Supporting Information

Diastereoselective Synthesis of β-Lactams by Ligand-Controlled Stereodivergent Intramolecular Tsuji–Trost Allylation

Matteo Faltracco,[†] Verena Sukowski,[†] Max van Druenen,[†] Trevor A. Hamlin,[*,§] F. Matthias Bickelhaupt,[§,‡] and Eelco Ruijter[*,†]

[†] Department of Chemistry & Pharmaceutical Sciences, Amsterdam Institute of Molecular and Life Sciences (AIMMS), Vrije Universiteit Amsterdam, De Boelelaan 1108, 1081 HZ Amsterdam, The Netherlands.

[§] Department of Theoretical Chemistry, Amsterdam Institute of Molecular and Life Sciences (AIMMS), Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands.

[‡] Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands.

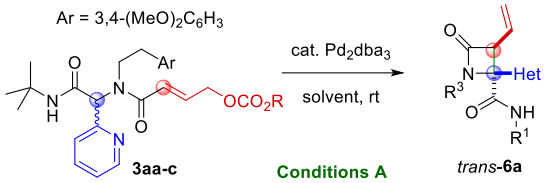
t.a.hamlin@vu.nl; e.ruijter@vu.nl

Table of Contents

Additional optimization studies

Under the initial conditions for the cyclization of **3aa** [Pd_2dba_3, dppe (**L1**), CH_2Cl_2, rt, 24 h, Table S1, entry 1], we observed the formation of β-lactam **6a** in 75% yield as a 31:69 *trans*/*cis* diastereomeric mixture. We then proceeded to screen a wide range of monodentate (Table S1) and bidentate (Table S2) phosphine ligands to increase the diastereoselectivity of the reaction. We soon found that the use of monodentate phosphine ligands generally affords predominantly the *trans* isomer, while the *cis* isomer was the major product when bidentate phosphines were used. While triethyl phosphite (**L2**) and triphenylphosphine (**L3**) proved to be unsuitable ligands for β-lactam formation (entries 2, 3), while the use of Buchwald-type biarylphosphines **L4-9** did result in the formation of **6a**, albeit with varying yields and diastereselectivities (entries 4-9). SPhos (**L9**) proved to be the optimal ligand, affording **6a** in near-quantitative yield as a 91:9 mixture of diastereomers (entry 9). The stereoselectivity was lower in more polar solvents (DMF, MeCN; entries 10,11), but even higher in toluene and 1,4-dioxane (entries 12, 12). Having selected the latter as the optimal solvent, we studied the influence of the carbonate leaving group. We found that the ethyl carbonate is superior to the corresponding methyl and *tert*-butyl carbonates (**3ab** and **3ac**, respectively; entries 14, 15).

Table S1. Optimization of Tsuji-Trost conditions for *trans* selectivity[a]

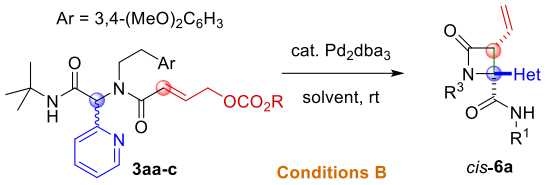


Entry	R^1	Ligand	Solvent	Conc.	Yield[b]	*trans*/*cis*[C]
1	Et	**L1**	CH_2Cl_2	0.2 M	75%	31:69
2	Et	**L2**	CH_2Cl_2	0.2 M	n.d.	-
3	Et	**L3**	CH_2Cl_2	0.2 M	n.d.	-
4	Et	**L4**	CH_2Cl_2	0.2 M	79%	89:11
5	Et	**L5**	CH_2Cl_2	0.2 M	15%	93:7
6	Et	**L6**	CH_2Cl_2	0.2 M	41%	78:22
7	Et	**L7**	CH_2Cl_2	0.2 M	14%	31:69
8	Et	**L8**	CH_2Cl_2	0.2 M	80%	90:10
9	Et	**L9**	CH_2Cl_2	0.2 M	99%	91:9
10	Et	**L9**	DMF	0.2 M	91%	62:38
11	Et	**L9**	MeCN	0.2 M	92%	69:31
12	Et	**L9**	toluene	0.2 M	91%	>95:5
13	**Et**	**L9**	**1,4-dioxane**	**0.2 M**	**92%**	**>95:5**
14	Me	**L9**	1,4-dioxane	0.2 M	87%	>95:5
15	*t*Bu	**L9**	1,4-dioxane	0.2 M	85%	94:6
16[d]	Et	L9	**1,4-dioxane**	0.2 M	87%	94:6

[a] All reactions were performed at rt with 0.2 mmol of **3a-c**, 0.01 mmol of $Pd_2(dba)_3$, 0.04 mmol of monodentate ligand (**L2-L9**) or 0.02 mmol of bidentate ligand (**L10-L19**) until full consumption of **3** (1 – 24 h). [b] ^{1}H NMR yield with 2,5-dimethylfuran as the internal standard. [c] Determined by ^{1}H NMR analysis of the crude product. [d] 0.02 mmol of **L9** was used.

The optimization of the *cis*-selective cyclization (Table S2) proved more challenging. First, we evaluated a range of relatively rigid bidentate phosphine ligands (**L10-15**), but all proved inferior to dppe (**L1**) in terms of yield and/or selectivity (entries 2-7). We thus evaluated a series of 1,ω-bis(diphenylphosphino)alkanes (**L16-19**, entries 8-11) and noted a marked dependence of the selectivity on the bite angle, with dppp providing the optimal selectivity(11:89, entry 11), albeit in lower yield than dppe (**L1**). In order to further improve conversion and selectivity, we screened various solvents. Interestingly, in this case, solvents such as toluene and 1,4-dioxane gave lower yield and selectivity (entries, 12, 13), while the selectivity was maintained in polar solvents (entries 14, 15). Performing the reaction in 1,2-dichloroethane gave **6a** with 9:91 *dr*, albeit still in only modest yield (entry 16). Next, we performed the reaction at different concentrations (entries 17-19) and found that the yield increases with decreasing concentration, down to 0.066 M (entry 19). Further lowering the concentration to 0.05 M led to lower yield and selectivity. Finally, we investigated the role of the carbonate again. While the *t*-Bu carbonate **3ac** gave similar results (entry 22), the methyl carbonate **3ab** gave lower yield and selectivity (entry 21).

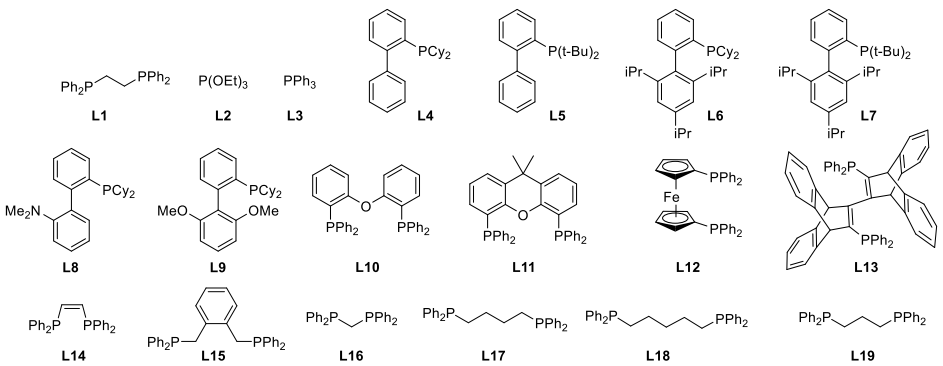
Table S2. Optimisation of Tsuji-Trost conditions for *cis* selectivity[a]



Entry	R^1	Ligand	Solvent	Conc.	Yield[b]	*trans/cis*[C]
1	Et	**L1**	CH_2Cl_2	0.2 M	75%	31:69
2	Et	**L10**	CH_2Cl_2	0.2 M	24%	50:50
3	Et	**L11**	CH_2Cl_2	0.2 M	11%	36:64
4	Et	**L12**	CH_2Cl_2	0.2 M	27%	44:56
5	Et	**L13**	CH_2Cl_2	0.2 M	22%	23:77
6	Et	**L14**	CH_2Cl_2	0.2 M	48%	37:63
7	Et	**L15**	CH_2Cl_2	0.2 M	50%	36:64
8	Et	**L16**	CH_2Cl_2	0.2 M	53%	57:43
9	Et	**L17**	CH_2Cl_2	0.2 M	62%	19:81
10	Et	**L18**	CH_2Cl_2	0.2 M	23%	53:43
11	Et	**L19**	DCM	0.2 M	45%	11:89
12	Et	**L19**	toluene	0.2 M	17%	24:76
13	Et	**L19**	1,4-dioxane	0.2 M	n.d.	-
14	Et	**L19**	DMF	0.2 M	30%	11:89
15	Et	**L19**	MeCN	0.2 M	47%	11:89
16	Et	**L19**	1,2-dichloroethane	0.2 M	50%	9:91
17	Et	**L19**	1,2-dichloroethane	0.4 M	42%	10:90
18	Et	**L19**	1,2-dichloroethane	0.1 M	55%	9:91
19	**Et**	**L19**	**1,2-dichloroethane**	**0.066 M**	**70%**	**9:91**
20	Et	**L19**	1,2-dichloroethane	0.05 M	61%	10:90
21	Me	**L19**	1,2-dichloroethane	0.066 M	73%	27:73
22	*t*Bu	**L19**	1,2-dichloroethane	0.066 M	70%	10:90

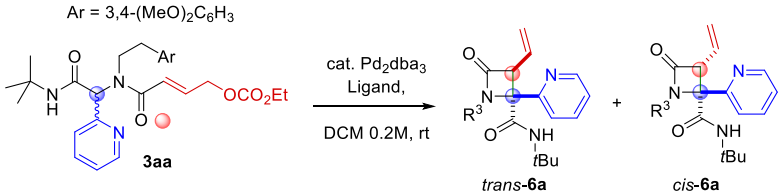
[a] All reaction were performed at rt with 0.2 mmol of **3a-c**, 0.01 mmol of $Pd_2(dba)_3$, 0.04 mmol of monodentate ligand (**L2-L9**) or 0.02 mmol of bidentate ligand (**L10-L19**) for 24 h. [b] ^{1}H NMR yield with 2,5-dimethylfuran as the internal standard. [c] Determined by ^{1}H NMR analysis of the crude product.

Figure S1. Ligands used for optimization of *cis/trans* selectivity.



Encouraged by the possibilities to control the relative stereochemistry, we tested a variety of chiral mono- and bidentate ligands (Figure S2) in an attempt to also control the absolute stereochemistry of the product (Table S3). The use of *t*BuPHOX (**L20**, entry 1) as a ligand afforded **6a** in excellent yield with reasonable diastereoselectivity for the *trans* isomer, but with low enantioselectivity for both the *trans* and *cis* isomer. Ligand **L21a** proved more efficient in controlling the absolute stereochemistry (72% ee for the *trans* isomer; entry 2), albeit at the expense of the diastereoselectivity. The isopropyl-substituted ligand **L21b** showed nearly identical results, although the yield was lower (entry 3). Reasoning that efficient transfer of chirality might require a chiral bidentate Pd complex, we tested several chiral bisphosphine ligands (**L22-31**, entries 4-15). Indeed, these ligands appear to follow the bidentate scenario, affording *cis*-**6a** as the main product. However, a range of structurally diverse chiral bisphosphine ligands (**L22-28**) only gave **6a** in low yield and with mostly low diastereo- and enantioselectivity (entries 4-10). (*R*)-BINAP (**L29a**) gave **6a** with good selectivity for the *cis* isomer (albeit in low yield) in encouraging *ee* (56%, entry 11). Increasing the steric bulk (**L29b**) did not improve either the diastereoselectivity or the enantioselectivity (entry 12). (*S*)-C_3-TunePhos (**L30**) gave very similar results, not surprisingly giving the opposite enantioselectivity. We then moved to MeOBIPHEP-type ligands (**L31a-c**), but they gave only traces of **6a**, moreover with very low selectivity (entries 13-15). We also tested three chiral phosphoramidites (**L32-34**), but no product formation was observed with these ligands (entries 16-19). Finally, we tested **L32-34** with iridium catalysis [5% $[Ir(cod)Cl]_2$, 10% **L**, 1.5 eq. Et_3N, CH_2Cl_2, 50 °C, 30 min.] but no conversion took place.

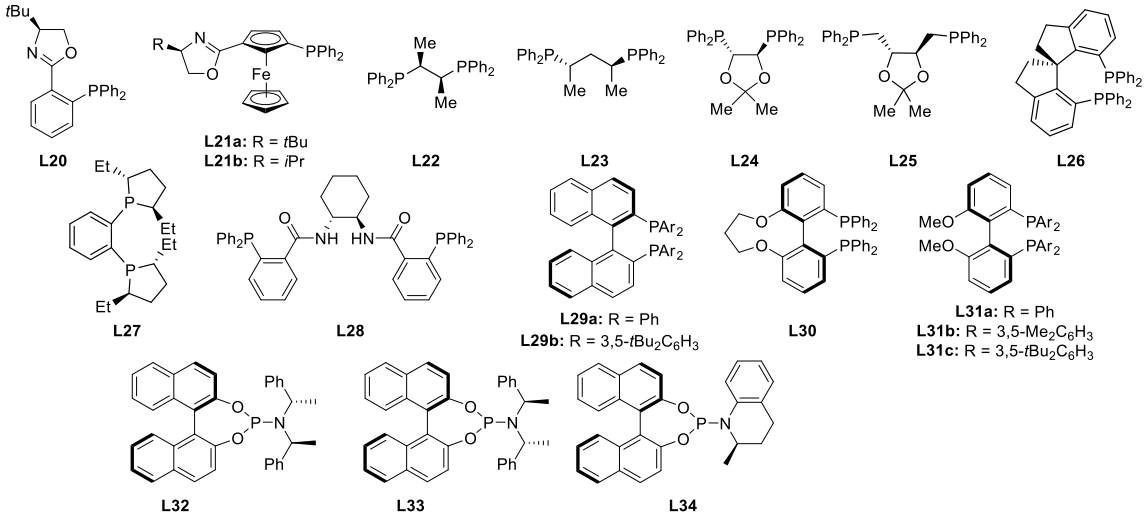
Table S3. Chiral ligand screening[a]



Entry	Catalyst	Ligand	Yield[b]	*trans*/*cis*[c]	*ee trans*[d]	*ee cis*[d]
1	$Pd_2(dba)_3$	**L20**	95%	81:19	24%	33%
2	$Pd_2(dba)_3$	**L21a**	87%	60:40	**72%**	−16%
3	$Pd_2(dba)_3$	**L21b**	72%	60:40	70%	−15%
4	$Pd_2(dba)_3$	**L22**	61%	25:75	n.d.	22%
5	$Pd_2(dba)_3$	**L23**	42%	10:90	n.d.	-20%
6	$Pd_2(dba)_3$	**L24**	18%	33:67	n.d.	12%
7	$Pd_2(dba)_3$	**L25**	22%	45:55	n.d.	−4%
8	$Pd_2(dba)_3$	**L26**	5%	27:73	n.d.	−5%
9	$Pd_2(dba)_3$	**L27**	10%	40:60	n.d.	20%
10	$Pd_2(dba)_3$	**L28**	18%	33:67	n.d.	−33%
11	$Pd_2(dba)_3$	**L29a**	22%	14:86	n.d.	56%
11	$Pd_2(dba)_3$	**L29b**	14%	13:87	n.d.	54%
12	$Pd_2(dba)_3$	**L30**	19%	11:89	n.d.	**−56%**
13	$Pd_2(dba)_3$	**L31a**	8%	19:81	n.d.	−12%
14	$Pd_2(dba)_3$	**L31b**	7%	14:86	n.d.	−10%
15	$Pd_2(dba)_3$	**L31c**	7%	14:86	n.d.	−11%
16	$Pd_2(dba)_3$	**L32**	0%	-	-	-
17	$Pd_2(dba)_3$	**L33**	0%	-	-	-
18	$Pd_2(dba)_3$	**L34**	0%	-	-	-

[a] All reaction were performed with 0.2 mmol of **3a**, 0.01 mmol of $Pd_2(dba)_3$, 0.04 mmol of monodentate ligand (**L20-L21; L32-34**) or 0.02 mmol of bidentate ligand (**L22-L31**). [b] Isolated yield. [c] Determined by ^1H NMR analysis of the crude product. [d] Determined by chiral SFC. *trans*-**6a** (method 1) t_{ret} = 6.631, 6.873 min; *cis*-**6a** (method 2) t_{ret} = 5.822, 6.047 min. Positive and negative signs refer to the earlier or later eluting enantiomer, respectively, being the major enantiomer.

Figure S2. Ligands used for enantioselectivity screening.



In light of our mechanistic considerations, it is perhaps not surprising **L20** gives only low *ee*: the observed *dr* suggests it acts as a monodentate ligand, and the oxazoline is likely displaced by the pyridine of the substrate. In fact, our DFT calculations suggests Pd already coordinates to the pyridine prior to generation of the π-allyl complex, which is the enantiodetermining step. Ligand **L21a** proved more efficient in controlling the absolute stereochemistry (72% *ee* for the *trans* isomer), albeit at the expense of the diastereoselectivity. Unfortunately, our attempts to further improve the *ee* remained fruitless. All chiral bisphosphine ligands appear to follow the bidentate scenario, affording *cis*-**6a** as the main product. However, the conversion was very slow, resulting in modest yields even after one week of reaction time. (*R*)-BINAP (**L29a**) gave the highest *ee* for the *cis* isomer, but also in this case any modifications made to the reaction conditions or the ligand structure proved counterproductive.

X-Ray crystallographic Analysis of *cis*-6s

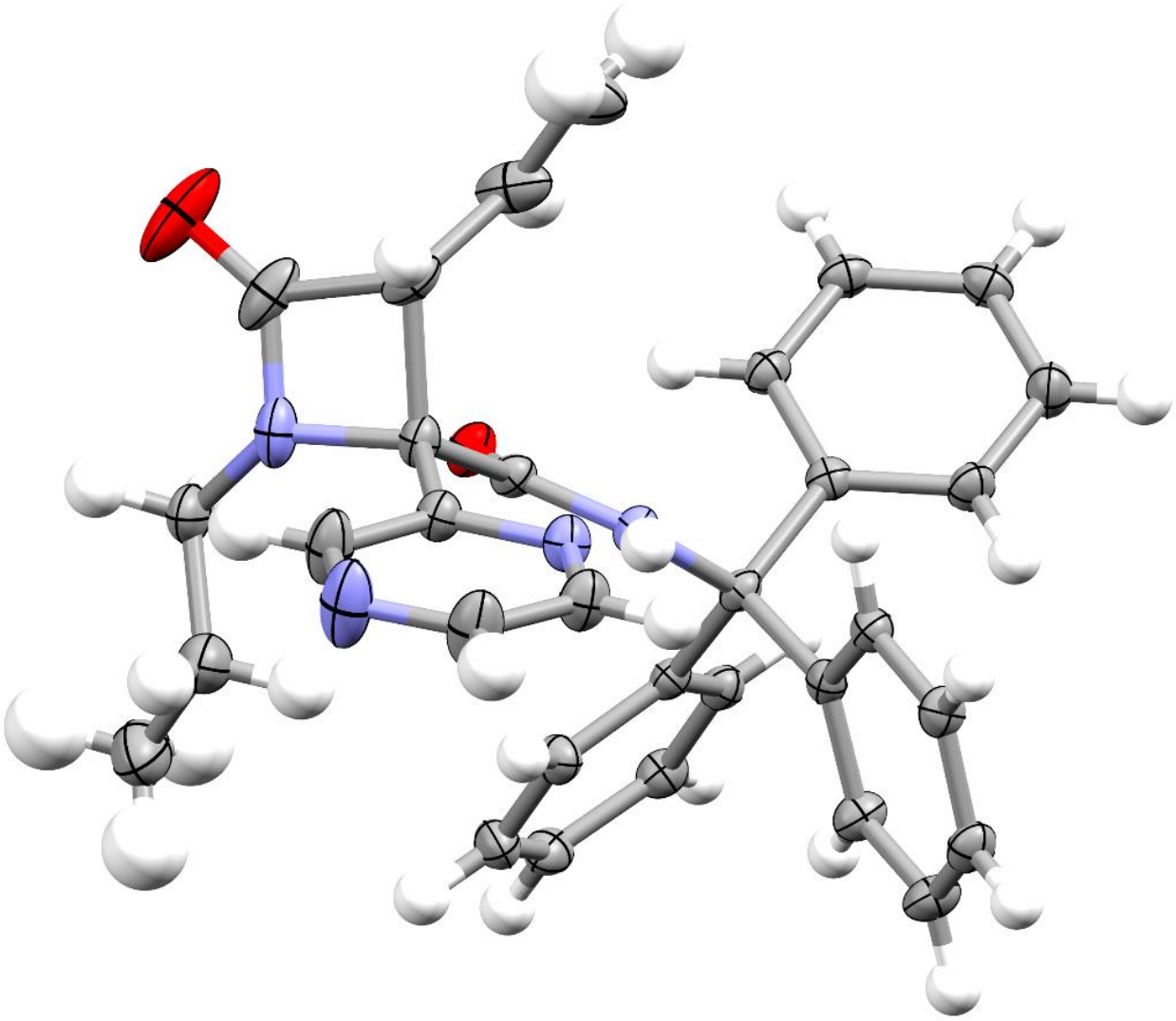


Fig. S3. Thermal displacement ellipsoid plot of *cis*-**6s** with ellipsoids shown at the 50% probability level. Suitable crystals were obtained from cyclohexane by slow evaporation. Hydrogens diameters at 1.2 times the isotropic equivalent displacement parameter of the atom on which they are refined as riding, except for H14 (on N14) which was refined freely, and the isotropic displacement parameter is shown on the same scale. The minor conformation of the disordered propyl side chain has been omitted for clarity.

Crystal data

$C_{32}H_{30}N_4O_2$	
M_r = 502.60	D_x = 1.260 Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, λ = 1.54184 Å
a = 9.2121 (1) Å	Cell parameters from 9625 reflections
b = 38.9320 (5) Å	θ = 4.5–75.0°
c = 8.1281 (1) Å	μ = 0.63 mm^{-1}
β = 114.645 (2)°	T = 100 K
V = 2649.57 (7) Å^3	Block, colourless

***Z* = 4**	0.4 × 0.3 × 0.3 mm
***F*(000) = 1064**	

Data collection

SuperNova, Dual, Cu at home/near, Atlas diffractometer	5384 independent reflections
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source	4679 reflections with $I > 2\sigma(I)$
Mirror monochromator	R_{int} = 0.041
Detector resolution: 10.4839 pixels mm^{-1}	θ_{max} = 75.3°, θ_{min} = 4.5°
	h = −11 10
Absorption correction: multi-scan CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	k = −48 45
T_{min} = 0.128, T_{max} = 1.000	l = −10 10
19985 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.045	H atoms treated by a mixture of independent (H14) and constrained refinement
$wR(F^2)$ = 0.114	$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 1.2904P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.01	$(\Delta/\sigma)_{max} < 0.001$
5384 reflections	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
372 parameters	$\Delta\rho_{min}$ = −0.40 e Å^{-3}
0 restraints	Extinction correction: SHELXL-2016/4 (Sheldrick 2016), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00134 (17)

Consideration of alternative reaction intermediates

To further support our proposed mechanism, additional DFT calculations were performed to determine relative energies of other organopalladium intermediates that could potentially form, as well as potential pathways for their interconversion under both conditions A (Fig. S4) and Conditions B (Fig. S5). Activation of the *E*-configured substrate **3zd** by the palladium catalyst leads to the stereospecific formation of the proposed *syn*-π-allylpalladium intermediate, under conditions A with intramolecular coordination to the pyridine nitrogen (intermediate **A**, Fig. S4). Somewhat to our surprise, its *anti*-isomer **B** was found to be slightly lower in energy ($\Delta\Delta G^{\ddagger}$ = −1.9 kcal mol^{-1}), however its potential involvement also depends on the availability of feasible pathways for its formation. We disregarded the involvement of σ-allyl intermediate **C**, as its formation involves unfavorable dissociation of the pyridine ligand. In addition, it is highly unlikely this species is directly converted to the product. Moreover, its conversion to a π-allylpalladium intermediate occurs stereospecifically, thus leading exclusively to **A**. We also considered the branched, deconjugated σ-allylpalladium intermediate **D**, which would represent a viable intermediate for the interconversion of **A** and **B**, however no stationary point could be location despite exhaustive searching of the potential energy surface. In addition, we considered the O-coordinated palladium enolates **E** (both *E* and *Z* isomer) and found that they undergo rapid ring contraction to give the five-membered palladacycles **F** that are >10 kcal mol^{-1} higher in energy than **A**. Moreover, intermediates **F** are geometrically incapable of forming the observed β-lactam product. Thus, although **B** is lower in energy than **A**, we could not identify a feasible pathway for its formation.

From these calculations, we can confidently conclude that only *syn*-π-allylpalladium intermediate **A** is involved in the reaction. As shown by the proposed mechanism, this hypothesis is furthermore in very good agreement with experimental observations.

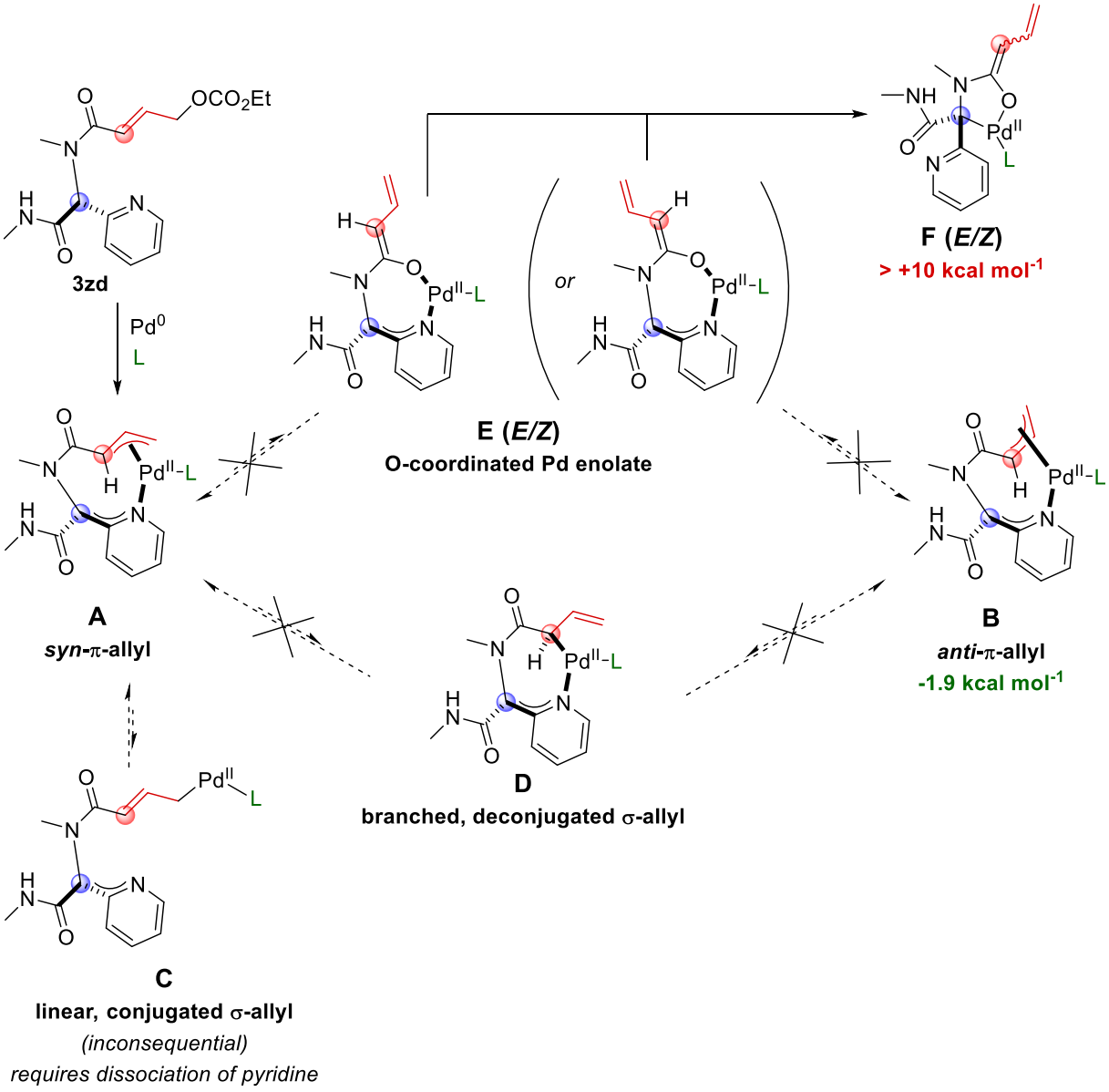


Fig. S4. Potentially involved organopalladium intermediates under conditions A

Under conditions B, similar considerations were made. However, in this case the *anti*-π-allylpalladium intermediate **B'** is disfavored with respect to **A'** ($\Delta\Delta G^{\ddagger}$ = +1.9 kcal mol^{-1}). Still, given the possibility of the *syn*- and *anti*-isomers displaying significantly different reactivities, we wanted to rule out its potential involvement. Again, intermediate **C'** was disregarded based on aforementioned considerations. Also, under conditions B, we were unable to locate the branched, deconjugated σ-allylpalladium intermediate **D'**. In this case, the O-coordinated palladium enolates **E`** are unstable and spontaneously relax to form **A'** exclusively. This leads us to the conclusion that the *anti*-π-allylpalladium intermediate **B'** is not involved in reactions under conditions B either, and that the observed diastereoselectivity (or lack thereof) results primarily from the enolate geometry, which may or may not be stabilized by subtle substrate-ligand interactions.

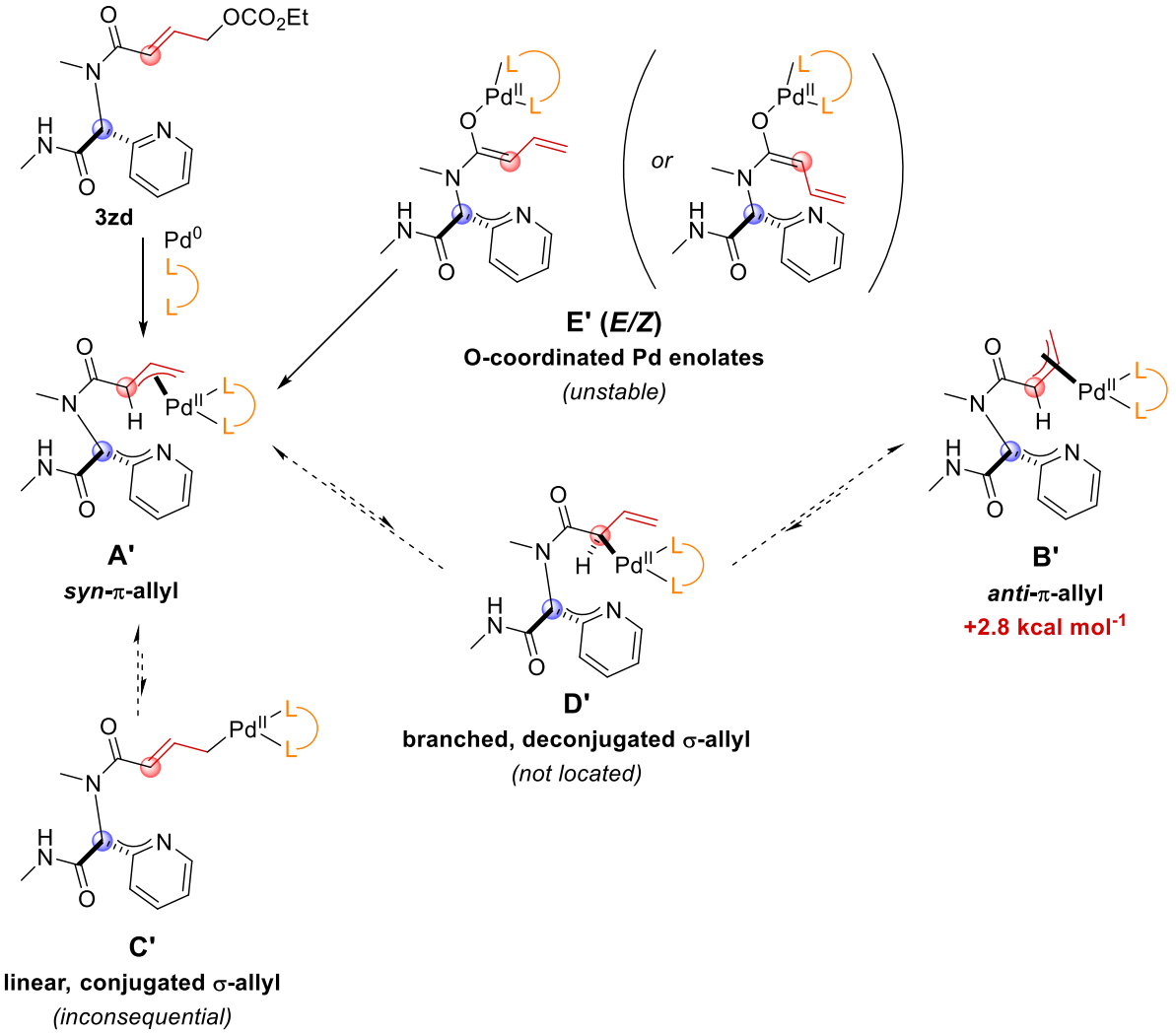


Fig. S5. Potentially involved organopalladium intermediates under conditions B

Computational section

Computational Details

All optimizations of stationary points and vibrational analyses were carried out at BLYP[1]/TZ2P[2] using ADF.[3] The zeroth-order regular approximation (ZORA)[4] accounted for scalar relativistic effects. Solvation effects of either dioxane or dichloroethane as in conditions A and B, respectively, were included in all computations using the COnductor-like Screening MOdel (COSMO).[5] This level is referred to as COSMO(dioxane/dichloroethane)-ZORA-BLYP/TZ2P. The ZORA-BLYP/TZ2P approach has been extensively tested against ab initio reference benchmarks from hierarchical series up till CCSD(T).[6] Energy minima and transition states were verified through vibrational analysis. All minima were found to have zero imaginary frequencies, while all transition states had a single imaginary frequency. Multiple conformations were screened for flexible systems and the lowest energy structure was used for the potential energy surface and subsequent analysis. Optimized structures were illustrated using CYLview.[7]

Quantitative analyses of the activation barriers associated with the studied Pd catalyzed C–C bond lactam formation reactions were obtained by means of the activation strain model (ASM), which involves decomposing the electronic energy of the transition structure $\Delta E^{\ddagger}$ into the strain $\Delta E_{strain}^{\ddagger}$ associated with the structural deformation of the reactants from their equilibrium geometry and the interaction $\Delta E_{int}^{\ddagger}$ between the deformed reactants (Eq. 1).[8] The $\Delta E_{strain}^{\ddagger}$ is determined by the rigidity of the reactants and by the extent to which they must deform in order to achieve the geometry of the transition state. The $\Delta E_{int}^{\ddagger}$ is usually stabilizing and is related to the electronic structure of the reactants and how they are mutually oriented over the course of the reaction. This analysis was performed using the PyFrag 2019 program.[9]

$$\Delta E^{\ddagger} = \Delta E_{strain}^{\ddagger} + \Delta E_{int}^{\ddagger} \quad (1)$$

For the thermochemistry calculations of the stepwise coordination reactions we used a standard approach. Geometries were optimized and the vibrational frequencies were obtained through numerical differentiation of the analytical gradient. Enthalpies at 298.15 K and 1 atm ($\Delta H°$) were calculated from the electronic bond energies and vibrational frequencies by using a standard thermochemistry relation for an ideal gas [Eq. 2].

$$\Delta H° = \Delta E_{trans,298} + \Delta E_{rot,298} + \Delta E_{vib,0} + \Delta(\Delta E_{vib,298}) + \Delta(pV) \quad (2)$$

$\Delta E_{trans,298}$, $\Delta E_{rot,298}$, and $\Delta E_{vib,0}$ are the differences between the reactants in the translational, rotational, and zero-point vibrational energy, respectively, whereas $\Delta E_{vib,298}$ takes the vibrational energy change upon going from 0 to 298.15 K into account. The vibrational energy corrections and the entropic term $T\Delta S°$ are based on frequency calculations. Thermal corrections for the electronic term are neglected and $\Delta(pV) \approx \Delta(nRT)$ was used. The change of the Gibbs free energy (ΔG) in both the gas and condensed phase was then calculated for 298.15 K and 1 atm ($\Delta G°$) [Eq. 3].

$$\Delta G° = \Delta H - T\Delta S° \quad (3)$$

Computed Activation Barrier at Multiple Levels of Theory

Table S4. Relative energies (in kcal mol^{-1}) of the transition structures for the Pd-catalyzed reactions computed at multiple levels of theory.[a]

Level of theory	monodentate (conditions **A**)		bidentate (conditions **B**)	
	trans	*cis*	*trans*	*cis*
COSMO-ZORA-BLYP/TZ2P	–4.6 (24.0)	0.3 (28.5)	–4.8 (8.4)	–8.5 (4.2)
COSMO-ZORA-BLYP-D3(BJ)/TZ2P	–2.4 (26.9)	1.0 (30.1)	–23.5 (–13.6)	–27.7 (–15.9)
COSMO-ZORA-M06// COSMO-ZORA-BLYP-D3(BJ)/TZ2P	3.0 (32.3)	11.7 (40.8)	–6.6 (–3.3)	–15.9 (–4.1)

[a] Gibbs free activation energies and electronic energies (in parentheses).

General ADF Input Script for a Geometry Optimization in Dioxane

```
XC
GGA BLYP
END

RELATIVISTIC SCALAR ZORA

BeckeGrid
  Quality Good
END

ZLMFIT
  Quality Good
END
```

```
BASIS
  TYPE  TZ2P
  Core Large
END

SCF
  ITERATIONS 99
  CONVERGE 0.000001
  MIXING 0.20
END

Geometry
  Optim Delocal
  ITERATIONS 999
  CONVERGE 0.0001
End

AnalyticalFreq
End
ScanFreq -9999 0 Num=6 Disrad=0.0035

SYMMETRY  AUTO
CHARGE    0

ATOMS
END

SOLVATION
  Solv name=dioxane
  Radii
!   ------------------------------------------------------------
!   radii taken from Allinger et al. J.Mol.Struct.(THEOCHEM) 312 (1994) 69
!   actual values used are MM3 radii divided by 1.2 and in Angstrom
!
!   see also: J.Org.Chem. 70 (2005) 3542, [supporting information p. 49]
!   ------------------------------------------------------------
    H  = 1.350
    C  = 1.700
    N  = 1.608
    O  = 1.517
    P  = 1.850
    Pd = 1.975
SubEnd
END
```

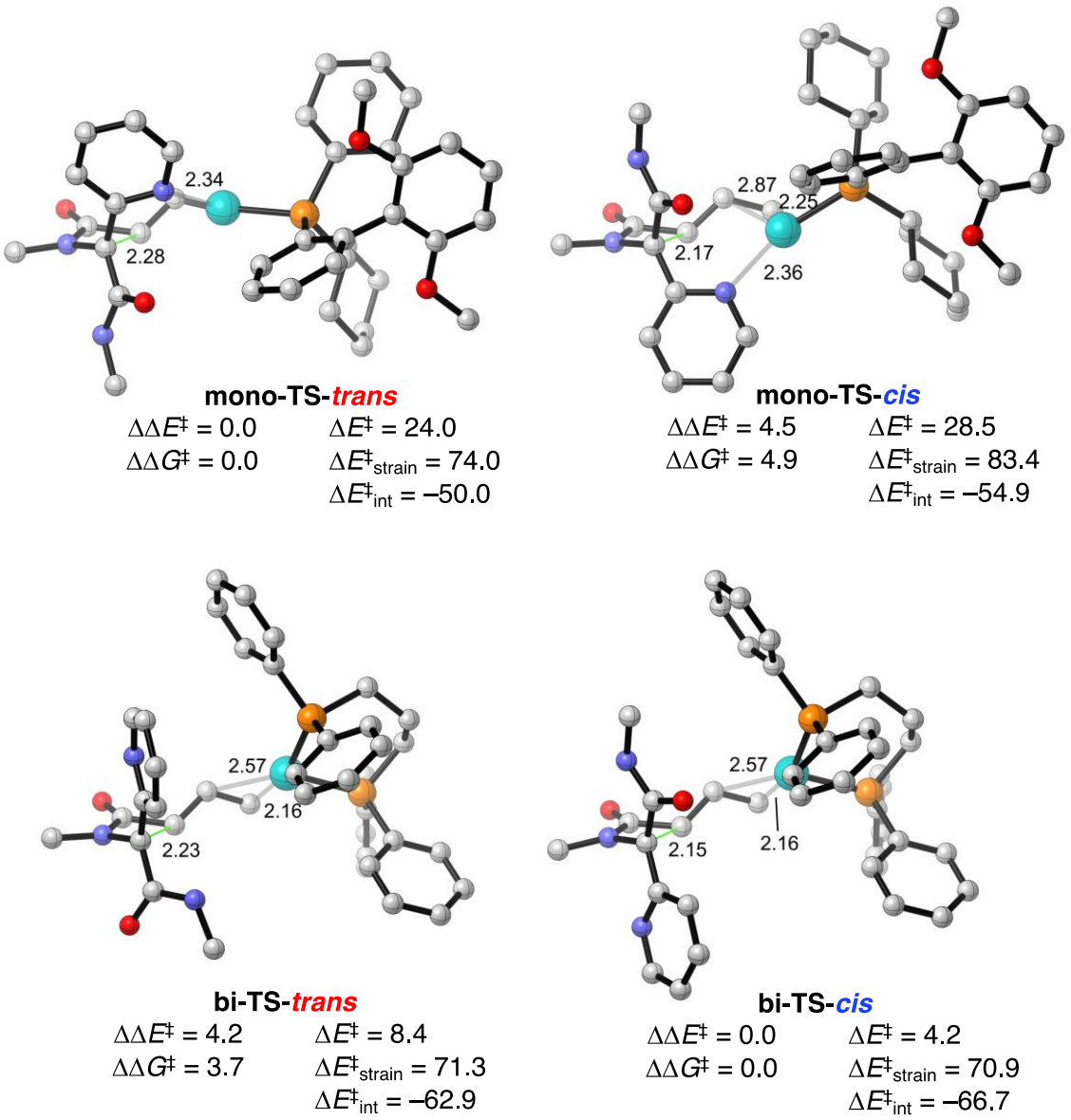


Figure S6. Results of the activation strain analysis performed on the optimized transition structures for the (top) mono- and (bottom) bidentate Pd catalyzed reactions.

Table S5. Cartesian coordinates (Å), energies (kcal mol^{-1}), and imaginary vibrational frequencies (cm^{-1}) of the optimized structures shown in Figure 3 (left panel) computed at COSMO(dioxane)-ZORA-BLYP/TZ2P.

R
E = −6135.01
G = −5950.83
N_{imag} = 0

N	0.791060	-0.253392	0.082922
C	1.395034	0.552361	-0.999923
H	0.747220	0.499090	-1.877864
H	1.466149	1.601514	-0.705572
H	2.389197	0.183798	-1.282693
C	-0.077413	-1.395215	-0.296264
H	-0.125962	-2.022467	0.601865
C	1.136586	-0.124116	1.422769
O	0.577843	-0.798193	2.302675
C	2.203588	0.871995	1.761117
H	2.810180	1.295400	0.964768
C	2.445152	1.216772	3.033687
H	1.832100	0.791021	3.827870
C	3.559902	2.122117	3.449664
H	4.307372	1.577555	4.040872
H	4.061336	2.592492	2.597250
O	2.980213	3.174476	4.303277
C	3.887822	3.964765	4.934999
O	5.100333	3.875267	4.846356
O	3.196812	4.861613	5.670880
C	4.016748	5.819733	6.439389
H	4.661070	5.248918	7.116141
H	4.648292	6.369504	5.733788
C	3.061422	6.733111	7.189295
H	3.642929	7.457280	7.772493
H	2.417547	7.286528	6.496590
H	2.429632	6.163089	7.879608
C	0.579726	-2.241312	-1.398564
C	0.098546	-2.320648	-2.712802
C	2.354331	-3.635593	-1.903611
C	0.794694	-3.098214	-3.642608
H	-0.811580	-1.804768	-3.000581
C	1.946950	-3.772721	-3.234788
H	3.246180	-4.148112	-1.541790
H	0.437333	-3.176032	-4.667147
H	2.516425	-4.392208	-3.923470
N	1.694583	-2.890133	-1.000421
C	-1.559996	-1.018936	-0.576731
O	-2.354700	-1.876684	-0.983496
N	-1.921995	0.261346	-0.308620
H	-1.237164	0.861697	0.135867
C	-3.315024	0.712017	-0.379578
H	-3.906831	0.317873	0.456737
H	-3.331424	1.804202	-0.349339
H	-3.766558	0.366613	-1.313890

Pd^0L_2 (L = Sphos)
E = −16726.4
G = −16106.7
N_{imag} = 0

H	-1.433702	-6.525275	4.971384
C	-4.005824	-2.753100	0.360203
C	-4.628815	-3.514043	1.351193
C	-4.144984	-3.452856	2.658479
C	-3.053478	-2.637786	3.023434
C	-2.423994	-1.845899	2.020061
C	-2.922423	-1.941374	0.701742
H	-5.475601	-4.155408	1.113141
H	-4.617877	-4.055903	3.431539
O	-1.449393	-4.699982	3.925762
P	-1.003039	-0.592864	2.143388
H	-2.424231	-1.352360	-0.068635
C	-2.655949	-2.743781	4.475135
C	-3.198880	-1.889903	5.462051
C	-2.890658	-2.058393	6.824911
C	-2.070509	-3.118839	7.212394
C	-1.567311	-4.022264	6.274615

C	-1.873506	-3.839571	4.914821
O	-4.058356	-0.915566	5.001850
H	-3.291696	-1.385356	7.574459
H	-1.829874	-3.251376	8.265354
H	-0.950717	-4.852350	6.601115
C	-4.780162	-0.130228	5.973190
H	-5.356585	-0.773285	6.650594
H	-5.460492	0.495793	5.392947
H	-4.104070	0.507333	6.557885
C	-0.792490	-5.923485	4.314224
H	0.165105	-5.726716	4.813323
H	-0.611011	-6.462408	3.381923
H	-3.307066	4.534500	3.672510
H	3.867687	-2.898159	4.324654
C	-1.776838	0.855472	3.127284
C	-3.790396	2.465129	3.180032
C	-3.158776	1.218756	2.520169
C	-0.850542	2.100224	3.083913
C	-1.485944	3.334924	3.761174
C	-2.851667	3.685406	3.143383
H	-1.918134	0.533667	4.168842
H	-4.036221	2.236641	4.227977
H	-4.740987	2.697845	2.678925
H	-3.027281	1.410711	1.443988
H	-3.844299	0.371479	2.613230
H	-0.633535	2.329666	2.029616
H	0.113399	1.890127	3.555549
H	-0.797575	4.187994	3.678149
H	-1.613608	3.138451	4.838062
H	-2.706162	4.003755	2.099259
C	0.276776	-1.443037	3.270388
C	2.491659	-1.222314	4.555810
C	1.379202	-0.480756	3.778537
C	0.906411	-2.612627	2.466017
C	2.021137	-3.340524	3.248511
C	3.111921	-2.365370	3.730440
H	-0.251975	-1.847702	4.141065
H	2.069961	-1.636136	5.485269
H	3.266076	-0.502322	4.856216
H	1.824727	0.046497	2.921315
H	0.944043	0.281837	4.433523
H	1.323972	-2.203762	1.533500
H	0.128603	-3.328742	2.178116
H	2.460465	-4.123672	2.614351
H	1.586217	-3.850495	4.121386
H	3.634896	-1.942675	2.858338
Pd	-0.137187	0.090636	0.052209
H	5.760302	1.069044	-5.980266
C	3.540695	3.054797	-0.042586
C	4.215353	3.830814	-0.987174
C	3.863099	3.718146	-2.332343
C	2.853845	2.838981	-2.778050
C	2.165584	2.042279	-1.822266
C	2.533658	2.185378	-0.465160
H	5.001374	4.520735	-0.685245
H	4.379897	4.326306	-3.072616
O	4.227045	1.169062	-4.542684
P	0.800014	0.742900	-2.035520
H	1.990797	1.588658	0.269378
C	2.617151	2.874385	-4.265149
C	1.784402	3.868131	-4.830302
C	1.668450	4.019311	-6.223068
C	2.400845	3.176451	-7.060931
C	3.254112	2.201220	-6.541210
C	3.371604	2.066064	-5.145680
O	1.116009	4.663735	-3.923384
H	1.021325	4.776530	-6.651391
H	2.309925	3.285794	-8.139843
H	3.823352	1.569097	-7.213587
C	0.323496	5.760677	-4.423061
H	0.936563	6.458178	-5.008402
H	-0.062713	6.266279	-3.535508
H	-0.514666	5.403896	-5.035523
C	5.121771	0.408393	-5.379705

H	4.570619	-0.272170	-6.042020
H	5.738727	-0.173071	-4.691804
H	-3.566403	2.035169	-5.757097
H	3.197840	-4.400783	-3.299707
C	-0.449149	1.464221	-3.310169
C	-2.940712	1.978137	-3.665781
C	-1.892752	1.287009	-2.766342
C	-0.368598	0.961406	-4.773274
C	-1.421418	1.649224	-5.675423
C	-2.851968	1.489047	-5.125031
H	-0.221579	2.538973	-3.303264
H	-2.780898	3.067738	-3.637402
H	-3.947738	1.798950	-3.263246
H	-2.124535	0.213337	-2.698916
H	-1.952668	1.670838	-1.740567
H	-0.549692	-0.121459	-4.801694
H	0.629450	1.128303	-5.188930
H	-1.354829	1.236014	-6.691919
H	-1.181154	2.719361	-5.758558
H	-3.141501	0.427006	-5.168294
C	1.677346	-0.717249	-2.892612
C	1.405677	-3.183341	-3.561511
C	0.724493	-1.940904	-2.944802
C	2.976621	-1.093315	-2.137084
C	3.657631	-2.342153	-2.741785
C	2.701949	-3.549426	-2.812484
H	1.942348	-0.415537	-3.914566
H	1.639744	-2.987202	-4.620073
H	0.704691	-4.029933	-3.547361
H	0.400462	-2.168845	-1.918139
H	-0.185644	-1.705767	-3.508892
H	2.728083	-1.289819	-1.083024
H	3.675715	-0.250761	-2.150774
H	4.548632	-2.595548	-2.149740
H	4.012271	-2.106092	-3.756903
H	2.449026	-3.872909	-1.790818
H	-4.354235	-2.790578	-0.670457
H	3.788178	3.126975	1.014979

L (L = Sphos)
E = -8329.6
G = -8028.2
N_{imag} = 0

H	-0.831250	-5.374806	6.573040
C	-3.609623	-3.976894	0.673804
C	-4.260894	-4.547304	1.769249
C	-4.021119	-4.036341	3.045970
C	-3.132626	-2.966025	3.272821
C	-2.461483	-2.380199	2.164936
C	-2.734739	-2.907842	0.881243
H	-4.952898	-5.376839	1.635653
H	-4.531716	-4.474815	3.901576
O	-1.213757	-4.069206	4.967454
P	-1.214386	-0.965817	2.038292
H	-2.242061	-2.455231	0.022827
C	-2.998811	-2.544463	4.711305
C	-3.936993	-1.657252	5.286881
C	-3.908247	-1.353290	6.659064
C	-2.937700	-1.949998	7.466173
C	-2.009811	-2.850402	6.939230
C	-2.054582	-3.156055	5.566756
O	-4.864476	-1.130074	4.412370
H	-4.624603	-0.666199	7.095328
H	-2.907840	-1.713715	8.527920
H	-1.275650	-3.311050	7.590834
C	-5.904100	-0.282625	4.942754
H	-6.514175	-0.818663	5.681380
H	-6.521407	-0.009745	4.084250
H	-5.487350	0.624519	5.399273
C	-0.296433	-4.805426	5.801828
H	0.436413	-4.140321	6.277317
H	0.218818	-5.493717	5.128932
H	-2.068375	3.909639	5.191084
H	4.181969	-2.963095	2.828570

C	-1.808461	0.430777	3.219086
C	-2.271699	2.965571	3.234294
C	-1.707299	1.770579	2.434760
C	-1.146101	0.570195	4.610979
C	-1.722560	1.766390	5.405817
C	-1.610420	3.088716	4.621633
H	-2.875132	0.211829	3.366117
H	-3.357927	2.833746	3.361473
H	-2.133721	3.892990	2.660732
H	-0.652142	1.968542	2.188362
H	-2.233149	1.678928	1.475488
H	-0.064865	0.727237	4.494026
H	-1.271381	-0.349224	5.190761
H	-1.203388	1.849349	6.371193
H	-2.781361	1.573095	5.635275
H	-0.547286	3.348369	4.495183
C	0.392662	-1.664754	2.798837
C	2.913102	-1.197179	3.009733
C	1.549455	-0.670241	2.508401
C	0.727805	-3.050811	2.194453
C	2.094412	-3.581391	2.684849
C	3.237314	-2.582228	2.415930
H	0.276236	-1.777041	3.885140
H	2.896130	-1.266308	4.108762
H	3.702798	-0.477204	2.752759
H	1.606148	-0.503927	1.421431
H	1.346913	0.308395	2.959976
H	0.747882	-2.970810	1.095873
H	-0.058890	-3.768928	2.447216
H	2.309233	-4.544799	2.201156
H	2.037656	-3.778630	3.766579
H	3.384875	-2.483401	1.328925
H	-3.783901	-4.350430	-0.333602

EtO^-
E = −982.2
G = −958.8
N_{imag} = 0

O	1.757224	0.426358	0.000000
C	0.663746	-0.383081	0.000000
C	-0.701959	0.377258	0.000000
H	-0.771409	1.022571	0.888936
H	-1.561070	-0.319703	0.000000
H	-0.771409	1.022571	-0.888936
H	0.606106	-1.086673	0.889987
H	0.606106	-1.086673	-0.889987

EtOH
E = −1037.3
G = −1005.0
N_{imag} = 0

O	-2.429997	-0.068244	0.000000
C	-1.285740	0.831383	0.000000
C	-0.017255	-0.012606	0.000000
H	0.023759	-0.651961	0.890077
H	0.866442	0.637498	0.000000
H	0.023759	-0.651961	-0.890077
H	-1.318409	1.476552	0.891345
H	-1.318409	1.476552	-0.891345
H	-3.239076	0.472825	0.000000

CO_2
E = −513.69
G = −519.76
N_{imag} = 0

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.172397
O	0.000000	0.000000	-1.172397

mono-RC-*cis*
E = −513.69
G = −519.76
N_{imag} = 0

C	5.515516	-11.086002	-10.797398

C	5.553738	-10.460749	-9.535512
C	4.604689	-9.429765	-9.261392
C	3.677176	-9.090174	-10.269775
H	4.588089	-11.254908	-12.736872
H	6.245980	-11.865469	-11.005103
O	8.169198	-9.604285	-9.809493
P	4.262499	-8.522357	-7.644597
H	2.940761	-8.307480	-10.105152
C	6.644760	-10.968190	-8.625304
C	6.420007	-12.021142	-7.708131
C	7.467324	-12.557877	-6.938002
C	8.763423	-12.072957	-7.118634
C	9.038493	-11.082487	-8.062699
C	7.983750	-10.548308	-8.823111
O	5.125973	-12.496205	-7.648377
H	7.283706	-13.351122	-6.222113
H	9.576156	-12.486628	-6.525158
H	10.057637	-10.741249	-8.205765
C	4.861246	-13.669093	-6.848872
H	5.475691	-14.516256	-7.177883
H	3.805684	-13.896870	-7.009647
H	5.038105	-13.476767	-5.782778
H	7.554570	-8.290191	-4.433706
C	9.516805	-9.213410	-10.147897
H	10.012768	-8.713887	-9.306022
H	9.413562	-8.512741	-10.979078
H	0.348550	-11.813503	-4.785104
H	9.053577	-6.419050	-5.072463
C	3.233045	-9.872900	-6.761239
C	0.917485	-10.977601	-6.719025
C	1.779331	-9.836849	-7.303663
C	3.246056	-9.871186	-5.214038
H	6.944916	-6.799238	-3.715803
H	5.263345	-6.559884	-5.532312
H	5.084374	-8.095754	-4.695276
H	6.370438	-6.422088	-7.803134
H	6.999936	-7.867638	-8.599182
H	8.841780	-6.528317	-7.599199
H	8.743344	-8.120345	-6.843584
H	7.686007	-5.482525	-5.677153
H	2.916348	-9.435418	-12.247540
C	2.367539	-11.008422	-4.637240
H	10.111295	-10.079113	-10.466330
C	0.926034	-10.965776	-5.178438
H	3.701753	-10.805153	-7.098655
H	1.298659	-11.945421	-7.079355
H	-0.109589	-10.886234	-7.097474
H	1.323331	-8.870523	-7.046181
H	1.777453	-9.896577	-8.397367
H	2.878273	-8.910382	-4.829595
H	4.268725	-9.995587	-4.841254
H	2.368807	-10.942580	-3.540540
H	2.820022	-11.978267	-4.893565
H	0.427904	-10.051776	-4.818459
C	5.906060	-8.247559	-6.734268
C	7.105296	-7.313943	-4.673064
C	5.739883	-7.534965	-5.364752
C	6.851081	-7.395518	-7.624461
C	8.220435	-7.158195	-6.947768
C	8.072645	-6.506777	-5.559243
H	6.356145	-9.236227	-6.572929
C	3.657066	-9.734051	-11.509395
C	4.582952	-10.741302	-11.777115
N	0.603599	-3.912675	-9.547477
C	-0.358274	-3.093949	-10.323289
H	-0.848028	-3.747268	-11.047812
H	-1.100615	-2.647379	-9.654253
H	0.155573	-2.280577	-10.852863
C	1.250671	-5.074940	-10.105860
H	4.570310	-3.052092	-12.678027
C	1.088095	-3.389454	-8.377900
O	0.846225	-2.235342	-7.971663
C	1.962222	-4.264150	-7.508380
H	2.873294	-3.766787	-7.172486

C	1.494369	-5.354832	-6.778401
H	0.498651	-5.743023	-6.991640
C	2.356386	-6.104619	-5.923140
H	1.936826	-6.940720	-5.371610
H	3.174709	-5.589706	-5.421435
H	6.304549	-4.678441	-11.805491
N	3.625098	-5.710723	-10.009604
C	0.543397	-6.318294	-10.228143
O	1.003683	-7.346865	-10.798924
N	-0.773061	-6.346626	-9.735574
H	-1.041485	-5.622730	-9.079729
C	-1.533236	-7.592441	-9.698844
H	-1.143027	-8.313735	-8.962794
H	-2.574295	-7.362517	-9.448802
Pd	3.142577	-6.430832	-7.932982
H	-1.501613	-8.074654	-10.680559
C	2.630345	-4.911589	-10.544453
C	2.999603	-3.918787	-11.488055
C	4.881052	-5.635823	-10.503805
C	4.308571	-3.804577	-11.936502
H	2.224628	-3.278070	-11.899415
C	5.274430	-4.706802	-11.461054
H	5.599765	-6.333294	-10.082546

mono-RC-*trans*
E = −12958.9
G = −12511.1
N_{imag} = 0

N	-6.246205	0.073872	-4.086686
C	-7.586029	-0.405792	-4.501649
H	-7.454692	-1.184445	-5.256953
H	-8.134712	-0.826764	-3.647681
H	-8.170086	0.423797	-4.909892
C	-5.163028	-0.883477	-3.969897
H	1.433997	3.048856	1.485376
C	-6.184754	1.297841	-3.459380
O	-7.186050	1.987875	-3.179301
C	-4.797317	1.741981	-3.167574
H	-4.033647	1.436729	-3.881123
C	-4.531256	2.761347	-2.236146
H	-5.364956	3.174392	-1.669507
C	-3.197829	3.028201	-1.854097
H	-3.012976	3.732368	-1.048600
H	-2.389118	2.903869	-2.572100
H	0.616529	4.505030	0.917817
H	-1.166727	3.147392	-0.144847
H	-1.045111	2.778089	1.567432
H	-0.173459	1.487713	-1.918239
H	0.664099	0.043954	-1.351720
H	2.273542	1.821590	-2.055782
H	2.471353	1.396519	-0.356496
H	1.020997	3.875487	-1.446984
H	-1.470169	-3.084669	-3.393346
Pd	-3.672764	0.880588	-1.373697
H	3.757843	-2.085167	1.859408
C	-5.116507	-1.674683	-2.729084
C	-5.450358	-3.051821	-2.764794
C	-5.050016	-1.808351	-0.376256
C	-5.614476	-3.784122	-1.597467
H	-5.610542	-3.510908	-3.734582
C	-5.447495	-3.137993	-0.363973
H	-4.860479	-1.284315	0.555413
H	-5.898740	-4.833787	-1.642429
H	-5.591296	-3.655657	0.580110
N	-4.837323	-1.098034	-1.510801
C	-4.530232	-1.378869	-5.164988
O	-3.747145	-2.370469	-5.187876
N	-4.746135	-0.652991	-6.341015
H	-5.468629	0.056282	-6.333049
C	-4.279579	-1.140594	-7.634759
H	-4.815378	-2.043765	-7.968140
H	-4.423970	-0.351947	-8.380033
H	-3.214374	-1.388364	-7.582022
C	-1.216781	-2.949197	-2.344417

C	-0.561374	-3.941957	-1.615165
C	-0.284813	-3.725500	-0.265165
C	-0.643411	-2.534924	0.400452
C	-1.323093	-1.525557	-0.333276
C	-1.585004	-1.768574	-1.700186
H	-0.271144	-4.879030	-2.086523
H	0.228314	-4.496871	0.305895
O	1.831320	-1.553074	1.199565
P	-1.916251	0.181820	0.200358
H	-2.110007	-1.012931	-2.279152
C	-0.236854	-2.491112	1.848532
C	-1.056042	-3.069157	2.845454
C	-0.611316	-3.193948	4.173126
C	0.666915	-2.742456	4.506797
C	1.510298	-2.178294	3.547655
C	1.059776	-2.066302	2.220147
O	-2.296759	-3.492336	2.418518
H	-1.243779	-3.634147	4.935875
H	1.014041	-2.834936	5.533846
H	2.501667	-1.843312	3.831521
C	-3.137544	-4.202082	3.352098
H	-2.639133	-5.105054	3.726949
H	-4.026964	-4.483301	2.784743
H	-3.427556	-3.563721	4.196812
C	3.205439	-1.214541	1.483778
H	3.273928	-0.393418	2.209291
H	3.628541	-0.895726	0.529190
H	-4.068107	1.016967	5.603620
H	2.555860	3.860660	-0.578344
C	-2.591887	0.137938	1.992728
C	-4.532392	0.932773	3.474772
C	-3.830598	1.071995	2.105981
C	-1.613551	0.434939	3.159202
C	-2.314760	0.289239	4.531479
C	-3.561329	1.187135	4.643895
H	-2.936635	-0.901784	2.093227
H	-4.952849	-0.081158	3.564046
H	-5.380875	1.628810	3.521702
H	-3.510839	2.115711	1.970006
H	-4.542304	0.867353	1.296648
H	-1.239716	1.462946	3.074384
H	-0.744726	-0.224999	3.121700
H	-1.597865	0.528271	5.328819
H	-2.605853	-0.761102	4.679184
H	-3.251824	2.243972	4.634538
C	-0.304496	1.193850	0.234761
C	0.814536	3.453226	0.669847
C	-0.523728	2.680933	0.609595
C	0.459347	1.091475	-1.110318
C	1.788897	1.879916	-1.071697
C	1.585914	3.351443	-0.660370
H	0.311462	0.717149	1.010493

mono-TS-*cis*
E = −12952.3
G = −12504.2
N_{imag} = 1, ν = −165.87i

C	-15.043467	15.694939	-3.820270
C	-14.699081	17.048505	-3.630140
C	-15.679692	18.047168	-3.906749
C	-16.947746	17.618948	-4.359432
H	-16.530110	14.240421	-4.391190
H	-14.288407	14.939118	-3.612551
O	-12.567787	17.016347	-5.403005
P	-15.604807	19.930141	-3.668300
H	-17.715536	18.363433	-4.570219
C	-13.281193	17.273195	-3.163802
C	-12.951518	17.322807	-1.789099
C	-11.618928	17.454064	-1.358561
C	-10.596193	17.478001	-2.307590
C	-10.872851	17.345182	-3.669276
C	-12.208943	17.220179	-4.088815
O	-14.013042	17.202221	-0.915925
H	-11.377449	17.519591	-0.303613

H	-9.564043	17.580978	-1.978839
H	-10.059599	17.330045	-4.386187
C	-13.732737	17.108323	0.496703
H	-13.074153	16.257700	0.712380
H	-14.702247	16.953165	0.974188
H	-13.279213	18.032088	0.878940
H	-11.609766	22.185618	-4.188936
C	-11.524971	16.812770	-6.379404
H	-10.897309	17.706002	-6.489220
H	-12.044660	16.614826	-7.319150
H	-16.654074	20.945098	1.999036
H	-11.275003	22.439257	-6.634256
C	-15.622174	20.009114	-1.755087
C	-17.182275	19.723439	0.269687
C	-17.074205	19.747782	-1.271297
C	-15.047394	21.291857	-1.106589
H	-12.401835	23.667717	-4.724337
H	-14.613552	22.527405	-4.763609
H	-13.868578	22.418802	-3.173958
H	-14.590274	20.530846	-6.358394
H	-13.821243	19.015391	-5.884984
H	-12.364121	20.297845	-7.445577
H	-11.582045	20.103087	-5.875688
H	-13.011657	22.625210	-6.888076
H	-18.261963	15.995779	-4.881362
C	-15.167321	21.256924	0.436303
H	-10.898965	15.951195	-6.114180
C	-16.614196	21.008121	0.902835
H	-15.004668	19.164104	-1.432605
H	-16.634428	18.852675	0.660980
H	-18.233359	19.587137	0.559668
H	-17.732344	20.532670	-1.669737
H	-17.441417	18.799292	-1.680882
H	-15.576105	22.180160	-1.479648
H	-13.991873	21.412721	-1.374035
H	-14.787657	22.201350	0.850192
H	-14.518360	20.459345	0.829958
H	-17.242320	21.865354	0.613960
C	-13.916222	20.528078	-4.302552
C	-12.442894	22.571958	-4.796794
C	-13.781741	22.072496	-4.206725
C	-13.753165	20.101693	-5.786241
C	-12.420057	20.598024	-6.389827
C	-12.258811	22.124853	-6.259135
H	-13.130118	20.054351	-3.698338
C	-17.268105	16.270936	-4.534956
C	-16.306531	15.297855	-4.261658
N	-21.893573	22.284879	-5.398029
C	-23.315068	22.071583	-5.691389
H	-23.676808	21.147709	-5.223217
H	-23.871336	22.923043	-5.288061
H	-23.488758	22.006911	-6.771443
C	-20.804445	21.336745	-5.579600
H	-20.315883	22.020605	-10.171597
C	-21.390631	23.315004	-4.639404
O	-22.011416	24.221203	-4.078890
C	-19.890724	23.094401	-4.688726
H	-19.454032	23.466394	-5.617525
C	-18.994653	22.898884	-3.633725
H	-19.383141	22.600905	-2.659584
C	-17.598874	22.880190	-3.843305
H	-16.951859	22.874472	-2.972085
H	-17.203158	23.434869	-4.697237
H	-17.915160	21.227285	-10.051097
N	-18.741655	20.924639	-6.772113
C	-20.789727	20.153340	-4.667994
O	-20.203947	19.085312	-4.933191
N	-21.503771	20.276999	-3.496538
H	-21.975946	21.144117	-3.278738
C	-21.600500	19.174785	-2.541031
H	-20.608670	18.877753	-2.179790
H	-22.209575	19.503007	-1.694654
Pd	-17.349609	20.887752	-4.861535
H	-22.067520	18.294290	-2.999792

C	-20.066640	21.295786	-6.837235
C	-20.630533	21.729635	-8.061897
C	-18.030794	20.902180	-7.926351
C	-19.874744	21.712819	-9.225668
H	-21.666970	22.051726	-8.089280
C	-18.542559	21.273457	-9.164849
H	-16.996507	20.577234	-7.835384

mono-TS-*trans*
E = −12956.8
G = −12509.2
N_{imag} = 1, ν = −100.01i

N	-6.315420	0.332177	-4.795122
C	-7.198617	-0.082852	-5.895644
H	-6.710864	-0.881269	-6.461398
H	-8.168550	-0.443101	-5.528419
H	-7.383449	0.773556	-6.552732
C	-5.352956	-0.473018	-4.076736
H	1.262919	3.220503	0.937518
C	-6.419321	1.541775	-4.154774
O	-7.320776	2.378718	-4.273991
C	-5.180924	1.665681	-3.299481
H	-4.268953	1.810952	-3.879628
C	-5.171584	2.118972	-1.962080
H	-6.116268	2.126009	-1.418502
C	-3.994881	2.605067	-1.312593
H	-4.106717	3.128553	-0.365167
H	-3.169821	2.959502	-1.931061
H	0.266277	4.507714	0.257909
H	-1.441467	2.861827	-0.478556
H	-1.167250	2.737607	1.251071
H	-0.411156	1.080446	-2.099982
H	0.603802	-0.194158	-1.425563
H	1.978622	1.612060	-2.475005
H	2.331450	1.438327	-0.756416
H	0.568893	3.606152	-2.032337
H	-1.570869	-3.640402	-3.031006
Pd	-3.773527	0.473650	-1.141405
H	4.041864	-1.750099	1.554170
C	-5.841786	-1.273633	-2.934360
C	-7.080121	-1.950702	-3.007833
C	-5.508418	-2.167519	-0.794929
C	-7.520360	-2.744997	-1.953221
H	-7.674604	-1.884298	-3.912777
C	-6.705940	-2.876993	-0.823207
H	-4.850452	-2.230929	0.068982
H	-8.468262	-3.274417	-2.023578
H	-6.991658	-3.502705	0.018413
N	-5.089442	-1.352546	-1.789673
C	-4.119285	-0.897483	-4.772919
O	-3.374137	-1.810948	-4.360403
N	-3.815898	-0.213733	-5.934988
H	-4.387294	0.577632	-6.202390
C	-2.596836	-0.488311	-6.691878
H	-2.535285	-1.551732	-6.949648
H	-2.617618	0.102297	-7.611960
H	-1.695220	-0.229693	-6.119907
C	-1.238437	-3.386289	-2.027411
C	-0.434567	-4.250093	-1.283252
C	-0.044466	-3.874327	0.002940
C	-0.427078	-2.645839	0.579912
C	-1.252366	-1.764592	-0.172516
C	-1.638590	-2.171490	-1.468722
H	-0.114642	-5.207315	-1.691296
H	0.580650	-4.544563	0.590104
O	2.029703	-1.420039	1.033679
P	-1.911697	-0.040602	0.247747
H	-2.283335	-1.530913	-2.064790
C	0.109626	-2.427484	1.969340
C	-0.562637	-2.964528	3.091326
C	0.009027	-2.921039	4.374724
C	1.268552	-2.341197	4.537938
C	1.971724	-1.816351	3.451747
C	1.395296	-1.874705	2.170122

O	-1.794605	-3.526352	2.827798
H	-0.512069	-3.329389	5.233430
H	1.713041	-2.301615	5.530361
H	2.953144	-1.381252	3.604202
C	-2.498017	-4.177877	3.905880
H	-1.904942	-4.999863	4.326957
H	-3.410477	-4.575998	3.457065
H	-2.759554	-3.467811	4.701261
C	3.393470	-0.963464	1.147491
H	3.465098	-0.065953	1.775846
H	3.704172	-0.722035	0.129106
H	-3.676458	0.964520	5.772416
H	2.154275	3.847349	-1.296642
C	-2.418222	-0.023496	2.102745
C	-4.317910	0.577281	3.722837
C	-3.785834	0.692803	2.277655
C	-1.400743	0.537283	3.129657
C	-1.932924	0.425453	4.579012
C	-3.301381	1.112177	4.750113
H	-2.571340	-1.090445	2.317770
H	-4.538455	-0.478851	3.944529
H	-5.269566	1.120258	3.806956
H	-3.674361	1.756119	2.019021
H	-4.517454	0.283963	1.570264
H	-1.210062	1.597185	2.917669
H	-0.441493	0.018961	3.054694
H	-1.196853	0.862397	5.268072
H	-2.021120	-0.636416	4.850746
H	-3.184679	2.198691	4.611710
C	-0.368086	1.062635	0.073555
C	0.551039	3.454016	0.130351
C	-0.703105	2.562166	0.274473
C	0.313155	0.853995	-1.302861
C	1.556959	1.756871	-1.470561
C	1.236782	3.245971	-1.234166
H	0.333485	0.740234	0.855179

mono-PC-*cis*
E = −12971.6
G = −12524.1
N_{imag} = 0

N	-0.007850	0.262189	-0.468528
C	0.376427	0.564968	-1.845934
H	-0.276631	0.048743	-2.558762
H	0.279050	1.645021	-1.988760
H	1.416820	0.272417	-2.037106
C	0.027849	-1.034127	0.289087
H	4.524700	-1.060169	0.447671
C	-0.010567	1.074657	0.644936
O	0.005923	2.290154	0.760777
C	-0.009072	-0.137220	1.627301
H	0.970235	-0.181333	2.112362
C	-1.125142	-0.240036	2.628361
H	-2.129900	-0.372023	2.224217
C	-0.996708	0.265421	3.917704
H	-0.055210	0.691119	4.261355
H	-1.878603	0.535025	4.495190
H	-3.430937	-2.988901	-1.163127
H	-4.180526	-1.386951	-1.403172
H	-4.073011	-2.098642	0.231326
C	-3.562908	-1.990296	-0.733940
H	-2.159095	-0.367541	-0.874203
C	-1.240943	-1.906263	0.111384
N	2.457207	-1.097232	0.384380
O	-1.320857	-3.038479	0.601987
H	2.749258	-4.635430	-1.182832
H	4.816981	-3.337944	-0.551311
N	-2.263749	-1.331037	-0.578393
C	1.346657	-1.793854	0.060496
C	1.418866	-3.072962	-0.512698
C	3.657312	-1.658152	0.165573
C	2.674082	-3.643975	-0.741180
H	0.515291	-3.619766	-0.754655
C	3.821533	-2.929398	-0.393887

H	1.546023	-8.315535	8.984122
C	-4.314246	-7.209506	7.550823
H	-4.432895	-8.278173	7.771426
H	-5.100668	-6.885600	6.865978
H	-4.377877	-6.632080	8.482332
C	2.882171	-7.848969	6.887983
H	3.478577	-3.065297	7.944057
H	3.227958	-7.300128	7.773714
H	3.574325	-7.679908	6.060773
H	-3.285290	-2.725557	10.664057
H	5.261324	-2.822643	6.231170
C	-1.511257	-3.719040	7.216849
C	-3.249008	-2.345012	8.514979
C	-2.260648	-2.363371	7.328574
C	-0.806115	-4.048982	8.556356
C	-1.797845	-4.028348	9.744364
H	3.575755	-1.375400	7.447191
H	1.624418	-1.656297	5.926175
H	1.203311	-2.117437	7.569295
H	2.107109	-3.512667	4.134878
H	2.019390	-5.206466	4.624459
H	4.389989	-4.419764	4.471770
H	3.986099	-4.942636	6.106736
H	4.134421	-2.036913	5.123018
H	-1.236960	-6.067973	1.407349
Pd	-0.852783	-1.934214	4.098623
H	2.833785	-8.921695	7.115625
C	-2.552003	-2.688401	9.846225
H	-2.260258	-4.498446	7.020157
H	-4.053417	-3.073799	8.327426
H	-3.729053	-1.358318	8.577930
H	-1.527339	-1.552516	7.453766
H	-2.786123	-2.151861	6.389499
H	-0.021811	-3.306064	8.753355
H	-0.315531	-5.025472	8.509141
H	-1.252081	-4.231970	10.676396
H	-2.523796	-4.846044	9.623599
H	-1.839138	-1.887535	10.098820
C	1.377730	-3.794803	6.159916
C	3.307566	-2.382048	7.097049
C	1.813035	-2.408824	6.706106
C	2.285962	-4.203424	4.972988
C	3.783815	-4.166267	5.352989
C	4.208508	-2.796022	5.917182
H	1.476903	-4.548028	6.952794
C	-1.123715	-6.264092	2.471281
C	-1.200156	-7.561434	2.980539
C	-1.060305	-7.761238	4.354727
C	-0.836464	-6.697234	5.252394
C	-0.754638	-5.373561	4.740076
C	-0.908940	-5.197721	3.346056
H	-1.372788	-8.410690	2.321655
H	-1.126041	-8.770125	4.758048
O	1.607052	-7.356757	6.427265
P	-0.445312	-3.730060	5.618730
H	-0.862933	-4.191213	2.929253
C	-0.726223	-7.111677	6.695487
C	-1.892578	-7.311426	7.469940
C	-1.824455	-7.842681	8.769450
C	-0.578937	-8.187348	9.297479
C	0.592776	-8.027051	8.555411
C	0.512332	-7.504809	7.251608
O	-3.075326	-6.955114	6.857025
H	-2.720538	-7.986462	9.362669
H	-0.520582	-8.594198	10.305046

mono-PC-*trans*
E = −12973.0
G = −12525.7
N_{imag} = 0

N	-0.070253	0.461513	-0.482535
C	-0.197254	0.770341	-1.901538
H	-1.165291	0.426549	-2.288820
H	-0.139237	1.857485	-2.007673

H	0.610400	0.298409	-2.467750
C	-0.169933	-0.827888	0.258303
H	-4.660634	-0.587849	-0.111599
C	-0.133887	1.268914	0.619535
O	-0.197501	2.483142	0.752011
C	-0.045174	0.050100	1.598945
H	0.984463	-0.002558	1.971365
C	-1.009997	-0.060269	2.738513
H	-2.063402	-0.126002	2.475054
C	-0.661896	0.313706	4.026040
H	0.346376	0.652562	4.260445
H	-1.429549	0.560400	4.756601
H	2.421154	-4.111499	0.082745
H	2.599623	-4.046899	1.857649
H	3.522420	-2.928888	0.816606
C	2.565738	-3.450354	0.943711
H	0.996371	-2.377406	1.957137
C	1.036643	-1.761725	-0.012925
N	-2.604183	-0.728047	0.061676
O	1.559301	-1.837490	-1.133989
H	-2.982367	-4.507407	-0.753070
H	-5.006456	-3.010455	-0.638521
N	1.454346	-2.499356	1.049195
C	-1.519099	-1.529026	0.014063
C	-1.621642	-2.897482	-0.279108
C	-3.811787	-1.270496	-0.164194
C	-2.883115	-3.450076	-0.517754
H	-0.735983	-3.522867	-0.332923
C	-4.006266	-2.624245	-0.457795
H	1.523503	-8.313931	9.054893
C	-4.272250	-7.193061	7.391190
H	-4.399123	-8.257513	7.626006
H	-5.031155	-6.881803	6.670457
H	-4.371355	-6.598720	8.308601
C	2.925416	-7.957730	6.978418
H	3.388405	-3.142728	8.177595
H	3.274411	-7.413479	7.865498
H	3.643261	-7.829842	6.165950
H	-3.609733	-2.675784	10.312383
H	5.315340	-2.969553	6.621106
C	-1.537706	-3.724631	7.054240
C	-3.414885	-2.367810	8.160764
C	-2.334592	-2.391939	7.057258
C	-0.932495	-3.988889	8.456101
C	-2.016693	-3.960374	9.560064
H	3.567083	-1.463831	7.667323
H	1.746093	-1.725080	5.989977
H	1.177095	-2.148842	7.597555
H	2.334844	-3.606263	4.280771
H	2.164834	-5.297116	4.769038
H	4.558130	-4.569113	4.811340
H	4.005740	-5.060116	6.411605
H	4.309638	-2.172168	5.410560
H	-1.047634	-6.184209	1.351078
Pd	-0.646880	-1.914656	4.071666
H	2.823271	-9.023983	7.217140
C	-2.815552	-2.642765	9.553739
H	-2.244788	-4.533973	6.828140
H	-4.178901	-3.128703	7.936504
H	-3.928050	-1.396217	8.149748
H	-1.639713	-1.552964	7.211337
H	-2.793234	-2.230305	6.073945
H	-0.188075	-3.216649	8.689858
H	-0.413269	-4.951674	8.481402
H	-1.540788	-4.114892	10.538459
H	-2.706377	-4.804554	9.412391
H	-2.148906	-1.811271	9.831968
C	1.430577	-3.854381	6.233829
C	3.306539	-2.469573	7.309737
C	1.849905	-2.468698	6.794047
C	2.424931	-4.297809	5.132559
C	3.886752	-4.289443	5.635313
C	4.294793	-2.921699	6.217025
H	1.449176	-4.596847	7.042219

C	-0.949662	-6.351417	2.421642
C	-1.013164	-7.641577	2.949840
C	-0.901037	-7.816535	4.329514
C	-0.713148	-6.735998	5.215360
C	-0.629295	-5.420052	4.682087
C	-0.764490	-5.269726	3.284029
H	-1.156914	-8.503247	2.300821
H	-0.963771	-8.819401	4.747423
O	1.683307	-7.415795	6.481490
P	-0.341619	-3.766566	5.548924
H	-0.729345	-4.261422	2.871456
C	-0.653154	-7.123693	6.669238
C	-1.848863	-7.299862	7.404453
C	-1.831600	-7.805792	8.715303
C	-0.608978	-8.151943	9.293531
C	0.589251	-8.021249	8.588965
C	0.560278	-7.525382	7.272998
O	-3.006327	-6.950908	6.741249
H	-2.749532	-7.930798	9.278440
H	-0.590260	-8.539019	10.310218

mono-P-*cis*
E = -4585.7
G = -4454.3
N_{imag} = 0

N	-1.20361357	0.09425916	-0.12723537
C	-1.76078319	0.66097567	-1.35528740
H	-2.59114585	0.05223349	-1.73051690
H	-2.12996209	1.66304734	-1.11936115
H	-0.99193263	0.73781326	-2.13447438
C	-0.44832899	-1.18282854	0.10217830
H	3.18488797	0.29379125	-2.10380274
C	-0.72192578	0.74002417	0.99211890
O	-0.89021471	1.87436156	1.40875070
C	0.10341869	-0.49781817	1.45539555
H	1.16990551	-0.28118307	1.34377832
C	-0.19987923	-1.09269167	2.79220408
H	-1.23681361	-1.37147969	2.98650631
C	0.71041935	-1.25281064	3.75844092
H	1.75504109	-0.98294667	3.61001518
H	0.43872707	-1.65798682	4.73061831
H	-3.29377094	-4.20508025	0.37371183
H	-4.60896099	-2.99607701	0.36091420
H	-3.73053000	-3.35582597	1.87281371
C	-3.63373396	-3.25094357	0.78402631
H	-2.99679934	-1.24639119	0.34984223
C	-1.33095953	-2.42185994	0.38923894
N	1.53036144	-0.42943842	-1.09422311
O	-0.81542716	-3.52670893	0.60261642
H	1.64748900	-3.49681571	-3.47045792
H	3.34650239	-1.64575859	-3.67939772
N	-2.67223961	-2.20388126	0.42705606
C	0.62642569	-1.42460009	-0.97166355
C	0.63795752	-2.54476823	-1.81651984
C	2.47296735	-0.53013185	-2.04521541
C	1.62115979	-2.63567399	-2.80628284
H	-0.09093540	-3.33785723	-1.69493291
C	2.56308358	-1.61283371	-2.92614571

mono-P-*trans*
E = -4584.3
G = -4453.0
N_{imag} = 0

N	-0.930335	0.630334	0.021276
C	-1.740027	0.993842	-1.135380
H	-2.758771	0.604579	-1.023957
H	-1.774910	2.086275	-1.178174
H	-1.296327	0.599542	-2.054096
C	-0.593224	-0.687769	0.625088
H	-4.857496	-0.804017	2.115139
C	-0.385260	1.395941	1.010821
O	-0.340569	2.604317	1.193832
C	0.164522	0.149410	1.779868
H	1.253263	0.100034	1.661407

C	-0.215331	-0.018643	3.214895
H	-1.279719	0.017883	3.444030
C	0.670361	-0.161924	4.207880
H	1.743936	-0.186264	4.022267
H	0.350127	-0.247780	5.243848
H	1.745734	-3.591172	-1.246439
H	2.908205	-3.559970	0.110620
H	2.994861	-2.329579	-1.179611
C	2.318503	-2.945958	-0.574283
H	1.626372	-1.936794	1.182959
C	0.300239	-1.526595	-0.331395
N	-2.907801	-0.770897	1.422608
O	-0.015606	-1.663522	-1.519706
H	-2.937378	-4.645661	1.724222
H	-4.973641	-3.293410	2.342677
N	1.399512	-2.114468	0.212246
C	-1.820339	-1.492913	1.087512
C	-1.796897	-2.893299	1.183626
C	-3.998743	-1.424989	1.858545
C	-2.934490	-3.560976	1.643118
H	-0.911097	-3.456402	0.904505
C	-4.064154	-2.815530	1.986865

B

E = -12962.6

G = -12512.96

N_{imag} = 0

N	-5.817785	0.647952	-3.102268
C	-6.845754	1.236942	-2.215434
H	-7.838437	0.952560	-2.575179
H	-6.719169	0.857435	-1.193100
H	-6.743233	2.324048	-2.210519
C	-6.002093	-0.731715	-3.509611
H	0.232271	3.609943	1.726884
C	-4.736736	1.422118	-3.462745
O	-4.609596	2.622102	-3.143850
C	-3.708739	0.674087	-4.261200
H	-4.085115	-0.067337	-4.960841
C	-2.339817	0.988668	-4.296619
H	-1.723969	0.461251	-5.024738
C	-1.712472	1.719394	-3.258037
H	-0.630160	1.806742	-3.268928
H	-2.264938	2.515465	-2.768820
H	-0.520432	4.712510	0.573991
H	-1.310396	2.822045	-0.810309
H	-1.881198	2.644959	0.838833
H	0.763744	1.337174	-1.629287
H	1.508749	0.251999	-0.457885
H	2.850513	2.340092	-0.771043
H	2.309739	2.150205	0.896486
H	1.049712	3.997798	-1.211271
H	1.022885	-3.279051	-2.988156
Pd	-2.709213	-0.044424	-2.313626
H	3.486904	-1.041821	3.687172
C	-5.395508	-1.824880	-2.798213
C	-6.054373	-3.104190	-2.780223
C	-3.711281	-2.803241	-1.432889
C	-5.530910	-4.187032	-2.111050
H	-6.993483	-3.183054	-3.311356
C	-4.318130	-4.044035	-1.406395
H	-2.773501	-2.659419	-0.908895
H	-6.067930	-5.134338	-2.109288
H	-3.857800	-4.864608	-0.863732
N	-4.184263	-1.719265	-2.109893
C	-6.937471	-0.933433	-4.616833
O	-7.300691	-2.045704	-5.083062
N	-7.443084	0.223583	-5.216855
H	-6.995198	1.106908	-5.009889
C	-8.214302	0.142881	-6.455538
H	-9.080358	-0.513436	-6.321952
H	-8.565408	1.147888	-6.709391
H	-7.623454	-0.251813	-7.296056
C	0.796940	-3.069764	-1.944838
C	1.338700	-3.851854	-0.923477

C	1.018332	-3.554736	0.400106
C	0.168732	-2.485303	0.753990
C	-0.392686	-1.691888	-0.281997
C	-0.056456	-2.017246	-1.616857
H	1.998710	-4.686533	-1.150826
H	1.435518	-4.162592	1.200246
O	1.895855	-0.970601	2.310743
P	-1.505587	-0.170087	-0.190528
H	-0.492945	-1.428760	-2.421331
C	-0.034919	-2.326782	2.235654
C	-1.049681	-3.049519	2.903567
C	-1.136333	-3.051897	4.306367
C	-0.197244	-2.330798	5.046153
C	0.826187	-1.614530	4.421889
C	0.909852	-1.624436	3.018508
O	-1.919847	-3.736500	2.085745
H	-1.916469	-3.604829	4.817333
H	-0.262667	-2.328841	6.132157
H	1.545851	-1.068361	5.021351
C	-2.943075	-4.551275	2.699325
H	-2.500083	-5.336900	3.324184
H	-3.489098	-5.002749	1.869221
H	-3.629613	-3.942529	3.301284
C	2.954776	-0.324506	3.049666
H	2.568667	0.499373	3.663781
H	3.636099	0.070495	2.293590
H	-5.468633	0.480574	4.098697
H	1.975474	4.505265	0.201239
C	-2.740156	-0.281835	1.273167
C	-5.174189	0.144603	1.964461
C	-4.104287	0.346534	0.868134
C	-2.281538	0.305033	2.634559
C	-3.355158	0.096887	3.730032
C	-4.715856	0.694870	3.327889
H	-2.888250	-1.364355	1.390780
H	-5.394068	-0.930069	2.058785
H	-6.109115	0.628346	1.650765
H	-3.972790	1.423450	0.688190
H	-4.454176	-0.088574	-0.071983
H	-2.106528	1.383449	2.529931
H	-1.340681	-0.142662	2.960587
H	-2.999887	0.545852	4.667701
H	-3.470527	-0.979448	3.923913
H	-4.629715	1.791148	3.267493
C	-0.301193	1.228420	0.270815
C	-0.014187	3.741832	0.661859
C	-0.980886	2.620946	0.215328
C	1.002996	1.216703	-0.564204
C	1.960049	2.350647	-0.127764
C	1.284457	3.735384	-0.168083
H	-0.025019	1.012853	1.312696

F (*E*)
E = -12951.33
G = -12499.99
N_{imag} = 0

N	-5.70304070	1.05020351	-3.50572282
C	-6.00865006	1.61237333	-4.83746659
H	-5.08086959	1.77442485	-5.38711767
H	-6.63502813	0.91637882	-5.41081581
H	-6.52411312	2.57222300	-4.72993567
C	-4.51189455	0.22672915	-3.36771658
H	1.54504982	1.92325700	-0.73784237
C	-6.71350670	0.89982563	-2.56054935
O	-6.39426679	0.25901319	-1.47389929
C	-7.99650478	1.44333349	-2.74790877
H	-8.31625588	1.71186976	-3.75096471
C	-8.93923451	1.57062971	-1.68363498
H	-8.57593584	1.30296235	-0.69002592
C	-10.22631573	1.99848695	-1.80838215
H	-10.87312110	2.09864220	-0.94079876
H	-10.65439417	2.25182525	-2.77774590
H	0.75709807	3.00738764	-1.88311997
H	-1.33182262	1.65892081	-1.79582901

H	-0.86386380	2.18059747	-0.18484372
H	-0.85428464	-0.79508241	-2.56233162
H	-0.07301481	-1.90880464	-1.42850171
H	1.53143514	-1.06370969	-3.15041049
H	2.02698738	-0.59475761	-1.52360332
H	0.60864852	1.19443234	-3.57427826
H	-3.69265467	-5.01926966	-1.11295440
Pd	-4.33032855	0.01964570	-1.09708331
H	3.27923339	-3.31746115	1.29970897
C	-4.67987762	-1.20331987	-3.79944157
C	-3.59581736	-2.10289679	-3.92606098
C	-6.15641645	-2.83727728	-4.53429144
C	-3.83291891	-3.39543012	-4.38579956
H	-2.59313661	-1.78082472	-3.68011529
C	-5.14086135	-3.78472621	-4.69587782
H	-7.19176119	-3.09382080	-4.76457402
H	-3.00517568	-4.09325611	-4.49627482
H	-5.36977812	-4.78666082	-5.05142141
N	-5.94442277	-1.58236686	-4.11013951
C	-3.26347290	0.97496615	-3.84363157
O	-2.32042090	0.43524614	-4.44455834
N	-3.27220433	2.31605096	-3.55588882
H	-4.07558688	2.67510828	-3.05151044
C	-2.27284311	3.25984857	-4.04699173
H	-2.70845967	3.94859176	-4.78362757
H	-1.85957740	3.85008013	-3.22052329
H	-1.46949760	2.69368081	-4.52211613
C	-3.03704856	-4.48367141	-0.42980990
C	-2.25020120	-5.17154463	0.49426316
C	-1.43409141	-4.44747463	1.36403575
C	-1.36497187	-3.03983467	1.34044715
C	-2.15416083	-2.33459227	0.38865103
C	-2.98133096	-3.08962496	-0.47033165
H	-2.27444122	-6.25822644	0.54818367
H	-0.82934822	-4.97898816	2.09618365
O	1.35422163	-2.57735919	0.88492612
P	-2.27784225	-0.47768827	0.06780242
H	-3.60364336	-2.55762829	-1.18536754
C	-0.46147851	-2.44712127	2.39020191
C	-0.93973353	-2.25594860	3.70837494
C	-0.08034498	-1.85961021	4.74721330
C	1.27427619	-1.66578530	4.47106429
C	1.79017317	-1.87619251	3.19114390
C	0.92417942	-2.28571693	2.16097293
O	-2.28607360	-2.49371956	3.88755064
H	-0.45378057	-1.70571648	5.75339720
H	1.94271591	-1.35367605	5.27085691
H	2.84976692	-1.73771689	3.00745432
C	-2.82385893	-2.44218193	5.22631924
H	-2.31791049	-3.16128137	5.88292814
H	-3.87686179	-2.71255180	5.12491407
H	-2.74313930	-1.43388133	5.65242649
C	2.77536408	-2.60597868	0.63318646
H	3.22395342	-1.61093820	0.74965202
H	2.87979244	-2.93401299	-0.40272873
H	-3.15724798	2.87718571	4.81983653
H	2.28447972	1.35041685	-3.03730732
C	-2.53101121	0.33699963	1.79509769
C	-4.11235252	1.83097696	3.16197142
C	-3.76563932	1.27854823	1.76132666
C	-1.32270225	1.06754253	2.43274247
C	-1.67166922	1.62075497	3.83547642
C	-2.90563322	2.54338443	3.80379353
H	-2.78570949	-0.52166025	2.42994206
H	-4.43374142	1.00045291	3.80911282
H	-4.96646624	2.51698642	3.08310020
H	-3.56834036	2.11809264	1.07899604
H	-4.63954215	0.74543236	1.35381681
H	-1.02192692	1.91179767	1.79940625
H	-0.45919882	0.39986535	2.50873920
H	-0.80204321	2.15854983	4.23771831
H	-1.86257731	0.78117299	4.51955386
H	-2.66896188	3.44951362	3.22421589
C	-0.57158865	0.03822617	-0.57496533

C	0.80694180	1.95998296	-1.55453955
C	-0.57501507	1.52525647	-1.01375219
C	-0.11763609	-0.86374739	-1.75090398
C	1.26173998	-0.42741485	-2.29627878
C	1.27683105	1.05670551	-2.71188556
H	0.13448880	-0.09256368	0.25612177

F (*Z*)
E = -12947.36
G = -12495.03
N_{imag} = 0

N	-5.775781	0.944956	-3.543320
C	-6.060717	1.508687	-4.874079
H	-5.132641	1.860955	-5.327550
H	-6.502459	0.749769	-5.532141
H	-6.744374	2.355605	-4.770441
C	-4.543901	0.179383	-3.379272
H	1.524358	1.933095	-0.753052
C	-6.757037	0.809236	-2.580602
O	-6.392555	0.242813	-1.465634
C	-8.087867	1.286519	-2.652402
H	-8.511431	1.467892	-1.664151
C	-8.991121	1.326709	-3.755938
H	-8.627188	1.012652	-4.732791
C	-10.301733	1.698712	-3.673706
H	-10.942587	1.696578	-4.551050
H	-10.748933	2.008359	-2.730259
H	0.722618	3.007288	-1.898393
H	-1.351994	1.637776	-1.803795
H	-0.887074	2.169861	-0.194681
H	-0.856159	-0.810919	-2.562499
H	-0.060872	-1.915315	-1.430102
H	1.530019	-1.059348	-3.159211
H	2.027155	-0.582358	-1.535233
H	0.584361	1.189699	-3.584439
H	-3.645145	-5.045203	-1.138884
Pd	-4.330982	-0.007660	-1.110881
H	3.297944	-3.289684	1.315467
C	-4.653469	-1.253862	-3.815329
C	-3.532889	-2.104236	-3.966367
C	-6.069931	-2.955937	-4.516514
C	-3.721010	-3.406776	-4.420431
H	-2.540696	-1.736026	-3.744216
C	-5.016294	-3.856181	-4.701427
H	-7.097609	-3.259829	-4.722628
H	-2.864848	-4.066141	-4.549013
H	-5.206978	-4.867831	-5.052016
N	-5.906467	-1.691990	-4.097514
C	-3.323357	0.983013	-3.829671
O	-2.360448	0.493082	-4.442299
N	-3.377954	2.316466	-3.509072
H	-4.188383	2.637554	-2.990949
C	-2.408337	3.304512	-3.972043
H	-2.867679	4.007471	-4.680333
H	-2.003834	3.875625	-3.127767
H	-1.593825	2.777471	-4.472403
C	-2.999593	-4.507634	-0.447772
C	-2.215086	-5.193656	0.479726
C	-1.410957	-4.467328	1.358685
C	-1.351567	-3.059118	1.340737
C	-2.139284	-2.355462	0.386893
C	-2.954442	-3.113051	-0.481555
H	-2.231864	-6.280718	0.528975
H	-0.807780	-4.997423	2.093169
O	1.364737	-2.572237	0.898439
P	-2.275916	-0.498747	0.069127
H	-3.575128	-2.582471	-1.199164
C	-0.457895	-2.463786	2.397007
C	-0.944128	-2.278952	3.712999
C	-0.092522	-1.879374	4.757019
C	1.262042	-1.675619	4.488019
C	1.785597	-1.878103	3.209862
C	0.927308	-2.290078	2.174245
O	-2.290061	-2.524749	3.884316

H	-0.471858	-1.730536	5.761793
H	1.924394	-1.361387	5.292044
H	2.844940	-1.731010	3.031572
C	-2.836656	-2.472432	5.219390
H	-2.332581	-3.188373	5.880921
H	-3.888037	-2.746740	5.111732
H	-2.762201	-1.462915	5.643819
C	2.786712	-2.582060	0.650450
H	3.222300	-1.581811	0.771941
H	2.898002	-2.904670	-0.386477
H	-3.140612	2.876239	4.808848
H	2.261083	1.361980	-3.054379
C	-2.526057	0.320069	1.794474
C	-4.099209	1.832195	3.151430
C	-3.752745	1.271814	1.754101
C	-1.313822	1.042407	2.433986
C	-1.662789	1.603657	3.833555
C	-2.888662	2.536647	3.794786
H	-2.789900	-0.535384	2.430199
H	-4.429726	1.006779	3.800552
H	-4.947344	2.525090	3.067463
H	-3.545995	2.107395	1.069567
H	-4.628873	0.744580	1.344527
H	-1.003189	1.881497	1.798444
H	-0.456510	0.367636	2.515507
H	-0.789975	2.135312	4.237076
H	-1.863257	0.767990	4.519802
H	-2.642376	3.438682	3.212749
C	-0.574305	0.029035	-0.578845
C	0.783300	1.961190	-1.567438
C	-0.592923	1.514674	-1.022023
C	-0.115629	-0.871161	-1.753939
C	1.257599	-0.423545	-2.305531
C	1.257366	1.059747	-2.724569
H	0.135530	-0.093365	0.250271

Table S6. Cartesian coordinates (Å), energies (kcal mol^{-1}), and imaginary vibrational frequencies (cm^{-1}) of the optimized structures shown in Figure 3 (right panel) computed at COSMO(dichlorobenzene)-ZORA-BLYP/TZ2P.

R
E = −6143.4
G = −5958.4
N_{imag} = 0

N	0.839790	-0.273709	0.098204
C	1.423498	0.555532	-0.981972
H	0.770431	0.504516	-1.854951
H	1.481770	1.600696	-0.674102
H	2.419947	0.203874	-1.274581
C	-0.043534	-1.405675	-0.278941
H	-0.080429	-2.043768	0.610289
C	1.191923	-0.148234	1.432120
O	0.650736	-0.842713	2.315074
C	2.244544	0.859754	1.770648
H	2.841087	1.292557	0.972688
C	2.483558	1.209635	3.042528
H	1.880803	0.779401	3.841951
C	3.585179	2.133445	3.451936
H	4.338462	1.602115	4.046690
H	4.075793	2.609275	2.597289
O	2.987344	3.181247	4.303569
C	3.874912	3.986789	4.940652
O	5.091441	3.911370	4.867013
O	3.166118	4.877436	5.662417
C	3.960552	5.856638	6.439653
H	4.598283	5.298172	7.131867
H	4.593459	6.409081	5.738301
C	2.979523	6.761321	7.164586
H	3.542731	7.496442	7.751608
H	2.342042	7.302644	6.456589
H	2.344285	6.188637	7.849571
C	0.573760	-2.246289	-1.405236
C	0.158831	-2.165740	-2.741554
C	2.196515	-3.804866	-1.946064
C	0.805950	-2.947802	-3.701984
H	-0.661034	-1.514372	-3.029272
C	1.846712	-3.787162	-3.299643
H	3.000320	-4.449458	-1.590726
H	0.499148	-2.901407	-4.744211
H	2.376005	-4.415585	-4.011424
N	1.580354	-3.056405	-1.011773
C	-1.528246	-1.021576	-0.533714
O	-2.335754	-1.897585	-0.889199
N	-1.880605	0.262049	-0.308942
H	-1.179021	0.892717	0.061276
C	-3.268030	0.730521	-0.399911
H	-3.880741	0.310244	0.407015
H	-3.269926	1.819501	-0.324369
H	-3.702352	0.431882	-1.358688

Pd^0L_2 (L = dppp)
E = −7656.5
G = −7418.9
N_{imag} = 0

Pd	-1.280702	2.444947	0.926247
P	0.917656	1.885497	1.318043
P	-1.900874	4.615092	1.392488
C	-0.437393	5.187252	2.454320
C	0.973083	4.764167	1.959319
C	1.467755	3.351615	2.380346
H	-0.606515	4.791420	3.462421
H	-0.482567	6.280543	2.534003
H	1.683098	5.484921	2.388564
H	1.044924	4.889795	0.871038
H	1.099218	3.115051	3.386788
H	2.563664	3.345072	2.448575
H	3.340055	3.572347	0.446059
H	3.654397	0.643381	1.828139
C	2.103452	1.878585	-0.120039
C	1.897124	0.903794	-1.117715
C	2.723115	0.839544	-2.242992

C	3.762314	1.766875	-2.406957
C	3.968624	2.749221	-1.433147
C	3.149373	2.802376	-0.296312
H	1.078981	0.192317	-1.012592
H	2.550755	0.073254	-2.996514
H	4.399571	1.725542	-3.287961
H	4.769695	3.476556	-1.551980
C	1.561913	0.482070	2.374177
C	0.637970	-0.222265	3.167654
C	1.060898	-1.252916	4.015962
C	2.415398	-1.603765	4.072009
C	3.343374	-0.916288	3.278474
C	2.920694	0.120526	2.437805
H	-0.418554	0.037615	3.114985
H	0.332775	-1.785980	4.624574
H	2.745354	-2.409979	4.724159
H	4.397286	-1.186482	3.314017
H	-2.621194	4.207850	4.236883
H	-2.064522	4.294026	-1.489713
C	-1.878444	5.849745	-0.007364
C	-1.754116	7.238315	0.192744
C	-1.725227	8.116596	-0.895710
C	-1.823801	7.621500	-2.203469
C	-1.950382	6.244325	-2.415654
C	-1.974968	5.366441	-1.323830
H	-1.686436	7.645065	1.199578
H	-1.628165	9.186929	-0.723308
H	-1.801900	8.305981	-3.049178
H	-2.027174	5.851513	-3.427714
C	-3.348671	5.174465	2.431017
C	-4.443728	5.866628	1.876716
C	-5.574502	6.159888	2.648664
C	-5.637875	5.766683	3.990924
C	-4.560409	5.068971	4.552781
C	-3.433469	4.769665	3.780196
H	-4.417568	6.183732	0.837305
H	-6.405526	6.700101	2.198427
H	-6.515579	5.997784	4.590942
H	-4.597241	4.752746	5.593740

EtO^-
E = −1010.6
G = −986.6
N_{imag} = 0

O	1.766255	0.430943	0.000000
C	0.650422	-0.388710	0.000000
C	-0.701305	0.376099	0.000000
H	-0.775050	1.019047	0.889260
H	-1.559534	-0.317033	0.000000
H	-0.775050	1.019047	-0.889260
H	0.612742	-1.080461	0.885718
H	0.612742	-1.080461	-0.885718

EtOH
E = −1038.9
G = −1006.7
N_{imag} = 0

O	-2.433627	-0.068590	0.000000
C	-1.283650	0.830762	0.000000
C	-0.015223	-0.012251	0.000000
H	0.030072	-0.650729	0.890776
H	0.865642	0.641195	0.000000
H	0.030072	-0.650729	-0.890776
H	-1.320021	1.474671	0.890738
H	-1.320021	1.474671	-0.890738
H	-3.239158	0.479085	0.000000

CO_2
E = −514.9
G = −521.0
N_{imag} = 0

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.172202
O	0.000000	0.000000	-1.172202

bi-RC-*cis*
E = −12252.15
G = −11867.8
N_{imag} = 0

C	0.628099	-5.983560	8.606803
H	1.693880	-6.177245	8.751493
H	0.157331	-5.822424	9.586242
H	0.153230	-6.840139	8.121064
C	-0.864522	-4.614685	7.128727
H	-2.074875	-2.504513	10.882350
C	1.254812	-3.714138	7.979699
O	2.131675	-3.701741	8.870970
C	1.047722	-2.546528	7.074413
H	0.427636	-2.685905	6.192808
C	1.338361	-1.256156	7.537905
H	1.771708	-1.170873	8.534202
C	1.281401	-0.115661	6.711994
H	0.625354	-0.100911	5.842200
H	1.551180	0.853540	7.119735
H	-0.694978	-7.681978	4.399005
H	0.902591	-7.115567	3.845304
H	-0.577301	-6.299956	3.293224
C	-0.097912	-6.792465	4.146355
H	0.889640	-5.895496	5.809444
C	-1.084031	-5.287405	5.869297
N	-1.514974	-3.476758	9.150337
O	-2.197067	-5.367282	5.260387
H	-5.112960	-2.783138	7.837678
H	-4.412242	-2.004623	10.148504
N	0.032429	-5.871700	5.271567
C	-1.871679	-3.912565	7.892877
C	-3.198419	-3.655720	7.412380
C	-2.419753	-2.823314	9.894936
C	-4.107355	-2.976206	8.210661
H	-3.470401	-4.006977	6.424266
C	-3.728514	-2.539684	9.493550
N	0.437574	-4.796800	7.746775
C	3.515357	4.158108	6.679501
C	4.159686	4.061936	7.917425
C	4.814974	2.874309	8.267402
C	4.827096	1.790818	7.384281
H	3.023413	3.171145	4.832649
H	2.999383	5.074466	6.400807
H	4.148245	4.903077	8.607043
H	5.313624	2.787393	9.230284
C	3.529356	3.077420	5.789205
P	4.178665	0.404873	5.018909
C	5.992654	-0.000874	4.847455
C	6.317130	-1.229547	3.970383
C	6.051095	-2.600628	4.630133
H	6.382452	-0.146433	5.862016
H	6.488295	0.889602	4.443515
H	7.389540	-1.185814	3.740476
H	5.800850	-1.155438	3.005152
H	6.467881	-2.616857	5.645507
H	6.566860	-3.393446	4.075525
H	5.326461	0.872602	7.685617
H	1.856048	-0.151759	3.320873
C	3.672218	1.020915	3.354180
C	4.465319	1.940170	2.638500
C	4.061408	2.387297	1.377333
C	2.862050	1.927814	0.817120
C	2.068058	1.016927	1.521191
C	2.472396	0.564148	2.782551
H	5.393867	2.317609	3.059654
H	4.682213	3.096432	0.834165
H	2.550377	2.278570	-0.164275
H	1.136480	0.655689	1.091816
C	4.193575	1.885201	6.128827
H	5.591670	-3.633152	2.144538
H	4.355124	-5.973492	3.867110
C	3.656336	-3.500566	3.127070
C	2.266035	-3.606623	2.930263

C	1.745912	-3.909367	1.668631
C	2.607070	-4.100284	0.581389
C	3.990131	-3.993868	0.764540
C	4.513790	-3.700039	2.029279
H	0.669612	-3.991083	1.534984
H	2.202564	-4.328906	-0.402242
H	4.666379	-4.142198	-0.074676
C	4.512504	-5.967652	4.942104
C	4.478303	-4.758288	5.660713
C	4.675772	-4.780959	7.053180
C	4.928556	-5.989008	7.711215
C	4.968093	-7.188339	6.990453
C	4.754182	-7.175471	5.606903
H	4.611267	-3.861969	7.630522
H	5.078907	-5.992540	8.788488
H	5.156478	-8.128420	7.504616
H	4.777372	-8.104637	5.041141
P	4.264932	-3.114632	4.831213
H	1.585742	-3.462117	3.766525
Pd	2.915137	-1.405927	5.864424

bi-RC-*trans*
E = -12249.7
G = -11865.2
N_{imag} = 0

C	0.248295	-6.423177	8.060213
H	1.296375	-6.723382	7.978067
H	-0.054296	-6.480140	9.115152
H	-0.376529	-7.093999	7.468357
C	-1.192671	-4.625282	7.057512
H	-0.339914	-6.949827	3.339419
C	1.011539	-4.104407	7.890866
O	1.898904	-4.298466	8.759751
C	0.903932	-2.847062	7.125016
H	0.352782	-2.867206	6.189168
C	1.392045	-1.641251	7.629119
H	1.848139	-1.667352	8.619034
C	1.394539	-0.420972	6.907494
H	0.696280	-0.288099	6.080639
H	1.686167	0.491212	7.419934
H	-4.163285	-2.505539	9.081132
H	-4.513525	-1.589938	7.595240
H	-3.085400	-1.185428	8.585832
C	-3.714940	-2.007227	8.215189
H	-2.982378	-2.844809	6.404894
C	-1.941627	-3.728955	7.951272
N	-0.730857	-5.860207	5.047275
O	-1.695263	-3.636092	9.185594
H	-4.480630	-5.951473	3.993678
H	-2.704597	-7.023609	2.536557
N	-2.959239	-2.966118	7.410119
C	-1.674438	-5.241439	5.839673
C	-3.052398	-5.287326	5.453808
C	-1.130553	-6.469798	3.921427
C	-3.429372	-5.915191	4.275043
H	-3.812285	-4.861423	6.100859
C	-2.452317	-6.521421	3.467251
N	0.077034	-5.052908	7.547551
C	3.076900	4.017855	6.894291
C	3.902334	4.035233	8.024102
C	4.786486	2.972996	8.251247
C	4.847977	1.902856	7.353402
H	2.489959	2.956399	5.118698
H	2.382752	4.835469	6.711237
H	3.854343	4.866096	8.724580
H	5.428242	2.973505	9.129767
C	3.138415	2.950761	5.990388
P	4.071063	0.413080	5.082620
C	5.896459	0.178556	4.758507
C	6.250962	-1.003618	3.829309
C	6.197399	-2.403234	4.484613
H	6.384407	0.051196	5.731944
H	6.274482	1.115348	4.332035
H	7.283642	-0.846345	3.491461

H	5.632435	-0.971576	2.923661
H	6.700679	-2.376496	5.460139
H	6.754772	-3.122553	3.872870
H	5.530421	1.082297	7.561918
H	1.806291	-0.451687	3.437530
C	3.399285	1.007684	3.464423
C	4.000783	2.072528	2.764235
C	3.482679	2.491318	1.535573
C	2.357769	1.856421	0.991557
C	1.753893	0.799507	1.679906
C	2.273493	0.376291	2.909178
H	4.868081	2.584493	3.174442
H	3.955712	3.314652	1.004643
H	1.956250	2.185707	0.035634
H	0.881323	0.301647	1.262976
C	4.032779	1.885124	6.203532
H	5.600919	-3.263215	1.988665
H	5.973582	-5.568195	3.939117
C	3.839173	-3.663633	3.197472
C	2.513462	-4.140352	3.160799
C	1.943388	-4.565968	1.957863
C	2.683125	-4.514164	0.769305
C	3.998999	-4.041511	0.794341
C	4.575486	-3.620822	2.000045
H	0.919724	-4.933041	1.949519
H	2.236174	-4.839076	-0.167867
H	4.582974	-3.998769	-0.122858
C	5.712970	-5.701264	4.986813
C	4.979144	-4.712771	5.672024
C	4.634309	-4.921882	7.016473
C	5.030060	-6.096120	7.671460
C	5.768677	-7.068300	6.990103
C	6.106093	-6.870954	5.643490
H	4.032277	-4.192154	7.552462
H	4.748955	-6.249467	8.711059
H	6.073405	-7.980361	7.499559
H	6.671641	-7.628478	5.104402
P	4.505536	-3.119732	4.841956
H	1.922563	-4.189500	4.073962
Pd	3.036301	-1.526733	5.925593

bi-TS-*cis*
E = −12241.9
G = −11858.1
N_{imag} = 1, ν = −210.0i

N	4.716305	-19.986019	-7.397061
C	4.197627	-20.582664	-8.630944
H	4.549578	-21.614848	-8.744725
H	3.105544	-20.579633	-8.574932
H	4.522043	-19.993211	-9.494740
C	6.112791	-19.775963	-7.062751
H	5.969132	-16.390134	-9.980059
C	3.987974	-19.436571	-6.392725
O	2.762139	-19.499660	-6.205806
C	5.013021	-18.700789	-5.555013
H	5.291319	-17.745254	-6.003880
C	4.990236	-18.727606	-4.131294
H	4.501960	-19.576290	-3.653605
C	5.294574	-17.585259	-3.343978
H	5.484768	-16.642631	-3.858453
H	4.785632	-17.475921	-2.385524
H	7.278869	-23.694061	-6.060481
H	5.729185	-23.866431	-5.196283
H	7.059967	-22.924001	-4.474621
C	6.555643	-23.184620	-5.410422
H	5.025991	-21.980441	-6.294664
C	6.799979	-20.929157	-6.407608
N	6.054146	-17.965157	-8.643521
O	8.024849	-20.950205	-6.153219
H	9.921935	-17.592888	-8.756667
H	8.444140	-16.074450	-10.132667
N	6.009012	-21.992646	-6.058882
C	6.841665	-18.800641	-7.903655
C	8.253044	-18.670912	-7.927198

C	6.642766	-17.030196	-9.407487
C	8.838498	-17.694475	-8.729221
H	8.851068	-19.334495	-7.315968
C	8.025981	-16.849027	-9.494340
Pd	7.126038	-18.536909	-2.707265
C	5.538186	-13.285123	-1.551786
C	4.652626	-13.454995	-0.480410
C	4.762819	-14.591303	0.329781
C	5.751896	-15.548137	0.074725
H	7.208294	-14.085724	-2.642340
H	5.459861	-12.408265	-2.191684
H	3.882872	-12.712324	-0.281614
H	4.077846	-14.737405	1.162787
C	6.529967	-14.238361	-1.806504
P	7.878980	-16.711113	-1.418133
C	8.519339	-17.249209	0.260453
C	9.597571	-18.356740	0.222490
C	9.087444	-19.785939	-0.085970
H	7.655547	-17.597838	0.838660
H	8.914997	-16.364651	0.774463
H	10.057686	-18.385063	1.219505
H	10.402513	-18.074788	-0.468255
H	8.140490	-19.966175	0.439312
H	9.796802	-20.527890	0.300280
H	5.804933	-16.425878	0.714039
H	9.267318	-16.902028	-3.977416
C	9.313866	-15.775556	-2.138016
C	9.968014	-14.748932	-1.429358
C	11.051685	-14.073796	-1.999109
C	11.493877	-14.411506	-3.285924
C	10.849170	-15.427469	-3.998664
C	9.765918	-16.106767	-3.426442
H	9.631614	-14.465325	-0.434488
H	11.548556	-13.282653	-1.441084
H	12.336097	-13.883454	-3.728307
H	11.188193	-15.693285	-4.997726
C	6.660405	-15.379264	-0.989864
H	11.606698	-20.329625	-0.829019
H	10.073148	-22.921037	-1.934183
C	10.420123	-20.357164	-2.651369
C	10.488340	-20.439215	-4.055972
C	11.723924	-20.562953	-4.700751
C	12.911608	-20.586361	-3.958607
C	12.854832	-20.495600	-2.563427
C	11.618454	-20.387066	-1.913618
H	11.758676	-20.635182	-5.786296
H	13.872279	-20.672372	-4.462714
H	13.771017	-20.512847	-1.975973
C	9.014133	-23.059195	-1.731458
C	8.152820	-21.948817	-1.683428
C	6.785541	-22.163687	-1.427450
C	6.293270	-23.454204	-1.206142
C	7.159479	-24.553911	-1.256095
C	8.518741	-24.352917	-1.523887
H	6.101310	-21.316318	-1.408335
H	5.233784	-23.601164	-1.005116
H	6.776760	-25.559536	-1.093768
H	9.197616	-25.202566	-1.569563
P	8.731258	-20.186687	-1.890430
H	9.575471	-20.421584	-4.648144

bi-TS-*trans*
E = −12237.7
G = −11854.3
N_{imag} = 1, ν = −175.2i

C	-1.956959	-5.179559	9.324790
H	-1.627377	-6.197505	9.076501
H	-1.919210	-5.048478	10.409861
H	-2.982629	-5.033686	8.972879
C	-0.949369	-3.965479	7.286140
H	2.129884	-7.213685	7.210968
C	-0.080513	-3.517172	9.324126
O	0.294296	-3.614313	10.505521
C	0.462449	-2.557970	8.287662

H	-0.206016	-1.714863	8.101932
C	1.848023	-2.282547	8.170756
H	2.535535	-3.021962	8.579250
C	2.351902	-0.997263	7.828656
H	1.636941	-0.184448	7.695041
H	3.299400	-0.689218	8.272354
H	-3.751323	-2.032360	4.829348
H	-2.422769	-1.543435	3.751870
H	-2.680730	-0.696496	5.302219
C	-2.718969	-1.670479	4.796219
H	-0.921518	-2.809189	4.981429
C	-2.004582	-3.091352	6.704513
N	0.733087	-5.693428	7.218580
O	-2.994198	-2.707723	7.371522
H	-0.358533	-6.950320	3.704522
H	1.512160	-8.096547	4.956619
N	-1.819820	-2.645170	5.419329
C	-0.269436	-5.054523	6.549197
C	-0.668853	-5.495738	5.263347
C	1.332453	-6.741135	6.635851
C	-0.037135	-6.594219	4.681134
H	-1.497371	-5.018121	4.750586
C	0.992251	-7.237737	5.372618
N	-1.081957	-4.183802	8.708701
C	3.340875	3.609673	7.518129
C	4.455682	3.601801	8.365176
C	5.423497	2.600523	8.220403
C	5.281310	1.617740	7.234426
H	2.325770	2.656353	5.880835
H	2.579310	4.379823	7.624137
H	4.566898	4.364724	9.132696
H	6.291632	2.580293	8.876254
C	3.197999	2.630386	6.529003
P	3.922847	0.249207	5.148235
C	5.628904	0.037980	4.398417
C	5.734136	-1.049467	3.304111
C	5.747106	-2.513092	3.807641
H	6.315979	-0.197698	5.219659
H	5.939082	1.006833	3.988431
H	6.683771	-0.879612	2.779148
H	4.948689	-0.904918	2.551096
H	6.367205	-2.593115	4.710008
H	6.214261	-3.163755	3.058442
H	6.042361	0.845374	7.153952
H	1.365793	-0.409795	3.909381
C	2.956165	1.038443	3.772675
C	3.422780	2.180299	3.092359
C	2.675338	2.739317	2.051443
C	1.451008	2.168366	1.677369
C	0.977929	1.035995	2.348074
C	1.728161	0.474588	3.389041
H	4.365219	2.643858	3.375172
H	3.047016	3.621525	1.534186
H	0.870644	2.606094	0.867876
H	0.028530	0.588885	2.061168
C	4.172733	1.626774	6.363633
H	4.937930	-3.271837	1.337919
H	4.591254	-5.916985	2.898333
C	3.243424	-3.574093	2.664913
C	1.871165	-3.884720	2.702830
C	1.156754	-4.134029	1.527548
C	1.800325	-4.058308	0.285863
C	3.161895	-3.741407	0.232063
C	3.879738	-3.505553	1.411819
H	0.098430	-4.381637	1.578365
H	1.244416	-4.242164	-0.631019
H	3.671207	-3.680141	-0.727675
C	4.842872	-6.023960	3.950461
C	4.669305	-4.943894	4.833849
C	4.993509	-5.119276	6.191589
C	5.497887	-6.339501	6.653650
C	5.669201	-7.409110	5.765900
C	5.335911	-7.249258	4.415586
H	4.843523	-4.299107	6.892144

H	5.746754	-6.457168	7.706545
H	6.053020	-8.361756	6.125379
H	5.460016	-8.077986	3.720878
P	4.089035	-3.257575	4.290794
H	1.363397	-3.943310	3.663289
Pd	3.059053	-1.799619	5.951955

bi-PC-*cis*
E = −12253.9
G = −11869.7
N_{imag} = 0

N	4.889530	-19.478318	-7.493951
C	4.394269	-19.853182	-8.818740
H	4.157261	-20.921716	-8.859062
H	3.483883	-19.278892	-9.010239
H	5.133152	-19.622071	-9.595985
C	6.136773	-19.889857	-6.756116
H	9.200267	-17.361319	-8.926531
C	4.650272	-18.362899	-6.734278
O	3.786425	-17.494284	-6.820885
C	5.860546	-18.634649	-5.792877
H	6.624002	-17.872860	-5.973150
C	5.535025	-18.773871	-4.322634
H	5.047395	-19.700807	-4.024192
C	5.266351	-17.608529	-3.581230
H	5.385275	-16.627140	-4.038613
H	4.579826	-17.642577	-2.736118
H	4.956711	-23.915764	-5.803956
H	3.472398	-23.190524	-5.133822
H	5.022784	-23.047581	-4.255113
C	4.551536	-23.064778	-5.242905
H	4.017712	-21.291239	-6.331355
C	6.042724	-21.264143	-6.049647
N	7.834869	-18.537271	-7.905151
O	7.054085	-21.806553	-5.582745
H	9.374868	-21.590345	-9.748401
H	10.262809	-19.264290	-10.152805
N	4.802911	-21.803390	-5.947036
C	7.371283	-19.781359	-7.669886
C	7.904527	-20.904456	-8.323536
C	8.851383	-18.382720	-8.773155
C	8.952496	-20.731964	-9.230992
H	7.515080	-21.897620	-8.125366
C	9.445271	-19.445399	-9.459470
Pd	7.167215	-18.323977	-2.743207
C	4.819232	-13.837977	-0.471359
C	4.243817	-14.258901	0.735159
C	4.774465	-15.373042	1.395225
C	5.871758	-16.058634	0.858298
H	6.342216	-14.180178	-1.947643
H	4.415442	-12.974205	-0.996635
H	3.392104	-13.726304	1.153244
H	4.337045	-15.712468	2.332491
C	5.913581	-14.522565	-1.008368
P	7.809915	-16.625611	-1.177599
C	8.821700	-17.255853	0.276136
C	9.993124	-18.178823	-0.139988
C	9.593202	-19.635853	-0.483893
H	8.144213	-17.809440	0.937007
H	9.201772	-16.399000	0.845938
H	10.690198	-18.222887	0.708118
H	10.556217	-17.722686	-0.965006
H	8.824809	-19.978531	0.221443
H	10.451572	-20.306400	-0.349785
H	6.254927	-16.923863	1.393070
H	8.975325	-16.194853	-3.810907
C	8.927592	-15.292780	-1.853674
C	9.395285	-14.222731	-1.066455
C	10.246774	-13.256346	-1.611072
C	10.645222	-13.344658	-2.952676
C	10.187024	-14.402894	-3.744618
C	9.333610	-15.370139	-3.196786
H	9.089263	-14.133525	-0.025951
H	10.597982	-12.433772	-0.990685

H	11.306746	-12.591206	-3.375696
H	10.491347	-14.476935	-4.786916
C	6.466462	-15.640059	-0.348866
H	11.883806	-19.562063	-1.860078
H	10.256411	-22.648836	-2.260385
C	10.346501	-20.118331	-3.291995
C	10.118590	-20.485903	-4.634210
C	11.183202	-20.595593	-5.533535
C	12.493890	-20.319556	-5.118794
C	12.729911	-19.942229	-3.793060
C	11.665515	-19.847023	-2.885160
H	10.988546	-20.890507	-6.562837
H	13.320433	-20.396423	-5.822623
H	13.742588	-19.724805	-3.457964
C	9.214747	-22.808986	-1.991615
C	8.327410	-21.720074	-1.925506
C	6.985715	-21.962967	-1.582604
C	6.542130	-23.259431	-1.297490
C	7.433118	-24.337624	-1.369042
C	8.769484	-24.108911	-1.720964
H	6.285294	-21.129757	-1.548074
H	5.500788	-23.428397	-1.028983
H	7.088512	-25.347990	-1.157266
H	9.467676	-24.942025	-1.782646
P	8.853747	-19.946555	-2.191382
H	9.105570	-20.699290	-4.971868

bi-PC-*trans*
E = −12253.5
G = −11868.5
N_{imag} = 0

C	-1.350606	-2.039565	0.002679
H	-1.973923	-2.923024	0.190942
H	-1.999748	-1.192995	-0.238364
H	-0.681128	-2.240865	-0.837918
C	0.341292	-2.489854	2.046496
H	-3.195184	-4.408592	4.092547
C	-0.721854	-0.653623	2.073139
O	-1.449144	0.338299	2.069669
C	0.396085	-1.206636	3.011518
H	1.308730	-0.645021	2.775885
C	0.196978	-1.229485	4.499467
H	-0.581759	-1.887221	4.874143
C	0.569154	-0.101430	5.241419
H	1.034577	0.752652	4.751241
H	0.082240	0.118121	6.190422
H	4.130649	-4.066071	1.097458
H	4.773238	-3.264680	2.552829
H	4.481135	-2.323975	1.064273
C	4.115122	-3.145982	1.690508
H	2.624330	-2.705328	3.175628
C	1.690072	-2.790858	1.349387
N	-1.550712	-3.548444	3.176219
O	1.772611	-2.949448	0.119273
H	-0.205450	-7.154955	2.643435
H	-2.410509	-6.764740	3.799194
N	2.758483	-2.869983	2.177454
C	-0.360620	-3.753358	2.572445
C	0.152873	-5.041828	2.365214
C	-2.242734	-4.617274	3.604790
C	-0.582128	-6.147553	2.804728
H	1.101218	-5.188640	1.857778
C	-1.804379	-5.935994	3.442472
N	-0.583613	-1.684874	1.191966
C	2.719489	3.733544	8.138064
C	1.732709	3.567475	9.115915
C	1.349774	2.273219	9.494153
C	1.949308	1.159535	8.898569
H	4.095585	2.771926	6.794264
H	3.021883	4.733399	7.831875
H	1.262711	4.434707	9.574925
H	0.578449	2.129883	10.248662
C	3.328556	2.617800	7.548333
P	3.638722	-0.215762	7.108696

C	4.391196	-1.110505	8.578797
C	4.954145	-2.509296	8.233696
C	3.898503	-3.636904	8.120921
H	3.597831	-1.202096	9.330608
H	5.174884	-0.486716	9.024558
H	5.643925	-2.793921	9.040077
H	5.568501	-2.448845	7.325863
H	3.155769	-3.513938	8.919463
H	4.375100	-4.610969	8.285781
H	1.618330	0.164545	9.191291
H	4.184402	0.039642	4.279356
C	5.131890	0.403873	6.182466
C	6.301621	0.870710	6.812522
C	7.388662	1.321262	6.055586
C	7.322646	1.319871	4.655992
C	6.164520	0.862809	4.017380
C	5.081237	0.404331	4.776878
H	6.373264	0.894097	7.897323
H	8.285521	1.676922	6.559231
H	8.168697	1.671880	4.069260
H	6.104571	0.858954	2.930936
C	2.959458	1.313262	7.925374
H	5.848975	-4.386604	6.307471
H	2.829768	-6.624834	7.515133
C	3.909186	-4.920648	5.485894
C	3.268888	-5.718480	4.516476
C	4.002364	-6.564276	3.680022
C	5.398883	-6.620345	3.782023
C	6.049729	-5.823654	4.729758
C	5.312925	-4.983156	5.575152
H	3.484528	-7.182616	2.949120
H	5.971161	-7.277206	3.130431
H	7.133874	-5.857475	4.820557
C	1.823085	-6.220957	7.597458
C	1.546278	-4.911197	7.159974
C	0.232854	-4.426433	7.272571
C	-0.782549	-5.224830	7.815266
C	-0.496589	-6.524361	8.246663
C	0.809265	-7.021404	8.134466
H	0.008421	-3.418814	6.927886
H	-1.794674	-4.832674	7.894460
H	-1.284149	-7.148521	8.664497
H	1.038377	-8.032746	8.465600
P	2.880798	-3.762063	6.528191
H	2.185625	-5.689768	4.425165
Pd	2.106033	-1.588126	5.829919

bi-P-*cis*
E = -4591.6
G = -4460.6
N_{imag} = 0

N	-1.199413	0.102756	-0.141276
C	-1.803001	0.631079	-1.365737
H	-2.608264	-0.021597	-1.718288
H	-2.217093	1.616429	-1.136654
H	-1.052441	0.732810	-2.159084
C	-0.434679	-1.167308	0.109523
H	3.435490	0.028304	-1.890286
C	-0.743534	0.754422	0.975497
O	-0.929574	1.894135	1.388402
C	0.090563	-0.466298	1.459431
H	1.157011	-0.243990	1.363618
C	-0.234177	-1.049924	2.798166
H	-1.272645	-1.333807	2.976357
C	0.660472	-1.191864	3.782446
H	1.705500	-0.914972	3.650033
H	0.373924	-1.588951	4.753797
H	-3.367819	-4.199172	0.176527
H	-4.584143	-2.968298	0.611383
H	-3.466269	-3.603045	1.849162
C	-3.566823	-3.318586	0.794723
H	-3.000232	-1.299319	0.338143
C	-1.297093	-2.418717	0.397354
N	1.676611	-0.557316	-0.967141

O	-0.748869	-3.512843	0.612009
H	1.368885	-3.288781	-3.712226
H	3.329713	-1.703800	-3.691210
N	-2.635820	-2.238860	0.446236
C	0.636582	-1.416330	-0.965213
C	0.492525	-2.410177	-1.944992
C	2.608420	-0.680522	-1.929259
C	1.463018	-2.524877	-2.944081
H	-0.354257	-3.088481	-1.929521
C	2.548872	-1.647698	-2.937128

bi-P-*trans*
E = -4590.3
G = - -4459.0
N_{imag} = 0

N	-0.928167	0.636287	0.028876
C	-1.717474	1.010683	-1.139317
H	-2.715215	0.562985	-1.078610
H	-1.810255	2.100369	-1.138973
H	-1.225736	0.682940	-2.059855
C	-0.593440	-0.687290	0.627196
H	-4.888187	-0.822666	2.040020
C	-0.374525	1.389693	1.014896
O	-0.323583	2.604456	1.199567
C	0.165556	0.146475	1.784937
H	1.254116	0.090016	1.673166
C	-0.226094	-0.017802	3.218481
H	-1.291497	0.028069	3.442239
C	0.653129	-0.176179	4.214995
H	1.726572	-0.218736	4.033362
H	0.325711	-0.264305	5.248592
H	1.730152	-3.680887	-1.167058
H	2.978282	-3.464697	0.091353
H	2.897962	-2.345179	-1.295471
C	2.306344	-2.946897	-0.595518
H	1.636179	-1.930161	1.163089
C	0.295704	-1.525107	-0.332982
N	-2.925442	-0.775946	1.380647
O	-0.041221	-1.667530	-1.520016
H	-2.896527	-4.639822	1.809346
H	-4.966052	-3.302880	2.345212
N	1.401285	-2.100259	0.192731
C	-1.821090	-1.491691	1.088097
C	-1.775845	-2.887189	1.230581
C	-4.014341	-1.435356	1.818377
C	-2.910758	-3.558991	1.691067
H	-0.875056	-3.444061	0.990030
C	-4.058490	-2.821704	1.989717

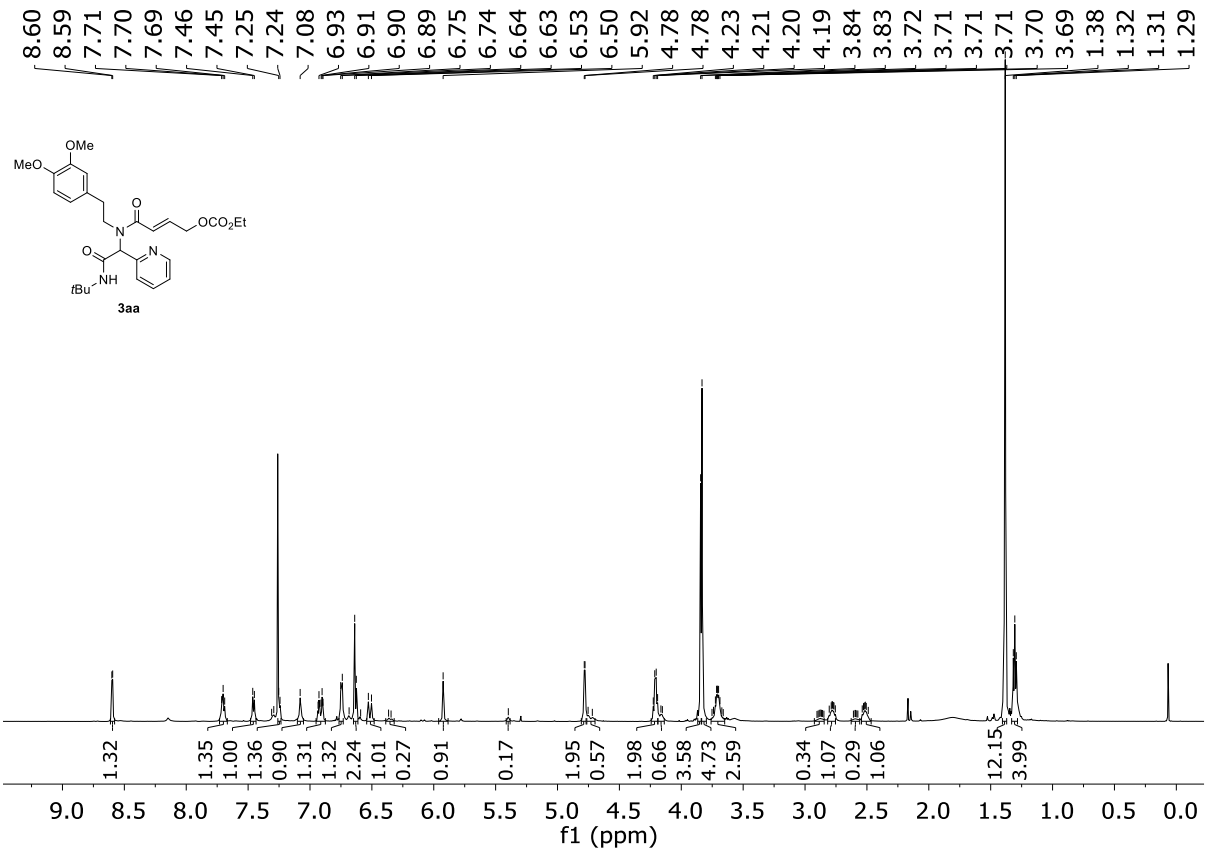
B′ anti-p-allyl
E = -12250.74
G = -11865.04
N_{imag} = 0

C	0.160684	1.775075	6.323976
H	0.812451	1.804427	7.201073
H	0.463903	2.567689	5.626949
H	-0.877513	1.938863	6.624265
C	-0.797630	0.072819	4.738995
H	1.527144	2.235784	1.590085
C	1.481526	-0.139569	5.566201
O	2.533196	0.373878	6.013018
C	1.448980	-1.490051	4.921643
H	0.524819	-2.048724	5.028489
C	2.371568	-1.947716	3.962372
H	2.100630	-2.857793	3.426180
C	3.676914	-1.445030	3.784183
H	3.933702	-0.444774	4.119569
H	4.308002	-1.887063	3.018815
H	-3.951115	-1.035869	7.241940
H	-2.749422	-1.663988	8.394537
H	-3.145343	-2.582606	6.918809
C	-3.000632	-1.574511	7.334240
H	-1.035713	-0.760166	7.143318
C	-1.974027	-0.551920	5.308215

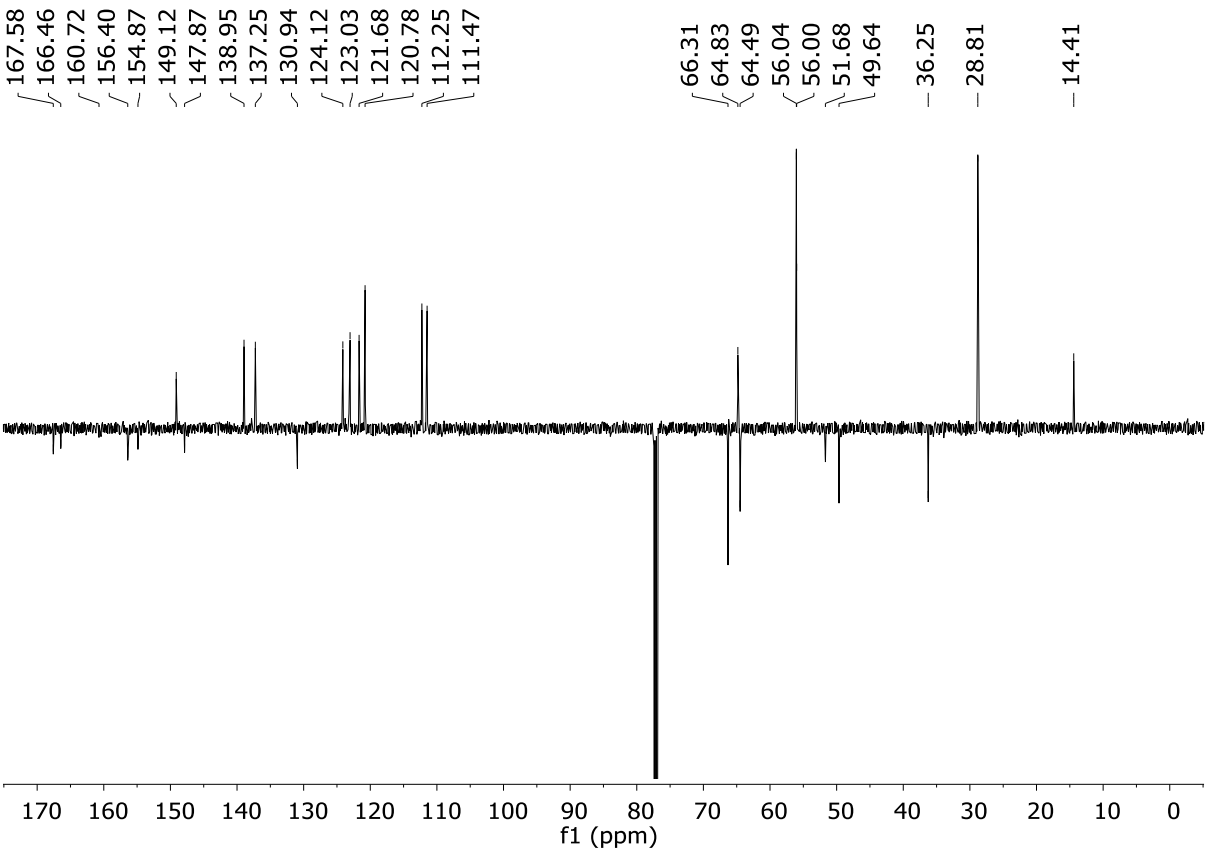
N	0.454591	1.239444	3.044847
O	-3.032873	-0.840237	4.669250
H	-2.070014	0.282148	0.240843
H	-0.027933	1.689871	-0.289468
N	-1.923679	-0.850900	6.665676
C	-0.649067	0.478315	3.357463
C	-1.577181	0.126361	2.324858
C	0.632794	1.634947	1.775075
C	-1.361576	0.554934	1.022504
H	-2.442820	-0.471211	2.583854
C	-0.231137	1.334382	0.718002
N	0.250444	0.456586	5.665812
C	8.437974	-0.715569	3.519672
C	8.529249	0.499339	4.207524
C	7.848222	0.661129	5.420745
C	7.082280	-0.385235	5.943172
H	7.618482	-2.703693	3.493162
H	8.959185	-0.849504	2.574086
H	9.121937	1.315637	3.800466
H	7.906873	1.604210	5.959885
C	7.676744	-1.768071	4.041971
P	5.906773	-2.947124	5.946841
C	6.527319	-3.152744	7.697160
C	5.742210	-4.170522	8.555669
C	4.382681	-3.665055	9.089888
H	6.498226	-2.162566	8.167225
H	7.582063	-3.445803	7.640341
H	6.365336	-4.405134	9.428247
H	5.621225	-5.116393	8.012154
H	4.492673	-2.647452	9.486711
H	4.049220	-4.285133	9.930383
H	6.545332	-0.228471	6.875840
H	4.478932	-4.828978	4.214088
C	6.421941	-4.509376	5.102244
C	7.728069	-5.021162	5.235794
C	8.088988	-6.211099	4.597314
C	7.154035	-6.903358	3.815868
C	5.855917	-6.401999	3.676026
C	5.491517	-5.212020	4.317511
H	8.471439	-4.494211	5.829161
H	9.100551	-6.595671	4.708109
H	7.438086	-7.829006	3.319961
H	5.125092	-6.934678	3.071569
C	6.998470	-1.617968	5.265220
H	3.464661	-6.230280	9.232208
H	0.738938	-4.598317	9.590381
C	2.397545	-5.288285	7.588916
C	1.515033	-5.524409	6.516602
C	1.023291	-6.808072	6.265321
C	1.419962	-7.881636	7.072655
C	2.303884	-7.661245	8.134287
C	2.787089	-6.372889	8.395416
H	0.337403	-6.970225	5.436655
H	1.044766	-8.883012	6.873013
H	2.618446	-8.489886	8.765194
C	0.748031	-3.513819	9.657674
C	1.673585	-2.762299	8.911885
C	1.655836	-1.358178	9.010511
C	0.740321	-0.720589	9.855202
C	-0.175483	-1.475373	10.599190
C	-0.172103	-2.871056	10.494466
H	2.347089	-0.760823	8.419366
H	0.740245	0.364878	9.928697
H	-0.889540	-0.978263	11.252254
H	-0.884148	-3.463814	11.065010
P	2.980631	-3.551590	7.858236
H	1.211949	-4.700277	5.874437
Pd	3.597684	-2.484233	5.803393

NMR spectra

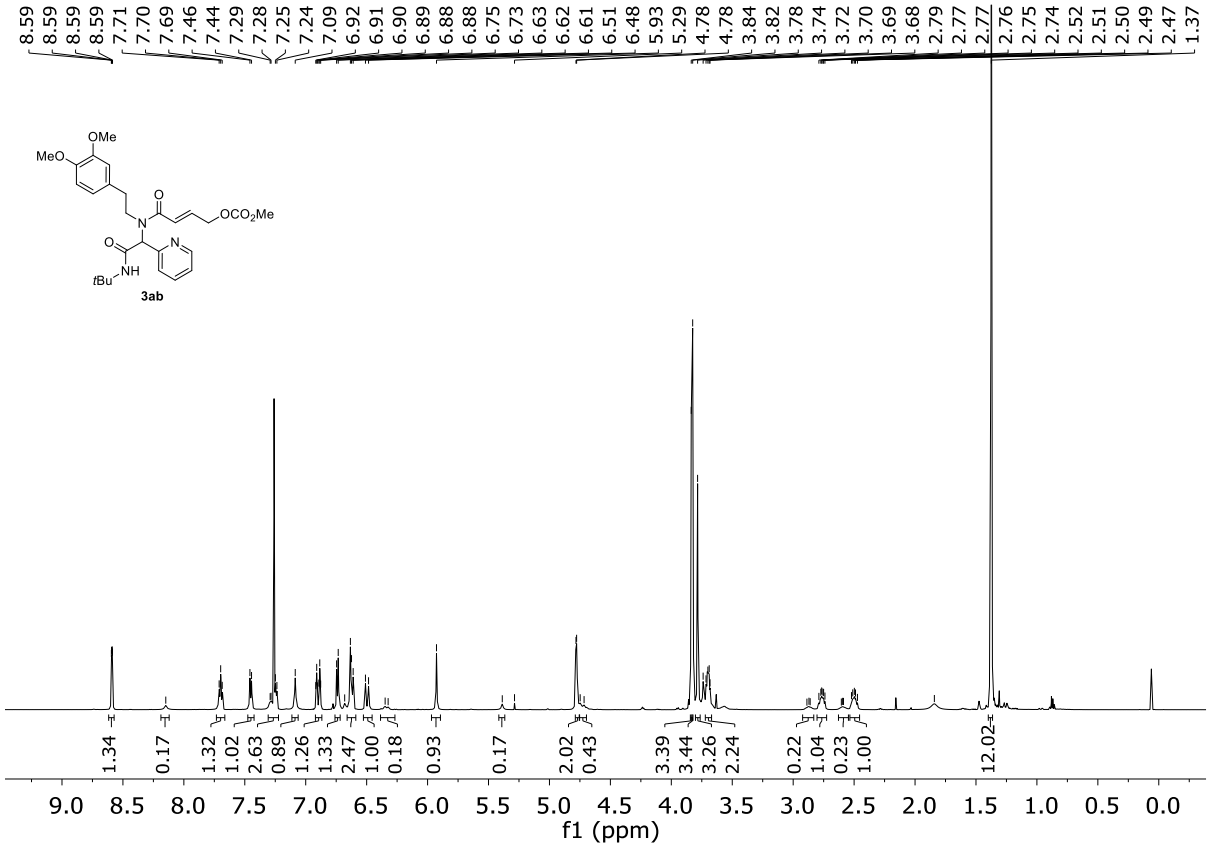
^{1}H NMR (3aa) 600 MHz, $CDCl_3$



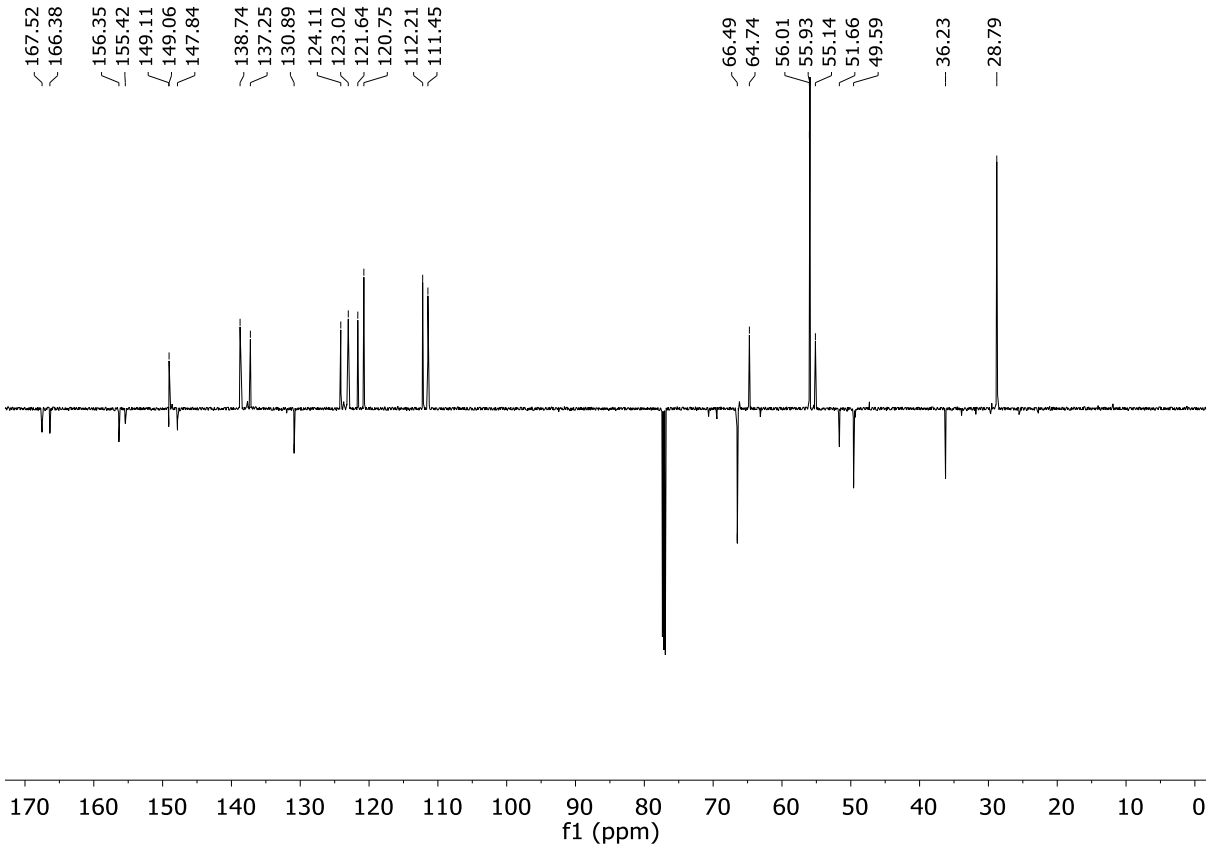
^{13}C NMR (3aa) 151 MHz, $CDCl_3$



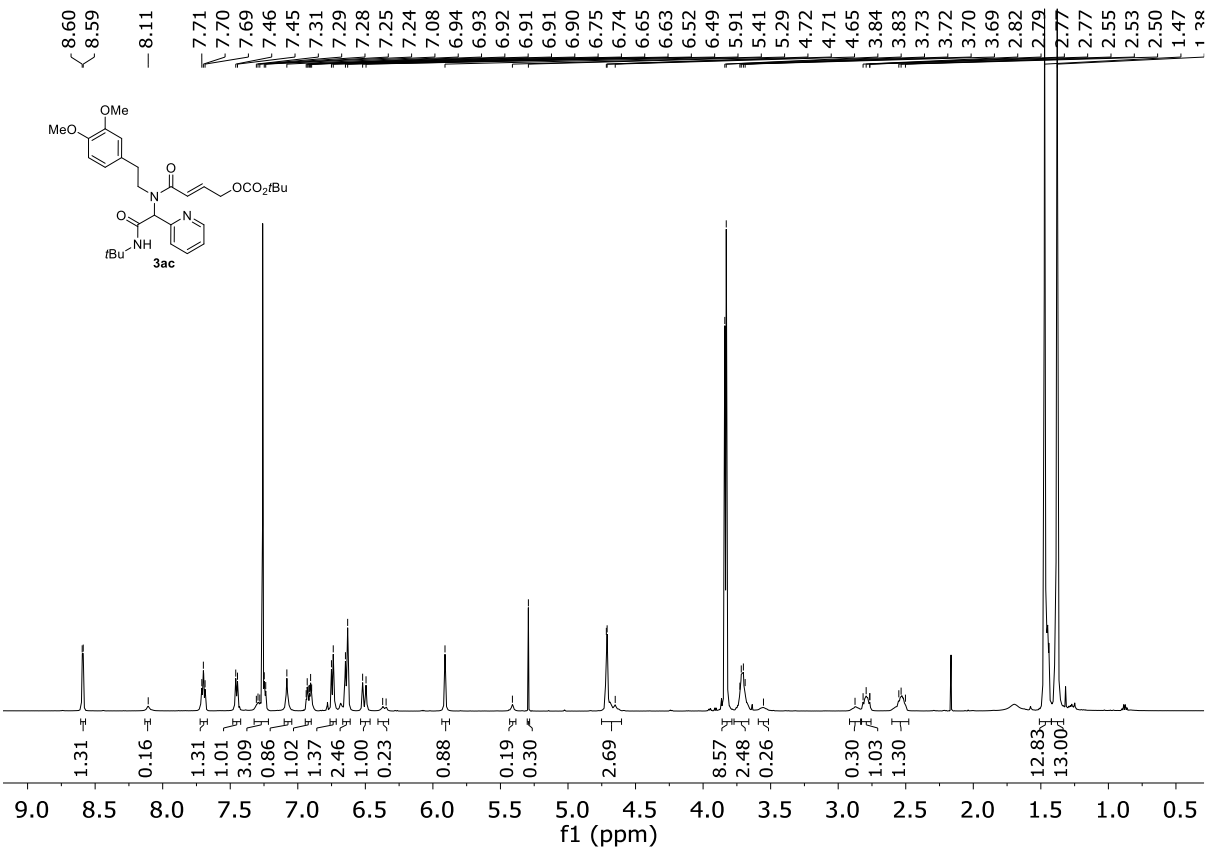
^{1}H NMR (3ab) 600 MHz, $CDCl_3$



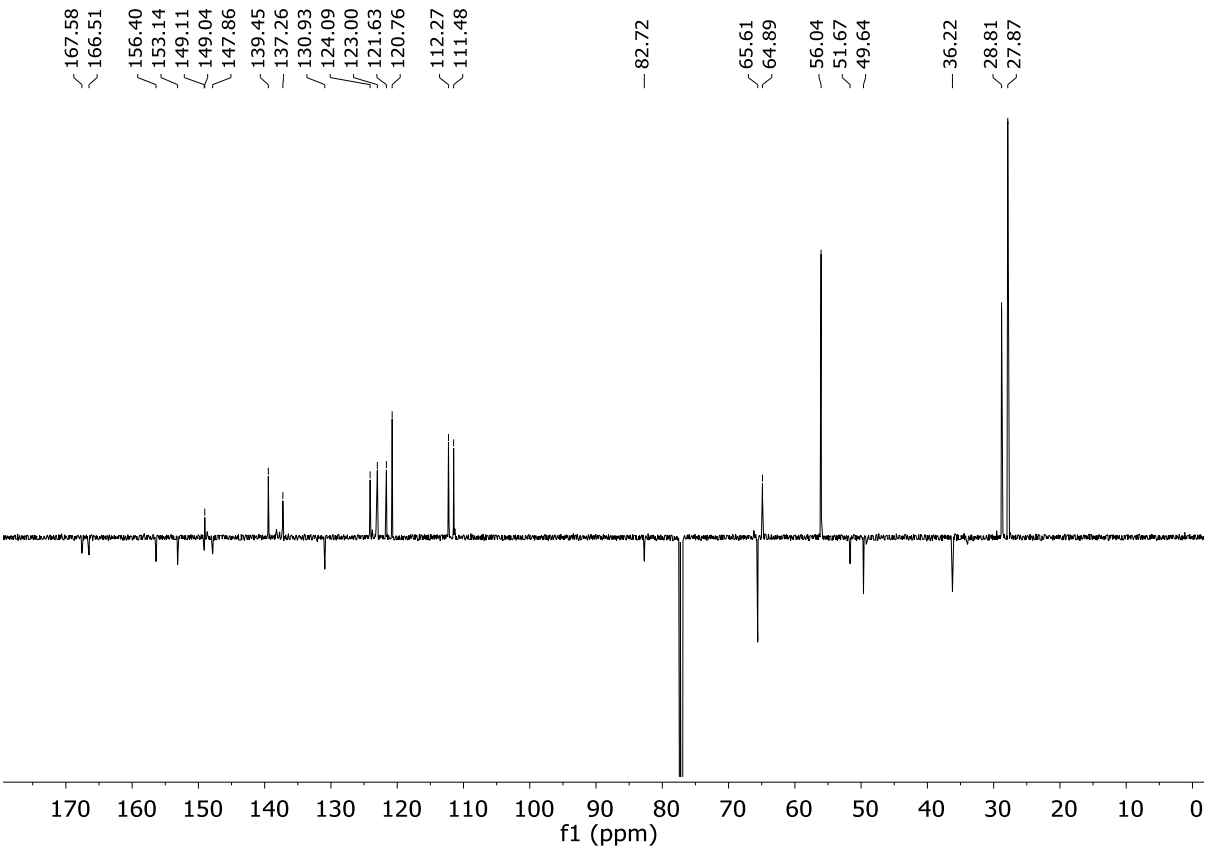
^{13}C NMR (3ab) 151 MHz, $CDCl_3$



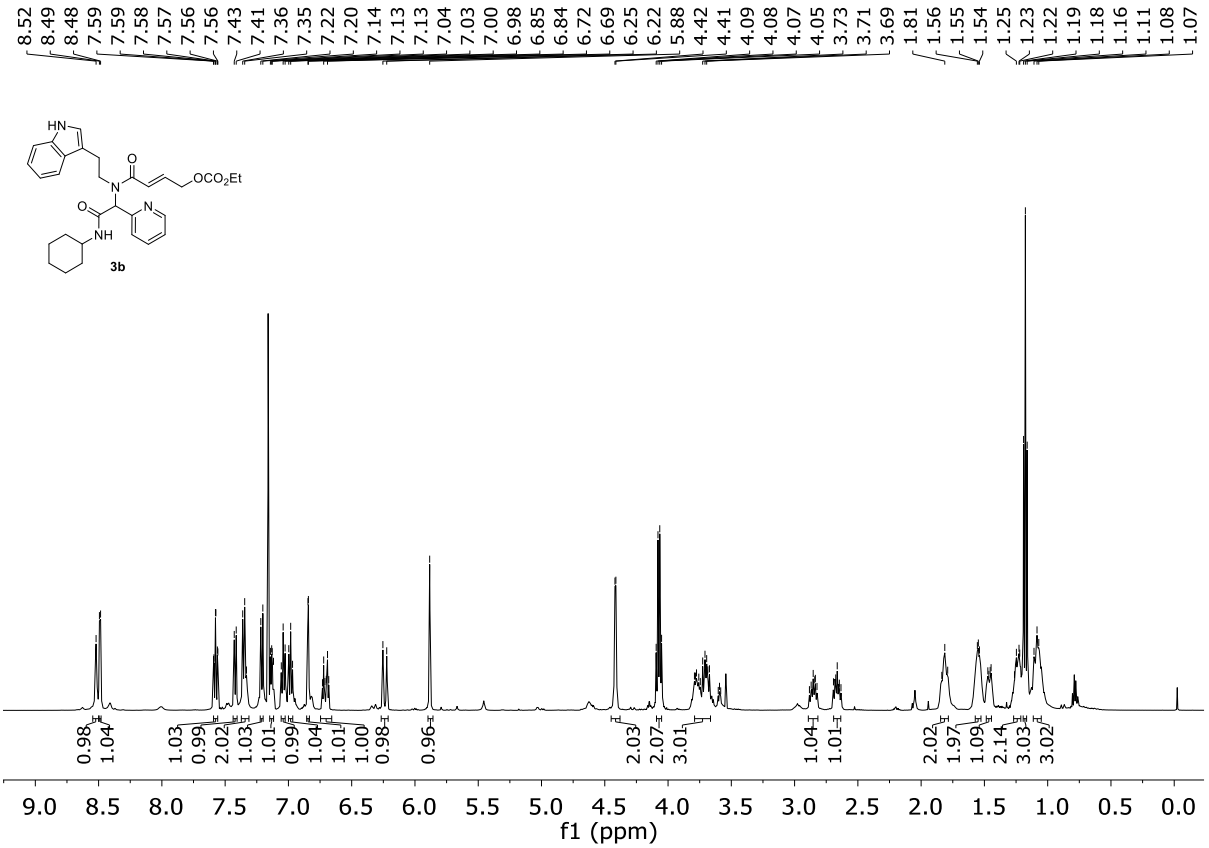
^{1}H NMR (3ac) 600 MHz, $CDCl_3$



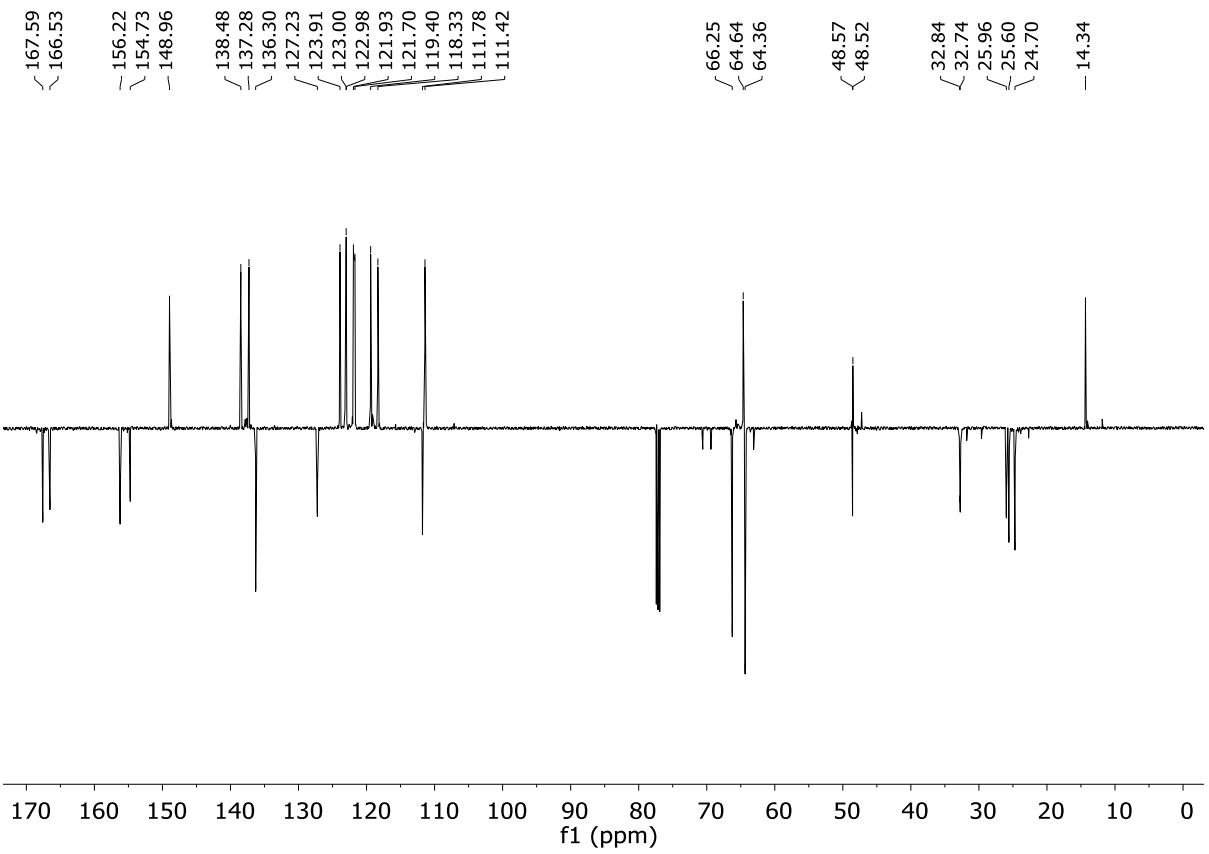
^{13}C NMR (3ac) 151 MHz, $CDCl_3$



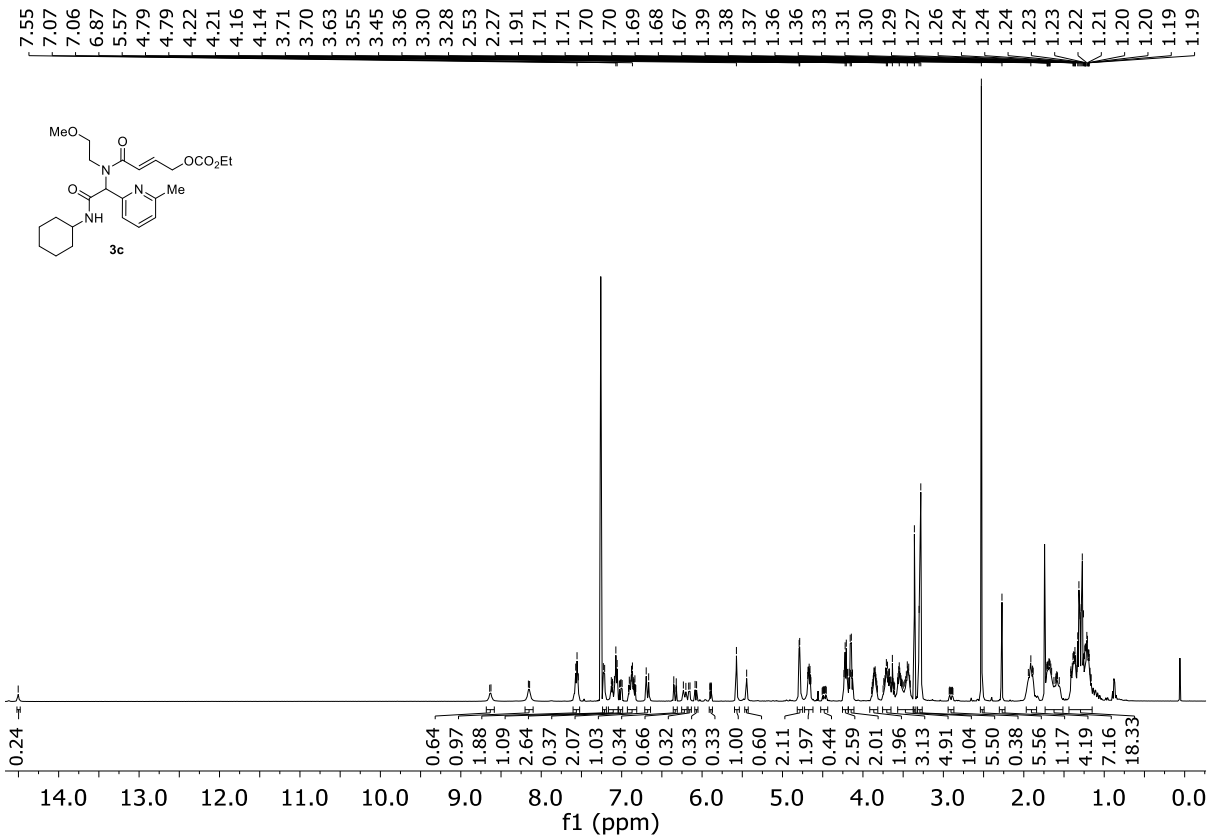
^{1}H NMR (3b) 500 MHz, $CDCl_3$



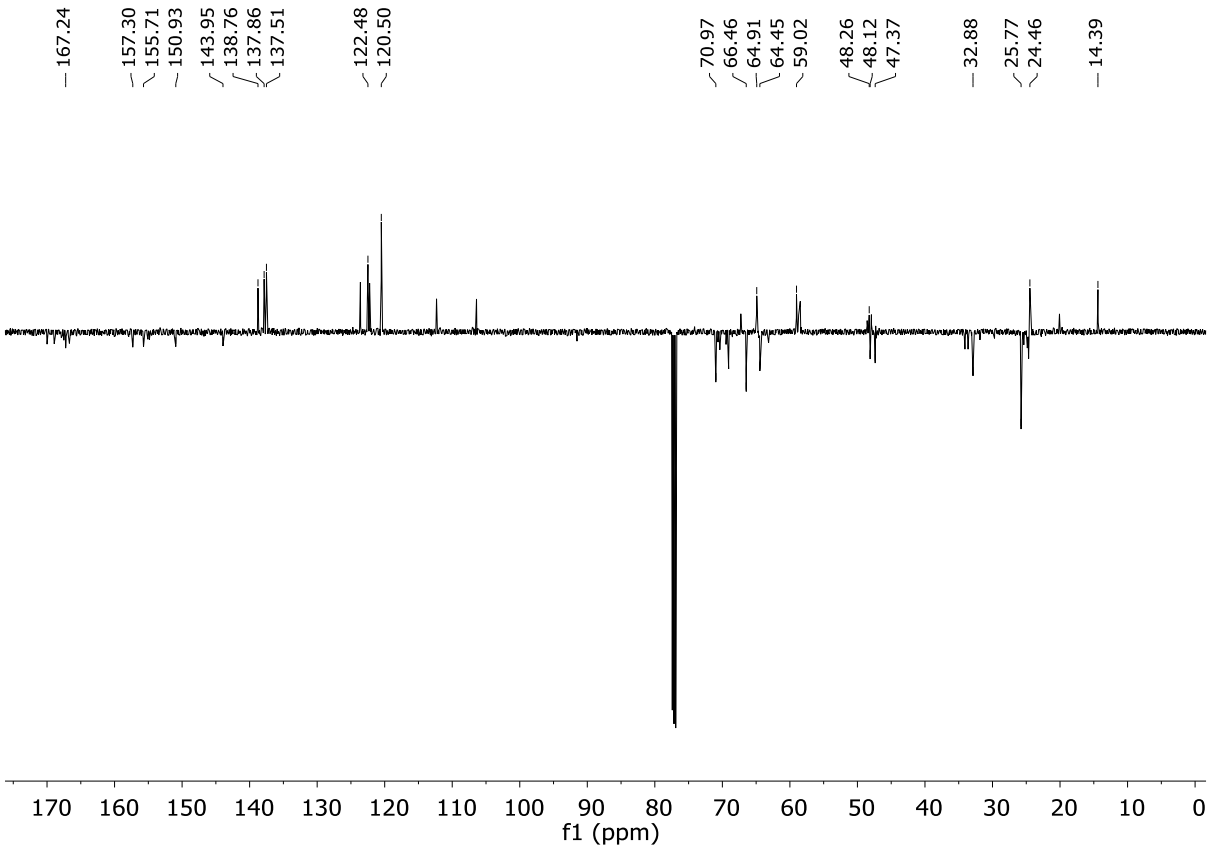
^{13}C NMR (3b) 126 MHz, $CDCl_3$



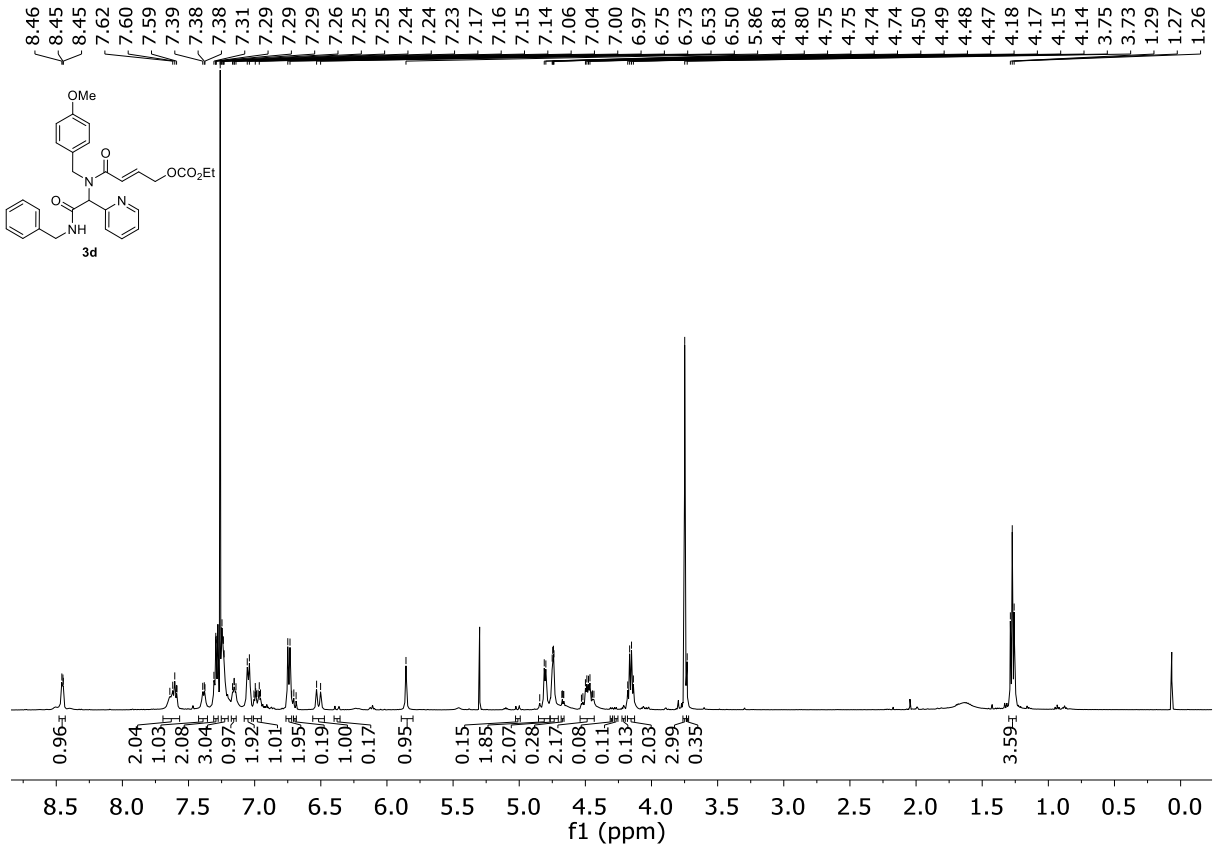
^{1}H NMR (3c) 500 MHz, $CDCl_3$



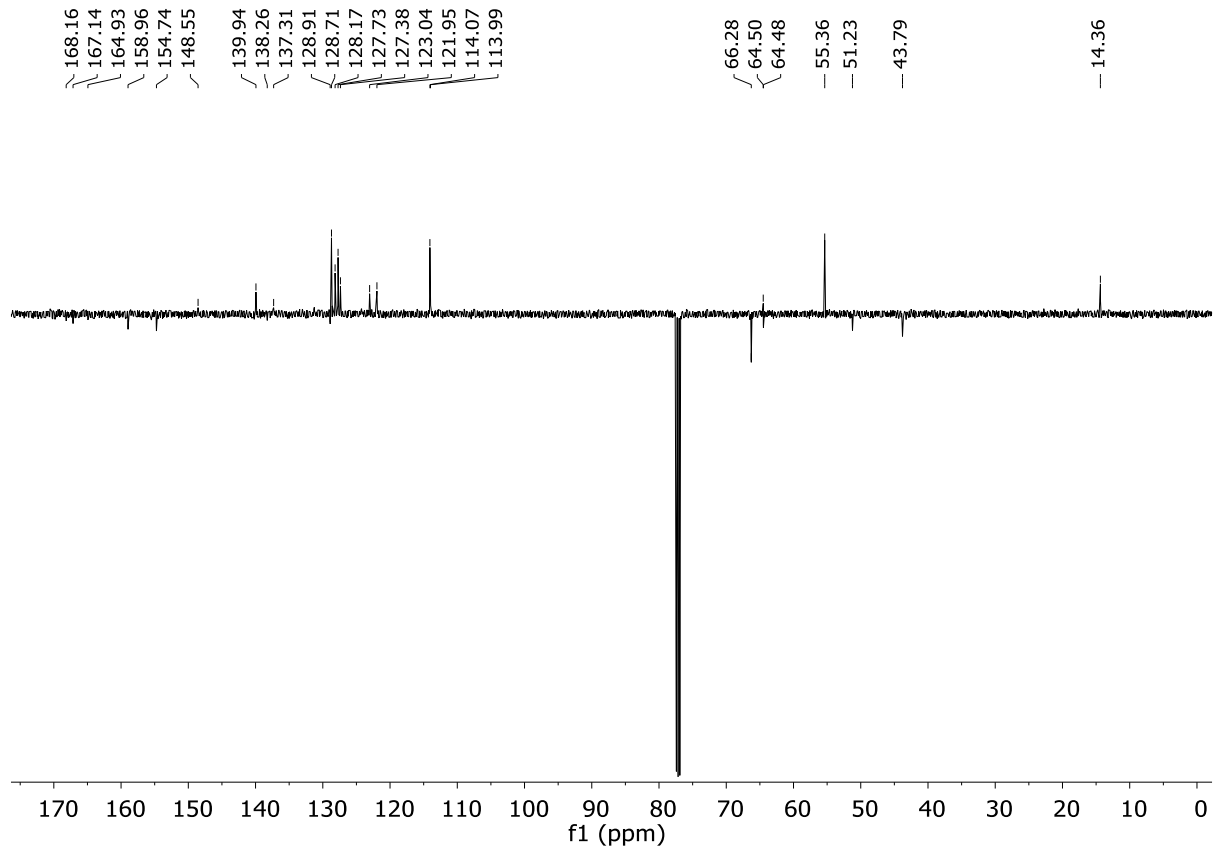
^{13}C NMR (3c) 126 MHz, $CDCl_3$



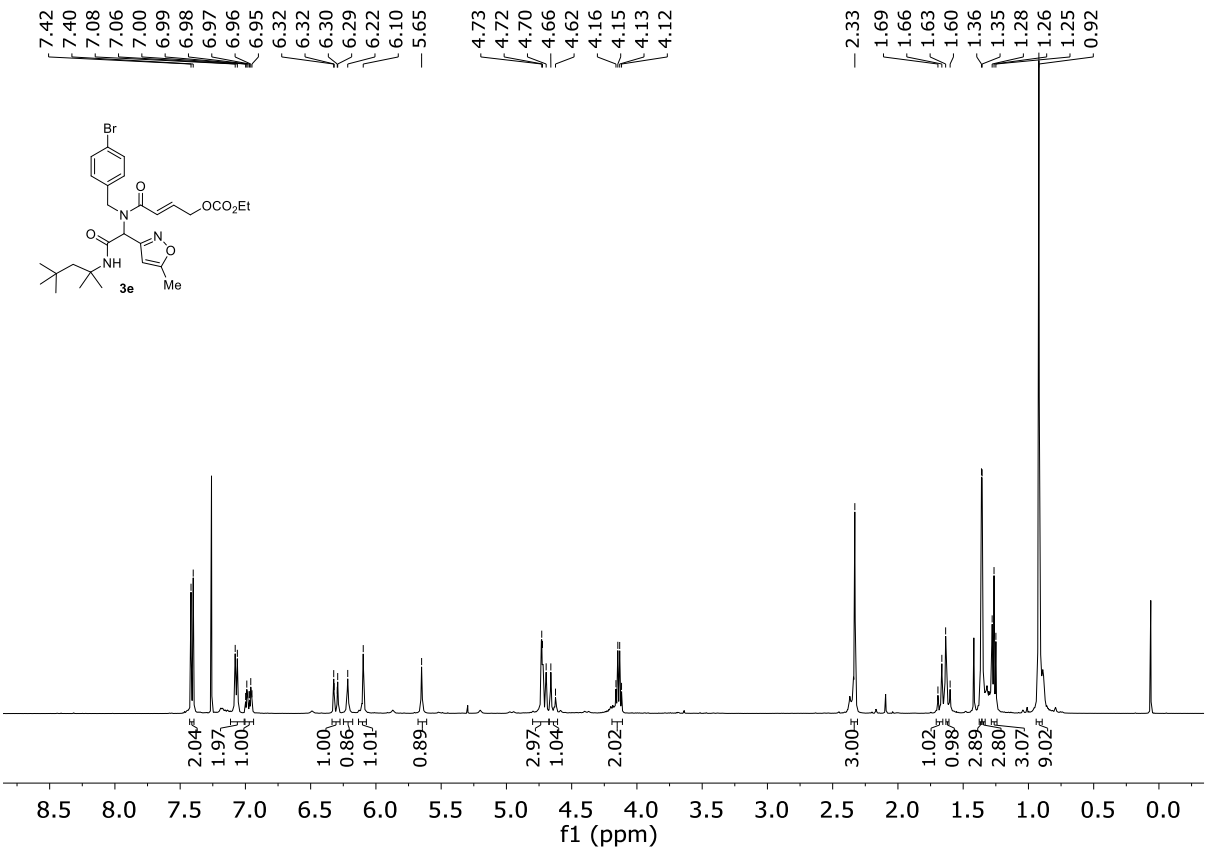
^{1}H NMR (3d) 500 MHz, $CDCl_3$



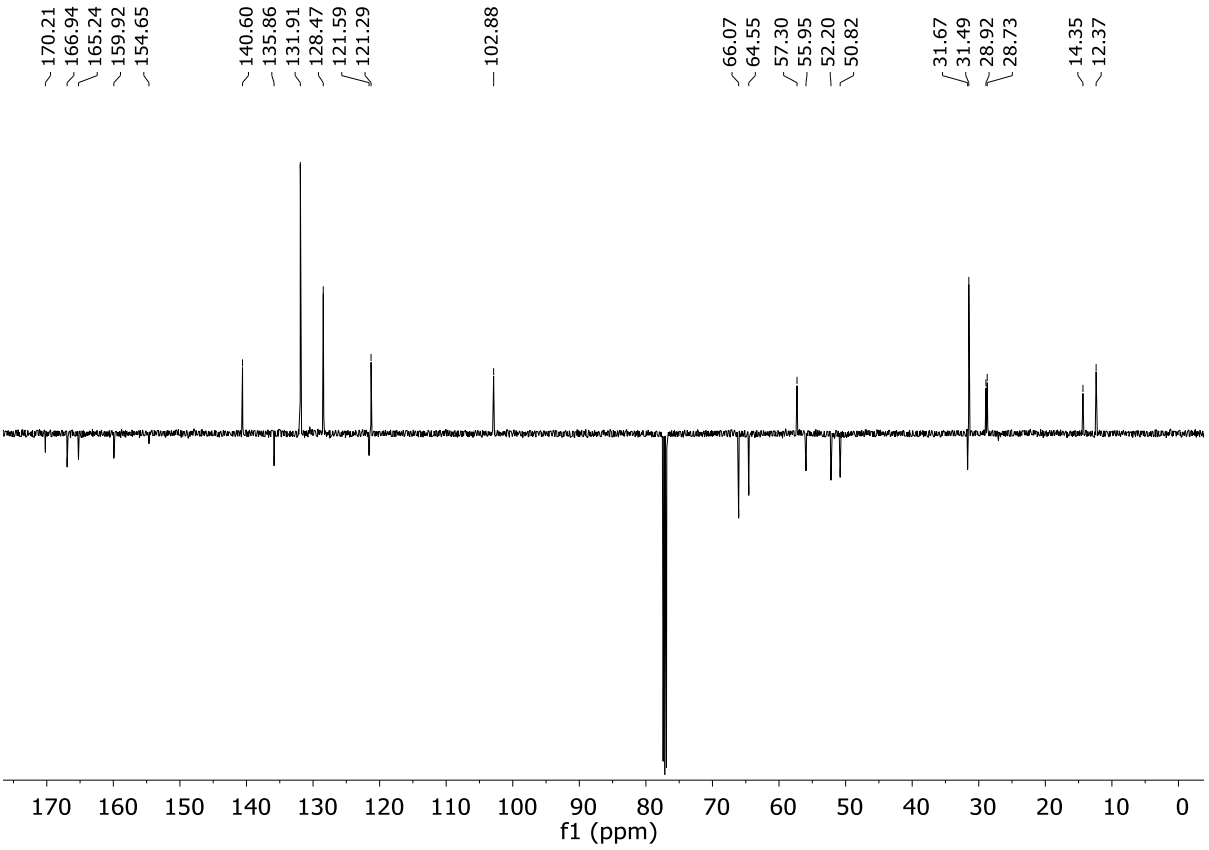
^{13}C NMR (3d) 126 MHz, $CDCl_3$



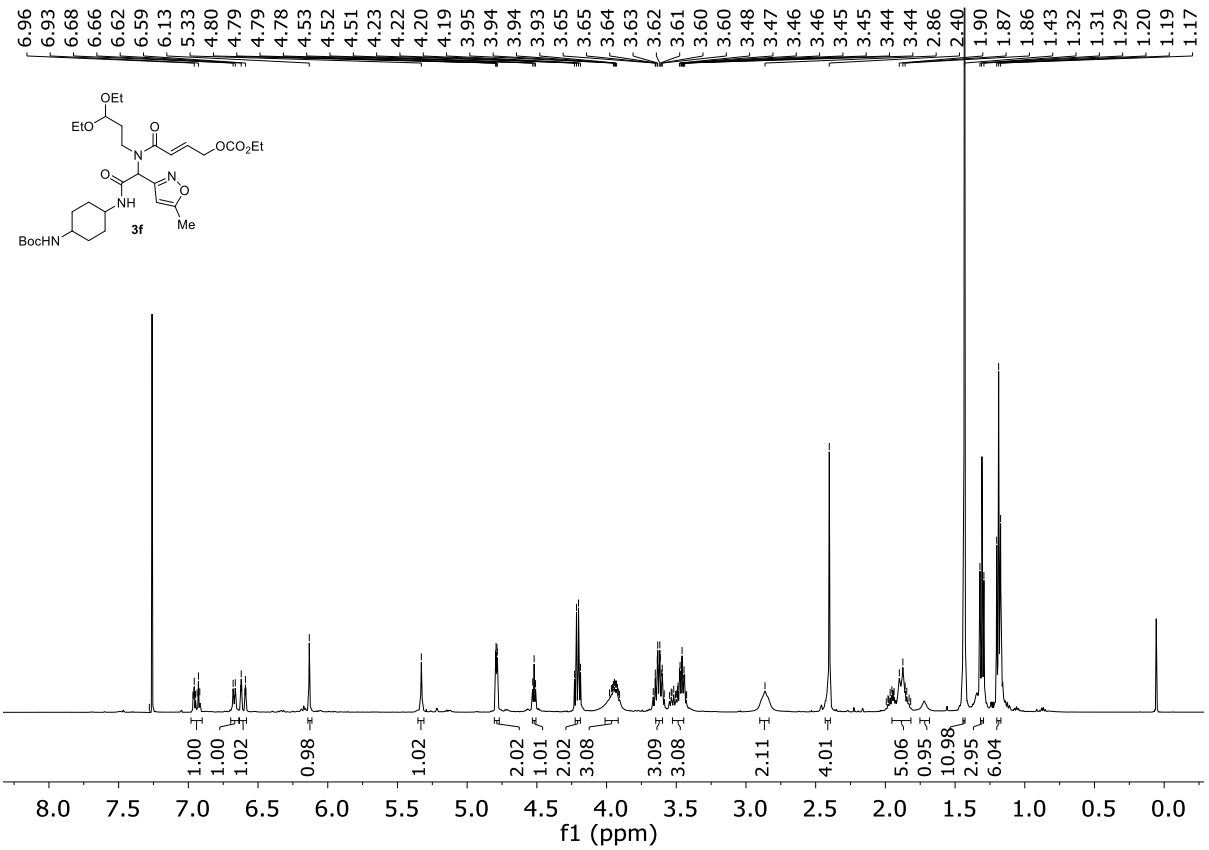
^{1}H NMR (3e) 500 MHz, $CDCl_3$



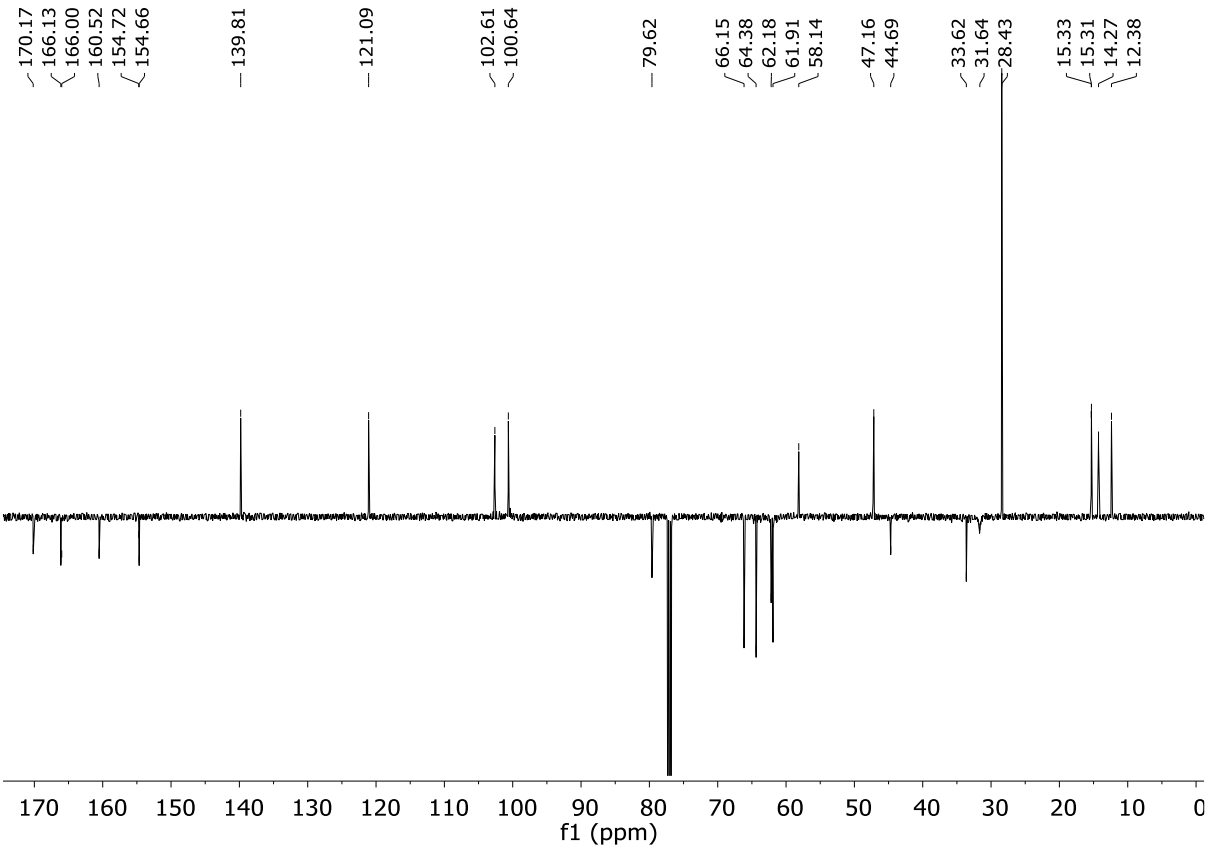
^{13}C NMR (3e) 126 MHz, $CDCl_3$



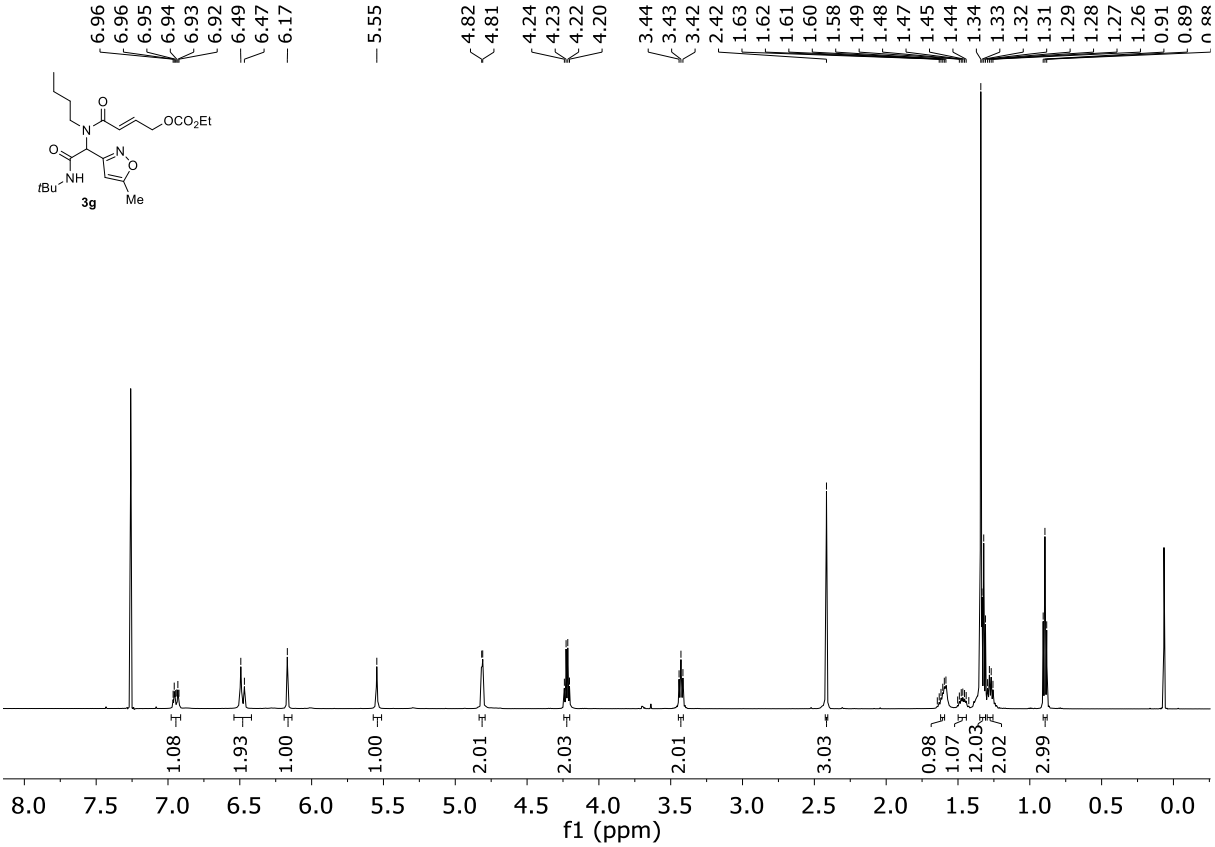
^{1}H NMR (3f) 500 MHz, $CDCl_3$



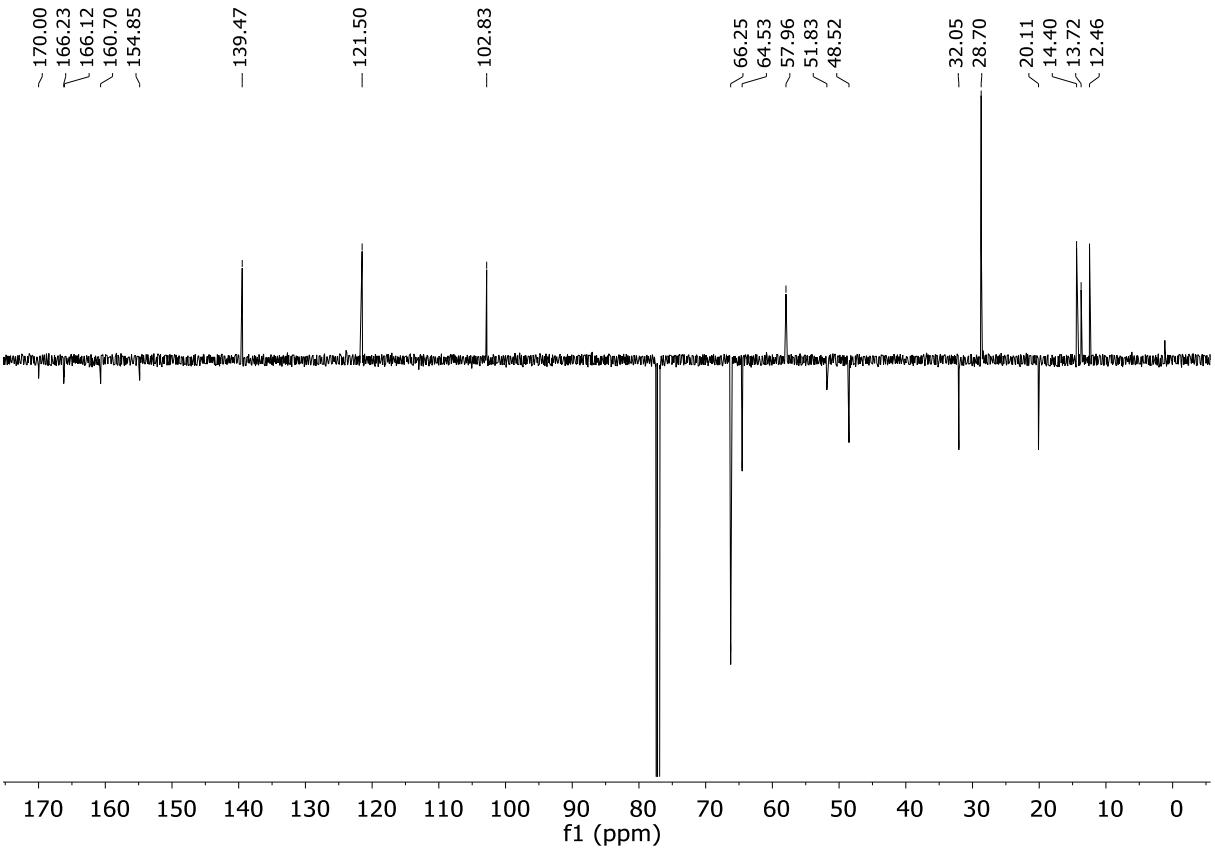
^{13}C NMR (3f) 126 MHz, $CDCl_3$



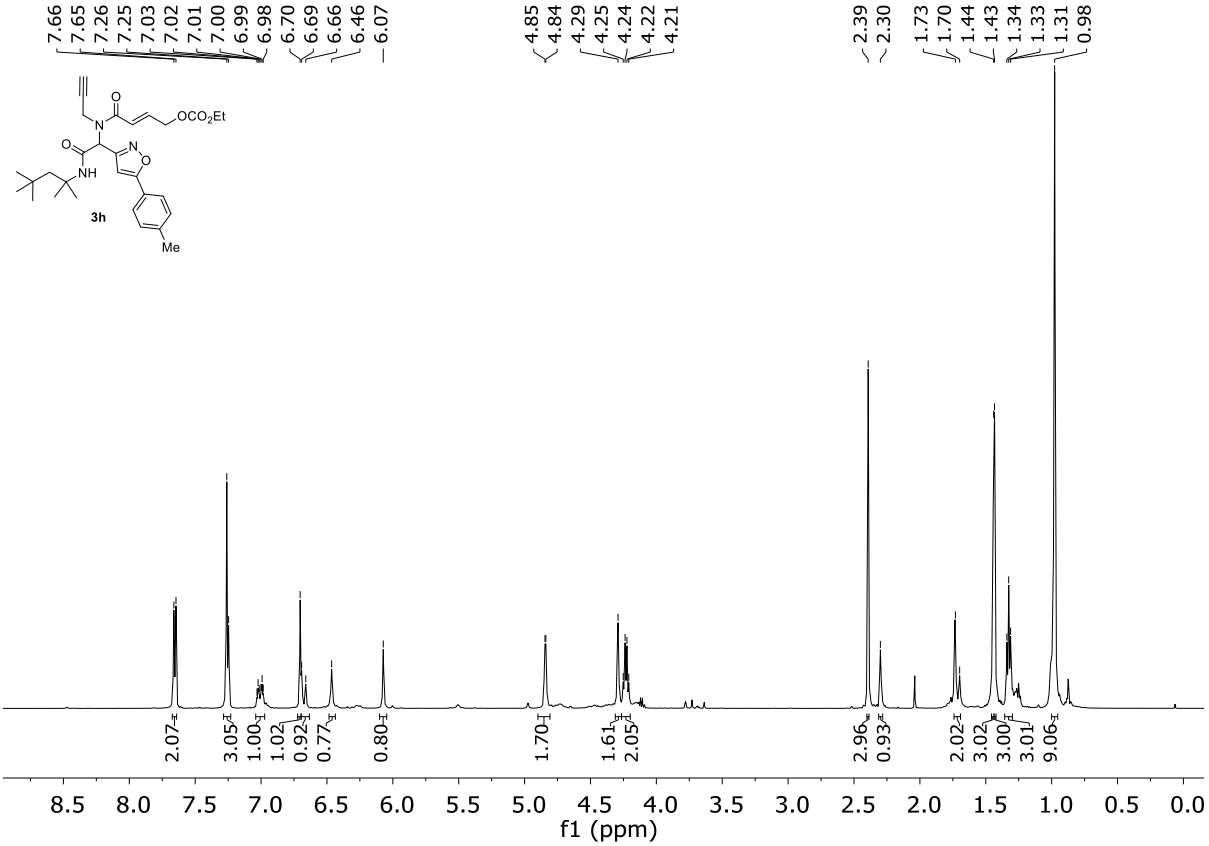
^{1}H NMR (3g) 600 MHz, $CDCl_3$



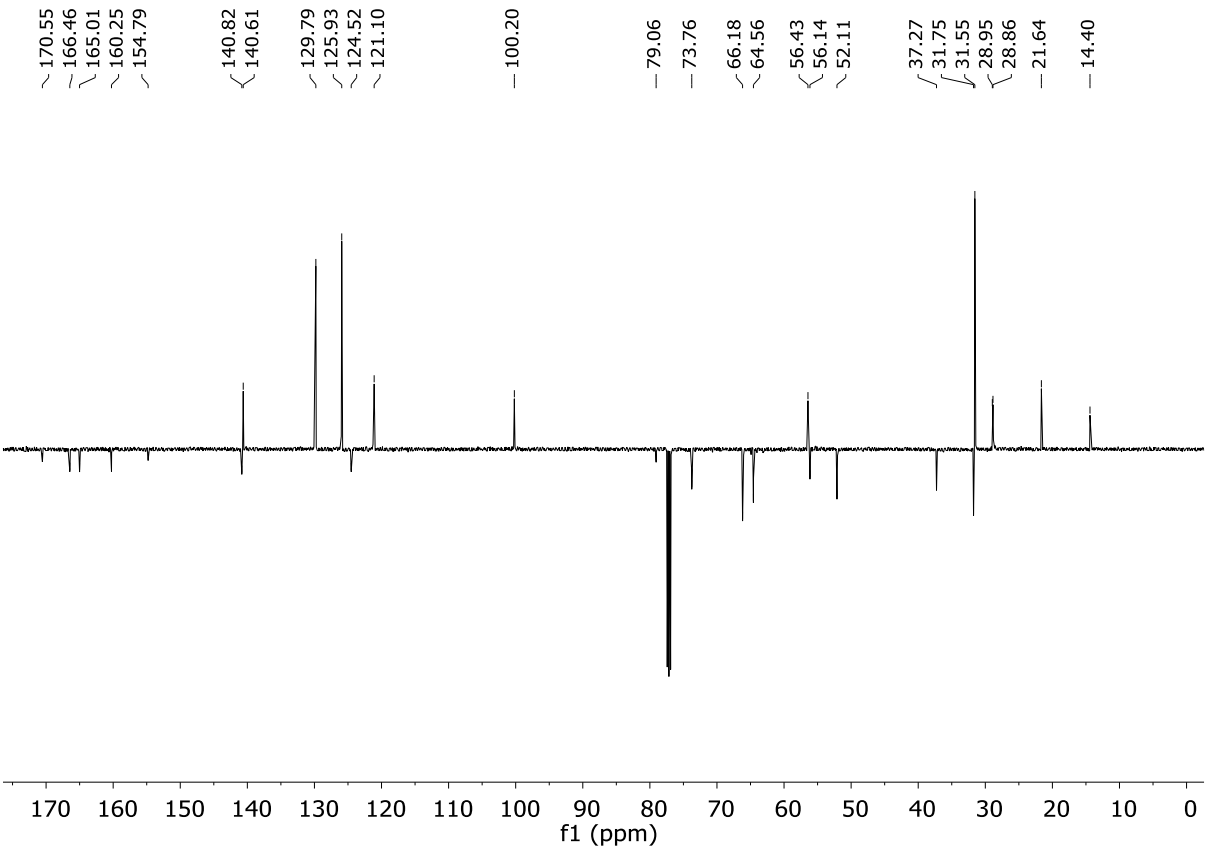
^{13}C NMR (3g) 151 MHz, $CDCl_3$



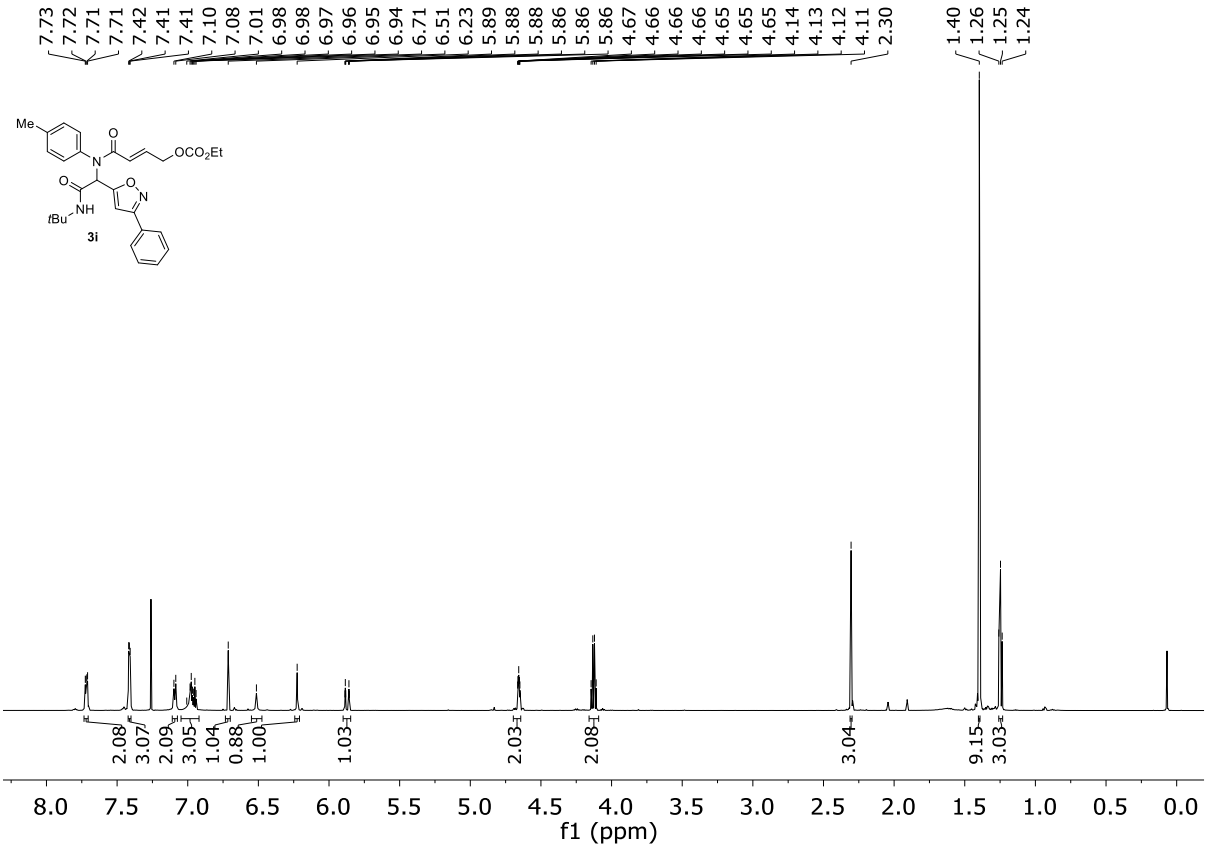
^{1}H NMR (3h) 500 MHz, $CDCl_3$



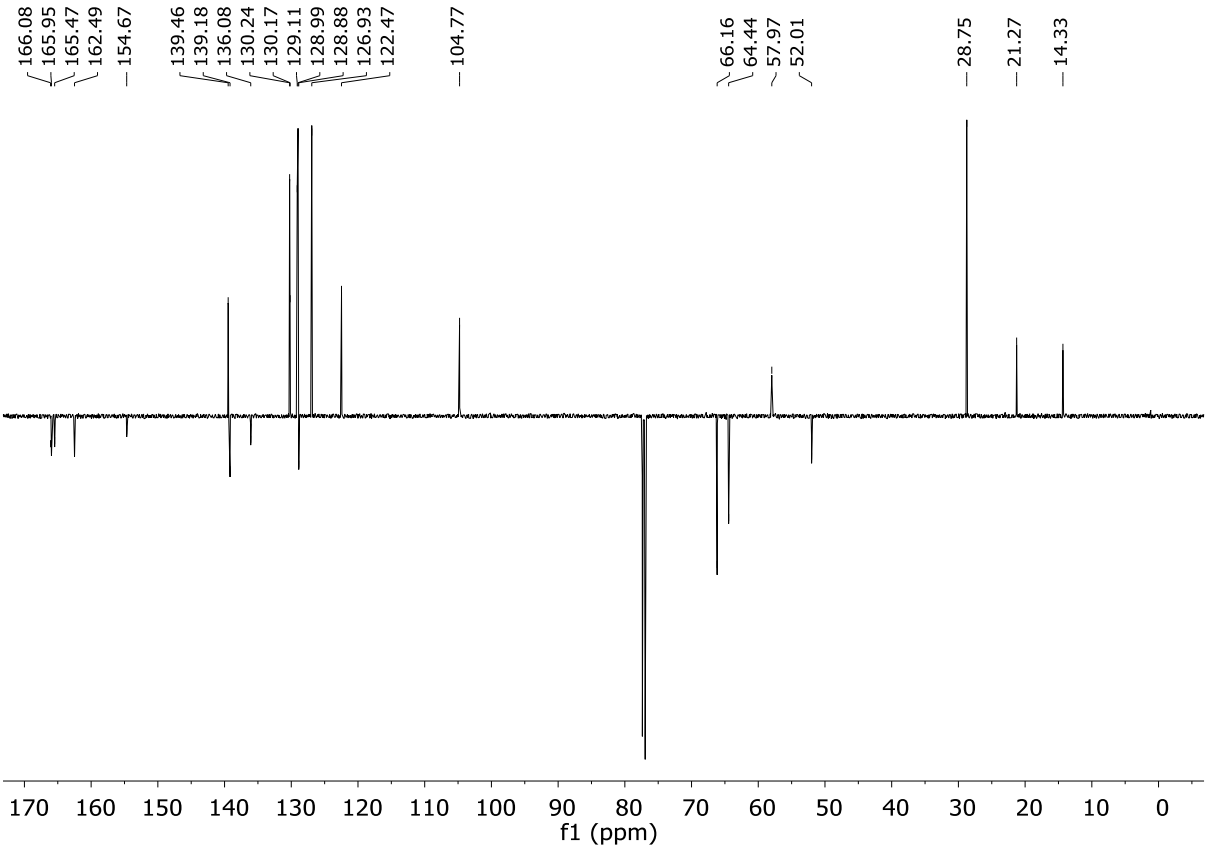
^{13}C NMR (3h) 126 MHz, $CDCl_3$



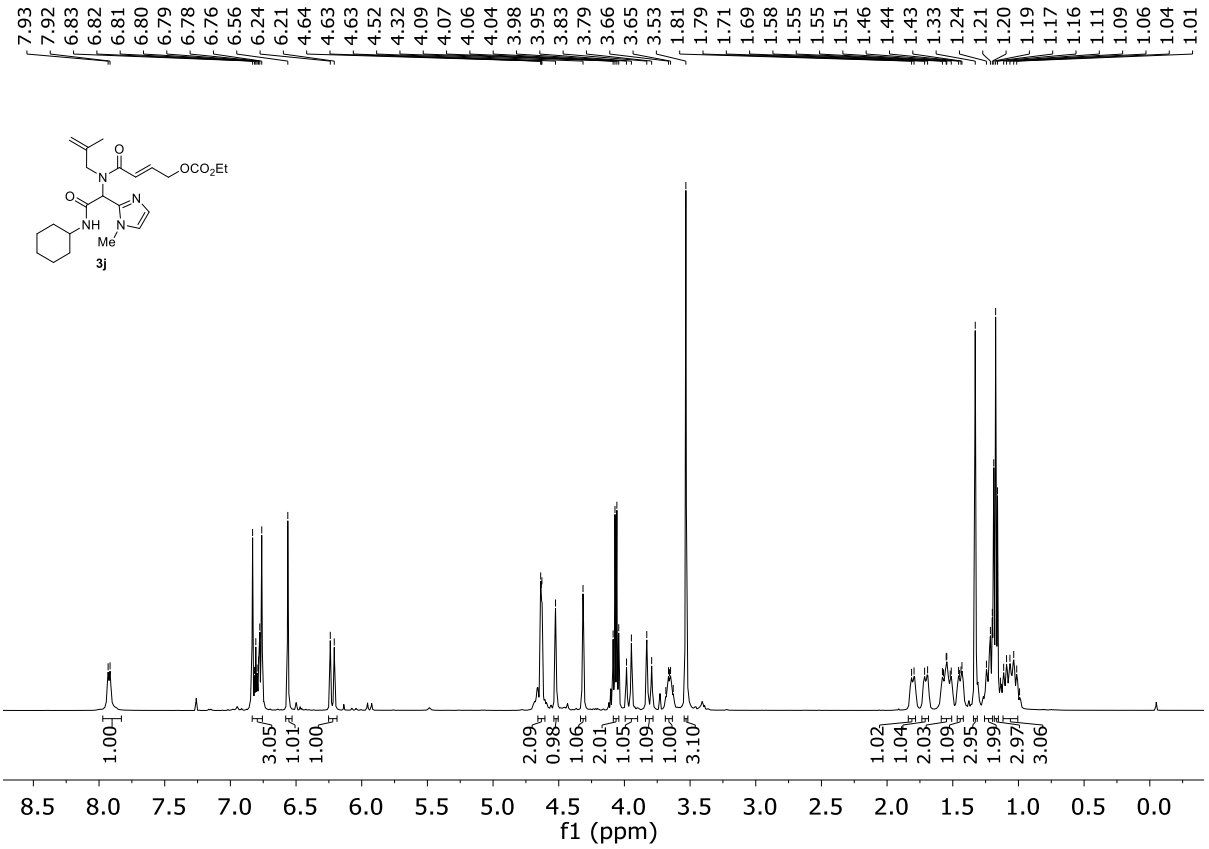
^{1}H NMR (3i) 600 MHz, $CDCl_3$



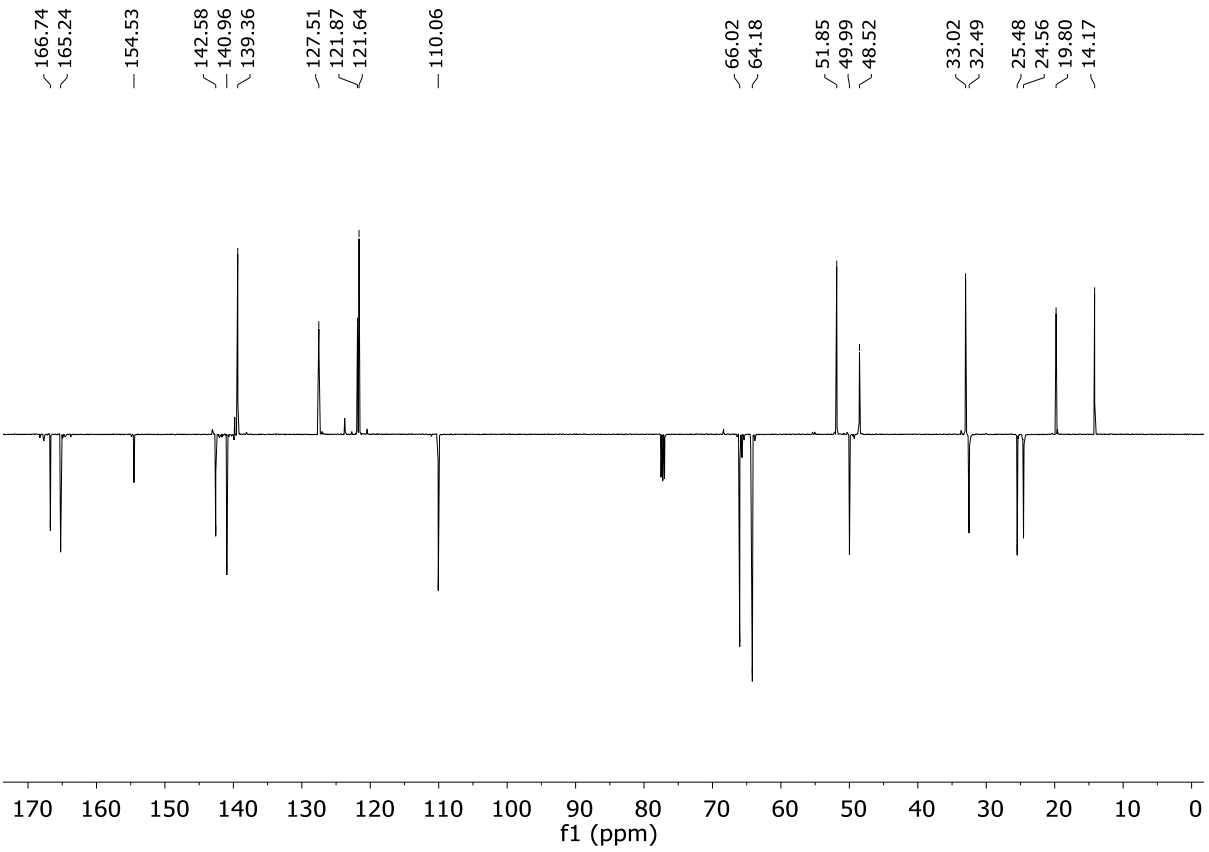
^{13}C NMR (3i) 151 MHz, $CDCl_3$



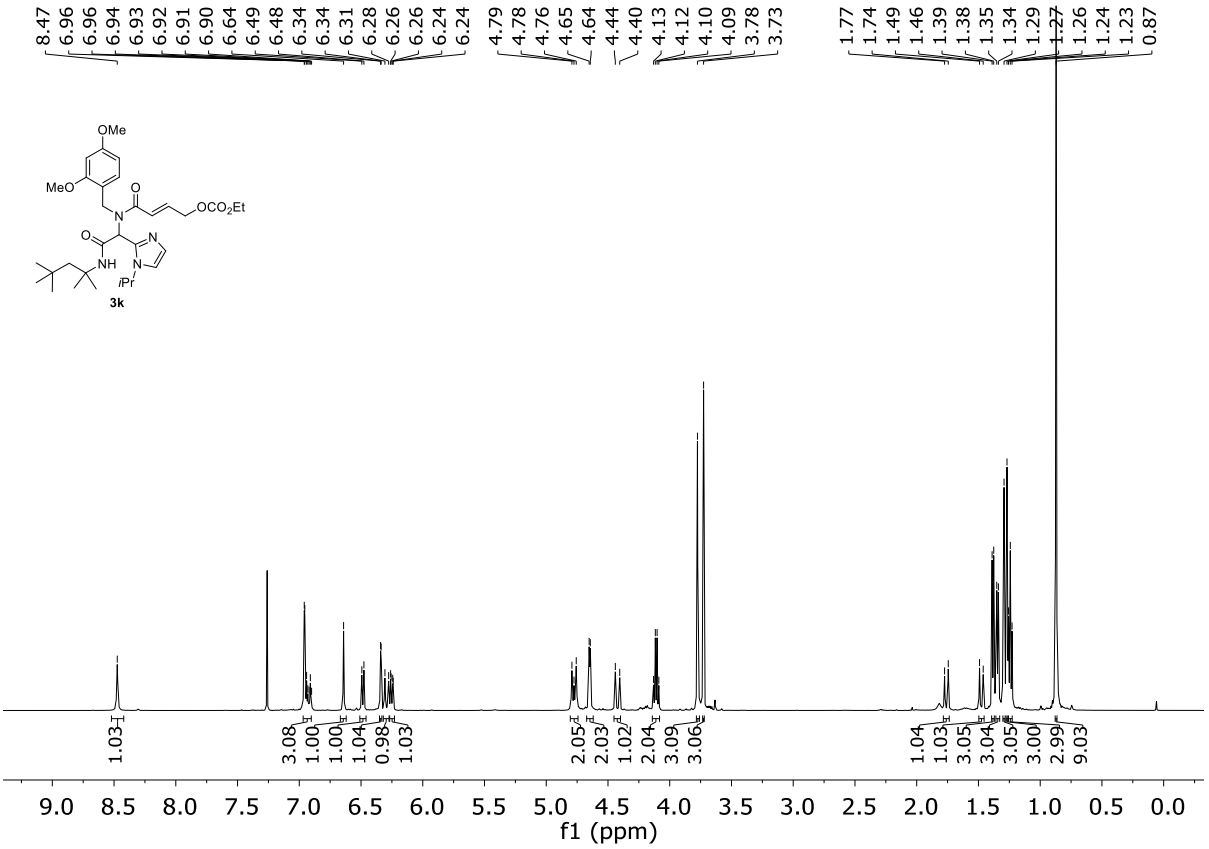
^{1}H NMR (3j) 500 MHz, $CDCl_3$



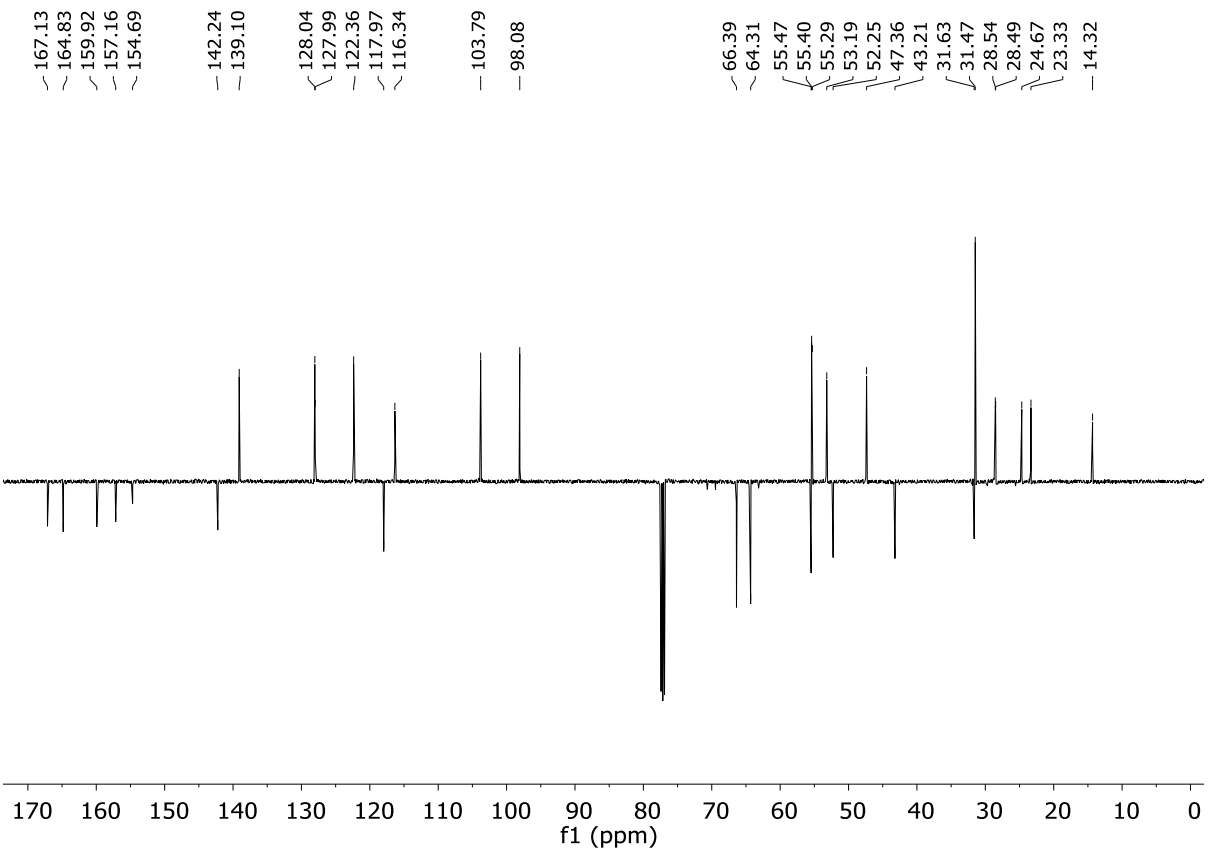
^{13}C NMR (3j) 126 MHz, $CDCl_3$



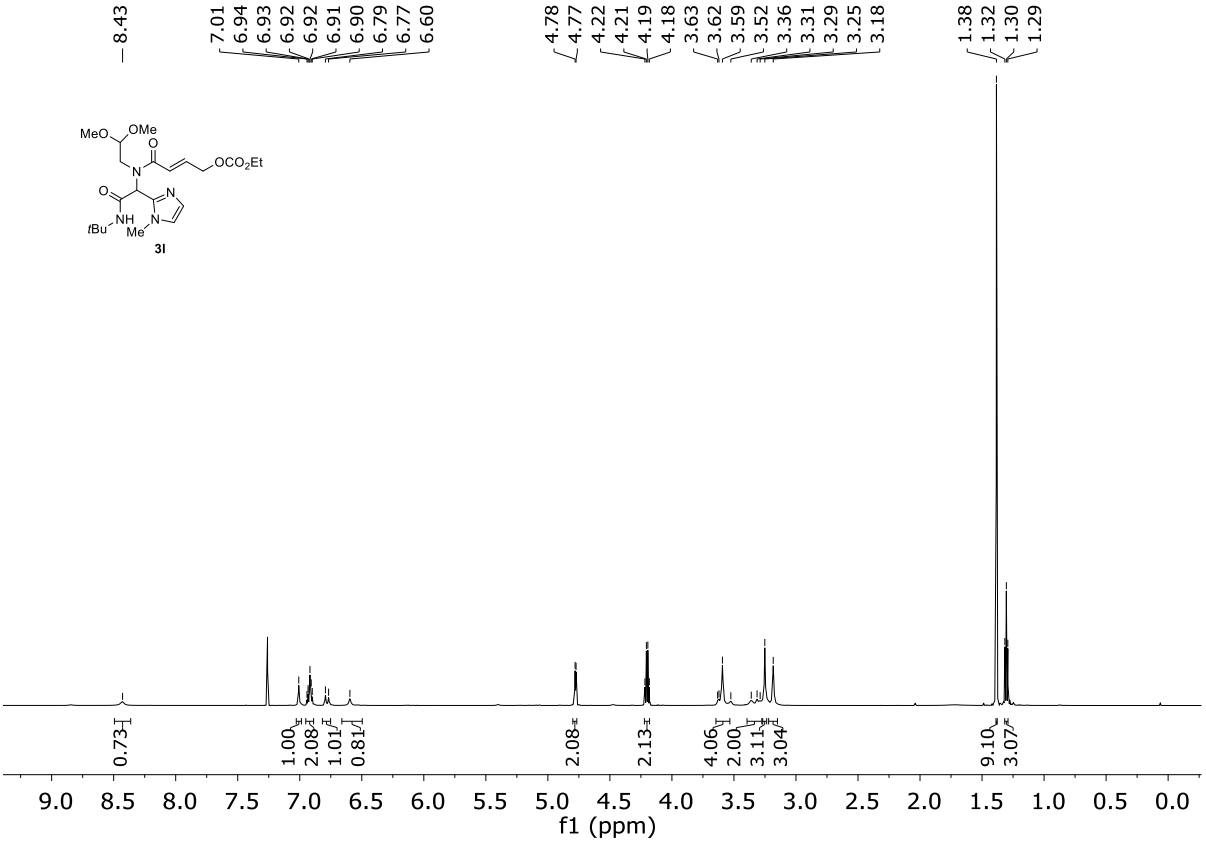
^{1}H NMR (3k) 500 MHz, $CDCl_3$



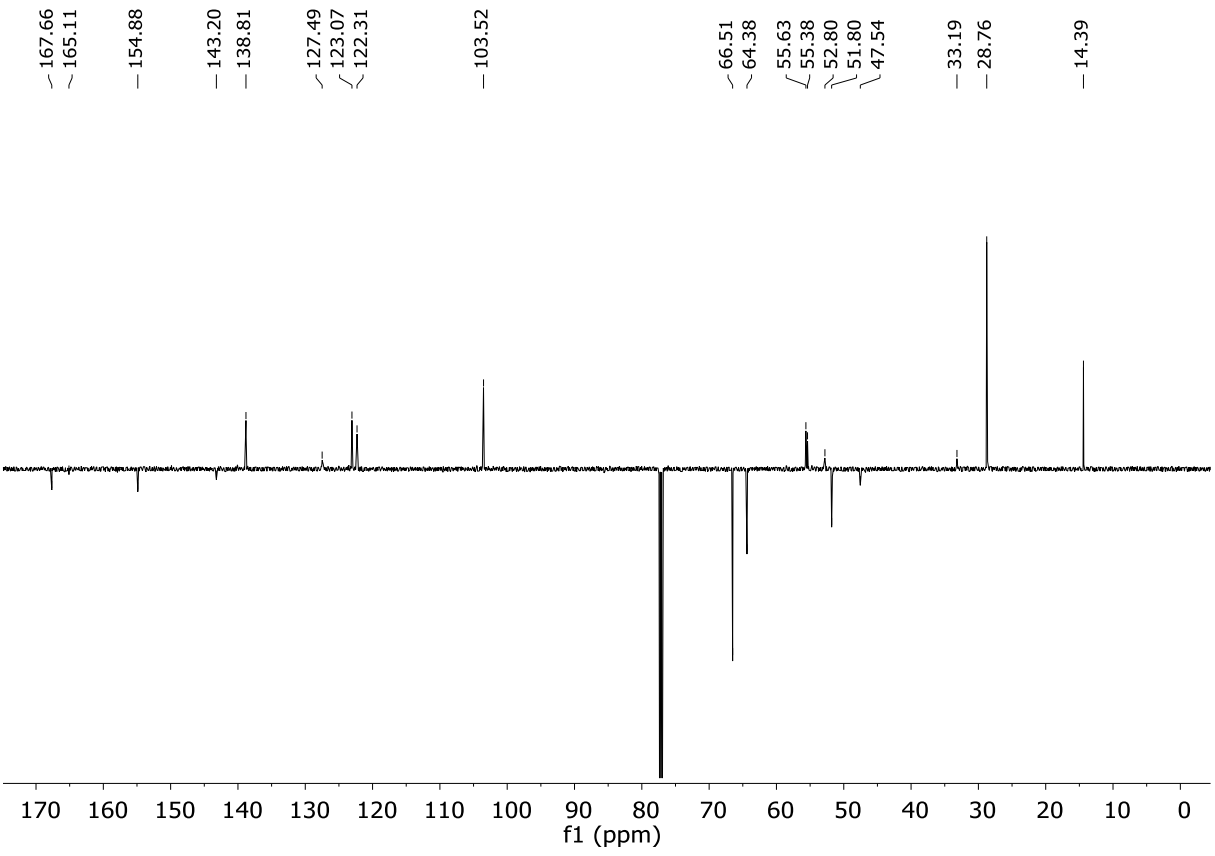
^{13}C NMR (3k) 126 MHz, $CDCl_3$



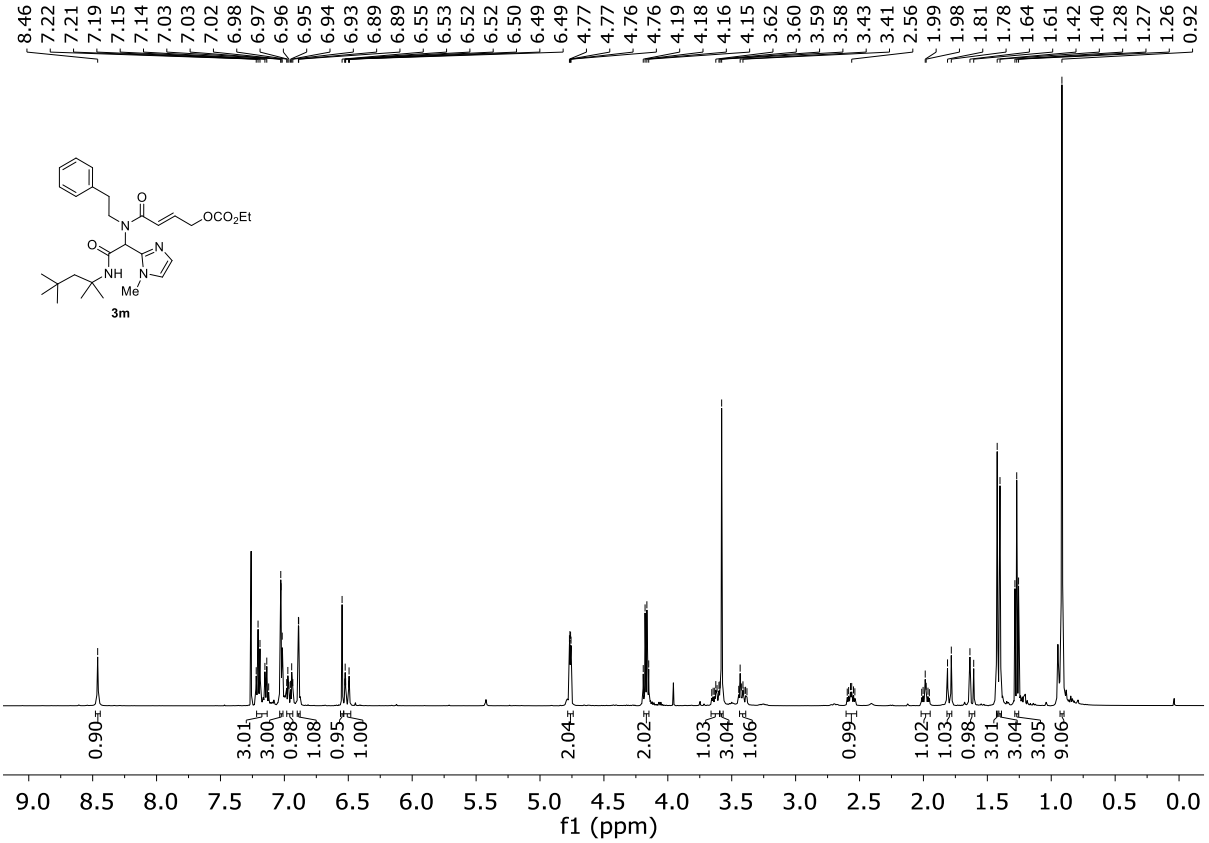
^{1}H NMR (3l) 600 MHz, $CDCl_3$



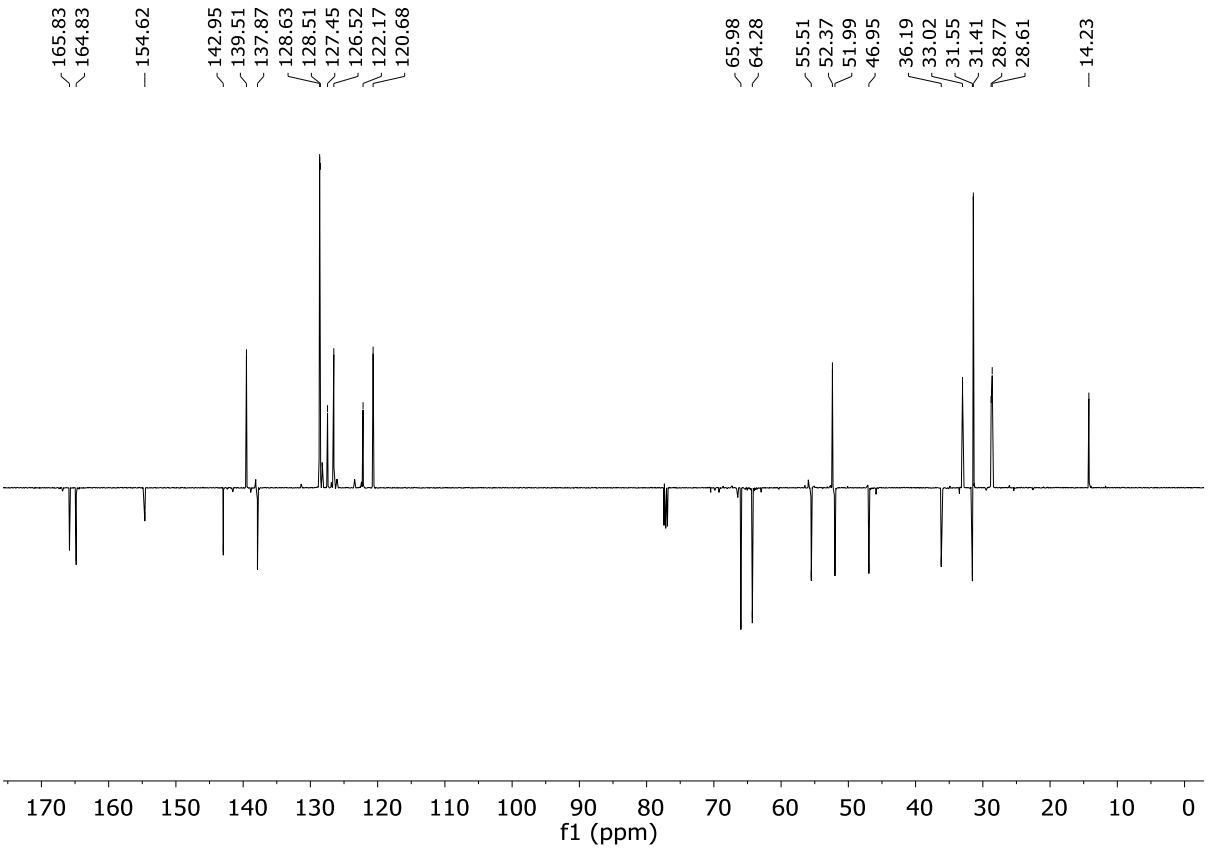
^{13}C NMR (3l) 151 MHz, $CDCl_3$



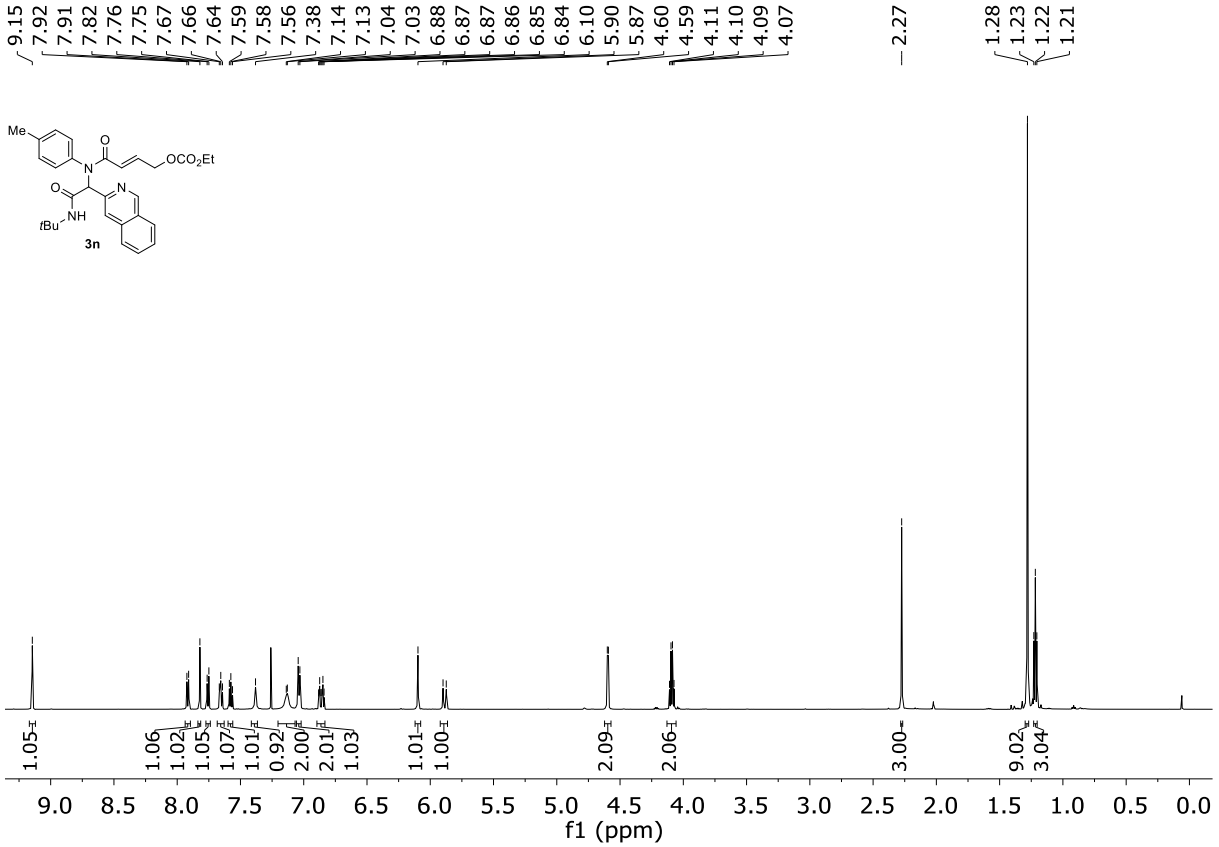
^{1}H NMR (3m) 500 MHz, $CDCl_3$



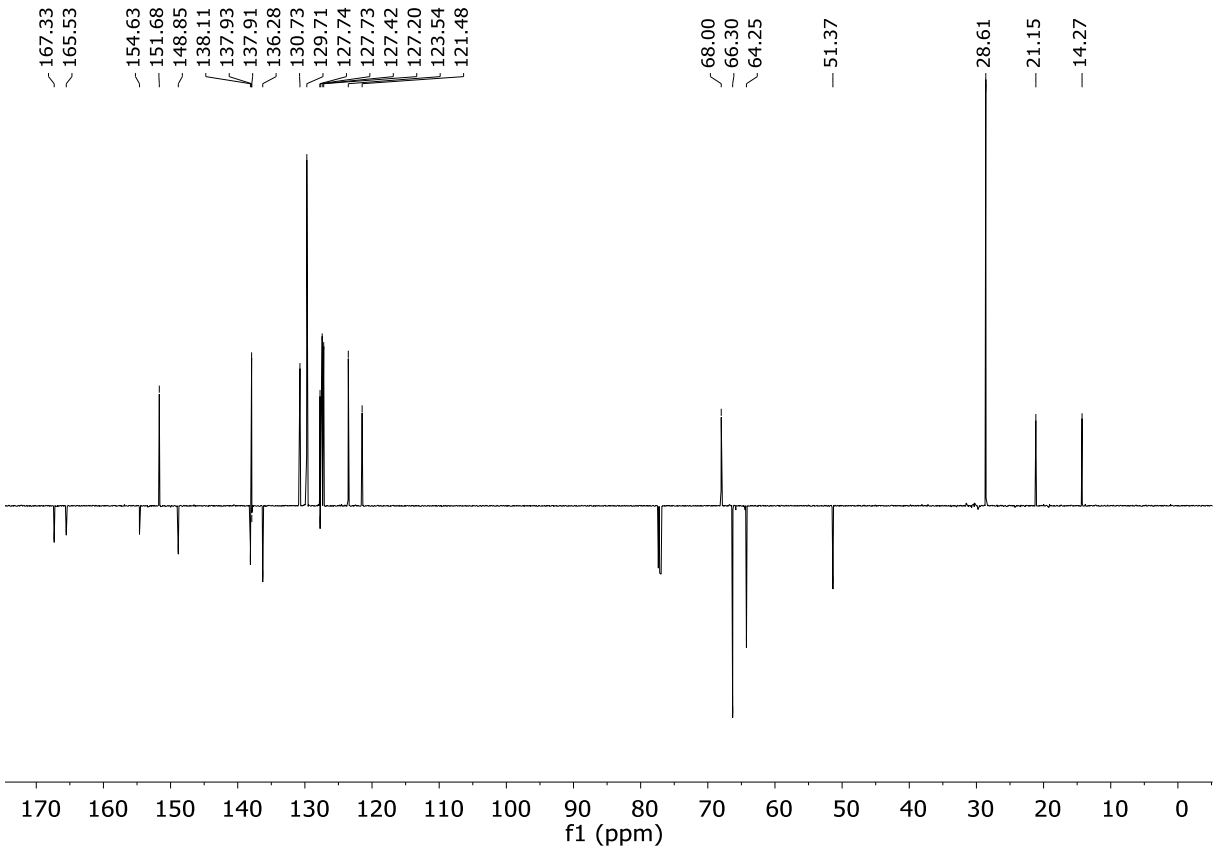
^{13}C NMR (3m) 126 MHz, $CDCl_3$



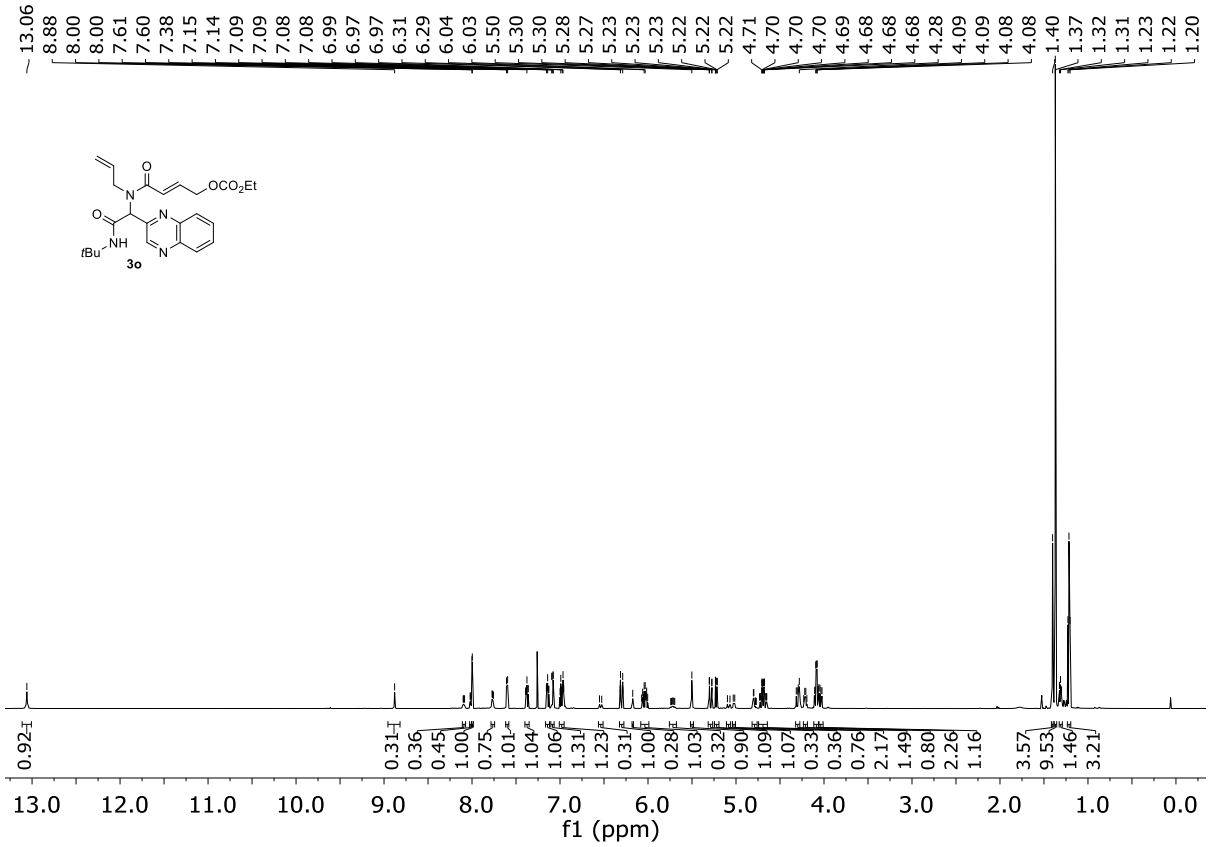
^{1}H NMR (3n) 600 MHz, $CDCl_3$



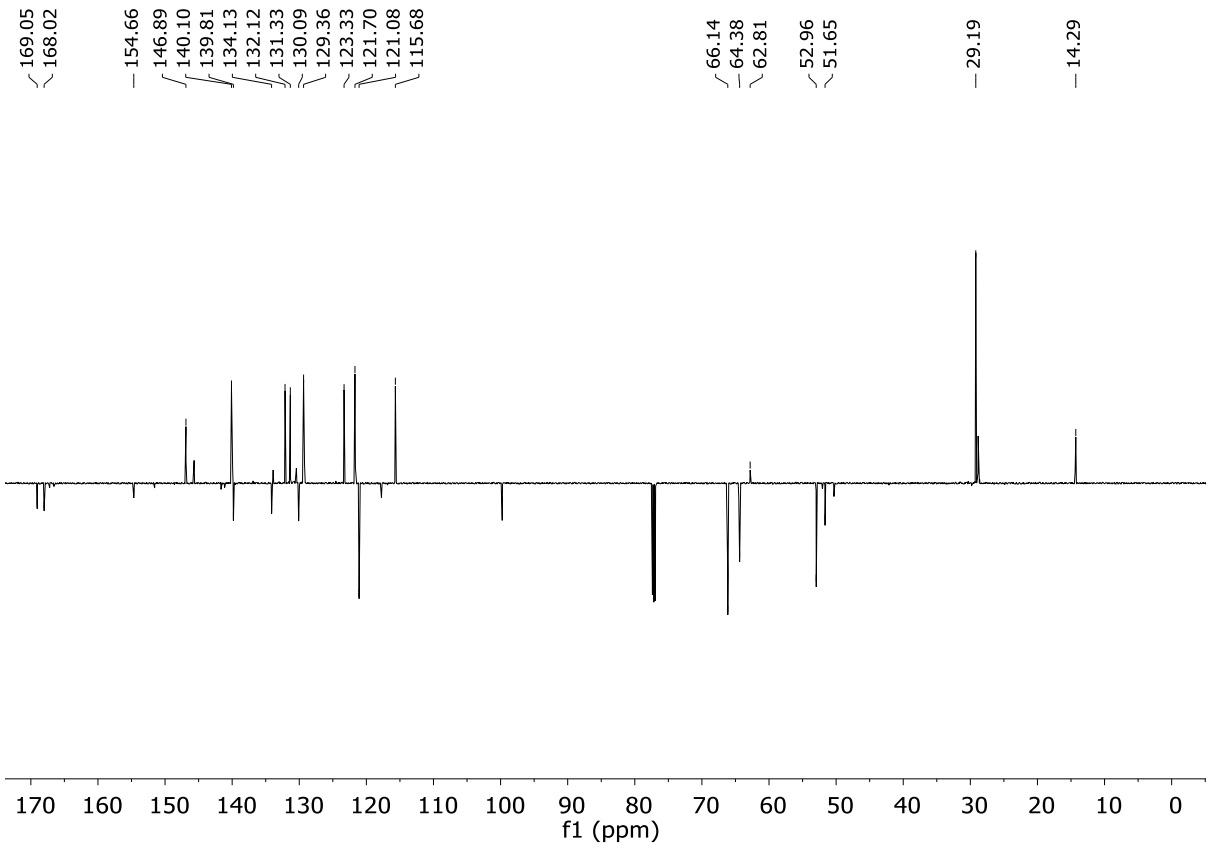
^{13}C NMR (3n) 151 MHz, $CDCl_3$



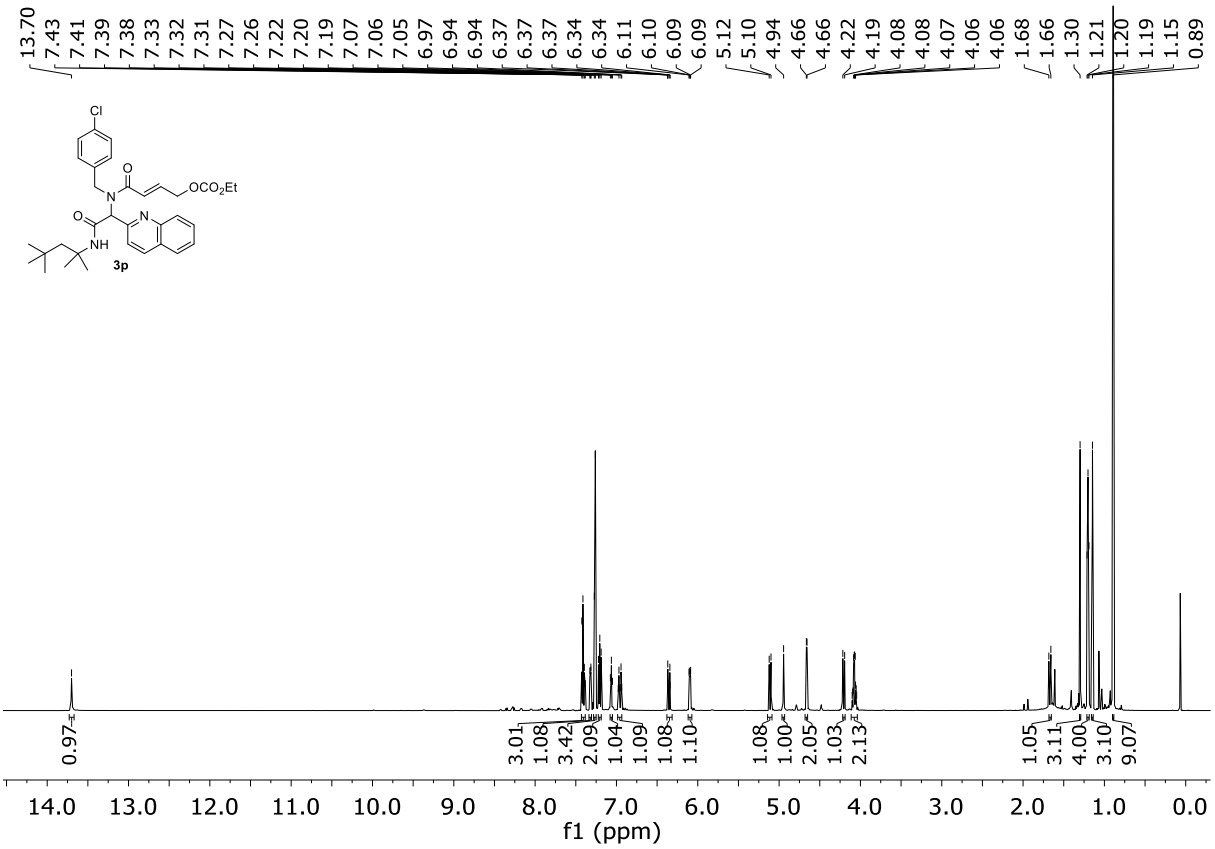
^{1}H NMR (3o) 600 MHz, $CDCl_3$



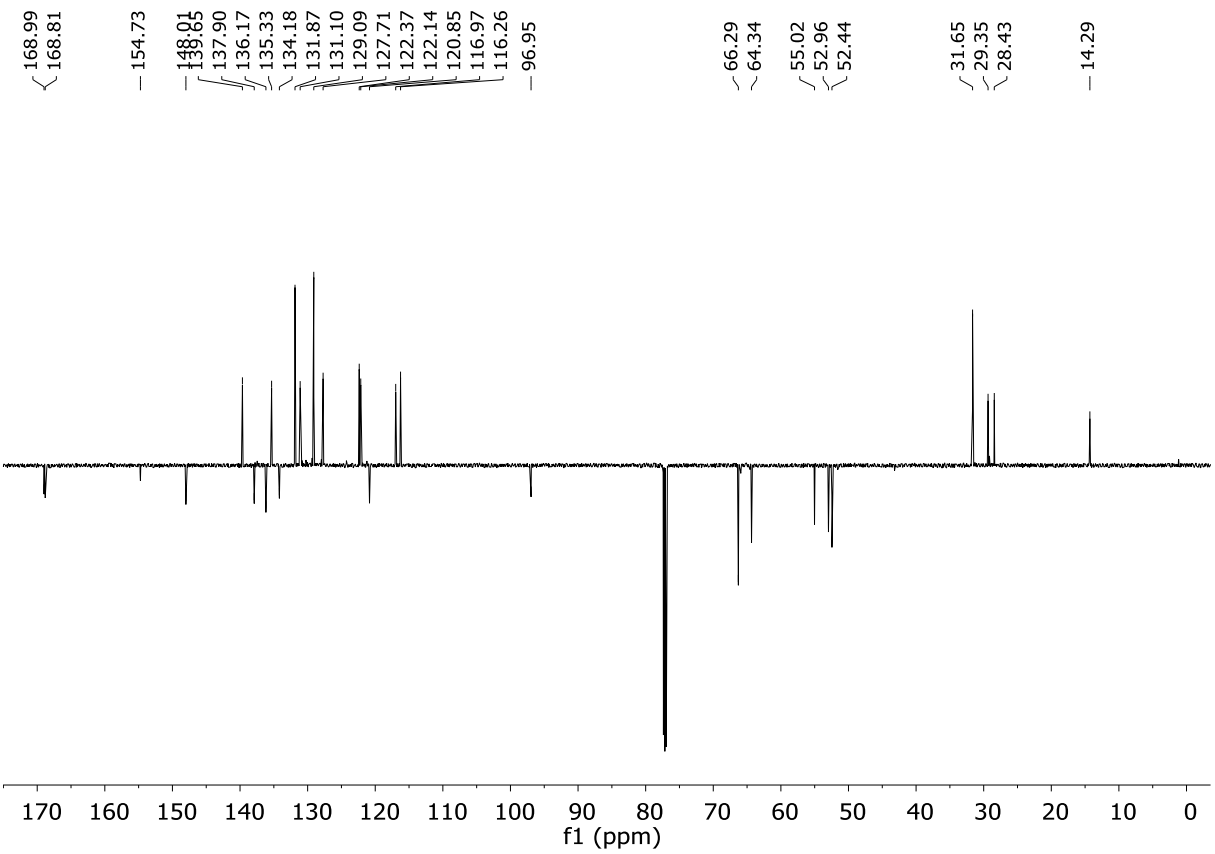
^{13}C NMR (3o) 151 MHz, $CDCl_3$



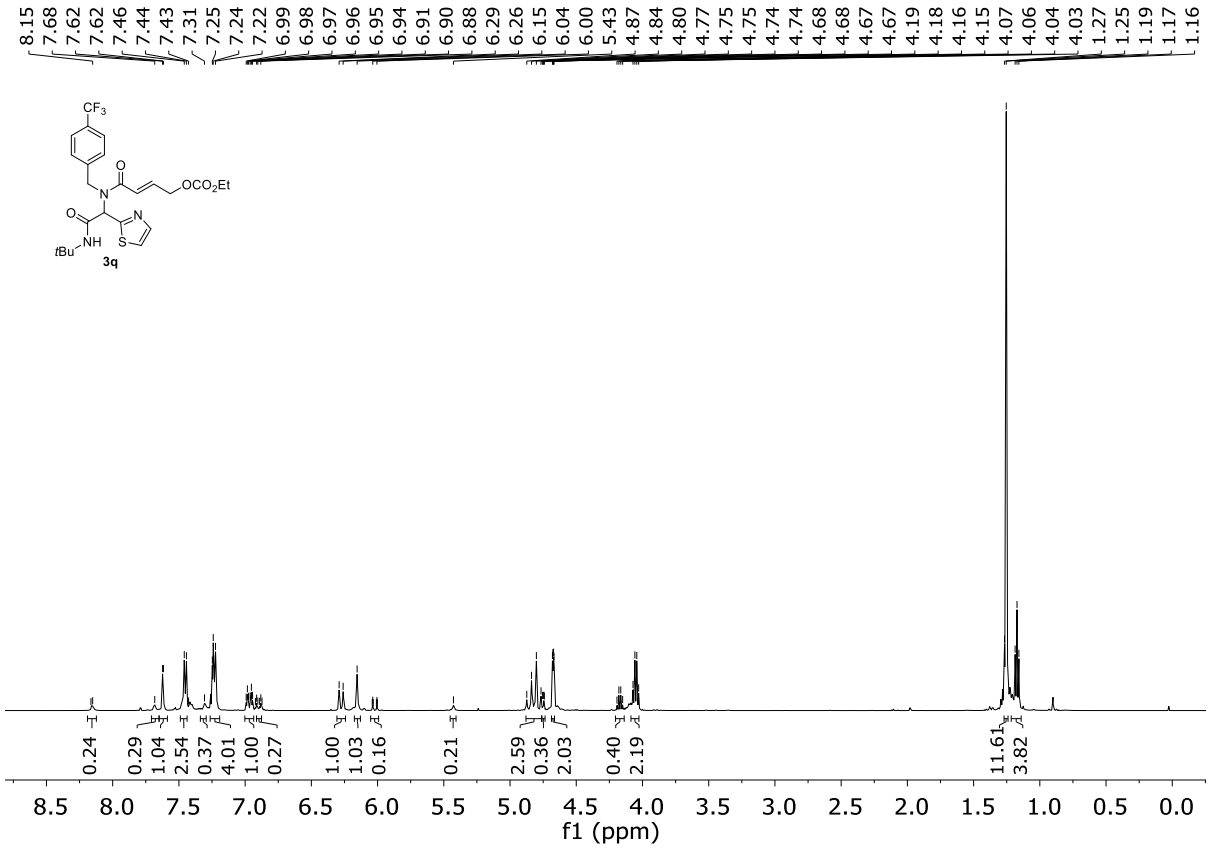
^{1}H NMR (3p) 500 MHz, $CDCl_3$



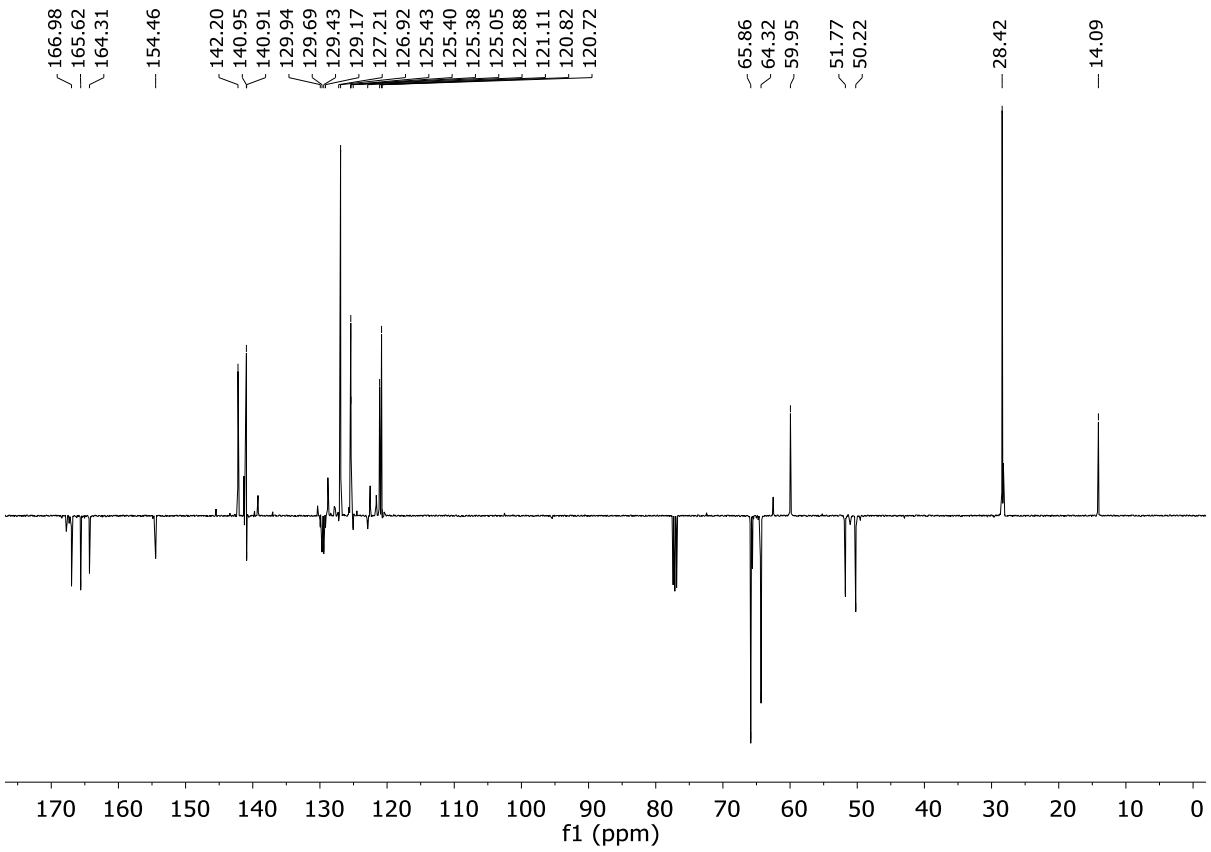
^{13}C NMR (3p) 126 MHz, $CDCl_3$



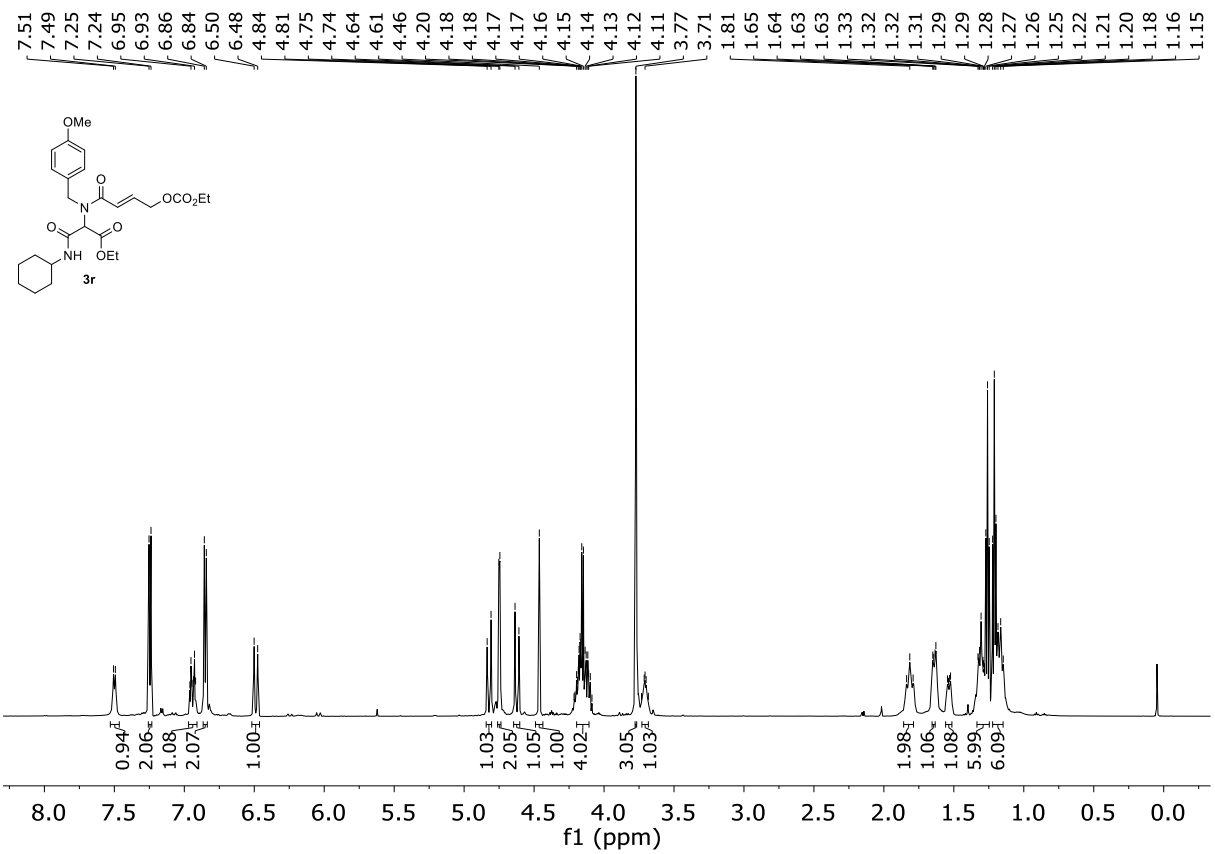
^{1}H NMR (3q) 500 MHz, $CDCl_3$



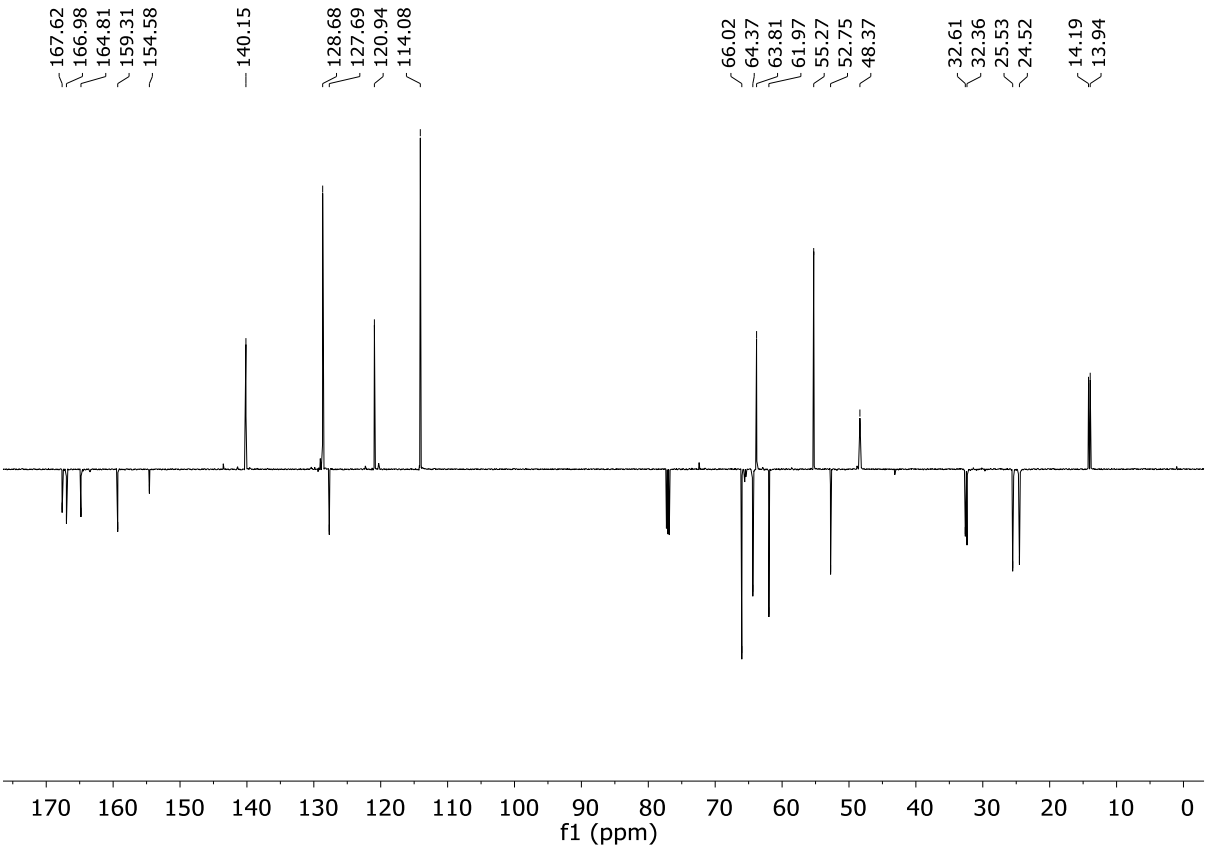
^{13}C NMR (3q) 126 MHz, $CDCl_3$



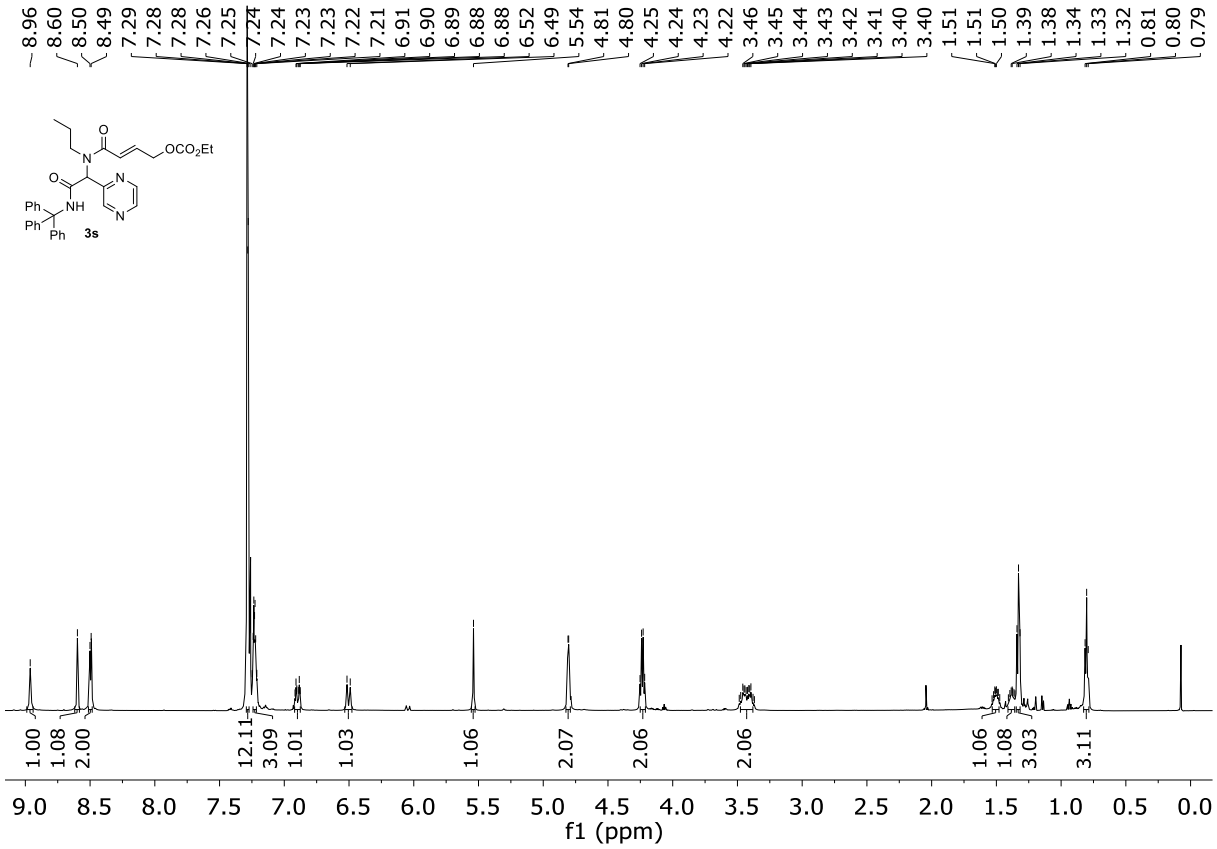
^{1}H NMR (3r) 600 MHz, $CDCl_3$



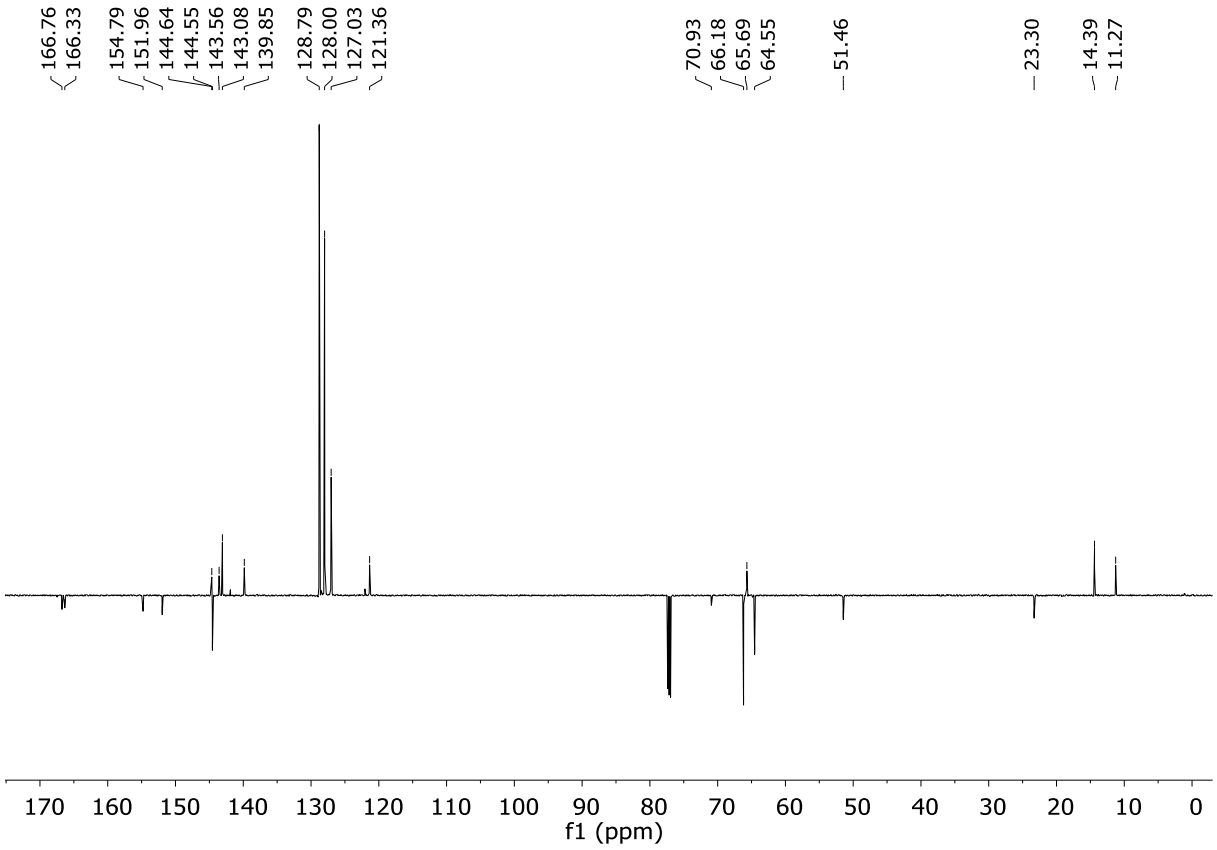
^{13}C NMR (3r) 151 MHz, $CDCl_3$



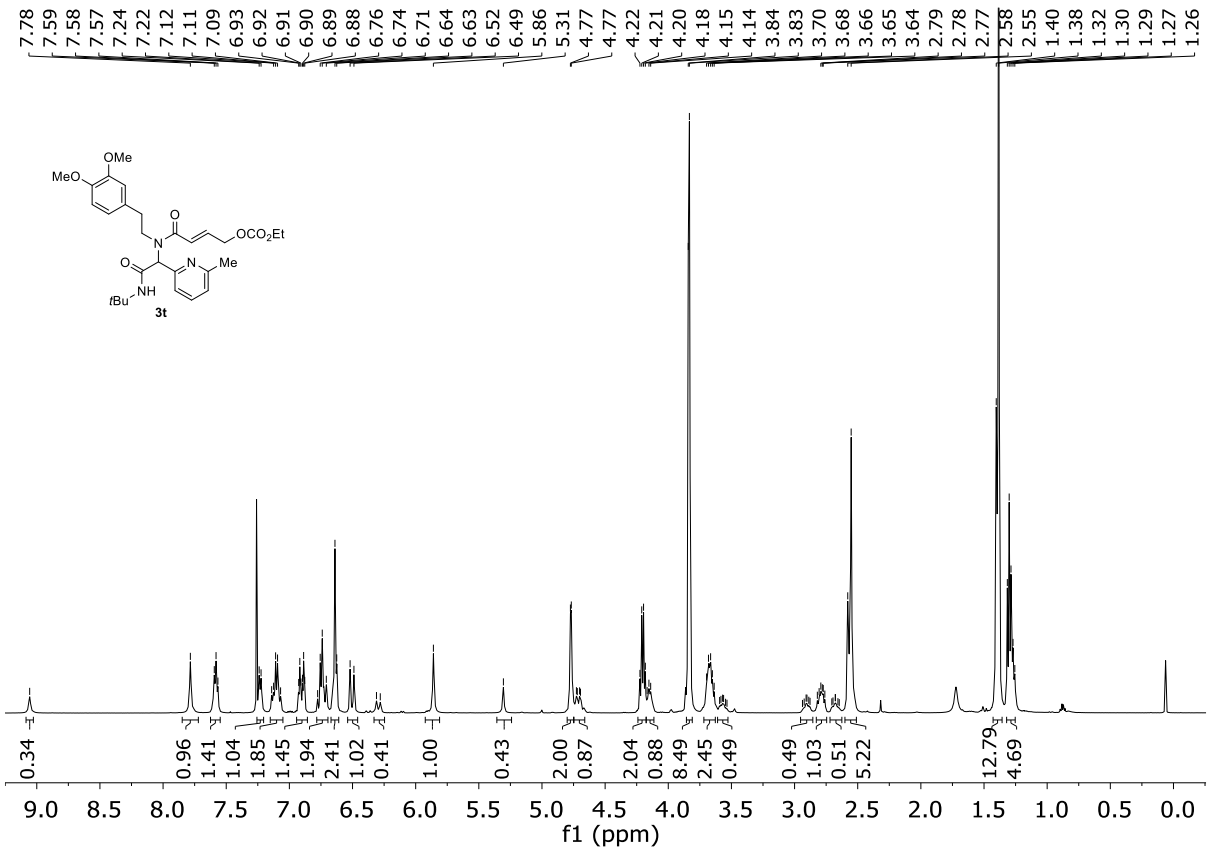
^{1}H NMR (3s) 600 MHz, $CDCl_3$



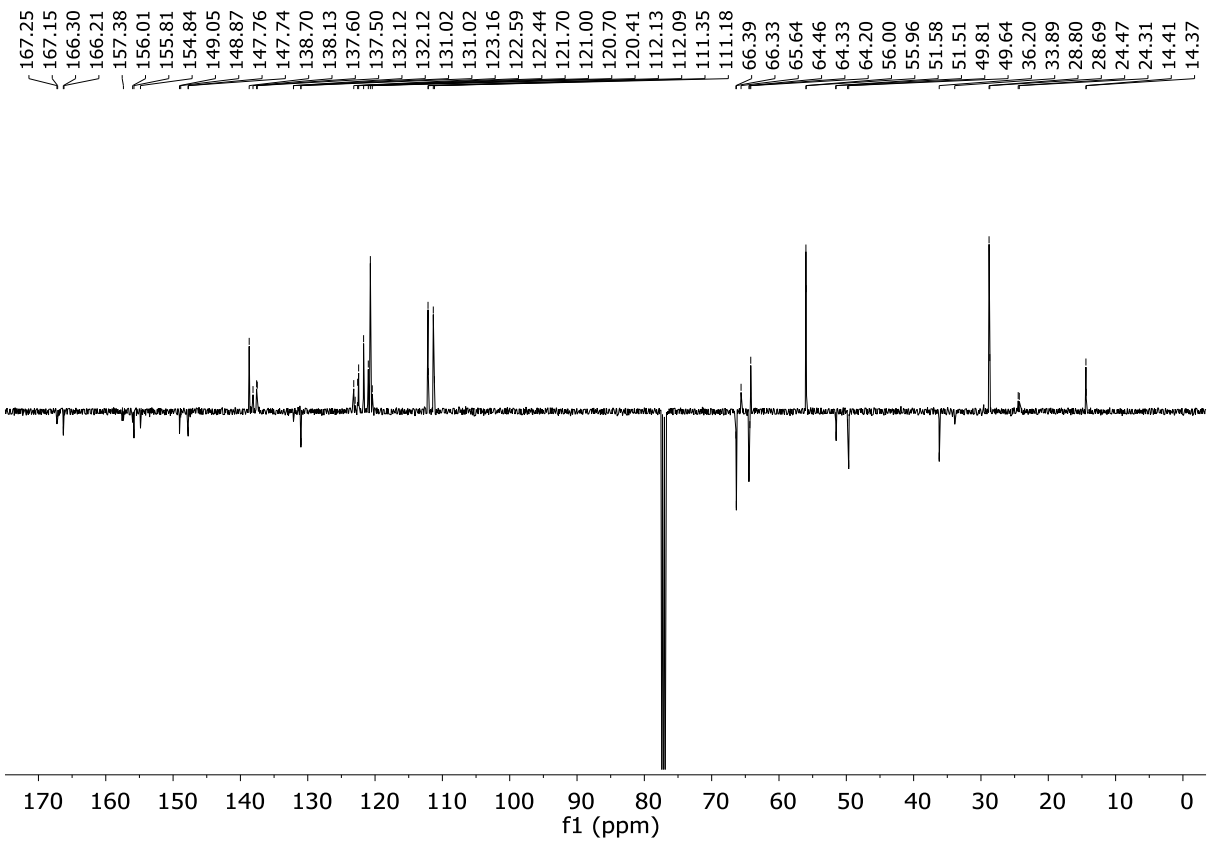
^{13}C NMR (3s) 151 MHz, $CDCl_3$



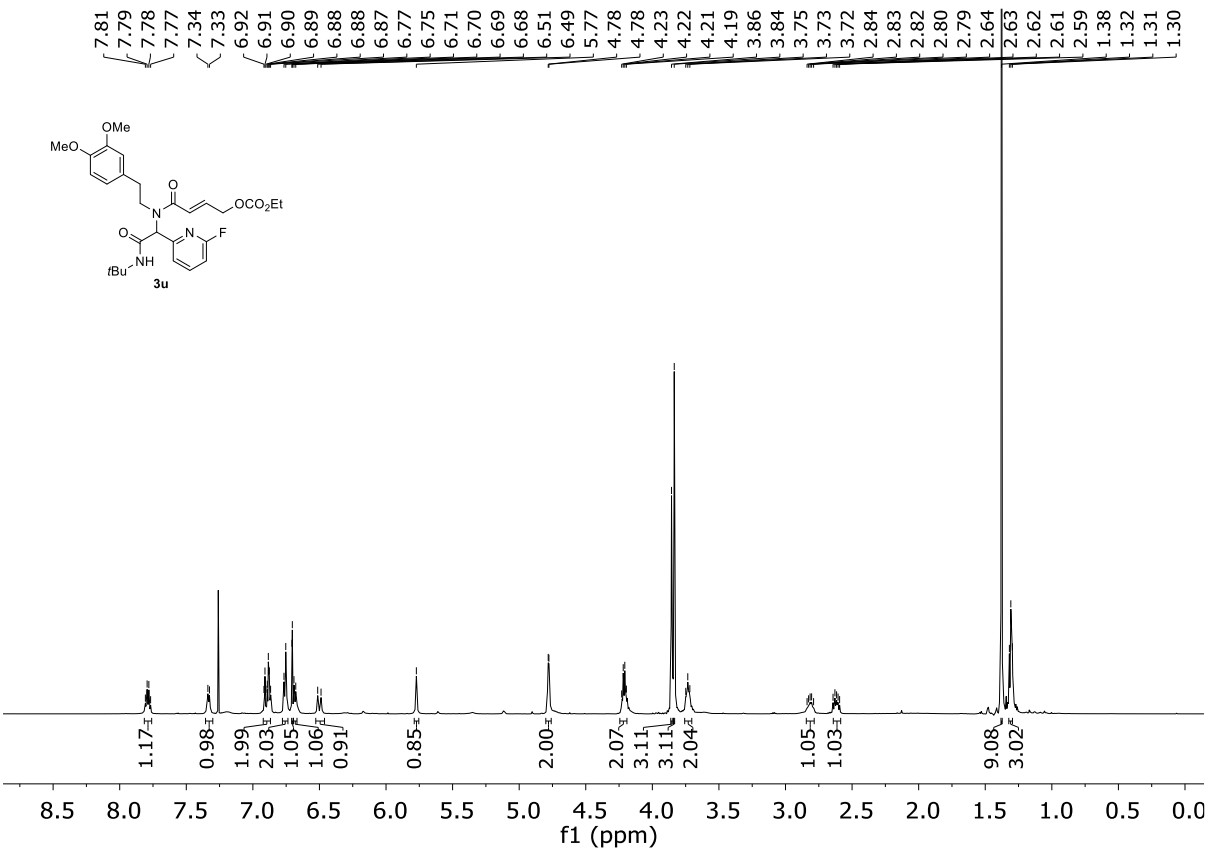
^{1}H NMR (3t) 500 MHz, $CDCl_3$



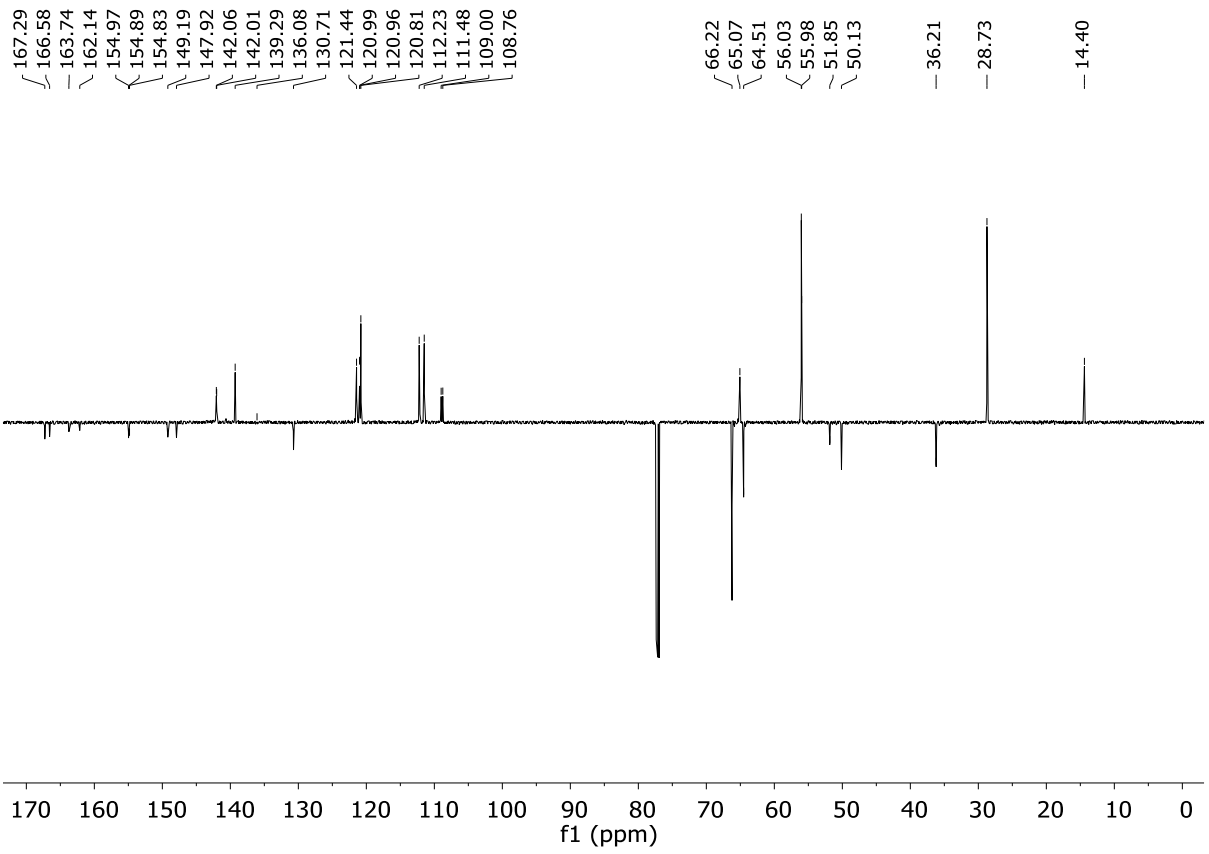
^{13}C NMR (3t) 126 MHz, $CDCl_3$



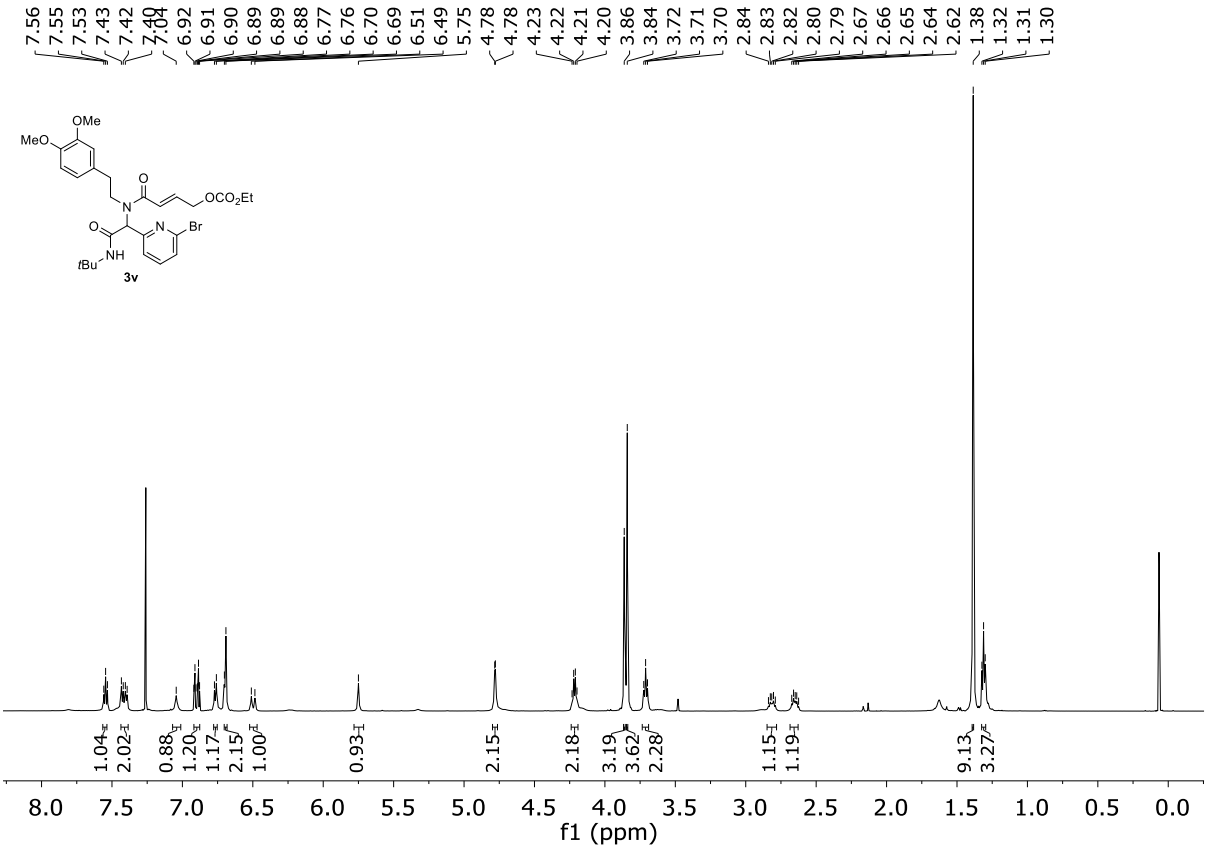
^{1}H NMR (3u) 600 MHz, $CDCl_3$



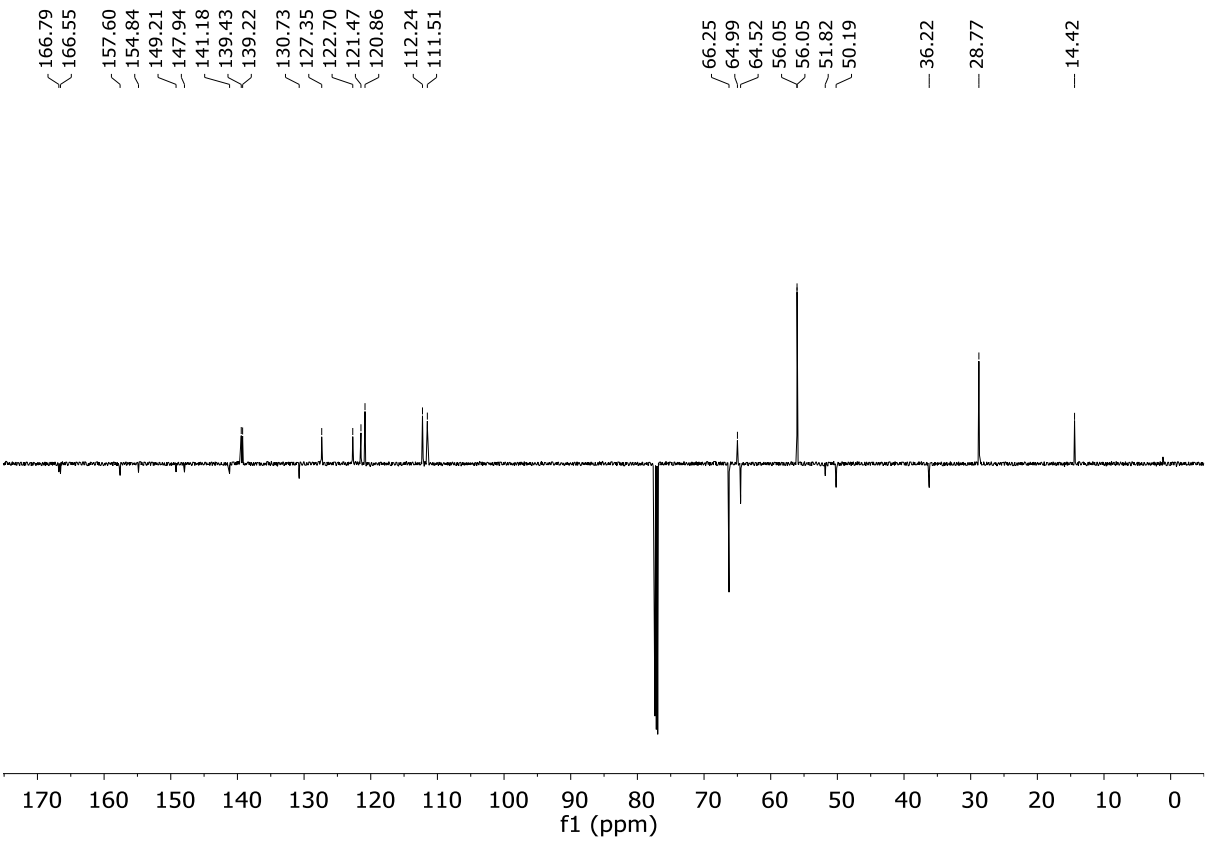
^{13}C NMR (3u) 151 MHz, $CDCl_3$



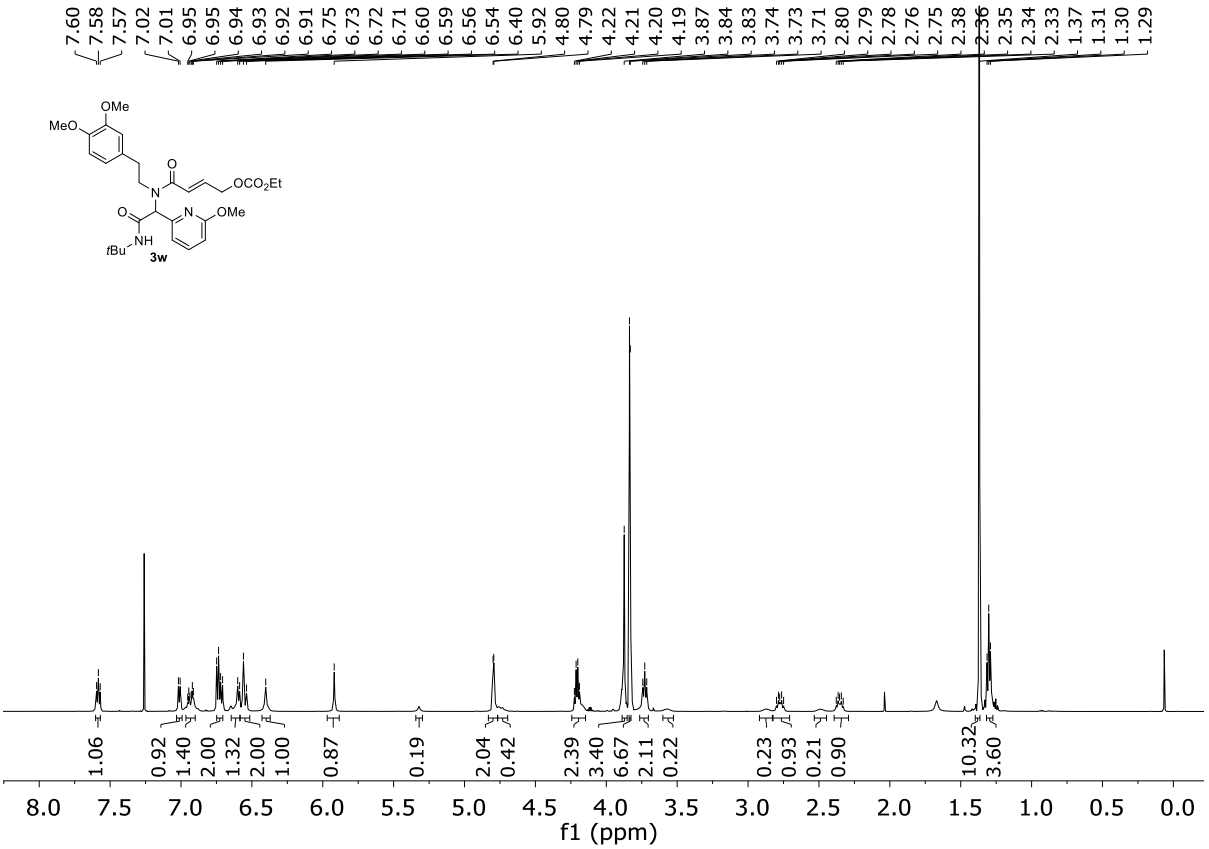
^{1}H NMR (3v) 600 MHz, $CDCl_3$



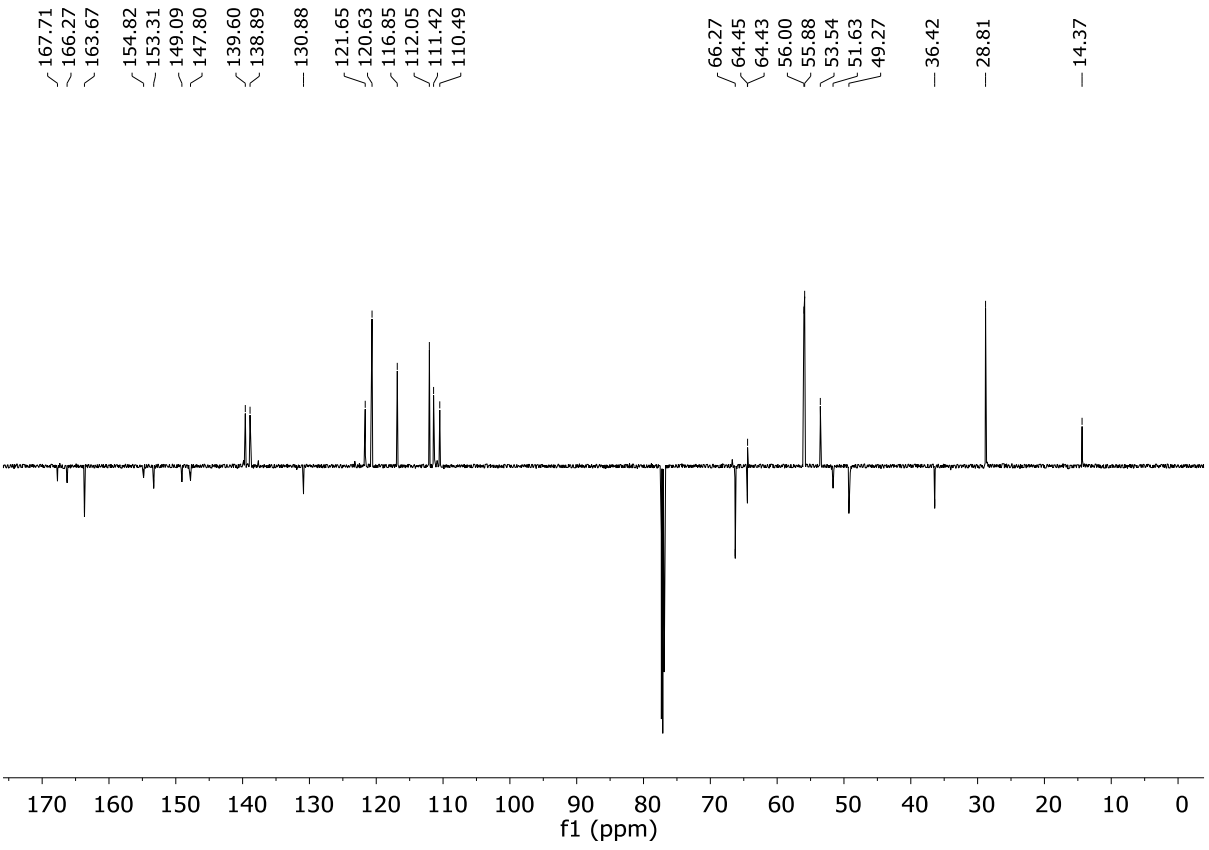
^{13}C NMR (3v) 126 MHz, $CDCl_3$



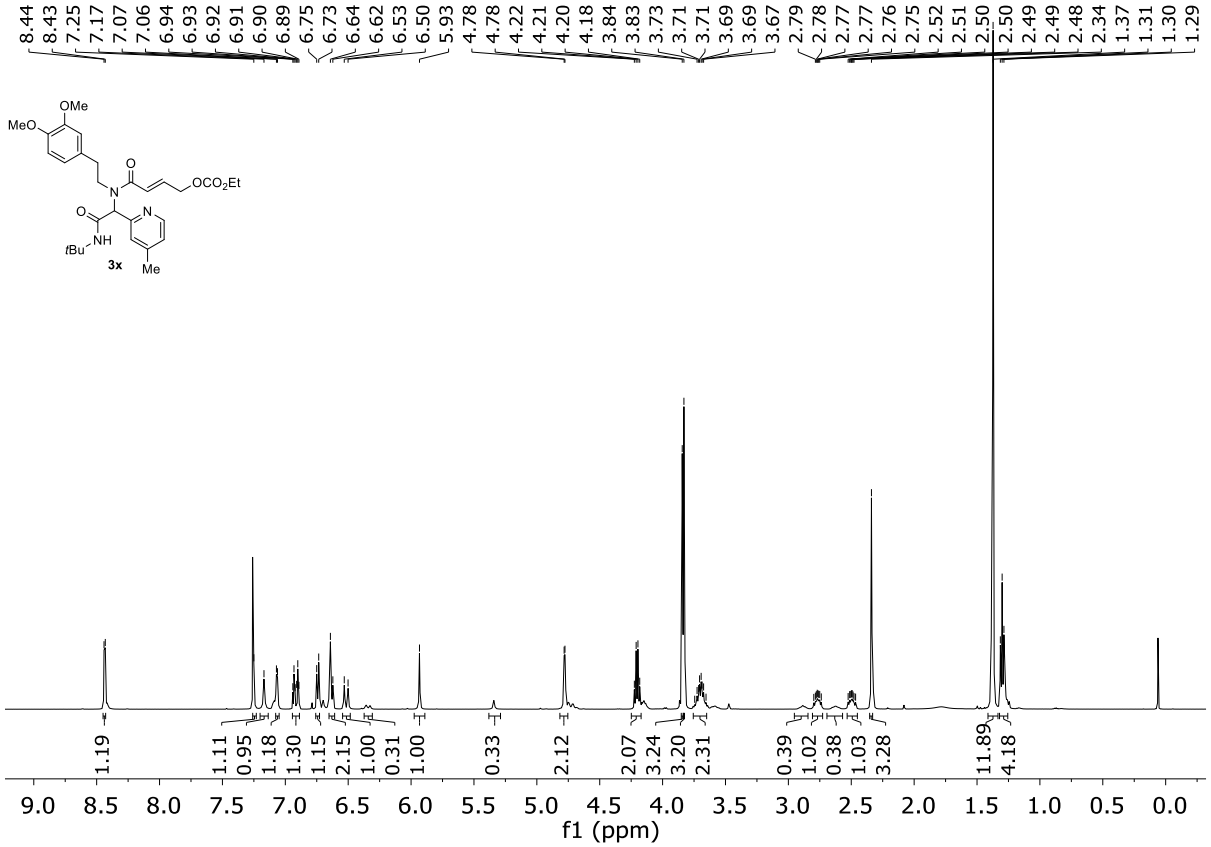
^{1}H NMR (3w) 600 MHz, $CDCl_3$



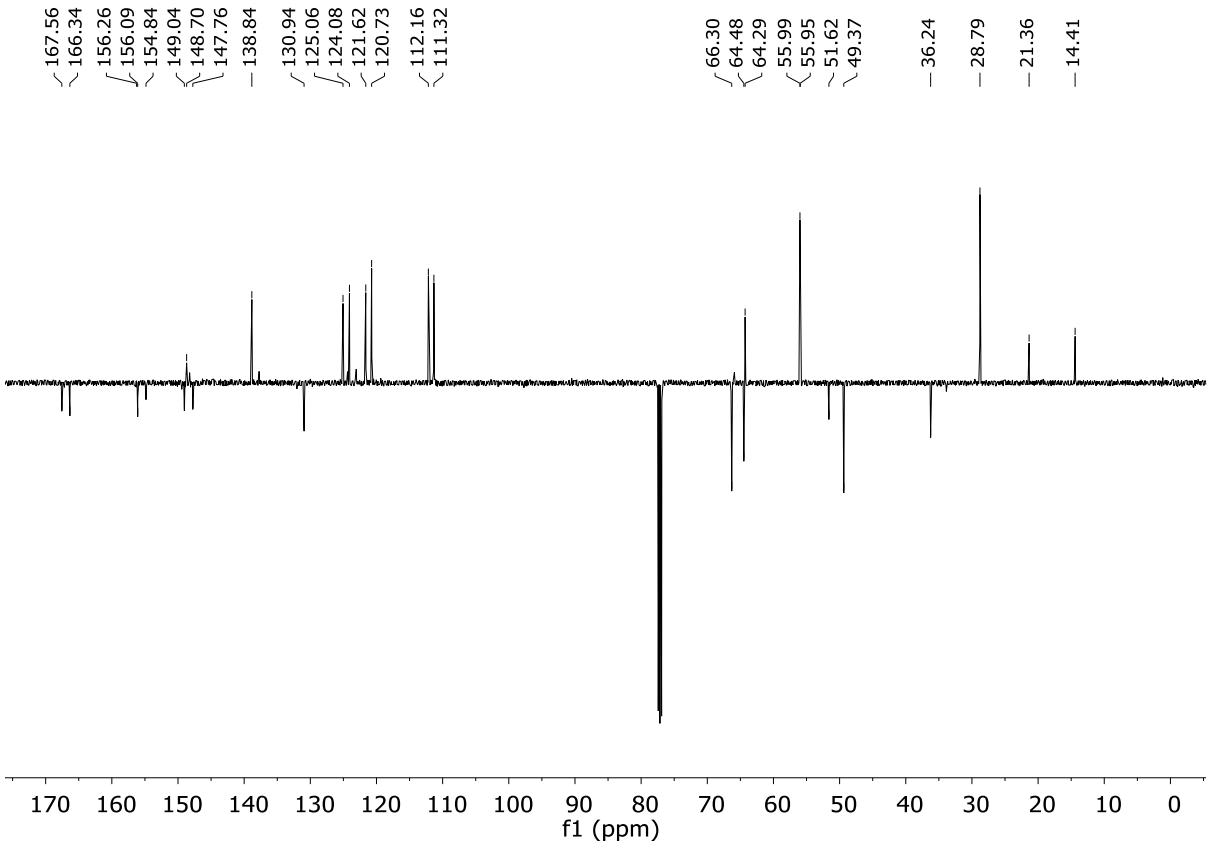
^{13}C NMR (3b) 151 MHz, $CDCl_3$



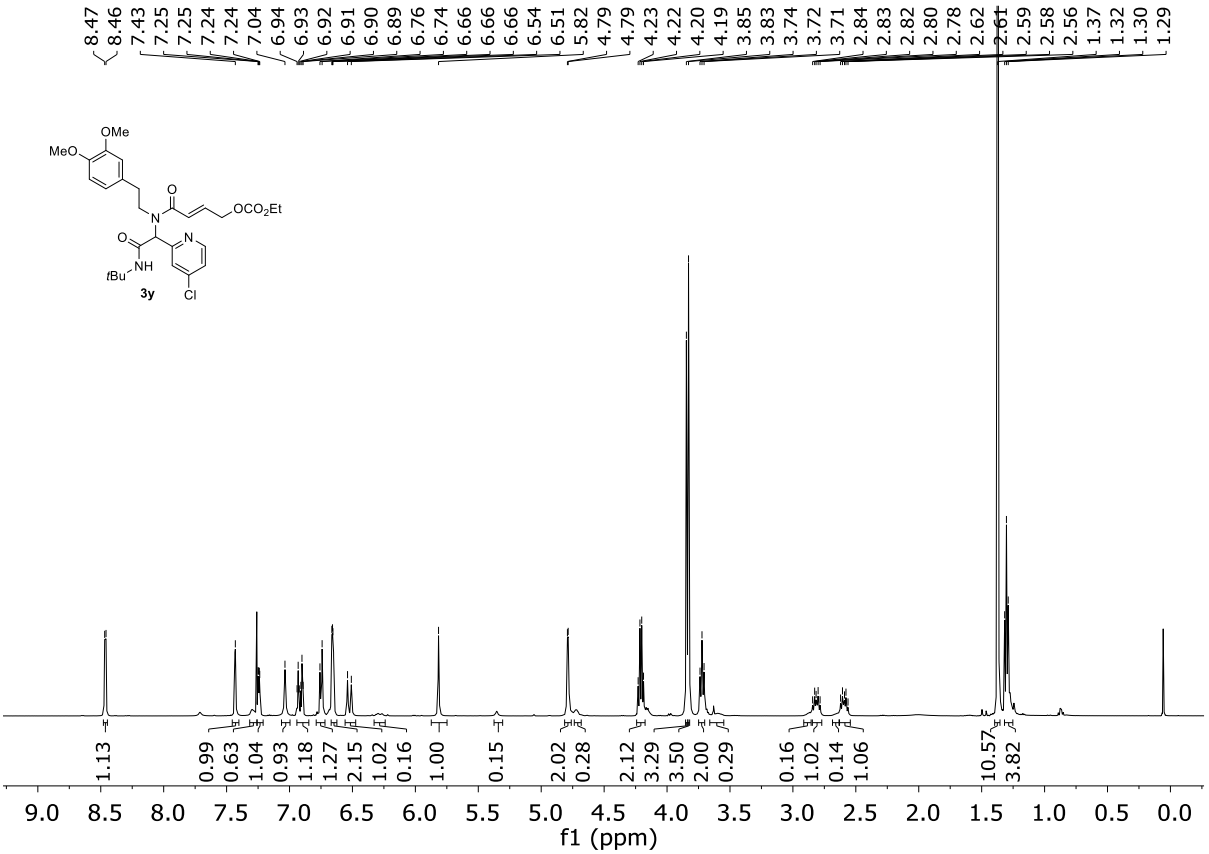
^{1}H NMR (3x) 500 MHz, $CDCl_3$



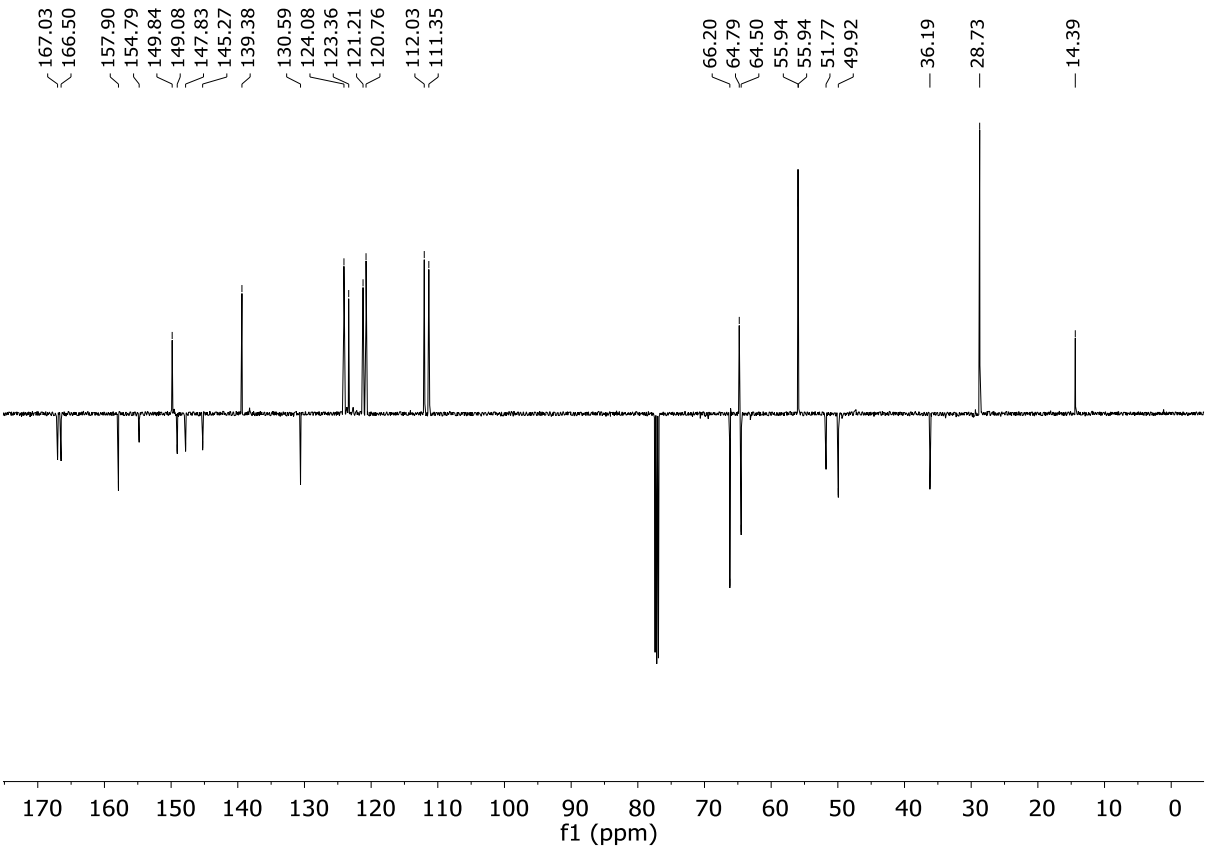
^{13}C NMR (3x) 126 MHz, $CDCl_3$



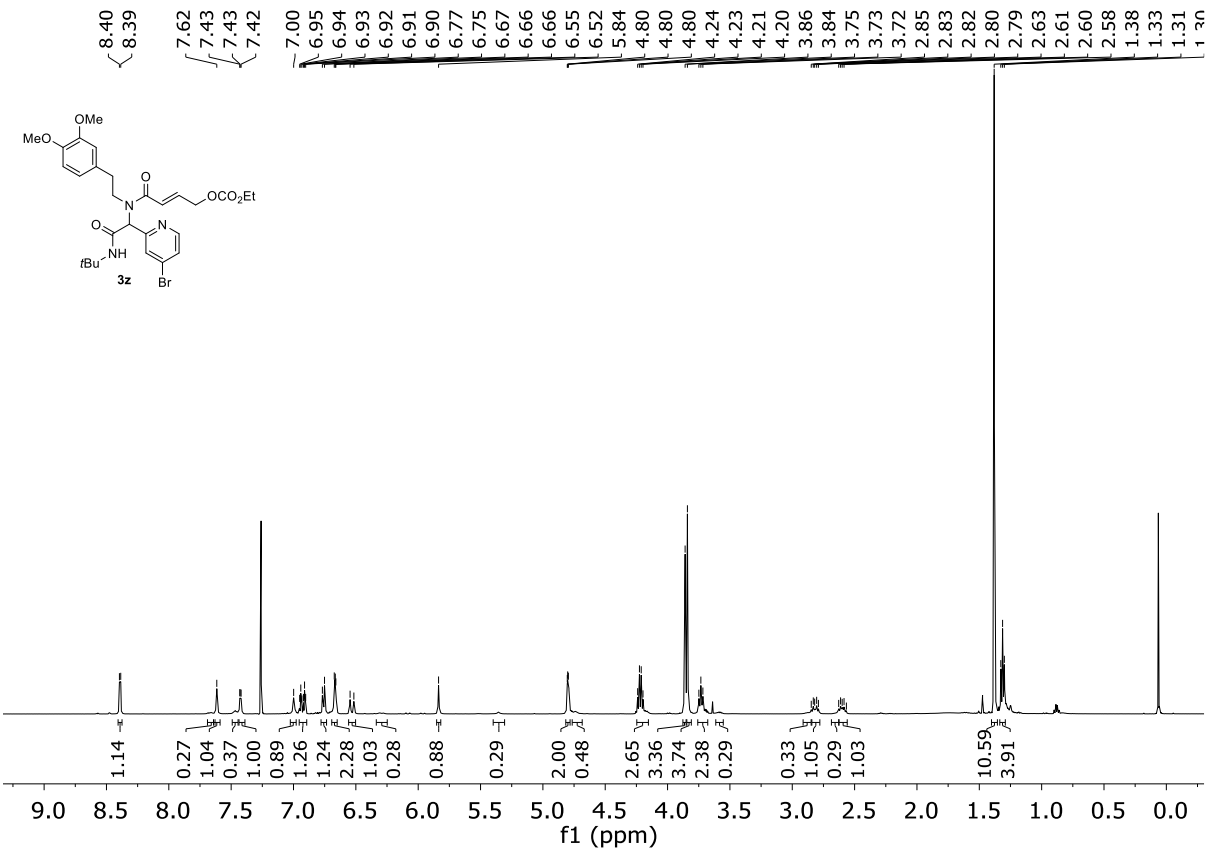
^{1}H NMR (3y) 500 MHz, $CDCl_3$



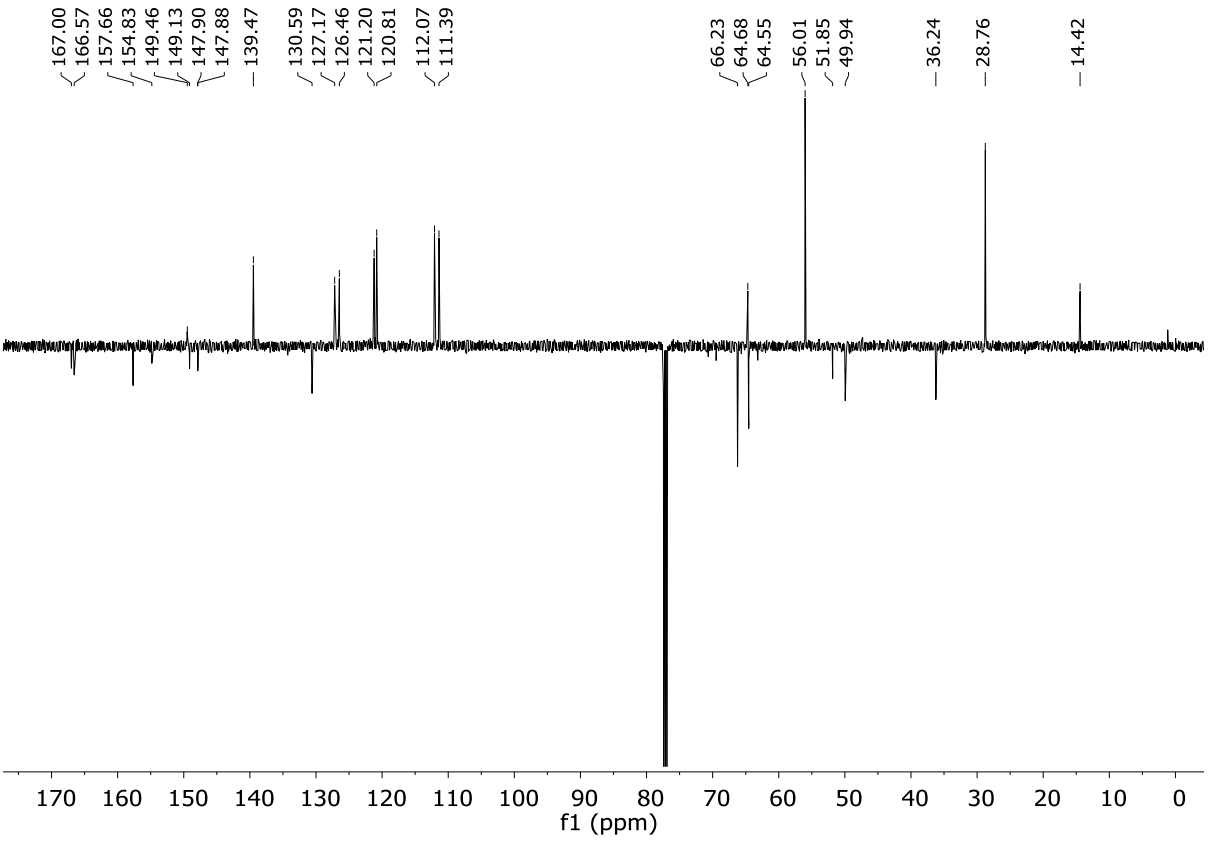
^{1}H NMR (3y) 500 MHz, $CDCl_3$



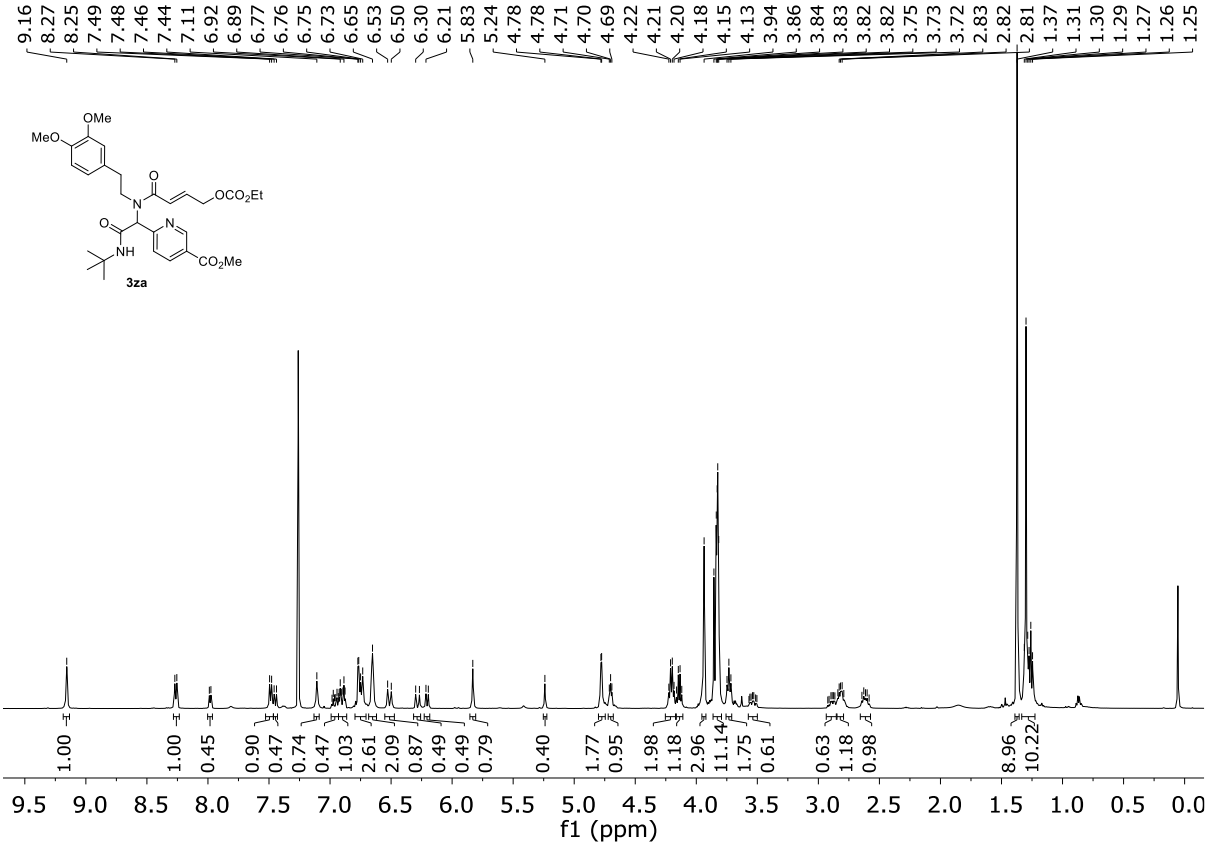
^{1}H NMR (3z) 500 MHz, $CDCl_3$



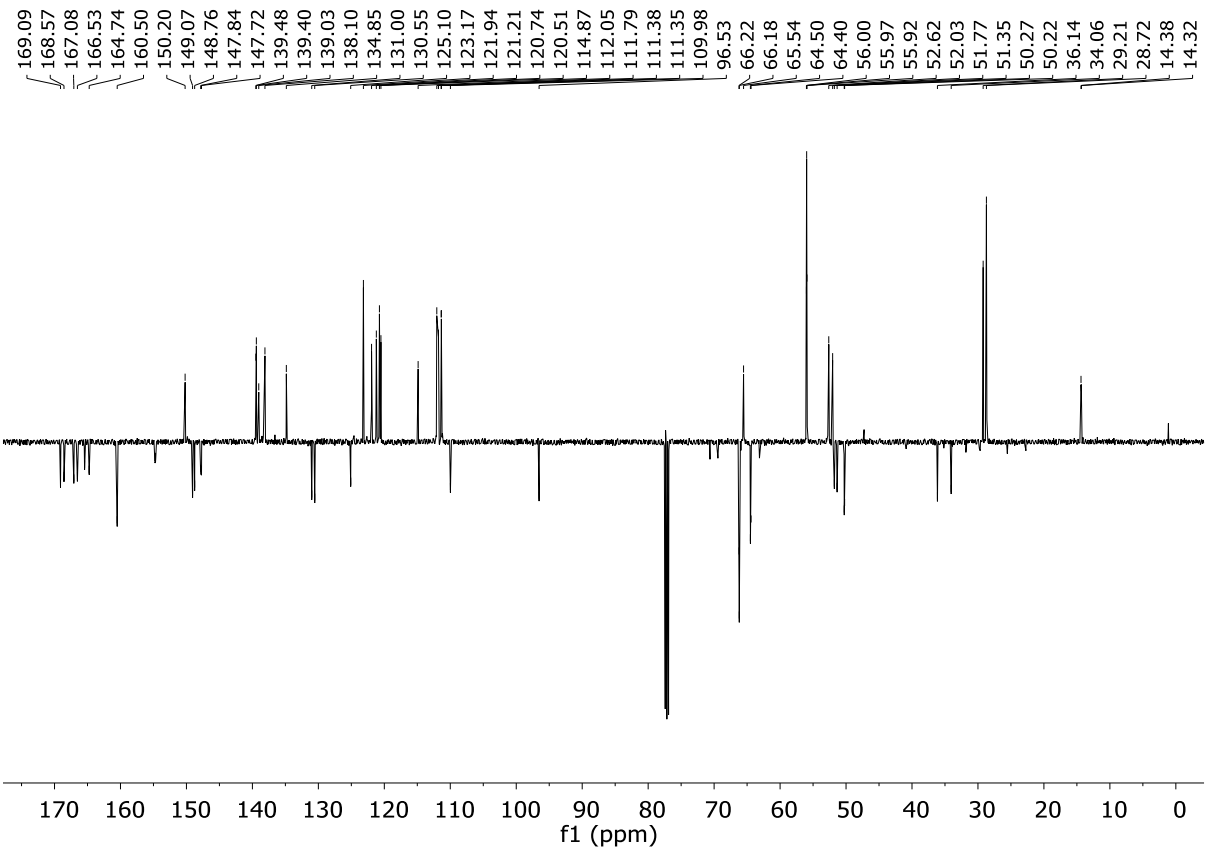
^{13}C NMR (3z) 126 MHz, $CDCl_3$



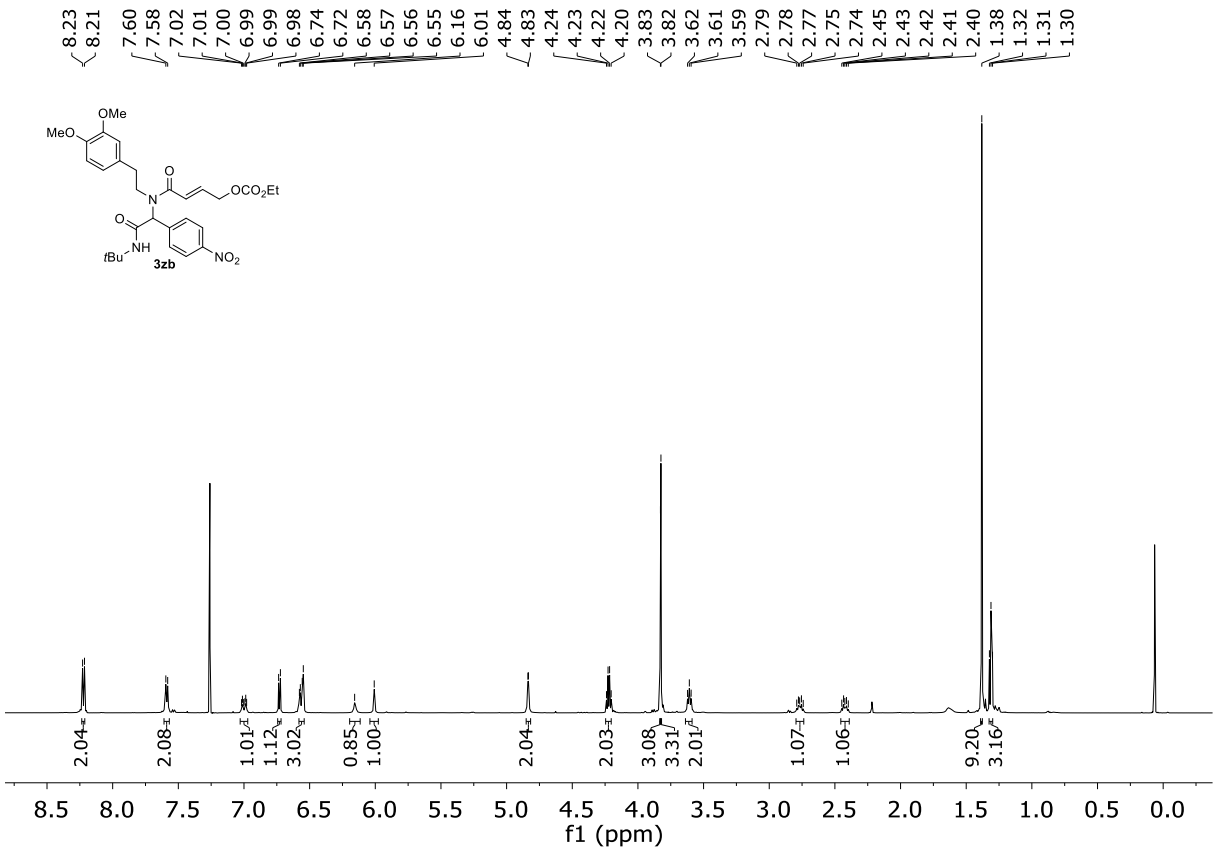
^{1}H NMR (3za) 500 MHz, $CDCl_3$



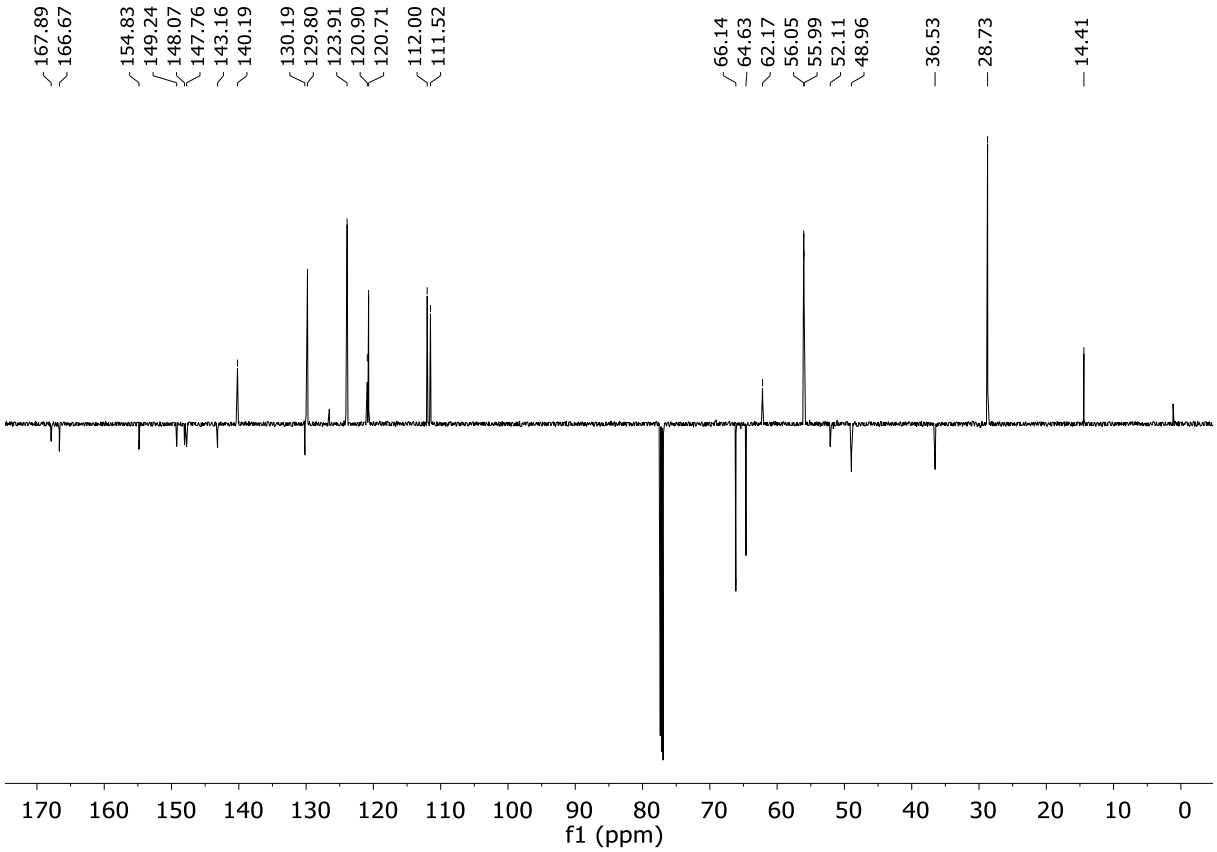
^{13}C NMR (3za) 126 MHz, $CDCl_3$



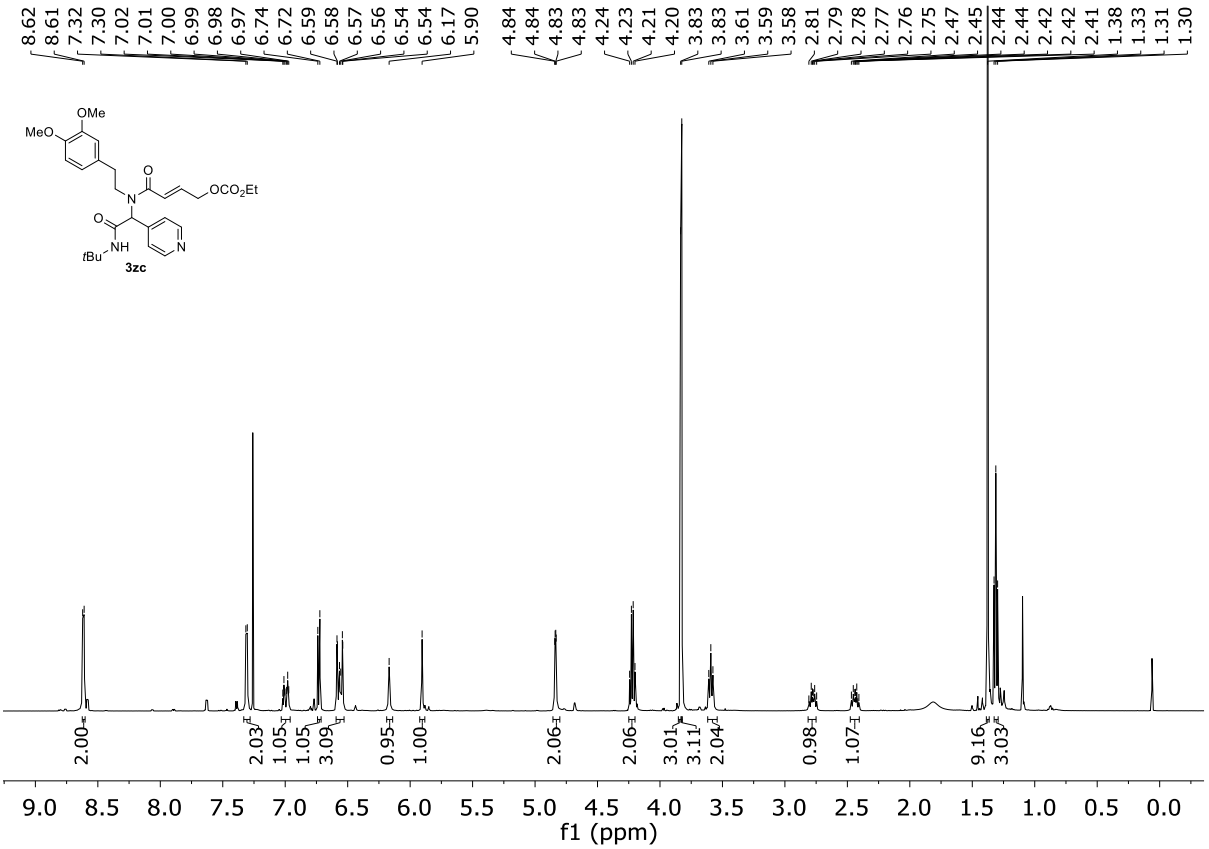
^{1}H NMR (3zb) 600 MHz, $CDCl_3$



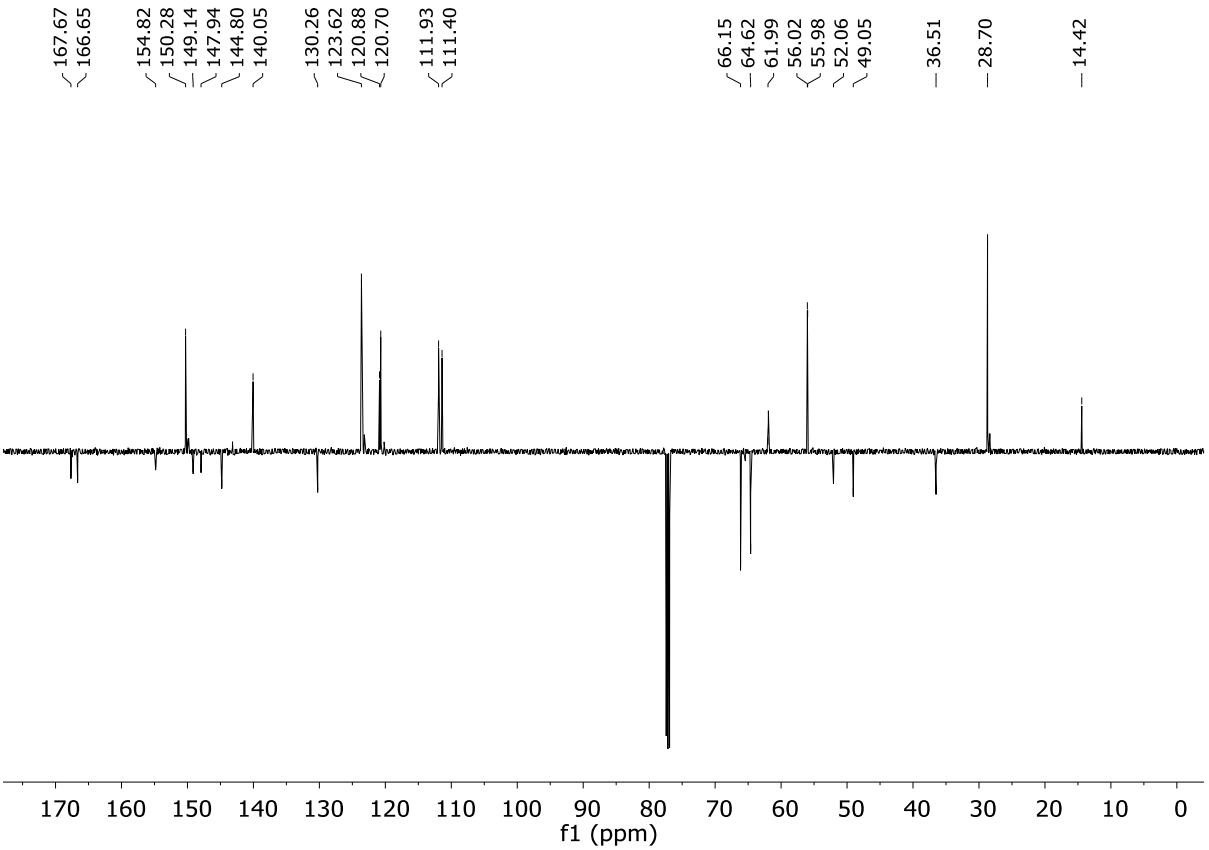
^{13}C NMR (3zb) 151 MHz, $CDCl_3$



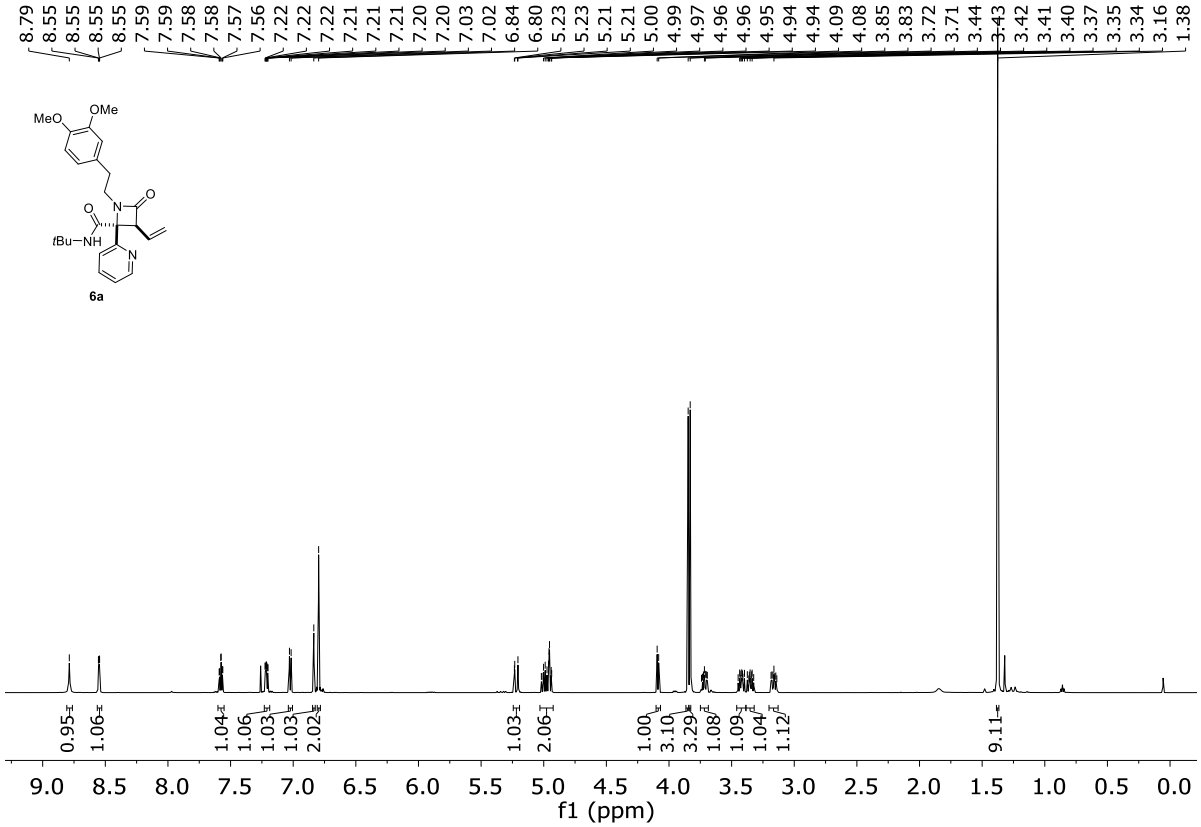
^{1}H NMR (3zc) 500 MHz, $CDCl_3$



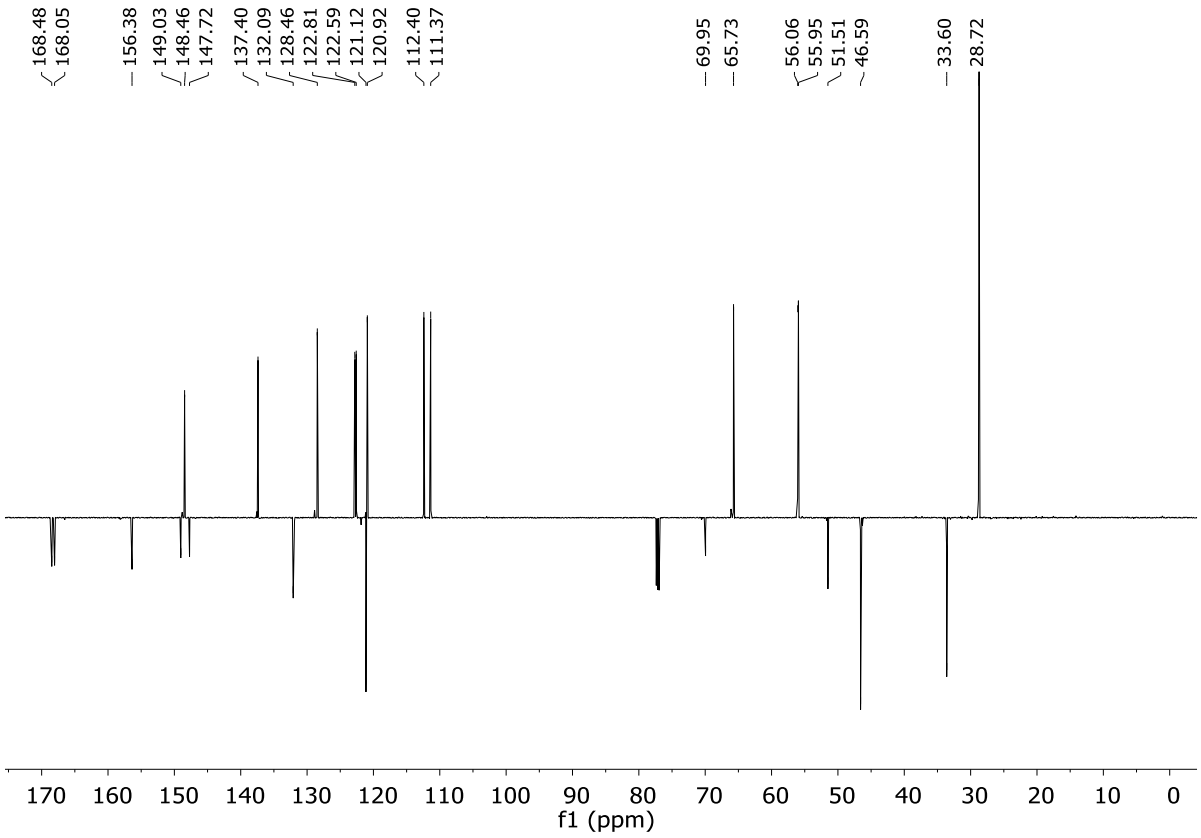
^{13}C NMR (3zc) 126 MHz, $CDCl_3$



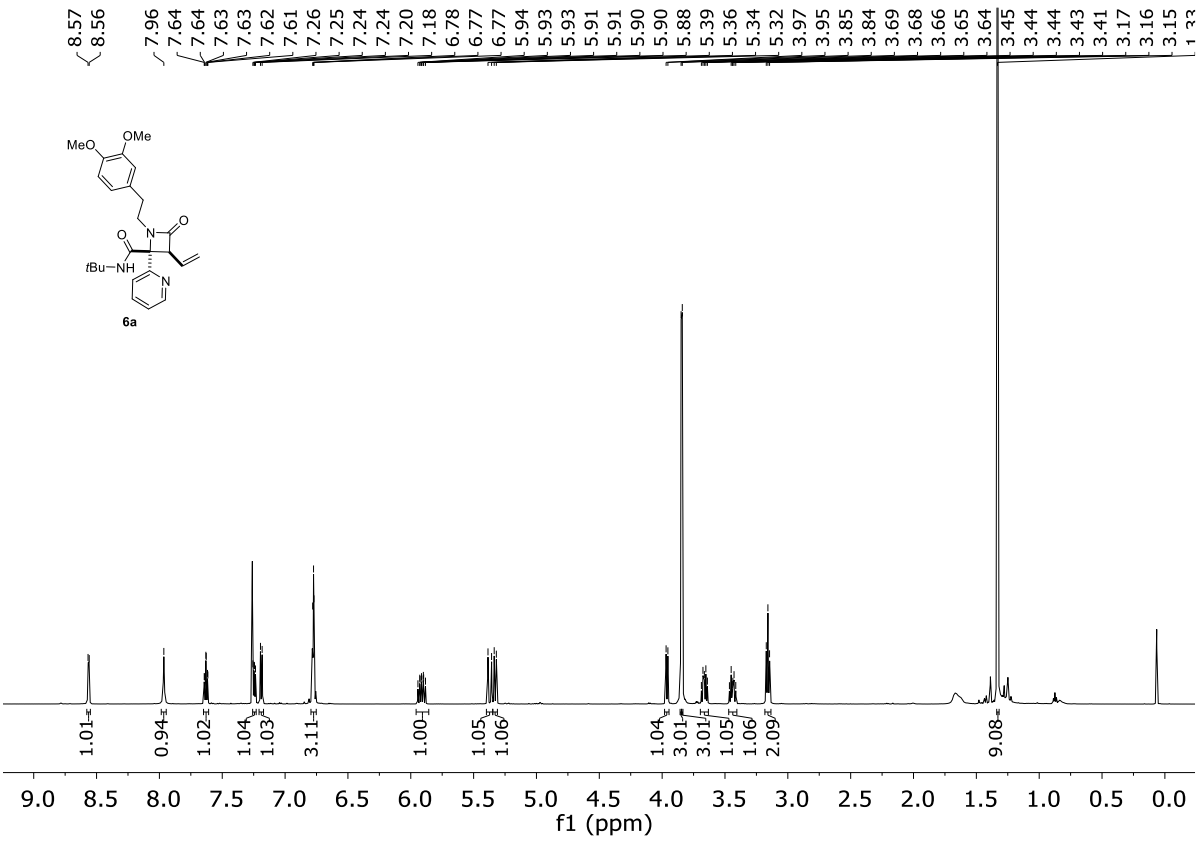
^{1}H NMR (*trans*-6a) 600 MHz, $CDCl_3$



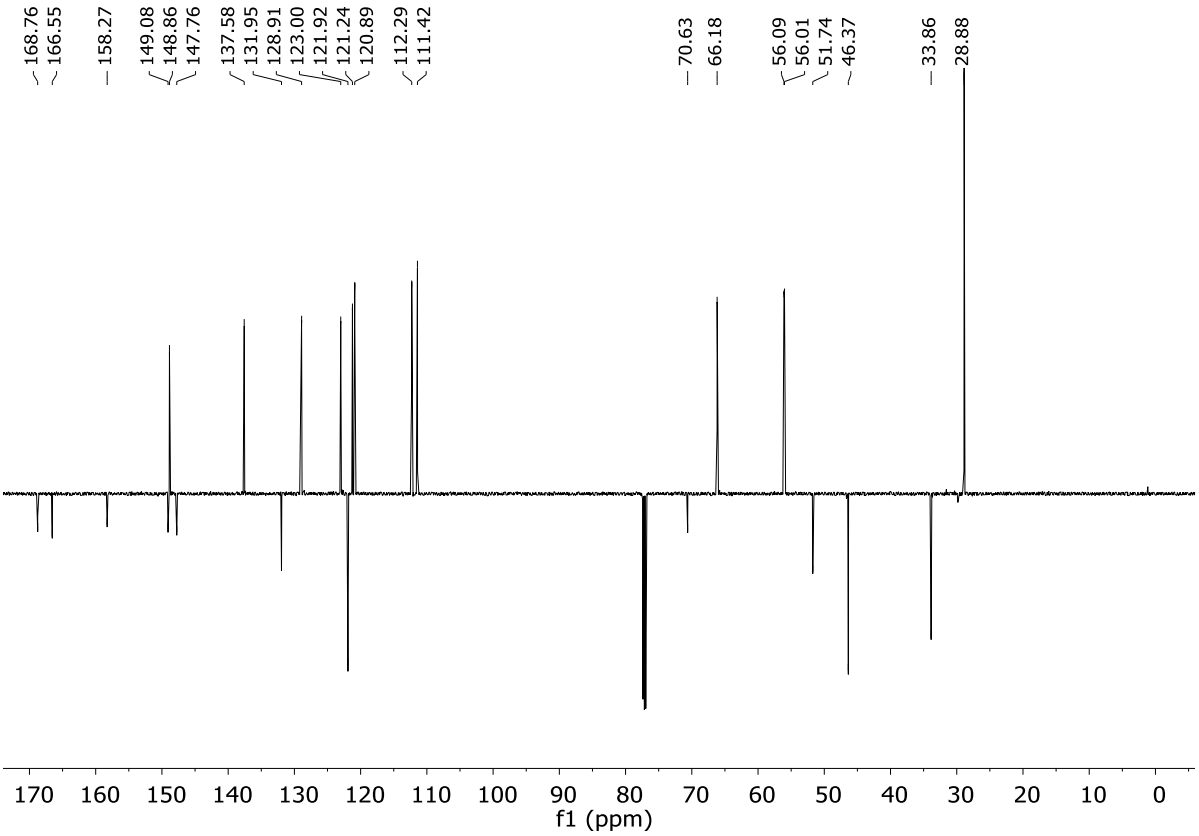
^{13}C NMR (*trans*-6a) 151 MHz, $CDCl_3$



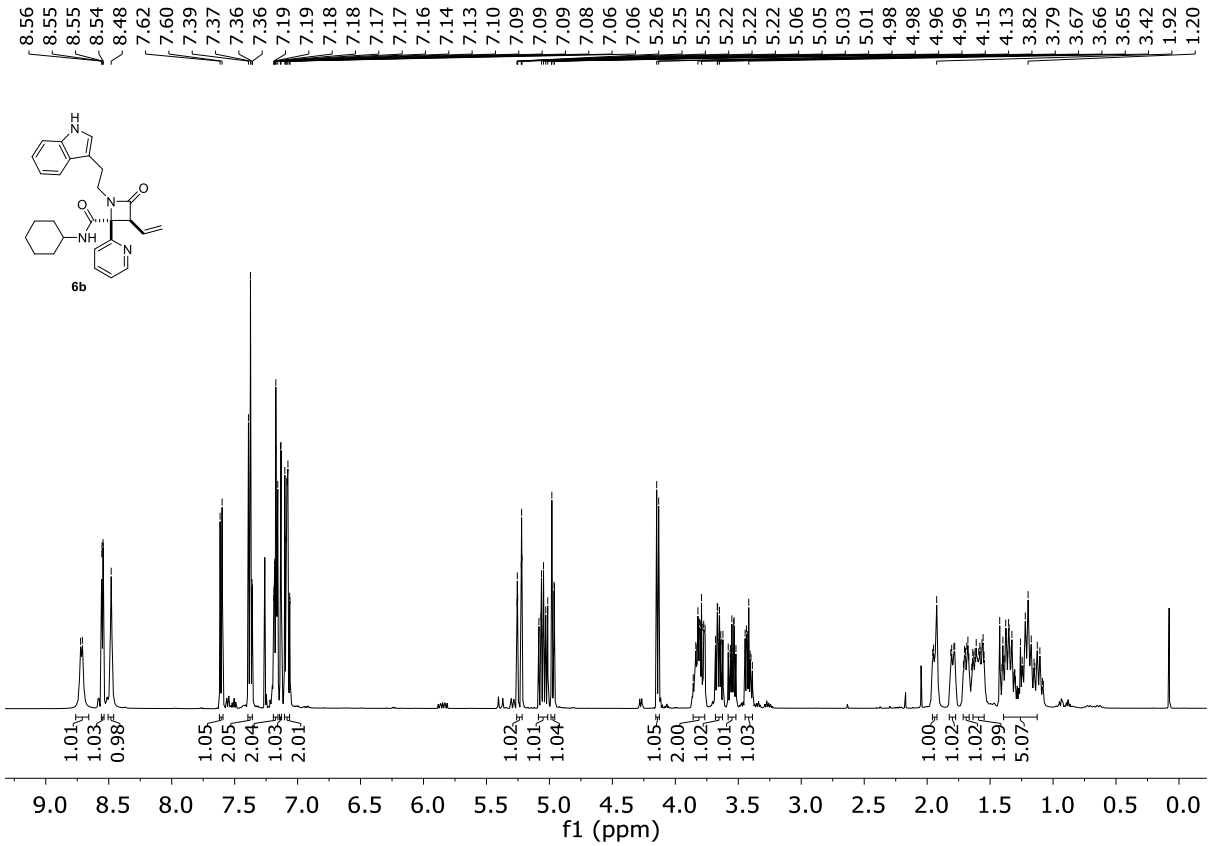
^{1}H NMR (*cis*-6a) 600 MHz, $CDCl_3$



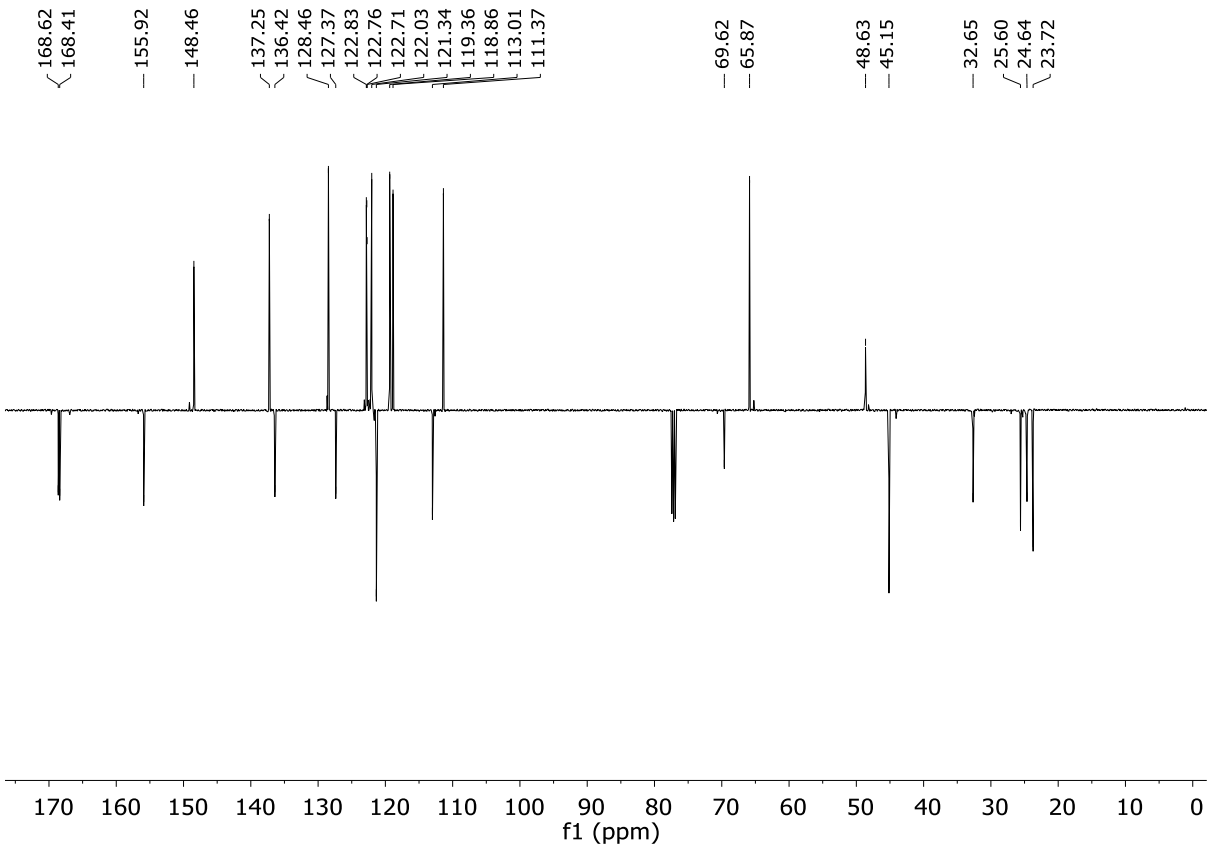
^{13}C NMR (*cis*-6a) 151 MHz, $CDCl_3$



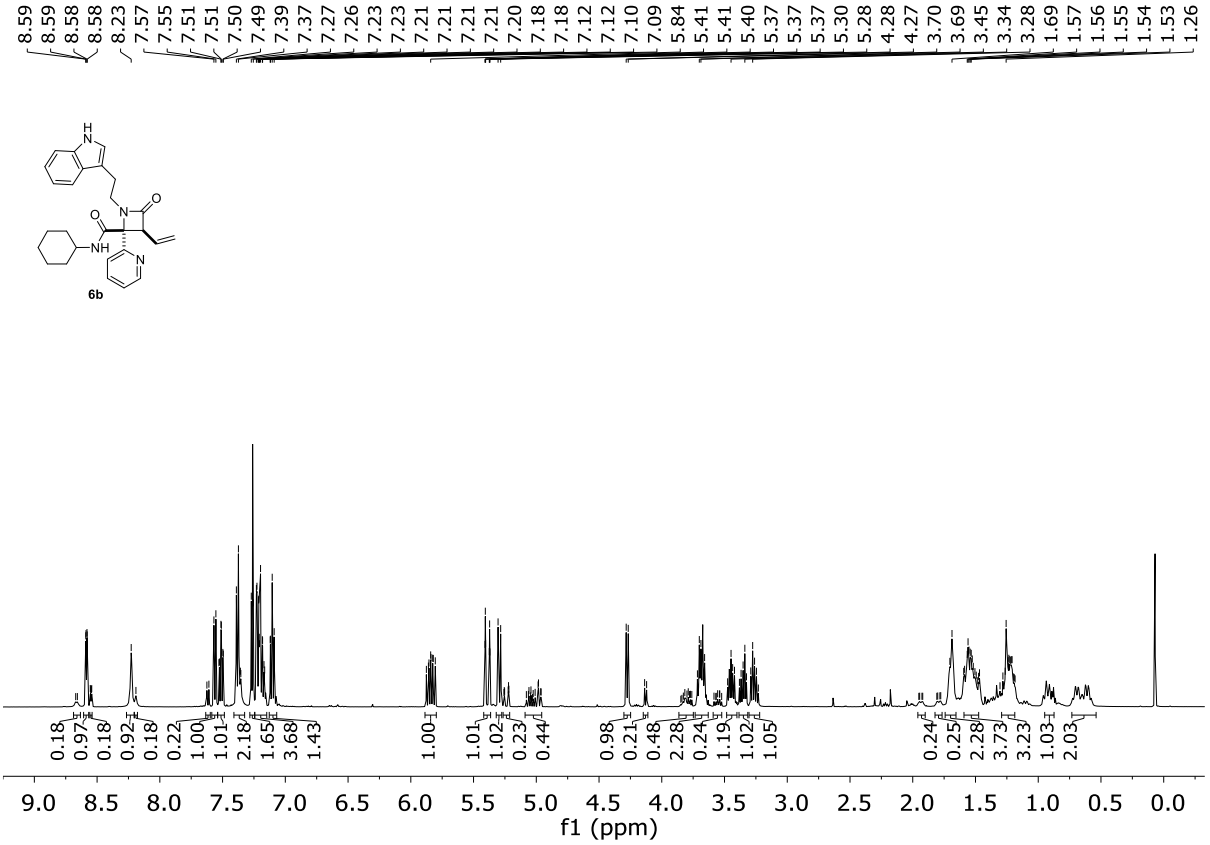
^{1}H NMR (*trans*-6b) 500 MHz, $CDCl_3$



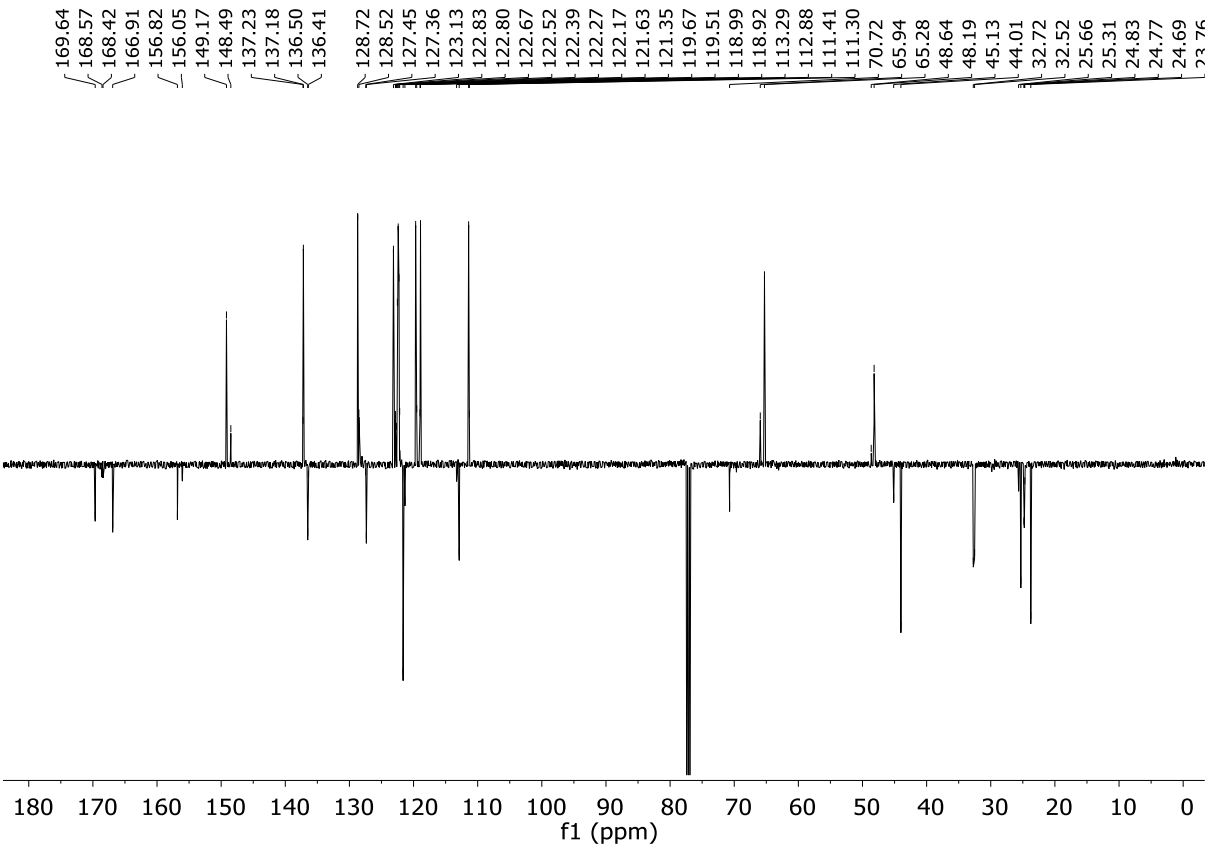
^{13}C NMR (*trans*-6b) 126 MHz, $CDCl_3$



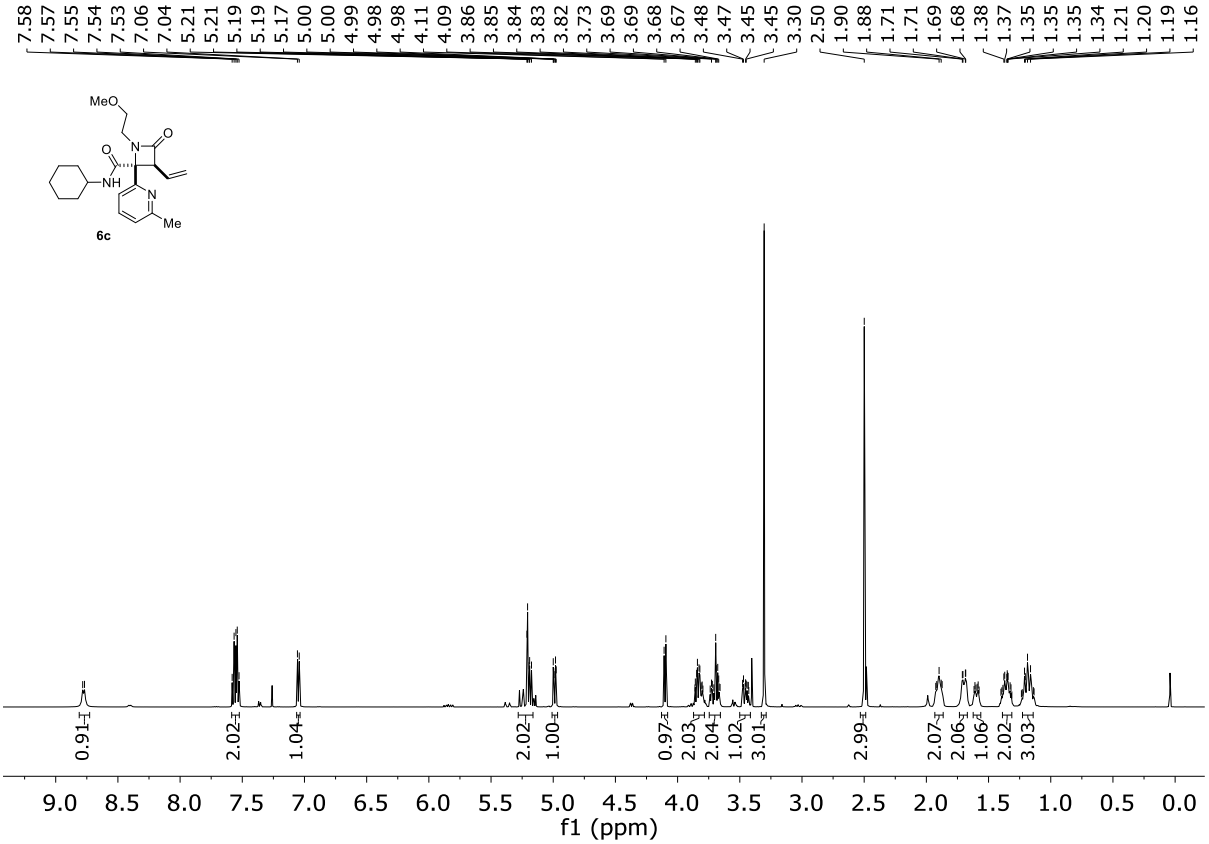
^{1}H NMR (*cis*-6b) 500 MHz, $CDCl_3$



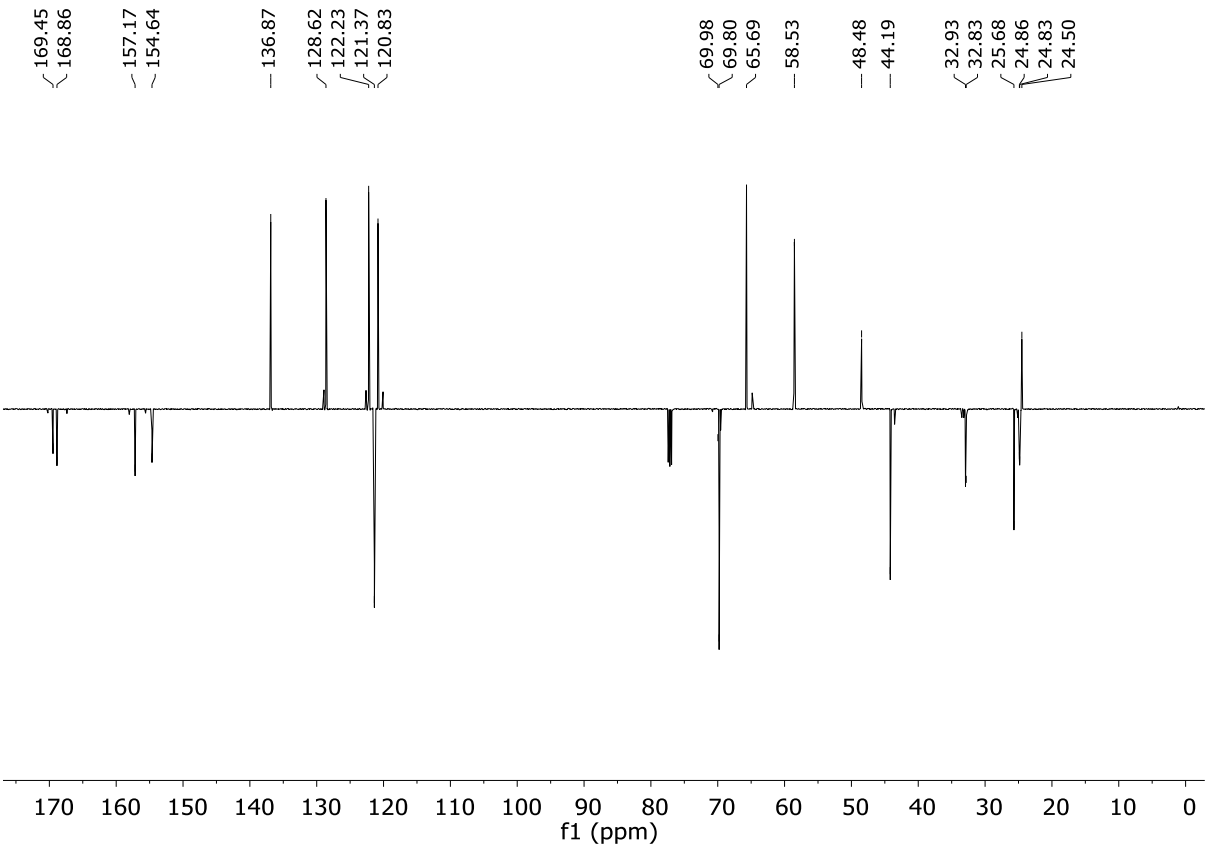
^{13}C NMR (*cis*-6b) 126 MHz, $CDCl_3$



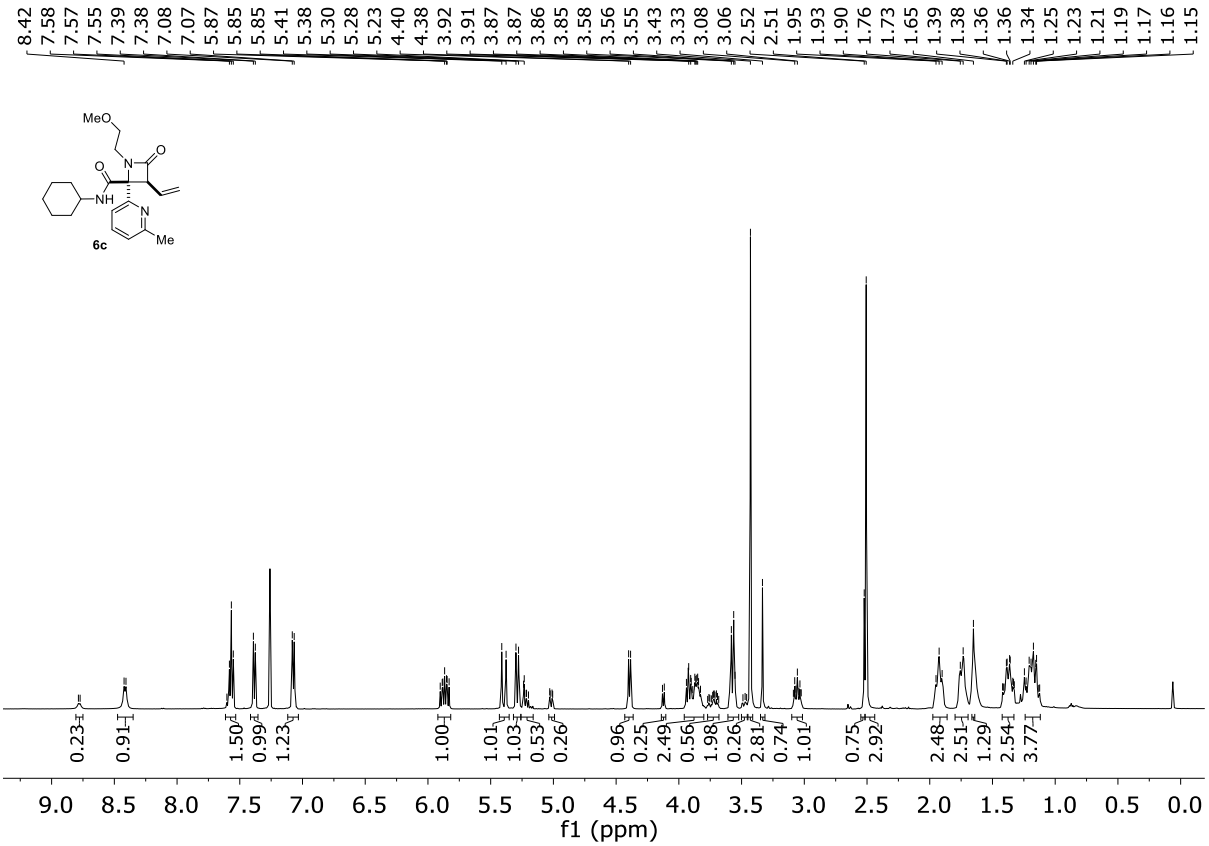
^{1}H NMR (*trans*-6c) 500 MHz, $CDCl_3$



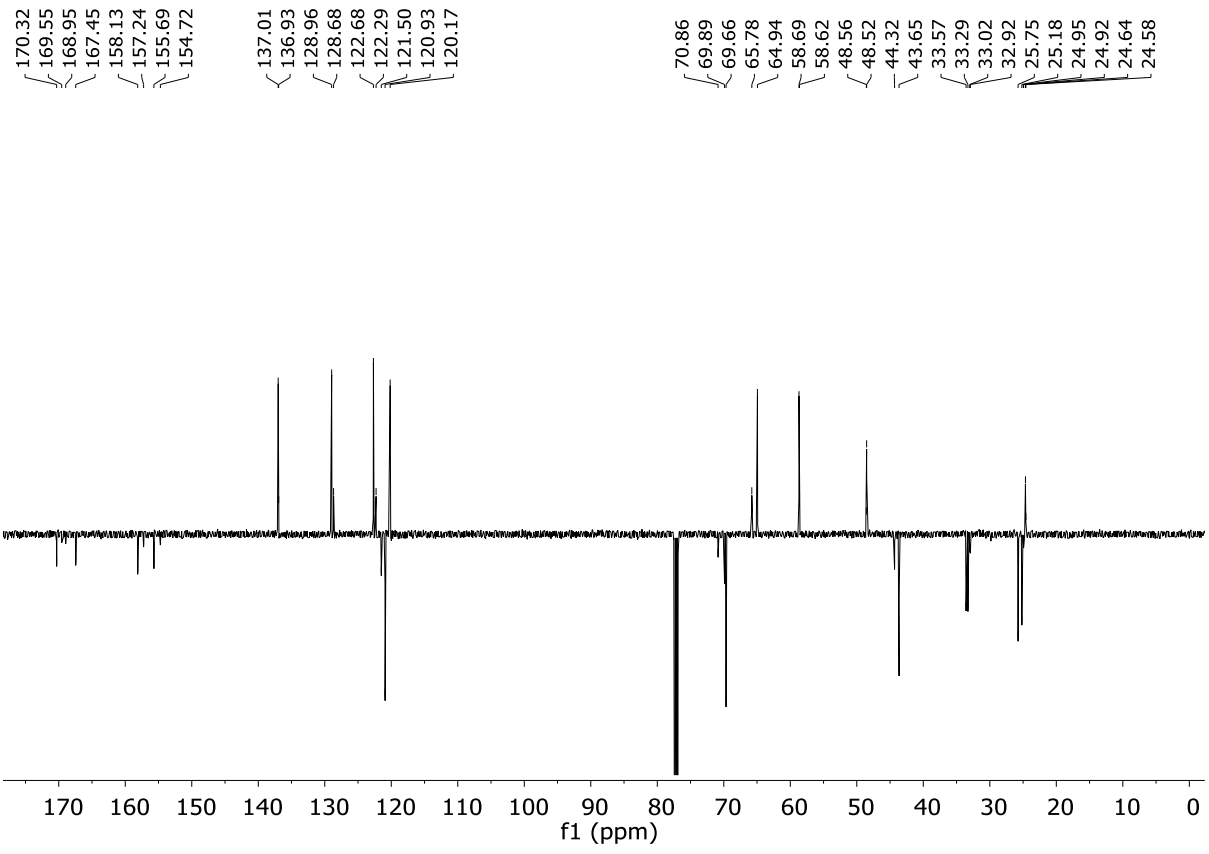
^{13}C NMR (*trans*-6c) 126 MHz, $CDCl_3$



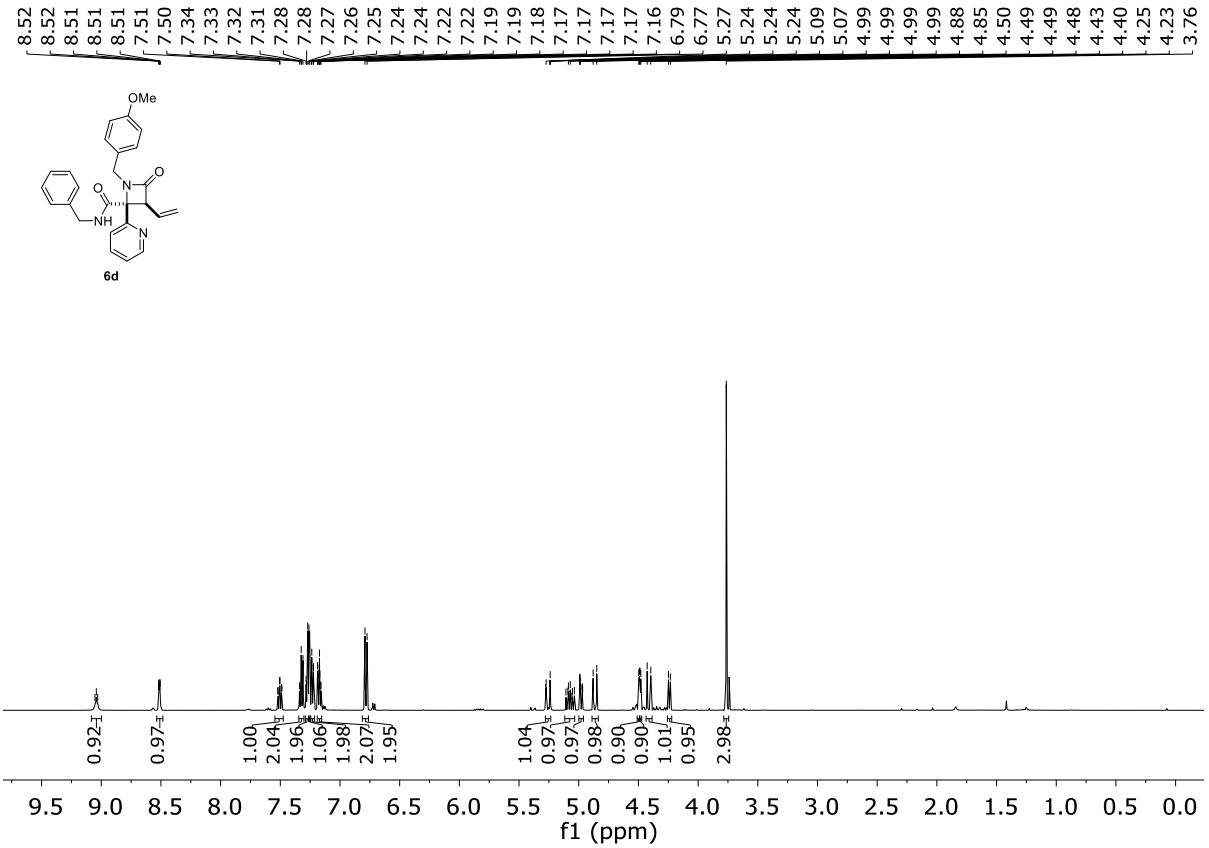
^{1}H NMR (*cis*-6c) 500 MHz, $CDCl_3$



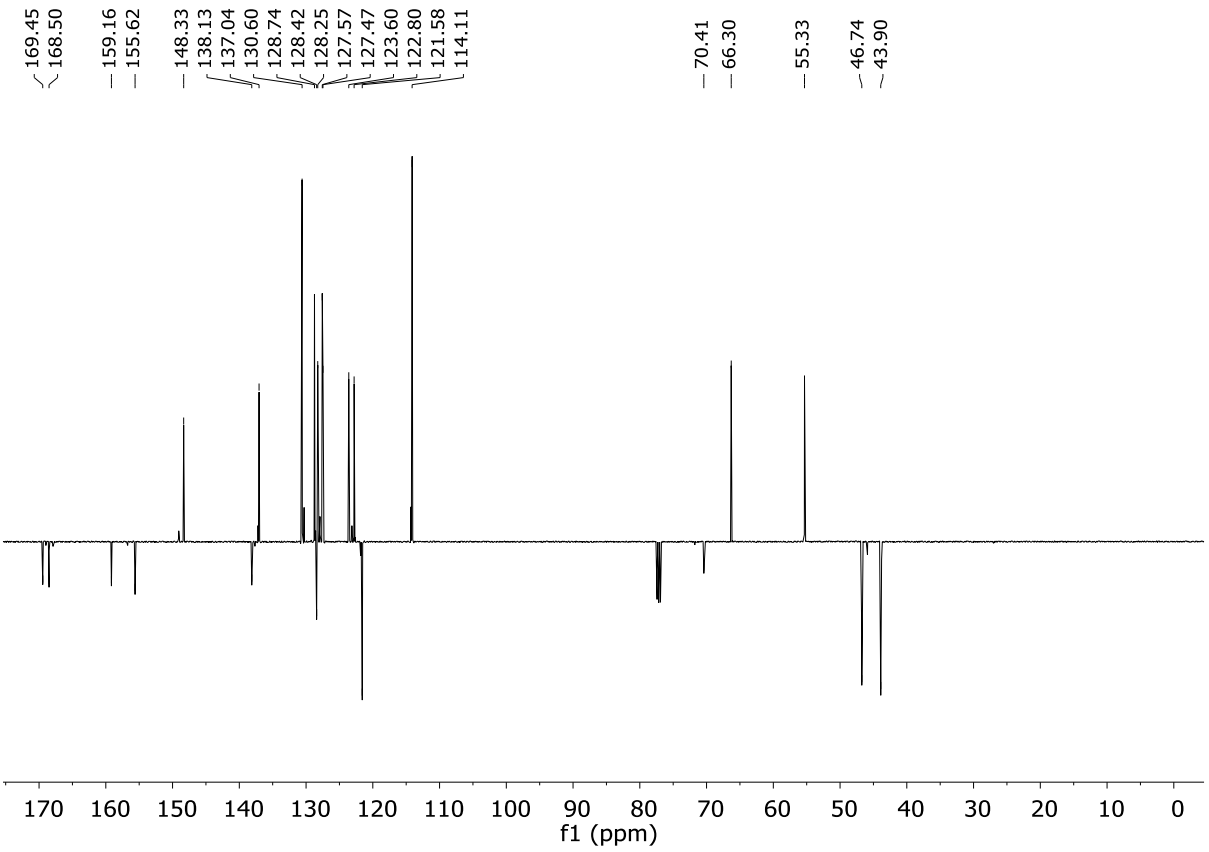
^{13}C NMR (*cis*-6c) 126 MHz, $CDCl_3$



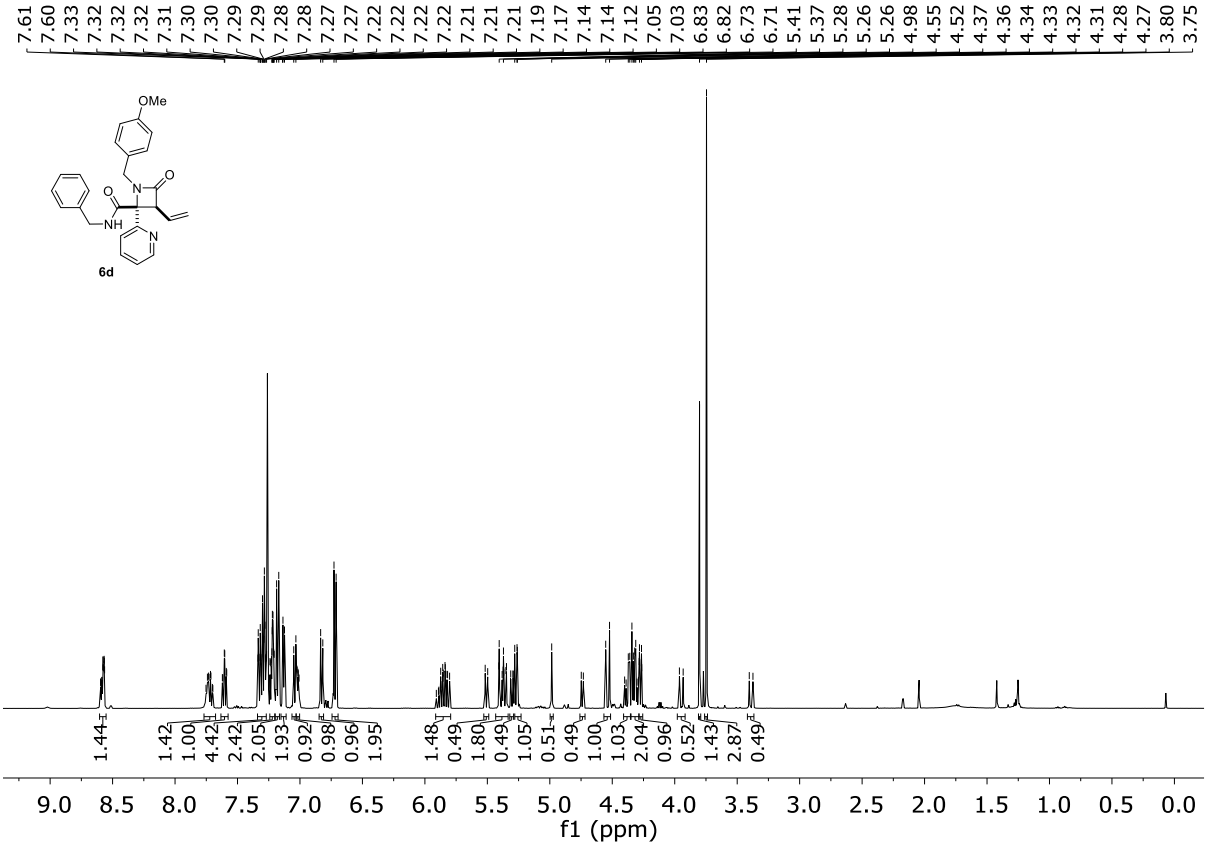
^{1}H NMR (*trans*-6d) 500 MHz, $CDCl_3$



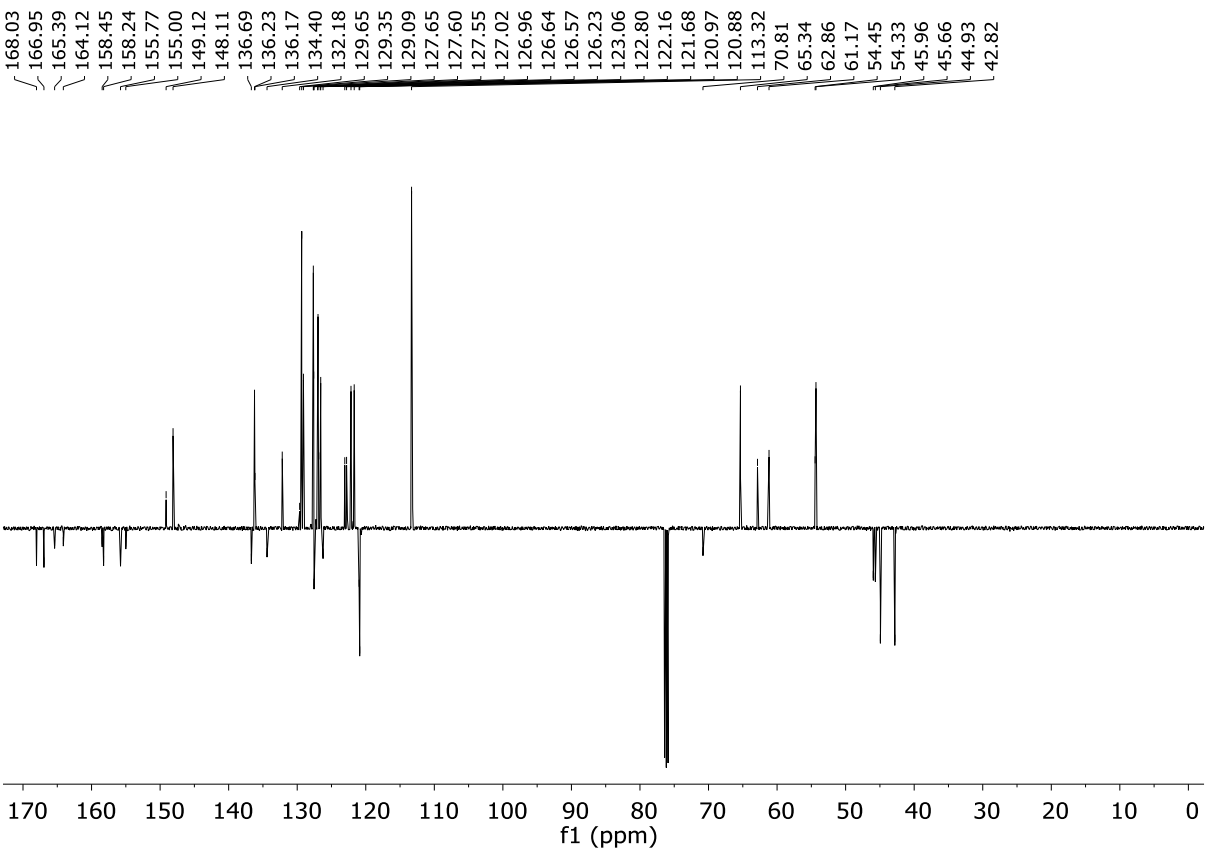
^{13}C NMR (*trans*-6d) 126 MHz, $CDCl_3$



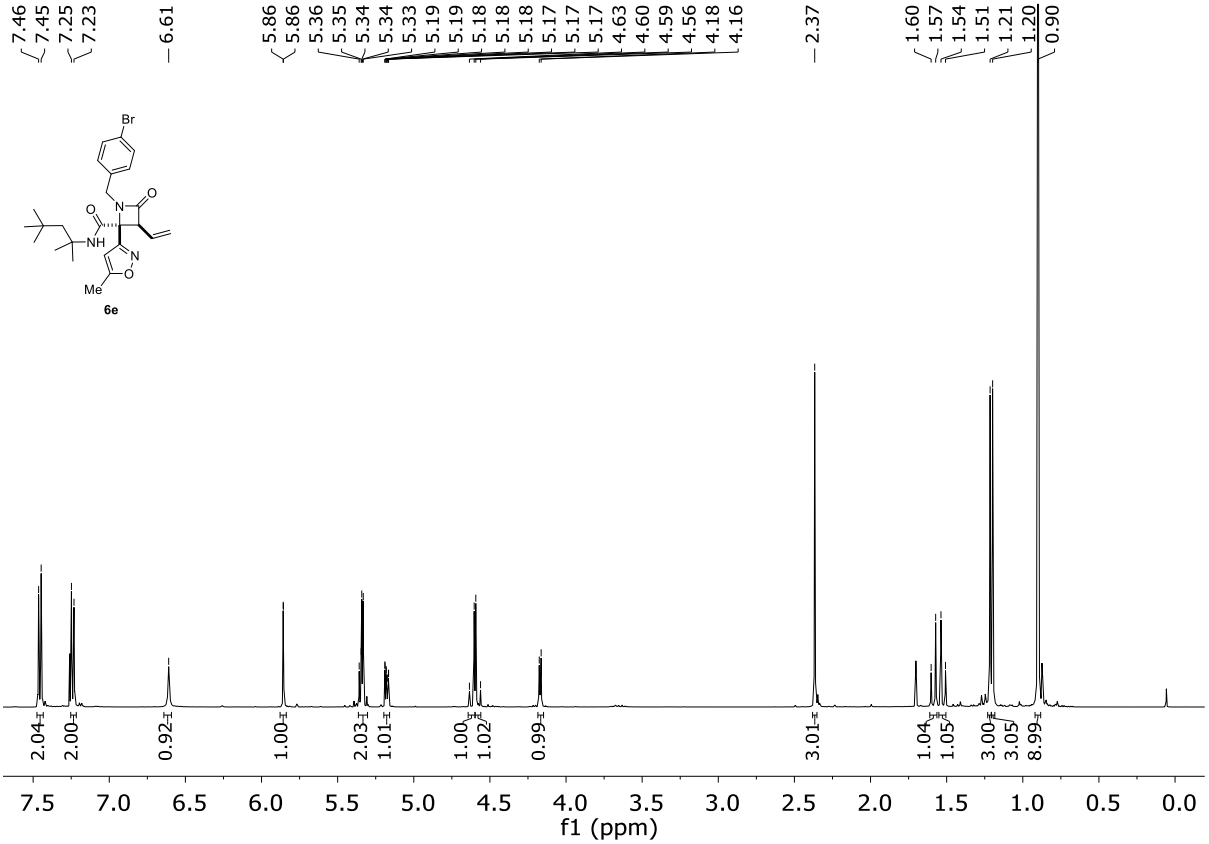
^{1}H NMR (*cis*-6d) 500 MHz, $CDCl_3$



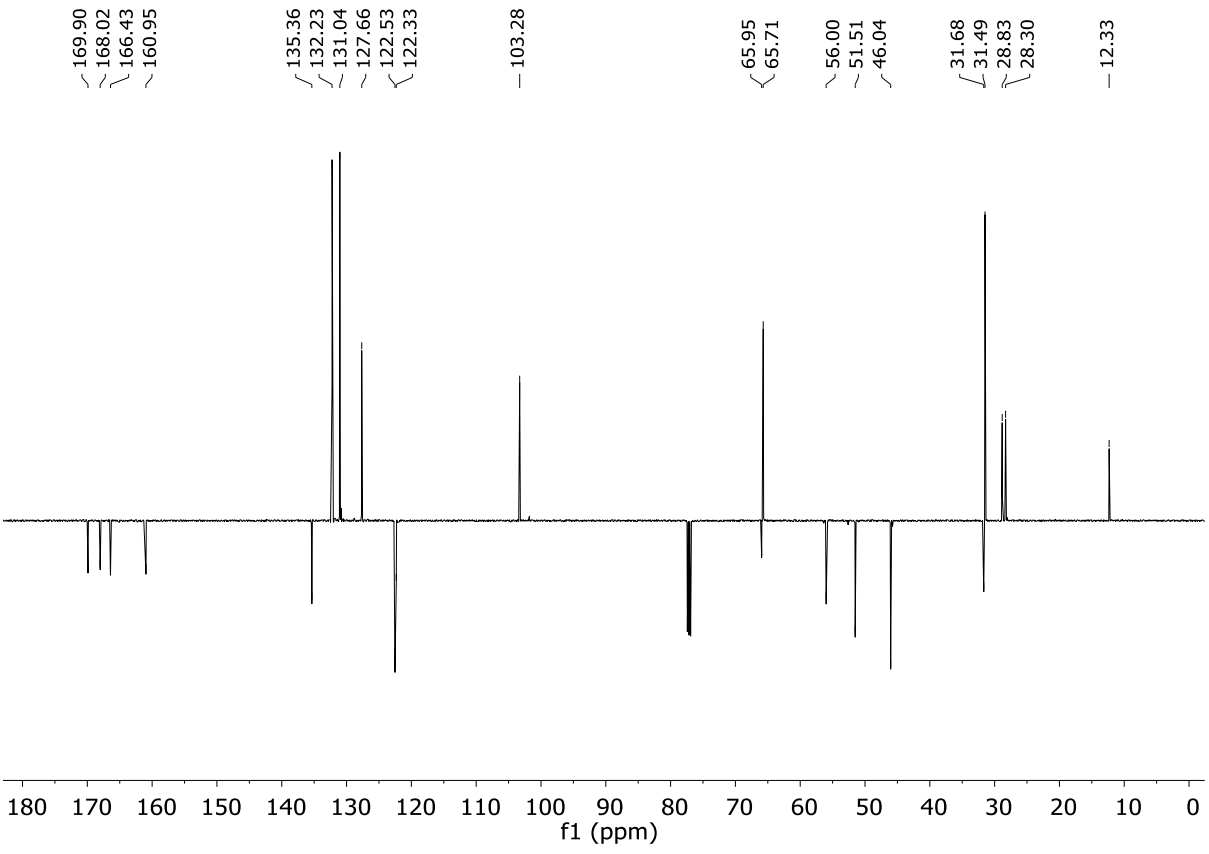
^{13}C NMR (*cis*-6d) 126 MHz, $CDCl_3$



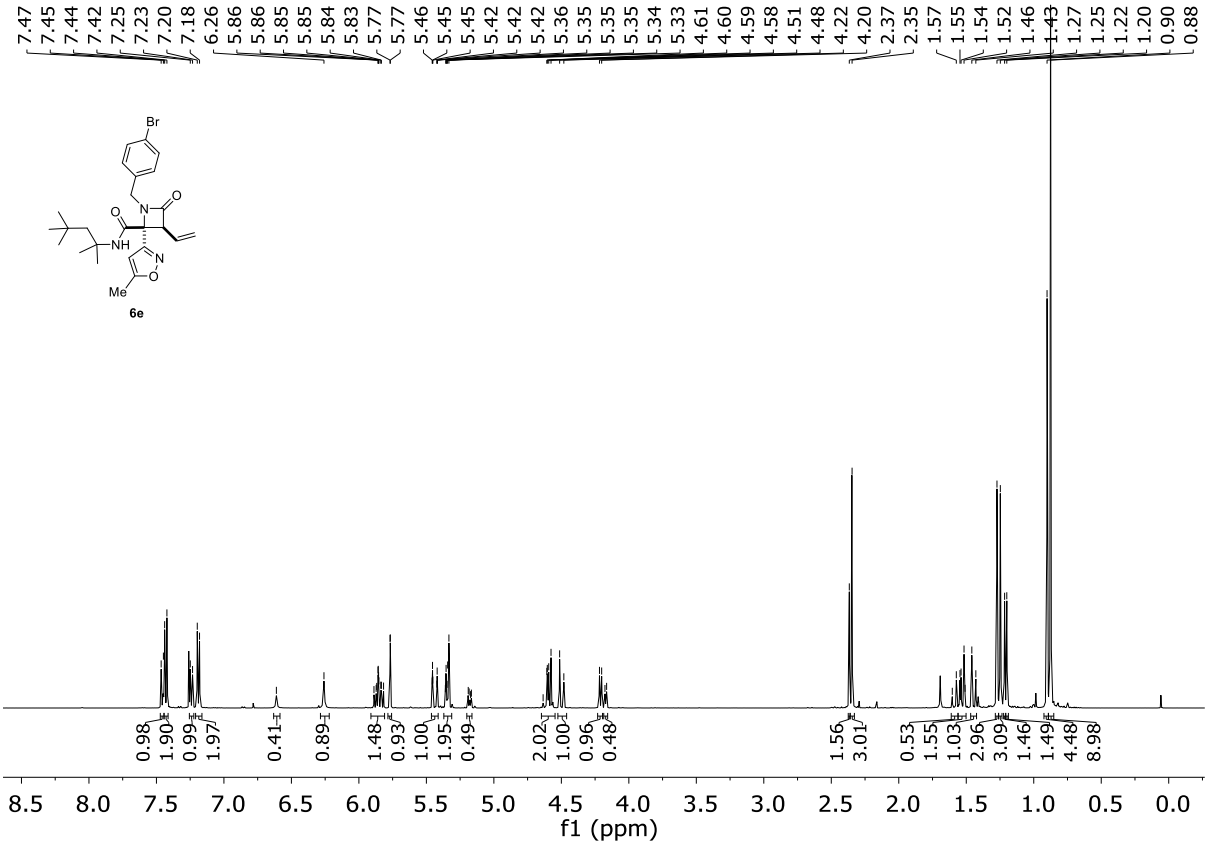
^{1}H NMR (*trans*-6e) 500 MHz, $CDCl_3$



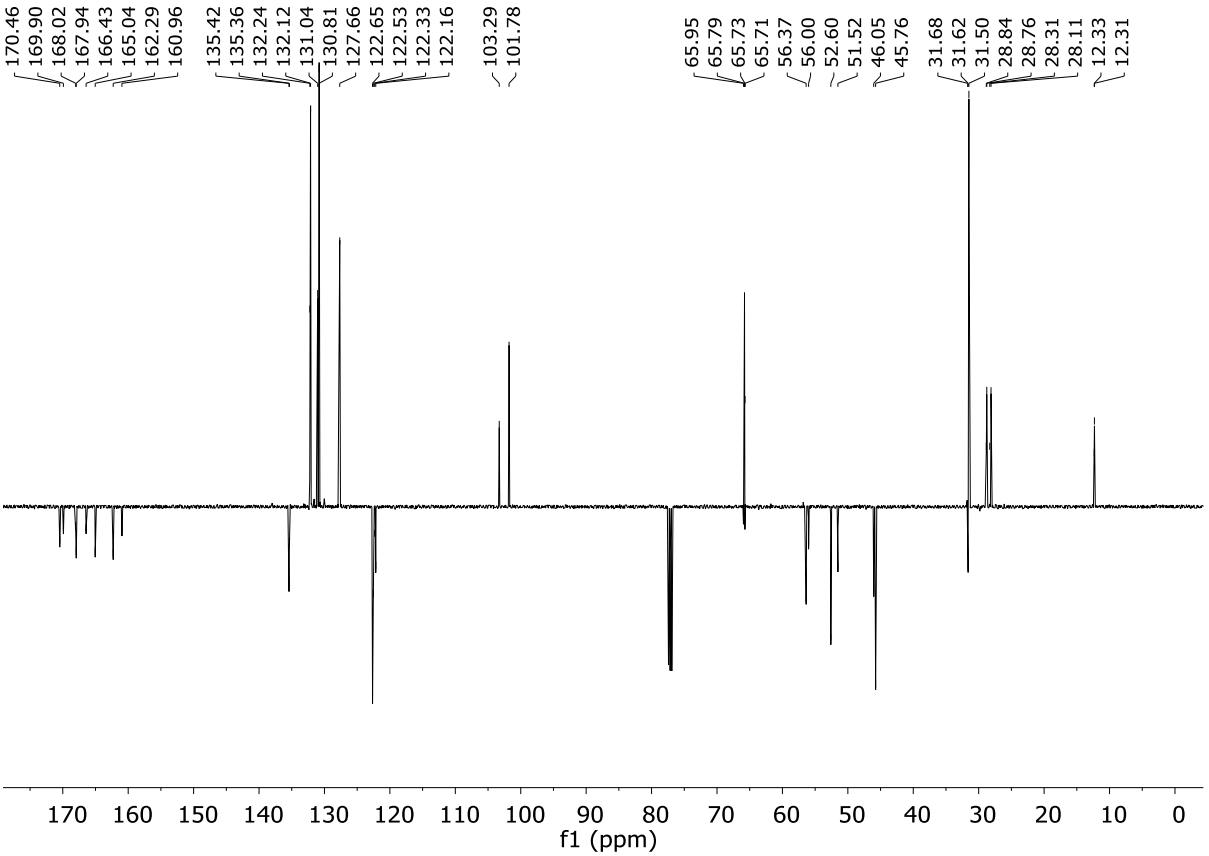
^{13}C NMR (*trans*-6e) 126 MHz, $CDCl_3$



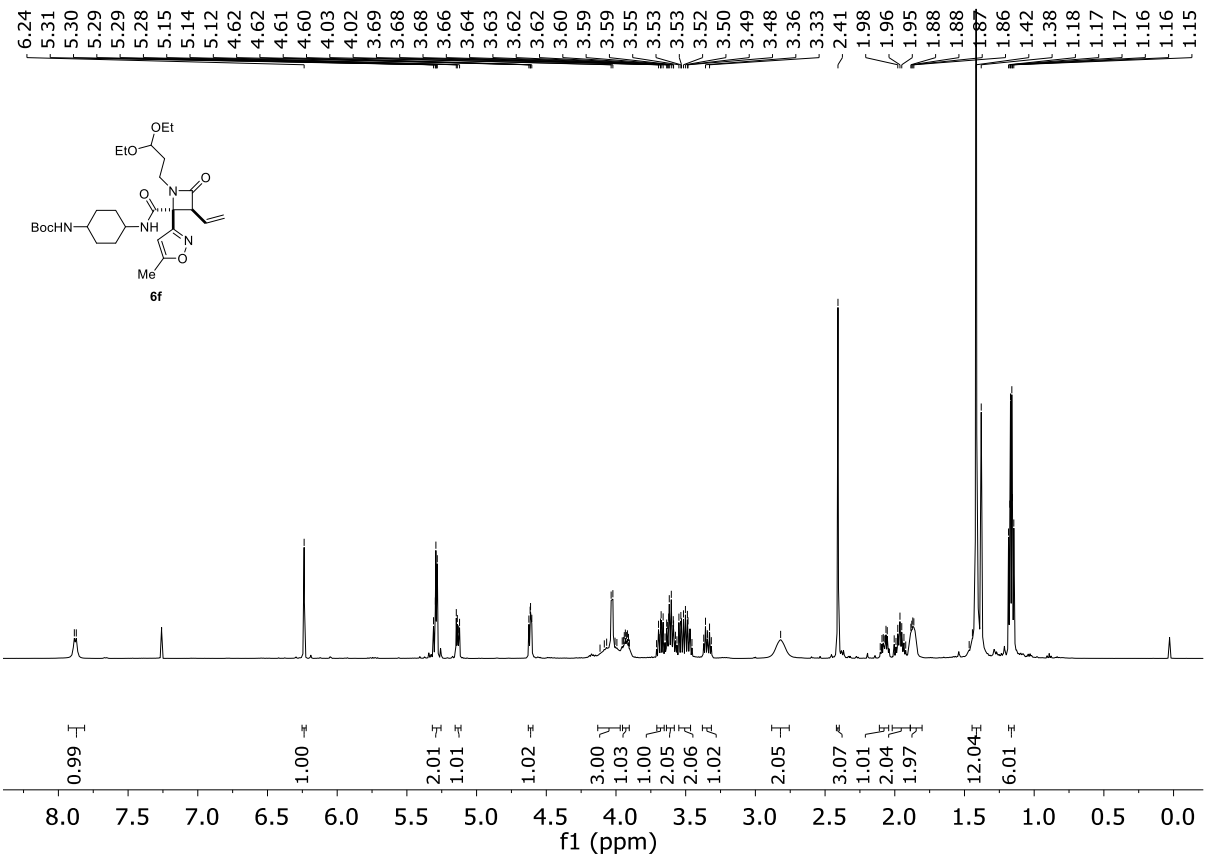
^{1}H NMR (*cis*-6e) 500 MHz, $CDCl_3$



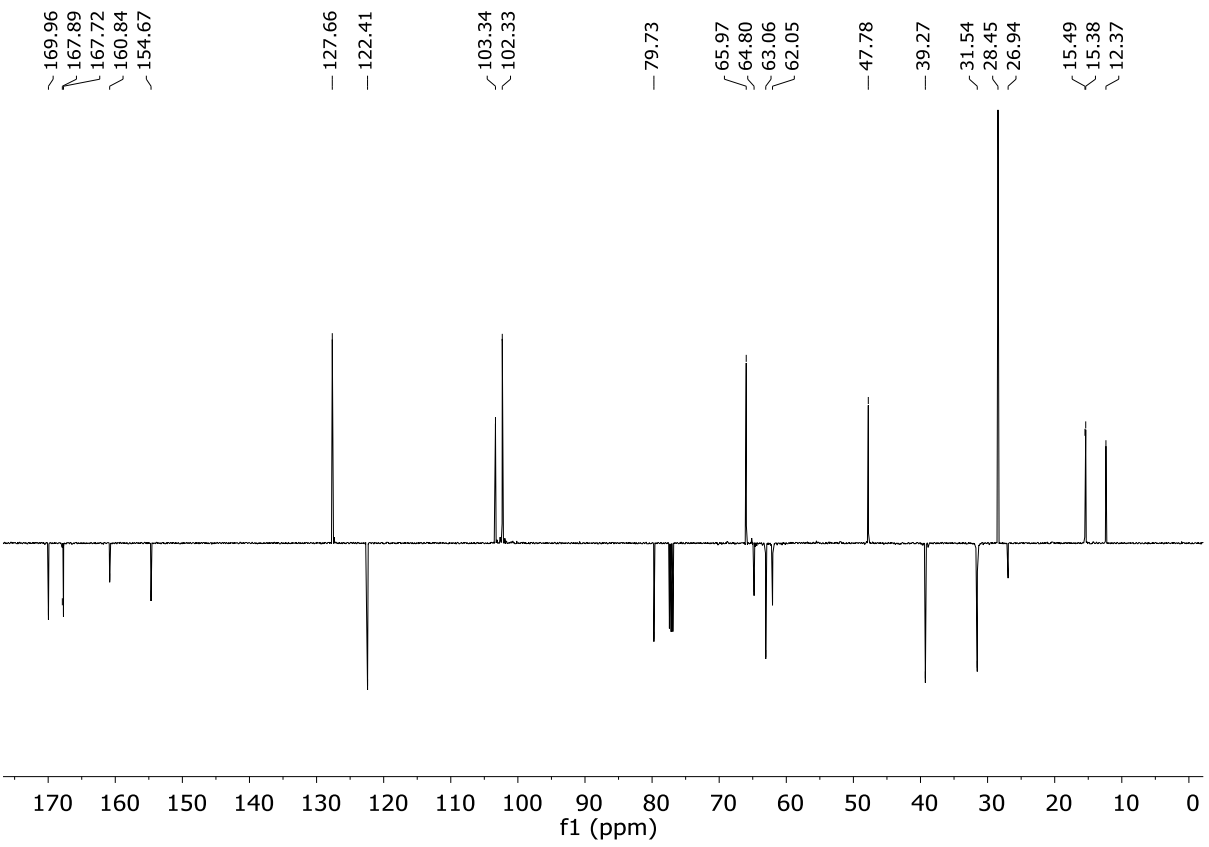
^{13}C NMR (*cis*-6e) 126 MHz, $CDCl_3$



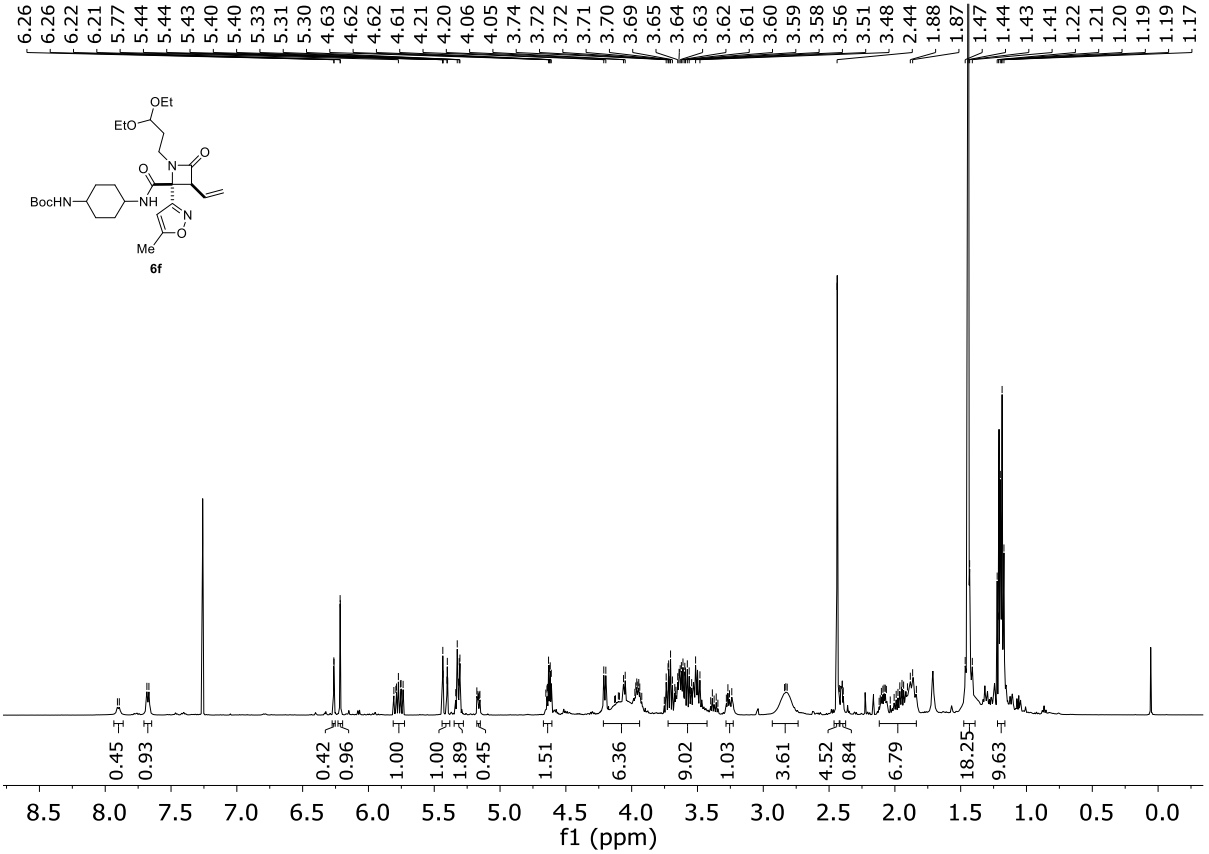
^{1}H NMR (*trans*-6f) 500 MHz, $CDCl_3$



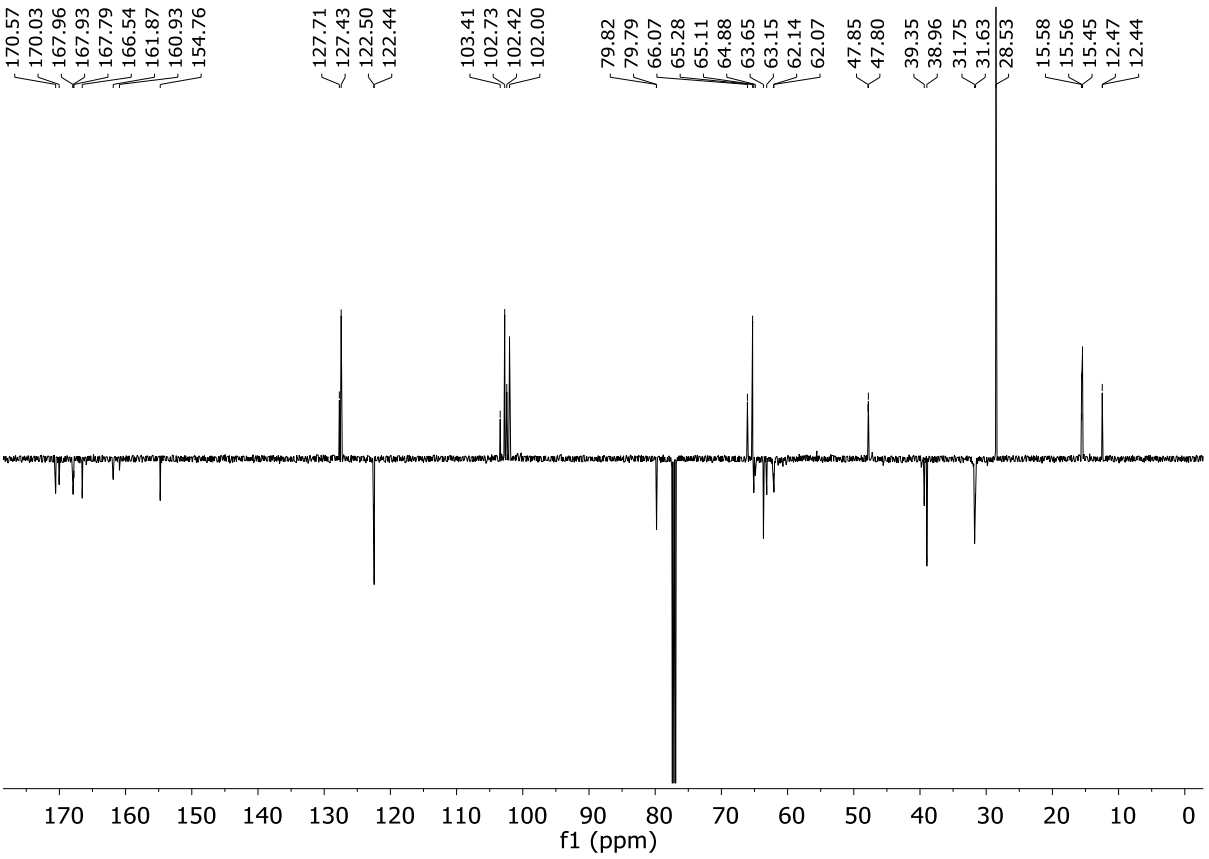
^{13}C NMR (*trans*-6f) 126 MHz, $CDCl_3$



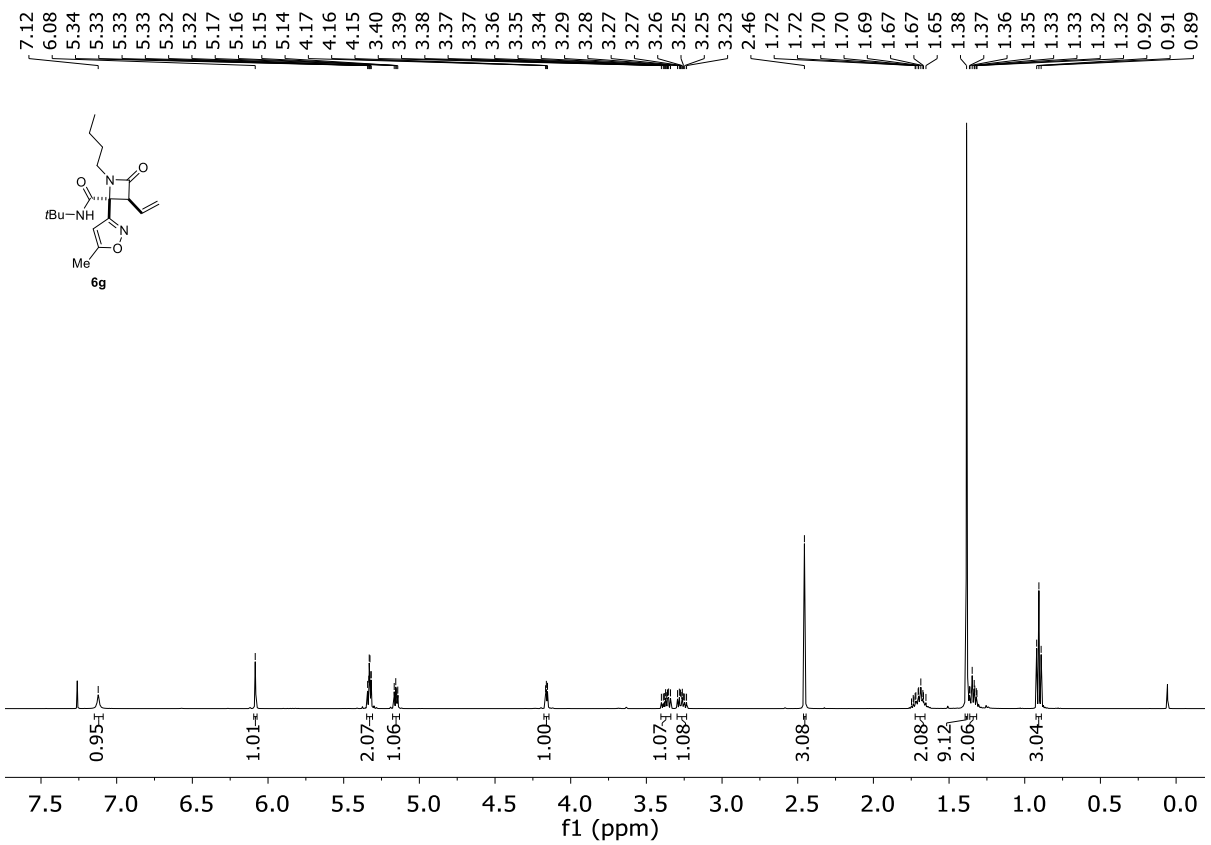
^{1}H NMR (*cis*-6f) 500 MHz, $CDCl_3$



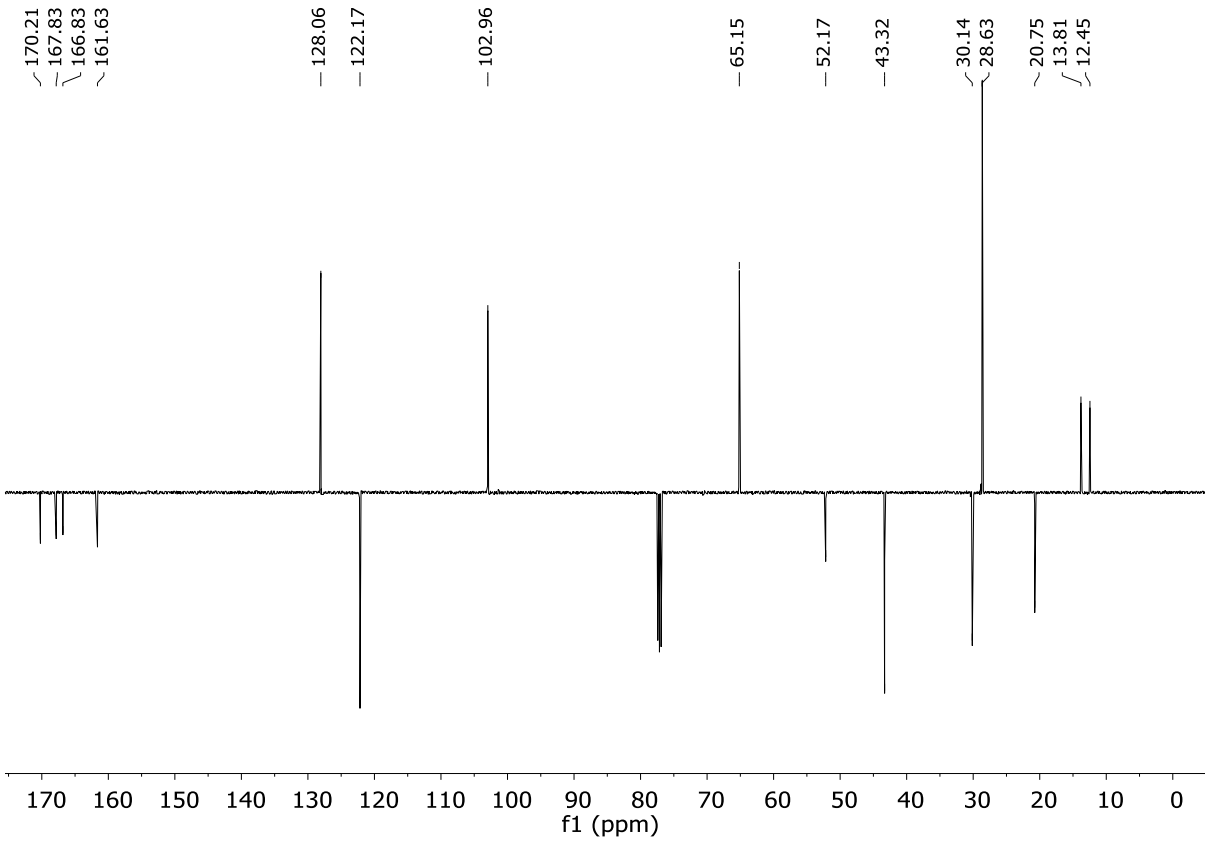
^{13}C NMR (*cis*-6f) 126 MHz, $CDCl_3$



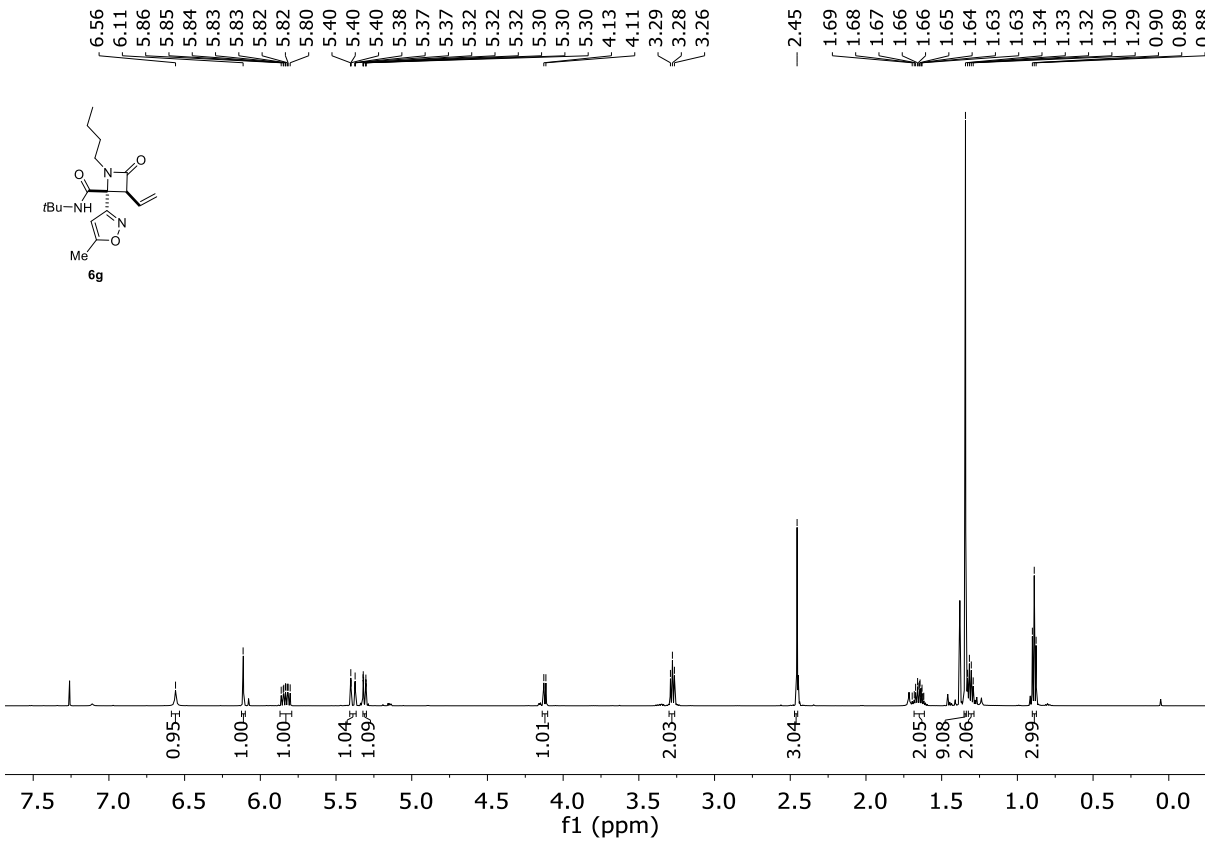
^{1}H NMR (*trans*-6g) 500 MHz, $CDCl_3$



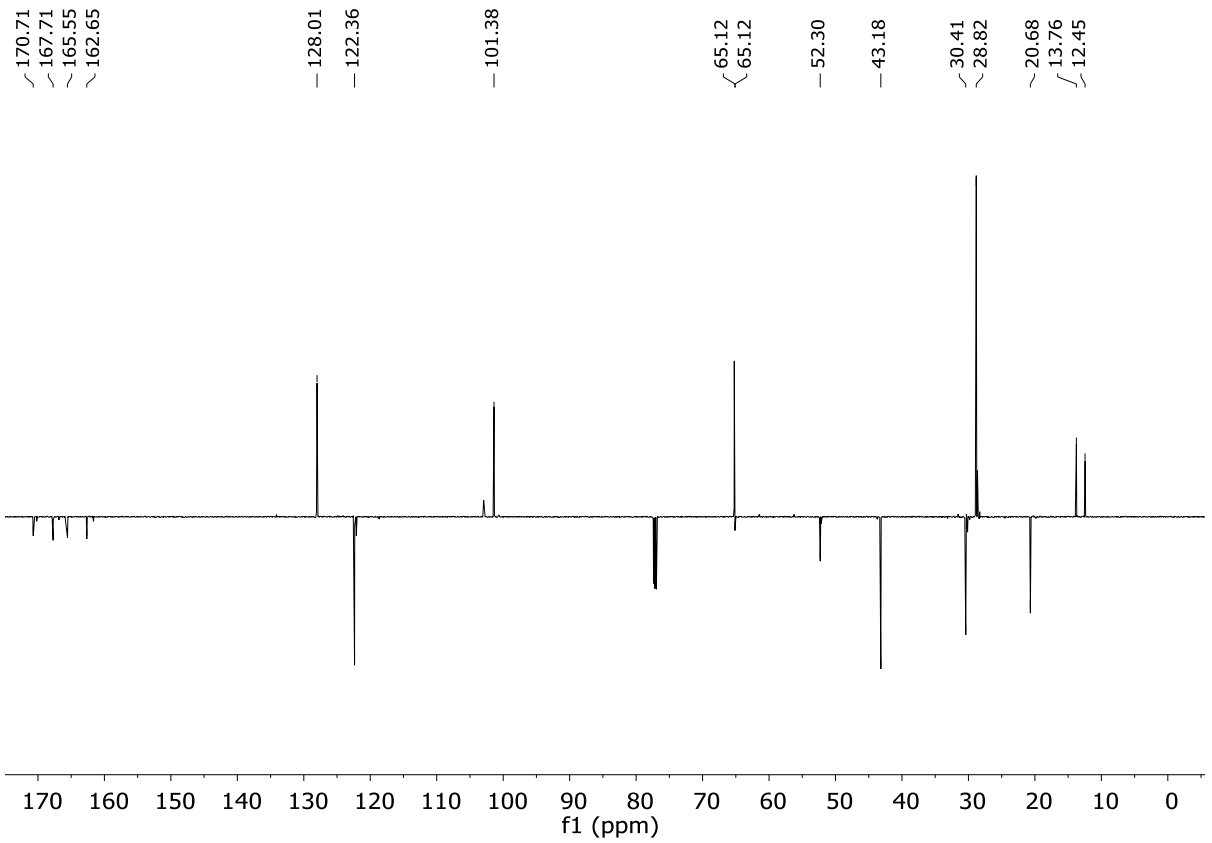
^{13}C NMR (*trans*-6g) 126 MHz, $CDCl_3$



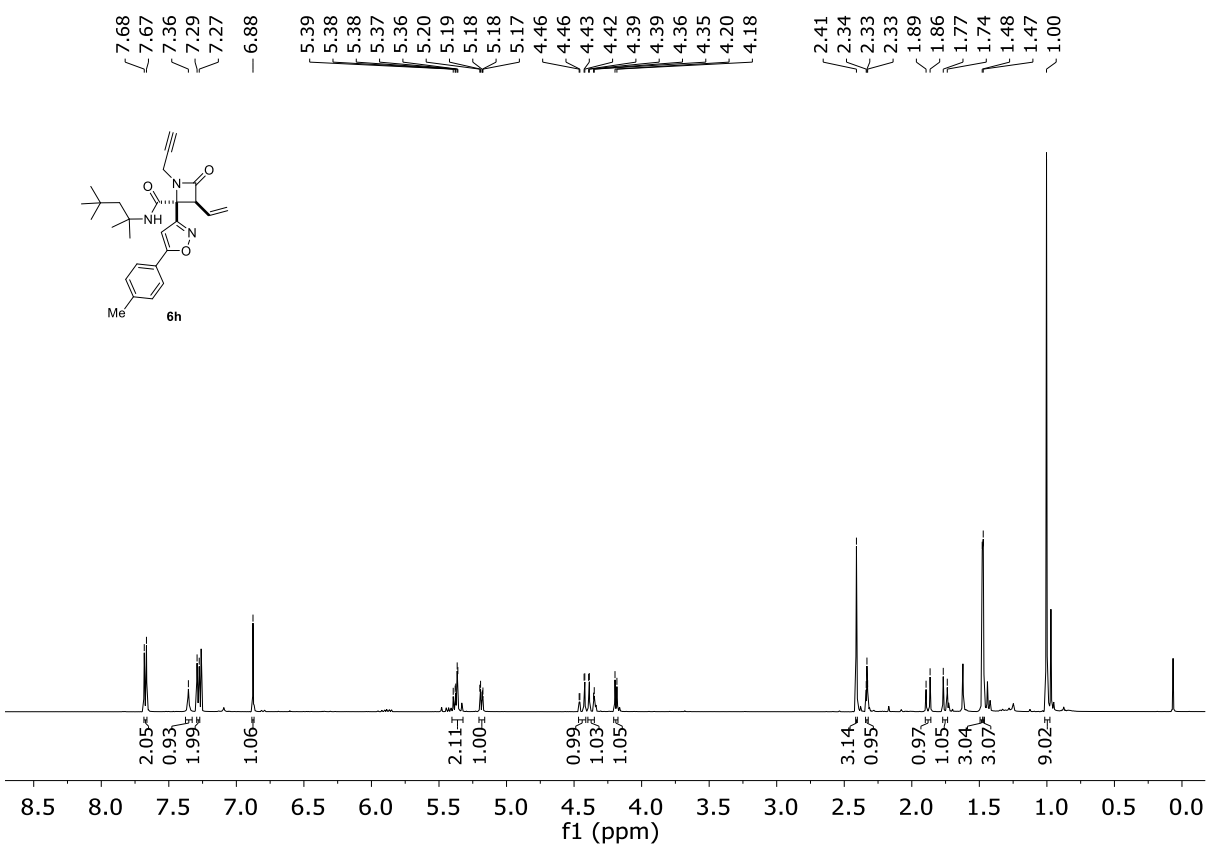
^{1}H NMR (*cis*-6g) 500 MHz, $CDCl_3$



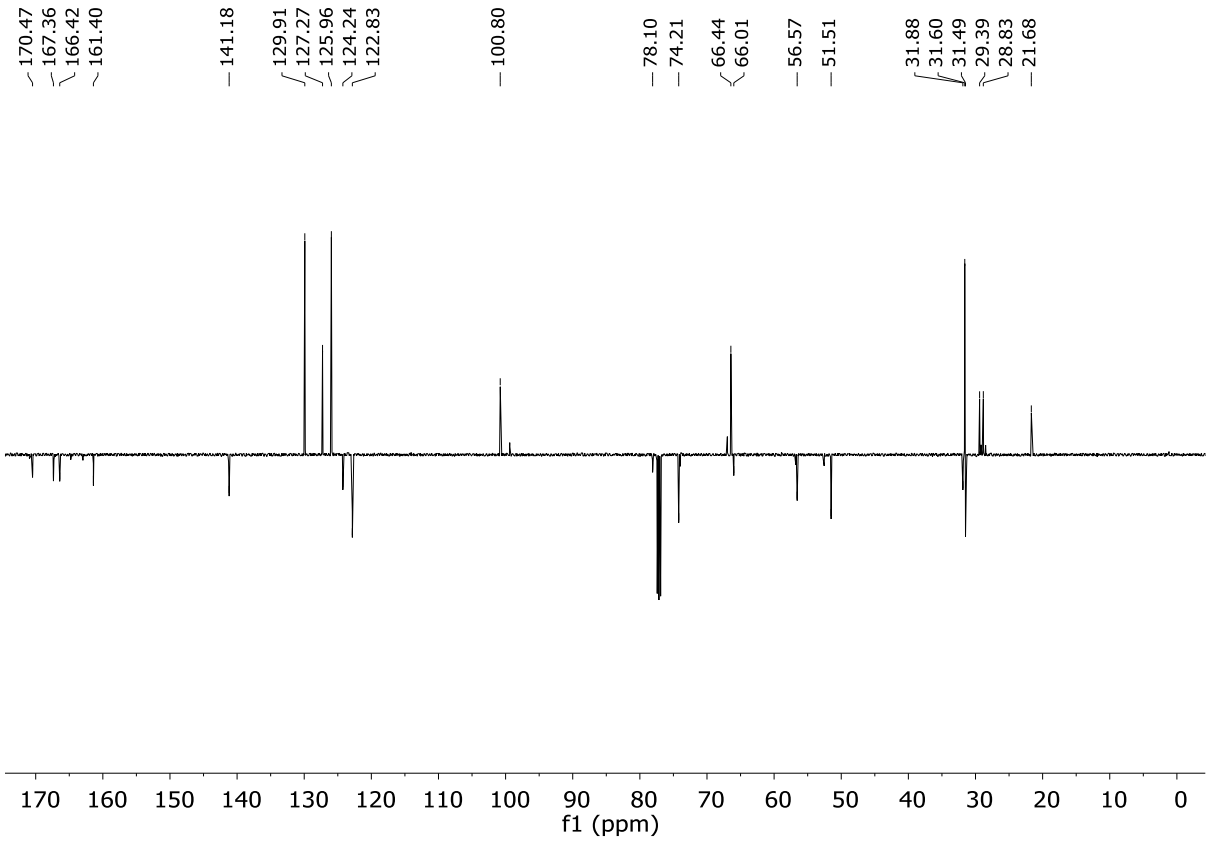
^{13}C NMR (*cis*-6g) 126 MHz, $CDCl_3$



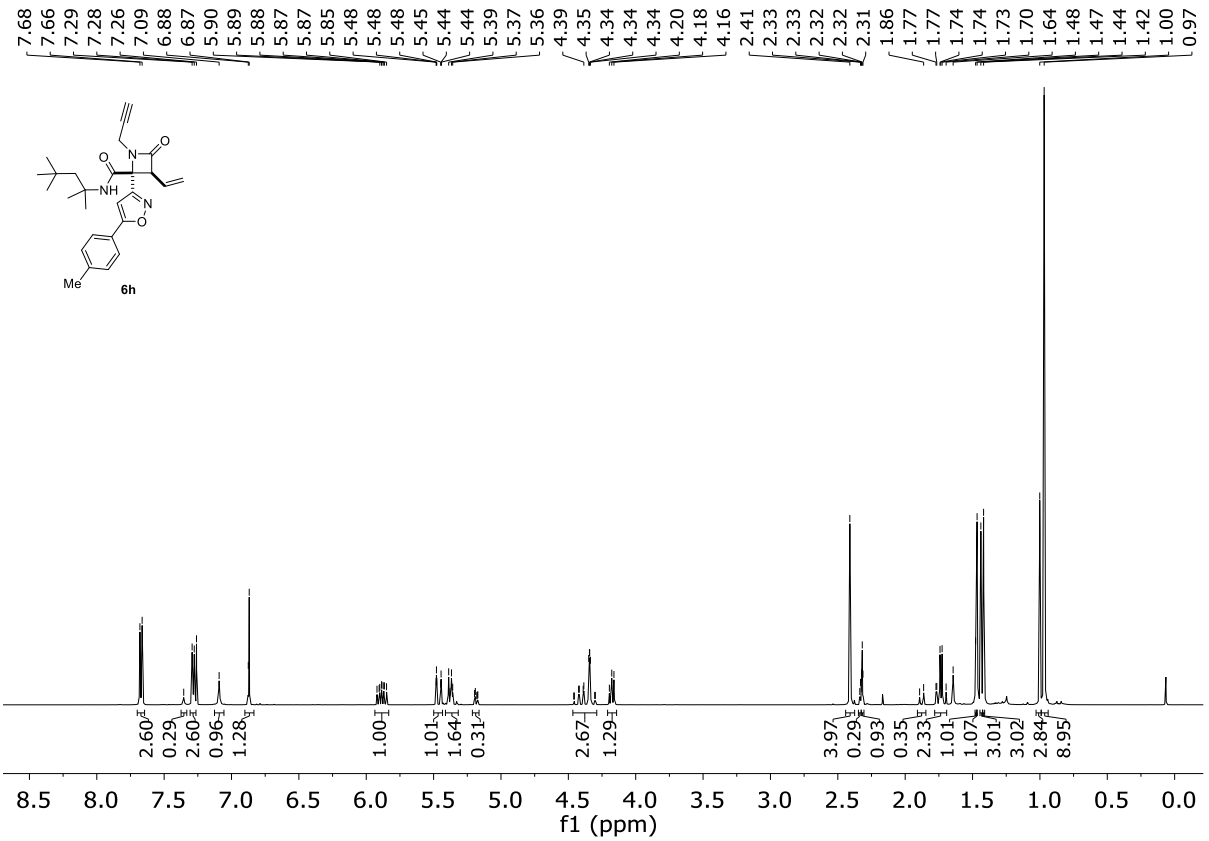
^{1}H NMR (*trans*-6h) 500 MHz, $CDCl_3$



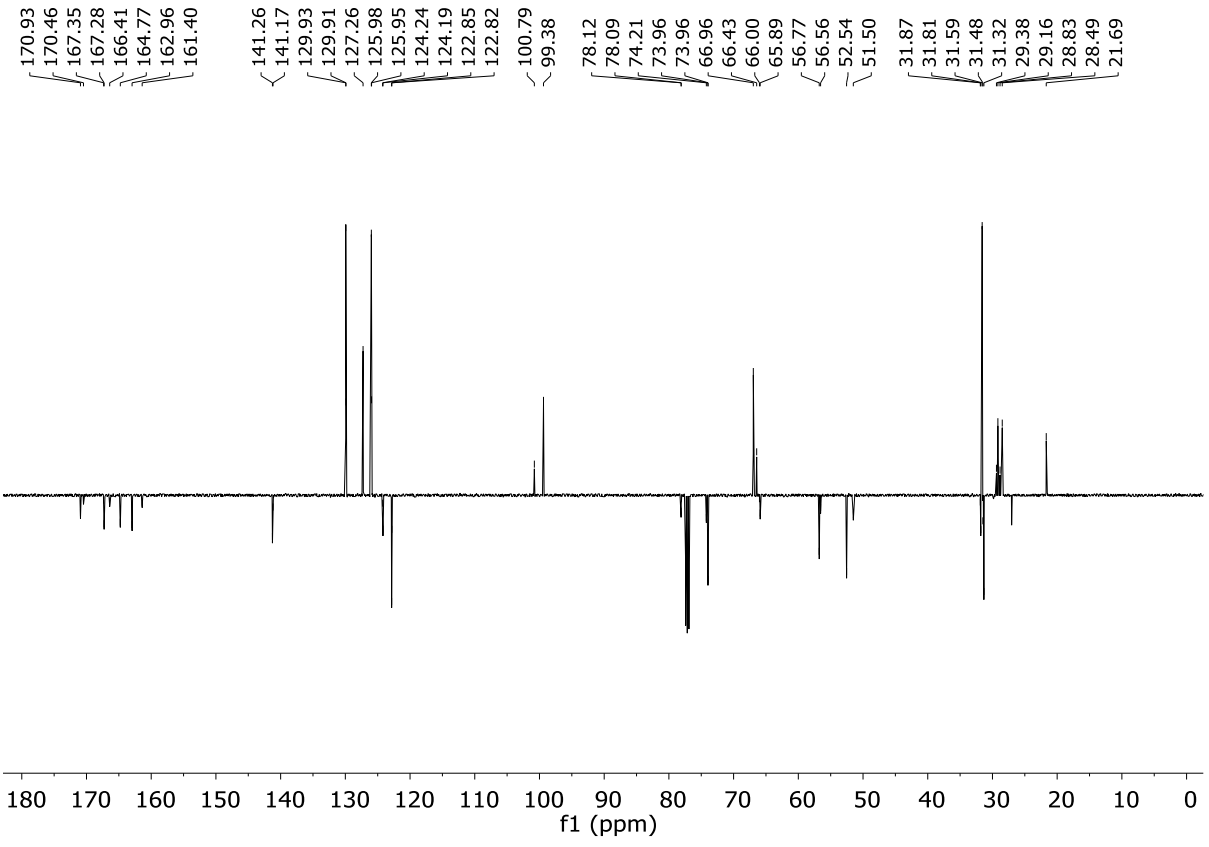
^{13}C NMR (*trans*-6h) 126 MHz, $CDCl_3$



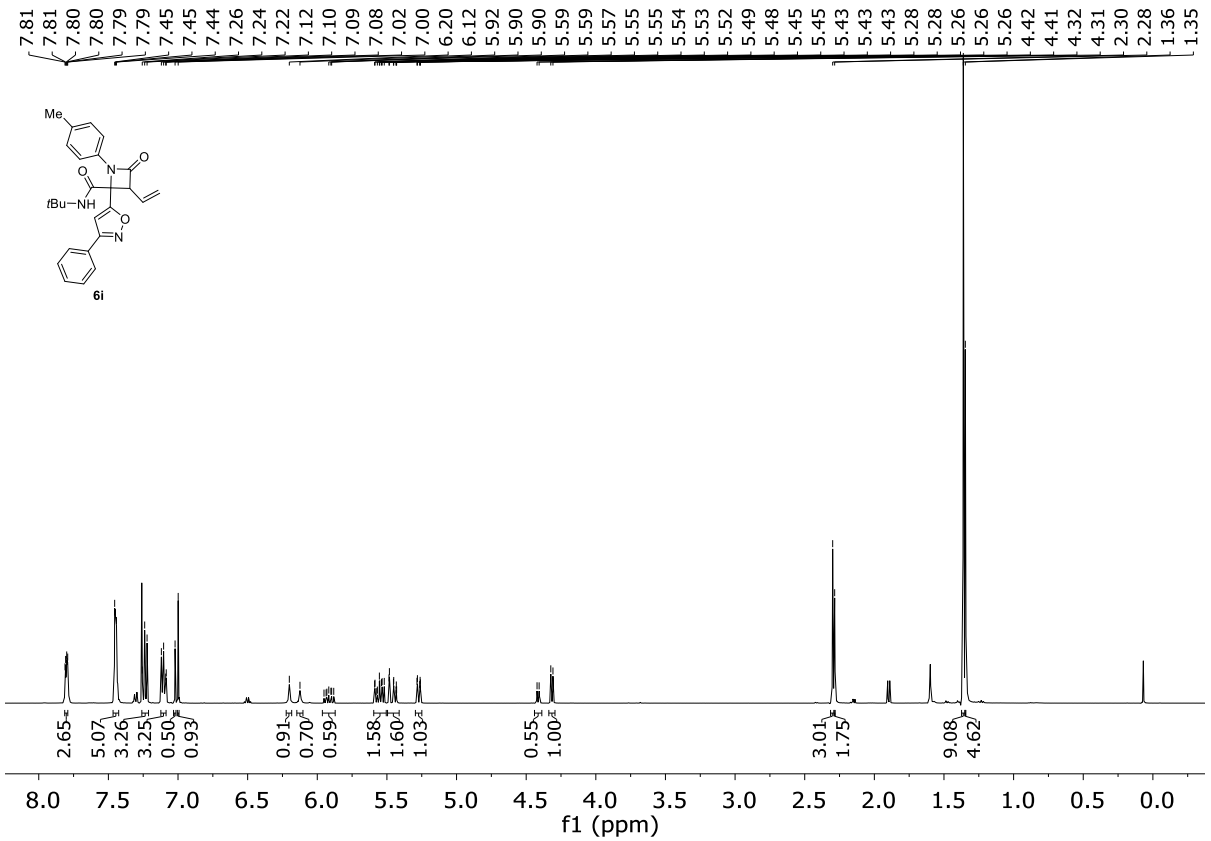
^{1}H NMR (*cis*-6h) 500 MHz, $CDCl_3$



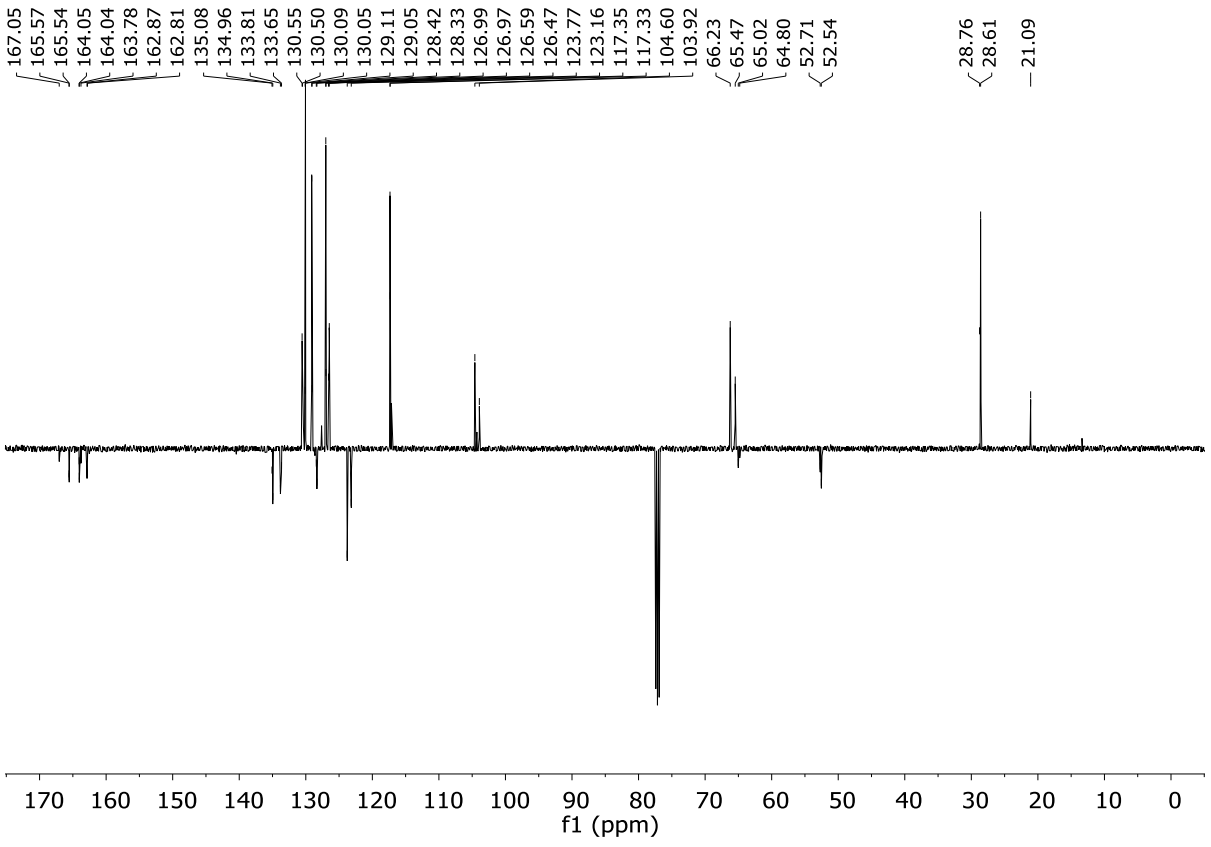
^{13}C NMR (*cis*-6h) 126 MHz, $CDCl_3$



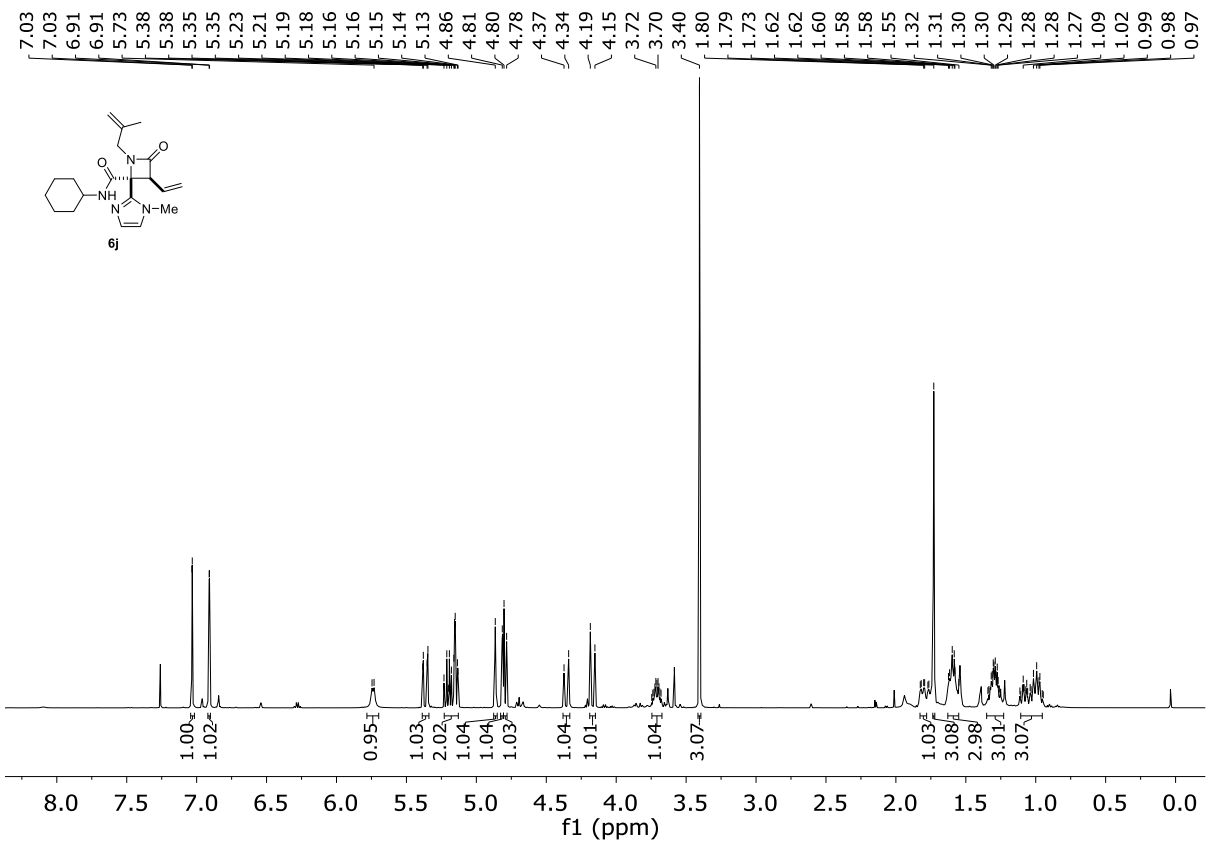
^{1}H NMR (*trans/cis*-6i) 500 MHz, $CDCl_3$



^{13}C NMR (*trans/cis*-6i) 126 MHz, $CDCl_3$

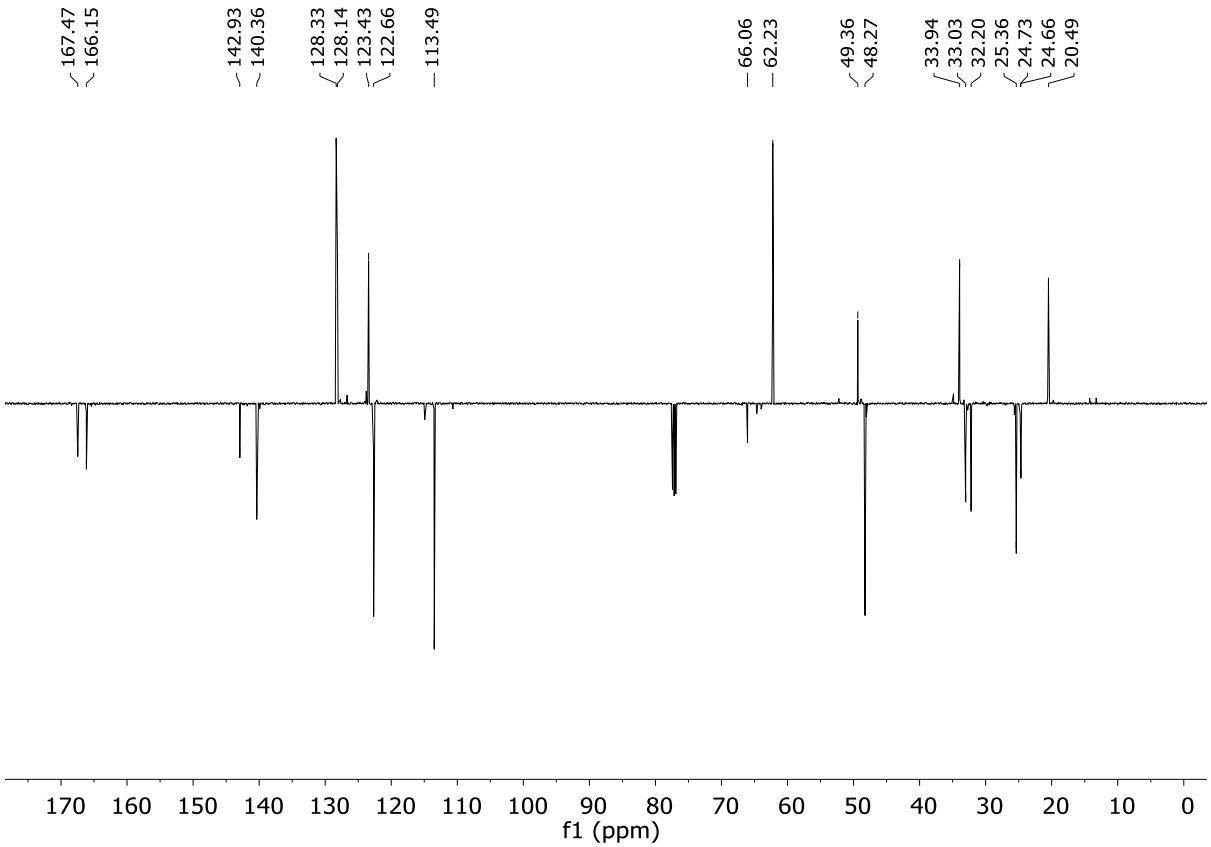


^{1}H NMR (*trans*-6j) 500 MHz, $CDCl_3$

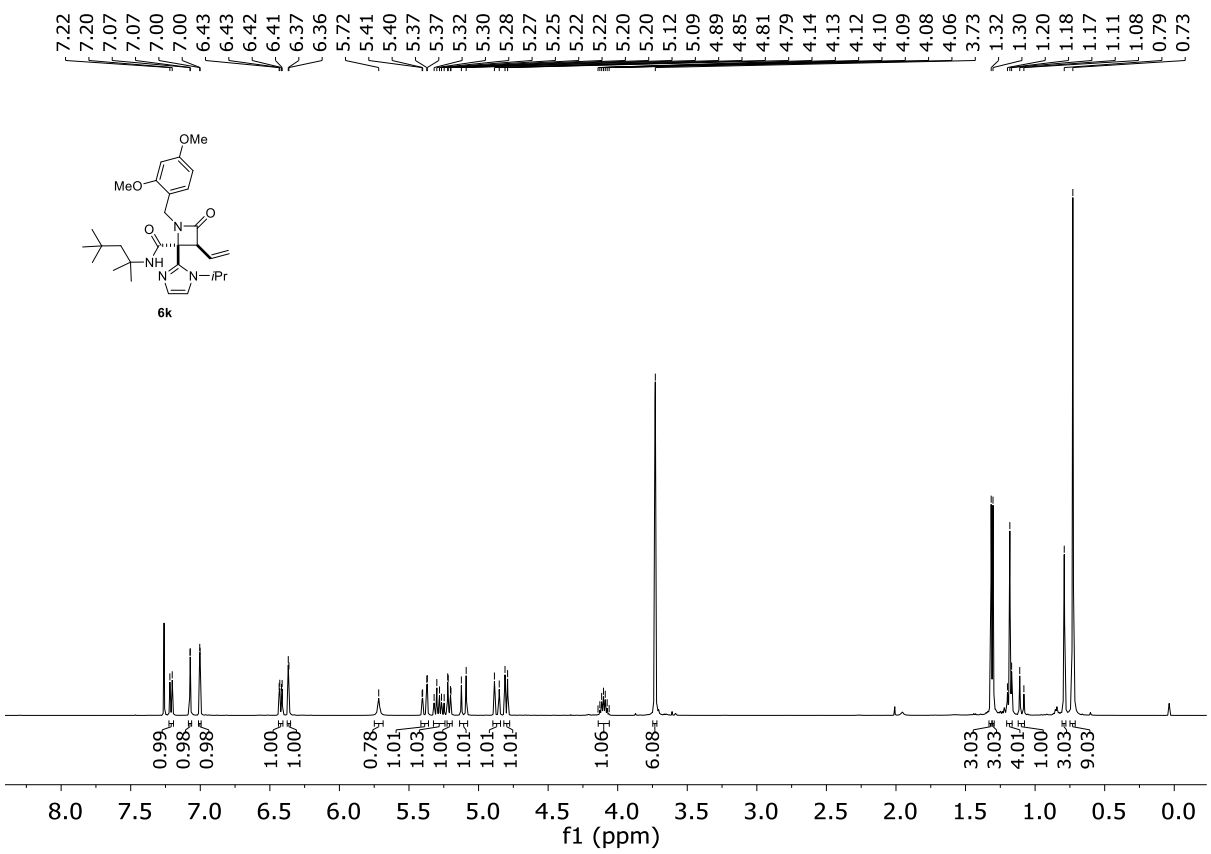


6j

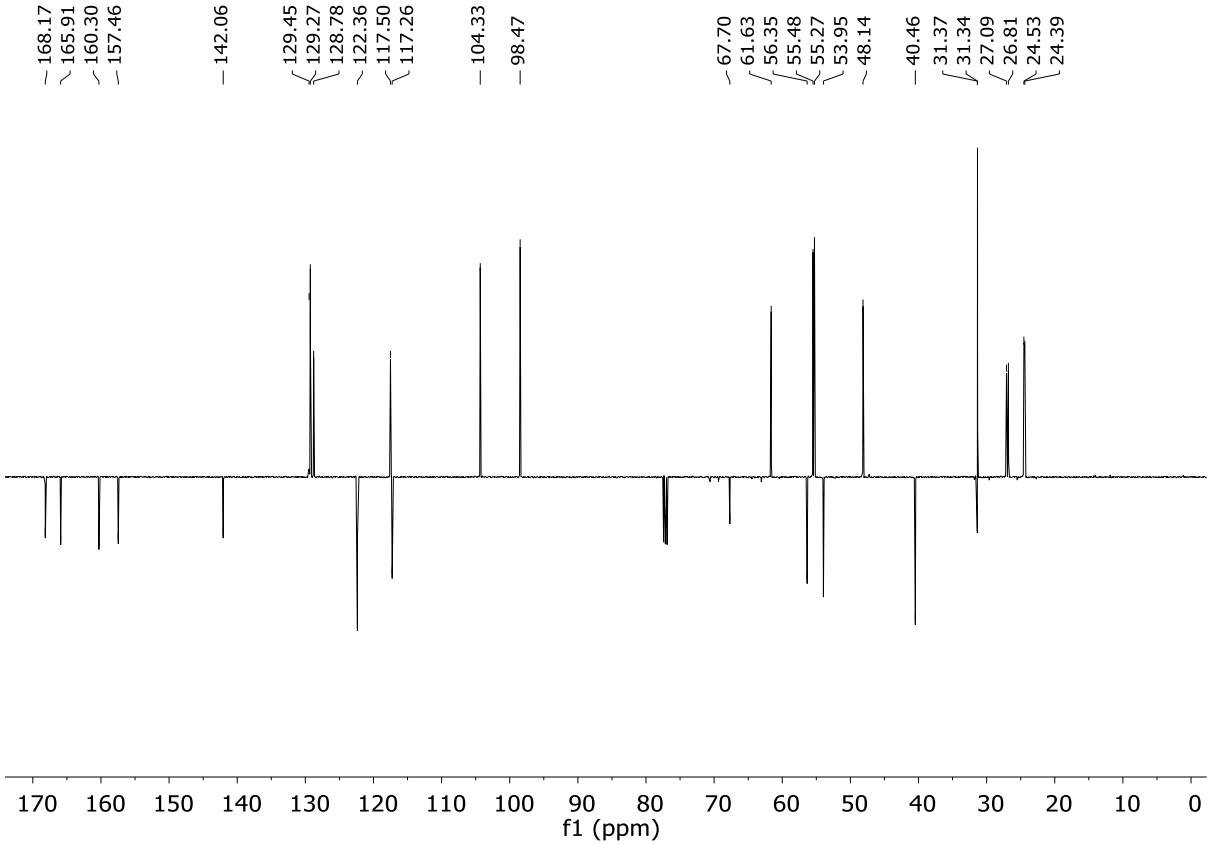
^{13}C NMR (*trans*-6j) 126 MHz, $CDCl_3$



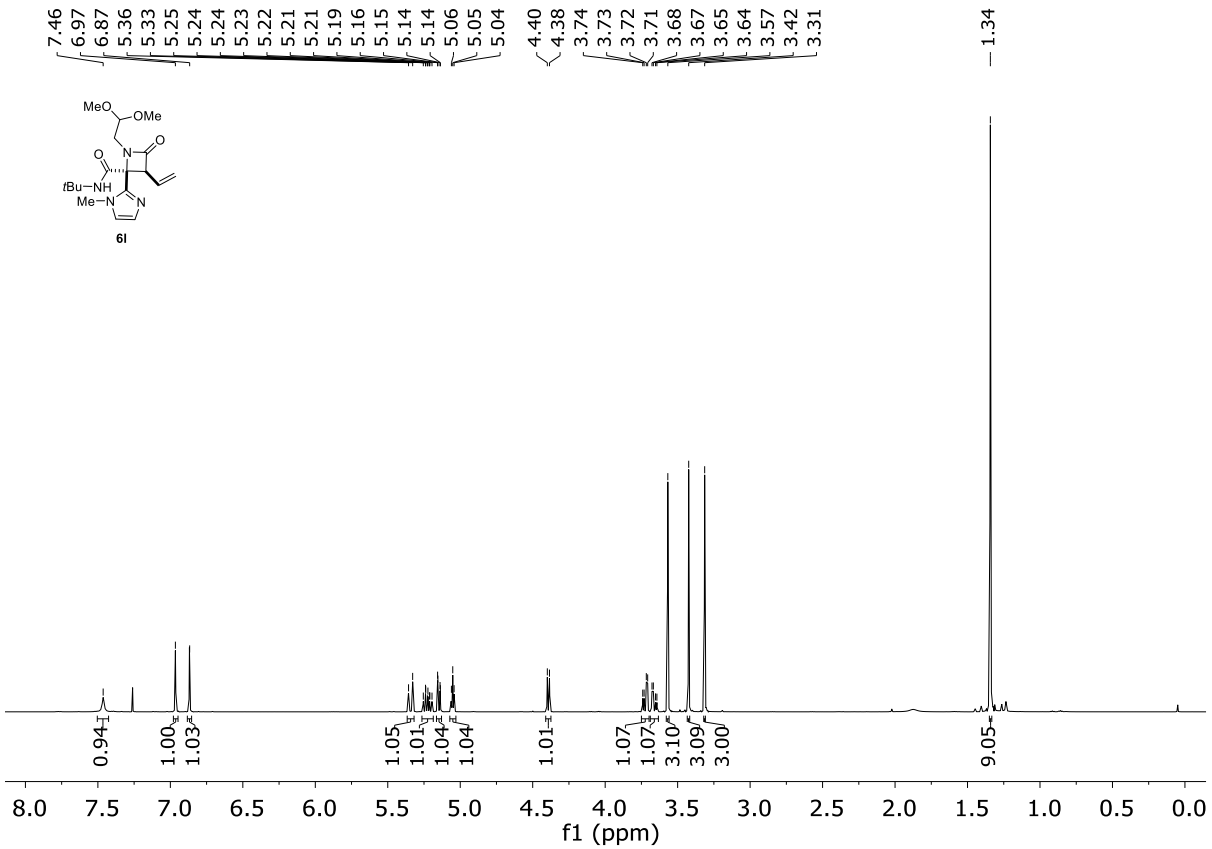
^{1}H NMR (*trans*-6k) 500 MHz, $CDCl_3$



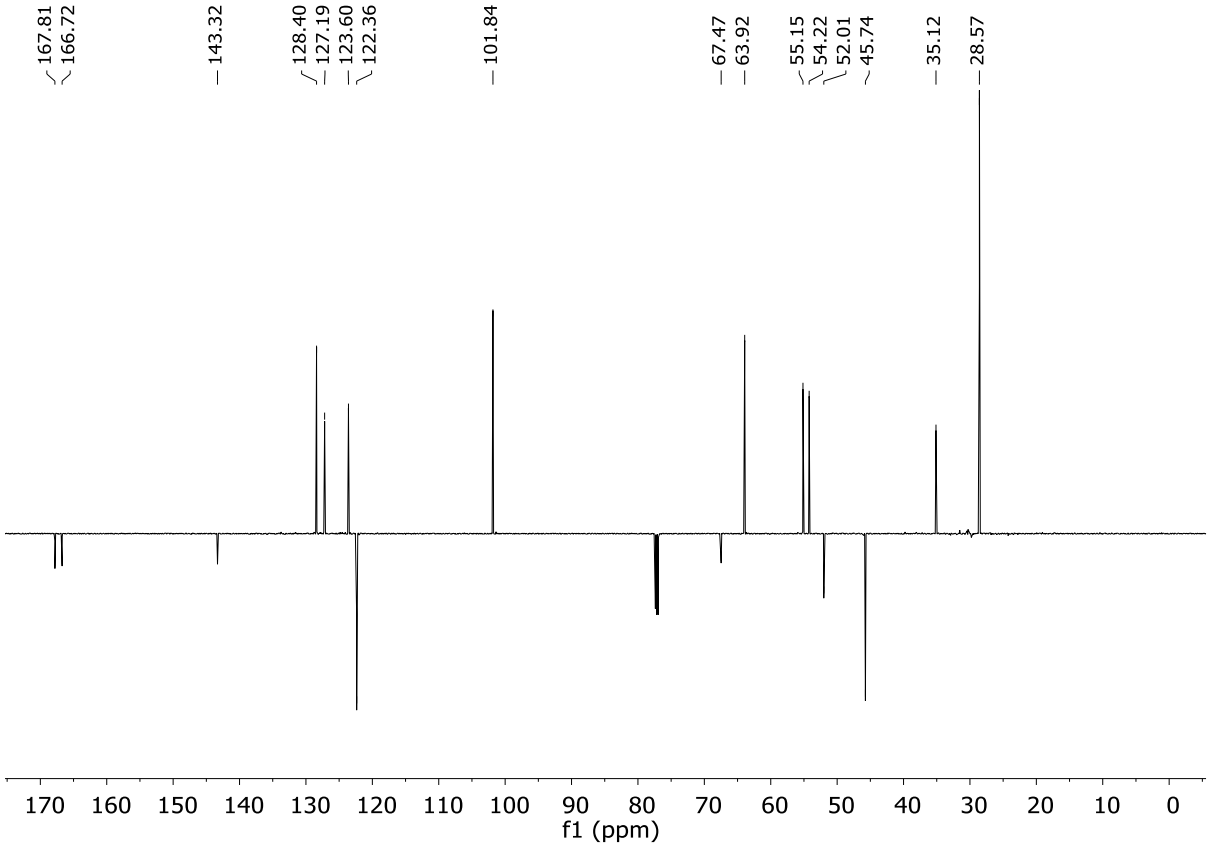
^{13}C NMR (*trans*-6k) 126 MHz, $CDCl_3$



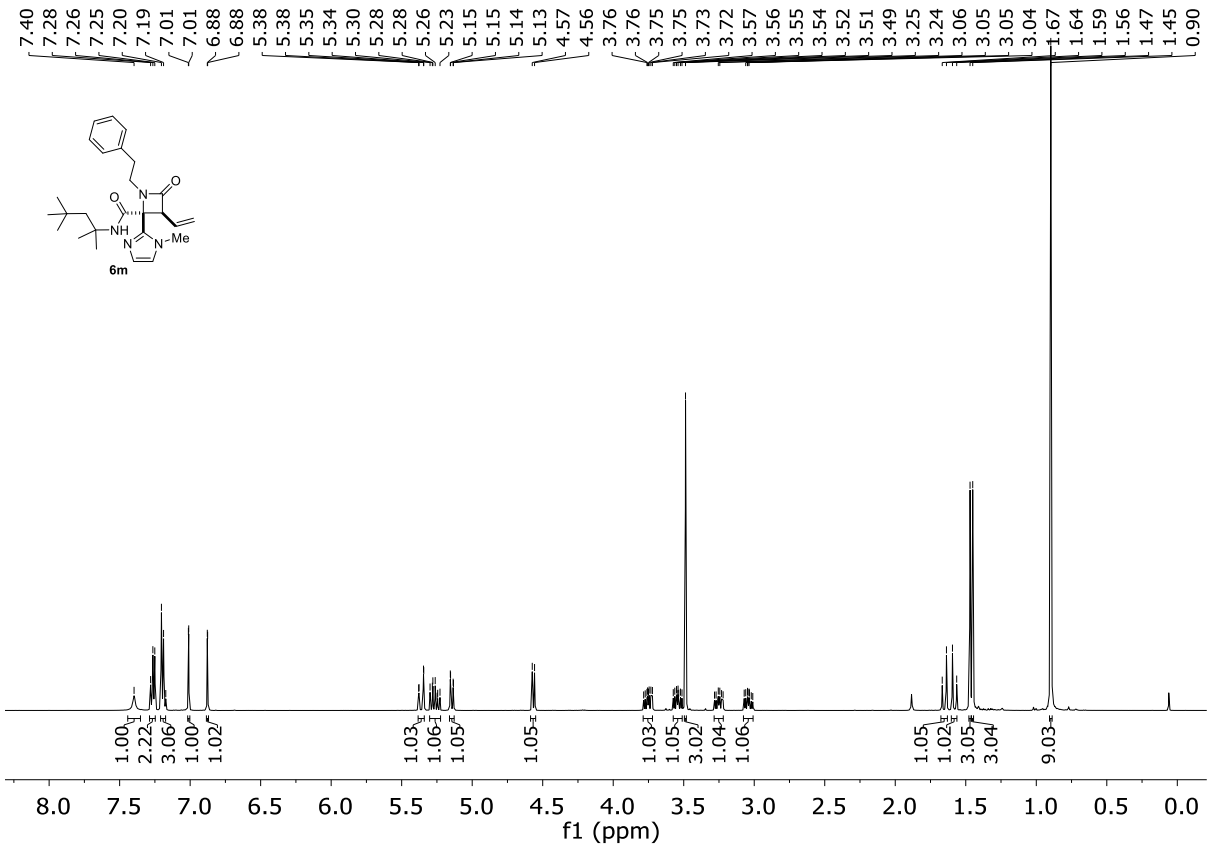
^{1}H NMR (*trans*-6l) 600 MHz, $CDCl_3$



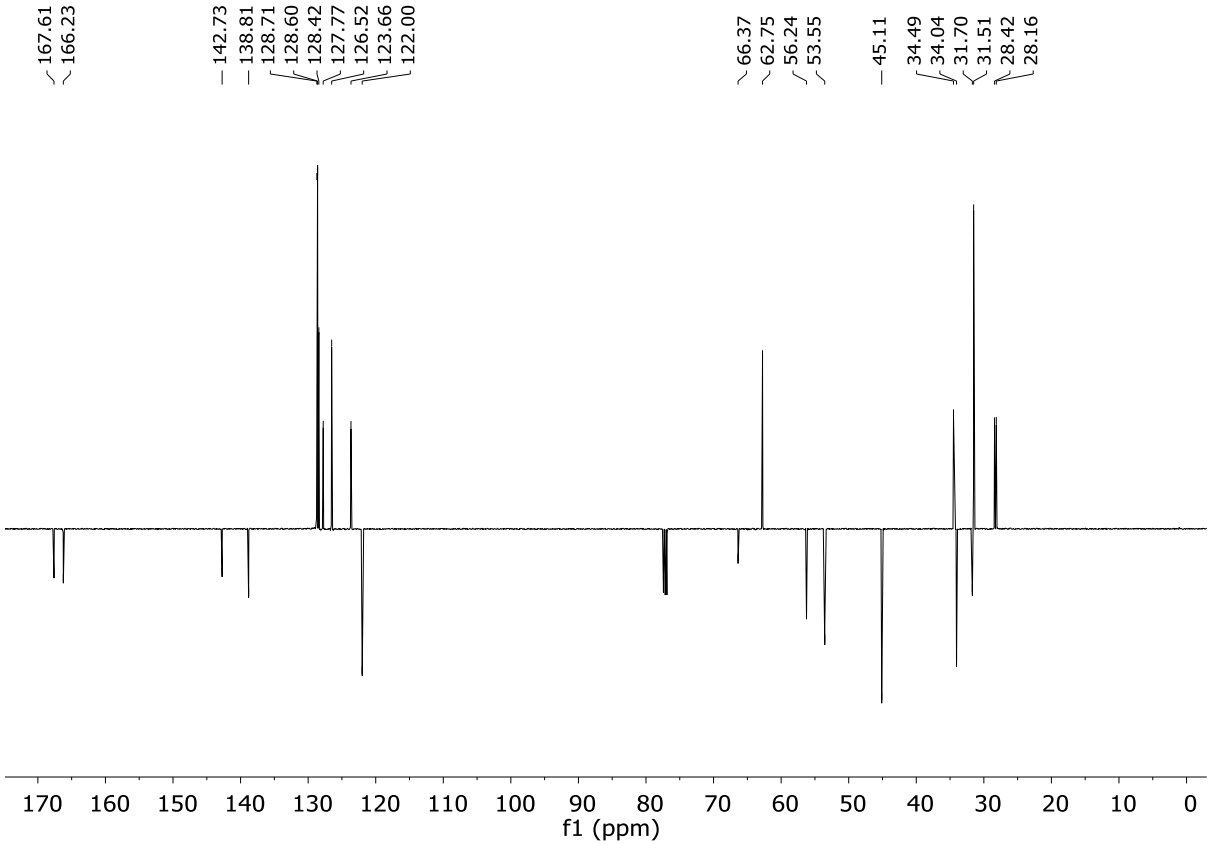
^{13}C NMR (*trans*-6l) 126 MHz, $CDCl_3$



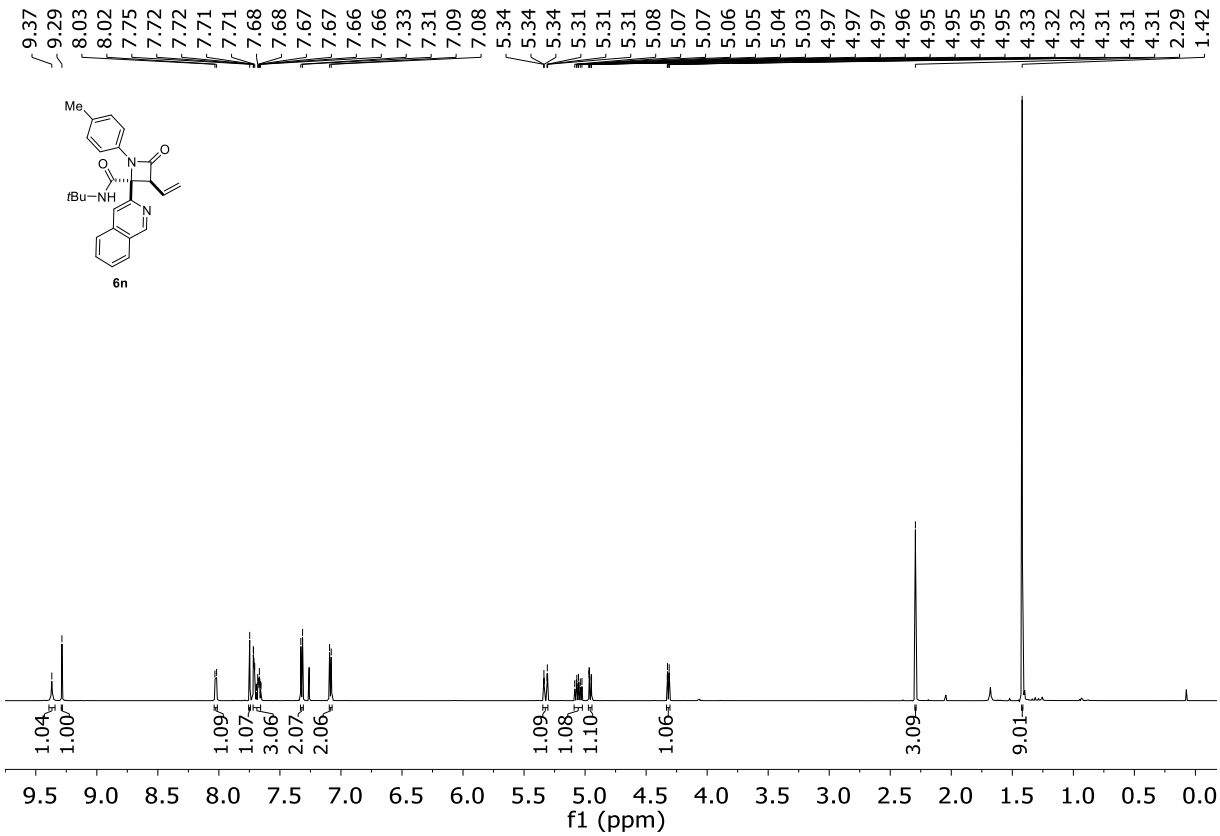
^{1}H NMR (*trans*-6m) 500 MHz, $CDCl_3$



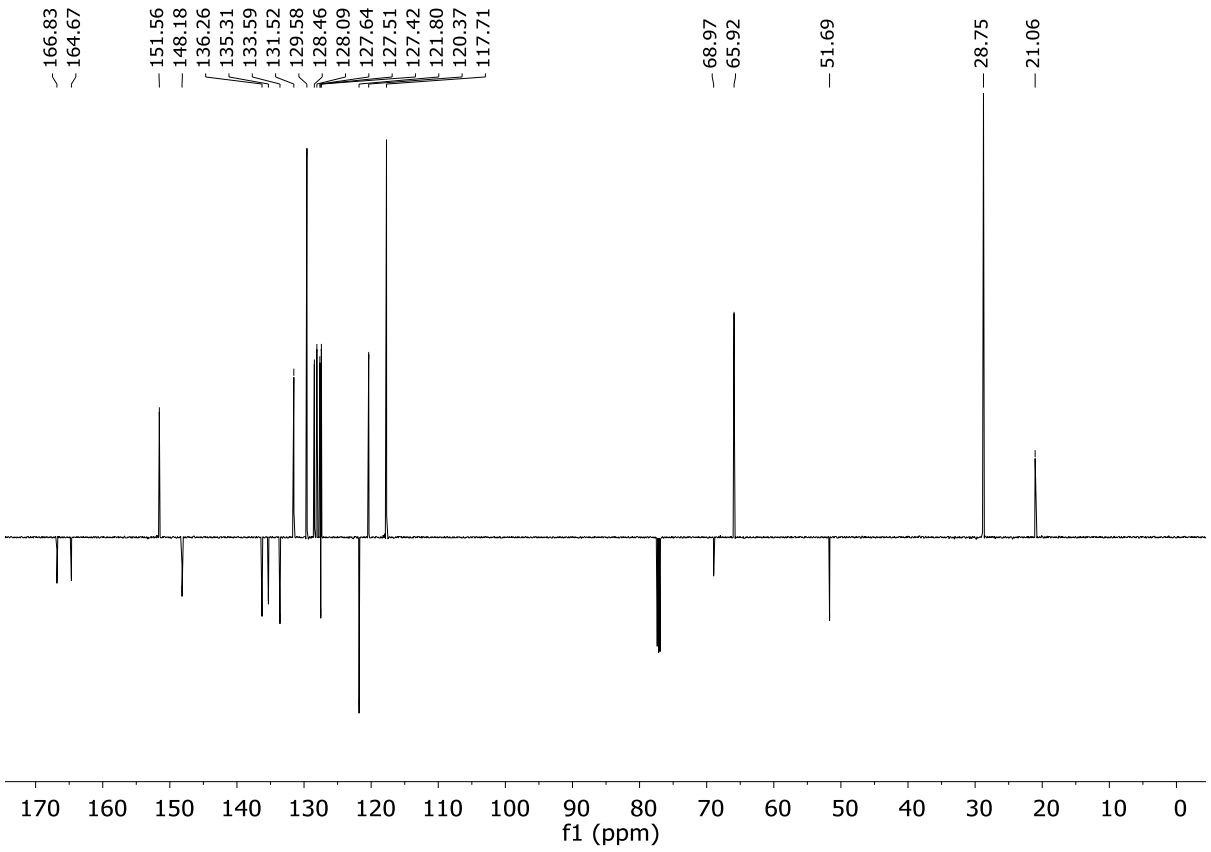
^{13}C NMR (*trans*-6m) 126 MHz, $CDCl_3$



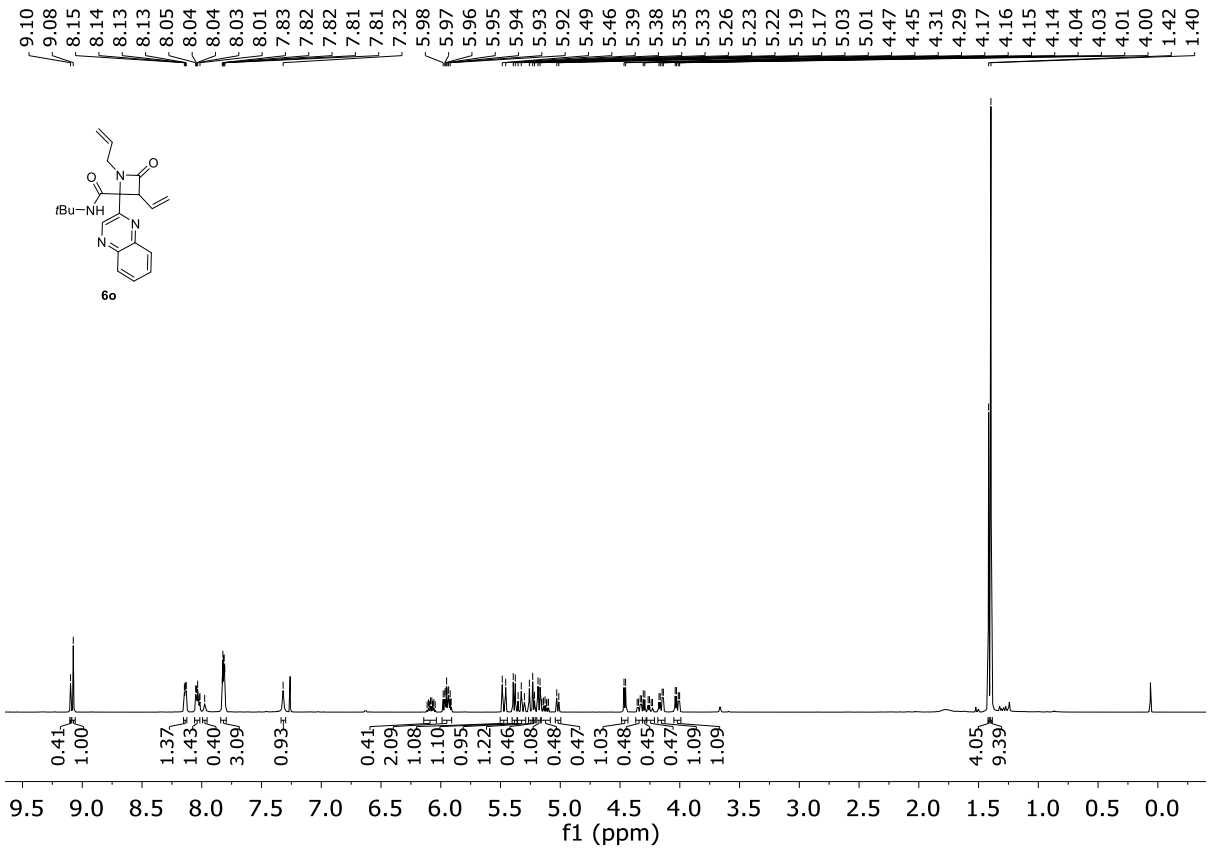
^{1}H NMR (*trans*-6n) 600 MHz, $CDCl_3$



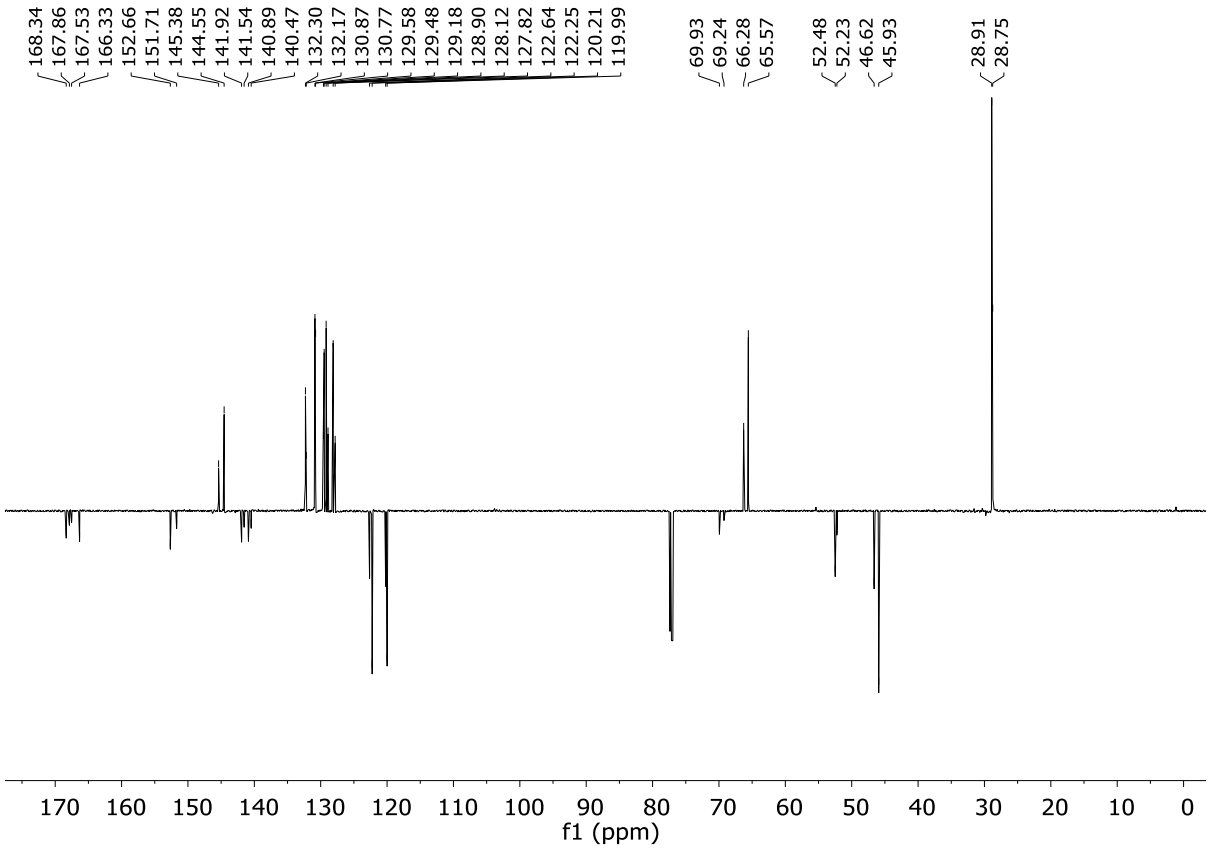
^{13}C NMR (*trans*-6n) 151 MHz, $CDCl_3$



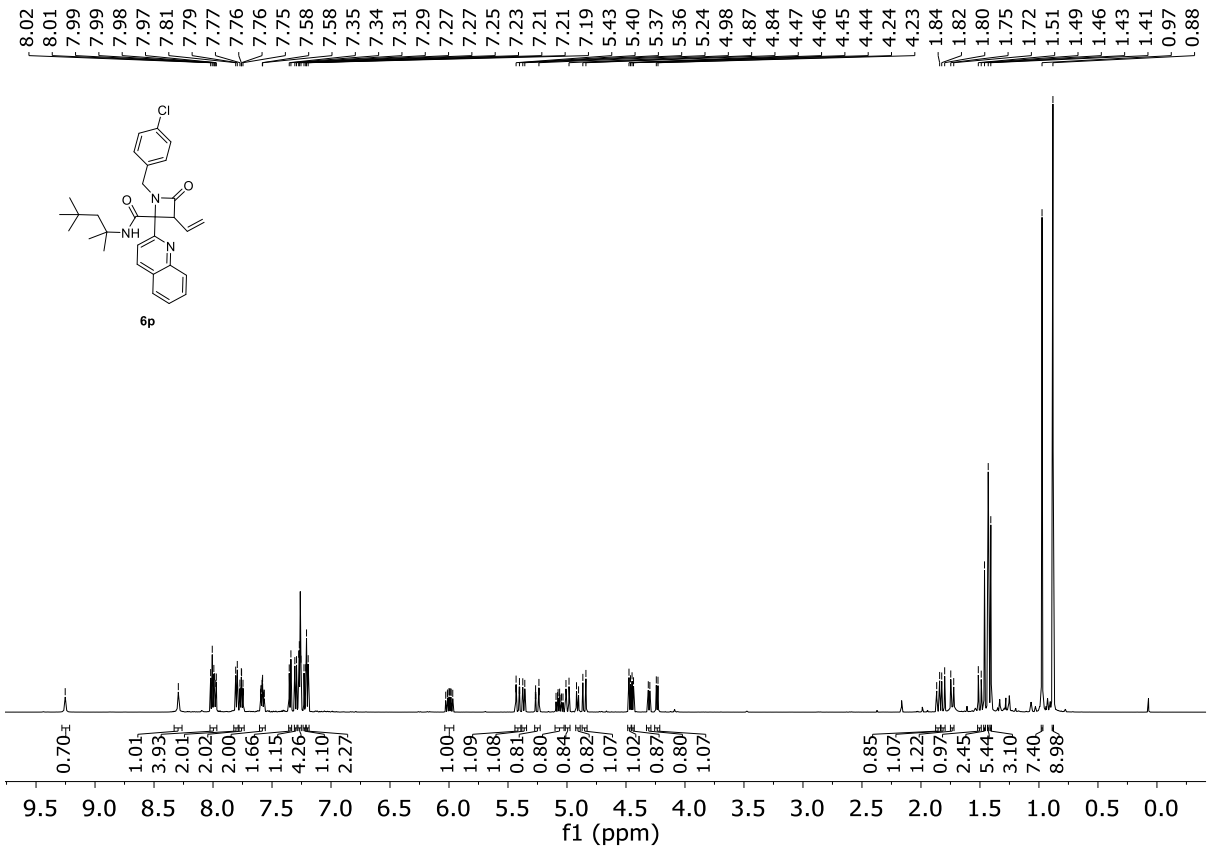
^{1}H NMR (*trans/cis*-6o) 600 MHz, $CDCl_3$



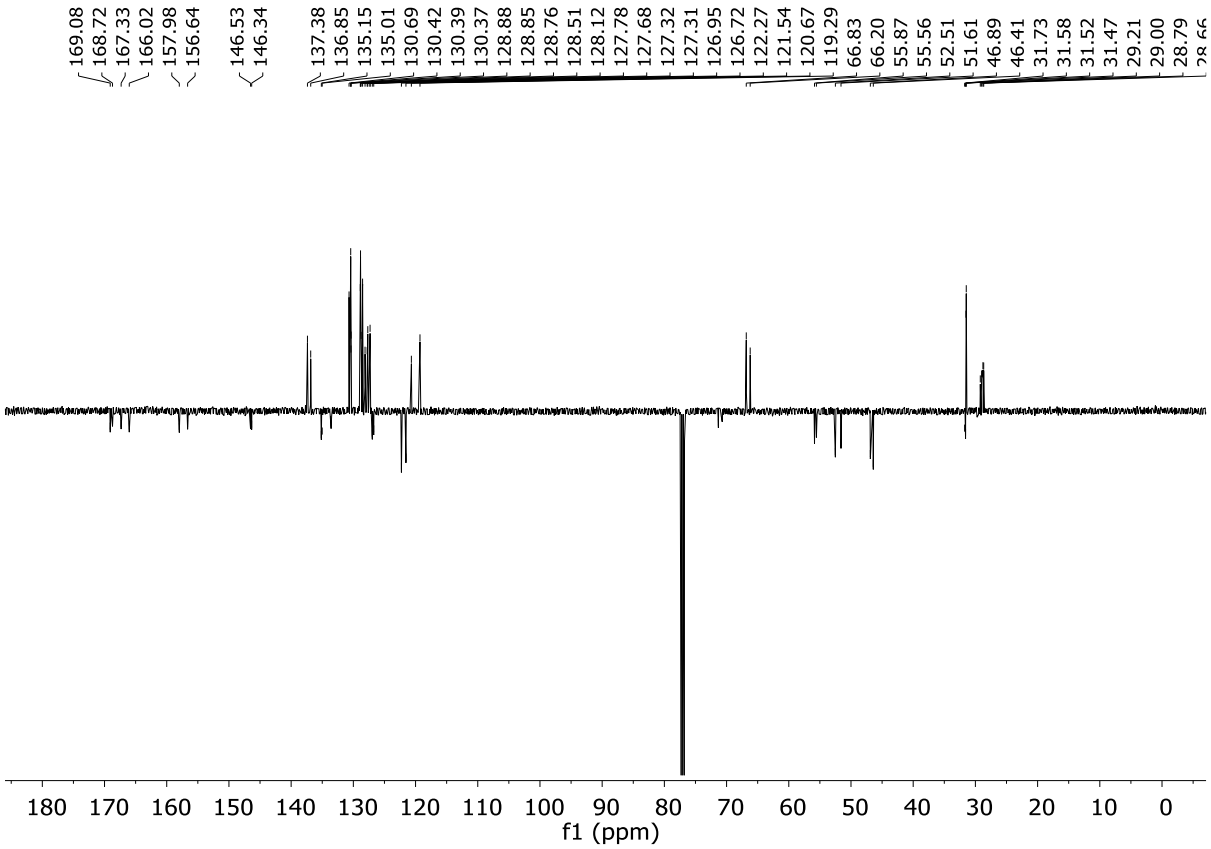
^{13}C NMR (*trans/cis*-6o) 151 MHz, $CDCl_3$



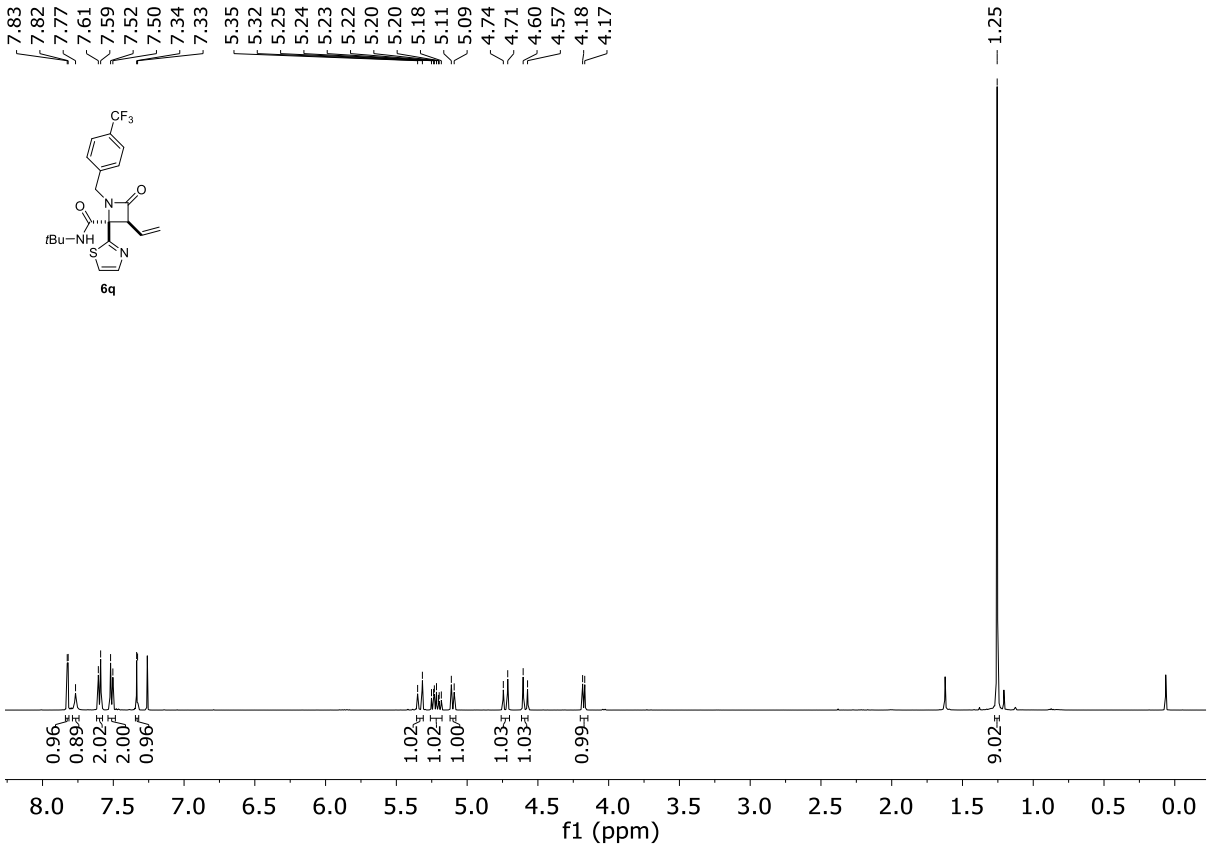
^{1}H NMR (*trans/cis*-6p) 500 MHz, $CDCl_3$



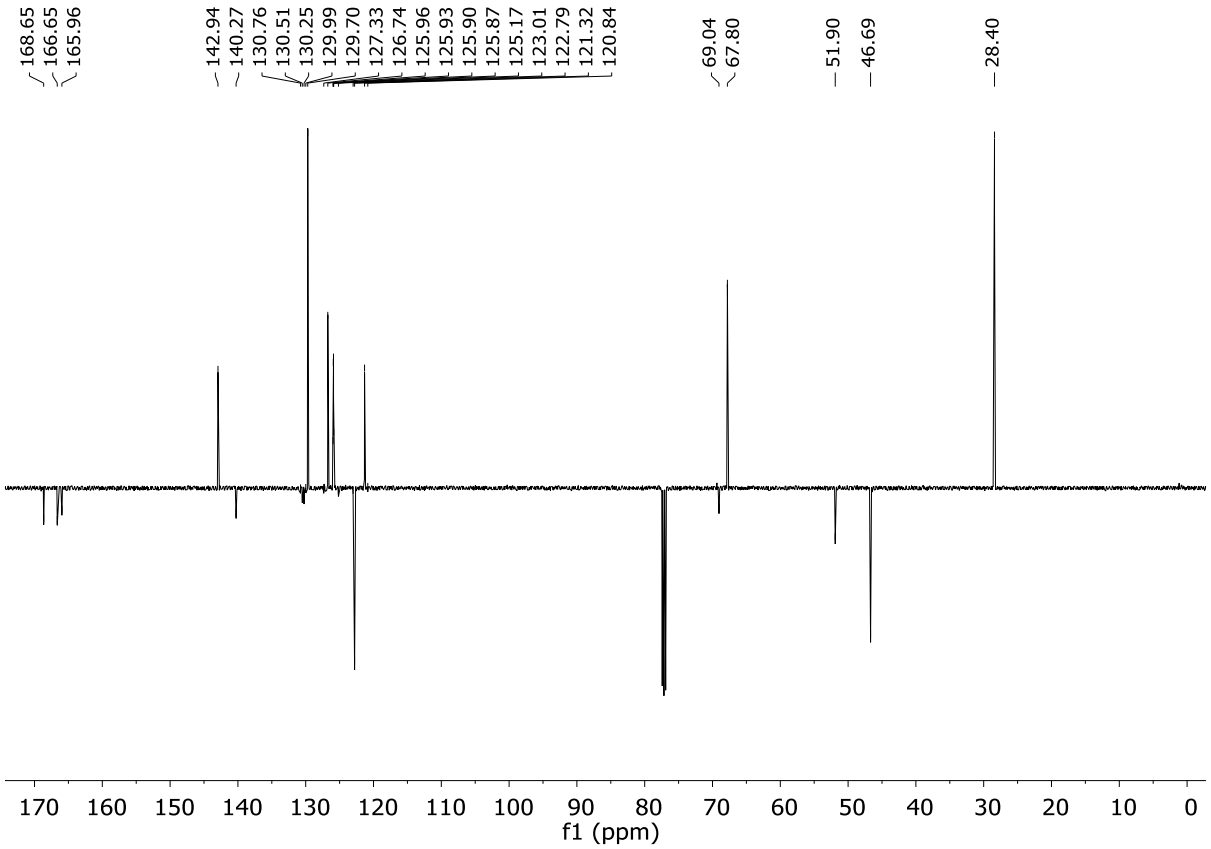
^{13}C NMR (*trans/cis*-6p) 126 MHz, $CDCl_3$



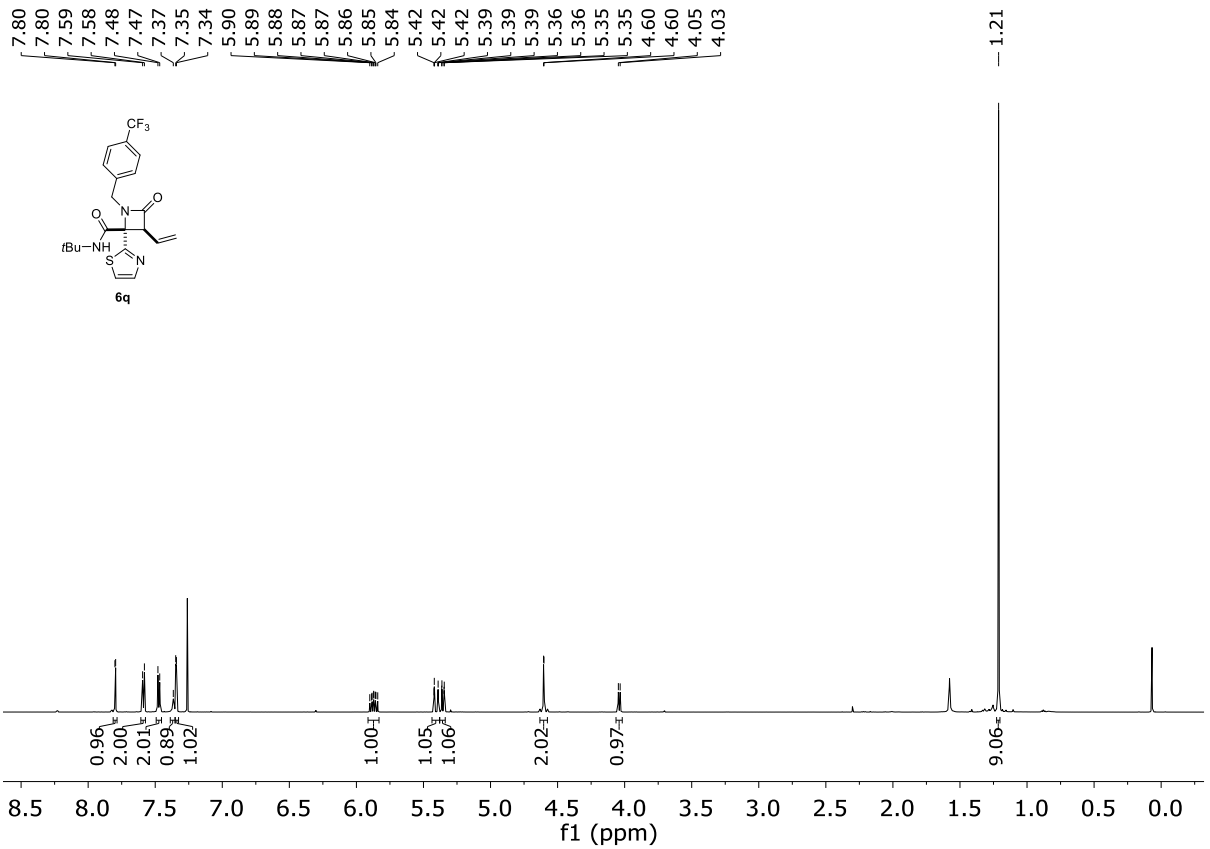
^{1}H NMR (*trans*-6q) 500 MHz, $CDCl_3$



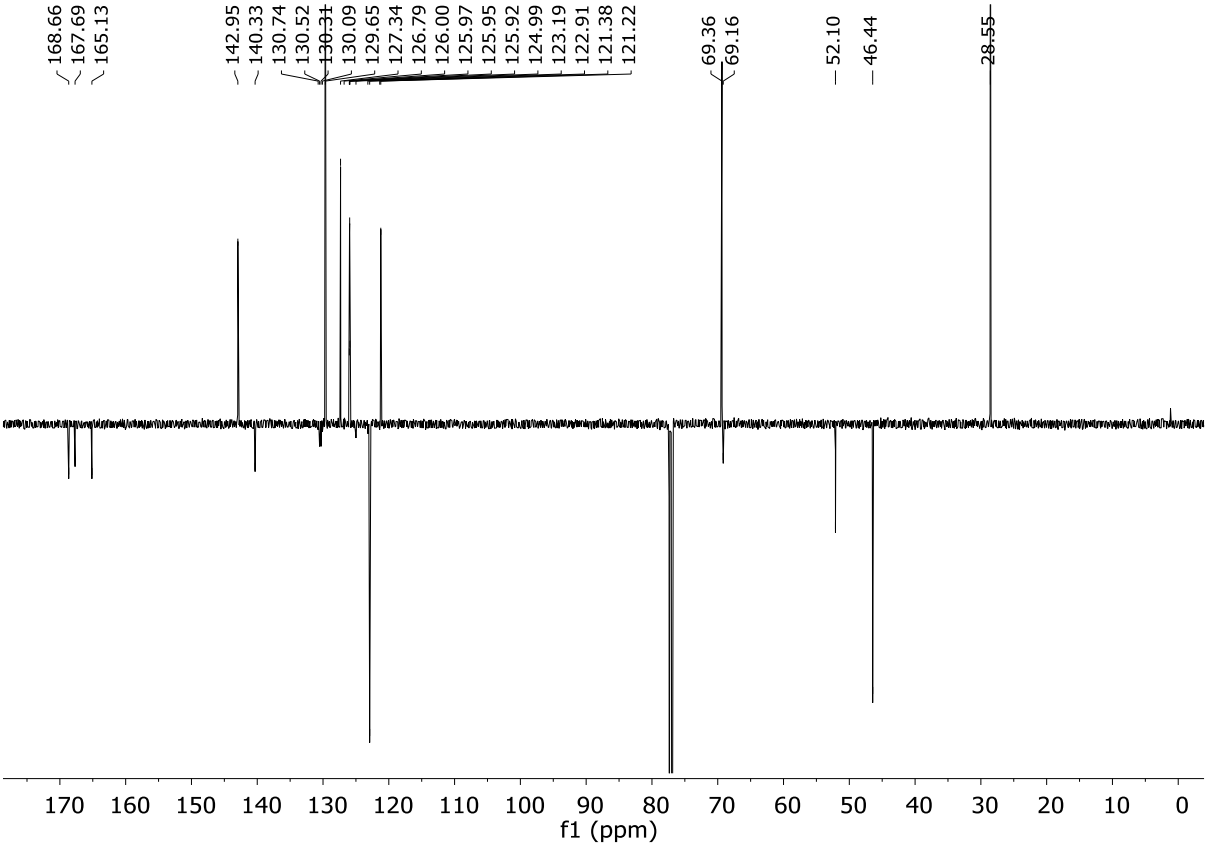
^{13}C NMR (*trans*-6q) 126 MHz, $CDCl_3$



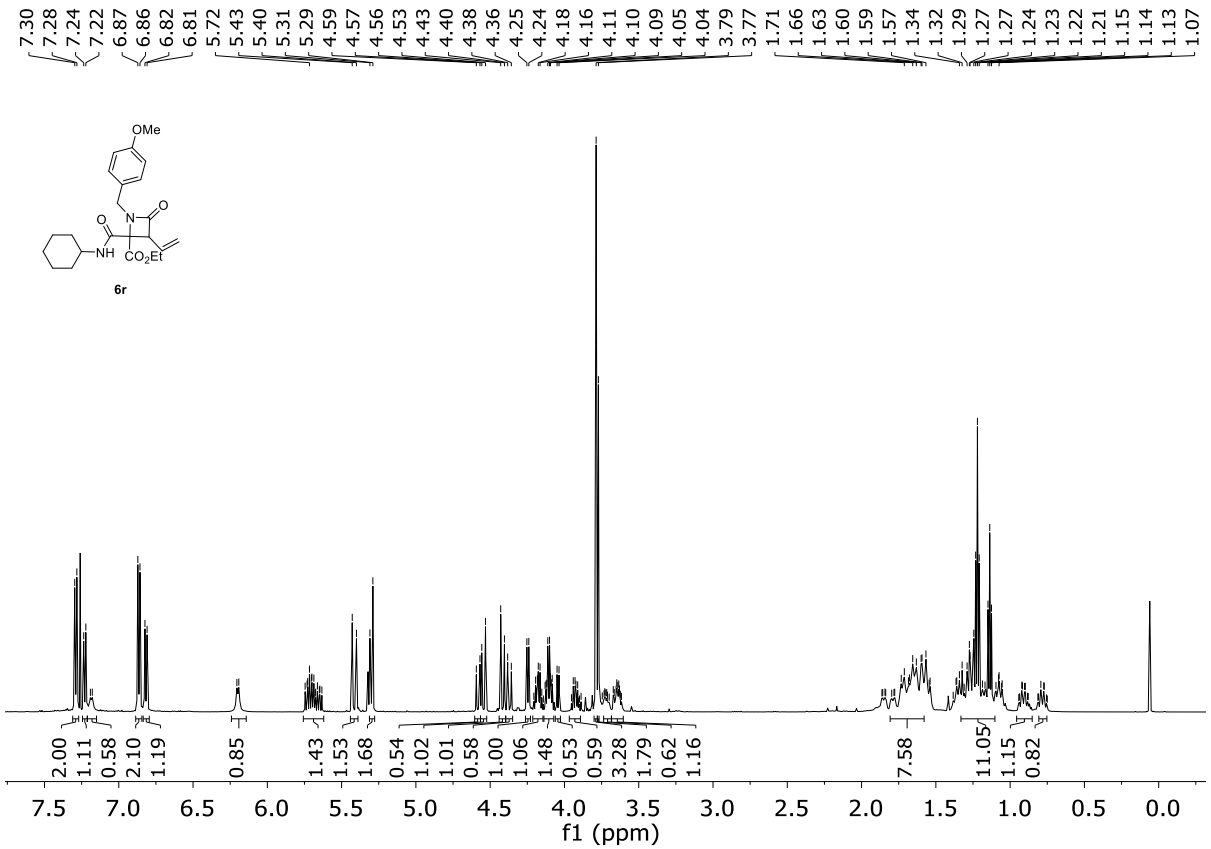
^{1}H NMR (*cis*-6q) 600 MHz, $CDCl_3$



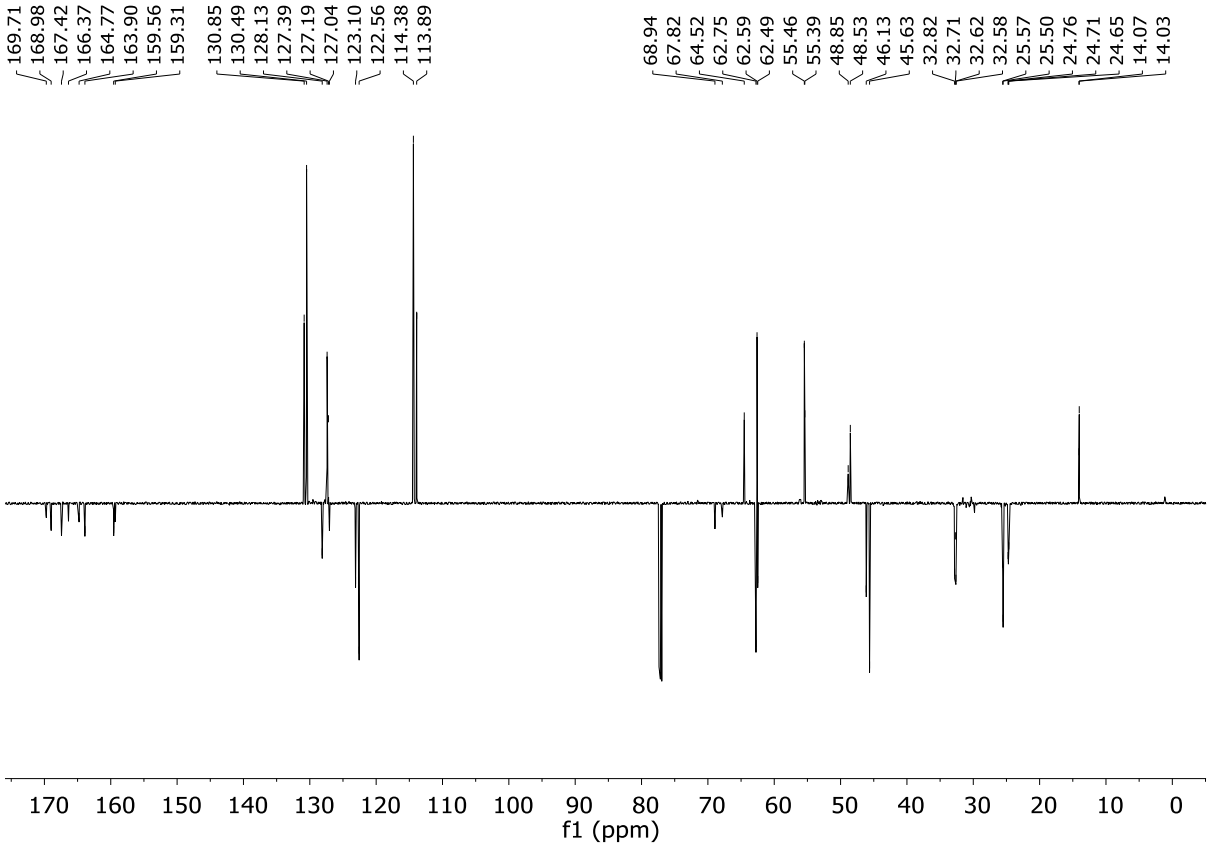
^{13}C NMR (cis-6b) 151 MHz, $CDCl_3$



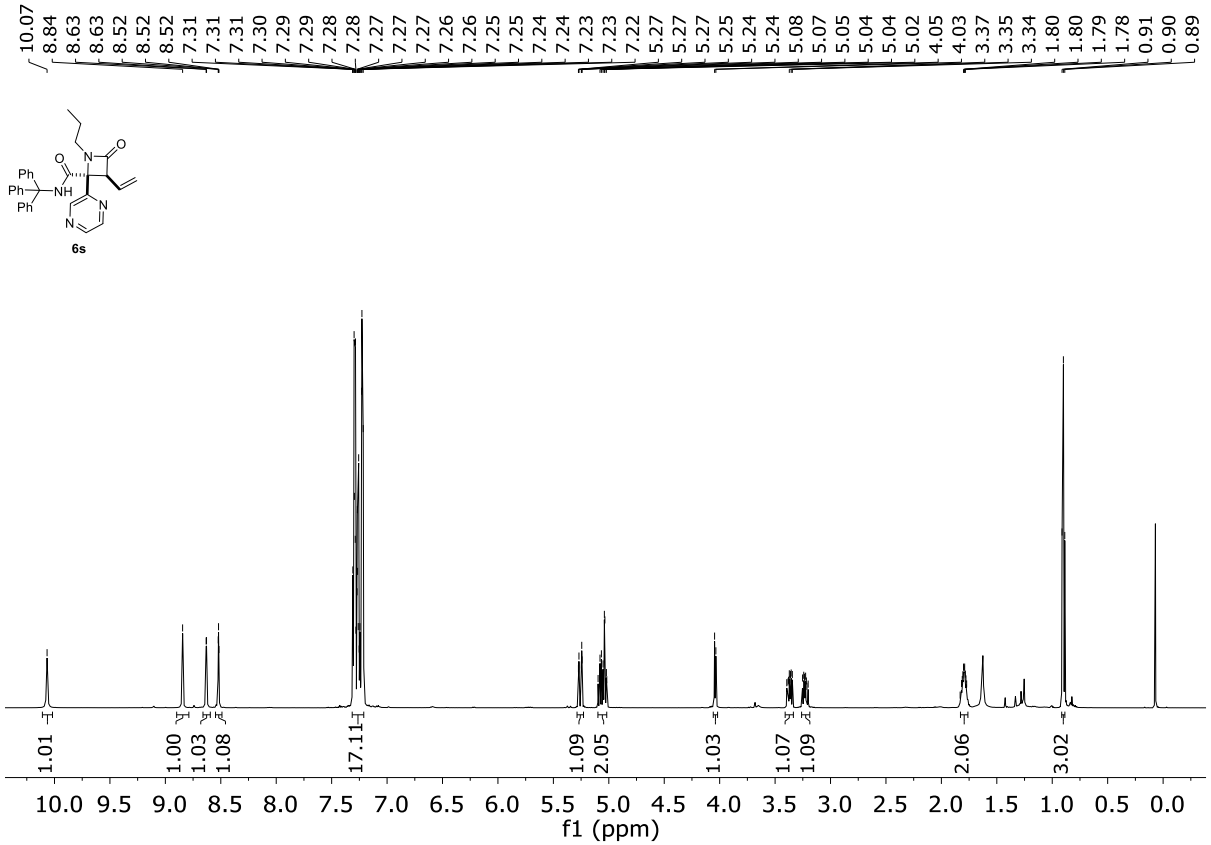
^{1}H NMR (*trans/cis*-6r) 600 MHz, $CDCl_3$



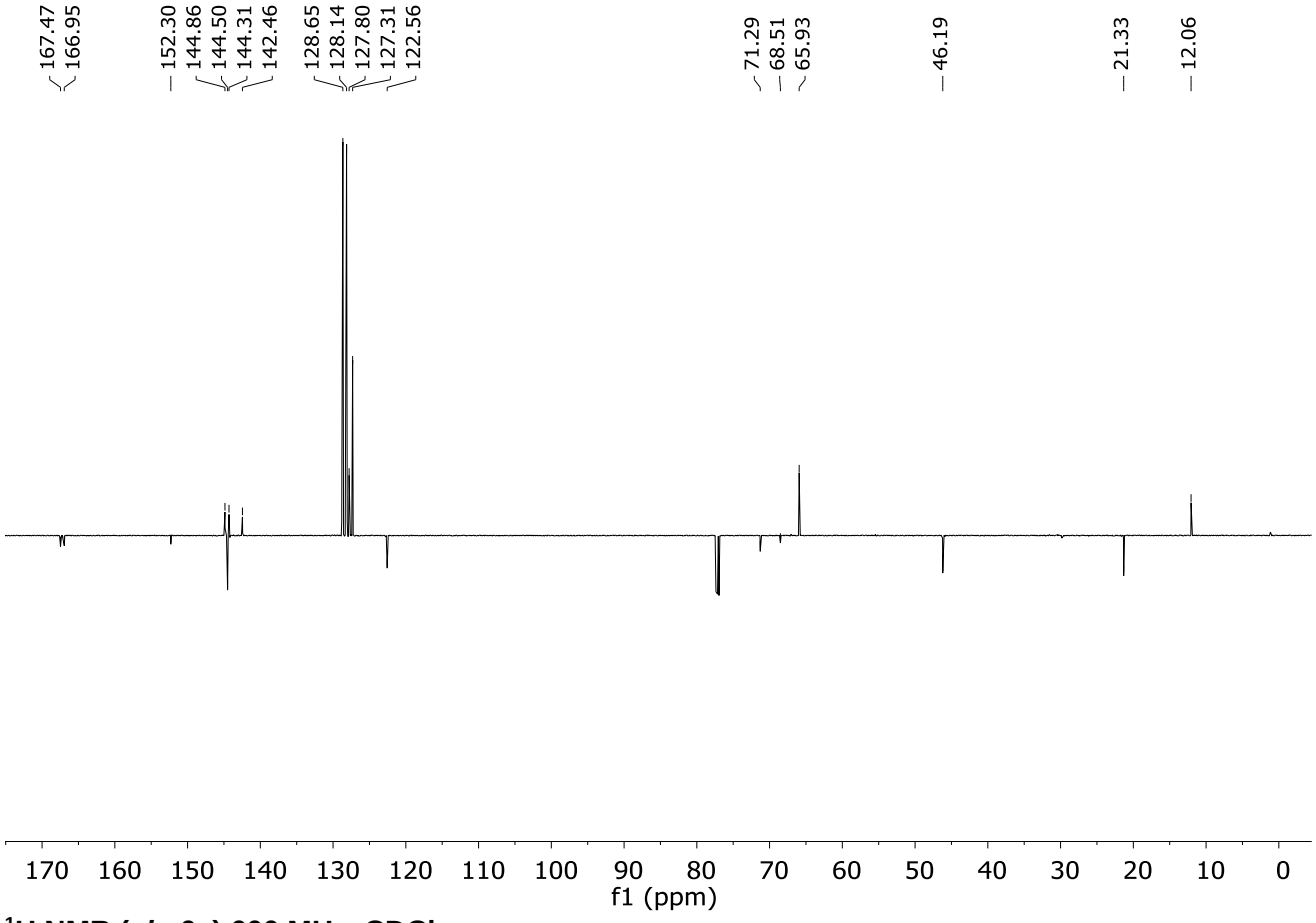
^{13}C NMR (*trans/cis*-6r) 151 MHz, $CDCl_3$



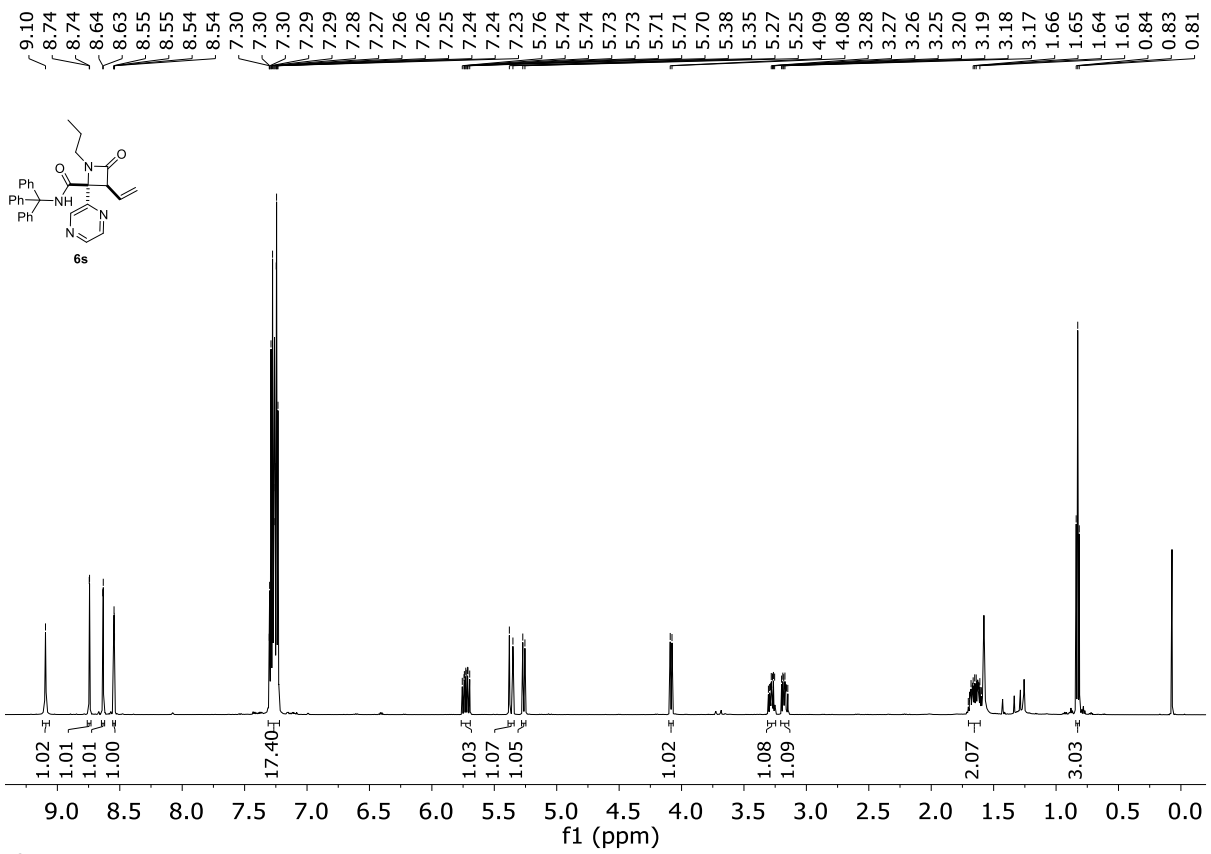
^{1}H NMR (*trans*-6s) 600 MHz, $CDCl_3$



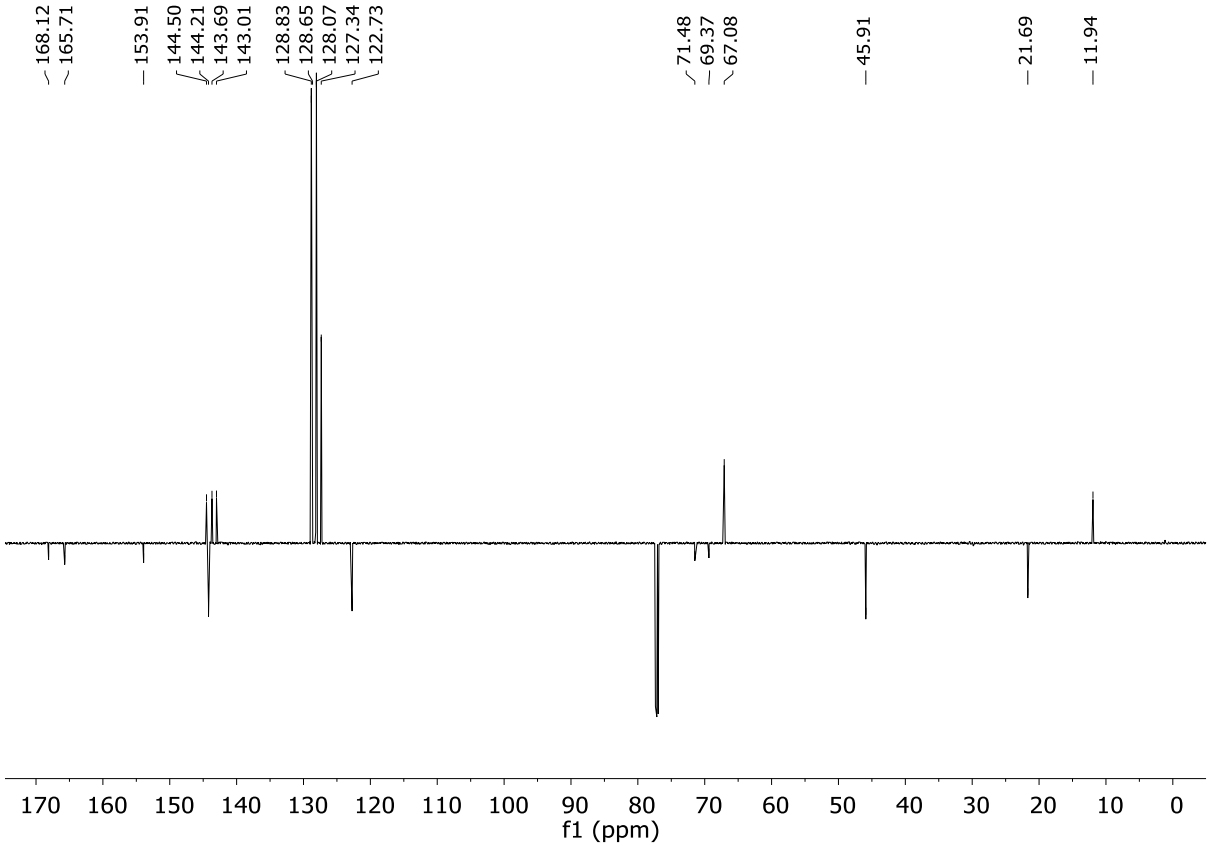
^{13}C NMR (*trans*-6s) 151 MHz, $CDCl_3$



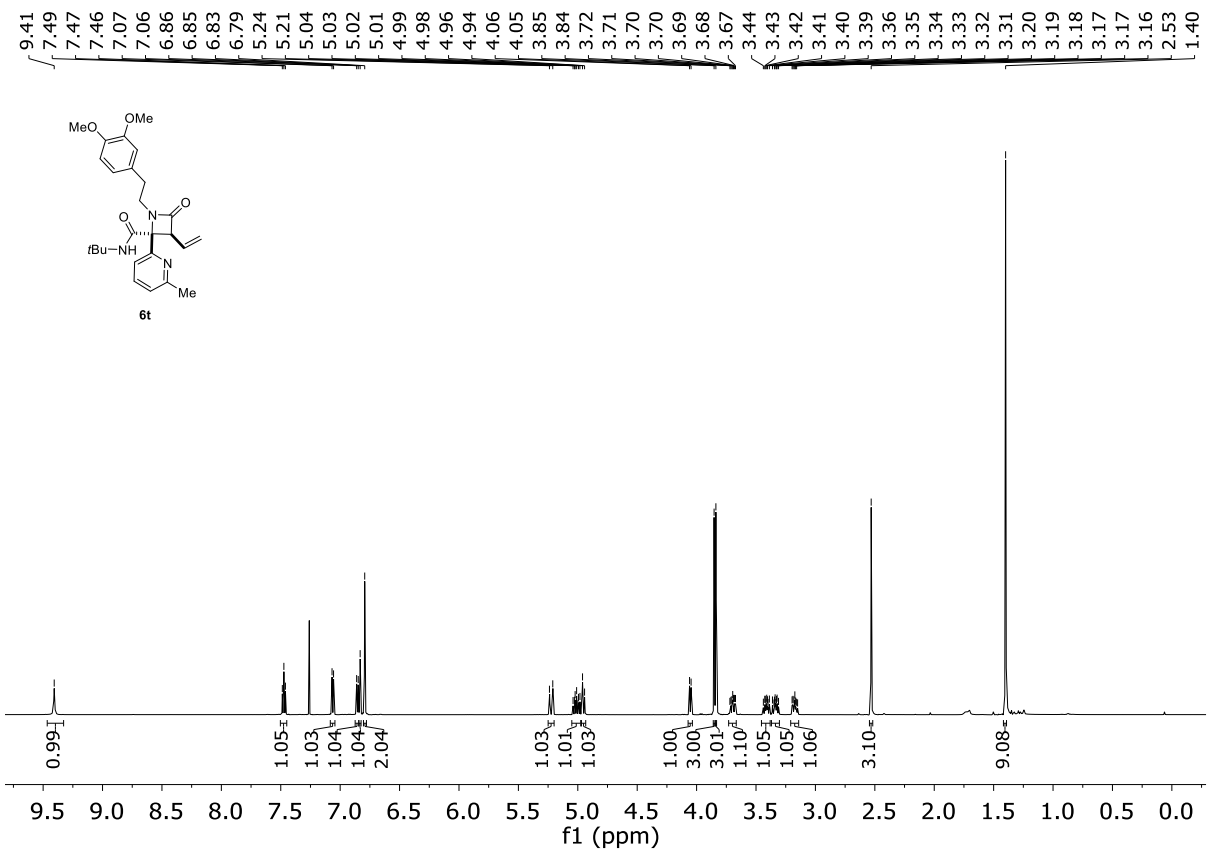
^{1}H NMR (*cis*-6s) 600 MHz, $CDCl_3$



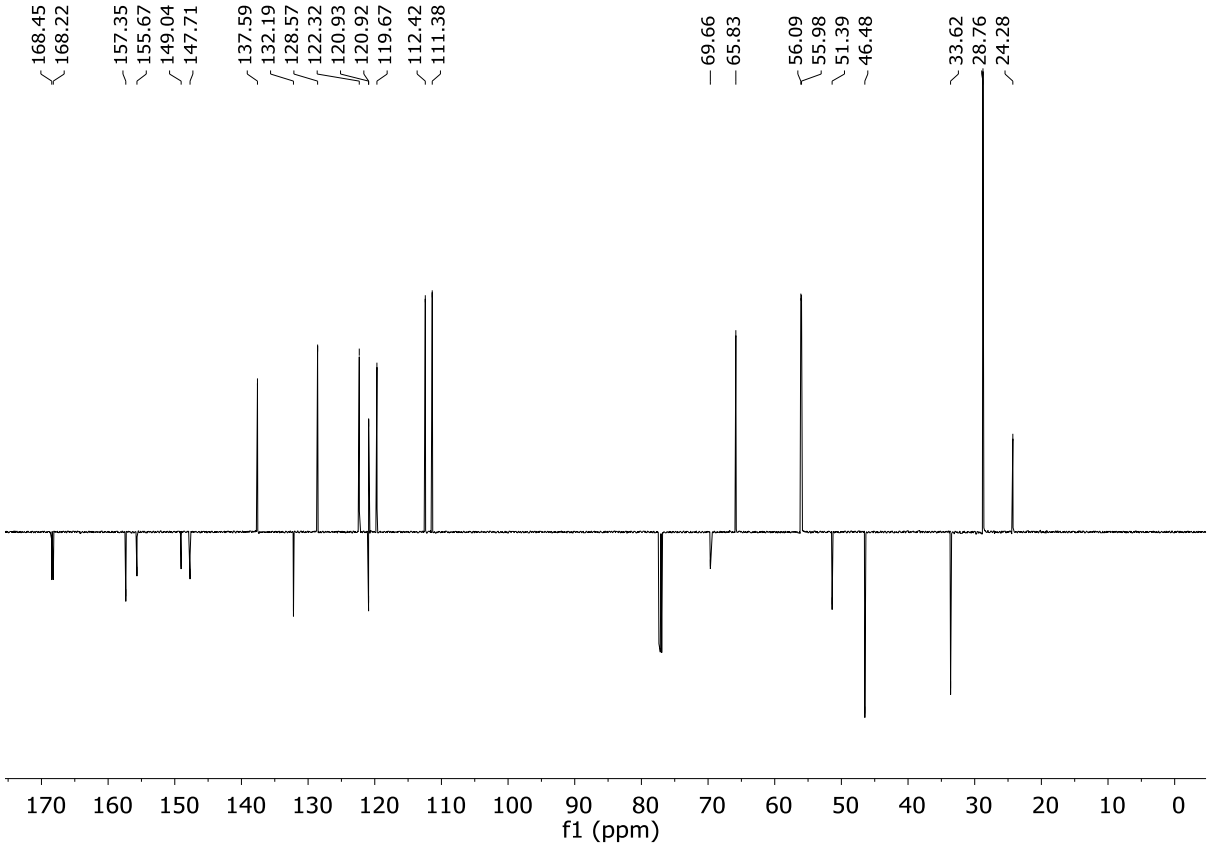
^{13}C NMR (*cis*-6s) 151 MHz, $CDCl_3$



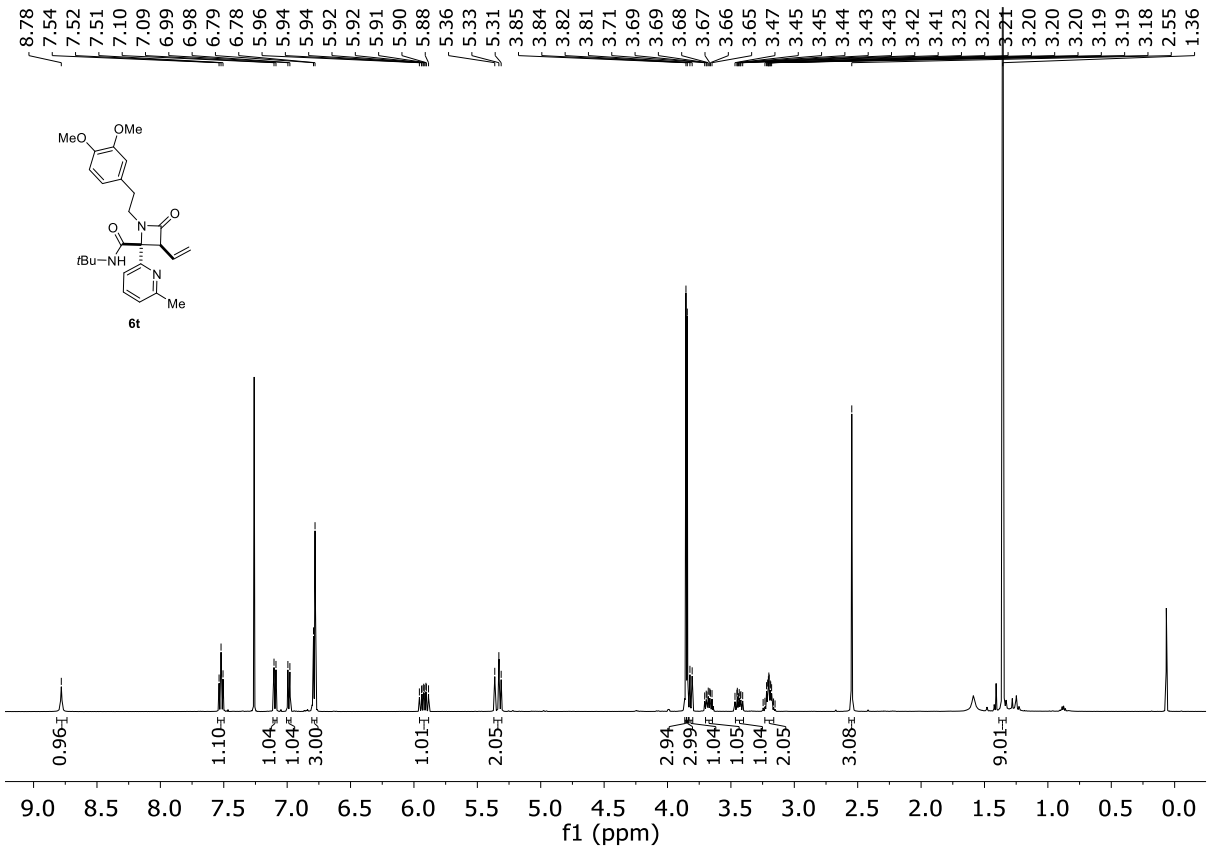
^{1}H NMR (*trans*-6t) 600 MHz, $CDCl_3$



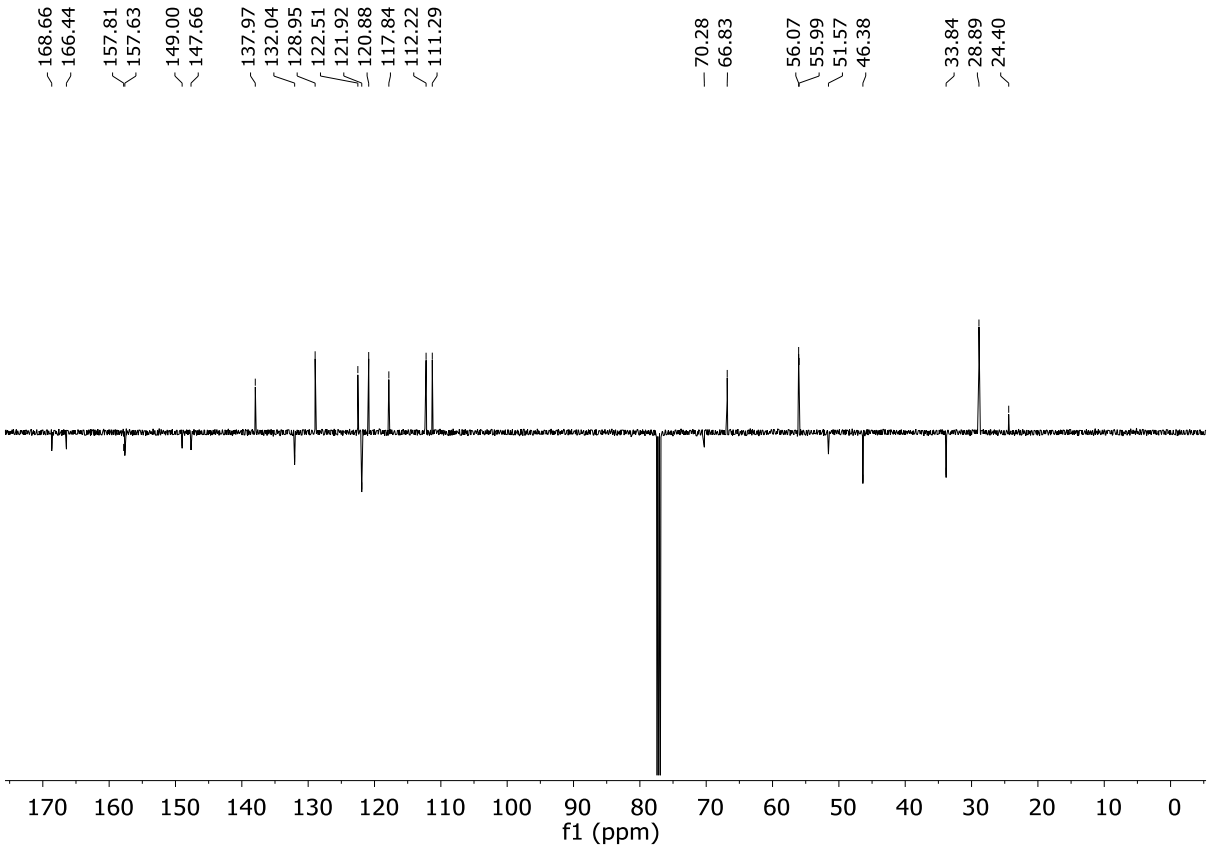
^{13}C NMR (*trans*-6t) 151 MHz, $CDCl_3$



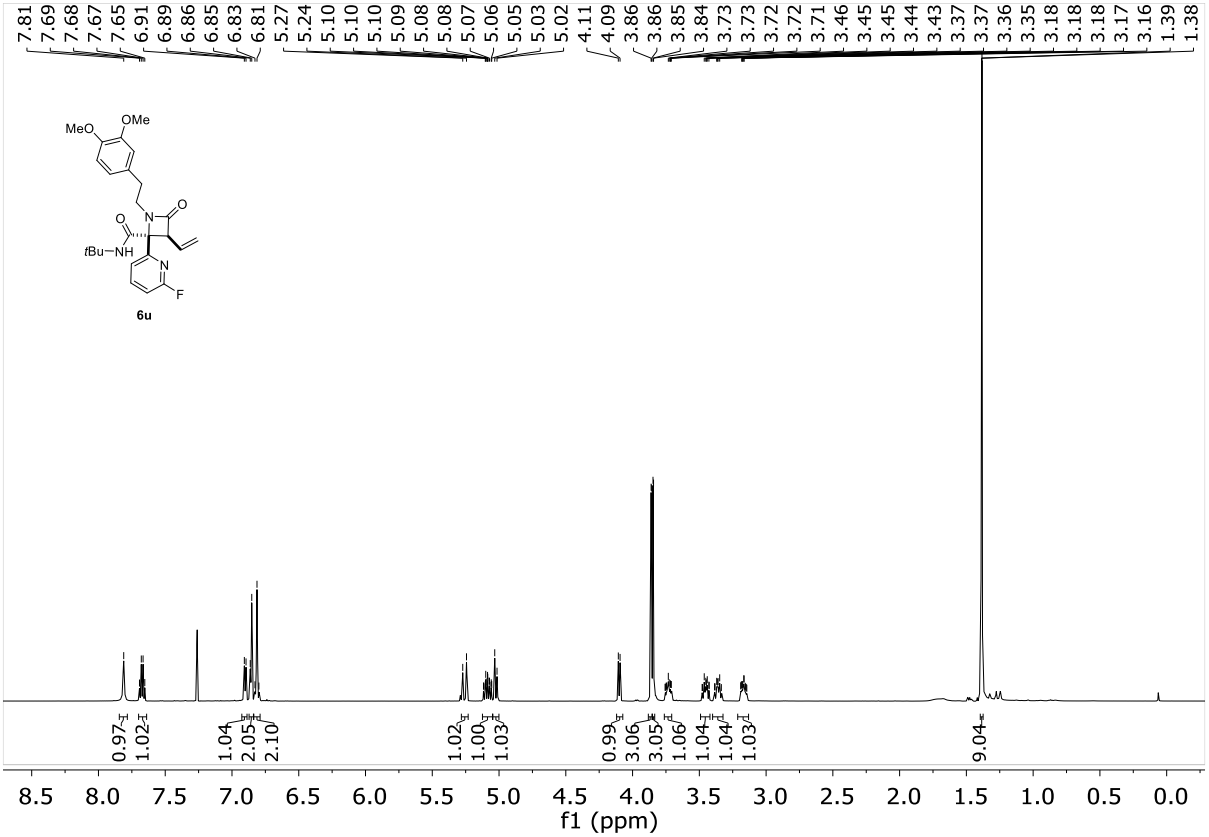
^{1}H NMR (*cis*-6t) 500 MHz, $CDCl_3$



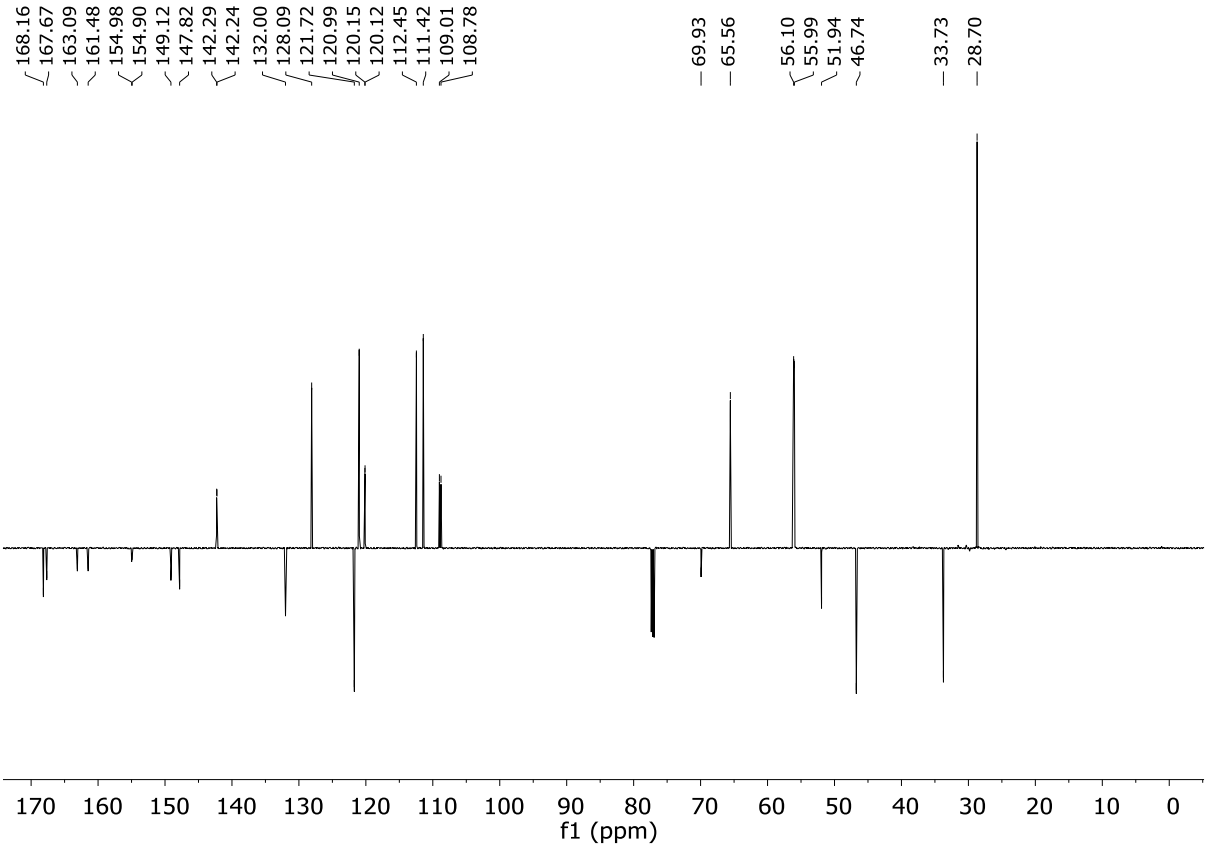
^{13}C NMR (*cis*-6t) 126 MHz, $CDCl_3$



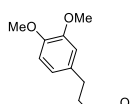
^{1}H NMR (*trans*-6u) 600 MHz, $CDCl_3$

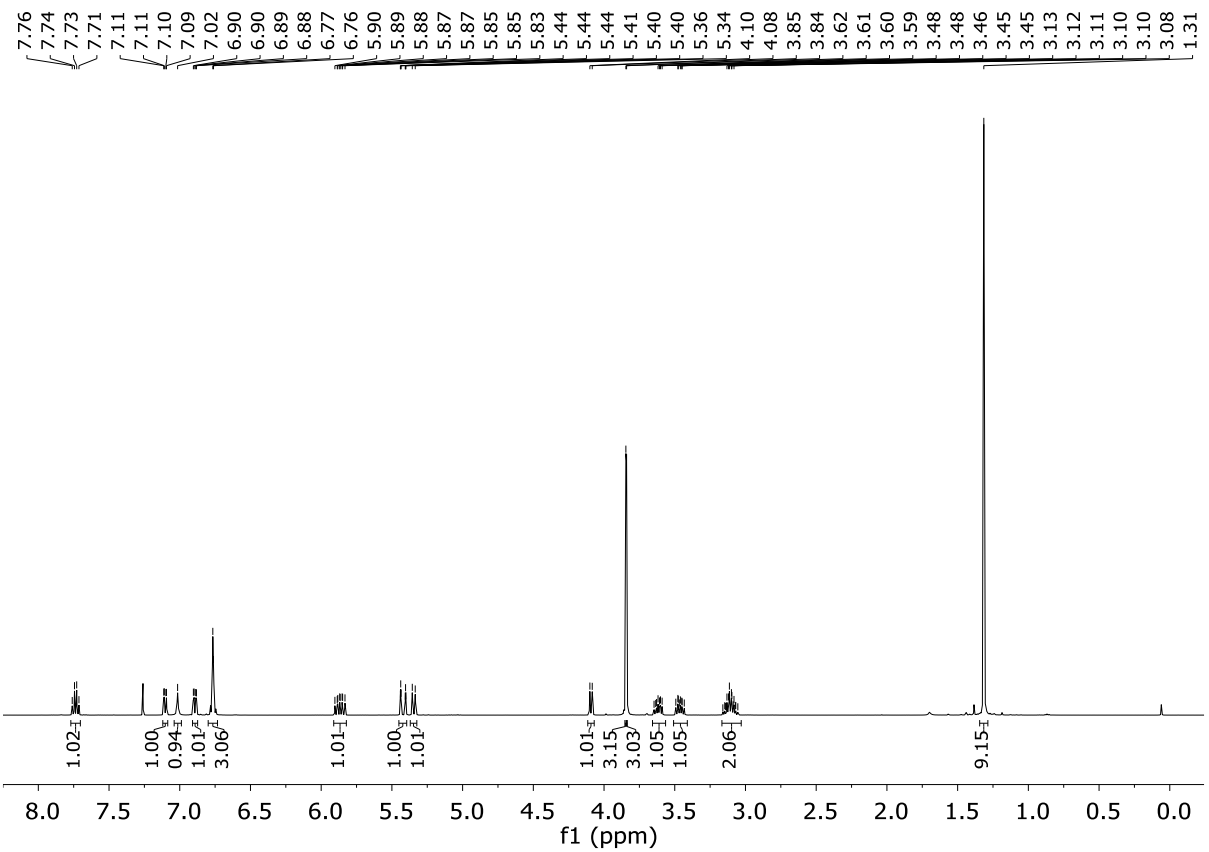


^{13}C NMR (*trans*-6u) 151 MHz, $CDCl_3$

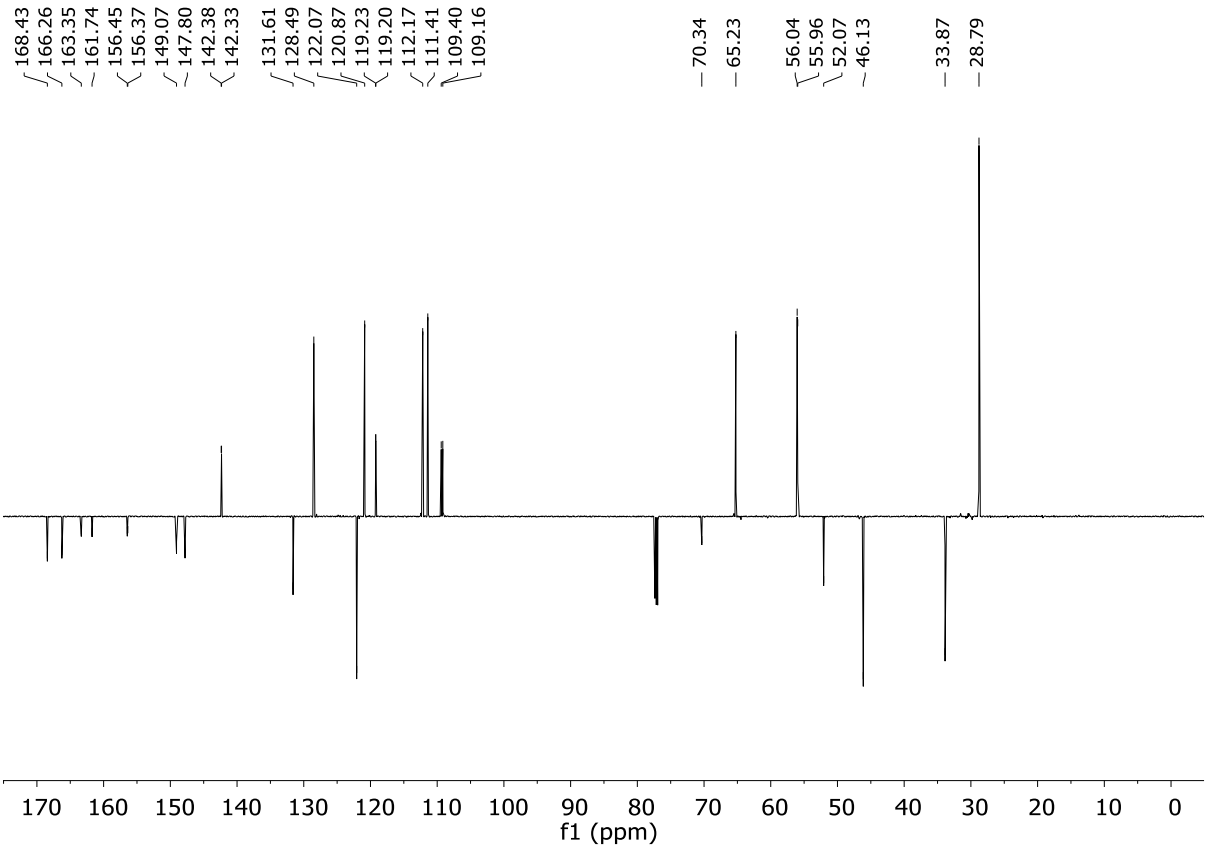


^{1}H NMR (*cis*-6u) 500 MHz, $CDCl_3$

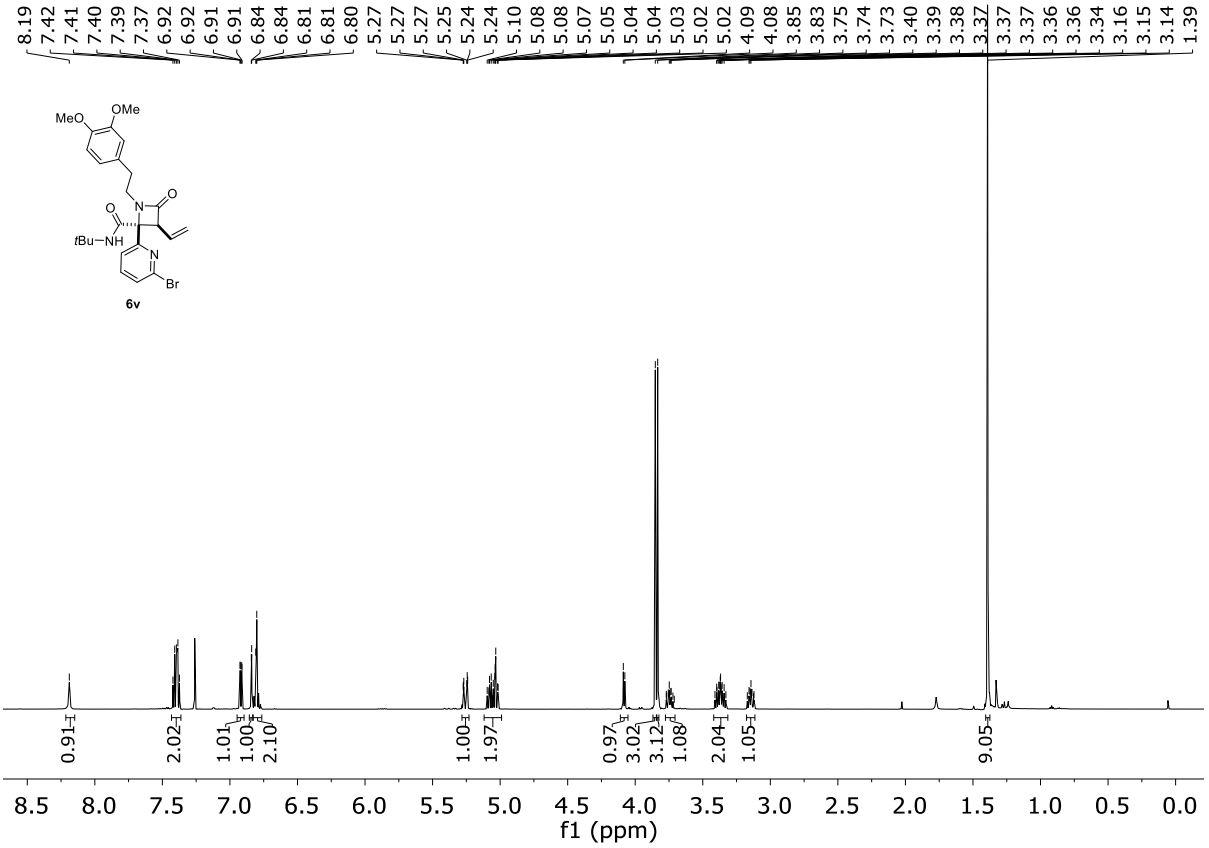




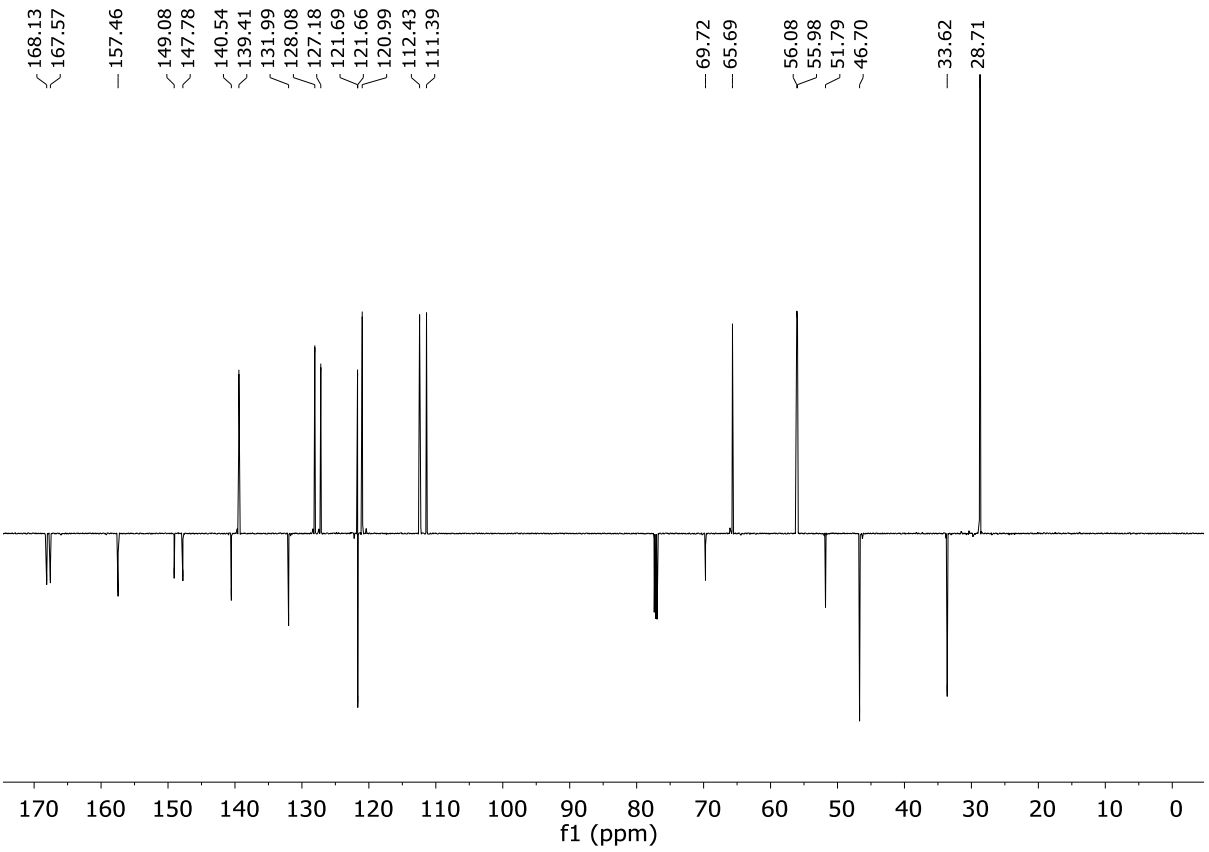
^{13}C NMR (*cis*-6b) 126 MHz, $CDCl_3$



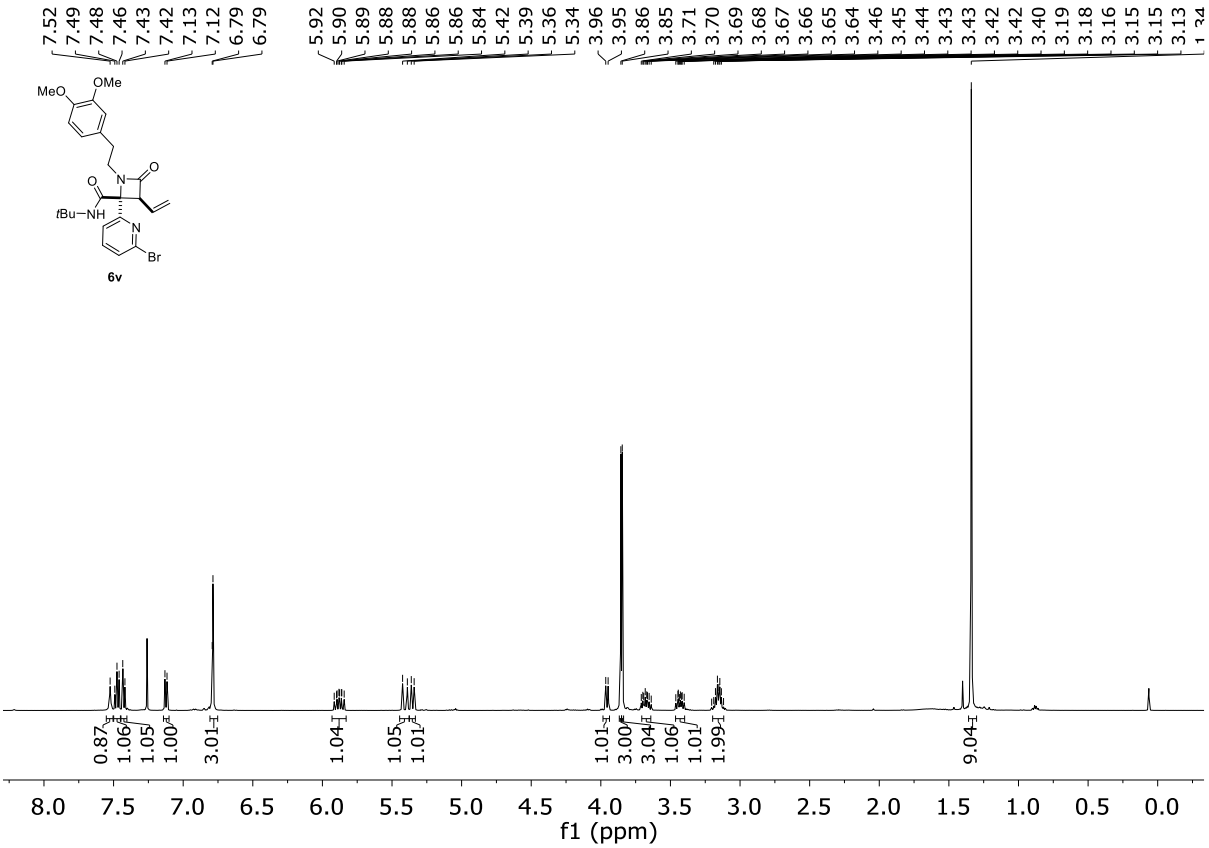
^{1}H NMR (*trans*-6v) 600 MHz, $CDCl_3$



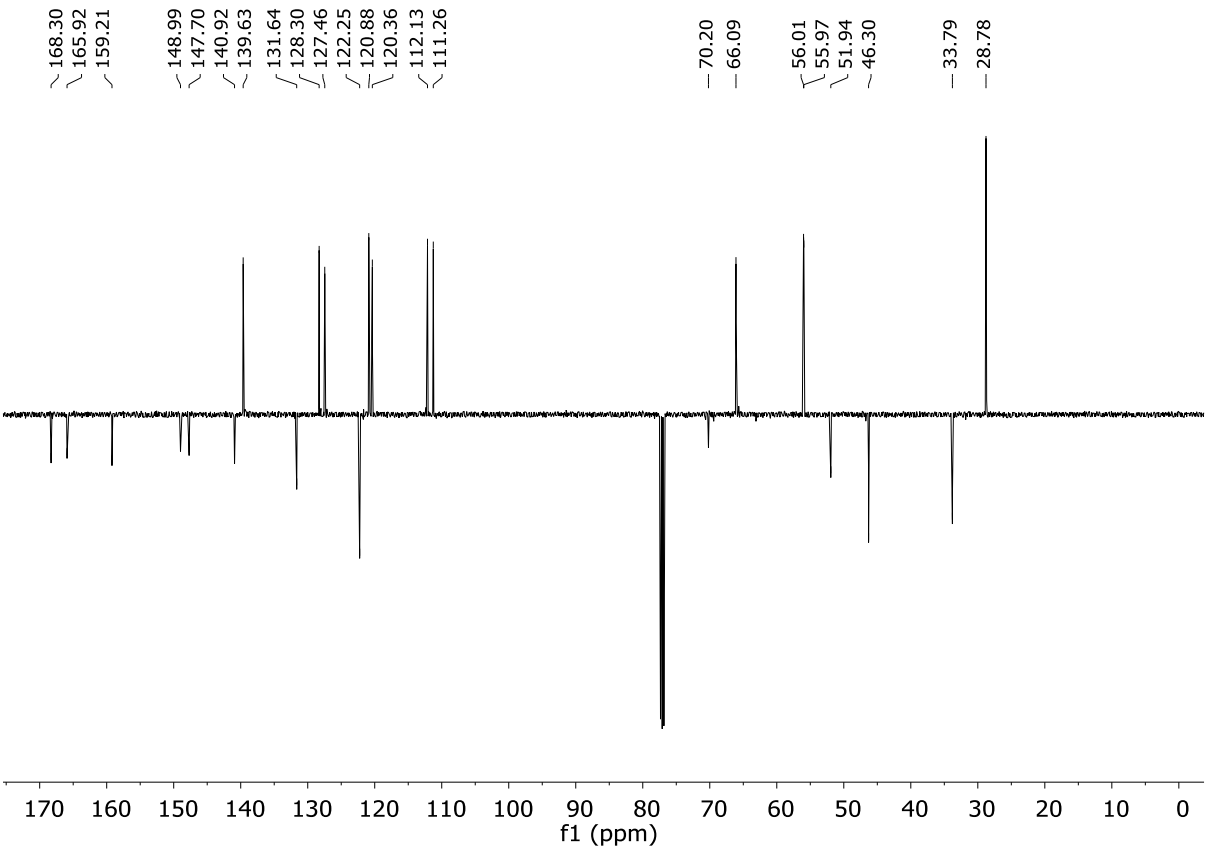
^{13}C NMR (*trans*-6v) 151 MHz, $CDCl_3$



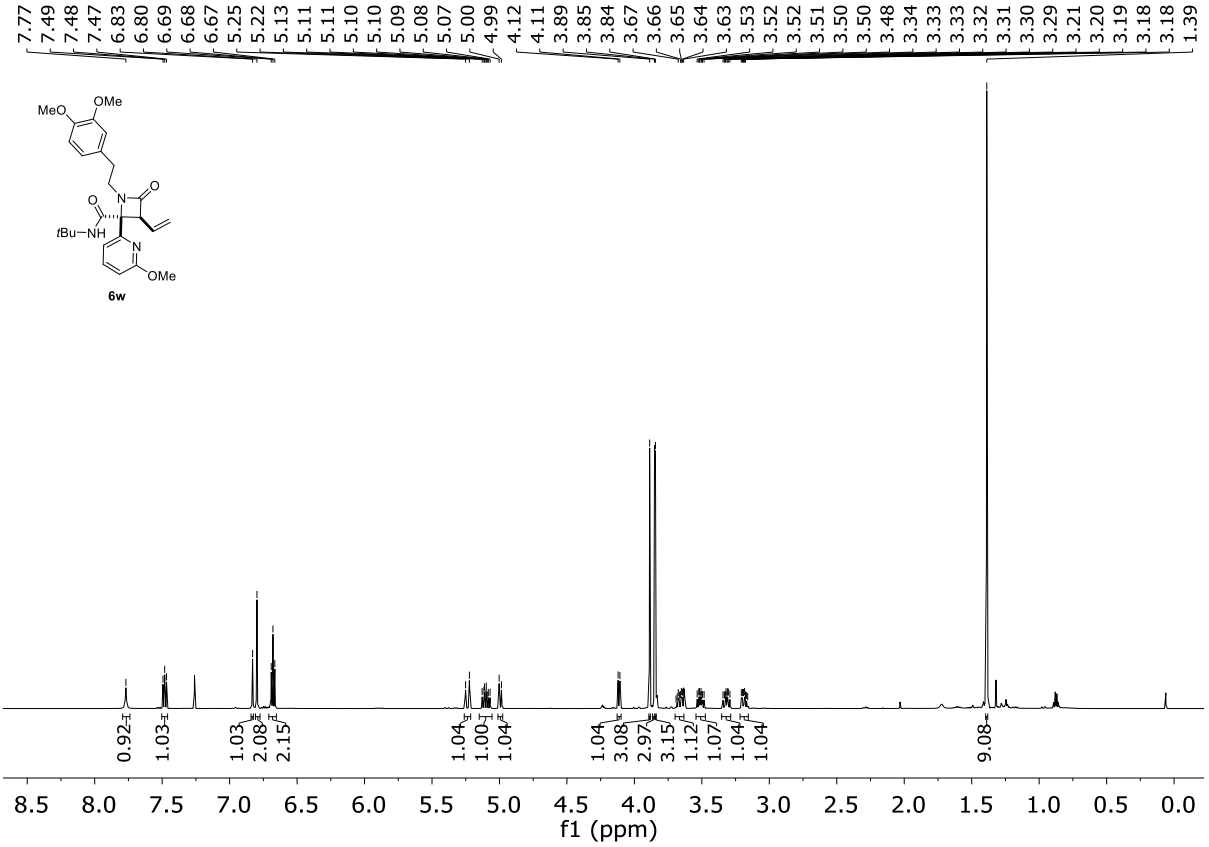
^{1}H NMR (*cis*-6v) 500 MHz, $CDCl_3$



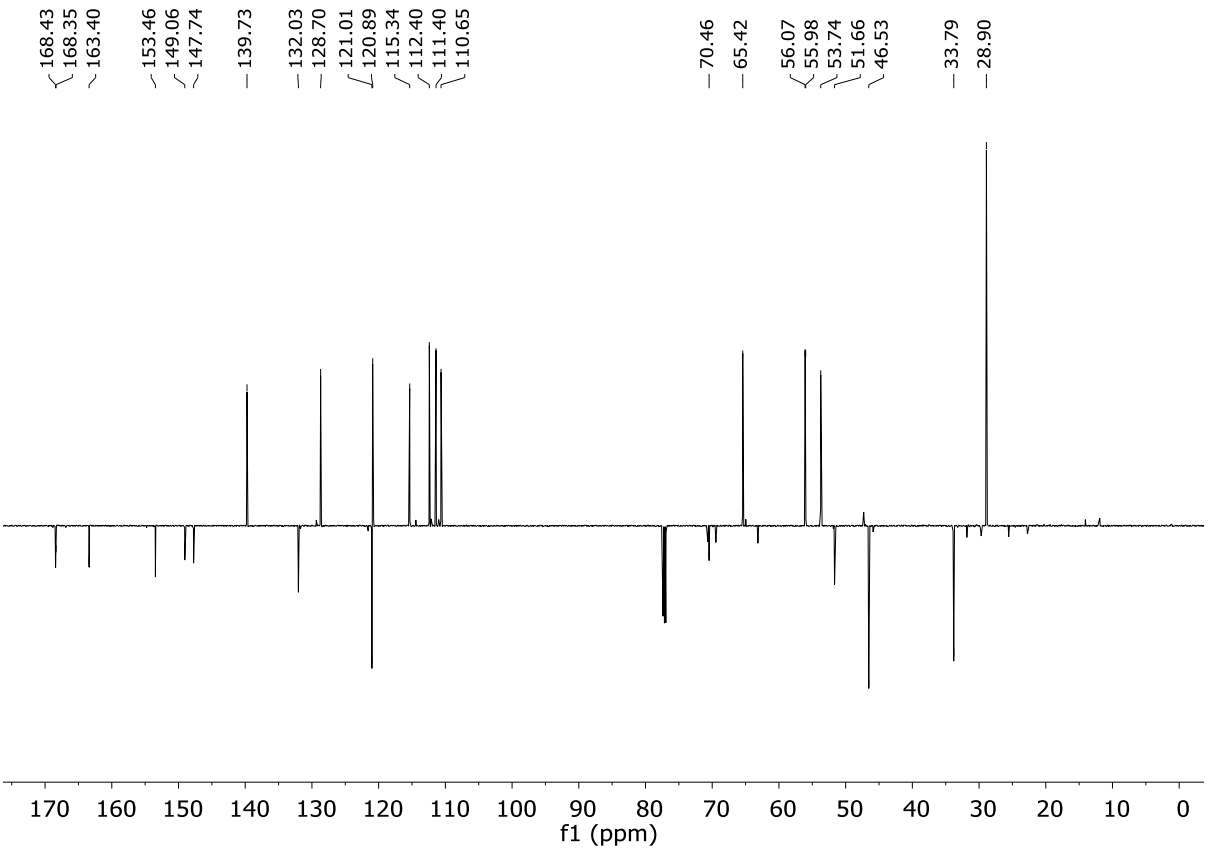
^{13}C NMR (*cis*-6v) 126 MHz, $CDCl_3$



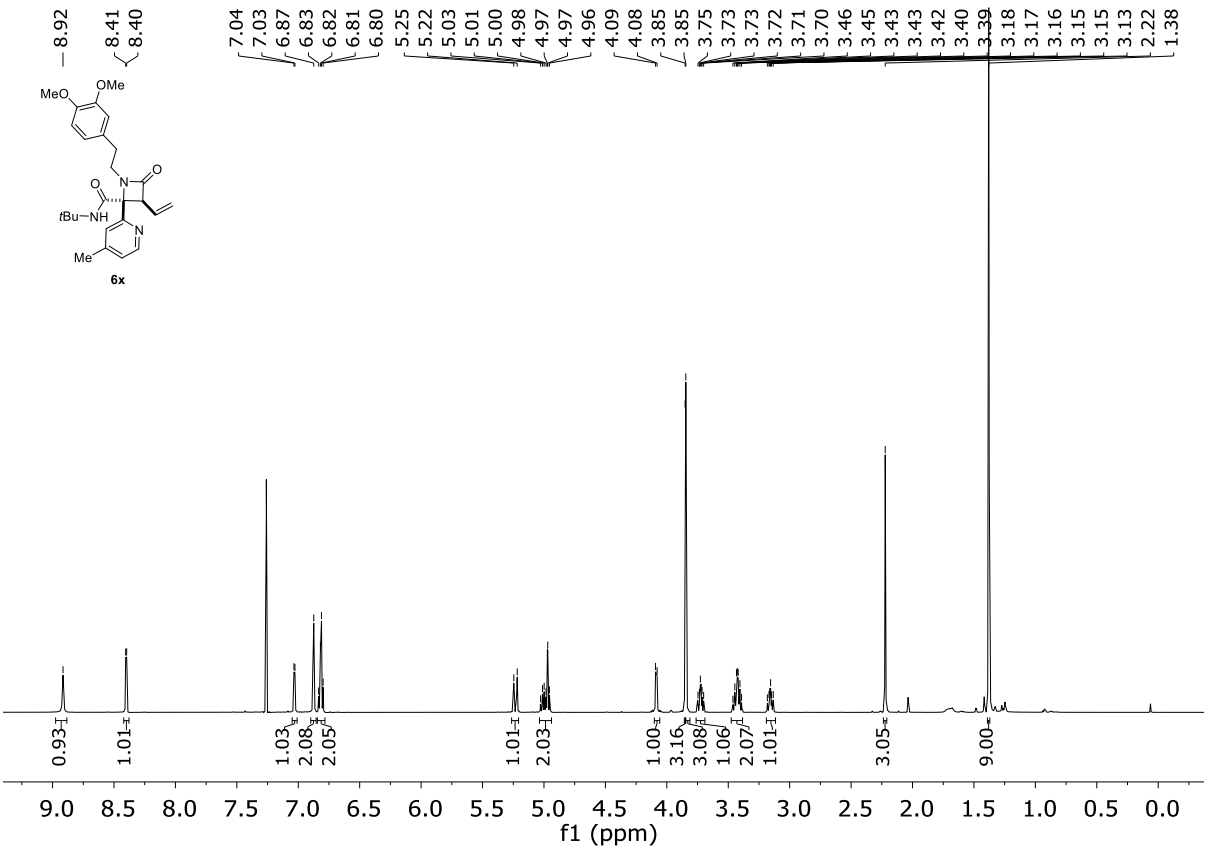
^{1}H NMR (*trans*-6w) 600 MHz, $CDCl_3$



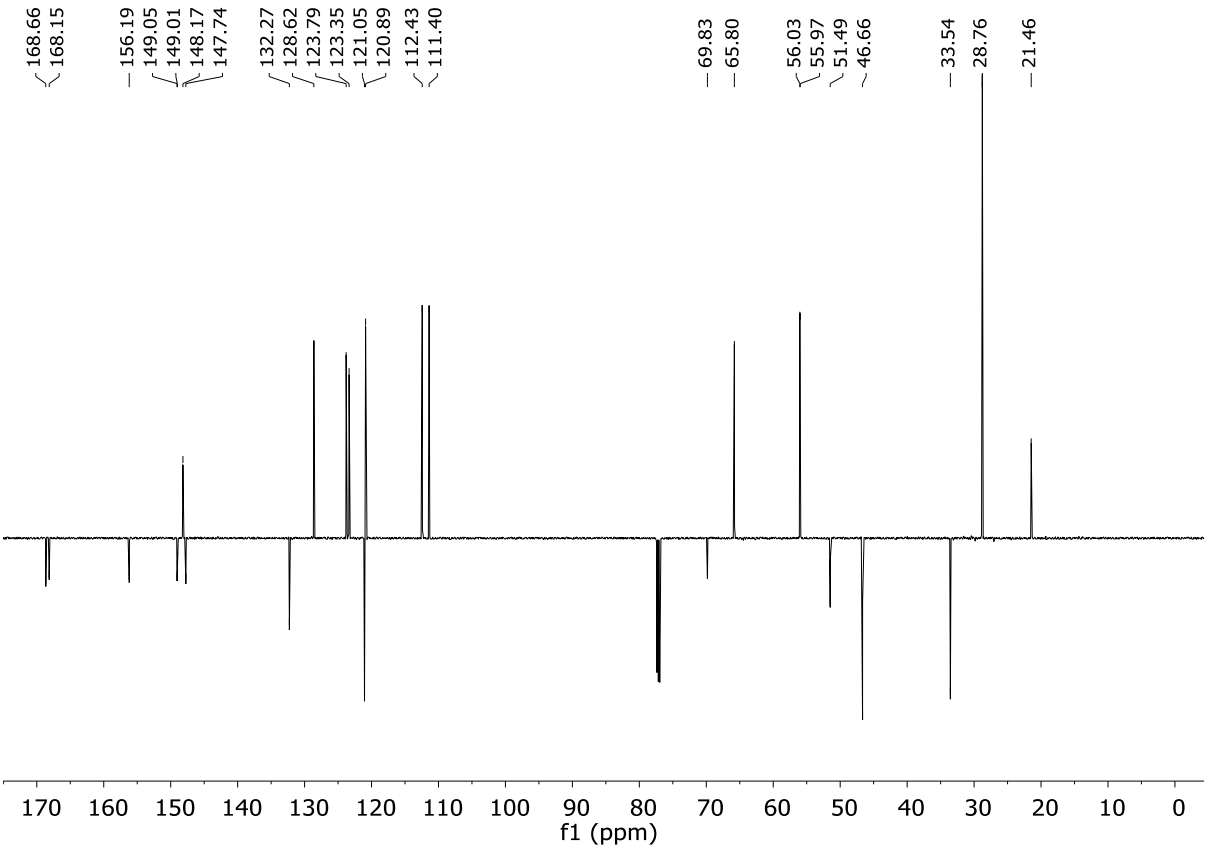
^{13}C NMR (*trans*-6w) 151 MHz, $CDCl_3$



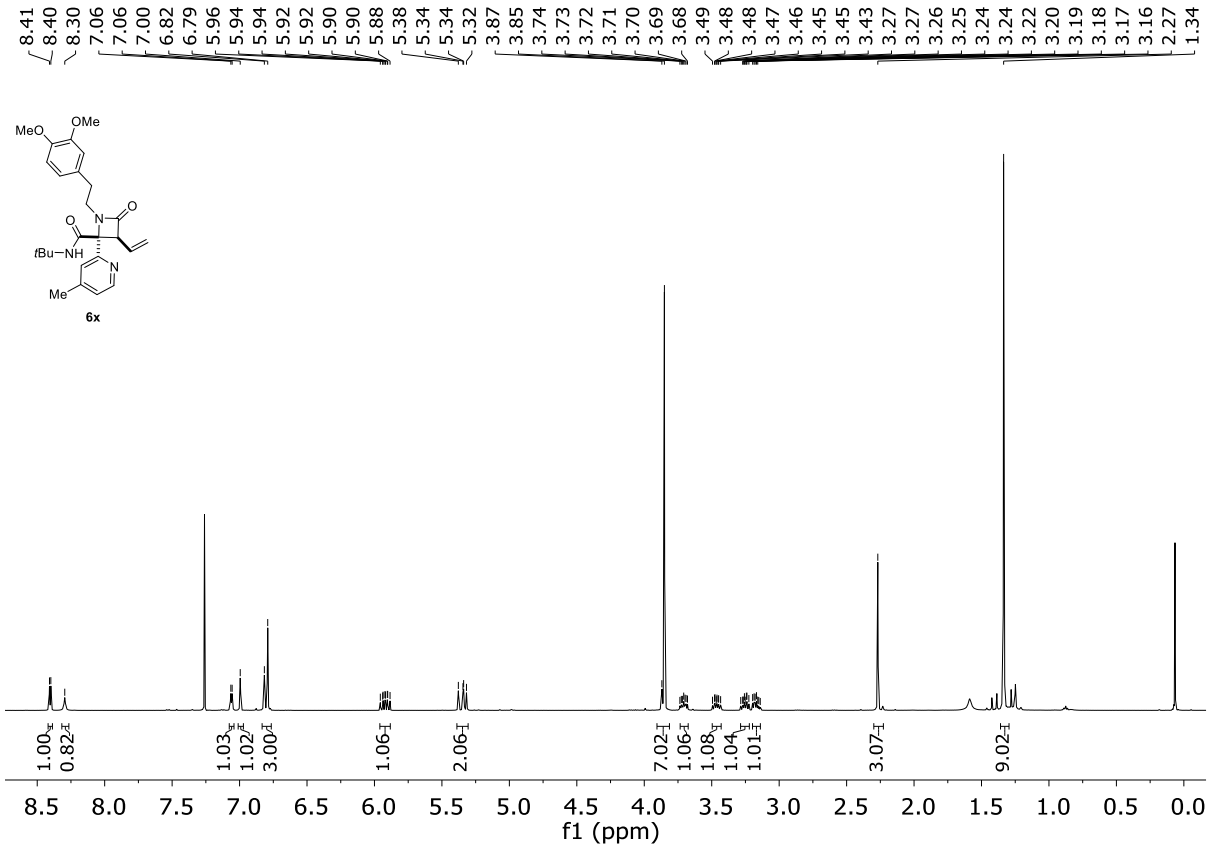
^{1}H NMR (*trans*-6x) 600 MHz, $CDCl_3$



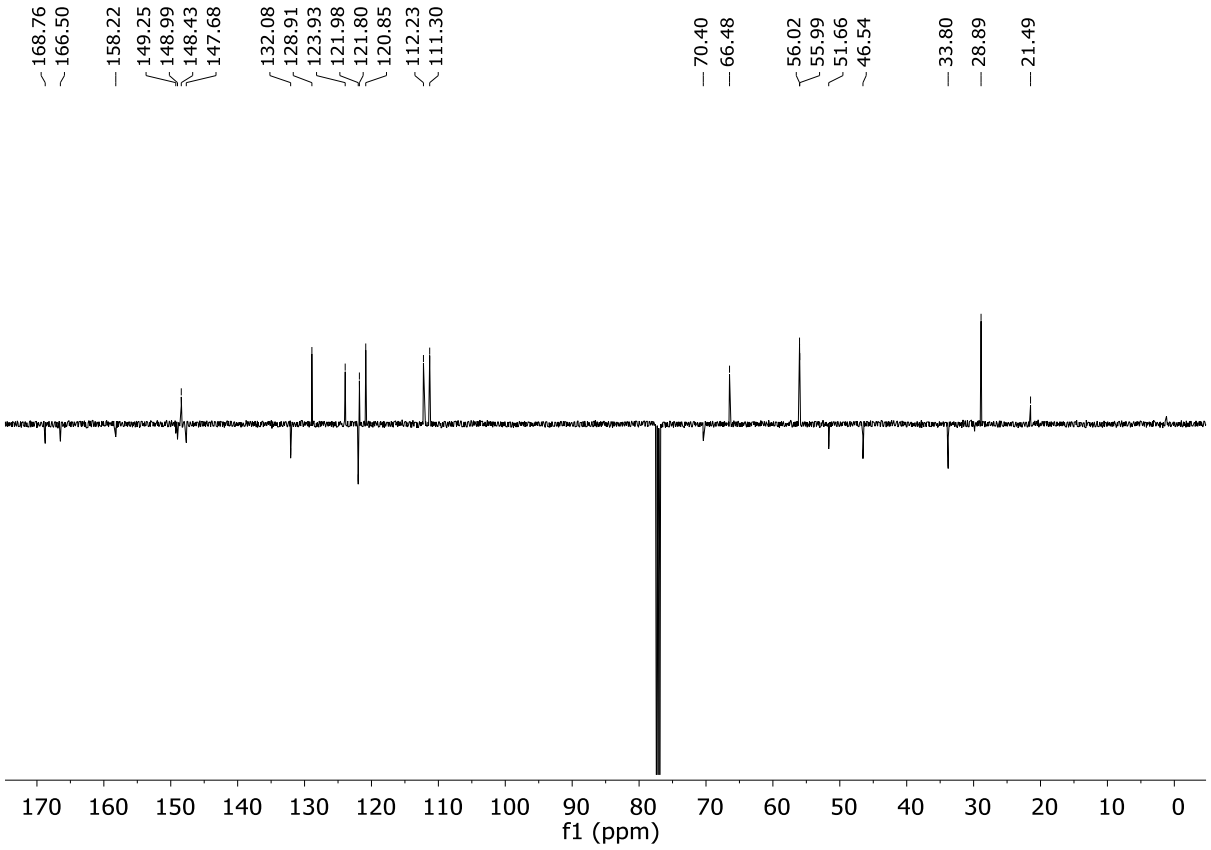
^{13}C NMR (*trans*-6x) 151 MHz, $CDCl_3$



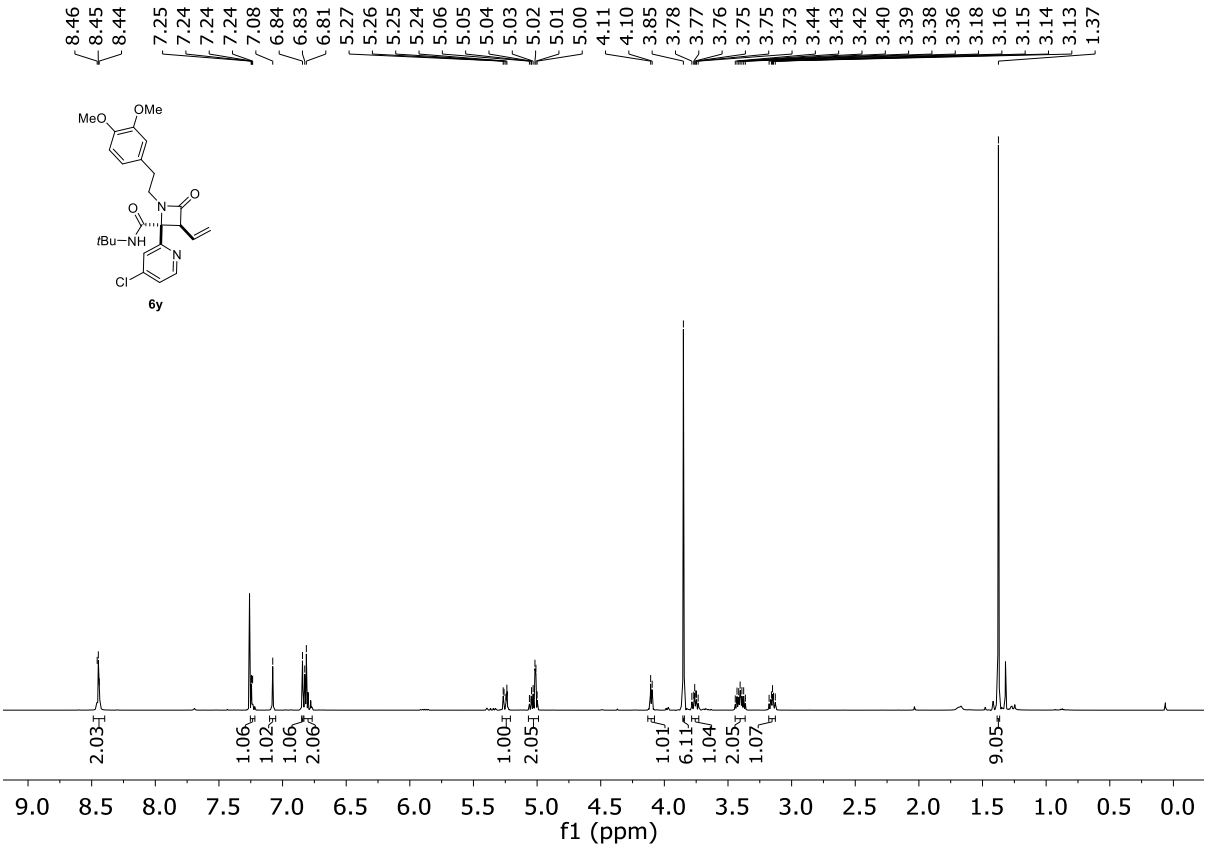
^{1}H NMR (*cis*-6x) 500 MHz, $CDCl_3$



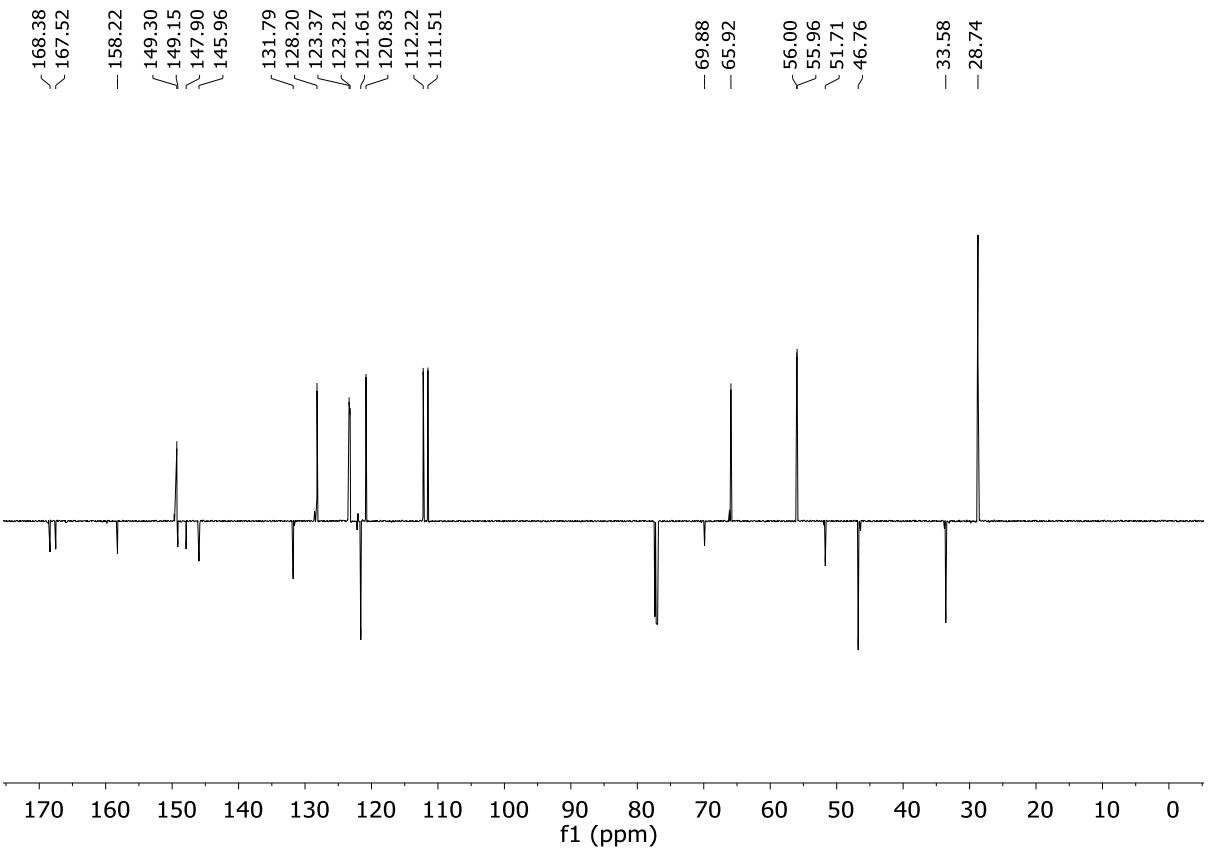
^{13}C NMR (*cis*-6x) 126 MHz, $CDCl_3$



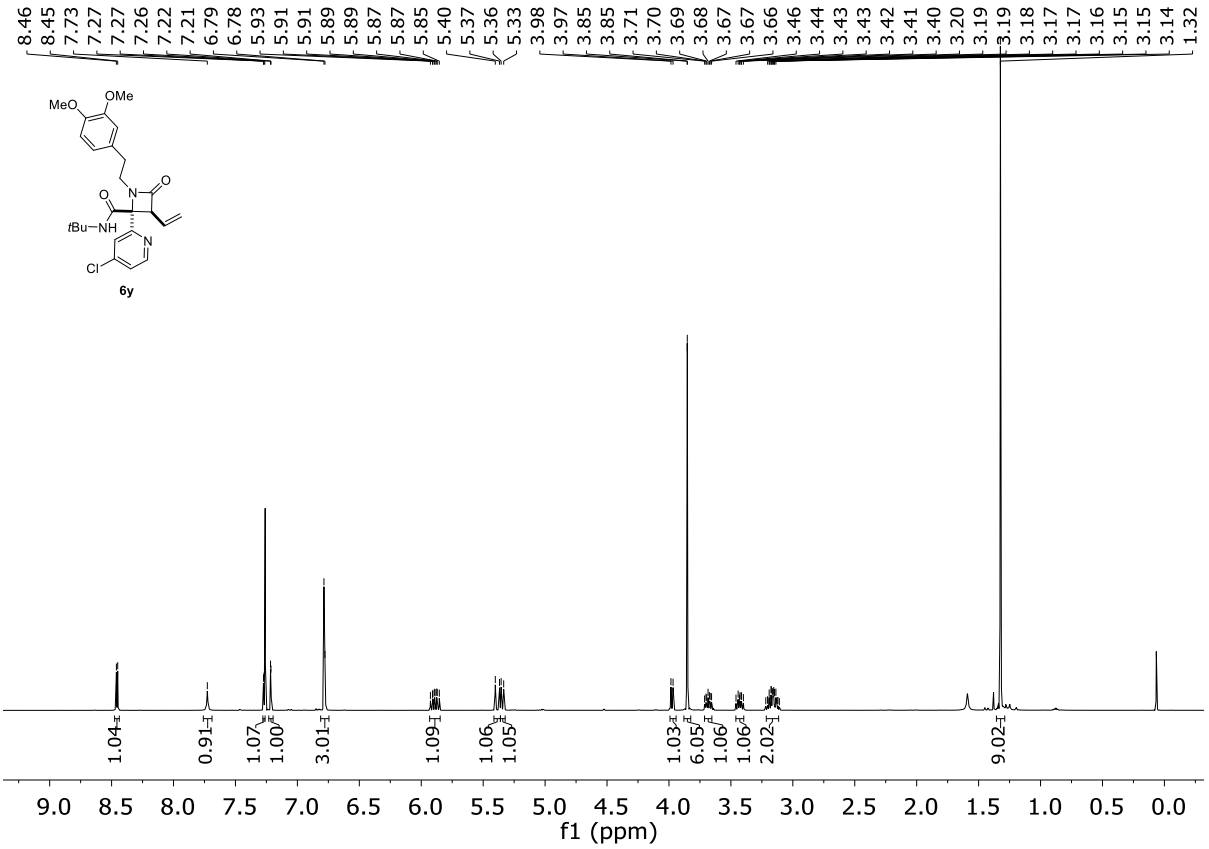
^{1}H NMR (*trans*-6y) 600 MHz, $CDCl_3$



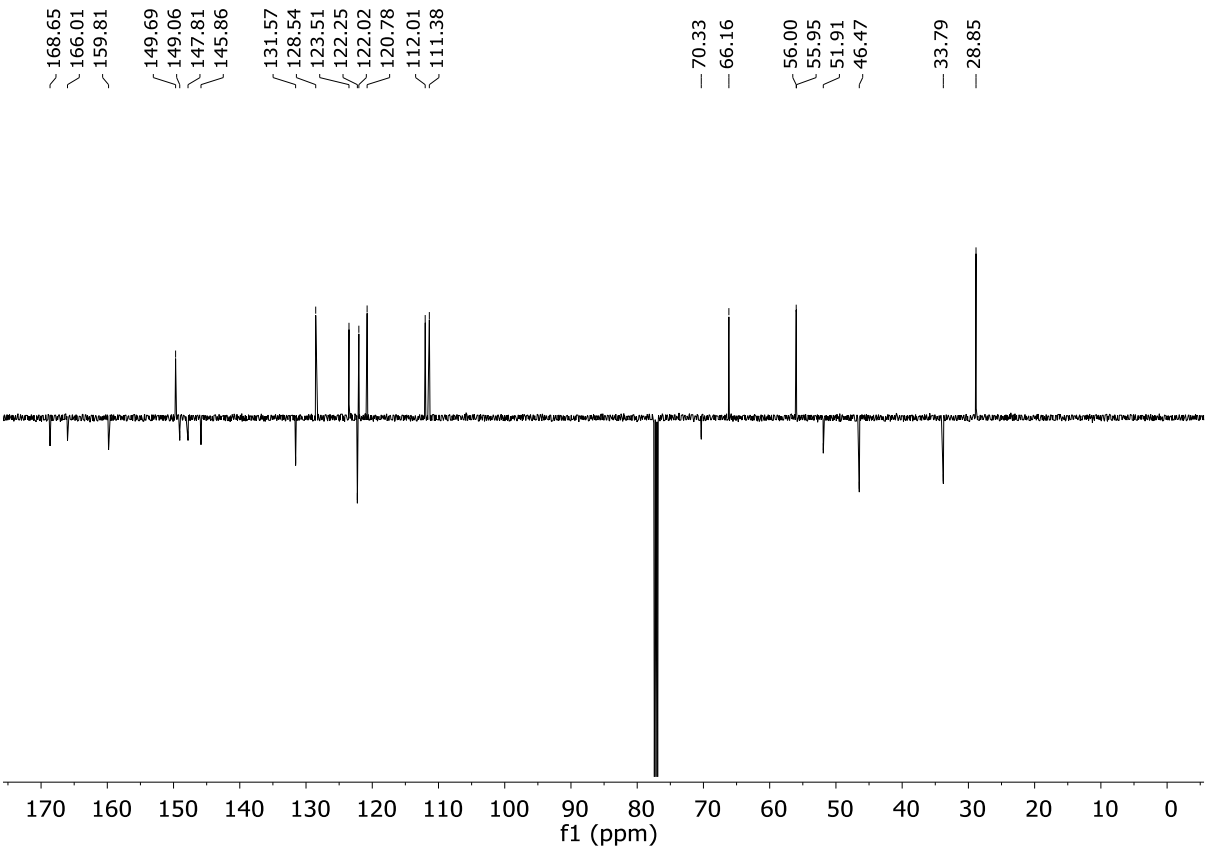
^{13}C NMR (*trans*-6y) 151 MHz, $CDCl_3$



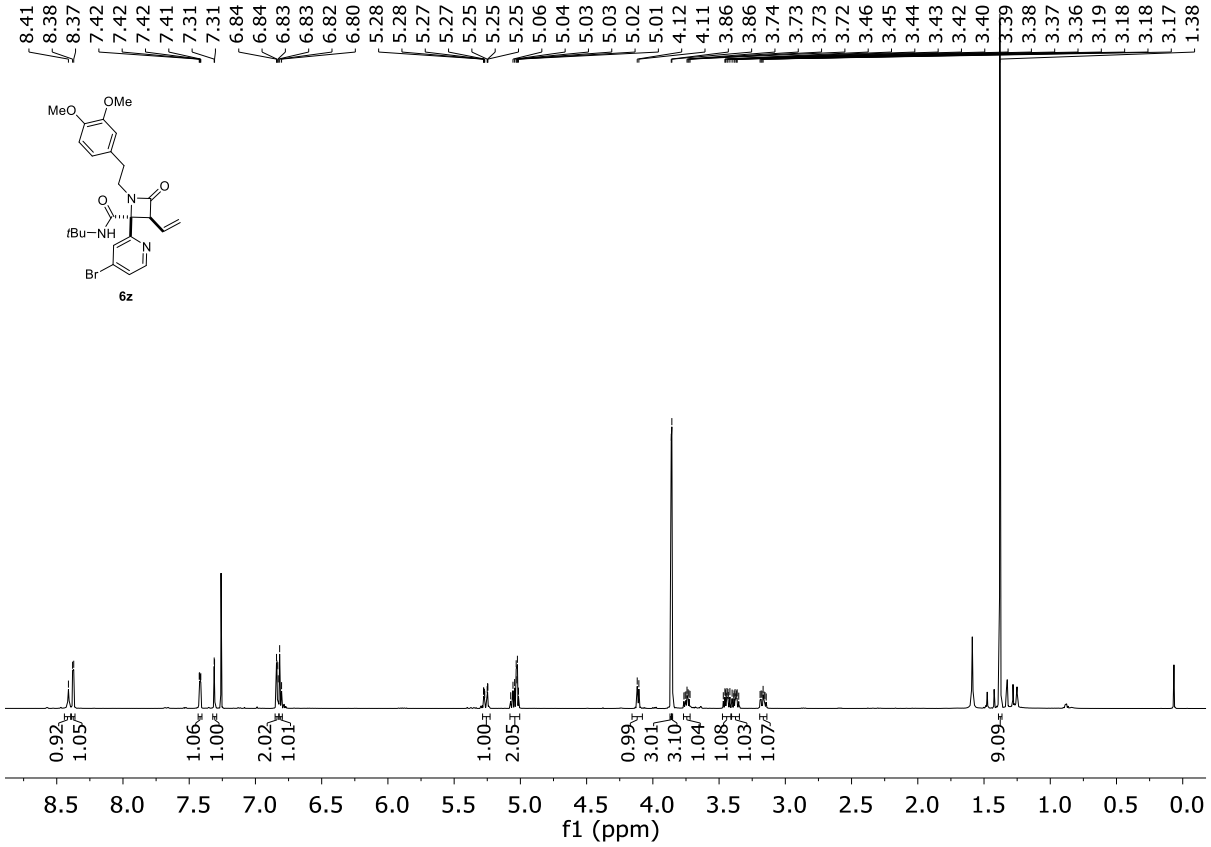
^{1}H NMR (*cis*-6y) 500 MHz, $CDCl_3$



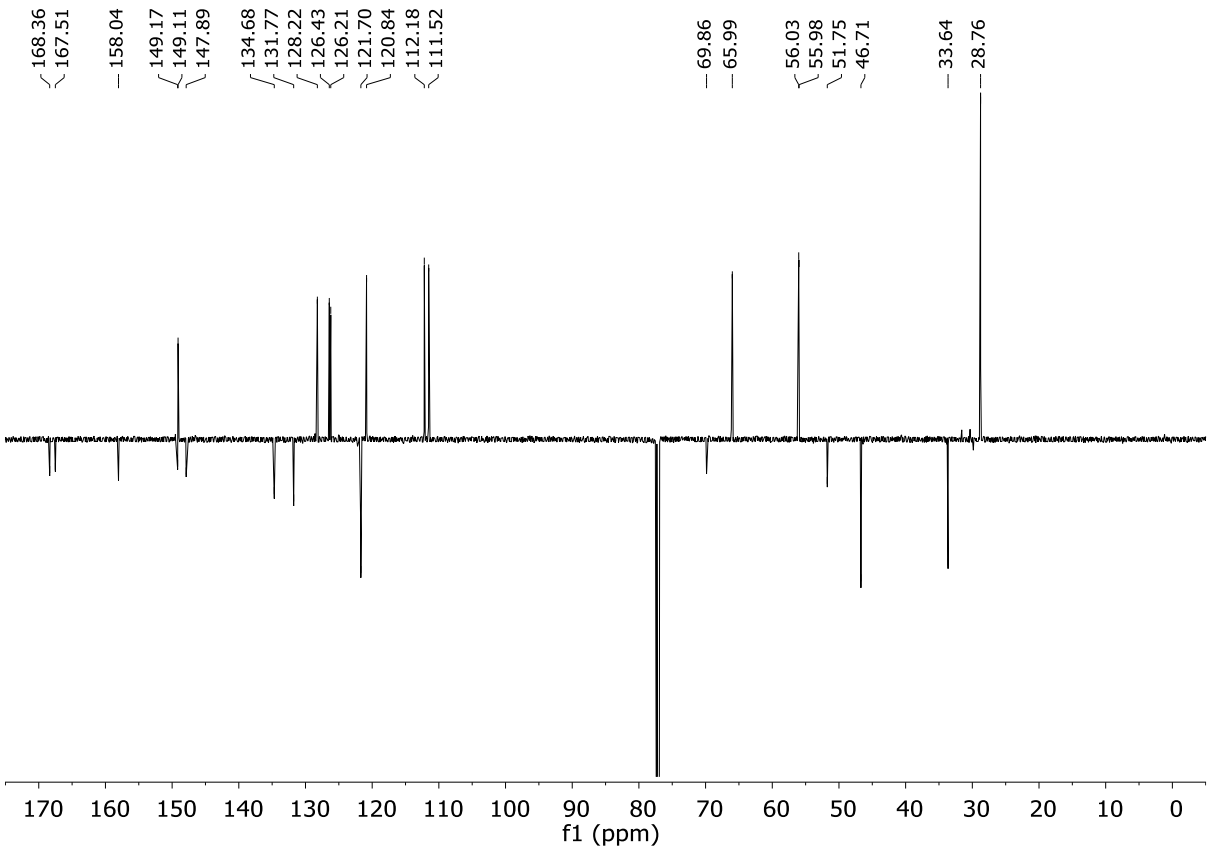
^{13}C NMR (*cis*-6y) 126 MHz, $CDCl_3$



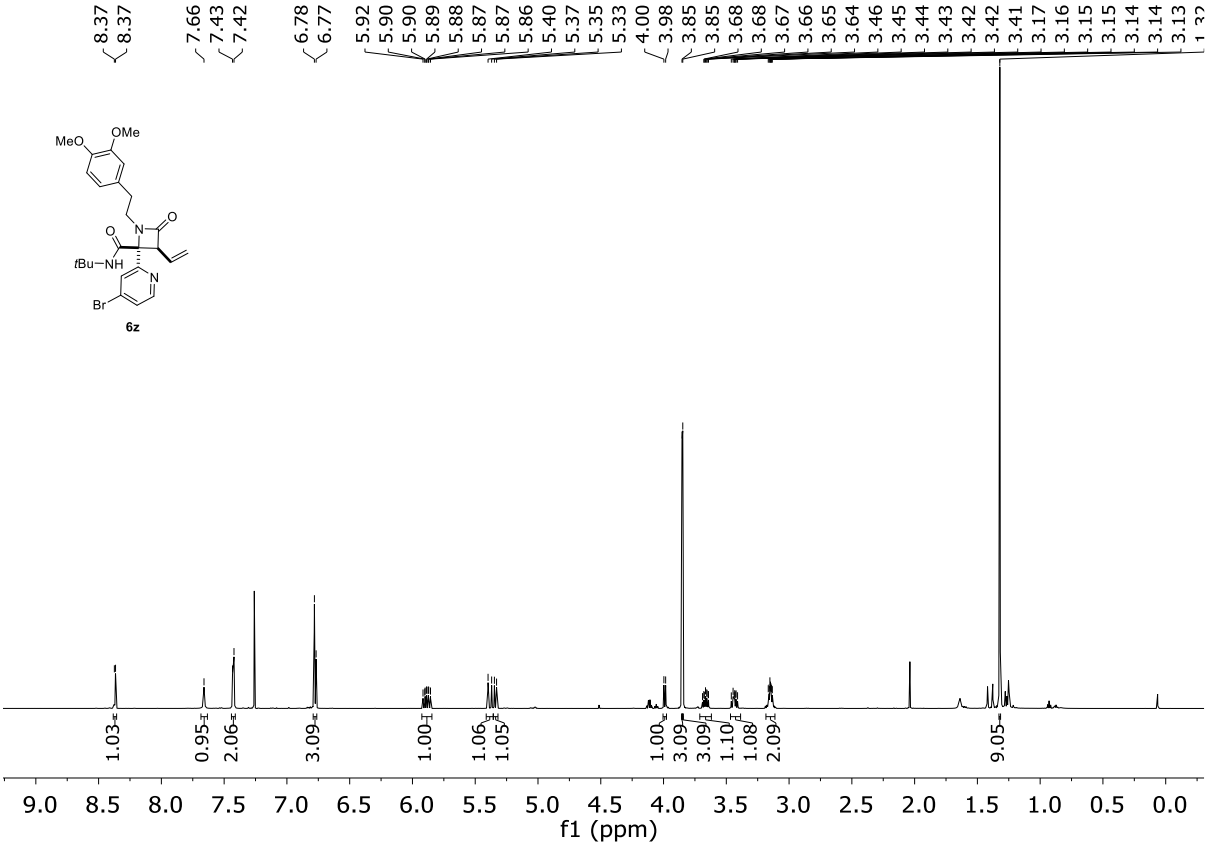
^{1}H NMR (*trans*-6z) 600 MHz, $CDCl_3$



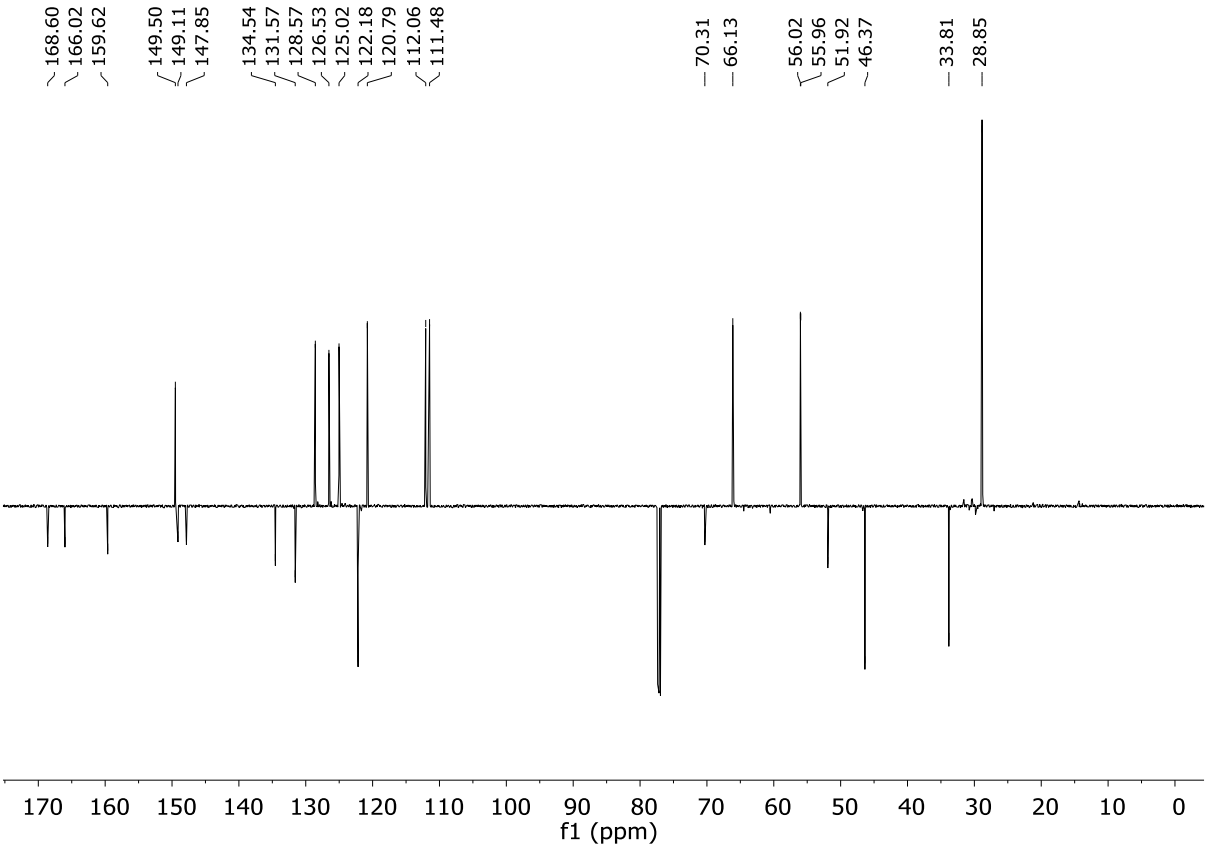
^{13}C NMR (*trans*-6z) 151 MHz, $CDCl_3$



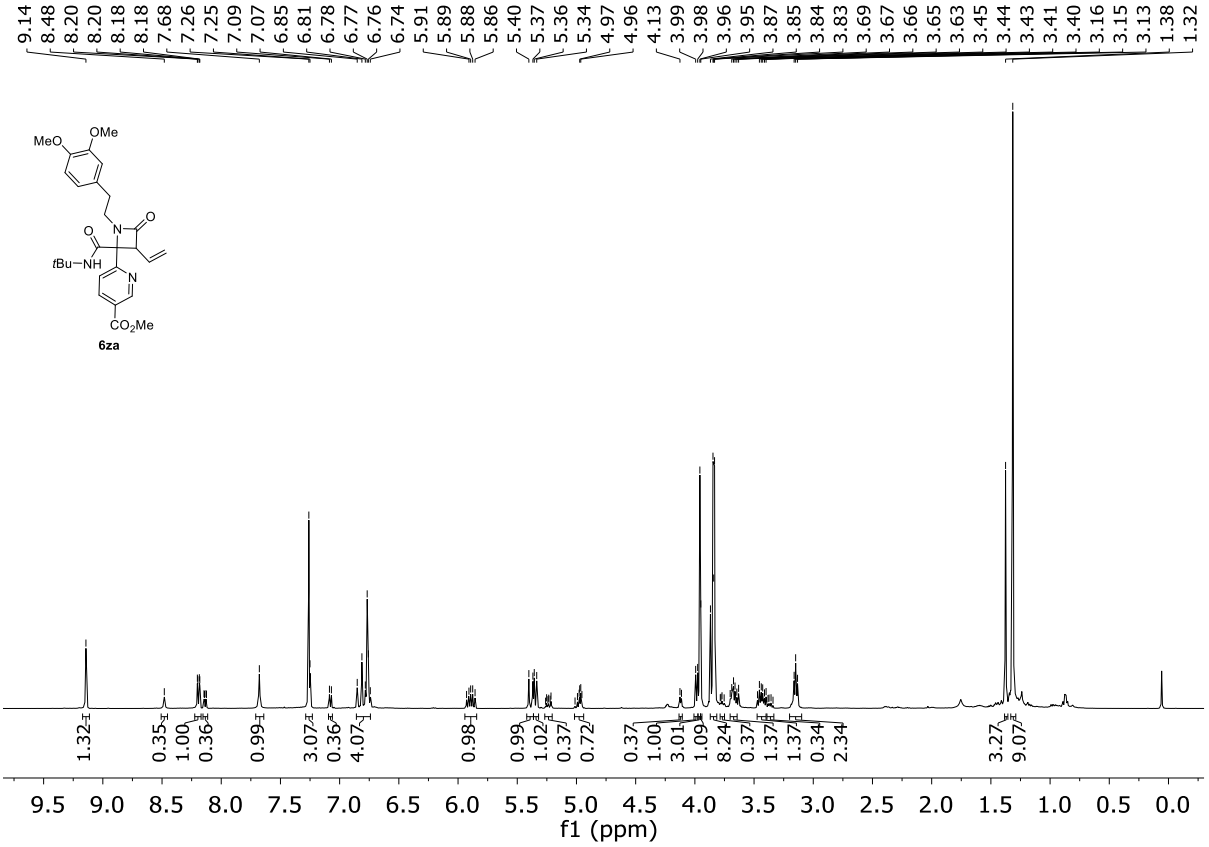
^{1}H NMR (*cis*-6z) 600 MHz, $CDCl_3$



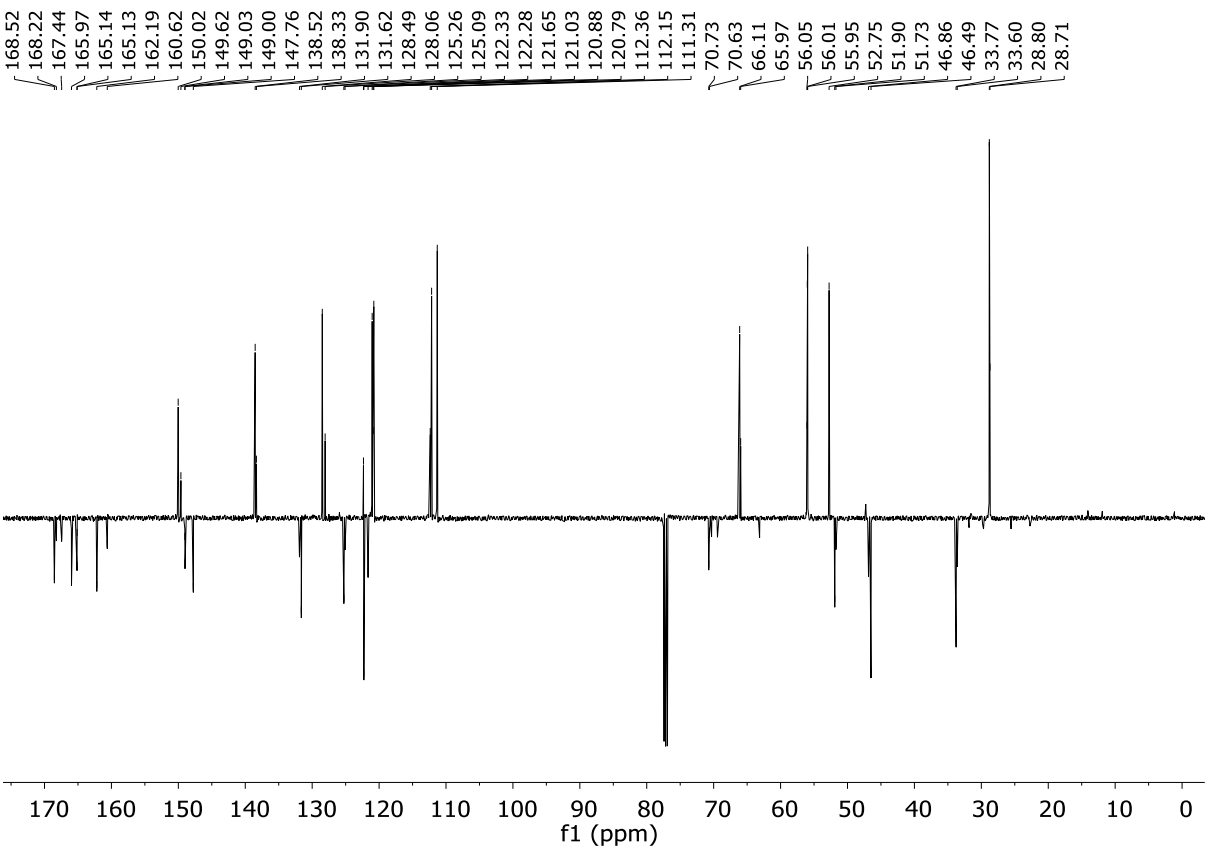
^{13}C NMR (*cis*-6z) 151 MHz, $CDCl_3$



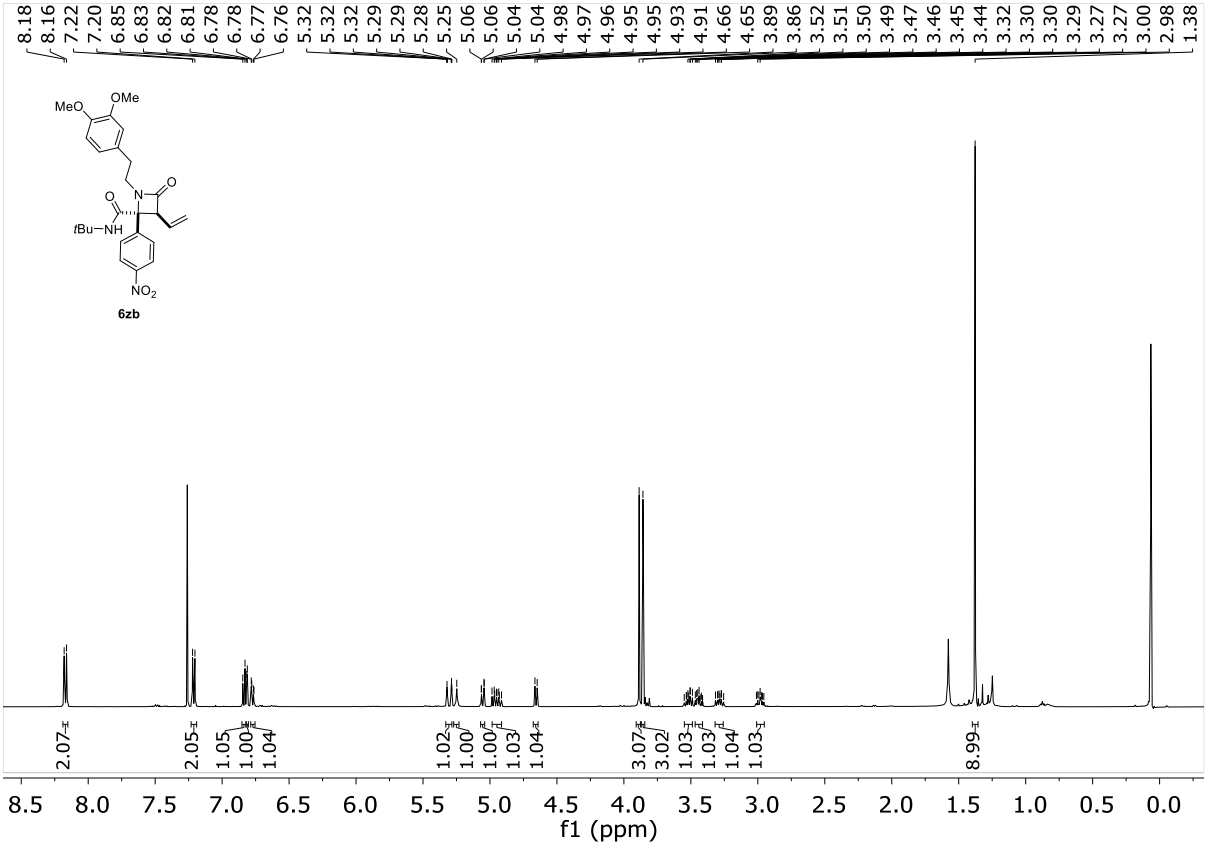
^{1}H NMR (*trans/cis*-6za) 500 MHz, $CDCl_3$



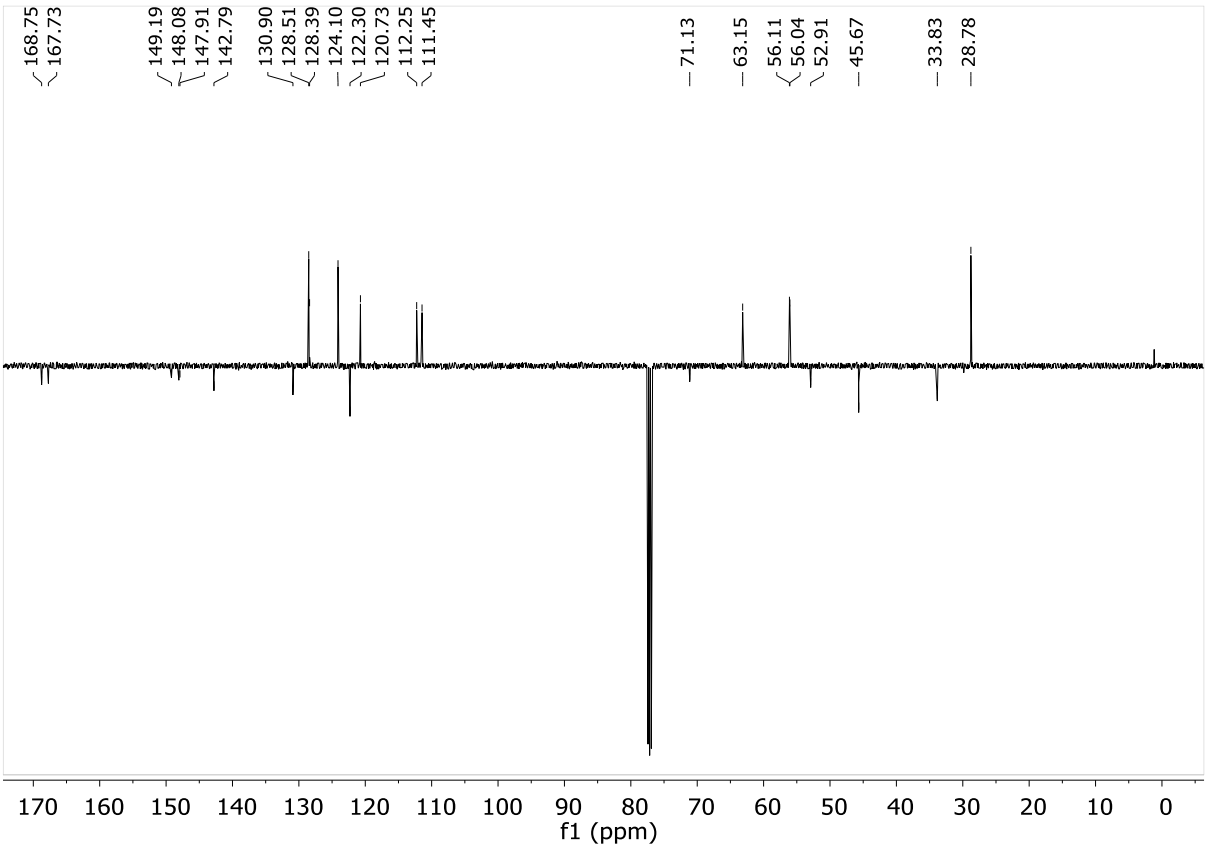
^{13}C NMR (*trans/cis*-6za) 151 MHz, $CDCl_3$



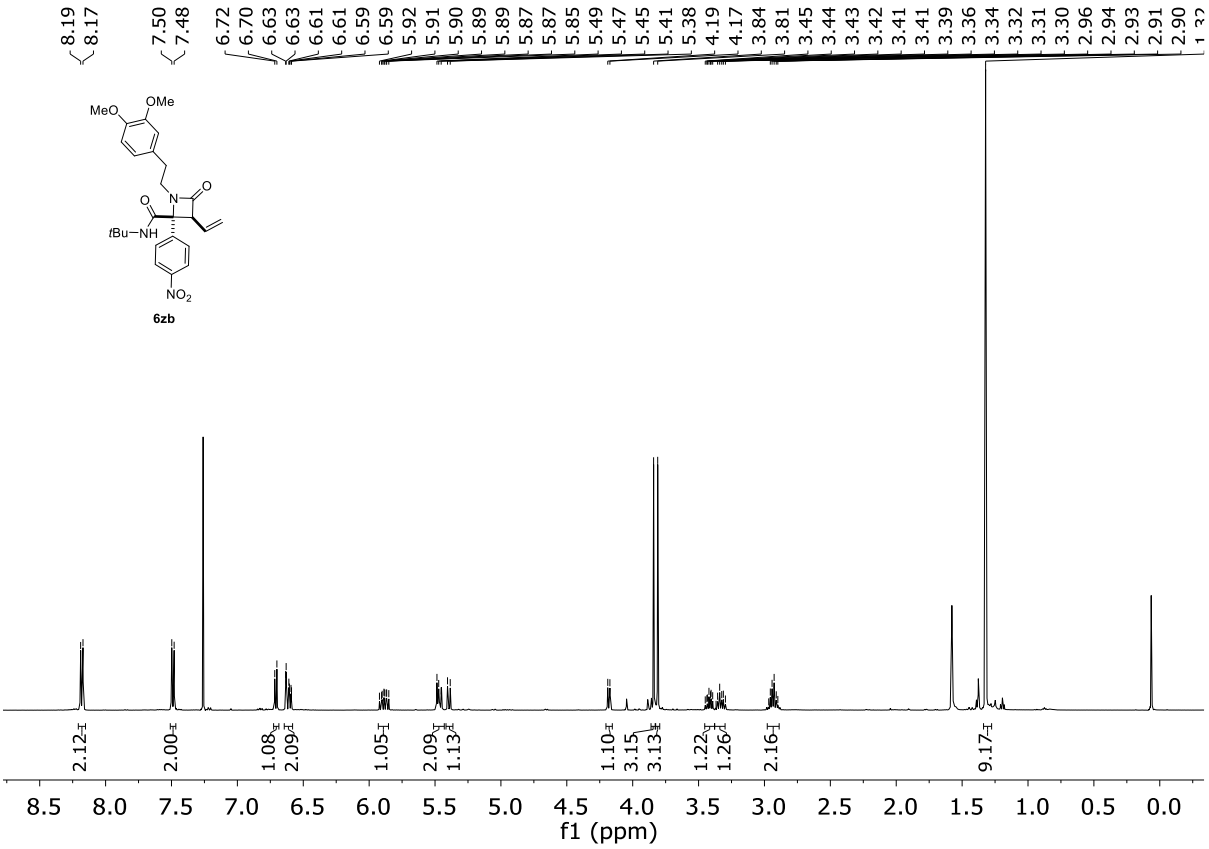
^{1}H NMR (*trans*-6zb) 500 MHz, $CDCl_3$



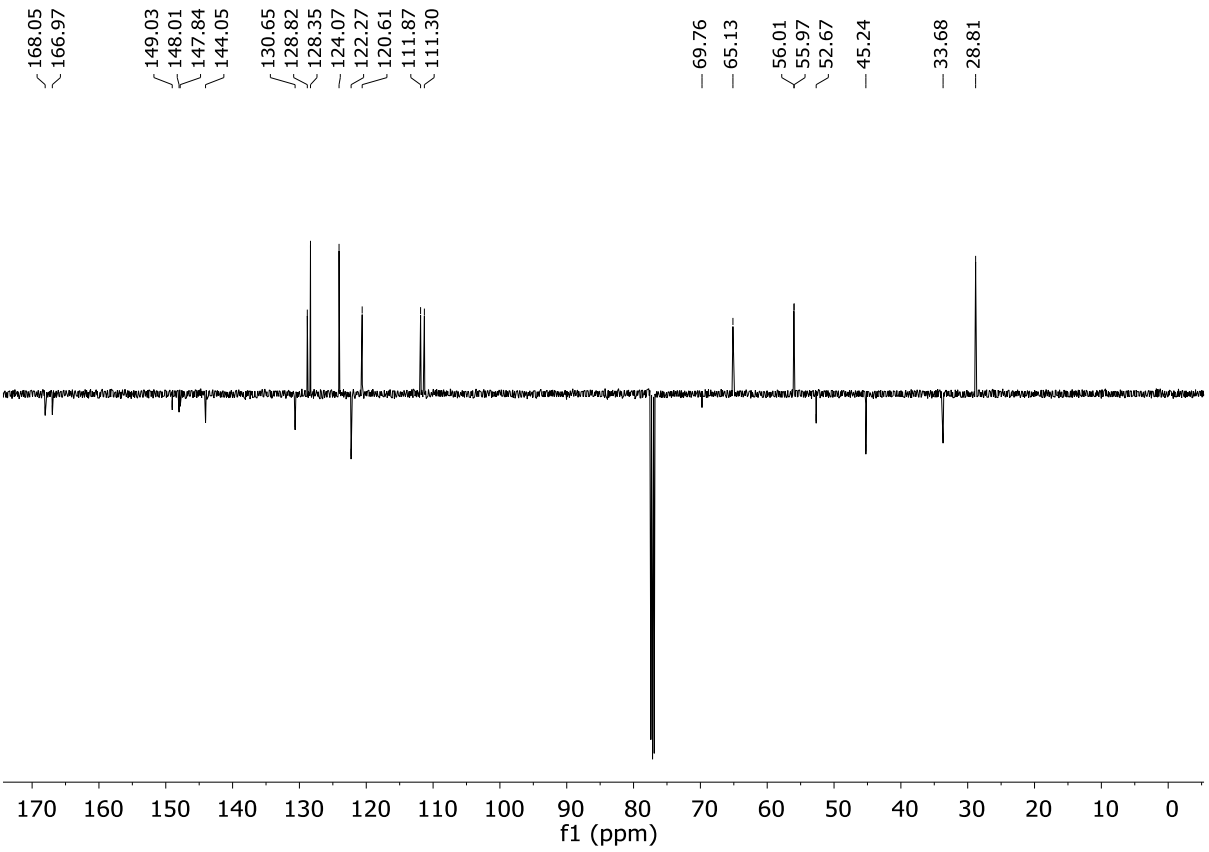
^{13}C NMR (*trans*-6zb) 126 MHz, $CDCl_3$



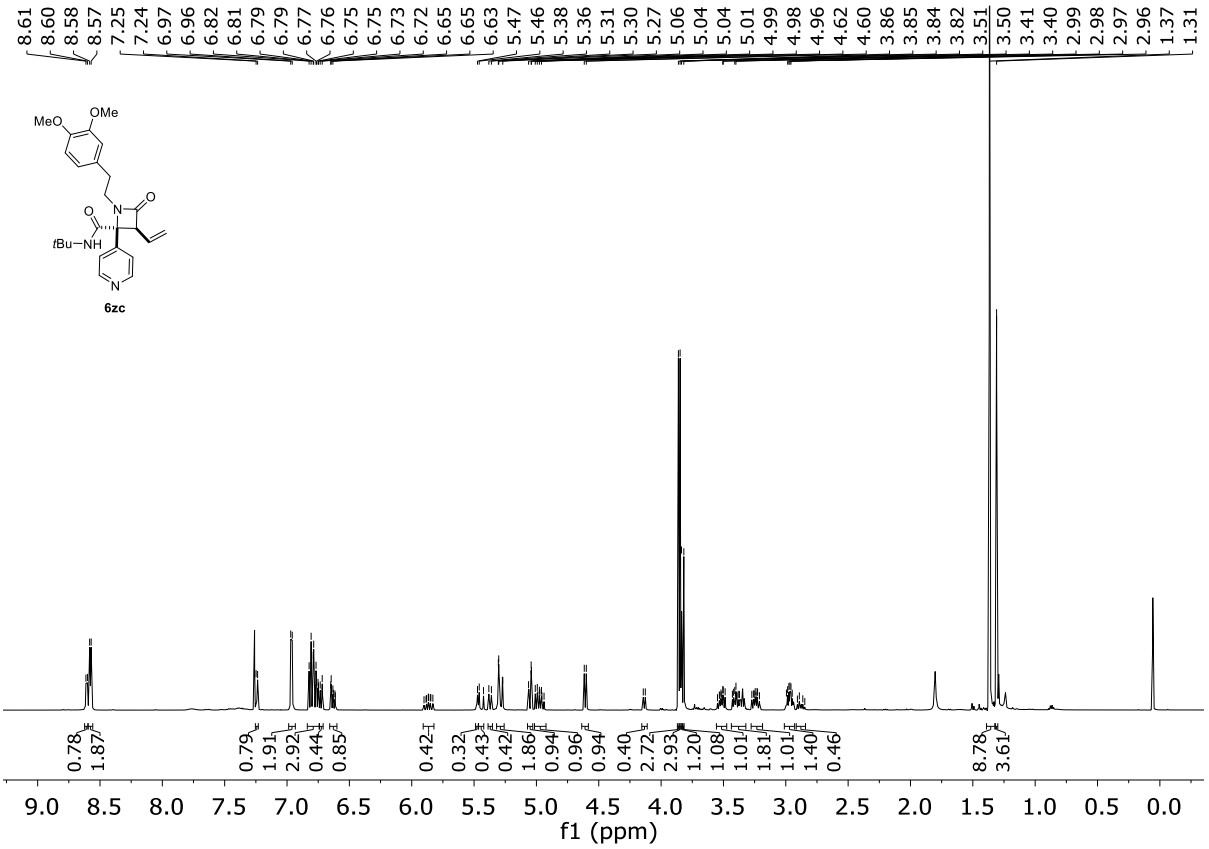
^{1}H NMR (*cis*-6zb) 500 MHz, $CDCl_3$



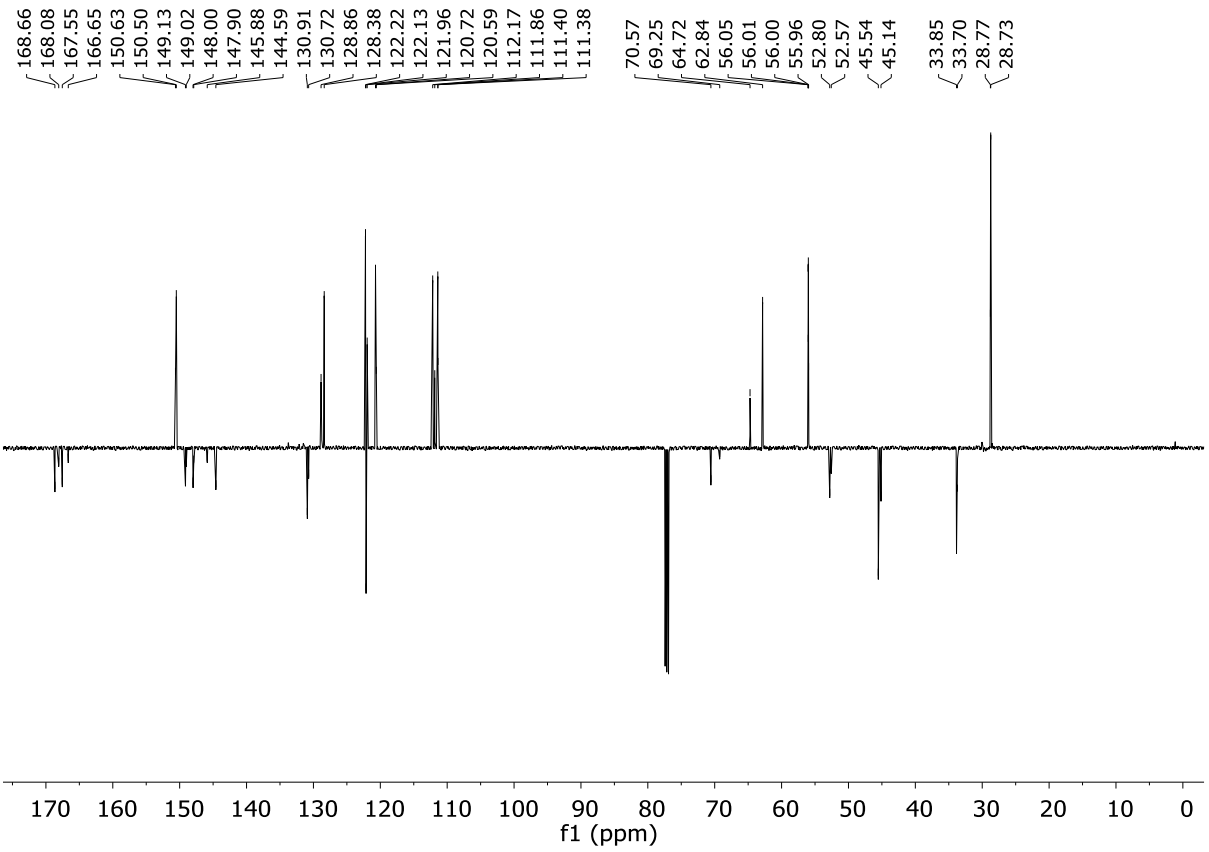
^{13}C NMR (*cis*-6zb) 126 MHz, $CDCl_3$



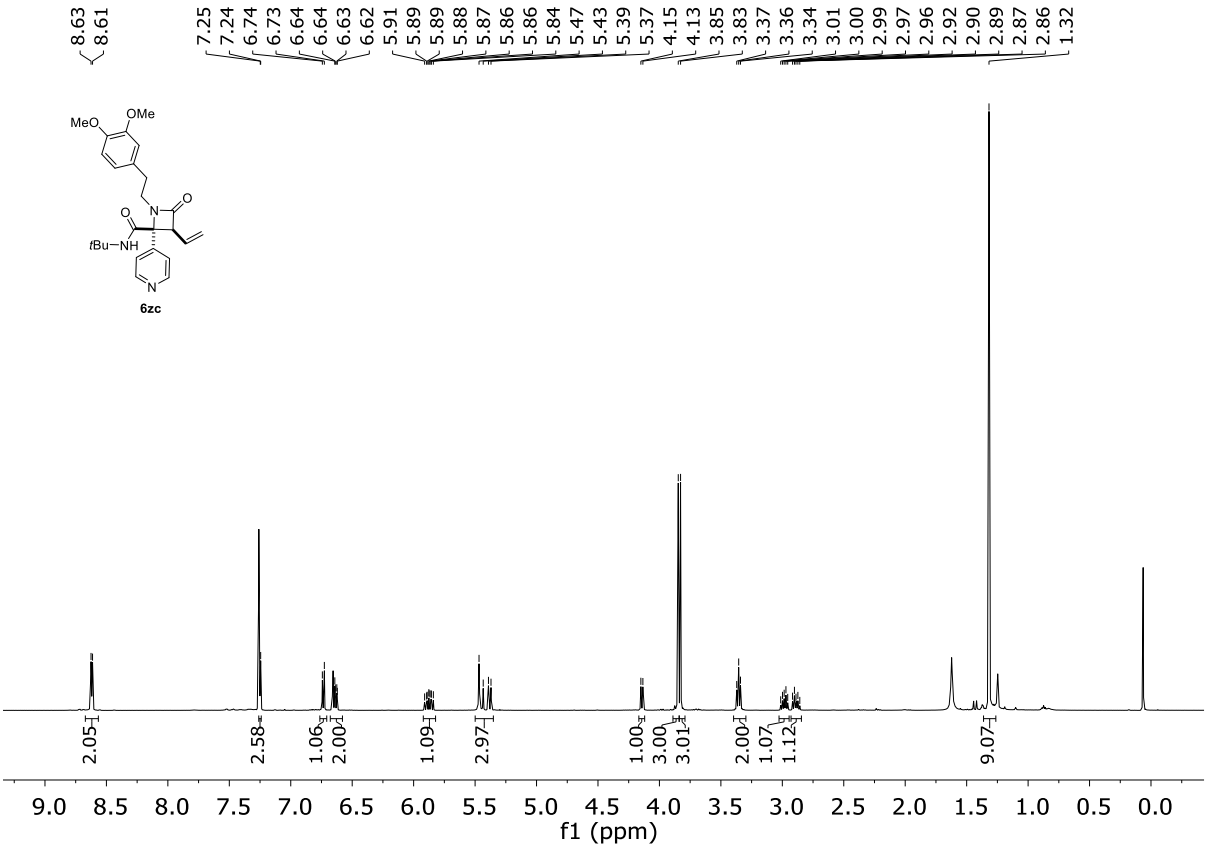
^{1}H NMR (*trans*-6zc) 500 MHz, $CDCl_3$



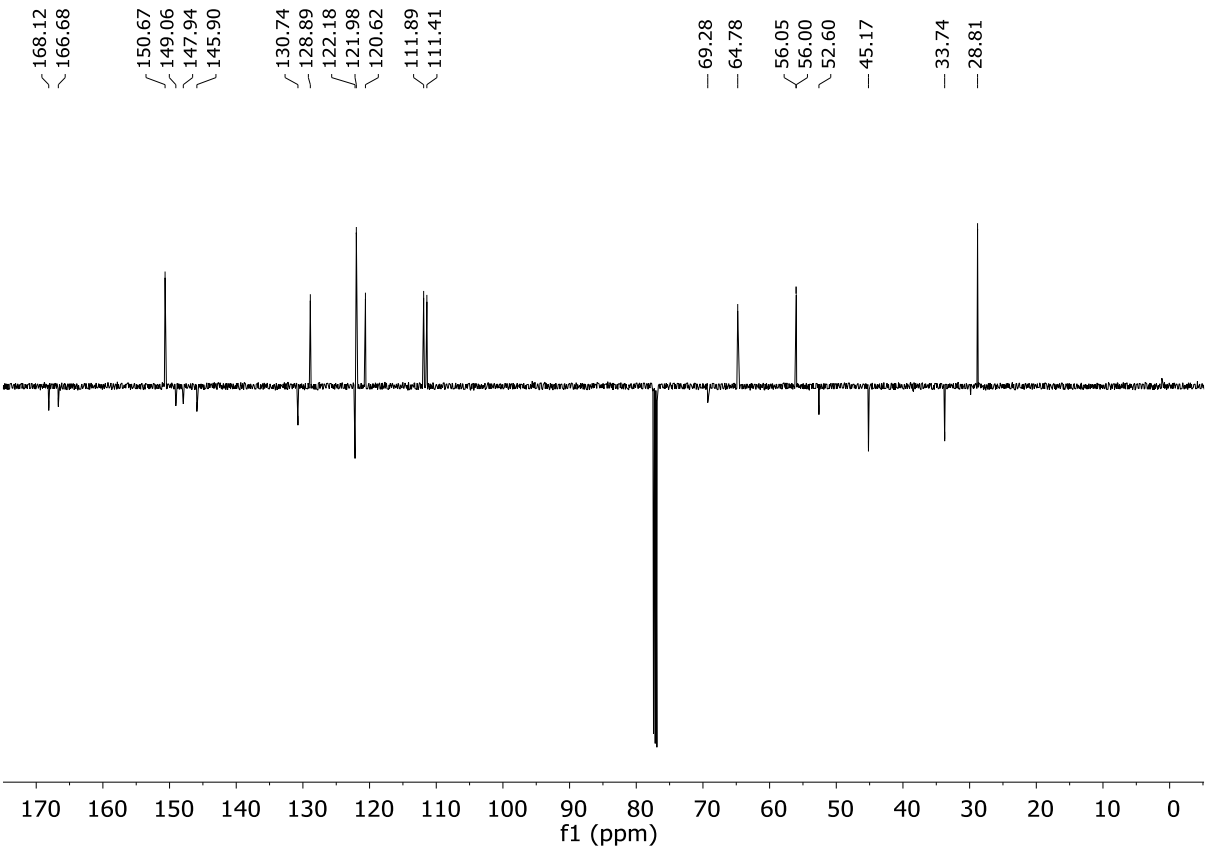
^{13}C NMR (*trans*-6zc) 126 MHz, $CDCl_3$



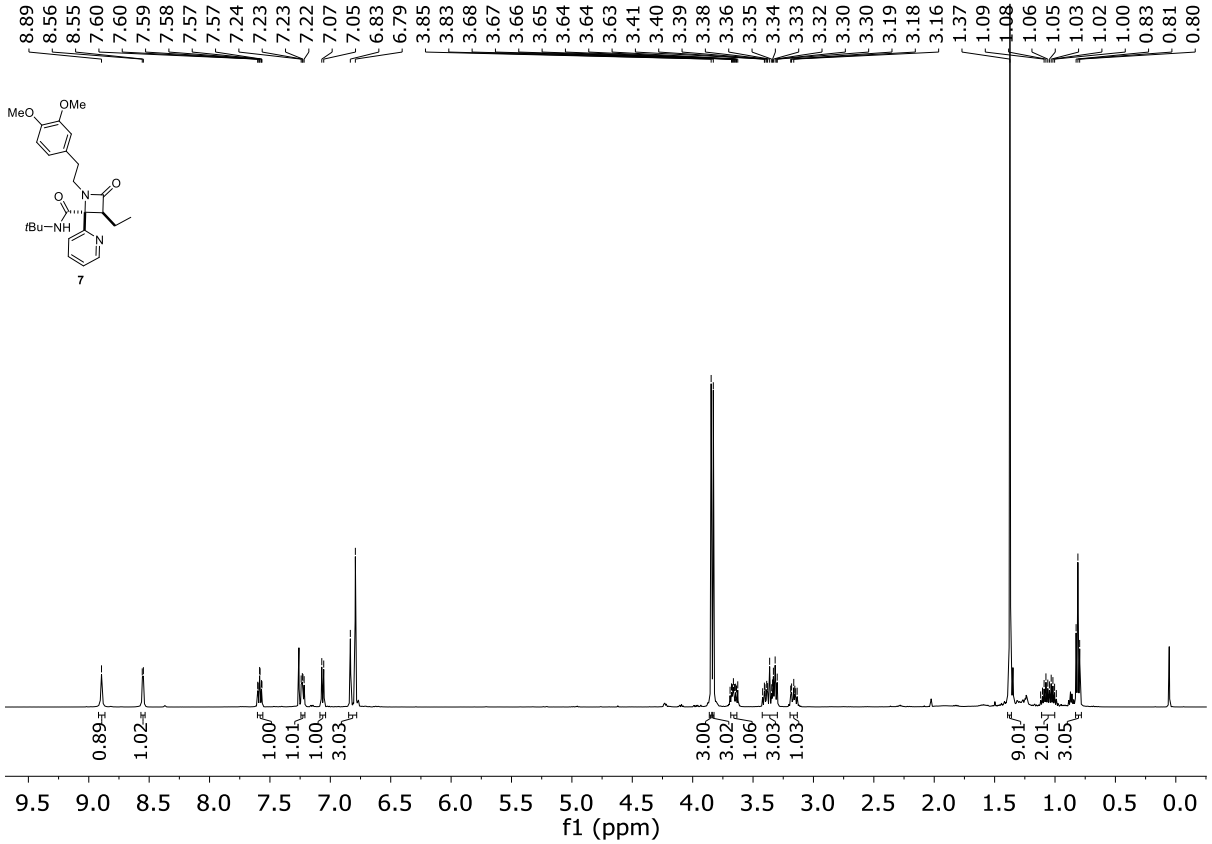
^{1}H NMR (*cis*-6zc) 500 MHz, $CDCl_3$



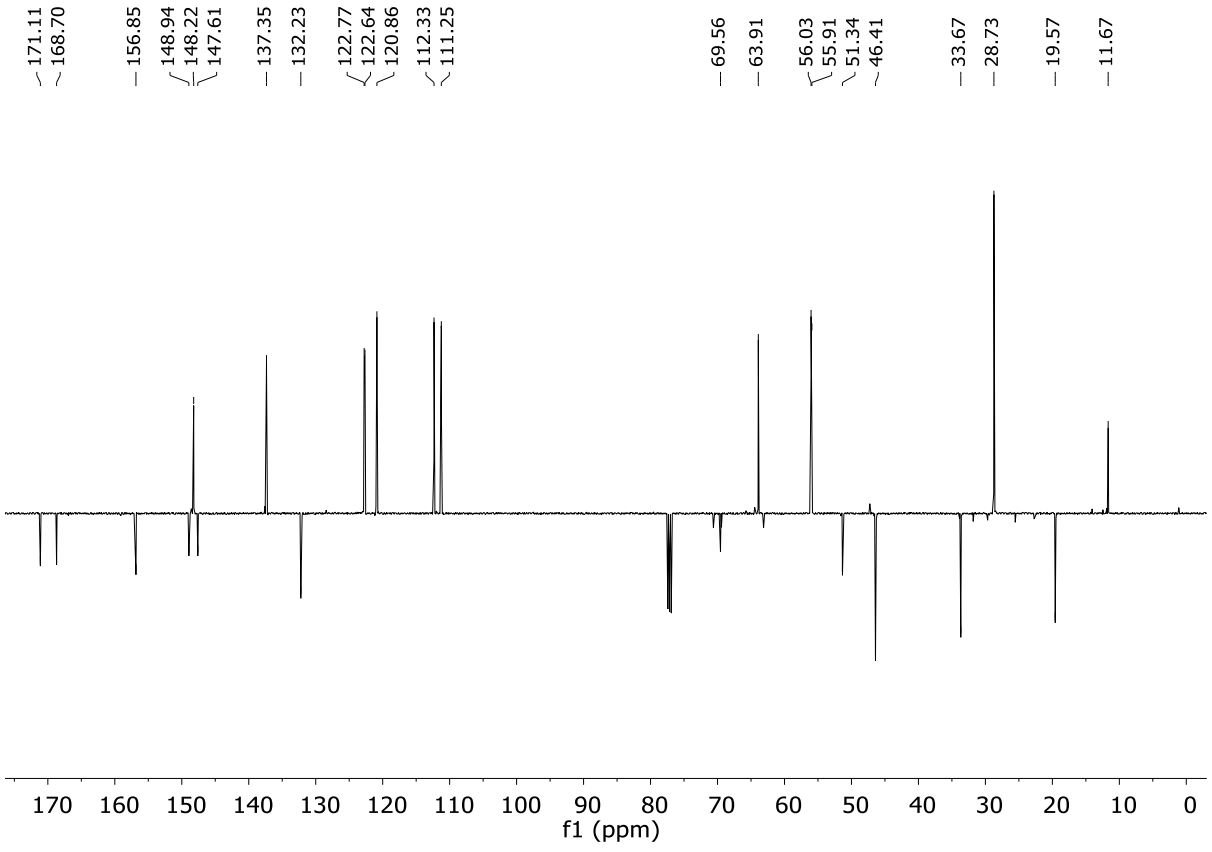
^{13}C NMR (*cis*-6zc) 126 MHz, $CDCl_3$



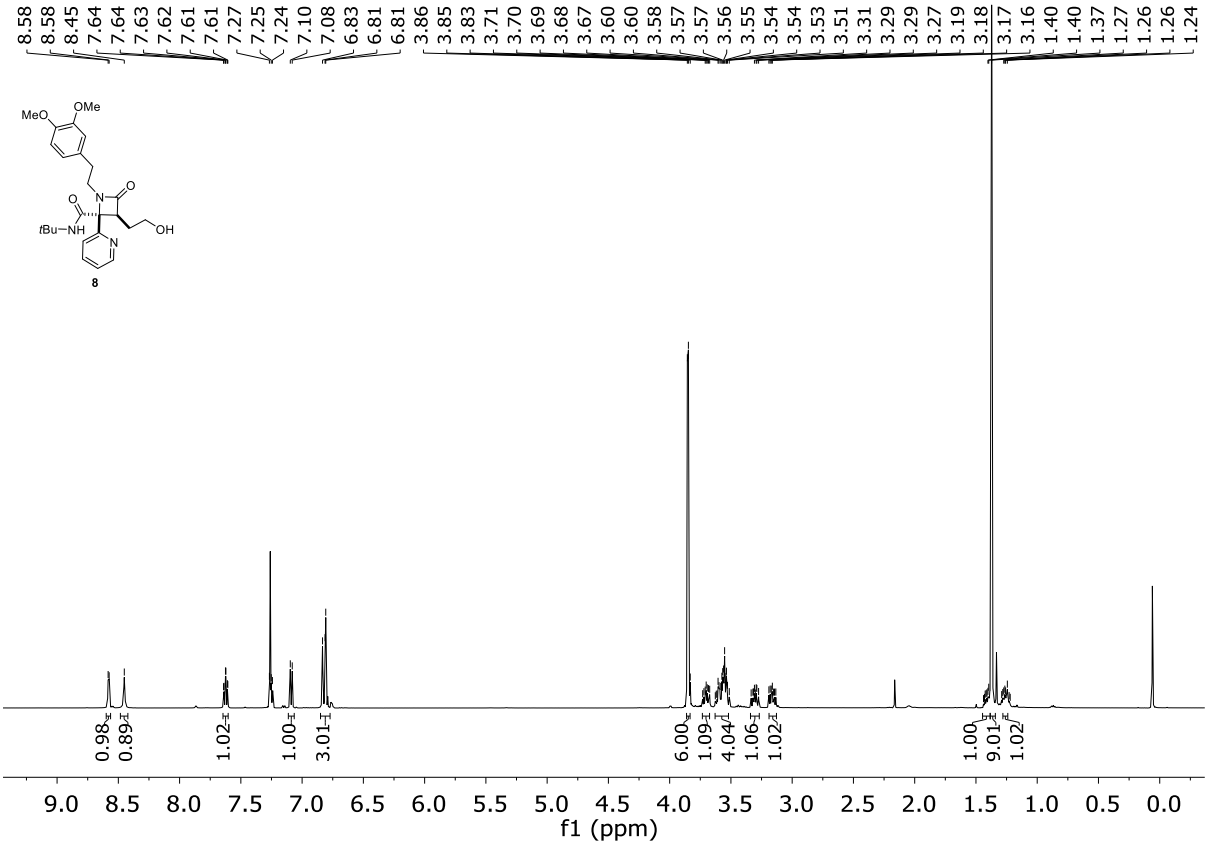
^{1}H NMR (7) 500 MHz, $CDCl_3$



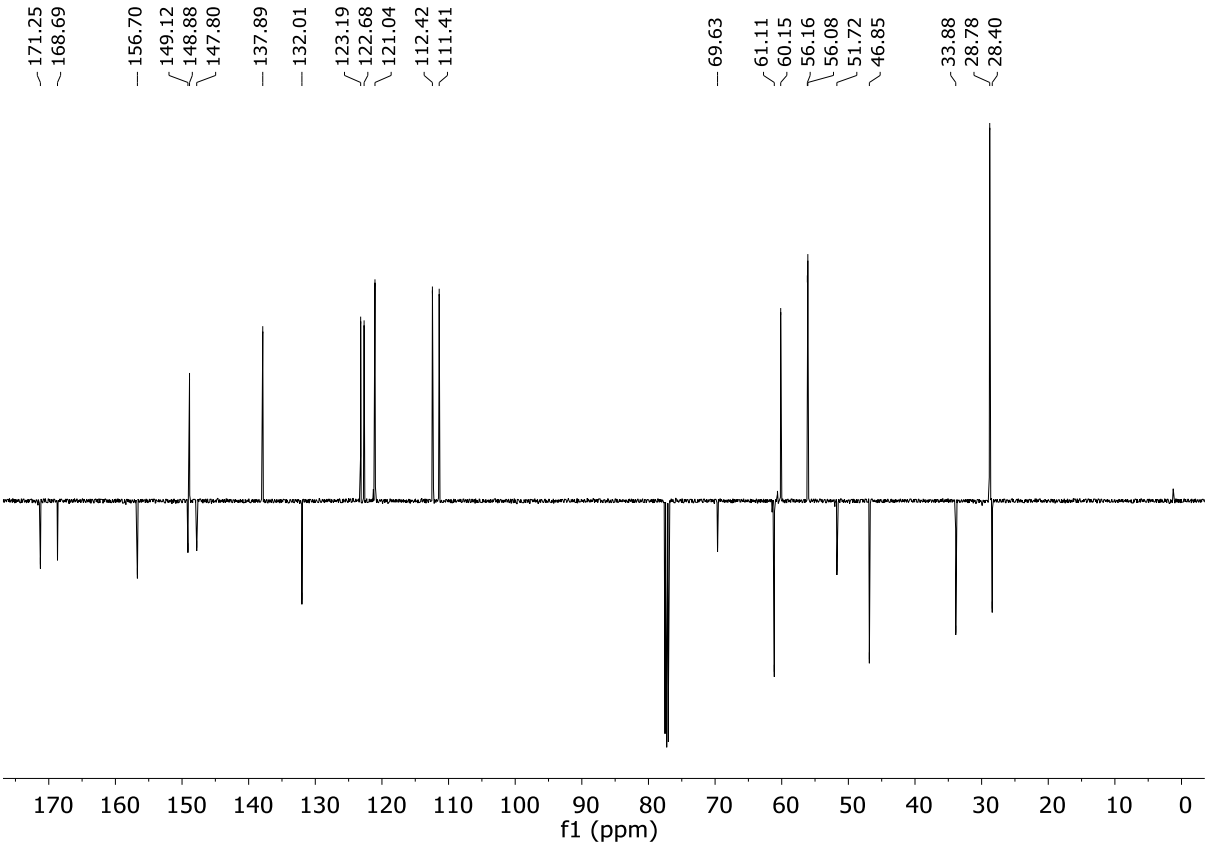
^{13}C NMR (7) 126 MHz, $CDCl_3$



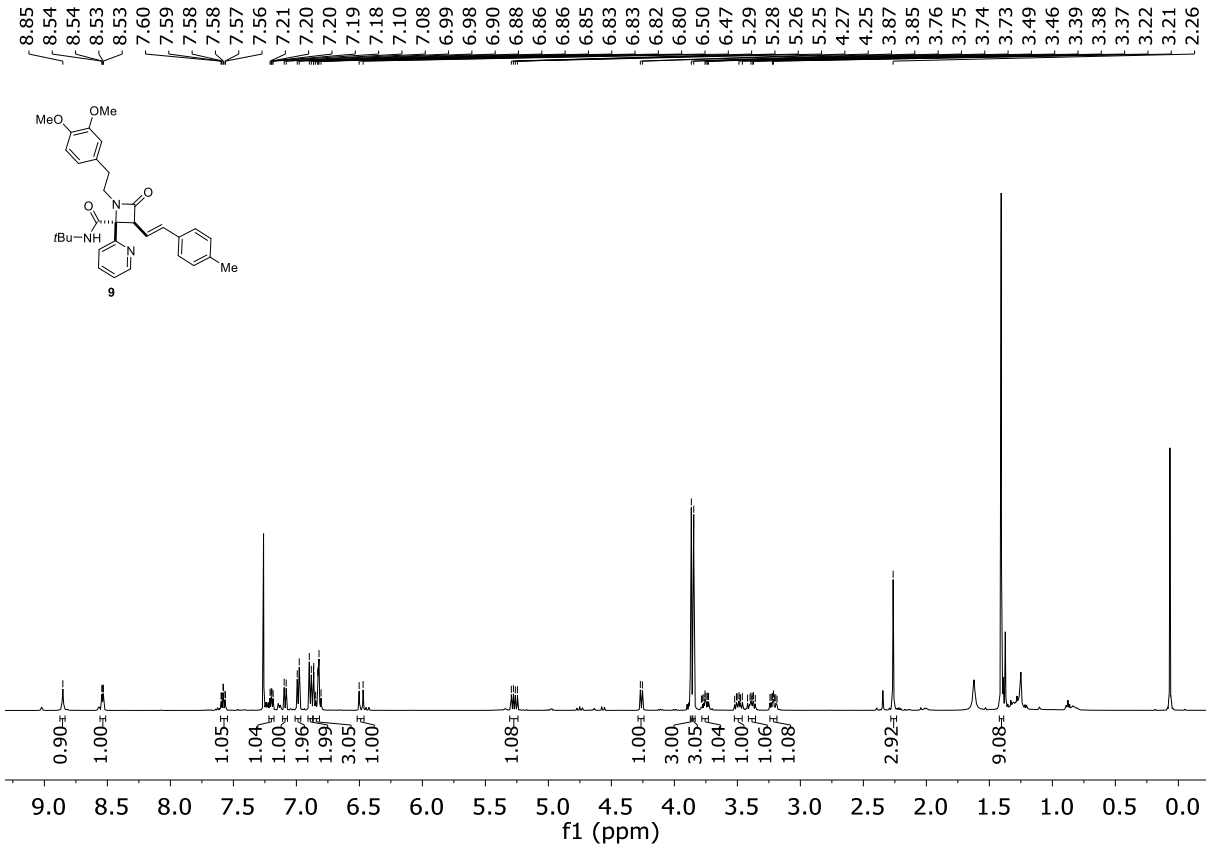
^{1}H NMR (8) 500 MHz, $CDCl_3$



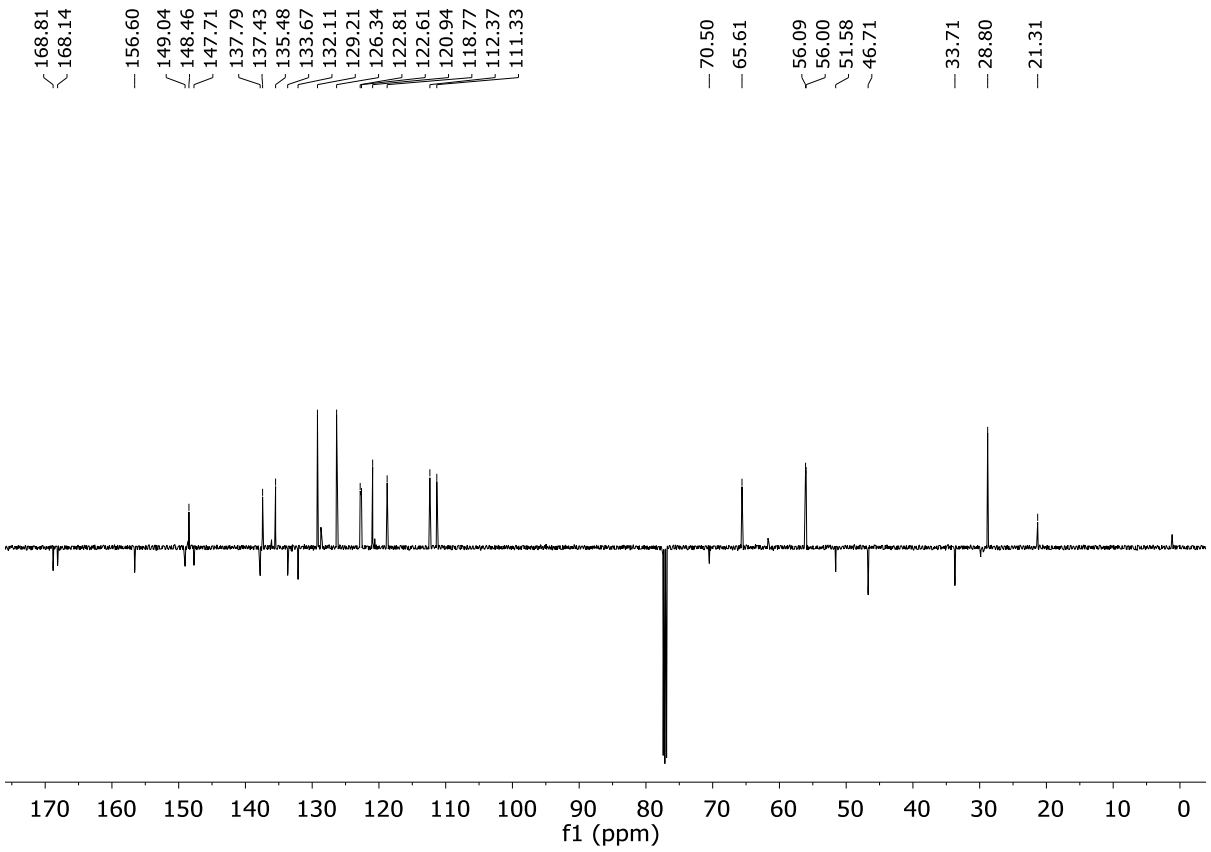
^{13}C NMR (8) 126 MHz, $CDCl_3$



^{1}H NMR (9) 500 MHz, $CDCl_3$



^{13}C NMR (9) 126 MHz, $CDCl_3$



References

(1) (a) Becke, A. D. Density functional calculations of molecular bond energies, *J. Chem. Phys.* **1986**, *84*, 4524; (b) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* **1988**, *38*, 3098.

(2) van Lenthe E.; Baerends, E. J. Optimized Slater‐type basis sets for the elements 1–118, *J. Comput. Chem.* **2003**, *24*, 1142.

(3) (a) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders J. G.; Ziegler, T. Chemistry with ADF, *J. Comput. Chem.* **2001**, *22*, 931; (b) Fonseca Guerra, C.; Snijders, J. G.; te Velde G.; Baerends, E. J. owards an order-N DFT method, *Theor. Chem. Acc.* **1998**, *99*, 391; (c) ADF2017, SCM Theoretical Chemistry, Vrije Universiteit: Amsterdam (The Netherlands), 2017. http:// www.scm.com.

(4) (a) van Lenthe, E.; Baerends E. J.; Snijders, J. G. Relativistic regular two‐component Hamiltonians, *J. Chem. Phys.* **1993**, *99*, 4597; (b) van Lenthe, E.; Baerends E. J.; Snijders, J. G. Relativistic total energy using regular approximations *J. Chem. Phys.* **1994**, *101*, 9783.

(5) (a) Klamt A.; Schüürmann, G. COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient *J. Chem. Soc. Perkin Trans. 2* **1993**, *2*, 799; (b) Klamt, A. Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena, *J. Phys. Chem.* **1995**, *99*, 2224; (c) Klamt A. Jones, V. Treatment of the outlying charge in continuum solvation models, *J. Chem. Phys.* **1996**, *105*, 9972.

(6) (a) de Jong, G. T.; Solà, M.; Visscher, L.; Bickelhaupt, F. M. Ab initio benchmark study for the oxidative addition of CH4 to Pd: Importance of basis-set flexibility and polarization, *J. Chem. Phys.* **2004**, *121*, 9982; (b) de Jong, G. T.; Bickelhaupt, F. M. Oxidative Addition of the Fluoromethane C-F Bond to Pd. An ab Initio Benchmark and DFT Validation Study, *J. Phys. Chem. A.* **2005**, *109*, 9685; (c) de Jong, G. T.; Bickelhaupt, F. M. Oxidative Addition of the Chloromethane C-Cl Bond to Pd, an ab Initio Benchmark and DFT Validation Study, *J. Chem. Theory Comput.* **2006**, *2*, 322.

(7) Legault, C. Y. CYLview (Unversité de Sherbrooke: Sherbrooke, QC, Canada, 1.0b, **2009**) http://www.cylview.org.

(8) (a) Bickelhaupt, F. M.; Houk, K. N., Analyzing Reaction Rates with the Distortion/Interaction‐Activation Strain Model, *Angew. Chem. Int. Ed.* **2017**, *56*, 10070; (b) Wolters, L. P.; Bickelhaupt, F. M. The Activation Strain Model and Molecular Orbital Theory, *WIRES Comput. Mol. Sci.* **2015**, *5*, 324; (c) Fernández, I.; Bickelhaupt, F. M. The Activation Strain Model and Molecular Orbital Theory: Understanding and Designing Chemical Reactions, *Chem. Soc. Rev.* **2014**, *43*, 4953; (d) van Zeist, W.-J.; Bickelhaupt, F. M., The activation strain model of chemical reactivity, *Org. Biomol. Chem.* **2010**, *8*, 3118.

(9) Sun, X.; Soini, T. M.; Poater, J.; Hamlin, T. A.; Bickelhaupt, F. M. PyFrag 2019—Automating the exploration and analysis of reaction mechanisms, *J. Comput. Chem*. **2019**, *40*, 2227.