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

Stability and Reactivity Trends of Alkylidene Dihydropyridines

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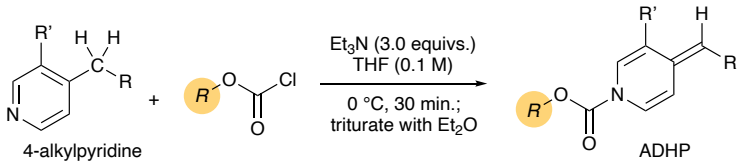
General Experimental

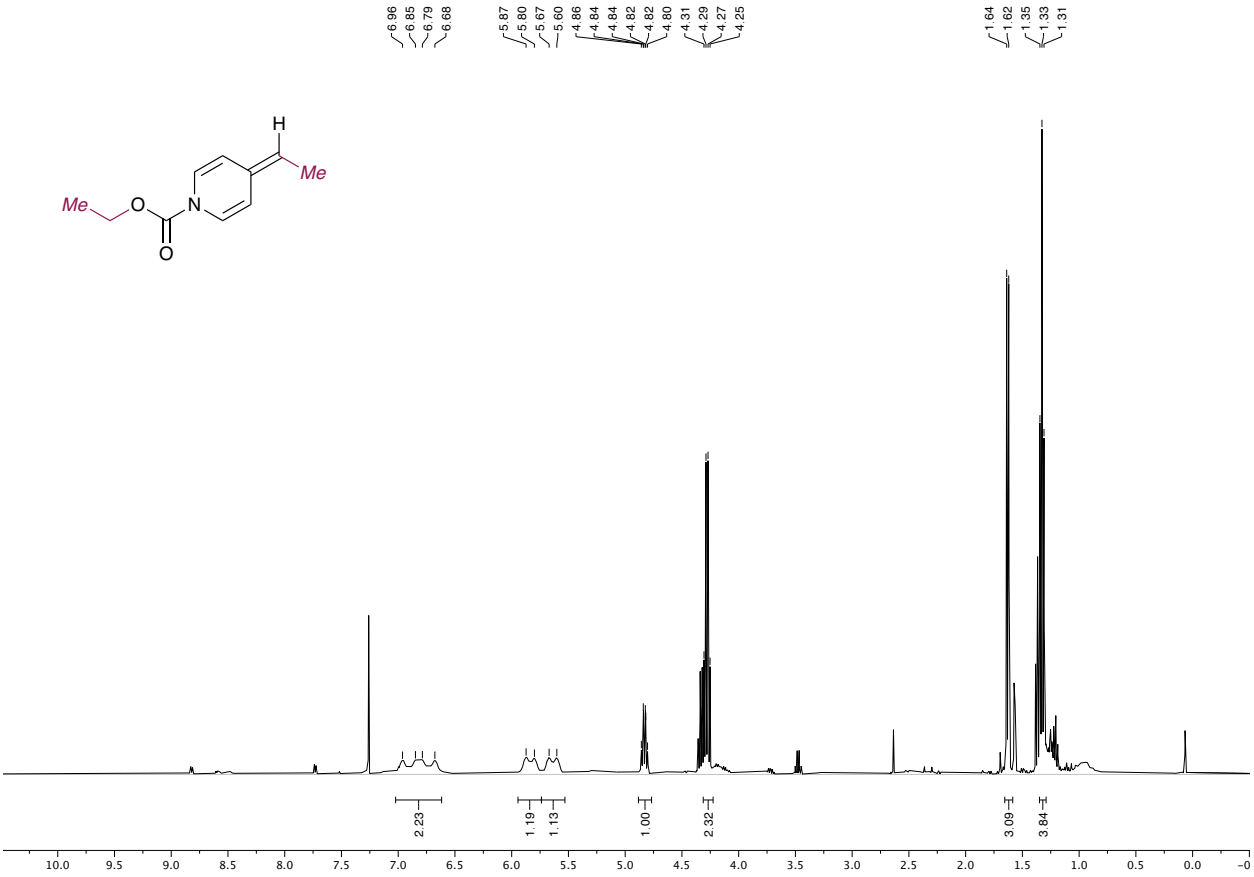
All reactions were conducted in flame- or oven-dried glassware under an atmosphere of argon using anhydrous solvents unless specified otherwise. Oxygen atmosphere conditions obtained using a balloon–needle through a rubber septum. Tetrahydrofuran (THF), diethylether (Et_2O), dichloromethane (DCM), acetonitrile (MeCN) and toluene (PhMe) were dried using an INERT® PureSolv solvent purification system. Commercial alkylpyridines and chloroformates were used as received. Triethyl amine (Et_3N) and di-isopropyl amine ($^iPr_2NH$) was distilled over CaH_2 under an argon atmosphere prior to use. Thin-layer chromatography was performed on SiliCycle® silica gel 60 F254 plates. Visualization was carried out using UV light (254 nm) and/or KMnO4, iodine stains. Flash column chromatography was carried out using SiliCycle® SiliaFlash® silica gel (230-400 mesh, 40- 63 µ, 60 Å pore size). Hexanes (ACS grade), acetone (ACS grade), isopropanol (ACS grade) and ethyl acetate (ACS grade) were used as received. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 400 AV, Bruker DRX 600, or Bruker 300 AV spectrometer in chloroform-d (99.8 % deuterated). Spectra recorded using chloroform were calibrated to 7.26 ppm ^{1}H and 77.16 ppm ^{13}C. Chemical shifts (δ) are reported in ppm and multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), sext (sextet), td (triplet of doublets), tt (triplet of triplets), dd (doublet of doublets), dddd (doublet of doublet of doublet of doublets), m (multiplet), and br (broad). Coupling constants *J* are reported in Hertz (Hz). Infrared (IR) spectra were recorded as thin films (neat) using Alpha Platinum ATR, Bruker, diamond crystal FT-IR instrument.

General Procedure 1: Synthesis of alkylidene dihydropyridines.



A flame-dried round-bottomed flask equipped with a stir bar, is charged with a 4-alkyl pyridine (100 mg, 1.0 equiv.) and anhydrous anhydrous THF to prepare a 0.1M solution. Freshly distilled Et_3N (3.0 equiv.) is added, and the solution is stirred vigorously while cooled in an ice bath. After 5 minutes, neat chloroformate ($ClCO_2R$, 2.0 equivs.) is added in a dropwise manner and the mixture is stirred for 30 minutes. The resulting bright yellow cloudy mixture is concentrated *in vacuo* and the crude material is suspended in anhydrous Et_2O (20 mL). The suspension is filtered through a cotton plug to remove the solids and the filtrate is concentrated *in vacuo* to give the crude ADHP as clear yellow oil. *The crude ADHPs are used without further purification due to their decomposition upon excessive handling and exposure to air or, conversely, to their instability towards hydrolysis. For the same reasons ADHPs were characterized as mixtures of rotamers only by ^{1}H- and ^{13}C-NMR spectroscopy as well as High Resolution Mass Spectrometry.*

^{1}H-NMR of ADHP derived from 4-ethylpyridine and ethyl chloroformate



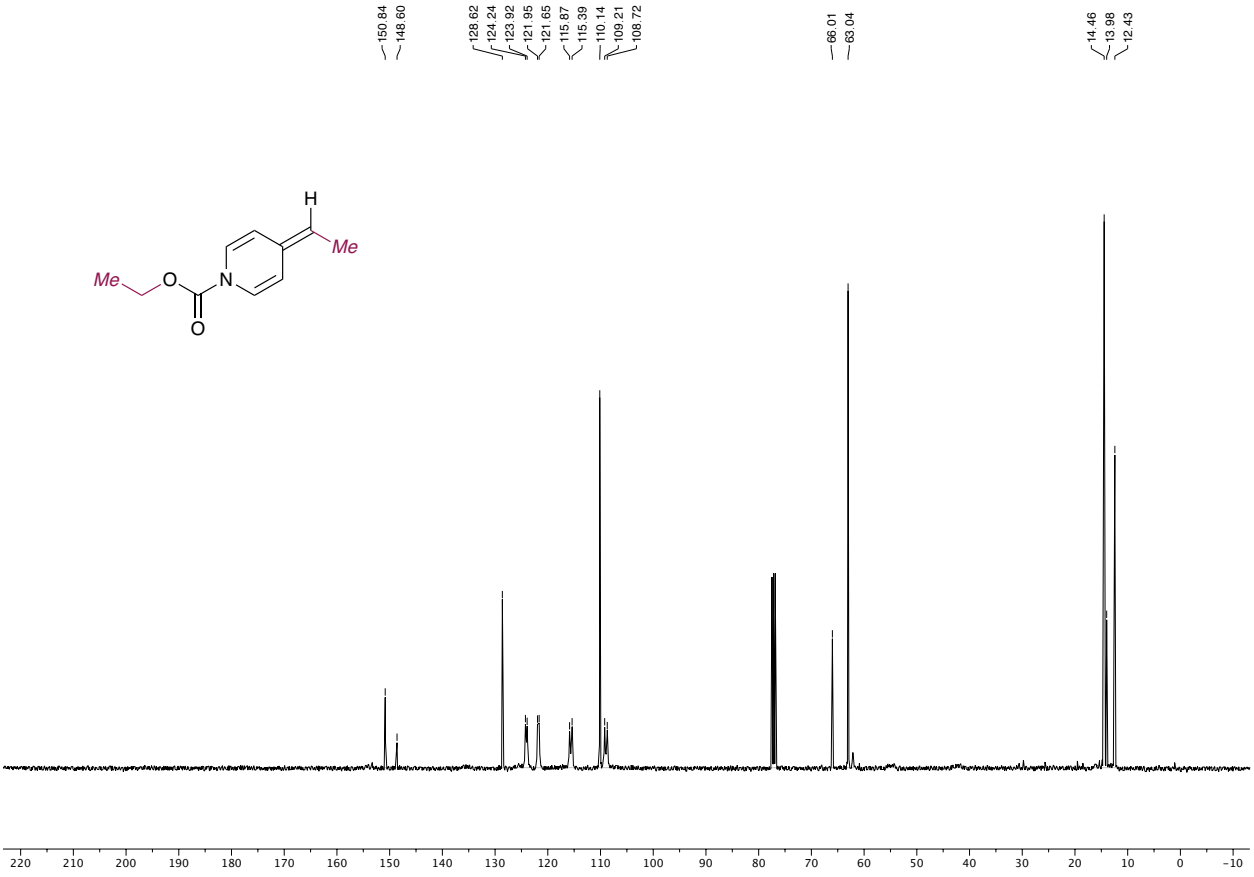
^{1}H-NMR (400 MHz, $CDCl_3$)

δ 6.96-6.68 (br m, 2H), 5.84-5.64 (br m, 2H), 4.81 (q, J = 8.0 Hz, 1H), 4.28 (q, J = 7.4 Hz, 2H), 1.63 (d, J = 8.0 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{10}H_{14}NO_2$ 180.1025; Found 180.1020

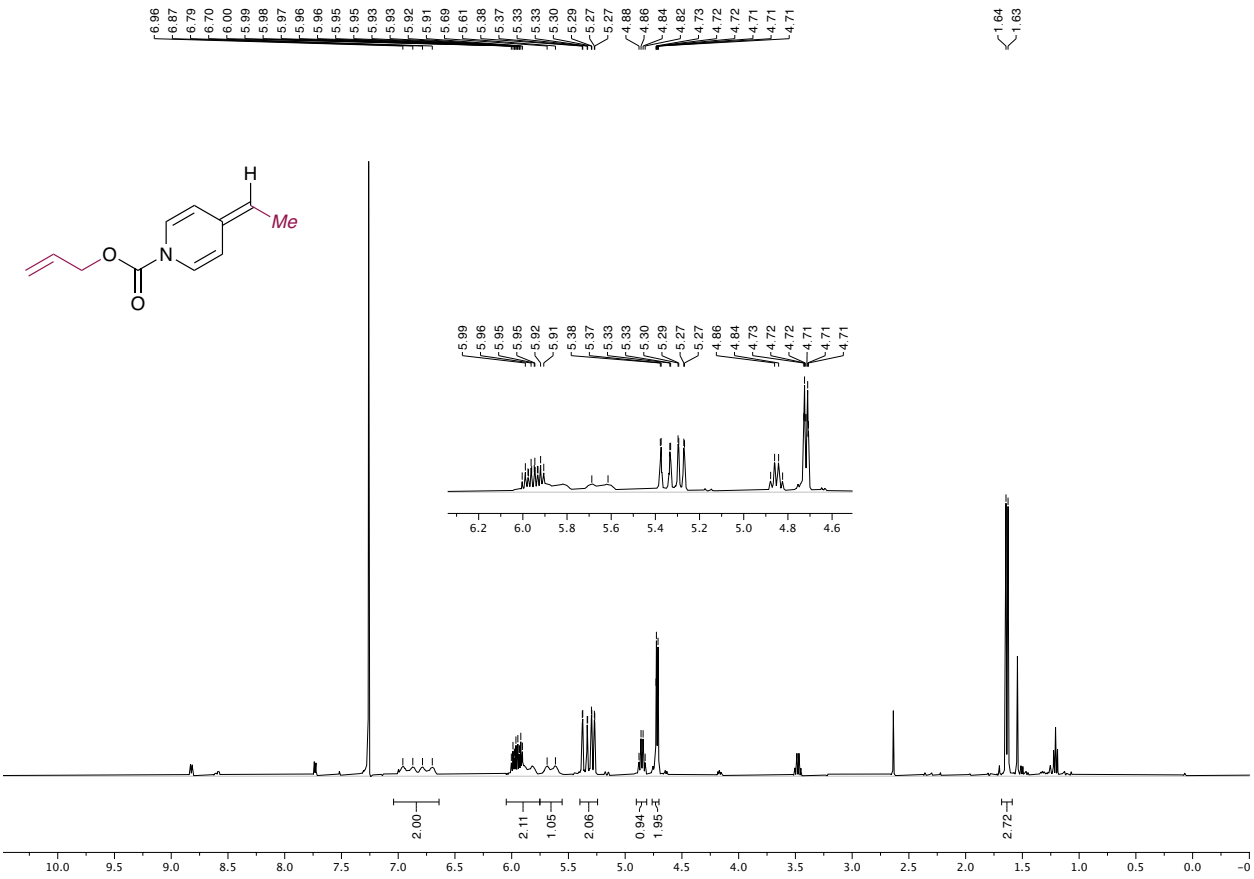
^{13}C-NMR of ADHP derived from 4-ethylpyridine and ethyl chloroformate



^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)

δ 150.8, 148.6, 128.6, 124.2, 123.9, 122.0, 121.7, 115.9, 115.4, 110.1, 109.2, 108.7, 66.0, 63.0, 14.5, 14.0,12.4.

^{1}H-NMR of ADHP derived from 4-ethylpyridine and allyl chloroformate



^{1}H-NMR (400 MHz, $CDCl_3$)

δ 6.95-6.70 (m, 2H), 6.00-5.82 (m, 2H), 5.65 (br m, 1H),

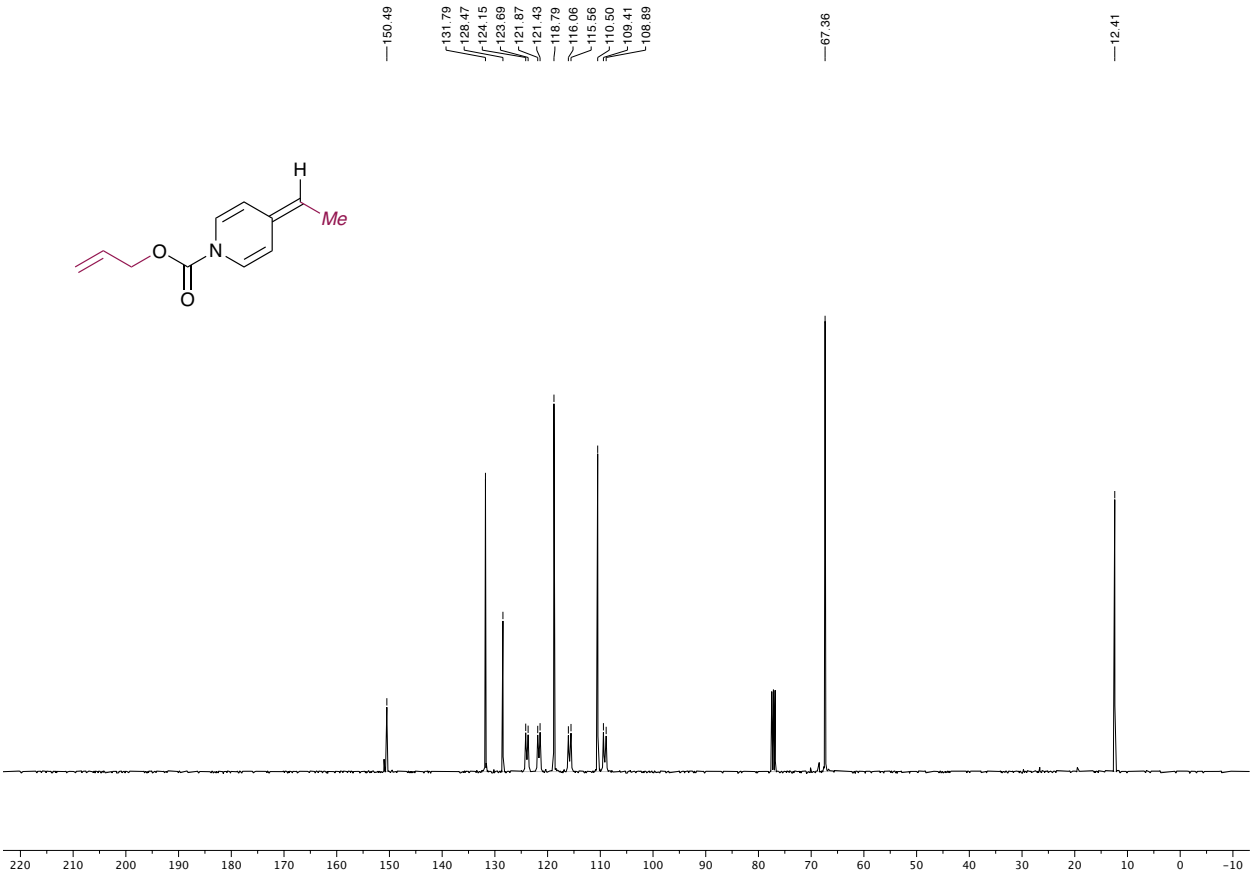
5.35 (dq, J = 17.2, 1.4 Hz, 1H), 5.28 (dq, J = 10.4, 1.3 Hz, 1H),

4.85 (q, J = 7.2 Hz, 1H), 4.71 (dt, J = 5.7, 1.4 Hz, 2H), 1.63 (d, J = 7.3 Hz, 3H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{11}H_{14}NO_2$ 192.1025; Found 192.1020

$^{13}C\{^{1}H\}$-NMR of ADHP derived from 4-ethylpyridine and allyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

δ 150.5, 131.8, 128.5, 124.2, 123.7, 121.9, 121.4, 118.9, 116.1, 115.6, 110.5, 109.4, 108.9, 67.4, 12.4.

^{1}H-NMR of ADHP derived from 4-ethylpyridine and benzyl chloroformate

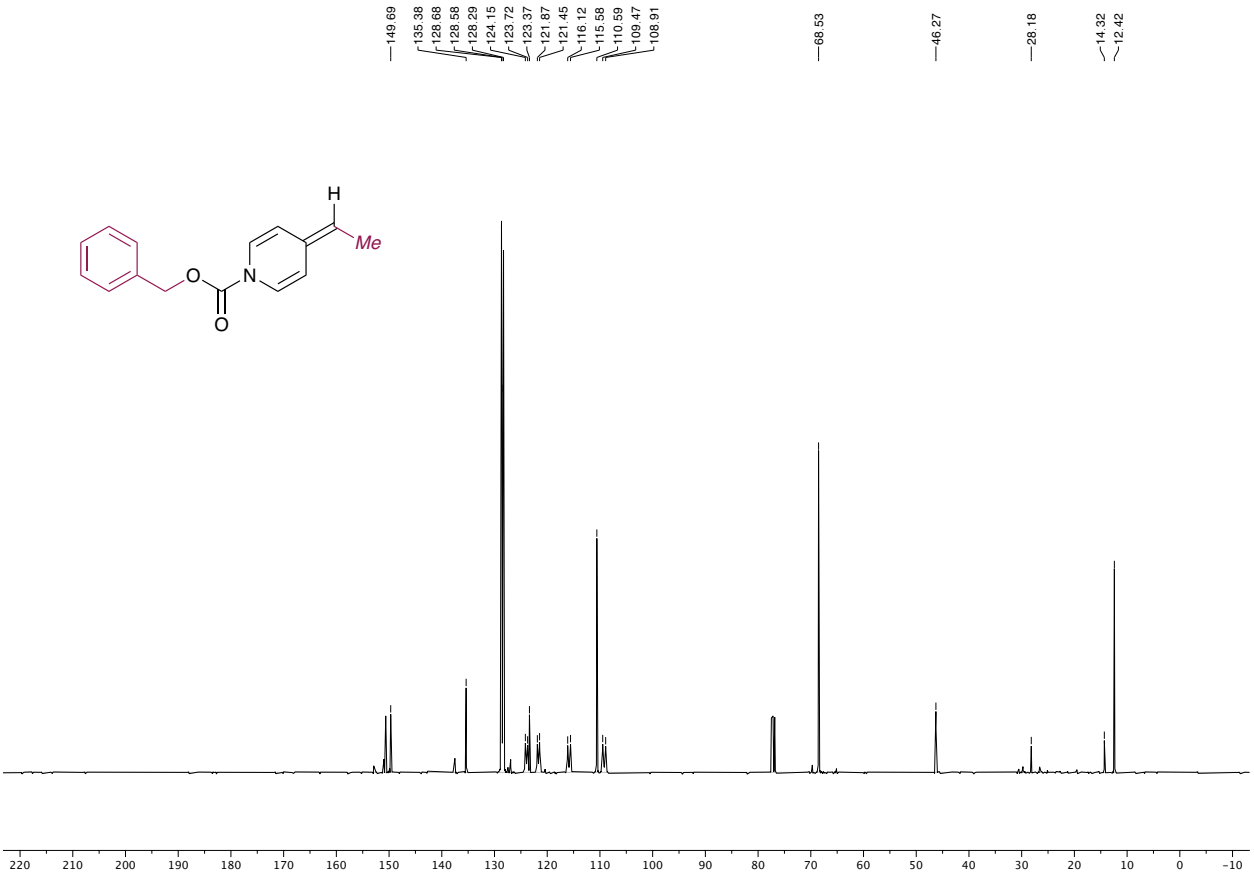
^{1}H-NMR (400 MHz, $CDCl_3$)

δ = 7.39-7.36 (m, 5H), 6.98-6.68 (br m, 2H), 5.87-5.58 (br m, 2H), 5.25 (s, 2H), 4.85 (q, J = 7.4 Hz, 1H), 1.63 (d, J = 7.4 Hz, 3H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{15}H_{16}NO_2$ 242.1181; Found 242.1173

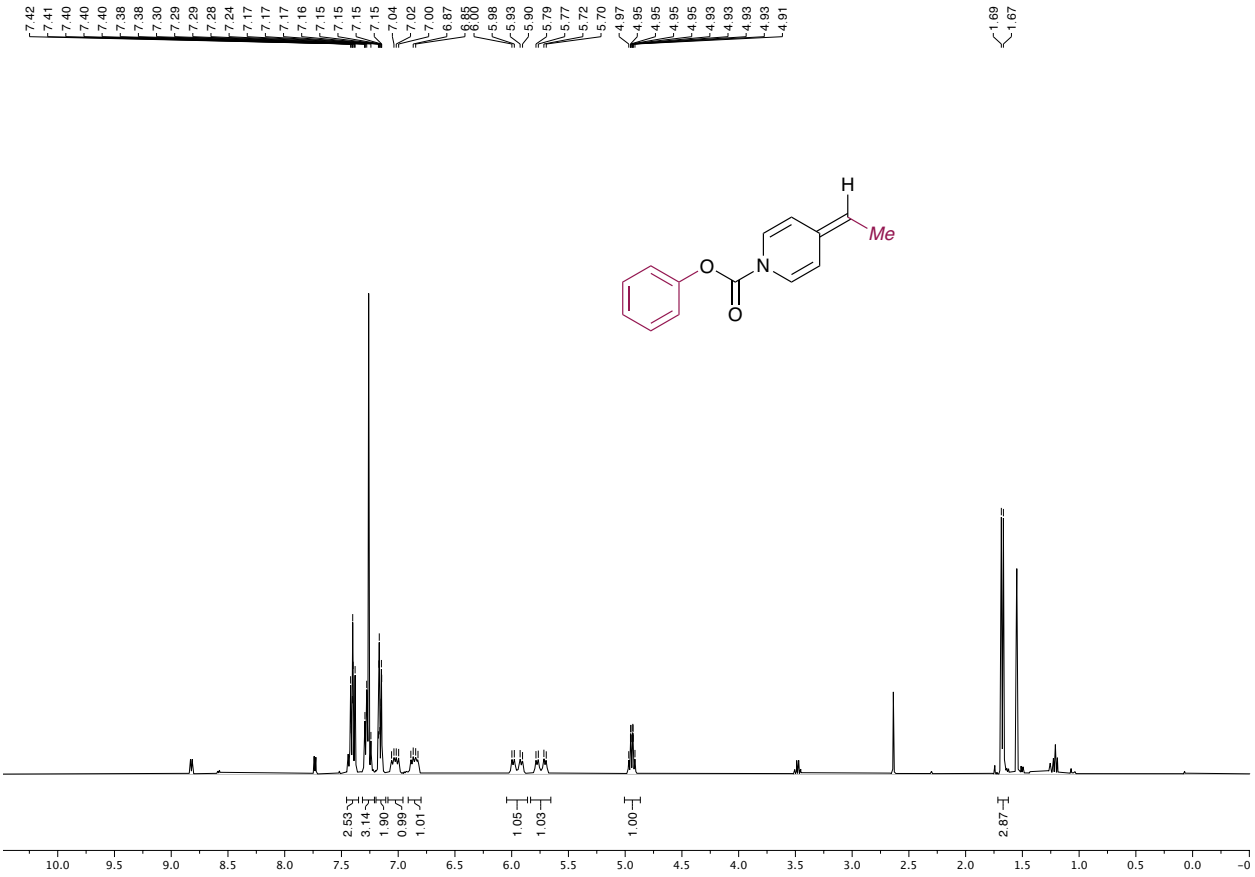
$^{13}C\{^{1}H\}$-NMR of ADHP derived from 4-ethylpyridine and benzyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

δ = 150.6, 149.68, 135.38, 129.0, 128.7, 128.60, 128.3, 124.2, 123.7, 123.4, 121.9, 121.5, 116.14, 115.60, 110.6, 109.50, 108.9, 68.5, 12.4.

^{1}H-NMR of ADHP derived from 4-ethylpyridine and phenyl chloroformate



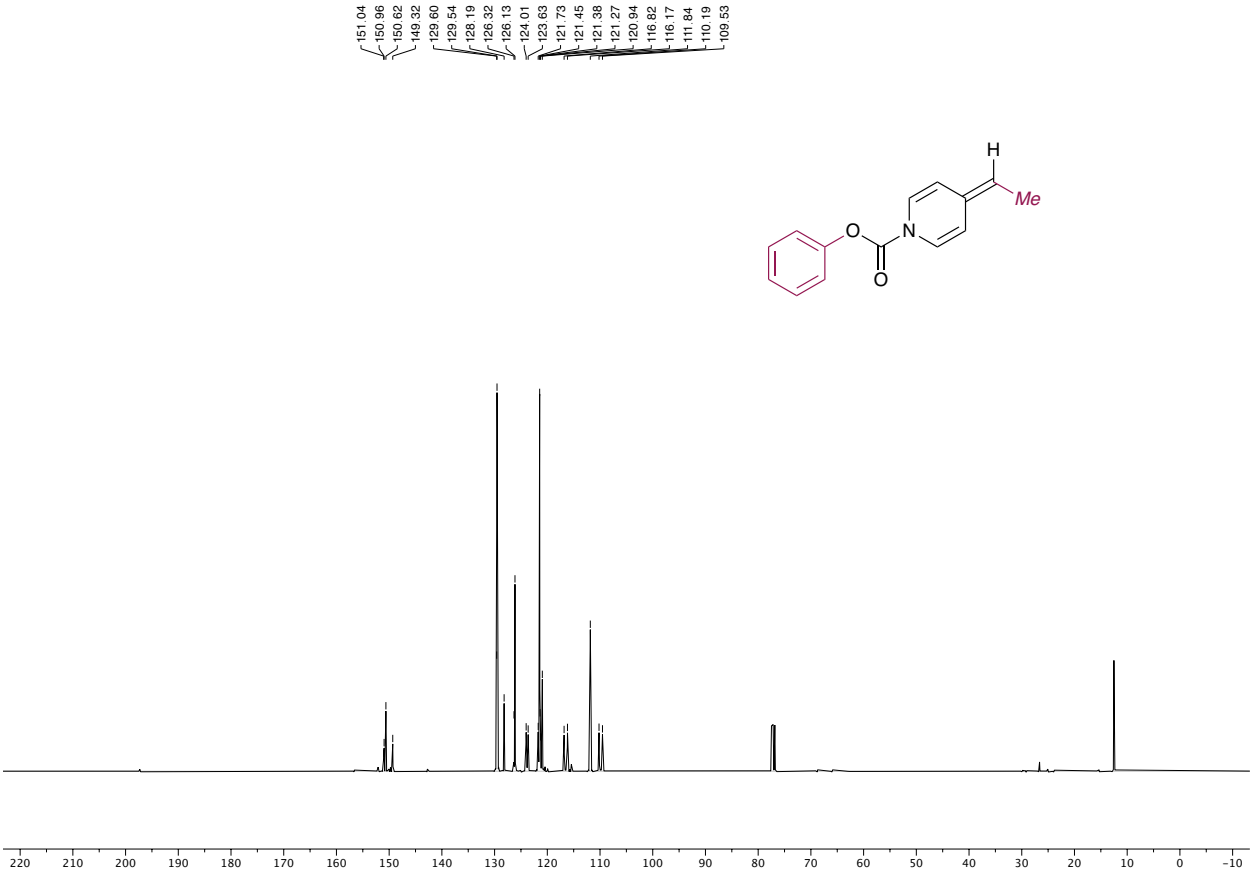
^{1}H-NMR (400 MHz, $CDCl_3$)

δ = 7.43-7.35 (m, 2H), 7.28-7.26 (m, 1H), 7.15-7.12 (m, 2H),
6.98 (dd, *J* = 16.0, 8.0 Hz 1H), 6.85 (dd, *J* = 15.0, 8.0 Hz, 1H),
5.93 (dd, *J* = 19.0, 8.0 Hz, 1H), 5.75 (dd, *J* = 16.0, 8.0 Hz, 1H),
4.93 (q, *J* = 7.3 Hz, 1H), 1.68 (d, *J* = 7.3 Hz, 3H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{14}H_{14}NO_2$ 228.1025; Found 228.1020

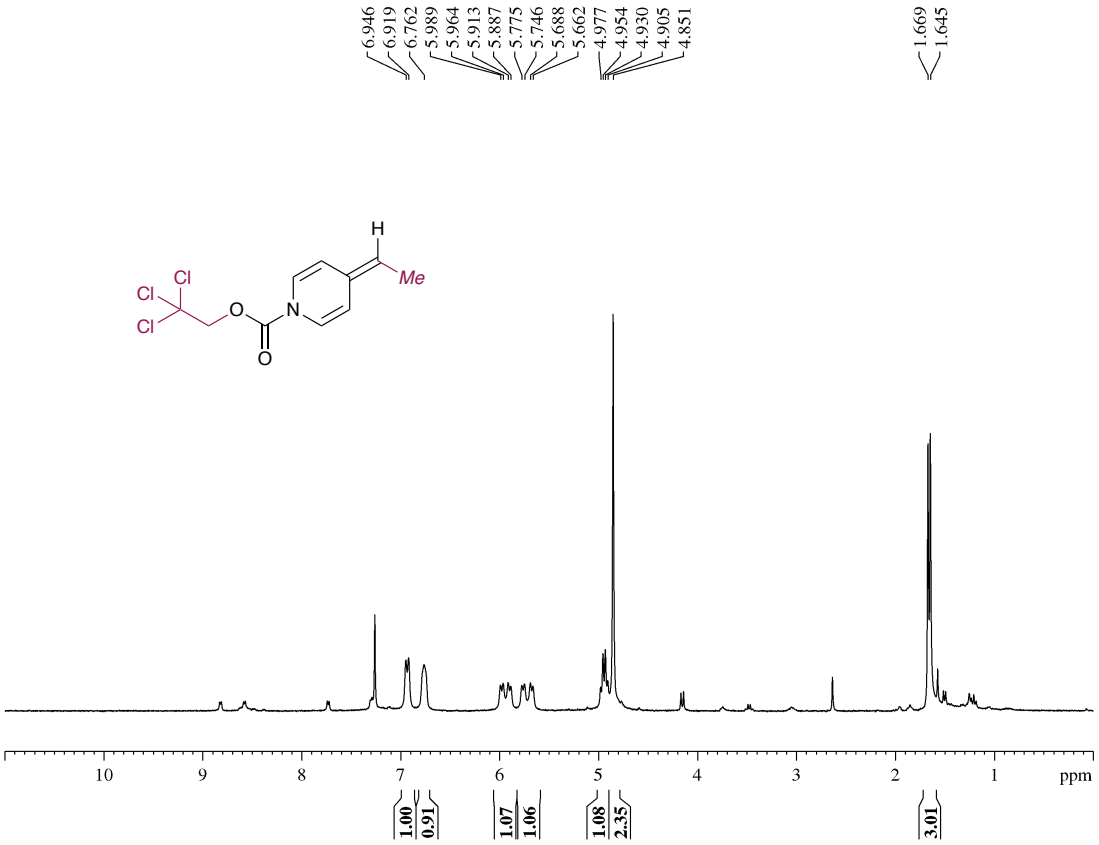
$^{13}C\{1H\}$-NMR of ADHP derived from 4-ethylpyridine and phenyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

δ 150.6, 149.3, 129.5, 128.2, 126.3, 126.1, 124.0, 123.6, 121.7, 121.4, 121.3, 120.9, 116.8, 116.2, 111.8, 110.2, 109.5, 12.5.

[1]H-NMR of ADHP derived from 4-ethylpyridine and trichloroethyl chloroformate



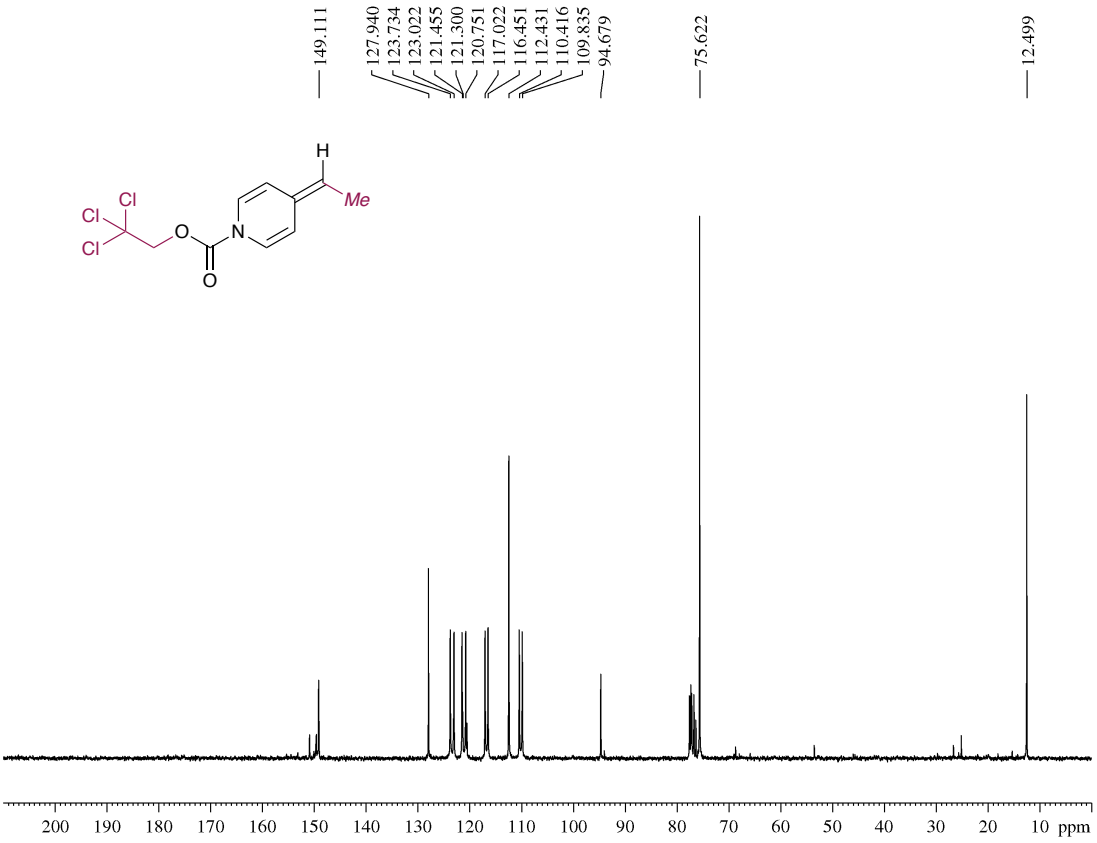
[1]H-NMR (400 MHz, $CDCl_3$)

δ 6.93 (d, J = 10.8 Hz, 1H), 6.76 (br s, 1H), 5.94 (dd, J = 10.8, 2.4 Hz, 1H), 5.72 (dd, J = 10.8, 2.3 Hz 1H), 4.94 (q, J = 7.3 Hz, 1H), 4.85 (s, 2H), 1.65 (d, J = 7.3 Hz, 3H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{10}H_{11}Cl_3NO_2$ 281.9855; Found 281.9851

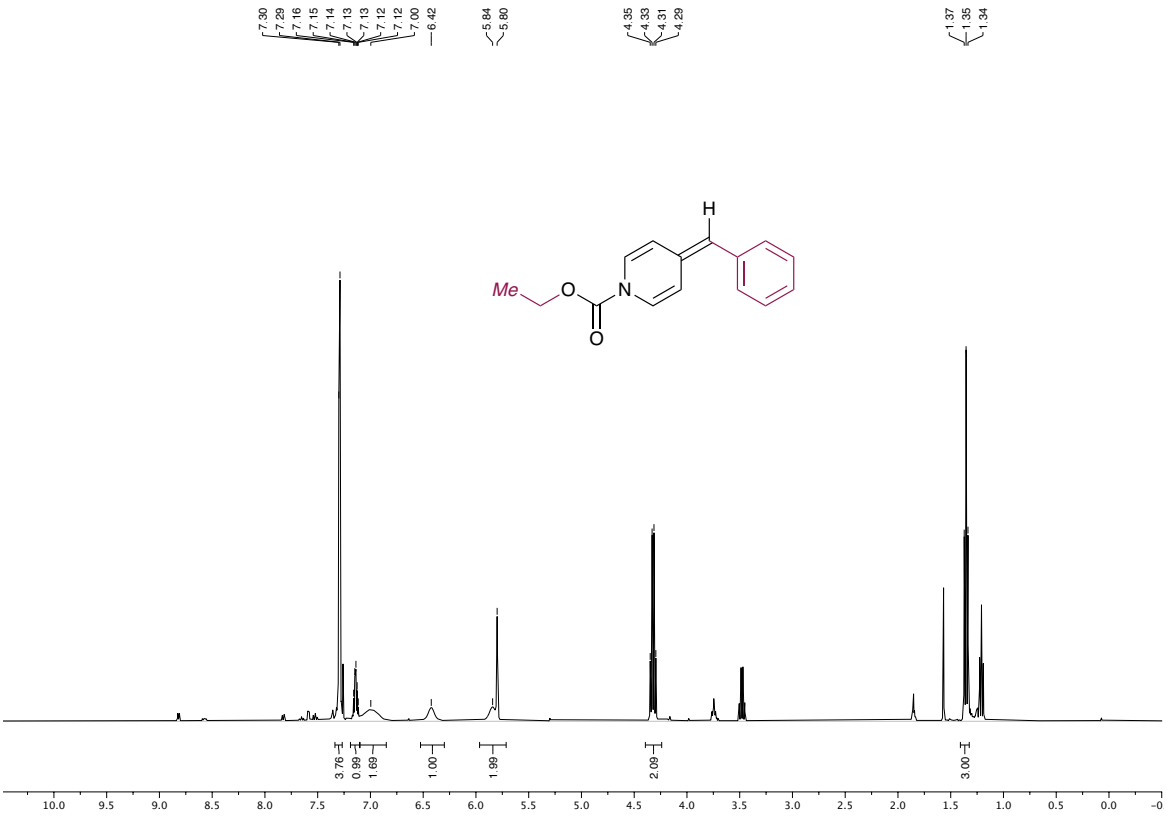
$^{13}C\{^{1}H\}$-NMR of ADHP derived from 4-ethylpyridine and trichloroethyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

δ 149.1, 127.9, 123.7, 123.0, 121.5, 121.3, 120.8, 117.0, 116.5, 112.4, 110.4, 109.8, 94.7, 75.6,12.5.

^{1}H-NMR of ADHP derived from 4-benzylpyridine and ethyl chloroformate



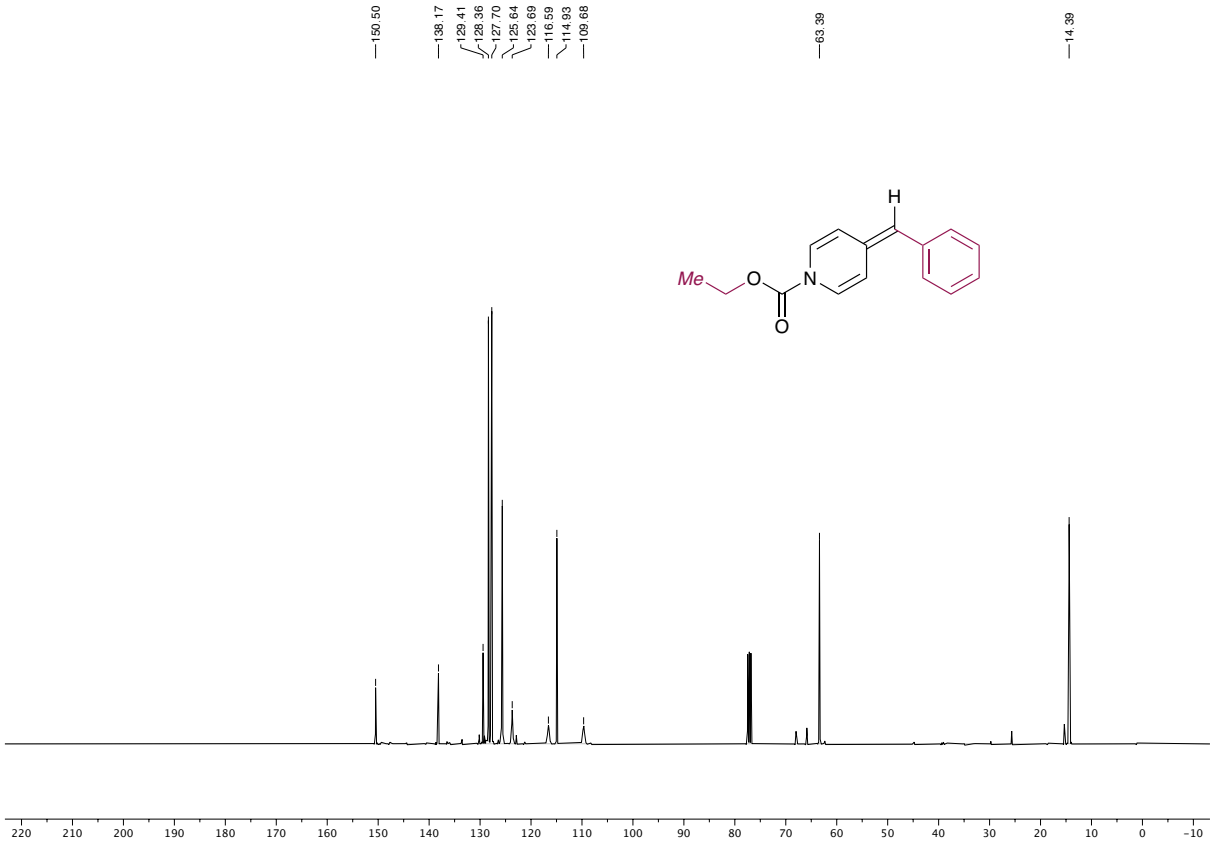
^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.30-7.29 (m, 4H), 7.14 (m, 1H), 7.00 (br s, 2H), 6.42 (br s, 1H), 5.84 (br s, 1H), 5.80 (s, 1H), 4.32 (q, J = 7.1, 2H), 1.35 (t, J = 7.1 Hz, 3H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{15}H_{16}NO_2$ 242.1181; Found 242.1170

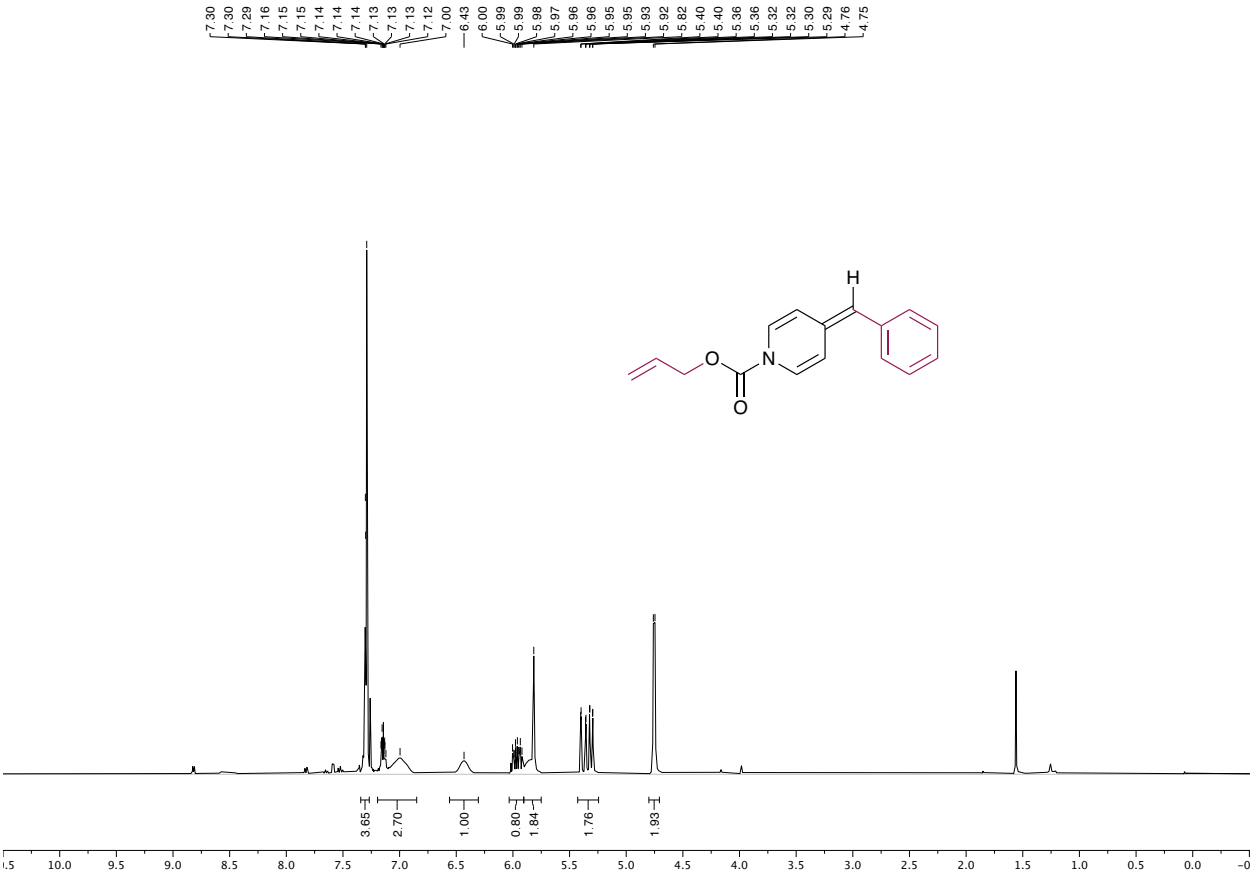
$^{13}C\{^{1}H\}$-NMR of ADHP derived from 4-benzylpyridine and ethyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

δ 150.5, 138.2, 129.4, 128.4, 127.7, 125.6, 123.7, 116.6, 114.9, 109.6, 63.4, 14.4.

^{1}H-NMR of ADHP derived from 4-benzylpyridine and allyl chloroformate



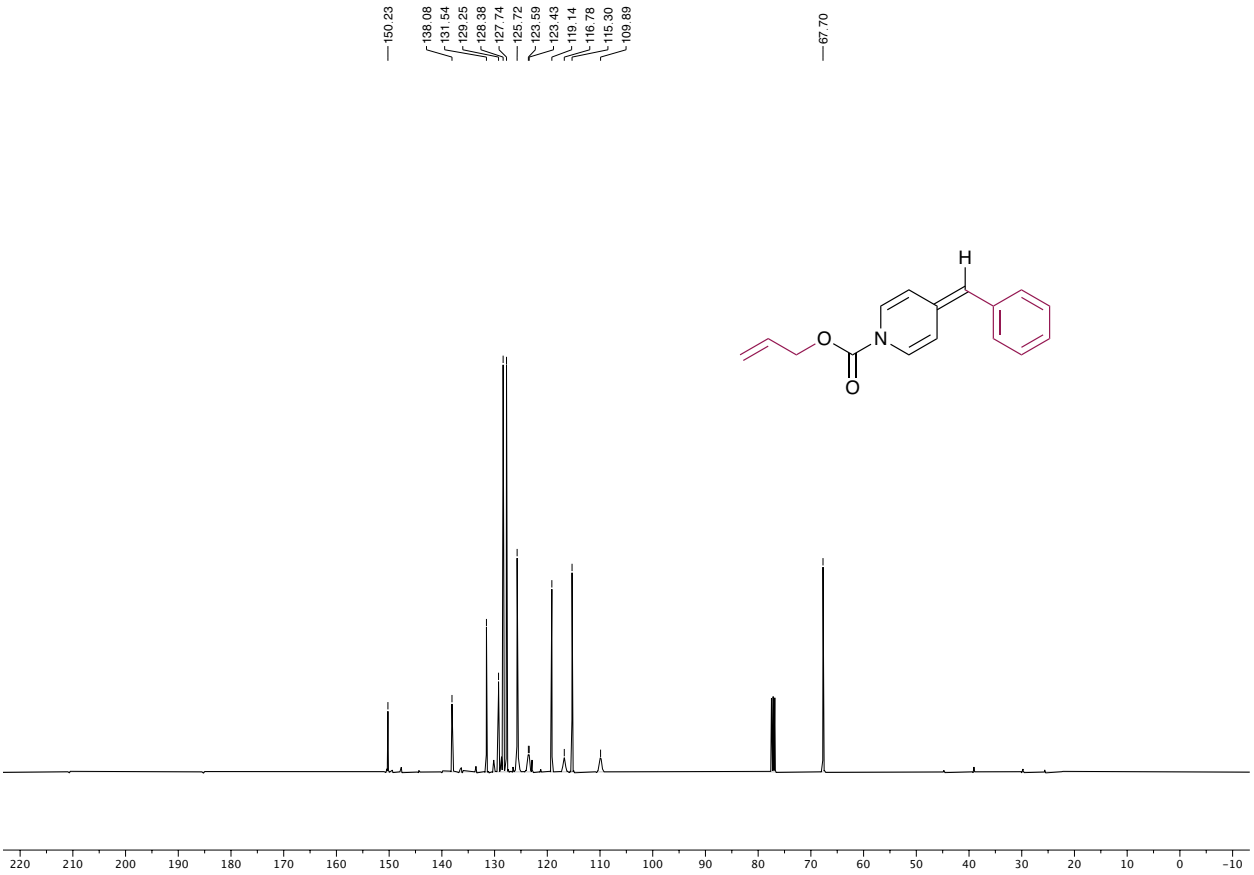
^{1}H NMR (400 MHz, $CDCl_3$):

δ 7.30-7.29 (m, 4H), 7.12-7.17 (m, 1H), 7.00 (br s, 2H), 6.43 (br s, 1H), 5.92-6.02 (m, 1H), 5.85 (br s, 1H), 5.81 (s, 1H), 5.38 (dq, J = 15.2, 1.7 Hz, 1H), 5.31 (dq, J = 10.4, 1.8 Hz, 1H), 4.75 (dt, J = 5.8, 1.3 Hz, 2H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{16}H_{16}NO_2$ 254.1181; Found 254.1174

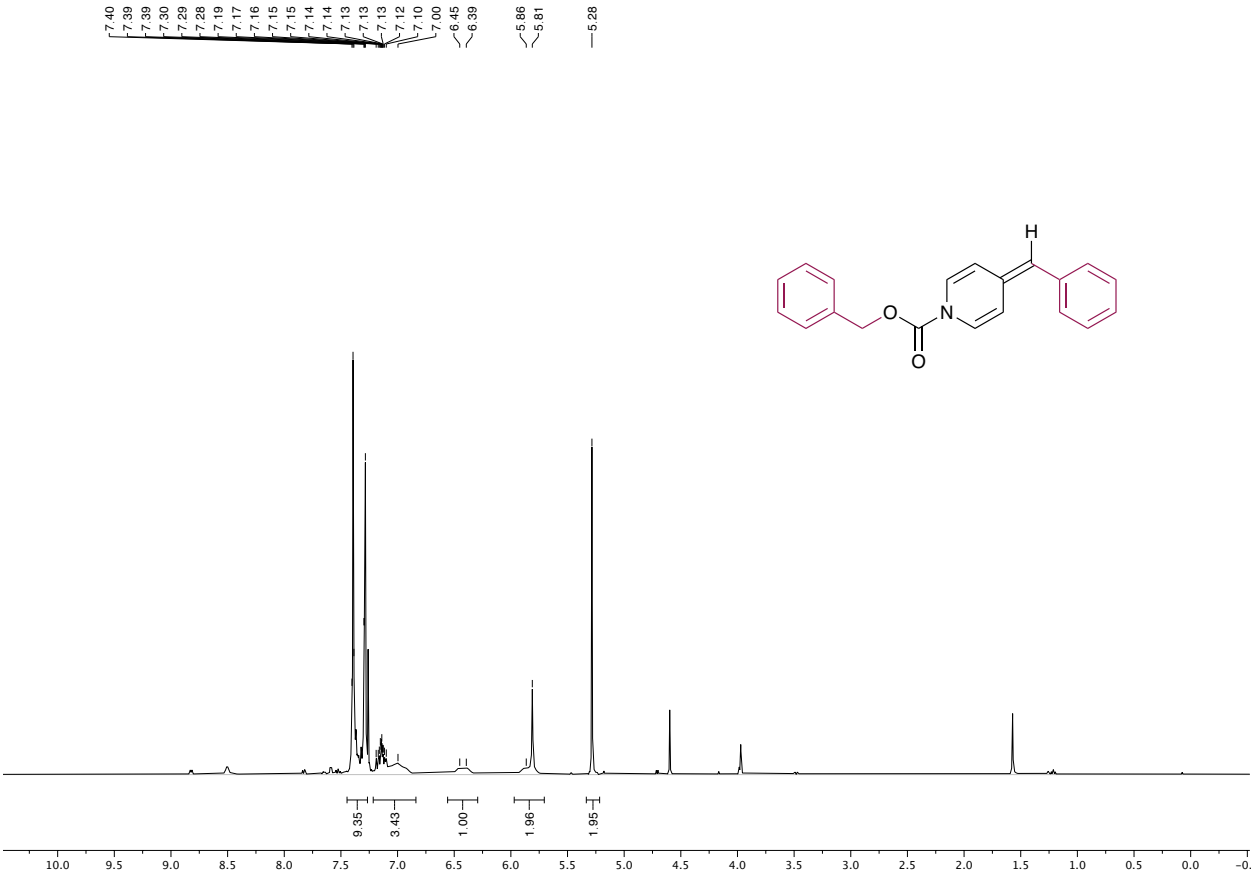
$^{13}C\{^{1}H\}$-NMR of ADHP derived from 4-benzylpyridine and allyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$):

δ 150.2, 138.1, 131.5, 129.2, 128.4, 127.7, 125.7, 125.6, 123.6, 119.1, 116.8, 115.3, 109.9, 67.7.

^{1}H-NMR of ADHP derived from 4-benzylpyridine and benzyl chloroformate



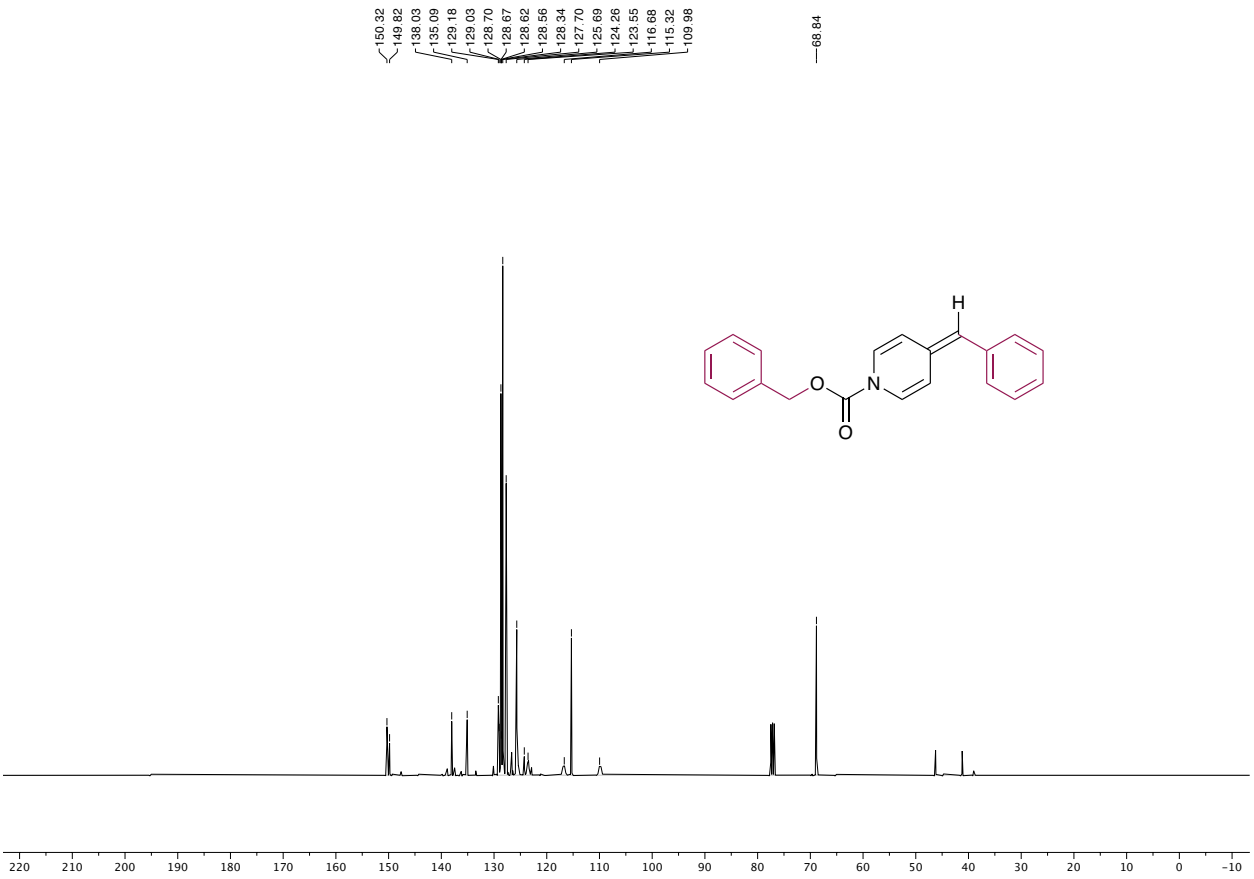
^{1}H NMR (400 MHz, $CDCl_3$):

δ 7.39-7.40 (m, 4H), 7.28-7.30 (m, 4H), 7.14 (m, 2H), 7.00 (br s, 2H), 6.42 (br s, 1H), 5.87 (br s, 1H), 5.81 (s, 1H), 5.28 (s, 2H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{20}H_{18}NO_2$ 304.1338; Found 304.1328

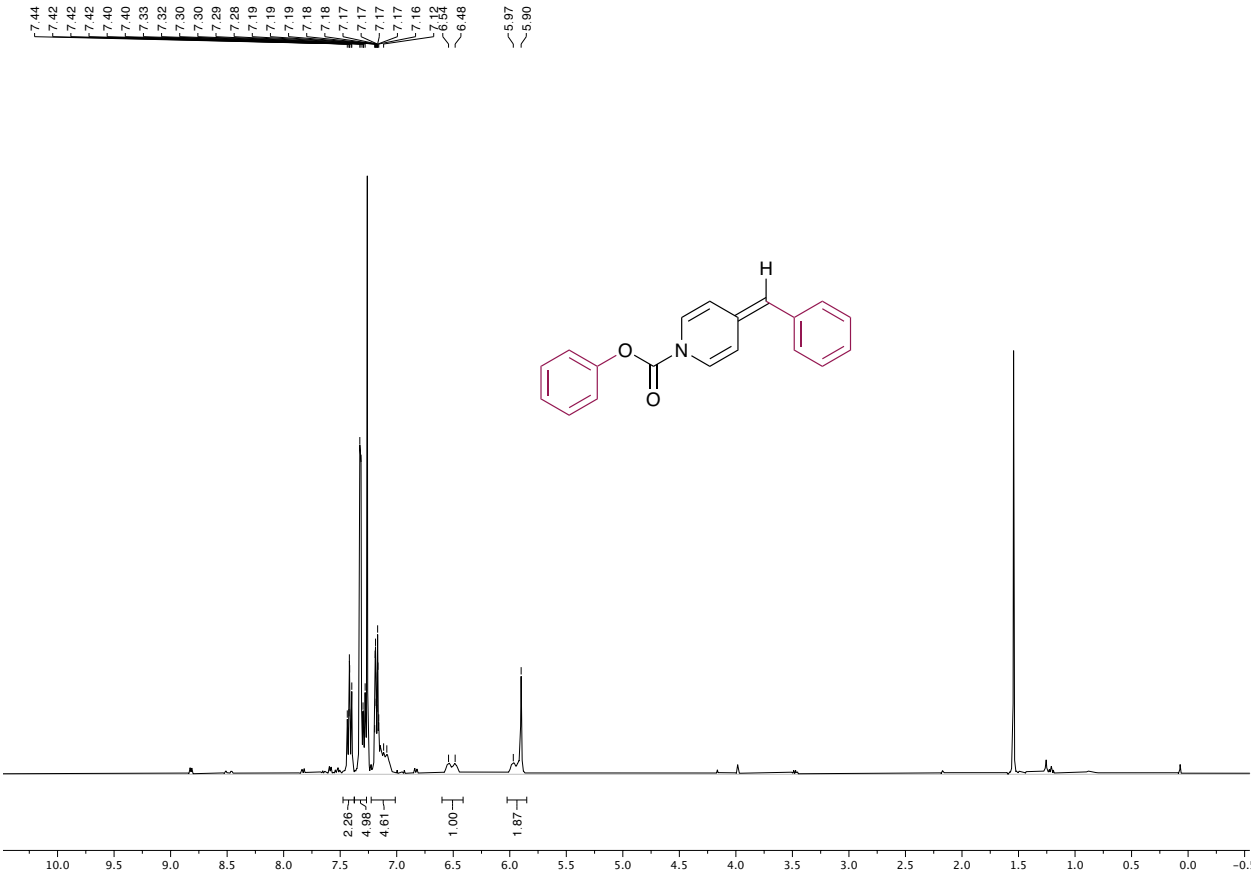
$^{13}C\{^{1}H\}$-NMR of ADHP derived from 4-benzylpyridine and benzyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$):

δ 150.3, 149.8, 138.1, 135.2, 129.3, 129.1, 128.8, 128.6, 128.4, 127.8, 125.8, 125.6, 123.7, 116.9, 115.4, 110.0, 68.9.

[1]H-NMR of ADHP derived from 4-benzylpyridine and phenyl chloroformate



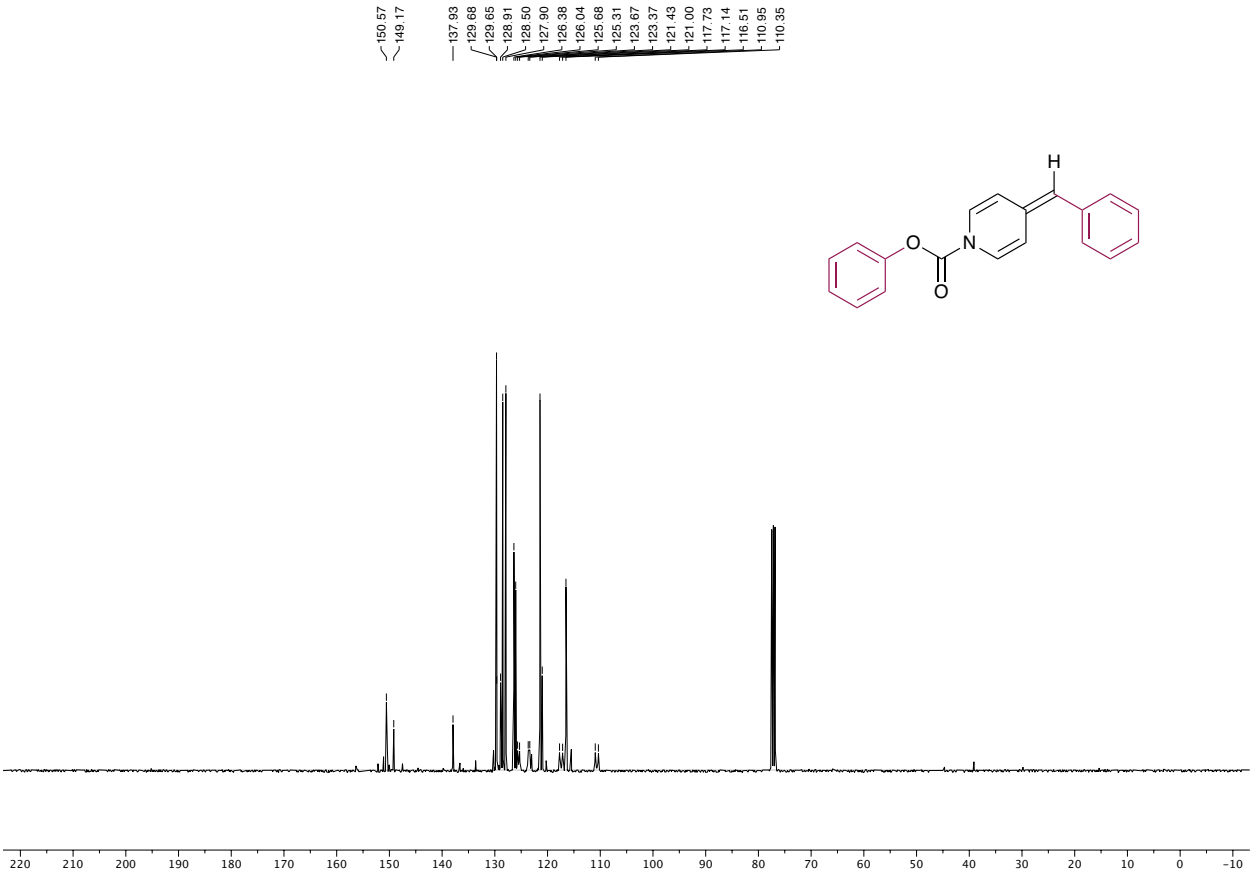
[1]H-NMR (400 MHz, $CDCl_3$):

δ 7.45-7.39 (m, 2H), 7.35-7.27 (m, 5H), 7.21-7.15 (m, 3H), 7.14-7.02 (br m, 2H), 6.51 (br d, J = 24 Hz, 1H), 6.02-5.91 (br s, 1H), 5.90 (s, 1H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{19}H_{16}NO_2$ 290.1181; Found 290.1175

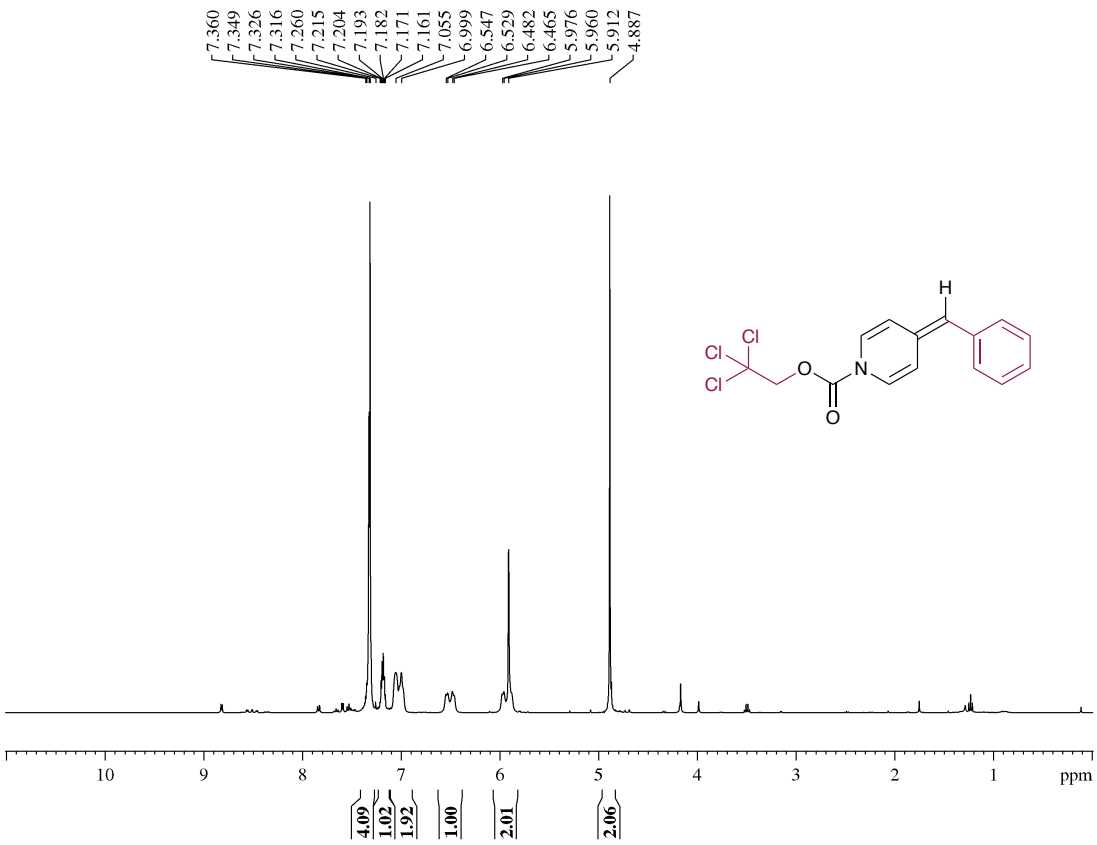
$^{13}C\{^{1}H\}$-NMR of ADHP derived from 4-benzylpyridine and phenyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$):

δ 150.6, 149.2, 137.9, 129.7, 128.9, 128.5, 127.9, 126.4, 126.0, 125.7, 125.3, 123.6, 123.4, 121.4, 121.0, 117.7, 117.1, 116.5, 110.9, 110.4.

[1]H-NMR of ADHP derived from 4-benzylpyridine and trichloroethyl chloroformate



[1]H-NMR (400 MHz, $CDCl_3$)

δ 7.22-7.36 (m, 4H), 7.18 (t, J = 8.0 Hz, 1H), 7.03 (br m, 2H),

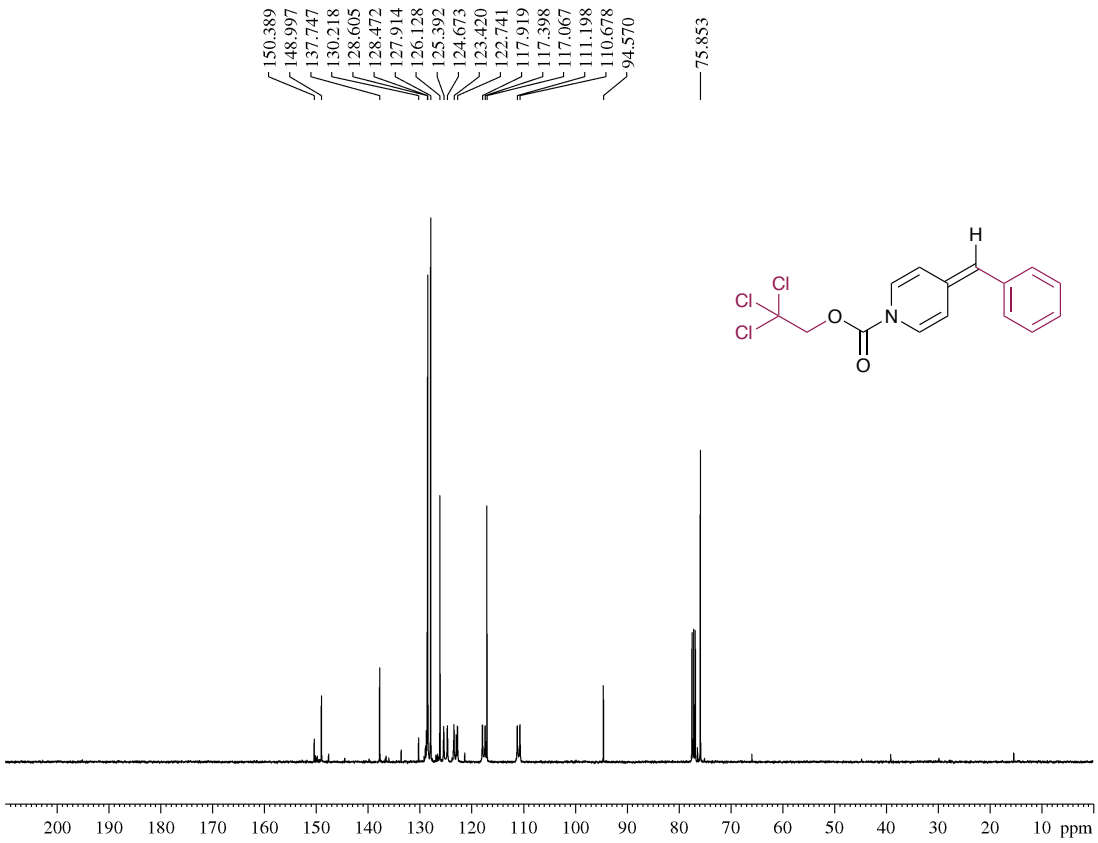
6.51 (br dd, J = 18.9, 6.9 Hz, 1H), 5.96 (d, J = 6.6 Hz, 1H), 5.91 (s, 1H),

4.89 (s, 2H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{15}H_{13}Cl_3NO_2$ 344.0012; Found 344.0006

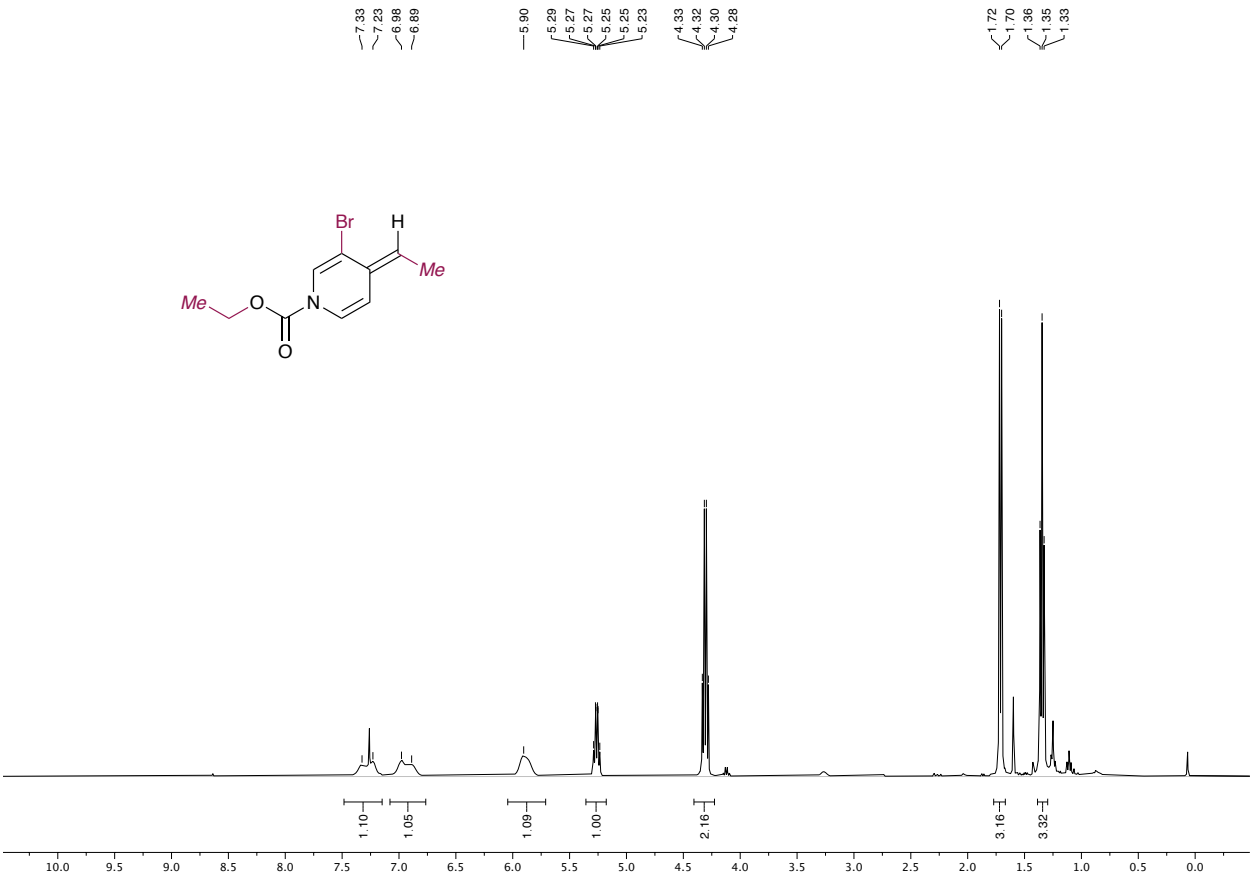
$^{13}C\{^{1}H\}$-NMR of ADHP derived from 4-benzylpyridine and trichloroethyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

δ 150.4, 149.0, 137.7, 130.2, 128.6, 128.4, 127.9, 126.1, 125.4, 124.6, 123.4, 122.7, 117.9, 117.4, 117.0, 111.2, 110.7, 94.6, 75.9.

^{1}H-NMR of ADHP derived from 3-bromo-4-ethylpyridine and ethyl chloroformate



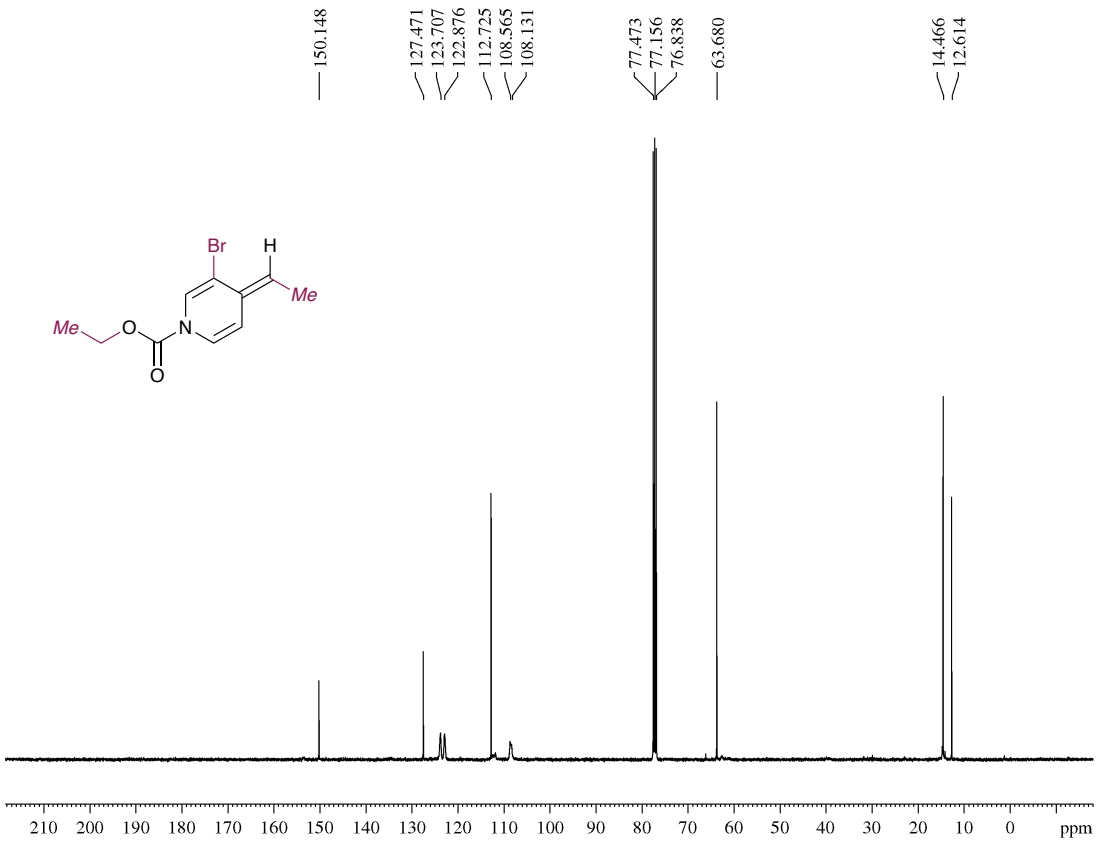
^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.39-7.29 (br m, 1H), 7.12-6.93 (br m, 1H), 5.90 (br s, 1H),
5.26 (q, J = 7.3 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.71 (d, J = 7.3 Hz, 3H),
1.35 (t, J = 7.1 Hz, 3H).

HRMS ESI-TOF

m/z [M+H] + calculated for $C_{10}H_{13}BrNO_2$ 258.0130; Found 258.0127

$^{13}C\{^{1}H\}$-NMR of ADHP derived from 3-bromo-4-ethylpyridine and ethyl chloroformate



$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

δ 150.1, 127.5, 123.7, 122.9, 112.7, 108.6, 108.1, 63.7, 14.5, 12.6.

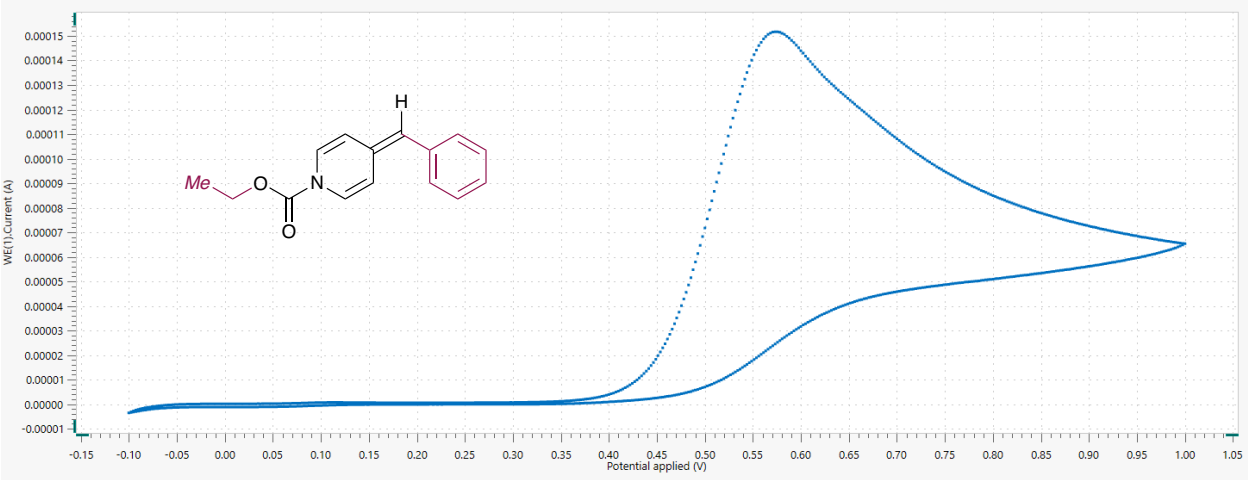
Measurement of oxidation potential of ADHPs by cyclic voltammetry

General cyclic voltammetry procedure

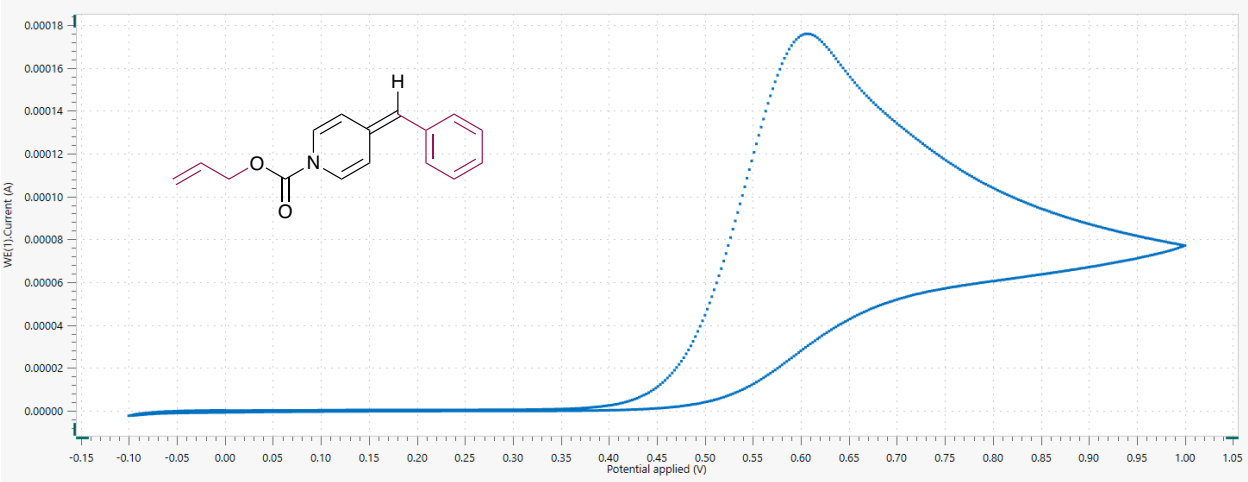
Cyclic voltammetry was performed with an Auto lab PGSTAT204 Potentiostat. The ADHP was prepared using general procedure 1, the resulting analyte was dissolved in anhydrous acetonitrile (0.1M) containing 0.0065M tetrabutylammonium hexafluorophosphate (NBu_4PF_6). Before the measurement was taken, this solution was purged with nitrogen gas for 5 minutes then sealed in a CV compatible chamber. A typical three-electrode cell was used with a Pt wire counter electrode, an Ag/AgCl reference electrode, and a glassy carbon working electrode were used to take oxidation potential measurements using a scan rate of 100 mV/s.

Only the ADHPs prepared from 4-benzylpyridine and 3-bromo-4-ethylpyridine were stable enough for cyclic voltammetry measurement.

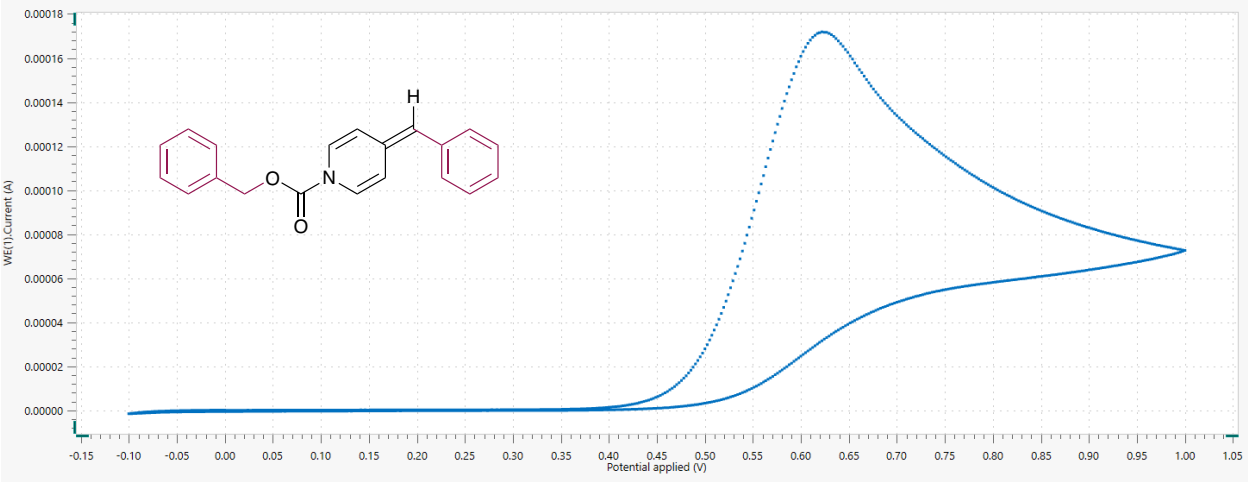
Cyclic voltammetry plot for the ADHP prepared from 4-benzylpyridine and ethyl chloroformate



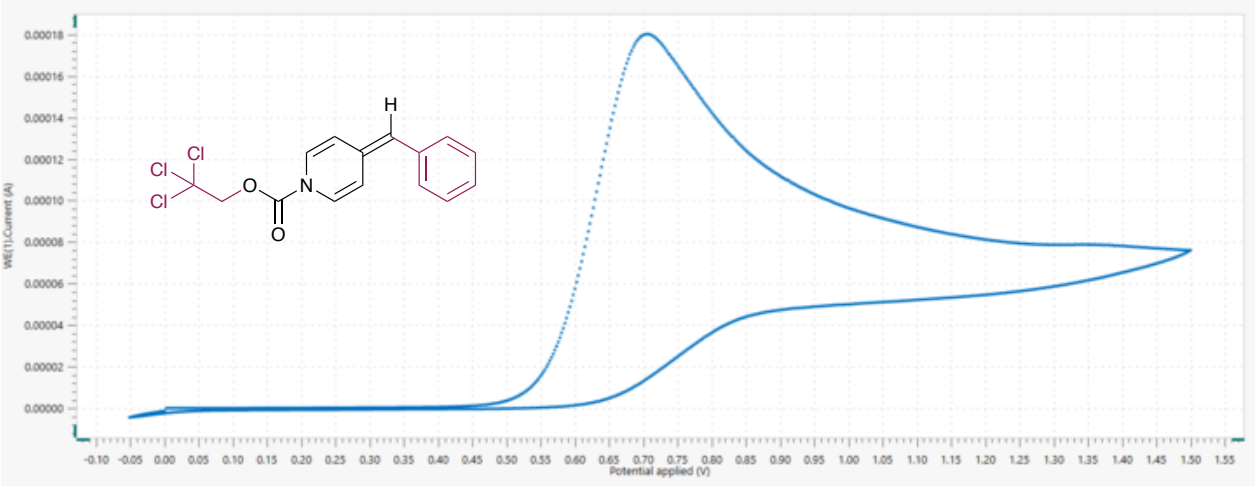
Cyclic voltammetry plot for the ADHP prepared from 4-benzylpyridine and allyl chloroformate



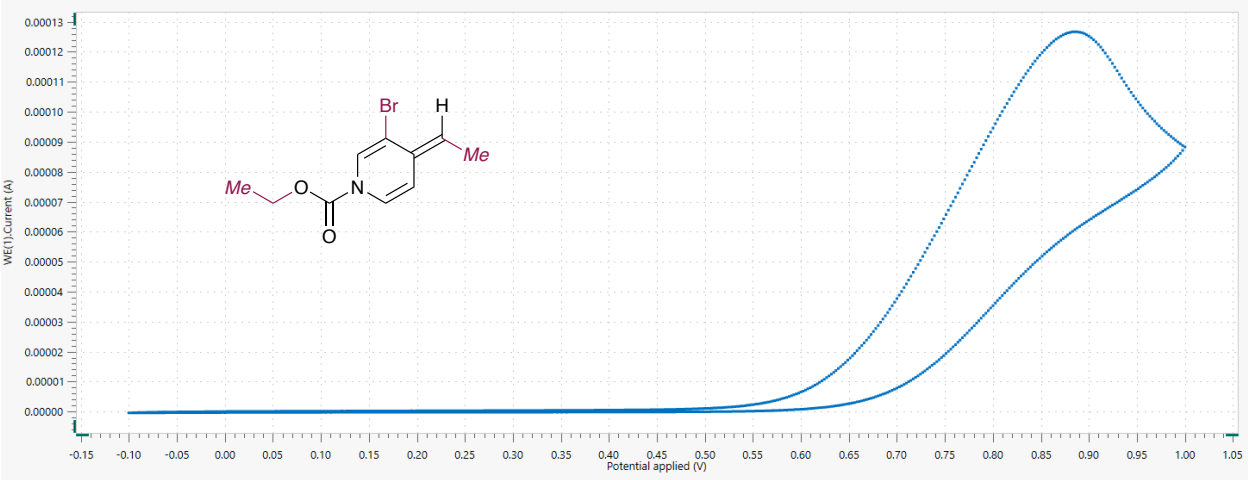
Cyclic voltammetry plot for the ADHP prepared from 4-benzylpyridine and benzyl chloroformate



Cyclic voltammetry plot for the ADHP prepared from 4-benzylpyridine and trichloroethyl chloroformate



Cyclic voltammetry plot for the ADHP prepared from 3-bromo-4-ethylpyridine and ethyl chloroformate



Calculation of oxidation potentials

Computational Methodology:

The oxidation potentials and ionization energies of the ADHPs were calculated using a well-established computational method, described in detail by Neese and co-workers.[1] In our study, the oxidation potential in the context of redox reactions was calculated using the Nernst equation (eq. 1), which is a standard method for evaluating the potential in redox reactions.

$$E^0_{RED/OX} = E^0_{SHE}(Ox) - \frac{\Delta G^0_{RED/OX}}{nF} \quad (1)$$

Where $E^0_{RED/OX}$ is the oxidation potential of the molecule of interest, $E^0_{SHE}(Ox)$ is the oxidation potential of standard hydrogen electrode, and $\Delta G^0_{RED/OX}$ is the free energy change for the molecule in going from reduced form to oxidized form in solution, i.e., the ionization potential. For a single-electron transfer redox reaction, such as the oxidation of ADHP, the aforementioned equation can be further simplified to

$$E^0_{RED/OX} = E^0_{SHE}(Ox) - \Delta G^0_{RED/OX} \quad (2)$$

where the energy unit has been chosen to eV, n is equal to 1 and F represents the elementary charge e. To calculate the oxidation potentials of the ADHPs, we followed the Born-Haber cycle methodology (see Figure S1), which enables the determination of ionization potentials in solution. The ionization potential represents the energy required to remove an electron from a neutral species, resulting in the formation of a monocationic species. This approach involves evaluating the energy difference between the oxidant and reductant using a combination of computational methods.

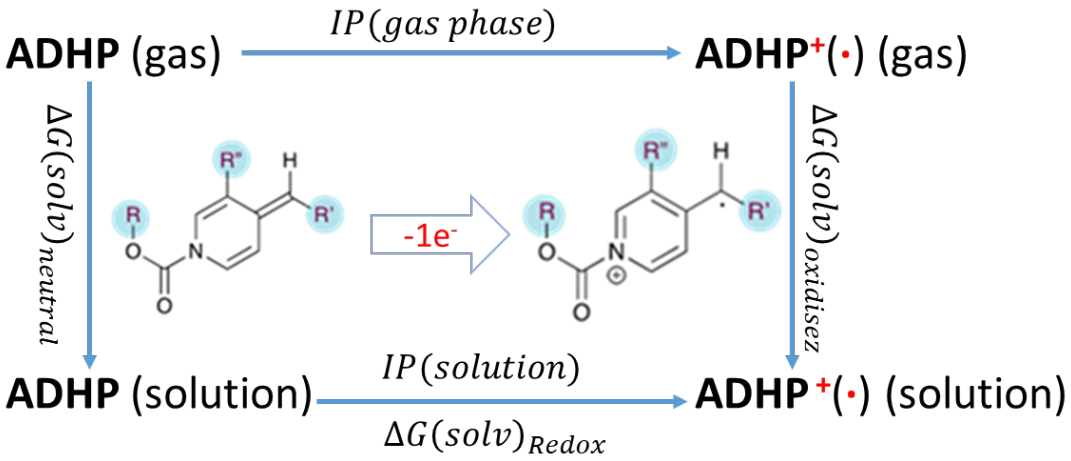


Figure S1. Born-Haber cycle for the one electron redox reaction of ADHP molecules.

The electronic structure calculations in this study were performed using the ORCA[2] quantum chemistry package. All structures of the neutral and monocationic forms of ADHPs were optimized at the ωB97X/cc-pVTZ/CPCM(acetonitrile)[3,4] basis set. The optimized geometries were confirmed to be minima on potential energy surfaces the absence of imaginary frequencies through hessian calculations. The zero-point energy (ZPE) and thermal energy corrections for the cationic and neutral species are obtained in these hessian calculations.

At the optimized structures of the cationic and neutral form of each ADHP species, single point calculations were performed at the DLPNO-CCSD(T)/cc-pVTZ/CPCM(acetonitrile)[5] level to obtain the electronic energies of the two forms. The two electronic energies are corrected with the ZPE and thermal energy corrections obtained in the respective hessian calculations. The subtraction of the so-obtained energies of the cationic and neutral forms gives the ionization potential of an ADHP species.

Finally, the calculated ionization potential was subtracted by the computationally estimated potential of 4.28 V, widely recognized as the standard hydrogen electrode (SHE) potential. The result of this subtraction is the calculated oxidation potential which is ready for comparison with experimental value.

By employing this well-established computational method, which includes the use of the Nernst equation and the Born-Haber cycle, we obtained accurate oxidation potentials and ionization energies of the ADHPs in solution, enabling meaningful correlations with experimental measurements.

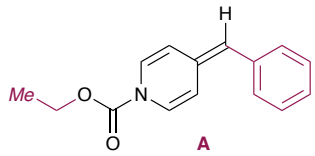
Results and Discussion:

All the calculated results are summarized in Table S1. All the optimized structures are summarized in the **Optimized Structures Section**. The calculated oxidation potentials (in V) for the series of ADHPs with different substituents are as follows: 0.57 for ethyl, 0.62 for allyl, 0.63 for benzyl, 0.67 for trichloroethyl, and 0.68 for phenyl-substituted ADHPs. Correspondingly, the ionization potentials for the same series of substituted ADHPs are 4.85, 4.90, 4.91, 4.95, and 4.96 eV, respectively.

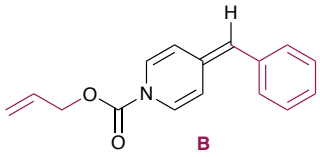
These calculated oxidation potentials and ionization potentials provide valuable insights into the trends observed in the electronic nature of ADHPs and their reactivity. Electron-donating groups, such as ethyl, result in the ADHP core structure with higher electron density, leading to lower ionization potentials or oxidation potentials. On the contrary, electron-withdrawing groups, such as allyl, benzyl, trichloroethyl, and phenyl, reduce the electron density in the ADHP core structure, leading to higher oxidation potentials.

Table S1: Computational results for ADHP molecules including solvent Gibbs free energy (G(solv)), energy corrections (ZPE and thermal), corrected G(solv), ionization energies (eV), and oxidation potentials (V)

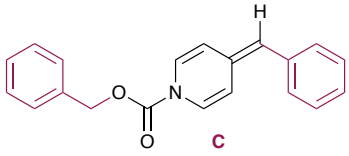
pyridine	$ClCO_2$ ***R***		G(solv)	Energy Corrections	Corrected G(solv)	IE	V_{ox}
4-benzyl	ethyl	$A^+(\cdot)$ A	-784.2758272	0.28655459	-783.98927	4.85	0.57
			-784.45401	0.28644215	-784.16757		
4-benzyl	allyl	$B^+(\cdot)$ B	-822.279838	0.29474267	-821.9851	4.90	0.62
			-822.458517	0.29310402	-822.16541		
4-benzyl	benzyl	$C^+(\cdot)$ C	-975.6433828	0.34568991	-975.29769	4.91	0.63
			-975.8226947	0.34442274	-975.47827		
4-benzyl	phenyl	$D^+(\cdot)$ D	-936.3993626	0.31492688	-936.08444	4.96	0.68
			-936.5811769	0.31449576	-936.26668		
4-benzyl	Cl_3CH_2-	$E^+(\cdot)$ E	-2161.65378	0.26343745	-2161.39034	4.95	0.67
			-2161.834545	0.26237318	-2161.57217		
4-ethyl	ethyl	$F^+(\cdot)$ F	-592.8957385	0.23149826	-592.66424	4.94	0.66
			-593.0764067	0.2305738	-592.84583		
3-bromo-4-ethyl	ethyl	$G^+(\cdot)$ G	-3164.993655	0.22227945	-3164.77137	5.13	0.85
			-3165.181714	0.22193379	-3164.95978		



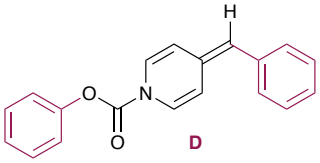
A



B



C



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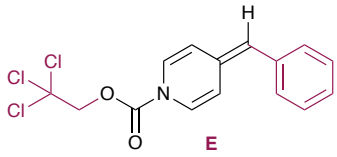

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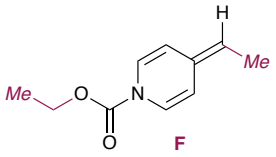

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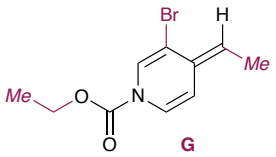
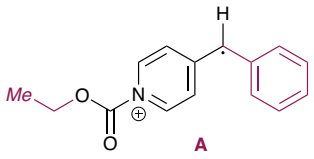


G

Optimized Structures:

compound_A_CH2CH3_cat_wb97x_ccPVTZ_opt_freq_opt.xyz

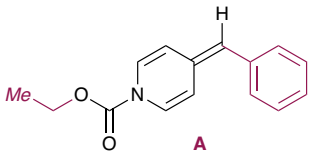
C	-2.030612	2.917075	0.663036
C	-3.226345	2.273061	0.626831
C	-0.819384	2.181881	0.688895
C	0.413383	2.864395	0.830700
C	-0.928418	0.779019	0.537741
C	-2.144302	0.178188	0.504148
N	-3.283582	0.916267	0.581751
H	-2.020679	3.996155	0.721645
H	-4.177979	2.780383	0.653771
H	0.391721	3.924854	0.604108
H	-0.054595	0.160510	0.415187
H	-2.264444	-0.887486	0.403756
C	-4.591514	0.291326	0.633997
O	-5.590795	0.948212	0.648250
O	-4.473953	-1.003475	0.682305
C	1.675916	2.328471	1.237869
C	1.826855	1.101966	1.913666
H	0.959441	0.522442	2.192169
C	3.076138	0.648823	2.283739
H	3.168266	-0.294423	2.804937
C	4.210074	1.403476	2.006771
H	5.183963	1.038286	2.307999
C	4.081084	2.633336	1.369735
H	4.959074	3.229722	1.159144
C	2.834037	3.096609	1.002345
H	2.737862	4.056820	0.510818
C	-5.715616	-1.760606	0.824536
H	-6.264465	-1.332421	1.659397
H	-6.287835	-1.618217	-0.089741
C	-5.340033	-3.198752	1.056236
H	-4.686678	-3.302490	1.920254
H	-6.247166	-3.770309	1.249554
H	-4.834271	-3.614130	0.184681



A

compound_A_CH2CH3_neu_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-2.075450	2.957088	0.607732
C	-3.241560	2.309462	0.591951
C	-0.800106	2.250122	0.712856
C	0.356109	2.910453	0.927653
C	-0.929611	0.803904	0.550532
C	-2.115786	0.196014	0.512554
N	-3.309745	0.914228	0.605426
H	-2.081206	4.039234	0.592898
H	-4.198353	2.806478	0.569424
H	0.317361	3.995777	0.906460
H	-0.048393	0.194193	0.420635
H	-2.218676	-0.868195	0.379089
C	-4.553036	0.302348	0.691654
O	-5.589067	0.922015	0.779738
O	-4.448967	-1.017624	0.677318
C	1.670612	2.334893	1.252567
C	1.808724	1.149452	1.981833
H	0.927711	0.614922	2.309991
C	3.056223	0.663433	2.337623
H	3.126804	-0.255107	2.906063
C	4.206650	1.354977	1.988515
H	5.177011	0.975835	2.285482
C	4.089329	2.542879	1.277551
H	4.975669	3.100500	1.000017
C	2.840046	3.027133	0.921884
H	2.765432	3.964129	0.382650
C	-5.680341	-1.766341	0.811297
H	-6.239547	-1.360164	1.650594
H	-6.263443	-1.622712	-0.097447
C	-5.311216	-3.212435	1.021734
H	-4.662191	-3.332641	1.887426
H	-6.218210	-3.790111	1.198346
H	-4.797628	-3.615168	0.148185



A

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C	-2.112197	2.762861	-0.199781
C	-3.397152	2.327615	-0.237202
C	-1.105250	2.008324	0.454479
C	0.197980	2.546864	0.537774
C	-1.519601	0.791433	1.047465
C	-2.816060	0.393603	0.981880
N	-3.747150	1.152765	0.348552
H	-1.868350	3.701992	-0.675705
H	-4.196611	2.868745	-0.717736
H	0.283218	3.579687	0.217416
H	-0.838778	0.171409	1.604512
H	-3.165348	-0.519535	1.433283
C	-5.142429	0.756546	0.285553
O	-5.979642	1.507220	-0.118860
O	-5.292465	-0.468098	0.704349
C	1.397049	1.959815	1.058180
C	1.638569	0.576063	1.150585
H	0.929376	-0.129178	0.744618
C	2.810403	0.101264	1.704667
H	2.991181	-0.964552	1.756654
C	3.767374	0.988892	2.183896
H	4.676952	0.610222	2.631329
C	3.563990	2.359458	2.069816
H	4.314939	3.049853	2.428733
C	2.408066	2.840910	1.488765
H	2.257319	3.907868	1.377748
C	-6.644876	-1.021737	0.589457
H	-7.309969	-0.376221	1.159097
H	-6.927991	-1.002683	-0.461765
C	-6.588655	-2.406779	1.134152
H	-6.520665	-2.501764	2.212215
C	-6.605467	-3.480172	0.361642
H	-6.563261	-4.474466	0.787283
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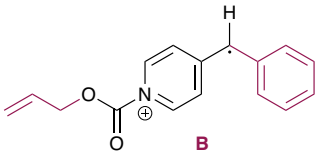

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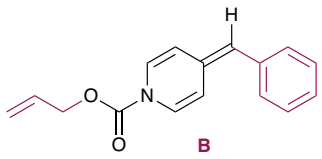
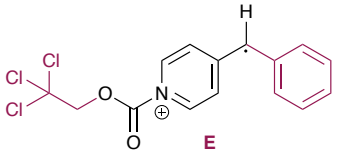
C	-2.300008	3.072601	0.948698
C	-3.563679	2.657283	0.857483
C	-1.158495	2.159994	0.900122
C	0.087326	2.637045	1.106601
C	-1.549545	0.768858	0.683504
C	-2.830204	0.397540	0.594734
N	-3.880352	1.308005	0.683104
H	-2.116853	4.131675	1.073526
H	-4.403695	3.329709	0.896933
H	0.144158	3.694125	1.352333
H	-0.805016	-0.009265	0.631765
H	-3.132723	-0.628858	0.460179
C	-5.188500	0.850310	0.571038
O	-5.469956	-0.277055	0.238517
O	-6.059600	1.799771	0.888351
C	1.385473	1.954063	1.165848
C	1.712342	0.772258	0.491837
H	0.996343	0.296462	-0.162211
C	2.972684	0.206228	0.617895
H	3.201709	-0.706622	0.082141
C	3.941831	0.803137	1.410806
H	4.919749	0.351080	1.519313
C	3.646408	1.995052	2.059267
H	4.398092	2.489309	2.661638
C	2.389702	2.559156	1.933241
H	2.169754	3.489183	2.444780
C	-7.465576	1.527117	0.678516
H	-7.653835	0.474054	0.882561
H	-7.977113	2.140767	1.415011
C	-7.864353	1.922963	-0.707981
H	-7.390306	1.384689	-1.523666
C	-8.753083	2.876288	-0.942481
H	-9.055010	3.154963	-1.944866
H	-9.221328	3.411965	-0.124641



compound_E_CH2CCl3_cat_wb97x_ccPVTZ_opt_freq_opt.xyz

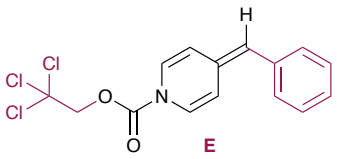
C	-5.583078	4.087556	1.580245
C	-6.006088	3.025306	0.852035
C	-5.881831	4.176540	2.960391
C	-5.390486	5.280176	3.693873
C	-6.709537	3.162360	3.504585
C	-7.166027	2.151997	2.720627
N	-6.792866	2.070586	1.417922
H	-4.991221	4.849951	1.095496
H	-5.768831	2.896888	-0.191436
H	-5.090536	6.144106	3.110614
H	-7.036659	3.197315	4.531752
H	-7.824835	1.374055	3.075058
C	-7.364218	1.028665	0.601320
O	-8.465429	0.617117	0.787251
O	-6.487709	0.671583	-0.312888
C	-6.947932	0.005110	-1.491563
H	-6.692791	-1.050798	-1.434317
H	-8.021581	0.138817	-1.610746
C	-6.212042	0.653375	-2.661569
C	-5.253440	5.379108	5.113439
C	-5.125339	4.252637	5.947038
H	-5.051580	3.264150	5.514720
C	-5.038755	4.399739	7.315541
H	-4.938110	3.524121	7.942572
C	-5.058090	5.668599	7.883899
H	-4.993940	5.779455	8.958438
C	-5.122758	6.796834	7.071090
H	-5.105965	7.784179	7.512684
C	-5.203746	6.657170	5.700204
H	-5.259808	7.531015	5.063014
Cl	-4.467832	0.413345	-2.518319
Cl	-6.788639	-0.067368	-4.155397
Cl	-6.542532	2.392449	-2.693675



E

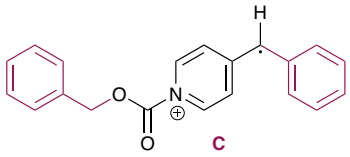
compound_E_CH2CCl3_neu_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-5.708860	4.228705	1.441650
C	-6.095723	3.137707	0.784238
C	-5.904127	4.362503	2.881197
C	-5.252082	5.296786	3.595546
C	-6.844910	3.383348	3.429755
C	-7.268962	2.337244	2.722027
N	-6.823309	2.117076	1.416388
H	-5.177268	4.998189	0.898360
H	-5.898989	2.989305	-0.263500
H	-4.676163	6.037921	3.050041
H	-7.227928	3.512297	4.431564
H	-7.960772	1.599695	3.096794
C	-7.175580	0.950256	0.771559
O	-8.057843	0.207557	1.123064
O	-6.372522	0.743055	-0.280700
C	-6.877864	0.022770	-1.391643
H	-6.579824	-1.023442	-1.347257
H	-7.962443	0.105619	-1.450834
C	-6.255084	0.666392	-2.628384
Cl	-4.493334	0.518097	-2.588275
Cl	-6.880995	-0.133998	-4.062831
Cl	-6.670573	2.384032	-2.705078
C	-5.206528	5.372604	5.063337
C	-5.086910	4.215747	5.838781
H	-4.997636	3.253943	5.350202
C	-5.057420	4.281439	7.221598
H	-4.973424	3.368824	7.798357
C	-5.114785	5.511816	7.860923
H	-5.088087	5.565702	8.941655
C	-5.181675	6.673937	7.102178
H	-5.204980	7.638843	7.592421
C	-5.223520	6.605269	5.717948
H	-5.285798	7.514974	5.132199



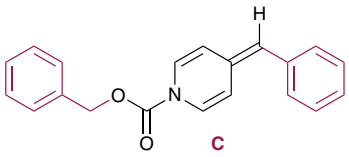
compound_C_CH2Ph_cat_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-2.057785	2.654885	-0.203699
C	-3.364717	2.301751	-0.288482
C	-1.150861	1.933611	0.615522
C	0.197660	2.367846	0.609514
C	-1.706973	0.856719	1.352534
C	-3.021942	0.536020	1.234007
N	-3.844821	1.244091	0.415622
H	-1.713557	3.499581	-0.780977
H	-4.083332	2.818823	-0.902852
H	0.353798	3.264358	0.022086
H	-1.128352	0.263857	2.037802
H	-3.469023	-0.277895	1.778753
C	-5.252363	0.923607	0.263096
O	-5.968962	1.610004	-0.403298
O	-5.542436	-0.154858	0.936000
C	1.395302	1.846312	1.188424
C	1.502952	0.684103	1.978809
H	0.637599	0.094049	2.225492
C	2.725842	0.266721	2.458810
H	2.783210	-0.629134	3.060994
C	3.882646	0.982101	2.167329
H	4.836207	0.636516	2.547456
C	3.804896	2.133273	1.389316
H	4.699747	2.692765	1.149483
C	2.583527	2.561153	0.913186
H	2.526610	3.460407	0.313261
C	-6.936644	-0.578765	0.981067
H	-7.555043	0.300277	0.811261
H	-7.098682	-1.287770	0.171776
C	-7.177875	-1.208909	2.323649
C	-7.924611	-2.376937	2.416797
H	-8.299391	-2.853254	1.517342
C	-8.193854	-2.935776	3.659676
H	-8.770890	-3.848636	3.725054
C	-7.712103	-2.336701	4.813406
H	-7.928984	-2.778098	5.778688
C	-6.947061	-1.179273	4.722398
H	-6.550750	-0.712848	5.616468
C	-6.685921	-0.616479	3.483346
H	-6.096224	0.289293	3.418551



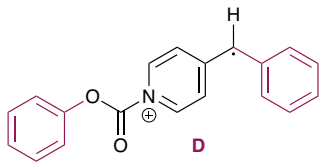
compound_C_CH2Ph_neu_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-1.953916	2.573260	-0.513973
C	-3.249875	2.278700	-0.421842
C	-0.936496	1.906698	0.296237
C	0.349659	2.301795	0.234004
C	-1.479335	0.870912	1.173334
C	-2.789009	0.620506	1.246359
N	-3.721366	1.310195	0.470247
H	-1.646491	3.336466	-1.214656
H	-4.013237	2.762298	-1.008601
H	0.559210	3.155277	-0.402099
H	-0.824766	0.299109	1.812878
H	-3.196911	-0.119737	1.912242
C	-5.089781	1.091298	0.542420
O	-5.880432	1.653806	-0.178435
O	-5.394841	0.208296	1.488435
C	1.516933	1.795374	0.973249
C	1.748505	0.445790	1.253273
H	1.053249	-0.302784	0.895844
C	2.882911	0.045979	1.947809
H	3.051438	-1.004002	2.156151
C	3.810160	0.984663	2.375806
H	4.691675	0.671438	2.919482
C	3.604463	2.327042	2.087586
H	4.325334	3.066426	2.412233
C	2.478182	2.723423	1.387351
H	2.330947	3.769985	1.145679
C	-6.773556	-0.153790	1.656567
H	-7.155870	0.400683	2.513240
H	-7.334150	0.149498	0.775077
C	-6.893870	-1.635700	1.890618
C	-8.170002	-2.167946	2.058692
H	-9.032822	-1.512546	2.017077
C	-8.340092	-3.524827	2.274478
H	-9.335104	-3.929306	2.411084
C	-7.234553	-4.366568	2.321941
H	-7.366411	-5.425816	2.502273
C	-5.964043	-3.839220	2.157161
H	-5.096092	-4.484408	2.204120
C	-5.793110	-2.478614	1.938624
H	-4.797456	-2.078863	1.805313



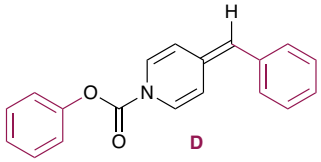
compound_D_Ph_cat_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-2.108578	2.883007	0.136625
C	-3.356410	2.389051	-0.064566
C	-1.139630	2.144614	0.862824
C	0.166174	2.681207	0.962701
C	-1.579665	0.925855	1.432856
C	-2.831922	0.463240	1.196342
N	-3.703321	1.172917	0.432760
H	-1.855604	3.842169	-0.292060
H	-4.121639	2.906034	-0.621313
H	0.248051	3.714272	0.642215
H	-0.955506	0.341574	2.084636
H	-3.191792	-0.467333	1.601332
C	-5.026175	0.676440	0.144832
O	-5.893925	1.380832	-0.264746
O	-5.077932	-0.616166	0.393408
C	1.402673	2.060309	1.315385
C	1.584427	0.677312	1.520607
H	0.754707	-0.007379	1.465311
C	2.843493	0.157084	1.731048
H	2.960869	-0.909609	1.868561
C	3.957739	0.989828	1.755767
H	4.942176	0.568253	1.911324
C	3.802943	2.359947	1.574405
H	4.666464	3.011217	1.591429
C	2.547076	2.887780	1.354749
H	2.428097	3.951898	1.189486
C	-6.333249	-1.241164	0.230977
C	-7.087541	-1.455604	1.363205
H	-6.728848	-1.110300	2.324149
C	-8.302398	-2.109982	1.221332
H	-8.908775	-2.305216	2.095558
C	-8.734724	-2.516973	-0.032477
H	-9.687143	-3.019002	-0.136872
C	-7.949311	-2.289086	-1.153723
H	-8.291824	-2.614602	-2.127741
C	-6.724231	-1.650822	-1.026559
H	-6.089446	-1.465402	-1.883015



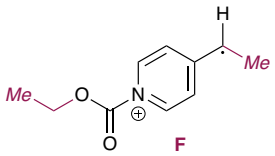
compound_D_Ph_neu_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-2.066715	2.934445	-0.349852
C	-3.293267	2.425884	-0.454516
C	-0.982649	2.222263	0.323508
C	0.241471	2.754079	0.468963
C	-1.374169	0.914174	0.840517
C	-2.617090	0.448549	0.729279
N	-3.621356	1.175281	0.080605
H	-1.869779	3.903350	-0.790090
H	-4.106682	2.932499	-0.948206
H	0.406662	3.764488	0.106450
H	-0.646523	0.301904	1.351974
H	-2.916466	-0.505379	1.129345
C	-4.919773	0.723041	-0.047208
O	-5.794952	1.333962	-0.605864
O	-5.072792	-0.473390	0.537044
C	1.394128	2.074684	1.099316
C	1.893723	0.877405	0.589527
H	1.415983	0.428970	-0.273452
C	2.995827	0.262118	1.167118
H	3.378487	-0.659234	0.744930
C	3.616397	0.834126	2.269112
H	4.470768	0.350870	2.725426
C	3.127470	2.024891	2.788080
H	3.605961	2.480029	3.646121
C	2.032362	2.642699	2.201958
H	1.650905	3.569899	2.614755
C	-6.313315	-1.110895	0.461152
C	-6.964426	-1.355123	1.653739
H	-6.543327	-0.979580	2.577507
C	-8.144387	-2.087195	1.631610
H	-8.658225	-2.307286	2.558594
C	-8.663089	-2.540470	0.428466
H	-9.587473	-3.102156	0.414637
C	-7.993025	-2.277405	-0.759314
H	-8.396541	-2.637458	-1.697829
C	-6.801388	-1.566808	-0.749206
H	-6.257435	-1.371031	-1.663444



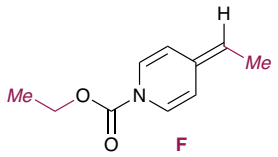
compound_F_C2H5_Me_cat_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-5.484356	4.247822	1.558280
C	-5.994011	3.266824	0.773329
C	-5.541735	4.156949	2.974393
C	-5.089635	5.235022	3.744881
C	-6.100691	2.967024	3.513280
C	-6.579393	2.003152	2.685496
N	-6.544871	2.154625	1.332654
H	-5.048940	5.116982	1.087138
H	-5.996959	3.317399	-0.302418
H	-4.651796	6.060942	3.197582
H	-6.150571	2.794193	4.578787
H	-7.010577	1.079085	3.038754
C	-7.065750	1.073387	0.514895
O	-7.437642	0.053712	1.015948
O	-7.034242	1.400521	-0.745729
C	-7.353759	0.359646	-1.725917
H	-6.774045	0.656543	-2.594816
H	-6.978888	-0.582158	-1.332450
C	-8.829039	0.311786	-2.027789
H	-9.184251	1.281351	-2.377231
H	-9.003826	-0.414082	-2.821097
H	-9.400818	-0.003903	-1.155562
C	-5.184265	5.384526	5.208876
H	-5.550213	4.495610	5.717607
H	-4.214694	5.682649	5.615823
H	-5.863032	6.208436	5.444967



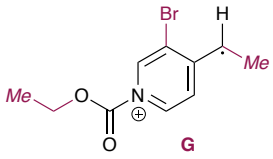
compound_F_C2H5_Me_neu_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-5.404201	4.222168	1.532004
C	-5.898516	3.263032	0.752151
C	-5.507194	4.190595	2.994057
C	-5.128216	5.241684	3.735603
C	-6.082032	2.941451	3.502930
C	-6.548003	1.996132	2.685534
N	-6.520930	2.128026	1.291955
H	-4.927164	5.071657	1.060904
H	-5.849503	3.299973	-0.323296
H	-4.711448	6.090147	3.201480
H	-6.130151	2.750054	4.566783
H	-6.974574	1.069709	3.038364
C	-7.070124	1.124861	0.511465
O	-7.520247	0.100781	0.975013
O	-7.037393	1.429381	-0.780896
C	-7.373878	0.379598	-1.723516
H	-6.828223	0.662453	-2.620548
H	-6.980804	-0.558475	-1.336963
C	-8.856678	0.296004	-1.991658
H	-9.241332	1.257542	-2.333605
H	-9.042083	-0.435307	-2.778131
H	-9.397994	-0.025357	-1.102237
C	-5.236528	5.405533	5.218470
H	-5.588614	4.503141	5.718902
H	-4.275936	5.699653	5.650024
H	-5.936233	6.203603	5.474890



compound_G_Br_Me_cat_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-1.861609	3.109241	0.454694
C	-3.075712	2.559839	0.725846
C	-0.676693	2.310406	0.435283
C	0.583412	2.874528	0.216372
C	-0.876083	0.922799	0.665323
C	-2.108438	0.414645	0.927017
N	-3.195099	1.231249	0.975688
Br	-1.803692	4.955904	0.121856
H	-3.988062	3.132661	0.778118
H	0.615340	3.941883	0.041694
H	-0.041744	0.238737	0.638536
H	-2.283700	-0.632150	1.112559
C	-4.520914	0.742618	1.339824
O	-5.472859	1.463001	1.296444
O	-4.464439	-0.501959	1.707376
C	-5.713371	-1.081619	2.207920
H	-6.025531	-0.488965	3.066197
H	-6.455403	-0.985378	1.418410
C	-5.424482	-2.515547	2.559086
H	-4.640008	-2.596163	3.308471
H	-6.330902	-2.960132	2.970661
H	-5.116361	-3.072479	1.674153
C	1.884746	2.187453	0.170372
H	1.849523	1.125129	0.403390
H	2.317397	2.339484	-0.824427
H	2.573383	2.678184	0.860085



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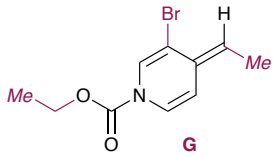
compound_G_Br_Me_neu_wb97x_ccPVTZ_opt_freq_opt.xyz

C	-1.901930	3.003460	0.106007
C	-3.100767	2.490473	0.388476
C	-0.638328	2.274348	0.310564
C	0.572570	2.823945	0.144079
C	-0.880688	0.887448	0.722317
C	-2.094418	0.401864	0.980779
N	-3.245279	1.192559	0.876507
Br	-1.858124	4.763673	-0.590710
H	-4.022048	3.035414	0.259901
H	0.610487	3.854343	-0.189305
H	-0.042649	0.213090	0.824610
H	-2.258404	-0.617523	1.288768
C	-4.501865	0.770039	1.301461
O	-5.493874	1.458770	1.230816
O	-4.463251	-0.458911	1.786371
C	-5.698289	-0.991341	2.328183
H	-5.992780	-0.380938	3.181875
H	-6.468439	-0.912460	1.563282
C	-5.429310	-2.425404	2.712322
H	-4.637667	-2.503606	3.455201
H	-6.335756	-2.855091	3.140069
H	-5.133539	-3.005232	1.837208
C	1.913756	2.198392	0.357710
H	2.514661	2.304636	-0.548687
H	2.457555	2.726245	1.143096
H	1.877074	1.145178	0.640050



G

References for computational studies.

1. [**Redox Computation**] Isegawa, M.; Neese, F.; Pantazis, D. A. Ionization Energies and Aqueous Redox Potentials of Organic Molecules: Comparison of DFT, Correlated Ab Initio Theory and Pair Natural Orbital Approaches. *J. Chem. Theory Comput*. **2016**, 12, 2272–2284. https://doi.org/10.1021/acs.jctc.6b00252.

2. [**ORCA 5.0**] Neese, F. Software Update: The ORCA Program System—Version 5.0. *WIREs Comput. Mol. Sci.* **2022**, 12. https://doi.org/10.1002/wcms.1606.

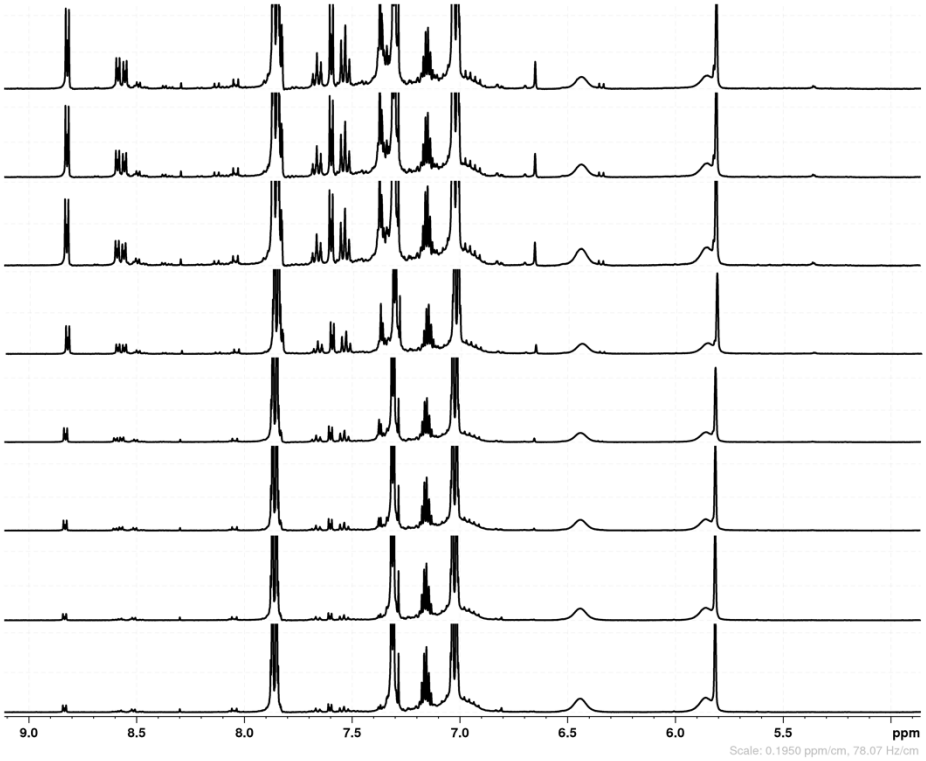
3. [**WB97X**] Chai, J.-D.; Head-Gordon, M. Systematic Optimization of Long-Range Corrected Hybrid Density Functionals. *J. Chem. Phys*. **2008**, 128, 084106. https://doi.org/10.1063/1.2834918.

4. [**CPCM**] Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A.* **1998**, 102, 1995–2001. https://doi.org/10.1021/jp9716997.

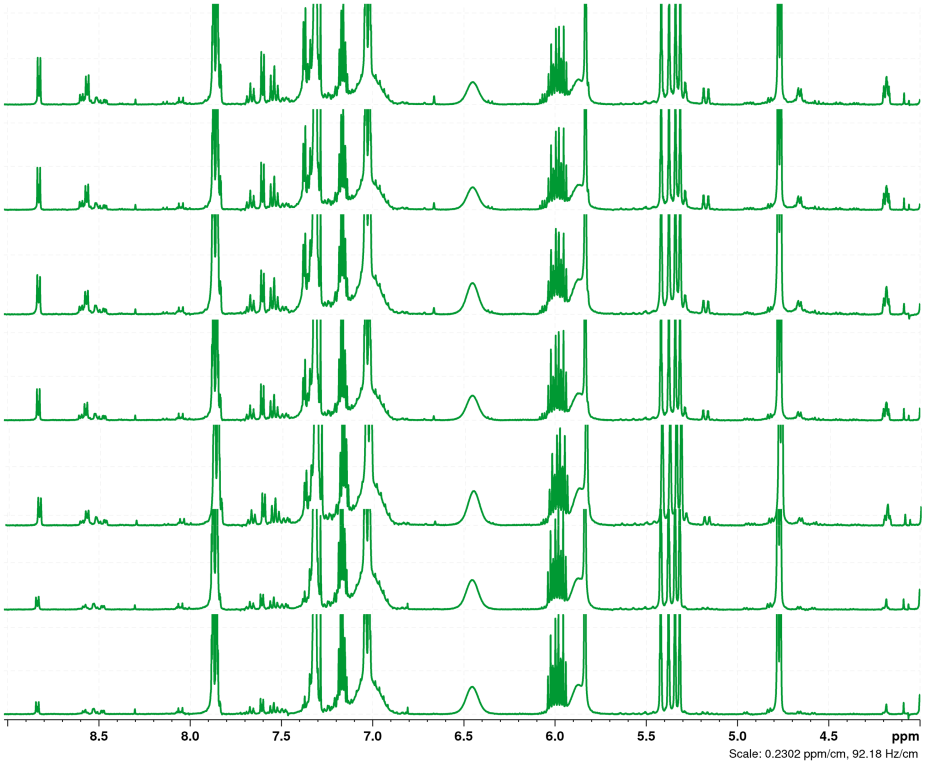
5. [**DLPNO-CCSD(T)**] Guo, Y.; Riplinger, C.; Becker, U.; Liakos, D. G.; Minenkov, Y.; Cavallo, L.; Neese, F. Communication: An improved linear scaling perturbative triples correction for the domain based local pair-natural orbital based singles and doubles coupled cluster method DLPNO-CCSD(T). *J. Chem. Phys*. **2018**, 148, 011101. https://doi.org/10.1063/1.5011798

NMR reaction progress experiments – An oven-dried NMR tube was charged with AHDP 1' (0.05 mmol) and *p*-anisaldehyde as an internal standard (1 eq., 0.05 mmol) in $CDCl_3$ (0.79 mL). The NMR tube containing the mixture was purged with oxygen for 1 minute prior to capping and sealing the tube with parafilm. The reaction was monitored for approximately 6.5 hours, recording a scan approximately every hour on a Bruker 400 AV spectrometer with the relaxation delay set to 35 seconds. The reaction mixture was vortexed for 2 minutes prior to each scan. The collected scans were then analyzed using Bruker Dynamics Center 2.5.5 to obtain the decay of the ADHP intermediate and formation of pyridylic ketone product.

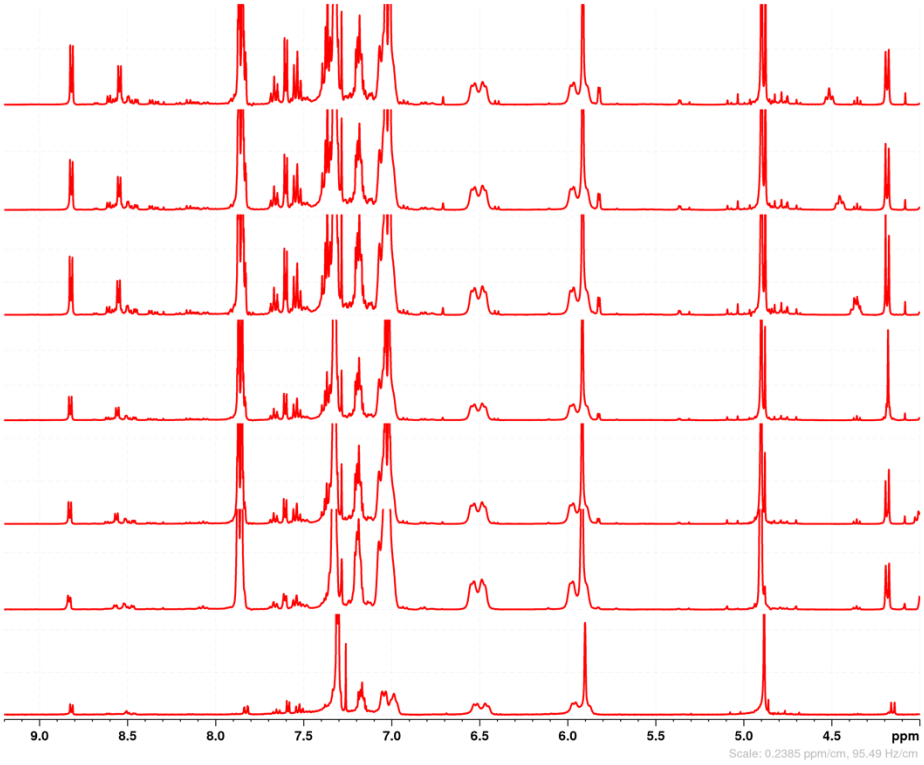
NMR data for the decomposition of the ADHP prepared from 4-benzylpyridine and **ethyl** chloroformate (Figure 3 and Figure 5, black traces). Anisaldehyde internal standard signal omitted.



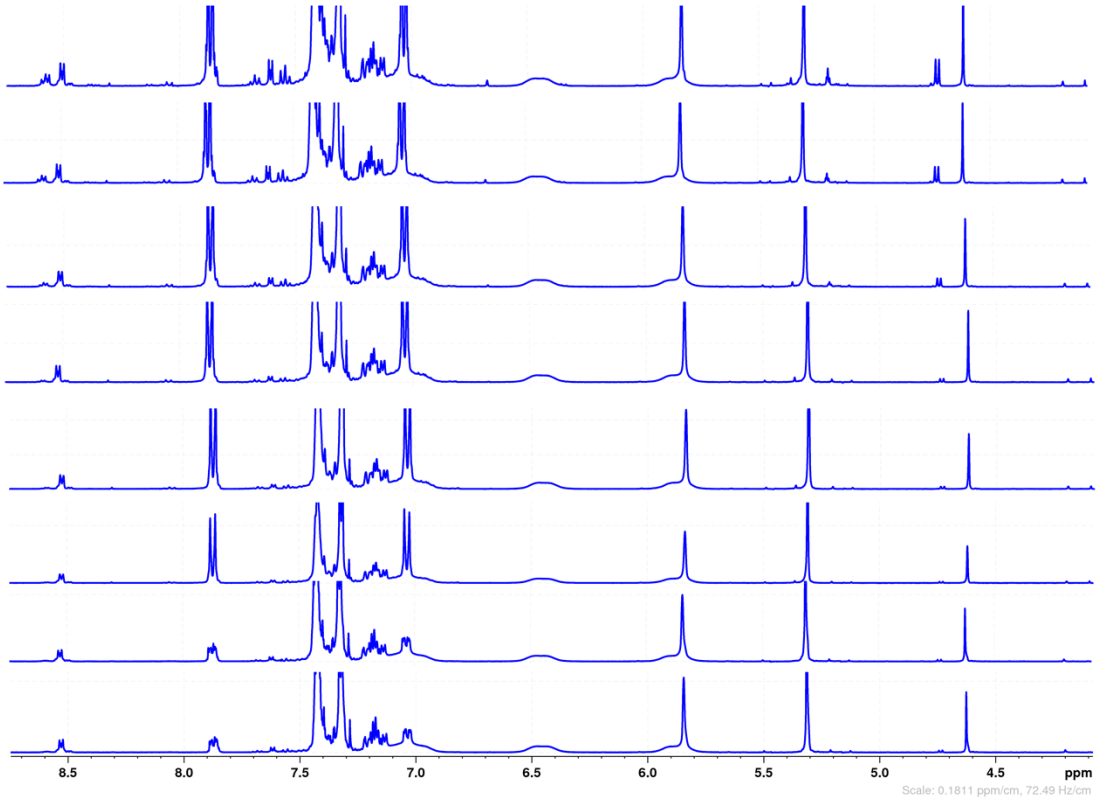
NMR data for the decomposition of the ADHP prepared from 4-benzylpyridine and **allyl** chloroformate (Figure 3, green traces). Anisaldehyde internal standard signal omitted.



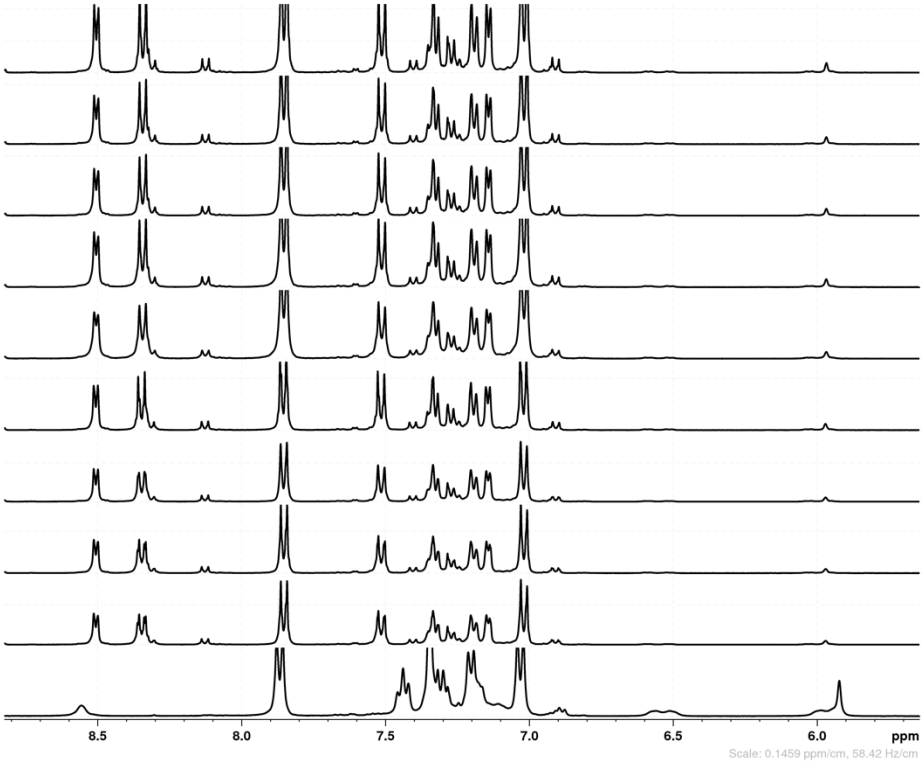
NMR data for the decomposition of the ADHP prepared from 4-benzylpyridine and **trichloroethyl** chloroformate (Figure 3, red traces). Anisaldehyde internal standard signal omitted.



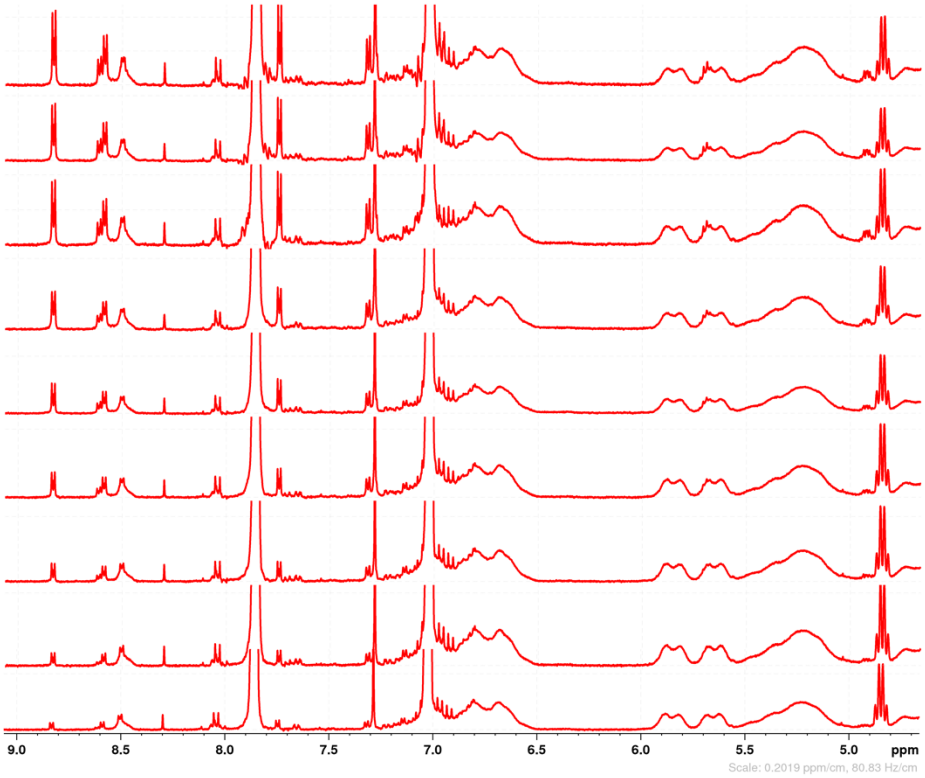
NMR data for the decomposition of the ADHP prepared from 4-benzylpyridine and **benzyl** chloroformate (Figure 3, blue traces). Anisaldehyde internal standard signal omitted.



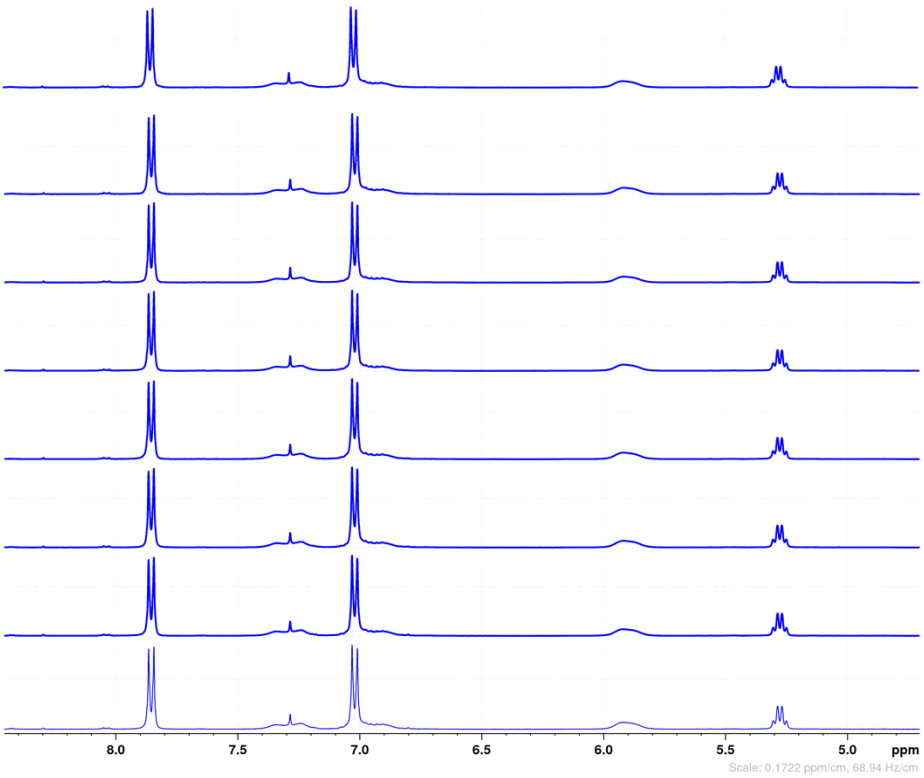
NMR data for the decomposition of the ADHP prepared from 4-benzylpyridine and **phenyl** chloroformate (Figure 4). Anisaldehyde internal standard signal omitted.



NMR data for the decomposition of the ADHP prepared from 4-ethylpyridine and ethyl chloroformate (Figure 5, red traces). Note appearance of 4-benzoylpyridine. Anisaldehyde internal standard signal omitted.



NMR data for the decomposition of the ADHP prepared from 3-bromo-4-ethylpyridine and ethyl chloroformate (Figure 5, blue trace). Anisaldehyde internal standard signal omitted.



Tabulated chemical shift of the alkylidene proton of the ADHP prepared from 4-*benzyl*pyridine and various chloroformates. (Figure 1).

ethyl	allyl	benzyl	phenyl	trichloroethyl
5.7963	5.811	5.8208	5.9444	5.8943
5.7902	5.8106	5.8225	5.946	5.8928
5.7894	5.8097	5.8136	5.945	5.8919
5.788	5.8096	5.8126	5.9471	5.8907
5.7867	5.8092	5.8116	5.9446	5.8901

Tabulated chemical shift of the alkylidene proton of the ADHP prepared from 4-*ethyl*pyridine and various chloroformates. (Figure 1).

ethyl	allyl	benzyl	phenyl	trichloroethyl
4.8222	4.8442	4.8467	4.9406	4.9273
4.8221	4.843	4.8476	4.9407	4.9256
4.822	4.8416	4.8481	4.9409	4.9239
4.8191	4.839	4.8471	4.9407	4.9233
4.8161	4.8407	4.8463	4.9411	4.9231

Summarized data for Figures 3 and 4.

ADHP from ethyl chloroformate										
time [min]:	0	35	47	97	145	198	244	295	344	393
delta ketone		0	1	4	11	19	28	31	35	38
delta ADHP		0	-4	-8	-21	-25	-43	-46	-51	-54

ADHP from allyl chloroformate										
time [min]:	0	35	47	96	147	198	248	299	347	398
delta ketone		0	1	7	9	12	13	15	17	19
delta ADHP		0	-1	-8	-13	-17	-19	-22	-25	-28

ADHP from trichloroethyl chloroformate							
time [min]:	0	35	98	156	274	335	424
delta ketone		0	7	9	11	12	13
delta ADHP		0	-8	-14	-22	-25	-27

ADHP from benzyl chloroformate										
time [min]:	0	35	47	77	126	178	227	277	327	381
delta ketone			0	0	1	1	1	1	1	1
delta ADHP			0	0	0	-1	-1	-1	-1	-1

ADHP from phenyl chloroformate										
time [min]:	0	35	46	87	136	189	237	286	336	391
delta ketone		0	0	1	1	1	2	2	3	3
delta ADHP		0	-1	-4	-7	-11	-15	-17	-19	-18

Summarized data for Figure 5

% ketone formation as a function of time
comparison of 4-ethylpyridine and 4benzylpyridine

4-ethylpyridine & ethyl chloroformate									
time [min]:	0	35	56	89	133	188	236	283	334
%Ketone	0	4	6	10	14	19	24	28	33

4-benzylpyridine & ethyl chloroformate										
time [min]:	0	35	47	97	145	198	244	295	344	393
%ketone	0	6	7	11	19	27	39	43	48	51

ADHP decomposition as a function of time
comparison of 4-ethylpyridine, 4-benzylpyridine and 3-bromo-4-ethylpyridine

4-ethylpyridine & ethyl chloroformate									
time [min]:	0	35	56	89	133	188	236	283	334
%ADHP	100	96	94	90	84	79	74	69	64

4-benzylpyridine & ethyl chloroformate										
time [min]:	0	35	47	97	145	198	244	295	344	393
%ADHP	100	94	92	88	79	72	58	54	49	45

3-bromo-4ethylpyridine & ethyl chloroformate								
time [min]:	0	35	49	136	183	265	315	370
%ADHP	100	100	99	99	98	98	98	98