Supplementary Information

$n \rightarrow \pi^*$ Interactions as A Versatile Tool for Controlling Dynamic Imine Chemistry in Both Organic and Aqueous Media

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TABLE OF CONTENTS

1. General Methods

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III spectrometer. The chemical shifts (δ) for ^{1}H NMR spectra, given in ppm, are referenced to the residual proton signal of the deuterated solvent. Mass spectra were recorded on a Bruker IMPACT-II spectrometer. pH was measured on a Sartorius PB-10 pH meter. All reagents were obtained from commercial sources and were used without further purification, unless indicated otherwise.

DCRs in Acetonitrile. Dynamic covalent reactions (DCRs) were performed *in situ* in the presence of molecular sieves (3 Å) in CD_3CN at room temperature without isolation and purification. For imine formation reactions, to an aldehyde (~39 mM, 1.0 equiv.) in CD_3CN (0.60 mL), was added an amine (RNH_2, 1.2 equiv.). For imine exchange reaction series 1 two aldehydes (~39 mM each, 1.0 equiv.) were mixed with 1-butylamine (1.0 equiv.) in CD_3CN (0.60 mL). For imine exchange reaction series 2 two aldehydes, 1.2 equiv. of DBU was also added. The mixture was stirred and characterized by ^{1}H NMR and ESI mass spectral analysis after the equilibrium was reached. See figure captions for specific conditions if necessary.

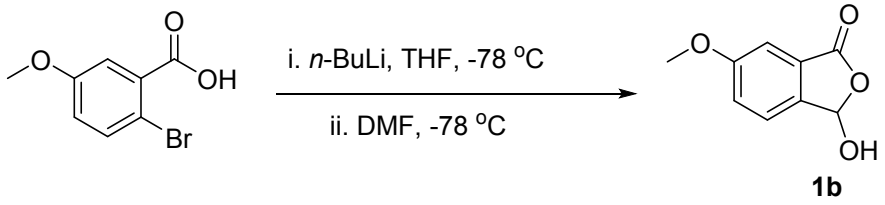
DCRs in Aqueous Solution. For imine formation in water an aldehyde (~39 mM, 1.0 equiv.) and ethanolamine (2.0 equiv.) were dissolved in D_2O (0.60 mL). For imine exchange reaction series 3 two aldehydes (~39 mM each, 1.0 equiv.) were mixed with ethanolamine (2.0 equiv.) in D_2O (0.60 mL, with 10% DMSO-d_6). For imine exchange reaction series 4 two aldehydes (~39 mM each, 1.0 equiv.) were mixed with ethanolamine (3.0 equiv.) in D_2O (0.60 mL). For imine formation in 50 mM phosphate buffer (PB) in D_2O, the stock solutions of aldehyde **1g** (60 mM) and amines (ethanolamine: 120 mM; amino acids: 120 mM; peptides: 20 mM) were prepared in PB buffer, respectively, and the desired pH (7.0, 7.4, or 7.8) was adjusted with concentrated NaOH or HCl solution. **1g** (40 mmol, 20 equiv.) and amine (2 mmol, 1.0 equiv.) were mixed under the same pH and stirred at room temperature. The mixture was characterized by ^{1}H NMR and ESI-MS after the equilibrium was reached. See figure captions for specific conditions if necessary.

DFT Calculations. All calculations were performed by using Gaussian 09 packages.[S1] The method and basis set of M06-2X-D3/def2-TZVP with an ultrafine integration grid were employed for the optimization and frequency analysis. PCM solvent model was included for acetonitrile or water. By frequency analysis, the number of imaginary frequencies for minima is 0. NBO analysis was implemented by NBO 3.1 module in Gaussian 09 packages and presented by VMD_1.90. For simplicity methylamine and dimethylamine were employed to create imine and iminium ion for calculation, respectively. Conformational search and rigid scan of potential energy surface (PES) were run for $\mathbf{1a_{ocb}}$ and $\mathbf{2a_{ocb}}$, and the major isomers were subjected for

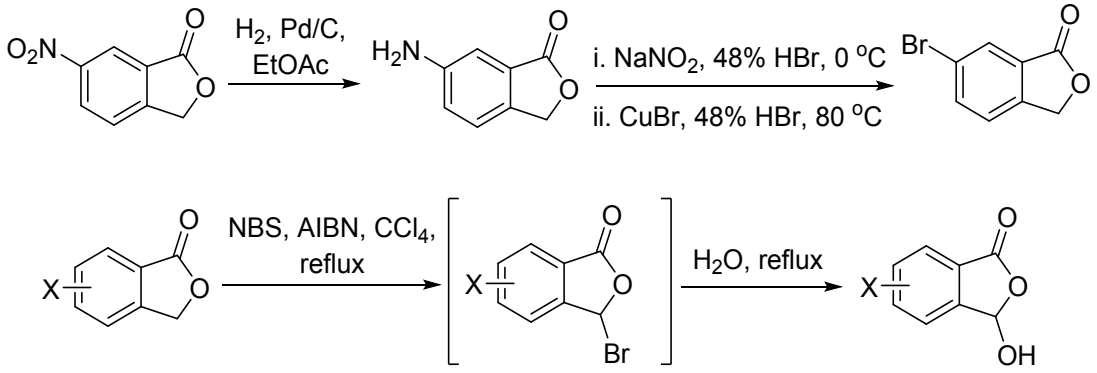
NBO analysis. For substituent effect (**1b**-**1g** and **2b**-**2g**) the open conjugate base form was studied. See more details in associated Figures and Tables if necessary.

2. Synthesis and Characterization

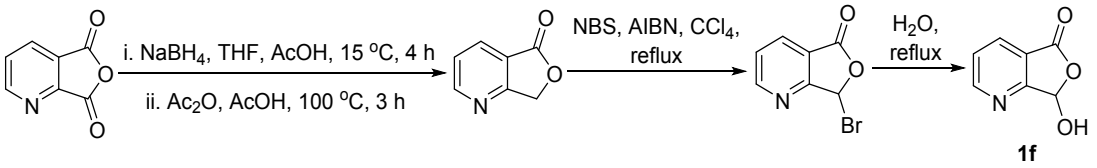
Scheme S1. Synthesis of **1b**.



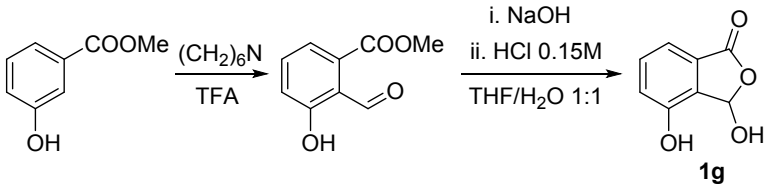
Scheme S2. General synthetic routes of **1c**, **1d**, and **1e**.

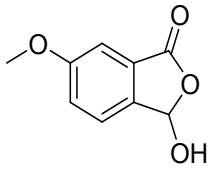


Scheme S3. Synthesis of **1f**.

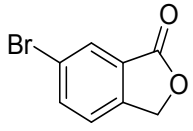


Scheme S4. Synthesis of **1g**.

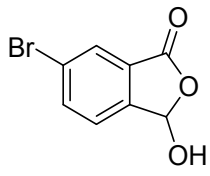




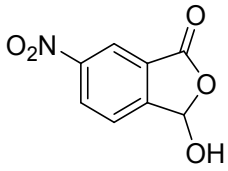
3-Hydroxy-6-methophthalide (1b): The reported procedure[S2] was used to afford the title compound as a white solid.



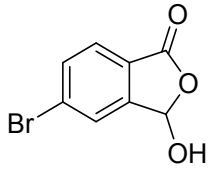
6-Bromophthalide: The reported procedure[S3] was used to afford the title compound as a yellow solid.



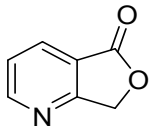
3-Hydroxy-6-bromophthalide (1c): The reported procedure[S4] was used to afford the title compound as a white solid.



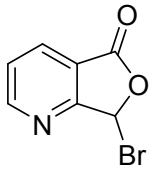
3-Hydroxy-6-nitrophthalide (1d): The reported procedure[S4] was used to afford the title compound as a yellow solid.



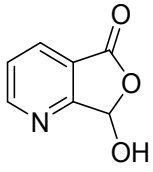
3-Hydroxy-5-bromophthalide (1e): The reported procedure[S5] was used to afford the title compound as a white solid.



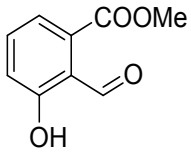
4-Azaphthalide: The reported procedure[S6] was used to afford the title compound as a yellow solid.



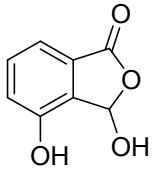
4-Aza-3-bromophthalide: The reported procedure[S6] was used to afford the title compound as a colorless solid.



4-Aza-3-hydroxyphthalide (1f): The reported procedure[S6] was used to afford the title compound as a yellow solid.



Methyl 2-formyl-3-hydroxybenzoate: The reported procedure[S7] was used to afford the title compound as a white solid.



2-Formyl-3-hydroxybenzoic acid (1g): The reported procedure[S7] was used to afford the title compound as a white solid.

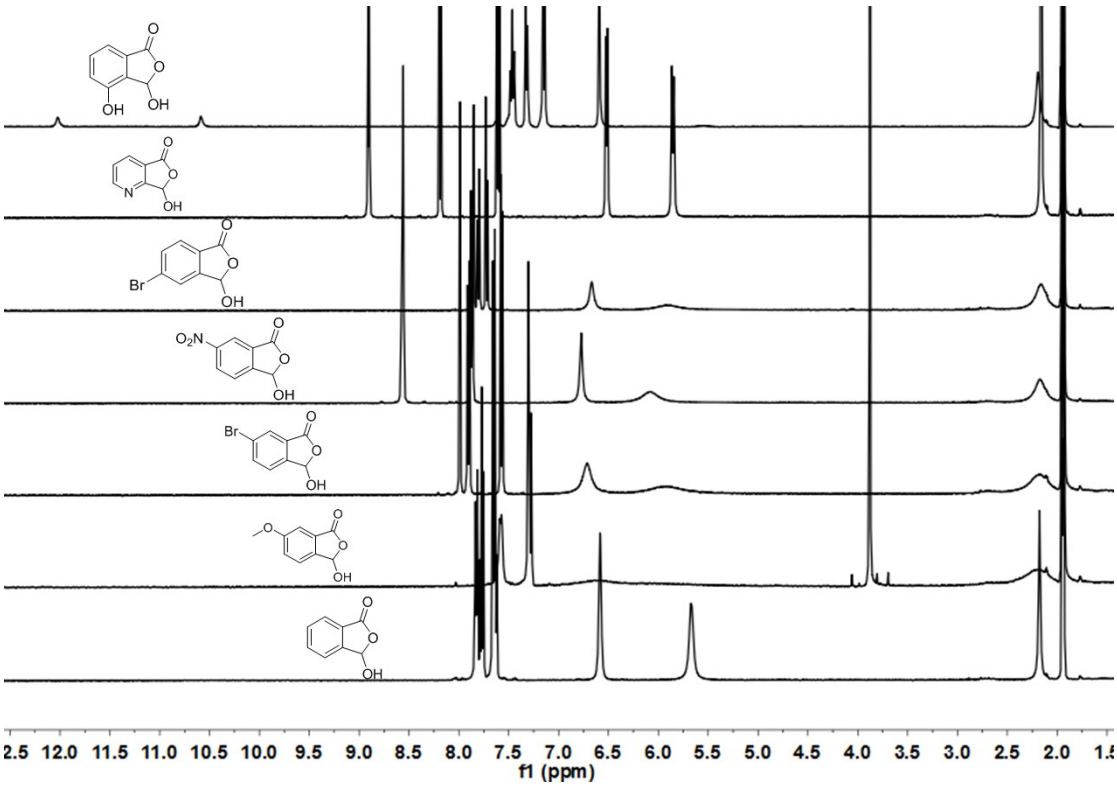


Figure S1. ^{1}H NMR spectra of **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, and **1g** (from bottom to top) in CD_3CN.

3. Dynamic Covalent Reactions (DCRs)

(1) Imine Formation

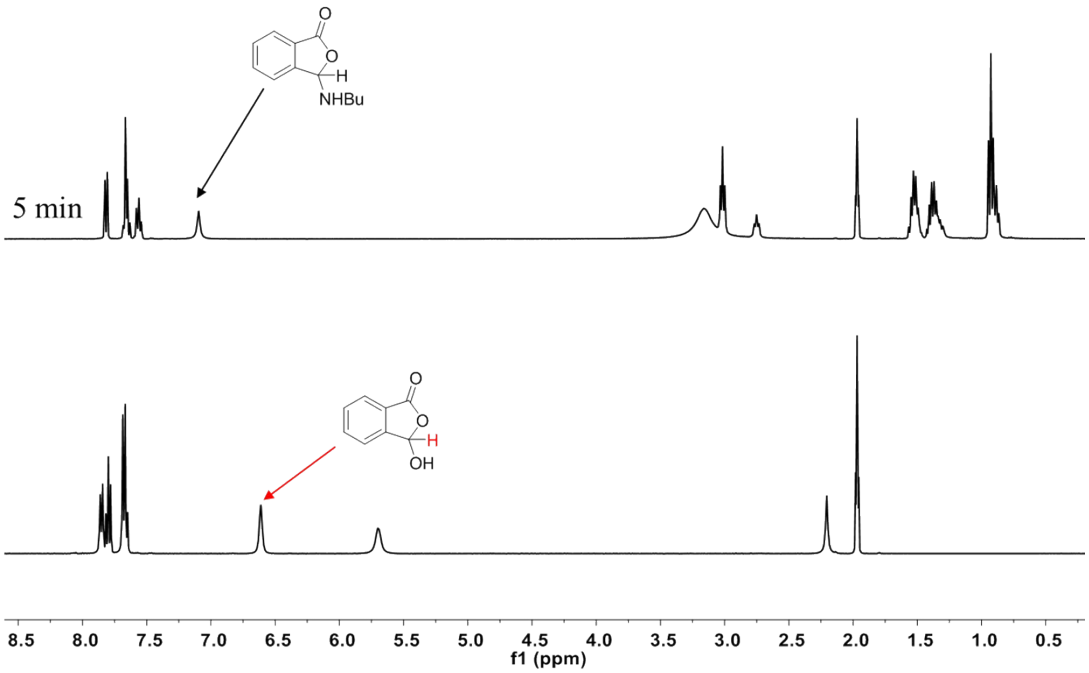


Figure S2. ^{1}H NMR spectra of the reaction between **1a** (39 mM) and 1-butylamine (1.2 equiv.) in CD_3CN. The reaction was complete after 5 min.

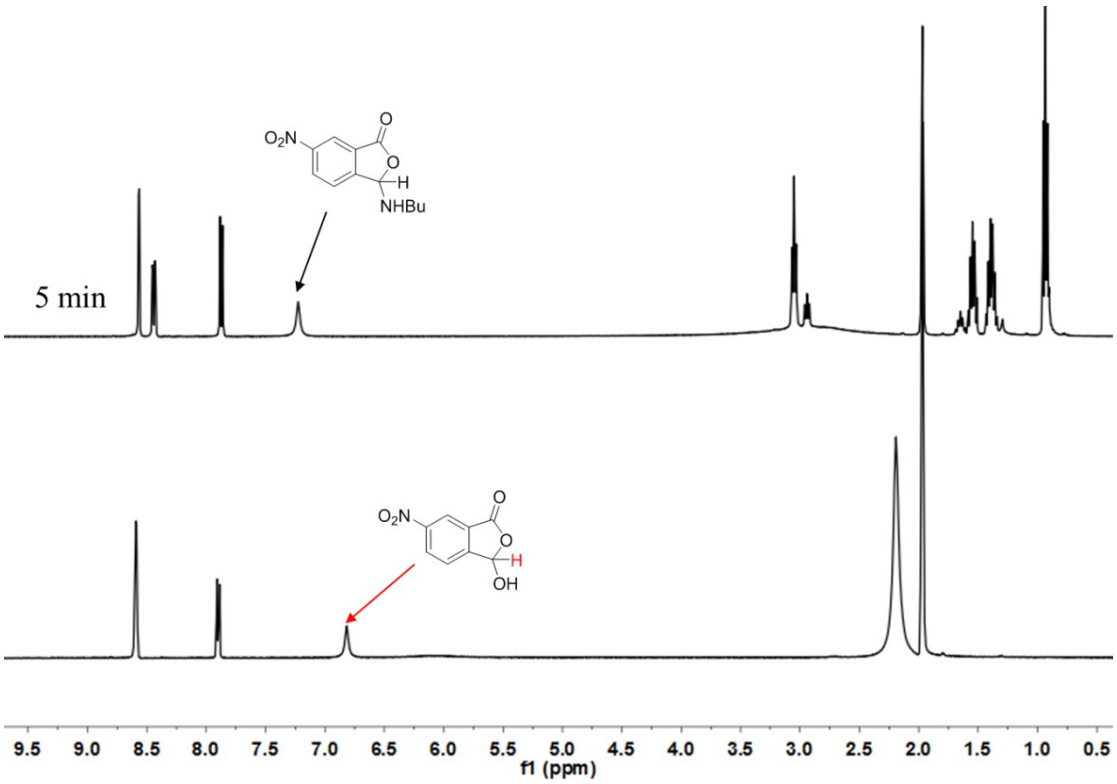


Figure S3. ^{1}H NMR spectra of the reaction between **1d** (39 mM) and 1-butylamine (1.2 equiv.) in CD_3CN. The reaction was complete after 5 min.

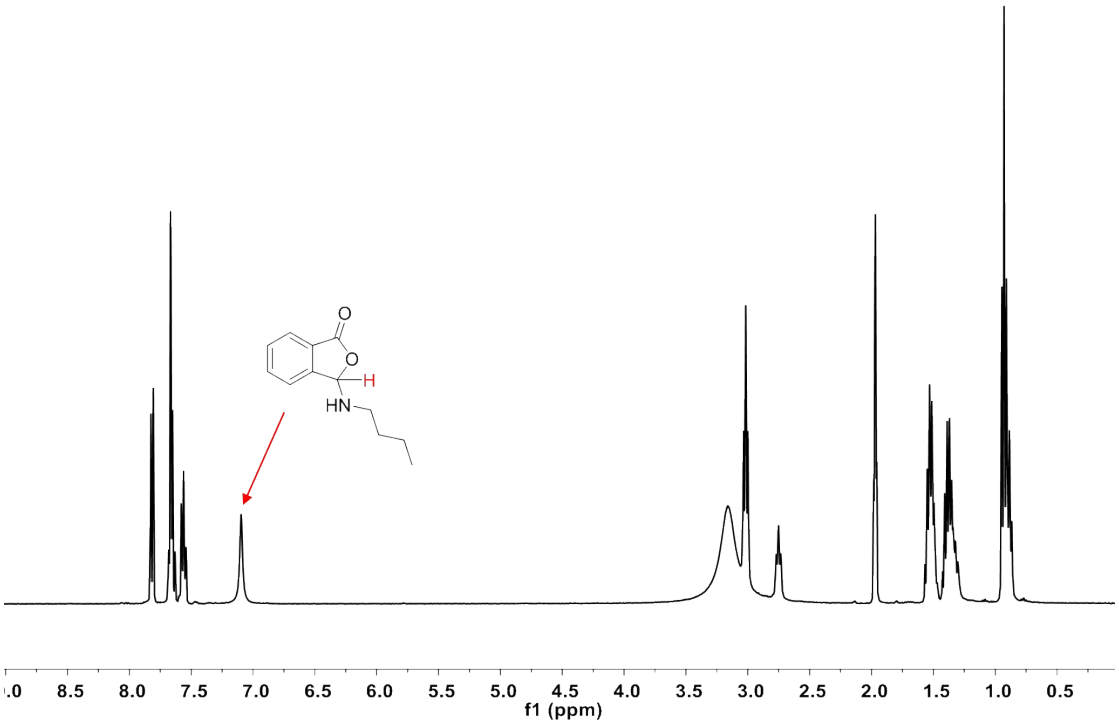


Figure S4. ^{1}H NMR spectrum of the reaction between **1a** and 1-butylamine in CD_3CN.

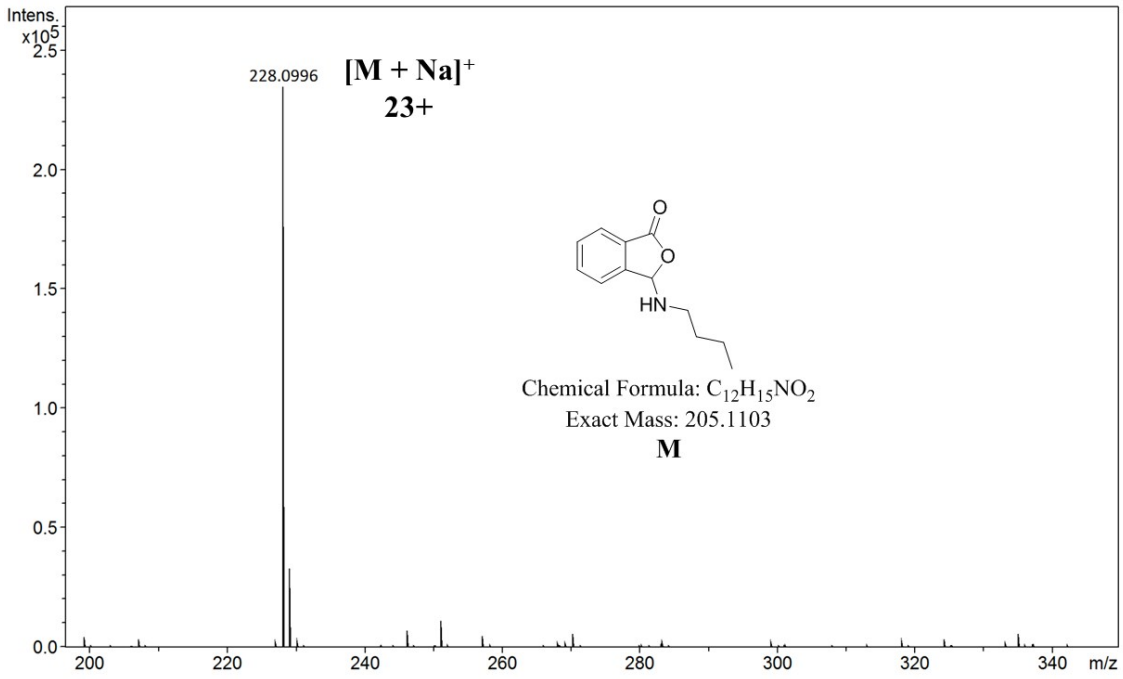


Figure S5. ESI-MS spectrum of the reaction between **1a** and 1-butylamine in CD_3CN.

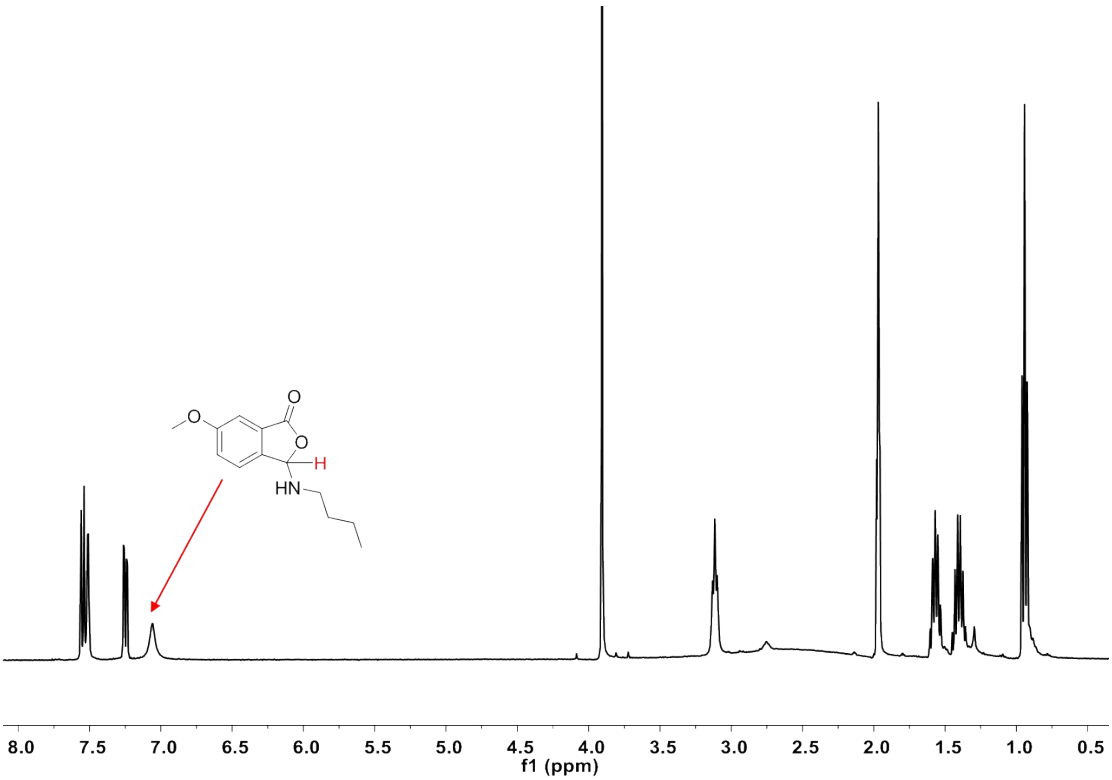


Figure S6. ^{1}H NMR spectrum of the reaction between **1b** and 1-butylamine in CD_3CN.

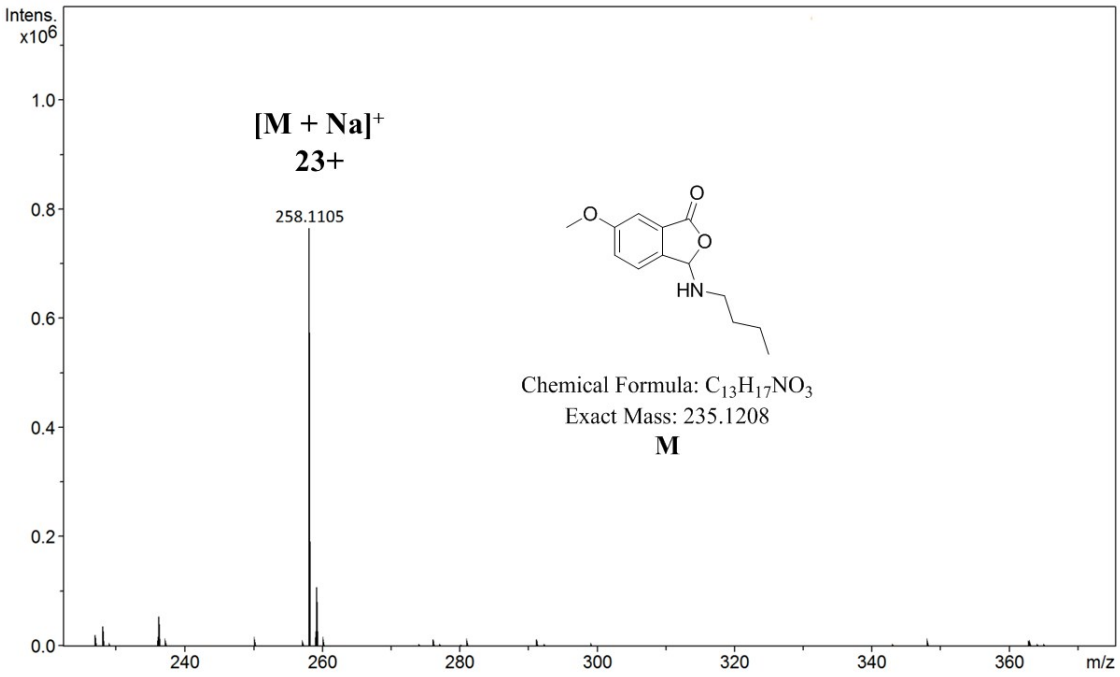


Figure S7. ESI-MS spectrum of the reaction between **1b** and 1-butylamine in CD_3CN.

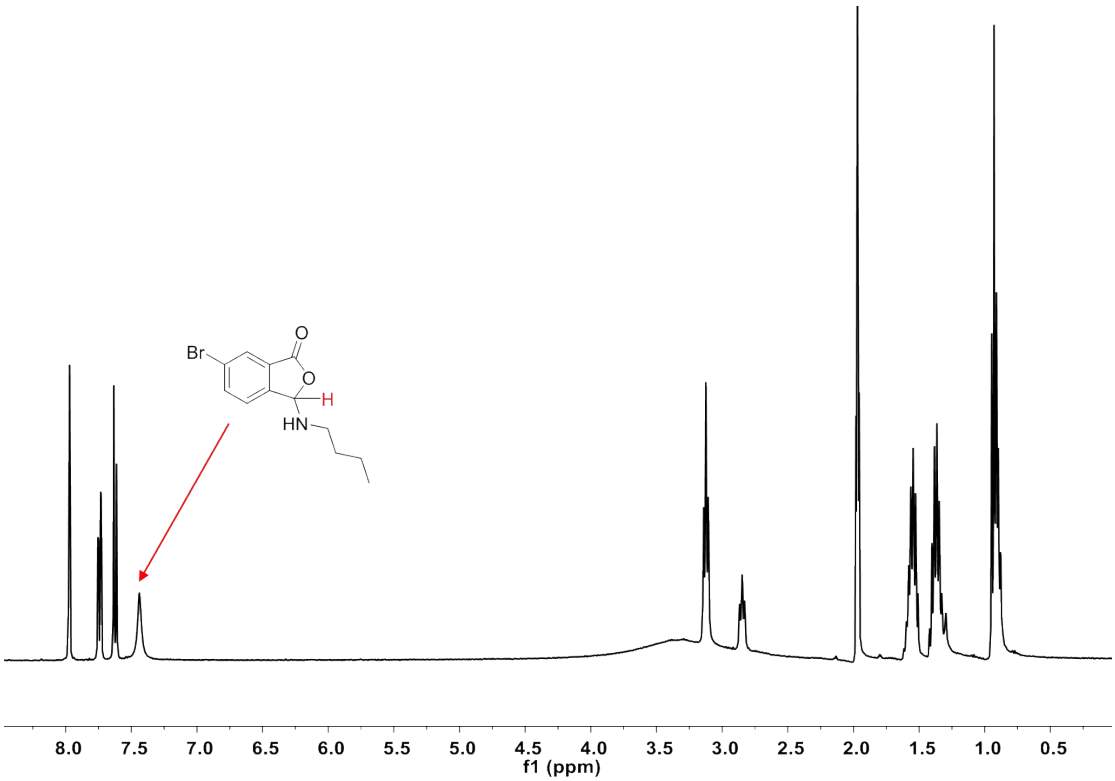


Figure S8. ^{1}H NMR spectrum of the reaction between **1c** and 1-butylamine in CD_3CN.

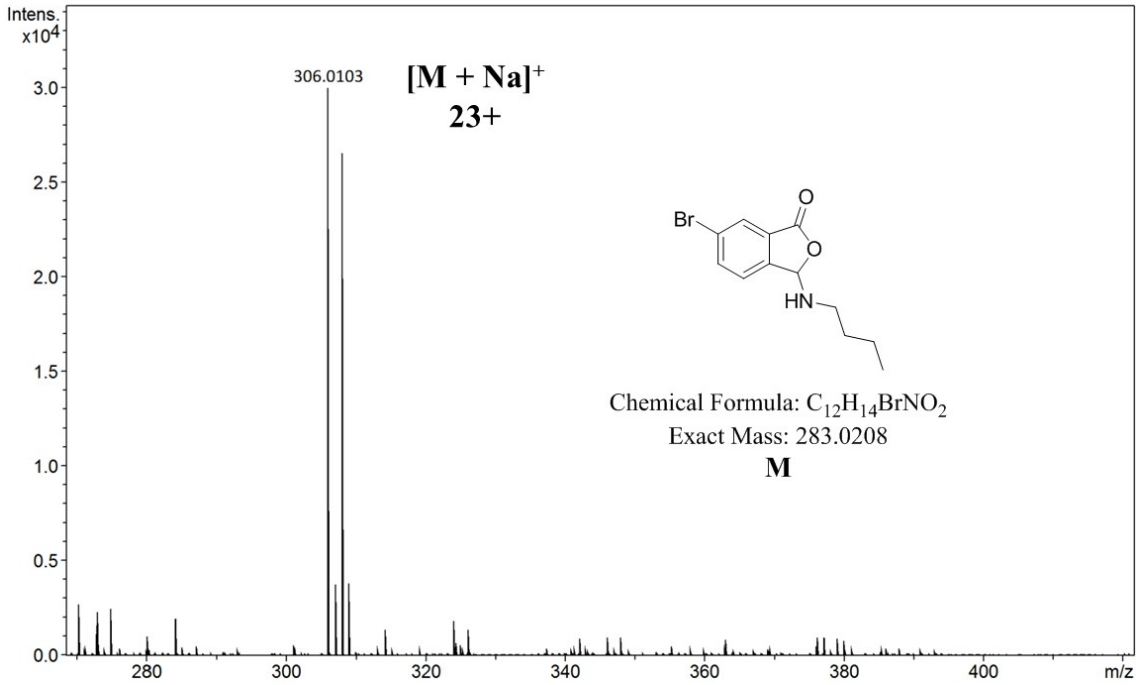


Figure S9. ESI-MS spectrum of the reaction between **1c** and 1-butylamine in CD_3CN.

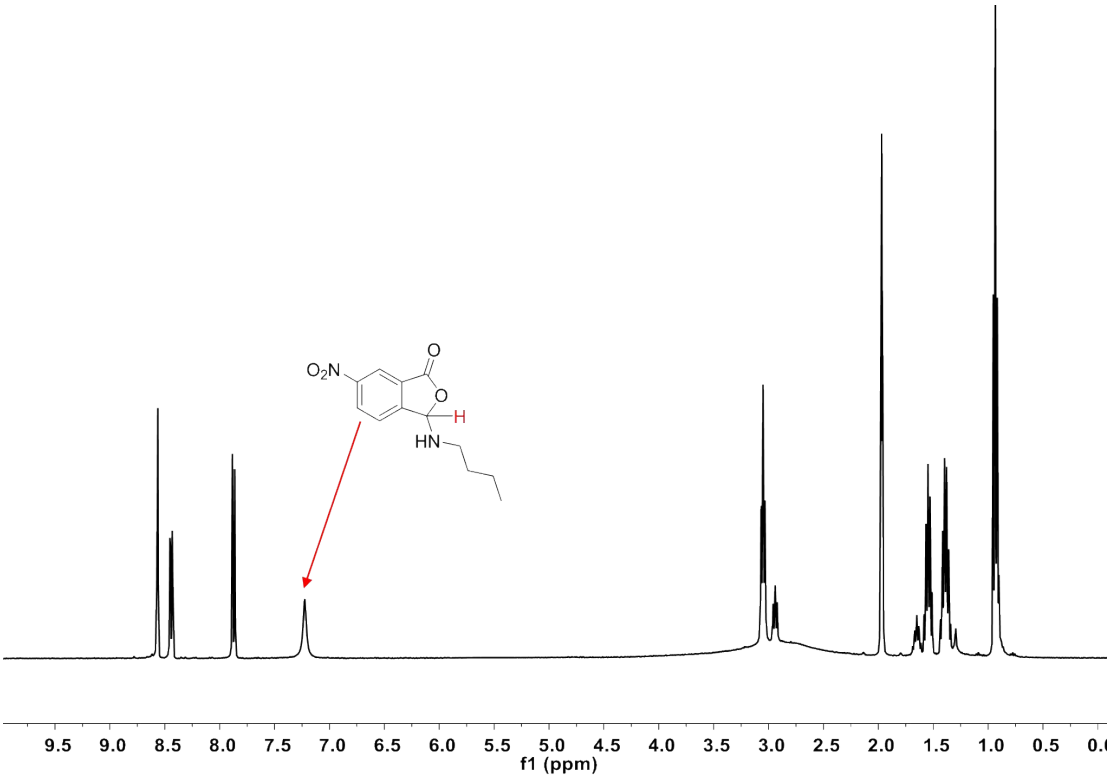


Figure S10. ^{1}H NMR spectrum of the reaction between **1d** and 1-butylamine in CD_3CN.

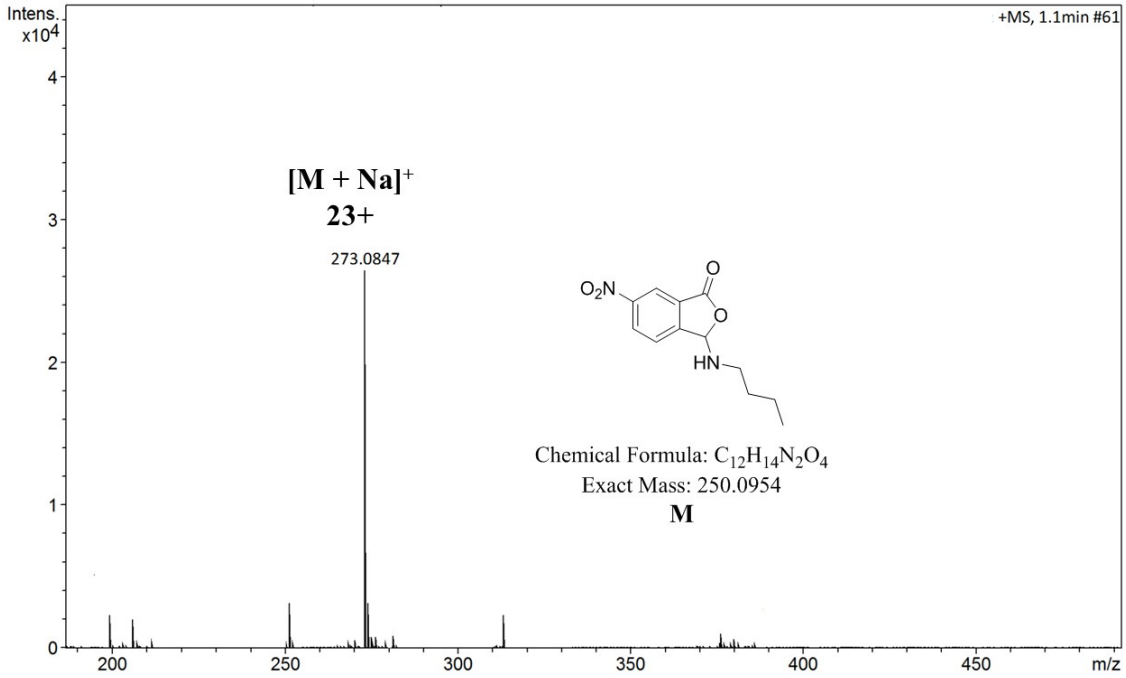


Figure S11. ESI-MS spectrum of the reaction between **1d** and 1-butylamine in CD_3CN.

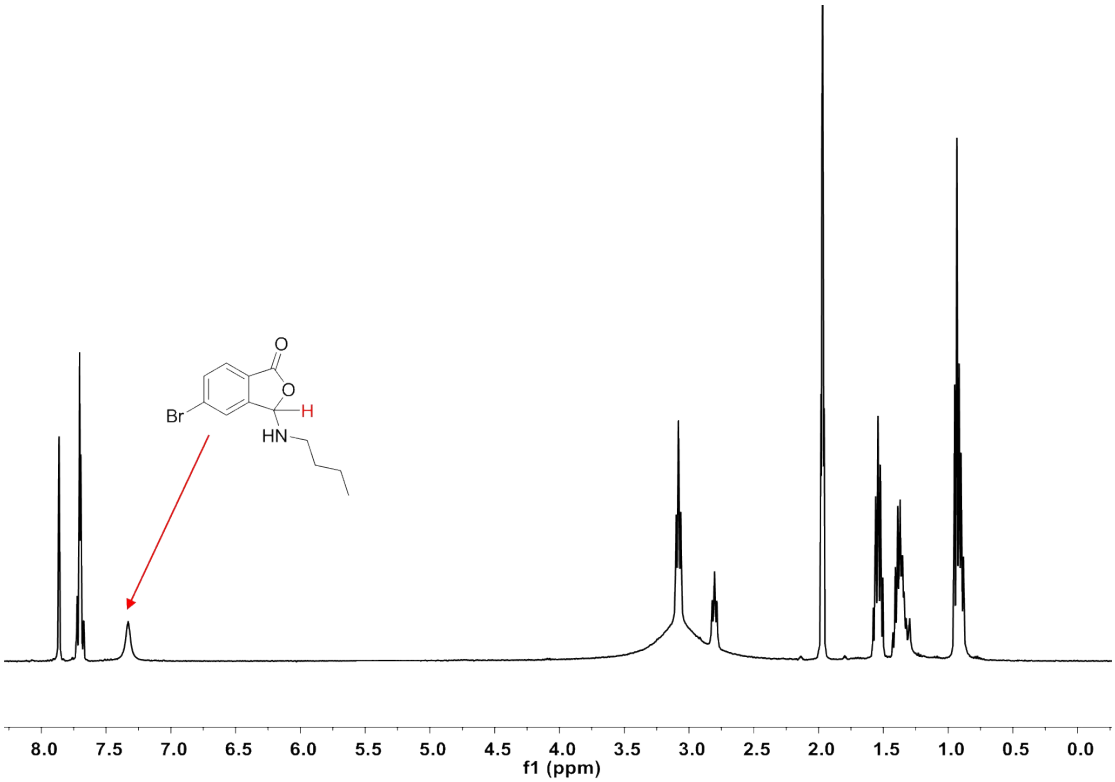


Figure S12. ^{1}H NMR spectrum of the reaction between **1e** and 1-butylamine in CD_3CN.

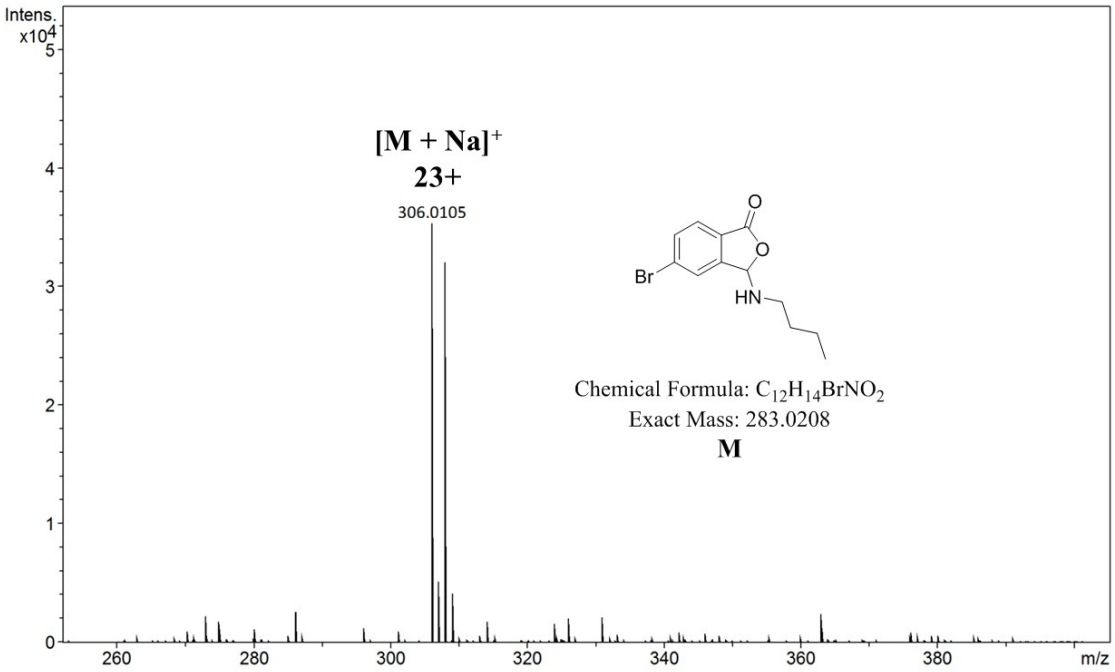


Figure S13. ESI-MS spectrum of the reaction between **1e** and 1-butylamine in CD_3CN.

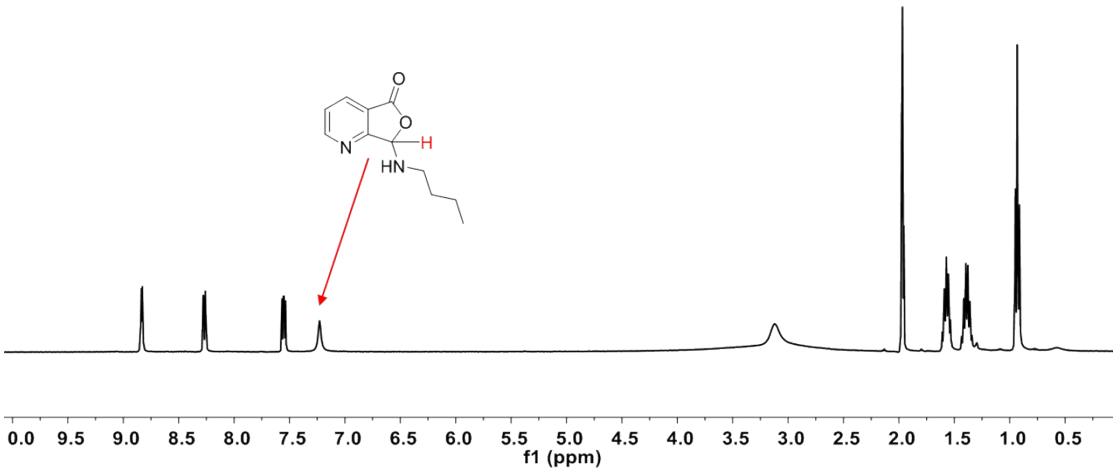


Figure S14. ^{1}H NMR spectrum of the reaction between **1f** and 1-butylamine in CD_3CN.

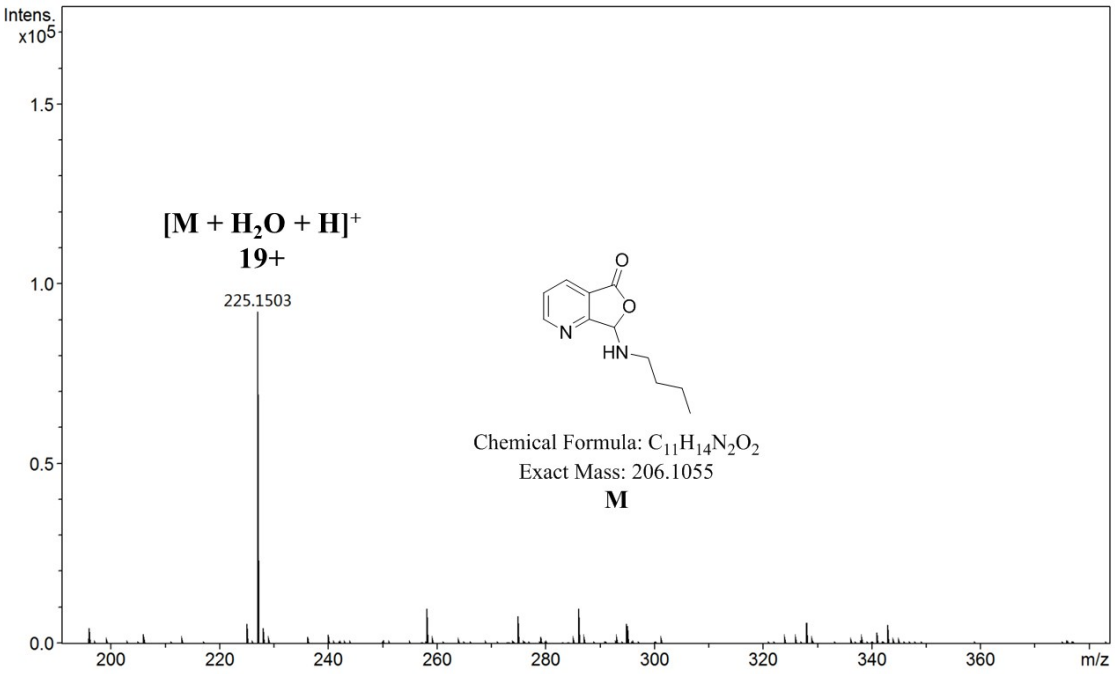


Figure S15. ESI-MS spectrum of the reaction between **1f** and 1-butylamine in CD_3CN.

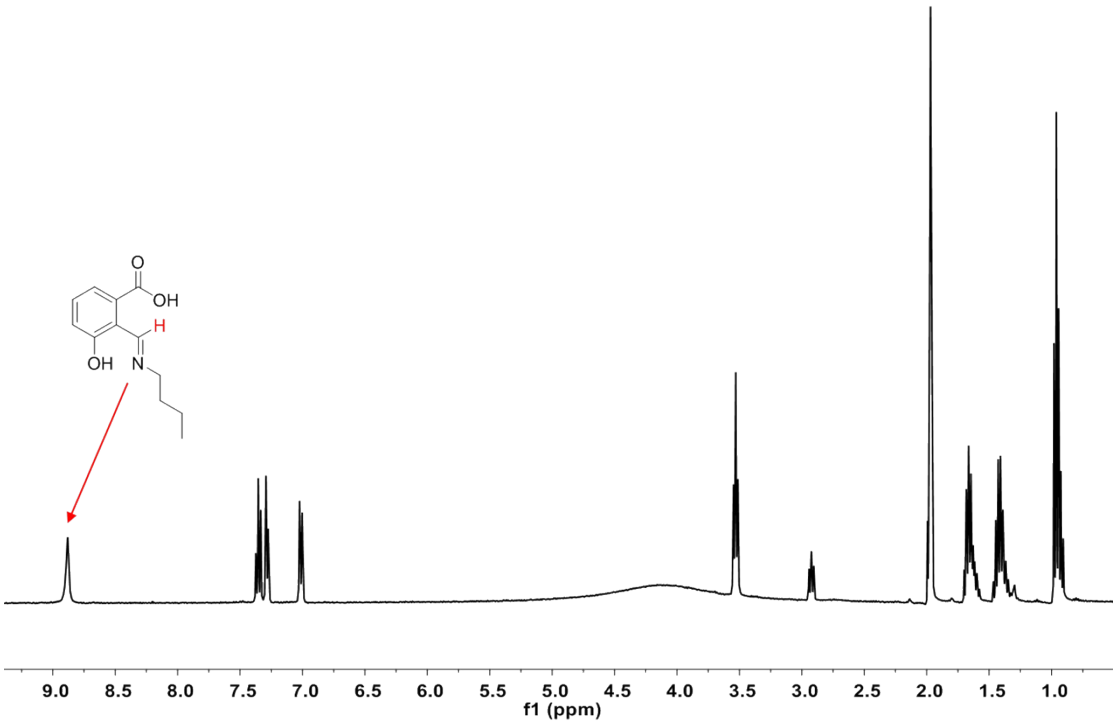


Figure S16. ^{1}H NMR spectrum of the reaction between **1g** and 1-butylamine in CD_3CN.

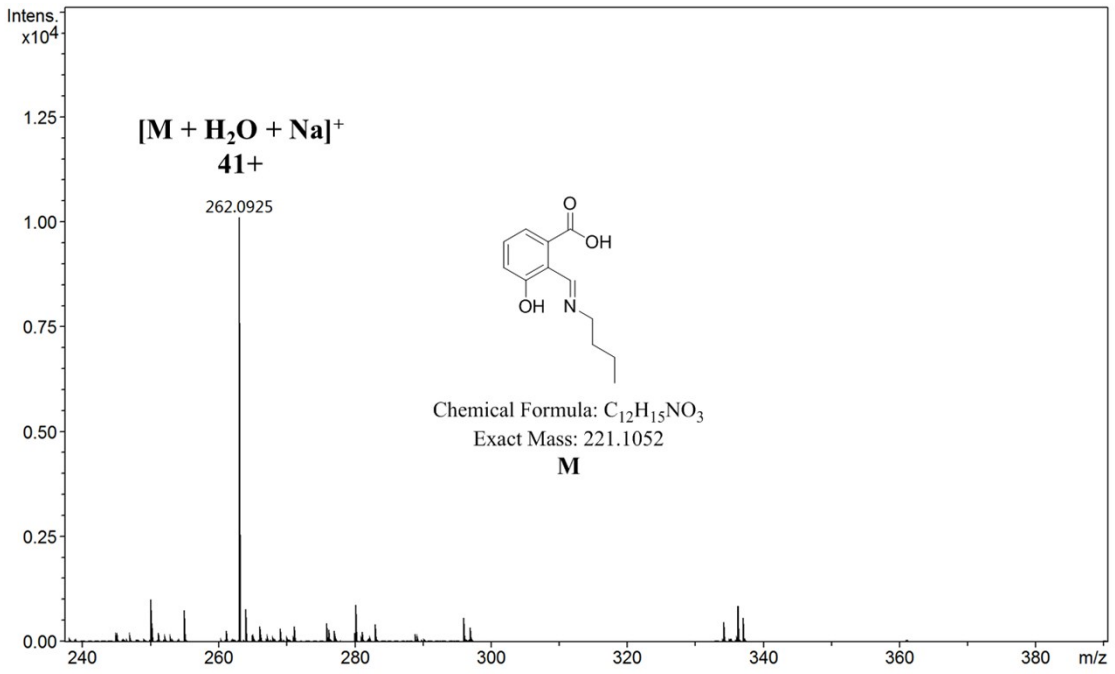


Figure S17. ESI-MS spectrum of the reaction between **1g** and 1-butylamine in CD_3CN.

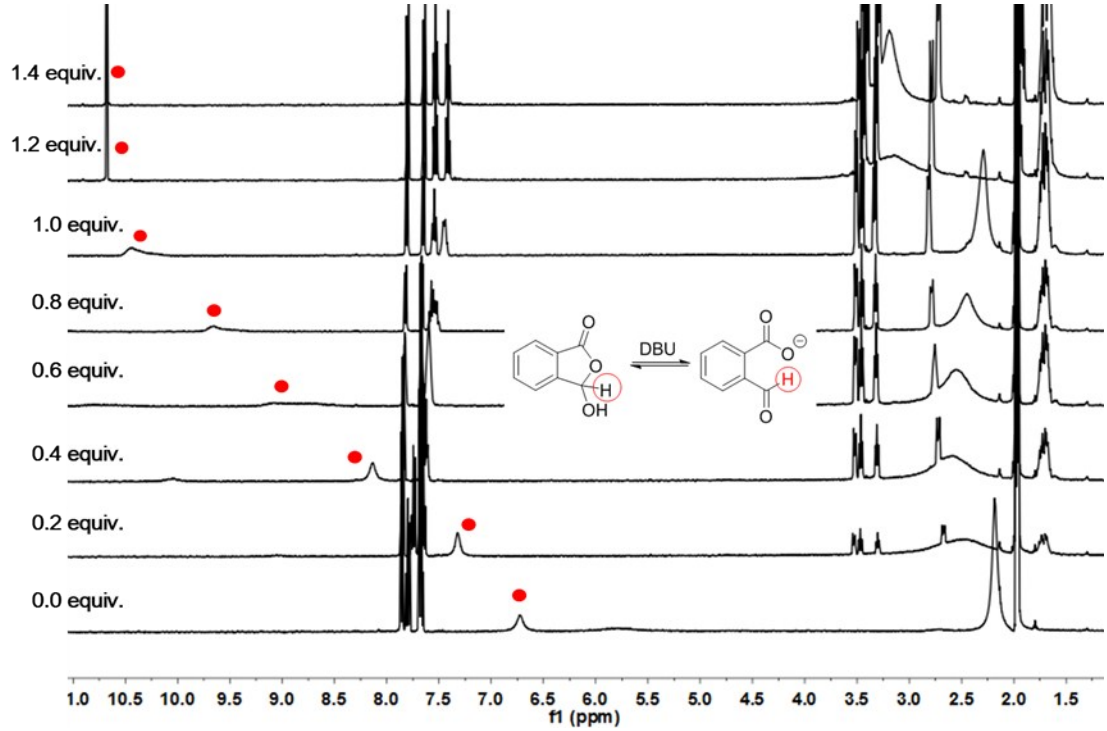


Figure S18. ^{1}H NMR spectra of the titration of **1a** with DBU in CD_3CN.

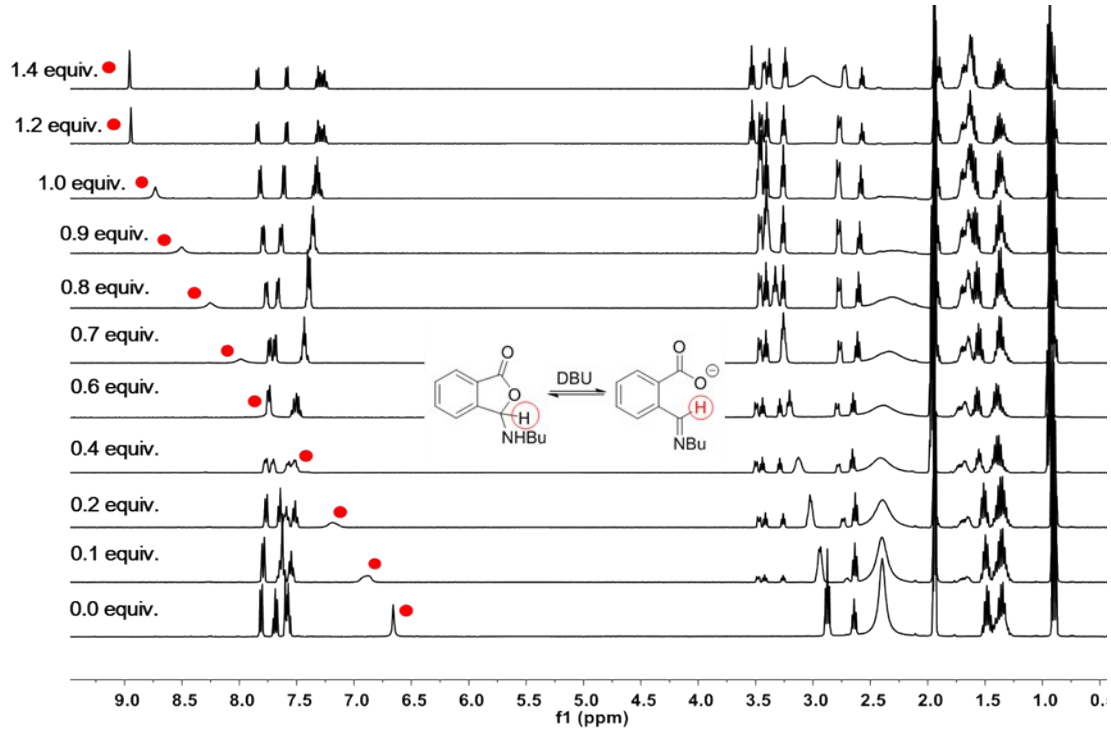


Figure S19. ^{1}H NMR spectra of the titration of **2a** with DBU in CD_3CN.

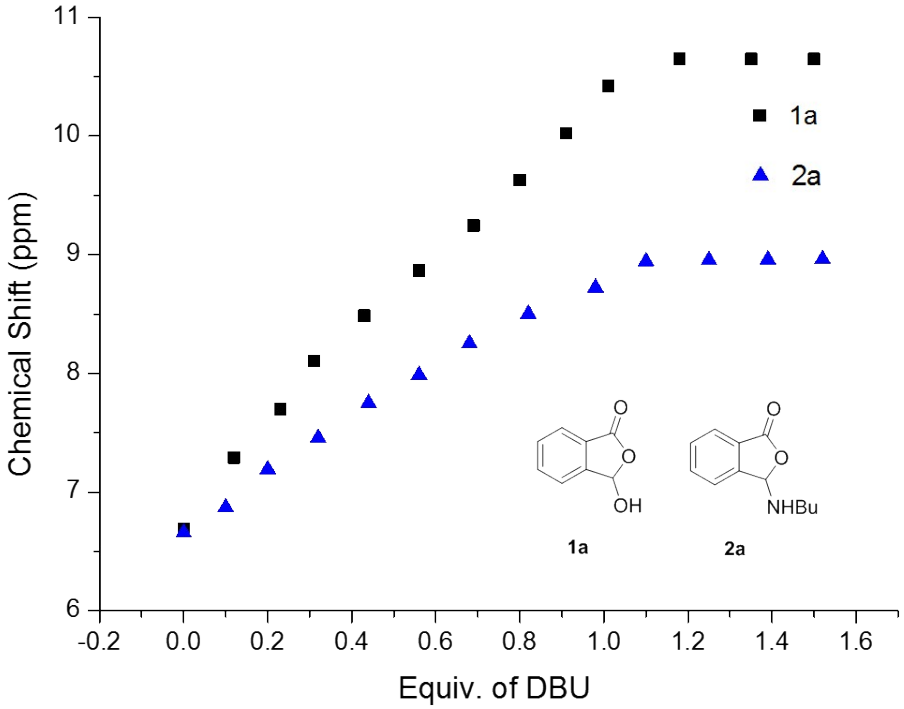


Figure S20. Titration curves of **1a** and **2a** with DBU in CD_3CN. The chemical shift of hemiacetal/hemiaminal ether methine proton was tracked.

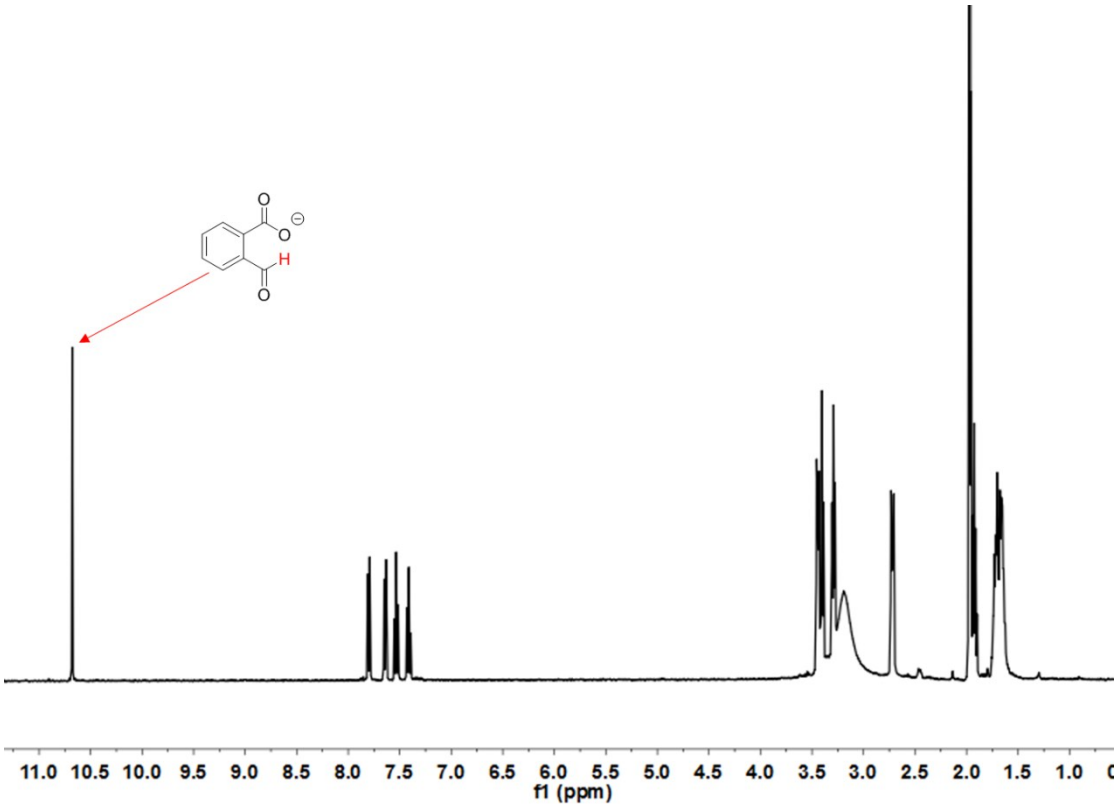


Figure S21. ^1H NMR spectrum of **1a** with DBU (1.2 equiv.) in CD_3CN.

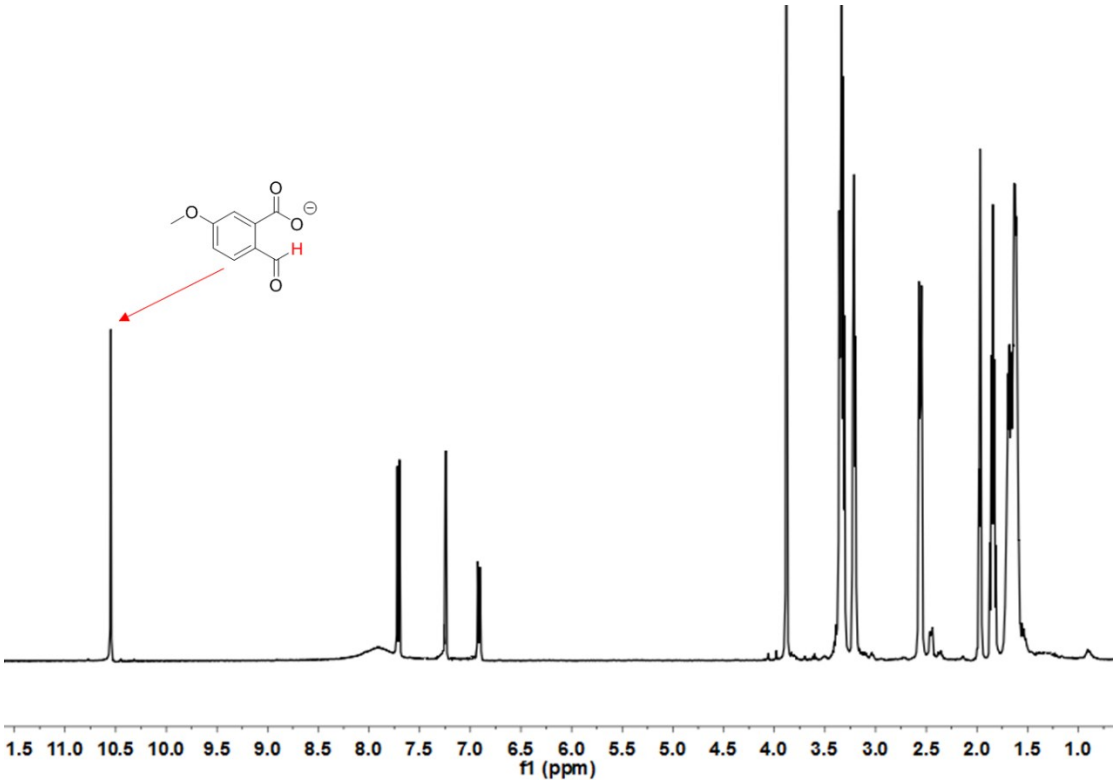


Figure S22. ^{1}H NMR spectrum of **1b** with DBU (1.2 equiv.) in CD_3CN.

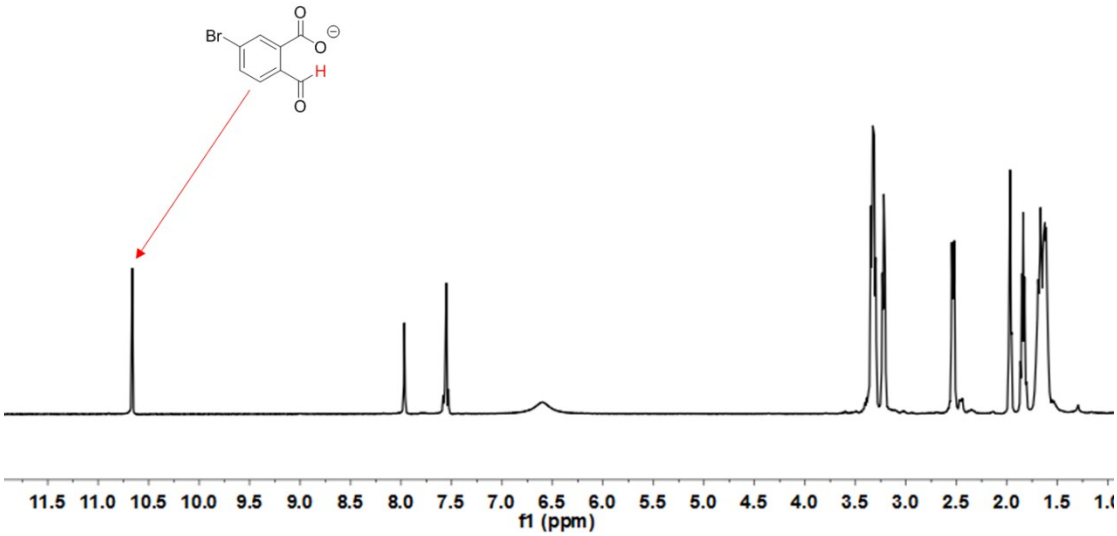


Figure S23. ^{1}H NMR spectrum of **1c** with DBU (1.2 equiv.) in CD_3CN.

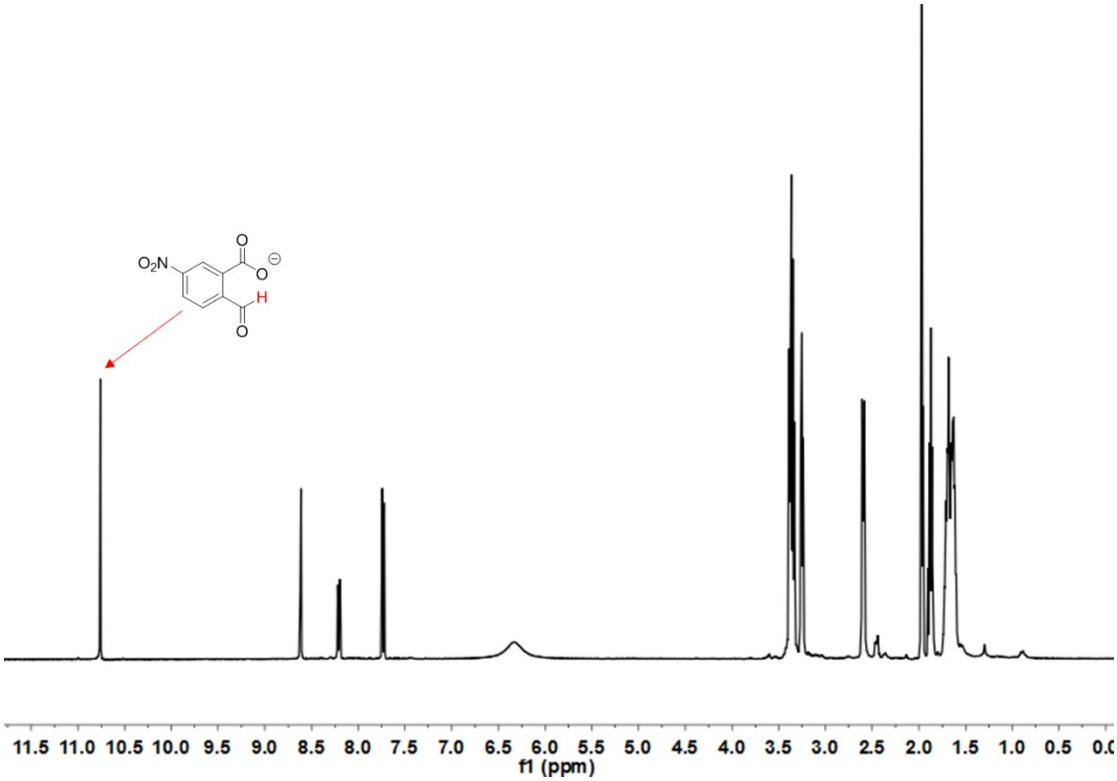


Figure S24. ^{1}H NMR spectrum of **1d** with DBU (1.2 equiv.) in CD_3CN.

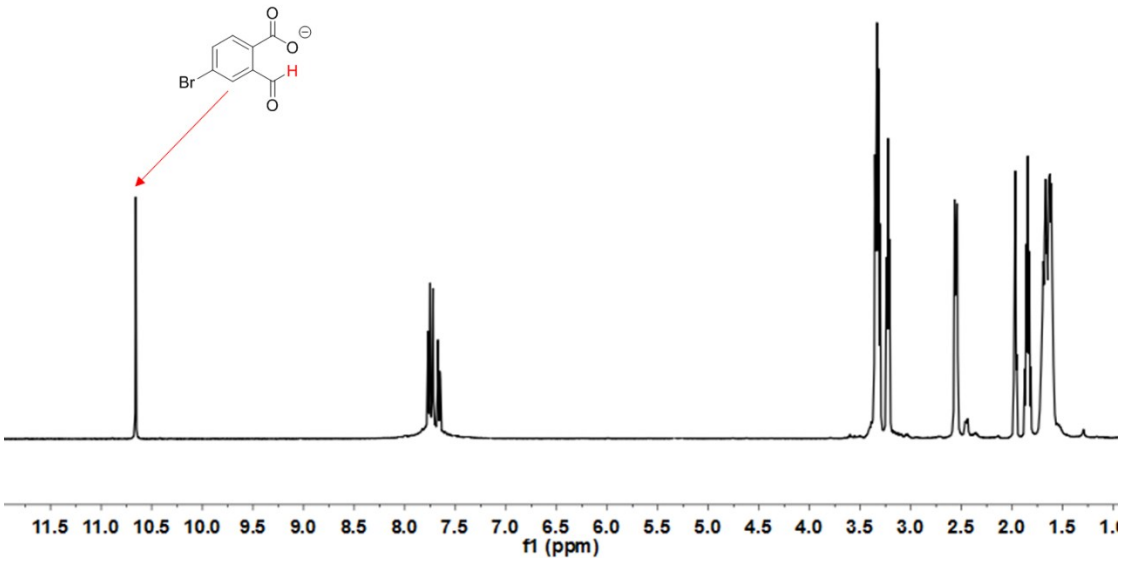


Figure S25. ^{1}H NMR spectrum of **1e** with DBU (1.2 equiv.) in CD_3CN.

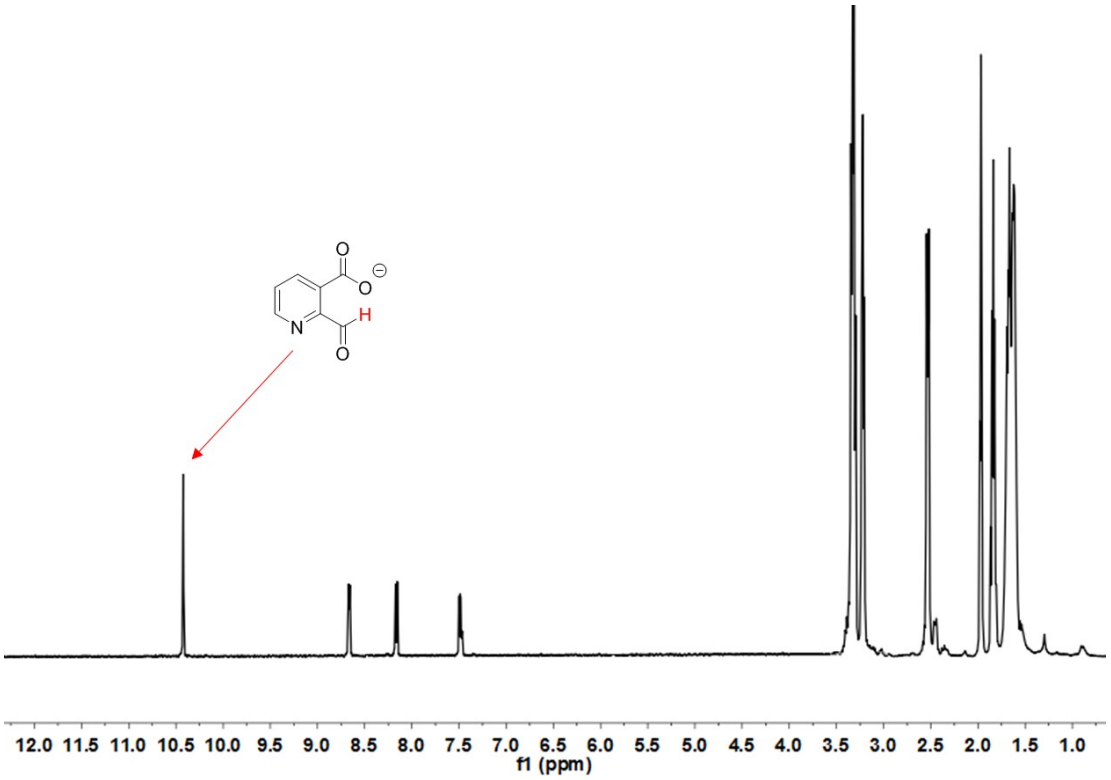


Figure S26. ^{1}H NMR spectrum of **1f** with DBU (1.2 equiv.) in CD_3CN.

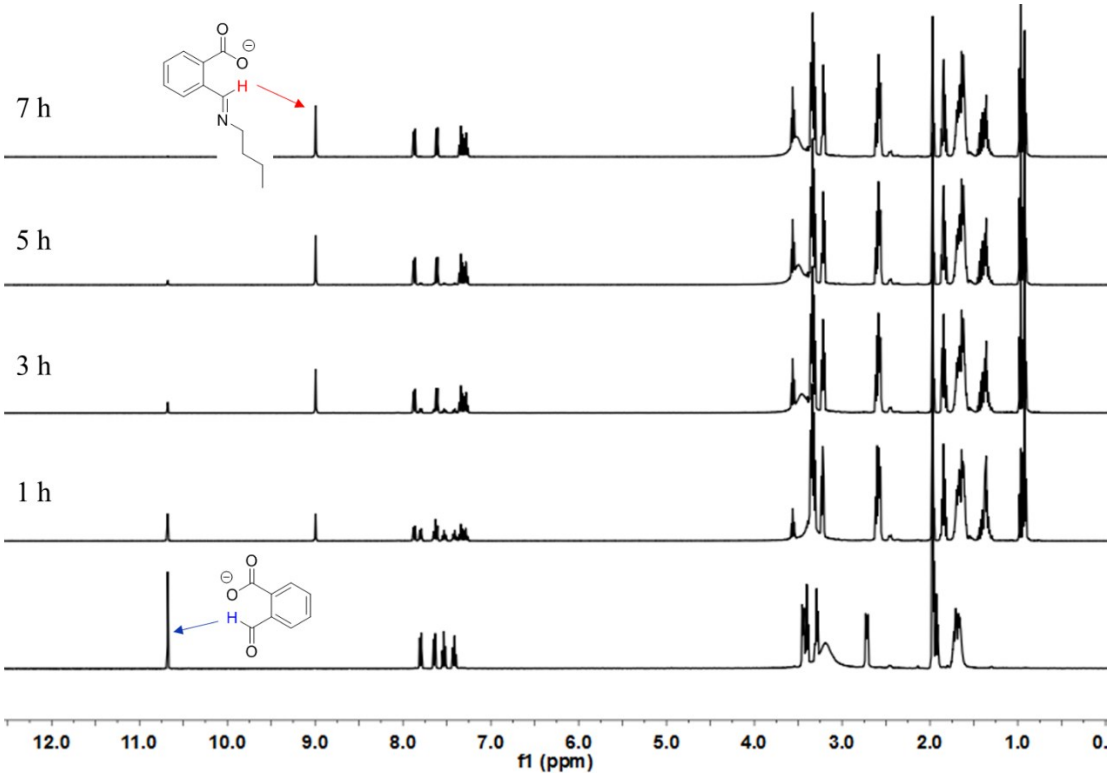


Figure S27. ^{1}H NMR spectra of the reaction between **1a** (39 mM) and 1-butylamine (1.2 equiv.) in the presence of DBU (1.2 equiv.) in CD_3CN. The reaction was complete after 7 h.

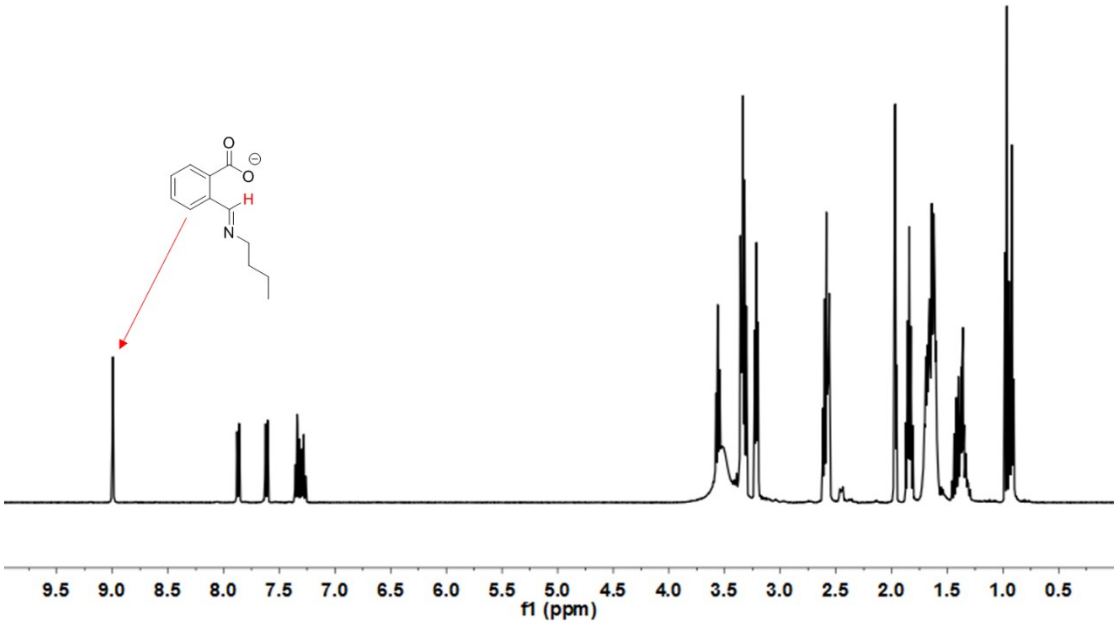


Figure S28. ^{1}H NMR spectrum of the reaction between **1a** and 1-butylamine in the presence of DBU (1.2 equiv.) in CD_3CN.

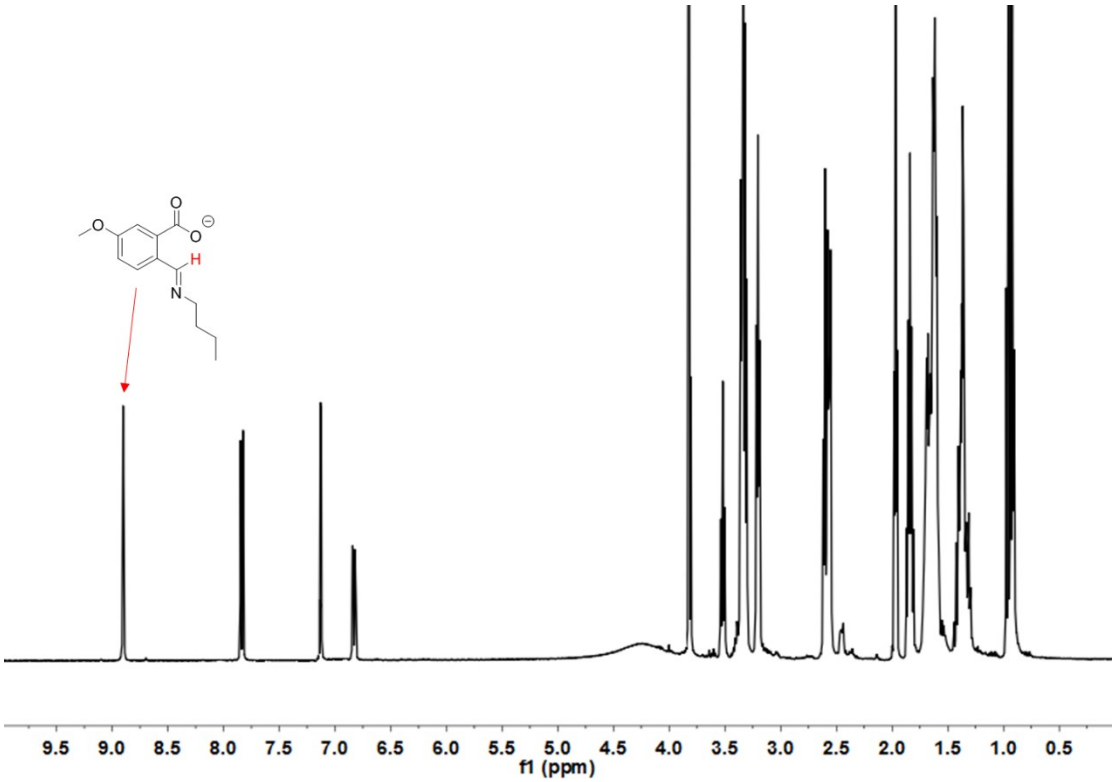


Figure S29. ^{1}H NMR spectrum of the reaction between **1b** and 1-butylamine in the presence of DBU (1.2 equiv.) in CD_3CN.

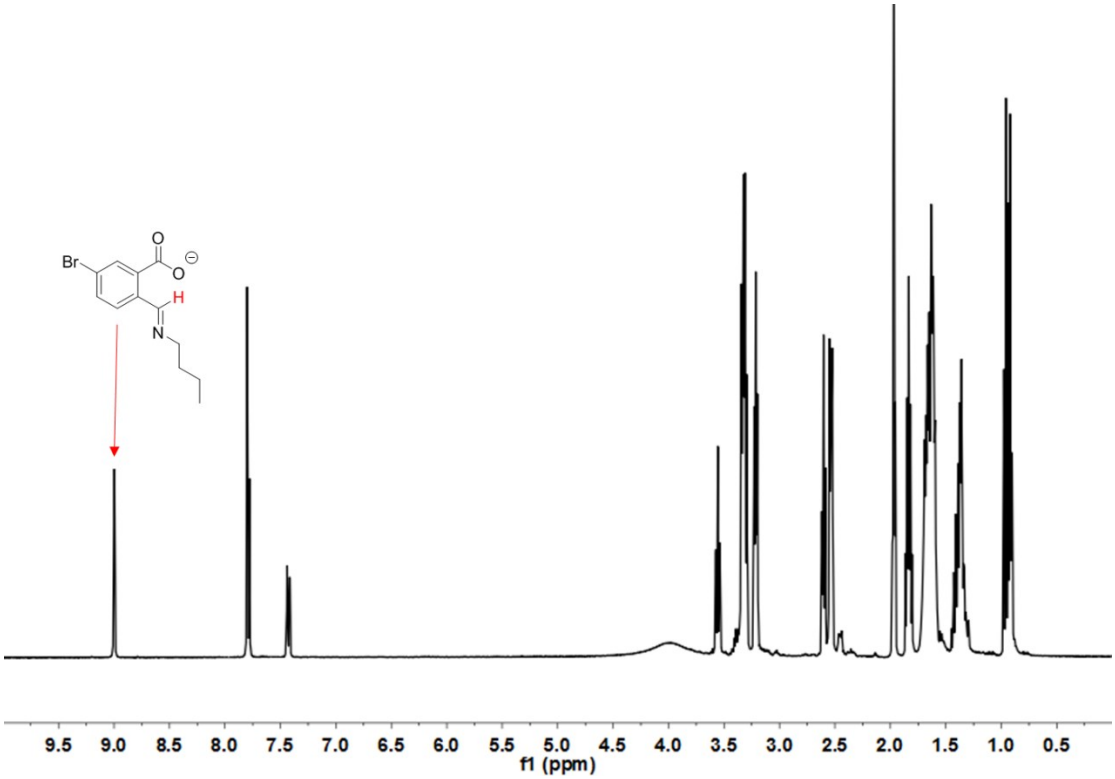


Figure S30. ^{1}H NMR spectrum of the reaction between **1c** and 1-butylamine in the presence of DBU (1.2 equiv.) in CD_3CN.

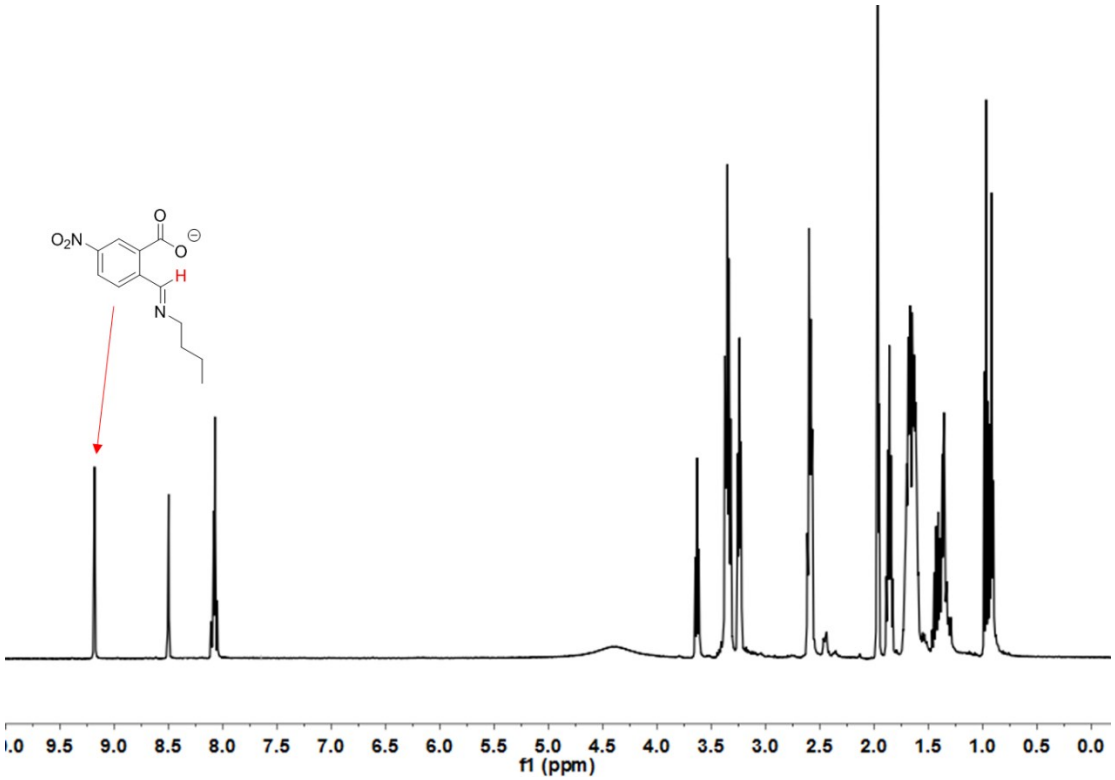


Figure S31. ^{1}H NMR spectrum of the reaction between **1d** and 1-butylamine in the presence of DBU (1.2 equiv.) in CD_3CN.

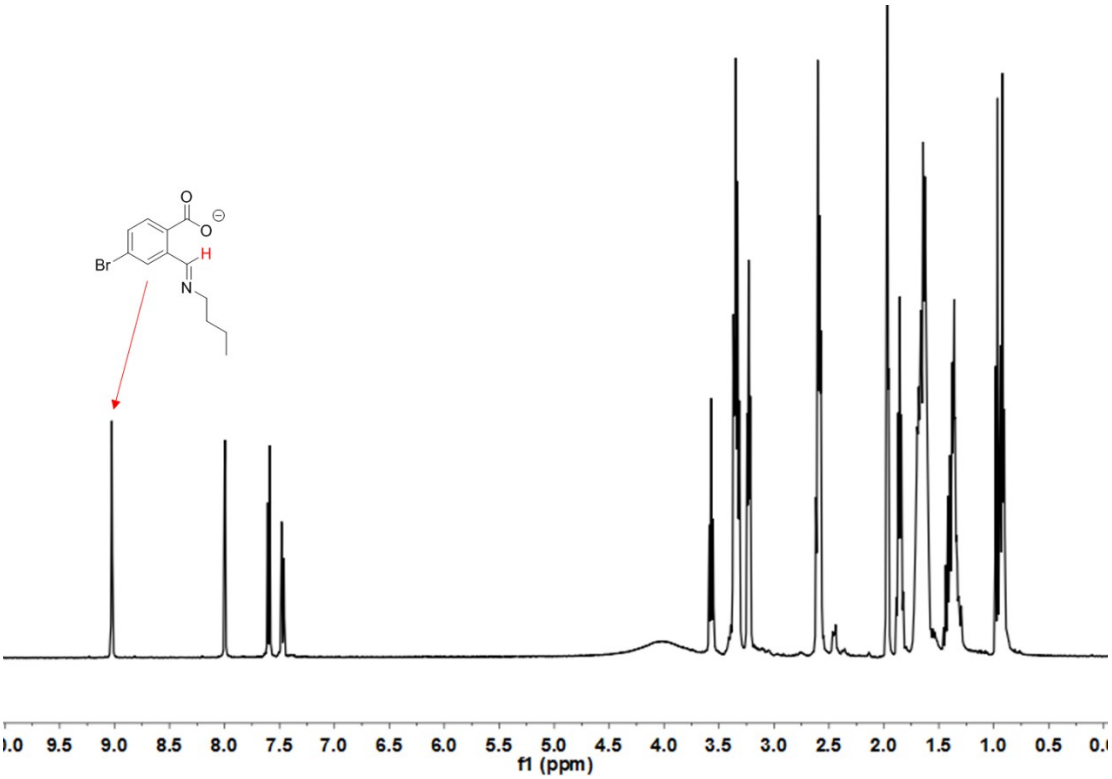


Figure S32. ^{1}H NMR spectrum of the reaction between **1e** and 1-butylamine in the presence of DBU (1.2 equiv.) in CD_3CN.

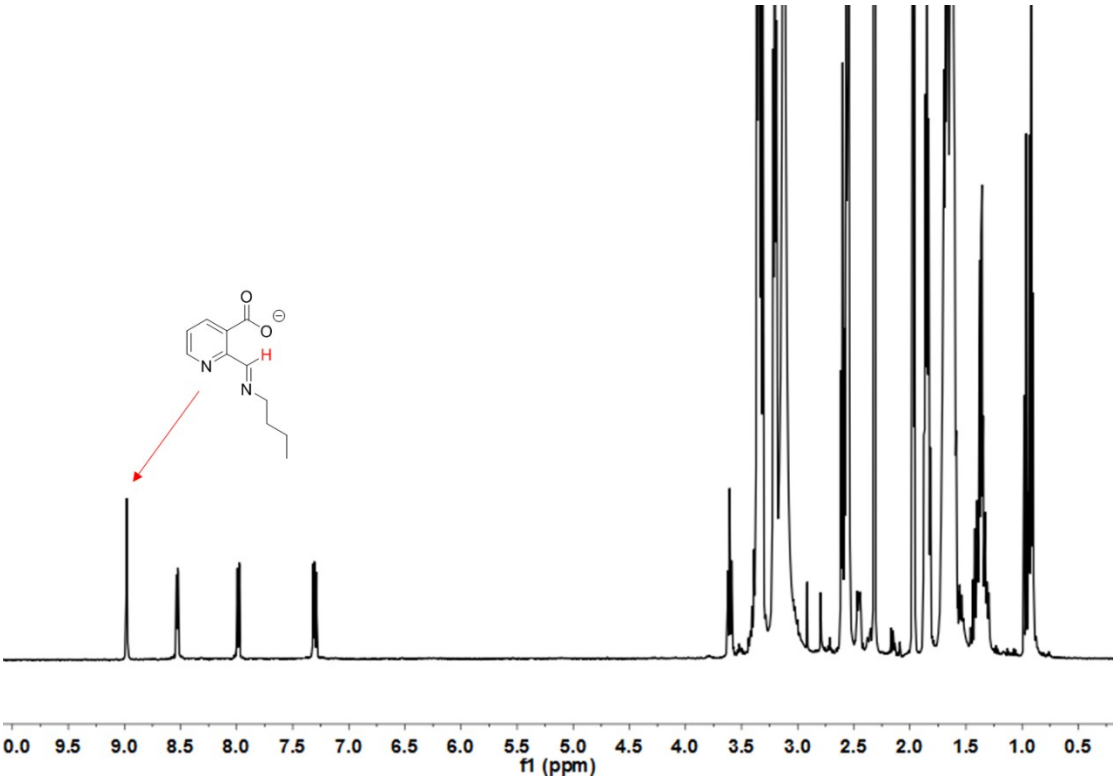


Figure S33. ^{1}H NMR spectrum of the reaction between **1f** and 1-butylamine in the presence of DBU (1.2 equiv.) in CD_3CN.

(2) Imine Exchange

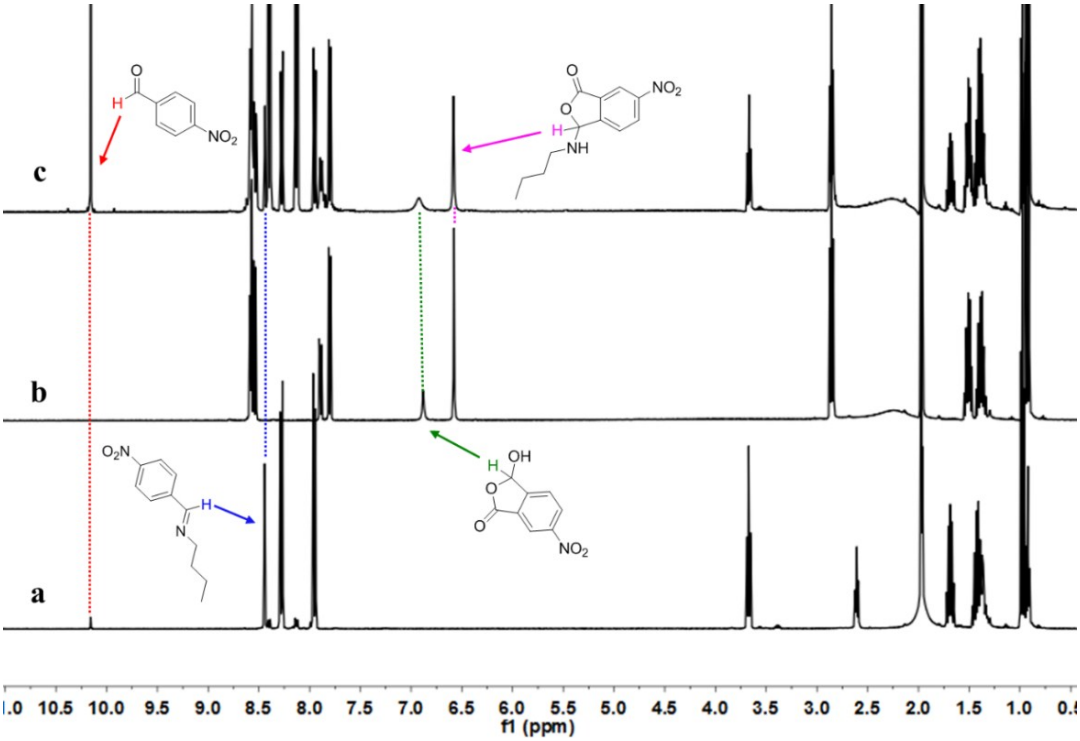


Figure S34. ^{1}H NMR spectra of (a) the reaction of **3d** with 1-butylamine (0.9 equiv.), (b) the reaction of **1d** with 1-butylamine (0.9 equiv.), (c) the reaction of **1d** and **3d** (1.0 equiv.) with 1-butylamine (1.0 equiv.) in CD_3CN.

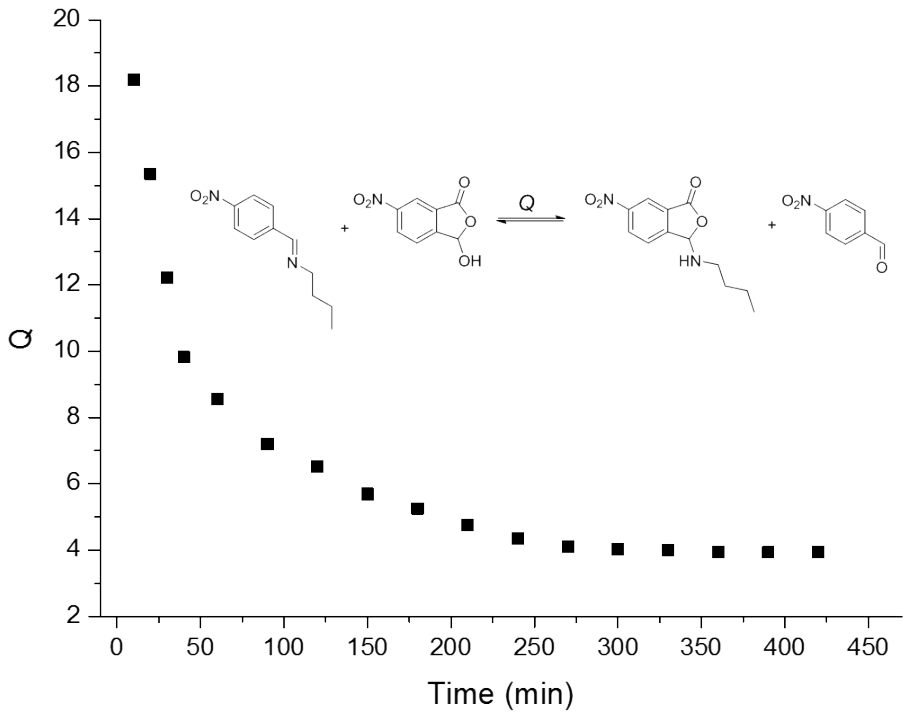


Figure S35. Kinetic profile of the competition reaction between **1d** and **3d** with 1-butylamine in CD_3CN.

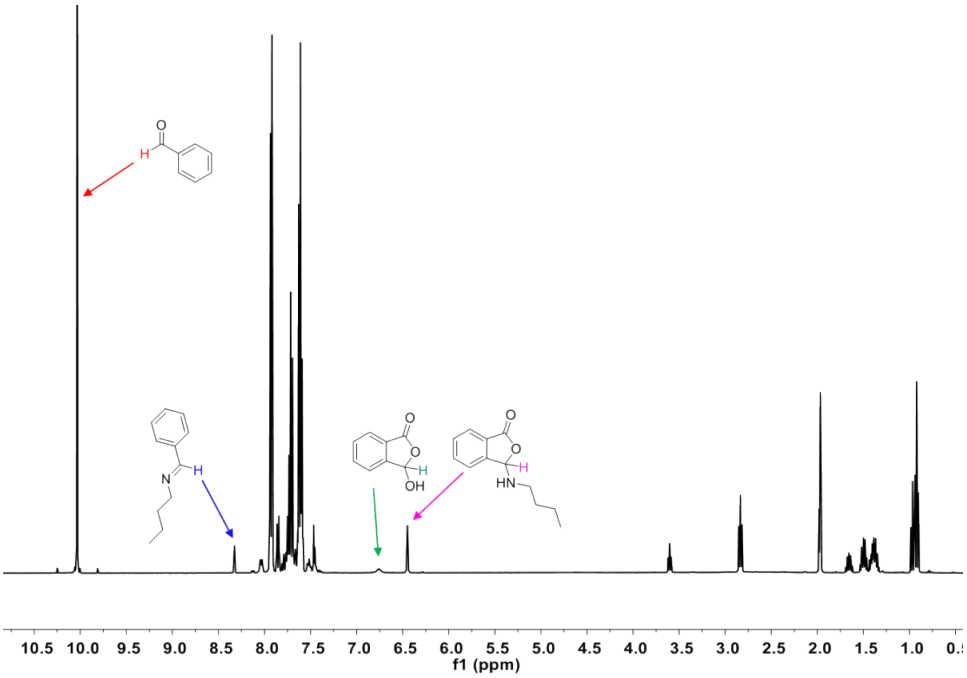


Figure S36. ^{1}H NMR spectrum of the competition between **1a** and **3a** for the reaction with 1-butylamine in CD_3CN.

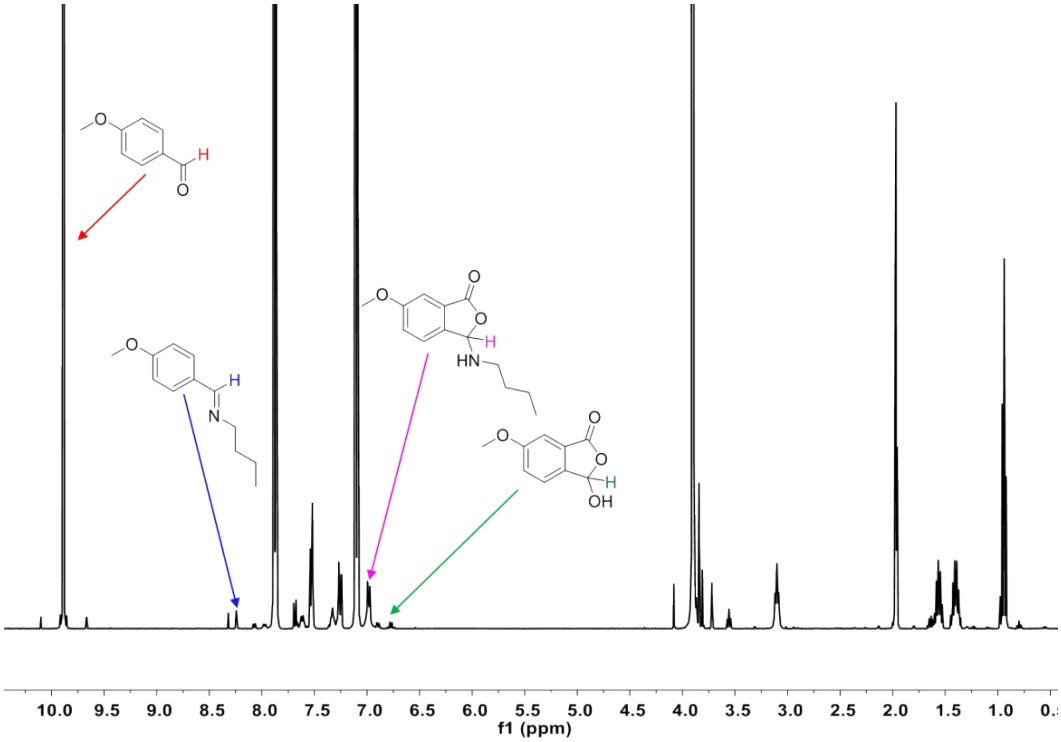


Figure S37. ^{1}H NMR spectrum of the competition between **1b** and **3b** for the reaction with 1-butylamine in CD_3CN.

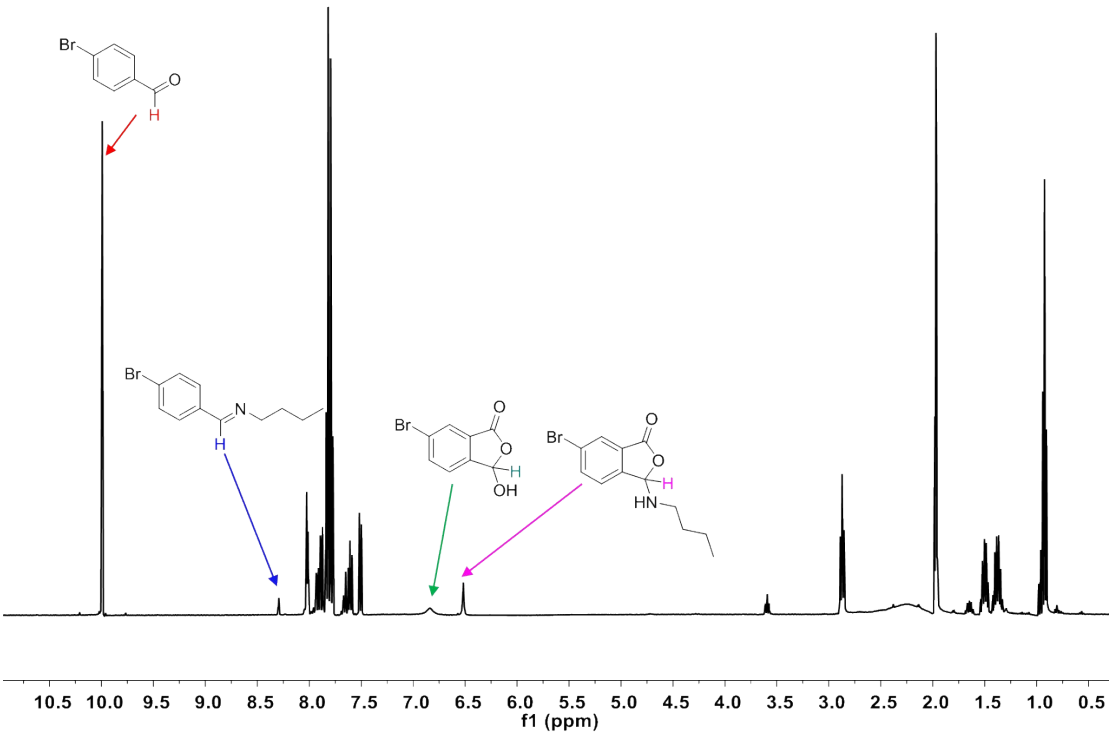


Figure S38. ^{1}H NMR spectrum of the competition between **1c** and **3c** for the reaction with 1-butylamine in CD_3CN.

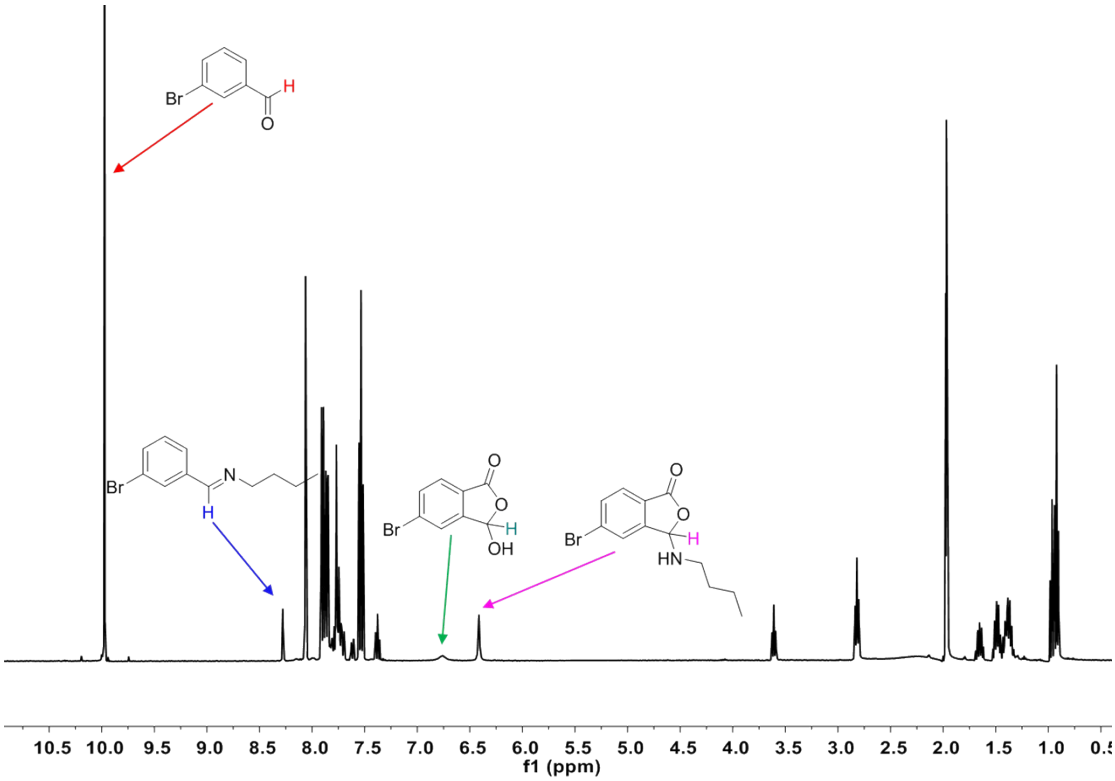


Figure S39. ^{1}H NMR spectrum of the competition between **1e** and **3e** for the reaction with 1-butylamine in CD_3CN.

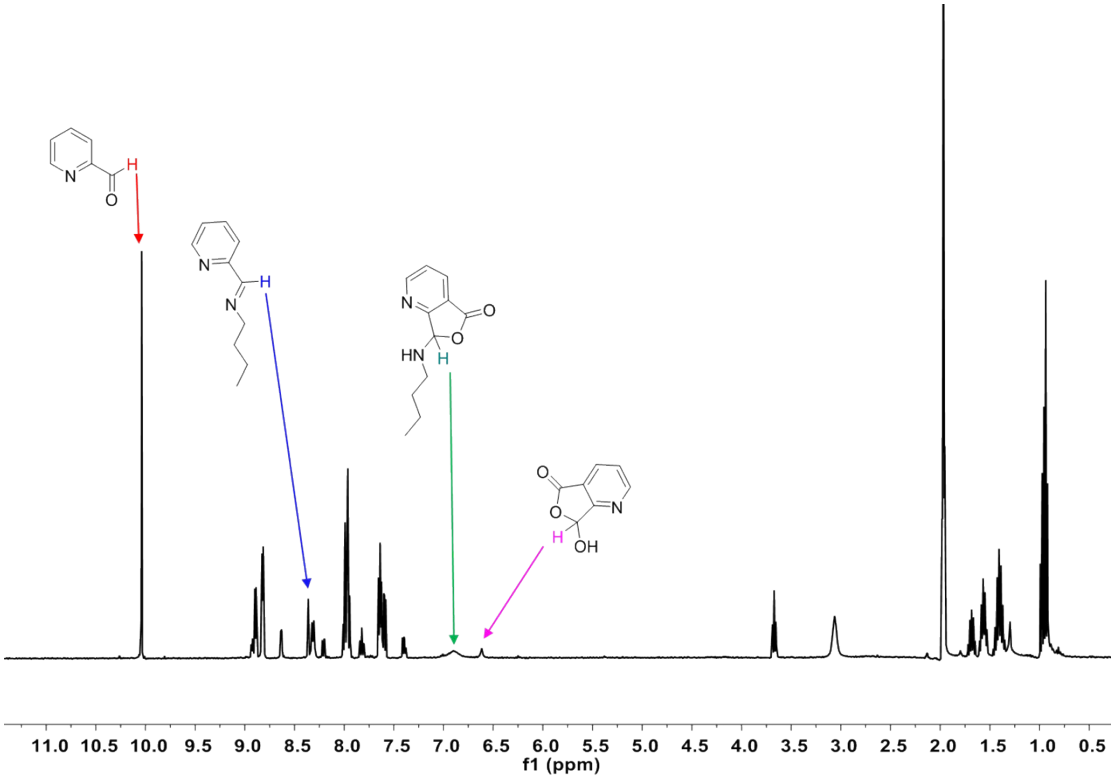


Figure S40. ^{1}H NMR spectrum of the competition between **1f** and **3f** for the reaction with 1-butylamine in CD_3CN.

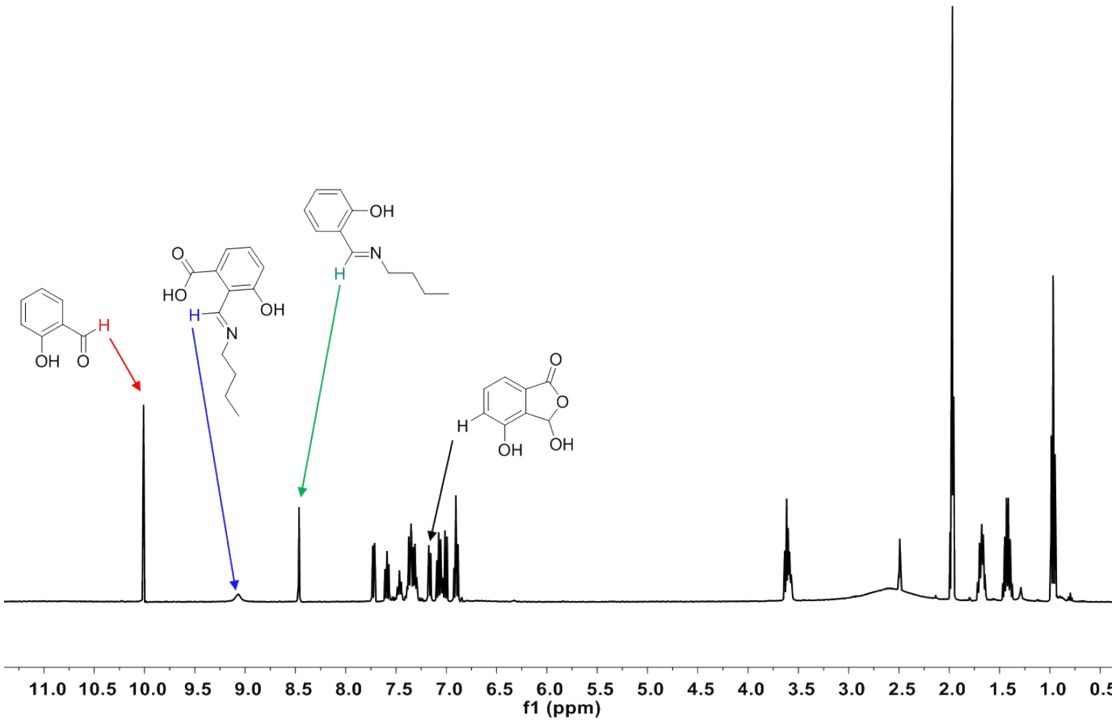


Figure S41. ^{1}H NMR spectrum of the competition between **1g** and **3g** for the reaction with 1-butylamine in CD_3CN.

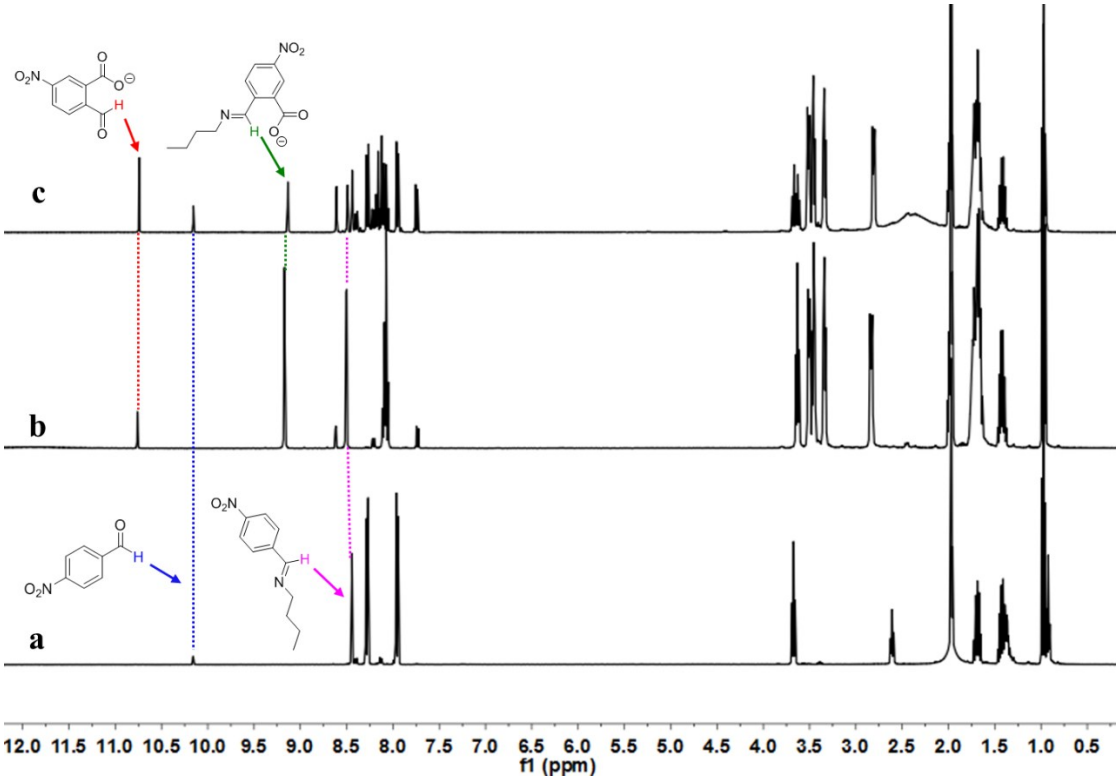


Figure S42. ^{1}H NMR spectra of (a) the reaction of **3d** with 1-butylamine (0.9 equiv.), (b) the reaction of $\mathbf{1d_{ocb}}$ with 1-butylamine (0.9 equiv.), (c) the reaction of **3d** and $\mathbf{1d_{ocb}}$ (1.0 equiv.) with 1-butylamine (1.0 equiv.) in CD_3CN.

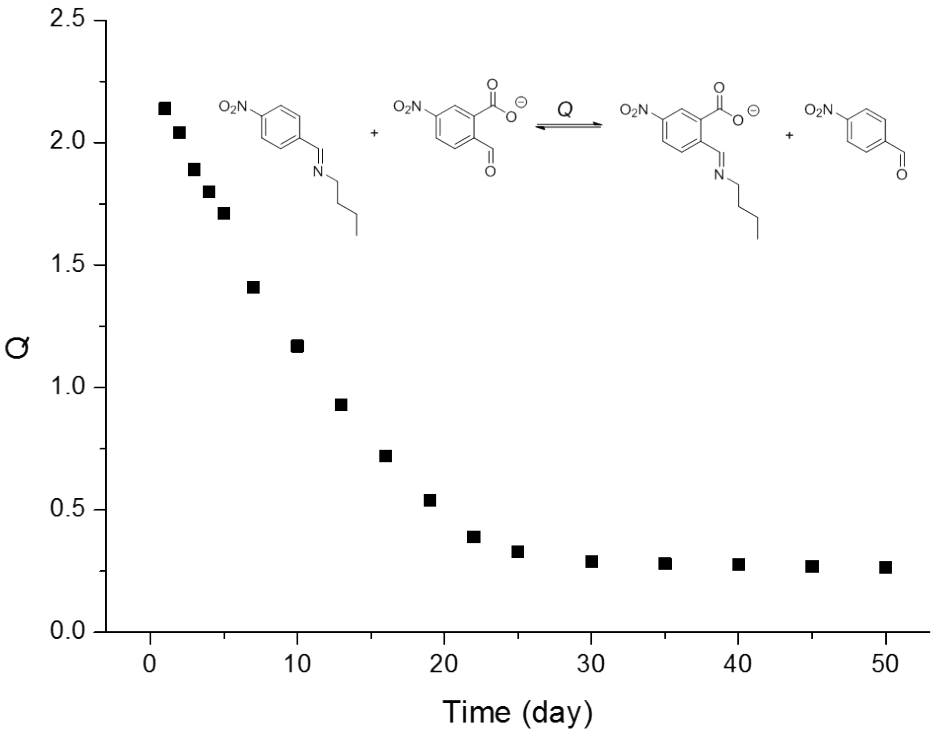


Figure S43. Kinetic profile of the competition reaction between $\mathbf{1d_{ocb}}$ and **3d** with 1-butylamine in CD_3CN.

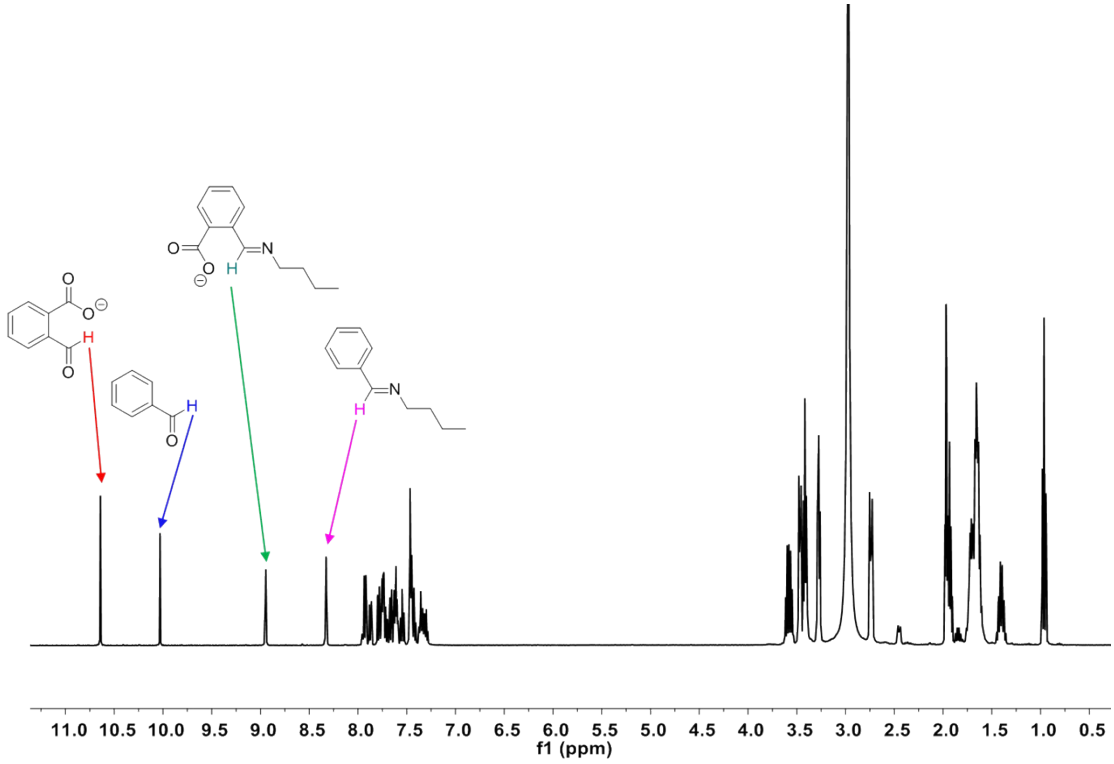


Figure S44. ^{1}H NMR spectrum of the competition between $\mathbf{1a_{ocb}}$ and **3a** for the reaction with 1-butylamine in CD_3CN.

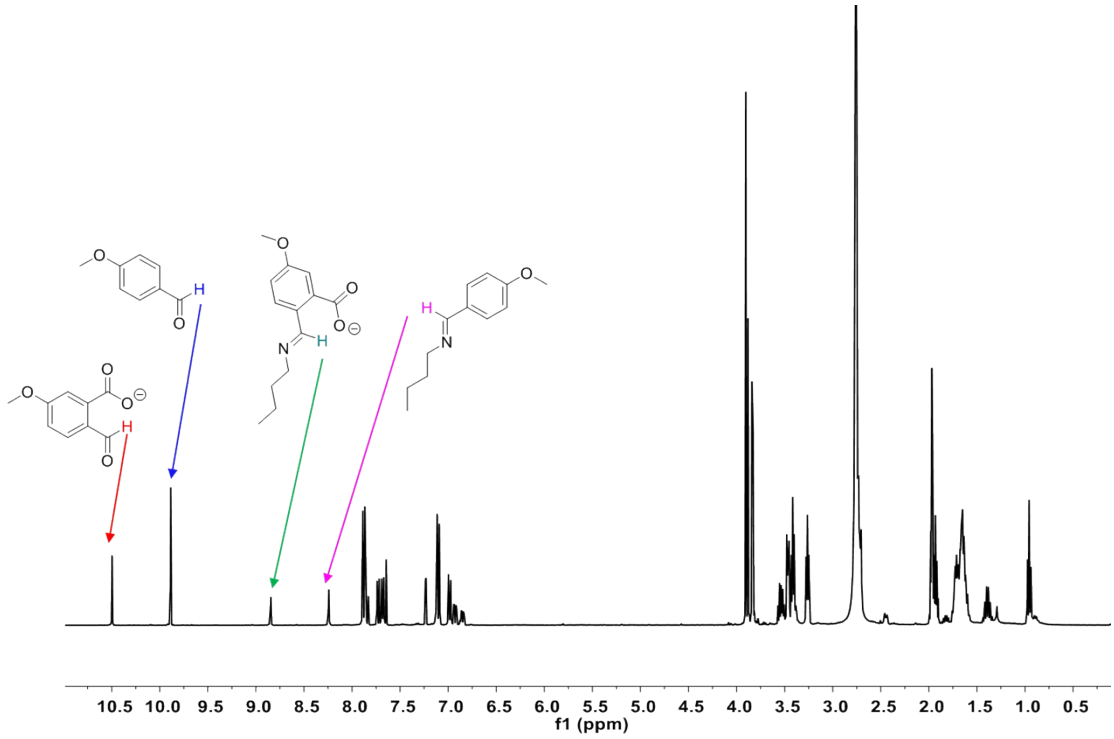


Figure S45. ^{1}H NMR spectrum of the competition between $\mathbf{1b_{ocb}}$ and **3b** for the reaction with 1-butylamine in CD_3CN.

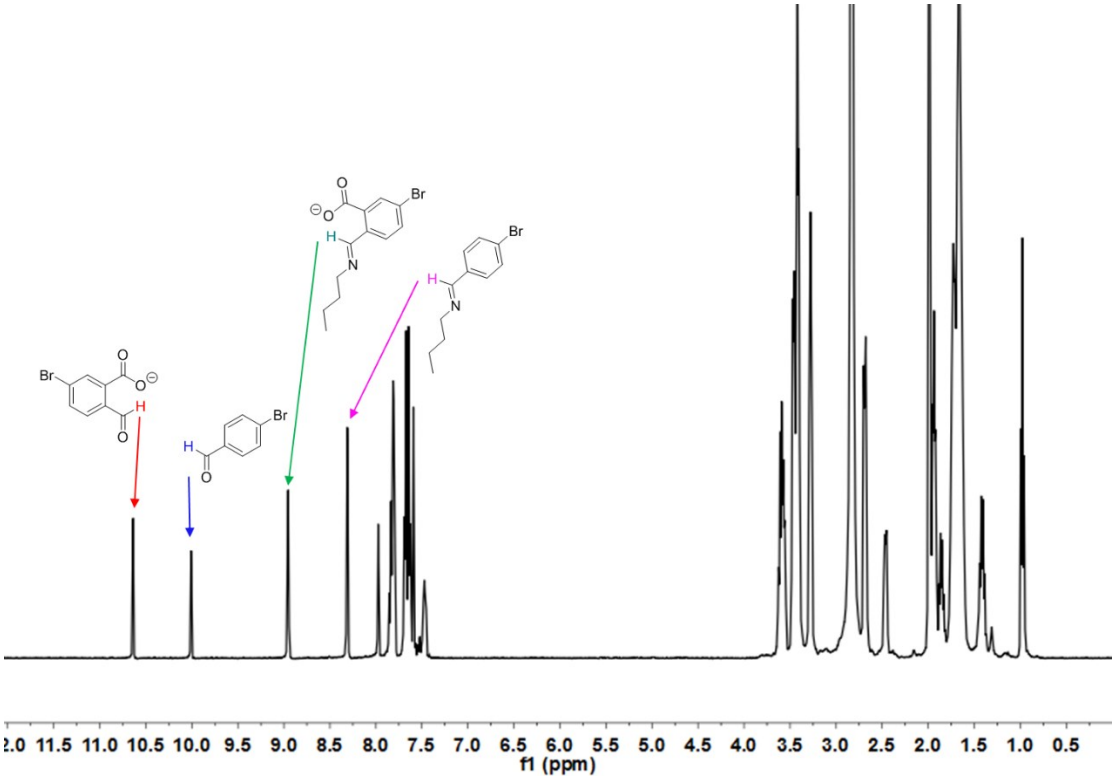


Figure S46. ^{1}H NMR spectrum of the competition between **1c$_{ocb}$** and **3c** for the reaction with 1-butylamine in CD_3CN.

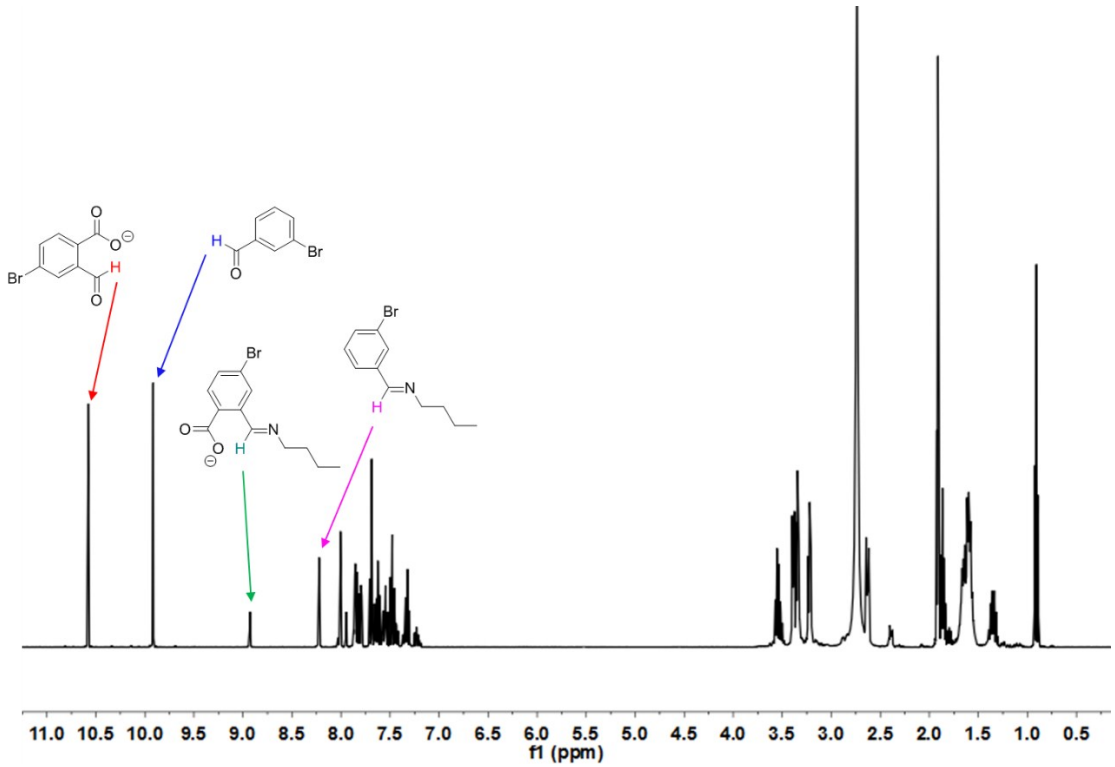


Figure S47. ^{1}H NMR spectrum of the competition between **1e$_{ocb}$** and **3e** for the reaction with 1-butylamine in CD_3CN.

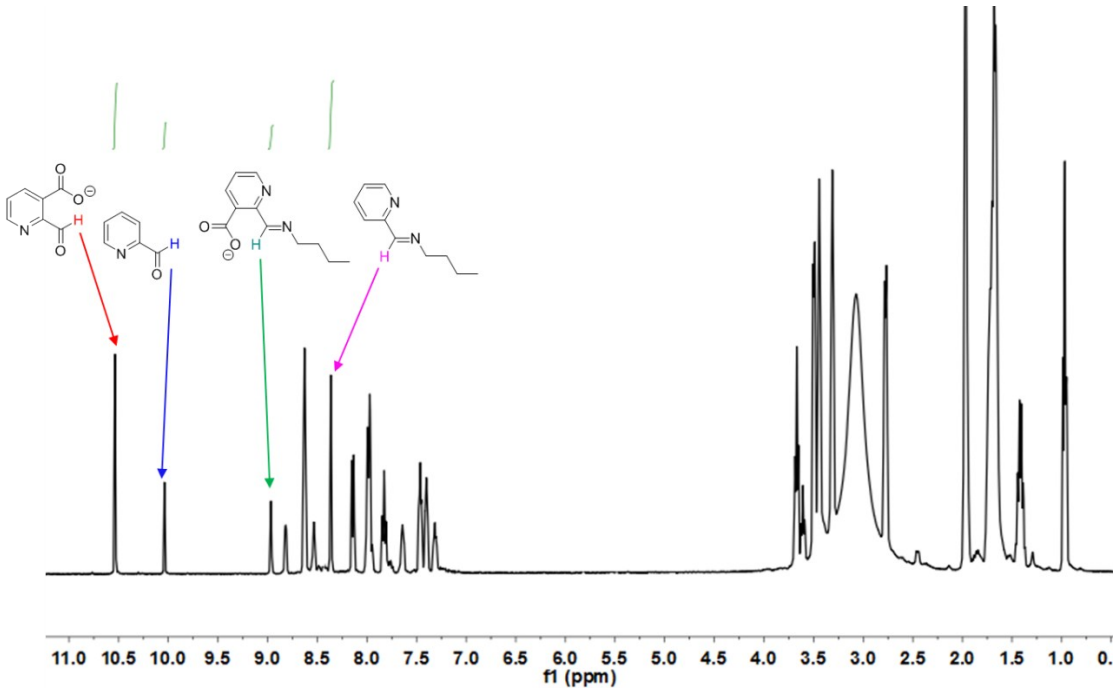


Figure S48. ^{1}H NMR spectrum of the competition between **1f**$_{\mathbf{ocb}}$ and **3f** for the reaction with 1-butylamine in CD_3CN.

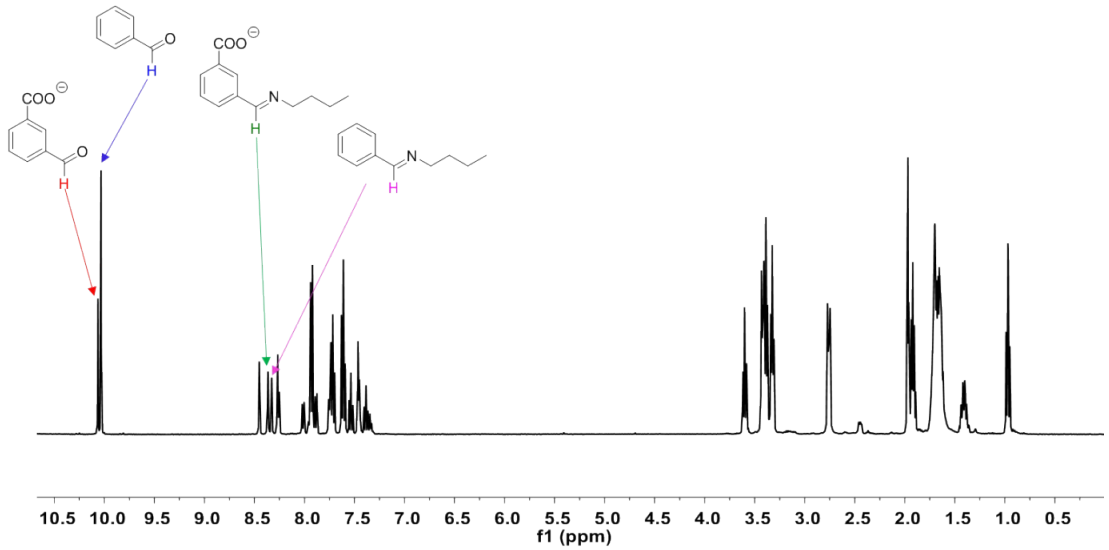


Figure S49. ^{1}H NMR spectrum of the competition between **1a**(*meta*)$_{\mathbf{ocb}}$ and **3a** for the reaction with 1-butylamine in CD_3CN.

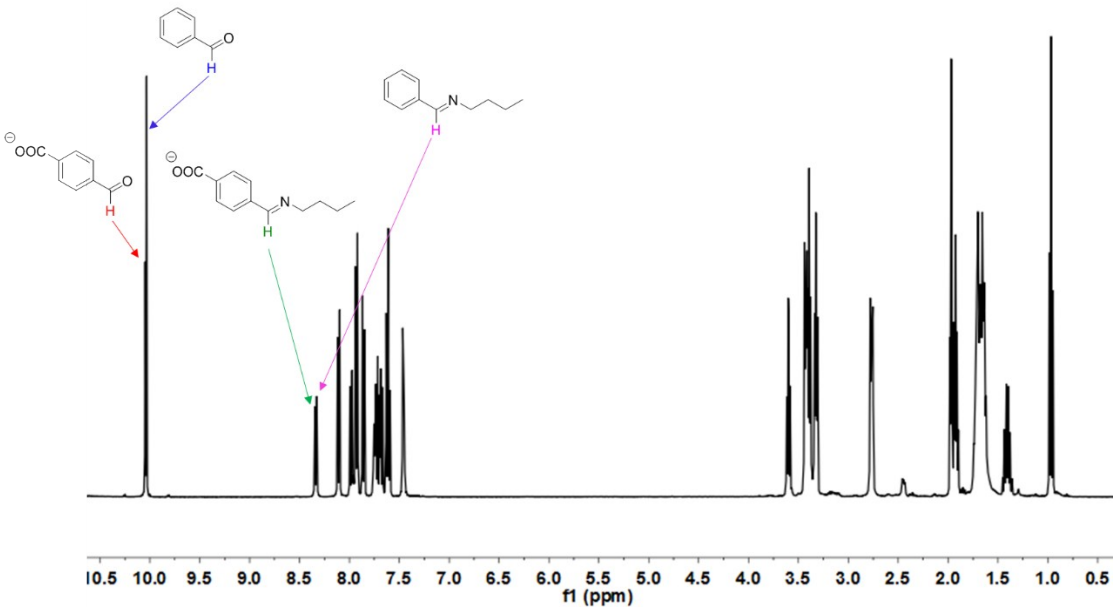


Figure S50. ^{1}H NMR spectrum of the competition between **1a**(*para*)$_{\mathbf{ocb}}$ and **3a** for the reaction with 1-butylamine in CD_3CN.

4. Crystal Structures

Table S1. Summary of crystallographic data for **2a$_{ocb}$** and **2f$_{ocb}$**.

Compound	**2a$_{ocb}$**	**2f$_{ocb}$**
Formula	$C_{20}H_{30}N_2O_2$	$C_{13}H_{29}N_3O_2$
Formula weight	330.46	331.45
T/*K*	293(2)	173(2)
Crystallization solvent	acetonitrile	acetonitrile
Color	Colorless	Orange
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$I2/a$
a / Å	11.012(9)	17.030(2)
b / Å	16.138(13)	10.580(10)
c / Å	11.225(9)	22.260(4)
α / °	90.000	90.000
β / °	96.899(12)	103.23(3)
γ / °	90.000	90.000
V/ Å^3	1980.0(3)	3903.0(9)
Z	4	8
D_x / g cm^{-3}	1.108	1.128
μ / mm^{-1}	0.071	0.074
F(000)	720	1440
θ range / °	2.22 to 26.14	3.42 to 27.48
GOF on F^2	1.093	1.072
R_1 [$I > 2\sigma(I)$]	0.0547	0.0880
wR_2 (all data)	0.1445	0.2777

5. DFT Calculations

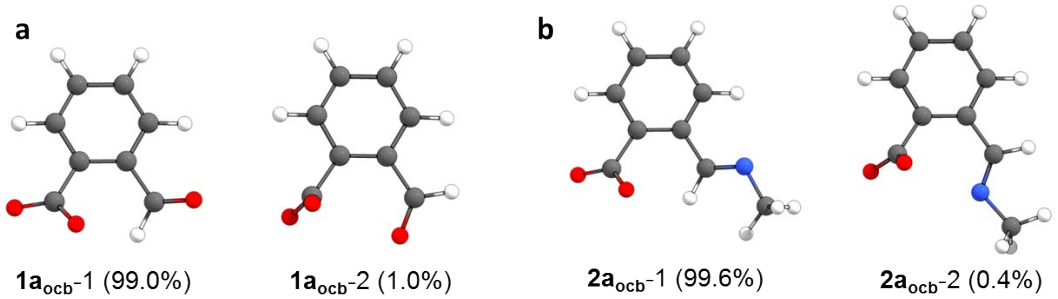


Figure S51. Optimized structures and populations of isomers for **1a$_{ocb}$** (a) and **2a$_{ocb}$** (b), respectively.

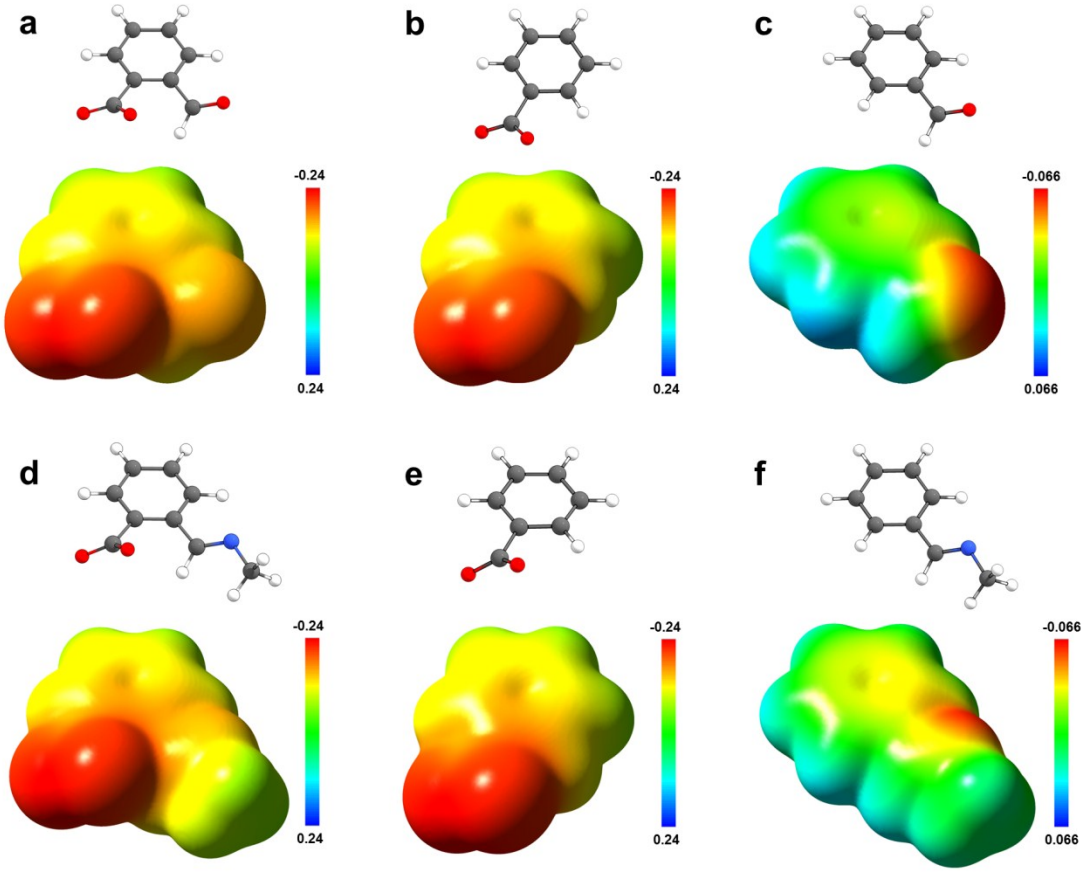
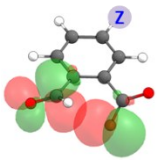
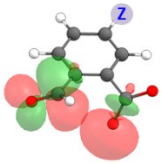
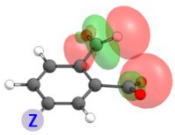
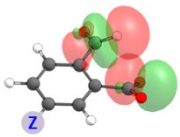
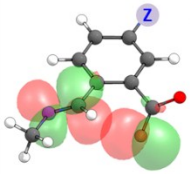
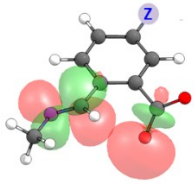
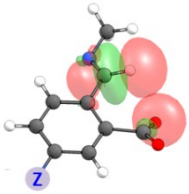
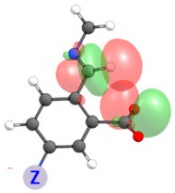


Figure S52. 3D MEP maps (0.001 isodensity surface) of **1a$_{ocb}$/2a$_{ocb}$** and its carboxylate and aldehyde/imine fragments (**1a$_{ocb}$**: a-c, **2a$_{ocb}$**: d-f). The unit of color scale is a.u.

Table S2. Individual $n\rightarrow\pi^*$ and $n\rightarrow\sigma^*$ interactions (kcal/mol) of $\mathbf{1}_{ocb}$ and $\mathbf{2}_{ocb}$ with varied substituents, respectively.

$\mathbf{1}_{ocb}$				
	n_1(O)→π^*	n_2(O)→π^*	n_1(O)→σ^*(CH)	n_2(O)→σ^*(CH)
1a (*p*-H)	1.90	0.39	0.03	0.00
1b(*p*-OMe)	0.60	0.12	0.13	0.06
1c (*p*-Br)	1.80	0.37	0.04	0.00
1d (*p*-NO_2)	3.76	0.73	0.00	0.03
1e (*m*-Br)	2.35	0.48	0.03	0.00
1f	4.78	0.89	0.05	0.00
1g	0.51	0.11	0.26	0.01
$\mathbf{2}_{ocb}$				
	n_1(O)→π^*	n_2(O)→π^*	n_1(O)→σ^*(CH)	n_2(O)→σ^*(CH)
2a (*p*-H)	1.04	0.28	0.04	0.00
2b(*p*-OMe)	0.65	0.17	0.08	0.02
2c (*p*-Br)	1.05	0.27	0.06	0.01
2d (*p*-NO_2)	1.21	0.31	0.05	0.00
2e (*m*-Br)	1.29	0.32	0.06	0.01
2f	1.45	0.37	0.02	0.00
2g	0.41	0.10	0.28	0.01

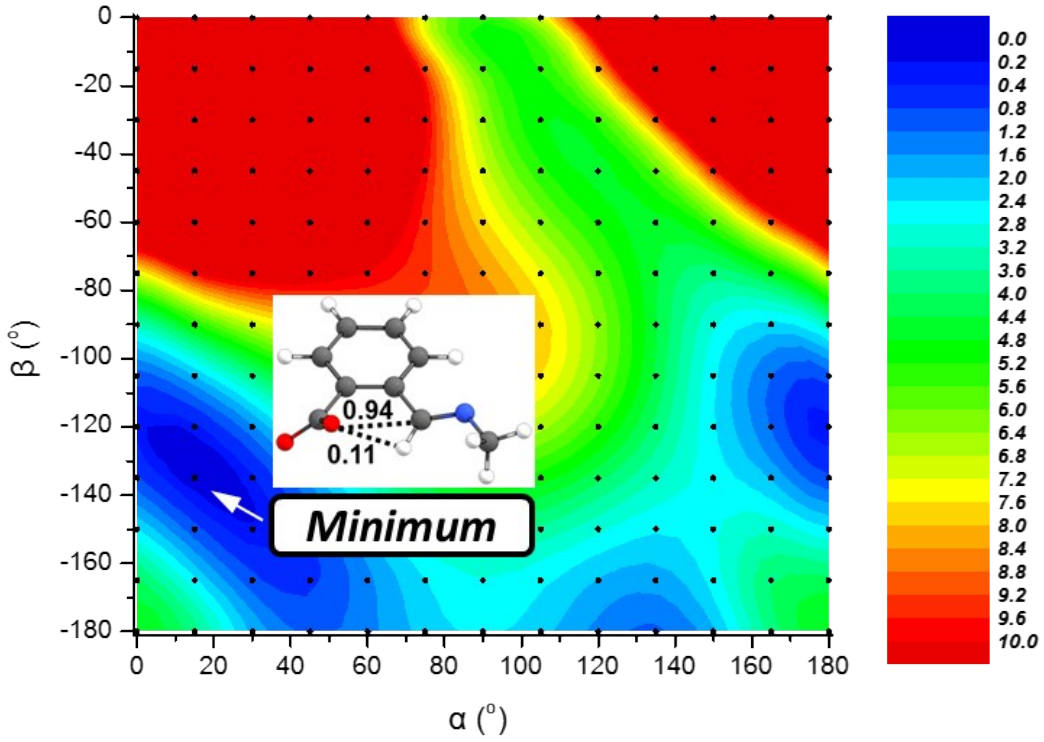
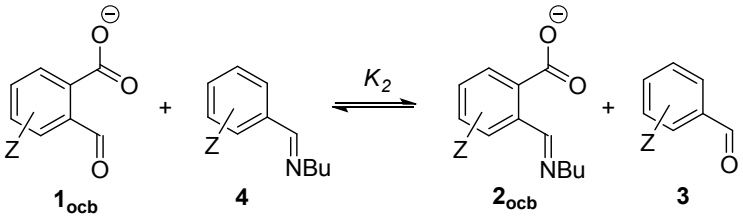


Figure S53. A heat map of the energies of $\mathbf{2a_{ocb}}$ (in kcal/mol) versus (α, β) coordinates (the definition of α and β is shown in Figure 8b in main text).

Table S3. Correlation of experimental equilibrium constants of imine exchange reactions with NBO energies of $n\rightarrow\pi^*$ interactions of the open conjugate base form of aldehyde/imine (the plot of log K_2 versus $\Delta\Delta E^{(2)}$ is shown in Figure 6b in main text).

Exchange 2



$\mathbf{1_{ocb}}$ 4 $\mathbf{2_{ocb}}$ 3

	$\Delta E^{(2)}$-$\mathbf{1_{ocb}}$	$\Delta E^{(2)}$-$\mathbf{2_{ocb}}$	$\Delta\Delta E^{(2)}$ [a]	log K_2
a (*p*-H)	2.29	1.32	-0.97	-0.174
b (*p*-OMe)	0.72	0.82	0.10	0.173
c (*p*-Br)	2.17	1.32	-0.85	-0.252
d (*p*-NO_2)	4.49	1.52	-2.97	-0.585
e (*m*-Br)	2.83	1.61	-1.22	-0.337
f	5.67	1.82	-3.85	-0.854

[a] $\Delta\Delta E^{(2)} = \Delta E^{(2)}$-$\mathbf{2_{ocb}}$ -$\Delta E^{(2)}$-$\mathbf{1_{ocb}}$

The quality of linear regression of log K_2 and $\Delta\Delta E^{(2)}$ was supported by a good linear relationship ($Y = 0.232*X + 0.0394$, $R^2 = 0.945$).

6. Imine DCC in Aqueous Phase

(1) Imine Chemistry in Water

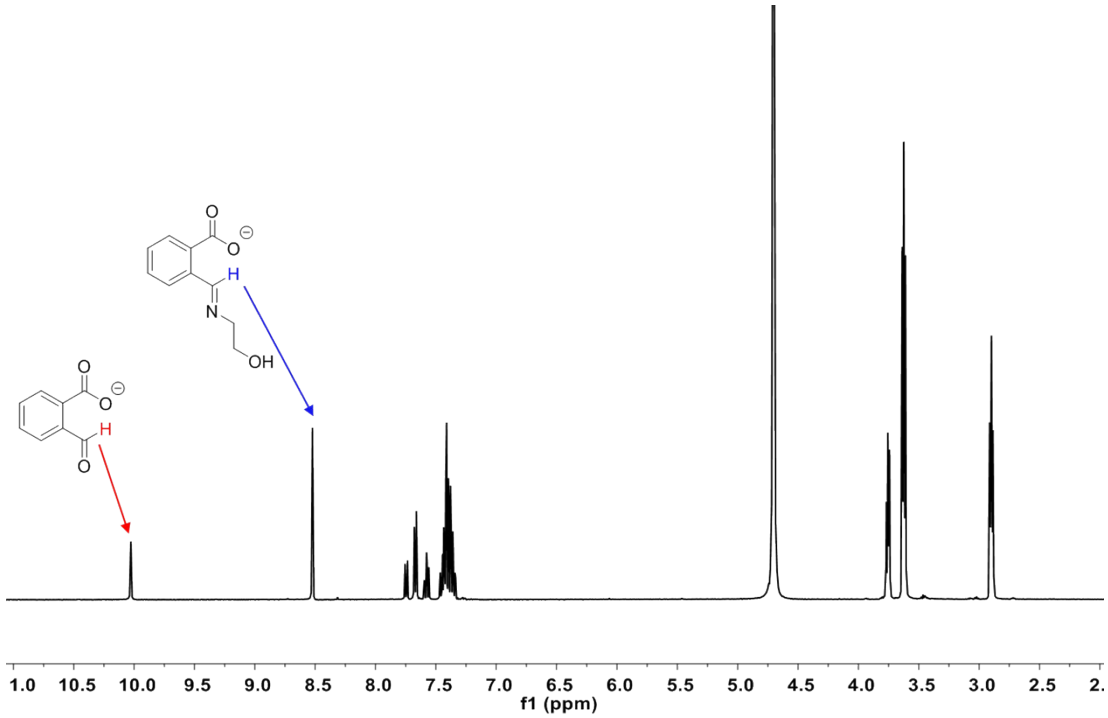


Figure S54. ^{1}H NMR spectrum of the reaction between **1a** and ethanolamine in D_2O. The yield of imine is 73%.

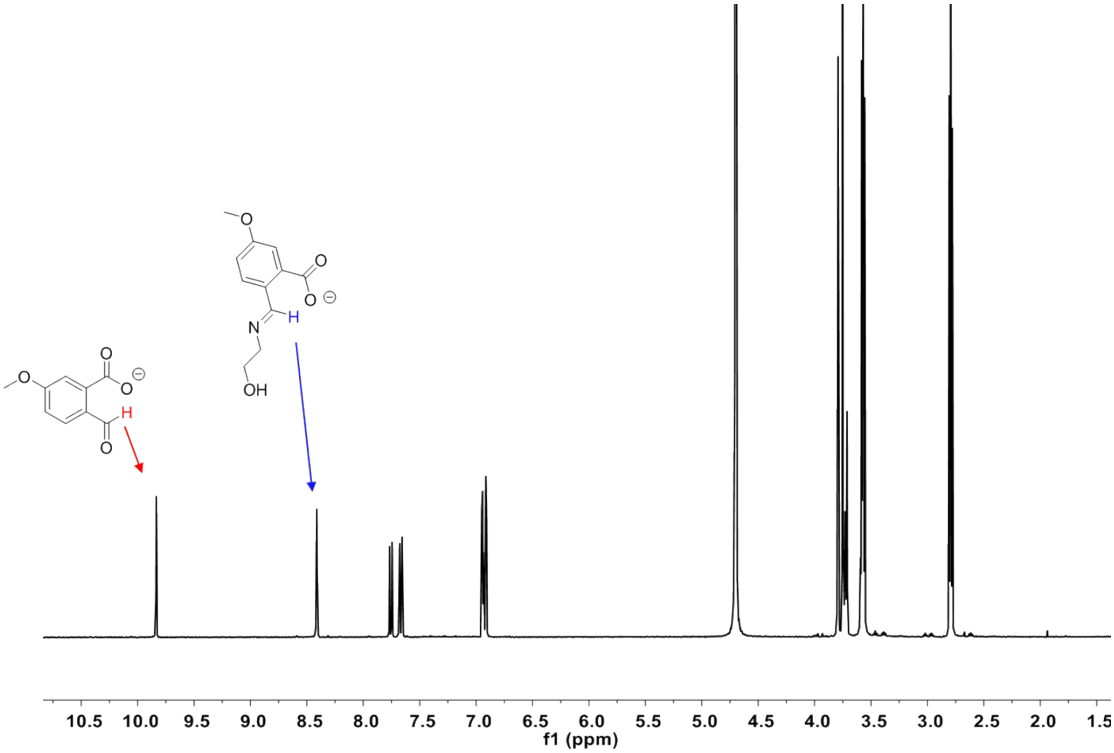


Figure S55. ^{1}H NMR spectrum of the reaction between **1b** and ethanolamine in D_2O. The yield of imine is 60%.

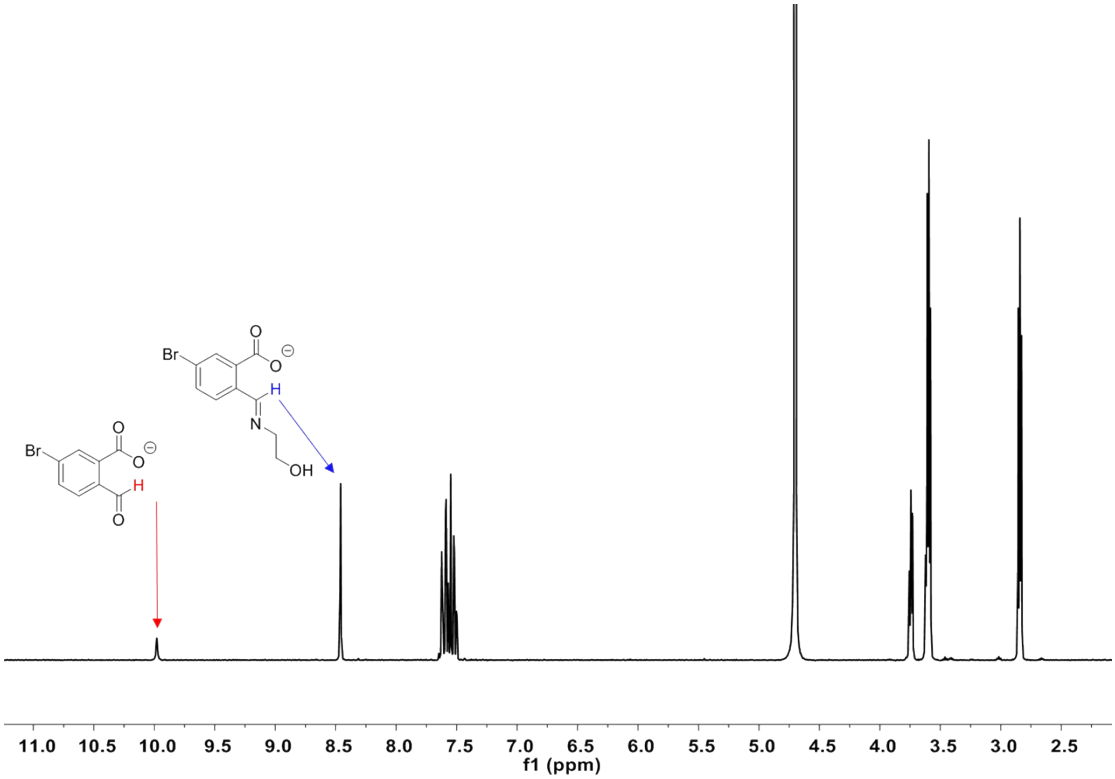


Figure S56. ^{1}H NMR spectrum of the reaction between **1c** and ethanolamine in D_2O. The yield of imine is 80%.

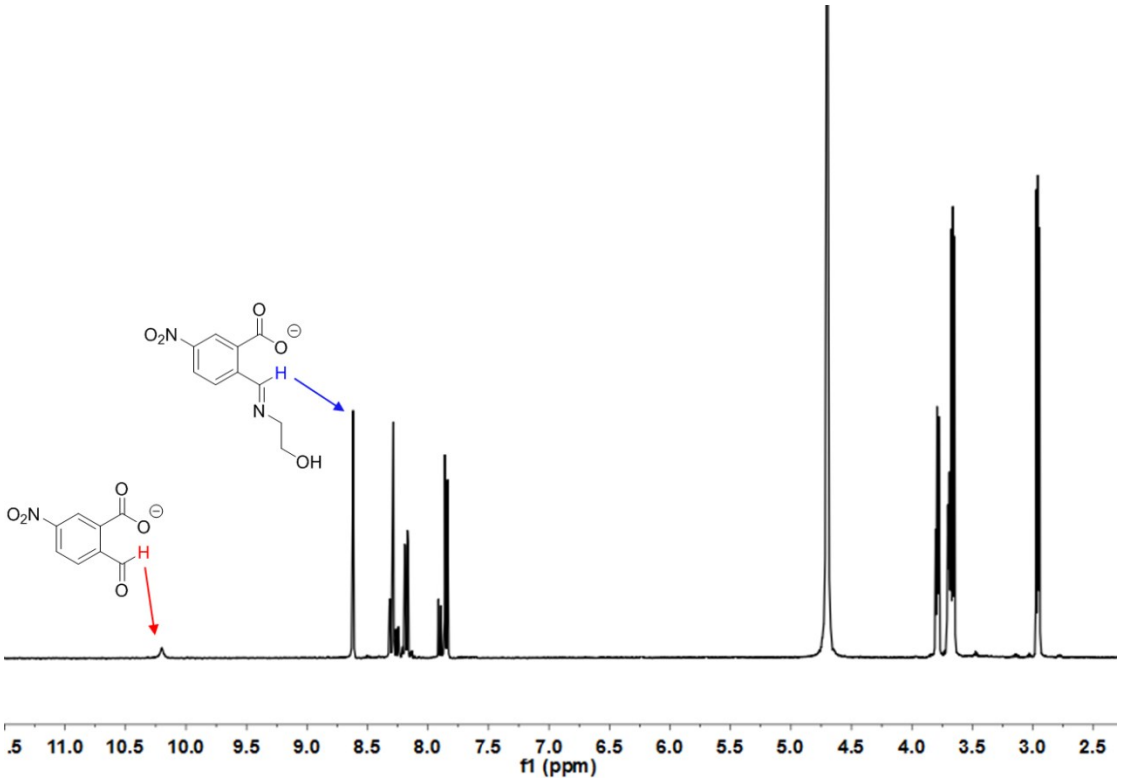


Figure S57. ^{1}H NMR spectrum of the reaction between **1d** and ethanolamine in D_2O. The yield of imine is 92%.

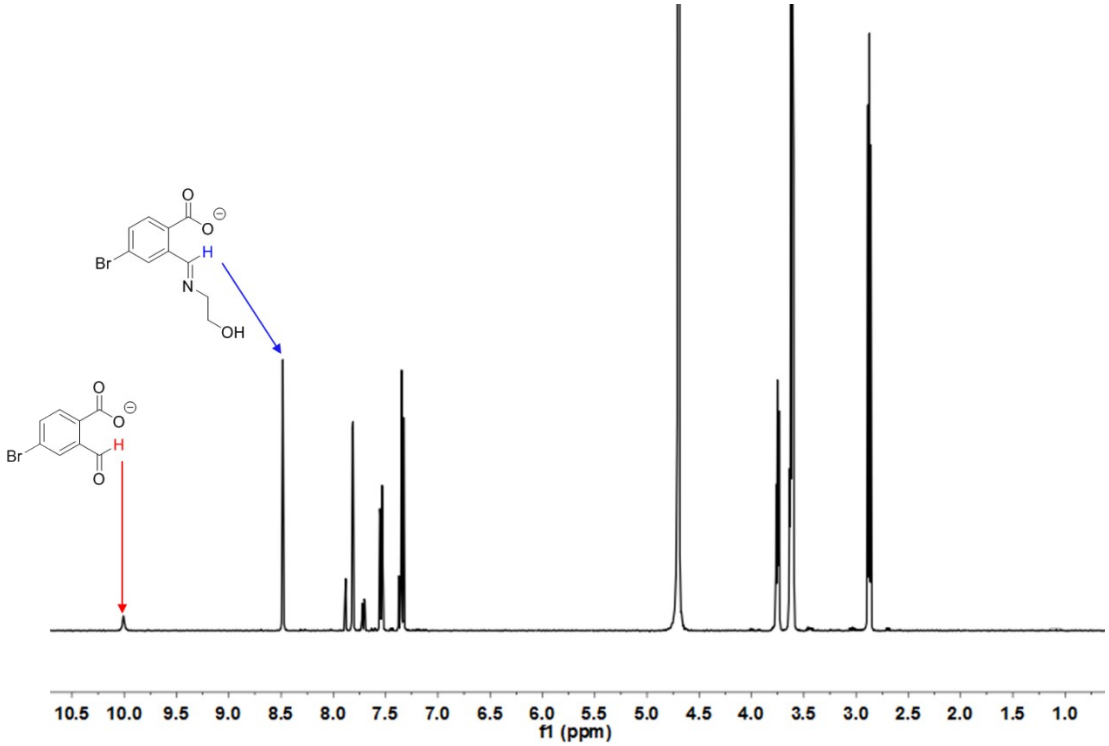


Figure S58. ^{1}H NMR spectrum of the reaction between **1e** and ethanolamine in D_2O. The yield of imine is 85%.

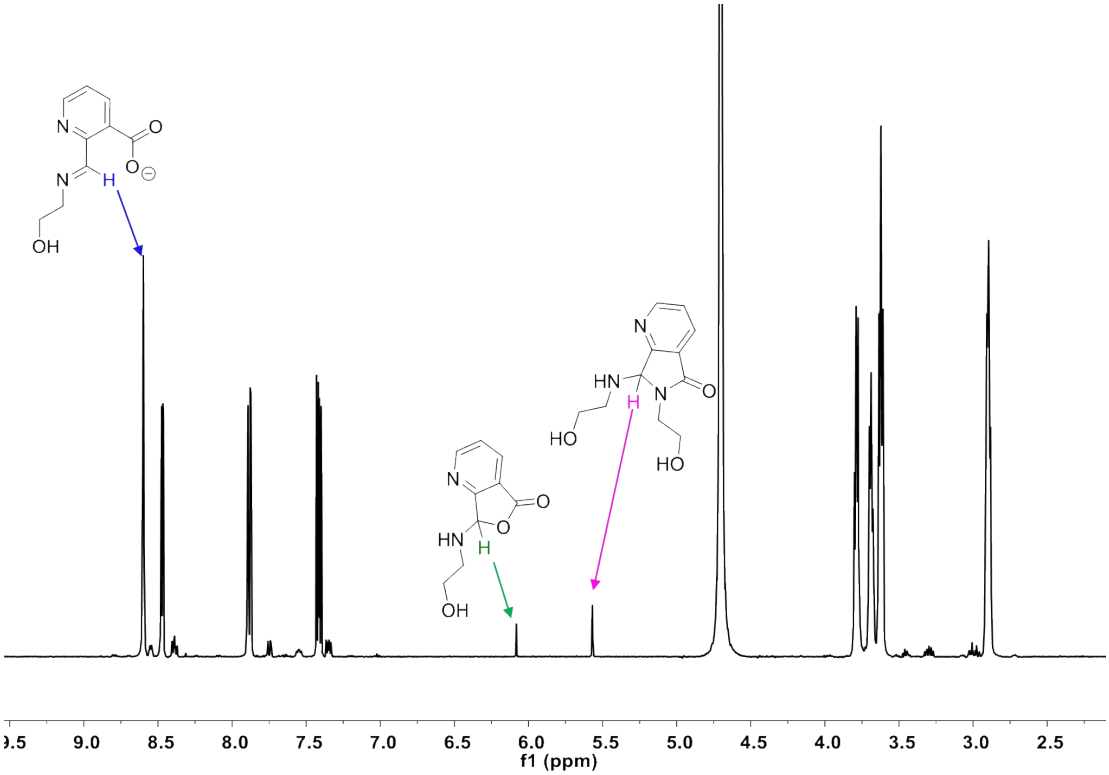


Figure S59. ^{1}H NMR spectrum of the reaction between **1f** and ethanolamine in D_2O. In addition to open imine (91%) cyclic structures (9%) were also observed. No aldehyde was apparent.

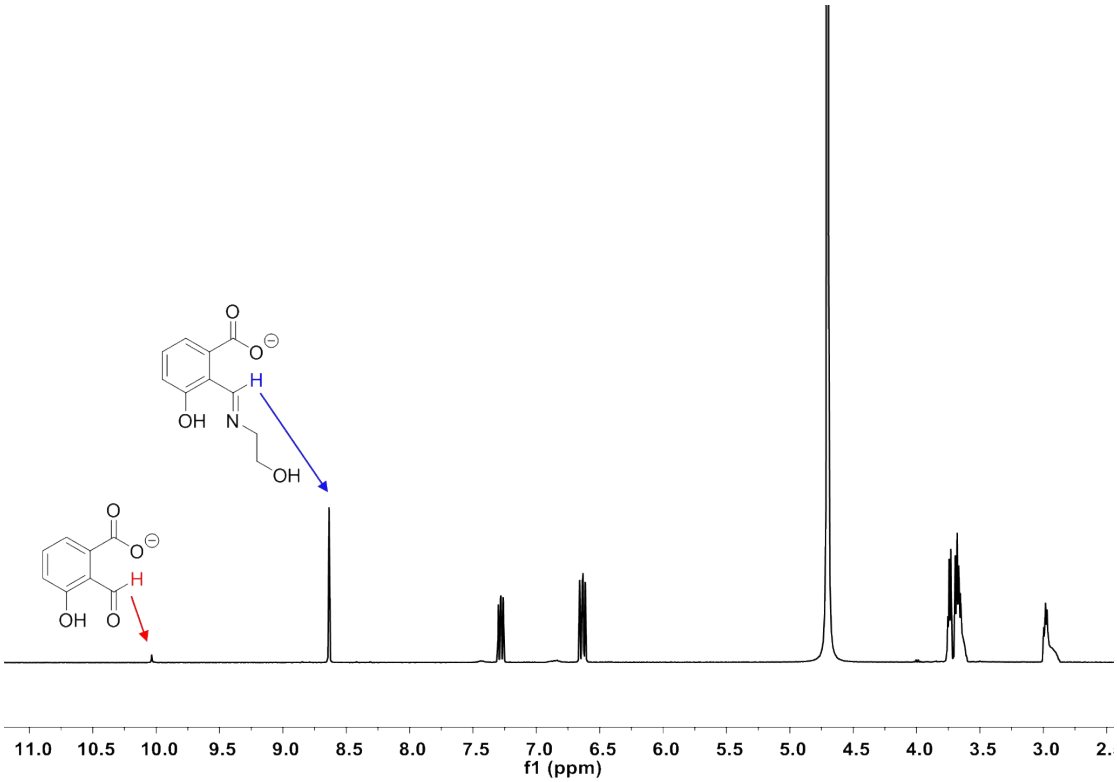


Figure S60. ^{1}H NMR spectrum of the reaction between **1g** and ethanolamine in D_2O. The yield of imine is 95%.

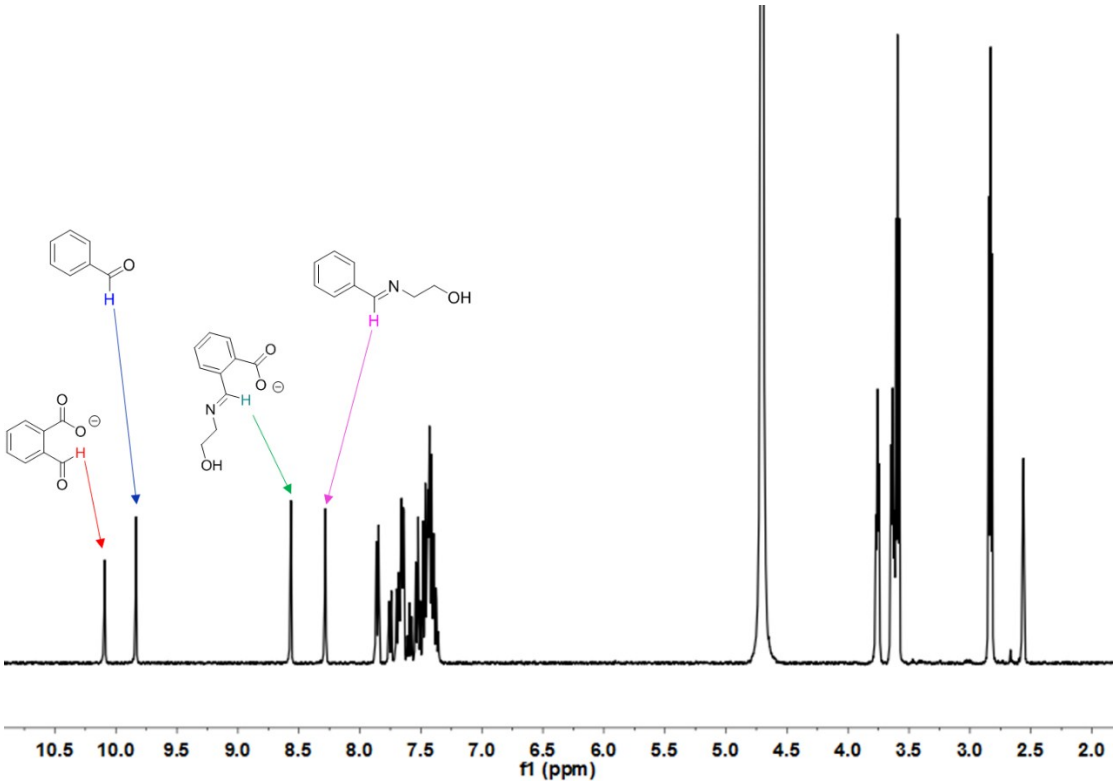


Figure S61. ^{1}H NMR spectrum of the competition between **1a** and **3a** for the reaction with ethanolamine in D_2O (with 10% DMSO-d_6).

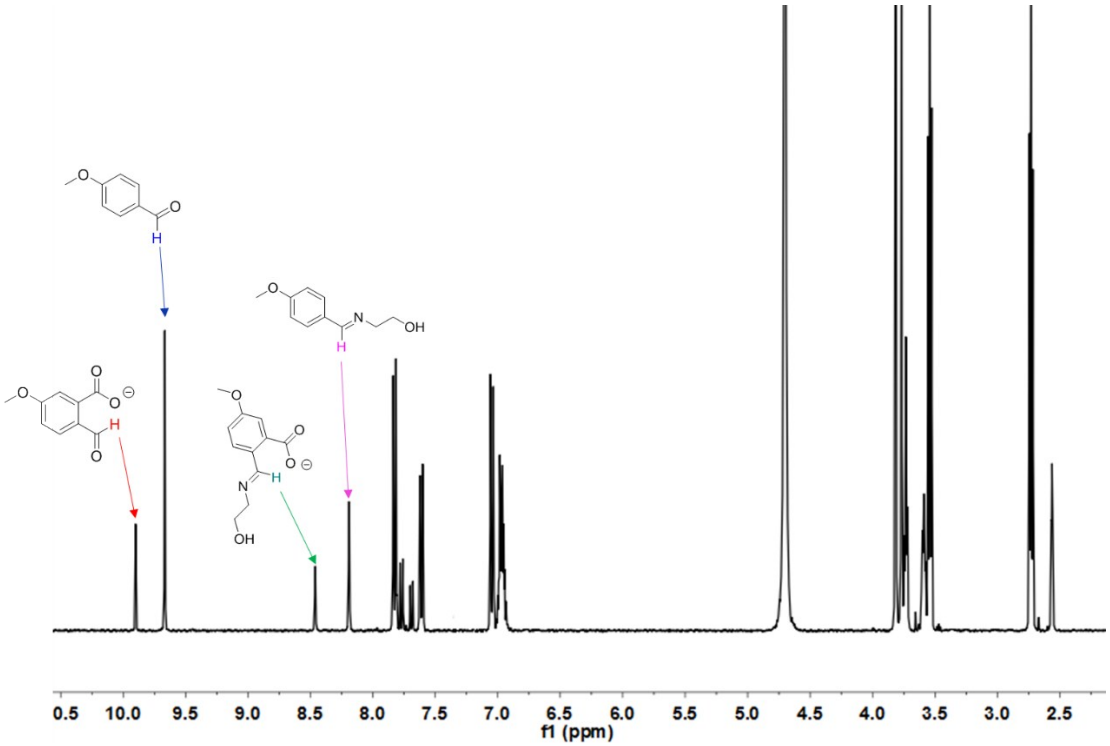


Figure S62. ^{1}H NMR spectrum of the competition between **1b** and **3b** for the reaction with ethanolamine in D_2O (with 10% DMSO-d_6).

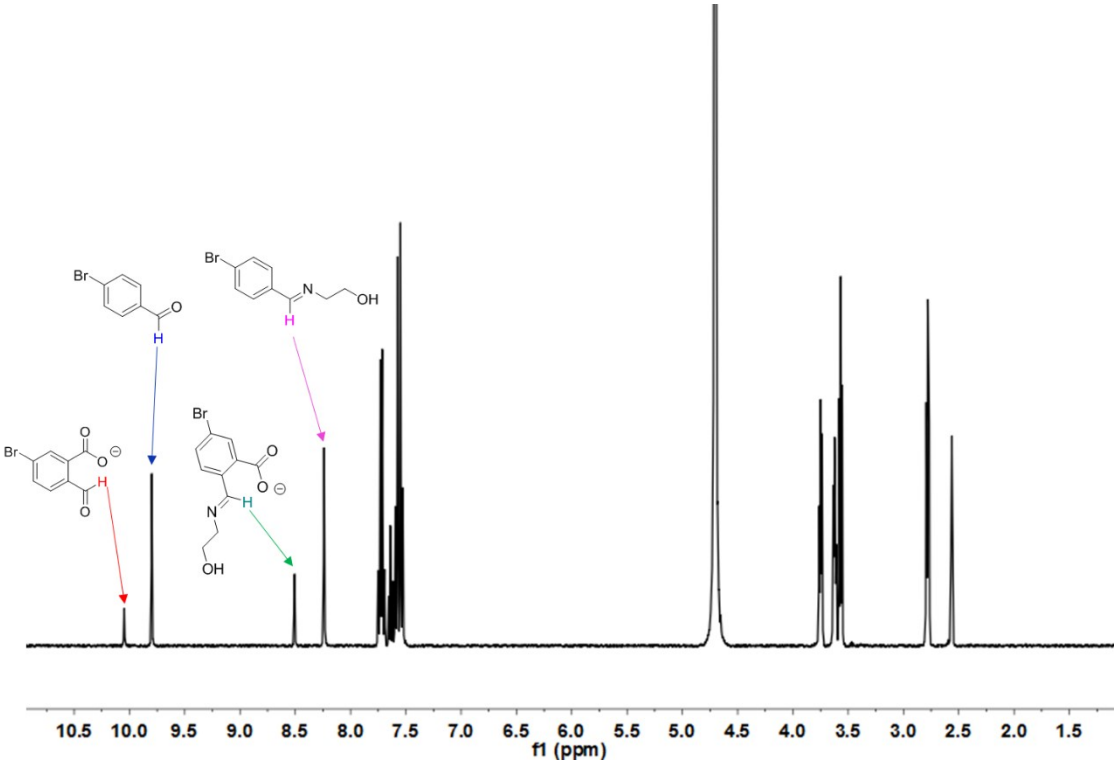


Figure S63. ^{1}H NMR spectrum of the competition between **1c** and **3c** for the reaction with ethanolamine in D_2O (with 10% DMSO-d_6).

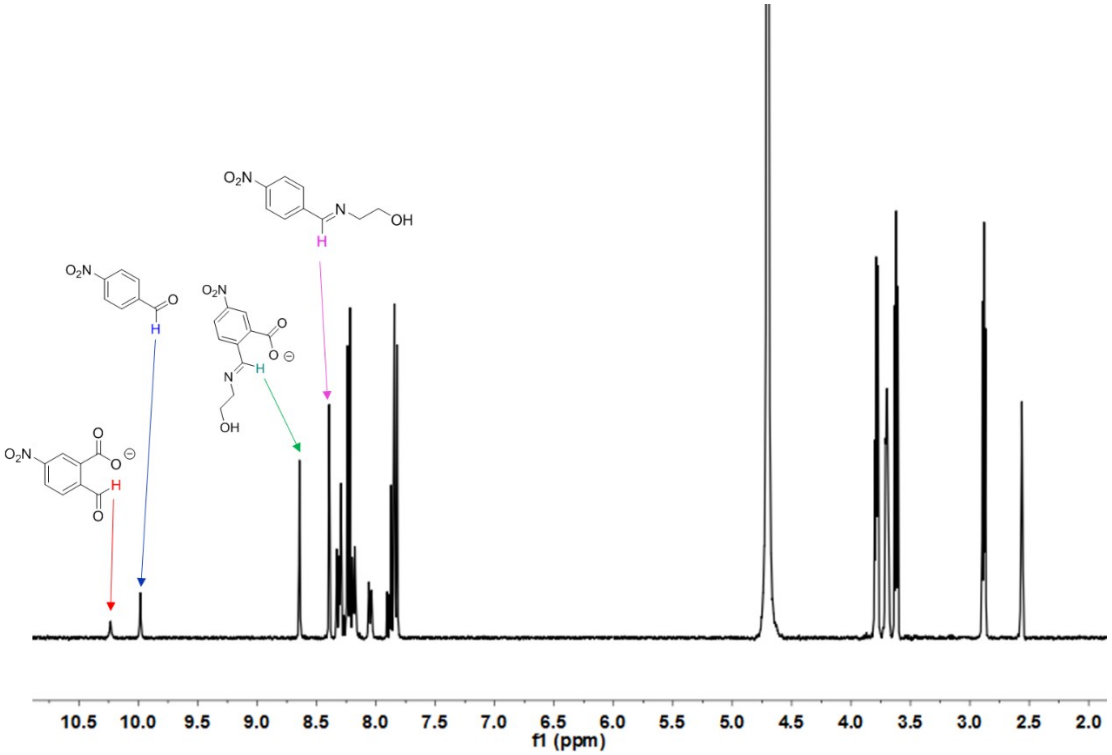


Figure S64. ^{1}H NMR spectrum of the competition between **1d** and **3d** for the reaction with ethanolamine in D_2O (with 10% DMSO-d_6).

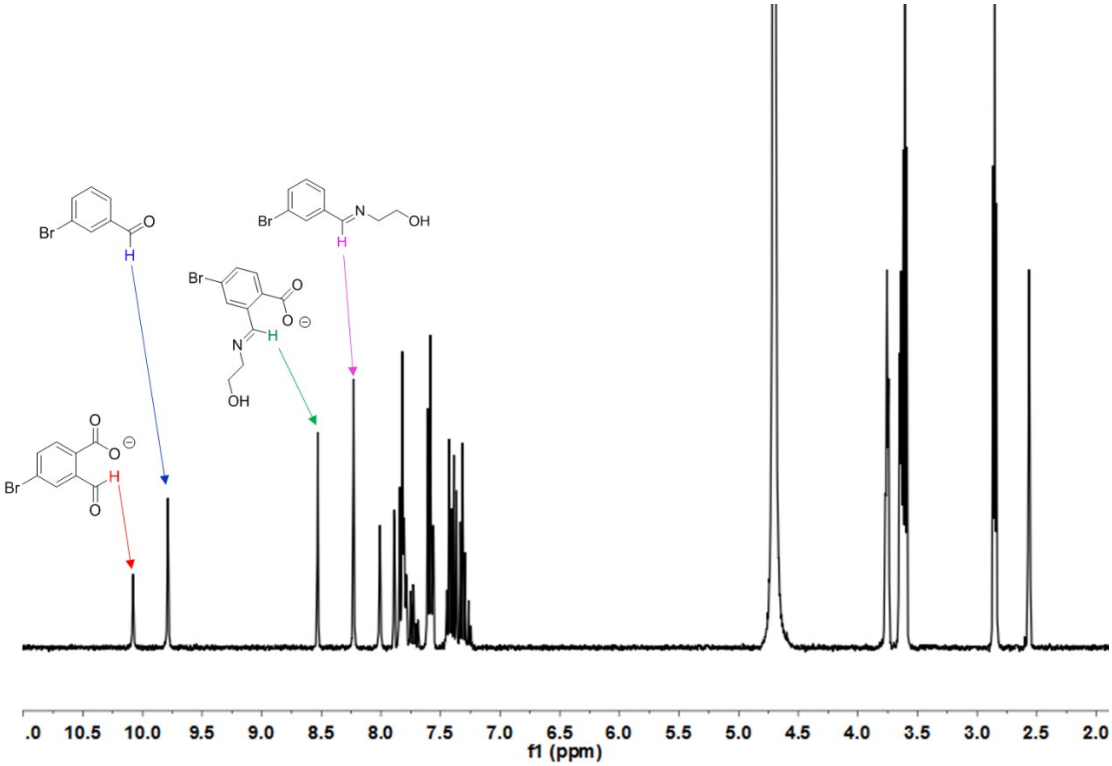


Figure S65. ^{1}H NMR spectrum of the competition between **1e** and **3e** for the reaction with ethanolamine in D_2O (with 10% DMSO-d_6).

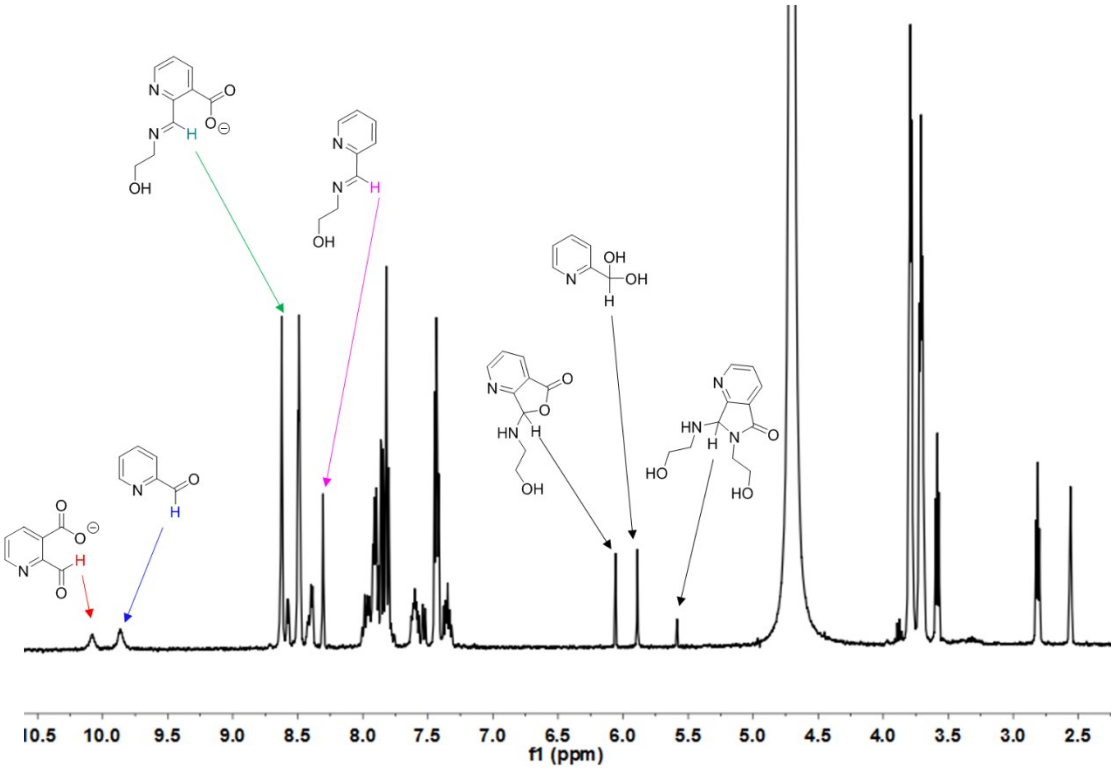


Figure S66. ^{1}H NMR spectrum of the competition between **1f** and **3f** for the reaction with ethanolamine in D_2O (with 10% DMSO-d_6).

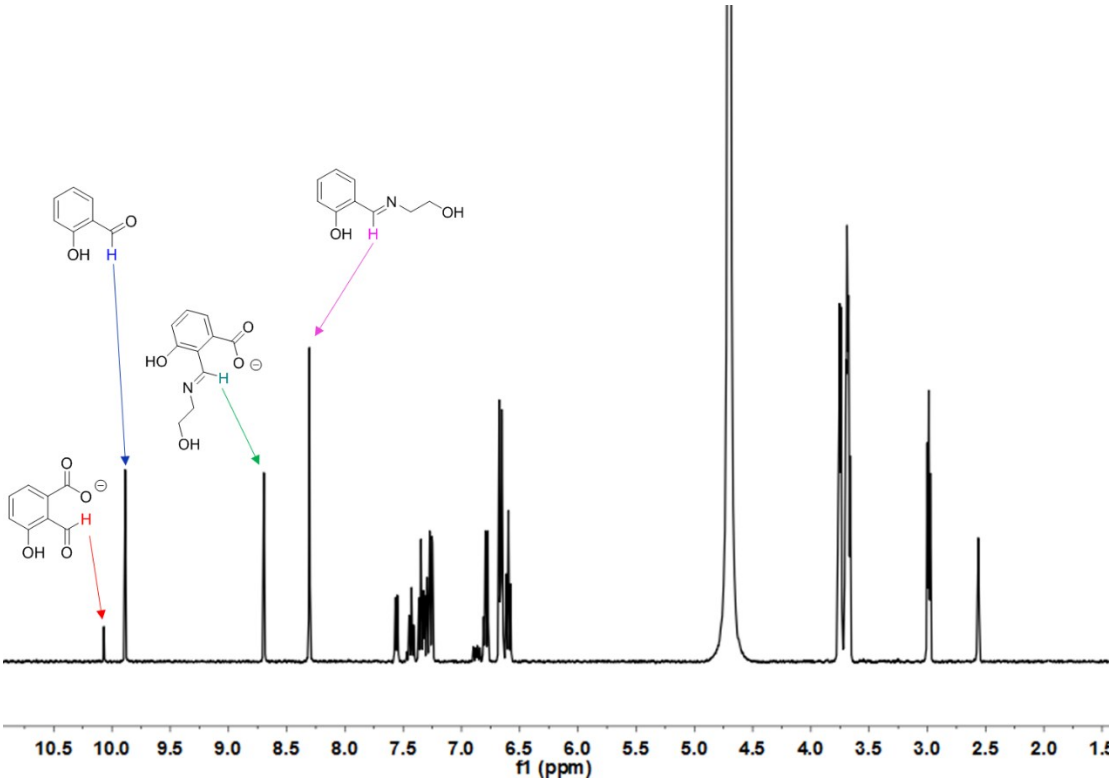


Figure S67. ^{1}H NMR spectrum of the competition between **1g** and **3g** for the reaction with ethanolamine in D_2O (with 10% DMSO-d_6).

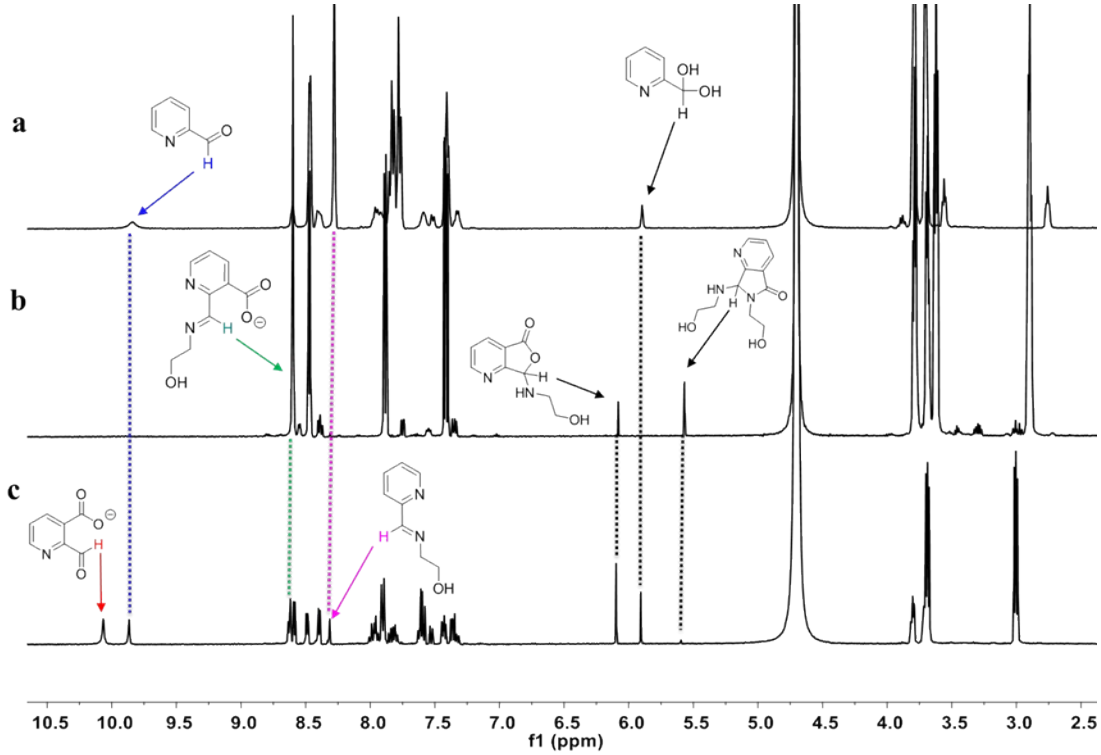


Figure S68. ^{1}H NMR spectra of (a) the reaction of **3f** with ethanolamine (1.0 equiv.), (b) the reaction of **1f** with ethanolamine (2.0 equiv.), (c) the reaction of **1f** and **3f** (1.0 equiv.) with ethanolamine (2.0 equiv.) in D_2O.

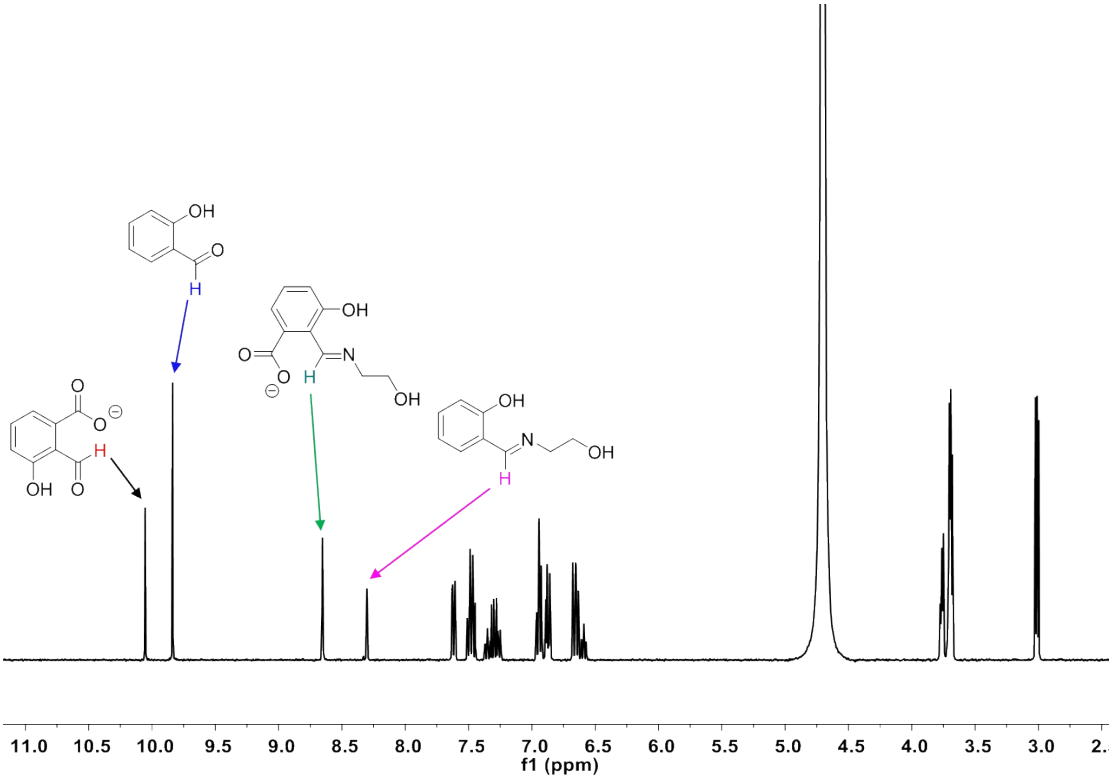


Figure S69. ^{1}H NMR spectrum of the competition between **1g** and **3g** (1.0 equiv.) for the reaction with ethanolamine (2.0 equiv.) in D_2O.

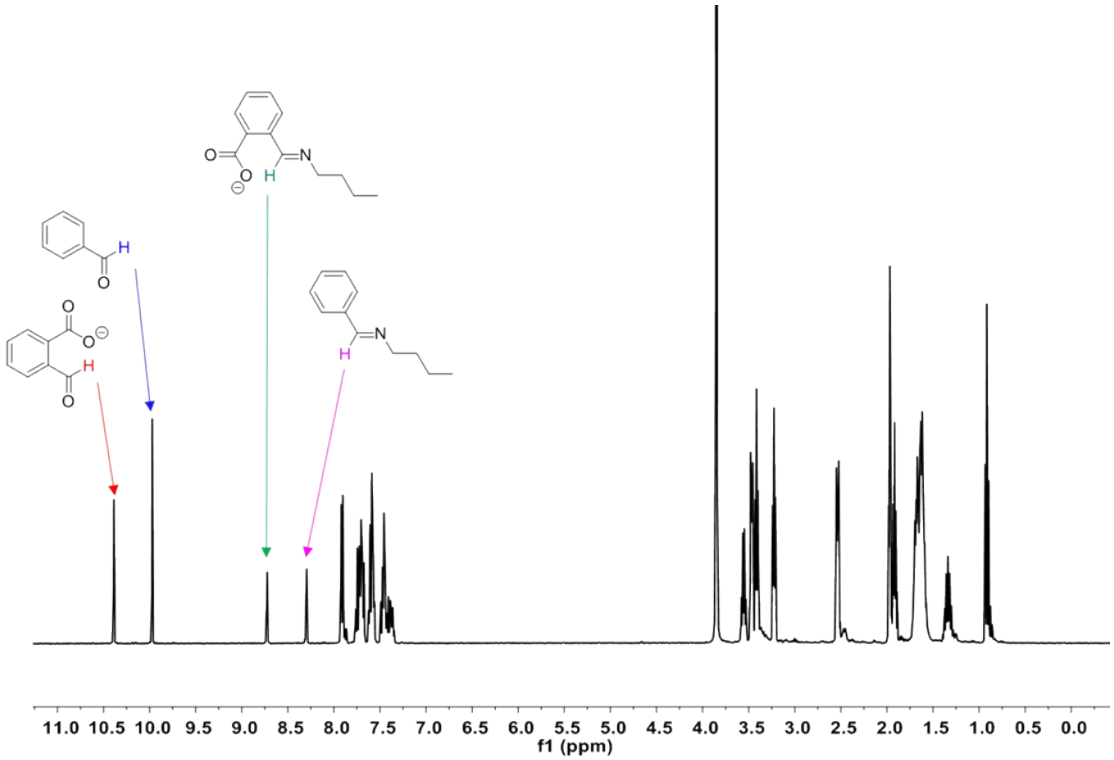


Figure S70. ^{1}H NMR spectrum of the competition between **1a**$_{\mathbf{ocb}}$ and **3a** (1.0 equiv.) for the reaction with 1-butylamine (1.0 equiv.) in CD_3CN/D_2O (3:1).

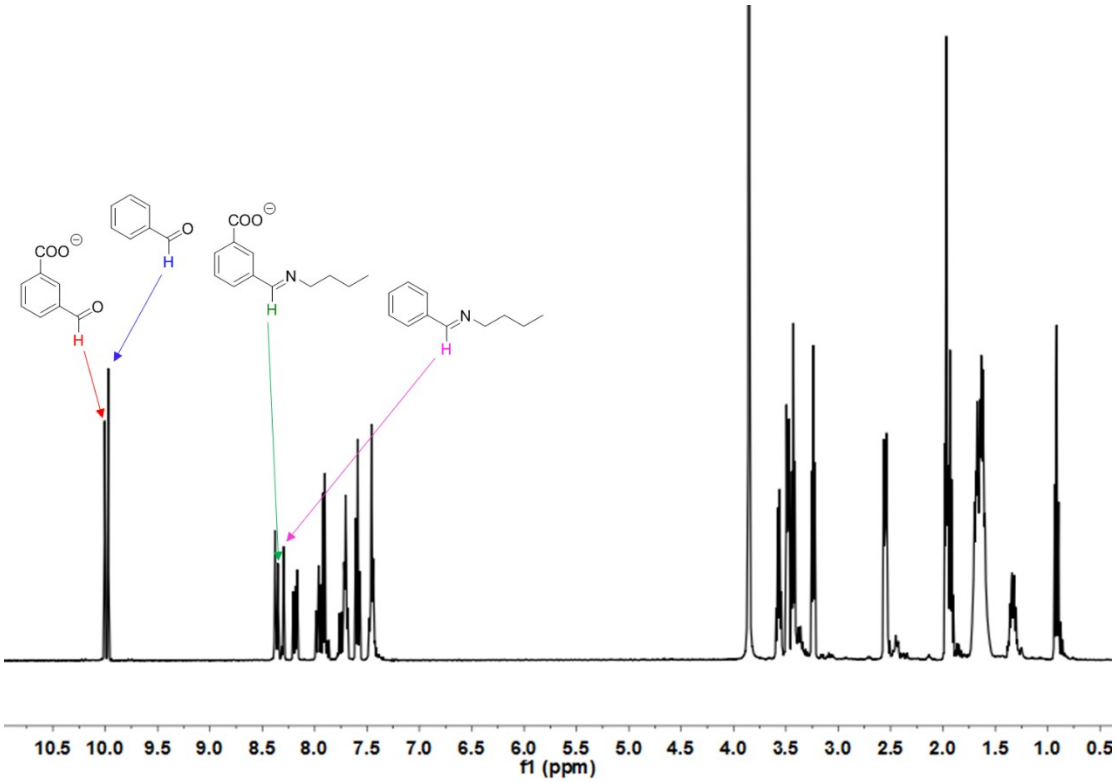


Figure S71. ^{1}H NMR spectrum of the competition between **1a**(*meta*)$_{\mathbf{ocb}}$ and **3a** (1.0 equiv.) for the reaction with 1-butylamine (1.0 equiv.) in CD_3CN/D_2O (3:1).

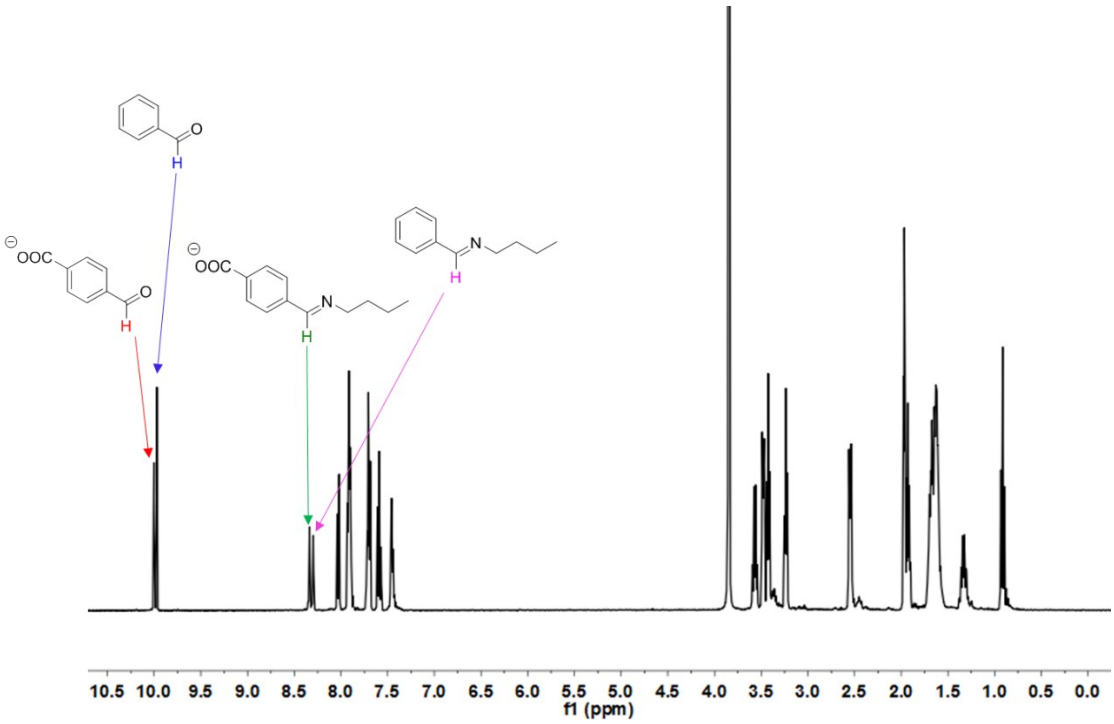


Figure S72. ^{1}H NMR spectrum of the competition between **1a**(*para*)$_{\mathbf{ocb}}$ and **3a** (1.0 equiv.) for the reaction with 1-butylamine (1.0 equiv.) in CD_3CN/D_2O (3:1).

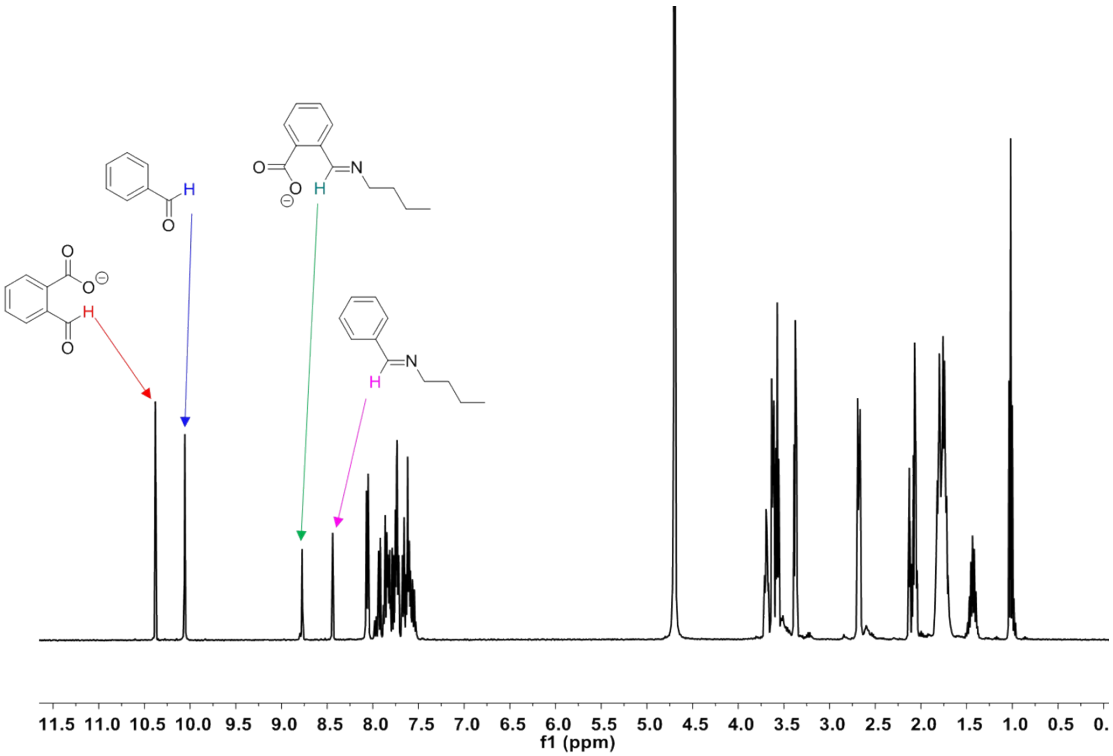


Figure S73. ^{1}H NMR spectrum of the competition between **1a**$_{\mathbf{ocb}}$ and **3a** (1.0 equiv.) for the reaction with 1-butylamine (1.0 equiv.) in CD_3CN/D_2O (1:3).

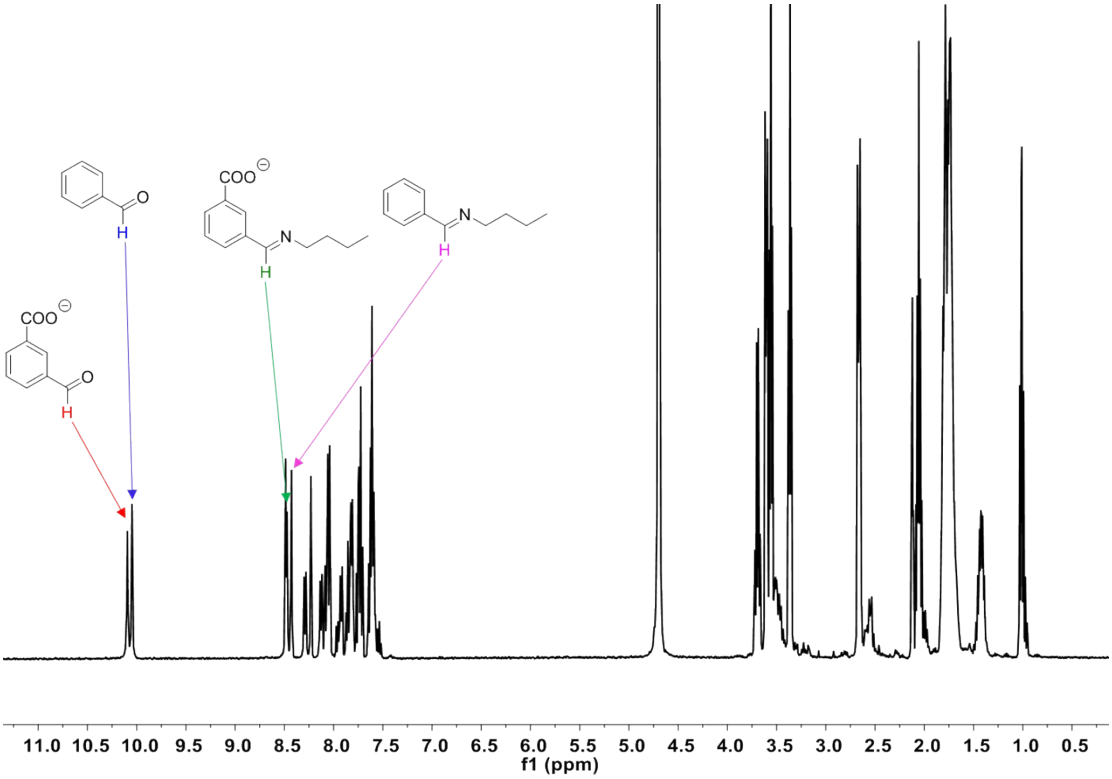


Figure S74. ^{1}H NMR spectrum of the competition between **1a**(*meta*)$_{\mathbf{ocb}}$ and **3a** (1.0 equiv.) for the reaction with 1-butylamine (1.0 equiv.) in CD_3CN/D_2O (1:3).

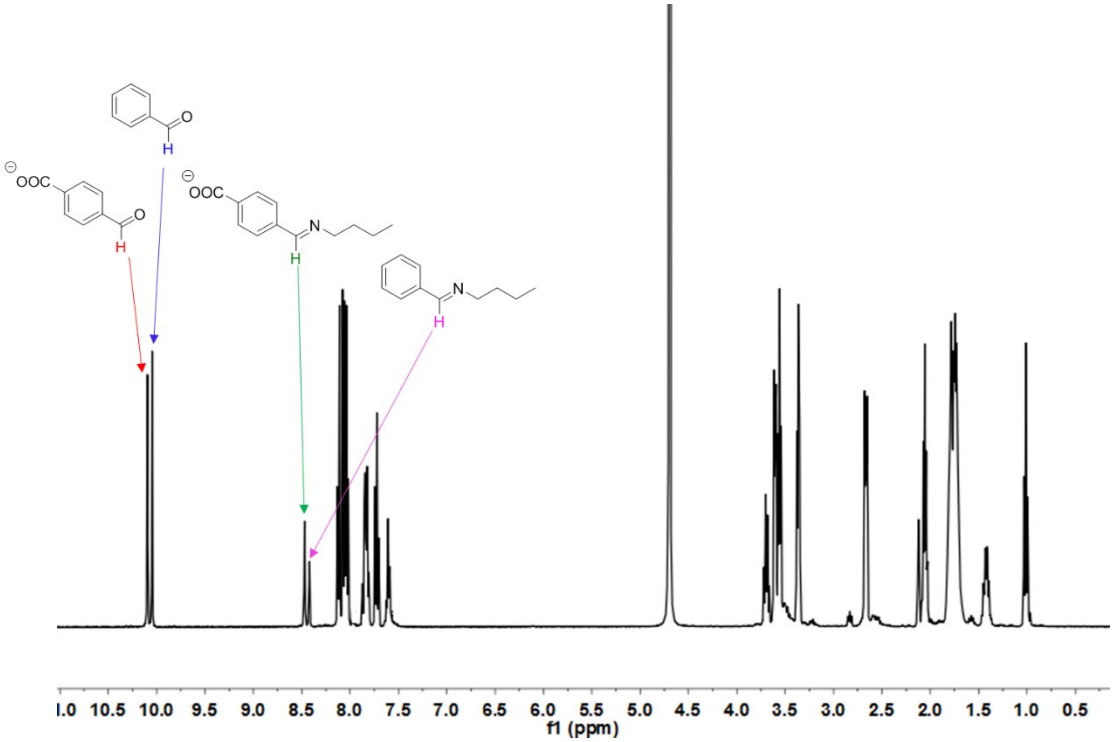


Figure S75. ^{1}H NMR spectrum of the competition between **1a**(*para*)$_{\mathbf{ocb}}$ and **3a** (1.0 equiv.) for the reaction with 1-butylamine (1.0 equiv.) in CD_3CN/D_2O (1:3).

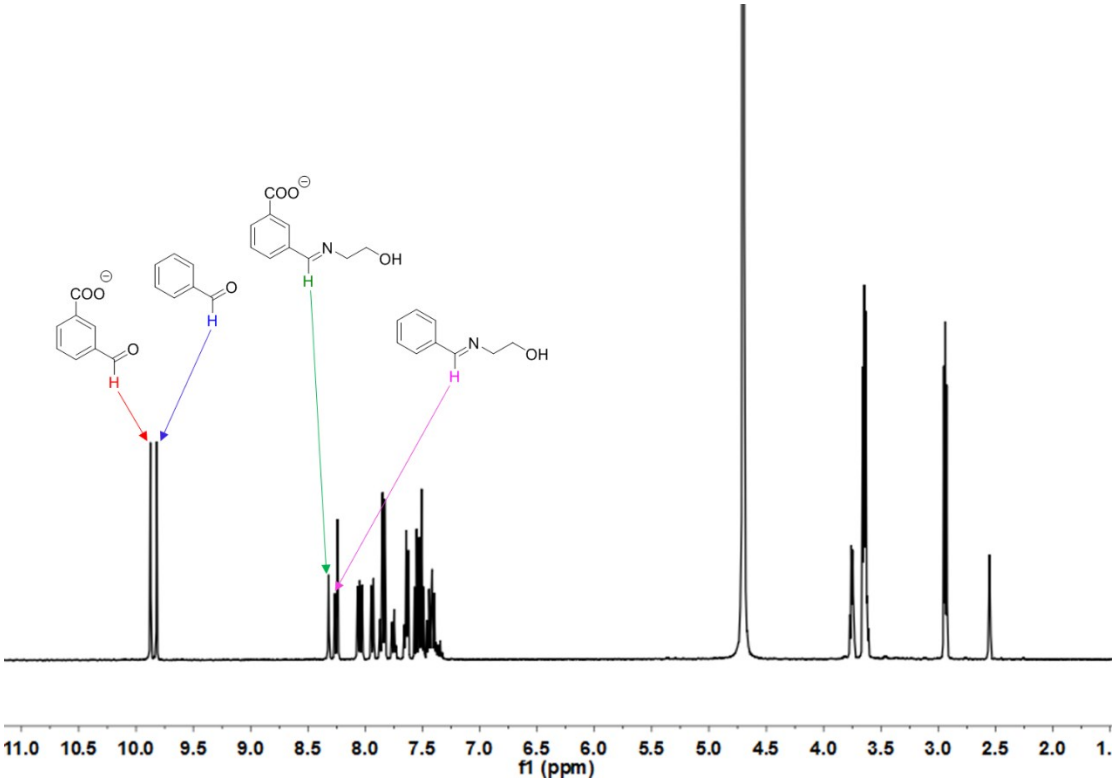


Figure S76. ^{1}H NMR spectrum of the competition between **1a**(*meta*)$_{\mathbf{ocb}}$ and **3a** (1.0 equiv.) for the reaction with ethanolamine (2.0 equiv.) in D_2O (with 10% DMSO-d_6).

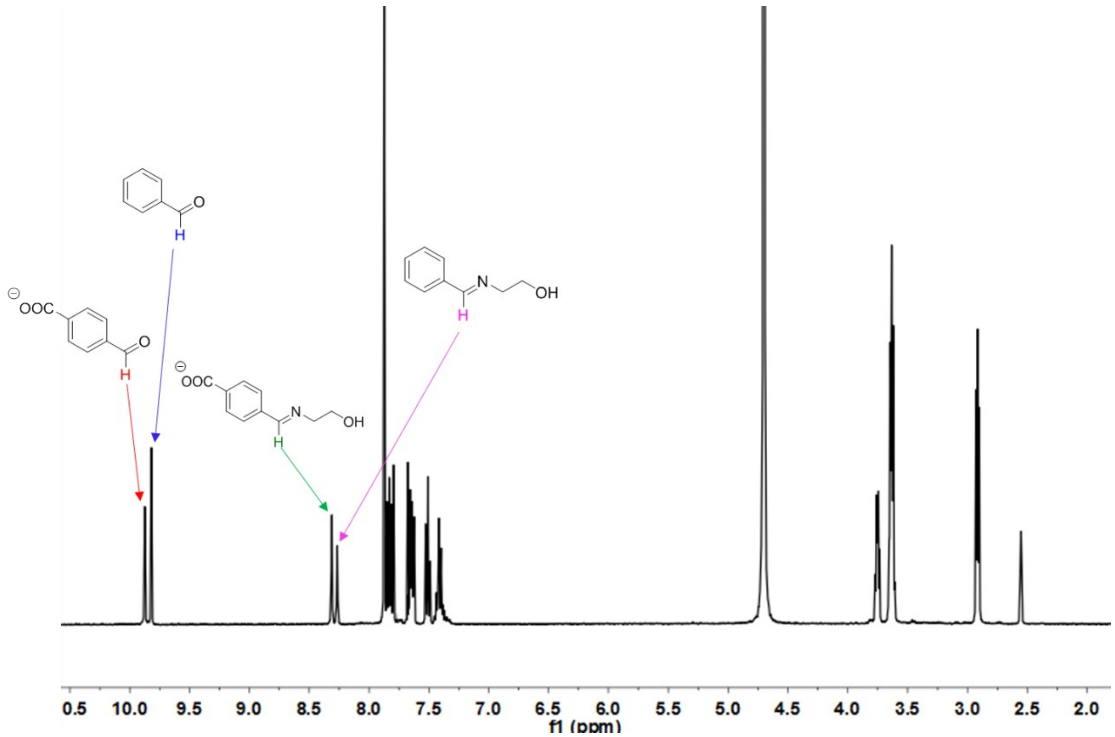
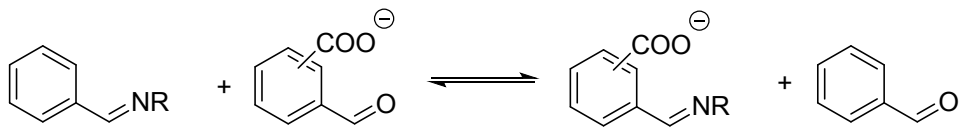


Figure S77. ^{1}H NMR spectrum of the competition between **1**(*para*)$_{\mathbf{ocb}}$ and **3a** (1.0 equiv.) for the reaction with ethanolamine (2.0 equiv.) in D_2O (with 10% DMSO-d_6).

Table S4. The equilibrium constants of imine exchange reactions in different solvents.



Solvent	**1a**	**1a**(*meta*)	**1a**(*para*)
CD_3CN	0.67	2.01	1.65
CD_3CN/D_2O 3:1	0.86	1.21	1.78
CD_3CN/D_2O 1:3	1.22	1.21	1.80
D_2O/DMSO-d_6 9:1 [a]	1.31	1.20	1.80

[a] D_2O/DMSO-d_6 (9:1) was used to solubilize the components.

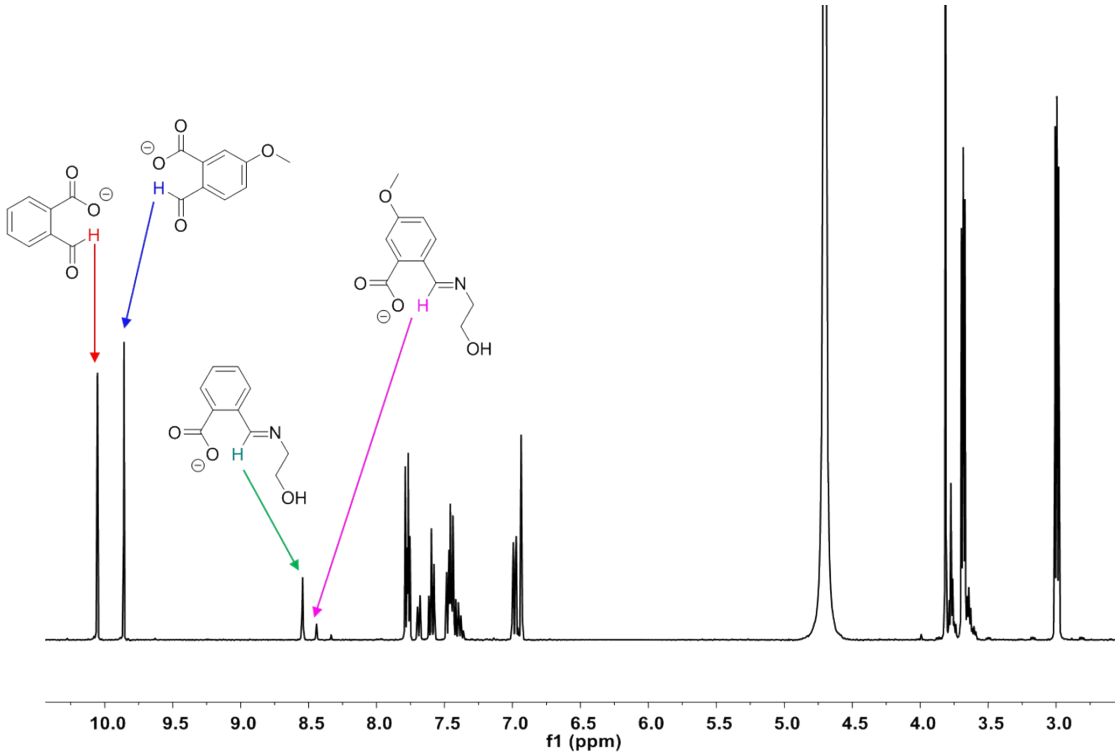


Figure S78. ^1H NMR spectrum of the competition between **1a** and **1b** for the reaction with ethanolamine in D_2O.

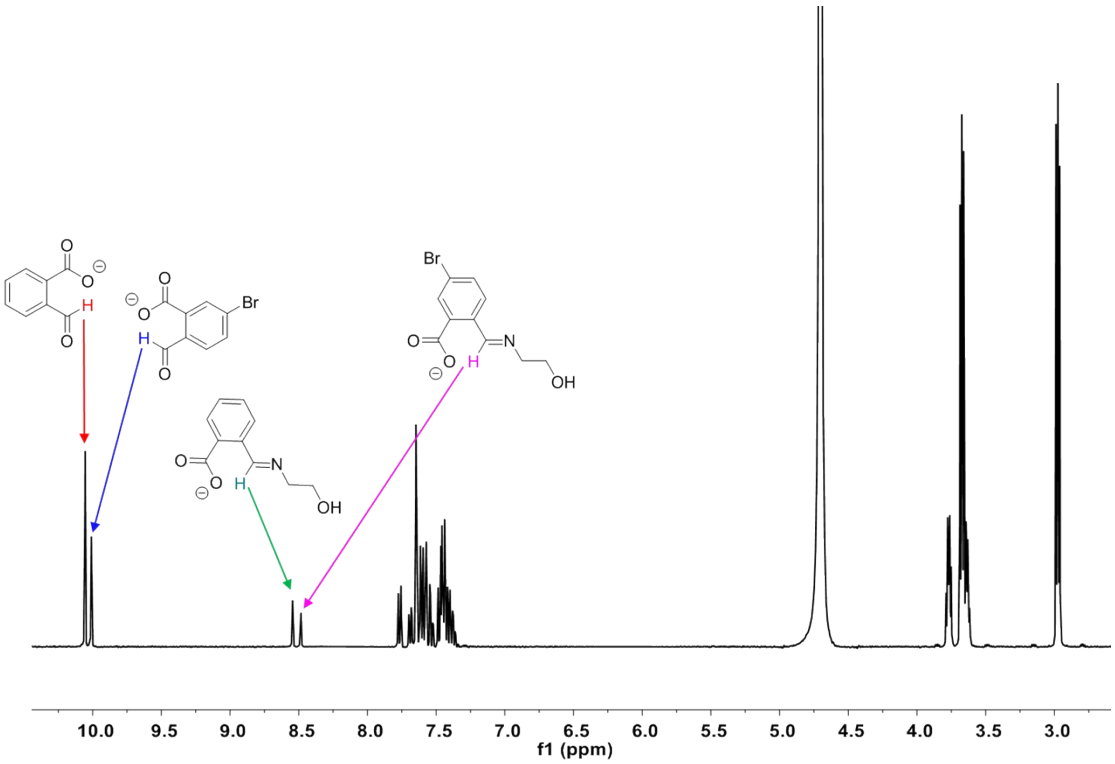


Figure S79. ^{1}H NMR spectrum of the competition between **1a** and **1c** for the reaction with ethanolamine in D_2O.

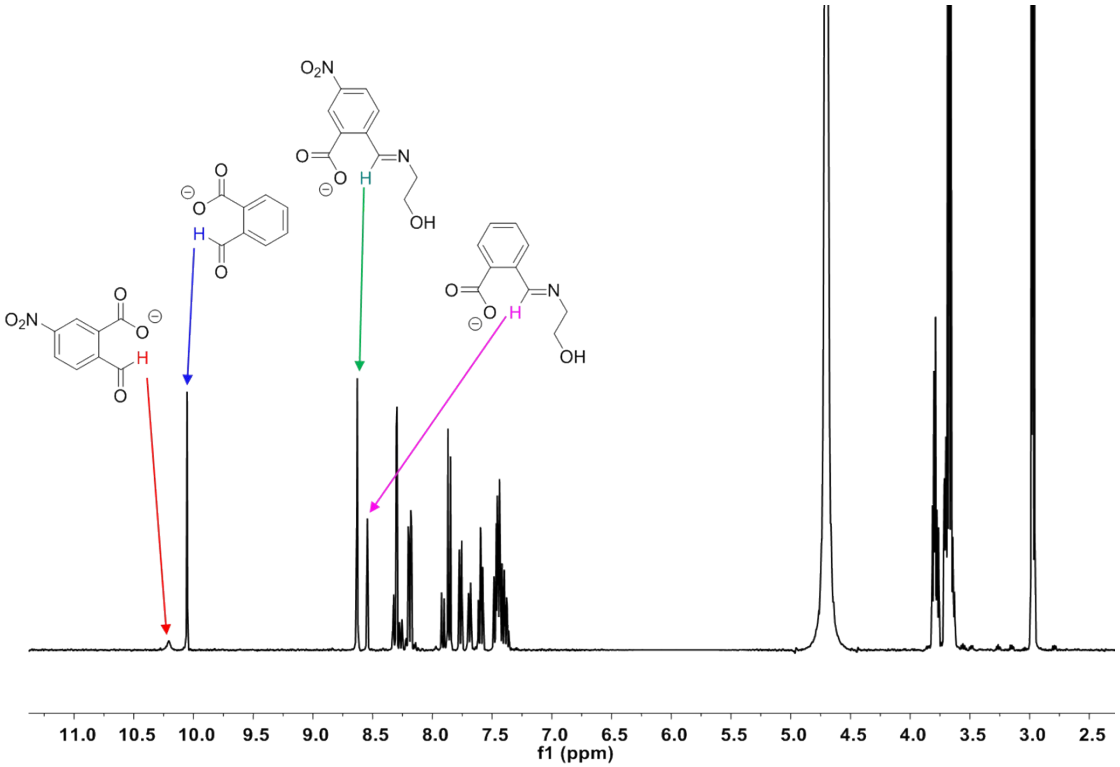


Figure S80. ^{1}H NMR spectrum of the competition between **1a** and **1d** for the reaction with ethanolamine in D_2O.

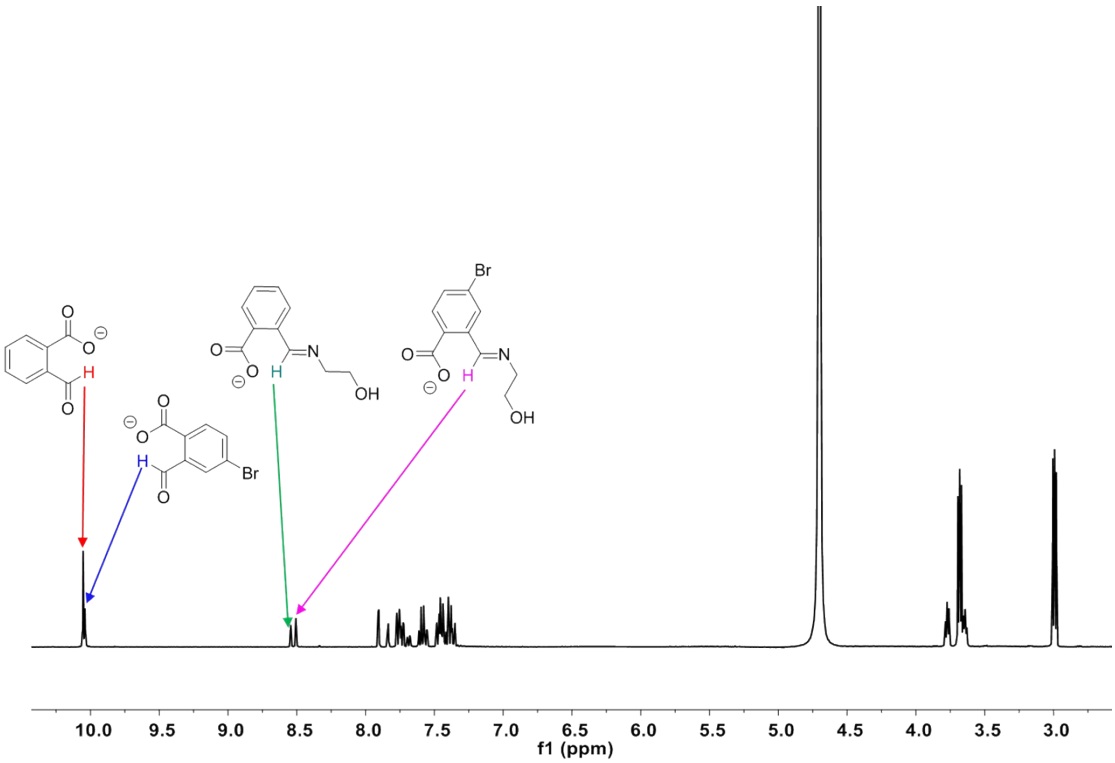


Figure S81. ^{1}H NMR spectrum of the competition between **1a** and **1e** for the reaction with ethanolamine in D_2O.

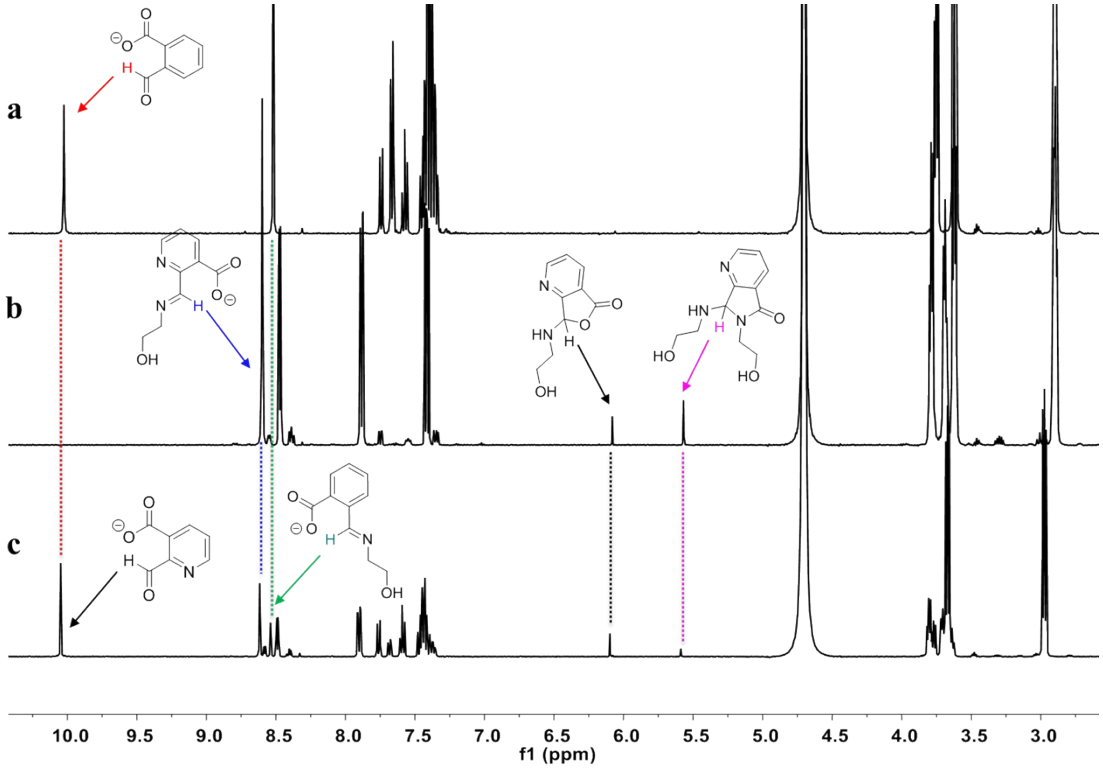


Figure S82. ^{1}H NMR spectra of (a) the reaction of **1a** with ethanolamine (2.0 equiv.), (b) the reaction of **1f** with ethanolamine (2.0 equiv.), (c) the reaction of **1a** and **1f** (1.0 equiv.) with ethanolamine (3.0 equiv.) in D_2O.

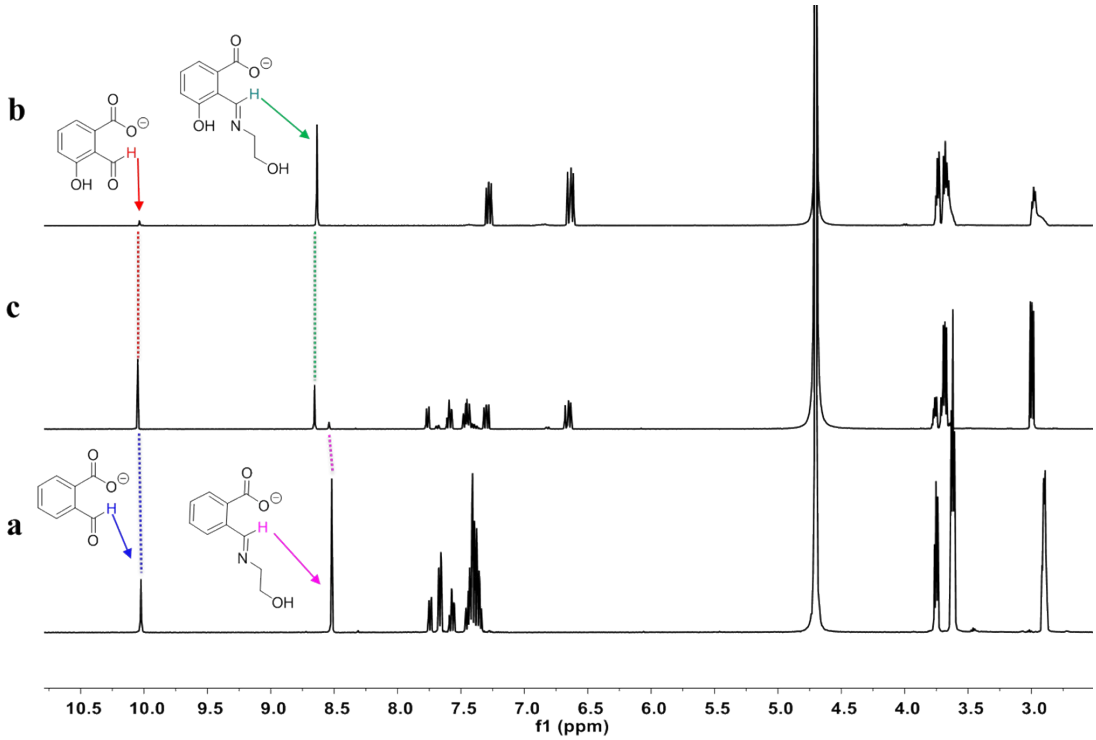


Figure S83. ^{1}H NMR spectra of (a) the reaction of **1a** with ethanolamine (2.0 equiv.), (b) the reaction of **1g** with ethanolamine (2.0 equiv.), (c) the reaction of **1a** and **1g** (1.0 equiv.) with ethanolamine (3.0 equiv.) in D_2O.

(2) Imine Chemistry in Buffer

Figure S84. ^{1}H NMR spectrum of the competition between **1g** and **3g** (1.0 equiv.) for the reaction with ethanolamine (1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

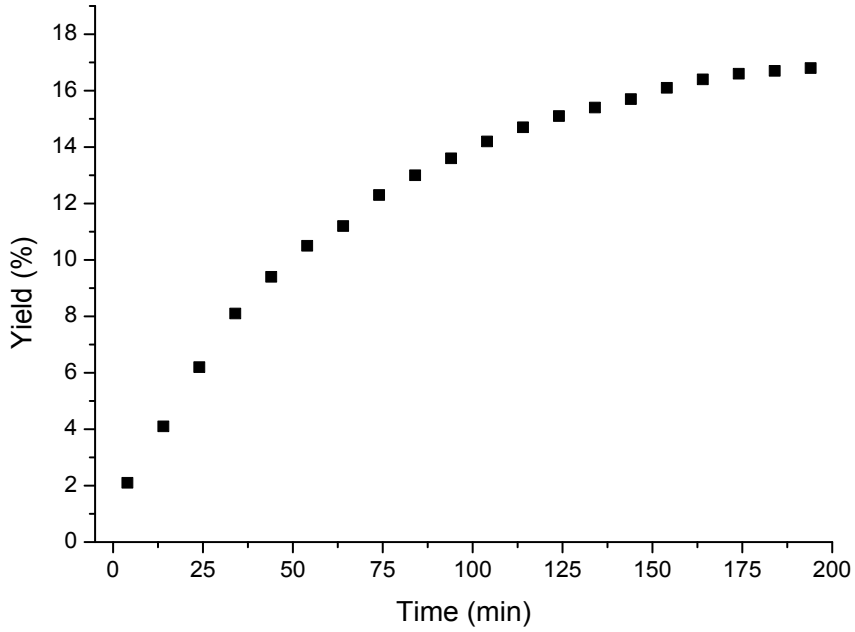


Figure S85. Kinetic profile of the reaction between **1g** (10 mM, 1.0 equiv.) and ethanolamine (1.2 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

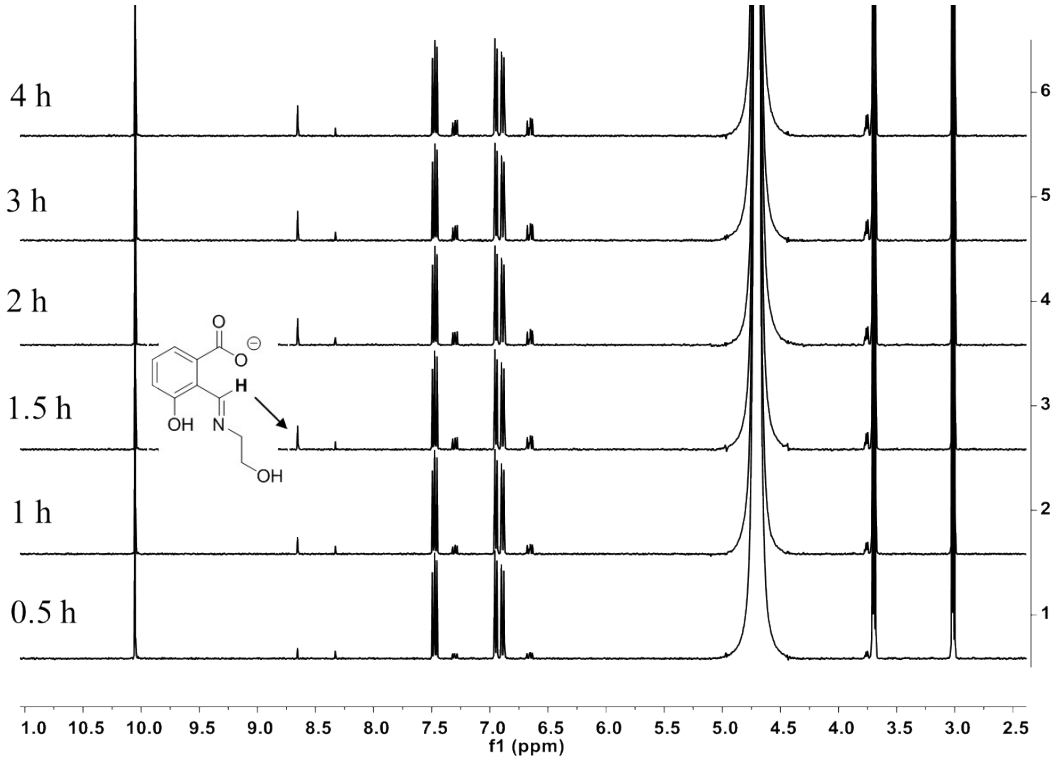


Figure S86. ^{1}H-NMR Spectra of the reaction between **1g** (10 mM, 1.0 equiv.) and ethanolamine (1.2 equiv.) at different reaction times (0.5 h, 1 h, 1.5 h, 2 h, 3 h, and 4 h) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

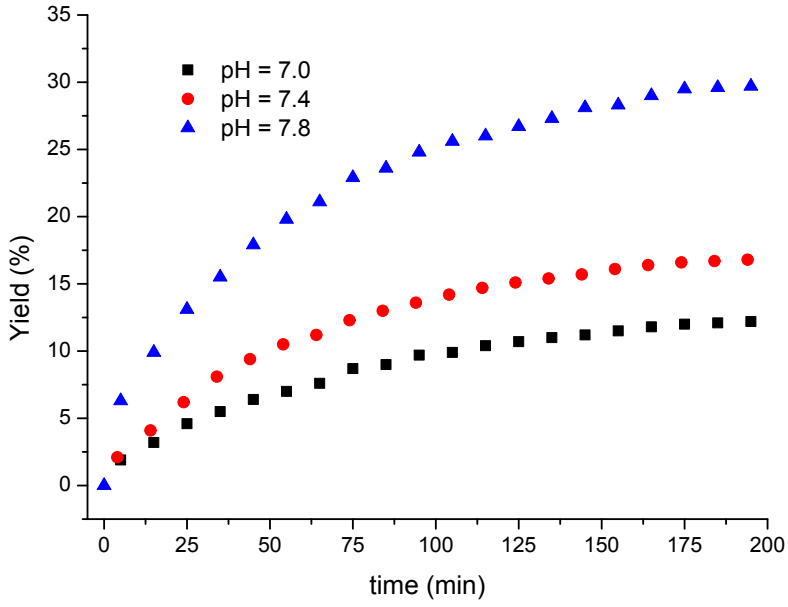


Figure S87. Kinetic profiles of the reaction between **1g** (10 mM, 1.0 equiv.) and ethanolamine (1.2 equiv.) at different pH in KPi buffer solution in D_2O (50 mM). The yield of imine was tracked.

Table S5. The reaction between **1g** (10 mM, 1.0 equiv.) and ethanolamine (1.2 equiv.) at different pH in KPi buffer solution in D_2O (50 mM), and corresponding yields of imines were obtained through ^{1}H-NMR spectra.

pH	3 hours	1 day	7 days
7.0	**12%**	**12%**	**12%**
7.4	**17%**	**17%**	**17%**
7.8	**30%**	**30%**	**30%**

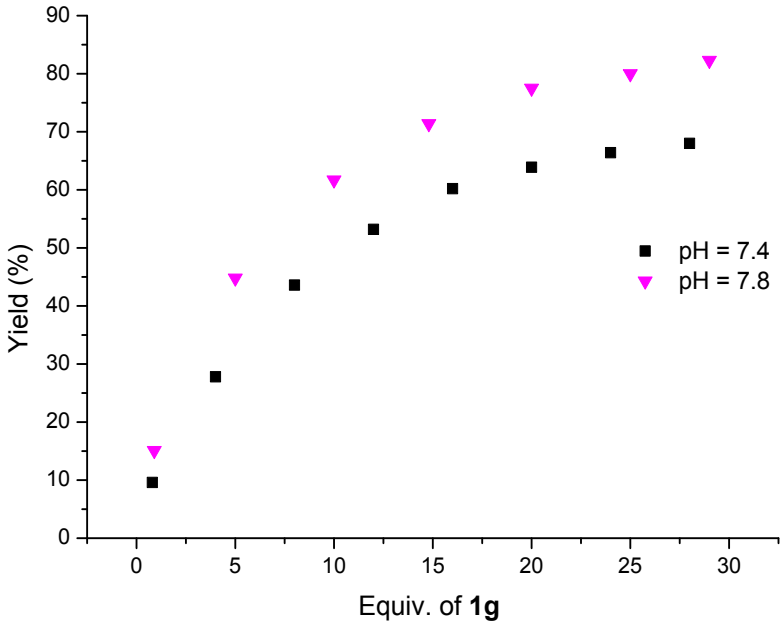


Figure S88. The yields of the reaction of varied concentration of **1g** and ethanolamine at different pH in KPi buffer solution in D_2O (50 mM).

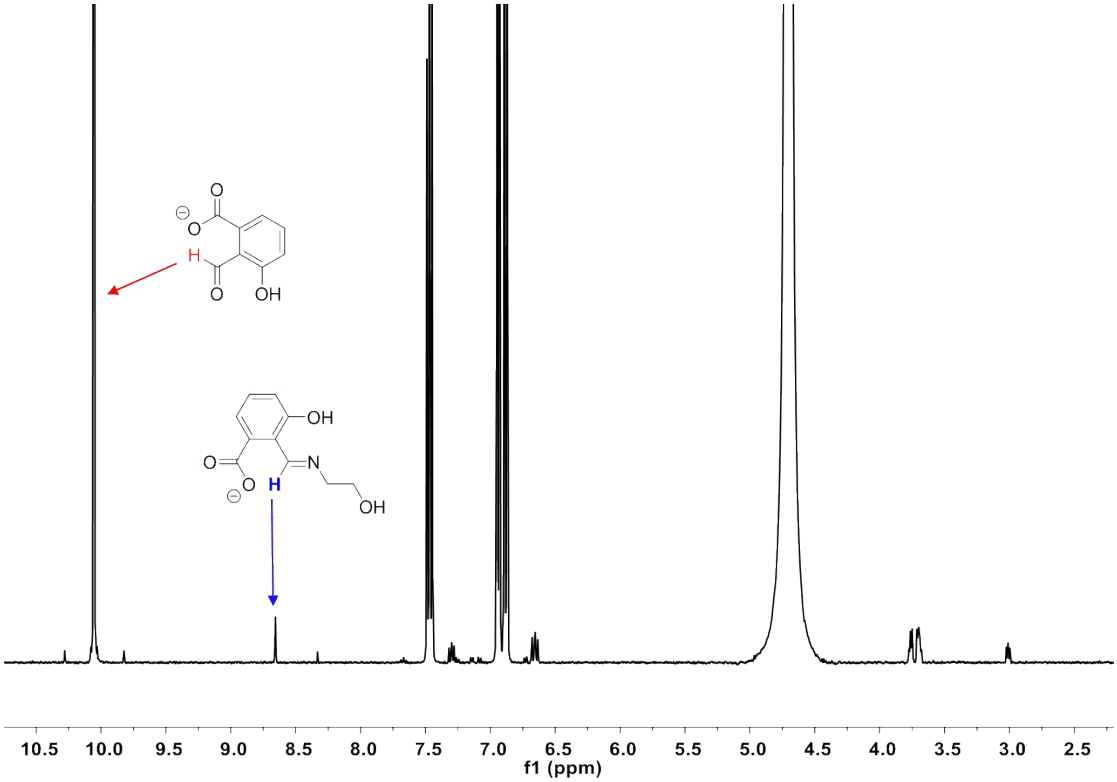


Figure S89. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and ethanolamine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4). The yield of imine is 63%.

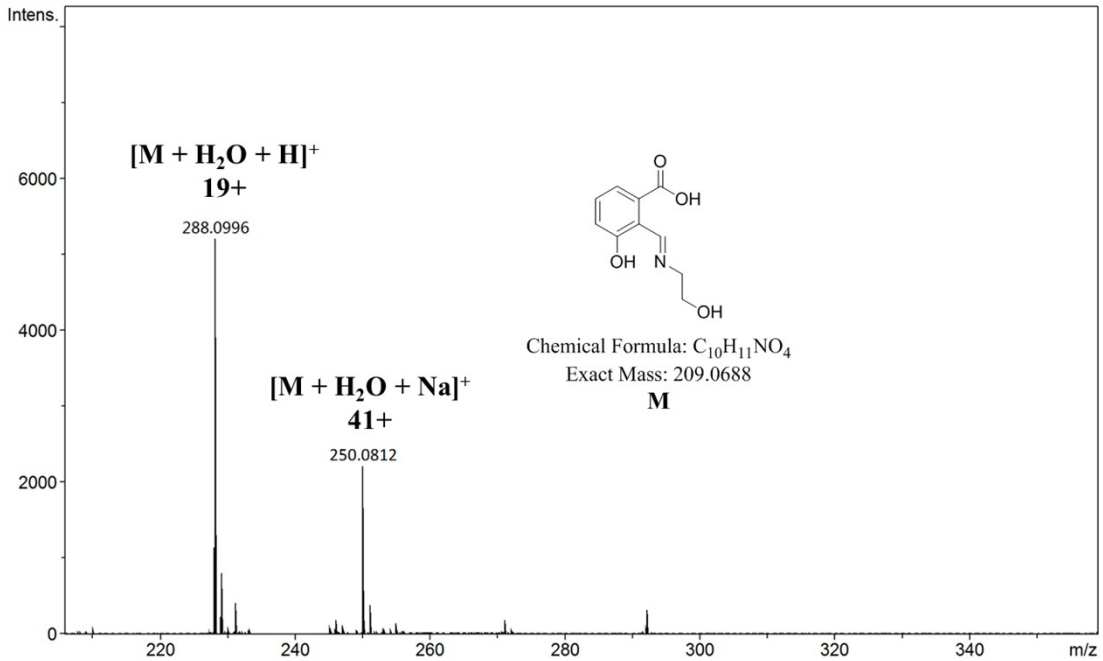


Figure S90. ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and ethanolamine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

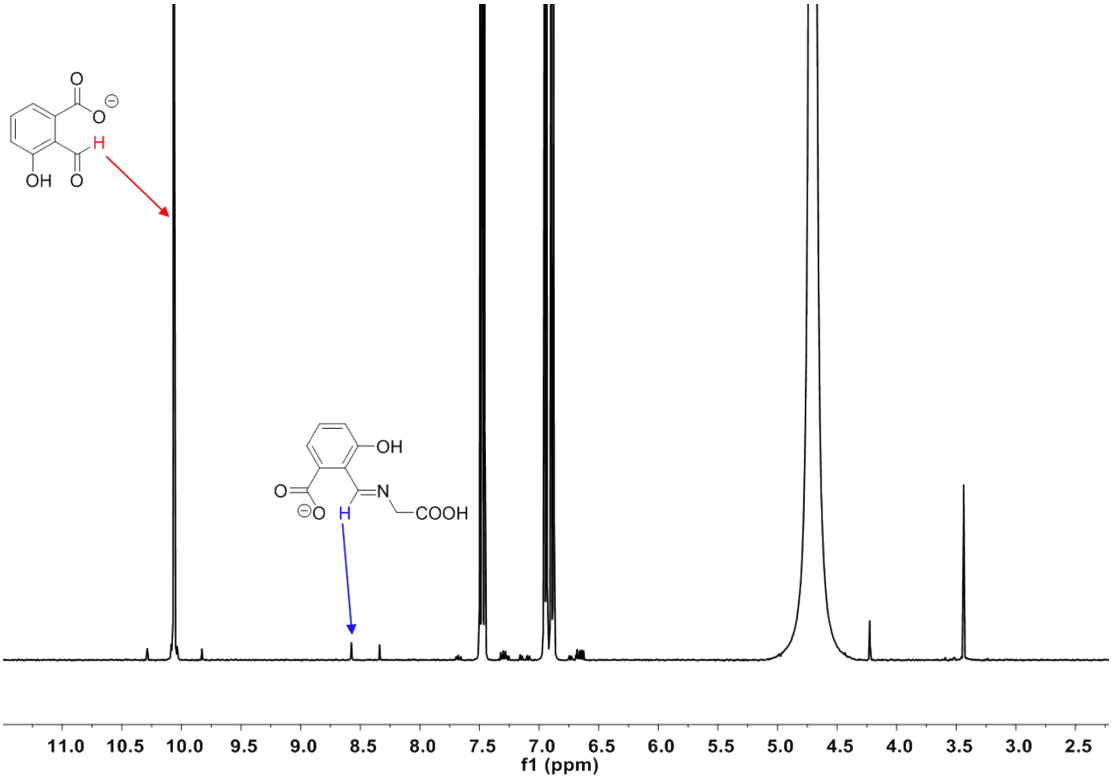


Figure S91. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and glycine(2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4). The yield of imine is 28%.

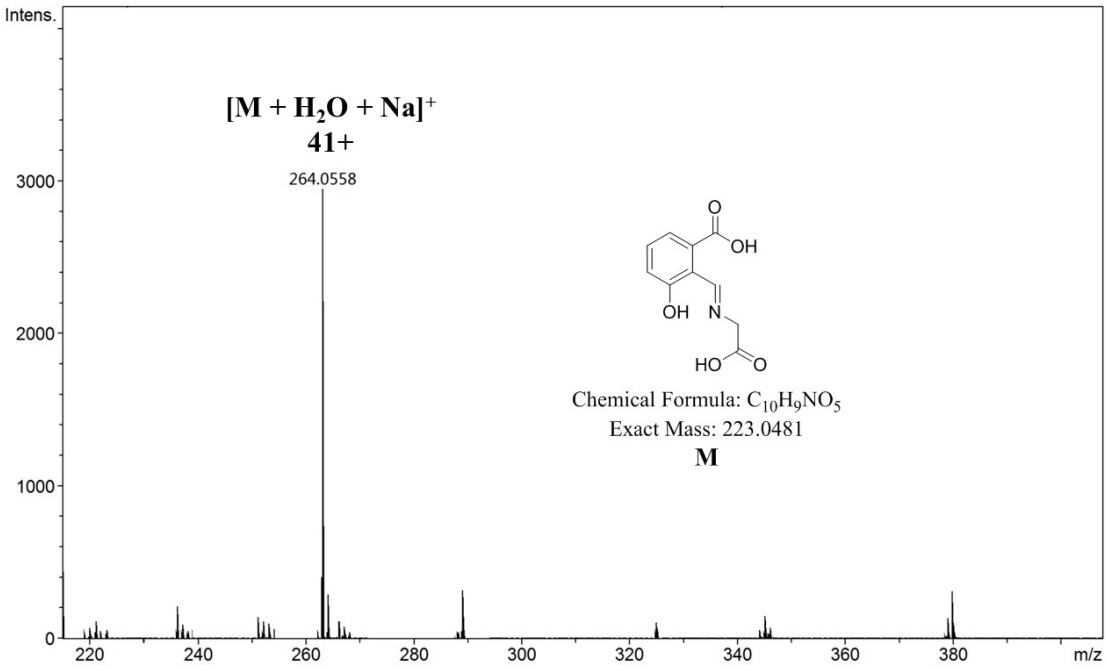


Figure S92. ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and glycine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

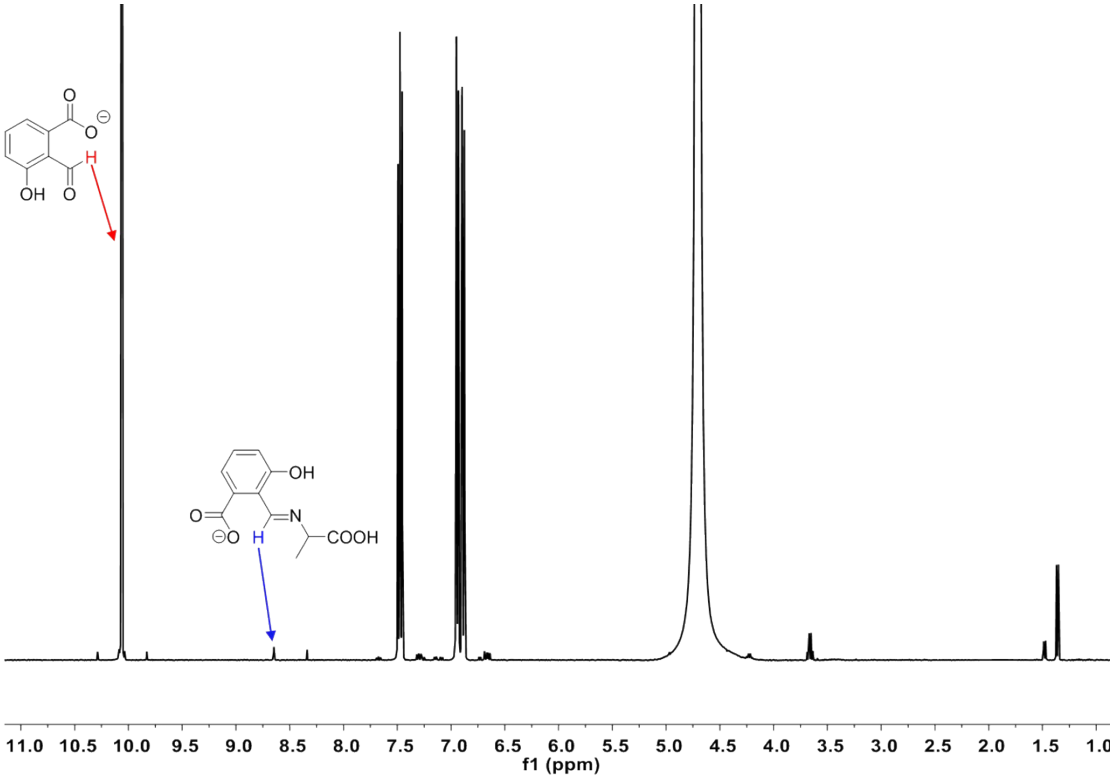


Figure S93. 1H NMR spectrum of the reaction between 1g (40 mM, 20.0 equiv.) and alanine(2 mM, 1.0 equiv.) in KPi buffer solution in D2O (50 mM, pH = 7.4). The yield of imine is 22%.

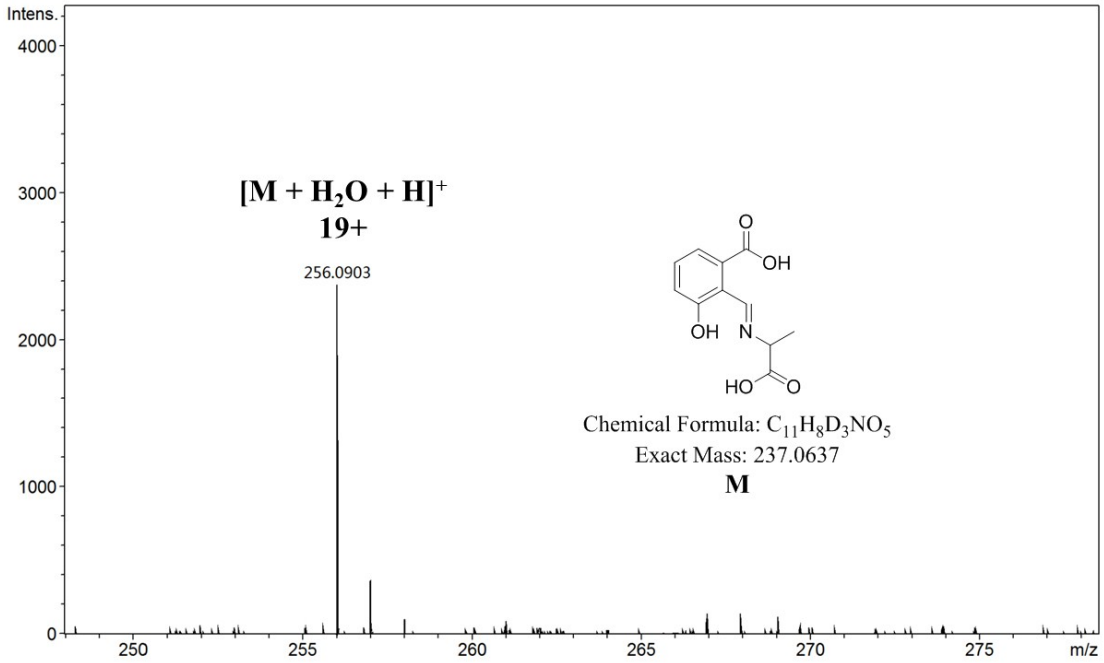


Figure S94. ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and alanine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

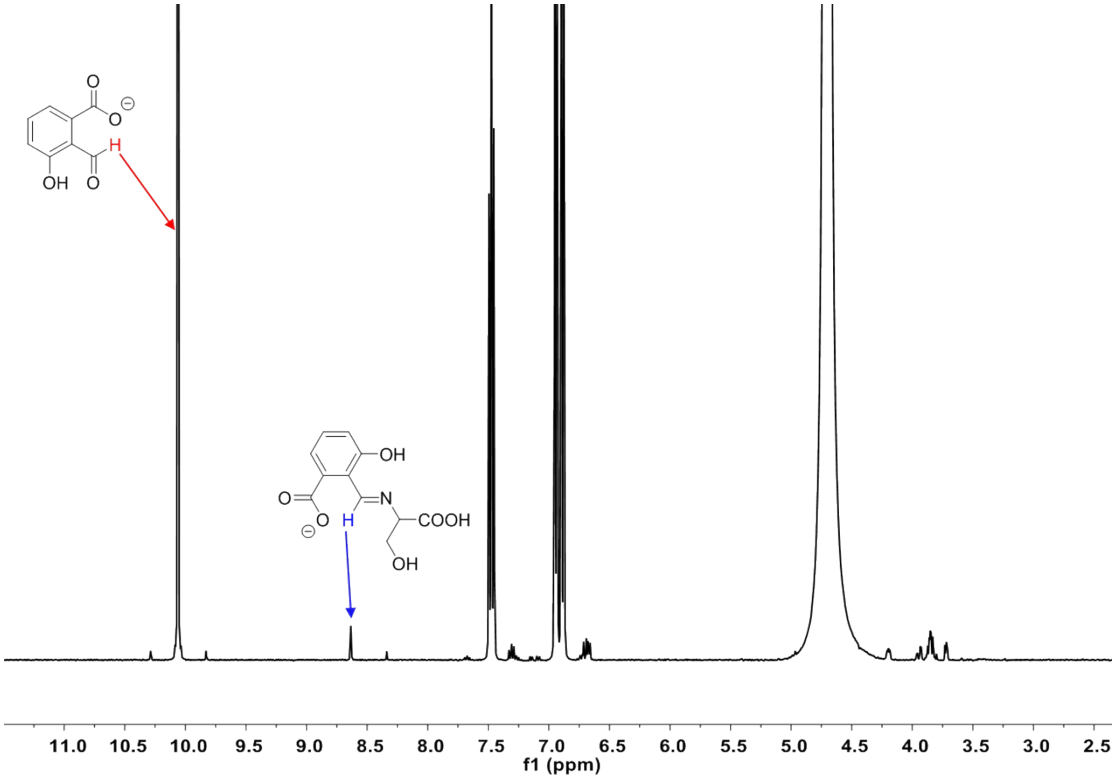


Figure S95. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and serine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4). The yield of imine is 65%.

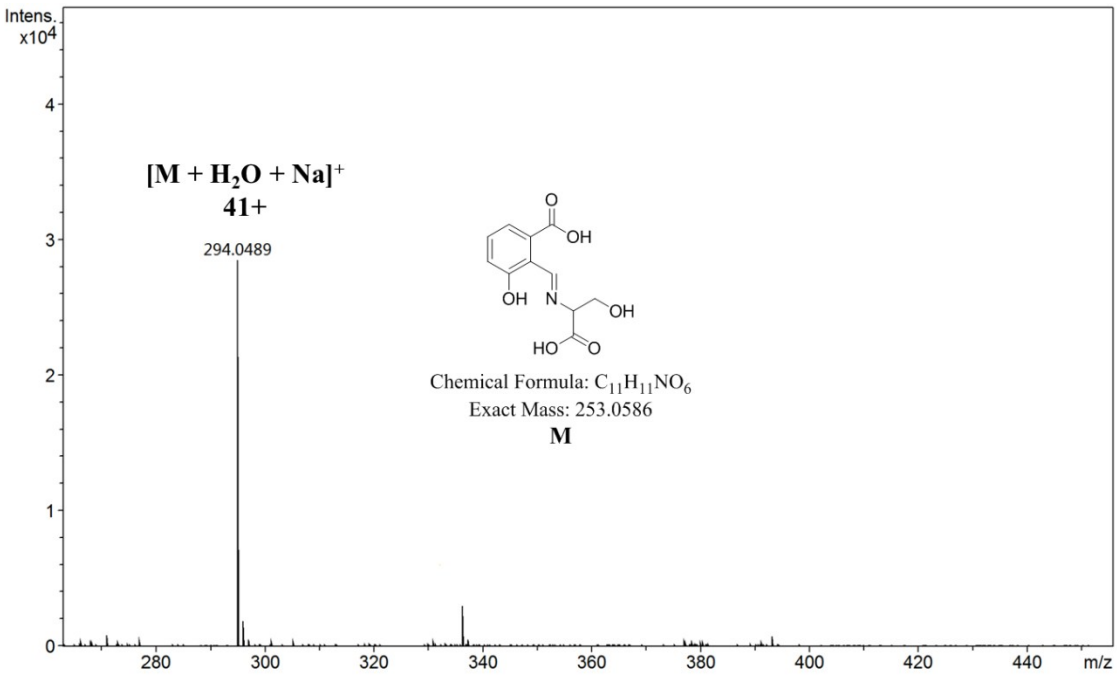


Figure S96. ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and serine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

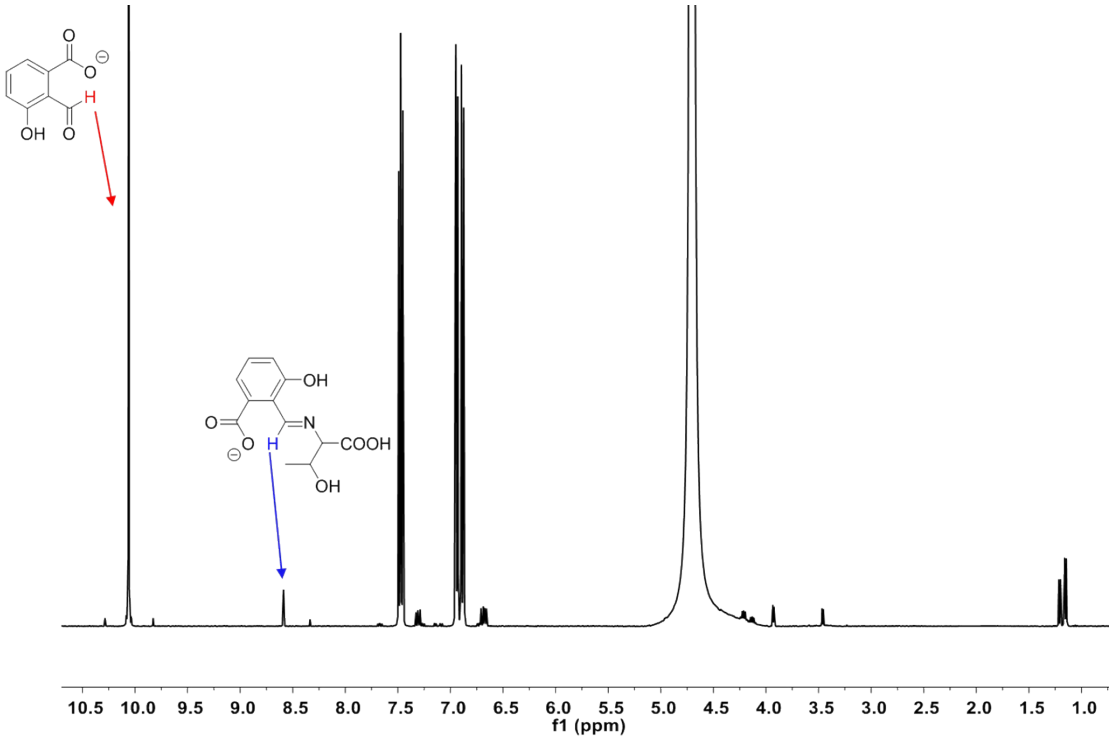


Figure S97. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and threonine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4). The yield of imine is 64%.

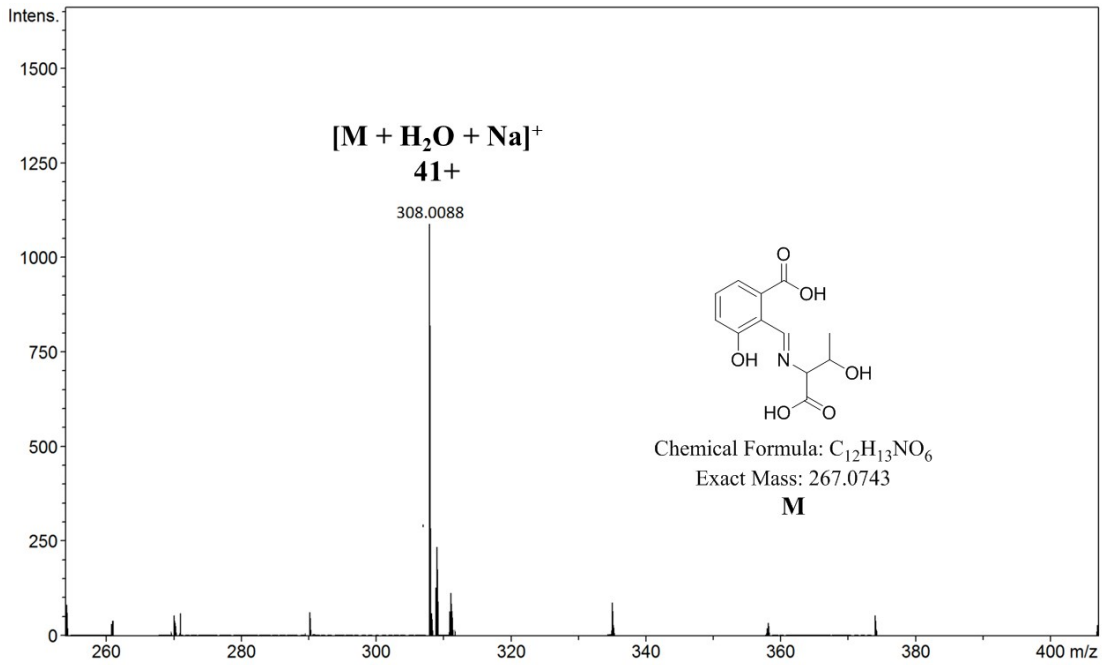


Figure S98. ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and threonine(2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

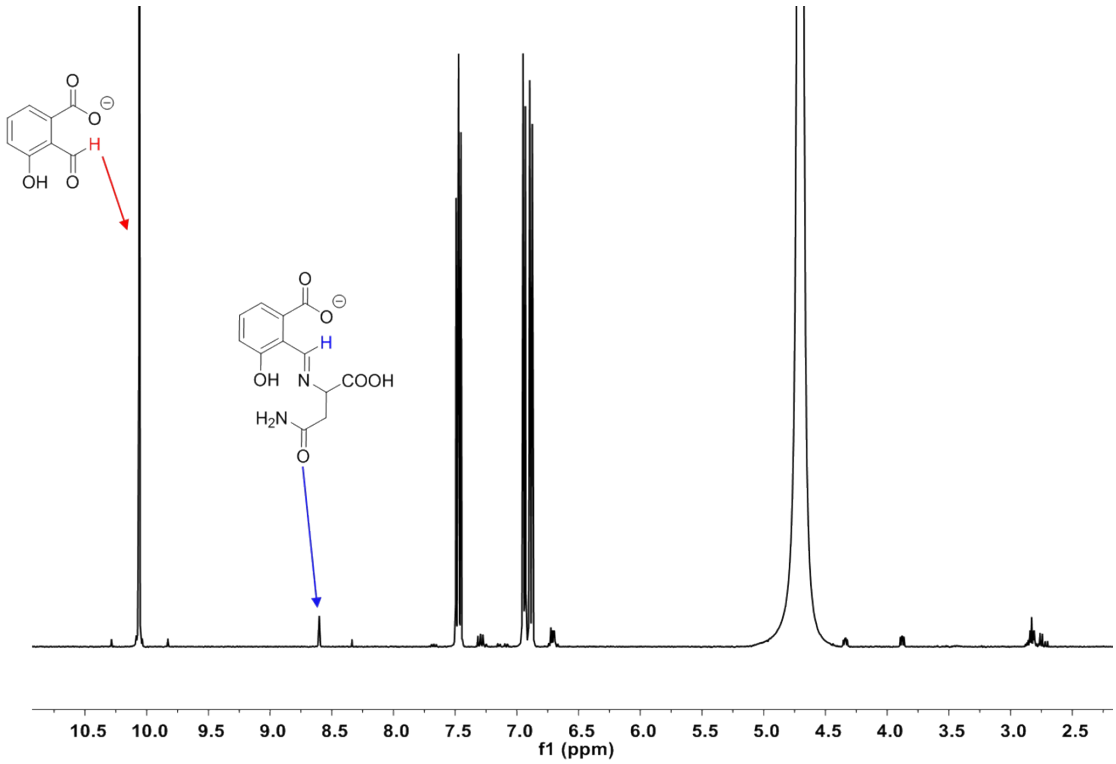


Figure S99. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and asparagine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4). The yield of imine is 54%.

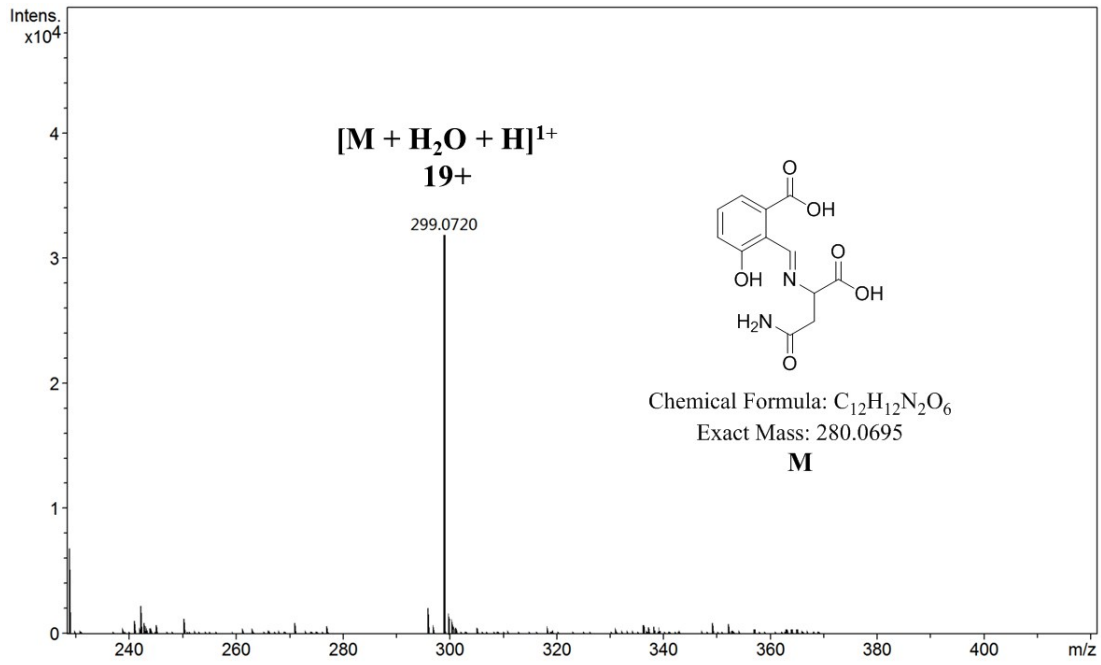


Figure S100. ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and asparagine(2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

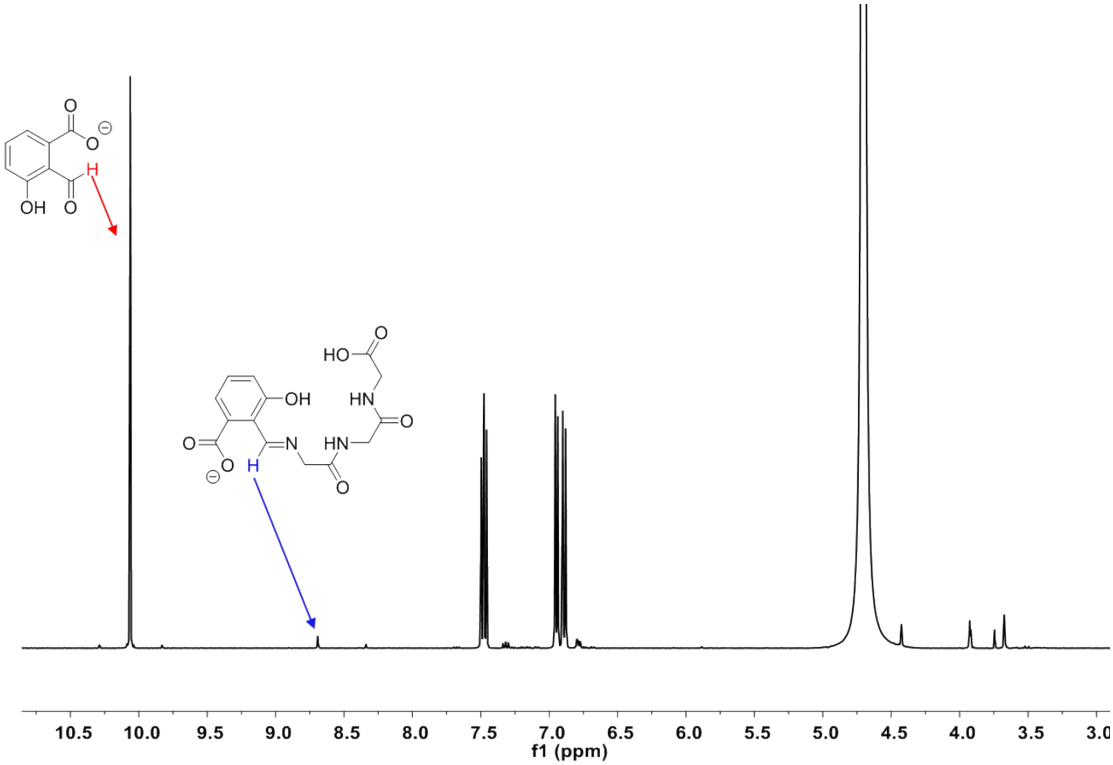


Figure S101. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and triglycine (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4). The yield of imine is 67%.

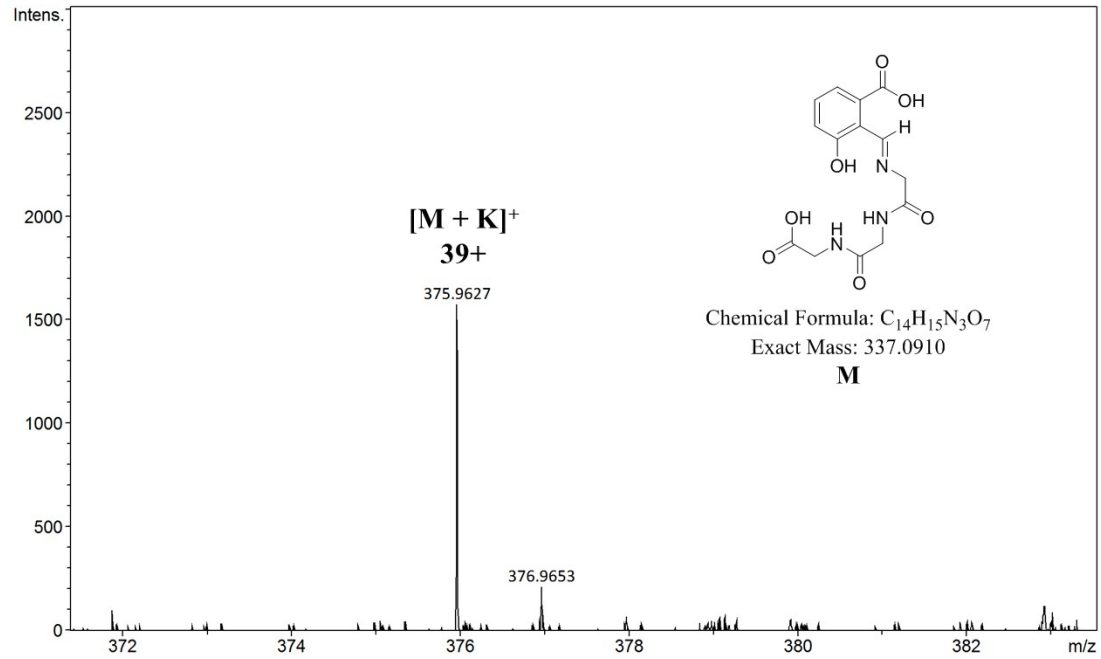


Figure S102. ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and triglycine(2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

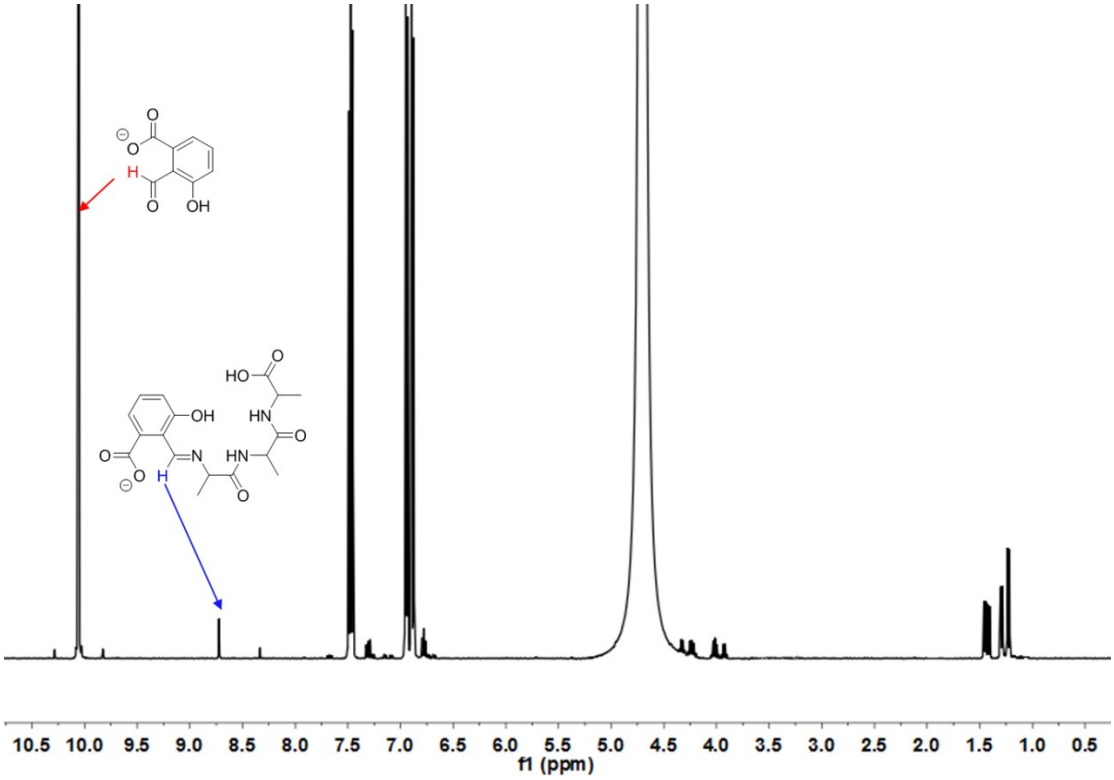


Figure S103. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and trialanine(2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4). The yield of imine is 57%.

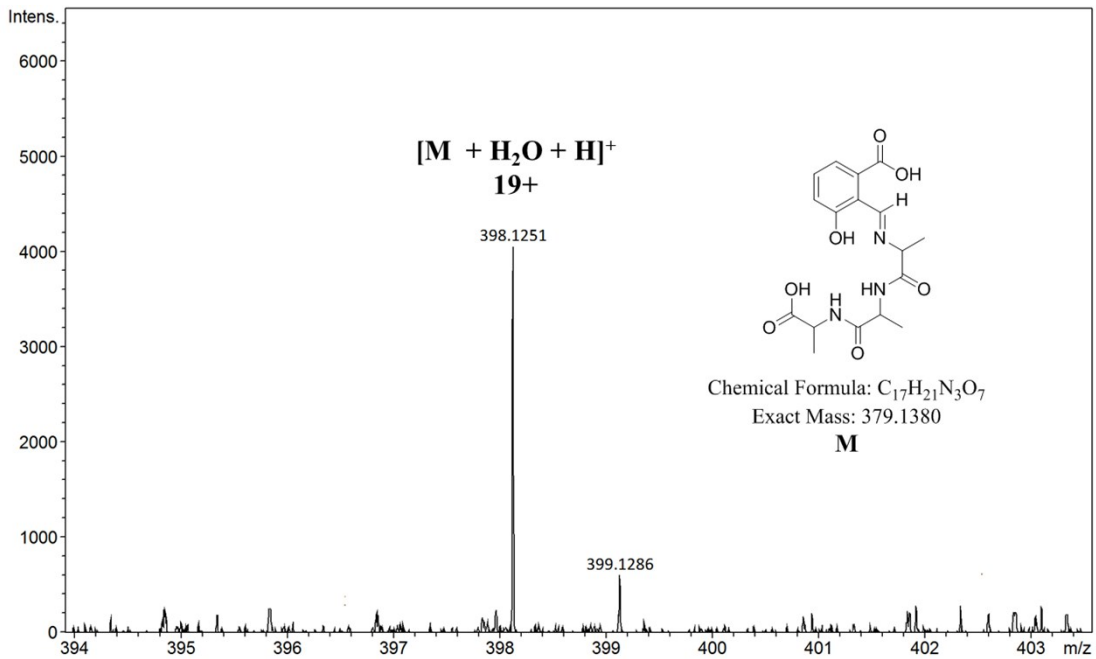


Figure S104. ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and trialanine(2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

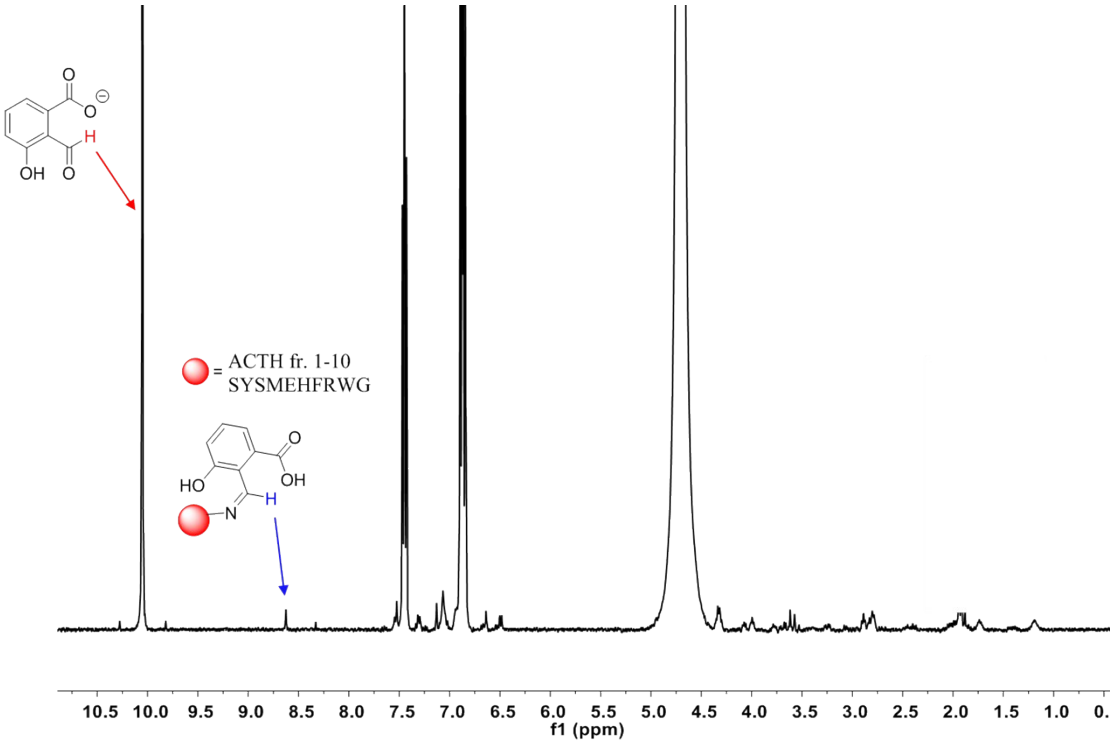


Figure S105. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and ACTH fr. 1-10 (SYSMEHFRWG) (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

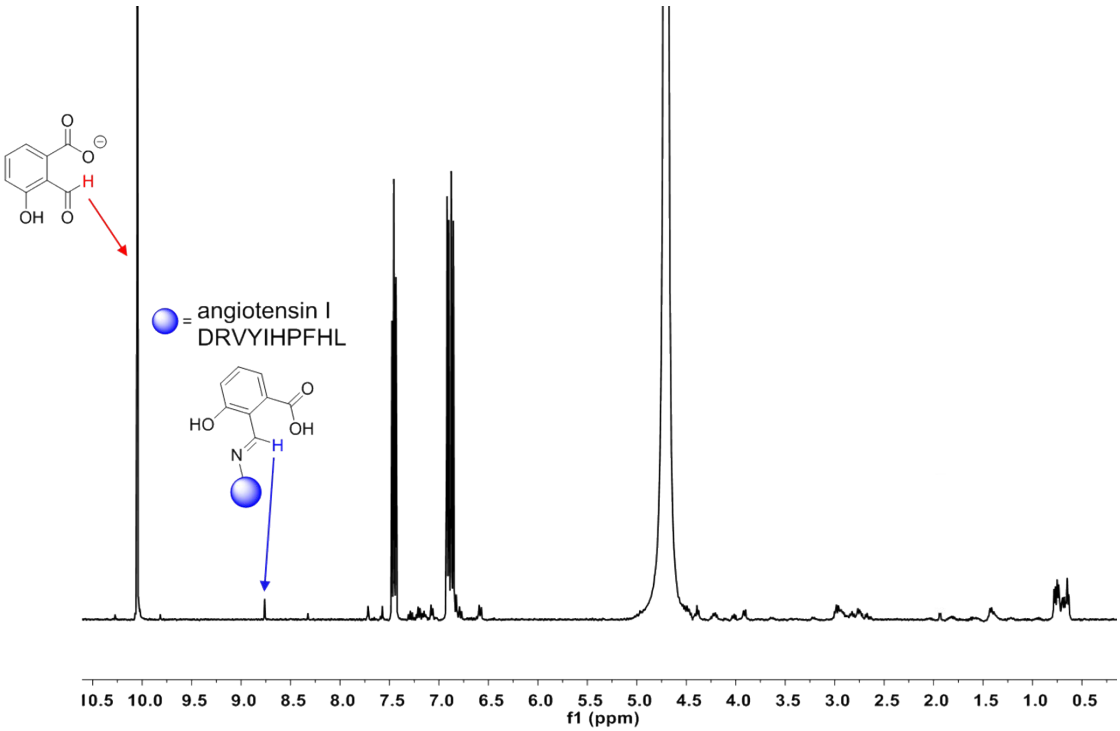


Figure S106. ^{1}H NMR spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and angiotensin I (DRVYIHPFHL) (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4).

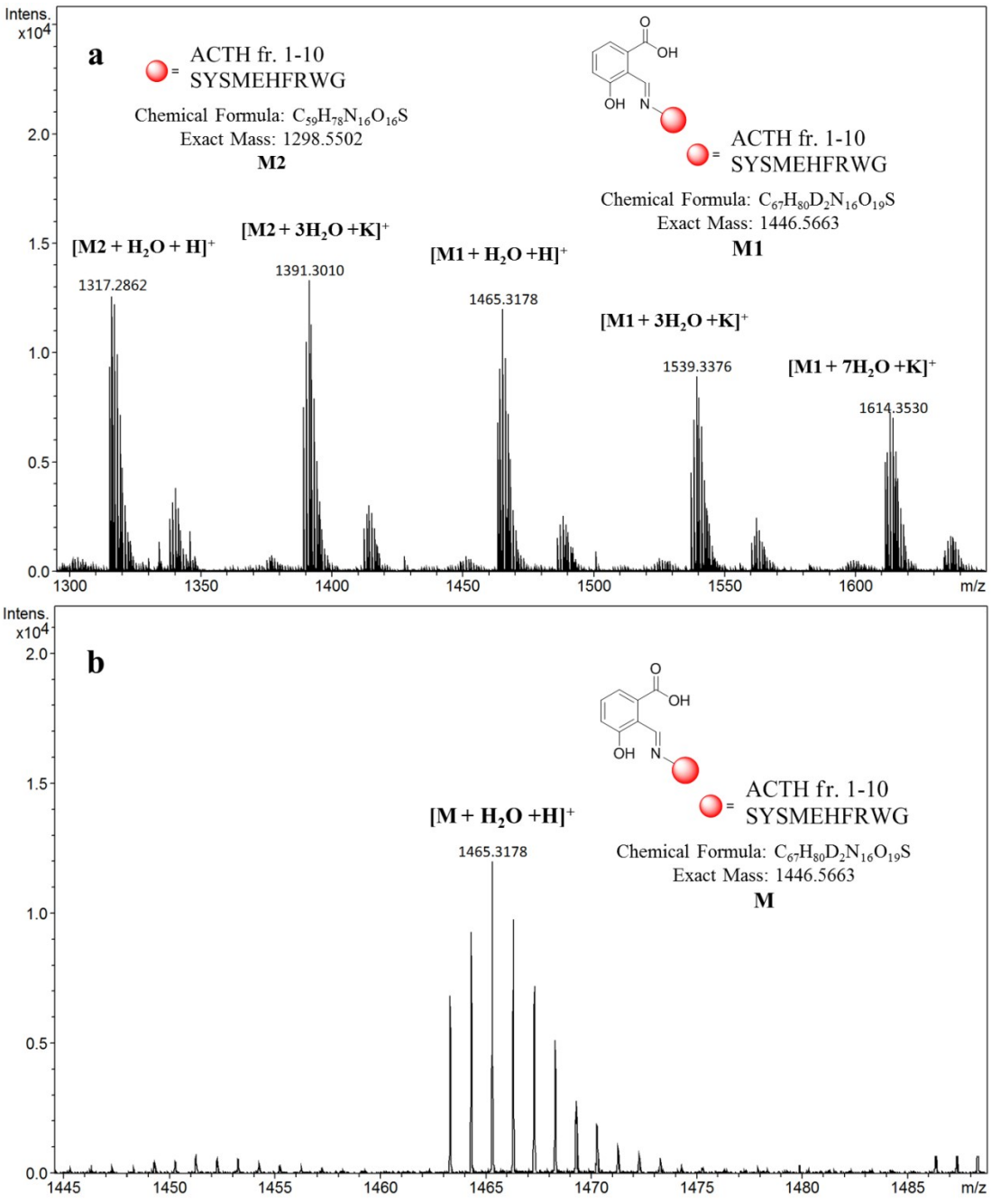


Figure S107. (a) ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and ACTH fr. 1-10 (SYSMEHFRWG) (2 mM, 1.0 equiv.) in KPi buffer solution in D2O(50 mM, pH = 7.4). (b) Partial enlargement of (a).

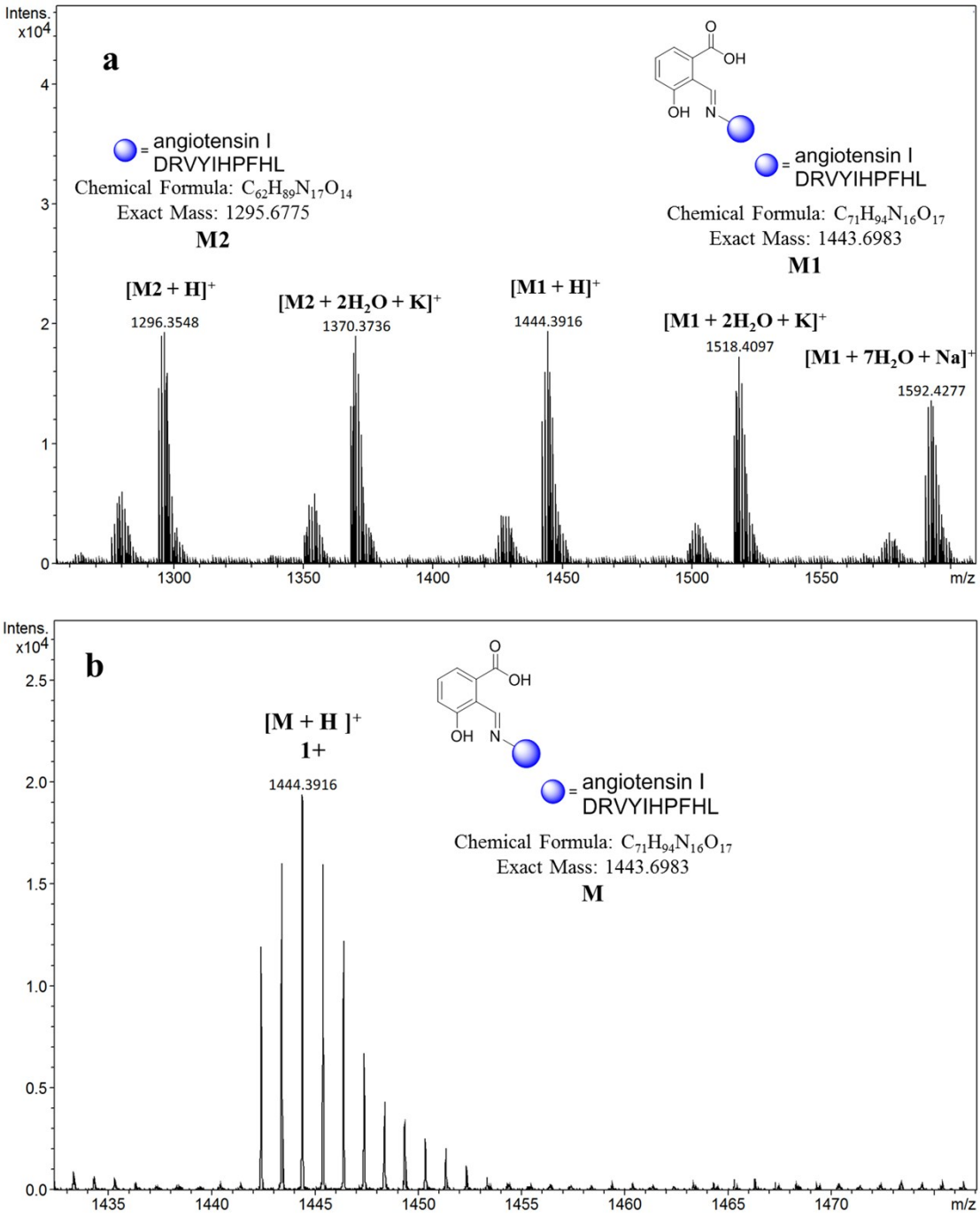


Figure S108. (a) ESI-MS spectrum of the reaction between **1g** (40 mM, 20.0 equiv.) and angiotensin I (DRVYIHPFHL) (2 mM, 1.0 equiv.) in KPi buffer solution in D_2O (50 mM, pH = 7.4). (b) Partial enlargement of (a).

7. Molecular Coordinates

1a$_{ocb}$-1 (acetonitrile)
Imaginary frequency: 0
G = -533.615244 hartree

C	0.49658700	0.60022400	0.09449700
C	1.88449600	0.47411400	0.05855500
C	2.47250700	-0.77571200	-0.04918600
C	1.66800300	-1.90806800	-0.11195200
C	0.28586400	-1.78463800	-0.06853500
C	-0.31715400	-0.53513600	0.02212200
H	3.55027900	-0.86942200	-0.07573900
H	2.11998500	-2.88836400	-0.19560600
H	-0.34819400	-2.65985400	-0.11947000
C	-0.07120800	1.96041500	0.28789400
O	0.50254500	2.96705700	-0.06250400
H	-1.03120000	2.01738700	0.81541300
C	-1.84243400	-0.43144600	-0.04039300
O	-2.29642100	0.60669500	-0.57176200
O	-2.48638500	-1.39453100	0.42001900
H	2.49124400	1.36795300	0.13136500

1a$_{ocb}$-2 (acetonitrile)
Imaginary frequency: 0
G = -533.610872 hartree

C	-0.40767400	0.85248900	0.01755200
C	-1.77254700	1.14612400	0.03489800
C	-2.71611500	0.13345300	0.01619200
C	-2.28556700	-1.18754700	-0.02024300
C	-0.92866500	-1.48546400	-0.03055400
C	0.03037500	-0.47813000	-0.00306700
H	-3.77211200	0.36714300	0.02734700
H	-3.01061100	-1.99164000	-0.03821100
H	-0.60584200	-2.51944100	-0.05599700
C	0.51649400	2.00219300	-0.01783100
O	1.70707000	1.94745000	-0.21002500
H	0.02359200	2.98123000	0.13018400
C	1.49897600	-0.89212000	0.05142400
O	2.00011600	-1.27677600	-1.02358800
O	2.02285300	-0.86654800	1.18251400
H	-2.08698300	2.18371700	0.05524200

2a$_{ocb}$-1 (acetonitrile)
Imaginary frequency: 0
G = -552.993645 hartree

C	0.16868600	-0.52194600	0.06462600
C	-0.02174100	-1.90529200	0.04925100
C	-1.29233400	-2.44782700	-0.04233700
C	-2.39750200	-1.60512600	-0.09740600
C	-2.21705700	-0.23090400	-0.05863400
C	-0.94285800	0.32809900	0.00687600
H	-1.42351200	-3.52223200	-0.05852600
H	-3.39546600	-2.01977300	-0.16407900
H	-3.06877000	0.43600700	-0.08945600
C	1.54212400	0.01293500	0.20602300
H	1.63253800	1.01899500	0.62144500
C	-0.81626800	1.85233900	-0.04182400

O	0.13588700	2.31037100	-0.71090200
O	-1.69259100	2.49979400	0.56847500
H	0.84771900	-2.54606500	0.11948900
N	2.56050700	-0.66140200	-0.12131600
C	3.85953500	-0.05893600	0.09924700
H	4.44988100	-0.70542000	0.75107200
H	4.39155300	0.00712700	-0.85145000
H	3.80062900	0.93980200	0.54520200

2a$_{ocb}$-2 (acetonitrile)
Imaginary frequency: 0
G = -552.988364 hartree

C	0.24540200	-0.80355900	0.08611100
C	1.22758100	-1.79608900	0.09449800
C	2.57294800	-1.47878300	-0.00728700
C	2.94802900	-0.14635500	-0.11680800
C	1.97808400	0.84740700	-0.11503700
C	0.62439200	0.54287900	-0.00000700
H	3.31964800	-2.26189400	-0.00264000
H	3.99437600	0.12036800	-0.19718600
H	2.27343900	1.88709600	-0.19369900
C	-1.15835900	-1.25666500	0.13797100
H	-1.30509000	-2.26367000	0.55287500
C	-0.34737900	1.71714900	0.09798000
O	-0.48288900	2.40866400	-0.93282600
O	-0.84902200	1.91724300	1.22321000
H	0.92273800	-2.83385500	0.17145800
N	-2.13381600	-0.58386500	-0.29495400
C	-3.45347800	-1.16928600	-0.18998000
H	-3.44689500	-2.17030900	0.25572800
H	-4.08623100	-0.51562400	0.41310400
H	-3.90330100	-1.22250400	-1.18267700

1$_{ocb}$-minimum (acetonitrile)

C	-0.45873700	0.62923400	-0.12470800
C	-1.86155900	0.64812200	-0.13432800
C	-2.56610900	-0.50621700	-0.00721100
C	-1.90052800	-1.73300800	0.13542900
C	-0.50129200	-1.77295200	0.14741900
C	0.22397900	-0.58466300	0.01656000
H	-3.63574600	-0.47973000	-0.01591900
H	-2.46244900	-2.63811600	0.23505000
H	0.00987700	-2.70666200	0.25600300
C	0.33003500	1.94394200	-0.26956200
O	-0.16117100	3.02233000	0.15395400
H	1.29574300	1.94046900	-0.73031700
C	1.76371000	-0.61117900	0.02777800
O	2.40683400	0.37702500	0.46756800
O	2.37876500	-1.62105100	-0.40284300
H	-2.37984400	1.57794900	-0.24251100

2$_{ocb}$-minimum (acetonitrile)

C	-0.45873700	0.62923400	-0.12470800
C	-1.86155900	0.64812200	-0.13432800
C	-2.56610900	-0.50621700	-0.00721100
C	-1.90052800	-1.73300800	0.13542900
C	-0.50129200	-1.77295200	0.14741900
C	0.22397900	-0.58466300	0.01656000

H	-3.63574600	-0.47973000	-0.01591900
H	-2.46244900	-2.63811600	0.23505000
H	0.00987700	-2.70666200	0.25600300
C	0.33003500	1.94394200	-0.26956200
O	-0.16117100	3.02233000	0.15395400
H	1.29574300	1.94046900	-0.73031700
C	1.76371000	-0.61117900	0.02777800
O	2.40683400	0.37702500	0.46756800
O	2.37876500	-1.62105100	-0.40284300
H	-2.37984400	1.57794900	-0.24251100

1b$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -648.116209 hartree

C	-1.05587900	-0.74912500	-0.05332600
C	-0.27861500	-1.91430000	-0.04640500
C	1.09374200	-1.85308300	-0.00028800
C	1.72578100	-0.60369000	0.02499000
C	0.96682500	0.56184200	0.00107100
C	-0.42330200	0.49699400	-0.02330100
H	1.70305600	-2.74711200	0.00506600
H	1.42896600	1.53778000	0.00523400
C	-2.52044700	-0.88300300	-0.16753400
O	-3.10684400	-1.93864700	-0.04220400
H	-3.07291100	0.03664200	-0.39773500
C	-1.19206500	1.82334100	0.03059600
O	-2.20360400	1.84750000	0.76298400
O	-0.71394200	2.75840200	-0.64189000
H	-0.78193600	-2.87178500	-0.09125300
O	3.07453800	-0.62659500	0.06877900
C	3.76165000	0.61396000	0.07715600
H	3.49402300	1.20165100	0.95731900
H	4.81984700	0.37224300	0.10737000
H	3.54163000	1.18768500	-0.82510400

1c$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -3107.226605 hartree

C	-1.54652700	-0.79764500	-0.10366000
C	-0.62738600	-1.84483300	-0.09808500
C	0.73335500	-1.59508600	-0.04754500
C	1.15953900	-0.27522800	-0.01312400
C	0.26438500	0.78066400	-0.02423000
C	-1.10147400	0.52653100	-0.05689800
H	1.44825400	-2.40574400	-0.04453100
H	0.60657200	1.80562700	0.00389000
C	-2.98776400	-1.14205700	-0.23564900
O	-3.44043700	-2.20271700	0.12973800
H	-3.62381900	-0.39774000	-0.72895100
C	-2.07072800	1.71100400	0.03897700
O	-3.16036200	1.47211100	0.60195300
O	-1.66915900	2.79312300	-0.42829400
H	-0.99150200	-2.86300600	-0.14866100
Br	3.02227900	0.09087500	0.04949600

1d$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -738.136495 hartree

C	-1.13020100	-0.81482800	-0.13228300
C	-0.18945300	-1.84254200	-0.12008700
C	1.16230100	-1.55465200	-0.05627200
C	1.53818000	-0.22264800	-0.00885300
C	0.62558400	0.81557600	-0.01727300
C	-0.72840600	0.52076500	-0.07007700
H	1.90868900	-2.33441800	-0.04745700
H	0.94714200	1.84531200	0.02679400
C	-2.56849700	-1.19975400	-0.27243100
O	-3.03025600	-2.16409400	0.28803700
H	-3.16760600	-0.60345700	-0.97041600
C	-1.75258200	1.65597500	0.02229100
O	-2.89173600	1.31176200	0.40553100
O	-1.34875900	2.79536400	-0.26933000
H	-0.52568900	-2.86959200	-0.17192300
N	2.97367100	0.09967700	0.05678400
O	3.29233700	1.26600400	0.12896500
O	3.76343900	-0.81940200	0.03372400

1e$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -3107.225763 hartree

C	1.00289200	0.69850200	-0.11765900
C	-0.38046700	0.86136900	-0.10116800
C	-1.18995800	-0.25447600	-0.00368800
C	-0.65014800	-1.53030300	0.06861400
C	0.72896400	-1.67722400	0.04681300
C	1.57136900	-0.57446300	-0.03382200
H	-1.29710100	-2.39370000	0.14255100
H	1.17138900	-2.66248300	0.10740200
C	1.82911100	1.92633800	-0.29765600
O	1.47434500	3.01128400	0.10003400
H	2.76125600	1.80712300	-0.86208100
C	3.08651800	-0.77211600	0.05391700
O	3.72908500	0.18844300	0.53258300
O	3.52894100	-1.86953600	-0.33516800
H	-0.80218200	1.85463300	-0.17721100
Br	-3.07662900	-0.03751100	0.02050400

1f$_{ocb}$-1 (acetonitrile)
Imaginary frequency: 0
G = -549.667979 hartree

C	0.43014100	0.64473900	0.13313200
C	2.51057000	-0.27918400	-0.00972700
C	1.98852400	-1.56254700	-0.10663300
C	0.61298900	-1.71655200	-0.08408100
C	-0.19701400	-0.59528800	0.02957600
H	3.58289300	-0.11944600	-0.02642800
H	2.65026300	-2.41248900	-0.20167500
H	0.14720100	-2.69018200	-0.16333700
C	-0.35712700	1.91173400	0.33183200
O	-0.11909300	2.92057000	-0.28373900
H	-1.11615600	1.89162300	1.12427800
C	-1.71752100	-0.70940500	-0.02456000
O	-2.32357100	0.35724300	-0.27503200
O	-2.20324000	-1.83871500	0.16792600
N	1.75423800	0.80810300	0.11095500

1f$_{ocb}$-2 (acetonitrile)
Imaginary frequency: 0
G = -549.66637 hartree

C	-0.43966300	0.83075000	-0.00378100
C	-2.63565400	0.19285900	-0.00411300
C	-2.28202000	-1.15398700	0.00158800
C	-0.94133200	-1.48903900	0.00284200
C	0.02379100	-0.48431300	-0.00244200
H	-3.67805500	0.48995100	-0.00636400
H	-3.04945500	-1.91614400	0.00471200
H	-0.63435100	-2.52811000	0.00759500
C	0.46720700	2.00879400	0.00627900
O	1.66954500	1.96089100	0.05527600
H	-0.07276700	2.97123400	-0.03052800
C	1.49715000	-0.88546800	-0.01327500
O	2.01548700	-0.99945000	-1.13960600
O	1.99700900	-1.12200100	1.10270100
N	-1.73693900	1.16428000	-0.00642400

1g$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -608.853877 hartree

C	0.40464700	-0.33681400	-0.02614000
C	1.64344800	0.33617400	0.01613400
C	1.68241000	1.72744400	0.07960600
C	0.49872100	2.43900700	0.09105600
C	-0.73336300	1.78844000	0.03972500
C	-0.79174400	0.40738400	-0.00171700
H	2.64426600	2.22114600	0.11567900
H	0.53175700	3.52022900	0.14357500
H	-1.65497200	2.35353600	0.04506300
C	0.38561700	-1.79001400	-0.17779500
O	1.39419700	-2.48618800	-0.16042000
H	-0.59332000	-2.25415000	-0.33104300
C	-2.17081200	-0.26315800	0.04041900
O	-2.28458900	-1.23956000	0.81206300
O	-3.05146000	0.25145100	-0.67511900
O	2.81123400	-0.32637300	-0.01331100
H	2.60367200	-1.28617000	-0.04670400

2b$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -667.493393 hartree

C	-0.77687300	-0.45400800	-0.04880800
C	-0.22919000	-1.74328400	-0.05373600
C	1.13152100	-1.94659400	-0.00944100
C	1.99330100	-0.84599300	0.02042100
C	1.46885800	0.43941300	0.00078800
C	0.08865800	0.64235600	-0.01883500
H	1.55435500	-2.94286700	-0.01074700
H	2.10725300	1.31055300	0.00350600
C	-2.24073600	-0.28695300	-0.13778700
H	-2.59858300	0.70840700	-0.41067000
C	-0.40089900	2.09368800	0.03158300
O	-1.37083000	2.33120800	0.78273200
O	0.23696400	2.91169500	-0.66375300
H	-0.90264900	-2.58918600	-0.10242500
O	3.31841400	-1.12856300	0.06068200

C	4.22430100	-0.04005800	0.07200700
H	4.07253500	0.58669600	0.95334800
H	5.21958500	-0.47404300	0.10095200
H	4.11651100	0.56867600	-0.82820600
N	-3.04591000	-1.23997200	0.07781900
C	-4.45964500	-0.96704300	-0.07955200
H	-4.87502600	-1.63662000	-0.83518200
H	-4.97642400	-1.18435400	0.85705400
H	-4.66834900	0.06866900	-0.36948800

2c$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -3126.605846 hartree

C	1.30031600	-0.42518600	0.08711800
C	0.55182800	-1.60321300	0.10546100
C	-0.83060700	-1.57956300	0.05506800
C	-1.46752000	-0.34798600	0.00865500
C	-0.75298000	0.83498700	0.01369200
C	0.63903100	0.80739200	0.03720400
H	-1.40270800	-2.49683700	0.06535100
H	-1.25672200	1.79129300	-0.00650400
C	2.77515400	-0.51399100	0.18706400
H	3.29164400	0.36543300	0.57605200
C	1.37581500	2.15041600	-0.03776000
O	2.43333300	2.16501800	-0.70173400
H	1.07445900	-2.54848000	0.16961400
Br	-3.36762400	-0.28921400	-0.05006400
O	0.83192600	3.10602000	0.55125400
N	3.40071600	-1.56117800	-0.14477100
C	4.83832300	-1.56584600	0.03435700
H	5.11398200	-2.38837300	0.69677300
H	5.31977800	-1.75432900	-0.92664200
H	5.22315900	-0.62834800	0.44968500

2d$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -757.517283 hartree

C	0.91854200	-0.42996700	0.09569100
C	0.20922100	-1.63405200	0.10499300
C	-1.16984100	-1.65074000	0.04344200
C	-1.83011200	-0.43277000	-0.00375200
C	-1.16103000	0.77539800	0.00881700
C	0.22763800	0.78709000	0.04201300
H	-1.72661100	-2.57562100	0.04388800
H	-1.70259100	1.70916500	-0.01170200
C	2.39657300	-0.47827200	0.20693100
H	2.88458800	0.39831000	0.63562900
C	0.93212700	2.14807200	-0.03079800
O	2.00849500	2.17570800	-0.66171900
O	0.34305200	3.09567900	0.52432900
H	0.76267100	-2.56076300	0.16862900
N	-3.29806600	-0.42835200	-0.05899400
O	-3.86522200	0.64120300	-0.12284300
O	-3.87201500	-1.49686600	-0.03780100
N	3.04654700	-1.49613600	-0.16311900
C	4.48341900	-1.47550000	0.02055800
H	4.77518100	-2.32617500	0.63857900
H	4.96900200	-1.60259300	-0.94826300

H	4.84469700	-0.55226200	0.48492400

2e$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -3126.605268 hartree

C	0.90809300	0.25382200	-0.08335100
C	-0.42858600	0.65647000	-0.08244700
C	-1.42951200	-0.29020300	0.00500500
C	-1.13930300	-1.64484200	0.07124200
C	0.18958500	-2.03610300	0.04803700
C	1.22531500	-1.10768800	-0.01428700
H	-1.93361100	-2.37588400	0.13416300
H	0.44486200	-3.08650900	0.08729800
C	1.95197200	1.29789100	-0.22086400
H	2.89961000	0.98370100	-0.66128700
C	2.66541300	-1.62687000	0.04841200
O	3.49703200	-0.89356800	0.62483600
O	2.86654800	-2.74904700	-0.45918000
H	-0.66144000	1.70957800	-0.15894600
N	1.74413100	2.49122200	0.13888700
C	2.80939100	3.44940100	-0.07744900
H	2.43791200	4.26221500	-0.70382700
H	3.09627000	3.88862100	0.87939900
H	3.69444500	3.00941700	-0.54891300
Br	-3.24599500	0.27428400	0.01453900

2f$_{ocb}$-1 (acetonitrile)
Imaginary frequency: 0
G = -569.047756 hartree

C	0.14458800	-0.55324800	0.09088700
C	-1.21278700	-2.39408100	-0.03144700
C	-2.36000500	-1.61574100	-0.11152000
C	-2.21524500	-0.24065400	-0.07654600
C	-0.94629500	0.31947200	0.00796300
H	-1.28170900	-3.47658400	-0.04757000
H	-3.33261400	-2.08161000	-0.19227100
H	-3.07248600	0.41834600	-0.12228800
C	1.52885300	-0.03040700	0.25822100
H	1.62257800	0.92230800	0.78330500
C	-0.80277700	1.84190800	-0.04082900
O	0.21836700	2.28524100	-0.60759200
O	-1.73667100	2.49415400	0.46793400
N	0.00738900	-1.88370100	0.08159500
N	2.53475100	-0.65445300	-0.17805400
C	3.83715400	-0.06877300	0.07028000
H	4.45363100	-0.78697500	0.61348800
H	4.33214100	0.11992800	-0.88380700
H	3.78899200	0.86565400	0.63957300

2f$_{ocb}$-2 (acetonitrile)
Imaginary frequency: 0
G = -569.045712 hartree

C	-0.26328300	-0.80225300	0.09290800
C	-2.44018600	-1.52221700	0.00391600
C	-2.91501300	-0.22478200	-0.12629700
C	-1.99682600	0.81151400	-0.12746800
C	-0.63914800	0.54171400	0.00281000
H	-3.12516000	-2.36255500	0.02416700

H	-3.97630700	-0.03677000	-0.21540300
H	-2.32717300	1.83938800	-0.21945900
C	1.14522600	-1.25775600	0.15041600
H	1.27778600	-2.26099800	0.57375900
C	0.32234200	1.72440600	0.10102100
O	0.83091600	1.91768200	1.22269100
O	0.43789100	2.42004600	-0.92788600
N	-1.14776700	-1.80704200	0.10829900
N	2.10915900	-0.58190700	-0.29827000
C	3.43511600	-1.15510100	-0.20240300
H	3.44192100	-2.15104300	0.25320500
H	3.87234700	-1.21272100	-1.20022900
H	4.06701800	-0.48762700	0.38590900

2g$_{ocb}$ (acetonitrile)
Imaginary frequency: 0
G = -628.236484 hartree

C	0.16128400	0.24027200	0.00627100
C	0.40535600	1.63066000	0.02718100
C	-0.65915900	2.52958900	0.05180300
C	-1.95782900	2.05501100	0.04050900
C	-2.21347500	0.68794100	0.00369900
C	-1.16644500	-0.22183200	0.00405700
H	-0.44185500	3.58944500	0.07544100
H	-2.78184300	2.75759400	0.06082300
H	-3.22914200	0.31719800	-0.01553600
C	1.28642500	-0.69481500	-0.07385600
H	1.04148200	-1.75343500	-0.16396200
C	-1.51655400	-1.71285200	0.04395800
O	-0.89722200	-2.41056700	0.87660000
O	-2.41346100	-2.08632600	-0.73876000
O	1.65482900	2.12383900	0.01927500
H	2.27614100	1.33615000	0.00762700
N	2.49660100	-0.29921800	-0.04875400
C	3.55517000	-1.28043100	-0.15779800
H	4.17581300	-1.04767100	-1.02399300
H	4.19306100	-1.22307700	0.72511300
H	3.16832300	-2.29850800	-0.25609500

1f$_{ocb}$ (water)
Imaginary frequency: 0
G = -626.095475 hartree

C	0.25519300	-0.09699200	-0.10789000
C	1.01120900	2.05683100	0.04999600
C	-0.28318600	2.55547600	0.11323500
C	-1.33722600	1.65980800	0.06800300
C	-1.07711000	0.29940000	-0.03221400
H	1.86506300	2.72326400	0.08680900
H	-0.45012000	3.61997000	0.20103900
H	-2.36616300	1.99077600	0.12083300
C	0.64423100	-1.53567000	-0.30332100
O	1.60073400	-2.02089900	0.24916000
H	0.05046600	-2.10659700	-1.02614400
C	-2.20855700	-0.72499400	0.01822000
O	-1.86664700	-1.88039800	0.35647600
O	-3.34866800	-0.31171200	-0.25863300
H	3.83990500	-1.17722900	0.16208600
O	3.98925300	-0.25773800	-0.07911900

H	3.08558000	0.11474700	-0.08394700
N	1.27865300	0.75969800	-0.06284500

2f$_{ocb}$ (water)
Imaginary frequency: 0
G = -645.477049 hartree

C	-0.02551700	0.19151700	0.07811000
C	0.03138800	2.48535700	-0.05230000
C	1.41736800	2.50372200	-0.11321200
C	2.08523600	1.29356200	-0.06763200
C	1.36820500	0.10524100	0.01034900
H	-0.53755700	3.40808600	-0.07943300
H	1.94848100	3.44230500	-0.18928000
H	3.16569100	1.24510900	-0.10063400
C	-0.86689100	-1.02524700	0.24440800
H	-0.40157700	-1.86443000	0.76319400
C	2.12710400	-1.22385600	-0.03172000
O	1.54086700	-2.17953000	-0.58195800
O	3.27137900	-1.21231200	0.46329600
H	-2.55904000	1.51545600	0.10417000
H	-3.73044400	0.64348700	-0.22969000
O	-3.53696200	1.54295700	0.05587100
N	-2.05243500	-1.07757800	-0.18481900
C	-2.79936400	-2.29519400	0.06392700
H	-3.11123800	-2.72301300	-0.89000000
H	-2.22993800	-3.04276900	0.62519000
H	-3.70755400	-2.04749400	0.61658500
N	-0.67103300	1.36382500	0.05491100

1g$_{ocb}$ (water)
Imaginary frequency: 0
G = -608.855478 hartree

C	0.40456400	-0.33707700	-0.02633700
C	1.64377800	0.33526900	0.01609500
C	1.68344000	1.72659000	0.07950800
C	0.50030800	2.43892800	0.09127600
C	-0.73224000	1.78902600	0.04025300
C	-0.79122500	0.40804300	-0.00197600
H	2.64549300	2.21992000	0.11544500
H	0.53408800	3.52007600	0.14397200
H	-1.65335200	2.35496800	0.04643700
C	0.38417600	-1.79023500	-0.17812200
O	1.39162800	-2.48785300	-0.16047200
H	-0.59522700	-2.25335500	-0.33185600
C	-2.17024100	-0.26168900	0.04030800
O	-2.28601900	-1.23587300	0.81461100
O	-3.05056800	0.25057300	-0.67756400
O	2.81122000	-0.32775500	-0.01325300
H	2.60354500	-1.28748100	-0.04660400

2g$_{ocb}$ (water)
Imaginary frequency: 0
G = -628.238203 hartree

C	0.16111200	0.24007700	0.00643100
C	0.40546100	1.63036900	0.02719800
C	-0.65890900	2.52959900	0.05163000
C	-1.95769300	2.05541800	0.04041000
C	-2.21370600	0.68830800	0.00381600

C	-1.16671100	-0.22152700	0.00415200
H	-0.44152600	3.58945300	0.07498600
H	-2.78150300	2.75819000	0.06059300
H	-3.22968400	0.31828700	-0.01502000
C	1.28613900	-0.69520500	-0.07392800
H	1.04141500	-1.75391200	-0.16482600
C	-1.51637500	-1.71217400	0.04415100
O	-0.90204300	-2.40873100	0.88154300
O	-2.40842200	-2.08794800	-0.74327500
O	1.65506900	2.12286300	0.01935900
H	2.27613500	1.33480300	0.00741700
N	2.49614600	-0.29957700	-0.04841800
C	3.55526700	-1.28016000	-0.15842300
H	4.17525800	-1.04633100	-1.02476600
H	4.19355200	-1.22275900	0.72415500
H	3.16896800	-2.29837500	-0.25725000

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