# The Effect of Additives on the Zinc Carbenoid-Mediated Cyclopropanation of a Dihydropyrrole

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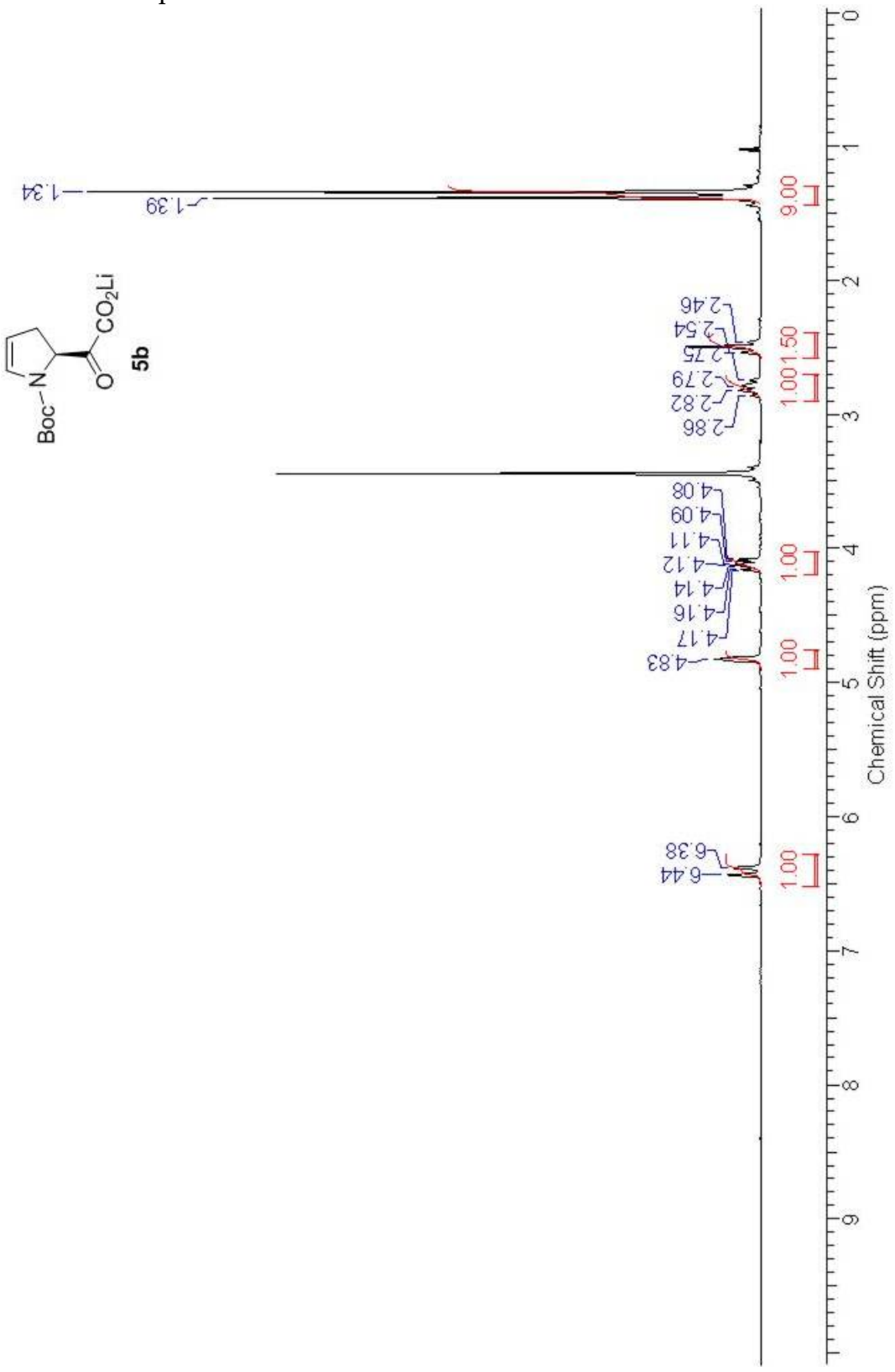
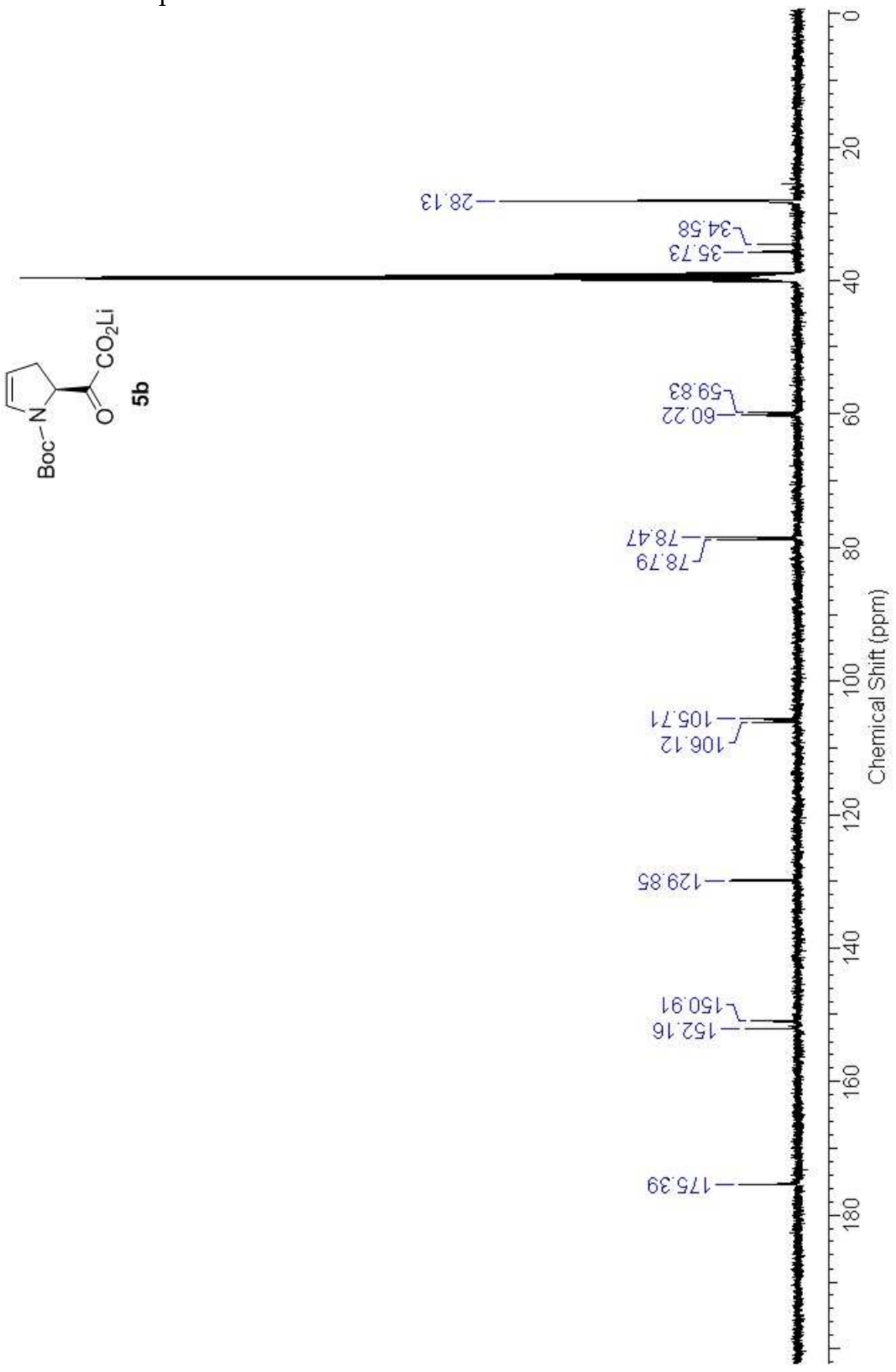
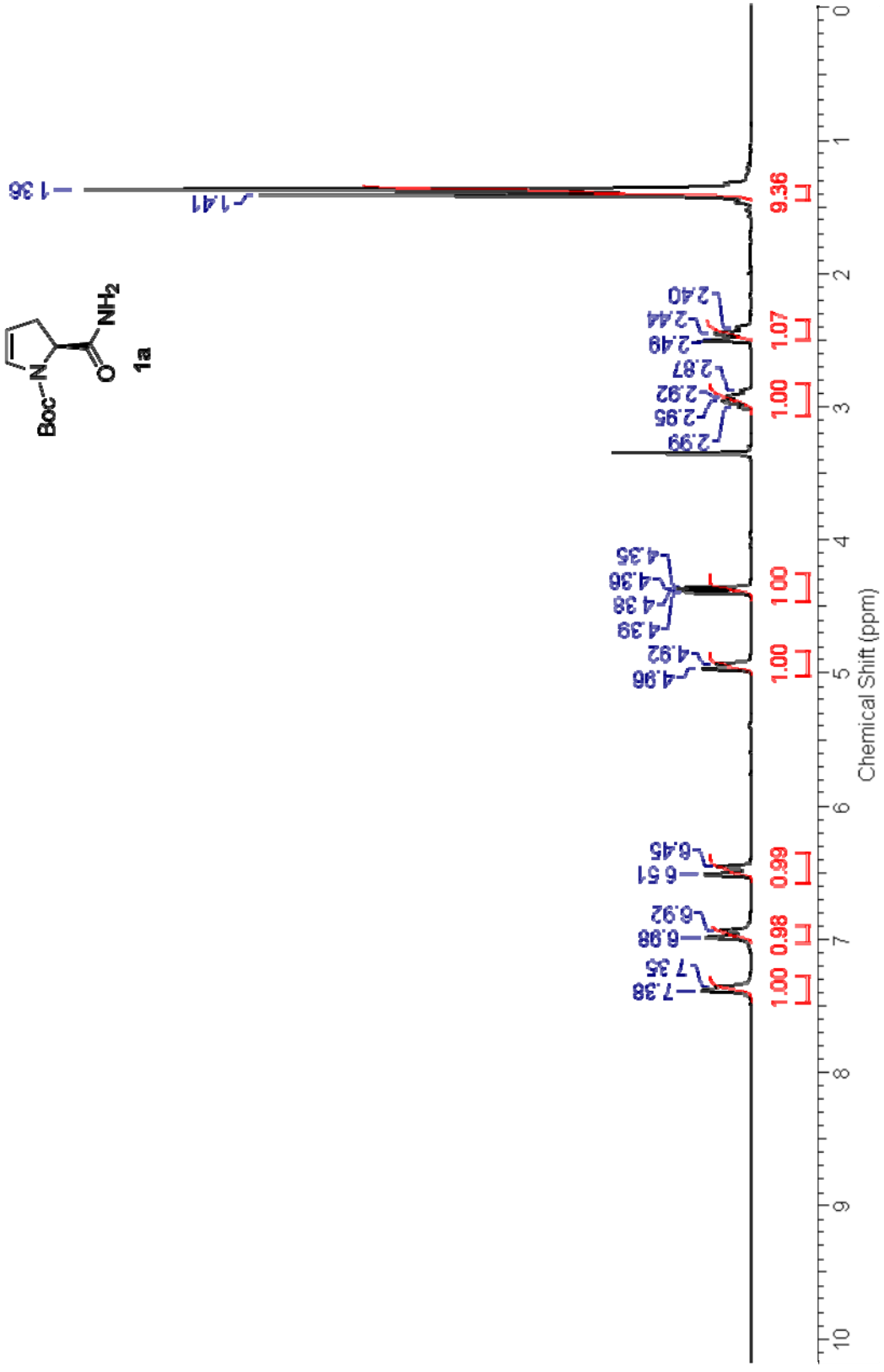


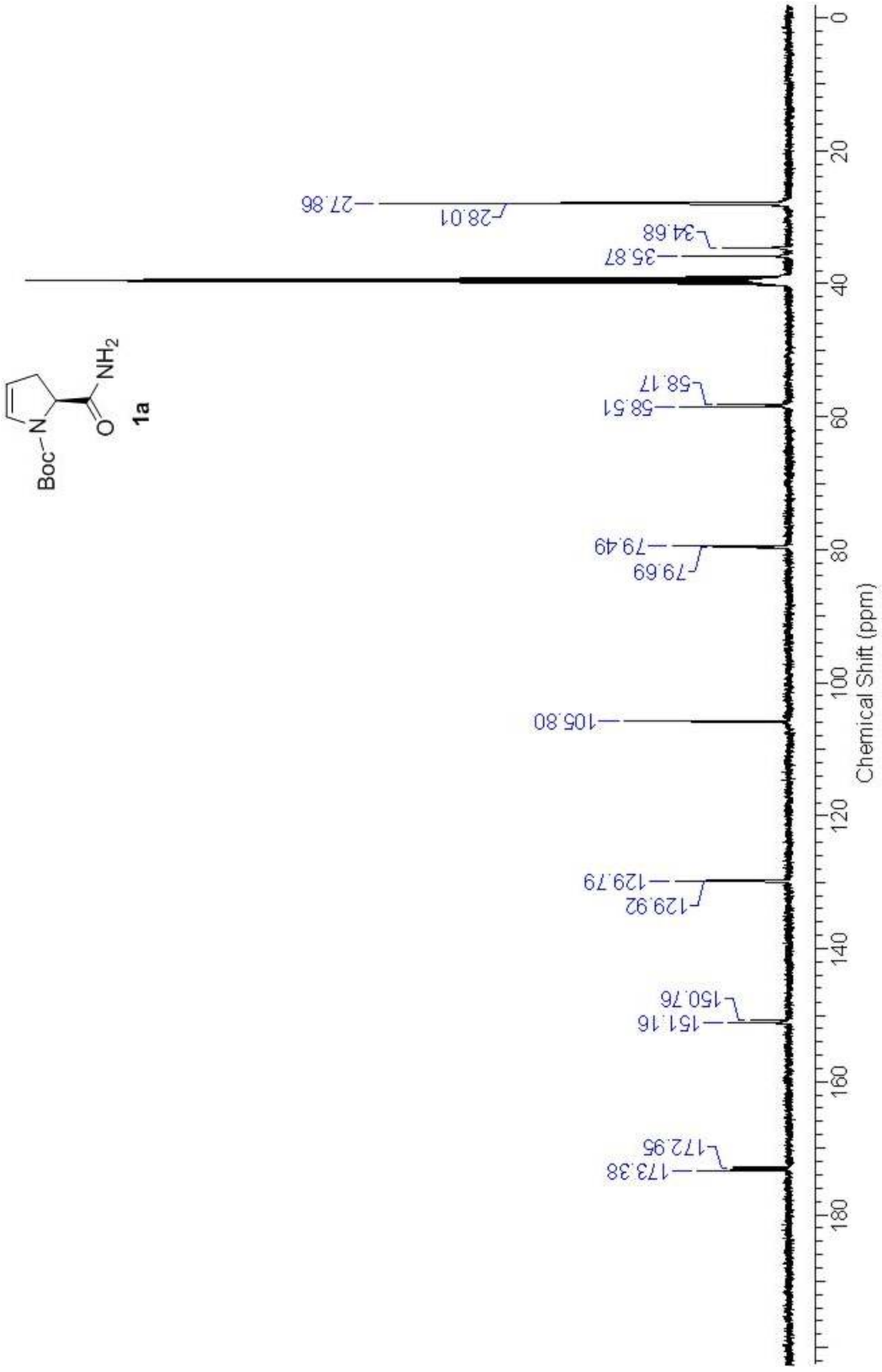
B. $^{13}C$ NMR Spectra of **5b**



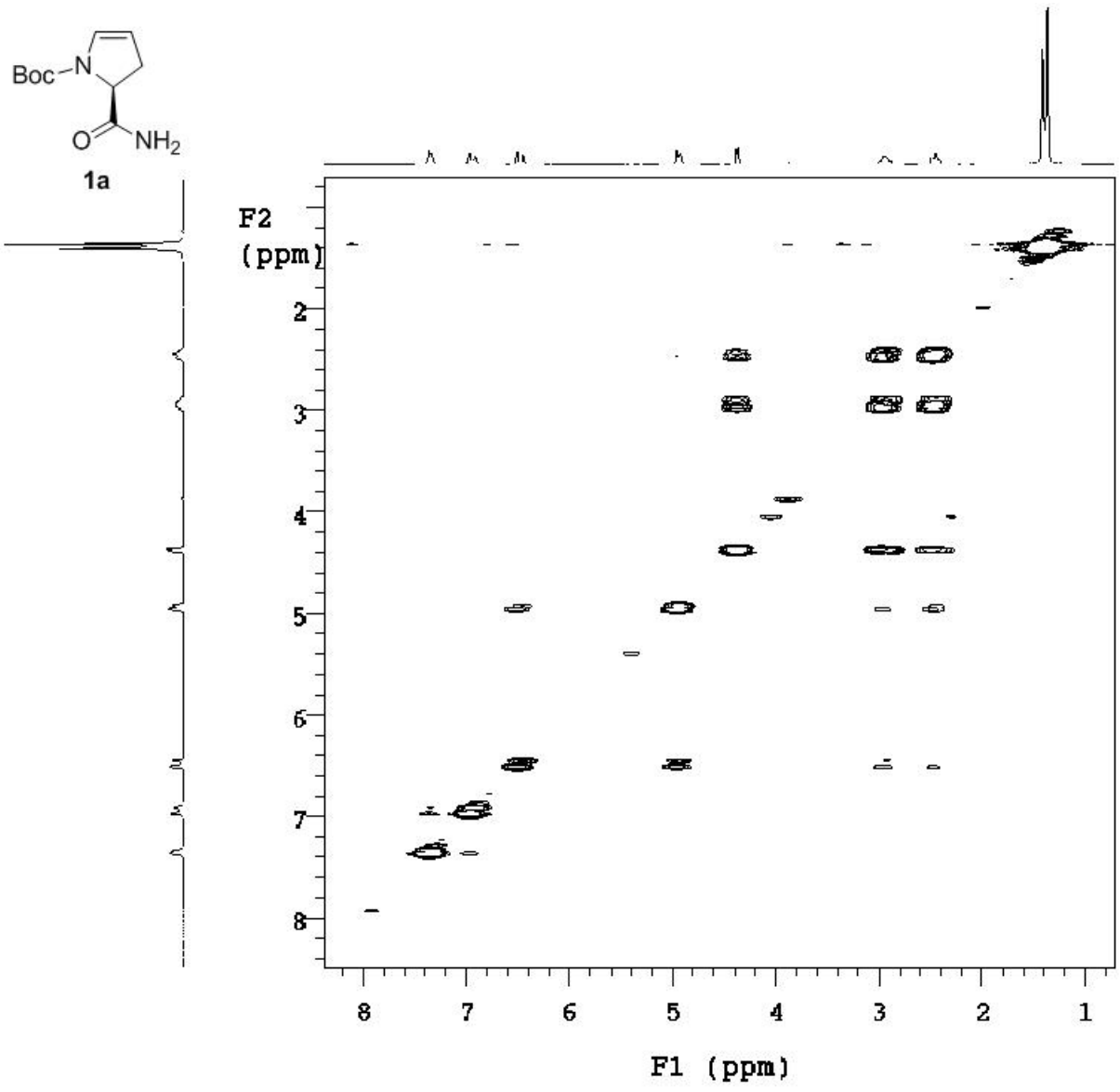
C. $^{1}$H NMR Spectra of **1a**



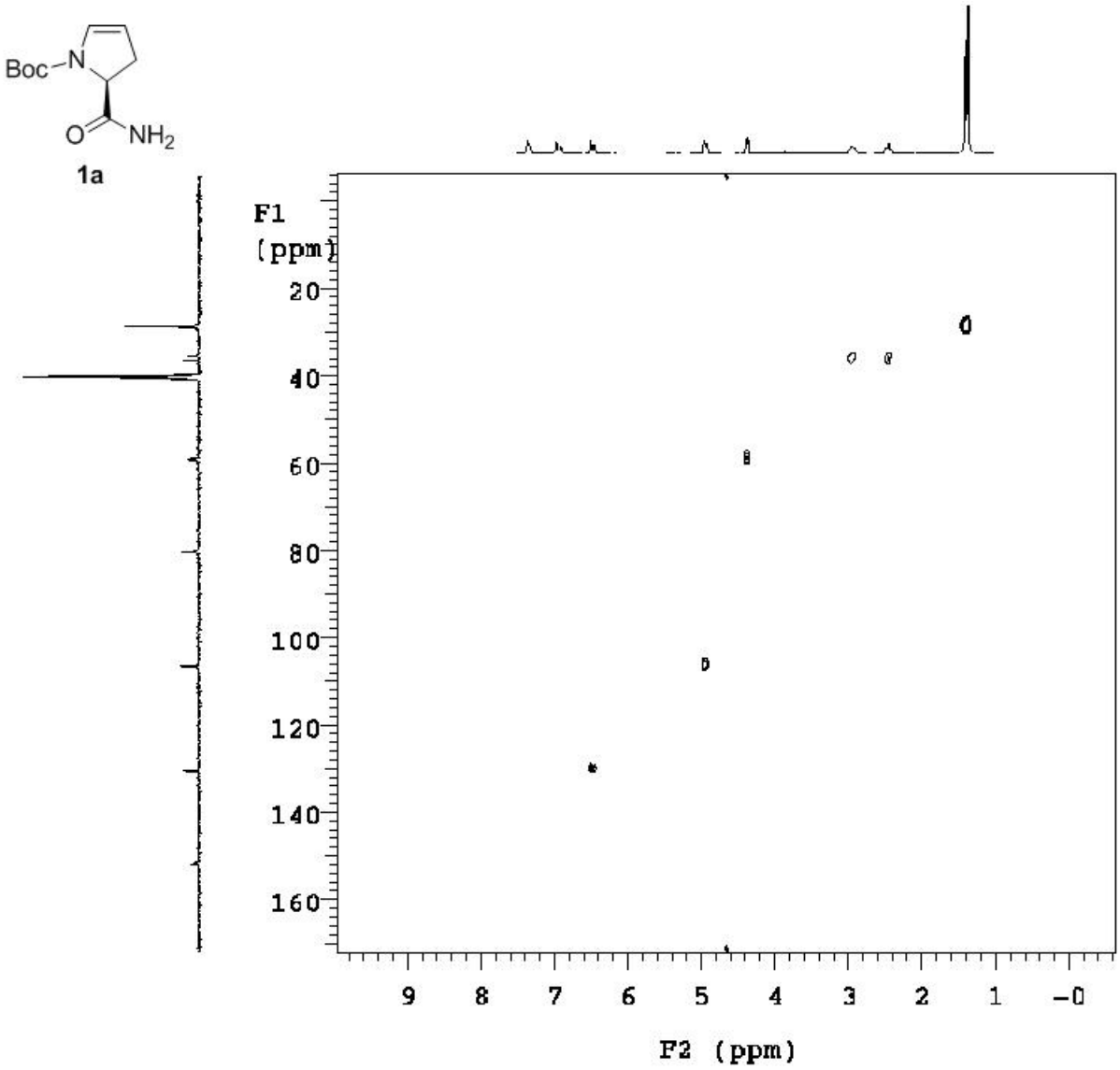
D. $^{13}C$ NMR Spectra of **1a**



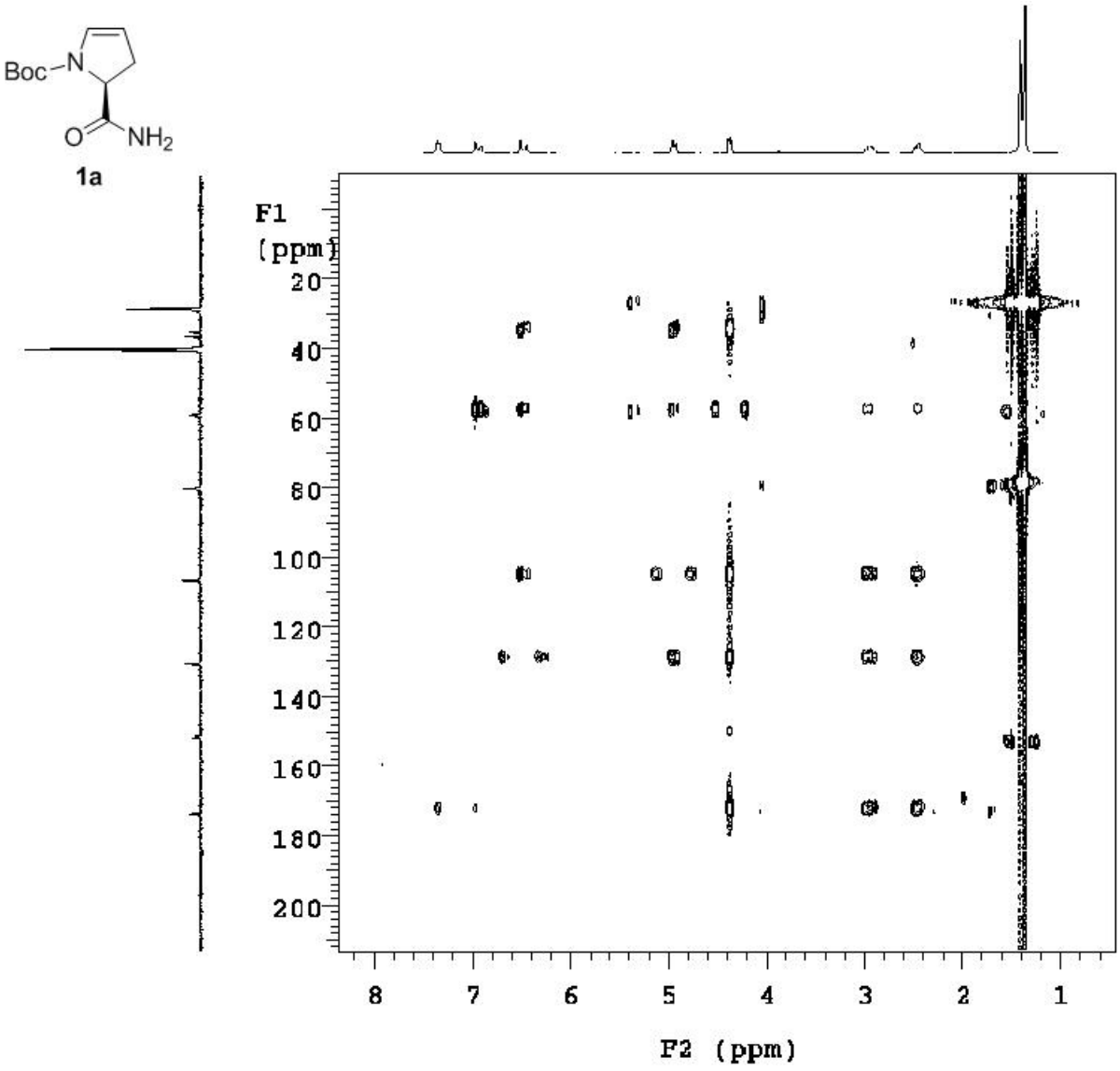
E. $^{1}$H-$^{1}$H COSY NMR Spectra of **1a**



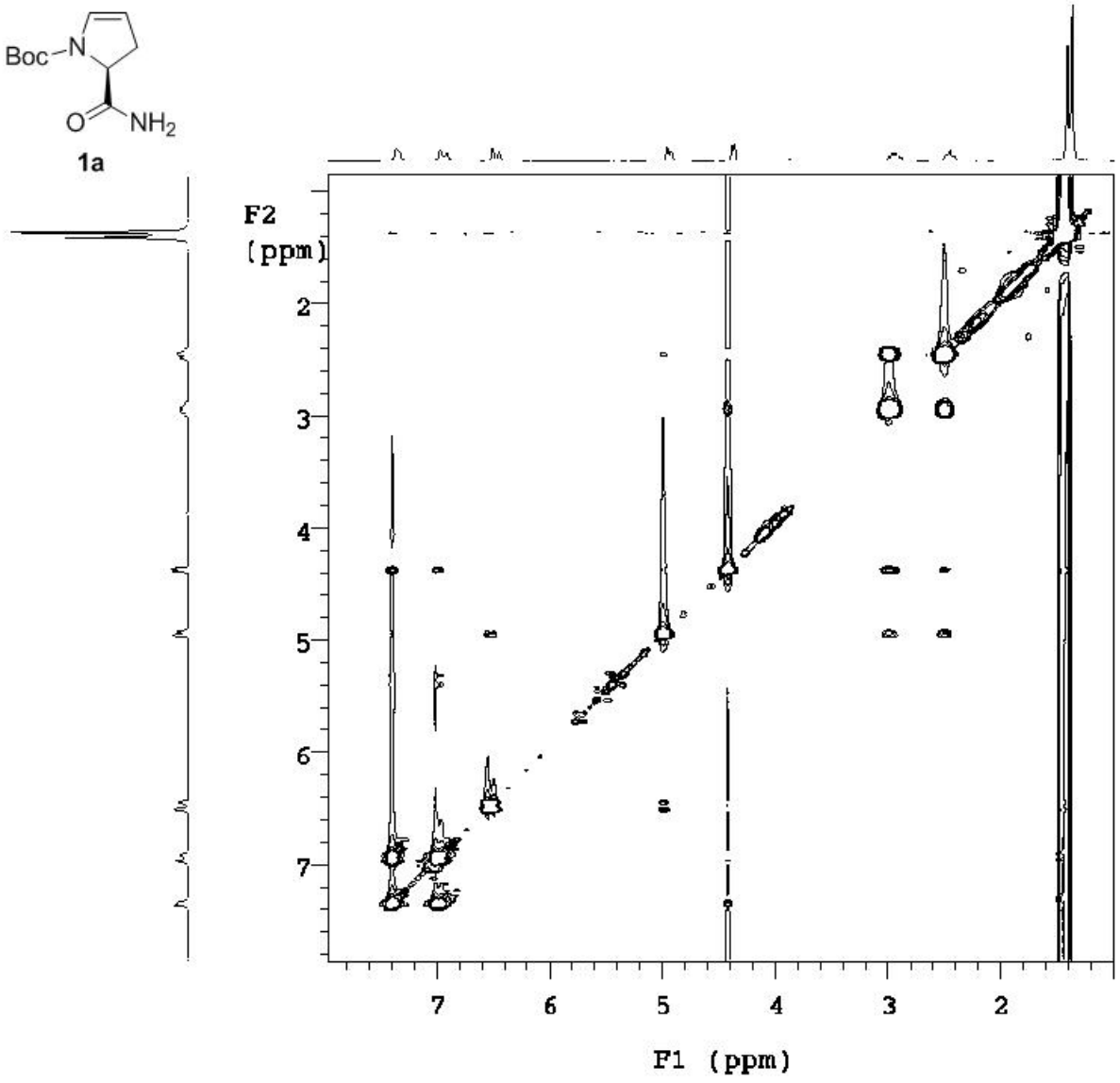
F. $^{1}H$-$^{13}C$ HSQC NMR Spectra of **1a**



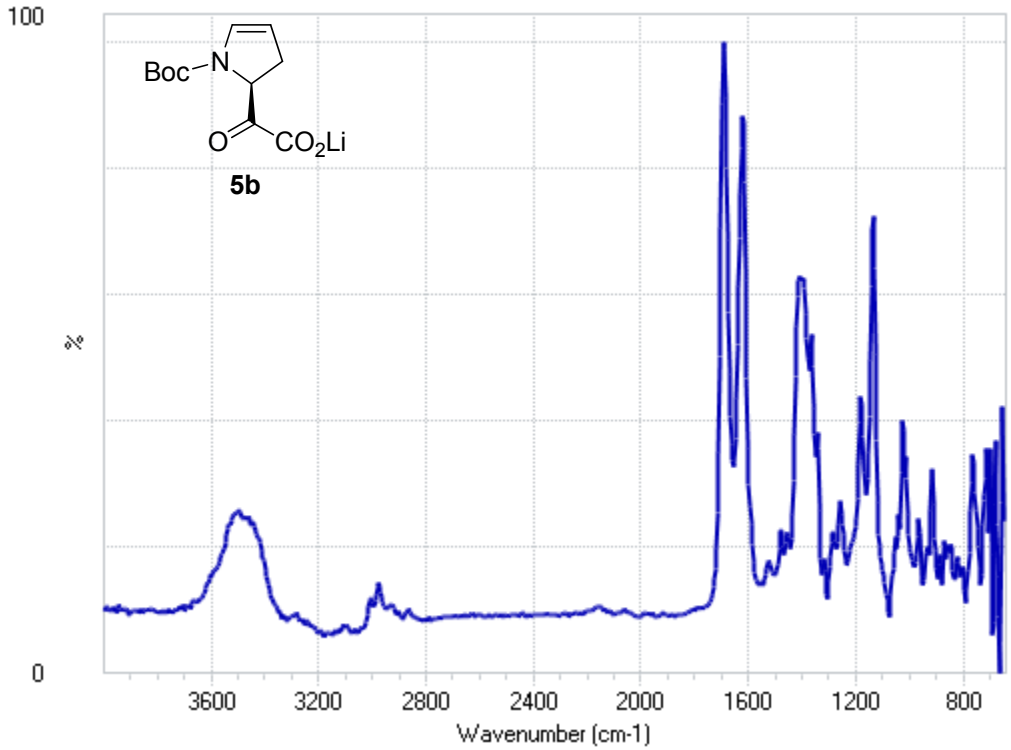
G. $^{1}H$-$^{13}C$ HMBC NMR Spectra of **1a**

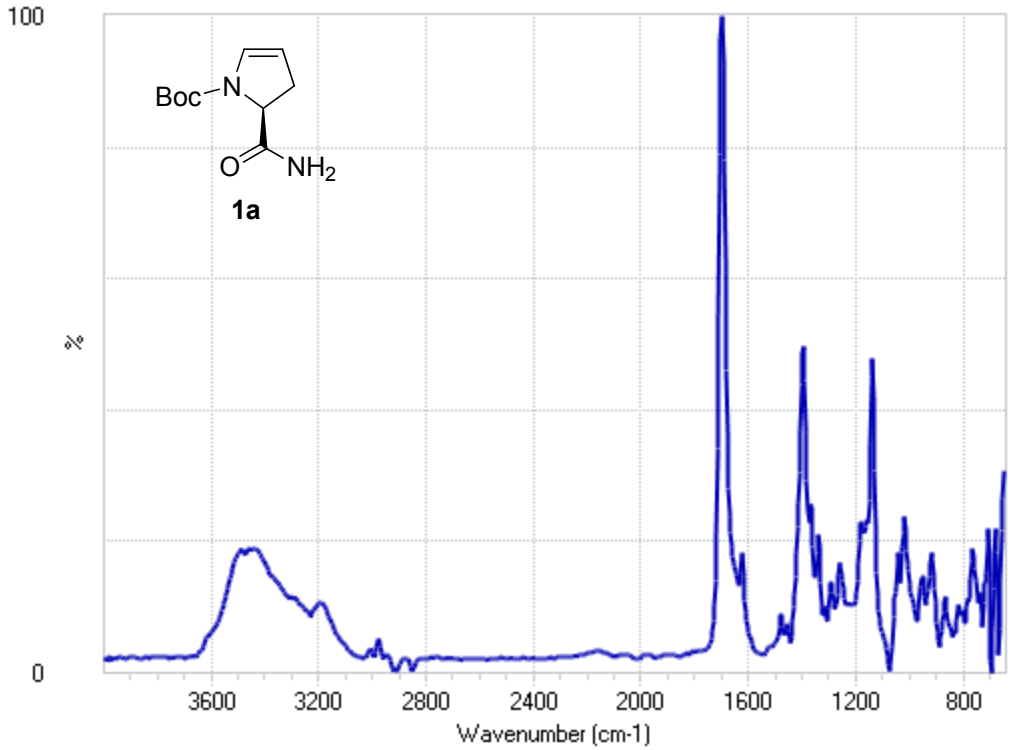


H. NOESY NMR Spectra of **1a**

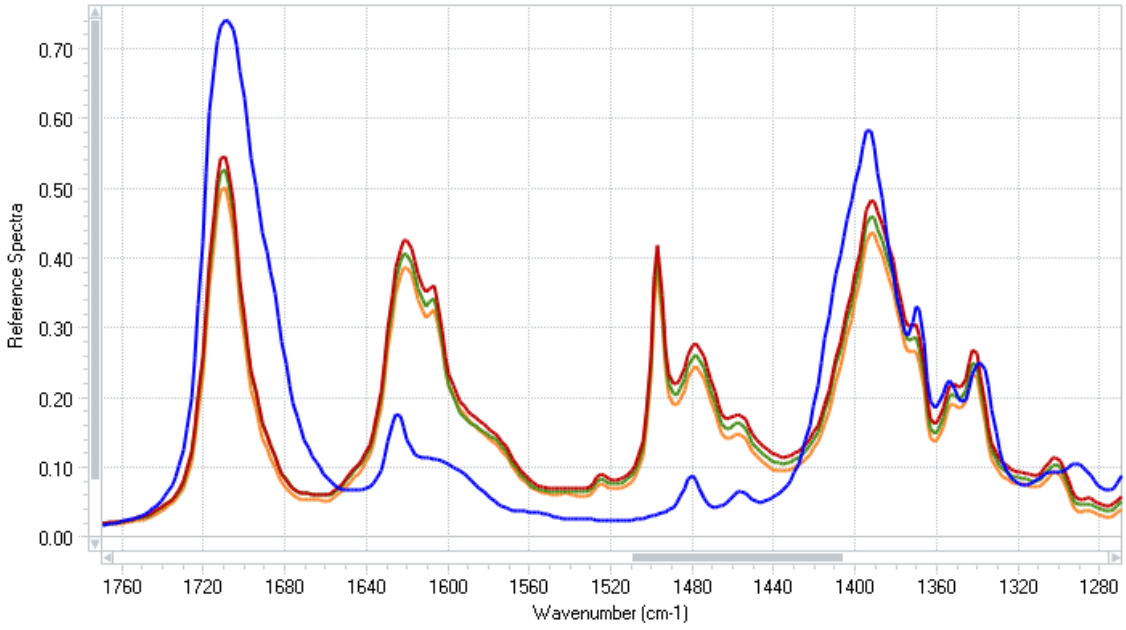


I. IR Spectra of **5b** and **1a**

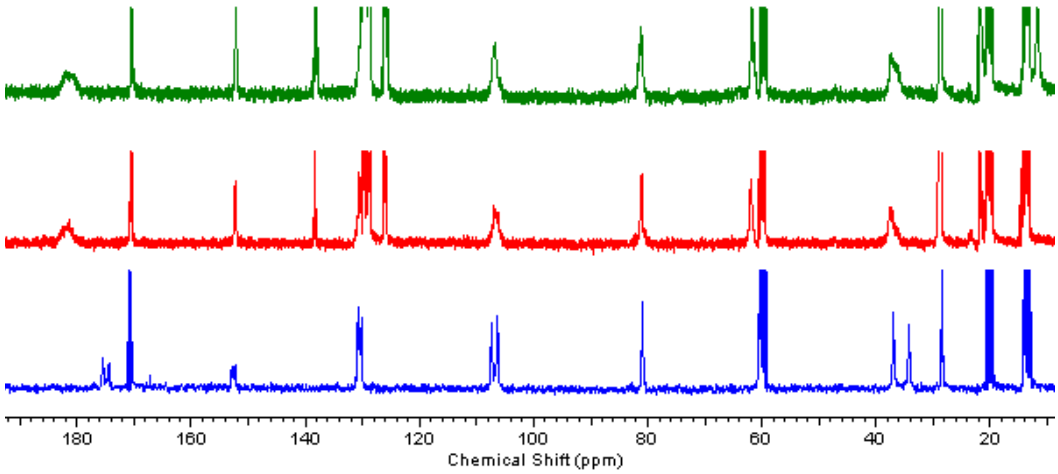


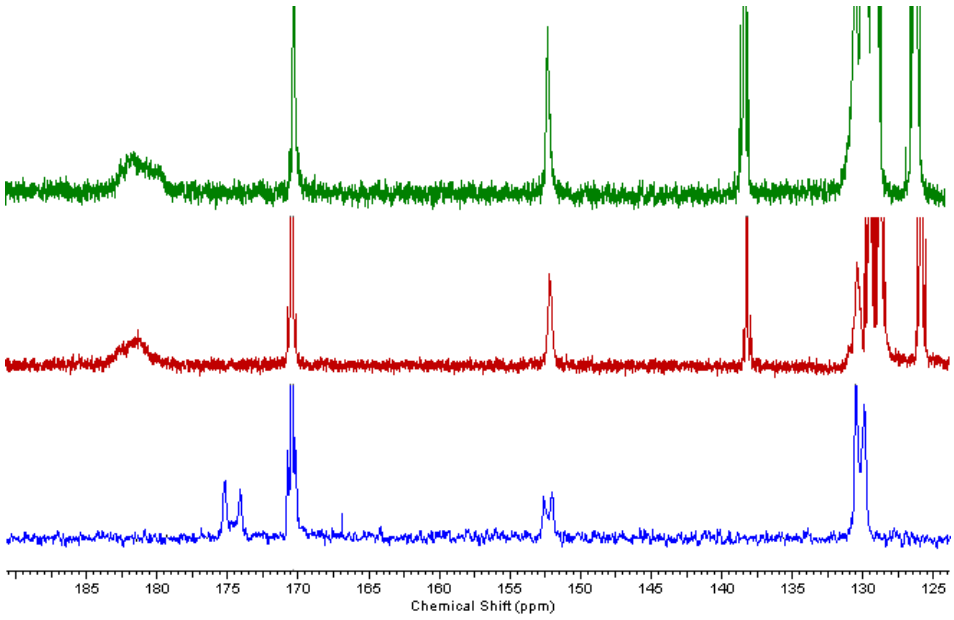
## II. IR and $^{13}C$ NMR Spectra of the Reaction of 1a with $Et_2Zn$




A. Overlay of IR spectra showing diagnostic bands[1] for dihydropyrrole **1a (**1710 and 1685 $cm^{-1}$, blue line) and **7a** (1710, 1620 and 1580 $cm^{-1}$, red line) upon treatment of **1a** (0.47 M in AcOEt) with 1 equiv $Et_2Zn$ (1.1 M in toluene) at 0 °C. The IR frequencies were insensitive to the charge of a second equiv of $Et_2Zn$ (green line) or the addition of 1 equiv $Zn(CH_2I_2)_2$ (orange line).

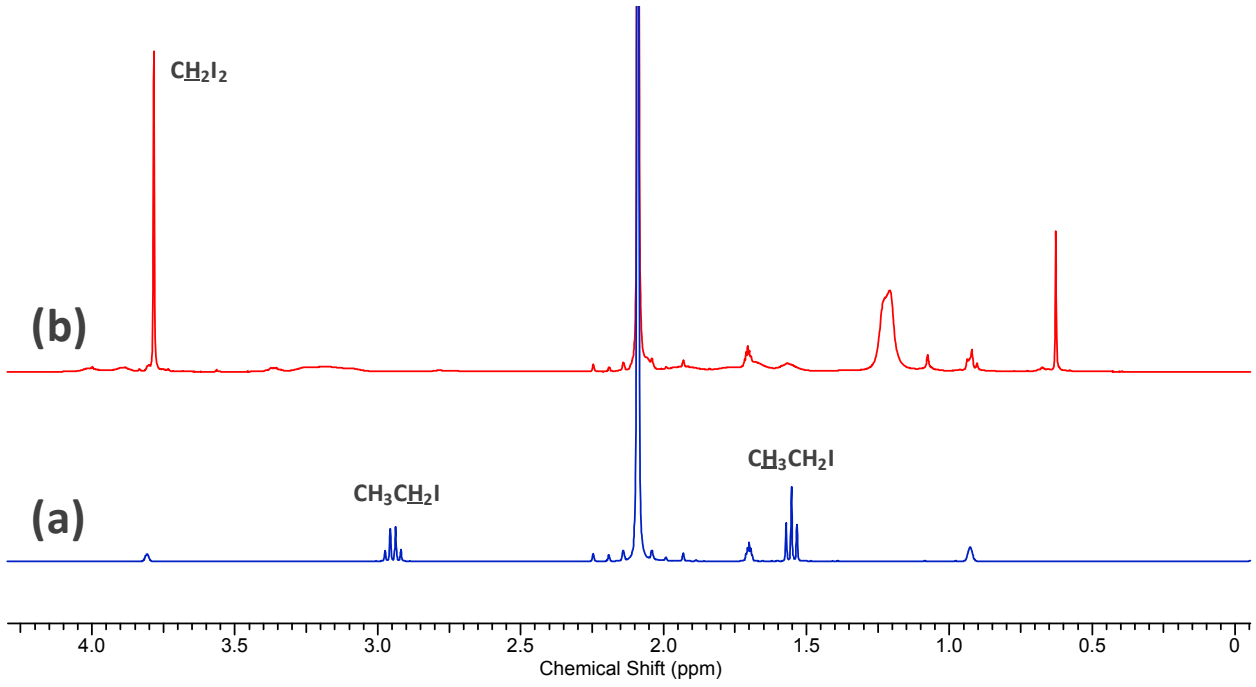



B. Representative titration of dihydropyrrole **1a** (0.41 M in AcOEt-$d_8$) with $Et_2Zn$ (2.0 equiv, 1.1 M in toluene) at 25.0 °C as monitored by $^{13}C$ NMR. Blue spectrum: mixture before the addition of $Et_2Zn$; red spectrum: mixture after the addition of 1.0 equiv $Et_2Zn$; (c) green spectrum: mixture after the addition of 2.0 equiv $Et_2Zn$.

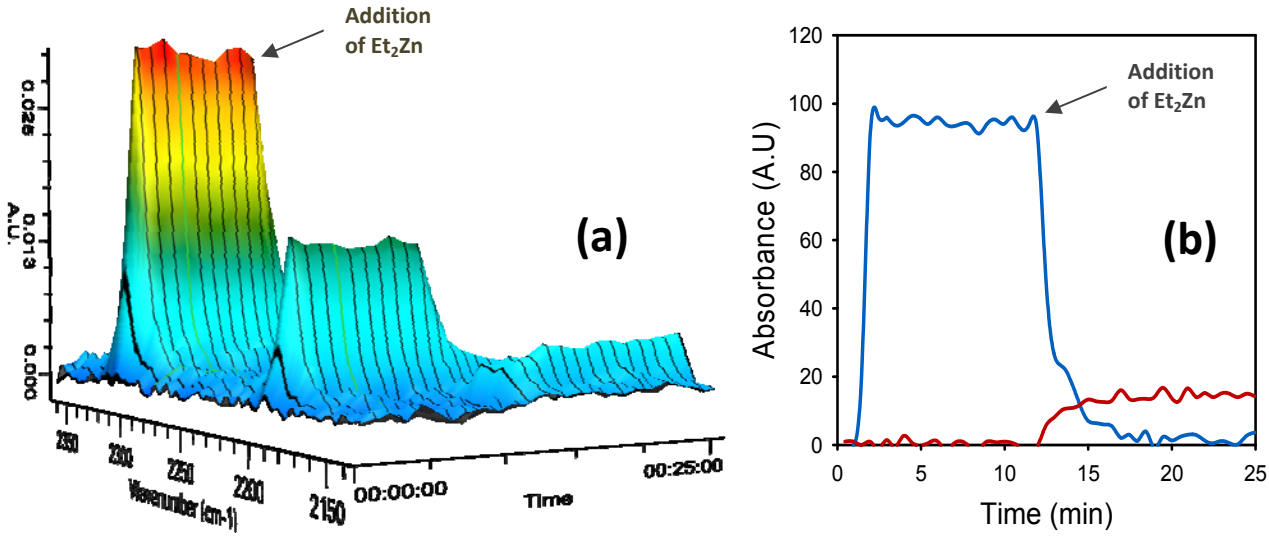



C. Expansion of $^{13}C$ NMR spectra in Section II.B between 125 and 190 ppm. Blue spectrum: mixture before the addition of $Et_2Zn$; red spectrum: mixture after the addition of 1.0 equiv $Et_2Zn$; (c) green spectrum: mixture after the addition of 2.0 equiv $Et_2Zn$.

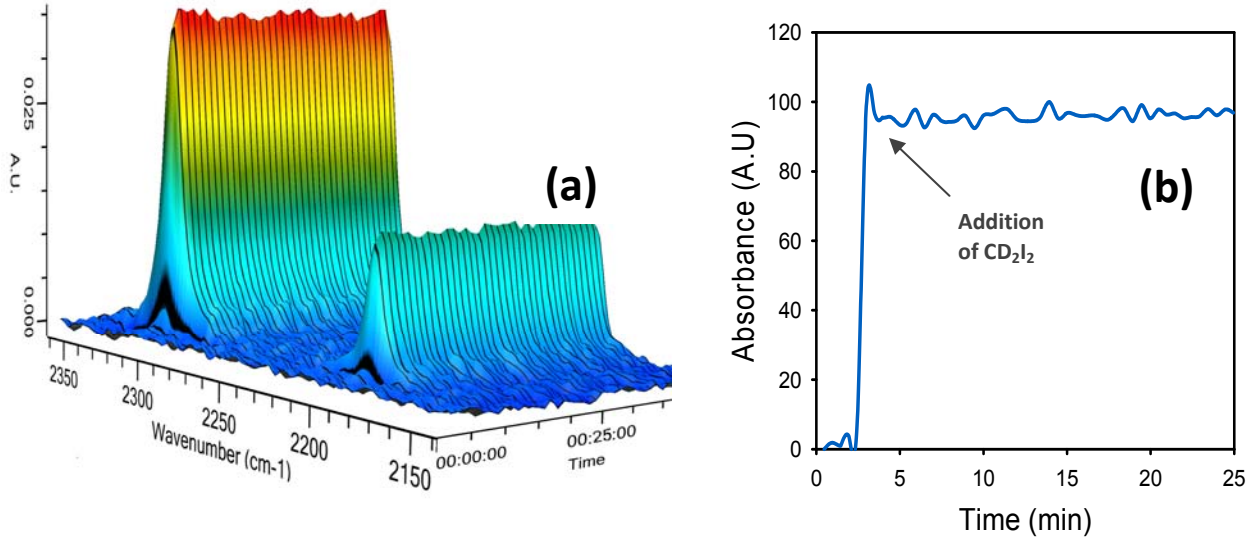
### III. $^1H$ NMR and IR Spectra of the Reaction of 7b with $CH_2I_2/CD_2I_2$




A. $^1H$ spectra of reaction mixtures containing (a) $Et_2Zn$ (0.12 M) and $CH_2I_2$, and (b) zinc amidate **7b** (0.12 M) and $CH_2I_2$ (0.24 M) in AcOEt-$d_8$/toluene at 25.0 °C. The spectra are referenced to the resonance corresponding to the methyl group of toluene at 2.08 ppm.

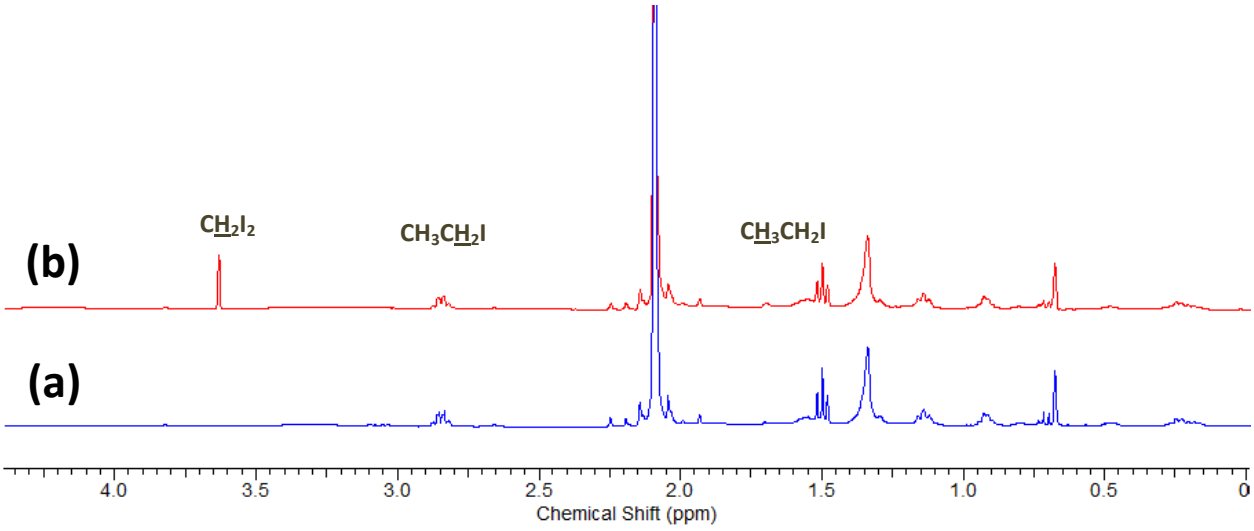



B. (a) In situ IR spectra of a reaction mixture containing $Et_2Zn$ (0.32 M) and $CD_2I_2$ (0.64 M) in AcOEt/toluene solution at 0 °C. (b) Disappearance of $CD_2I_2$ (2310 $cm^{-1}$, blue line) and concomitant formation of $Zn(CD_2I)_2$ (2160 $cm^{-1}$, red line) in the same reaction.

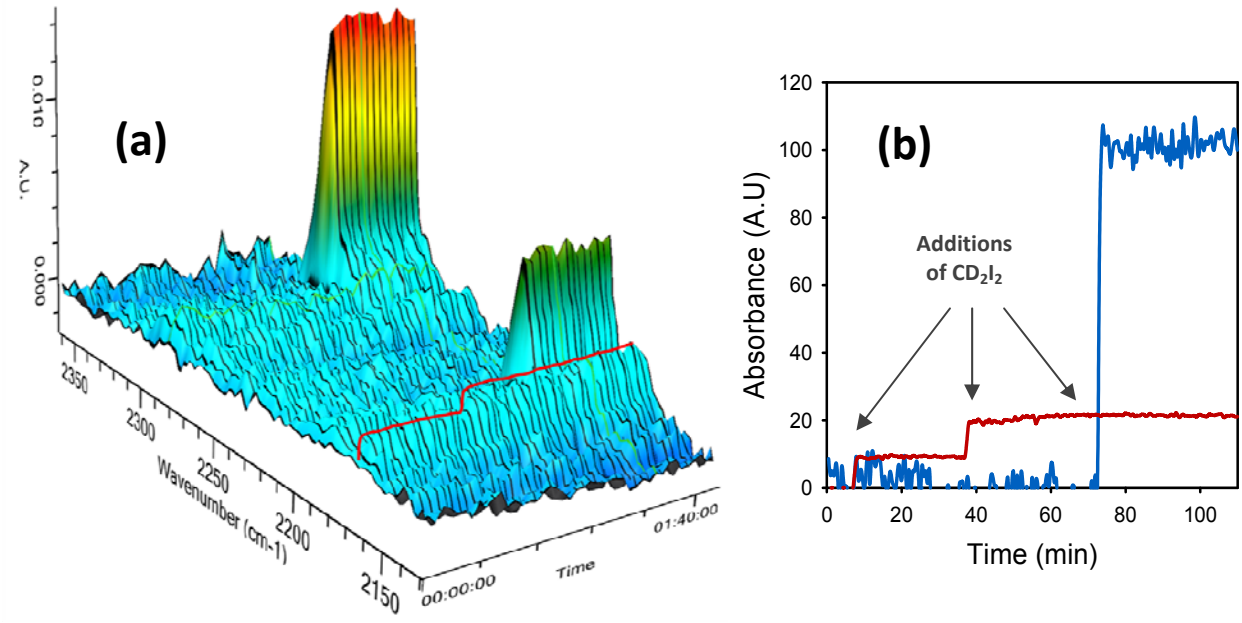



C. (a) In situ IR spectra of a reaction mixture containing amidate **7b** (0.32 M) and $CD_2I_2$ (0.64 M) in AcOEt/toluene solution at 25.0 °C. (b) Profile of the $CD_2I_2$ absorbance at 2310 $cm^{-1}$ (blue line) in the same reaction.

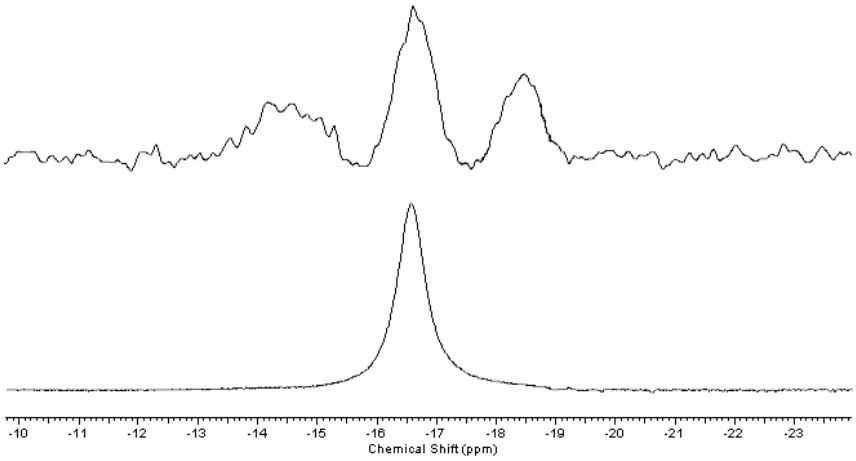
## IV. NMR and IR Spectra of the Reaction of 7b and $Et_2Zn$ with $CH_2I_2/CD_2I_2$




A. $^1H$ spectra of reaction mixtures containing (a) zinc amidate **7b** (0.12 M), $Et_2Zn$ (0.12 M) and $CH_2I_2$ (0.24 M), and (b) zinc amidate **7b** (0.12 M), $Et_2Zn$ (0.12 M) and $CH_2I_2$ (0.36 M) in AcOEt-$d_8$/toluene at 25.0 °C. The spectra are referenced to the resonance corresponding to the methyl group of toluene at 2.08 ppm.

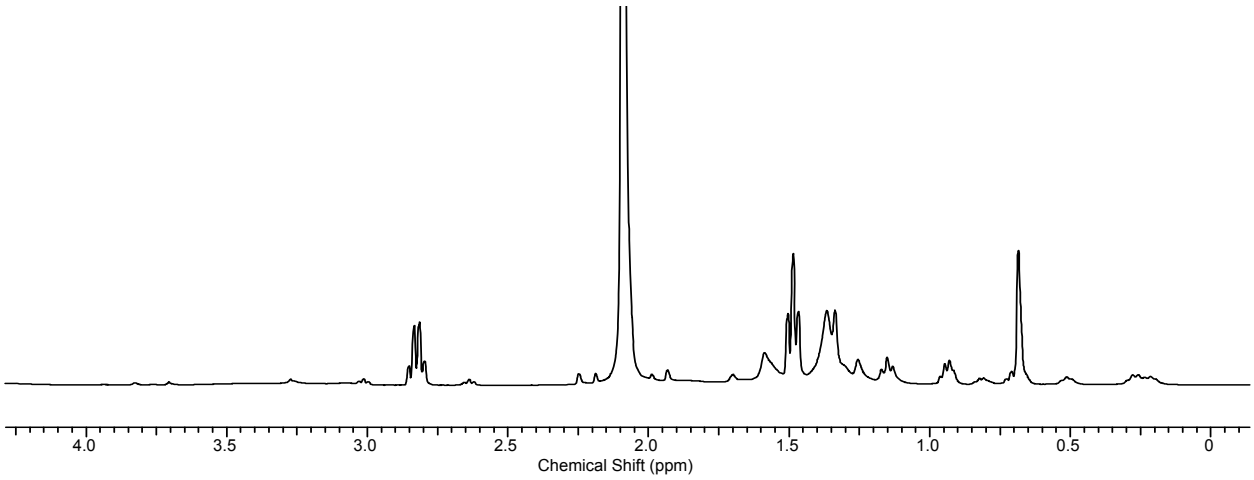



B. (a) In situ IR spectra of a reaction mixture containing amidate **7b** (0.32 M) and $Et_2Zn$ (0.32 M) that was titrated with 3 equiv of $CD_2I_2$ (0.96 M) at intervals of 1 equiv of $CD_2I_2$ in AcOEt/toluene solution at 25.0 °C. (b) Profile of the $CD_2I_2$ (2310 $cm^{-1}$, blue line) and $Zn(CD_2I)_2$ (2160 $cm^{-1}$, red line) absorbances in the same reaction.

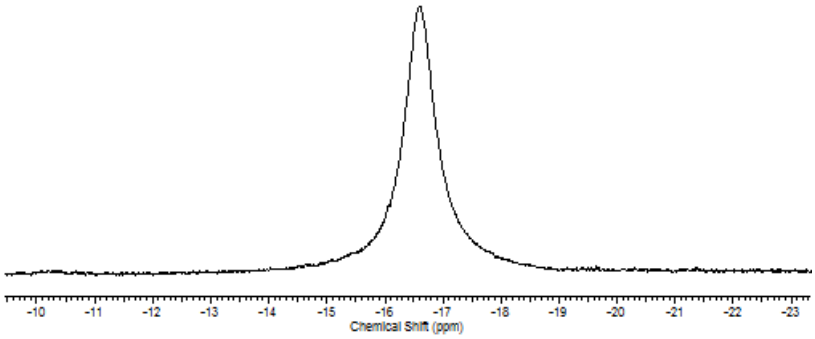



C. $^{13}C$ spectra of reaction mixtures containing (a) zinc amidate **7b** (0.12 M), $Et_2Zn$ (0.12 M) and $^{13}CH_2I_2$ (0.12 M), and (b) zinc amidate **7b** (0.12 M), $Et_2Zn$ (0.12 M) and $^{13}CH_2I_2$ (0.24 M) in AcOEt-$d_8$/toluene at 25.0 °C. The spectra are referenced to the resonance corresponding to the methyl group of toluene at 20.4 ppm.

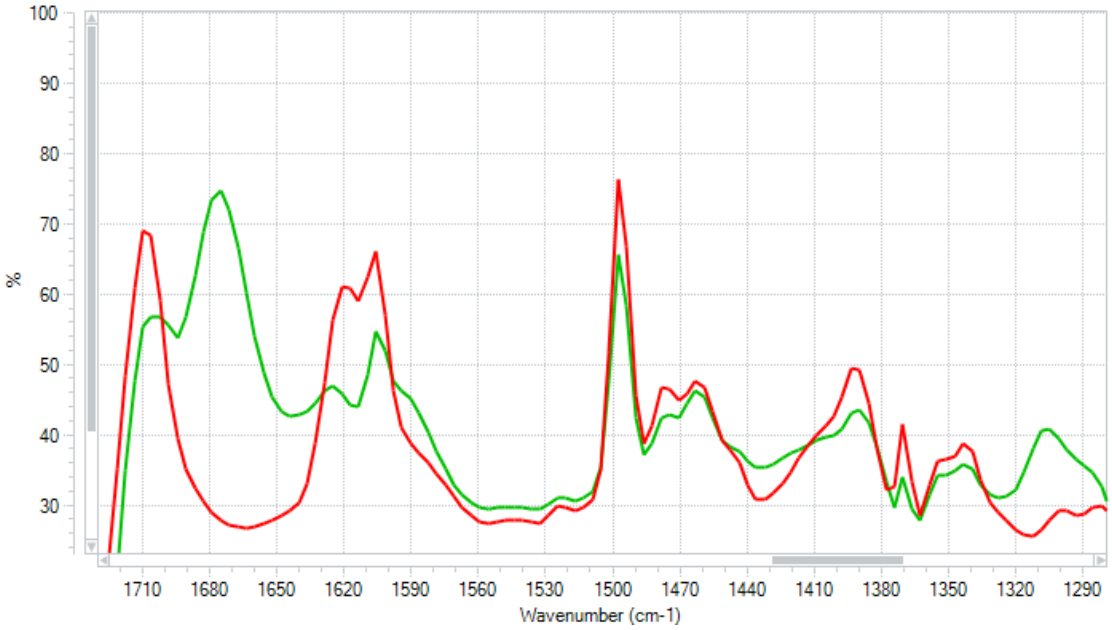
## V. IR and NMR Spectra of the Reaction of 7b/$Zn(CH_2I)_2$ with TFA




A. $^1H$ spectrum of reaction mixtures containing zinc amidate **7b** (0.12 M), $Zn(CH_2I)_2$ (0.12 M) and TFA (0.02 M). The spectrum is referenced to the resonance corresponding to the methyl group of toluene at 2.08 ppm.

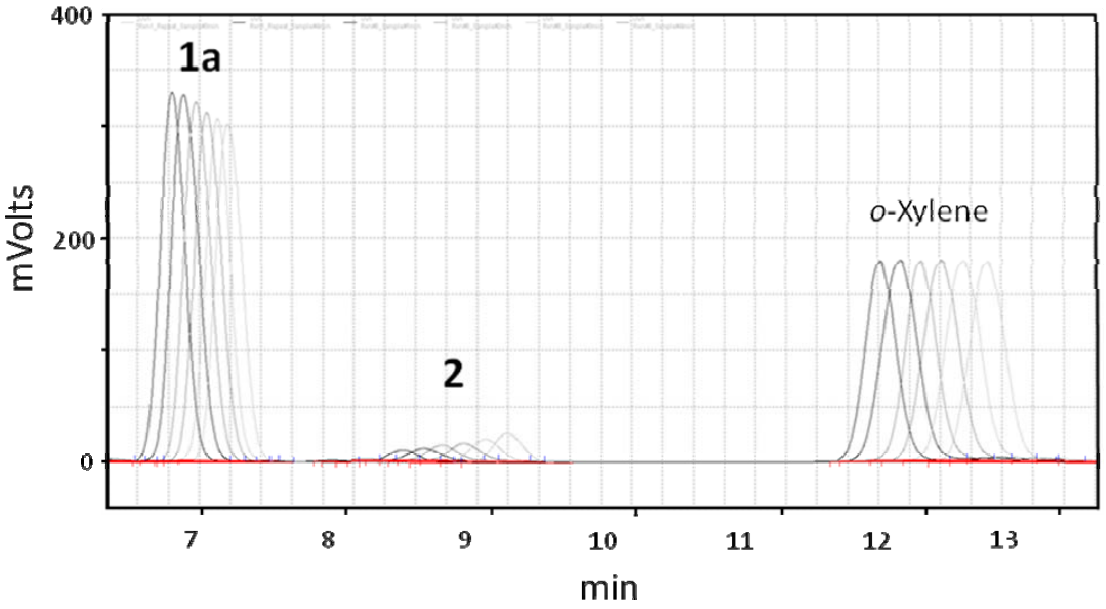



B. $^{13}C$ spectra of a reaction mixtures containing zinc amidate **7b** (0.12 M), $Zn(^{13}CH_2I)_2$ (0.12 M) and TFA (0.02 M). The spectrum is referenced to the resonance corresponding to the methyl group of toluene at 20.4 ppm.




C. Overlay of IR spectra showing changes on the diagnostic bands[1] for amidate **7b** (1710, 1620 and 1580 $cm^{-1}$) upon treatment of an equimolar mixture of **7b** and $Zn(CD_2I)_2$ (0.47 M in AcOEt, red line) with TFA (0.09 M) at 0 °C (green line).

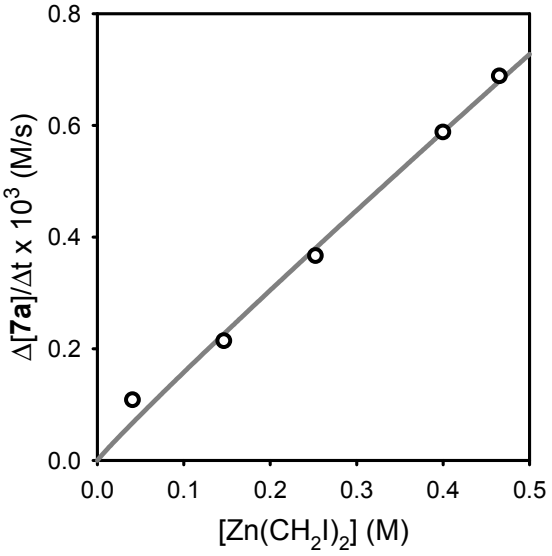
## VI. Kinetic Studies




Representative overlay of HPLC traces with UV detection at 205 nm for the cyclopropanation of dihydropyrrole **1a** at 1 min intervals. [**1a**] = 0.048 M; [$Zn(CH_2I)_2$] = 0.253 M; [AcOEt] = 5.230 M. Analogous plots normalized to *o*-xylene internal standard were used to calculate the initial rates within the first 0-10% of substrate conversion using a linear fit.

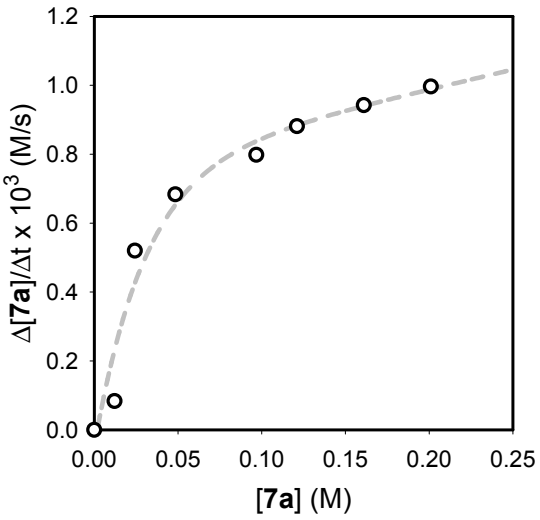
Plot of $k_{obsd}$ versus [$Zn(CH_2I)_2$] for the cyclopropanation of **7a** (0.048 M) by $Zn(CH_2I)_2$ at 0 °C ([AcOEt] = 5.2 M in toluene). The curve depicts an unweighted least-squares fit to $k_{obsd} = k[Zn(CH_2I)_2]^n$ ($k$ = 0.0014 ± 0.0001; n = 0.95 ± 0.08).

| [$Zn(CH_2I)_2$] (M) | Δ[**7a**]/Δt (M/s) |
|---|---|
| 0.041 | 0.00011 ± 2E-5 |
| 0.147 | 0.00021 ± 2E-5 |
| 0.253 | 0.00037 ± 4E-5 |
| 0.400 | 0.00059 ± 7E-5 |
| 0.465 | 0.00068 ± 6E-5 |



Plot of $k_{obsd}$ versus [**7a**] for the cyclopropanation of **7a** by $Zn(CH_2I)_2$ (0.465 M) at 0 °C ([AcOEt] = 5.2 M in toluene).

| [**7a**] (M) | Δ[**7a**]/Δt (M/s) |
|---|---|
| 0.012 | 0.00008 ± 1E-5 |
| 0.024 | 0.00052 ± 7E-5 |
| 0.048 | 0.00068 ± 6E-5 |
| 0.097 | 0.00080 ± 9E-5 |
| 0.121 | 0.00088 ± 9E-5 |
| 0.161 | 0.0009 ± 1E-4 |
| 0.201 | 0.0010 ± 1E-4 |



## VII. B3LYP and PCM Calculations

### A. Computational Methods.

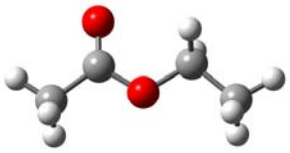
All calculations were executed using Gaussian 09, Revision B.01.[2] A series of geometries were systematically tested for reactants, intermediates, and transition structures at the B3LYP/6-311+G(2d,2p) level for all the atoms except iodine, which was described by Glukhovtsev's modification of the 6-311G basis set.[3] Then, the lowest energy forms were submitted to single point B3LYP/6-311+G(2d,2p) calculations incorporating Tomasi's Polarized Continuum Model (PCM) corrections[4] for AcOEt[5] as the bulk solvent. The calculation of solution-phase energies using gas-phase geometries has been reported previously.[6] All reactants and intermediates containing Zn atoms were reoptimized after the explicit addition of a molecule of AcOEt as coordinating solvent, and the resulting structures were only considered when their energies were lower than those of the unsolvated analogues. The calculated energies ($\Delta G$, 298.15 K, 1.0 atm) result from the sum of thermal corrections to Gibbs free energy (TCGFE) as obtained from the frequency analysis at the B3LYP/6-311+G(2d,2p) level, and single point PCM corrections. Plausible structures for monomeric zinc amidate **7a** and its complexes with $Et_2Zn$, $Zn(CH_2I)_2$, and $IZnCH_2I$ are presented in Figure 2. Calculated structures for transition states **TS1** and **TS2** are shown in Figures 5 and 6. Energy values are given relative to zinc amidate **10** in $kcal \cdot mol^{-1}$. In the absence of structural data on the aggregation and solvation states of zinc amidate **7a** and plausible intermediates under the reaction conditions, these energies represent reactivity trends rather than precise values. Frequency calculations for all stationary points were carried out to describe them either as minima ($i = 0$) or as first-order transition states ($i = 1$). For all transition structures, visualization of the imaginary frequencies corresponded to the expected normal mode for the elementary step under investigation. Intrinsic reaction coordinate calculations (IRC) were performed from the transition states in forward and reverse directions to confirm the lowest energy reaction pathways that connect the corresponding minima.

## B. Calculated B3LYP/6-311+G(2d,2p) Energies

| Structure[a] | TCGFE (Hartree) | B3LYP/PCM (Hartree) | $\Delta G$ (kcal·mol$^{-1}$) | Imaginary ν (cm$^{-1}$) |
|---|---|---|---|---|
| **AcOEt** | 0.085623 | -307.820080 | --- | --- |
| **$Et_2Zn$** | 0.095996 | -1937.848463 | --- | --- |
| **$Zn(CH_2I)_2$** | 0.013464 | -15697.070394 | --- | --- |
| **$IZnCH_2I$** | -0.008393 | -15657.814317 | --- | --- |
| **9a** (n = 0) | 0.259140 | -2584.171319 | 1.1 | --- |
| **9b** (n = 1) | 0.363952 | -2891.994255 | 11.4 | --- |
| **9c** (n = 2) | 0.469066 | -3199.812806 | 24.5 | --- |
| **10** (n = 0) | 0.260308 | -2584.174263 | 0.0 | --- |
| **11** (n = 0) | 0.371042 | -4522.001204 | 22.7 | --- |
| **12** (n = 0) | 0.294878 | -18281.246947 | 11.8 | --- |
| **13** (n = 0) | 0.269480 | -18242.000708 | 3.4 | --- |
| **14** (n = 0) | 0.370959 | -4522.024458 | 8.1 | --- |
| **15** (n = 0) | 0.293860 | -18281.254540 | 6.4 | --- |
| **16** (n = 0) | 0.272002 | -18242.005233 | 2.1 | --- |
| **TS1a-*syn*** | 0.295945 | -18281.212266 | 34.2 | -323 |
| **TS1b-*syn*** | 0.297744 | -18281.220151 | 30.4 | -375 |
| **TS1c-*anti*** | 0.291755 | -18281.216925 | 31.6 | -315 |
| **TS2a-*syn*** | 0.272710 | -18241.961639 | 30.0 | -306 |
| **TS2b-*syn*** | 0.274393 | -18241.965834 | 28.4 | -354 |
| **TS2c-*anti*** | 0.269907 | -18241.958816 | 31.8 | -299 |

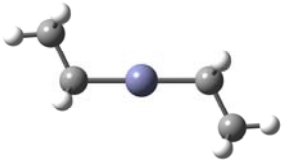
[a] Multiple unconstrained searches for stationary points corresponding to structures **12** and **13** converged into related geometries lacking the C=O—Zn interaction.

## C. Calculated Coordinates



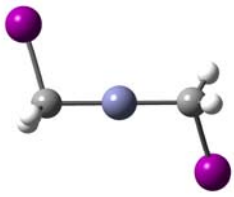
AcOEt

| | | | |
|---|---|---|---|
| C | -1.039351 | 0.145032 | -0.000149 |
| O | -1.203552 | 1.339854 | 0.000030 |
| O | 0.176570 | -0.440906 | -0.000120 |
| C | 1.316983 | 0.452581 | -0.000011 |
| H | 1.256907 | 1.091738 | 0.879968 |
| H | 1.257064 | 1.091742 | -0.879998 |
| C | -2.138571 | -0.884997 | 0.000057 |
| H | -3.101652 | -0.385483 | -0.000321 |
| H | -2.050670 | -1.524713 | -0.877718 |
| H | -2.051012 | -1.523919 | 0.878452 |
| C | 2.567519 | -0.398726 | 0.000097 |
| H | 3.448044 | 0.244408 | 0.000173 |
| H | 2.608775 | -1.034350 | 0.884008 |
| H | 2.608928 | -1.034348 | -0.883809 |



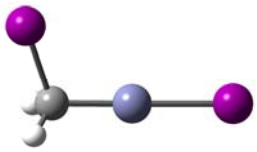
$Et_2Zn$

| | | | |
|---|---|---|---|
| Zn | -0.000001 | 0.000015 | -0.000057 |
| C | -1.853155 | -0.679573 | -0.000055 |
| H | -1.968365 | -1.330980 | -0.871142 |
| H | -1.968276 | -1.331209 | 0.870873 |
| C | -2.956617 | 0.393138 | 0.000143 |
| H | -2.896447 | 1.040128 | -0.876930 |
| H | -3.955916 | -0.051336 | 0.000133 |
| H | -2.896360 | 1.039890 | 0.877386 |
| C | 1.853168 | 0.679560 | -0.000053 |
| H | 1.968301 | 1.331191 | 0.870877 |
| H | 1.968391 | 1.330968 | -0.871138 |
| C | 2.956609 | -0.393173 | 0.000143 |
| H | 2.896427 | -1.040159 | -0.876932 |
| H | 3.955919 | 0.051280 | 0.000134 |
| H | 2.896339 | -1.039926 | 0.877384 |



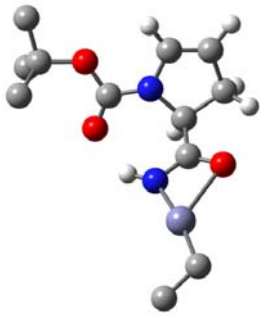
$Zn(CH_2I)_2$

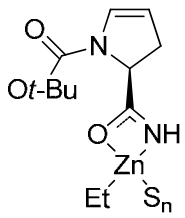
| | | | |
|---|---|---|---|
| Zn | 0.000036 | 0.000177 | 0.435018 |
| C | -1.554316 | -1.176107 | 0.424161 |
| H | -1.531644 | -1.976431 | -0.306965 |
| H | -1.847230 | -1.575058 | 1.388892 |
| C | 1.554450 | 1.176389 | 0.423742 |
| I | 3.255972 | -0.098048 | -0.191503 |
| I | -3.256014 | 0.097905 | -0.191529 |
| H | 1.531865 | 1.976505 | -0.307615 |
| H | 1.847347 | 1.575576 | 1.388386 |



$IZnCH_2I$

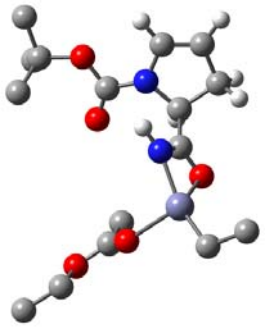
| | | | |
|---|---|---|---|
| Zn | 0.000000 | 0.791320 | 0.000000 |
| C | -1.903837 | 0.361188 | 0.000000 |
| H | -2.430862 | 0.692698 | 0.887284 |
| H | -2.430862 | 0.692698 | -0.887284 |
| I | -2.091197 | -1.833449 | 0.000000 |
| I | 2.398457 | 1.318503 | 0.000000 |

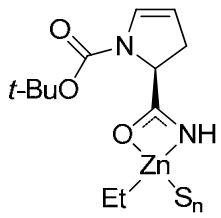





**9a** (n=0)

| | | | |
|---|---|---|---|
| C | 0.174763 | 1.773715 | 0.721348 |
| C | 0.209202 | 3.272427 | 0.333107 |
| C | 1.226124 | 3.326641 | -0.778480 |
| C | 1.820608 | 2.148351 | -0.930540 |

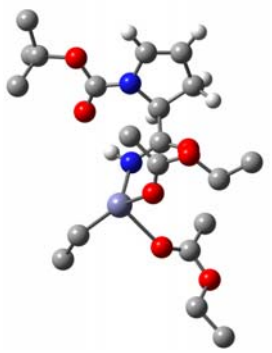


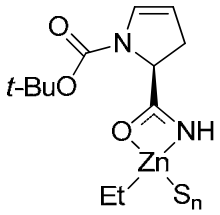



**9b** (n=1)

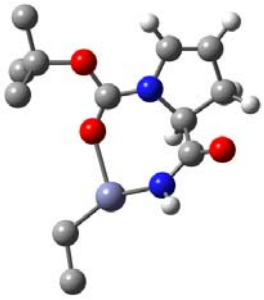
| | | | |
|---|---|---|---|
| C | -1.182344 | -1.904332 | 1.097073 |
| C | -1.442322 | -3.444160 | 1.129283 |
| C | -2.584055 | -3.628421 | 0.160494 |
| C | -3.015599 | -2.454446 | -0.289679 |

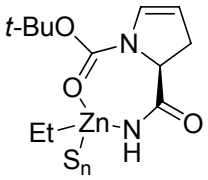
| | | | |
|---|---|---|---|
| H | 0.340756 | 1.611413 | 1.785492 |
| H | -0.783626 | 3.585775 | 0.015804 |
| H | 0.502882 | 3.900803 | 1.176994 |
| N | 1.314471 | 1.186494 | -0.028079 |
| H | 1.440392 | 4.204597 | -1.364878 |
| H | 2.591932 | 1.856979 | -1.620252 |
| C | -1.167035 | 1.096024 | 0.368654 |
| N | -1.320410 | -0.214036 | 0.531021 |
| H | -0.533361 | -0.734232 | 0.896193 |
| O | -2.139132 | 1.771057 | -0.040574 |
| C | 1.933329 | 0.035013 | 0.363098 |
| O | 1.504080 | -0.684091 | 1.253456 |
| O | 3.045965 | -0.190032 | -0.360477 |
| C | 3.861871 | -1.407427 | -0.159897 |
| C | 3.031536 | -2.654067 | -0.461668 |
| H | 3.682136 | -3.529112 | -0.456599 |
| H | 2.249243 | -2.798497 | 0.277373 |
| H | 2.576869 | -2.577517 | -1.449539 |
| C | 4.967660 | -1.231573 | -1.198357 |
| H | 5.657208 | -2.073909 | -1.152652 |
| H | 4.549085 | -1.182837 | -2.203050 |
| H | 5.528567 | -0.316478 | -1.011803 |
| C | 4.444534 | -1.419643 | 1.252531 |
| H | 4.987786 | -0.494563 | 1.446141 |
| H | 3.666122 | -1.535592 | 2.000605 |
| H | 5.146171 | -2.249193 | 1.345990 |
| Zn | -3.153999 | -0.408776 | -0.001059 |
| C | -4.988475 | -0.908341 | -0.478425 |
| H | -5.650964 | -0.288720 | 0.130557 |
| H | -5.145242 | -0.584074 | -1.509910 |
| C | -5.357354 | -2.392067 | -0.324637 |
| H | -6.396687 | -2.578106 | -0.609307 |
| H | -4.734785 | -3.034081 | -0.949712 |
| H | -5.240832 | -2.736379 | 0.704082 |
| H | -1.255291 | -1.461088 | 2.086740 |
| H | -0.548053 | -3.994427 | 0.837973 |
| H | -1.704246 | -3.781197 | 2.133704 |
| N | -2.266972 | -1.383797 | 0.241020 |
| H | -2.995651 | -4.584166 | -0.118582 |
| H | -3.817470 | -2.241184 | -0.973540 |
| C | 0.218397 | -1.592903 | 0.581749 |
| N | 0.476914 | -1.218725 | -0.653805 |
| H | -0.303794 | -1.104809 | -1.281502 |
| O | 1.180477 | -1.740953 | 1.385766 |
| C | -2.617681 | -0.061687 | 0.268497 |
| O | -1.997247 | 0.775538 | 0.898731 |
| O | -3.708238 | 0.164040 | -0.493530 |
| C | -4.274102 | 1.520941 | -0.640359 |
| C | -3.254098 | 2.446590 | -1.302118 |
| H | -3.727430 | 3.402888 | -1.527089 |
| H | -2.402122 | 2.623387 | -0.652655 |
| H | -2.902369 | 2.015604 | -2.239746 |
| C | -5.464169 | 1.279791 | -1.566776 |
| H | -5.981693 | 2.219049 | -1.759061 |
| H | -5.133763 | 0.866915 | -2.519389 |
| H | -6.169681 | 0.583941 | -1.113980 |
| C | -4.744145 | 2.044409 | 0.716220 |
| H | -5.424814 | 1.331675 | 1.182212 |
| H | -3.906473 | 2.220456 | 1.384254 |
| H | -5.282744 | 2.981863 | 0.573858 |
| Zn | 2.459981 | -1.129117 | -0.465047 |
| C | 4.302244 | -1.667582 | -0.955293 |
| H | 4.618321 | -1.048637 | -1.799459 |
| H | 4.947473 | -1.379179 | -0.121033 |
| C | 4.511898 | -3.153125 | -1.287877 |
| H | 5.555247 | -3.378106 | -1.531981 |
| H | 4.233714 | -3.797513 | -0.451934 |
| H | 3.910187 | -3.466425 | -2.143484 |
| C | 2.153687 | 1.868135 | 0.848072 |
| O | 2.609844 | 1.087331 | 0.026889 |
| O | 2.401757 | 3.177832 | 0.777767 |
| C | 3.223754 | 3.635399 | -0.330045 |
| H | 2.732410 | 3.354773 | -1.260323 |
| H | 4.179945 | 3.117001 | -0.284806 |
| C | 1.267844 | 1.502479 | 1.995380 |
| H | 0.235097 | 1.477176 | 1.638584 |
| H | 1.512804 | 0.502351 | 2.342346 |
| H | 1.344587 | 2.234954 | 2.793989 |
| C | 3.377454 | 5.133510 | -0.194400 |
| H | 3.990497 | 5.511952 | -1.012649 |
| H | 2.409691 | 5.632142 | -0.233015 |
| H | 3.863280 | 5.393893 | 0.745173 |






**9c** (n=2)



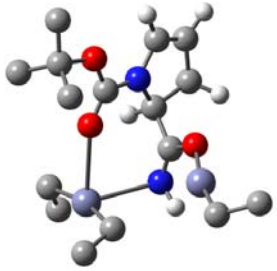


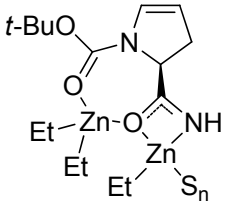

**10** (n=0)

| | | | |
|---|---|---|---|
| C | -1.630425 | 1.105282 | -1.779567 |
| C | -1.658945 | 2.573270 | -2.265475 |
| C | -2.739787 | 3.206892 | -1.427534 |
| C | -3.377376 | 2.287306 | -0.710670 |
| H | -1.725934 | 0.390254 | -2.594907 |
| H | -0.679288 | 3.017249 | -2.096492 |
| H | -1.884970 | 2.647567 | -3.332271 |
| N | -2.844787 | 0.996029 | -0.924019 |
| H | -2.965574 | 4.260548 | -1.415910 |
| H | -4.200772 | 2.404228 | -0.029188 |
| C | -0.318333 | 0.755993 | -0.998781 |
| N | -0.235645 | -0.476595 | -0.499047 |
| H | -1.059175 | -1.030149 | -0.706322 |
| O | 0.572775 | 1.615880 | -0.911255 |
| C | -3.509788 | -0.182124 | -0.743844 |
| O | -3.078381 | -1.261462 | -1.118333 |
| O | -4.677987 | 0.012078 | -0.097075 |
| C | -5.549793 | -1.123212 | 0.266997 |
| C | -4.818168 | -2.064792 | 1.222919 |
| H | -5.515052 | -2.818686 | 1.590764 |
| H | -3.990969 | -2.567264 | 0.730753 |
| H | -4.436533 | -1.511768 | 2.081497 |
| C | -6.709225 | -0.429083 | 0.979243 |
| H | -7.440218 | -1.168484 | 1.304856 |
| H | -6.353976 | 0.113627 | 1.854671 |
| H | -7.204476 | 0.275537 | 0.312001 |
| C | -6.041670 | -1.835383 | -0.992627 |
| H | -6.510371 | -1.122990 | -1.671924 |
| H | -5.226695 | -2.332597 | -1.509762 |
| H | -6.788604 | -2.580533 | -0.716480 |
| Zn | 1.113940 | -1.285498 | 0.667757 |
| C | 1.409152 | -2.868541 | 1.841746 |
| H | 2.293988 | -2.651006 | 2.446843 |
| H | 0.579890 | -2.951143 | 2.550522 |
| C | 1.597628 | -4.211799 | 1.117400 |
| H | 1.798383 | -5.036999 | 1.809432 |
| H | 0.712144 | -4.489811 | 0.541419 |
| H | 2.432878 | -4.175646 | 0.414509 |
| C | 3.586042 | -0.728218 | -1.486100 |
| O | 3.105692 | -1.197553 | -0.469264 |
| O | 4.902389 | -0.750349 | -1.716104 |
| C | 5.734815 | -1.359867 | -0.691439 |

| | | | |
|---|---|---|---|
| C | 0.091606 | 2.132618 | -0.567617 |
| C | -0.532781 | 3.487261 | -0.977734 |
| C | -1.966705 | 3.372650 | -0.534809 |
| C | -2.229916 | 2.153770 | -0.081986 |
| H | 0.579920 | 1.630548 | -1.400652 |
| H | -0.010810 | 4.288485 | -0.457119 |
| H | -0.455033 | 3.664457 | -2.052643 |
| N | -1.085343 | 1.319314 | -0.154216 |
| H | -2.679738 | 4.179633 | -0.571308 |
| H | -3.145445 | 1.748893 | 0.308451 |
| C | 1.104422 | 2.294519 | 0.605598 |
| N | 1.908730 | 1.236841 | 0.832174 |
| H | 2.540430 | 1.462132 | 1.591933 |
| O | 1.132889 | 3.347177 | 1.236017 |
| C | -1.094879 | -0.026990 | -0.160710 |
| O | -0.094337 | -0.719983 | -0.405027 |
| O | -2.301400 | -0.531426 | 0.109050 |
| C | -2.561658 | -1.992503 | 0.177851 |
| C | -1.728856 | -2.623925 | 1.291046 |
| H | -2.049696 | -3.655953 | 1.434503 |
| H | -0.670497 | -2.624713 | 1.049353 |
| H | -1.879603 | -2.090759 | 2.229584 |
| C | -4.047498 | -2.032727 | 0.526472 |
| H | -4.380217 | -3.067017 | 0.604733 |
| H | -4.234229 | -1.537606 | 1.478599 |
| H | -4.637818 | -1.538177 | -0.243894 |
| C | -2.307719 | -2.631254 | -1.185703 |
| H | -2.878269 | -2.116484 | -1.958721 |
| H | -1.254475 | -2.607995 | -1.448155 |
| H | -2.636348 | -3.670490 | -1.159912 |
| Zn | 2.005051 | -0.503936 | 0.044901 |
| C | 2.904731 | -2.172885 | -0.496745 |
| H | 2.453534 | -2.984395 | 0.080916 |
| H | 4.755802 | -2.079406 | 0.672807 |
| C | 4.434404 | -2.220602 | -0.360716 |
| H | 4.919457 | -1.442567 | -0.952622 |
| H | 4.844206 | -3.178783 | -0.694117 |
| H | 2.615483 | -2.360533 | -1.534495 |

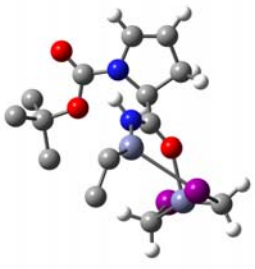
| | | | |
|---|---|---|---|
| H | 5.422180 | -2.395351 | -0.567946 |
| H | 5.555440 | -0.841436 | 0.248743 |
| C | 2.805694 | -0.082615 | -2.587460 |
| H | 3.458960 | 0.309723 | -3.360519 |
| H | 2.130739 | -0.823501 | -3.016186 |
| H | 2.186549 | 0.705957 | -2.156370 |
| C | 7.172573 | -1.246174 | -1.145520 |
| H | 7.826577 | -1.696953 | -0.398765 |
| H | 7.327418 | -1.763329 | -2.091735 |
| H | 7.463474 | -0.203663 | -1.269847 |
| C | 1.156997 | 1.515399 | 2.150204 |
| O | 1.814005 | 0.574403 | 1.737171 |
| C | -0.209599 | 1.391281 | 2.757213 |
| H | -0.915423 | 1.188703 | 1.950938 |
| H | -0.228081 | 0.544505 | 3.439806 |
| H | -0.503546 | 2.302447 | 3.269044 |
| O | 1.592876 | 2.768652 | 2.106211 |
| C | 2.831864 | 3.001854 | 1.378450 |
| H | 3.626883 | 2.441963 | 1.868672 |
| H | 2.693226 | 2.612036 | 0.372712 |
| C | 3.089795 | 4.491449 | 1.391428 |
| H | 3.196475 | 4.865822 | 2.409250 |
| H | 4.012338 | 4.705185 | 0.850809 |
| H | 2.277284 | 5.030176 | 0.905844 |

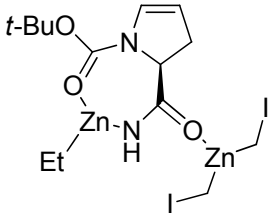





**11**

| | | | |
|---|---|---|---|
| C | 0.738809 | 0.151027 | 2.232414 |
| C | -0.772925 | -0.398308 | 3.693909 |
| C | -1.742954 | -1.551163 | 3.618863 |
| C | -2.135224 | -1.752019 | 2.364816 |
| H | -1.200327 | 1.133157 | 2.171157 |
| H | 0.216801 | -0.732791 | 4.010268 |
| H | -1.087663 | 0.378352 | 4.390382 |
| N | -1.558037 | -0.822895 | 1.482339 |
| H | -2.047743 | -2.145138 | 4.464202 |
| H | -2.800706 | -2.499000 | 1.971061 |
| C | 0.679638 | 0.287732 | 1.705347 |
| N | 1.159411 | 1.473091 | 1.605455 |
| H | 2.143376 | 1.446421 | 1.343593 |
| O | 1.287835 | -0.857803 | 1.460116 |
| C | -1.798432 | -0.676141 | 0.151805 |
| O | -1.283831 | 0.205034 | -0.521557 |
| O | -2.647909 | -1.617457 | -0.302427 |
| C | -3.076637 | -1.651378 | -1.717690 |
| C | -1.872120 | -1.897288 | -2.625438 |
| H | -2.217342 | -2.056509 | -3.647464 |

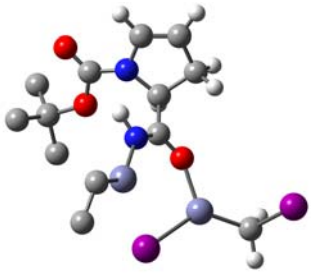


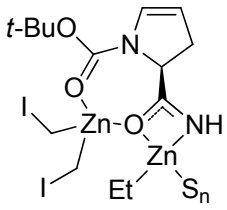



**12**

| | | | |
|---|---|---|---|
| C | -1.630786 | -0.783556 | 1.747673 |
| C | -1.386964 | -0.674267 | 3.288510 |
| C | -1.847373 | -2.013592 | 3.808745 |
| C | -2.396022 | -2.732998 | 2.835920 |
| H | -2.235990 | 0.039386 | 1.378797 |
| H | -0.339013 | -0.468076 | 3.503092 |
| H | -1.961640 | 0.147255 | 3.719829 |
| N | -2.349803 | -2.062232 | 1.594818 |
| H | -1.760178 | -2.327303 | 4.835525 |
| H | -2.853097 | -3.706501 | 2.870718 |
| C | -0.300841 | -0.710734 | 0.989071 |
| N | 0.214127 | -1.799877 | 0.443471 |
| H | -0.400504 | -2.596462 | 0.558196 |
| O | 0.249439 | 0.413141 | 0.978719 |
| C | -3.197924 | -2.396016 | 0.558813 |
| O | -3.889391 | -3.393201 | 0.564061 |
| O | -3.108799 | -1.483353 | -0.425072 |
| C | -3.930624 | -1.596549 | -1.653132 |
| C | -5.414063 | -1.531924 | -1.293501 |
| H | -6.003118 | -1.480692 | -2.209585 |

| | | | |
|---|---|---|---|
| H | -1.190251 | -1.052315 | -2.617730 |
| H | -1.335370 | -2.791958 | -2.308518 |
| C | -4.022260 | -2.850277 | -1.742155 |
| H | -4.414111 | -2.992745 | -2.748695 |
| H | -3.500804 | -3.758938 | -1.442962 |
| H | -4.861073 | -2.693100 | -1.065023 |
| C | -3.824530 | -0.366876 | -2.071035 |
| H | -4.644186 | -0.201260 | -1.371805 |
| H | -3.165634 | 0.495769 | -2.051774 |
| H | -4.248042 | -0.460852 | -3.071457 |
| Zn | 0.262313 | 2.474421 | -0.570041 |
| C | -1.131064 | 3.783698 | -0.032066 |
| H | -1.608486 | 4.187265 | -0.929780 |
| C | -0.634226 | 4.937759 | 0.854701 |
| H | -1.444408 | 5.609183 | 1.158737 |
| H | -0.162564 | 4.568059 | 1.767124 |
| H | 0.108370 | 5.552242 | 0.340450 |
| Zn | 2.547657 | -1.196927 | 0.157797 |
| C | 1.717934 | 1.473479 | -1.526669 |
| H | 2.670614 | 1.667239 | -1.019114 |
| H | 1.473246 | 0.412667 | -1.354859 |
| C | 3.922882 | -1.921243 | -1.024394 |
| C | 1.891688 | 1.703114 | -3.035687 |
| H | 2.147128 | 2.743116 | -3.247487 |
| H | 2.679821 | 1.084712 | -3.477876 |
| H | 0.970949 | 1.487745 | -3.581174 |
| H | -1.913006 | 3.225700 | 0.491530 |
| H | 4.642723 | -1.117049 | -1.184990 |
| H | 3.440542 | -2.093562 | -1.987888 |
| C | 4.627397 | -3.193456 | -0.531960 |
| H | 5.379879 | -3.526304 | -1.251464 |
| H | 5.138964 | -3.036748 | 0.418247 |
| H | 3.929698 | -4.019693 | -0.391521 |
| H | -5.724941 | -2.405817 | -0.728560 |
| H | -5.623702 | -0.636523 | -0.708266 |
| C | -3.511402 | -0.359541 | -2.443188 |
| H | -4.061685 | -0.317677 | -3.382519 |
| H | -3.719171 | 0.549157 | -1.880008 |
| H | -2.446172 | -0.390485 | -2.670034 |
| C | -3.566758 | -2.873358 | -2.408822 |
| H | -2.494047 | -2.908841 | -2.600539 |
| H | -3.857579 | -3.760209 | -1.853703 |
| H | -4.080149 | -2.878943 | -3.370732 |
| Zn | 1.913518 | -2.128042 | -0.405756 |
| C | 3.071677 | -3.325112 | -1.470628 |
| H | 3.947056 | -3.557973 | -0.860215 |
| C | 3.511426 | -2.773855 | -2.835832 |
| H | 4.166212 | -3.477021 | -3.357458 |
| H | 2.659957 | -2.583207 | -3.491105 |
| H | 4.059264 | -1.835562 | -2.739314 |
| Zn | 1.112106 | 1.983757 | -0.066755 |
| C | -0.229798 | 2.658954 | -1.354791 |
| H | 0.105240 | 3.416007 | -2.055472 |
| H | -0.788156 | 1.899585 | -1.892473 |
| C | 2.917317 | 1.987886 | 0.777508 |
| H | 2.932099 | 1.970131 | 1.862834 |
| H | 2.535568 | -4.267829 | -1.601627 |
| H | 3.656976 | 2.695793 | 0.417616 |
| I | 3.869635 | 0.039692 | 0.254803 |
| I | -1.795472 | 3.709371 | -0.180415 |



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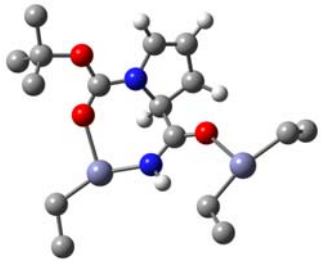
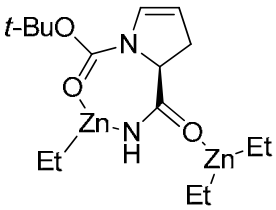


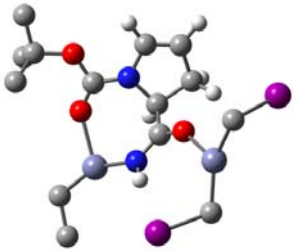


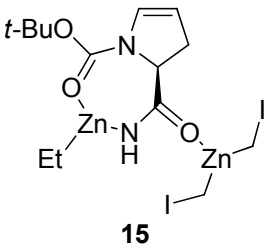

14

| | | | |
|---|---|---|---|
| C | 1.78032 | -2.19783 | 0.42229 |
| C | 1.15476 | -3.30123 | 1.33908 |
| C | 2.16772 | -3.44686 | 2.44796 |
| C | 3.23828 | -2.69735 | 2.20999 |
| H | 1.88265 | -2.54075 | -0.60301 |
| H | 0.17049 | -3.002 | 1.69844 |
| H | 1.0153 | -4.2343 | 0.79093 |
| N | 3.10388 | -1.95246 | 1.0183 |
| H | 2.03794 | -4.08633 | 3.30484 |
| H | 4.14736 | -2.59024 | 2.77557 |
| C | 0.204440 | -1.072396 | -1.486858 |
| C | -0.412358 | -2.333819 | -2.137759 |
| C | 0.133309 | -3.467871 | -1.311306 |
| C | 1.025923 | -3.031073 | -0.432759 |
| H | 0.727544 | -0.448033 | -2.208392 |
| H | -1.497421 | -2.277323 | -2.082405 |
| H | -0.127186 | -2.428016 | -3.187702 |
| N | 1.200794 | -1.626399 | -0.531264 |
| H | -0.170094 | -4.495962 | -1.418614 |
| H | 1.594907 | -3.575525 | 0.298261 |

| | | | |
|---|---|---|---|
| C | 0.87784 | -0.96201 | 0.3733 |
| N | 1.16848 | 0.105 | 1.07294 |
| H | 2.03774 | -0.03699 | 1.57584 |
| O | -0.15171 | -1.12624 | -0.35109 |
| C | 4.19371 | -1.40969 | 0.36835 |
| O | 5.30126 | -1.36058 | 0.85987 |
| O | 3.82579 | -0.9433 | -0.83904 |
| C | 4.79825 | -0.26049 | -1.72605 |
| C | 5.9232 | -1.2216 | -2.10555 |
| H | 6.55657 | -0.75178 | -2.85851 |
| H | 6.53528 | -1.47658 | -1.2456 |
| H | 5.51355 | -2.13668 | -2.53357 |
| C | 3.9448 | 0.08373 | -2.94404 |
| H | 4.55187 | 0.6018 | -3.68569 |
| H | 3.54132 | -0.81945 | -3.40053 |
| H | 3.11485 | 0.73149 | -2.66475 |
| C | 5.3151 | 1.00781 | -1.04978 |
| H | 4.48329 | 1.64745 | -0.75412 |
| H | 5.91347 | 0.77582 | -0.17362 |
| H | 5.93243 | 1.56462 | -1.75518 |
| Zn | 0.43172 | 1.92035 | 1.3274 |
| C | 0.69894 | 3.40713 | 2.6151 |
| H | 0.19019 | 3.11942 | 3.53876 |
| C | 0.21601 | 4.78763 | 2.15371 |
| H | 0.3802 | 5.54942 | 2.92106 |
| H | 0.73637 | 5.12061 | 1.25425 |
| H | -0.85008 | 4.78754 | 1.92292 |
| Zn | -1.72864 | -0.19399 | -1.01879 |
| C | -3.31299 | -1.17936 | -1.66382 |
| H | -3.10844 | -2.1037 | -2.19236 |
| H | 1.76337 | 3.44011 | 2.86117 |
| H | -4.04451 | -0.59605 | -2.21003 |
| I | -4.39648 | -1.83138 | 0.15768 |
| I | -1.28803 | 2.39666 | -0.80797 |

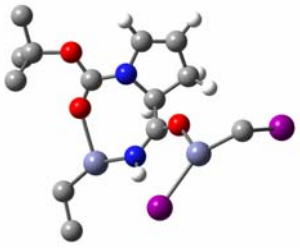
| | | | |
|---|---|---|---|
| C | -0.850756 | -0.214592 | -0.738494 |
| N | -0.493528 | 1.035117 | -0.445458 |
| H | -1.249872 | 1.513887 | 0.031460 |
| O | -1.947098 | -0.734843 | -0.471378 |
| C | 2.267528 | -0.930253 | -0.090113 |
| O | 2.458538 | 0.268443 | -0.352096 |
| O | 3.095382 | -1.674204 | 0.642256 |
| C | 4.333233 | -1.127501 | 1.262318 |
| C | 3.979232 | -0.020922 | 2.252350 |
| H | 4.871649 | 0.250323 | 2.816707 |
| H | 3.610573 | 0.866906 | 1.747922 |
| H | 3.226388 | -0.367566 | 2.959997 |
| C | 4.886304 | -2.349372 | 1.991149 |
| H | 5.818481 | -2.088941 | 2.490795 |
| H | 4.181069 | -2.704799 | 2.741381 |
| H | 5.085790 | -3.159009 | 1.290340 |
| C | 5.296441 | -0.662476 | 0.173035 |
| H | 5.478014 | -1.464009 | -0.542857 |
| H | 4.913981 | 0.205488 | -0.355390 |
| H | 6.250176 | -0.397132 | 0.629734 |
| Zn | 1.176454 | 1.967812 | -0.663902 |
| C | 2.297869 | 3.565462 | -0.932449 |
| H | 2.919448 | 3.672263 | -0.039331 |
| C | 1.571818 | 4.886525 | -1.228937 |
| H | 2.274238 | 5.713705 | -1.366510 |
| H | 0.969391 | 4.824617 | -2.136650 |
| H | 0.897981 | 5.171072 | -0.419270 |
| Zn | -3.890764 | -0.083605 | 0.697932 |
| C | -3.409308 | 1.753758 | 1.330042 |
| H | -2.475380 | 1.687173 | 1.900006 |
| H | -3.184159 | 2.371418 | 0.452045 |
| C | -4.910184 | -1.764668 | 0.390510 |
| H | -5.863335 | -1.718564 | 0.924446 |
| C | -4.473086 | 2.466222 | 2.183059 |
| H | -4.704654 | 1.902838 | 3.089345 |
| H | -4.160590 | 3.466614 | 2.500282 |
| H | -5.412159 | 2.583917 | 1.638581 |
| H | 2.992502 | 3.328525 | -1.742907 |
| C | -5.160731 | -2.115103 | -1.086142 |
| H | -5.778926 | -1.363184 | -1.582170 |
| H | -4.225950 | -2.176571 | -1.646343 |
| H | -5.673404 | -3.075603 | -1.206998 |
| H | -4.343188 | -2.572443 | 0.864285 |

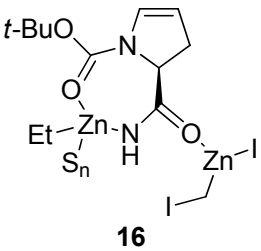





15

| | | | |
|---|---|---|---|
| C | 1.03834 | -1.36821 | -1.2956 |
| C | 0.11915 | -2.52715 | -1.7542 |

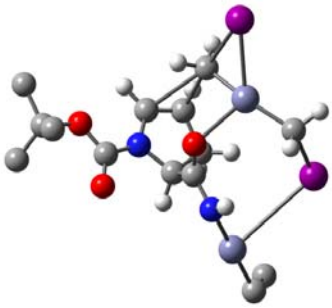


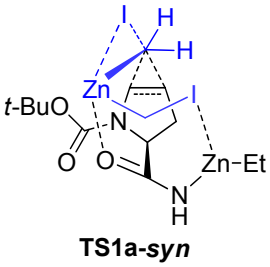



16

| | | | |
|---|---|---|---|
| C | -1.054478 | -1.491498 | 1.052075 |
| C | -0.208761 | -2.768989 | 1.281460 |

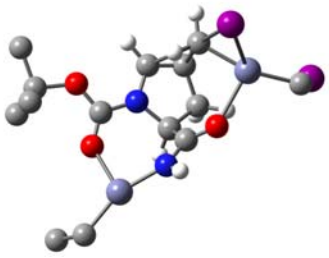
| | | | |
|---|---|---|---|
| C | 0.43728 | -3.63929 | -0.79031 |
| C | 1.44954 | -3.31085 | 0.0007 |
| H | 1.64988 | -0.97952 | -2.10725 |
| H | -0.92469 | -2.22744 | -1.69117 |
| H | 0.32711 | -2.81939 | -2.7856 |
| N | 1.93051 | -2.00748 | -0.29325 |
| H | -0.0994 | -4.57219 | -0.74871 |
| H | 1.91832 | -3.87173 | 0.78814 |
| C | 0.25686 | -0.20106 | -0.64576 |
| N | 0.87868 | 0.96332 | -0.56643 |
| H | 0.29392 | 1.67049 | -0.12672 |
| O | -0.90092 | -0.4435 | -0.23667 |
| C | 3.14385 | -1.5172 | 0.03081 |
| O | 3.57947 | -0.435 | -0.3963 |
| O | 3.82068 | -2.32573 | 0.84289 |
| C | 5.1877 | -2.0085 | 1.34287 |
| C | 5.15923 | -0.7285 | 2.17376 |
| H | 6.12199 | -0.60645 | 2.67026 |
| H | 4.97848 | 0.14726 | 1.55822 |
| H | 4.38963 | -0.78908 | 2.94295 |
| C | 5.48904 | -3.21876 | 2.22265 |
| H | 6.48586 | -3.12279 | 2.65106 |
| H | 4.77006 | -3.29376 | 3.03751 |
| H | 5.45161 | -4.13844 | 1.64025 |
| C | 6.16038 | -1.93233 | 0.16894 |
| H | 6.10973 | -2.84293 | -0.42777 |
| H | 5.95163 | -1.07813 | -0.46808 |
| H | 7.17626 | -1.83768 | 0.55287 |
| Zn | 2.71009 | 1.44549 | -0.96831 |
| C | 4.13567 | 2.68762 | -1.51895 |
| H | 4.78368 | 2.83016 | -0.64999 |
| C | 3.69578 | 4.04956 | -2.07701 |
| H | 4.55374 | 4.66922 | -2.35297 |
| H | 3.07801 | 3.94279 | -2.96999 |
| H | 3.11062 | 4.61693 | -1.35202 |
| Zn | -2.74562 | 0.45687 | 0.31015 |
| C | -3.60596 | -1.05245 | 1.26393 |
| H | -2.94034 | -1.66551 | 1.86275 |
| H | -4.50947 | -0.84618 | 1.82711 |
| C | -2.77806 | 2.30326 | -0.43067 |
| H | -3.74326 | 2.79896 | -0.42609 |
| H | 4.74686 | 2.15786 | -2.25439 |
| H | -2.31251 | 2.45259 | -1.39994 |
| I | -1.5612 | 3.59854 | 0.91428 |
| I | -4.31225 | -2.46532 | -0.30739 |
| C | -0.709996 | -3.721727 | 0.227904 |
| C | -1.748530 | -3.213454 | -0.421908 |
| H | -1.560790 | -1.165295 | 1.958147 |
| H | 0.849912 | -2.547726 | 1.163139 |
| H | -0.357317 | -3.169912 | 2.286100 |
| N | -2.076431 | -1.920514 | 0.063284 |
| H | -0.275508 | -4.687887 | 0.032749 |
| H | -2.334455 | -3.631893 | -1.219504 |
| C | -0.233484 | -0.311727 | 0.487544 |
| N | -0.726389 | 0.896905 | 0.644948 |
| H | -0.115034 | 1.606818 | 0.243191 |
| O | 0.853390 | -0.601907 | -0.083020 |
| C | -3.255150 | -1.283039 | -0.098240 |
| O | -3.544889 | -0.228567 | 0.490015 |
| O | -4.066070 | -1.916593 | -0.940149 |
| C | -5.410730 | -1.391975 | -1.315537 |
| C | -5.267282 | -0.038561 | -2.005959 |
| H | -6.232536 | 0.252463 | -2.420358 |
| H | -4.946136 | 0.734304 | -1.314365 |
| H | -4.553848 | -0.101296 | -2.827231 |
| C | -5.899077 | -2.453290 | -2.297355 |
| H | -6.894183 | -2.192229 | -2.655020 |
| H | -5.232260 | -2.522925 | -3.155838 |
| H | -5.951261 | -3.429588 | -1.817222 |
| C | -6.307295 | -1.337716 | -0.081480 |
| H | -6.327698 | -2.306507 | 0.417322 |
| H | -5.974426 | -0.582313 | 0.623774 |
| H | -7.324605 | -1.097347 | -0.390968 |
| Zn | -2.469767 | 1.456589 | 1.287442 |
| C | -3.722146 | 2.695843 | 2.165050 |
| H | -4.447695 | 3.001554 | 1.406714 |
| C | -3.114150 | 3.932316 | 2.844037 |
| H | -2.407846 | 3.659248 | 3.629368 |
| H | -2.574312 | 4.561663 | 2.135298 |
| H | -3.883344 | 4.556768 | 3.307024 |
| Zn | 2.449433 | 0.389735 | -0.857788 |
| H | -4.288872 | 2.106632 | 2.890775 |
| C | 3.943141 | -0.884270 | -1.149566 |
| H | 3.705573 | -1.732782 | -1.782916 |
| H | 4.875634 | -0.440526 | -1.479036 |
| I | 1.918307 | 2.883678 | -1.147315 |
| I | 4.467900 | -1.817841 | 0.793705 |

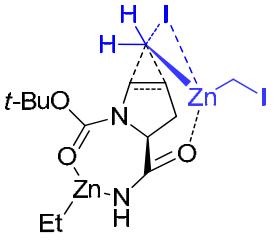





**TS1a-*syn***

| | | | |
|---|---|---|---|
| N | 1.898826 | -1.558408 | 0.902710 |
| C | 2.064566 | -0.659351 | 1.932111 |
| C | 0.879261 | -0.231110 | 2.427823 |
| C | -0.226280 | -1.071719 | 1.823358 |
| C | 0.472053 | -1.775232 | 0.617619 |
| C | 0.064822 | -1.136691 | -0.724815 |
| N | -0.931713 | -1.734532 | -1.390333 |
| Zn | -2.330969 | -2.819740 | -0.731267 |
| Zn | -0.341618 | 1.822527 | -0.072377 |
| C | -2.155649 | 1.849296 | -0.888104 |
| C | 1.088113 | 1.766339 | 1.300708 |
| C | -3.776374 | -3.941012 | -0.049969 |
| O | 0.614119 | -0.089597 | -1.097211 |
| C | 2.877118 | -2.122667 | 0.096555 |
| O | 4.091866 | -1.694718 | 0.455042 |
| C | 5.308118 | -2.126136 | -0.285473 |
| O | 2.597315 | -2.907497 | -0.781408 |
| H | 1.128444 | 2.314751 | 2.236015 |
| H | 2.083871 | 1.583796 | 0.917783 |
| H | -1.100207 | -0.500343 | 1.516939 |
| H | -2.645028 | 2.814021 | -0.800758 |
| H | -2.177153 | 1.550296 | -1.931681 |
| H | -1.145954 | -1.195357 | -2.222491 |
| H | 3.059372 | -0.373933 | 2.225287 |
| H | 0.773153 | 0.301490 | 3.356832 |
| H | 0.272884 | -2.844075 | 0.583462 |
| H | -0.570074 | -1.812595 | 2.548655 |
| H | -4.650997 | -3.709767 | -0.661625 |
| H | -3.528881 | -4.984562 | -0.251980 |
| I | 1.149524 | 4.183531 | -0.162531 |
| I | -3.676375 | 0.495321 | 0.033955 |
| C | 6.416034 | -1.376366 | 0.448445 |
| H | 6.449446 | -1.665321 | 1.498476 |
| H | 7.379825 | -1.609467 | -0.002573 |
| H | 6.259673 | -0.300137 | 0.387716 |
| C | 5.210933 | -1.671078 | -1.739518 |
| H | 4.423876 | -2.198375 | -2.270412 |
| H | 5.015770 | -0.600341 | -1.791939 |
| H | 6.159764 | -1.867277 | -2.239567 |
| C | 5.487394 | -3.636257 | -0.149831 |
| H | 6.446787 | -3.921477 | -0.582139 |
| H | 5.491306 | -3.927788 | 0.900663 |
| H | 4.700411 | -4.178540 | -0.665609 |
| C | -4.101443 | -3.744404 | 1.439126 |
| H | -4.364455 | -2.711405 | 1.667253 |

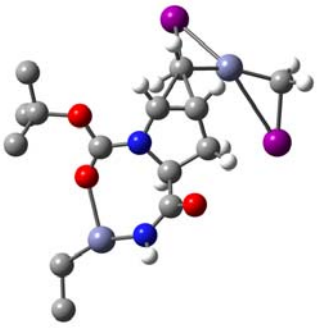


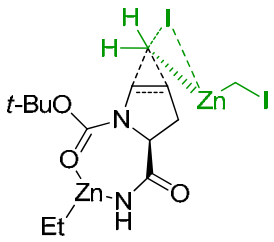



**TS1b-*syn***

| | | | |
|---|---|---|---|
| N | 1.608541 | -0.218021 | 1.144941 |
| C | 0.745114 | 0.338391 | 2.097351 |
| C | -0.447675 | -0.303491 | 2.105740 |
| C | -0.328251 | -1.568911 | 1.285827 |
| C | 0.917207 | -1.319055 | 0.413990 |
| C | 0.567680 | -0.931864 | -1.054395 |
| N | 1.576742 | -0.957578 | -1.922966 |
| Zn | 3.452396 | -1.368883 | -1.751846 |
| Zn | -2.366110 | 0.341274 | -0.438090 |
| C | -3.920124 | -0.839759 | -0.795614 |
| C | -1.174295 | 1.338903 | 0.850600 |
| C | 5.192228 | -2.012121 | -2.412472 |
| O | -0.603190 | -0.665310 | -1.373840 |
| C | 2.934932 | 0.057685 | 1.019364 |
| O | 3.324097 | 1.029418 | 1.831933 |
| C | 4.732110 | 1.533833 | 1.881722 |
| O | 3.678315 | -0.558299 | 0.246297 |
| H | -1.497057 | 1.982370 | 1.663972 |
| H | -0.243553 | 1.699976 | 0.429171 |
| H | -1.201883 | -1.799910 | 0.686901 |
| H | -4.857552 | -0.314663 | -0.943951 |
| H | -3.782312 | -1.552182 | -1.602569 |
| H | 1.228679 | -0.713379 | -2.844082 |
| H | 1.074113 | 1.177642 | 2.681513 |
| H | -1.200597 | -0.165343 | 2.862213 |
| H | 1.578919 | -2.181587 | 0.387885 |
| H | -0.167613 | -2.414304 | 1.958117 |
| H | 5.008647 | -2.764259 | -3.182138 |
| H | 5.672777 | -1.175491 | -2.926354 |
| I | -2.398350 | 3.050038 | -1.088181 |
| I | -4.368729 | -2.148785 | 0.951769 |
| C | 4.632751 | 2.635432 | 2.932068 |
| H | 4.302449 | 2.230955 | 3.887880 |
| H | 5.610039 | 3.094885 | 3.073420 |
| H | 3.932193 | 3.408072 | 2.618555 |
| C | 5.122404 | 2.109044 | 0.523757 |
| H | 5.220622 | 1.333945 | -0.230142 |
| H | 4.386354 | 2.840573 | 0.191466 |
| H | 6.081865 | 2.617420 | 0.618195 |
| C | 5.658830 | 0.415023 | 2.346643 |
| H | 6.653988 | 0.826396 | 2.515603 |
| H | 5.306289 | -0.007450 | 3.287352 |
| H | 5.735906 | -0.377905 | 1.608801 |
| C | 6.132160 | -2.574730 | -1.335307 |
| H | 5.706597 | -3.448966 | -0.840086 |

| | | | |
|---|---|---|---|
| H | -4.947659 | -4.367199 | 1.739020 |
| H | -3.261636 | -4.015746 | 2.080318 |

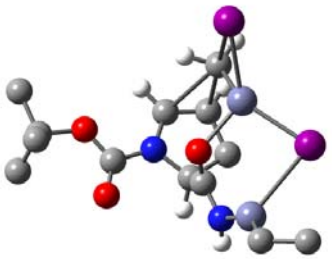


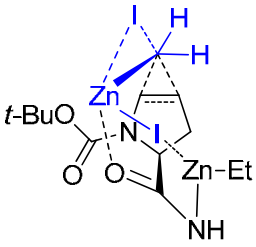



**TS1c-*anti***

| | | | |
|---|---|---|---|
| N | 1.731182 | 0.343713 | 1.310495 |
| C | 0.789023 | 0.949178 | 2.135734 |
| C | 0.233590 | 0.113707 | 2.419163 |
| C | 0.055735 | -1.259903 | 1.866575 |
| C | 1.424606 | -1.108717 | 1.160212 |
| C | 2.524693 | -1.971225 | 1.849445 |
| N | 3.604881 | -2.253607 | 1.097279 |
| Zn | 4.184734 | -1.594526 | -0.598544 |
| C | 5.113500 | -1.564275 | -2.331218 |
| O | 2.348229 | -2.343347 | 3.004951 |
| C | 2.623903 | 1.002637 | 0.512962 |
| O | 2.647923 | 2.305810 | 0.762194 |
| C | 3.517183 | 3.256782 | 0.002102 |
| O | 3.303699 | 0.431145 | -0.340189 |
| H | 0.165548 | -1.975745 | 2.680483 |
| H | 4.235119 | -2.842464 | 1.629718 |
| H | 0.940695 | 1.965287 | 2.452523 |
| H | 1.372967 | -1.340595 | 0.098698 |
| H | 0.717985 | -1.622279 | 1.191185 |
| H | 5.772306 | -0.692033 | -2.324108 |
| H | 4.355482 | -1.351349 | -3.089660 |
| C | 3.177209 | 4.588826 | 0.663186 |
| H | 2.116514 | 4.813066 | 0.559955 |
| H | 3.744586 | 5.387976 | 0.188204 |
| H | 3.430007 | 4.571137 | 1.722653 |
| C | 4.985090 | 2.900462 | 0.216103 |
| H | 5.248809 | 1.967403 | -0.272316 |
| H | 5.209788 | 2.823230 | 1.279679 |
| H | 5.605371 | 3.693532 | -0.201665 |
| C | 3.110457 | 3.255191 | -1.468324 |
| H | 3.658111 | 4.041400 | -1.988152 |
| H | 2.045887 | 3.463749 | -1.571863 |
| H | 3.335738 | 2.306947 | -1.947256 |
| C | 5.906358 | -2.822314 | -2.717803 |
| H | 6.381339 | -2.715833 | -3.697141 |
| H | 5.268469 | -3.706112 | -2.766202 |
| H | 6.699341 | -3.040340 | -2.000523 |
| H | 0.973977 | 0.309106 | 3.175259 |
| C | 1.481990 | 1.351700 | 0.876882 |
| Zn | 3.114077 | 0.285054 | 0.545381 |
| I | 3.295519 | 2.626826 | -0.867181 |

| | | | |
|---|---|---|---|
| H | 7.091295 | -2.882626 | -1.760452 |
| H | 6.345280 | -1.839862 | -0.557922 |

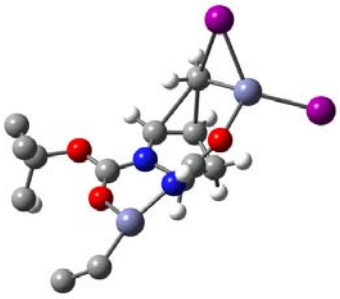


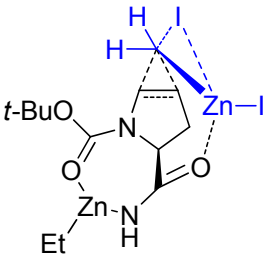



**TS2a-*syn***

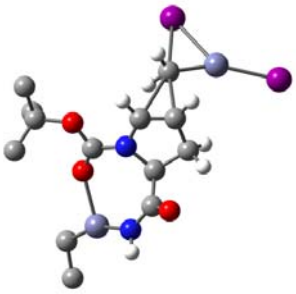
| | | | |
|---|---|---|---|
| N | 2.62260900 | -0.74599800 | 1.28190500 |
| C | 2.71080600 | 0.44828500 | 1.96041700 |
| C | 1.66866500 | 0.63244700 | 2.80292400 |
| C | 0.85140000 | -0.64073600 | 2.85892300 |
| C | 1.41858700 | -1.49404200 | 1.67586700 |
| C | 0.38989000 | -1.60579700 | 0.54111700 |
| N | -0.40239800 | -2.64978600 | 0.50230400 |
| Zn | -2.01218500 | -2.48052300 | -0.61715700 |
| Zn | -0.75657700 | 1.06798300 | 0.30151100 |
| C | 0.68104300 | 2.10541400 | 1.22735300 |
| C | -3.18522900 | -3.19104000 | -2.03913500 |
| O | 0.25016800 | -0.64703000 | -0.27297800 |
| C | 3.48284400 | -1.24597600 | 0.31434700 |
| O | 4.46116800 | -0.37426300 | 0.05265200 |
| C | 5.51072400 | -0.67832500 | -0.95878500 |
| O | 3.31523800 | -2.34171700 | -0.17148300 |
| H | 0.56667200 | 2.90466000 | 1.95610300 |
| H | 1.58773100 | 2.24965600 | 0.65151200 |
| H | -0.22065700 | -0.47560700 | 2.76401300 |
| H | -0.18312100 | -3.38820100 | 1.15570300 |
| H | 3.54109300 | 1.10336600 | 1.76312400 |
| H | 1.62584900 | 1.40419200 | 3.55216600 |
| H | 1.70537500 | -2.49380800 | 1.99251400 |
| H | 1.01078600 | -1.15490600 | 3.80842700 |
| H | -2.90151300 | -2.66784200 | -2.95560900 |
| H | -2.91864600 | -4.23884000 | -2.19557100 |
| I | -0.62149300 | 3.48049100 | -0.92082300 |
| C | 6.36930500 | 0.58253000 | -0.92338500 |
| H | 6.78664700 | 0.73937000 | 0.07077800 |
| H | 7.19264200 | 0.48585600 | -1.62994400 |
| H | 5.78222900 | 1.45801000 | -1.19785000 |
| C | 4.86600200 | -0.86163000 | -2.33032300 |
| H | 4.25450900 | -1.75821800 | -2.36817900 |
| H | 4.24649200 | -0.00033500 | -2.57888300 |
| H | 5.64977300 | -0.94305800 | -3.08380400 |
| C | 6.31373000 | -1.89868500 | -0.51489500 |
| H | 7.15713300 | -2.03568100 | -1.19192400 |
| H | 6.70962100 | -1.75067800 | 0.49003600 |
| H | 5.70890200 | -2.80061300 | -0.52918900 |
| C | -4.69343100 | -3.05113200 | -1.79595300 |
| H | -4.98416700 | -2.01068000 | -1.64914000 |

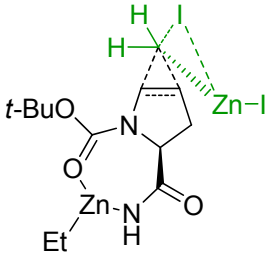
| | | | |
|---|---|---|---|
| C | 4.359899 | -1.227777 | 0.593948 |
| H | 4.550144 | -1.674786 | 1.563270 |
| H | 5.298491 | -1.061902 | 0.078240 |
| I | 3.395307 | -2.858133 | -0.561679 |
| H | 0.712658 | 1.423269 | 0.117769 |
| H | 1.503689 | 2.235520 | 1.501858 |
| H | -5.27221800 | -3.43356900 | -2.64139800 |
| H | -5.01624600 | -3.60197100 | -0.91086100 |
| I | -3.09598000 | -0.06819300 | 0.69311700 |






**TS2b-*syn***






**TS2c-*anti***

| | | | |
|---|---|---|---|
| N | 1.614753 | 0.241117 | 1.217562 |
| C | 0.829100 | 1.066733 | 2.034089 |
| C | -0.294612 | 0.428485 | 2.431326 |
| C | -0.187886 | -1.036996 | 2.073807 |
| C | 0.940578 | -1.074313 | 1.022172 |
| C | 0.434783 | -1.266567 | -0.437071 |
| N | 1.344691 | -1.667143 | -1.318042 |
| Zn | 3.250715 | -1.945010 | -1.182483 |
| Zn | -2.435894 | -0.004973 | 0.003517 |
| C | -1.325990 | 1.507455 | 0.775907 |
| C | 4.945906 | -2.813406 | -1.679976 |
| O | -0.763113 | -1.093725 | -0.733125 |
| C | 2.890933 | 0.498699 | 0.820308 |
| O | 3.286677 | 1.715194 | 1.163918 |
| C | 4.644900 | 2.253614 | 0.834958 |
| O | 3.589567 | -0.331638 | 0.227433 |
| H | -1.677851 | 2.345460 | 1.372290 |
| H | -0.474194 | 1.802993 | 0.173020 |
| H | -1.108542 | -1.475881 | 1.699999 |
| H | 0.904801 | -1.791570 | -2.223797 |
| H | 1.156956 | 2.068160 | 2.242792 |
| H | -0.967794 | 0.804105 | 3.182463 |
| H | 1.660142 | -1.862193 | 1.231544 |
| H | 0.099053 | -1.602709 | 2.962827 |
| H | 4.814060 | -3.890096 | -1.551535 |
| H | 5.089141 | -2.663299 | -2.752804 |
| I | -2.901350 | 2.230699 | -1.487095 |
| C | 5.708738 | 1.419081 | 1.540721 |
| H | 5.762217 | 0.411486 | 1.139643 |
| H | 6.679802 | 1.895301 | 1.405043 |
| H | 5.506788 | 1.367839 | 2.610417 |
| C | 4.572330 | 3.660283 | 1.419937 |
| H | 3.778223 | 4.236678 | 0.947392 |
| H | 4.387452 | 3.624621 | 2.492715 |
| H | 5.517081 | 4.175449 | 1.251993 |
| C | 4.827156 | 2.300984 | -0.678720 |
| H | 5.743765 | 2.844615 | -0.907330 |

| | | | |
|---|---|---|---|
| N | 1.734578 | -0.080070 | -1.230060 |
| C | 0.702652 | 0.303844 | -2.086014 |
| C | -0.294491 | -0.602144 | -2.096956 |
| C | 0.087569 | -1.804488 | -1.272560 |
| C | 1.500328 | -1.468404 | -0.736843 |
| C | 2.574828 | -2.443005 | -1.308038 |
| N | 3.723135 | -2.523324 | -0.610043 |
| Zn | 4.416547 | -1.482377 | 0.833071 |
| C | 5.490851 | -1.050711 | 2.422961 |
| O | 2.318518 | -3.074934 | -2.327491 |
| C | 2.662709 | 0.758148 | -0.684416 |
| O | 2.613600 | 1.973157 | -1.217610 |
| C | 3.522285 | 3.080011 | -0.786697 |
| O | 3.434985 | 0.408838 | 0.210175 |
| H | 0.158106 | -2.688285 | -1.905564 |
| H | 4.330117 | -3.206819 | -1.048149 |
| H | 0.786265 | 1.226704 | -2.631220 |
| H | 1.543402 | -1.457962 | 0.350224 |
| H | -0.622596 | -2.012567 | -0.473219 |
| H | 6.212459 | -0.285686 | 2.124312 |
| H | 4.819241 | -0.557826 | 3.130749 |
| C | 3.267837 | 3.408391 | 0.681311 |
| H | 3.581488 | 2.599893 | 1.334754 |
| H | 3.830002 | 4.303776 | 0.946801 |
| H | 2.211039 | 3.614024 | 0.850044 |
| C | 3.072714 | 4.224366 | -1.689768 |
| H | 3.210763 | 3.966979 | -2.739133 |
| H | 2.022701 | 4.460279 | -1.522579 |
| H | 3.662392 | 5.114369 | -1.474332 |
| C | 4.971797 | 2.697995 | -1.070366 |
| H | 5.606404 | 3.568072 | -0.901678 |
| H | 5.311529 | 1.896677 | -0.421347 |
| H | 5.091267 | 2.391209 | -2.109247 |
| C | 6.215531 | -2.219647 | 3.107799 |
| H | 6.781140 | -1.888026 | 3.983082 |
| H | 5.518335 | -2.986353 | 3.448959 |
| H | 6.923347 | -2.708773 | 2.436613 |

| | | | |
|---|---|---|---|
| H | 4.905987 | 1.306789 | -1.107923 |
| H | 3.997850 | 2.828921 | -1.148583 |
| C | 6.186300 | -2.337265 | -0.910552 |
| H | 6.089786 | -2.507563 | 0.162754 |
| H | 7.087721 | -2.860996 | -1.239891 |
| H | 6.365802 | -1.270300 | -1.049665 |
| I | -4.163131 | -1.688538 | 0.815996 |
| H | -1.116228 | -0.588778 | -2.791653 |
| C | -1.494366 | 0.951909 | -0.687663 |
| Zn | -3.074339 | -0.068923 | -0.077814 |
| I | -3.190065 | 2.432649 | 0.953793 |
| H | -0.660438 | 1.139850 | -0.023194 |
| H | -1.572037 | 1.703752 | -1.462762 |
| I | -4.483844 | -2.098986 | 0.084782 |

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