Supporting Information

Pd-Catalyzed Direct C-H Alkenylation and Allylation of Azine *N*-Oxides

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I. General remarks

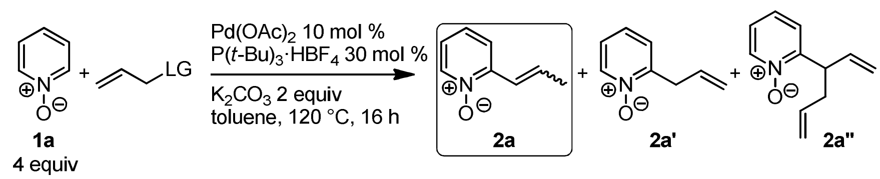
All reactions were carried out under an argon atmosphere by standard syringe and septa techniques. Glassware was flame-dried under vacuum or taken directly from the oven (100 °C) and let cool under vacuum prior to every use. Reagents and solvents were purchased from commercial sources and generally used as received. DCM, THF and Et_2O were dried on a Mbraun purification system MB SPS-800. Toluene was dried on an Innovative Technology PureSolv Micro purification system. Where necessary, other organic compounds were dried and/or distilled.

NMR spectra (^1H, ^{13}C, ^{19}F) were recorded on a Bruker AM 300 MHz or on a Bruker AVANCE 400 MHz spectrophotometer. NMR experiments were carried out at room temperature in $CDCl_3$. Chemical shifts are given in parts per million (ppm) using the $CDCl_3$ residual non-deuterated signals as reference (δ ^1H = 7.26 ppm; δ ^{13}C = 77.16 ppm). The terms m, s, d, t and q represent multiplet, singlet, doublet, triplet and quartet, respectively. The term (br.) is used when the peak is broad, and the correct multiplicity cannot be surely assigned. Coupling constants (*J*) are given in Hertz (Hz). For previously unknown compounds, a combination of ^{13}C DEPT and 2D experiments (COSY, HSQC, HMBC) were often used to complete assignment of ^1H and ^{13}C signals.

IR spectra were recorded with a Tensor 27 (ATR diamond) Bruker spectrometer, and reported as characteristic bands (cm^{-1}). High resolution mass spectra (HRMS) were recorded using a mass spectrometer MicroTOF from Bruker with an electron spray ion source (ESI) and a TOF detector and an atmospheric pressure chemical ionisation (APCI) source at Institut Parisien de Chimie Moléculaire. Melting points were measured in capillary tubes on Stuart Scientific SMP3 apparatus and are uncorrected. TLC were performed on Merck 60 F254 silica gel and revealed with either a ultra-violet lamp (λ = 254 nm) or a specific color reagent (potassium permanganate, *p*-anisaldehyde, etc.). A silica gel Merck Geduran® SI 60 (40-63 µm) was used for flash column chromatography. Preparative thin layer chromatography was realized with PLC silica gel 60 F_{254} (1 mm, 20x20 cm).

II. Further optimizations

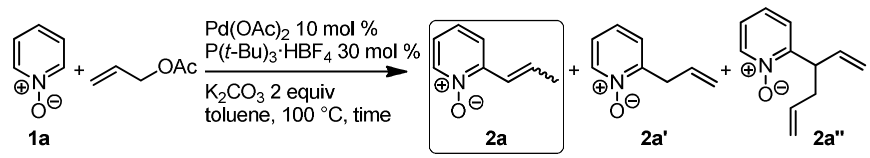
Table S1. *Optimization of allyl partner and temperature*



entry	LG	ratio (2a:2a':2a'')[a]	2a, yield (%) (*E/Z*)[a]
1	OAc	95:3:2	54 (81/19)
2	OCO_2Me	24:0:76	18 (89/11)
3	$OP(O)(OEt)_2$	61:traces:39	25 (89/11)
4	**OAc (100 °C)**	**86:4:10**	**62 (68/32)**

[a] Determined by ^1H NMR analysis of the crude mixture using dimethylsulfone as an internal standard

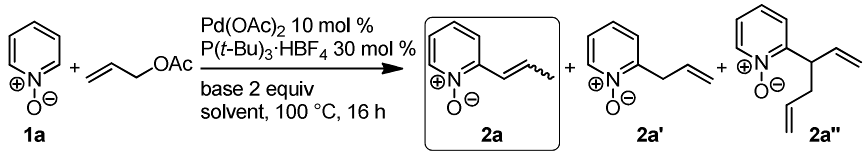
Table S2. *Optimization of ratio PNO **1a**/allyl acetate, concentration and time*



entry	ratio **1a**/allyl acetate	Concentration [M]	time (h)	ratio (**2a**:**2a'**:**2a''**)[a]	**2a**, yield (%) (*E/Z*)[a]
1	3/1	0,25	16	53:traces:47	40 (81/19)
2	**2/1**	**0,25**	**16**	**78:4:12**	**56 (75/25)**
3	1/1	0,25	16	53:traces:47	27 (78/22)
4	1/2	0,25	16	39:traces:61	36 (75/25)
5	2/1	0,5	16	54:traces:46	34 (79/21)
6	2/1	0,1	16	58:11:31	36 (78/22)
7	2/1	0,25	24	71:traces:29	39 (82/18)
8	2/1	0,25	7	58:10:32	45 (71/29)

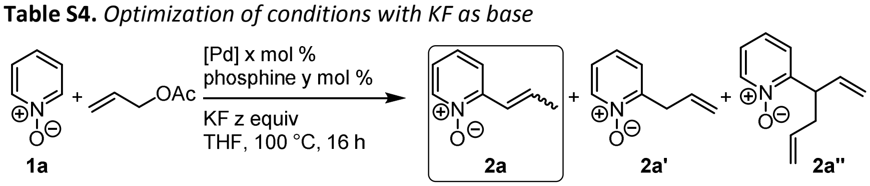
[a] Determined by ^1H NMR analysis of the crude mixture using dimethylsulfone as an internal standard

Table S3. *Optimization of base and solvent*



entry	base	solvent	ratio (**2a**:**2a'**:**2a''**)[a]	**2a**, yield (%) (*E*/*Z*)[a]
1	K_2CO_3	THF	38:0:62	20 (85/15)
2	KF	Toluene	100:traces:0	70 (86/14)
3	**KF**	**THF**	**100:0:0**	**80 (84/16)**
4	KF	Xylene	100:0:traces	74 (92/8)
5	KF	MeCN	100:0:traces	3 (100/0)
6	CsF	THF	91:0:9	70 (87/13)
7	NaOAc	THF	100:0:0	32 (65/35)
8	KOAc	THF	100:0:0	58 (84/16)

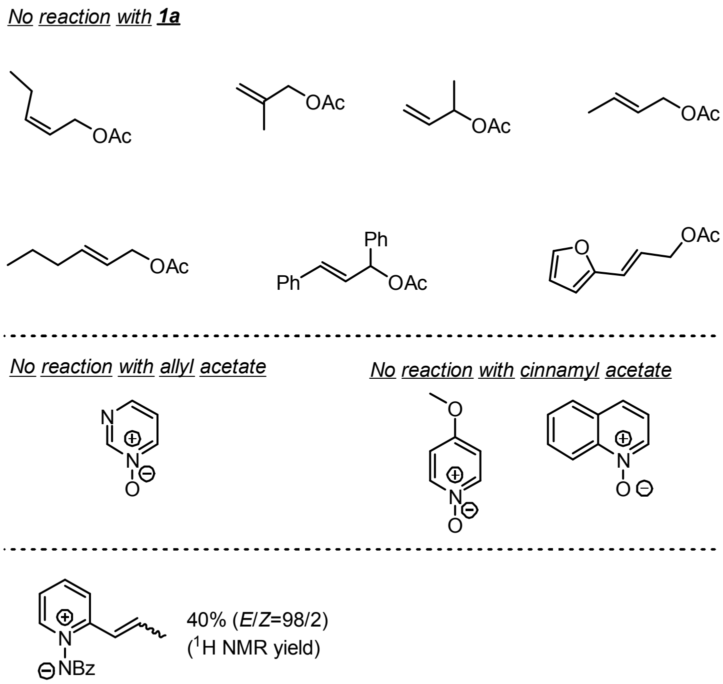
Table S4. *Optimization of conditions with KF as base*



entry	[Pd] (x)	phosphine (y)	KF (z)	ratio (**2a**:**2a'**:**2a''**)[a]	**2a**, yield (%) (*E*/*Z*)[a]
1[b]	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	1	92:0:8	59 (75/25)
2[b]	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	2	100:traces:0	70 (86/14)
3[b]	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	3	100:0:0	21 (71/29)
4	**$Pd(OAc)_2$ (10)**	**P(*t*-Bu)$_3$·HBF_4 (30)**	**2**	**100:0:0**	**80 (84/16)**
5	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (20)	2	100:0:0	68 (82/18)
6	$Pd(OAc)_2$ (5)	P(*t*-Bu)$_3$·HBF_4 (15)	2	100:0:0	65 (73/27)
7	$[PdCl(\eta^3C_3H_5)]_2$ (5)	P(*t*-Bu)$_3$·HBF_4 (15)	2	100:0:0	<1%
8	$PdCl_2(CH_3CN)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	2	Traces:0:0	-
9	$Pd(dba)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	2	100:0:0	13 (92/8)
10	$Pd(TFA)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	2	100:0:0	53 (72/28)
11	$Pd(OAc)_2$ (10)	PPh_3 (30)	2	0:0:0	-
12	$Pd(OAc)_2$ (10)	SPhos (30)	2	100:0:0	13 (99/1)
13	$Pd(OAc)_2$ (10)	dppe (30)	2	traces:0:0	-
14	$Pd(OAc)_2$ (10)	Xantphos (30)	2	0:0:0	-
15	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$ (30)	2	100:0:0	31 (50/50)
16	$Pd(OAc)_2$ (10)	-	2	0:0:0	-
17	-	P(*t*-Bu)$_3$·HBF_4 (30)	2	0:0:0	-
18[c]	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	2	0:0:0	-
19[d]	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	2	76:0:24	13 (81/19)
20[e]	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	2	100:0:0	12 (58/42)
21[f]	$Pd(OAc)_2$ (10)	P(*t*-Bu)$_3$·HBF_4 (30)	2	100:0:0	22 (99/1)

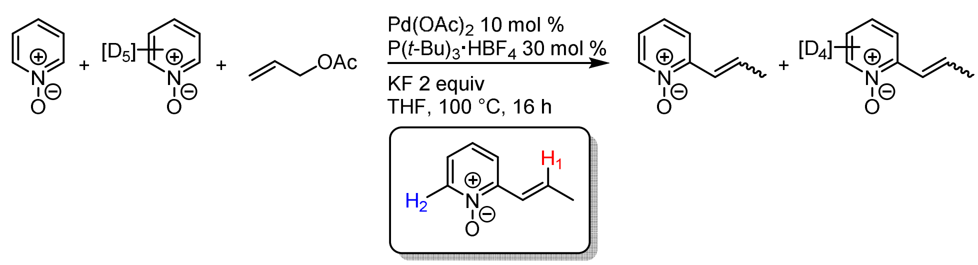
[a] Determined by ^{1}H NMR analysis of the crude mixture using dimethylsulfone as an internal standard. [b] In toluene. [c] Without KF. [d] With allyl methyl carbonate. [e] With allyl benzoate. [f] with allyl pivalate.

Figure S1. *Other azine N-oxides (or N-iminopyridiniumylides) and allyl acetates tested in the reaction.*

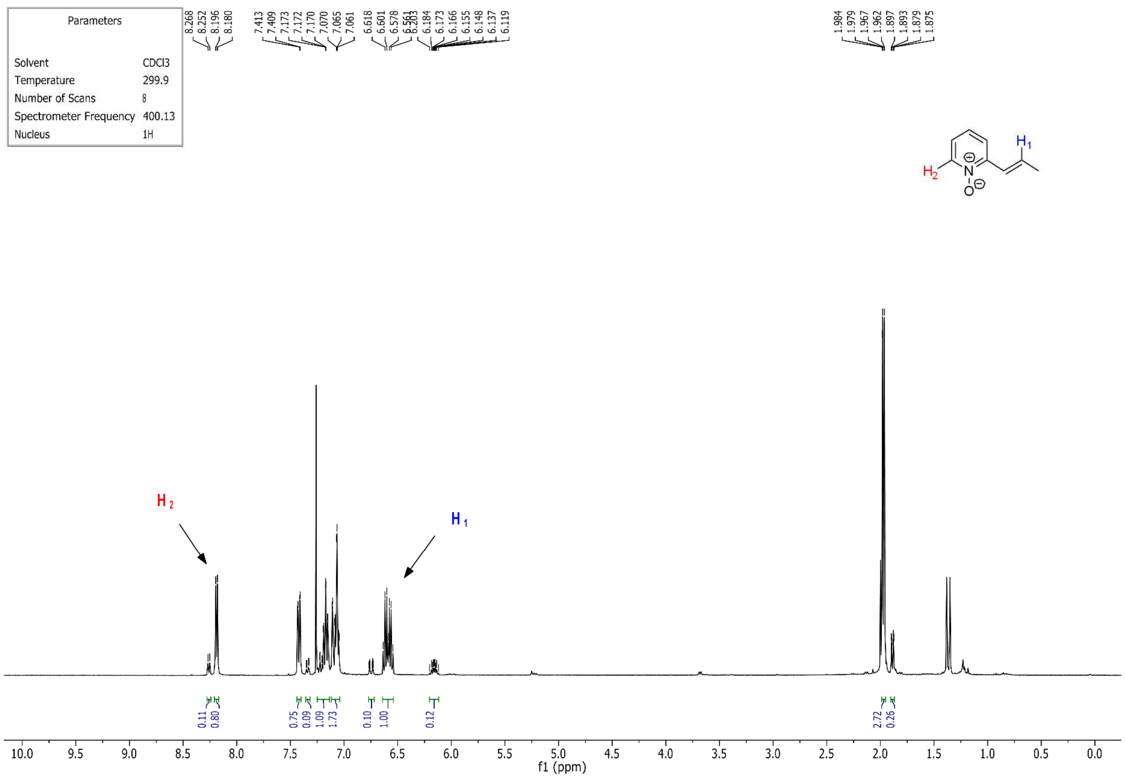


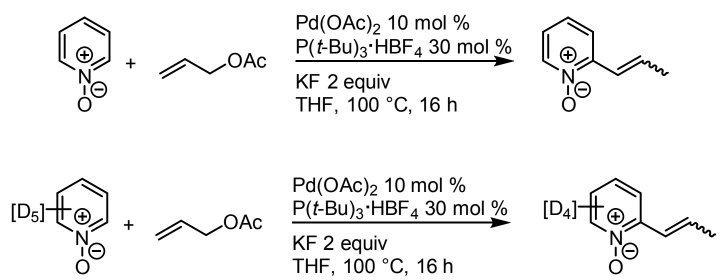
III. Mechanistic studies

1. Kinetic isotopic effect experiments for the olefination of Pyridine N-oxide



To a dried tube, were added: pyridine *N*-oxide **1a** (142.7 mg, 1.5 mmol, 3 equiv), pyridine-d_5 *N*-oxide (150.2 mg, 1.5 mmol, 3 equiv), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol, 0.1 equiv), $P(t\text{-}Bu)_3.HBF_4$ (43.6 mg, 0.15 mmol, 0.3 equiv) and KF (58.1 mg, 1 mmol, 2 equiv). The content was purged with Argon. THF (2 mL) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv) were then added, and the reaction mixture was heated at 100 °C for 16 h. The reaction mixture was filtered over Celite and washed with DCM. The volatiles were removed under reduced pressure and the resulting crude product was purified by silica gel column chromatography eluting with EtOAc/EtOH (90/10). The integration value of the proton H_1 is used as reference to integrate H_2. See **2a** for the NMR spectrum.





To a tube, dried under vacuum, were added pyridine *N*-oxide (142.7 mg, 1.5 mmol, 3 equiv), or pyridine-d_5 *N*-oxide (150.2 mg, 1.5 mmol, 3 equiv), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol, 0.1 equiv), $P(t\text{-}Bu)_3.HBF_4$ (43.6 mg, 0.15 mmol, 0.3 equiv) and KF (58.1 mg, 1 mmol, 2 equiv). The content was purged under Argon. THF (2 mL) and allylacetate (0.054 mL, 0.5 mmol, 1 equiv) were then added and the reaction mixture was heated at 100 °C for 16 h. The resulting reaction mixture was filtered over Celite and washed with DCM. The volatiles were removed under reduced pressure. ^{1}H NMR yield was determined using dimethylsulfone as an internal standard.

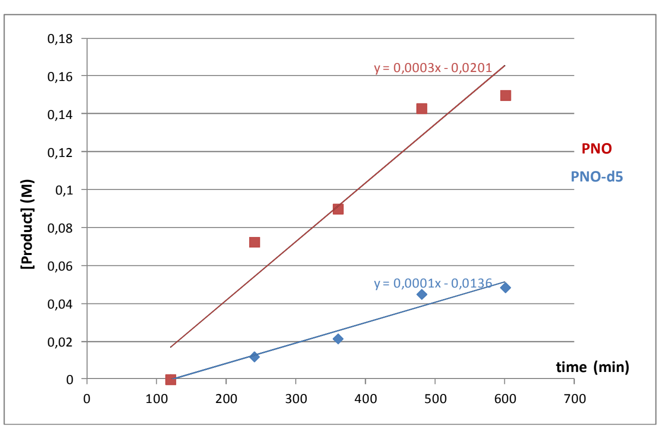
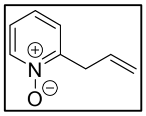


Figure S2. Product formation over time for the alkenylation of pyridine *N*-oxide and pyridine-d_5 *N*-oxide

2. Isomerization of the double bond



Preparation of 2-allylpyridine *N*-oxide 2a': Following a slightly modified version of a reported procedure,[1] a three-necked flask equipped with a magnetic stirrer was charged with 2-iodopyridine *N*-oxide (331.5 mg, 1.5 mmol, 1 equiv) in 10 mL of THF. The mixture was cooled to -60 °C, and *i*-PrMgCl·LiCl (6.3 mL, 1.6 mmol, 1.05 equiv)[2] was added slowly with a syringe. The mixture was stirred at -60 for 2 h. A solution of CuI·2LiCl in THF (1.6 mL, 1.6 mmol, 1.05 equiv.) was added with a syringe and the resulting mixture was stirred at -60 °C for 20 min. Allyl bromide (148 µL, 1.75 mmol, 1.16 equiv) was then added and the resuting mixture was stirred under the same temperature for 2 h. The reaction was quenched with 10% aqueous NH_4Cl solution and extracted with EtOAc. The organic layer was collected, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (90/10) to afford 80.5 mg of **2a'** (40% yield) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.30 (d, *J* = 6.1 Hz, 1H), 7.25-7.12 (m, 3H), 6.10-5.93 (m, 1H), 5.30-5.17 (m, 2H), 3.69 (dt, *J* = 6.9, 1.4 Hz, 2H). These data are in agreement with those reported in the literature.[1]

[1] Duan, X.-F.; Z.-Q. Ma, F. Zhang, Z.-B. Zhang, *J. Org. Chem.* **2009**, *74*, 939.

[2] Prepared and titrated according to the following procedure: (a) Krasovskiy, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 3333. (b) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890.

IV. DFT study

Calculations were performed using the GAUSSIAN 09 software package,[3] and the PBE0 functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25 % mixture of Hartree-Fock[4] exchange with DFT[5] exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE).[6] The optimized geometries were obtained with the Stuttgart Effective Core Potentials and associated basis set[7] augmented with a f-polarization function[8] for Pd, and a standard 6-31G(d,p)[9] for the remaining elements (basis b1). Transition state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQN) developed by Schlegel *et al*,[10] following extensive searches of the Potential Energy Surface. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profile. The electronic energies (E_{b1}) obtained at the PBE0/b1 level of theory were converted to free energy at 298.15 K and 1 atm (G_{b1}) by using zero point energy and thermal energy corrections based on structural and vibration frequency data calculated at the same level.

Single point energy calculations were performed on the geometries obtained at the PBE0/b1 level using the M06 functional, and an improved basis set (b2) corresponding to the same basis set for Pd and a 6-311++G(d,p) basis set[11] for the rest of the elements. The M06 functional is a hybrid meta-GGA functional developed by Truhlar and Zhao,[12] and it was shown to perform very well for the kinetics of transition metal molecules, providing a good description of weak and long range interactions.[13] Solvent effects (THF) were accounted for in the M06/b2//PBE0/b1 calculations by means of the Polarisable Continuum Model (PCM) initially devised by Tomasi and coworkers[14] with radii and non-electrostatic terms of the SMD solvation model, developed by Truhlar *et al*.[15]

The free energy values presented (G_{b2}^{soln}) were derived from the electronic energy values obtained at the M06/b2//PBE0/b1 level, including solvent effects (E_{b2}^{soln}), according to the following expression: $G_{b2}^{soln} = E_{b2}^{soln} + G_{b1} - E_{b1.}$

[3] Gaussian 09, Revision A.01, Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT **2009**.

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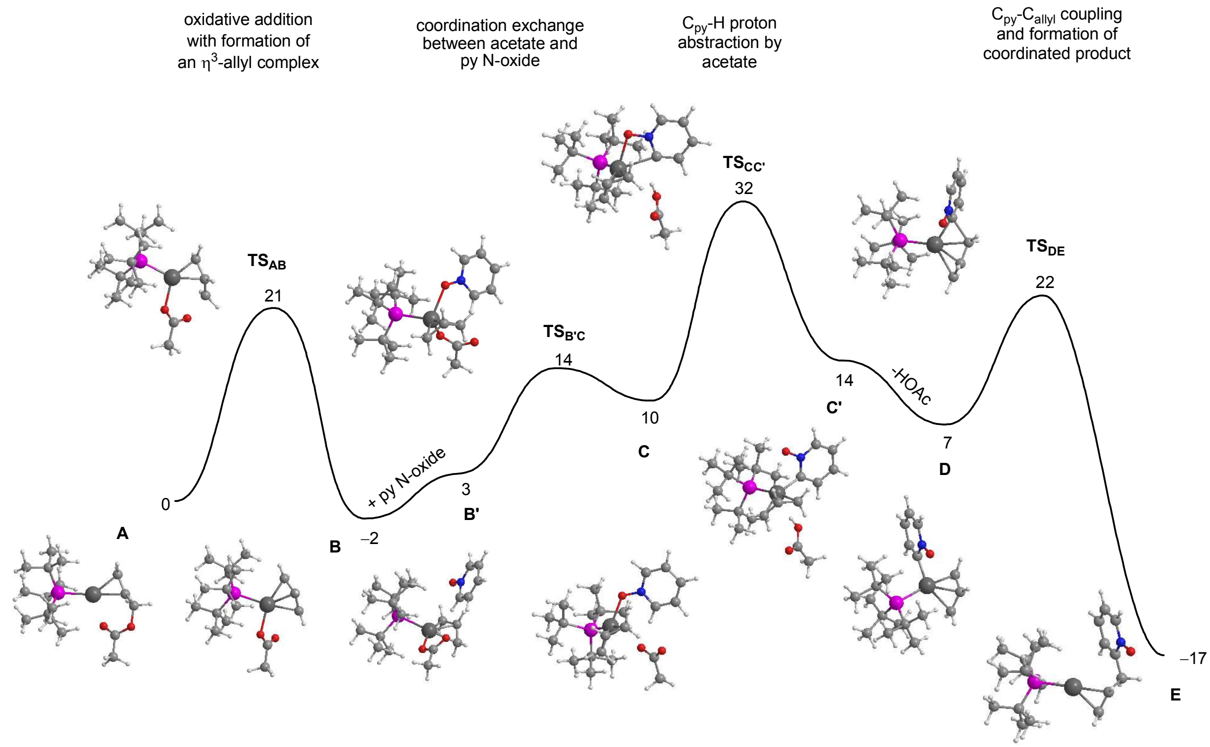

Figure S3. Free energy profile (kcal/mol) for allylation of **1a** to **2a'** with [Pd(P^{t}Bu$_3$)] as active species.

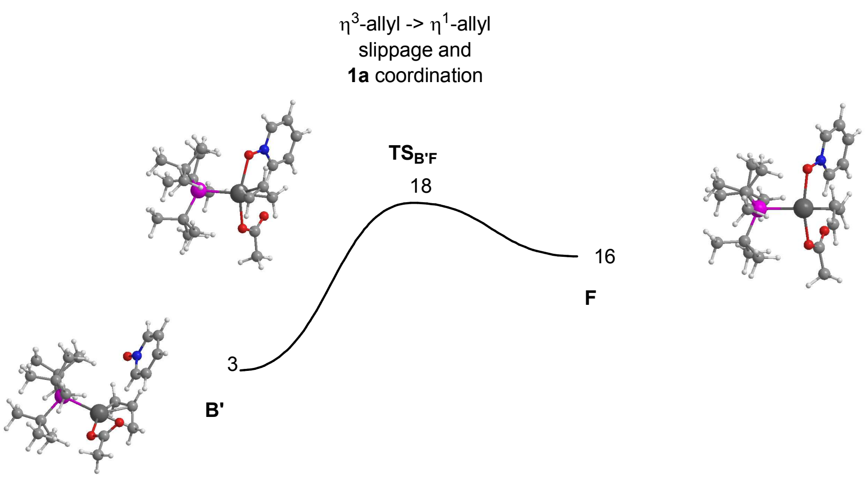

Figure S4. Free energy profile (kcal/mol) for η^3-η^1 allyl slippage following coordination of **1a** to intermediate B'.

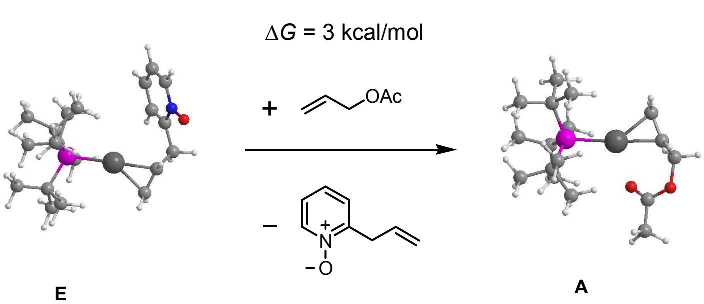

Figure S5. Free energy balance for closing the catalytic cycle.

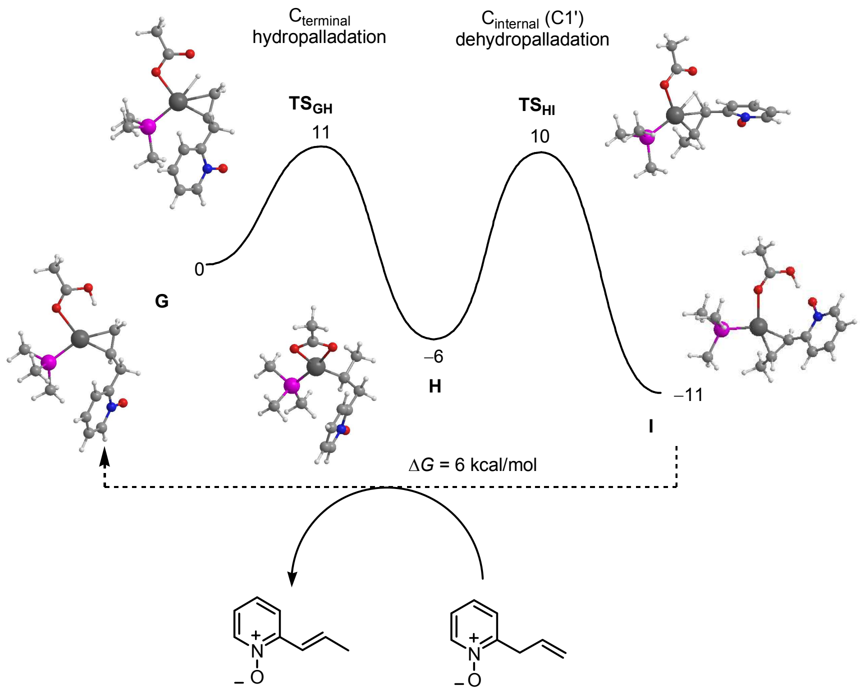

Figure S6. Free energy profile (kcal/mol) for **2a'-2a** isomerization with [Pd(PMe_3)] as active species.[16]

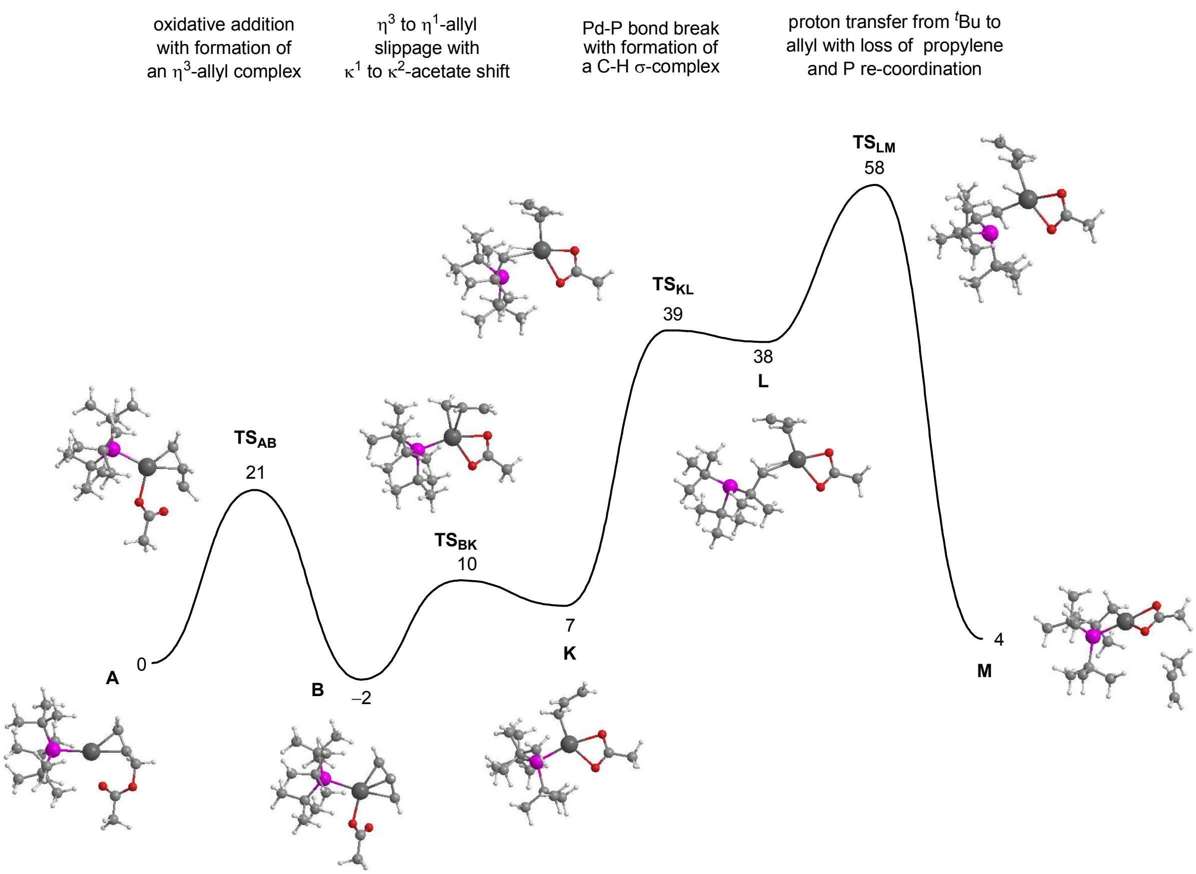

Figure S7. Free energy profile (kcal/mol) for C–H activation of the ^{t}Bu group by coordinated allyl, with [Pd(P^tBu_3)] as active species.

[16] An alternative, slightly modified, isomerization mechanism with HF instead of AcOH as the Brönsted acid cannot be ruled out.

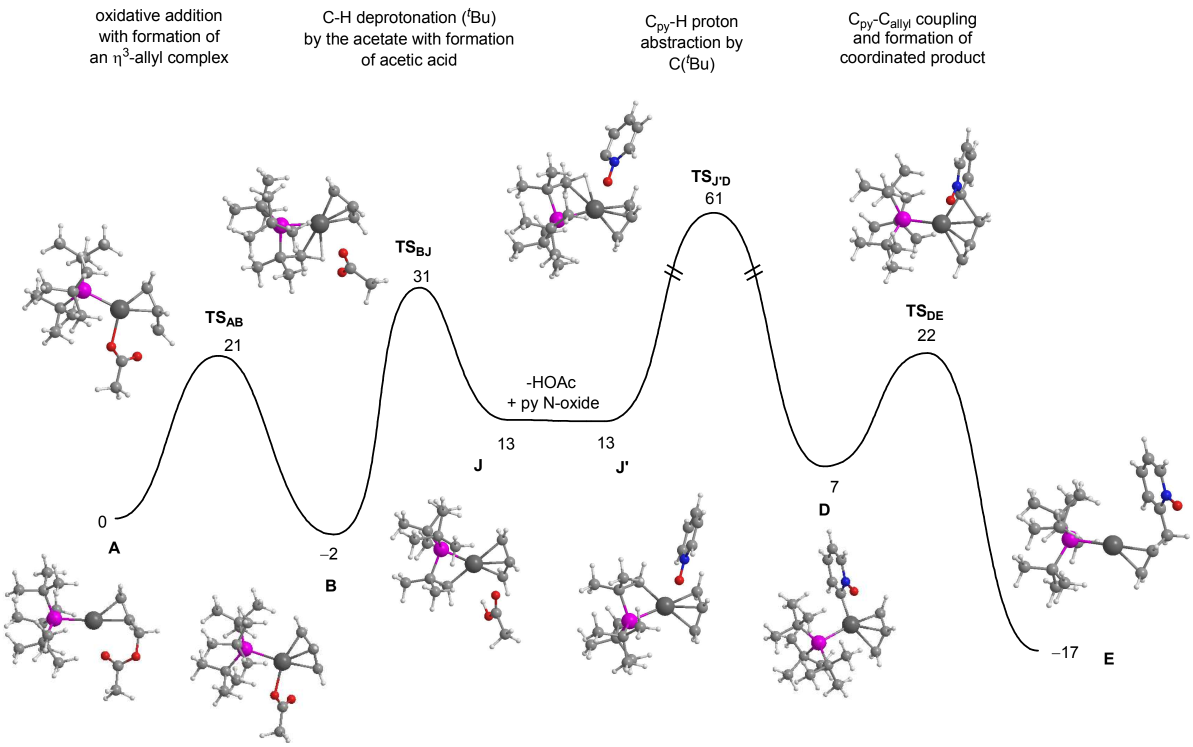

Figure S8. Free energy profile (kcal/mol) for allylation of **1a** with [Pd(P^tBu_3)] as active species and C–H activation of the ^{t}Bu group by coordinated acetate.

Atomic coordinates of the optimized species

1a

O	-1.882457	-1.882457	0.000000
N	-0.989716	-0.989716	0.000000
C	-0.165765	1.128913	0.760569
H	-2.056763	0.176970	1.311764
C	1.128913	-0.165765	-0.760569
H	0.176970	-2.056763	-1.311764
C	-1.132860	0.145032	0.750364
H	1.758485	1.758485	0.000000
C	0.145032	-1.132860	-0.750364
C	0.992097	0.992097	0.000000
H	-0.334358	2.007323	1.375507
H	2.007323	-0.334358	-1.375507

2a

N	1.396010	-1.127303	1.391745
C	2.102618	-0.442645	2.339645
O	1.585826	-2.372025	1.252505
H	2.779341	-1.074523	2.899076
H	-1.340001	-1.496842	-3.388419
C	1.950399	0.911871	2.531276
H	2.543393	1.397309	3.298979
C	-0.944090	-0.788749	-1.402378
H	-2.762086	-1.406560	-2.360124
C	1.042350	1.623689	1.749380
H	0.895619	2.688923	1.887696
C	-1.692498	-1.651082	-2.361196
C	0.319368	0.924385	0.797349
H	-0.417129	1.434235	0.185341
C	0.488801	-0.444462	0.597750
H	-0.135135	-2.326674	-0.206333
C	-0.231828	-1.256930	-0.369054
H	-1.583714	-2.710752	-2.116555
H	-0.990845	0.284833	-1.588881

2a’

C	-1.281224	-0.207459	0.675031
N	1.066877	-0.828553	0.545309
O	0.750186	-1.875156	1.191062
H	-1.881670	0.706350	0.633411
H	-1.217295	-0.542668	1.718502
H	-1.399751	-2.245715	-0.137401
C	0.110217	0.104266	0.219017
H	-0.305297	1.947638	-0.741812
C	0.475402	1.235159	-0.494074
H	2.065511	2.346166	-1.439908
C	1.791143	1.457581	-0.882620
H	3.785975	0.616344	-0.804576
C	2.741750	0.503371	-0.533021
H	3.030948	-1.410155	0.485395
C	2.363297	-0.617938	0.173787
C	-1.923722	-1.292764	-0.145328
H	-3.587958	-0.191788	-0.848133
H	-3.482218	-1.953572	-1.406373
C	-3.050072	-1.137505	-0.835066

AcOH

O	-1.534272	0.750072	0.491126
O	-0.503510	-1.214531	0.808940
C	-0.580084	0.034378	0.306622
C	0.646498	0.385357	-0.482155
H	1.532205	0.310608	0.154639
H	0.550397	1.396947	-0.872840
H	0.776219	-0.324469	-1.303669
H	-1.328754	-1.352262	1.296937

Allyl acetate

O	-0.571353	0.256988	0.260846
O	-1.302088	0.722038	-1.815558
C	-1.192289	1.026474	-0.651910
C	-1.712949	2.287667	-0.023067
C	-0.040820	-0.977916	-0.245741
C	0.439718	-1.781216	0.913722
C	1.656320	-2.311901	0.992429
H	-2.207699	2.892763	-0.781293
H	-0.889098	2.849036	0.425902
H	-2.415257	2.043626	0.778802
H	0.765111	-0.768180	-0.956810
H	-0.835041	-1.496892	-0.796110
H	-0.284821	-1.946629	1.709688
H	2.396908	-2.154423	0.211874
H	1.955357	-2.927834	1.834826

A

Pd	0.403917	0.318629	-0.793088
P	-0.056941	-1.882418	-0.135847
O	1.398526	3.343608	0.606168
O	2.330227	1.498423	1.517659
C	1.203591	1.330817	-2.478395
C	0.861969	2.279555	-1.515493
C	1.651679	2.497489	1.614415
C	1.901920	2.984931	-0.693922
H	2.799536	2.371712	-0.578858
H	-0.083515	2.815778	-1.614379
H	-3.674571	-1.373902	0.892887
H	-3.154907	-2.469987	-0.383181
H	2.240297	1.022389	-2.610381
H	-2.731280	-0.743936	-0.466653
H	0.550370	1.144097	-3.327643
H	-1.331758	0.301668	1.306242
H	-0.572288	-0.645819	2.593678
H	2.172140	3.946608	-1.144821
C	0.966837	2.945426	2.875068
H	-2.332348	-0.492289	2.539719
H	1.461853	2.498889	3.737289
H	-2.721757	-2.939123	2.499979
H	-0.992932	-3.251948	2.618060
H	-0.072821	2.602210	2.849018
H	0.957423	4.033967	2.953500
H	-1.940141	-3.994450	1.322079
H	-1.278066	-4.923685	-2.225569
H	-2.150979	-4.199634	-0.879871
C	-1.581822	-1.847663	1.032434
C	-2.851002	-1.600928	0.204091
H	-0.581237	-4.967557	-0.604910
C	-1.430072	-0.601221	1.923581
H	0.591728	-3.819129	-3.329583
C	-1.807093	-3.082962	1.909992
H	1.514947	-3.995770	-1.840016
C	-0.455579	-3.023945	-1.629042
H	1.388214	-2.403879	-2.623858
C	-1.153177	-4.348223	-1.299135
H	-0.848706	-1.273960	-2.866252
C	0.847249	-3.324978	-2.383936
H	-2.325803	-2.019635	-2.247359
C	-1.323465	-2.228844	-2.619435
H	-1.430379	-2.816658	-3.540266
C	1.429052	-2.635503	0.826387
H	0.737202	-2.245023	2.888974
C	1.541926	-1.966099	2.205025
H	1.594609	-0.875665	2.124437
H	2.480509	-2.300156	2.664798
C	1.402695	-4.155390	1.022066
H	2.268220	-4.448936	1.629907
C	2.716888	-2.235915	0.083092
H	1.477292	-4.702893	0.079382
H	0.506290	-4.498531	1.544289
H	3.577992	-2.573867	0.674155
H	2.777383	-1.148201	-0.022155
H	2.804957	-2.680171	-0.908128

TS_{AB}

Pd	0.292958	0.506335	-0.474204
P	-0.107517	-1.745950	-0.056724
O	2.347705	2.574515	0.529882

O	0.751998	1.301364	1.511884
C	0.296743	1.040703	-2.442460
C	0.470984	2.261727	-1.693110
C	1.700320	2.123981	1.527823
C	1.731409	2.739743	-1.269800
H	2.618900	2.236979	-1.642370
H	-0.386799	2.916671	-1.548974
H	-3.837854	-1.615181	0.627982
H	-3.106558	-2.600052	-0.634200
H	1.163926	0.617921	-2.954468
H	-2.833967	-0.840796	-0.604912
H	-0.624834	0.954331	-3.016632
H	-1.732838	0.218897	1.413872
H	-1.017955	-0.752894	2.692855
H	1.854526	3.802730	-1.093246
C	2.128239	2.673177	2.872887
H	-2.768674	-0.778306	2.459625
H	1.943634	1.937872	3.657629
H	-2.898808	-3.213240	2.216966
H	-1.170984	-3.363898	2.509759
H	1.526263	3.561829	3.090681
H	3.177966	2.969069	2.859206
H	-1.894755	-4.111404	1.079069
H	-0.776829	-4.836639	-2.315873
H	-1.864501	-4.249598	-1.063417
C	-1.735931	-1.917775	0.953025
C	-2.936995	-1.737672	0.014096
H	-0.255418	-4.843770	-0.630458
C	-1.803106	-0.738510	1.938846
H	1.019169	-3.456855	-3.248199
C	-1.917864	-3.230481	1.724473
H	1.821617	-3.619024	-1.690247
C	-0.252961	-2.870024	-1.615533
H	1.594972	-2.009666	-2.408784
C	-0.816986	-4.275323	-1.373501
H	-0.761966	-1.170252	-2.879343
C	1.134635	-2.991857	-2.261370
H	-2.178959	-2.088318	-2.365367
C	-1.134510	-2.171862	-2.662917
H	-1.103782	-2.762047	-3.587656
C	1.349108	-2.414794	1.016197
H	0.435853	-2.270138	3.017369
C	1.249113	-1.833225	2.434128
H	1.135001	-0.745908	2.417652
H	2.182034	-2.068502	2.962333
C	1.465642	-3.939058	1.128847
H	2.295032	-4.175989	1.807583
C	2.656976	-1.852177	0.429667
H	1.689077	-4.418524	0.173246
H	0.565892	-4.400729	1.542409
H	3.486994	-2.146636	1.084964
H	2.628427	-0.758710	0.384725
H	2.881047	-2.224765	-0.569717

B

Pd	0.341781	0.700350	-0.479494
P	-0.000955	-1.635339	-0.056551
O	3.053120	1.639938	0.244575
O	1.196722	1.134560	1.392943
C	-0.547521	1.029494	-2.376137
C	-0.628392	2.236145	-1.630944
C	2.400301	1.598100	1.289970
C	0.554045	2.777101	-1.126991
H	1.504743	2.649981	-1.638870
H	-1.586323	2.561891	-1.227997
H	-3.785276	-1.413544	0.156789
H	-2.905381	-2.413915	-0.994829
H	0.279802	0.902293	-3.074590
H	-2.626517	-0.656589	-0.942485
H	-1.468829	0.533427	-2.663568
H	-1.752589	0.426172	1.143959
H	-1.184079	-0.516297	2.515918
H	0.520492	3.549632	-0.365315
C	2.988897	2.081785	2.603061
H	-2.905149	-0.523563	2.108201
H	3.095917	1.234643	3.288297
H	-3.087187	-2.946651	1.900702
H	-1.412188	-3.124209	2.408879
H	2.313874	2.797619	3.080178
H	3.964934	2.538782	2.437665
H	-1.975957	-3.907854	0.925695
H	-0.455949	-4.806637	-2.232959
H	-1.711291	-4.100270	-1.223259
C	-1.743787	-1.724119	0.750110
C	-2.814518	-1.547895	-0.335849
H	-0.224550	-4.715834	-0.487958
C	-1.891166	-0.513667	1.688218
H	1.472971	-3.524151	-3.008844
C	-2.054375	-3.004932	1.534331
H	2.051102	-3.675728	-1.354242
C	0.030302	-2.815677	-1.583986
H	2.021000	-2.084787	-2.140933
C	-0.628975	-4.181515	-1.347829
H	-0.097598	-1.293455	-3.134405
C	1.484915	-3.032361	-2.028412
H	-1.688027	-1.859768	-2.604300
C	-0.658278	-2.162486	-2.790845
H	-0.673273	-2.893456	-3.608973
C	1.300037	-2.310781	1.196161
H	0.144562	-2.077829	3.056769
C	1.049849	-1.693393	2.581754
H	1.010977	-0.602710	2.534026
H	1.890671	-1.978176	3.226906
C	1.330970	-3.835257	1.370845
H	2.074400	-4.068658	2.143384
C	2.693807	-1.839959	0.740084
H	1.638430	-4.366111	0.467937
H	0.376715	-4.247594	1.707698
H	3.400171	-2.025386	1.558833
H	2.726401	-0.773317	0.505689
H	3.062530	-2.387748	-0.127311

B’

Pd	0.102135	-1.402730	-1.981850
P	-1.764736	0.087375	-2.034800
C	1.604581	-2.967029	-1.865516
C	0.758966	-3.033538	-0.752352
C	-0.633181	-3.136624	-0.988518
H	-1.502157	1.068722	-5.703510
H	-1.381574	2.201054	-4.363375
H	-0.248651	0.826063	-4.472522
H	-1.089140	-1.500716	-4.448265
H	-2.772433	-1.907065	-4.071163
H	1.361620	-3.513611	-2.775860
H	2.631444	-2.634987	-1.755511
H	-2.384451	-1.079935	-5.582645
H	1.093128	-2.701294	0.229241
H	-0.984580	-3.742302	-1.825387
H	-3.826295	0.873456	-5.227287
H	-1.312702	-3.070861	-0.146922
O	2.916375	-0.000305	-1.877088
H	-4.467375	0.079578	-3.794232
O	1.233035	-0.273863	-3.342108
C	2.416890	0.107183	-3.002174
H	-3.867996	1.744894	-3.694609
C	3.195422	0.764261	-4.128640
H	-1.973174	3.869797	-1.277160
H	2.729728	1.723085	-4.379685
H	3.162170	0.143656	-5.027929
H	-2.232886	3.143335	-2.859224
C	-2.274396	0.242541	-3.884177
H	4.229528	0.937148	-3.828627
C	-1.281596	1.147239	-4.631141
O	0.433328	-0.980310	1.773019
N	1.528886	-0.390935	2.067818
H	-3.313128	2.749567	-1.515763
C	3.585015	0.629682	1.412765
C	-2.124561	-1.151998	-4.518772
C	3.019668	0.483115	3.722477
H	-0.816436	2.700887	0.537157
C	-3.691495	0.764566	-4.143673
C	2.398148	-0.001153	1.093992
C	1.841778	-0.146904	3.371990
H	-2.287467	1.739550	0.619753
C	3.919584	0.885495	2.739247
C	-1.317651	1.825578	-1.353816

H	4.230040	0.907616	0.585945
H	−0.706261	0.933516	0.568674
H	3.219896	0.651621	4.775606
C	−2.274003	2.945299	−1.786166
H	2.109568	−0.218725	0.069534
H	0.846387	1.502101	−1.385043
C	−1.288204	1.776447	0.181644
H	1.092380	−0.492044	4.071975
H	4.848928	1.379567	3.000264
H	0.236185	2.227468	−2.871836
C	0.107281	2.196478	−1.790801
H	0.328524	3.196283	−1.395587
C	−3.276873	−0.541755	−1.020284
H	−4.284934	−1.620689	−2.654107
C	−3.805833	−1.818353	−1.692771
H	−3.018351	−2.560243	−1.843372
H	−4.566008	−2.264141	−1.040241
C	−4.455234	0.432989	−0.878544
H	−5.249293	−0.073557	−0.315028
C	−2.811807	−0.913643	0.409377
H	−4.186735	1.325997	−0.310346
H	−4.881699	0.746213	−1.832509
H	−3.375429	−1.788687	0.754095
H	−1.748043	−1.144012	0.486054
H	−3.013950	−0.108810	1.118110

$TS_{B'C}$

Pd	0.015136	−1.384916	−1.278600
P	−1.828499	0.132645	−1.735060
C	1.372328	−3.014228	−0.891776
C	0.044154	−3.470532	−0.849931
C	−0.721140	−3.233263	−2.016263
H	−0.980684	1.265227	−5.257091
H	−1.053453	2.348470	−3.874121
H	0.043352	0.938163	−3.838696
H	−0.896896	−1.339597	−4.142079
H	−2.630404	−1.694083	−4.019813
H	1.957742	−3.013178	−1.807876
H	1.947733	−2.958446	0.027858
H	−2.015224	−0.790330	−5.404356
H	−0.432252	−3.753872	0.086089
H	−0.244761	−3.314157	−2.992164
H	−3.396471	1.196791	−5.116193
H	−1.783072	−3.452242	−2.003748
O	1.457111	−0.105257	−2.576202
H	−4.268509	0.389185	−3.819477
O	3.386651	−1.228724	−2.312667
C	2.621485	−0.480166	−2.947853
H	−3.589553	2.001587	−3.560319
C	3.078751	0.074032	−4.293431
H	−2.119932	3.894937	−0.829538
H	3.004773	1.165774	−4.292728
H	2.416003	−0.291135	−5.084985
H	−2.184609	3.245107	−2.461888
C	−2.070501	0.412004	−3.620721
H	4.104390	−0.227602	−4.511209
C	−0.938879	1.300672	−4.160661
O	0.709269	−0.447280	0.847779
N	1.867706	−0.007829	1.222637
H	−3.437726	2.816530	−1.286353
C	4.192635	0.331101	0.878680
C	−1.899110	−0.943883	−4.324049
C	3.173815	1.079786	2.898439
H	−1.292229	2.669112	1.051321
C	−3.411978	1.032621	−4.031225
C	2.968147	−0.143960	0.441528
C	1.966662	0.596955	2.436752
H	−2.686392	1.607599	0.928553
C	4.318560	0.952355	2.115484
C	−1.489705	1.845825	−0.915956
H	5.039730	0.196468	0.214537
H	−1.038993	0.918482	1.010706
H	3.202544	1.553858	3.873745
C	−2.369381	2.999933	−1.414045
H	2.838851	−0.636292	−0.526604
H	0.651497	1.438554	−0.785354
C	−1.650275	1.730824	0.608139
H	1.032258	0.652795	2.979250
H	5.275825	1.326412	2.461943
H	0.228701	2.385753	−2.198276
C	−0.016786	2.217825	−1.151797
H	0.187232	3.147018	−0.603374
C	−3.486898	−0.532326	−1.002062
H	−4.445262	−1.273789	−2.846702
C	−4.071884	−1.639824	−1.889351
H	−3.353951	−2.436267	−2.083350
H	−4.921955	−2.088361	−1.360344
C	−4.595160	0.510175	−0.800737
H	−5.485750	−0.001011	−0.413163
C	−3.161213	−1.192736	0.348039
H	−4.329303	1.280505	−0.075908
H	−4.883355	1.000657	−1.733453
H	−4.073991	−1.655262	0.744988
H	−2.400401	−1.970060	0.230241
H	−2.794100	−0.488028	1.093655

C

Pd	−0.039651	−1.179741	−0.888264
P	−1.844423	0.245023	−1.627493
C	1.421770	−2.740100	−0.400184
C	0.232837	−3.313520	−0.856675
C	−0.233598	−2.872556	−2.124035
H	−0.898100	1.393244	−5.134046
H	−1.072568	2.470348	−3.757769
H	0.103829	1.117207	−3.695983
H	−0.619721	−1.148923	−4.016424
H	−2.311181	−1.689788	−3.918434
H	2.208658	−2.418819	−1.094445
H	1.697561	−2.861022	0.645323
H	−1.767787	−0.739270	−5.300454
H	−0.424865	−3.857869	−0.181276
H	0.500443	−2.668943	−2.901199
H	−3.277161	1.118060	−5.116052
H	−1.204127	−3.204601	−2.477607
O	1.632369	−0.030473	−2.634766
H	−4.141756	0.227532	−3.869846
O	3.444891	−1.326806	−2.369917
C	2.671283	−0.633664	−3.063767
H	−3.651247	1.903857	−3.583668
C	2.960287	−0.488375	−4.556585
H	−2.465944	4.005092	−0.916848
H	2.905342	0.562959	−4.853939
H	2.192814	−1.021995	−5.128955
H	−2.362617	3.289133	−2.519312
C	−1.978678	0.467336	−3.537018
H	3.939660	−0.898949	−4.808101
C	−0.889951	1.431022	−4.036931
O	0.497659	−0.037575	0.909048
N	1.768097	0.118995	1.189433
H	−3.663400	2.812301	−1.417365
C	4.038753	0.275505	0.538155
C	−1.655657	−0.871072	−4.216909
C	3.441707	0.411968	2.848164
H	−1.696360	2.941512	1.064681
C	−3.345496	0.957471	−4.032798
C	2.699143	0.145603	0.211625
C	2.118271	0.255610	2.491882
H	−3.016657	1.793385	0.886731
C	4.429554	0.414419	1.863367
C	−1.686731	2.007332	−0.861943
H	4.747529	0.238171	−0.281564
H	−1.347514	1.212872	1.150971
H	3.687495	0.515654	3.899351
C	−2.604516	3.071955	−1.477698
H	2.324470	0.045802	−0.814924
H	0.435785	1.807796	−0.442818
C	−1.964211	1.961642	0.648790
H	1.288171	0.219754	3.185084
H	5.476107	0.516188	2.130019
H	0.129415	2.485333	−2.038053
C	−0.224904	2.463069	−1.010135
H	−0.140913	3.477198	−0.597994
C	−3.487378	−0.528814	−0.979979
H	−4.161533	−1.503735	−2.844832
C	−3.858659	−1.754611	−1.826604
H	−3.039603	−2.476580	−1.870640

H	-4.710254	-2.255641	-1.349769
C	-4.702723	0.406562	-0.941018
H	-5.571589	-0.165582	-0.591025
C	-3.228462	-1.064240	0.439028
H	-4.570641	1.238629	-0.247102
H	-4.956232	0.814796	-1.921209
H	-4.125847	-1.595459	0.781679
H	-2.387076	-1.764714	0.446521
H	-3.011768	-0.279798	1.163337

$TS_{CC'}$

Pd	-0.021070	-1.285537	-0.774396
P	-1.724254	0.231880	-1.541195
C	1.225805	-2.964466	-0.209516
C	0.054471	-3.417462	-0.841479
C	-0.163288	-2.930899	-2.150965
H	-0.757805	1.423186	-5.028170
H	-0.971779	2.492145	-3.650389
H	0.217976	1.172737	-3.573954
H	-0.556824	-1.179345	-3.952474
H	-2.265731	-1.637752	-3.911111
H	2.115968	-2.783038	-0.806743
H	1.358989	-3.110511	0.858651
H	-1.651727	-0.668230	-5.248718
H	-0.742627	-3.898638	-0.277706
H	0.701062	-2.784018	-2.796814
H	-3.158624	1.187282	-5.017500
H	-1.098459	-3.154946	-2.652540
O	2.267944	0.164769	-2.714015
H	-4.026820	0.271978	-3.791921
O	2.974716	-1.963737	-2.915136
C	2.847834	-0.840790	-3.362237
H	-3.527232	1.937352	-3.465370
C	3.323125	-0.425133	-4.728915
H	-2.371325	3.986649	-0.772309
H	3.968804	0.453711	-4.652954
H	2.463962	-0.142417	-5.345020
H	-2.284868	3.300769	-2.387690
C	-1.866267	0.485755	-3.449949
H	3.859057	-1.248536	-5.199217
C	-0.776243	1.456202	-3.931237
O	0.070066	-0.515634	1.367120
N	1.308704	-0.072141	1.356976
H	-3.569451	2.797921	-1.277185
C	3.293093	0.394832	0.239076
C	-1.570780	-0.838158	-4.167567
C	3.148879	0.761286	2.599125
H	-1.593204	2.885332	1.190977
C	-3.227083	1.001298	-3.938017
C	1.963744	-0.047533	0.161302
C	1.844222	0.319300	2.537744
H	-2.900697	1.728649	0.985140
C	3.898736	0.795500	1.426035
C	-1.580027	1.995212	-0.757653
H	3.867774	0.430486	-0.682833
H	-1.231965	1.146682	1.233527
H	3.560381	1.065314	3.555504
C	-2.512692	3.062397	-1.346877
H	1.945345	-0.120695	-1.805244
H	0.585998	1.760526	-0.521167
C	-1.849407	1.912224	0.753012
H	1.179322	0.241448	3.388797
H	4.931619	1.131482	1.440254
H	0.143218	2.707700	-1.941272
C	-0.131456	2.486013	-0.910587
H	-0.024115	3.414910	-0.336498
C	-3.375386	-0.545489	-0.912302
H	-4.068767	-1.483120	-2.789757
C	-3.748617	-1.754470	-1.781644
H	-2.923965	-2.468286	-1.850709
H	-4.590249	-2.271529	-1.304451
C	-4.587610	0.393373	-0.860352
H	-5.460015	-0.186711	-0.533103
C	-3.125604	-1.107975	0.498463
H	-4.459952	1.204688	-0.141725
H	-4.833876	0.829047	-1.830543
H	-4.049274	-1.588404	0.846469
H	-2.329404	-1.858427	0.489558
H	-2.845373	-0.350406	1.228209

C’

Pd	0.151756	-1.236860	-0.817126
P	-1.620195	0.271606	-1.512423
C	1.516043	-2.816752	-0.388609
C	0.268720	-3.411252	-0.704478
C	-0.317590	-3.183411	-1.948240
H	-0.674152	1.440411	-5.014104
H	-0.922719	2.528147	-3.654501
H	0.305188	1.246805	-3.557387
H	-0.428704	-1.151232	-3.924844
H	-2.121170	-1.638404	-3.818749
H	2.271789	-2.721300	-1.166572
H	1.891345	-2.888547	0.627226
H	-1.565862	-0.688041	-5.197199
H	-0.337335	-3.811653	0.107878
H	0.311185	-2.990357	-2.814606
H	-3.064616	1.181455	-4.992704
H	-1.314759	-3.562217	-2.142682
O	2.309330	-0.153612	-2.987684
H	-3.930682	0.289789	-3.749596
O	2.097921	-2.117456	-4.060547
C	2.623018	-1.031173	-3.949603
H	-3.422305	1.956537	-3.450218
C	3.692786	-0.498537	-4.858976
H	-2.369193	3.989258	-0.669839
H	4.594990	-0.279249	-4.281113
H	3.361888	0.440229	-5.311830
H	-2.275829	3.348170	-2.303809
C	-1.764079	0.506319	-3.420533
H	3.913613	-1.231622	-5.633204
C	-0.697058	1.493161	-3.918254
O	-0.209587	-0.835372	2.008224
N	0.900612	-0.231913	1.748398
H	-3.533524	2.776527	-1.196140
C	2.564029	0.485080	0.239040
C	-1.454741	-0.828753	-4.114422
C	2.811846	0.947115	2.570361
H	-1.399433	2.820856	1.271404
C	-3.128579	1.011826	-3.910334
C	1.333734	-0.144471	0.448586
C	1.605651	0.311952	2.777865
H	-2.778269	1.752492	1.048060
C	3.312950	1.036148	1.275392
C	-1.507137	2.027640	-0.723491
H	2.933656	0.549213	-0.779866
H	-1.160993	1.061823	1.232236
H	3.342565	1.359664	3.421925
C	-2.487572	3.076203	-1.266984
H	1.616124	-0.545717	-2.398726
H	0.669282	1.897793	-0.542073
C	-1.725294	1.889554	0.792155
H	1.134644	0.181854	3.743991
H	4.262841	1.522342	1.075716
H	0.143865	2.818965	-1.957220
C	-0.088194	2.583622	-0.919210
H	-0.009586	3.517530	-0.348744
C	-3.270977	-0.529352	-0.890223
H	-4.029711	-1.387185	-2.782438
C	-3.684067	-1.698350	-1.795089
H	-2.875367	-2.418926	-1.916637
H	-4.518989	-2.219311	-1.310981
C	-4.474323	0.417964	-0.792295
H	-5.346423	-0.171678	-0.482485
C	-3.011892	-1.141481	0.496792
H	-4.339891	1.198213	-0.041751
H	-4.725966	0.891062	-1.743900
H	-3.934197	-1.635986	0.828739
H	-2.213574	-1.887956	0.468516
H	-2.725437	-0.415095	1.254749

D

Pd	0.512487	-1.450932	0.037571
P	-1.158311	0.152771	-0.619833
C	1.906000	-3.043313	0.334651
C	0.604661	-3.588187	0.398060

C	-0.278665	-3.468162	-0.680450
H	0.501404	1.452762	-3.767778
H	0.010239	2.483545	-2.428287
H	1.119216	1.123238	-2.141782
H	0.337104	-1.229604	-2.755713
H	-1.352561	-1.563516	-3.161272
H	2.452348	-3.045226	-0.607827
H	2.516989	-3.027553	1.231290
H	-0.367714	-0.590786	-4.256482
H	0.206190	-3.856968	1.375725
H	0.100447	-3.455245	-1.700343
H	-1.908000	1.306828	-4.253243
H	-1.297534	-3.819360	-0.557686
H	-3.036070	0.450090	-3.209967
H	-2.477836	2.067834	-2.768523
H	-2.092588	3.778789	0.387723
H	-1.665997	3.301610	-1.249348
C	-0.954379	0.507248	-2.498946
C	0.238694	1.451836	-2.702587
O	0.747577	-0.676812	2.821162
N	1.769108	-0.147870	2.241244
H	-3.091982	2.606366	-0.465881
C	3.069529	0.287122	0.315258
C	-0.569950	-0.805929	-3.199405
C	3.794942	1.113586	2.433616
H	-1.402300	2.507859	2.340172
C	-2.171469	1.115937	-3.205004
C	1.923393	-0.273262	0.880676
C	2.672356	0.538830	2.994378
H	-2.635226	1.346709	1.877083
C	4.012806	0.985015	1.064956
C	-1.158844	1.847893	0.312143
H	3.208604	0.172141	-0.756363
H	-0.971431	0.793670	2.227120
H	4.486330	1.648524	3.076203
C	-2.063785	2.926192	-0.302522
H	0.942399	1.811126	0.933042
C	-1.575802	1.586966	1.769368
H	2.422837	0.575713	4.047320
H	4.891439	1.416368	0.595442
H	0.690829	2.695389	-0.569280
C	0.250381	2.455343	0.396848
H	0.166636	3.395144	0.956958
C	-2.902679	-0.635228	-0.330536
H	-3.426423	-1.265524	-2.377778
C	-3.191638	-1.695058	-1.401817
H	-2.363280	-2.393280	-1.514709
H	-4.070521	-2.269987	-1.084270
C	-4.098915	0.324839	-0.318976
H	-5.011791	-0.271632	-0.195279
C	-2.849880	-1.379745	1.015017
H	-4.069961	1.034451	0.509258
H	-4.202954	0.882691	-1.253340
H	-3.814086	-1.878942	1.175659
H	-2.064131	-2.138732	1.012205
H	-2.665139	-0.726173	1.866474

TS_{DE}

Pd	0.303154	-1.404933	0.004747
P	-1.231317	0.197087	-0.662009
C	2.037173	-2.630693	0.666673
C	0.824059	-3.446611	0.518155
C	0.198902	-3.713320	-0.680314
H	0.369921	1.558153	-3.818027
H	-0.059034	2.544615	-2.424046
H	1.032729	1.154438	-2.226093
H	0.218718	-1.159981	-2.822273
H	-1.470465	-1.477422	-3.227590
H	2.747464	-2.699742	-0.157304
H	2.504828	-2.775880	1.639106
H	-0.485677	-0.494704	-4.315272
H	0.334029	-3.747168	1.443005
H	0.702445	-3.566768	-1.632933
H	-2.034031	1.420326	-4.263704
H	-0.713884	-4.300413	-0.696029
H	-3.143887	0.536338	-3.222461
H	-2.584274	2.147168	-2.753257
H	-1.929277	3.864527	0.428240
H	-1.620181	3.358450	-1.227590
C	-1.056351	0.583096	-2.537430
C	0.141395	1.520551	-2.745492
O	0.906853	-1.063177	2.908605
N	1.849181	-0.456559	2.284627
H	-3.051617	2.765332	-0.372921
C	3.112128	-0.068165	0.307317
C	-0.684899	-0.722942	-3.260054
C	3.654579	1.115783	2.309579
H	-1.349344	2.478023	2.356997
C	-2.281251	1.205632	-3.215950
C	2.057228	-0.732543	0.949147
C	2.633391	0.439023	2.943727
H	-2.659484	1.416334	1.861442
C	3.905111	0.863190	0.960341
C	-1.157080	1.860460	0.307481
H	3.287618	-0.304230	-0.738445
H	-1.041884	0.742851	2.192377
H	4.244930	1.826438	2.877550
C	-1.994667	3.012328	-0.260563
H	0.944944	1.552559	0.817172
C	-1.586192	1.589536	1.758333
H	2.366359	0.560892	3.985878
H	4.701709	1.379675	0.434393
H	0.726589	2.636062	-0.558220
C	0.304317	2.328418	0.397546
H	0.343156	3.198703	1.064873
C	-2.975781	-0.575470	-0.361367
H	-3.411539	-1.285141	-2.406502
C	-3.226948	-1.674459	-1.403090
H	-2.391666	-2.380923	-1.440864
H	-4.123106	-2.232827	-1.104668
C	-4.162917	0.393729	-0.382346
H	-5.089116	-0.183425	-0.264379
C	-2.943621	-1.300431	0.996010
H	-4.129959	1.112190	0.439671
H	-4.242914	0.948600	-1.320297
H	-3.898874	-1.823496	1.133846
H	-2.138170	-2.041566	1.021375
H	-2.804403	-0.634618	1.846172

E

Pd	-0.164247	-1.375006	0.454780
P	-1.582523	0.196539	-0.525681
C	2.563645	-2.751049	0.823689
C	1.151830	-2.833305	1.364579
C	0.129412	-3.491915	0.701888
H	0.793588	1.736394	-3.048285
H	0.092682	2.589489	-1.677647
H	1.047585	1.113132	-1.410899
H	0.269843	-1.092629	-2.360051
H	-1.240323	-1.222653	-3.264665
H	2.594866	-3.135408	-0.200873
H	3.213308	-3.379073	1.449364
H	0.070019	-0.234669	-3.910519
H	1.066490	-2.631916	2.431259
H	0.298594	-3.960206	-0.267185
H	-1.401439	1.762684	-4.088284
H	-0.752720	-3.831829	1.240565
H	-2.767999	0.852227	-3.456385
H	-2.303682	2.385923	-2.706015
H	-2.260602	3.833848	0.686937
H	-1.573415	3.400953	-0.874771
C	-0.931943	0.724202	-2.259237
C	0.317604	1.595766	-2.069380
O	3.190580	-1.498699	3.115079
N	3.411908	-0.831040	2.058626
H	-3.221667	2.905452	-0.466928
C	3.392232	-0.621669	-0.316953
C	-0.438412	-0.539333	-2.986291
C	4.198076	1.180615	1.016966
H	-2.401520	2.270548	2.544399
C	-1.917428	1.472279	-3.163922
C	3.130150	-1.366114	0.824018
C	3.936300	0.427150	2.141394
H	-3.591155	1.377299	1.603712
C	3.927567	0.659664	-0.245681
C	-1.671662	1.762513	0.587293

H	3.156875	−1.074348	−1.275223
H	−2.198042	0.528215	2.314963
H	4.617091	2.173314	1.144454
C	−2.213234	3.037589	−0.067304
H	0.135903	1.128780	1.636062
C	−2.524643	1.450953	1.825228
H	4.119026	0.746873	3.158832
H	4.130086	1.230762	−1.145088
H	0.465058	2.308593	0.361696
C	−0.253258	2.019935	1.128507
H	−0.298571	2.834985	1.862651
C	−3.361447	−0.504001	−0.736037
H	−3.257587	−1.076806	−2.863799
C	−3.350497	−1.532355	−1.875747
H	−2.547016	−2.264306	−1.743169
H	−4.303483	−2.075652	−1.861225
C	−4.464678	0.523657	−1.010324
H	−5.412805	−0.007042	−1.166691
C	−3.714548	−1.301632	0.531506
H	−4.617620	1.206183	−0.171053
H	−4.274276	1.121777	−1.904298
H	−4.661558	−1.829289	0.359465
H	−2.936972	−2.040489	0.750876
H	−3.844248	−0.677458	1.415219

TS$_{B'F}$

Pd	0.277989	−1.082182	−1.414750
P	−1.687092	0.269063	−1.829210
C	1.693729	−2.546883	−1.166491
C	0.576920	−3.367068	−0.747586
C	−0.346014	−3.869654	−1.609844
H	−1.301699	1.085525	−5.519861
H	−1.306278	2.288443	−4.235441
H	−0.112499	0.954609	−4.216924
H	−0.836869	−1.381160	−4.152508
H	−2.516889	−1.864297	−3.830943
H	2.101998	−2.728422	−2.160120
H	2.453768	−2.330358	−0.416932
H	−2.107453	−1.067707	−5.350051
H	0.390165	−3.459426	0.321731
H	−0.191040	−3.825599	−2.684911
H	−3.652413	0.808105	−5.129111
H	−1.238493	−4.373324	−1.251279
O	2.858833	0.422050	−2.225228
H	−4.319732	0.079659	−3.674206
O	1.217525	−0.682102	−3.303094
C	2.325741	−0.031741	−3.246429
H	−3.778746	1.765342	−3.653212
C	2.978295	0.194110	−4.601433
H	−2.143487	4.086222	−1.269891
H	2.390373	0.922524	−5.170032
H	2.989662	−0.733316	−5.179402
H	−2.374898	3.252409	−2.802029
C	−2.127599	0.311534	−3.699659
H	3.992588	0.575957	−4.478732
C	−1.145079	1.228617	−4.443092
O	0.365742	−0.776335	0.903064
N	1.438505	−0.307681	1.467038
H	−3.433995	2.894293	−1.429753
C	3.573898	0.723846	1.387540
C	−1.884786	−1.095706	−4.275261
C	2.610302	0.151808	3.492035
H	−1.016033	3.052019	0.643690
C	−3.552742	0.767330	−4.036726
C	2.456424	0.218927	0.743825
C	1.510459	−0.344434	2.823562
H	−2.393003	1.957797	0.736065
C	3.670635	0.699610	2.773513
C	−1.401602	2.068245	−1.228386
H	4.363530	1.132815	0.766460
H	−0.743434	1.297938	0.710695
H	2.623639	0.102189	4.575494
C	−2.404754	3.118879	−1.718521
H	2.347095	0.203952	−0.346248
H	0.770459	1.759427	−1.366456
C	−1.395028	2.078678	0.307710
H	0.643914	−0.784236	3.299426
H	4.543810	1.093539	3.282046

H	0.104666	2.630916	−2.740788
C	0.012930	2.489793	−1.664259
H	0.249511	3.449394	−1.186816
C	−3.200174	−0.461795	−0.886762
H	−4.167893	−1.549926	−2.548755
C	−3.677041	−1.739022	−1.592795
H	−2.850418	−2.438692	−1.751133
H	−4.410775	−2.233978	−0.944235
C	−4.396282	0.483215	−0.723672
H	−5.214015	−0.064885	−0.237951
C	−2.736027	−0.923423	0.504932
H	−4.164450	1.339884	−0.086915
H	−4.775383	0.858742	−1.676155
H	−3.594345	−1.375972	1.018854
H	−1.947762	−1.677257	0.430224
H	−2.358481	−0.118723	1.133385

F

Pd	0.333043	−1.010225	−1.313312
P	−1.661799	0.378963	−1.790323
C	1.657016	−2.533436	−0.971264
C	0.681634	−3.606174	−0.752035
C	0.247949	−4.470659	−1.687628
H	−1.188330	1.398026	−5.412910
H	−1.215789	2.519321	−4.057100
H	−0.034946	1.185900	−4.091853
H	−0.844899	−1.201958	−4.183550
H	−2.564397	−1.606919	−3.996847
H	2.264489	−2.660263	−1.868308
H	2.276495	−2.315523	−0.097099
H	−2.027133	−0.714722	−5.414061
H	0.250481	−3.670662	0.248756
H	0.645787	−4.448307	−2.699338
H	−3.564990	1.149125	−5.082868
H	−0.510643	−5.215592	−1.466408
O	2.706754	0.256143	−2.484887
H	−4.263744	0.314921	−3.702367
O	1.050420	−1.057810	−3.261094
C	2.145868	−0.384610	−3.382367
H	−3.720396	1.992318	−3.541169
C	2.749163	−0.444625	−4.773933
H	−2.236223	4.154192	−1.024805
H	1.977238	−0.301075	−5.534309
H	3.181052	−1.437727	−4.934621
H	−2.372423	3.422299	−2.619405
C	−2.076164	0.525870	−3.663760
H	3.532952	0.305957	−4.882372
C	−1.062719	1.471833	−4.325438
O	0.301788	−0.758719	0.835192
N	1.374876	−0.230515	1.365348
H	−3.487260	2.948070	−1.328579
C	3.485391	0.841169	1.238537
C	−1.865231	−0.843667	−4.335637
C	2.517650	0.365694	3.366524
H	−1.145876	3.041288	0.852265
C	−3.488021	1.026340	−3.994679
C	2.383287	0.276824	0.616042
C	1.434870	−0.191681	2.720518
H	−2.506184	1.924229	0.835885
C	3.570630	0.896134	2.623442
C	−1.447739	2.153622	−1.083504
H	4.271609	1.232741	0.602336
H	−0.848927	1.290177	0.834460
H	2.525084	0.375859	4.450894
C	−2.451135	3.214293	−1.550125
H	2.279406	0.194553	−0.472583
H	0.729607	1.904569	−1.120131
C	−1.496650	2.082476	0.449959
H	0.576190	−0.627623	3.213840
H	4.431170	1.337329	3.114408
H	0.118350	2.796097	−2.505113
C	−0.027115	2.626085	−1.439022
H	0.163123	3.577593	−0.925436
C	−3.177190	−0.442156	−0.927512
H	−4.096349	−1.448687	−2.662543
C	−3.600984	−1.687007	−1.719896
H	−2.751338	−2.347337	−1.921069
H	−4.319925	−2.250206	−1.111622

C	-4.403974	0.456992	-0.736883
H	-5.213522	-0.141889	-0.299472
C	-2.732052	-0.975023	0.444115
H	-4.213438	1.284137	-0.049028
H	-4.776601	0.873192	-1.674815
H	-3.587725	-1.481742	0.909334
H	-1.922743	-1.702682	0.339870
H	-2.391899	-0.199509	1.128156

G

Pd	-1.233198	1.712649	-3.654179
P	-2.594648	3.159000	-2.446070
C	-1.832729	4.664024	-1.706147
C	-3.910167	3.907828	-3.493779
C	-3.576285	2.519971	-1.029236
C	0.271395	0.019556	-1.574509
C	-0.724128	-0.052062	-2.720739
C	-0.235520	-0.124266	-4.058665
H	-1.294502	5.215165	-2.482014
H	-1.116156	4.363903	-0.936964
H	-2.586963	5.319102	-1.255905
H	-4.504834	4.642891	-2.940483
H	-4.570287	3.118377	-3.863820
H	-3.441226	4.385496	-4.357598
H	-4.257654	3.282210	-0.635164
H	-2.900103	2.198098	-0.233275
H	-4.154938	1.650671	-1.352543
H	1.173176	0.546805	-1.901946
H	0.552541	-1.010886	-1.311643
H	-1.625661	-0.606645	-2.464577
H	0.846226	-0.094432	-4.212772
H	-0.763703	-0.760547	-4.770326
O	-1.266138	3.197263	-5.455284
O	-0.025631	1.655155	-6.494200
C	-0.653628	2.808006	-6.446959
C	-0.556893	3.602445	-7.712662
H	0.493958	3.774893	-7.960183
H	-1.077338	4.551997	-7.598551
H	-0.994536	3.031464	-8.536286
O	-1.532975	-1.184822	0.021840
N	-1.125005	-0.052754	0.420627
C	0.211006	1.902156	0.141294
C	-1.158495	1.682665	2.078567
C	-0.218201	0.667607	-0.323626
C	-1.578486	0.457327	1.604777
C	-0.246833	2.434514	1.342209
H	0.926293	2.441490	-0.472274
H	-1.552615	2.035109	3.026086
H	-0.167122	1.208509	-5.603280
H	-2.279614	-0.194837	2.108655
H	0.103192	3.398011	1.696362

TS_{GH}

Pd	-1.256638	1.835778	-3.721292
P	-2.601260	3.165866	-2.452850
C	-1.824168	4.672546	-1.748088
C	-3.928437	3.868918	-3.505962
C	-3.531627	2.495121	-1.022545
C	0.232877	0.134656	-1.659744
C	-0.788142	0.106199	-2.788370
C	-0.264607	-0.046995	-4.150323
H	-1.309831	5.214360	-2.545905
H	-1.088906	4.384178	-0.992578
H	-2.572574	5.326873	-1.288154
H	-4.524331	4.612077	-2.965668
H	-4.582580	3.063345	-3.850281
H	-3.463323	4.323232	-4.384277
H	-4.228434	3.238972	-0.621600
H	-2.833098	2.198280	-0.236658
H	-4.089630	1.608600	-1.334482
H	1.123960	0.683574	-1.981665
H	0.529894	-0.903617	-1.449322
H	-1.671011	-0.476900	-2.528755
H	0.821476	-0.149544	-4.230045
H	-0.784809	-0.769450	-4.782124
O	-1.272355	3.239135	-5.389556
O	-0.060368	1.604753	-6.328809
C	-0.621088	2.739015	-6.352305
C	-0.505162	3.536016	-7.627432
H	0.547197	3.626117	-7.908227
H	-0.950733	4.524324	-7.515160
H	-1.008244	2.994820	-8.433971
O	-1.546168	-1.140817	-0.091248
N	-1.130708	-0.028683	0.352770
C	0.204640	1.936035	0.140496
C	-1.137720	1.632415	2.085388
C	-0.234794	0.724132	-0.372584
C	-1.565463	0.428626	1.565181
C	-0.235930	2.415662	1.369872
H	0.916200	2.499538	-0.455612
H	-1.517403	1.942894	3.053208
H	-0.294735	0.989824	-5.104542
H	-2.259176	-0.244984	2.050840
H	0.121284	3.361714	1.761635

H

Pd	-1.460697	2.141752	-3.571052
P	-3.359530	2.611115	-2.518688
C	-3.119221	4.020421	-1.372344
C	-4.636017	3.237848	-3.675499
C	-4.255328	1.387940	-1.499824
C	-0.131378	0.074756	-2.103795
C	-1.433182	0.235475	-2.898201
C	-1.438367	-0.654662	-4.130354
H	-2.645073	4.842977	-1.913937
H	-2.454660	3.716229	-0.559770
H	-4.074189	4.356899	-0.954970
H	-5.510474	3.614919	-3.134667
H	-4.945979	2.433494	-4.347363
H	-4.205436	4.040694	-4.279681
H	-5.125813	1.854946	-1.028198
H	-3.581367	0.983262	-0.735034
H	-4.594116	0.560504	-2.129564
H	0.721950	0.146136	-2.786678
H	-0.126548	-0.930072	-1.653207
H	-2.264939	-0.018222	-2.241943
H	-1.283223	-1.707385	-3.847265
H	-2.391540	-0.595904	-4.665124
O	-0.850691	3.997358	-4.626765
O	0.403485	2.182994	-4.665406
C	0.189152	3.389998	-5.013222
C	1.172933	4.076321	-5.919383
H	2.190918	3.757839	-5.686412
H	1.078873	5.159935	-5.837465
H	0.961524	3.785427	-6.953544
O	-1.665596	0.106561	0.142075
N	-0.748347	0.992851	0.080117
C	1.059495	2.056593	-1.047831
C	0.384194	2.846617	1.096871
C	0.077822	1.073366	-1.013718
C	-0.585687	1.866414	1.116102
C	1.229389	2.957243	-0.004185
H	1.680117	2.104308	-1.937071
H	0.467059	3.513326	1.948795
H	-0.639966	-0.379981	-4.829010
H	-1.280941	1.698806	1.928430
H	1.997972	3.721010	-0.047463

TS_{HI}

Pd	-1.776873	2.202052	-2.961661
P	-3.907884	2.966425	-3.087972
C	-4.023131	4.795887	-3.053304
C	-4.769068	2.541707	-4.651556
C	-5.117281	2.450684	-1.809475
C	-0.359505	0.726364	-2.202581
C	-1.789545	0.503399	-1.889406
C	-2.479664	-0.700799	-2.481834
H	-3.353524	5.197381	-3.818215
H	-3.681200	5.162898	-2.081969
H	-5.046116	5.143420	-3.231555
H	-5.769612	2.985164	-4.690816
H	-4.851644	1.455476	-4.741440
H	-4.176860	2.908863	-5.493722
H	-6.103420	2.893398	-1.984280

H	-4.753901	2.756861	-0.825043
H	-5.206511	1.361161	-1.812623
H	0.057857	1.732066	-3.118561
H	0.056972	-0.080700	-2.814234
H	-2.064050	0.687075	-0.847091
H	-2.153380	-1.607974	-1.957325
H	-3.568772	-0.629377	-2.388537
O	-0.878483	3.768145	-4.184824
O	0.916623	2.452788	-3.914958
C	0.333093	3.472204	-4.392335
C	1.153261	4.378628	-5.274349
H	0.592582	5.272638	-5.546651
H	1.436798	3.833440	-6.179353
H	2.078329	4.652284	-4.761063
O	0.672304	-1.263635	-0.771327
N	1.000409	-0.100039	-0.387364
C	0.881151	2.277242	-0.590709
C	2.183521	1.306817	1.152961
C	0.525729	1.016404	-1.045613
C	1.825878	0.058595	0.687652
C	1.705941	2.447730	0.515966
H	0.494524	3.129753	-1.140347
H	2.837727	1.369546	2.016363
H	-2.235950	-0.823870	-3.541909
H	2.144865	-0.879374	1.122654
H	1.975387	3.439376	0.862167

I

Pd	-1.840468	1.732401	-2.559948
P	-3.674998	2.986836	-3.160154
C	-3.443866	4.808264	-3.043540
C	-4.179165	2.800222	-4.920050
C	-5.281463	2.757221	-2.292929
C	-0.877859	0.126293	-1.558089
C	-2.269742	0.194752	-1.250453
C	-3.209222	-0.885337	-1.728877
H	-2.543544	5.073939	-3.603519
H	-3.286330	5.089439	-1.998761
H	-4.303066	5.359774	-3.440924
H	-5.010837	3.463927	-5.181438
H	-4.472427	1.763612	-5.106523
H	-3.319725	3.027454	-5.556501
H	-6.059712	3.415485	-2.694522
H	-5.152598	2.964039	-1.226957
H	-5.603674	1.717608	-2.397931
H	1.441357	1.552950	-3.425355
H	-0.522651	-0.561047	-2.322482
H	-2.560127	0.626101	-0.289263
H	-3.225837	-1.733239	-1.029647
H	-4.235496	-0.513347	-1.813297
O	-0.556511	3.051179	-3.911895
O	1.594190	2.368741	-4.090932
C	0.590130	3.138048	-4.363356
C	0.938405	4.228148	-5.345260
H	0.090079	4.895376	-5.493984
H	1.226165	3.776339	-6.299028
H	1.802692	4.790633	-4.982635
O	1.561971	0.442663	-2.574873
N	1.400543	0.829654	-1.330241
C	0.039814	1.147867	0.583478
C	2.348998	1.795785	0.629402
C	0.160760	0.707462	-0.747912
C	2.457771	1.351162	-0.667990
C	1.107290	1.692014	1.266681
H	-0.925364	1.035859	1.063714
H	3.219616	2.206278	1.126941
H	-2.909002	-1.267984	-2.708802
H	3.365648	1.377498	-1.257048
H	0.986331	2.020531	2.294164

TS_{BJ}

Pd	0.834708	0.180466	-0.684950
P	-0.182619	-1.831297	-0.153471
O	2.804765	1.054048	1.465635
O	0.657479	1.647847	1.723997
C	-0.472476	1.325808	-1.882552
C	0.513062	2.198397	-1.342220
C	1.873288	1.784073	1.956337
C	1.859699	1.921938	-1.583416
H	2.173046	1.453735	-2.515404
H	0.249078	2.843525	-0.507206
H	-3.940267	-1.789353	0.395659
H	-3.117295	-2.812284	-0.777168
H	-0.338673	0.932128	-2.890008
H	-2.960021	-1.041815	-0.869489
H	-1.505340	1.444760	-1.567451
H	-1.820177	0.226819	1.110395
H	-1.234153	-0.681206	2.493182
H	2.631635	2.412249	-1.000186
C	2.345307	2.895003	2.879992
H	-2.959876	-0.686947	2.124627
H	1.496998	3.428494	3.310715
H	-2.916537	-3.186444	2.174369
H	-1.170710	-3.275061	2.398436
H	2.972573	3.595129	2.318939
H	2.969084	2.477653	3.675509
H	-1.932585	-4.123324	1.047543
H	-0.566561	-5.041497	-2.261403
H	-1.699879	-4.469987	-1.039876
C	-1.837227	-1.941828	0.787624
C	-3.018929	-1.897069	-0.189115
H	-0.044688	-4.901250	-0.578831
C	-1.956897	-0.696160	1.679894
H	1.150503	-3.628096	-3.216098
C	-1.956293	-3.208534	1.643932
H	1.957232	-3.491172	-1.655062
C	-0.201679	-3.001167	-1.669355
H	1.536294	-2.027869	-2.563400
C	-0.653991	-4.430532	-1.354218
H	-0.839580	-1.363492	-2.965441
C	1.201202	-3.035071	-2.294856
H	-2.171267	-2.432992	-2.503844
C	-1.112125	-2.401204	-2.754538
H	-0.978076	-2.980378	-3.676388
C	1.313929	-2.207638	0.966322
H	0.421240	-2.241485	2.984137
C	1.113136	-1.646564	2.382225
H	0.792530	-0.602148	2.370585
H	2.087742	-1.678761	2.884552
C	1.770082	-3.660843	1.102503
H	2.674173	-3.683310	1.723872
C	2.346835	-1.281738	0.281050
H	2.023510	-4.135114	0.152739
H	1.015836	-4.278574	1.602908
H	3.284381	-1.309218	0.858638
H	2.348439	0.007662	0.689287
H	2.636443	-1.618022	-0.717957

J

Pd	0.853340	0.019776	-0.840038
P	-0.212046	-1.922146	-0.230106
O	2.731251	1.632489	1.550656
O	0.626124	2.083602	2.196669
C	-0.441825	1.420571	-1.997454
C	0.642234	2.094395	-1.418648
C	1.823045	2.223530	2.332350
C	1.980041	1.687244	-1.651613
H	2.258939	1.285938	-2.625625
H	0.443173	2.745798	-0.567723
H	-3.966996	-1.856778	0.407926
H	-3.173419	-2.912591	-0.756499
H	-0.345468	0.971964	-2.984998
H	-3.019054	-1.145590	-0.902916
H	-1.451740	1.663666	-1.682835
H	-1.829004	0.181425	0.974331
H	-1.199553	-0.667562	2.383255
H	2.784071	2.176873	-1.110558
C	2.470425	3.071996	3.391183
H	-2.934020	-0.680641	2.066696
H	1.703524	3.551711	3.997461
H	-2.890316	-3.190953	2.210162
H	-1.137409	-3.258606	2.390907
H	3.109157	3.826847	2.924342
H	3.112832	2.450570	4.021522
H	-1.926711	-4.162177	1.093593

H	-0.682457	-5.178843	-2.240617
H	-1.783893	-4.557680	-1.014460
C	-1.852293	-1.994581	0.746707
C	-3.060481	-1.981082	-0.197055
H	-0.124603	-4.996269	-0.573352
C	-1.945569	-0.714173	1.591396
H	1.033879	-3.828863	-3.264619
C	-1.943899	-3.225710	1.655576
H	1.870517	-3.668448	-1.720415
C	-0.273430	-3.127948	-1.713419
H	1.474998	-2.220999	-2.657668
C	-0.743859	-4.540033	-1.350473
H	-0.894710	-1.508164	-3.038413
C	1.116554	-3.211233	-2.361805
H	-2.244713	-2.524065	-2.515660
C	-1.191961	-2.532393	-2.794219
H	-1.098523	-3.139859	-3.702937
C	1.312293	-2.259687	0.848786
H	0.487338	-2.161278	2.897714
C	1.167217	-1.618669	2.234737
H	0.850949	-0.573901	2.176329
H	2.158468	-1.633714	2.705354
C	1.797474	-3.694321	1.049948
H	2.741690	-3.671120	1.608745
C	2.228287	-1.327929	0.014855
H	1.991947	-4.224410	0.115905
H	1.083559	-4.287045	1.634259
H	3.005169	-0.884440	0.650407
H	2.263229	1.090483	0.874668
H	2.739538	-1.861689	-0.791617

J’

Pd	-0.097880	-0.448942	-1.310138
P	-2.297439	0.201299	-1.316477
C	2.007269	-0.920892	-1.525057
C	1.334373	-2.020757	-0.937212
C	0.248701	-2.644032	-1.568213
H	-2.250583	1.235999	-4.965816
H	-1.840189	2.268405	-3.596653
H	-0.924770	0.779853	-3.876365
H	-1.996454	-1.466576	-3.702099
H	-3.724731	-1.638619	-3.365330
H	2.130781	-0.877868	-2.606712
H	2.778271	-0.409655	-0.955903
H	-3.199460	-0.836263	-4.842995
H	1.472344	-2.199147	0.129728
H	0.205471	-2.706302	-2.654346
H	-4.562854	1.222188	-4.265010
H	-0.326916	-3.387583	-1.026105
H	-5.102102	0.458704	-2.771928
H	-4.334889	2.054992	-2.722191
H	-1.780010	4.000239	-0.628437
H	-2.463045	3.298602	-2.092624
C	-2.934078	0.411561	-3.106063
C	-1.920657	1.230034	-3.919439
O	0.234354	-0.854363	2.474514
N	1.248136	-0.161965	2.800326
H	-3.365896	3.217798	-0.572524
C	3.013973	1.342659	2.219068
C	-2.969400	-0.971682	-3.778619
C	2.795986	0.586776	4.467134
H	-0.937757	2.685305	1.192614
C	-4.311210	1.075212	-3.206921
C	1.910555	0.589052	1.870939
C	1.695166	-0.156331	4.090167
H	-2.492024	1.884866	1.410076
C	3.481087	1.355598	3.530726
C	-1.657422	1.855504	-0.635951
H	3.502485	1.920732	1.441131
H	-1.004240	0.918811	1.239740
H	3.107969	0.552955	5.505902
C	-2.364456	3.155355	-1.014985
H	1.488027	0.525750	0.872863
H	0.519092	2.091757	-0.549029
C	-1.531702	1.812357	0.891422
H	1.110240	-0.778025	4.754975
H	4.347166	1.943407	3.812944
C	-0.233809	1.643156	-1.209871
H	-0.110349	2.089733	-2.200634
C	-3.653711	-0.580975	-0.220470
H	-4.967699	-1.457248	-1.756630
C	-4.328790	-1.763689	-0.925064
H	-3.597798	-2.492818	-1.288221
H	-4.971252	-2.275401	-0.197908
C	-4.729078	0.427990	0.200183
H	-5.450437	-0.071988	0.859411
C	-2.961392	-1.155523	1.025713
H	-4.312296	1.270793	0.756125
H	-5.285580	0.826617	-0.651502
H	-3.705235	-1.708023	1.613865
H	-2.156416	-1.843523	0.752172
H	-2.529232	-0.393969	1.672806

TS$_{J'D}$

Pd	-0.046495	-0.554588	-0.918513
P	-2.204157	0.245511	-1.129905
C	2.020898	-1.360936	-1.243846
C	1.166977	-2.316141	-0.703908
C	-0.057043	-2.596184	-1.382901
H	-1.876437	1.192598	-4.792416
H	-1.500758	2.222585	-3.412485
H	-0.640538	0.686614	-3.631883
H	-1.786325	-1.497542	-3.464148
H	-3.537664	-1.614216	-3.244543
H	2.068385	-1.199540	-2.319649
H	2.825027	-0.945527	-0.645860
H	-2.887235	-0.856397	-4.694915
H	1.261163	-2.581566	0.346522
H	-0.054907	-2.658043	-2.470689
H	-4.215657	1.235276	-4.272502
H	-0.793864	-3.223003	-0.888113
H	-4.890467	0.523993	-2.810253
H	-4.095396	2.105507	-2.739422
H	-1.801358	4.054445	-0.487532
H	-2.261411	3.318026	-2.019623
C	-2.705858	0.418442	-2.969761
C	-1.610883	1.184833	-3.728212
O	0.099684	-0.818242	1.765523
N	1.164813	-0.156151	2.145566
H	-3.350129	3.216654	-0.625878
C	2.782747	1.498061	1.859012
C	-2.736057	-0.977453	-3.615101
C	2.871470	0.103085	3.791967
H	-1.057259	2.798852	1.426800
C	-4.053708	1.112859	-3.194153
C	1.636244	0.863640	1.363850
C	1.740167	-0.530524	3.319359
H	-2.638699	2.025685	1.496851
C	3.418778	1.144622	3.047344
C	-1.600521	1.918871	-0.443219
H	3.193921	2.317198	1.269642
H	-1.141501	1.036051	1.510382
H	3.306236	-0.224588	4.730859
C	-2.299718	3.186252	-0.936662
H	0.629634	1.163466	-0.029091
H	0.409378	2.733631	-0.476319
C	-1.628117	1.923801	1.092526
H	1.238948	-1.345290	3.828071
H	4.310450	1.663065	3.390030
C	-0.107014	1.830791	-0.838605
H	0.068359	1.819813	-1.917591
C	-3.656301	-0.463371	-0.118171
H	-4.846051	-1.379106	-1.731070
C	-4.282150	-1.663909	-0.840044
H	-3.533150	-2.412597	-1.116682
H	-4.988304	-2.143879	-0.152203
C	-4.754724	0.569816	0.162996
H	-5.540430	0.093192	0.762734
C	-3.094404	-0.996523	1.209795
H	-4.385965	1.423514	0.734805
H	-5.222570	0.947241	-0.749077
H	-3.899413	-1.529455	1.731463
H	-2.260399	-1.685454	1.054945
H	-2.733039	-0.210868	1.869993

TS$_{BK}$

Pd	0.631636	0.522955	−0.210728
P	0.030912	−1.684064	0.010835
O	2.490845	2.092928	−0.241875
O	1.906858	0.868594	1.505653
C	−0.443040	1.010729	−1.861888
C	−0.981372	2.145024	−1.120598
C	2.655881	1.746993	0.947670
C	−0.268973	3.254678	−0.820845
H	0.726866	3.413534	−1.222286
H	−1.978481	2.035116	−0.692756
H	−3.769973	−1.435701	−0.183664
H	−2.756576	−2.354713	−1.290581
H	0.340665	1.252257	−2.588455
H	−2.522258	−0.602891	−1.109211
H	−1.186927	0.341031	−2.281151
H	−1.785070	0.376515	1.089470
H	−1.455628	−0.643738	2.488095
H	−0.670959	4.016862	−0.159813
C	3.764096	2.338646	1.782585
H	−3.097027	−0.556269	1.843068
H	4.501941	1.561881	2.007009
H	−3.297957	−2.974264	1.549613
H	−1.705674	−3.210024	2.255555
H	3.364884	2.691341	2.737225
H	4.251478	3.157327	1.252340
H	−2.099758	−3.938605	0.689994
H	−0.285025	−4.719268	−2.376556
H	−1.616256	−4.022099	−1.463825
C	−1.801678	−1.755237	0.609199
C	−2.750107	−1.528749	−0.576628
H	−0.239789	−4.738416	−0.614854
C	−2.034771	−0.575086	1.567848
H	1.772142	−3.515164	−2.834159
C	−2.229463	−3.050303	1.311575
H	2.140920	−3.758801	−1.131672
C	0.203938	−2.792596	−1.561029
H	2.275525	−2.136653	−1.848501
C	−0.530311	−4.138925	−1.478129
H	0.284195	−1.154067	−2.998623
C	1.690330	−3.061308	−1.839025
H	−1.357996	−1.774669	−2.752876
C	−0.305079	−2.052165	−2.805872
H	−0.188685	−2.721749	−3.667090
C	1.137677	−2.473907	1.383604
H	−0.192296	−2.161520	3.117165
C	0.781362	−1.842738	2.738916
H	0.830111	−0.752060	2.701500
H	1.529556	−2.176955	3.468173
C	1.031746	−3.999578	1.513694
H	1.631101	−4.303294	2.380978
C	2.613684	−2.118436	1.128617
H	1.442744	−4.524329	0.648544
H	0.014623	−4.356103	1.684040
H	3.198746	−2.522676	1.964603
H	2.755706	−1.037454	1.111626
H	3.017273	−2.551546	0.215196

K

Pd	0.938977	0.366664	−0.107059
P	0.093762	−1.762179	0.016699
O	2.036119	2.208593	0.042716
O	2.414248	0.679172	1.576727
C	−0.172835	1.064749	−1.652794
C	−1.011969	2.134463	−1.080930
C	2.648617	1.822723	1.084778
C	−0.678246	3.430383	−1.005145
H	0.285434	3.784079	−1.359696
H	−1.986248	1.832782	−0.692009
H	−3.670820	−1.222980	−0.201201
H	−2.727321	−2.226015	−1.296721
H	0.624339	1.453605	−2.298617
H	−2.357284	−0.497264	−1.126096
H	−0.760678	0.327955	−2.194057
H	−1.577356	0.428428	1.093972
H	−1.312522	−0.621092	2.486266
H	−1.350300	4.163322	−0.568252
C	3.671311	2.717574	1.726208
H	−2.944885	−0.418456	1.846482
H	4.669528	2.309069	1.539959
H	−3.324256	−2.813415	1.527112
H	−1.758390	−3.159783	2.247217
H	3.521457	2.735454	2.808280
H	3.615177	3.726881	1.317423
H	−2.185269	−3.854381	0.674224
H	−0.431793	−4.733238	−2.406934
H	−1.712824	−3.950200	−1.490686
C	−1.738880	−1.697294	0.604109
C	−2.659652	−1.398442	−0.588227
H	−0.394981	−4.771453	−0.644595
C	−1.887080	−0.507114	1.567576
H	1.712487	−3.668887	−2.846933
C	−2.261284	−2.961574	1.298595
H	2.042344	−3.980361	−1.147656
C	0.192979	−2.855788	−1.569054
H	2.312726	−2.357382	−1.824543
C	−0.638278	−4.145145	−1.503878
H	0.416843	−1.212084	−2.984909
C	1.656466	−3.232978	−1.842059
H	−1.274071	−1.692158	−2.751329
C	−0.248833	−2.058647	−2.805029
H	−0.186984	−2.723605	−3.675440
C	1.140877	−2.640856	1.381167
H	−0.160821	−2.210841	3.109843
C	0.837725	−1.978184	2.734490
H	0.975971	−0.894420	2.694336
H	1.553711	−2.369363	3.467377
C	0.916287	−4.153161	1.513938
H	1.488607	−4.503925	2.381753
C	2.640950	−2.403879	1.122756
H	1.285940	−4.707987	0.648490
H	−0.126309	−4.428303	1.681391
H	3.190356	−2.822081	1.975837
H	2.880908	−1.340652	1.069183
H	3.011332	−2.902040	0.228645

TS$_{KL}$

Pd	0.187570	1.244944	−0.324941
P	0.540569	−1.992535	0.136639
O	1.228821	2.407809	−1.679320
O	0.118213	0.718081	−2.552050
C	0.571085	2.441582	1.240304
C	−0.593090	3.334917	1.305573
C	0.887903	1.699901	−2.694486
C	−1.566154	3.263455	2.227649
H	−1.527157	2.534131	3.034431
H	−0.663196	4.092558	0.525043
H	1.059150	−1.713532	3.889427
H	−0.483495	−1.577857	3.051342
H	0.719050	1.858674	2.156722
H	0.847951	−0.470241	2.657748
H	1.497919	2.936720	0.936390
H	2.938315	−1.267889	1.578566
H	3.221785	−2.984331	1.268162
H	−2.417694	3.936648	2.213460
C	1.462429	2.061767	−4.032950
H	3.049279	−2.415147	2.927078
H	0.854986	1.635985	−4.832411
H	1.241407	−4.053762	3.381441
H	1.316257	−4.681295	1.738244
H	2.475802	1.653683	−4.105307
H	1.531363	3.146403	−4.136912
H	−0.225697	−4.128955	2.402340
H	−3.240065	−2.407844	1.074783
H	−1.882186	−2.722362	2.154116
C	1.156238	−2.497787	1.886374
C	0.597249	−1.504072	2.916441
H	−2.107832	−3.710180	0.707044
C	2.680867	−2.281492	1.901773
H	−3.001253	−1.291175	−1.055464
C	0.846036	−3.920293	2.365321
H	−2.000773	−2.626293	−1.612416
C	−1.359835	−1.697870	0.276318
H	−1.424675	−0.952430	−1.789254
C	−2.180611	−2.694936	1.103857

H	-0.527145	0.213025	1.069600
C	-1.964989	-1.644241	-1.136477
H	-1.947339	-0.274111	1.883534
C	-1.520716	-0.278409	0.874316
H	-2.164525	0.356929	0.257544
C	0.832677	-3.467133	-1.057796
H	2.447785	-4.499506	0.035792
C	2.279315	-3.957498	-0.897503
H	2.997600	-3.133631	-0.960003
H	2.503910	-4.651039	-1.717433
C	-0.105159	-4.670950	-0.928498
H	0.197080	-5.443119	-1.648618
C	0.746382	-2.896830	-2.485762
H	-1.143623	-4.416226	-1.153361
H	-0.073309	-5.120909	0.066711
H	1.069272	-3.669751	-3.195334
H	1.397198	-2.025945	-2.605651
H	-0.259647	-2.590855	-2.770931

L

Pd	-0.018766	1.872085	-0.927589
P	0.970845	-2.369553	0.357386
O	0.171235	3.491559	-2.185030
O	-0.779377	1.700904	-3.040106
C	0.795014	2.747102	0.689170
C	-0.326448	3.231332	1.505277
C	-0.373690	2.883008	-3.176700
C	-0.699801	2.714227	2.685987
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H	1.436885	2.033678	1.217753
H	0.950207	-0.739689	2.803643
H	1.388042	3.546794	0.234744
H	2.962947	-2.204591	2.433892
H	2.802521	-3.954480	2.255729
H	-1.550188	3.104007	3.237092
C	-0.479507	3.607248	-4.484920
H	2.350266	-3.188293	3.775795
H	-1.204275	3.113227	-5.132645
H	0.076568	-4.212931	3.690977
H	0.423529	-4.996306	2.152987
H	0.499152	3.598321	-4.975206
H	-0.757882	4.649967	-4.318688
H	-1.004627	-3.968152	2.316580
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C	0.885176	-2.851861	2.221369
C	0.381678	-1.647882	3.031488
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C	2.337939	-3.067279	2.684883
H	-1.696596	-0.863303	-1.905158
C	0.044810	-4.075097	2.601801
H	-1.040074	-2.488535	-2.086053
C	-0.720551	-1.571256	-0.114682
H	0.036143	-1.074610	-2.114597
C	-1.997215	-2.198084	0.457285
H	0.343575	0.300488	-0.025598
C	-0.850422	-1.509413	-1.642373
H	-0.599979	0.042463	1.431538
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H	-1.545264	0.431705	0.004401
C	1.144180	-3.993218	-0.659344
H	1.995597	-5.310704	0.892381
C	2.271612	-4.843061	-0.055019
H	3.185780	-4.259607	0.093946
H	2.510055	-5.652827	-0.755930
C	-0.101107	-4.874532	-0.803517
H	0.158027	-5.776506	-1.374024
C	1.648208	-3.589322	-2.057660
H	-0.906612	-4.375503	-1.347453
H	-0.495966	-5.200210	0.161749
H	1.877051	-4.498649	-2.628362
H	2.564519	-2.994906	-1.989144
H	0.920537	-3.018958	-2.634115

TS_{LM}

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O	-1.225630	1.641469	0.877678
C	0.880015	1.299032	-2.791374
C	2.270804	1.461187	-2.304898
C	-0.497225	2.676692	0.931907
C	3.312020	0.740201	-2.732287
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H	-0.118398	-1.818478	3.569324
H	4.311173	0.904351	-2.341242
C	-0.584286	3.607689	2.103247
H	-1.844390	-1.489102	3.713284
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H	1.594865	-1.380334	-2.014838
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C	1.572060	-3.038965	0.956452
H	0.987708	-3.518831	3.031299
C	1.806865	-3.059884	2.474477
H	1.977067	-2.053686	2.871151
H	2.708226	-3.651146	2.680178
C	1.342737	-4.477513	0.480901
H	2.186783	-5.103608	0.800948
C	2.887627	-2.508960	0.355742
H	1.286376	-4.554198	-0.607783
H	0.433416	-4.917916	0.896151
H	3.718716	-3.131256	0.712379
H	3.075954	-1.477993	0.671163
H	2.909735	-2.534588	-0.733417

M

Pd	-0.739220	0.087011	-0.083208
P	-0.373599	-2.042677	0.440109
O	0.392840	1.702855	0.890369
O	-1.178693	2.136460	-0.590273
C	2.277626	1.713636	-2.432035
C	3.143905	1.750472	-1.214090
C	-0.287888	2.538836	0.220337
C	4.466906	1.592167	-1.214978
H	5.020095	1.423445	-2.136981
H	2.623706	1.912278	-0.269131
H	-3.426052	-2.270248	2.674909
H	-3.373632	-2.586110	0.942487
H	2.858739	1.513592	-3.337586
H	-2.930316	-0.986087	1.558554
H	1.745208	2.663023	-2.568594
H	-0.884970	-0.602098	2.922038
H	0.063750	-1.966174	3.533858
H	5.045734	1.630564	-0.296529

C	-0.015130	4.009394	0.365214	C	-2.153925	-3.737623	-1.226670
H	-1.626152	-1.801298	3.996780	H	1.500811	0.944828	-2.334269
H	0.917280	4.250133	-0.156206	C	-0.307524	-2.552576	-2.371229
H	-2.044856	-4.181781	3.163939	H	-2.945122	-1.123788	-0.753385
H	-0.377981	-4.323584	2.614394	C	-1.941566	-1.119934	-1.188133
H	0.123805	4.261788	1.418775	H	-1.978506	-0.683424	-2.193845
H	-0.825622	4.597623	-0.066275	C	1.393970	-2.745686	0.564914
H	-1.711504	-4.619556	1.484552	H	1.490868	-3.165474	2.722886
H	-2.709371	-3.727950	-2.172842	C	1.973810	-2.539880	1.969087
H	-2.887842	-3.784468	-0.421417	H	1.922553	-1.493943	2.285117
C	-1.413728	-2.500165	1.973216	H	3.032273	-2.825696	1.944237
C	-2.869471	-2.060474	1.753687	C	1.433778	-4.239265	0.219262
H	-1.564269	-4.661110	-1.200599	H	2.473051	-4.586791	0.270639
C	-0.918137	-1.667755	3.169659	C	2.294001	-1.959326	-0.399996
H	-0.928158	-2.604331	-3.274110	H	1.071705	-4.442576	-0.790751
C	-1.375868	-3.992712	2.315399	H	0.850503	-4.845659	0.915992
H	0.351601	-3.424469	-2.379441	H	3.325821	-2.308806	-0.271414
C	-1.256264	-2.505436	-1.168833	H	2.275528	-0.886431	-0.188889
H	0.294625	-1.643686	-2.445943	H	2.030167	-2.107271	-1.446559

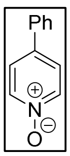
V. Preparation and characterization of starting materials

General procedure: Oxidation of azines (GP1)

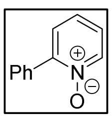
Following a slightly modified version of a reported procedure,[17] *m*-chloroperbenzoic acid (1.2 equiv for pyridines and 1 equiv. for diazine) was added to a solution of the corresponding pyridine or diazine (5 mmol, 1 equiv) in dry CH_2Cl_2 (0.2 M). The mixture was stirred overnight at room temperature. PPh_3 (655.7 mg, 2.5 mmol, 0.5 equiv) was added and the mixture was stirred for another 4 hours. After evaporation, the crude was purified by silica gel column chromatography affording the desired product.

General procedure: Palladium catalyzed arylation of pyridine *N*-oxide (GP2)

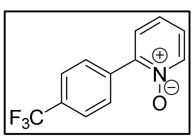
Following a reported procedure,[18] to a tube, dried under vacuum, were added pyridine *N*-oxide (4 mmol, 4 equiv), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol, 0.05 equiv), $P(t\text{-}Bu)_3{\cdot}HBF_4$ (43.6 mg, 0.15 mmol, 0.15 equiv) and K_2CO_3 (276.4 mg, 2 mmol, 2 equiv). The content was purged under Argon atmosphere. Toluene (0.33 M) and aryl bromide (1 mmol, 1 equiv) were added and the reaction mixture was then heated at 110 °C for 24 h. The reaction mixture was filtered over Celite and washed with CH_2Cl_2. The volatiles were removed under reduced pressure and the crude was then purified by silica gel column chromatography affording the corresponding product.



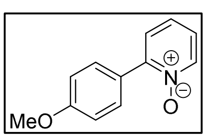
4-phenylpyridine *N*-oxide 1c: Prepared according to general procedure **GP1** from 2-phenylpyridine (0.776 mg, 5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/MeOH (90/10) to 845 mg of afford **1c** (99% yield) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.25 (d, *J* = 7.4 Hz, 2H), 7.57 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.55-7.34 (m, 5H). These data are in agreement with those reported in the literature.[19]



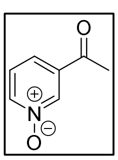
2-phenylpyridine *N*-oxide 1d: Prepared according to general procedure **GP1** from 2-phenylpyridine (0.715 mL, 5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/MeOH (90/10) to afford 850 mg of **1d** (quantitative yield) as white solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.33 (ddd, *J* = 6.3, 1.4, 0.6 Hz, 1H), 7.86-7.78 (m, 2H), 7.55-7.36 (m, 4H), 7.22 (ddd, *J* = 7.5, 6.4, 2.2 Hz, 1H), 7.29 (td, *J* = 7.7, 1.4 Hz, 1H). These data are in agreement with those reported in the literature.[19]



2-(4-(trifluoromethyl))-phenylpyridine *N*-oxide 1e: Prepared according to general procedure **GP2** from pyridine *N*-oxide (380.4 mg, 4 mmol, 2 equiv) and 4-(trifluoromethyl)bromobenzene (0.28 mL, 1 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/Acetone/MeOH (70/28/2) to afford 157 mg of **1e** (66% yield) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.42-8.25 (m, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.40-7.22 (m, 2H). These data are in agreement with those reported in the literature.[18]



2-(4-(methoxy))-phenylpyridine *N*-oxide 1f: Prepared according to general procedure **GP2** from pyridine *N*-oxide (380.4 mg, 4 mmol, 2 equiv) and 4-bromoanisole (0.125 mL, 1 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/Acetone/MeOH (70/28/2) to afford 176.6 mg of **1f** (88% yield) as a yellow solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.36 (d, *J* = 6.4 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.45 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.39-7.25 (m, 1H), 7.21 (ddd, *J* = 7.4, 6.4, 2.1 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H). These data are in agreement with those reported in the literature.[18]



3-acetylpyridine *N*-oxide 1h: Prepared according to general procedure **GP1** from 3-acetylpyridine (0.55 mL, 5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/MeOH (90/10) to afford 685 mg of **1h** (quantitative yield) as a white solid. **m.p.:** 144-145 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.72 (t, *J* = 1.8 Hz, 1H), 8.35 (ddd, *J* = 6.4, 1.7, 1.0 Hz, 1H), 7.77 (ddd, *J* = 8.0, 1.5, 1.0 Hz, 1H), 7.40 (ddd, *J* = 8.0, 6.5, 0.7 Hz, 1H), 2.61 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 193.8, 142.4, 139.6, 135.8, 126.2, 124.7, 26.9. **IR (cm^{-1})** ν: 3028, 1687, 1569, 1421, 920. **HRMS** m/z calculated for $C_7H_7NNaO_2$ $[M+Na]^+$: 160.0369; found 160.0364.

Pyridazine *N*-oxide 1i: Prepared according to general procedure **GP1** from pyridazine (0.363 mL, 5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/MeOH (90/10) to afford 419 mg

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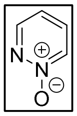
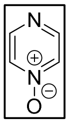
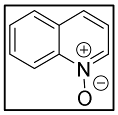
[17] Leclerc, J.-P.; Fagnou, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 7781.
[18] Ding, Y.; Zhao, W.; Song, W.; Zhang, Z.; Ma, B. *Green Chem.* **2011**, *13*, 1486.
[19] Kokatla, H. P.; Thomson, P. F.; Bae, S.; Doddi, V. R.; Lakshman, M. K. *J. Org. Chem.* **2011**, *76*, 7842.



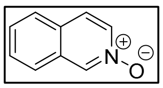
of **1i** (87% yield) as a brown solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.41 (br s, 1H), 8.12 (dt, *J* = 6.5, 1.0 Hz, 1H), 7.65-7.57 (m, 1H), 7.04 (ddd, *J* = 7.7, 5.4, 0.9 Hz, 1H). These data are in agreement with those reported in the literature.[17]



Pyrazine *N*-oxide 1j: Prepared according to general procedure **GP1** from pyrazine (0.404 mL, 5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/MeOH (90/10) to afford 433 mg of **1i** (90% yield) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.47 (dd, *J* = 3.6, 1.3 Hz, 2H), 8.10 (dd, *J* = 3.5, 1.4 Hz, 2H). These data are in agreement with those reported in the literature.[17]



Quinoline *N*-oxide 1k: Prepared according to general procedure **GP1** from quinoline (0.592 mL, 5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/MeOH (90/10) to afford 725 mg of **1k** (quantitative yield) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.75 (d, *J* = 9.2 Hz, 1H), 8.54 (dd, *J* = 6.0, 1.0 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.81-7.70 (m, 2H), 7.64 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.29 (dd, *J* = 8.5, 6.1 Hz, 1H). These data are in agreement with those reported in the literature.[18]

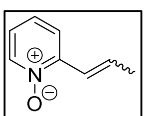


Isoquinoline *N*-oxide 1l: Prepared according to general procedure **GP1** from isoquinoline (0.588 mL, 5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/MeOH (90/10) to afford 727 mg of **1l** (quantitative yield) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.76 (s, 1H), 8.13 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.82-7.76 (m, 1H), 7.76-7.69 (m, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.63-7.54 (m, 2H). These data are in agreement with those reported in the literature.[1818]

VI. Preparation and characterization of C2-alkenylated and allylated *N*-Oxides

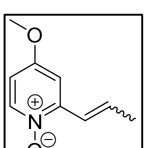
General procedure: Palladium catalyzed alkenylation or allylation of azine *N*-oxides (GP3)

To a tube, dried under vacuum, were added pyridine or diazine *N*-oxide (1 mmol, 2 equiv), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol, 0.1 equiv), $P(t\text{-}Bu)_3{\cdot}HBF_4$ (43.6 mg, 0.15 mmol, 0.3 equiv) and KF (58.1 mg, 1 mmol, 2 equiv). The content was purged with Argon atmosphere. THF (0.25 M) and the partner acetate (0.5 mmol, 1 equiv) were added and the reaction mixture was heated at 100 °C for 16-24 h. The reaction mixture was filtered over Celite and washed with CH_2Cl_2. The volatiles were removed under reduced pressure and the crude was then purified by silica gel column chromatography affording the corresponding product.



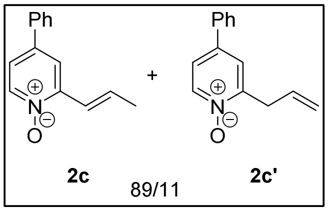
E/Z 90/10

2-(prop-1-enyl)pyridine *N*-oxide 2a: Prepared according to general procedure **GP3** from pyridine *N*-oxide **1a** (95.1 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (90/10) to afford 48.2 mg of **2a** (71% yield, with a 90/10 ratio of *E/Z* isomers or 66% from 5 mmol of allyl acetate) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.26 (d, *J* = 6.4 Hz, 1H, *Z* isomer), 8.20 (d, *J* = 6.4 Hz, 1H, *E* isomer), 7.43 (dd, *J* = 8.0, 2.1 Hz, 1H, *E* isomer), 7.35 (dd, *J* = 7.9, 2.1 Hz, 1H, *Z* isomer), 7.22-7.15 (m, 3H, 1H *E* isomer + 2H *Z* isomer), 7.11 (dd, *J* = 6.0, 1.9 Hz, 2H, *E* isomer), 6.75 (dd, *J* = 11.9, 2.0 Hz, 1H, *Z* isomer), 6.60 (dq, *J* = 16.1, 6.8 Hz, 1H, *E* isomer), 6.16 (dq, *J* = 11.8, 7.2 Hz, 1H, *Z* isomer), 1.98 (dd, *J* = 6.8, 1.7 Hz, 3H, *E* isomer), 1.89 (dd, *J* = 7.2, 1.8 Hz, 3H, *Z* isomer). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 148.4 (*E* isomer), 147.2 (*Z* isomer), 140.1 (*E* isomer), 135.0 (*E* isomer), 133.0 (*Z* isomer), 127.2 (*Z* isomer), 126.2 (*E* isomer), 125.8 (*Z* isomer), 125.6 (*Z* isomer), 124.3 (*Z* isomer), 123.7 (*E* isomer), 123.3 (*E* isomer), 122.5 (*E* isomer), 122.0 (*Z* isomer), 19.5 (*E* isomer), 15.3 (*Z* isomer). **IR (cm^{-1})** ν: 3394, 2917, 1647, 1488, 971, 769, 709. **HRMS** m/z calculated for $C_8H_{10}NO$ $[M+H]^+$: 136.0757; found 136.0754.

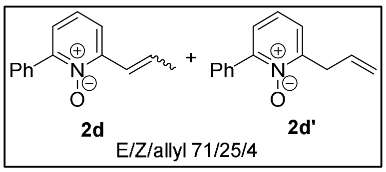


E/Z 93/7

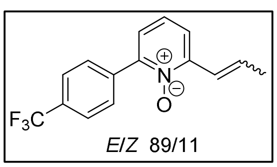
4-methoxy-2-(prop-1-en-1-yl)pyridine *N*-oxide 2b: Prepared according to general procedure **GP3** from 4-metoxypyridine *N*-oxide **1b** (125.1 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (90/10) to afford 55.3 mg of **2b** (67% yield with a 93/7 ratio of *E/Z* isomers) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 7.3 Hz, 1H, *Z* isomer), 8.11 (d, *J* = 7.3 Hz, 1H, *E* isomer), 7.09 (dq, *J* = 16.0, 1.8 Hz, 1H, *E* isomer), 6.91 (d, *J* = 3.4 Hz, 1H, *E* isomer), 6.84 (d, *J* = 3.4 Hz, 1H, *Z* isomer), 6.80-6.69 (m, 2H, *Z* isomer), 6.66 (dd, *J* = 7.3, 3.4 Hz, 1H, *E* isomer), 6.56 (dq, *J* = 16.1, 6.7 Hz, 1H, *E* isomer), 6.23-6.10 (m, 1H, *Z* isomer), 3.84 (s, 6H, 3H *E* isomer + 3H *Z* isomer), 1.98 (dd, *J* = 6.7, 1.7 Hz, 3H, *E* isomer), 1.90 (dd, *J* = 7.2, 1.8 Hz, 3H, *Z* isomer). **^{13}C NMR (101 MHz, $CDCl_3$):** only the *E* isomer δ 157.8, 148.7, 140.6, 135.0, 122.6, 110.3, 107.2, 56.1, 19.1. **IR (cm^{-1})** ν: 3003, 2920, 2849, 1622, 1553, 1480, 1371, 1196, 969, 819, 737. **HRMS** m/z calculated for $C_9H_{12}NO_2$ $[M]^+$: 166.0863; found 166.0858.



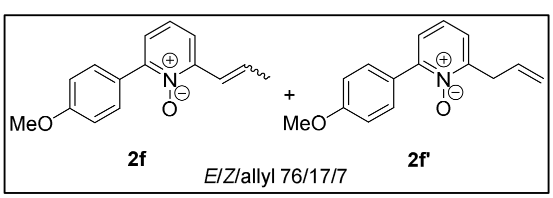
4-phenyl-(*E*)-2-(prop-1-en-1-yl)pyridine *N*-oxide 2c and **4-phenyl-2-allylpyridine *N*-oxide 2c':** Prepared according to general procedure **GP3** from 4-phenyl-pyridine *N*-oxide **1c** (171.2 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by two successive flash chromatographies on silica gel, eluting with EtOAc/EtOH (95/5) to afford 51 mg of **2c** and **2c'** (48% yield with a 89/11 ratio of **2cE**/**2c'**) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.30 (d, *J* = 6.8 Hz, 1H, **2c'**), 8.24 (d, *J* = 6.8 Hz, 1H, **2c**), 7.64 (d, *J* = 2.7 Hz, 1H, **2c**), 7.62-7.54 (m, 5H, 2H **2c** + 3H **2c'**), 7.54-7.33 (m, 7H, 3H **2c** + 4H **2c'**), 7.31 (dd, *J* = 6.8, 2.7 Hz, 1H, **2c**), 7.14 (dq, *J* = 16.1, 1.7 Hz, 1H, **2c**), 6.69 (dq, *J* = 16.1, 6.7 Hz, 1H, **2c**), 6.08 (ddt, *J* = 17.4, 9.7, 6.9 Hz, 1H, **2c'**), 5.37-5.23 (m, 2H, **2c'**), 3.75 (d, *J* = 7.0 Hz, 2H, **2c'**), 2.02 (dd, *J* = 6.8, 1.8 Hz, 3H, **2c**). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 150.8 (**2c'**), 147.9 (**2c**), 139.8 (**2c**), 139.6 (**2c'**), 138.6 (**2c'**), 136.9 (**2c**), 136.8 (**2c'**), 134.7 (**2c**), 132.2 (**2c'**), 129.8 (**2c** +**2c'**), 129.4 (**2c** +**2c'**), 129.1 (**2c** +**2c'**), 126.6 (**2c** +**2c'**), 126.6 (**2c** +**2c'**), 123.1 (**2c** +**2c'**), 122.6 (**2c**), 121.5 (**2c'**), 121.3 (**2c**), 120.6 (**2c**), 119.4 (**2c'**), 34.9 (**2c'**), 19.3 (**2c**). **IR (cm^{-1})** ν: 3058, 1649, 1607, 1447, 968, 822, 764. **HRMS** m/z calculated for $C_{14}H_{14}NO$ $[M]^+$: 212.1070; found 212.1072.



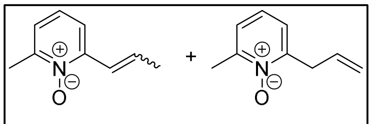
2-phenyl-6-(prop-1-en-1-yl)pyridine *N*-oxide 2d and **2-phenyl-6-allylpyridine *N*-oxide 2d':** Prepared according to general procedure **GP3** from 2-phenylpyridine *N*-oxide **1d** (171.2 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (95/5) to afford 40.7 mg of **2d**(E/Z) and **2d'** (38% yield with a 72/24/4 ratio of **2dE**/**2dZ**/**2d'**) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** Only the **2d**E/Z isomers δ 7.84-7.69 (m, 4H, 2H*E* isomer + 2H*Z* isomer), 7.52-7.35 (m, 8H, 4H*E* isomer + 4H*Z* isomer), 7.39-7.07 (m, 5H, 3H*E* isomer + 2H*Z* isomer), 6.81 (dq, *J* = 11.8, 1.9 Hz, 1H, *Z* isomer), 6.62 (dq, *J* = 16.0, 6.7 Hz, 1H, *E* isomer), 6.16 (dq, *J* = 11.8, 7.2 Hz, 1H, *Z* isomer), 1.99 (dd, *J* = 6.7, 1.8 Hz, 3H, *E* isomer), 1.94 (dd, *J* = 7.2, 1.8 Hz, 3H, *Z* isomer). Characteristic shifts of **2d'**: 6.1-6.02 (m, 1H), 5.34-5.22 (m, 2H), 3.74 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$):** Only the E/Z isomers δ 149.7 (*E* isomer), 148.8 (*E* isomer), 147.9 (*Z* isomer), 134.2 (*E* isomer), 133.6 (*E* isomer), 133.4 (*Z* isomer), 132.7 (*Z* isomer), 131.9 (*Z* isomer), 129.5 (*Z* isomer), 129.5 (*E* isomer), 129.4 (*E* and *Z*), 129.3 (*E* and *Z*), 128.2 (*Z* isomer), 128.2 (*E* isomer), 125.6 (*E* or *Z*), 125.4 (*E* or *Z*), 124.9 (*Z* isomer), 124.8 (*E* isomer), 124.2 (*E* isomer), 124.0 (*Z* isomer), 123.2 (*E* isomer), 122.6 (*Z* isomer), 121.9 (*E* and *Z*), 19.3 (*E* isomer), 15.1 (*Z* isomer). **IR (cm^{-1})** ν: 3060, 2918, 1644, 1553, 1476, 1377, 968, 840, 760. **HRMS** m/z calculated for $C_{14}H_{14}NO$ $[M]^+$: 212.1070; found 212.1071.



2-(4-(trifluoromethyl)-phenyl)-5-(prop-1-en-1-yl)pyridine *N*-oxide 2e: Prepared according to general procedure **GP3** from 2-(4-(trifluoromethyl)-phenyl)-pyridine *N*-oxide **1e** (239.2 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc 100% to afford 75 mg of **2e** (54% yield with a 89/11 ratio of *E/Z* isomers) as a white solid. **m.p.:** 70-71 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.96-7.85 (m, 4H, 2H*E* isomer + 2H*Z* isomer), 7.78-7.67 (m, 4H, 2H*E* isomer + 2H*Z* isomer), 7.51-7.45 (m, 1H, *E* isomer), 7.40 (dd, *J* = 7.1, 2.9 Hz, 1H, *Z* isomer), 7.37-7.20 (m, 4H, 2H*E* isomer + 2H*Z* isomer), 7.14 (dq, *J* = 16.1, 1.7 Hz, 1H, *E* isomer), 6.80 (dd, *J* = 11.8, 1.9 Hz, 1H, *Z* isomer), 6.67 (dq, *J* = 16.1, 6.7 Hz, 1H, *E* isomer), 6.21 (dq, *J* = 11.9, 7.2 Hz, 1H, *Z* isomer), 2.02 (dd, *J* = 6.8, 1.8 Hz, 3H, *E* isomer), 1.96 (dd, *J* = 7.2, 1.9 Hz, 3H, *Z* isomer). ^{13}C NMR (101 MHz, $CDCl_3$) : only E isomer δ 149.0, 148.2, 137.1 (q, *J* = 1.7 Hz), 134.7, 131.1 (q, *J* = 32.8 Hz), 129.9, 125.1 (q, *J* = 3.8 Hz), 125.0, 124.9, 124.0, (q, *J* = 272.3 Hz), 122.85, 122.60, 19.21. **^{19}F NMR (282 MHz, $CDCl_3$):** δ -62.9. **IR (cm^{-1})** ν: 3058, 2922, 1650, 1614, 1560, 1481, 1377, 1324, 1169, 969, 841, 777. **HRMS** m/z calculated for $C_{15}H_{12}F_3NNaO$ $[M+Na]^+$: 302.0763; found 302.0770.



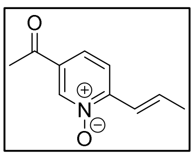
2-(4-(methoxy)phenyl)-6-(prop-1-en-1-yl)pyridine *N*-oxide 2f and **2-(4-(methoxy)phenyl)-6-allylpyridine *N*-oxide 2f':** Prepared according to general procedure **GP3** from 2-(**4**-(methoxy)-phenyl)-pyridine *N*-oxide **1f** (201.2 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc 100% to afford 25 mg of a non-separable mixture of **2f** and **2f'** (21% with a 76/17/7 ratio of **2f***E/***2f***Z*/**2f'**) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.84-7.73 (m, 6H, 2H *E* isomer + 2H *Z* isomer + 2H allyl), 7.46-7.26 (m, 2H, 1H *E* isomer +1 H *Z* isomer), 7.33-7.09 (m, 8H, 3H *E* isomer + 2H *Z* isomer + 3H allyl), 7.03-6.91 (m, 6H, 2H *E* isomer +2H *Z* isomer +2H allyl), 6.80 (dd, *J* = 11.8, 1.9 Hz, 1H, *Z* isomer), 6.60 (dq, *J* = 16.1, 6.8 Hz, 1H,*E* isomer), 6.22-6.01 (m, 2H, 1H *Z* isomer + 1H allyl), 5.33-5.21 (m, 2H,allyl), 3.85 (s, 9H, 3H *E* isomer + 3H *Z* isomer + 3H allyl), 3.74 (d, *J* = 6.9 Hz, 2H, allyl), 1.99 (dd, *J* = 6.7, 1.7 Hz, 3H, *E* isomer), 1.93 (dd, J = 7.2, 1.9 Hz, 3H, Z isomer). **^{13}C NMR (75 MHz, $CDCl_3$):** Only E/Z isomers δ 160.4 (E + Z isomers), 149.4 (E + Z isomers), 148.9 (E + Z isomers), 134.0 (E isomer), 131.7 (Z isomer), 131.1 (Z isomer), 131.0 (E isomer), 130.8 (E + Z isomers), 125.8 (E isomer), 125.1 (E + Z isomer), 125.0 (E + Z isomer), 124.8 (E isomer), 124.6 (E isomer), 124.2 (Z isomer), 123.4 (E isomer), 122.8 (Z isomer), 121.4 (Z isomer), 113.7 (Z isomer), 113.6 (E isomer), 55.5 (E + Z isomers), 19.3 (E isomer), 15.1 (Z isomer). **IR (cm^{-1})** ν: 2792, 2785, 1670, 1516, 1475, 1378, 1180, 836. **HRMS** m/z calculated for $C_{15}H_{16}NO_2$ $[M]^+$: 242.1176; found 242.1181.



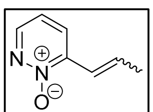
2g **2g'**

E/Z/allyl 71/21/8

5-(prop-1-enyl)-2-picoline *N*-oxide 2g and **5-allyl-2-picoline *N*-oxide 2g':**Prepared according to general procedure **GP3** from 2-picoline *N*-oxide **1g** (109.1 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by by two successive flash chromatography on silica gel eluting with EtOAc/EtOH (95/5) to afford 25 mg of a non-separable mixture of **2g** and **2g'** (33% with a 71/21/8 ratio of **2g***E*/**2g***Z*/**2g'**) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.36-7.24 (m, 1H, E isomer), 7.27-7.17 (m, 2H, 1H Z isomer +1H allyl), 7.18-7.01 (m, 6H, 2H + 2H Z isomer + 2H allyl) 6.79 (dq, J = 11.8, 1.9 E isomer Hz, 1H, Z isomer), 6.56 (dq, J = 16.1, 6.7 Hz, 1H E isomer), 6.12 (dq, J = 12.0, 7.3 Hz, 1H, Z isomer), 6.08-5.93 (m, 1H, Z isomer), 5.30-5.16 (m, 2H, allyl), 3.70 (d, J = 6.8 Hz, 2H, allyl), 2.53 (s, 3H, allyl), 2.52 (s, 3H, Z isomer), 2.50 (s, 3H, E isomer), 1.97 (dd, J = 6.7, 1.8 Hz, 3H, E isomer), 1.88 (dd, J = 7.2, 1.9 Hz, 2H, Z isomer). **^{13}C NMR (75 MHz, $CDCl_3$):** Only E/Z isomers δ 149.3 (E + Z isomers), 148.2 (E isomer), 133.9 (E isomer), 131.8 (Z isomer), 124.7 (E isomer), 124.5 (E isomer), 124.4 (Z isomer), 124.2 (Z isomer), 124.1 (Z isomer), 123.9 (Z isomer), 123.1 (E isomer), 122.5 (Z isomer), 120.7 (E isomer), 19.2 (E isomer), 18.5 (Z isomer), 18.4 (E isomer), 15.0 (Z isomer). **IR (cm^{-1})** ν: 3050, 2919, 1645, 1561, 1491, 1444, 971, 838, 770. **HRMS** m/z calculated for $C_9H_{11}NNaO$ $[M]^+$: 172.0733; found 172.0734.

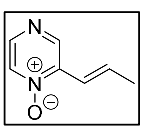


(*E*)-5-acetyl-2-(prop-1-enyl)pyridine *N*-oxide 2h: Prepared according to general procedure **GP3** from 3-acetylpyridine *N*-oxide **1h** (137.2 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (90/10) to afford 50 mg of **2h** (56% yield of the E isomer) as a yellow solid. **m.p.:** 134-135 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.73 (d, J = 1.5 Hz, 1H), 7.68 (dd, J = 8.3, 1.2 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.14 (dq, J = 16.2, 1.7 Hz, 1H), 6.80 (dq, J = 16.2, 6.8 Hz, 1H), 2.57 (s, 3H), 2.04 (dd, J = 6.7, 1.7 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 193.9, 151.2, 140.5, 137.6, 132.8, 124.2, 122.7, 122.0, 26.8, 19.5. **IR (cm^{-1})** ν: 3035, 1681, 1640, 1600, 1546, 974, 932, 841. **HRMS** m/z calculated for $C_{10}H_{11}NNaO_2$ $[M+Na]^+$: 200.0682; found 200.0690.

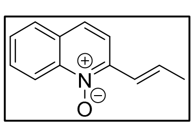


E/Z 89/11

6-(prop-1-en-1-yl)pyridazine *N*-oxide 2i: Prepared according to general procedure **GP3** from pyridazine *N*-oxide **1i** (96.1 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (95/5) to afford 42 mg of **2i** (62% yield with a 89/11 ratio of E/Z isomers) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.34 (dd, J = 5.7, 2.4 Hz, 1H, Z isomer), 8.28 (dd, J = 5.2, 2.4 Hz, 1H, E isomer), 7.70 (dd, J = 8.1, 2.5 Hz, 1H, E isomer), 7.64 (dd, J = 8.0, 2.5 Hz, 1H, Z isomer), 7.05-7.03 (m, 1H, , Z isomer), 7.00 (dd, J = 8.1, 5.1 Hz, 1H, E isomer), 6.87 (dq, J = 16.0, 1.7 Hz, 1H, E isomer), 6.72-6.57 (m, 2H, 1H , 1H E isomer + 1H Z isomer), 6.18 (dq, J = 11.8, 7.2 Hz, 1H, Z isomer), 1.97 (dd, J = 6.7, 1.6 Hz, 3H , E isomer), 1.87 (dd, J = 7.2, 1.9 Hz, 3H, Z isomer). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 148.5 (Z isomer), 148.1 (E isomer), 143.1 (E and Z isomers), 136.1 (E isomer), 134.1 (Z isomer), 133.8 (Z isomer), 130.7 (E isomer), 121.8 (E isomer), 121.0 (Z isomer), 116.3 (E isomer), 115.5 (Z isomer), 19.3 (E isomer), 15.0 (Z isomer). **IR (cm^{-1})** ν: 3060, 2918, 1642, 1588, 1538, 1376, 964, 784. **HRMS** m/z calculated for $C_7H_8N_2NaO$ $[M+Na]^+$: 159.0529; found 159.0533.

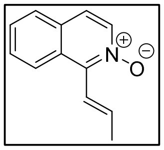


(*E*)-2-(prop-1-en-1-yl)pyrazine *N*-oxide 2j: Prepared according to general procedure **GP3** from pyrazine *N*-oxide **1j** (96.1 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (90/10) followed by preparative thin layer chromatography EtOAc/EtOH (90/10) to afford 40 mg of **2j** (59% yield of the E isomer) as a light brown solid. **m.p.:** 80-81 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.60 (s, 1H), 8.22 (d, J = 4.1 Hz, 1H), 8.05 (d, J = 4.1 Hz, 1H), 6.89-6.81 (m, 2H), 2.05-1.96 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 145.8, 144.1, 143.3, 136.4, 133.9, 119.5, 19.5. **IR (cm^{-1})** ν: 3055, 2922, 1644, 1588, 1454, 970, 869. **HRMS** m/z calculated for C_7H_9N2O $[M+H]^+$: 137.0709; found 137.0709.

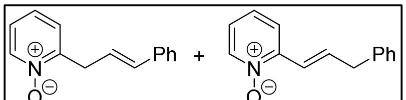


(*E*)-2-(prop-1-enyl)quinoline *N*-oxide 2k: Prepared according to general procedure **GP3** from quinoline *N*-oxide **1k** (145.2 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH

(95/5) to afford 52 mg of **2k** (57% yield of the *E* isomer) as a brown solid. **m.p.:** 65-66 °C. **^{1}H NMR (300 MHz, CDCl$_3$):** δ 8.75 (d, *J* = 8.7 Hz, 1H), 7.76 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.71 (ddd, *J* = 8.6, 7.0, 1.4 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.55 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.37 (dq, *J* = 16.1, 1.8 Hz, 1H), 6.81 (dq, *J* = 16.1, 6.8 Hz, 1H), 2.04 (dd, *J* = 6.8, 1.7 Hz, 3H). **^{13}C NMR (75 MHz, CDCl$_3$):** δ 144.3, 141.8, 136.1, 130.6, 128.9, 128.1, 128.0, 125.5, 123.3, 120.1, 119.3, 19.5. **IR (cm^{-1})** ν: 3061, 2919, 1602, 1560, 1512, 1442, 970, 765. **HRMS** m/z calculated for $C_{12}H_{12}NO$ [M]$^+$: 186.0913; found 186.0908.

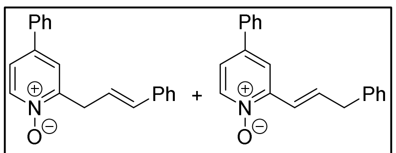


(*E*)-1-(prop-1-en-1-yl)isoquinoline *N*-oxide 2l: Prepared according to general procedure **GP3** from isoquinoline *N*-oxide **1l** (147.2 mg, 1 mmol, 2 equiv) and allyl acetate (0.054 mL, 0.5 mmol, 1 equiv). The crude product was purified by two successive flash chromatography on silica gel eluting with EtOAc/EtOH (95/5) to afford 44 mg of **2l** (48% yield of the *E* isomer with only traces of the allylated derivative) as a yellow oil. **^{1}H NMR (300 MHz, CDCl$_3$):** δ 8.19-7.98 (m, 2H), 7.75 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.63-7.51 (m, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.01-6.89 (m, 1H), 6.82 (dq, *J* = 16.1, 6.2 Hz, 1H), 2.13 (dd, *J* = 6.3, 1.3 Hz, 3H). **^{13}C NMR (75 MHz, CDCl$_3$):** δ 144.5, 138.9, 137.0, 129.4, 129.1, 128.8, 128.3, 127.4, 125.1, 122.0, 120.8, 19.9. **IR (cm^{-1})** ν: 3066, 2971, 1653, 1552, 1499, 1451, 970, 818, 756. **HRMS** m/z calculated for $C_{12}H_{11}LiNO$ [M+Li]$^+$: 192.0995; found 192.1001.



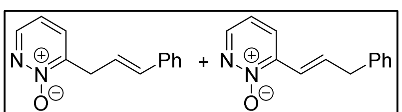
3a 4a
3a/4a 90/10

2-cinnamylpyridine *N*-oxide 3a and **(*E*)-2-(3-phenylprop-1-en-1-yl)pyridine *N*-oxide 4a:** Prepared according to general procedure **GP3** from pyridine *N*-oxide **1a** (95.1 mg, 1 mmol, 2 equiv) and cinnamyl acetate (88.1 mg, 0.5 mmol, 1 equiv) during 40 h. The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (95/5) to afford 32 mg of **3a** and **4a** (31% yield with a 90/10 ratio of **3a**/**4a**) as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.30 (d, *J* = 6.0 Hz, 1H, **3a**), 8.22 (d, *J* = 6.6 Hz, 1H, **4a**), 7.46 (d, *J* = 8.0 Hz, 2H, **4a**), 7.42-7.37 (m, 2H, **3a**), 7.34-7.28 (m, 6H, 3H **3a** + 3H **4a**), 7.26-7.15 (m, 6H, 3H **3a** + 3H **4a**), 7.14-7.05 (m, 1H, **4a**), 6.70 (dt, *J* = 15.9, 7.1 Hz, 1H, **4a**), 6.60 (d, *J* = 15.8 Hz, 1H, **3a**), 6.41 (dt, *J* = 15.8, 6.9 Hz, 1H, **3a**), 3.86 (d, *J* = 7.1 Hz, 2H, **3a**), 3.66 (d, *J* = 6.6 Hz, 2H, **4a**). **^{13}C NMR (101 MHz, CDCl$_3$):** only **3a** δ 151.2, 139.7, 137.0, 134.3, 128.7, 127.8, 126.4, 126.0, 125.6, 123.8, 123.4, 34.0. Some characteristic shifts of **4a**: 128.9, 128.8, 126.7, 39.9. **IR (cm^{-1})** ν: 3379, 3070, 2965, 1490, 1437, 974, 845, 694. **HRMS** m/z calculated for $C_{14}H_{13}NNaO$ [M+Na]$^+$: 234.0889; found 234.0898.



3c 4c
3c/4c 83/17

2-cinnamyl-4-phenylpyridine *N*-oxide 3c and (*E*)-4-phenyl-2-(3-phenylprop-1-en-1-yl)pyridine *N*-oxide 4c: Prepared according to general procedure **GP3** from 4-phenyl-pyridine *N*-oxide **1c** (171.2 mg, 1 mmol, 2 equiv) and cinnamyl acetate (88.1 mg, 0.5 mmol, 1 equiv) during 40 h. The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (95/5) to afford 31 mg of **3c** and **4c** (22% yield with a 83/17 ratio of **3c**/**4c**) as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$) :** δ 8.35 (d, *J* = 7.0 Hz, 1H, **3c**), 8.27 (d, *J* = 7.2 Hz, 1H, **4c**), 7.66 (d, *J* = 2.5 Hz, 1H, **4c**), 7.59-7.54 (m, 4H, 2H **3c** + 2H **4c**), 7.52-7.37 (m, 13H, 7H **3c** + 6H **4c**), 7.37-7.20 (m, 7H, 3H **3c** + 4H **4c**), 6.79 (dt, *J* = 16.1, 7.2 Hz, 1H, **4c**), 6.65 (d, *J* = 15.7 Hz, 1H, **3c**), 6.47 (dt, *J* = 15.8, 7.2 Hz, 1H, **3c**), 3.92 (d, *J* = 7.0 Hz, 2H, **3c**), 3.69 (d, *J* = 7.1 Hz, 2H, **4c**). **^{13}C NMR (101 MHz, CDCl$_3$)** : only **3a** δ 151.0, 139.7, 138.9, 137.0, 136.8, 134.4, 129.4, 129.1, 128.7, 127.8, 126.7, 126.5, 123.5, 123.2, 121.7, 34.3. **IR (cm^{-1})** ν 3060, 3031, 1601, 1545, 1475, 1453, 1245, 972, 765. **HRMS** m/z calculated for $C_{20}H_{18}NO$ [M+H]$^+$: 288.1383; found 288.1381.



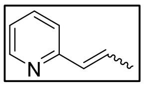
3i 4i
3i/4i 83/17

6-cinnamylpyridazine *N*-oxide 3i and (*E*)-6-(3-phenylprop-1-en-1-yl)pyridazine *N*-oxide 4i: Prepared according to general procedure **GP3** from pyridazine *N*-oxide **1i** (96.1 mg, 1 mmol, 2 equiv) and cinnamyl acetate (88.1 mg, 0.5 mmol, 1 equiv) during 40 h. The crude product was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (95/5) to afford 51 mg of **3i** and **4i** (48% yield with a 83/17 ratio of **3i**/**4i**) as a dark brown solid. **m.p.:** 72-73 °C. **^{1}H NMR (300 MHz, CDCl$_3$):** δ 8.38 (dd, *J* = 5.3, 2.4 Hz, 1H, **3i**), 8.31 (dd, *J* = 5.1, 2.4 Hz, 1H, **4i**), 7.72 (dd, *J* = 8.1, 2.4 Hz, 1H, **4i**), 7.61 (dd, *J* = 7.9, 2.4 Hz, 1H, **3i**), 7.43-7.17 (m, 11H, 5H **3i** + 6H **4i**), 7.08-6.91 (m, 2H, 1H **3i** + 1H **4i**), 6.79 (dt, *J* = 16.1, 6.9 Hz, 1H, **4i**), 6.62 (d, *J* = 15.9 Hz, 1H, **3i**), 6.35 (dt, *J* = 15.9, 7.1 Hz, 1H, **3i**), 3.77 (d, *J* = 7.1 Hz, 2H, **3i**), 3.64 (d, *J* = 6.9 Hz, 2H, **4i**). **^{13}C NMR (75 MHz, CDCl$_3$) :** δ 148.5 (**3i**), 148.3 (**4i**), 146.2 (**4i**), 139.1 (**4i**), 136.6 (**3i**), 135.2 (**3i**), 133.0 (**3i**), 130.9 (**4i**), 128.8 (**4i**), 128.7 (**3i**), 128.0 (**3i** + **4i**), 126.8 (**3i** + **4i**), 126.4 (**3i** + **4i**), 121.8 (**3i**), 121.5 (**4i**), 116.2 (**3i**), 39.9 (**4i**), 34.5 (**3i**). A quaternary carbon of **4i** could not be observed. **IR (cm^{-1})** ν: 3064, 3027, 1593, 1542, 1494, 973, 886, 741. **HRMS** m/z calculated for $C_{13}H_{12}N_2NaO$ [M+Na]$^+$:235.0842; found 235.0832.

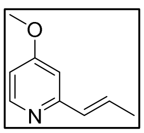
VII. Further derivatizations of C2-alkenylated *N*-Oxides

1. Deoxygenation of alkenylated pyridine *N*-oxides: General procedure (GP4)

Following a reported procedure,[20] a solution of alkenyated pyridine *N*-oxide (0.25 mmol, 1 equiv) in Toluene (1.25 mL) was prepared, PCl_3 (44 µL, 0.5 mmol, 2 equiv.) was added slowly and the reaction mixture stirred at room temperature. After reaction completion (followed by TLC), the mixture was quenched with a saturated solution of $NaHCO_3$ and stirred for 5 min. The aqueous layer was then extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ filtered and the volatiles were removed under reduced pressure. The crude was then purified by silica gel column chromatography, affording the corresponding product.

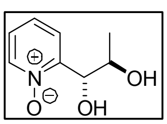


2-(prop-1-en-1-yl)pyridine 5a: Prepared according to general procedure **GP4** from 2-(prop-1-enyl)pyridine *N*-oxide **2a** (33.8 mg, 0.25 mmol, 1 equiv) during 4 h. The crude product was purified by flash chromatography on silica gel eluting with Pentane/Et_2O (70/30) to afford 20 mg of **5a** (67% yield with a 79/21 ratio of *E/Z* isomers) as a colorless oil (product volatile). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.61 (d, *J* = 4.1 Hz, 1H, *Z* isomer), 8.52 (d, *J* = 4.6 Hz, 1H, *E* isomer), 7.71-7.52 (m, 2H, 1H *E* isomer + 1H *Z* isomer), 7.29-7.17 (m, 2H, 1H *E* isomer + 1H *Z* isomer), 7.14-7.03 (m, 2H, 1H *E* isomer + 1H *Z* isomer), 6.74 (dq, *J* = 15.6, 6.7 Hz, 1H, *E* isomer), 6.55-6.43 (m, 2H, 1H *E* isomer + 1H *Z* isomer), 6.00 (dq, *J* = 11.8, 7.3 Hz, 1H, *Z* isomer), 2.09 (dd, *J* = 7.2, 1.8 Hz, 3H, *Z* isomer), 1.93 (dd, *J* = 6.7, 1.7 Hz, 3H, *E* isomer). **^{13}C NMR (75 MHz, $CDCl_3$):**) δ 156.3 (*E* isomer), 149.5 (*E* isomer), 149.4 (*Z* isomer), 136.5 (*E* isomer), 136.0 (*Z* isomer), 131.4 (*E* isomer), 131.3 (*Z* isomer), 130.9 (*E* isomer), 129.7 (*Z* isomer), 124.0 (*Z* isomer), 121.6 (*E* isomer), 121.2 (*Z* isomer), 120.9 (*E* isomer), 18.5 (*E* isomer), 15.1 (*Z* isomer). A quaternary carbon of the *Z* isomer could not be observed. **IR (cm^{-1})** ν 3007, 2913, 1587, 1564, 1470, 1430, 1150, 968, 730. **HRMS** m/z calculated for $C_8H_{10}N$ $[M+H]^+$: 120.0808; found 120.0806.



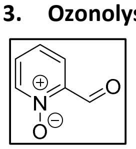
(*E*)-4-methoxy-2-(prop-1-en-1-yl)pyridine 5b: Prepared according to general procedure **GP4** from 4-methoxy-2-(prop-1-en-1-yl)pyridine *N*-oxide **2b** (41.3 mg, 0.25 mmol, 1 equiv) during 5 h. The crude product was purified by flash chromatography on silica gel eluting with Pentane/Et_2O (50/50) to afford 30 mg of **5b** (80% yield of *E* isomer with only traces of *Z* isomer) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.34 (d, *J* = 5.8 Hz, 1H), 6.80-6.67 (m, 2H), 6.63 (dd, *J* = 5.7, 2.5 Hz, 1H), 6.44 (dq, *J* = 15.5, 1.7 Hz, 1H), 3.83 (s, 3H), 1.92 (dd, *J* = 6.7, 1.7 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 166.2, 157.9, 150.7, 131.3, 131.0, 107.9, 106.9, 55.1, 18.4. **IR (cm^{-1})** ν 3000, 2945, 1580, 1560, 1475, 1030, 955, 735. **HRMS** m/z calculated for $C_9H_{12}NO$ $[M+H]^+$: 150.0913; found 150.0912.

2. Dihydroxylation of 2-(prop-1-enyl)pyridine *N*-oxide 2a



2-((1*R,2*R**)-1,2-dihydroxypropyl)pyridine 1-oxide 6a**: To a solution of 2-(prop-1-enyl)pyridine *N*-oxide **2a** (33.8 mg, 0.25 mmol, 1 equiv) in 4 mL of THF/H_2O (9/1) was added *N*-methyl morpholine-*N*-oxide (75.5 mg, 0.625 mmol, 2.5 equiv.) and a catalytic amount of $OsCl_3$. The reaction mixture was stirred at room temperature during 7 h. After completion, the mixture was quenched with a saturated solution of NaS_2O_3 and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ filtered and the volatiles were removed under reduced pressure. The crude was then purified by silica gel column chromatography flash chromatography on silica gel eluting with CH_2Cl_2/Acetone/MeOH (50/45/5) to afford 13.5 mg of **6a** (32% yield, *d.r.* 80/20) as a yellow oil. **m.p.:** 118-120 °C. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.22 (d, *J* = 6.3 Hz, 2H, 1H major + 1H minor), 7.46-7.37 (m, 4H, 2H major + 2H minor), 7.33-7.26 (m, 2H, 1H major + 1H minor), 5.94 (s, 1H, major), 5.69 (s, 1H, minor), 4.74 (s, 1H, minor), 4.65 (s, 1H, major), 4.33-4.22 (m, 2H, 1H major + 1H minor), 3.88 (s, 1H, minor), 3.74 (s, 1H, major), 1.25 (d, *J* = 6.4 Hz, 3H, minor), 1.22 (d, *J* = 6.3 Hz, 3H, major). **^{13}C NMR (101 MHz, $CDCl_3$)**:, δ 150.0 (major), 140.2 (major + minor), 128.1 (minor), 127.9 (major), 126.5 (minor), 126.1 (major), 125.0 (major), 124.9 (minor), 76.6 (minor), 76.5 (major), 70.4 (minor), 68.7 (major), 20.0 (minor), 19.5 (major). **IR (cm^{-1})** ν 3236, 2975, 2927, 1488, 1434, 1372, 1202, 1133. **HRMS** m/z calculated for $C_8H_{12}N_1O_3$ $[M+H]^+$: 170.0812; found 170.0811.

3. Ozonolysis of 2-(prop-1-enyl)pyridine *N*-oxide 2a



2-formylpyridine *N*-oxide 7a: 2-(prop-1-enyl)pyridine *N*-oxide **2a** (67.6 mg, 0.5 mmol, 1 equiv) was dissolved in dry DCM (2 mL) and MeOH (2 mL) and cooled to -78 °C. Ozone was bubbled through the

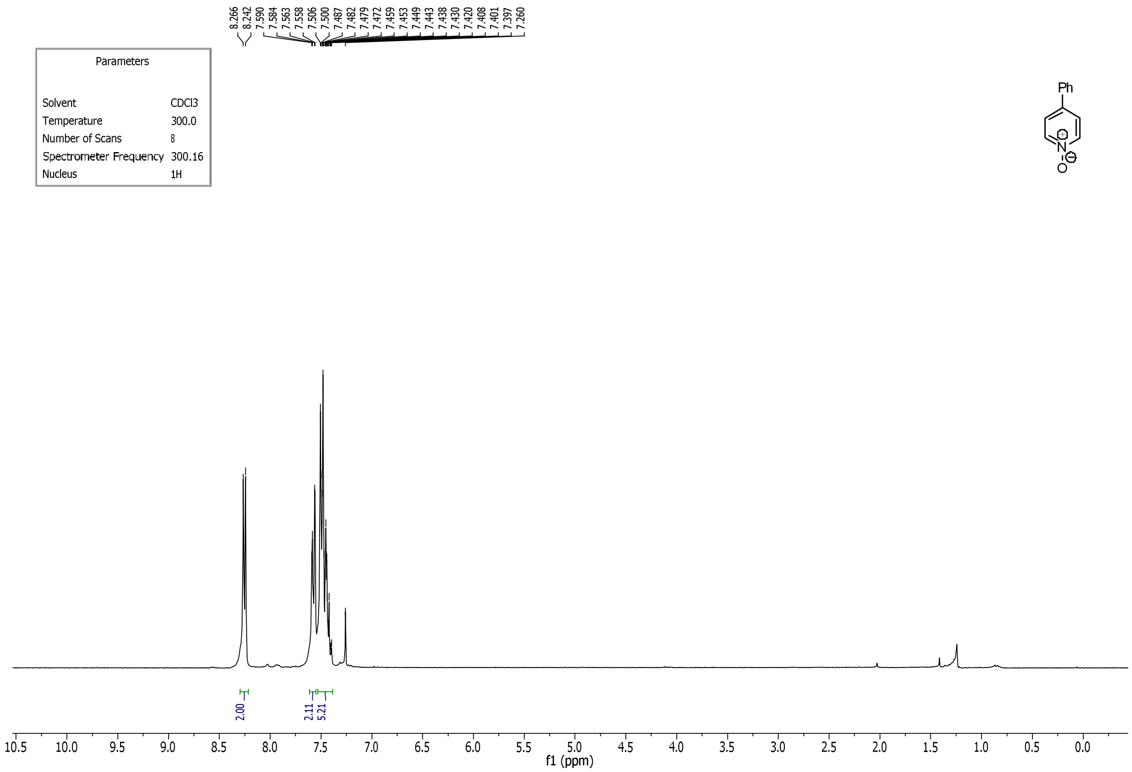
[20] Cho, S. H.; Hwang, S. J.; Chang, S. *J. Am. Chem. Soc.* **2008**, *130*, 9254.

mixture for 30 min. the reaction was then purged with N_2 for 5 min. Dimethyl sulfide (0.185 mL, 2.5 mmol, 5 equiv) was then added and the reaction was allowed to warm to room temperature and stirred for 3 h. The reaction mixture was concentrated under vacuum and the crude was purified by flash chromatography on silica gel eluting with EtOAc/EtOH (80/20) to afford 40 mg of 7a (65% yield) as yellow solid. **m.p.:** 63-65 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 10.63 (d, *J* = 0.7 Hz, 1H), 8.22 (ddd, *J* = 6.5, 1.1, 0.7 Hz, 1H), 7.82 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.46 (ddd, *J* = 7.2, 6.7, 2.3 Hz, 1H), 7.33 (tt, *J* = 7.7, 1.0 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 185.8, 143.9, 140.5, 130.1, 125.7, 125.4. **IR (cm^{-1})** ν 3115, 2950, 1695, 1603, 1434, 1296. **HRMS** m/z calculated for $C_6H_5NNaO_2$ $[M+Na]^+$: 146.0212; found 146.0210.

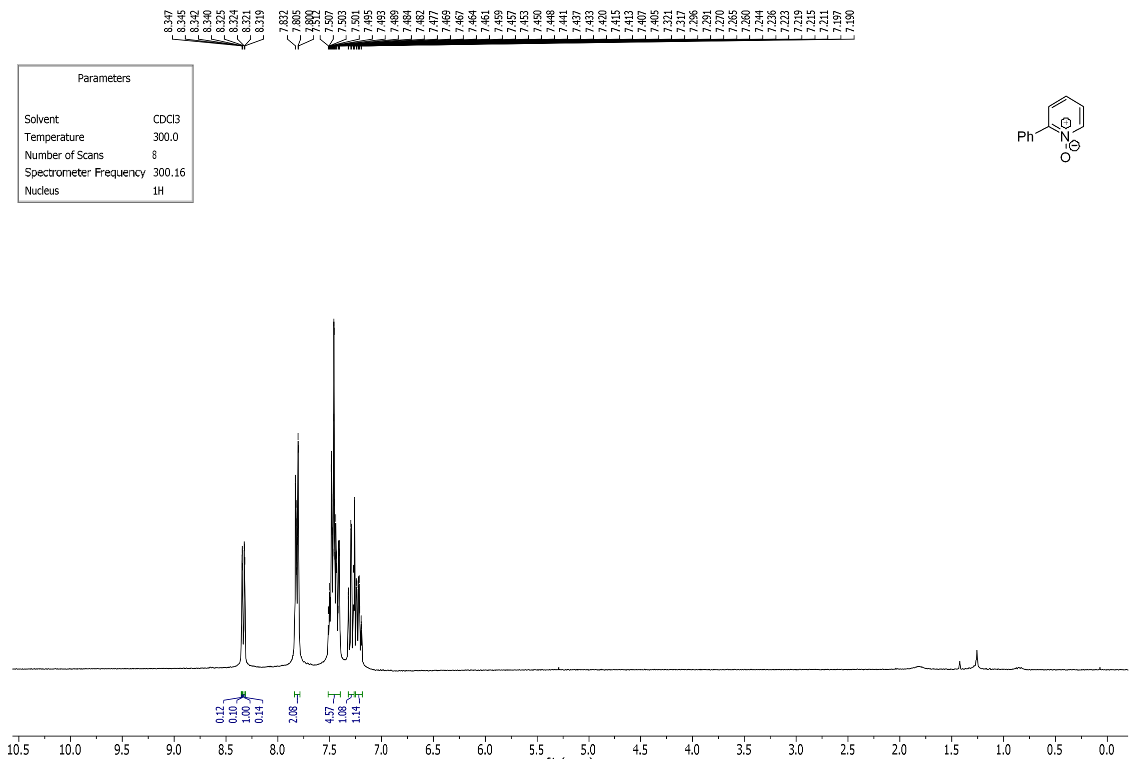
VIII. ^{1}H, ^{13}C and ^{19}F NMR Spectra

<u>Starting materials</u>

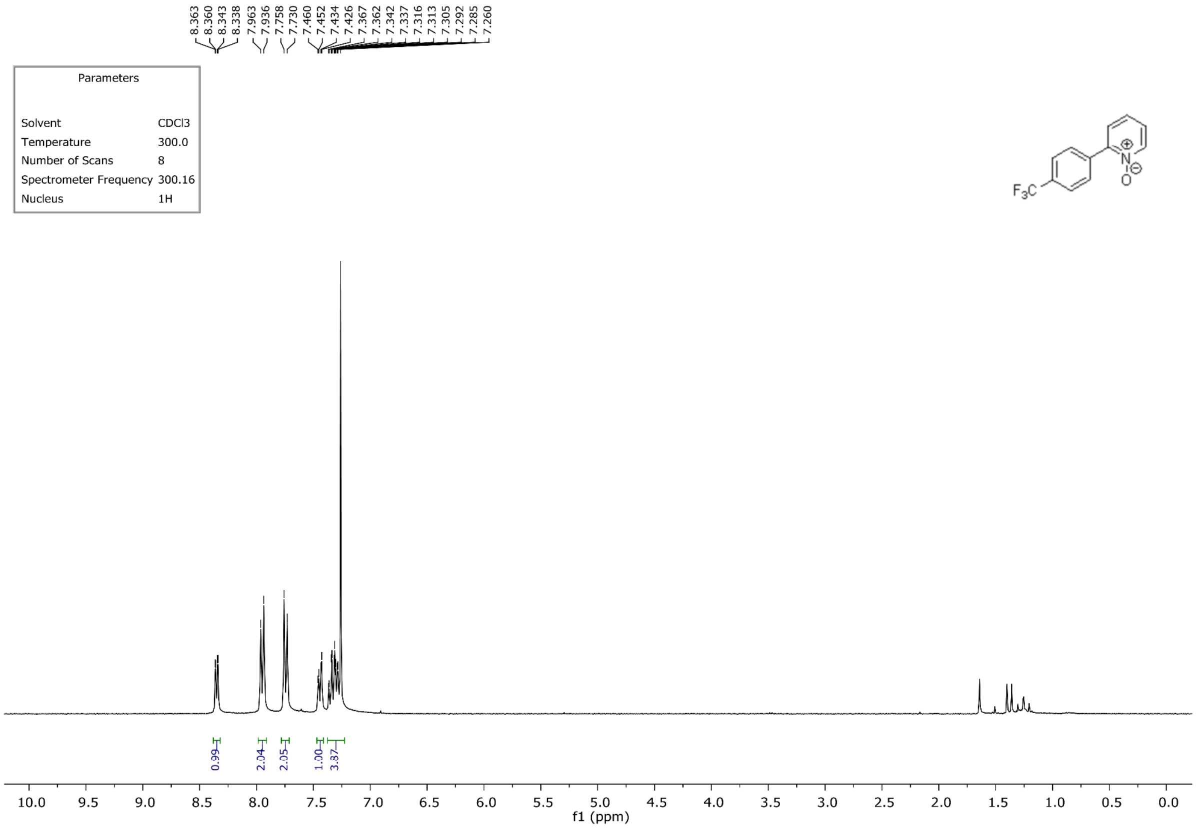
4-phenylpyridine *N*-oxide 1c



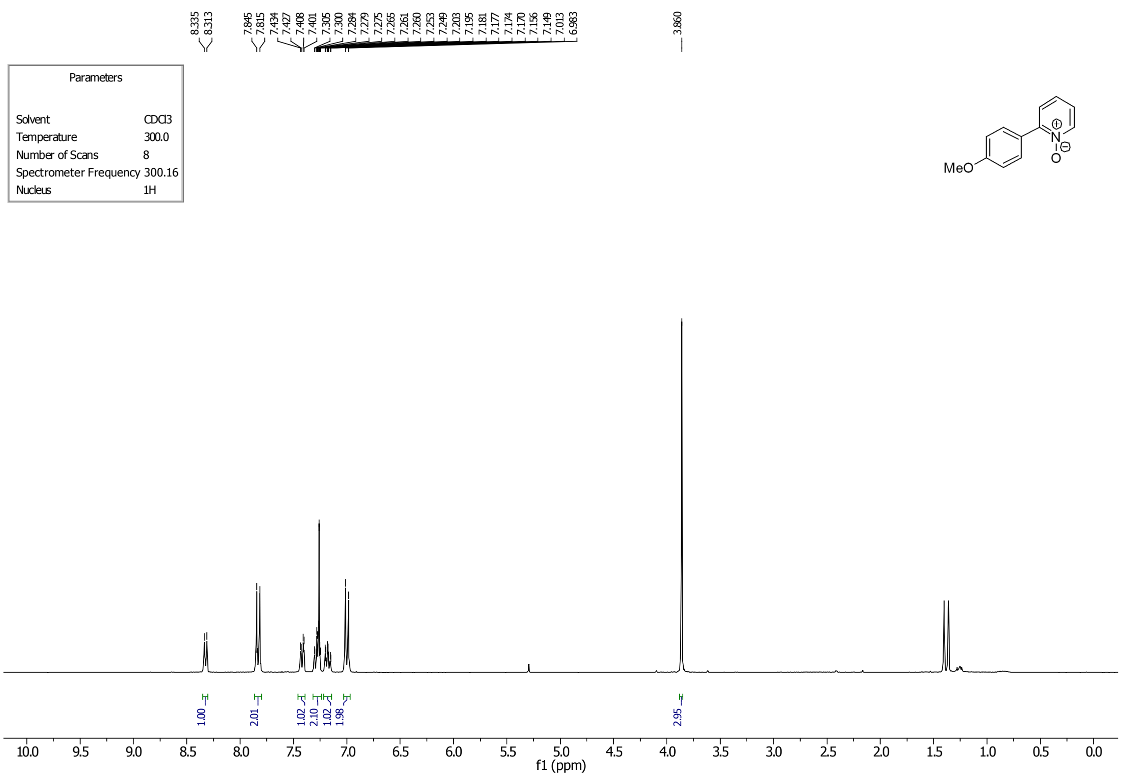
2-phenylpyridine *N*-oxide 1d



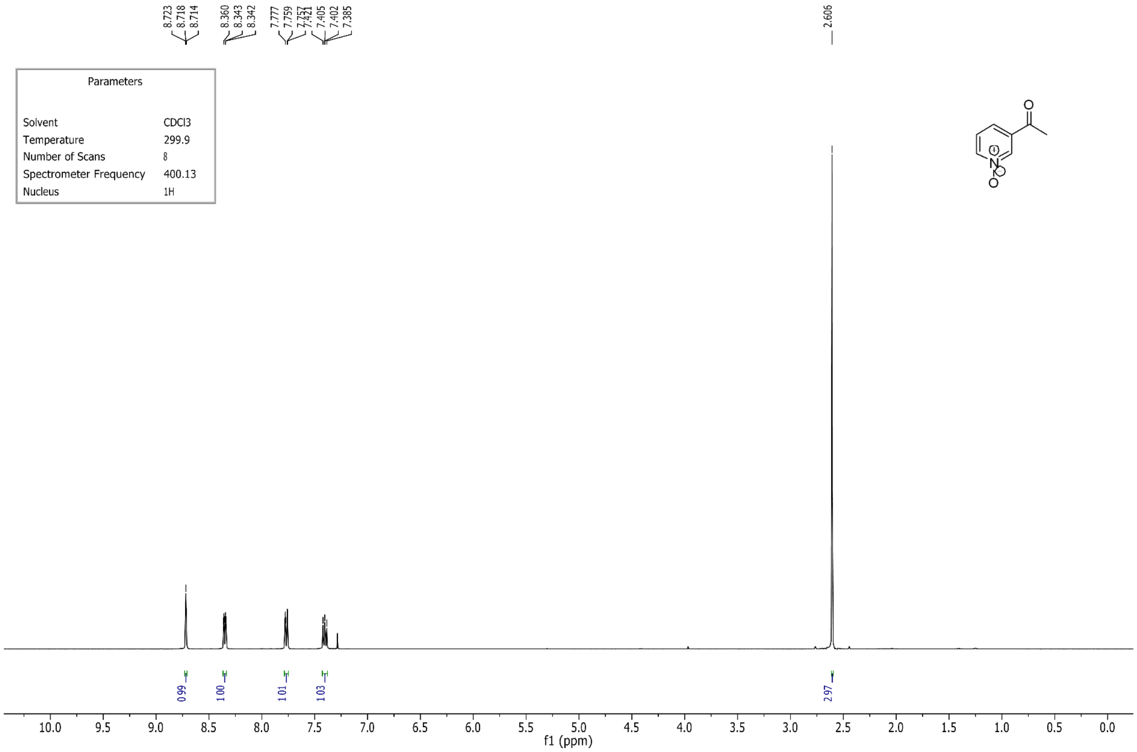
2-(4-(trifluoromethyl))-phenylpyridine *N*-oxide 1e

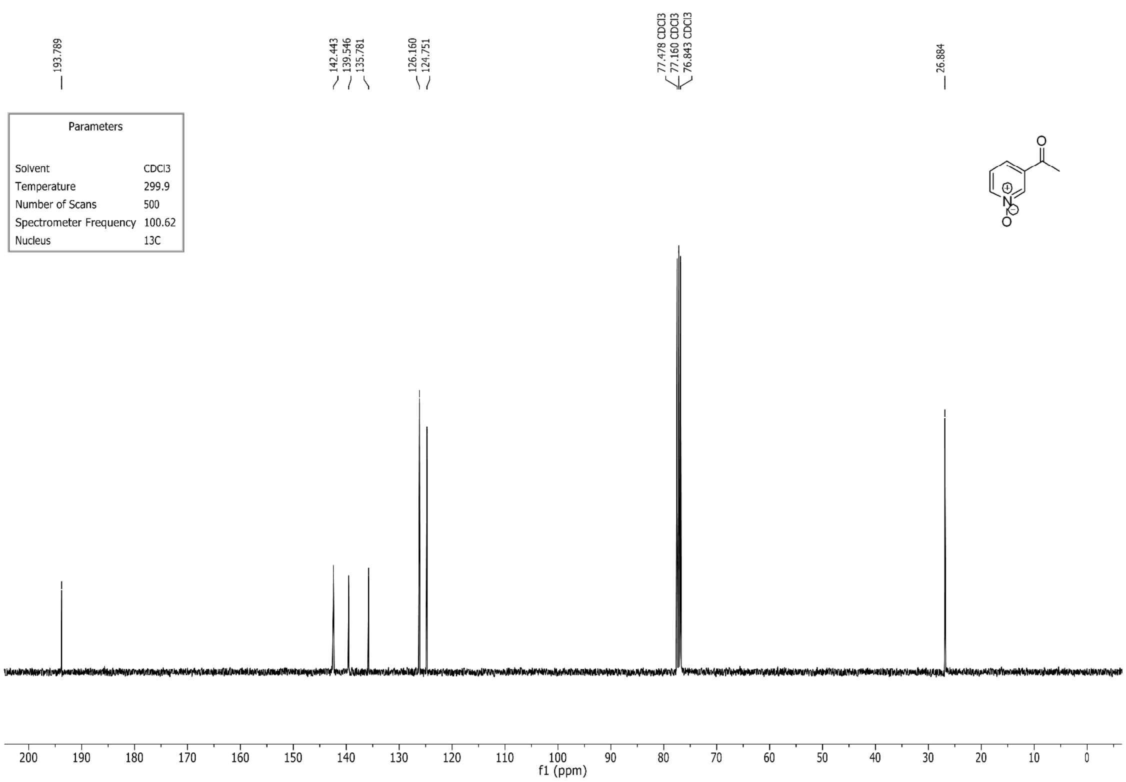


2-(4-(methoxy))phenylpyridine *N*-oxide 1f

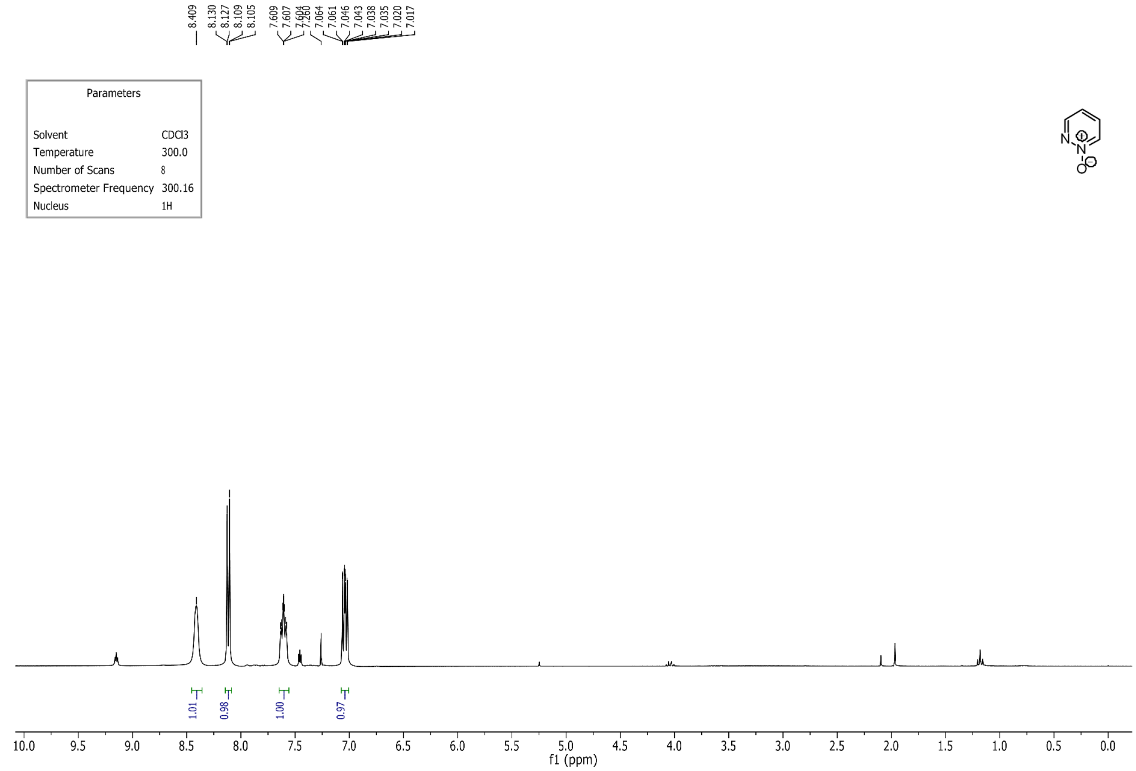


3-acetylpyridine *N*-oxide 1h

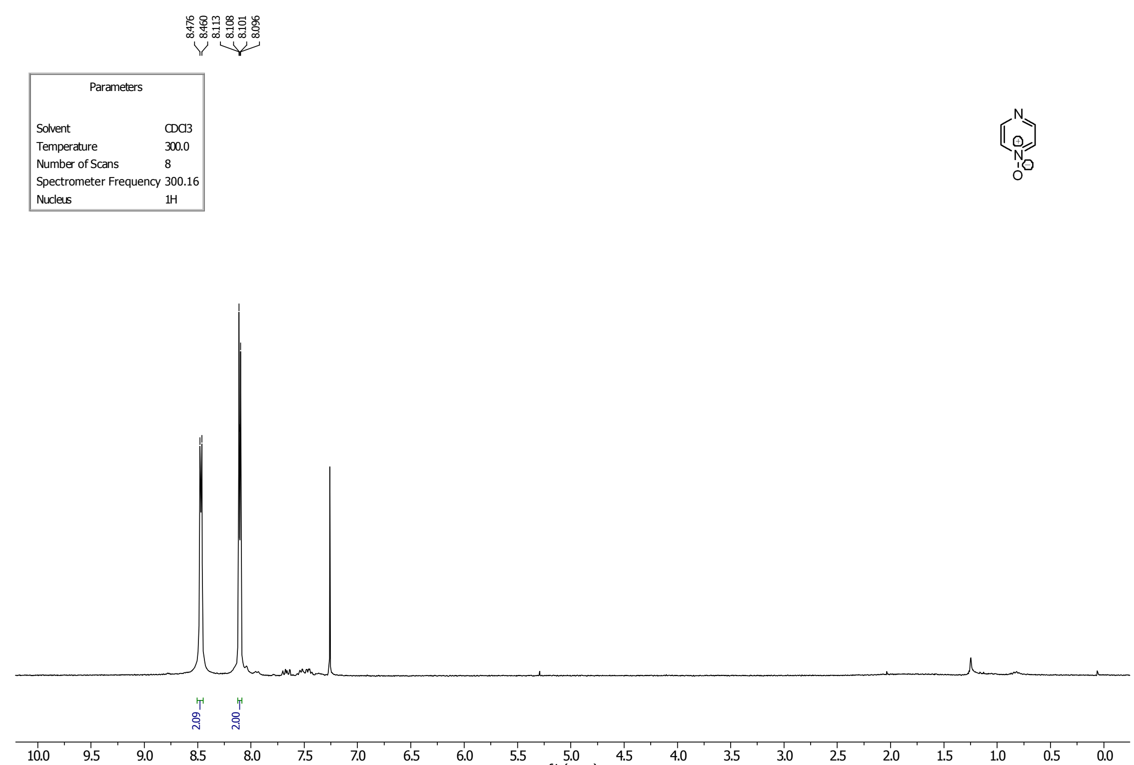




pyridazine *N*-oxide 1i



pyrazine *N*-oxide 1j



quinoline *N*-oxide 1k

Parameters	
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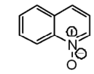
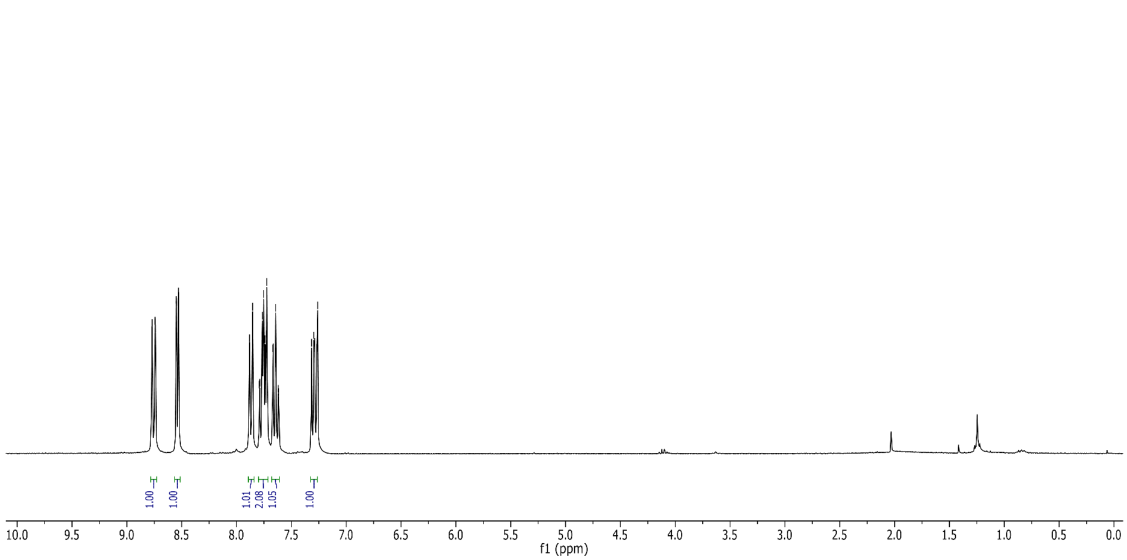
Temperature	300.0
Number of Scans	8
Spectrometer Frequency	300.16
Nucleus	1H





isoquinoline *N*-oxide 1l

Parameters	
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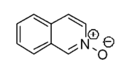
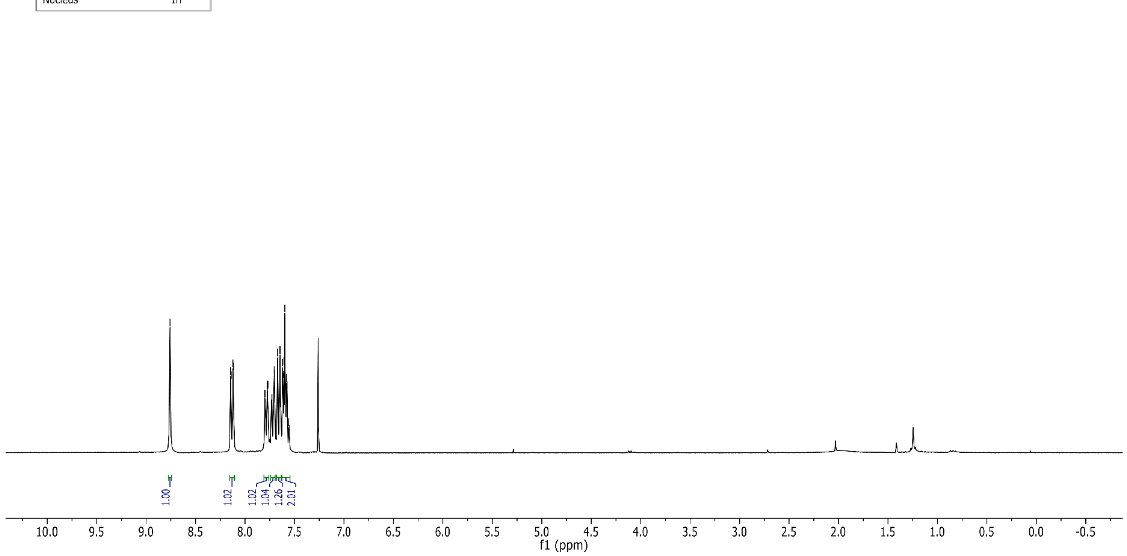
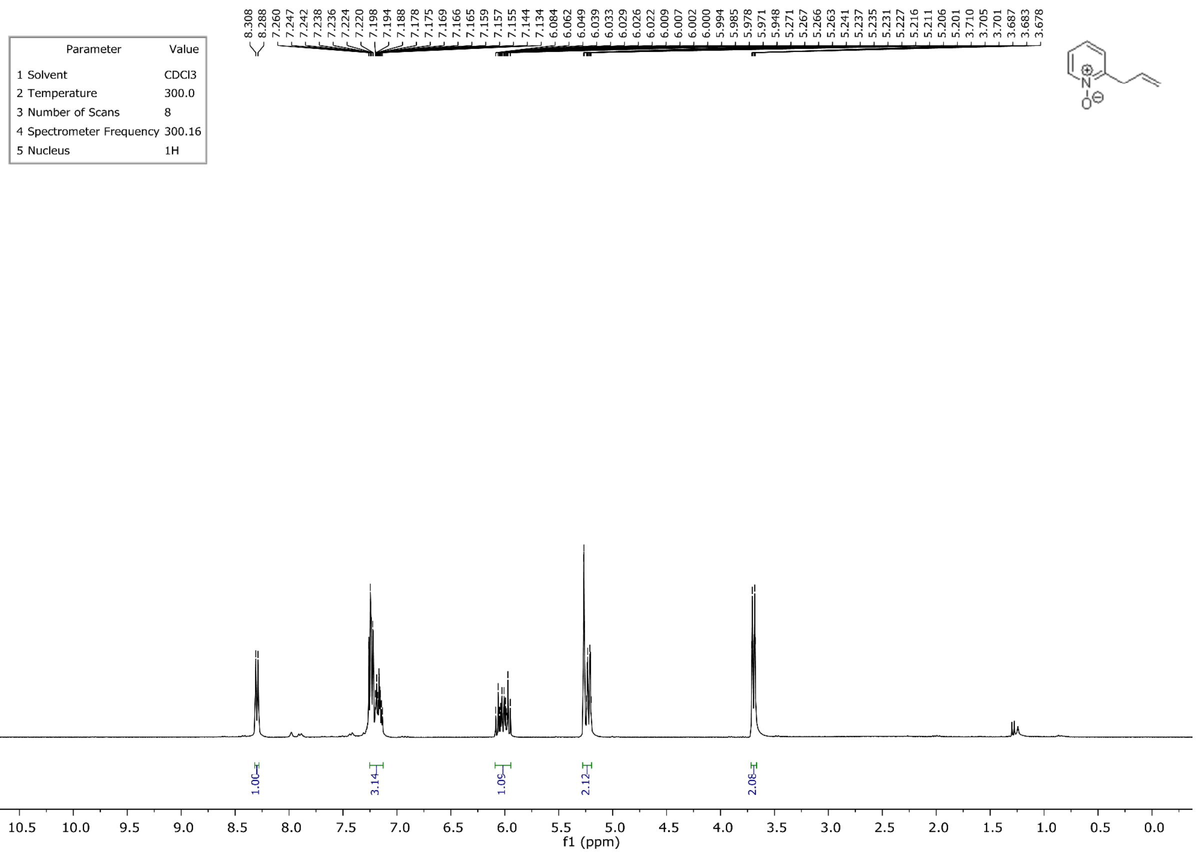
Temperature	300.0
Number of Scans	8
Spectrometer Frequency	300.16
Nucleus	1H



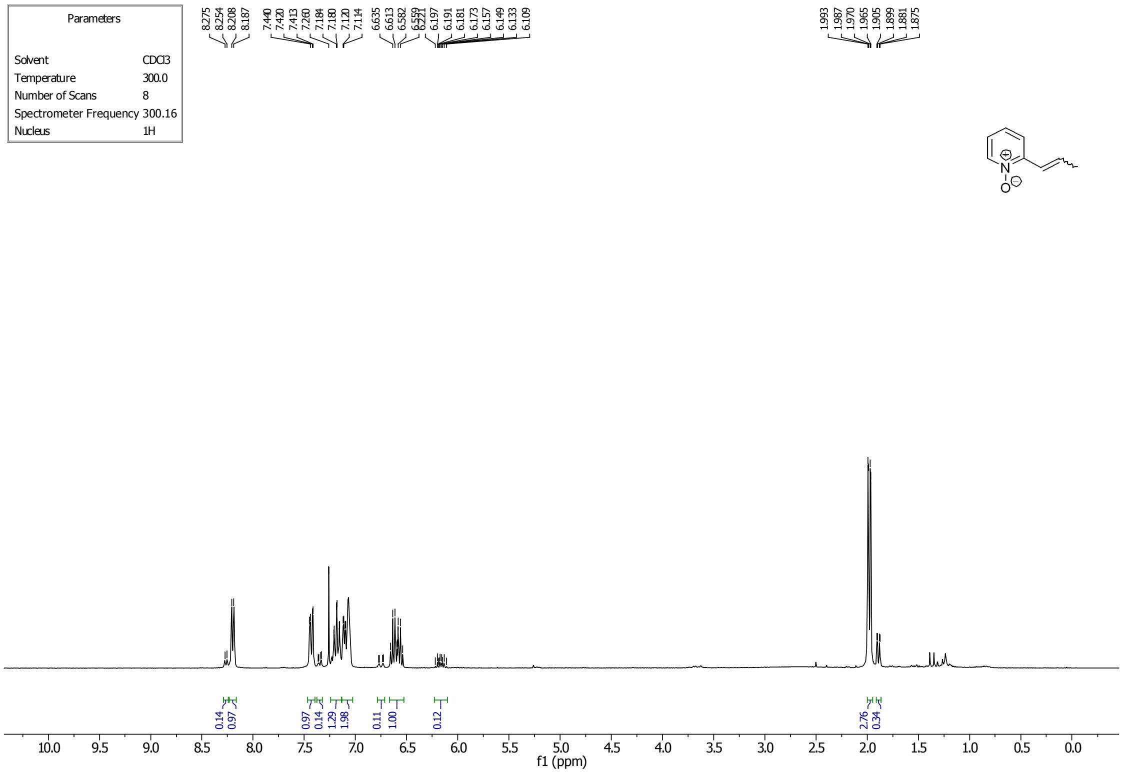


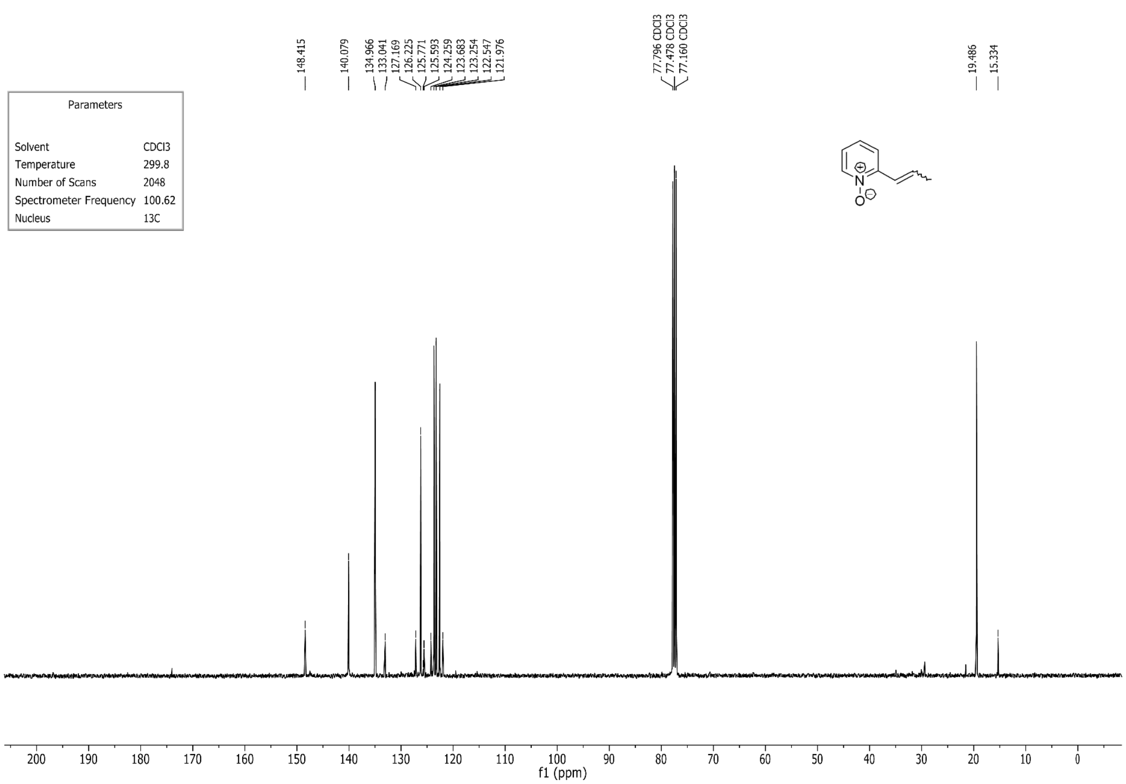
2-allylpyridine *N*-oxide 2a’



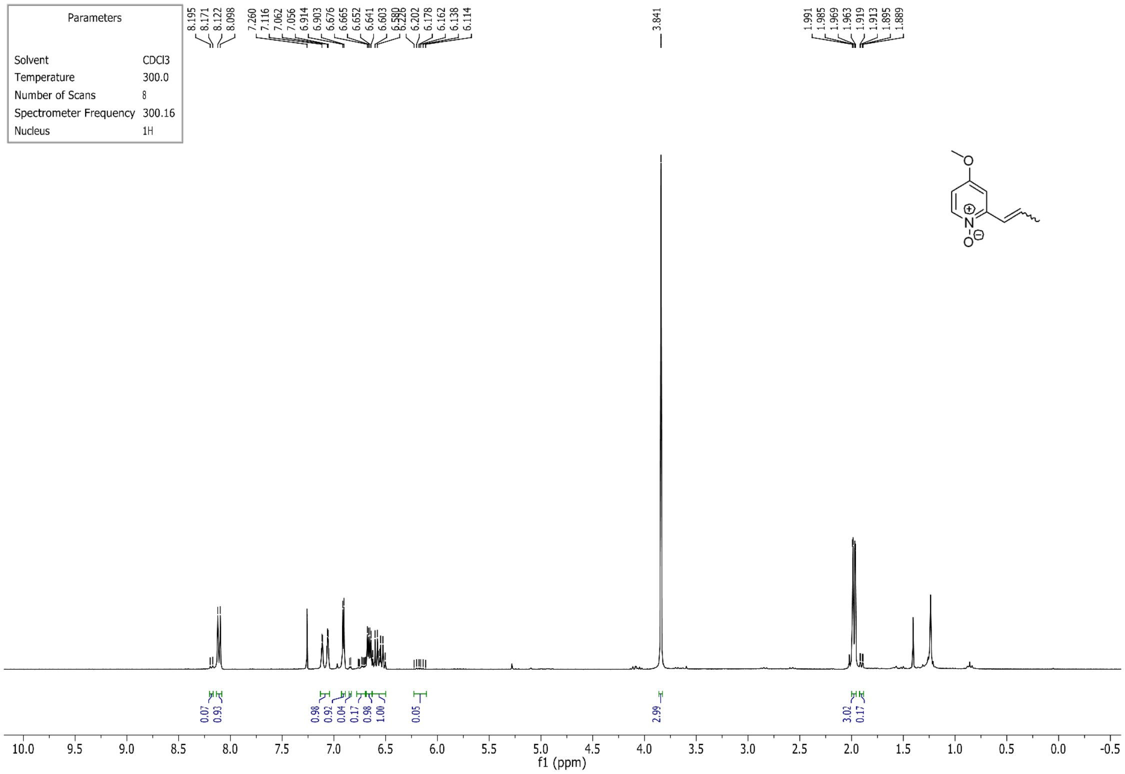
<u>C2-alkenylated and allylated *N*-Oxides</u>

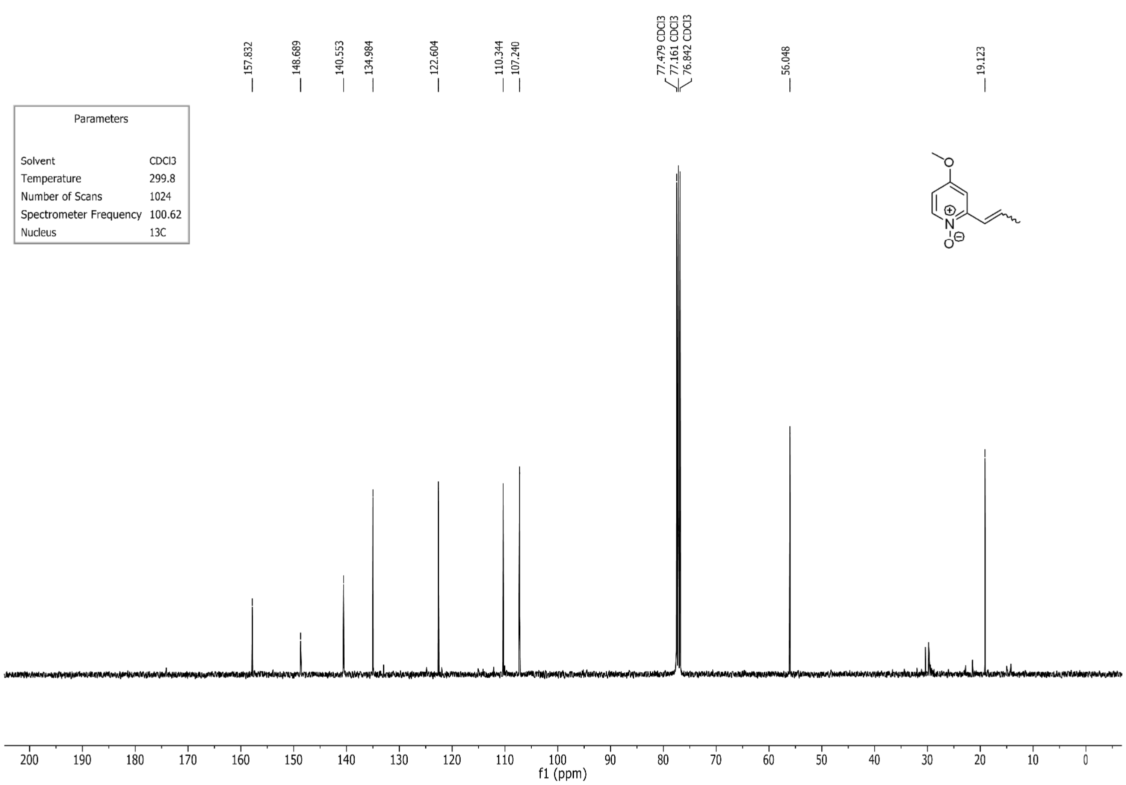
2-(prop-1-enyl)pyridine *N*-oxide 2a



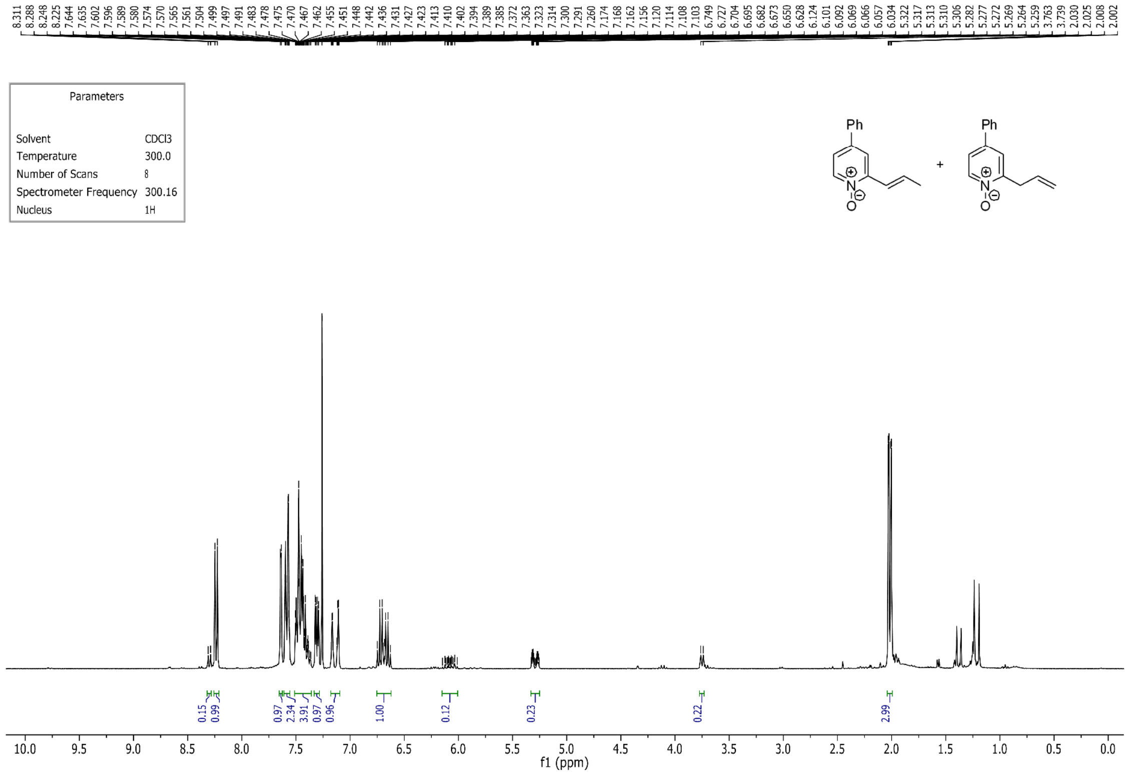


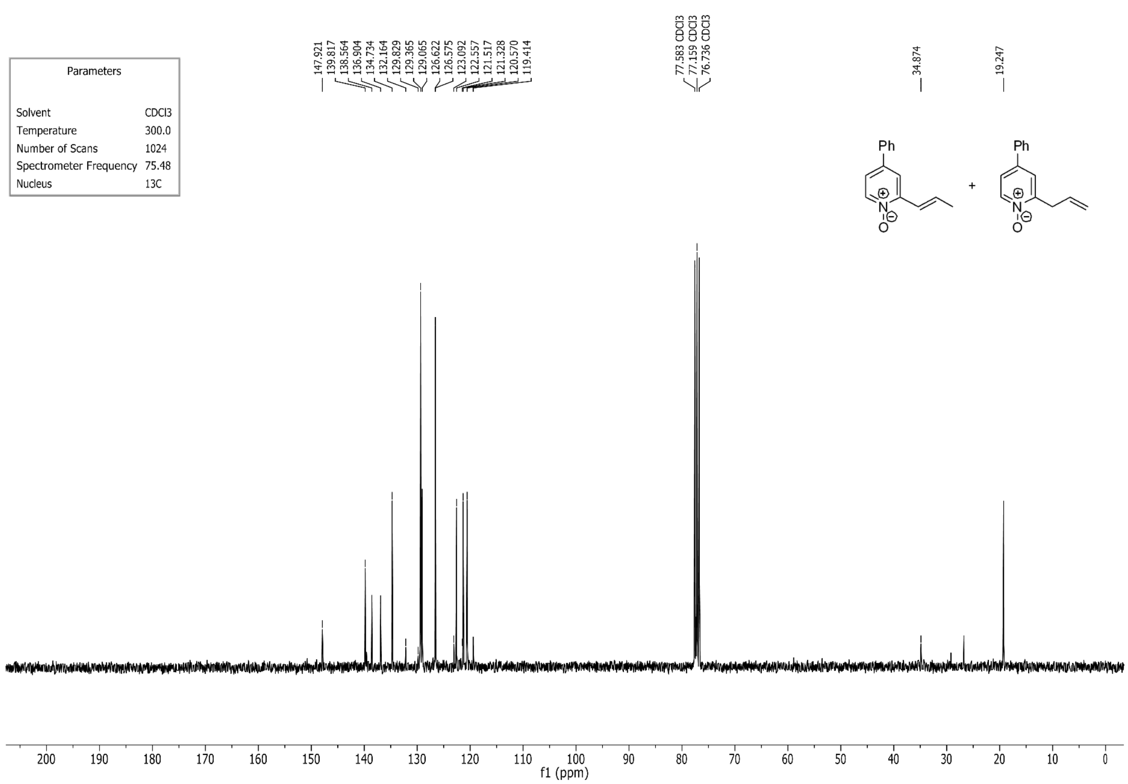
4-methoxy-2-(prop-1-en-1-yl)pyridine *N*-oxide 2b



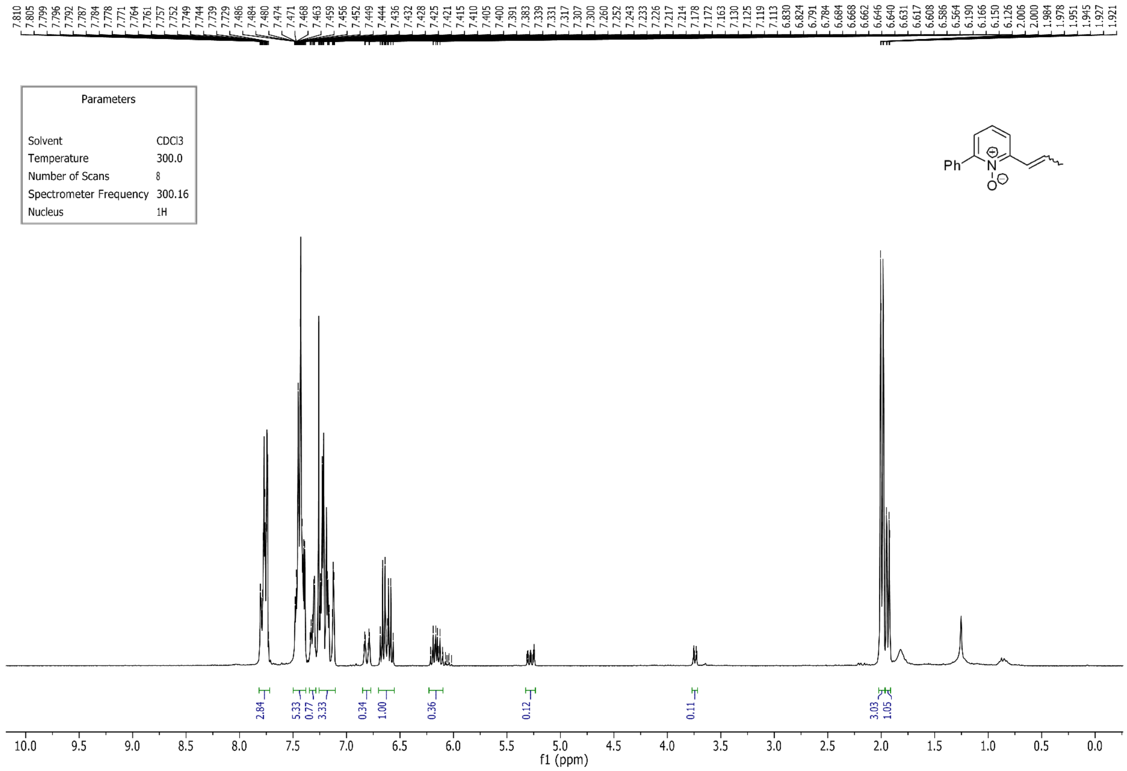


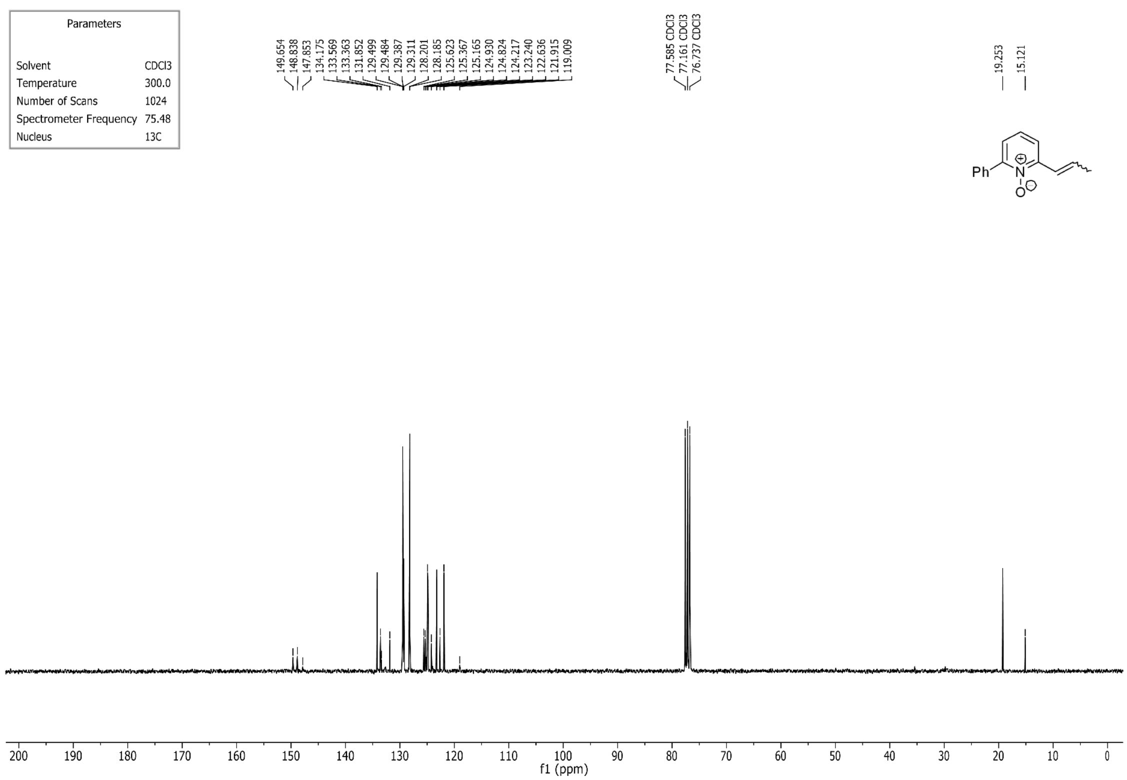
4-phenyl-(*E*)-2-(prop-1-en-1-yl)pyridine *N*-oxide 2c and 4-phenyl-2-allylpyridine *N*-oxide 2c'



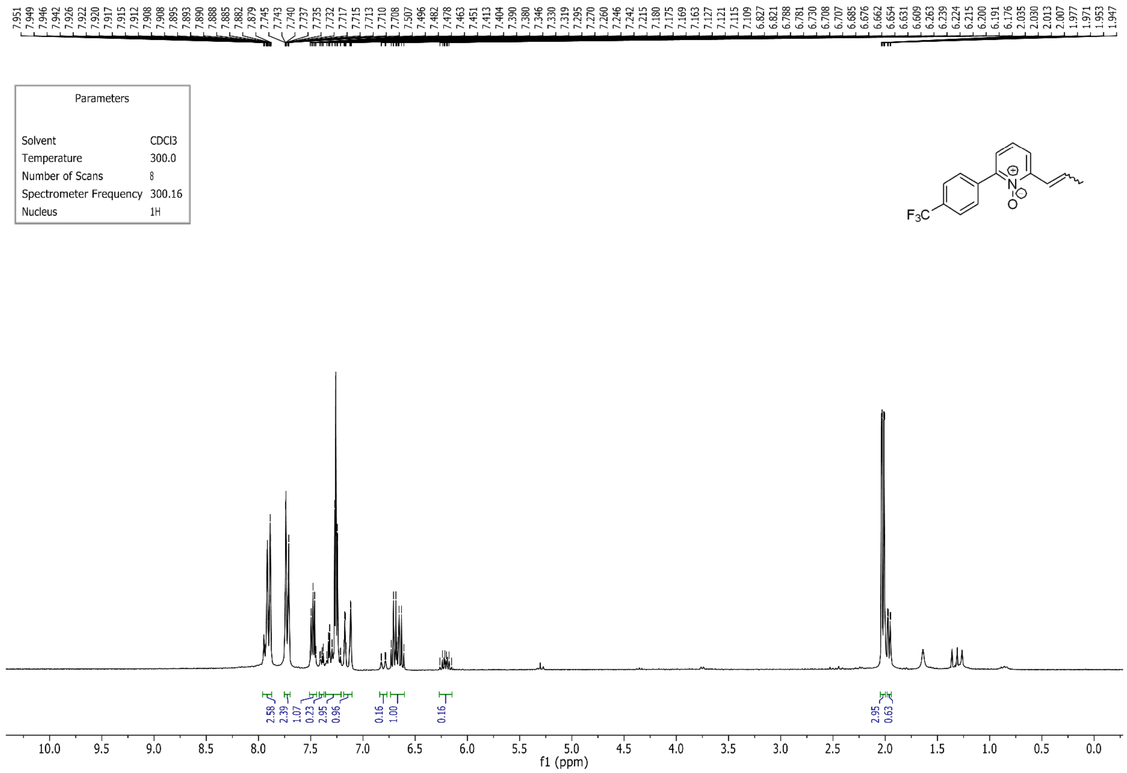


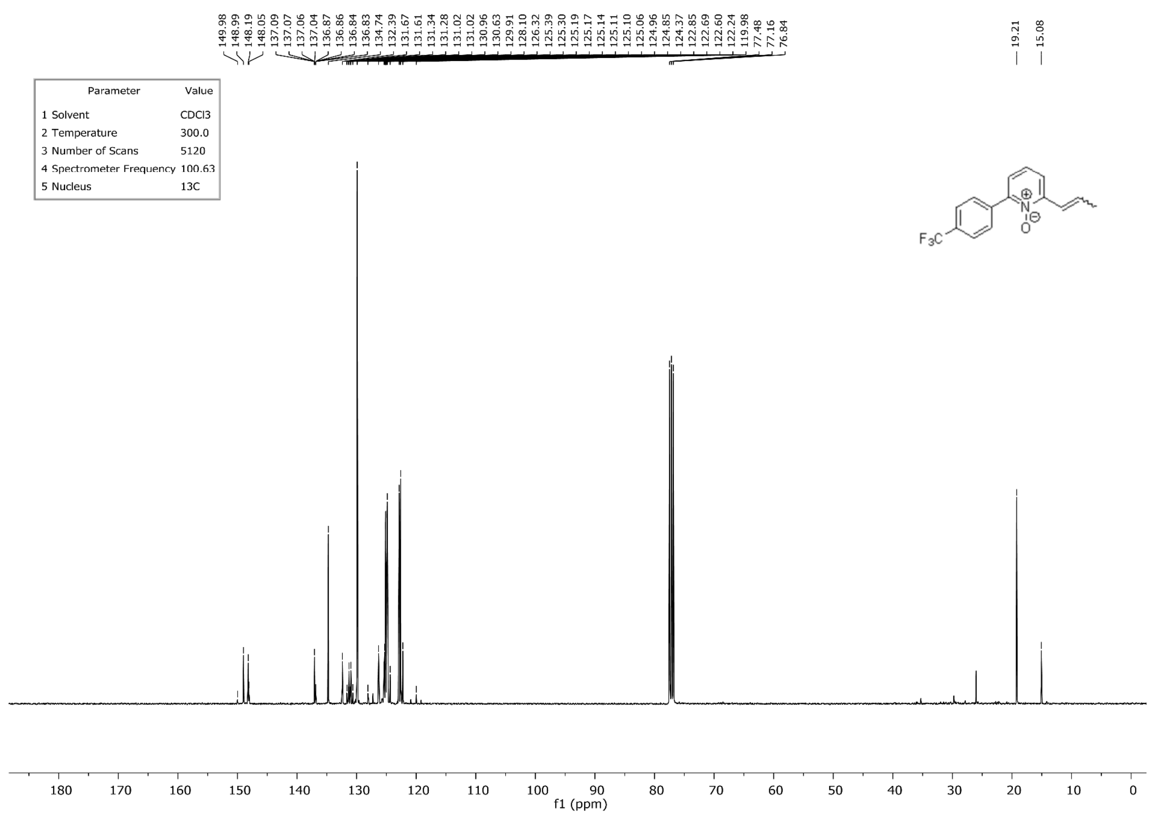
2-phenyl-5-(prop-1-en-1-yl)pyridine *N*-oxide 2d

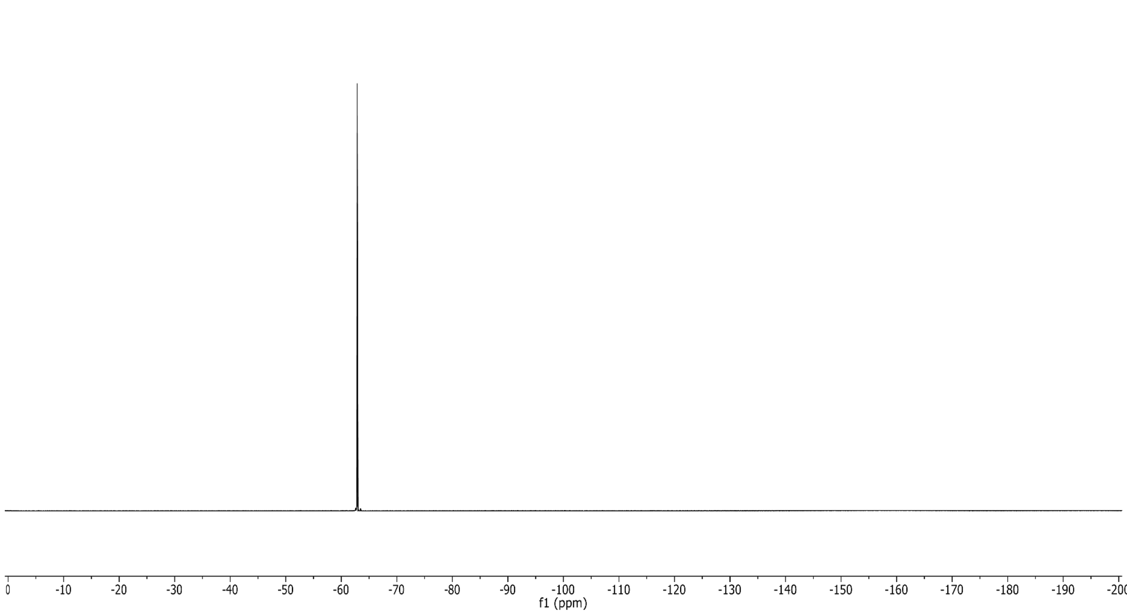


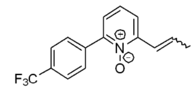


2-(4-(trifluoromethyl)Phenyl)-5-(prop-1-en-1-yl)pyridine *N*-oxide 2e

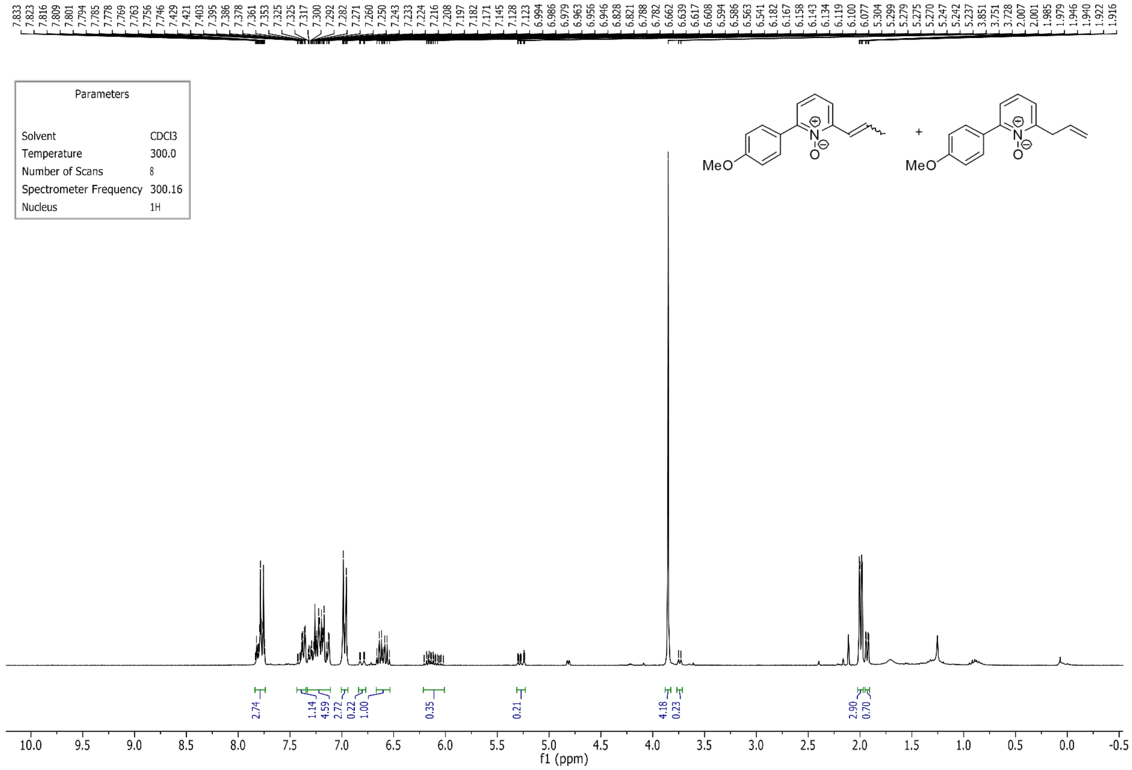

7.951 7.949 7.946 7.942 7.926 7.922 7.920 7.917 7.915 7.912 7.908 7.908 7.895 7.893 7.890 7.888 7.885 7.882 7.879 7.745 7.743 7.740 7.737 7.735 7.732 7.717 7.715 7.713 7.710 7.708 7.507 7.496 7.482 7.478 7.463 7.451 7.413 7.404 7.390 7.380 7.346 7.330 7.319 7.295 7.270 7.260 7.246 7.242 7.215 7.180 7.175 7.169 7.163 7.127 7.121 7.115 7.109 6.827 6.821 6.788 6.781 6.730 6.708 6.707 6.685 6.676 6.662 6.654 6.631 6.609 6.263 6.239 6.224 6.215 6.200 6.191 6.176 2.035 2.030 2.013 2.007 1.977 1.971 1.953 1.947
Parameters
Solvent CDCl3
Temperature 300.0
Number of Scans 8
Spectrometer Frequency 300.16
Nucleus 1H
F3C
N
O
2.58 2.39 1.07 0.23 2.95 0.96 0.16 1.00 0.16 2.95 0.63
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
f1 (ppm)

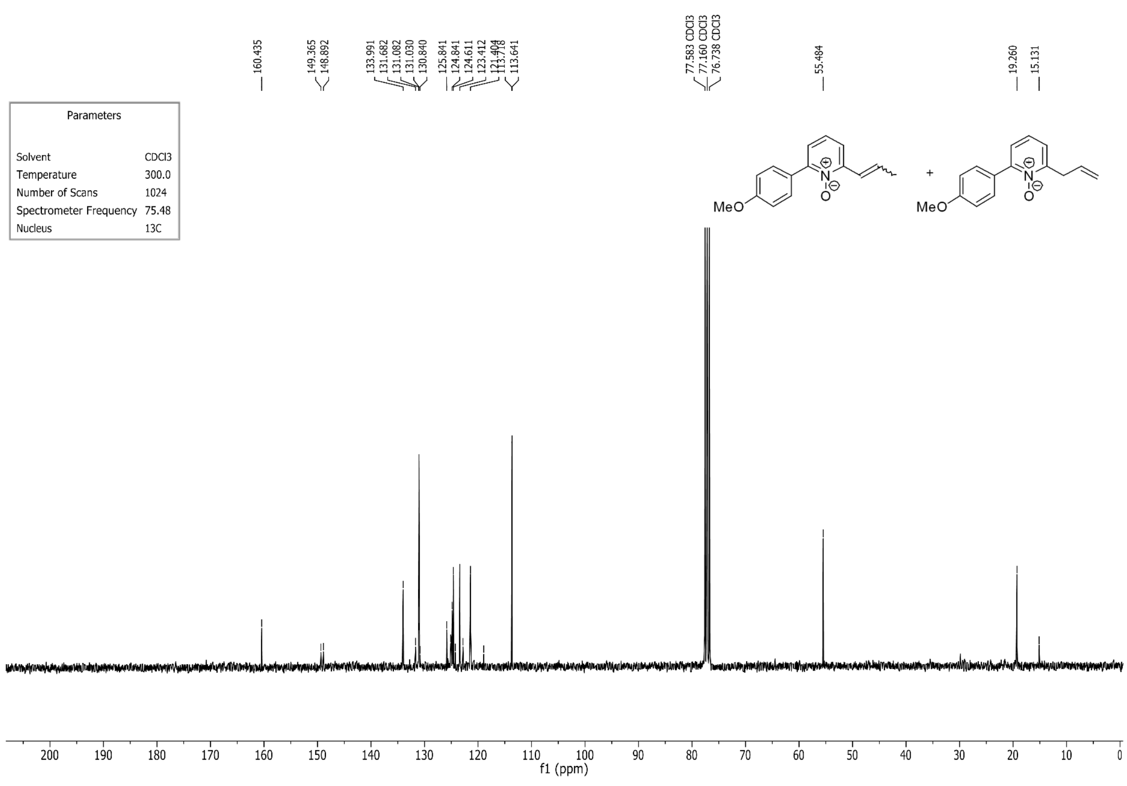

149.98 148.99 148.19 148.05 137.09 137.07 137.06 137.04 136.87 136.86 136.84 136.83 134.74 132.39 131.67 131.61 131.34 131.28 131.02 130.96 130.63 129.91 128.10 126.32 125.39 125.30 125.19 125.17 125.14 125.11 125.10 125.06 124.96 124.85 124.37 122.85 122.69 122.60 122.24 119.98 77.48 77.16 76.84
19.21
15.08
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 5120
4 Spectrometer Frequency 100.63
5 Nucleus 13C
F3C
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Parameters
Solvent CDCl3
Temperature 300.0
Number of Scans 32
Spectrometer Frequency 282.40
Nucleus 19F
-62.856
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

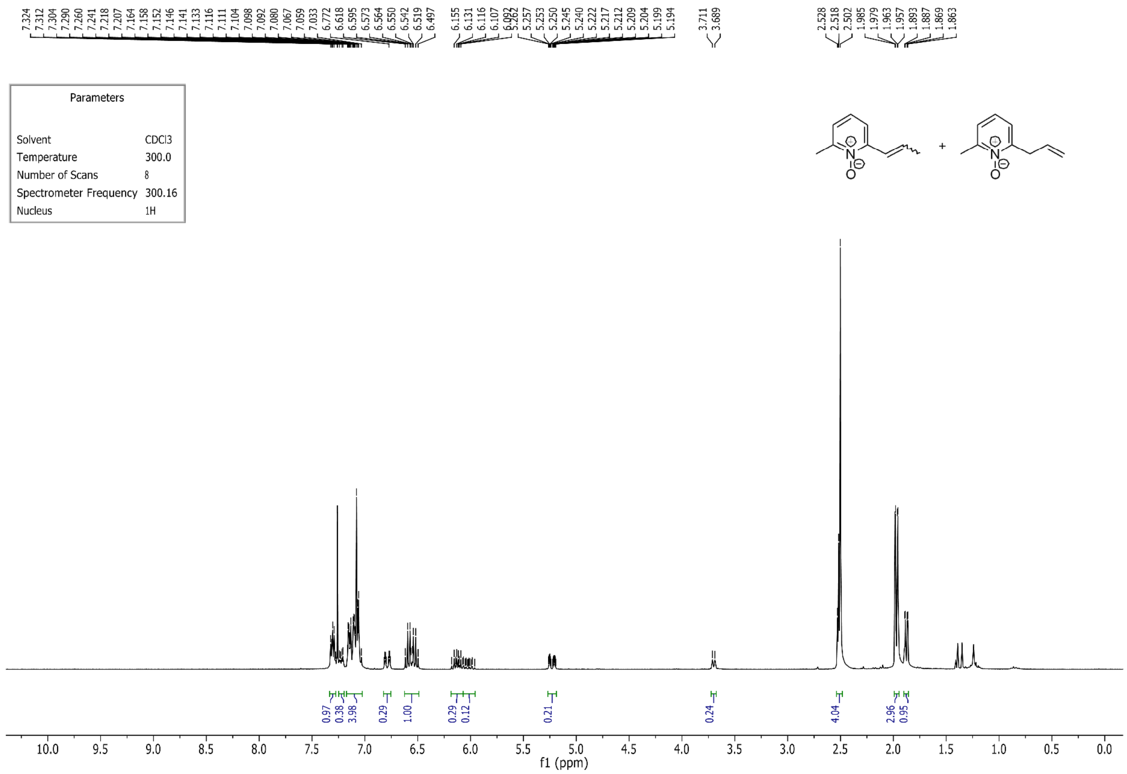

F3C
N
O

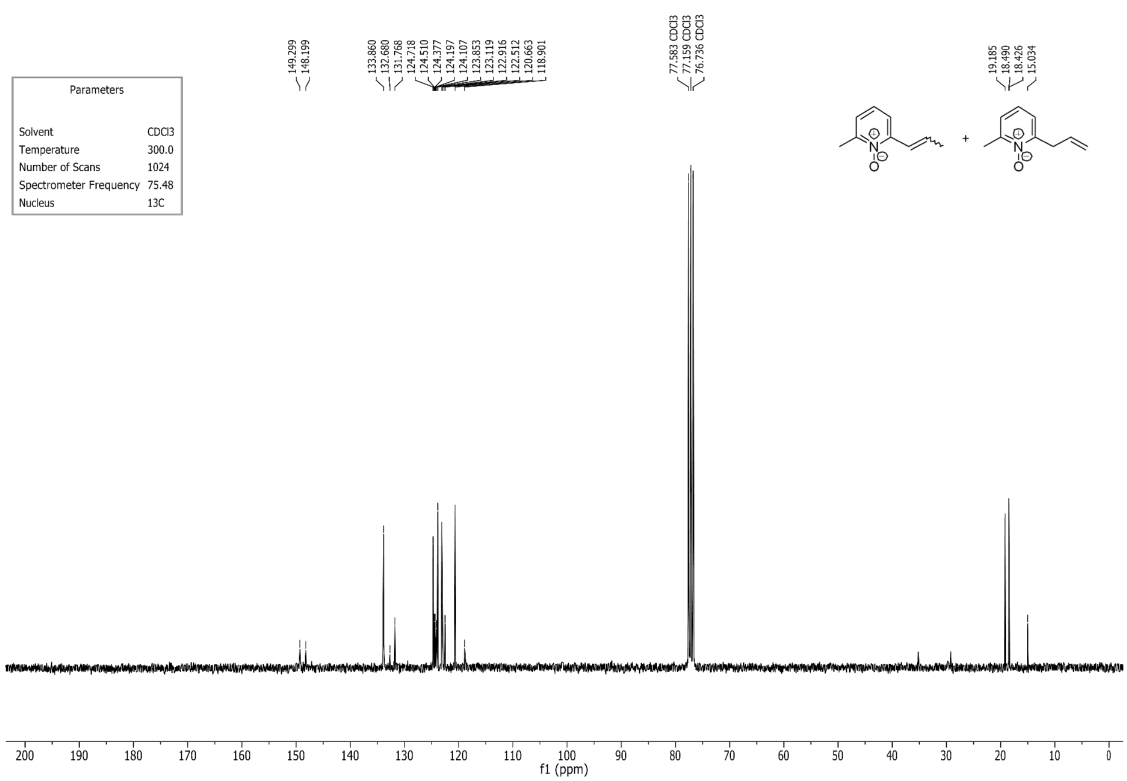
2-(4-(methoxy)phenyl)-5-(prop-1-en-1-yl)pyridine *N*-oxide 2f and **2-(4-(methoxy)phenyl)-5-allylpyridine *N*-oxide 2f'**



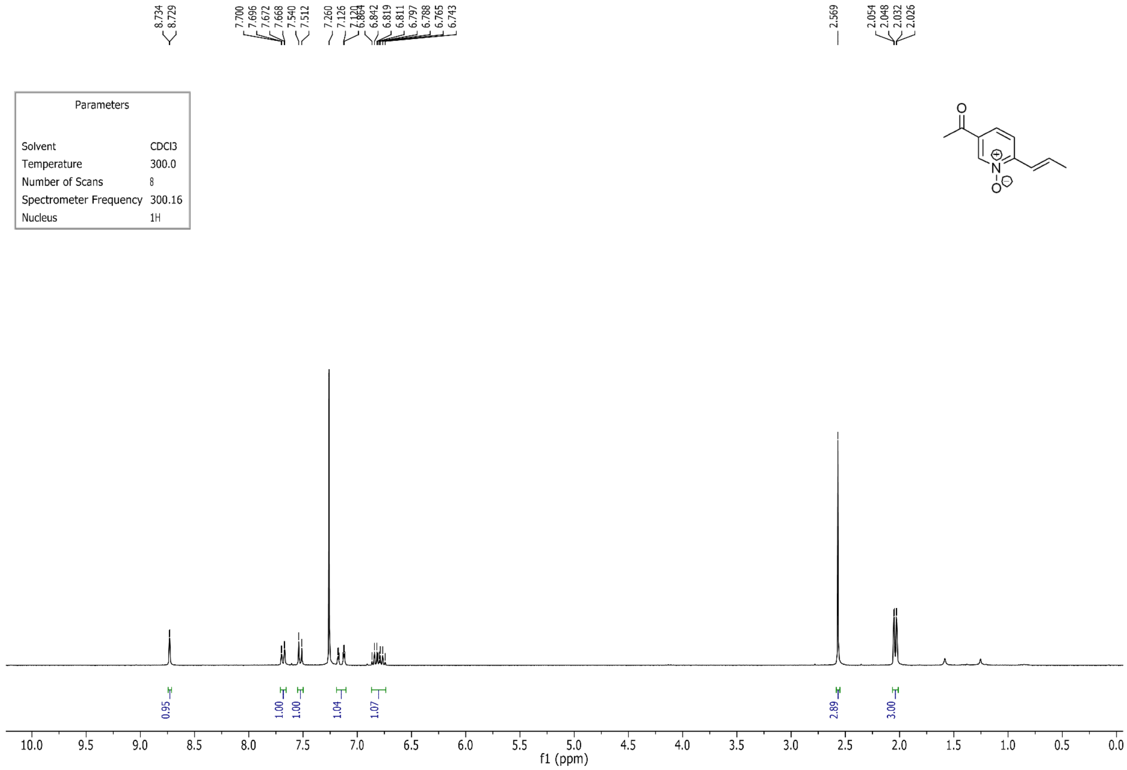


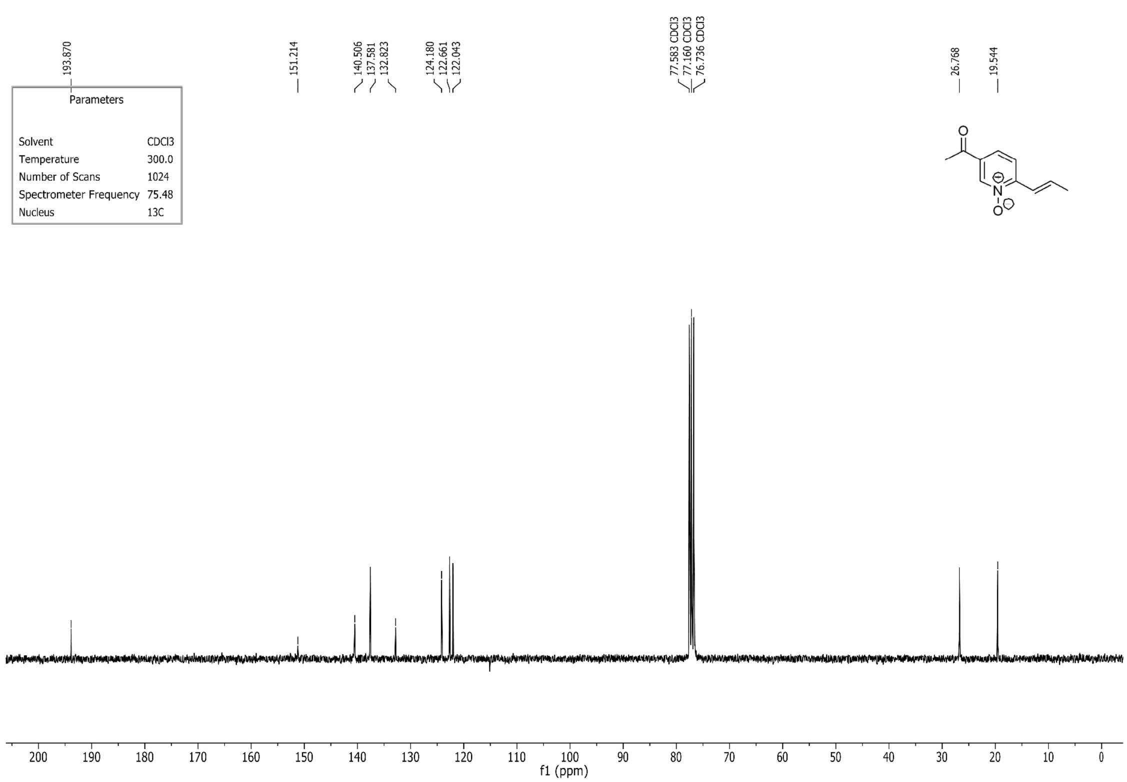
5-(prop-1-enyl)-2-picoline *N*-oxide 2g and 5-allyl-2-picoline *N*-oxide 2g'



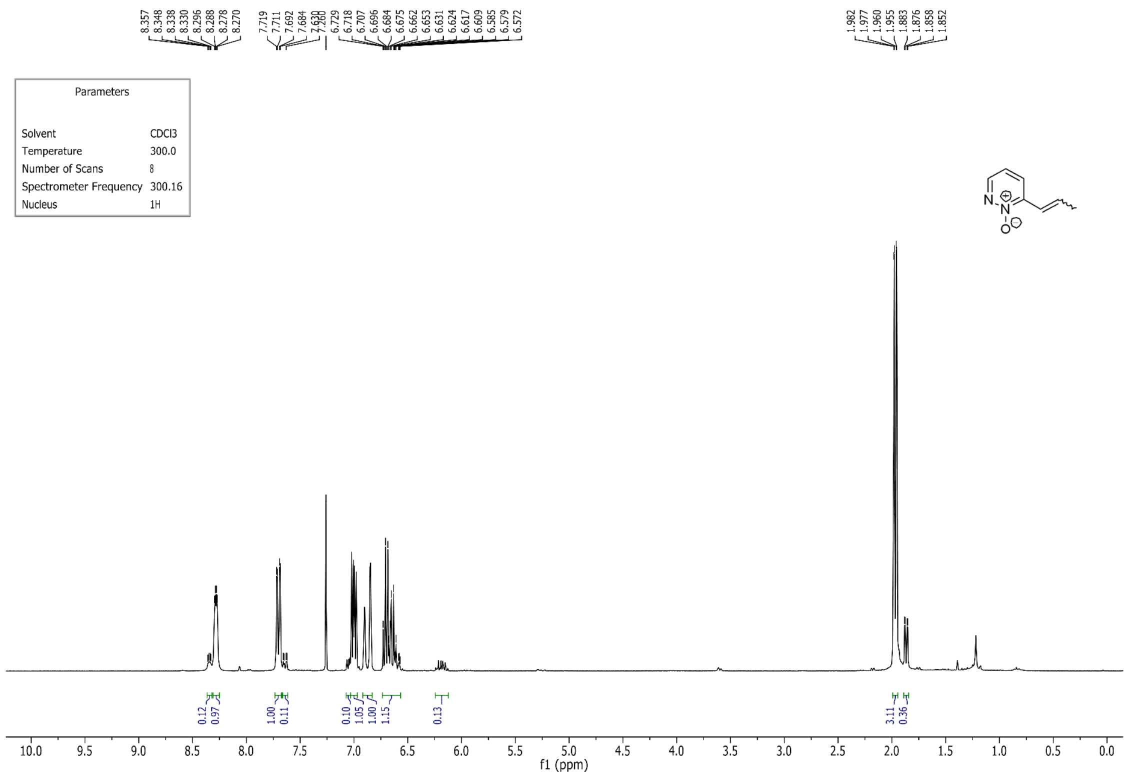


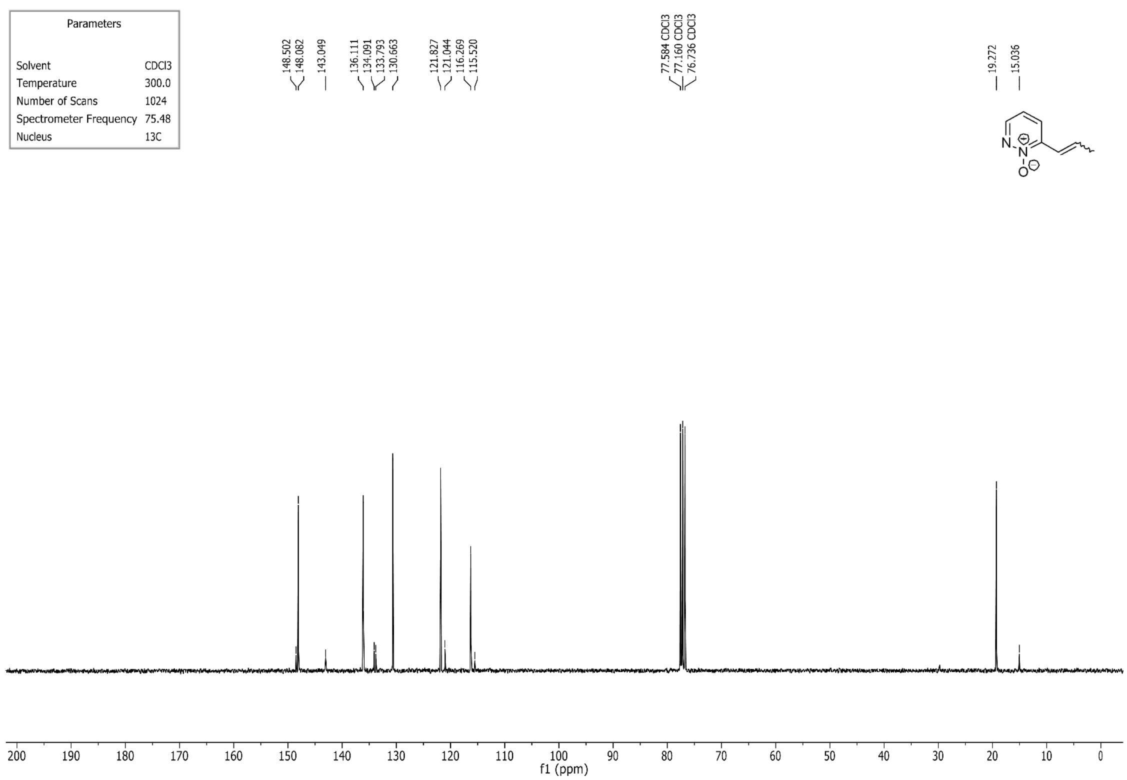
(*E*)-5-acetyl-2-(prop-1-en-1-yl)pyridine *N*-oxide 2h



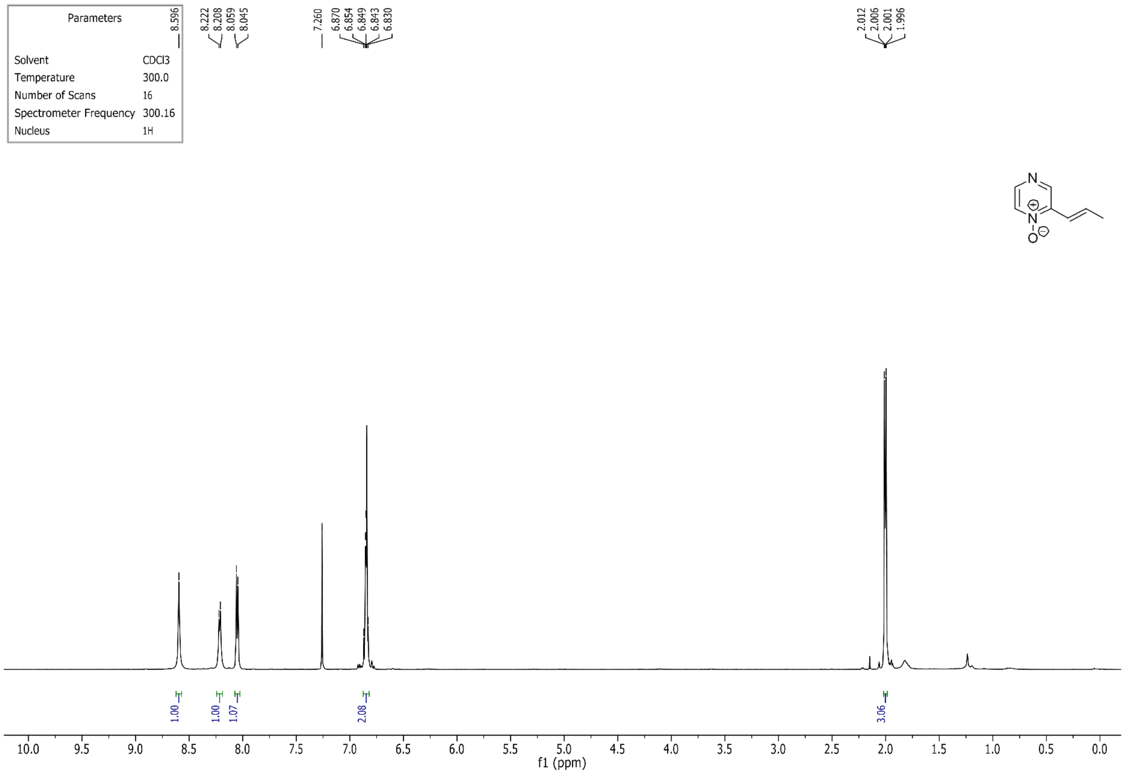


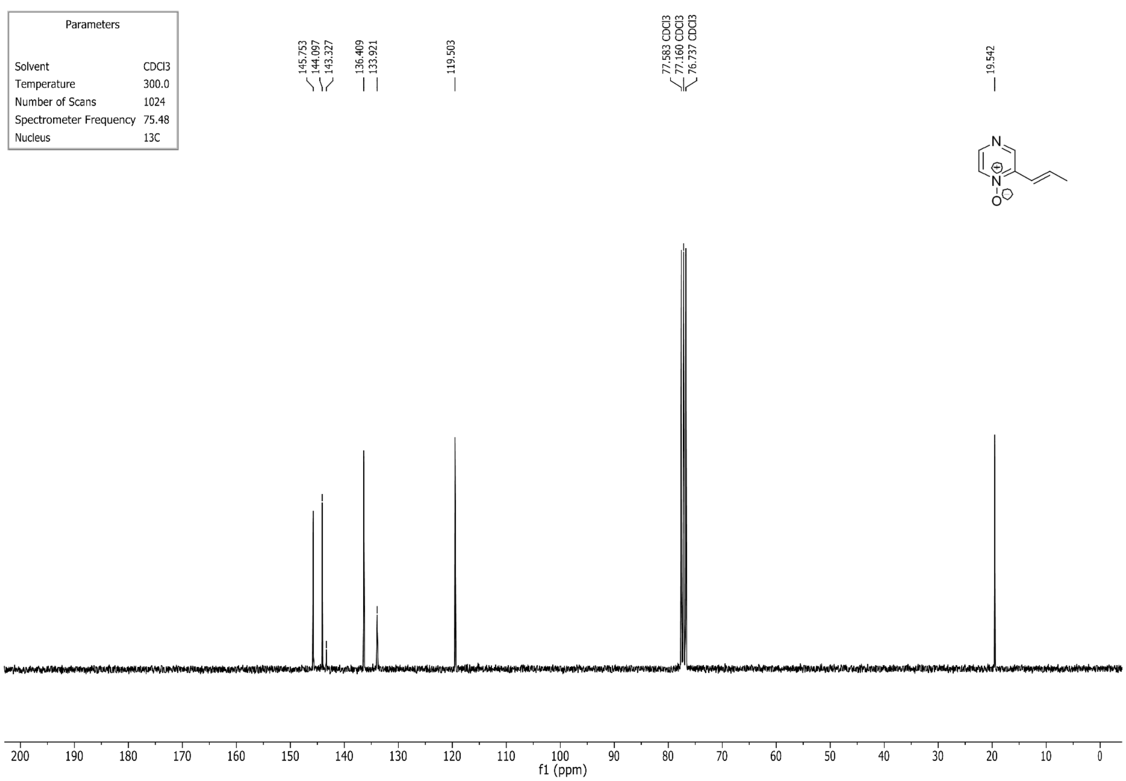
6-(prop-1-en-1-yl)pyridazine *N*-oxide 2i



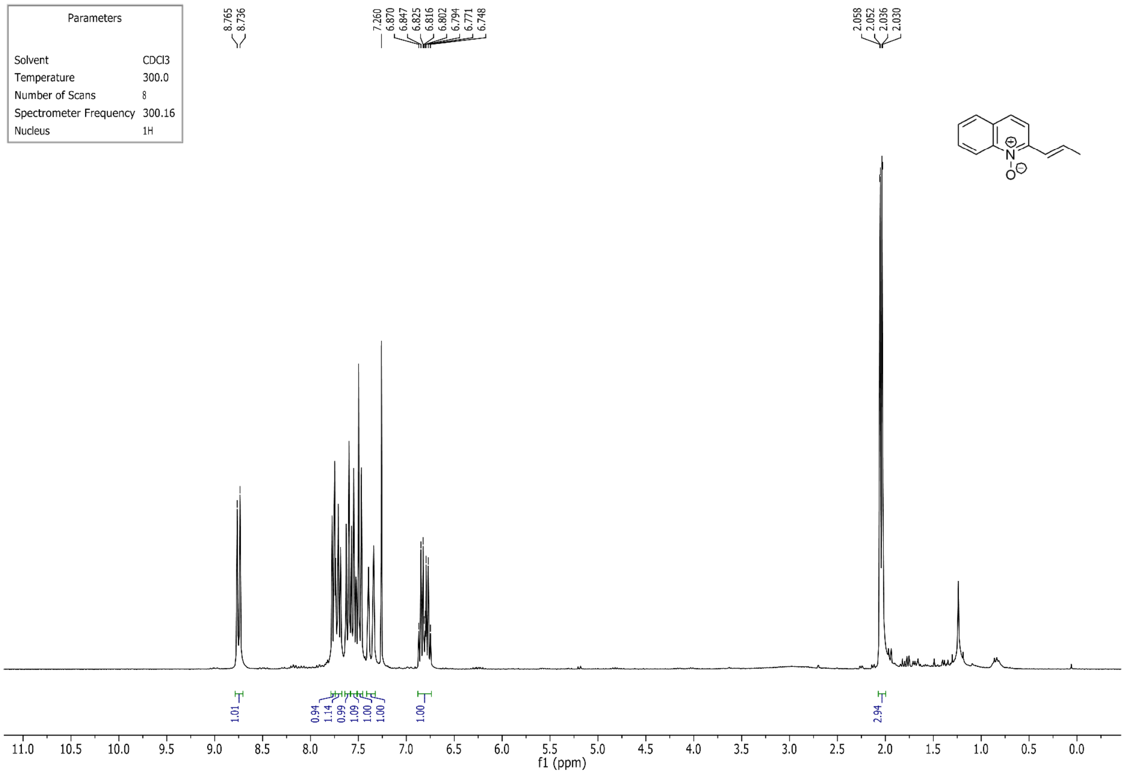


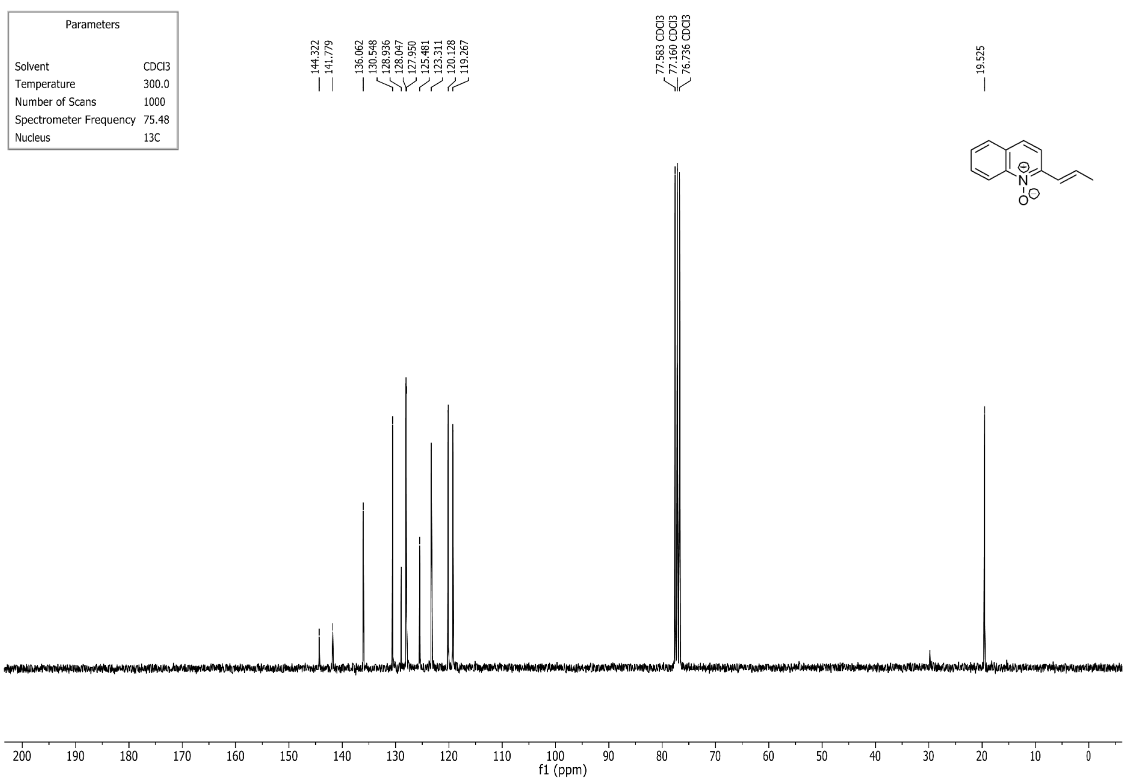
(*E*)-2-(prop-1-en-1-yl)pyrazine *N*-oxide 2j



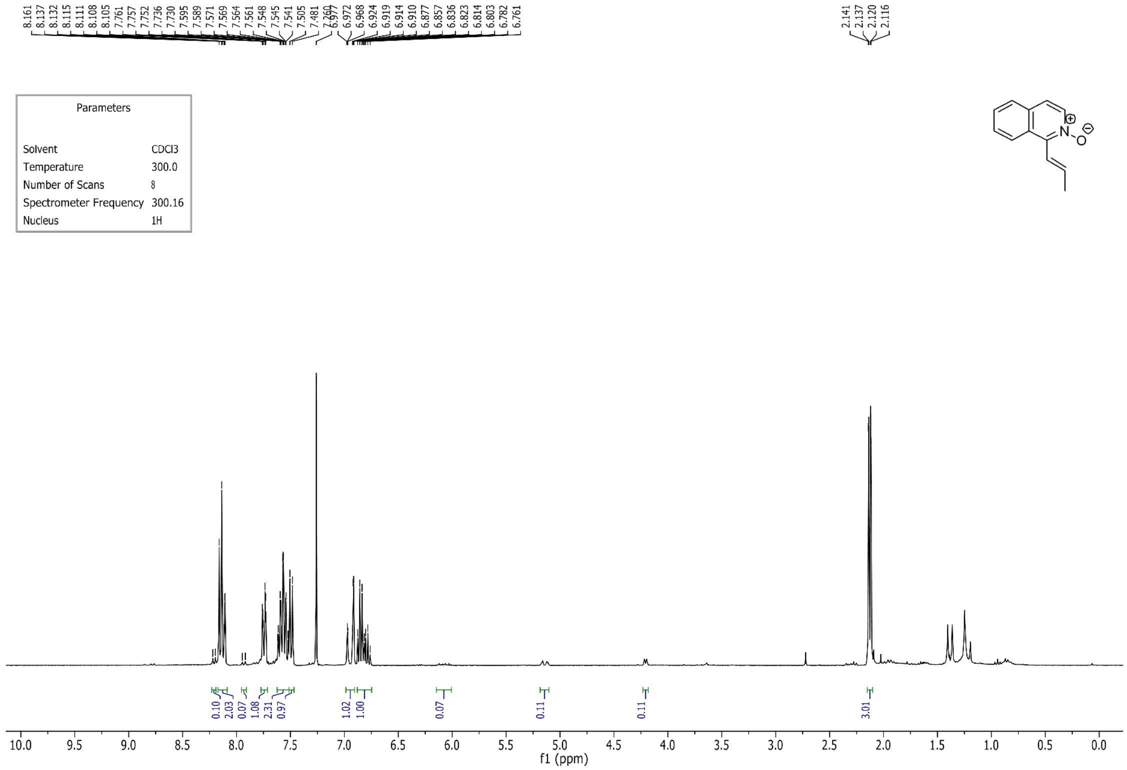


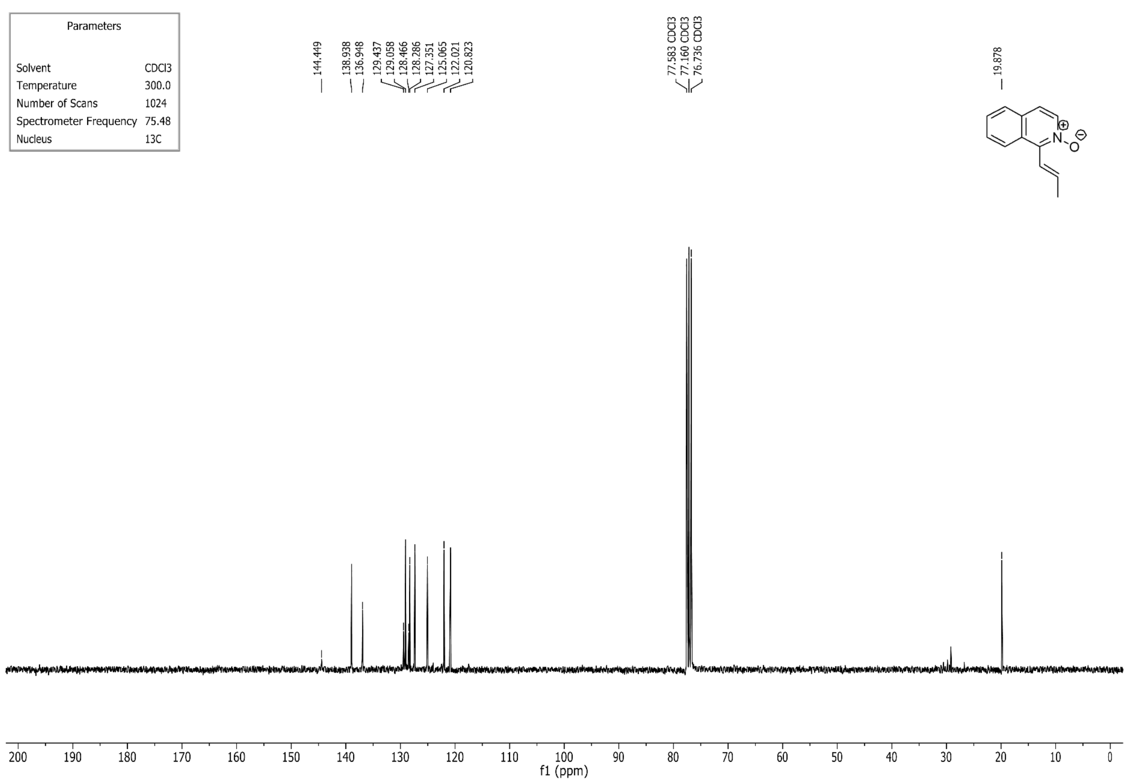
(*E*)-2-(prop-1-enyl)quinoline *N*-oxide 2k



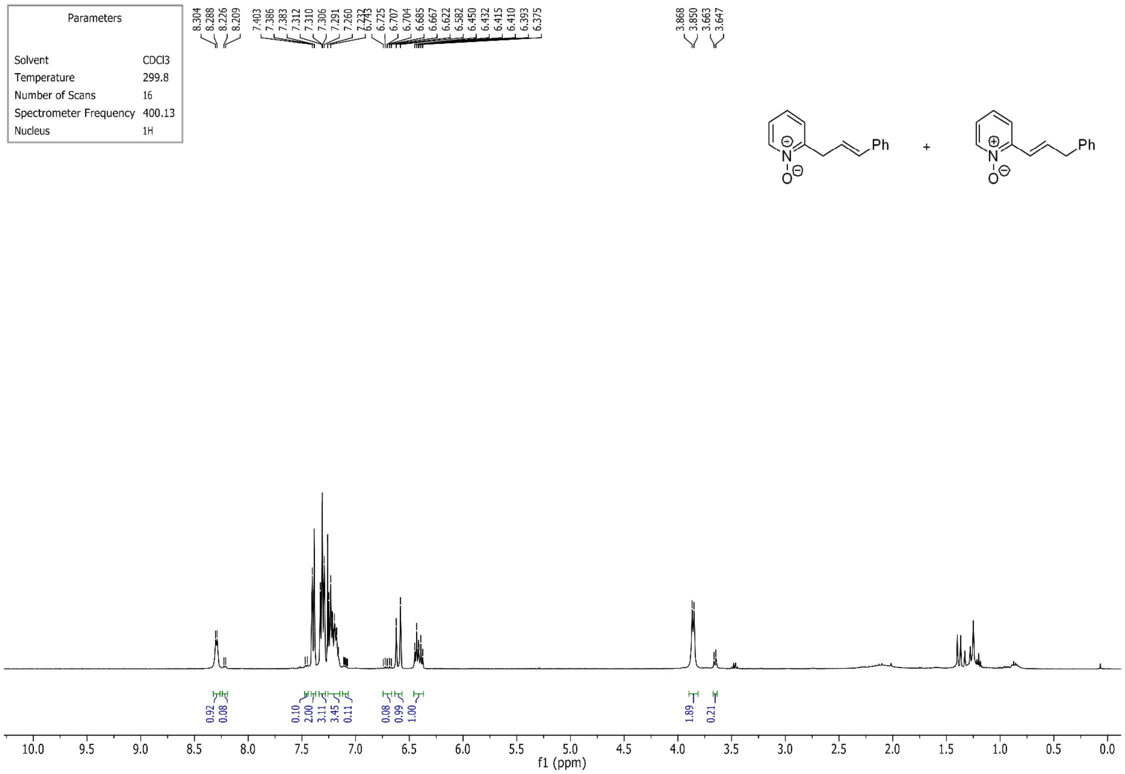


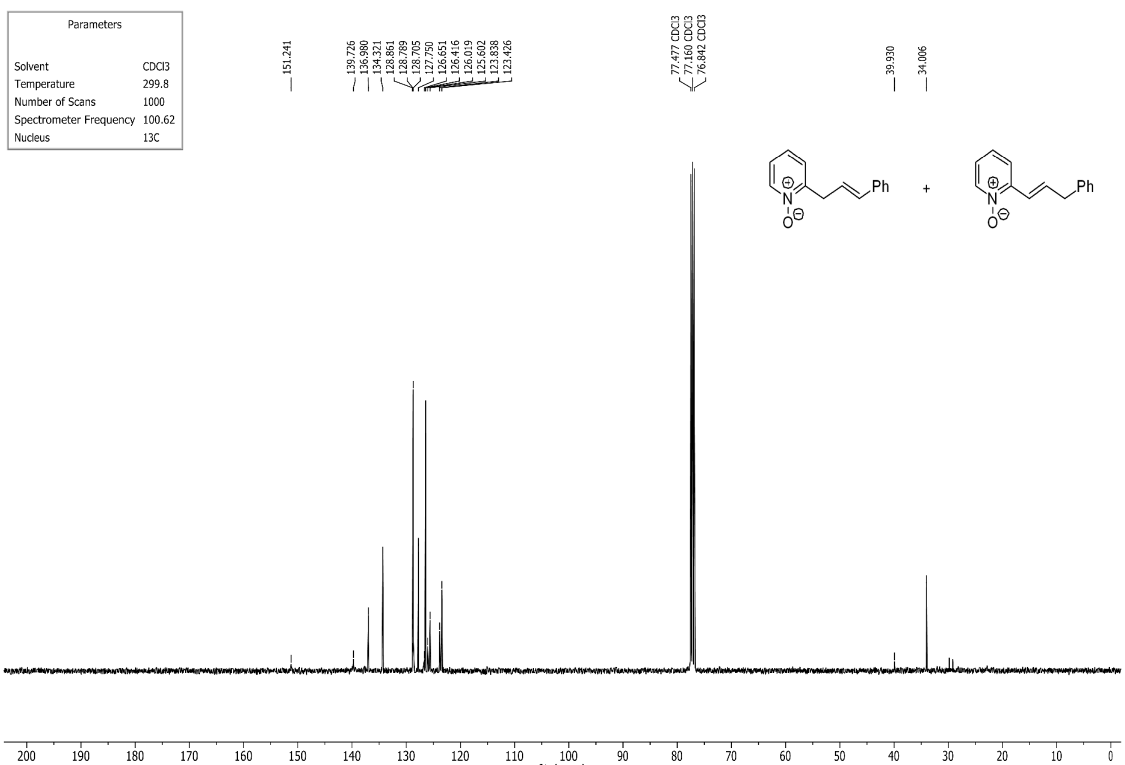
(*E*)-1-(prop-1-en-1-yl)isoquinoline *N*-oxide 2l



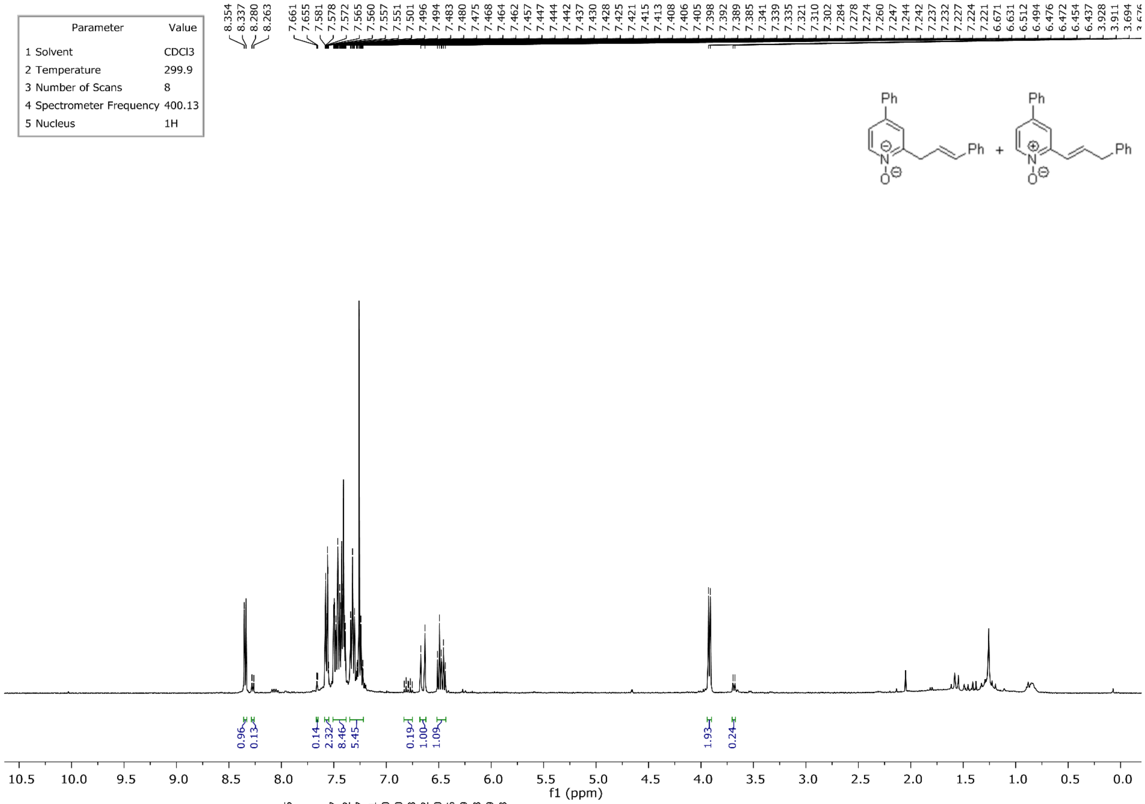


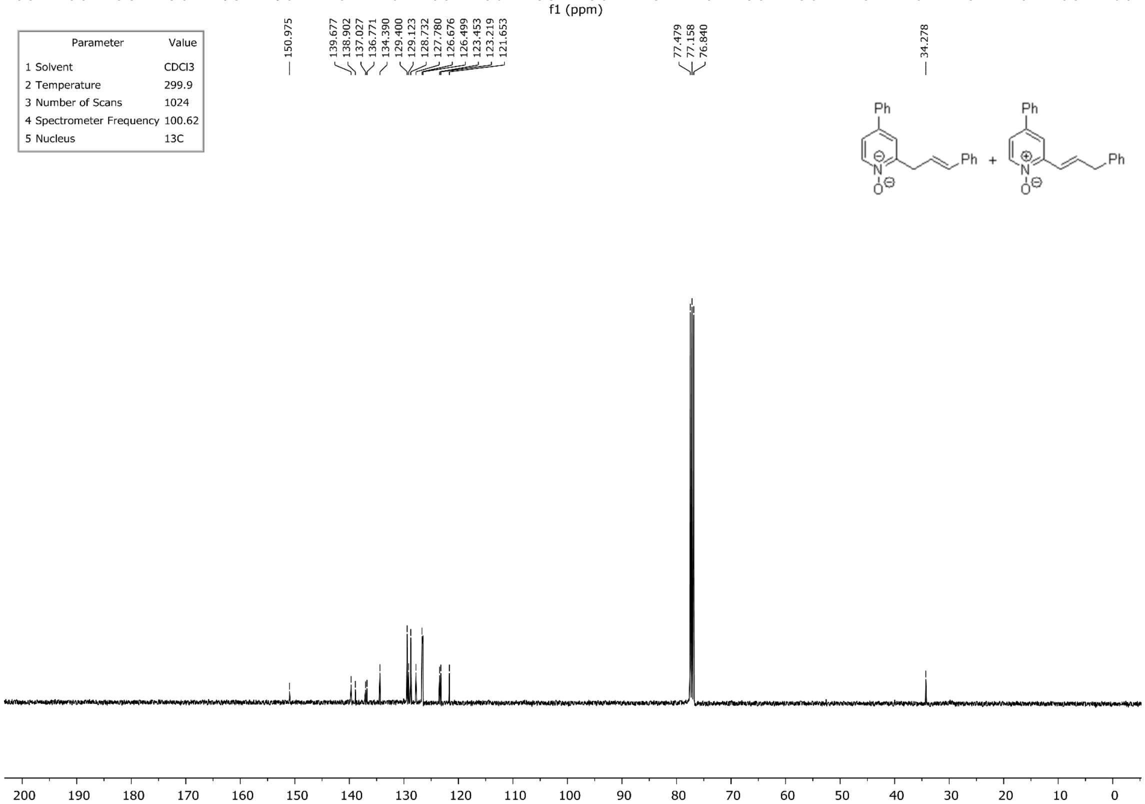
2-cinnamylpyridine *N*-oxide 4a and (E)-2-(3-phenylprop-1-en-1-yl)pyridine *N*-oxide 3a



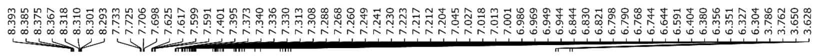


2-cinnamyl-4-phenylpyridine *N*-oxide 3c and (*E*)-4-phenyl-2-(3-phenylprop-1-en-1-yl)pyridine *N*-oxide 4c

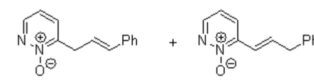


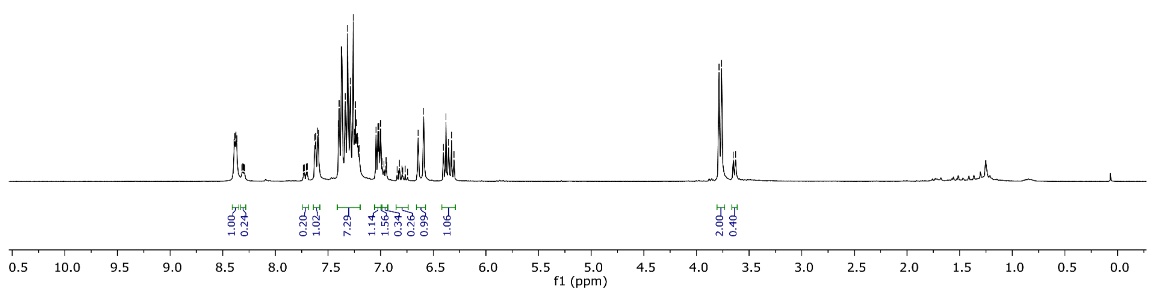


6-cinnamylpyridazine *N*-oxide 4i and (*E*)-6-(3-phenylprop-1-en-1-yl)pyridazine *N*-oxide 3i

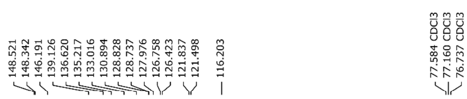


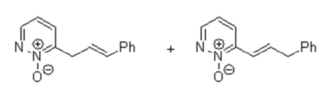
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.0
3 Number of Scans	8
4 Spectrometer Frequency	300.16
5 Nucleus	1H

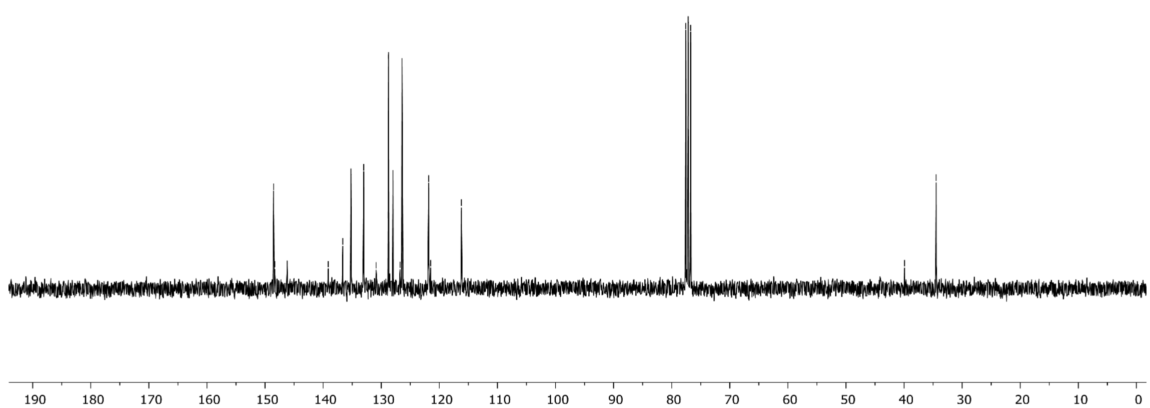




Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.0
3 Number of Scans	64
4 Spectrometer Frequency	75.48
5 Nucleus	13C

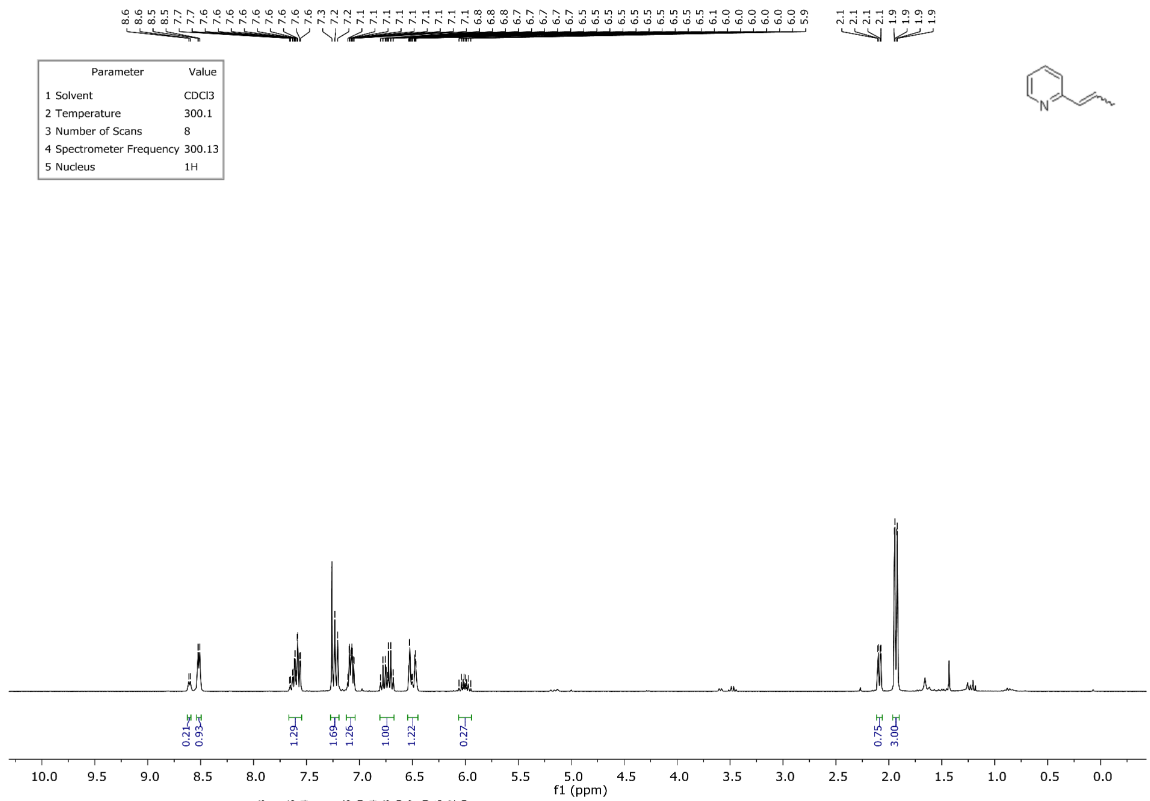




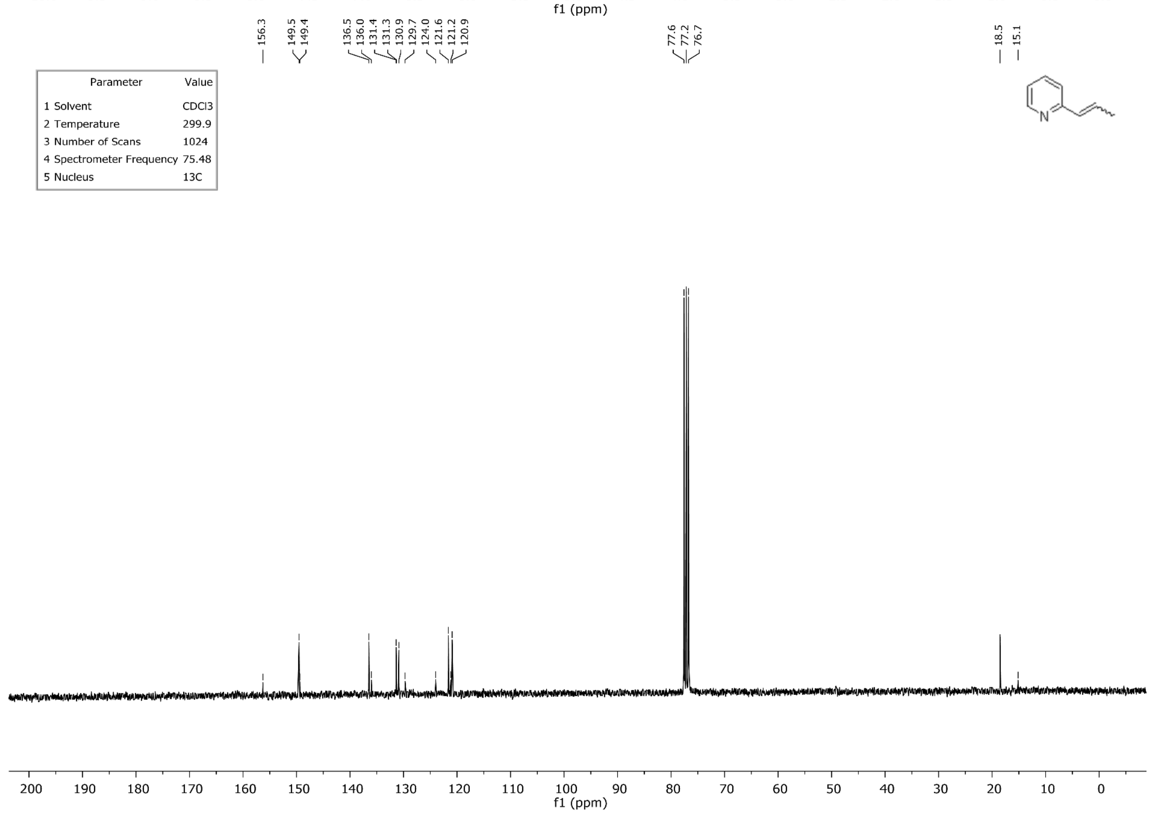


Further derivatizations products

(*E*)-2-(prop-1-en-1-yl)pyridine 5a:

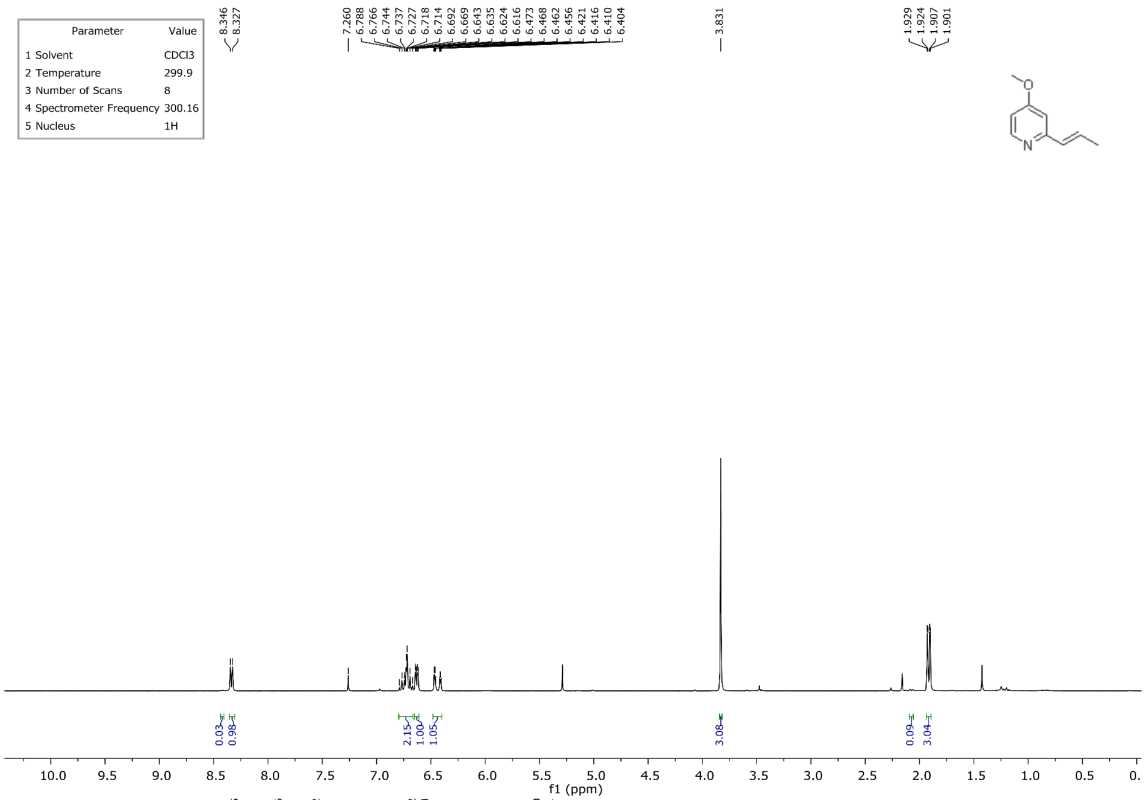


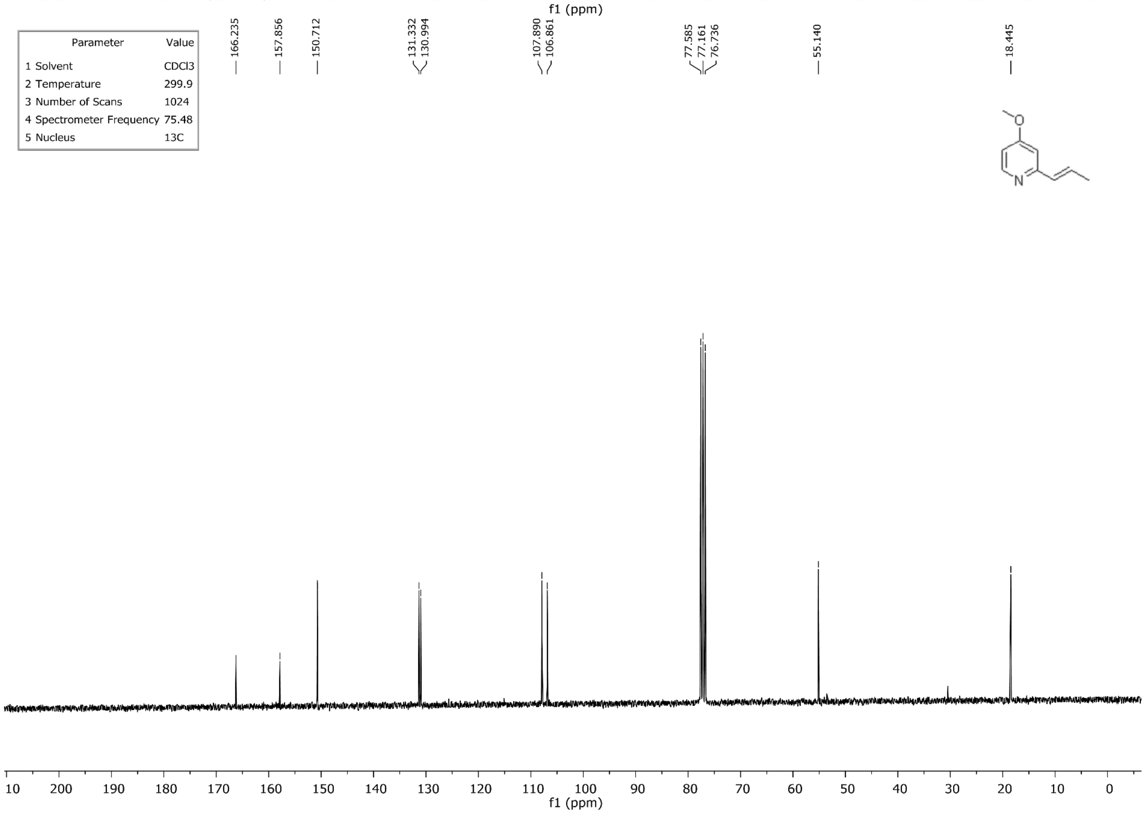
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.1
3 Number of Scans	8
4 Spectrometer Frequency	300.13
5 Nucleus	1H



Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.9
3 Number of Scans	1024
4 Spectrometer Frequency	75.48
5 Nucleus	13C

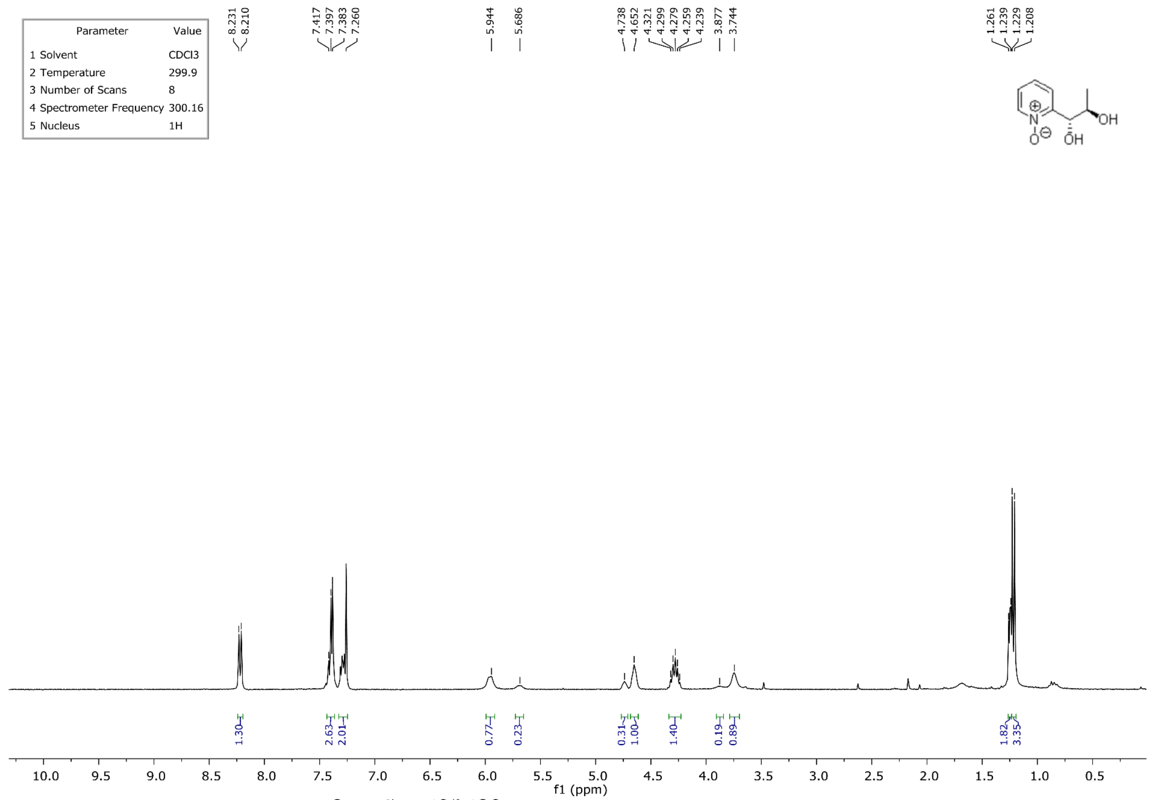
(*E*)-4-methoxy-2-(prop-1-en-1-yl)pyridine 5b



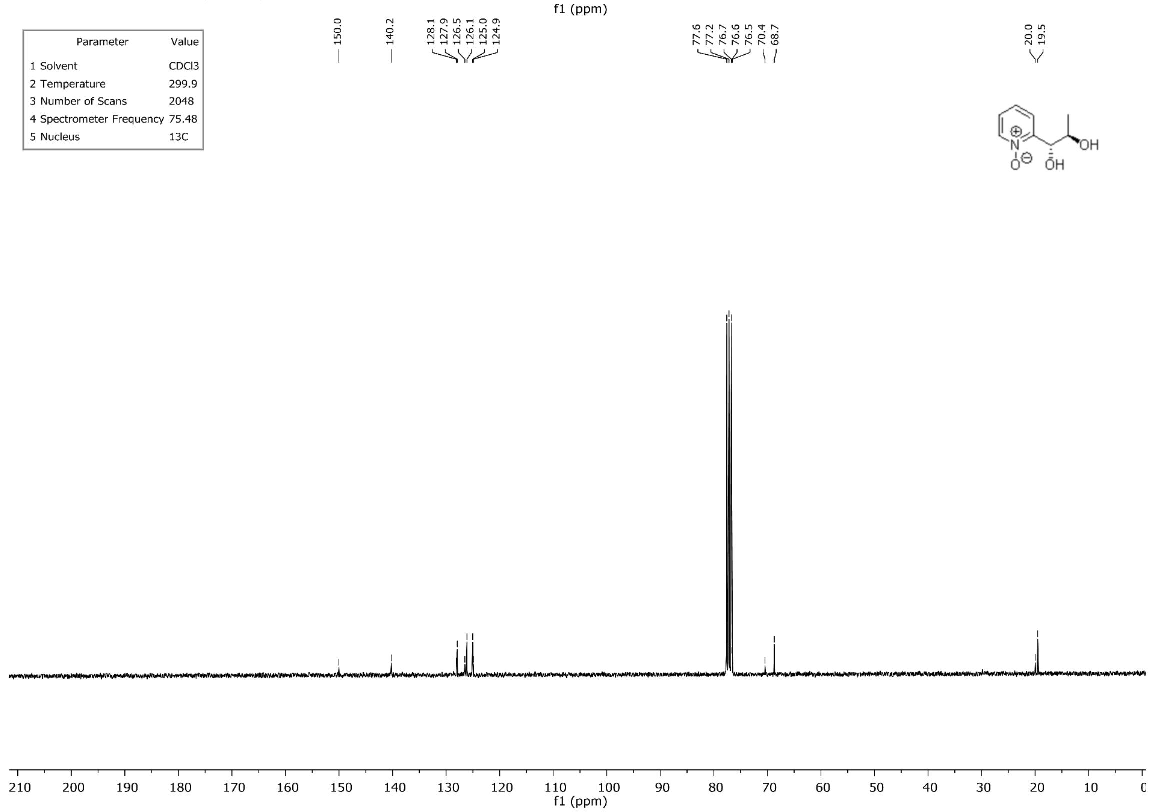


2-((1*R,2*R**)-1,2-dihydroxypropyl)pyridine 1-oxide 6a**

Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.9
3 Number of Scans	8
4 Spectrometer Frequency	300.16
5 Nucleus	1H

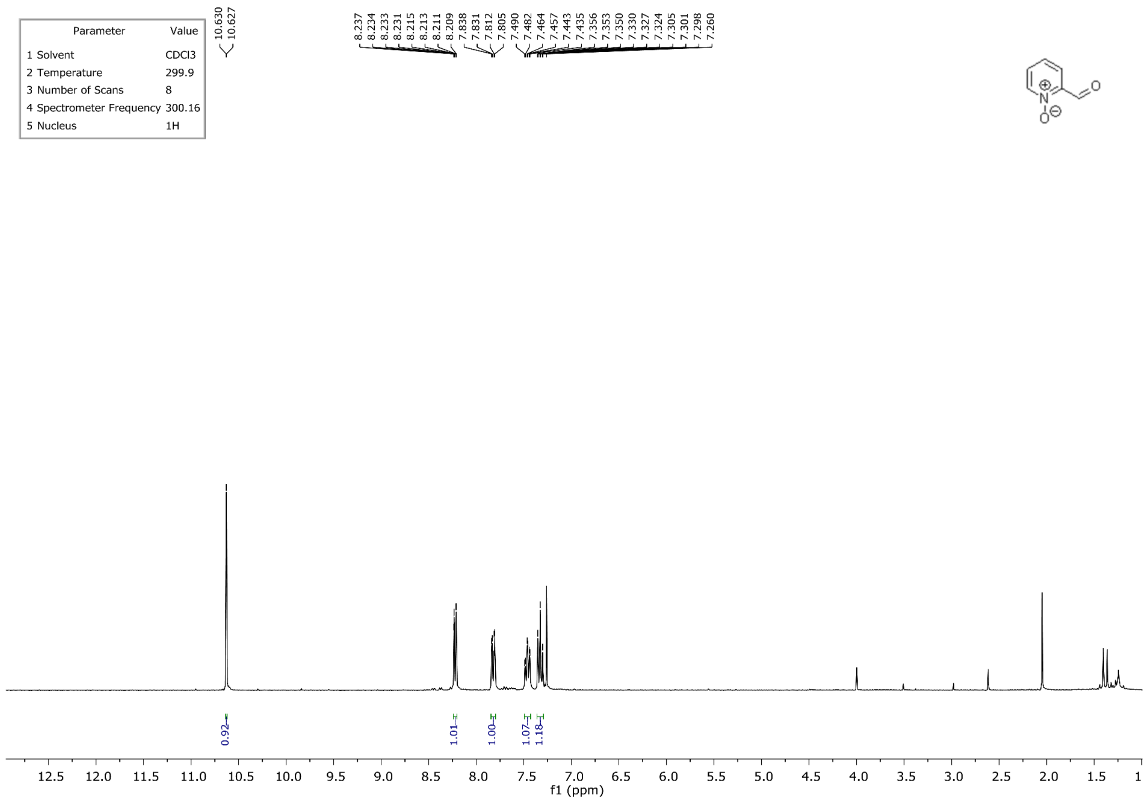


Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.9
3 Number of Scans	2048
4 Spectrometer Frequency	75.48
5 Nucleus	13C



2-formylpyridine *N*-oxide 7a

Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.9
3 Number of Scans	8
4 Spectrometer Frequency	300.16
5 Nucleus	1H



Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.9
3 Number of Scans	1024
4 Spectrometer Frequency	75.48
5 Nucleus	13C