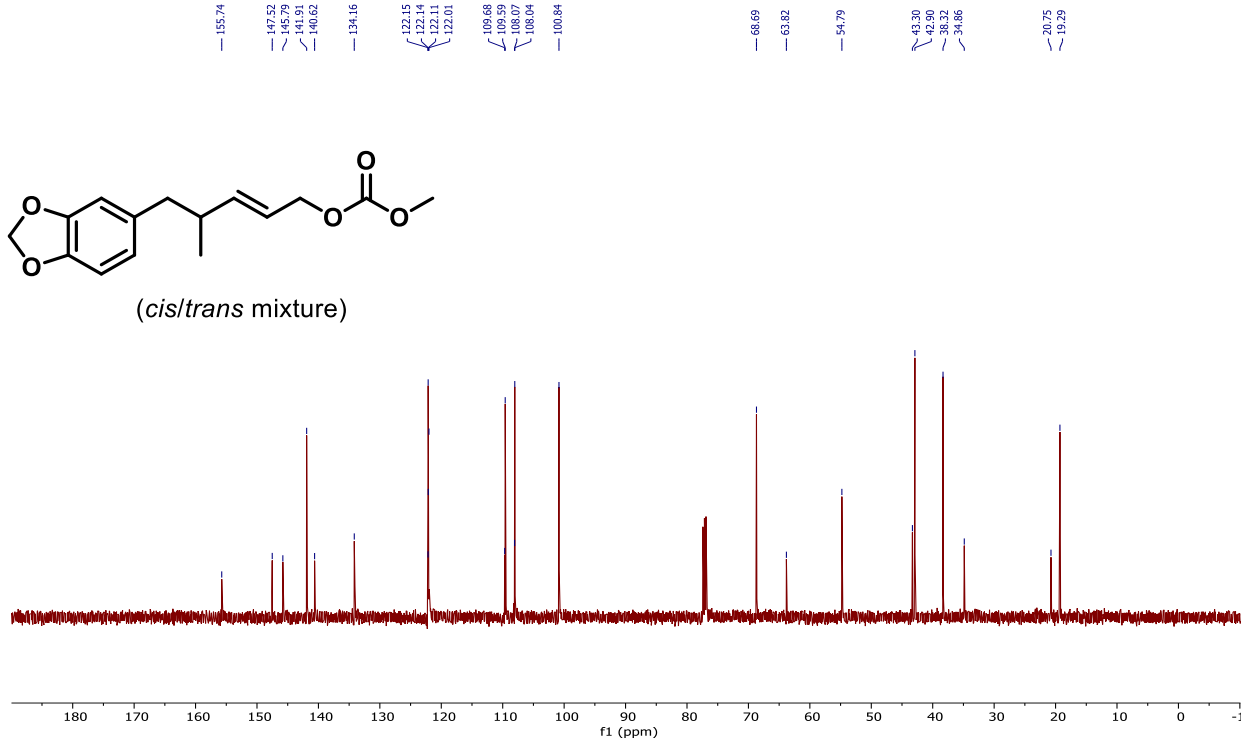


Figure 26: ^{13}C NMR (126 MHz, $CDCl_3$) of 5-(benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl methyl carbonate (**12**)

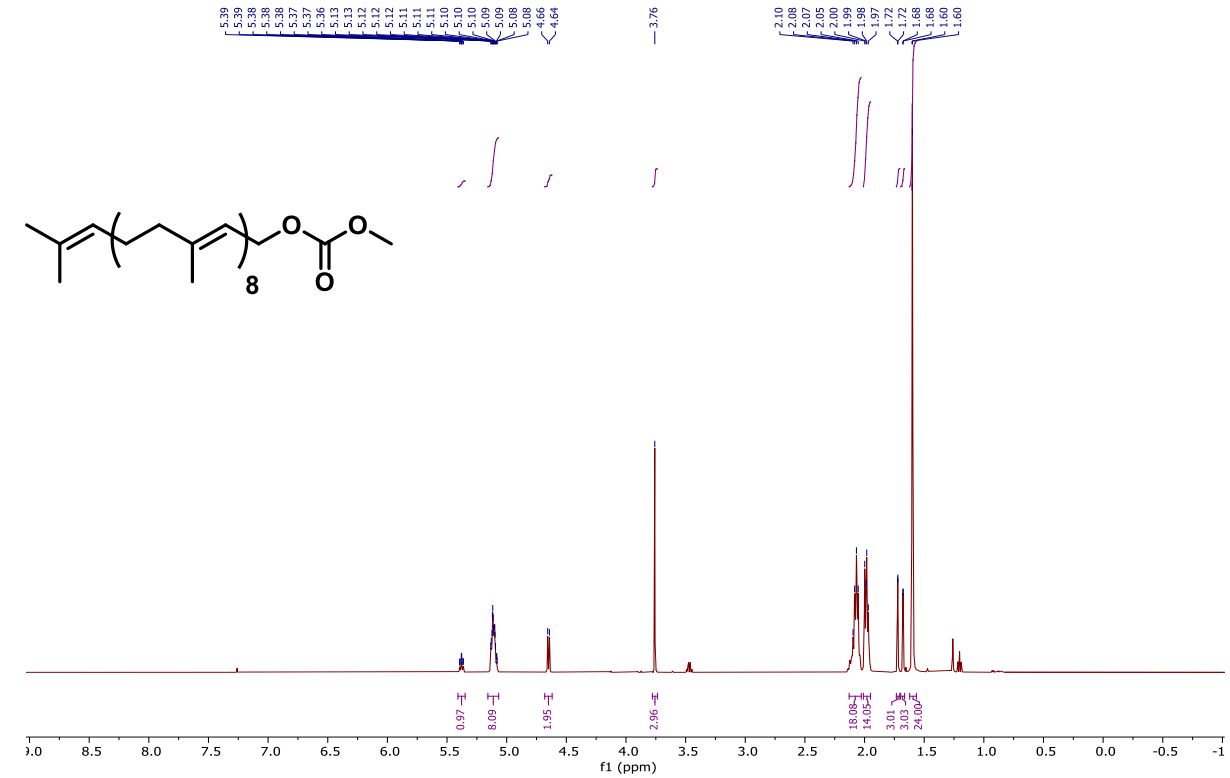


Figure 27: ^{1}H NMR (500 MHz, $CDCl_3$) of solanesyl methyl carbonate (**13**)

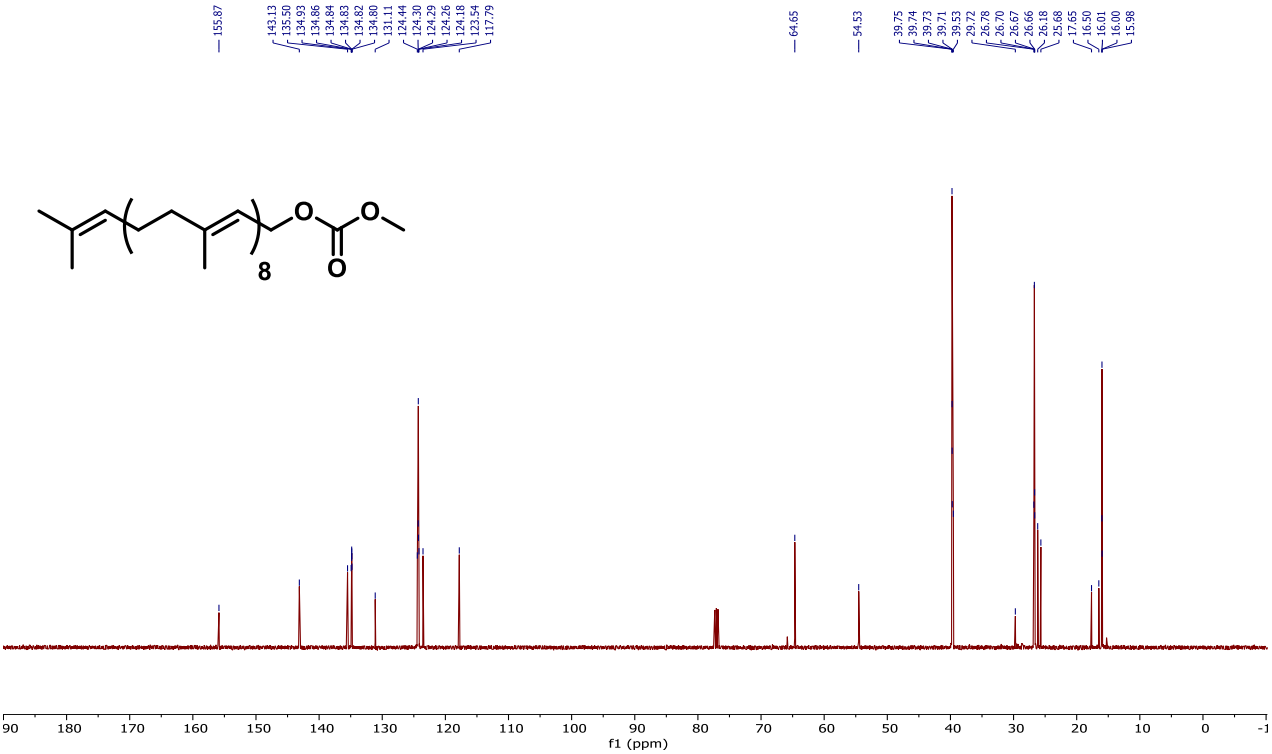


Figure 28: ^{13}C NMR (126 MHz, $CDCl_3$) of solanesyl methyl carbonate (**13**)

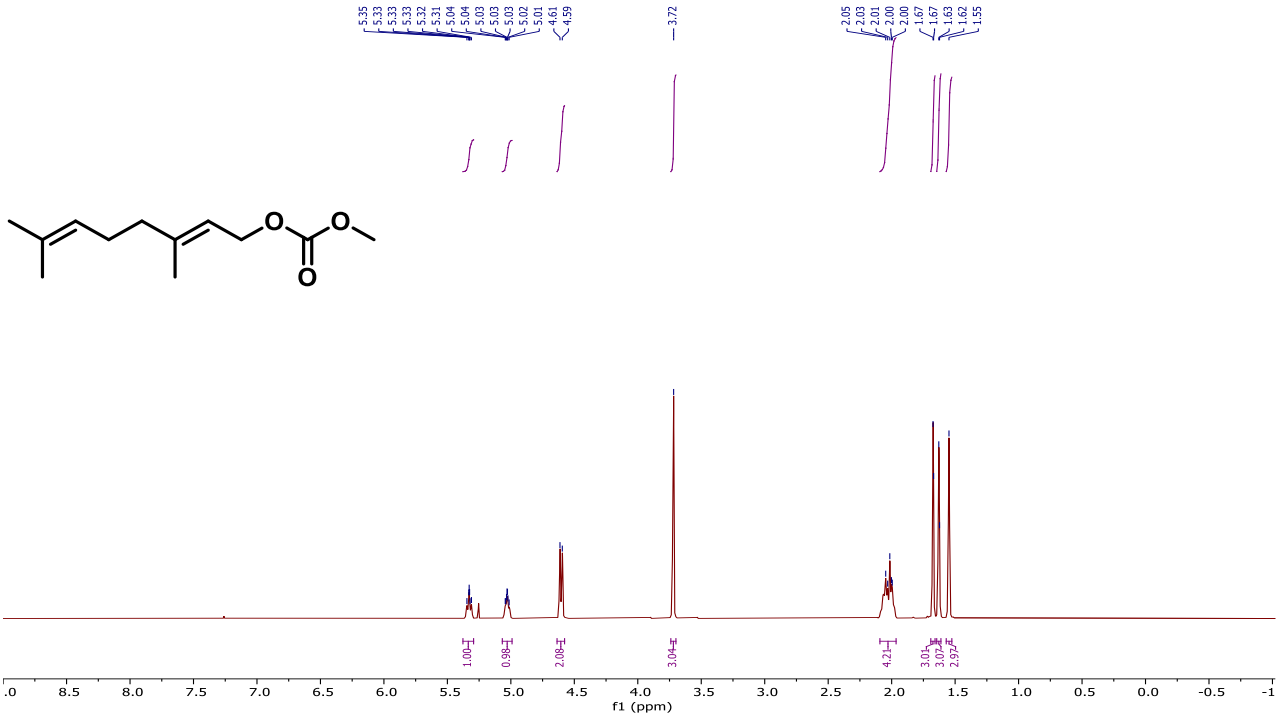


Figure 28: ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-3,7-dimethylocta-2,6-dien-1-yl methyl carbonate (**14**)

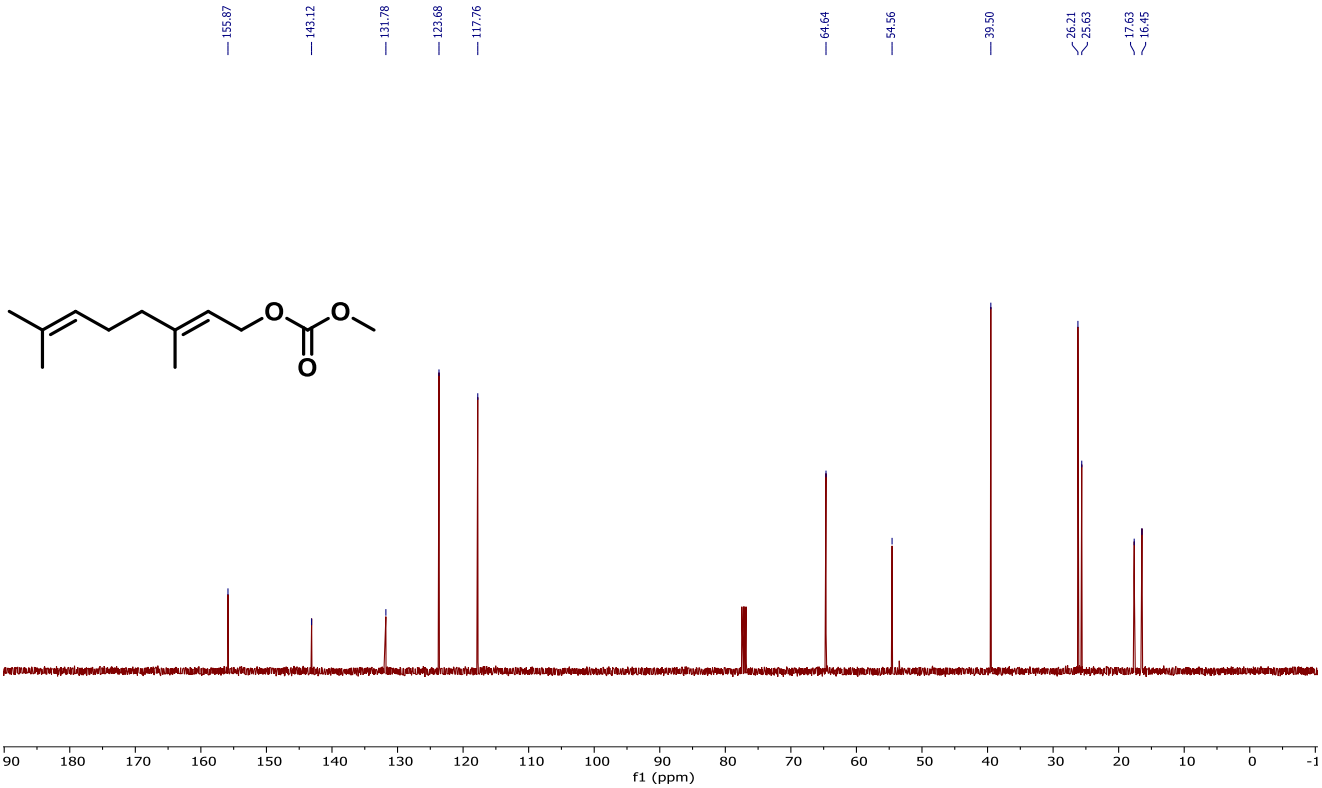


Figure 29: ^{13}C NMR (101 MHz, $CDCl_3$) of (*E*)-3,7-dimethylocta-2,6-dien-1-yl methyl carbonate (**14**)

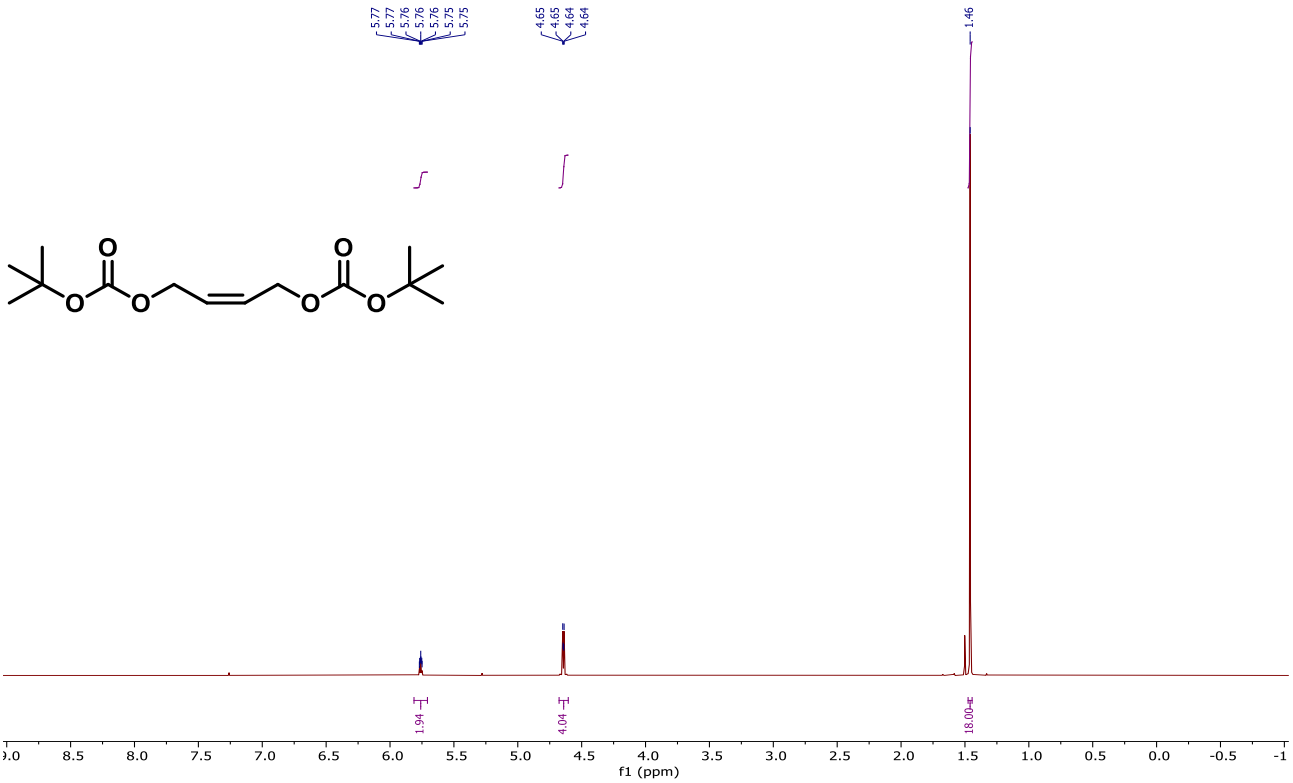


Figure 30: ^{1}H NMR (500 MHz, $CDCl_3$) of (*Z*)-but-2-ene-1,4-diyl di-*t*-butyl bis(carbonate) (**15**)

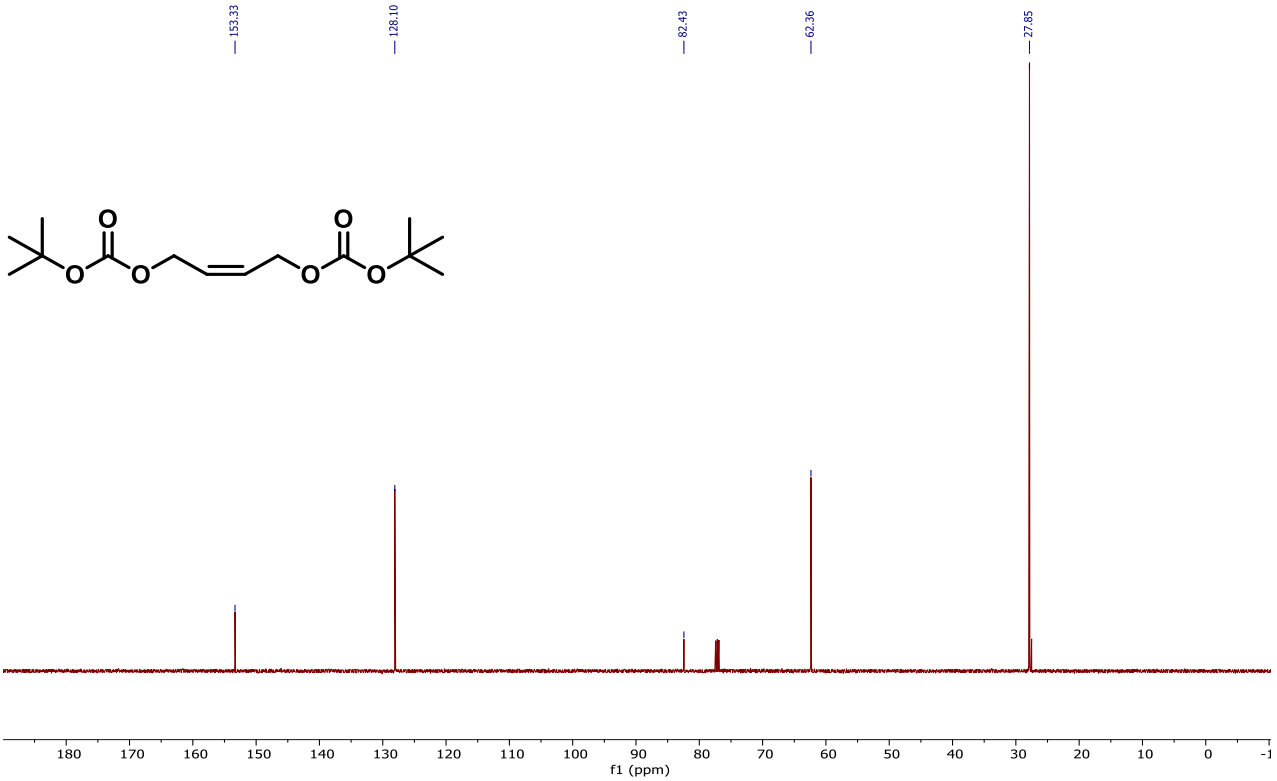


Figure 31: ^{13}C NMR (126 MHz, $CDCl_3$) of (*Z*)-but-2-ene-1,4-diyl di-*t*-butyl bis(carbonate) (**15**)

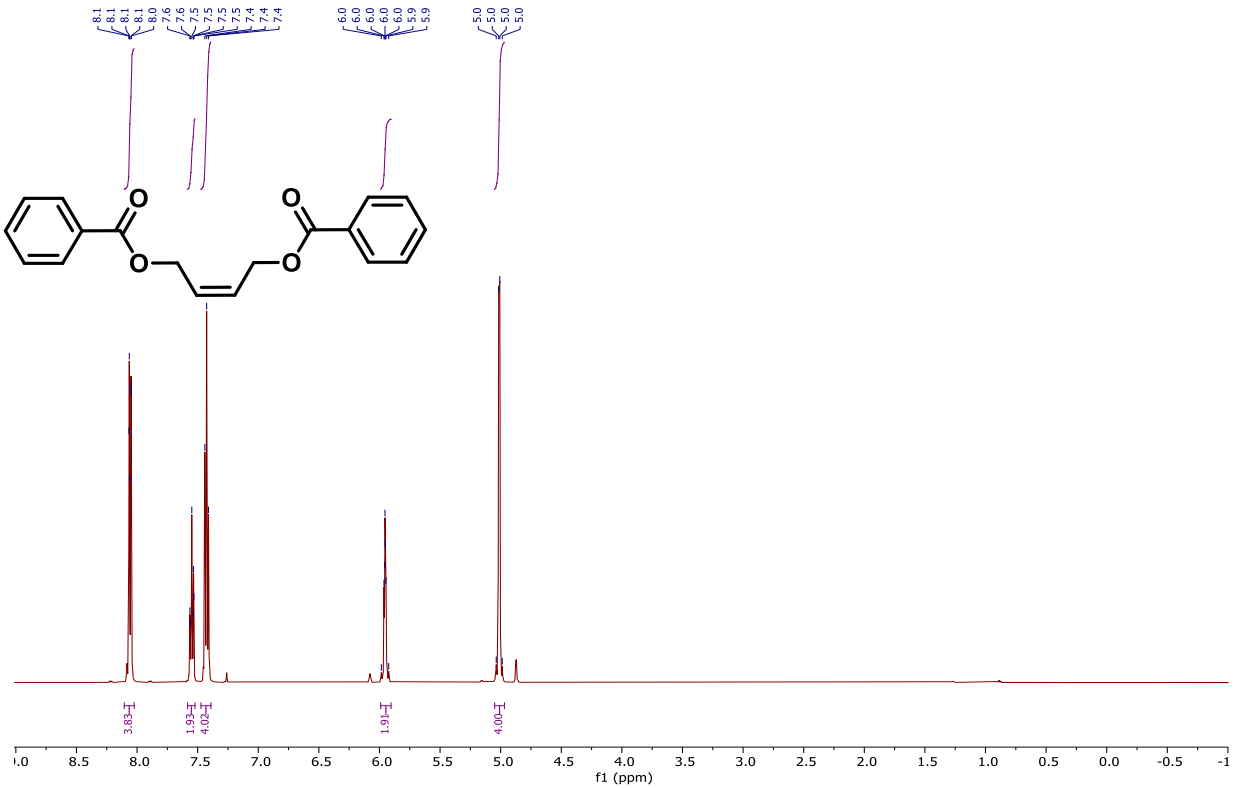


Figure 32: ^{1}H NMR (500 MHz, $CDCl_3$) of (*Z*)-but-2-ene-1,4-diyl dibenzoate (**16**)

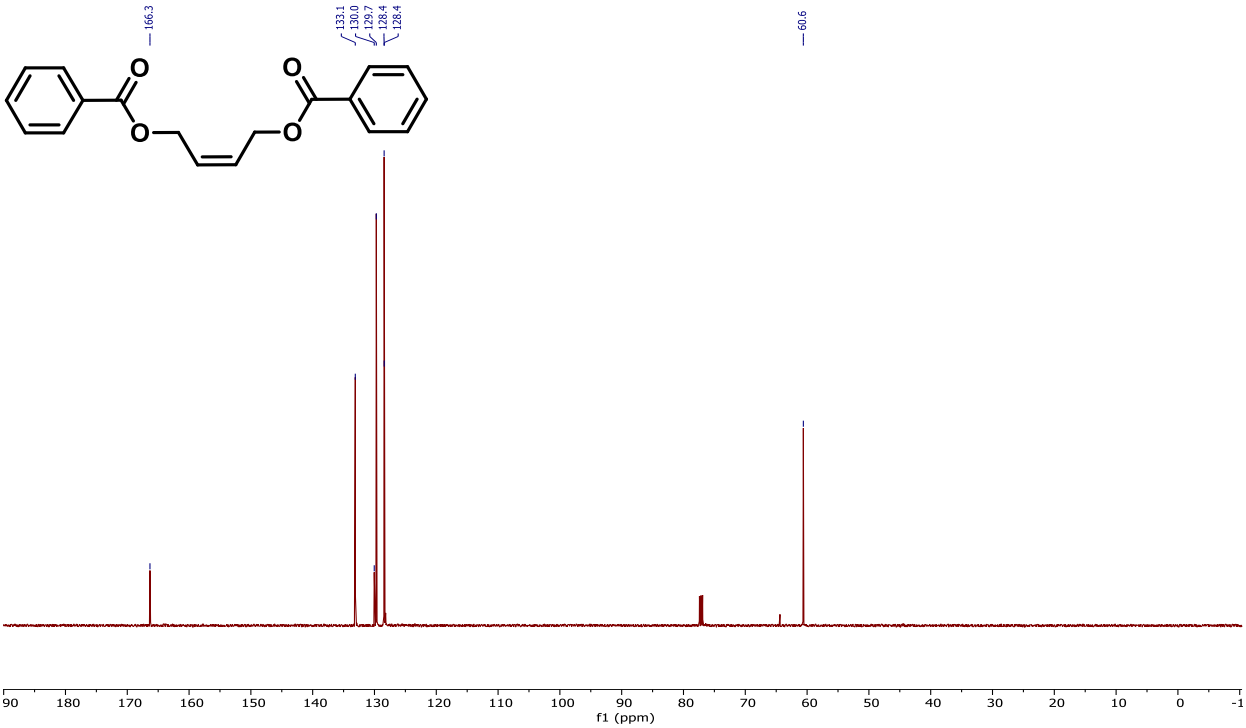


Figure 33: ^{13}C NMR (126 MHz, $CDCl_3$) of (*Z*)-but-2-ene-1,4-diyl dibenzoate (**16**)

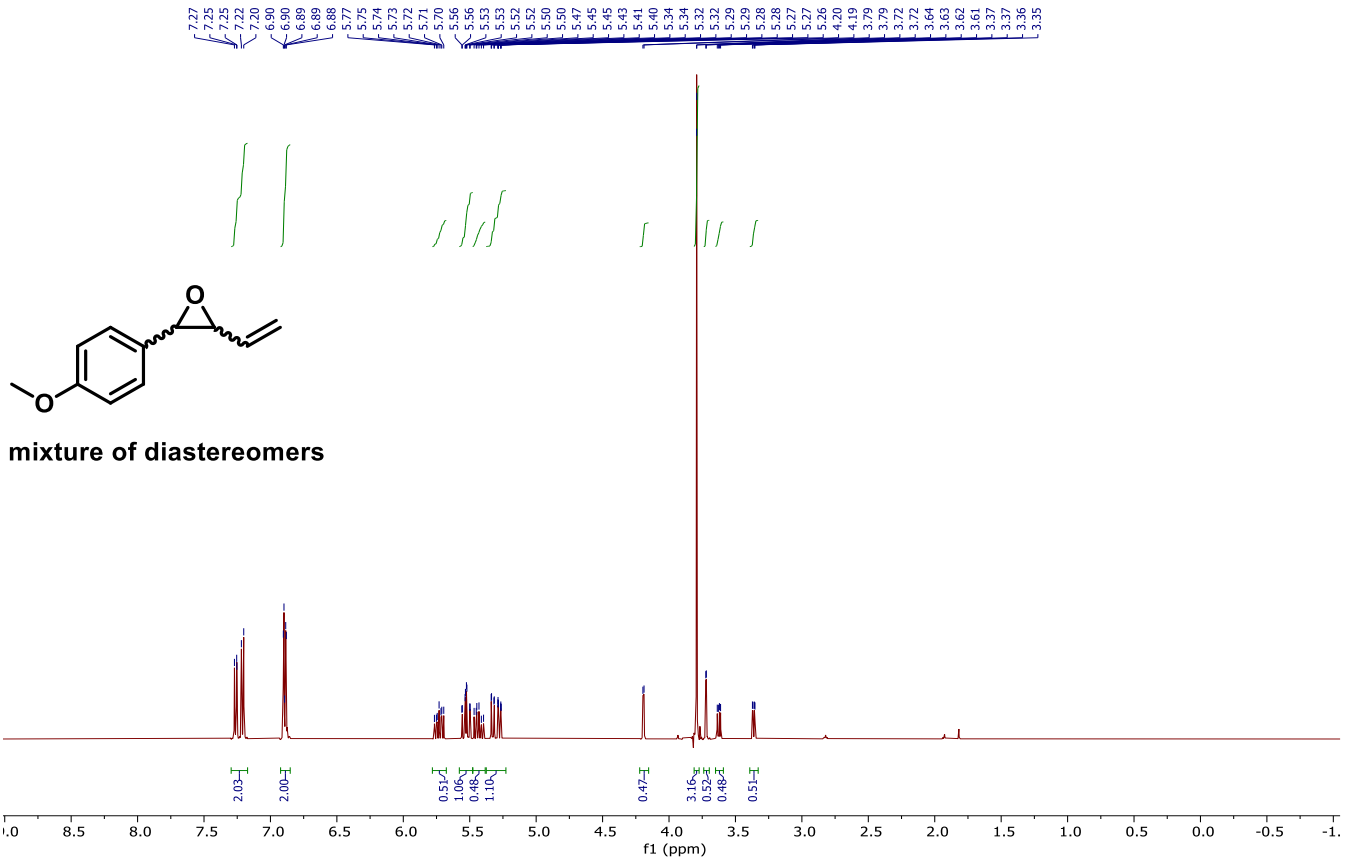


Figure 34: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-(4-Methoxyphenyl)-3-vinyloxirane (**17**)

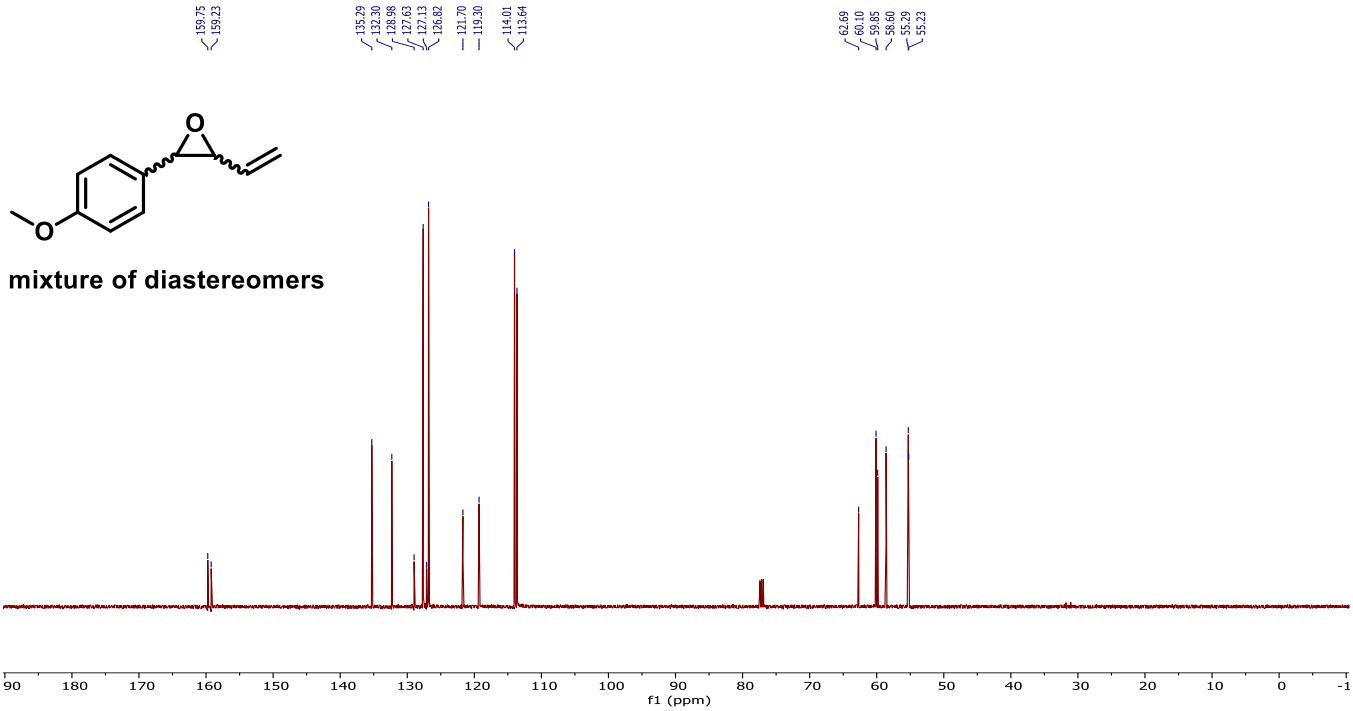


Figure 35: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-(4-Methoxyphenyl)-3-vinyloxirane (**17**)

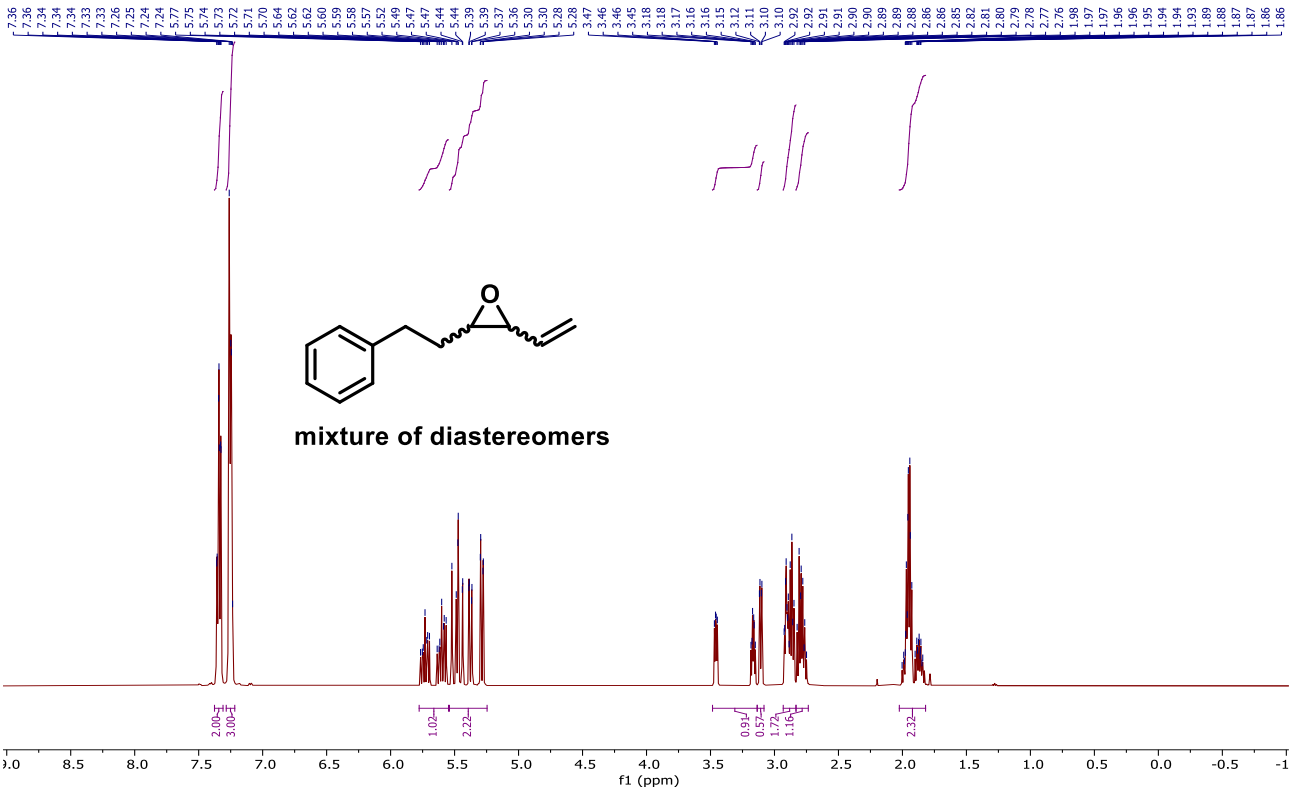


Figure 36: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-Phenethyl-3-vinyloxirane (**18**)

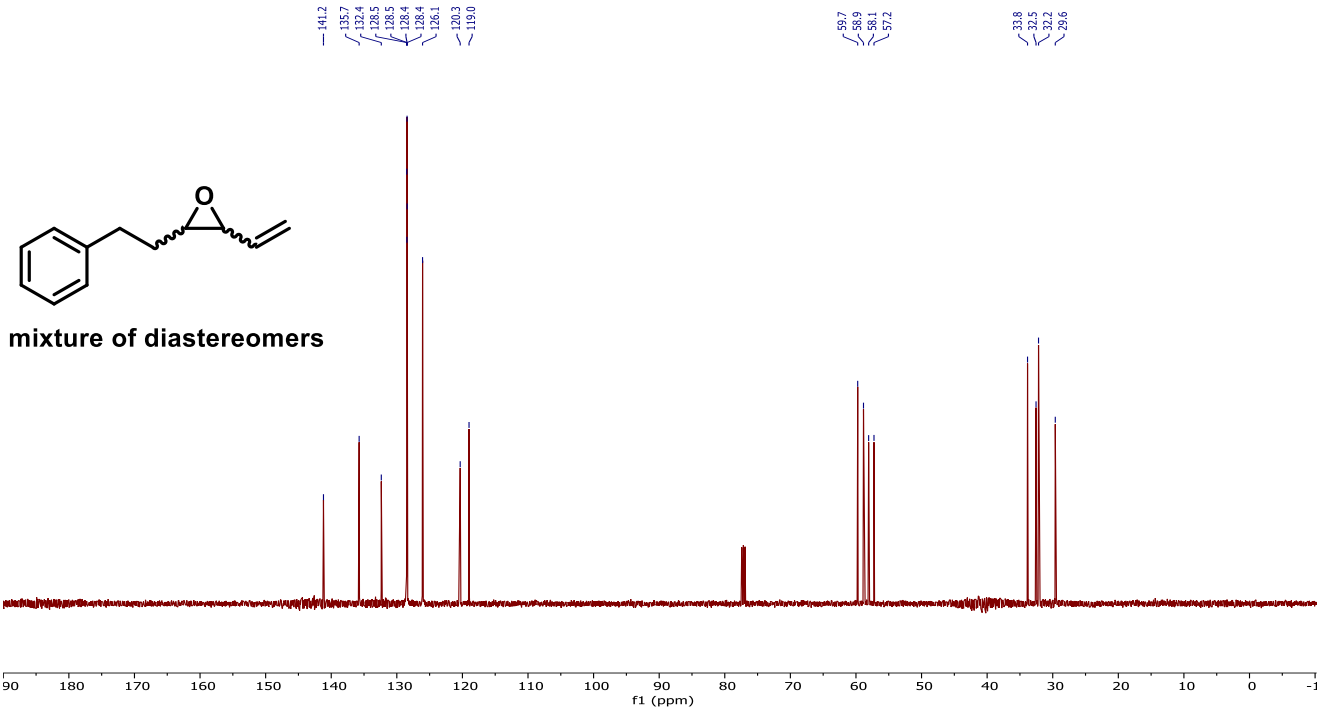


Figure 37: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-Phenethyl-3-vinyloxirane (**18**)

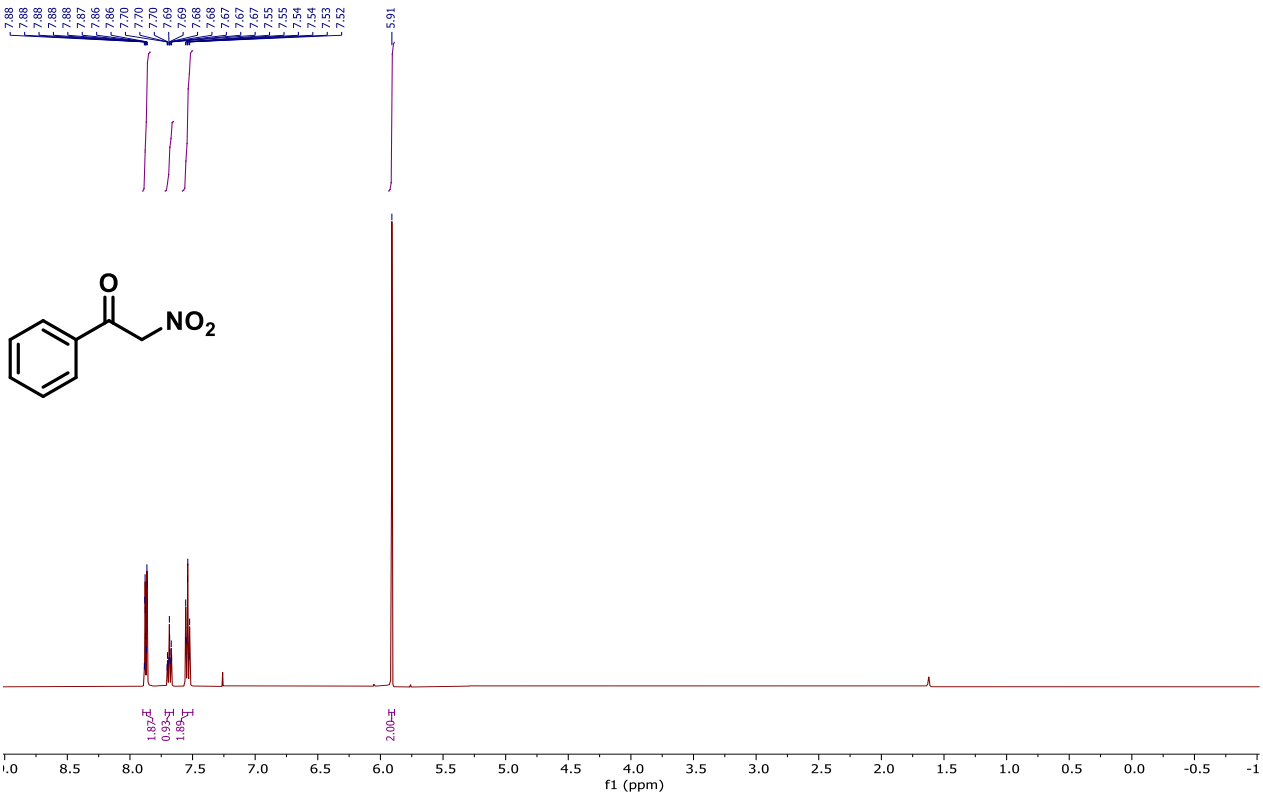


Figure 38: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-nitro-1-phenylethan-1-one (**19**)

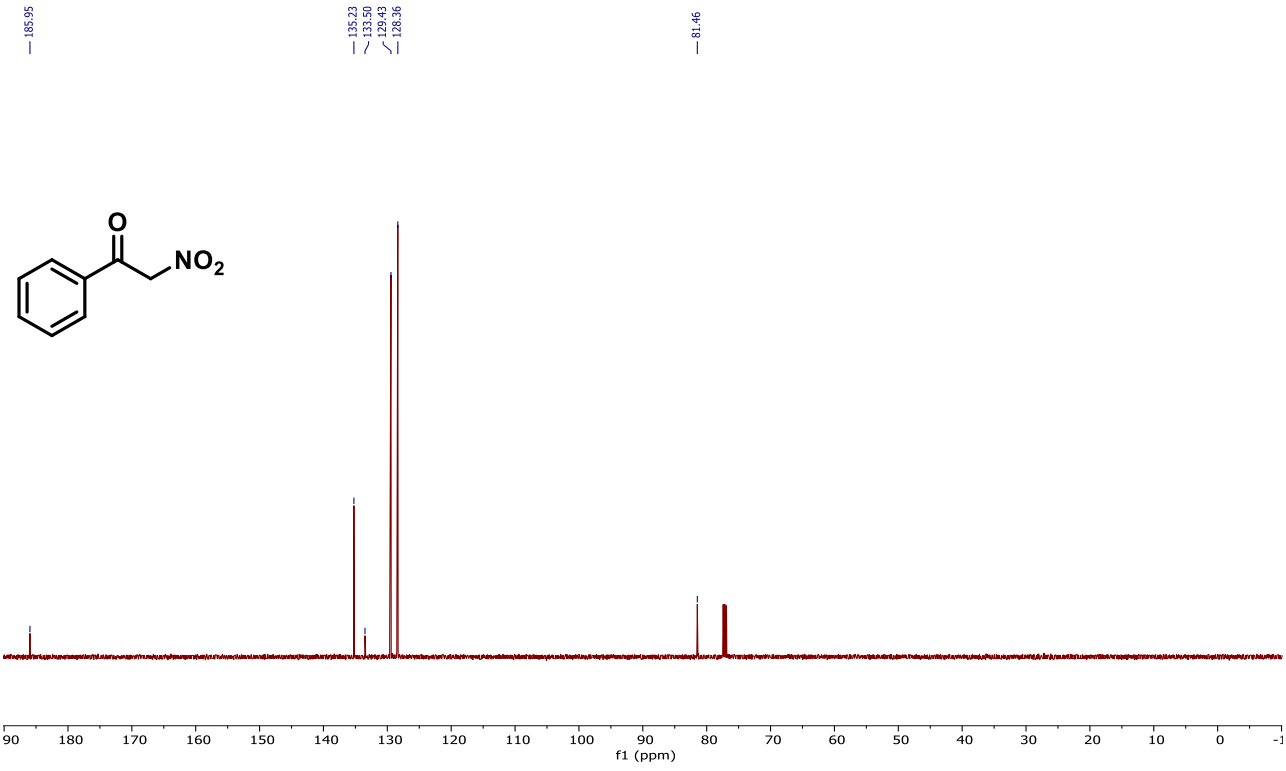


Figure 39: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-nitro-1-phenylethan-1-one (**19**)

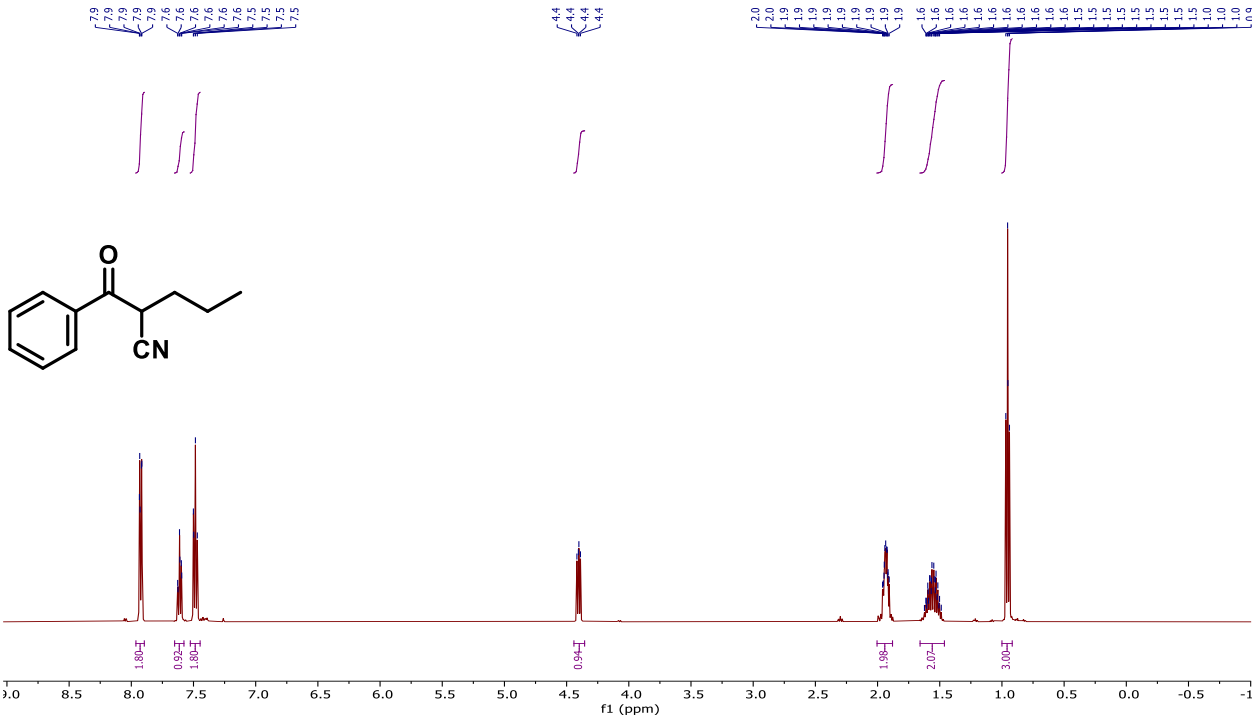


Figure 40: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-benzoylpentanenitrile (**20**)

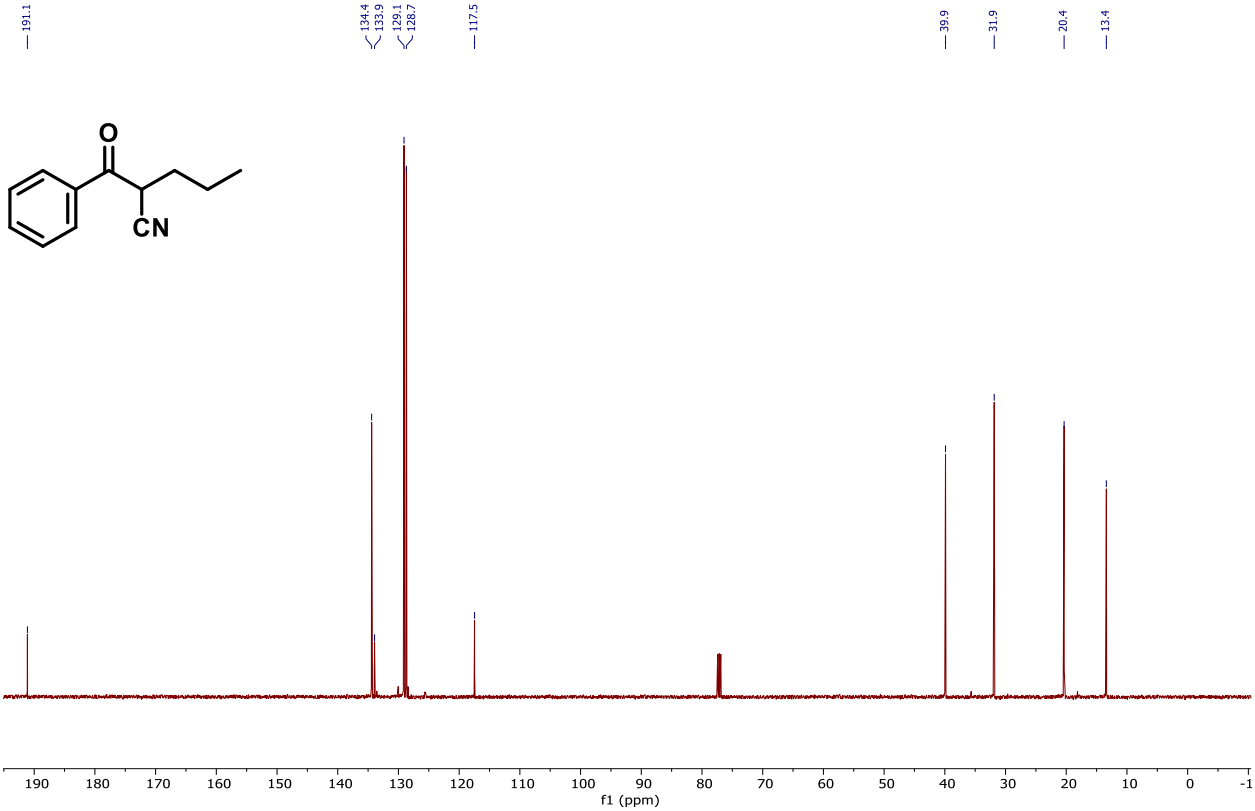


Figure 41: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-benzoylpentanenitrile (**20**)

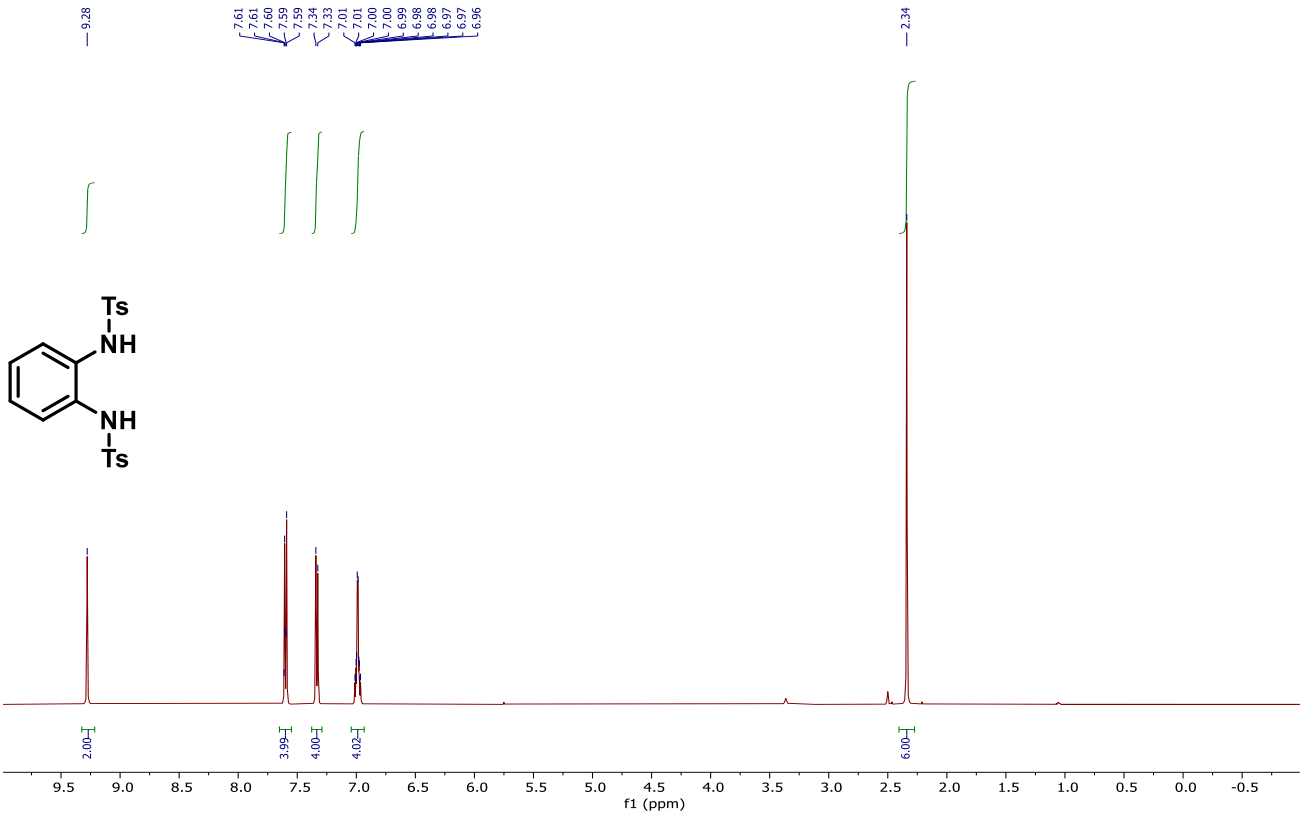


Figure 43: ^{1}H NMR (500 MHz, DMSO-d_6) of *N,N′*-(1,2-phenylene)bis(4-methylbenzenesulfonamide) (**21**)

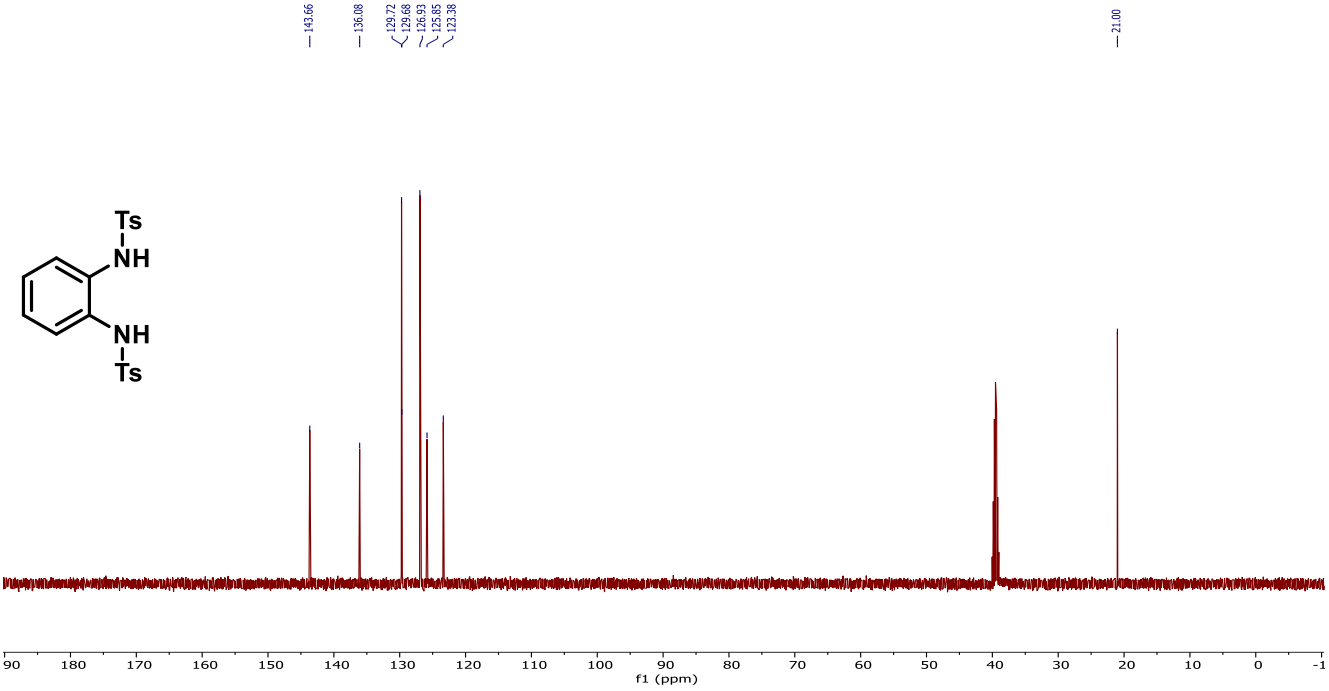


Figure 44: ^{13}C NMR (126 MHz, DMSO-d_6) of *N,N′*-(1,2-phenylene)bis(4-methylbenzenesulfonamide) (**21**)

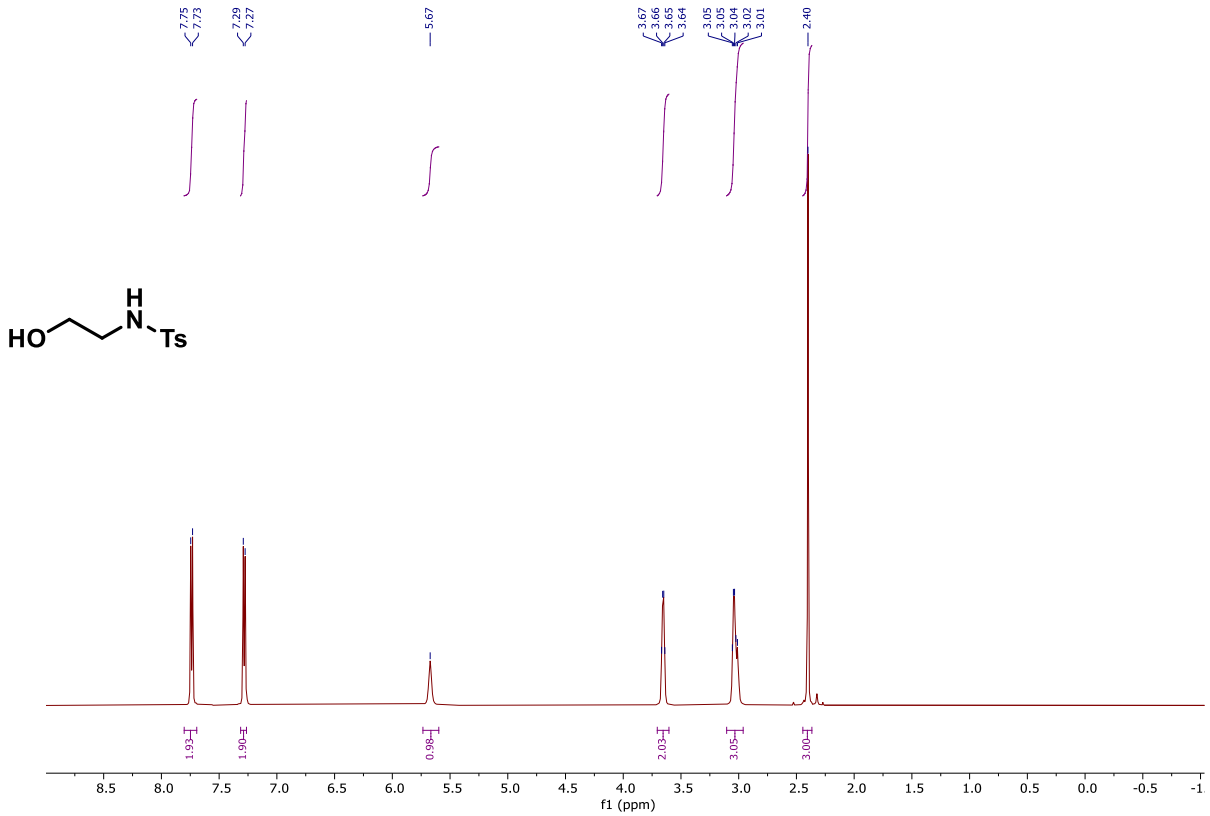


Figure 45: ^{1}H NMR (500 MHz, $CDCl_3$) of *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**22**)

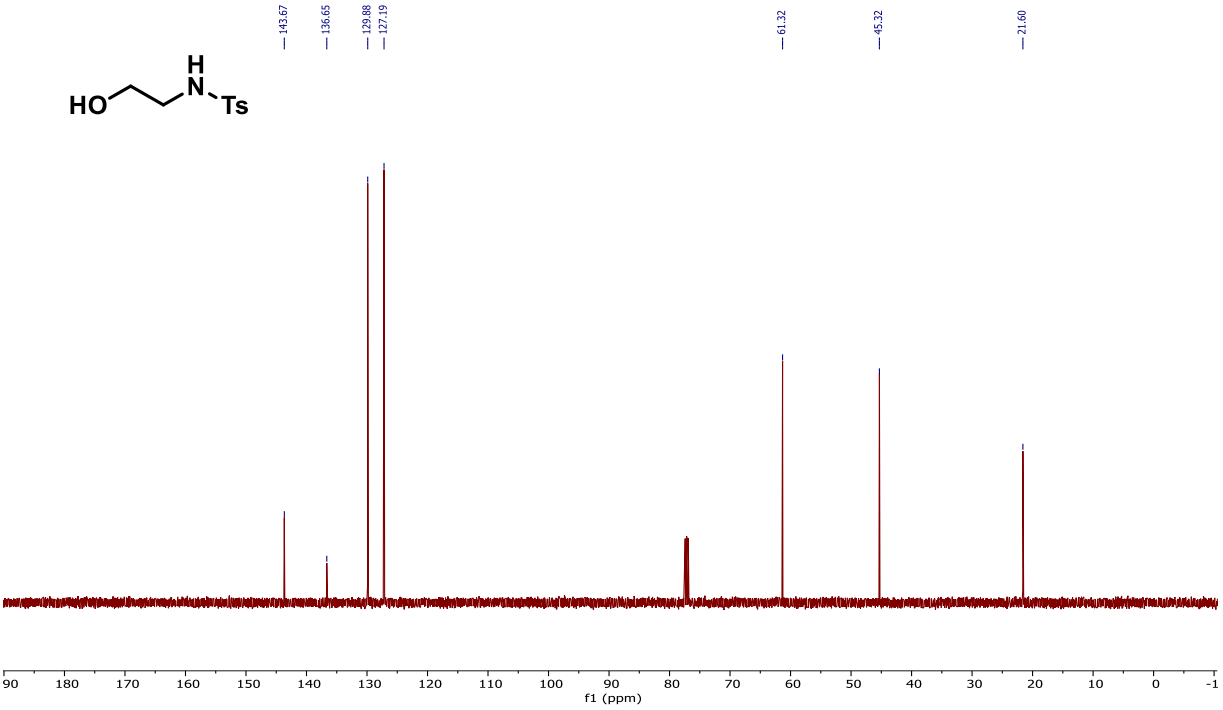


Figure 46: ^{13}C NMR (126 MHz, $CDCl_3$) of *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**22**)

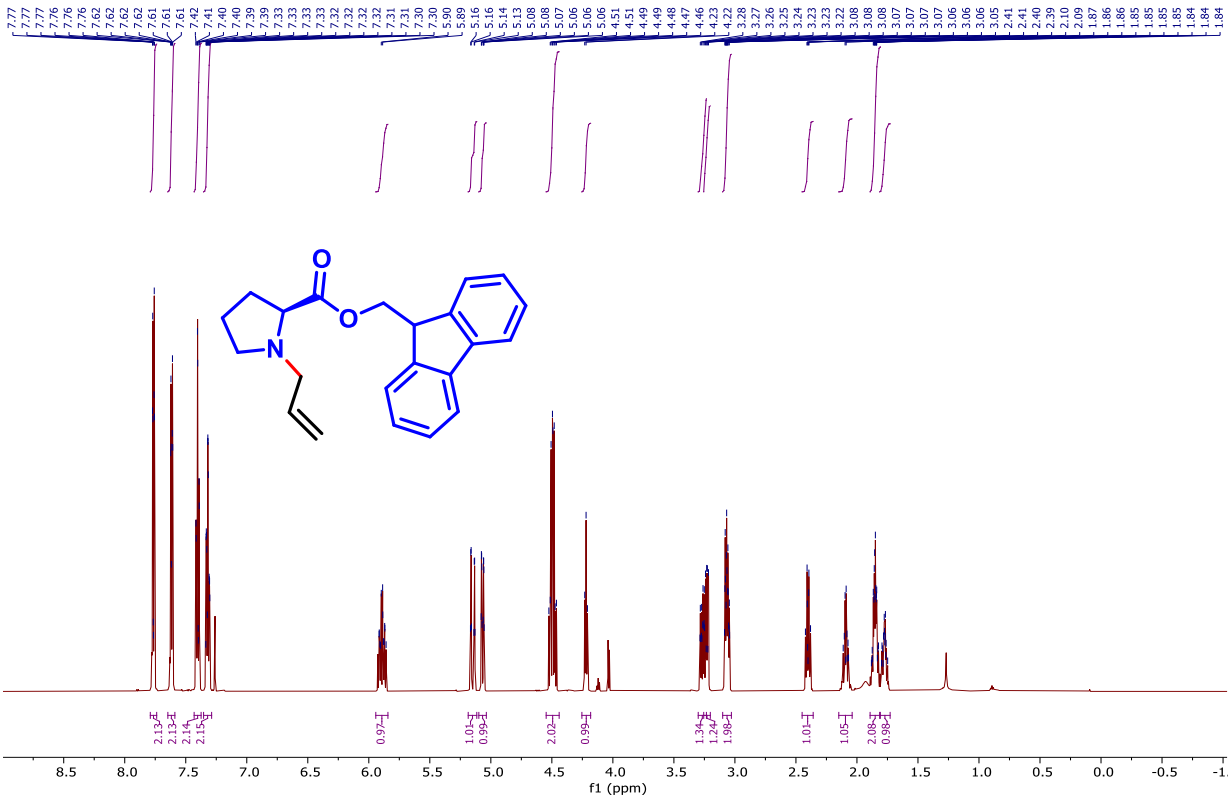


Figure 47: ^{1}H NMR (600 MHz, $CDCl_3$) of (9H-Fluoren-9-yl)methyl allyl-L-prolinate (**1a**)

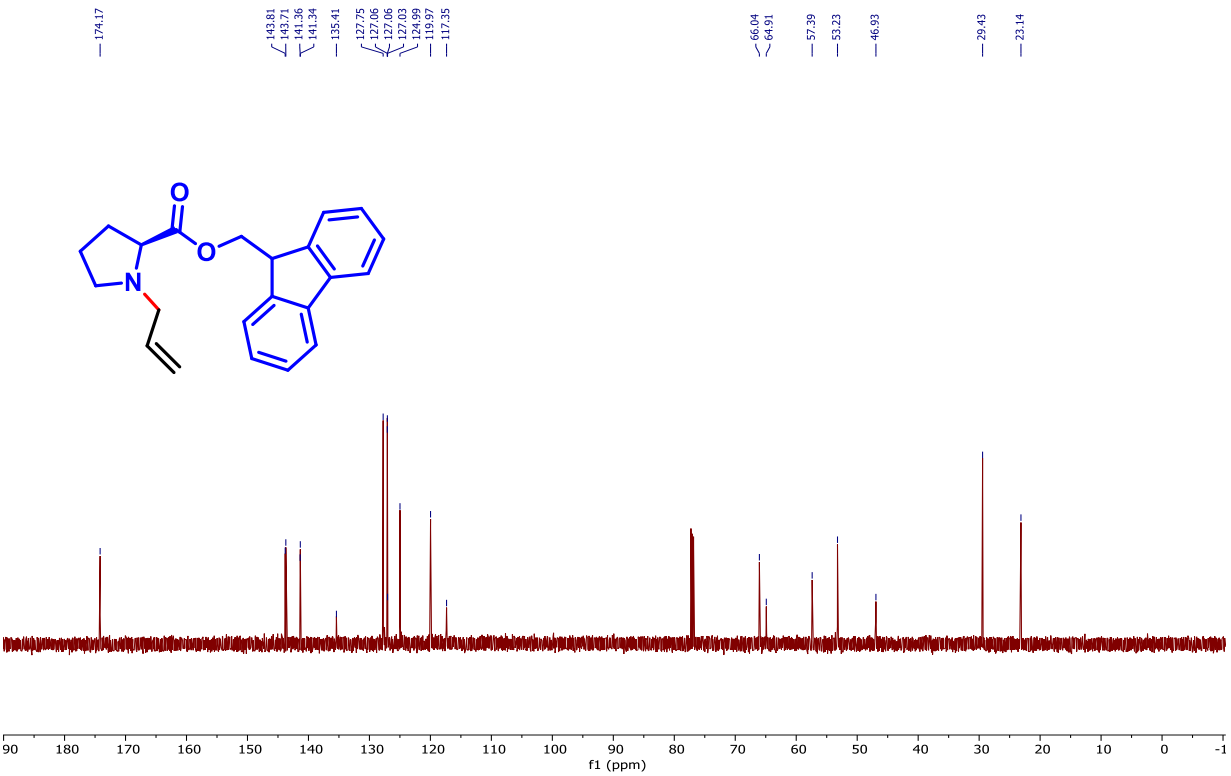


Figure 48: ^{13}C NMR (151 MHz, $CDCl_3$) of (9H-Fluoren-9-yl)methyl allyl-L-prolinate (**1a**)

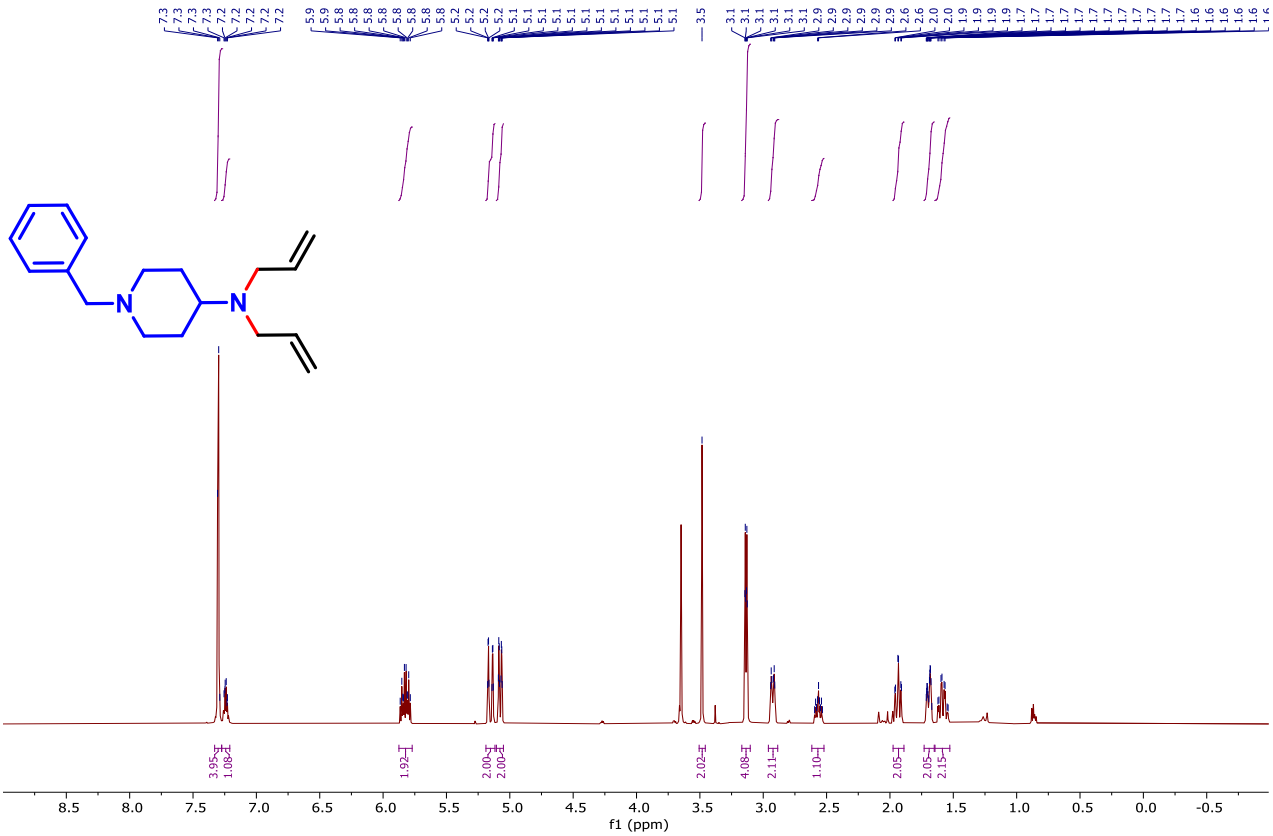


Figure 49: ^{1}H NMR (500 MHz, $CDCl_3$) of *N,N*-Diallyl-1-benzylpiperidin-4-amine (**1b**)

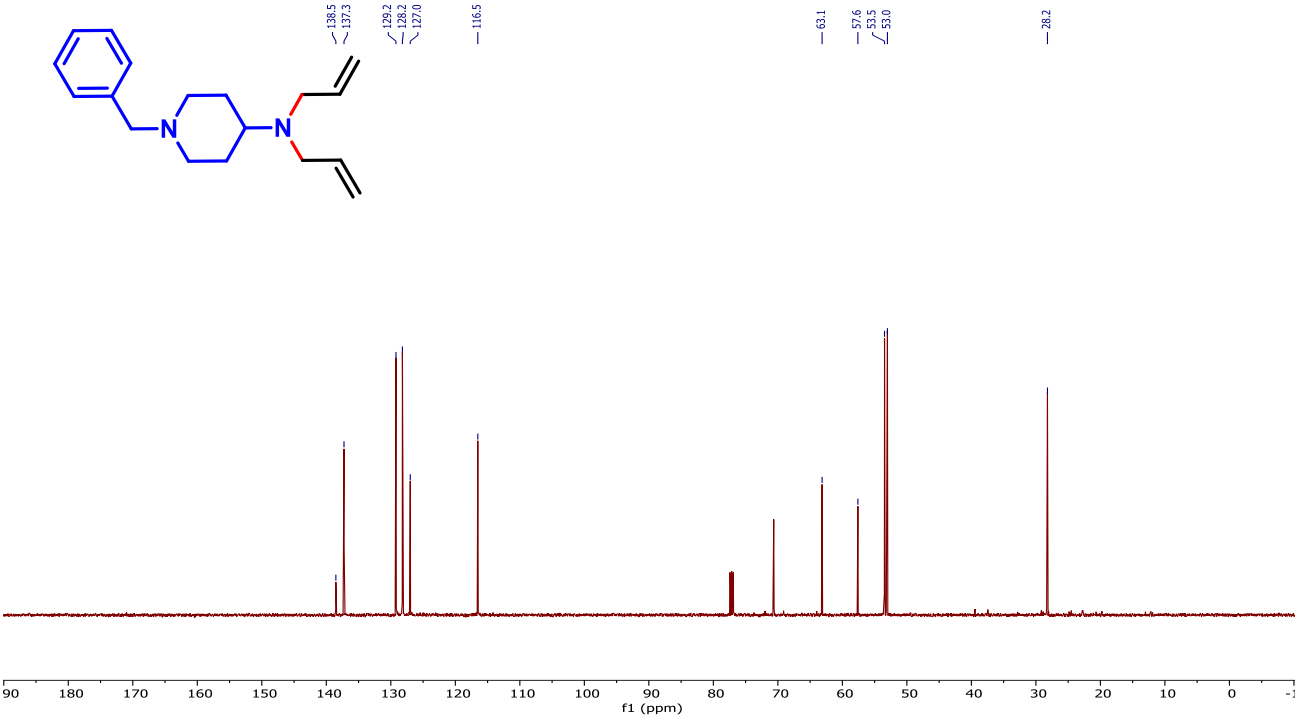


Figure 50: ^{13}C NMR (126 MHz, $CDCl_3$) of *N,N*-Diallyl-1-benzylpiperidin-4-amine (**1b**)

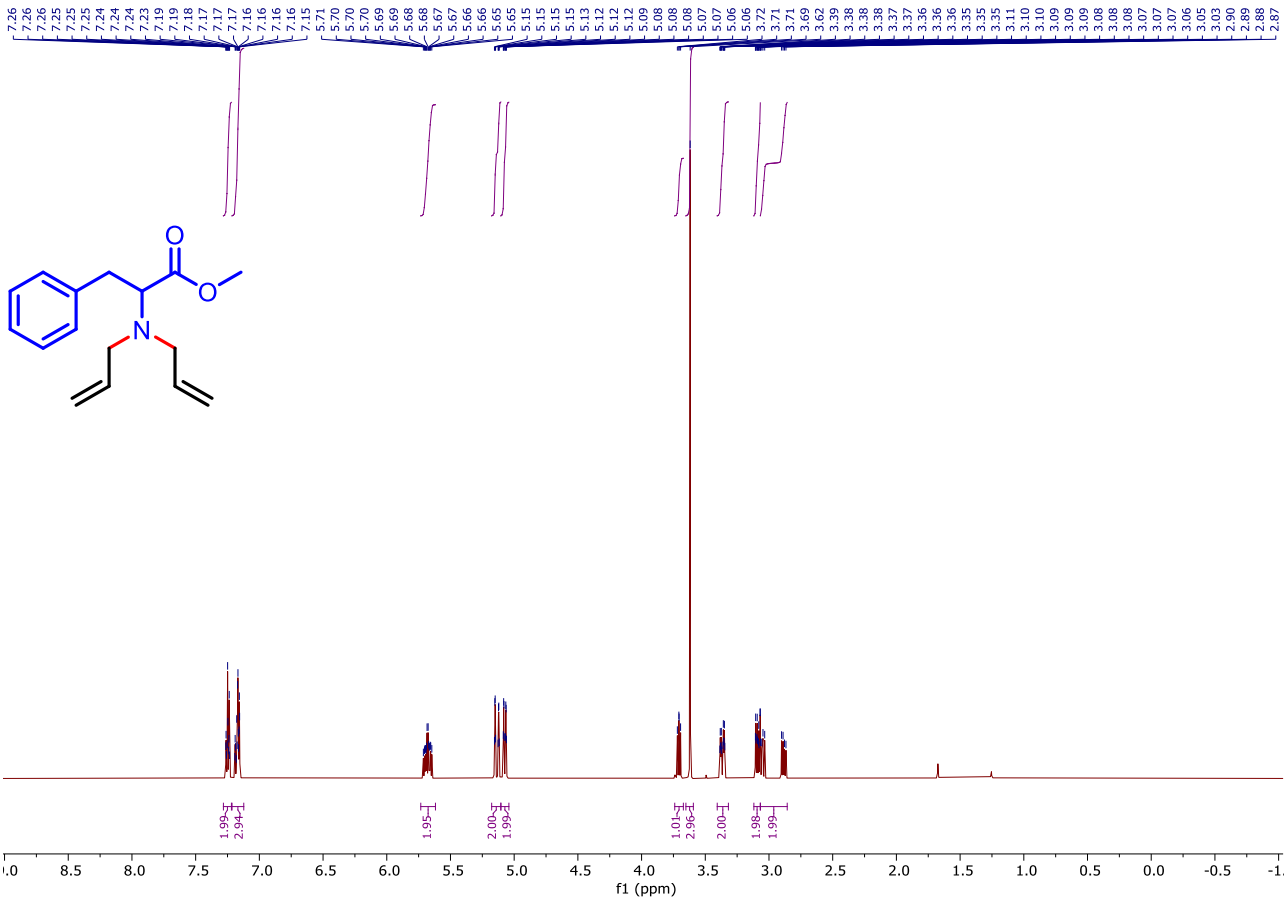


Figure 51: ^{1}H NMR (600 MHz, $CDCl_3$) of Methyl diallylphenylalaninate (**1c**)

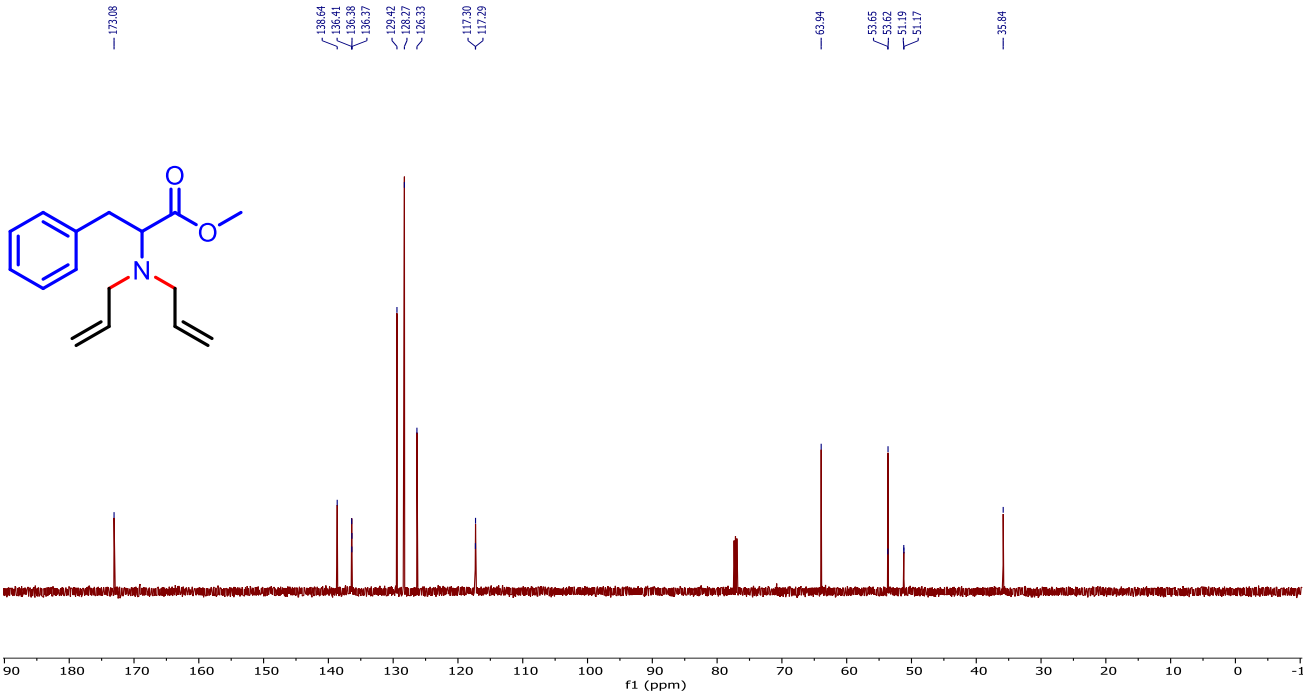


Figure 52: ^{13}C NMR (126 MHz, $CDCl_3$) of Methyl diallylphenylalaninate (**1c**)

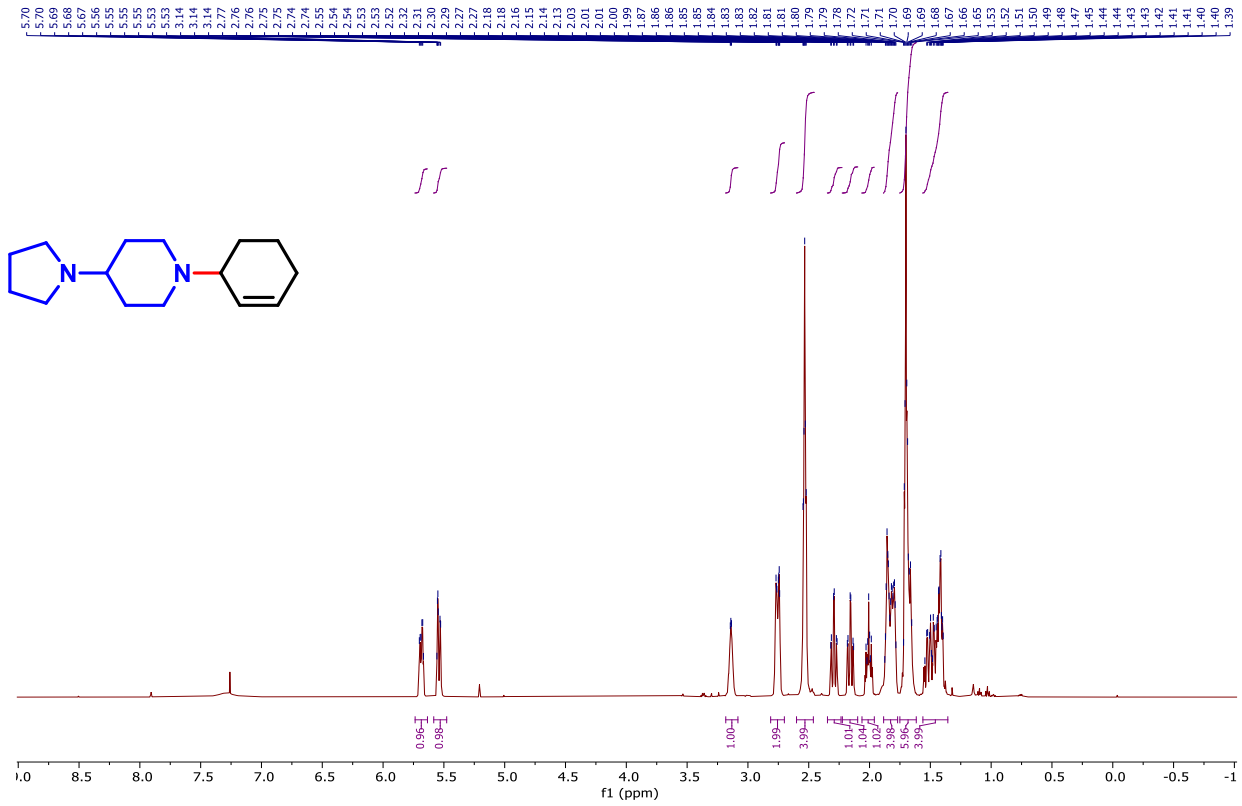


Figure 53: 1-(Cyclohex-2-en-1-yl)-4-(pyrrolidin-1-yl)piperidine (**1d**)

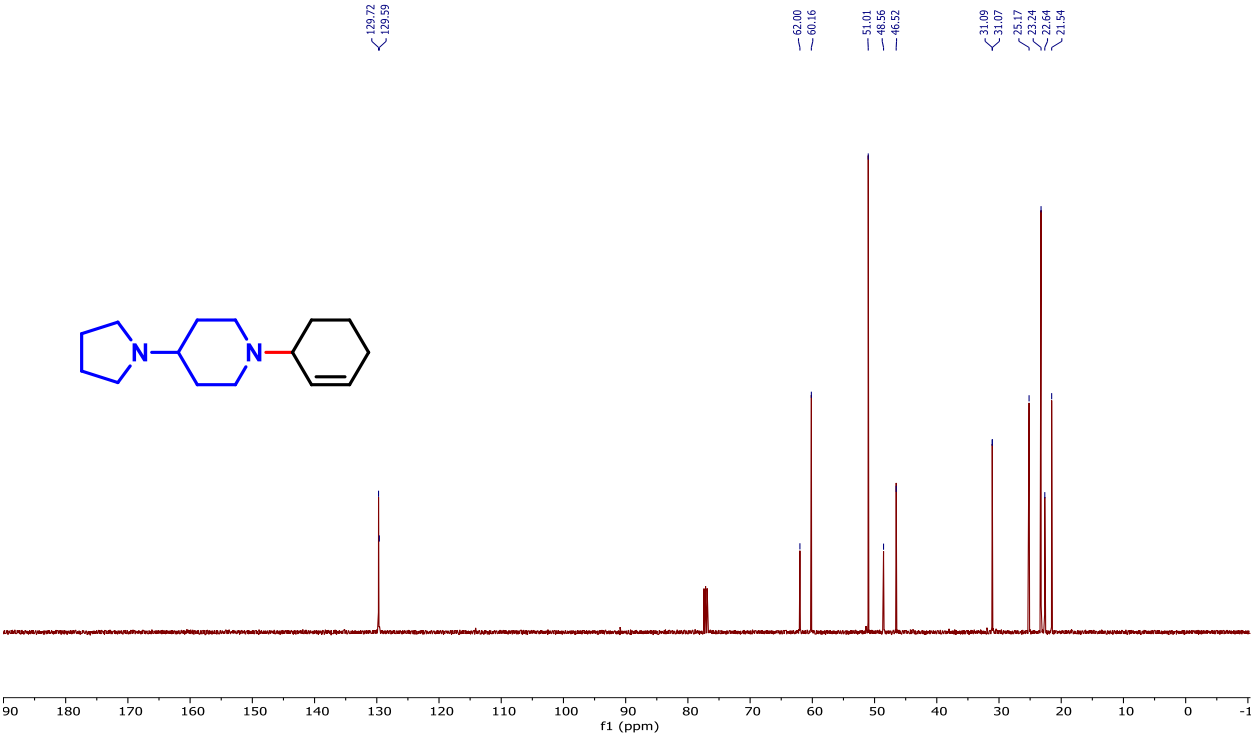


Figure 54: ^{13}C NMR (126 MHz, $CDCl_3$) of 1-(Cyclohex-2-en-1-yl)-4-(pyrrolidin-1-yl)piperidine (**1d**)

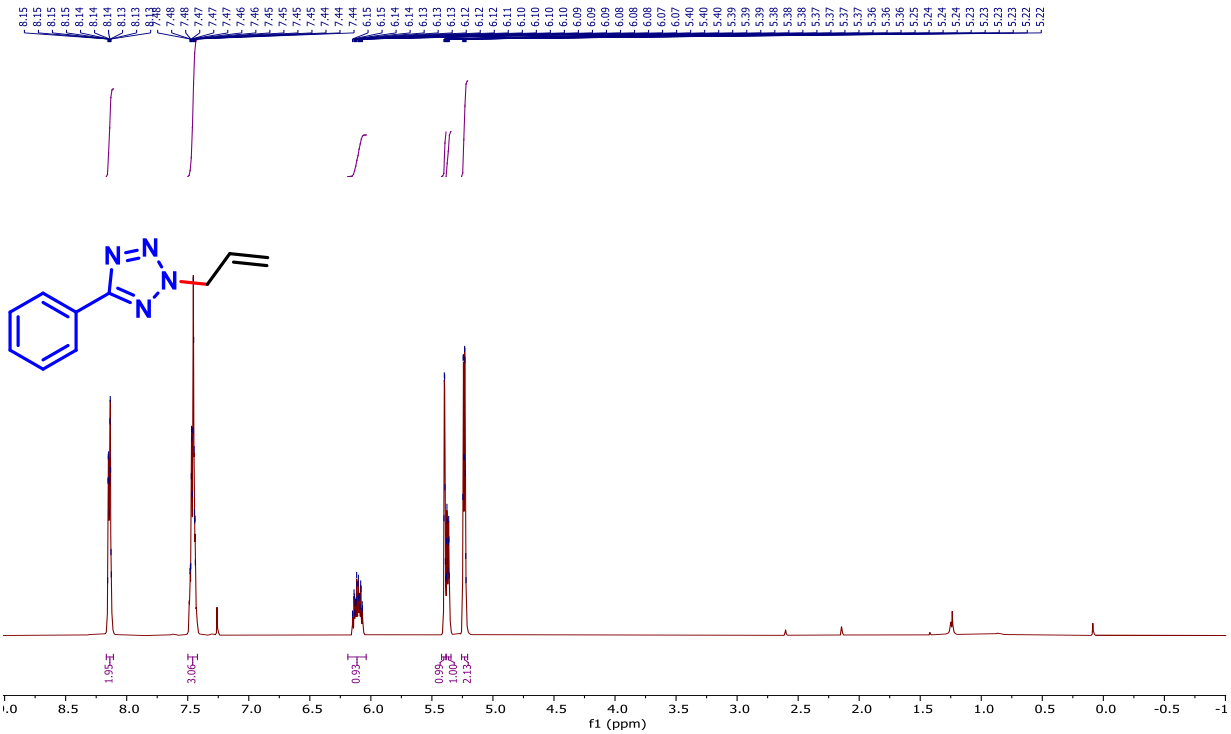


Figure 55: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-Allyl-5-phenyl-2H-tetrazole (**1e**)

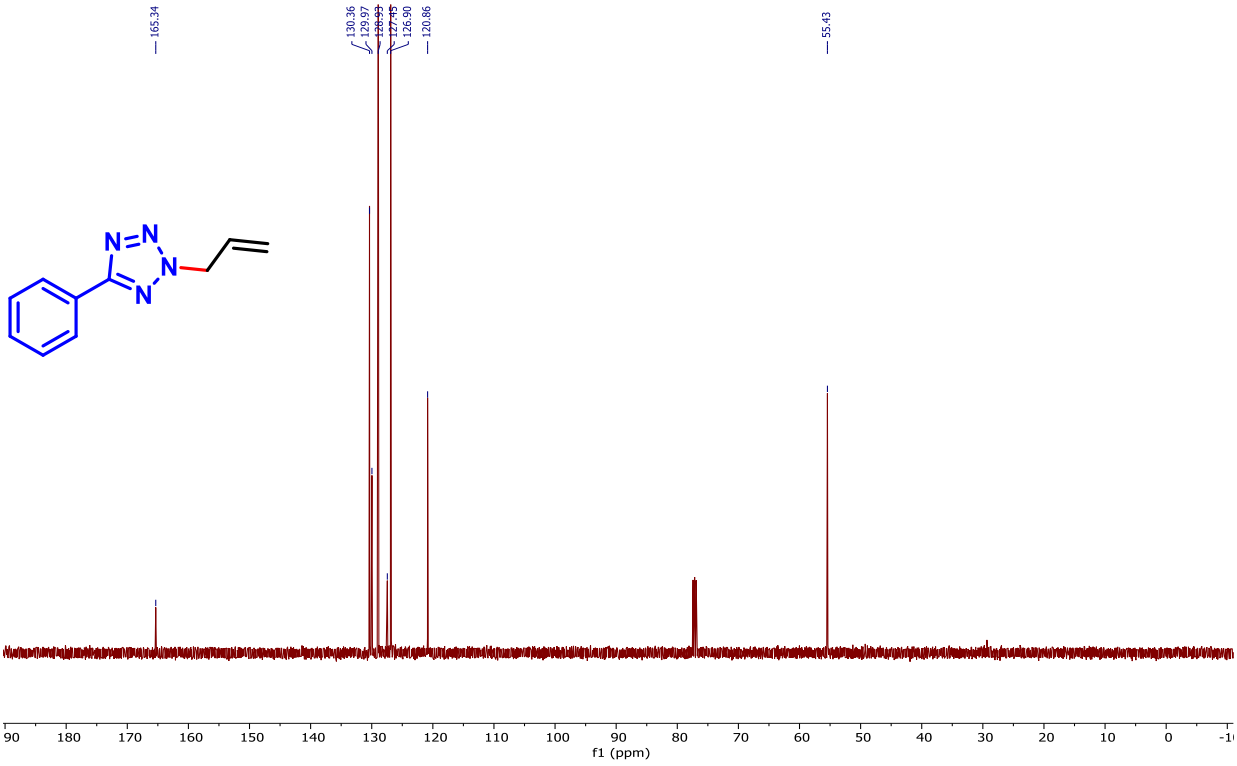


Figure 56: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-Allyl-5-phenyl-2H-tetrazole (**1e**)

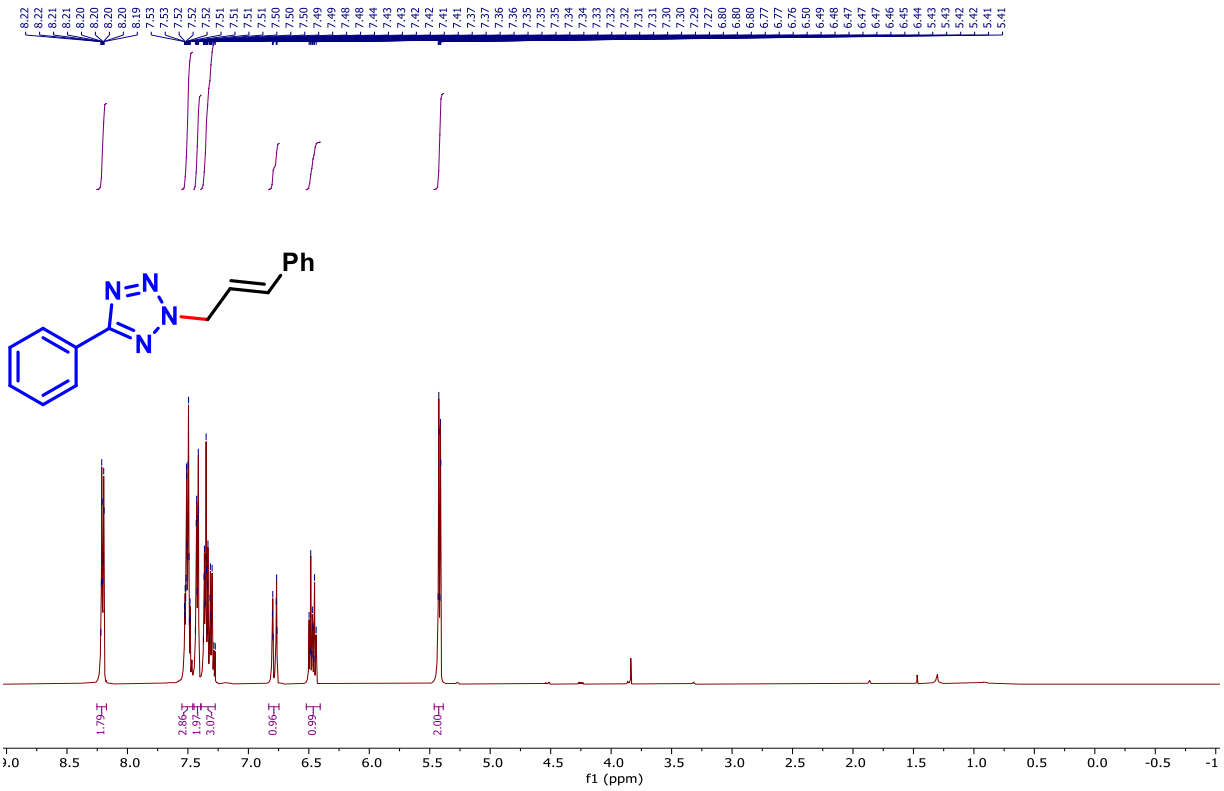


Figure 57: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-Cinnamyl-5-phenyl-2H-tetrazole (**1f**)

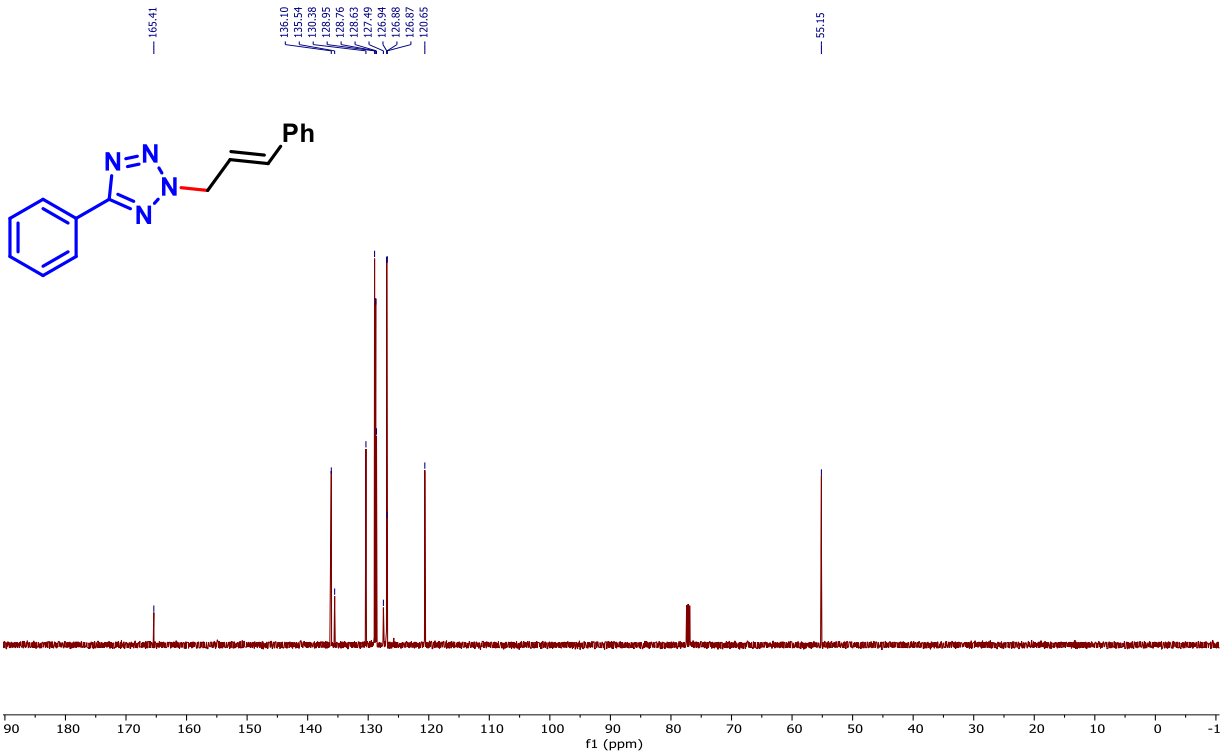


Figure 58: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-Cinnamyl-5-phenyl-2H-tetrazole (**1f**)

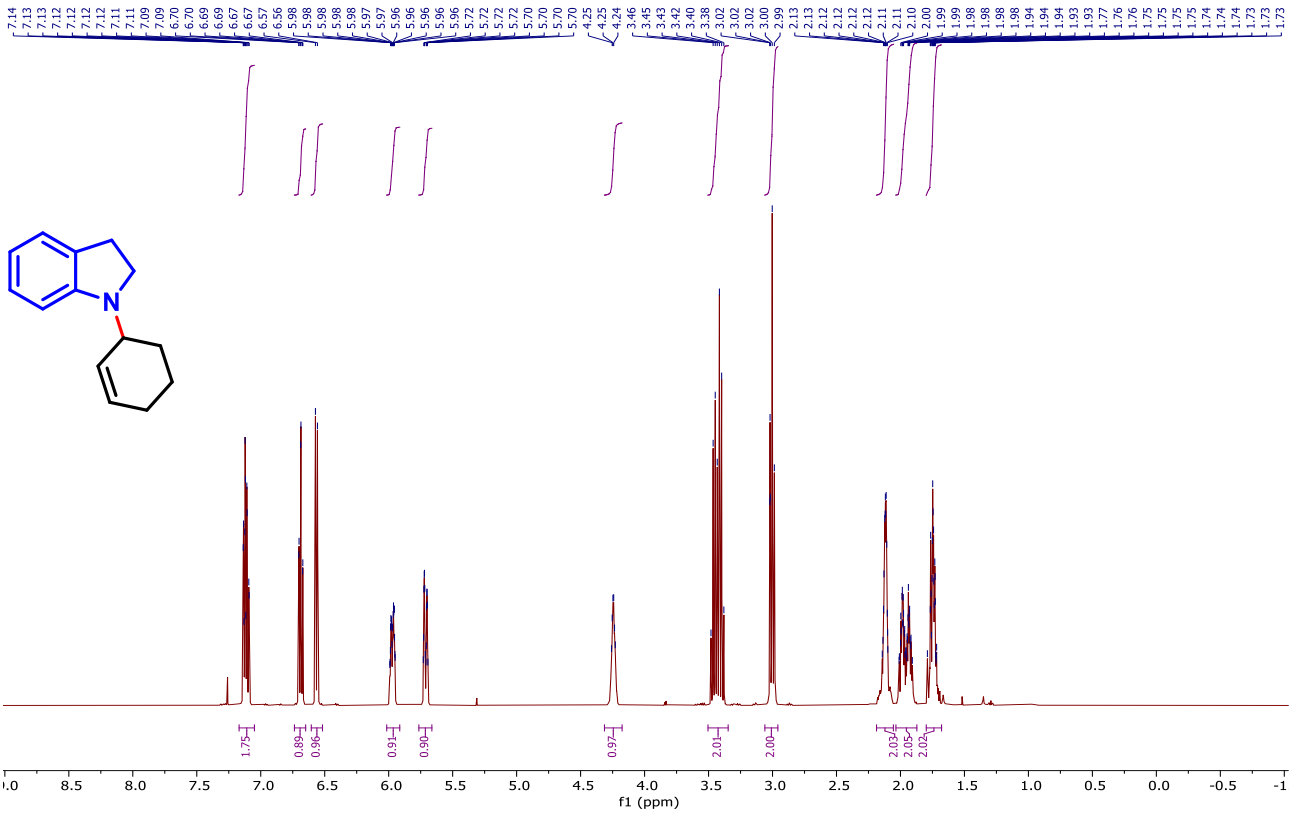


Figure 59: ^{1}H NMR (500 MHz, $CDCl_3$) of 1-(cyclohex-2-en-1-yl)indoline (**1g**)

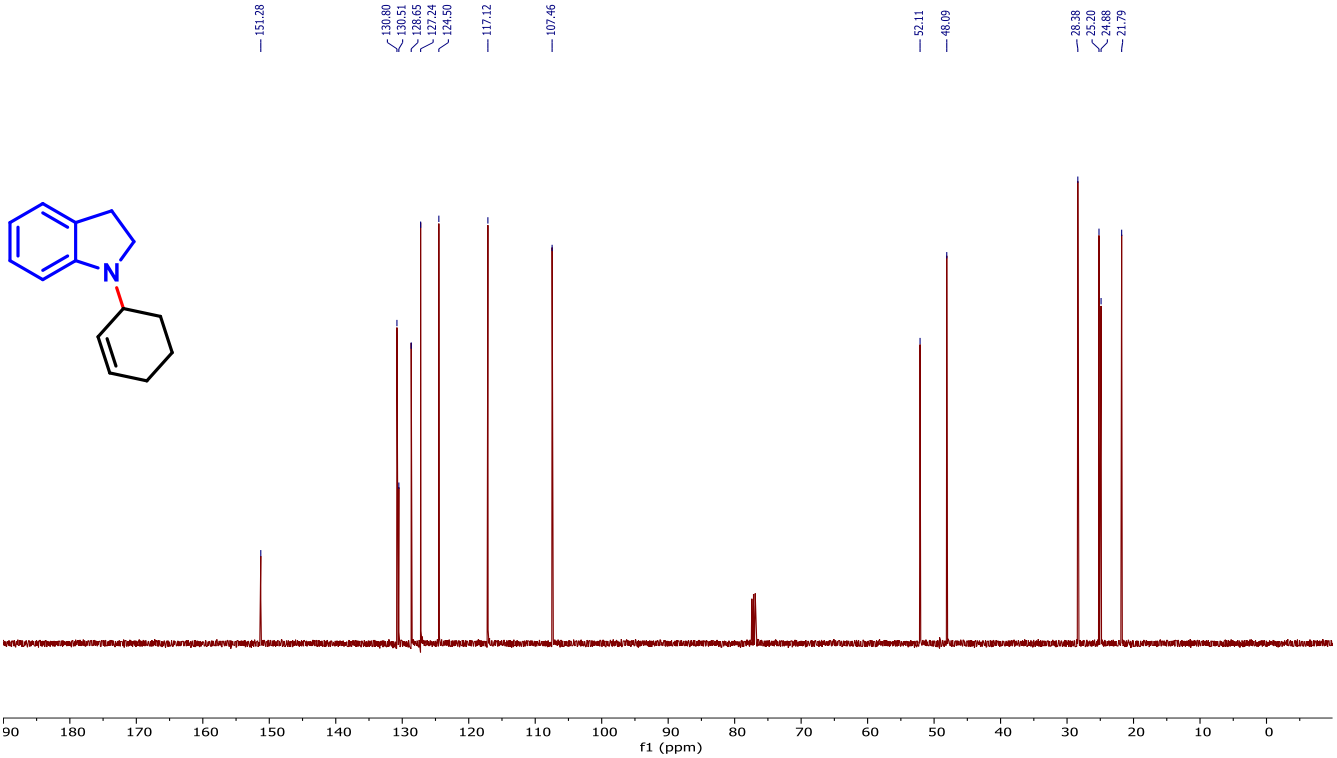


Figure 60: ^{13}C NMR (126 MHz, $CDCl_3$) of 1-(cyclohex-2-en-1-yl)indoline (**1g**)

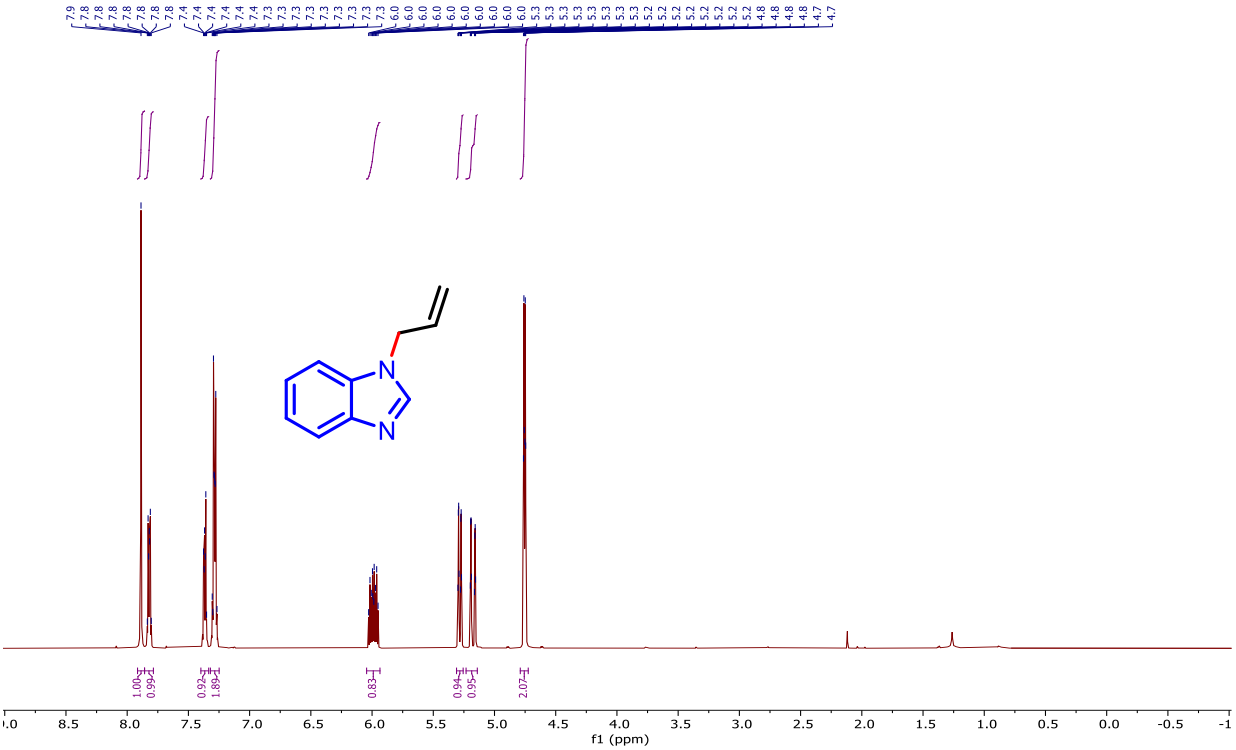


Figure 61: ^{1}H NMR (500 MHz, $CDCl_3$) of 1-Allyl-1H-benzo[d]imidazole (**1h**)

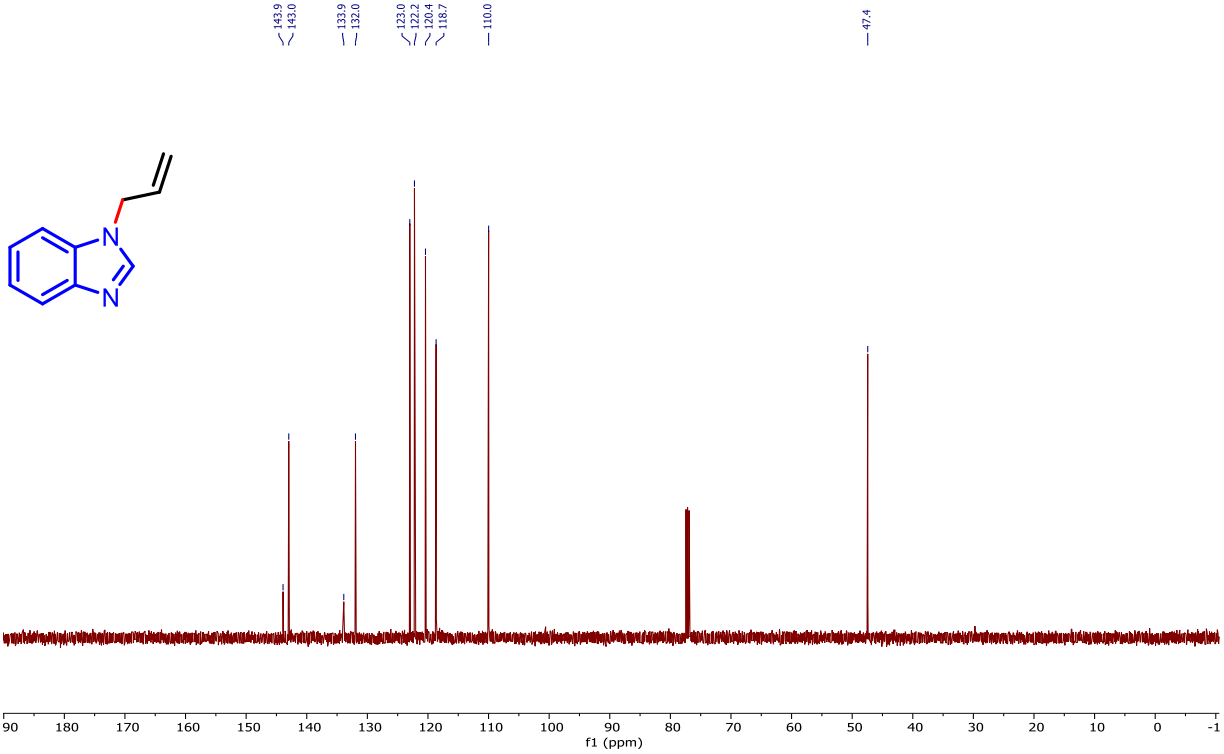


Figure 62: ^{13}C NMR (126 MHz, $CDCl_3$) of 1-Allyl-1H-benzo[d]imidazole (**1h**)

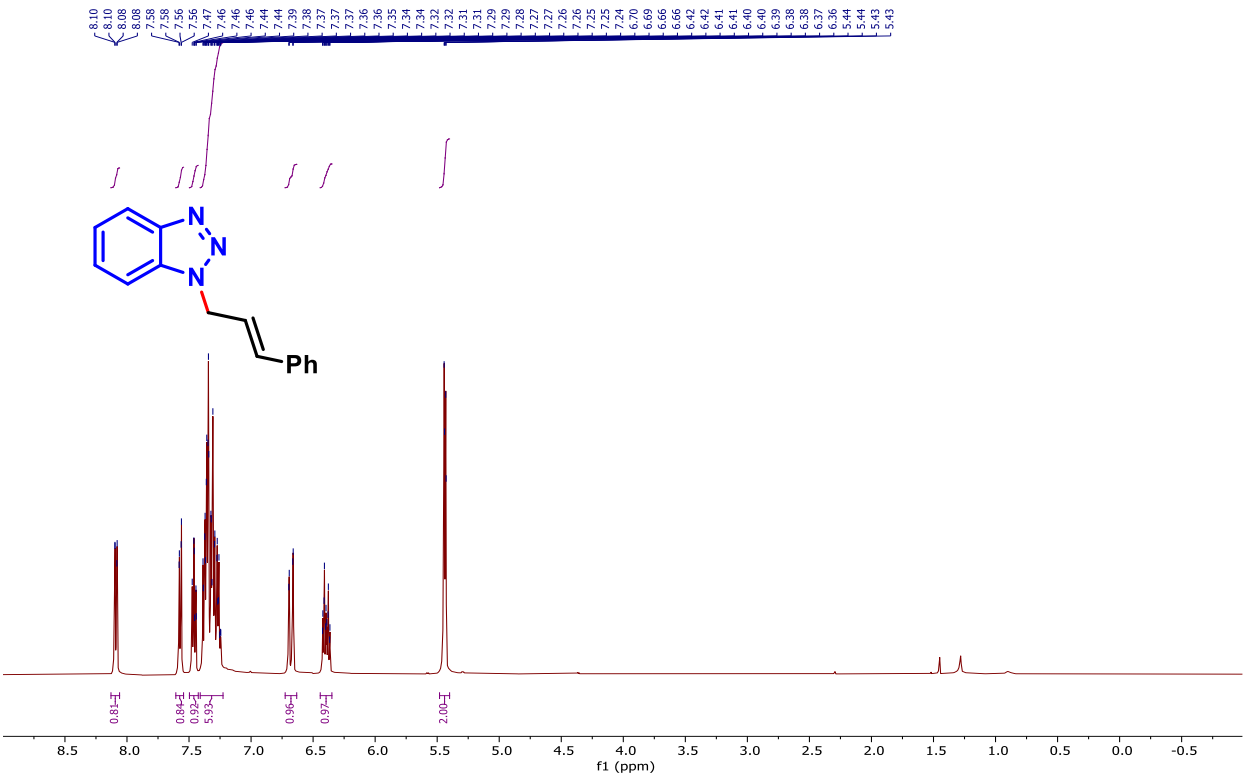


Figure 63: ^{1}H NMR (500 MHz, $CDCl_3$) of 1-Cinnamyl-1H-benzo[d][1,2,3]triazole (**1i**)

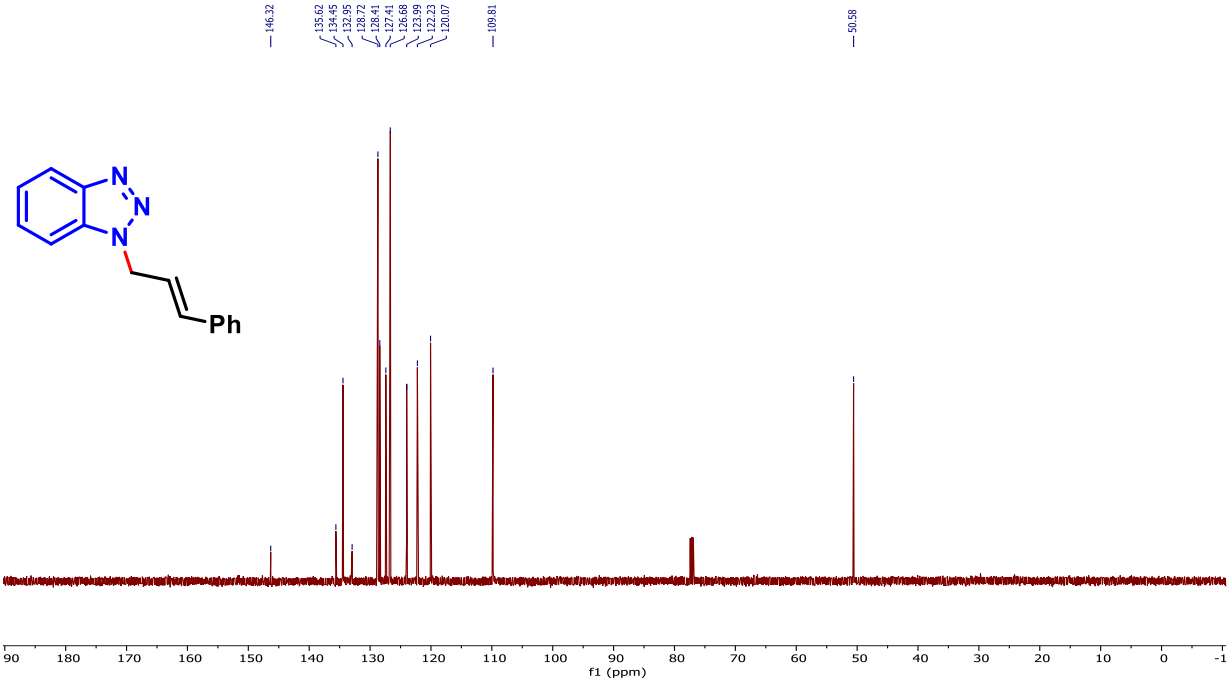


Figure 64: ^{13}C NMR (126 MHz, $CDCl_3$) of 1-Cinnamyl-1H-benzo[d][1,2,3]triazole (**1i**)

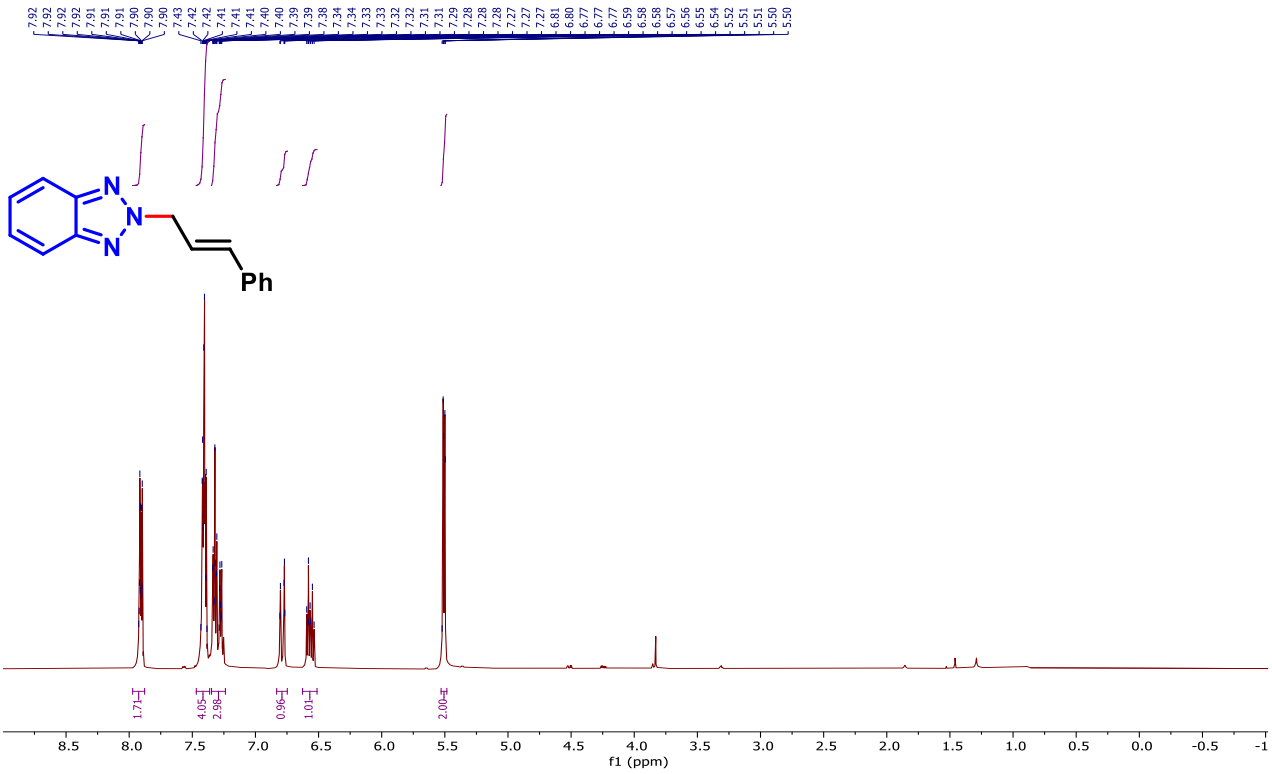


Figure 65: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-Cinnamyl-2H-benzo[d][1,2,3]triazole (**1i**)

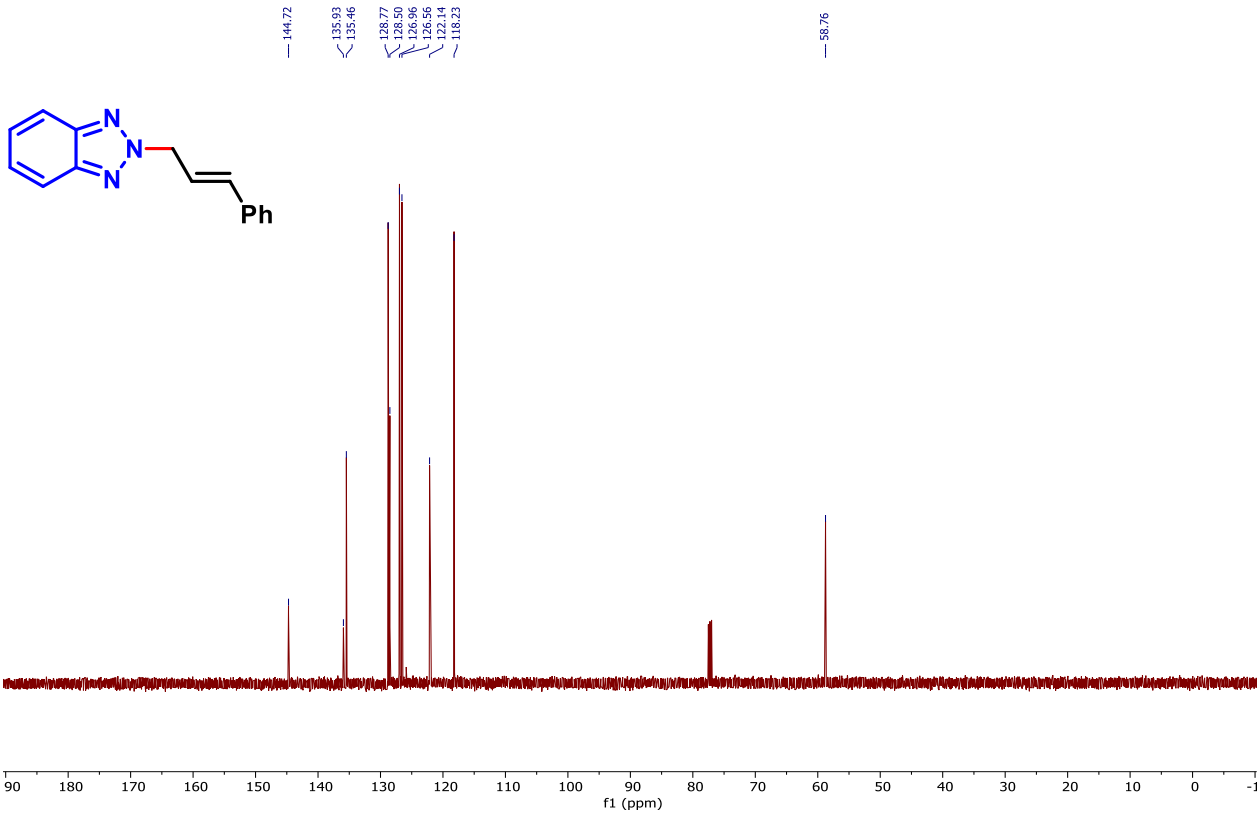


Figure 66: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-Cinnamyl-2H-benzo[d][1,2,3]triazole (**1i**)

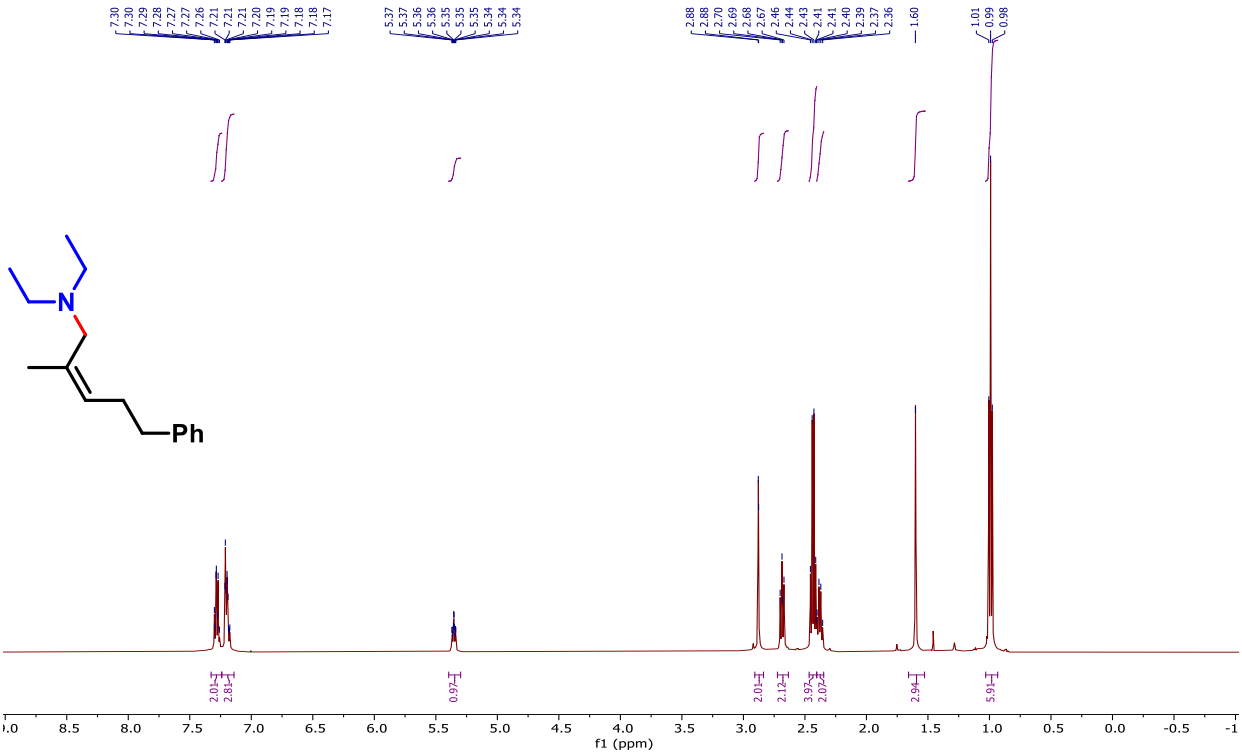


Figure 67: ^{1}H NMR (500 MHz, $CDCl_3$) of *(E)-N,N*-Diethyl-2-methyl-5-phenylpent-2-en-1-amine (**1j**)

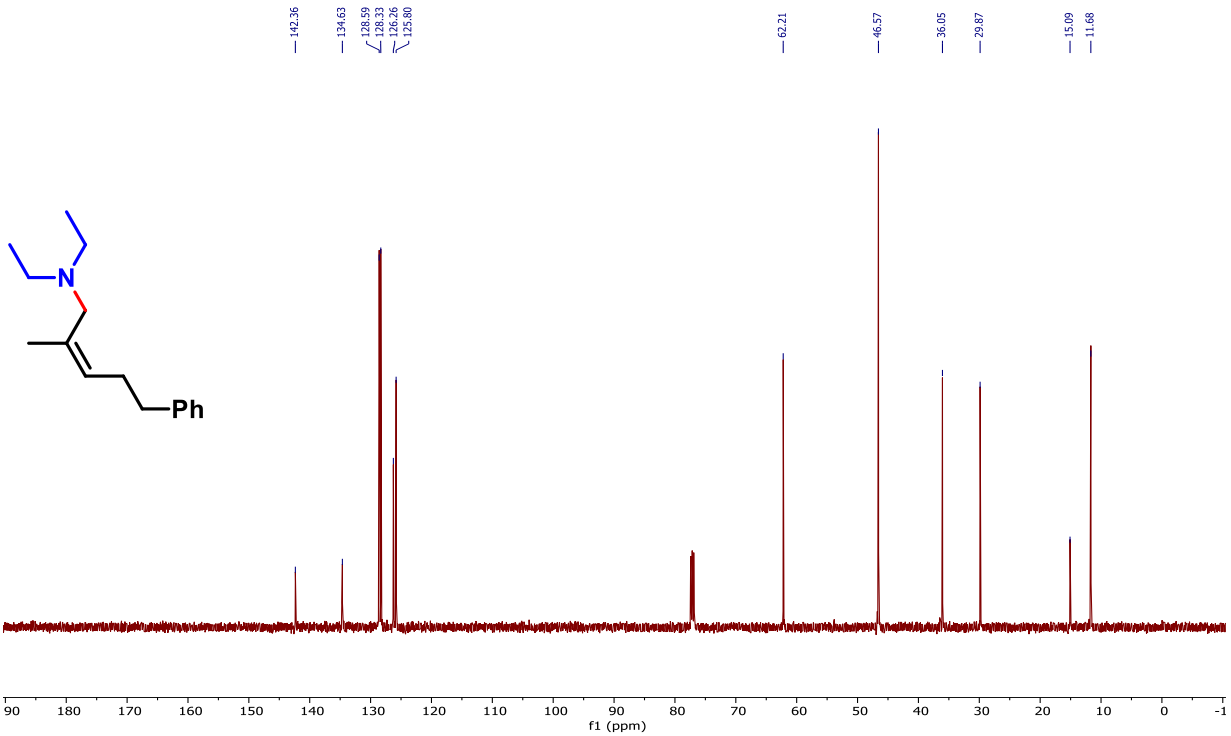


Figure 68: ^{13}C NMR (126 MHz, $CDCl_3$) of *(E)-N,N*-Diethyl-2-methyl-5-phenylpent-2-en-1-amine (**1j**)

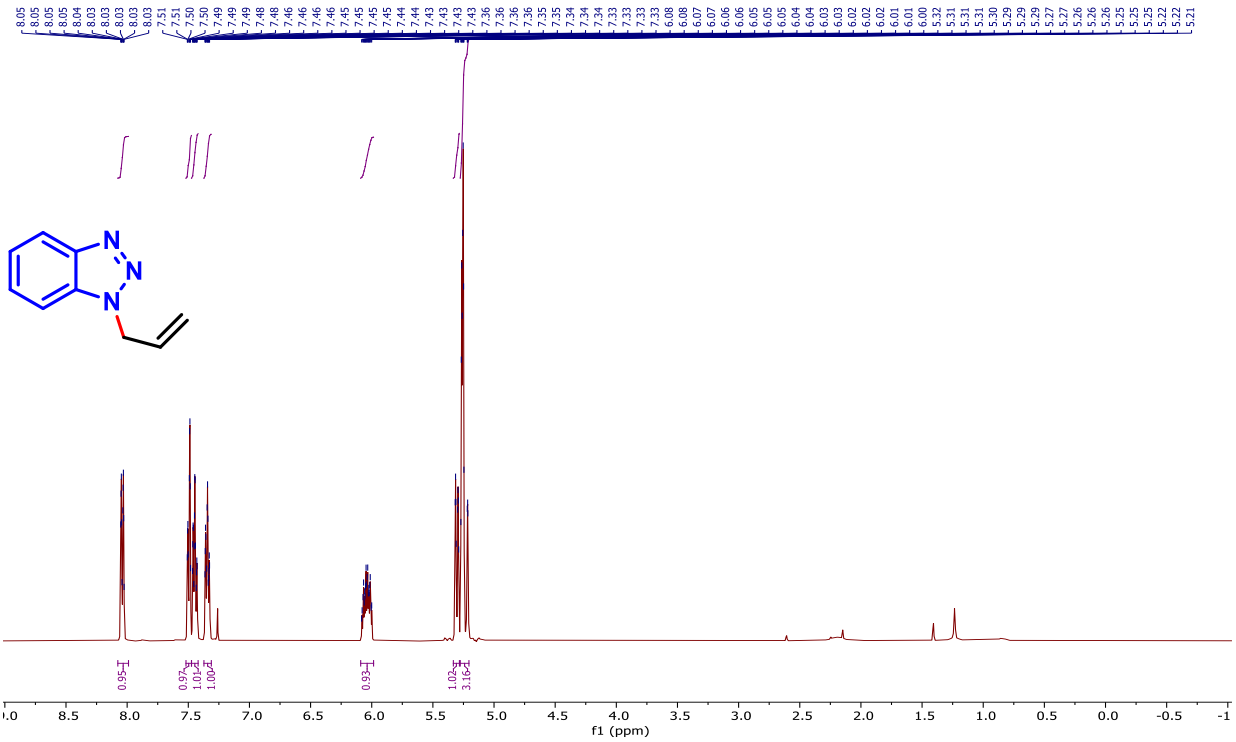


Figure 69: ^{1}H NMR (500 MHz, $CDCl_3$) of 1-Allyl-1H-benzo[d][1,2,3]triazole (**1k**)

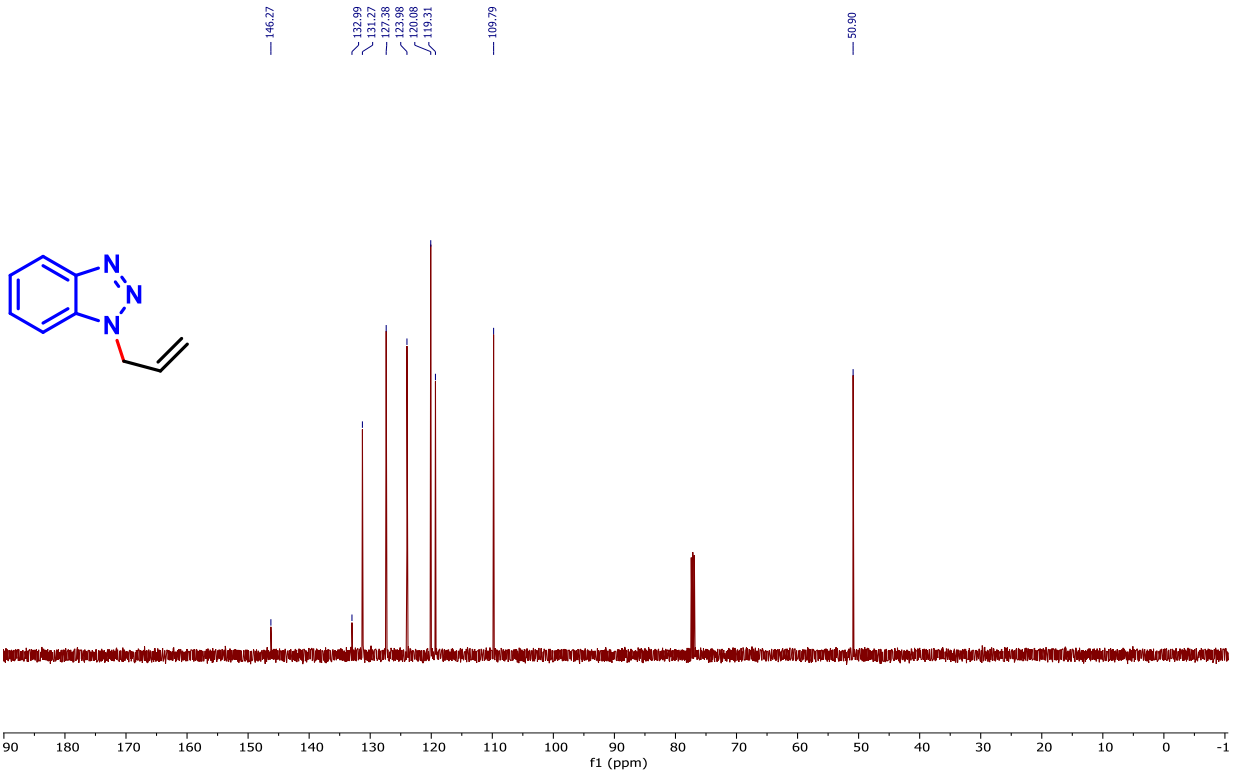


Figure 70: ^{13}C NMR (126 MHz, $CDCl_3$) of 1-Allyl-1H-benzo[d][1,2,3]triazole (**1k**)

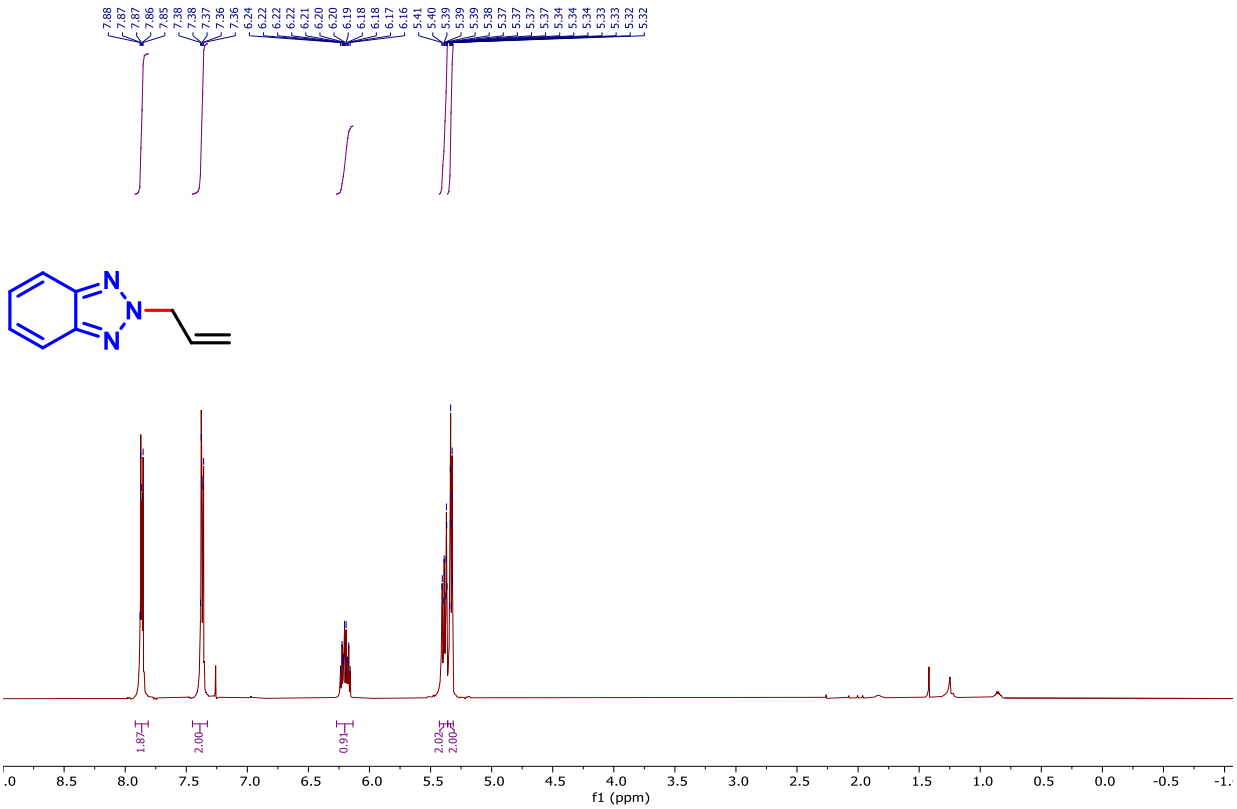


Figure 71: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-Allyl-2H-benzo[d][1,2,3]triazole (**1k**)

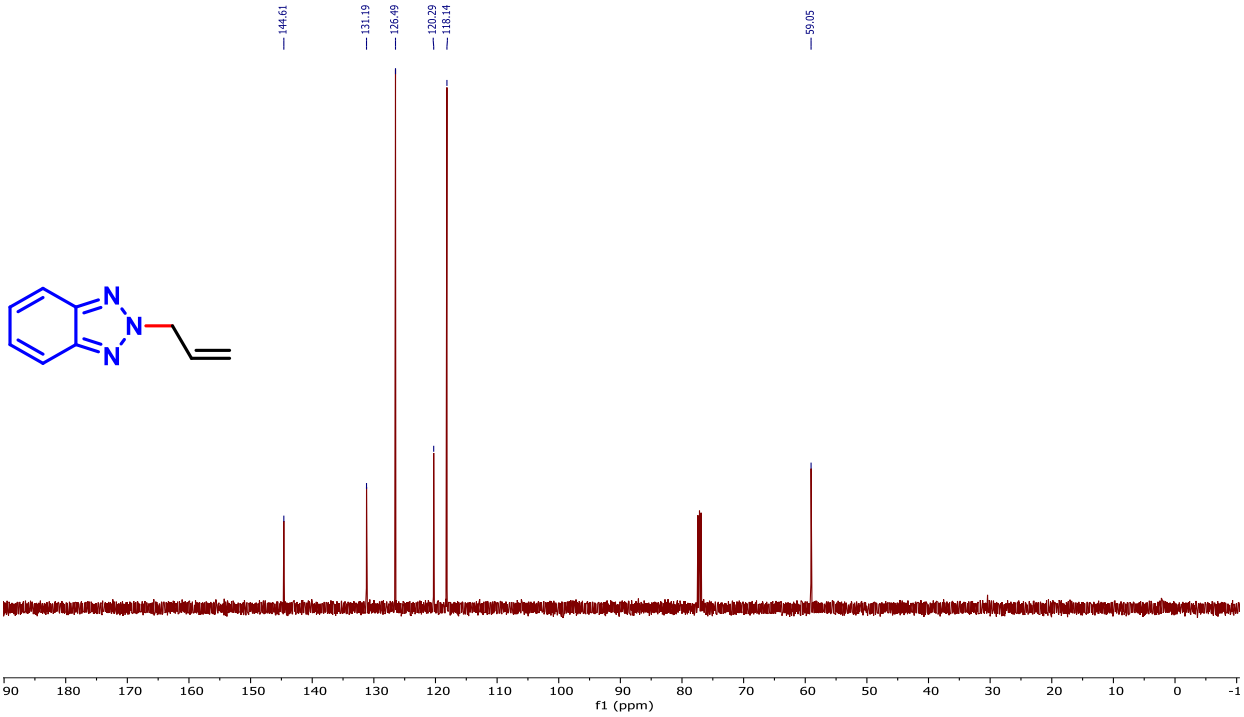


Figure 72: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-Allyl-2H-benzo[d][1,2,3]triazole (**1k**)

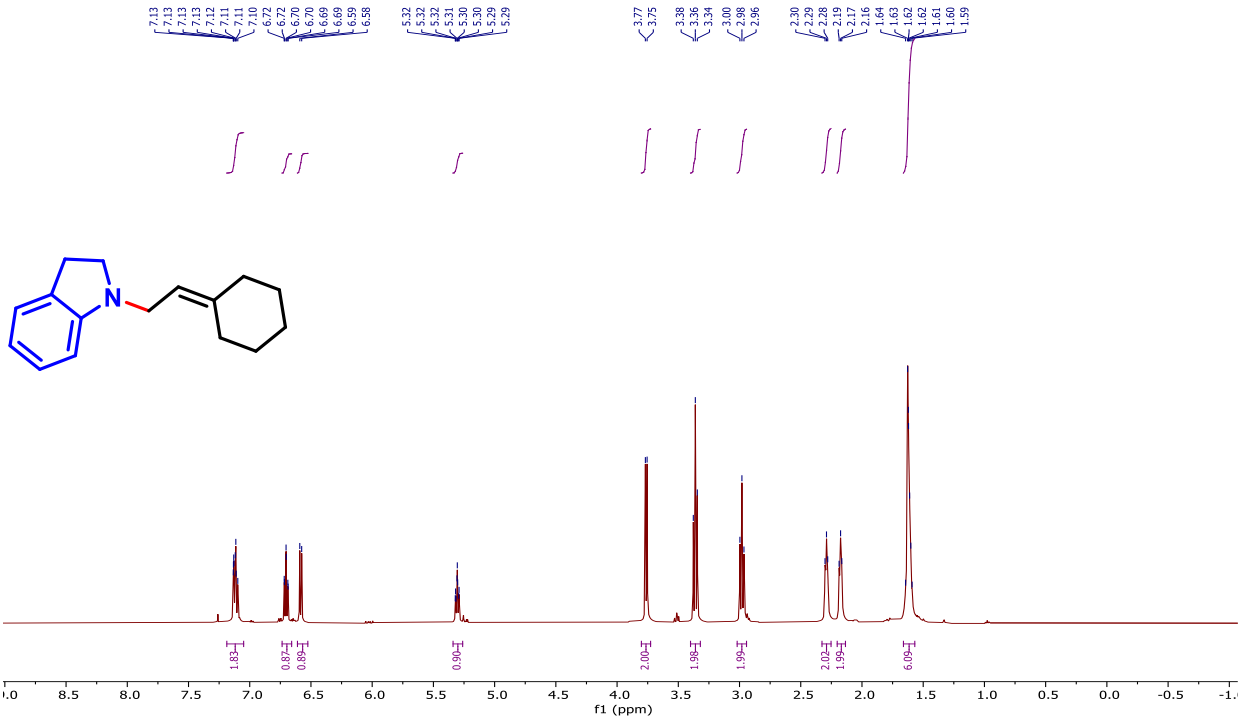


Figure 73: ^{1}H NMR (500 MHz, $CDCl_3$) of 1-(2-Cyclohexylideneethyl)indoline (**1l**)

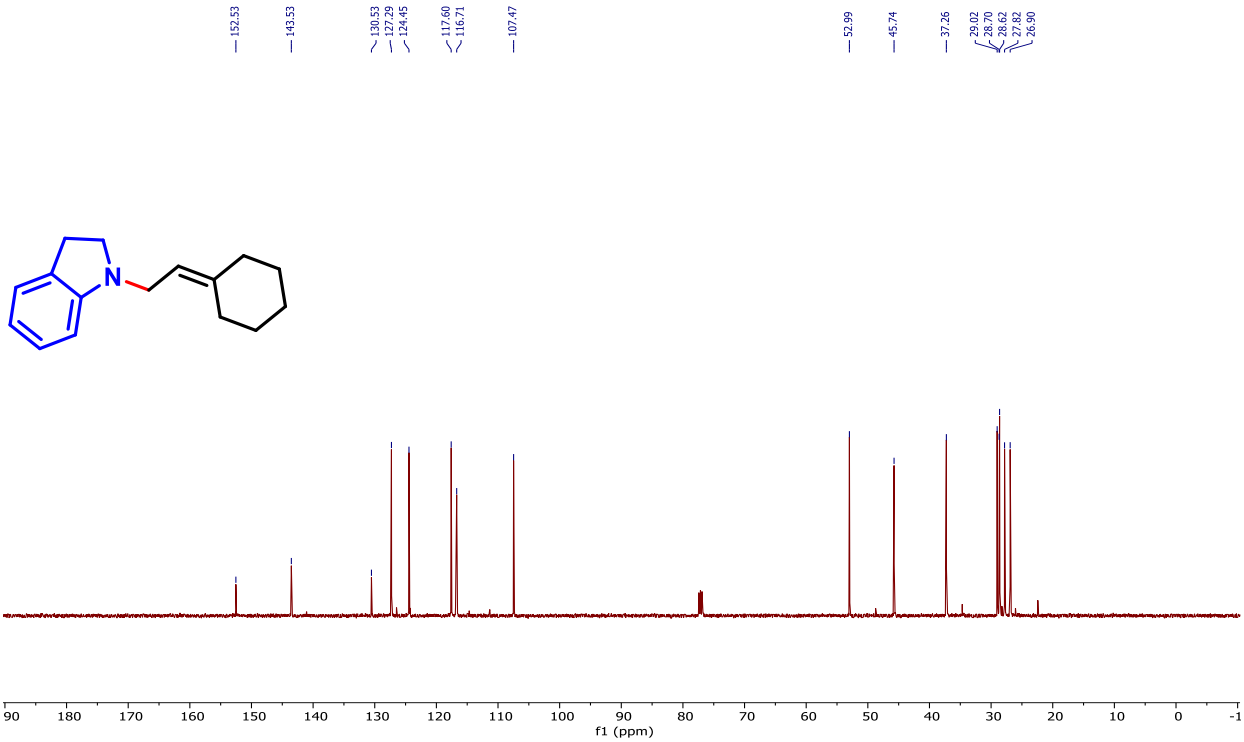


Figure 74: ^{13}C NMR (126 MHz, $CDCl_3$) of 1-(2-Cyclohexylideneethyl)indoline (**1l**)

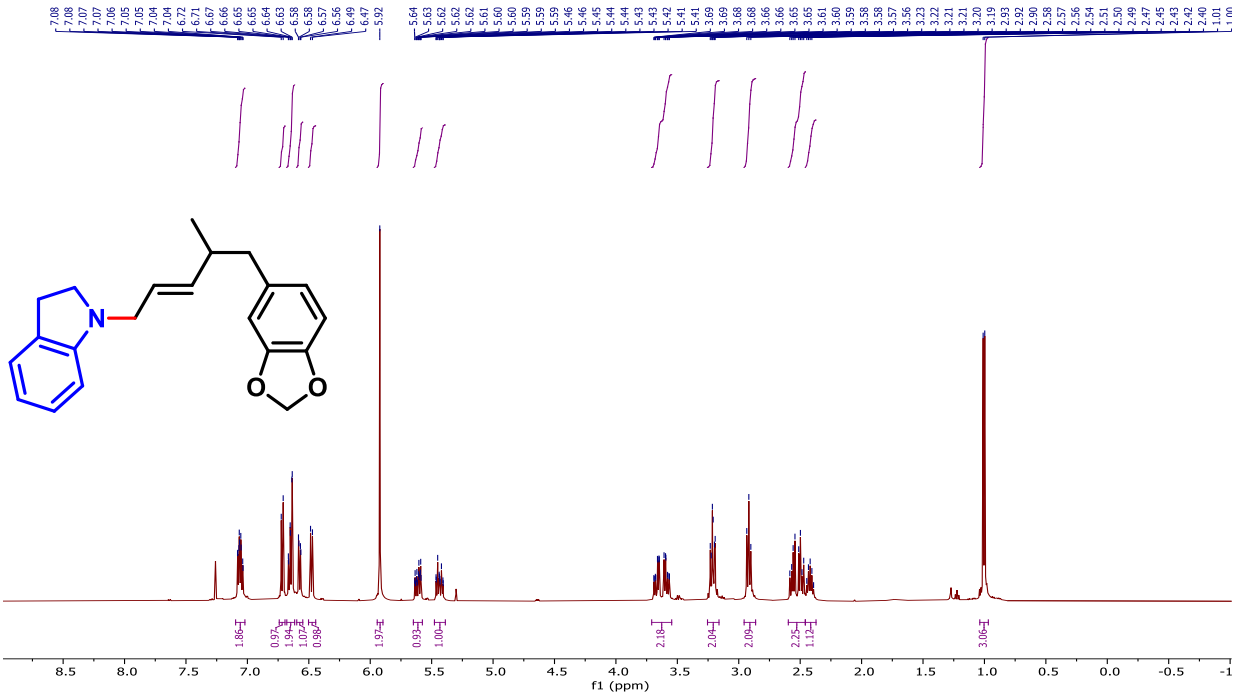


Figure 75: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-1-(5-(Benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl)indoline (**1m**)

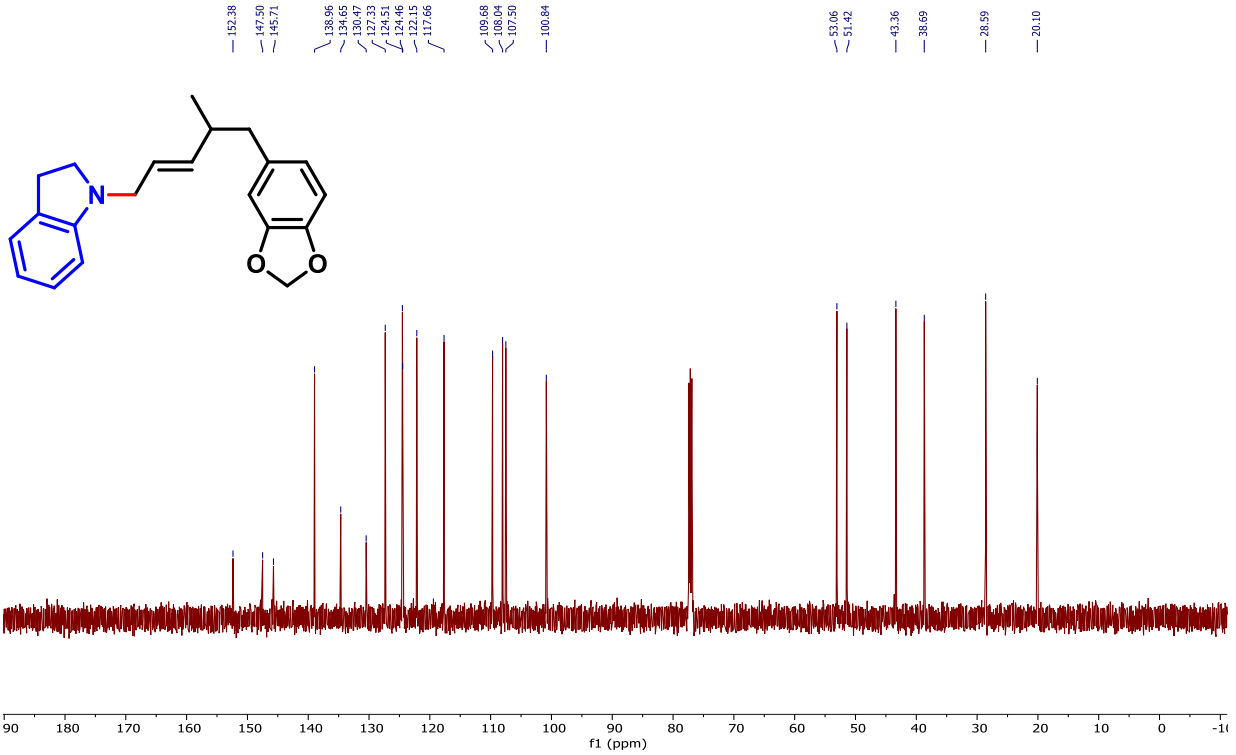


Figure 76: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-1-(5-(Benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl)indoline (**1m**)

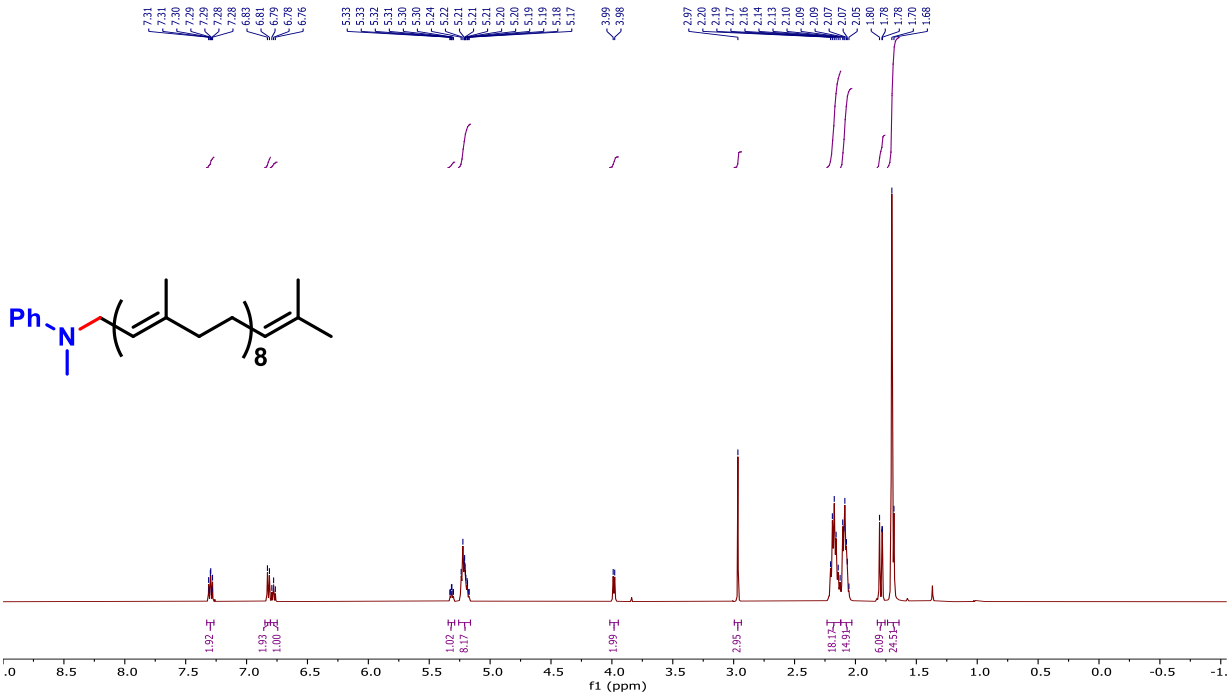


Figure 77: ^{1}H NMR (500 MHz, $CDCl_3$) of *N*-Methyl-*N*-((2E,6E,10E,14E,18E,22E,26E,30E)-3,7,11,15,19,23,27,31,35-nonamethylhexatriaconta-2,6,10,14,18,22,26,30,34-nonaen-1-yl)aniline (**1n**)

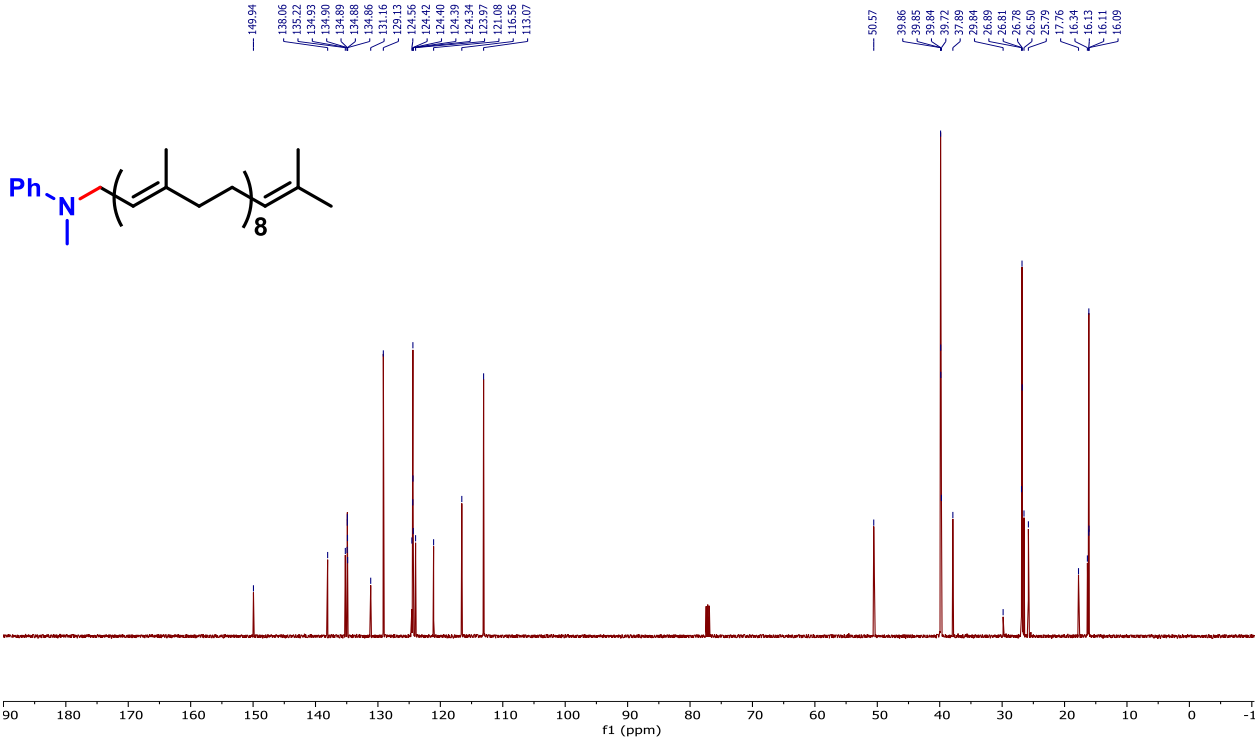


Figure 78: ^{13}C NMR (126 MHz, $CDCl_3$) of *N*-Methyl-*N*-((2E,6E,10E,14E,18E,22E,26E,30E)-3,7,11,15,19,23,27,31,35-nonamethylhexatriaconta-2,6,10,14,18,22,26,30,34-nonaen-1-yl)aniline (**1n**)

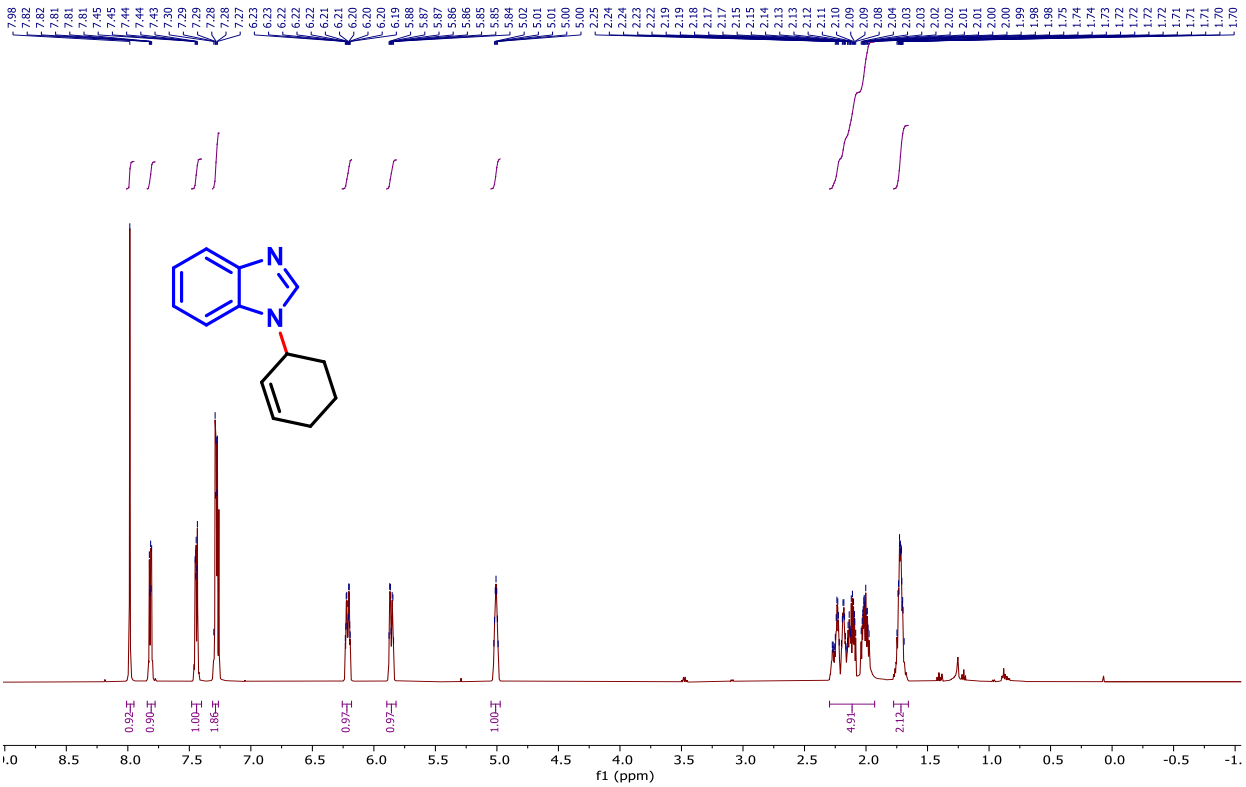


Figure 79: ^{1}H NMR (500 MHz, $CDCl_3$) of 1-(Cyclohex-2-en-1-yl)-1H-benzo[d]imidazole (**1o**)

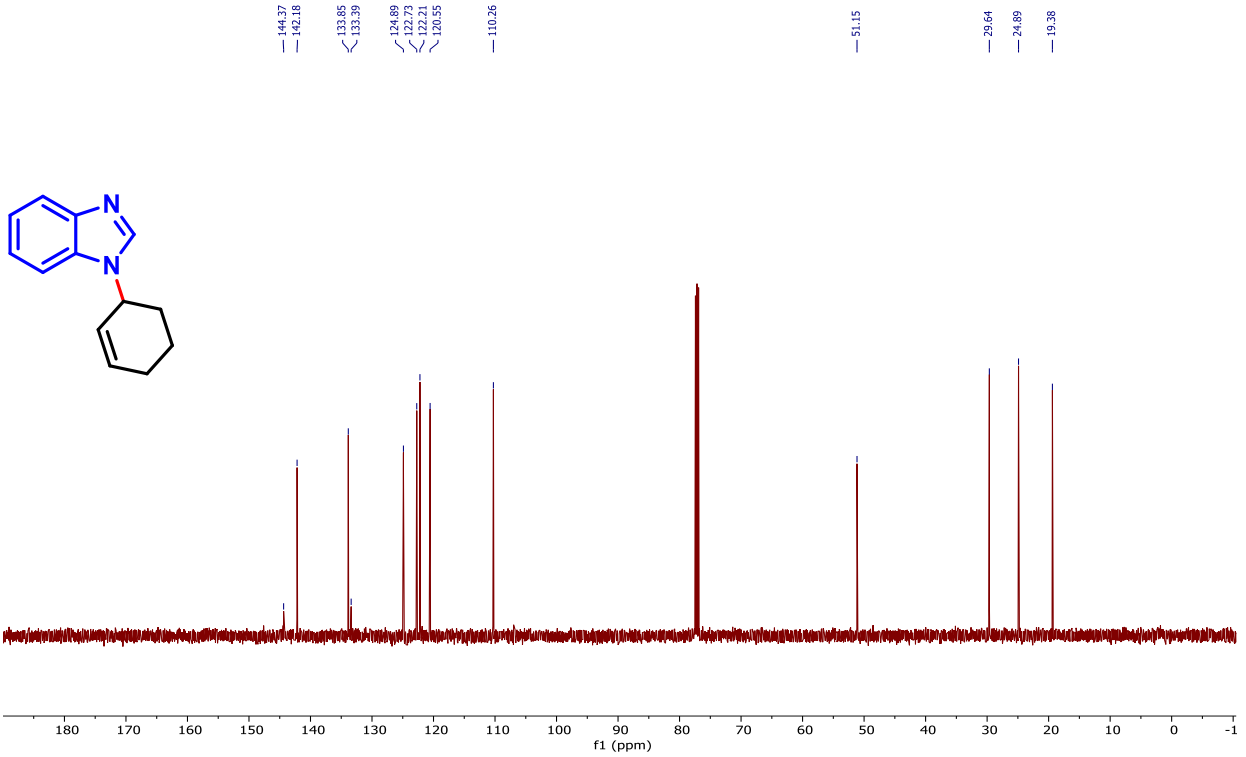


Figure 80: ^{13}C NMR (126 MHz, $CDCl_3$) of 1-(Cyclohex-2-en-1-yl)-1H-benzo[d]imidazole (**1o**)

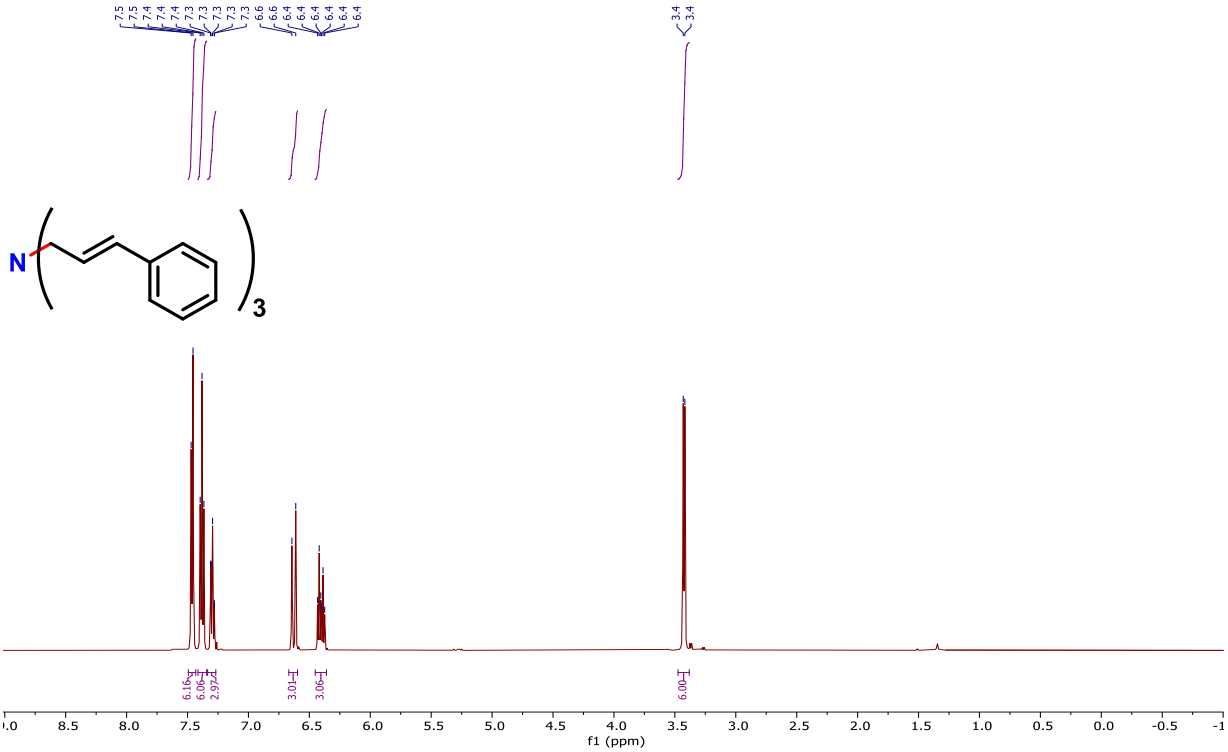


Figure 81: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-Tricinnamylamine (**1p**)

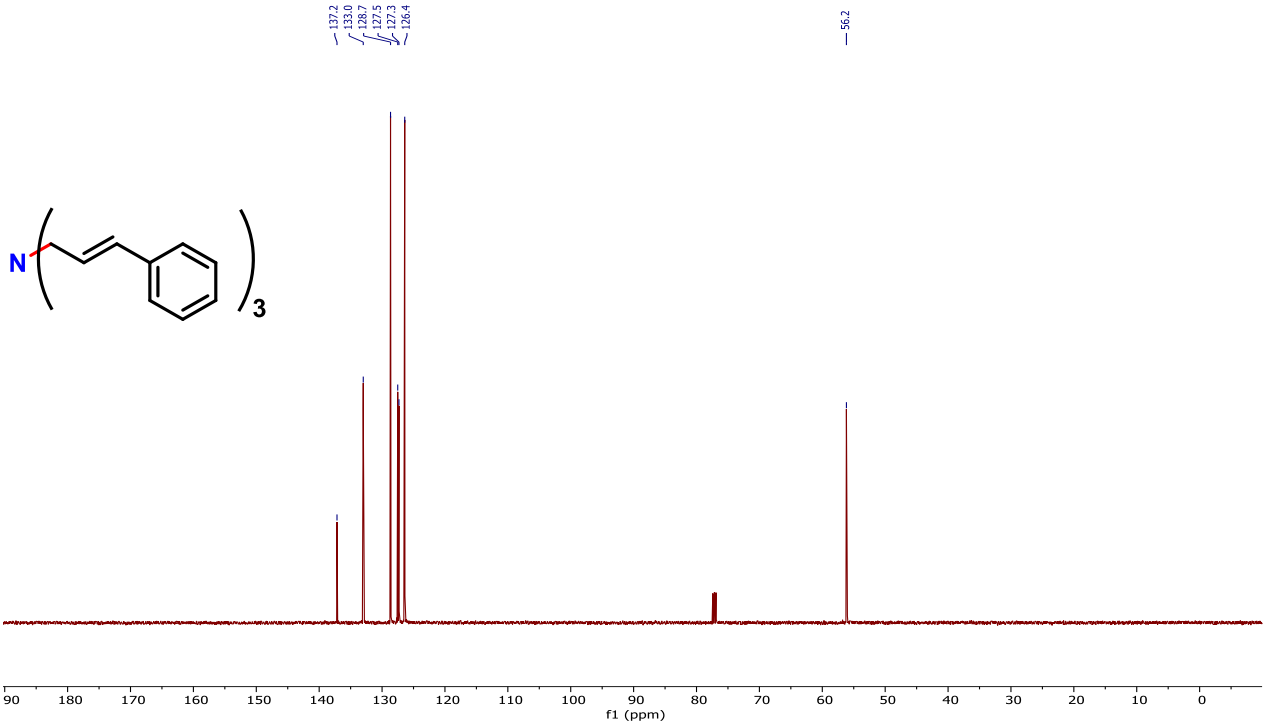


Figure 82: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-Tricinnamylamine (**1p**)

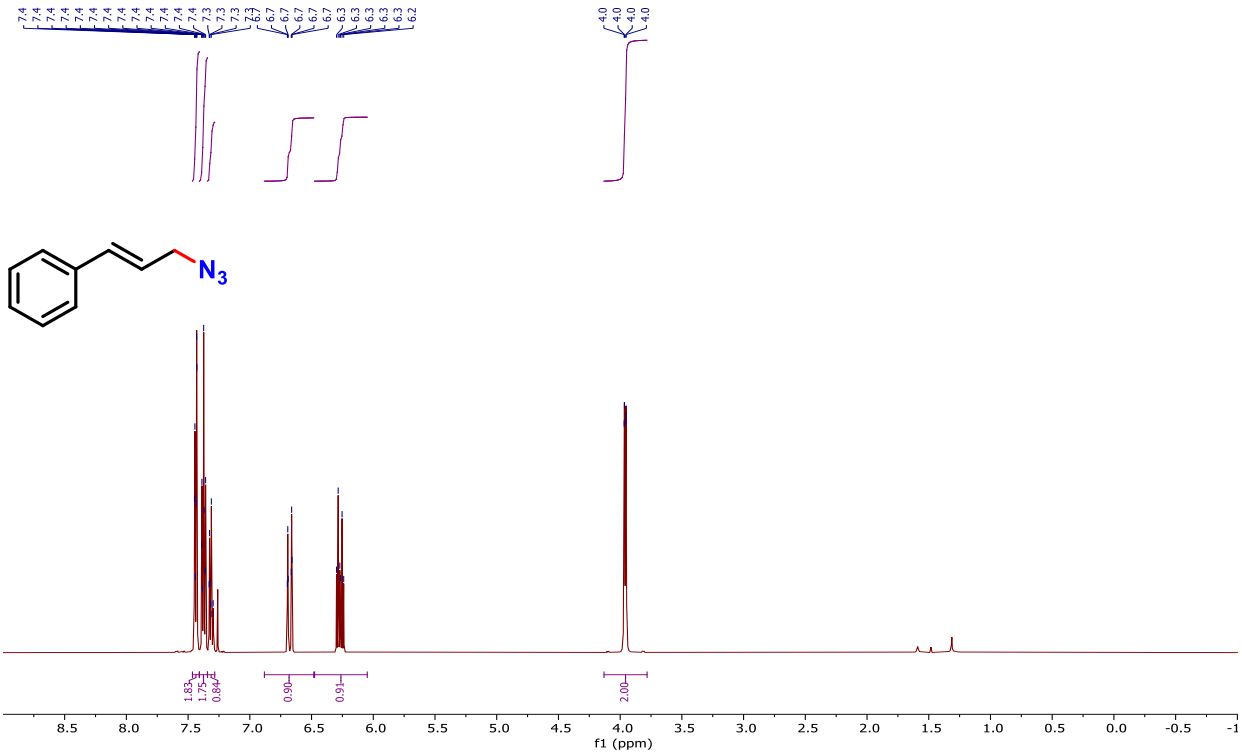


Figure 83: ^{1}H NMR (500 MHz, $CDCl_3$) of (E)-(3-azidoprop-1-en-1-yl)benzene (**1q**)

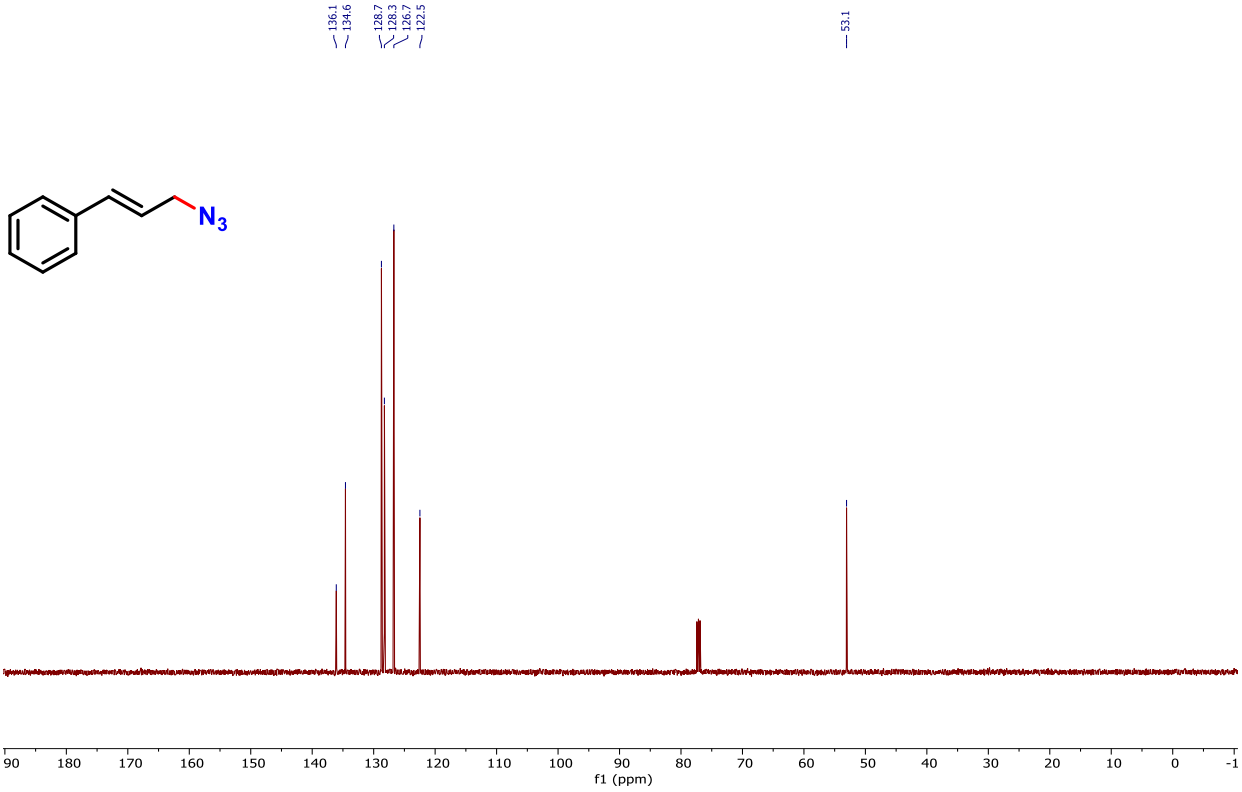


Figure 84: ^{13}C NMR (126 MHz, $CDCl_3$) of (E)-(3-azidoprop-1-en-1-yl)benzene (**1q**)

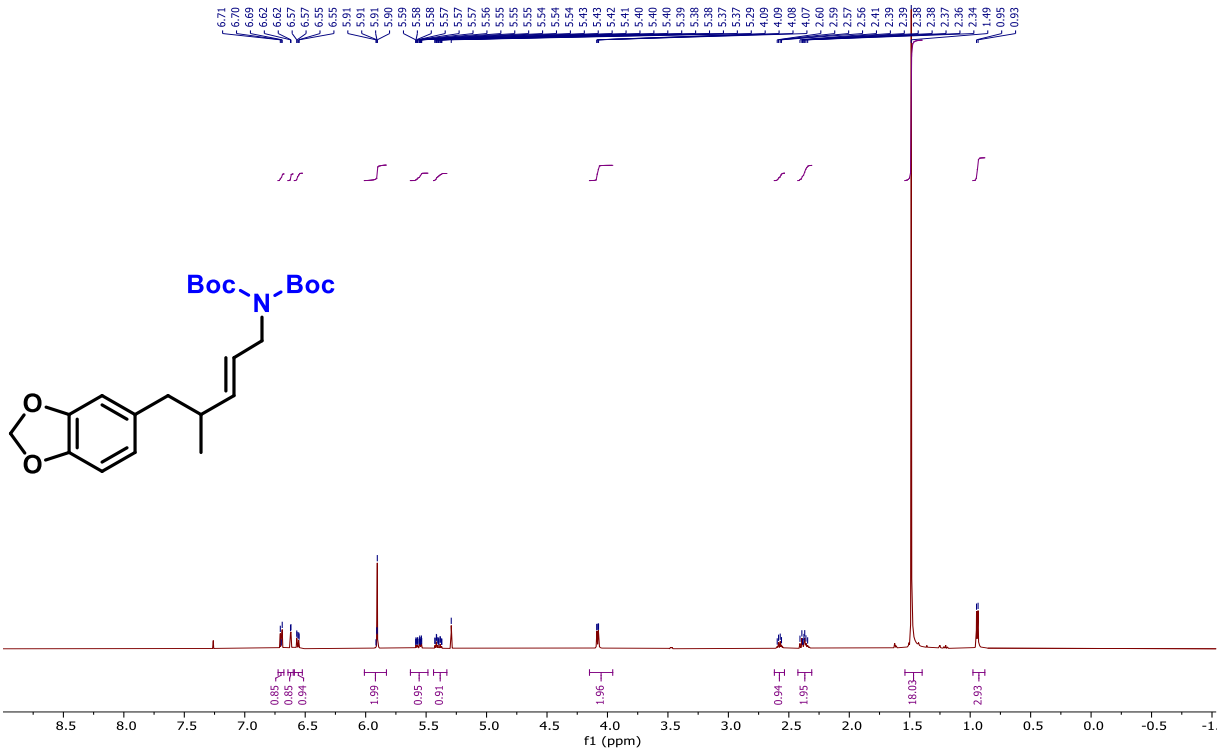


Figure 85: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-5-(Benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-(di-*tert*-butyl iminodicarboxylate) (**1r**)

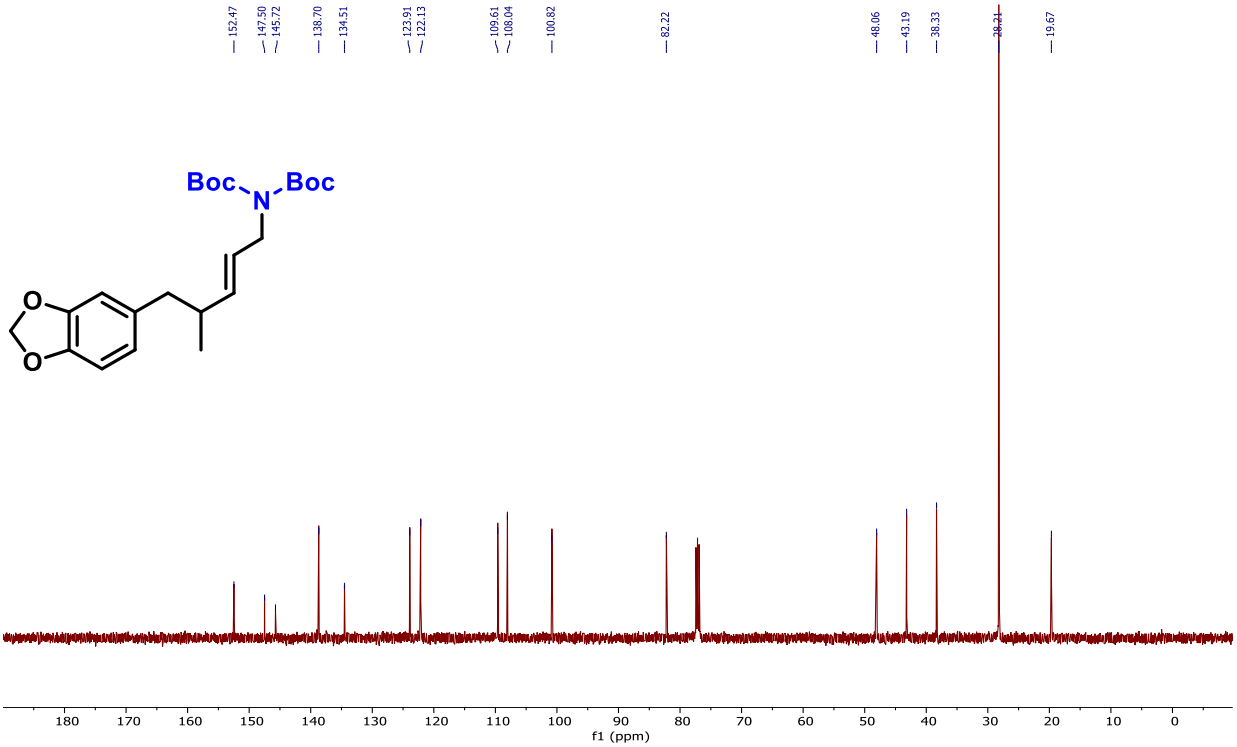


Figure 86: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-5-(Benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-en-1-(di-*tert*-butyl iminodicarboxylate) **(1r)**

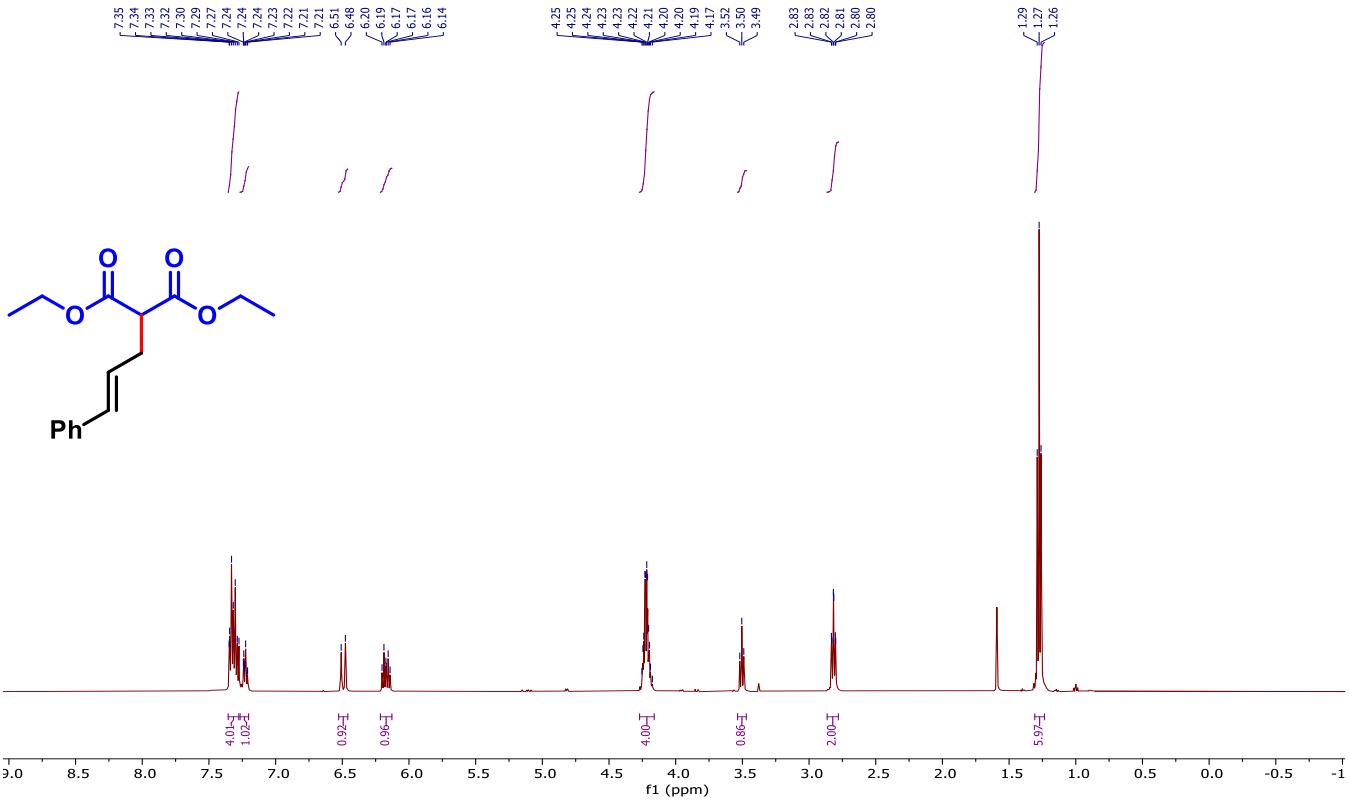


Figure 87: ^{1}H NMR (500 MHz, $CDCl_3$) of Diethyl 2-cinnamylmalonate (**2a**)

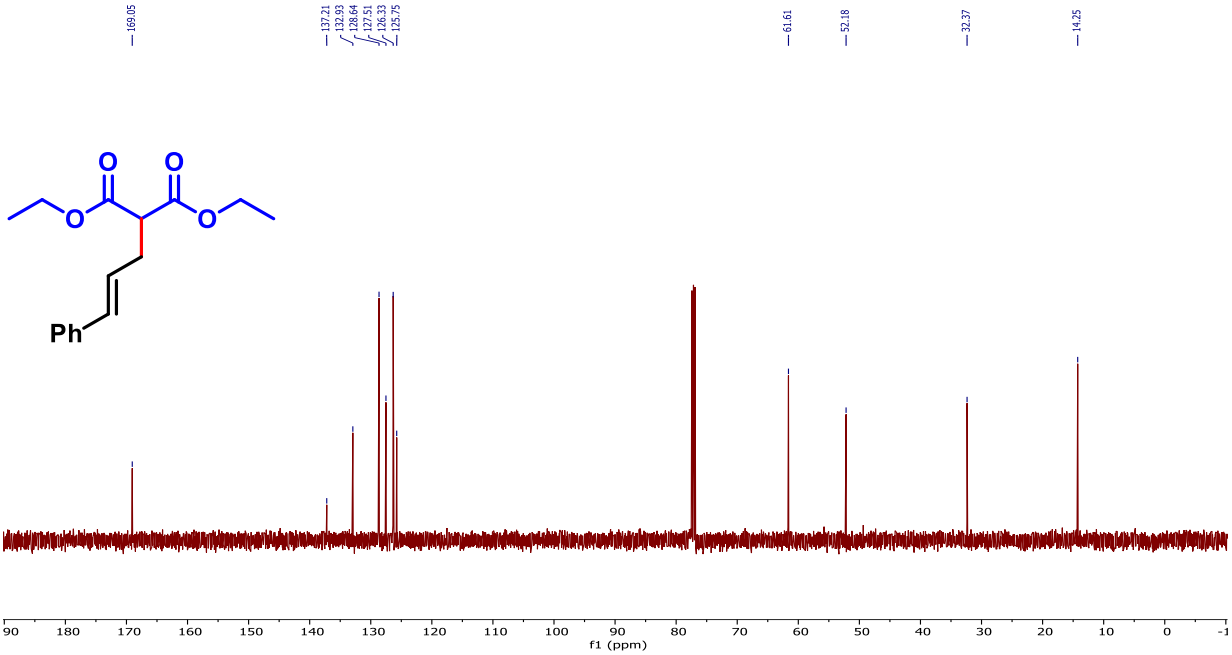


Figure 88: ^{13}C NMR (126 MHz, $CDCl_3$) of Diethyl 2-cinnamylmalonate (**2a**)

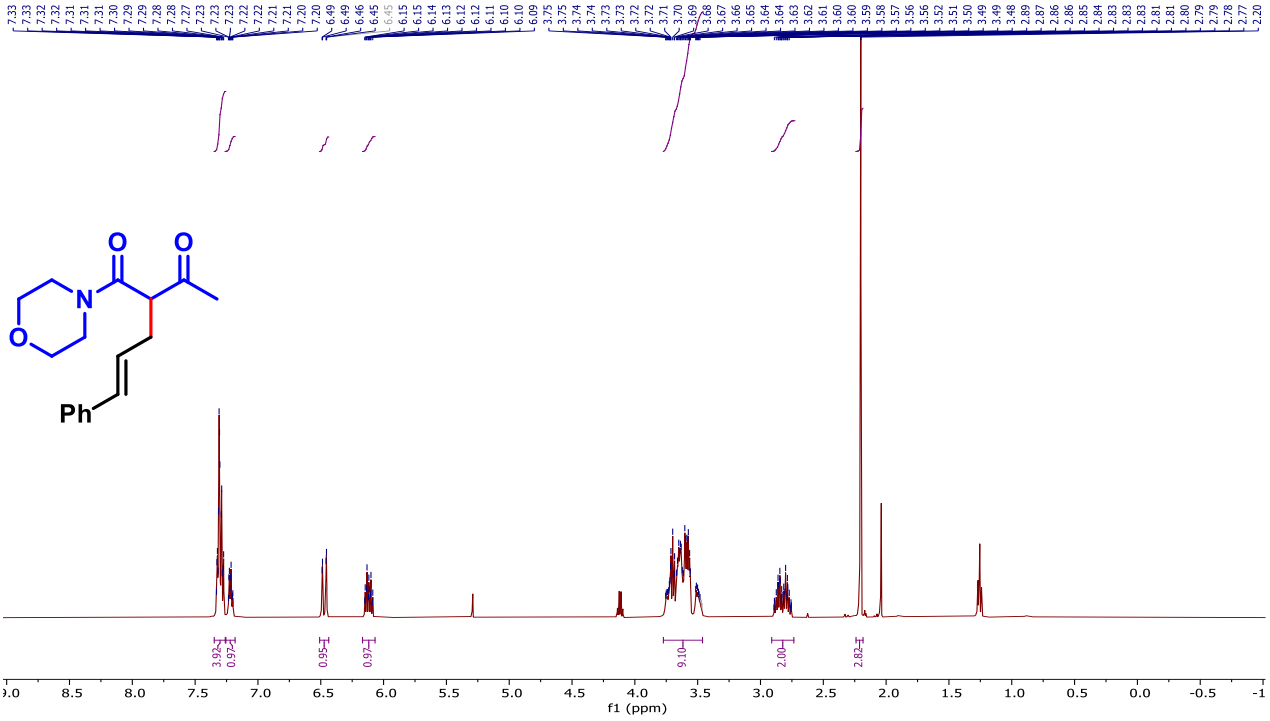


Figure 89: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-Cinnamyl-1-morpholinobutane-1,3-dione (**2b**)

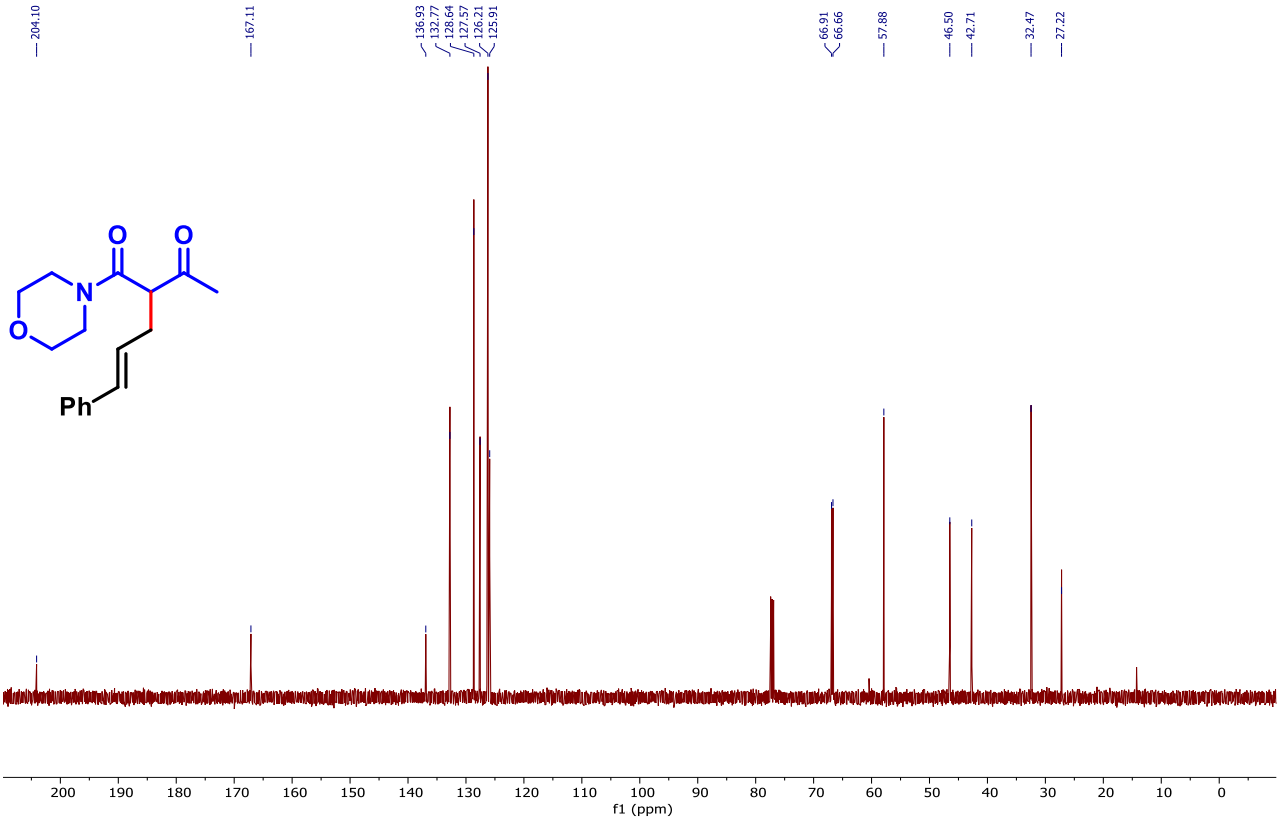


Figure 90: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-Cinnamyl-1-morpholinobutane-1,3-dione (**2b**)

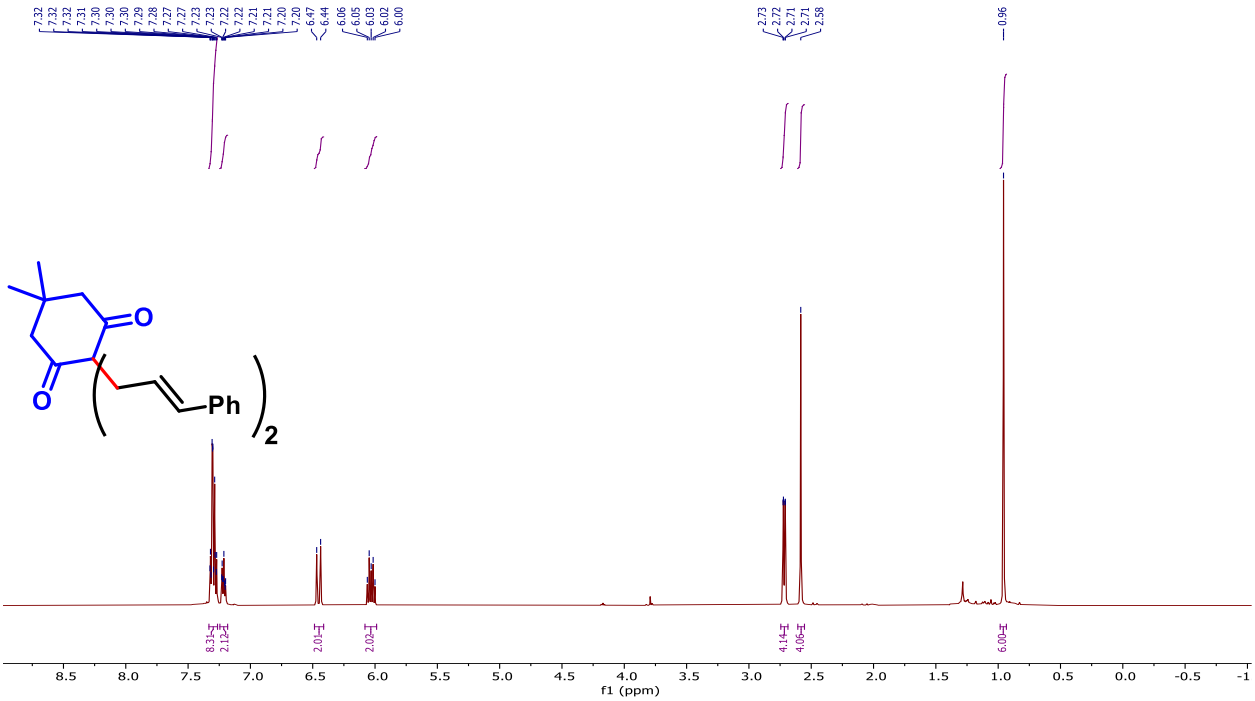


Figure 91: ^{1}H NMR (500 MHz, $CDCl_3$) of 2,2-Dicinnamyl-5,5-dimethylcyclohexane-1,3-dione (**2c**)

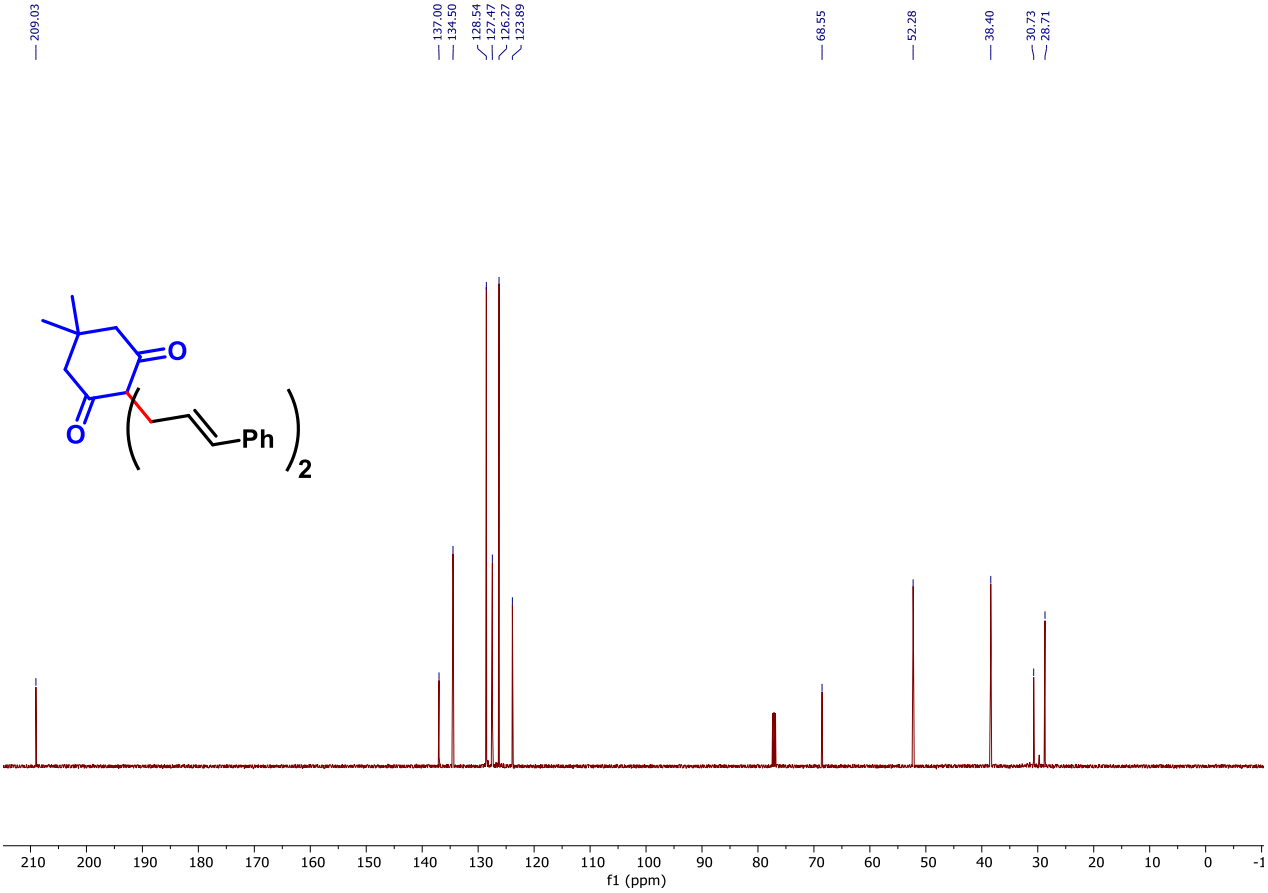


Figure 92: ^{13}C NMR (126 MHz, $CDCl_3$) of 2,2-Dicinnamyl-5,5-dimethylcyclohexane-1,3-dione (**2c**)

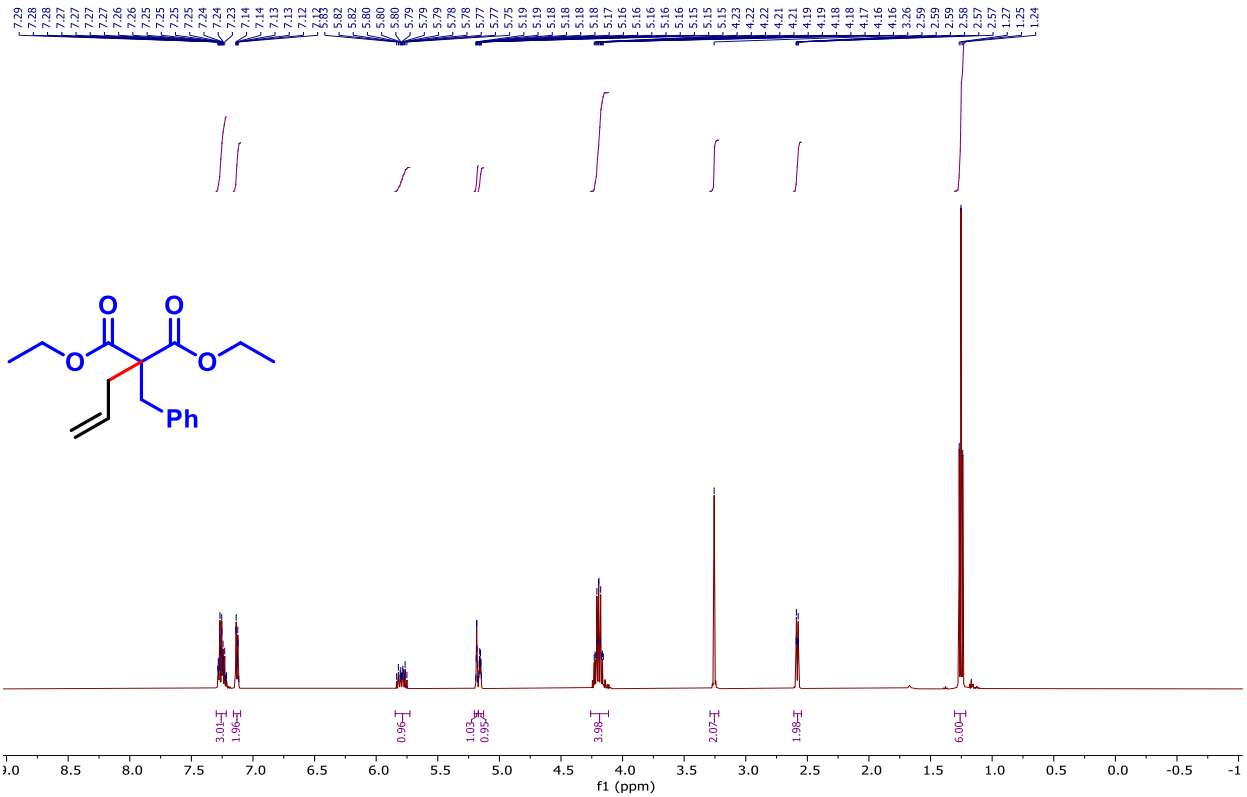


Figure 93: ^{1}H NMR (500 MHz, $CDCl_3$) of Diethyl 2-allyl-2-benzylmalonate (**2d**)

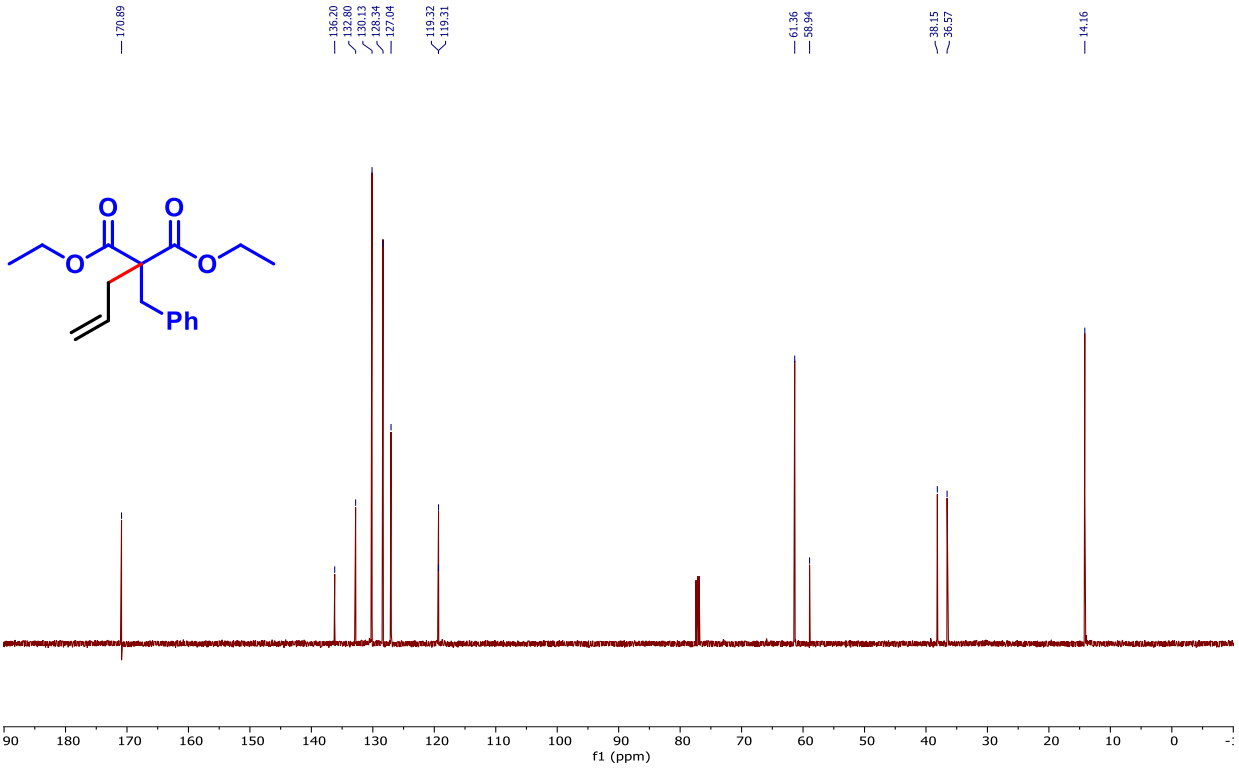


Figure 94: ^{13}C NMR (126 MHz, $CDCl_3$) of Diethyl 2-allyl-2-benzylmalonate (**2d**)

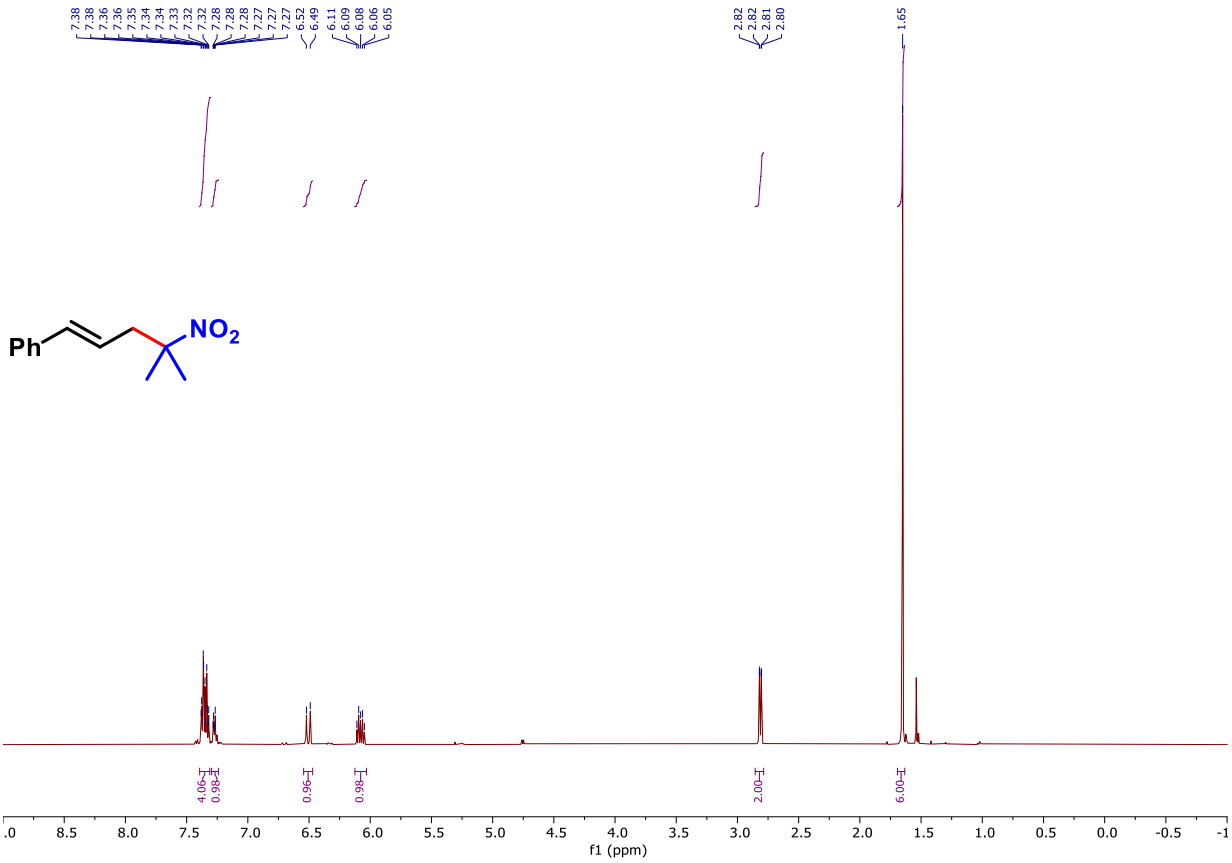


Figure 95: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-(4-Methyl-4-nitropent-1-en-1-yl)benzene (**2e**)

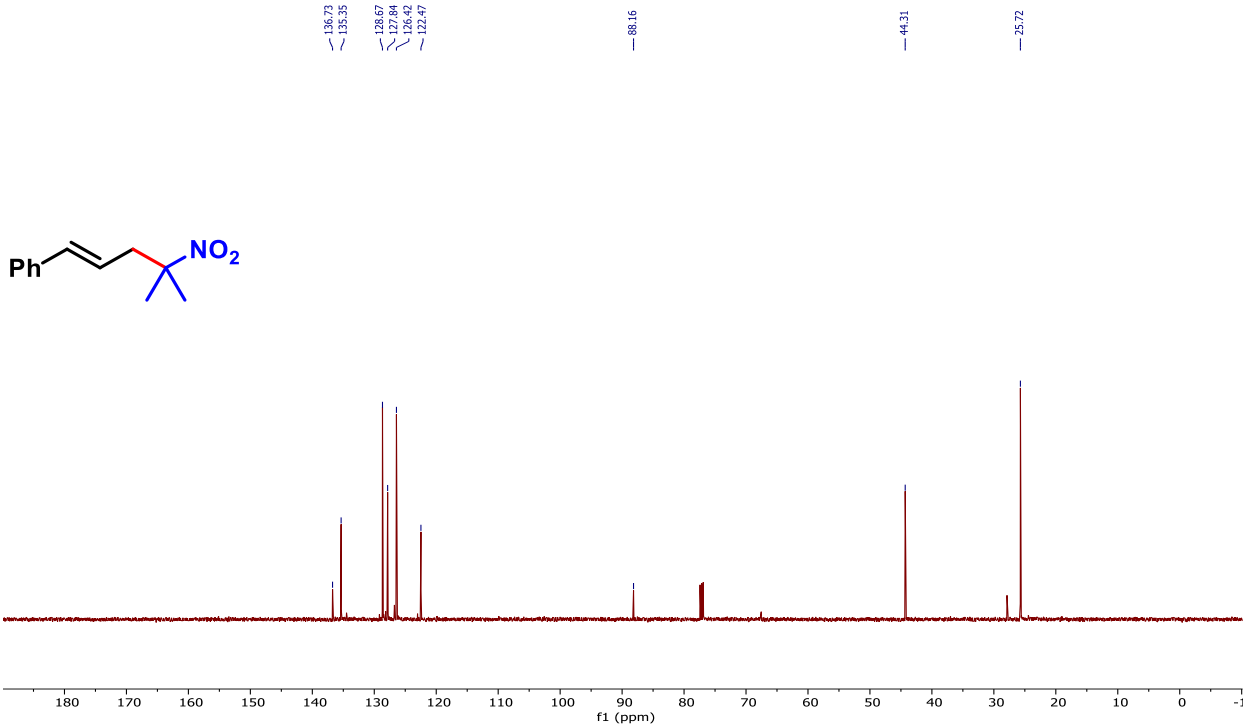


Figure 96: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-(4-Methyl-4-nitropent-1-en-1-yl)benzene (**2e**)

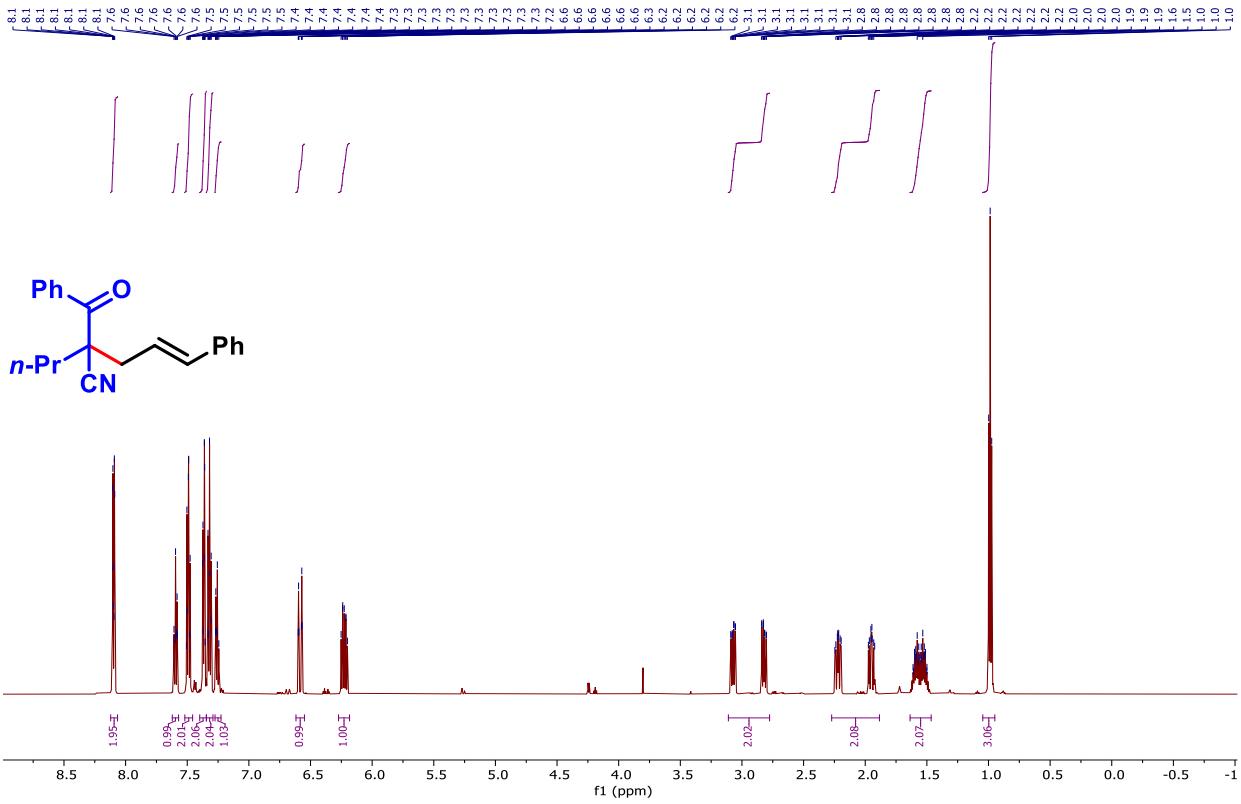


Figure 97: ^{1}H NMR (600 MHz, $CDCl_3$) of (*E*)-2-Benzoyl-5-phenyl-2-propylpent-4-enenitrile (**2f**)

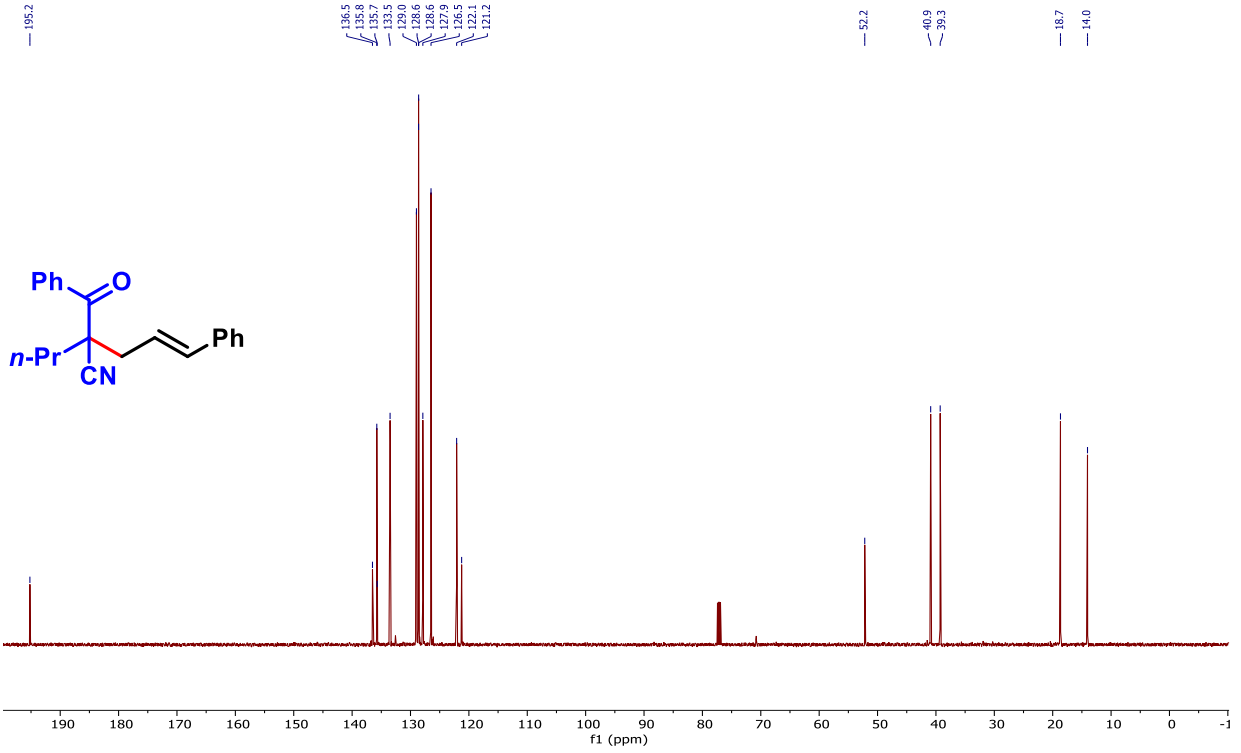


Figure 98: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-2-Benzoyl-5-phenyl-2-propylpent-4-enenitrile (**2f**)

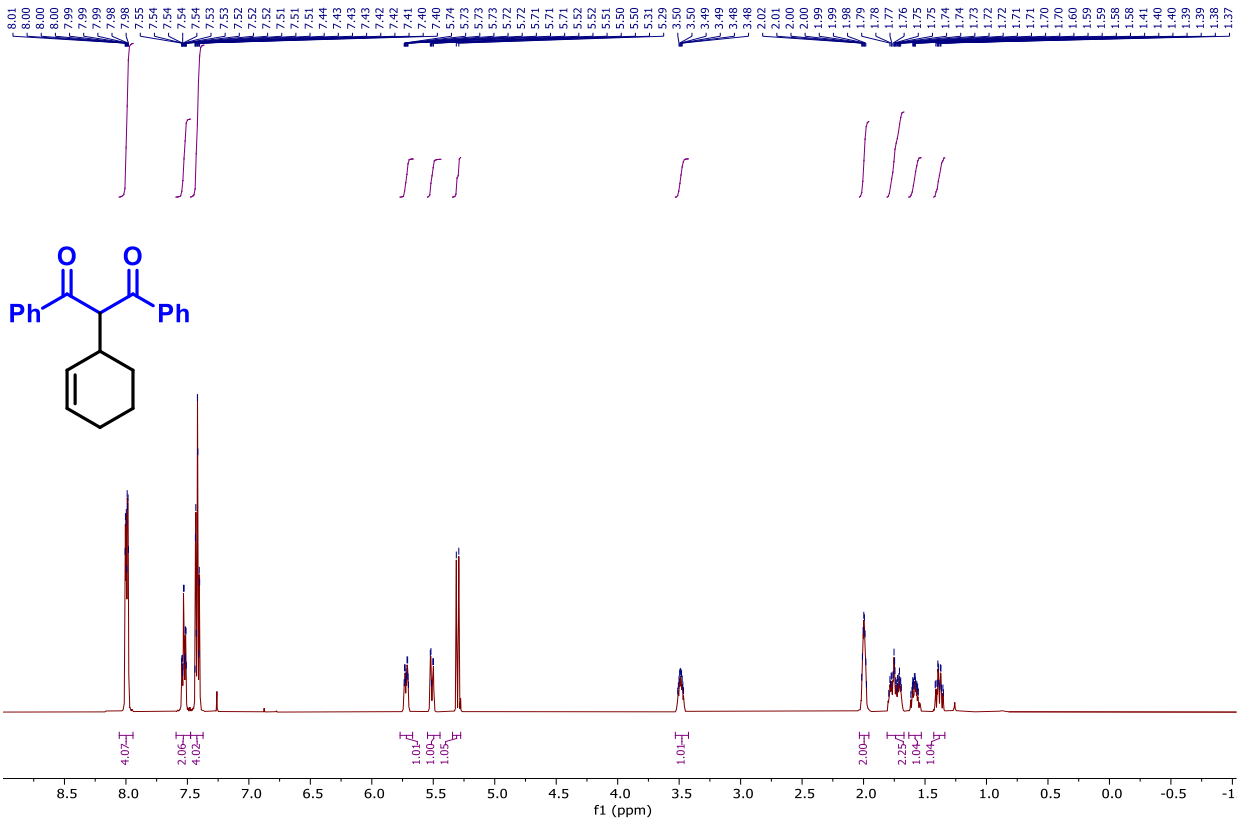


Figure 99: ^{1}H NMR (500 MHz, $CDCl_3$) of 2-(Cyclohex-2-en-1-yl)-1,3-diphenylpropane-1,3-dione (**2g**)

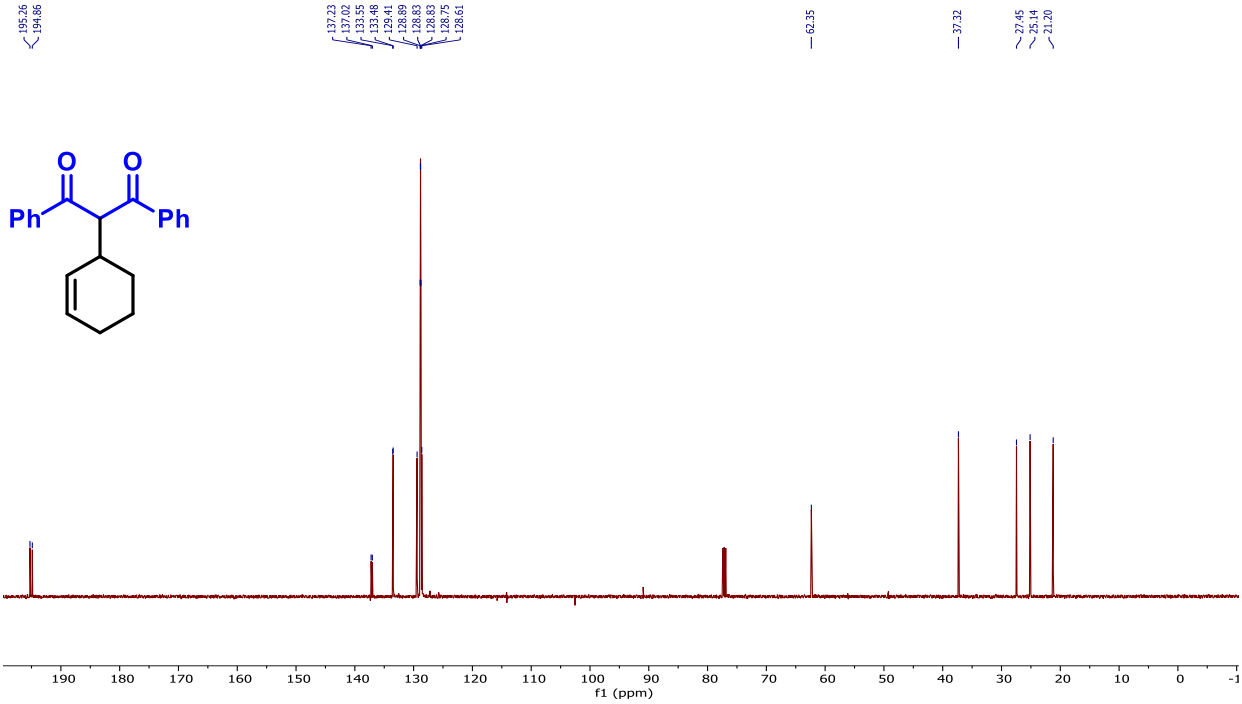


Figure 100: ^{13}C NMR (126 MHz, $CDCl_3$) of 2-(Cyclohex-2-en-1-yl)-1,3-diphenylpropane-1,3-dione (**2g**)

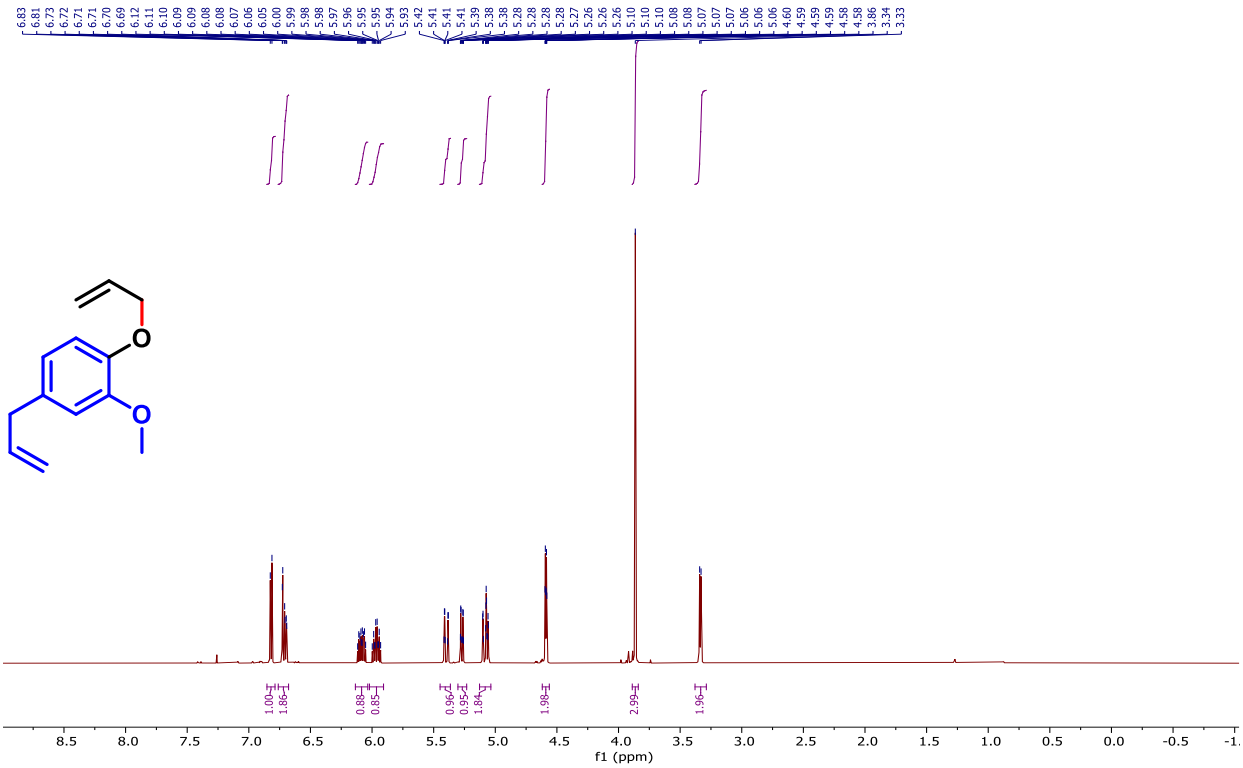


Figure 101: ^{1}H NMR (600 MHz, $CDCl_3$) of 4-Allyl-1-(allyloxy)-2-methoxybenzene (**3a**)

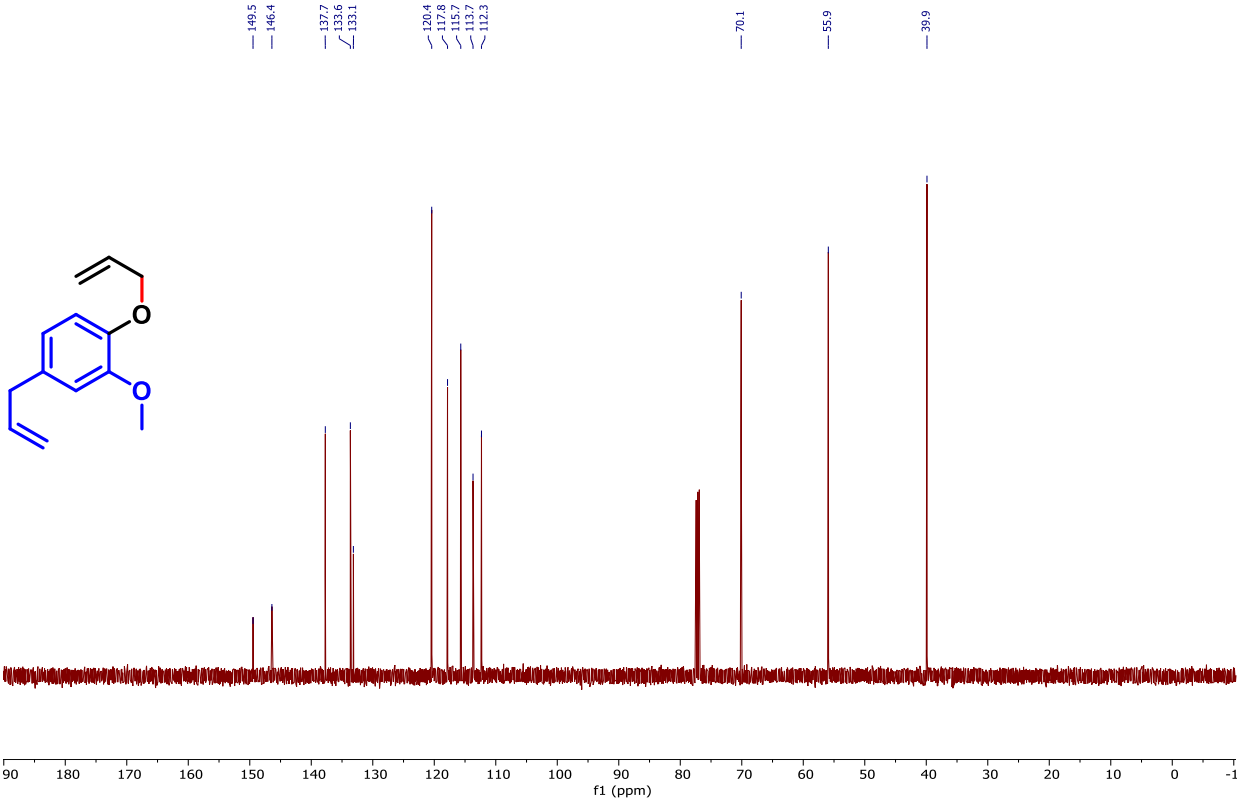


Figure 102: ^{13}C NMR (126 MHz, $CDCl_3$) of 4-Allyl-1-(allyloxy)-2-methoxybenzene (**3a**)

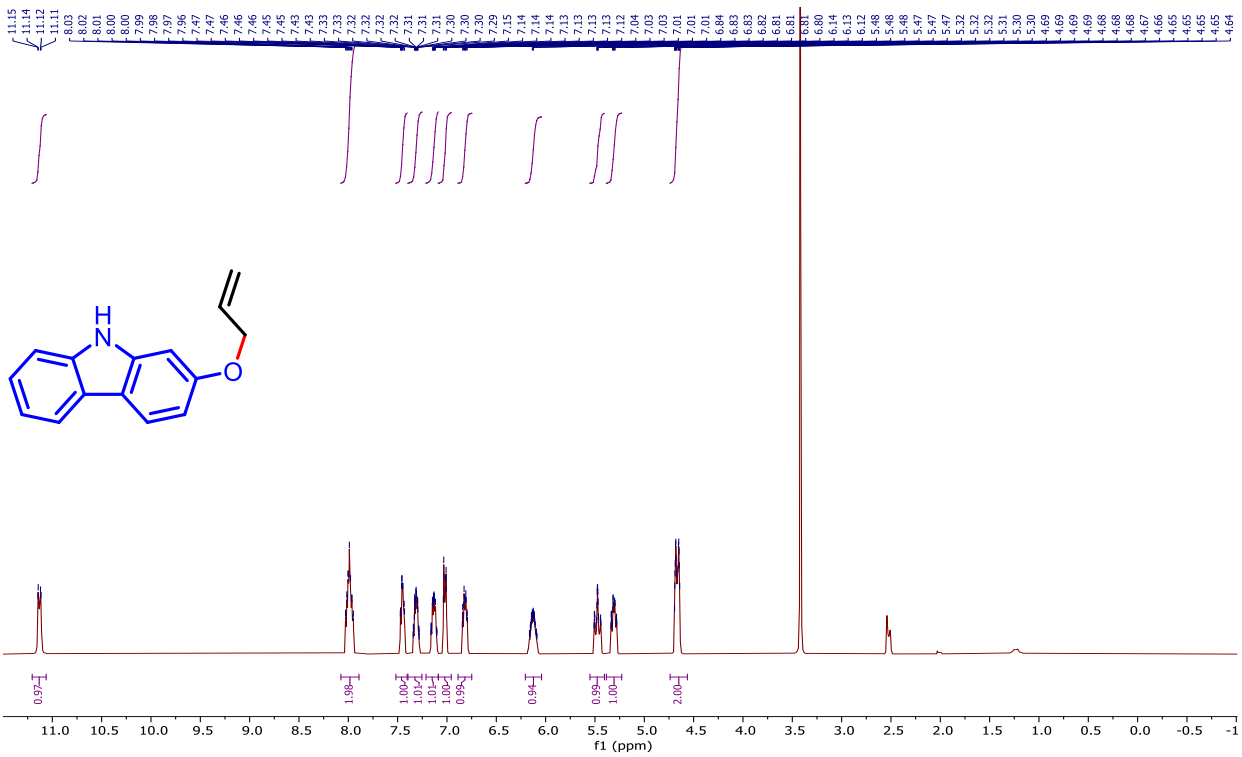


Figure 103: ^{1}H NMR (600 MHz, DMSO) of 2-(Allyloxy)-9H-carbazole (**3b**)

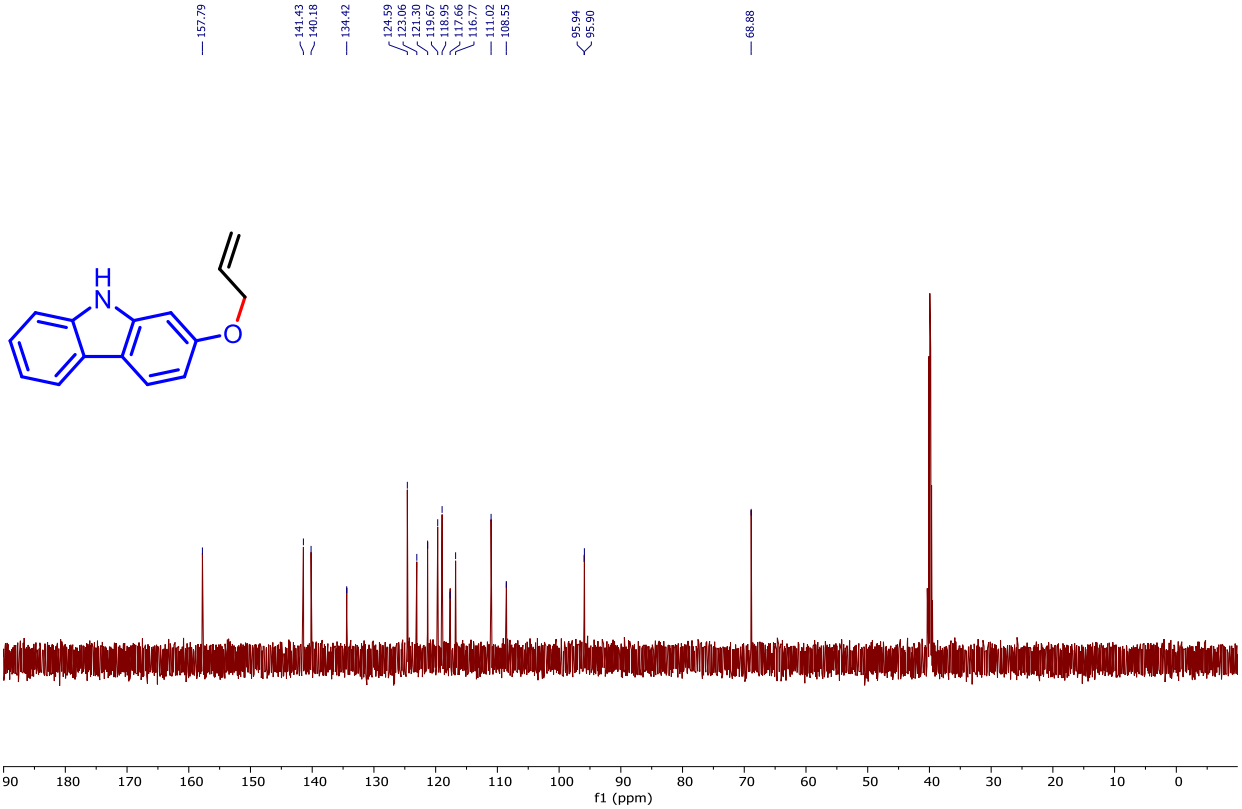


Figure 104: ^{13}C NMR (151 MHz, DMSO) of 2-(Allyloxy)-9H-carbazole (**3b**)

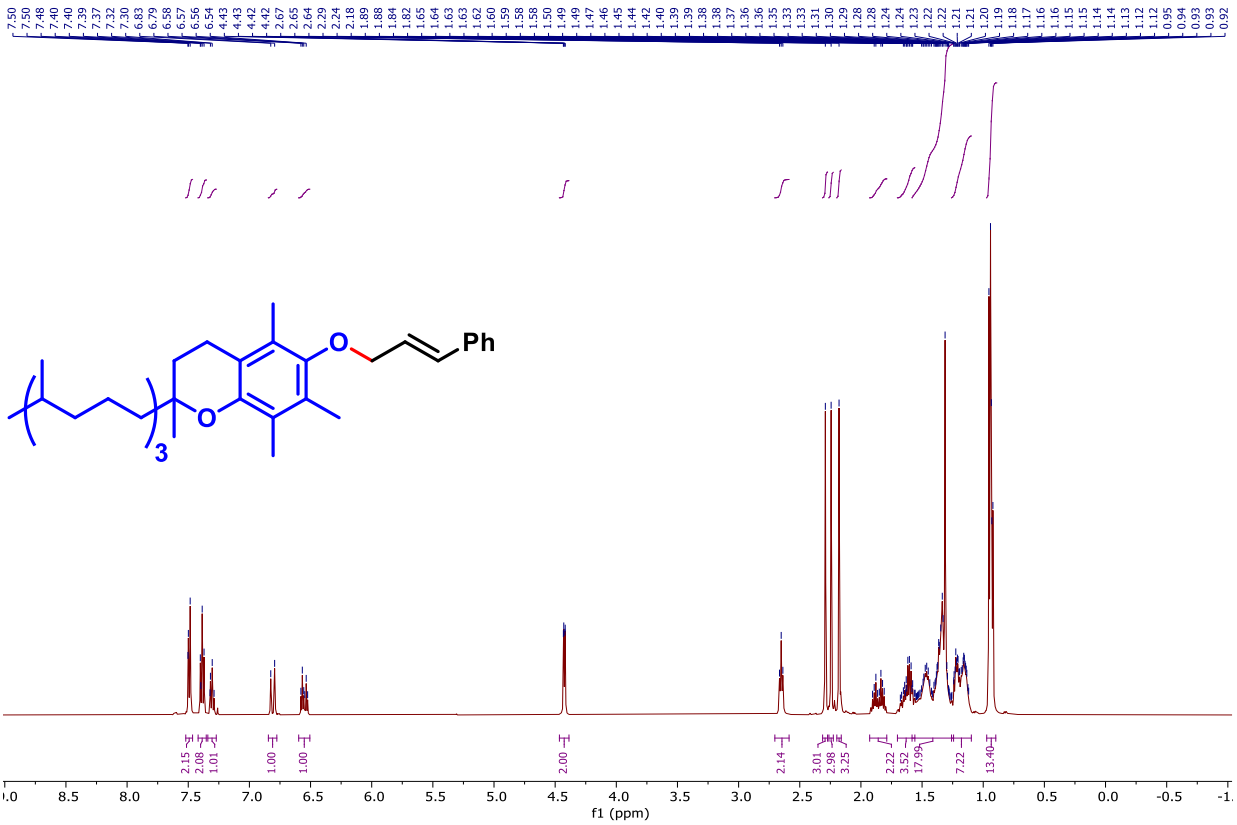


Figure 105: ^{1}H NMR (500 MHz, $CDCl_3$) of 6-(Cinnamyloxy)-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chromane (**3c**)

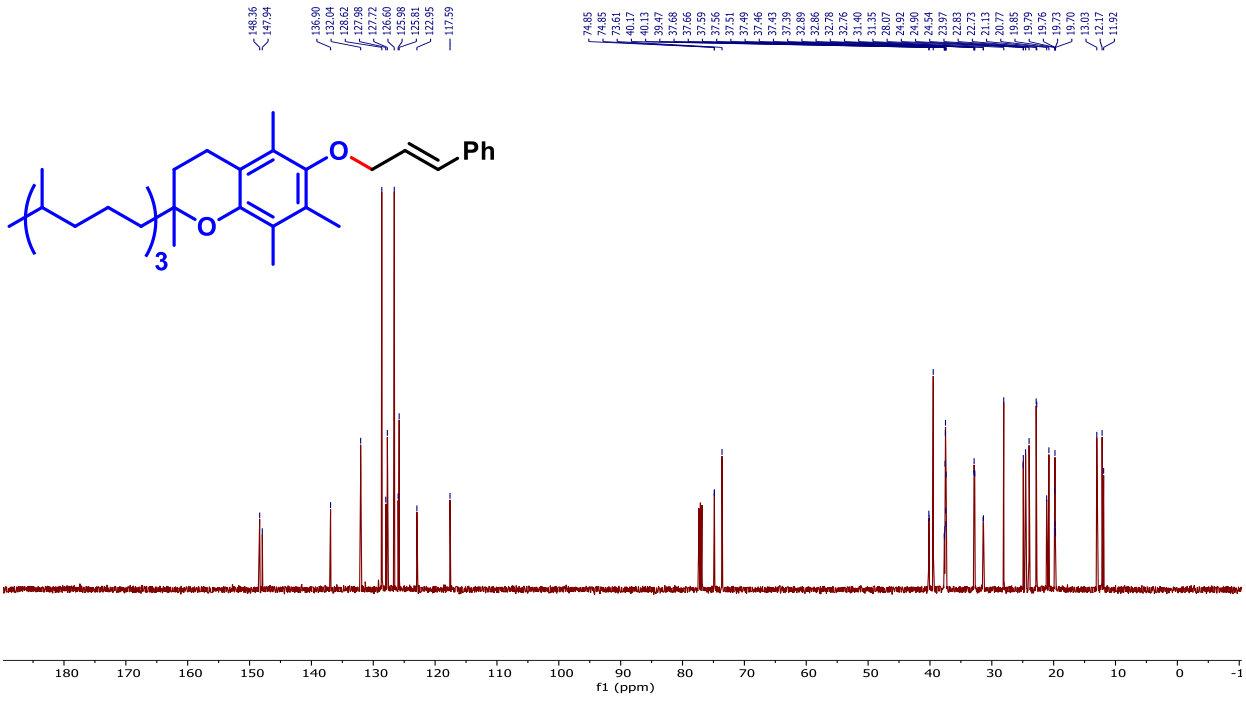


Figure 106: ^{13}C NMR (126 MHz, $CDCl_3$) of 6-(Cinnamyloxy)-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chromane (**3c**)

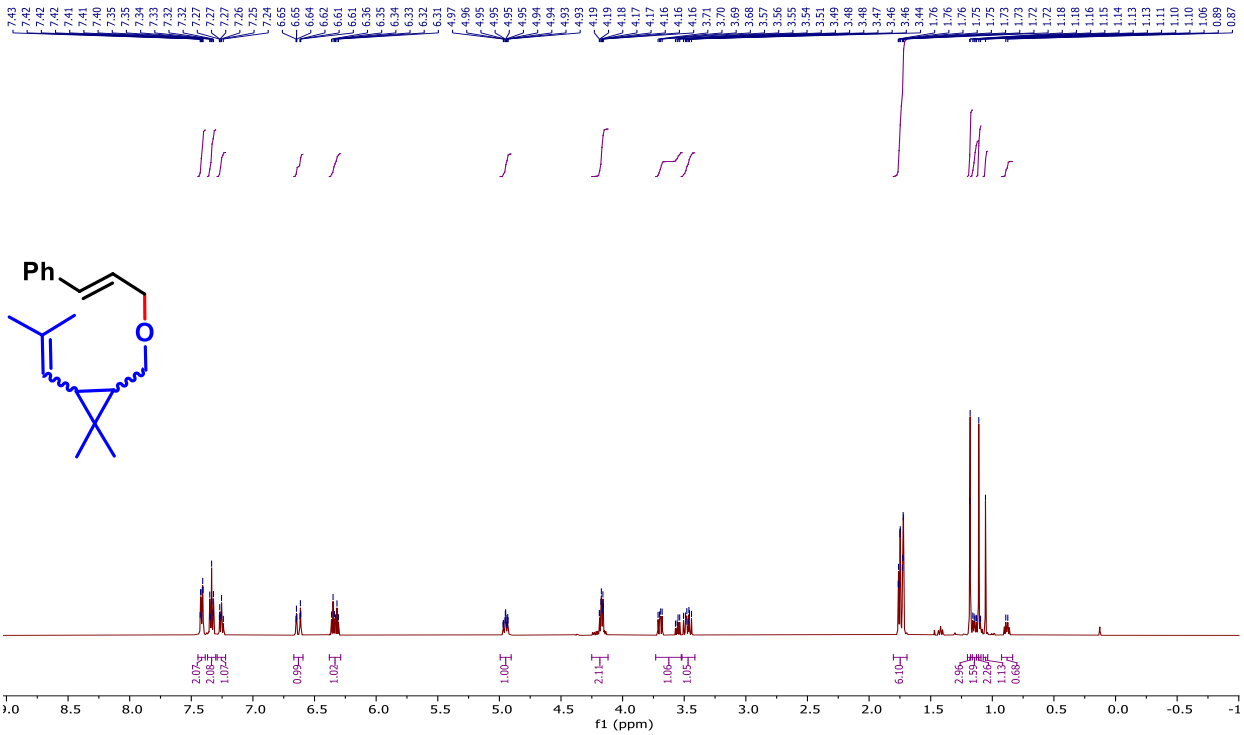


Figure 107: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-(3-((2,2-Dimethyl-3-(2-methylprop-1-en-1-yl)cyclopropyl)methoxy)prop-1-en-1-yl)benzene (**3d**)

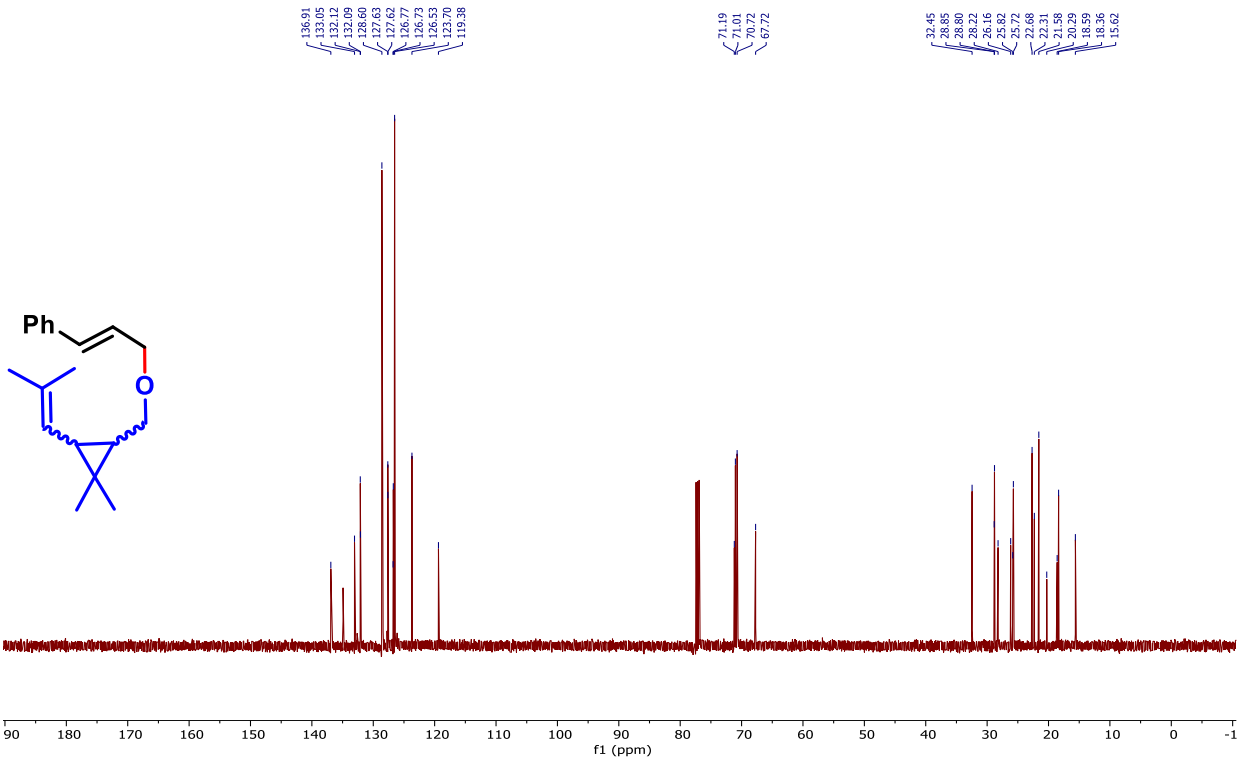


Figure 108: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-(3-((2,2-Dimethyl-3-(2-methylprop-1-en-1-yl)cyclopropyl)methoxy)prop-1-en-1-yl)benzene (**3d**)

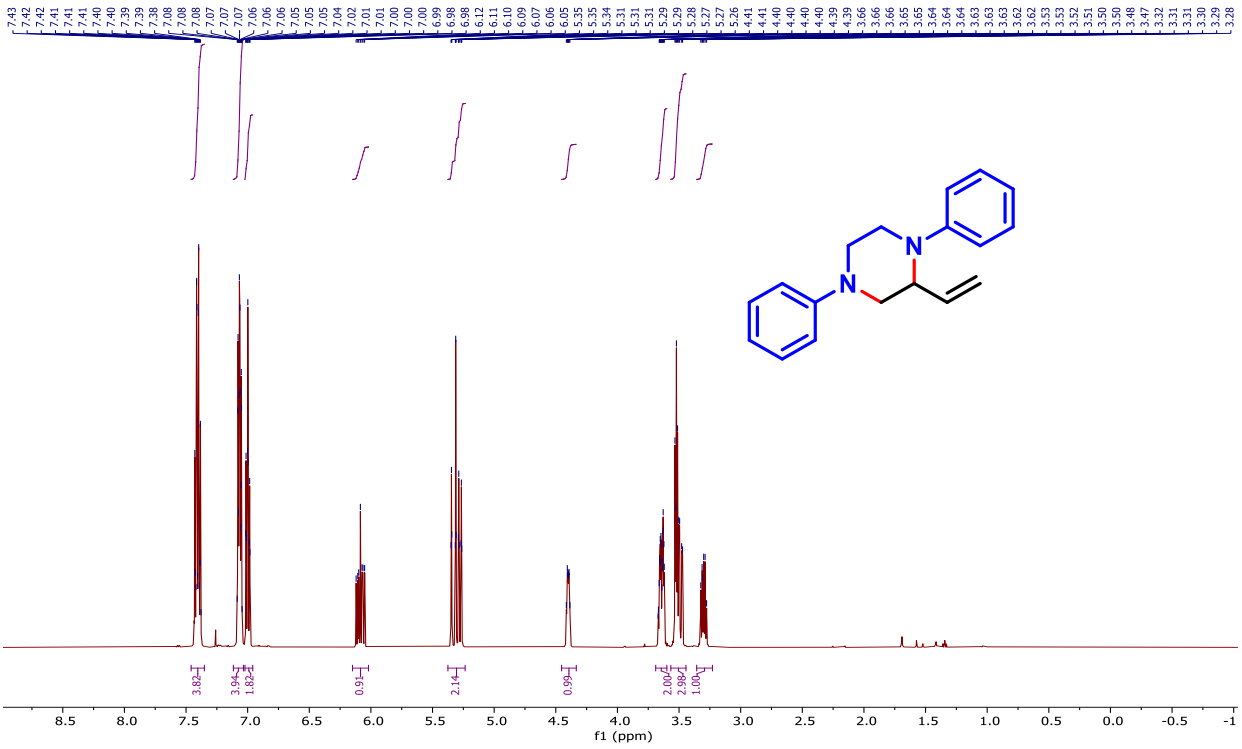


Figure 109: ^{1}H NMR (500 MHz, $CDCl_3$) of 1,4-Diphenyl-2-vinylpiperazine (**4a**)

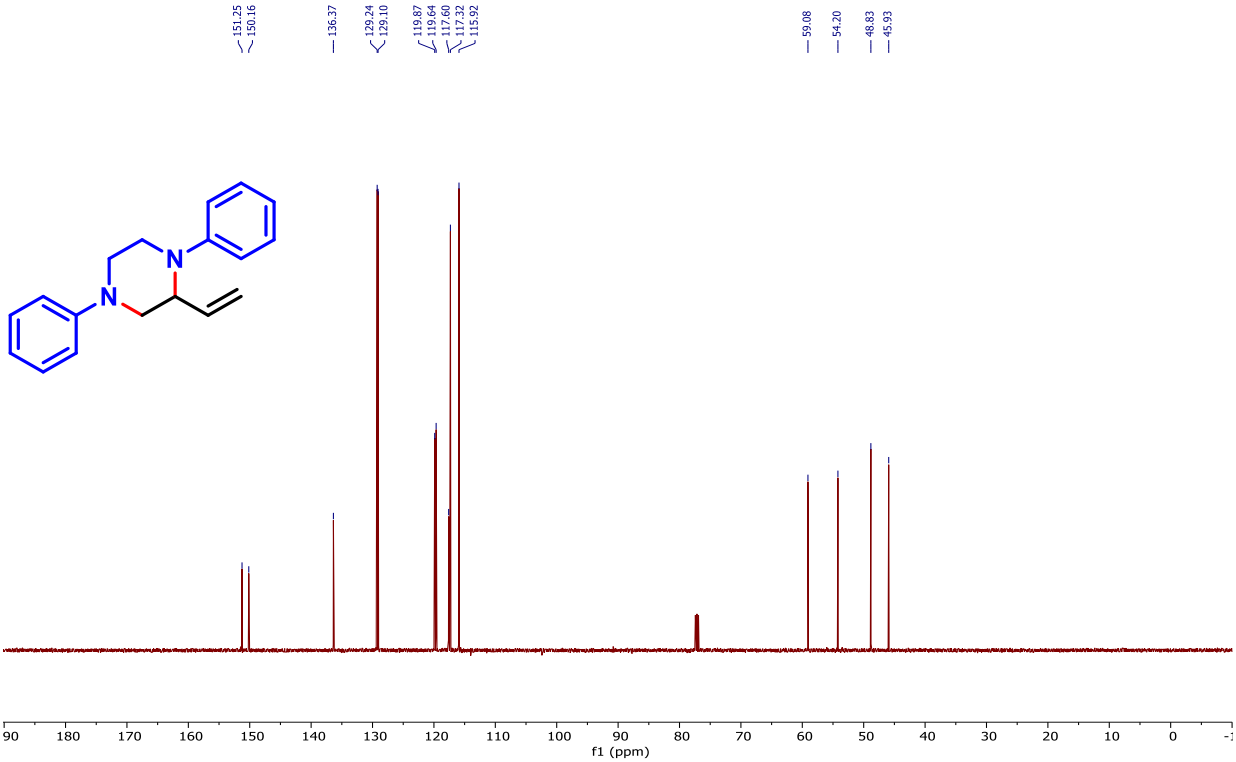


Figure 1110: ^{13}C NMR (126 MHz, $CDCl_3$) of 1,4-Diphenyl-2-vinylpiperazine (**4a**)

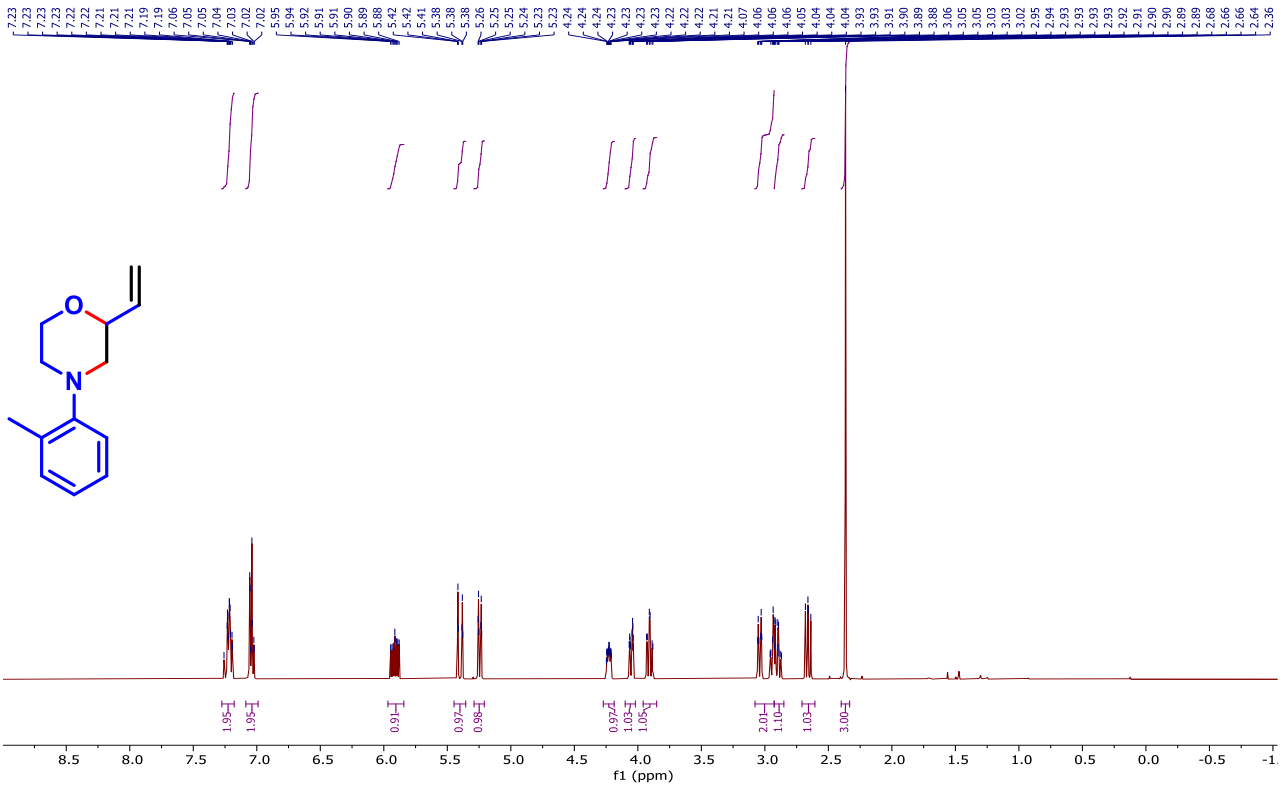


Figure 111: ^{1}H NMR (500 MHz, $CDCl_3$) of 4-(*o*-Tolyl)-2-vinylmorpholine (**4b**)

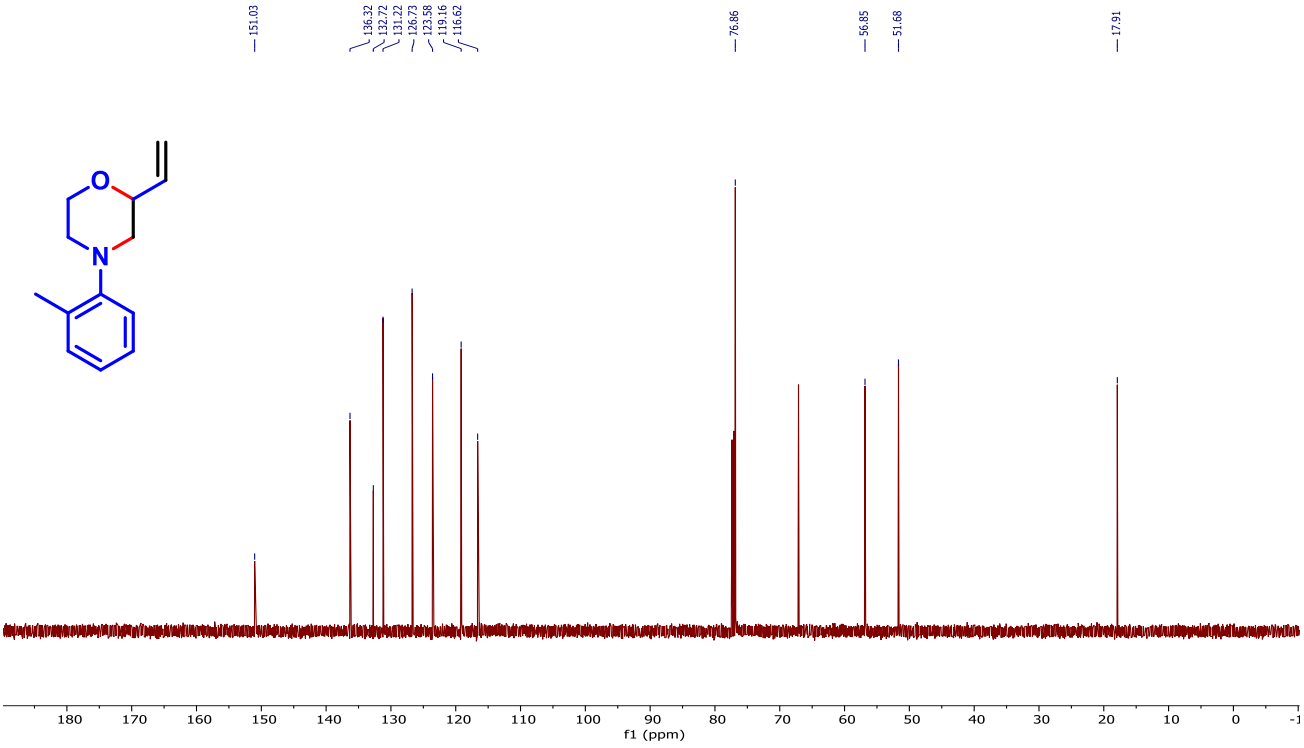


Figure 112: ^{13}C NMR (126 MHz, $CDCl_3$) of 4-(*o*-Tolyl)-2-vinylmorpholine (**4b**)

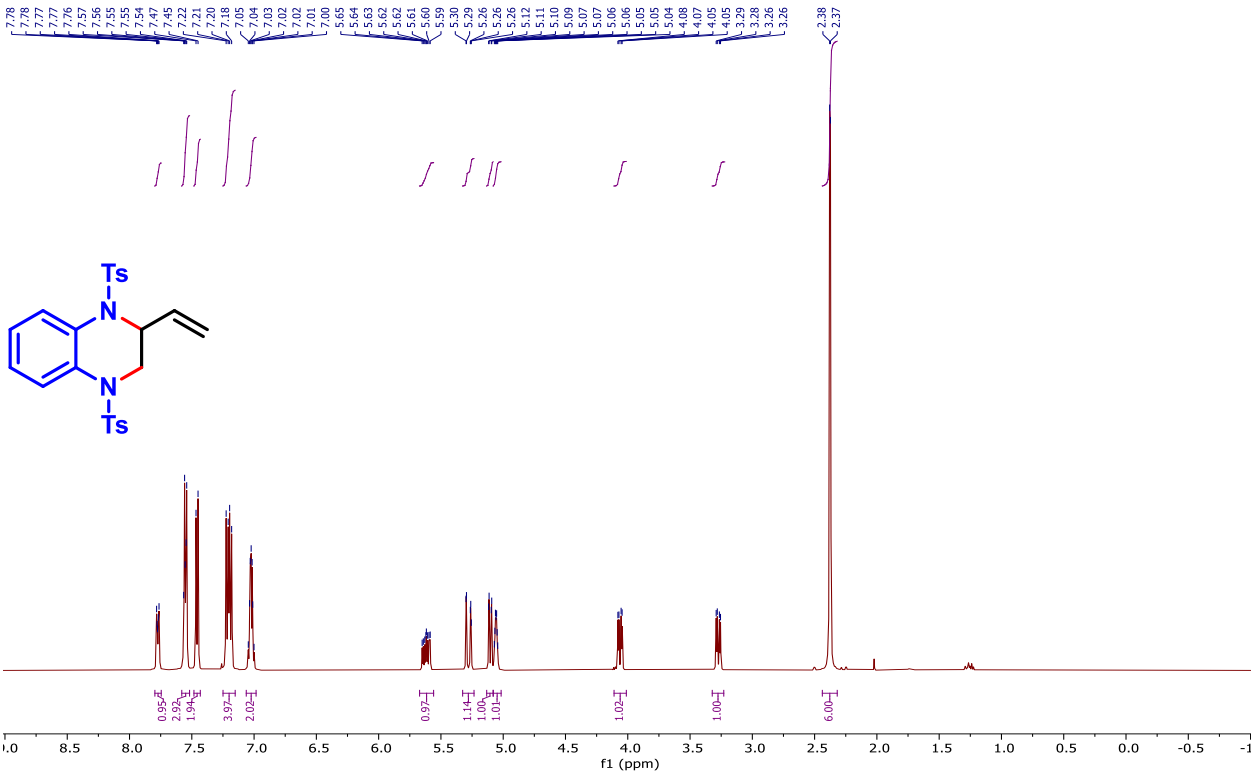


Figure 113: ^{1}H NMR (500 MHz, $CDCl_3$) of 1,4-Ditosyl-2-vinyl-1,2,3,4-tetrahydroquinoxaline (**4c**)

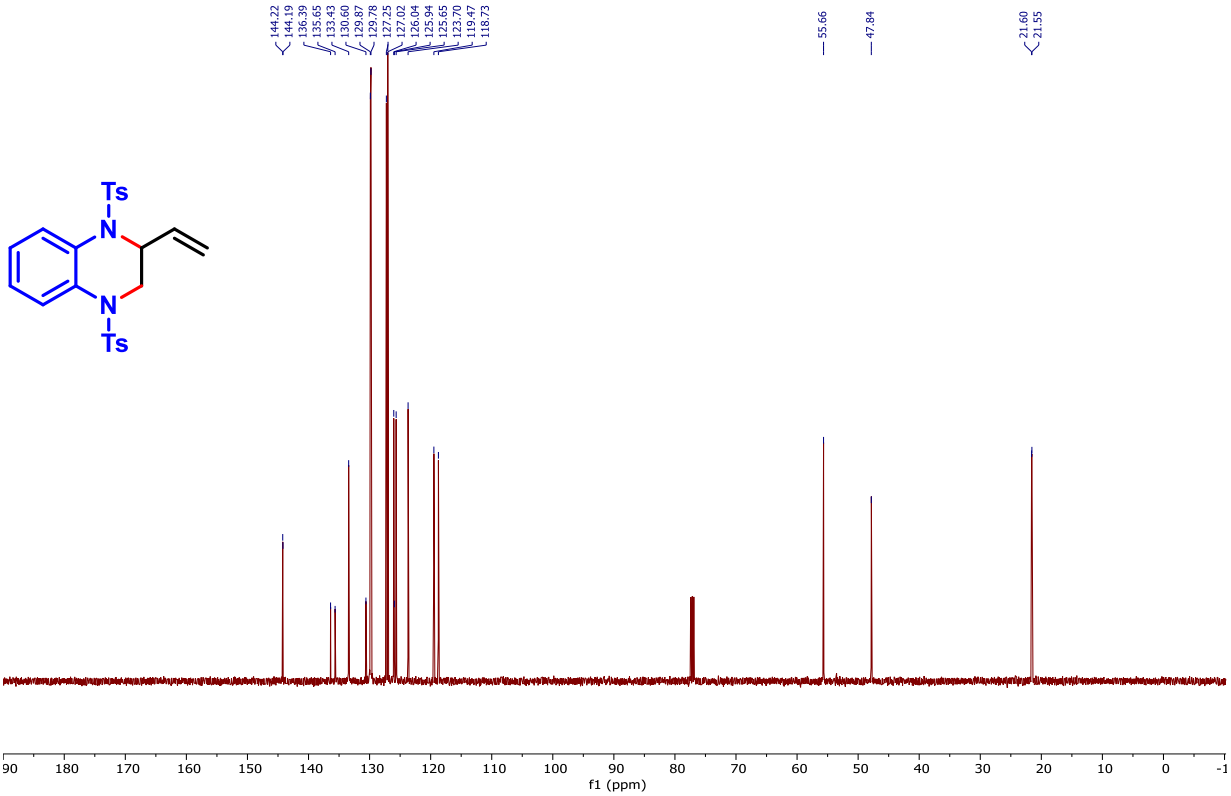


Figure 114: ^{13}C NMR (126 MHz, $CDCl_3$) of 1,4-Ditosyl-2-vinyl-1,2,3,4-tetrahydroquinoxaline (**4c**)

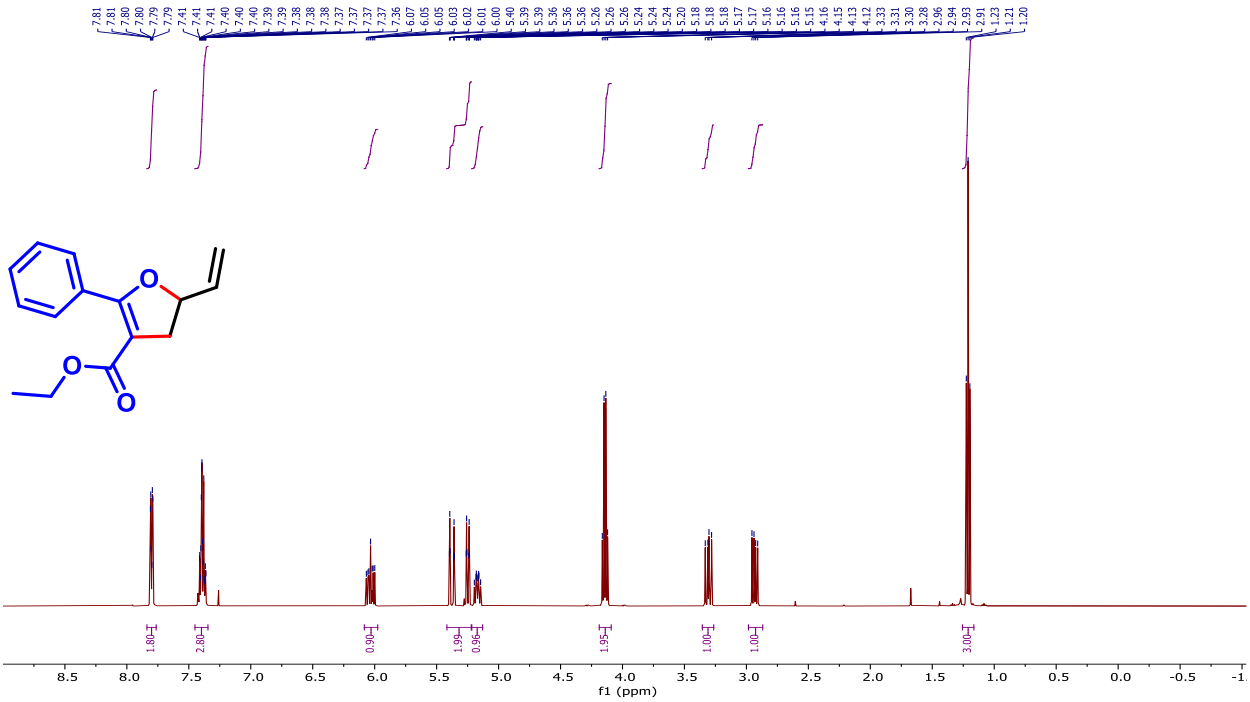


Figure 115: ^{1}H NMR (500 MHz, $CDCl_3$) of Ethyl 2-phenyl-5-vinyl-4,5-dihydrofuran-3-carboxylate (**4d**)

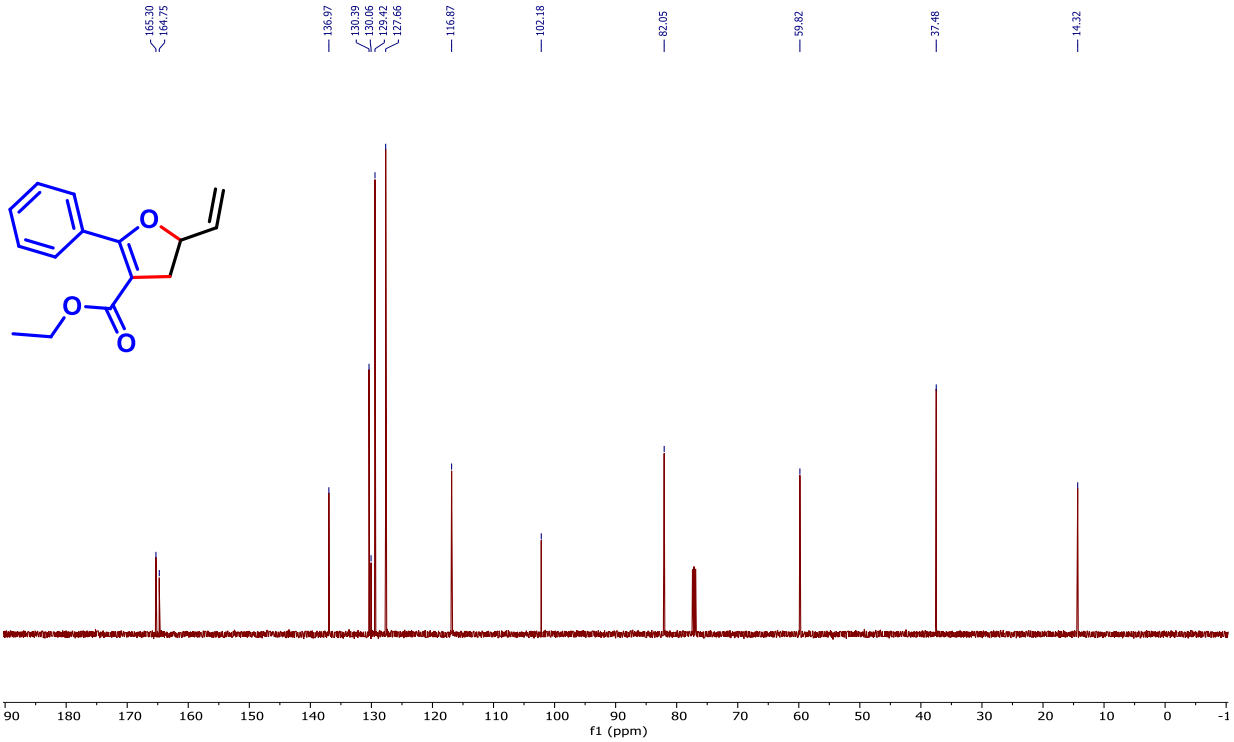


Figure 116: ^{13}C NMR (126 MHz, $CDCl_3$) of Ethyl 2-phenyl-5-vinyl-4,5-dihydrofuran-3-carboxylate (**4d**)

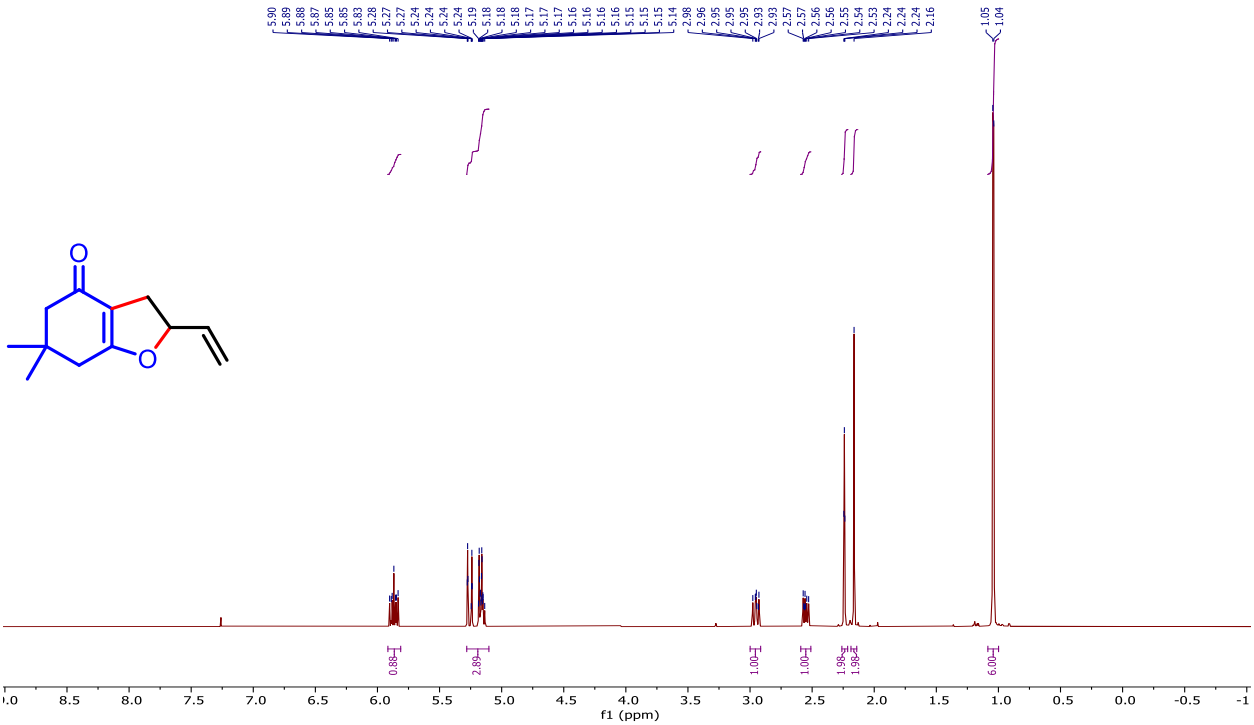


Figure 117: ^{1}H NMR (500 MHz, $CDCl_3$) of 6,6-Dimethyl-2-vinyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4e**)

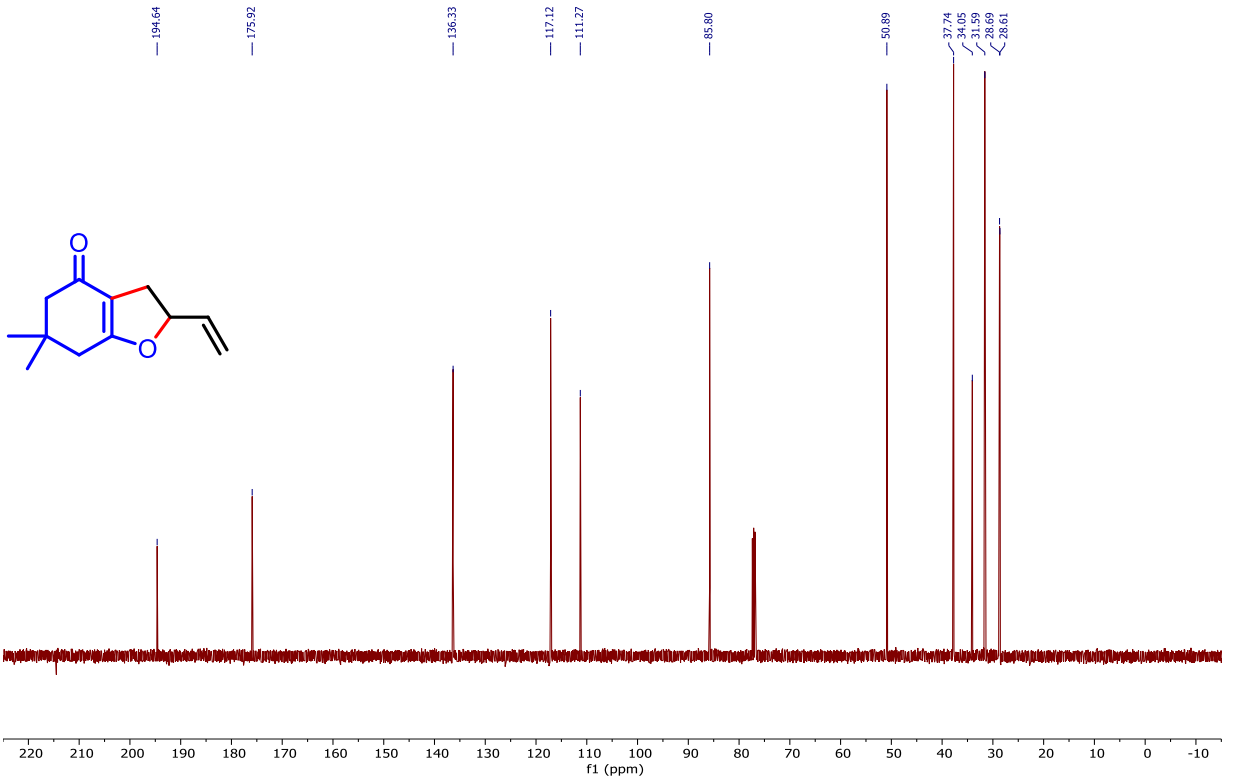


Figure 118: ^{13}C NMR (126 MHz, $CDCl_3$) of 6,6-Dimethyl-2-vinyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4e**)

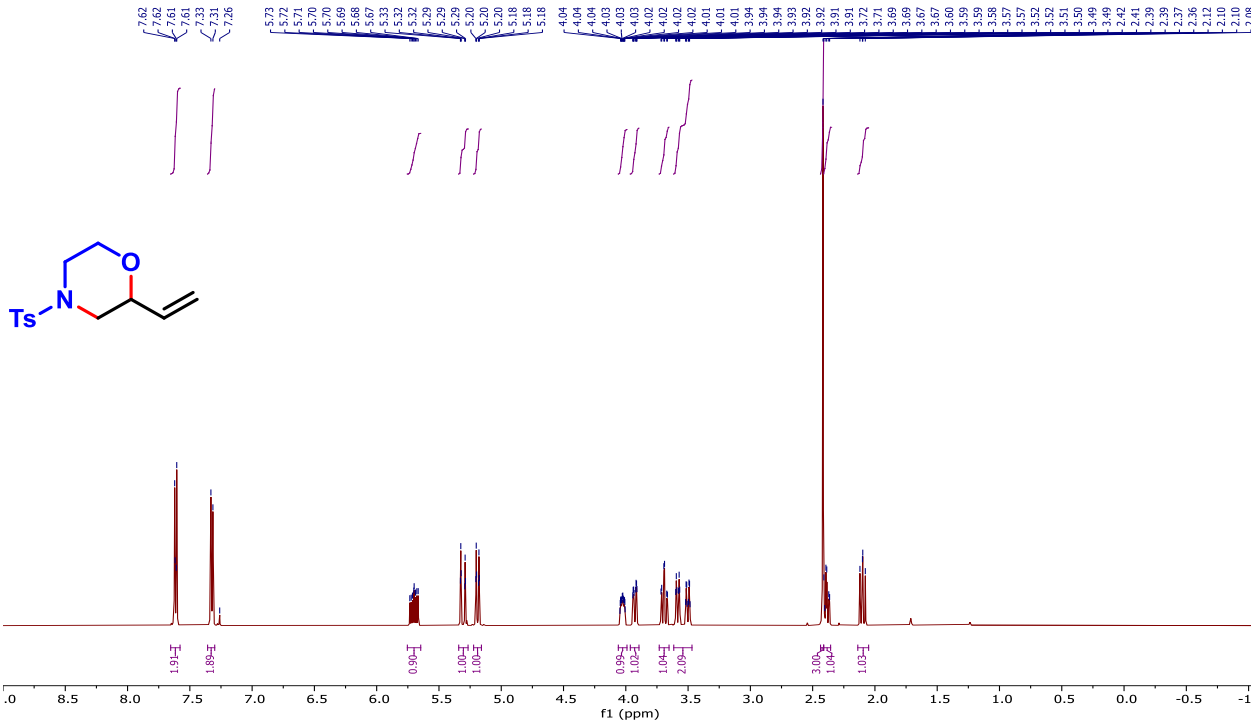


Figure 119: ^{1}H NMR (500 MHz, $CDCl_3$) of 4-*N*-Tosyl-2-vinylmorpholine (**4f**)

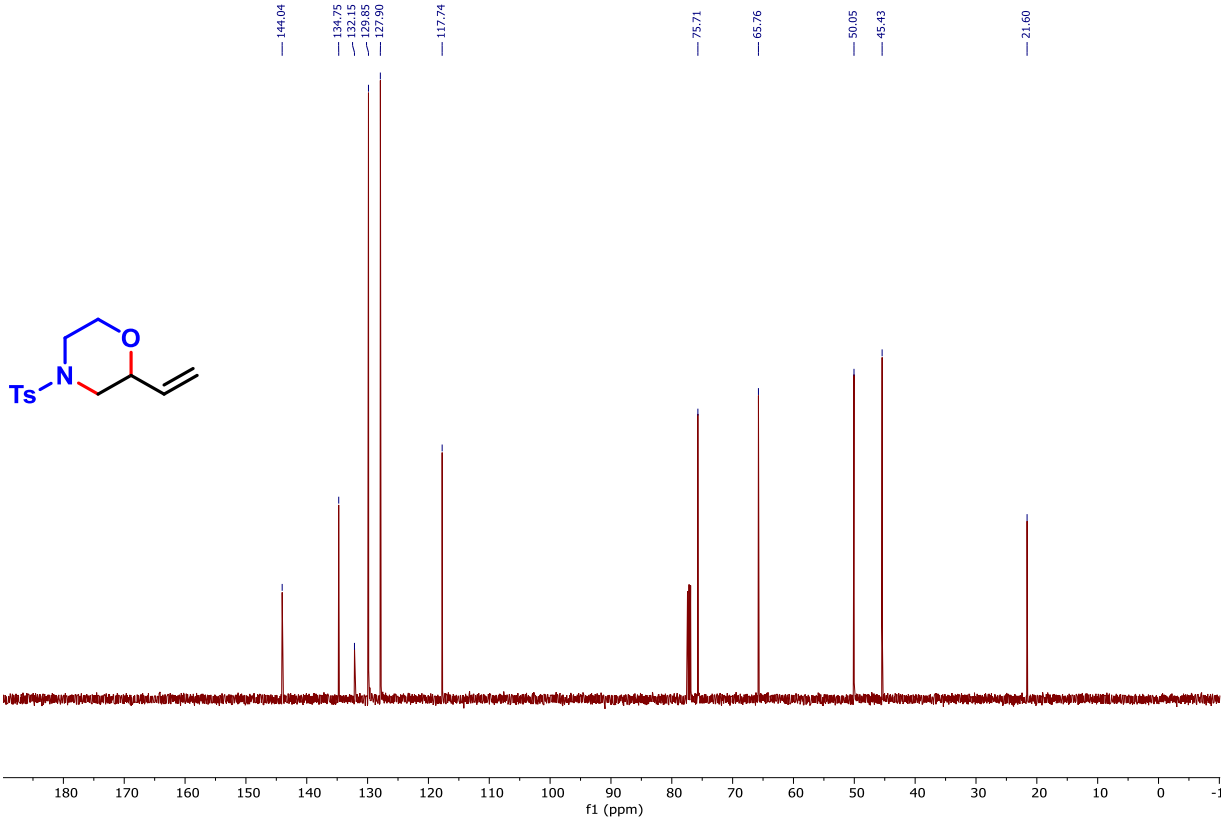


Figure 120: ^{13}C NMR (126 MHz, $CDCl_3$) of 4-*N*-Tosyl-2-vinylmorpholine (**4f**)

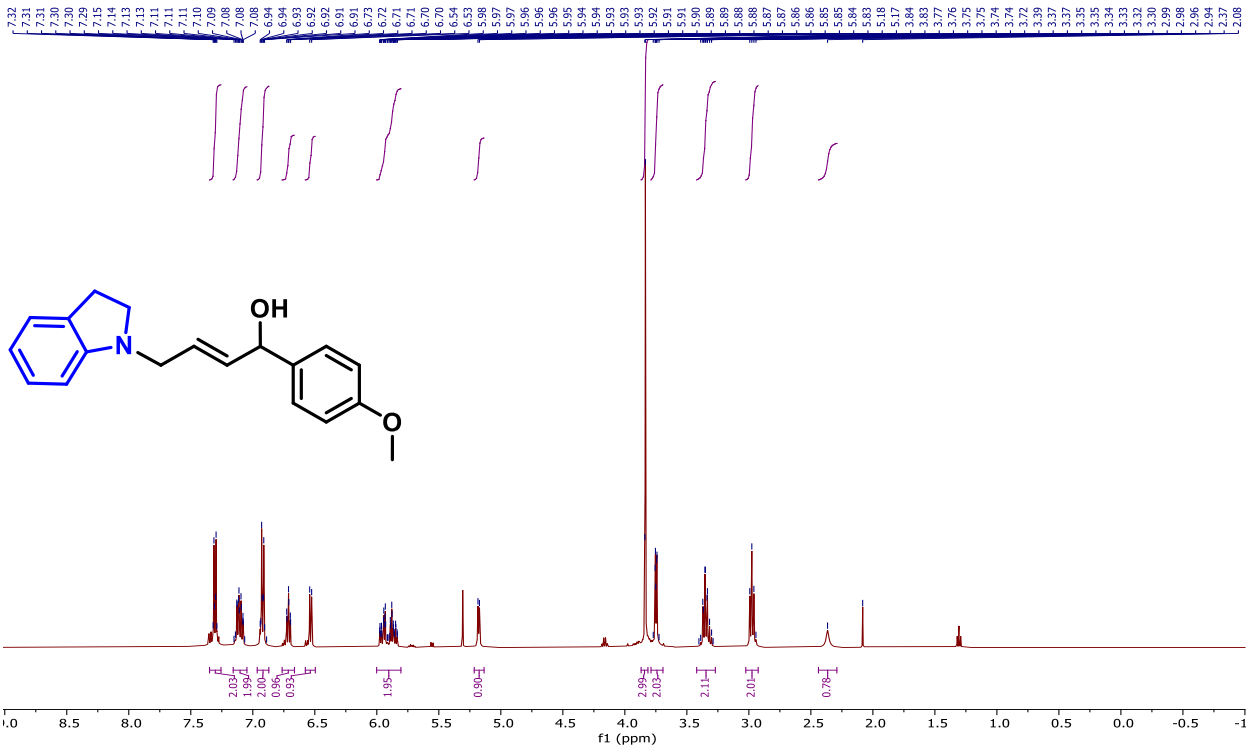


Figure 121: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-4-(Indolin-1-yl)-1-(4-methoxyphenyl)but-2-en-1-ol (**5a**)

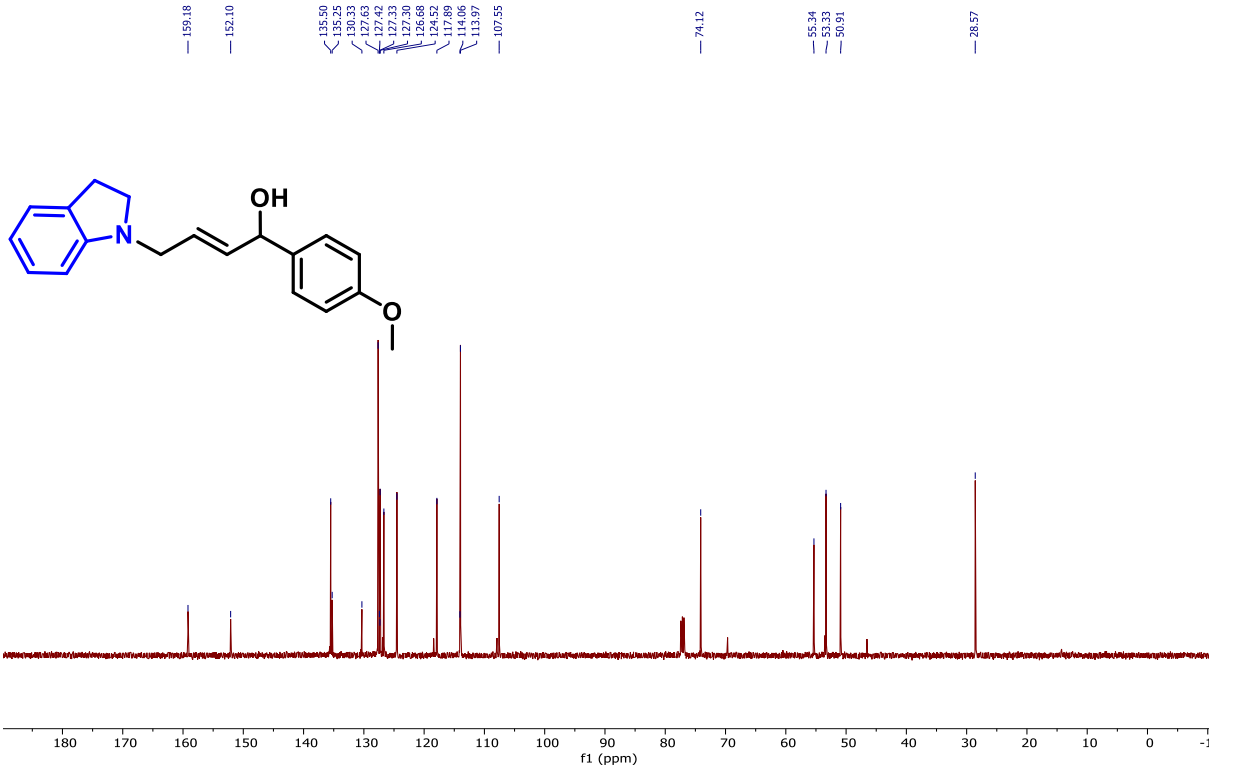


Figure 122: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-4-(Indolin-1-yl)-1-(4-methoxyphenyl)but-2-en-1-ol (**5a**)

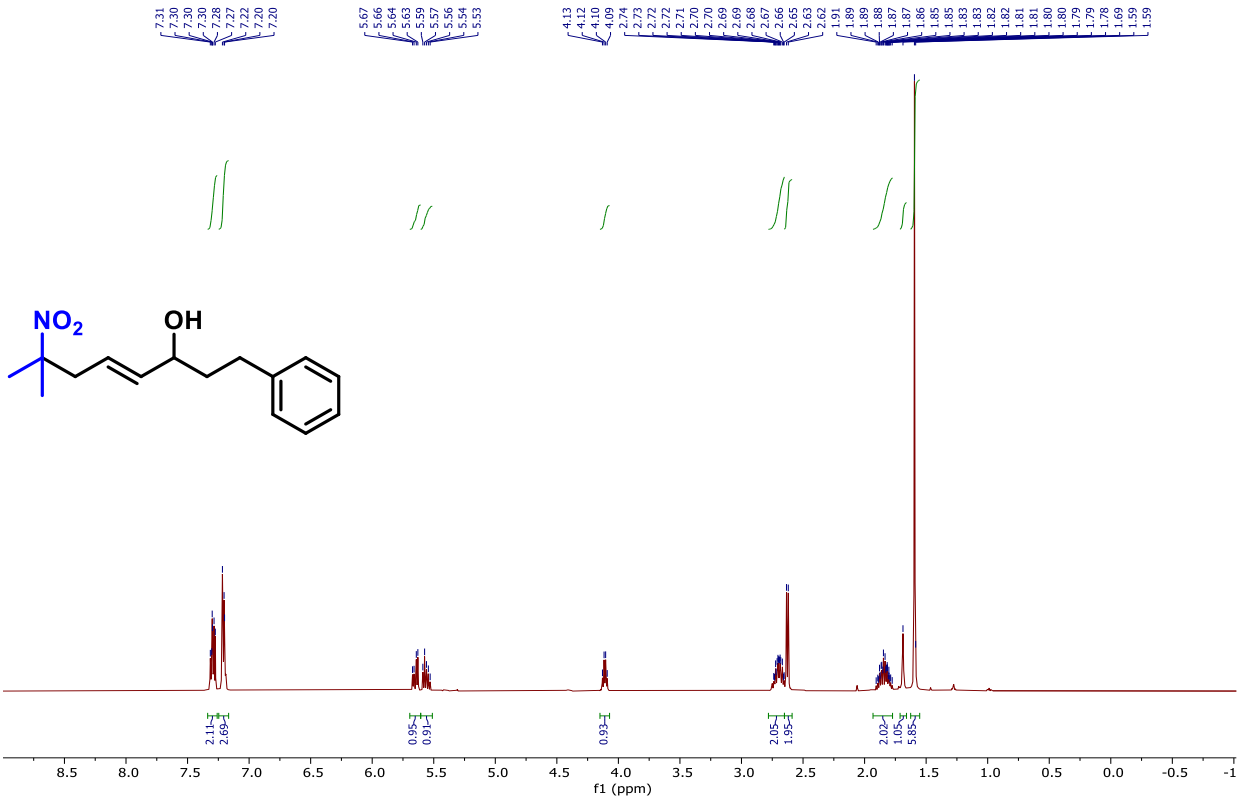


Figure 123: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-7-Methyl-7-nitro-1-phenyloct-4-en-3-ol (**5b**)

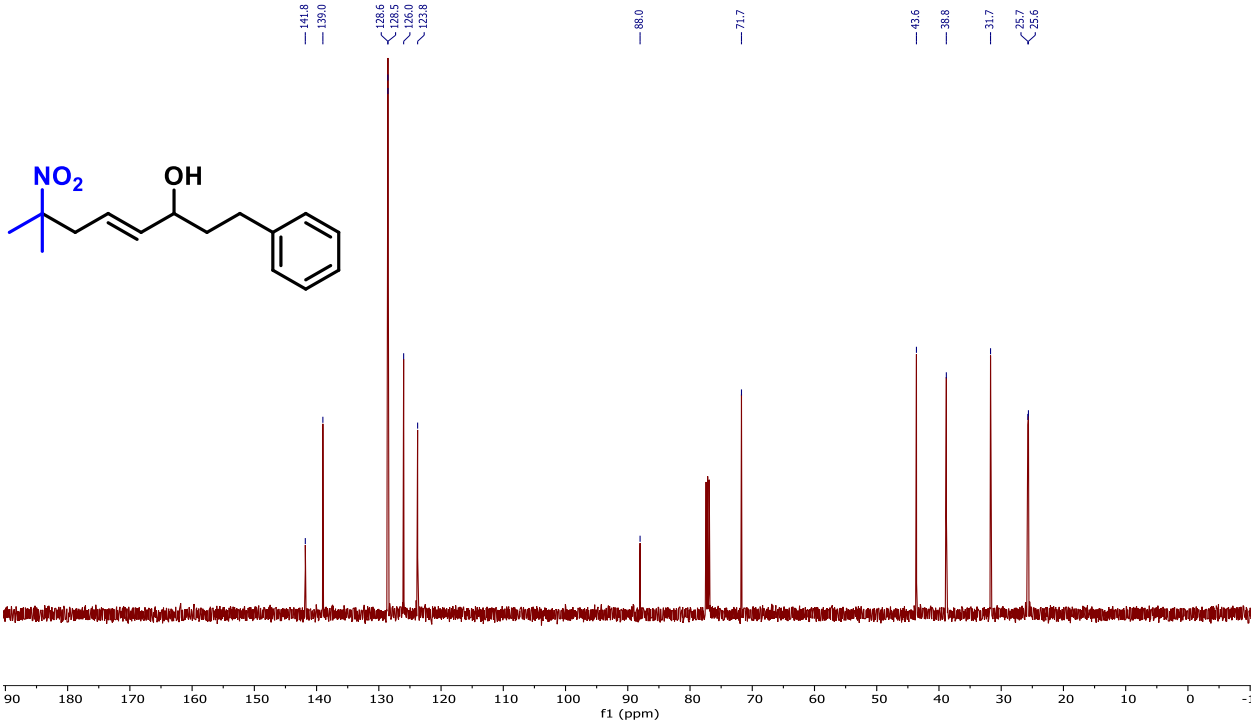


Figure 124: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-7-Methyl-7-nitro-1-phenyloct-4-en-3-ol (**5b**)

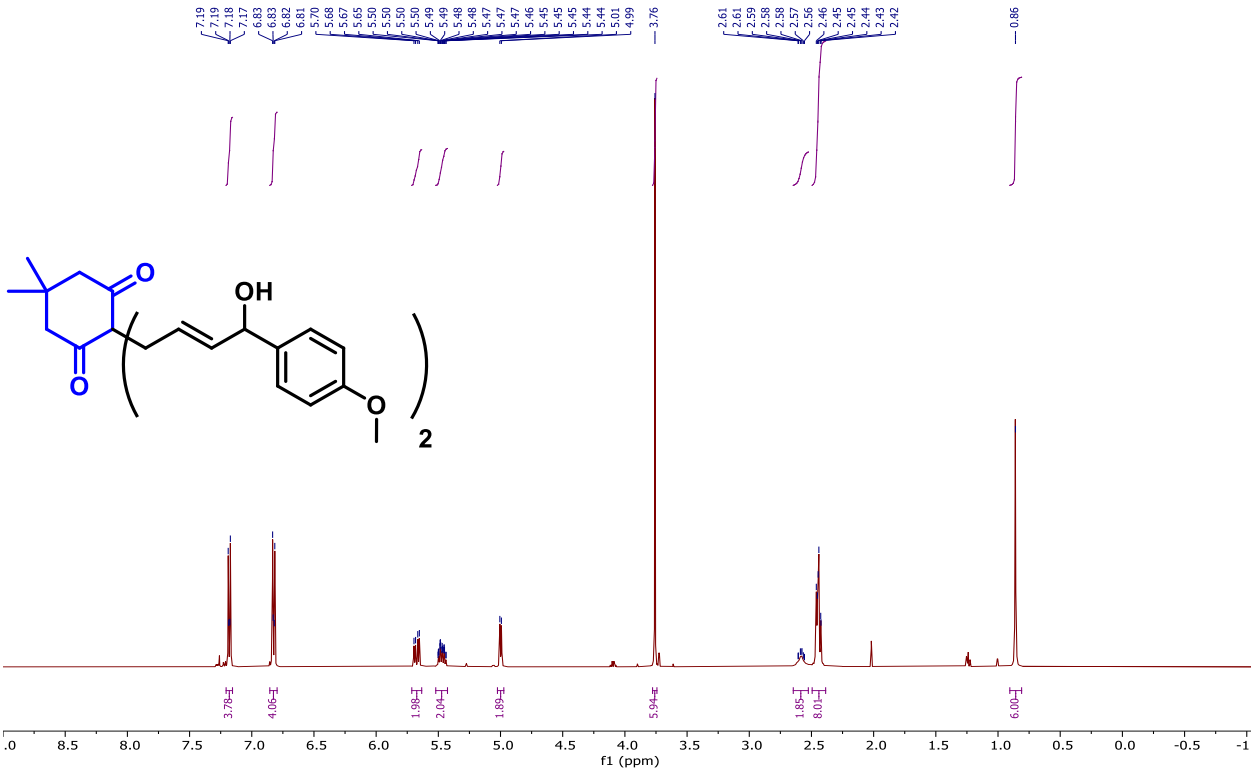


Figure 125: ^{1}H NMR (500 MHz, $CDCl_3$) of 2,2-bis((*E*)-4-Hydroxy-4-(4-methoxyphenyl)but-2-en-1-yl)-5,5-dimethylcyclohexane-1,3-dione (**5c**)

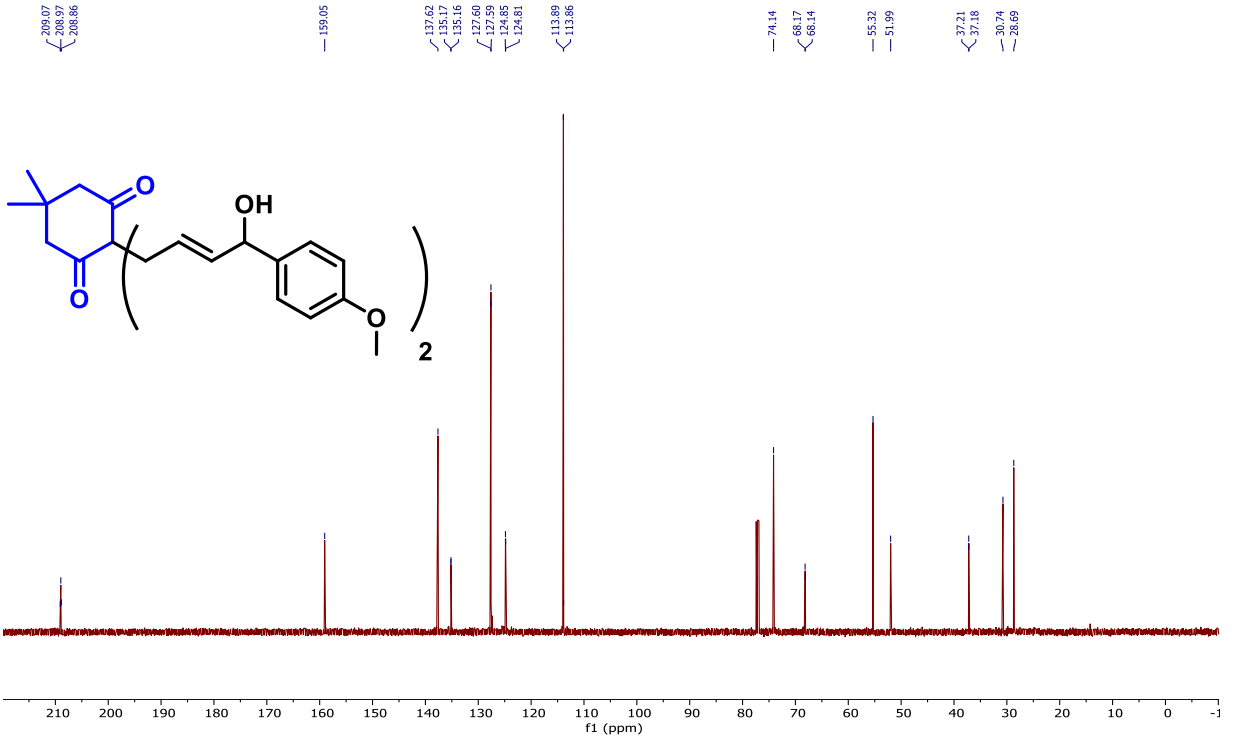


Figure 126: ^{13}C NMR (126 MHz, $CDCl_3$) of 2,2-bis((*E*)-4-Hydroxy-4-(4-methoxyphenyl)but-2-en-1-yl)-5,5-dimethylcyclohexane-1,3-dione (**5c**)

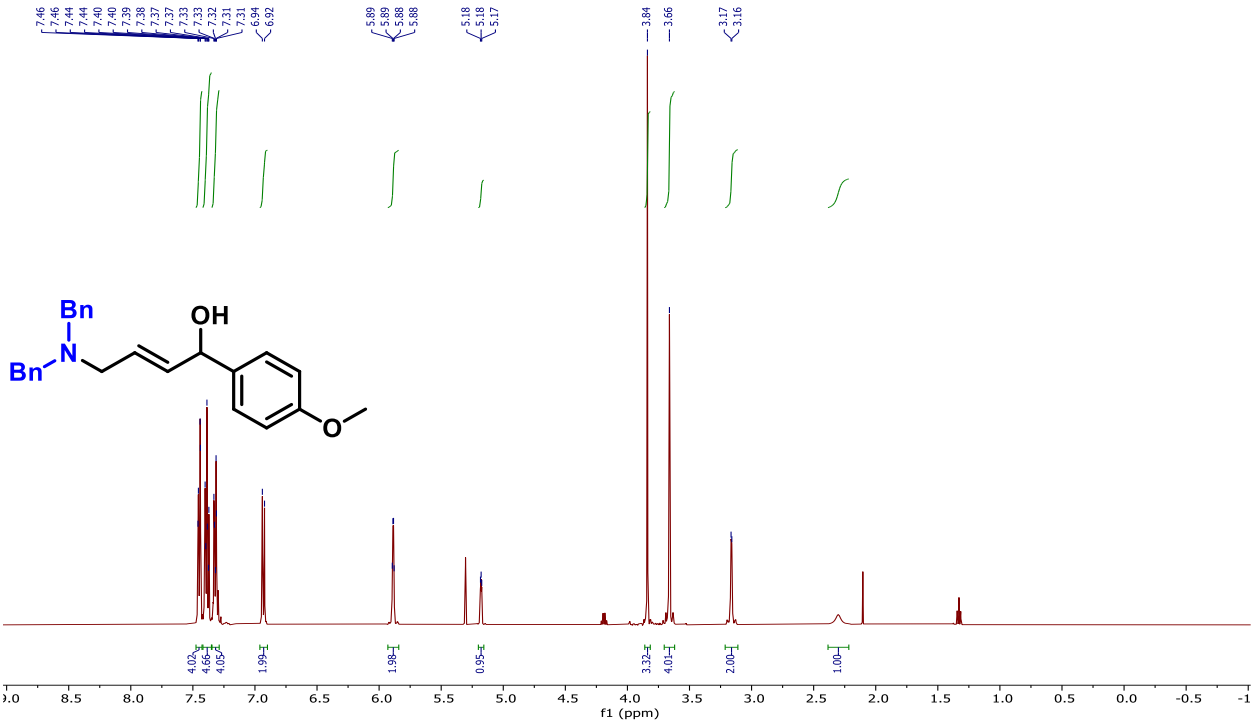


Figure 127: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-4-(Dibenzylamino)-1-(4-methoxyphenyl)but-2-en-1-ol (**5d**)

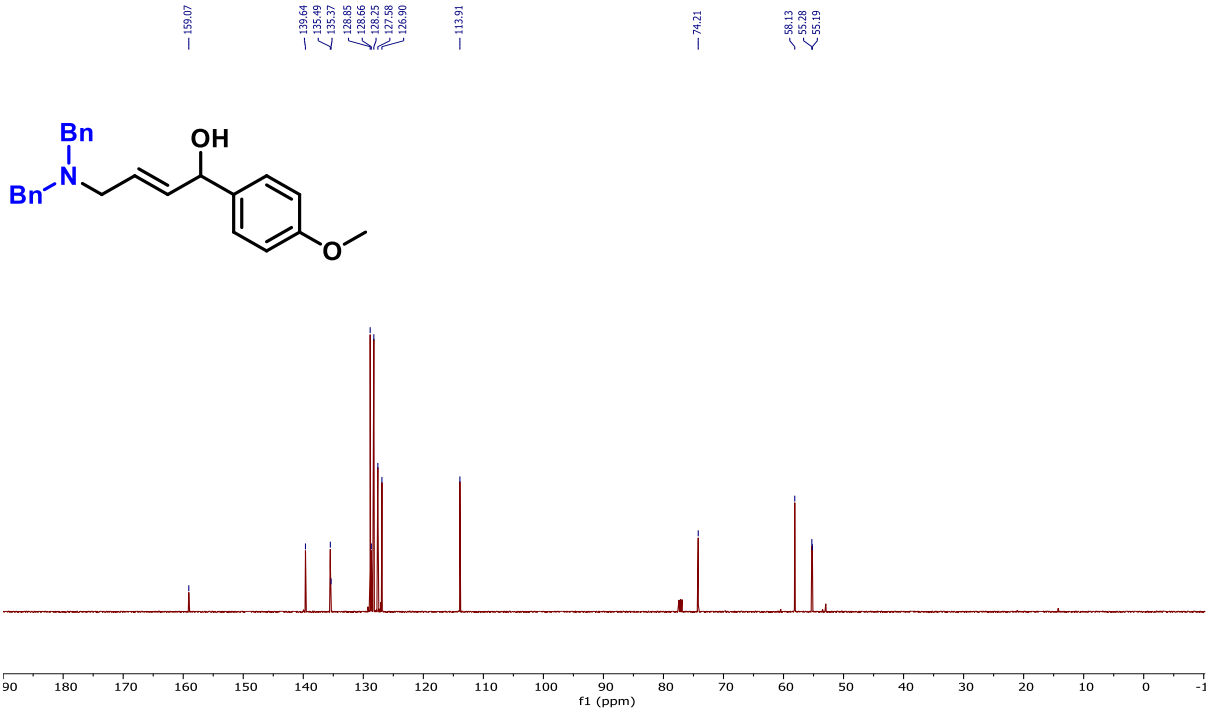


Figure 128: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-4-(Dibenzylamino)-1-(4-methoxyphenyl)but-2-en-1-ol (**5d**)

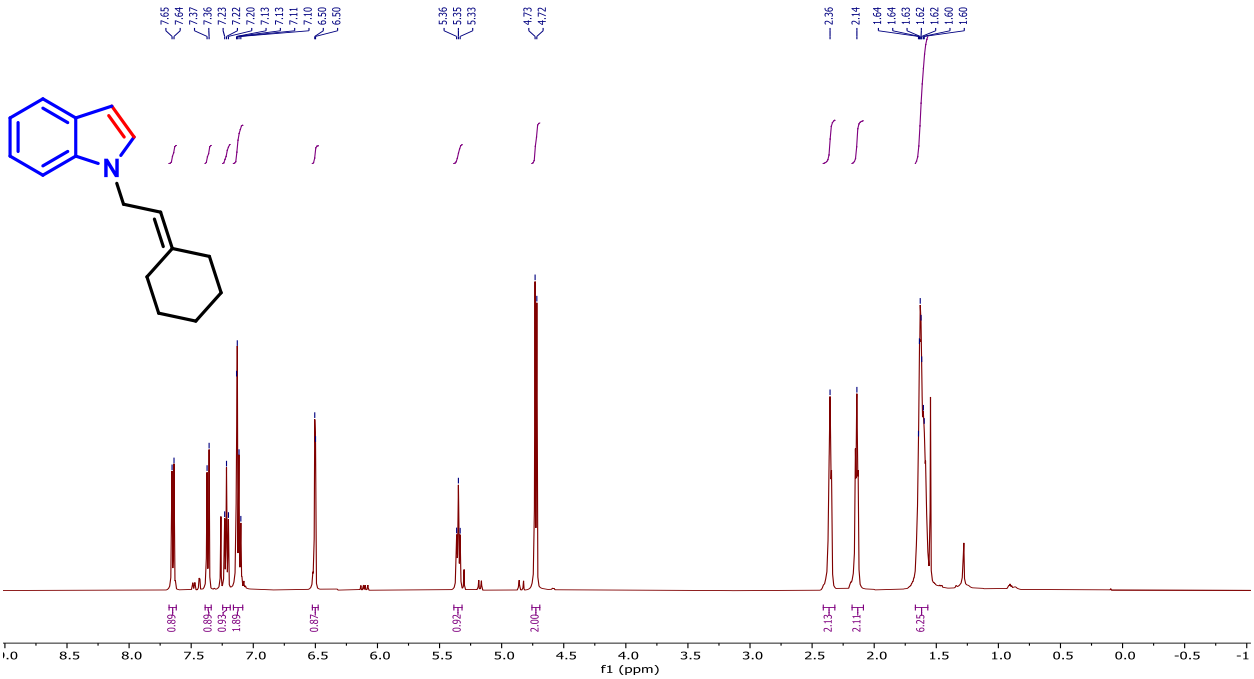


Figure 129: ^{1}H NMR (500 MHz, $CDCl_3$) of 1-(2-Cyclohexylideneethyl)-1H-indole (**6a**)

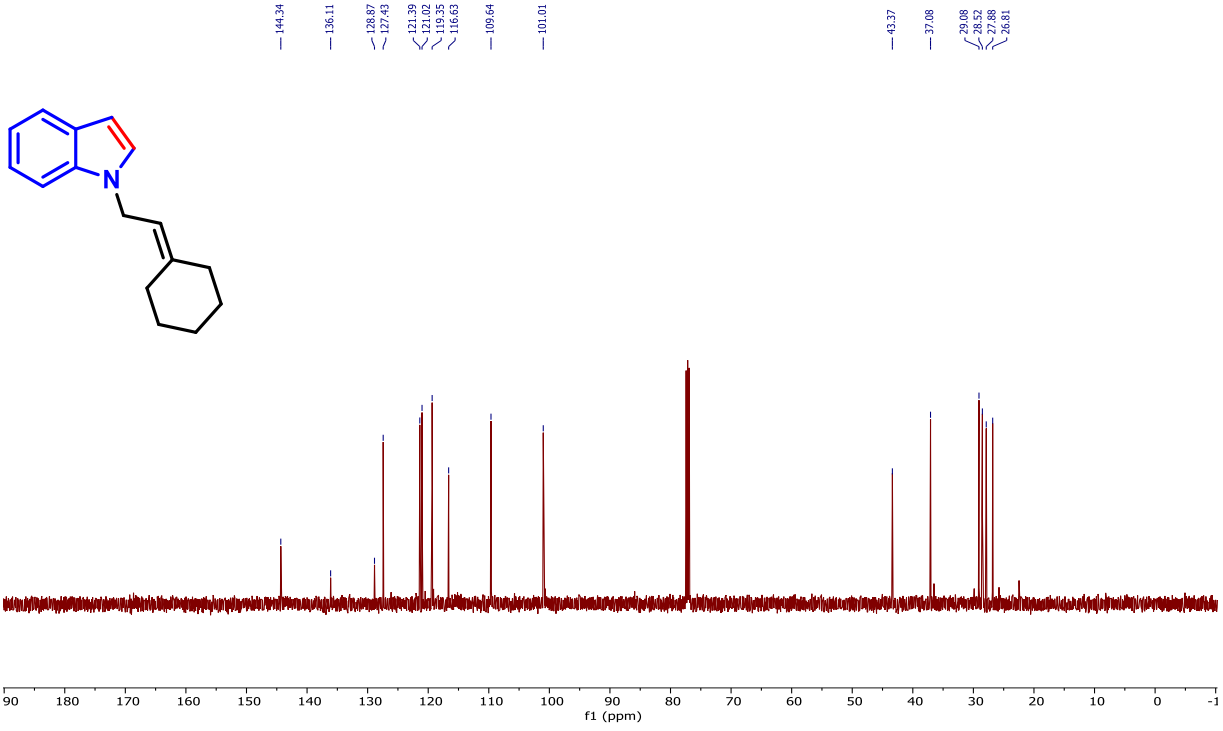


Figure 130: ^{13}C NMR (126 MHz, $CDCl_3$) of 1-(2-Cyclohexylideneethyl)-1H-indole (**6a**)

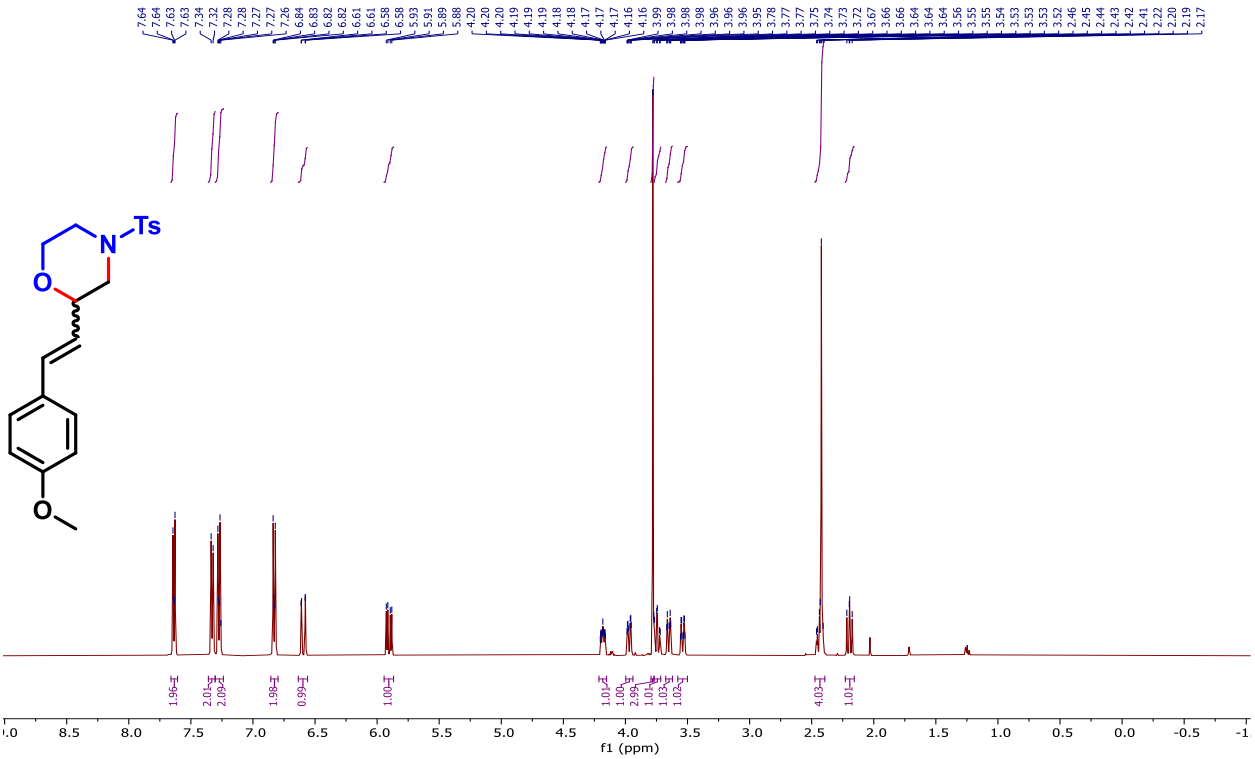


Figure 131: ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-2-(4-Methoxystyryl)-4-tosylmorpholine (**6b**)

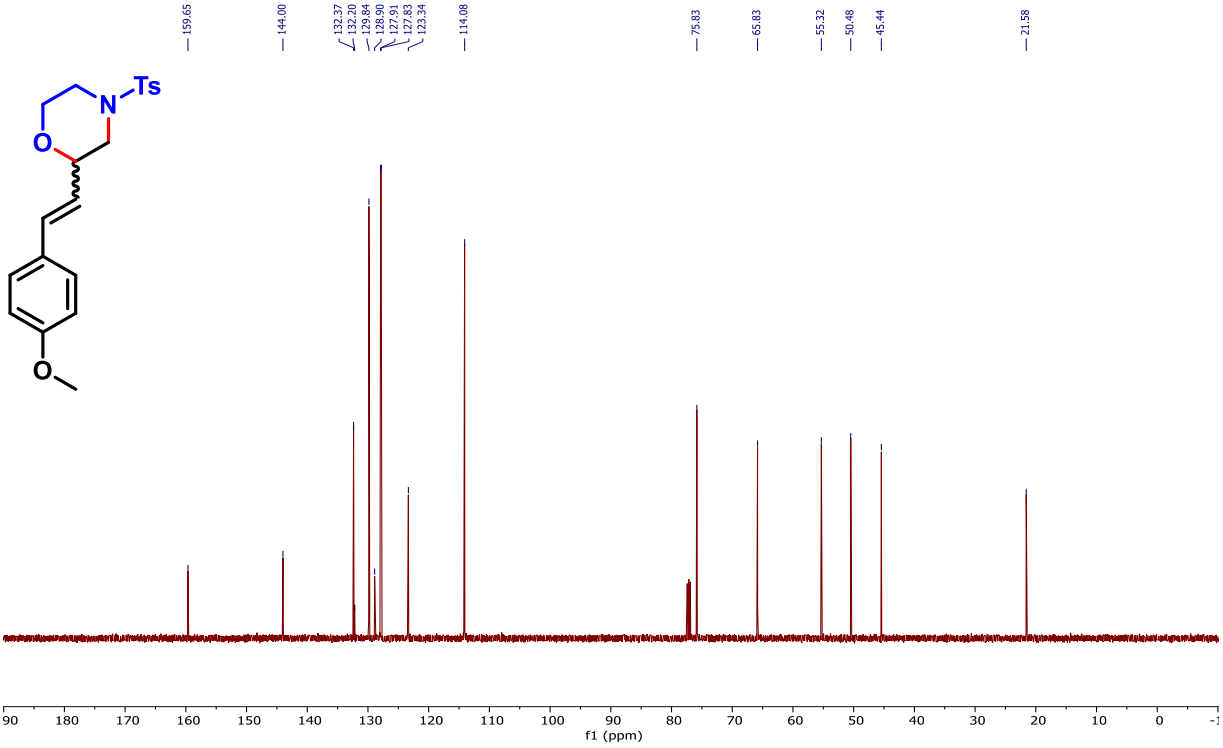


Figure 132: ^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-2-(4-Methoxystyryl)-4-tosylmorpholine (**6b**)