Supporting Information

for

How Intramolecular Coordination Bonding (ICB) Control the Homolysis of the C—ON Bond in Alkoxyamines

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1) Characterization of compounds

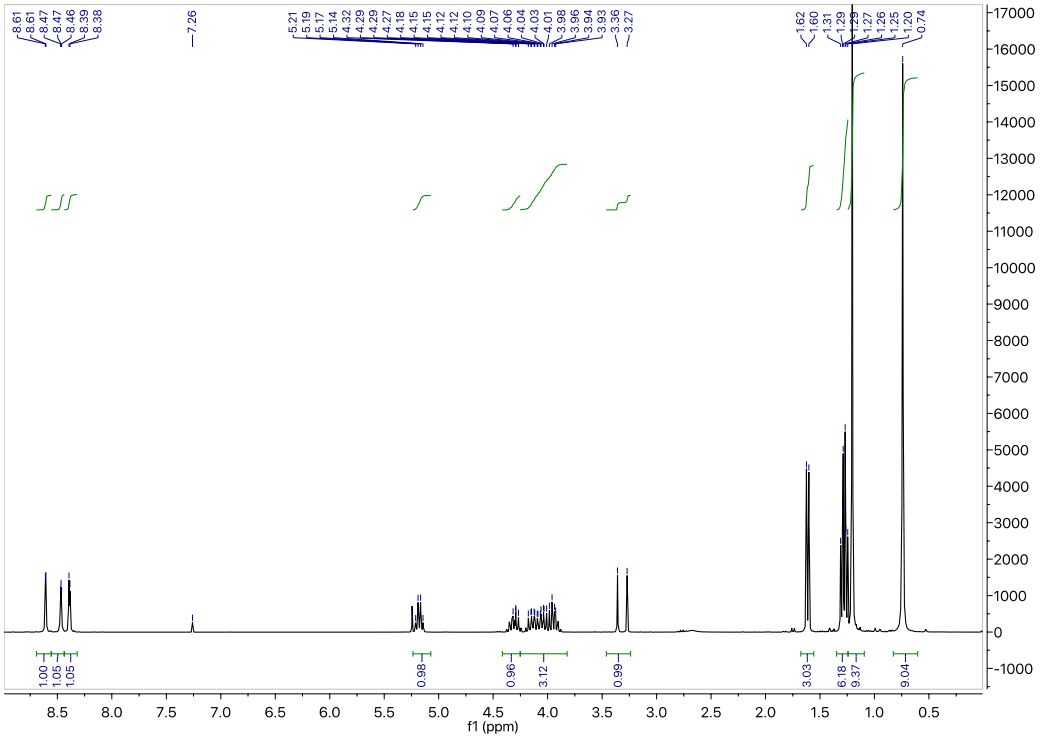
a. ^{1}H, ^{13}C NMR for **4-6** and HRMS data for **4-6**

b. Measurements of k_d for compounds **6**-*RS/SR*

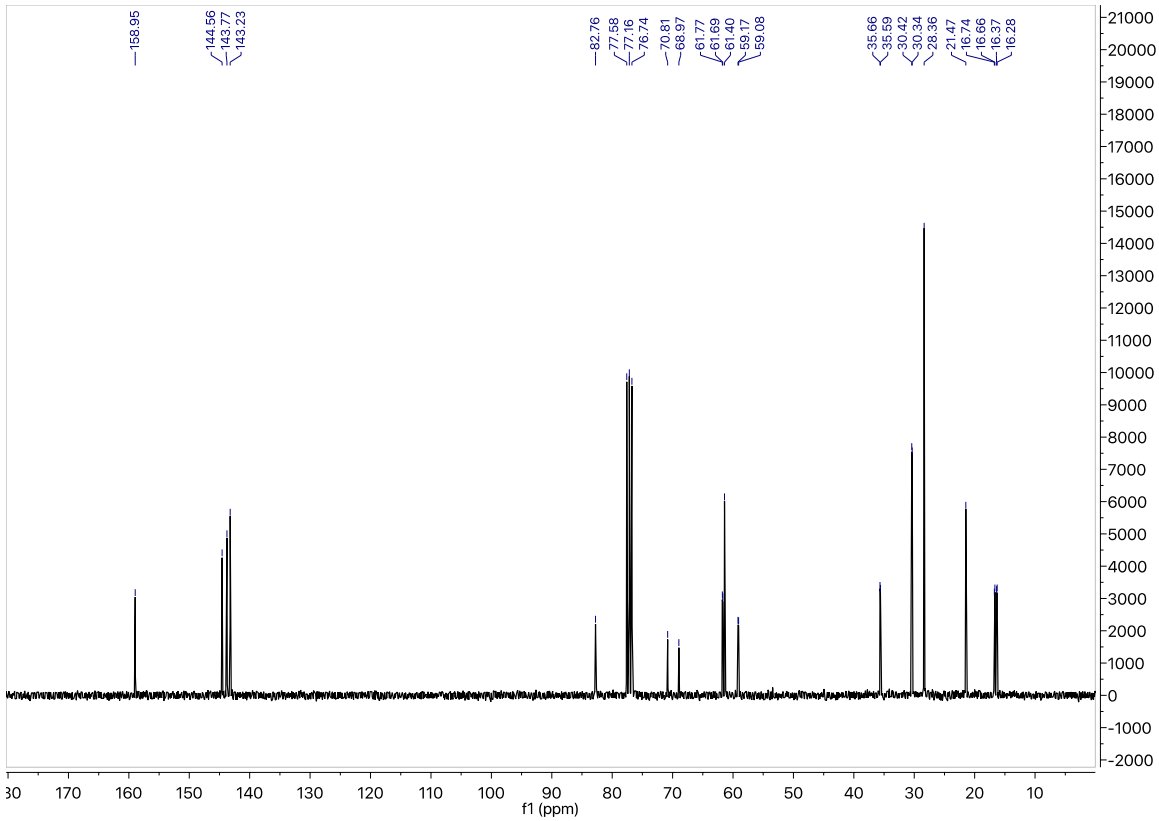
c. NMR data on py addition to the solution of [Zn(hfac)$_2$(**1**-RS/SR)], [Zn(hfac)$_2$(**3**-RS/SR)], [(Zn(hfac)$_2$)**3**(4-RS/SR)$_2$].

a) ^{1}H, ^{13}C NMR for **4-6** and HRMS data for **4-6**

RRSS-**4** (300 MHz, $CDCl_3$)



RRSS-**4** (75 MHz, $CDCl_3$)



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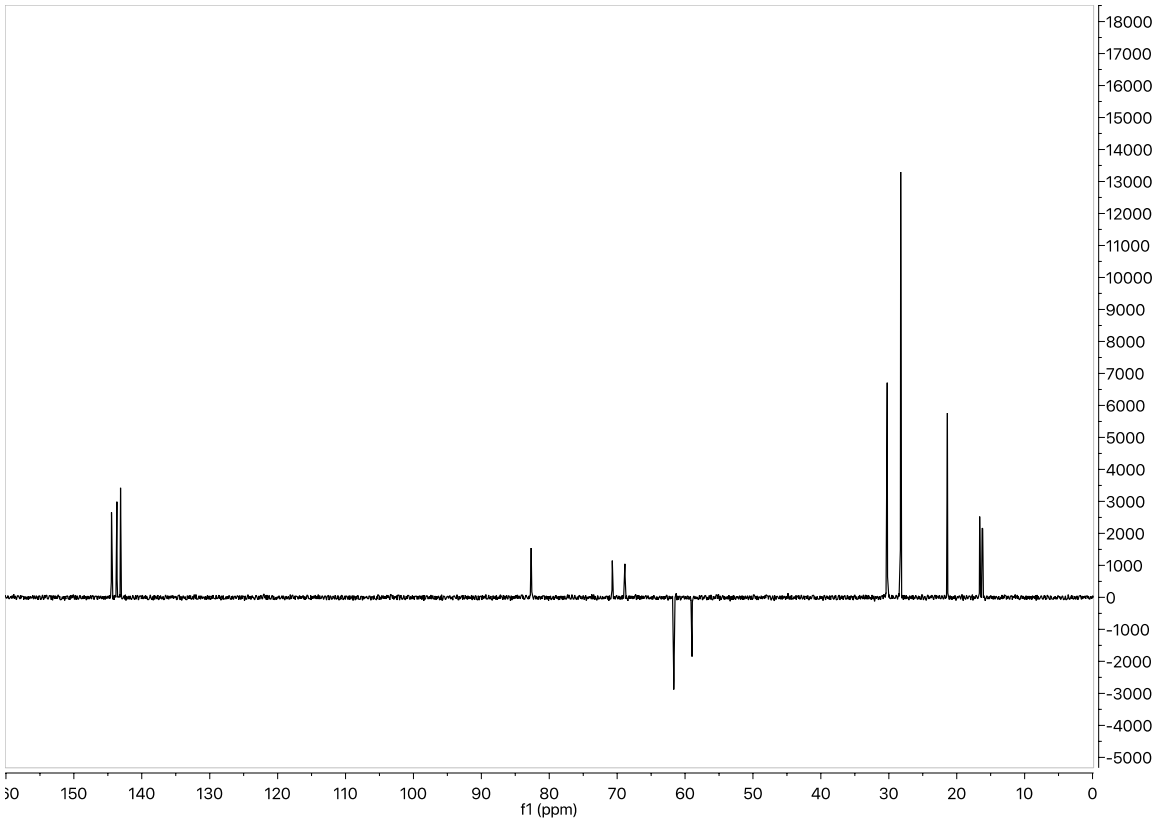
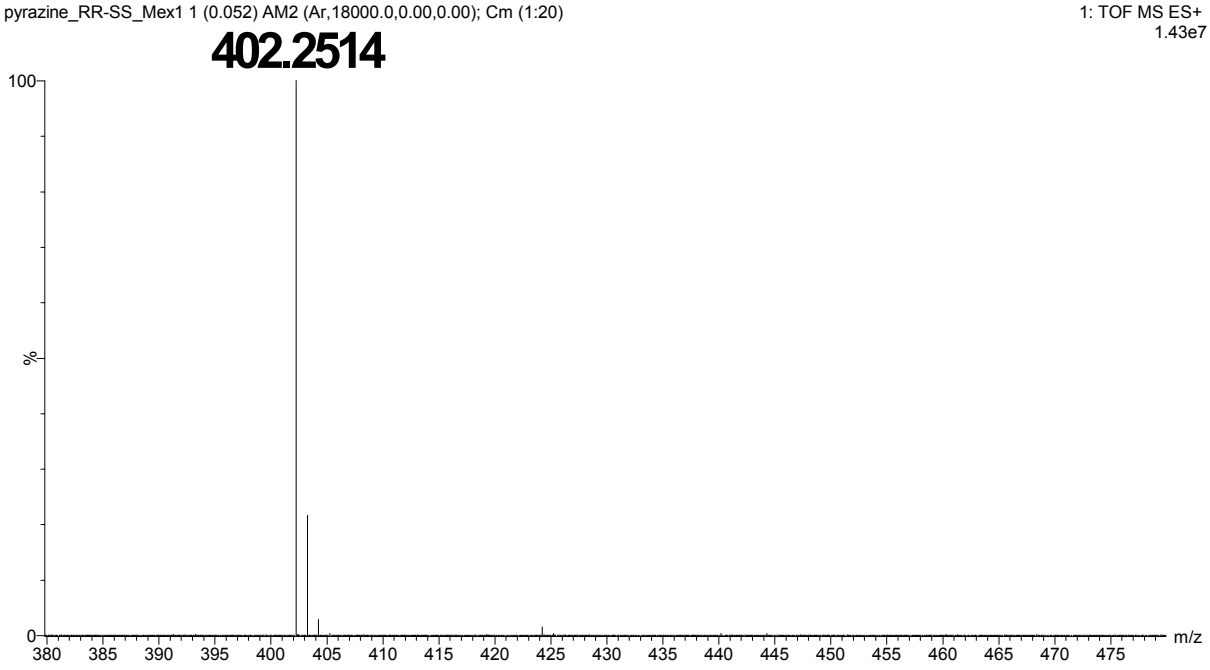
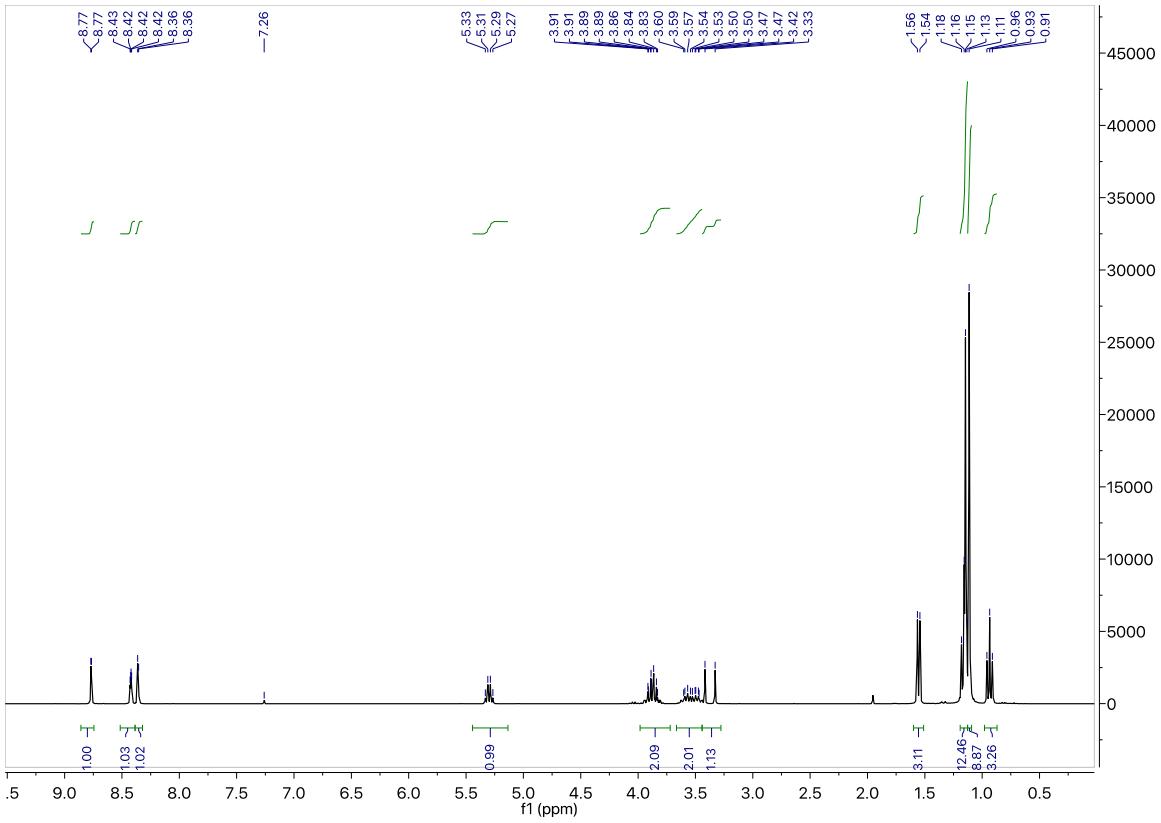


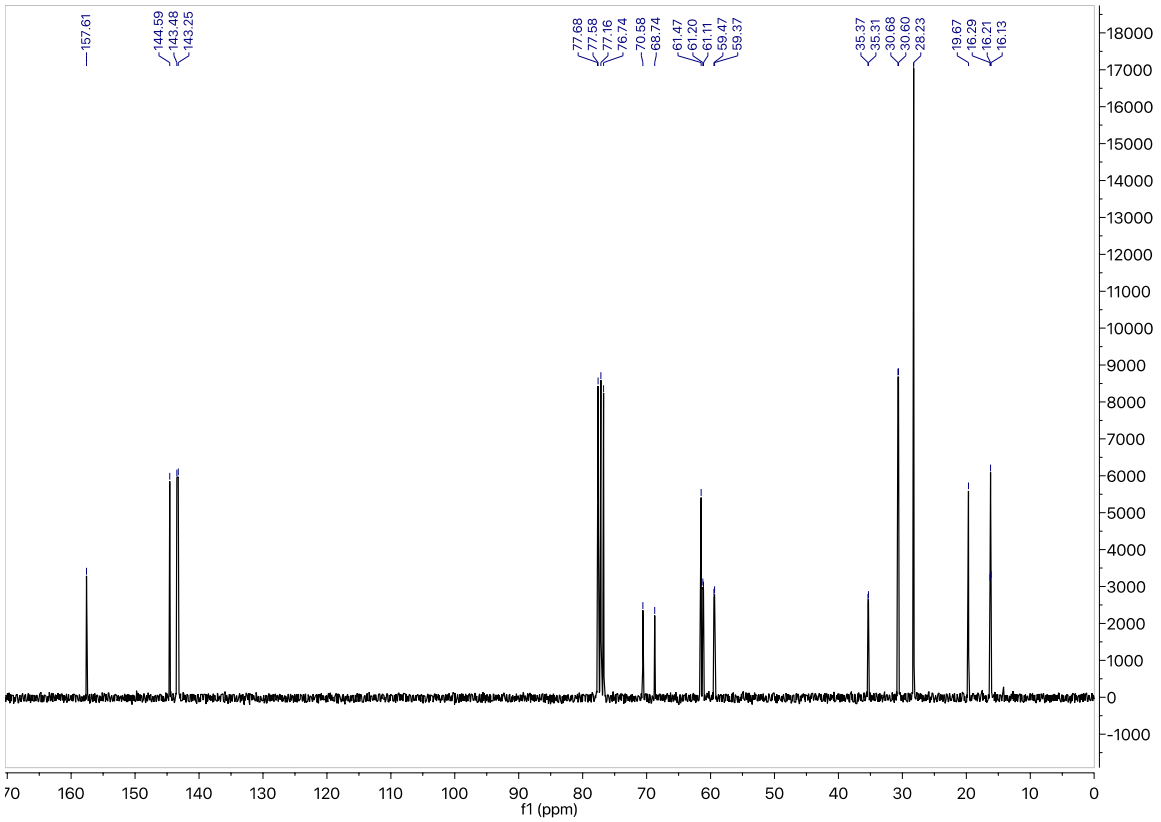
RRSS-**4** HRMS



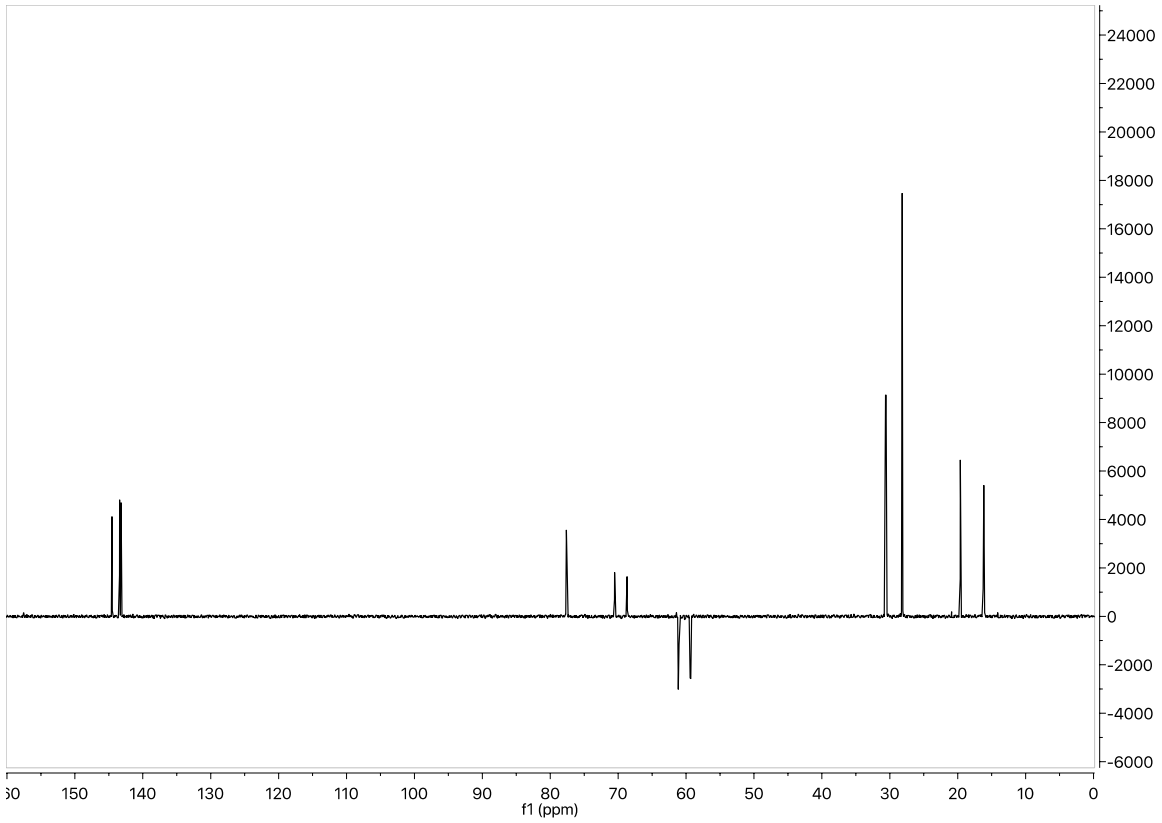
RSSR-**4** (300 MHz, $CDCl_3$)



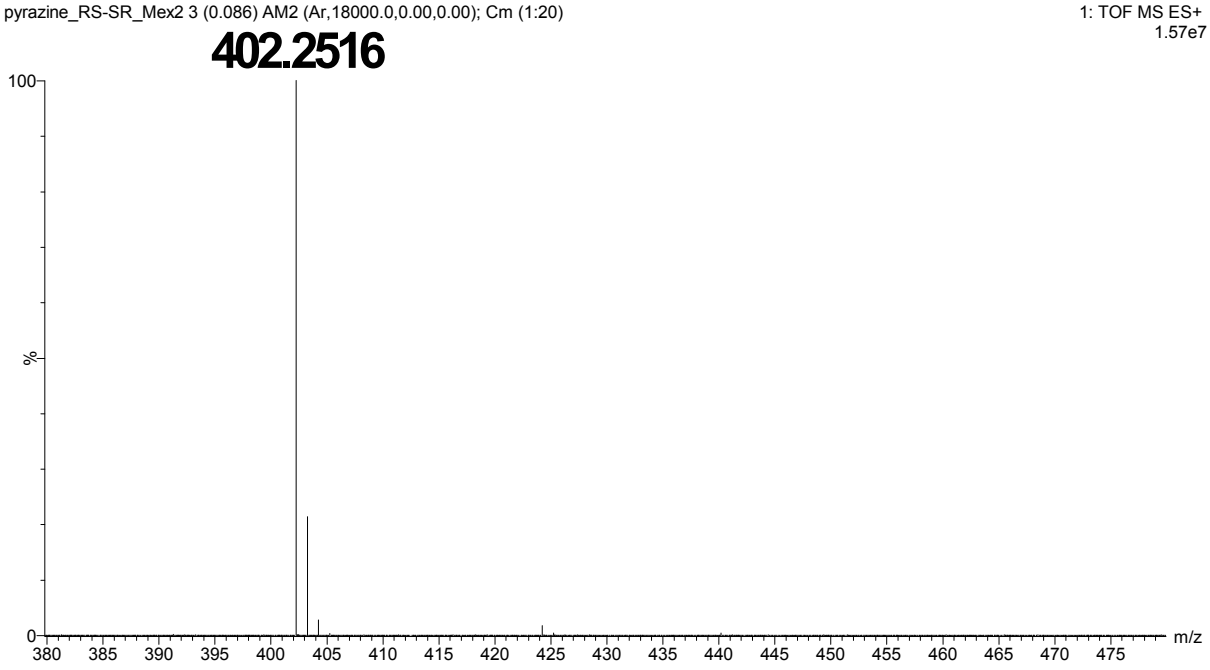
RSSR-**4** (75 MHz, $CDCl_3$)



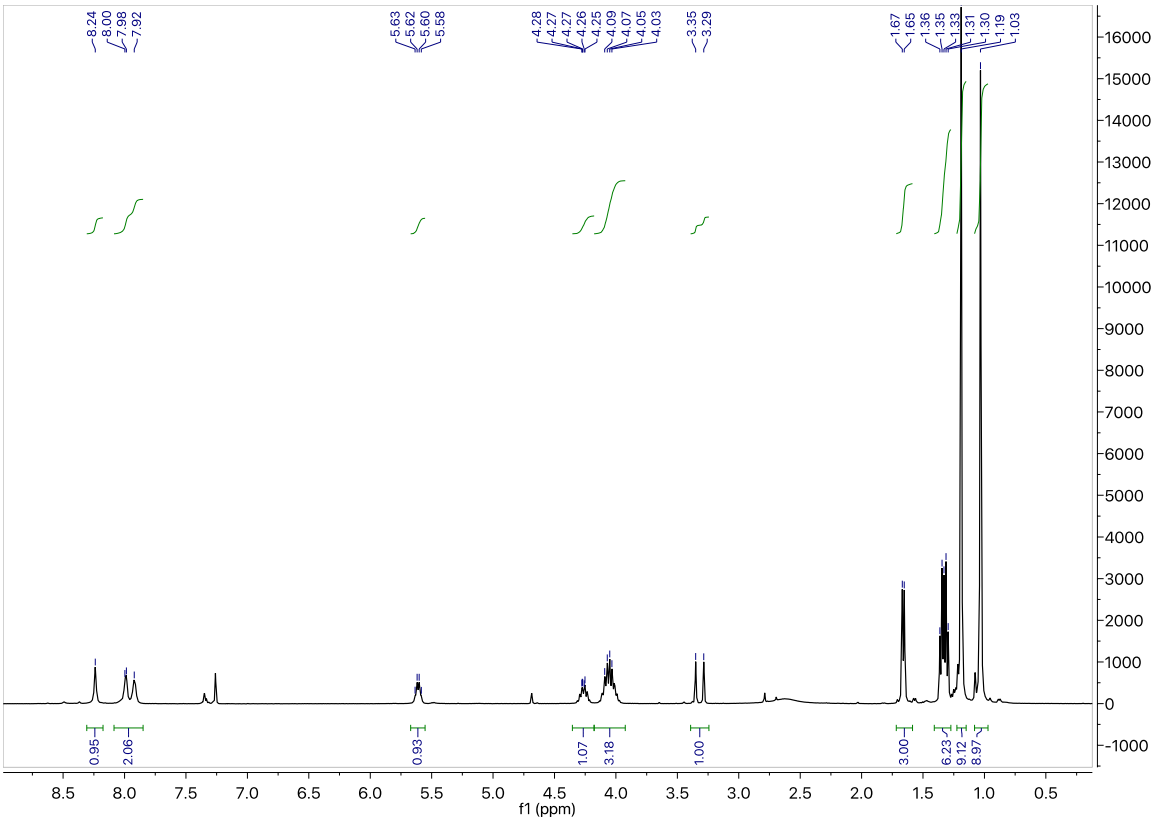
RSSR-**4** (DEPT 135, $CDCl_3$)



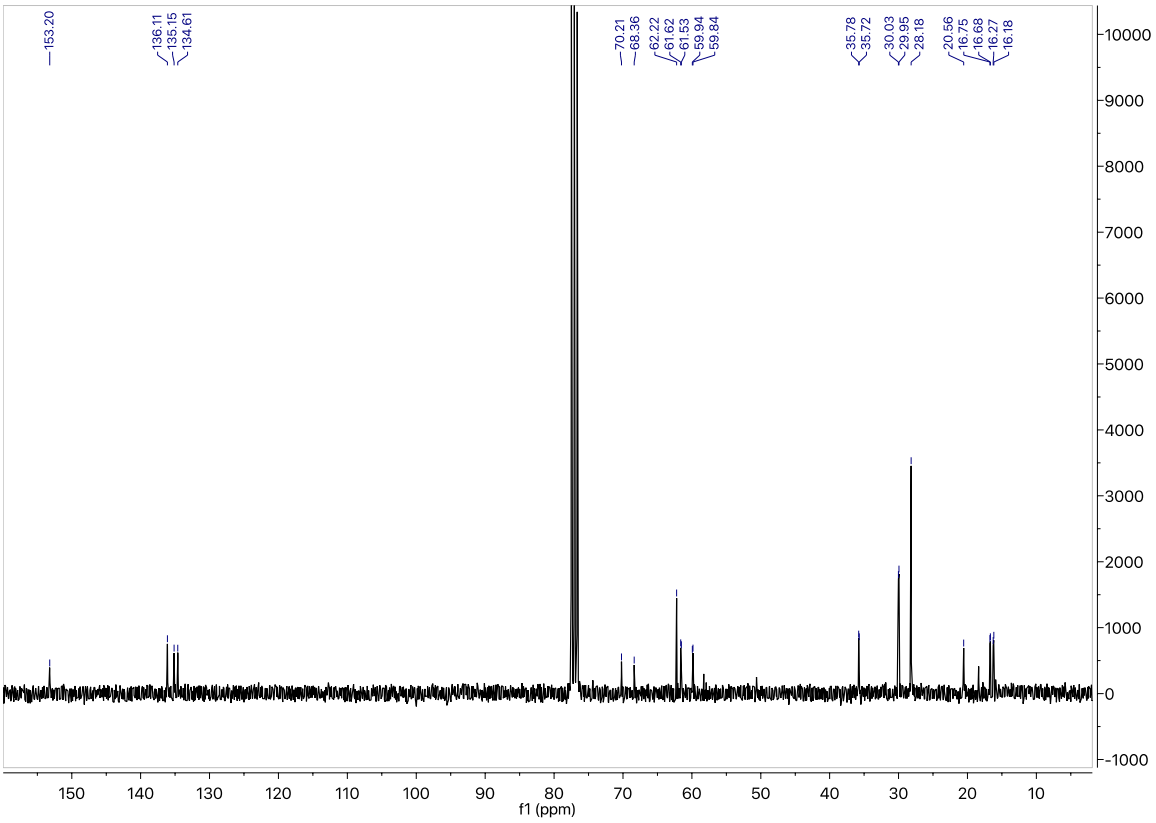
RSSR-**4** HRMS



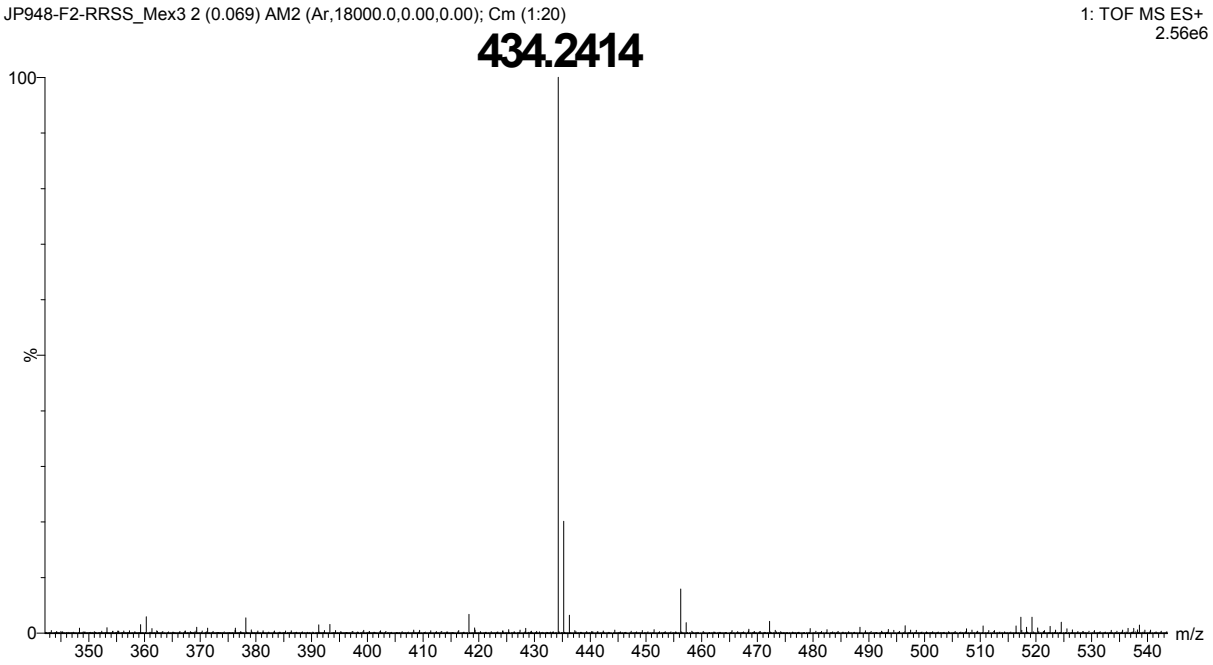
RRSS-**5** (400 MHz, $CDCl_3$)



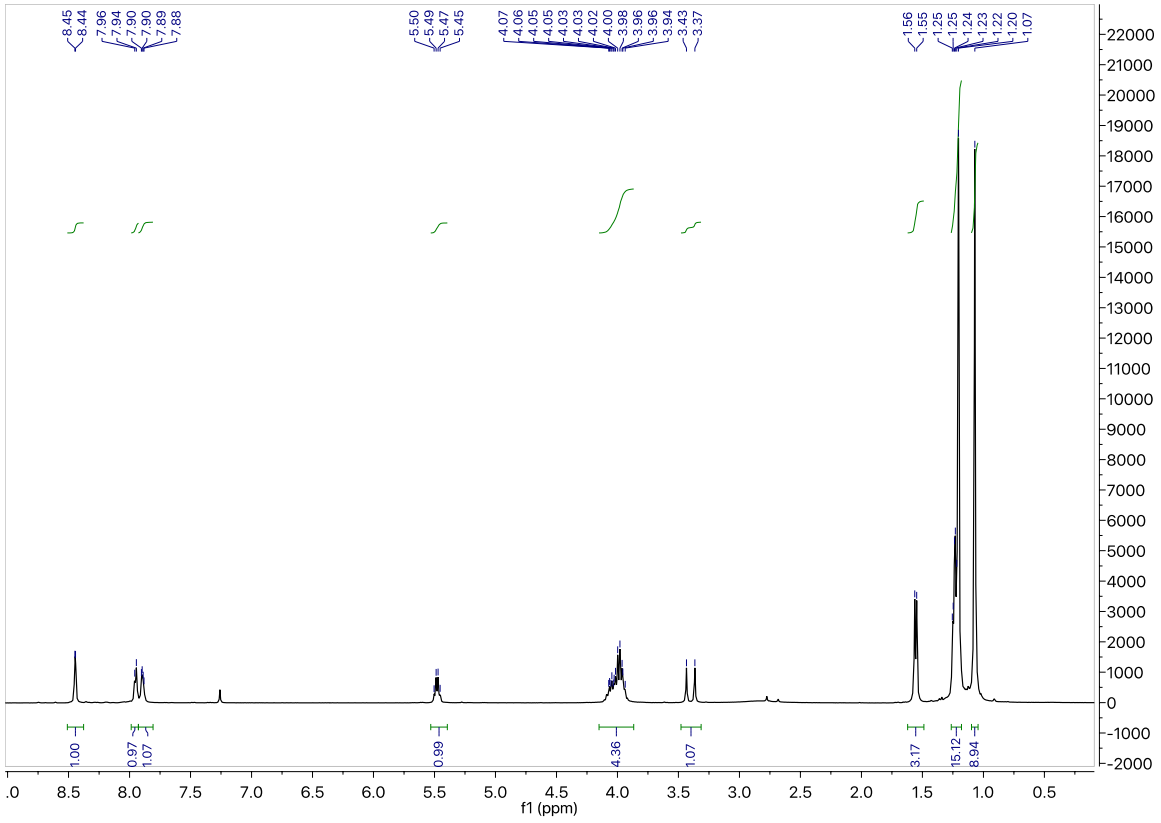
RRSS-**5** (75 MHz, $CDCl_3$)



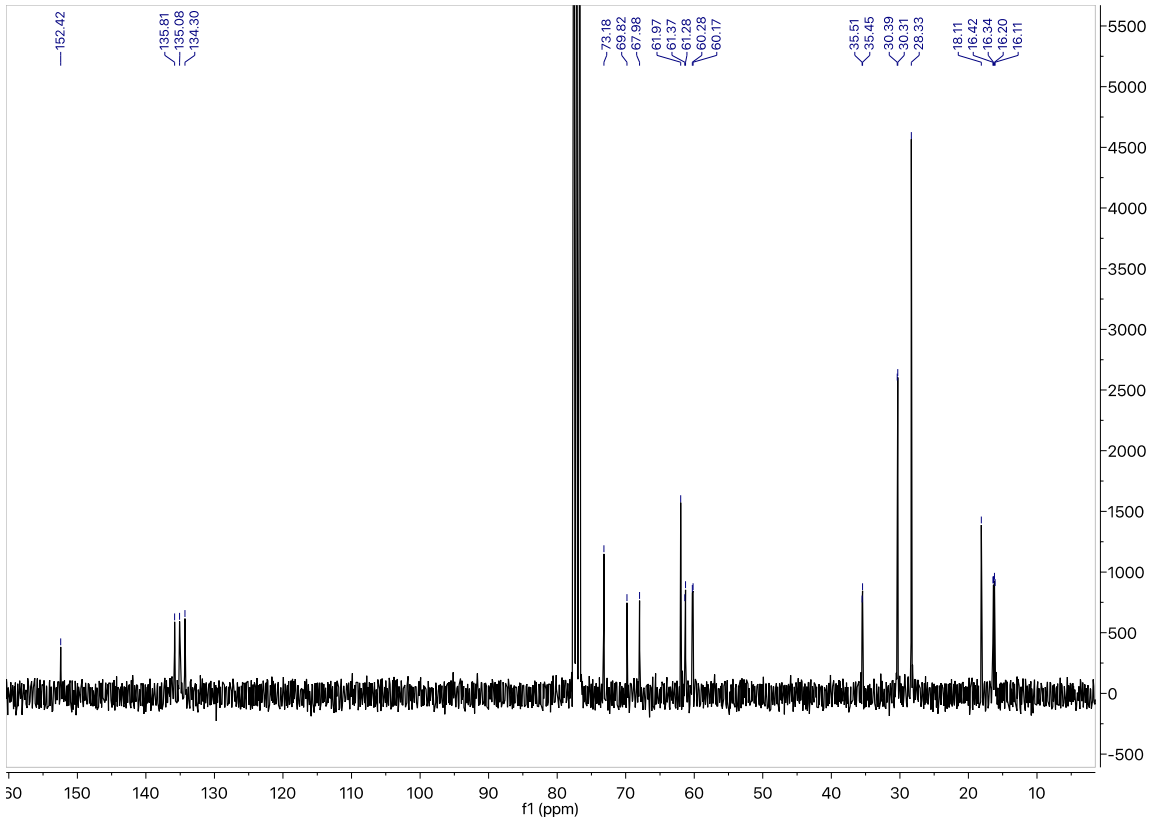
RRSS-**5** HRMS



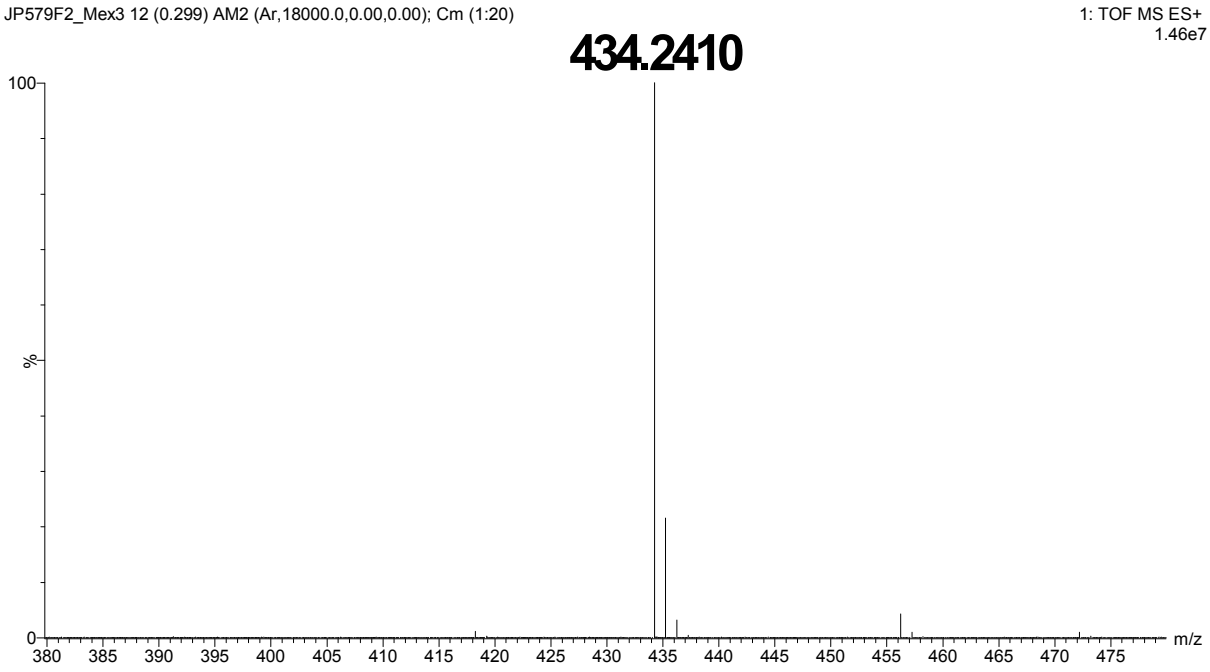
RSSR-**5** (400 MHz, $CDCl_3$)



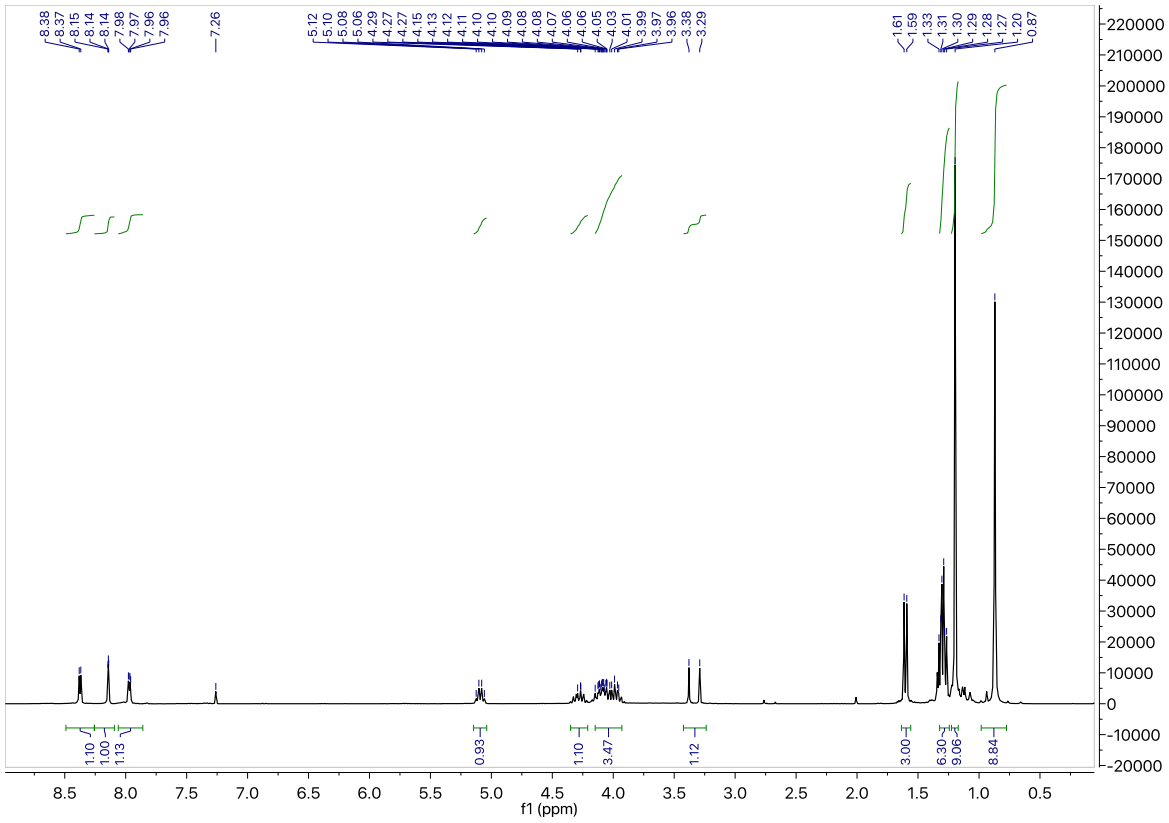
RSSR-**5** (75 MHz, $CDCl_3$)



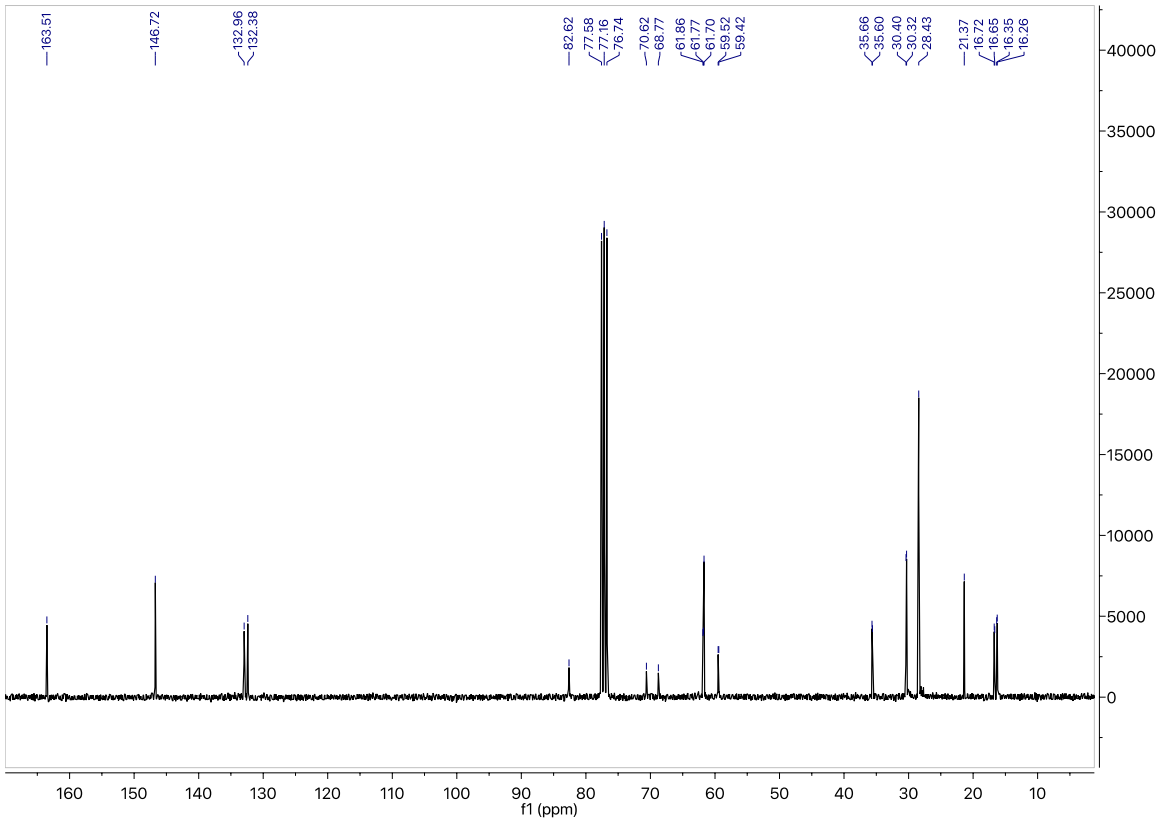
RSSR-**5** HRMS



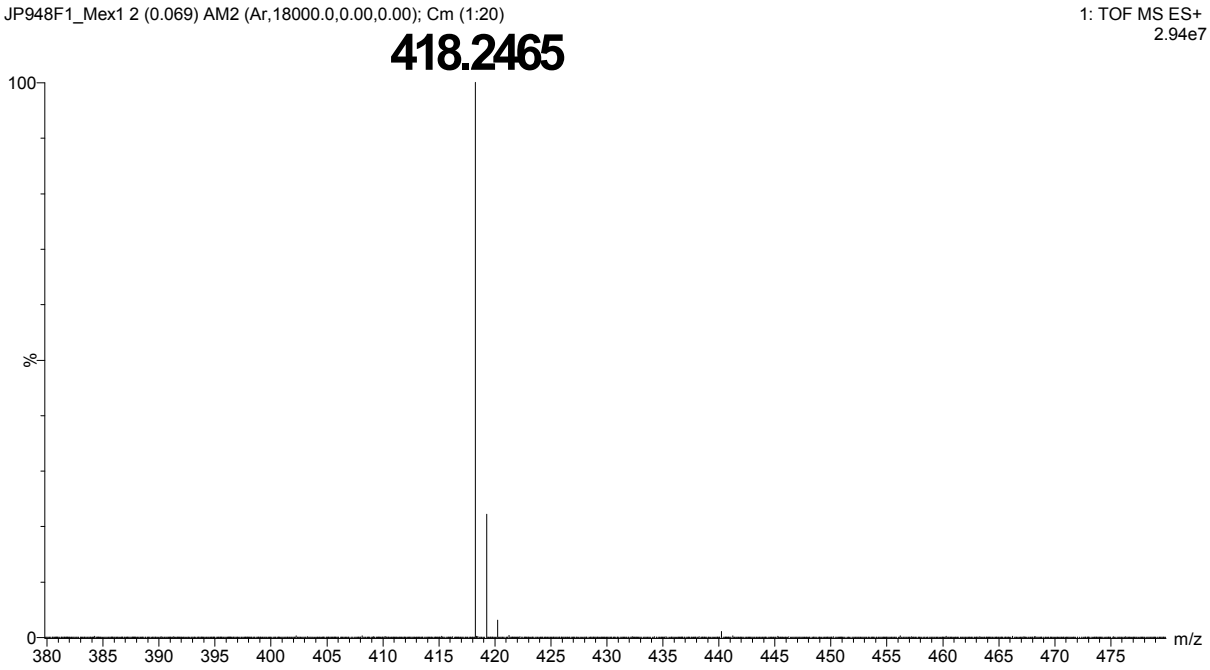
RRSS-**6** (300 MHz, $CDCl_3$)



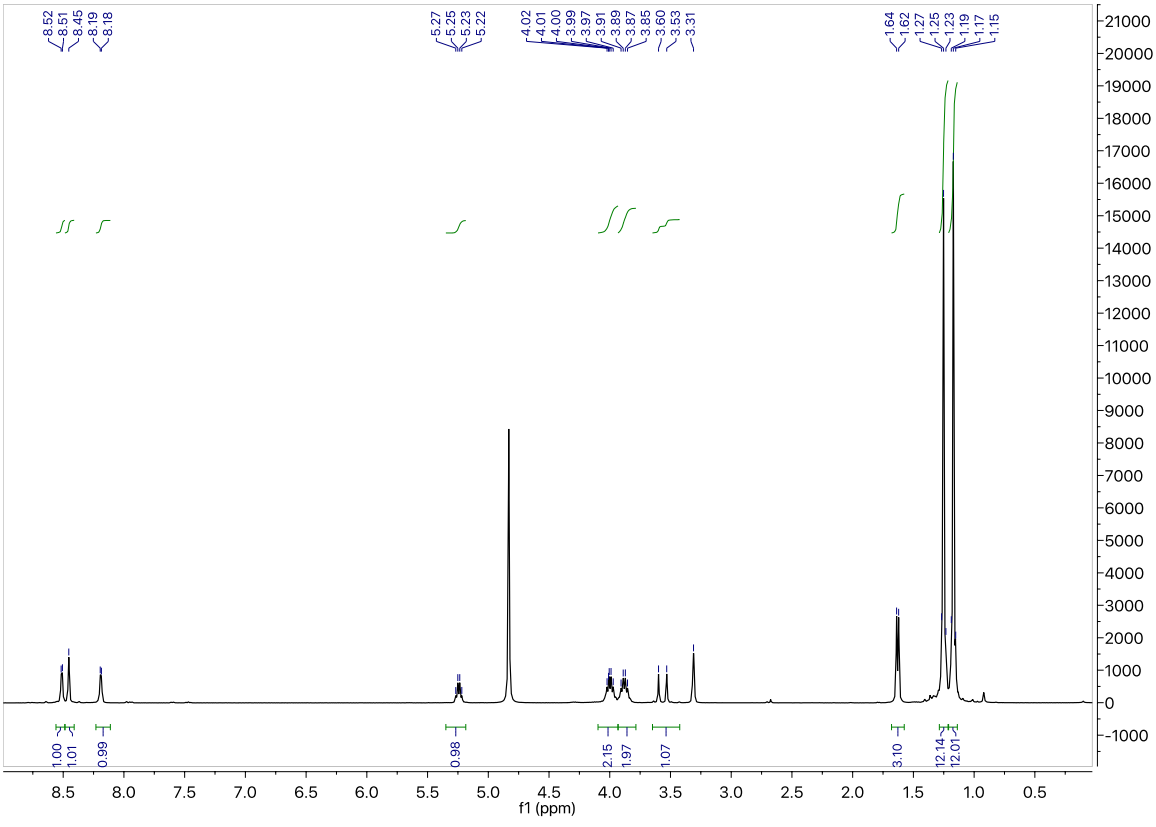
RRSS-**6** (75 MHz, $CDCl_3$)



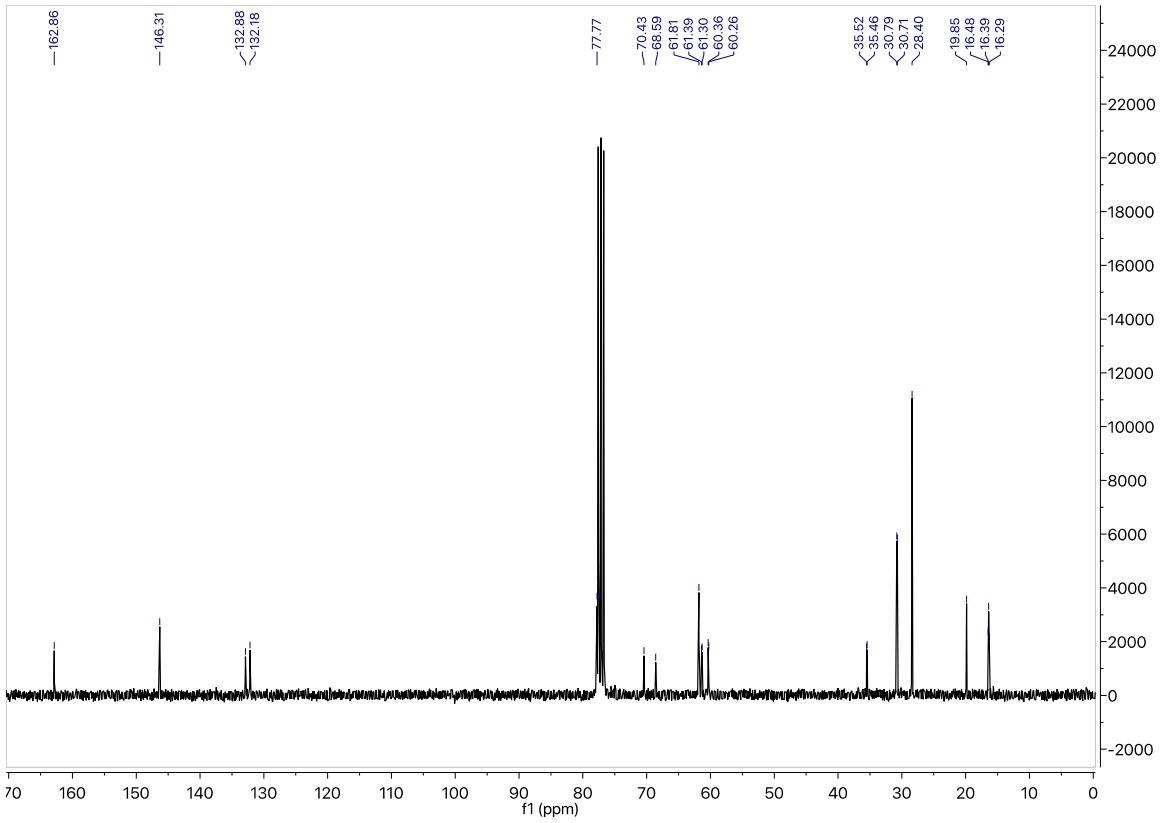
RRSS-**6** HRMS



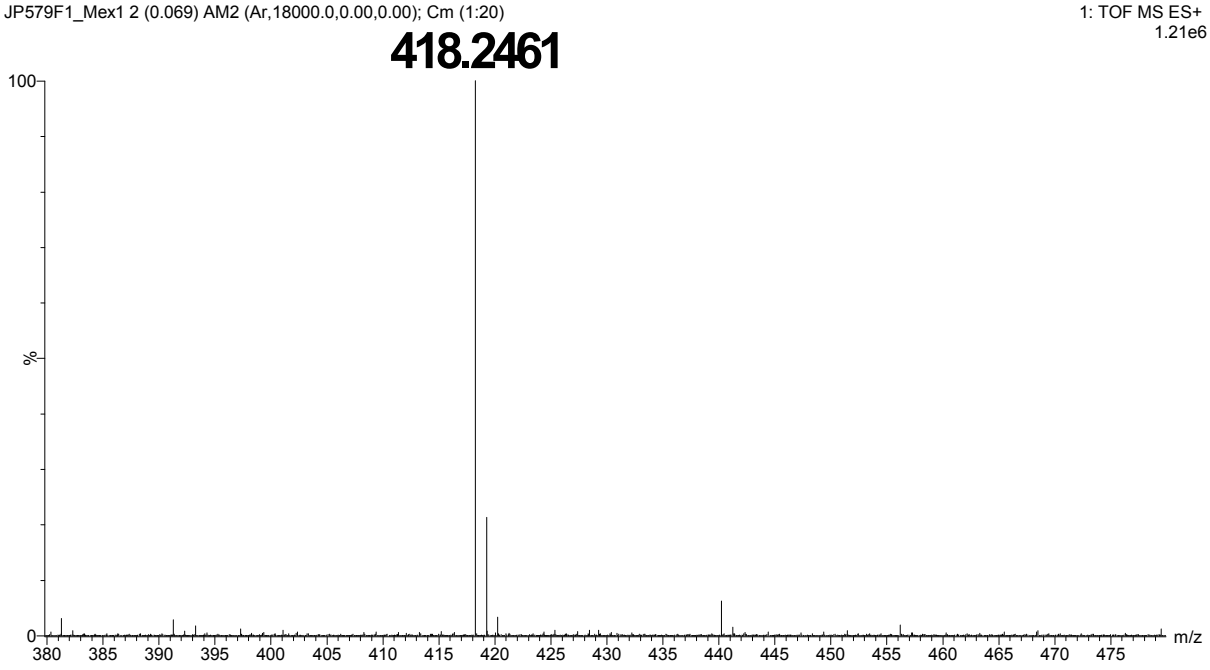
RSSR-**6** (400 MHz, CD_3OD)



RSSR-**6** (75 MHz, $CDCl_3$)



RSSR-**6** HRMS



b) Measurement temperature dependence of k_d for alkoxyamine RS/SR-6.

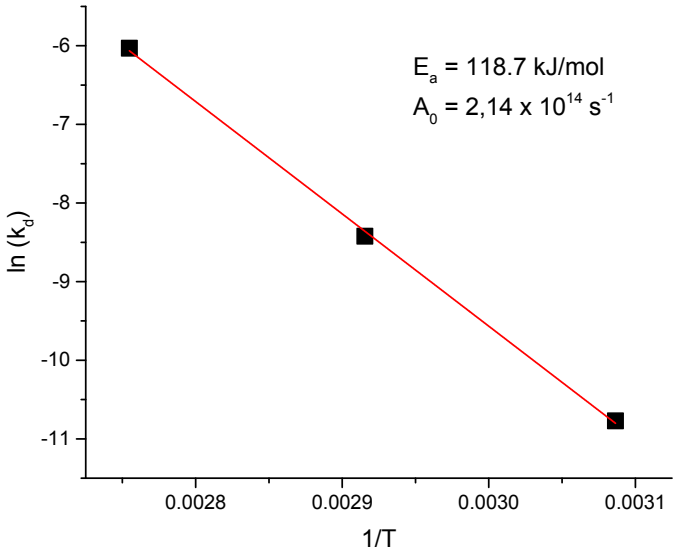
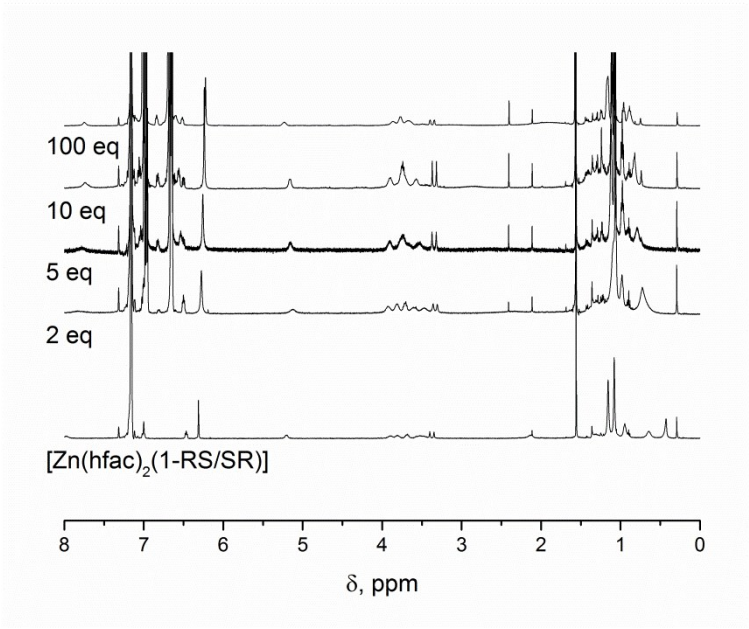


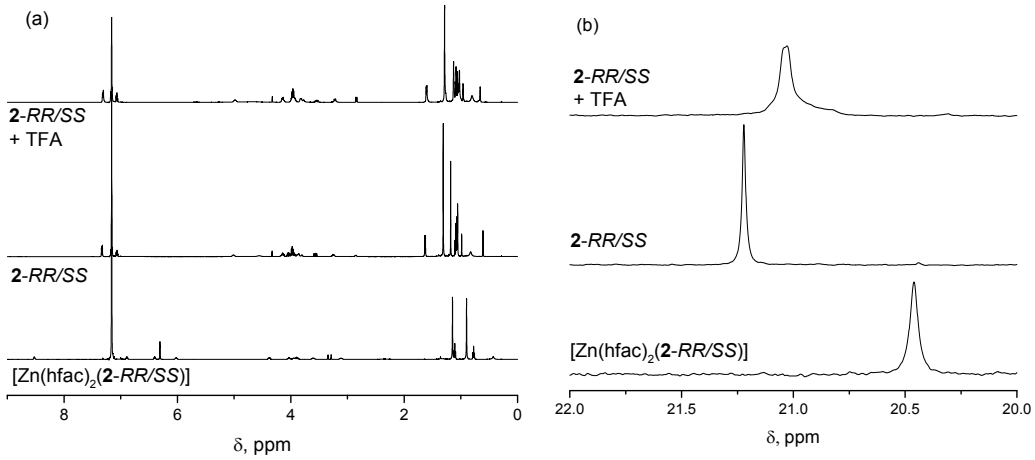
Table 1SI k_d values measured in *t*-Butylbenzene for alkoxyamine RS/SR-6

#	T, °C	k_d, s^{-1}
1	324	2.1E-5
2	343	2.2E-4
3	363	0.0024

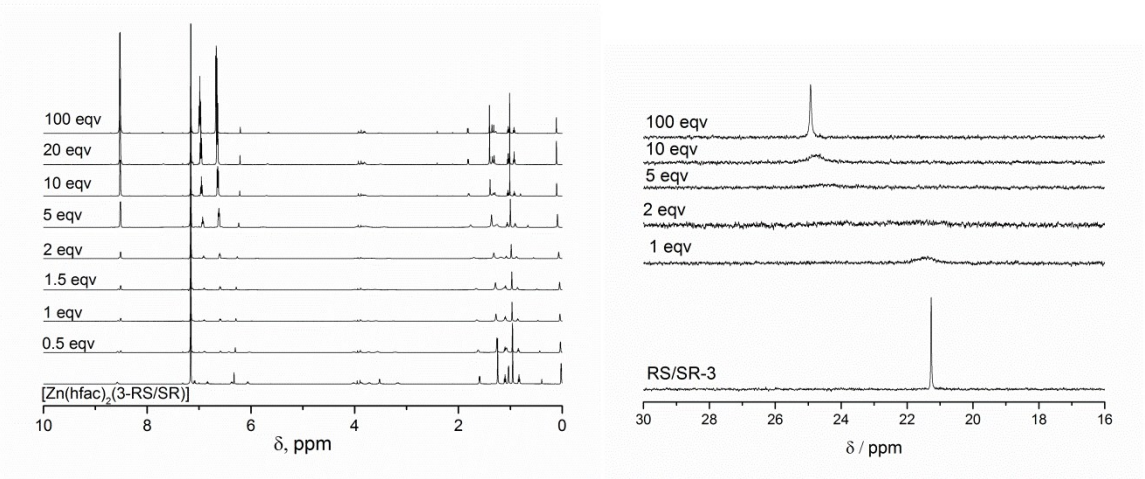
c) NMR data on Py addition to the solution of [Zn(hfac)$_2$(**1**-*RS/SR*)], [Zn(hfac)$_2$(**3**-*RS/SR*)], [(Zn(hfac)$_2$)$_3$(**4**-*RS/SR*)$_2$].



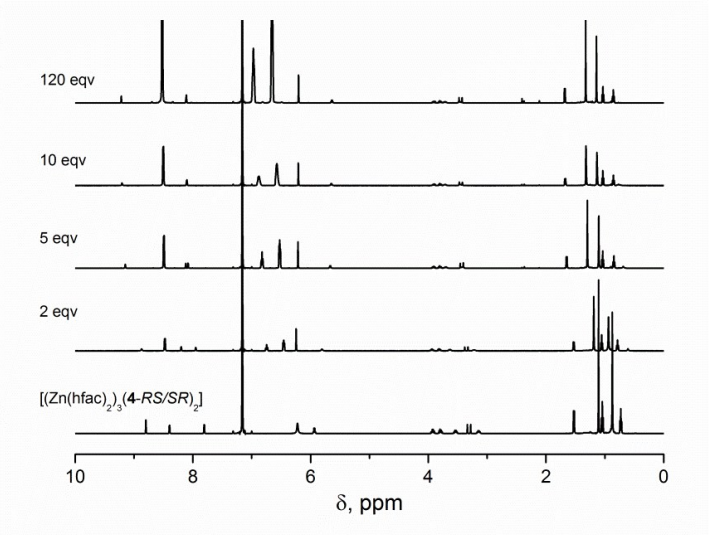
^{1}H NMR spectroscopy of the [Zn(hfac)$_2$(**1**-*RS/SR*)] (a) complex in C_6D_6 (0.02 M solution) with different amounts of Py as a competitor.



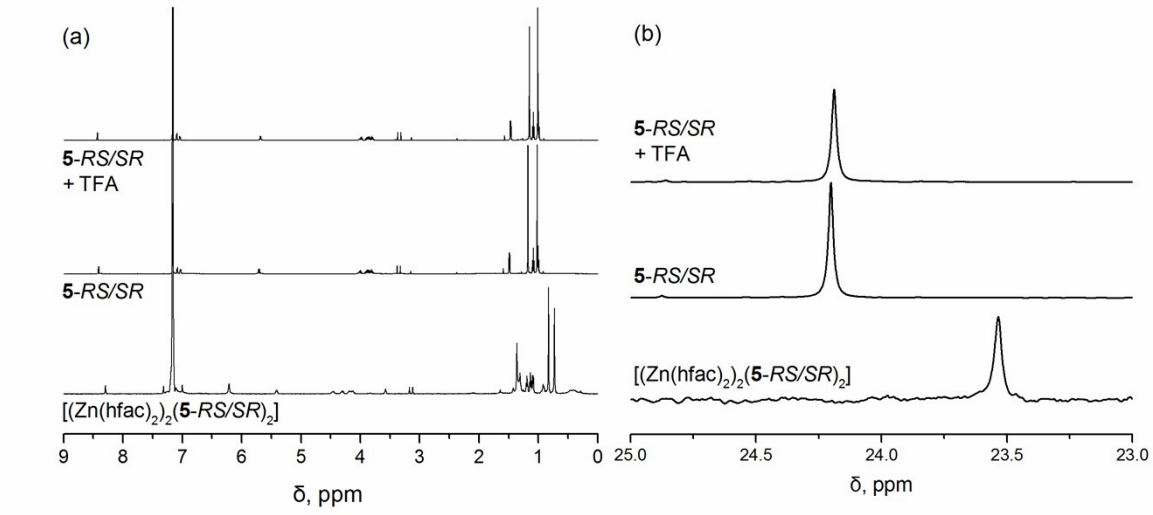
^{1}H and ^{31}P NMR spectroscopy of the [Zn(hfac)$_2$(**2**-*RR/SS*)] complex in C_6D_6 (0.02 M solution) along with **2**-*RR/SS* and **2**-*RR/SS* in the presence of 1 eqv. of TFA.



^{1}H and ^{31}P NMR spectroscopy of the [Zn(hfac)$_2$(**3**-*RS/SR*)] complex in C_6D_6 (0.02 M solution) with different amounts of Py as a competitor.



^{1}H NMR spectroscopy of the [(Zn(hfac)$_2$)$_3$(**4**-*RS/SR*)$_2$] complex in C_6D_6 (0.02 M solution) with different amounts of Py as a competitor.



^{1}H (a) and ^{31}P (b) NMR spectroscopy of the [Zn(hfac)$_2$(**5**-*RS/SR*)$_2$] complex in C_6D_6 (0.02 M solution) along with **5**-*RS/SR* and **5**-*RS/SR* in the presence of 1 eqv. of TFA.