Supplementary Material

Quinoidal alkali imidate salts: Dipotassium pyrazine-2,5-bis(olates), a novel class of quinoidal piperazine-2,5-dione derivatives

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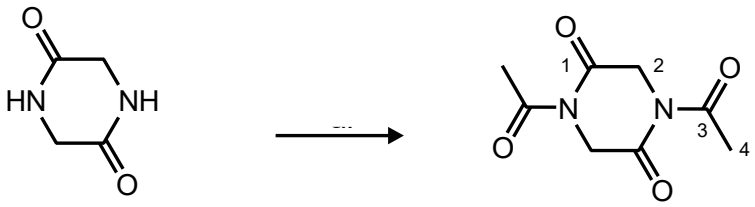
Synthesis results

Table S1 Isolated yields and purities of **4a**-**4m** and **6a**-**6m**.

4	Yield (%)	Purity (%)	**6**	Yield (%)	Purity (%)
4a	85	>95	**6a**	>99	>95
4b	84	>95	**6b**	>99	>95
4c	52	>95	**6c**	>99	>95
4d	65	>95	**6d**	>99	>95
4e	91	>95	**6e**	>99	>95
4f	66	>95	**6f**	>99	>95
4g	86	>95	**6g**	>99	>95
4h	92	>95	**6h**	>99	>95
4i	100	96	**6i**	>99	96
4j	60	>95	**6j**	>99	>95
4k	83	>95	**6k**	>99	>95
4l	82	>85	**6l**	>99	>85
4m	85	81	**6m**	>99	81

NMR spectra were only collected for the isolated precursors, selected piperazine-2,5-diones, and for the isolated pyrazine-2,5-bis(olates). The low solubility of certain piperazine-2,5-diones prohibited their analysis and is the primary reason for the omission of their NMR spectra. The purities of the piperazine-2,5-diones were obtained from the purities of their corresponding dipotassium pyrazine-2,5-bis(olates).

1,4-Diacetylpiperazine-2,5-dione (2)



1 **2**

Scheme S1 Synthesis of 1,4-diacetylpiperazine-2,5-dione (**2**).

Yield and purity: 100% (85.22 g) as a white solid, >99% pure based on ^{1}H NMR. M.P.: 99-101 °C.

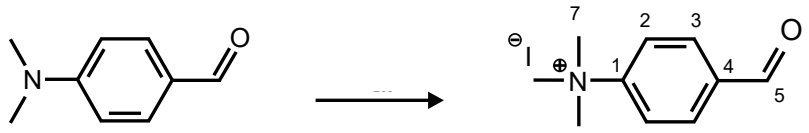
FTIR, wavenumber in cm^{-1}: 3051-2925 (CH_2 and CH_3 C-H stretches, possibly overtones, the intensity is very low), 1700 (convoluted imide C=O stretches), 1454, 1431, 1416, 1357, 1305, 1260, 1224, 1178, 1128, 1077, 1039, 974, 946, 813, 731, 689, 621, 596, 565, 550, 415.

Positive ion APCI-HRMS, m/z: 157.0610 (calculated M.W. of mother ion + [H$^+$]: 199.0718 g.mol^{-1}, calculated M.W. of product ion based on in-situ fragmentation + [H$^+$]: 157.0613 g.mol^{-1})

^{1}H NMR (DMSO-d_6, 600 MHz): δ 2.43 (proton 4, s, 6 H), 4.53 (proton 2, s, 4 H)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 170.3 (carbon 3), 166.7 (carbon 1), 46.9 (carbon 2), 26.1 (carbon 4)

4-Formyl-*N*,*N*,*N*-trimethylanilinium iodide (3i)



8 **3i**

Scheme S2 Synthesis of 4-formyl-*N*,*N*,*N*-trimethylanilinium iodide (**3i**).

Yield and purity: 37% (35.55 g) as translucent crystals, >99% pure based on ^{1}H NMR. M.P.: 142-144 °C.

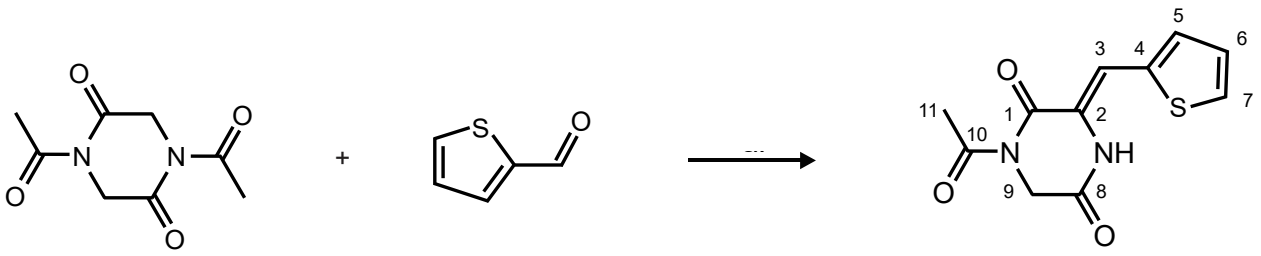
FTIR, wavenumber in cm^{-1}: 3134 and 3109 (aromatic =C-H stretches), 3045 (aromatic -C-H stretch), 3015 and 3000 (aliphatic C-H stretches), 1699 (carbonyl C=O stretch), 1600 (aromatic C=C stretch), 1475-1492 (aromatic C=C stretches), 1394-1306 (aromatic C-N stretch), 1225, 1178, 1116, 1014, 961, 941, 856, 846, 828, 717-631 (out of plane C-H bend), 594, 548, 486, 478, 426.

Negative ion ESI-HRMS, m/z: 164.1078 (calculated M.W. of product ion - [H^{+}]: 164.1075 g.mol^{-1})

^{1}H NMR (DMSO-d_6, 600 MHz): δ 3.68 (proton 7, s, 9 H), 8.15 and 8.16 (proton 3, m, 2 H), 8.23 and 8.24 (proton 2, m, 2 H), 10.13 (proton 5, s, 1 H)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 56.4 (carbon 7), 121.7 (carbon 3), 130.8 (carbon 2), 136.7 (carbon 4), 151.0 (carbon 1), 192.0 (carbon 5)

(3*Z*)-1-acetyl-3-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (9)



2 **3c** **9**

Scheme S3 Synthesis of (3*Z*)-1-acetyl-3-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (**9**).

Yield and purity: 64% (35.24 g) as a light brown solid, >99% pure based on ^{1}H NMR. M.P.: 174-176 °C.

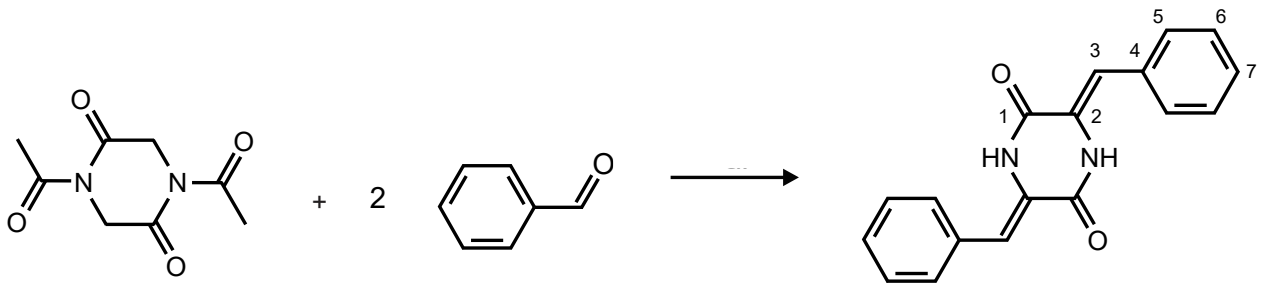
FTIR, wavenumber in cm^{-1}: 3254 (secondary amide N-H stretch), 3086 (aromatic C-H stretch), 2997 (aliphatic CH_2 or CH_3 C-H stretch), 1682 (convoluted amide and imide C=O stretch), 1614 (aromatic C=C stretch), 1507 and 1433 (aromatic C=C stretches), 1363, 1349, 1268, 1255, 1204, 1184, 1095, 1038, 1001, 974, 955, 901, 846, 820, 739-631 (out of plane C-H bend), 587, 565, 536, 476, 436.

Positive ion APCI-HRMS, m/z: 209.0362 (calculated M.W. of mother ion + [H$^+$]: 251.0490 g.mol^{-1}, calculated M.W. of product ion due to in-situ fragmentation + [H$^+$]: 209.0385 g.mol^{-1})

^{1}H NMR (DMSO-d_6, 600 MHz): δ 2.48 (proton 11, s, 3 H), 4.36 (proton 9, s, 2 H), 7.17 and 7.18 (proton 6 and proton 3, convoluted m, 2 H), 7.56 (proton 5, d, 1 H, J = 3.00 Hz), 7.76 (proton 7, d, 1 H, J = 4.80 Hz), 9.96 (NH proton, s, 1 H)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 26.5 (carbon 11), 45.5 (carbon 9), 113.6 (carbon 3), 124.6 (carbon 4), 128.2 (carbon 6), 129.6 (carbon 7), 131.2 (carbon 5), 135.7 (carbon 2), 161.8 (carbon 8), 164.3 (carbon 1), 171.7 (carbon 10)

(3*Z*,6*Z*)-3,6-bis(phenylmethylidene)piperazine-2,5-dione (4a)



2 **3a** **4a**

Scheme S4 Synthesis of (3*Z*,6*Z*)-3,6-bis(phenylmethylidene)piperazine-2,5-dione (**4a**).

Yield and purity: 85% (10 g) as an off-white solid, >95% pure based on ^{1}H NMR. M.P.: 294-296 °C.

FTIR, wavenumber in cm^{-1}: 3351 (amide N-H stretch), 3166, 3052 and 3026 (vinylic and aromatic C-H stretches), 2885, 1678 (amide C=O stretch), 1621 (aromatic C=C stretch), 1494 (aromatic C=C stretch), 1451, 1428, 1393, 1353, 1185, 1177, 1151, 1101, 1059, 942, 922, 856, 813, 765- 689 (out of plane C-H bend), 603, 553, 536, 482, 445.

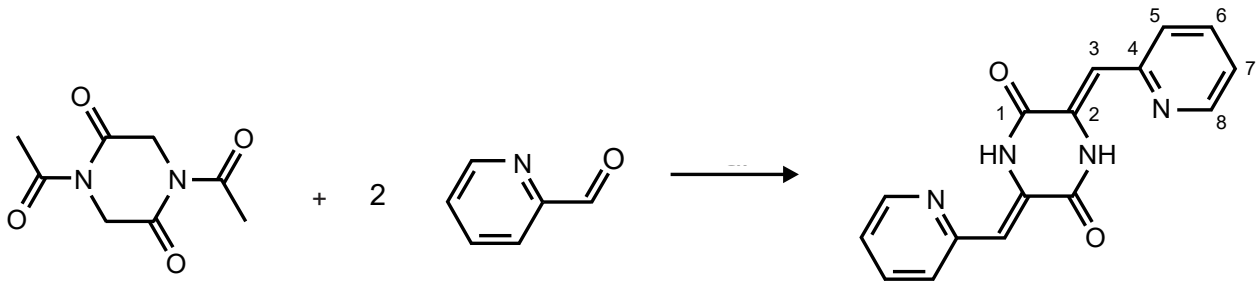
Negative ion APCI-HRMS, m/z: 289.1011 (calculated M.W. of mother ion - [H^{+}]: 289.0977 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 291.1115 (calculated M.W. of mother ion + [H^{+}]: 291.1133 g.mol^{-1})

^{1}H NMR (TFA-*d*, 600 MHz): δ 7.53 (proton 3, s, 2 H), 7.57-7.66 (proton 5, proton 6 and proton 7, convoluted multiplet, 10 H)

^{13}C NMR (TFA-*d*, 150 MHz): δ 123.7 (carbon 3), 128.4 (carbon 5), 129.1, 129.4 (carbon 6), 130.3 (carbon 7), 131.1 (carbon 2), 160.3 (carbon 1)

(3*Z*,6*Z*)-3,6-bis[(pyridine-2-yl)methylidene]piperazine-2,5-dione (4b)



2 **3b** **4b**

Scheme S5 Synthesis of (3*Z*,6*Z*)-3,6-bis[(pyridine-2-yl)methylidene]piperazine-2,5-dione (**4b**).

Yield and purity: 84% (4.97 g) as a bright yellow solid, >95% pure based on ^{1}H NMR. M.P.: 368-370 °C, a phase change and colour change were observed at 343-345 °C, the sample changed from a yellow powder to a black crystalline solid.

FTIR, wavenumber in cm^{-1}: 3118 (amide N-H stretch), 3074-3009 (vinylic and aromatic C-H stretches), 1686 (amide C=O stretch), 1641 (aromatic C=C stretch), 1584, 1559, 1537, 1471 (aromatic C=C stretch), 1450, 1411, 1345, 1295, 1244, 1153, 1140, 1096, 1046, 998, 936, 882, 855, 813-735 (out of plane C-H bend), 619, 545, 471.

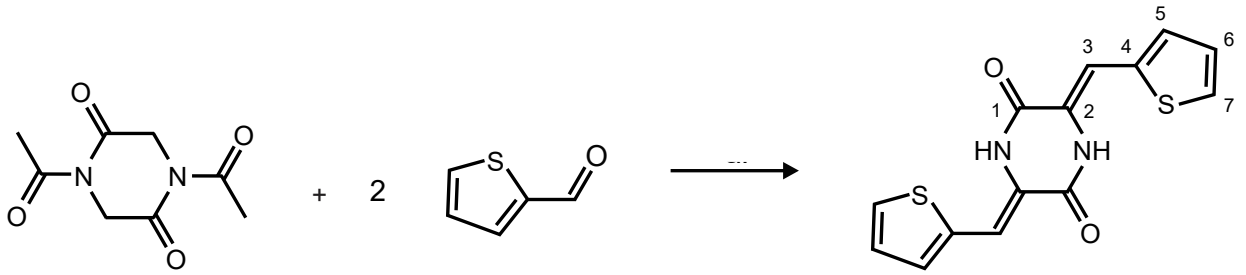
Negative ion APCI-HRMS, m/z: 291.0919 (calculated M.W. of mother ion - [H^{+}]: 291.0882 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 293.1022 (calculated M.W. of mother ion + [H^{+}]: 293.1038 g.mol^{-1})

^{1}H NMR (TFA-*d*, 600 MHz): δ 7.47 (proton 3, s, 2 H), 8.19 (proton 7, m, 2 H), 8.39 (proton 5, m, 2 H), 8.81 (proton 6, m, 2 H), 8.96 (proton 8, m, 2 H)

^{13}C NMR (TFA-*d*, 150 MHz): δ 107.8 (carbon 3), 127.0 (carbon 5), 128.6 (carbon 7), 131.8 (carbon 2), 142.7 (carbon 6), 145.0 (carbon 4), 148.3 (carbon 8), 157.9 (carbon 1)

(3*Z*,6*Z*)-3,6-bis[(thiophen-2-yl)methylidene]piperazine-2,5-dione (4c)



2 **3c** **4c**

Scheme S6 Synthesis of (3*Z*,6*Z*)-3,6-bis[(thiophen-2-yl)methylidene]piperazine-2,5-dione (**4c**).

Yield and purity: 52% (3.19 g) as a beige, light brown solid, >95% pure based on ^{1}H NMR. M.P.: 315-317 °C.

FTIR, wavenumber in cm^{-1}: 3170 (amide N-H stretch), 3095-3041 (vinylic and aromatic C-H stretches), 1674 (amide C=O stretch), 1608 (aromatic C=C stretch), 1439 (aromatic C=C stretch), 1414, 1385, 1348, 1257, 1166, 1124, 1065, 933, 869, 854, 749-699 (out of plane C-H bend), 574, 513, 470.

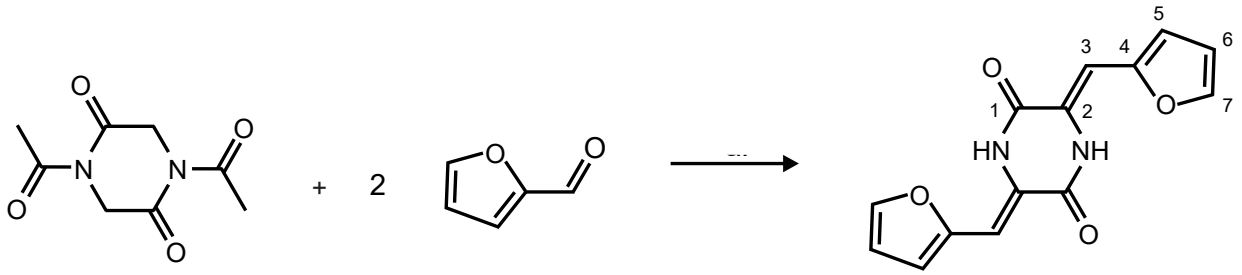
Negative ion APCI-HRMS, m/z: 301.0144 (calculated M.W. of mother ion - [H^{+}]: 301.0106 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 303.0238 (calculated M.W. of mother ion + [H^{+}]: 303.0262 g.mol^{-1})

^{1}H NMR (TFA-*d*, 600 MHz): δ 7.01 (proton 3, s, 2 H), 7.26 and 7.29 (proton 5 and proton 6, convoluted m, 4 H), 7.43 (proton 7, convoluted m, 2 H)

^{13}C NMR (TFA-*d*, 150 MHz): δ 116.0 (carbon 3), 120.5 (carbon 4), 128.6 (carbon 6), 130.2 (proton 7), 132.7 (proton 5), 133.8 (carbon 2)

(3*Z*,6*Z*)-3,6-bis[(furan-2-yl)methylidene]piperazine-2,5-dione (4d)



Scheme S7 Synthesis of (3*Z*,6*Z*)-3,6-bis[(furan-2-yl)methylidene]piperazine-2,5-dione (**4d**).

Yield and purity: 65% (3.56 g) yield as a beige, light brown solid, >95% pure based on ^{1}H NMR. M.P.: 282-284 °C.

FTIR, wavenumber in cm^{-1}: 3274 (amide N-H stretch), 3157-3056 (vinylic and aromatic C-H stretches), 1682, 1626 (amide C=O stretch), 1479 (aromatic C=C stretch), 1392 (aromatic C=C stretch), 1337, 1267, 1200, 1152, 1129, 1088, 1038, 1014, 942, 865, 809, 796-683 (out of plane C-H bend), 653, 588, 485.

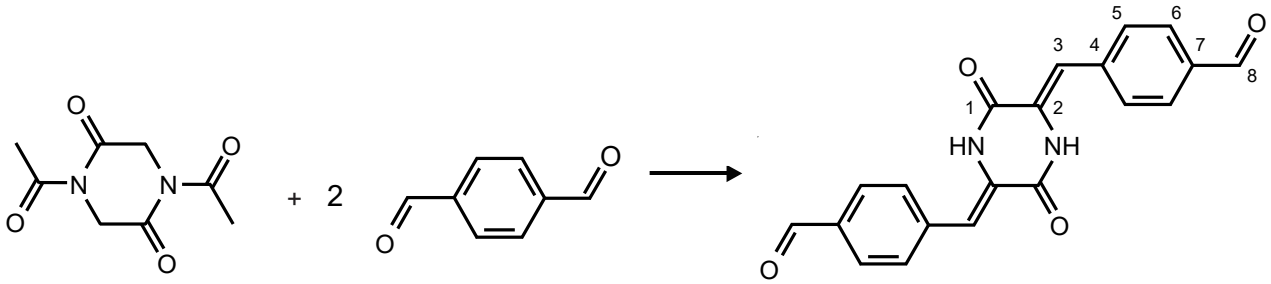
Negative ion APCI-HRMS, m/z: 269.0600 (calculated M.W. of mother ion - [H^{+}]: 269.0562 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 271.0699 (calculated M.W. of mother ion + [H^{+}]: 271.0718 g.mol^{-1})

^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.53 (proton 5, convoluted m, 2 H), 6.59 (proton 6, convoluted m, 2 H), 6.76 (proton 3, s, 2 H), 7.59 (proton 7, convoluted m, 2 H), 9.28 (NH proton, s, 2 H)

^{13}C NMR ($CDCl_3$, 150 MHz): δ 102.9 (carbon 3), 112.5 (carbon 5), 114.7 (carbon 6), 123.5 (carbon 2), 144.1 (carbon 7), 150.8 (carbon 4), 156.7 (carbon 1)

(3*Z*,6*Z*)-3,6-bis[(4-formylphenyl)methylidene]piperazine-2,5-dione (4e)



2 **3e** **4e**

Scheme S8 Synthesis of (3*Z*,6*Z*)-3,6-bis[(4-formylphenyl)methylidene]piperazine-2,5-dione (**4e**).

Yield and purity: 91% (11.74 g) as an orange-yellow solid, >95% pure based on ^{1}H NMR. M.P.: >400 °C, a darkening in the colour of the sample was observed at 350-352 °C.

FTIR, wavenumber in cm^{-1}: 3240 (amide N-H stretch), 2849, 2756, 1683 (aldehyde and amide C=O stretches), 1626 and 1600 (aromatic C=C stretch), 1567 and 1440 (aromatic C=C stretch), 1386, 1353, 1310, 1300, 1223, 1212, 1168, 1153, 1112, 1013, 928, 890, 867, 822, 769-637 (out of plane C-H bend), 628, 532, 464, 441.

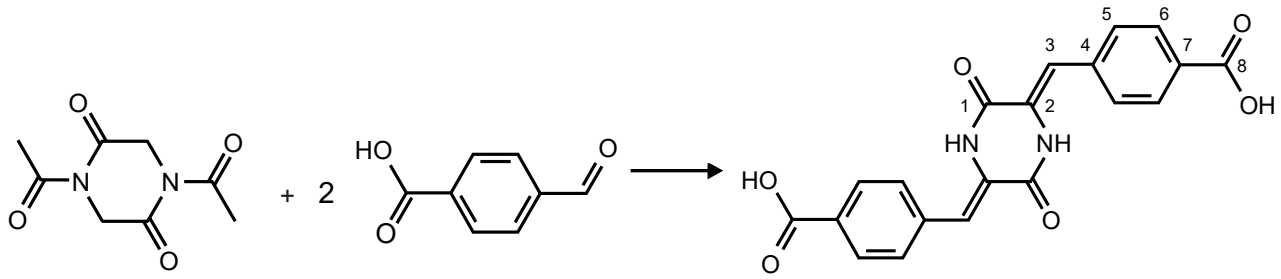
Negative ion APCI-HRMS, m/z: 345.0924 (calculated M.W.: 345.0876 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 347.1007 (calculated M.W.: 347.1032 g.mol^{-1})

^{1}H NMR (TFA-*d*, 600 MHz): δ 7.45 (proton 3, s, 2 H), 7.74 (proton 5, m, 4 H), 8.17 (proton 6, m, 4 H), 10.00 (proton 8, s, 2 H)

^{13}C NMR (TFA-*d*, 150 MHz): δ 120.7 (carbon 3), 125.7 (carbon 4), 129.5 (carbon 6), 131.7 (carbon 5), 135.7 (carbon 2), 139.3 (carbon 7), 159.6 (carbon 1), 196.8 (carbon 8)

(3*Z*,6*Z*)-3,6-bis[(4-carboxyphenyl)methylidene]piperazine-2,5-dione (4f)



2 **3f** **4f**

Scheme S9 Synthesis of (3*Z*,6*Z*)-3,6-bis[(4-carboxyphenyl)methylidene]piperazine-2,5-dione (**4f**).

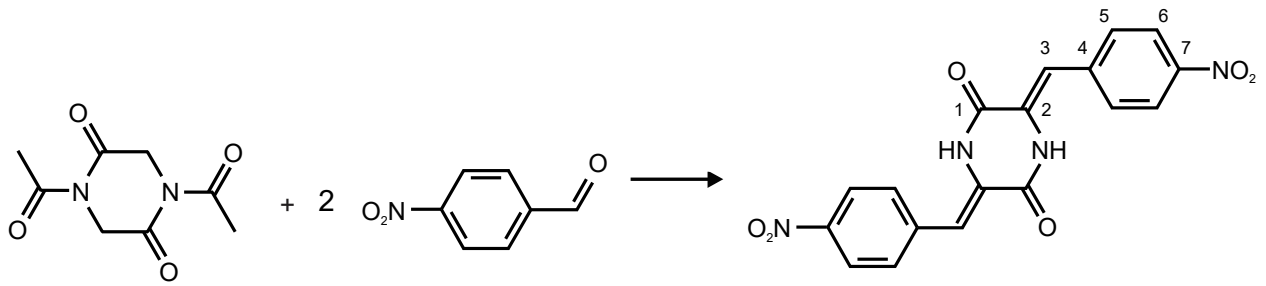
Yield and purity: 66% (3.02 g) light-yellow solid, >95% pure based on ^{1}H NMR of **6f**. M.P.: >400 °C, a darkening in the colour of the sample was observed at 367-369 °C.

FTIR, wavenumber in cm^{-1}: 3235 (amide N-H stretch), 2954, 2833, 2664, 2553, 1677 (carboxylic acid and amide C=O stretch), 1629 and 1605 (aromatic C=C stretch), 1567, 1511 and 1439 (aromatic C=C stretch), 1406, 1393, 1358, 1325, 1289, 1190, 1155, 1122, 1016, 928, 892, 853, 804, 775- 691 (out of plane C-H bend), 655, 630, 549, 529, 503, 456, 414.

Negative ion APCI-HRMS, m/z: 377.0794 (calculated M.W. of mother ion - [H^{+}]: 377.0774 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 379.0902 (calculated M.W. of mother ion + [H^{+}]: 379.0930 g.mol^{-1})

(3*Z*,6*Z*)-3,6-bis[(4-nitrophenyl)methylidene]piperazine-2,5-dione (4g)



2 **3g** **4g**

Scheme S10 Synthesis of (3*Z*,6*Z*)-3,6-bis[(4-nitrophenyl)methylidene]piperazine-2,5-dione (**4g**).

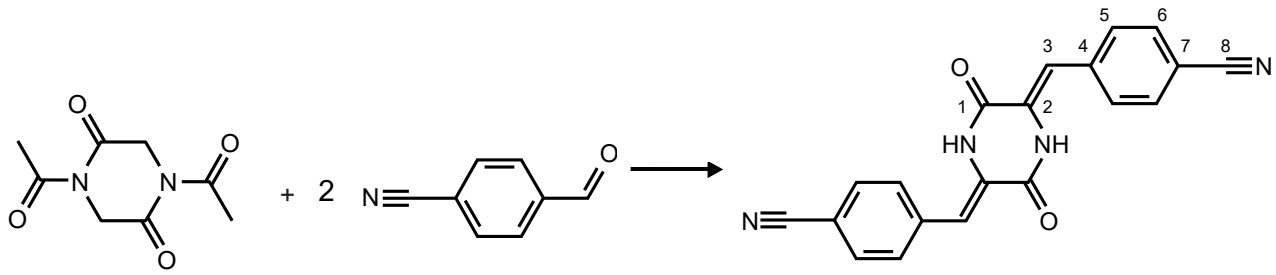
Yield and purity: 86% (4.04 g) as a beige, off-white solid, >95% pure based on ^{1}H NMR of **6g**. M.P.: No melting point was observed in the analytical range of the instrument. However, carbonisation occurred at 374-376 °C.

FTIR, wavenumber in cm^{-1}: 3263 (amide N-H stretch), 3112 and 3085 (vinylic and aromatic C-H stretches), 2851, 1682 (amide C=O stretch), 1628-1603 (aromatic C=C stretch), 1521-1435 (aromatic C=C stretch), 1404, 1389, 1343, 1319, 1215, 1188, 1148, 1109, 928, 887, 868, 835, 767-660 (out of plane C-H bend), 626, 524, 497, 454, 412.

Negative ion APCI-HRMS, m/z: 379.0712 (calculated M.W. of mother ion - $[H^+]$: 379.0679 $g.mol^{-1}$)

Positive ion APCI-HRMS, m/z: 381.0805 (calculated M.W. of mother ion + $[H^+]$: 381.0835 $g.mol^{-1}$)

(3*Z*,6*Z*)-3,6-bis[(4-cyanophenyl)methylidene]piperazine-2,5-dione (4h)



2 **3h** **4h**

Scheme S11 Synthesis of (3*Z*,6*Z*)-3,6-bis[(4-cyanophenyl)methylidene]piperazine-2,5-dione (**4h**).

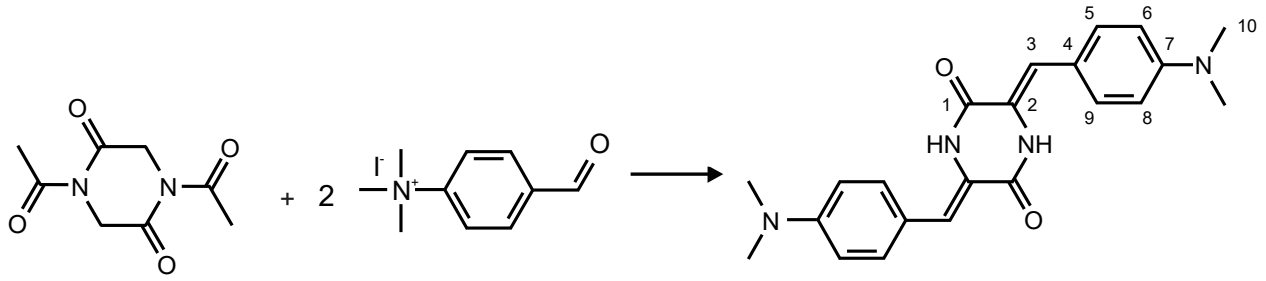
Yield and purity: 92% (10.87 g) as a yellow solid, >95% pure based on ^{1}H NMR of **6h**. M.P.: No melting point was observed in the analytical range of the instrument; however, decomposition occurred at 373-375 °C.

FTIR, wavenumber in cm^{-1}: 3212 (amide N-H stretch), 3111-3059 (vinylic and aromatic C-H stretches), 2221 (C≡N stretch), 1674 (amide C=O stretch), 1616 and 1600 (aromatic C=C stretch), 1504 and 1442 (aromatic C=C stretch), 1387, 1350, 1292, 1215, 1178, 1157, 934, 889, 862, 835, 791-705 (out of plane C-H bend), 639, 554, 523, 445.

Negative ion APCI-HRMS, m/z: 339.0912 (calculated M.W. of mother ion - [H^{+}]: 339.0882 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 341.1021 (calculated M.W. of mother ion + [H^{+}]: 341.1038 g.mol^{-1})

(3*Z*,6*Z*)-3,6-bis[(4-dimethylaminophenyl)methylidene]piperazine-2,5-dione (4i)



2 **3i** **4i**

Scheme S12 Synthesis of (3*Z*,6*Z*)-3,6-bis[(4-dimethylaminophenyl)methylidene]piperazine-2,5-dione (**4i**).

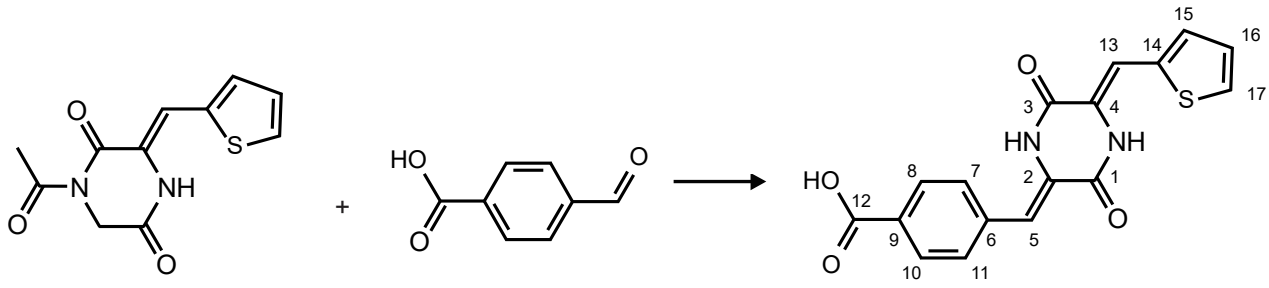
Yield and purity: 100% (10.22 g) as a dark orange solid. 95.77% pure based on ^{1}H NMR of **6i**, the primary impurity is *p*-(dimethylamino)benzaldehyde. M.P.: 332-334 °C, a darkening in the colour of the sample was observed at a temperature of 322-324 °C.

FTIR, wavenumber in cm^{-1}: 3214 (amide N-H stretch), 3153 (vinylic and aromatic C-H stretches), 2794 (aliphatic C-H stretch), 1662 (amide C=O stretch), 1592 and 1519 , 1391 (aromatic C=C stretch), 1338, 1199, 1160, 1122, 1058, 934, 894, 864, 813, 776-681 (out of plane C-H bend), 632, 551, 531, 486, 469, 414.

Negative ion APCI-HRMS, m/z: 375.1862 (calculated M.W.: 375.1821 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 377.1952 (calculated M.W.: 377.1977 g.mol^{-1})

(3*Z*,6*Z*)-3-[(4-carboxyphenyl)methylidene]-6-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (4j)



9 **3f** **4j**

Scheme S13 Synthesis of (3*Z*,6*Z*)-3-[(4-carboxyphenyl)methylidene]-6-[(thiophen-2-yl) methylidene]piperazine-2,5-dione (**4j**).

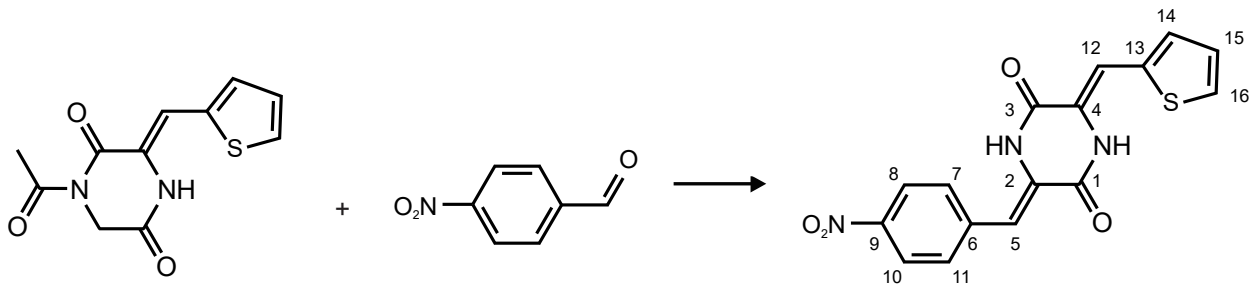
Yield and purity: 60% (8.27 g) as a yellow solid, >95% pure based on ^{1}H NMR of **6j**. M.P.: 387-389 °C.

FTIR, wavenumber in cm^{-1}: 3234 (amide N-H stretch), 3111-3051 (vinylic and aromatic C-H stretches), 1673 (carboxylic acid and amide C=O stretches), 1622-1566, 1511-1409 (aromatic C=C stretch), 1390, 1355, 1323, 1290, 1259, 1189, 1158, 1121, 1073, 1062, 1016, 978, 925, 892, 854, 827, 764-688 (out of plane C-H bend), 537, 520, 482.

Negative ion APCI-HRMS, m/z: 339.0474 (calculated M.W. of mother ion - [H^{+}]: 339.0440 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 341.0574 (calculated M.W. of mother ion + [H^{+}]: 341.0596 g.mol^{-1})

(3*Z*,6*Z*)-3-[(4-nitrophenyl)methylidene]-6-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (4k)



9 **3g** **4k**

Scheme S14 Synthesis of (3*Z*,6*Z*)-3-[(4-nitrophenyl)methylidene]-6-[(thiophen-2-yl) methylidene]piperazine-2,5-dione (**4k**).

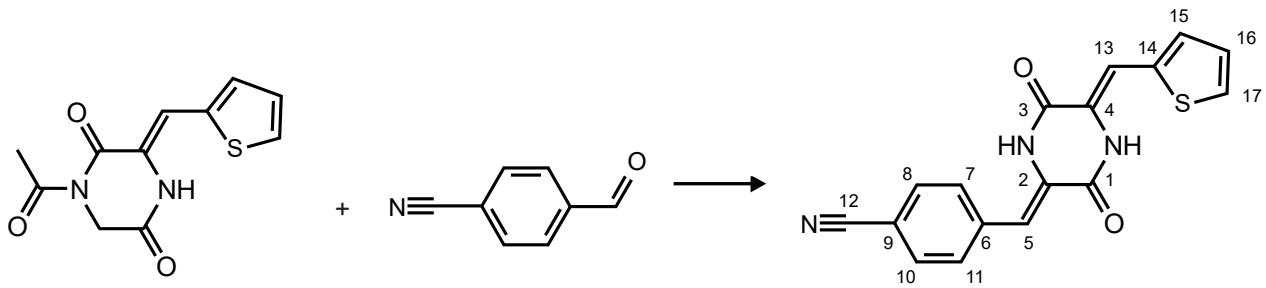
Yield and purity: 83% (7.92 g) as an orange solid, >95% pure based on ^{1}H NMR of **6k**. M.P.: No melting point was observed; however, decomposition was observed at 346-349 °C.

FTIR, wavenumber in cm^{-1}: 3248 (amide N-H stretch), 3104 (vinylic and aromatic C-H stretches), 1681 (amide C=O stretch), 1625 and 1597 (aromatic C=C stretch), 1513-1408 (aromatic C=C stretch), 1390, 1356, 1338, 1323, 1249, 1216, 1205, 1188, 1118, 1106, 1076, 1050, 929, 888, 869, 854, 839, 758-684 (out of plane C-H bend), 631, 584, 540, 520, 490, 456, 412.

Negative ion APCI-HRMS, m/z: 340.0431 (calculated M.W. of mother ion - [H$^+$]: 340.0392 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 342.0521 (calculated M.W. of mother ion + [H$^+$]: 342.0548 g.mol^{-1})

(3*Z*,6*Z*)-3-[(4-cyanophenyl)methylidene]-6-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (4l)



9 **3h** **4l**

Scheme S15 Synthesis of (3*Z*,6*Z*)-3-[(4-cyanophenyl)methylidene]-6-[(thiophen-2-yl) methylidene]piperazine-2,5-dione (**4l**).

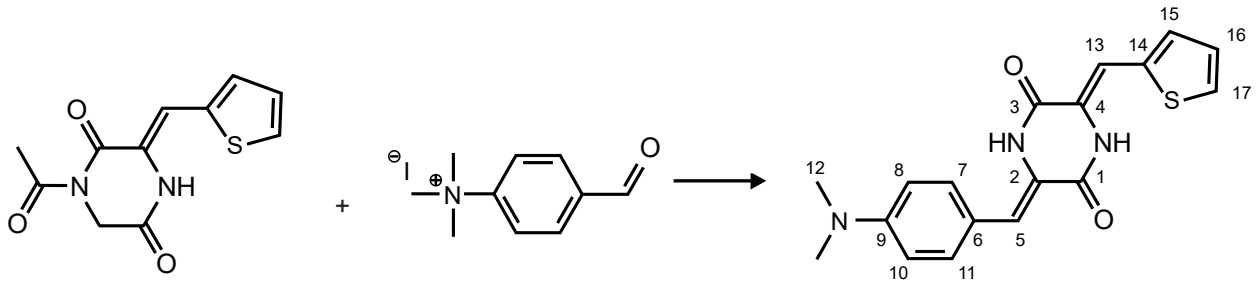
Yield and purity: 82% (10.54 g) as a yellow solid, 85-99% pure based on ^{1}H NMR of **6l**. The impurity is either the *E*,*Z* isomer, *E*,*E* isomer, or a rotamer that is visible on the NMR timescale. M.P.: No melting point was observed; however, carbonisation occurred at 301-304° C.

FTIR, wavenumber in cm^{-1}: 3190 (amide N-H stretch), 3106 and 3032 (vinylic and aromatic C-H stretches), 2226 (C≡N stretch), 1677 (amide C=O stretch), 1620 and 1502 (aromatic C=C stretch), 1438 (aromatic C=C stretch), 1390, 1348, 1248, 1173, 1157, 1125, 1109, 1075, 1049, 1018, 930, 881, 829, 783-712 (out of plane C-H bend), 587, 555, 529, 494, 450.

Negative ion APCI-HRMS, m/z: 320.0528 (calculated M.W. of mother ion - [H^{+}]: 320.0494 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 322.0630 (calculated M.W. of mother ion + [H^{+}]: 322.0650 g.mol^{-1})

(3*Z*,6*Z*)-3-[(4-dimethylaminophenyl)methylidene]-6-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (4m)



9 **3h** **4l**

Scheme S16 Synthesis of (3*Z*,6*Z*)-3-[(4-N,N-dimethylaminophenyl)methylidene]-6-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (**4m**).

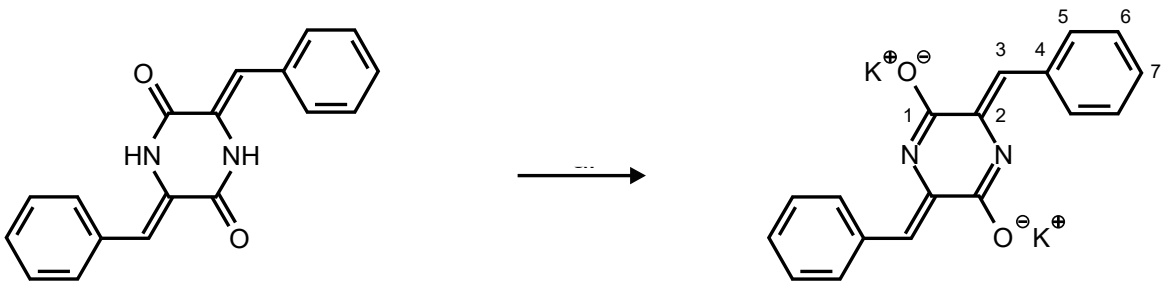
Yield and purity: 85% (8.06 g) as a orange solid, 80.66% pure based on ^{1}H NMR of **6l**. Unidentified impurity, possibly a benzylamine derivative based on the ^{1}H NMR. M.P.: 228-231 °C.

FTIR, wavenumber in cm^{-1}: 3247 (amide N-H stretch), 3085 and 2995 (vinylic and aromatic C-H stretches), 1675 (amide C=O stretch), 1612 and 1524 (aromatic C=C stretch), 1433 and 1412 (aromatic C=C stretch), 1393, 1361, 1348, 1255, 1198, 1184, 1163, 1093, 1038, 999, 973, 931, 900, 846, 817, 803, 751-685 (out of plane C-H bend), 630, 585, 564, 537, 524, 473, 435.

Negative ion APCI-HRMS, m/z: 338.1004 (calculated M.W. of mother ion - [H^{+}]: 338.0963 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 340.1084 (calculated M.W. of mother ion + [H^{+}]: 340.1119 g.mol^{-1})

Dipotassium (3*Z*,6*Z*)-3,6-bis(phenylmethylidene)pyrazine-2,5-bis(olate) (6a)



4a **6a**

Scheme S17 Synthesis of dipotassium (3*Z*,6*Z*)-3,6-bis(phenylmethylidene)pyrazine-2,5-bis(olate) (**6a**).

Yield and purity: Quantitative (1.26 g). Isolated as a yellow solid. M.P.: 302-304 °C.

FTIR, wavenumber in cm^{-1}: 3198, 3043 and 3023 (aromatic C-H stretch), 2815, 2166, 1649 (C=N stretch), 1594-1526 (aromatic C=C stretch), 1486-1442 (aromatic C=C stretch), 1391, 1344, 1321, 1307, 1184, 1155, 1129, 1072, 1045, 1027, 1000, 988, 958, 922, 912, 881, 851, 768-663 (out of plane C-H bend), 629, 618, 586, 537, 494, 477, 453.

Negative ion APCI-HRMS, m/z: 289.0977 (calculated M.W. of product - 2[K^+]: 288.0910 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 289.0983 $g.mol^{-1}$)

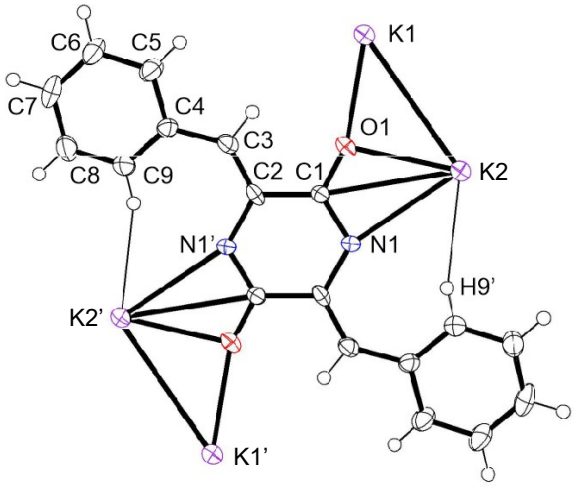
Positive ion APCI-HRMS, m/z: 291.1133 (calculated M.W. of product - 2[K^+]: 288.0910 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] + [H^+]: 291.1128 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.34 (proton 3, s, 2 H), 7.08 (proton 7, m, 2 H), 7.28 (proton 6, m, 4 H), 7.84 (proton 5, m, 4 H)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 108.2 (carbon 3), 125.2 (carbon 7), 128.4 (carbon 5), 129.3 (carbon 6), 138.6 (carbon 2), 163.3 (carbon 1)

XRD: The unit cell lengths are 8.719 Å, 7.249 Å, 25.695 Å, the unit cell angles are 90.000°, 94.921°, 90.000° and the crystal class is monoclinic. Selected bond lengths and bond angles obtained for **6a** are presented in **Table S2**.

Table S2 ORTEP and selected bond lengths and bond angles of **6a**.[a]



Bond lengths (Å)		Bond angles (°)	
N1-C1	1.334	N1-C1-O1	120.39
C1-O1	1.261	C1-C2-N1'	119.85
C1-C2	1.512	C1-N1-C2'	118.91
C2-C3	1.353	O1-C1-C2	118.41
C3-C4	1.446	C1-C2-C3	117.42
C4-C5	1.394	C2-C3-C4	132.34
C5-C6	1.382	C4-C5-C6	122.38
C6-C7	1.381	C5-C6-C7	119.70
C7-C8	1.378	C6-C7-C8	119.77
C8-C9	1.395	C7-C8-C9	119.83
C9-C4	1.393	C8-C9-C4	121.70
O1-K1	2.601	C9-C4-C5	116.52
K1-K2	3.805	O1-K1-K2	44.74
O1-K2	2.680	O1-K2-K1	43.08
C1-K2	3.254	N1-K2-K1	88.92
N1-K2	3.019	N1-K2-O1	46.07
K2-H9'	2.686	N1-K2-C1	24.18
		C2-C3-C4-C5	-172.65
		C2-C3-C4-C9	8.23
		N1-C1-C2-N1'	2.44
		C4-C5-C6-C7	1.14

a. Grey atoms represent carbon, red atoms represent oxygen, blue atoms represent nitrogen and purple atoms represent potassium. Solvent molecules omitted for clarity, every potassium ion is also coordinated to a single oxygen atom of two DMSO-d_6 molecules. K2 and K2' represent potassium ions of adjacent dipotassium pyrazine-2,5-bis(olates).

The bond lengths observed for piperazine-2,5-diones are generally; C-N ~1.349-1.362 Å and C=O ~1.229-1.236 Å.[1, 2] Based on the data represented in **Table S3.1**, the C-N bond length equates to 1.334 Å, whereas the C-O bond length equates to 1.261 Å. Therefore, a comparatively stronger double bond character exists for the carbon/nitrogen partial double bond, whereas a weaker double bond character exists for the carbon/oxygen partial double bond in the product versus the piperazine-2,5-dione core, suggesting formation of the pyrazine-2,5-bis(olate) core.

The crystal assumed a primitive monoclinic lattice and **6a** crystallised in a γ-herringbone packing regime, **Figure S1a**-**Figure S1d**. **6a** possesses a herringbone packing angle of θ = 38.66°, **Figure S1b**, with lattice constants of y = 7.25 Å and x = 25.49 Å, **Figure S1c**. Overlapping molecules within the same stack are separated by 7.25 Å, whereas overlapping molecules of adjacent stacks present with a 3.74 Å distance between them, adjacent stacks are separated by 6.01 Å, **Figure S1c** and **Figure S1d**. A single potassium atom is coordinated to the oxygen of a pyrazine-2,5-bis(olate) with a bond length of 2.601 Å, suggesting ionic bonding. The potassium also coordinates to an oxygen, nitrogen, carbon, and an aromatic hydrogen atom of an adjacent pyrazine-2,5-bis(olate), as well as to the oxygen atoms of two DMSO-d_6 molecules and a neighbouring potassium atom

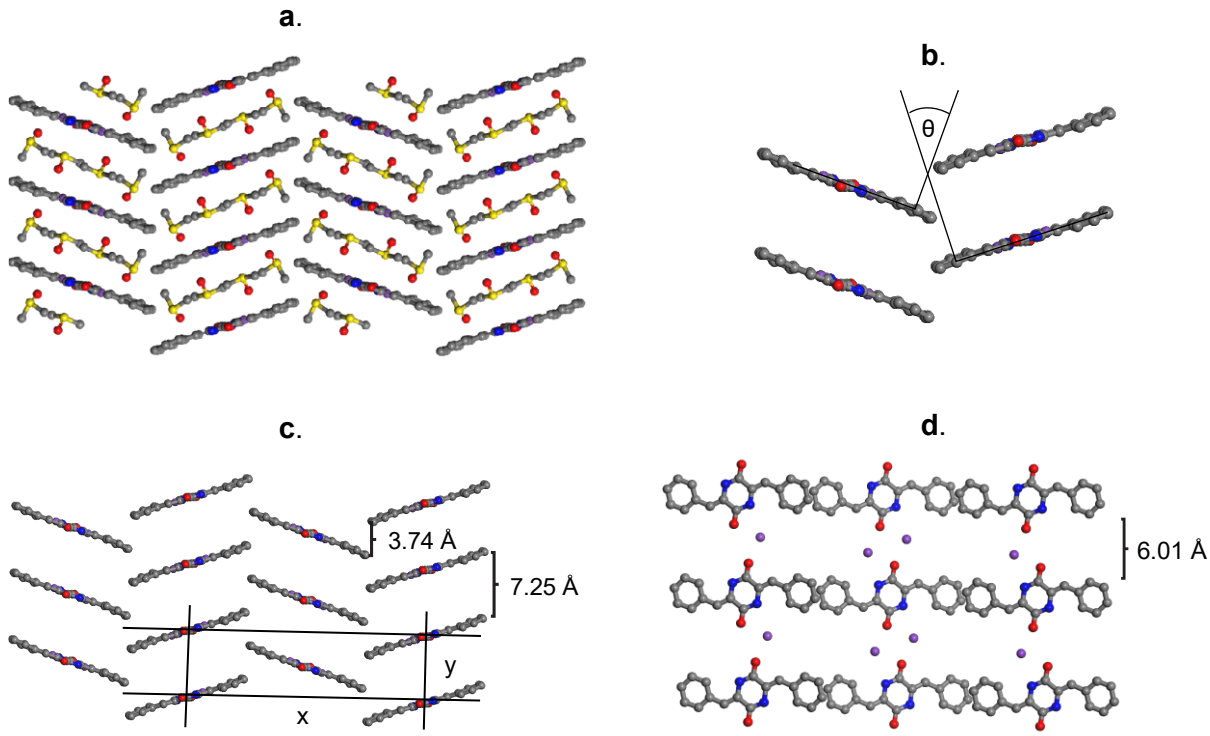
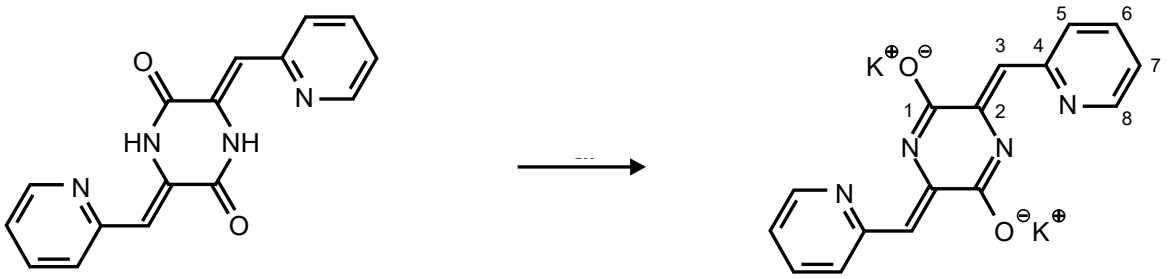


Figure S1 **a**. Front view of the crystal structure of **6a**, solvent molecules included. **b**. Herringbone packing angle of **6a**, θ = 38.66°. **c**. Front view of the crystal structure of **6a**, solvent molecules omitted, lattice constants x = 25.49 Å and y = 7.25 Å. **d**. Top view of the crystal structure of **6a**, solvent molecules omitted. Grey: carbon, red: oxygen, blue: nitrogen and purple: potassium, hydrogen atoms omitted for clarity.

Dipotassium (3*Z*,6*Z*)-3,6-bis[(pyridin-2-yl)methylidene]pyrazine-2,5-bis(olate) (6b)



4b **6b**

Scheme S18 Synthesis of dipotassium (3*Z*,6*Z*)-3,6-bis[(pyridin-2-yl)methylidene]pyrazine-2,5-bis(olate) (**6b**).

Yield and purity: Quantitative (1.26 g). Isolated as a orange solid. M.P.: 322-324 °C.

FTIR, wavenumber in cm^{-1}: 3154, 3053 (vinylic and aromatic C-H stretch), 2984, 1693, 1648, 1613, 1584, 1548 and 1501 (aromatic C=C stretch), 1471-1406 (aromatic C=C stretch), 1346, 1300, 1215, 1151, 1138, 1092, 985, 968, 862, 834, 778- 719 (out of plane C-H bend), 618, 548, 492, 465.

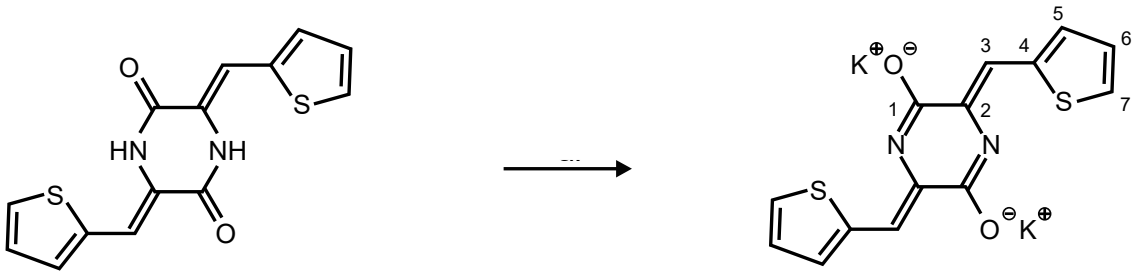
Negative ion APCI-HRMS, m/z: 291.0892 (calculated M.W. of product - 2[K^+]: 290.0815 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 291.0887 $g.mol^{-1}$)

Positive ion APCI-HRMS, m/z: 293.1035 (calculated M.W. of product - 2[K^+]: 290.0815 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] + [H^+]: 293.1033 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.38 (proton 3, s, 2 H), 6.49 (proton 3, s, 2 H), 6.99 (proton 7, m, 2 H), 7.20 (proton 7, m, 2 H), 7.42 (proton 5, m, 2 H), 7.64 (proton 6, m, 2 H), 7.78 (proton 6, m, 2 H), 8.42 (proton 8, m, 2 H), 8.61 (proton 8, m, 2 H), 9.07 (proton 5, m, 2 H), 12.21 (NH or OH proton)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 102.3 (carbon 3), 110.9 (carbon 3), 119.2 (carbon 7), 120.5 (carbon 7), 124.9 (carbon 5), 125.0 (carbon 5), 134.9 (carbon 6), 135.3 (carbon 2), 137.0 (carbon 6), 142.3 (carbon 2), 148.1 (carbon 8), 148.6 (carbon 8), 157.0 (carbon 4), 157.2 (carbon 4), 160.5 (carbon 1), 160.9 (carbon 1)

Dipotassium (3*Z*,6*Z*)-3,6-bis[(thiophen-2-yl)methylidene]pyrazine-2,5-bis(olate) (6c)



4c **6c**

Scheme S19 Synthesis of dipotassium (3*Z*,6*Z*)-3,6-bis[(thiophen-2-yl)methylidene]pyrazine-2,5-bis(olate) (**6c**).

Yield and purity: Quantitative (1.25 g). Isolated as a brown solid. M.P.: 324-326 °C.

FTIR, wavenumber in cm^{-1}: 3367, 3208, 3108 and 3066 (aromatic C-H stretch), 2946, 2818, 1647 (C=N stretch), 1596-1501 (aromatic C=C stretch), 1426 (aromatic C=C stretch), 1389, 1356, 1306, 1234, 1210, 1128, 1072, 1044, 995, 963, 853, 828, 809, 787-658 (out of plane C-H bend), 617, 576, 538, 518, 496, 471.

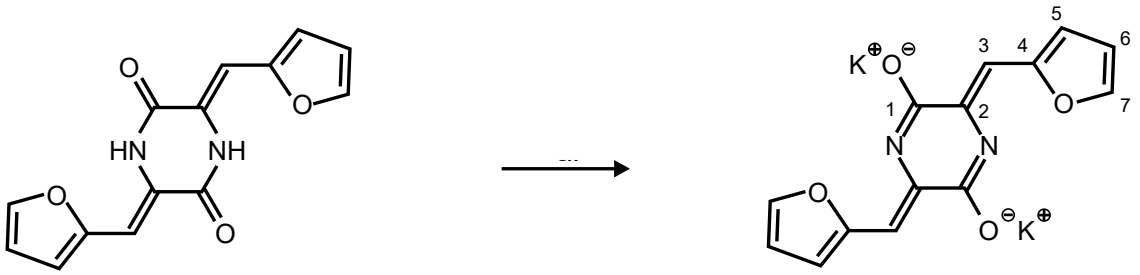
Negative ion APCI-HRMS, m/z: 301.0106 (calculated M.W. of product - 2[K^+]: 300.0038 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 301.0111 $g.mol^{-1}$)

Positive ion APCI-HRMS, m/z: 303.0260 (calculated M.W. of product - 2[K^+]: 300.0038 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] + [H^+]: 303.0256 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.68 (proton 3, s, 2 H), 7.02 (proton 5, convoluted m, 2 H), 7.17 (proton 6, convoluted m, 2 H), 7.38 (proton 7, convoluted m, 2 H), 8.57 (NH or OH proton), 8.67 (NH or OH proton)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 126.1 (carbon 5, carbon 6 and carbon 7), 161.3 (carbon 1)

Dipotassium (3*Z*,6*Z*)-3,6-bis[(furan-2-yl)methylidene]pyrazine-2,5-bis(olate) (6d)



4d **6d**

Scheme S20 Synthesis of dipotassium (3*Z*,6*Z*)-3,6-bis[(furan-2-yl)methylidene]pyrazine-2,5-bis(olate) (**6d**).

Yield and purity: Quantitative (1.28 g). Isolated as a brown solid. M.P.: No melting point was observed; however, decomposition was observed at 313-315 °C.

FTIR, wavenumber in cm^{-1}: 3351, 3109-3091 (aromatic C-H stretch), 1641 (C=N stretch), 1624 and 1515 (aromatic C=C stretch), 1477 and 1404 (aromatic C=C stretch), 1377, 1335, 1318, 1246, 1216, 1208, 1137, 1115, 1073, 1039, 1013, 994, 968, 940, 912, 880, 847, 787-689 (out of plane C-H bend), 666, 588, 563, 511, 497.

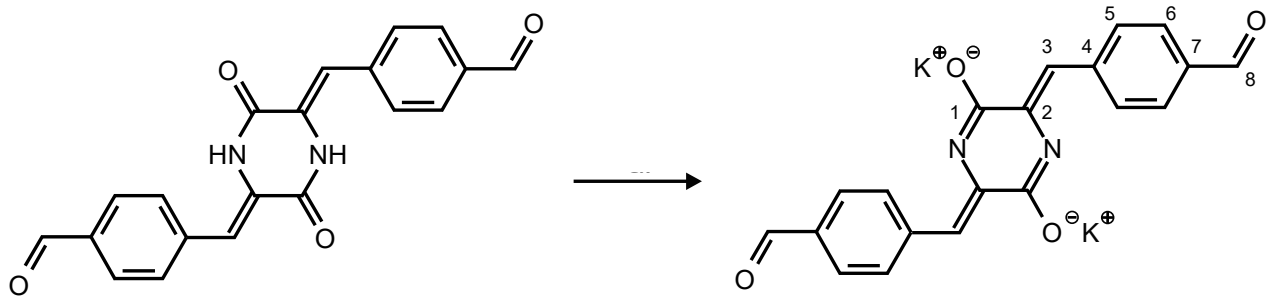
Negative ion APCI-HRMS, m/z: 296.0567 (calculated M.W. of product - 2[K^+]: 268.0495 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 269.0568 $g.mol^{-1}$)

Positive ion APCI-HRMS, m/z: 271.0715 (calculated M.W. of product - 2[K^+]: 268.0495 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] + [H^+]: 271.0713 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.30 (proton 3, s, 2 H), 6.52 (proton 6 convoluted with proton 5, m, 3 H), 7.12 (proton 5, m, 1 H), 7.52 and 7.75 (proton 7, m, 2 H), 9.00 (NH or OH proton)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 95.9 and 100.5 (carbon 3), 110.3 (carbon 5), 112.4 (carbon 6), 129.8 and 138.2 (carbon 2), 140.8 and 143.0 (carbon 7), 152.9 and 154.7 (carbon 4), 160.6 and 161.0 (carbon 1)

Dipotassium (3*Z*,6*Z*)-3,6-bis[(4-formylphenyl)methylidene]pyrazine-2,5-bis(olate) (6e)



Scheme S21 Synthesis of dipotassium (3*Z*,6*Z*)-3,6-bis[(4-formylphenyl)methylidene]pyrazine-2,5-bis(olate) (**6e**).

Yield and purity: Quantitative (1.22 g). Isolated as a dark, red-brown solid. M.P.: No melting point was observed; however, decomposition was observed at 386-389 °C.

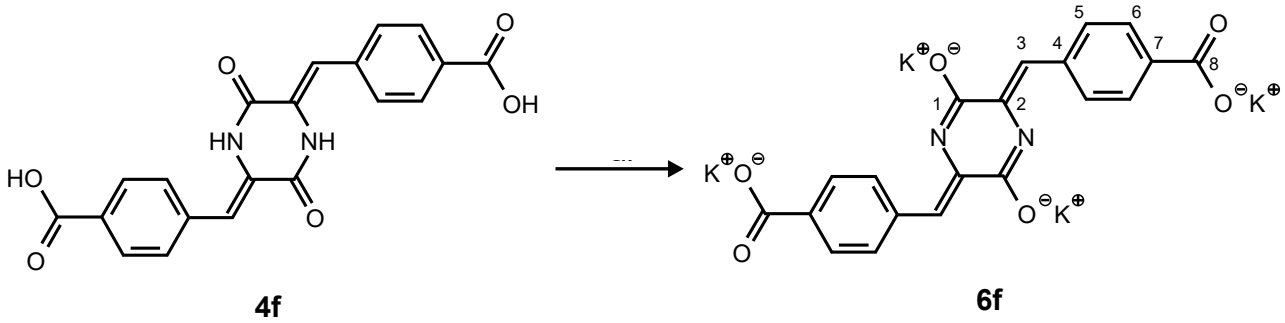
FTIR, wavenumber in cm^{-1}: 3200, 3088 (vinylic and aromatic C-H stretch), 2968, 1663 (aldehyde C=O and imidate C=N stretch), 1593-1502 (aromatic C=C stretch), 1476 and 1407 (aromatic C=C stretch), 1394, 1350, 1300, 1212, 1158, 991, 961, 866, 808, 784-707 (out of plane C-H bend), 648, 623, 600, 564, 535, 464, 443.

Negative ion APCI-HRMS, m/z: 345.0886 (calculated M.W. of product - 2[K^+]: 344.0808 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 345.0881 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.42 (proton 3, s, 2 H), 7.78 (proton 5, m, 4 H), 8.04 (proton 6, convoluted m, 4 H), 9.88 (proton 8, s, 2 H)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 106.9 (carbon 3), 129.0 (carbon 5), 129.2 (carbon 4), 129.4 (carbon 6), 132.3 (carbon 7), 144.6 (carbon 2), 162.8 (carbon 1), 191.8 (carbon 8)

Tetrapotassium (3*Z*,6*Z*)-3,6-bis[(4-carboxylatophenyl)methylidene]pyrazine-2,5-bis(olate) (6f)



Scheme S22 Synthesis of tetrapotassium (3*Z*,6*Z*)-3,6-bis[(4-carboxylatophenyl)methylidene] pyrazine-2,5-bis(olate) (**6f**).

Yield and purity: Quantitative (1.40 g). Isolated as an orange solid. M.P.: >400 °C.

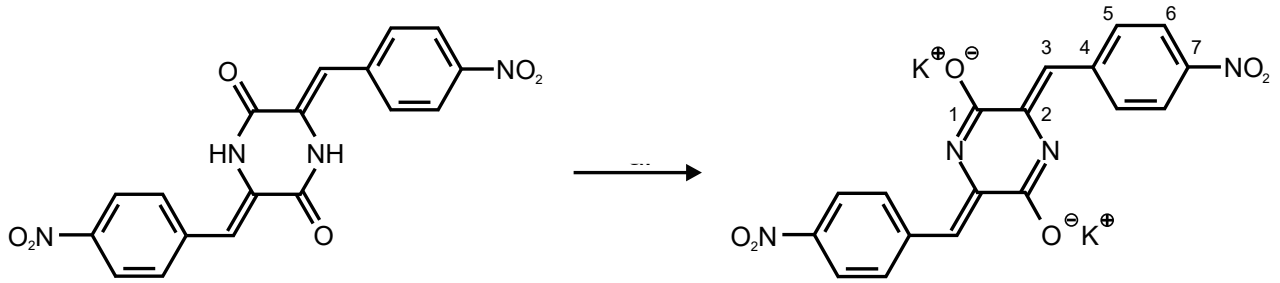
FTIR, wavenumber in cm^{-1}: 3191 (hydrogen bonding, broad O-H stretch), 2169, 1666 and 1596 (carboxylate C=O and imidate C=N stretch), 1541 (aromatic C=C stretch), 1488-1428 (aromatic C=C stretch), 1375, 1295, 1208, 1170, 1137, 1080, 1013, 967, 885, 825, 785-670 (out of plane C-H bend), 606, 538, 485, 412.

Negative ion APCI-HRMS, m/z: 377.0849 (calculated M.W. for product - 4[K^+]: 374.0561 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 377.0779 $g.mol^{-1}$)

^{1}H NMR (D_2O, 600 MHz): δ 6.68 (proton 3, s, 2 H), 7.78 (proton 5, m, 4 H), 7.90 (proton 6, m, 4 H)

^{13}C NMR (D_2O, 150 MHz): δ 115.6 (carbon 3), 129.7 (carbon 5), 130.0 (carbon 6), 132.8 (carbon 4), 135.7 (carbon 7), 138.2 (carbon 2), 163.7 (carbon 1), 175.7 (carbon 8)

Dipotassium (3*Z*,6*Z*)-3,6-bis[(4-nitrophenyl)methylidene]pyrazine-2,5-bis(olate) (6g)



4g **6g**

Scheme S23 Synthesis of dipotassium (3*Z*,6*Z*)-3,6-bis[(4-nitrophenyl)methylidene]pyrazine-2,5-bis(olate) (**6g**).

Yield and purity: Quantitative (1.20 g). Isolated as a black solid. M.P.: Explosive decomposition of the sample was observed at 324-326 °C.

FTIR, wavenumber in cm^{-1}: 3233, 3106 and 3090 (aromatic C-H stretch), 1668 (C=N stretch), 1577 and 1543 (aromatic C=C stretch), 1491-1401 (aromatic C=C stretch), 1307, 1291, 1220, 1176, 1129, 1108, 1008, 976, 960, 871, 840, 816, 777-696 (out of plane C-H bend), 547, 512, 463, 431.

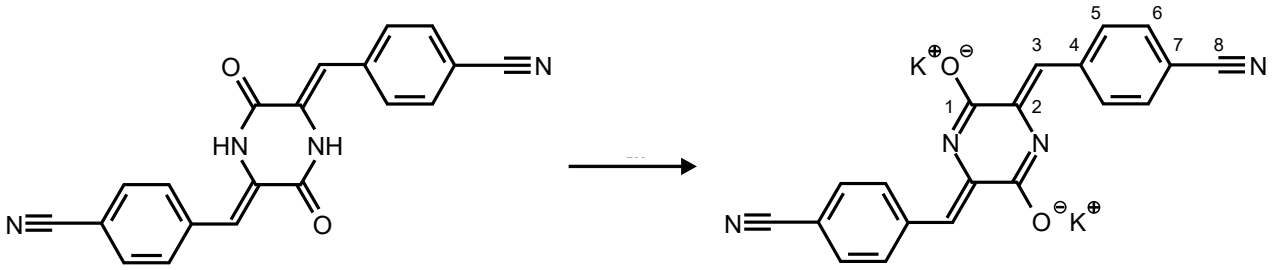
Negative ion APCI-HRMS, m/z: 379.0676 (calculated M.W. of product - 2[K^+]: 378.0611 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 379.0684 $g.mol^{-1}$)

Positive ion APCI-HRMS, m/z: 381.0828 (calculated M.W. of product - 2[K^+]: 378.0611 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] + [H^+]: 381.0830 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.35 (proton 3, s, 2 H), 8.04 (proton 5, m, 4 H), 8.11 (proton 6, m, 4 H), 9.96 (NH or OH proton)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 105.5 (carbon 3), 123.6 (carbon 6), 128.7 (carbon 5), 142.3 (carbon 2), 147.1 (carbon 7), 164.9 (carbon 1)

Dipotassium (3*Z*,6*Z*)-3,6-bis[(4-cyanophenyl)methylidene]pyrazine-2,5-bis(olate) (6h)



4h **6h**

Scheme S24 Synthesis of dipotassium (3*Z*,6*Z*)-3,6-bis[(4-cyanophenyl)methylidene]pyrazine-2,5-bis(olate) (**6h**).

Yield and purity: Quantitative (1.22 g). Isolated as a bright red solid. M.P.: 338-340 °C.

FTIR, wavenumber in cm^{-1}: 3228, 2218 (C≡N stretch), 1667 (C=N stretch), 1592 and 1549 (aromatic C=C stretch), 1465-1403 (aromatic C=C stretch), 1350, 1327, 1299, 1214, 1167, 1126, 1103, 987, 960, 866, 846, 838, 816, 765 and 728 (out of plane C-H bend), 642, 558, 528, 448.

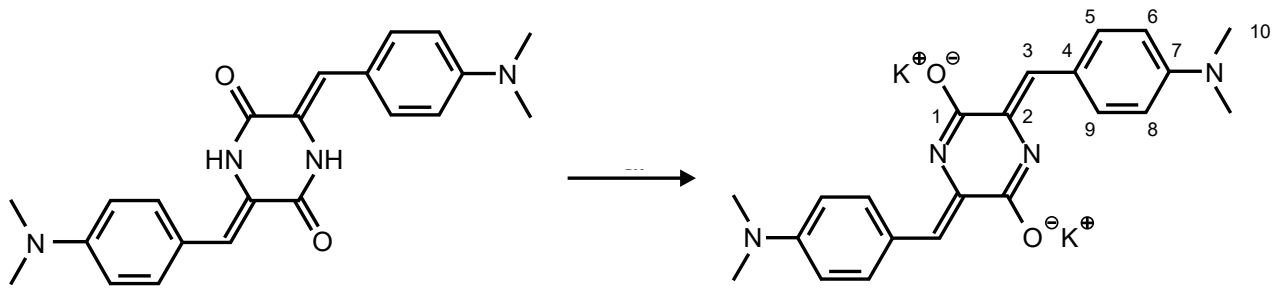
Negative ion APCI-HRMS, m/z: 339.0892 (calculated M.W. of product - 2[K^+]: 338.0814 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 339.0887 $g.mol^{-1}$)

Positive ion APCI-HRMS, m/z: 341.1031 (calculated M.W. of product - 2[K^+]: 338.0814 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] + [H^+]: 341.1033 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.33 (proton 3, s, 2 H), 7.62 (proton 5, m, 4 H), 8.02 (proton 6, m, 4 H), 9.72 (NH or OH proton)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 105.6 (carbon 7), 106.3 (carbon 3), 120.2 (carbon 8), 129.4 (carbon 5), 131.8 (carbon 6), 143.7 (carbon 2), 163.6 (carbon 1)

Dipotassium (3*Z*,6*Z*)-bis[(4-dimethylaminophenyl)methylidene]-3,6-dihydropyrazine-2,5-bis(olate) (6i)



4i **6i**

Scheme S25 Synthesis of dipotassium (3*Z*,6*Z*)-3,6-bis[(4-dimethylaminophenyl)methylidene] pyrazine-2,5-bis(olate) (**6i**).

Yield and purity: Quantitative (1.20 g). Isolated as a light brown solid. 95.77% pure based on ^{1}H NMR, 4-(dimethylamino)benzaldehyde is the primary impurity. M.P.: No melting point was observed; however, decomposition was observed at 312-317 °C.

FTIR, wavenumber in cm^{-1}: 2797 (aliphatic C-H stretch), 1650 and 1632 (C=N stretch), 1600 and 1576 (aromatic C=C stretch), 1498 and 1441 (aromatic C=C stretch), 1397, 1340, 1222, 1181, 1163, 1139, 1122, 1059, 943, 814, 788 and 759 (out of plane C-H bend), 509, 486, 473.

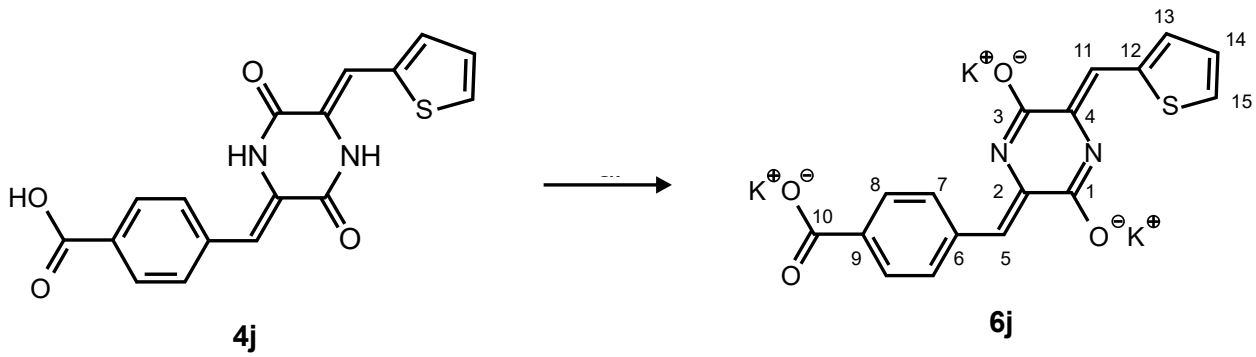
Negative ion APCI-HRMS, m/z: 375.1822 (calculated M.W. of product - 2[K^{+}]: 374.1754 g.mol^{-1}, calculated M.W. of mother ion + 2[H^{+}] - [H^{+}]: 375.1826 g.mol^{-1})

Positive ion APCI-HRMS, m/z: 377.1957 (calculated M.W. of product - 2[K^{+}]: 374.1754 g.mol^{-1}, calculated M.W. of mother ion + 2[H^{+}] + [H^{+}]: 377.1972)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 2.90 (proton 10, s, 12 H), 3.03 (4-(dimethylamino)benzaldehyde), 6.28 (proton 3, m, 2 H), 6.70 (proton 6 and proton 8, m, 4 H), 6.78 (4-(dimethylamino)benzaldehyde), 7.25 (proton 5, m, 2 H), 7.69 (4-(dimethylamino)benzaldehyde), 8.01 (proton 9, m, 2 H), 8.47 (NH or OH proton, s, 1 H), 8.60 (4-(dimethylamino)benzaldehyde), 9.67 (4-(dimethylamino)benzaldehyde)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 40.0 (carbon 10), 106.9 and 111.0 (carbon 3), 111.9 and 112.5 (carbon 6 and carbon 8), 123.6 and 127.5 (carbon 4), 129.0 (carbon 5), 130.7 (carbon 9), 136.9 (carbon 2), 148.0 and 148.7 (carbon 7), 161.2 (carbon 1)

Tripotassium (3*Z*,6*Z*)-3-[(4-carboxylatophenyl)methylidene]-6-[(thiophen-2-yl) methylidene]pyrazine-2,5-bis(olate) (6j)



Scheme S26 Synthesis of tripotassium (3*Z*,6*Z*)-3-[(4-carboxylatophenyl)methylidene]-6-[(thiophen-2-yl)methylidene]pyrazine-2,5-bis(olate) (**6j**).

Yield and purity: Quantitative (1.34 g). Isolated as an orange solid. M.P.: no melting point was observed; however, decomposition was observed at 316-318 °C.

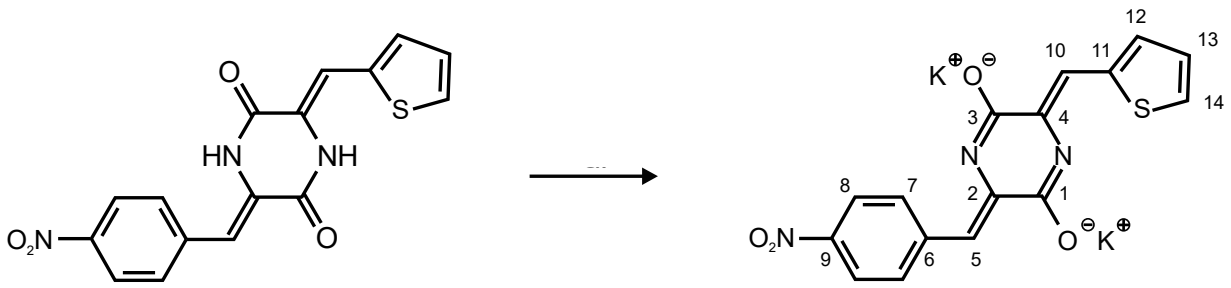
FTIR, wavenumber in cm^{-1}: 3630-3090 (broad O-H stretch and aromatic C-H stretch), 1651 and 1586 (carboxylate C=O stretch and imidate C=N stretch), 1533 and 1515 (aromatic C=C stretch), 1499 (aromatic C=C stretch), 1385, 1358, 1315, 1293, 1240, 1208, 1176, 1123, 1102, 1049, 1014, 969, 887, 853, 826, 801, 777-695 (out of plane C-H bend), 649, 590, 556, 527, 496, 481, 460, 407.

Negative ion APCI-HRMS, m/z: 339.0458 (calculated M.W. of product - 3[K^+]: 337.0299 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 339.0445 $g.mol^{-1}$)

^{1}H NMR (D_2O, 600 MHz): δ 6.66 (proton 11, s, 1 H), 6.98 (proton 5, s, 1 H), 7.08 (proton 14, m, 1 H), 7.32 (proton 13, m, 1 H), 7.53 (proton 15, m, 1 H), 7.59 (proton 7, m, 2 H), 7.92 (proton 8, m, 2 H)

^{13}C NMR (D_2O, 150 MHz): δ 112.8 (carbon 11), 113.7 (carbon 5), 127.5 (carbon 14), 129.3 (carbon 7), 129.9 (carbon 8), 129.9 (carbon 15), 130.4 (carbon 13), 130.5 (carbon 12), 132.9 (carbon 6), 135.7 (carbon 9), 137.8 and 139.1 (carbon 2 and carbon 4), 163.4 and 163.6 (carbon 1 and carbon 3), 175.6 (carbon 10)

Dipotassium (3*Z*,6*Z*)-3-(4-nitrophenyl)methylidene-6-(thiophen-2-yl)methylidene-3,6-dihydropyrazine-2,5-bis(olate) (6k)



4k **6k**

Scheme S27 Synthesis of dipotassium (3*Z*,6*Z*)-3-[(4-nitrophenyl)methylidene]-6-[(thiophen-2-yl)methylidene]pyrazine-2,5-bis(olate) (**6k**).

Yield and purity: Quantitative (1.22 g). Isolated as a black solid. M.P.: No melting point was observed; however, decomposition was observed at 298-300 °C.

FTIR, wavenumber in cm^{-1}: 3352, 3103 (aromatic C-H stretch), 2979, 2255, 1658, 1642 (C=N stretch), 1582, 1534 and 1523 (aromatic C=C stretch), 1459 and, 1407 (aromatic C=C stretch), 1380, 1331, 1304, 1267, 1209, 1165, 1106, 1090, 1073, 1046, 990, 967, 879, 862, 842, 809, 798-671 (out of plane C-H bend), 641, 559, 525, 492, 466, 417.

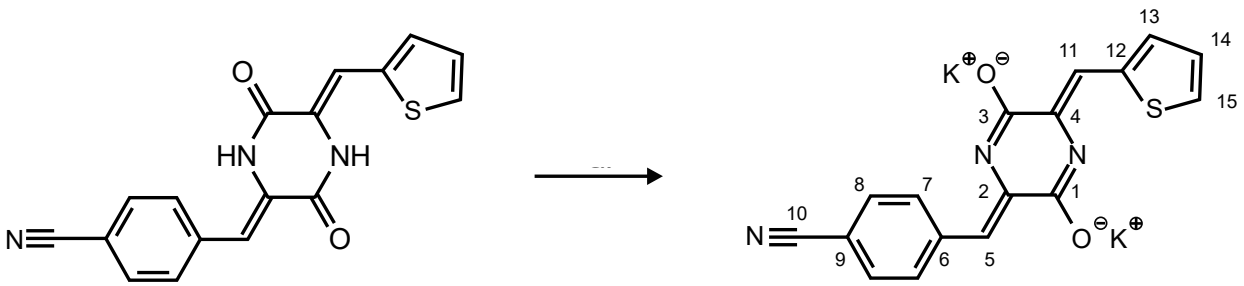
Negative ion APCI-HRMS, m/z: 340.0431 (calculated M.W. of product - 2[K^+]: 341.0470 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 340.0398 g,mol^{-1})

Positive ion APCI-HRMS, m/z: 342.0521 (calculated M.W. of product - 2[K^+]: 341.0470 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] + [H^+]: 342.0543 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.34 (proton 5, s, 1 H), 6.63 (proton 10, m, 1 H), 6.92 (proton 13, m, 1 H), 6.97 (proton 12, m, 1 H), 7.18 (proton 14, m, 1 H), 7.98 (proton 7, m, 2 H), 8.14 (proton 8, m, 2 H), 8.57 and 9.22 (NH or OH proton)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 103.6 (carbon 5), 104.3 (carbon 10), 123.3 (carbon 7), 123.6 (carbon 12), 124.5 (carbon 14), 125.8 (carbon 13), 127.5 (carbon 8), 140.4 and 141.9 (carbon 2 and carbon 4), 148.7 (carbon 9), 150.7 (carbon 11), 164.7 and 167.6 (carbon 1 and carbon 3)

Dipotassium (3*Z*,6*Z*)-3-[(4-cyanophenyl)methylidene]-6-[(thiophen-2-yl)methylidene] pyrazine-2,5-bis(olate) (6l)



4l **6l**

Scheme S28 Synthesis of dipotassium (3*Z*,6*Z*)-3-[(4-cyanophenyl)methylidene]-6-[(thiophen-2-yl)methylidene]pyrazine-2,5-bis(olate) (**6l**).

Yield and purity: Quantitative (1.24 g). Isolated as a red solid. M.P.: No melting point observed; however, decomposition observed at 302-306 °C.

FTIR, wavenumber in cm^{-1}: 3549, 3354, 3230, 2216 (C≡N stretch), 1651 (C=N stretch), 1597, 1577 and 1518 (aromatic C=C stretch), 1398, 1355, 1317, 1307, 1242, 1210, 1172, 1138, 1120, 1071, 1046, 996, 965, 868, 851, 822, 780-678 (out of plane C-H bend), 644, 620, 556, 539, 495, 450.

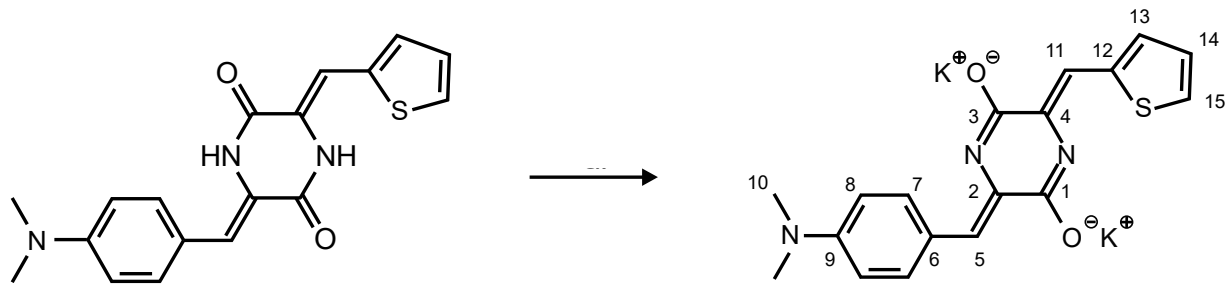
Negative ion APCI-HRMS, m/z: 320.0498 (calculated M.W. of product - 2[K^+]: 319.0426 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 320.0499 $g.mol^{-1}$)

Positive ion APCI-MS, m/z: 322.0644 (calculated M.W. of product - 2[K^+]: 319.0426 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] + [H^+]: 322.0645 $g.mol^{-1}$)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.34 and 6.48 (proton 5, s, 1 H), 6.66 and 6.70 (proton 11, s, 1 H), 6.96 (proton 13, convoluted m, 1 H), 7.06 and 7.11 (carbon 14, convoluted m, 1 H), 7.27 and 7.31 (carbon 15, convoluted m, 1 H), 7.60 (proton 7, m, 2 H), 7.86 and 7.98 (proton 8, convoluted m, 2 H), 8.58 and 9.22 (NH and OH protons)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 104.7 (carbon 11), 105.4 (carbon 5), 120.5 (carbon 10), 125.1 (carbon 13), 125.6 (carbon 15), 126.7 (carbon 14), 129.3 (carbon 8), 132.0 (carbon 7), 144.2 (carbon 12), 164.2 and 168.3 (carbon 1 and carbon 3)

Dipotassium (3*Z*,6*Z*)-3-[(4-dimethylaminophenyl)methylidene]-6-[(thiophen-2-yl) methylidene]pyrazine-2,5-bis(olate) (6m)



Scheme S29 Synthesis of dipotassium (3*Z*,6*Z*)-3-[(4-dimethylaminophenyl)methylidene]-6-[(thiophen-2-yl)methylidene]pyrazine-2,5-bis(olate) (**6m**).

Yield and purity: Quantitative (1.22 g). Isolated as a mustard brown solid. 80.66% pure based on 1H NMR, the impurity remains unidentified, however, it appears to be a benzylamine derivative. M.P.: 302-304 °C, decomposition was observed upon melting.

FTIR, wavenumber in cm^{-1}: 3545, 3353, 3116, 3081 (aromatic C-H stretch), 3065, 1691, 1655 (C=N stretch), 1636, 1607, 1577, 1530 (aromatic C=C stretch), 1459 and 1428 (aromatic C=C stretch), 1380, 1358, 1334, 1251, 1225, 1171, 1109, 1094, 1052, 1038, 1028, 979, 876, 854, 832, 812, 758-675 (out of plane C-H bend), 649, 611, 570, 521, 500, 480, 447.

Negative ion APCI-MS, m/z: 338.0949 (calculated M.W. of product - 2[K^+]: 337.0856 $g.mol^{-1}$, calculated M.W. of mother ion + 2[H^+] - [H^+]: 338.0969)

^{1}H NMR (DMSO-d_6, 600 MHz): δ 2.91 (proton 10, s, 6 H), 6.42 (proton 5, s, 1 H), 6.54, 6.60, 6.66 (proton 11, s, 1 H), 6.73 (proton 8, convoluted m, 2 H), 6.90, 6.94 (proton 14, convoluted m, 1 H), 7.06 (proton 13, convoluted m, 1 H), 7.17, 7.26 and 7.28 (convoluted peaks, proton 7 and proton 15, 3 H), 7.53, 8.67 (NH or OH proton)

^{13}C NMR (DMSO-d_6, 150 MHz): δ 39.9 (carbon 10), 46.3, 103.6, 105.1 (carbon 11), 108.5 (carbon 5), 112.5 (carbon 8), 123.3, 124.5 (carbon 13), 124.9, 125.3 (carbon 14), 125.5 (carbon 15), 129.2 (carbon 7), 138.5, 141.2, 141.6, 149.9 (carbon 9), 160.4, 161.8, 162.1, 167.4

FTIR spectra

Precursors

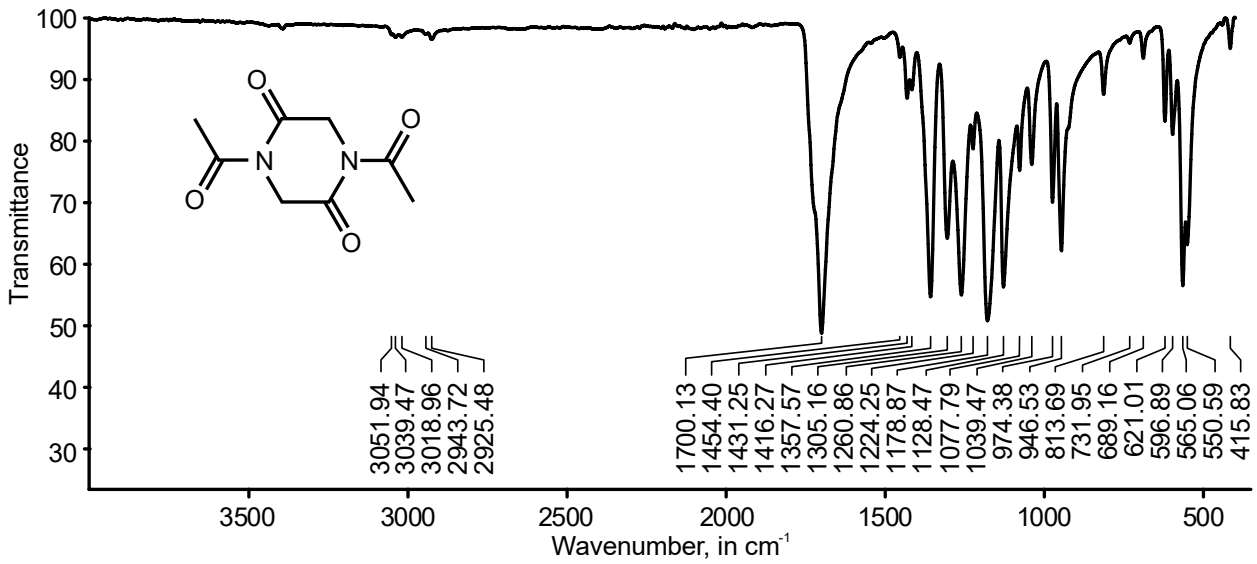


Figure S1.1 Solid-state FTIR of **2**.

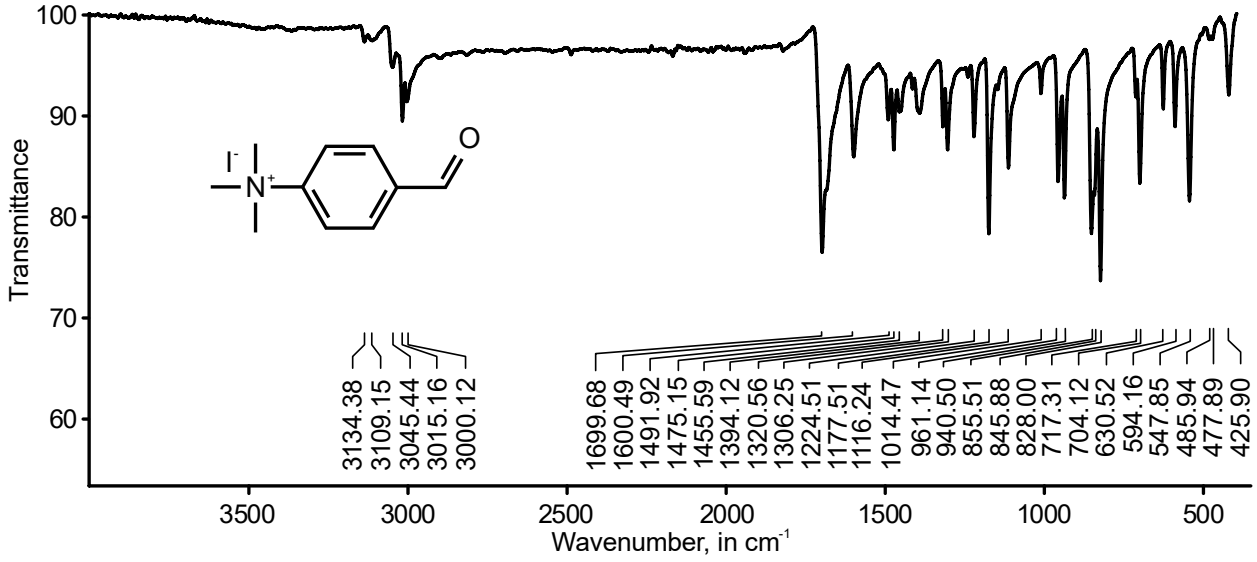


Figure S1.2 Solid-state FTIR of **3i**.

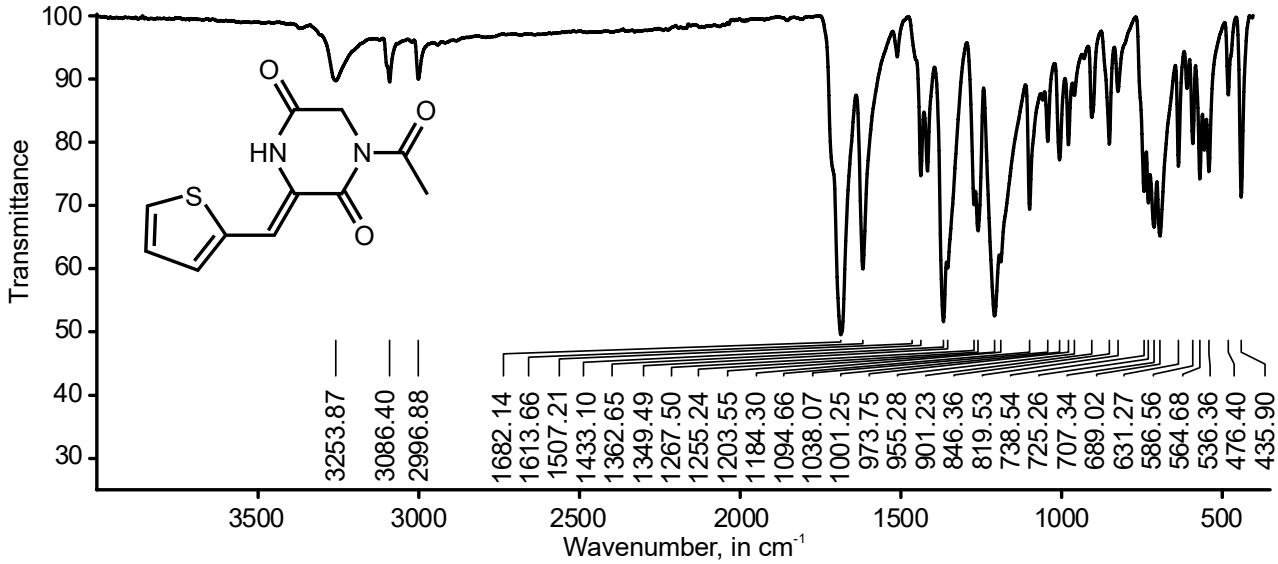


Figure S1.3 Solid-state FTIR of **9**.

4a and 6a

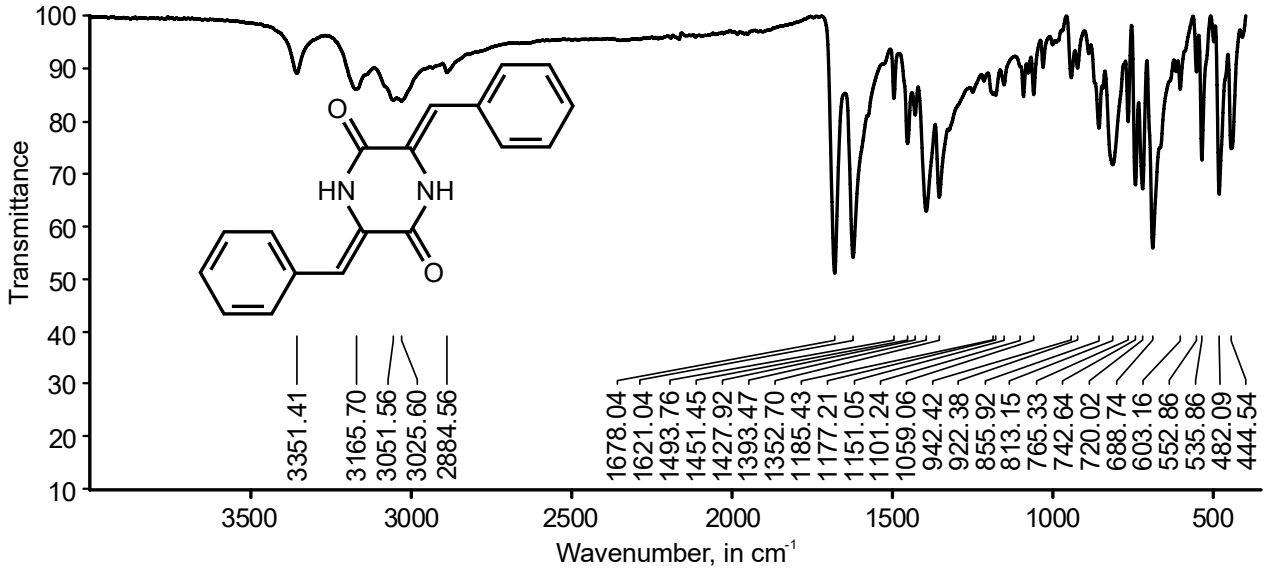


Figure S1.4 Solid-state FTIR of **4a**.

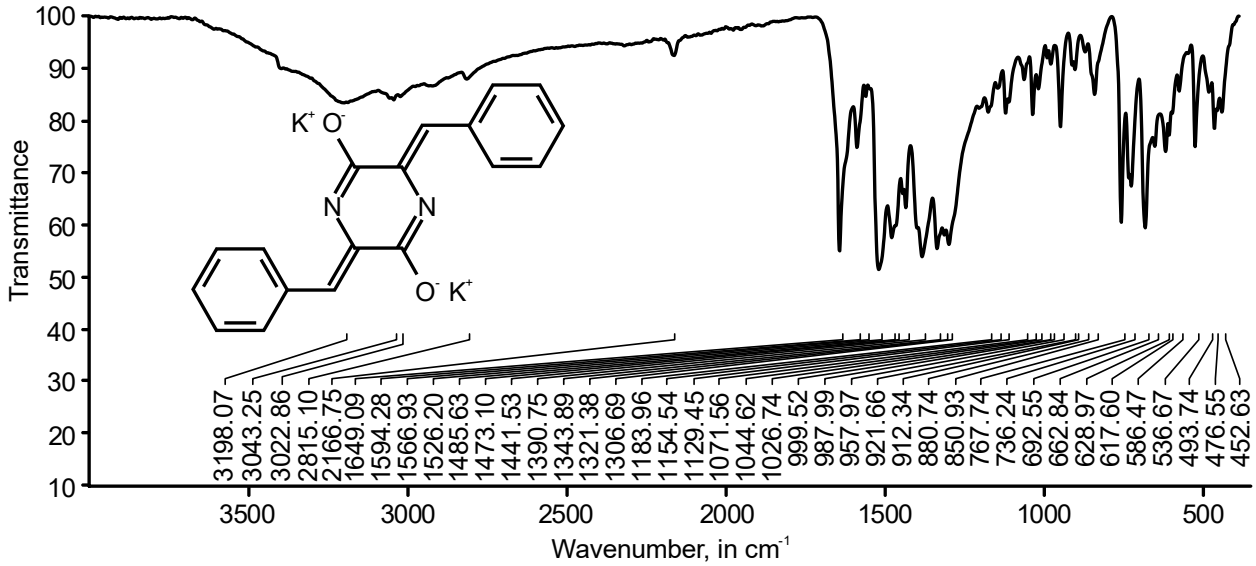


Figure S1.5 Solid-state FTIR of **6a**.

4b and 6b

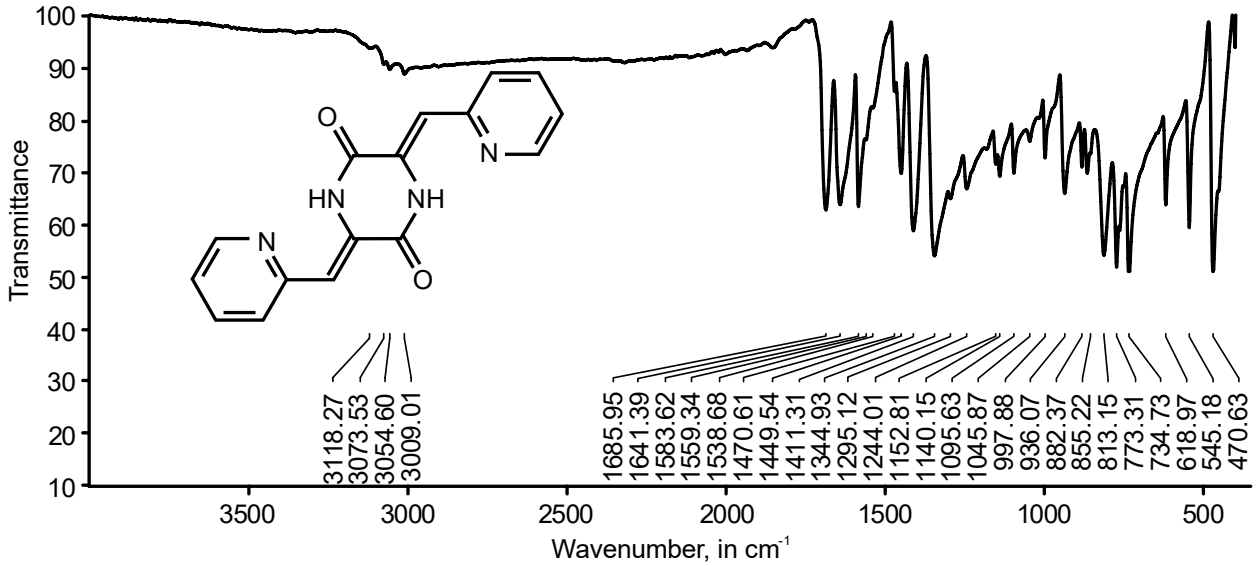


Figure S1.6 Solid-state FTIR of **4b**.

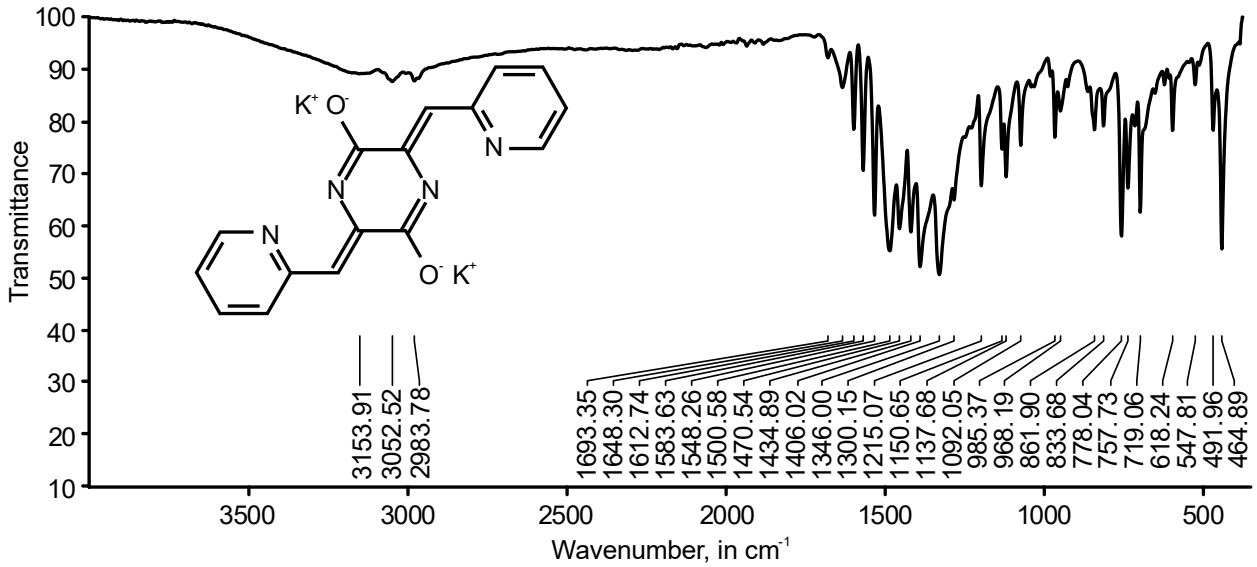


Figure S1.7 Solid-state FTIR of **6b**.

4c and 6c

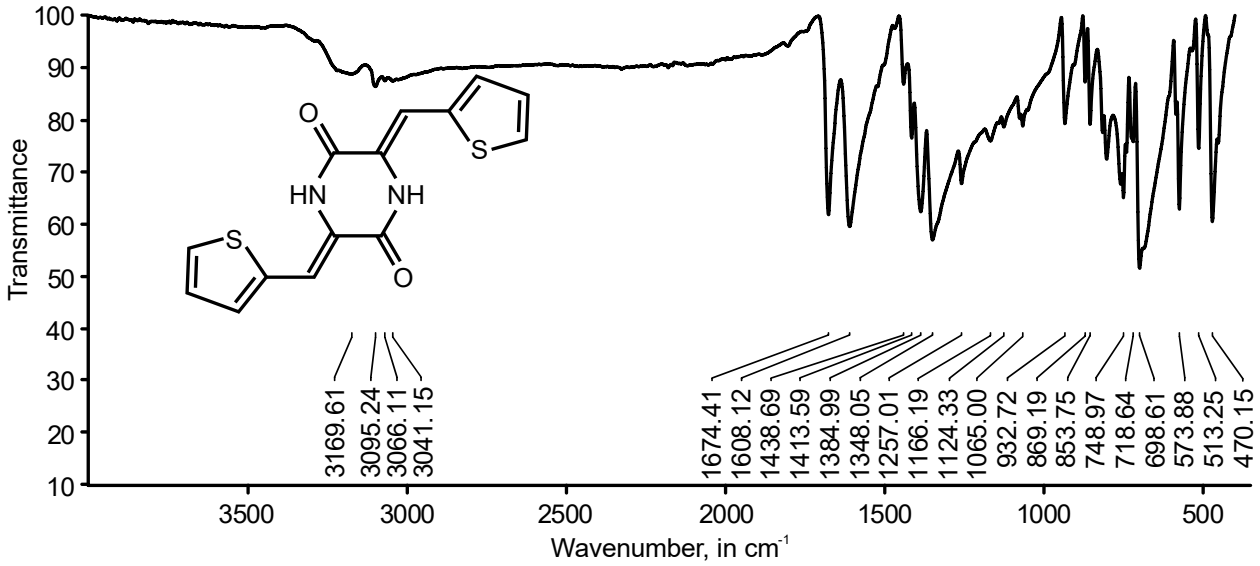


Figure S1.8 Solid-state FTIR of **4c**.

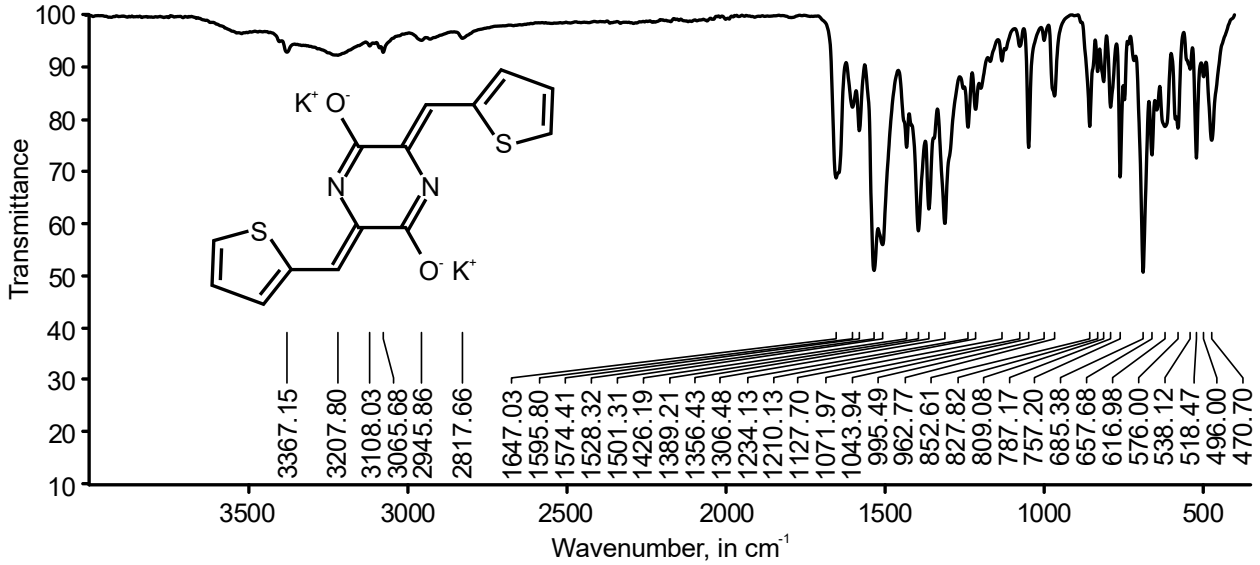


Figure S1.9 Solid-state FTIR of **6c**.

4d and 6d

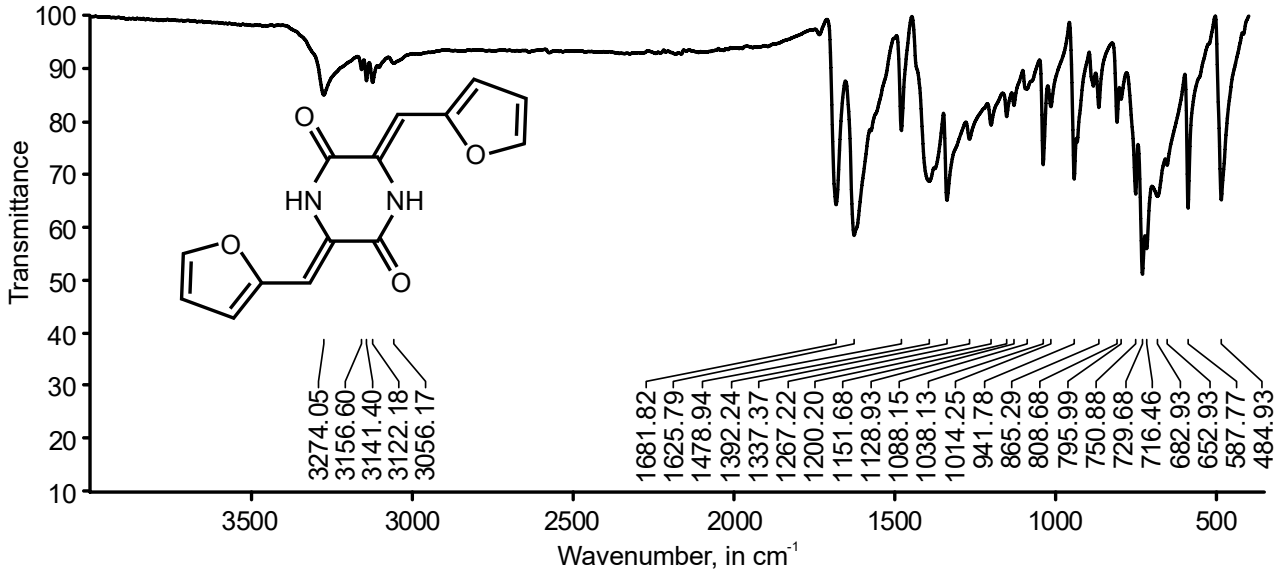


Figure S1.10 Solid-state FTIR of **4d**.

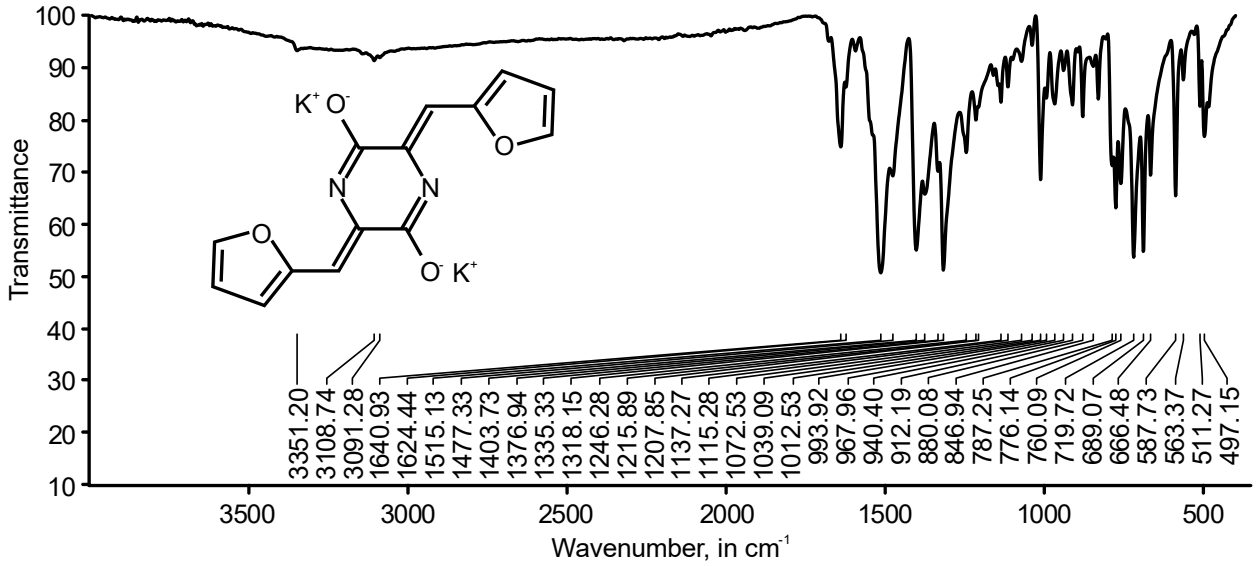


Figure S1.11 Solid-state FTIR of **6d**.

4e and 6e

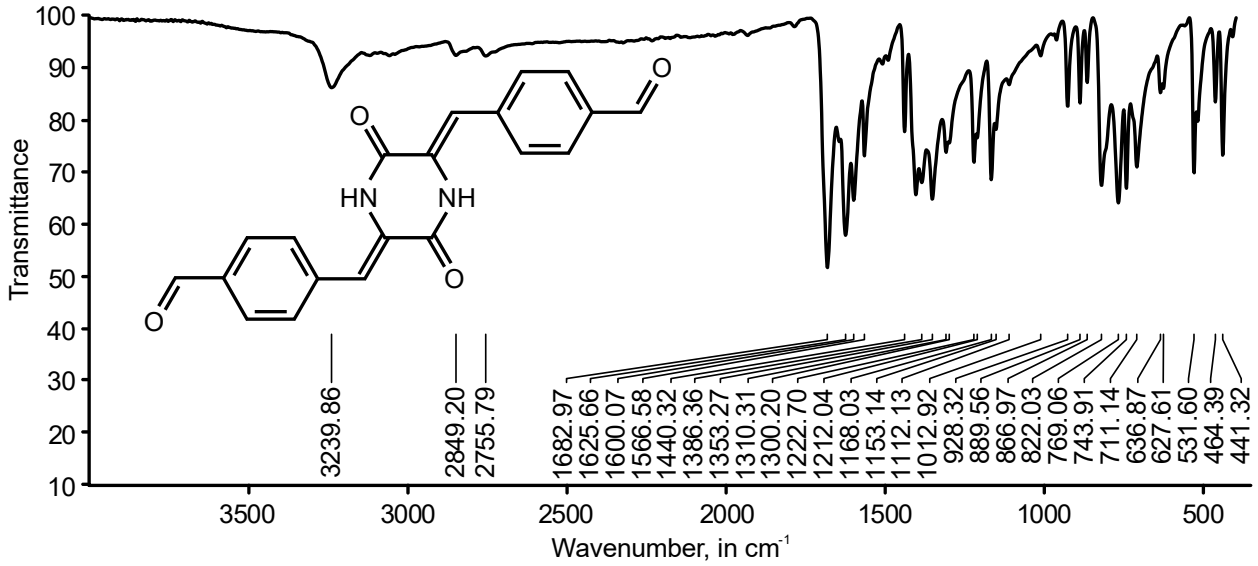


Figure S1.12 Solid-state FTIR of **4e**.

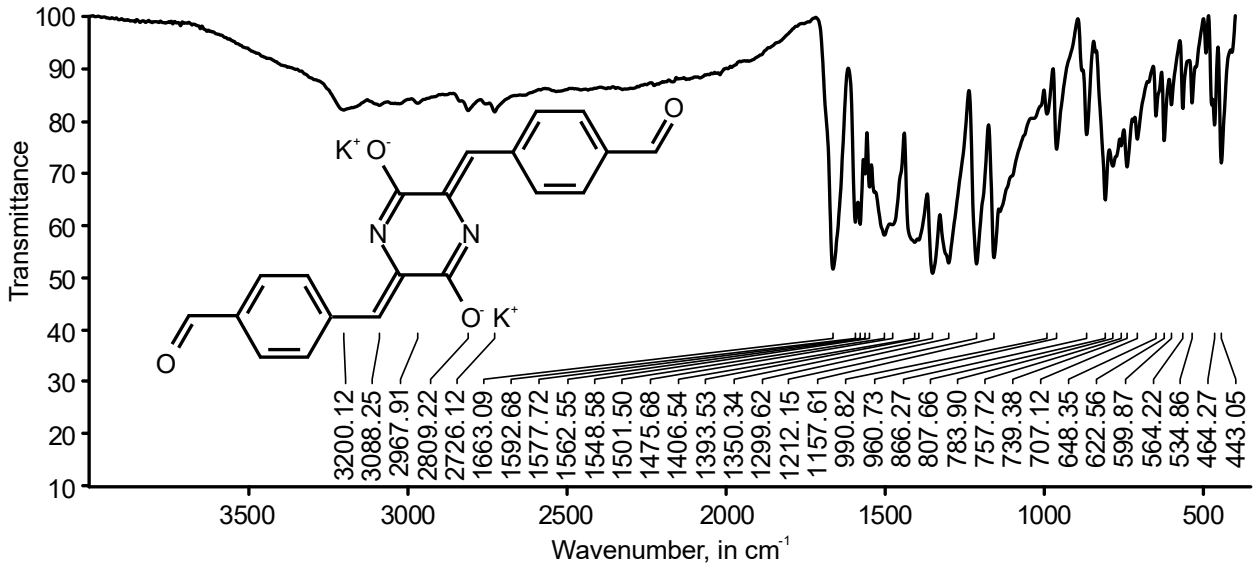


Figure S1.13 Solid-state FTIR of **6e**.

4f and 6f

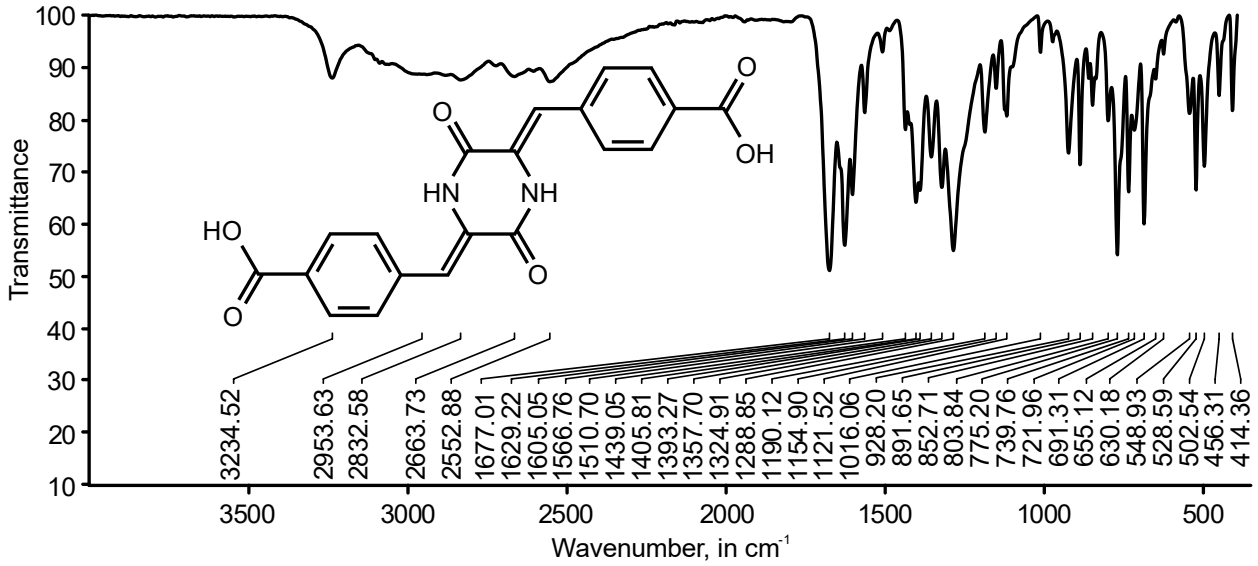


Figure S1.14 Solid-state FTIR of **4f**.

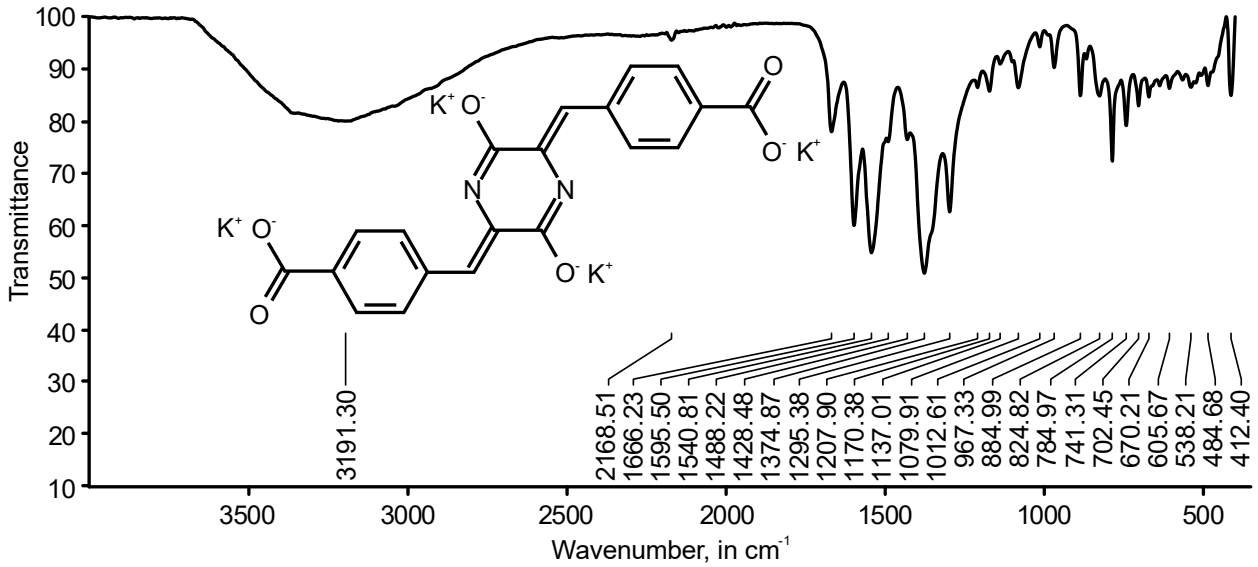


Figure S1.15 Solid-state FTIR of **6f**.

4g and 6g

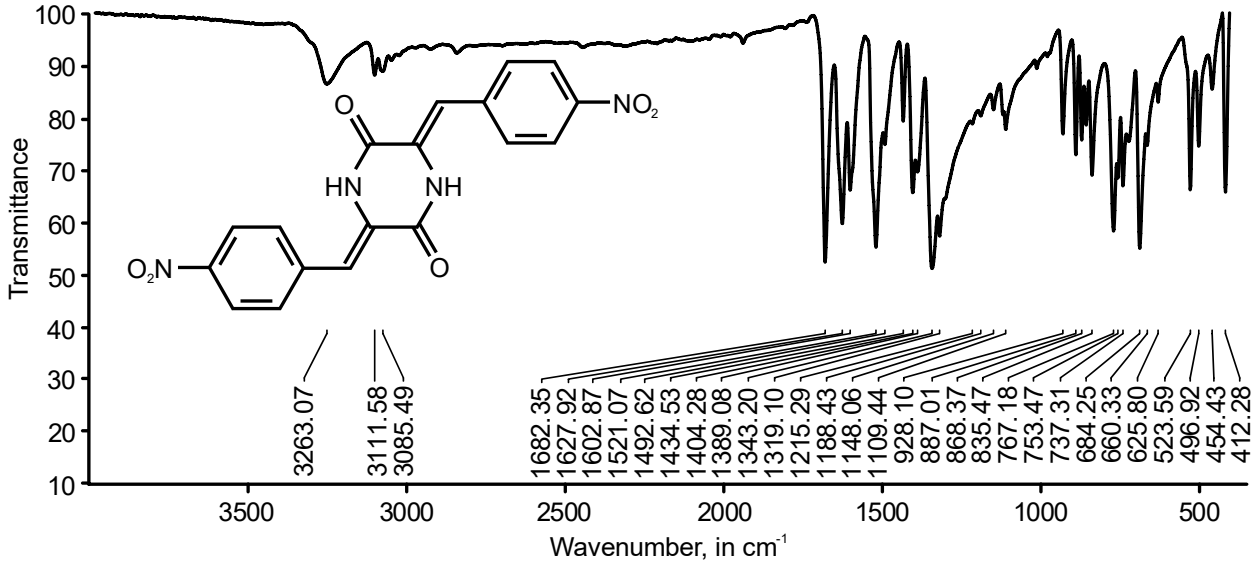


Figure S1.16 Solid-state FTIR of **4g**.

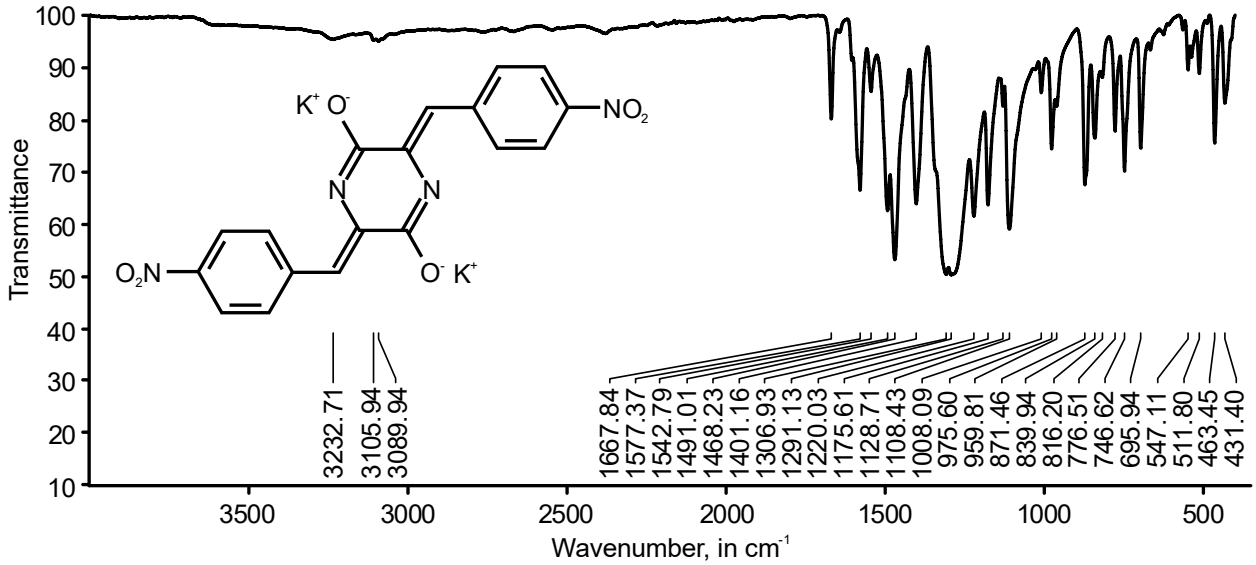


Figure S1.17 Solid-state FTIR of **6g**.

4h and 6h

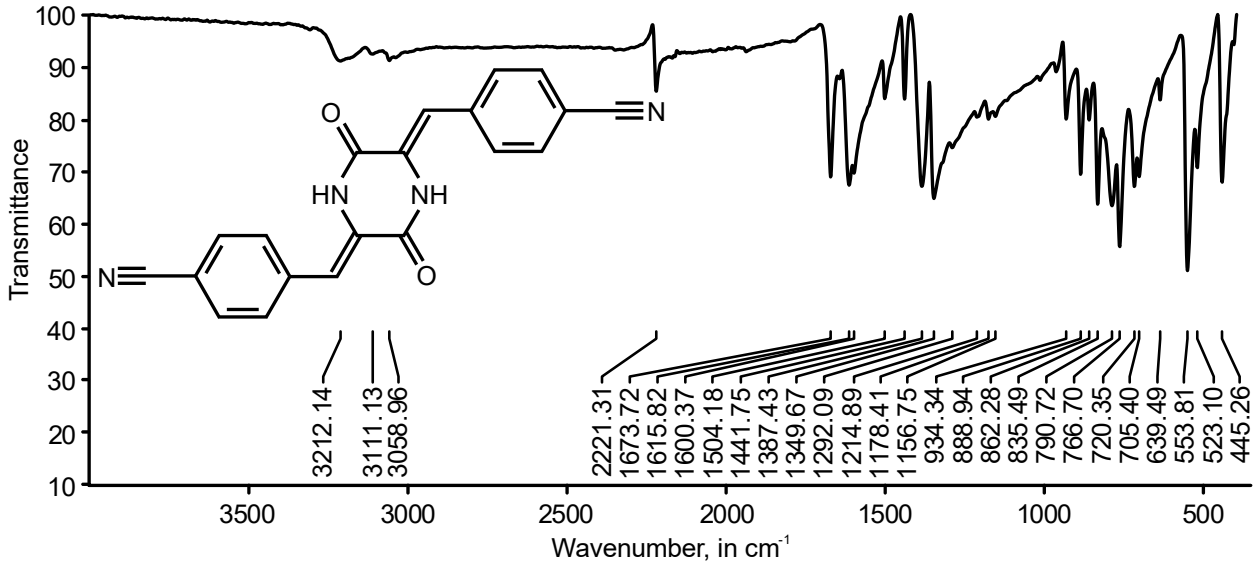


Figure S1.18 Solid-state FTIR of **4h**.

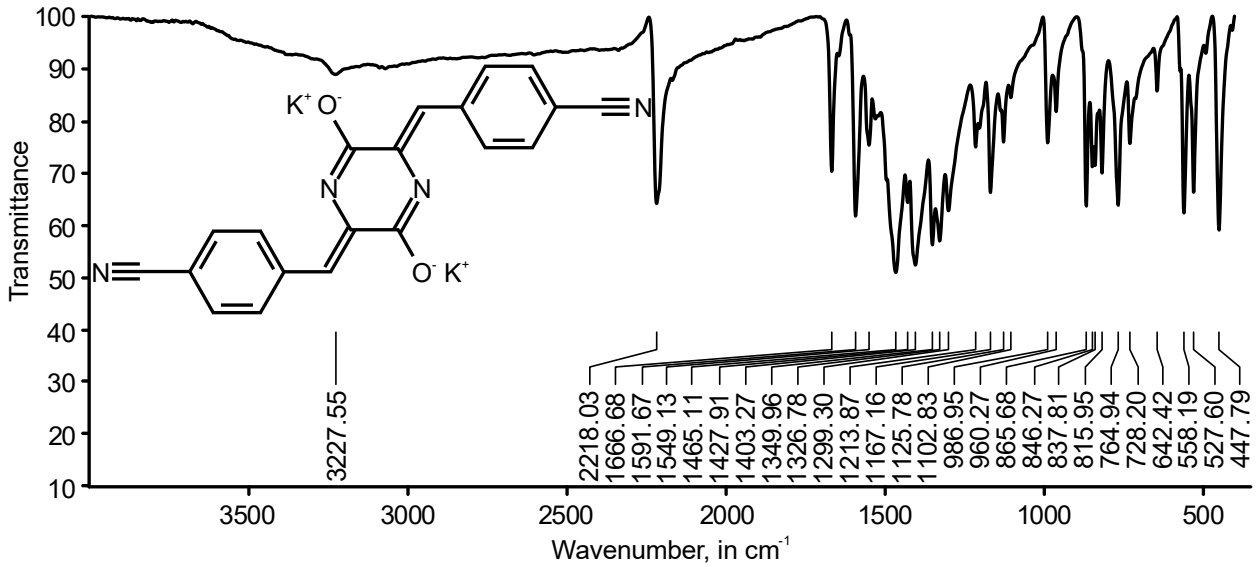


Figure S1.19 Solid-state FTIR of **6h**.

4i and 6i

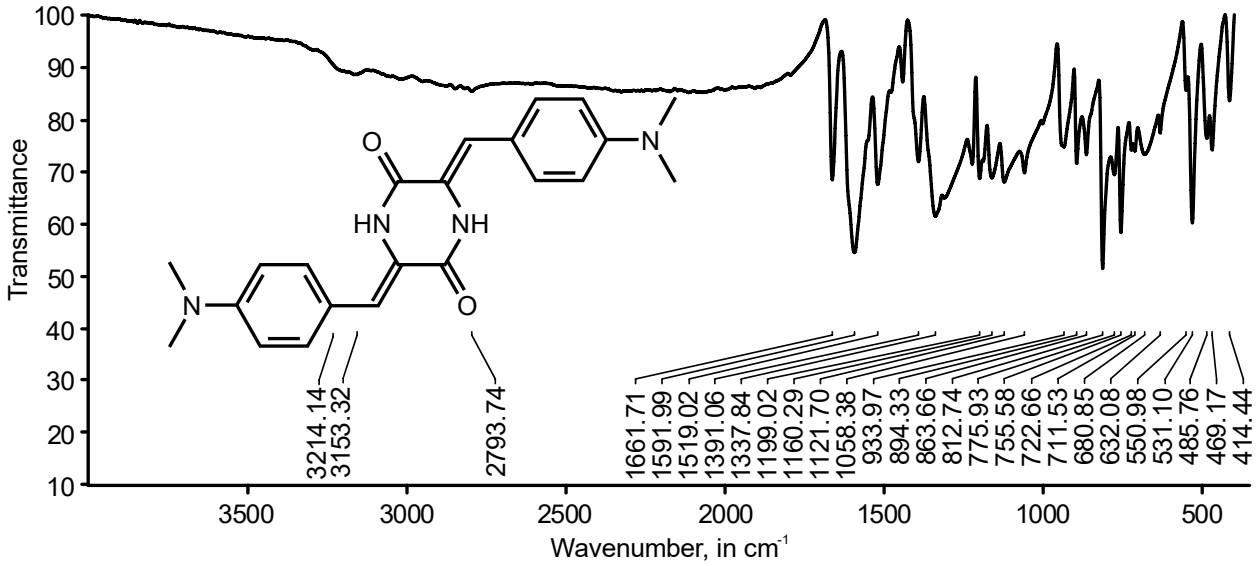


Figure S1.20 Solid-state FTIR of **4i**.

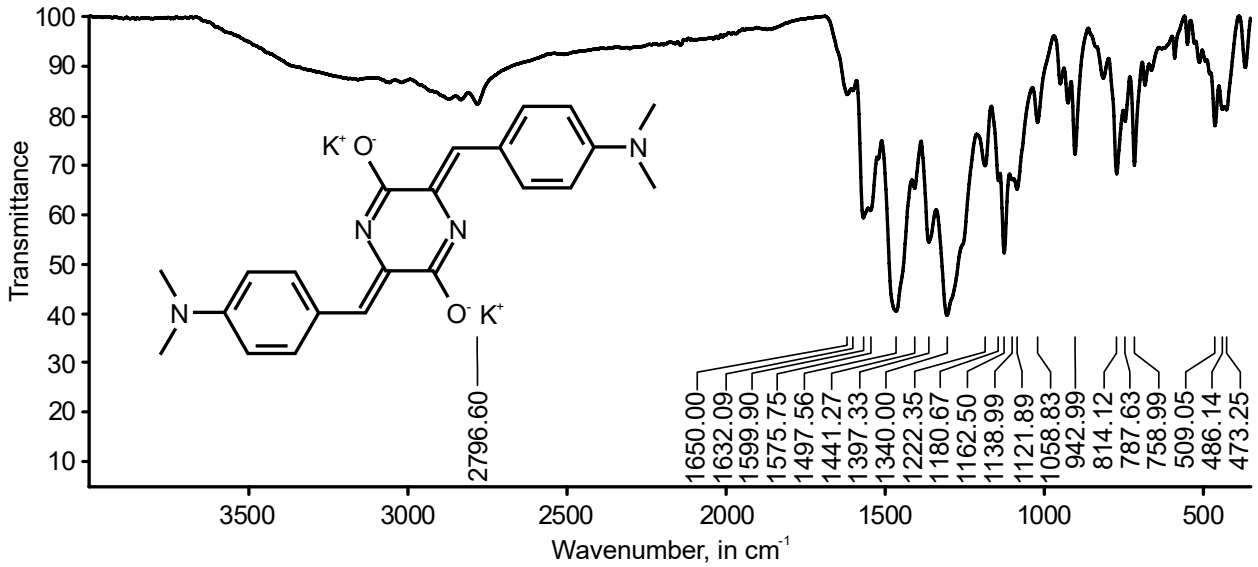


Figure S1.21 Solid-state FTIR of **6i**.

4j and 6j

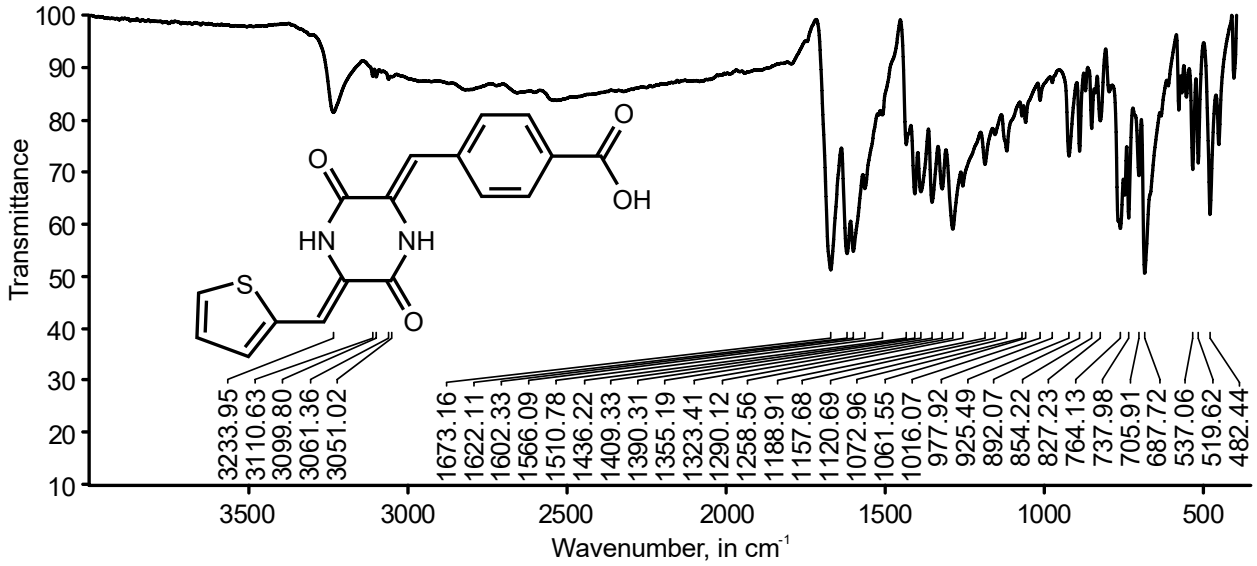


Figure S1.22 Solid-state FTIR of **4j**.

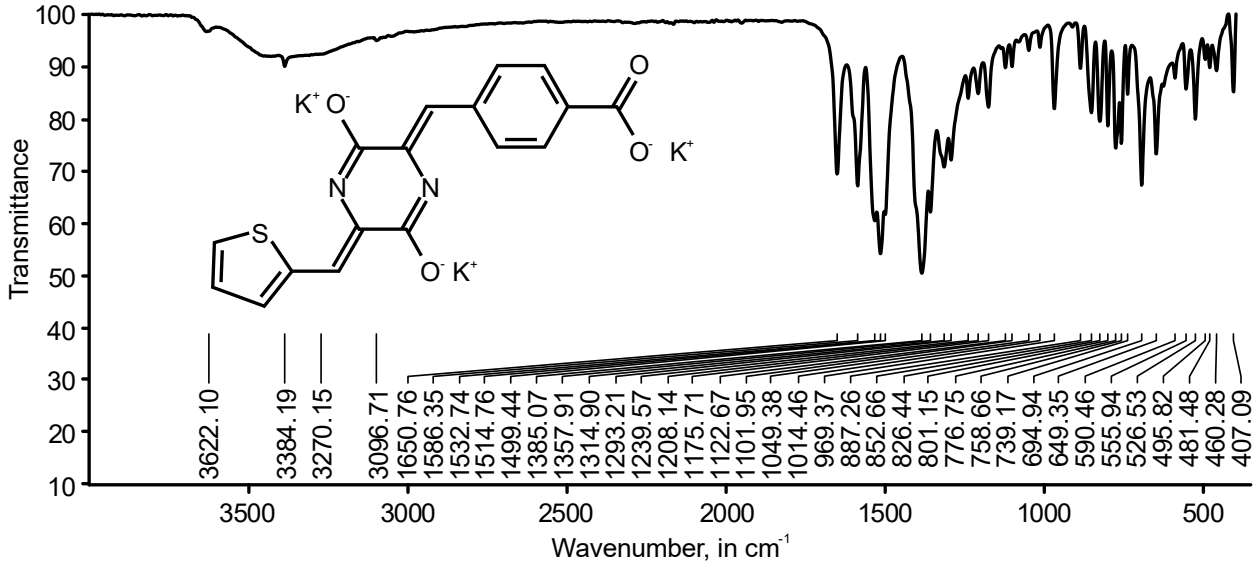


Figure S1.23 Solid-state FTIR of **6j**.

4k and 6k

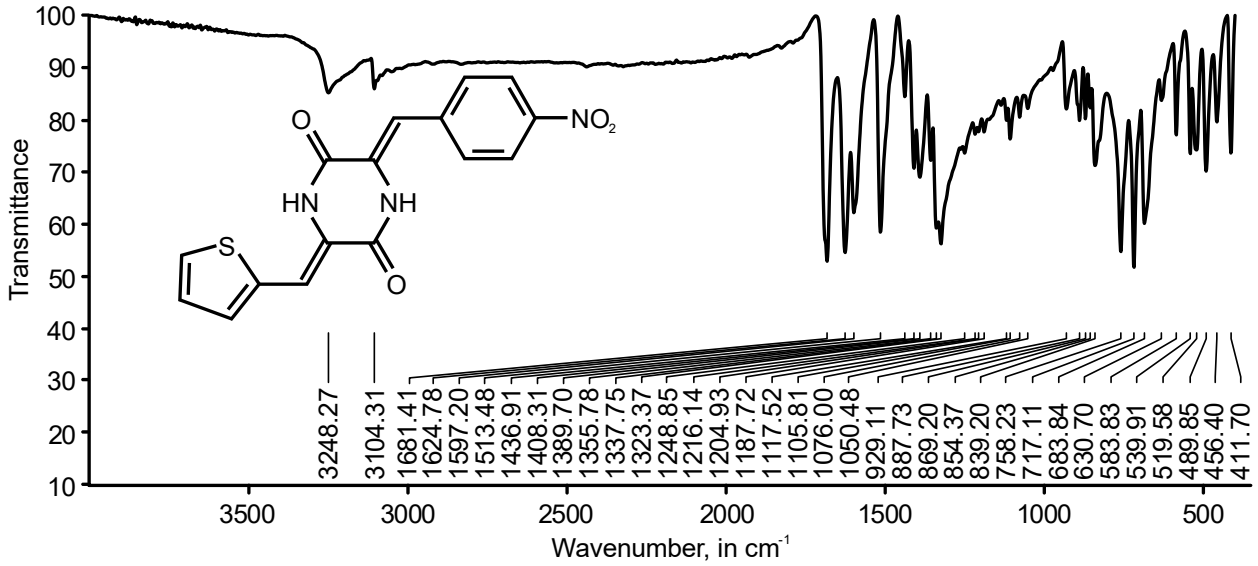


Figure S1.24 Solid-state FTIR of **4k**.

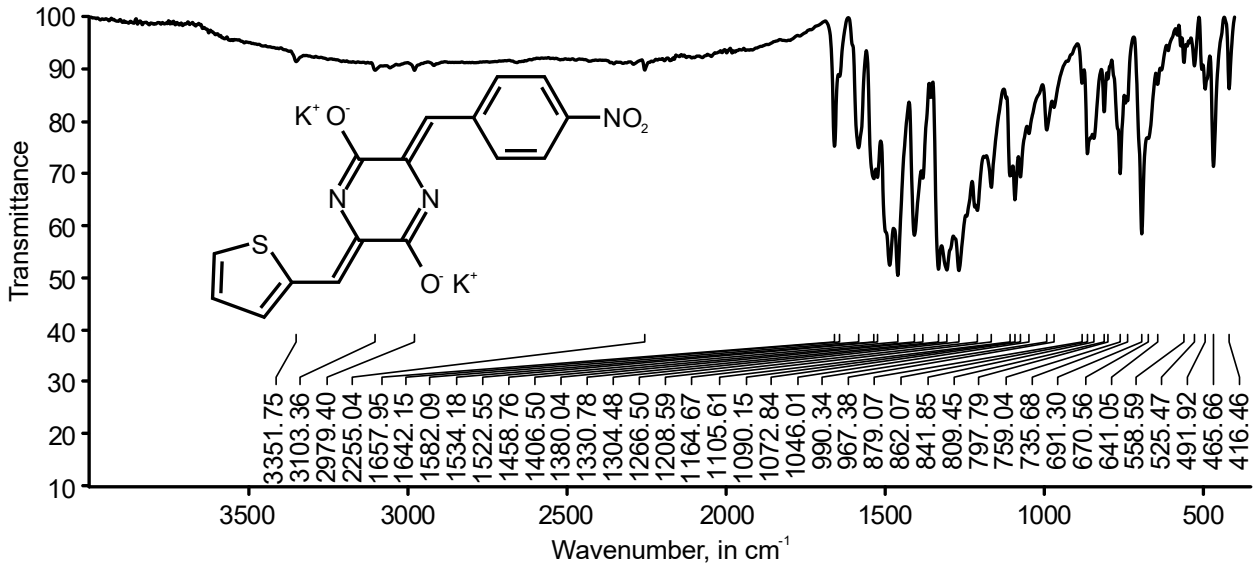


Figure S1.25 Solid-state FTIR of **6k**.

4l and 6l

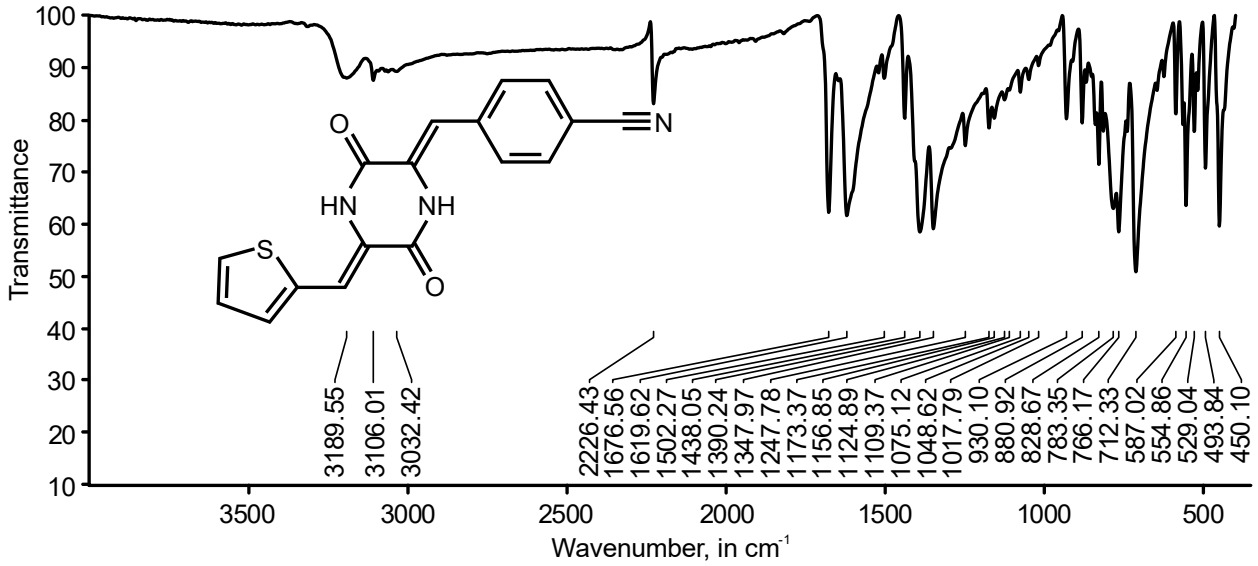


Figure S1.26 Solid-state FTIR of **4l**.

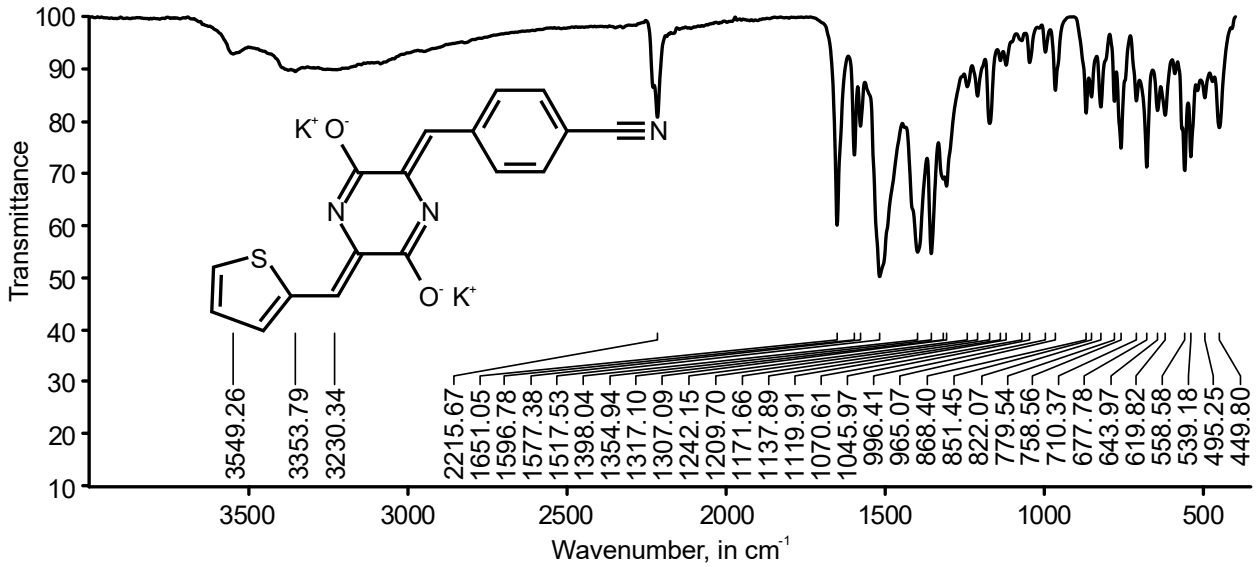


Figure S1.27 Solid-state FTIR **6l**.

4m and 6m

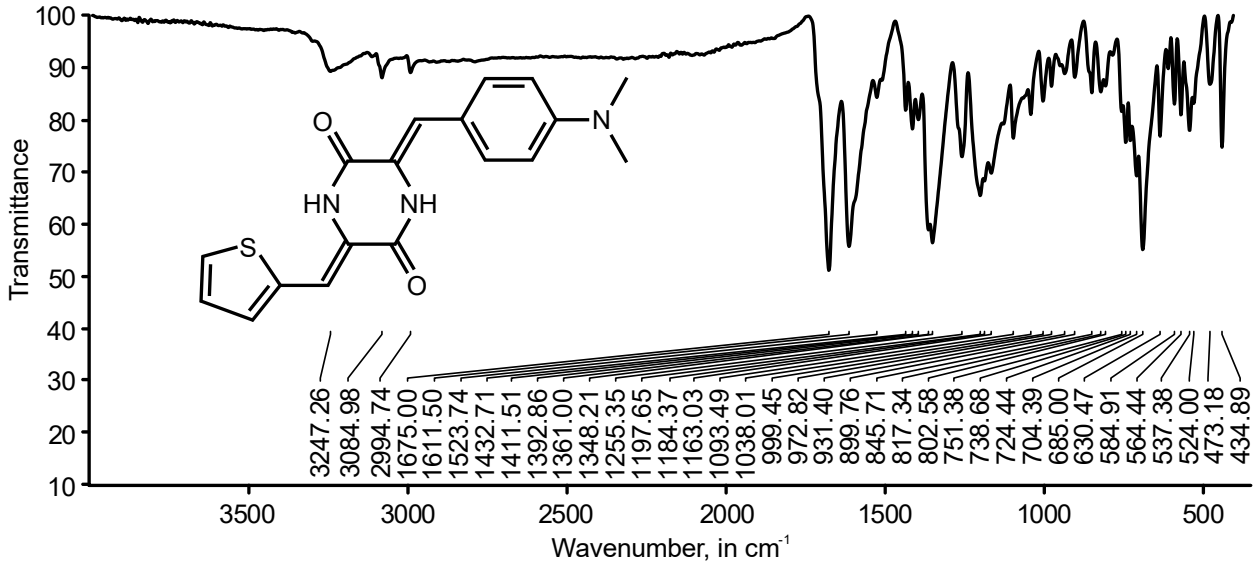


Figure S1.28 Solid-state FTIR of **4m**.

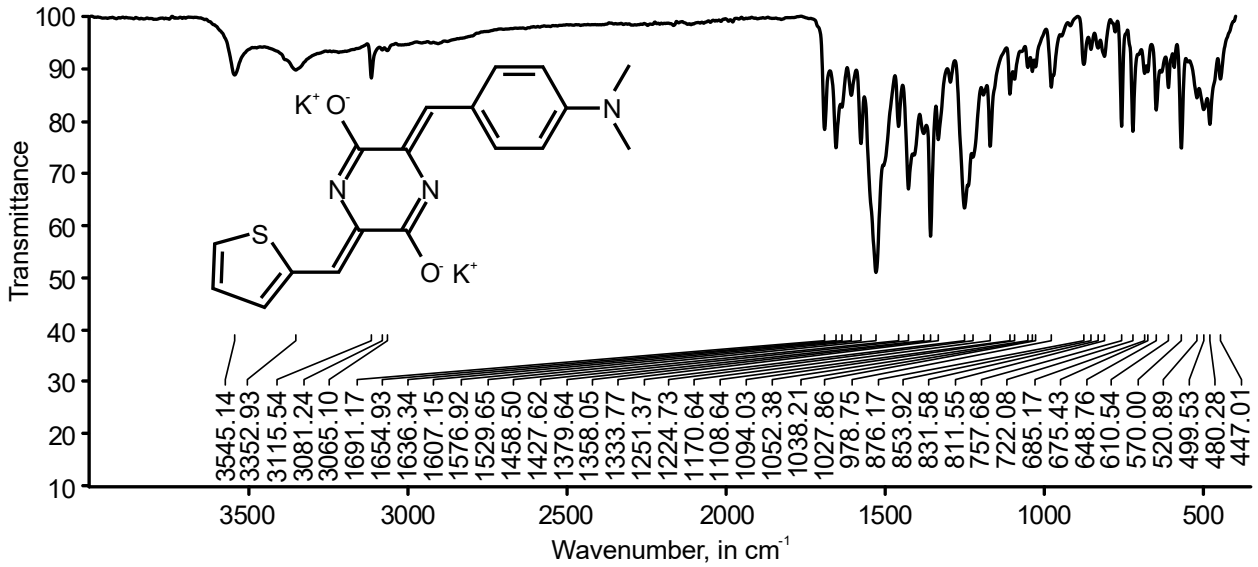


Figure S1.29 Solid-state FTIR of **6m**.

HR-MS spectra

Precursors

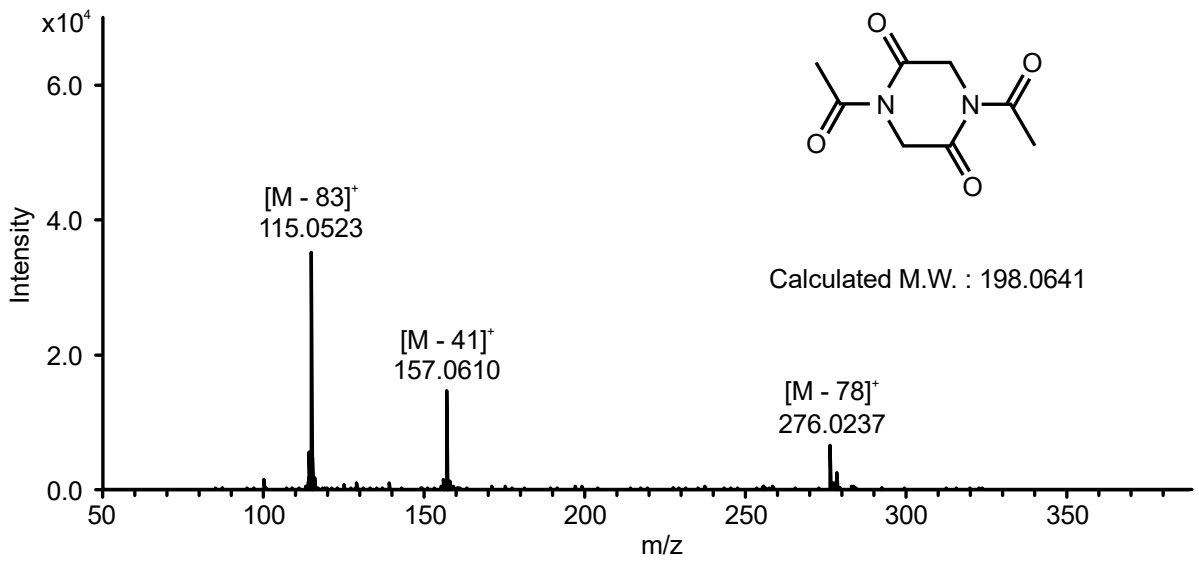


Figure S2.1 Positive ion APCI-MS of **2**.

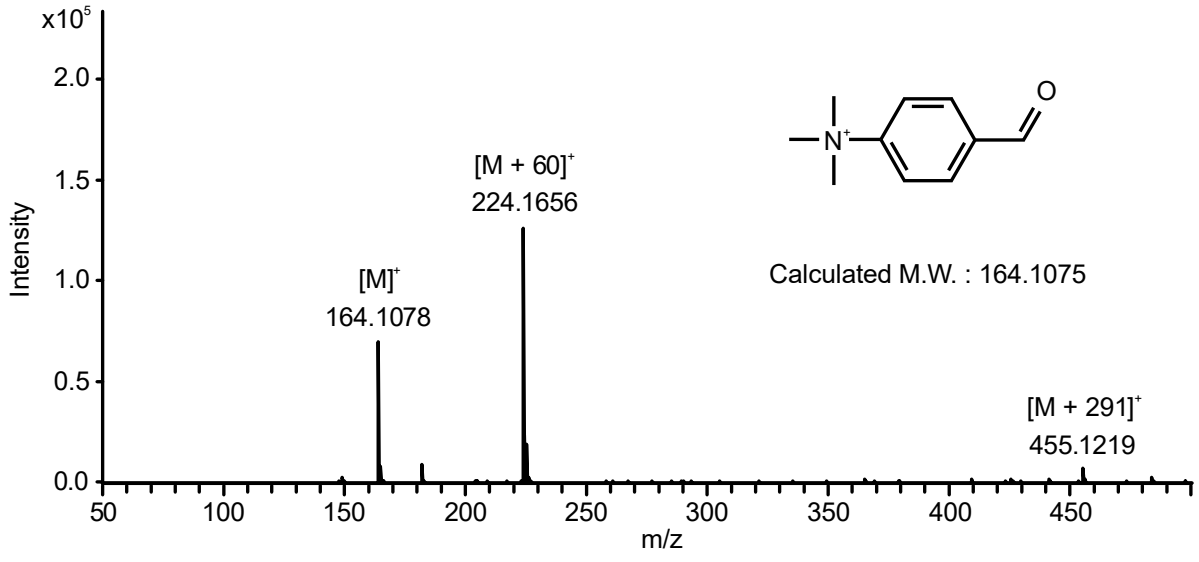


Figure S2.2 Positive ion ESI-MS of **3i**.

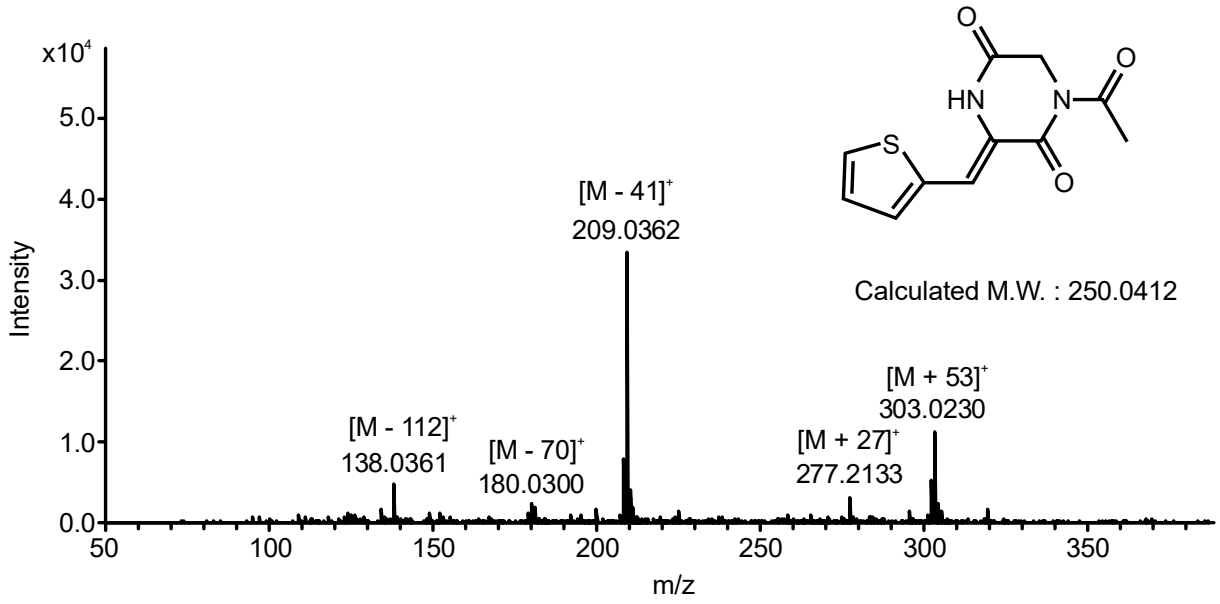


Figure S2.3 Positive ion APCI-MS of **9**.

4a and 6a

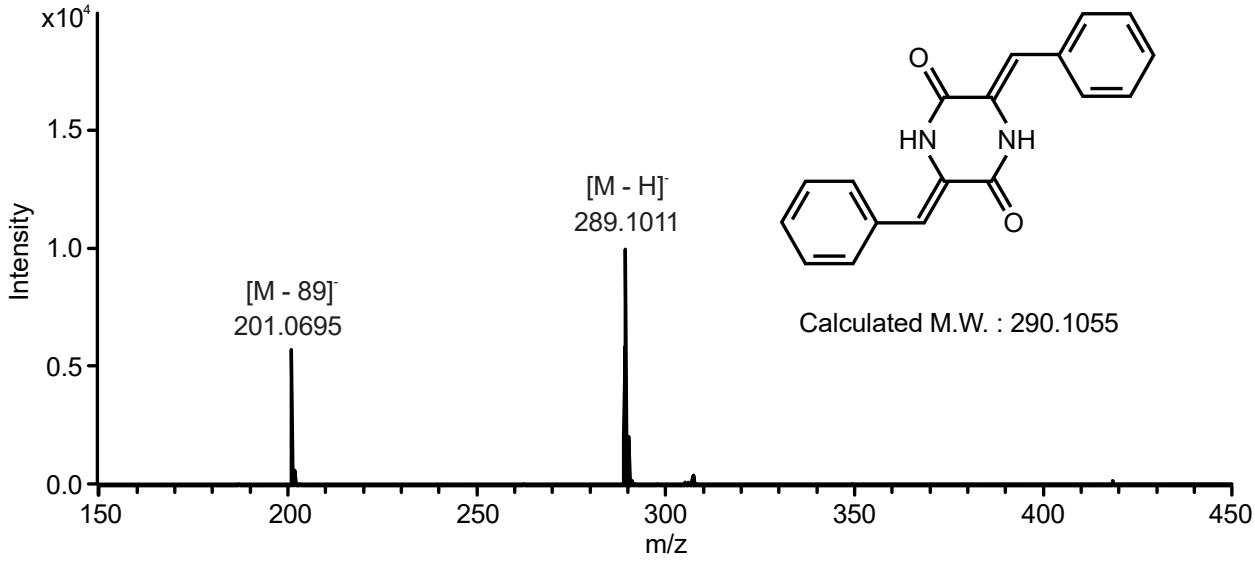


Figure S2.4 Negative ion APCI-MS of **4a**.

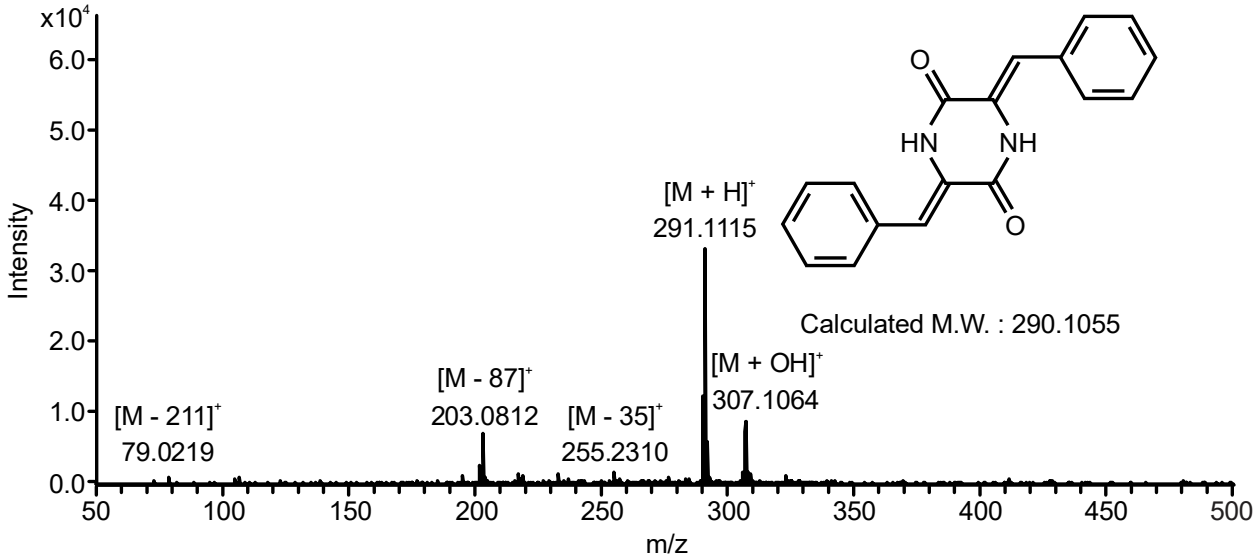


Figure S2.5 Positive ion APCI-MS of **4a**.

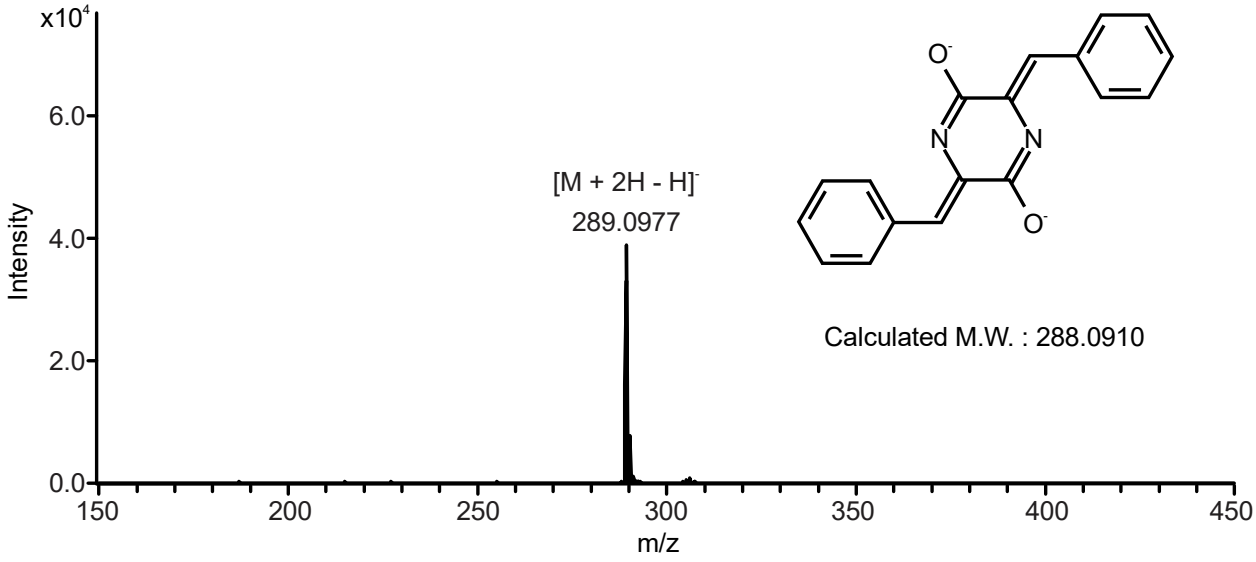


Figure S2.6 Negative ion APCI-MS of **6a**.

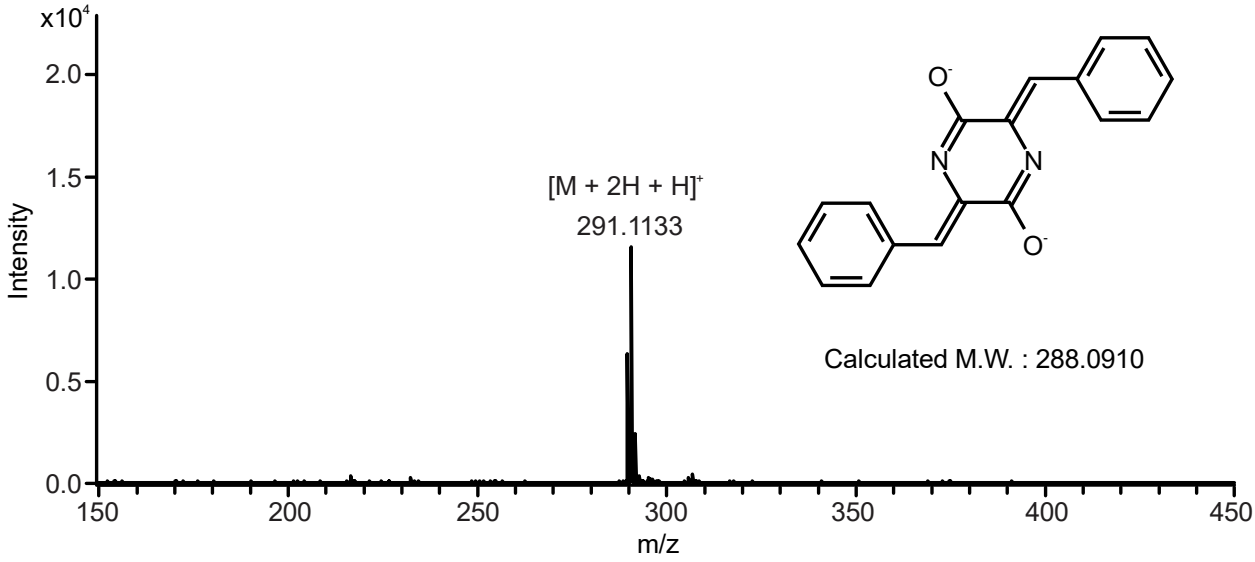


Figure S2.7 Positive ion APCI-MS of **6a**.

4b and 6b

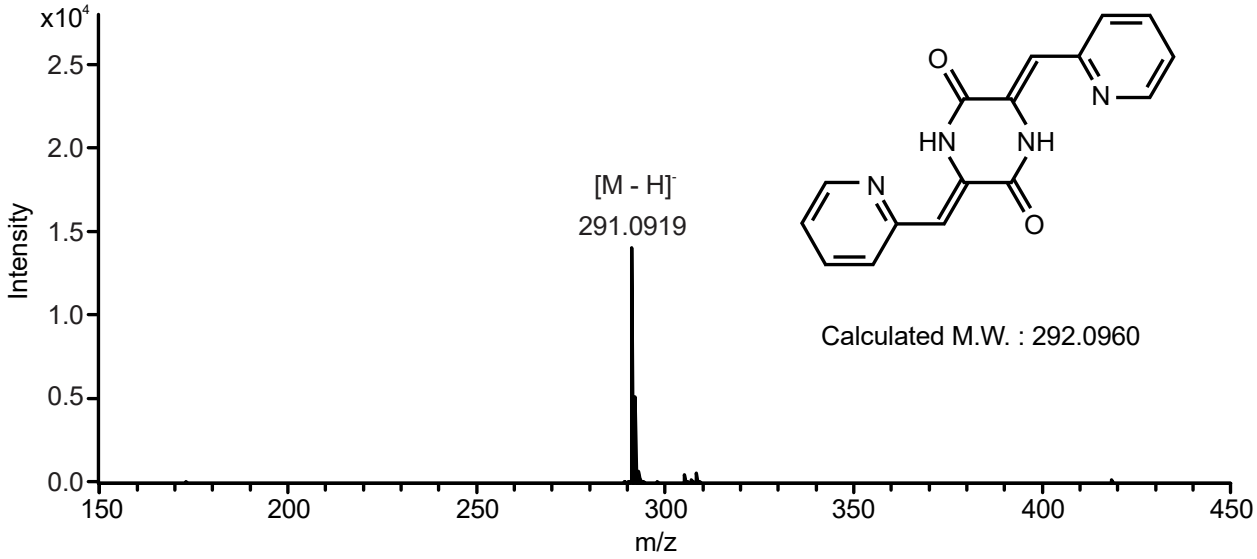


Figure S2.8 Negative ion APCI-MS of **4b**.

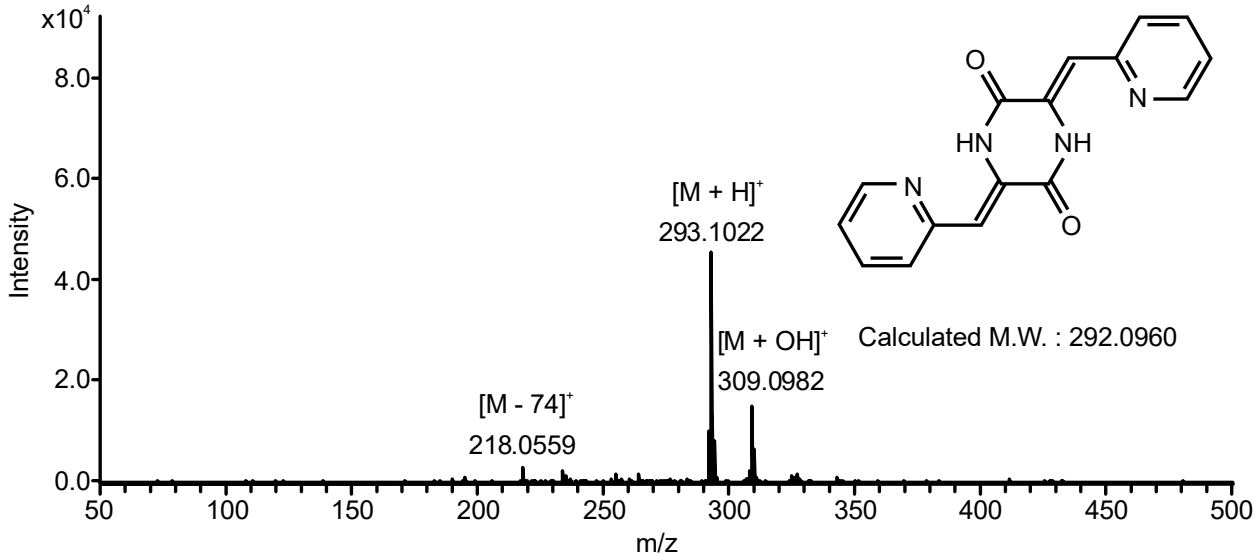


Figure S2.9 Positive ion APCI-MS of **4b**.

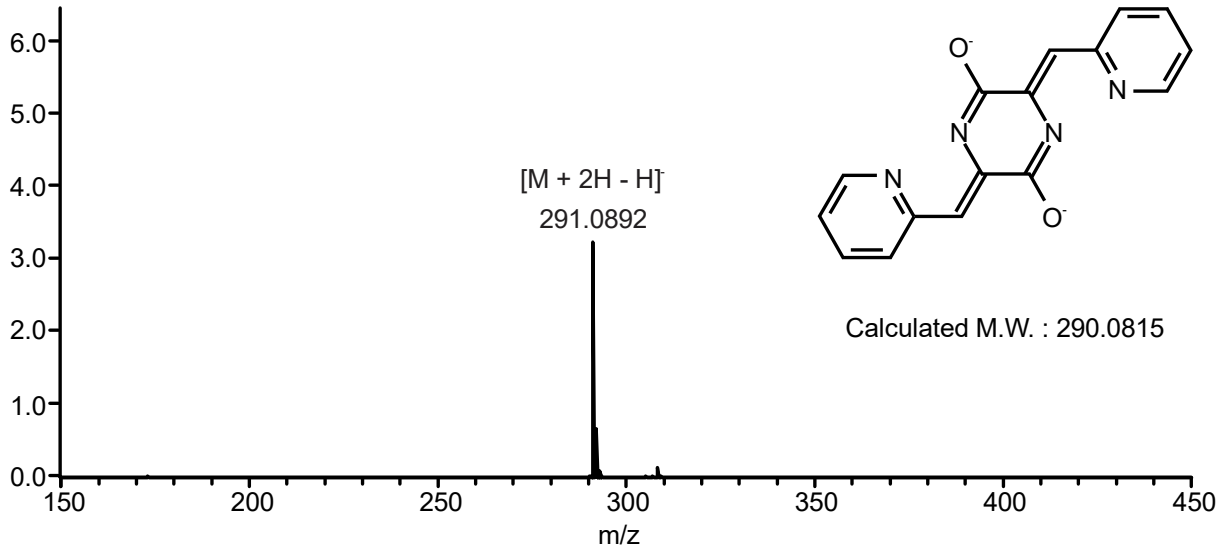


Figure S2.10 Negative ion APCI-MS of **6b**.

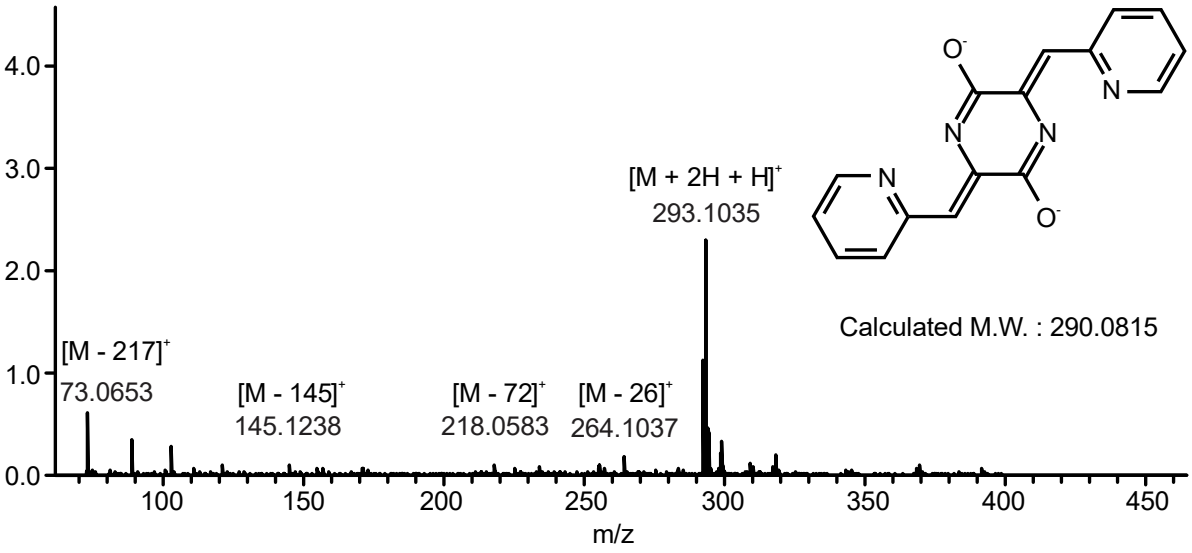


Figure S2.11 Positive ion APCI-MS of **6b**.

4c and 6c

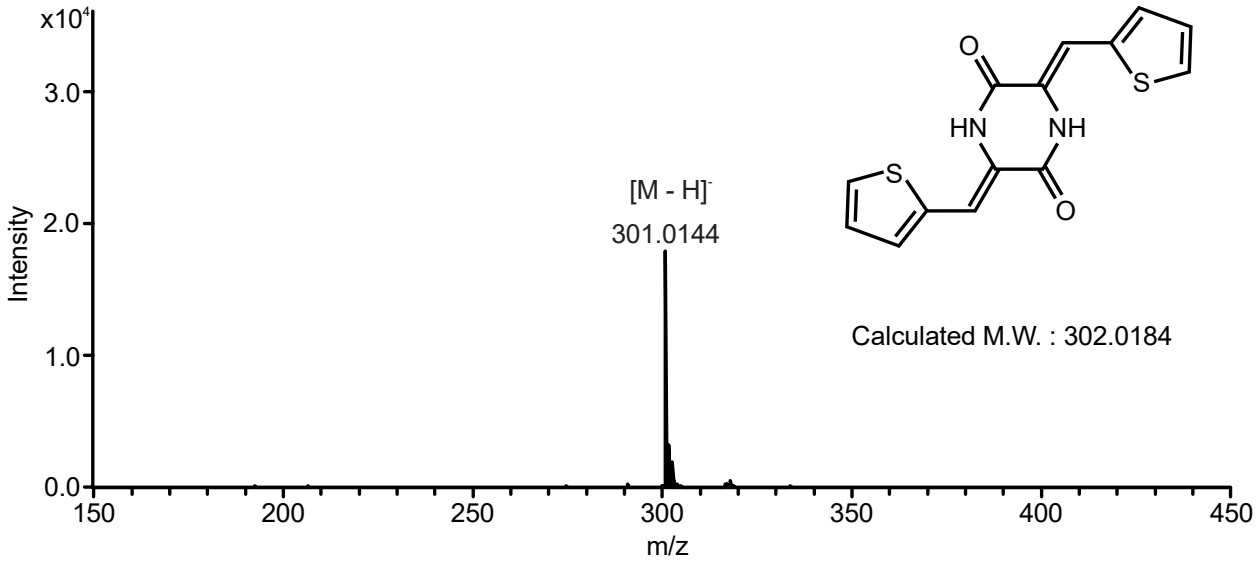


Figure S2.12 Negative ion APCI-MS of **4c**.

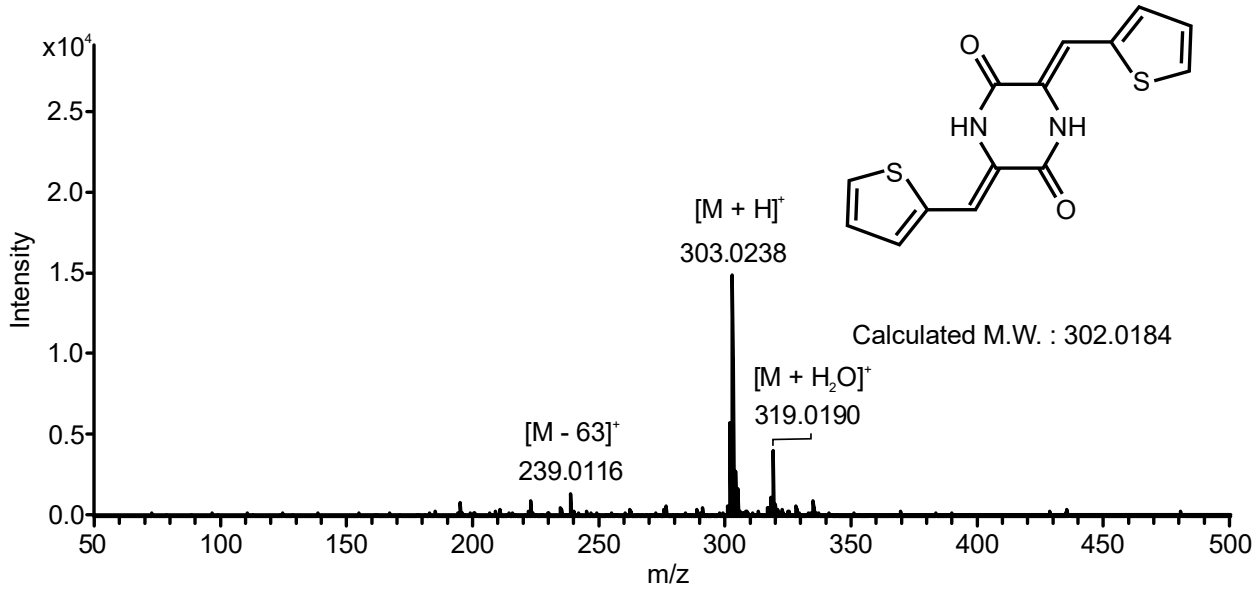


Figure S2.13 Positive ion APCI-MS of **4c**.

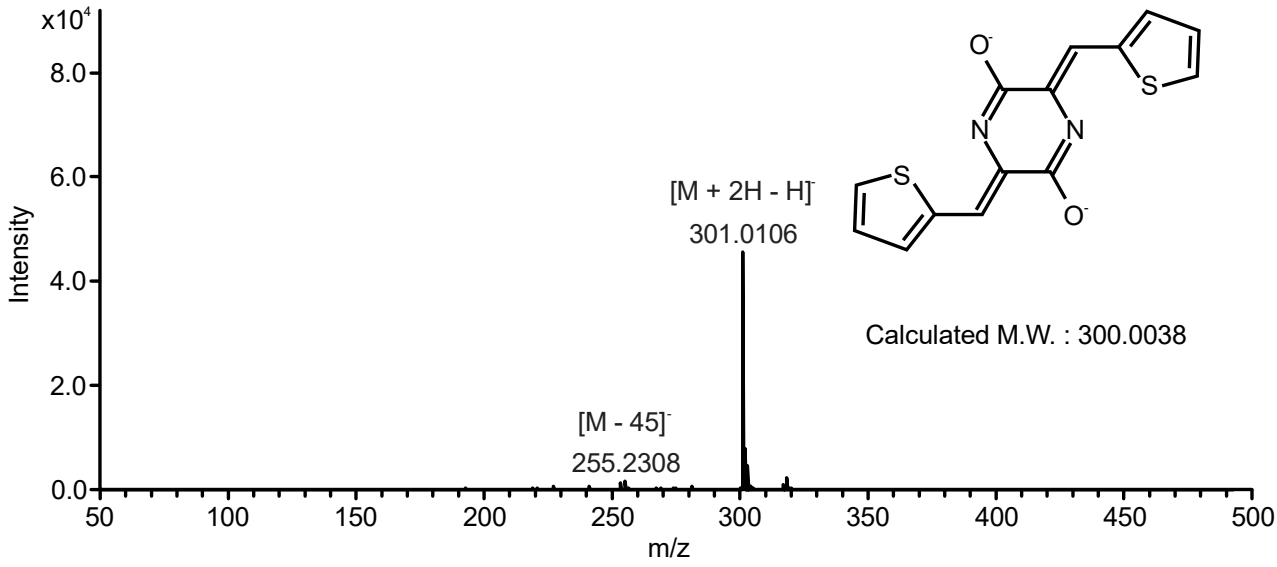


Figure S2.14 Negative ion APCI-MS of **6c**.

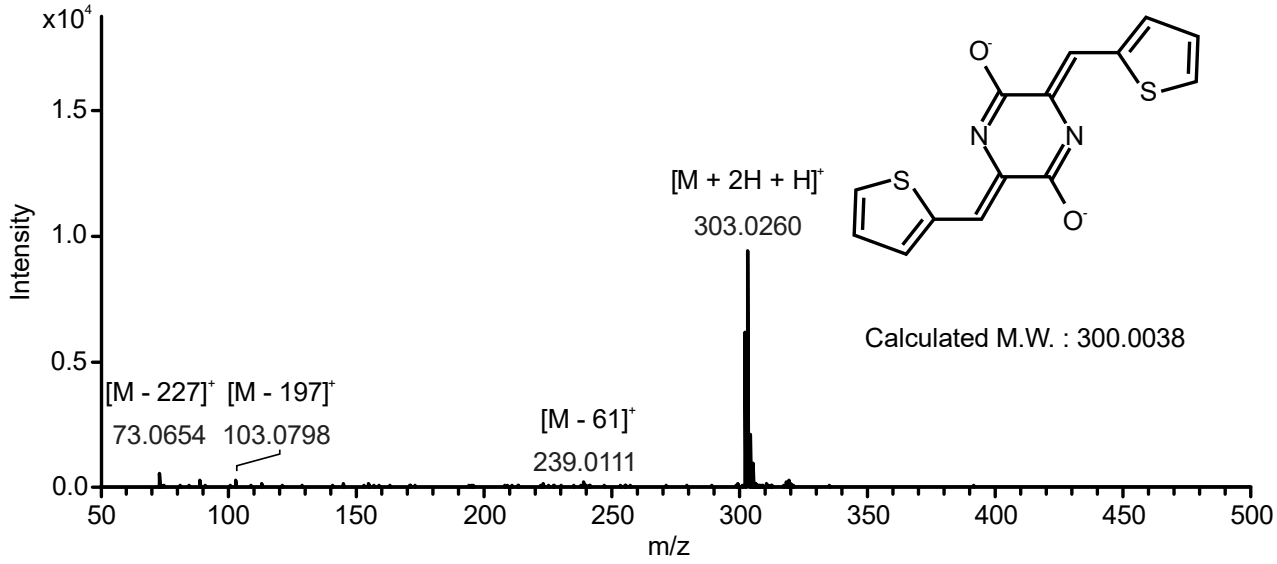


Figure S2.15 Positive ion APCI-MS of **6c**.

4d and 6d

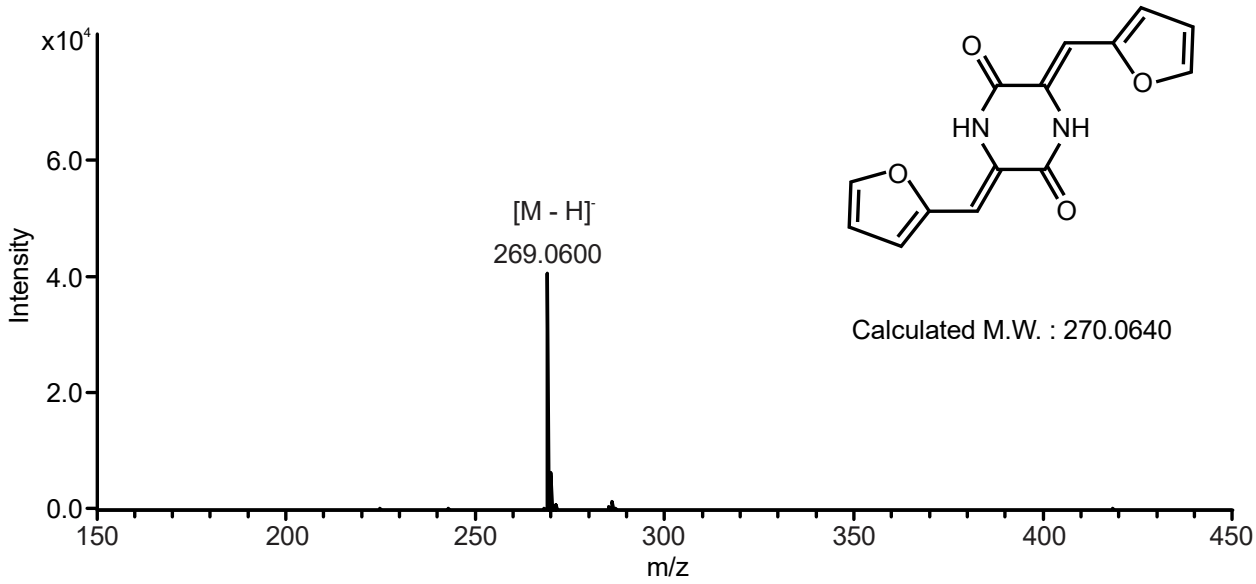


Figure S2.16 Negative ion APCI-MS of **4d**.

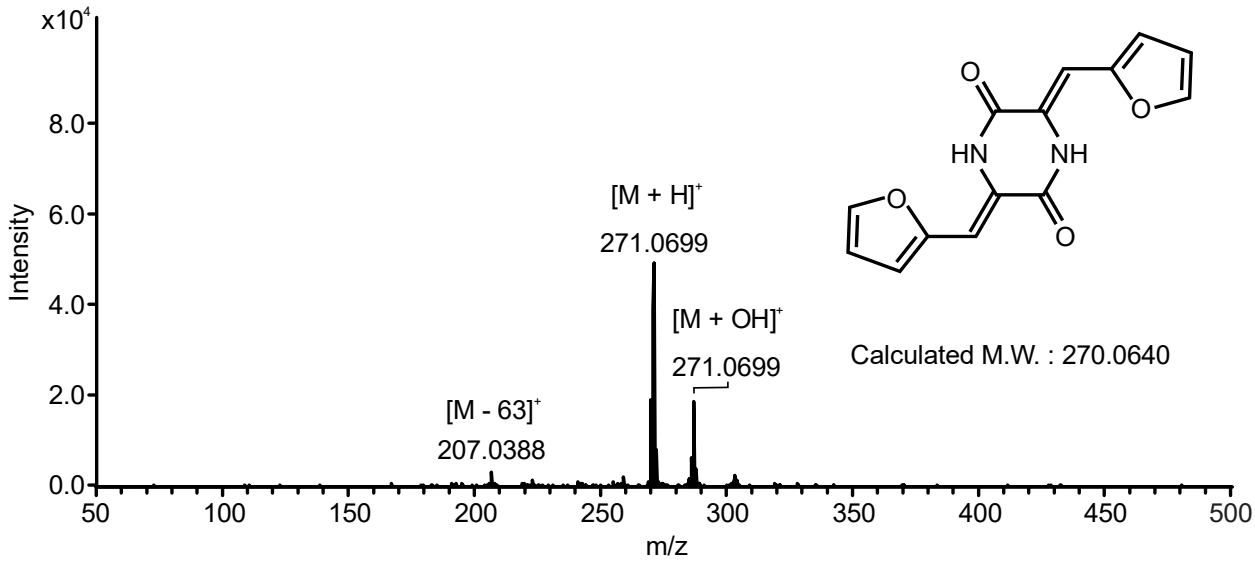


Figure S2.17 Positive ion APCI-MS of **4d**.

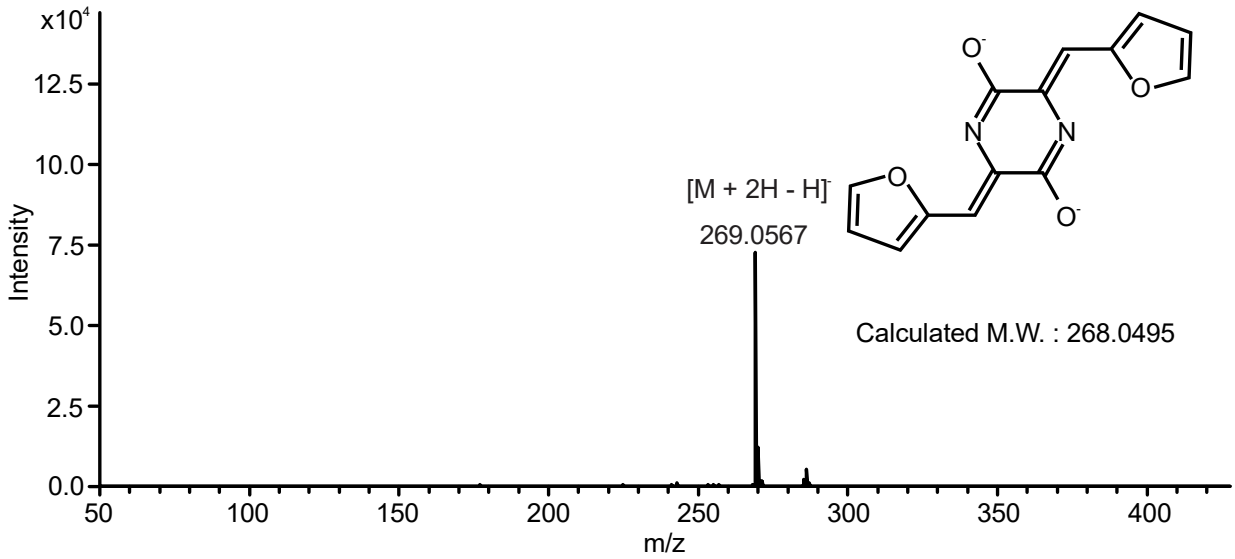


Figure S2.18 Negative ion APCI-MS of **6d**.

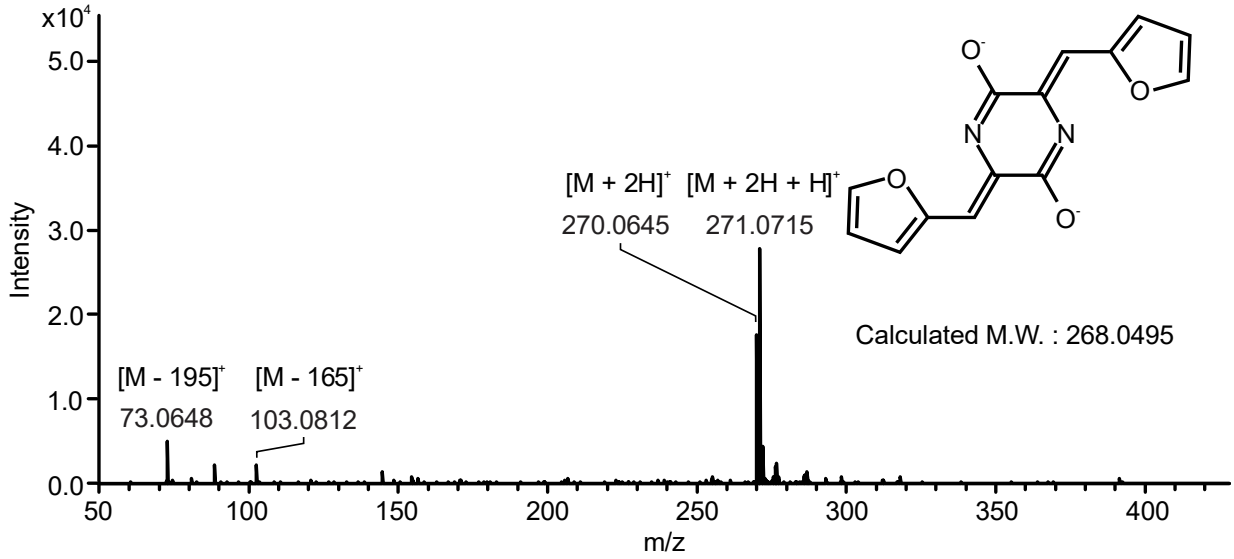


Figure S2.19 Positive ion APCI-MS of **6d**.

4e and 6e

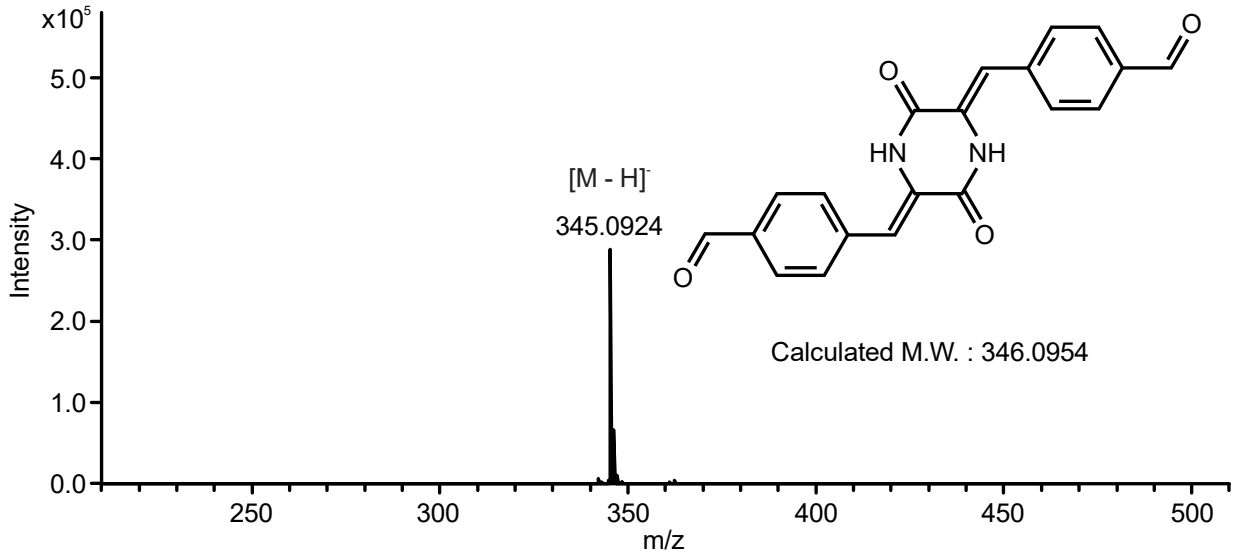


Figure S2.20 Negative ion APCI-MS of **4e**.

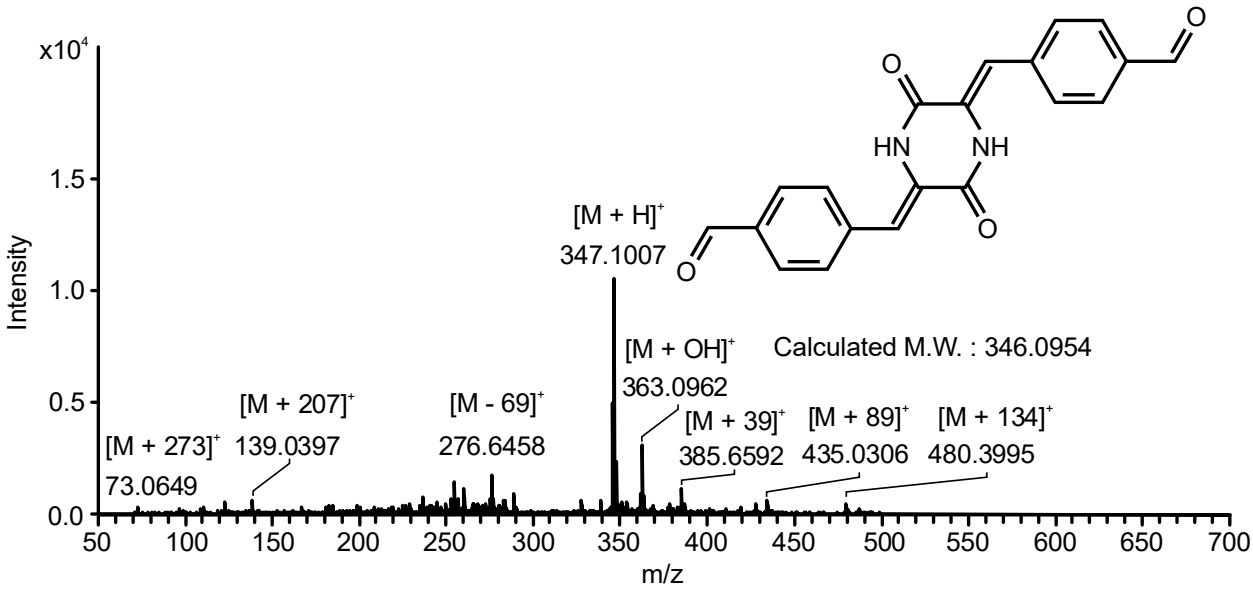


Figure S2.21 Positive ion APCI-MS of **4e**.

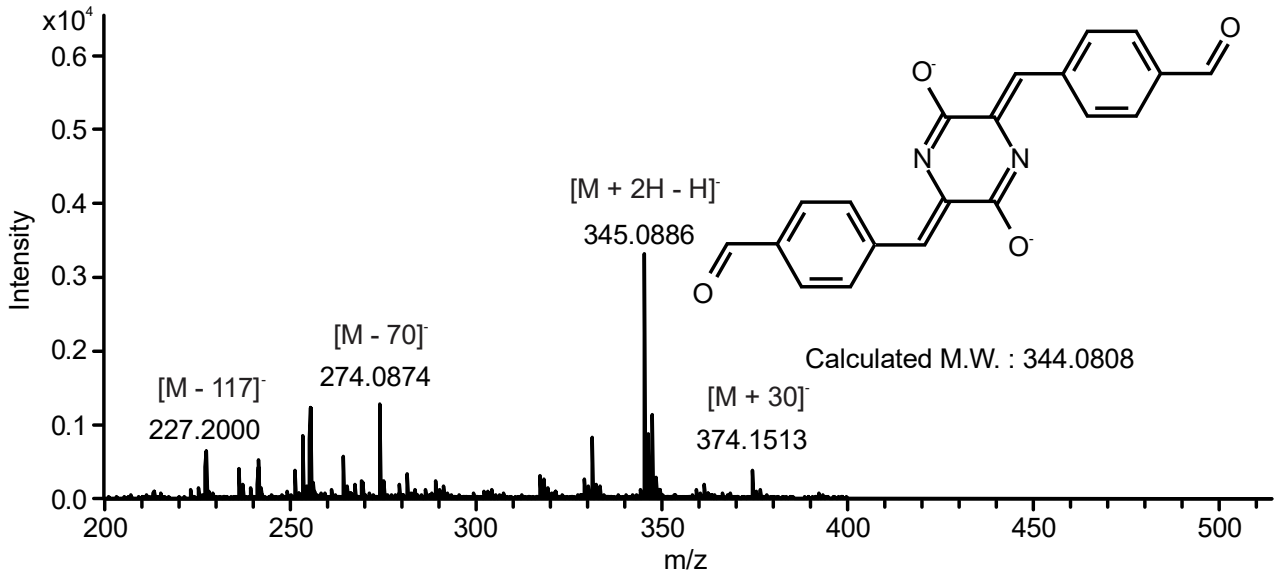


Figure S2.22 Negative ion APCI-MS of **6e**.

4f and 6f

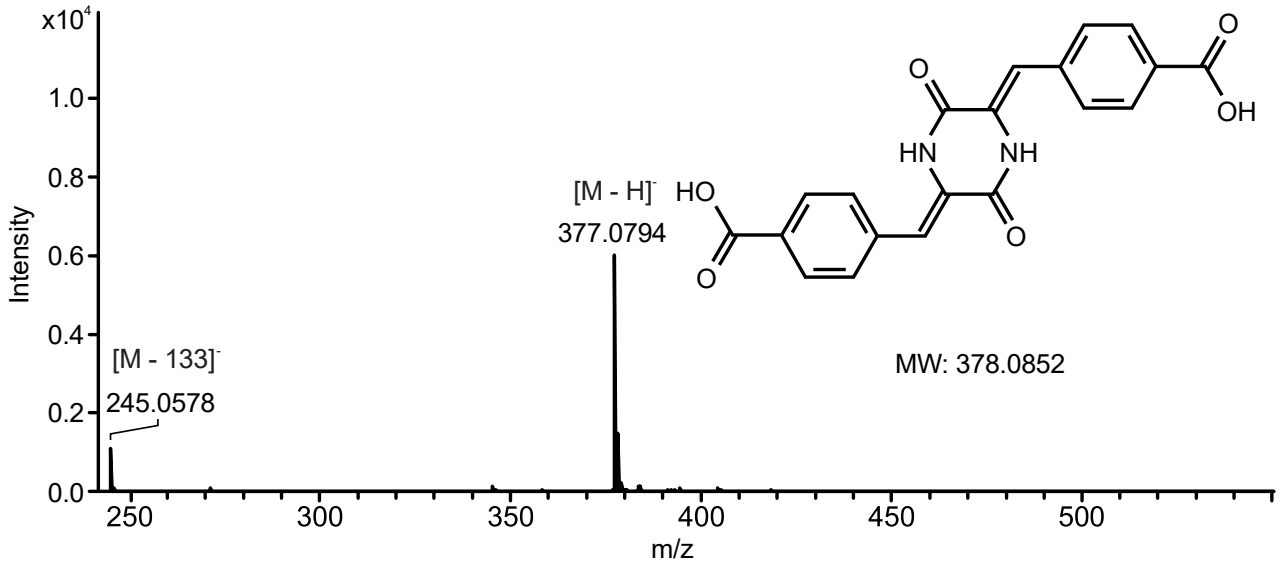


Figure S2.23 Negative ion APCI-MS of **4f**.

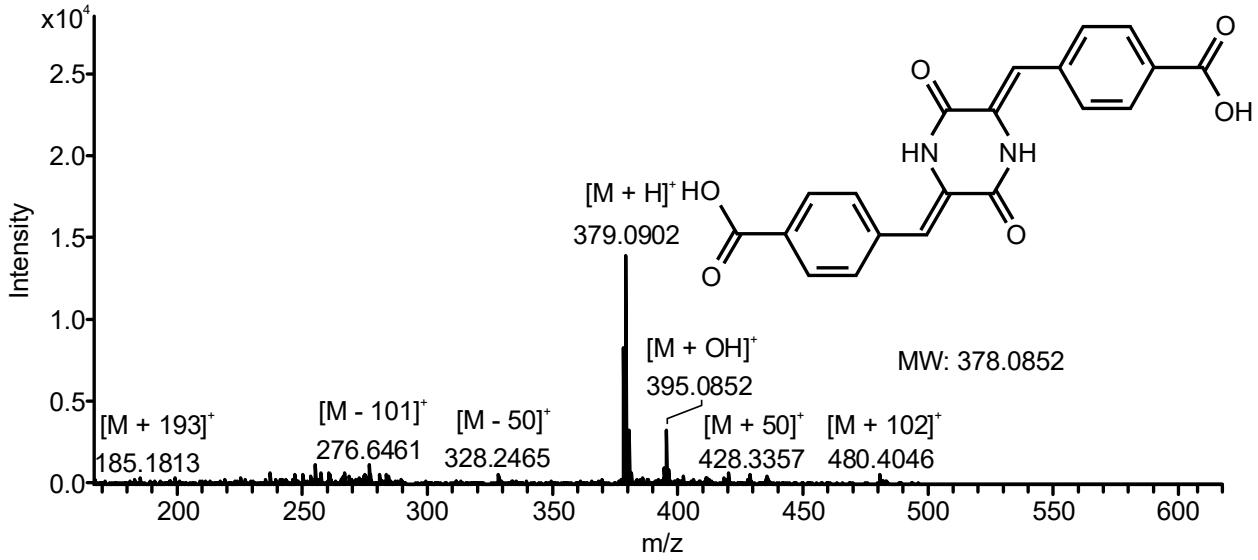


Figure S2.24 Positive ion APCI-MS of **4f**.

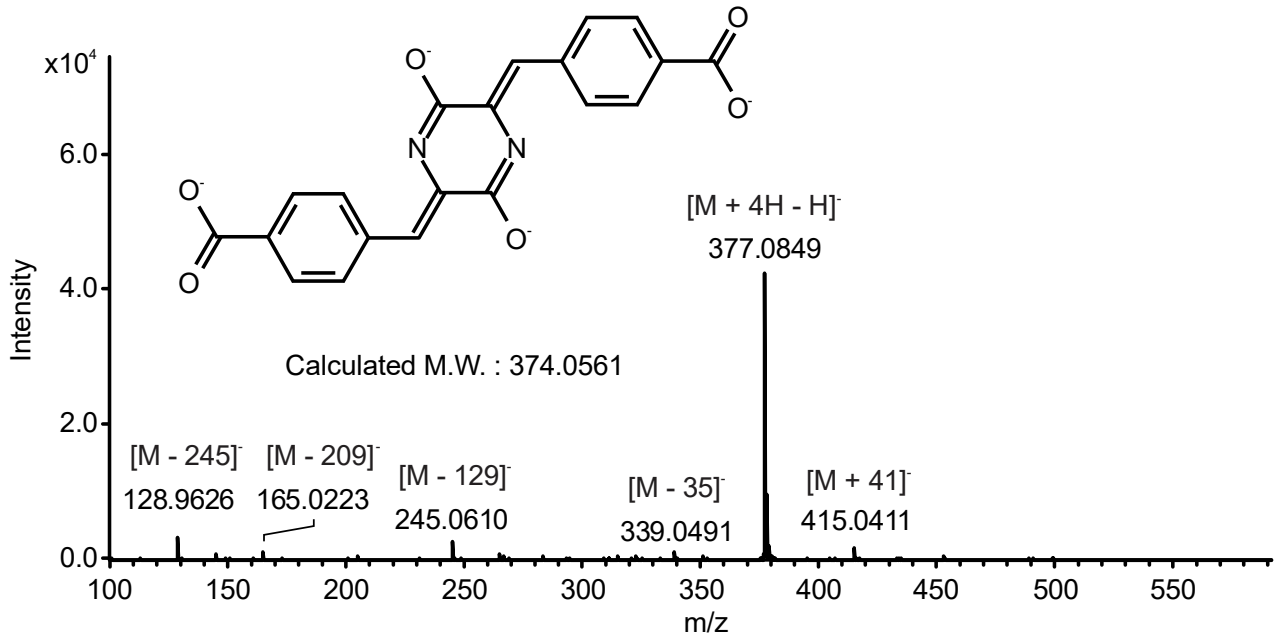


Figure S2.25 Negative ion ESI-MS of **6f**.

4g and 6g

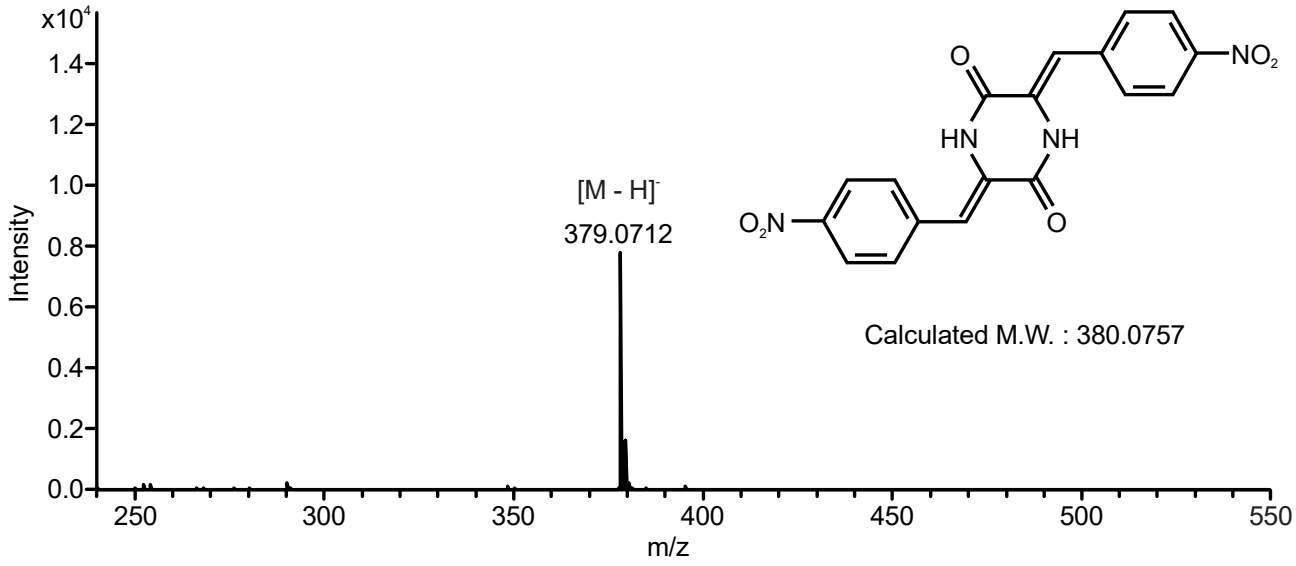


Figure S2.26 Negative ion APCI-MS of **4g**.

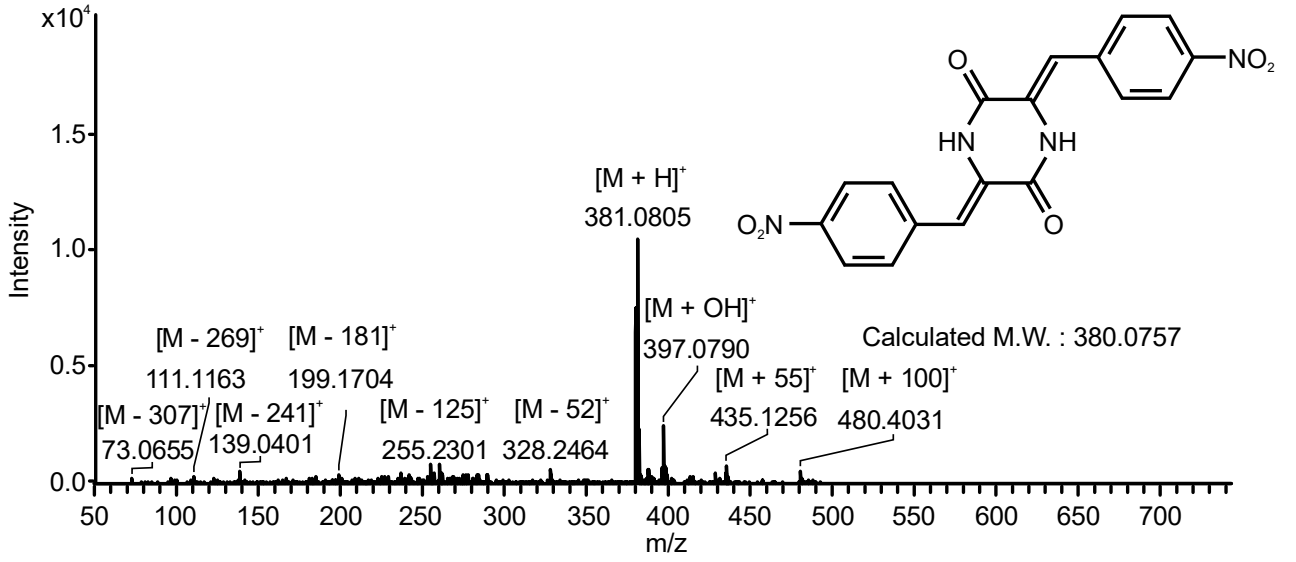


Figure S2.27 Positive ion APCI-MS of **4g**.

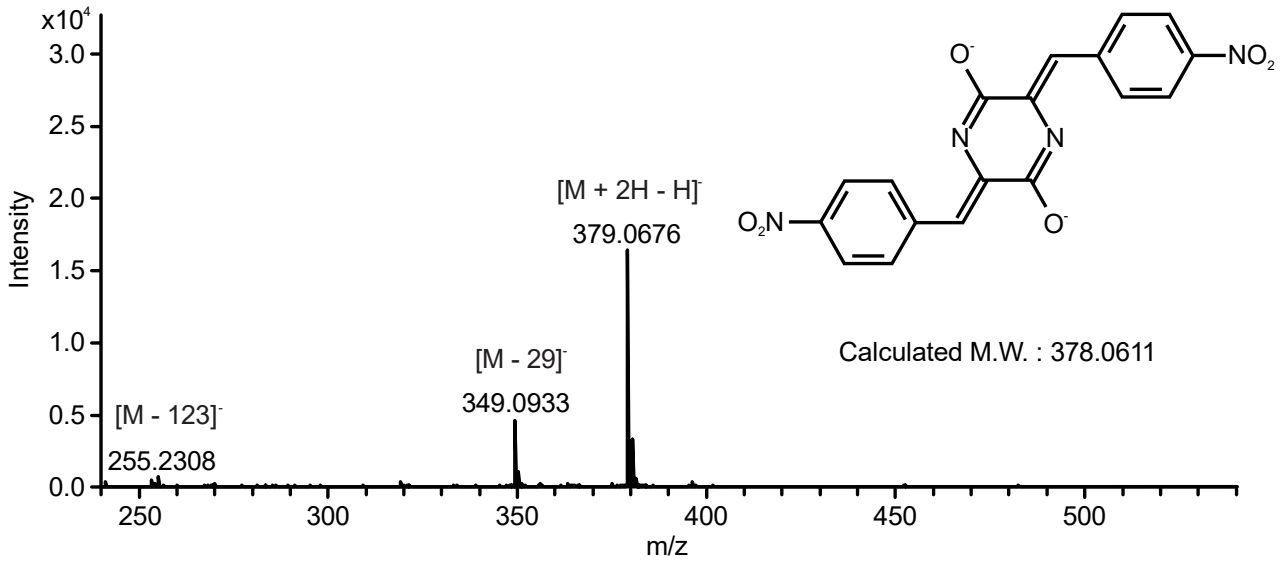


Figure S2.28 Negative ion APCI-MS of **6g**.

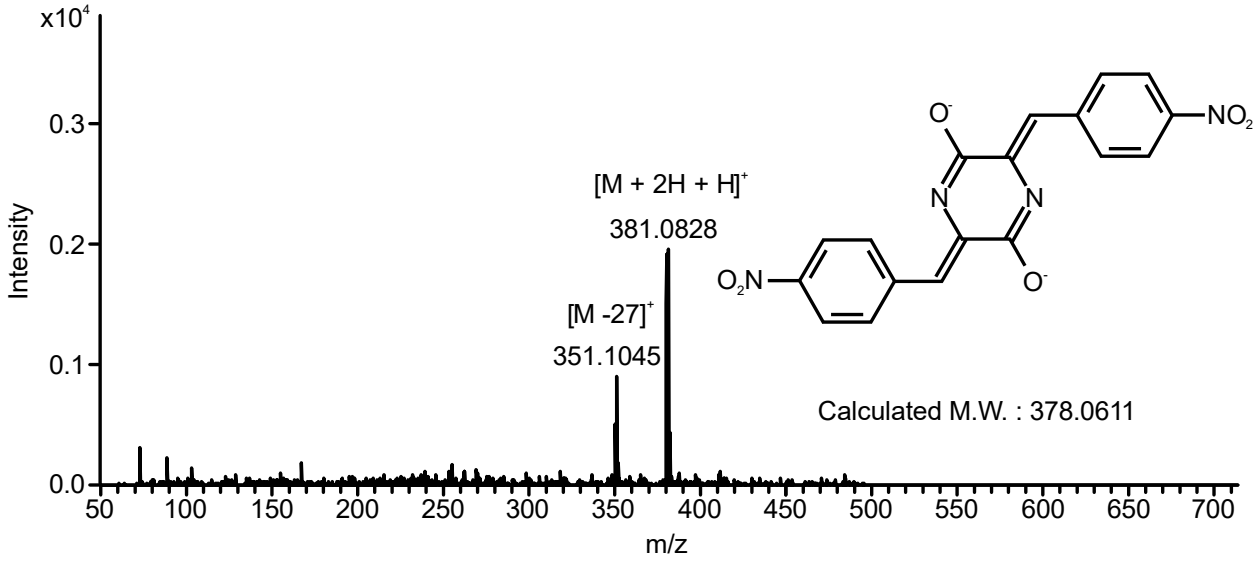


Figure S2.29 Positive ion APCI-MS of **6g**.

4h and 6h

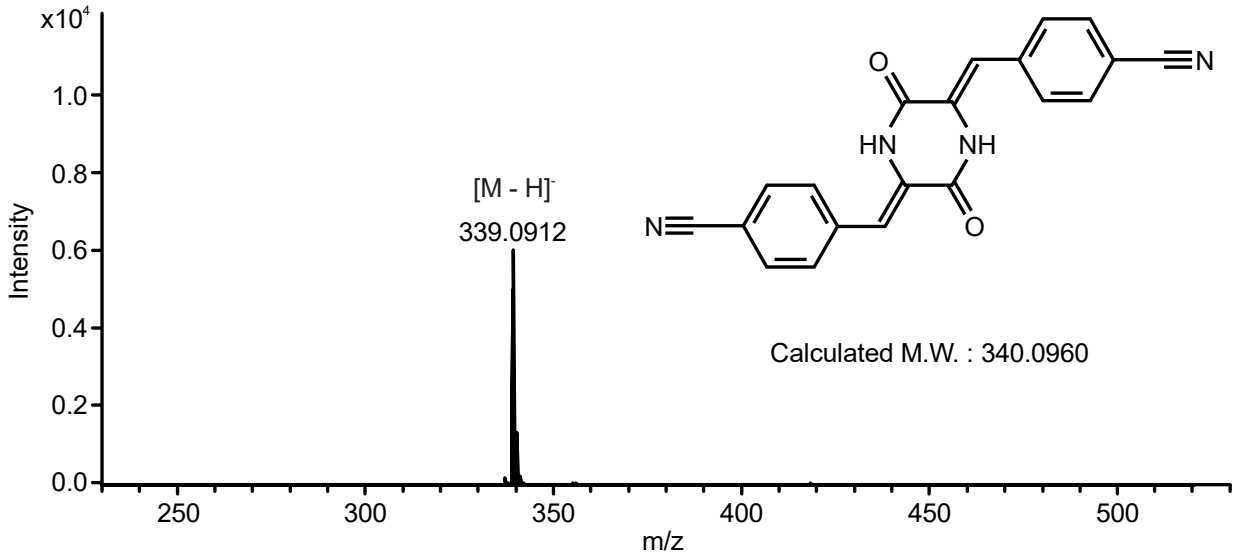


Figure S2.30 Negative ion APCI-MS of **4h**.

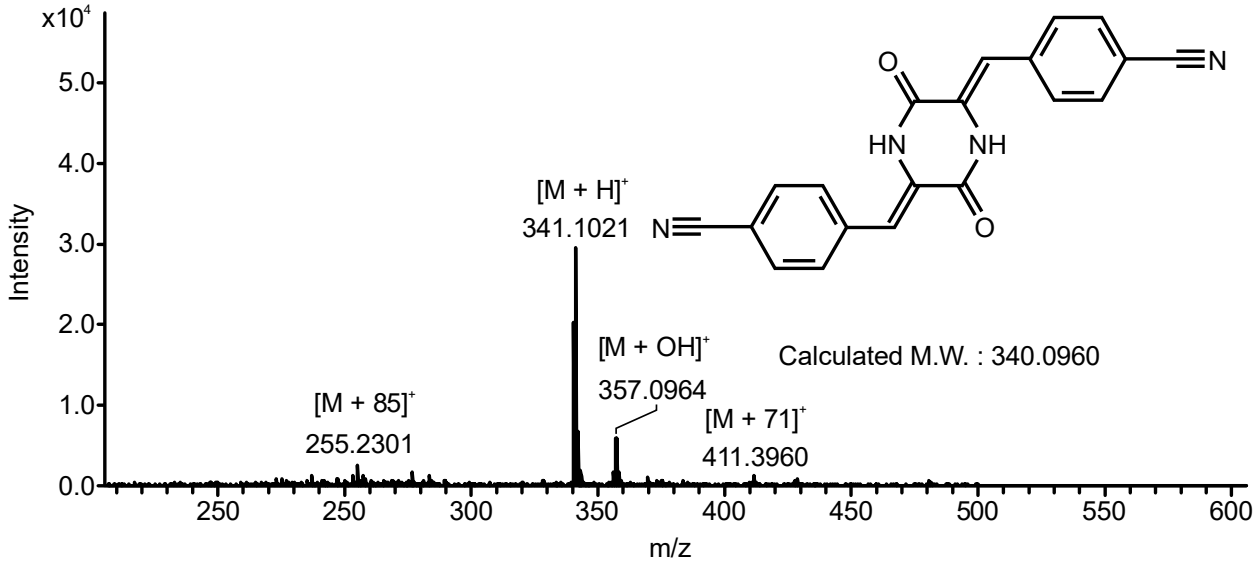


Figure S2.31 Positive ion APCI-MS of **4h**.

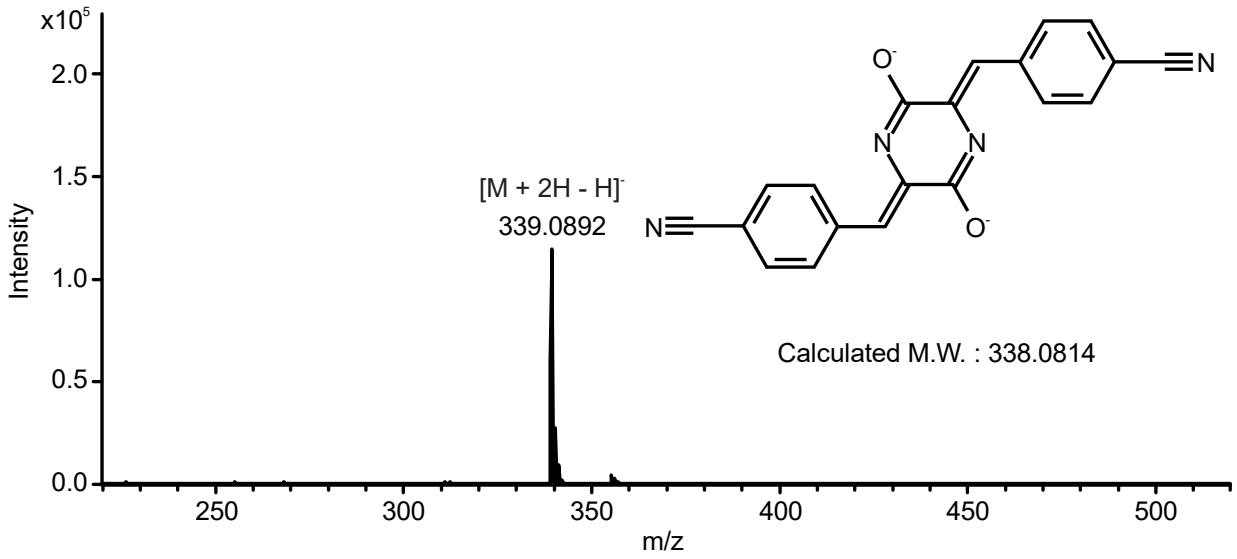


Figure S2.32 Negative ion APCI-MS of **6h**.

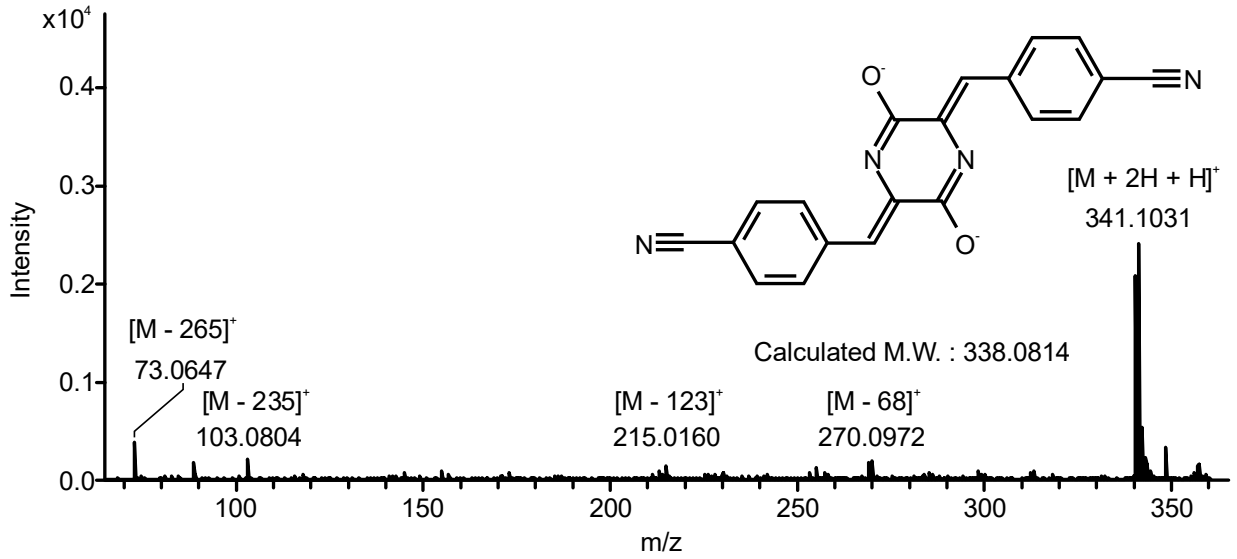


Figure S2.33 Positive ion APCI-MS of **6h**.

4i and 6i

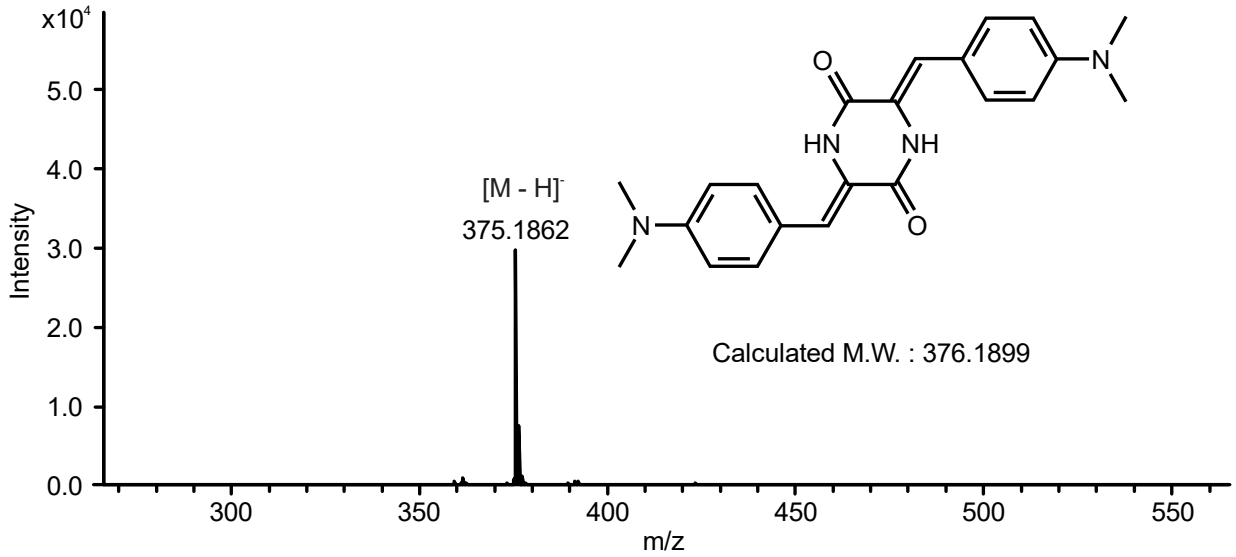


Figure S2.34 Negative ion APCI-MS of **4i**.

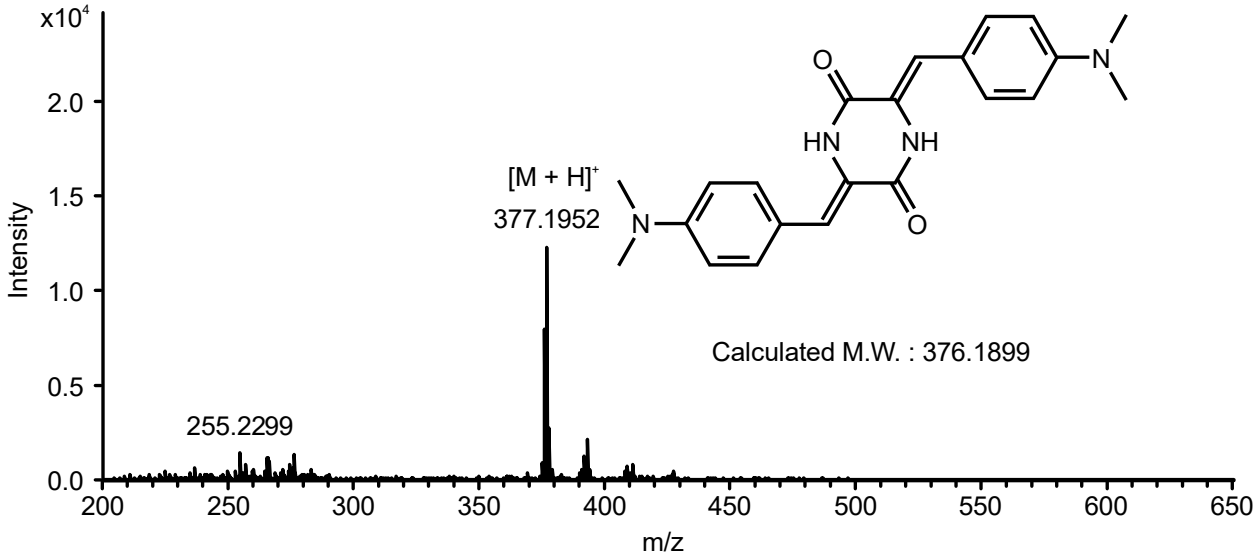


Figure S2.35 Positive ion APCI-MS of **4i**.

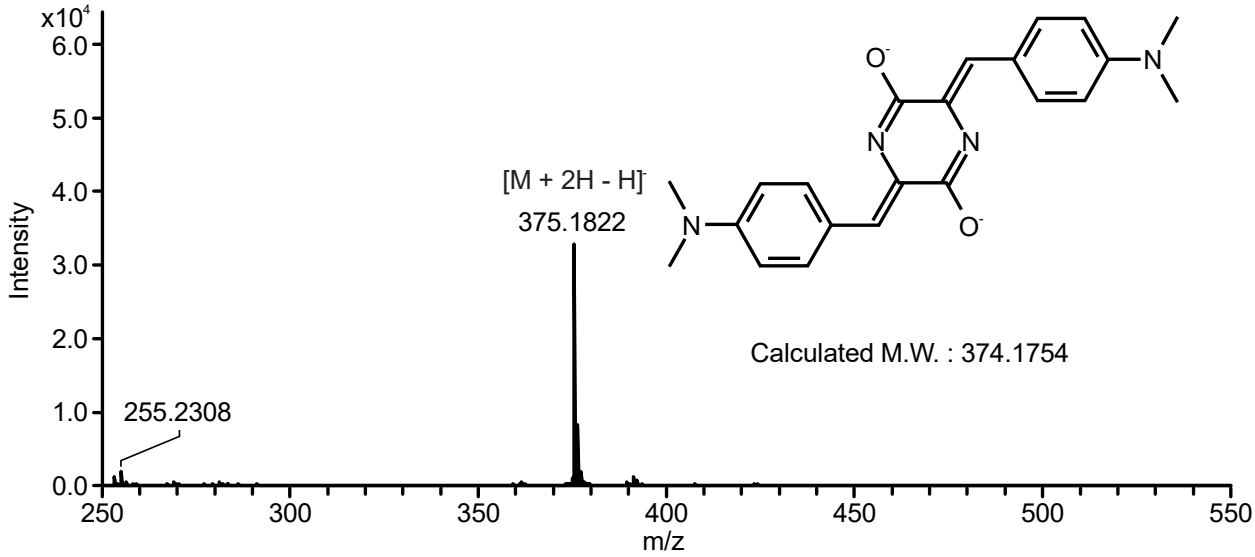


Figure S2.36 Negative ion APCI-MS of **6i**.

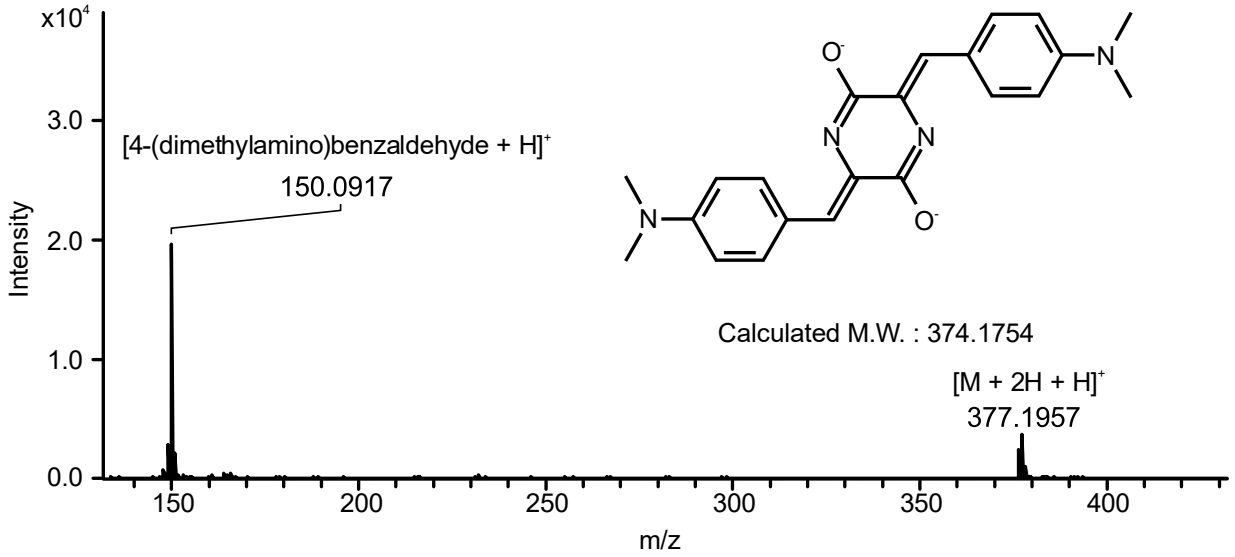


Figure S2.37 Positive ion APCI-MS of **6i**.

4j and 6j

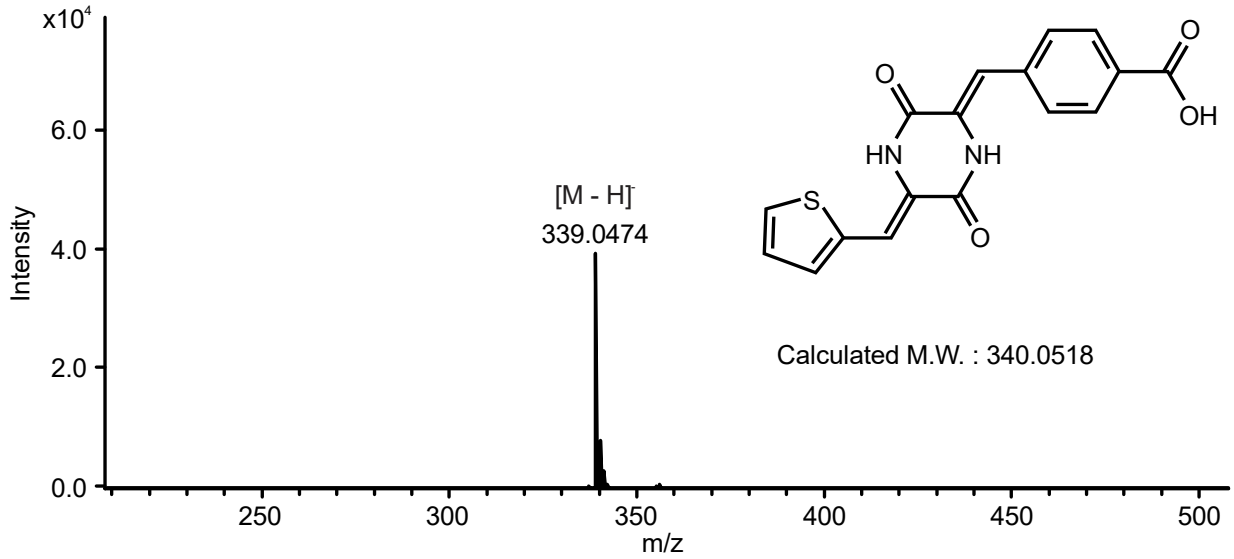


Figure S2.38 Negative ion APCI-MS of **4j**.

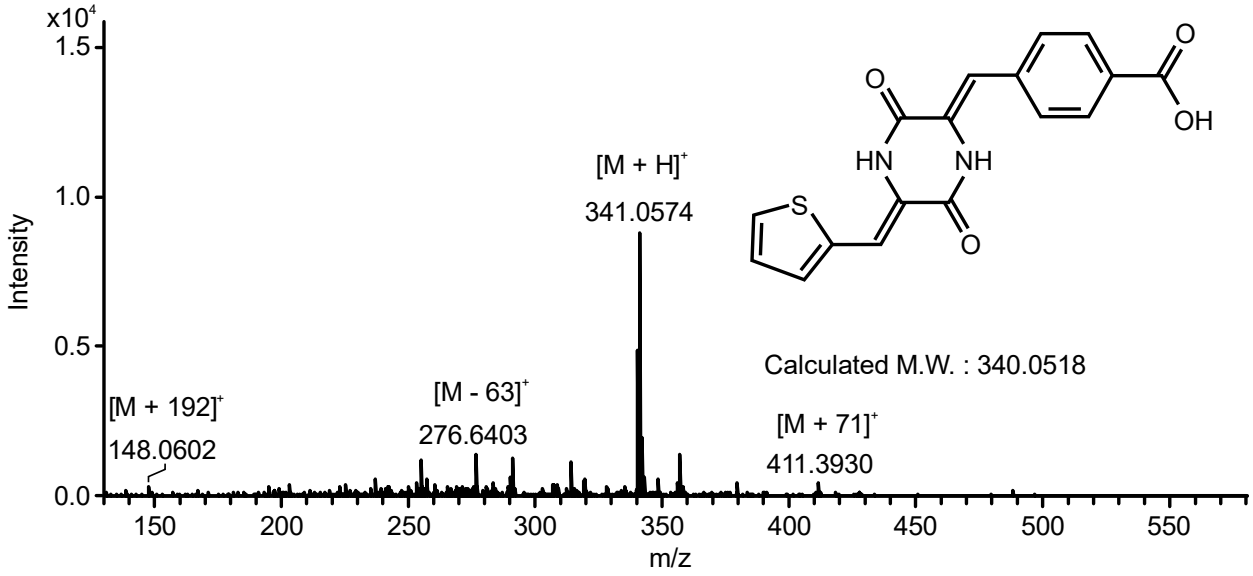


Figure 2.39 Positive ion APCI-MS of **4j**.

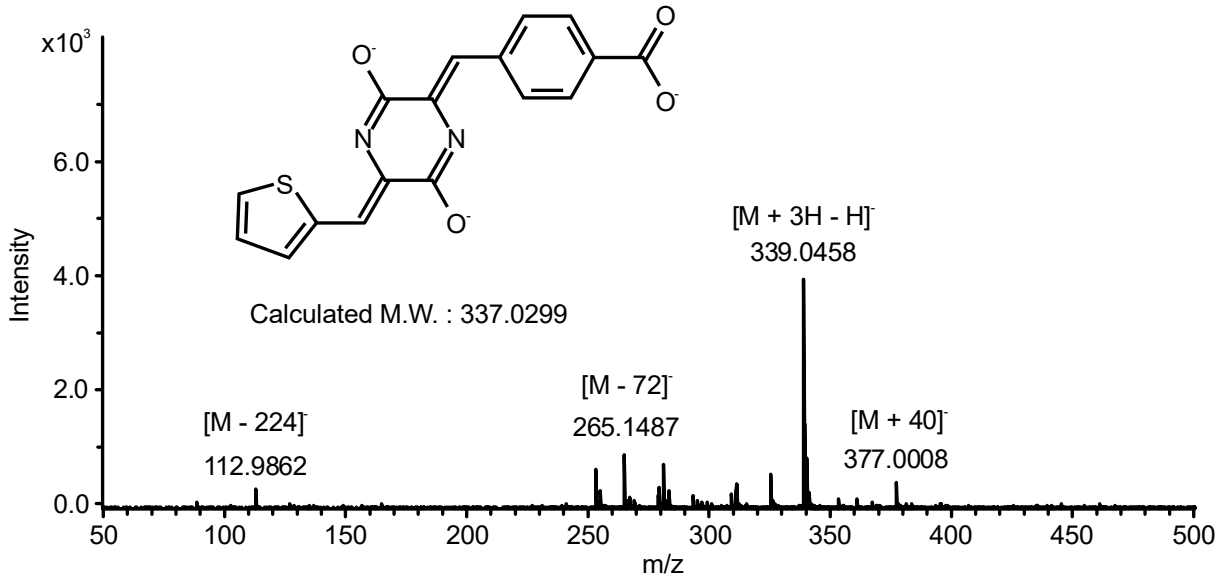


Figure S2.40 Negative ion APCI-MS of **6j**.

4k and 6k

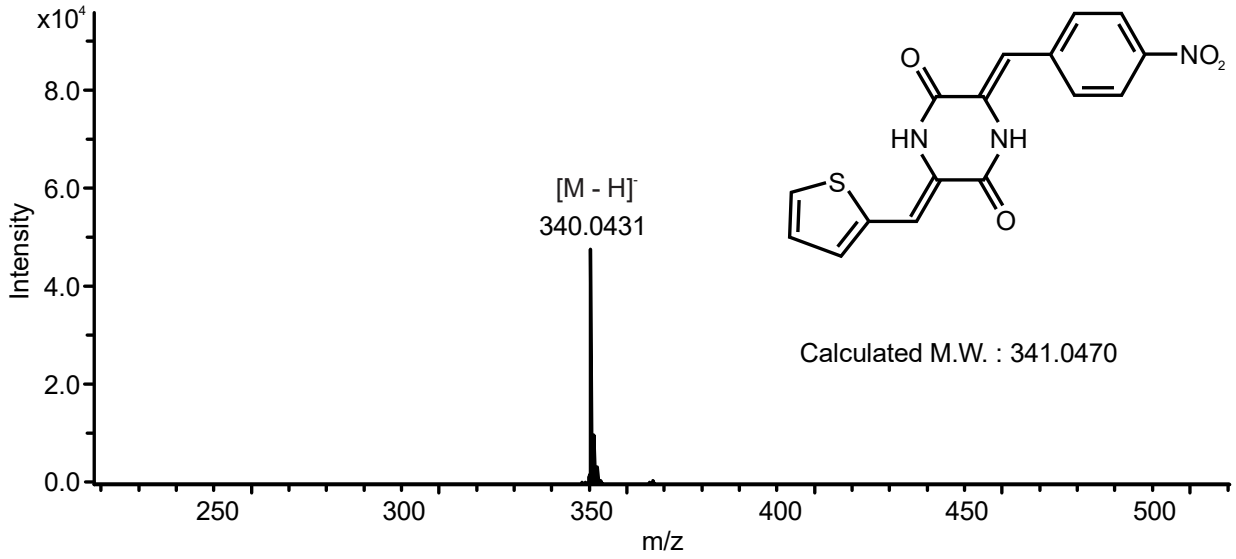


Figure S2.41 Negative ion APCI-MS of **4k**.

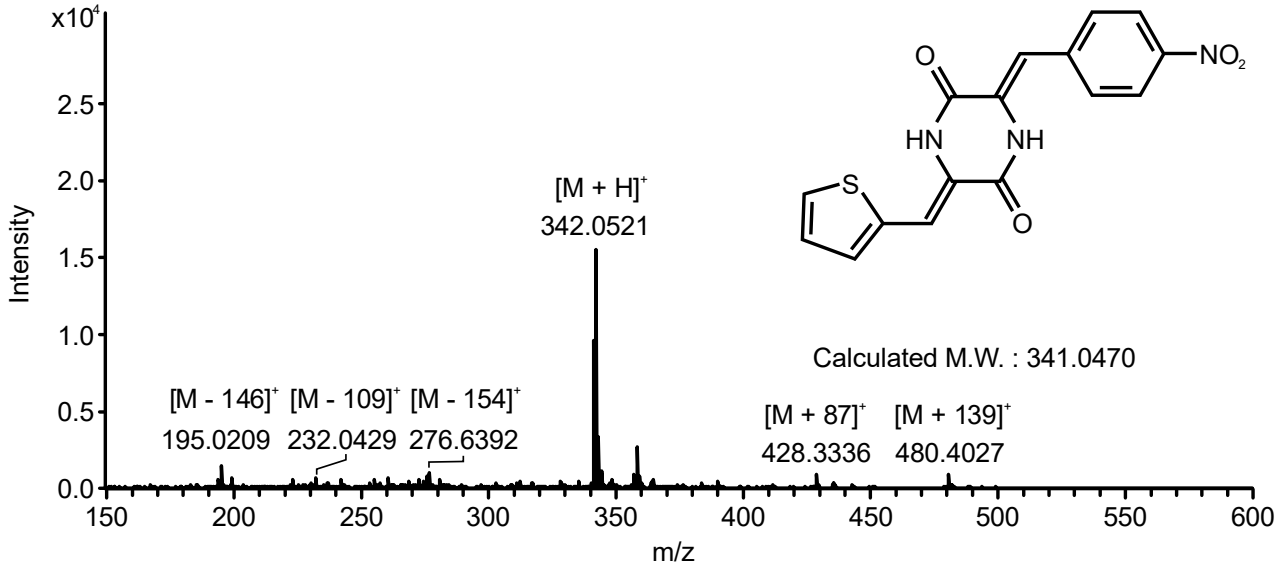


Figure S2.42 Positive ion APCI-MS of **4k**.

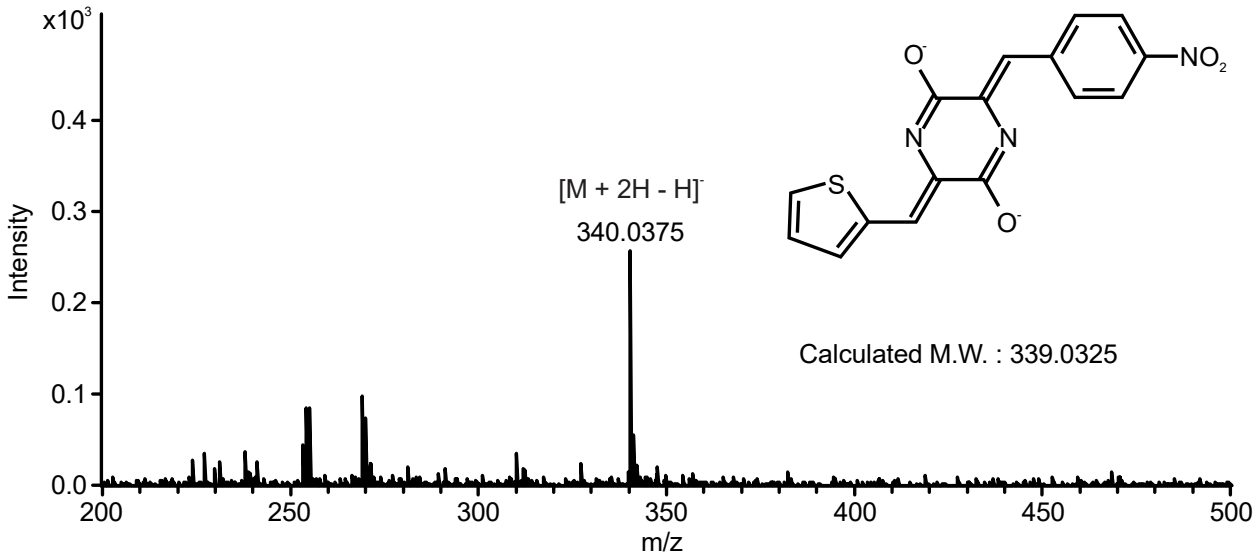


Figure S2.43 Negative ion APCI-MS of **6k**.

4l and 6l

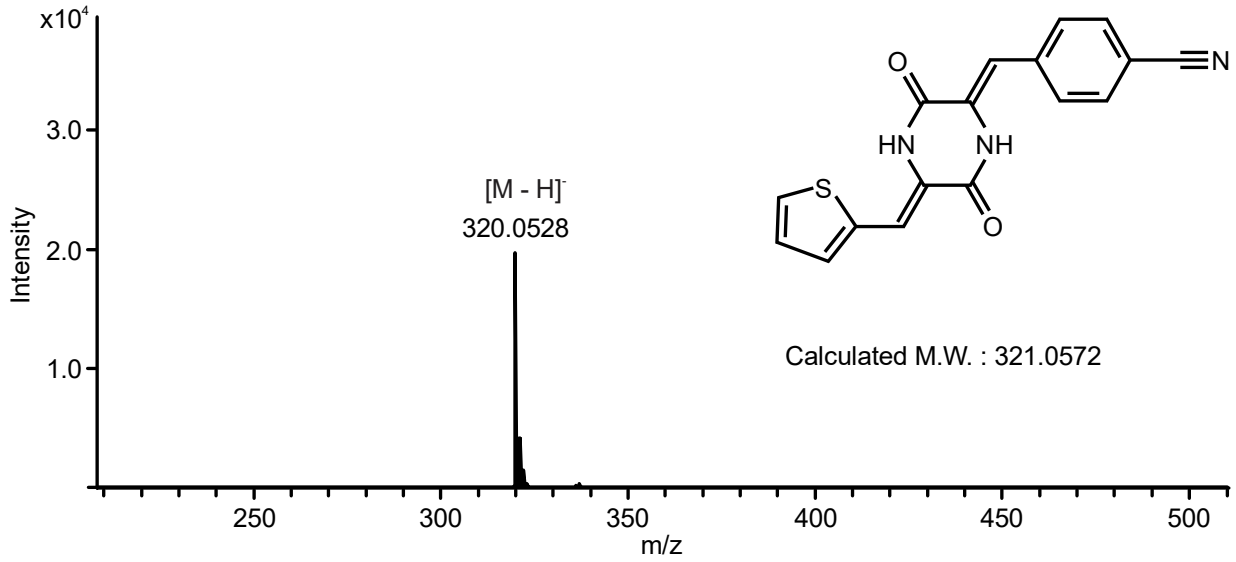


Figure S2.44 Negative ion APCI-MS of **4l**.

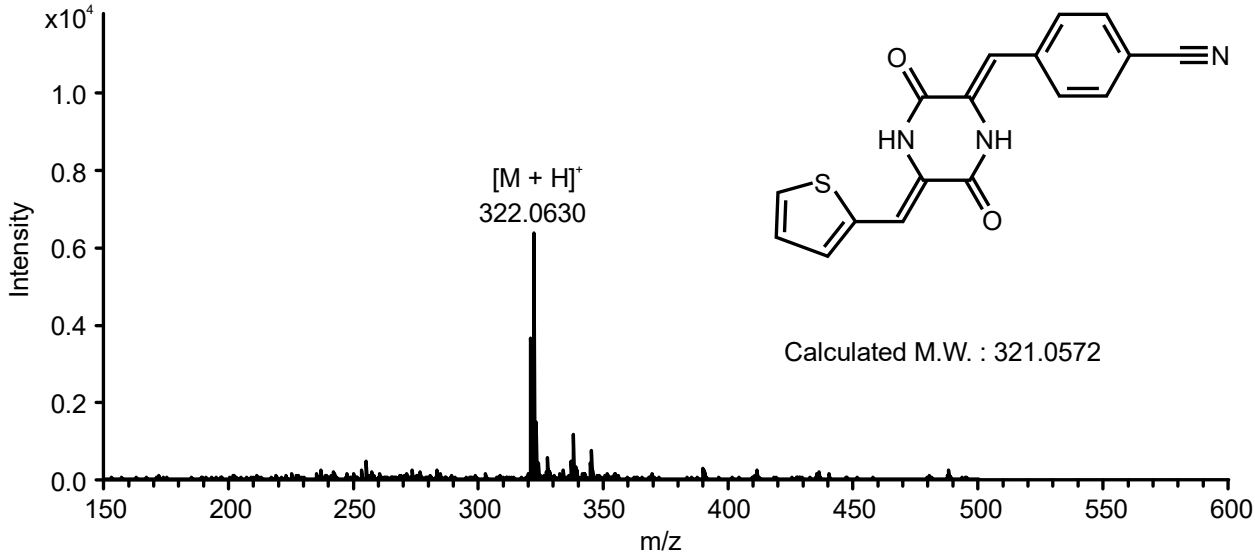


Figure S2.45 Positive ion APCI-MS of **4l**.

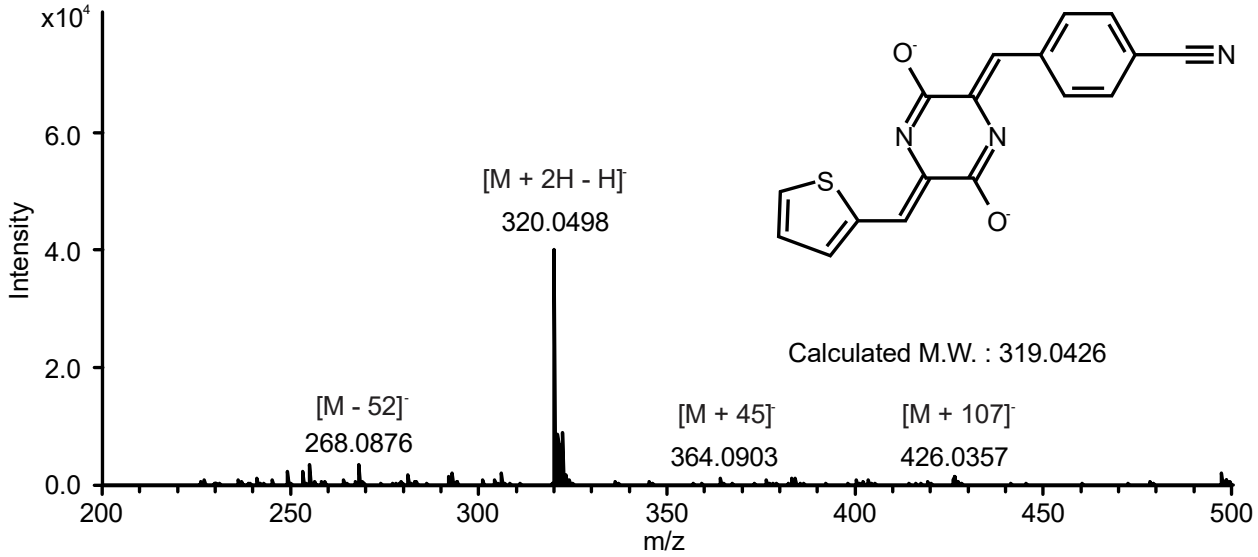


Figure S2.46 Negative ion APCI-MS of **6l**.

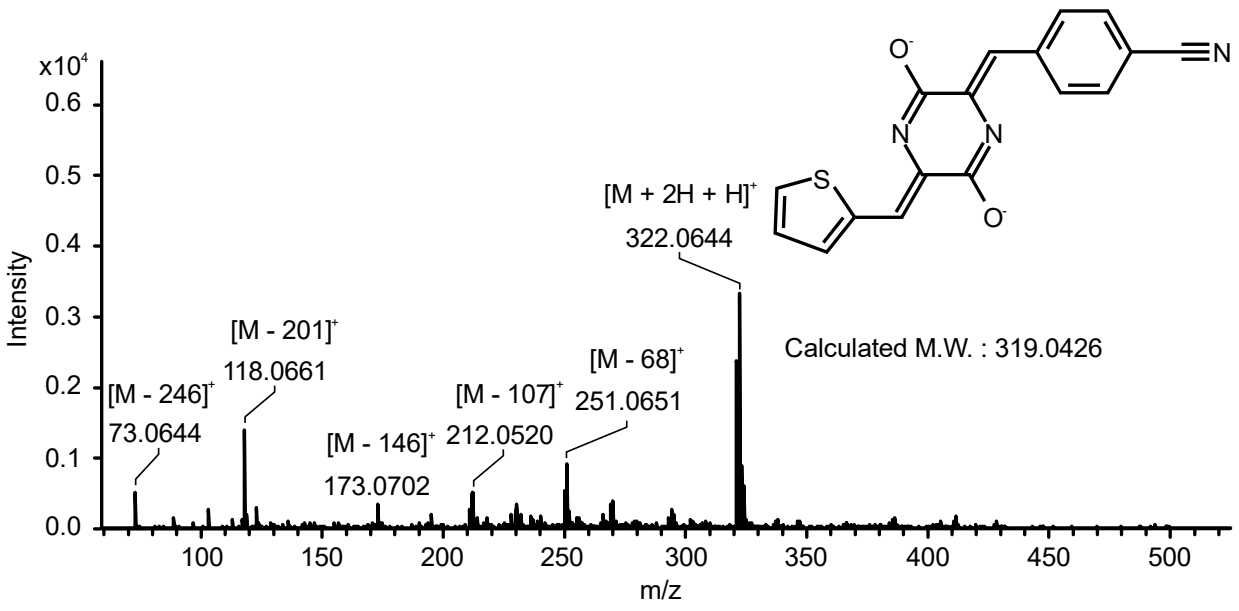


Figure S2.47 Positive ion APCI-MS of **6l**.

4m and 6m

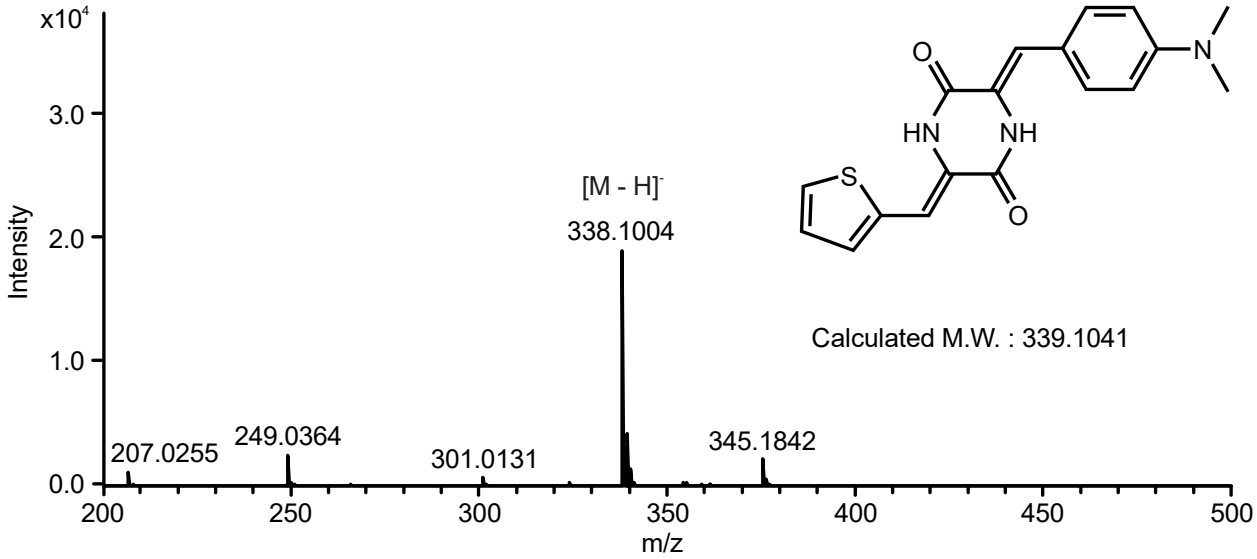


Figure S2.48 Negative ion APCI-MS of **4m**.

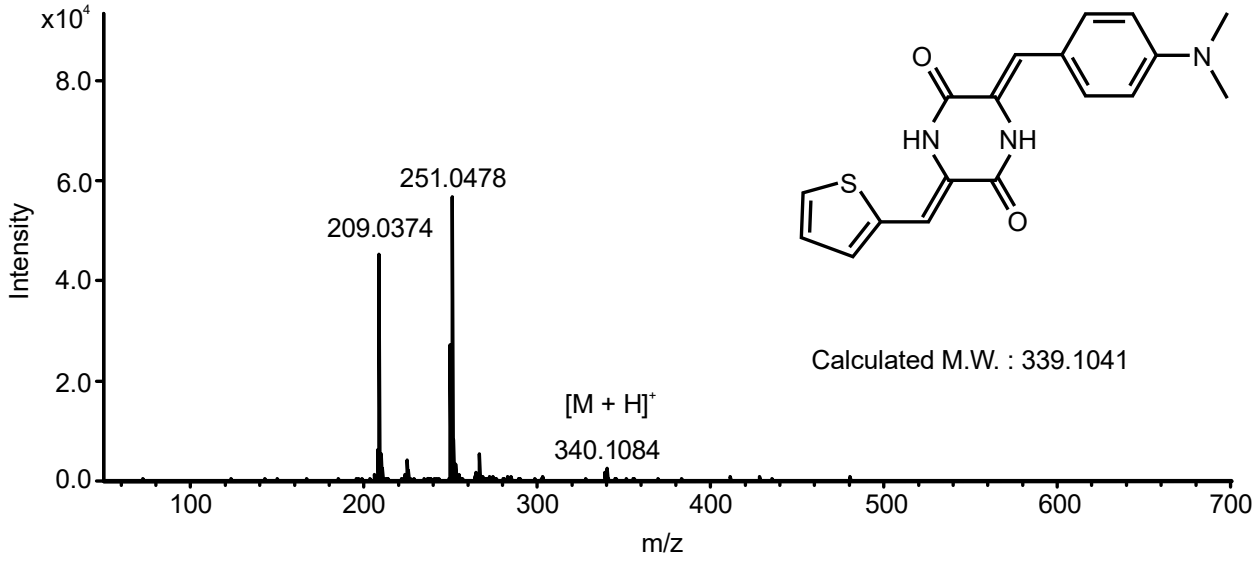


Figure S2.49 Positive ion APCI-MS of **4m**.

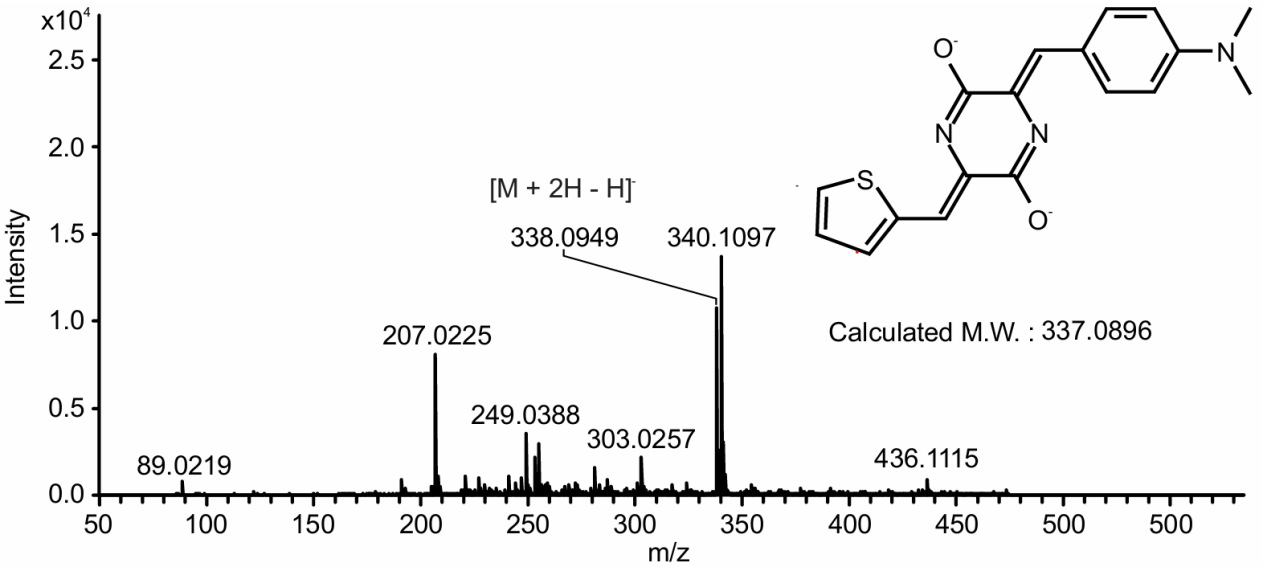


Figure S2.50 Negative ion APCI-MS of **6m**.

NMR spectra

Precursors

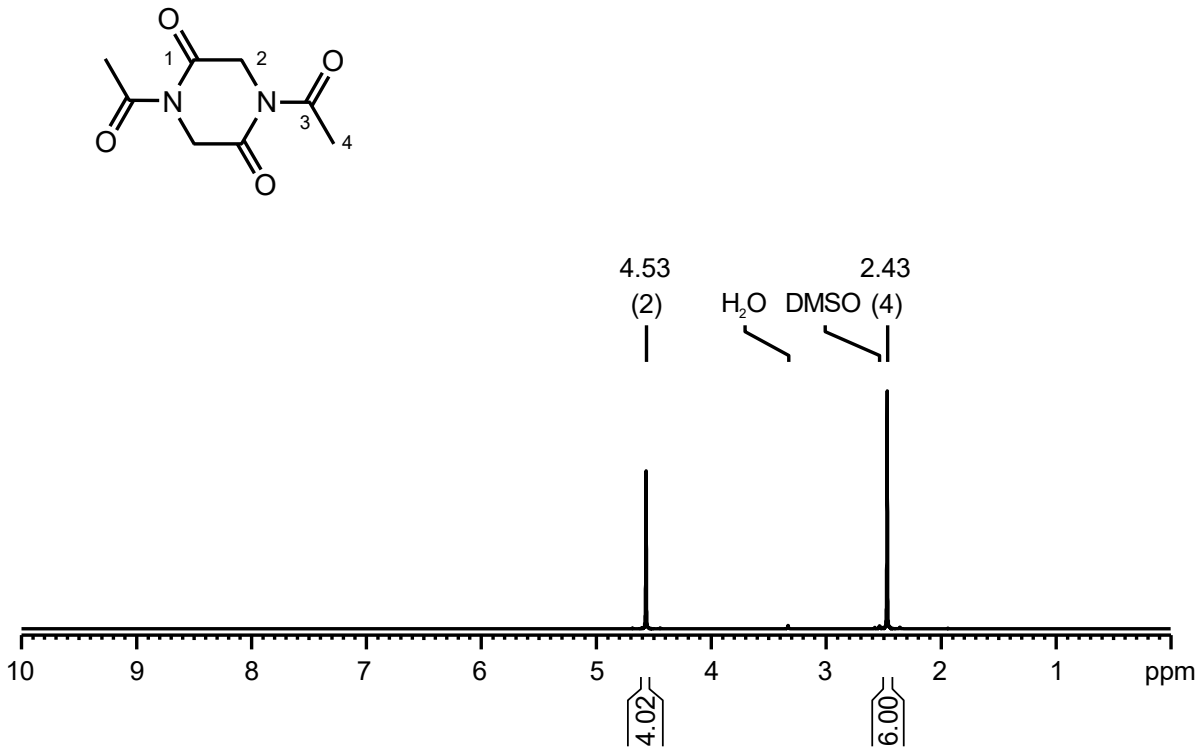


Figure S3.1 ^{1}H NMR of **2** in DMSO-d_6, numbering simplified for ease of interpretation.

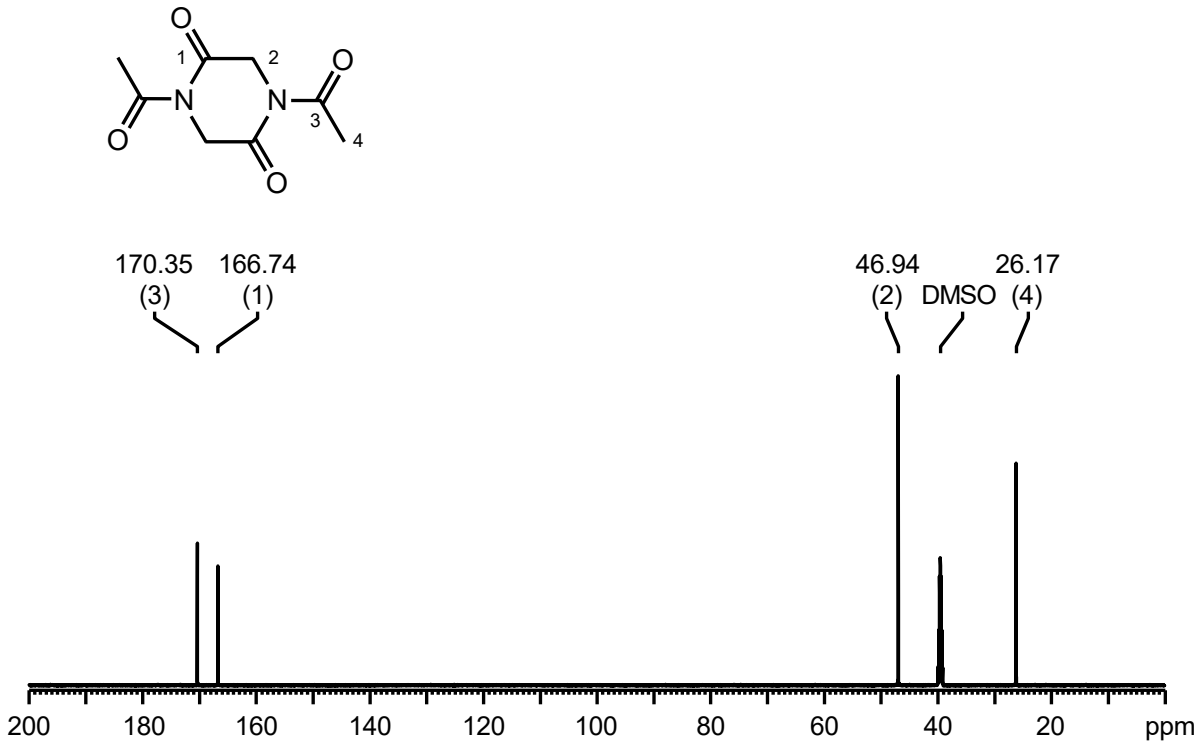


Figure S3.2 ^{13}C NMR of **2** in DMSO-d_6, numbering simplified for ease of interpretation.

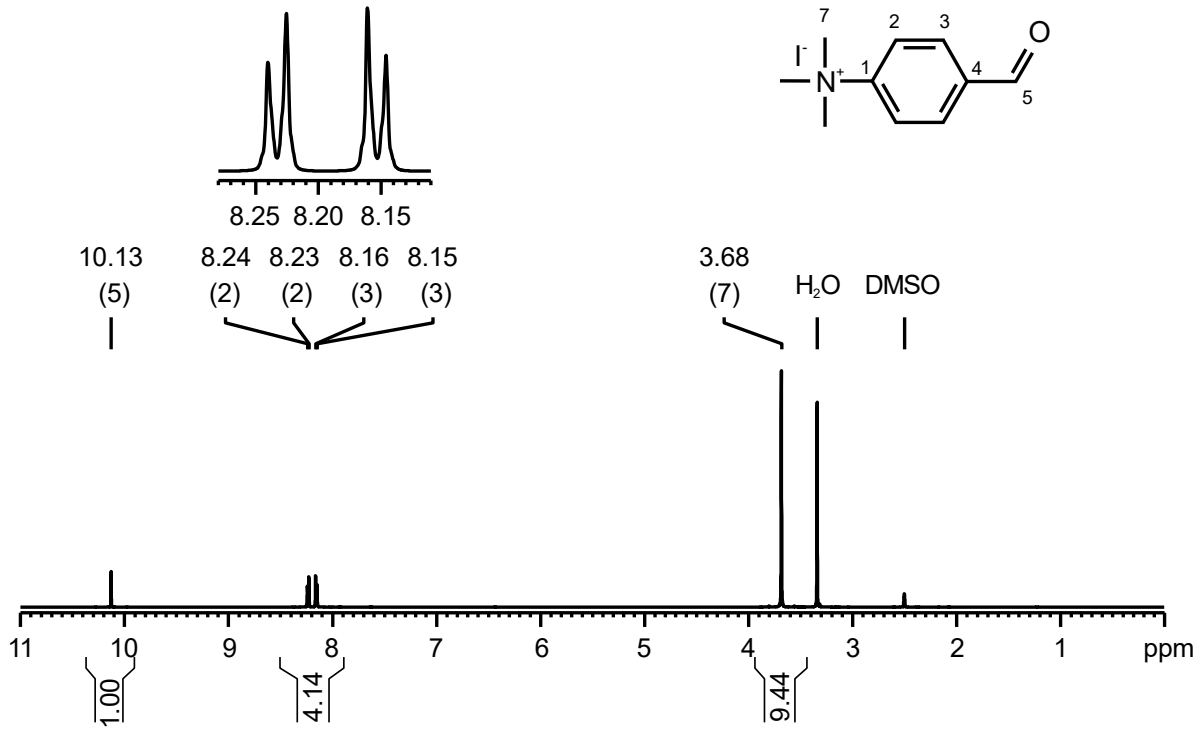


Figure S3.3 ^{1}H NMR of **3i** in DMSO-d_6, numbering simplified for ease of interpretation.

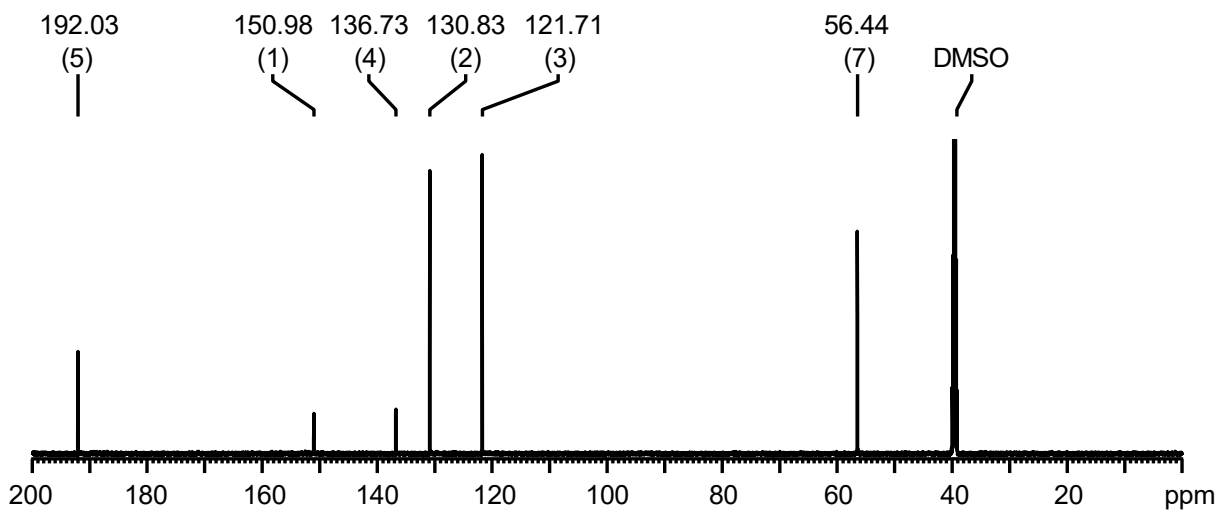


Figure S3.4 ^{13}C NMR of **3i** in DMSO-d_6, numbering simplified for ease of interpretation.

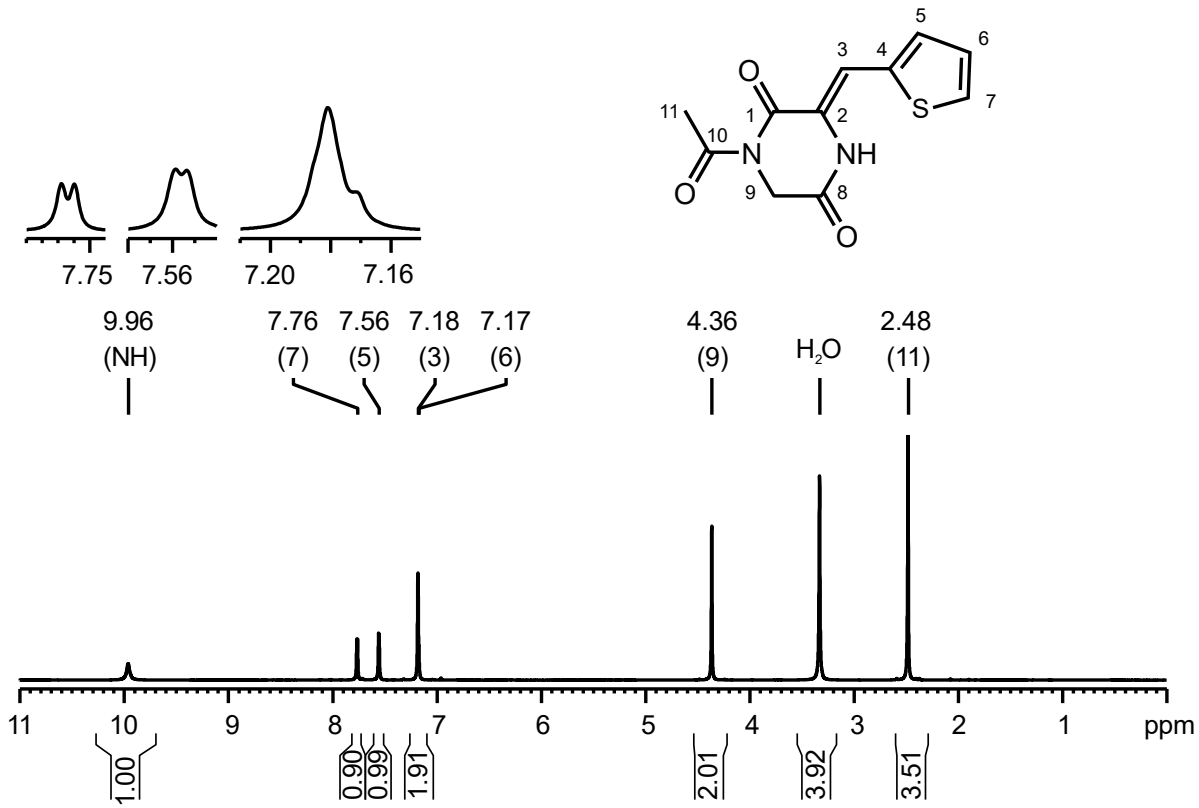


Figure S3.5 ^{1}H NMR of **9** in DMSO-d_6, numbering simplified for ease of interpretation.

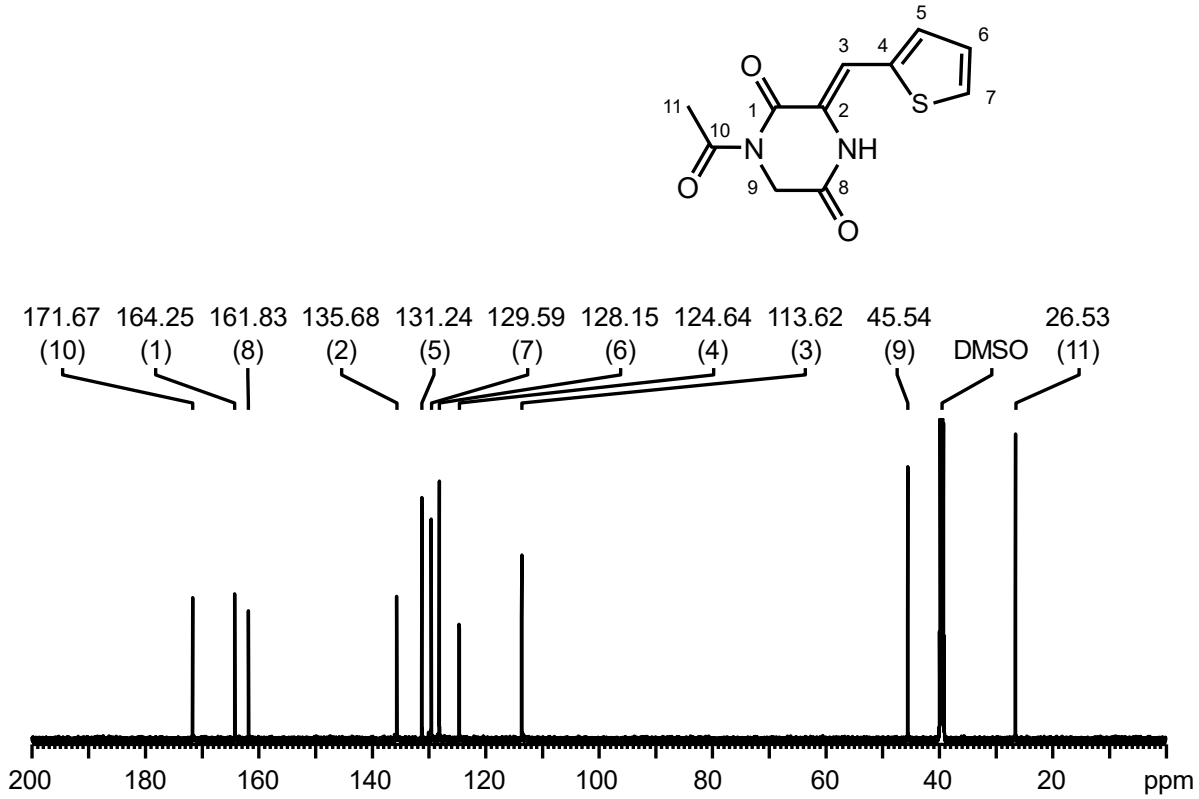


Figure S3.6 ^{13}C NMR of **9** in DMSO-d_6, numbering simplified for ease of interpretation.

4a

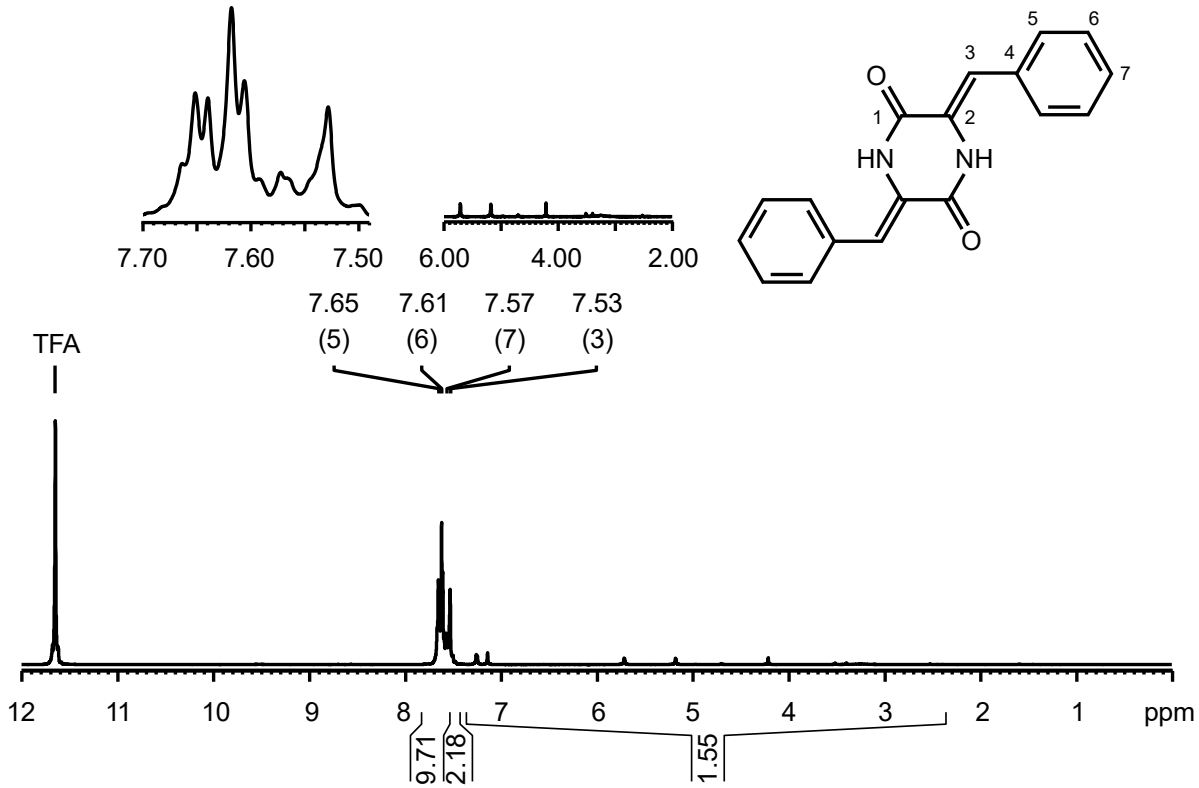


Figure S3.7 ^{1}H NMR of **4a** in TFA-*d*, numbering simplified for ease of interpretation.

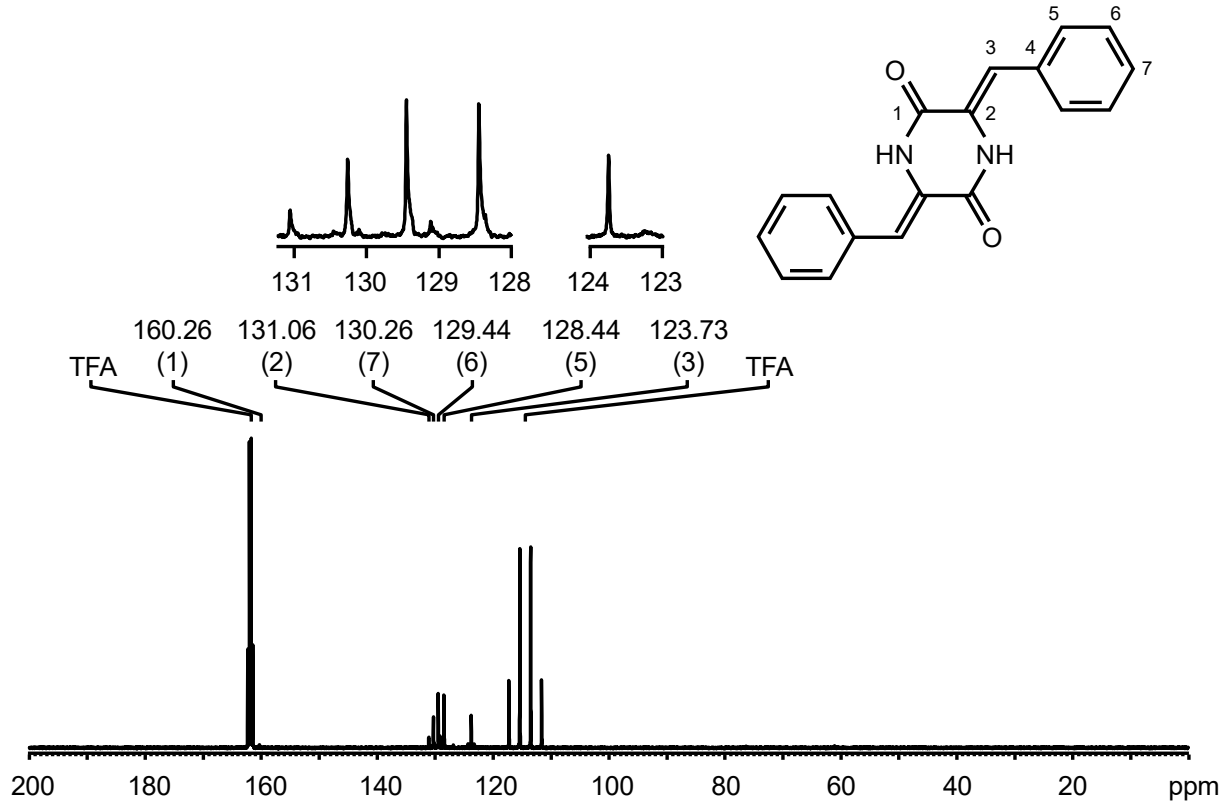


Figure S3.8 ^{13}C NMR of **4a** in TFA-*d*, numbering simplified for ease of interpretation.

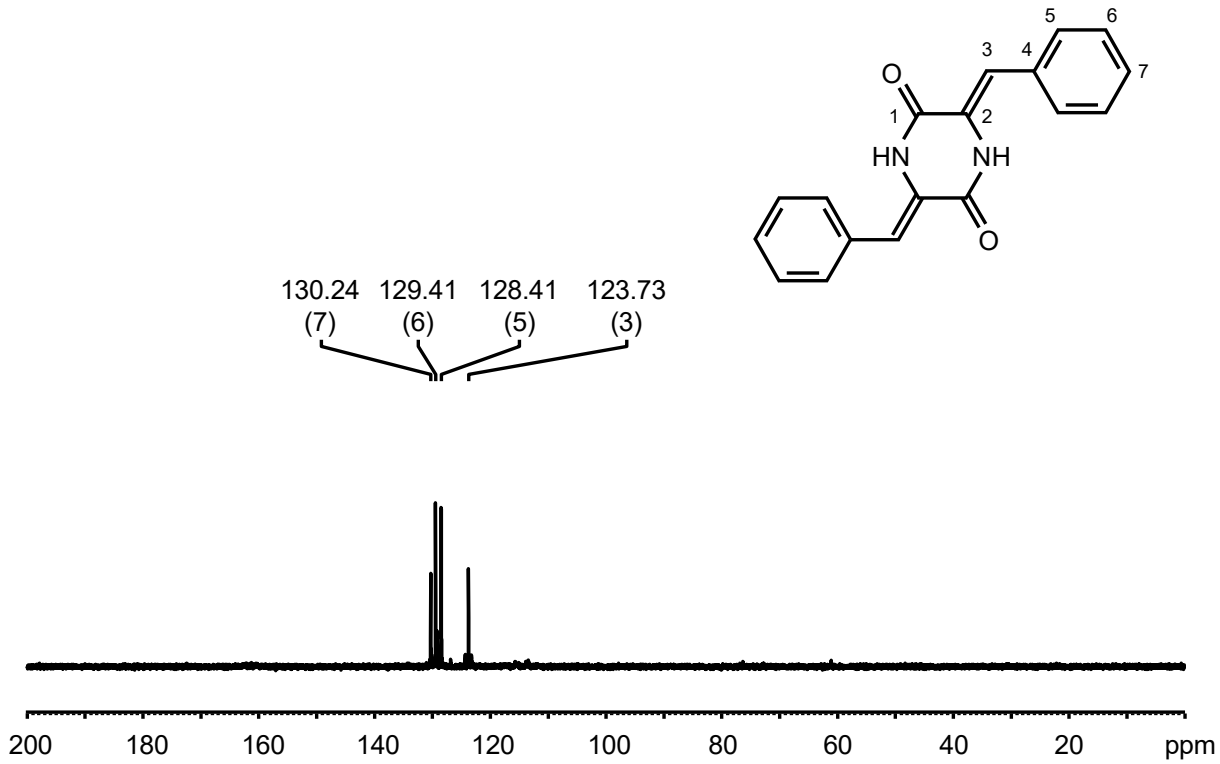


Figure S3.9 DEPT135 NMR of **4a** in TFA-*d*, numbering simplified for ease of interpretation.

6a

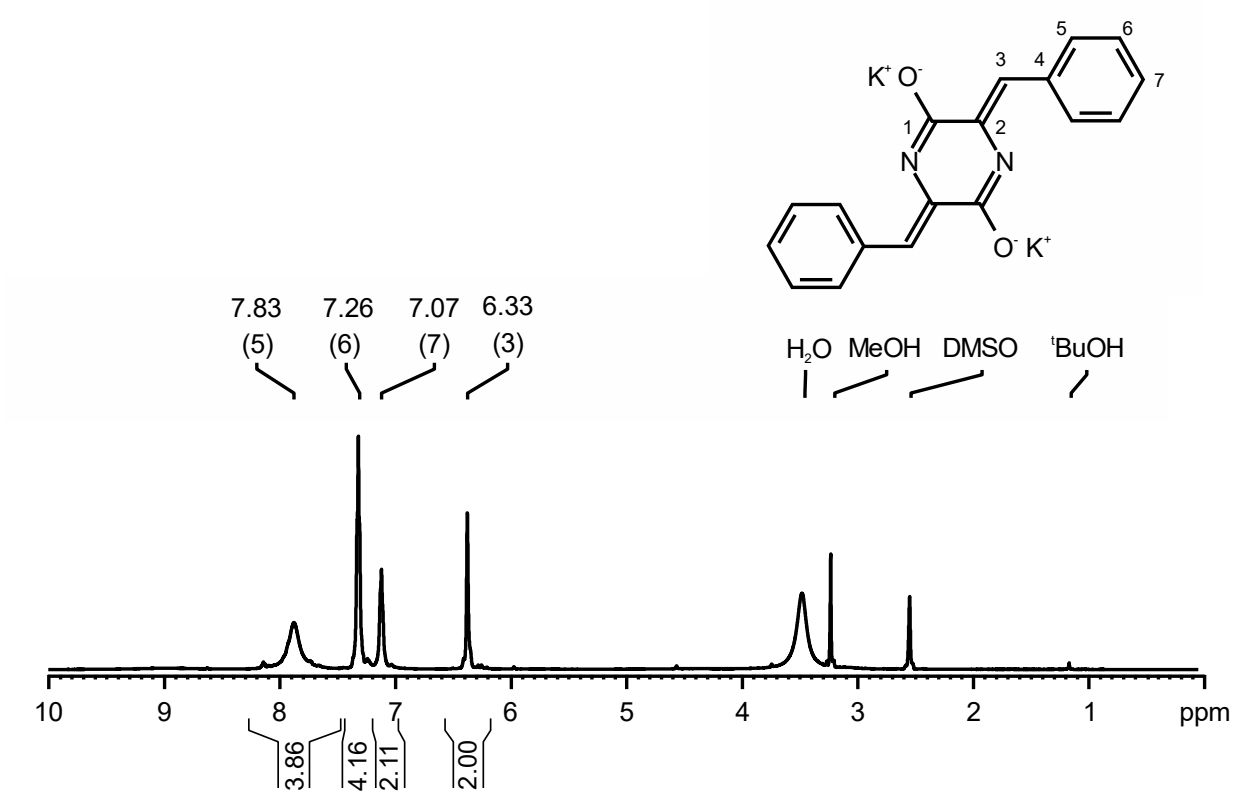


Figure S3.10 ^{1}H NMR of **6a** in DMSO-d_6, numbering simplified for ease of interpretation.

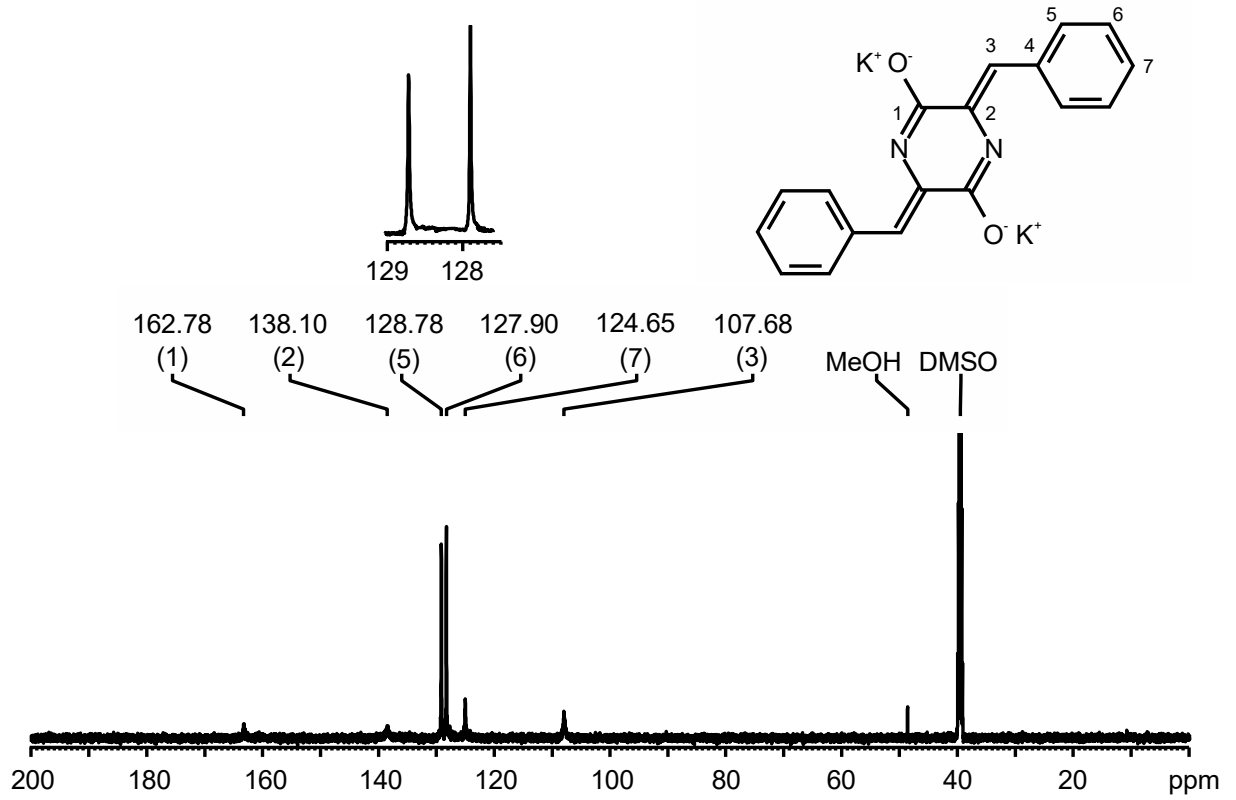


Figure S3.11 ^{13}C NMR of **6a** in DMSO-d_6, numbering simplified for ease of interpretation.

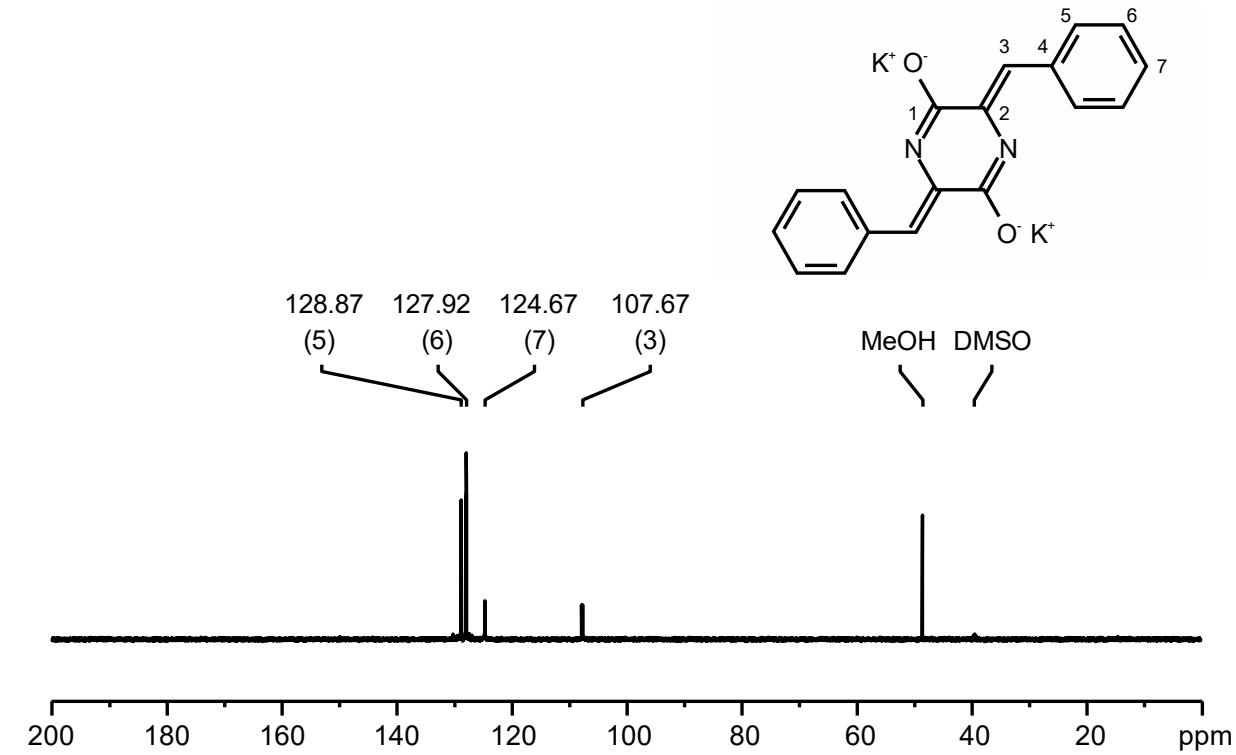


Figure S3.12 DEPT135 NMR of **6a** in DMSO-d_6, numbering simplified for ease of interpretation.

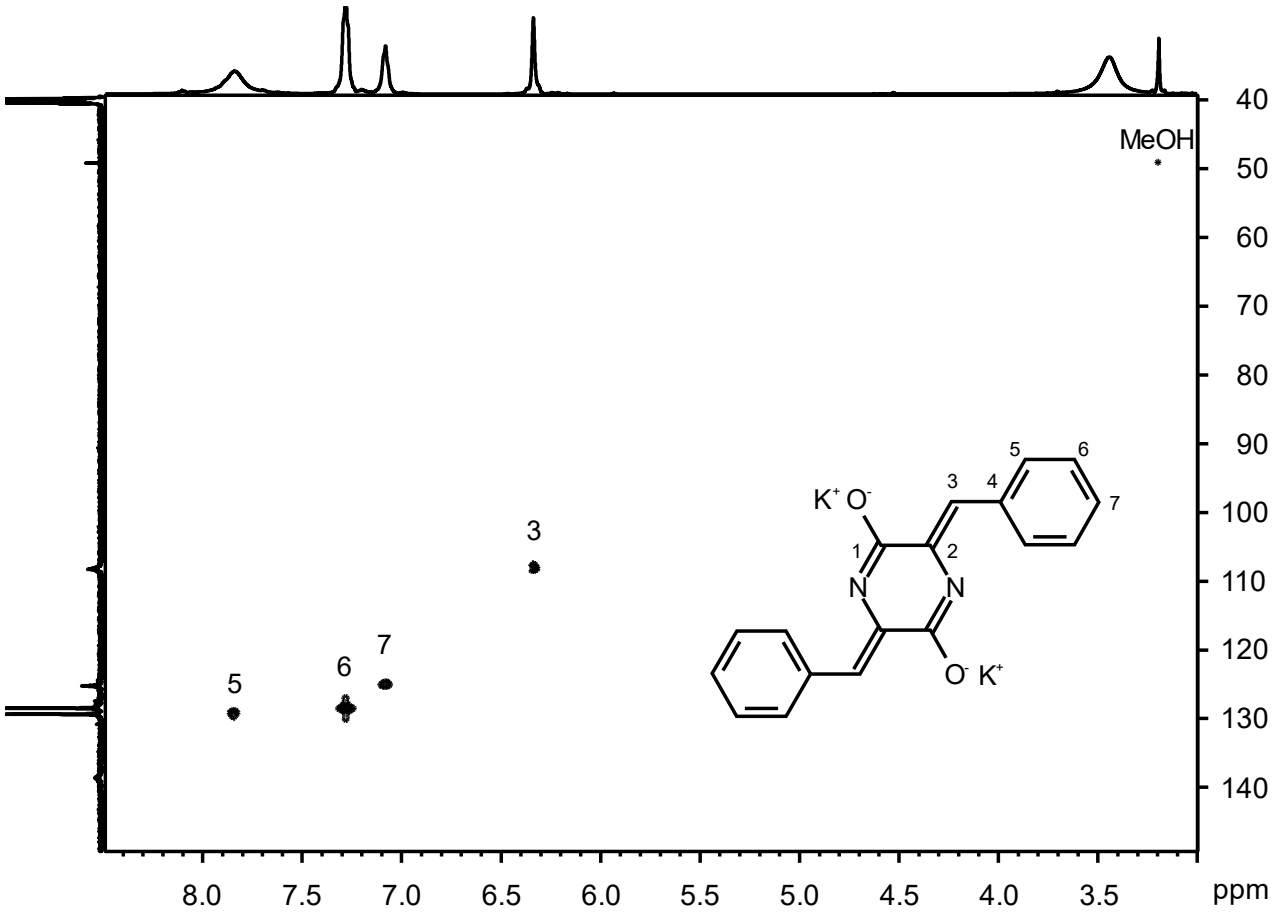


Figure S3.13 HSQC NMR of **6a** in DMSO-d_6, numbering simplified for ease of interpretation.

4b

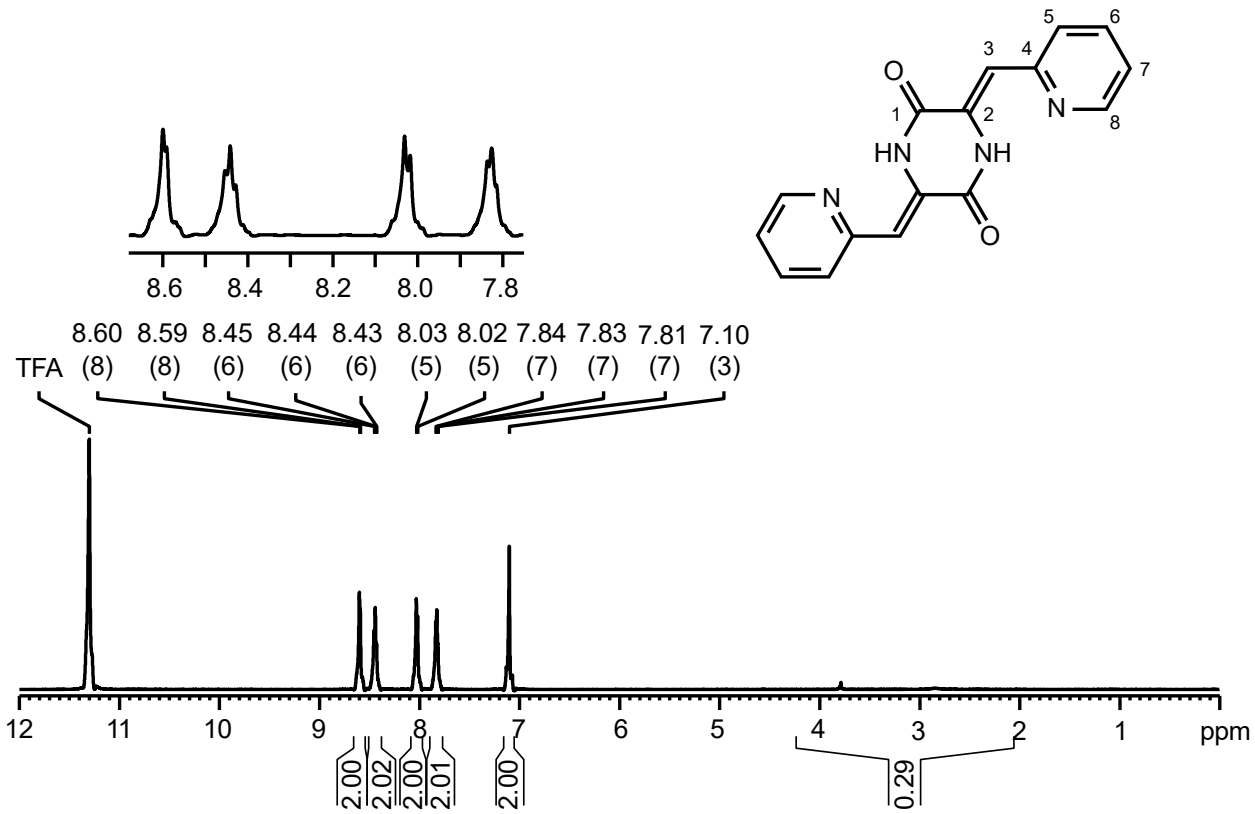


Figure S3.14 ^{1}H NMR of **4b** in TFA-*d*, numbering simplified for ease of interpretation.

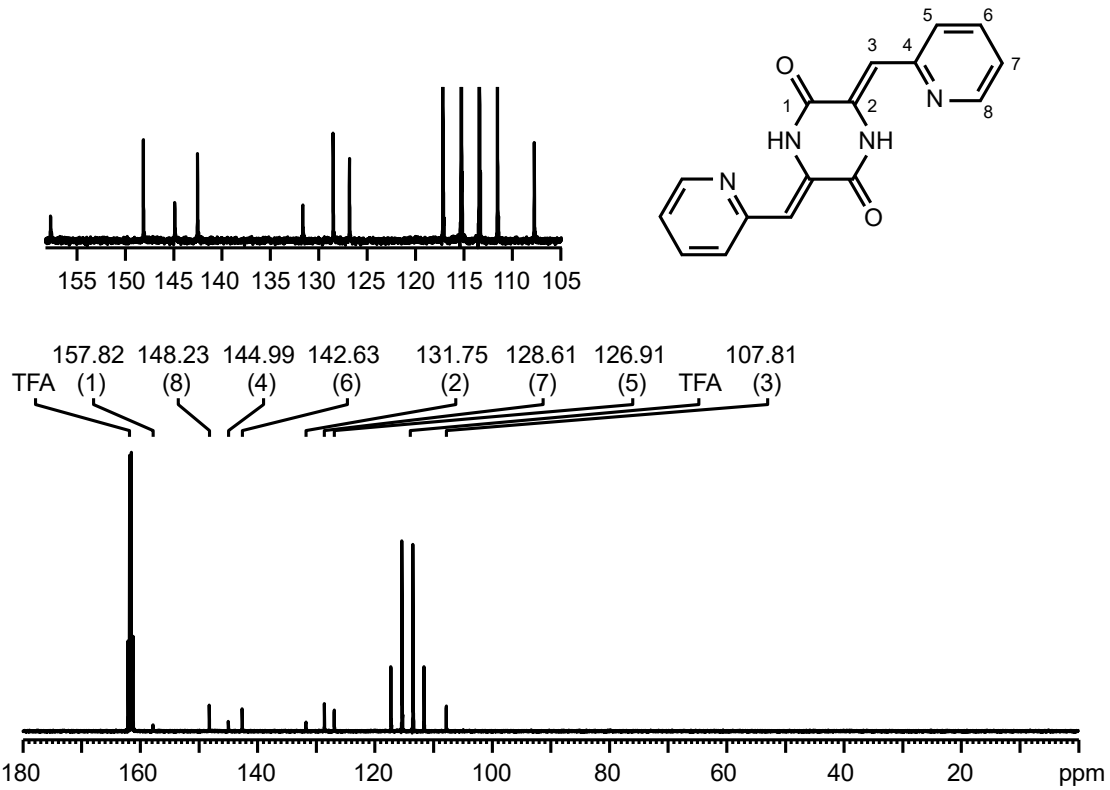


Figure S3.15 ^{13}C NMR of **4b** in TFA-*d*, numbering simplified for ease of interpretation.

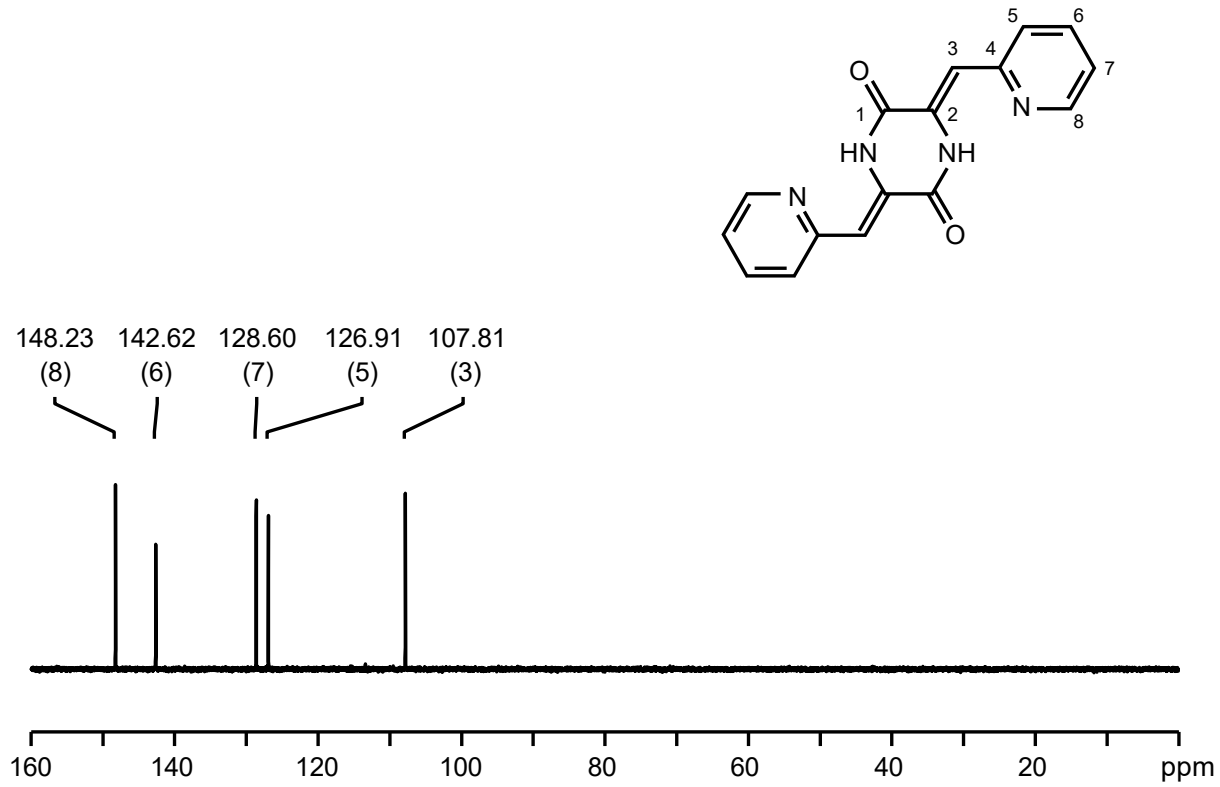


Figure S3.16 DEPT135 NMR of **4b** in TFA-*d*, numbering simplified for ease of interpretation.

6b

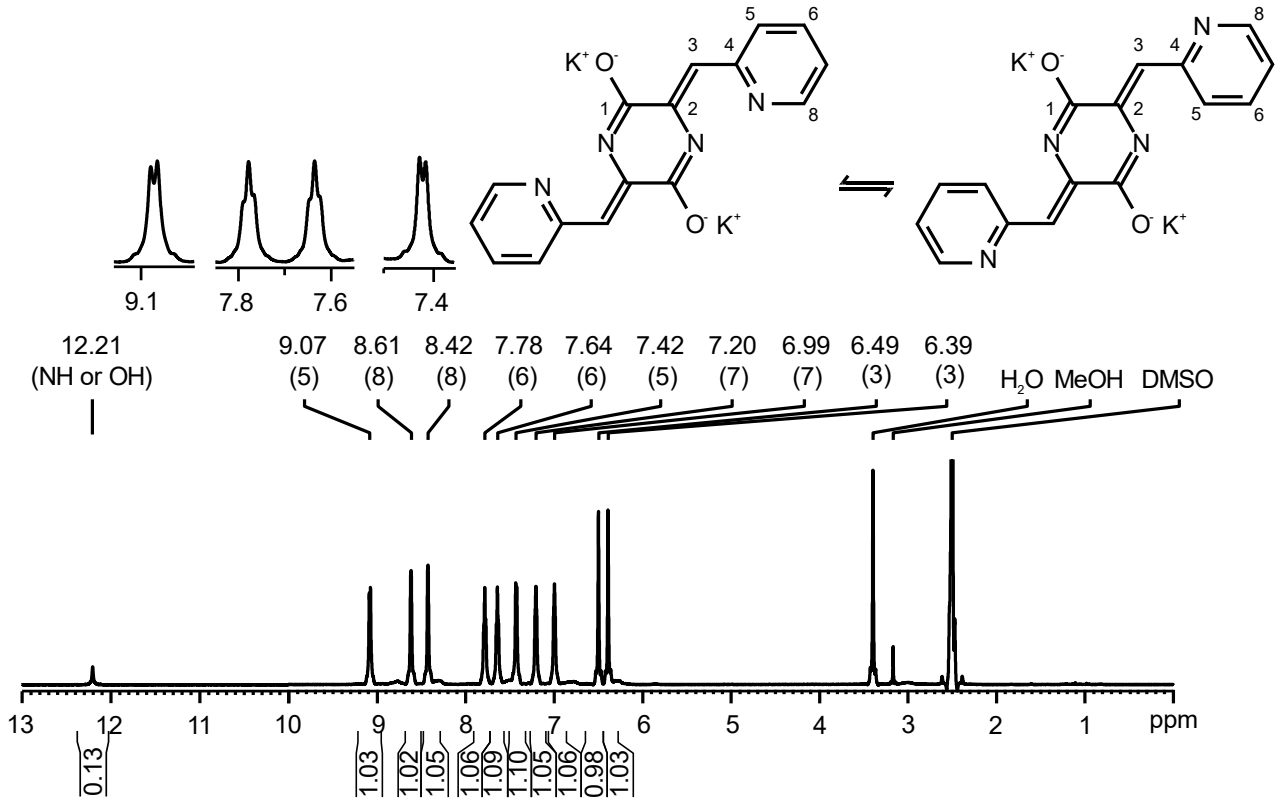


Figure S3.17 ^{1}H NMR of **6b** in DMSO-d_6, numbering simplified for ease of interpretation.

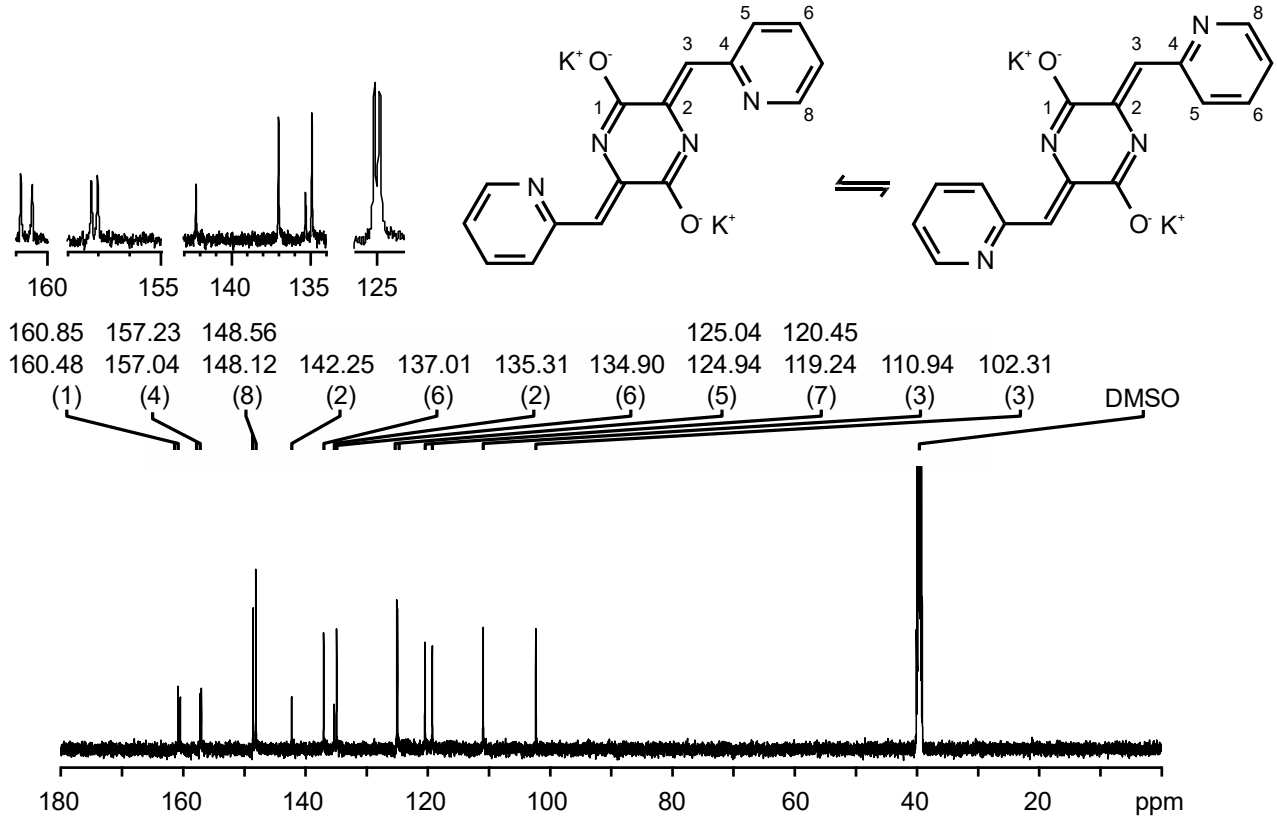


Figure S3.18 ^{13}C NMR of **6b** in DMSO-d_6, numbering simplified for ease of interpretation.

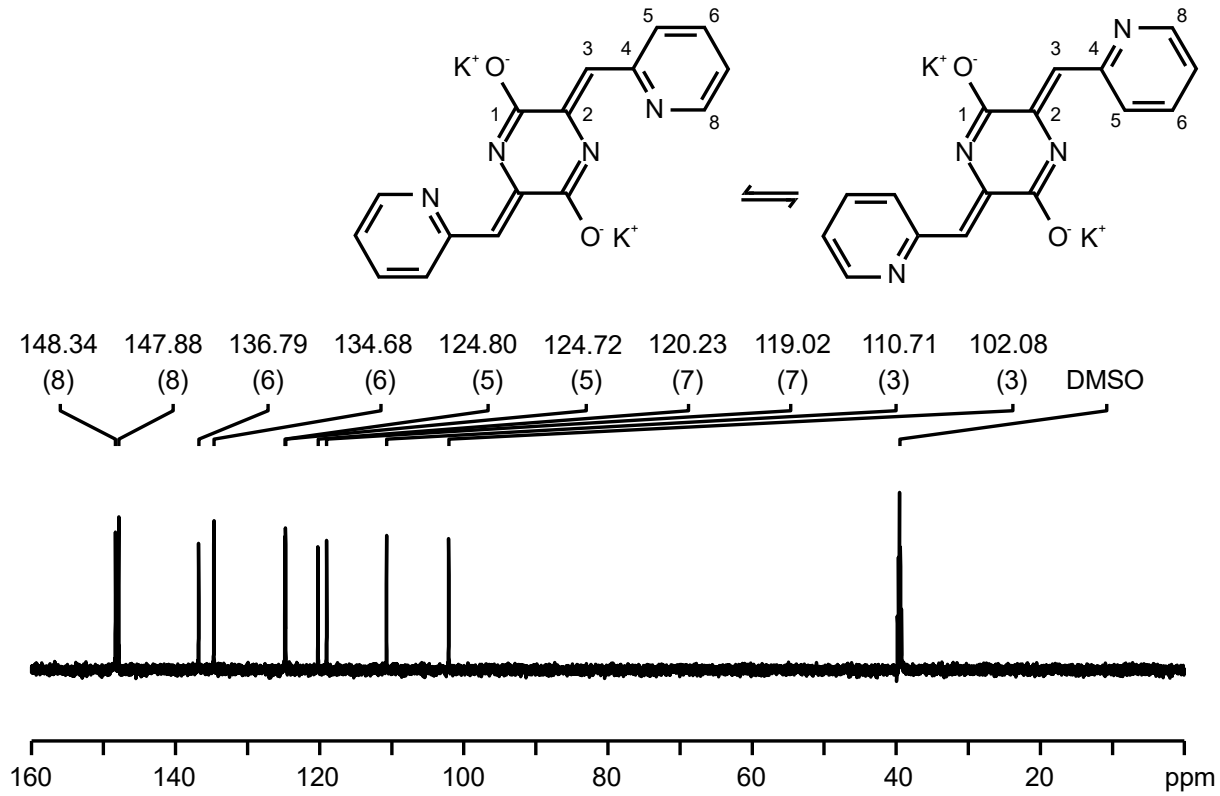


Figure S3.19 DEPT135 NMR of **6b** in DMSO-d_6, numbering simplified for ease of interpretation.

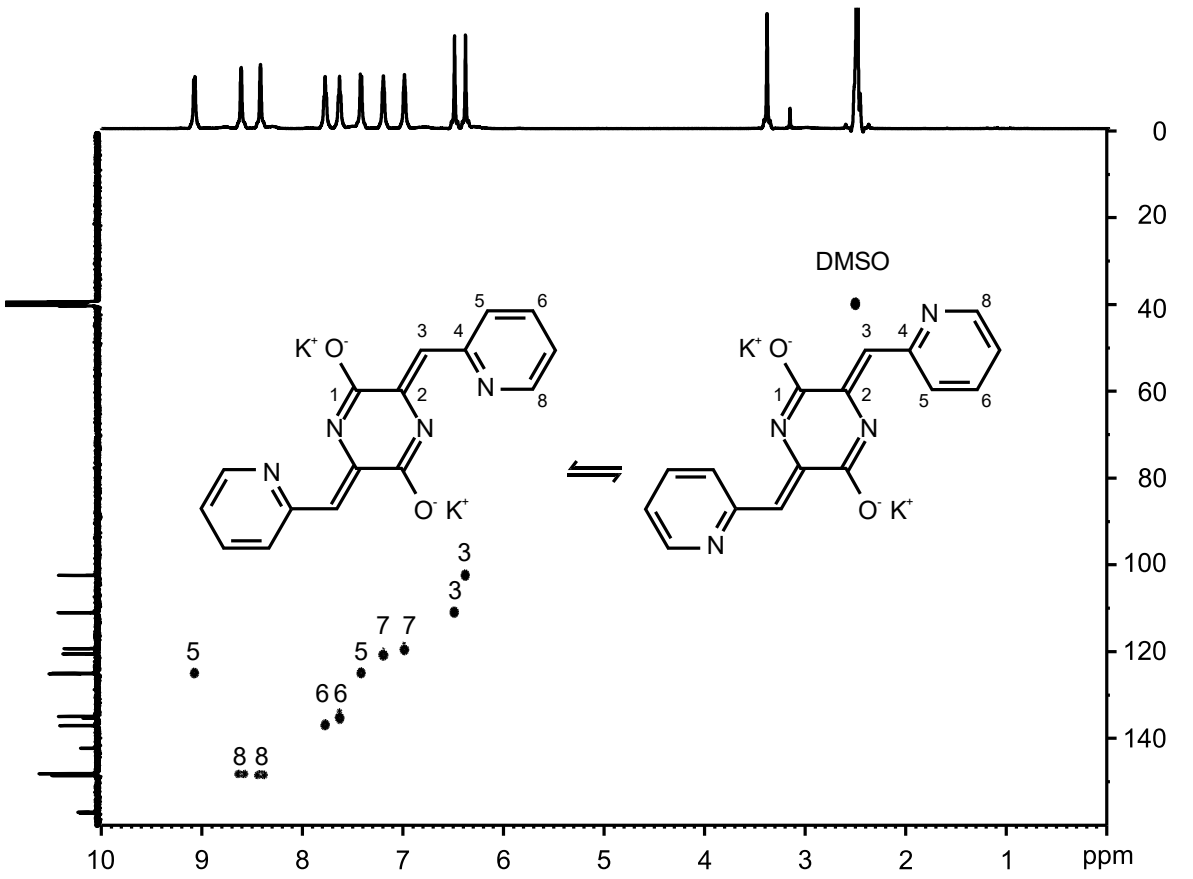


Figure S3.20 HSQC NMR of **6b** in DMSO-d_6, numbering simplified for ease of interpretation.

4c

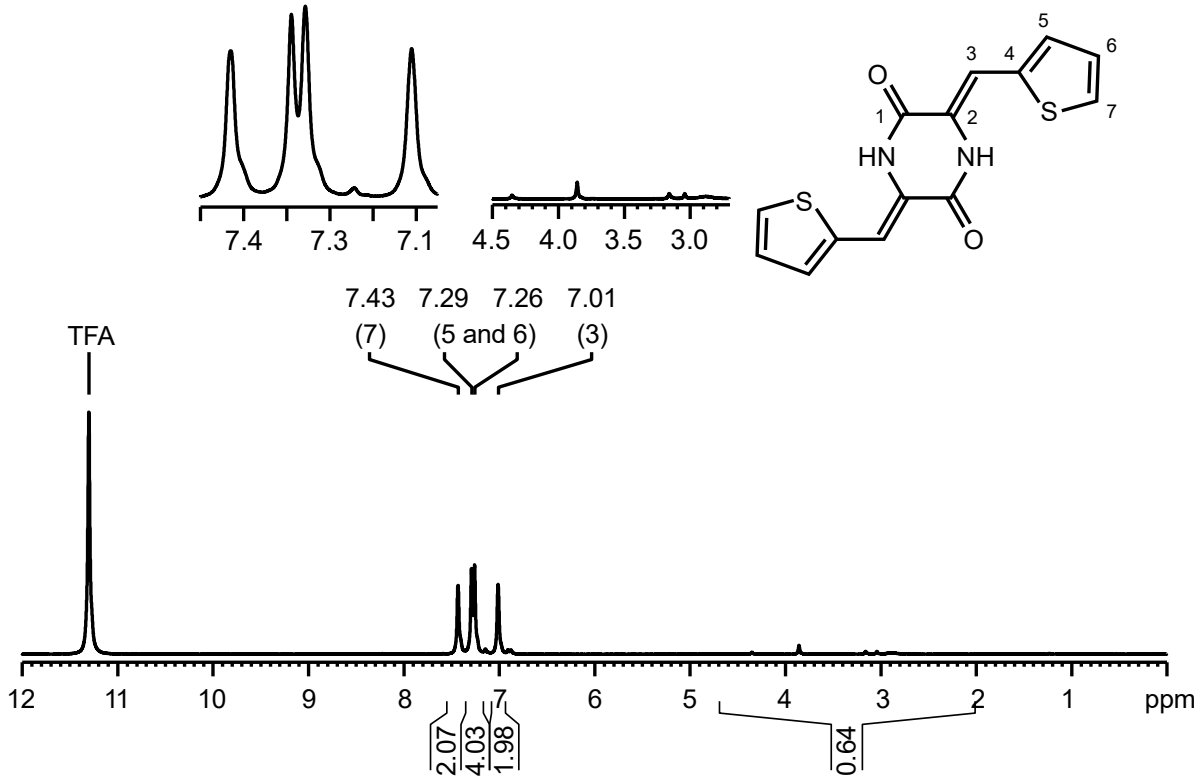


Figure S3.21 ^{1}H NMR of **4c** in TFA-*d*, numbering simplified for ease of interpretation.

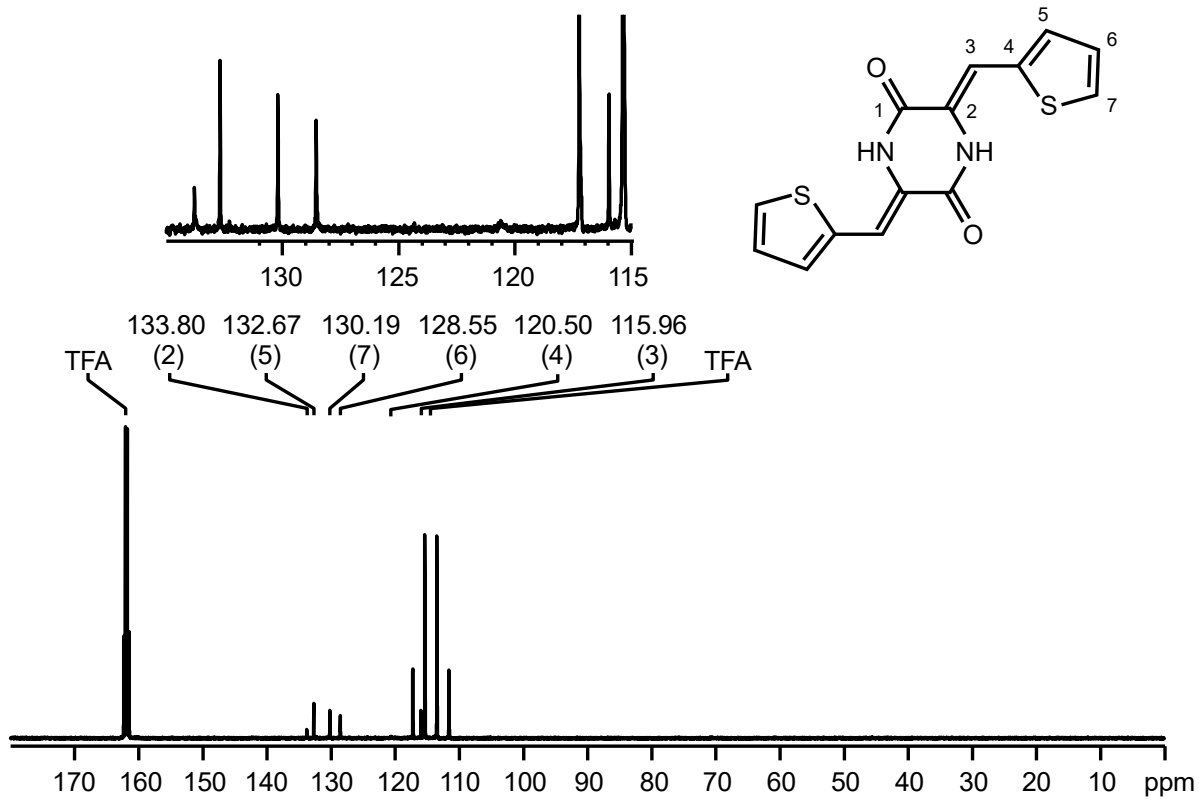


Figure S3.22 ^{13}C NMR of **4c** in TFA-*d*, numbering simplified for ease of interpretation.

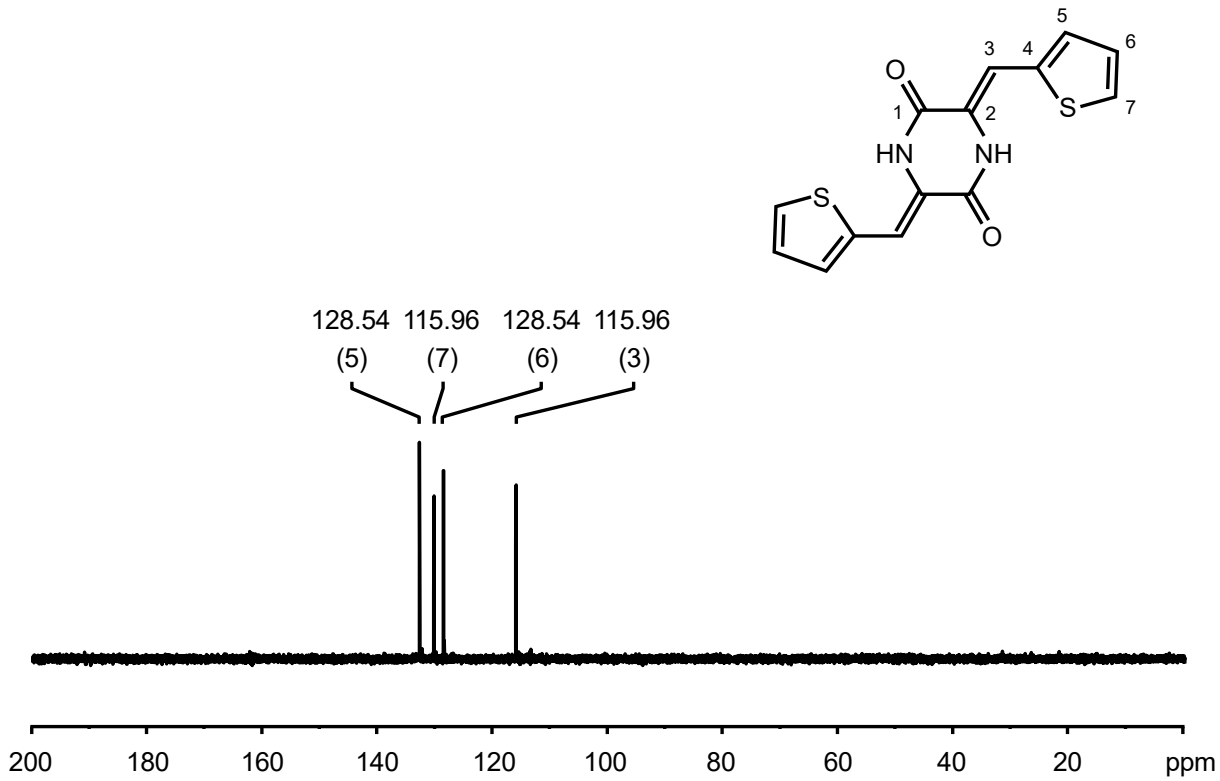


Figure S3.23 DEPT135 NMR of **4c** in TFA-*d*, numbering simplified for ease of interpretation.

6c

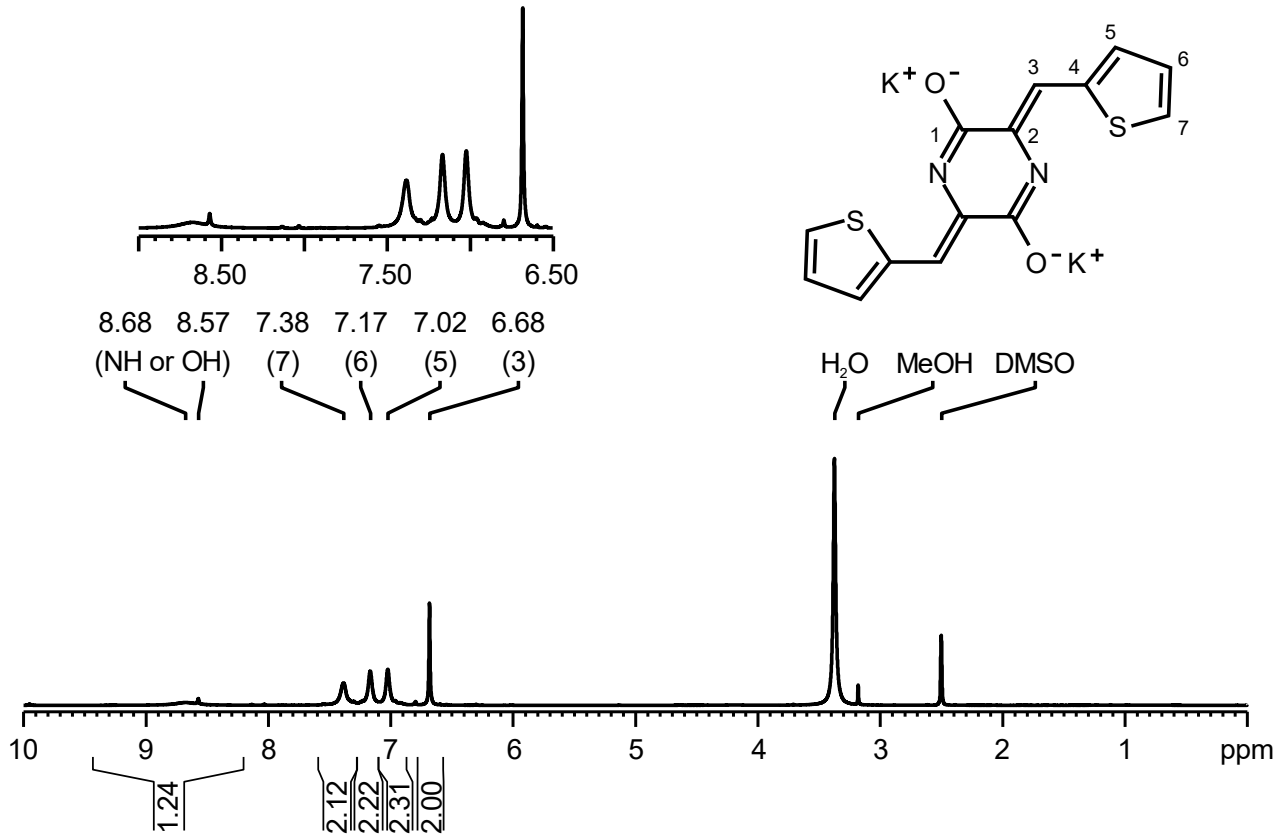


Figure S3.24 ^{1}H NMR of **6c** in DMSO-d_6, numbering simplified for ease of interpretation.

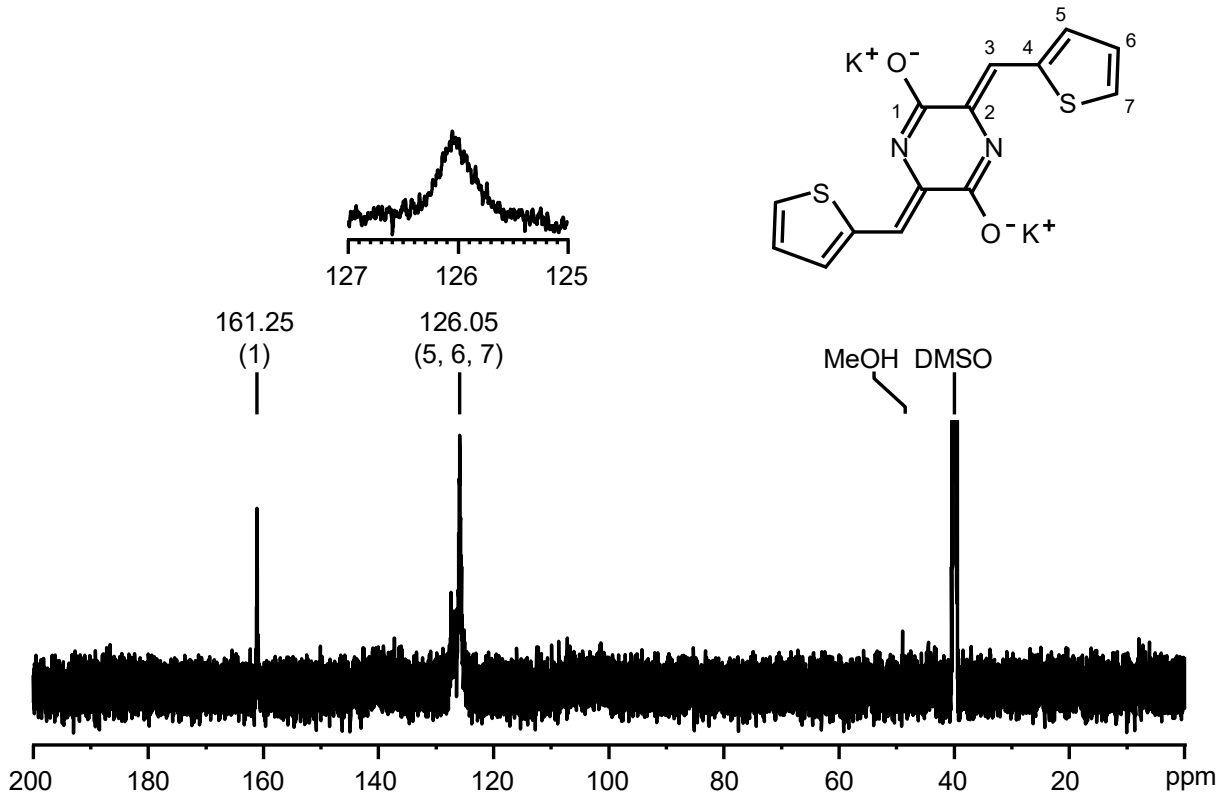


Figure S3.25 ^{13}C NMR of **6c** in DMSO-d_6, numbering simplified for ease of interpretation.

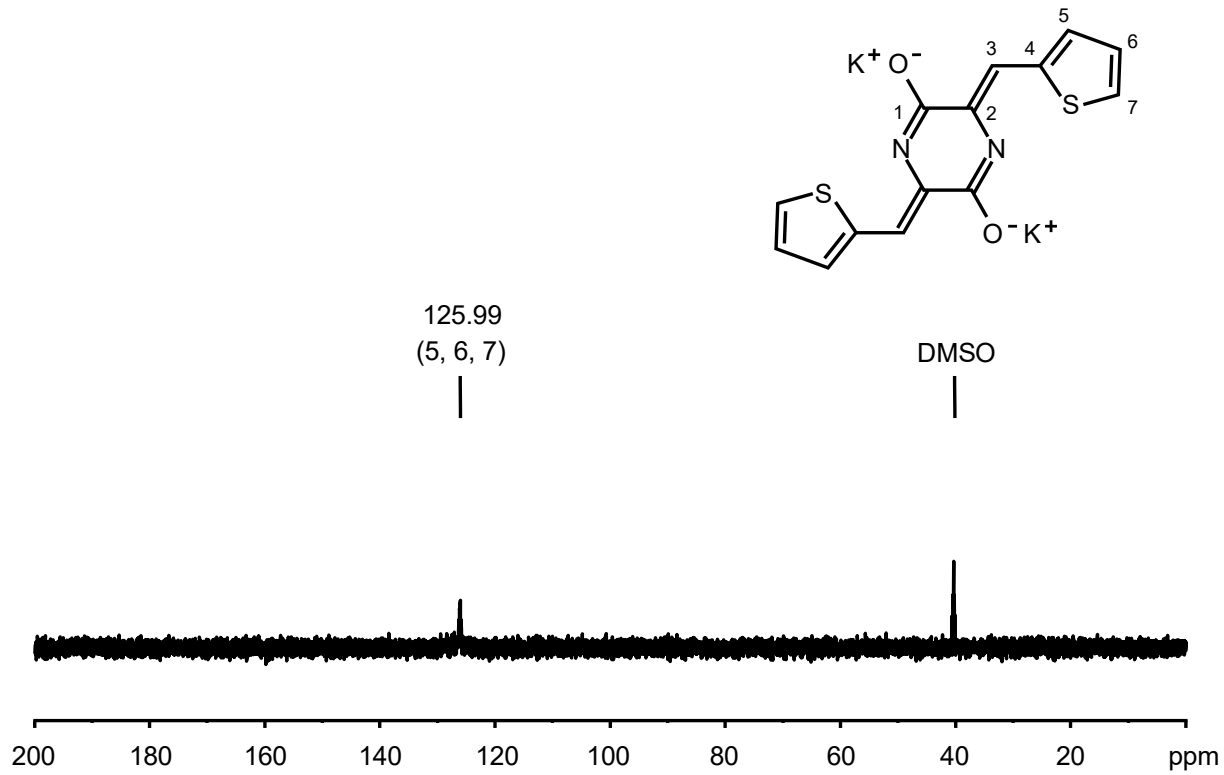


Figure S3.26 DEPT135 NMR of **6c** in DMSO-d_6, numbering simplified for ease of interpretation.

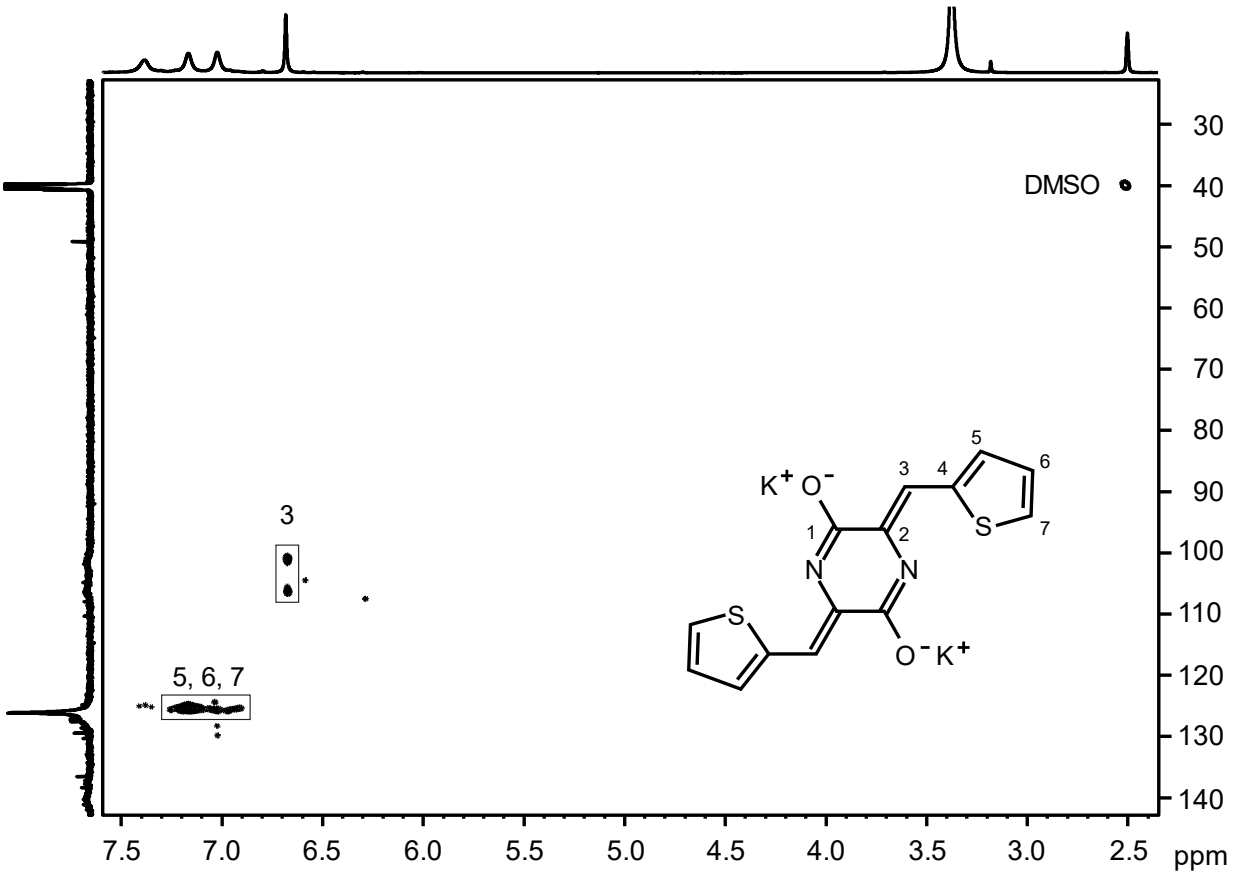


Figure S3.27 HSQC NMR of **6c** in DMSO-d_6, numbering simplified for ease of interpretation.

4d

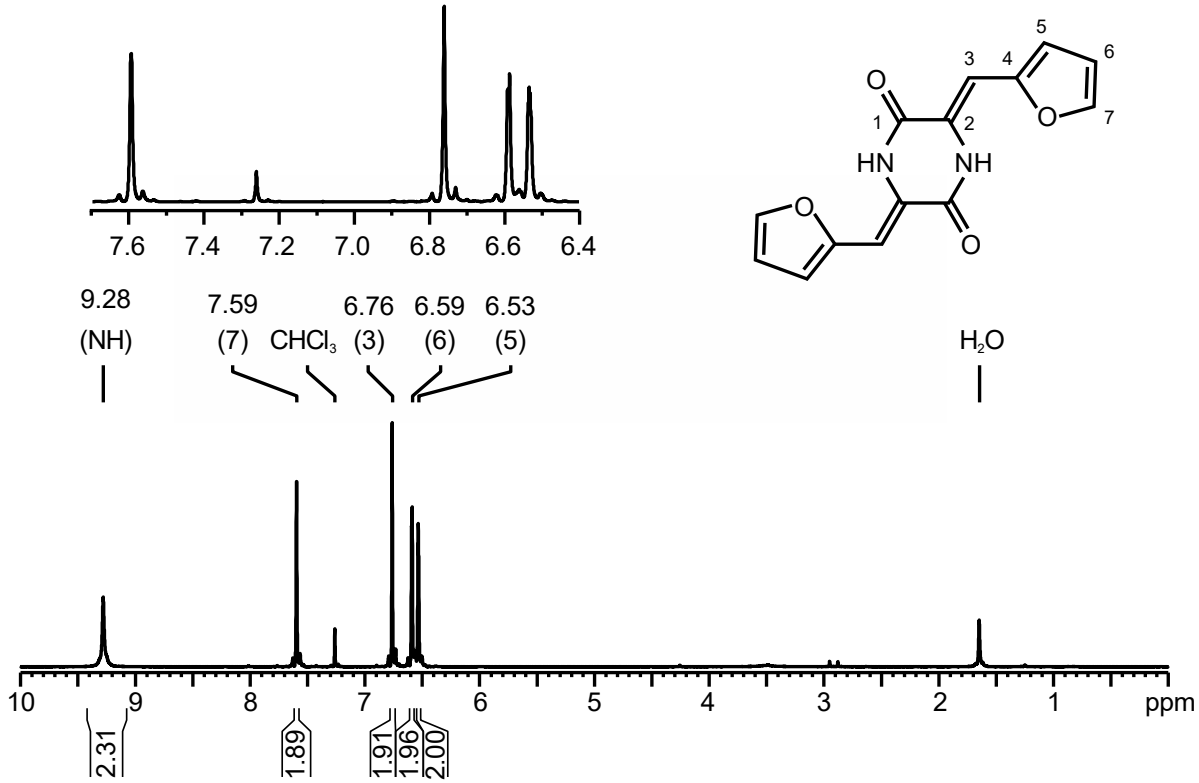


Figure S3.28 ^{1}H NMR of **4d** in $CDCl_3$, numbering simplified for ease of interpretation.

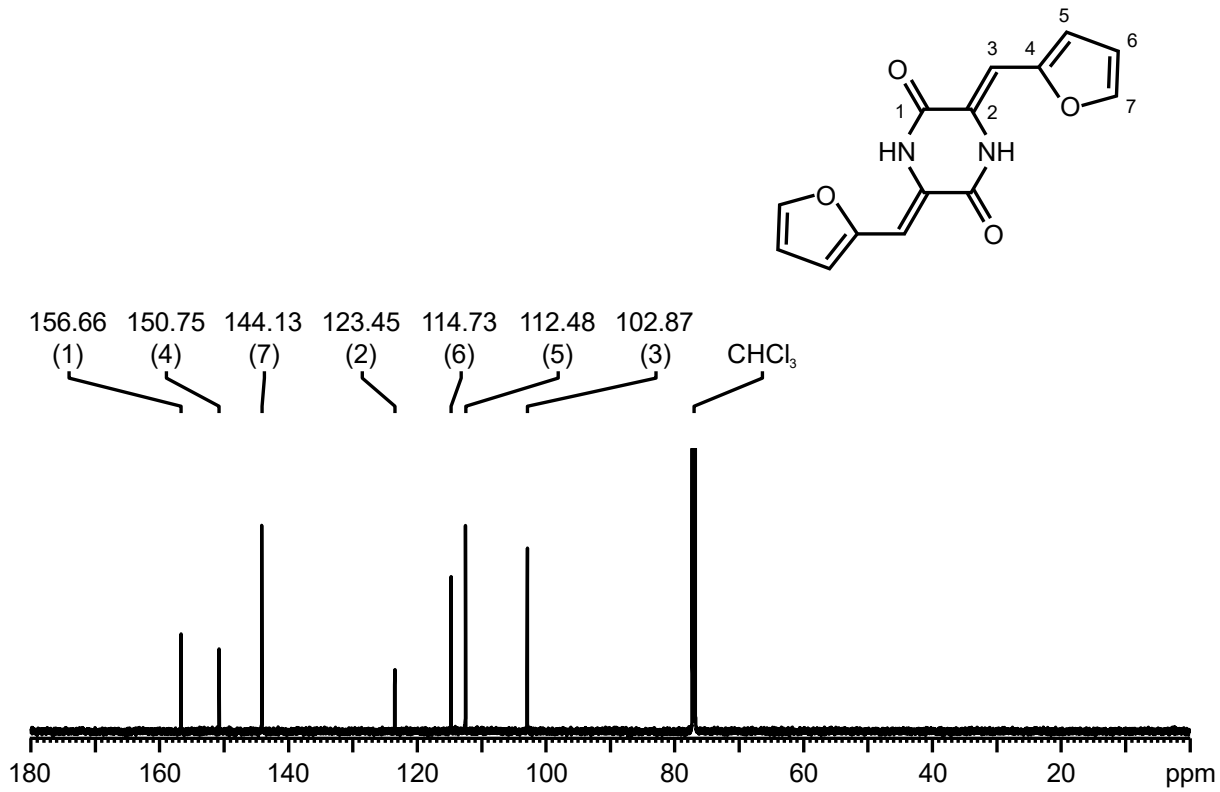


Figure S3.29 ^{13}C NMR of **4d** in $CDCl_3$, numbering simplified for ease of interpretation.

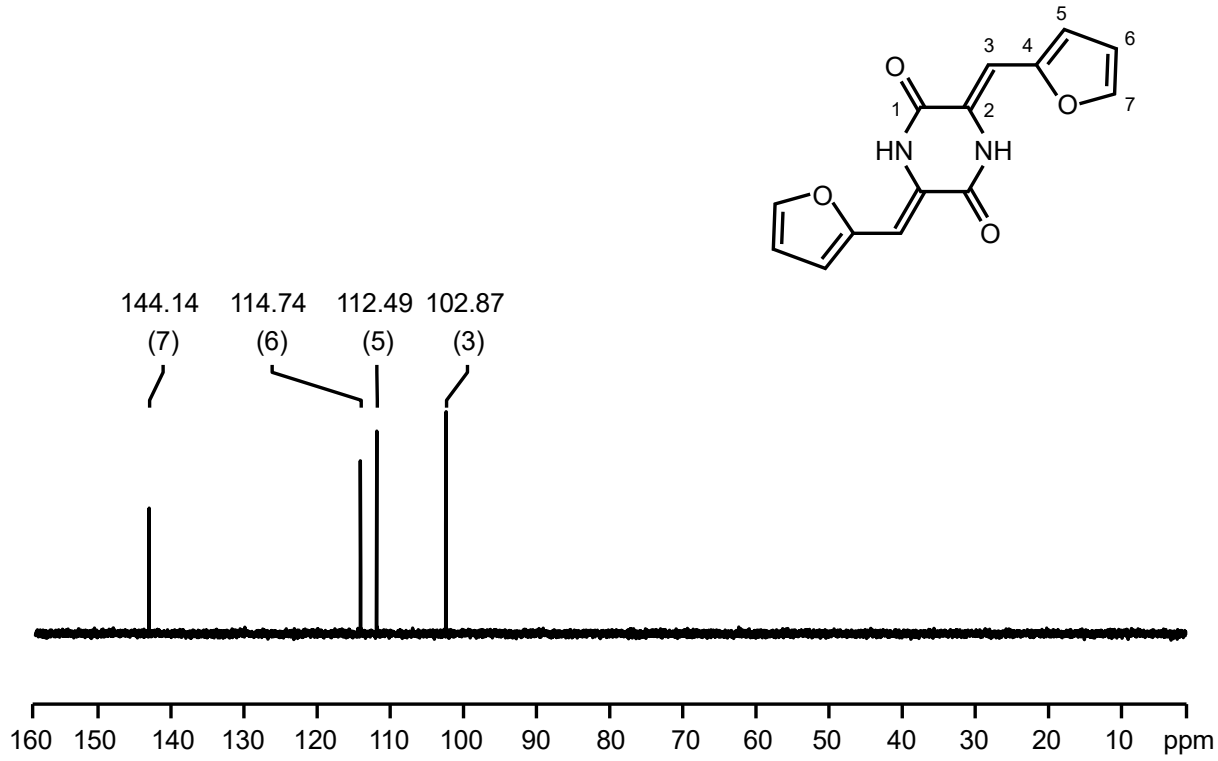


Figure S3.30 DEPT135 NMR of **4d** in $CDCl_3$, numbering simplified for ease of interpretation.

6d

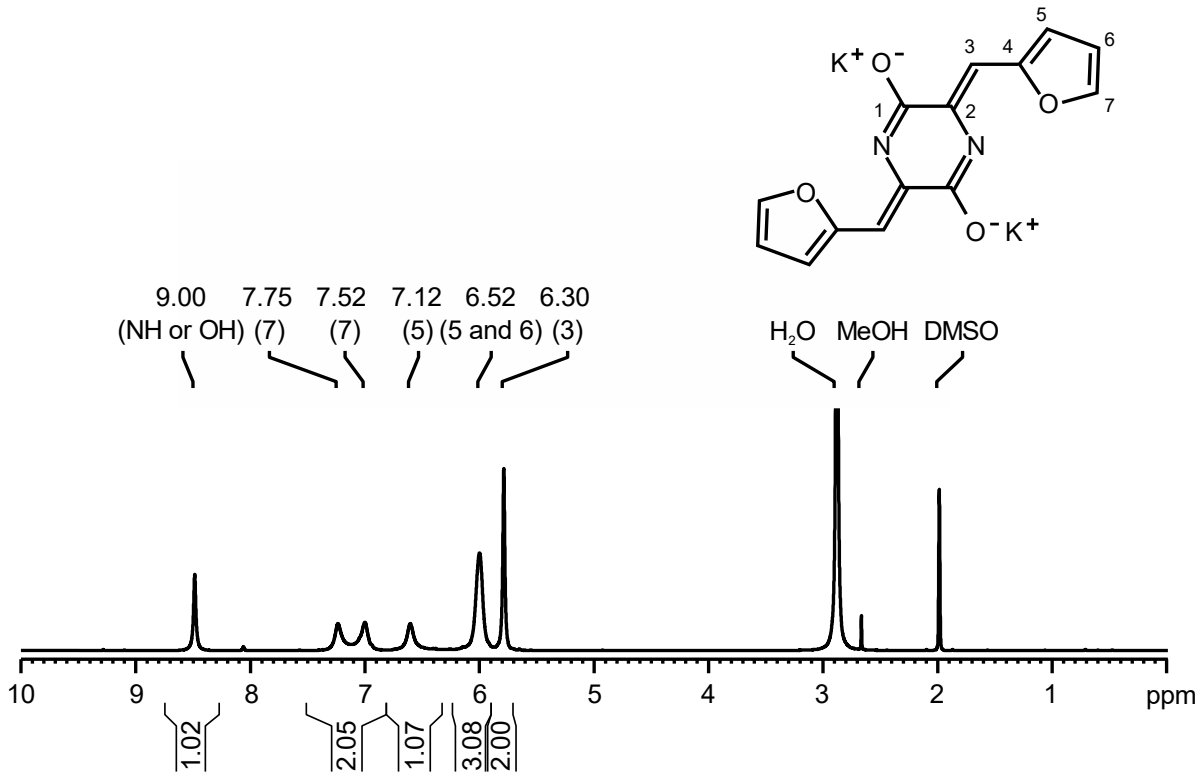


Figure S3.31 ^{1}H NMR of **6d** in DMSO-d_6, numbering simplified for ease of interpretation.

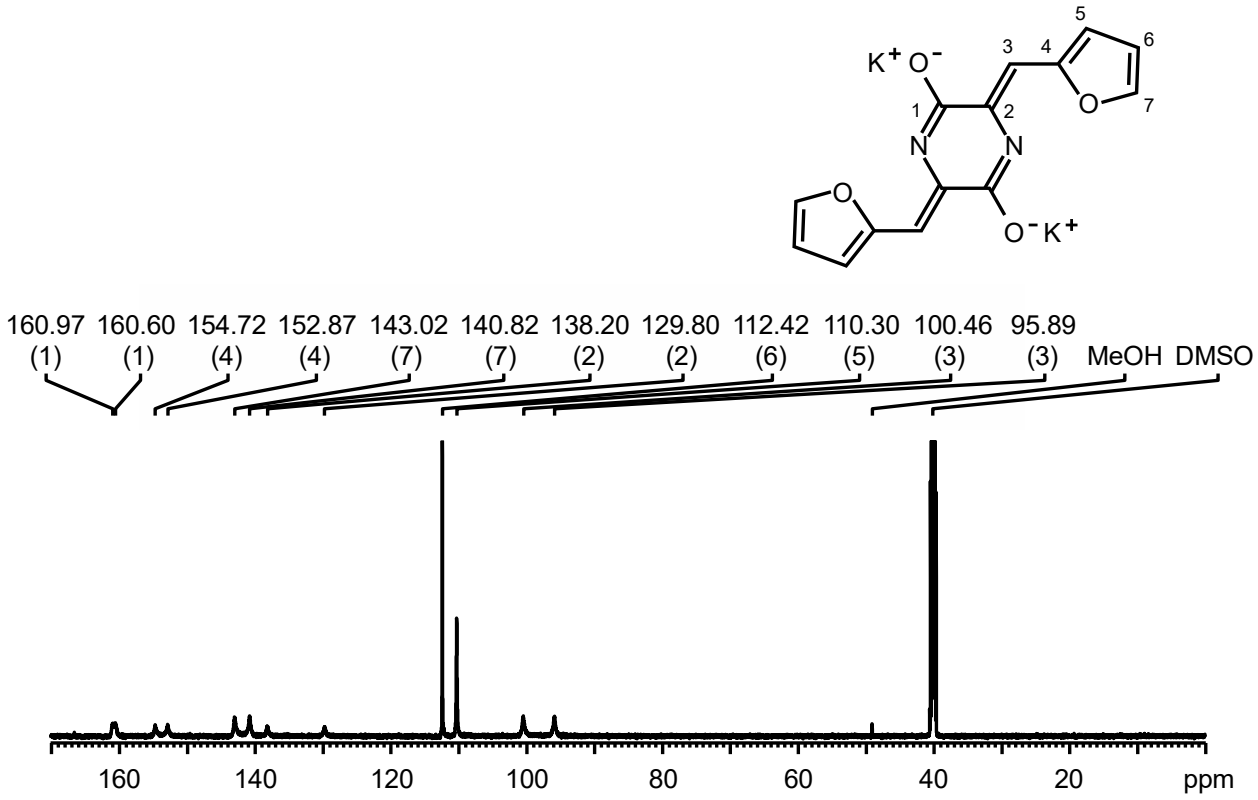


Figure S3.32 ^{13}C NMR of **6d** in DMSO-d_6, numbering simplified for ease of interpretation.

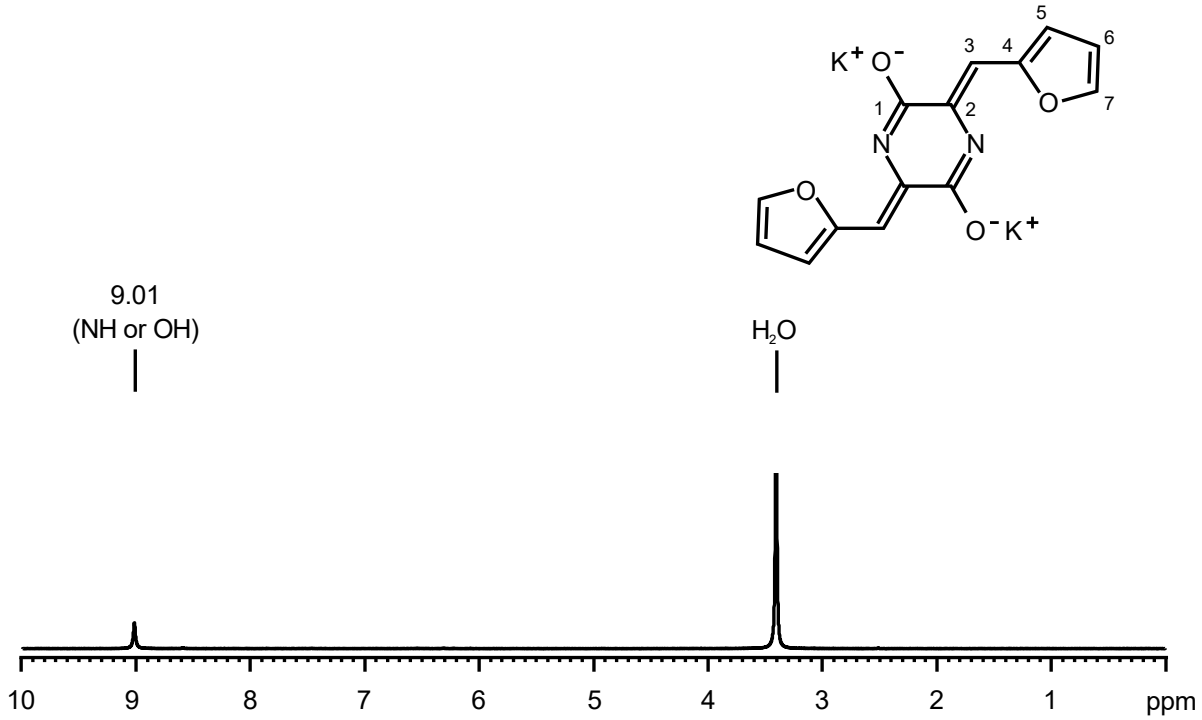


Figure S3.33 1D NOE NMR of **6d** in DMSO-d_6, numbering simplified for ease of interpretation. Shift at 9.01 ppm irradiated.

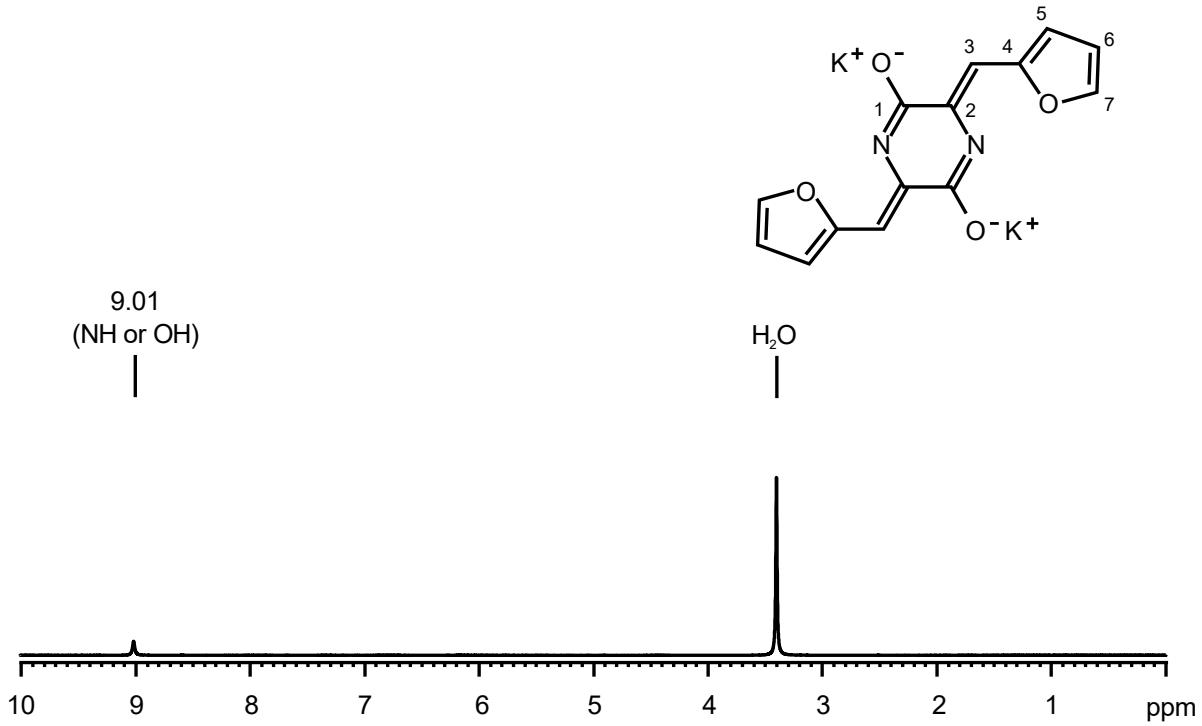


Figure S3.34 1D NOE NMR of **6d** in DMSO-d_6, numbering simplified for ease of interpretation. H_2O shift irradiated.

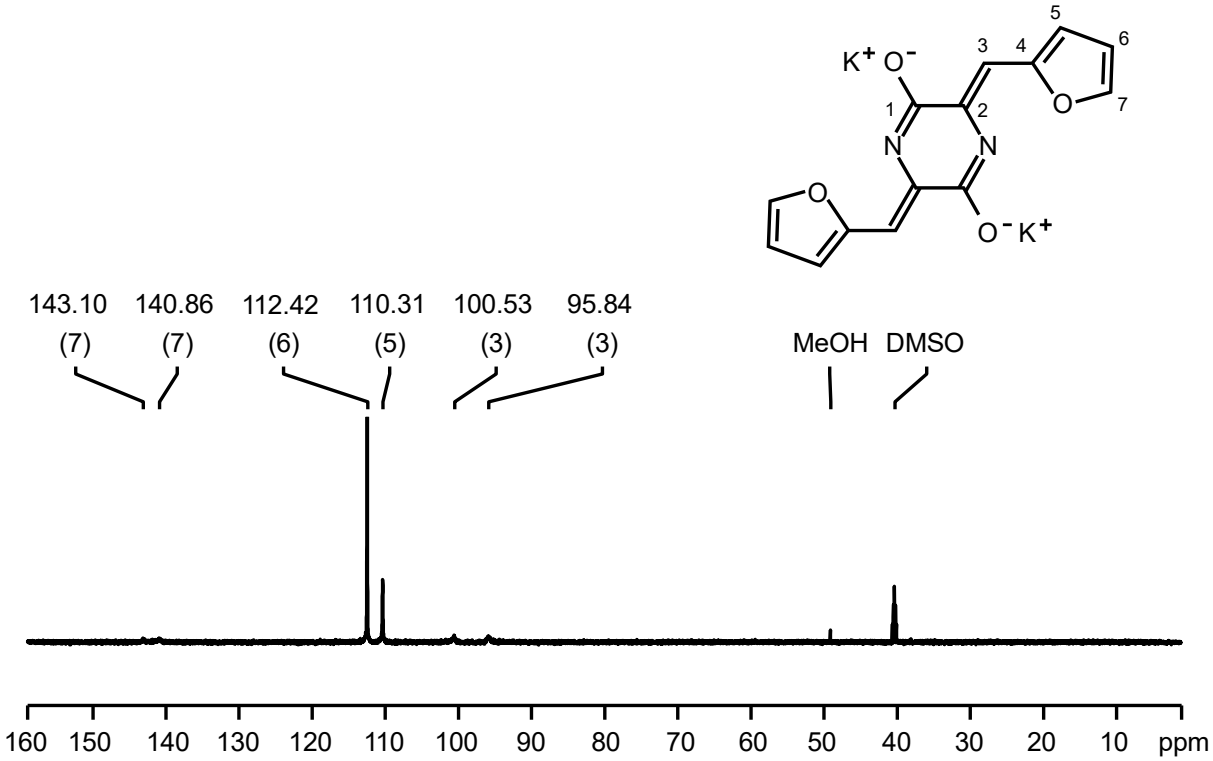


Figure S3.35 DEPT135 NMR of **6d** in DMSO-d_6, numbering simplified for ease of interpretation.

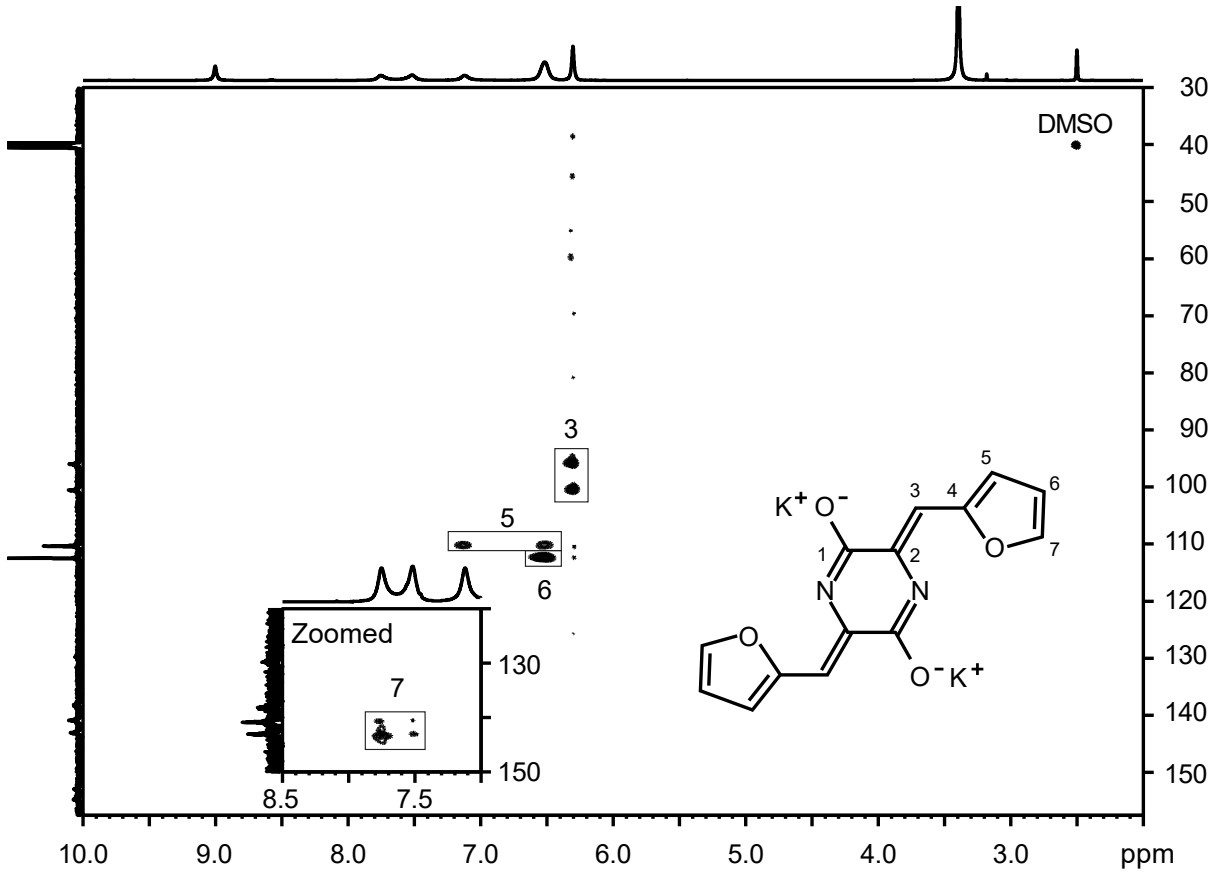


Figure S3.36 HSQC NMR of **6d** in DMSO-d_6, numbering simplified for ease of interpretation.

4e

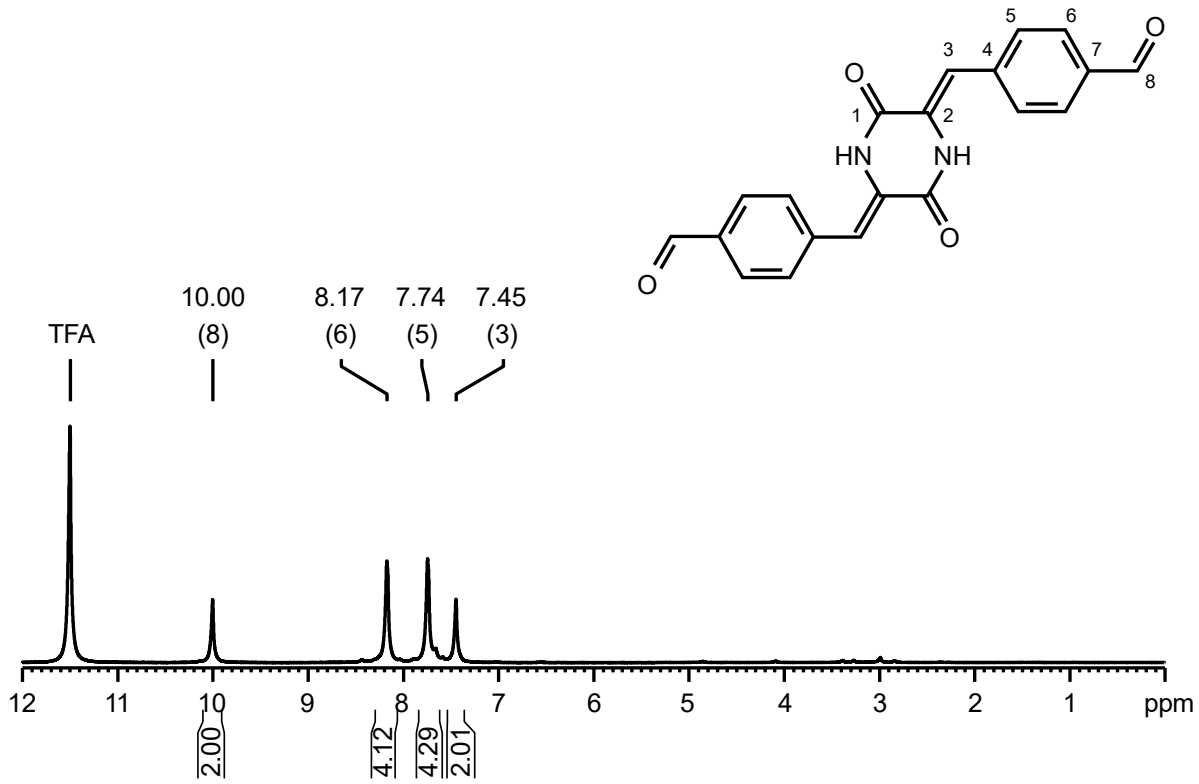


Figure S3.37 ^{1}H NMR of **4e** in TFA-*d*, numbering simplified for ease of interpretation.

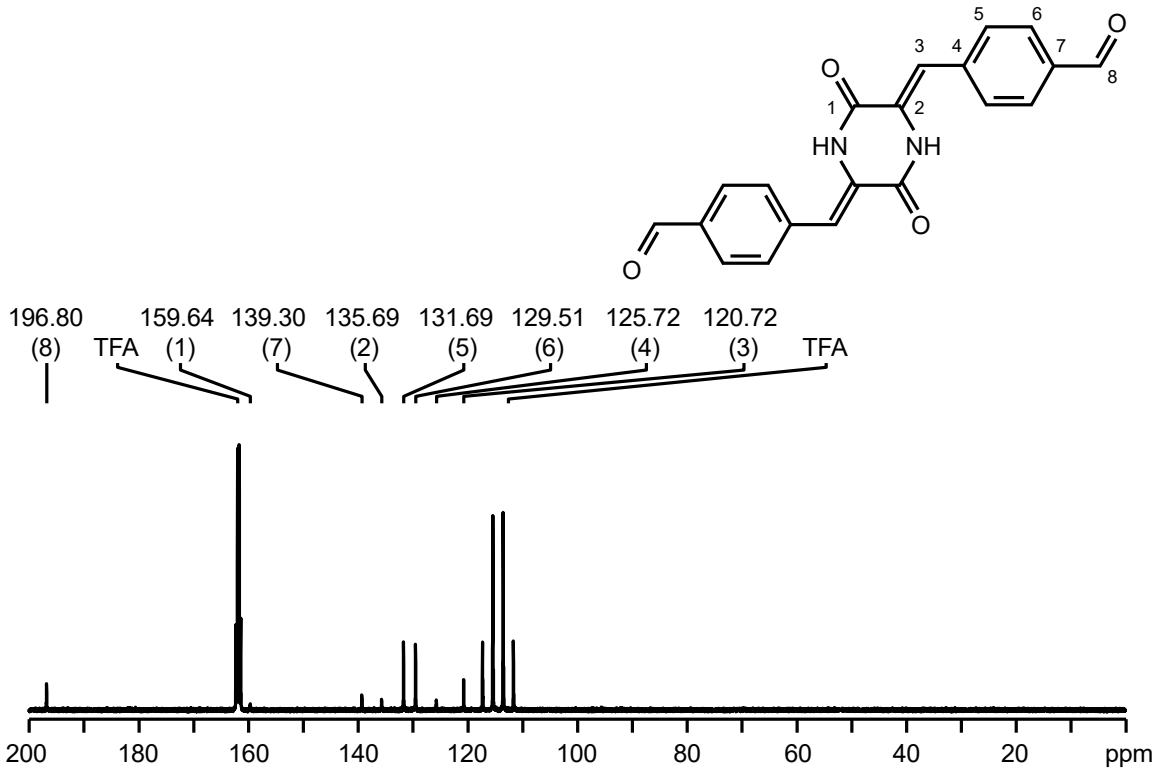


Figure S3.38 ^{13}C NMR of **4e** in TFA-*d*, numbering simplified for ease of interpretation.

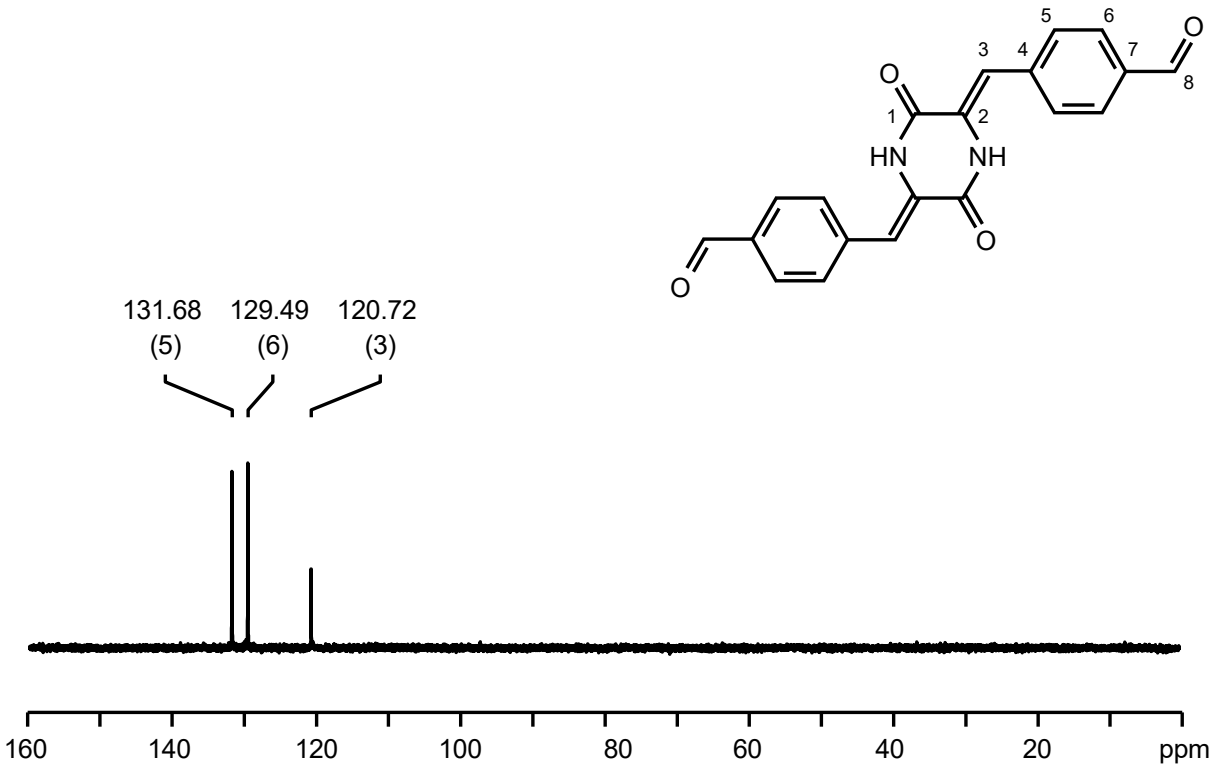


Figure S3.39 DEPT135 NMR of **4e** in TFA-*d*, numbering simplified for ease of interpretation.

6e

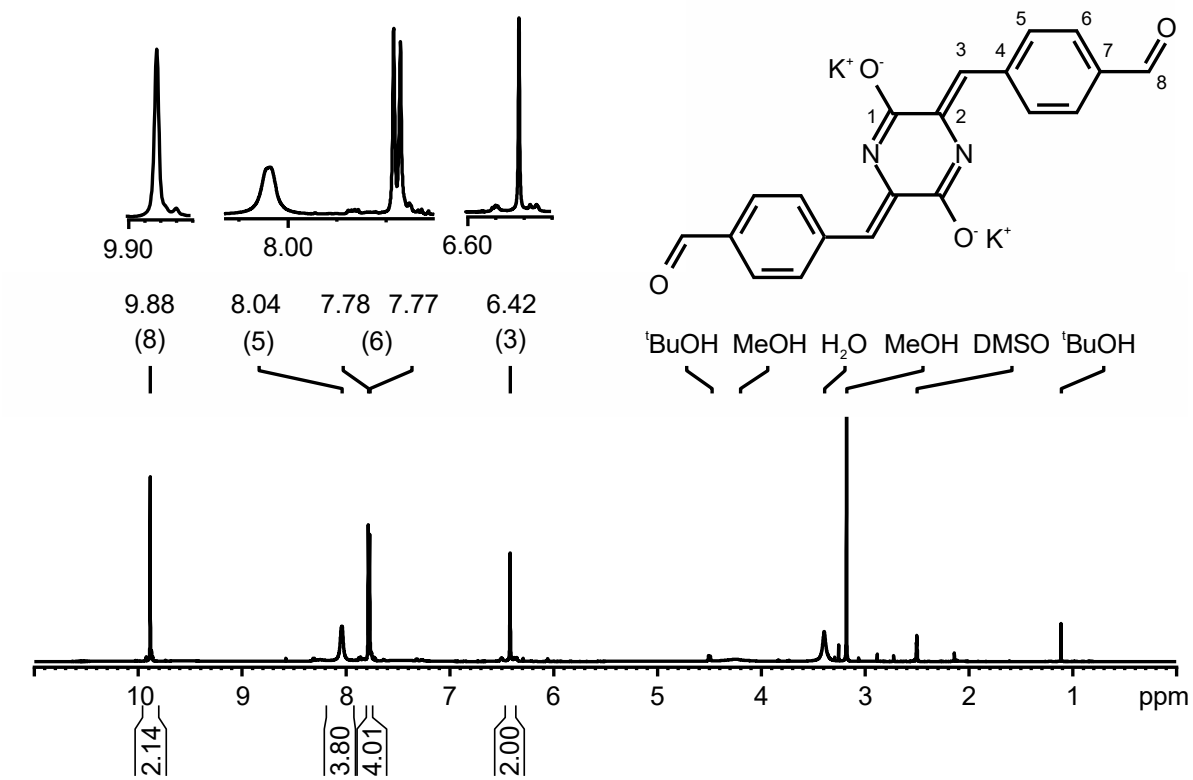


Figure S3.40 ^{1}H NMR of **6e** in DMSO-d_6, numbering simplified for ease of interpretation.

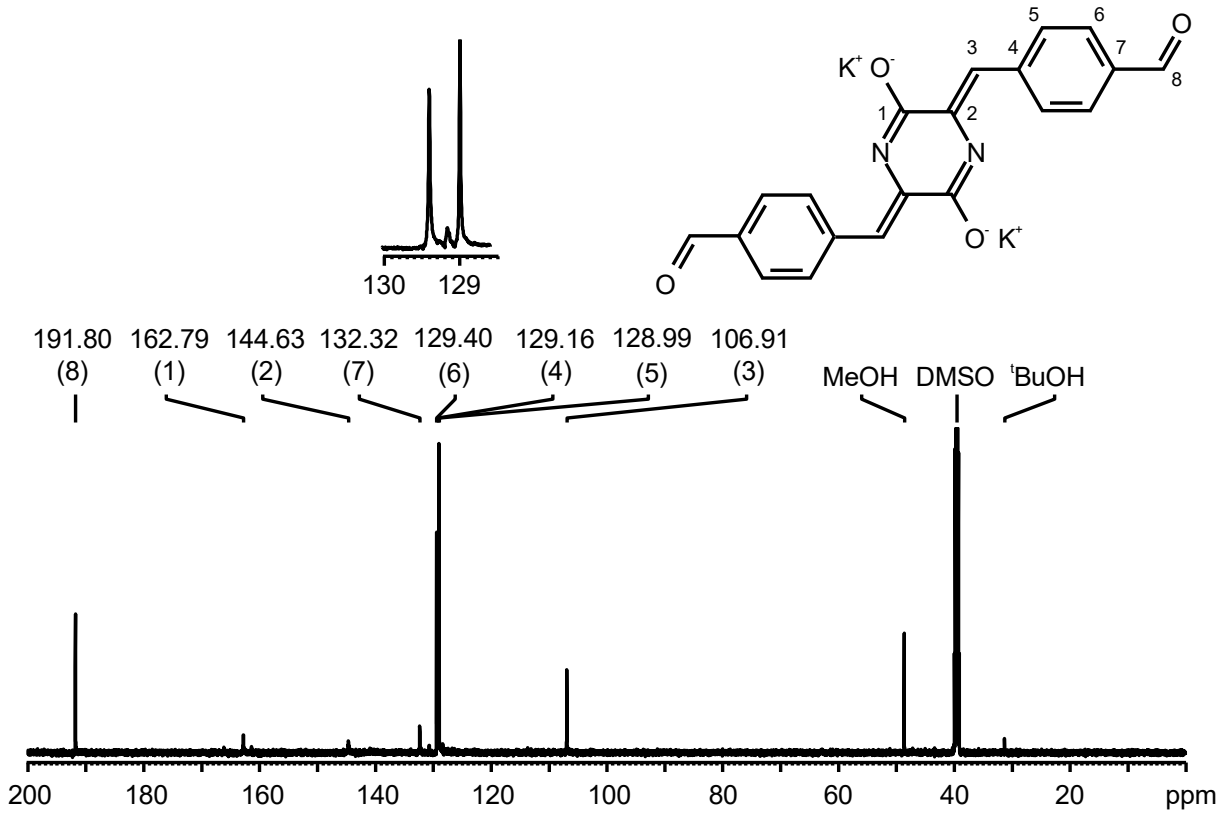


Figure S3.41 ^{13}C NMR of **6e** in DMSO-d_6, numbering simplified for ease of interpretation.

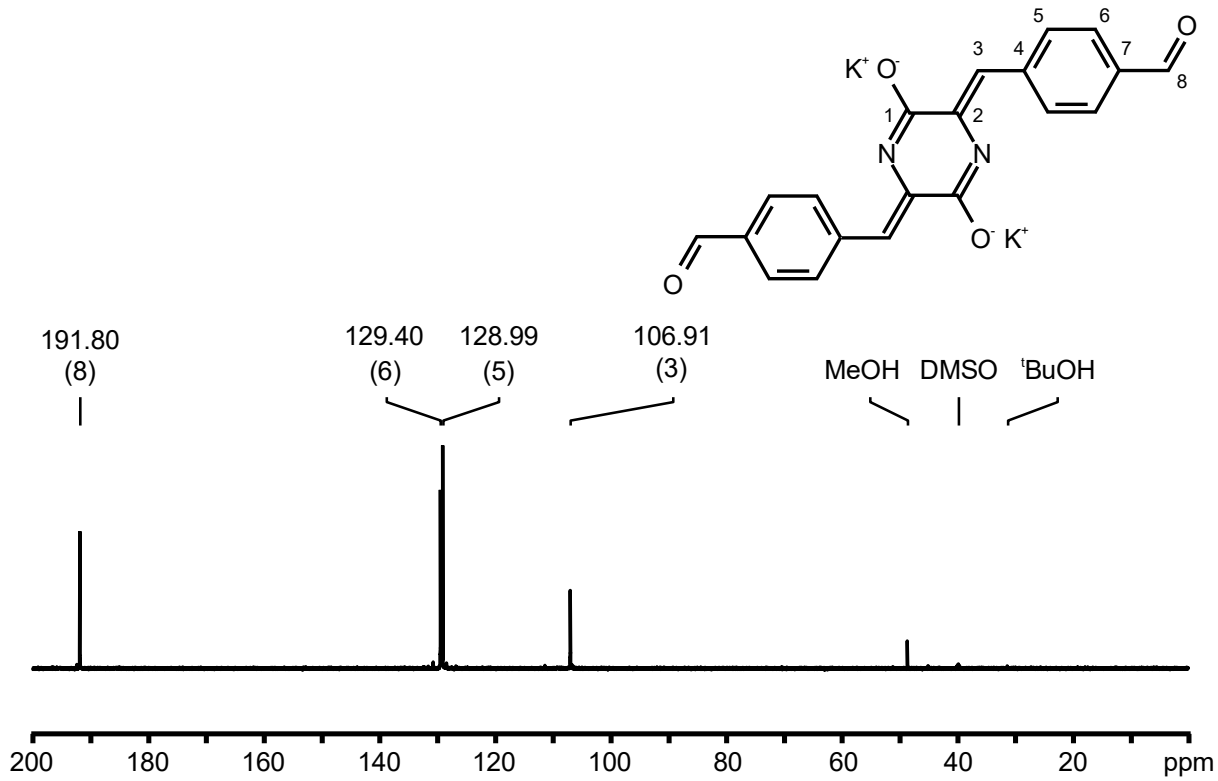


Figure S3.42 DEPT135 NMR of **6e** in DMSO-d_6, numbering simplified for ease of interpretation.

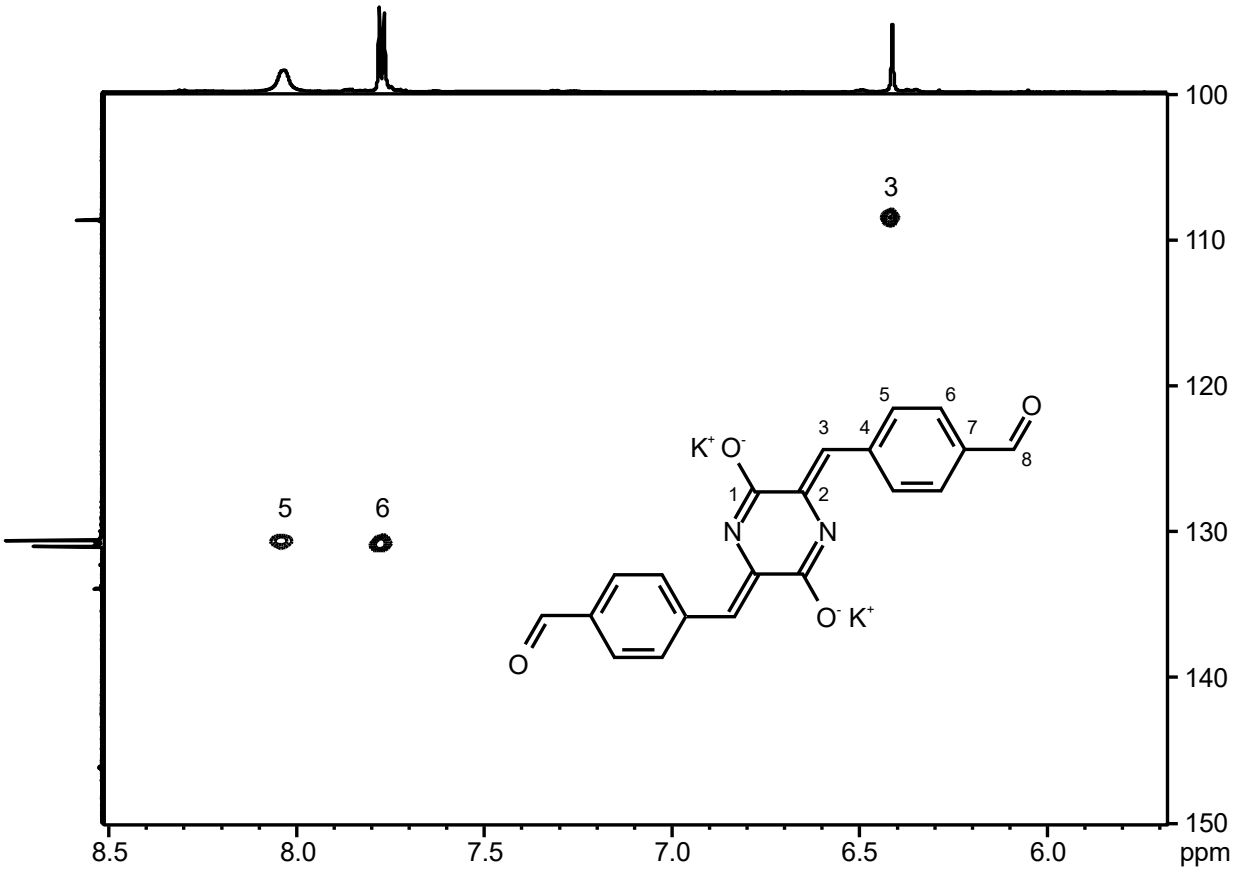


Figure S3.43 HSQC NMR of **6e** in DMSO-d_6, numbering simplified for ease of interpretation.

6f

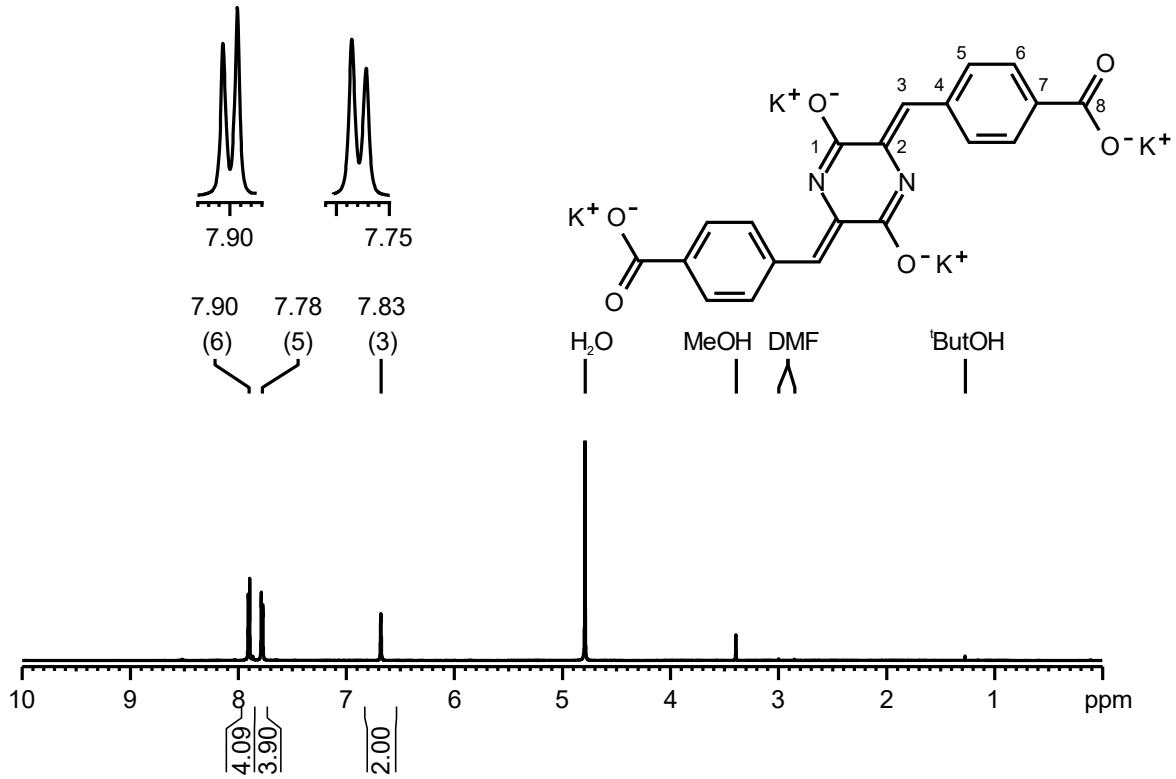


Figure S3.44 ^{1}H NMR of **6f** in D_2O, numbering simplified for ease of interpretation. MeOH utilised for peak calibration.

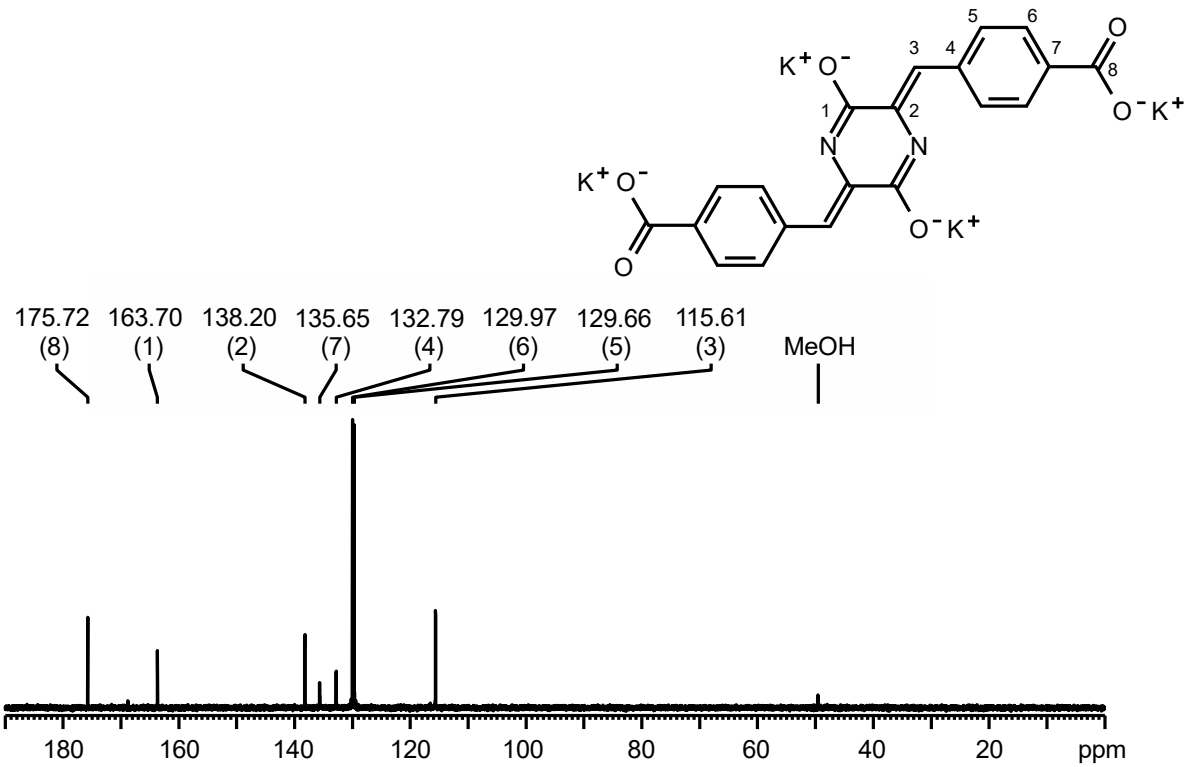


Figure S3.45 ^{13}C NMR of **6f** in D_2O, numbering simplified for ease of interpretation. MeOH utilised for peak calibration.

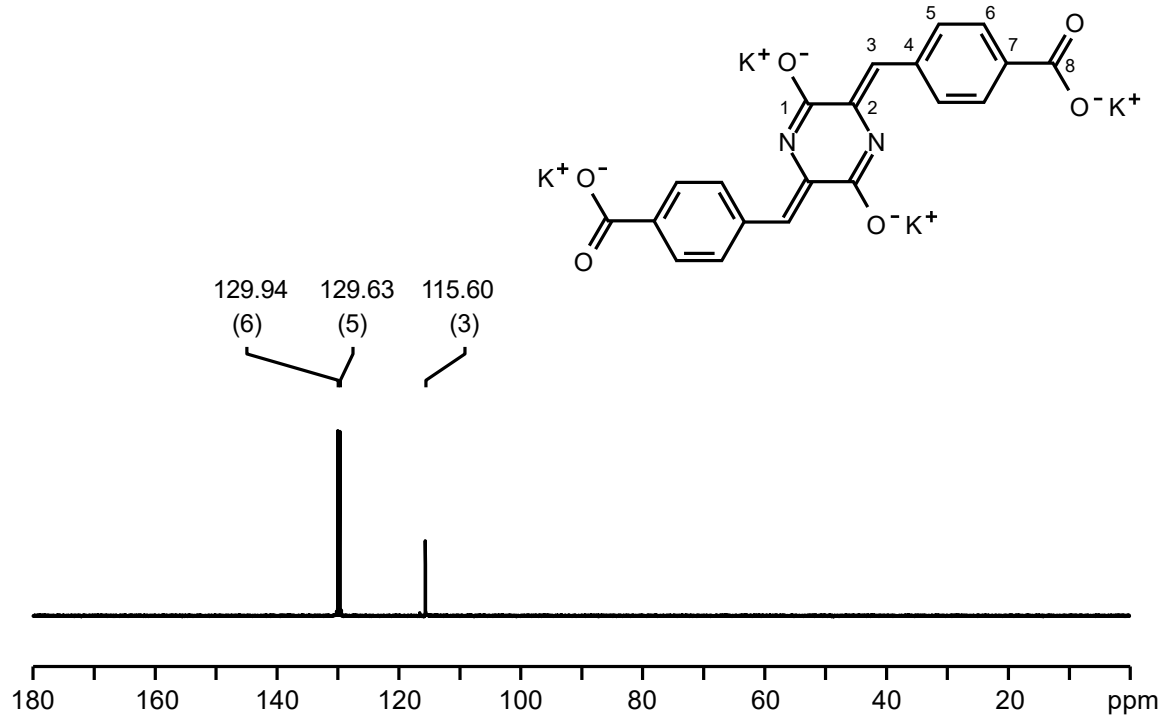


Figure S3.46 DEPT135 NMR of **6f** in D_2O, numbering simplified for ease of interpretation. MeOH utilised for peak calibration.

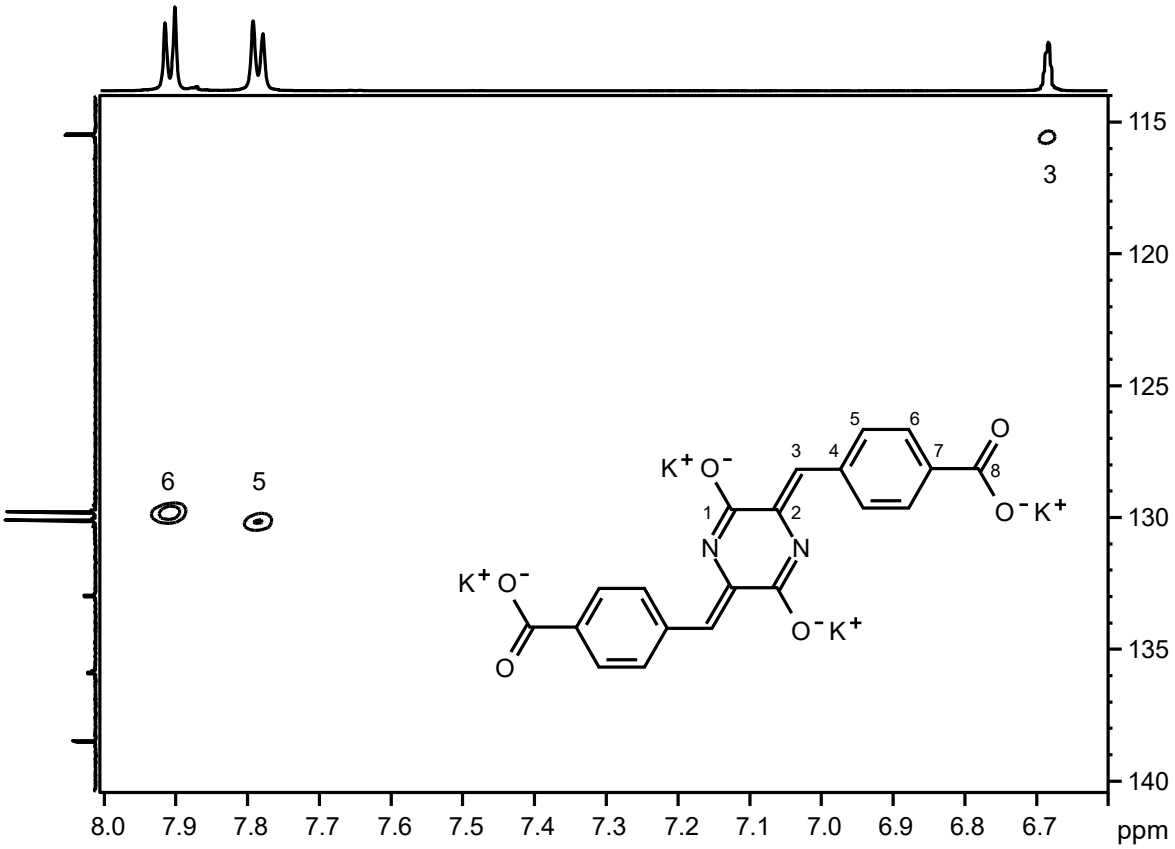


Figure S3.47 HSQC NMR of **6f** in D_2O, numbering simplified for ease of interpretation. MeOH utilised for peak calibration.

6g

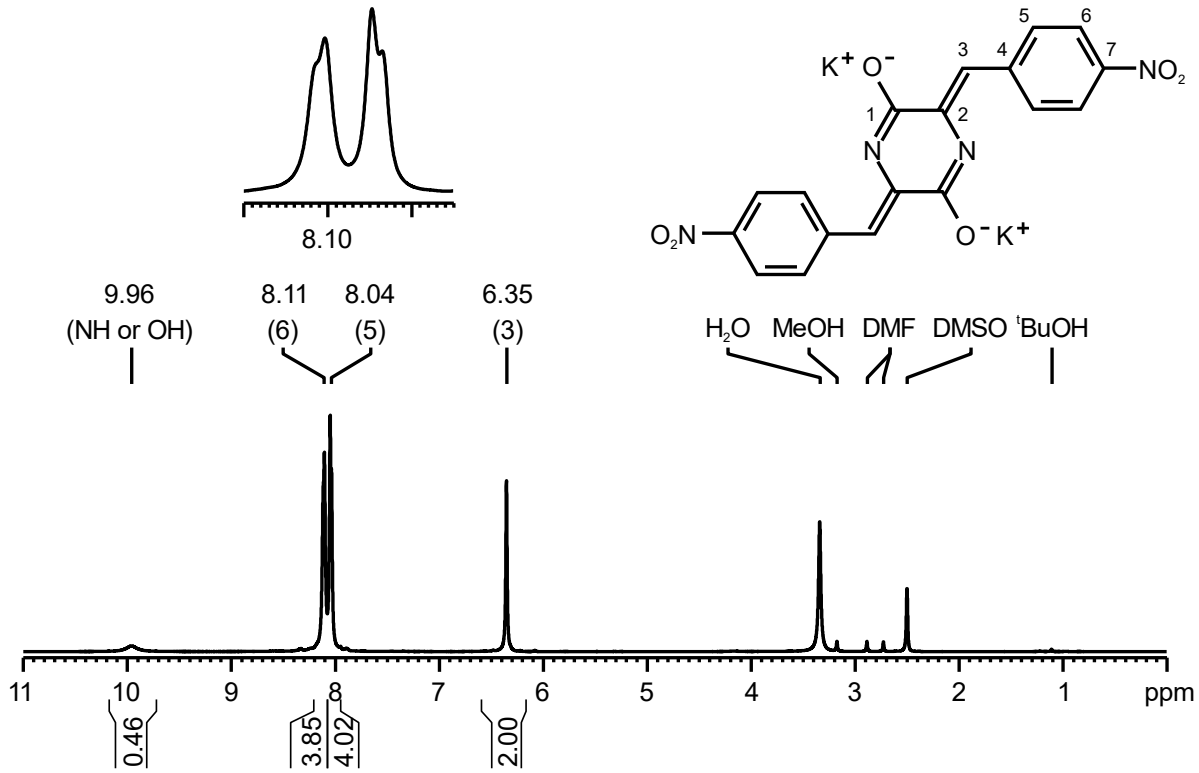


Figure S3.48 ^{1}H NMR of **6g** in DMSO-d_6, numbering simplified for ease of interpretation.

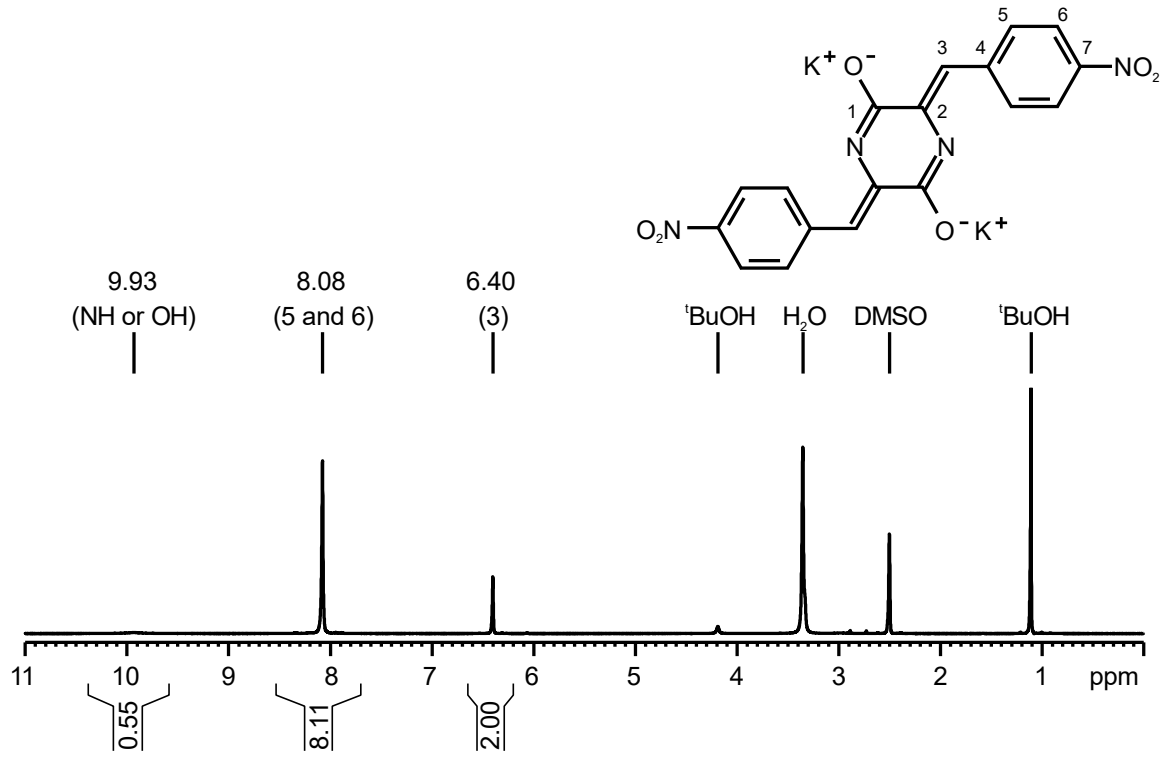


Figure S3.49 ^{1}H NMR of **6g** with excess ^{t}BuOH in DMSO-d_6, numbering simplified for ease of interpretation.

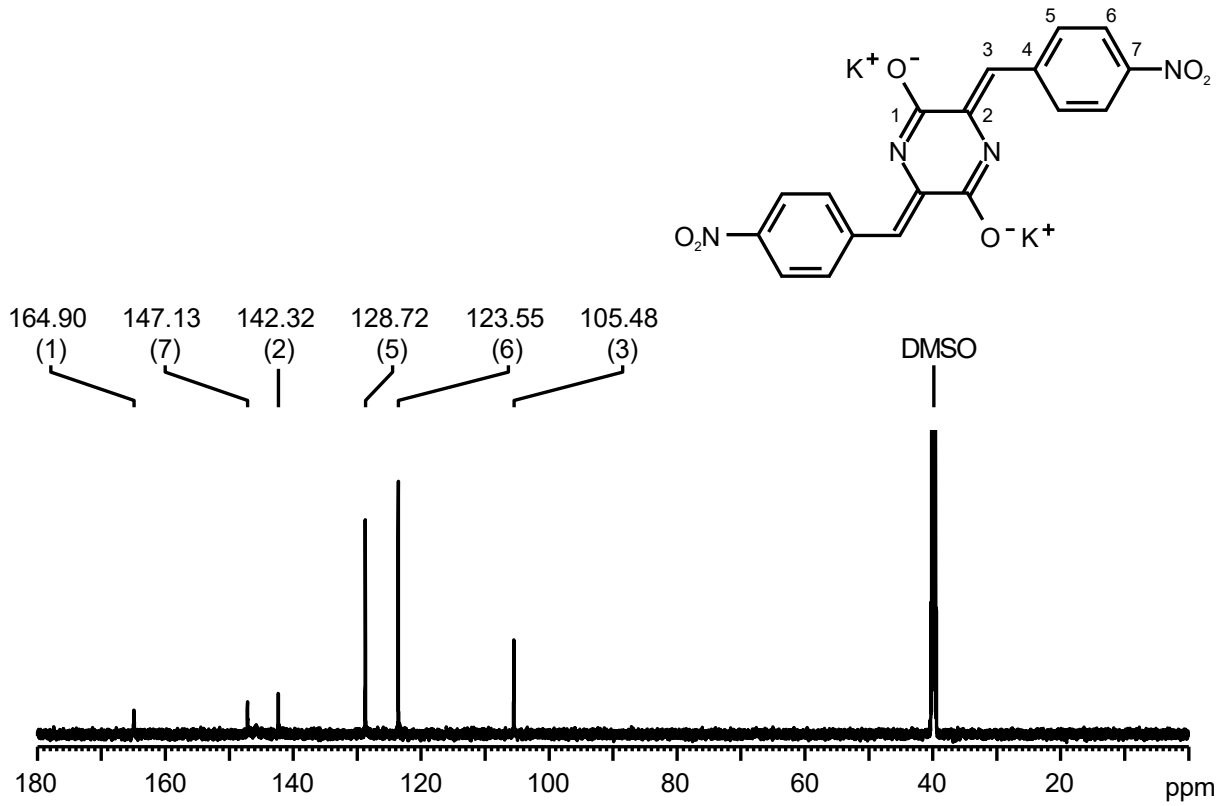


Figure S3.50 ^{13}C NMR of **6g** in DMSO-d_6, numbering simplified for ease of interpretation.

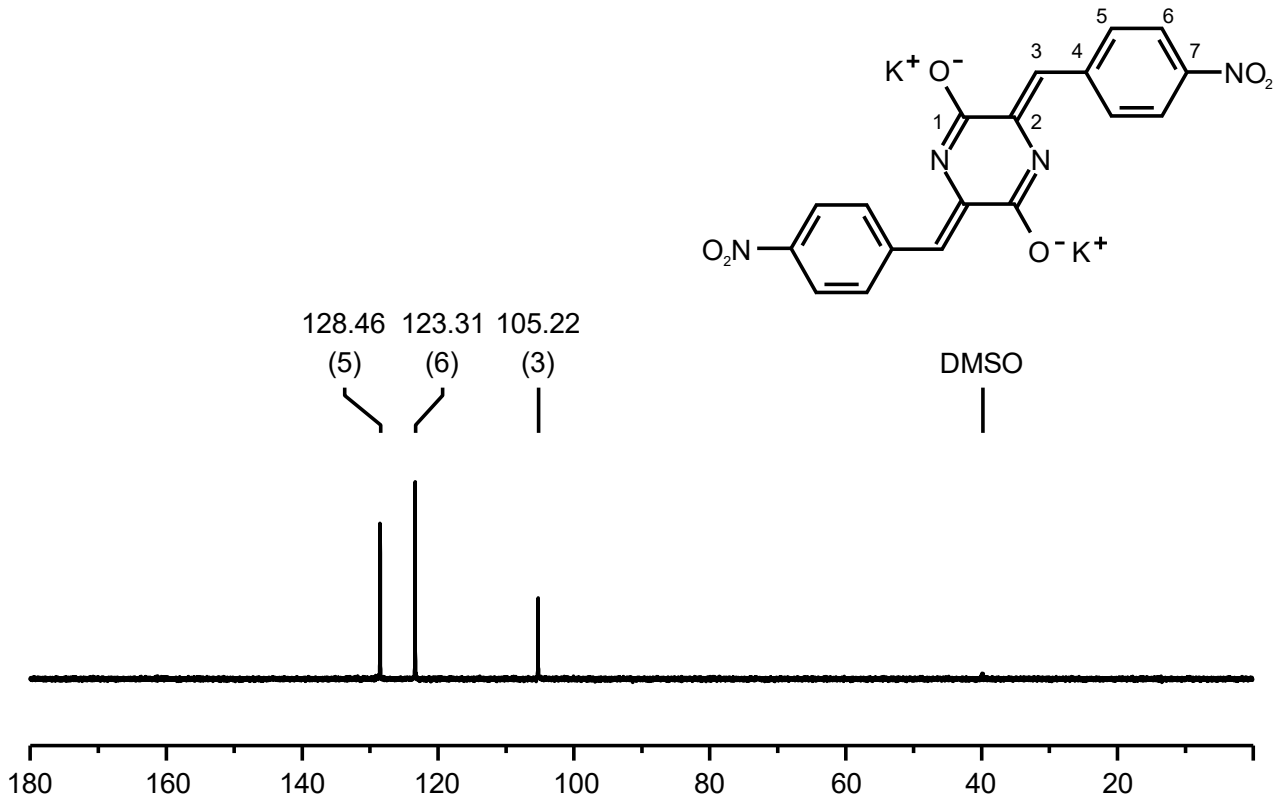


Figure S3.51 DEPT135 NMR of **6g** in DMSO-d_6, numbering simplified for ease of interpretation.

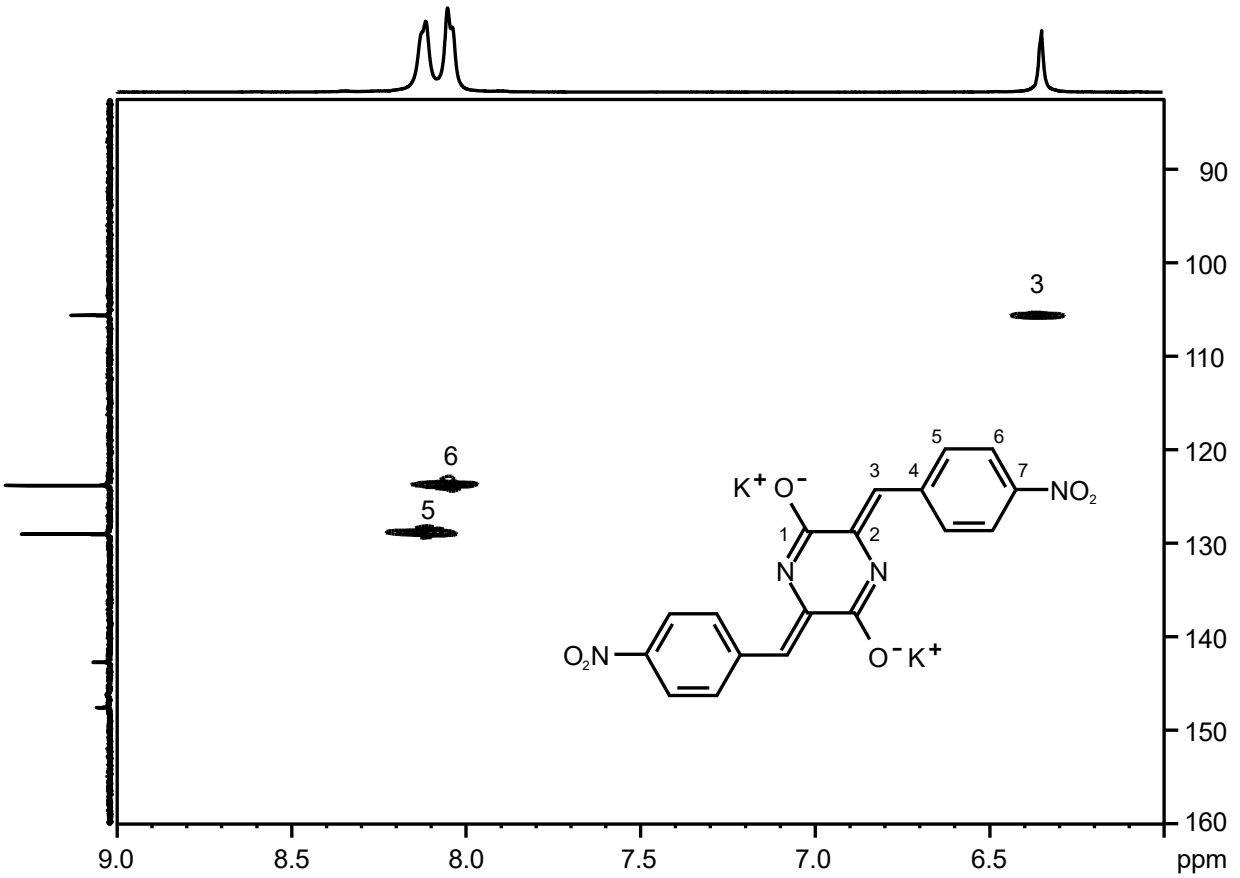


Figure S3.52 HSQC NMR of **6g** in DMSO-d_6, numbering simplified for ease of interpretation.

6h

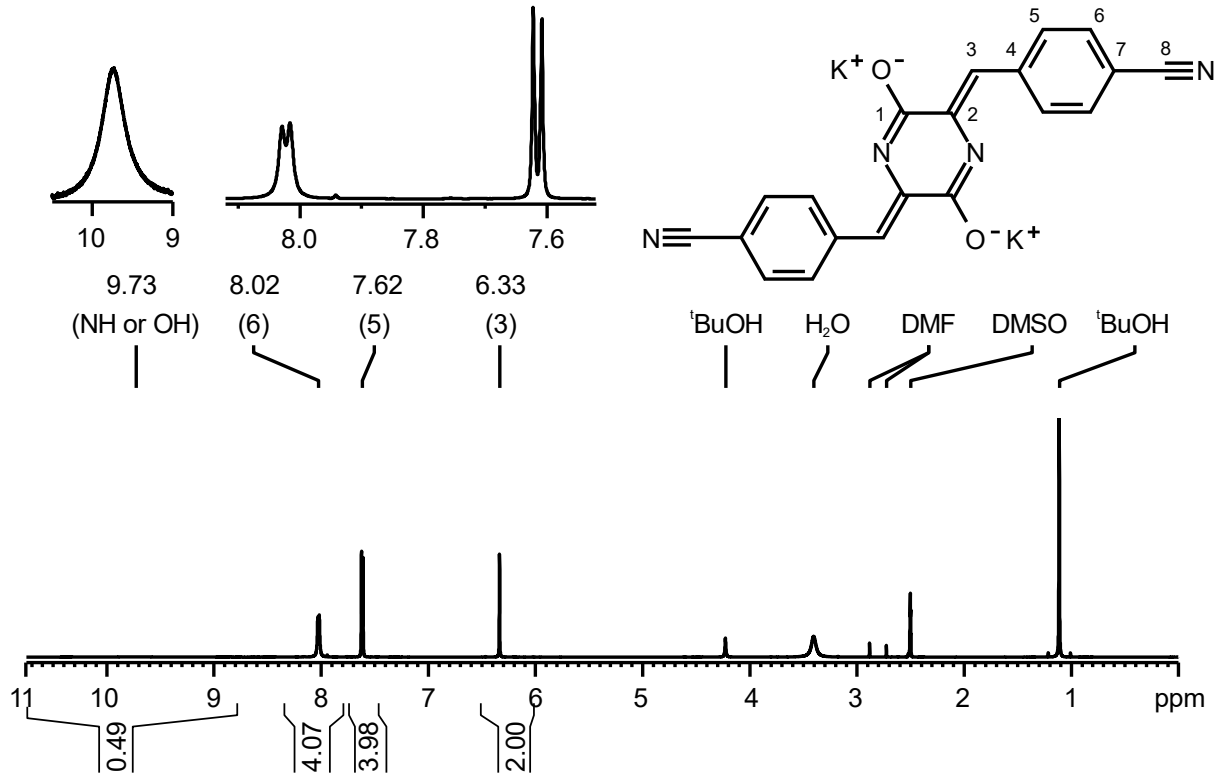


Figure S3.53 ^{1}H NMR of **6h** in DMSO-d_6, numbering simplified for ease of interpretation.

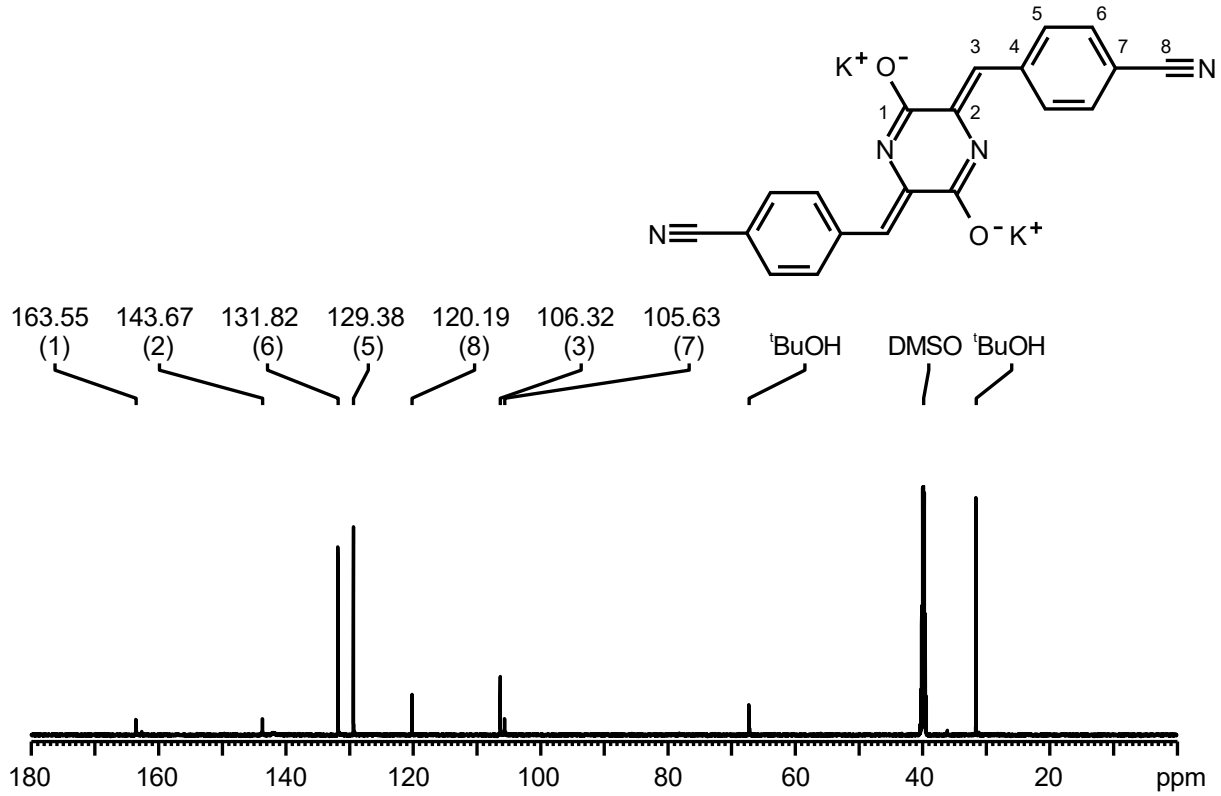


Figure S3.54 ^{13}C NMR of **6h** in DMSO-d_6, numbering simplified for ease of interpretation.

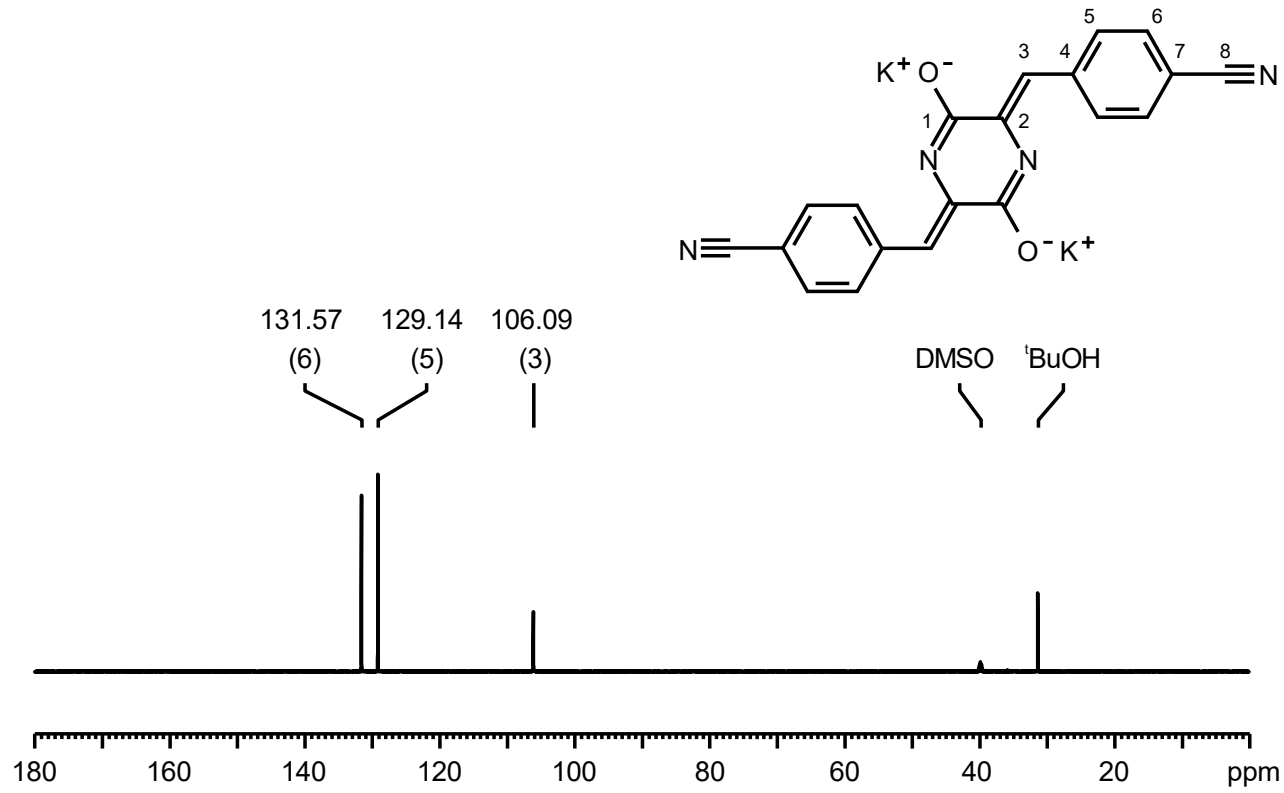


Figure S3.55 DEPT135 NMR of **6h** in DMSO-d_6, numbering simplified for ease of interpretation.

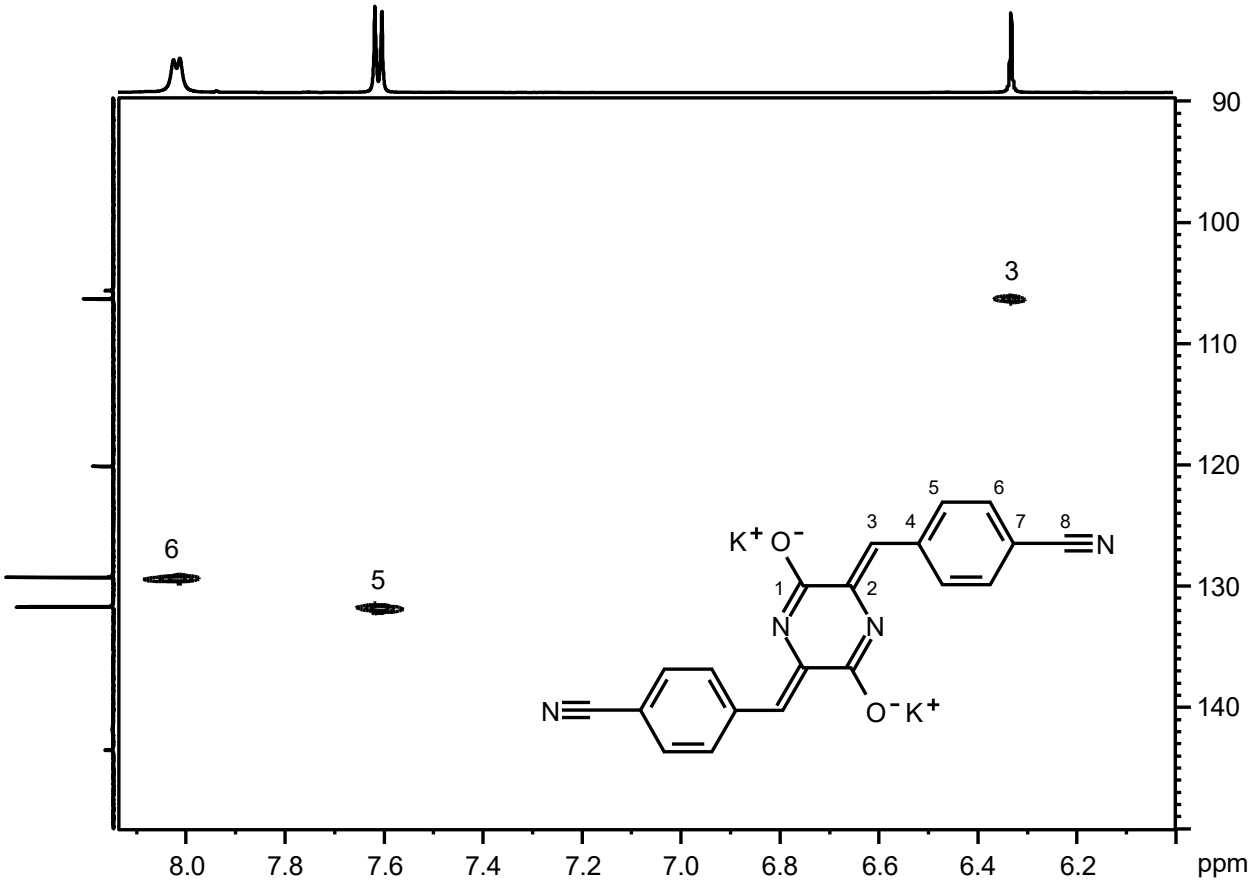


Figure S3.56 HSQC NMR of **6h** in DMSO-d_6, numbering simplified for ease of interpretation.

6i

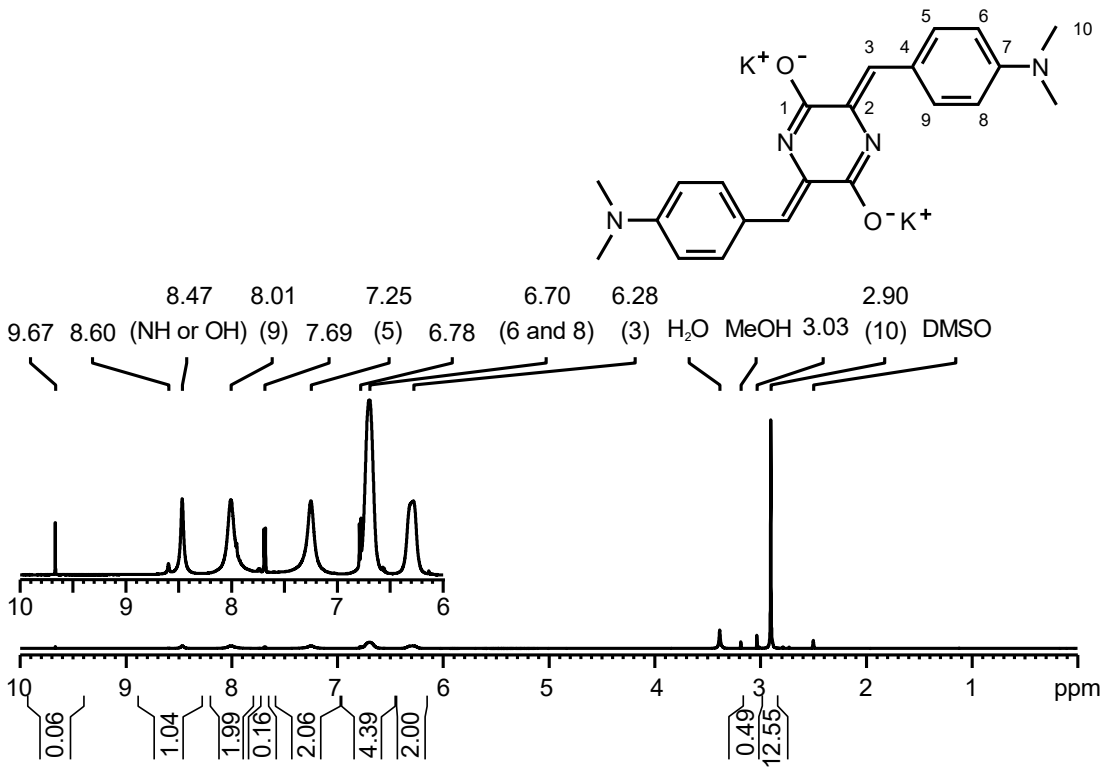


Figure S3.57 ^{1}H NMR of **6i** in DMSO-d_6, numbering simplified for ease of interpretation. Impurity is 4-(dimethylamino)benzaldehyde at a concentration of 4.33%.

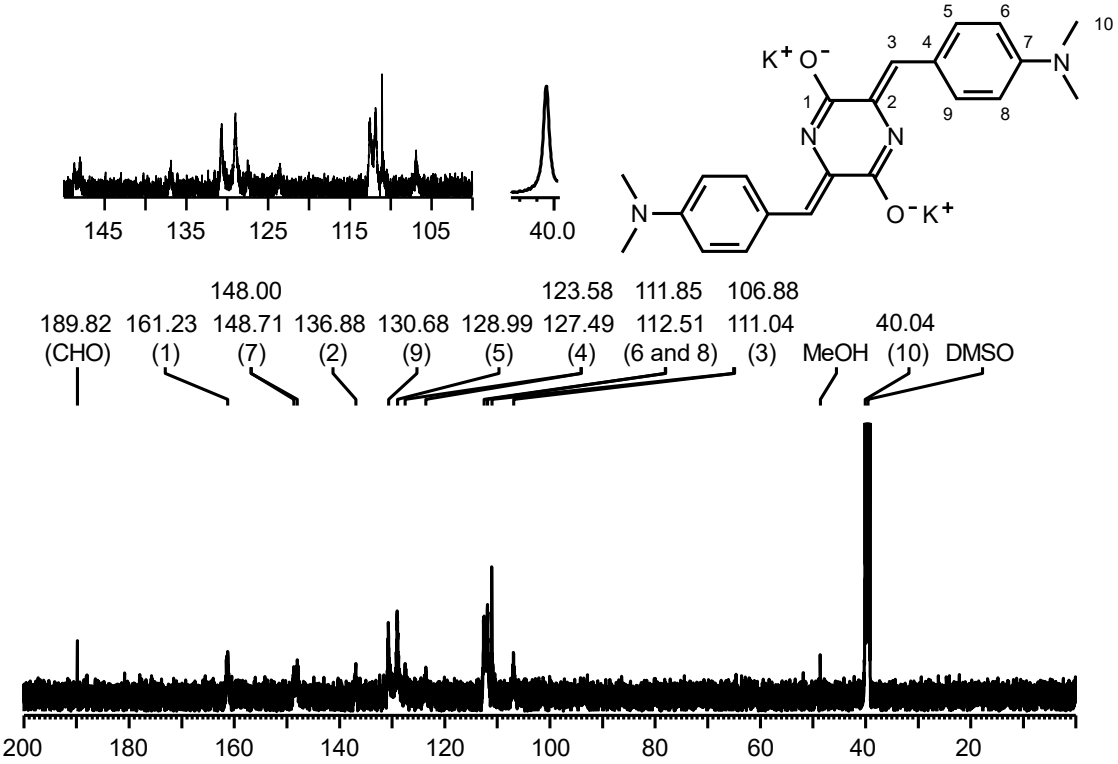


Figure S3.58 ^{13}C NMR of **6i** in DMSO-d_6, numbering simplified for ease of interpretation. Impurity is 4-(dimethylamino)benzaldehyde at a concentration of 4.33%.

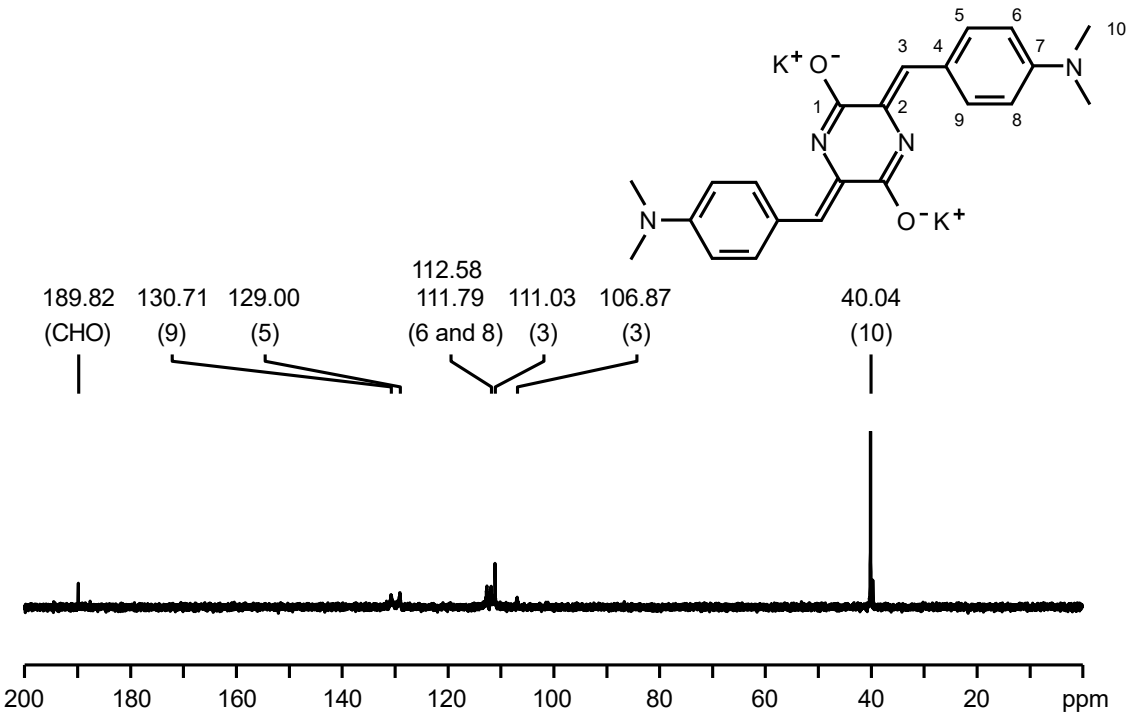


Figure S3.59 DEPT135 NMR of **6i** in DMSO-d_6, numbering simplified for ease of interpretation. Impurity is 4-(dimethylamino)benzaldehyde at a concentration of 4.33%.

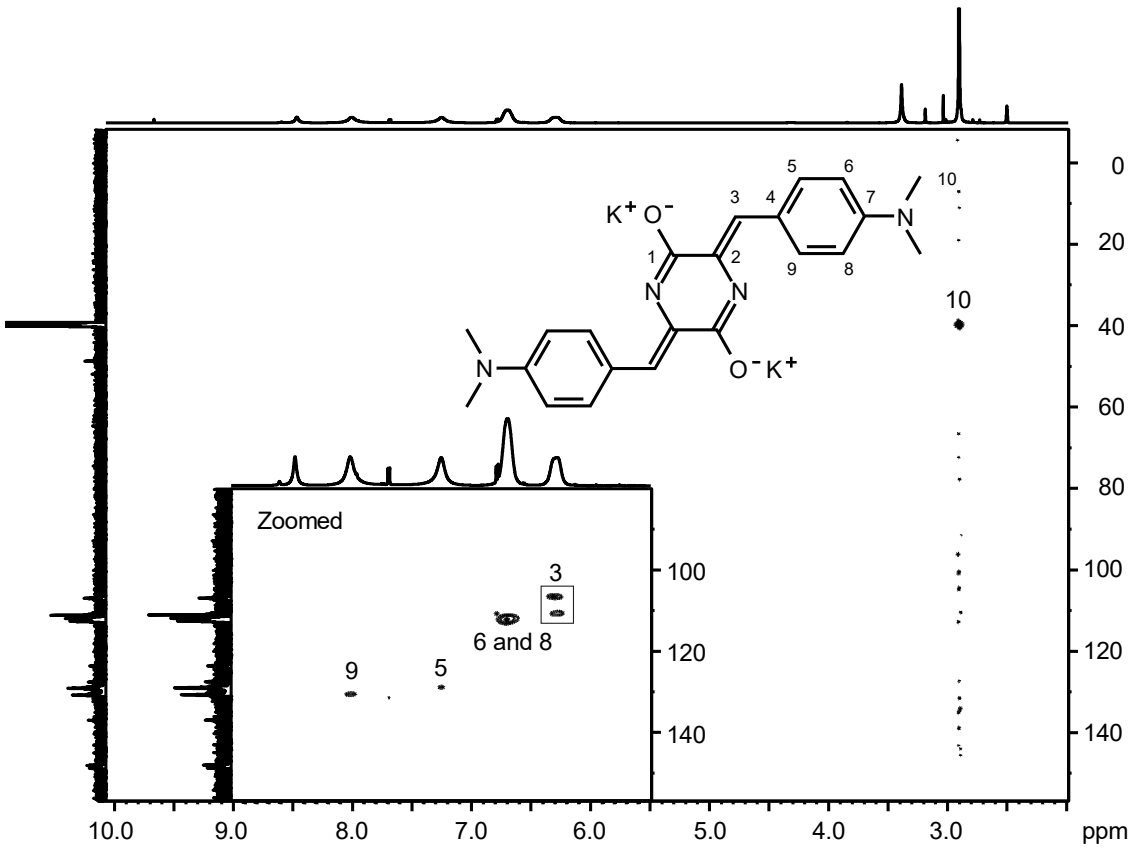


Figure S3.60 HSQC NMR of **6i** in DMSO-d_6, numbering simplified for ease of interpretation. Impurity is 4-(dimethylamino)benzaldehyde at a concentration of 4.33%.

6j

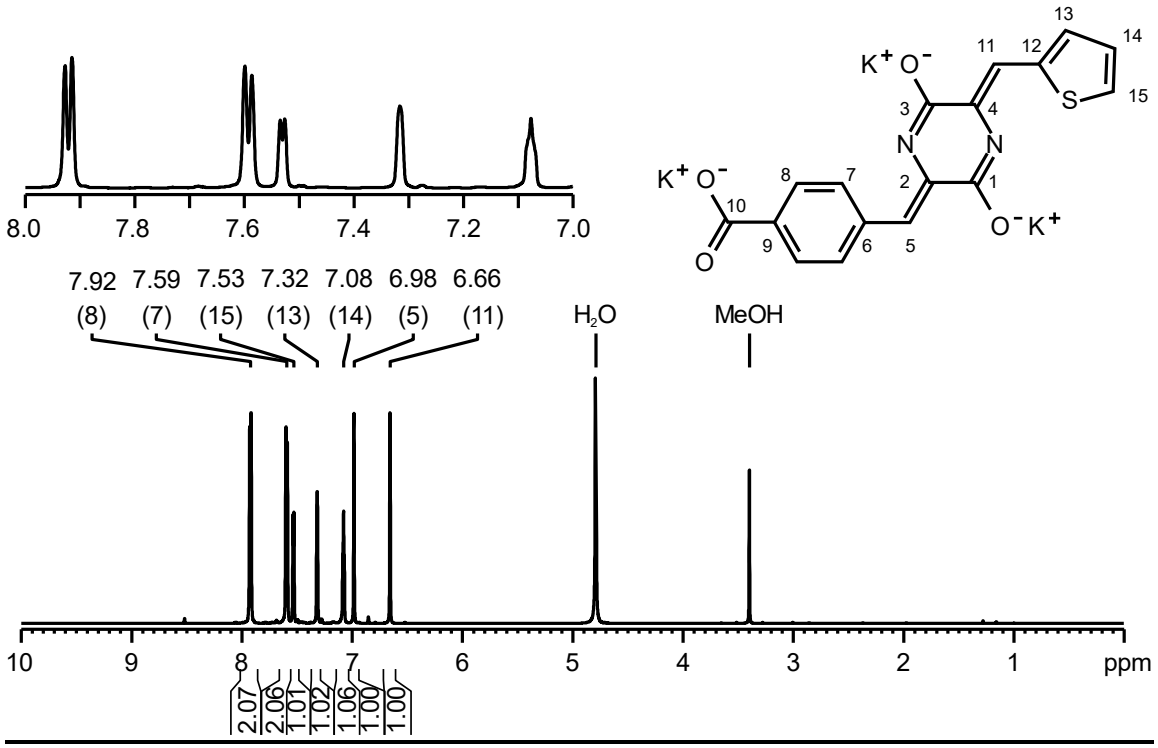


Figure S3.61 ^{1}H NMR of **6j** in D_2O, numbering simplified for ease of interpretation. MeOH utilised for peak calibration.

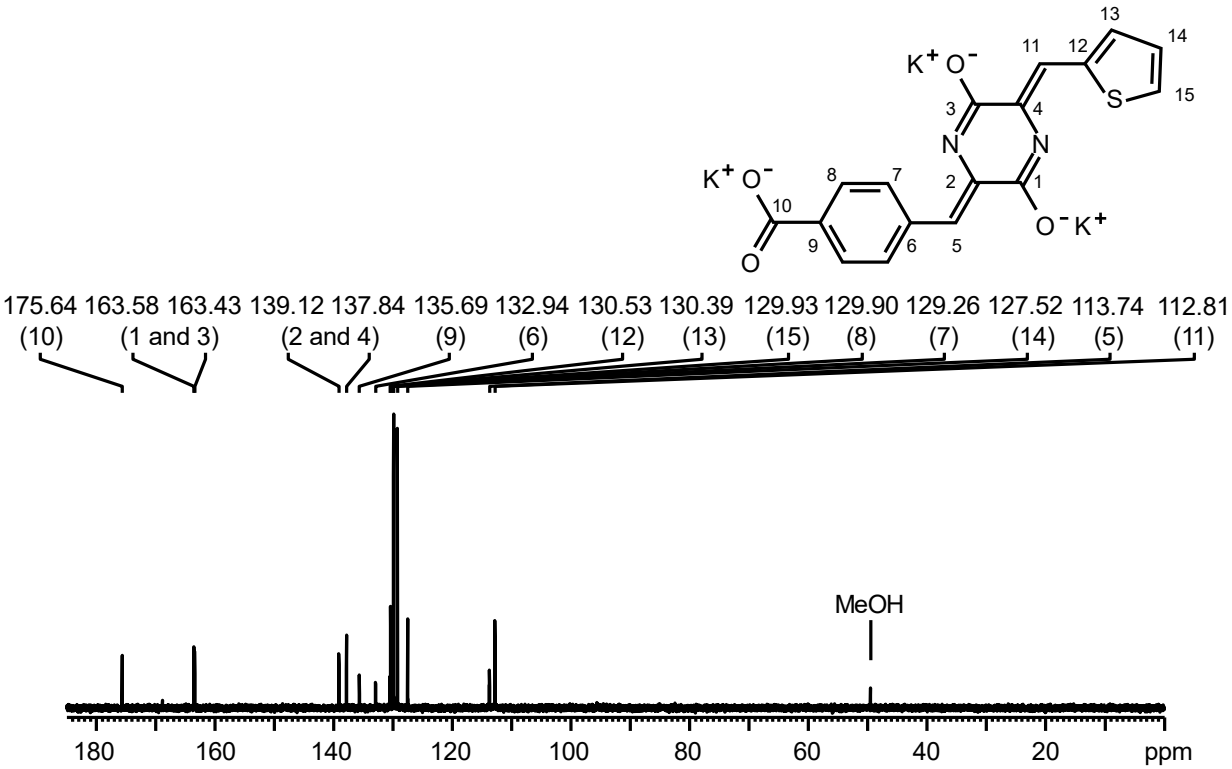


Figure S3.62 ^{13}C NMR of **6j** in D_2O, numbering simplified for ease of interpretation. MeOH utilised for peak calibration.

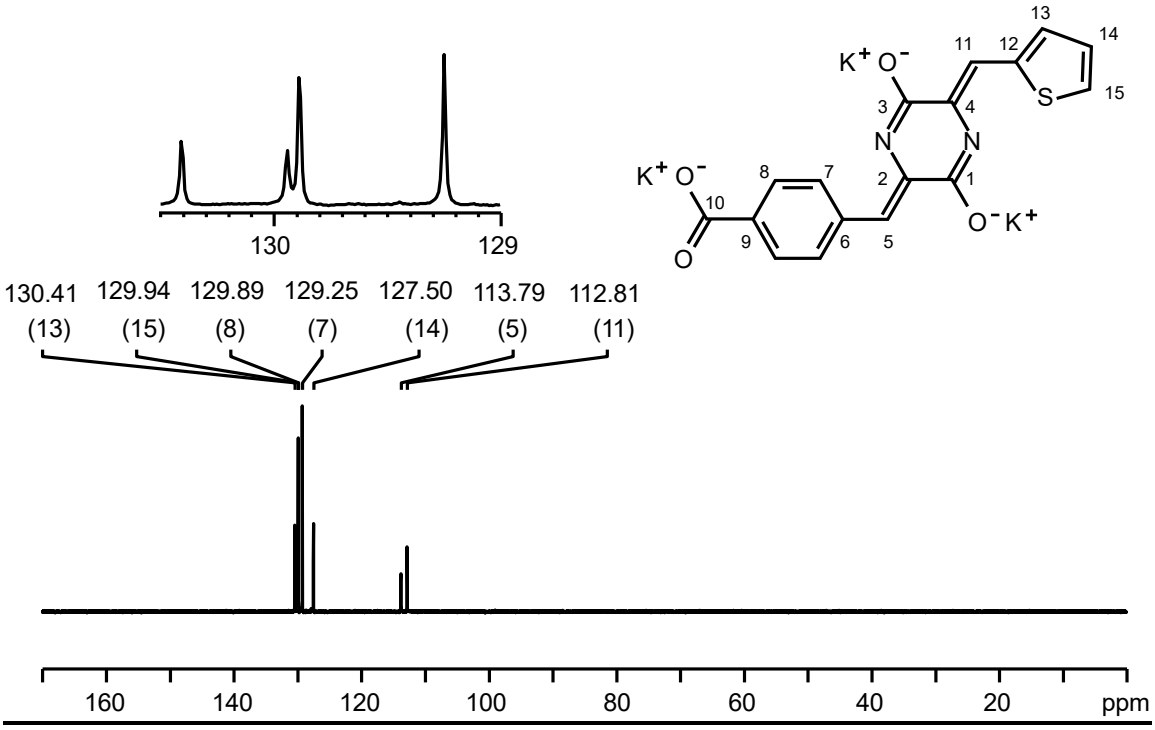


Figure S3.63 DEPT135 NMR of **6j** in D_2O, numbering simplified for ease of interpretation. MeOH utilised for peak calibration.

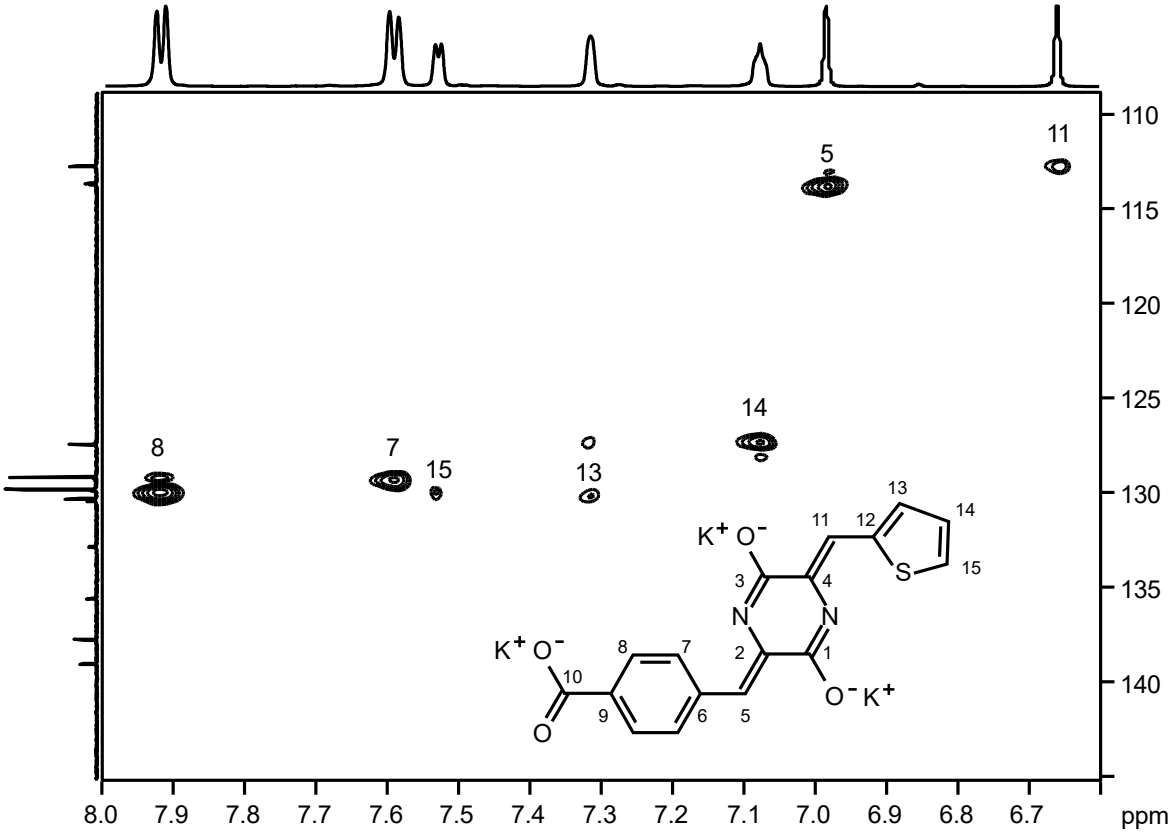


Figure S3.64 HSQC NMR of **6j** in D_2O, numbering simplified for ease of interpretation. MeOH utilised for peak calibration.

6k

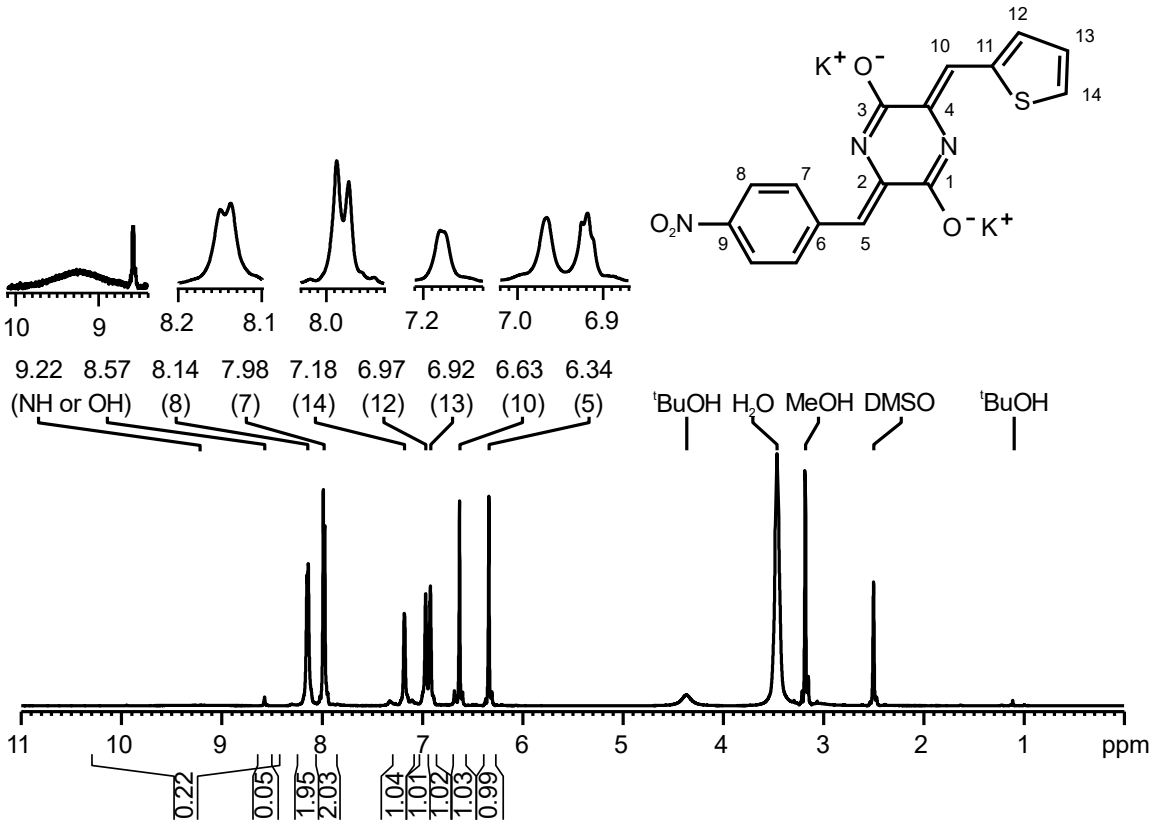


Figure S3.65 ^{1}H NMR of **6k** in DMSO-d_6, numbering simplified for ease of interpretation.

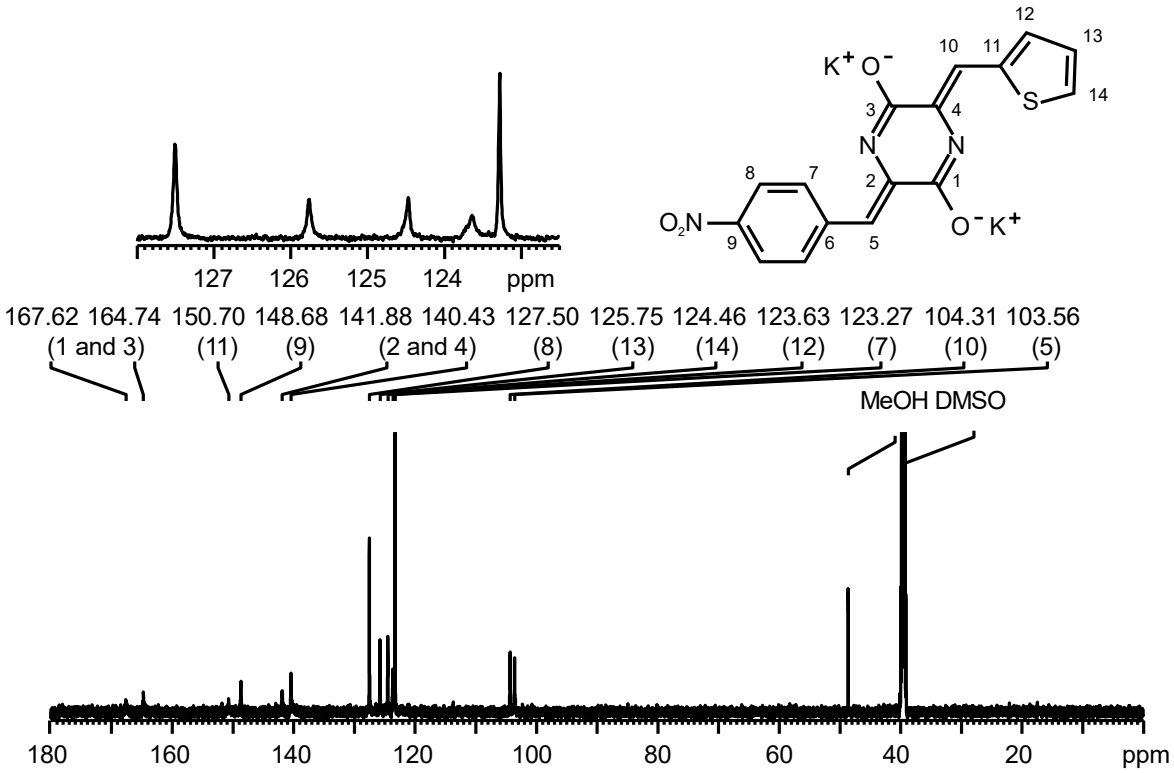


Figure S3.66 ^{13}C NMR of **6k** in DMSO-d_6, numbering simplified for ease of interpretation.

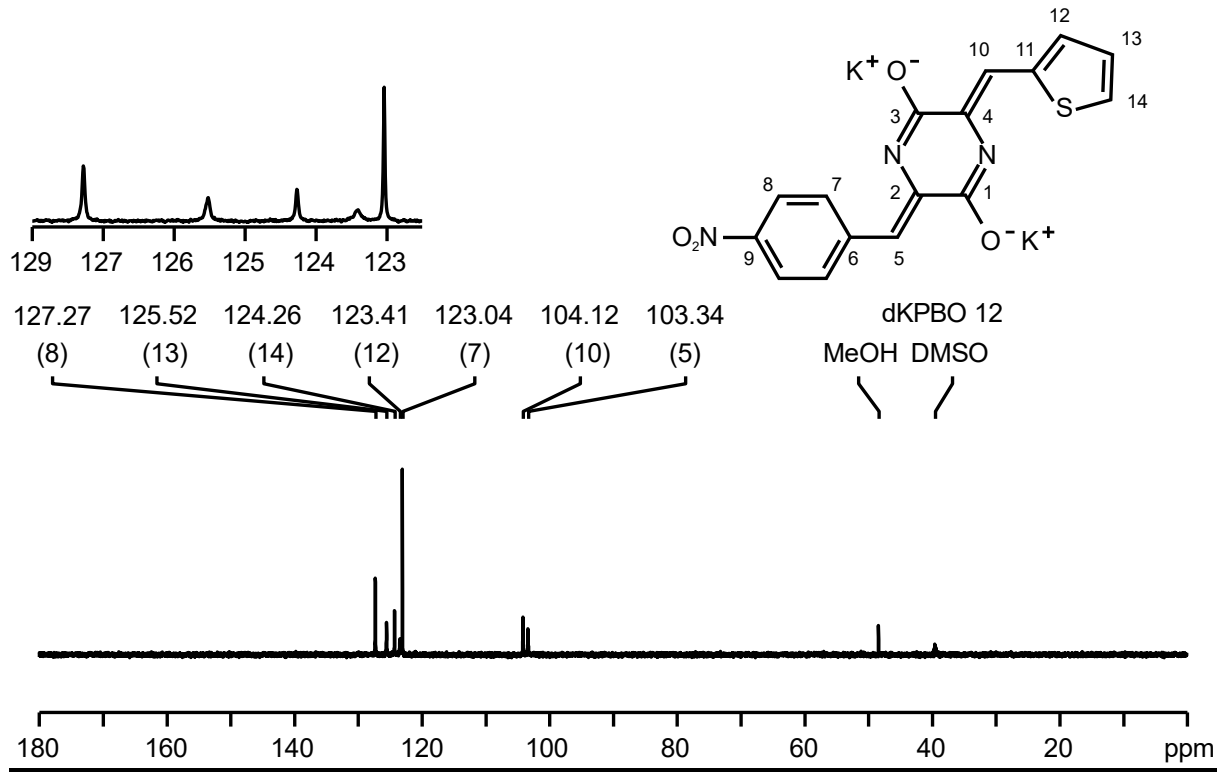


Figure S3.67 DEPT135 NMR of **6k** in DMSO-d_6, numbering simplified for ease of interpretation.

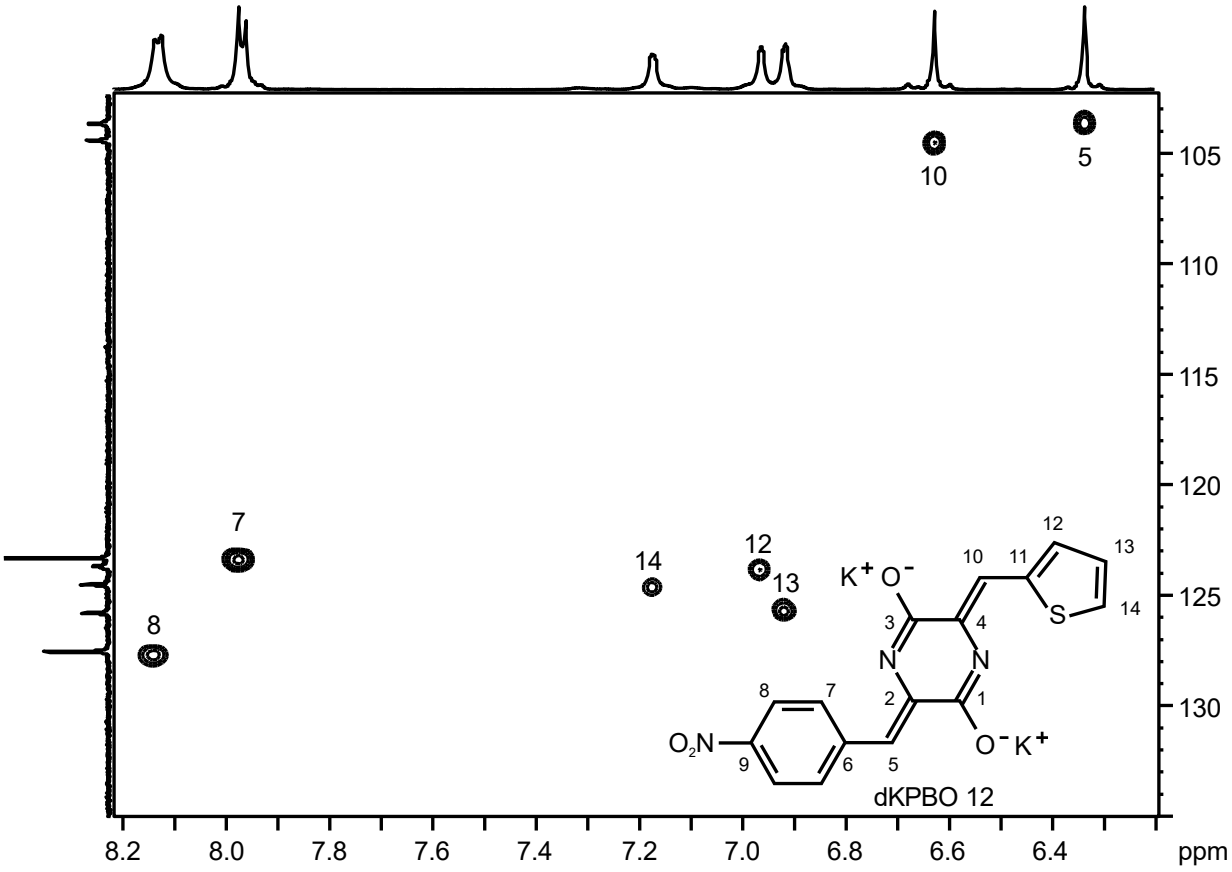


Figure S3.68 HSQC NMR of **6k** in DMSO-d_6, numbering simplified for ease of interpretation.

6l

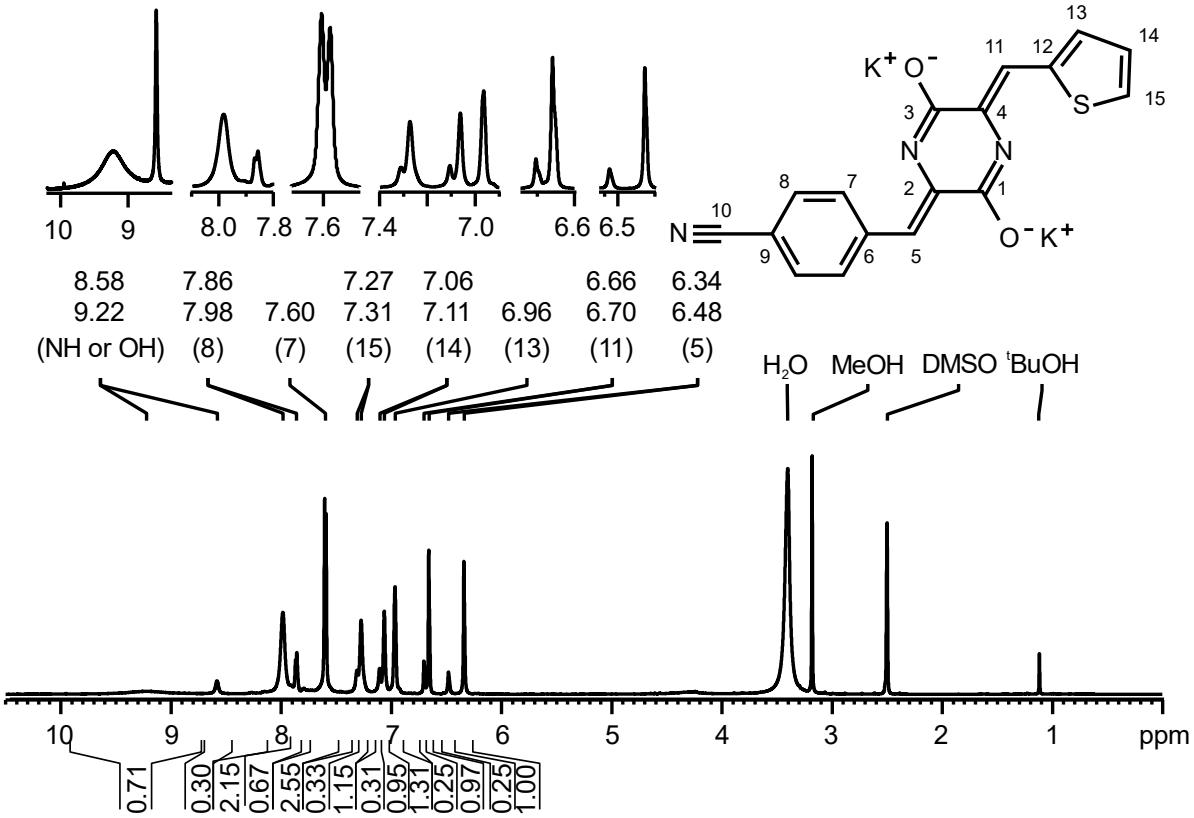


Figure S3.69 ^{1}H NMR of **6l** in DMSO-d_6, numbering simplified for ease of interpretation.

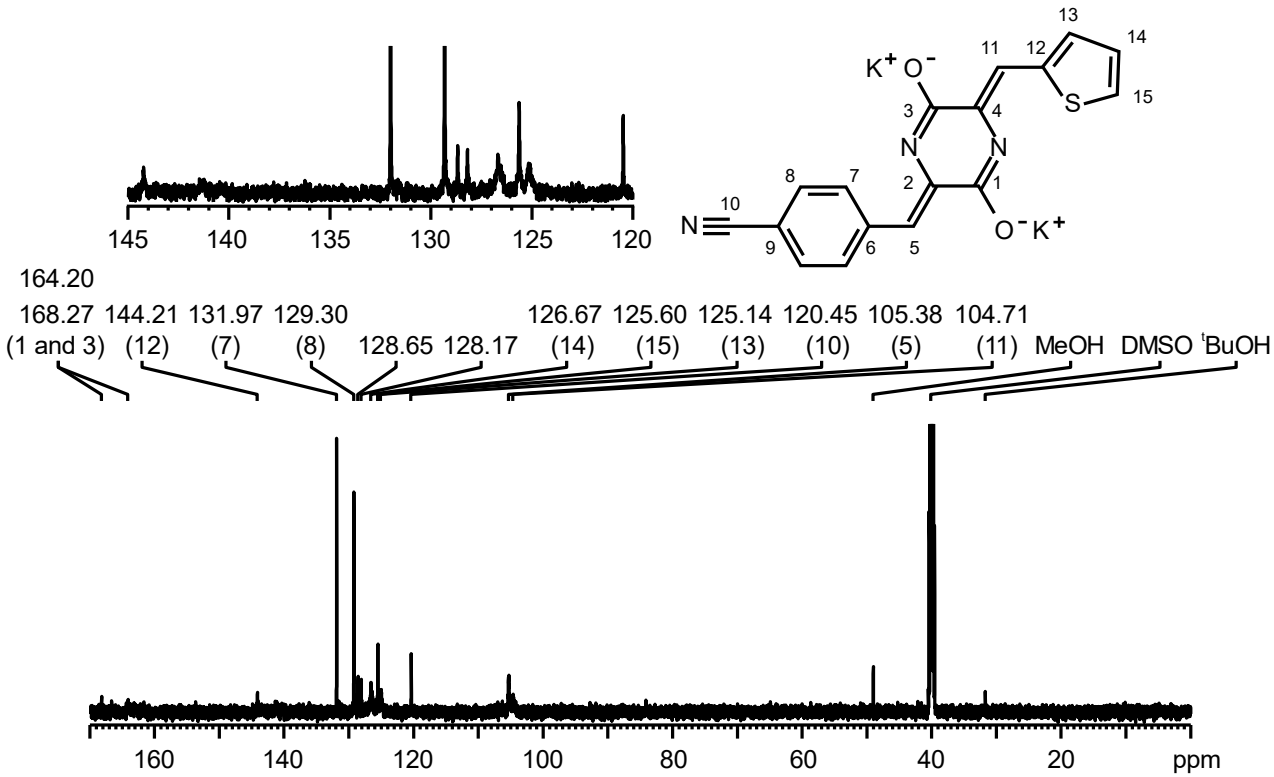


Figure S3.70 ^{13}C NMR of **6l** in DMSO-d_6, numbering simplified for ease of interpretation.

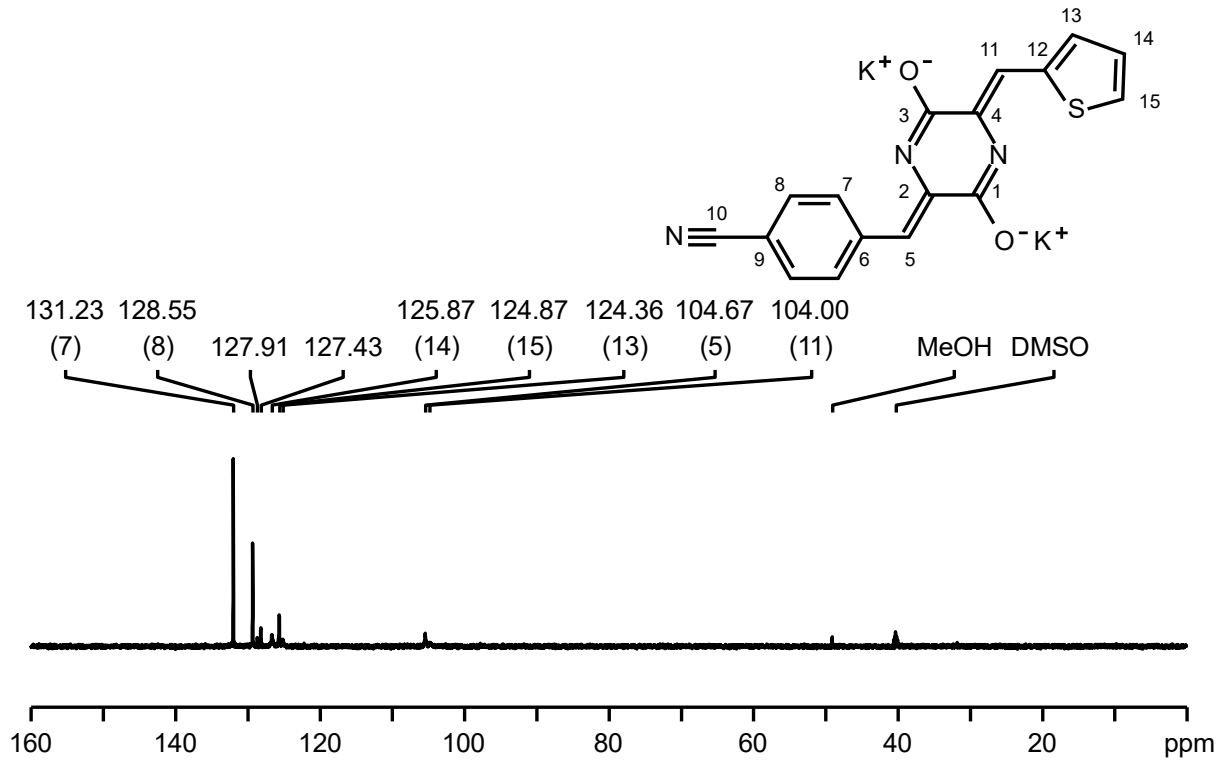


Figure S3.71 DEPT135 NMR of **6l** in DMSO-d_6, numbering simplified for ease of interpretation.

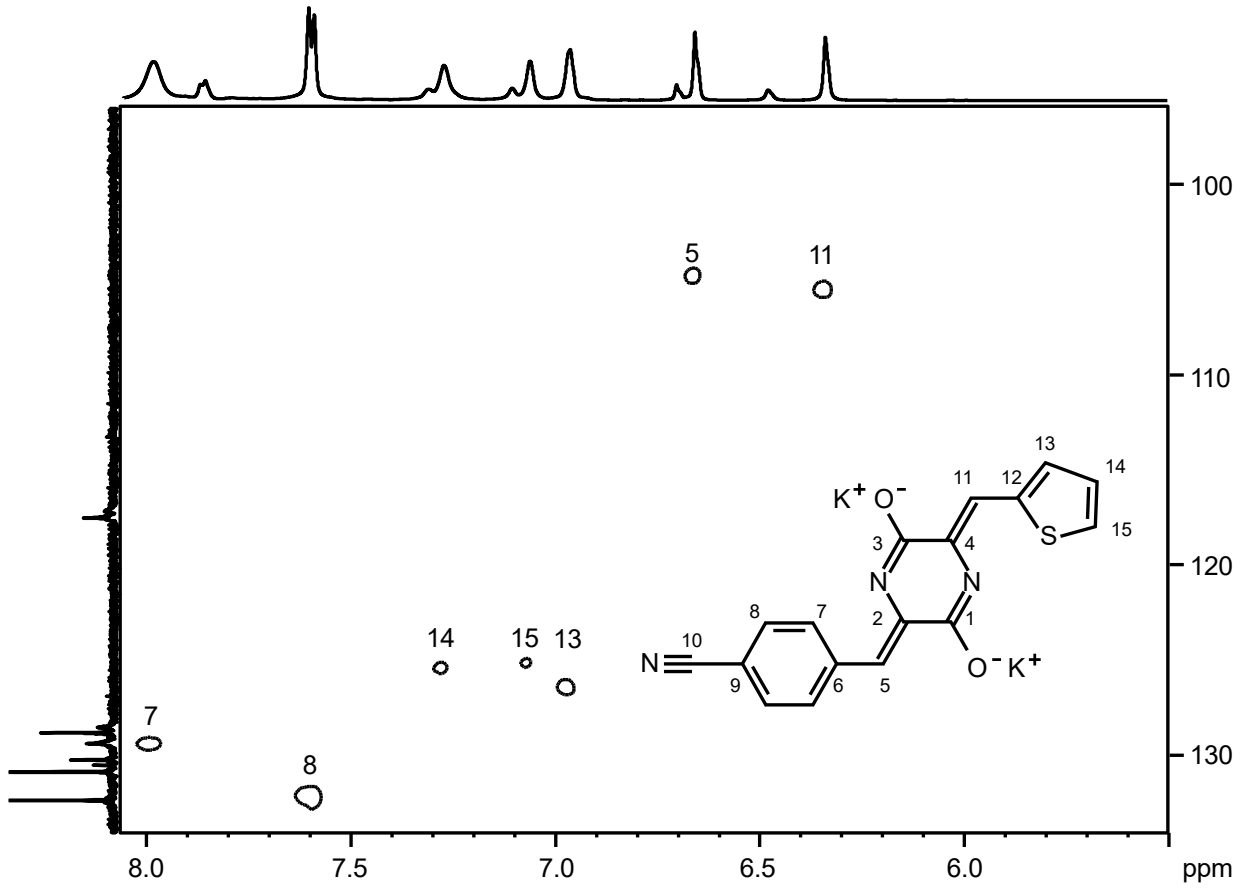


Figure S3.72 HSQC NMR of **6l** in DMSO-d_6, numbering simplified for ease of interpretation.

6m

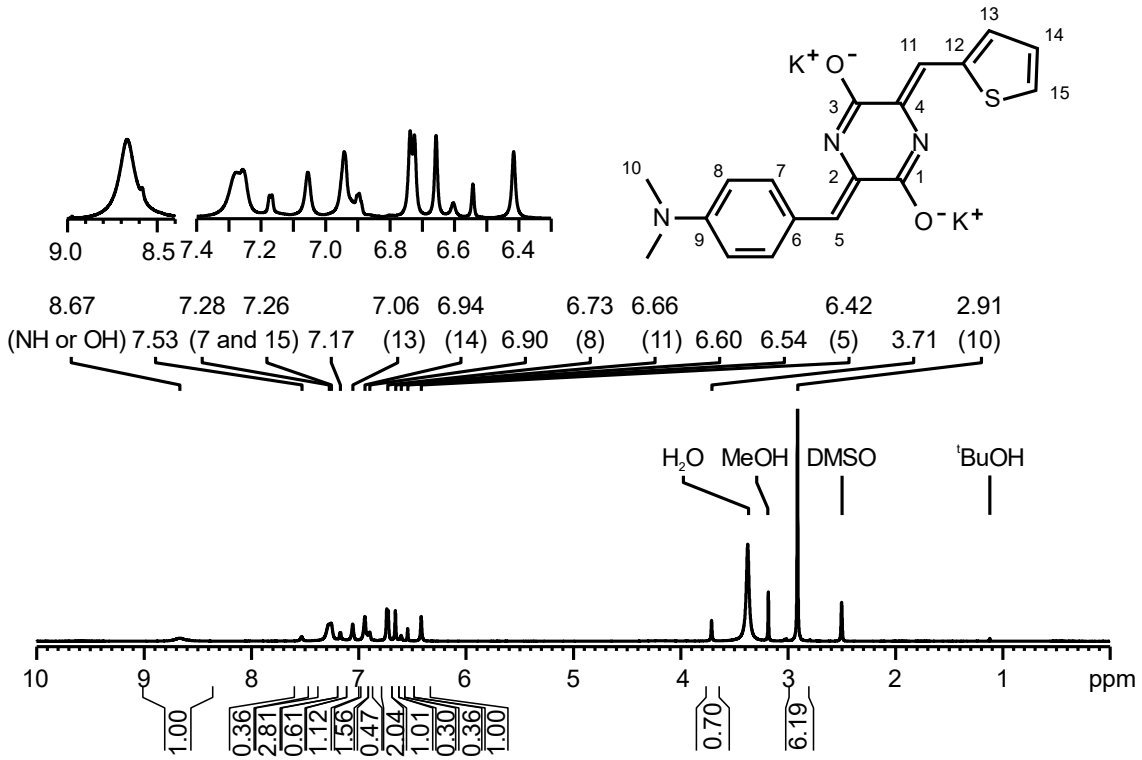


Figure S3.73 ^{1}H NMR of **6m** in DMSO-d_6, numbering simplified for ease of interpretation. Unidentifiable impurity present in a concentration of 19.34%.

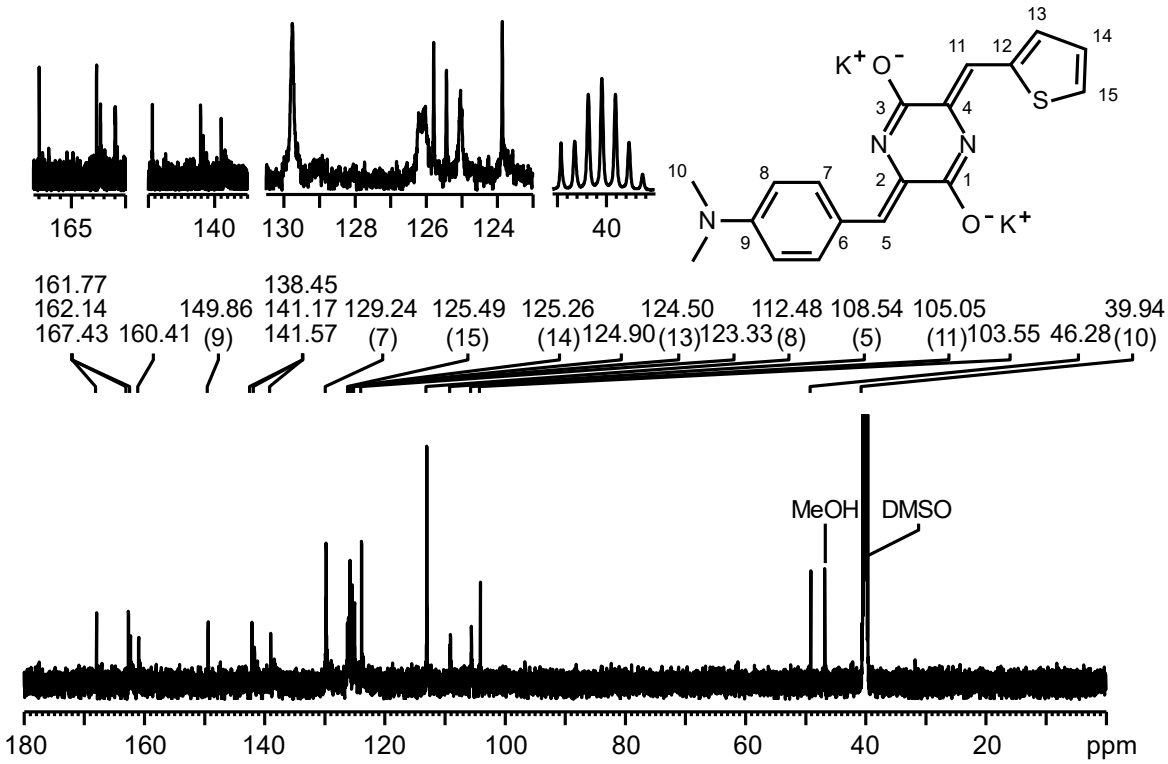


Figure S3.74 ^{13}C NMR of **6m** in DMSO-d_6, numbering simplified for ease of interpretation. Unidentifiable impurity present in a concentration of 19.34%.

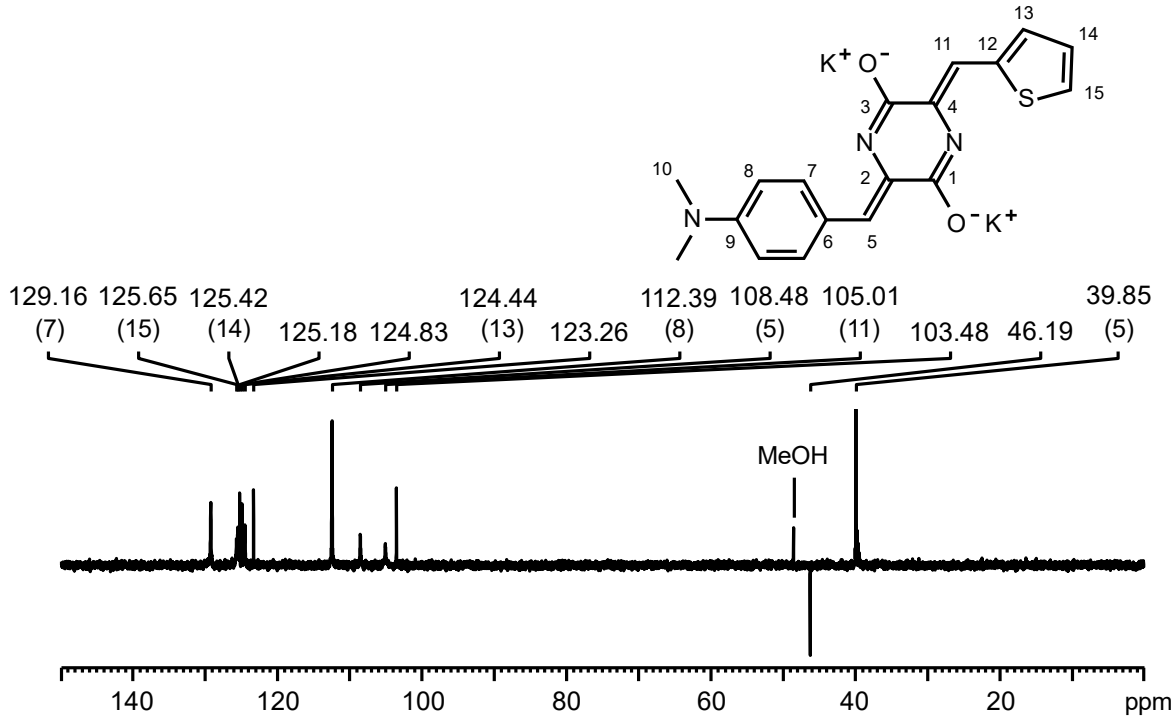


Figure S3.75 DEPT135 NMR of **6m** in DMSO-d_6, numbering simplified for ease of interpretation. Unidentifiable impurity present in a concentration of 19.34%.

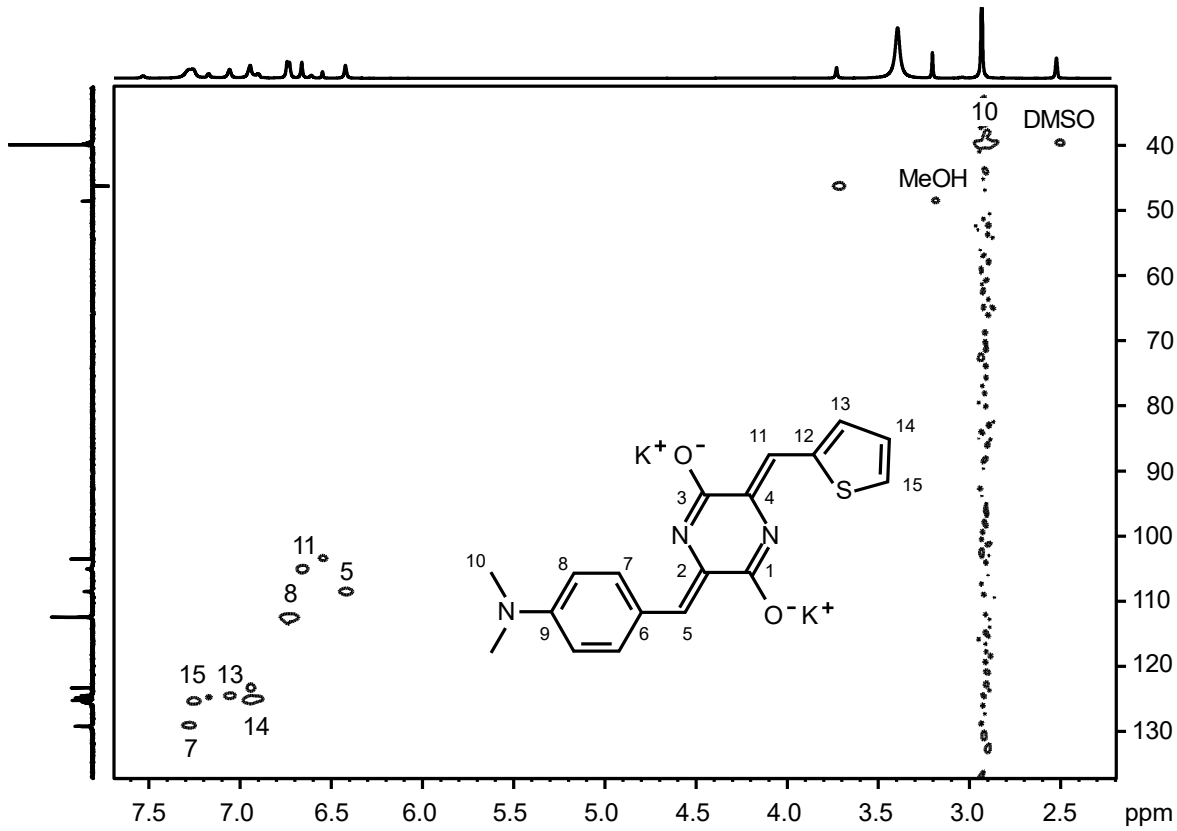


Figure S3.76 HSQC NMR of **6m** in DMSO-d_6, numbering simplified for ease of interpretation. Unidentifiable impurity present in a concentration of 19.34%.

References

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2. W. A. Loughlin, R. L. Marshall, K. E. Fairfull-Smith and P. C. Healy*, Acta Cryst.*, 2005, **E61**, o1443