Synthesis of amidines by palladium-mediated CO_2 extrusion followed by insertion of carbodiimides: translating mechanistic studies to develop a one-pot method.

Yang Yang,[a] Asif Noor,[a] Allan J. Canty,[b] Alireza Ariafard,[b]
Paul S. Donnelly*,[a] and Richard A. J. O'Hair*[a]

a. School of Chemistry, Bio21 Institute of Molecular Science and Biotechnology, The University of Melbourne, Victoria 3010, Australia.
b. School of Physical Sciences, University of Tasmania, Private Bag 75, Hobart, Tasmania 7001, Australia.

* Phone: +613 8344-2452. Fax: +613 9347-5180. E-mail: rohair@unimelb.edu.au; pauld@unimelb.edu.au

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Discussion of overall thermochemistry for the ExIn transformation of carboxylic acids to amidines.

DFT calculations were used to evaluate the enthalpy and Gibbs free energy (298K, gas phase) change associated with eq. 1 (Y = NR) for representative carboxylates and carbodiimides due to a dearth of literature on the heats of formation of amidines.[36] The M06/6-31G* method and level of theory was used as it closely matched the computationally more expensive G2 method for the model reaction shown in eq. S1 (B3LYP-D3BJ/BS2: $\Delta_r G$ = -24.7 kcal/mol; $\Delta_r H$ = -26.3 kcal/mol, M06/6-31G*: $\Delta_r G$ = -26.5 kcal/mol; $\Delta_r H$ = -28.1 kcal/mol versus G2: $\Delta_r G$ = -26.4 kcal/mol; $\Delta_r H$ = -28.0 kcal/mol). The energies associated with the aromatic systems shown in Scheme 2 were then examined. We note that the product amidines can exist as 4 different isomers (Figure S1) but **5-1** is the most stable (Table S2). DFT calculations (Table S1) indicate that ExIn reactions for amidine preparation (eq. 1, X = NR) are considerably exothermic for all the systems shown in Scheme 2.

$$HCO_2H + HNCNH \rightarrow HC(NH)NH_2 + CO_2 \qquad (S1)$$

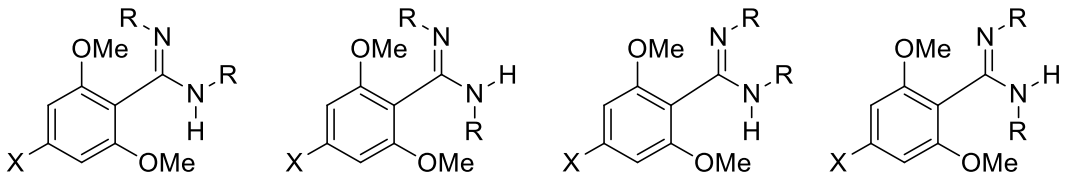
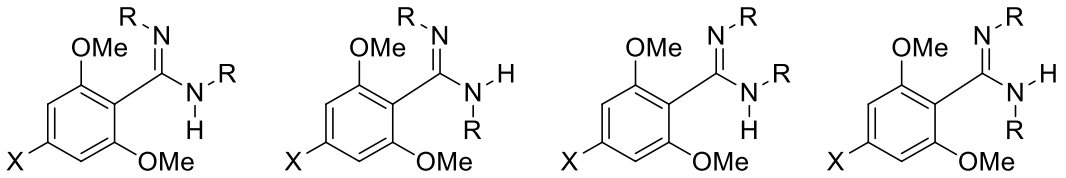


Figure S1: Conformers of amidines where X=H, OMe; R=^{i}Pr, ^{c}Hex, Ph. **5-1** is the *E-syn* isomer; **5-2** is the *E-anti* isomer; **5-3** is the *Z-syn* isomer; **5-4** is the *Z-anti* isomer.[37]

Table S1: B3LYP-D3BJ/BS2 DFT calculated enthalpy and Gibbs free energy change (kcal/mol) for ExIn reactions for amidine preparation (eq. 1, Y = NR).

Ar =	R =	$\Delta_r H$	$\Delta_r G$
2,6-$(MeO)_2C_6H_3$	^{i}Pr	-29.9	-24.8
2,6-$(MeO)_2C_6H_3$	^{c}Hex	-30.4	-27.2
2,6-$(MeO)_2C_6H_3$	Ph	-31.3	-26.5
2,4,6-$(MeO)_3C_6H_2$	^{i}Pr	-30.4	-26.1
2,4,6-$(MeO)_3C_6H_2$	^{c}Hex	-31.1	-28.2
2,4,6-$(MeO)_3C_6H_2$	Ph	-32.6	-29.2

Table S2: M06/6-31G* DFT calculated relative enthalpies and Gibbs free energies (kcal/mol) for the conformers of amidines. **5-1** is the *E-syn* isomer; **5-2** is the *E-anti* isomer; **5-3** is the *Z-syn* isomer; **5-4** is the *Z-anti* isomer.



5-1 **5-2** **5-3** **5-4**

X =	R =	5-1		5-2		5-3		5-4	
		Δ_rH	Δ_rG	Δ_rH	Δ_rG	Δ_rH	Δ_rG	Δ_rH	Δ_rG
H	Me	0.0	0.0	1.6	0.8	7.6	7.6	3.7	3.5
H	^{i}Pr	0.0	0.0	1.7	0.0	7.8	7.5	5.0	4.9
H	^{c}Hex	0.0	0.0	0.2	1.6	6.4	5.3	2.9	1.8
H	Ph	0.0	0.0	0.9	2.2	7.8	8.4	4.1	5.6
MeO	Me	0.0	0.0	1.5	1.1	9.6	10.4	2.1	4.1
MeO	^{i}Pr	0.0	0.0	1.8	1.0	10.9	10.4	8.2	7.3
MeO	^{c}Hex	0.0	0.0	0.5	2.2	7.1	7.6	3.4	4.1
MeO	Ph	0.0	0.0	0.9	0.7	11.2	11.6	4.0	4.1

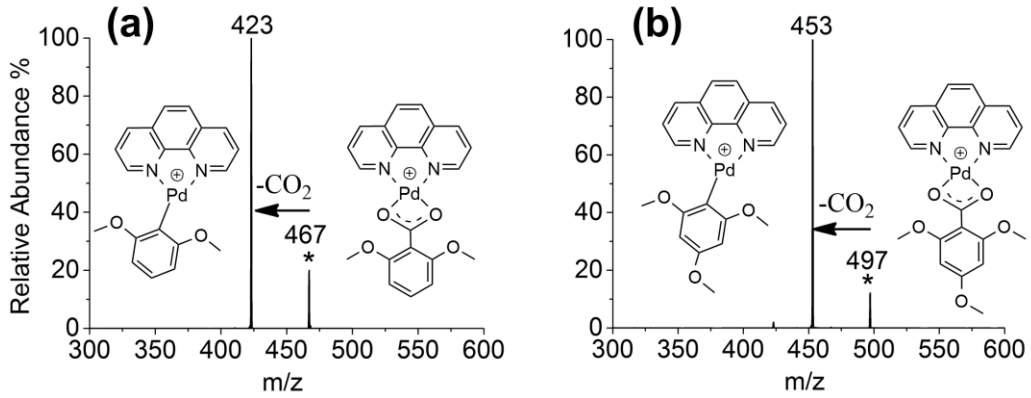


Figure S2. Decarboxylation of $[(Phen)Pd(O_2CAr)]^+$ under collision induced dissociation conditions: (a) $[(phen)Pd(O_2CC_6H_3(2,6\text{-}OMe)_2)]^+$ (*m/z*=467), 100 ms, 13 eV, (b) $[(phen)Pd(O_2CC_6H_2(2,4,6\text{-}OMe)_3)]^+$ (*m/z*=497), 100 ms, 13eV. The mass-selected precursor ions are denoted by a *.

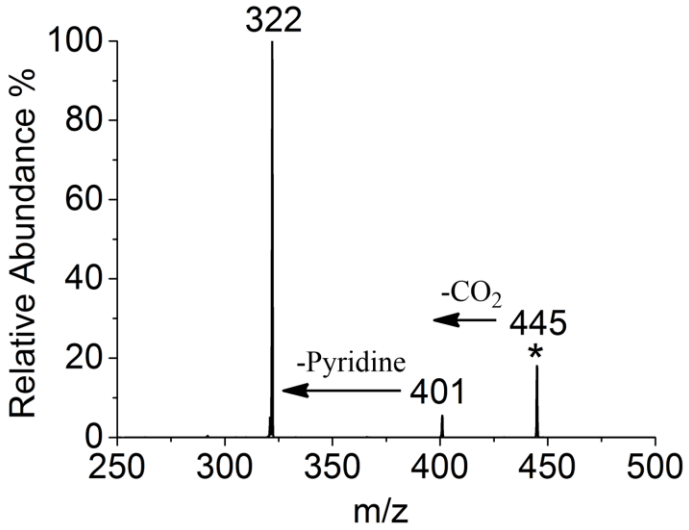


Figure S3. Decarboxylation of $[(Py)_2Pd(O_2CC_6H_3(2,6\text{-}OMe)_2)]^+$ (*m/z*=445) under CID conditions at a normalized collision energy of 14 eV. The mass-selected precursor ion is denoted by a *.

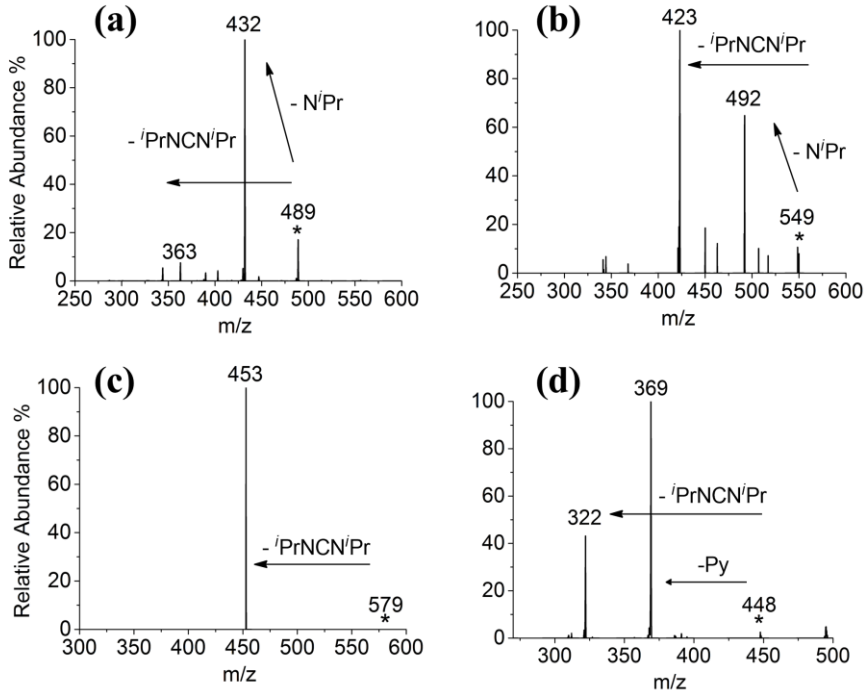
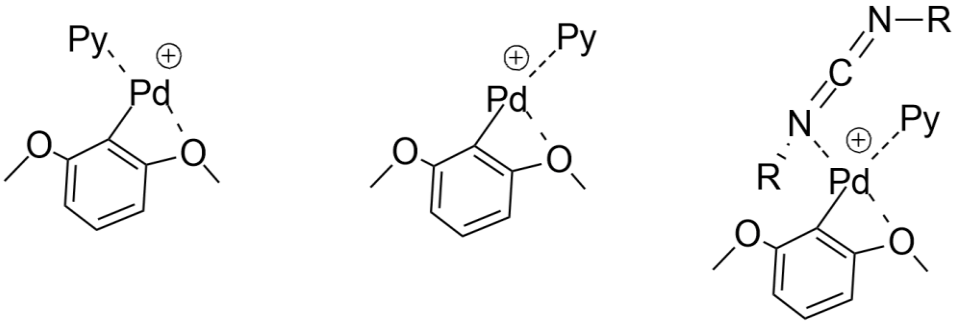


Figure S4. CID mass spectra at a normalized collision energy of 20 showing the fragmentation reactions of the products formed in the ion-molecule reaction between $[(L)Pd(Ar)]^+$ and $^{i}PrN{=}C{=}N^{i}Pr$: (a) L = phen, Ar = C_6H_5 (*m/z*=489), (b) L = phen, Ar = $C_6H_3(2,6\text{-}OMe)_2$ (*m/z*=549), (c) L = phen, Ar = $C_6H_2(2,4,6\text{-}OMe)_3$ (*m/z*=579), (d) L = py, Ar = $C_6H_3(2,6\text{-}OMe)_2$ (*m/z*=447). ^{i}Pr = isopropyl. The mass-selected precursor ion is denoted by a *.

Table S3. Ion-molecule kinetic data for reaction of $[(L)Pd(Ar)]^+$ and $^{i}PrN{=}C{=}N^{i}Pr$:

L =	**Ar =**	k_{expt} [a,b]	K_{ADO} [c]	Φ [d]
phen	C_6H_5	1.416 x 10^{-9}	1.179 x 10^{-9}	120
py	$C_6H_3(2,6\text{-}OMe)_2$)	1.105 x 10^{-9}	1.198 x 10^{-9}	92

(a) Rates measured for these reactions were determined from triplicate experiments Mean ± standard deviation (n=3). (b) In units of: cm^3 $molecules^{-1}$ s^{-1}. (c) The k_{ADO} is the theoretical ion-molecule collision rate constant obtained from the average-dipole orientation (ADO) theory,[1] which is calculated using the Colrate program.[2] (d). Reaction efficiency, φ, = (k_{expt}/k_{ADO}) x 100.



9d
0.0 (0.0)

9e
15.0 (17.2)

10e
-6.7 (-21.4)

Figure S5. Comparison between two isomers of **9d**, Py *trans* to OMe and **9e**, Py *cis* to OMe together with the complex **10e**. The relative Gibbs and enthalpy energies (in parentheses) are given in kcal/mol and were calculated at the M06/LANL2DZ6-31G+(d) level of theory.

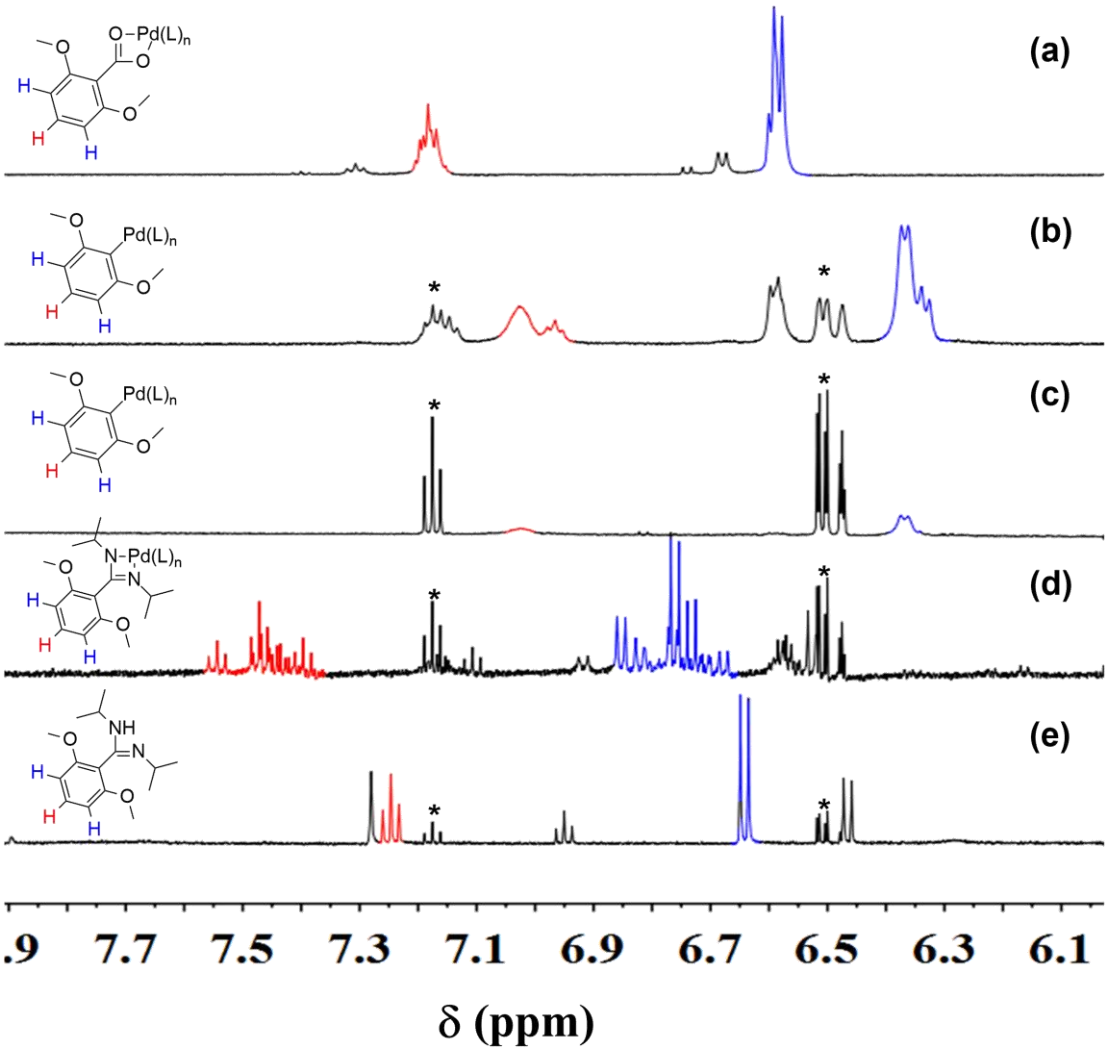


Figure S6. $Pd(O_2CCH_3)_2$ induced transformation of 2,6-dimethoxybenzoic acid to amidine **5AI** monitored by ^1H NMR spectroscopy (600Hz) in DMSO-d_6 (only the resonances due to the aromatic protons are shown): (a) 2,6-dimethoxybenzoic acid binding to the metal center (eq. 2); (b) decarboxylation for 4 hours (eq. 3); (c) showing heating for 24 hours to form the protodecarboxylation product completely (eq. 8); (d) insertion of ^{i}PrN=C=N^{i}Pr into the Pd-C bond (eq. 4) and (e) reaction of the palladium amidinate with $NaBH_4$ to release the free amidine (eq. 5). A * highlights peaks due to the product of protodecarboxylation, 1,3-dimethoxybenzene. Ligand 'L' is DMSO or acetate or both, ^{i}Pr=isopropyl.

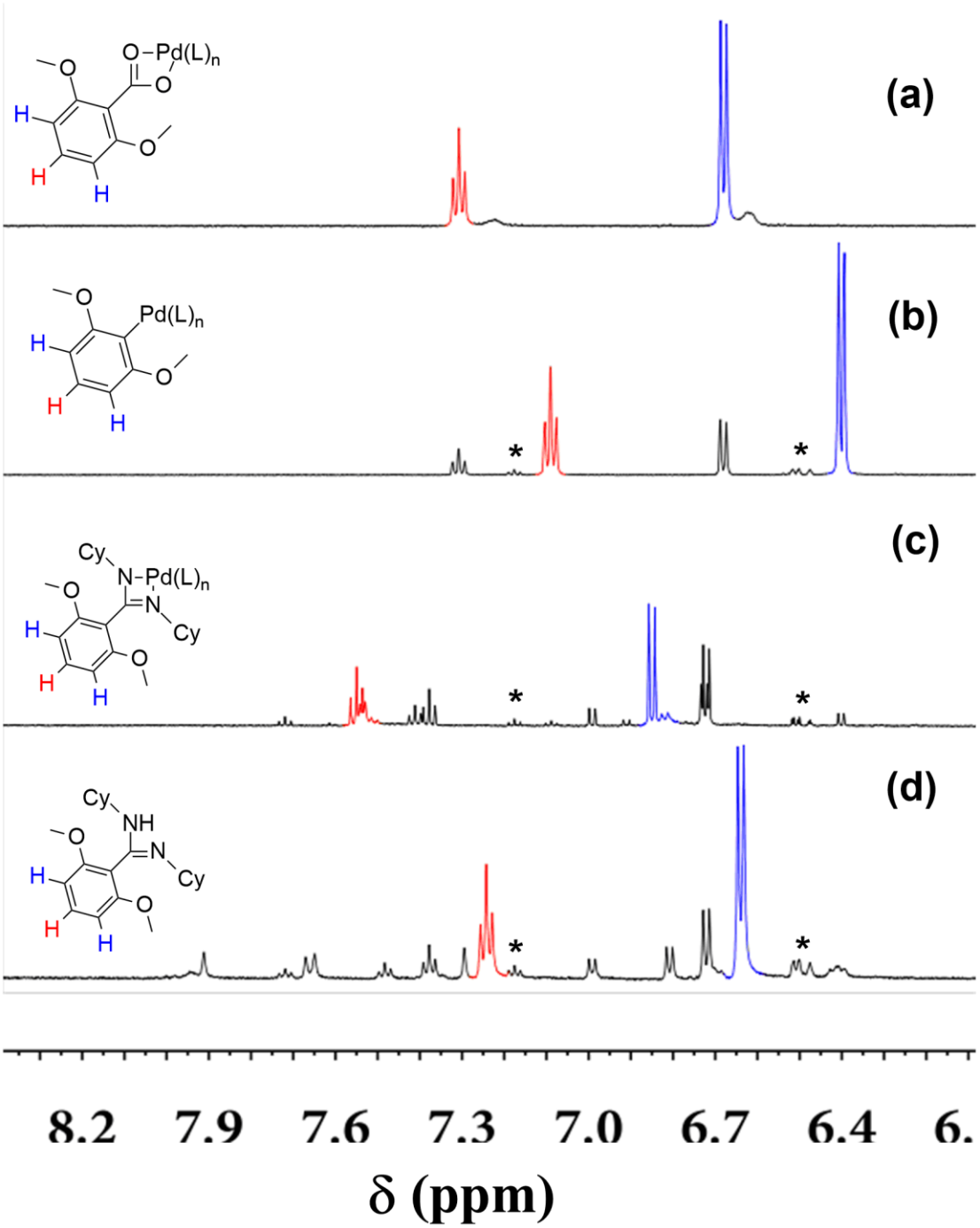


Figure S7. $Pd(O_2CCF_3)_2$ induced transformation of 2,6-dimethoxybenzoic acid to amidine **5AII** monitored by ^1H NMR spectroscopy (600Hz) in DMSO-d_6 (only the resonances due to the aromatic protons are shown): (a) 2,6-dimethoxybenzoic acid binding to the metal center (eq. 2); (b) decarboxylation for 6 hours (eq. 3); (c) insertion of ^{c}HexN=C=N^{c}Hex into the Pd-C bond (eq. 4) and (d) reaction of the palladium amidinate with $NaBH_4$ to release the free amidine (eq. 5). A * highlights peaks due to the product of protodecarboxylation, 1,3-dimethoxybenzene. Ligand 'L' is either DMSO or trifluroacetate or both, ^{c}Hex=cyclohexyl.

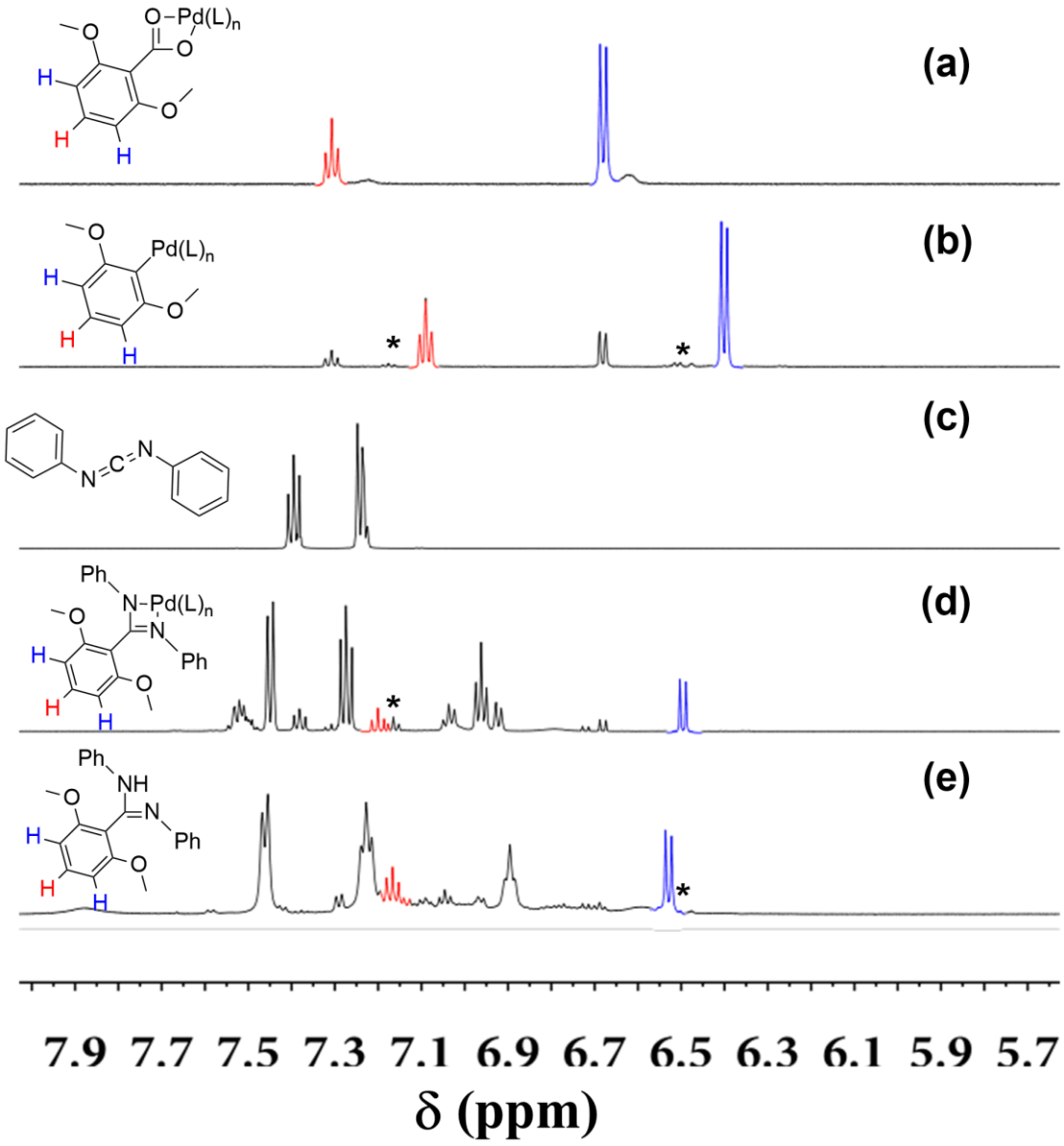


Figure S8. $Pd(O_2CCF_3)_2$ induced transformation of 2,6-dimethoxybenzoic acid to amidine **5AIII** monitored by ^1H NMR spectroscopy (600Hz) in DMSO-d_6 (only the resonances due to the aromatic protons are shown): (a) 2,6-dimethoxybenzoic acid binding to the metal center (eq. 2); (b) decarboxylation for 6 hours (eq. 3); (c) showing the peaks of PhN=C=NPh at aromatic range; (d) insertion of PhN=C=NPh into the Pd-C bond (eq. 4) and (e) reaction of the palladium amidinate with $NaBH_4$ to release the free amidine (eq. 5). A * highlights peaks due to the product of protodecarboxylation, 1,3-dimethoxybenzene. Ligand 'L' is either DMSO or trifluroacetate or both.

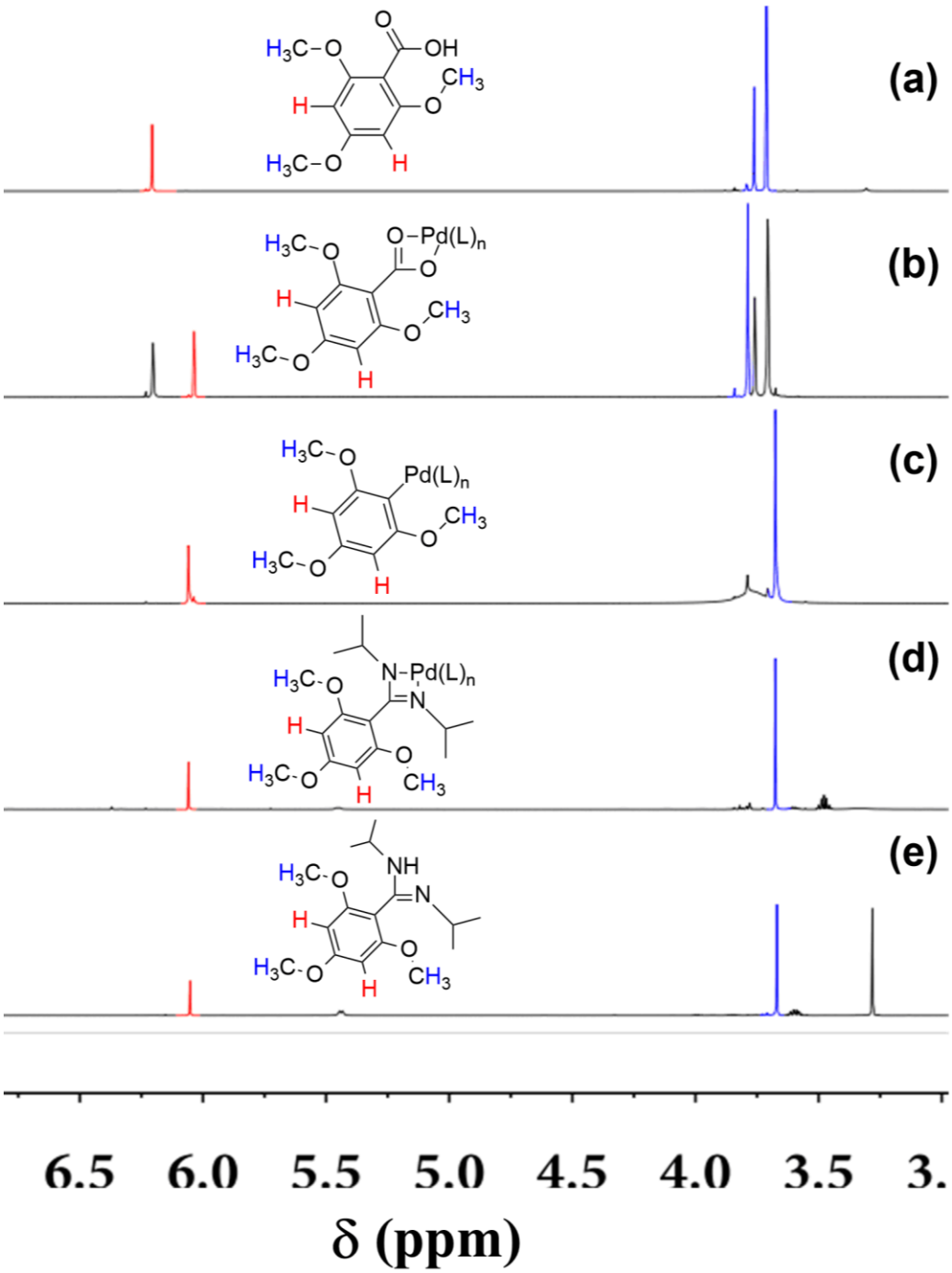


Figure S9. $Pd(O_2CCF_3)_2$ induced transformation of 2,4,6-trimethoxybenzoic acid to amidine **5BI** monitored by ^1H NMR spectroscopy (only the resonances due to the aromatic protons and methoxy protons are shown): (a) 2,4,6-trimethoxybenzoic acid; (b) 2,4,6-trimethoxybenzoic acid binding to the metal center (eq. 2); (c) decarboxylation for 6 hours (eq. 3); (d) insertion of ^{i}PrN=C=N^{i}Pr into the Pd-C bond (eq. 4) and (e) reaction of the palladium amidinate with $NaBH_4$ to release the free amidine (eq. 5). Ligand 'L' is either DMSO or trifluroacetate or both, ^{i}Pr=isopropyl.

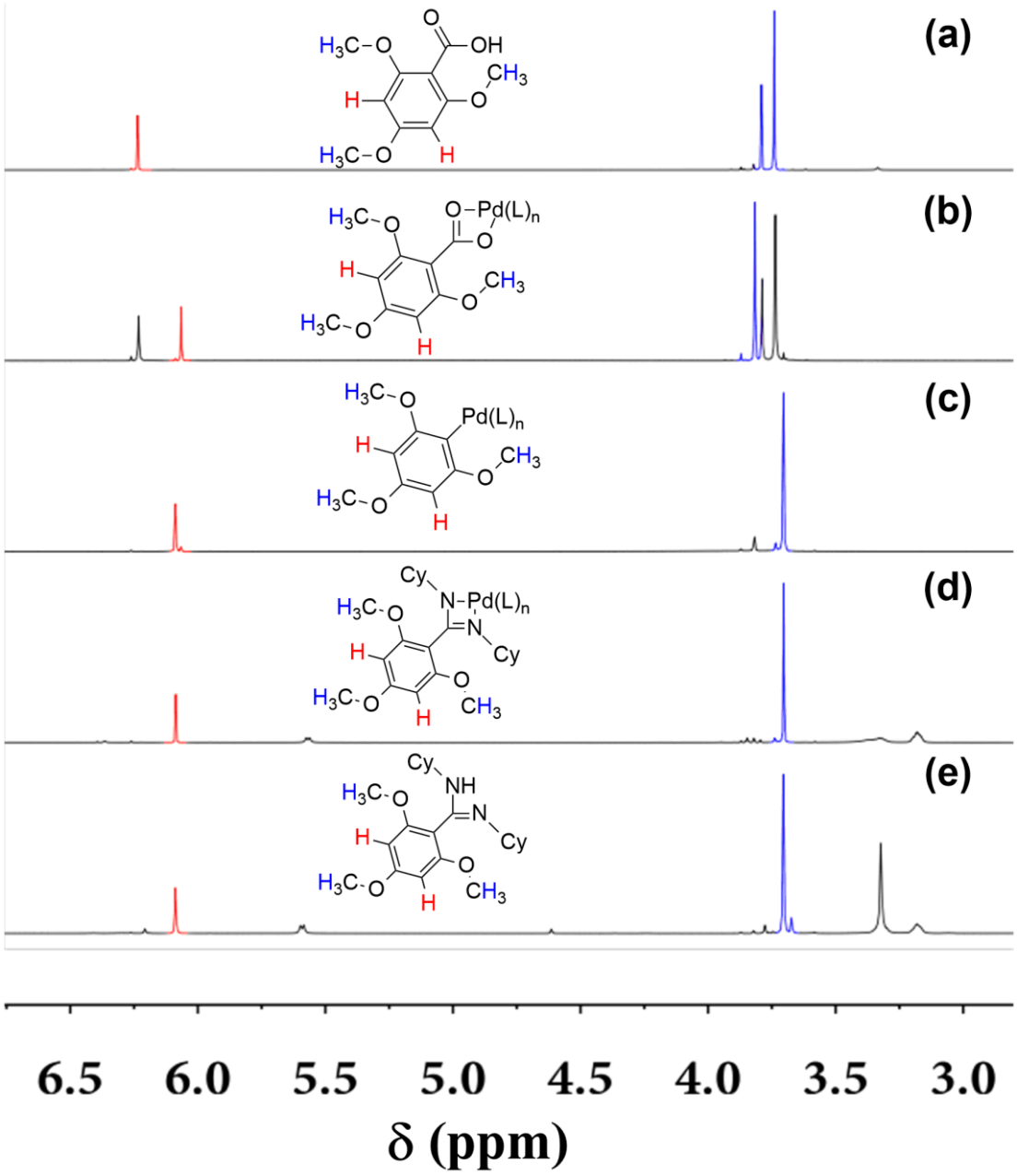


Figure S10. $Pd(O_2CCF_3)_2$ induced transformation of 2,4,6-trimethoxybenzoic acid to amidine **5BII** monitored by ^1H NMR spectroscopy (only the resonances due to the aromatic protons and methoxy protons are shown): (a) 2,4,6-trimethoxybenzoic acid; (b) 2,4,6-trimethoxybenzoic acid binding to the metal center (eq. 2); (c) decarboxylation for 6 hours (eq. 3); (d) insertion of ^{c}HexN=C=N^{c}Hex into the Pd-C bond (eq. 4) and (e) reaction of the palladium amidinate with $NaBH_4$ to release the free amidine (eq. 5). Ligand 'L' is either DMSO or trifluroacetate or both, ^{c}Hex=cyclohexyl.

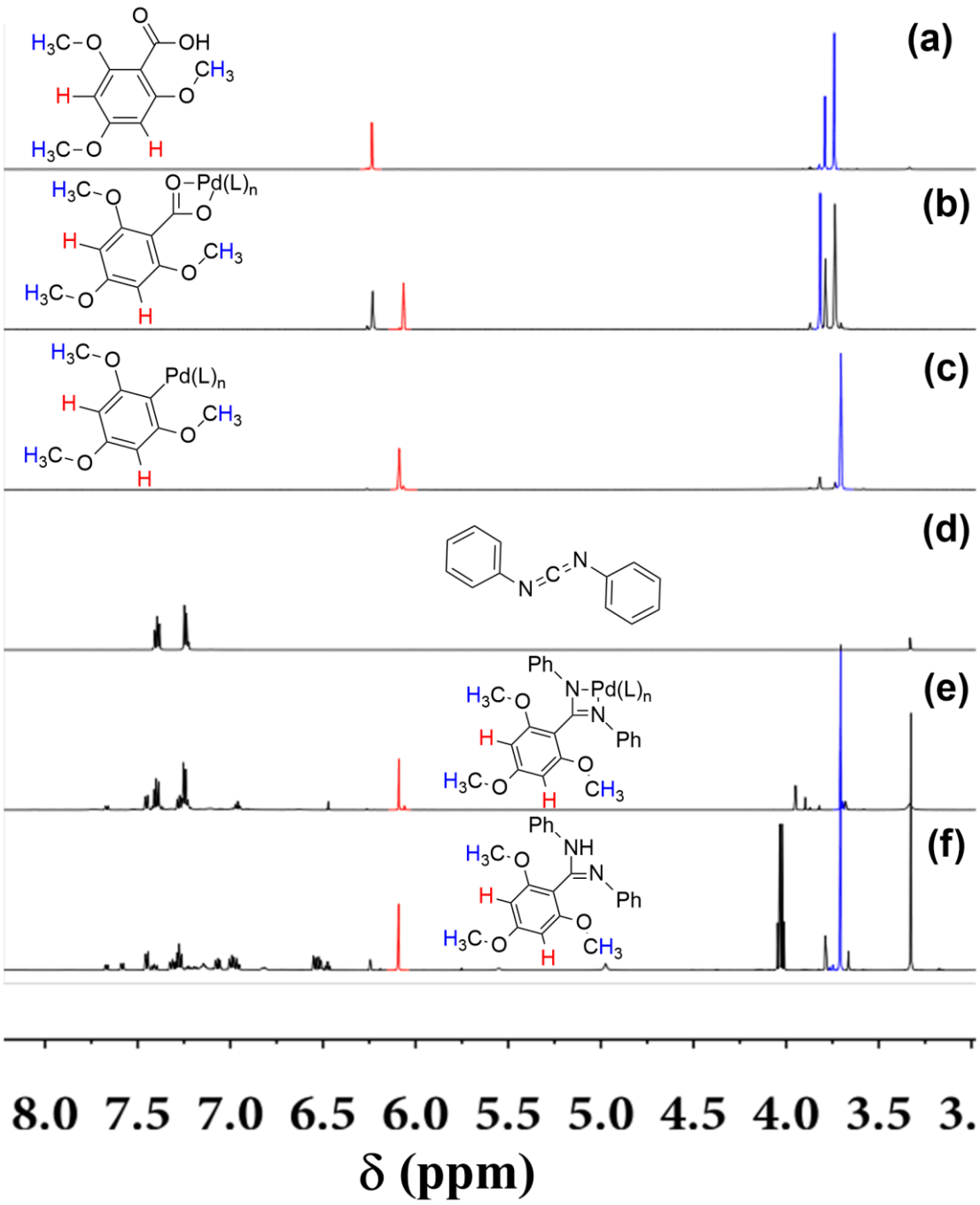


Figure S11. $Pd(O_2CCF_3)_2$ induced transformation of 2,4,6-trimethoxybenzoic acid to amidine **5BIII** monitored by ^1H NMR spectroscopy (only the resonances due to the aromatic protons and methoxy protons are shown): (a) 2,4,6-trimethoxybenzoic acid; (b) 2,4,6-trimethoxybenzoic acid binding to the metal center (eq. 2); (c) decarboxylation for 6 hours (eq. 3); (d) showing the peaks of PhN=C=NPh at aromatic range (e) insertion of PhN=C=NPh into the Pd-C bond (eq. 4) and (f) reaction of the palladium amidinate with $NaBH_4$ to release the free amidine (eq. 5). Ligand 'L' is either DMSO or trifluroacetate or both.

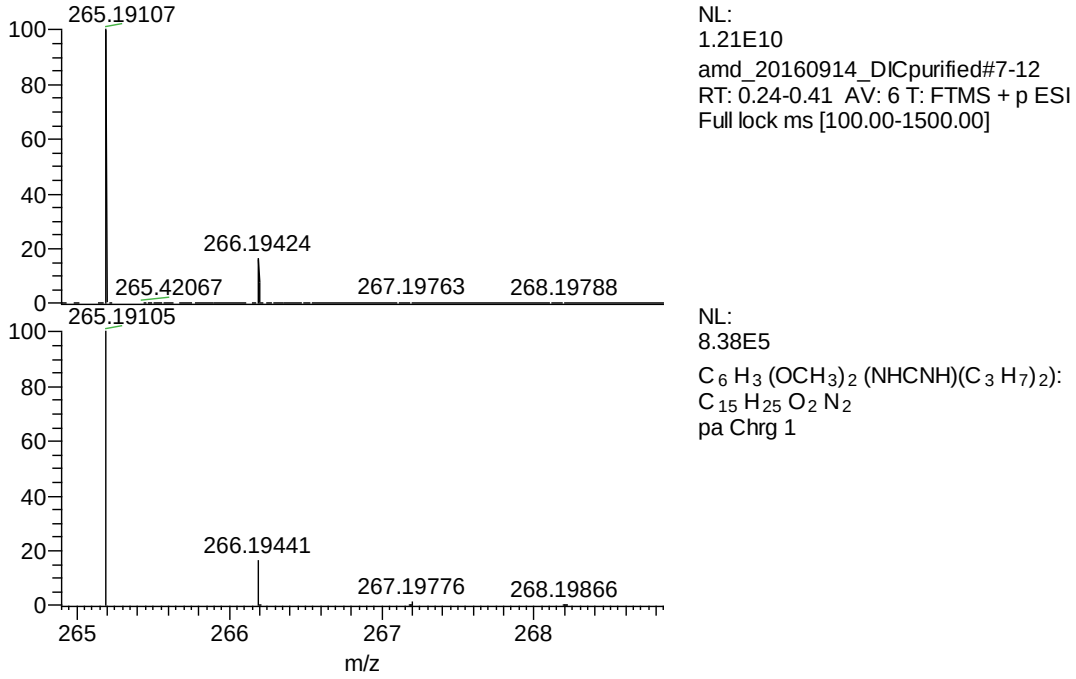


Figure S12. The ESI-HRMS spectrum (+ve, Thermo OrbiTrap MS) showing the isotope distribution patterns of the protonated amidine **5AI** formed in the ^{1}H NMR monitoring experiment (Figure S6). Observed (top) and calculated (bottom).

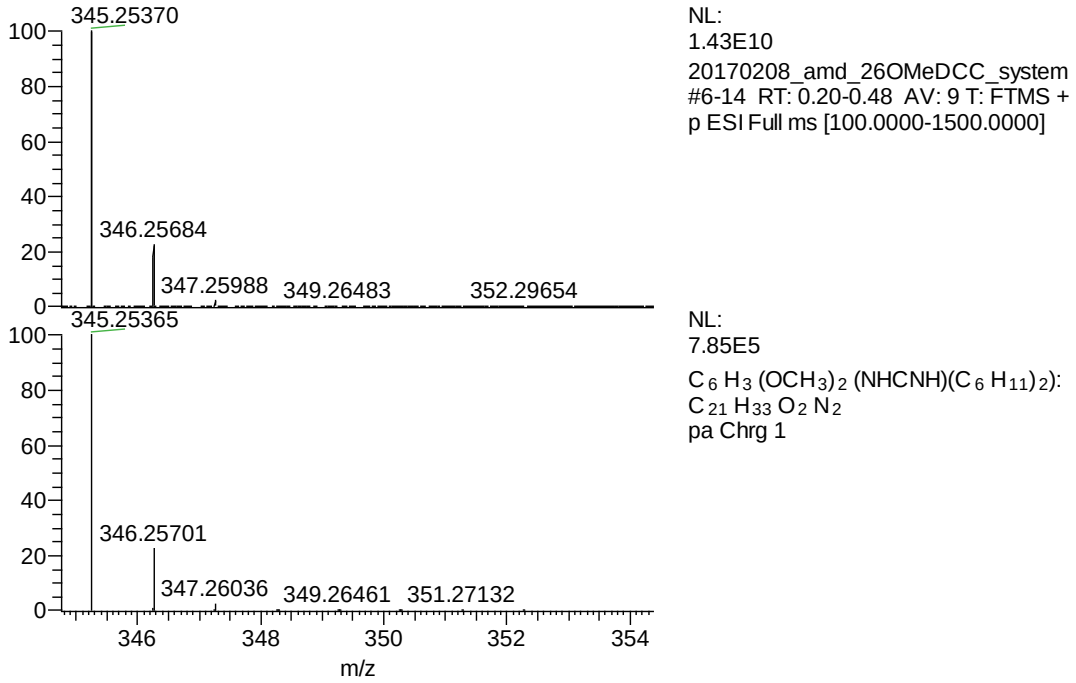


Figure S13. The ESI-HRMS spectrum (+ve, Thermo OrbiTrap MS) showing the isotope distribution patterns of the protonated amidine **5AII** formed in the ^{1}H NMR monitoring experiment (Figure S7). Observed (top) and calculated (bottom).

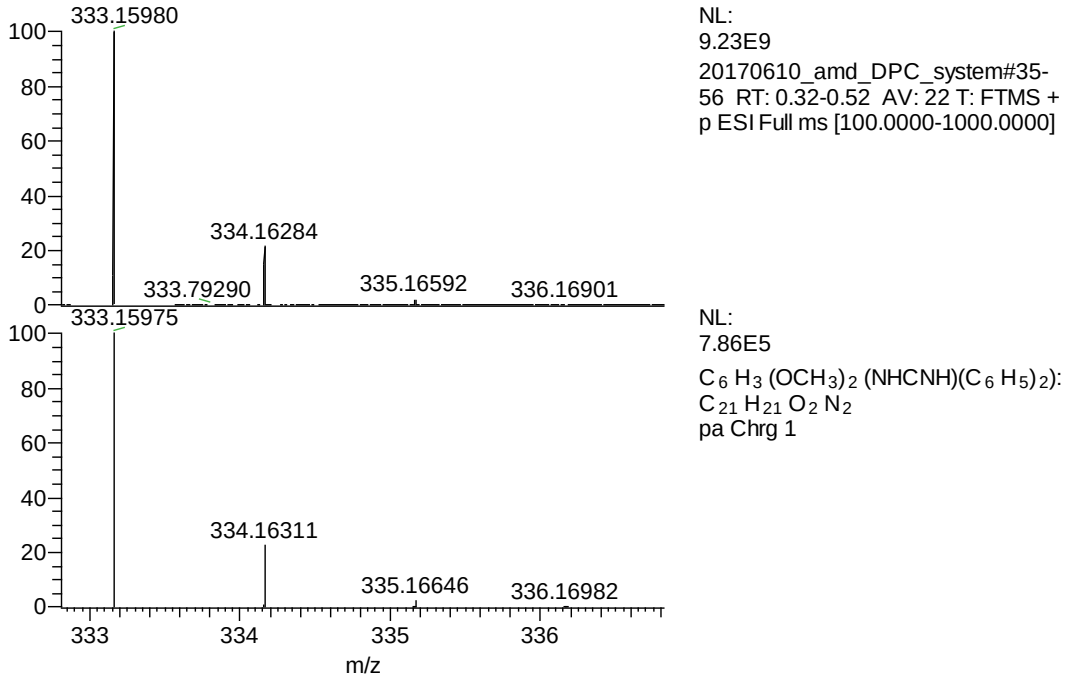


Figure S14. The ESI-HRMS spectrum (+ve, Thermo OrbiTrap MS) showing the isotope distribution patterns of the protonated amidine **5AIII** formed in the ^{1}H NMR monitoring experiment (Figure S8). Observed (top) and calculated (bottom).

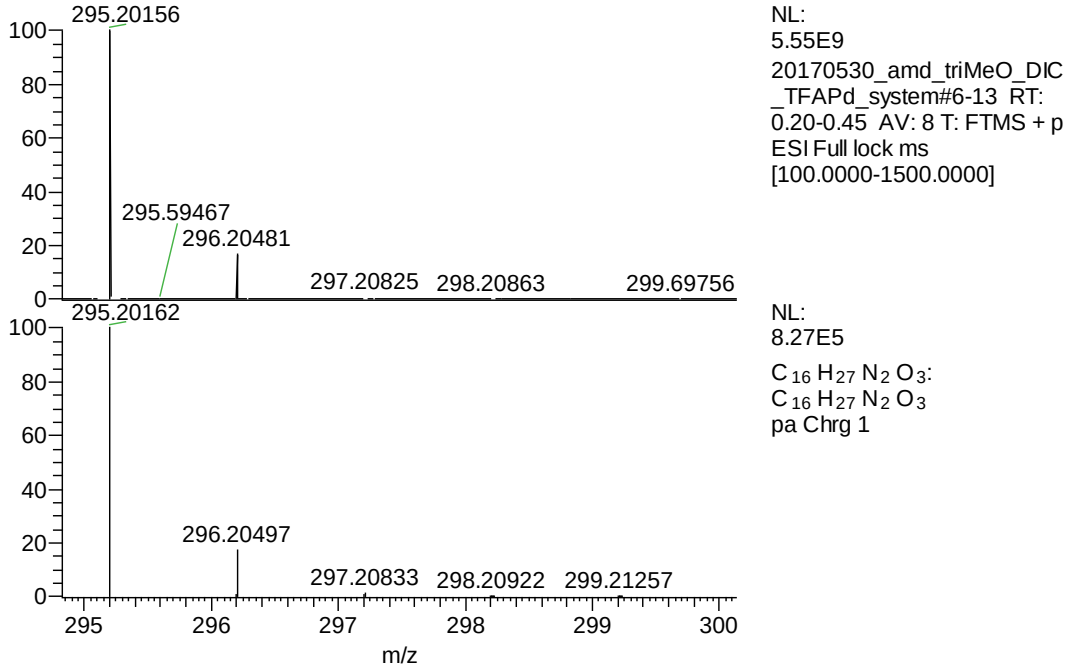


Figure S15. The ESI-HRMS spectrum (+ve, Thermo OrbiTrap MS) showing the isotope distribution patterns of the protonated amidine **5BI** formed in the ^{1}H NMR monitoring experiment (Figure S9). Observed (top) and calculated (bottom).

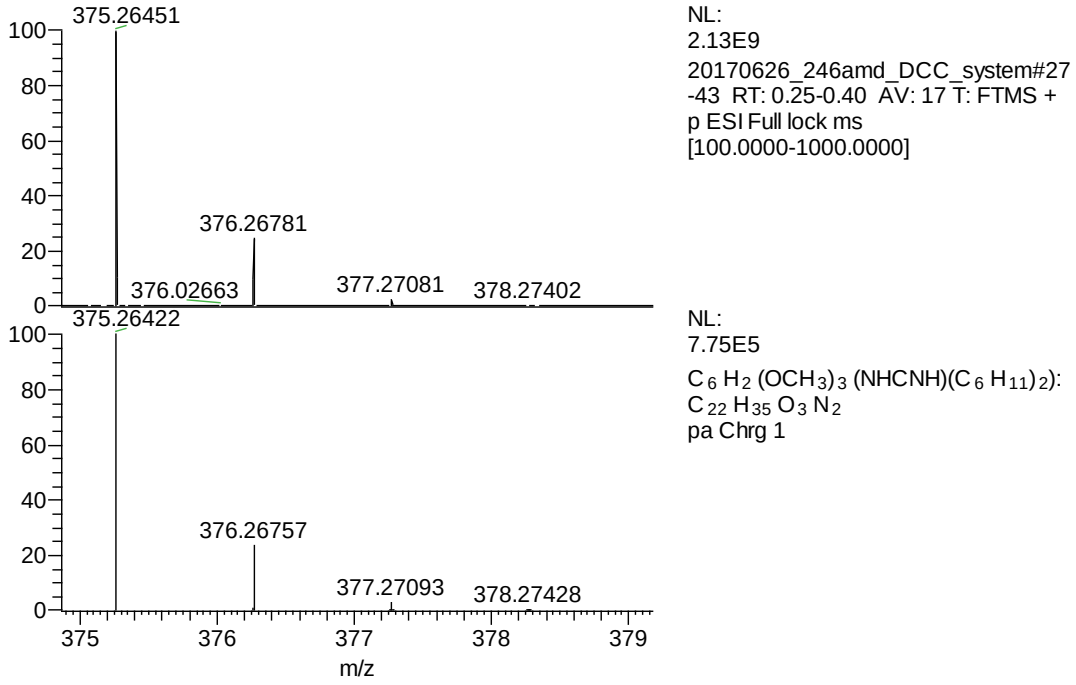


Figure S16. The ESI-HRMS spectrum (+ve, Thermo OrbiTrap MS) showing the isotope distribution patterns of the protonated amidine **5BII** formed in the ^{1}H NMR monitoring experiment (Figure S10). Observed (top) and calculated (bottom).

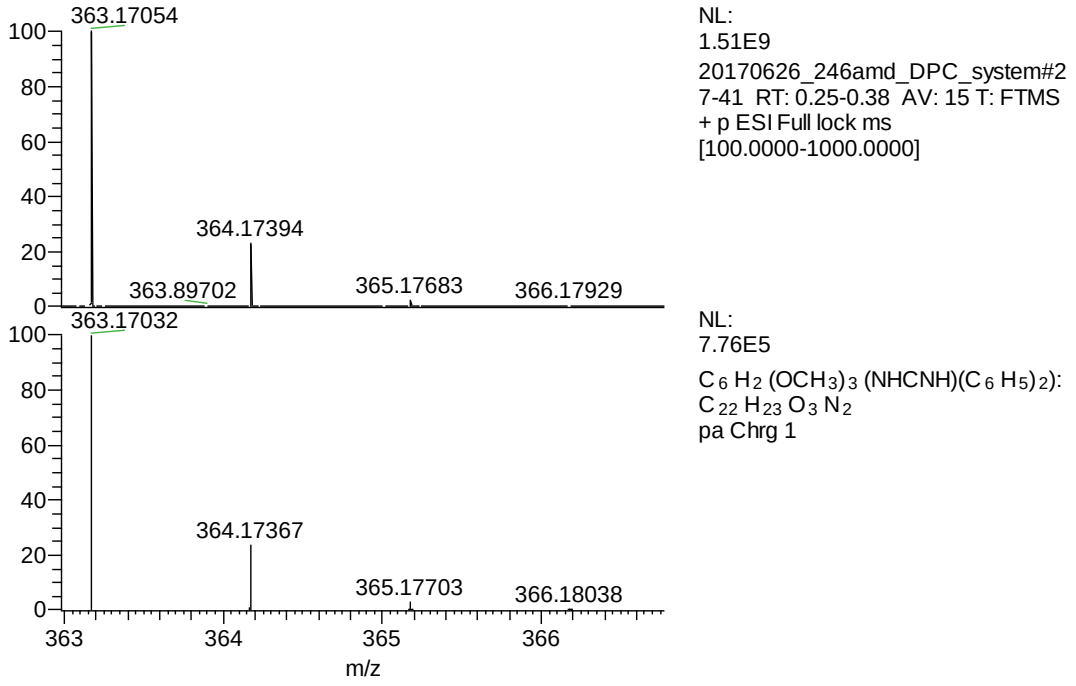


Figure S17. The ESI-HRMS spectrum (+ve, Thermo OrbiTrap MS) showing the isotope distribution patterns of the protonated amidine **5BIII** formed in the ^{1}H NMR monitoring experiment (Figure S11). Observed (top) and calculated (bottom).

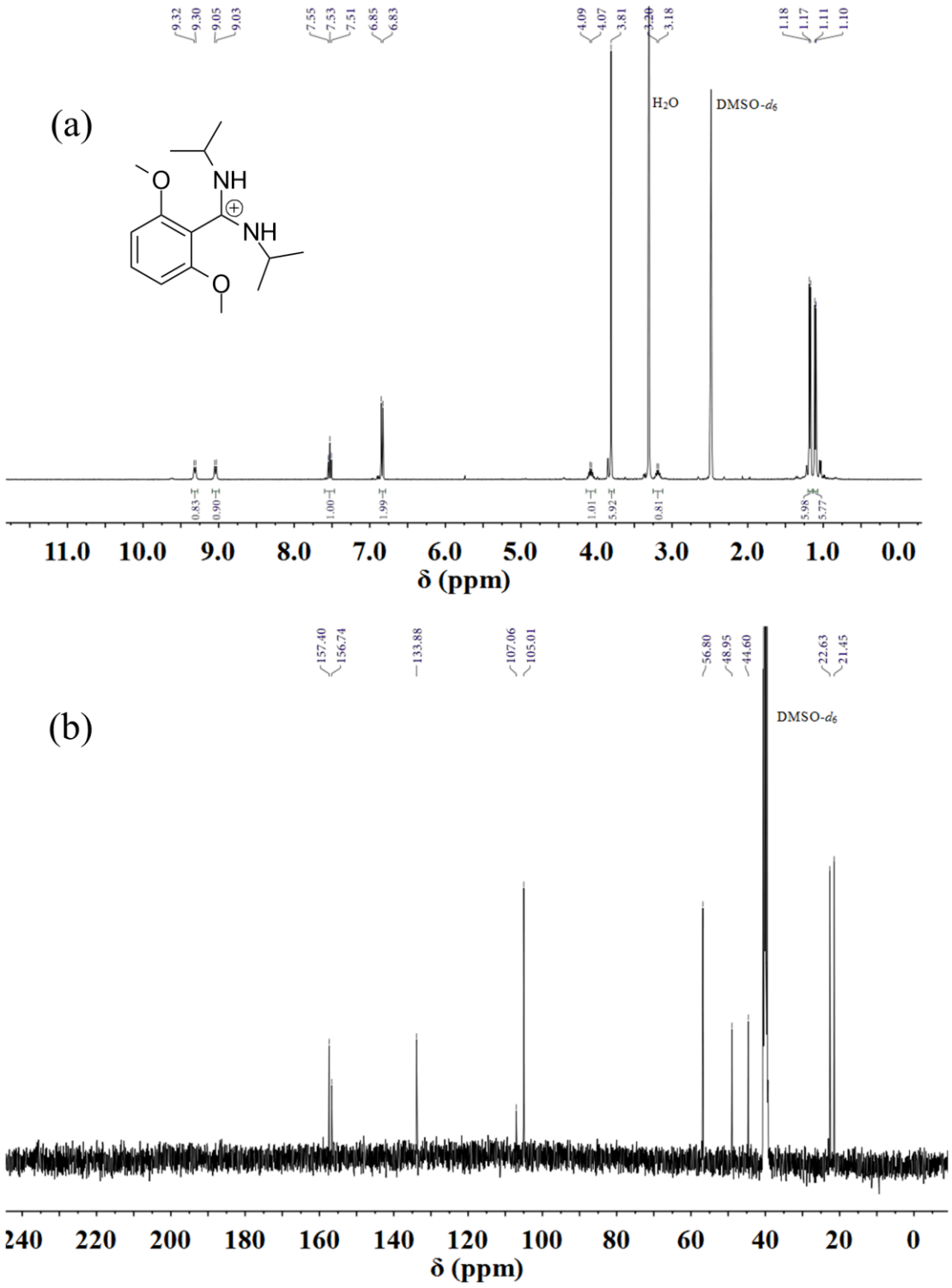


Figure S18. NMR spectra of isolated amidine **5AI**: (a) ^{1}H NMR (400MHz, DMSO-d_6); (b) ^{13}C NMR (400MHz, DMSO-d_6)

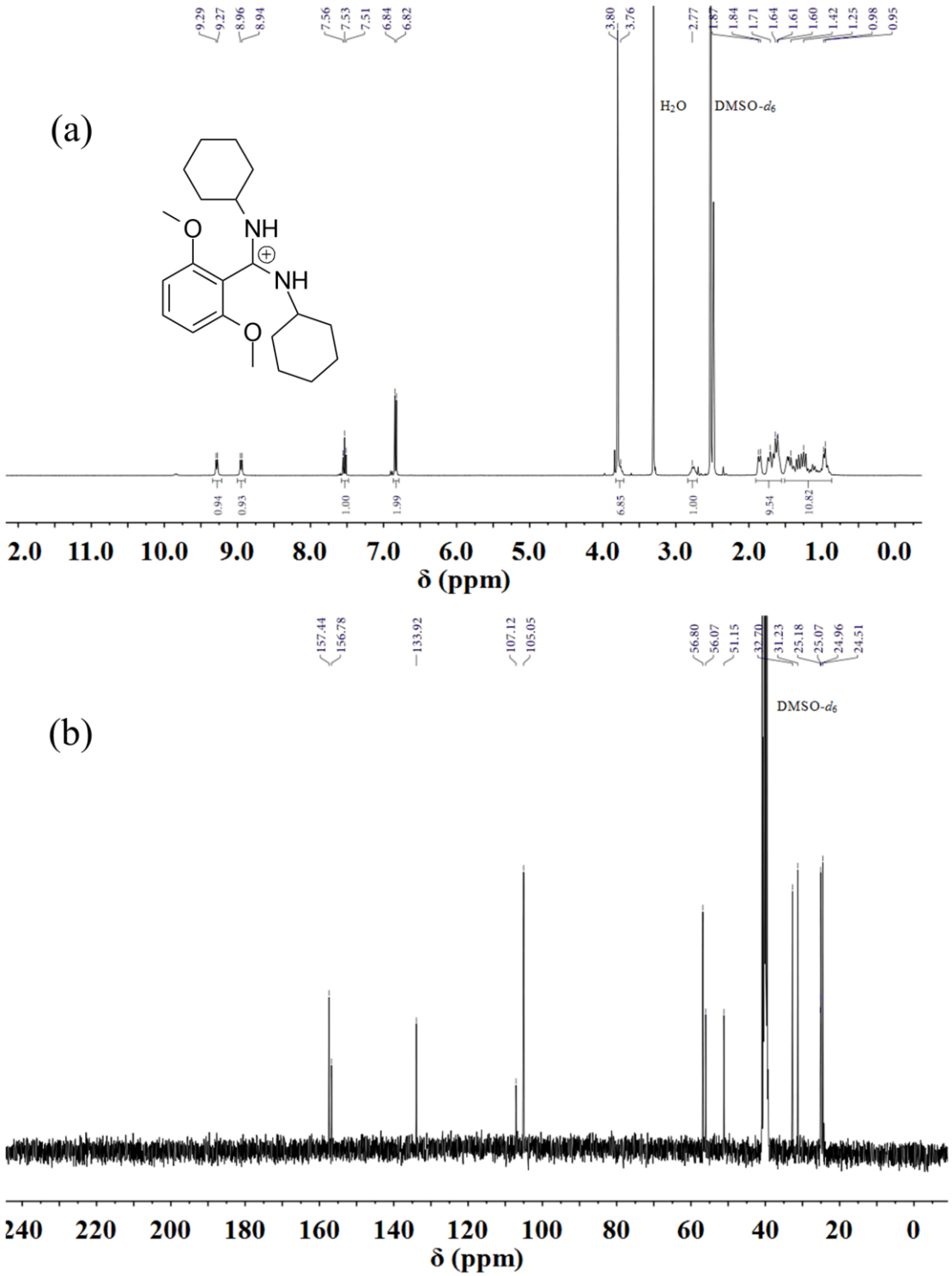


Figure S19. NMR spectra of isolated amidine **5AII**: (a) ^{1}H NMR (400MHz, DMSO-d_6); (b) ^{13}C NMR (400MHz, DMSO-d_6)

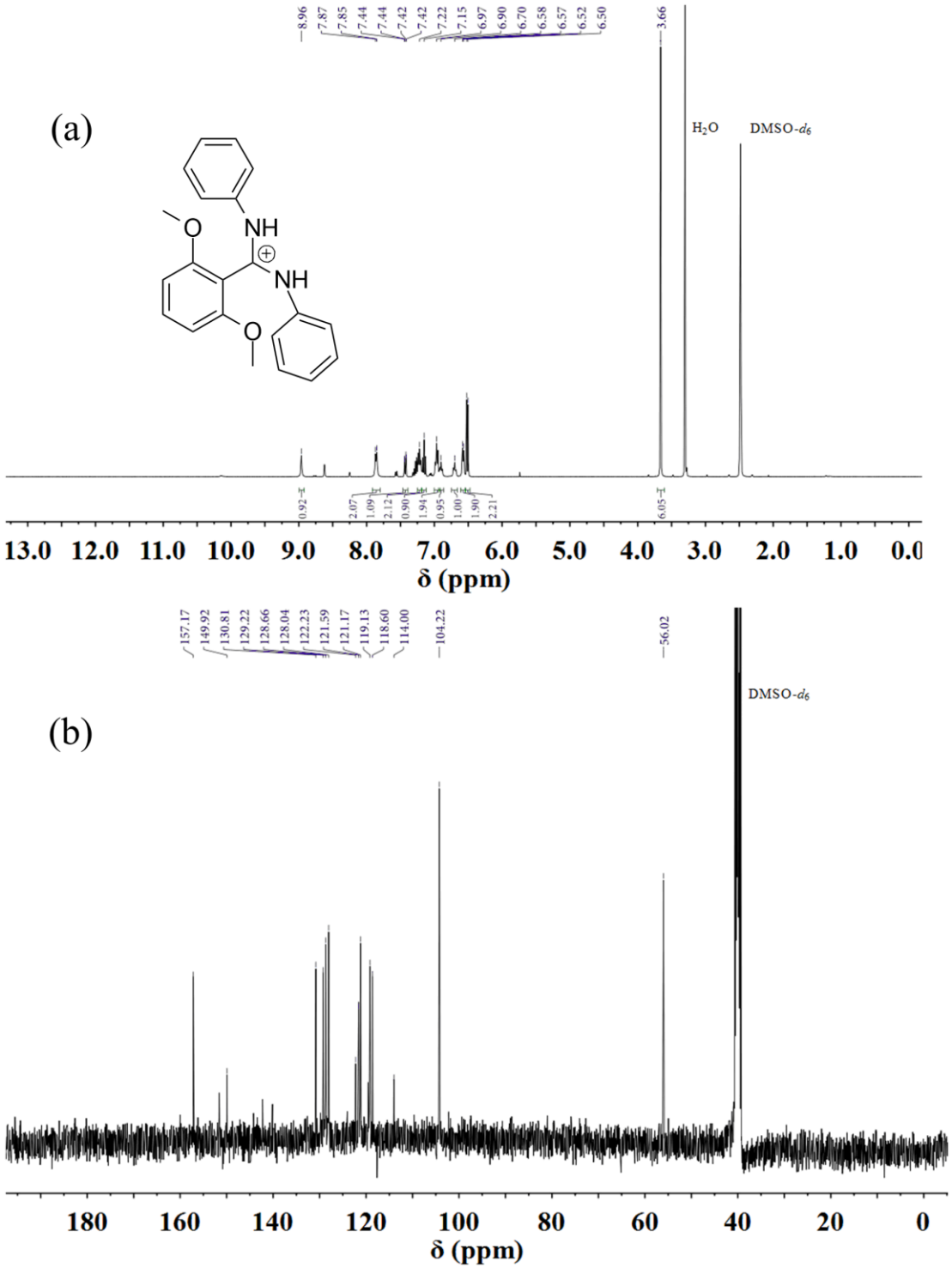


Figure S20. NMR spectra of isolated amidine **5AIII**: (a) ^{1}H NMR (400MHz, DMSO-d_6); (b) ^{13}C NMR (400MHz, DMSO-d_6)

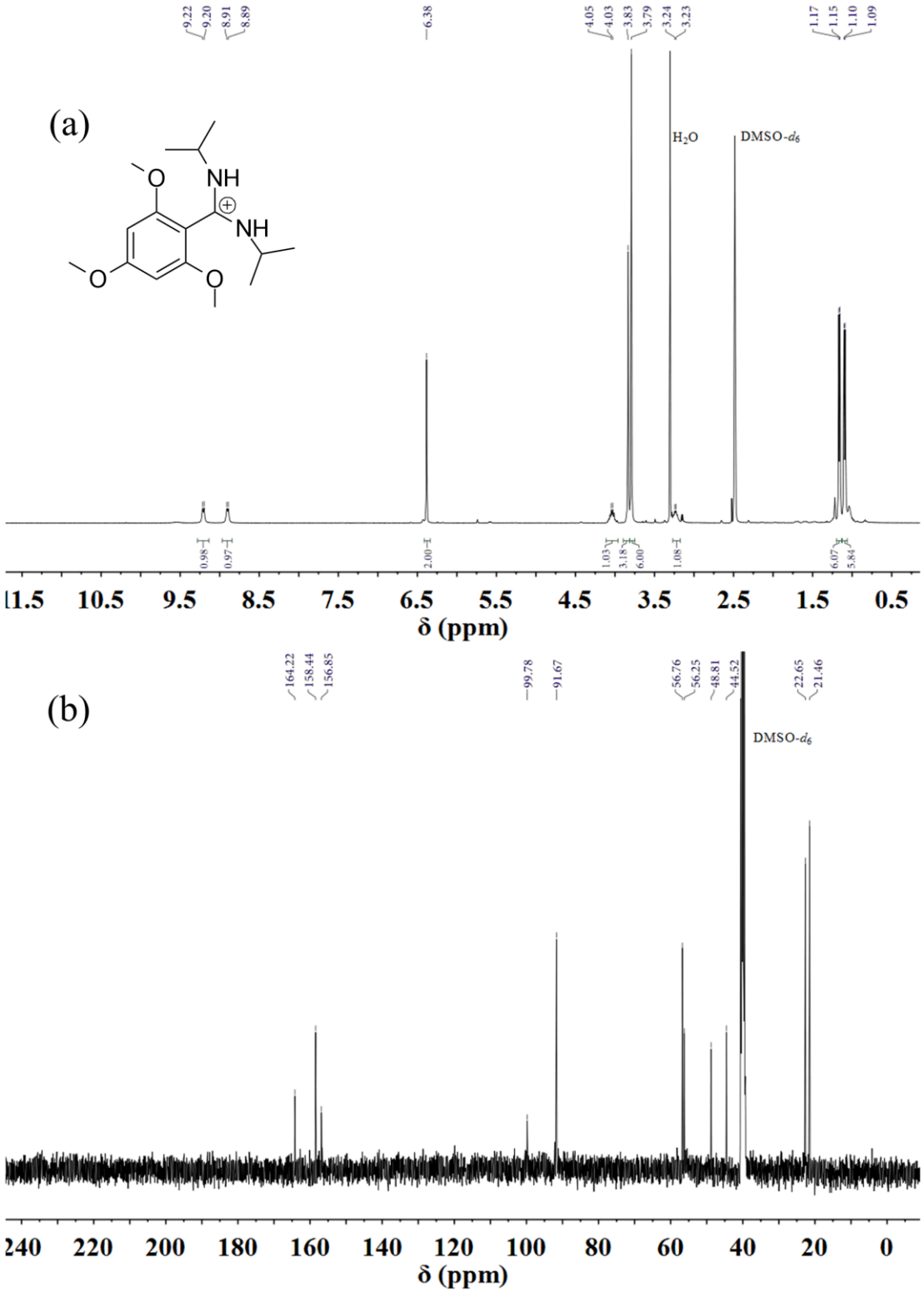


Figure S21. NMR spectra of isolated amidine **5BI**: (a) ^{1}H NMR (400MHz, DMSO-d_6); (b) ^{13}C NMR (400MHz, DMSO-d_6)

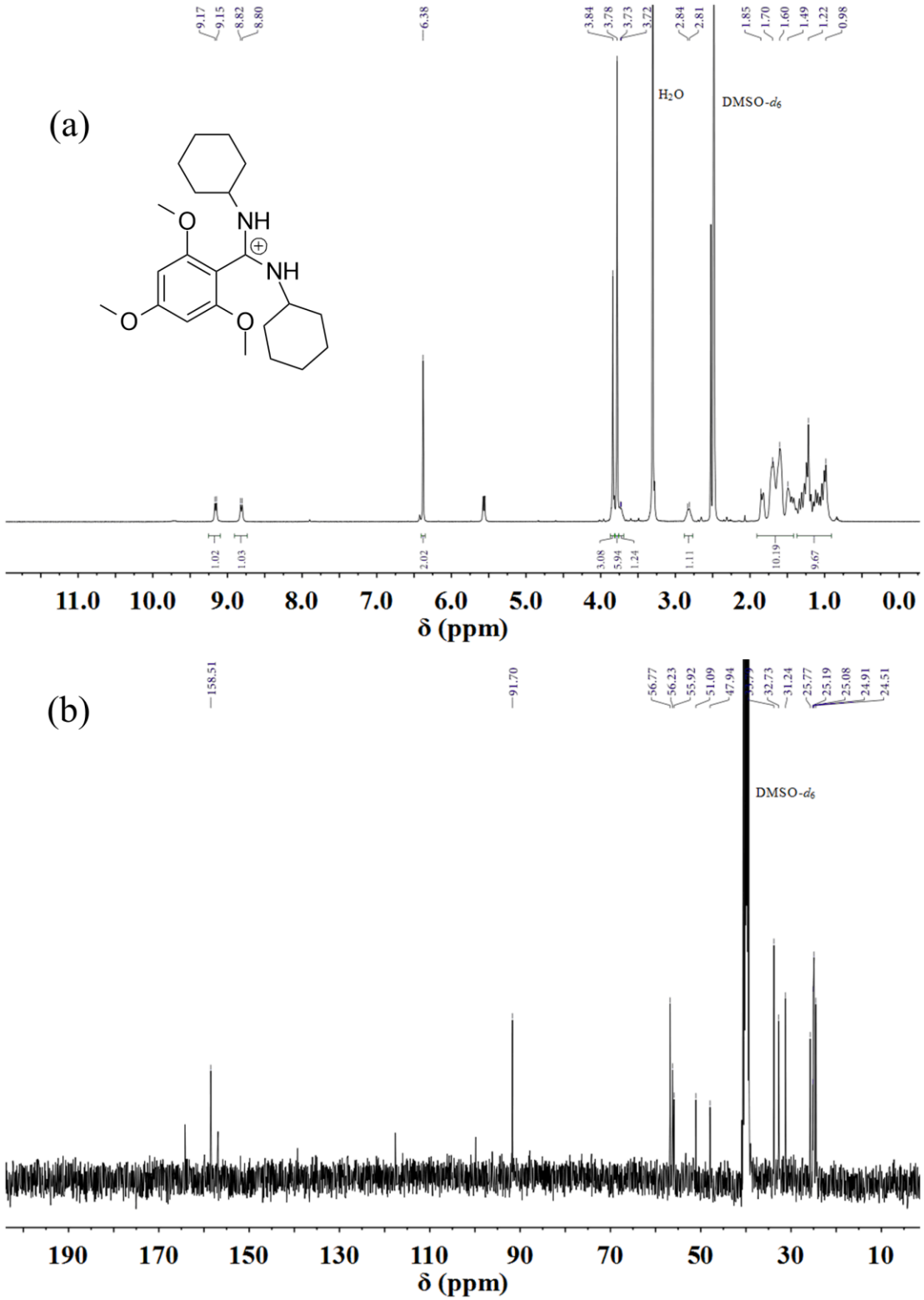


Figure S22. NMR spectra of isolated amidine **5BII**: (a) ^{1}H NMR (400MHz, DMSO-d_6); (b) ^{13}C NMR (400MHz, DMSO-d_6)

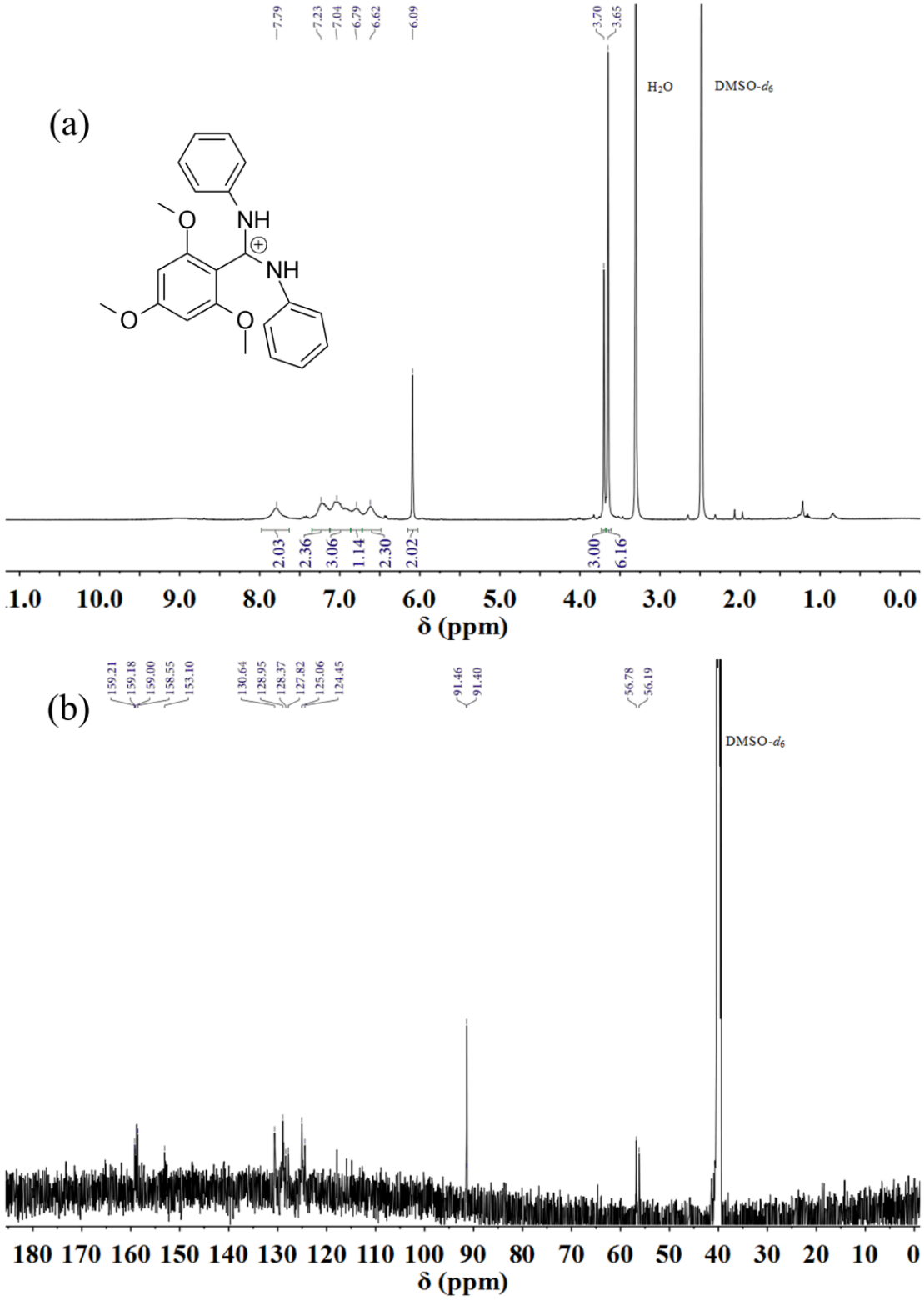


Figure S23. NMR spectra of isolated amidine **5BIII**: (a) ^{1}H NMR (400MHz, DMSO-d_6); (b) ^{13}C NMR (600MHz, DMSO-d_6)

X-ray Crystallography

The molecular structures of the synthesized benzamidines **5AII** and **5AIII** as their hydrochloride salts were confirmed by X-ray crystallography. For both compounds single crystals suitable for X-ray diffraction were obtained by slow evaporation of compounds dissolved in a mixture of pentane and dichloromethane (1:1). Both benzamidine hydrochlorides crystalized with one benzamidinium cation, a chlorine atom and one water molecule in their asymmetric units but both structures show different intermolecular hydrogen bonded arrangements (Figures S24 and S25). A dimeric arrangement is found in **5AII.HCl.H_2O** supported by two water molecules at the centre and a bridging chlorine atom between the water molecule and **5AII.H^+** due to strong hydrogen bonding through the Cl with O-H and N-H groups. In contrast, the hydrogen bonded arrangement in **5AIII** was different. Here two water molecules are bridged between a Cl atom and the **5AIII.H^+** cation forming a hydrogen bonded zigzag chain in an extended supramolecular structure.

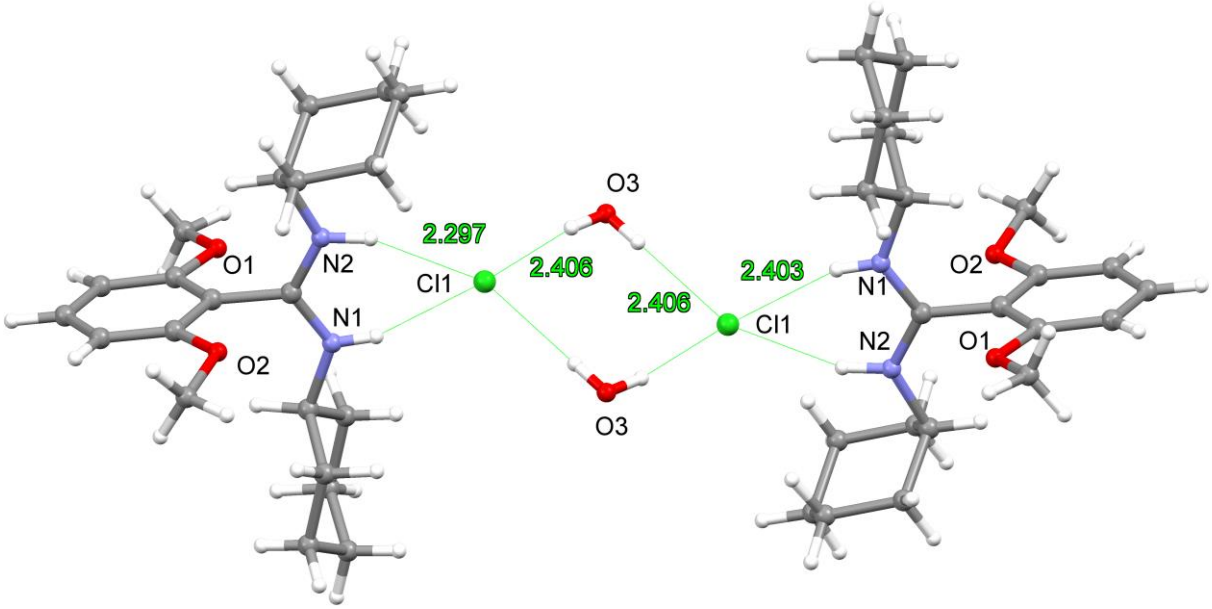


Figure S24. Mercury diagrams (capped stick) for the intermolecular hydrogen bonded arrangement of **5AII.HCl.H_2O**

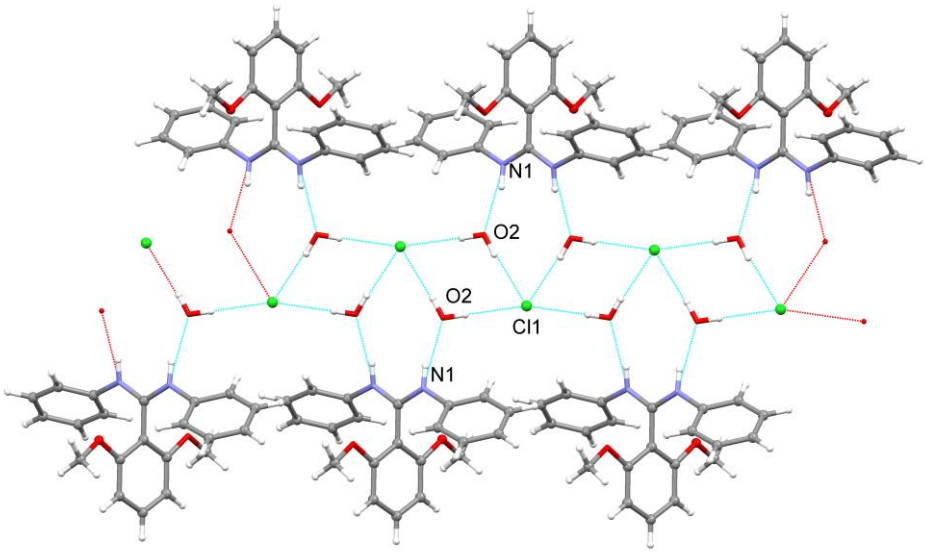


Figure S25. Mercury diagrams (capped stick) for the intermolecular hydrogen bonded arrangement of **5AII.HCl.H$_2$O**

Data Collection

X-ray data for amidines were collected at 130 K on an Agilent Technologies Dual source Supernova system using Mo and Cu Kα radiation, and data were treated using CrysAlisPro[*1] software. The structures were solved using SHELXT running within the WinGX*[2] package program.

Data Refinement

X-Ray data refinement for 5AII.HCl.H$_2$O

The structure was solved by direct methods using SHELXT running within the WinGX[*2] package. All non-hydrogen atoms were refined anisotropically. The structure was solved in the monoclinic space group $P2_1/n$ and refined to an R_1 value of 4.8%. Full details are given in Table S4.

X-Ray data refinement for 5AIII.HCl.H_2O

The structure was solved by direct methods using SHELXT[3] running within the WinGX[4] package. All non-hydrogen atoms were refined anisotropically. The structure was solved in the monoclinic space group *I*2/*a* and refined to an R_1 value of 3.2%. Full details are given in Table S5.

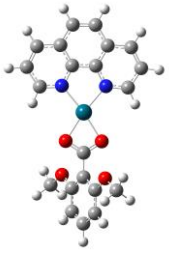
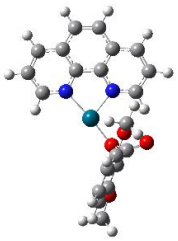
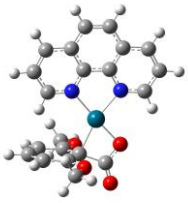
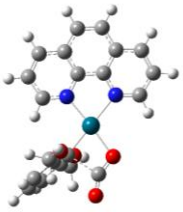
Table S4. Crystal data and structure refinement for **5AII.HCl.H_2O**

CCDC Number	1836504	
Identification code	5AII	
Empirical formula	C_{21} H_{35} C_l N_2 O_3	
Formula weight	398.96	
Temperature	130.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.1250(3) Å	α = 90°.
	b = 18.8393(5) Å	β = 108.937(4)°.
	c = 12.0041(4) Å	γ = 90°.
Volume	2165.83(12) $Å^3$	
Z	4	
Density (calculated)	1.224 Mg/m^3	
Absorption coefficient	0.199 mm^{-1}	
F(000)	864	
Crystal size	0.617 x 0.400 x 0.261 mm^3	
Theta range for data collection	3.153 to 36.448°.	
Index ranges	-16<=h<=16, -31<=k<=20, -19<=l<=18	
Reflections collected	23758	
Independent reflections	10003 [R(int) = 0.0356]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.944 and 0.898	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10003 / 0 / 384	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1149	
R indices (all data)	R1 = 0.0715, wR2 = 0.1314	
Largest diff. peak and hole	0.471 and -0.326 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for **5AIII.HCl.H_2O**

CCDC Number	1836505	
Identification code	5AIII	
Empirical formula	$C_{21}H_{25}ClN_2O_4$	
Formula weight	404.88	
Temperature	130(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 9.6185(2) Å	α = 90°.
	b = 16.7957(3) Å	β = 102.879(2)°.
	c = 12.7312(3) Å	γ = 90°.
Volume	2004.98(7) $Å^3$	
Z	4	
Density (calculated)	1.341 Mg/m^3	
Absorption coefficient	1.936 mm^{-1}	
F(000)	856	
Crystal size	0.391 x 0.275 x 0.141 mm^3	
Theta range for data collection	4.430 to 74.672°.	
Index ranges	-9<=h<=11, -17<=k<=20, -15<=l<=15	
Reflections collected	6781	
Independent reflections	2028 [R(int) = 0.0219]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.59845	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2028 / 0 / 179	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0867	
R indices (all data)	R1 = 0.0338, wR2 = 0.0878	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.243 and -0.331 $e.Å^{-3}$	

3D structures and energies for all M06/BS2 DFT calculated species (all energies are in Hartrees).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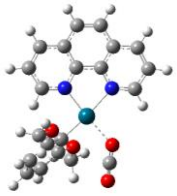	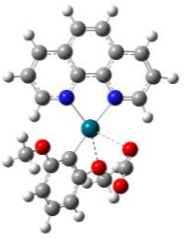	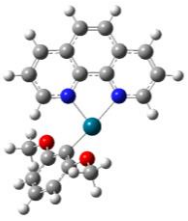	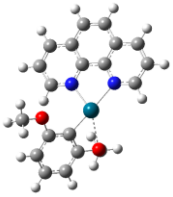
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	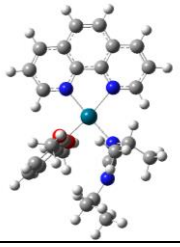	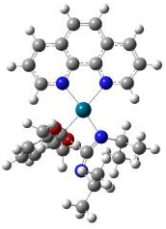	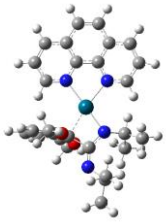
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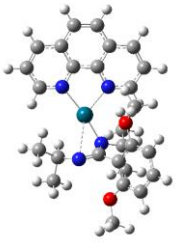	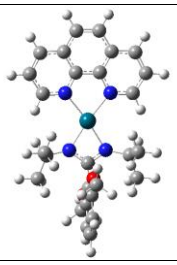		
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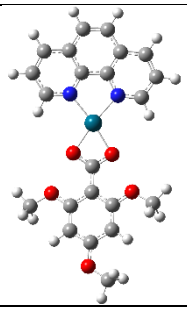	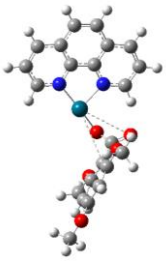	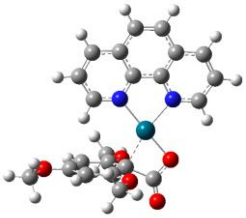	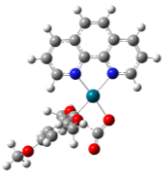
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	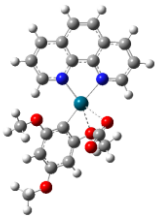	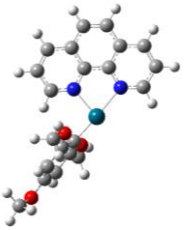	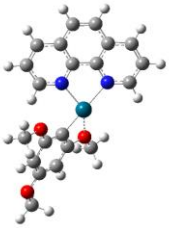
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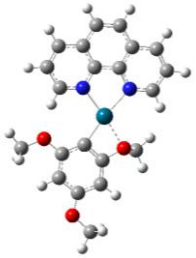	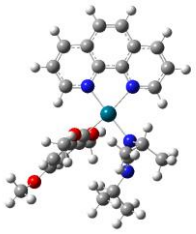	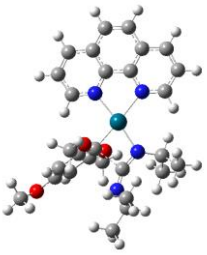	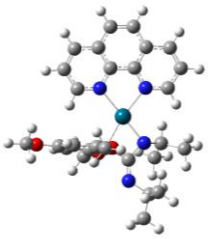
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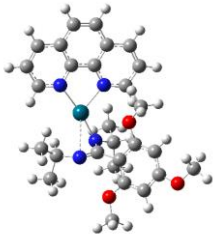	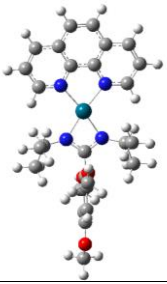		
11b-12b	**12b**		
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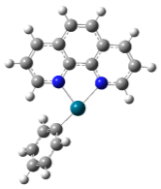	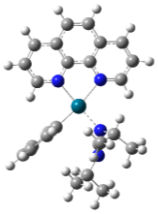	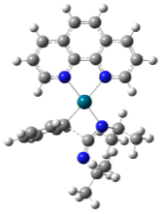	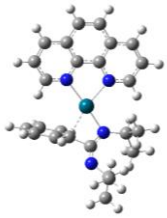
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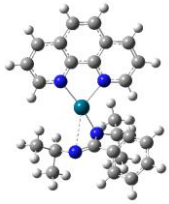	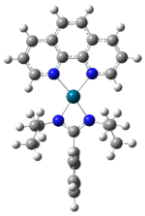		
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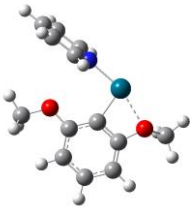
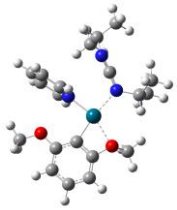
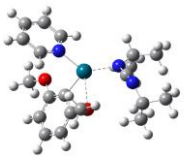
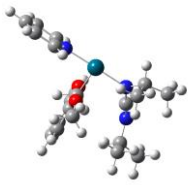
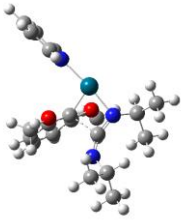
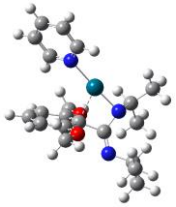
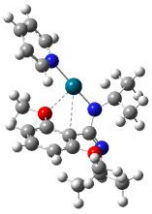
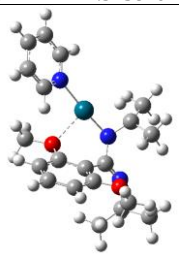
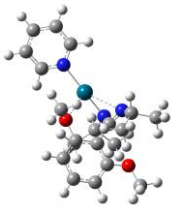
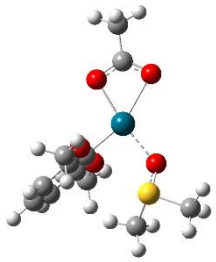
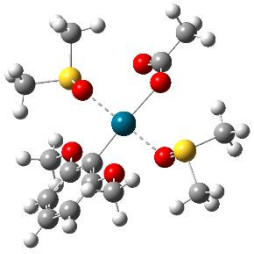
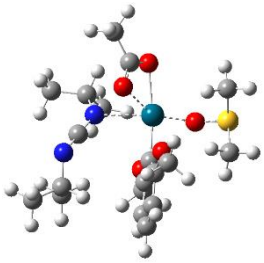
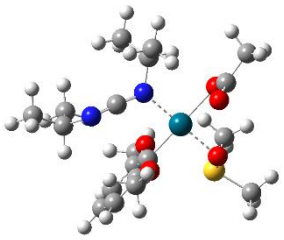
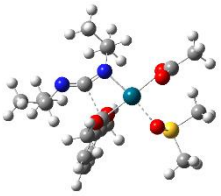
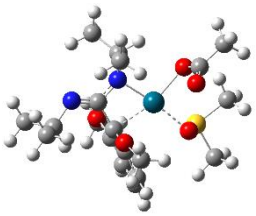
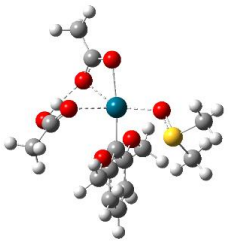
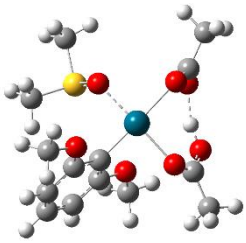
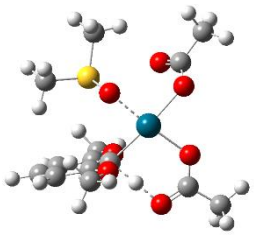
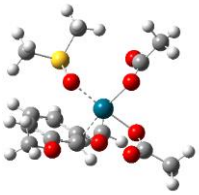
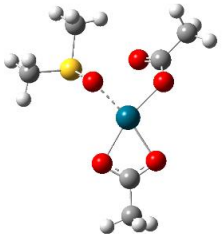
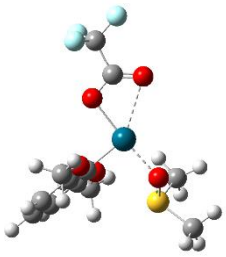
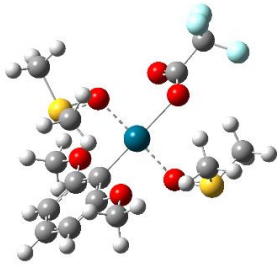
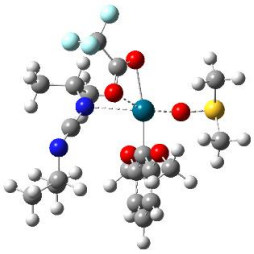
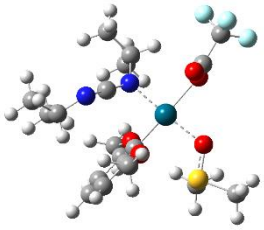
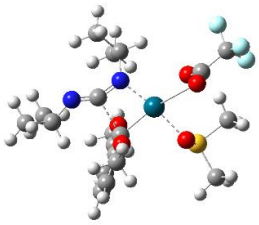
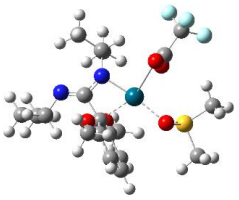
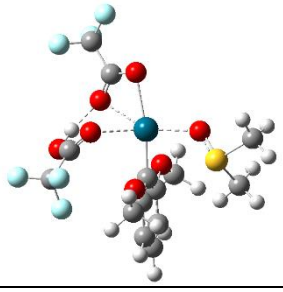
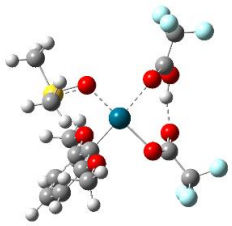
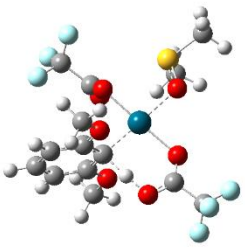
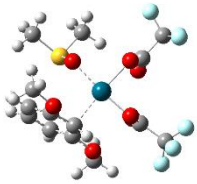
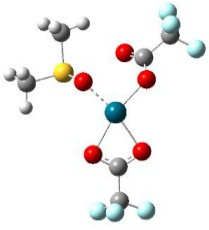
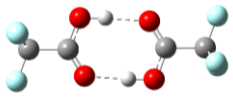
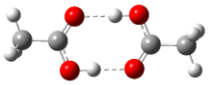
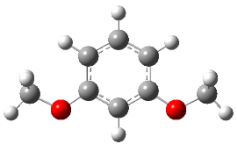
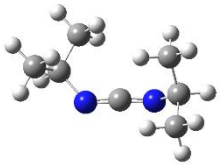
			
9d	**10d**	**TS10d-10d'**	**10d'**
E= -834.990386 H= -834.726368 G= -834.789694 SPE= -837.0588468	E= -1219.408456 H= -1218.926401 G= -1219.016422 SPE= -1221.962058	E= -1219.391818 H= -1218.910316 G= -1218.998211 SPE= -1221.942368	E= -1219.422793 H= -1218.940014 G= -1219.02863 SPE= -1221.973846
			
TS10d'-11d	**11d**	**TS11d-11d'**	**11d'**
E= -1219.38338 H= -1218.902672 G= -1218.989355 SPE= -1221.930513	E= -1219.399996 H= -1218.917426 G= -1219.004511 SPE= -1221.943792	E= -1219.375711 H= -1218.897839 G= -1218.983271 SPE= -1221.924234	E= -1219.376306 H= -1218.896253 G= -1218.981978 SPE= -1221.925086
			
TS11d'-12d	**12d**		
E= -1219.374665 H= -1218.89359 G= -1218.979207 SPE= -1221.919806	E= -1219.42047 H= -1218.937268 G= -1219.027492 SPE= -1221.97158		

		
13a1	**13a2**	**TS13a-14a**
E = -1368.580509 H = -1368.269103 G = -1368.345382 SPE = -1370.846982630	E = -1921.659037 H = -1921.258399 G = -1921.349693 SPE = -1924.195395050	E = -1752.954818 H = -1752.425937 G = -1752.528191 SPE = -1755.702346950
		
14a	**TS14a-15a**	**15a**
E = -1752.974198 H = -1752.443246 G = -1752.545146 SPE = -1755.725718240	E = -1752.950554 H = -1752.421521 G = -1752.523478 SPE = -1755.700271980	E = -1752.982071 H = -1752.450895 G = -1752.552188 SPE = -1755.727585860
		
TS13a-16a	**16a**	**TS16a-17a**
E = -1597.547468 H = -1597.166233 G = -1597.252927 SPE = -1600.049815500	E = -1597.565397 H = -1597.184293 G = -1597.271939 SPE = -1600.072961960	E = -1597.549975 H = -1597.168089 G = -1597.256653 SPE = -1600.050781170
		
17a	**18a**	
E = -1597.563914 H = -1597.182074 G = -1597.273094 SPE = -1600.068971240	E = -1136.569155 H = -1136.366067 G = -1136.431849 SPE = -1138.540605970	

		
13b1	**13b2**	**TS13b-14b**
E = -1666.223517 H = -1665.931735 G = -1666.015463 SPE = -1668.699794	E = -2219.308614 H = -2218.928027 G = -2219.0262 SPE = -2222.057655	E = -2050.602507 H = -2050.092194 G = -2050.195812 SPE = -2053.557664
		
14b	**TS14b-15b**	**15b**
E = -2050.628777 H = -2050.118724 G = -2050.228018 SPE = -2053.590696	E = -2050.603067 H = -2050.094018 G = -2050.200544 SPE = -2053.56168	E = -2050.632954 H = -2050.122025 G = -2050.228165 SPE = -2053.5868
		
TS13b-16b	**16b**	**TS16b-17b**
E = -2192.831448 H = -2192.491284 G = -2192.58732 SPE = -2195.748819	E = -2192.850642 H = -2192.510262 G = -2192.612636 SPE = -2195.776215	E = -2192.830835 H = -2192.495405 G = -2192.593724 SPE = -2195.755544
		
17b	**18b**	
E = -2192.85925 H = -2192.517678 G = -2192.617609 SPE = -2195.783198	E = -1731.847602 H = -1731.685348 G = -1731.762189 SPE = -1734.238212	

			
$(CF_3COOH)_2$	**$(CH_3COOH)_2$**	**DMSO**	**1,3-dimethoxy benzene**
E = -1053.2153 H = -1053.119511 G = -1053.178197 SPE = -1054.114081	E = -457.947255 H = -457.812168 G = -457.856 SPE = -458.428898430	E = -553.055231 H = -552.969371 G = -553.004256 SPE = -553.332269389	E = -460.976633 H = -460.801079 G = -460.84928 SPE = -461.515425887
			
***N,N'*-diisopropyl carbodiimide**			
E = -384.367711 H = -384.151883 G = -384.199959 SPE = -384.851308027			

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(1) Su, T.; Bowers, M. T. Ion-polar molecule collisions. Effect of size on ion-polar molecule rate constants. Paramterization of the average-dipole-orientation theory. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347–356.

(2) Lim, K. F. COLRATE. QCPE 643: Calculation of gas-kinetic collision rate coefficients. *QCPE Bull.* **1994**, *14*, 3.

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(4) Farrugia, L. J. WinGX suite for small-molecule single-crystal crystallography, J. Appl. Cryst. **1999**, *32*, 837-838.