“Supporting Information”

Cp_2TiCl_2-CATALYZED PHOTOREDOX ALLYLATION OF ALDEHYDES WITH VISIBLE LIGHT

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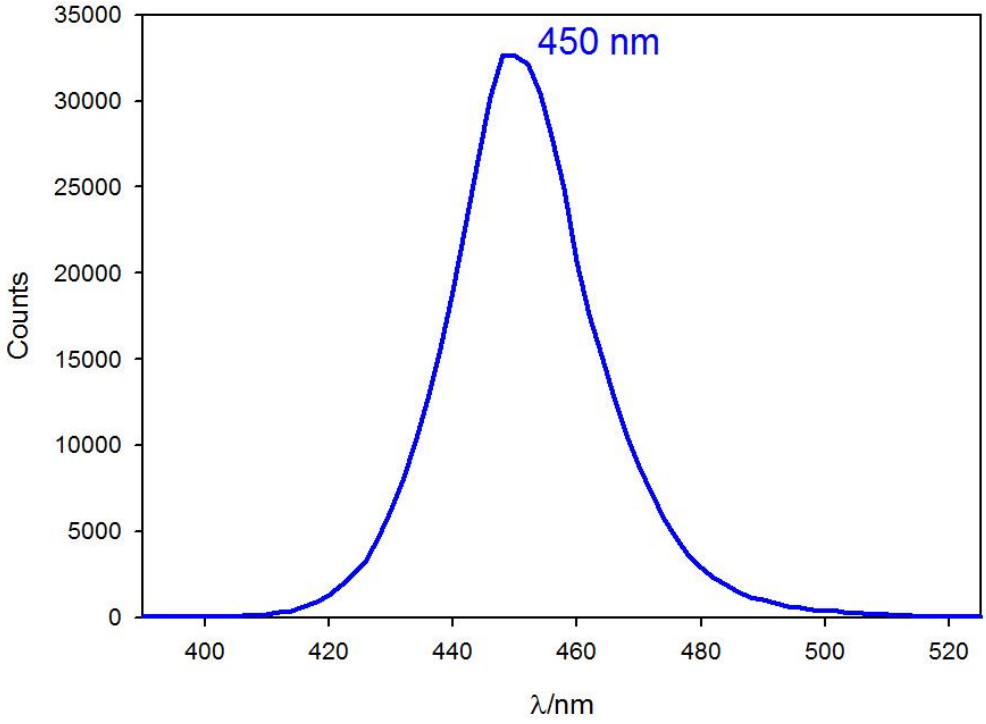
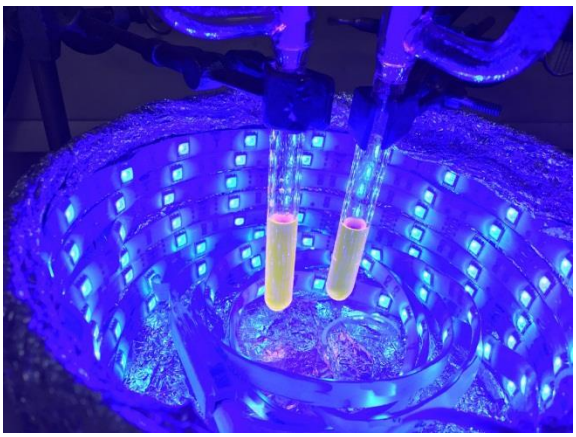
Experimental Procedures

General methods and materials

^{1}H-NMR spectra were recorded on Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard ($CHCl_3$: δ = 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, dd = double duplet, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on Varian MR400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard ($CDCl_3$: δ = 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. LC-electrospray ionization mass spectra (ESI-MS) were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques.
Anhydrous solvents were supplied by Aldrich in Sureseal® bottles and were used, unless otherwise noted, without further purification. All the reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Fluorochem, Strem Chemicals, TCI) and used without further purification unless specified.
Reaction mixture was irradiated with 16 W blue LEDs strip or Kessil® PR160L@456 nm.[1]
Aldehydes **1p**,[2] **1t**,[3] **1w**[4] and Hantzsch ester[5] were prepared according to literature procedure.

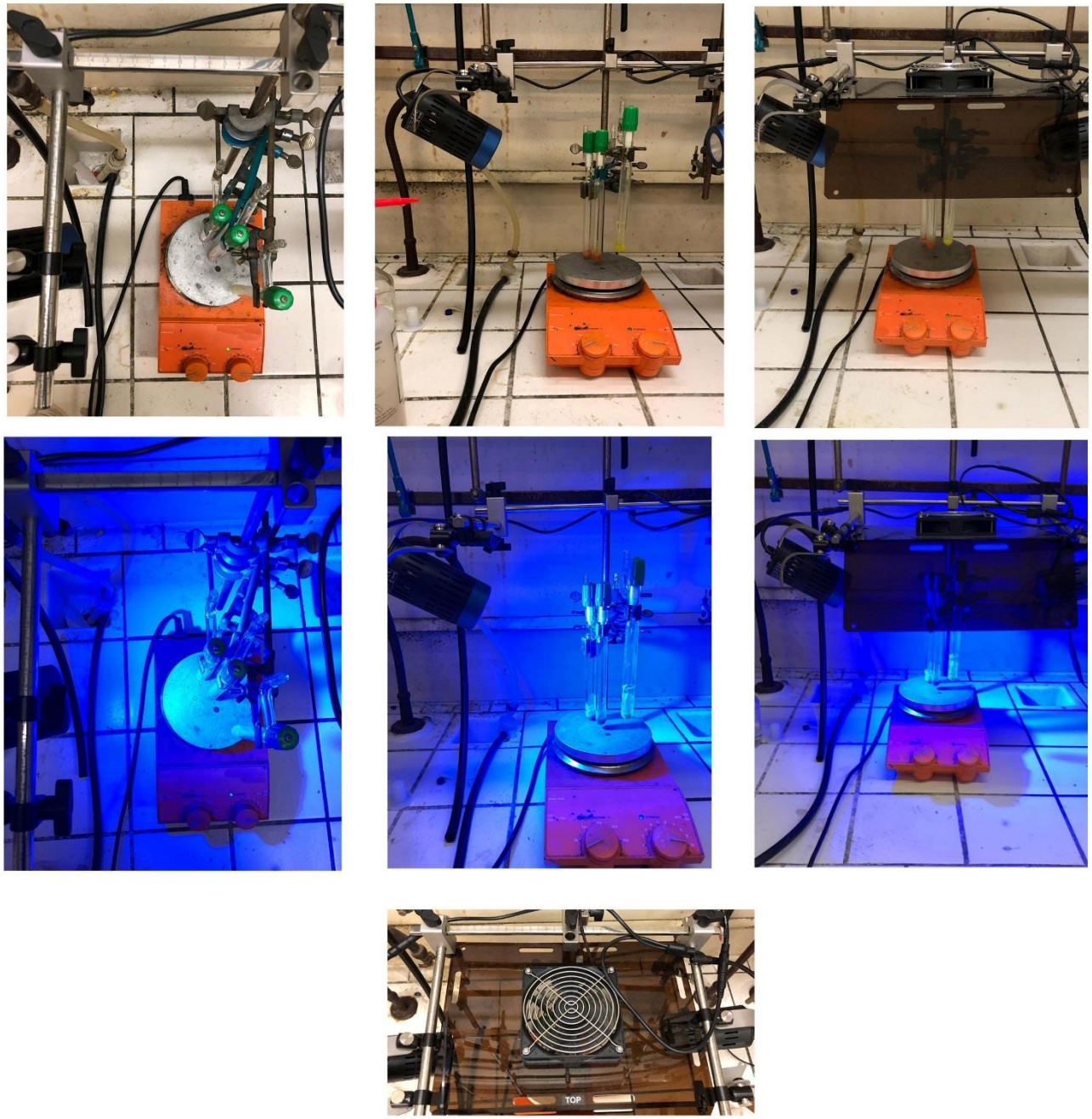
Figure S1. Emission profile of the 16W Blue LED strip used to irradiate the solutions and reaction setup.





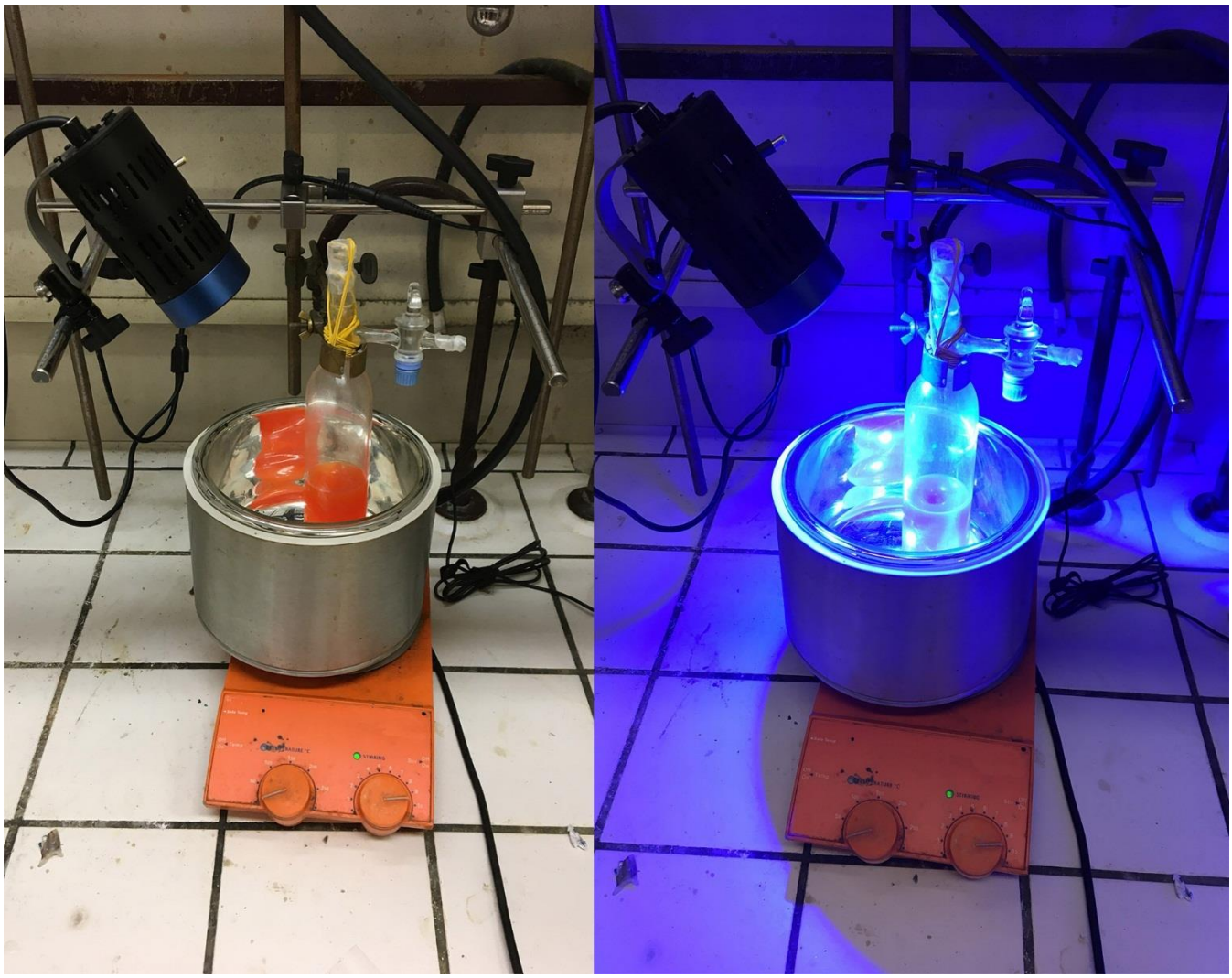
The reaction temperature was close to room temperature during the irradiation as measured with a thermometer at 2 cm from reaction flask.

Figure S2. Reaction set-up with Kessil® PR160L@456 nm lamp.



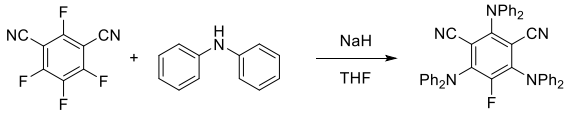
The reaction flasks were positioned approximatively at 18 cm from the light source and Kessil® PR160 Rig with Fan Kit[1] was used to control the temperature. The reaction temperature was close to room temperature during the irradiation as measured with a thermometer at 2 cm from reaction flask.

Figure S3. Reaction set-up with Kessil® PR160L@456 nm lamp for 5 mmol scale.



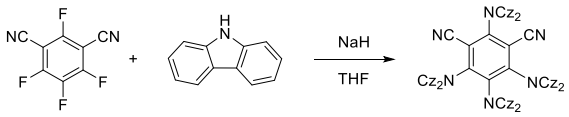
Synthesis and characterization of the photocatalysts

*Synthesis of 1,3-dicyano-2,4,5,6-tetrakis(diphenylamino)-benzene (**3DPAFIPN**)*



To a 50 mL round-bottom-flask was added diphenylamine (5.0 eq., 10 mmol, 1.69 g) and dry THF (20 mL). The solution was cooled down to 0 °C and NaH (60% in mineral oil) (7.5 eq., 15 mmol, 600 mg) was slowly added under vigorous stirring. After 2 hours tetrafluoroisophtalonitrile (1.0 eq., 2 mmol, 400 mg) was added and the mixture was stirred at room temperature. The solution slowly turned from colorless to dark brown. When the TLC showed a complete consumption of the starting material (usually 2 days are needed), water (1 mL) was added to neutralize the excess of NaH and the mixture was evaporated to give a yellow solid. The residue was purified by flash chromatography (cHex/AcOEt 2/1) to obtain **3DPAFIN** as bright yellow solid 80% yield. Spectroscopic data were according to the literature.[6]

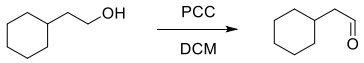
*Synthesis of 2,4,5,6-tetrakis(carbazol-9-yl)-4,6- dicyanobenzene (**4CzIPN**)*



To a 50 mL round-bottom-flask was added carbazole (5.0 eq., 10 mmol, 1.67 g) and dry THF (20 mL). The solution was cooled down to 0 °C and NaH (60% in mineral oil) (7.5 eq., 15 mmol, 600 mg) was slowly added under vigorous stirring. After 2 hours tetrafluoroisophtalonitrile (1.0 eq., 2 mmol, 400 mg) was added and the mixture was stirred at room temperature overnight. A yellow precipitate progressively appeared. When the TLC showed a complete consumption of the starting material water (1 mL) was added to neutralize the excess of NaH and the mixture was evaporated to give a yellow solid. The solid was successively washed with water and ethanol to afford the product in 69% yield. The spectroscopic data are in agreement with those reported in the literature.[6]

Synthesis and characterization of the substrates

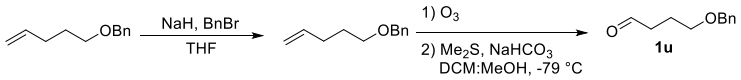
*Synthesis of aldehyde **1s***



S1s

To a solution of cyclohexylethanol (0.300 g, 2.34 mmol) in CH_2Cl_2 (60 mL) was added pyridinium chlorochromate (0.774 g, 3.56 mmol) and stirred at room temperature overnight. The reaction mixture was diluted with diethyl ether (50 mL) and stirred at room temperature for 1 h. The mixture was filtered through a pad of Celite® and silica gel more times until the solution became colorless. The filtrate was carefully concentrated to dryness to give 2-cyclopentylacetaldehyde in quantitative yield. Spectroscopic data were according to the literature.[7]

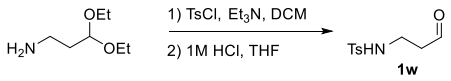
*Synthesis of aldehyde **1u***



1u

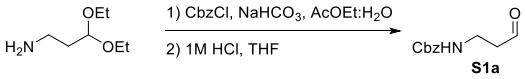
To a suspension of NaH (60% in mineral oil, 426 mg, 10.7 mmol, 1.1 equiv.) in dry THF (10 mL), 4-penten-1-ol (1 mL, 9.7 mmol) was slowly added at 0°C. The mixture was left stirring at room temperature for 2 hours. Benzyl bromide (1.27 mL, 10.6 mmol, 1.1 equiv.) was added at 0°C and the reaction mixture was stirred at room temperature overnight. After the consumption of the starting material, the mixture was quenched with H_2O (5 mL) and the aqueous phase extracted with Et_2O (3 x 10 mL). The combined organic phase dried over Na_2SO_4 and concentrated to obtain a yellow oil. The residue was dissolved in a mixture of DCM/MeOH 3/1 (40 mL), cooled down to -78°C and ozone was bubbled until the mixture turned blue. Oxygen was then bubbled for few minutes and dimethyl sulfide (2.3 mL, 31 mmol, 3.2 equiv.) and sodium bicarbonate (2.44 g, 30 mmol, 3 equiv.) were added. The suspension was warmed to room temperature overnight, then filtered on Celite® and the solvents removed under reduced pressure. The crude was purified by flash column chromatography (cHex/AcOEt 10/1) to obtain separately **1u** as colorless oil 68% yield (6.6 mmol, 1.2 g) Spectroscopic data were according to the literature.[8]

*Synthesis of aldehyde **1w***



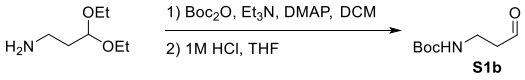
To a solution of 3,3-diethoxy-1-aminopropane (300 µL, 1.85 mmol) in DCM (8 mL) was added Et_3N (310 µL, 2.22 mmol, 1.2 equiv.). The solution was cooled to 0°C and *p*-toluenesulfonyl chloride (389 mg, 2.04 mmol, 1.1 equiv.) was carefully added. The resulting mixture was allowed to stir overnight at room temperature. The mixture was quenched with NH_4Cl sat. acq. (10 mL), the layers separated, and the aqueous phase was extracted with DCM (3 x 10 mL), dried over Na_2SO_4, and concentrated to a brownish oil. Intermediate tosyl amide (255 mg, 0.85 mmol) was dissolved in THF (2 mL), treated with 1M HCl (850 µL, 1 equiv.) and stirred at room temperature for 2.5 hours. After that the reaction mixture was extracted with AcOEt (3 x 10 mL), the combined organic phases were washed with brine (5 mL), dried over Na_2SO_4 and concentrated to obtain a brownish oil. The crude was further purified by flash column chromatography (cHex/AcOEt 8/2). **1w** was obtained as brown oil, 51% yield (0.44 mmol, 99 mg). Spectroscopic data were according to the literature.[9]

*Synthesis of aldehyde **S1a***



To a solution of 3,3-diethoxy-1-aminopropane (250 µL, 1.54 mmol) in AcOEt (3 mL) were added $NaHCO_3$ (650 mg, 7.7 mmol, 5 equiv.), water (3mL) and benzyl chloroformate (331 µL, 2.3 mmol, 1.5 equiv.). The resulting mixture was allowed to stir overnight at room temperature and checked by GC-MS and TLC (cHex/AcOEt 6/4) to complete conversion. After that, the layers were separated, and the aqueous phase was extracted with AcOEt (3 x 5 mL), dried over Na_2SO_4 and concentrated. The crude was dissolved in THF (0.5 mL), treated with 1M HCl (250 µL, 12 mol%) at 0°C and stirred overnight at room temperature. After the reaction mixture was diluted with Et_2O (10 mL) and washed with a saturated solution of $NaHCO_3$ (5 mL), the combined organic phase was dried over Na_2SO_4 and concentrated to obtain a yellowish oil. The crude was further purified by flash column chromatography (cHex/AcOEt 7/3) to obtain **S1a** as yellow solid, 51% yield (0.79 mmol, 164 mg). Spectroscopic data were according to the literature.[9]

*Synthesis of aldehyde **S1b***

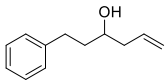


To a solution of 3,3-diethoxy-1-aminopropane (250 µL, 1.54 mmol) in DCM (3 mL) were added Et_3N (428 µL, 3.1 mmol, 2 equiv.), 4-(dimethylamino)pyridine (2 mg, 0.016 mmol, 1.0 mol%) and a solution of di-*tert*-butyl dicarbonate (371 mg, 1.7 mmol, 1.1 equiv.) in DCM (1.5 mL) drop-wise at 0°C. The resulting mixture was allowed to stir overnight at room temperature and checked by GC-MS and TLC (cHex/AcOEt 6/4). After the mixture was quenched with H_2O (10 mL), the layers separated, and the aqueous phase was extracted with Et_2O (3 x 10 mL), the combined organic phase washed with Brine (10 mL), dried over Na_2SO_4 and concentrated. The crude was dissolved in THF (1 mL), treated with 1M HCl (550 µL, 40 mol%) at 0°C and stirred at room temperature until disappearance of starting material (TLC cHex/AcOEt 7/3). A saturated solution of $NaHCO_3$ was added, extracted with Et_2O (3 x 10 mL), the combined organic phase was dried over Na_2SO_4 and concentrated to obtain a yellowish oil. The crude was further purified by flash column chromatography (cHex/AcOEt 8/2) to obtain **S1b** as yellowish oil, 31% yield (0.47 mmol, 82 mg). Spectroscopic data were according to the literature.[9]

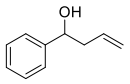
General procedure for photoredox titanium-catalyzed allylation of aldehydes

Standard procedure: All the reactions were performed in duplicate on 0.1 mmol scale of aldehyde. A dry 10 mL Schlenk tube, equipped with a Rotaflo stopcock, magnetic stirring bar and an argon supply tube, was first charged under argon with the organic photocatalyst 3DPAFIPN (5 mol%, 0.005 mmol, 3.2 mg), Cp_2TiCl_2 catalyst (10 mol%, 0.01 mmol, 2.5 mg), Dimethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate Hantzsch's ester (2 equivalents, 0.2 mmol, 45 mg). Inhibitor-free dry THF (2 mL in order to obtain a 0.05 M substrate solution) was then added and the reaction mixture was further subjected to a freeze-pump-thaw procedure (three cycles) and the vessel refilled with argon. Then, allyl bromide **2** (0.3 mmol, 3 equiv., 36 mg, 26 µL) and the substrate **1** (0.1 mmol) were added. The reaction was irradiated under vigorous stirring for the desired time. After that the two reaction mixtures were quenched with aqueous HCl 0.5 M (approx. 4 mL), combined together and extracted with AcOEt (4 x 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was subject of flash column chromatography (SiO_2) to afford the products **3** in the stated yields.

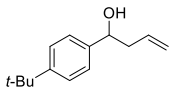
Procedure for 5 mmol scale: A dry 250 mL Schlenk tube, equipped with magnetic stirring bar and an argon supply tube, was first charged under argon with the organic photocatalyst 3DPAFIPN (3 mol%, 0.15 mmol, 95 mg), Cp_2TiCl_2 catalyst (8 mol%, 0.4 mmol, 0.100 g), Dimethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate Hantzsch's ester (2 equivalents, 10 mmol, 2.25 g). Inhibitor-free dry THF (100 mL in order to obtain a 0.05 M substrate solution) was then added and the reaction mixture was further subjected to a freeze-pump-thaw procedure (four cycles) and the vessel refilled with argon. Then, allyl bromide **2a** (15 mmol, 3 equiv., 1.8 g, 1.29 mL) and the substrate **1a** (5 mmol, 0.67 g, 0.66 mL) were added. The reaction was irradiated under vigorous stirring for 48 hours. After that the solvent was removed under reduced pressure. The crude was subject of flash column chromatography (SiO_2) to afford the products **3a** in 95% yield (4.75 mmol, 0.836 g).



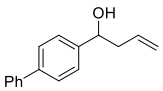
(**3a**): brown oil, 98% (0.195 mmol, 34 mg). The general procedure was applied using **1a** (0.1 mmol, 13 µL) previously distilled and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM).Spectroscopic data were according to the literature.[10]



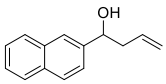
(**3b**): brown oil, 90% (0.18 mmol, 26 mg). The general procedure was applied using **1b** (0.1 mmol, 10.2 µL) previously distilled and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



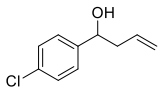
(**3c**): brown oil, 77% (0.15 mmol, 31.4 mg). The general procedure was applied using **1c** (0.1 mmol, 16 µL) previously distilled and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



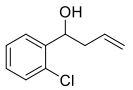
(**3d**): brown oil, 86% (0.17 mmol, 38.5 mg). The general procedure was applied using **1d** (0.1 mmol, 18 mg) and **2a** (0.6 mmol, 64 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



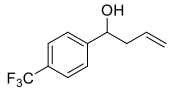
(**3e**): brown oil, 83% (0.17 mmol, 26 mg). The general procedure was applied using **1e** (0.1 mmol, 16 mg) and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



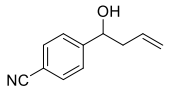
(**3f**): brown oil, 85% (0.17 mmol, 31 mg). The general procedure was applied using **1f** (0.1 mmol, 14 mg) and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature. [10]



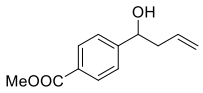
(**3g**): brown oil, 41% (0.08 mmol, 12 mg). The general procedure was applied using **1g** (0.1 mmol, 11.2 µL) previously distilled and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



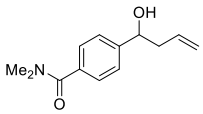
(**3h**): brown oil, 70% (0.14 mmol, 30 mg). The general procedure was applied using **1h** (0.1 mmol, 14 µL) previously distilled and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



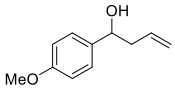
(**3i**): brown oil, 49% (0.1 mmol, 19 mg). The general procedure was applied using **1i** (0.1 mmol, 19 mg) and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



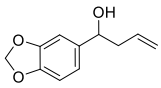
(**3j**): brown oil, 68% (0.13 mmol, 28 mg). The general procedure was applied using **1j** (0.1 mmol, 17 mg) and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (gradient to 100% DCM to 99.5/0.5 DCM/MeOH). Spectroscopic data were according to the literature.[10]



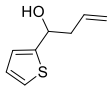
(**3k**): brown oil, 63% (0.13 mmol, 28 mg). The general procedure was applied using **1k** (0.1 mmol, 17 mg) and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (gradient to 100% DCM to 99.5/0.5 DCM/MeOH). Spectroscopic data were according to the literature.[10]



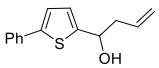
(**3l**): brown oil, 75% (0.15 mmol, 27 mg). The general procedure was applied using **1l** (0.1 mmol, 13 µL) and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



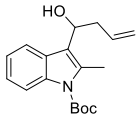
(**3m**): brown oil, 65% (0.13 mmol, 25 mg). The general procedure was applied using **1m** (0.1 mmol, 19 mg) and **2m** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography(100% DCM). Spectroscopic data were according to the literature.[10]



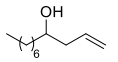
(**3n**): brown oil, 71% (0.14 mmol, 22 mg). The general procedure was applied using **1n** (0.1 mmol, 15.4 mg) and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature. [10]



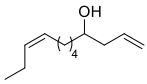
(**3o**): brown oil, 47% (0.09 mmol, 22 mg). The general procedure was applied using **1o** (0.2 mmol, 23 mg) and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



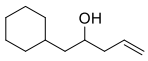
(**3p**): brown oil, 21% (0.04 mmol, 13 mg). The general procedure was applied using **1p** (0.1 mmol, 30 µL) and **2a** (0.6 mmol, 64 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



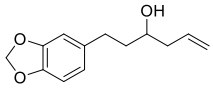
(**3q**): brown oil, 73% (0.14 mmol, 24 mg). The general procedure was applied using **1q** (0.1 mmol, 16 µL) freshly distilled at 59°C/21 mbar and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature. [10]



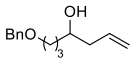
(**3r**): yellow oil, 40%. (0.08 mmol, 14 mg). The general procedure was applied using **1r** (0.1 mmol, 17 µL) freshly distilled at 68°C/13 mbar and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



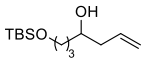
(**3s**): yellow oil, 60%. (0.12 mmol, 20 mg). The general procedure was applied using **1s** (0.1 mmol, 13 mg) at 68°C/13 mbar and **2a**(0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[11]



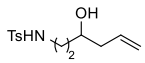
(**3t**): brown oil, 79% (0.16 mmol, 34.7 mg). The general procedure was applied using **1u** (0.1 mmol, 18 mg) previously synthesized and **2a** (0.6 mmol, 64 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



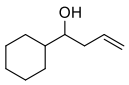
(**3u**): brown oil, 69% (0.14 mmol 27 mg). The general procedure was applied using **1u** (0.1 mmol, 15 mg) previously synthesized and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



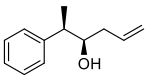
(**3v**): brown oil, 60% (0.12 mmol 29 mg). The general procedure was applied using **1v** (0.1 mmol, 15 mg) previously synthesized and **2a** (0.3 mmol, 28 µL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). ^{1}H NMR ($CDCl_3$, 401 MHz) δ 5.84 (m, J = 17.4, 10.3, 7.2 Hz, 1H), 5.17 – 5.01 (m, 1H), 3.66 (m, J = 5.0 Hz, 3H), 2.32 – 2.16 (m, 2H), 1.70 – 1.39 (m, 4H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz,) δ 135.11, 117.53, 70.58, 64.90, 63.44, 56.25, 41.90, 40.54, 33.94, 29.13, 25.89.



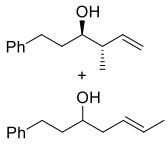
(**3w**): brown oil, 60% (0.12 mmol, 32 mg). The general procedure was applied using **1w** (, 0.1 mmol, 22 mg) previously synthesized and **2a** (0.3 mmol, 28 μL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (gradient to 100% DCM to 99.5/0.5 DCM/MeOH). Spectroscopic data were according to the literature.[10]



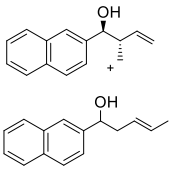
(**3x**): brown oil, 84% (0.12 mmol, 26 mg). The general procedure was applied using **1x** (, 0.1 mmol, 11 mg) freshly distilled at 68°C/13 mbar and **2a** (0.3 mmol, 28 μL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (gradient to 100% DCM to 99.5/0.5 DCM/MeOH). Spectroscopic data were according to the literature.[10]



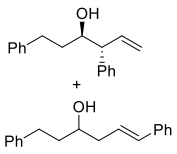
(**3y**): yellow oil, 90% (0.18 mmol, 32 mg) as *syn*:*anti* mixture dr of 1.2:1. The general procedure was applied using **1y** (0.1 mmol 13 μL) freshly distilled at 52°C/3 mbar and **2a** (0.3 mmol, 28 μL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[10]



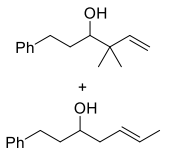
(**3ab-3ab'**): yellow oil, 50% as mixture regioisomer and distereoisomer **3ab**:**3ab'** of >99:1, **3ab**$_{syn}$:**3ab**$_{anti}$ dr of 91:9 (0.1 mmol, 19 mg). The general procedure was applied using **1a** (0.1 mmol 13 μL) freshly distilled at 52°C/3 mbar and **2b** 85% technical grade (0.3 mmol, 37 μL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[12]



(**3eb-3eb'**): brown oil, 82% as mixture regioisomer and distereoisomer **3eb**:**3eb'** of 84:16, **3eb**$_{anti}$:**3eb**$_{syn}$ dr of 94:6 (0.18 mmol, 32 mg). The general procedure was applied using **1e** (0.1 mmol) and **2b** 85% technical grade (0.3 mmol, 37 μL, 3 equiv.) and performed in duplicate. The title compound was isolated by flash column chromatography (100% DCM). Spectroscopic data were according to the literature.[13]



(**3ac-3ac'**): brown oil, 25% as mixture regioisomer and distereoisomer **3ac**:**3ac'** of 93:7, **3ac**$_{anti}$:**3ac**$_{syn}$ dr of 85:15 (0.05 mmol, 13 mg). The general procedure was applied using **1a** (0.1 mmol) and **2c** (0.3 mmol, 59 mg, 3 equiv.) and performed in duplicate. The title compound was not isolated, and the yield determined by ^{1}H NMR with internal standard method. Spectroscopic data were according to the literature.[13]



(**3ad-3ad'**): brown oil, 27% as mixture regioisomer **3ad**:**3ad'** of 69:31 (0.05 mmol, 11 mg). The general procedure was applied using **1a** (0.1 mmol) and **2d** (95%, 0.3 mmol, 36 μL, 3 equiv.) and performed in duplicate. The title compound was not isolated, and the yield determined by ^{1}H NMR with internal standard method. Spectroscopic data were according to the literature.[13]

Results and Discussion

Screening of reaction conditions

Scheme S1. Reaction in the presence of radical scavenger TEMPO. Trial was conducted using typical procedure, two reaction on 0.1 mmol scale performed in duplicate

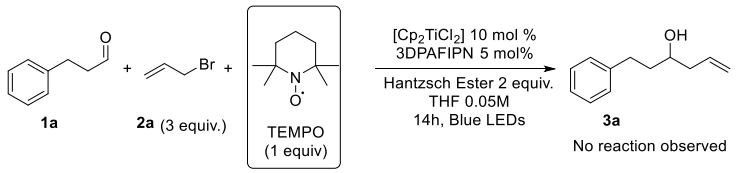
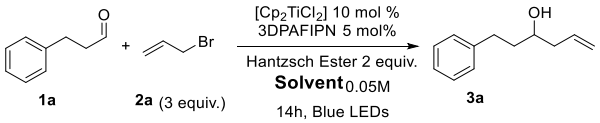


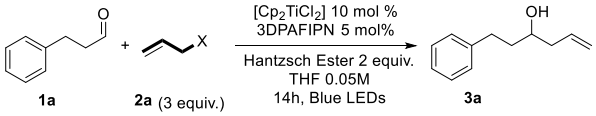
Table S1. Screening of reaction solvent.



Entry[a]	Solvent	Yield (%)[b]
1	THF	>99 (98)[c]
2	THF contains 250 ppm BHT as inhibitor	14
3	Toluene	60
4	MeCN	55
5	2MeTHF	39
6	DMF	0
7	DCM	0
8	MeOH	0
9	DMSO	0

[a] Reaction conditions reported in the above figure on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis. [c] Isolated yield after chromatographic purification.

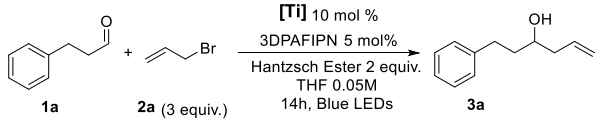
Table S2. Screening of allylating agent.



Entry[a]	X	Yield (%)[b]
1	Cl	92
2	OAc	Traces
3	Br	>99 (98)[c]

[a] Reaction conditions reported in the above figure on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis. [c] Isolated yield after chromatographic purification.

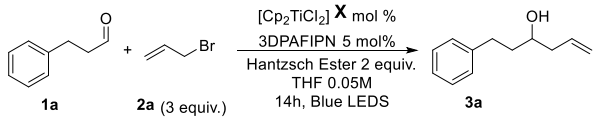
Table S3. Screening of titanium source.



Entry[a]	Titanium source	Yield (%)[b]
1	[Cp_2TiCl_2]	>99 (98)[c]
2	[$TiCl_4$]	24
3	[$CpTiCl_3$]	15

[a] Reaction conditions reported in the above figure on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis. [c] Isolated yield after chromatographic purification.

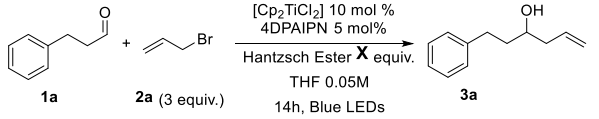
Table S4. Screening of [Cp_2TiCl_2] amount**.**



Entry[a]	Amount titanium complex	Yield (%)[b]
1	-	0
2	2.5 mol%	55
3	5 mol%	71
4	10 mol%	>99 (98)[c]

[a] Reaction conditions reported in the above figure on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis. [c] Isolated yield after chromatographic purification.

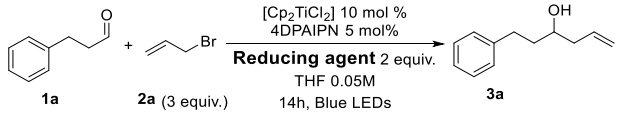
Table S5. Screening of reducing agent amount.



Entry[a]	Amount of Hatzsch ester	Yield (%)[b]
1	-	0
2	1.2 equivalents	45
3	2 equivalents	>99 (98)[c]

[a] Reaction conditions reported in the above figure on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis. [c] Isolated yield after chromatographic purification.

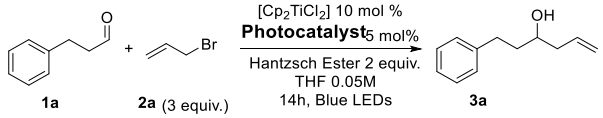
Table S6. Test with different reducing agent.

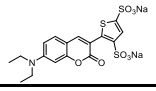


Entry[a]	Reducing agent	Yield (%)[b]
1	Hantzsch	>99 (98)[c]
2	DIPEA	0
3	Triphenylamine (TPA)	0

[a] Reaction conditions reported in the above figure on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis. [c] Isolated yield after chromatographic purification.

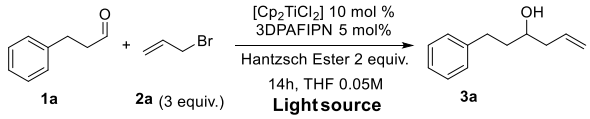
Table S7. Screening of photocatalyst.



Entry[a]	Photocatalyst	Yield (%)[b]
1	-	0
2	3DPAFIPN	>99 (98)[c]
3[d]	{Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}(PF$_6$)	96
4	4CZIPN	45
5[d]	[Ru(bpy)$_3$]Cl$_2$•6H$_2$O	0
6		17

[a] Reaction conditions reported in the above figure on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis. [c] Isolated yield after chromatographic purification. [d] 1% of the photocatalyst was used.

Table S8. Test with different light source.

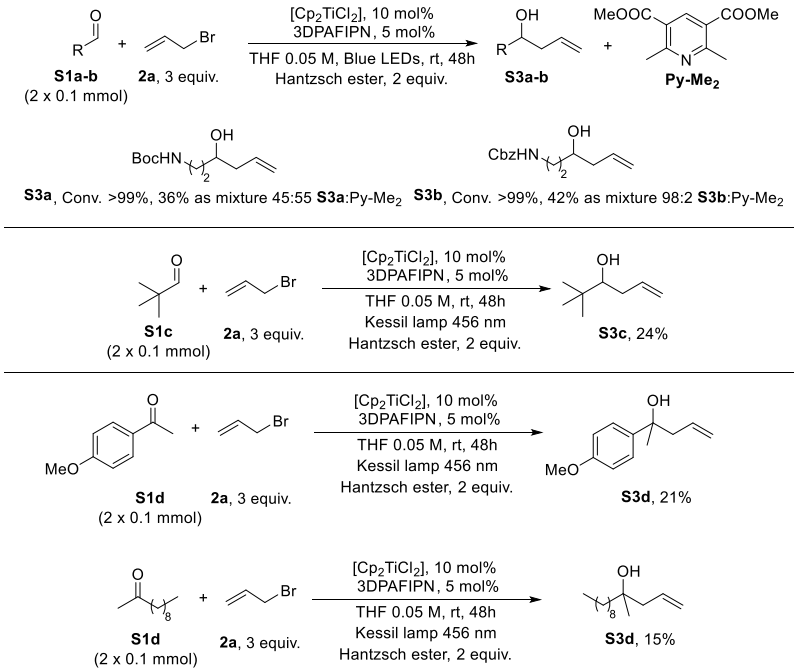


Entry[a]	Light source	Yield (%)[b]
1	Blue LED 450 nm 16W	>99 (98)[c]
2[d]	Green LED 550 nm 16W	0
3[e]	40W Kessil® lamp 456 nm	>99 (97)[c]
4	No light	0

[a] Reaction conditions reported in the above figure on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis. [c] Isolated yield after chromatographic purification. [d] Reaction performed in absence of the photocatalyst. [e] Reaction time 6h.

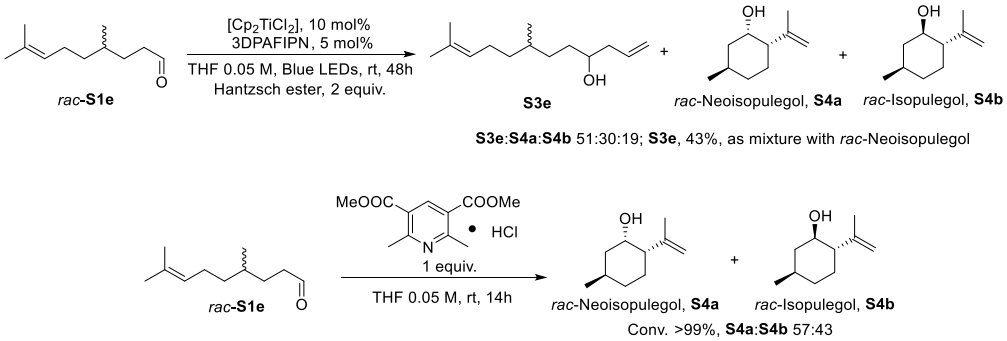
Further substrates and bromides studied

Scheme S2. Other substrate studies with poor yields or problematic purifications.



Aldehydes **S1a** and **S1b** gave complete conversion applying standard conditions with Blue LEDs but the corresponding products **S3a** and **S3b** were obtained as mixture with the oxidized Hantzsch ester after chromatographic purification. Any attempts to isolate pure products were useless.

Scheme S3. Reaction with citronellal.



Under the standard reaction condition *rac*-citronellal (*rac*-**S1e**) gave an inseparable mixture of desired product (**S3e**) and *rac*-Neoisopulegol (*rac*-**S4a**) and *rac*-Isopulegol (*rac*-**S4b**). We assumed that cyclizations occurred due to the presence in the reaction mixture of pyridinium salt derived from the oxidation of Hantzsch ester. To confirm our hypothesis *rac*-**S1e** was treated with 1 equivalent of pyridinium salt in THF for 14h gave a mixture of *rac*-Isopulegol and *rac*-Neoisopulegol. The acid catalyzed cyclization of citronellal to Pulegol isomers is already reported in literature.[14]

Figure S4. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of reaction crude. Reaction of aldehyde **1a** to give product **3a** (Table 1 entry 1).

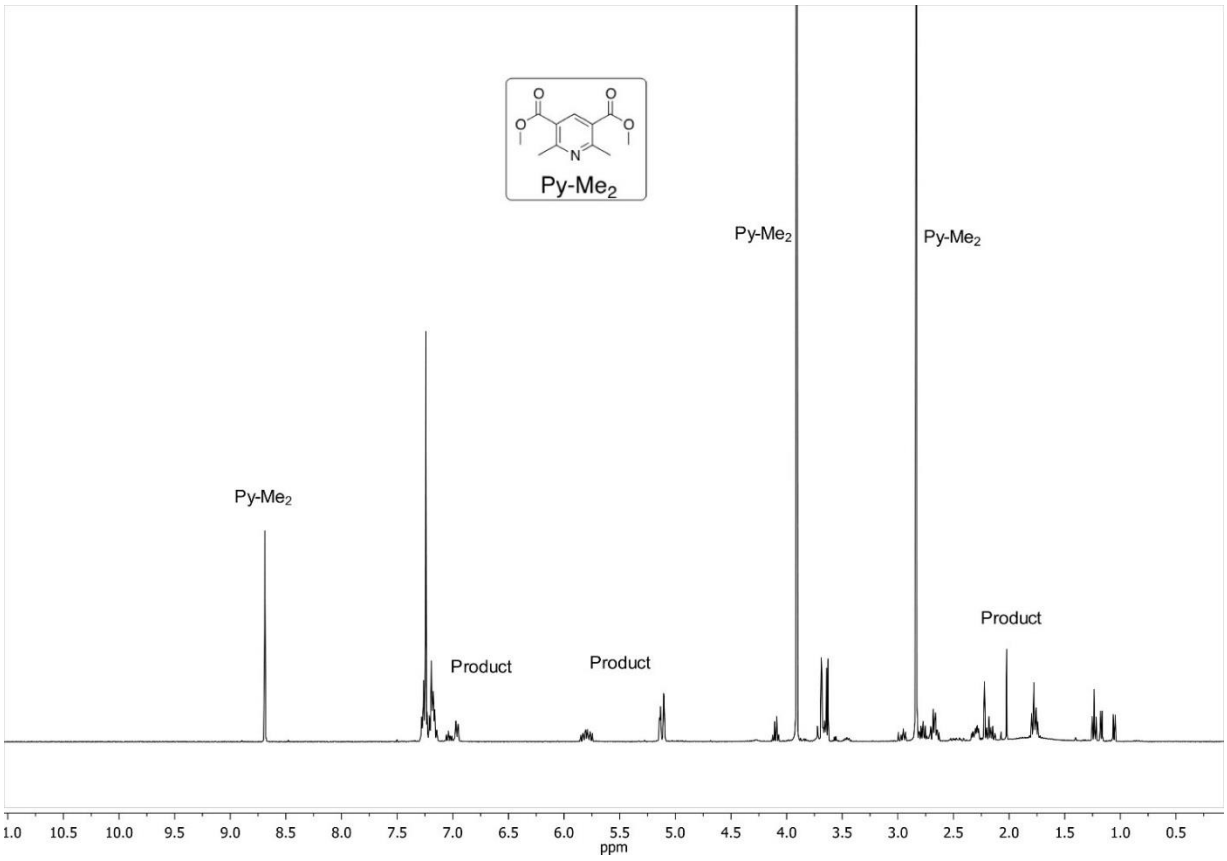
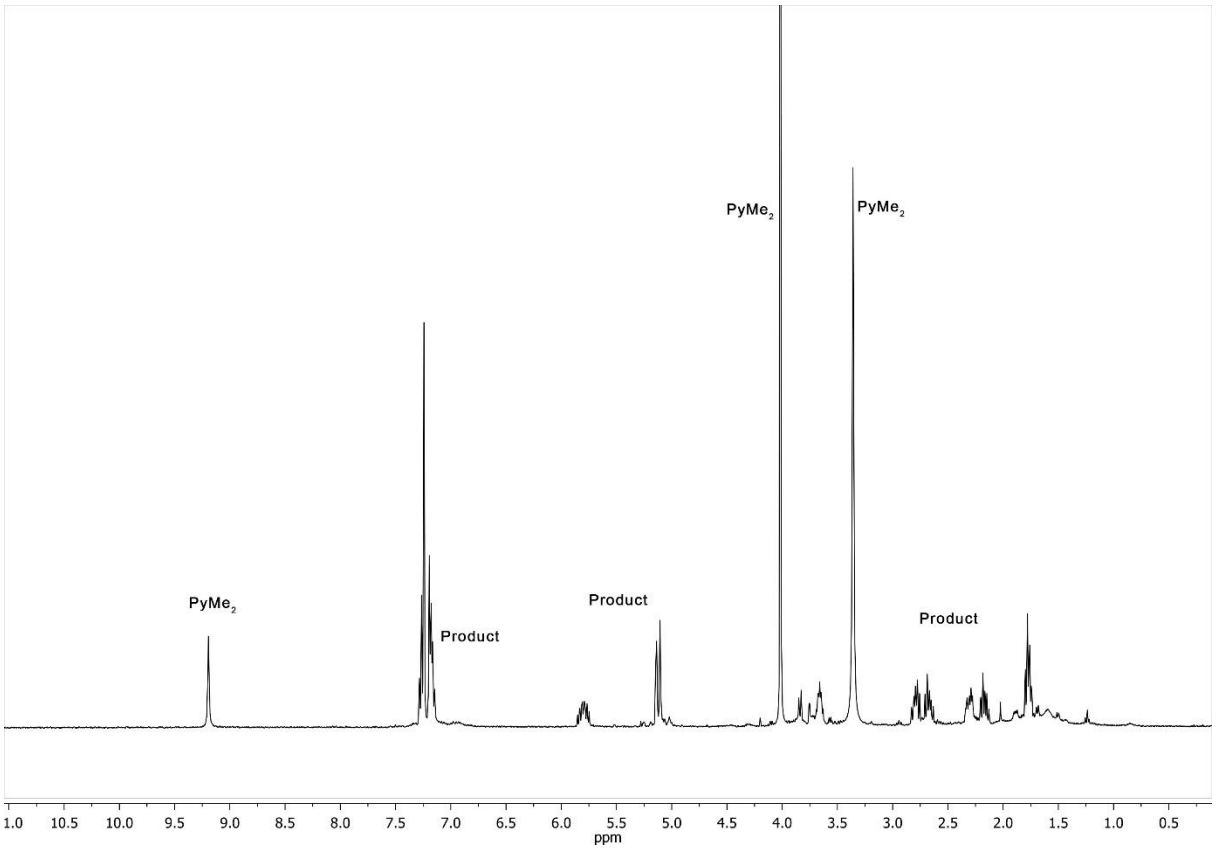


Figure S5. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of reaction crude. Reaction of aldehyde **1a** to give product **3a** (Table 1 entry 4) on 5 mmol scale.



Photophysical and mechanistic studies

All the photophysical analyses were carried out in air-equilibrated tetrahydrofuran at 298 K unless otherwise specified. Luminescence measurements at 77 K were performed in dichloromethane/methanol (1:1 v/v) mixture. UV–vis absorption spectra were recorded with a PerkinElmer λ40 spectrophotometer using quartz cells with path length of 1.0 cm. Luminescence spectra were performed with a PerkinElmer LS-50 or an Edinburgh FLS920 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Lifetimes shorter than 10 μs were measured by the above-mentioned Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution). The estimated experimental errors are 2 nm on the band maximum, 5% on the molar absorption coefficient and luminescence lifetime.

Figure S6. A: molar absorptivity spectrum of **Cp_2TiCl_2** recorded in air-equilibrated CH_3CN at r.t. **B**: phosphorescence spectrum of **Cp_2TiCl_2** recorded in CH_2Cl_2:CH_3OH (1:1 v/v) glassy matrix at 77 K; λ_{ex} = 520 nm. Inset: phosphorescence decay recorded on the same glassy matrix at λ_{em}= 660 nm.

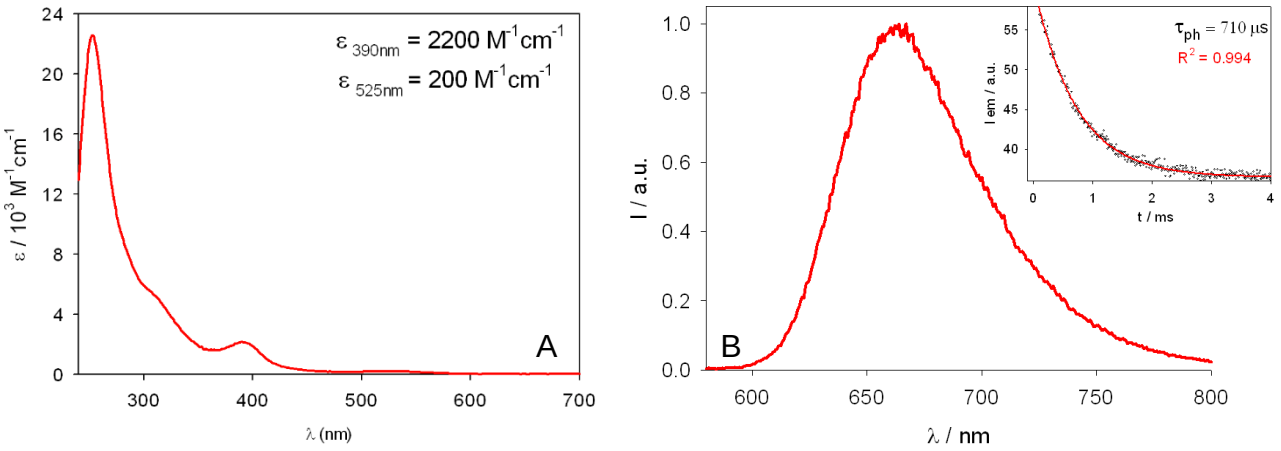


Figure S7. A: absorption (solid line) and emission spectrum (dashed line) recorded on a solution of **3-DPAFIPN** in air-equilibrated THF at r.t. λ_{ex}= 365 nm. For the fluorescence lifetime determination: λ_{ex}= 405 nm. **B:** absorption (solid line) and emission spectrum (dashed line) recorded on a solution of **Hantzsch ester** (**HE**) in air-equilibrated THF at r.t. λ_{ex}= 365 nm. For the fluorescence lifetime determination: λ_{ex}= 405 nm.

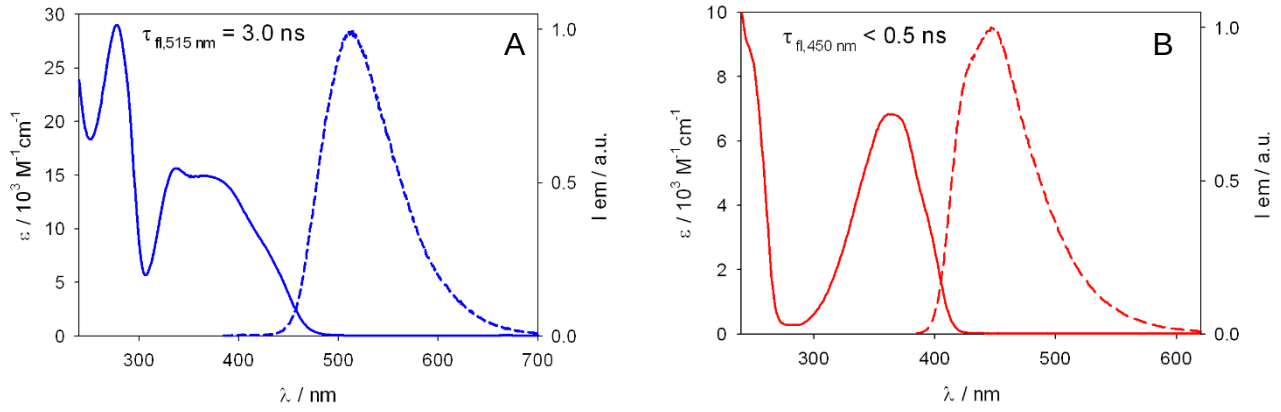


Figure S8. Emission decay of **3-DPAFIPN** in air equilibrated THF (blue dots). The decay is fitted with a monoexponential function (red line); the instrument response function is also shown (black dots). λ_{ex}=405 nm, λ_{em}=520 nm.

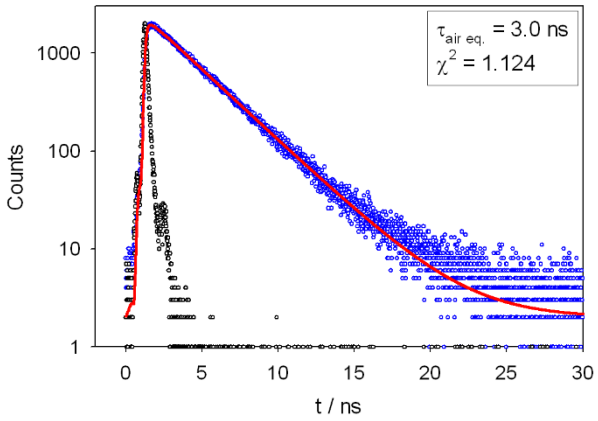


Figure S9. Comparison between normalized excitation (green dashed line) and emission (green solid line) spectra in degassed THF solutions of **3-DPAFIPN** at room temperature (λ_{em}=530 nm and λ_{ex}=410 nm) recorded in phoshorescence mode (delay=0.05 ms, gate 0.2 ms). The absorption spectrum is also shown (blue line).

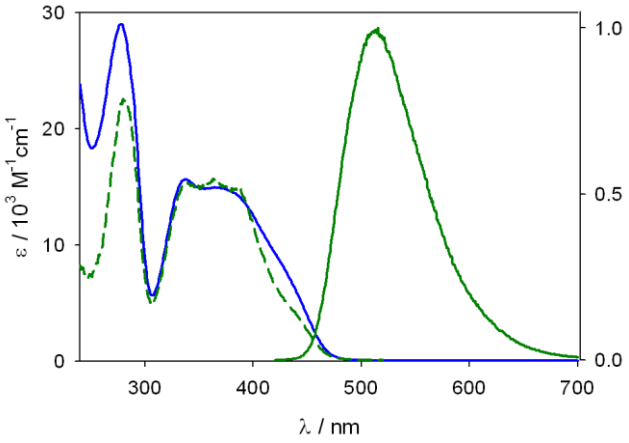


Figure S10. A: prompt fluorescence decay of **3-DPAFIPN** in degassed THF (pump-freeze-thaw, 3 cycles; blue dots). The decay is fitted with a monoexponential function (red line); the instrument response function is also shown (black dots). λ_{ex}=405 nm, λ_{em}=520 nm. **B**: emission decay of **3-DPAFIPN** in degassed THF (pump-freeze-thaw, 3 cycles; blue dots). The decay is fitted with a monoexponential function (red line). λ_{ex}=410 nm, λ_{em}=520 nm; delay = 0.05 ms.

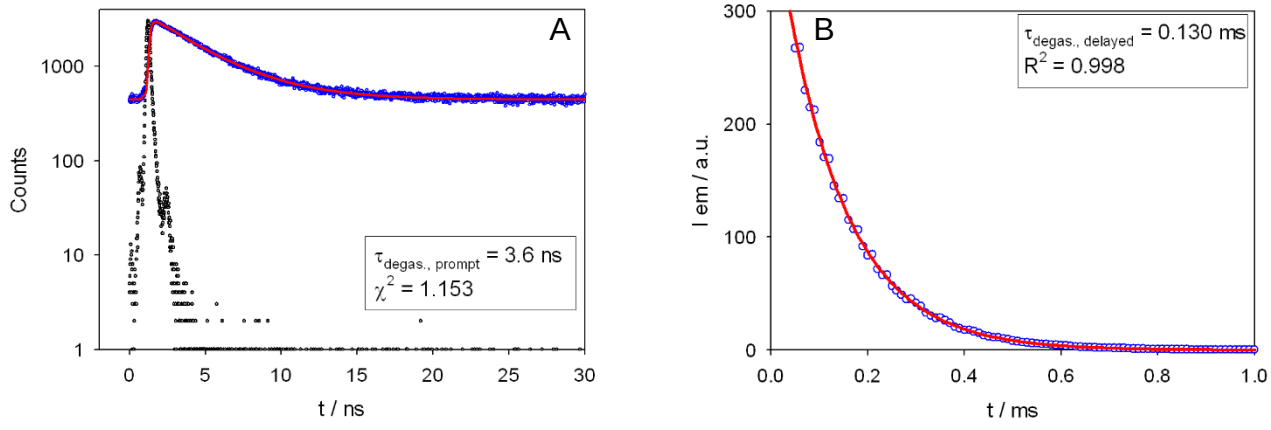


Figure S11. Luminescence spectra detected for a sample of **3-DPAFIPN** in rigid matrix at 77 K (CH_2Cl_2:CH_3OH 1:1, v/v) at different instrumental setups: fluorescence mode (blue line); gated phosphorescence (green line; gate=3 ms, delay=0.05 ms); undelayed phosphorescence (gate=100 ms). λ_{ex}=410 nm.

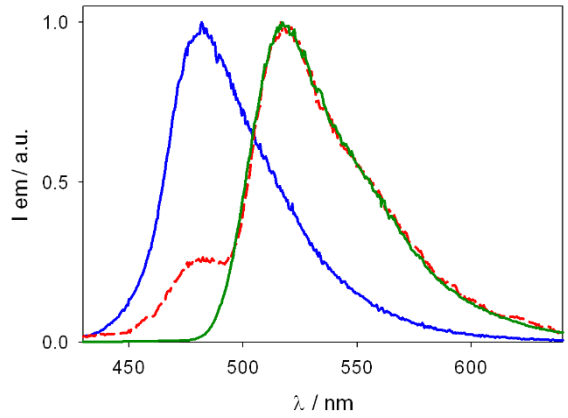


Figure S12. A: fluorescence decay of **3-DPAFIPN** in rigid matrix at 77 K (CH_2Cl_2:CH_3OH 1:1, v/v; blue dots). The decay is fitted with a biexponential function (red line); the instrument response function is also shown (black dots). λ_{ex}=405 nm, λ_{em}=470 nm. **B**: phosphorescence decay of **3-DPAFIPN** in rigid matrix at 77 K (CH_2Cl_2:CH_3OH 1:1, v/v; blue dots). The decay is fitted with a monoexponential function (red line). λ_{ex}=410 nm, λ_{em}=520 nm; delay = 5 ms.

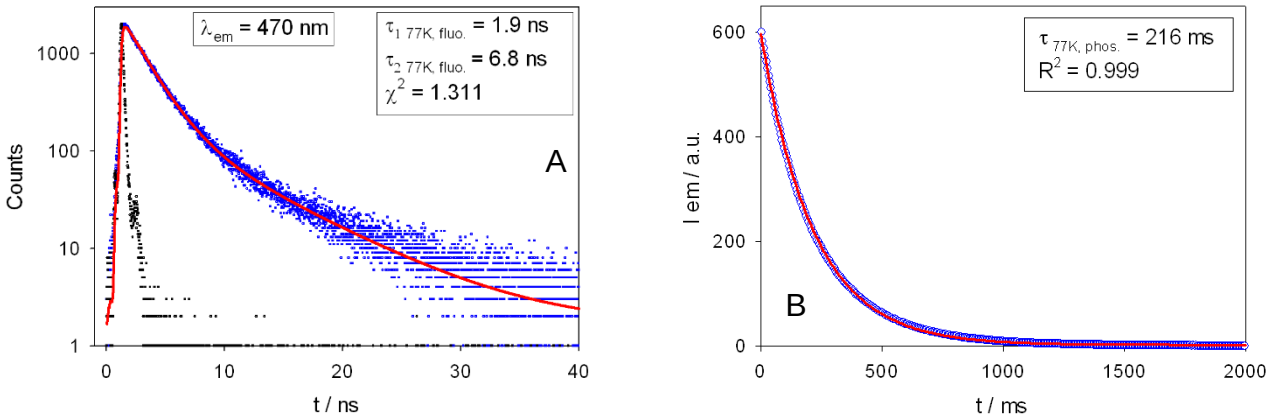


Figure S13. A: evolution of absorption spectra recorded for a solution of **Cp_2TiCl_2** (ca. 2.3 mM, blue line) in air-equilibrated commercial THF kept in the dark for total ca. 200 minutes (red line). Similar results were observed for **Cp_2TiCl_2** solutions at the same concentrations in distilled and degassed THF. **B**: evolution of absorption spectra recorded for the same solution as in **A**, upon irradiation with a blue-emitting LED strip ($\lambda_{ex} \approx$ 460 nm).

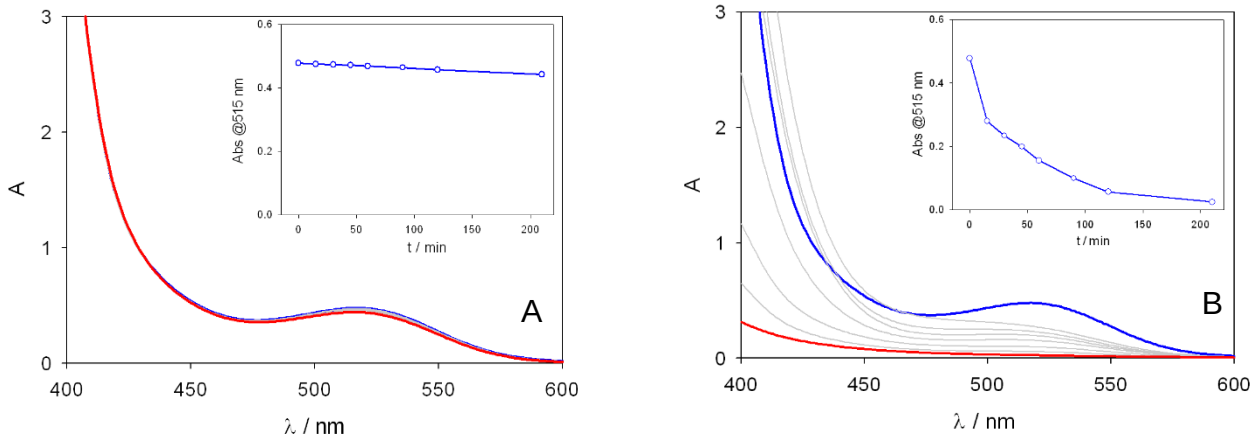


Figure S14. **A**: evolution of absorption spectra recorded from a solution containing **Cp_2TiCl_2** and **Hantzsch ester** (**HE**) (ca. 2.5 mM and 45 mM, respectively; blue line) in air-equilibrated THF, kept in the dark for a total ca. 110 minutes (red line). **B**: evolution of absorption spectra recorded from the same solution as **A**, upon irradiation with a blue-emitting LED strip ($\lambda_{ex} \approx 460$ nm).

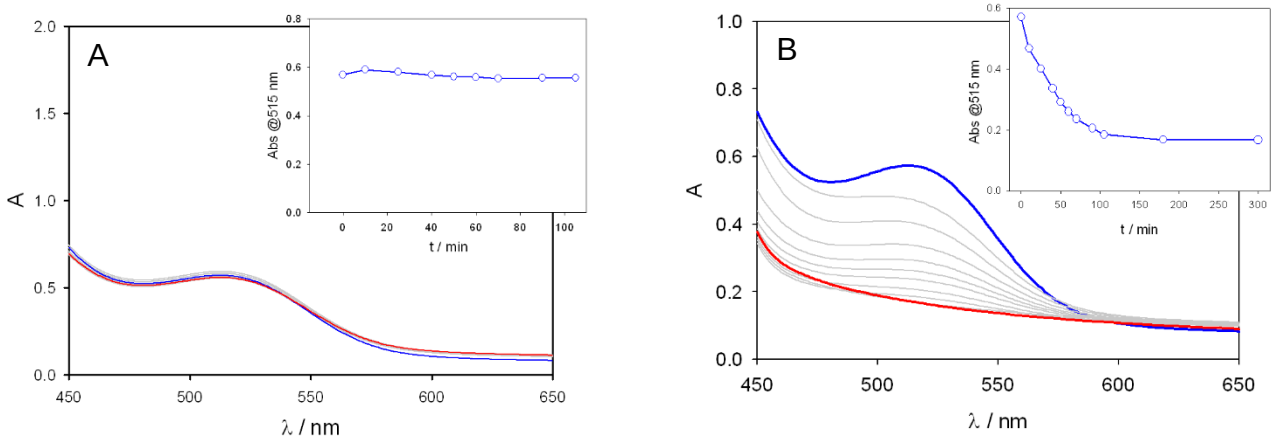
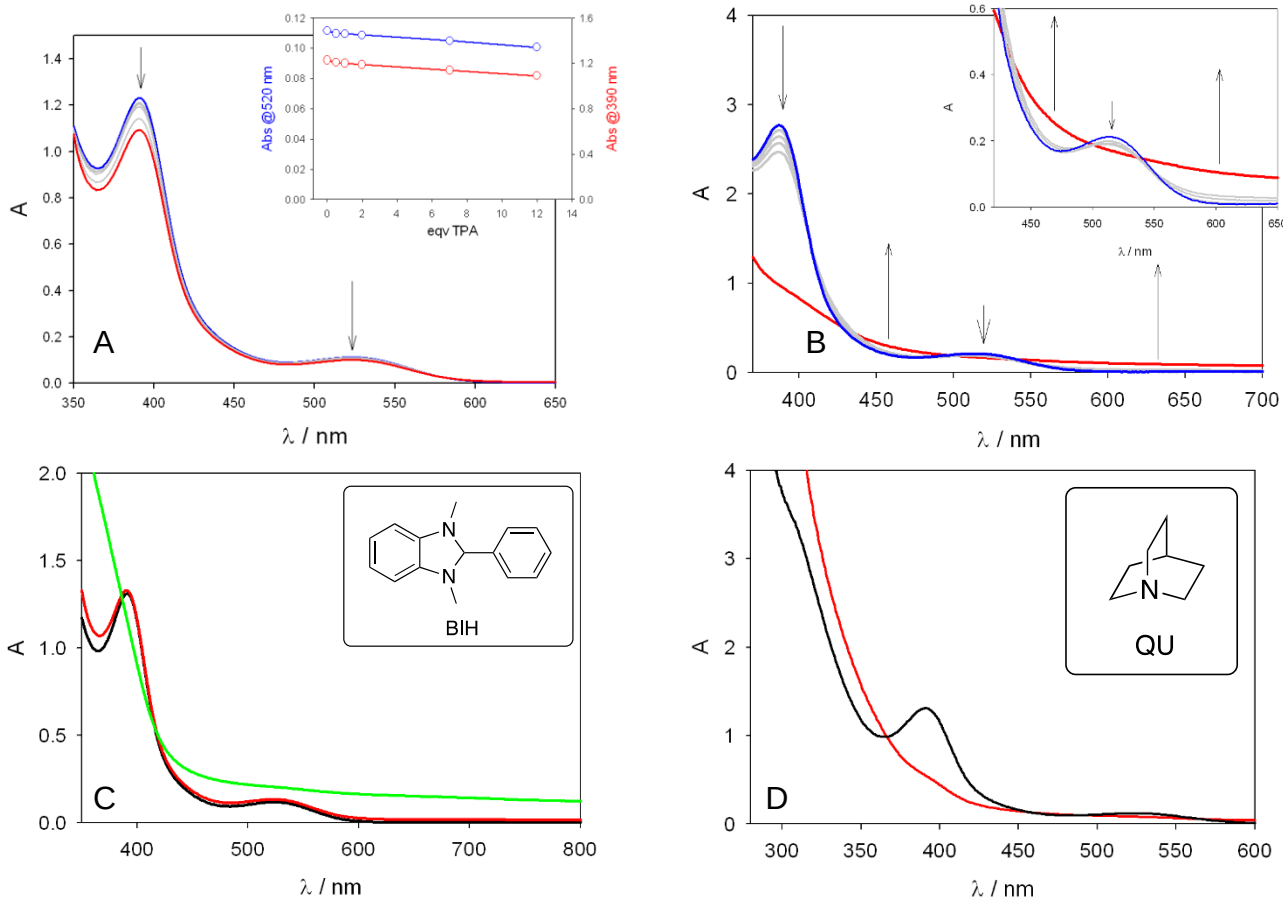


Figure S15. A: absorption spectra of a solution of **Cp_2TiCl_2** (ca. 0.72 mM, blue line) in air-equilibrated CH_3CN recorded upon addition of increasing amounts of triphenylamine (**TPA**, from a 6.6 mM solution in CH_3CN). Inset: absorption profiles at 520 and 390 nm. **B**: Evolution of absorption spectra recorded from a solution containing **Cp_2TiCl_2** and **TPA** (ca. 0.96 mM and 10 mM, respectively; blue line) in air-equilibrated CH_3CN at r.t., upon irradiation with a blue-emitting LED strip ($\lambda_{ex} \approx 460$ nm). Total irradiation time ≈ 18 hours (red line). **C**: Absorption spectra of a solution of **Cp_2TiCl_2** (ca. 0.72 mM, black line) in air-equilibrated CH_3CN at r.t recorded upon additions of 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (**BIH**, 1.52 mM an d 4.29 mM, red and green line, respectively). **D**: Absorption spectra of a solution of **Cp_2TiCl_2** (ca. 0.72 mM, black line) in air-equilibrated CH_3CN at r.t recorded upon addition of quinuclidine (**QU**, ca. 14.0 mM, red line).



NOTE. From the plots in figure, the general behaviour of **Cp_2TiCl_2** in solution with amines is highlighted. In the presence of aliphatic and aromatic amines in various air-equilibrated and degassed CH_3CN at r.t. the concentration of **Cp_2TiCl_2** is decreasing, probably in reason of its decomposition or ligand substitution. Since changes in concentration were detected both in solutions kept in the dark and under irradiation, the decomposition is likely occurring even on **Cp_2TiCl_2** at the ground state.

The Stern-Volmer relationship has been employed to evaluate in several experimental conditions the diffusional quenching occurring between **3-DPAFIPN** and the several species involved in the photoreactions taken into exam.
The Stern-Volmer kinetics show a linear correlation between the ratio τ_0/τ or I_0/I and the quencher concentration, as expected for a dynamic quenching process according to the Stern-Volmer equations:

$$\tau_0/\tau = 1 + k_{SV}[\mathbf{Q}] = 1 + k_q \tau_0 [\mathbf{Q}] \qquad I_0/I = 1 + k_{SV}[\mathbf{Q}] = 1 + k_q \tau_0 [\mathbf{Q}]$$

where τ_0 and τ are the lifetimes, and I_0 and I are the emission intensities in the absence and in the presence of the quencher **Q**, respectively, k_{SV} is the Stern-Volmer constant and k_q is the quenching constant.

Figure S16. A: absorption spectra of solutions of **3-DPAFIPN** in air-equilibrated THF (blue line) obtained upon addition of increasing amounts of **Cp_2TiCl_2** (up to ca. 31 mM, red line). **B**: normalised fluorescence decays of **3-DPAFIPN** obtained from the same solutions at λ_{em} = 590 nm (λ_{ex}= 405 nm). **C**: Stern-Volmer diagram relative to the fluorescence lifetimes shown in **B**.

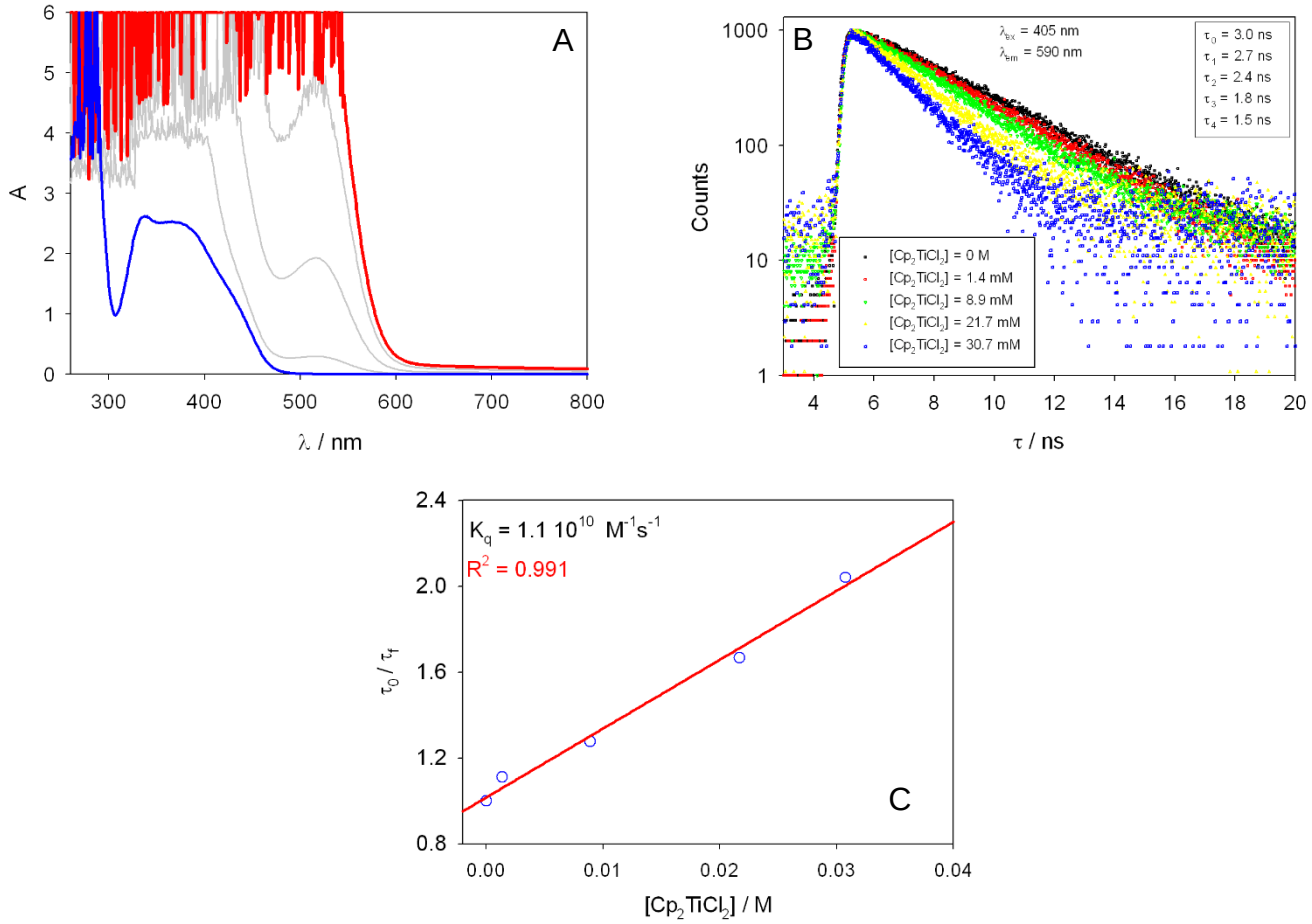


Figure S17. A: normalised emission decays of **3-DPAFIPN** in degassed THF (black dots) obtained upon addition of increasing amounts of **Cp_2TiCl_2** (up to ca. 65 □M, yellow line). λ_{em} = 560 nm (λ_{ex}= 410 nm). **B**: Stern-Volmer diagram relative to the emission lifetimes shown in **B**.

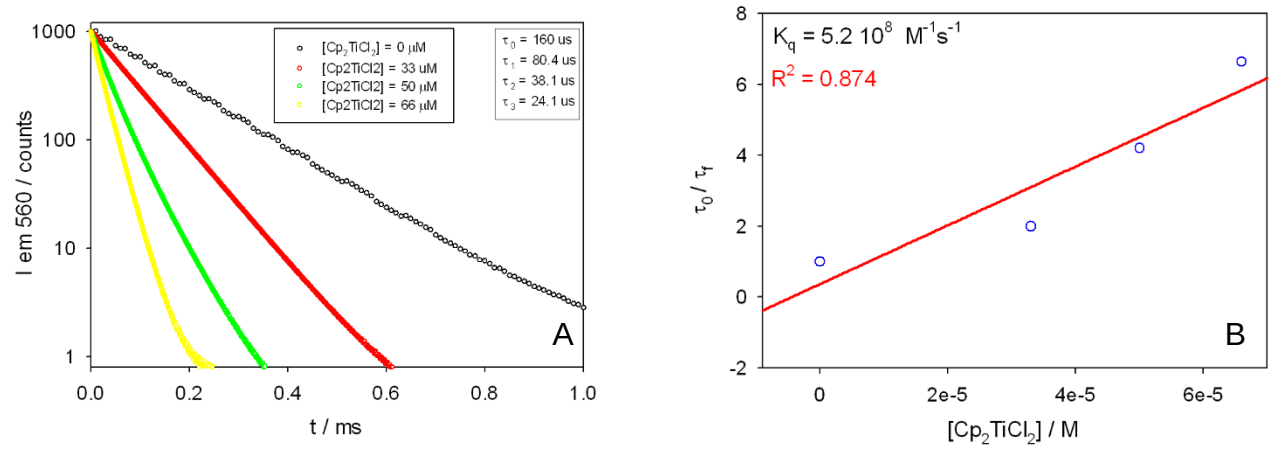


Figure S18. A: absorption spectra of solutions of **3-DPAFIPN** in air-equilibrated THF (blue line) obtained upon addition of increasing amounts of **Hantzsch ester** (up to ca. 14 mM, red line). **B**: fluorescence spectra of **3-DPAFIPN** obtained from the same solutions at λ_{ex}= 460 nm. **C**: Stern-Volmer diagram relative to the fluorescence spectra shown in **B**.

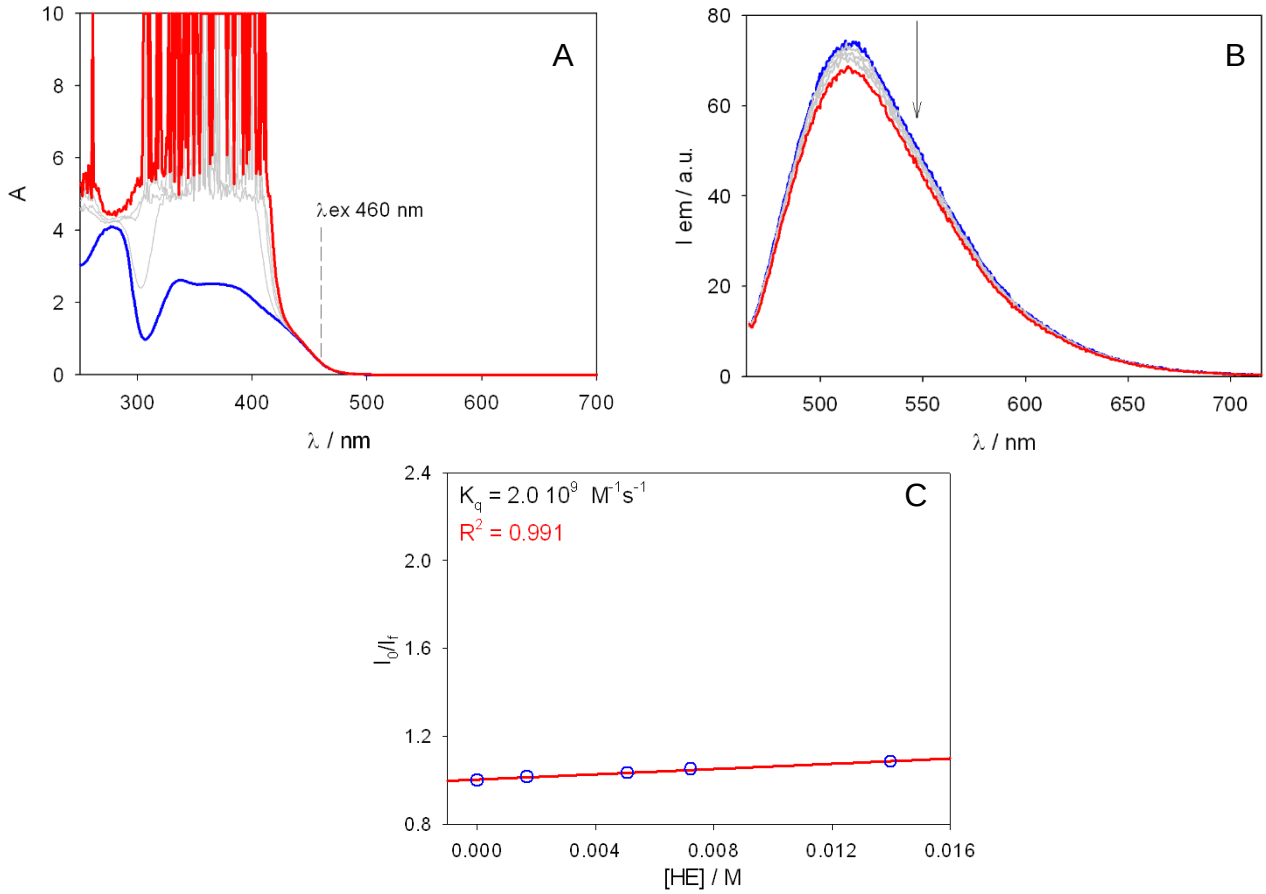
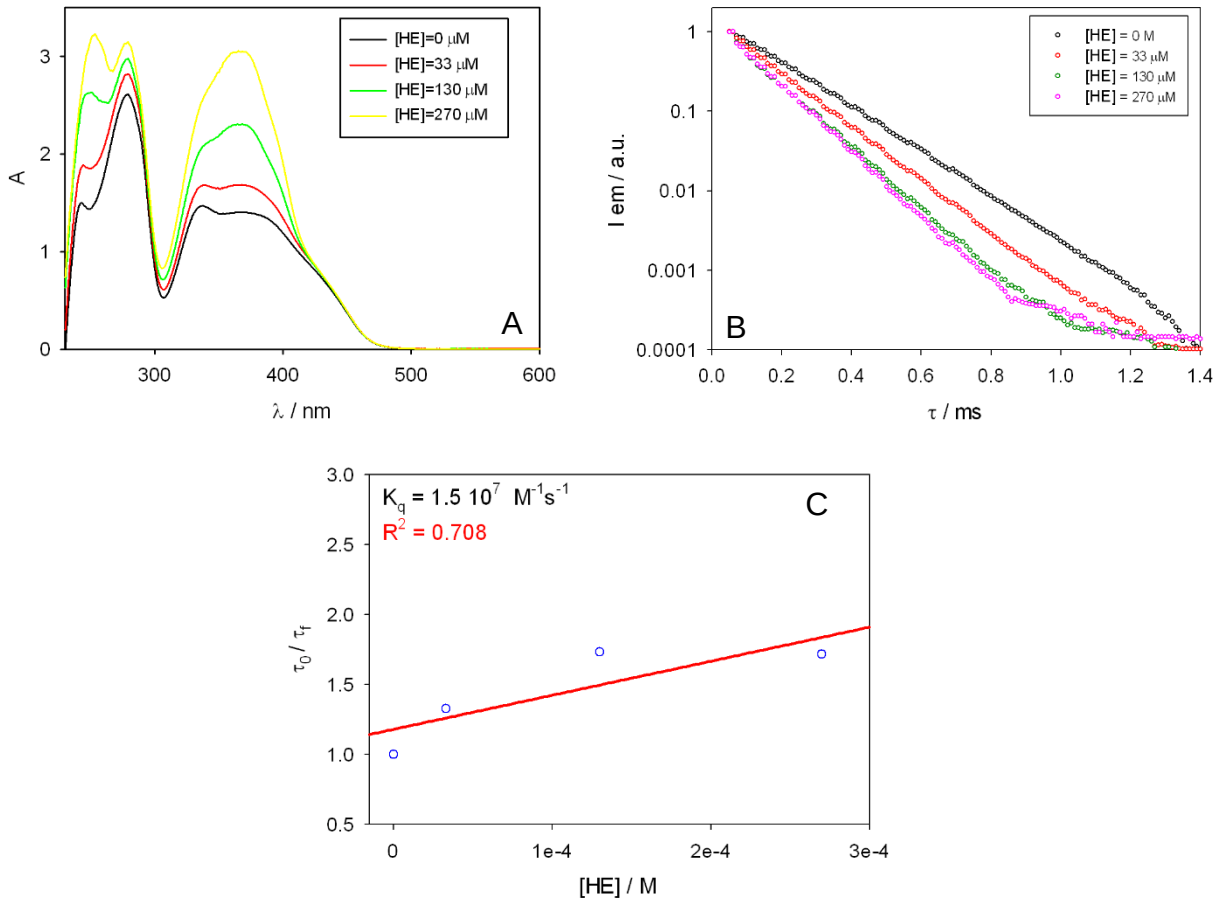
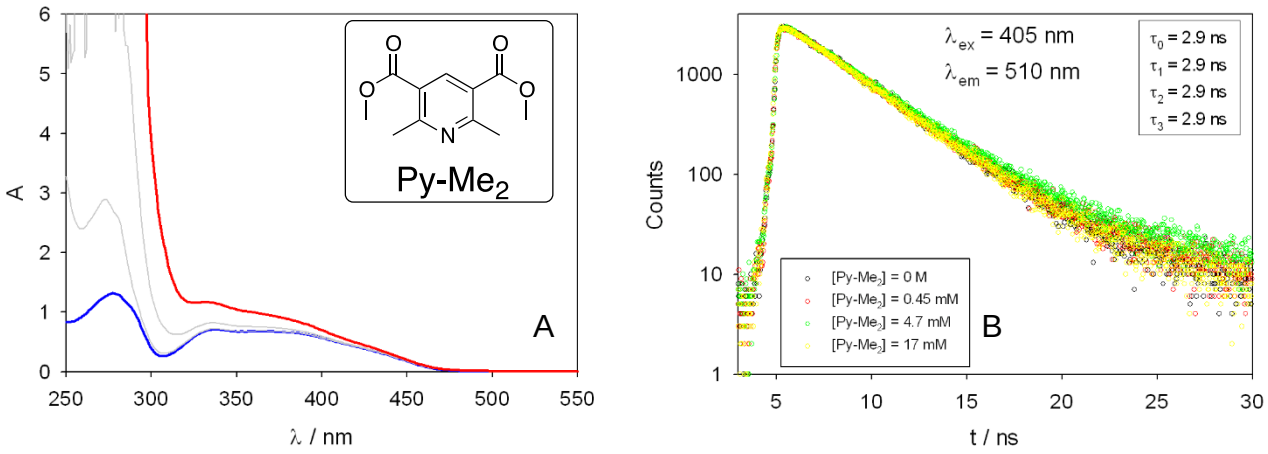


Figure S19. A: absorption spectra of solutions at r.t. of **3-DPAFIPN** in deoxygenated THF (argon purging, ca. 30 min. for each measurement) obtained upon addition of increasing amounts of **Hantzsch ester** (up to ca. 0.27 mM, yellow line). **B**: normalized emission decays of **3-DPAFIPN** obtained from the same solutions at λ_{em}= 520 nm (λ_{ex}= 430 nm). **C**: Stern-Volmer diagram relative to the emission decays shown in **B**.



In order to rule out the interaction of pyridine derived from the Hantzsch's ester (**Py-Me$_2$**) with the excited state of **3-DPAFIPN**, quenching experiment of **3-DPAFIPN** with increasing amounts of **Py-Me$_2$** has been performed.

Figure S20. A: absorption spectra of solutions of **3-DPAFIPN** in THF (blue line) obtained upon addition of increasing amounts of **Py-Me$_2$** (up to ca. 17 mM, red line). **B**: normalised fluorescence decays of **3-DPAFIPN** obtained from the same solutions at λ_{em} = 510 nm (λ_{ex}= 405 nm). Since the fluorescence lifetime of **3-DPAFIPN** is not significantly changing upon increasing additions of **Py-Me$_2$**, no Stern-Volmer plot is shown.



Determination of quantum yield

General procedure was applied on aldehyde **1a** (0.1 mmol scale) using allyl bromide **2a** under irradiation with Kessil® PR160L@456 nm. Three identical reactions were started, and one was stopped after 60 min., one after 90 and one after 120 min. Yield of the product **3a** was determined by ^{1}H NMR analysis on the reaction crude using benzyl alcohol as internal standard.
A LP 10-BB sensor manufactured by Laserpoint connected to a Gentec TPM-300CE power meter was used to determine the total radiant power of the excitation light at the same distance from the source and with the same total irradiation area of the reaction vessel.
The photon flux F_{ph} was calculated by taking into account the emission maximum of the lamp (456 nm, 2.72 eV; FWHM=0.12 eV) and approximated to monochromatic.[15]
The energy associated to a photon at a wavelength λ, E_{ph}, is calculated as

$$E_{ph} = \frac{h \cdot c}{\lambda}$$

where h is the Planck constant and c the speed of light. At 456 nm, E_{ph} corresponds to $4.36 \cdot 10^{-19}$ J.

The total photon flux F_{ph} was calculated as:

$$F_{ph} = \frac{P_i}{E_{ph}}$$

where P_i is the measured power (123 mW) and E_{ph} is the photon energy ($4.36 \cdot 10^{-19}$ J). From these data, a photon flux of $2.82 \cdot 10^{17}$ photons$\cdot$s^{-1} was determined, corresponding to $1.02 \cdot 10^{21}$ photons$\cdot$h^{-1} or $1.69 \cdot 10^{-3}$ E$\cdot$h^{-1}.

Considering that in our experimental condition the number of transmitted photons is neglegible in the whole range of emission of the lamp, it can be assumed that all of the photons are absorbed by the **3DPAFIPN** photocatalyst.

Quantum yield was determined as:

$$\Phi_{\%} = \frac{\text{mmol of } \mathbf{3a} \text{ formed}}{\text{mEinstein of light absorbed}} \cdot 100$$

Table S9. Determination of quantum yield.

Time (min)	**3a** (mmol)	Yield **3a** (%)	Light absorbed (mEinstein)	Φ (%)
60	0.0189	18.9	1.7	1.1
90	0.0335	33.5	2.4	1.3
120	0.0530	53.0	3.5	1.6

Quantum yield could be considered, within the experimental error, constant during the time interval studied and the average quantum yield is 1.3%.

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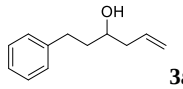
Copies of NMR spectra



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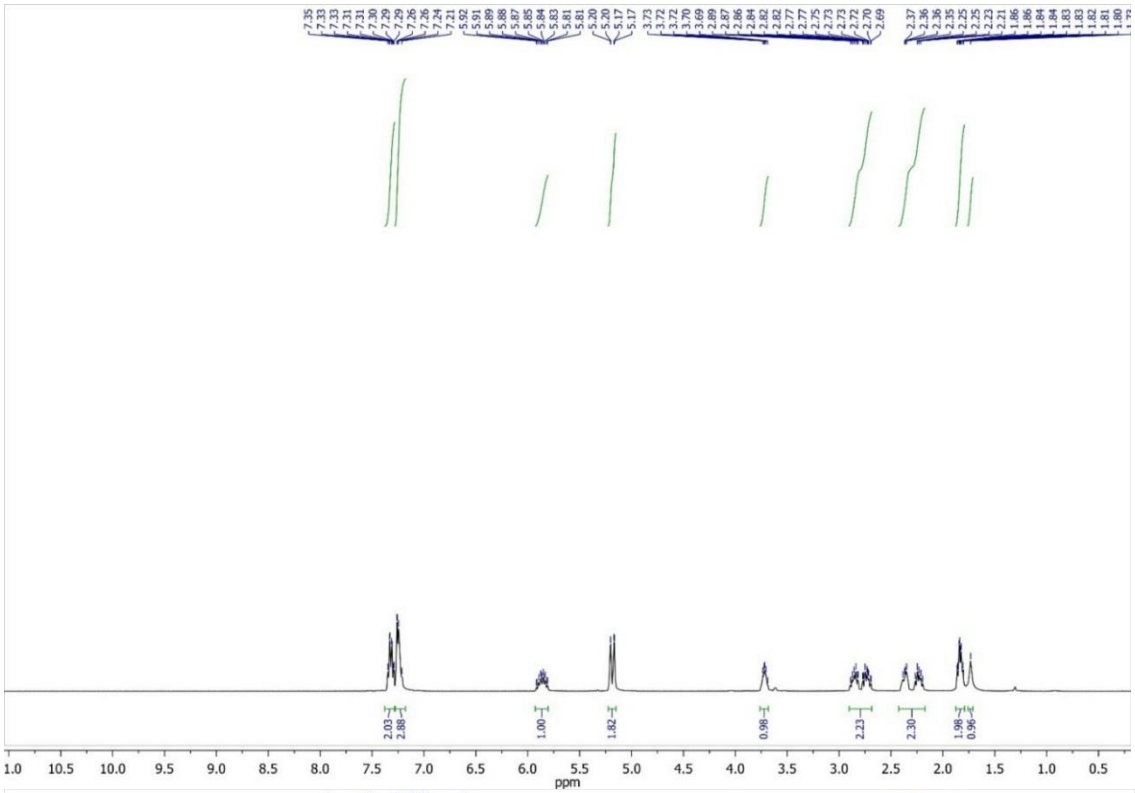

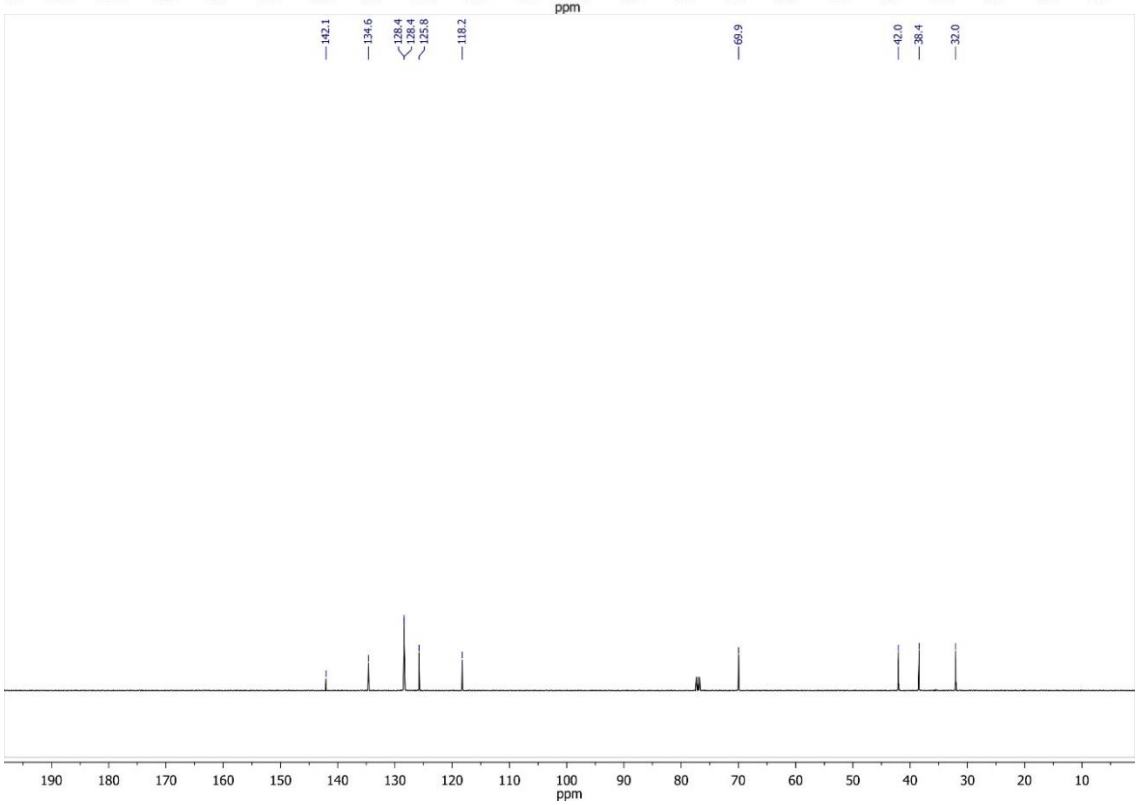

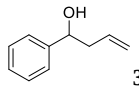
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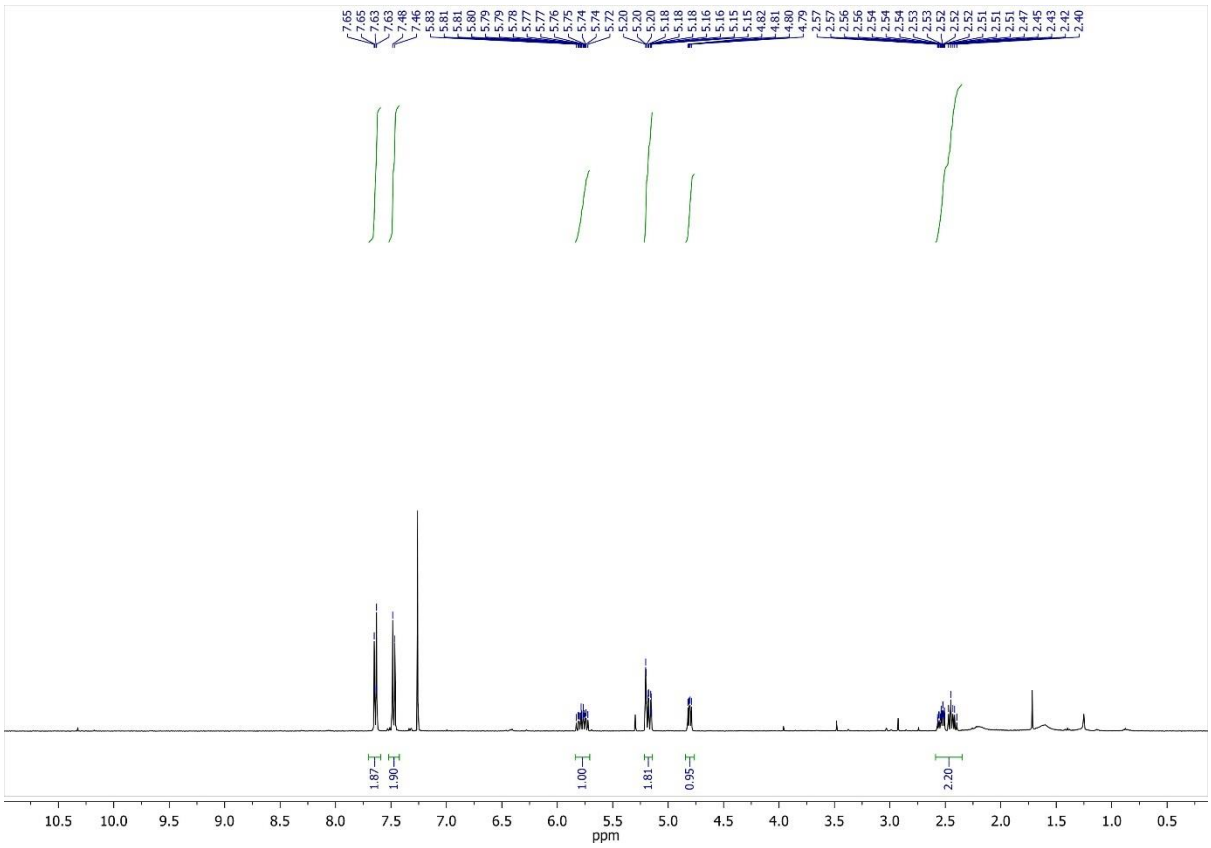
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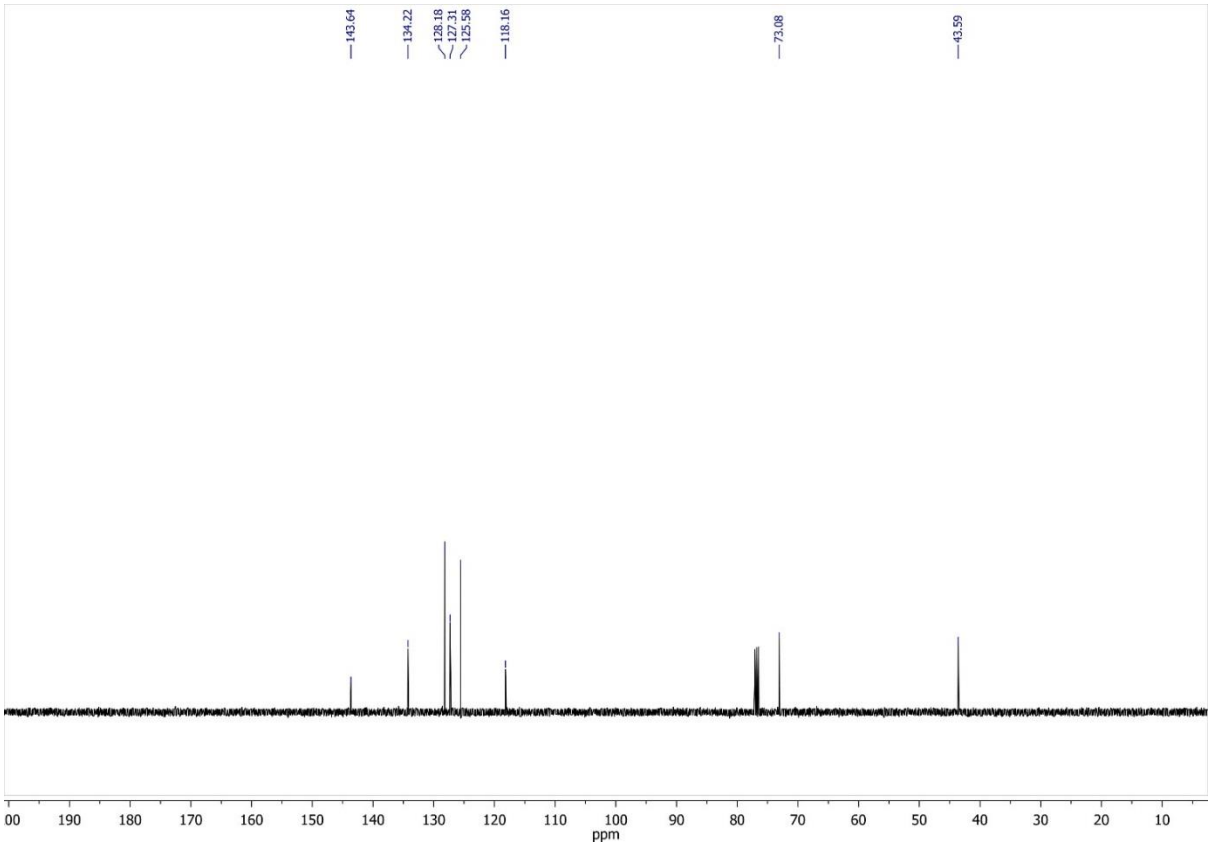
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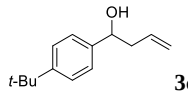
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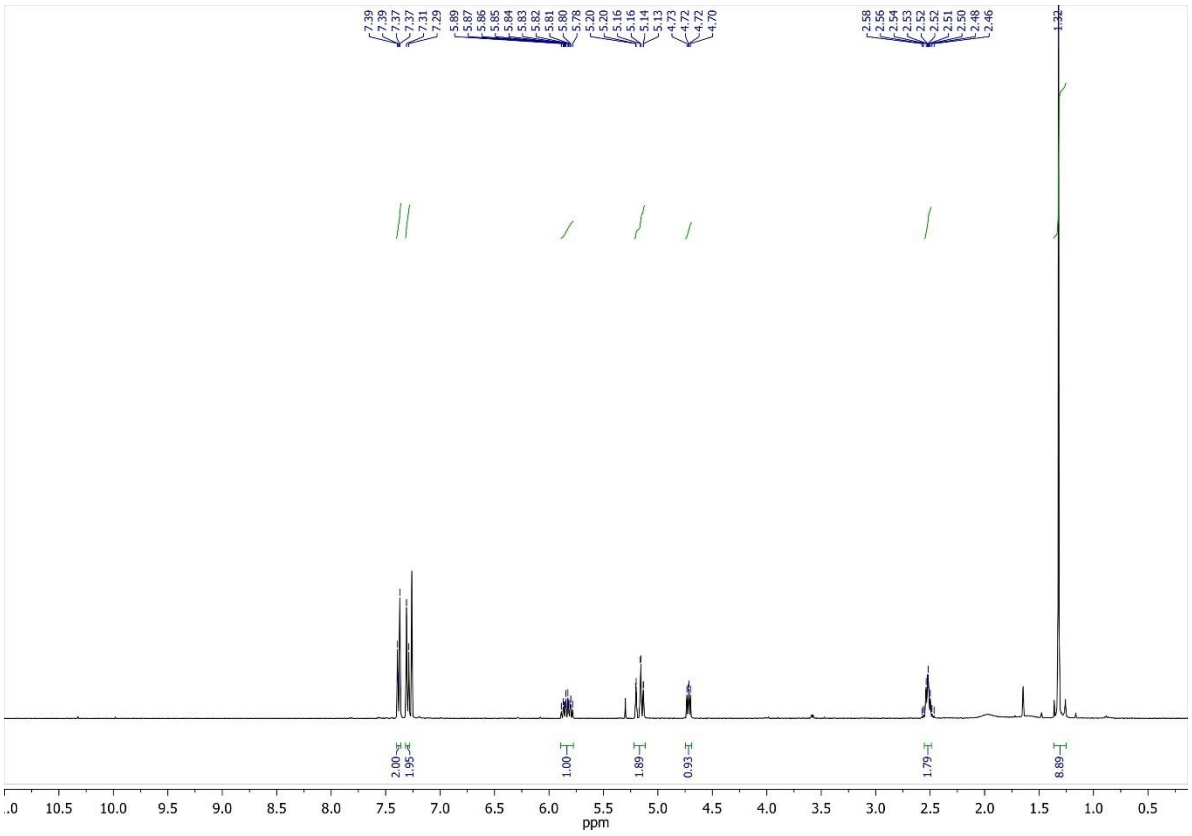
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5.16
5.16
5.14
5.13
4.73
4.72
4.72
4.70
2.58
2.56
2.54
2.53
2.52
2.52
2.51
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1.32
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1.00
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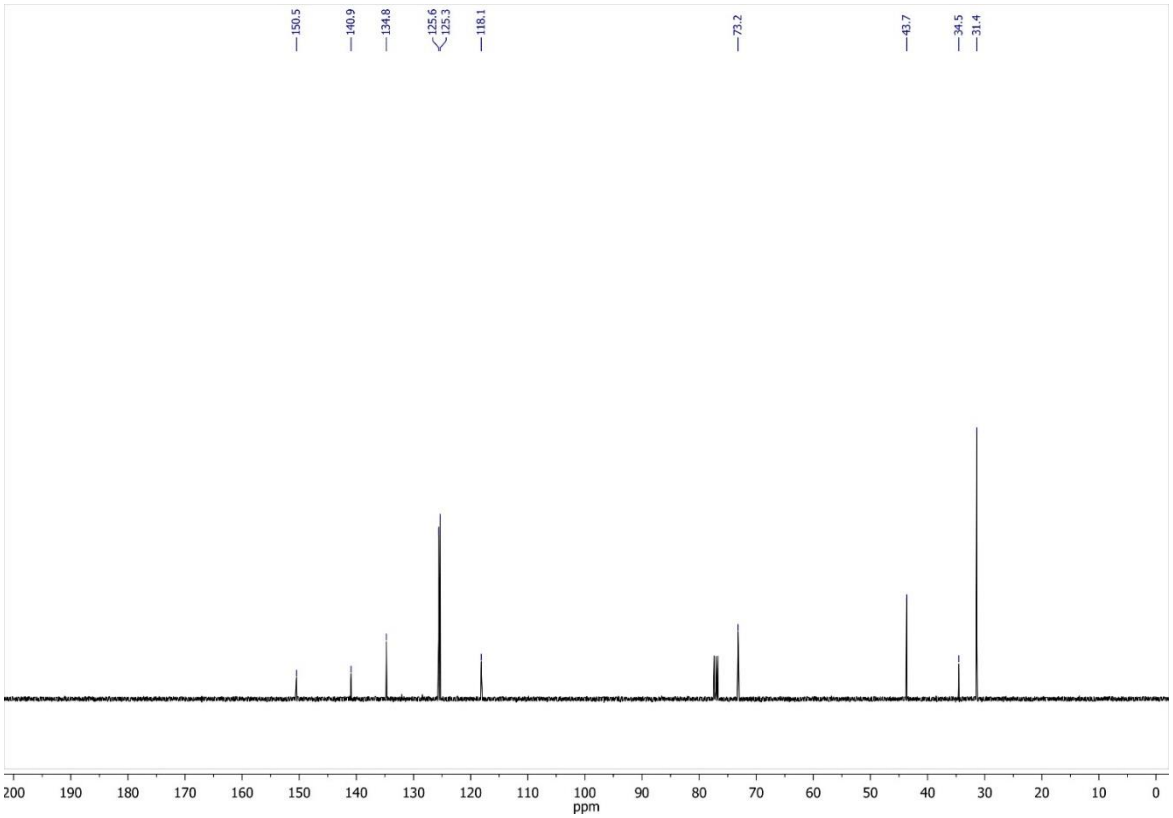
1.79
8.89
ppm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125.3
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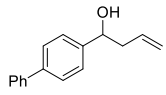
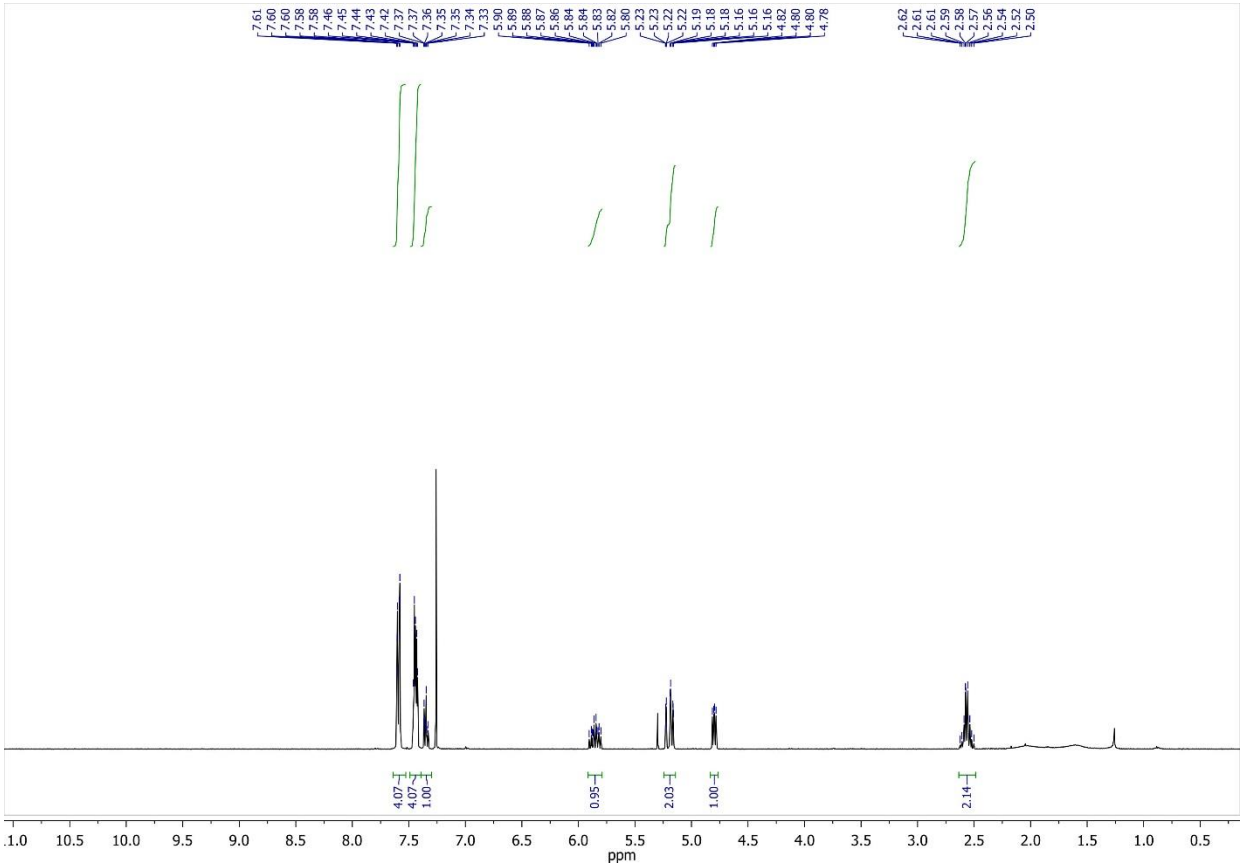
73.2
43.7
34.5
31.4
ppm


OH
Ph

3d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7.60
7.60
7.58
7.58
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7.44
7.43
7.42
7.37
7.37
7.36
7.35
7.35
7.34
7.33
5.90
5.89
5.88
5.87
5.86
5.84
5.84
5.83
5.82
5.80
5.23
5.23
5.22
5.22
5.19
5.18
5.18
5.16
5.16
5.16
4.82
4.80
4.80
4.78
2.62
2.61
2.61
2.59
2.58
2.57
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2.52
2.50
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4.07
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0.95
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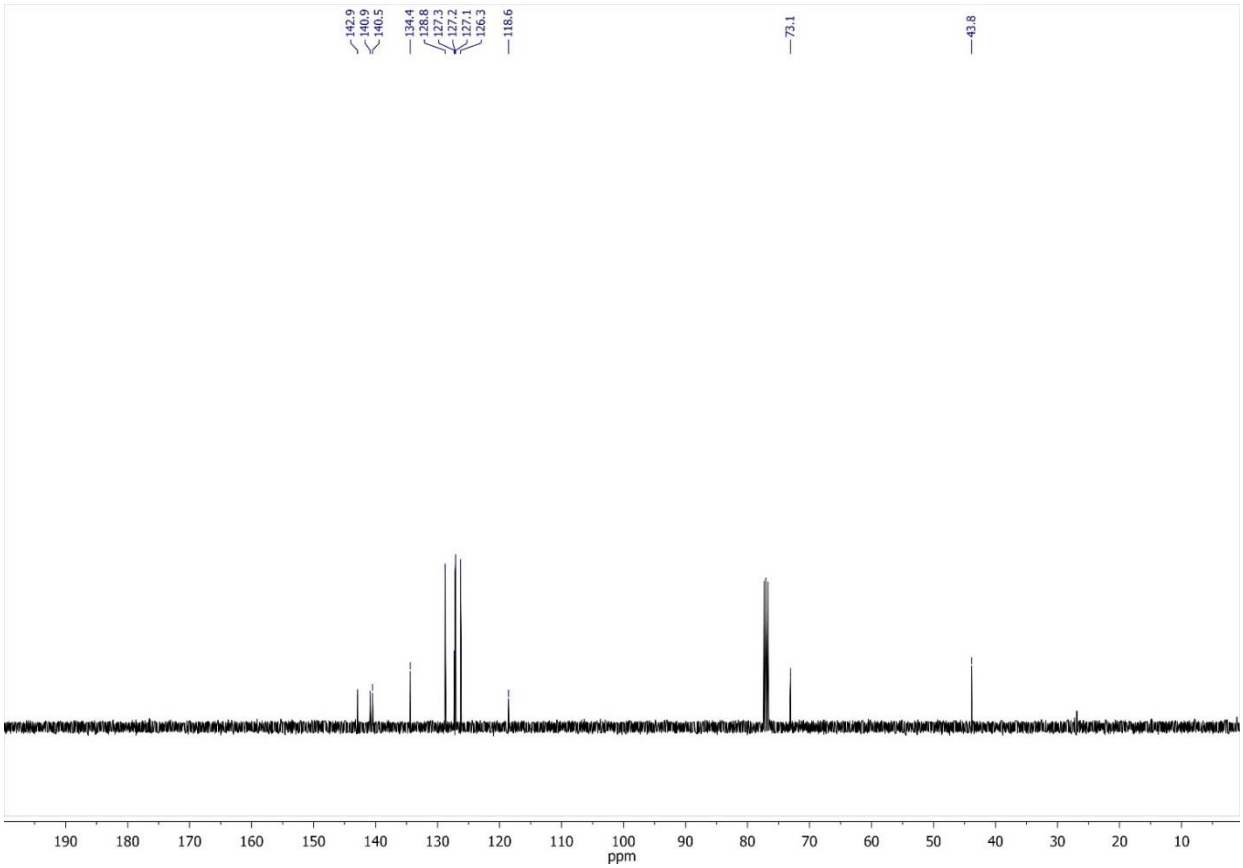
1.00
2.14
ppm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140.9
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127.3
127.2
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126.3
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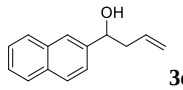
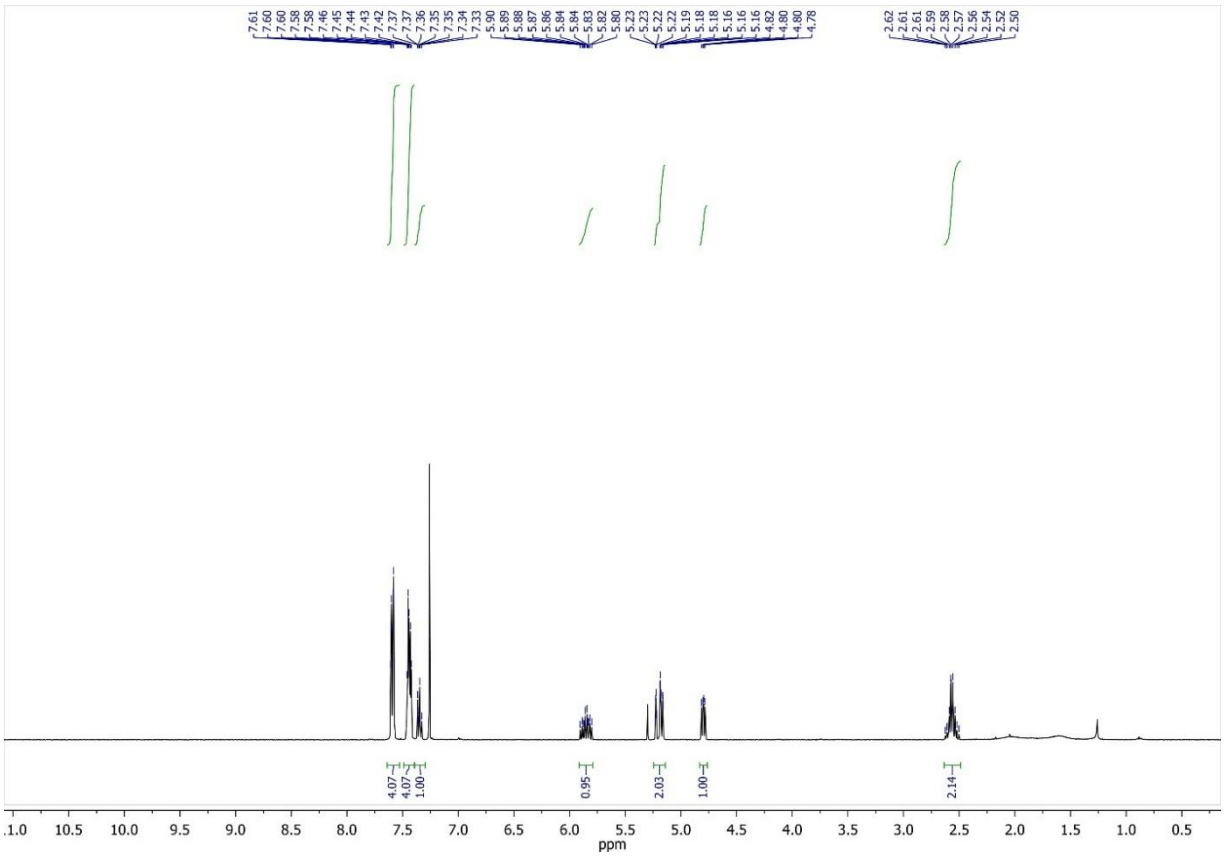
73.1
43.8
ppm


OH

3e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7.60
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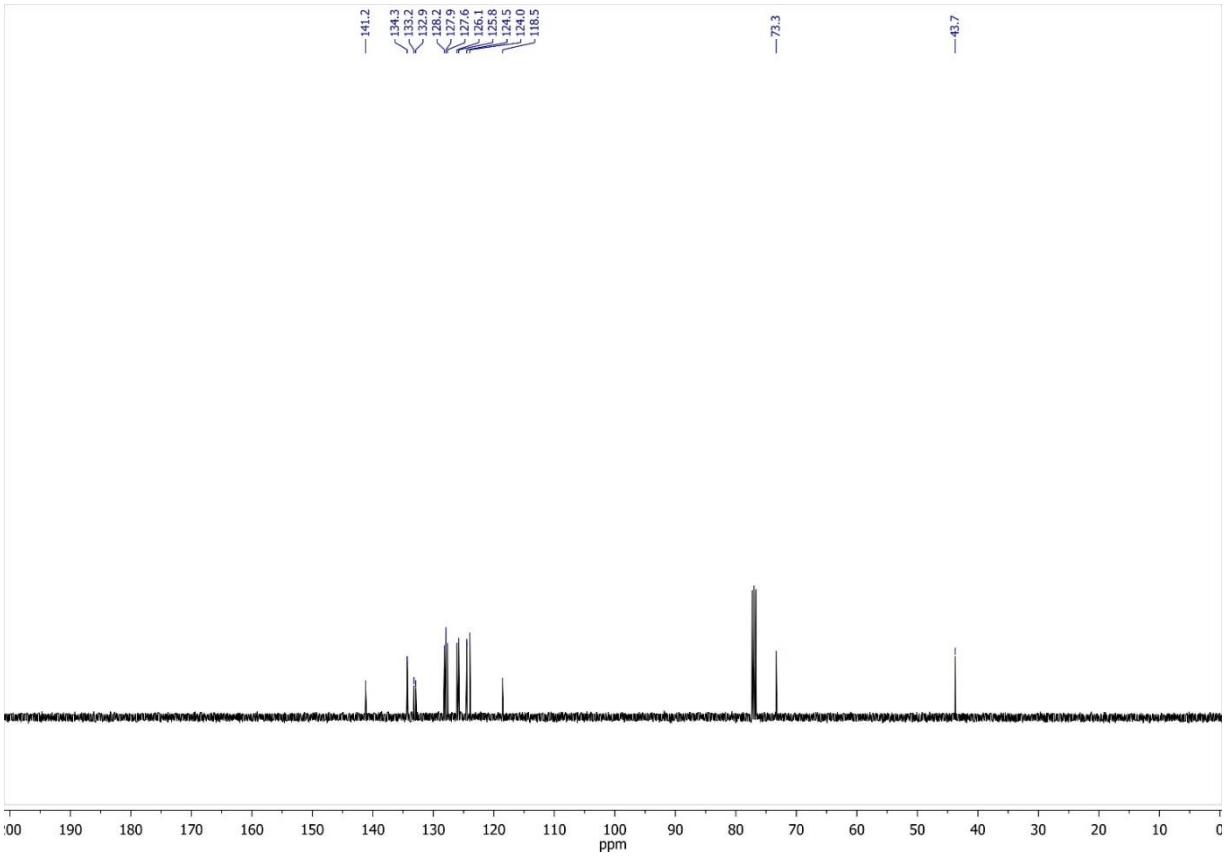
7.45
7.44
7.43
7.42
7.37
7.37
7.36
7.35
7.35
7.34
7.33
5.90
5.89
5.88
5.87
5.86
5.84
5.84
5.83
5.82
5.80
5.23
5.23
5.22
5.22
5.19
5.18
5.18
5.16
5.16
5.16
4.82
4.80
4.80
4.78
2.62
2.61
2.61
2.59
2.58
2.57
2.56
2.54
2.52
2.50
4.07
4.07
1.00
0.95
2.03
1.00
2.14
ppm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134.3
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127.6
126.1
125.8
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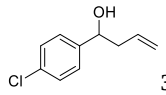
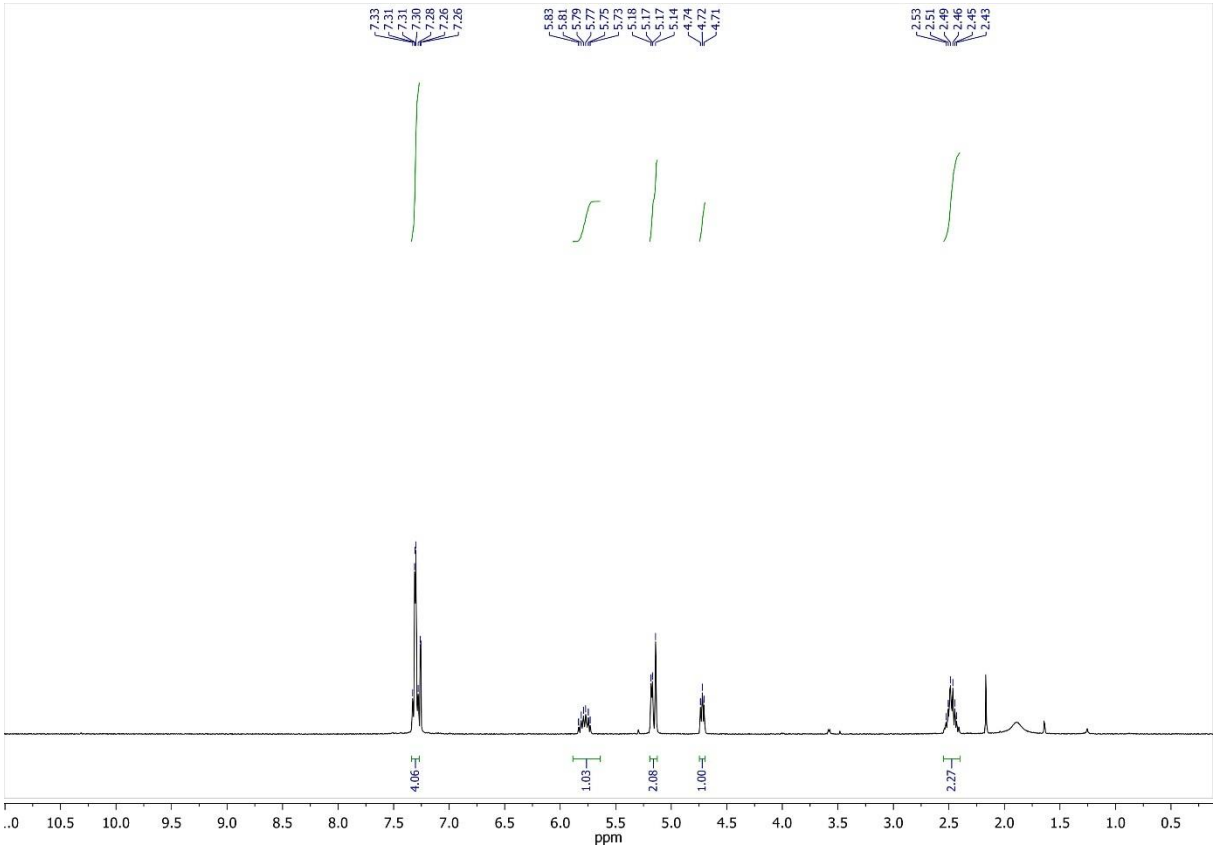
124.0
118.5
73.3
43.7
ppm


OH
Cl

3f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7.26
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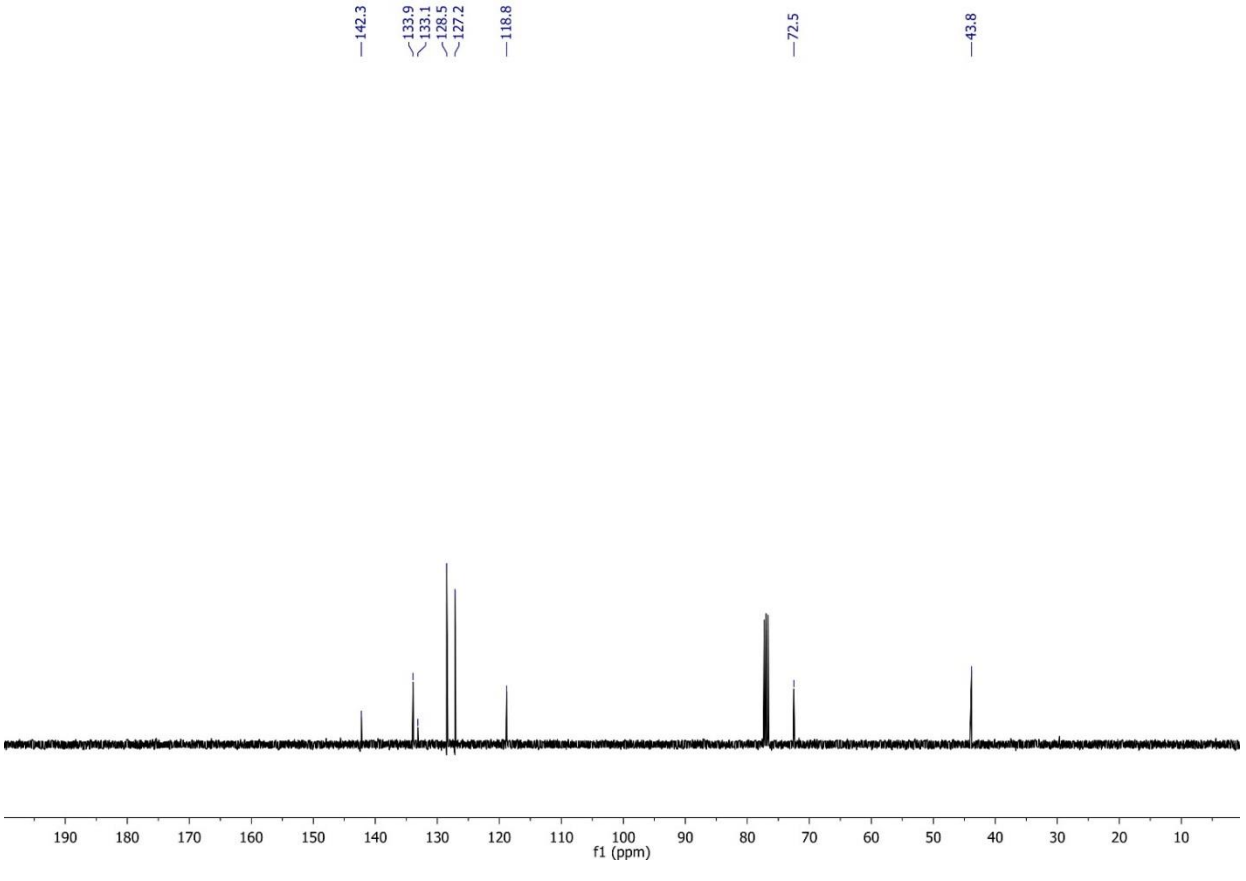
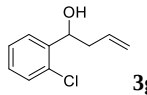
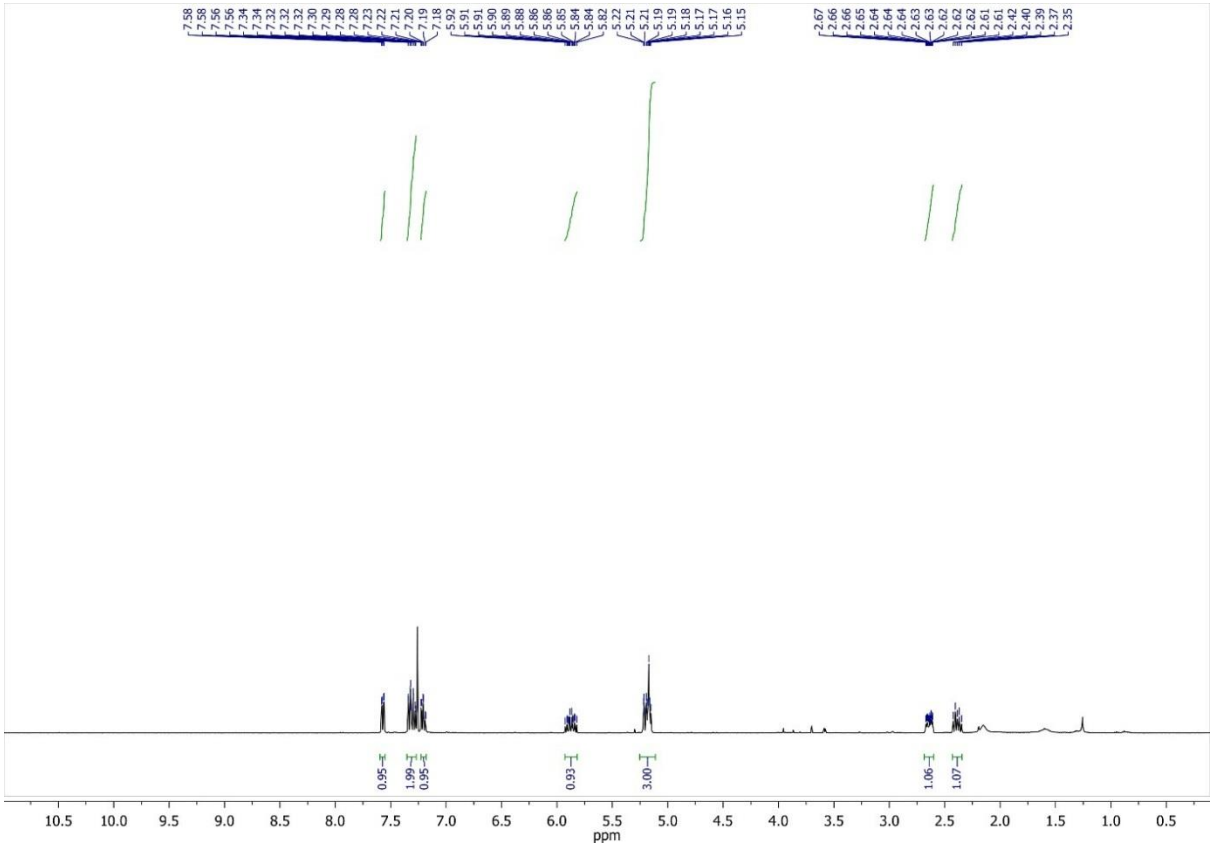
5.81
5.79
5.77
5.75
5.73
5.18
5.17
5.17
5.14
4.74
4.72
4.71
2.53
2.51
2.49
2.46
2.45
2.43
4.06
1.03
2.08
1.00
2.27
ppm


142.3
133.9
133.1
128.5
127.2
118.8
72.5
43.8
f1 (ppm)


OH
Cl

3g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7.56
7.56
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7.34
7.32
7.32
7.30
7.29
7.28
7.28
7.23
7.22
7.21
7.20
7.19
7.18
5.92
5.91
5.91
5.90
5.89
5.88
5.86
5.86
5.85
5.84
5.84
5.82
5.22
5.21
5.21
5.19
5.19
5.18
5.17
5.17
5.16
5.15
2.67
2.66
2.66
2.65
2.64
2.64
2.64
2.63
2.63
2.62
2.62
2.62
2.61
2.61
2.42
2.40
2.39
2.37
2.35
0.95
1.99
0.95
0.93
3.00
1.06
1.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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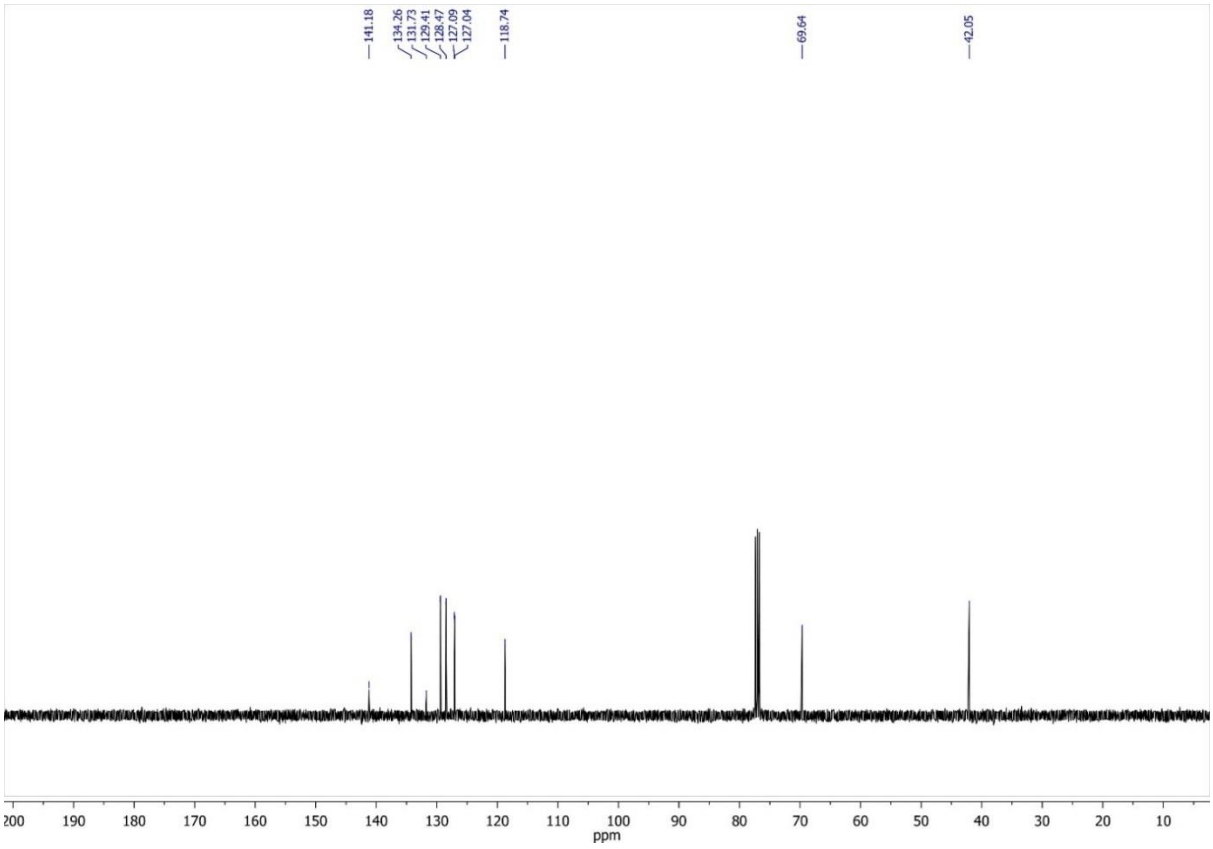
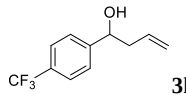
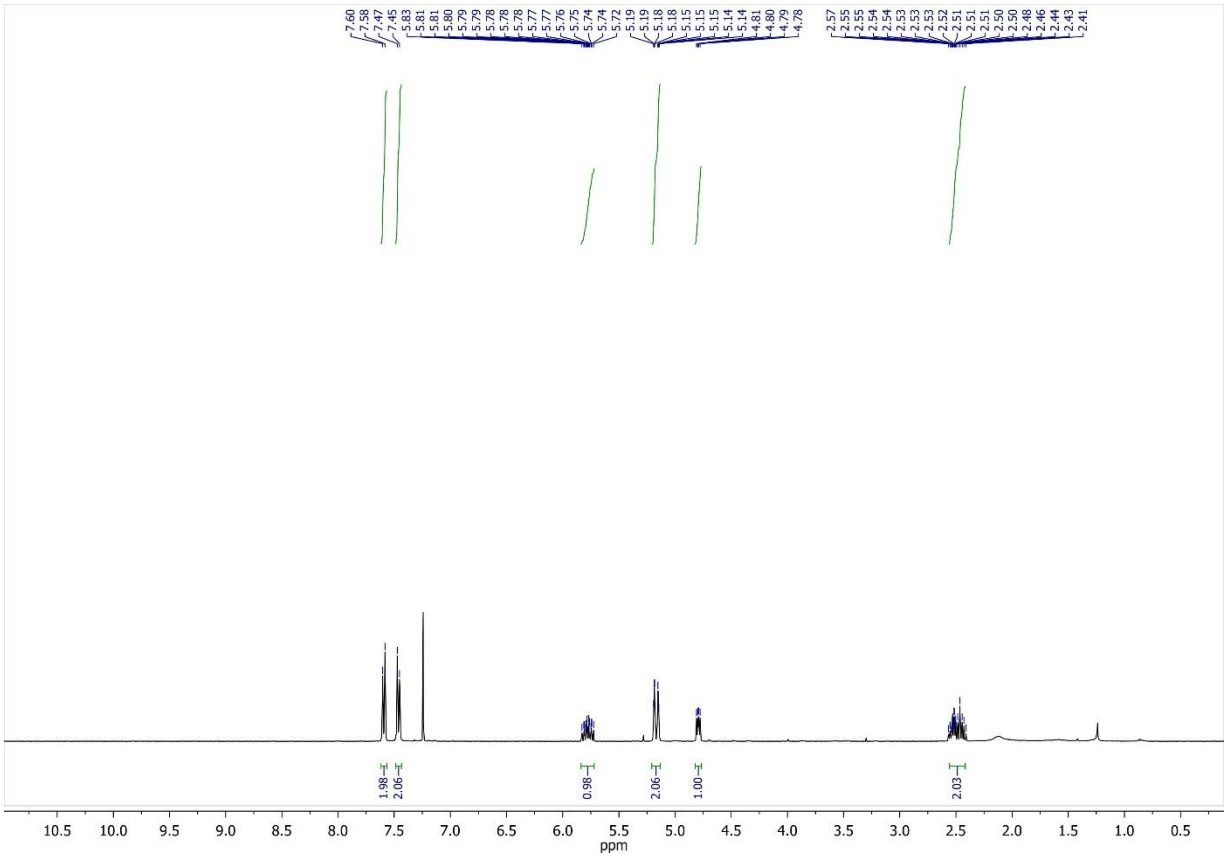
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


141.18
134.26
131.73
129.41
128.47
127.09
127.04
118.74
69.64
42.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OH
CF3

3h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5.81
5.80
5.79
5.79
5.78
5.78
5.78
5.77
5.77
5.76
5.75
5.74
5.74
5.72
5.19
5.19
5.18
5.18
5.15
5.15
5.15
5.14
5.14
4.81
4.80
4.79
4.78
2.57
2.55
2.55
2.54
2.54
2.53
2.53
2.53
2.52
2.51
2.51
2.51
2.50
2.50
2.48
2.46
2.44
2.43
2.41
1.98
2.06
0.98
2.06
1.00
2.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
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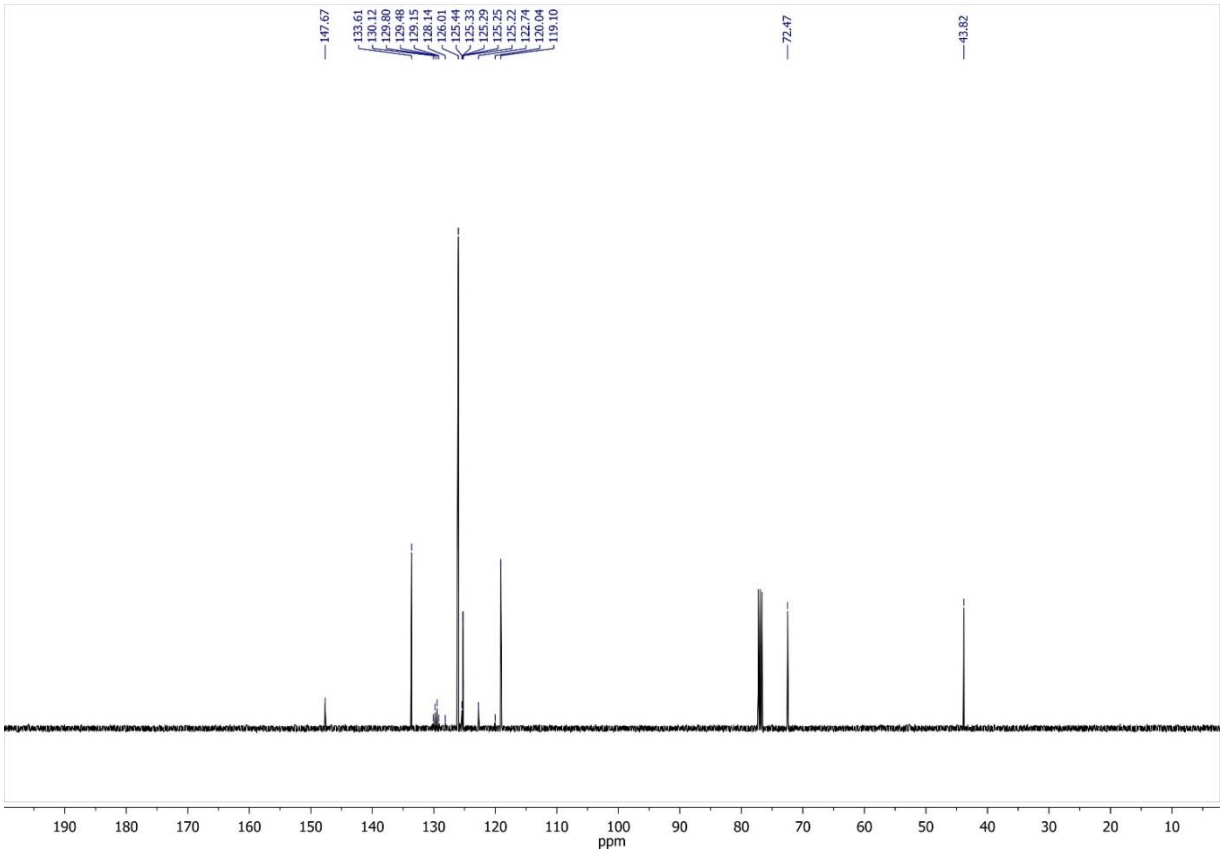
2.0
1.5
1.0
0.5
ppm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129.48
129.15
128.14
126.01
125.44
125.33
125.29
125.25
125.22
122.74
120.04
119.10
72.47
43.82
190
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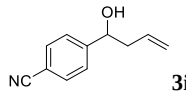
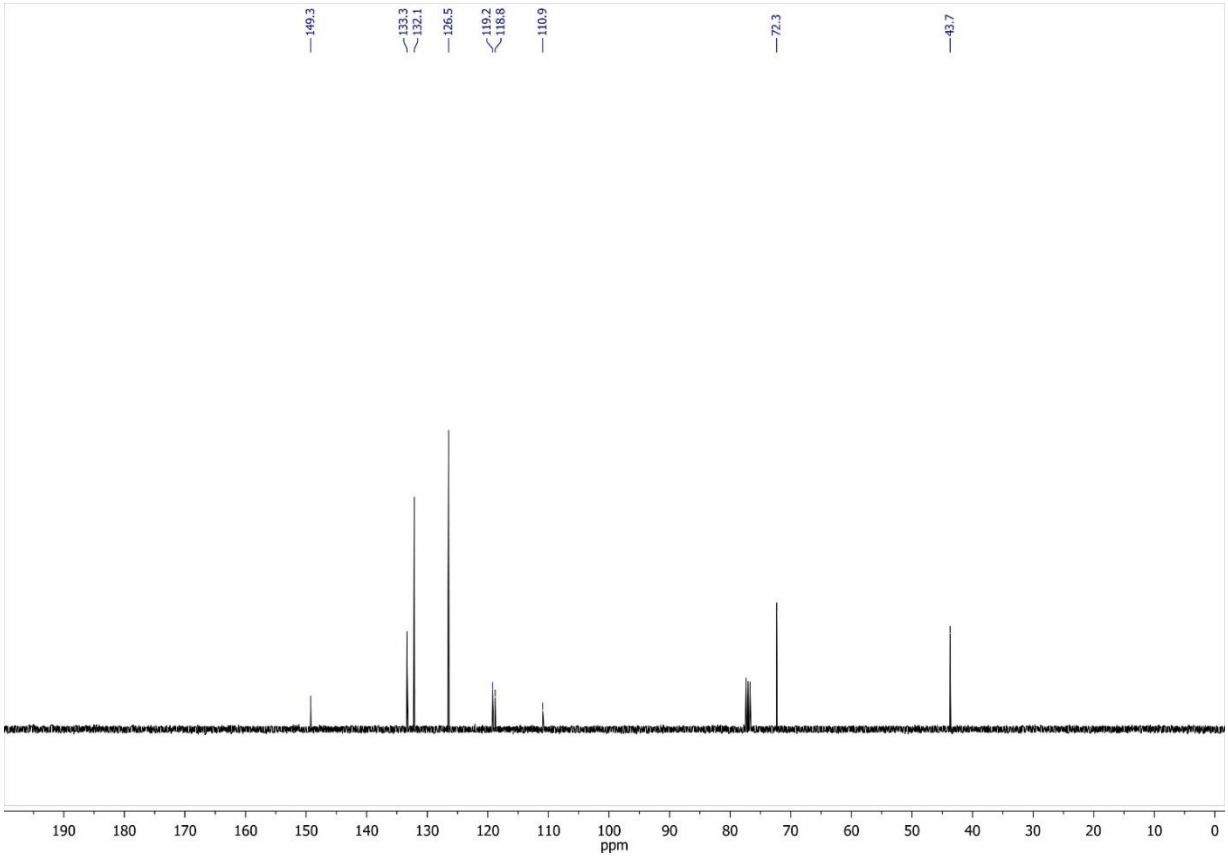
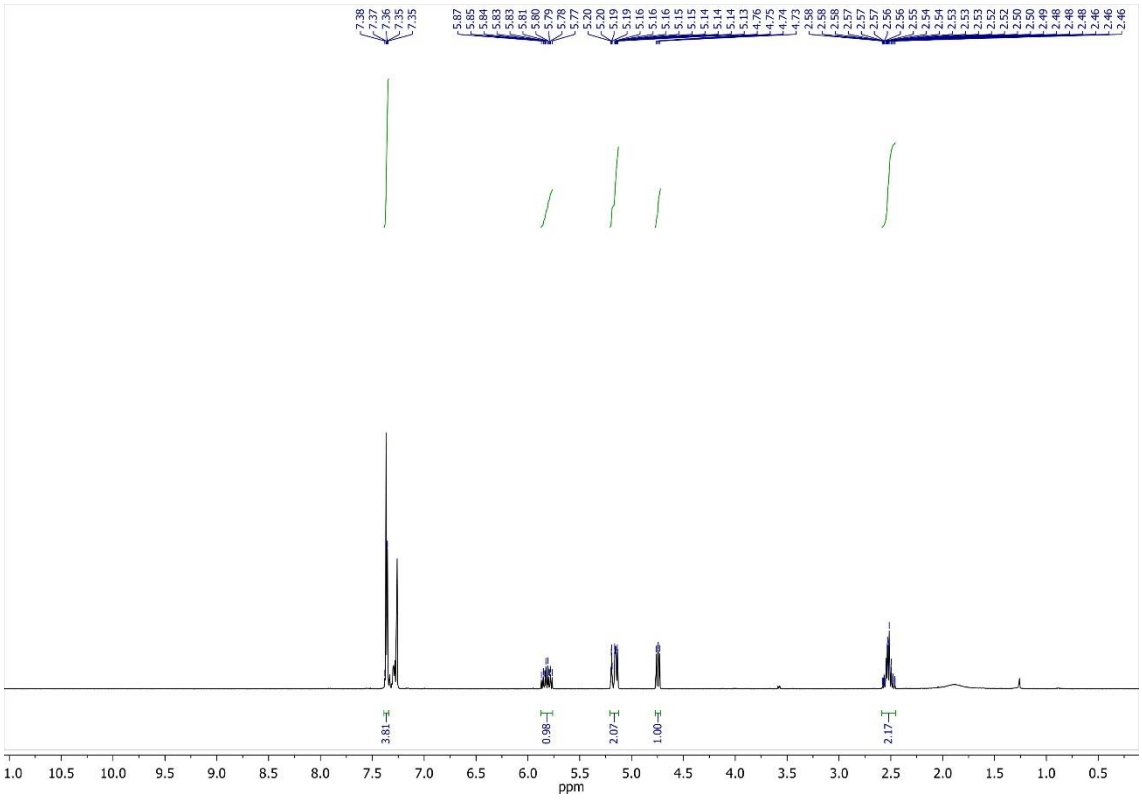
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OH
NC

3i


149.3
133.3
132.1
126.5
119.2
118.8
110.9
72.3
43.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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5.83
5.81
5.80
5.79
5.78
5.77
5.20
5.20
5.19
5.19
5.16
5.16
5.16
5.15
5.15
5.14
5.14
5.14
5.13
4.76
4.75
4.74
4.73
2.58
2.58
2.58
2.57
2.57
2.57
2.56
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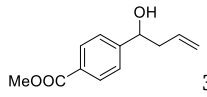
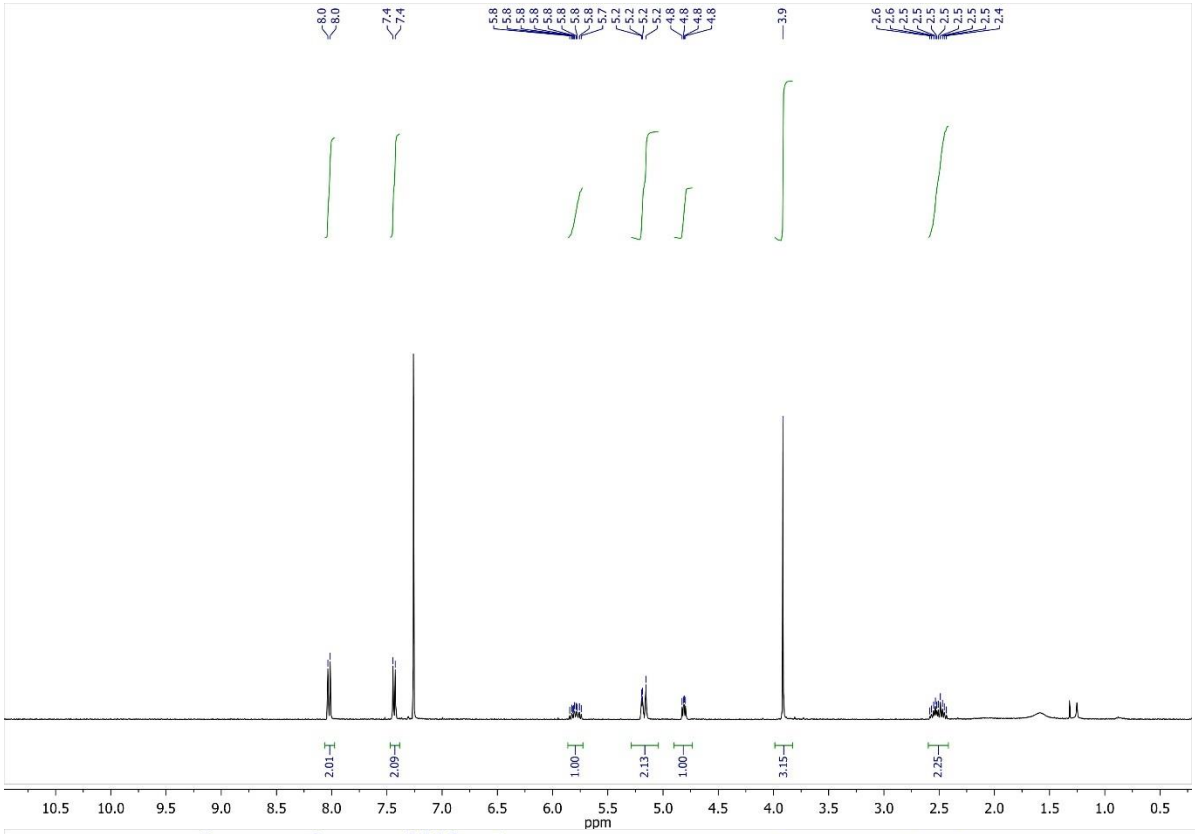
2.53
2.52
2.52
2.50
2.50
2.49
2.48
2.48
2.46
2.46
2.46
3.81
0.98
2.07
1.00
2.17
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


OH
MeOOC

3j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8.0
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5.8
5.8
5.8
5.8
5.8
5.8
5.8
5.8
5.7
5.2
5.2
5.2
5.2
4.8
4.8
4.8
4.8
3.9
2.6
2.6
2.5
2.5
2.5
2.5
2.5
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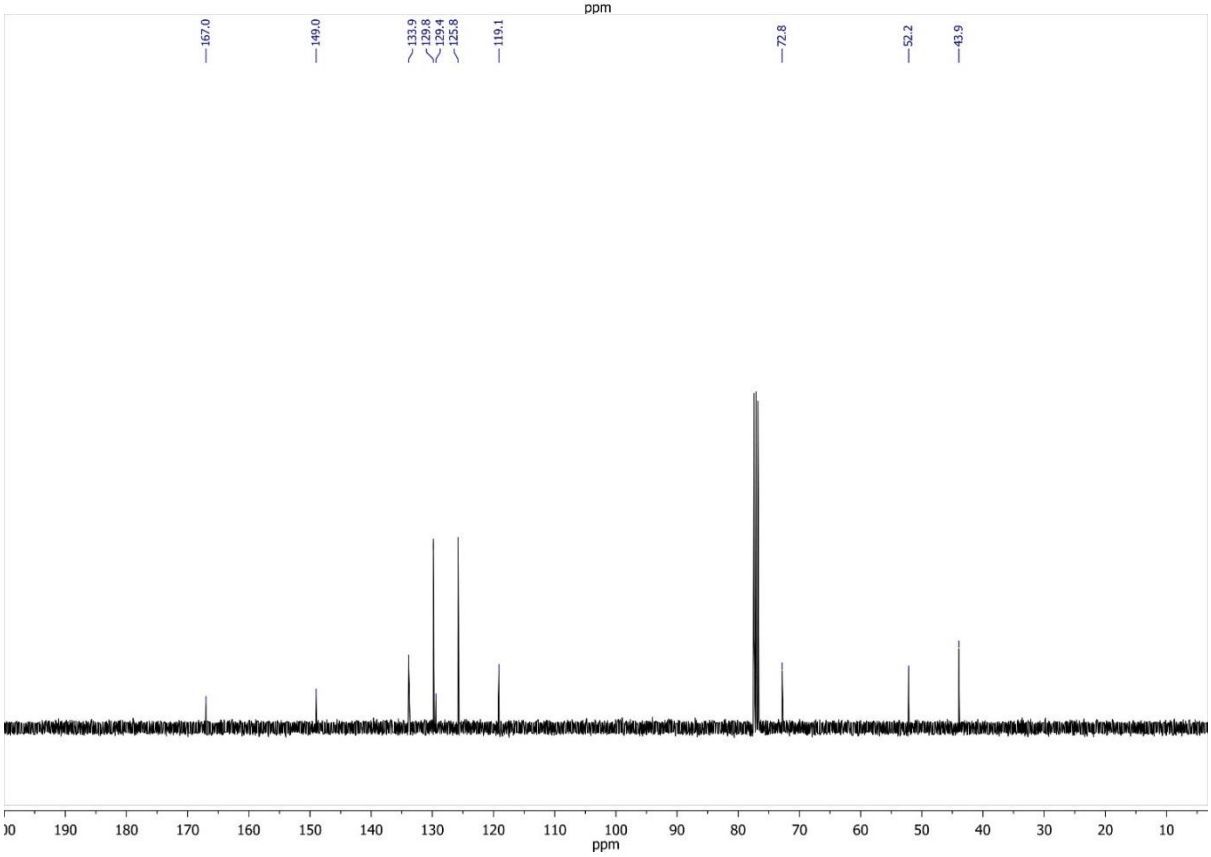
2.5
2.4
2.01
2.09
1.00
2.13
1.00
3.15
2.25
ppm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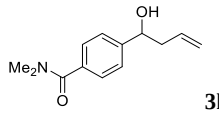
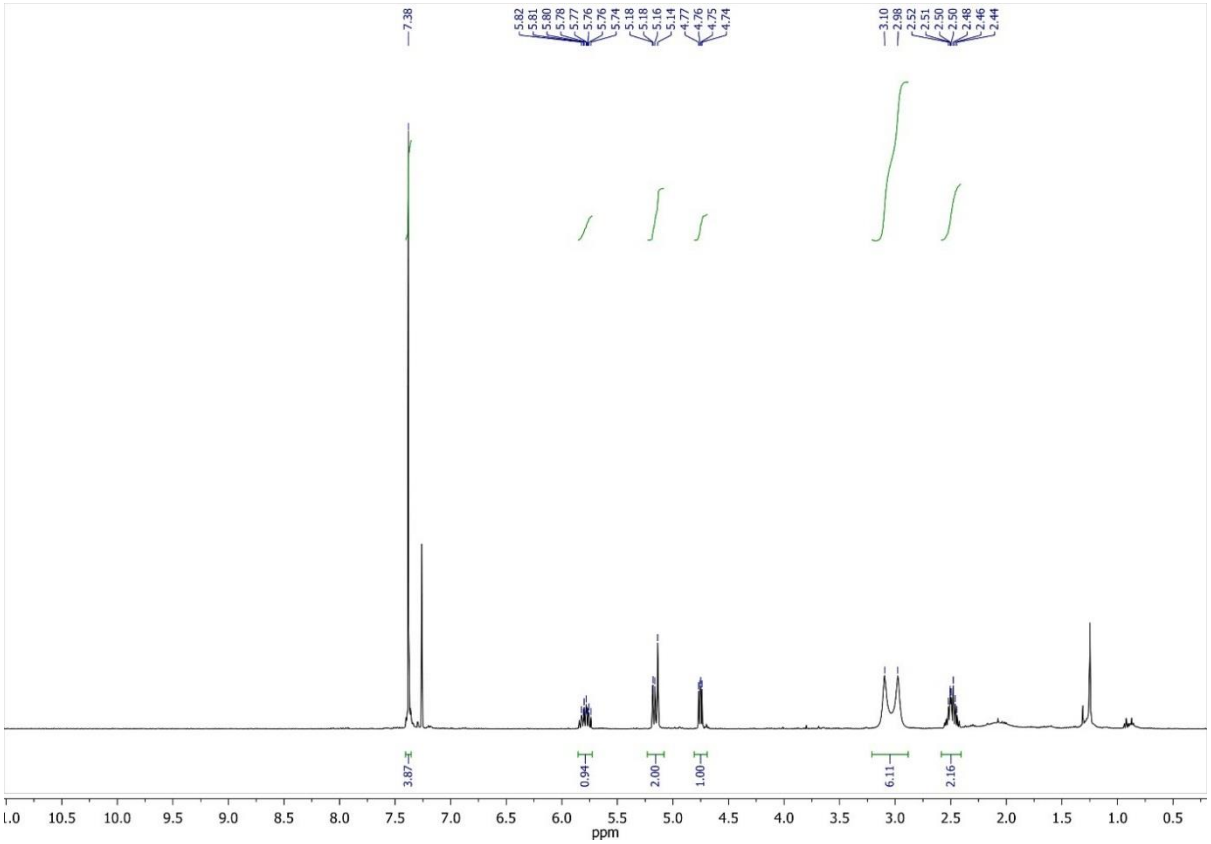
129.4
125.8
119.1
72.8
52.2
43.9
ppm


OH
Me2N
O

3k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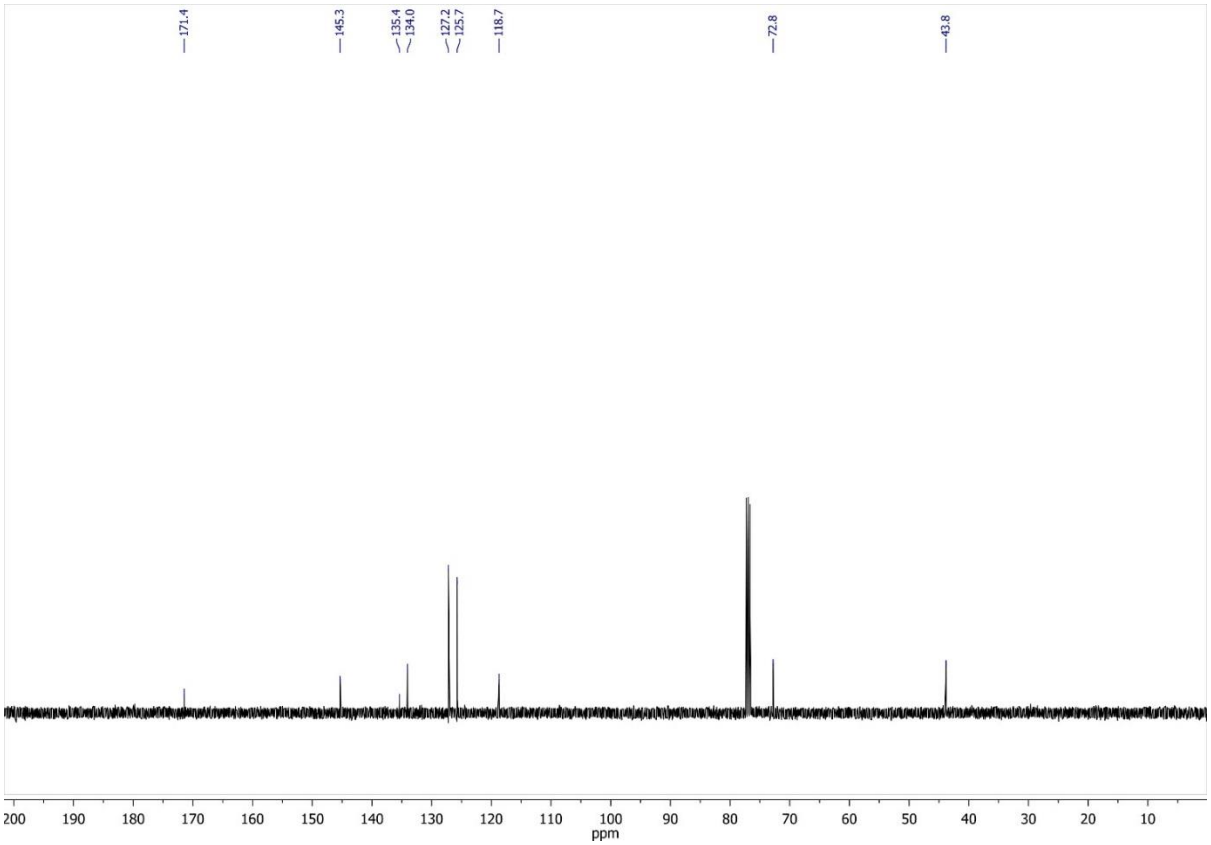
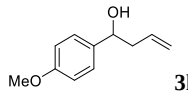
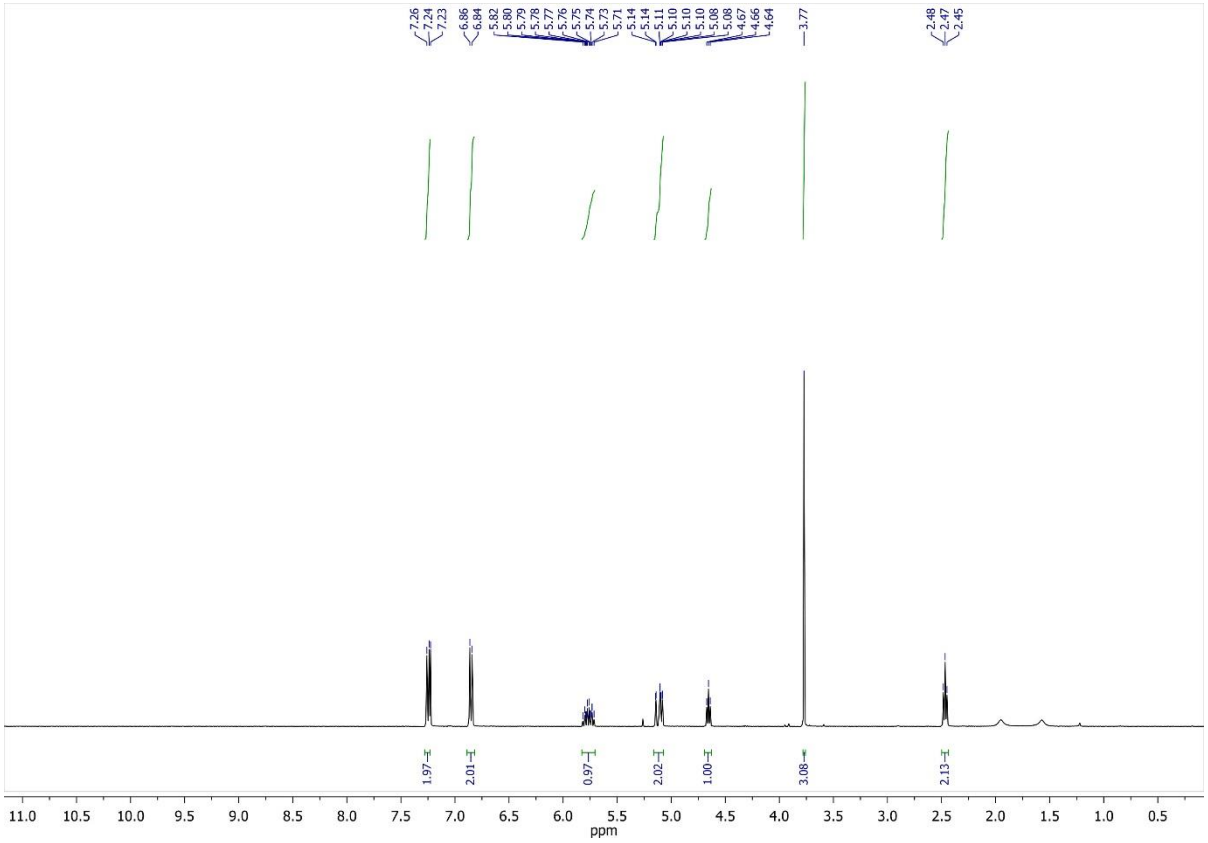
5.81
5.80
5.78
5.77
5.76
5.76
5.74
5.18
5.16
5.14
4.77
4.76
4.75
4.74
3.10
2.98
2.52
2.51
2.50
2.50
2.48
2.46
2.44
3.87
0.94
2.00
1.00
6.11
2.16
ppm


171.4
145.3
135.4
134.0
127.2
125.7
118.7
72.8
43.8
ppm


OH
MeO

3l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7.24
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6.84
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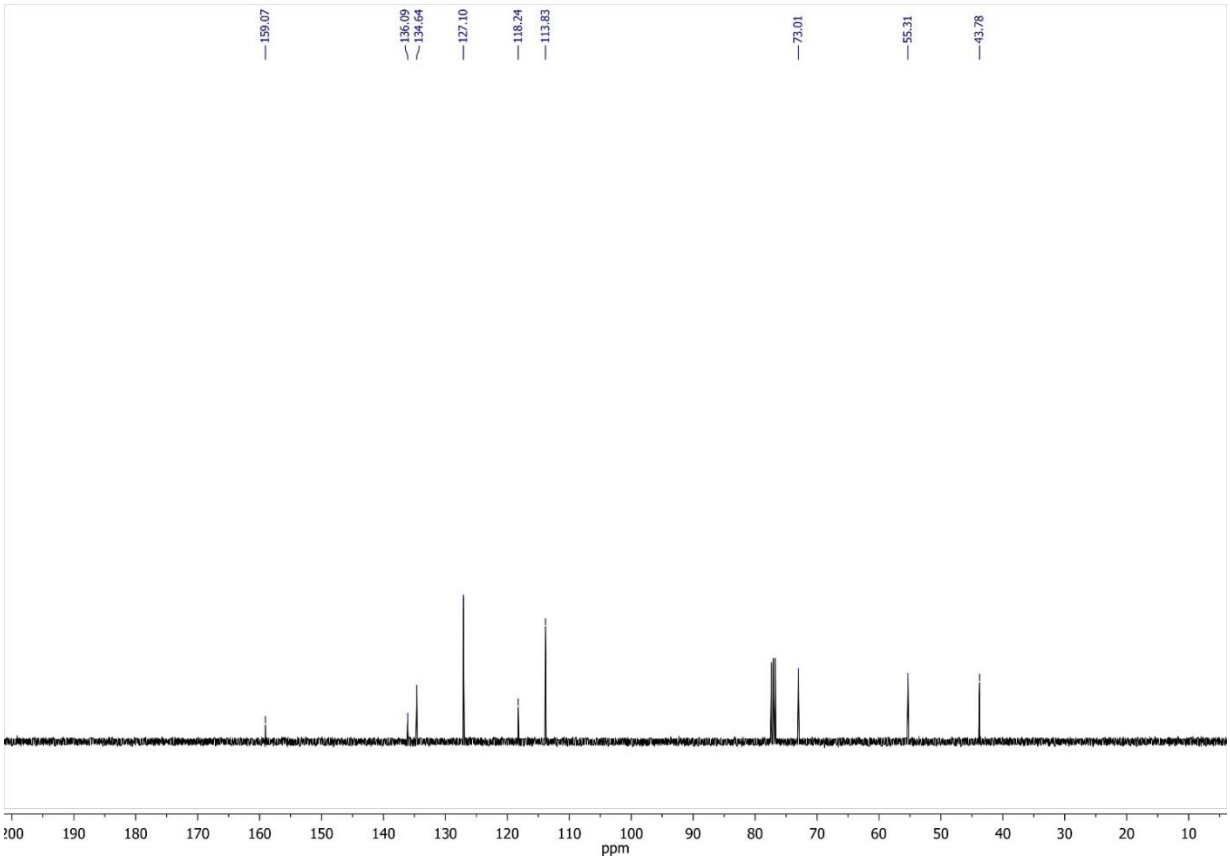
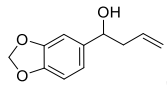
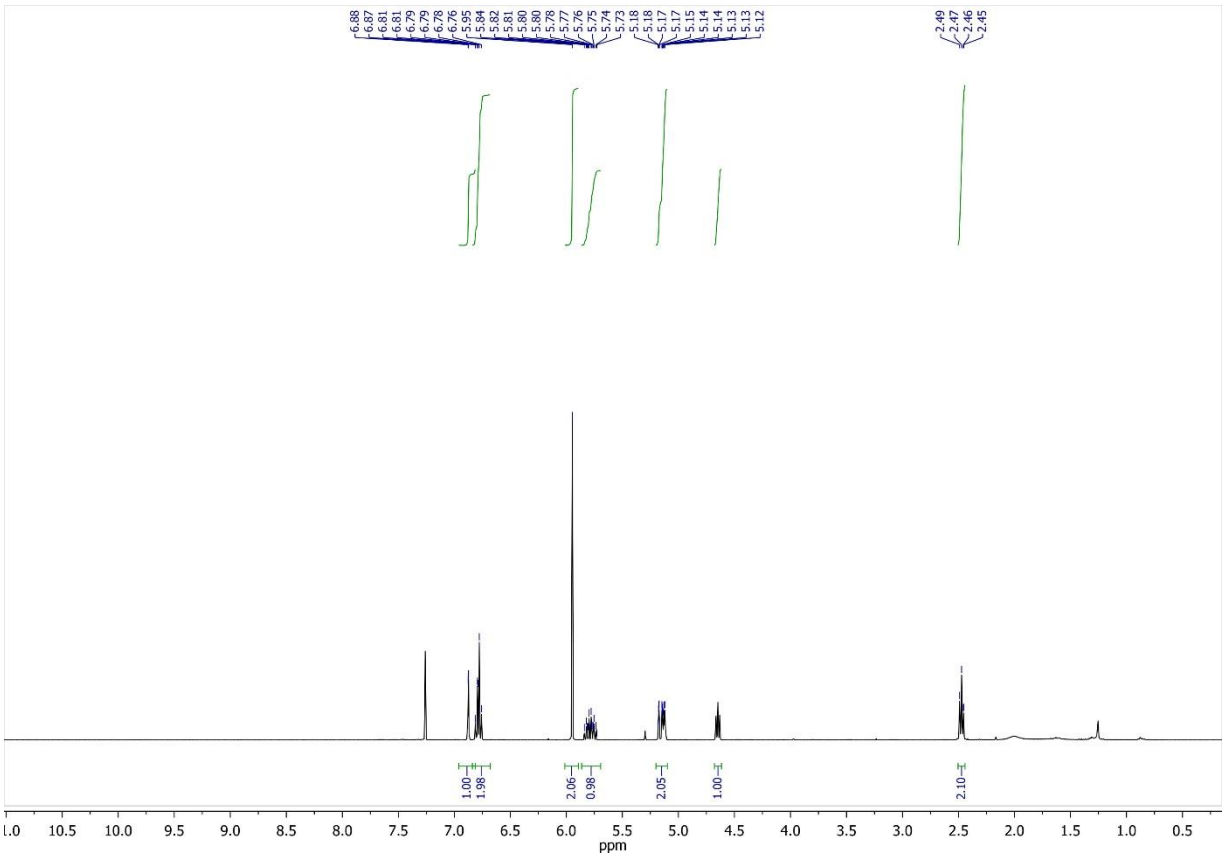
5.80
5.79
5.78
5.77
5.76
5.75
5.74
5.73
5.71
5.14
5.14
5.11
5.10
5.10
5.10
5.08
5.08
4.67
4.66
4.64
3.77
2.48
2.47
2.45
1.97
2.01
0.97
2.02
1.00
3.08
2.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


159.07
136.09
134.64
127.10
118.24
113.83
73.01
55.31
43.78
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm



3m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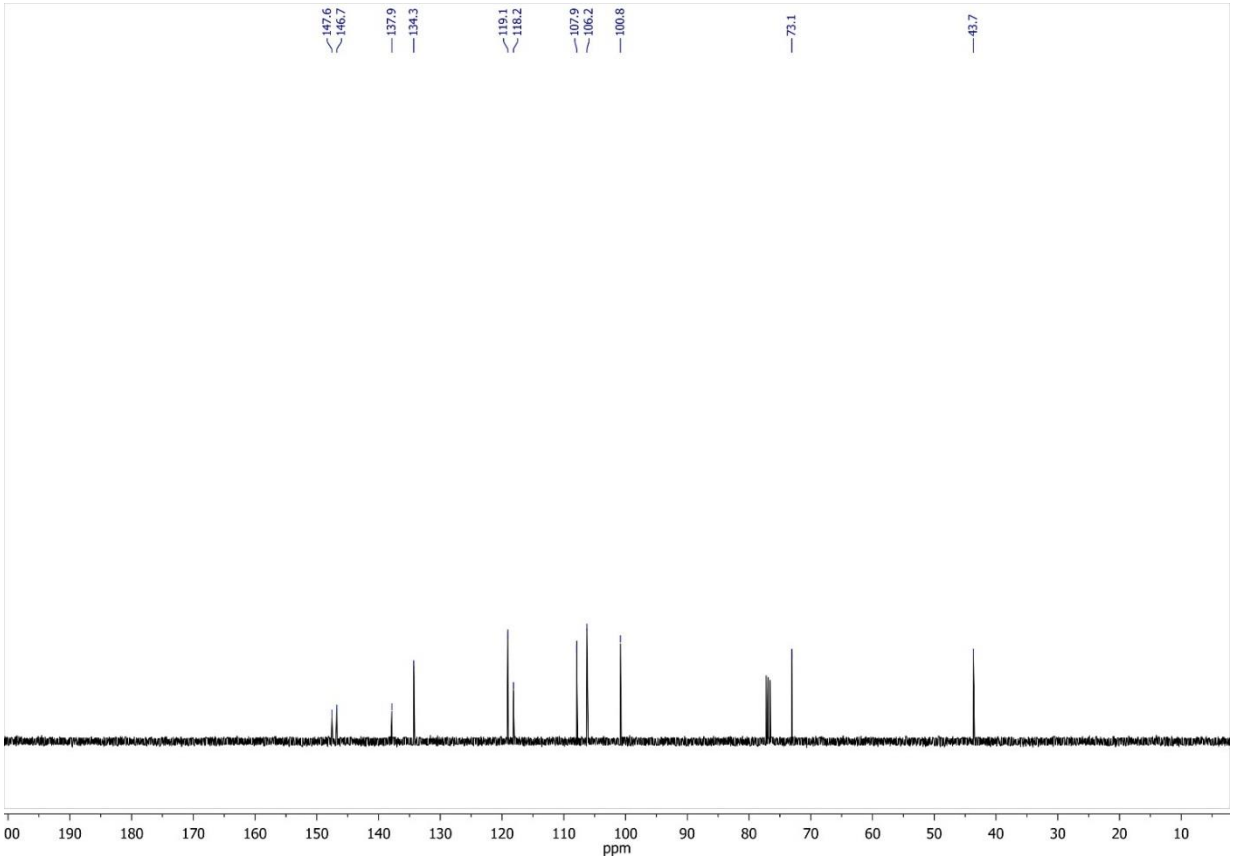
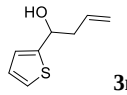
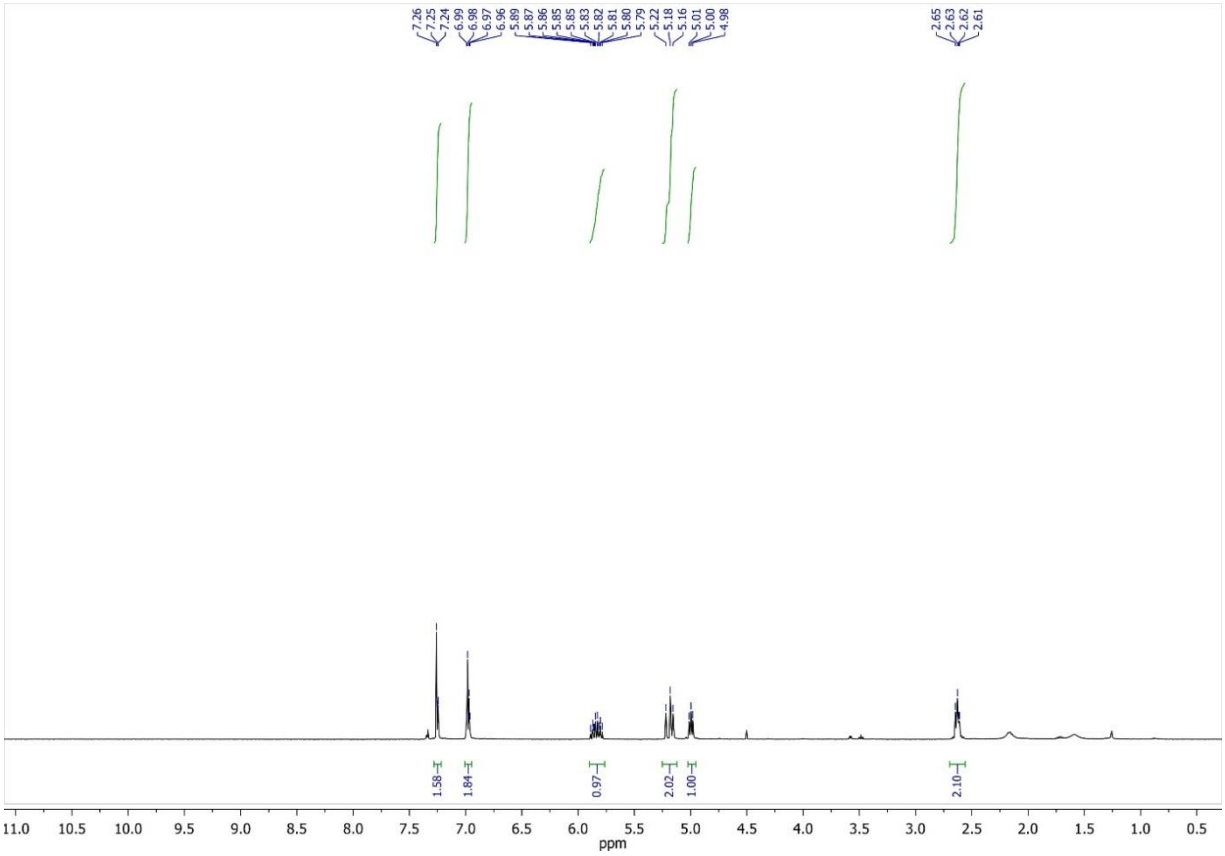
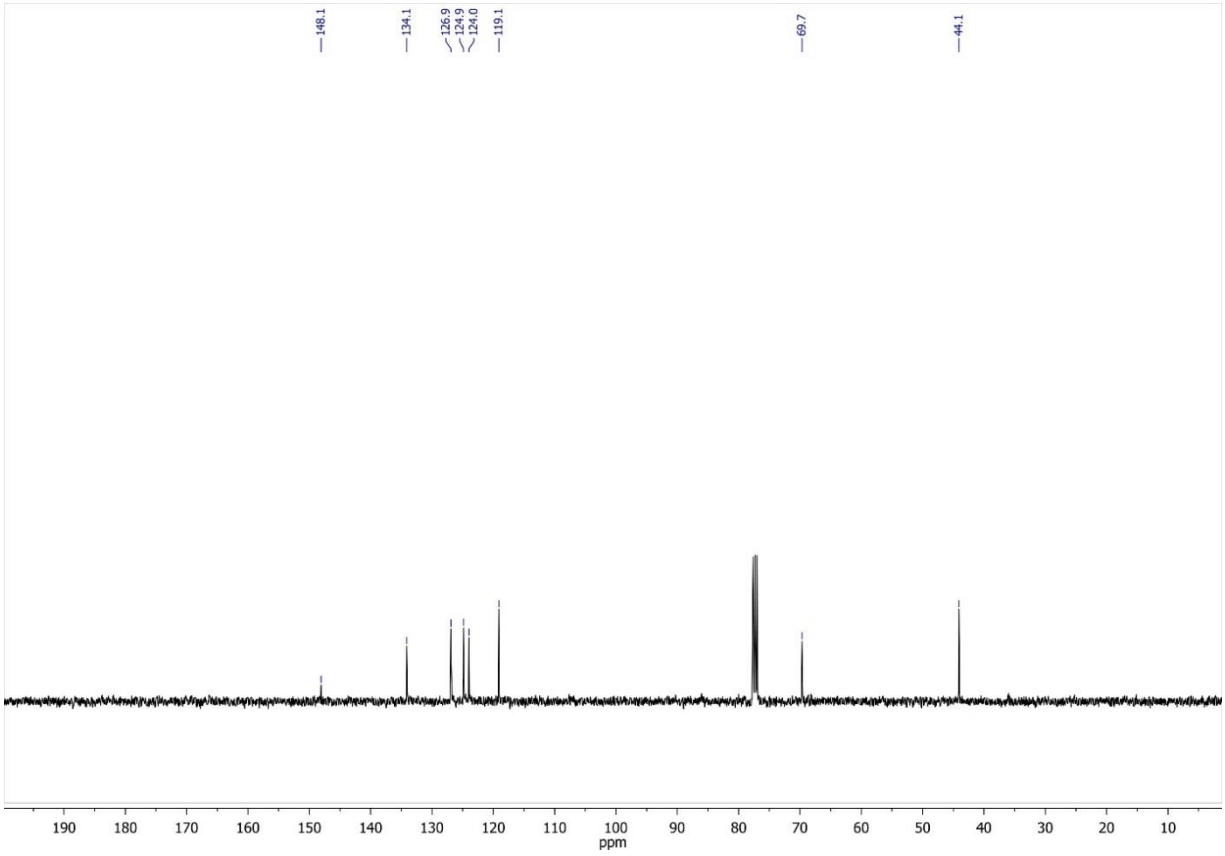
6.81
6.79
6.79
6.78
6.76
5.95
5.84
5.82
5.81
5.80
5.80
5.78
5.77
5.76
5.75
5.74
5.73
5.18
5.18
5.17
5.17
5.15
5.14
5.14
5.13
5.13
5.12
2.49
2.47
2.46
2.45
1.00
1.98
2.06
0.98
2.05
1.00
2.10
ppm

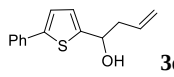

147.6
146.7
137.9
134.3
119.1
118.2
107.9
106.2
100.8
73.1
43.7
ppm


HO
S

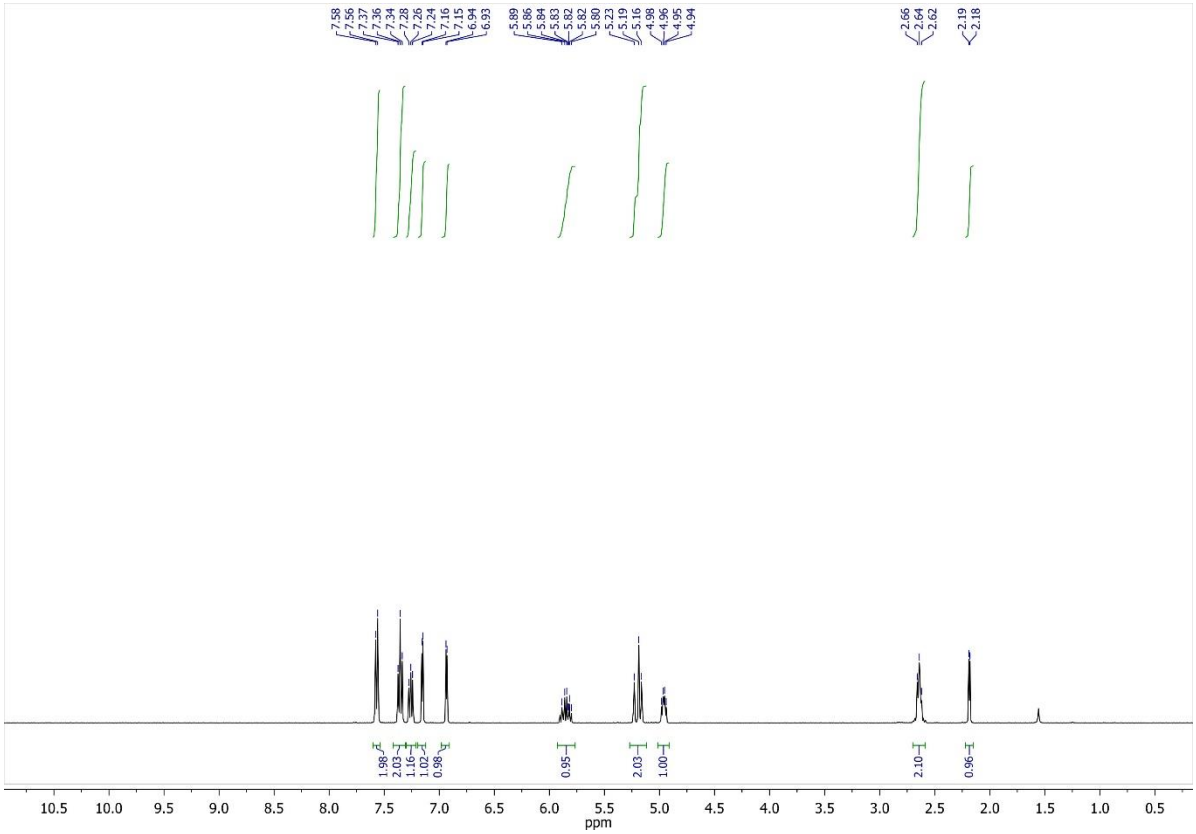
3n


7.26
7.25
7.24
6.99
6.98
6.97
6.96
5.89
5.87
5.86
5.85
5.85
5.83
5.82
5.81
5.80
5.79
5.22
5.18
5.16
5.01
5.00
4.98
2.65
2.63
2.62
2.61
1.58
1.84
0.97
2.02
1.00
2.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


148.1
134.1
126.9
124.9
124.0
119.1
69.7
44.1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


Ph
S
OH

3o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7.56
7.37
7.36
7.34
7.28
7.26
7.24
7.16
7.15
6.94
6.93
5.89
5.86
5.84
5.83
5.82
5.82
5.80
5.23
5.19
5.16
4.98
4.96
4.95
4.94
2.66
2.64
2.62
2.19
2.18
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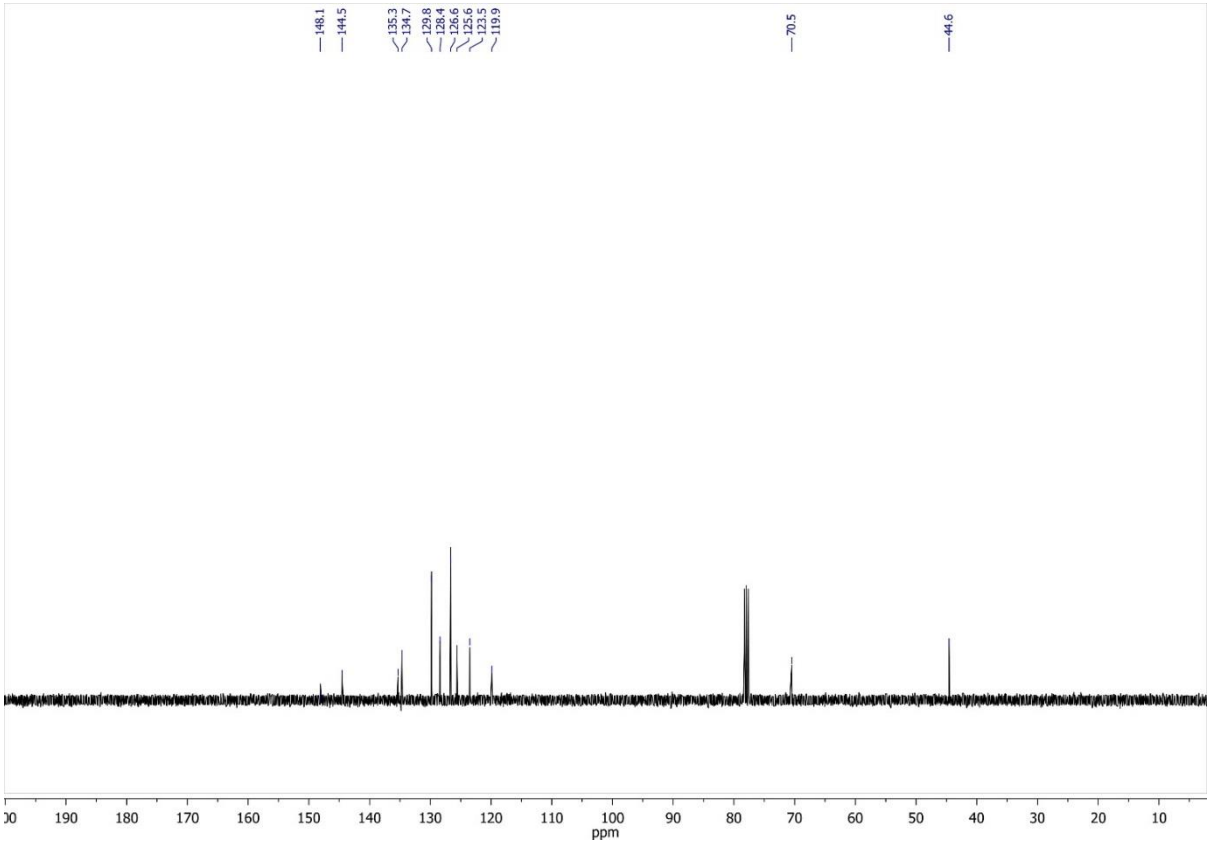
2.03
1.16
1.02
0.98
0.95
2.03
1.00
2.10
0.96
ppm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144.5
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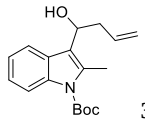
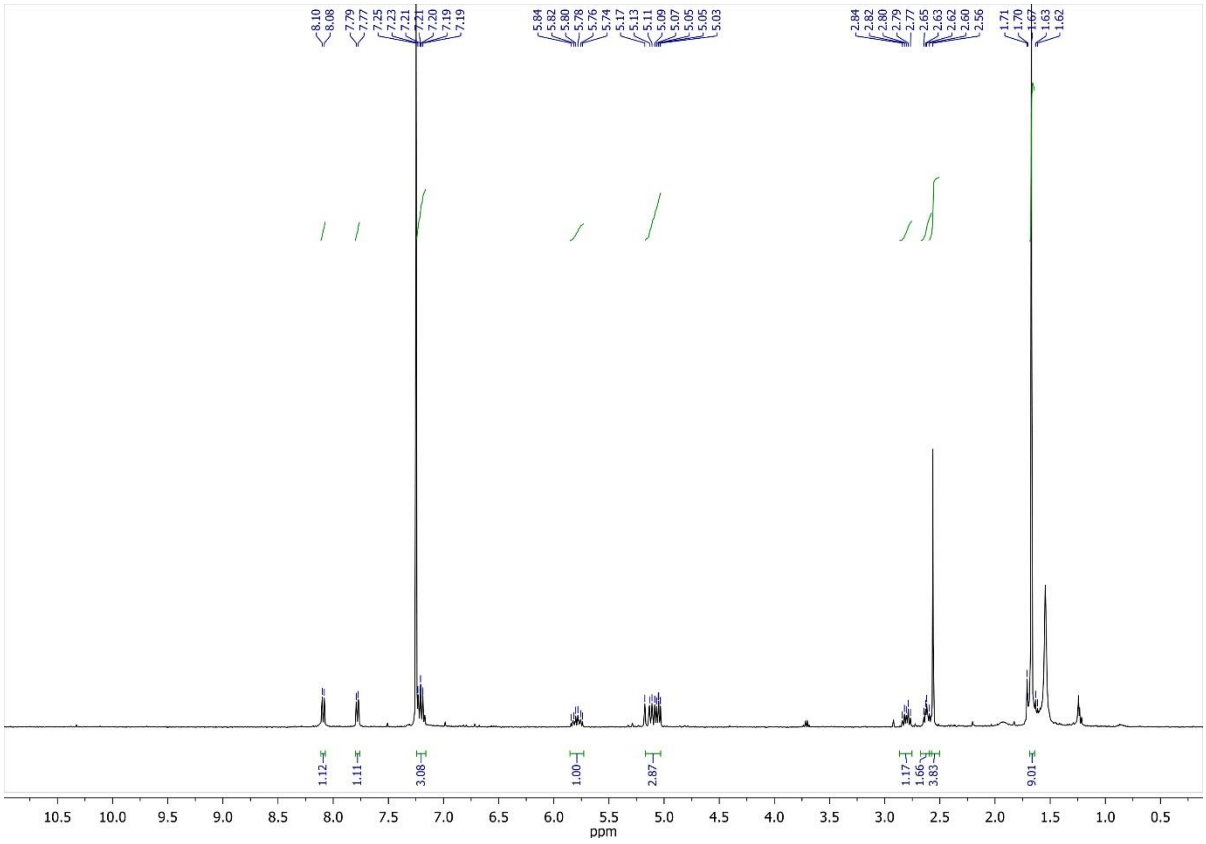
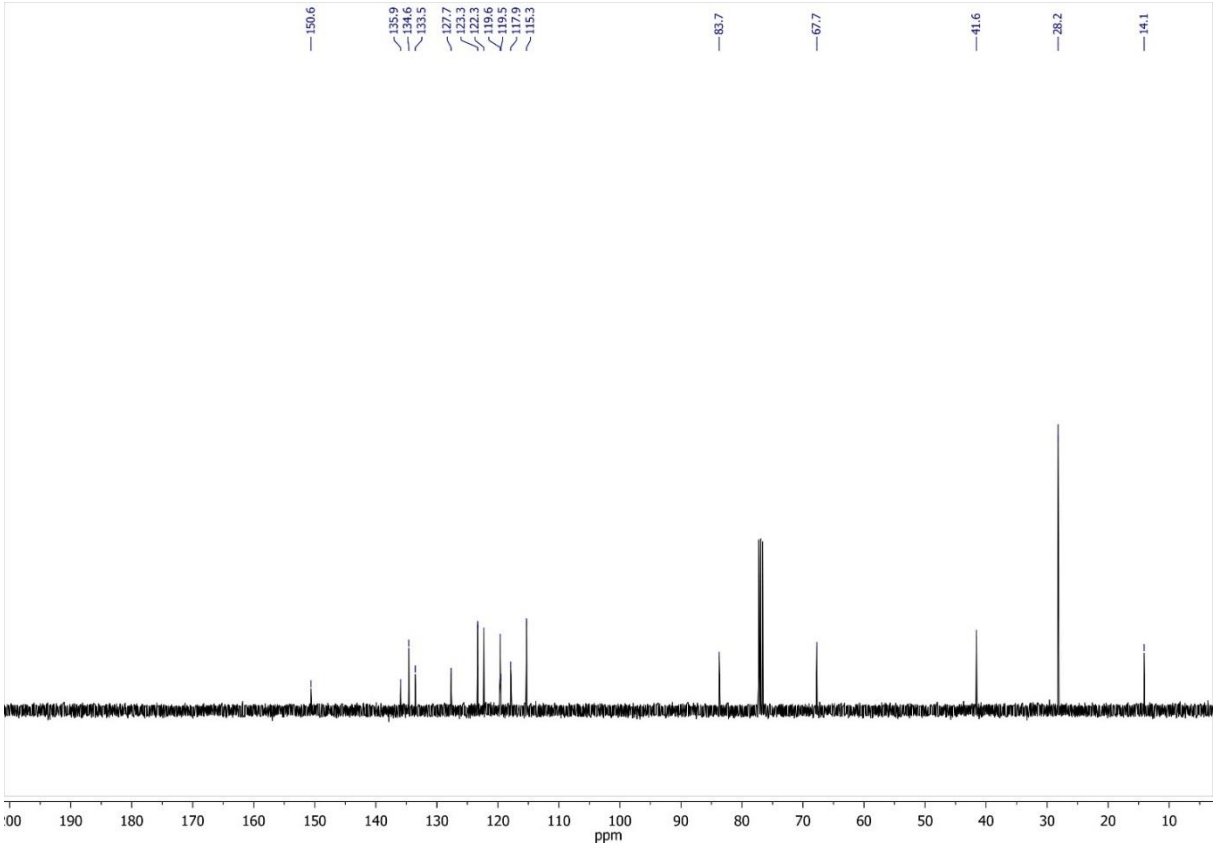
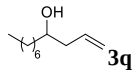
134.7
129.8
128.4
126.6
125.6
123.5
119.9
70.5
44.6
ppm


HO
N
Boc

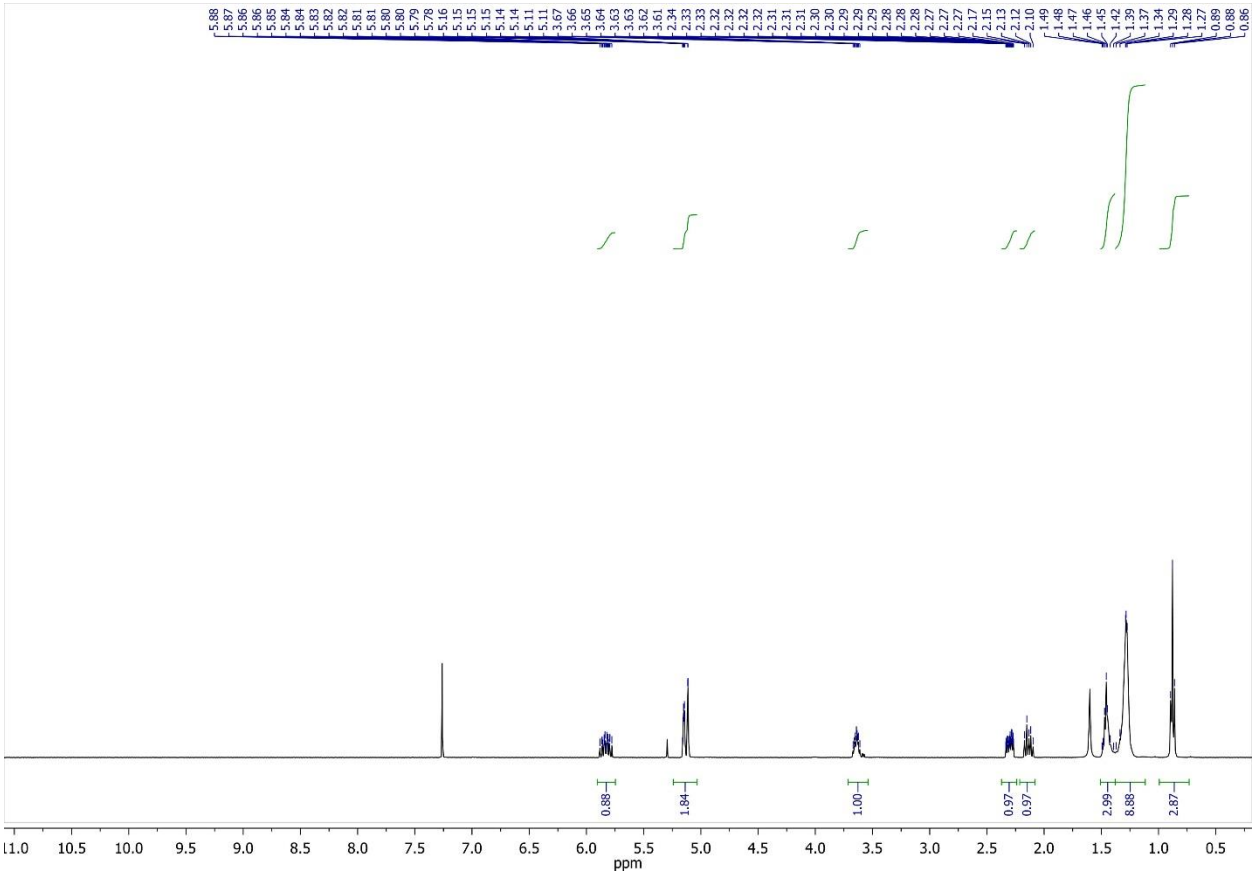
3p

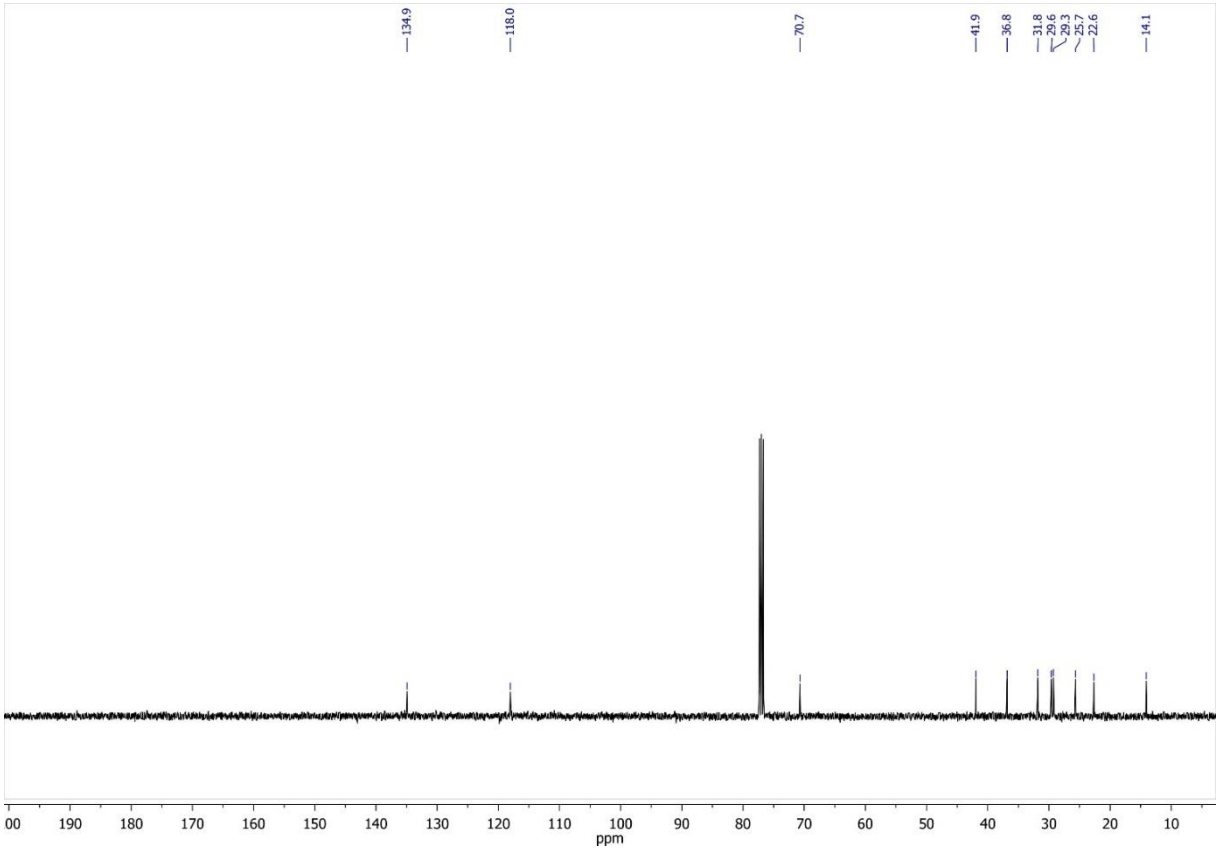

8.10
8.08
7.79
7.77
7.25
7.23
7.21
7.21
7.20
7.19
7.19
5.84
5.82
5.80
5.78
5.76
5.74
5.17
5.13
5.11
5.09
5.07
5.05
5.05
5.03
2.84
2.82
2.80
2.79
2.77
2.65
2.63
2.62
2.60
2.56
1.71
1.70
1.67
1.63
1.62
1.12
1.11
3.08
1.00
2.87
1.17
1.66
3.83
9.01
ppm

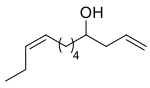

150.6
135.9
134.6
133.5
127.7
123.3
122.3
119.6
119.5
117.9
115.3
83.7
67.7
41.6
28.2
14.1
ppm


OH
6

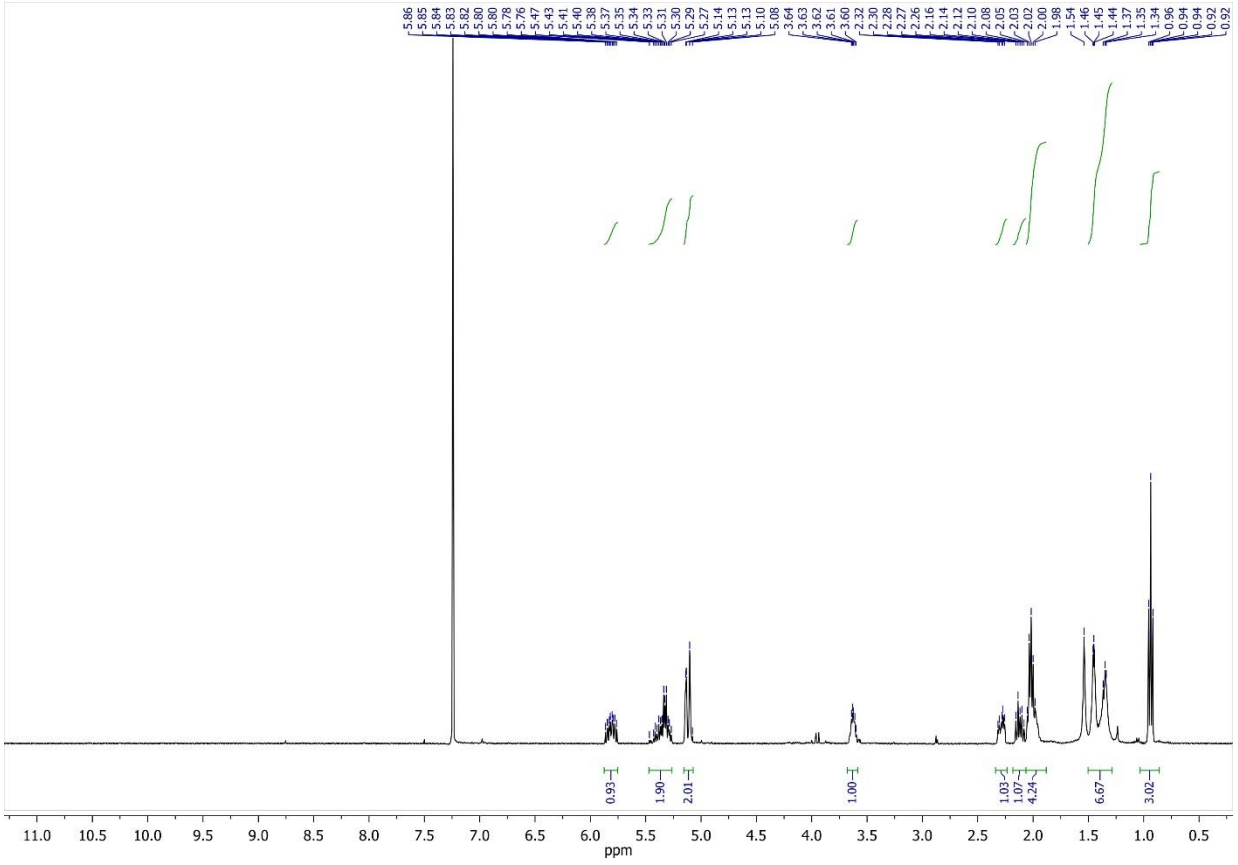
3q

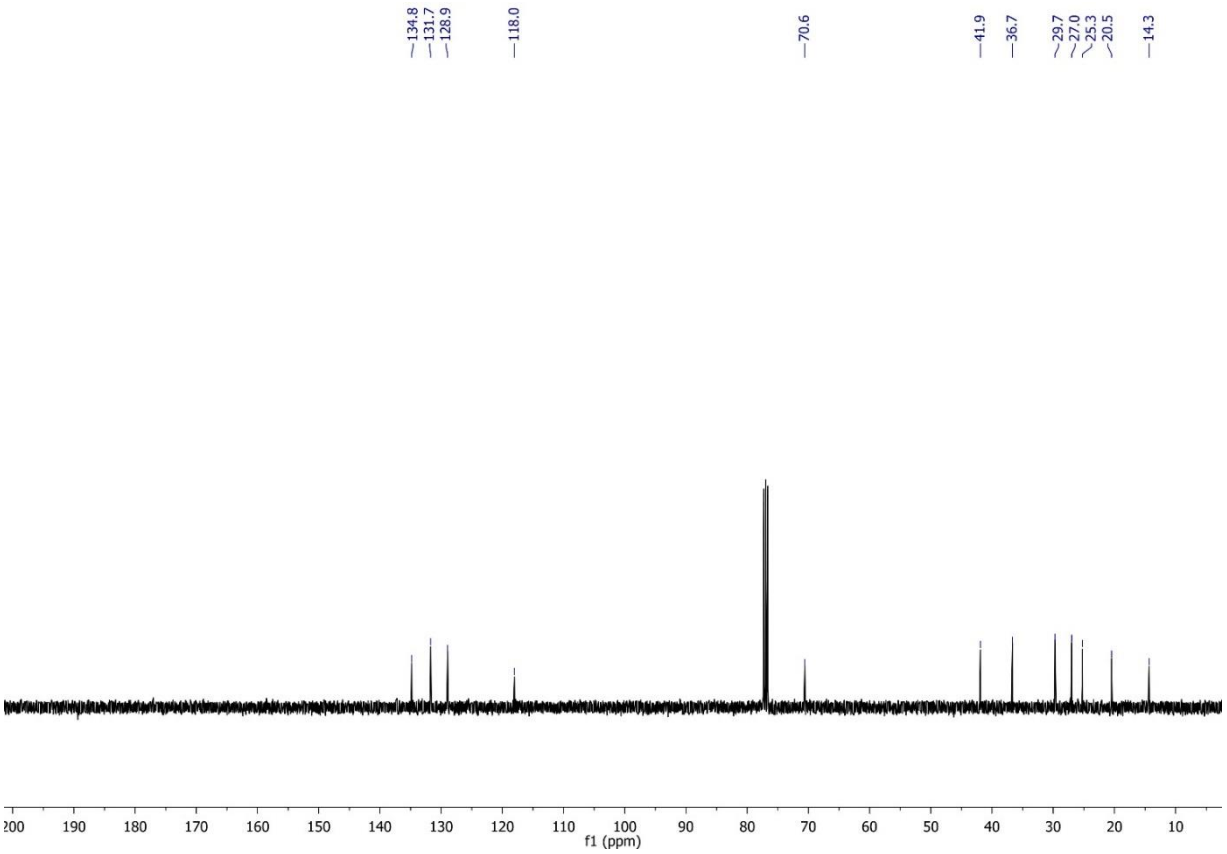

0.88
1.84
1.00
0.97
0.97
2.99
8.88
2.87
ppm

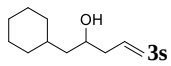

134.9
118.0
70.7
41.9
36.8
31.8
29.6
29.3
25.7
22.6
14.1
ppm


OH
4

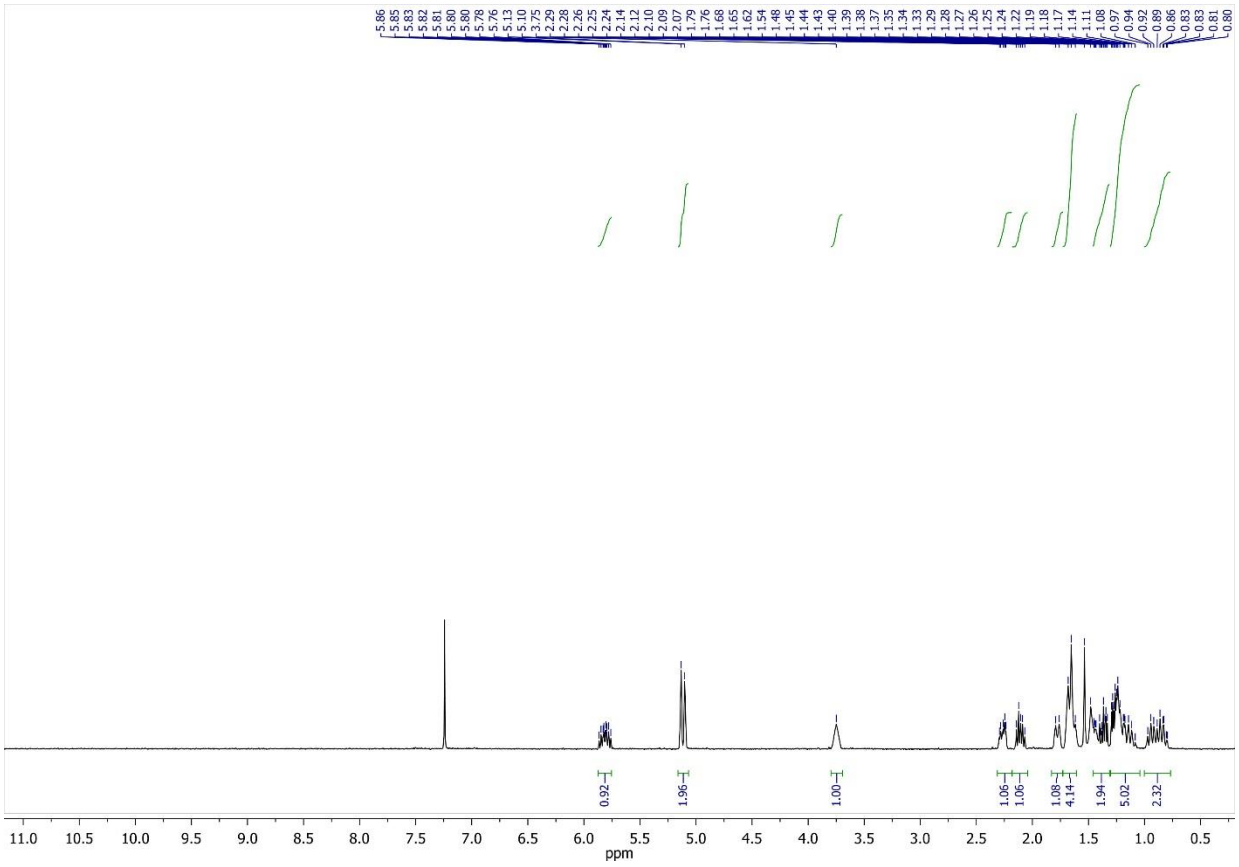
3r

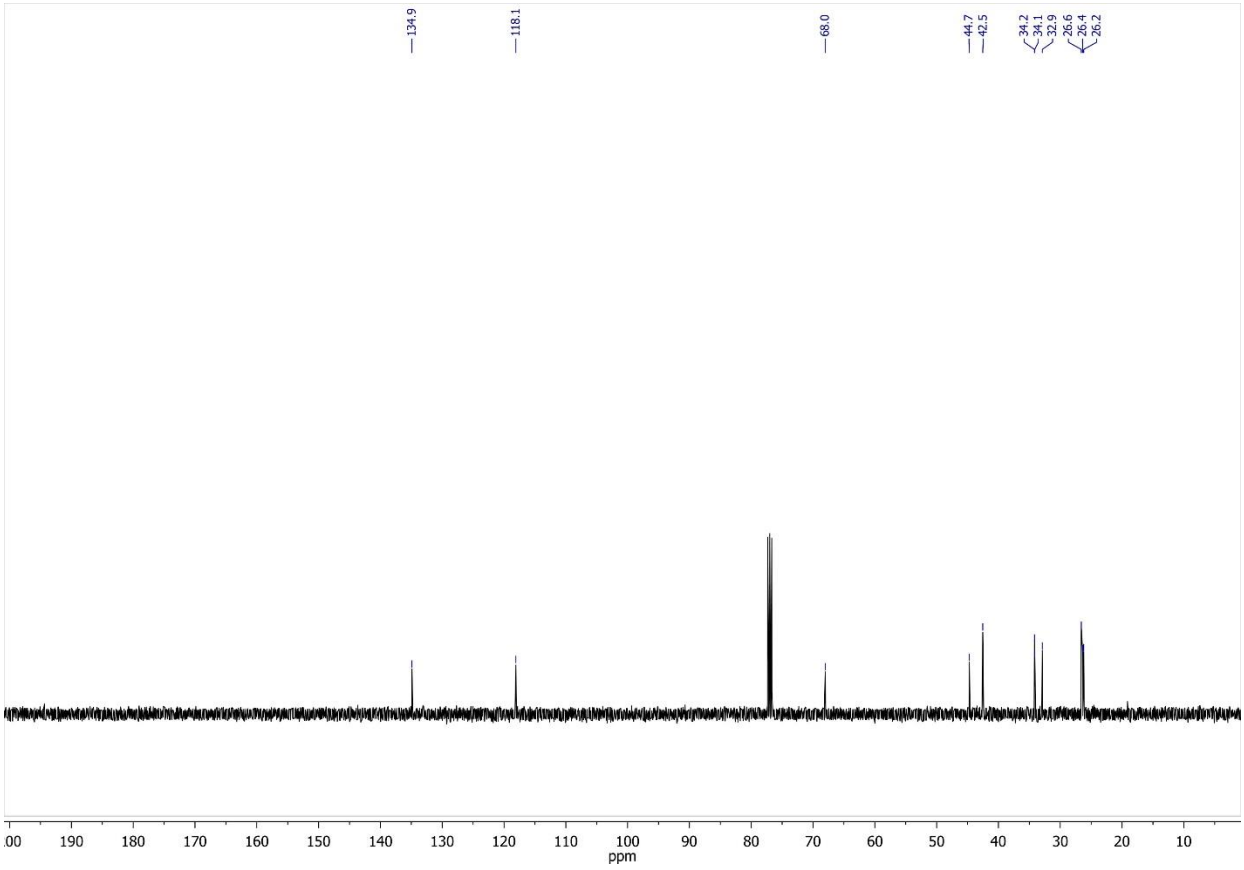

5.86 5.85 5.84 5.83 5.82 5.80 5.80 5.78 5.76 5.47 5.43 5.41 5.40 5.38 5.37 5.35 5.34 5.33 5.31 5.30 5.29 5.27 5.14 5.13 5.13 5.10 5.08 3.64 3.63 3.62 3.61 3.60 2.32 2.30 2.28 2.27 2.26 2.16 2.14 2.12 2.10 2.08 2.05 2.03 2.02 2.00 1.98 1.54 1.46 1.45 1.44 1.37 1.35 1.34 0.96 0.94 0.94 0.92 0.92
0.93 1.90 2.01 1.00 1.03 1.07 4.24 6.67 3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

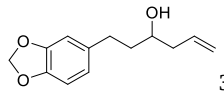

134.8 131.7 128.9 118.0 70.6 41.9 36.7 29.7 27.0 25.3 20.5 14.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


OH

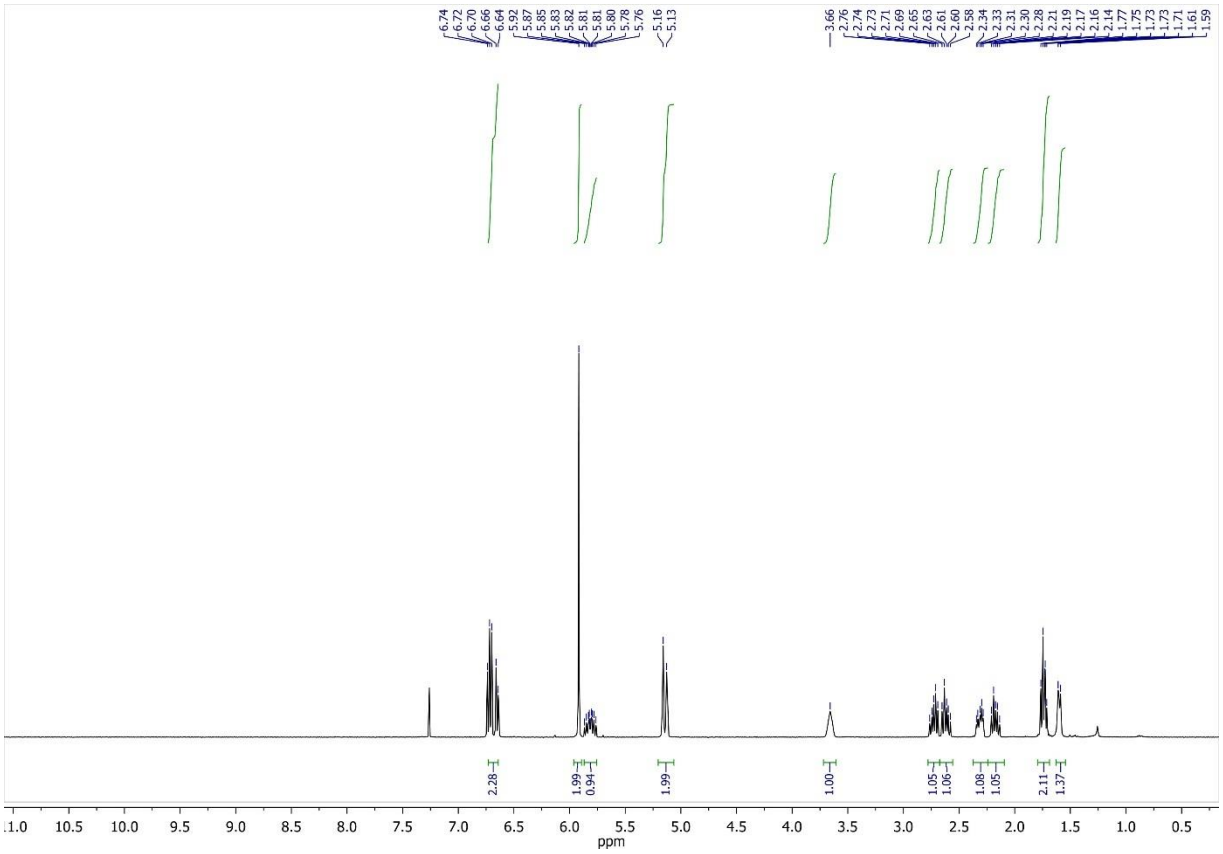
3s


5.86 5.85 5.83 5.82 5.81 5.80 5.80 5.78 5.76 5.13 5.10 3.75 2.29 2.28 2.26 2.25 2.24 2.14 2.12 2.10 2.09 2.07 1.79 1.76 1.68 1.65 1.62 1.54 1.48 1.45 1.44 1.43 1.40 1.39 1.38 1.37 1.35 1.34 1.33 1.29 1.28 1.27 1.26 1.25 1.24 1.22 1.19 1.18 1.17 1.14 1.11 1.08 0.97 0.94 0.92 0.89 0.86 0.83 0.83 0.81 0.80
0.92 1.96 1.00 1.06 1.06 1.08 4.14 1.94 5.02 2.32
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

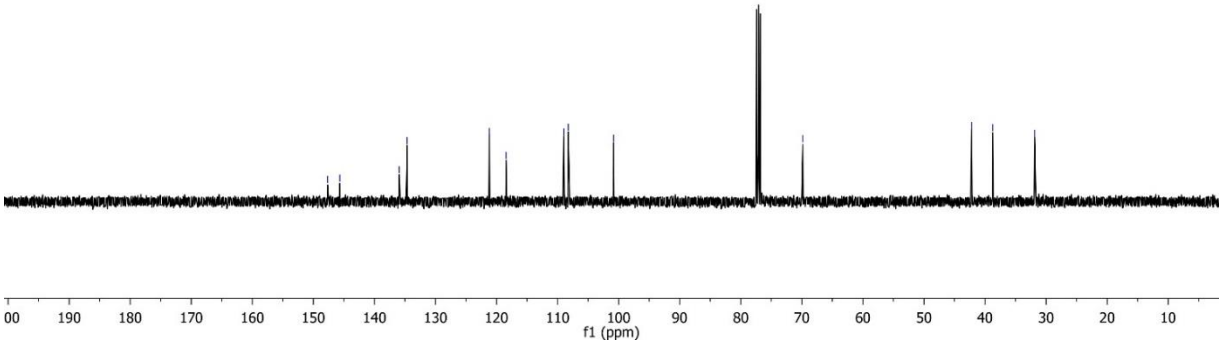

134.9 118.1 68.0 44.7 42.5 34.2 34.1 32.9 26.6 26.4 26.2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

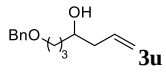

OH
O
O

3t

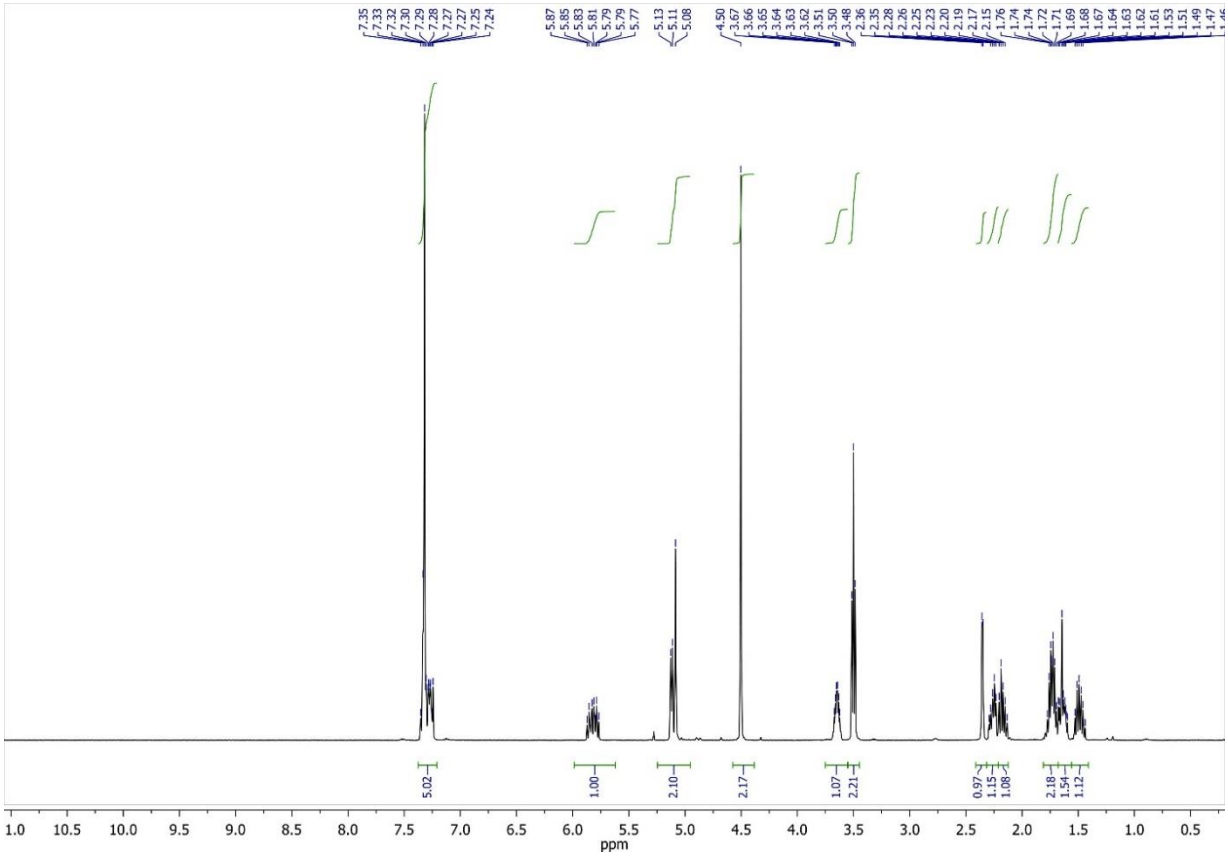

6.74
6.72
6.70
6.66
6.64
5.92
5.87
5.85
5.83
5.82
5.81
5.81
5.80
5.78
5.76
5.16
5.13
3.66
2.76
2.74
2.73
2.71
2.69
2.65
2.63
2.61
2.60
2.58
2.34
2.33
2.31
2.30
2.28
2.21
2.19
2.17
2.16
2.14
1.77
1.75
1.73
1.73
1.71
1.61
1.59
2.28
1.99
0.94
1.99
1.00
1.05
1.06
1.08
1.05
2.11
1.37
ppm

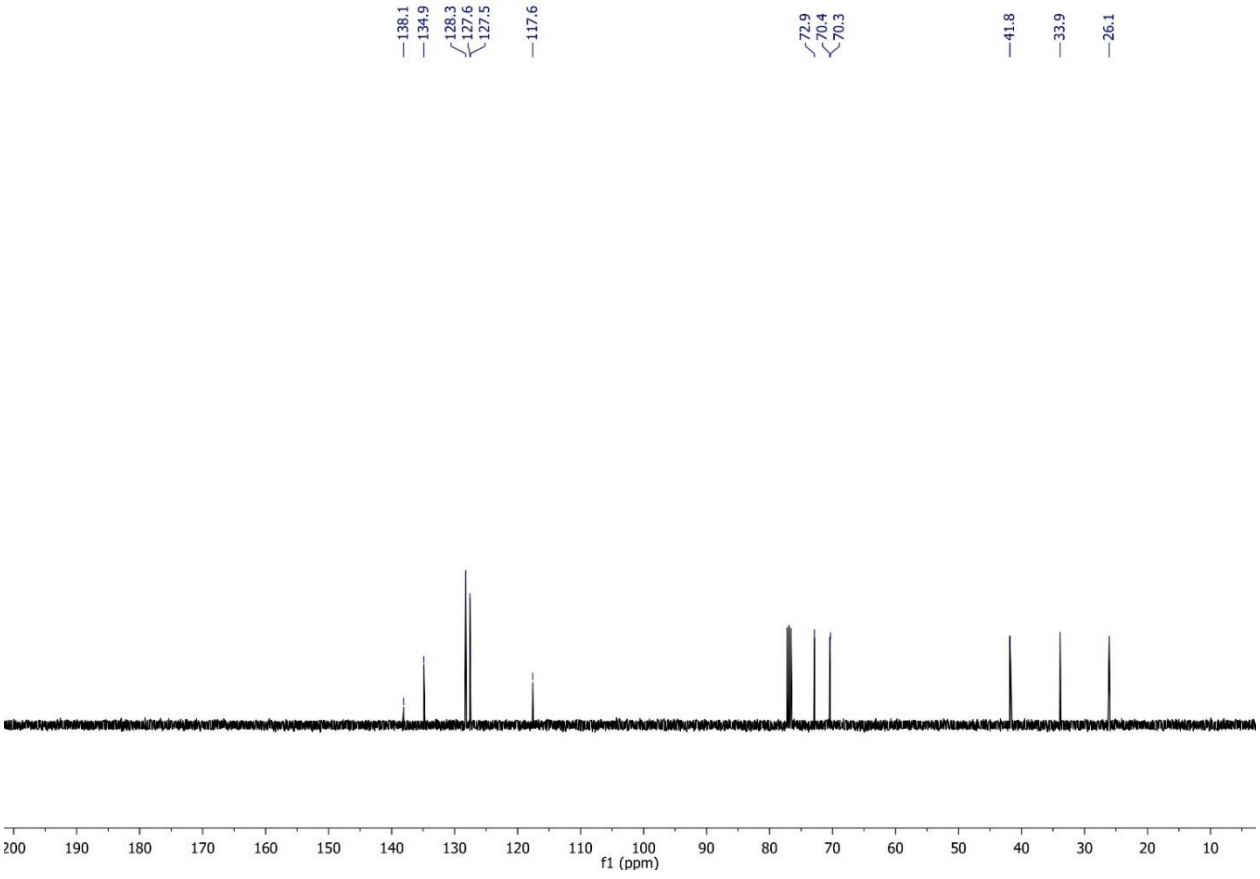

147.7
145.7
136.0
134.7
121.2
118.4
109.0
108.3
100.8
69.9
42.2
38.7
31.9

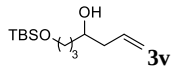

f1 (ppm)

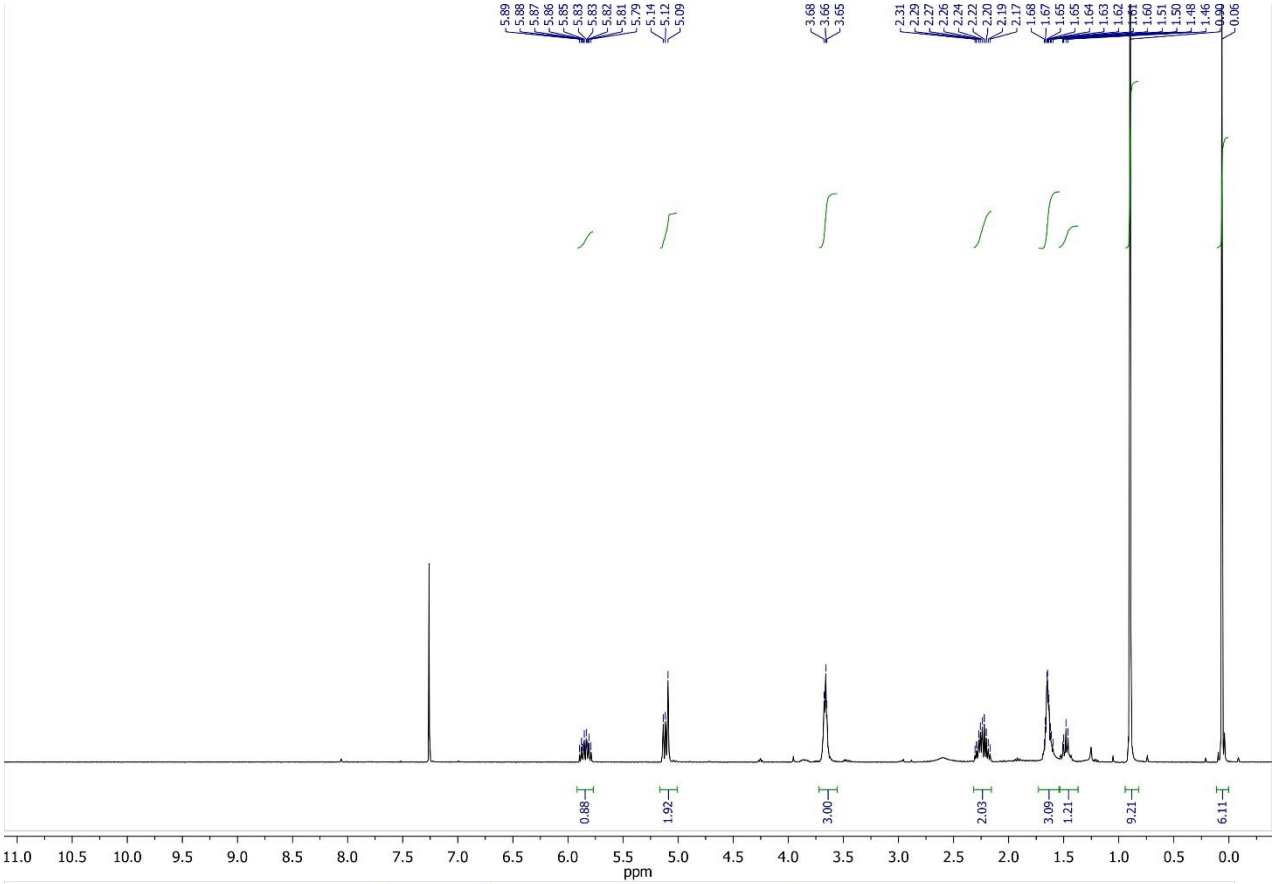

OH
BnO
3

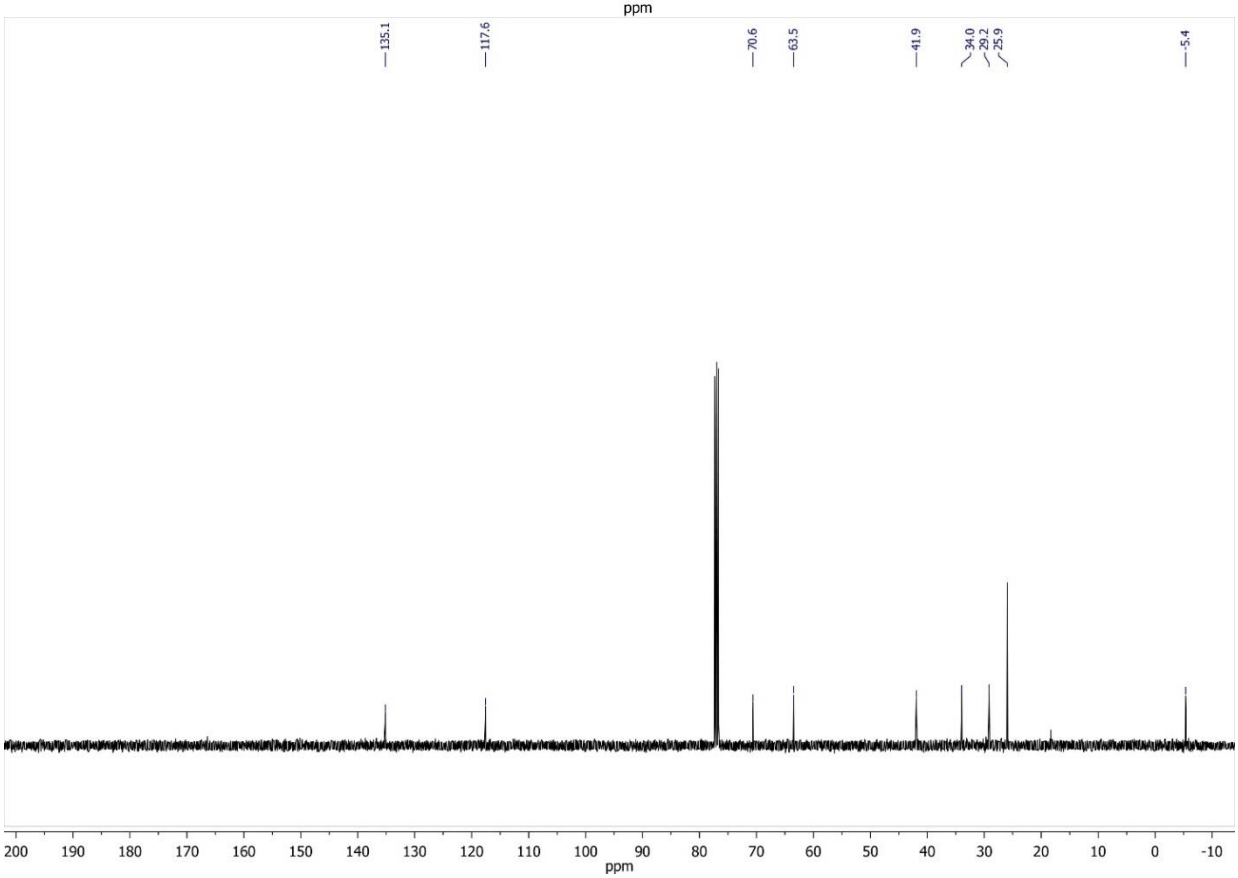
3u

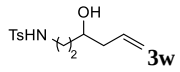

7.35
7.33
7.32
7.30
7.29
7.28
7.27
7.27
7.25
7.24
5.87
5.85
5.83
5.81
5.79
5.79
5.77
5.13
5.11
5.08
4.50
3.67
3.66
3.65
3.64
3.63
3.62
3.51
3.50
3.48
2.36
2.35
2.28
2.26
2.25
2.23
2.20
2.19
2.17
2.15
1.76
1.74
1.74
1.72
1.71
1.69
1.68
1.67
1.64
1.63
1.62
1.61
1.53
1.51
1.49
1.47
5.02
1.00
2.10
2.17
1.07
2.21
0.97
1.15
1.08
2.18
1.54
1.12
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


138.1
134.9
128.3
127.6
127.5
117.6
72.9
70.4
70.3
41.8
33.9
26.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

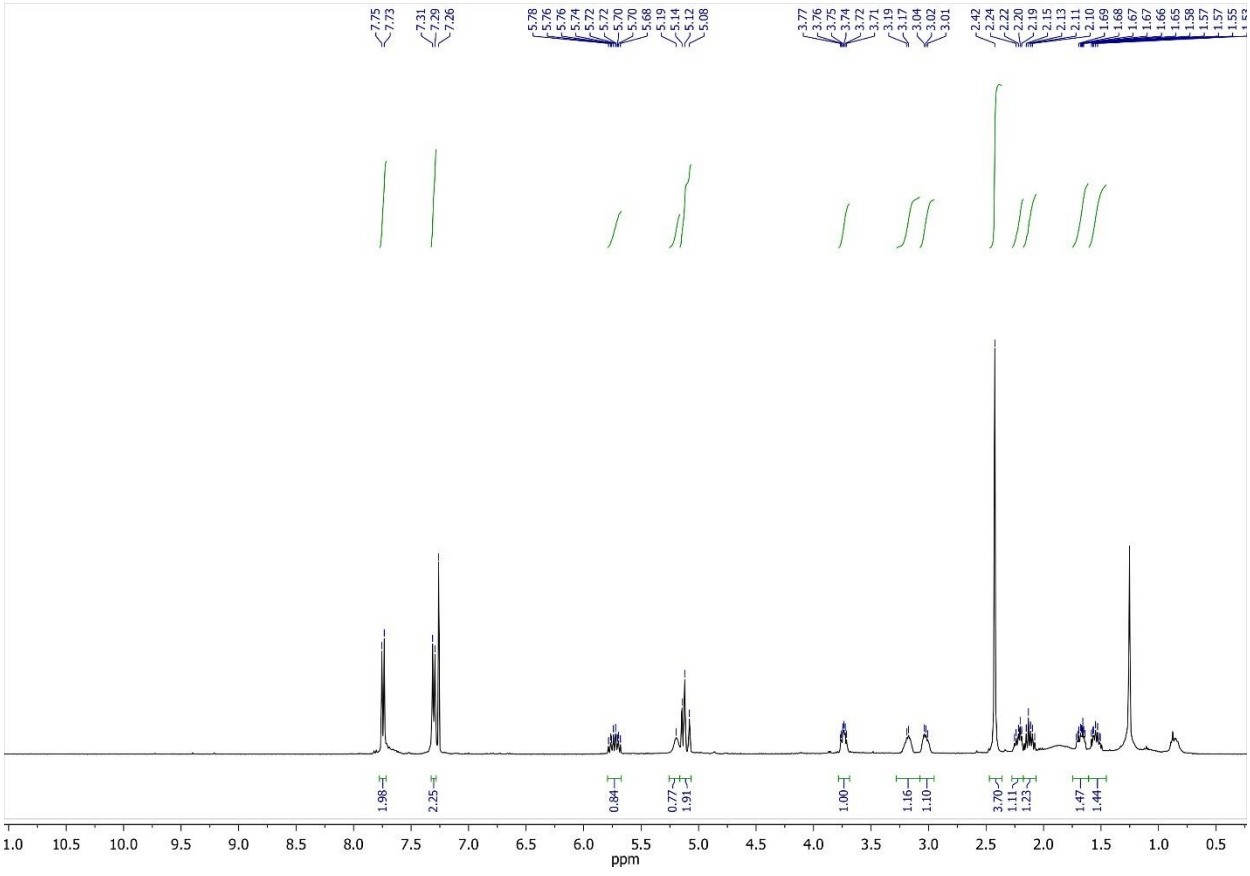

OH
TBSO
3
3v


5.89
5.88
5.87
5.86
5.85
5.83
5.83
5.82
5.81
5.79
5.14
5.12
5.09
3.68
3.66
3.65
2.31
2.29
2.27
2.26
2.24
2.22
2.20
2.19
2.17
1.68
1.67
1.65
1.65
1.64
1.63
1.62
1.61
1.60
1.51
1.50
1.48
1.46
0.90
0.06
0.88
1.92
3.00
2.03
3.09
1.21
9.21
6.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


135.1
117.6
70.6
63.5
41.9
34.0
29.2
25.9
-5.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


OH
TsHN
2

3w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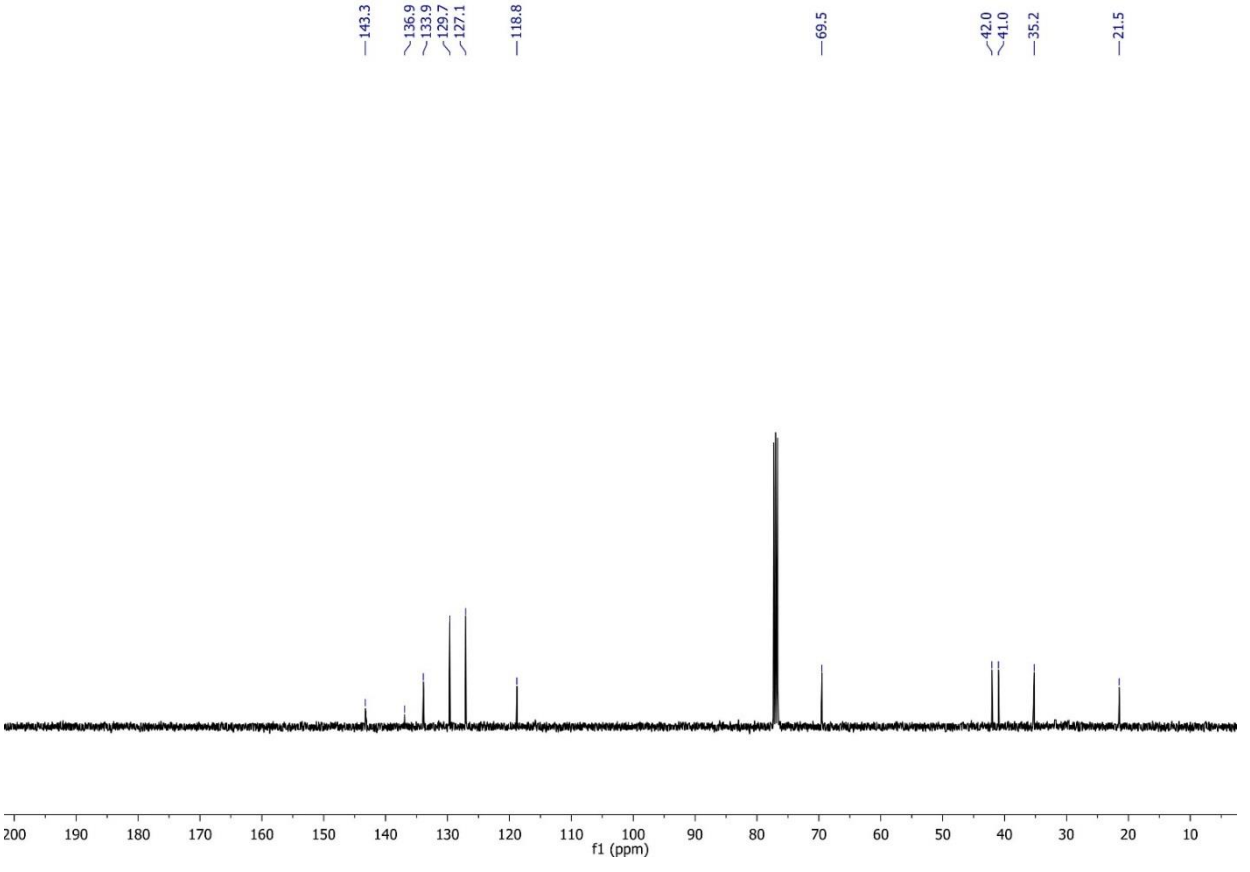
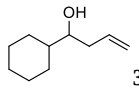
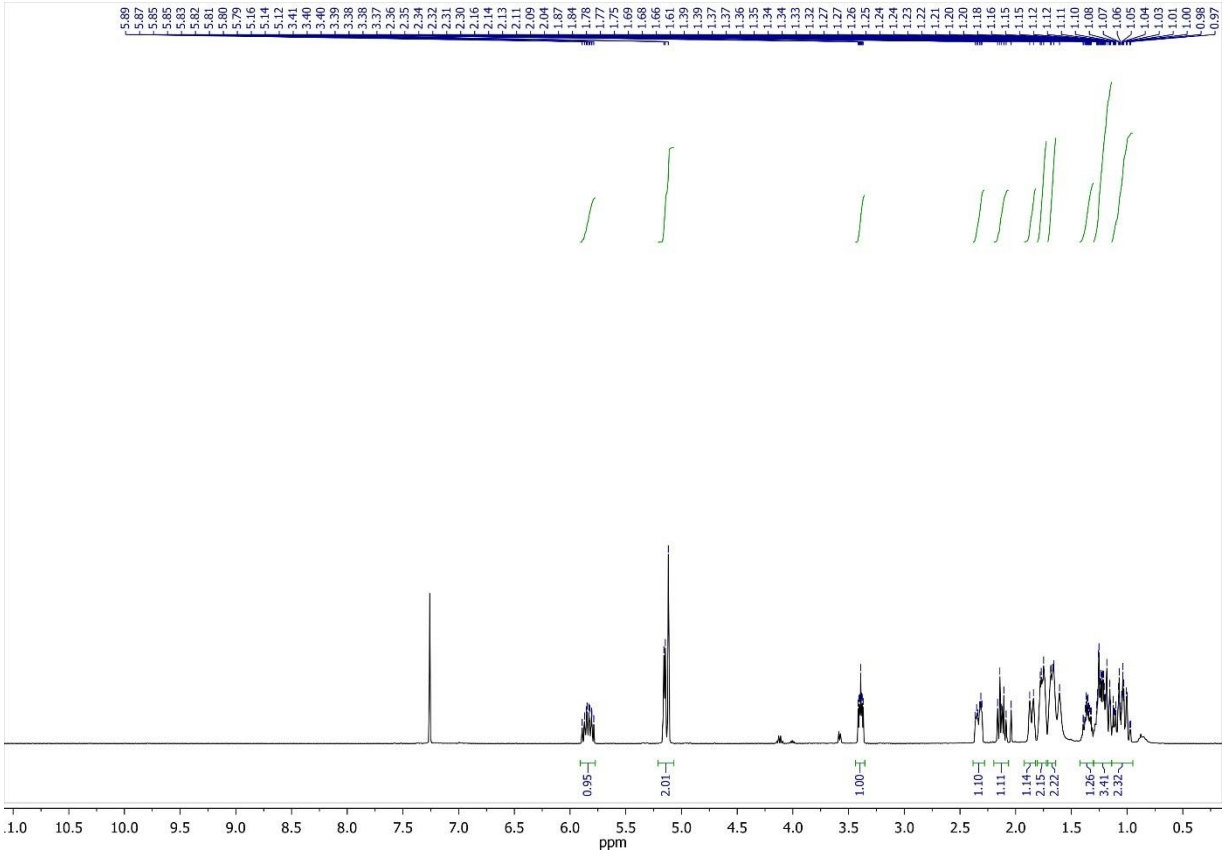
7.29
7.26
5.78
5.76
5.76
5.74
5.72
5.72
5.70
5.70
5.68
5.19
5.14
5.12
5.08
3.77
3.76
3.75
3.74
3.72
3.71
3.19
3.17
3.04
3.02
3.01
2.42
2.24
2.22
2.20
2.19
2.15
2.13
2.11
2.10
1.69
1.68
1.67
1.67
1.66
1.65
1.58
1.57
1.57
1.55
1.98
2.25
0.84
0.77
1.91
1.00
1.16
1.10
3.70
1.11
1.23
1.47
1.44
ppm

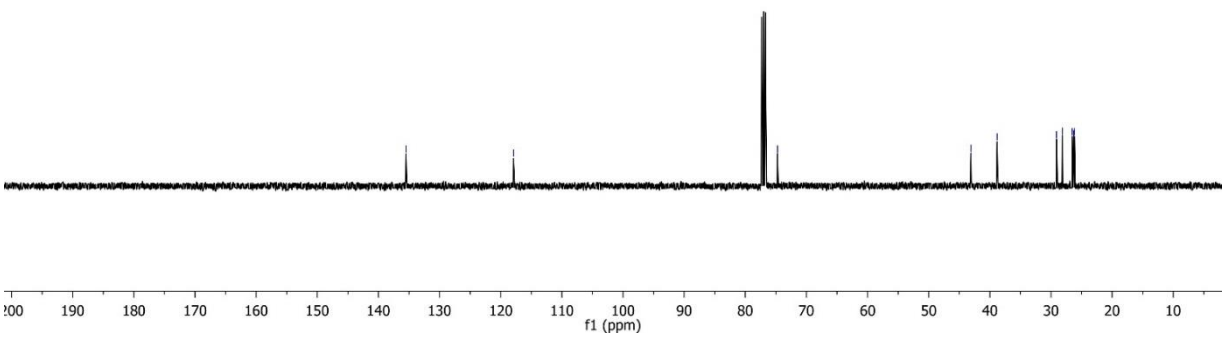

143.3
136.9
133.9
129.7
127.1
118.8
69.5
42.0
41.0
35.2
21.5
f1 (ppm)

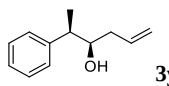

OH

3x

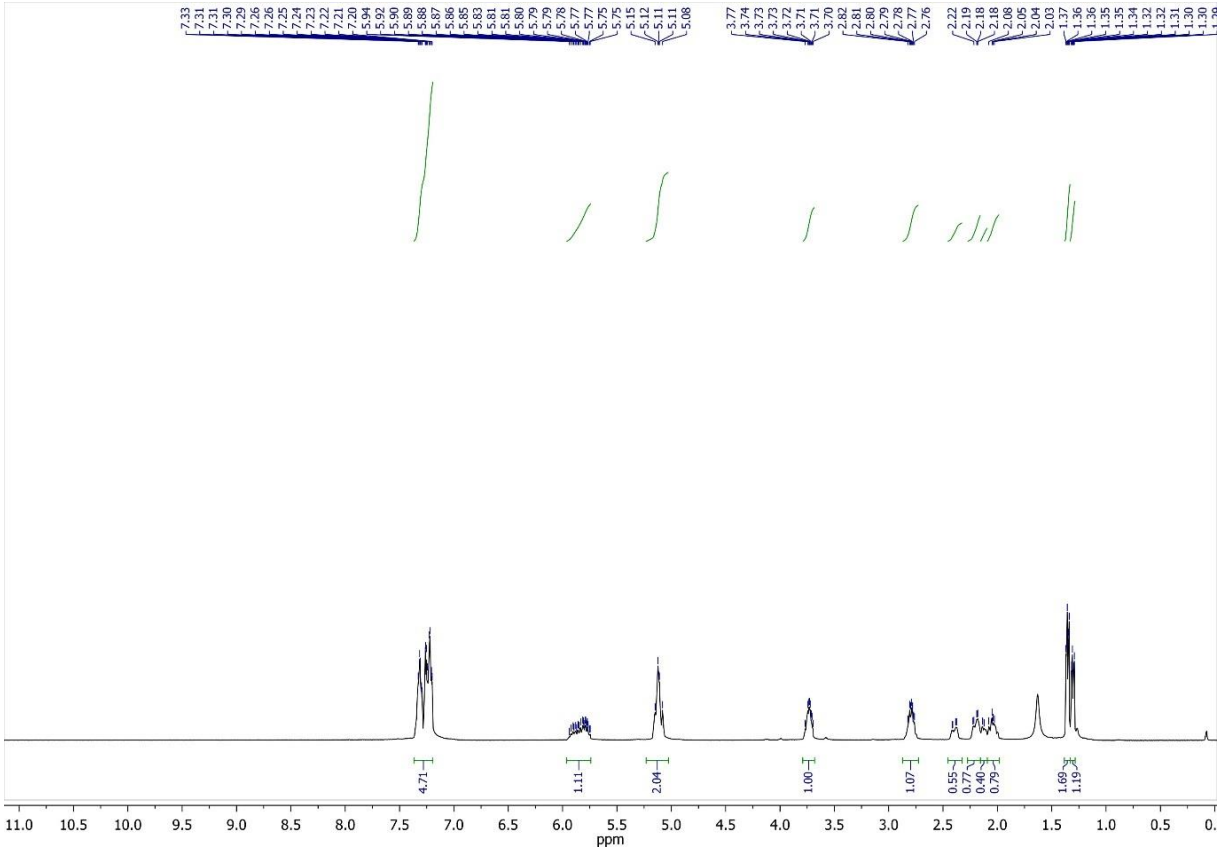

0.95
2.01
1.00
1.10
1.11
1.14
2.15
2.22
1.26
3.41
2.32
ppm

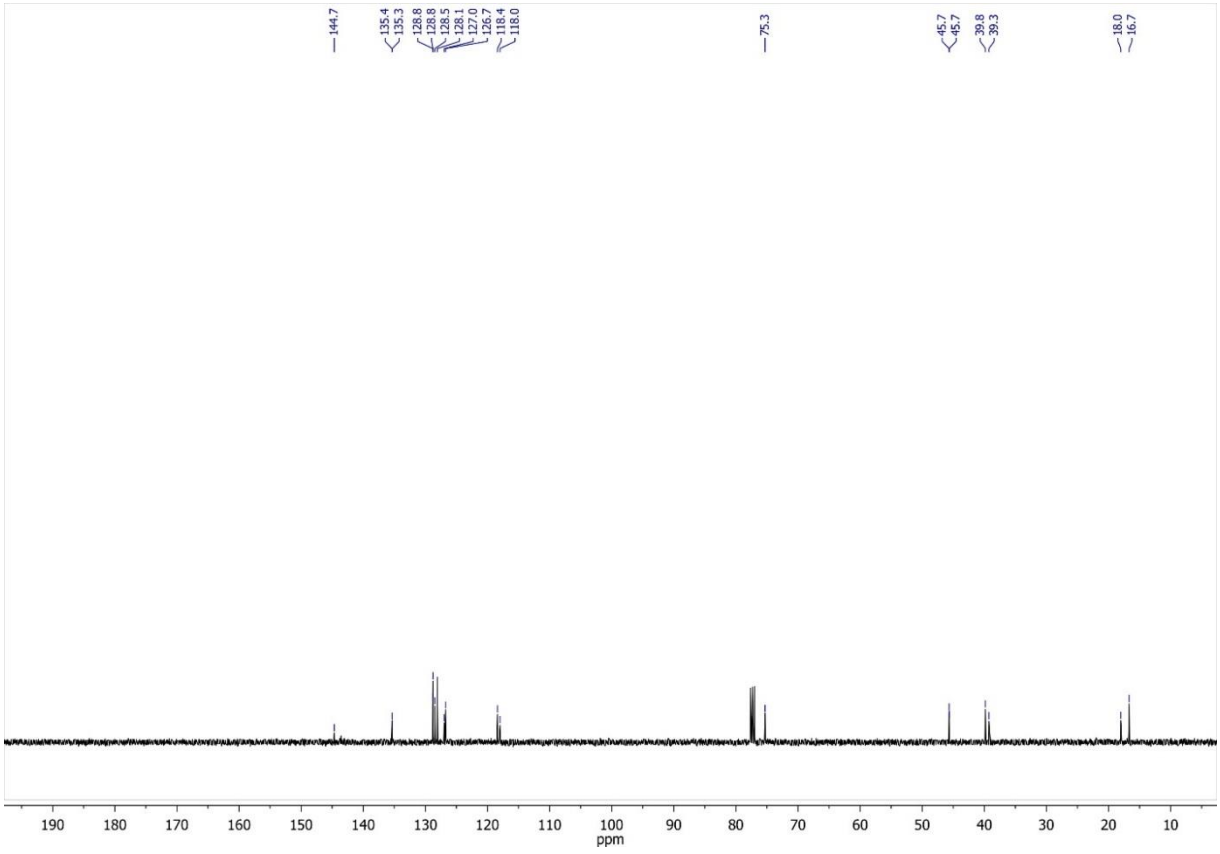

135.5
117.9
74.7
43.1
38.8
29.1
28.1
26.5
26.3
26.1

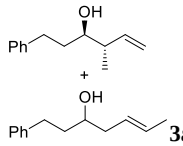

f1 (ppm)


OH

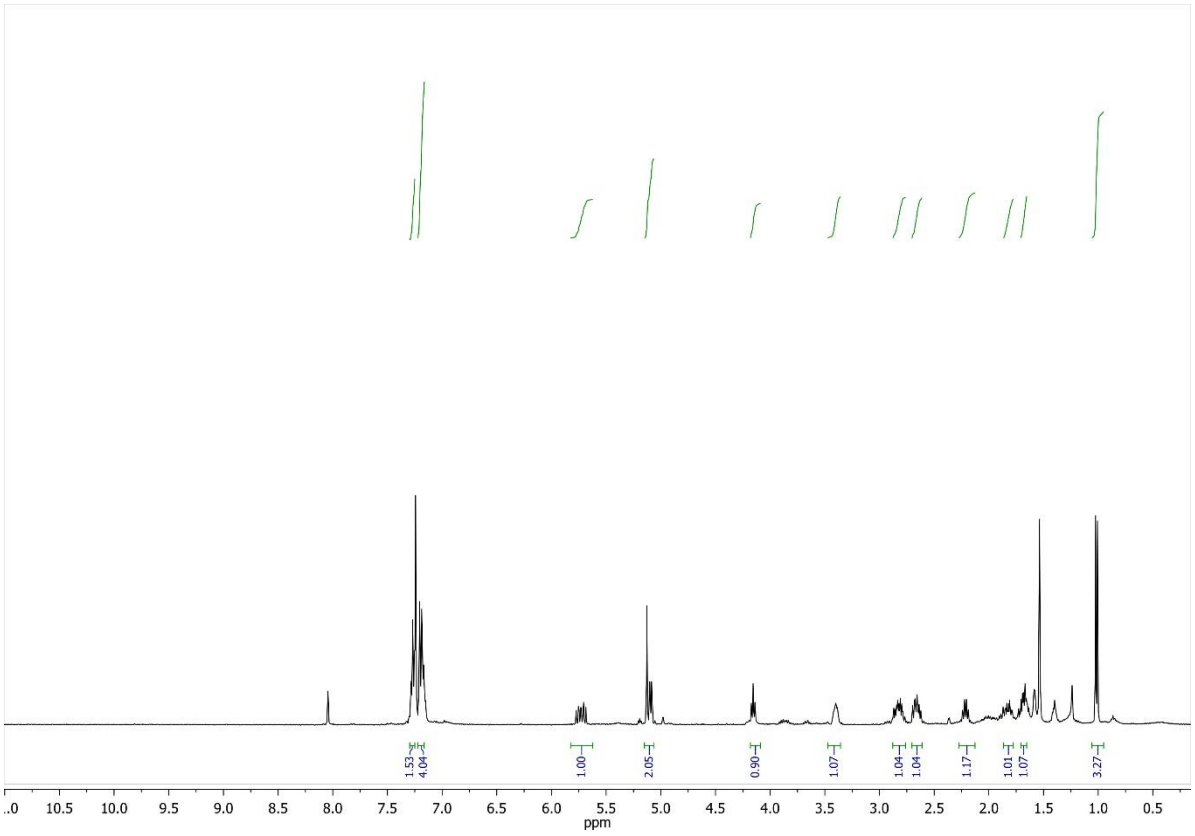
3y

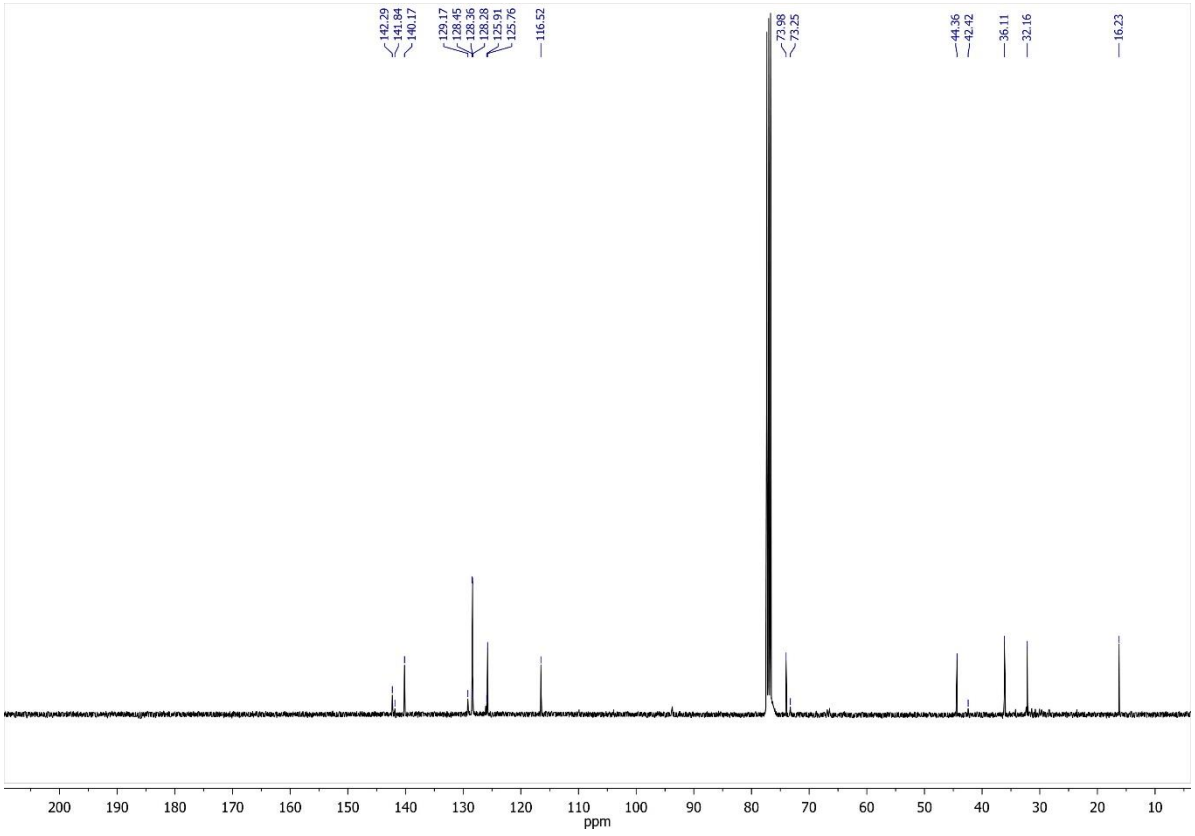

4.71
1.11
2.04
1.00
1.07
0.55
0.77
0.40
0.79
1.69
1.19
ppm

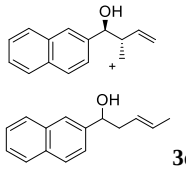

144.7
135.4
135.3
128.8
128.8
128.5
128.1
127.0
126.7
118.4
118.0
75.3
45.7
45.7
39.8
39.3
18.0
16.7
ppm


OH
Ph
+
OH
Ph

3ab+3ab'


1.53
4.04
1.00
2.05
0.90
1.07
1.04
1.04
1.17
1.01
1.07
3.27
ppm


142.29
141.84
140.17
129.17
128.45
128.36
128.28
125.91
125.76
116.52
73.98
73.25
44.36
42.42
36.11
32.16
16.23
ppm



3eb+3eb'