Supplementary Material

A convenient approach to the synthesis of bio-promising 4-amino-substituted pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acids

Anton Bentya,[a]* Mariia Litvinchuk,[a] Svitlana Shishkina,[a,b] and Mykhailo Vovk[a]

[a]*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, 5 Academician Kukhar Str., Kyiv 02660, Ukraine*

[b]*Institute for Single Crystals, National Academy of Sciences of Ukraine, 60 Nauky Ave., Kharkiv 61072, Ukraine*

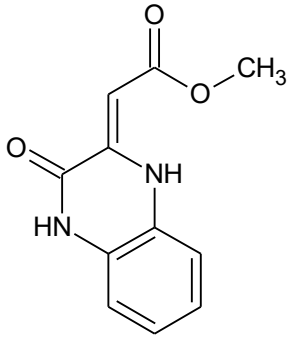
Email: bentya@gmail.com

Table of Contents

Materials and Methods

^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Varian Mercury 200 (^{19}F: 188 MHz), Varian Mercury Plus 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), Varian UNITY INOVA 400 (^{1}H: 400 MHz), Bruker AVANCE III 400 (^{13}C: 100 MHz, ^{19}F: 376 MHz), Varian VNMRS 500 (^{13}C: 125 MHz), Bruker AVANCE DRX 500 (^{13}C: 125 MHz) and Agilent ProPulse 600 (^{13}C: 150 MHz), using solvent peak as internal reference or apparatus SR. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and hertz respectively. IR spectra were recorded on a Bruker Vertex 70 instrument in KBr pellets and are reported in cm^{-1}. Melting points were determined on a Kofler bench and are uncorrected. Mass spectrometry was performed using a Agilent LC/MSD SL instrument , at atmospheric pressure, electrospray ionization. X-ray difraction study of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8j**) was solved by direct method using SHELXTL package. Other reagents and starting materials were directly used as obtained commercially.

Chemical characterization of 1a-f



Chemical characterization of methyl 2-(3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate (**1a**).[1, 2, 3]. Yellow solid (4.059 g, 93%). mp 229-230 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.68 (3H, s, CH_3), 5.52 (1H, s, C<u>H</u>=CNH), 6.99 – 7.08 (3H, m, 3CH aromatic), 7.38 – 7.41 (1H, m, CH aromatic), 11.03 (1H, s, NH), 11.73 (1H, s, NH). ESI-MS: m/z 219.0 [M+H]+. Anal. calcd for $C_{11}H_{10}N_2O_3$ (218.21): C, 60.55; H, 4.62; N, 12.84. Found: C, 60.37; H, 4.65; N, 12.77.

Literature:

1. Sadjadi, S.; Hekmatshoar, R.; Ahmadi, S. J.; at al. *Synthetic Communications* **2010**, *40,* (4), 607. https://doi.org/10.1080/00397910903007103
2. Maik W.; Markus Z.; Katharina J. at al. *Chemistry - A European Journal* **2015**, *21*, (17), 6511. https://doi.org/10.1002/chem.201406306
3. Garima C.; Rama Krishna P. *Green Chemistry* **2011**, *13*, (11), 3290. https://doi.org/10.1039/C1GC15701A

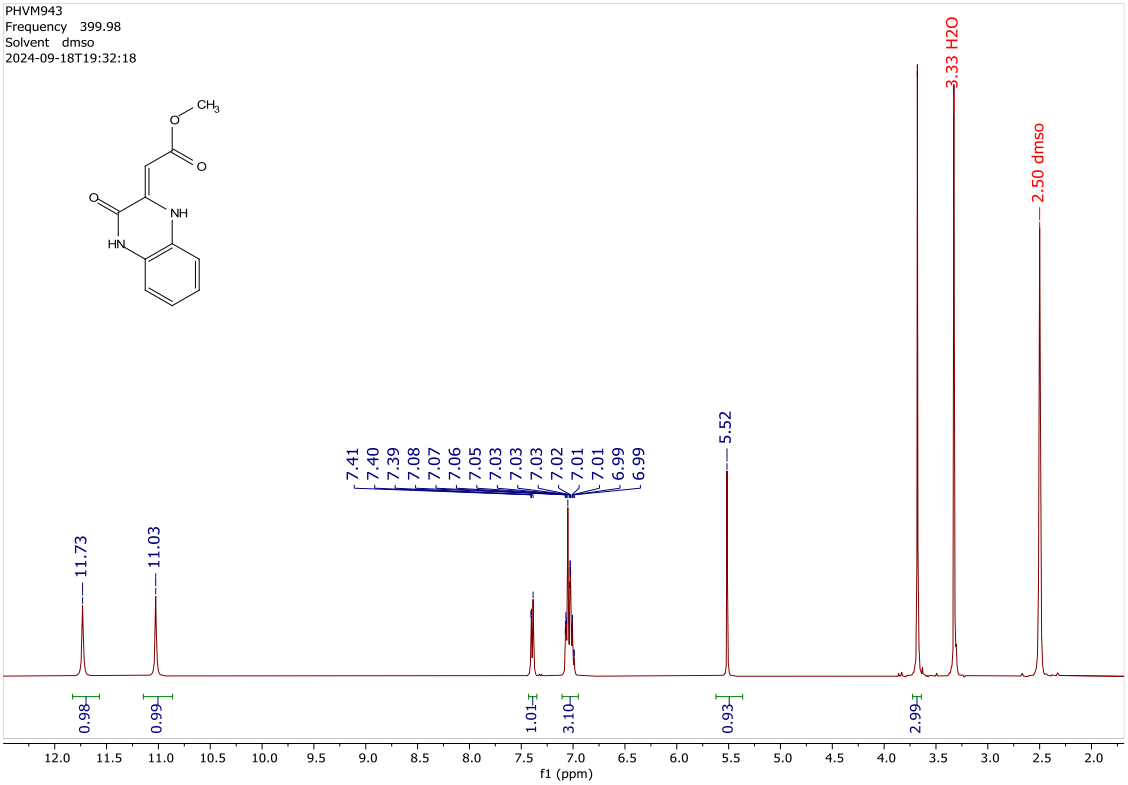
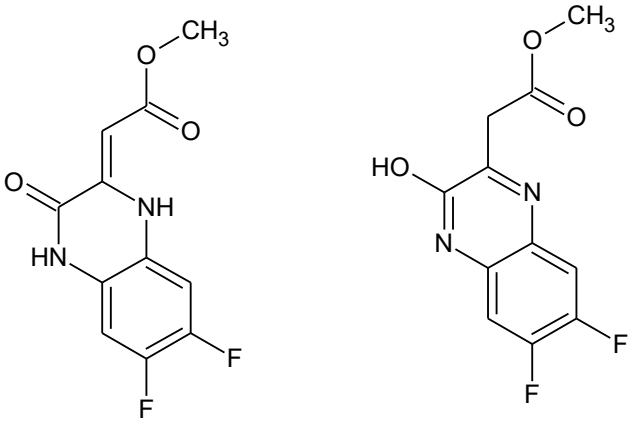


Figure S1. ^{1}H NMR spectrum of methyl 2-(3-oxo-3,4-dihydroquinoxalin-2(*1H*)-*ylidene)acetate* (**1a**) in DMSO-*d*$_6$



Chemical characterization of methyl 2-(6,7-difluoro-3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate (**1b**) + *methyl (6,7-difluoro-3-hydroxyquinoxalin-2-yl)acetate* (**1b'**). Gray solid (4.423 g, 87%). mp 239-240 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 3.63 (3H, s, CH_3O, **1b'**), 3.68 (3H, s, CH_3O, **1b**), 3.82 (2H, s, CH_2, **1b'**), 5.53 (1H, s, CH-CO, **1b**), 6.98 (1H, dd, $^{3}J_{HF}$ 10.7, $^{4}J_{HF}$ 7.9 Hz, CH aromatic, **1b**), 7.23 (1H, dd, $^{3}J_{HF}$ 11.7, $^{4}J_{HF}$ 7.8 Hz, CH aromatic, **1b'**), 7.72 (1H, dd, $^{3}J_{HF}$ 11.8, $^{4}J_{HF}$ 7.7 Hz, CH aromatic, **1b**), 7.87 (1H, dd, $^{3}J_{HF}$ 11.1, $^{4}J_{HF}$ 7.4 Hz, CH aromatic, **1b**), 10.98 (1H, s, NH, **1b**), 11.74 (1H, s, NH-CO, **1b**), 12.61 (1H, s, OH, **1b'**). ^{13}C NMR (DMSO-*d*$_6$, 101 MHz): δ_C 50.73 (CH_3O, **1b**), 51.93 (CH_3O, **1b'**), 84.58 (CH-CO, **1b**), 103.31 (d, $^{2}J_{CF}$ 21.1 Hz, CH aromatic, **1b'**), 103.59 (d, $^{2}J_{CF}$ 22.3 Hz, CH aromatic, **1b**), 104.59 (d, $^{2}J_{CF}$ 23.4 Hz, CH aromatic, **1b**), 116.15 (d, $^{2}J_{CF}$ 18.0 Hz, CH aromatic, **1b'**), 121.65, 121.74, 143.05, 144.63 (dd, $^{1}J_{CF}$ 240.0, $^{2}J_{CF}$ 13.7 Hz, CF aromatic, **2d**), 145.19 (dd, $^{1}J_{CF}$ 239.3, $^{2}J_{CF}$ 13.5 Hz, CF aromatic, **2d**), 153.98, 155.32 (C=O, **1b**), 156.56, 169.03 ($COOCH_3$, **1b**), 169.33 ($COOCH_3$, **1b'**). ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ_H -145.78 (ddd, $^{3}J_{FF}$ 23.8, $^{3}J_{HF}$ 11.1, $^{4}J_{HF}$ 7.6 Hz, **1b**), -144.39 (ddd, $^{3}J_{FF}$ 23.7, $^{3}J_{HF}$ 12.1, $^{4}J_{HF}$ 7.6 Hz, **1b**), -143.64 (ddd, $^{3}J_{FF}$ 23.3, $^{3}J_{HF}$ 11.2, $^{4}J_{HF}$ 8.0 Hz, **1b'**), -133.47 (ddd, $^{3}J_{FF}$ 22.9, $^{3}J_{HF}$ 11.0, $^{4}J_{HF}$ 8.3 Hz, **1b'**). ESI-MS: m/z 255.0 [M+H]+. Anal. calcd for $C_{11}H_8F_2N_2O_3$ (254.19): C, 51.98; H, 3.17; N, 11.02. Found: C, 52.10; H, 3.14; N, 10.89.

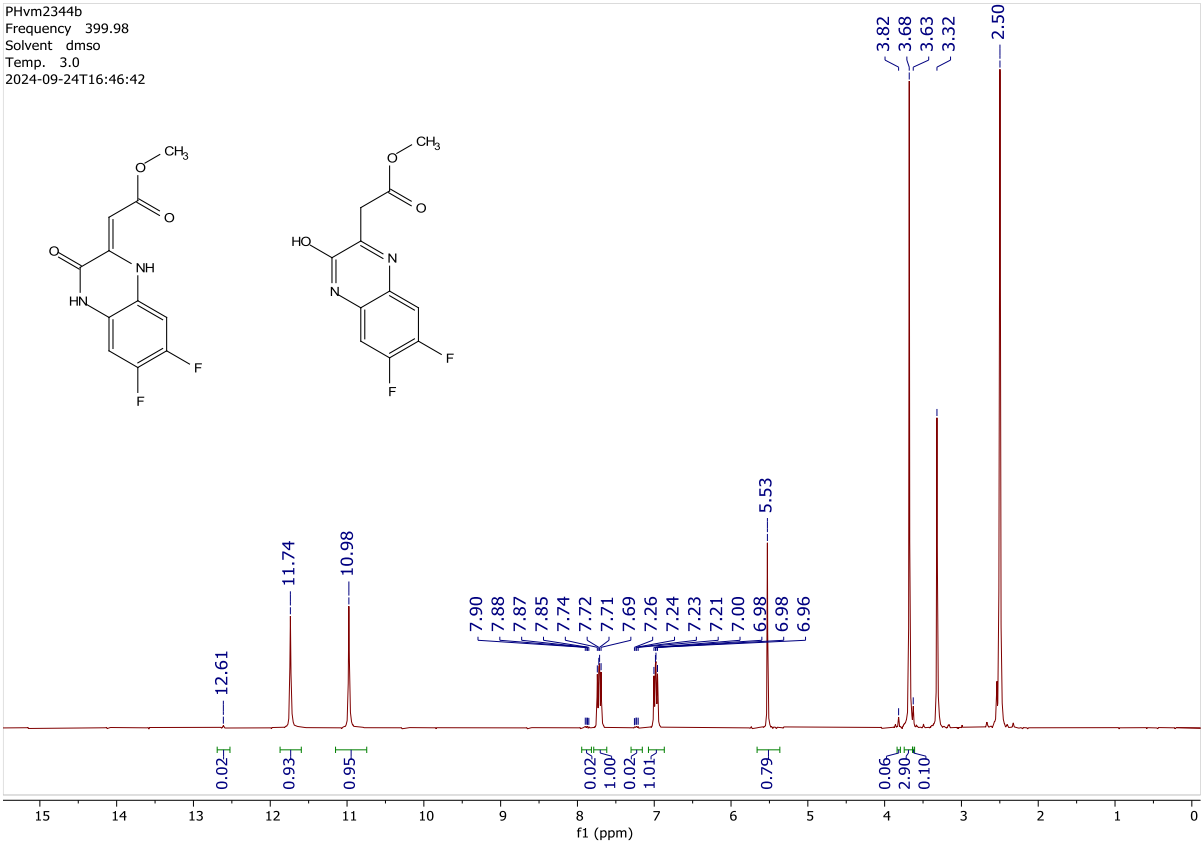


Figure S2. [1]H NMR spectrum of methyl 2-(6,7-difluoro-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1b**) + methyl (6,7-difluoro-3-hydroxyquinoxalin-2-yl)acetate (**1b'**) in DMSO-d_6

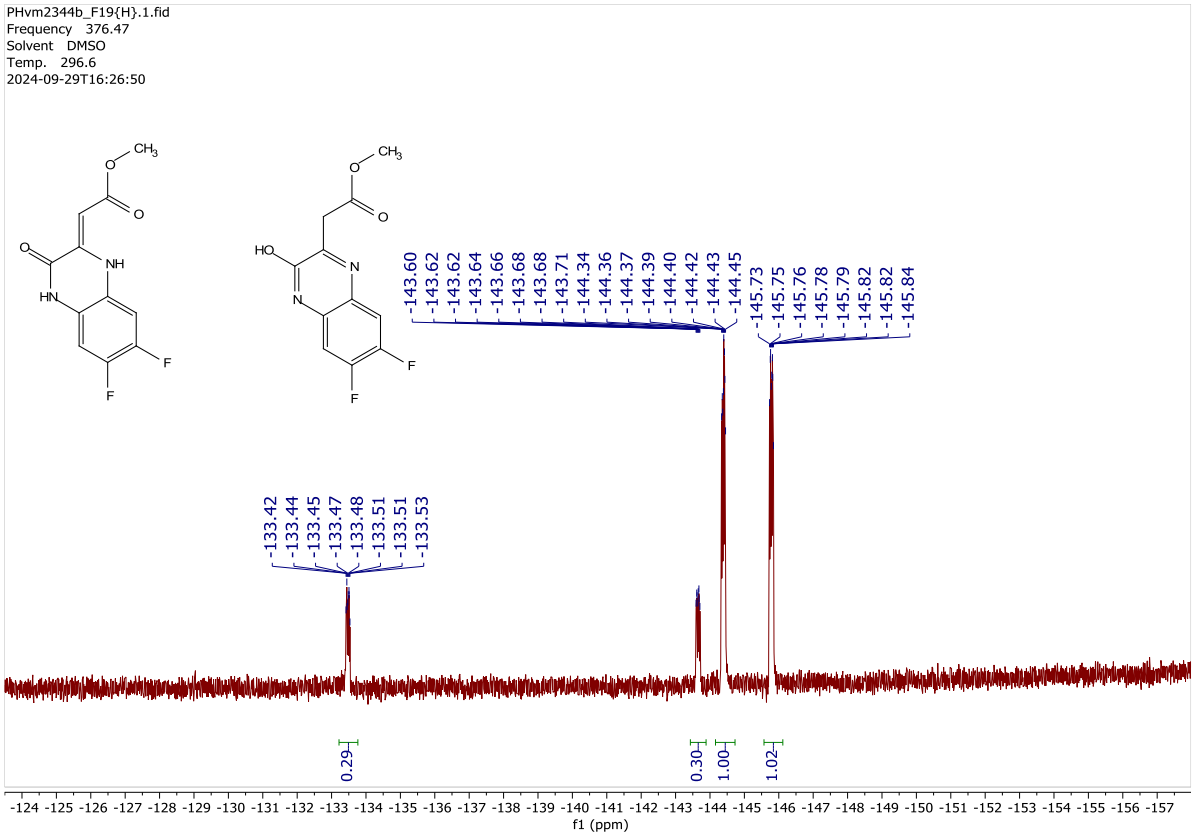


Figure S3. [19]F NMR spectrum of methyl 2-(6,7-difluoro-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1b**) + methyl (6,7-difluoro-3-hydroxyquinoxalin-2-yl)acetate (**1b'**) in DMSO-d_6

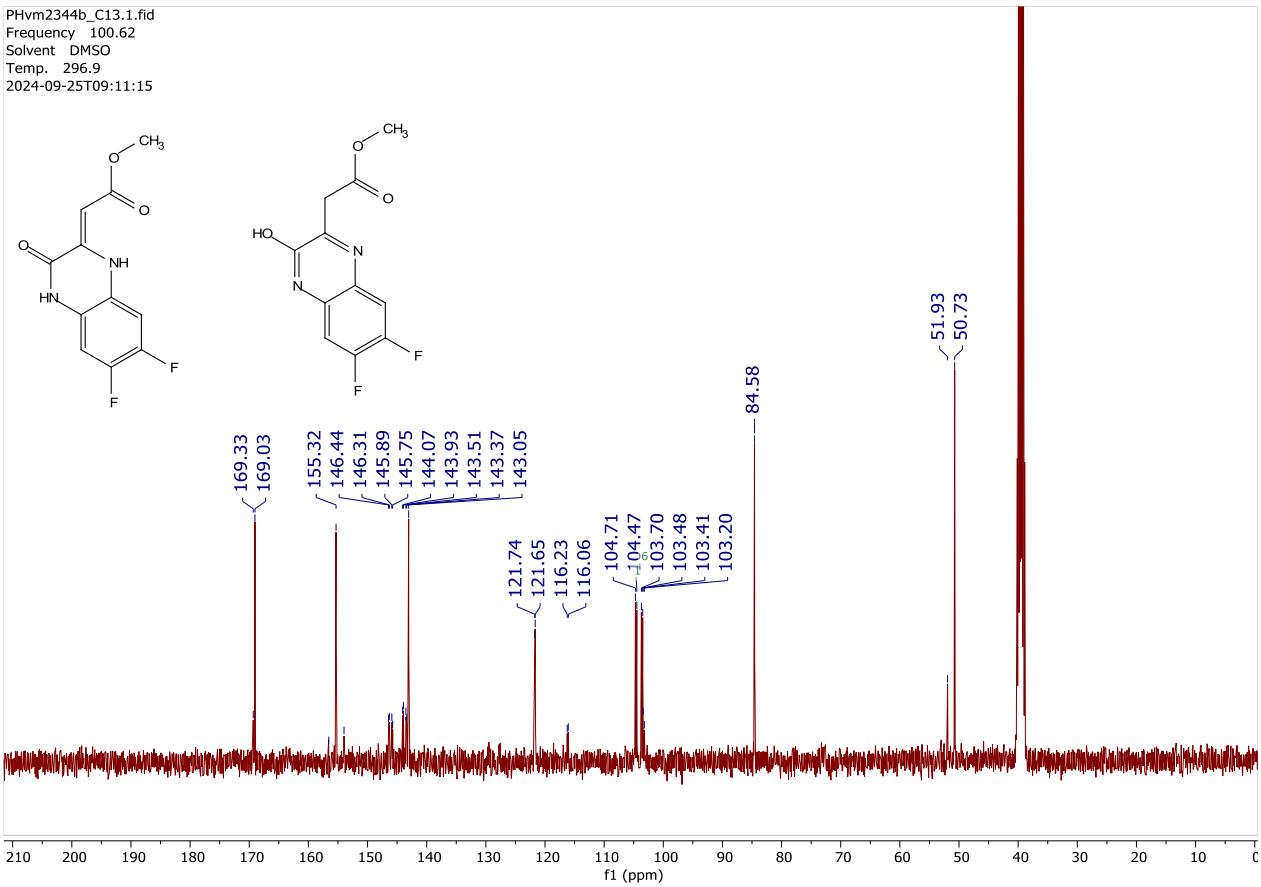
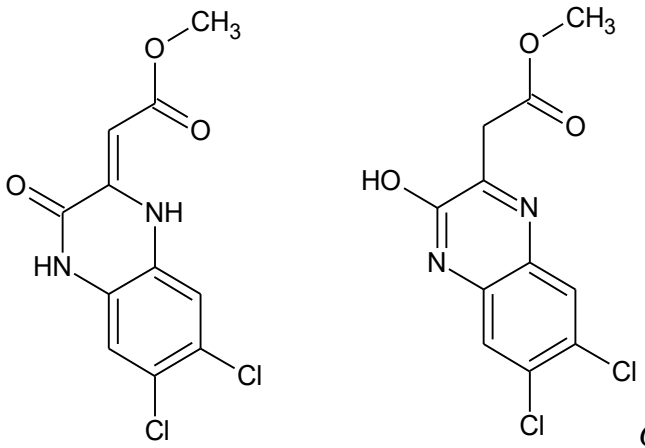


Figure S4. ^{13}C NMR spectrum of methyl 2-(6,7-difluoro-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1b**) + methyl (6,7-difluoro-3-hydroxyquinoxalin-2-yl)acetate (**1b'**) in DMSO-*d*$_6$



Chemical characterization of methyl 2-(6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate (**1c**) + *methyl (6,7-dichloro-3-hydroxyquinoxalin-2-yl)acetate* (**1c'**). Beige solid (5.397 g, 94%). mp 252-253 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 3.63 (3H, s, CH_3O **1c'**), 3.69 (3H, s, CH_3O **1c**), 3.83 (2H, s, CH_2 **1c'**), 5.56 (1H, s, C<u>H</u>=CNH **1c**), 7.14 (1H, s, CH aromatic **1c**), 7.46 (1H, s, CH aromatic **1c'**), 7.85 (1H, s, CH aromatic **1c**), 8.01 (1H, s, CH aromatic **1c'**), 10.95 (1H, s, NH **1c**), 11.80 (1H, s, NH **1c**), 12.63 (1H, s, OH **1c'**). ^{13}C NMR (DMSO-*d*$_6$, 151 MHz): δ_C 39.42 (CH_2 **1c'**), 50.81 (CH_3O **1c**), 51.94 (CH_3O **1c'**), 85.60 (<u>C</u>H-CO **1c**), 115.81, 116.51, 116.76, 123.47, 124.77, 125.17, 125.21, 125.36, 129.29, 130.74, 131.94, 132.31, 142.67, 153.87, 155.35, 157.76, 168.82 (<u>C</u>OOCH$_3$ **1c**), 169.17 (<u>C</u>OOCH$_3$ **1c'**). ESI-MS: m/z 287.0 $[M+H]^+$. Anal. calcd for $C_{11}H_8Cl_2N_2O_3$ (287.10): C, 46.02; H, 2.81; N, 9.76. Found: C, 45.83; H, 2.79; N, 9.84.

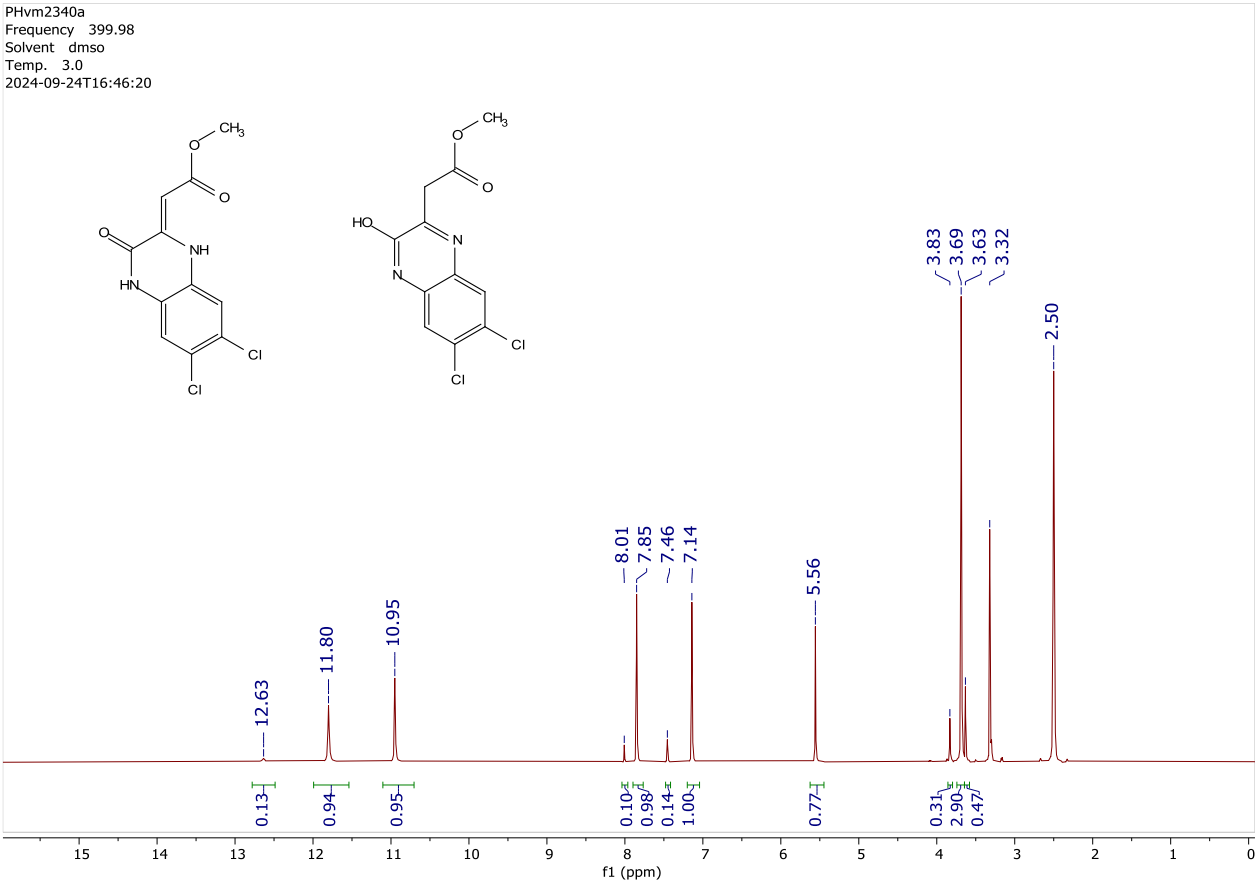


Figure S5. [1]H NMR spectrum of methyl 2-(6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1c**) + methyl (6,7-dichloro-3-hydroxyquinoxalin-2-yl)acetate (**1c'**) in DMSO-d_6

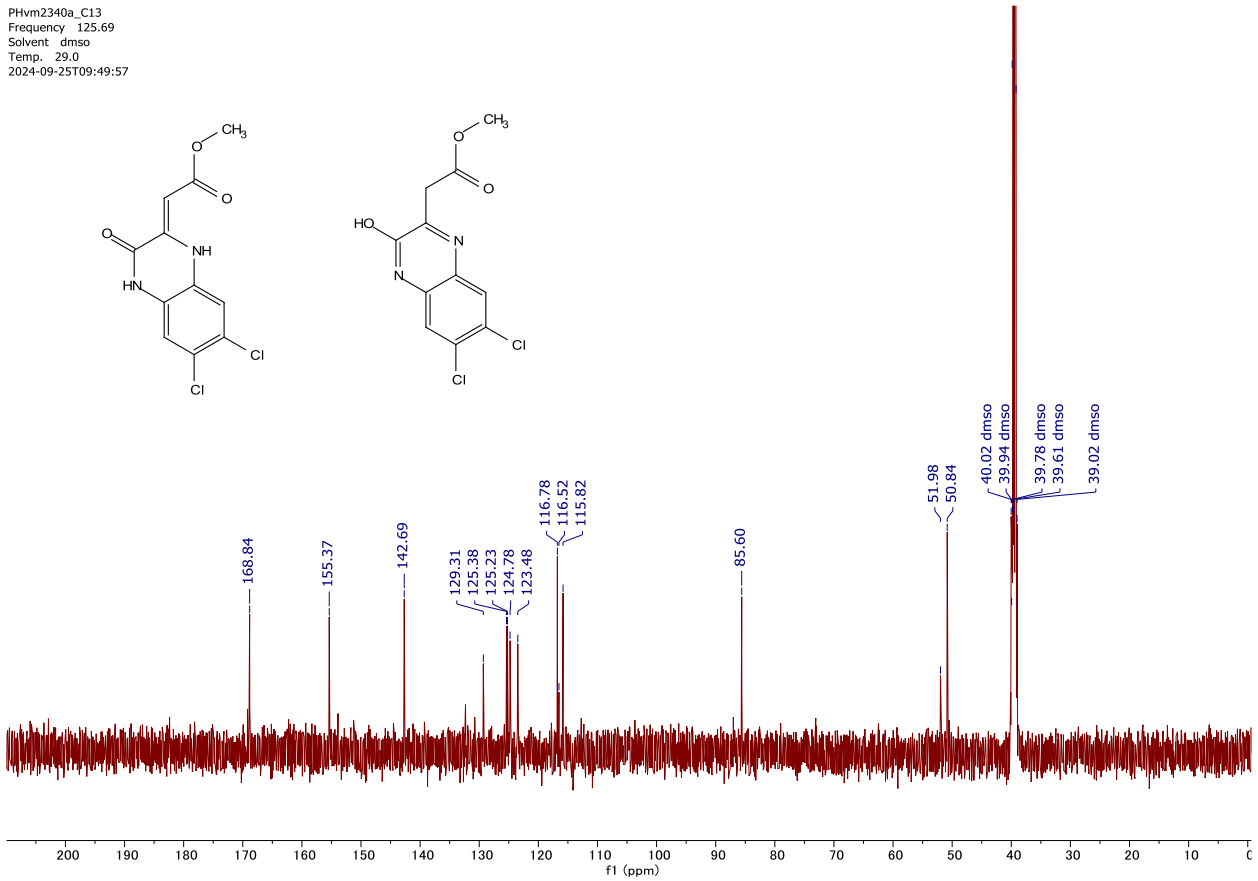
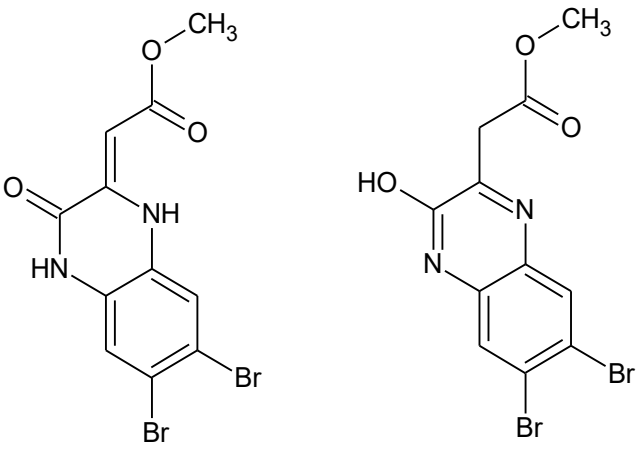


Figure S6. [13]C NMR spectrum of methyl 2-(6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1c**) + methyl (6,7-dichloro-3-hydroxyquinoxalin-2-yl)acetate (**1c'**) in DMSO-d_6



Chemical characterization of methyl 2-(6,7-dibromo-3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate (**1d**) + *methyl (6,7-dibromo-3-hydroxyquinoxalin-2-yl)acetate* (**1d'**). Light yellow solid (6.317 g, 84%). mp 253-254 (decomp.) °C. IR (solid, KBr, νmax, cm^{-1}): 3204, 1693, 1643, 1348, 1235, 771, 596, 532. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 3.64 (3H, s, CH_3O **1d'**), 3.70 (3H, s, CH_3O **1d**), 3.83 (2H, s, CH_2 **1d'**), 5.59 (1H, s, C<u>H</u>=CNH **1d**), 7.31 (1H, s, CH aromatic **1d**), 7.64 (1H, s, CH aromatic **1d'**), 7.92 (1H, s, CH aromatic **1d**), 8.08 (1H, s, CH aromatic **1d'**), 10.90 (1H, s, NH **1d**), 11.64 (1H, s, NH **1d**), 12.47 (1H, s, OH **1d'**). ^{13}C NMR (DMSO-*d*$_6$, 151 MHz): δ_C 51.29 (CH_3O), 86.12 (<u>C</u>H-CO), 115.74, 117.16, 119.25, 120.21, 126.29, 126.47, 143.14, 155.84, 169.25 (<u>C</u>OOCH$_3$). ESI-MS: m/z 378.8 $[M+H]^+$. Anal. calcd for $C_{11}H_8Br_2N_2O_3$ (376.00): C, 35.14; H, 2.14; N, 7.45. Found: C, 35.30; H, 2.10; N, 7.39.

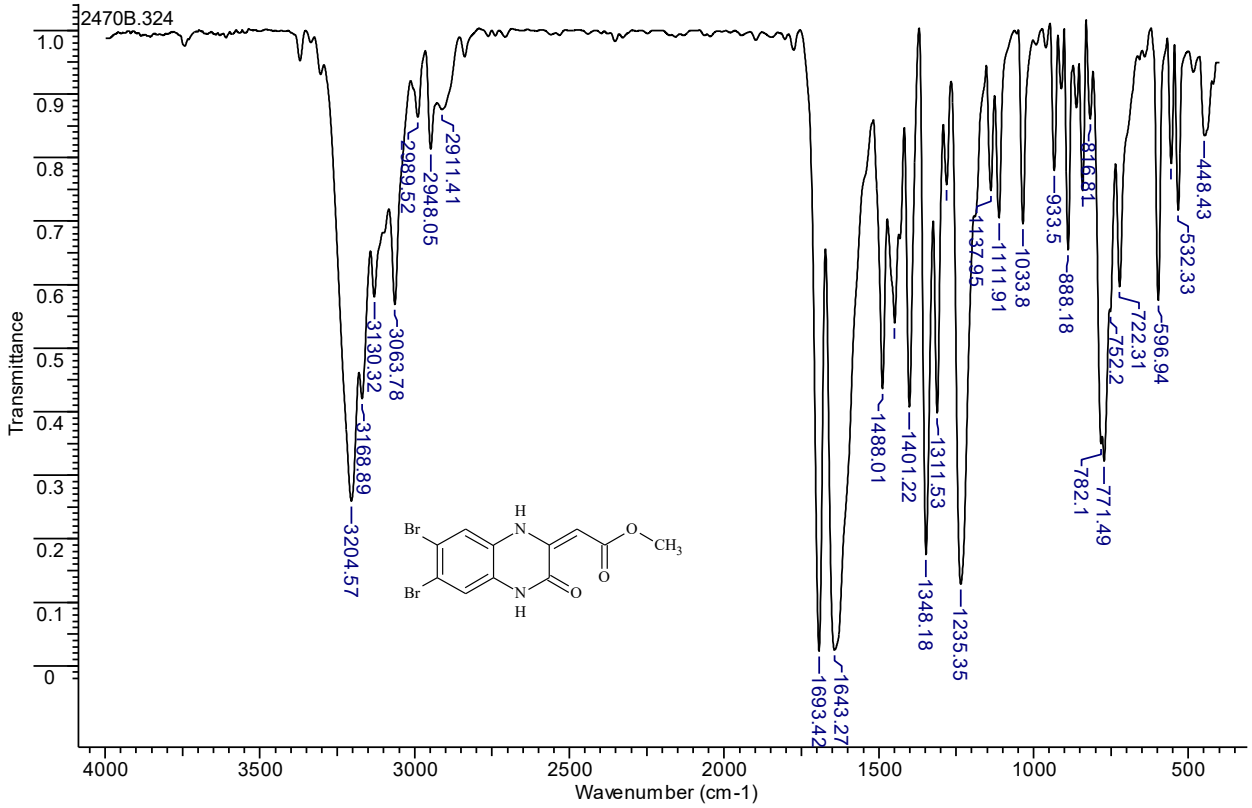


Figure S7. IR spectrum of methyl 2-(6,7-dibromo-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1d**) + methyl (6,7-dibromo-3-hydroxyquinoxalin-2-yl)acetate (**1d'**) in KBr pellet

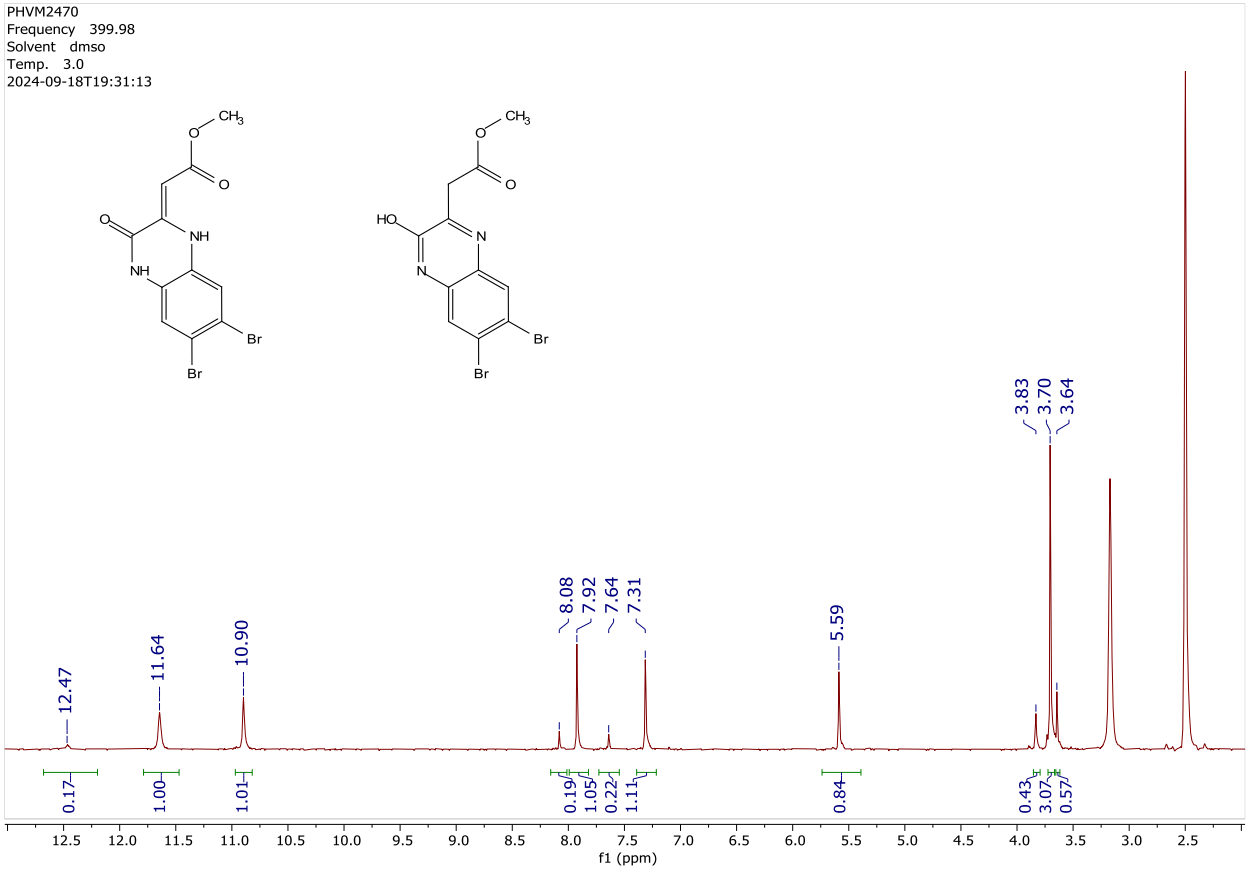


Figure S8. ^{1}H NMR spectrum of methyl 2-(6,7-dibromo-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1d**) + methyl (6,7-dibromo-3-hydroxyquinoxalin-2-yl)acetate (**1d'**) in DMSO-d_6

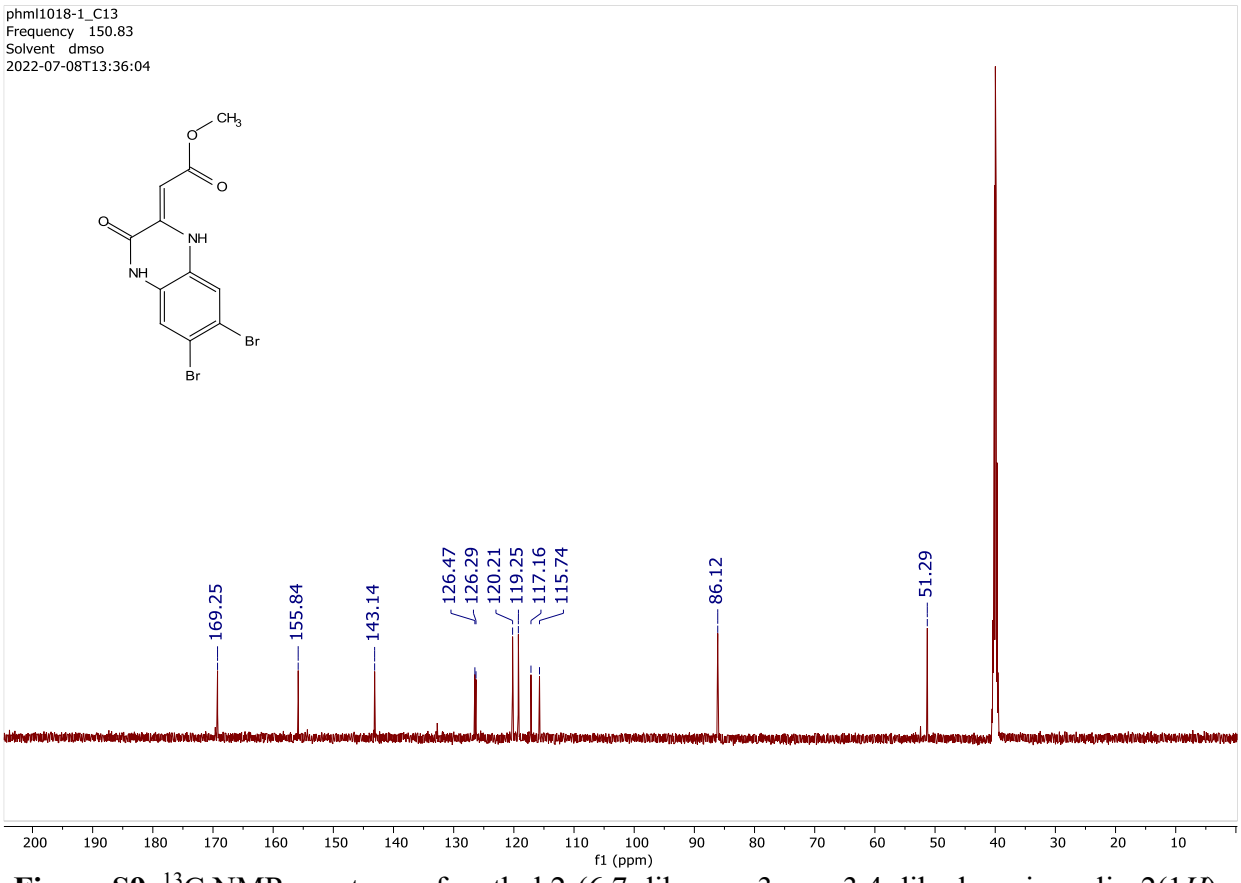
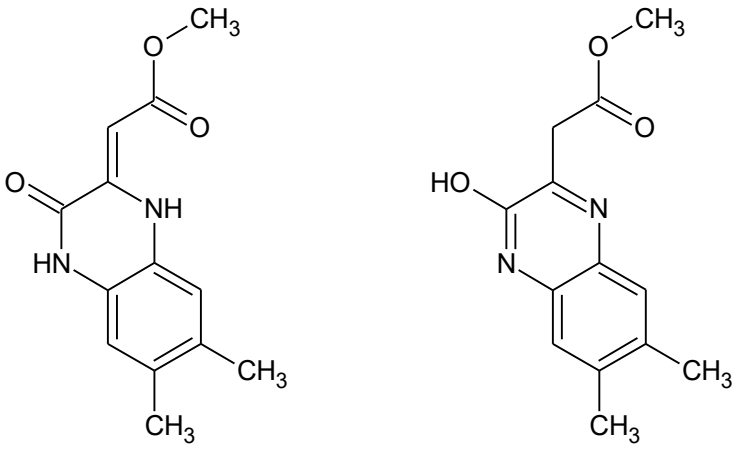


Figure S9. ^{13}C NMR spectrum of methyl 2-(6,7-dibromo-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1d**) + methyl (6,7-dibromo-3-hydroxyquinoxalin-2-yl)acetate (**1d'**) in DMSO-d_6



Chemical characterization of methyl 2-(6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate (**1e**) + *methyl (3-hydroxy-6,7-dimethylquinoxalin-2-yl)acetate* (**1e'**). Yellow solid (4.039 g, 82%). mp 224-225 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 2.16 + 2.17 (3H+3H, s + s, 2 CH_3 **1e**), 2.28 + 2.30 (1H+1H, s + s, 2CH_3 **1e'**), 3.63 (3H, s, CH_3O **1e'**), 3.67 (3H, s, CH_3O **1e**), 3.79 (2H, s, CH_2 **1e'**), 5.47 (1H, s, C<u>H</u>=CNH **1e**), 6.82 (1H, s, CH aromatic **1e**), 7.06 (1H, s, CH aromatic **1e'**), 7.13 (1H, s, CH aromatic **1e**), 7.49 (1H, s, CH aromatic **1e'**), 10.95 (1H, s, NH **1e**), 11.56 (1H, s, NH **1e**), 12.27 (1H, s, OH **1e'**). ^{13}C NMR (DMSO-*d*$_6$, 126 MHz): δ_C 18.87 + 18.89 + 18.95 + 19.71 (4CH_3 **1e** and **1e'**), 39.40 (CH_2 **1e'**), 50.60 + 51.80 (2CH_3O **1e** and **1e'**), 82.52 (<u>C</u>H-CO **1e**), 115.41, 115.78, 115.95, 122.49, 122.91, 128.14, 129.98, 130.12, 130.71, 131.58, 131.97, 139.69, 144.15, 154.43 + 155.44 (2CO-NH **1e** and **1e'**), 169.63 + 169.72 (2<u>C</u>OOCH$_3$ **1e** and **1e'**). ESI-MS: m/z 247.2 [M+H]+. Anal. calcd for $C_{13}H_{14}N_2O_3$ (246.26): C, 63.40; H, 5.73; N, 11.38. Found: C, 63.19; H, 5.77; N, 11.42.

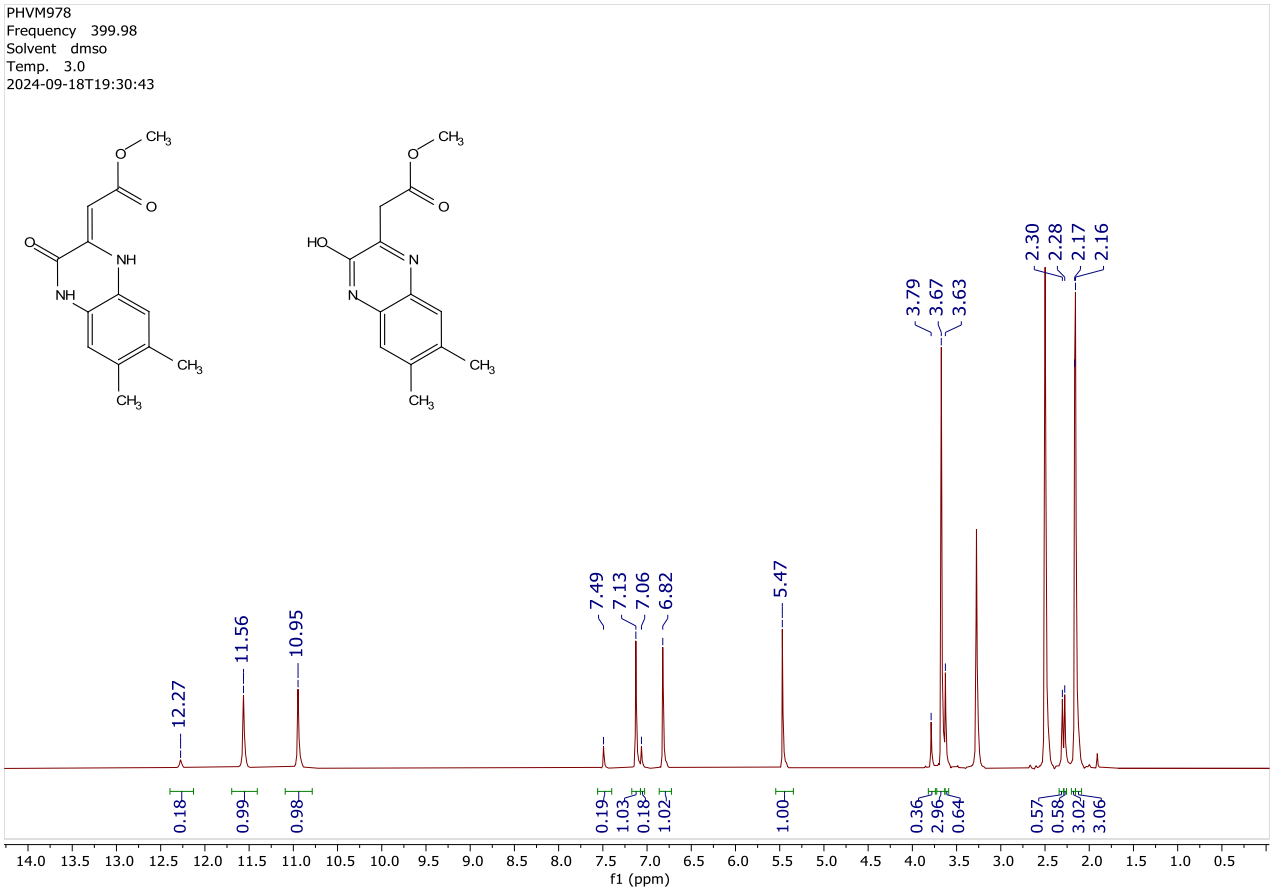


Figure S10. ^{1}H NMR spectrum of methyl 2-(6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1e**) + methyl (3-hydroxy-6,7-dimethylquinoxalin-2-yl)acetate (**1e'**) in DMSO-*d*$_6$

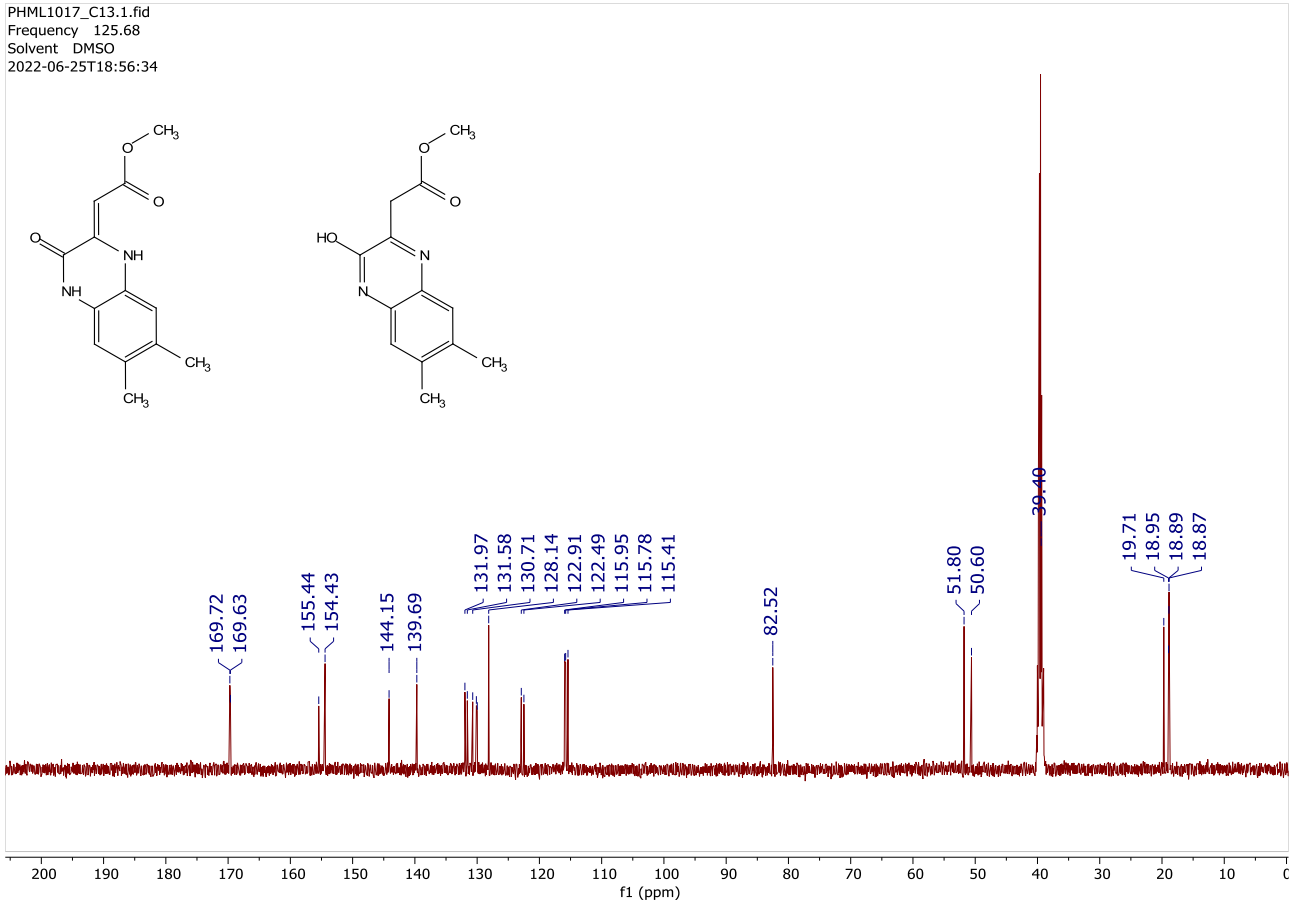
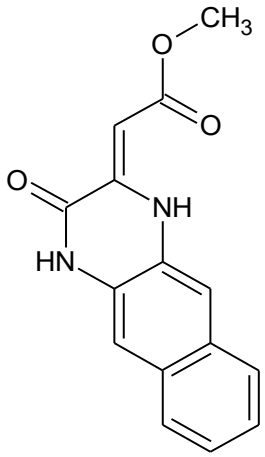


Figure S11. ^{13}C NMR spectrum of methyl 2-(6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (**1e**) + methyl (3-hydroxy-6,7-dimethylquinoxalin-2-yl)acetate (**1e'**) in DMSO-d_6



Chemical characterization of methyl 2-(3-oxo-3,4-dihydrobenzo[g]quinoxalin-2(1H)-ylidene)acetate (**1f**). Yellow solid (4.292 g, 80%). mp 253-254 (decomp.) °C. IR (solid, KBr, νmax, cm^{-1}): 3229, 1697, 1650, 1227, 772, 742. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.72 (3H, s, CH_3), 5.61 (1H, s, CH-CO), 7.33 – 7.39 (2H, m, CH aromatic), 7.46 (1H, s, CH aromatic), 7.74 – 7.79 (2H, m, CH aromatic), 7.84 (7H, s, CH aromatic), 11.09 (1H, s, NH), 11.96 (1H, s, NH-CO). ^{13}C NMR (DMSO-d_6, 151 MHz): δ_C 51.30 (CH_3O), 85.64 (CH-CO), 111.25, 111.36, 125.15, 125.47, 125.49, 126.32, 126.99, 127.11, 129.54, 130.34, 143.73, 156.19 (CO-NH), 169.79 (COOCH$_3$). ESI-MS: m/z 267.0 [M+H]+. Anal. calcd for $C_{15}H_{12}N_2O_3$ (268.27): C, 67.16; H, 4.51; N, 10.44. Found: C, 67.30; H, 4.53; N, 10.30.

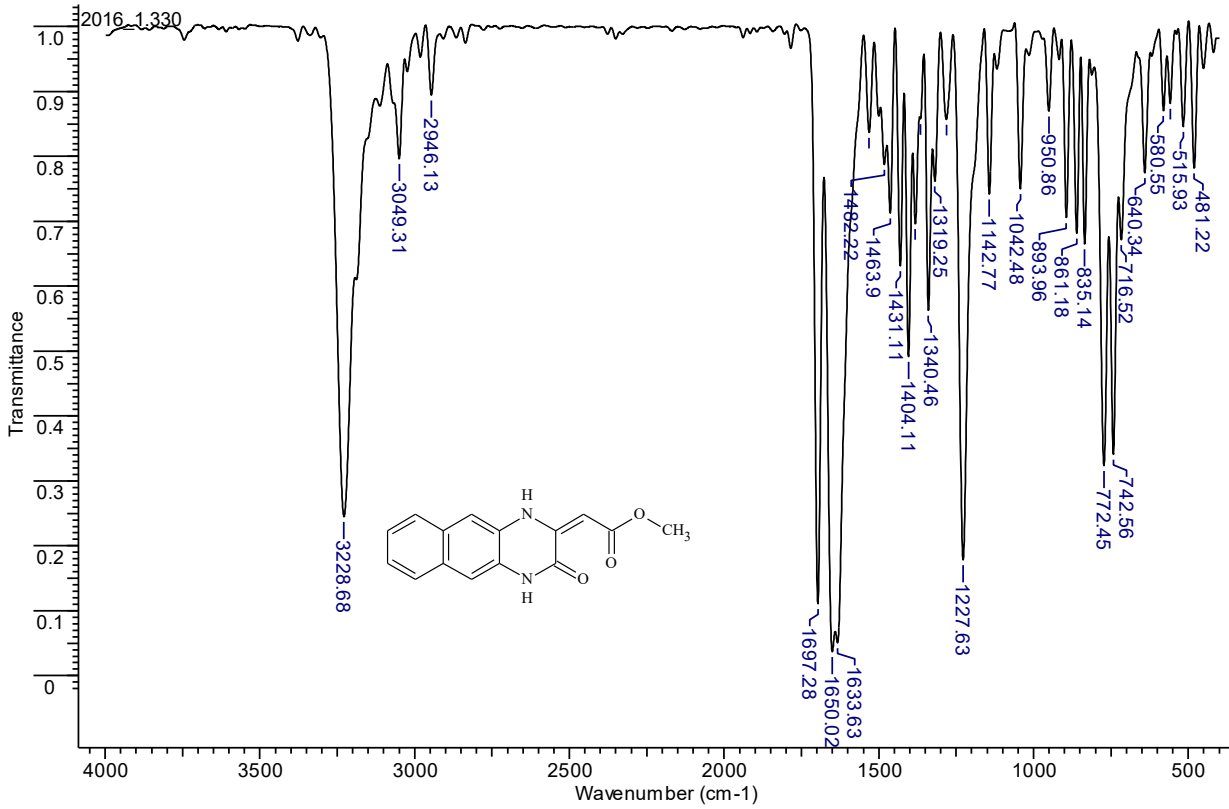


Figure S12. IR spectrum of methyl 2-(3-oxo-3,4-dihydrobenzo[*g*]quinoxalin-2(1*H*)-ylidene)acetate (**1f**) in KBr pellet

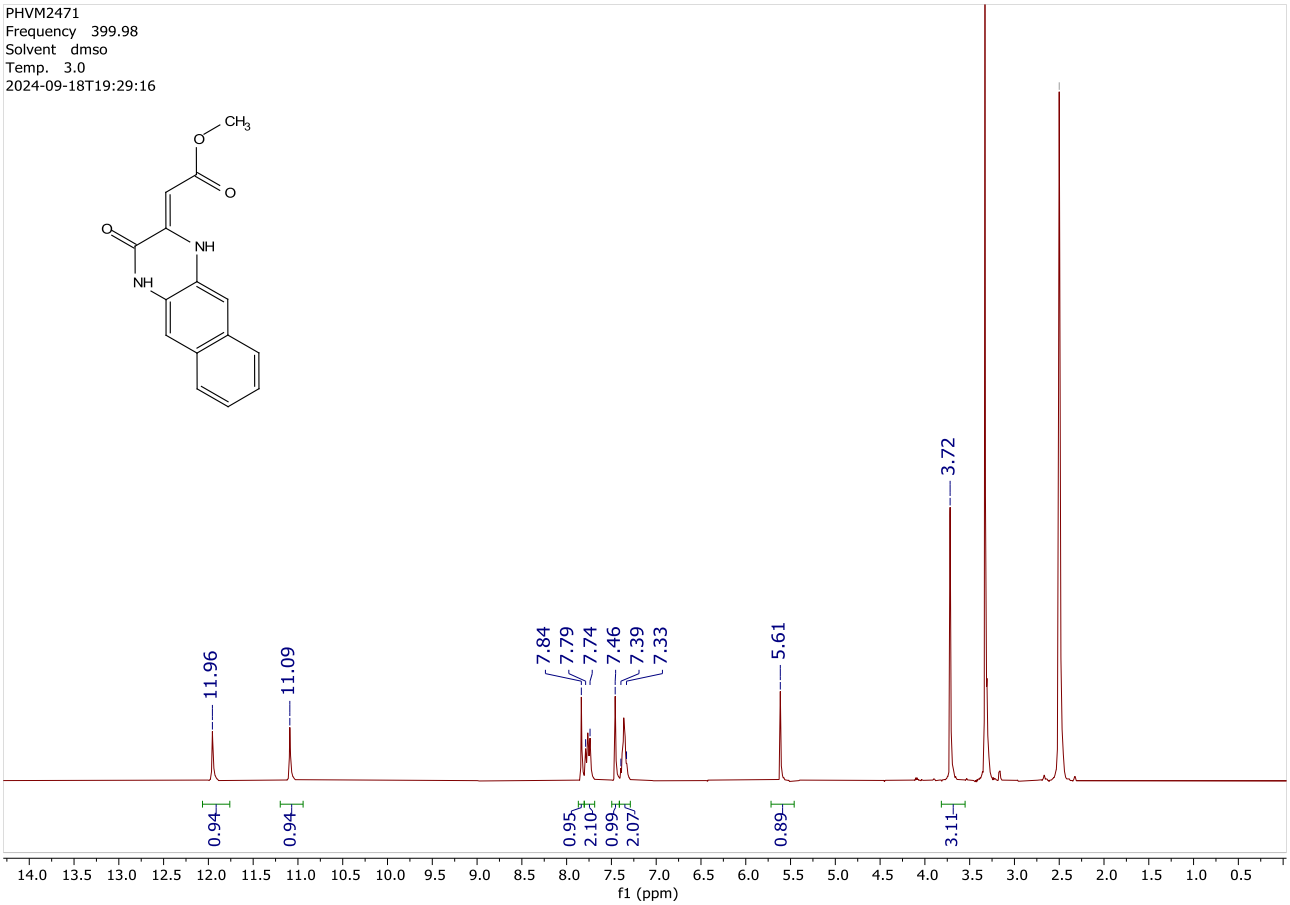


Figure S13. ^{1}H NMR spectrum of methyl 2-(3-oxo-3,4-dihydrobenzo[*g*]quinoxalin-2(1*H*)-ylidene)acetate (**1f**) in DMSO-d_6

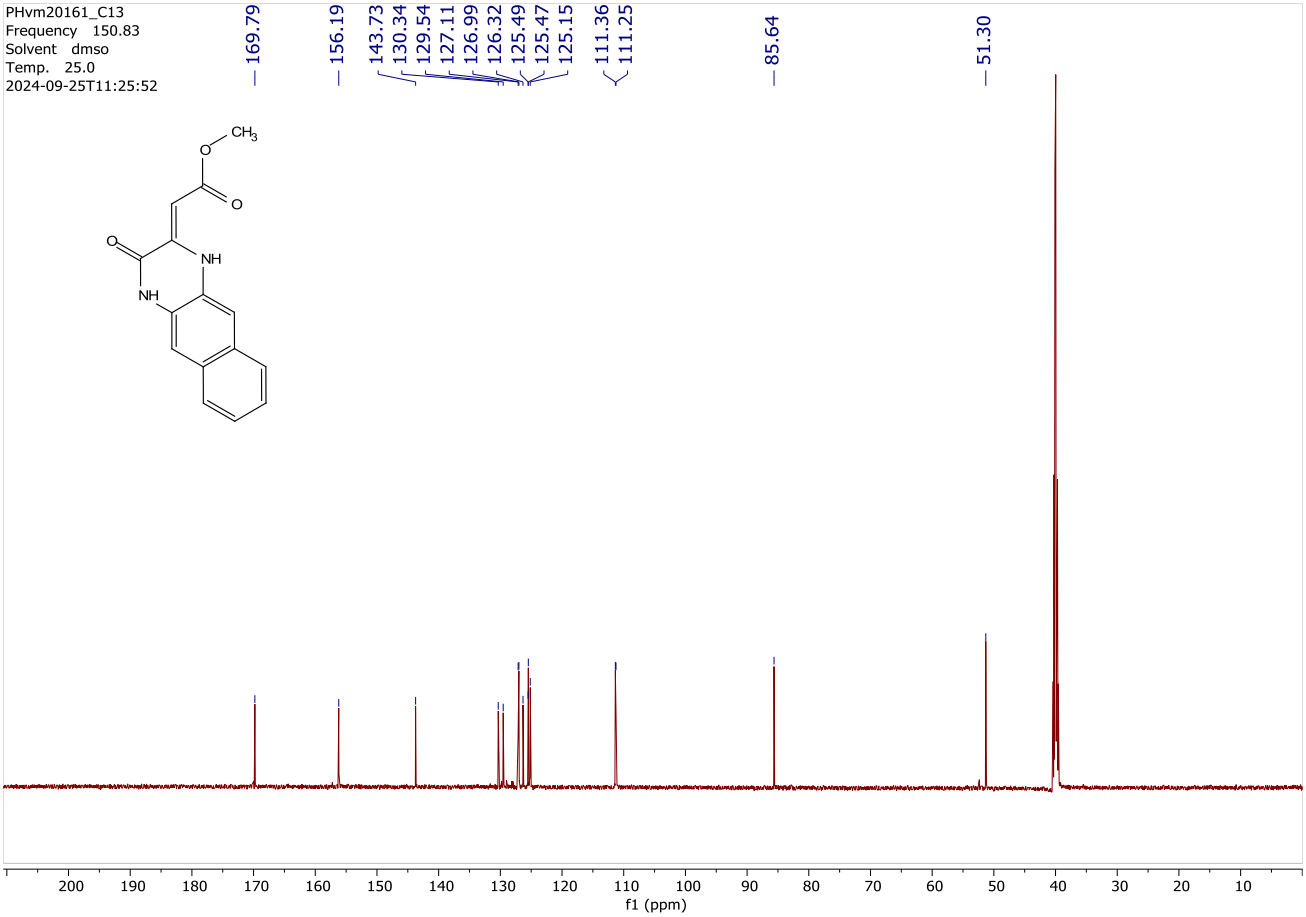


Figure S14. ^{13}C NMR spectrum of methyl 2-(3-oxo-3,4-dihydrobenzo[*g*]quinoxalin-2(1*H*)-ylidene)acetate (**1f**) in DMSO-d_6

Variation in the tautomeric ratio of 1a-f and 1a'–f' in DMSO-d_6 solution in time

For 2-[3,4-dihydro-3-oxoquinoxalin-2(1*H*)-ylidene]carboxylates **1a-f** in DMSO-d_6 solution, a tautomeric equilibrium with (3-hydroxyquinoxalin-2-yl)carboxylates is observed. The rate of tautomerization significantly depends on the nature of the substituents in the quinoxaline nucleus.

Table S1. Variation in the tautomeric ratio of **1a-f** and **1a'–f'** in DMSO-d_6 solution in time

Time	ω, mol %		ω, mol %		ω, mol %		ω, mol %		ω, mol %		ω, mol %	
	1a	**1a'**	**1b**	**1b'**	**1c**	**1c'**	**1d**	**1d'**	**1e**	**1e'**	**1f**	**1f'**
5 min	100	0	100	0	95	5	100	0	98	2	100	0
24 h	95	5	89	11	88	12	91	9	86	14	95	5
48 h	94	6	74	26	86	14	87	13	69	22	91	9
72 h	92	8	72	28	86	14	85	15	50	50	92	8

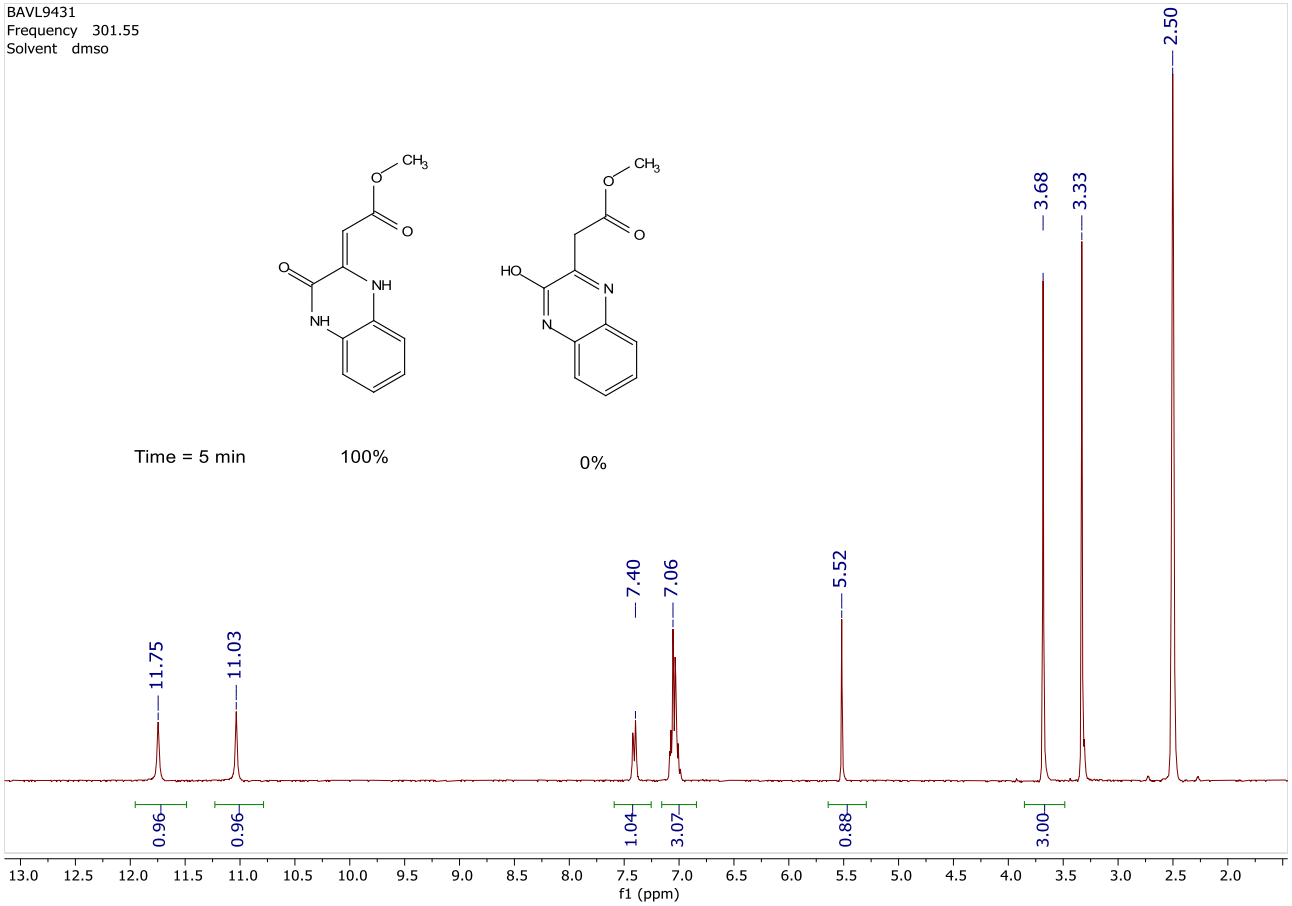


Figure S15. [1]H NMR spectrum of **1a** in DMSO-d_6 5 min after dissolution

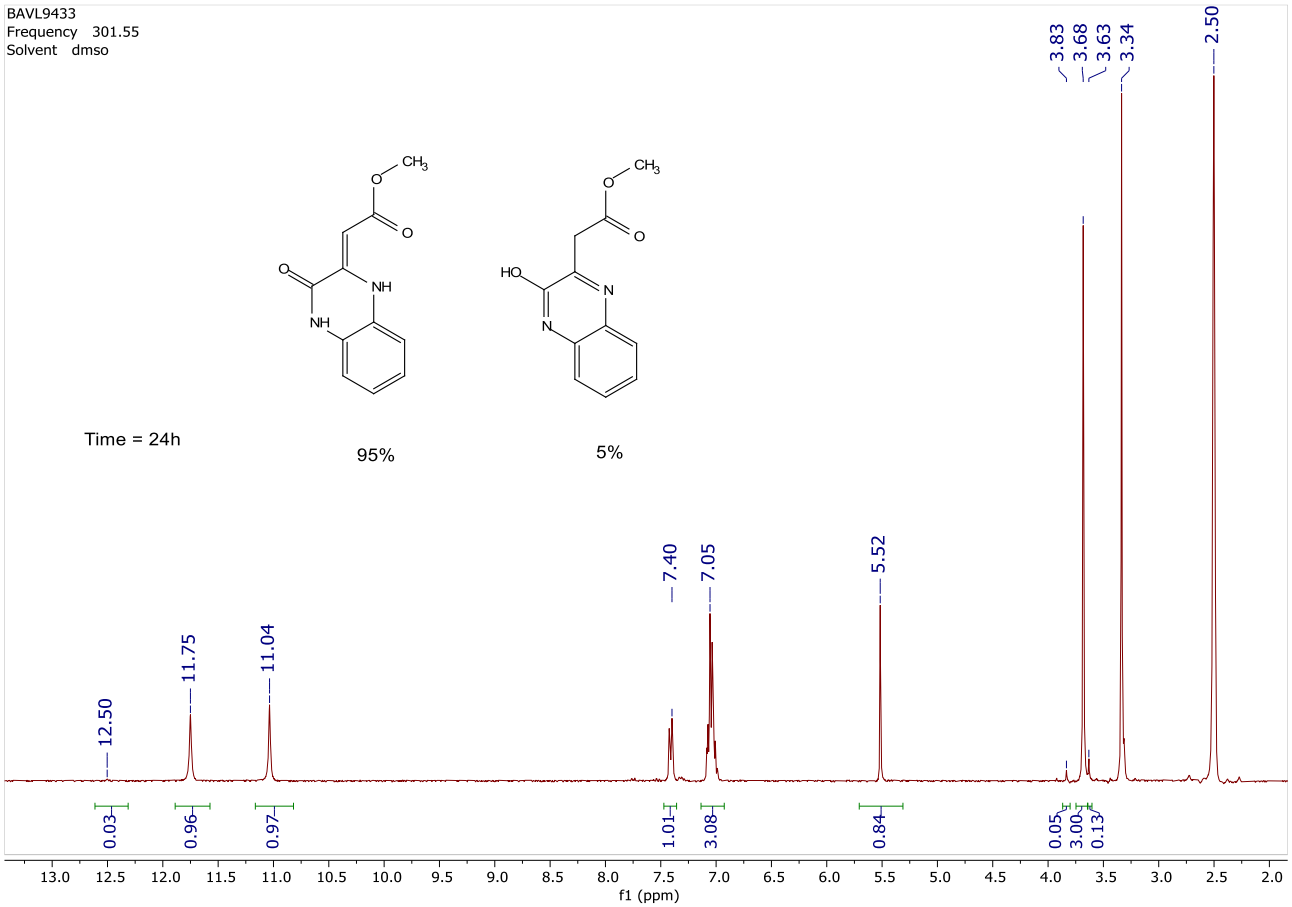


Figure S16. [1]H NMR spectrum of **1a** in DMSO-d_6 24h after dissolution

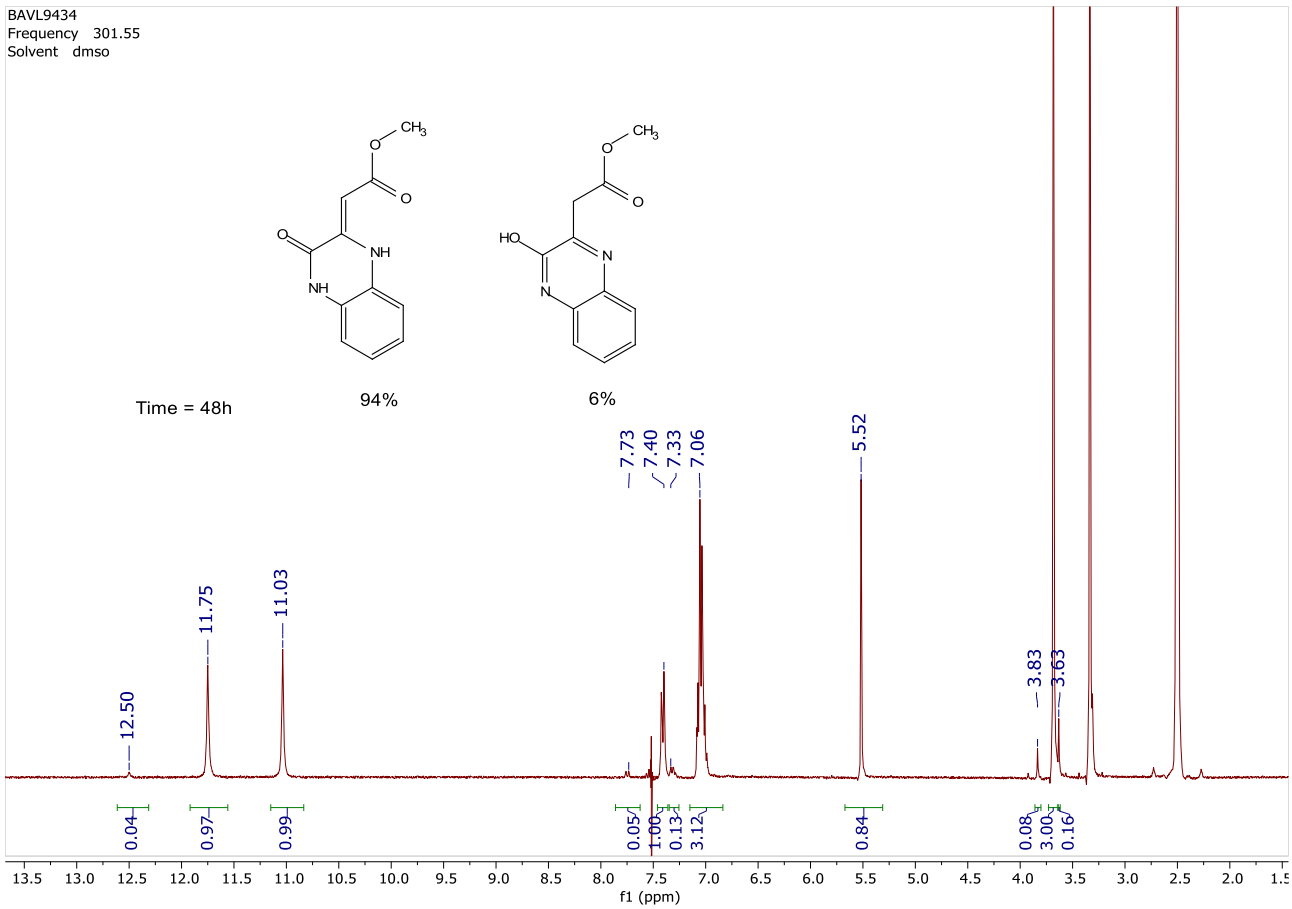


Figure S17. ^{1}H NMR spectrum of **1a** in DMSO-d_6 48h after dissolution

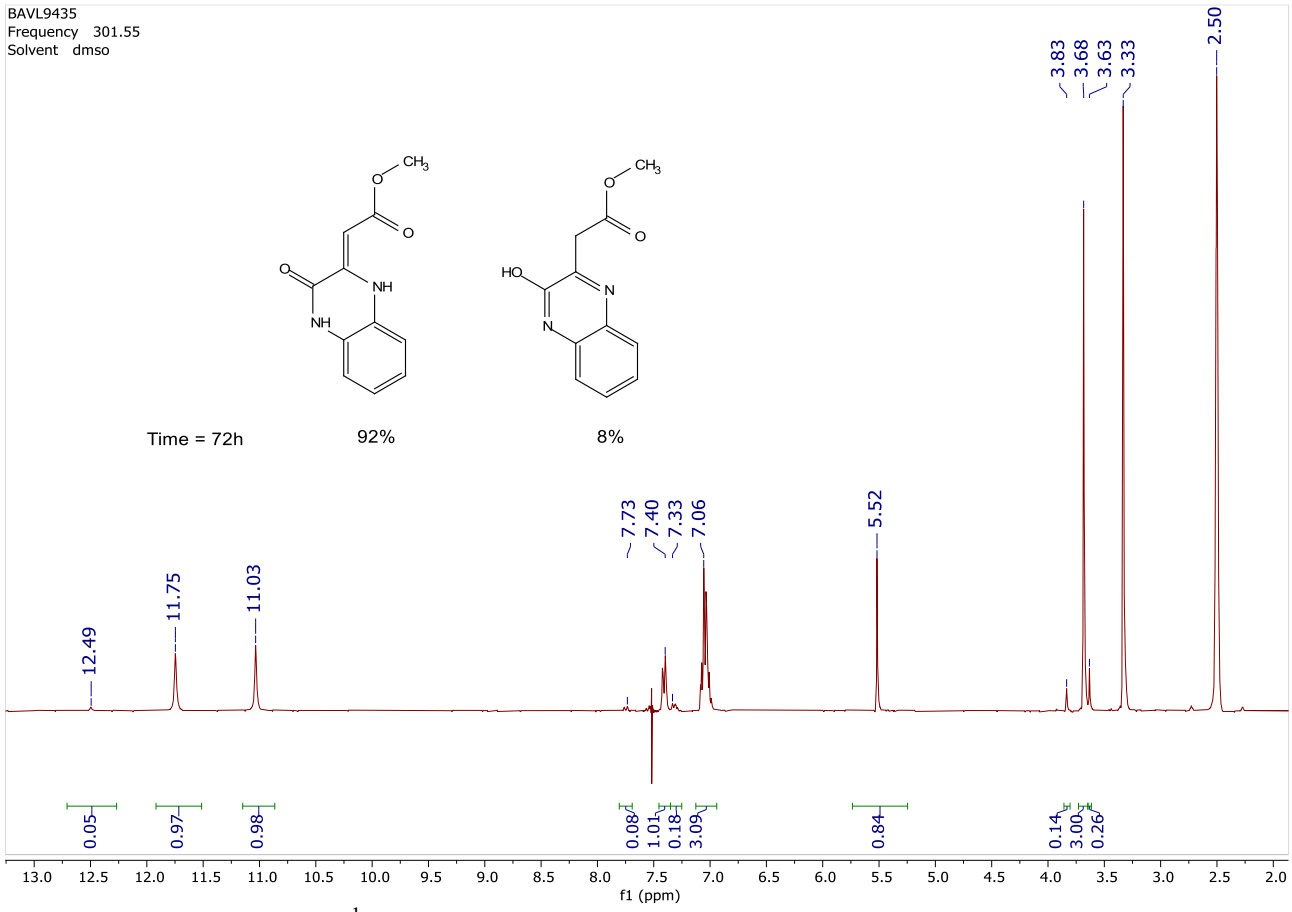


Figure S18. ^{1}H NMR spectrum of **1a** in DMSO-d_6 72h after dissolution

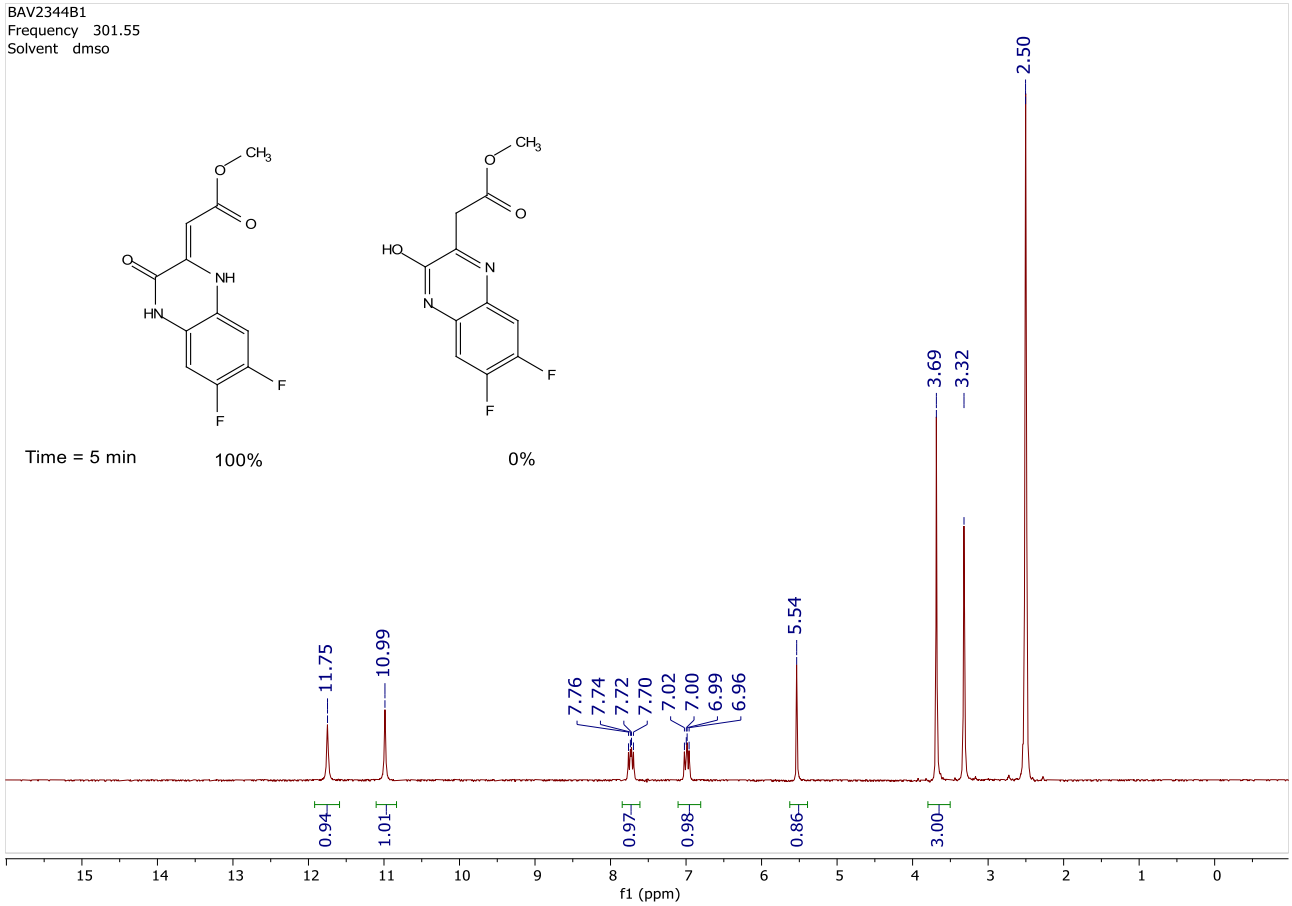


Figure S19. ^{1}H NMR spectrum of **1b** in DMSO-d_6 5min after dissolution

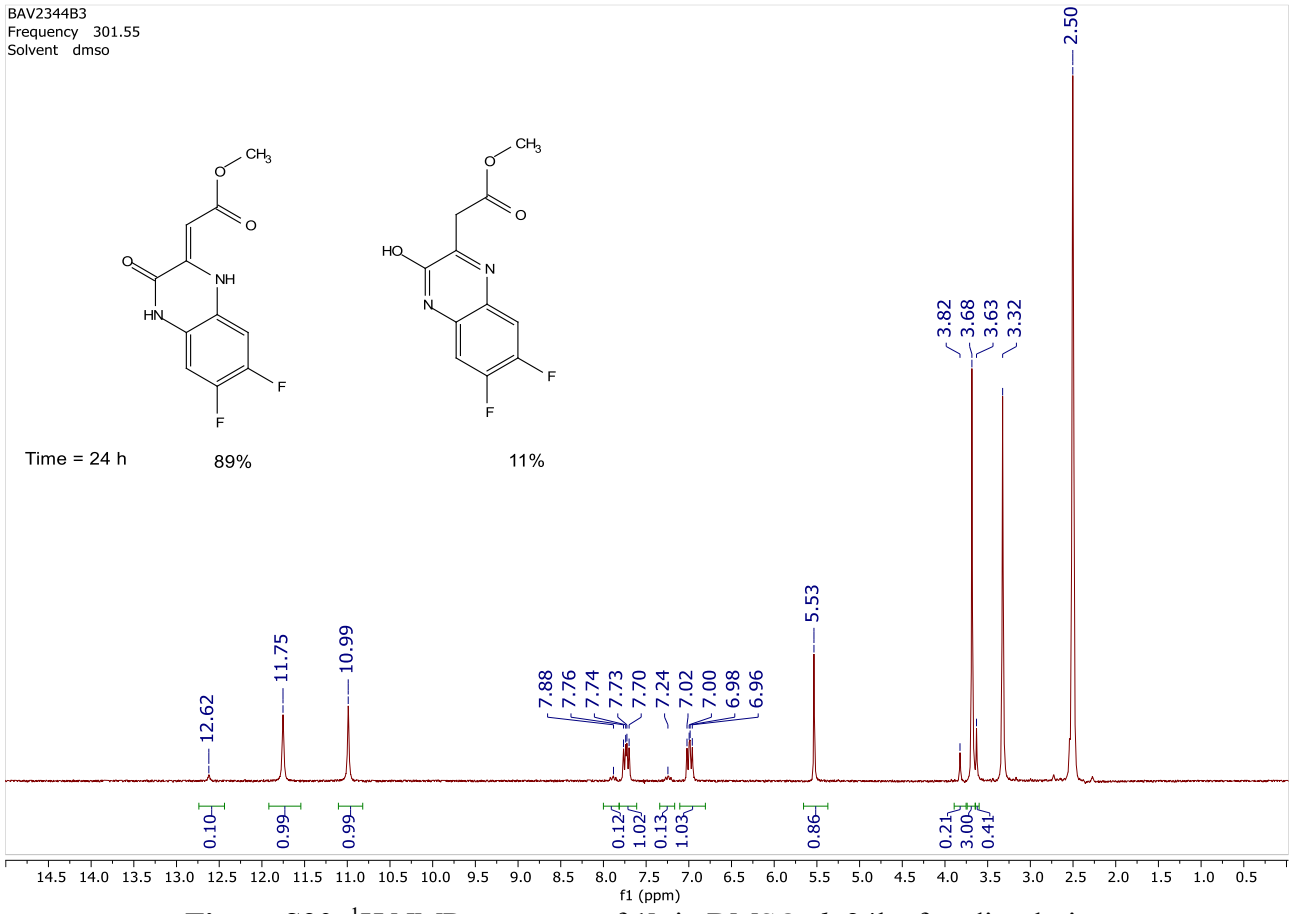


Figure S20. ^{1}H NMR spectrum of **1b** in DMSO-d_6 24h after dissolution

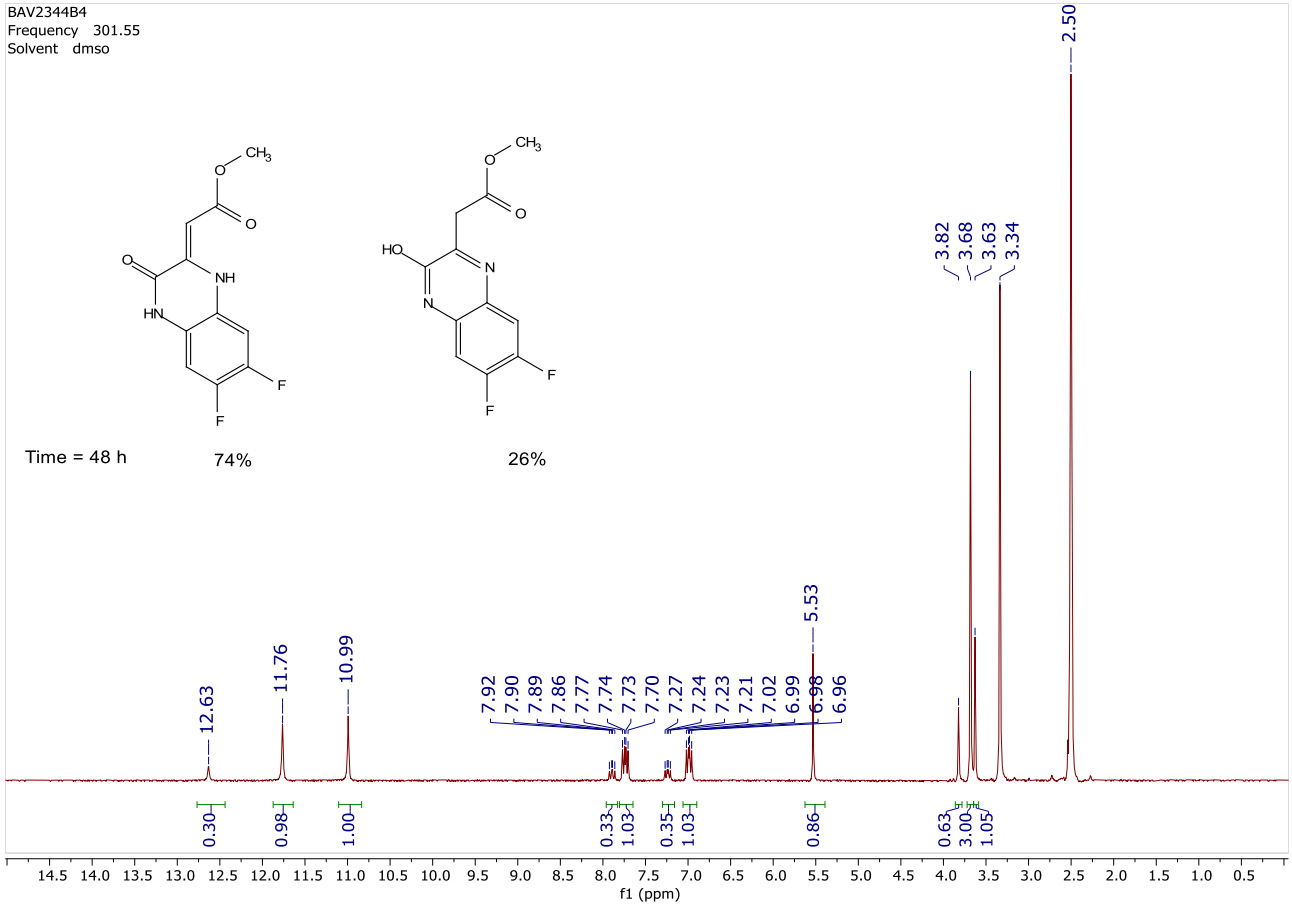


Figure S21. ^{1}H NMR spectrum of **1b** in DMSO-d_6 48h after dissolution

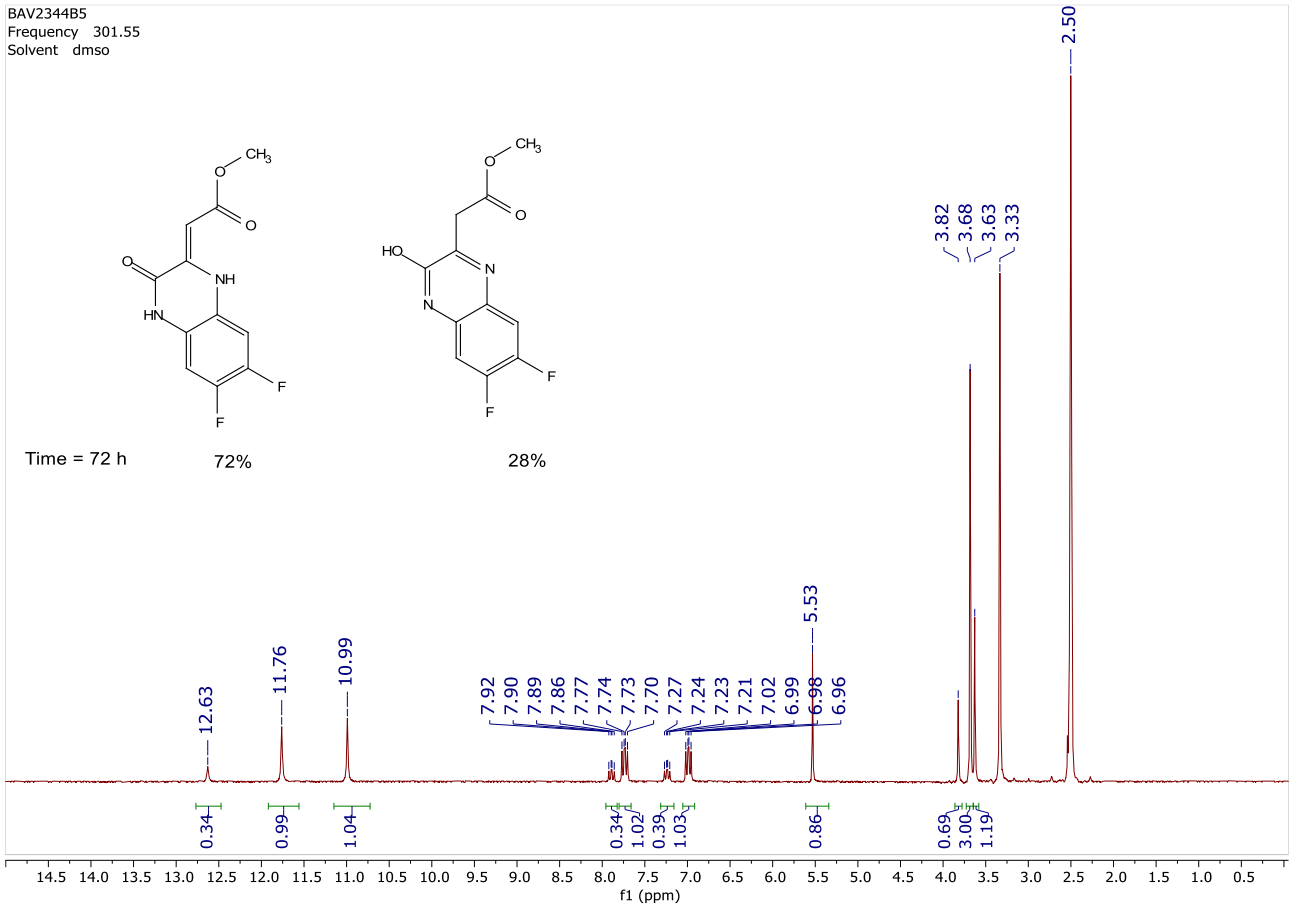


Figure S22. ^{1}H NMR spectrum of **1b** in DMSO-d_6 72h after dissolution

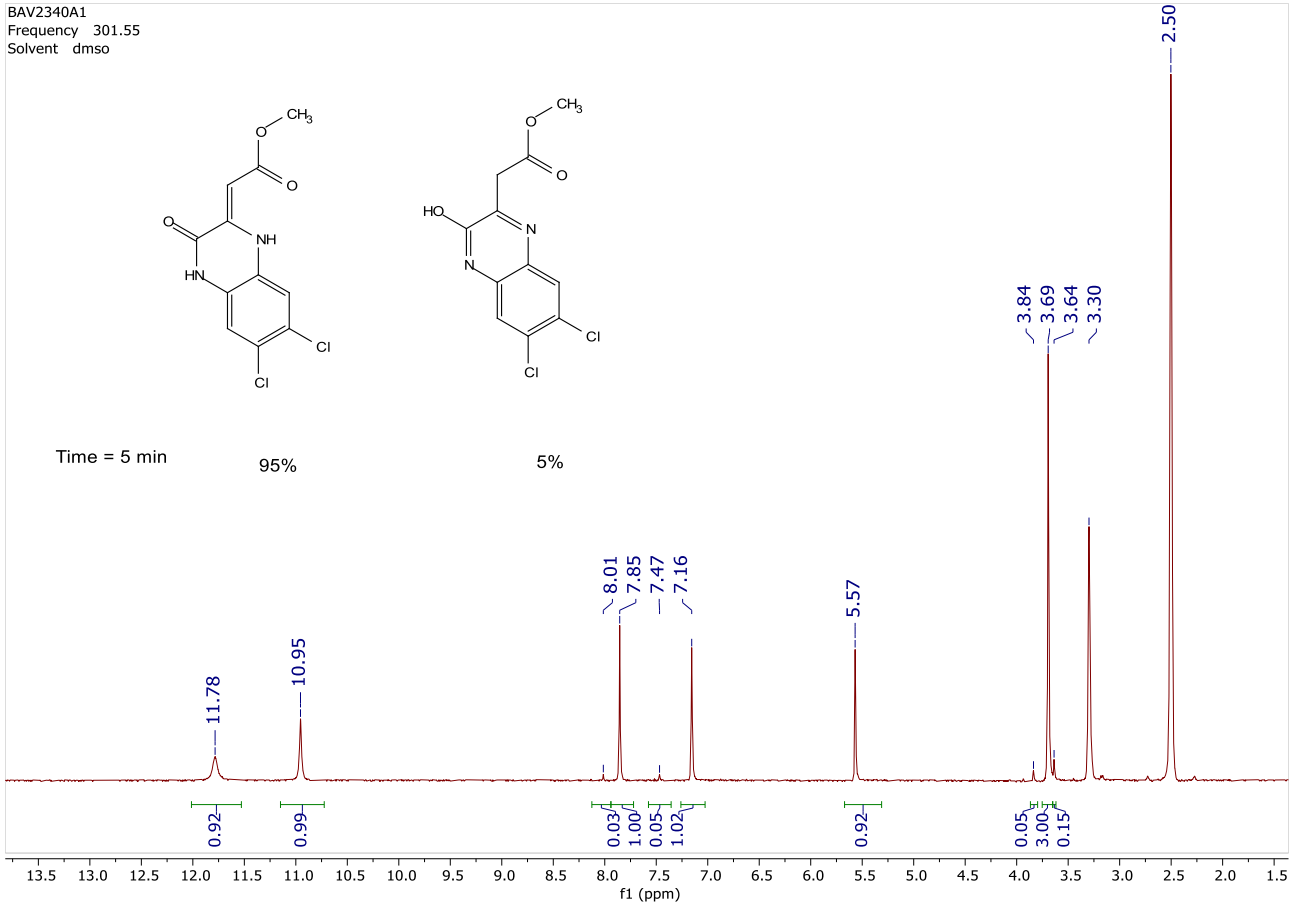


Figure S23. ^{1}H NMR spectrum of **1c** in DMSO-d_6 5min after dissolution

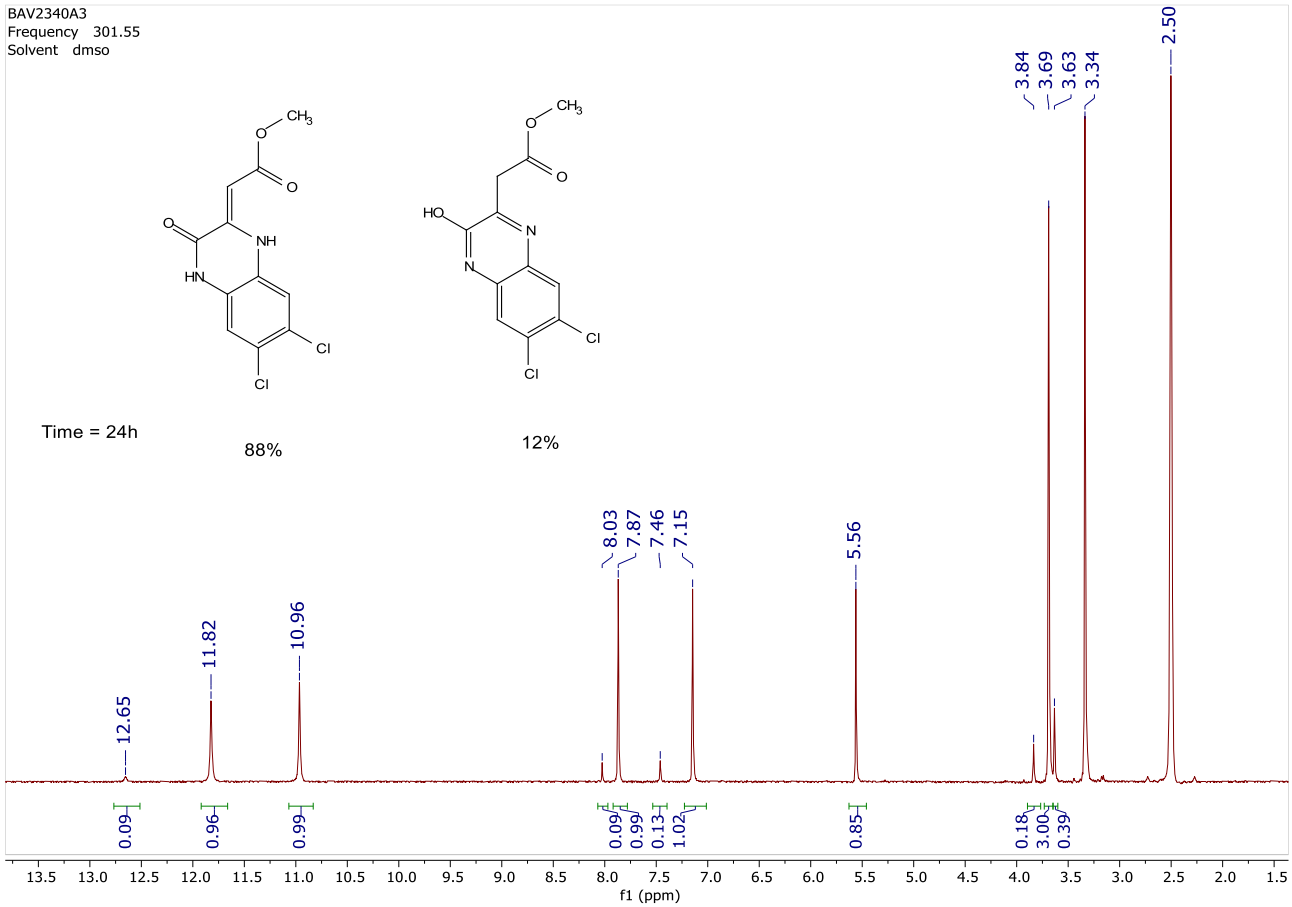


Figure S24. ^{1}H NMR spectrum of **1c** in DMSO-d_6 24h after dissolution

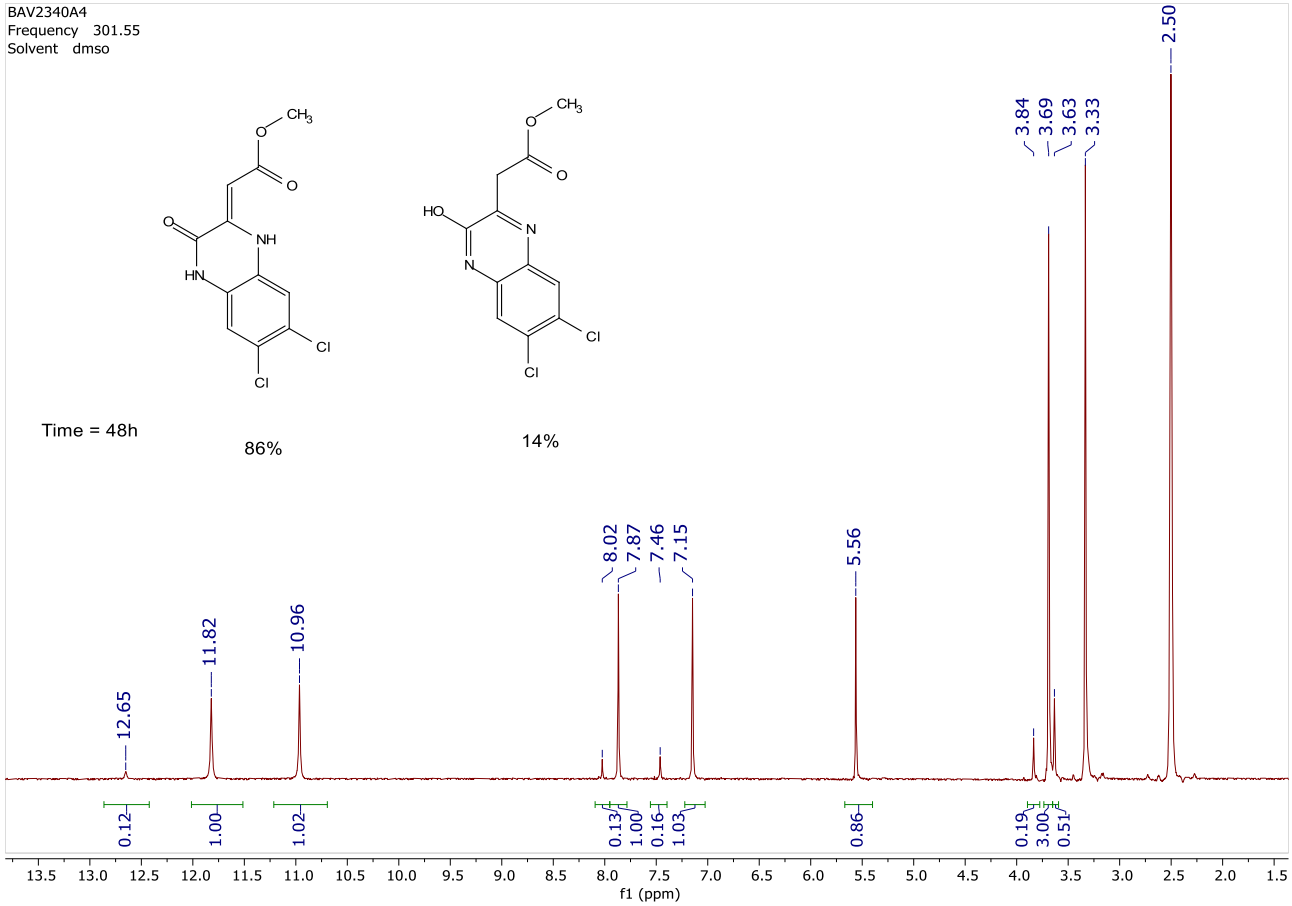


Figure S25. ^{1}H NMR spectrum of **1c** in DMSO-d_6 48h after dissolution

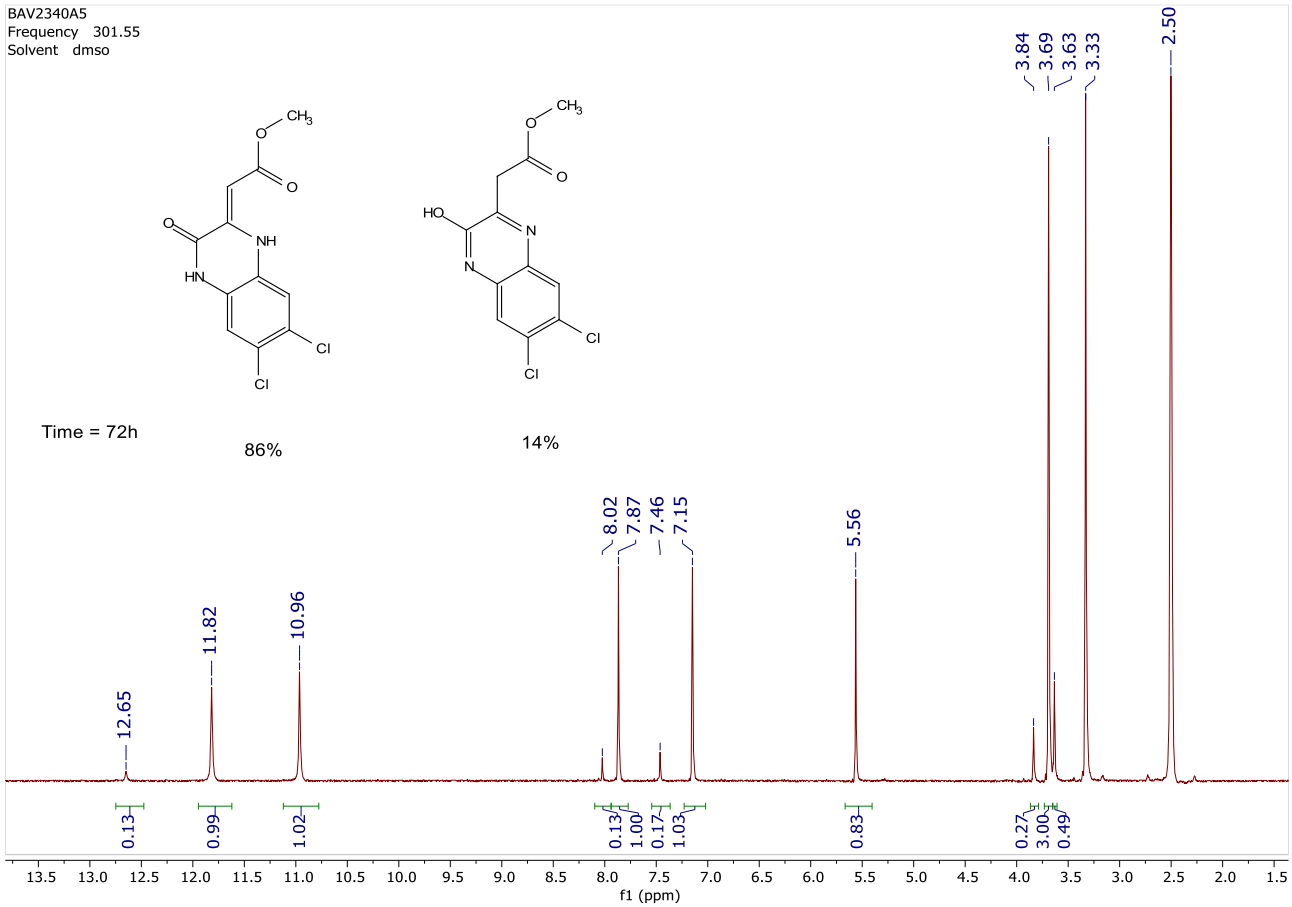


Figure S26. ^{1}H NMR spectrum of **1c** in DMSO-d_6 72h after dissolution

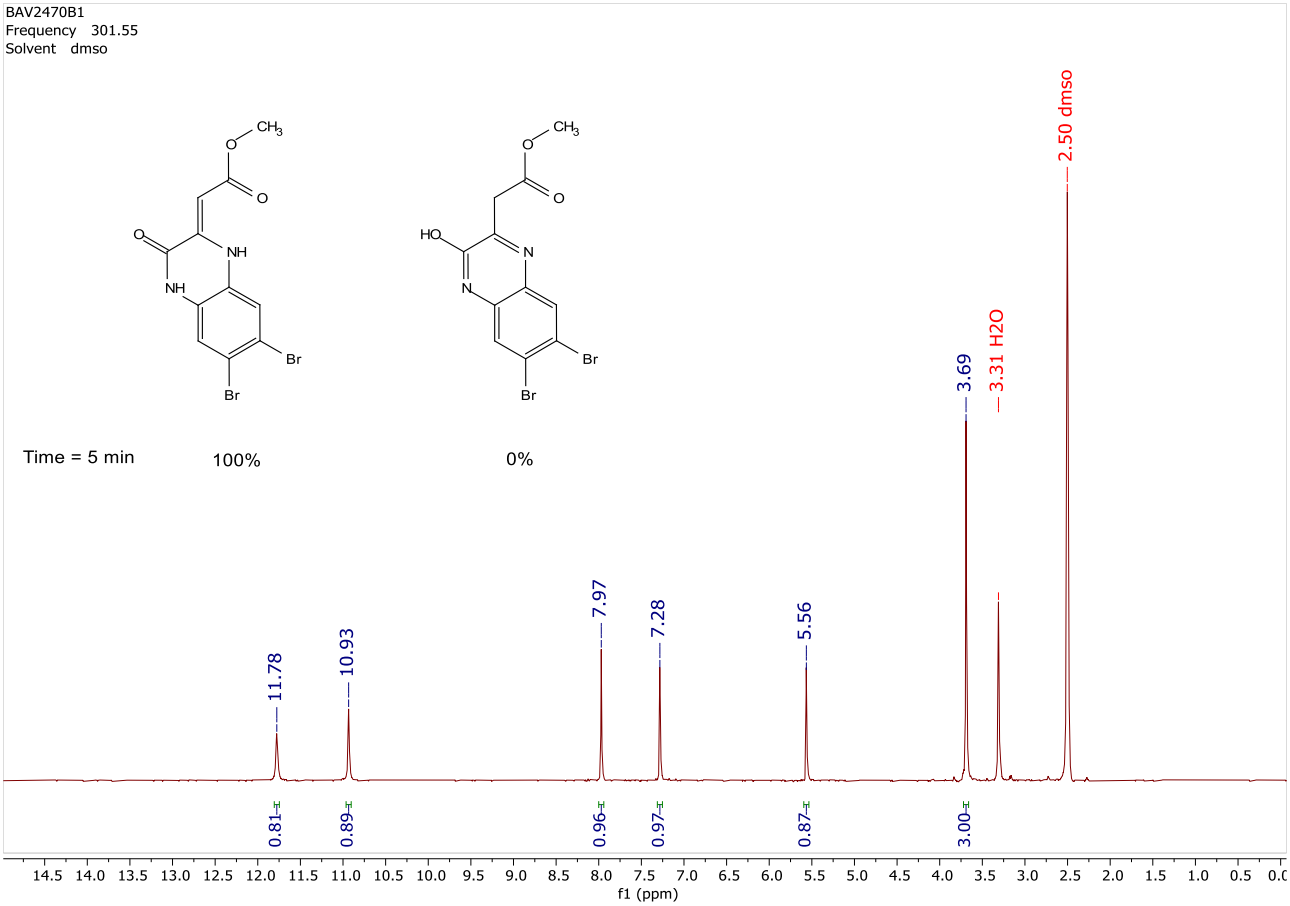


Figure S27. ^{1}H NMR spectrum of **1d** in DMSO-d_6 5min after dissolution

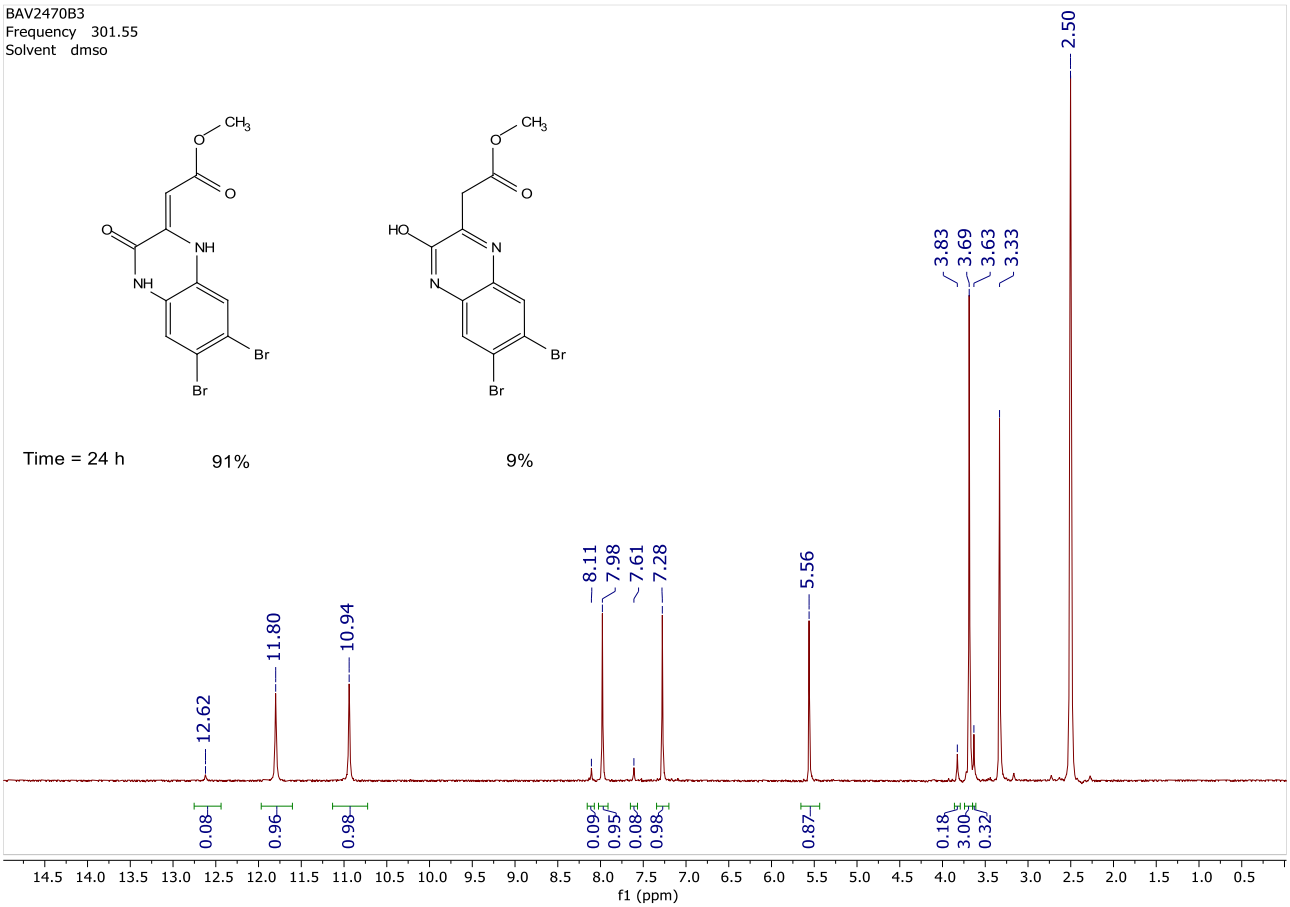


Figure S28. ^{1}H NMR spectrum of **1d** in DMSO-d_6 24h after dissolution

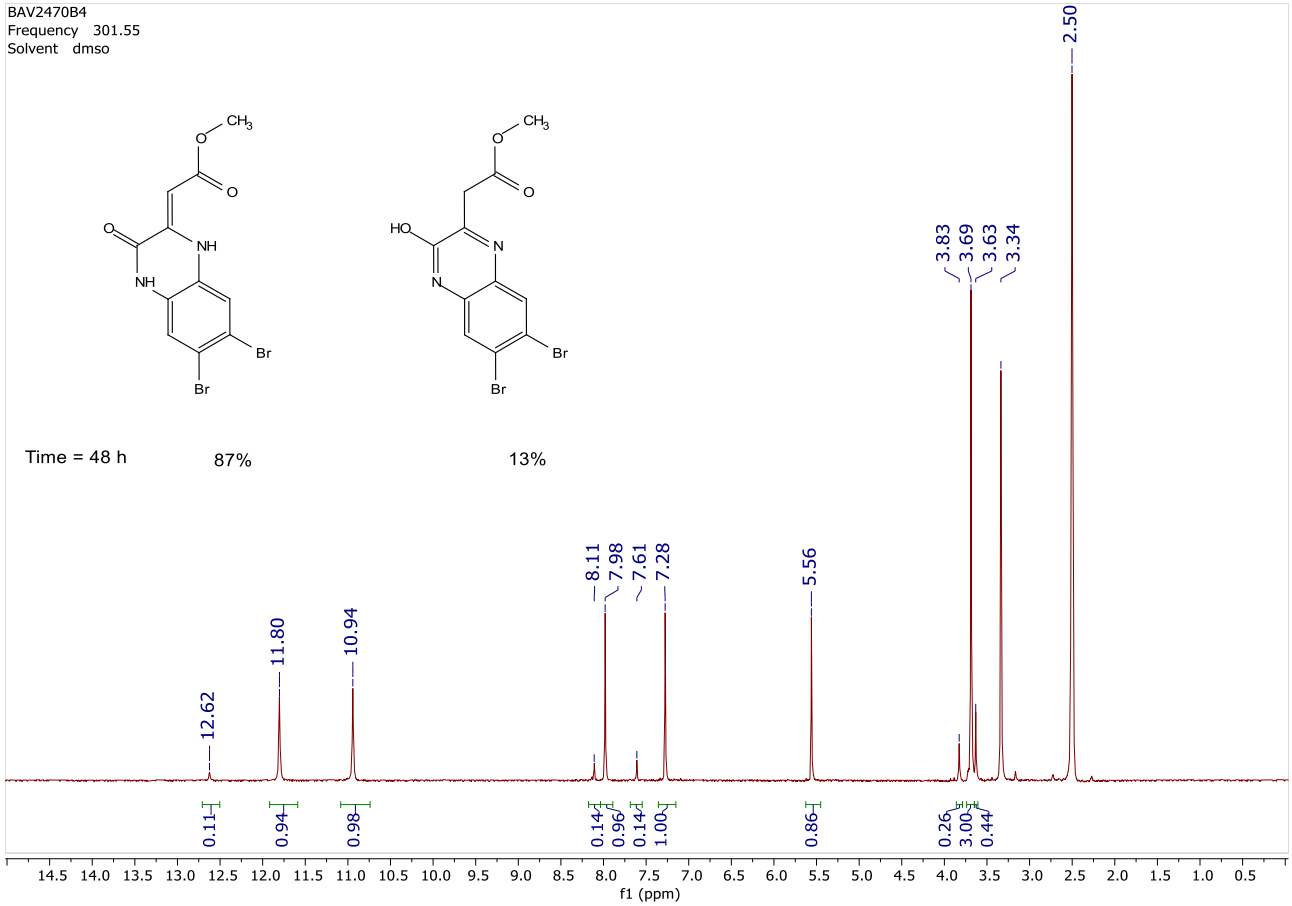


Figure S29. ^{1}H NMR spectrum of **1d** in DMSO-d_6 48h after dissolution

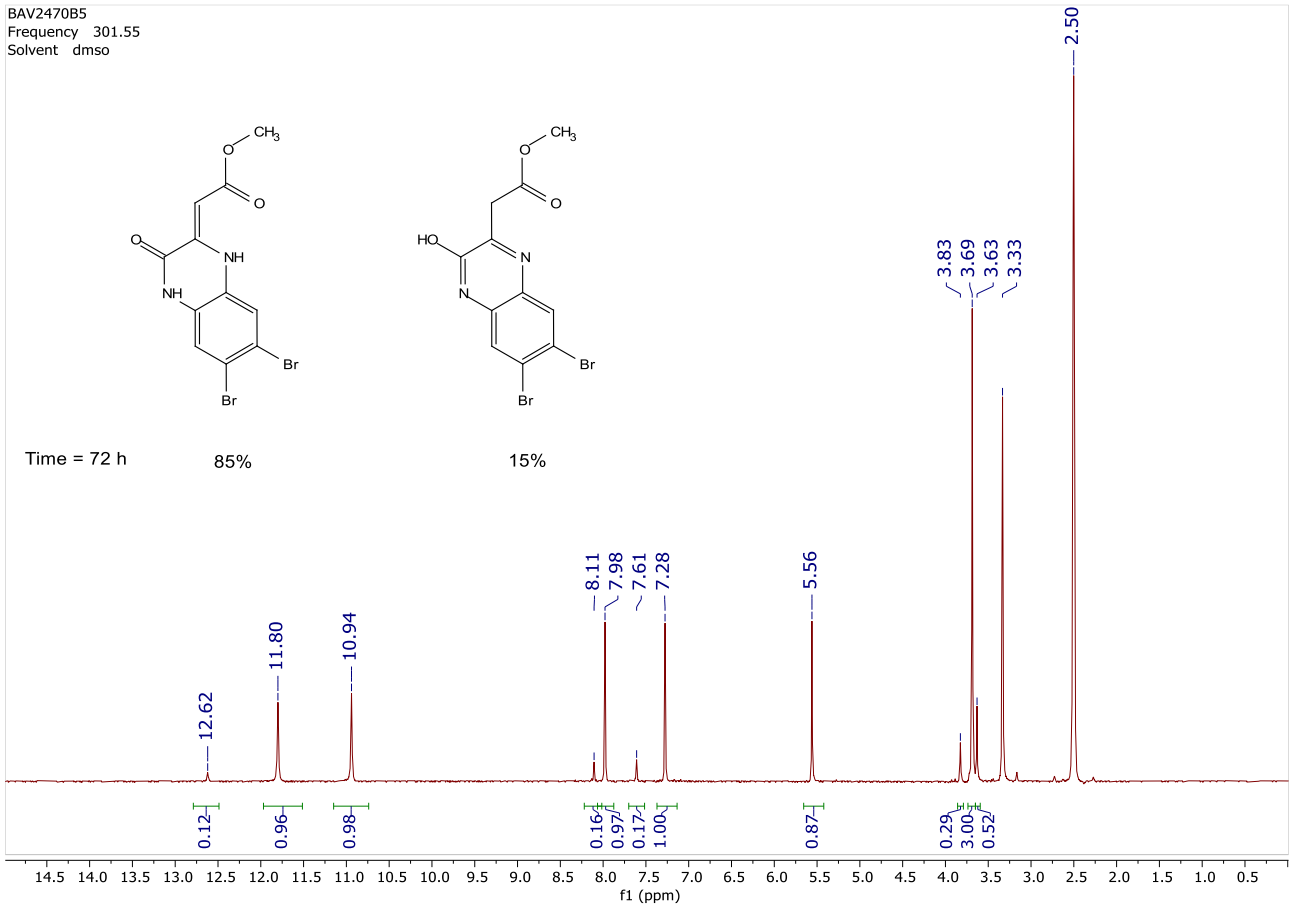


Figure S30. ^{1}H NMR spectrum of **1d** in DMSO-d_6 72h after dissolution

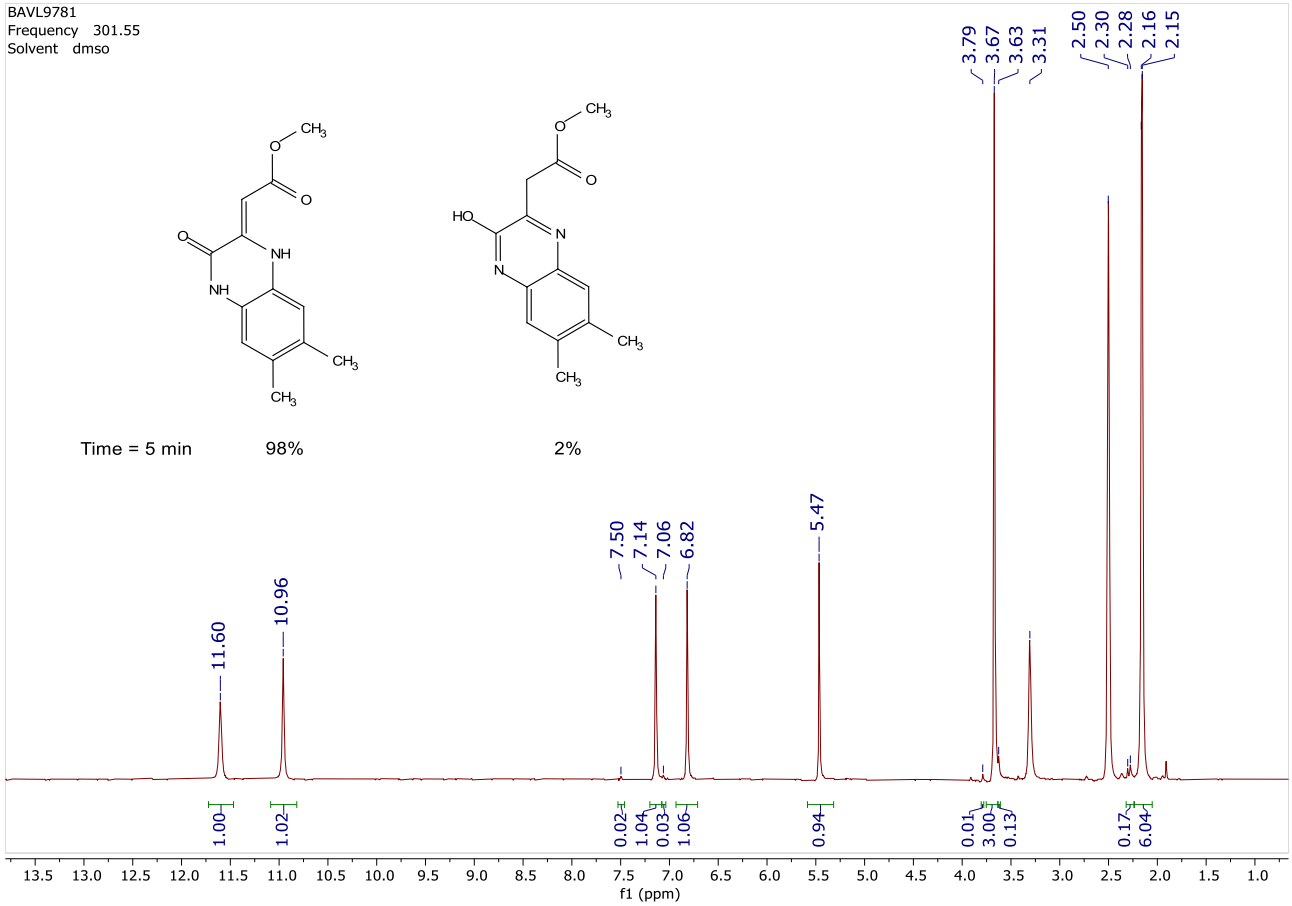


Figure S31. ^{1}H NMR spectrum of **1e** in DMSO-d_6 5min after dissolution

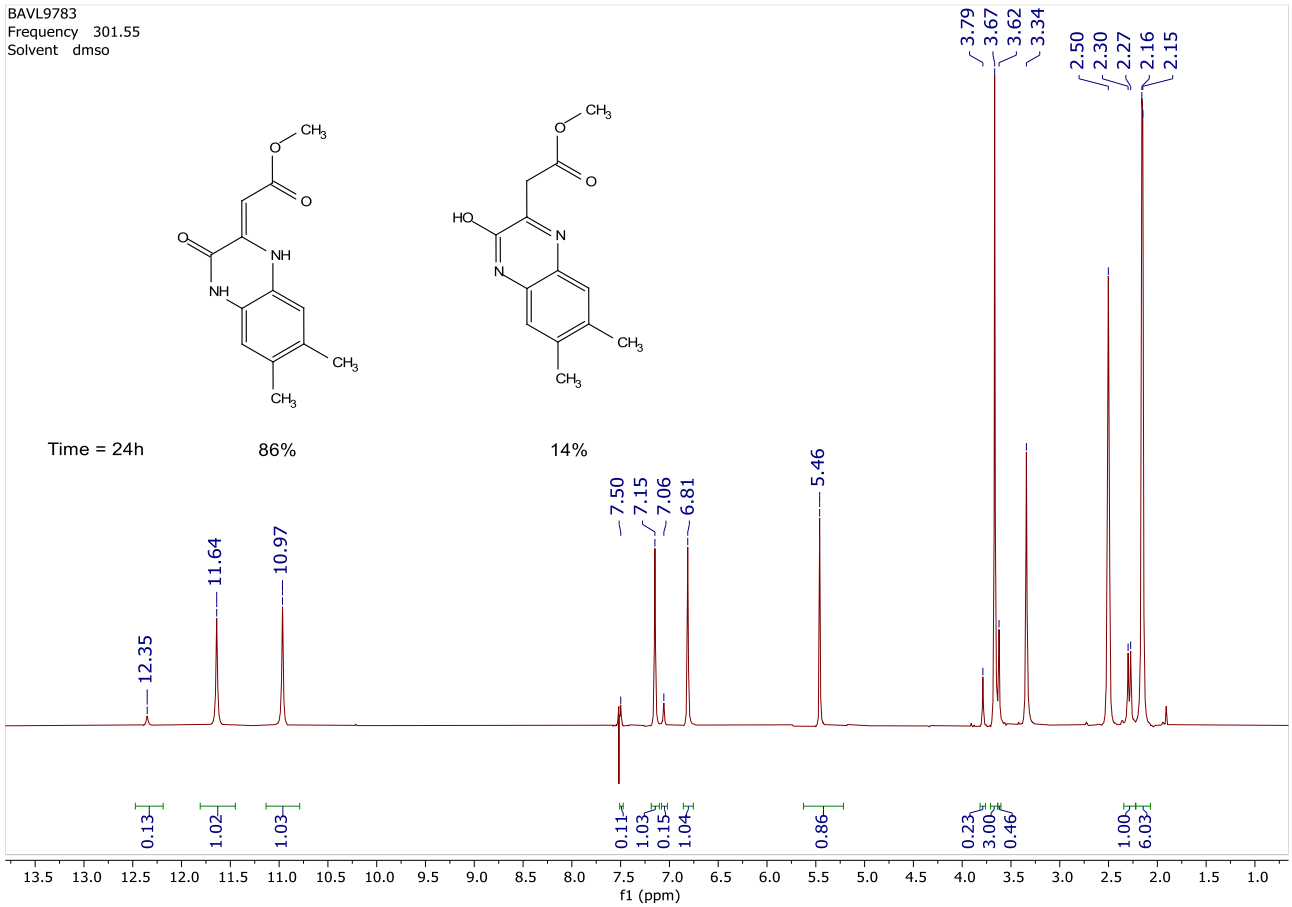


Figure S32. ^{1}H NMR spectrum of **1e** in DMSO-d_6 24h after dissolution

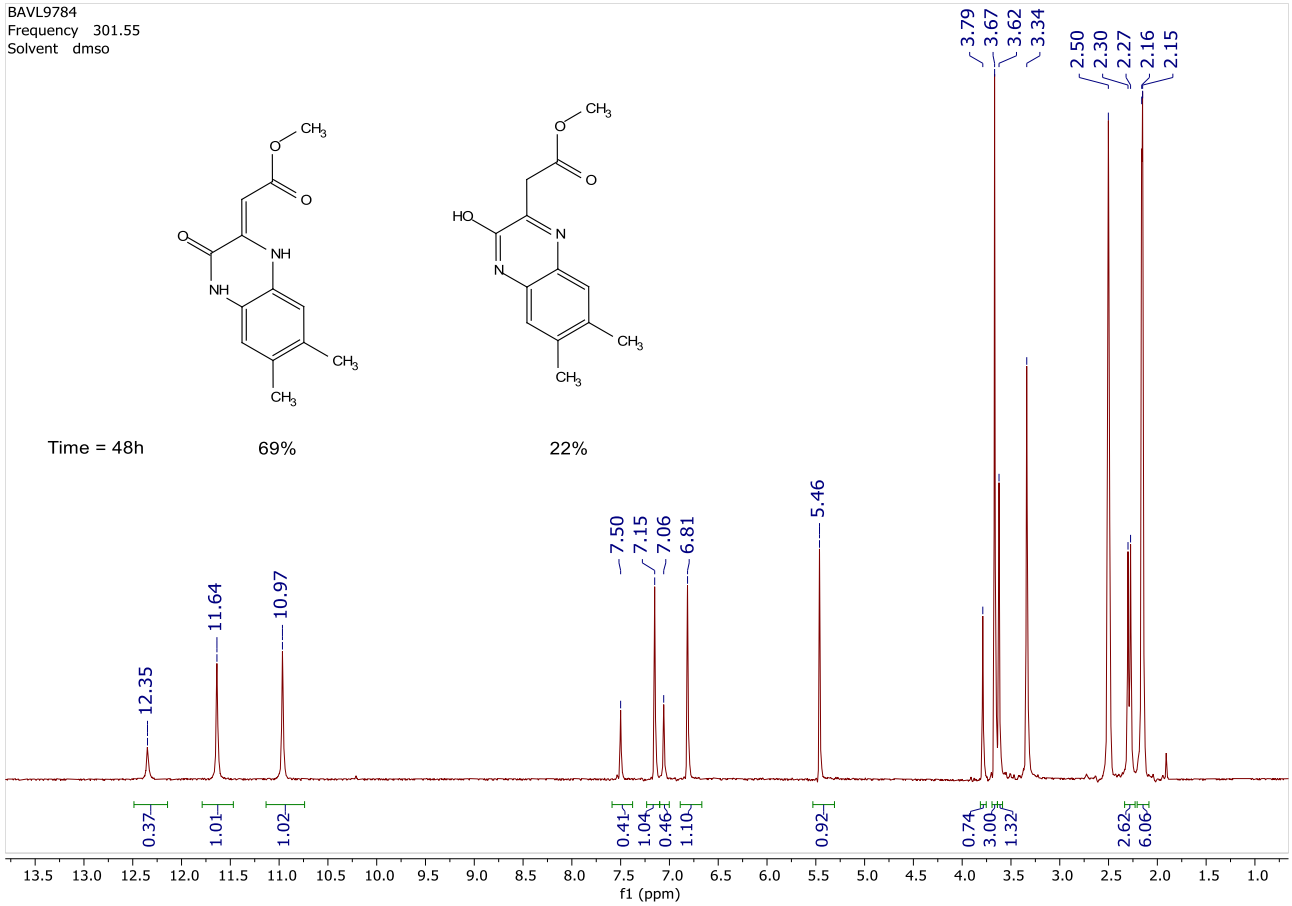


Figure S33. ^{1}H NMR spectrum of **1e** in DMSO-d_6 48h after dissolution

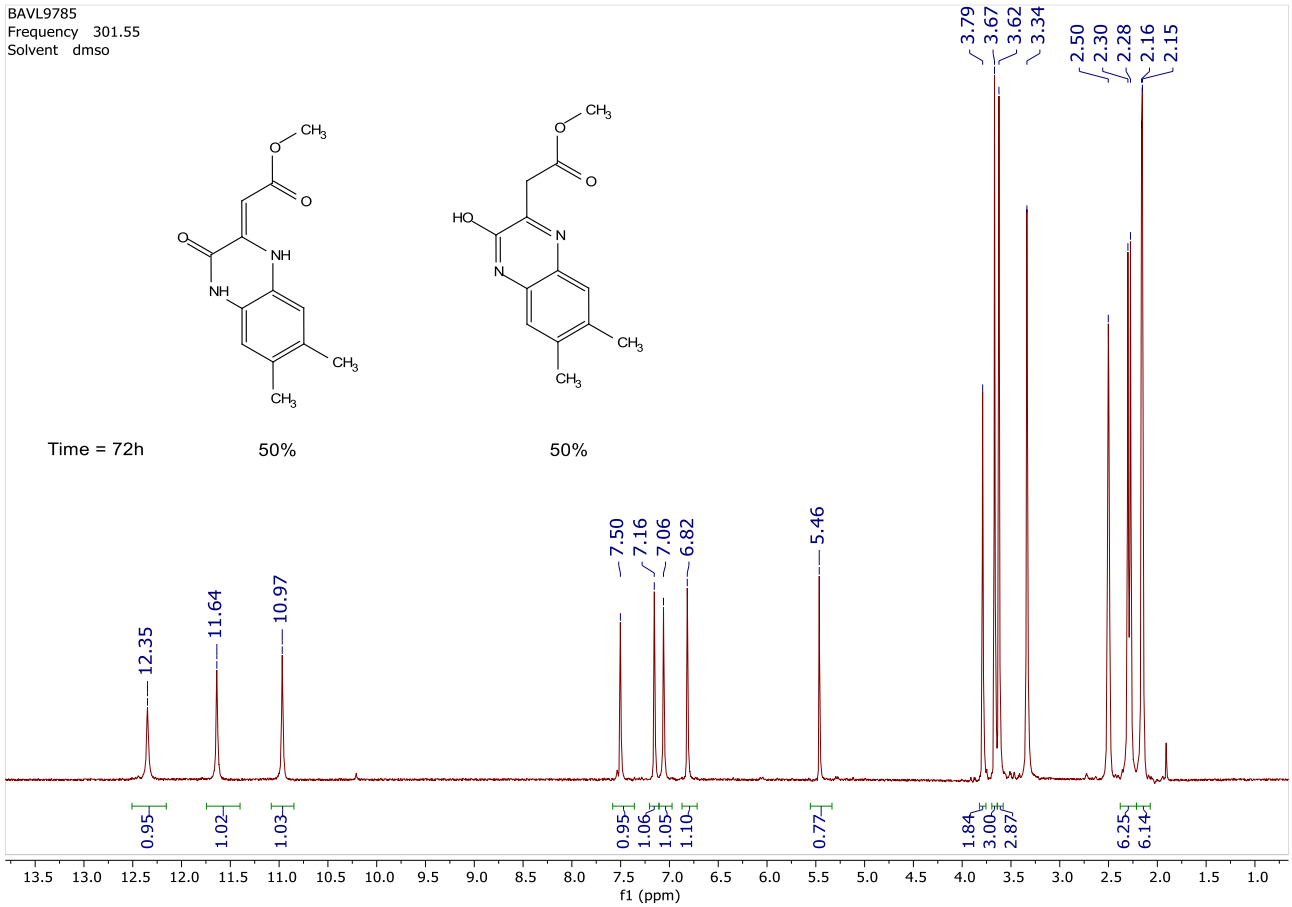


Figure S34. ^{1}H NMR spectrum of **1e** in DMSO-d_6 72h after dissolution

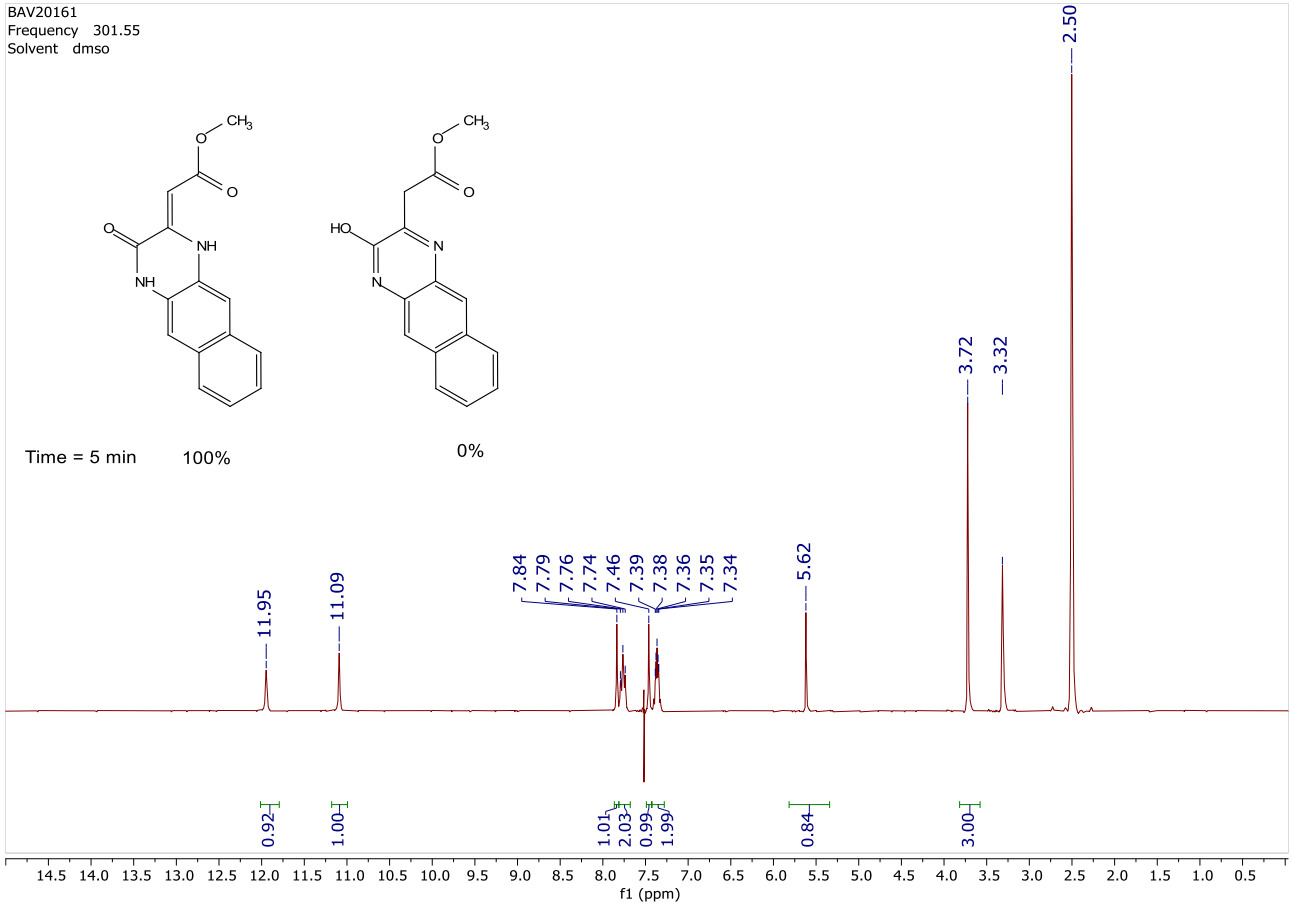


Figure S35. ^{1}H NMR spectrum of **1f** in DMSO-d_6 5min after dissolution

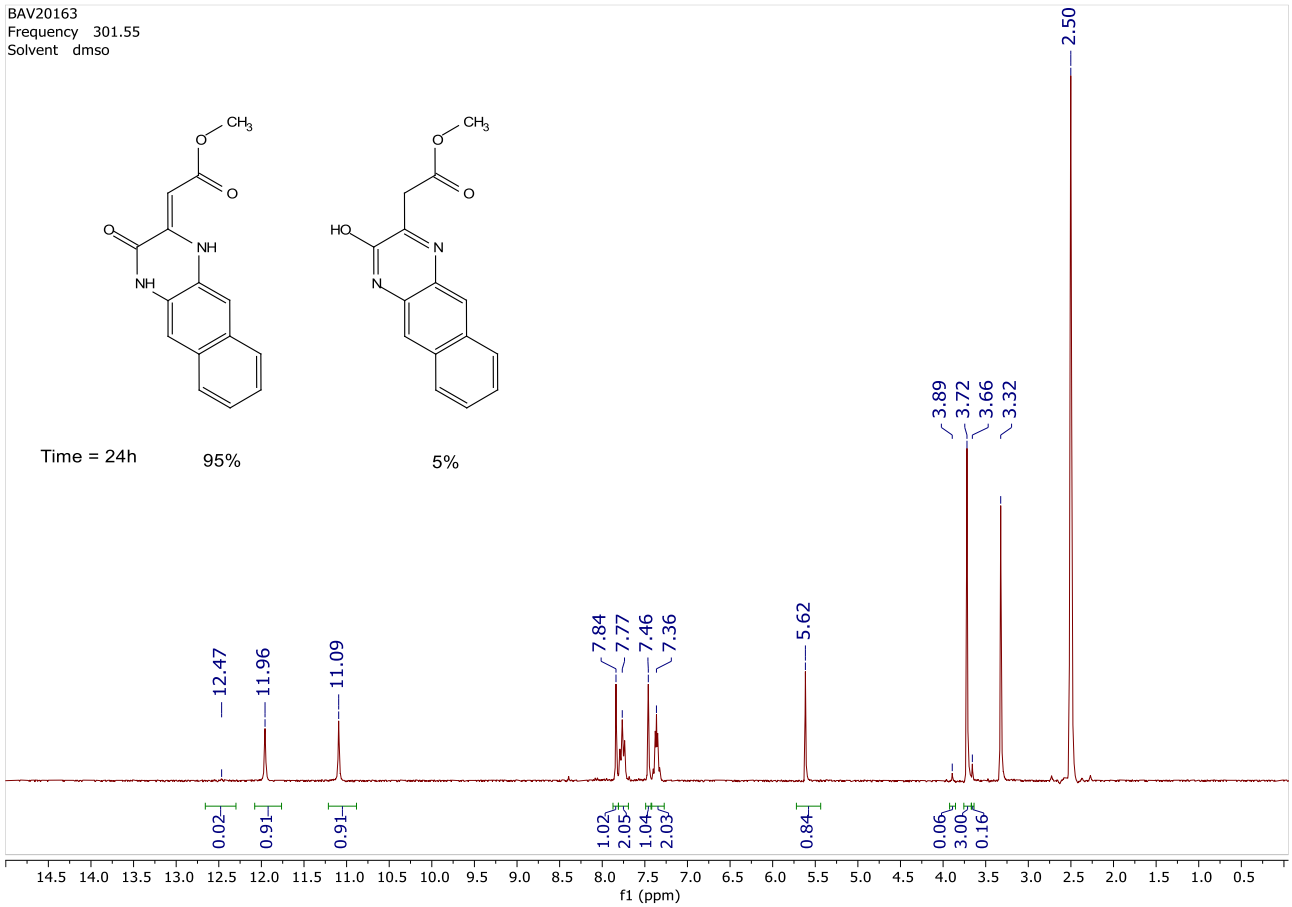


Figure S36. ^{1}H NMR spectrum of **1f** in DMSO-d_6 24h after dissolution

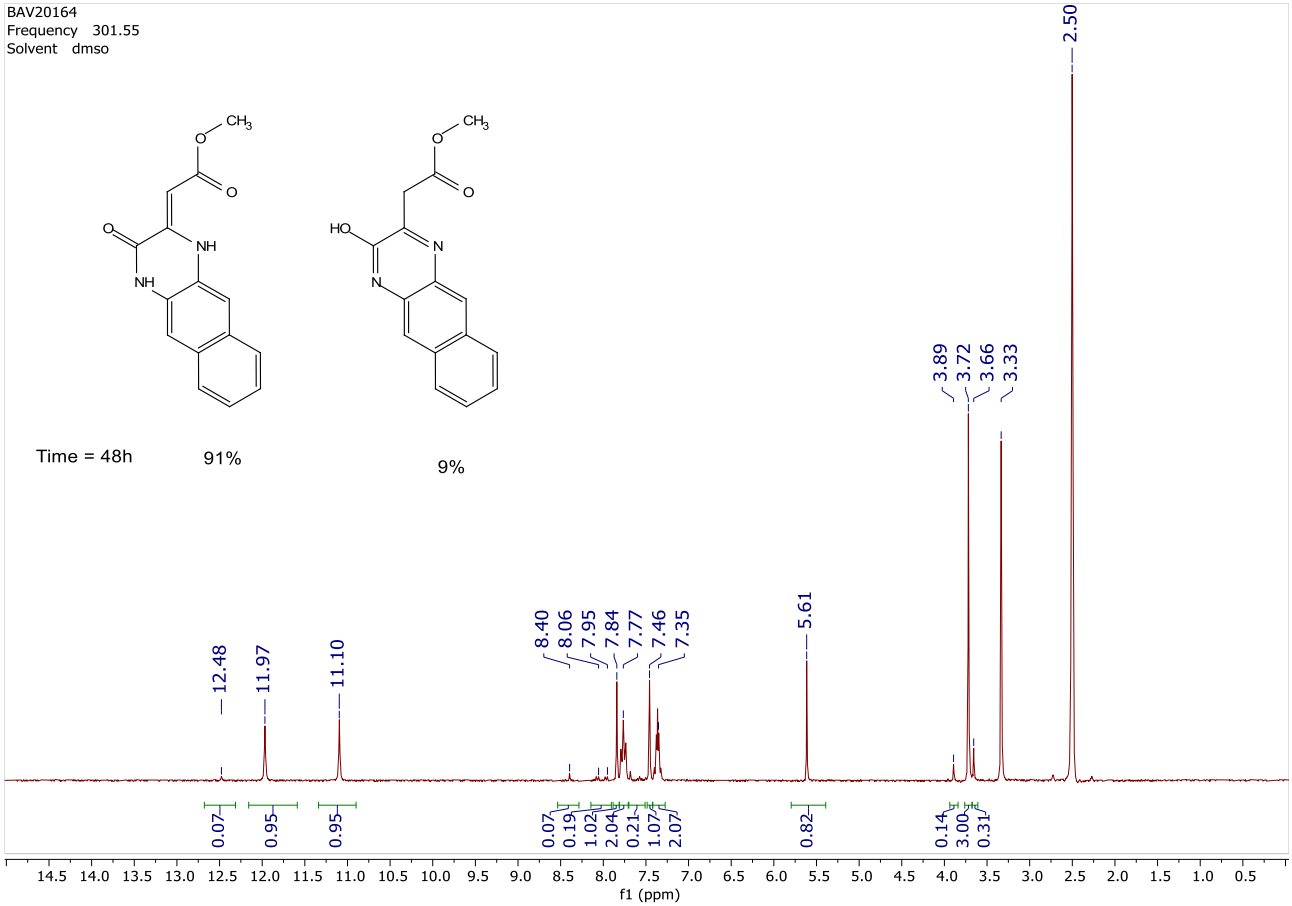


Figure S37. ^{1}H NMR spectrum of **1f** in DMSO-d_6 48h after dissolution

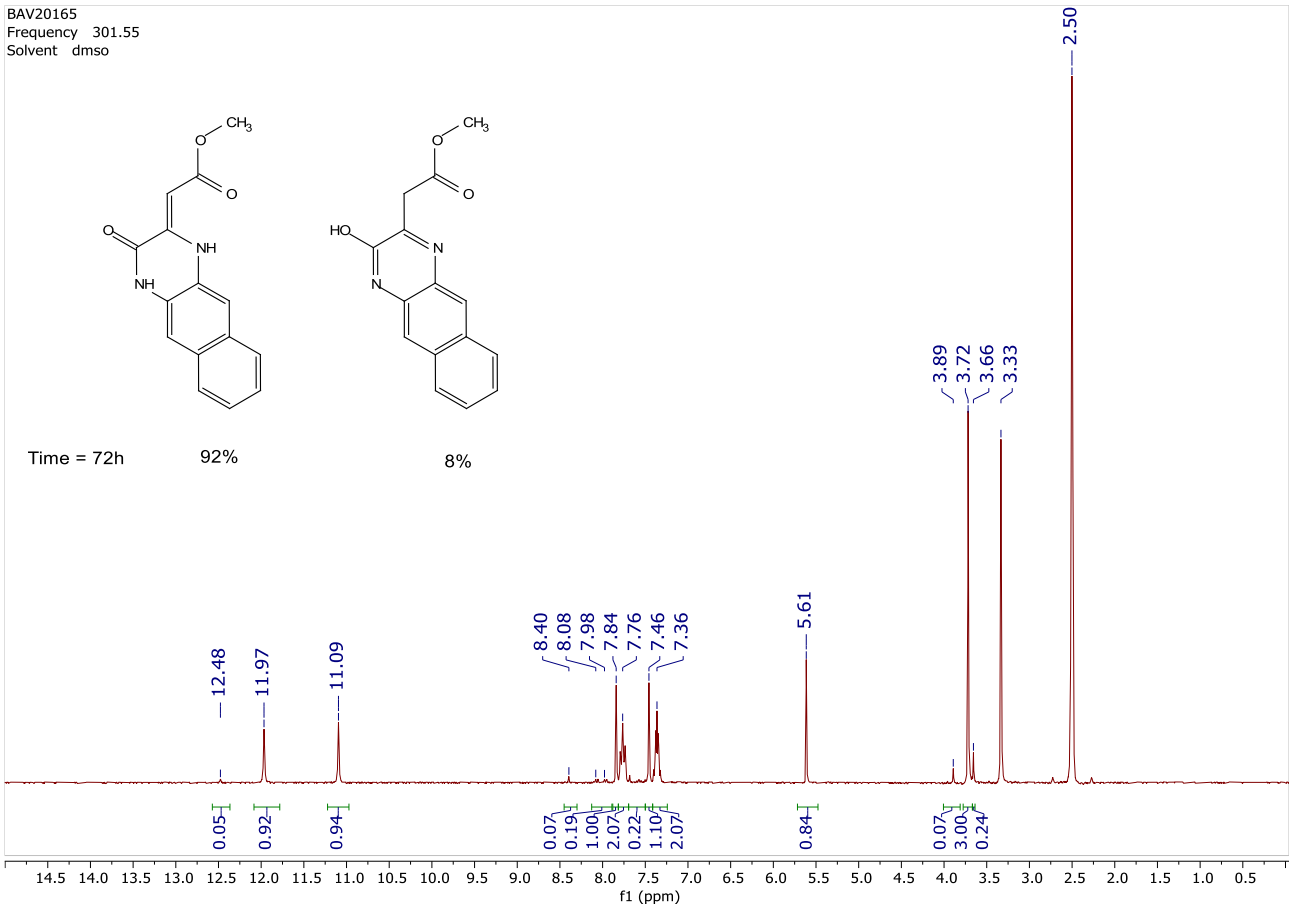
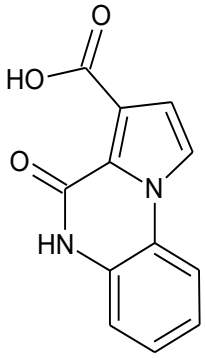


Figure S38. ^{1}H NMR spectrum of **1f** in DMSO-d_6 72h after dissolution

Chemical characterization of 3a-f



Chemical characterization of 4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**3a**). Light yellow solid (3.252 g, 95%). mp >290 (decomp.) °C. IR (solid, KBr, νmax, cm^{-1}): 3143, 2999, 1703, 1619, 1508, 1384, 748, 539. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 7.22 (1H, d, $^{3}J_{HH}$ 2.8 Hz, CH pyrrole), 7.38 – 7.49 (3H, m, 3CH aromatic), 8.26 (1H, d, $^{3}J_{HH}$ 8.2 Hz, CH aromatic), 8.44 (1H, d, $^{3}J_{HH}$ 2.9 Hz, CH pyrrole), 12.64 (1H, s, NH), 15.42 (1H, s, OH). ^{13}C NMR (DMSO-*d*$_6$, 126 MHz): δ_C 115.76, 116.94, 117.43, 118.89, 119.99, 120.19, 122.44, 124.45, 126.99, 127.23, 157.37 (CO-NH), 162.24 (COOH). ESI-MS: m/z 228.9 $[M+H]^+$. Anal. calcd for $C_{12}H_8N_2O_3$ (228.20): C, 63.16; H, 3.53; N, 12.28. Found: C, 62.94; H, 3.56; N, 12.40.

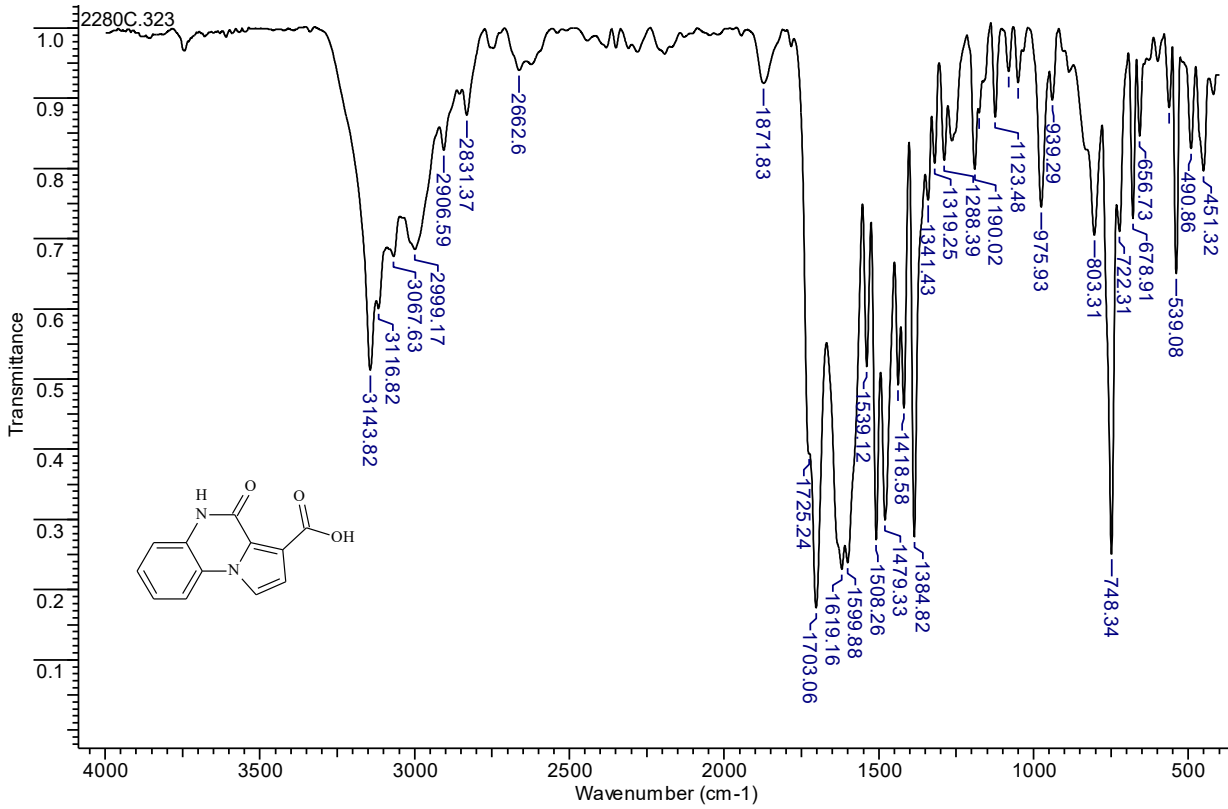


Figure S39. IR spectrum of 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3a**) in KBr pellet

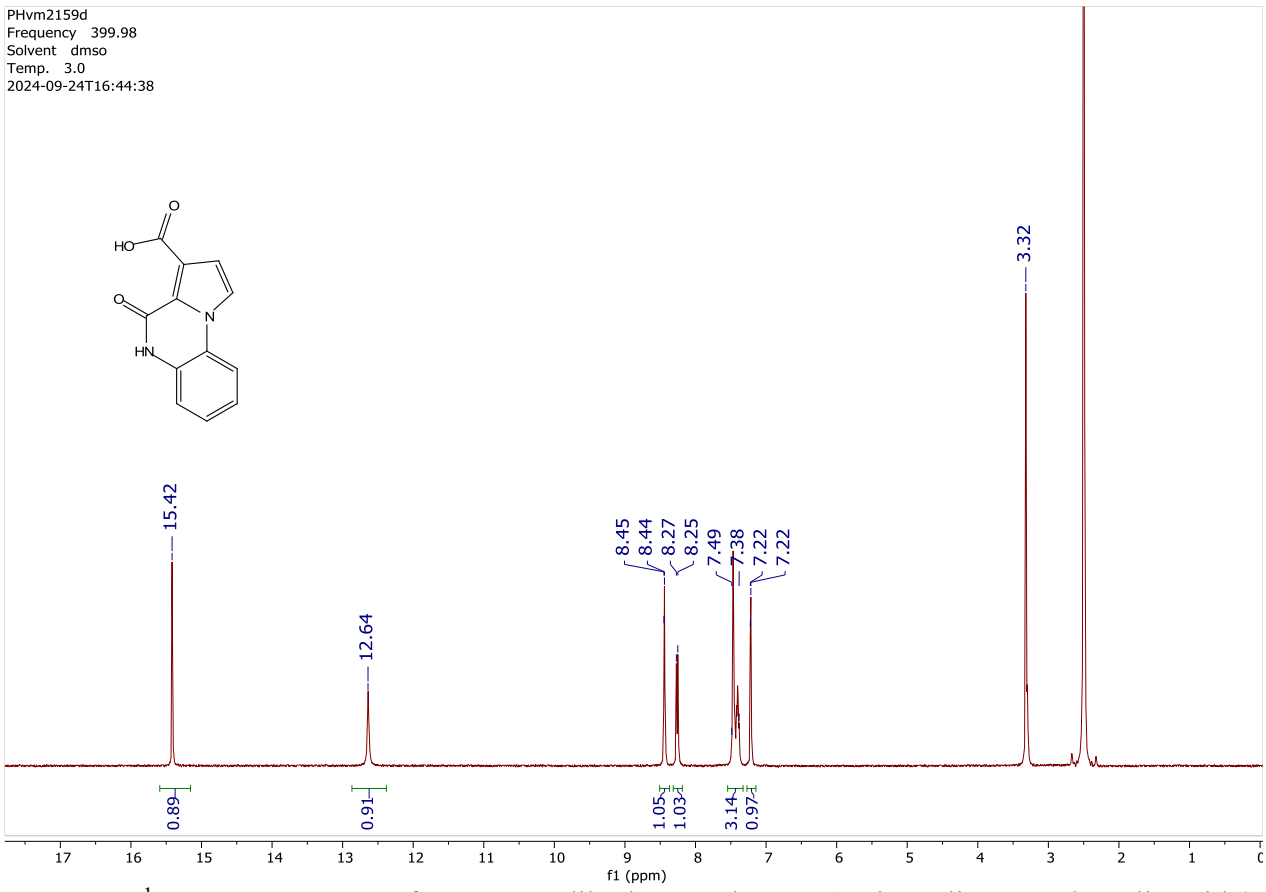


Figure S40. ^{1}H NMR spectrum of 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3a**) in DMSO-d_6

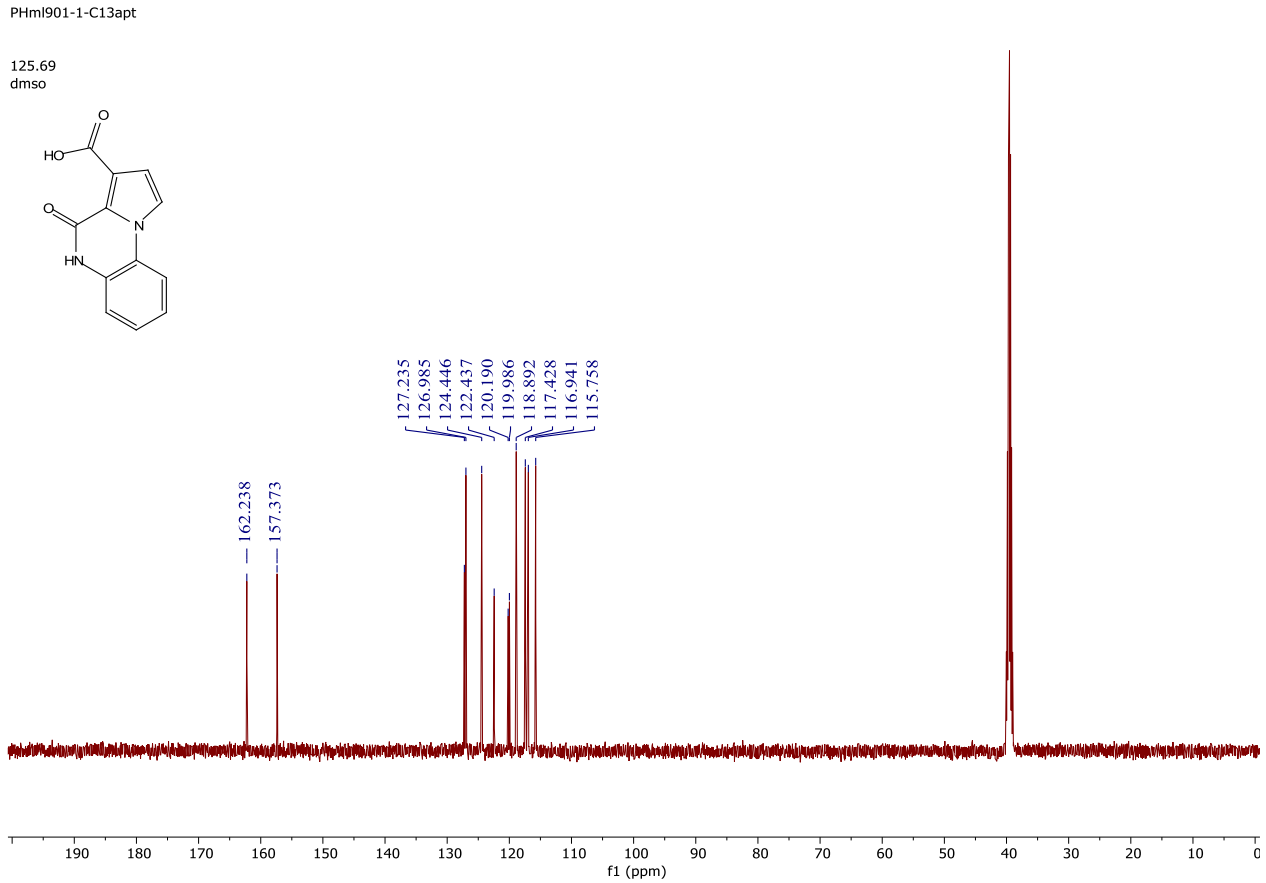
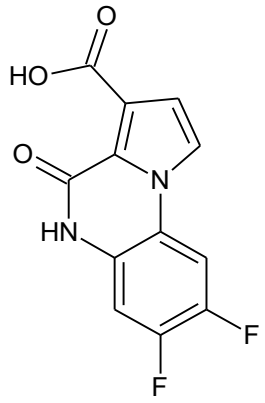


Figure S41. ^{13}C NMR spectrum of 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3a**) in DMSO-d_6



Chemical characterization of 7,8-difluoro-4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**3b**). Gray solid (3.844 g, 97%). mp >290 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 7.17 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.35 (1H, dd, $^{3}J_{HF}$ 10.9, $^{3}J_{HH}$ 7.5 Hz, CH aromatic), 8.29 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 8.47 (1H, dd, $^{3}J_{HF}$ 11.5, $^{3}J_{HH}$ 7.4 Hz, CH aromatic), 12.59 (1H, s, NH), 15.15 (1H, s, OH). ^{13}C NMR (DMSO-d_6, 101 MHz): δ_C 106.3 (d, $^{2}J_{CF}$ 23.8 Hz, CH aromatic), 106.12 (d, $^{2}J_{CF}$ 22.4 Hz, CH aromatic), 117.53, 119.25 (d, $^{3}J_{CF}$ 9.6 Hz, C aromatic), 119.84, 120.11, 120.70, 124.54 (d, $^{3}J_{CF}$ 9.1 Hz, C aromatic), 146.44 (dd, $^{1}J_{CF}$ 243.1, $^{2}J_{CF}$ 13.9 Hz, CF aromatic), 148.01 (dd, $^{1}J_{CF}$ 246.1, $^{2}J_{CF}$ 13.6 Hz, CF aromatic), 157.54 (CO-NH), 162.26 (COOH). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -141.12 (ddd, $^{3}J_{FF}$ 23.8, $^{3}J_{HF}$ 11.5, $^{4}J_{HF}$ 7.6 Hz), -138.42 (ddd, $^{3}J_{FF}$ 23.7, $^{3}J_{HF}$ 10.8, $^{4}J_{HF}$ 7.6 Hz). ESI-MS: m/z 265.0 $[M+H]^+$. Anal. calcd for $C_{12}H_6F_2N_2O_3$ (264.18): C, 54.56; H, 2.29; N, 10.60. Found: C, 54.71; H, 2.26; N, 10.44.

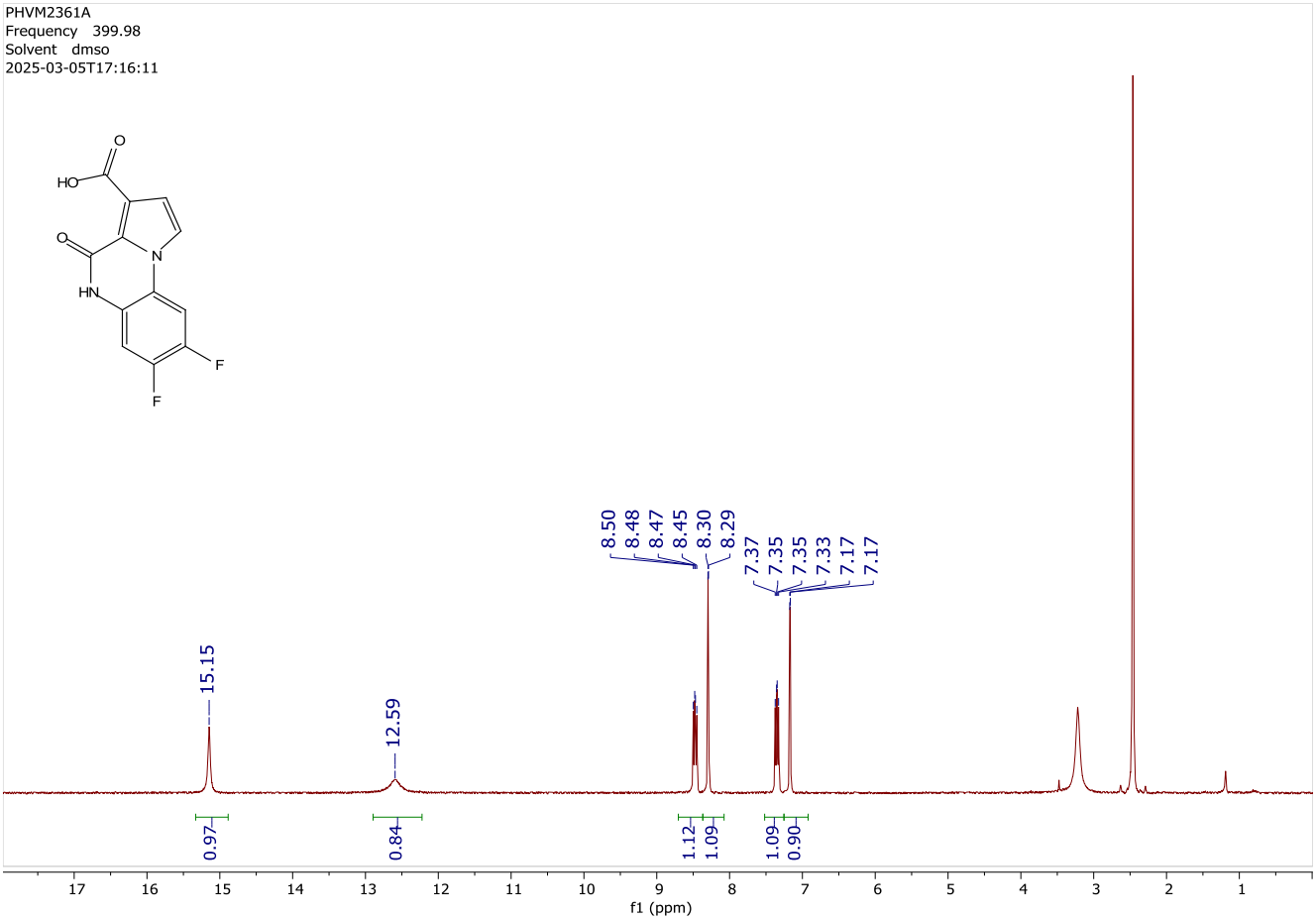


Figure S42. ^{1}H NMR spectrum of 7,8-difluoro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3b**) in DMSO-d_6

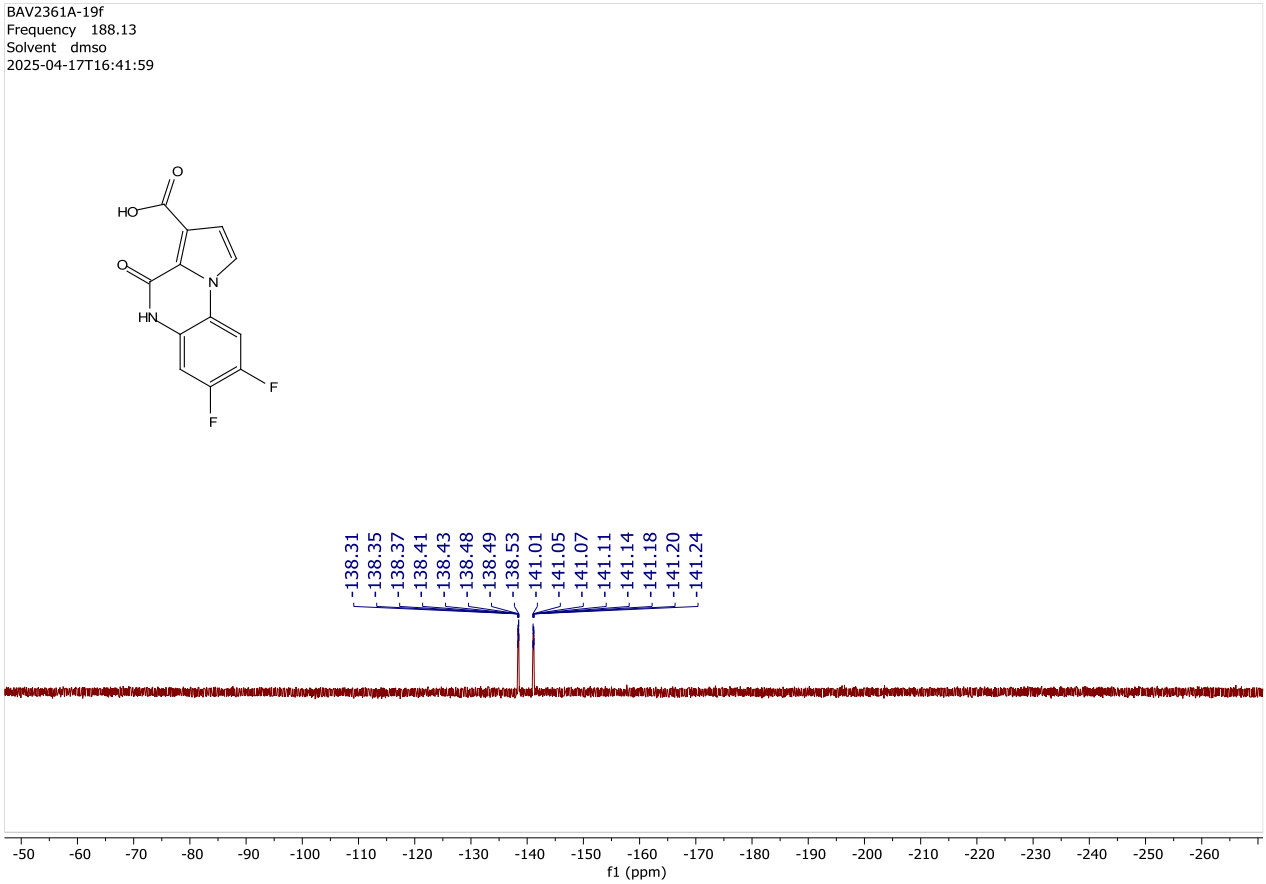


Figure S43. ^{19}F NMR spectrum of 7,8-difluoro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3b**) in DMSO-d_6

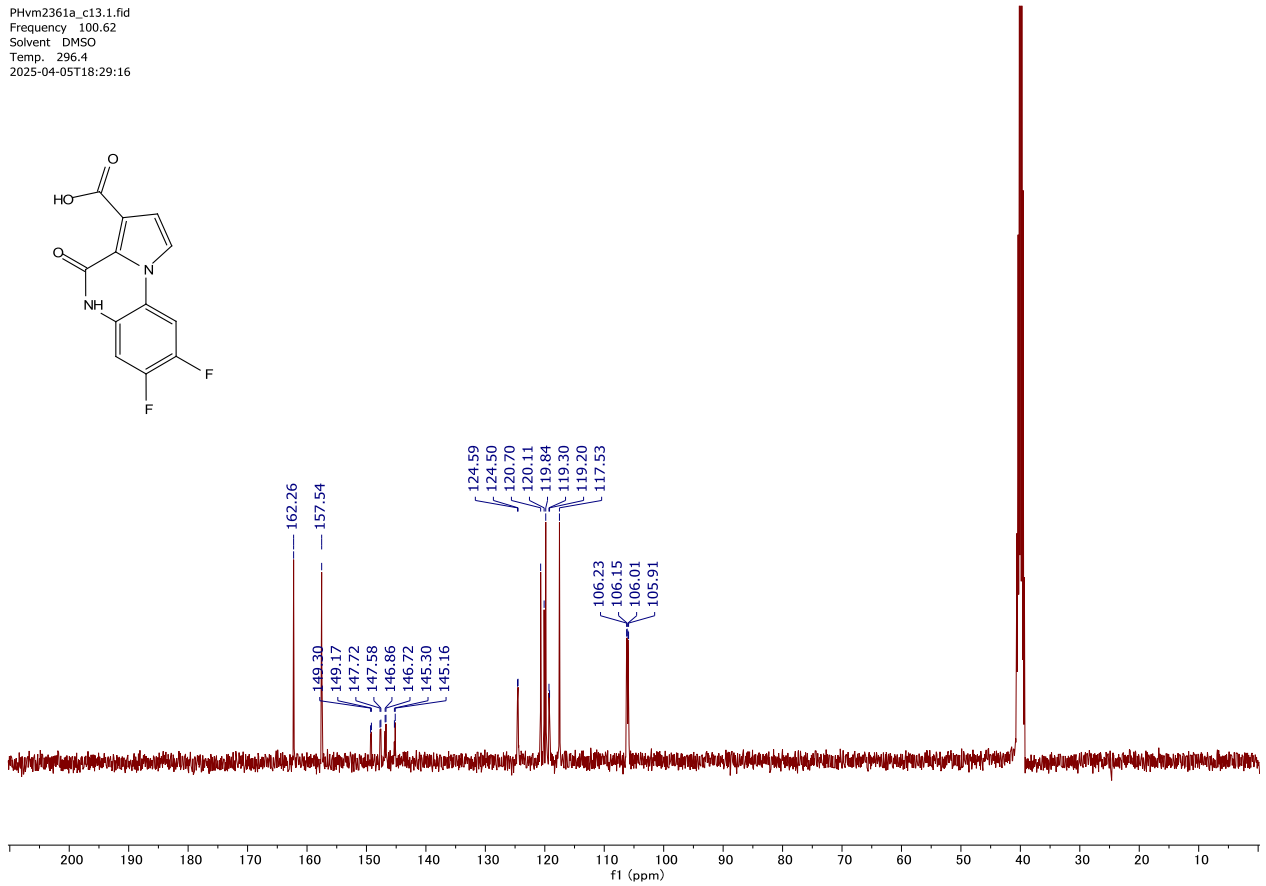
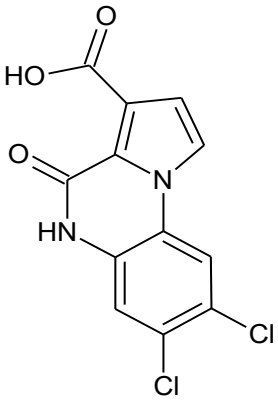


Figure S44. ^{13}C NMR spectrum of 7,8-difluoro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3b**) in DMSO-d_6



Chemical characterization of 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**3c**). Gray solid (4.048 g, 94%). mp >290 (decomp.) °C. IR (solid, KBr, νmax, cm^{-1}): 3116, 3051, 1667, 1629, 1497, 1379, 750, 545, 481. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 7.21 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 7.54 (1H, s, CH aromatic), 8.44 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 8.64 (1H, s, CH aromatic), 12.73 (1H, s, NH), 15.11 (1H, s, OH). ^{13}C NMR (DMSO-d_6, 126 MHz): δ_C 117.25, 117.59, 118.05, 119.67, 119.91, 120.60, 122.14, 126.43, 127.23, 128.82, 157.21 (CO-NH), 161.77 (COOH). ESI-MS: m/z 297.0 $[M+H]^+$. Anal. calcd for $C_{12}H_6Cl_2N_2O_3$ (297.09): C, 48.51; H, 2.04; N, 9.43. Found: C, 48.69; H, 2.07; N, 9.56.

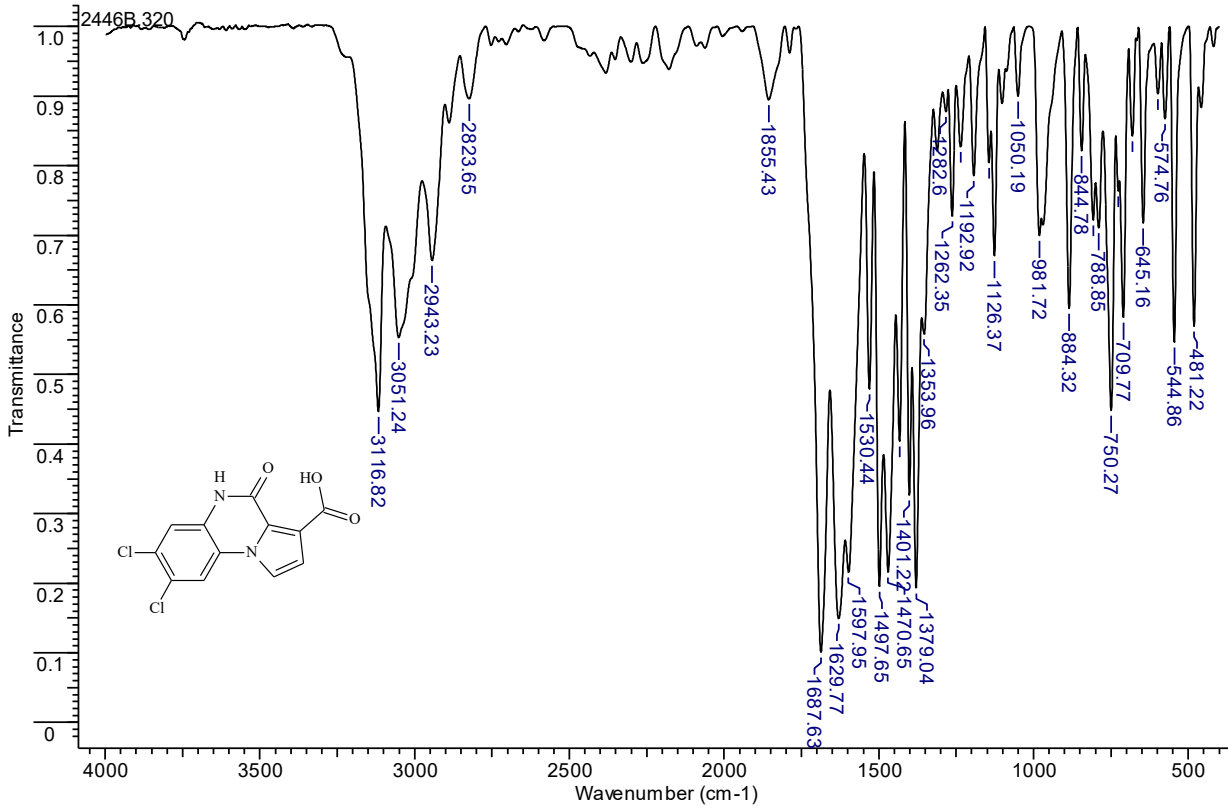


Figure S45. IR spectrum of 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3c**) in KBr pellet

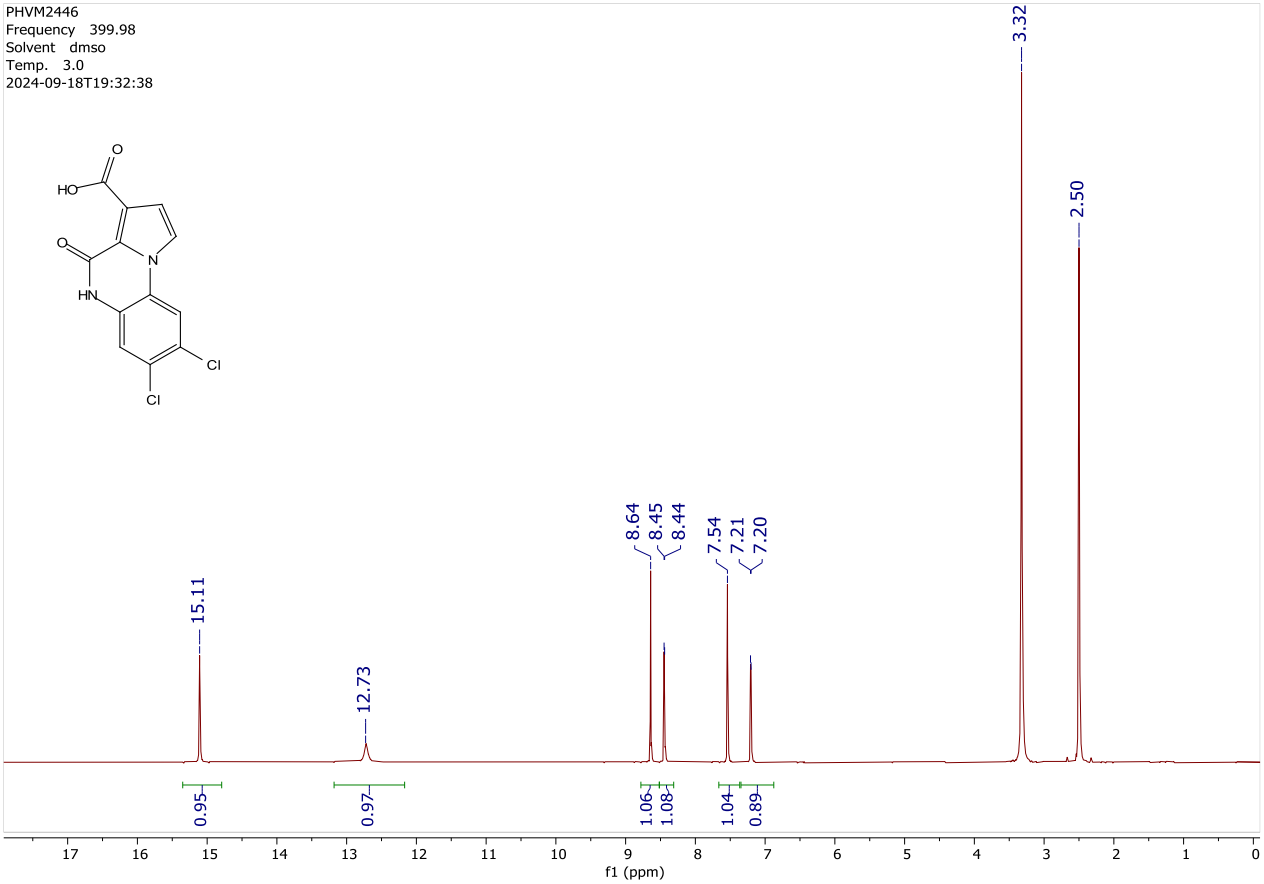


Figure S46. ^{1}H NMR spectrum of 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3c**) in DMSO-d_6

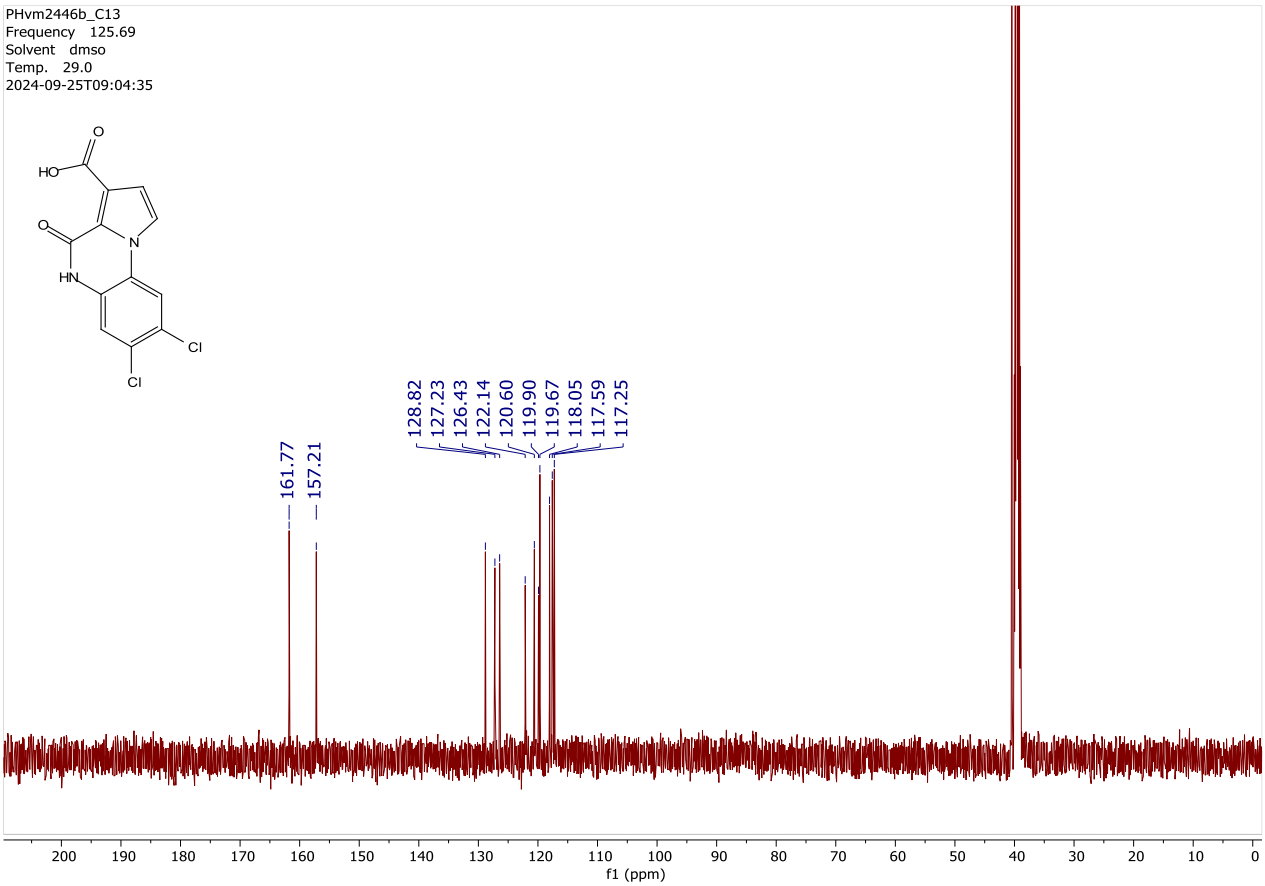
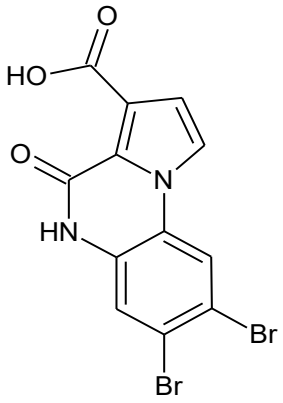


Figure S47. ^{13}C NMR spectrum of 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3c**) in DMSO-d_6



Chemical characterization of 7,8-dibromo-4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**3d**). Gray solid (4.921 g, 85%). mp >290 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 7.20 (1H, d, $^{3}J_{HH}$ 2.9 Hz, CH pyrrole), 7.68 (1H, s, CH aromatic), 8.48 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole) 8.72 (1H, s, CH aromatic), 12.69 (1H, s, NH), 15.11 (1H, s, OH). ^{13}C NMR (DMSO-*d*$_6$, 101 MHz): δ_C 117.24, 118.43, 119.72, 120.10, 120.48, 120.59, 121.12, 121.18, 122.86, 127.86, 157.31 (CO-NH), 161.83 (COOH). ESI-MS: m/z 388.8 $[M+H]^+$. Anal. calcd for $C_{12}H_6Br_2N_2O_3$ (386.00): C, 37.34; H, 1.57; N, 7.26. Found: C, 37.20; H, 1.60; N, 7.35.

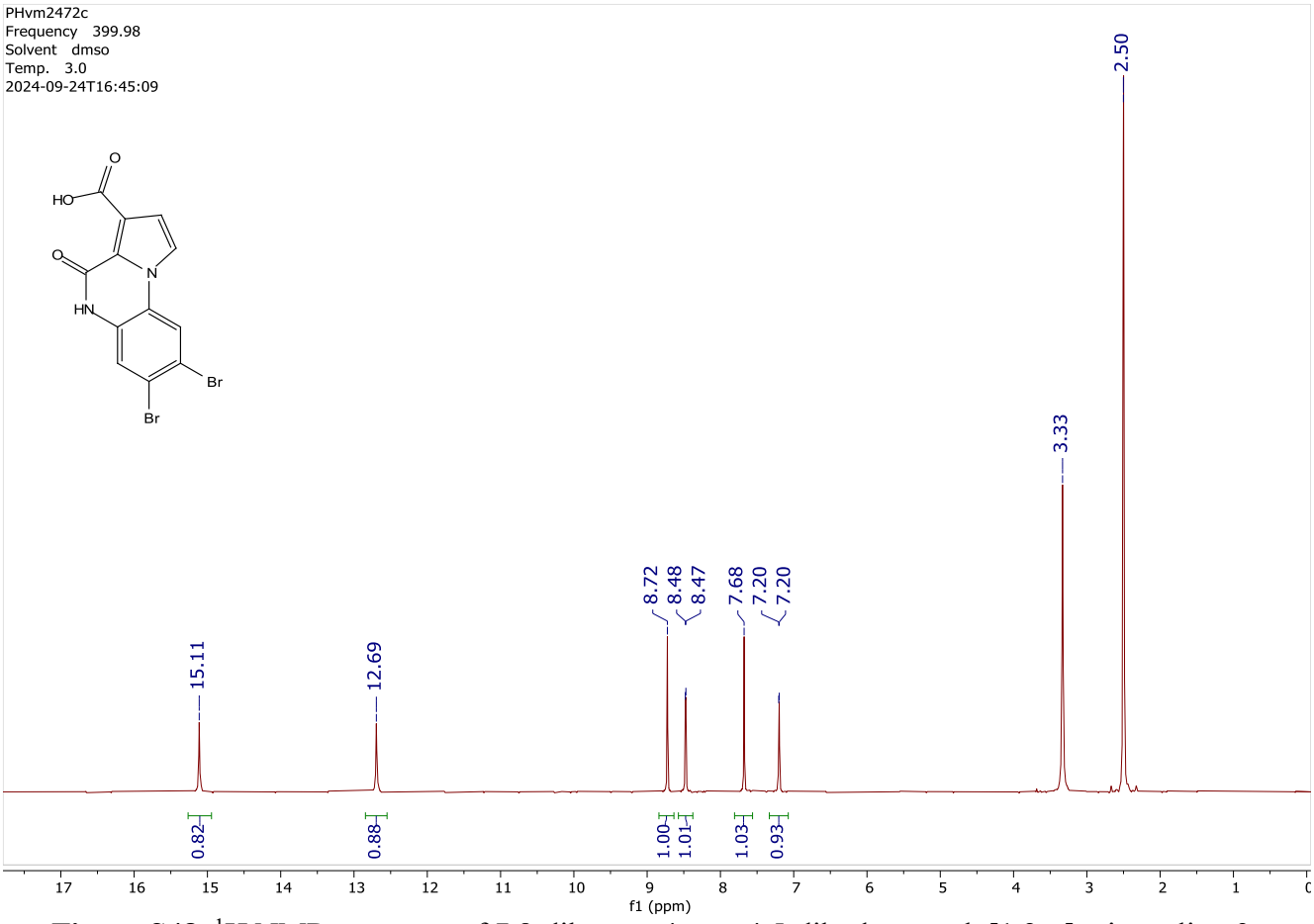


Figure S48. ^{1}H NMR spectrum of 7,8-dibromo-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3d**). in DMSO-*d*$_6$

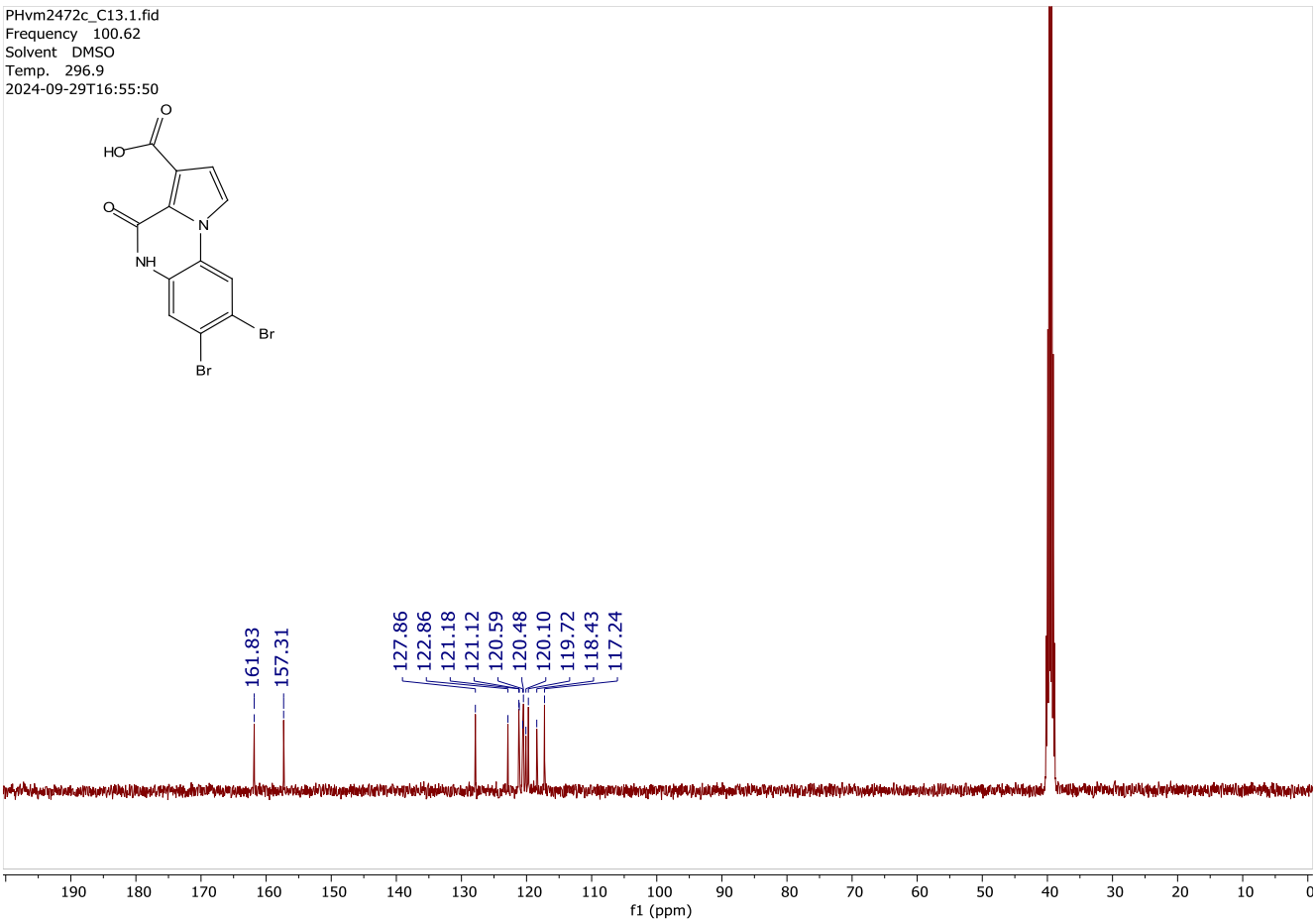
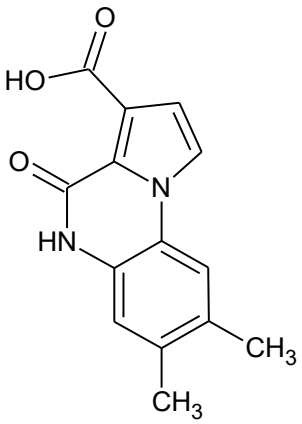


Figure S49. ^{13}C NMR spectrum of 7,8-dibromo-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3d**). in DMSO-*d*$_6$



Chemical characterization of 7,8-dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**3e**). Gray solid (3.421 g, 89%). mp 282-283 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 2.25 (3H, s, CH_3), 2.29 (3H, s, CH_3), 7.12 – 7.16 (2H, m, CH pyrrole + CH aromatic), 7.93 (1H, s, CH aromatic), 8.26 (1H, s, CH pyrrole), 12.40 (1H, s, NH), 15.42 (1H, s, OH). ^{13}C NMR (DMSO-*d*$_6$, 126 MHz): δ_C 19.08 + 19.13 ($2CH_3$), 115.65, 116.66, 117.29, 118.25, 119.56, 119.81, 120.03, 124.69, 133.19, 135.55, 156.97 (CO-NH), 162.32 (COOH). ESI-MS: m/z 257.2 $[M+H]^+$. Anal. calcd for $C_{14}H_{12}N_2O_3$ (256.26): C, 65.62; H, 4.72; N, 10.93. Found: C, 65.73; H, 4.75; N, 11.00.

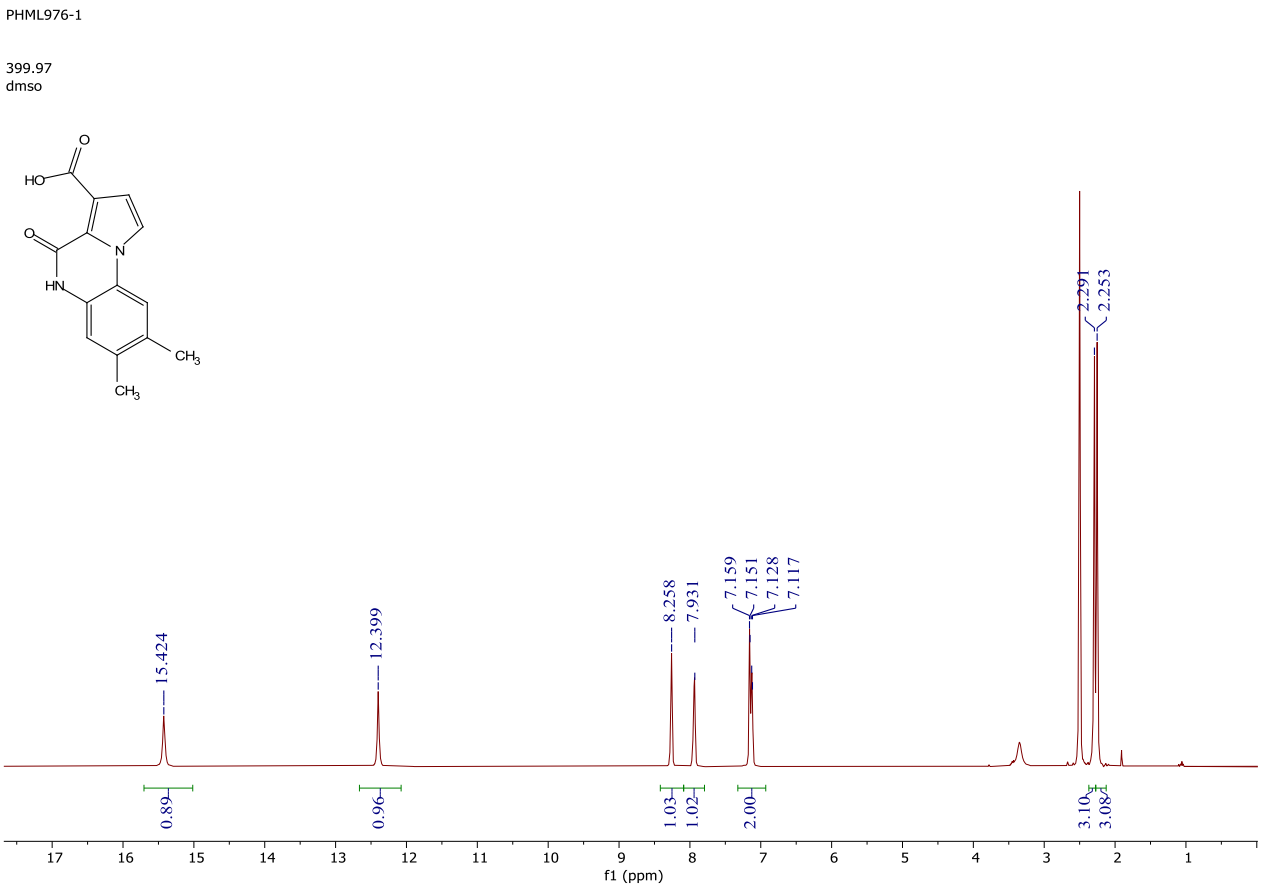


Figure S50. ^{1}H NMR spectrum of 7,8-dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3e**) in DMSO-d_6

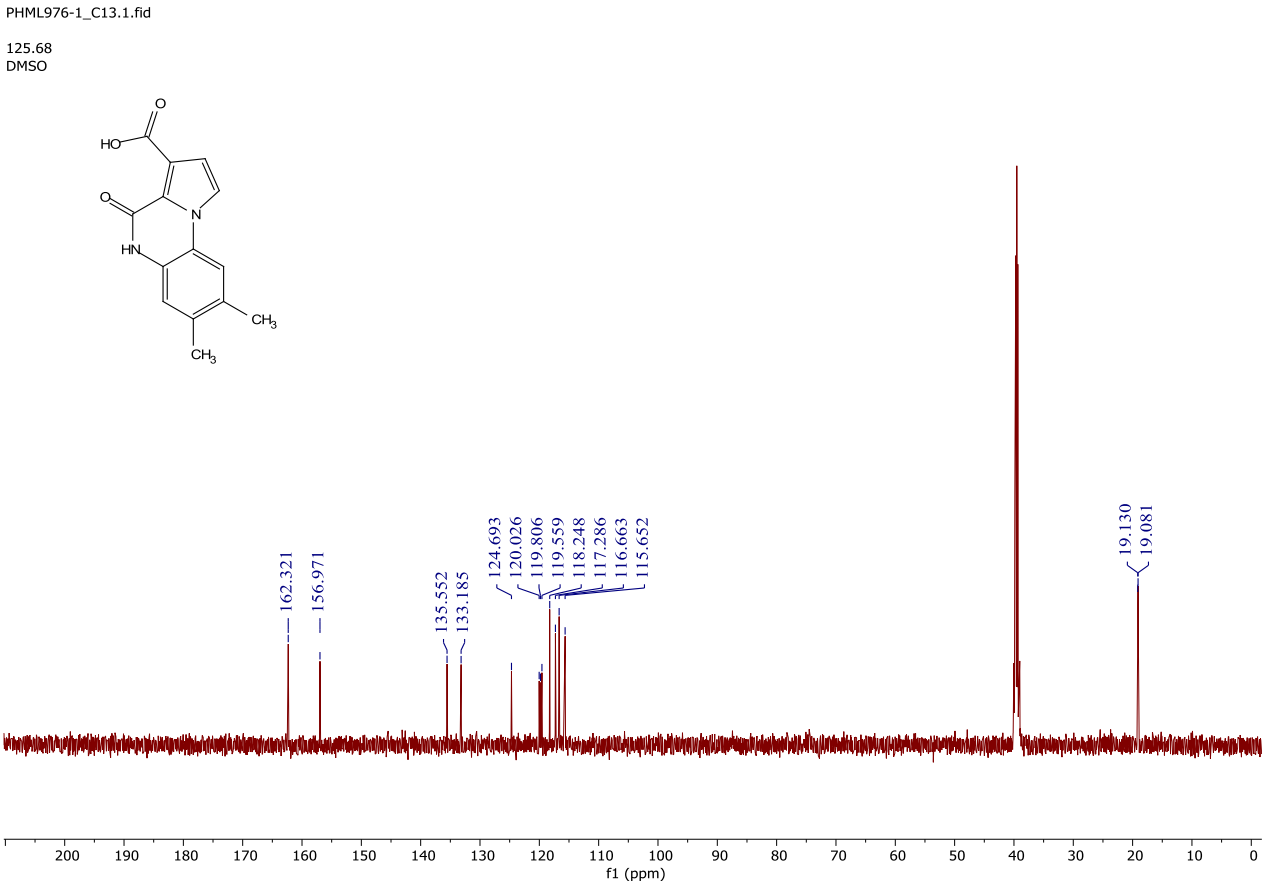
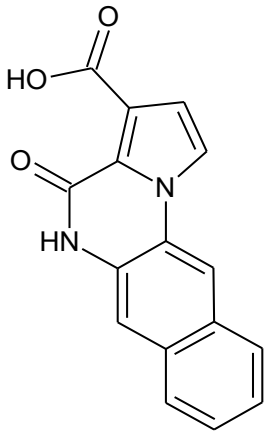


Figure S51. ^{13}C NMR spectrum of 7,8-dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3e**) in DMSO-d_6



Chemical characterization of 4-oxo-4,5-dihydrobenzo[g]pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**3f**). Gray solid (3.756 g, 90%). mp >290 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 7.24 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.53 – 7.57 (2H, m, 2CH aromatic), 7.86 (1H, s, CH aromatic), 7.95 – 7.99 (2H, m, 2CH aromatic), 8.53 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 8.81 (1H, s, CH aromatic), 12.74 (1H, s, NH), 15.37 (1H, s, OH). ^{13}C NMR (DMSO-d_6, 101 MHz): δ_C 113.70, 113.98, 117.33, 119.97, 120.44, 121.33, 122.68, 126.41, 126.91, 127.15, 127.39, 127.80, 129.90, 131.35, 157.99 (CO-NH), 162.58 (COOH). ESI-MS: m/z 279.0 $[M+H]^+$. Anal. calcd for $C_{16}H_{10}N_2O_3$ (278.26): C, 69.06; H, 3.62; N, 10.07. Found: C, 69.17; H, 3.58; N, 10.15.

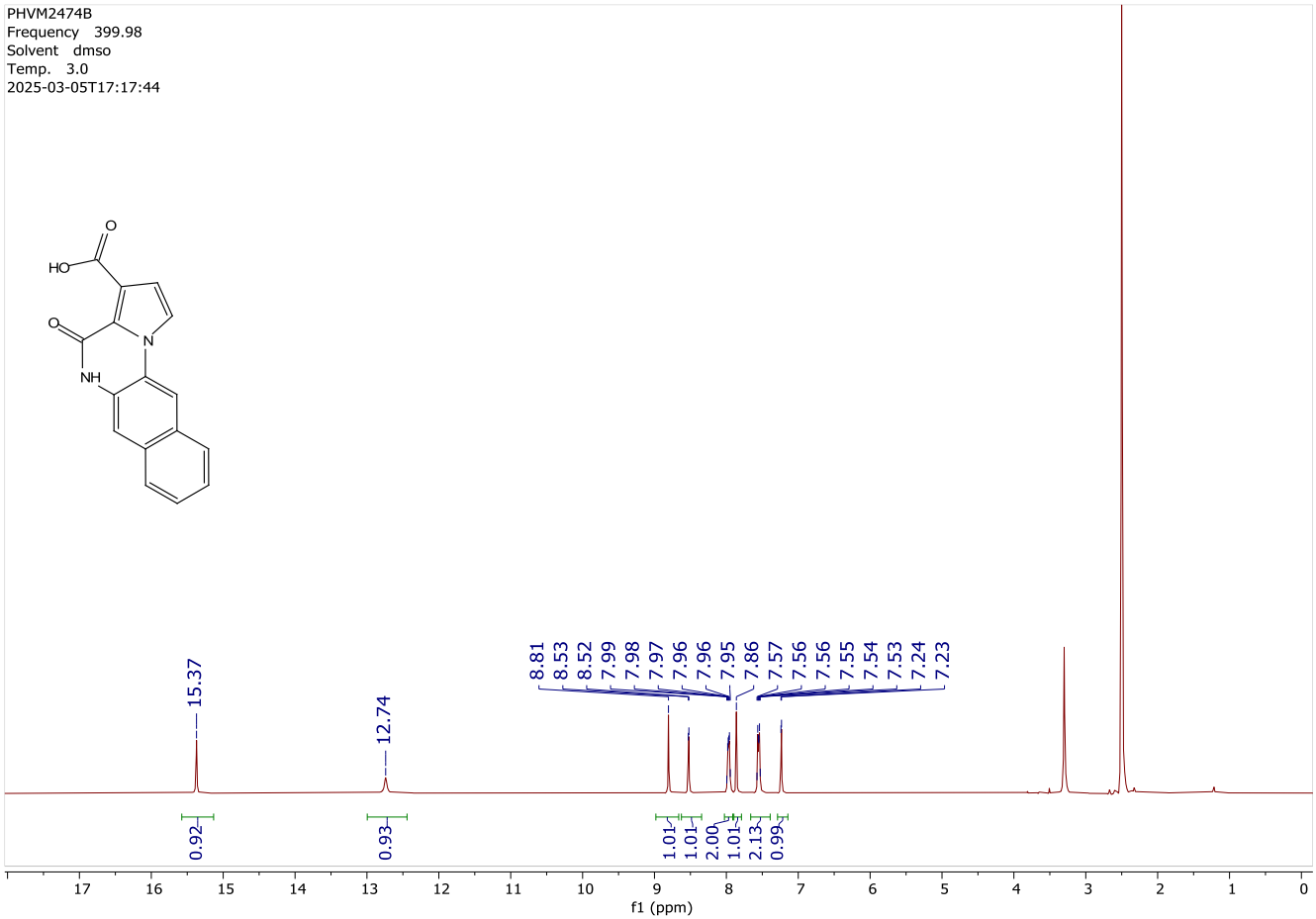


Figure S52. ^{1}H NMR spectrum of 4-oxo-4,5-dihydrobenzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3f**) in DMSO-d_6

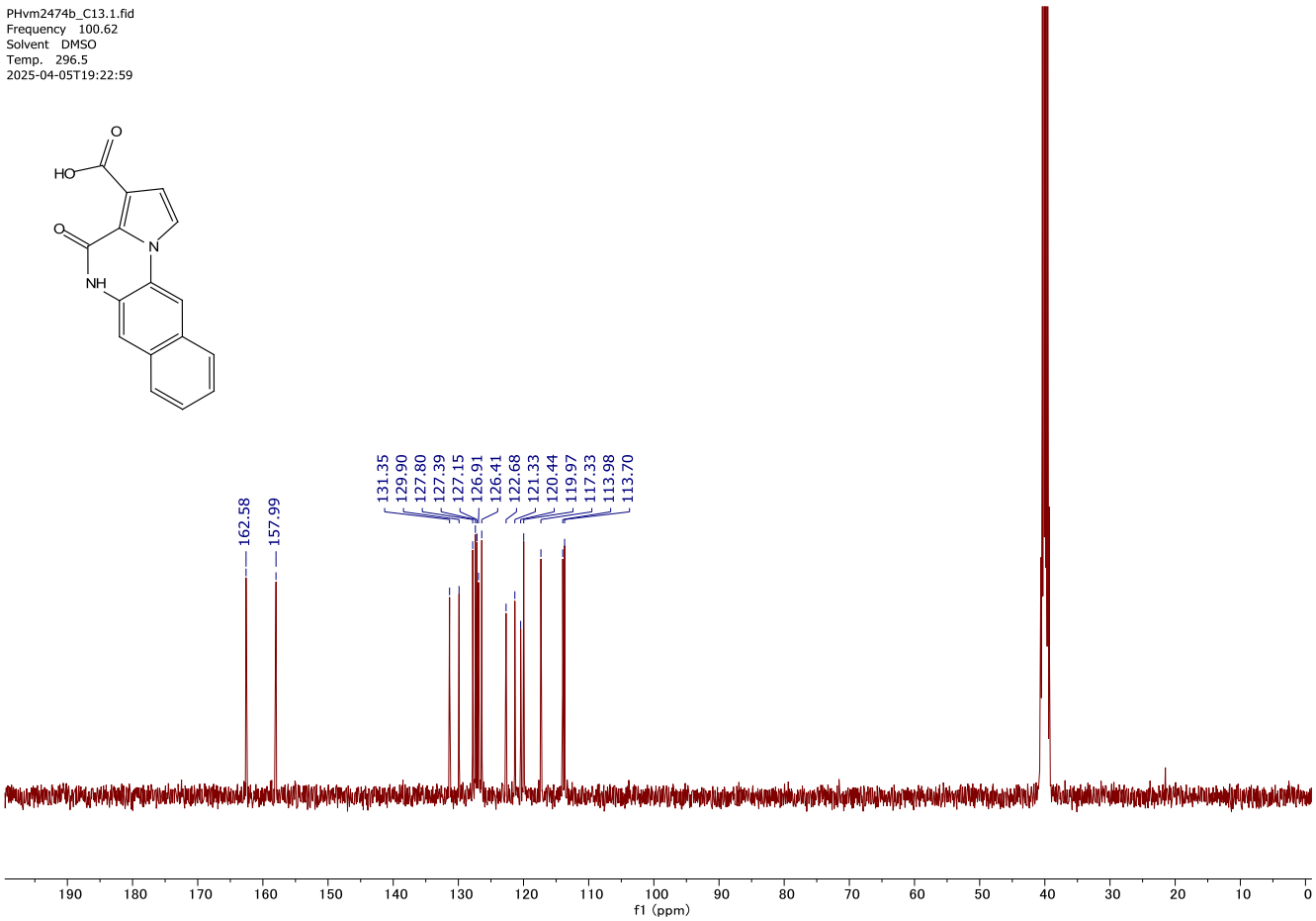
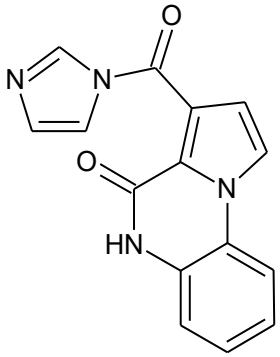


Figure S53. ^{13}C NMR spectrum of 4-oxo-4,5-dihydrobenzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**3f**) in DMSO-d_6

Chemical characterization of 4a-f



Chemical characterization of 3-(1H-imidazole-1-carbonyl)pyrrolo[1,2-a]quinoxalin-4(5H)-one (**4a**). Beige solid (2.504 g, 90%). mp 275-276 °C. ^{1}H NMR (302 MHz, DMSO-d_6): δ_H 7.06 (1H, dd, $^3J_{HH}$ 1.7, $^4J_{HH}$ 0.8 Hz, CH imidazole), 7.08 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole), 7.26 – 7.41 (3H, m, 3CH aromatic), 7.68 (1H, t, $^3J_{HH}$ 1.5 Hz, CH imidazole), 8.14 (1H, t, $^4J_{HH}$ 1.1 Hz, CH imidazole), 8.19 (1H, d, $^3J_{HH}$ 7.6 Hz, CH aromatic), 8.38 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 11.58 (1H, s, NH). Anal. calcd for $C_{15}H_{10}N_4O_2$ (278.26): C, 64.74; H, 3.62; N, 20.13. Found: C, 64.61; H, 3.58; N, 20.02.

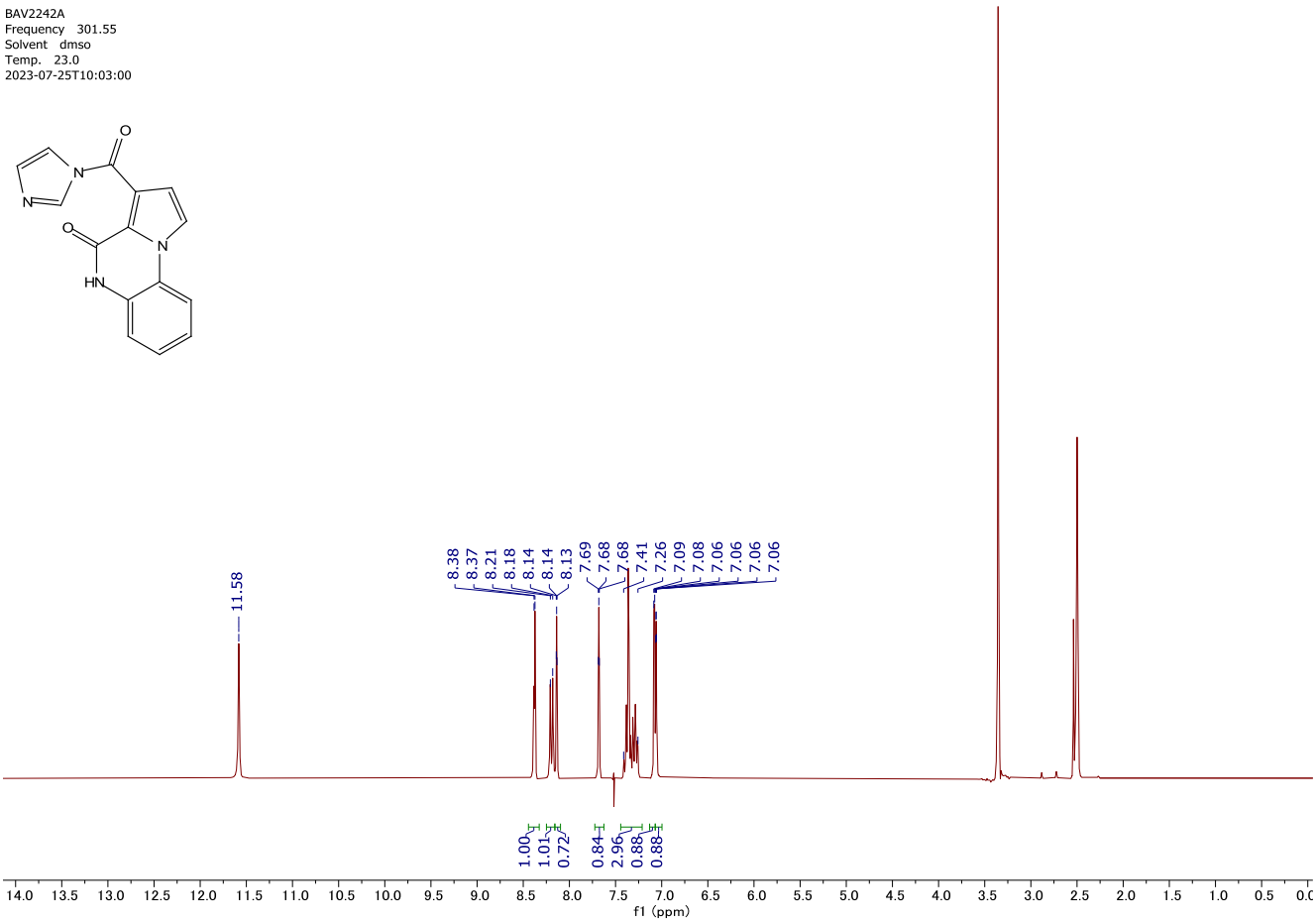
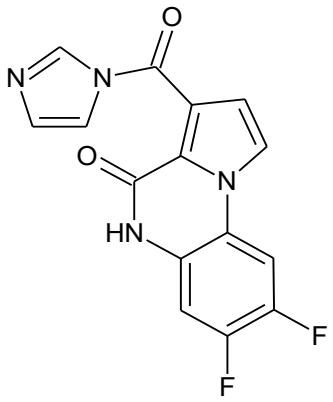


Figure S54. ^{1}H NMR spectrum of 3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4a**) in DMSO-*d*$_6$



Chemical characterization of 7,8-difluoro-3-(1H-imidazole-1-carbonyl)pyrrolo[1,2-a]quinoxalin-4(5H)-one (**4b**). Gray solid (2.577 g, 82%). mp 281-282 °C. IR (solid, KBr, νmax, cm^{-1}): 3114, 1691, 1663, 1529, 1304, 1219, 873, 751. ^{1}H NMR (302 MHz, DMSO-*d*$_6$): δ_H 7.06 (1H, s, CH imidazole), 7.10 (1H, d, $^{3}J_{HH}$ 2.9 Hz, CH pyrrole), 7.29 (1H, dd, $^{3}J_{HF}$ 11.2, $^{4}J_{HF}$ 7.5 Hz, CH aromatic), 7.68 (1H, s, CH imidazole), 8.13 (1H, s, CH imidazole), 8.32 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 8.50 (1H, dd, $^{3}J_{HF}$ 11.6, $^{4}J_{HF}$ 7.5 Hz, CH aromatic), 11.65 (1H, s, NH). ^{19}F NMR (DMSO-*d*$_6$, 188 MHz): δ_F -143.70 (ddd, $^{3}J_{FF}$ 23.7, $^{3}J_{HF}$ 11.6, $^{4}J_{HF}$ 7.6 Hz), -139.61 (ddd, $^{3}J_{FF}$ 23.7, $^{3}J_{HF}$ 11.3, $^{4}J_{HF}$ 8.3 Hz). Anal. calcd for $C_{15}H_8F_2N_4O_2$ (314.25): C, 57.33; H, 2.57; N, 17.83. Found: C, 57.24; H, 2.54; N, 17.75.

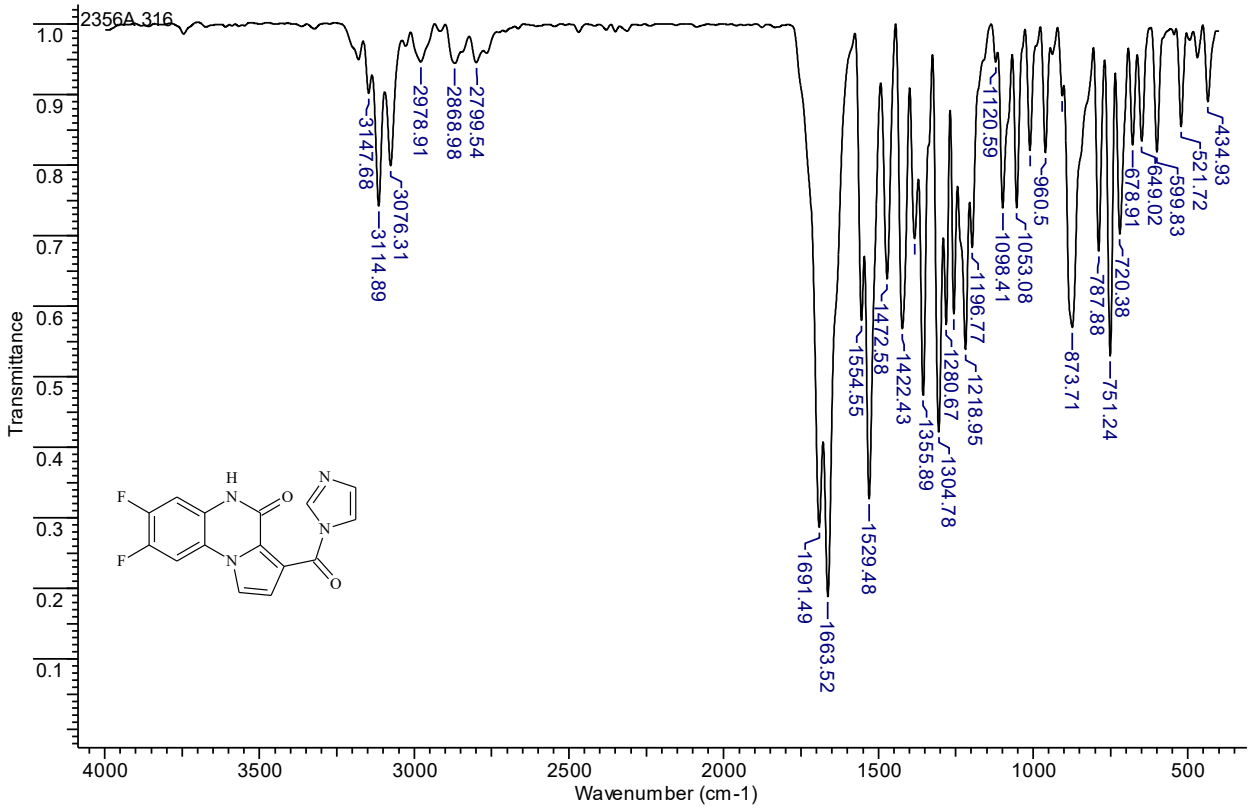


Figure S55. IR spectrum of 7,8-difluoro-3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4b**) in KBr pellet

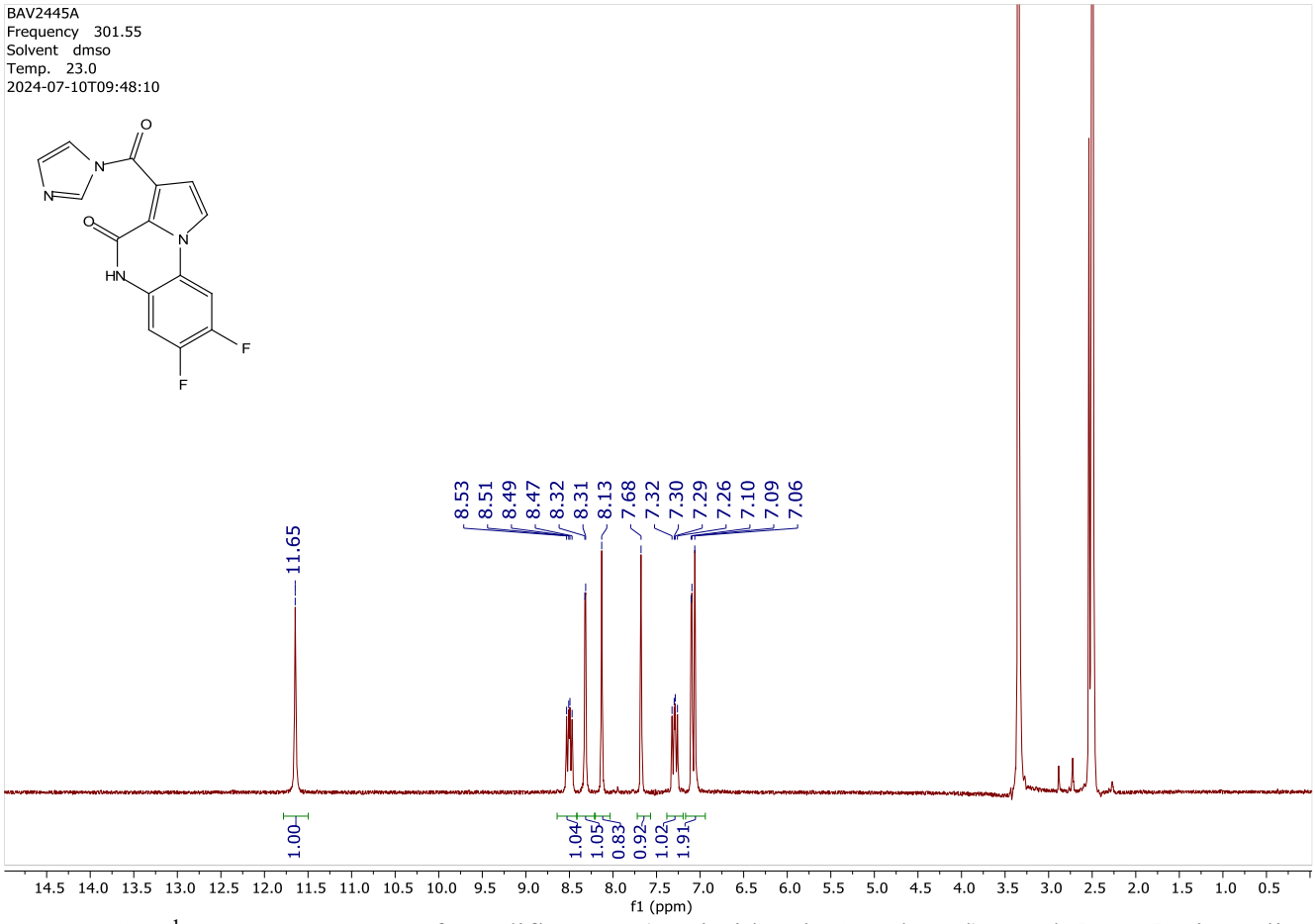


Figure S56. ^{1}H NMR spectrum of 7,8-difluoro-3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4b**) in DMSO-d_6

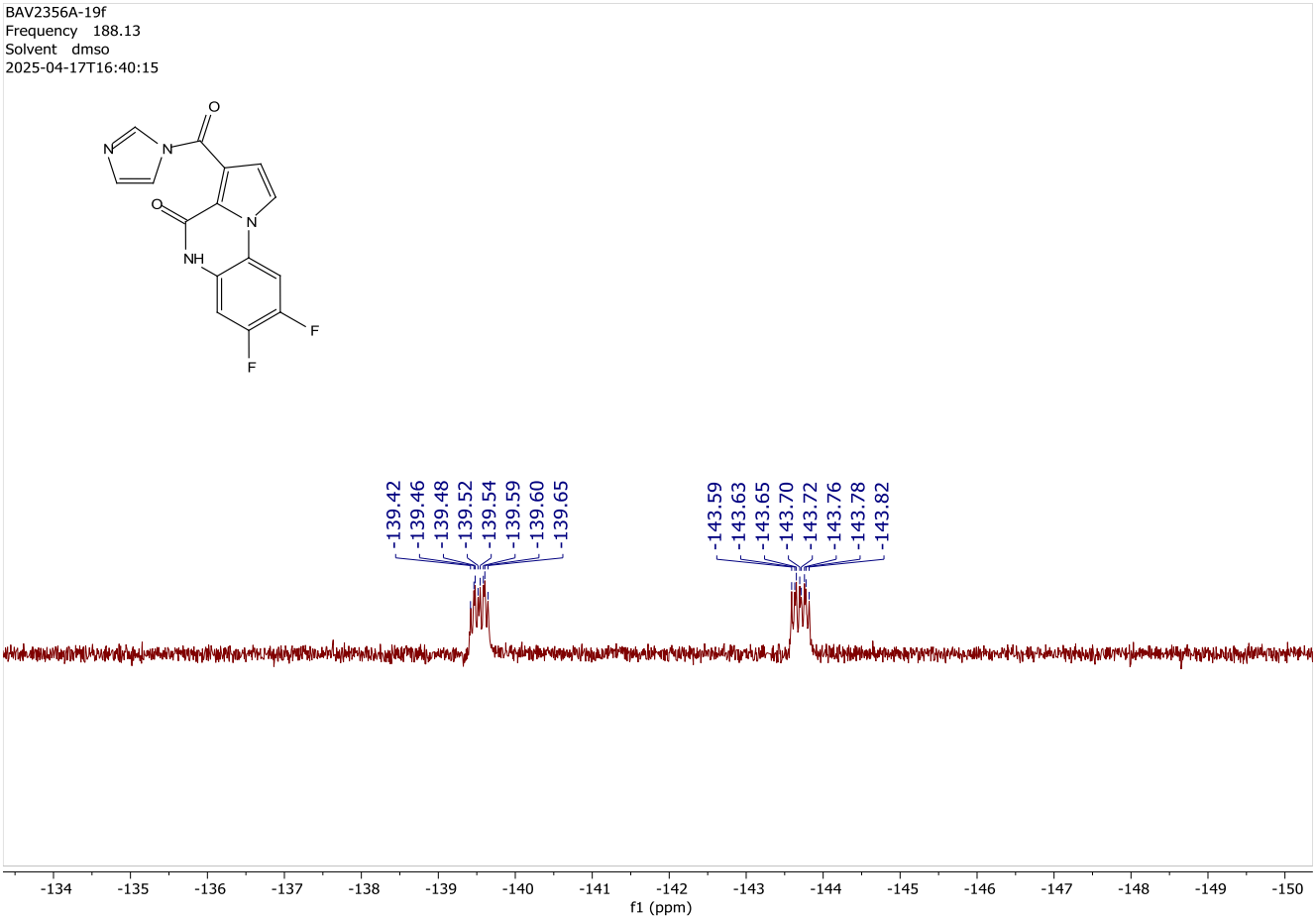
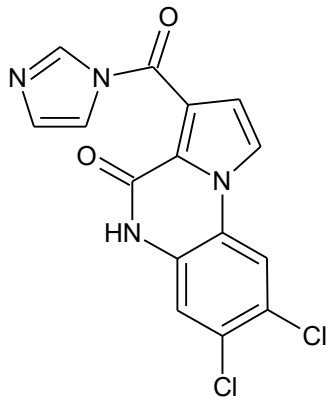


Figure S57. ^{19}F NMR spectrum of 7,8-difluoro-3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4b**) in DMSO-d_6



Chemical characterization of 7,8-dichloro-3-(1H-imidazole-1-carbonyl)pyrrolo[1,2-a]quinoxalin-4(5H)-one (**4c**). Gray solid (2.742 g, 79%). mp 269-270 (decomp.) °C. ^{1}H NMR (302 MHz, DMSO-d_6): δ_H 7.07 (1H, s, CH imidazole), 7.09 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 7.47 (1H, s, CH aromatic), 7.68 (1H, s, CH imidazole), , 8.13 (1H, s, CH imidazole), 8.41 (1H, d, $^3J_{HH}$ 2.8 Hz, CH pyrrole), 8.60 (1H, s, CH aromatic), 11.71 (1H, s, NH). Anal. calcd for $C_{15}H_8Cl_2N_4O_2$ (347.16): C, 51.90; H, 2.32; N, 16.14. Found: C, 51.74; H, 2.35; N, 16.06.

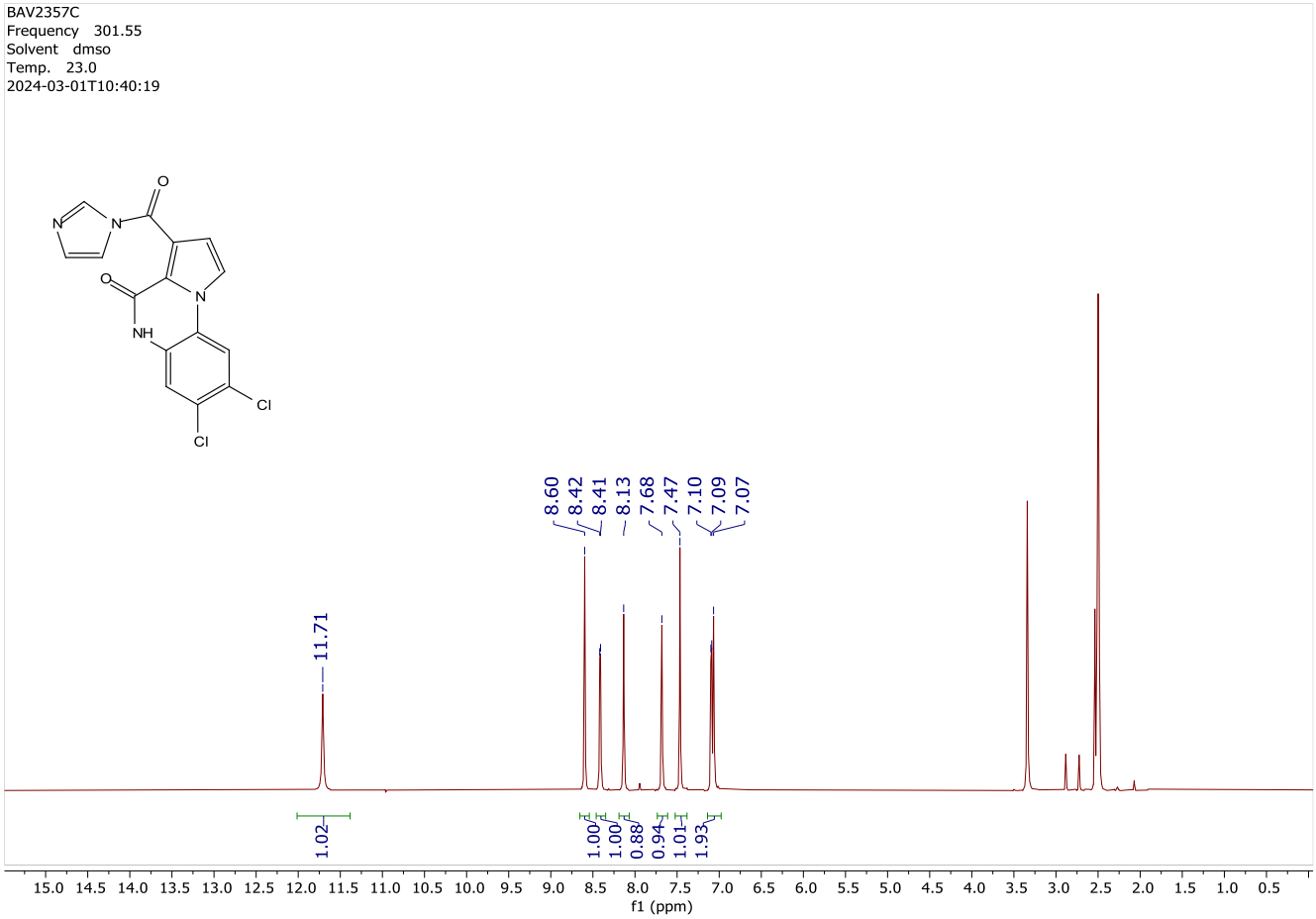
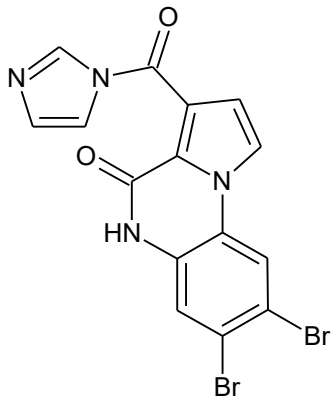


Figure S58. ^{1}H NMR spectrum of 7,8-dichloro-3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4c**) in DMSO-d_6



Chemical characterization of 7,8-dibromo-3-(1H-imidazole-1-carbonyl)pyrrolo[1,2-a]quinoxalin-4(5H)-one (**4d**). Gray solid (3.183 g, 73%). mp >290 °C. ^{1}H NMR (302 MHz, DMSO-d_6): δ_H 7.06-7.10 (2H, m, CH pyrrole + CH imidazole), 7.10 (1H, s, CH aromatic), 7.62 + 7.68 (2H, s + s, CH imidazole + CH aromatic), 8.13 (1H, s, CH imidazole), 8.44 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 8.69 (1H, s, CH aromatic), 11.69 (1H, s, NH).Anal. calcd for $C_{15}H_8Br_2N_4O_2$ (436.06): C, 41.32; H, 1.85; N, 12.85. Found: C, 41.12; H, 1.89; N, 12.92.

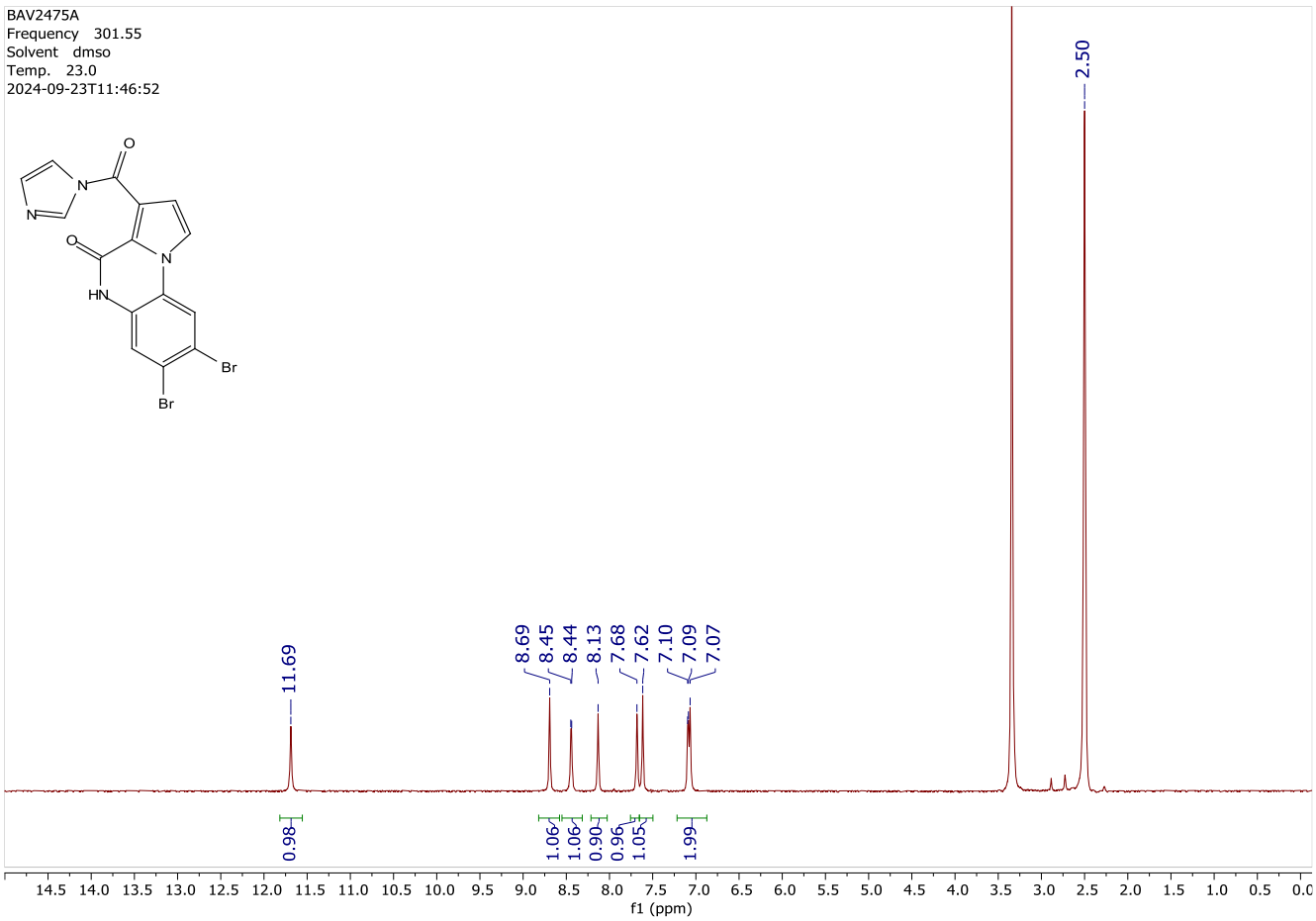
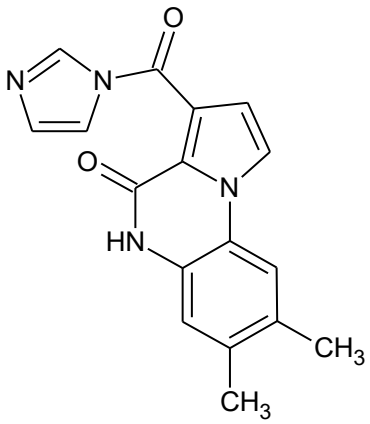


Figure S59. ^{1}H NMR spectrum of 7,8-dibromo-3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4d**) in DMSO-d_6



Chemical characterization of 3-(1H-imidazole-1-carbonyl)-7,8-dimethylpyrrolo[1,2-a]quinoxalin-4(5H)-one (**4e**). Beige solid (2.726 g, 89%). mp 270-271 °C. IR (solid, KBr, νmax, cm^{-1}): 3147, 2856, 1738, 1659, 1374, 1216, 867, 751. ^{1}H NMR (302 MHz, DMSO-d_6): δ_H 2.27 (3H, s, CH_3), 2.32 (3H, s, CH_3), 7.04-7.06 (2H, m, CH pyrrole + CH imidazole), 7.10 (1H, s, CH aromatic), 7.66 (1H, t, $^{3}J_{HH}$ 1.5 Hz, CH imidazole), 8.01 (1H, s, CH aromatic), 8.11 (1H, t, $^{4}J_{HH}$ 0.9 Hz, CH imidazole), 8.29 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 11.46 (1H, s, NH). Anal. calcd for $C_{17}H_{14}N_4O_2$ (306.32): C, 66.66; H, 4.61; N, 18.29. Found: C, 66.82; H, 4.59; N, 18.42.

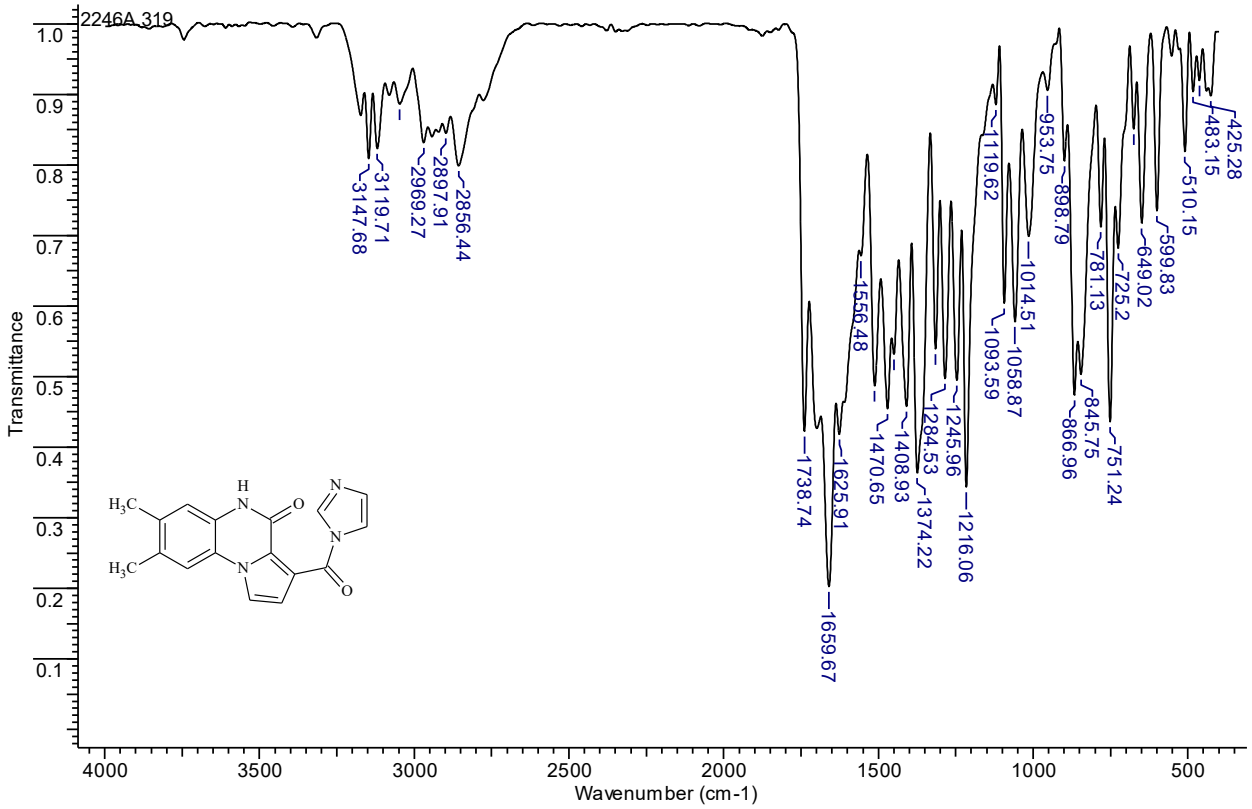


Figure S60. IR spectrum of 3-(1*H*-imidazole-1-carbonyl)-7,8-dimethylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4e**) in KBr pellet

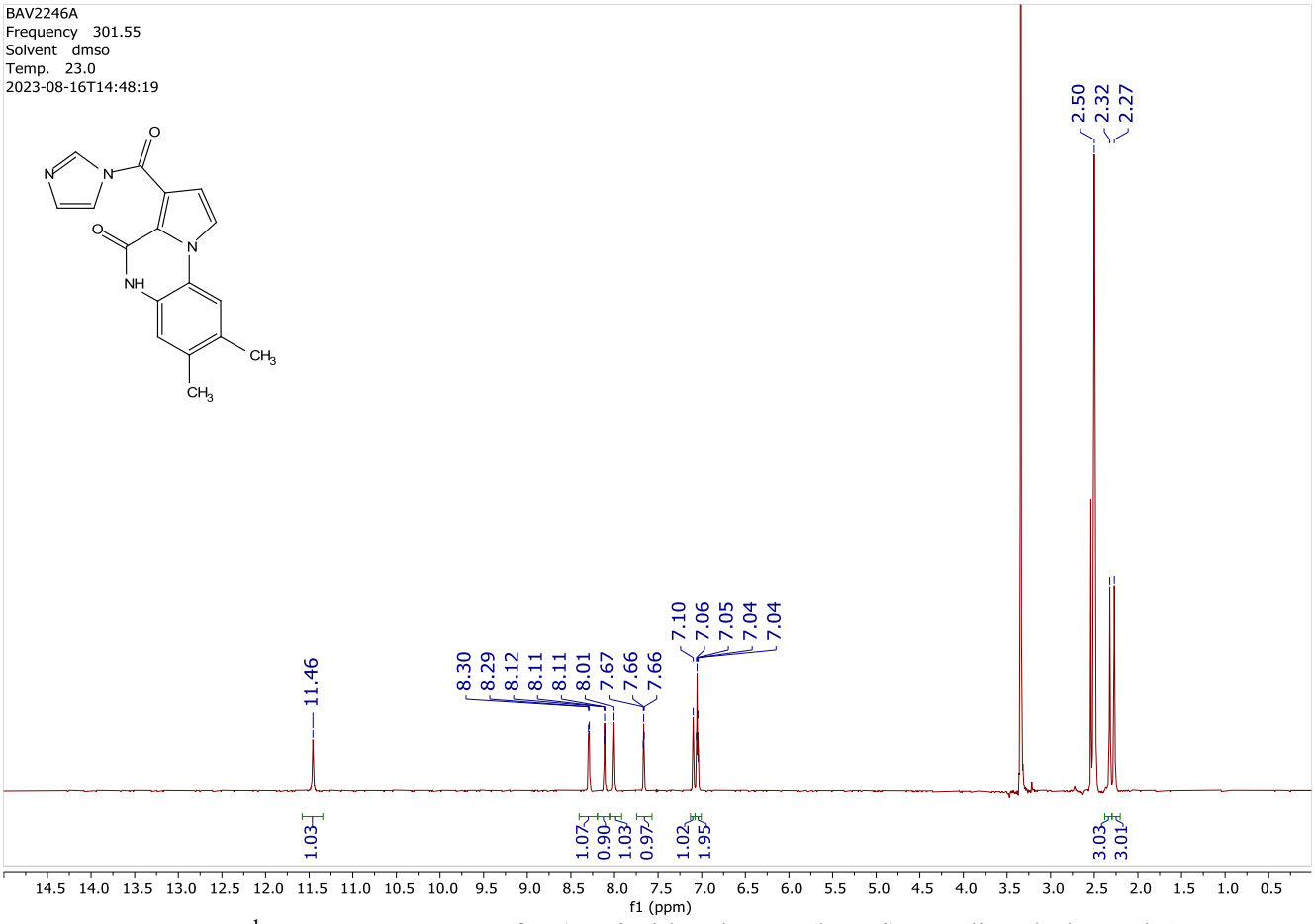
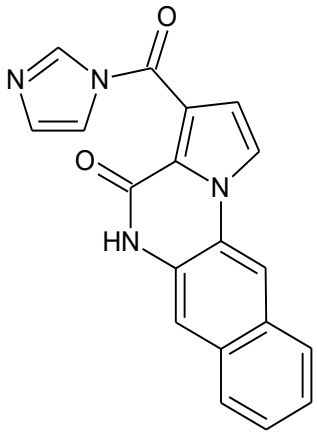


Figure S61. ^{1}H NMR spectrum of 3-(1*H*-imidazole-1-carbonyl)-7,8-dimethylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4e**) in DMSO-d_6



Chemical characterization of 3-(1H-imidazole-1-carbonyl)benzo[g]pyrrolo[1,2-a]quinoxalin-4(5H)-one (**4f**). Gray solid (2.462 g, 75%). mp >290 °C. ^{1}H NMR (302 MHz, DMSO-d_6): δ_H 7.08 (1H, s, CH imidazole), 7.11 (1H, d, $^{3}J_{HH}$ 2.9 Hz, CH pyrrole), 7.48 – 7.55 (2H, m, 2CH aromatic), 7.71 (1H, t, $^{3}J_{HH}$ 1.5 Hz, CH imidazole), 7.73 (1H, s, CH aromatic), 7.90 – 7.99 (2H, m, 2CH aromatic), 8.19 (1H, s, CH imidazole), 8.50 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 8.77 (1H, s, CH aromatic), 11.74 (1H, s, NH). Anal. calcd for $C_{19}H_{12}N_4O_2$ (328.32): C, 69.51; H, 3.68; N, 17.06. Found: C, 69.23; H, 3.70; N, 16.94.

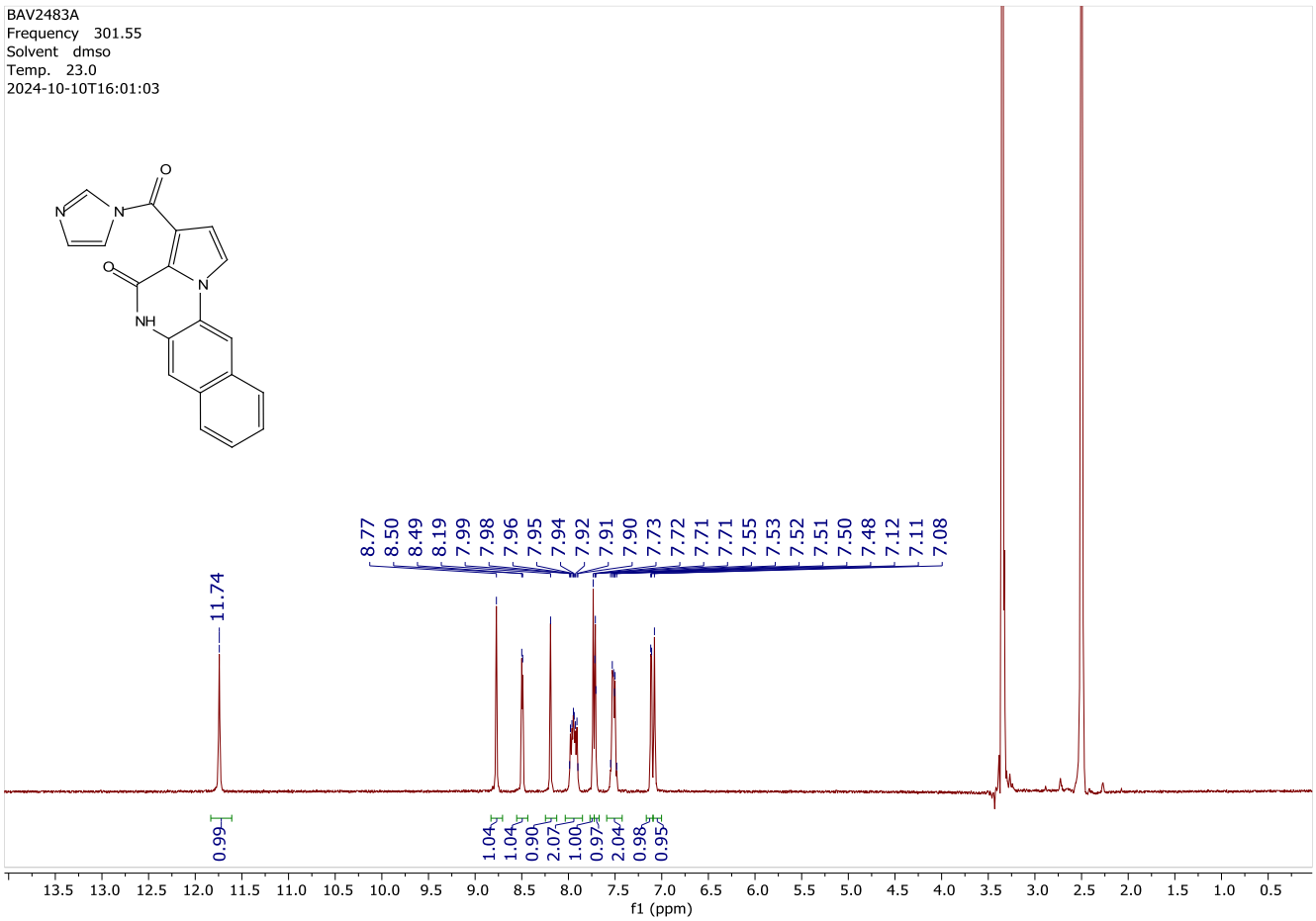
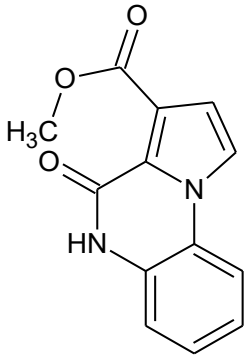


Figure S62. ^{1}H NMR spectrum of 3-(1*H*-imidazole-1-carbonyl)benzo[*g*]pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**4f**) in DMSO-d_6

Chemical characterization of 5a-f



Chemical characterization of methyl 4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylate (**5a**). Light yellow solid (2.228 g, 92%). mp 246-247 (decomp.) °C. IR (solid, KBr, νmax, cm^{-1}): 3136, 3027, 2896, 1724, 1655, 1359, 1288, 1050, 757, 451. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.79 (3H, s, CH_3O), 6.97 (1H, d, $^{3}J_{HH}$ 2.5 Hz, CH pyrrole), 7.20 – 7.36 (3H, m, 3CH aromatic), 8.12 (1H, d, $^{3}J_{HH}$ 8.2 Hz, CH aromatic), 8.23 (1H, d, $^{3}J_{HH}$ 2.9 Hz, CH pyrrole), 11.48 (1H, s, NH). ^{13}C NMR (DMSO-d_6, 126 MHz): δ_C 51.69 (CH_3O), 114.58, 115.54, 116.35, 117.45, 118.33, 121.79, 121.85, 122.64, 126.52, 128.80, 153.44 (CO-NH), 164.11 (COOCH$_3$). ESI-MS: m/z 243.2 $[M+H]^+$. Anal. calcd for $C_{13}H_{10}N_2O_3$ (242.23): C, 64.46; H, 4.16; N, 11.56. Found: C, 64.63; H, 4.20; N, 11.61.

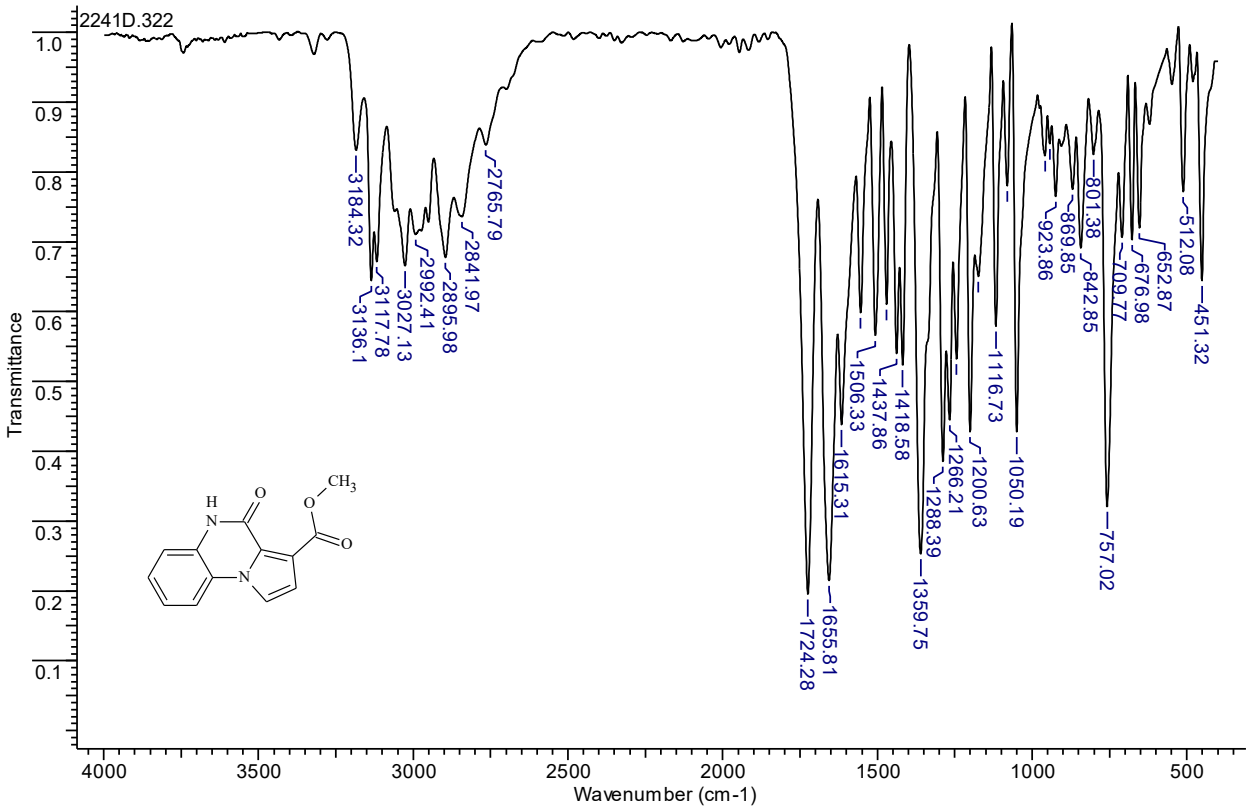


Figure S63. IR spectrum of 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5a**) in KBr pellet

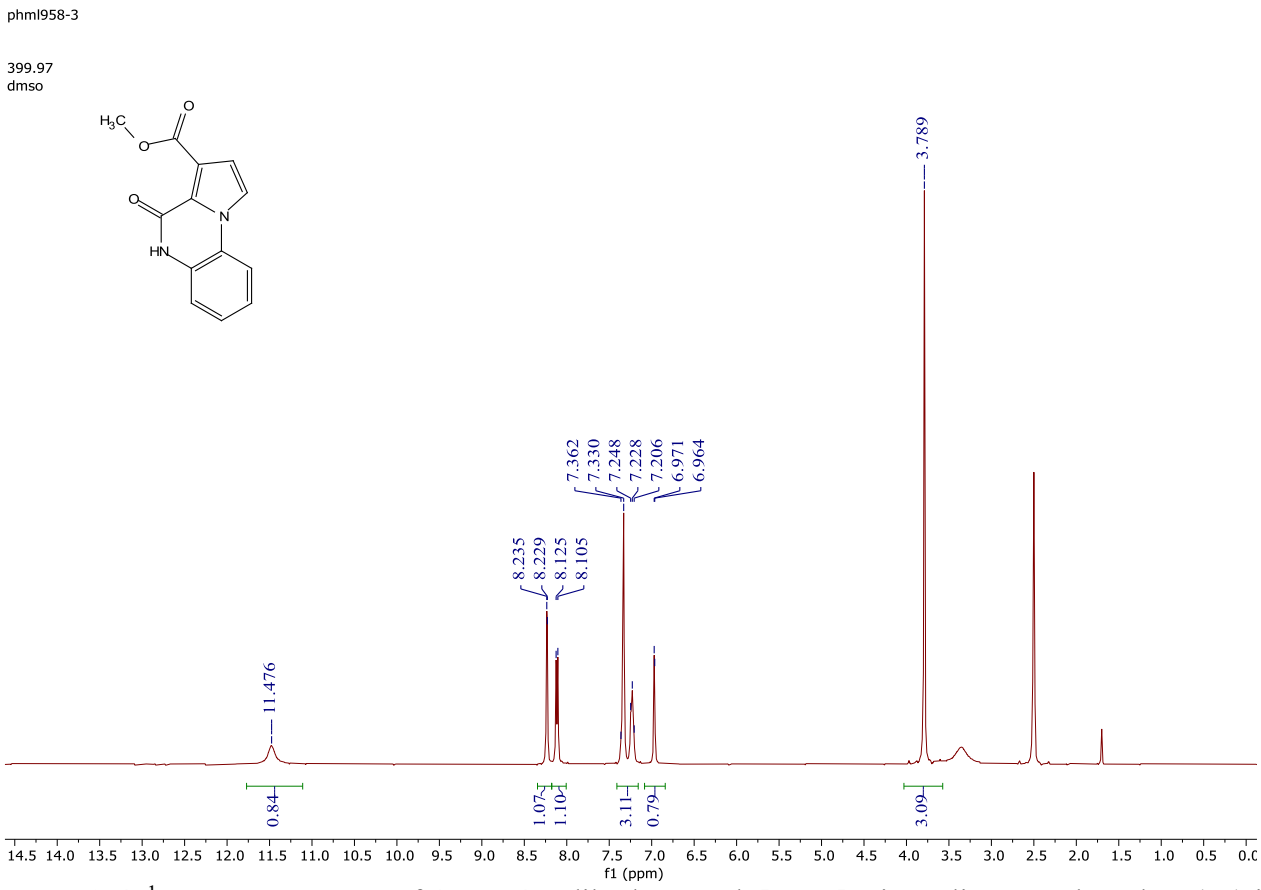


Figure S64. ^{1}H NMR spectrum of 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5a**) in DMSO-d_6

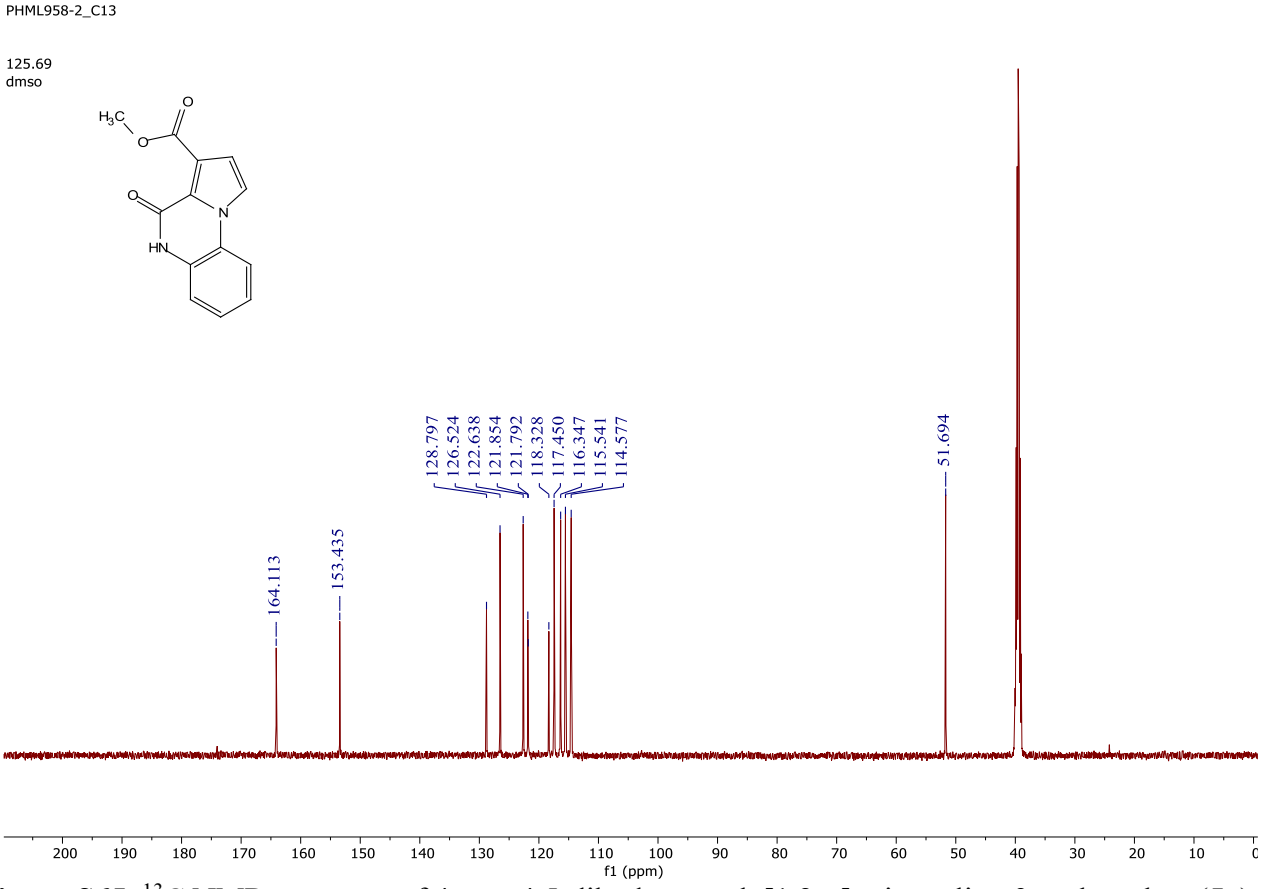
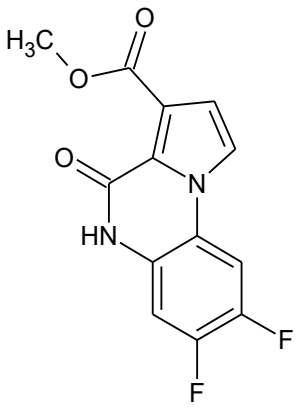


Figure S65. ^{13}C NMR spectrum of 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5a**) in DMSO-d_6



Chemical characterization of methyl 7,8-difluoro-4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylate (**5b**). Colorless solid (2.699 g, 97%). mp 280-281 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.80 (3H, s, CH_3O), 6.95 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.27 (1H, dd, $^{3}J_{HF}$ 11.2, $^{3}J_{HH}$ 7.5 Hz, CH aromatic), 8.12 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 8.31 (1H, dd, $^{3}J_{HF}$ 11.5, $^{3}J_{HH}$ 7.6 Hz, CH aromatic), 11.28 (1H, s, NH). ^{13}C NMR (TFA-d_1, 151 MHz,): δ_C 56.66 (OCH_3) 107.43 (d, $^{2}J_{CF}$ 24.1 Hz, CH aromatic), 110.76 (d, $^{2}J_{CF}$ 23.7 Hz, CH aromatic), 119.46, 122.14 (d, $^{3}J_{CF}$ 8.3 Hz, C aromatic), 122.72, 122.98 (d, $^{3}J_{CF}$ 9.1 Hz, C aromatic), 124.70, 152.67 (dd, $^{1}J_{CF}$ 256.5, $^{2}J_{CF}$ 13.1 Hz, CF aromatic), 152.90 (dd, $^{1}J_{CF}$ 256.4, $^{2}J_{CF}$ 13.5 Hz, CF aromatic), 158.62 (CO-NH), 171.62 (COOH). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -144.06 (ddd, $^{3}J_{FF}$ 23.4, $^{3}J_{HF}$ 11.7, $^{4}J_{HF}$ 8.0 Hz), -139.73 (ddd, $^{3}J_{FF}$ 24.3, $^{3}J_{HF}$ 11.2, $^{4}J_{HF}$ 8.2 Hz). ESI-MS: m/z 279.0 $[M+H]^+$. Anal. calcd for $C_{13}H_8F_2N_2O_3$ (278.21): C, 56.12; H, 2.90; N, 10.07. Found: C, 55.91; H, 2.93; N, 9.91.

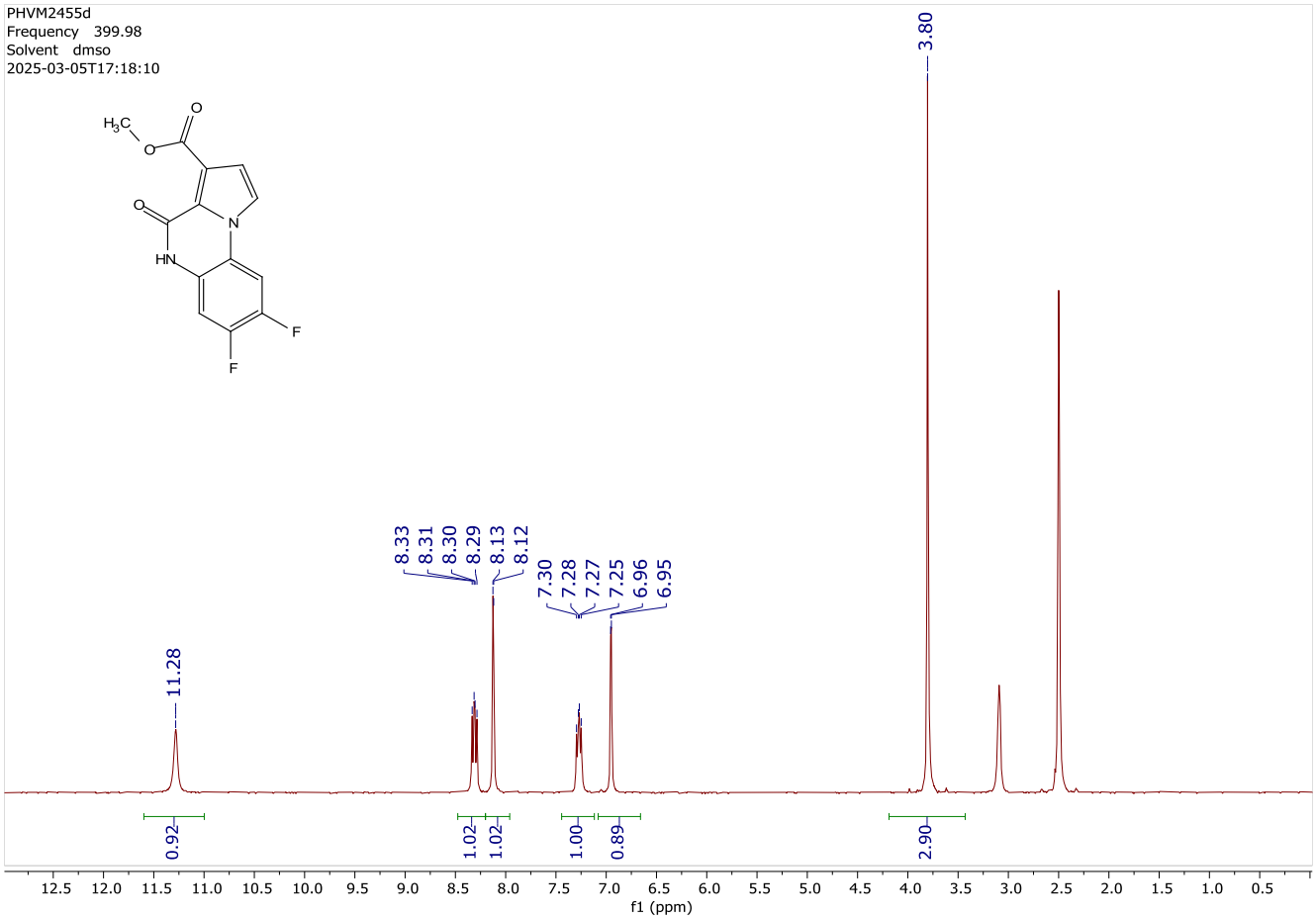


Figure S66. ^{1}H NMR spectrum of methyl 7,8-difluoro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5b**) in DMSO-d_6

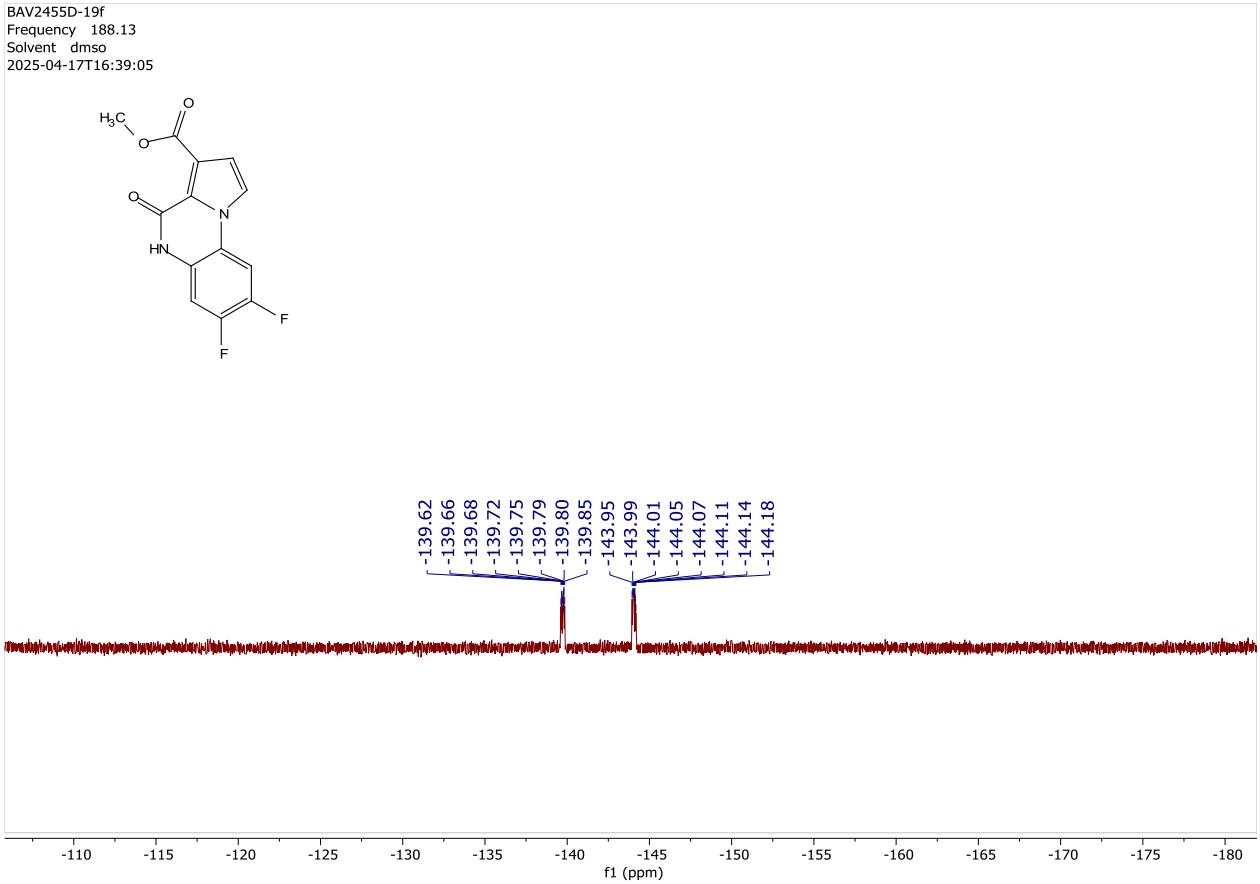


Figure S67. ^{19}F NMR spectrum of methyl 7,8-difluoro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5b**) in DMSO-d_6

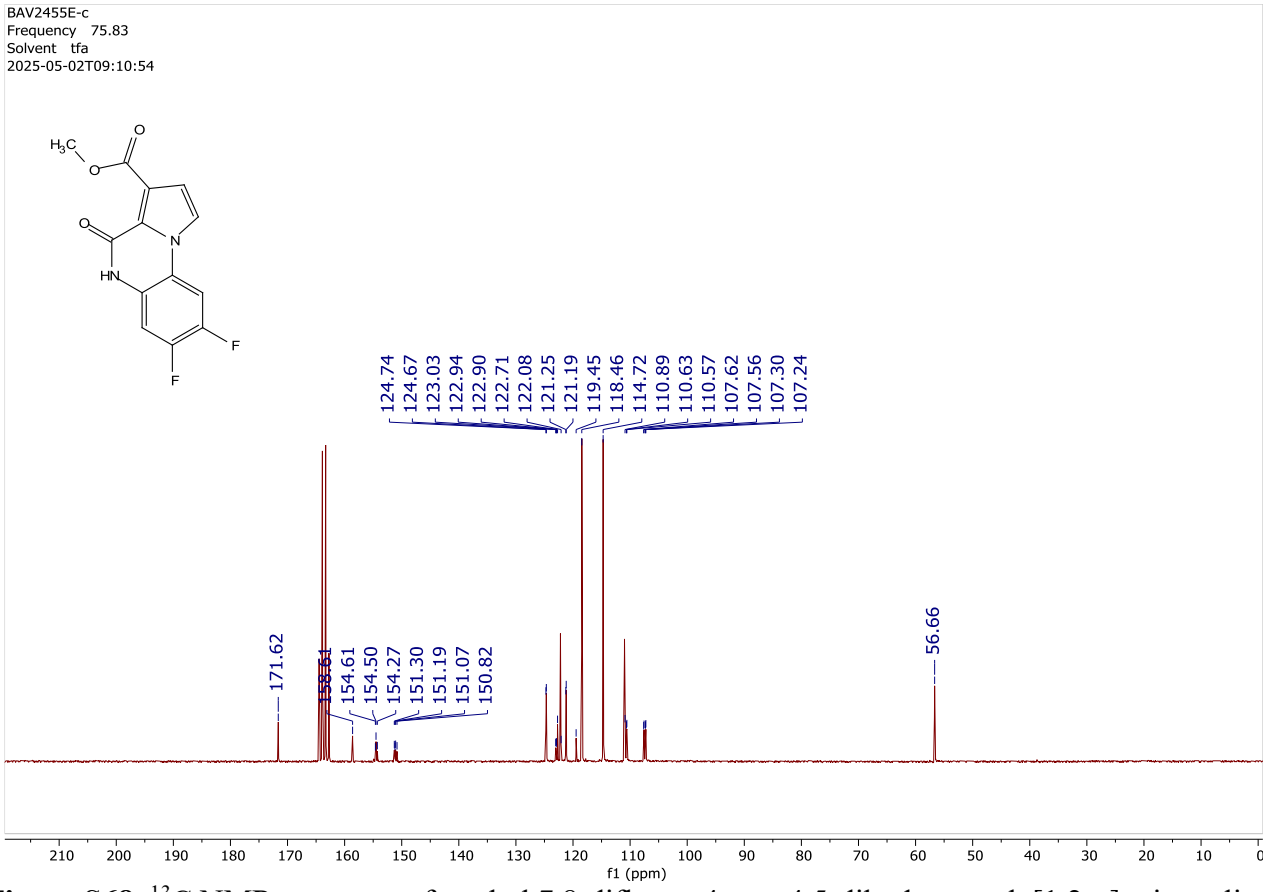
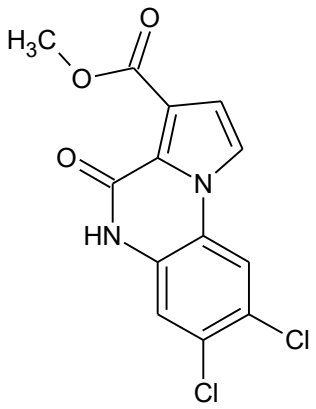


Figure S68. ^{13}C NMR spectrum of methyl 7,8-difluoro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5b**) in TFA-d_1



Chemical characterization of methyl 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylate (**5c**). Gray solid (3.049 g, 98%). mp 285-286 °C. IR (solid, KBr, νmax, cm^{-1}): 3254, 1716, 1665, 1346, 1295, 1052, 754, 483. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.78 (1H, s, CH_3O), 6.97 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.43 (1H, s, CH aromatic), 8.27 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 8.51 (1H, s, CH aromatic), 11.60 (1H, broad s, NH). ^{13}C NMR (TFA-d_1, 151 MHz): δ_C 56.80 (CH_3O), 119.52, 119.70, 121.30, 123.00, 123.03, 124.51, 124.81, 125.43, 136.48, 136.82, 158.76 (CO-NH), 171.67 (COOCH$_3$). ESI-MS: m/z 311.0 [M+H]+. Anal. calcd for $C_{13}H_8Cl_2N_2O_3$ (311.12): C, 50.19; H, 2.59; N, 9.00. Found: C, 49.89; H, 2.62; N, 8.86.

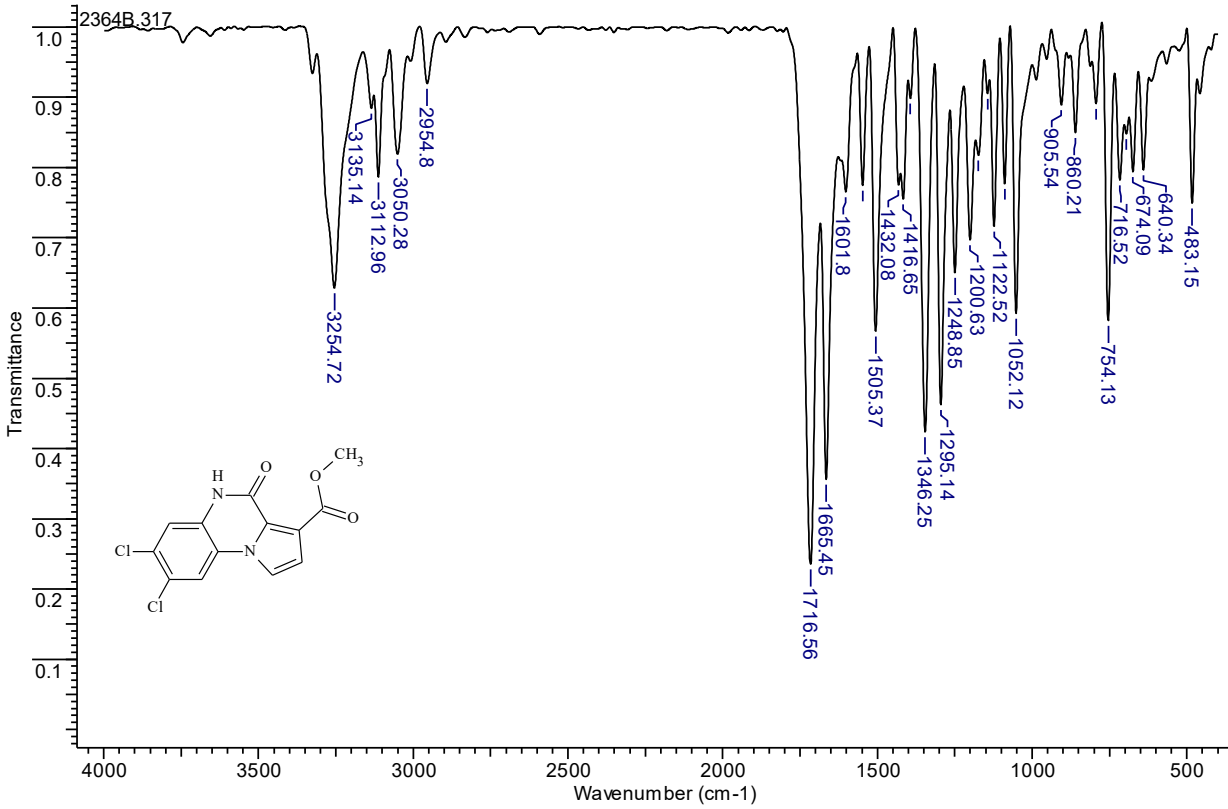


Figure S69. IR spectrum of methyl 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5c**) in KBr pellet

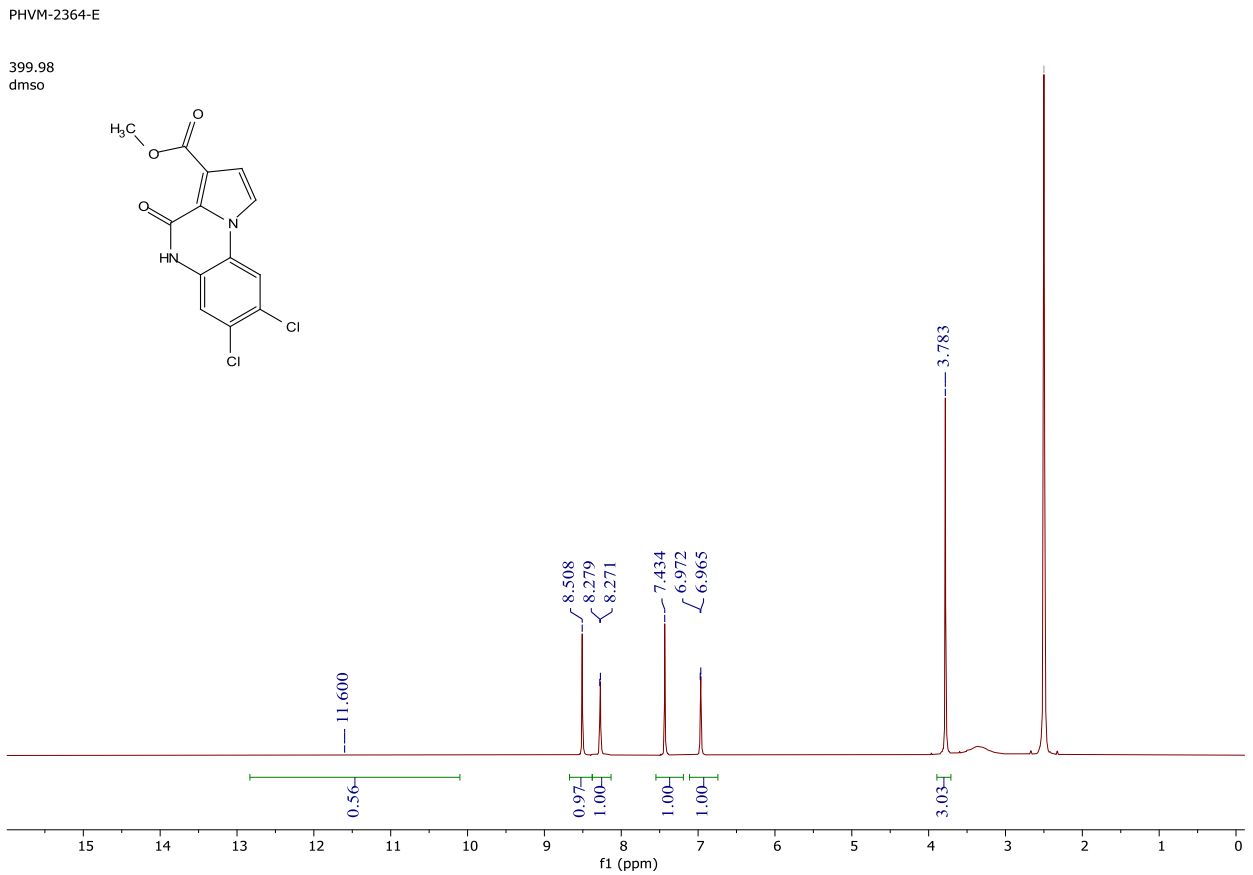


Figure S70. [1]H NMR spectrum of methyl 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5c**) in DMSO-d_6

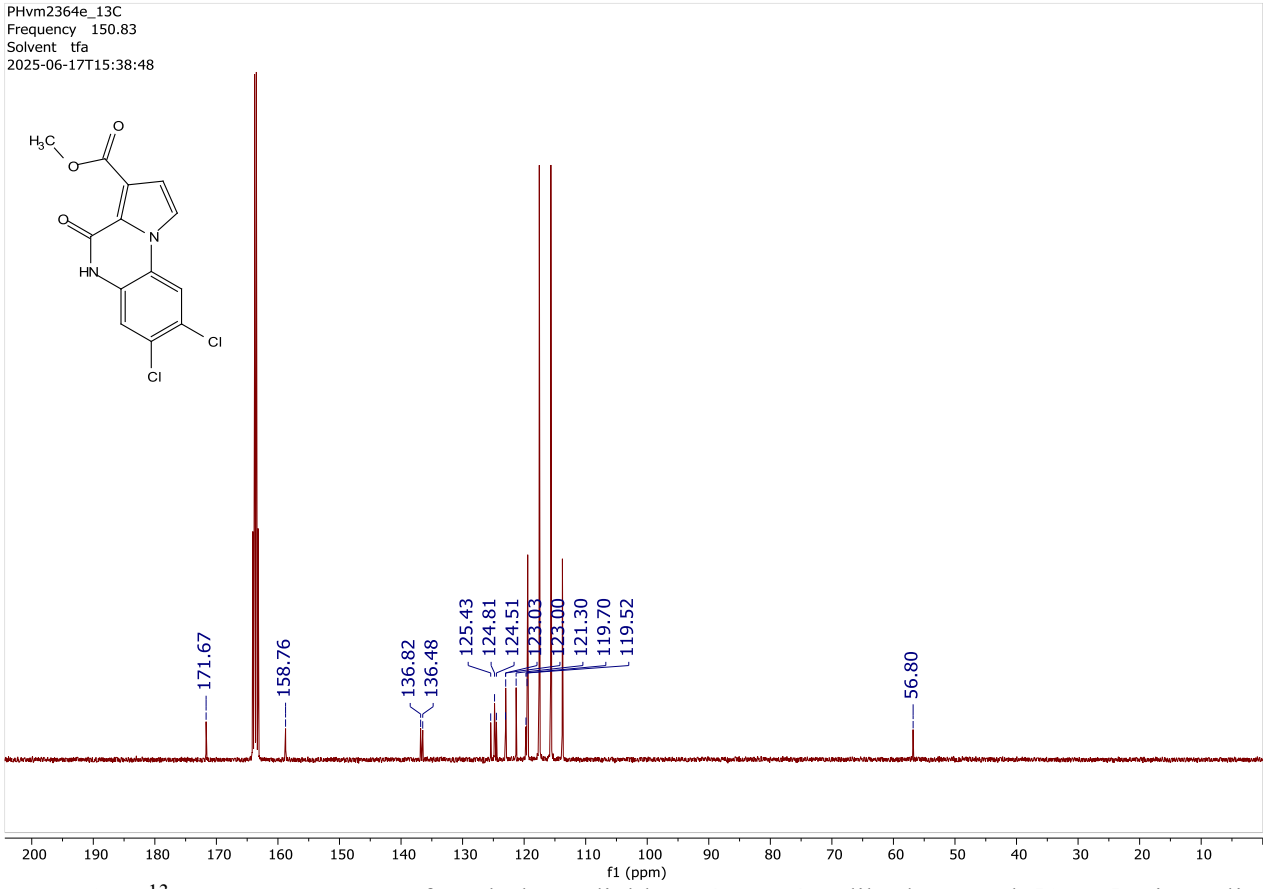
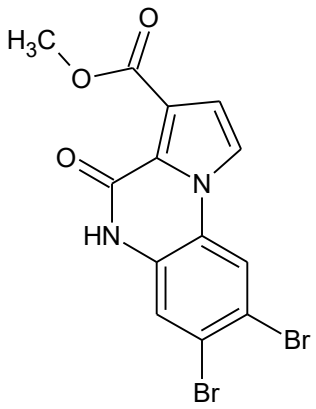


Figure S71. [13]C NMR spectrum of methyl 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5c**) in TFA-d_1



Chemical characterization of methyl 7,8-dibromo-4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylate (**5d**). Gray solid (3.840 g, 96%). mp 278-279 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.79 (3H, s, CH_3O), 6.97 (1H, d, $^{3}J_{HH}$ 2.9 Hz, CH pyrrole), 7.58 (1H, s, CH aromatic), 8.31 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole) 8.60 (1H, s, CH aromatic), 11.58 (1H, s, NH). ^{13}C NMR (DMSO-d_6, 126 MHz): δ_C 51.81 (CH_3O), 114.84, 116.16, 118.41, 119.08, 120.05, 120.27, 120.53, 121.44, 122.46, 129.47, 153.06 (CO-NH), 163.87 (COOCH$_3$). ESI-MS: m/z 402.8 $[M+H]^+$. Anal. calcd for $C_{13}H_8Br_2N_2O_3$ (400.02): C, 39.03; H, 2.02; N, 7.00. Found: C, 39.24; H, 2.05; N, 6.87.

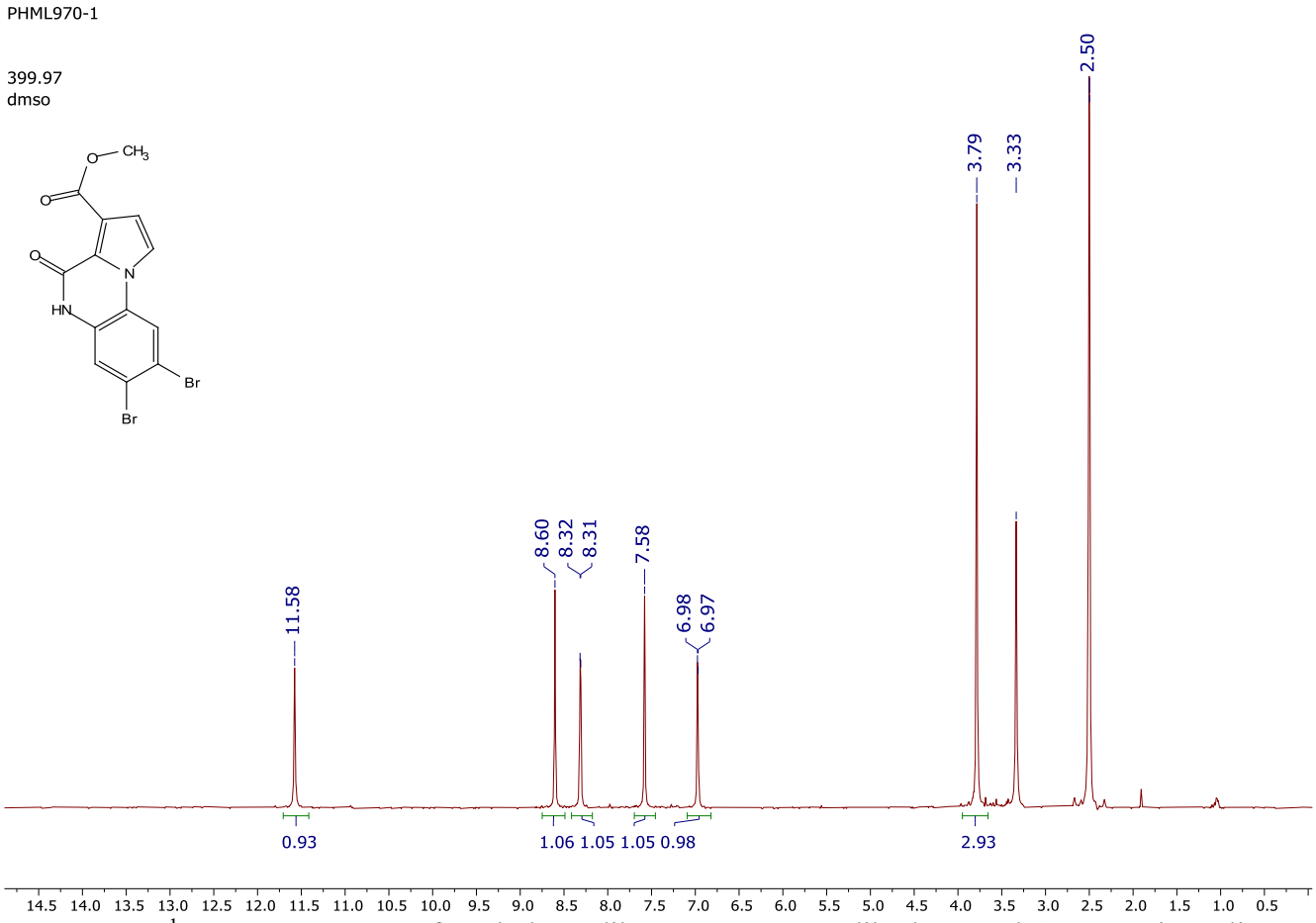


Figure S72. ^{1}H NMR spectrum of methyl 7,8-dibromo-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5d**) in DMSO-d_6

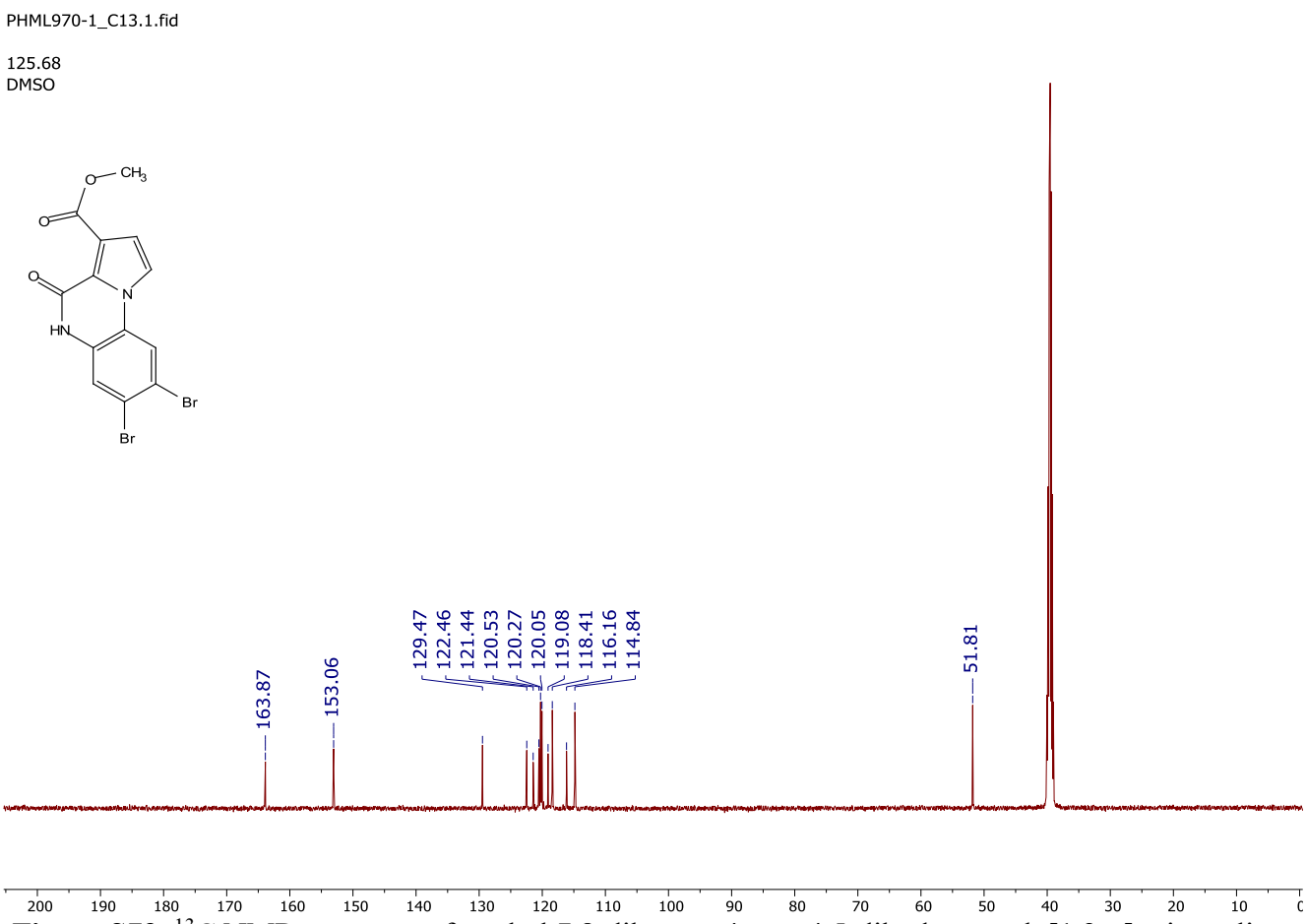
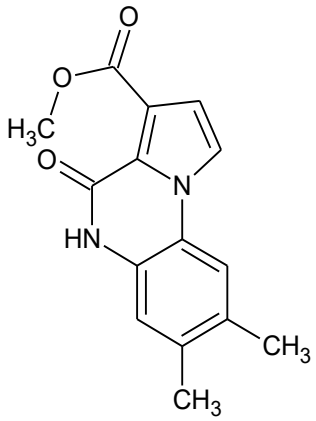


Figure S73. ^{13}C NMR spectrum of methyl 7,8-dibromo-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5d**) in DMSO-d_6



Chemical characterization of methyl 7,8-dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-3-carboxylate (**5e**). Light yellow solid (2.649 g, 98%). mp 284-285 (decomp.) °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 2.24 (3H, s, CH_3), 2.28 (3H, s, CH_3), 3.78 (3H, s, CH_3O), 6.92 (1H, d, *J*=3.0 Hz, CH pyrrole), 7.06 (1H, s, CH aromatic), 7.88 (1H, s, CH aromatic), 8.12 (1H, d, *J*=3.0 Hz, CH pyrrole), 11.23 (1H, s, NH). ^{13}C NMR (DMSO-d_6, 126 MHz): δ_C 19.01 + 19.15 ($2CH_3$), 51.62 (CH_3O), 114.35, 115.87, 116.64, 116.93, 117.94, 119.72, 121.71, 126.51, 131.12, 134.96, 153.44 (CO-NH), 164.17 ($\underline{C}OOCH_3$). ESI-MS: m/z 271.2 $[M+H]^+$.Anal. calcd for $C_{15}H_{14}N_2O_3$ (270.28): C, 66.66; H, 5.22; N, 10.36. Found: C, 66.79; H, 5.17; N, 10.22.

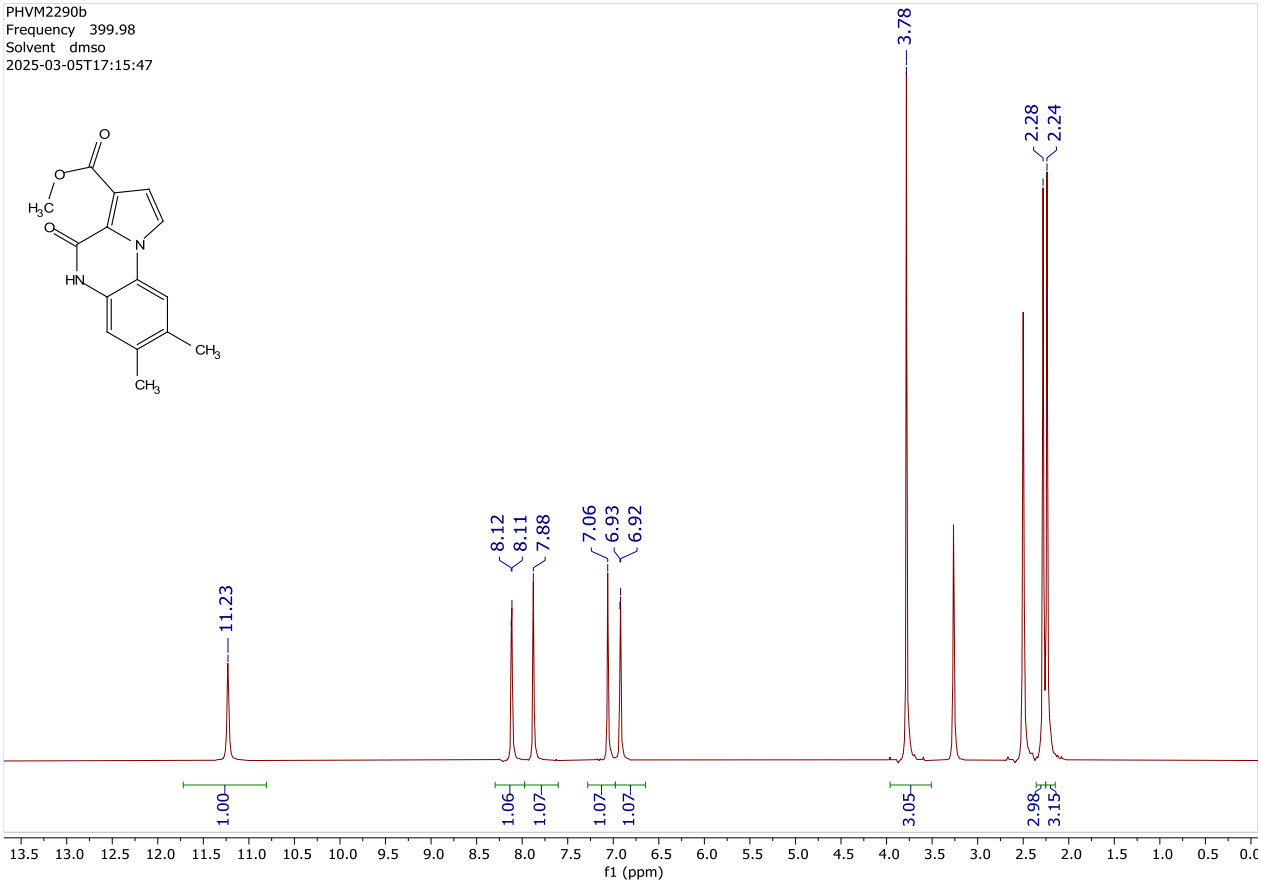


Figure S74. [1]H NMR spectrum of methyl 7,8-dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5e**) in DMSO-d_6

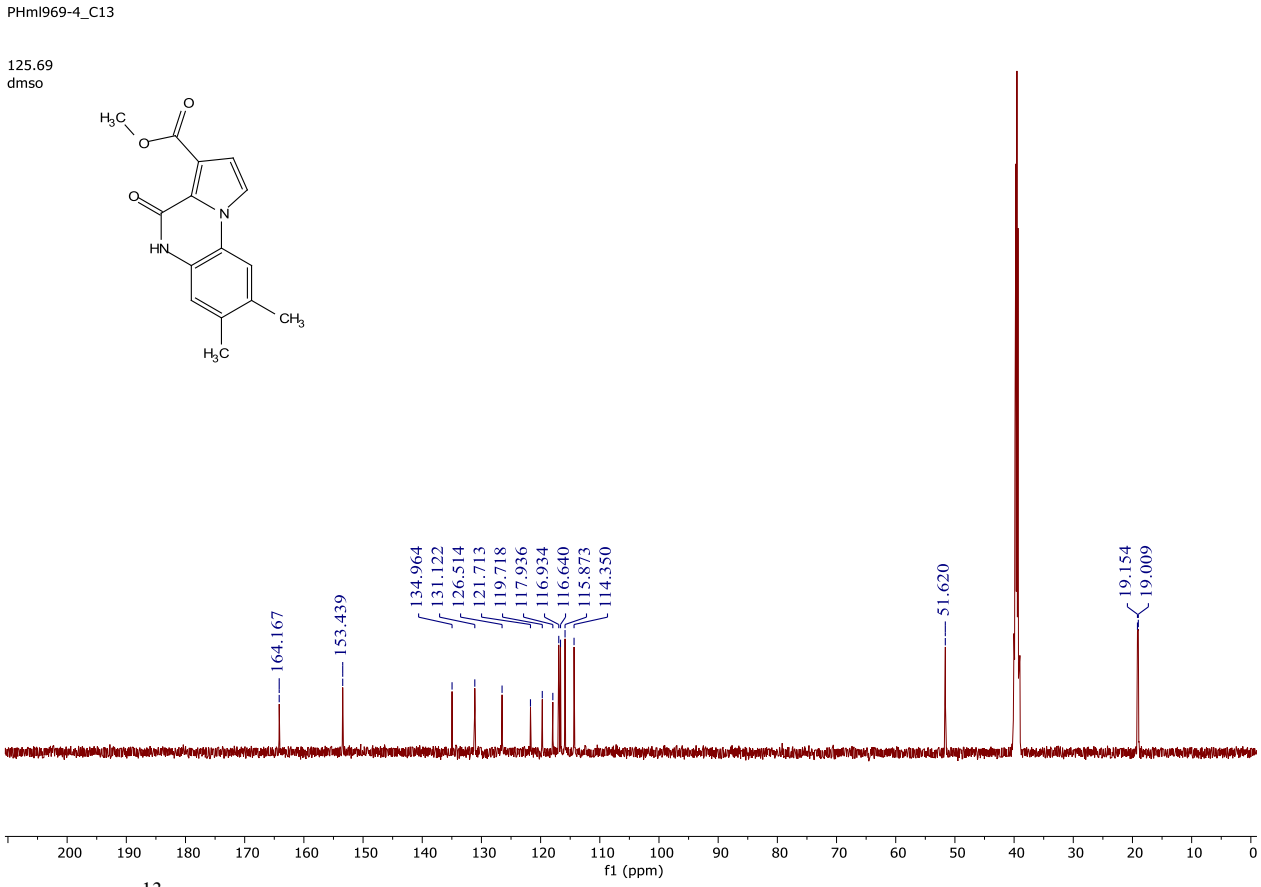
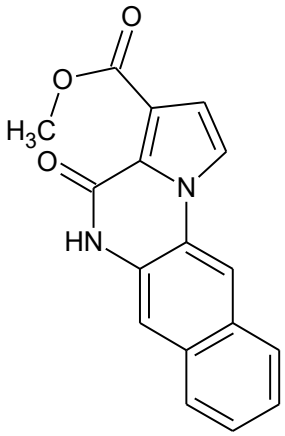


Figure S75. [13]C NMR spectrum of methyl 7,8-dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5e**) in DMSO-d_6



Chemical characterization of methyl 4-oxo-4,5-dihydrobenzo[g]pyrrolo[1,2-a]quinoxaline-3-carboxylate (**5f**). Light yellow solid (2.835 g, 97%). mp 283-284 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.81 (3H, s, CH_3O), 7.01 (1H, s, CH pyrrole), 7.45 – 7.52 (2H, m, 2CH aromatic), 7.69 (1H, s, CH aromatic), 7.87 – 7.93 (2H, m, 2CH aromatic), 8.37 (1H, s, CH pyrrole), 8.69 (1H, s, CH aromatic), 11.63 (1H, s, NH). ^{13}C NMR (DMSO-d_6, 126 MHz): δ_C 51.82 (CH_3O), 111.71, 112.92, 114.61, 118.21, 119.30, 121.55, 122.38, 125.20, 126.42, 126.69, 127.40, 128.28, 128.82, 131.16, 153.54 (CO-NH), 164.15 ($\underline{C}OOCH_3$). ESI-MS: m/z 293.0 $[M+H]^+$. Anal. calcd for $C_{17}H_{12}N_2O_3$ (292.29): C, 69.86; H, 4.14; N, 9.58. Found: C, 69.68; H, 4.06; N, 9.71.

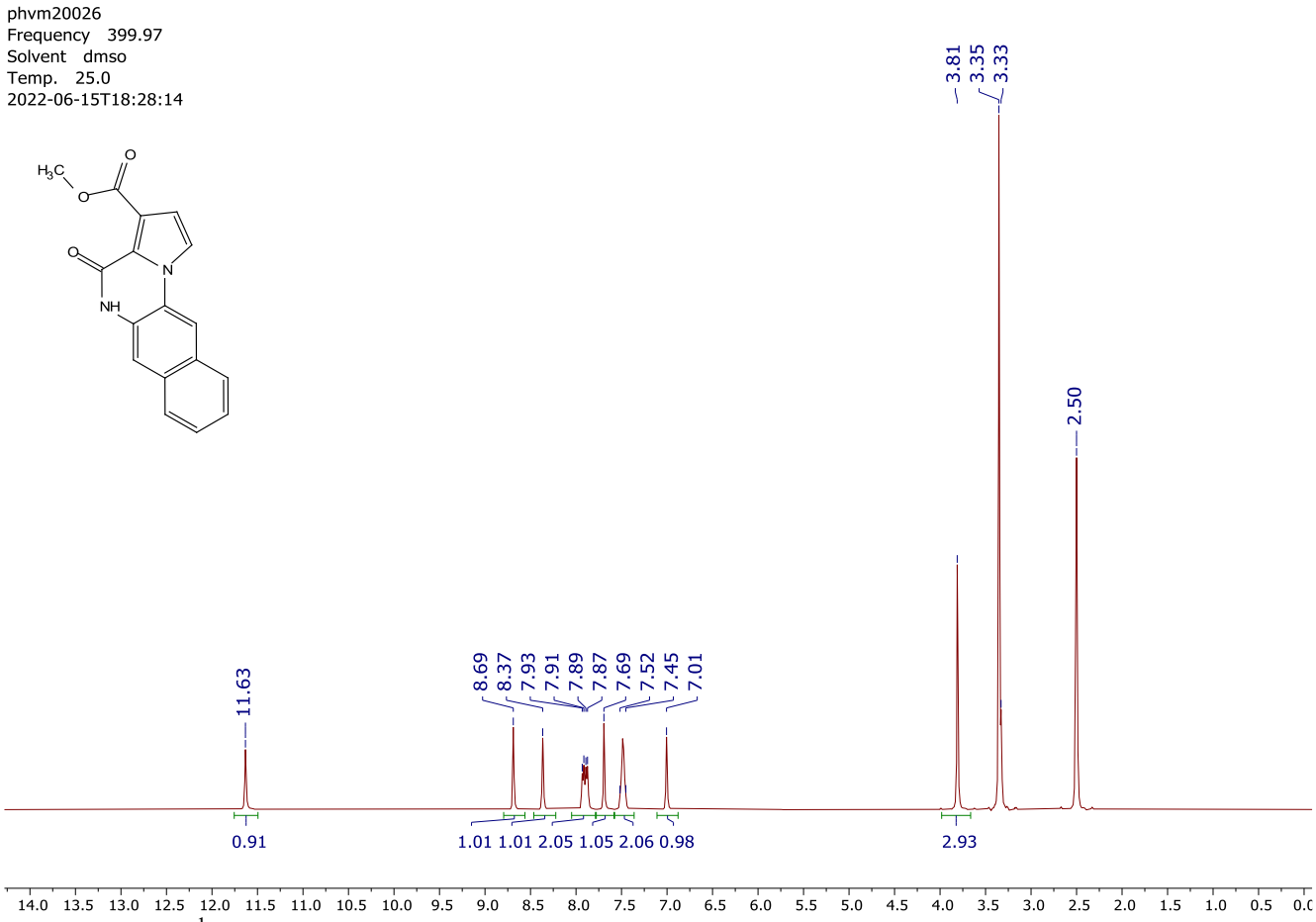


Figure S76. ^{1}H NMR spectrum of methyl 4-oxo-4,5-dihydrobenzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5f**) in DMSO-d_6

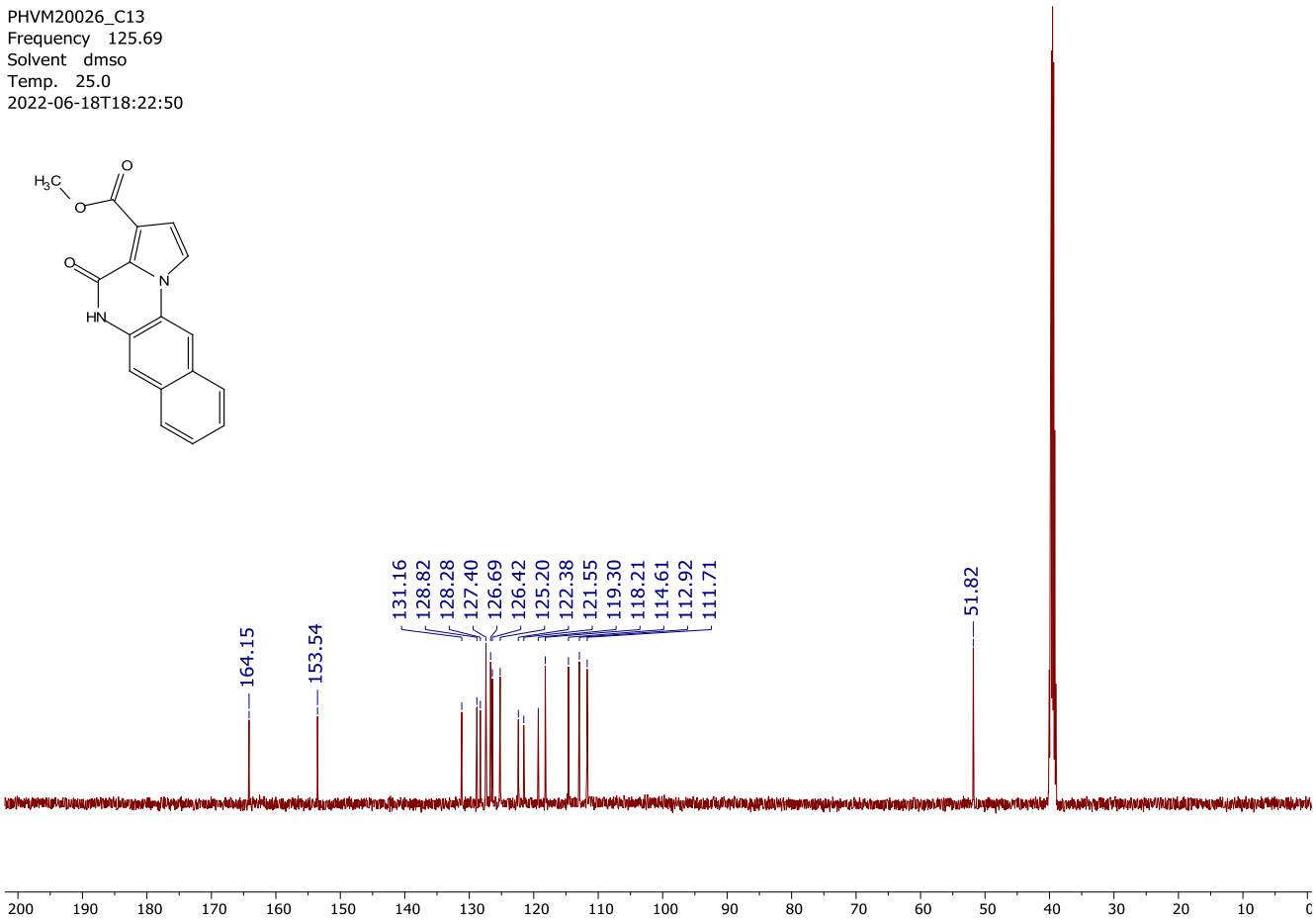
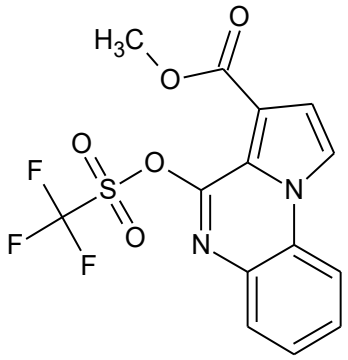


Figure S77. ^{13}C NMR spectrum of methyl 4-oxo-4,5-dihydrobenzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**5f**) in DMSO-d_6

Chemical characterization of 6a-f



Chemical characterization of methyl 4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**6a**). Light yellow solid (1.628 g, 87%). mp 163-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.98 (3H, s, CH_3O), 7.44 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole), 7.57 (1H, t, $^3J_{HH}$ 7.6 Hz, CH aromatic), 7.67 (1H, t, $^3J_{HH}$ 7.8 Hz, CH aromatic), 7.93 (2H, d, $^3J_{HH}$ 9.1 Hz, CH aromatic), 8.04 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole). ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 52.25 (CH_3O), 113.84, 114.14, 116.65, 116.81, 118.49, 118.70 (q, $^1J_{CF}$ 321.1 Hz, CF_3), 126.49, 127.10, 129.72, 129.75, 132.51, 146.09, 163.04 (COO-CH_3). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -74.16. EI-MS: m/z 374 $[M]^+$. Anal. calcd for $C_{14}H_9F_3N_2O_5S$ (374.29): C, 44.92; H, 2.42; N, 7.48; S, 8.57. Found: C, 45.11; H, 2.39; N, 7.55; S, 8.68.

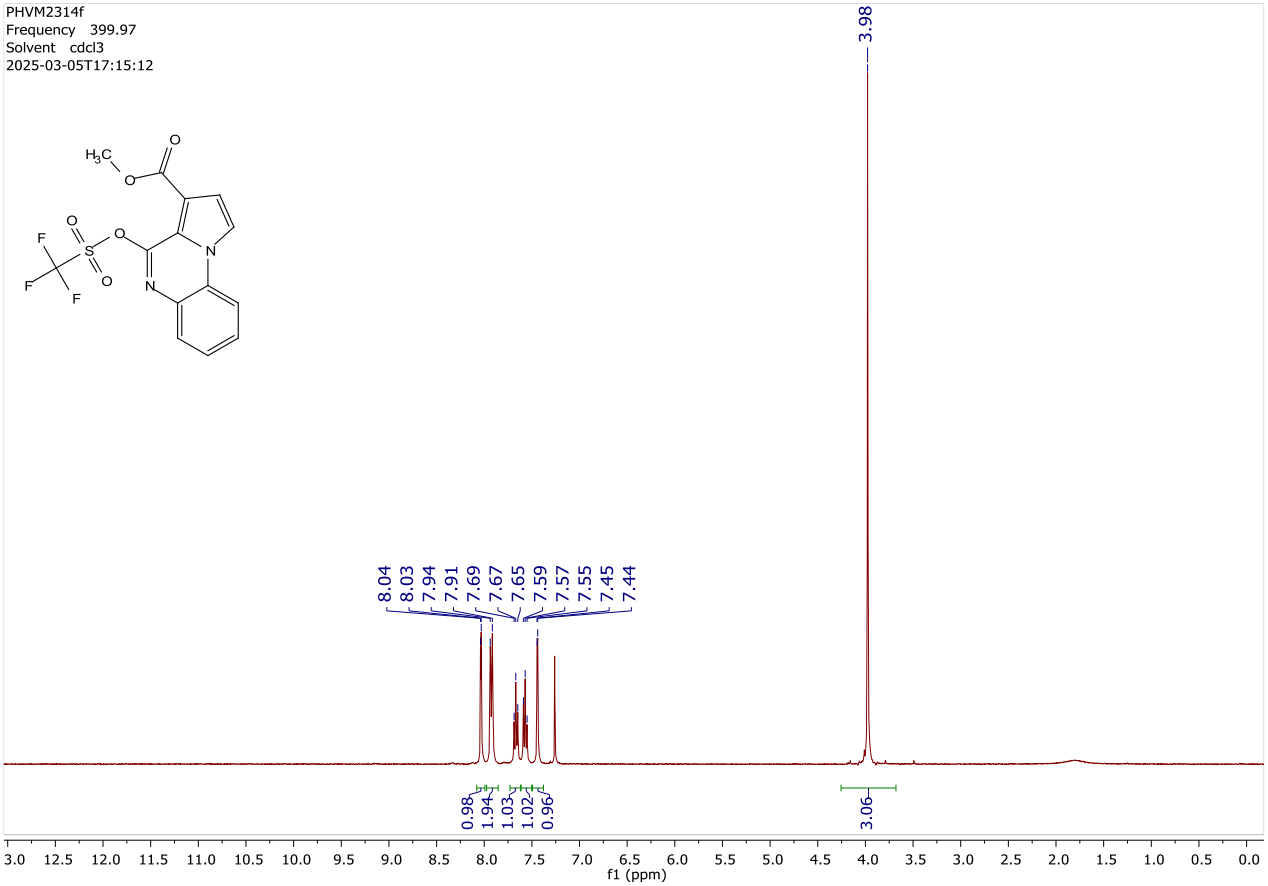


Figure S78. ^{1}H NMR spectrum of methyl 4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6a**) in $CDCl_3$

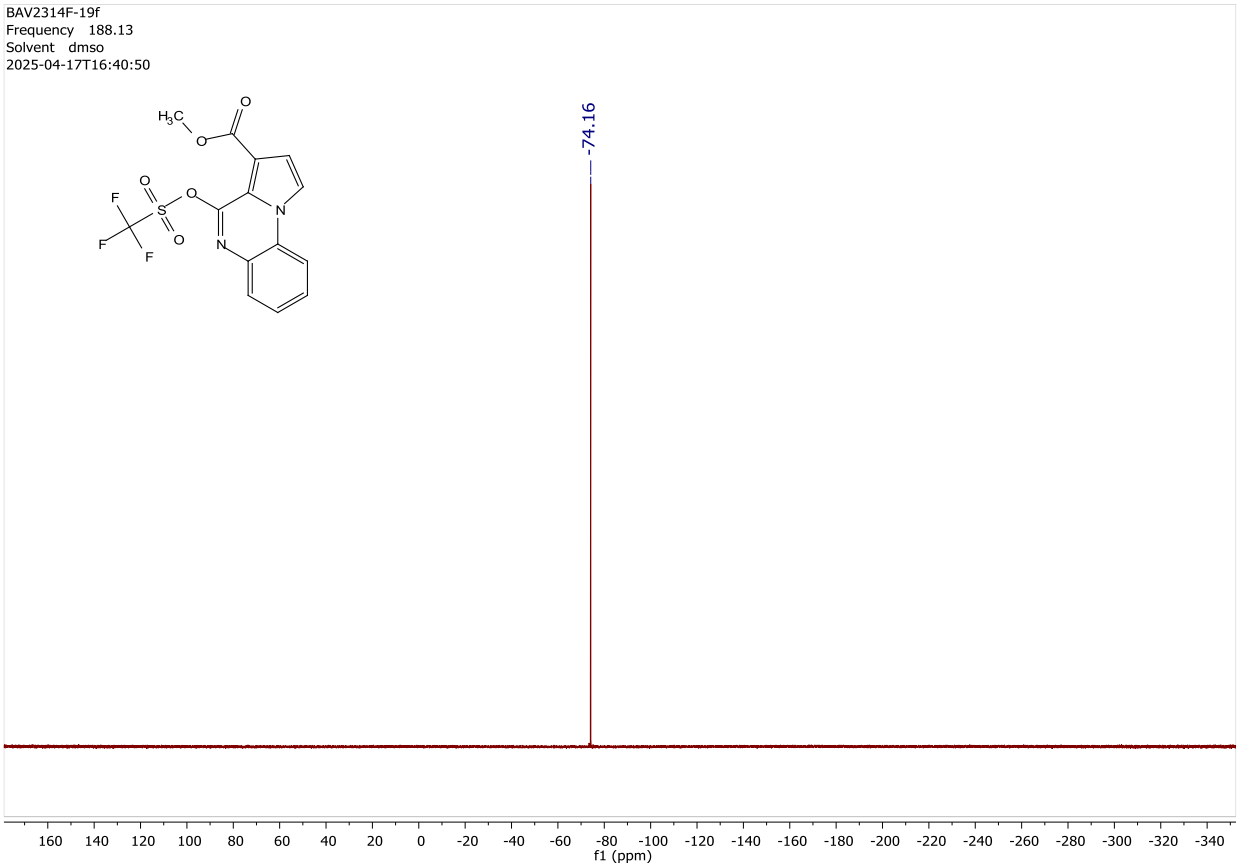


Figure S79. ^{19}F NMR spectrum of methyl 4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6a**) in DMSO-d_6

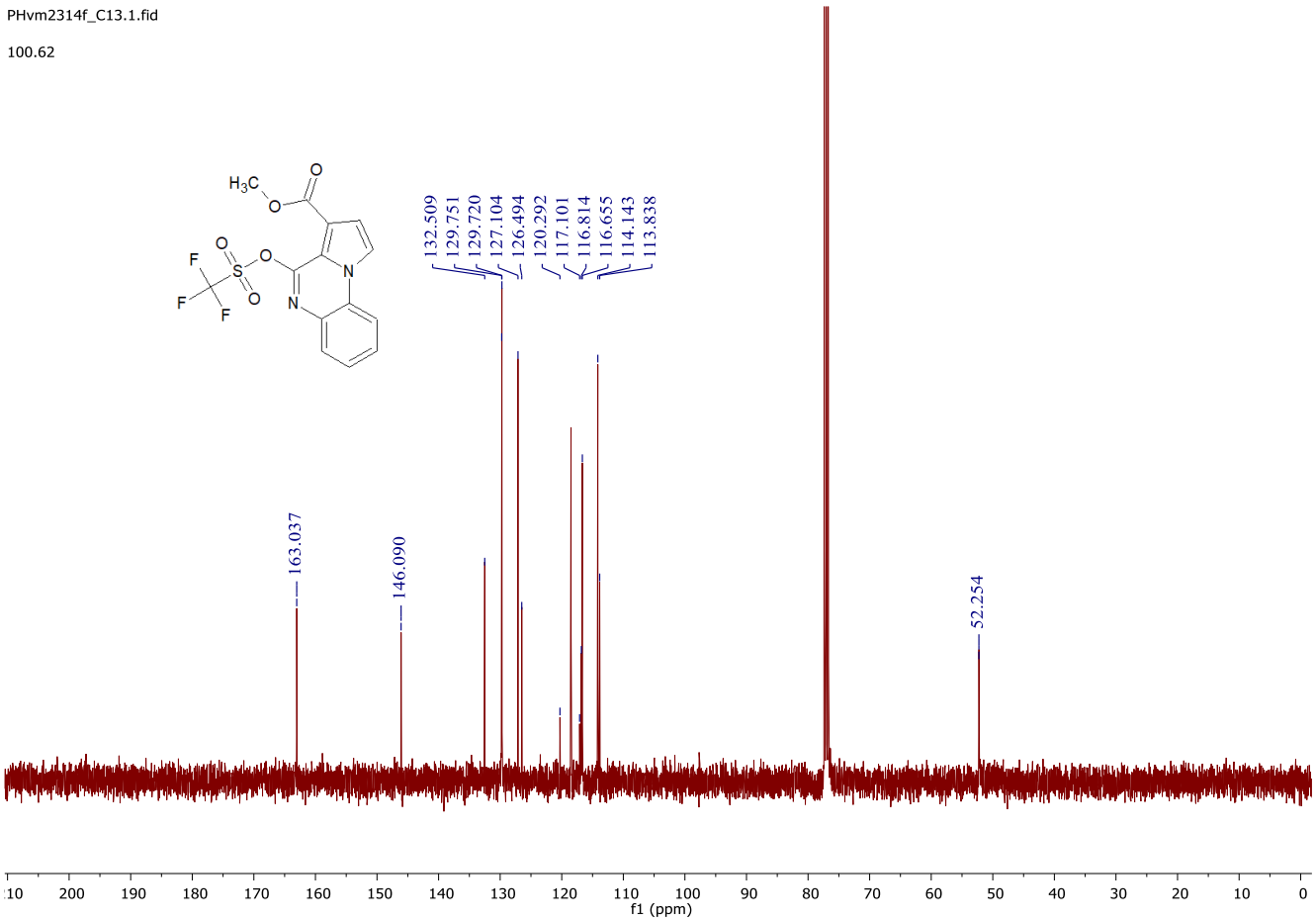
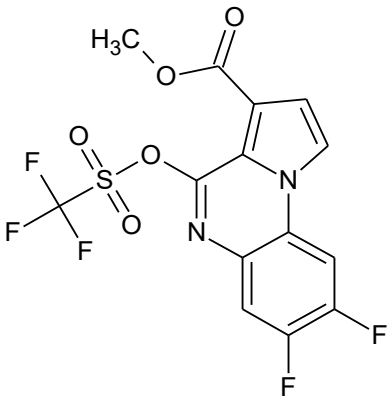


Figure S80. ^{13}C NMR spectrum of methyl 4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6a**) in $CDCl_3$



Chemical characterization of methyl 7,8-difluoro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**6b**). Light yellow solid (1.785 g, 87%). mp 230-231 °C. IR (solid, KBr, νmax, cm^{-1}): 1741, 1402, 1215, 1125, 813, 739, 597, 579. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.97 (3H, s, CH_3O), 7.47 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole), 7.72 – 7.79 (2H, m, 2CH aromatic), 7.90 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 52.54 (OCH_3) 103.26 (d, $^2J_{CF}$ 22.9 Hz, CH aromatic), 114.82, 116.65, 117.12, 117.63 (d, $^2J_{CF}$ 18.8 Hz, CH aromatic), 118.77 (q, $^1J_{CF}$ 321.7 Hz, CF_3), 119.26, 123.40 (d, $^3J_{CF}$ 8.2 Hz, C aromatic), 129.40 (d, $^3J_{CF}$ 9.7 Hz, C aromatic), 146.84 (C=N), 149.43 (dd, $^1J_{CF}$ 251.4, $^2J_{CF}$ 13.7 Hz, CF aromatic), 151.17 (dd, $^1J_{CF}$ 255.5, $^2J_{CF}$ 14.9 Hz, CF aromatic), 162.86 (COO-CH_3). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -139.15 (ddd, $^3J_{FF}$ 22.3, $^3J_{HF}$ 10.6, $^4J_{HF}$ 7.4 Hz), -133.31 (ddd, $^3J_{FF}$ 22.2, $^3J_{HF}$ 11.2, $^4J_{HF}$ 8.2 Hz), -74.26. EI-MS: m/z 410 $[M]^+$. Anal. calcd for $C_{14}H_7F_5N_2O_5S$ (410.27): C, 40.98; H, 1.72; N, 6.83; S, 7.82. Found: C, 41.11; H, 1.69; N, 6.75; S, 7.98.

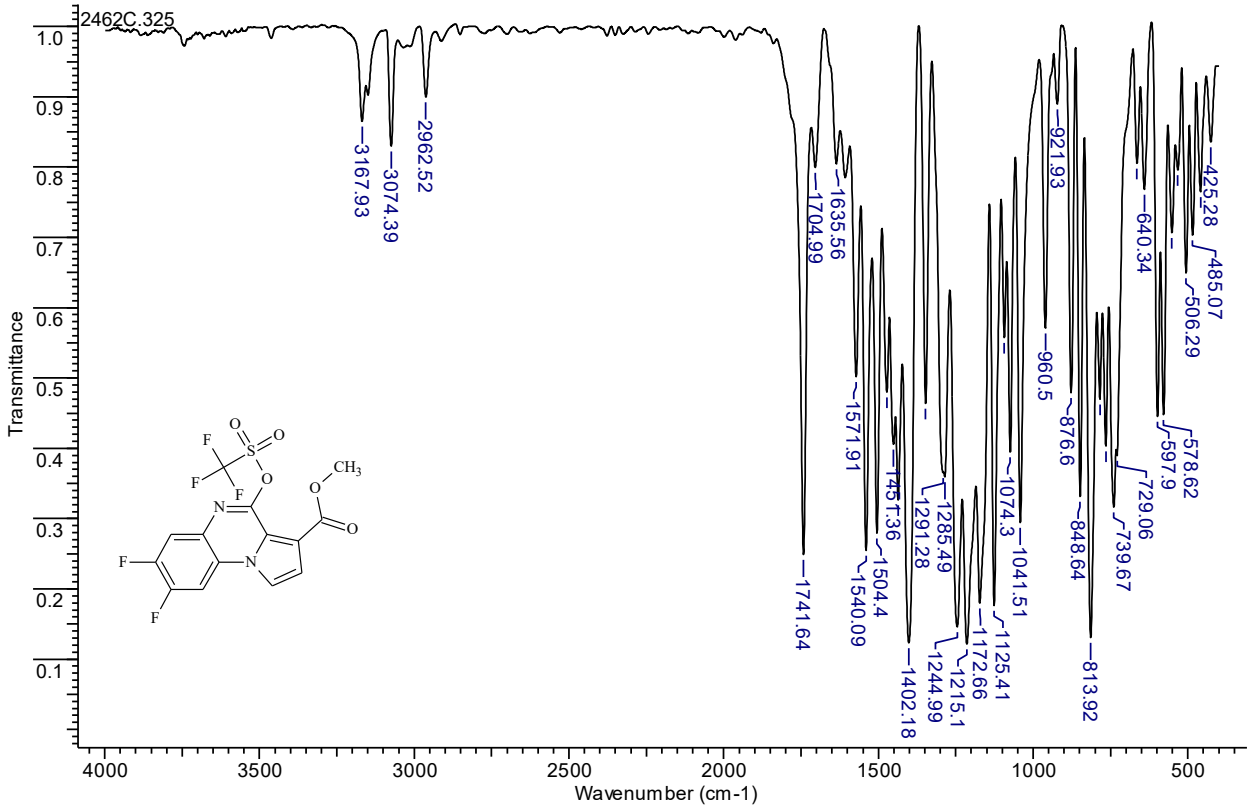


Figure S81. IR spectrum of methyl 7,8-difluoro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6b**) in KBr pellet

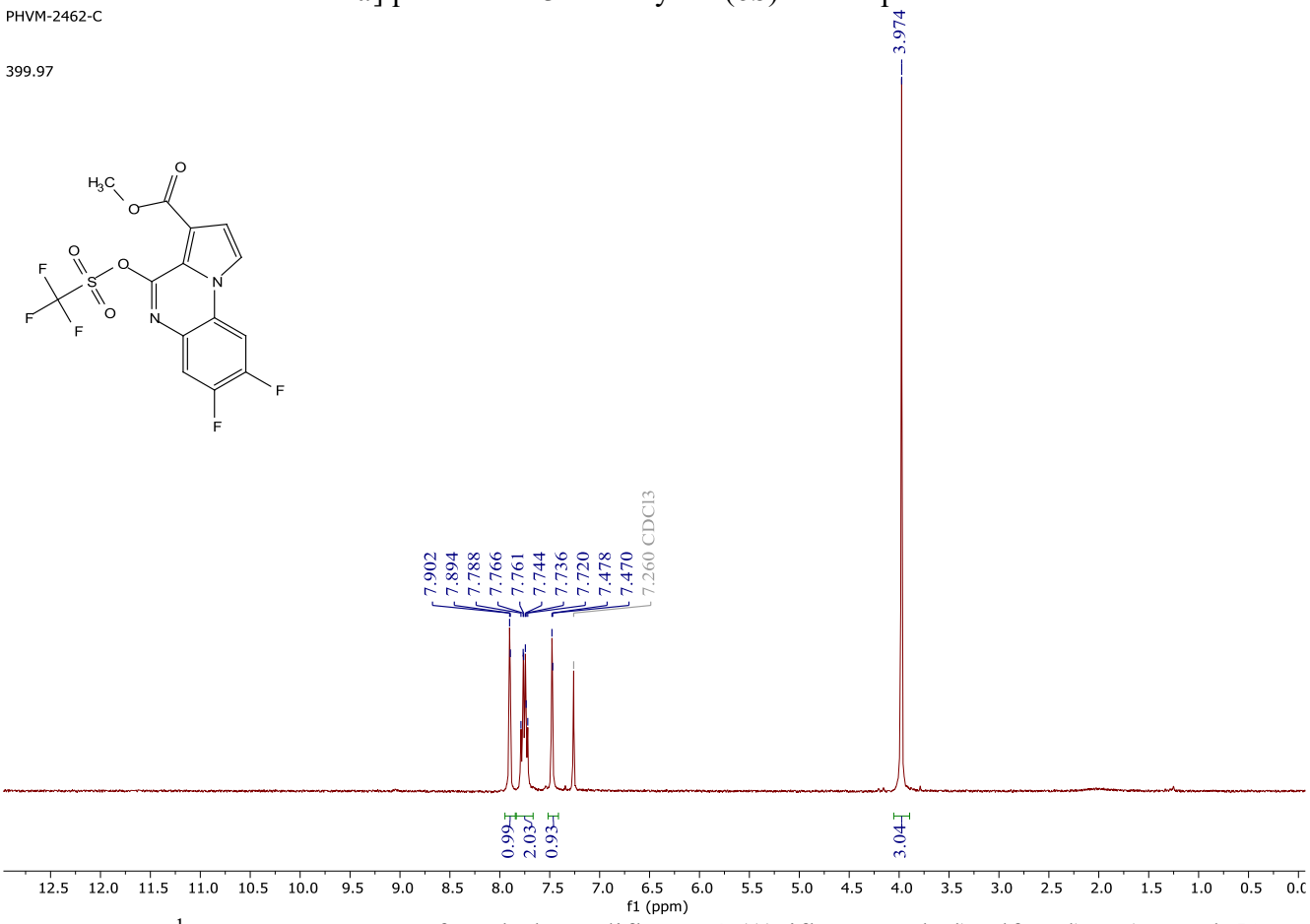


Figure S82. ^{1}H NMR spectrum of methyl 7,8-difluoro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6b**) in $CDCl_3$

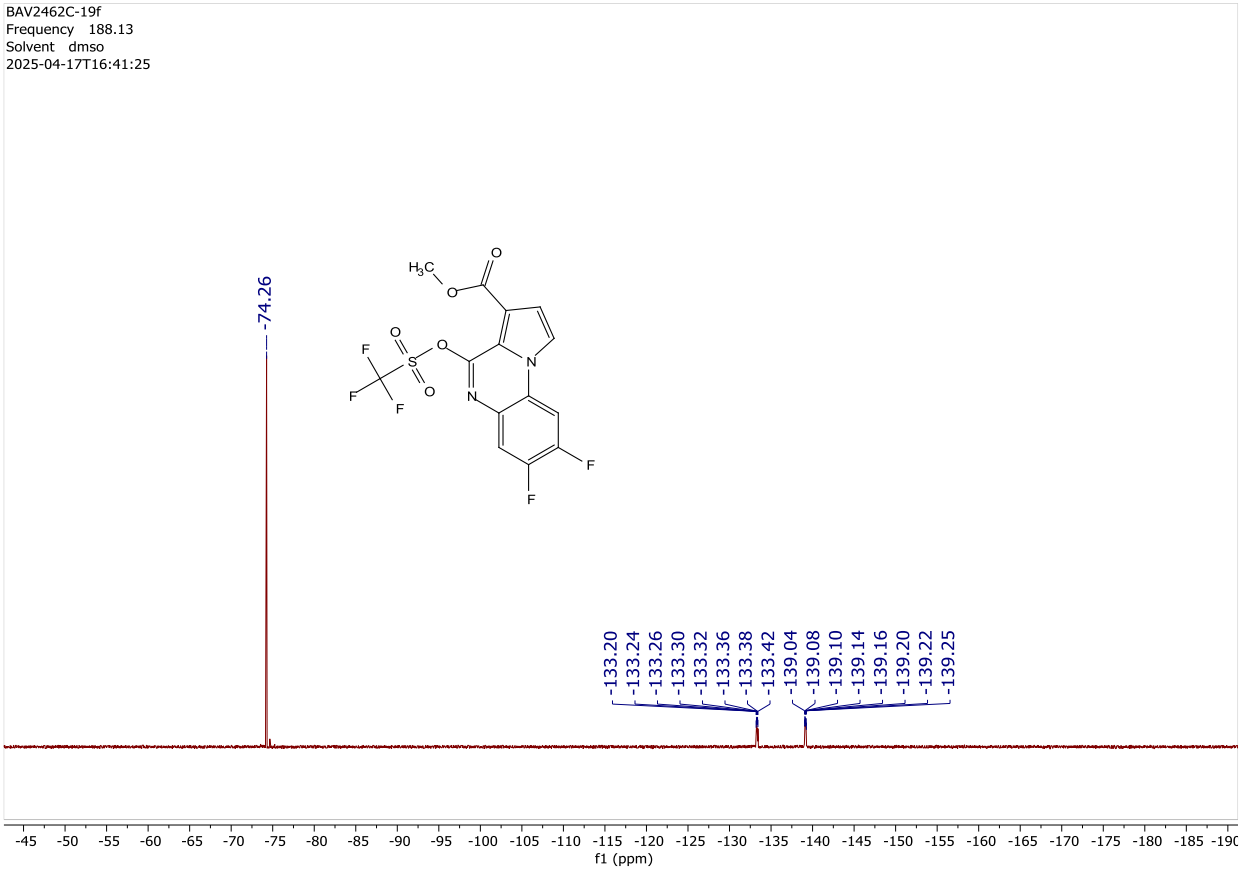


Figure S83. ^{19}F NMR spectrum of methyl 7,8-difluoro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6b**) in DMSO-d_6

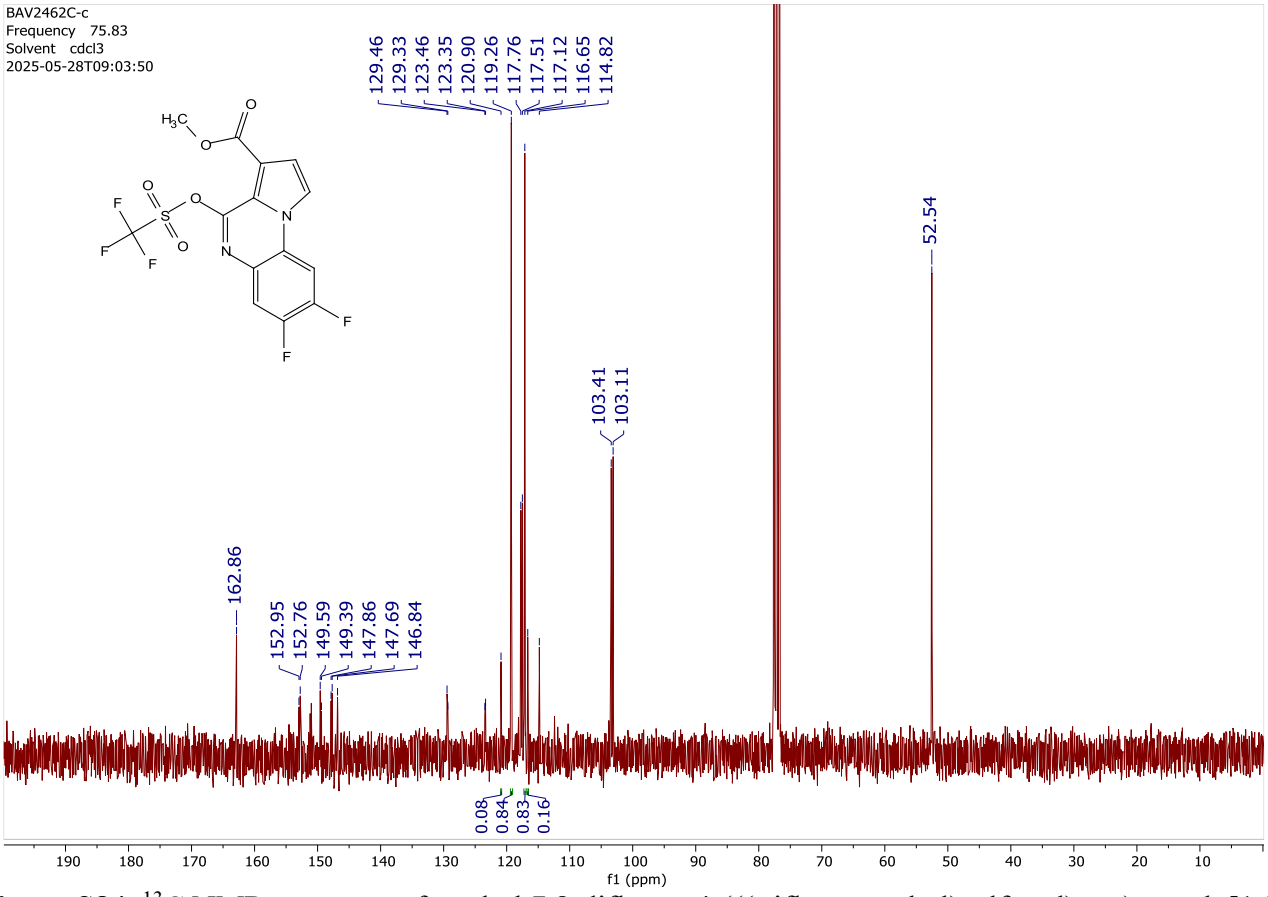
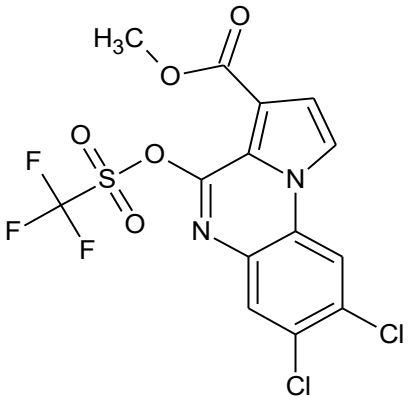


Figure S84. ^{13}C NMR spectrum of methyl 7,8-difluoro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6b**) in $CDCl_3$



Chemical characterization of methyl 7,8-dichloro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**6c**). Light yellow solid (1.861 g, 84%). mp 242-243 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.97 (3H, s, CH_3O), 7.46 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.96 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 8.03 (1H, s, CH aromatic), 8.03 (1H, s, CH aromatic). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 52.58 (CH_3O), 115.32, 116.01, 116.69, 117.34, 118.76 (q, $^{1}J_{CF}$ 321.1 Hz, CF_3), 119.32, 125.76, 130.76, 131.59, 132.04, 134.06, 147.27 (C=N), 162.80 (C=O). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -74.32. ESI-MS: m/z 443.0 $[M+H]^+$. Anal. calcd for $C_{14}H_7Cl_2F_3N_2O_5S$ (443.18): C, 37.94; H, 1.59; N, 6.32; S, 7.24. Found: C, 38.07; H, 1.62; N, 6.17; S, 7.40.

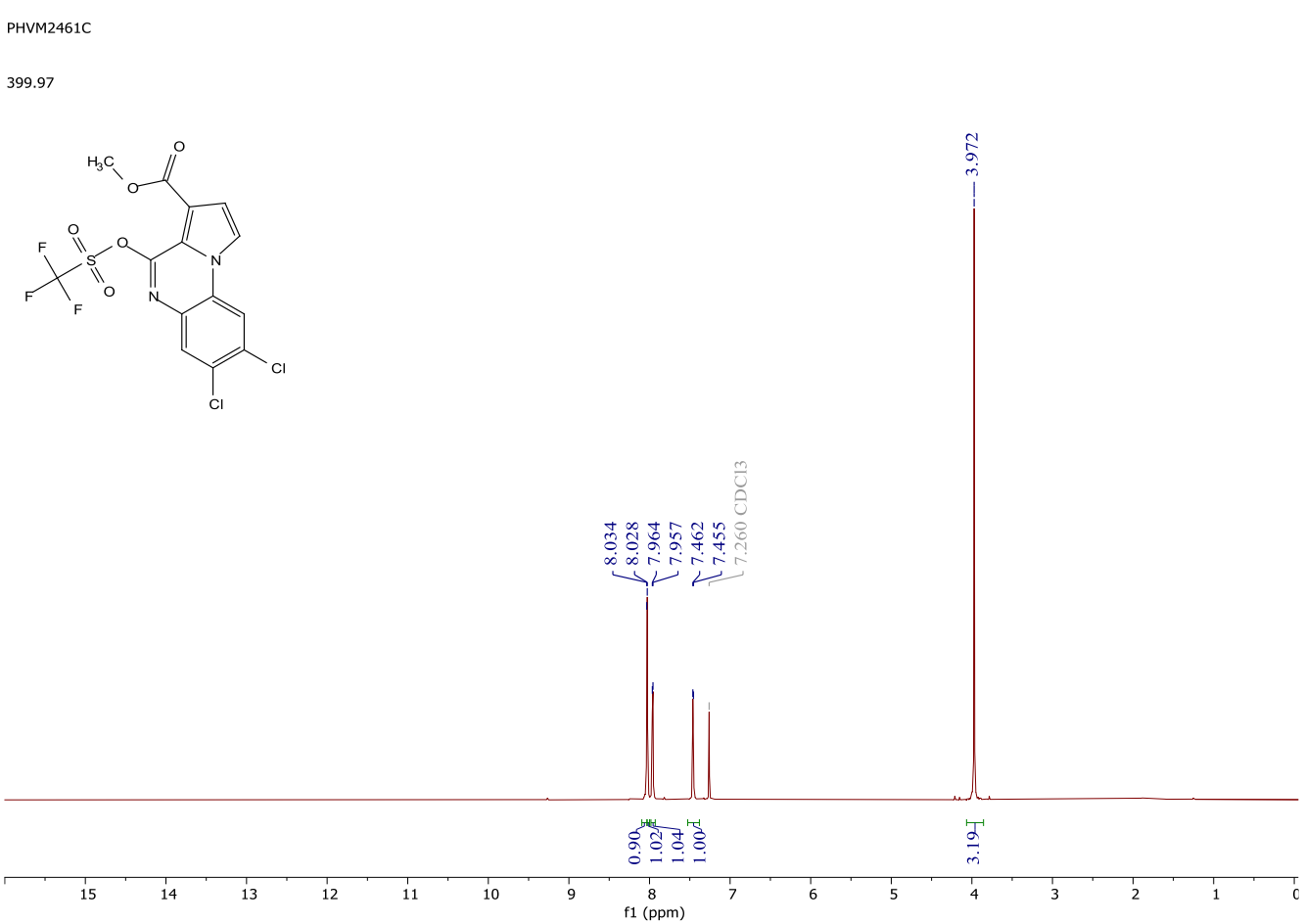


Figure S85. ^{1}H NMR spectrum of methyl 7,8-dichloro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6c**) in $CDCl_3$

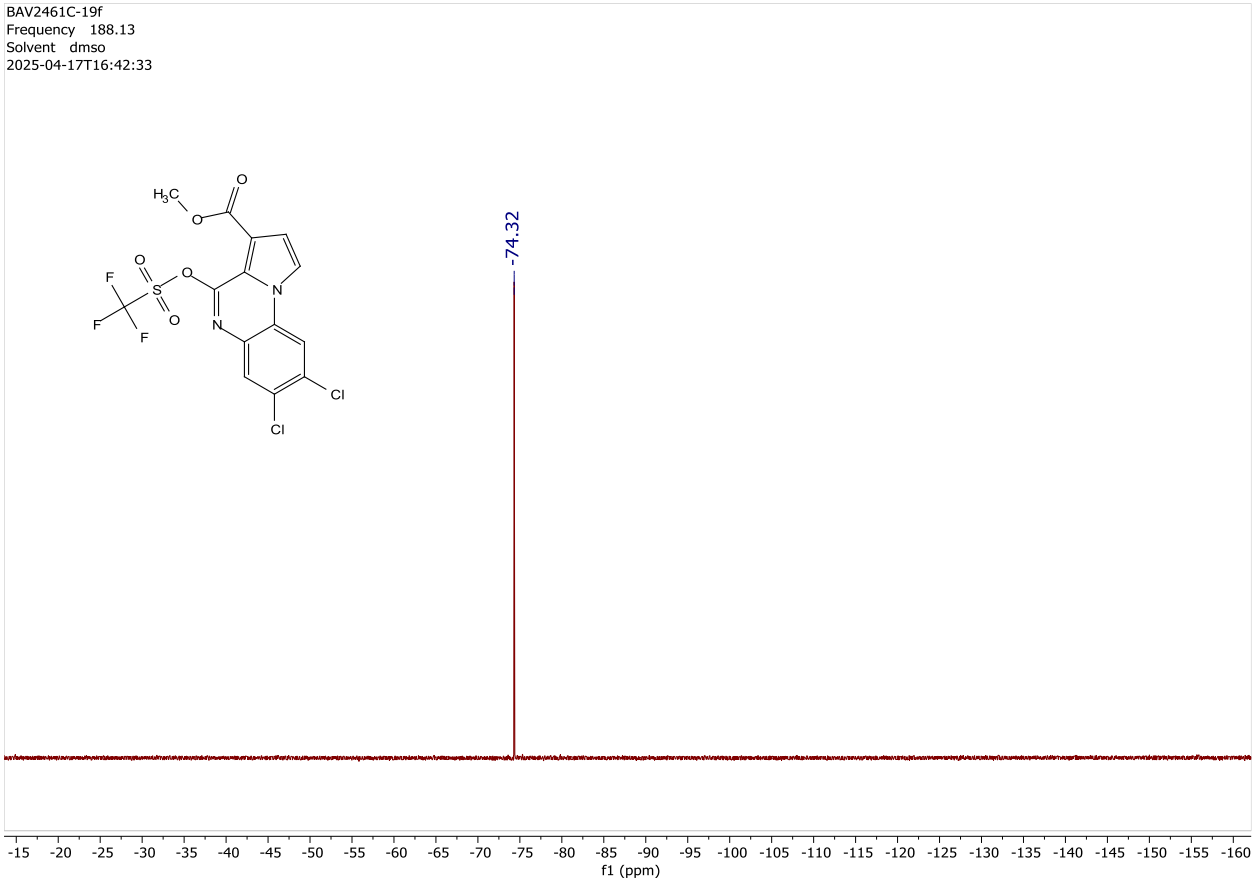


Figure S86. ^{19}F NMR spectrum of methyl 7,8-dichloro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6c**) in DMSO-d_6

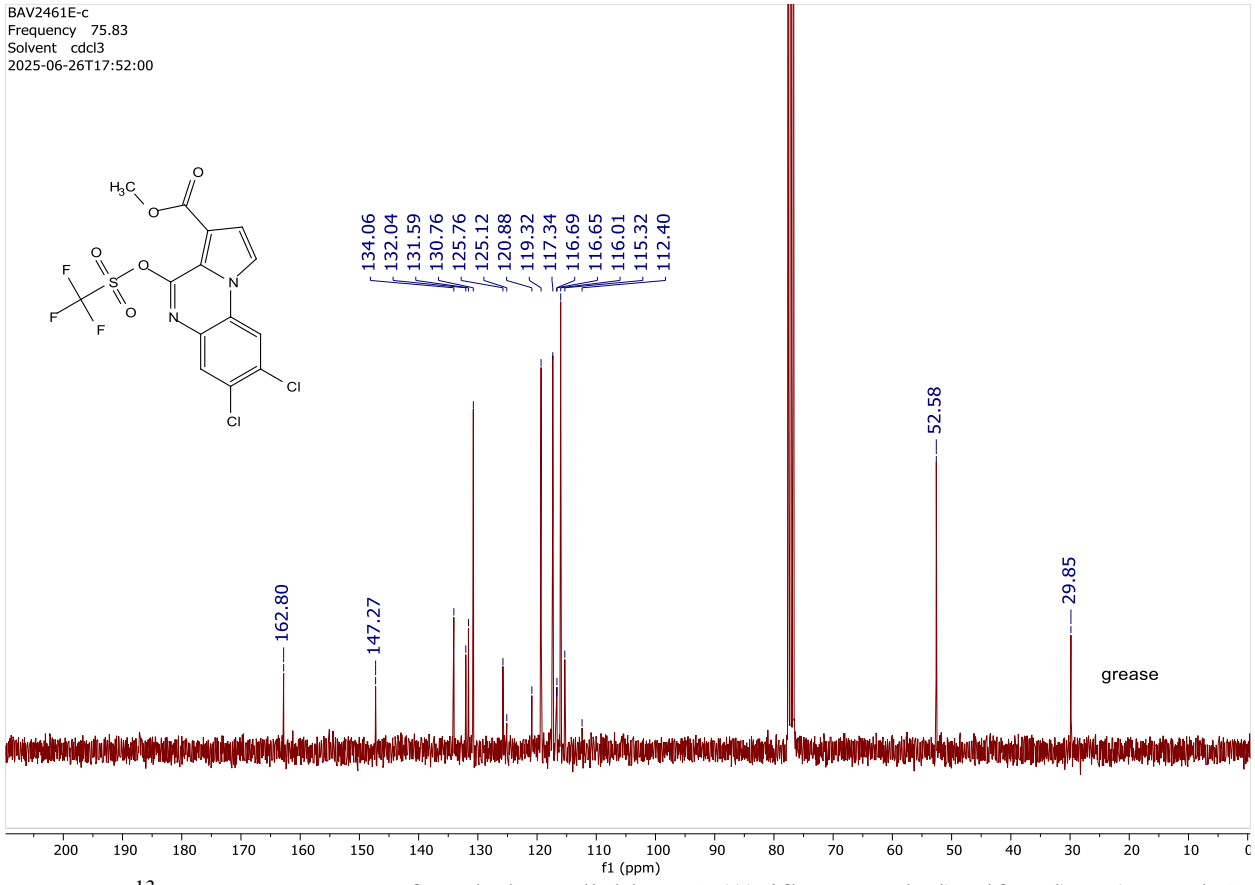
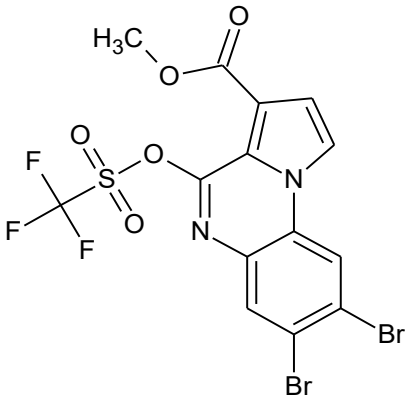


Figure S87. ^{13}C NMR spectrum of methyl 7,8-dichloro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6c**) in $CDCl_3$



Chemical characterization of methyl 7,8-dibromo-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**6d**). Light yellow solid (2.394 g, 90%). mp 236-237 °C. IR (solid, KBr, νmax, cm^{-1}): 1730, 1527, 1407, 1209, 1087, 826, 749, 618. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.97 (3H, s, CH_3O), 7.45 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.97 (1H, d, $^{3}J_{HH}$ 2.9 Hz, CH pyrrole), 8.18 (1H, s, CH aromatic), 8.19 (1H, s, CH aromatic). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 52.58 (CH_3O), 115.40, 116.71, 117.33, 118,75 (q, $^{1}J_{CF}$ 321.2 Hz, CF_3), 119.08, 119.30, 123.14, 125.94, 126.33, 132.64, 133.87, 147.27 (C=N), 162.76 (COOCH$_3$). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -74.34. ESI-MS: m/z 534.8 $[M+H]^+$. Anal. calcd for $C_{14}H_7Br_2F_3N_2O_5S$ (532.08): C, 31.60; H, 1.33; N, 5.26; S, 6.03. Found: C, 31.45; H, 1.35; N, 5.17; S, 6.17.

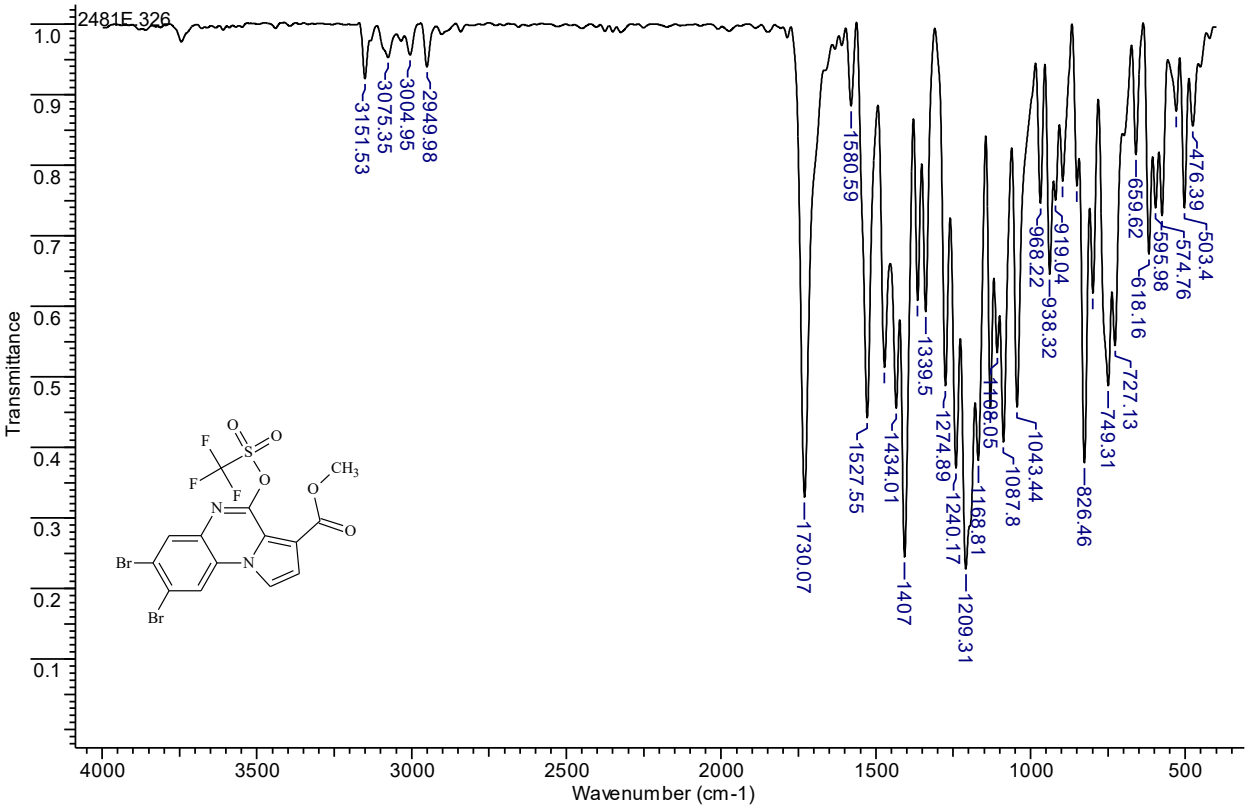


Figure S88. IR spectrum of methyl 7,8-dibromo-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6d**) in KBr pellet

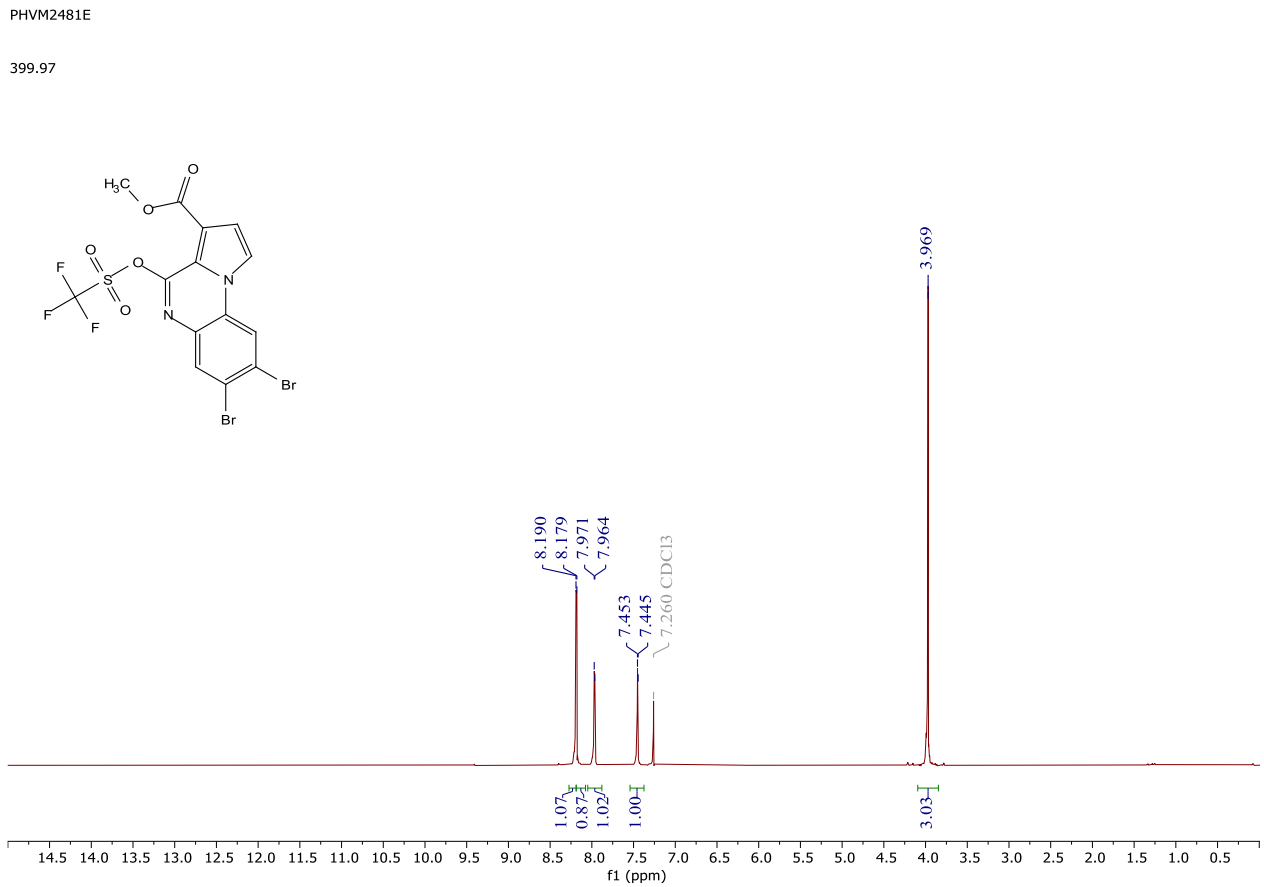


Figure S89. ^{1}H NMR spectrum of methyl 7,8-dibromo-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6d**) in $CDCl_3$

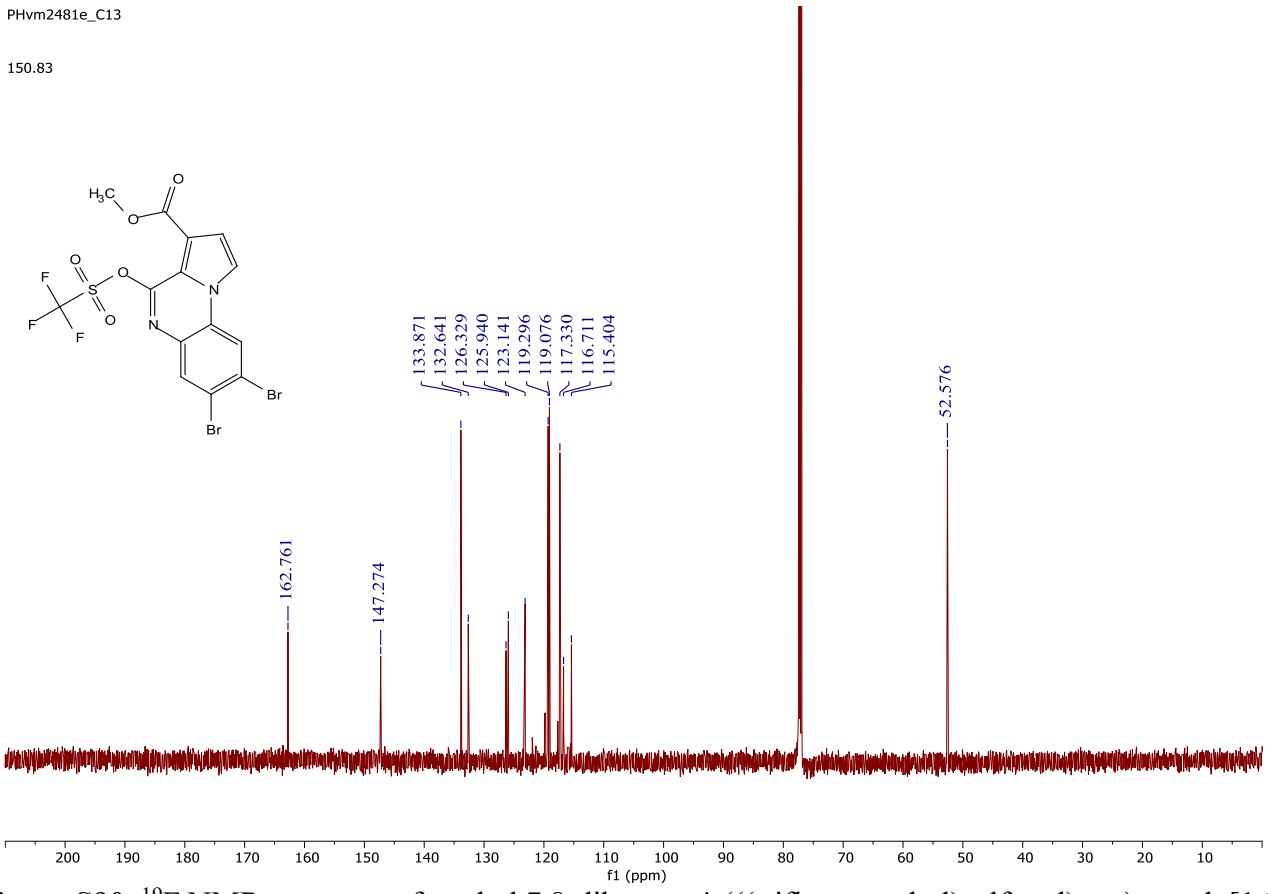


Figure S90. ^{19}F NMR spectrum of methyl 7,8-dibromo-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6d**) in DMSO-d_6

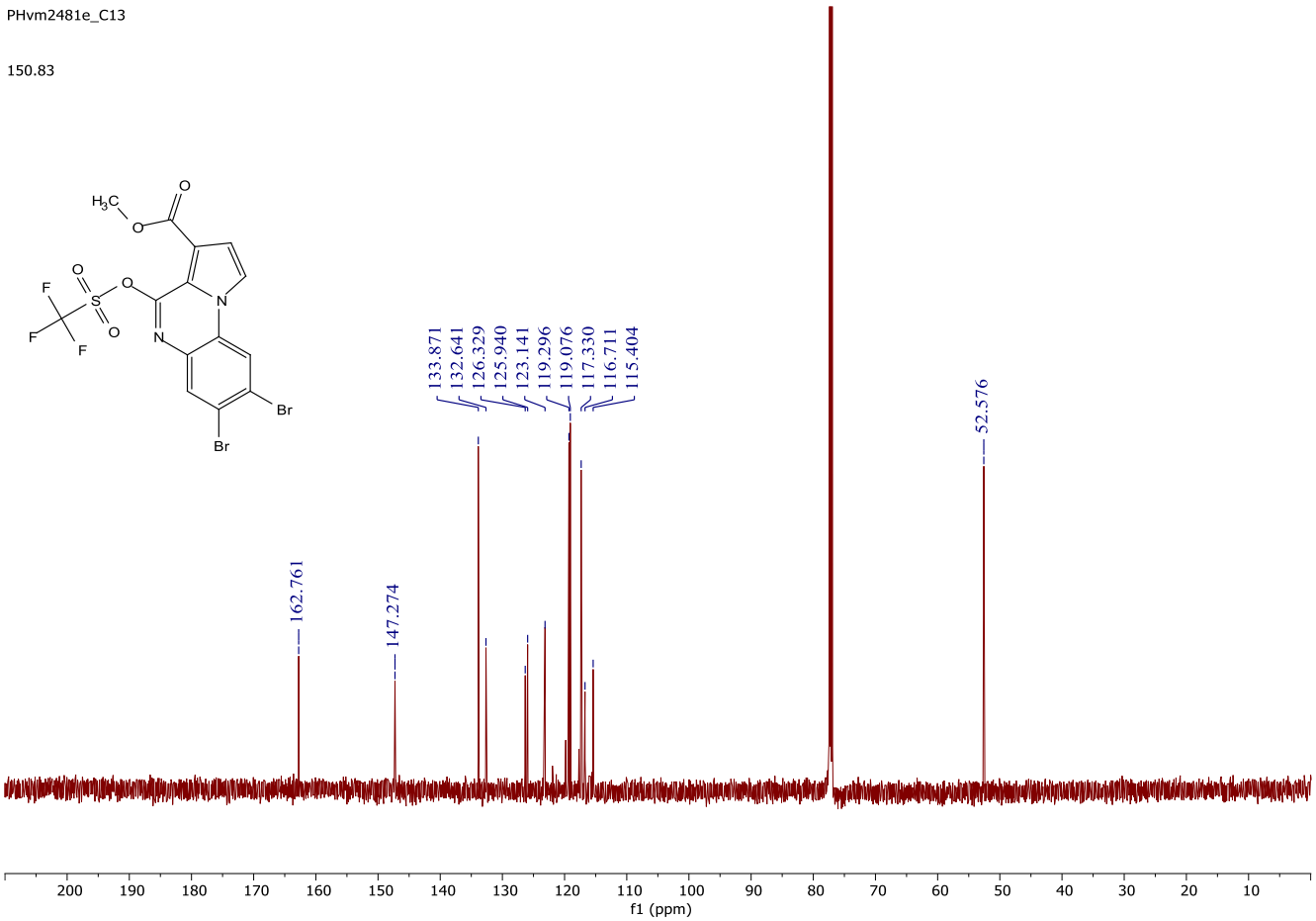
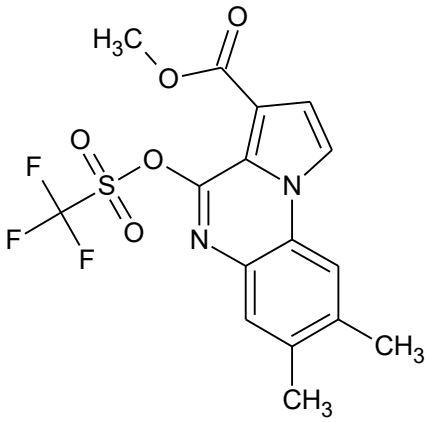


Figure S91. ^{13}C NMR spectrum of methyl 7,8-dibromo-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6d**) in $CDCl_3$



Chemical characterization of methyl 7,8-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**6e**). Light yellow solid (1.790 g, 89%). mp 215-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.38 (3H, s, CH_3), 2.46 (3H, s, CH_3), 3.96 (3H, s, CH_3O), 7.36 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole), 7.61 (2H, s, 2CH aromatic), 7.90 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 19.64 (CH_3), 20.59 (CH_3), 52.28 (CH_3O), 113.29, 114.51, 116.20, 117.01, 118.42, 118.85 (q, $^1J_{CF}$ 320.4 Hz, CF_3), 124.66, 129.68, 130.79, 136.75, 140.04, 145.62, 163.34 (C=O). ^{19}F NMR (DMSO-*d*$_6$, 188 MHz): δ_F -74.21. EI-MS: m/z 402 $[M]^+$. Anal. calcd for $C_{16}H_{13}F_3N_2O_5S$ (402.34): C, 47.76; H, 3.26; N, 6.96; S, 7.97. Found: C, 47.90; H, 3.24; N, 7.03; S, 7.88.

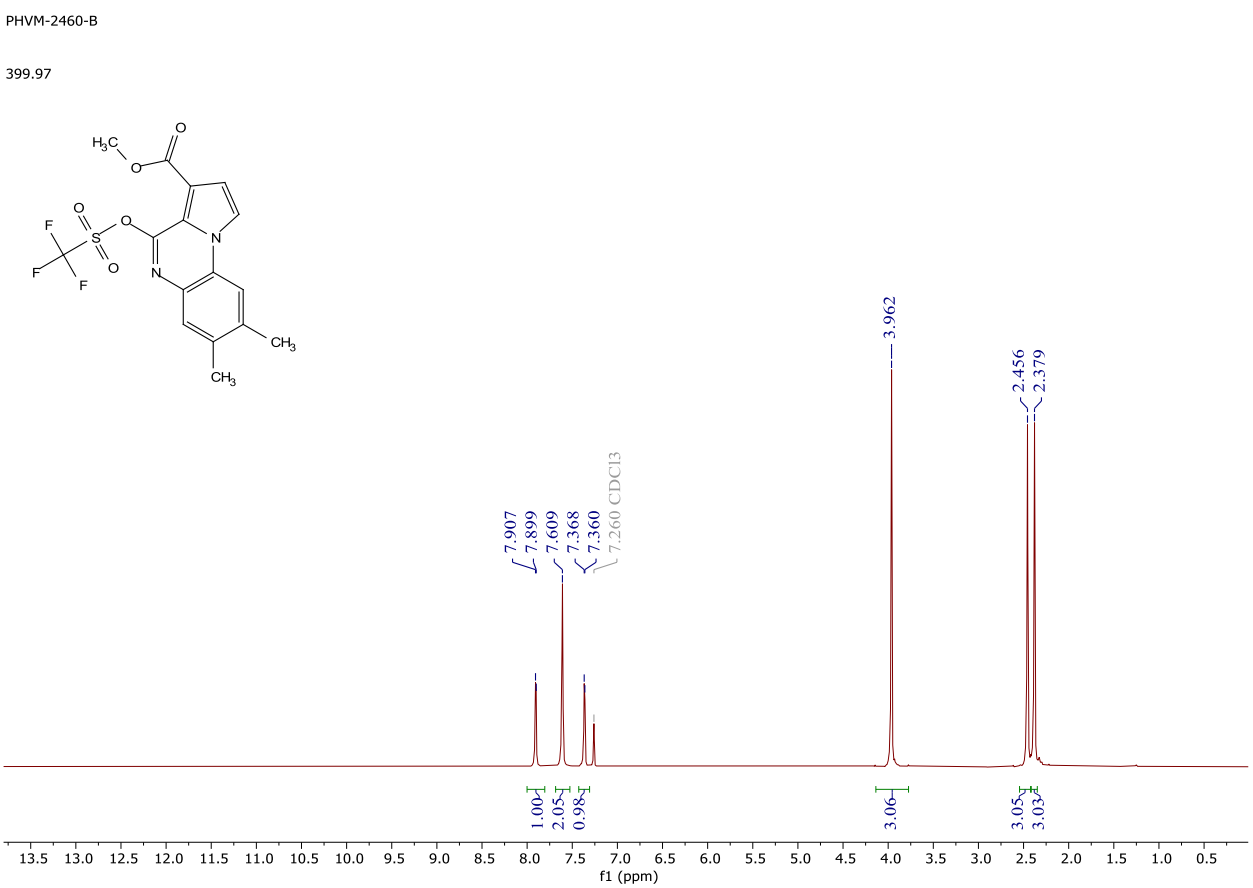


Figure S92. ^{1}H NMR spectrum of methyl 7,8-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6e**) in $CDCl_3$

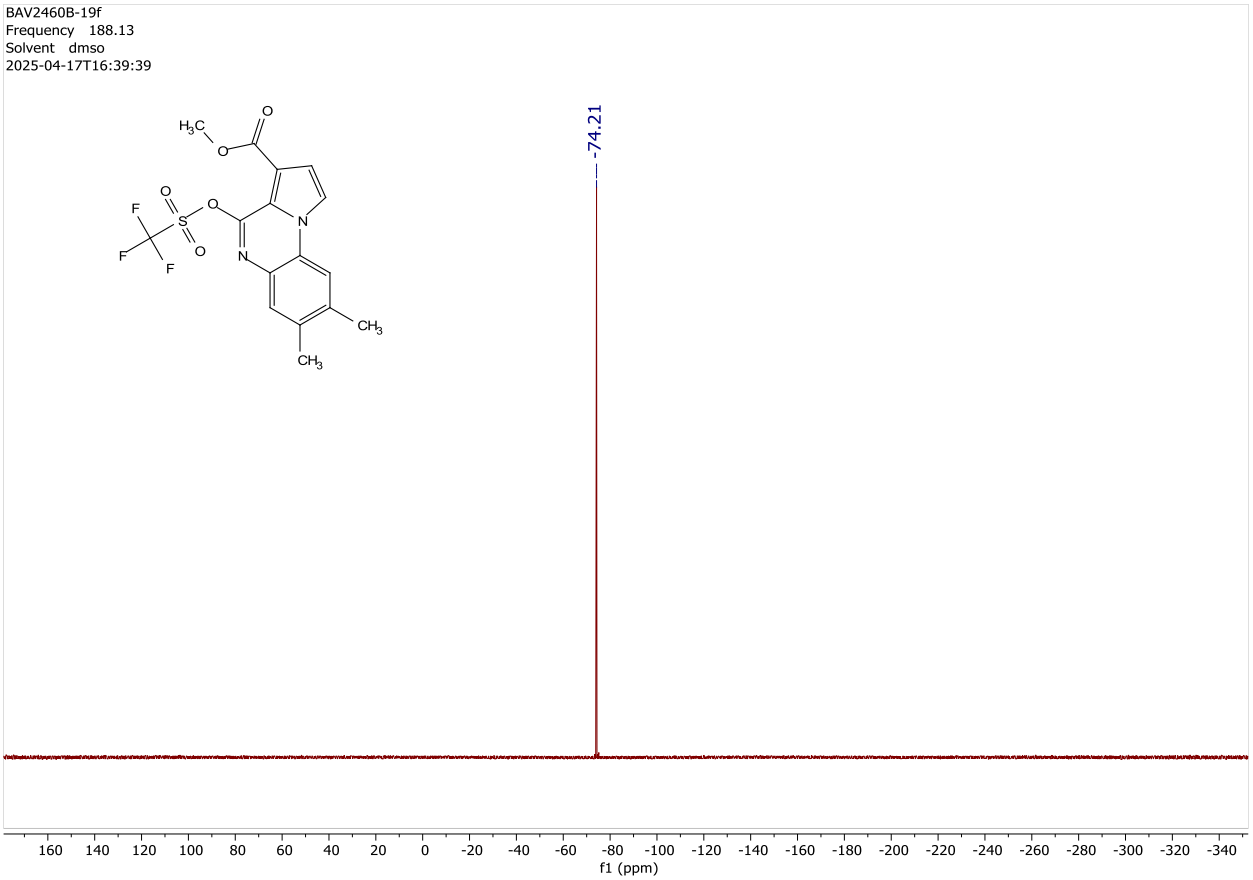


Figure S93. ^{19}F NMR spectrum of methyl 7,8-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6e**) in DMSO-d_6

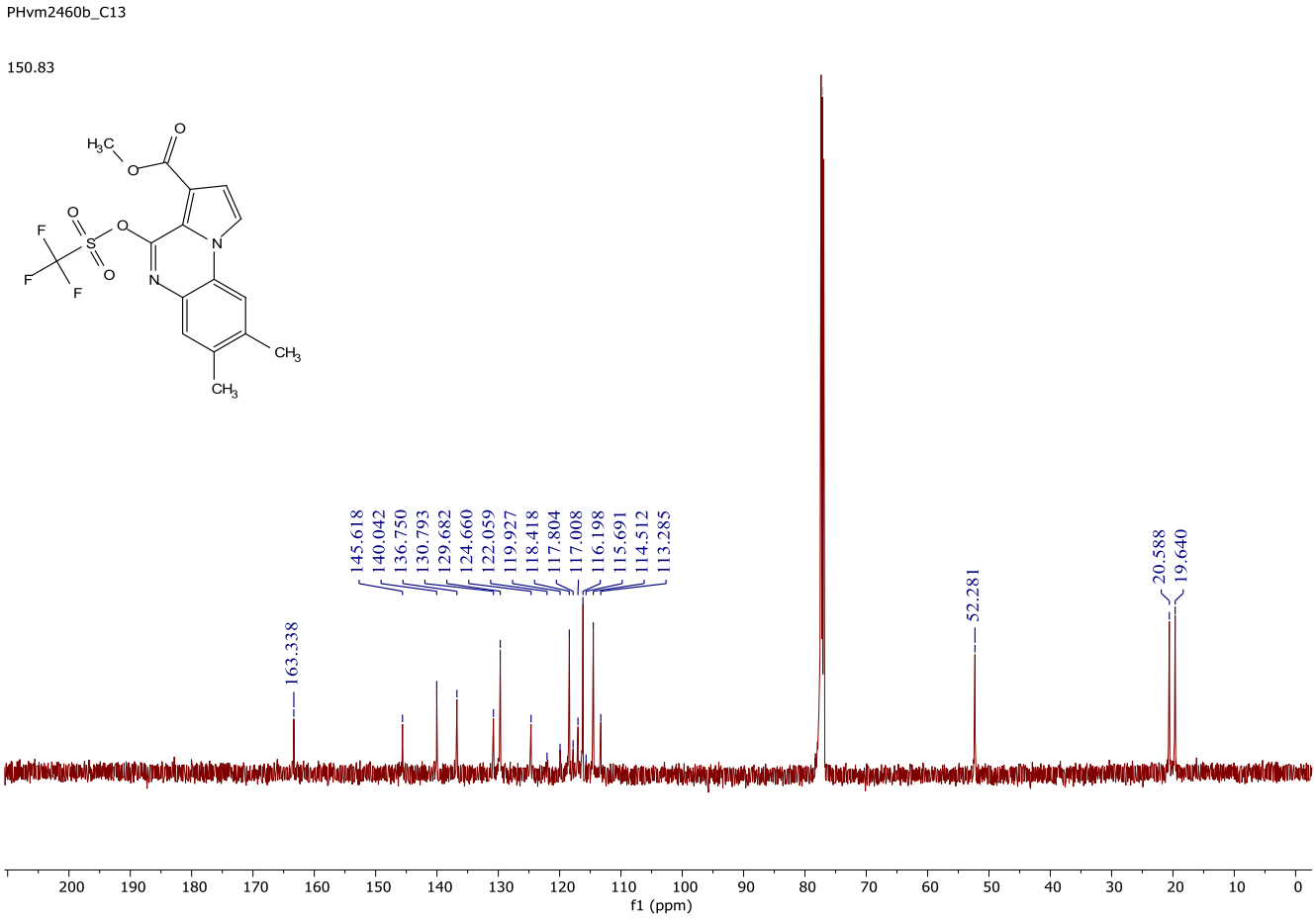
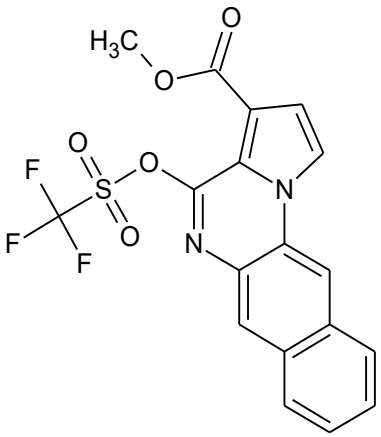


Figure S94. ^{13}C NMR spectrum of methyl 7,8-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6e**) in $CDCl_3$



Chemical characterization of methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzo[g]pyrrolo[1,2-a]quinoxaline-3-carboxylate (**6f**). Light yellow solid (1.931 g, 91%). mp 231-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.97 (3H, s, CH_3O), 7.32 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 7.53 (1H, t, $^3J_{HH}$ 7.3 Hz, CH aromatic), 7.60 (1H, t, $^3J_{HH}$ 7.5 Hz, CH aromatic), 7.93 (2H, t, $^3J_{HH}$ 7.9 Hz, 2CH aromatic), 8.05 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 8.16 (1H, s, CH aromatic), 8.30 (1H, s, CH aromatic). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 52.41 (CH_3O), 111.35, 115.54, 116.27, 117.88, 117.99, 118.84 (q, $^1J_{CF}$ 321.2 Hz, CF_3), 124.94, 126.66, 127.46, 128.17, 128.37, 128.74, 130.99, 131.68, 132.87, 146.24, 163.08 (COO-CH_3). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -74.28. ESI-MS: m/z 425.0 $[M+H]^+$. Anal. calcd for $C_{18}H_{11}F_3N_2O_5S$ (424.35): C, 50.95; H, 2.61; N, 6.60; S, 7.56. Found: C, 51.07; H, 2.58; N, 6.53; S, 7.49.

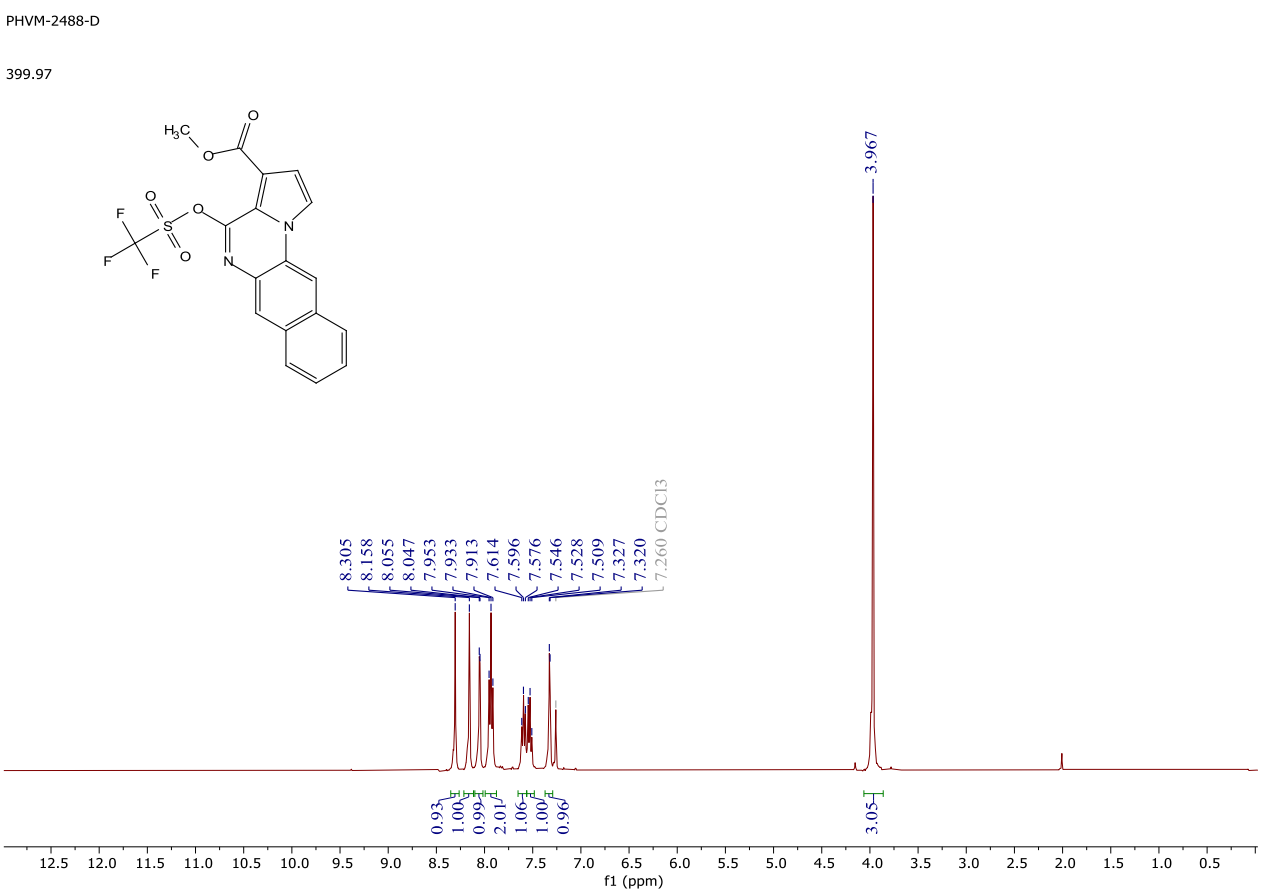


Figure S95. ^{1}H NMR spectrum of methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6e**) in $CDCl_3$

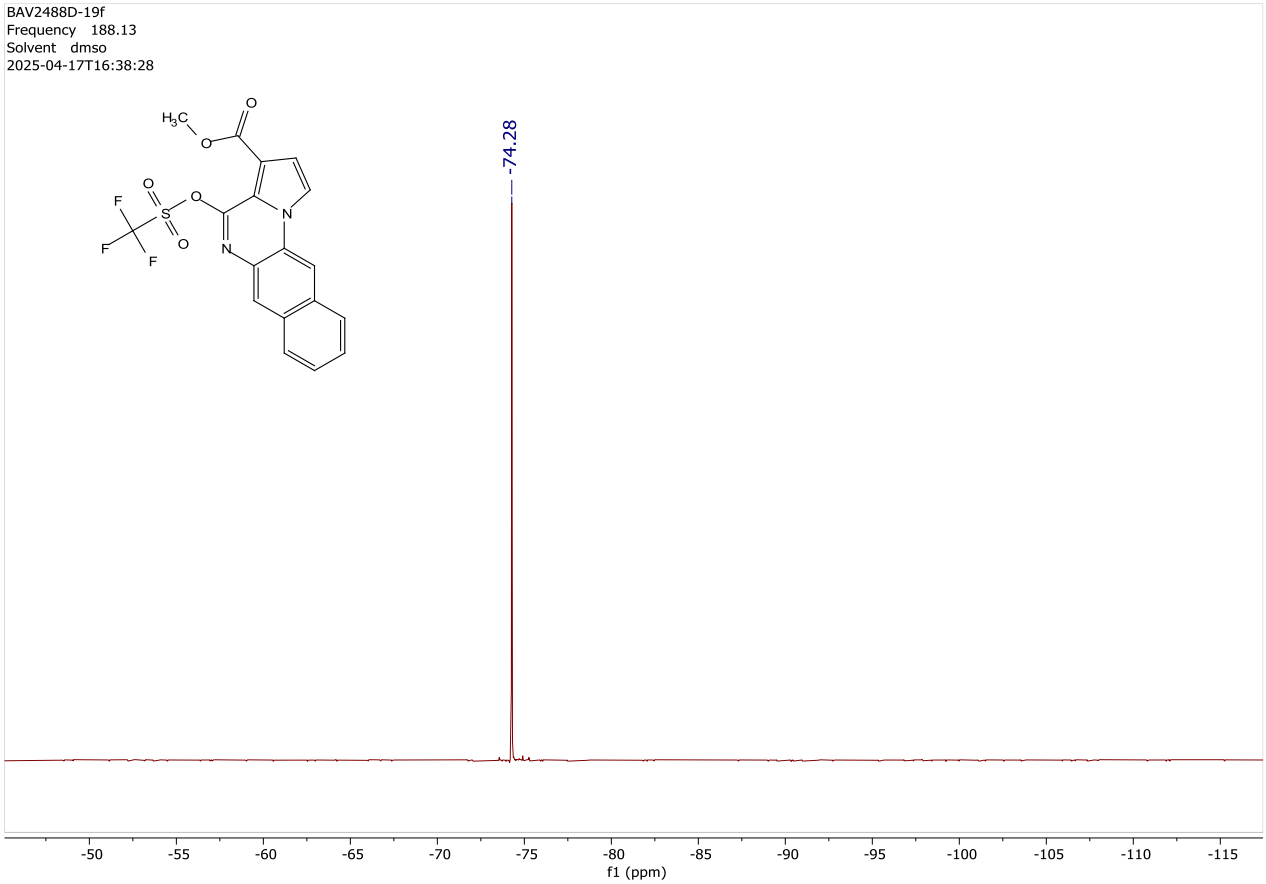


Figure S96. ^{19}F NMR spectrum of methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6e**) in DMSO-d_6

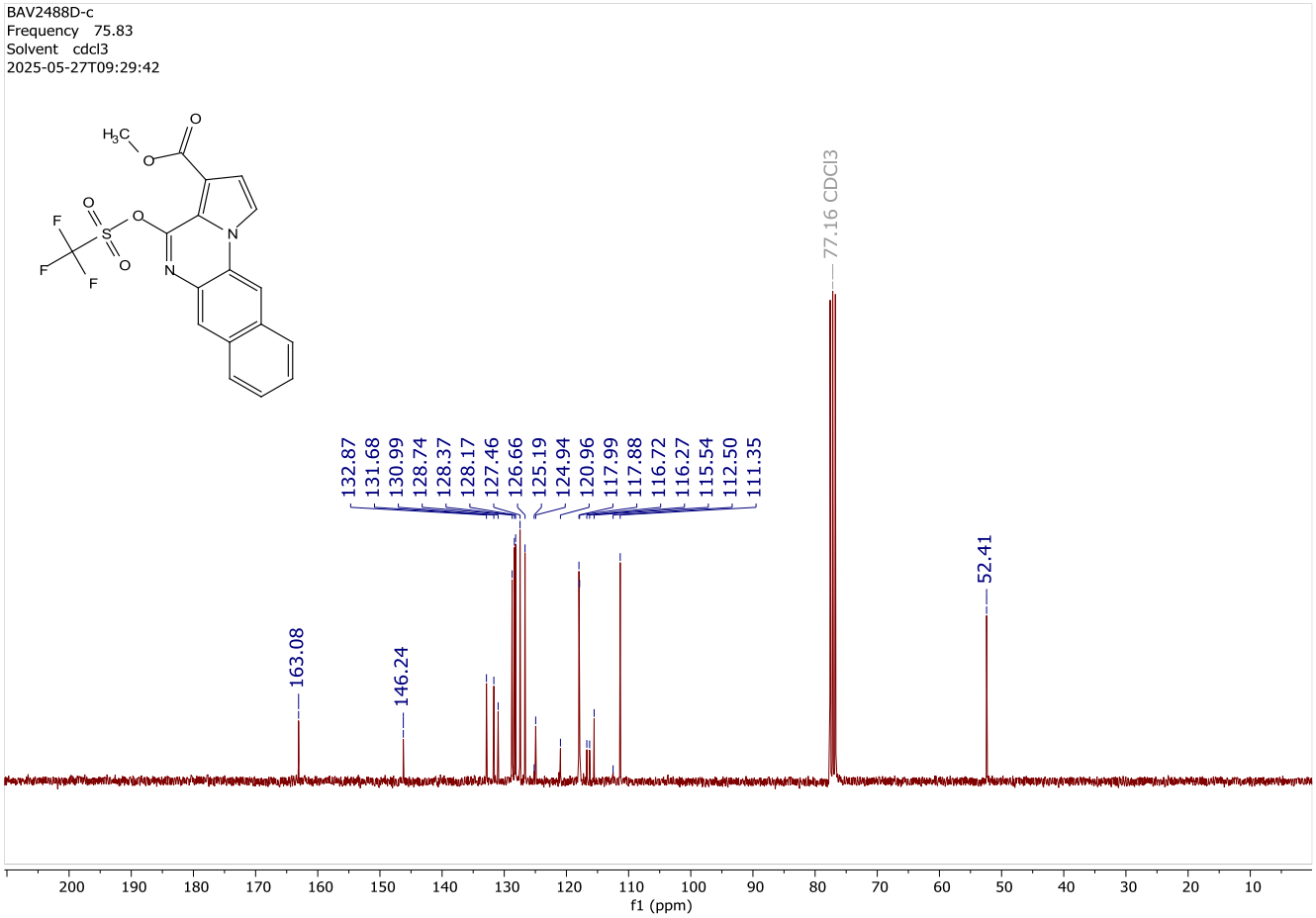
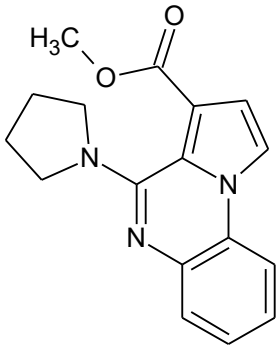


Figure S97. ^{13}C NMR spectrum of methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**6e**) in $CDCl_3$

Chemical characterization of 8a-p



Chemical characterization of methyl 4-pyrrolidin-1-ylpyrrolo[1,2-a]quinoxaline-3-carboxylate (**8a**). Beige solid (762 mg, 86%). mp 128-129 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.88-1.92 (4H, m, $2CH_2$ pyrrolidine), 3.70-3.74 (4H, m, $2CH_2$ pyrrolidine), 3.89 (3H, s, OCH_3), 7.09 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole), 7.18-7.23 (1H, m, CH aromatic), 7.31-7.37 (1H, m, CH aromatic), 7.64-7.70 (2H, m, 2 CH aromatic), 7.74 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole). ^{13}C NMR ($CDCl_3$, 151 MHz): δ_C 25.56 ($2CH_2$ pyrrolidine), 49.46 ($2CH_2$ pyrrolidine), 51.99 (OCH_3), 113.32, 113.57, 114.05, 115.45, 120.04, 123.01, 124.91, 126.26, 126.91, 137.16, 151.40 (N=C), 165.50 (C=O). ESI-MS: *m/z* 296.2 $[M+H]^+$. Anal. calcd for $C_{17}H_{17}N_3O_2$ (295.34): C, 69.14; H, 5.80; N, 14.23. Found: C, 68.93; H, 5.78; N, 14.34.

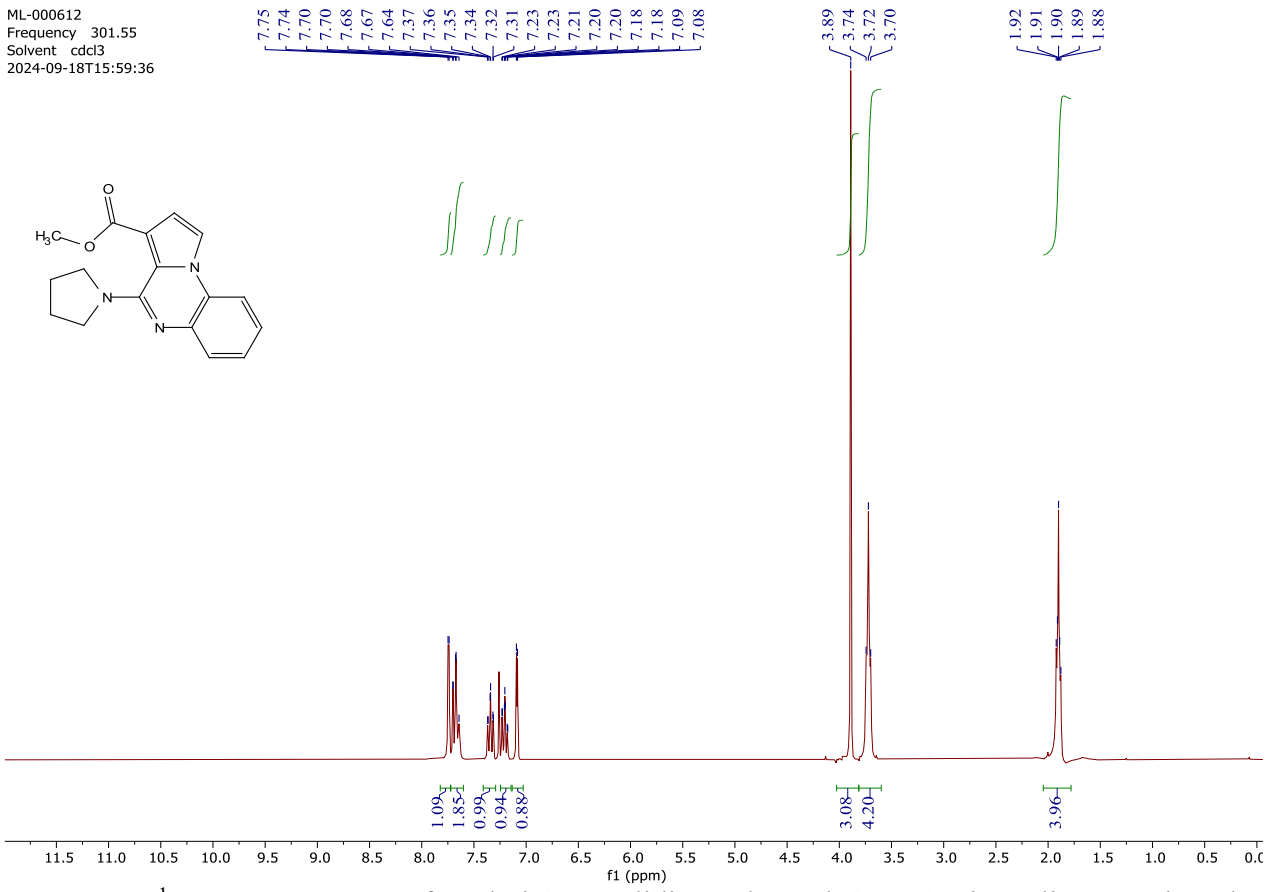


Figure S98. ^{1}H NMR spectrum of methyl 4-pyrrolidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8a**) in $CDCl_3$

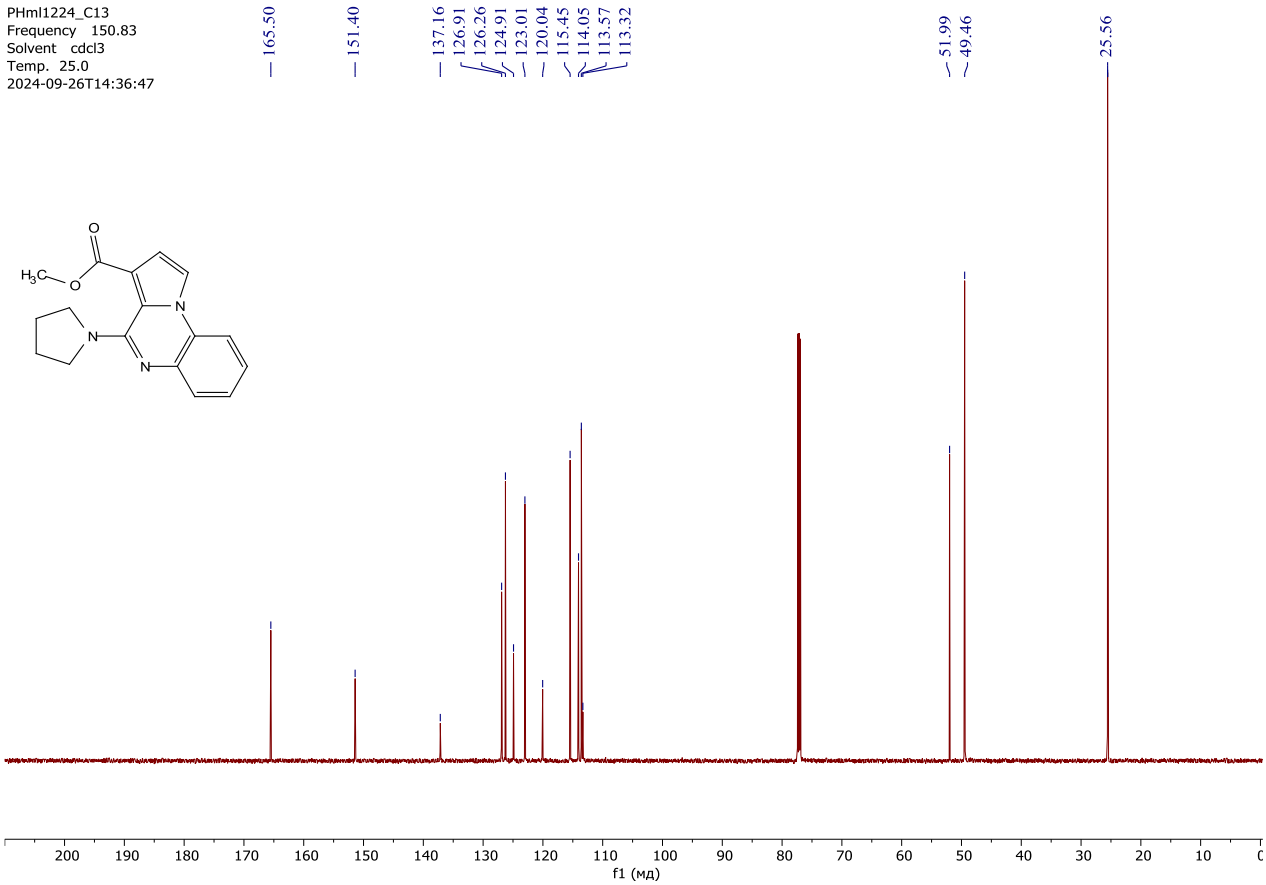
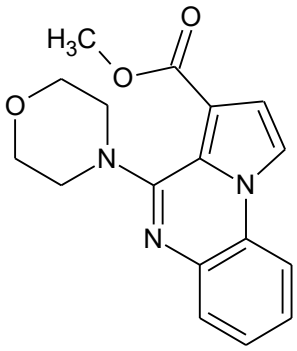


Figure S99. ^{13}C NMR spectrum of methyl 4-pyrrolidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8a**) in $CDCl_3$



Chemical characterization of methyl 4-morpholin-4-ylpyrrolo[1,2-a]quinoxaline-3-carboxylate (**8b**). White solid (869 mg, 93%). mp 139-140 °C. ^{1}H NMR (302 MHz, DMSO-d_6): δ_H 3.31-3.43 (4H, m, 2CH_2 morpholine), 3.74 (4H, t, $^{3}J_{HH}$ 4.6 Hz, 2CH_2 morpholine), 3.83 (3H, s, CH_3O), 7.20 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.40-7.48 (2H, m, 2CH aromatic), 7.60-7.73 (1H, m, CH aromatic), 8.23-8.26 (1H, m, CH aromatic), 8.45 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole). ^{13}C NMR ($CDCl_3$, 151 MHz): δ_C 50.19 (2CH_2 morpholine), 52.07 (CH_3O), 66.62 (2CH_2 morpholine), 112.35, 113.74, 114.50, 116.46, 119.95, 125.21, 125.28, 126.34, 128.13, 135.99, 152.99 (N=C), 164.37 (C=O). ESI-MS: *m/z* 312.0 $[M+H]^+$. Anal. calcd for $C_{17}H_{17}N_3O_3$ (311.34): C, 65.58; H, 5.50; N, 13.50. Found: C, 65.77; H, 5.48; N, 13.36.

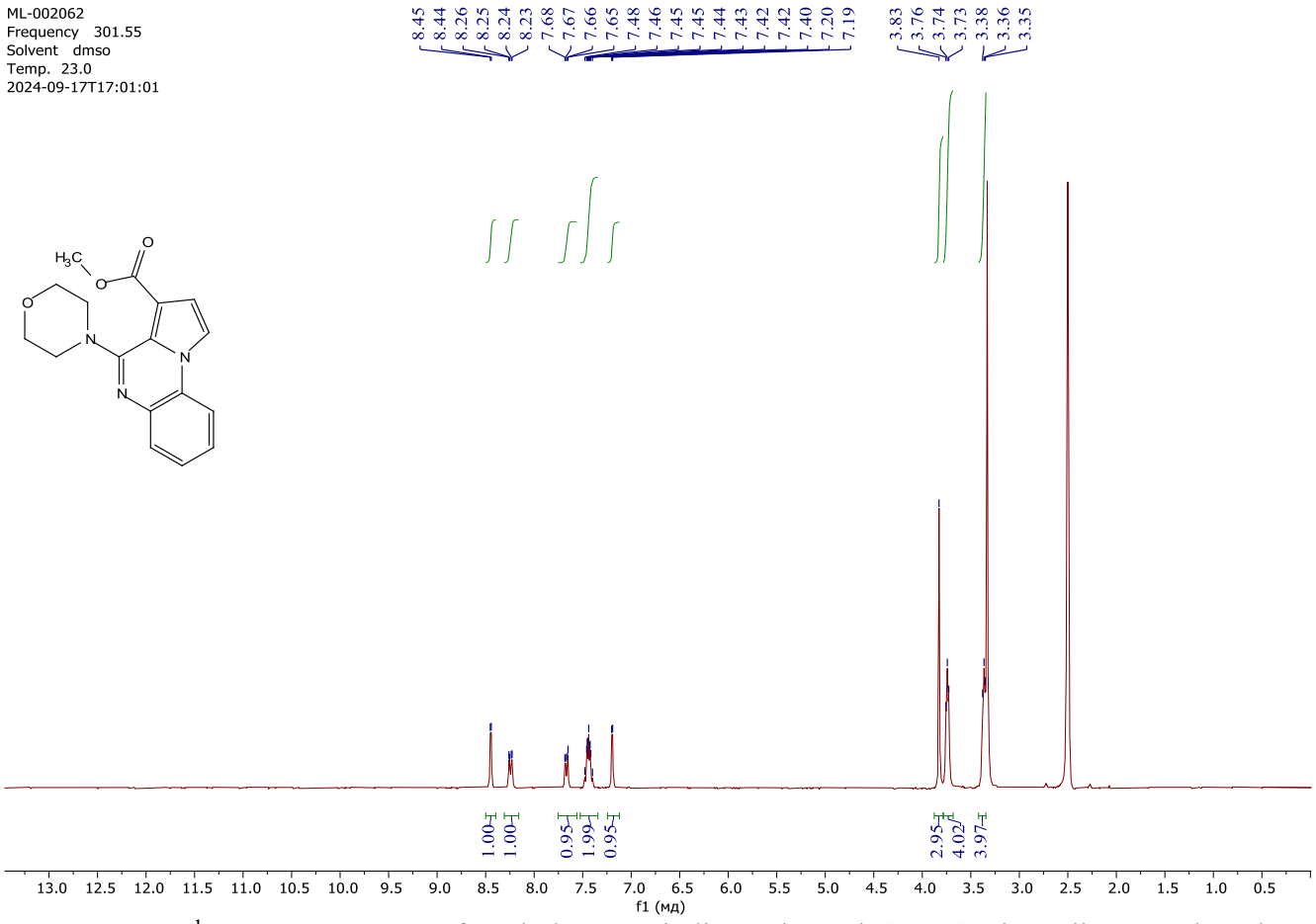


Figure S100. ^{1}H NMR spectrum of methyl 4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8b**) in DMSO-d_6

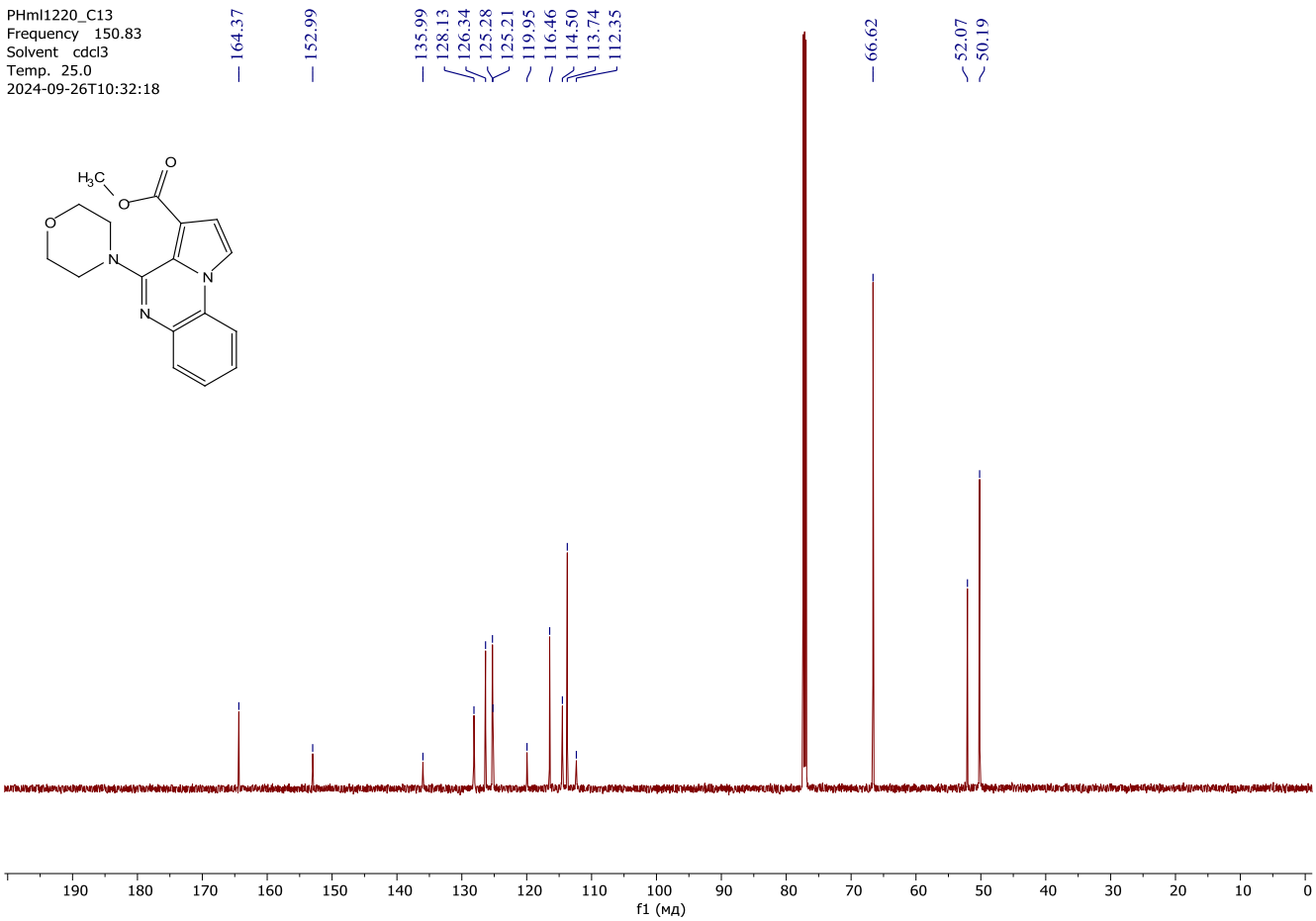
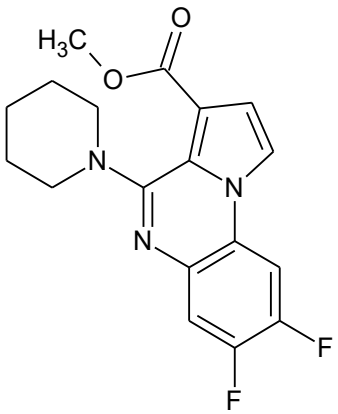


Figure S101. ^{13}C NMR spectrum of methyl 4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8b**) in $CDCl_3$



Chemical characterization of methyl 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-a]quinoxaline-3-carboxylate (**8c**). Beige solid (901 mg, 87%). mp 164-165 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 1.57-1.63 (6H, m, 3CH_2 piperidine), 3.37-3.42 (4H, m, 2CH_2 piperidine), 3.83 (3H, s, OCH_3), 7.15 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 7.59 (1H, dd, $^3J_{HF}$ 11.7, $^3J_{HH}$ 8.1 Hz, CH aromatic), 8.34 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole), 8.43 (1H, dd, $^3J_{HF}$ 11.8, $^3J_{HH}$ 7.8 Hz, CH aromatic). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 24.94 (CH_2 piperidine), 25.57 (2CH_2 piperidine), 50.55 (2CH_2 piperidine), 52.16 (CH_3O), 102.31 (d, $^2J_{CF}$ 23.6 Hz, CH aromatic), 113.24, 114.47, 114.85 (d, $^2J_{CF}$ 16.5 Hz, CH aromatic) 116.28, 119.51, 120.99, 133.35, 147.51 (dd, $^1J_{CF}$ 249.0, $^2J_{CF}$ 16.9 Hz, CF aromatic), 148.85 (dd, $^1J_{CF}$ 248.8, $^2J_{CF}$ 15.9 Hz, CF aromatic), 153.30 (C=N), 164.34 (C=O). ^{19}F NMR (DMSO-d_6, 376 MHz): δ_F -140.06-(-139.77) (m, 2CF aromatic). ESI-MS: *m/z* 346.2 $[M+H]^+$. Anal. calcd for $C_{18}H_{17}F_2N_3O_2$ (345.34): C, 62.60; H, 4.96; N, 12.17. Found: C, 62.38; H, 4.99; N, 12.24.

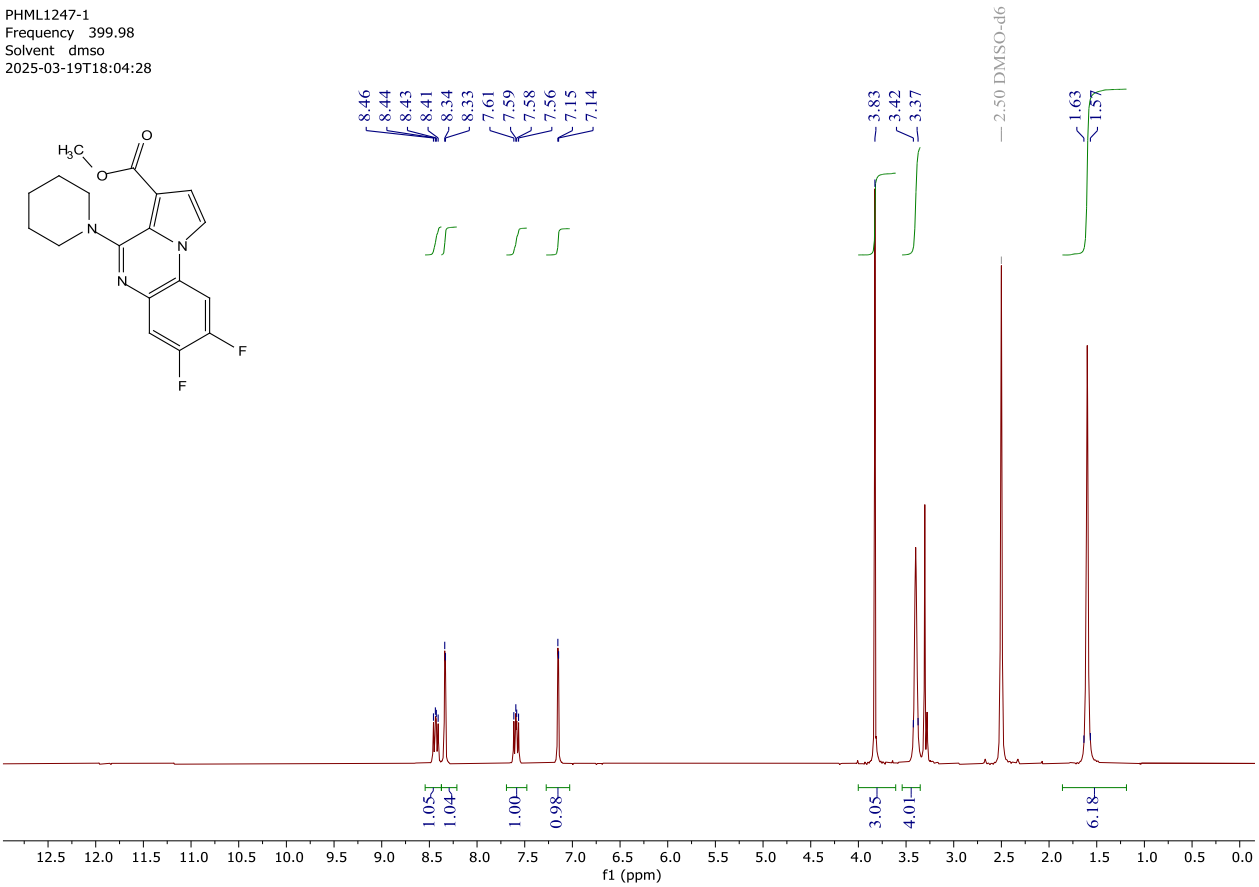


Figure S102. ^{1}H NMR spectrum of methyl 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8c**) in DMSO-d_6

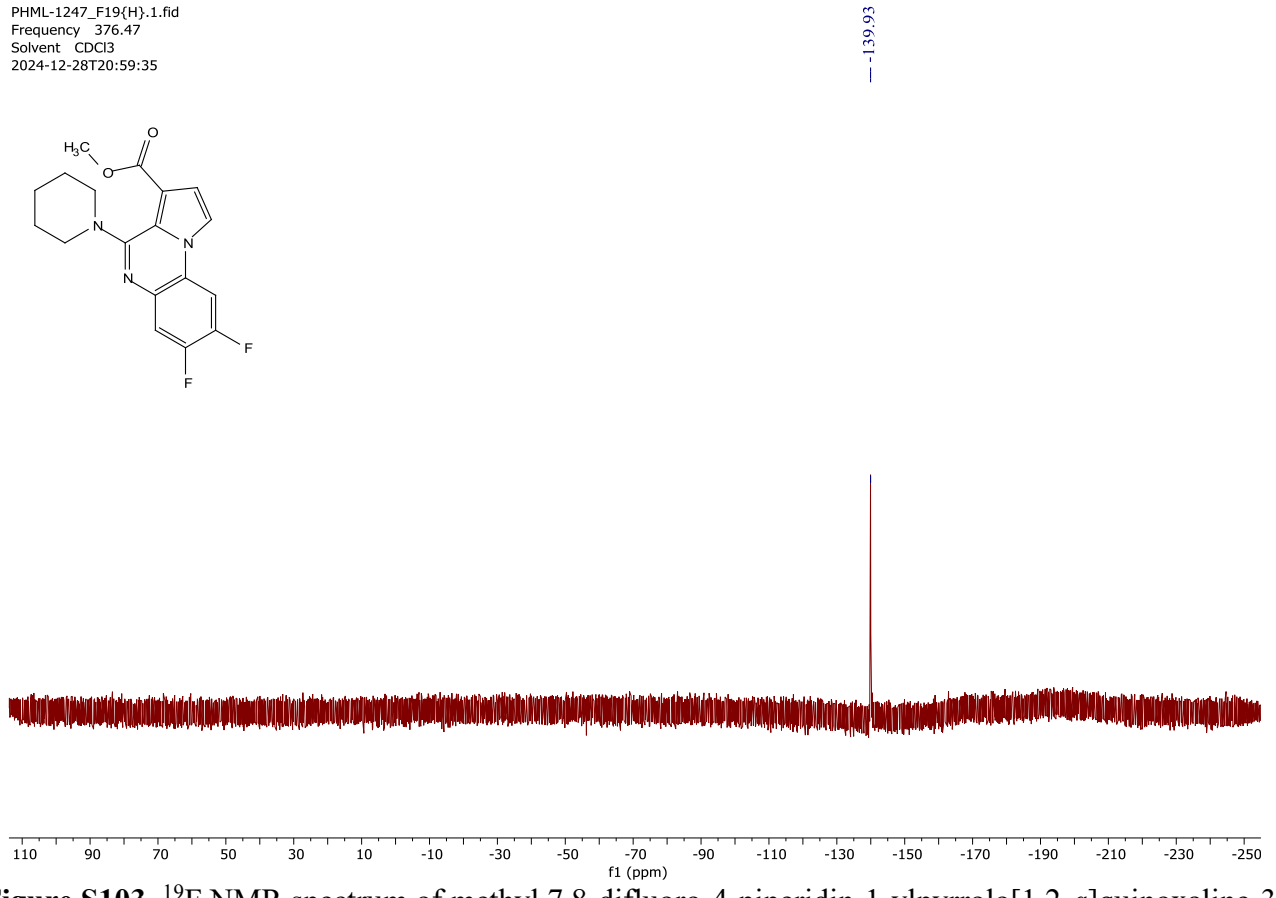


Figure S103. ^{19}F NMR spectrum of methyl 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8c**) in DMSO-d_6

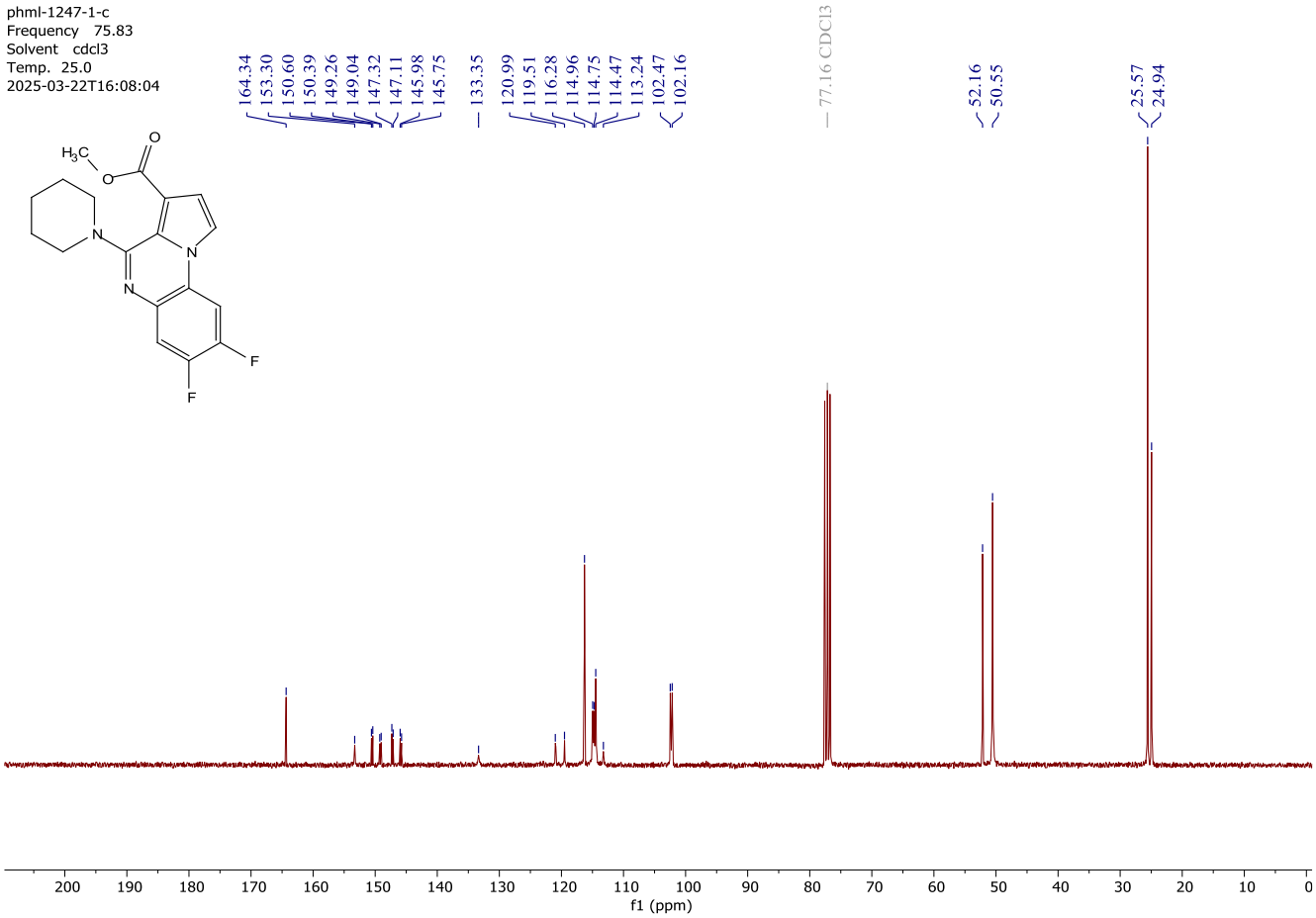
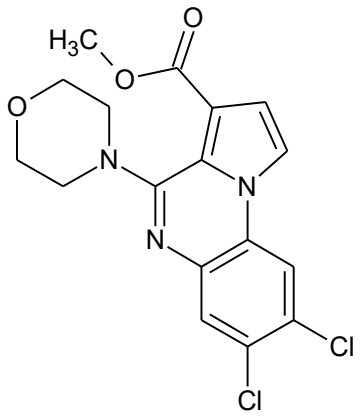


Figure S104. ^{13}C NMR spectrum of methyl 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8c**) in $CDCl_3$



Chemical characterization of methyl 7,8-dichloro-4-morpholin-4-ylpyrrolo[1,2-a]quinoxaline-3-carboxylate (**8d**). Yellow solid (1.072 g, 94%). mp 203-204 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.42 (4H, t, $^{3}J_{HH}$ 4.7 Hz, 2CH_2 morpholine), 3.72 (4H, t, $^{3}J_{HH}$ 4.7 Hz, 2CH_2 morpholine), 3.83 (3H, s, OCH_3), 7.20 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 7.80 (1H, s, CH aromatic), 8.49 (1H, d, $^{3}J_{HH}$ 3.2 Hz, CH pyrrole), 8.63 (1H, s, CH aromatic). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 50.11 (2CH_2 morpholine), 52.28 (OCH_3), 66.56 (2CH_2 morpholine), 113.69, 115.16, 115.31, 116.97, 119.32, 124.22, 128.20, 128.54, 130.08, 135.38, 153.22 (C=N), 164.07 (C=O). ESI-MS: *m/z* 380.2 $[M+H]^+$. Anal. calcd for $C_{17}H_{15}Cl_2N_3O_3$ (380.23): C, 53.70; H, 3.98; N, 11.05. Found: C, 53.86; H, 4.01; N, 10.97.

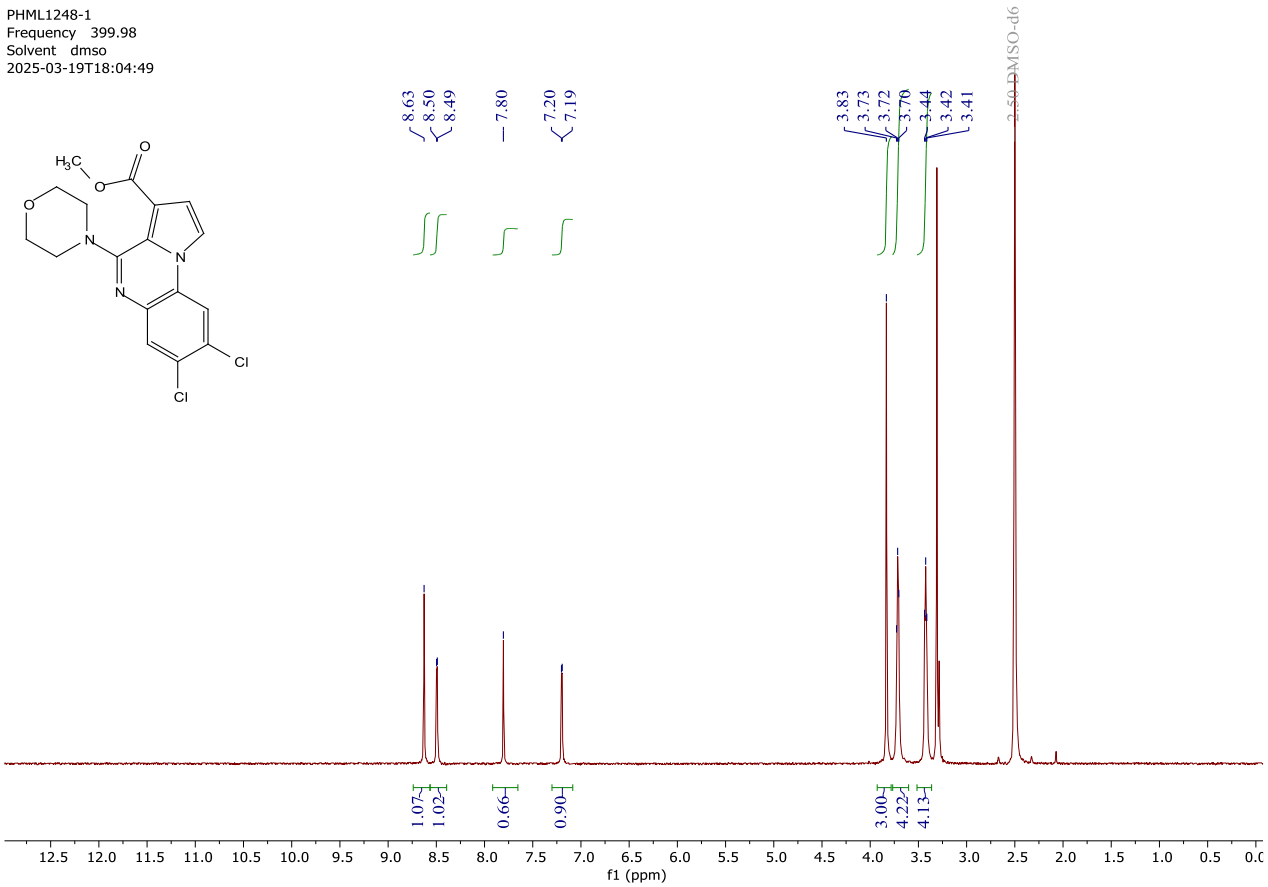


Figure S105. ^{1}H NMR spectrum of methyl 7,8-dichloro-4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8d**) in DMSO-d_6

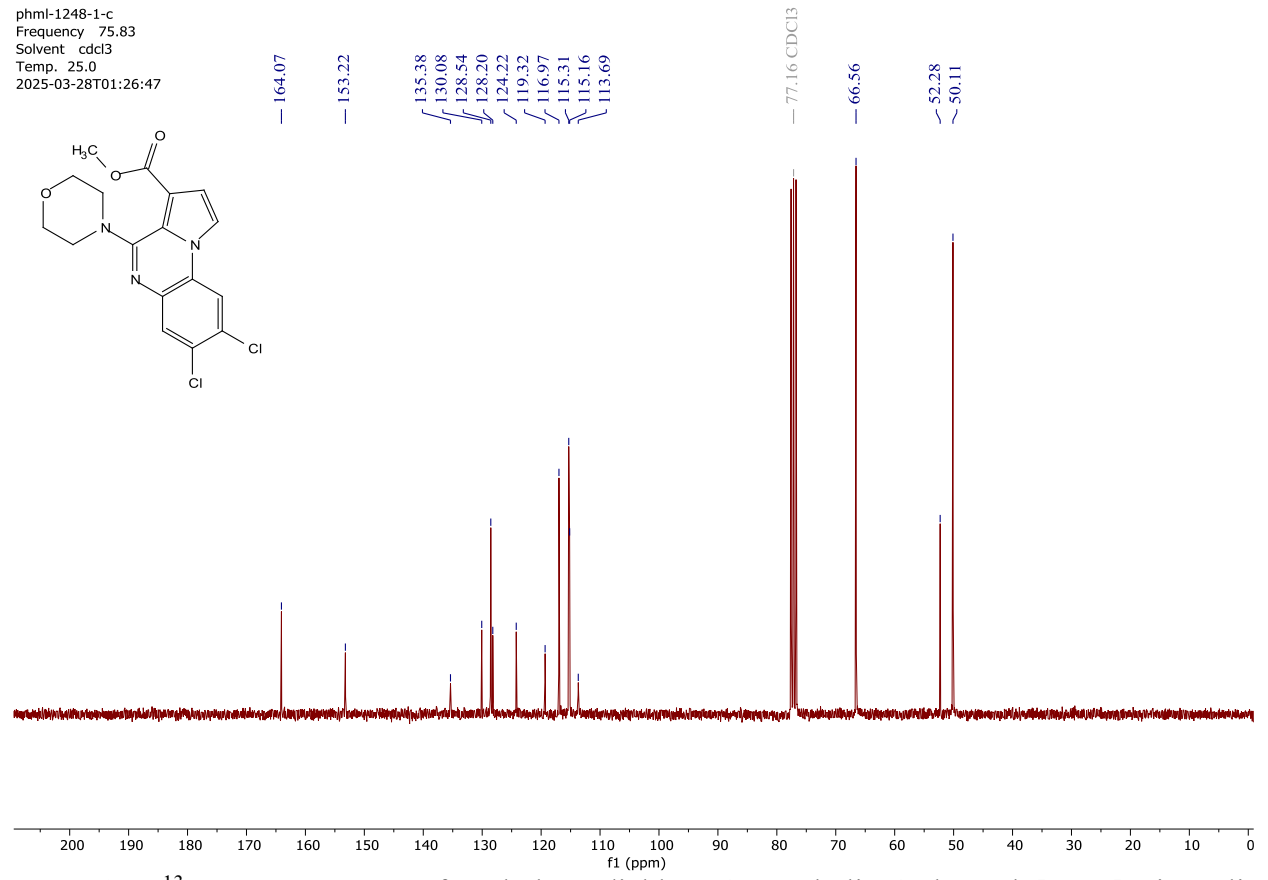
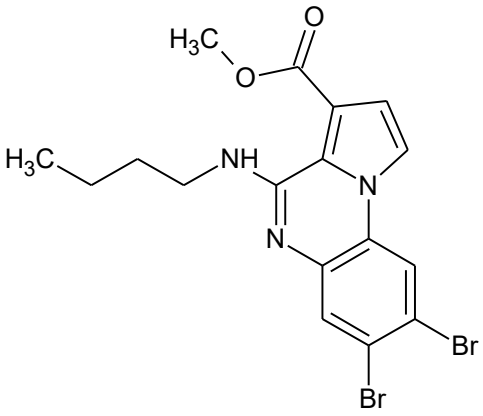


Figure S106. ^{13}C NMR spectrum of methyl 7,8-dichloro-4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8d**) in $CDCl_3$



Chemical characterization of methyl 7,8-dibromo-4-(butylamino)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8e**). Beige solid (1.215 g, 89%). mp 162-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.00 (3H, t, $^{3}J_{HH}$ 7.4 Hz, CH_3), 1.47-1.56 (2H, m, CH_2), 1.71-1.78 (2H, m, CH_2), 3.60-3.68 (2H, m, CH_2), 3.93 (3H, s, OCH_3), 7.20 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.60 (1H, d, $^{3}J_{HH}$ 3.2 Hz, CH pyrrole), 7.89-7.95 (2H, m, 2CH aromatic), 9.77 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_C 14.04 (CH_3), 20.56 (CH_2), 31.31 (CH_2), 40.90 (CH_2), 52.41 (OCH_3), 111.10, 114.03, 116.25, 116.51, 118.22, 121.54, 121.78, 123.69, 130.40, 138.50, 149.70 (N=C), 166.61 (C=O). ESI-MS: *m/z* 456.0 $[M+H]^+$. Anal. calcd for $C_{17}H_{17}Br_2N_3O_2$ (455.14): C, 44.86; H, 3.76; N, 9.23. Found: C, 45.02; H, 3.77; N, 9.14.

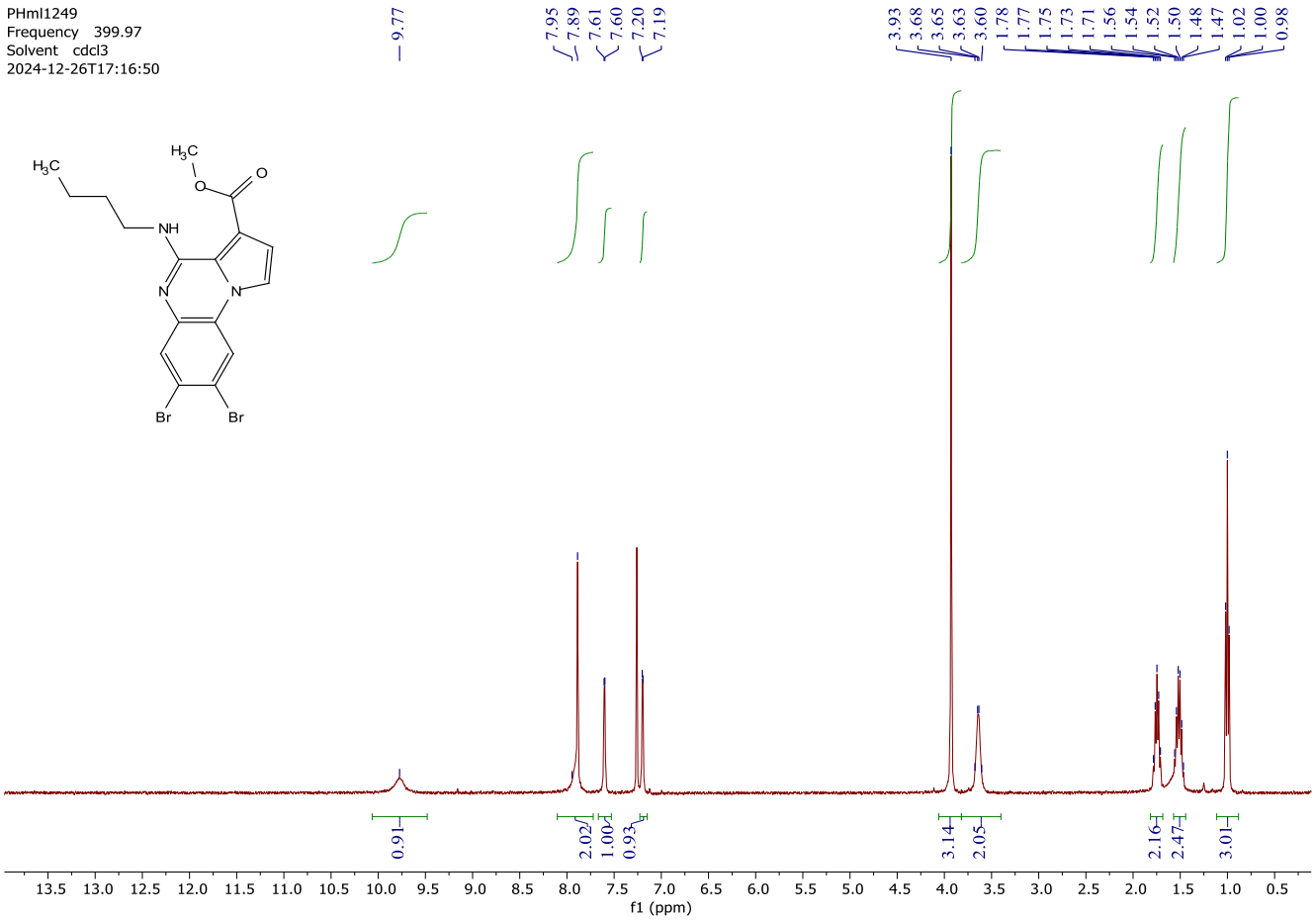


Figure S107. ^{1}H NMR spectrum of methyl 7,8-dibromo-4-(butylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8e**) in $CDCl_3$

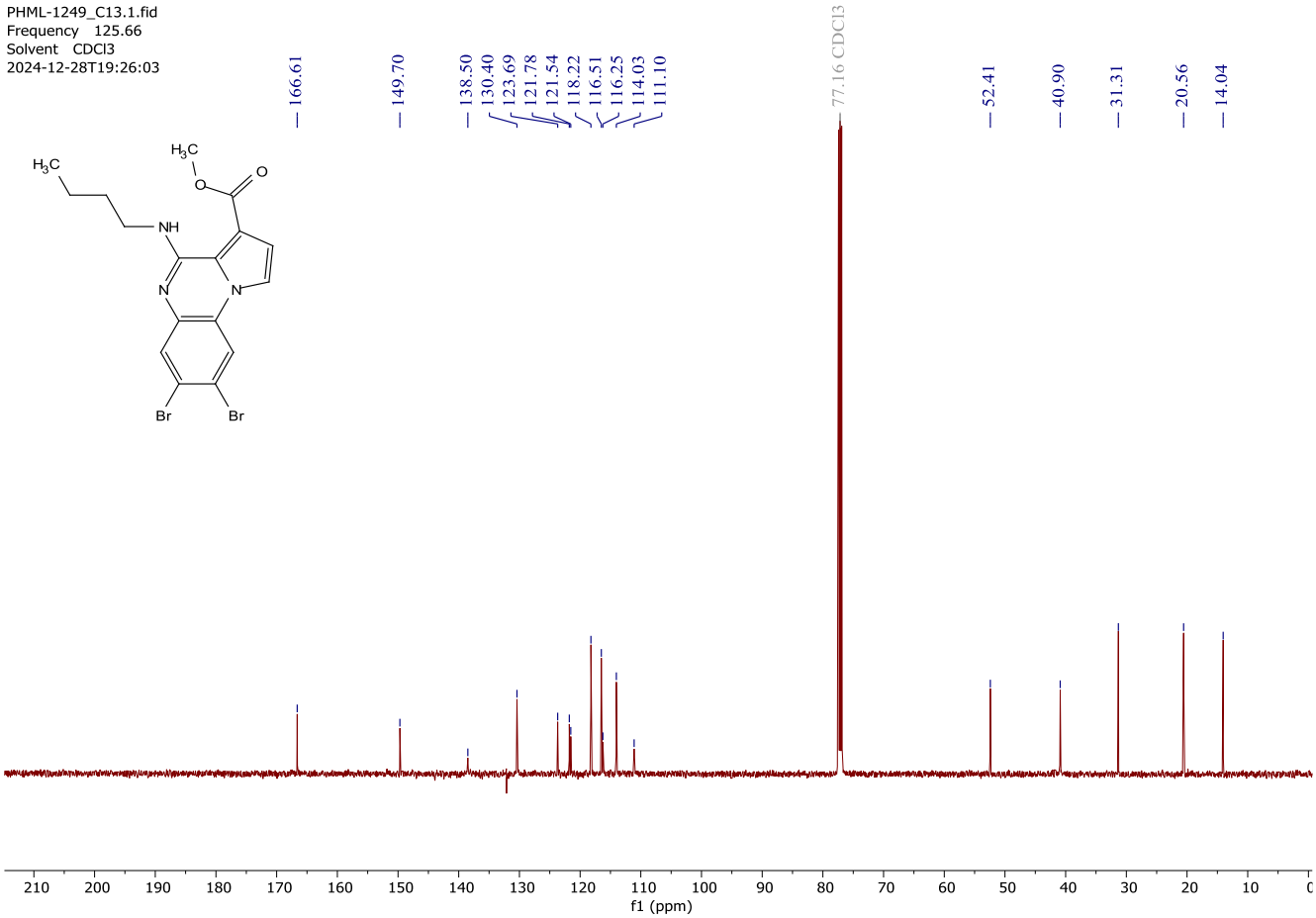
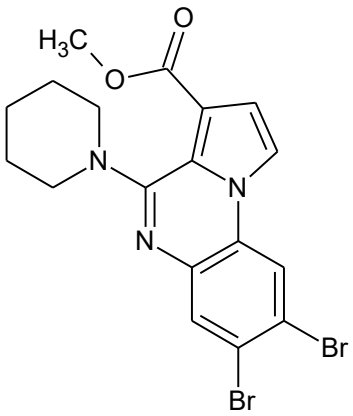


Figure S108. ^{13}C NMR spectrum of methyl 7,8-dibromo-4-(butylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8e**) in $CDCl_3$



Chemical characterization of methyl 7,8-dibromo-4-piperidin-1-ylpyrrolo[1,2-a]quinoxaline-3-carboxylate (**8f**). Yellow solid (1.275 g, 91%). mp 177-178 °C. IR (solid, KBr, νmax, cm^{-1}): 2945, 1725, 1518, 1483, 1229, 1187, 1046, 870, 717. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 1.57-1.63 (6H, m, 3CH_2 piperidine), 3.41-3.49 (4H, m, 2CH_2 piperidine), 3.84 (3H, s, OCH_3), 7.13 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 7.86 (1H, s, CH aromatic), 8.44 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole), 8.64 (1H, s, CH aromatic). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_C 24.95 (CH_2 piperidine), 25.67 (2CH_2 piperidine), 50.47 (2CH_2 piperidine), 52.16 (OCH_3), 113.81, 114.73, 116.34, 118.18, 118.42, 119.45, 121.37, 124.84, 131.43, 136.85, 153.41 (N=C aromatic), 164.25 (C=O). ESI-MS: *m/z* 468.0 [M+H]$^+$. Anal. calcd for $C_{18}H_{17}Br_2N_3O_2$ (467.16): C, 46.28; H, 3.67; N, 8.99. Found: C, 46.51; H, 3.71; N, 8.86.

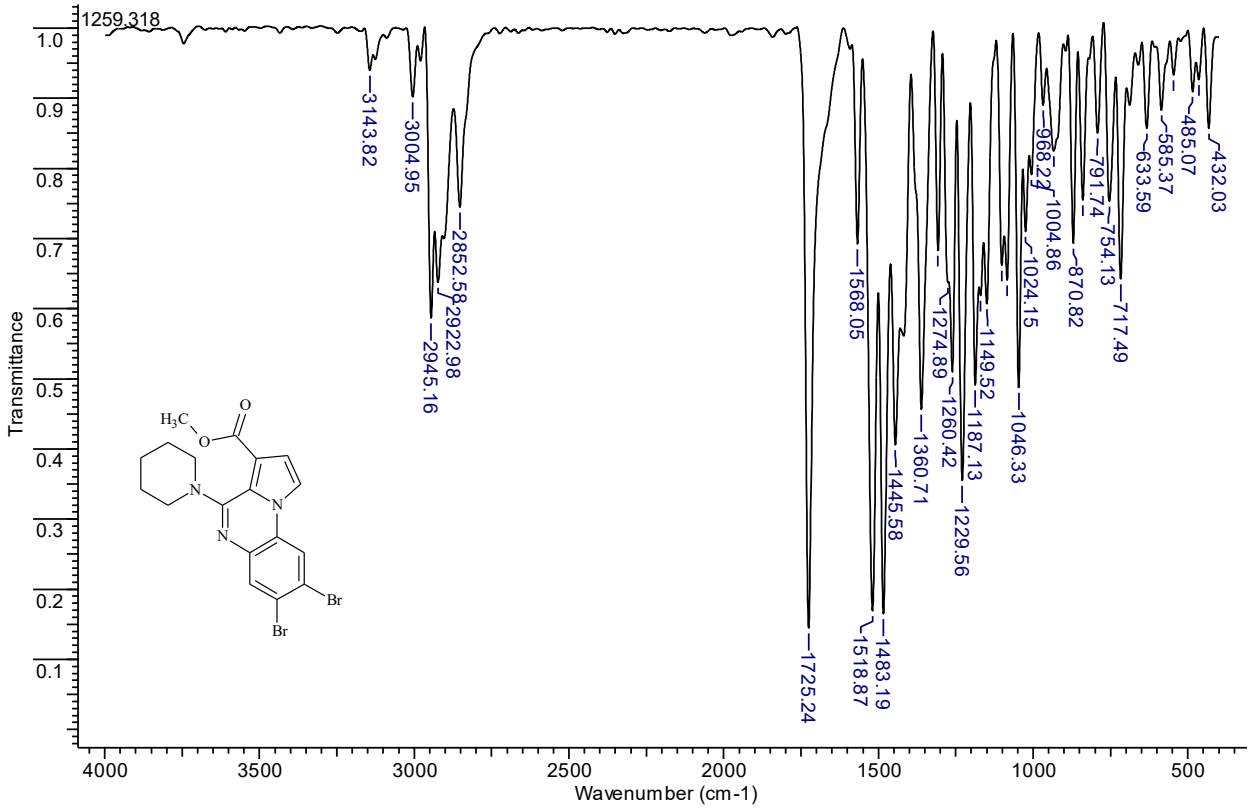


Figure S109. IR spectrum of methyl 7,8-dibromo-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8f**) in KBr pellet

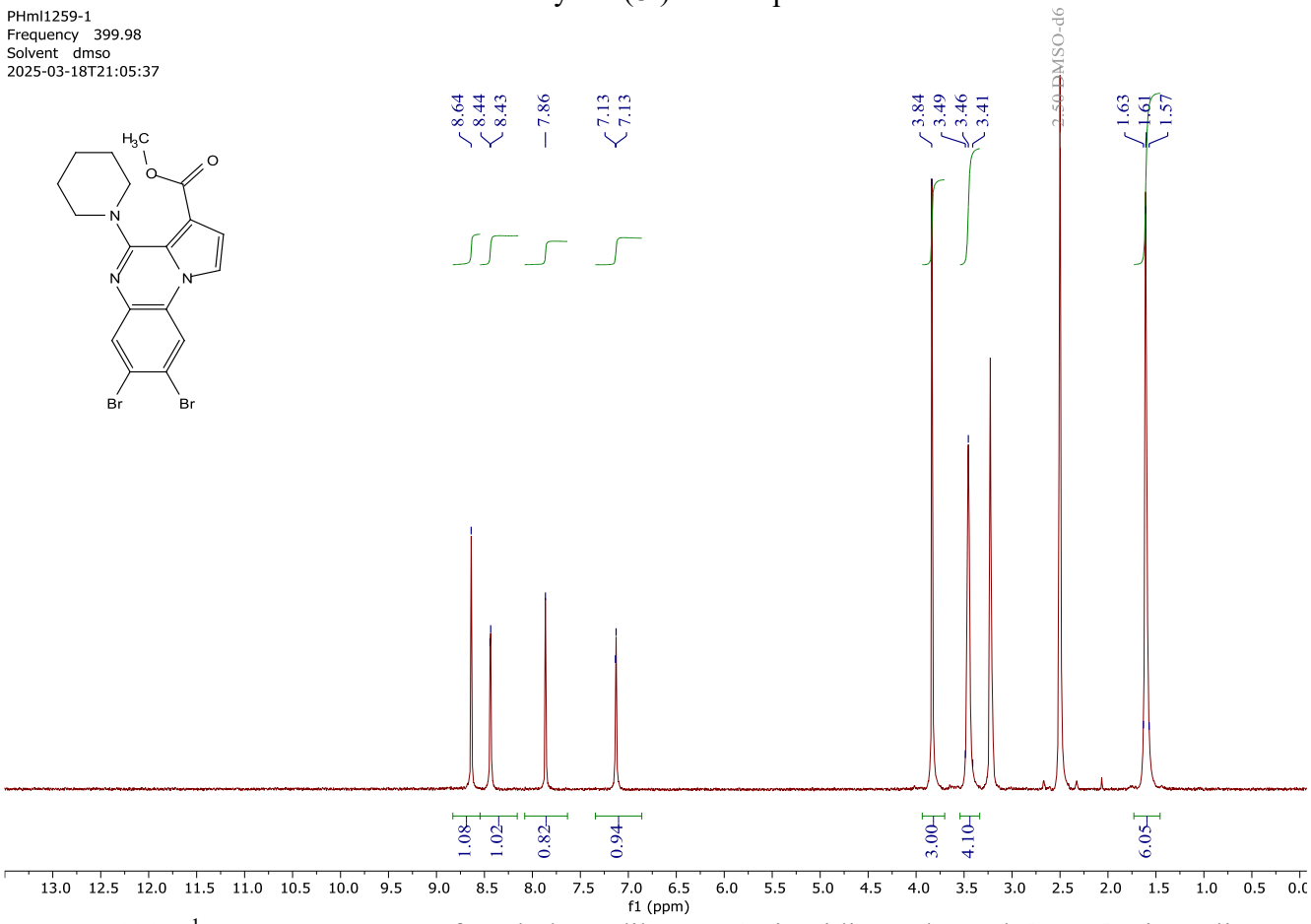


Figure S110. ^{1}H NMR spectrum of methyl 7,8-dibromo-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8f**) in DMSO-d_6

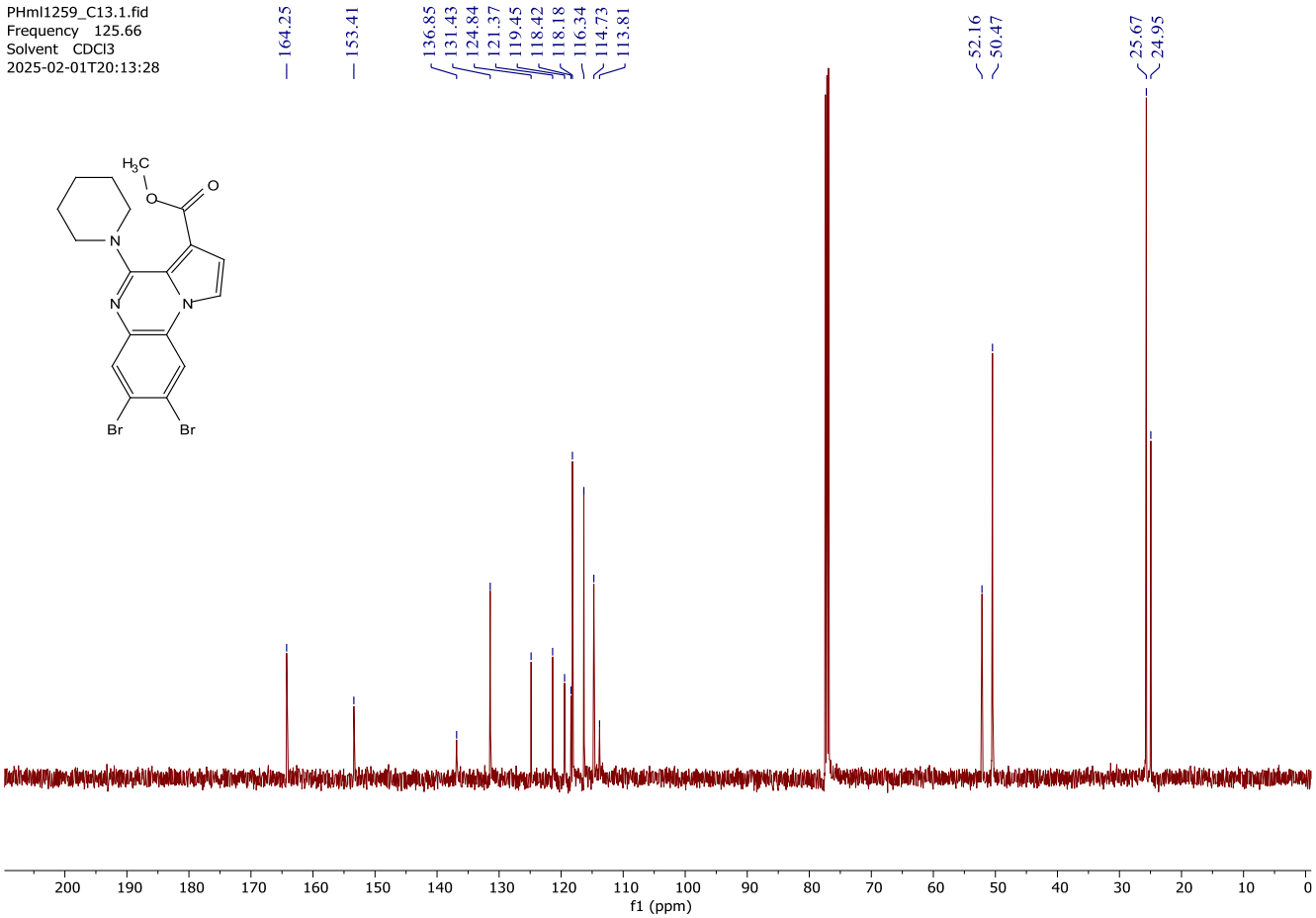
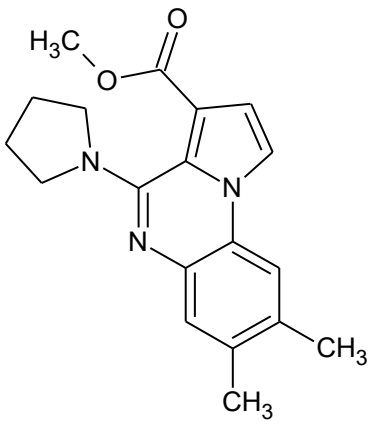


Figure S111. ^{13}C NMR spectrum of methyl 7,8-dibromo-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8f**) in $CDCl_3$



Chemical characterization of methyl 7,8-dimethyl-4-(pyrrolidin-1-yl)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8g**). Beige solid (941 mg, 97%). mp 207-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.90 (4H, s, $2CH_2$), 2.33 (3H, s, CH_3), 2.37 (3H, s, CH_3), 3.70 (4H, s, $2N\text{-}CH_2$), 3.88 (3H, s, CH_3O), 7.07 (1H, s, CH pyrrole), 7.45 (2H, s, 2CH aromatic), 7.70 (1H, s, CH pyrrole). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_C 19.62 (CH_3), 19.99 (CH_3), 25.50 ($2CH_2$), 49.49 ($N(CH_2)_2$), 51.91 (OCH_3), 112.91, 113.64, 114.12, 115.41, 120.21, 122.94, 127.31, 132.38, 135.12, 151.23 (C=N), 165.60 (C=O). ESI-MS: m/z 324.2 $[M+H]^+$. Anal. calcd for $C_{19}H_{21}N_3O_2$ (323.39): C, 70.57; H, 6.55; N, 12.99. Found: C, 70.71; H, 6.47; N, 13.06.

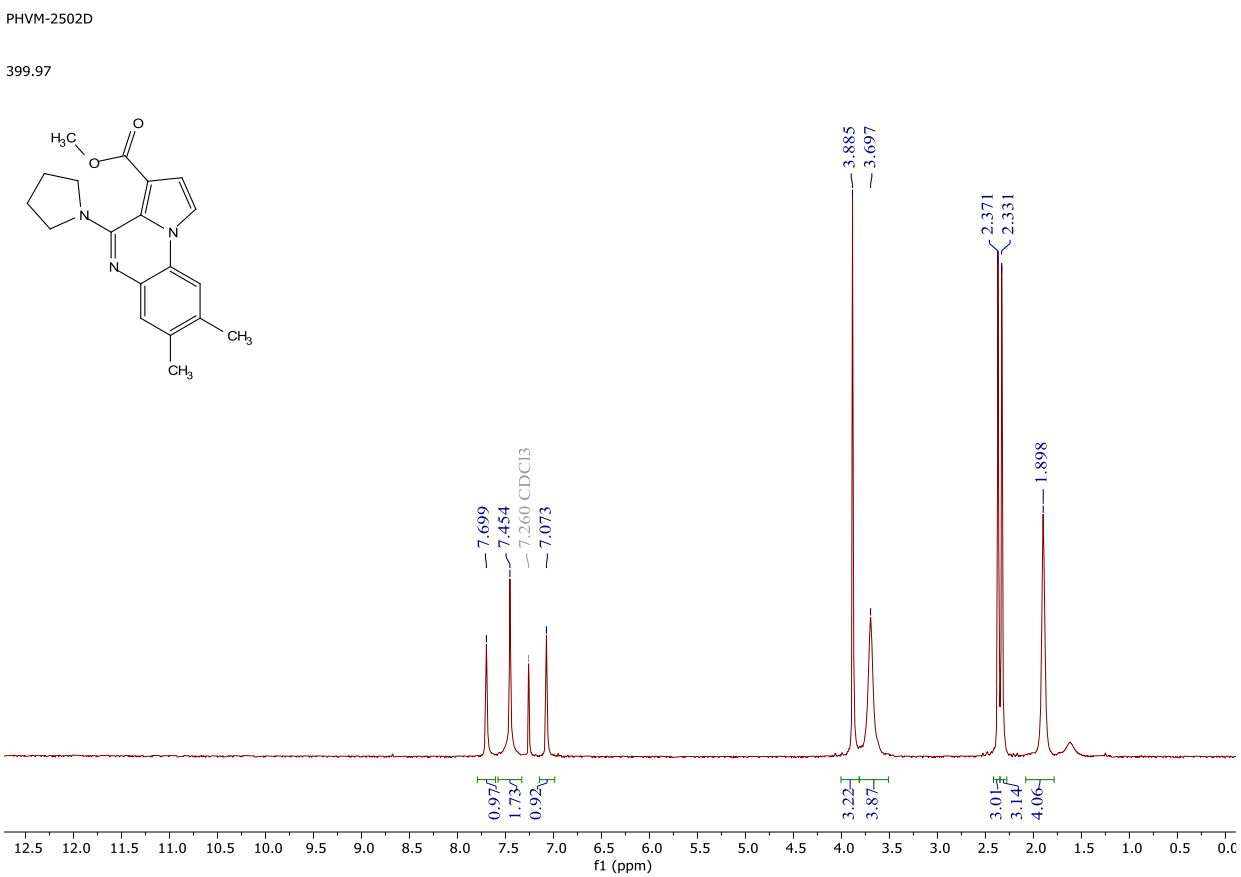


Figure S112. ^{1}H NMR spectrum of methyl 7,8-dimethyl-4-(pyrrolidin-1-yl)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8g**) in $CDCl_3$

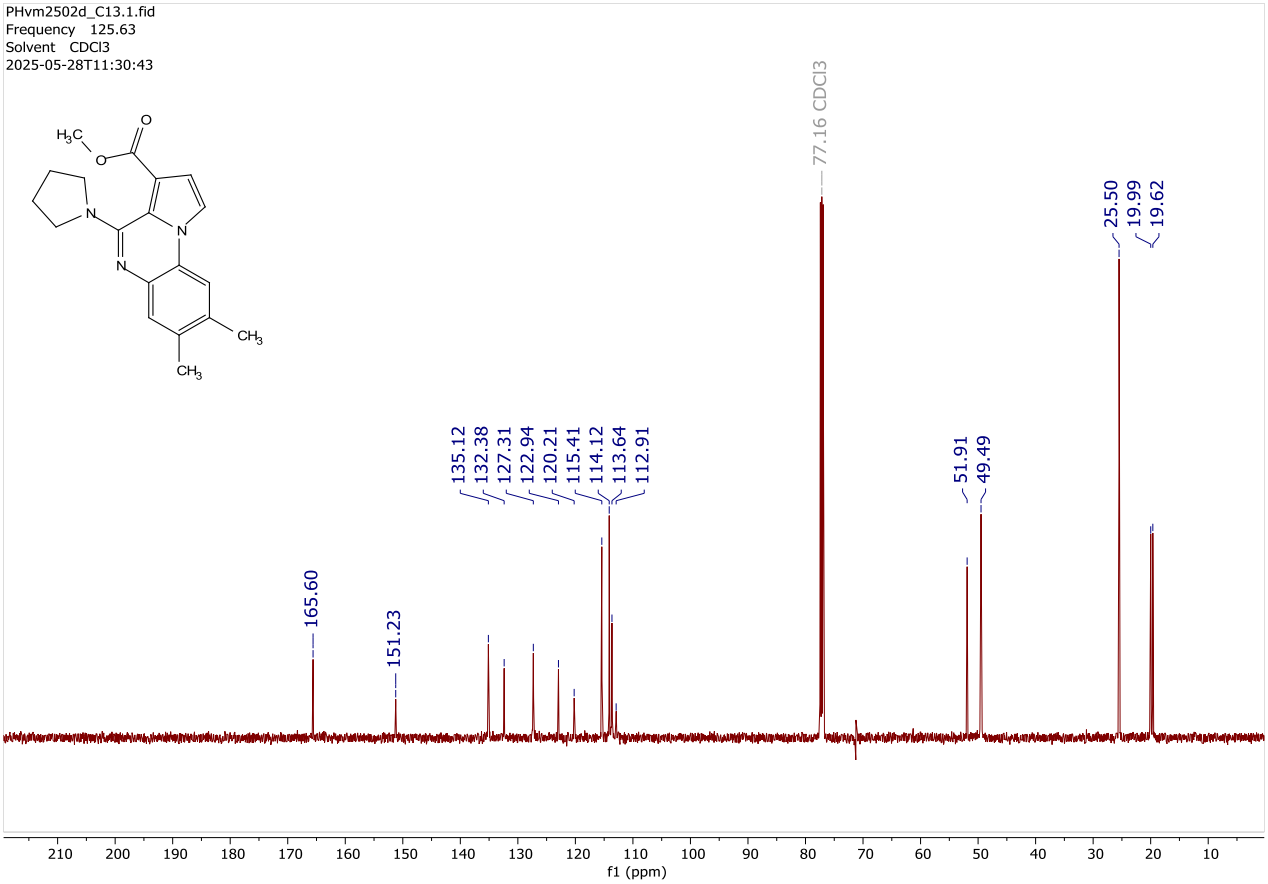
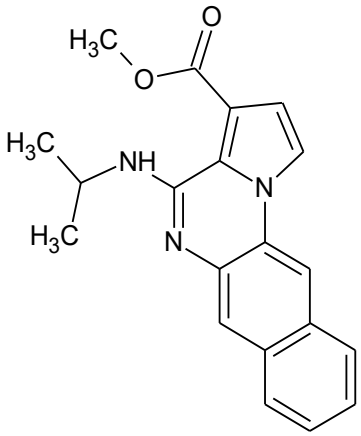


Figure S113. ^{13}C NMR spectrum of methyl 7,8-dimethyl-4-(pyrrolidin-1-yl)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8g**) in $CDCl_3$



Chemical characterization of methyl 4-(isopropylamino)benzo[g]pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8h**). Light yellow solid (870 mg, 87%). mp 214-215 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.43 (6H, d, $^{3}J_{HH}$ 6.5 Hz, $(C\underline{H}_3)_2CH$), 3.94 (3H, s, CH_3O), 4.49 – 4.79 (1H, m, $(CH_3)_2C\underline{H}$), 7.21 (1H, d, J = 3.1 Hz, CH pyrrole), 7.37 – 7.44 (2H, m, CH aromatic), 7.84 – 7.88 (3H, m, 2CH aromatic + CH pyrrole), 8.07 (2H, s, 2CH aromatic), 9.65 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_C 22.80 ($(CH_3)_2CH$), 42.24 $(CH_3)_2\underline{C}H$), 52.27 (CH_3O), 110.73, 111.27, 114.72, 115.86, 122.23, 122.43, 124.38, 124.66, 125.51, 127.26, 127.29, 129.38, 132.66, 136.92, 148.03 (C=N), 166.79 (C=O). ESI-MS: m/z 334.2 $[M+H]^+$. Anal. calcd for $C_{20}H_{19}N_3O_2$ (333.38): C, 72.05; H, 5.74; N, 12.60. Found: C, 72.26; H, 5.71; N, 12.44.

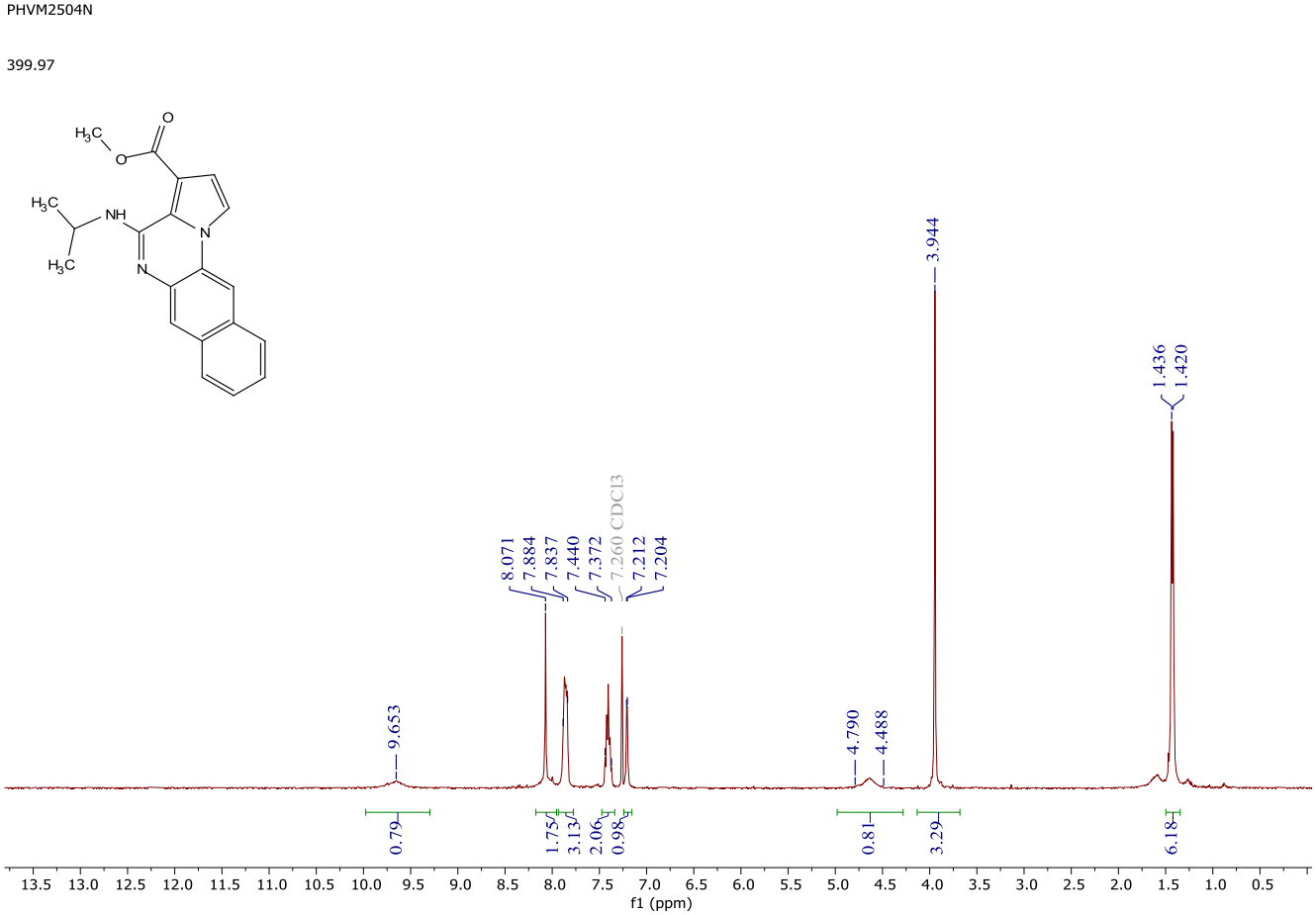


Figure S114. ^{1}H NMR spectrum of methyl 4-(isopropylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8h**) in $CDCl_3$

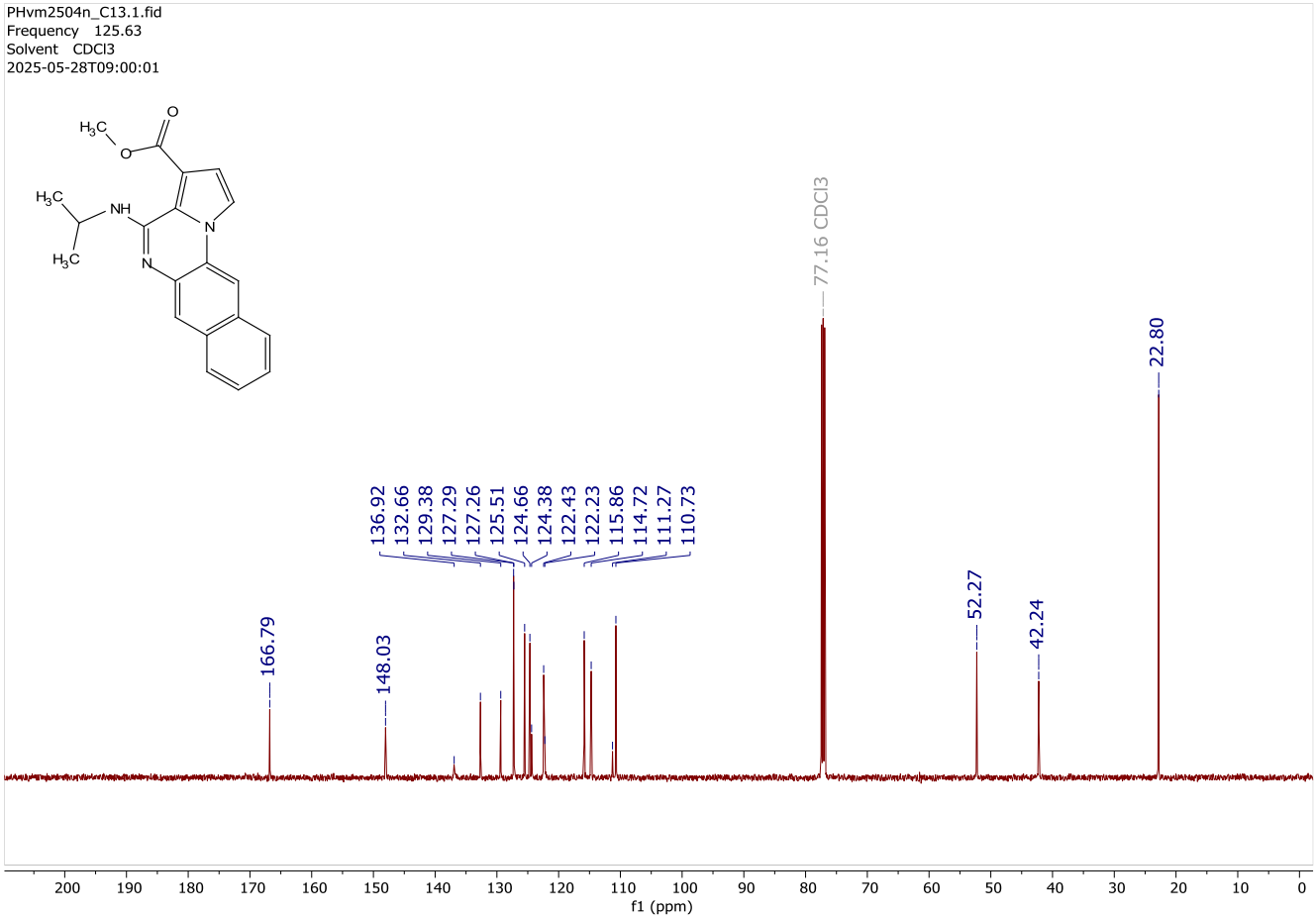
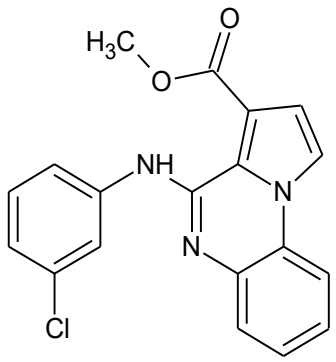


Figure S115. ^{13}C NMR spectrum of methyl 4-(isopropylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8h**) in $CDCl_3$



Chemical characterization of methyl 4-((3-chlorophenyl)amino)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8i**). Beige solid (992 mg, 94%). mp 250-251 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.98 (3H, s, CH_3O), 7.11 (1H, d, $^3J_{HH}$ 8.0 Hz, CH aromatic), 7.33 (1H, d, $^3J_{HH}$ 3.2 Hz, CH pyrrole), 7.42 (2H, t, $^3J_{HH}$ 7.9 Hz, CH aromatic), 7.49 (1H, t, $^3J_{HH}$ 7.6 Hz, CH aromatic), 7.70 (1H, d, $^3J_{HH}$ 8.1 Hz, CH aromatic), 7.78 (1H, d, $^3J_{HH}$ 8.4 Hz, CH aromatic), 8.24 (1H, d, $^3J_{HH}$ 8.3 Hz, CH aromatic), 8.32 (1H, s, CH aromatic), 8.45 (1H, d, *J* 3.2 Hz, CH pyrrole), 12.06 (1H, s, NH). ^{13}C NMR (TFA-d_1, 76 MHz): δ_C 55.22 (CH_3O), 117.32, 118.73, 120.58, 121.51, 122.07, 122.37, 125.05, 126.13, 126.31, 128.34, 130.07, 130.85, 132.55, 134.01, 134.97, 139.15, 148.12 (C=N), 169.64 (COOCH$_3$). ESI-MS: m/z 352.2 $[M+H]^+$. Anal. calcd for $C_{19}H_{14}ClN_3O_2$ (351.79): C, 64.87; H, 4.01; N, 11.94. Found: C, 64.70; H, 3.98; N, 11.99.

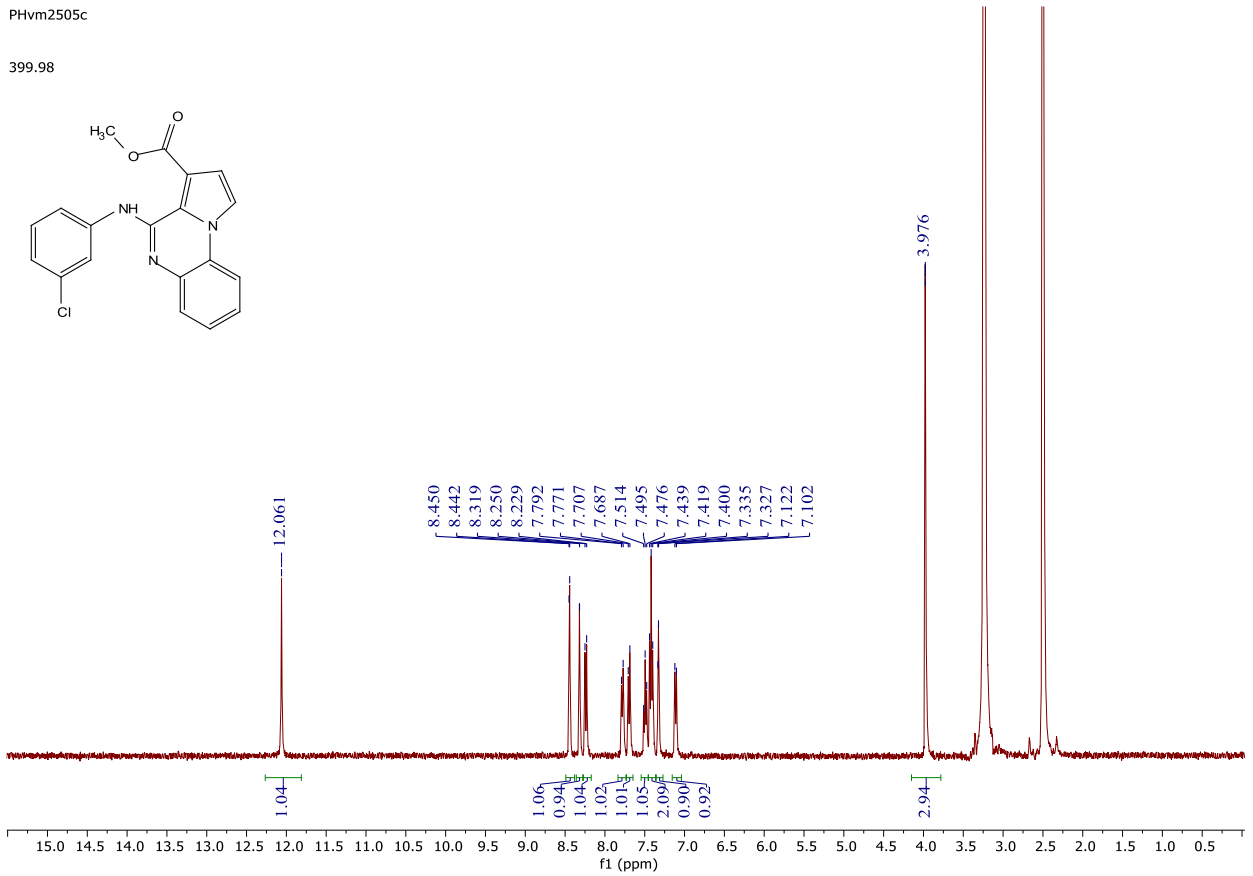


Figure S116. ^{1}H NMR spectrum of methyl 4-((3-chlorophenyl)amino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8i**) in DMSO-d_6

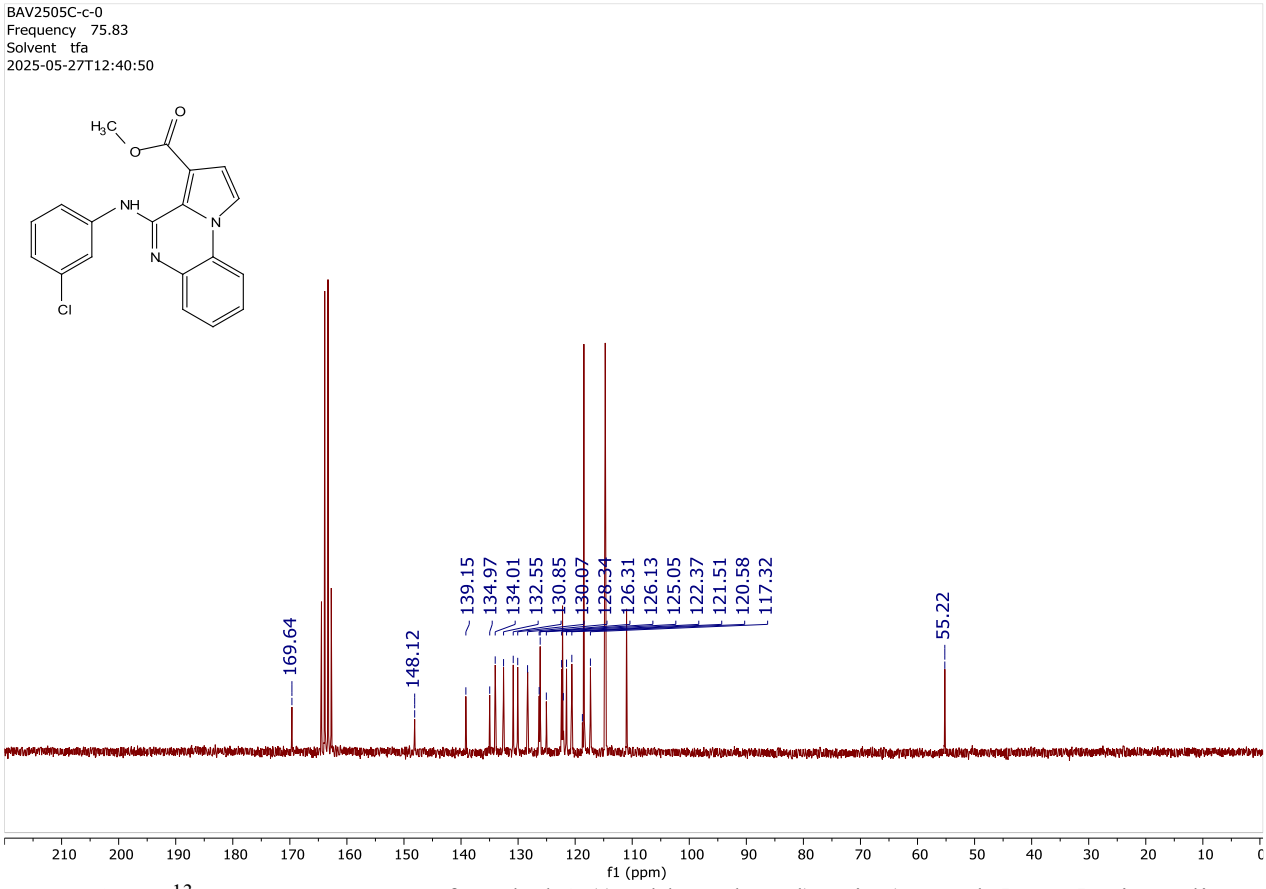
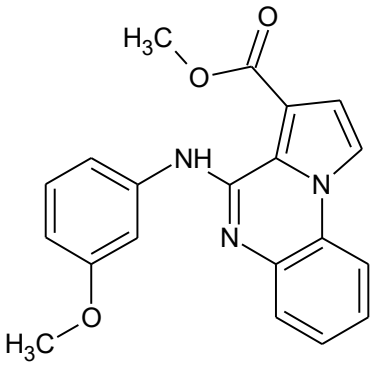


Figure S117. ^{13}C NMR spectrum of methyl 4-((3-chlorophenyl)amino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8i**) in TFA-d_1



Chemical characterization of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8j**). Beige solid (792 mg, 76%). mp 165-166 °C. IR (solid, KBr, νmax, cm^{-1}): 3050, 1683, 1651, 1534, 1483, 1280, 1198, 1045, 748. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.81 (3H, s, OCH_3), 3.93 (3H, s, OCH_3), 6.62-6.65 (1H, m, CH aromatic), 7.24-7.30 (3H, m, 3CH aromatic), 7.35 (1H, t, $^{3}J_{HH}$ 7.8 Hz, CH aromatic), 7.44 (1H, t, $^{3}J_{HH}$ 7.6 Hz, CH aromatic), 7.63 (1H, d, $^{3}J_{HH}$ 7.9 Hz, CH aromatic), 7.99 (1H, d, $^{3}J_{HH}$ 2.1 Hz, CH pyrrole), 8.18 (1H, d, $^{3}J_{HH}$ 8.2 Hz, CH aromatic), 8.38 (1H, d, $^{3}J_{HH}$ 3.5 Hz, CH pyrrole), 11.92 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 52.55 (CH_3O), 55.40 (CH_3O), 105.97, 108.28, 109.92, 112.64, 113.80, 114.14, 116.45, 121.88, 124.01, 124.12, 126.63, 127.44, 129.45, 136.84, 141.75, 146.27 (N=C aromatic), 160.18 (O-C aromatic), 167.25 (C=O). ESI-MS: *m/z* 348.2 $[M+H]^+$. Anal. calcd for $C_{20}H_{17}N_3O_3$ (347.37): C, 69.15; H, 4.93; N, 12.10. Found: C, 69.34; H, 4.92; N, 12.16.

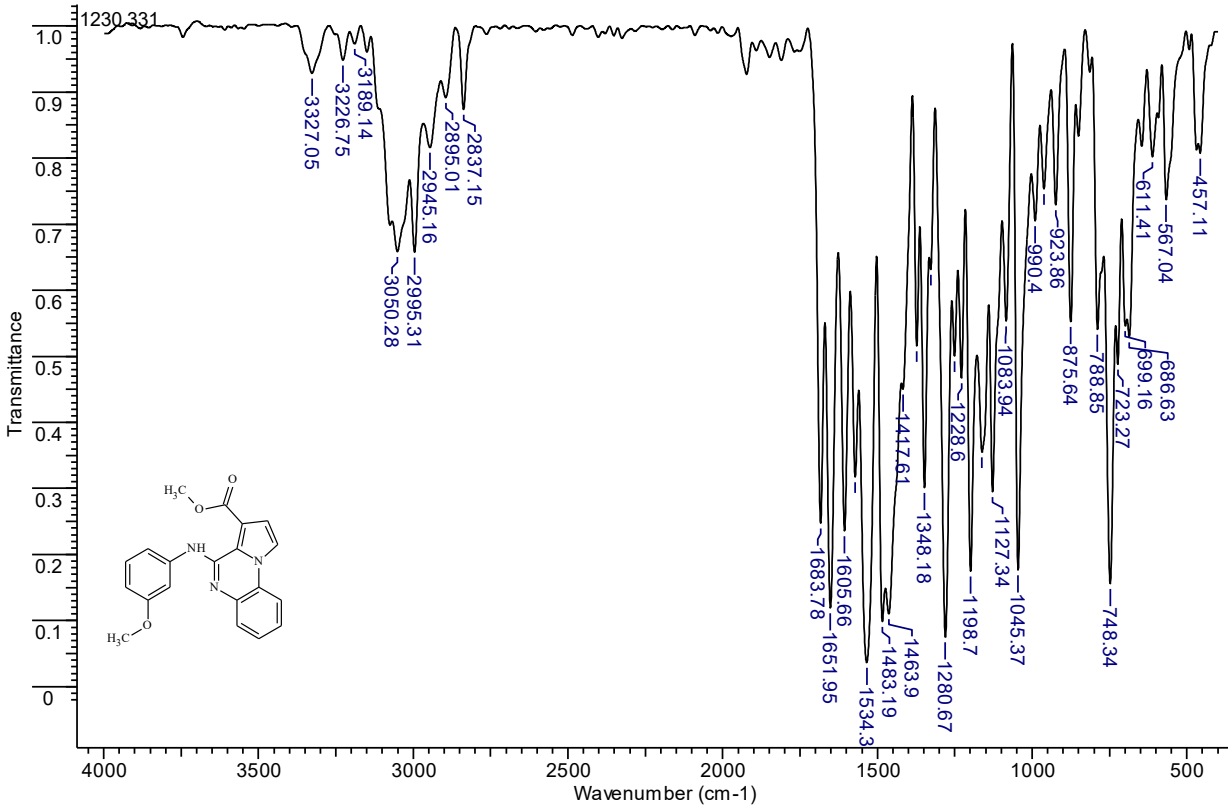


Figure S118. IR spectrum of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8j**) in KBr pellet

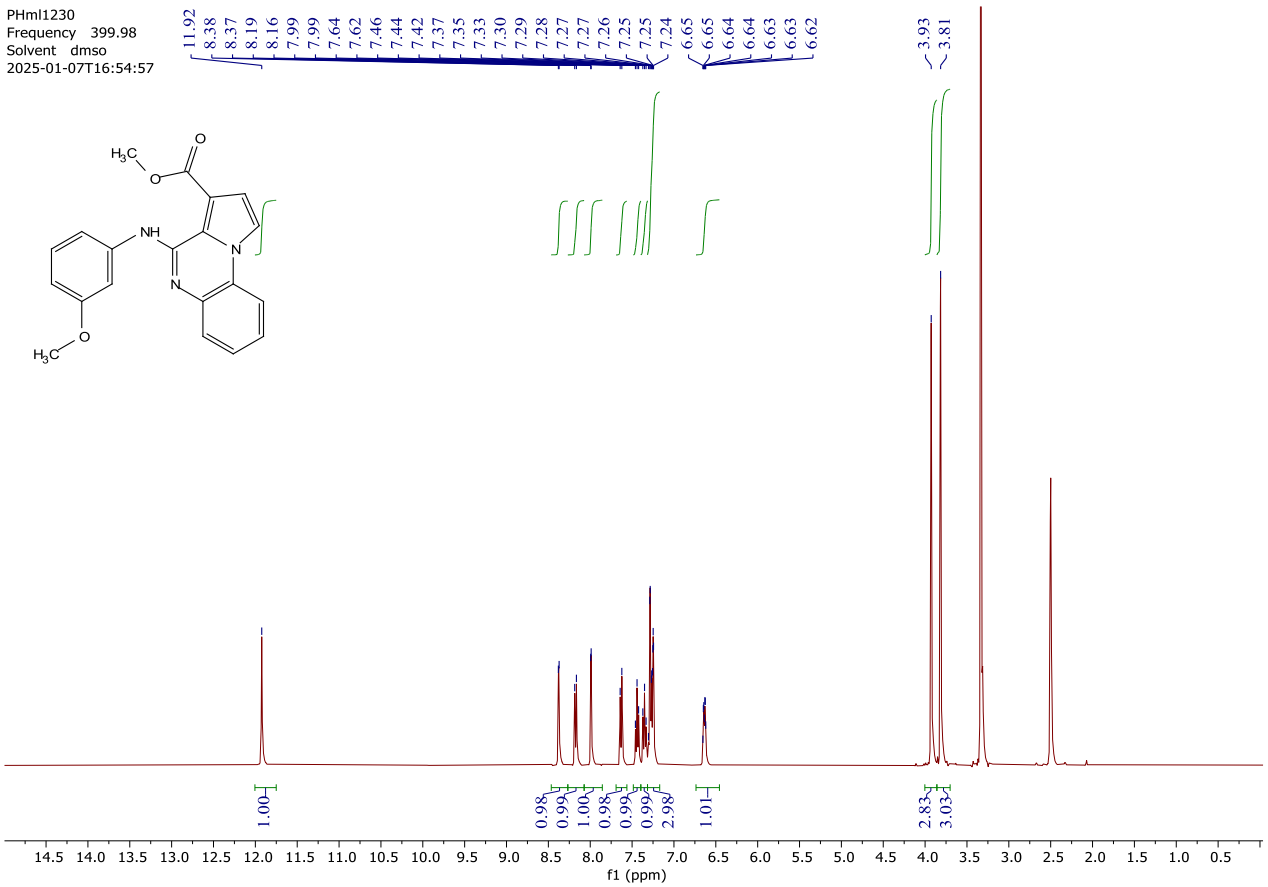


Figure S119. ^{1}H NMR spectrum of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8j**) in DMSO-d_6

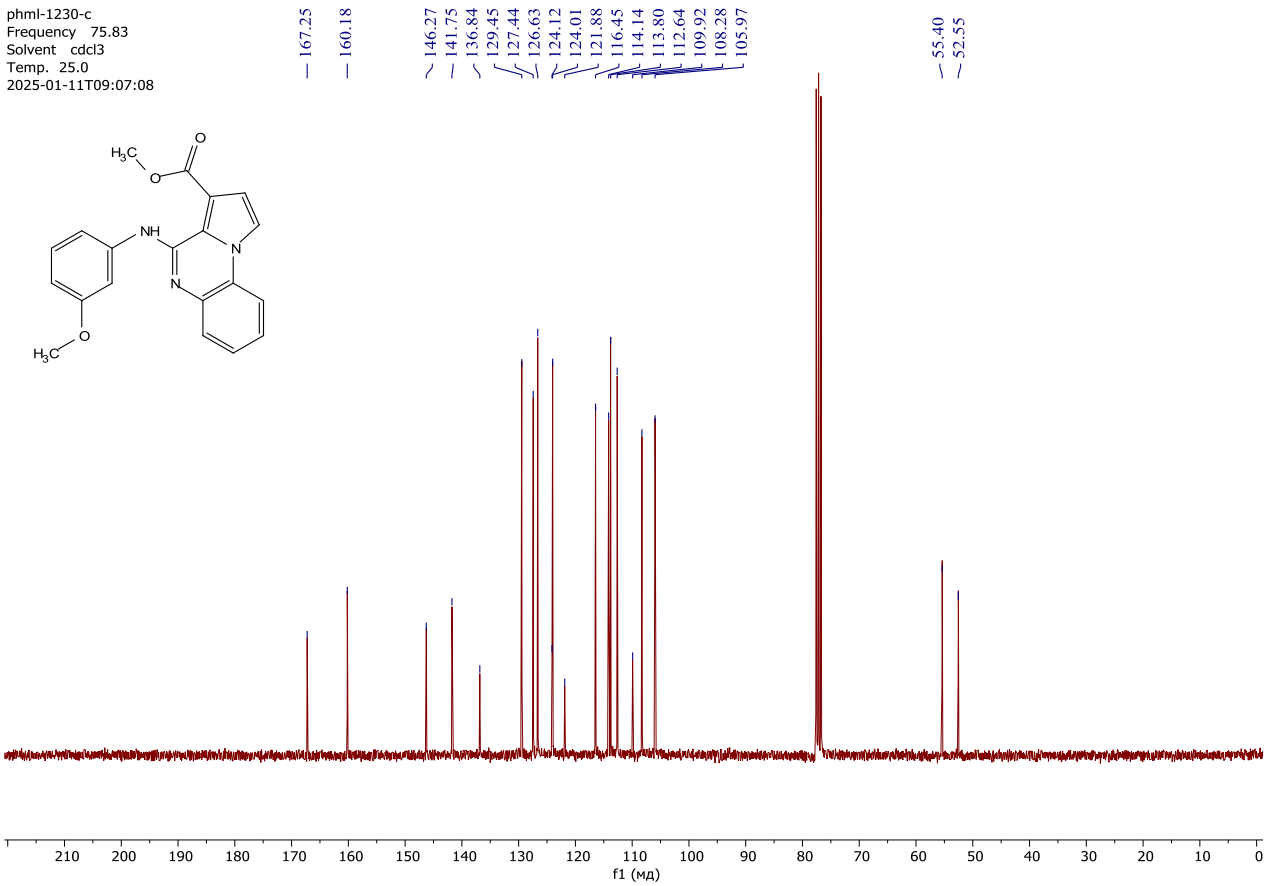


Figure S120. ^{13}C NMR spectrum of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8j**) in $CDCl_3$

X-ray of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8j**).
The colourless crystals of compound **8j** ($C_{20}H_{17}N_3O_3$) are triclinic. At 173 K a = 7.5231(3), b = 9.8646(3), c = 11.4752(3) Å, α = 99.718(2)°, β = 94.883(2)°, γ = 97.226(2)°, V = 827.77(5) Å^3, M_r = 347.36, Z = 2, space group $P\bar{1}$, d_{calc}= 1.394 g/cm^3, $\mu(MoK_\alpha)$ = 0.096 mm^{-1}, F(000) = 364. Intensities of 12074 reflections (2904 independent, R_{int}=0.0312) were measured on the Bruker APEX II diffractometer (graphite monochromated MoK_α radiation, CCD detector, φ- and ω-scaning, $2\Theta_{max}$ = 50°). The structure was solved by direct method using OLEX2 [4] package with SHELXT [5] and SHELXL modules [6]. Positions of the hydrogen atoms were located from electron density difference maps and refined using "riding" model with U_{iso} = nU_{eq} of the carrier atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms). Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 2904 reflections was converged to wR_2 = 0.1113 (R_1 = 0.0413 for 2289 reflections with F>4σ(F), S = 1.018). The final atomic coordinates, and crystallographic data for molecule **8j** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 2453292).

Literature

4. O. V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2 : a complete structure solution, refinement and analysis program, J. Appl. Crystallogr. 42 (2009) 339–341. https://doi.org/10.1107/S0021889808042726.
5. G.M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination, Acta Crystallogr. Sect. A Found. Adv. 71 (2015) 3–8. https://doi.org/10.1107/S2053273314026370.
6. G.M. Sheldrick, Crystal Structure Refinement with SHELXL, Acta Crystallogr. Sect. C, 71 (2015) 3–8. http://dx.doi.org/10.1107/S2053229614024218.

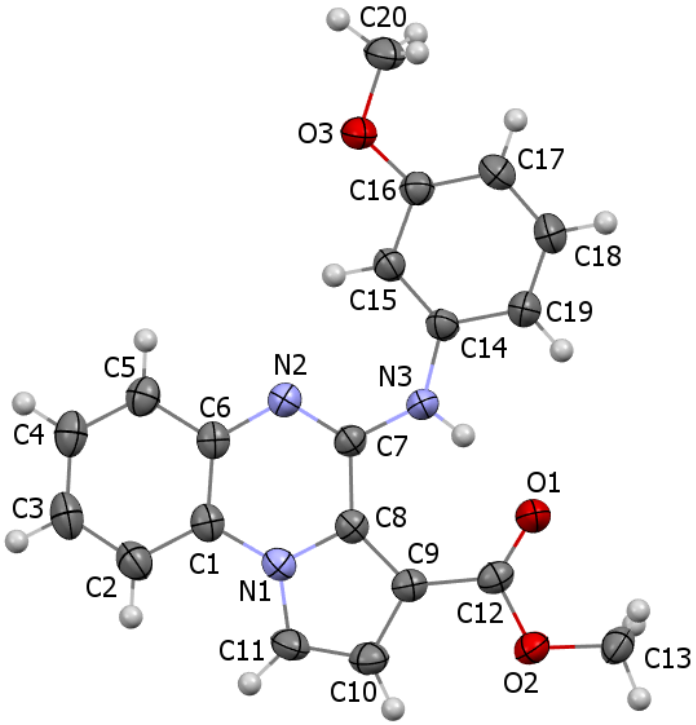
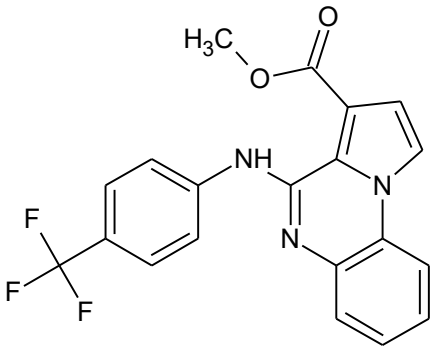


Figure S121. X-ray of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8j**).



Chemical characterization of methyl 4-{[4-(trifluoromethyl)phenyl]amino}pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8k**). White solid (902 mg, 78%). mp 214-215 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.96 (3H, s, OCH_3), 7.31 (1H, d, $^{3}J_{HH}$ 2.8 Hz, CH pyrrole), 7.42 (1H, t, $^{3}J_{HH}$ 7.7 Hz, CH aromatic), 7.49 (1H, t, $^{3}J_{HH}$ 7.6 Hz, CH aromatic), 7.72 (3H, d, $^{3}J_{HH}$ 8.4 Hz, 3CH aromatic), 8.19-8.24 (3H, m, 3CH aromatic), 8.44 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 12.21 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 52.71 (OCH_3), 110.04, 113.91, 114.40, 116.69, 119.49, 121.74, 123.84 (q, $^{2}J_{CF}$ 32.7 Hz, C aromatic), 124.34, 124.70, 124.73 (q, $^{1}J_{CF}$ 270.8 Hz, CF_3), 126.11 (q, $^{3}J_{CF}$ 3.6 Hz, 2CH aromatic), 126.87, 127.70, 136.59, 143.72, 146.08, 167.44. ^{19}F NMR ($CDCl_3$, 376 MHz): δ_F -62.16. ESI-MS: *m/z* 386.2 $[M+H]^+$. Anal. calcd for $C_{20}H_{14}F_3N_3O_2$ (385.34): C, 62.34; H, 3.66; N, 10.90. Found: C, 62.49; H, 3.64; N, 10.79.

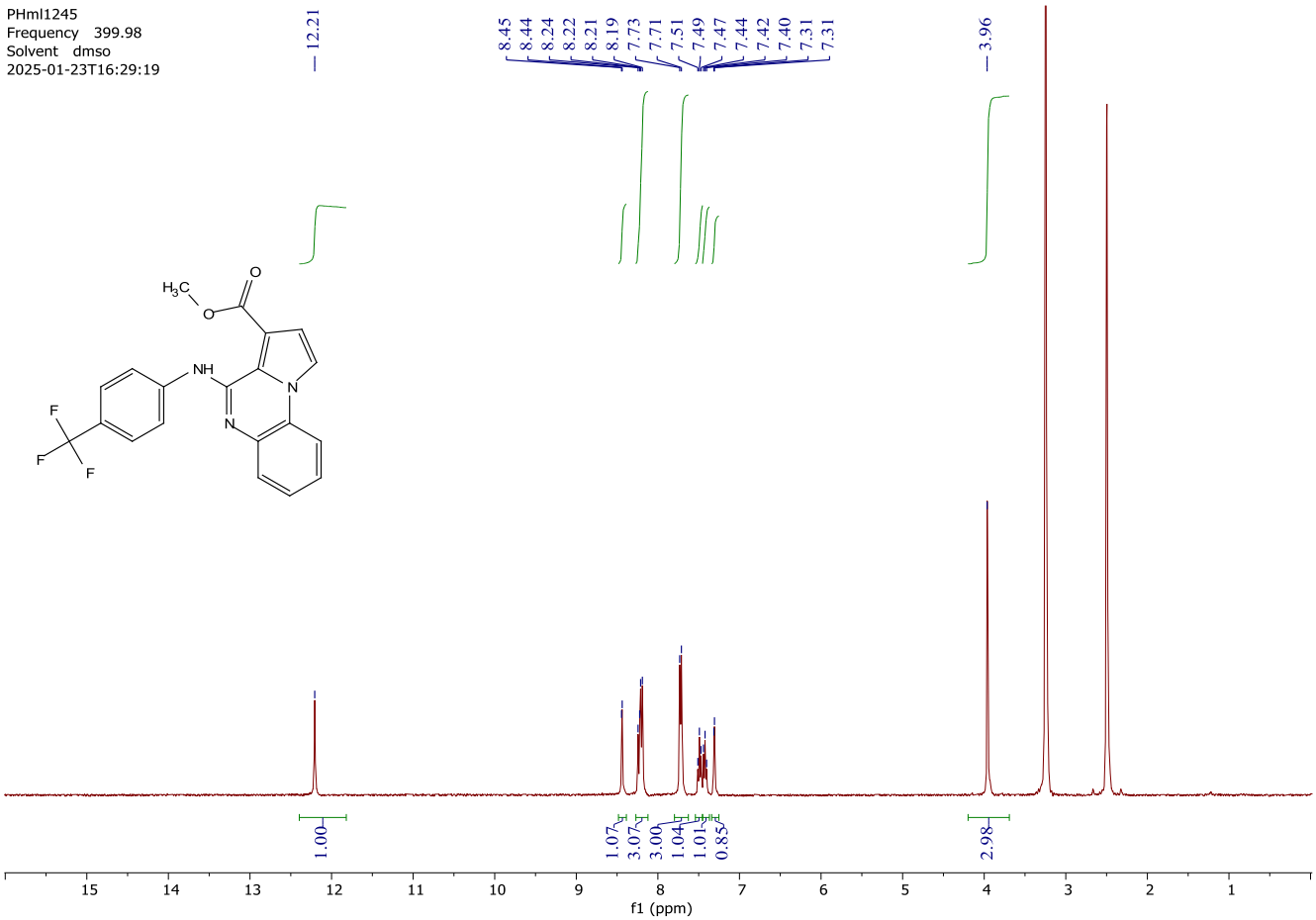


Figure S122. ^{1}H NMR spectrum of methyl 4-{[4-(trifluoromethyl)phenyl]amino}pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8k**) in DMSO-d_6

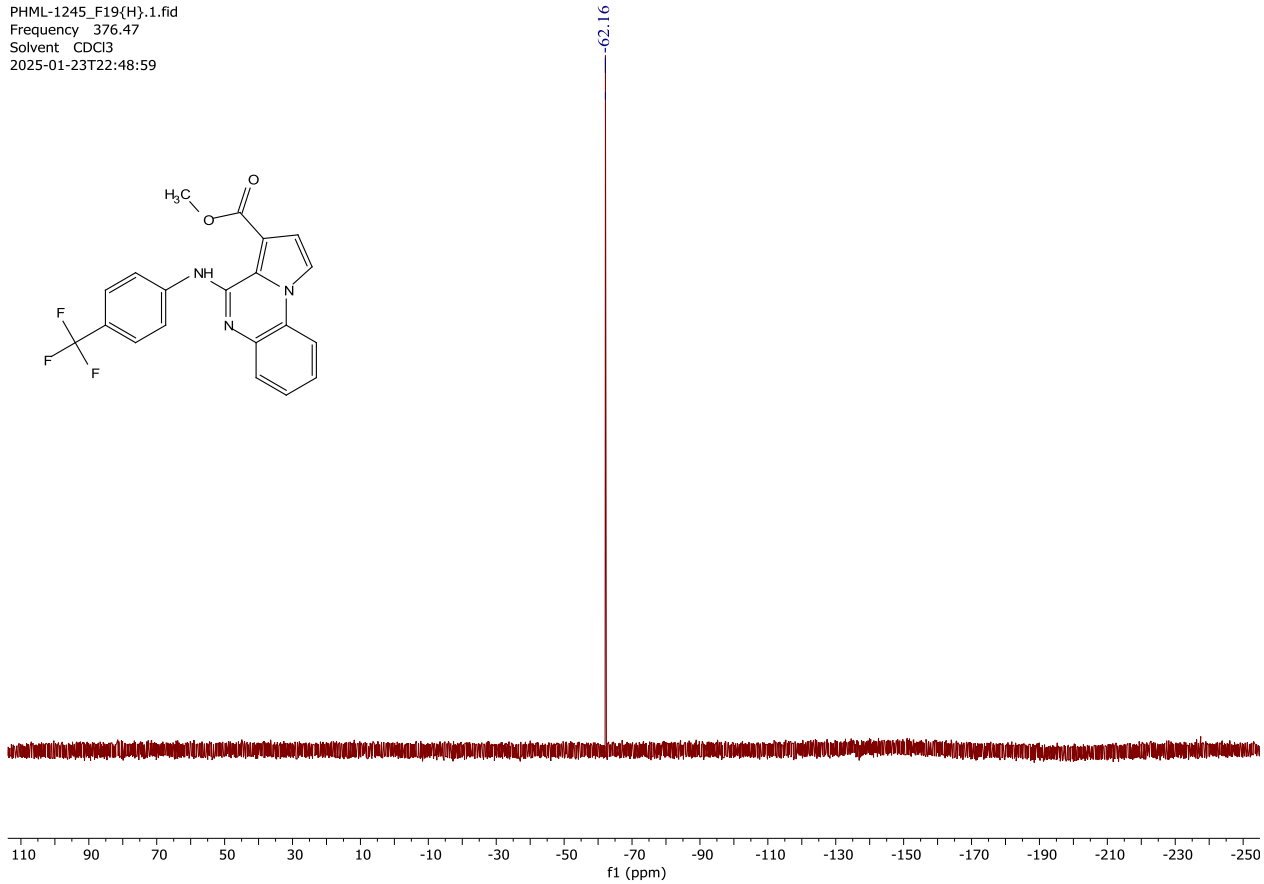


Figure S123. ^{19}F NMR spectrum of methyl 4-{[4-(trifluoromethyl)phenyl]amino}pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8k**) in $CDCl_3$

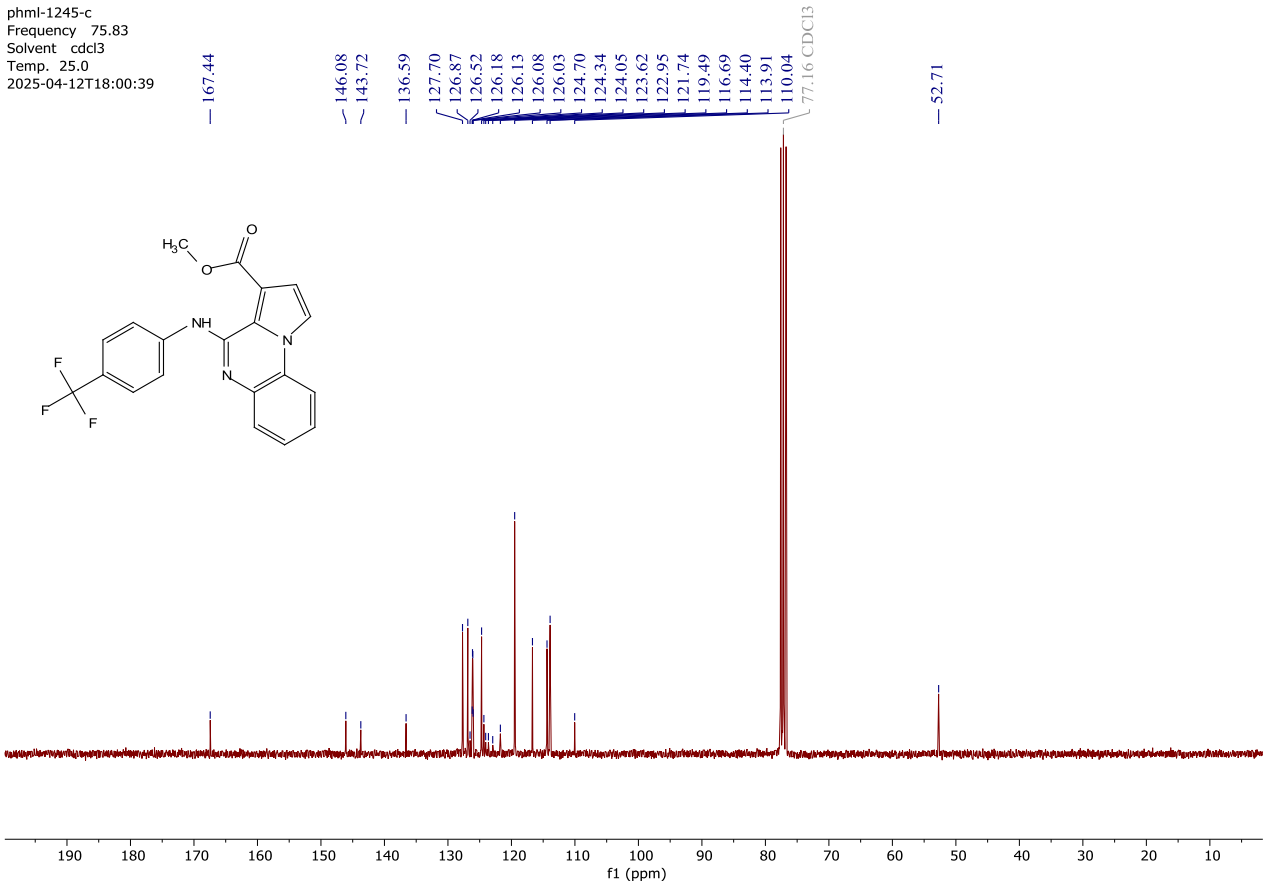
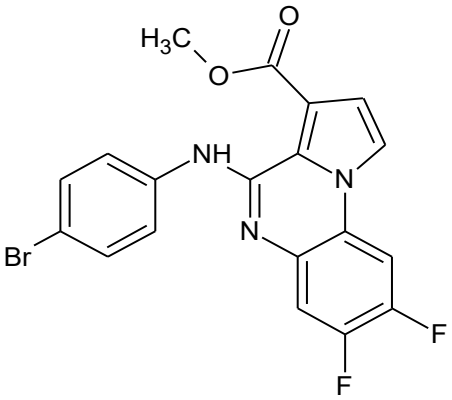


Figure S124. ^{13}C NMR spectrum of methyl 4-{[4-(trifluoromethyl)phenyl]amino}pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8k**) in $CDCl_3$



Chemical characterization of methyl 4-((4-bromophenyl)amino)-7,8-difluoropyrrolo[1,2-a]quinoxaline-3-carboxylate (**8l**). Beige solid (1.089 g, 84%). mp 282-283 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.96 (3H, s, CH_3O), 7.30 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 7.54 (2H, d, $^{3}J_{HH}$ 7.6 Hz, 2CH aromatic), 7.63 (1H, dd, $^{3}J_{HF}$ 11.6, $^{3}J_{HH}$ 8.0 Hz, CH aromatic), 7.92 (2H, d, $^{3}J_{HH}$ 9.0 Hz, 2CH aromatic), 8.35 (1H, d, $^{3}J_{HH}$ 3.3 Hz, CH pyrrole), 8.42 (1H, dd, $^{3}J_{HF}$ 11.4, $^{3}J_{HH}$ 7.9 Hz, CH aromatic), 11.98 (1H, s, NH). ^{13}C NMR (TFA-d_1,101 MHz): δ_C 55.35 (OCH_3) 107.19 (d, $^{2}J_{CF}$ 24.2 Hz, CH aromatic), 109.80 (d, $^{2}J_{CF}$ 23.9 Hz, CH aromatic), 118.69, 121.55 (d, $^{3}J_{CF}$ 7.9 Hz, C aromatic), 121.81, 122.73, 122.77, 123.15 (d, $^{3}J_{CF}$ 9.0 Hz, C aromatic), 126.89, 129.60, 132.47, 136.49, 148.43 (C=N), 151.73 (dd, $^{1}J_{CF}$ 253.6, $^{2}J_{CF}$ 13.6 Hz, CF aromatic), 152.30 (dd, $^{1}J_{CF}$ 253.3, $^{2}J_{CF}$ 12.9 Hz, CF aromatic), 169.40 ($COOCH_3$). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -140.68 (ddd, $^{3}J_{FF}$ 23.6, $^{3}J_{HF}$ 11.7, $^{4}J_{HF}$ 8.1 Hz), -139.62 (ddd, $^{3}J_{FF}$ 23.6, $^{3}J_{HF}$ 11.3, $^{4}J_{HF}$ 7.6 Hz). ESI-MS: m/z 434.0, 432.0 [M+H]+. Anal. calcd for $C_{19}H_{12}BrF_2N_3O_2$ (432.22): C, 52.80; H, 2.80; N, 9.72. Found: C, 53.03; H, 2.82; N, 9.60.

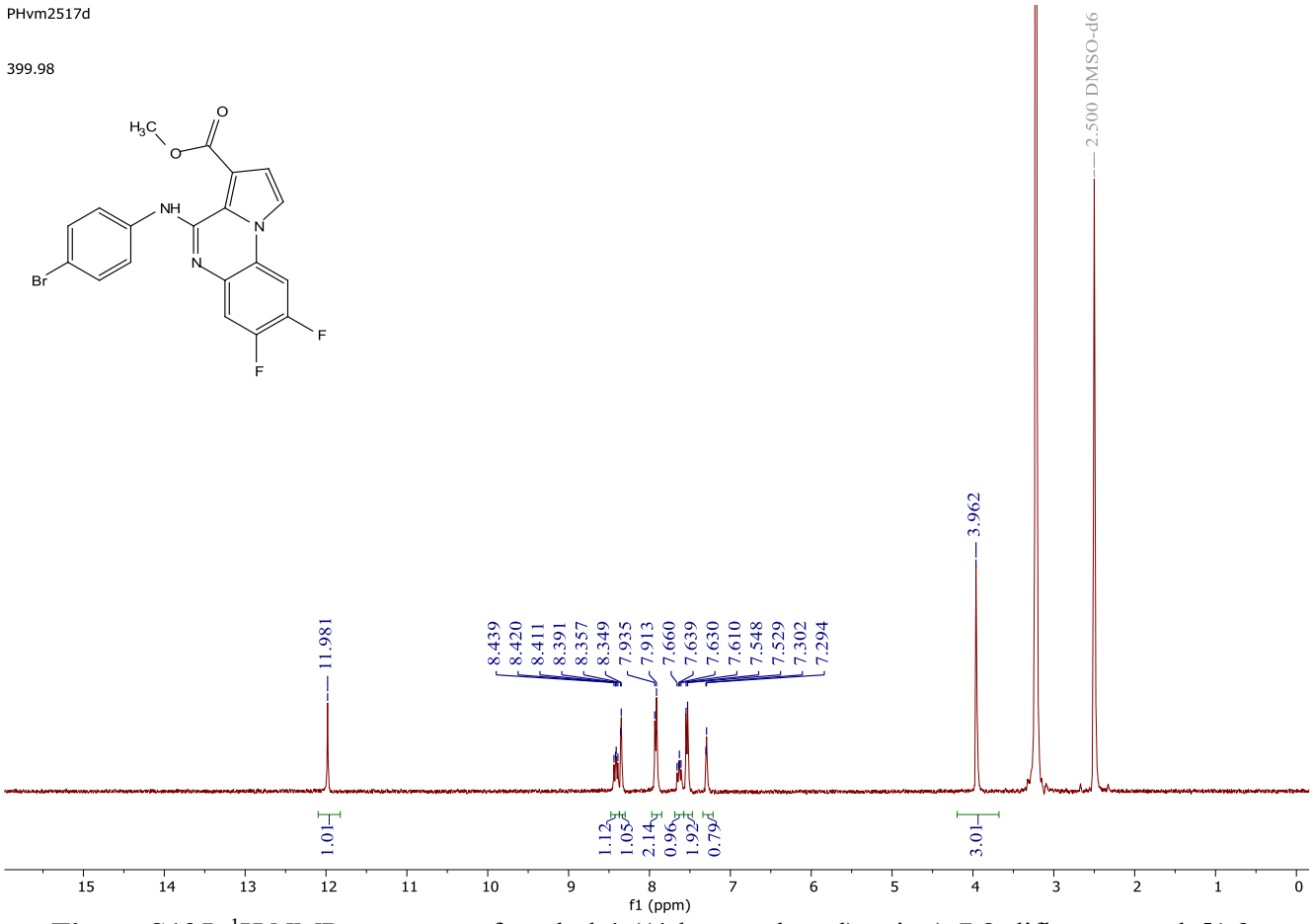


Figure S125. ^{1}H NMR spectrum of methyl 4-((4-bromophenyl)amino)-7,8-difluoropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8l**) in DMSO-d_6

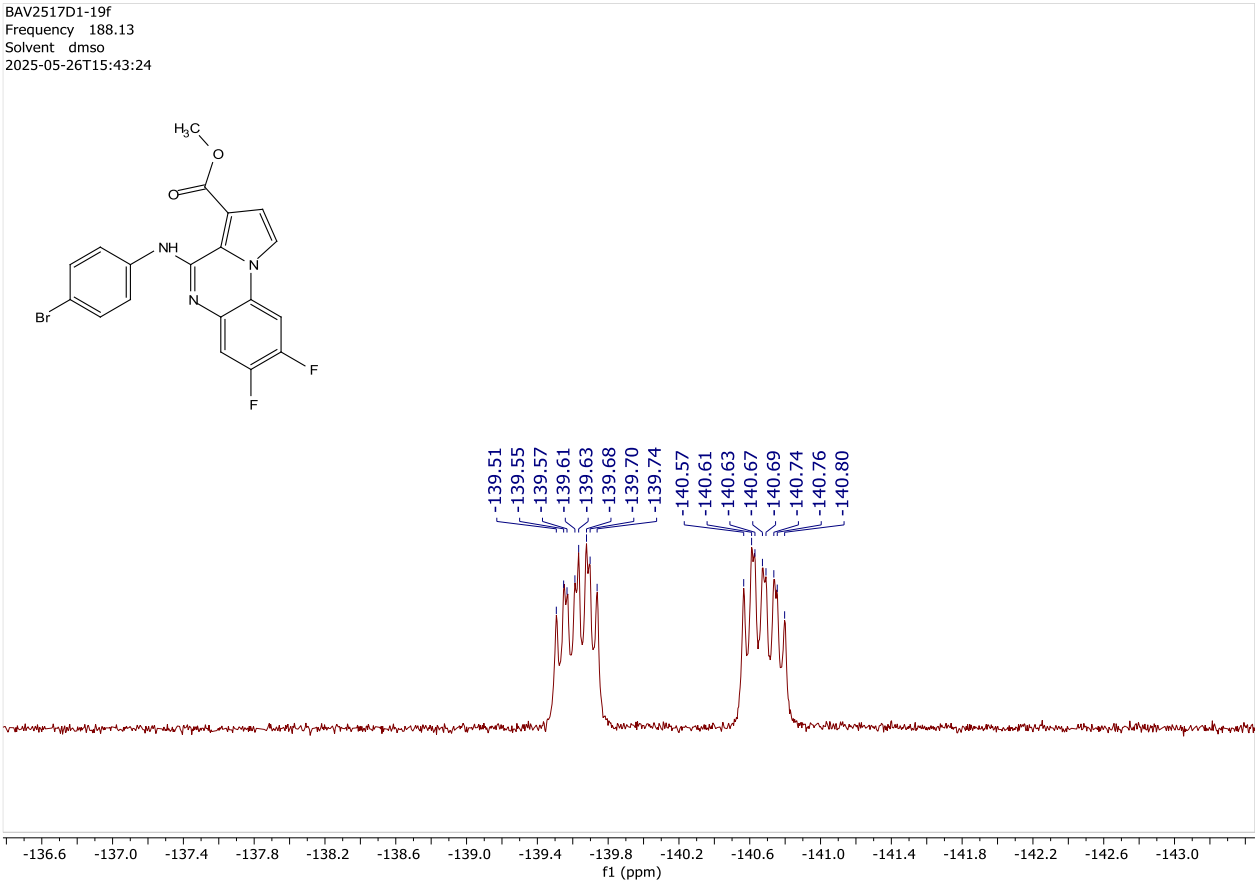


Figure S126. ^{19}F NMR spectrum of methyl 4-((4-bromophenyl)amino)-7,8-difluoropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8l**) in DMSO-d_6

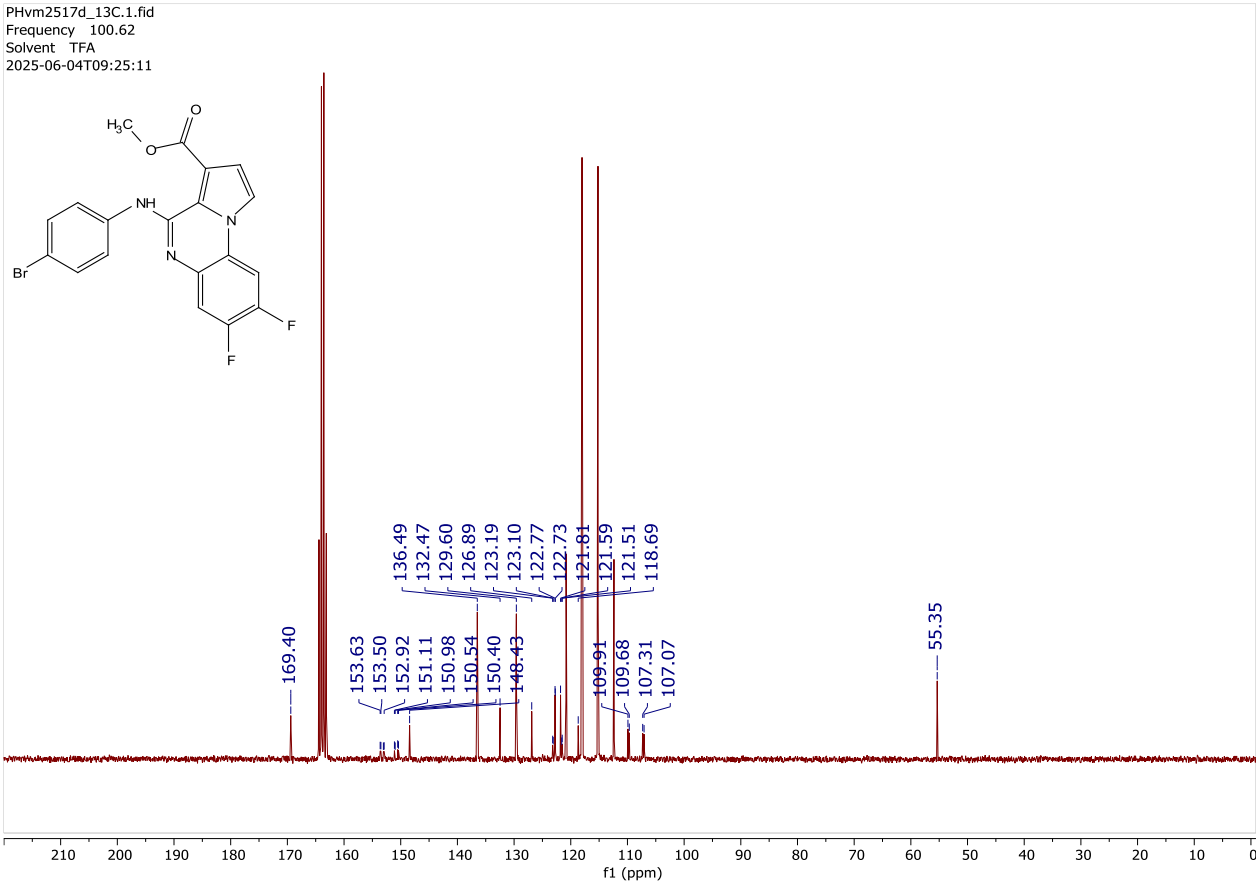
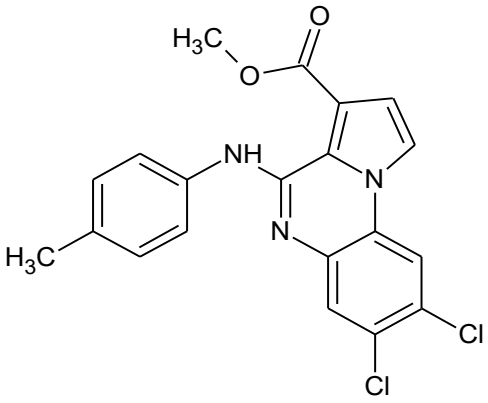


Figure S127. ^{13}C NMR spectrum of methyl 4-((4-bromophenyl)amino)-7,8-difluoropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8l**) in TFA-d_1



Chemical characterization of methyl 7,8-dichloro-4-(p-tolylamino)pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8m**). Light yellow solid (1.057 g, 88%). mp 283-284 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 2.31 (3H, s, CH_3), 3.92 (3H, s, CH_3O), 7.11-7.17 (3H, m, 2CH aromatic + CH pyrrole), 7.60 (1H, s, CH aromatic), 7.76 (2H, d, $^{3}J_{HH}$ 7.9 Hz, 2CH aromatic), 8.29 (1H, s, CH aromatic), 8.36 (1H, d, $^{3}J_{HH}$ 3.6 Hz, CH pyrrole), 11.76 (1H, s, NH). ^{13}C NMR (TFA-d_1, 151 MHz): δ_C 21.60 (CH_3), 55.24 (CH_3O), 118.84, 119.10, 121.65, 121.78, 122.54, 122.83, 124.05, 125.79, 127.56, 130.50, 133.67, 134.25, 135.38, 144.06, 148.40 (C=N), 169.23 ($COOCH_3$). ESI-MS: m/z 400.0 $[M+H]^+$. Anal. calcd for $C_{20}H_{15}Cl_2N_3O_2$ (400.26): C, 60.01; H, 3.78; N, 10.50. Found: C, 59.85; H, 3.80; N, 10.43.

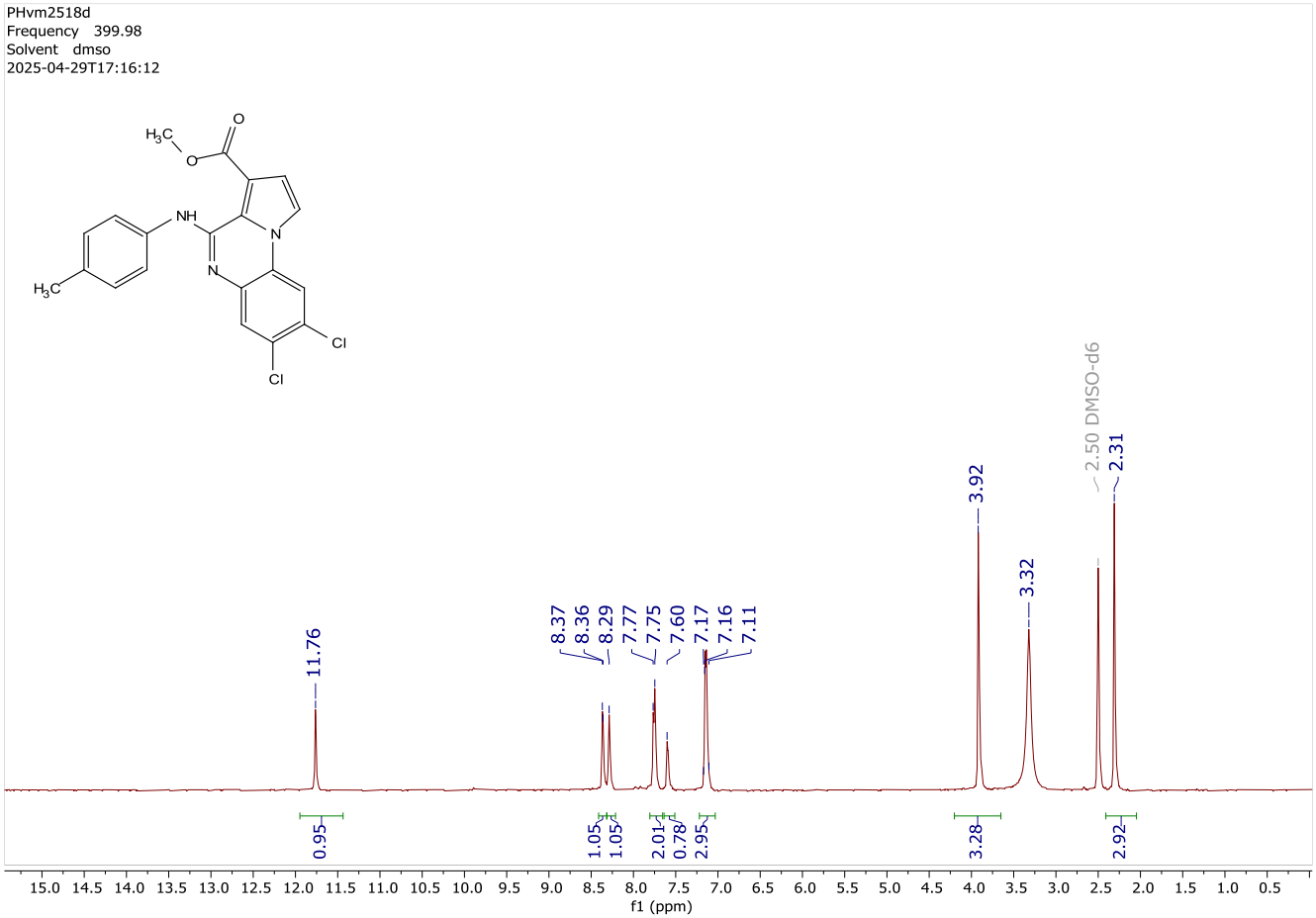


Figure S128. ^{1}H NMR spectrum of methyl 7,8-dichloro-4-(*p*-tolylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8m**) in DMSO-d_6

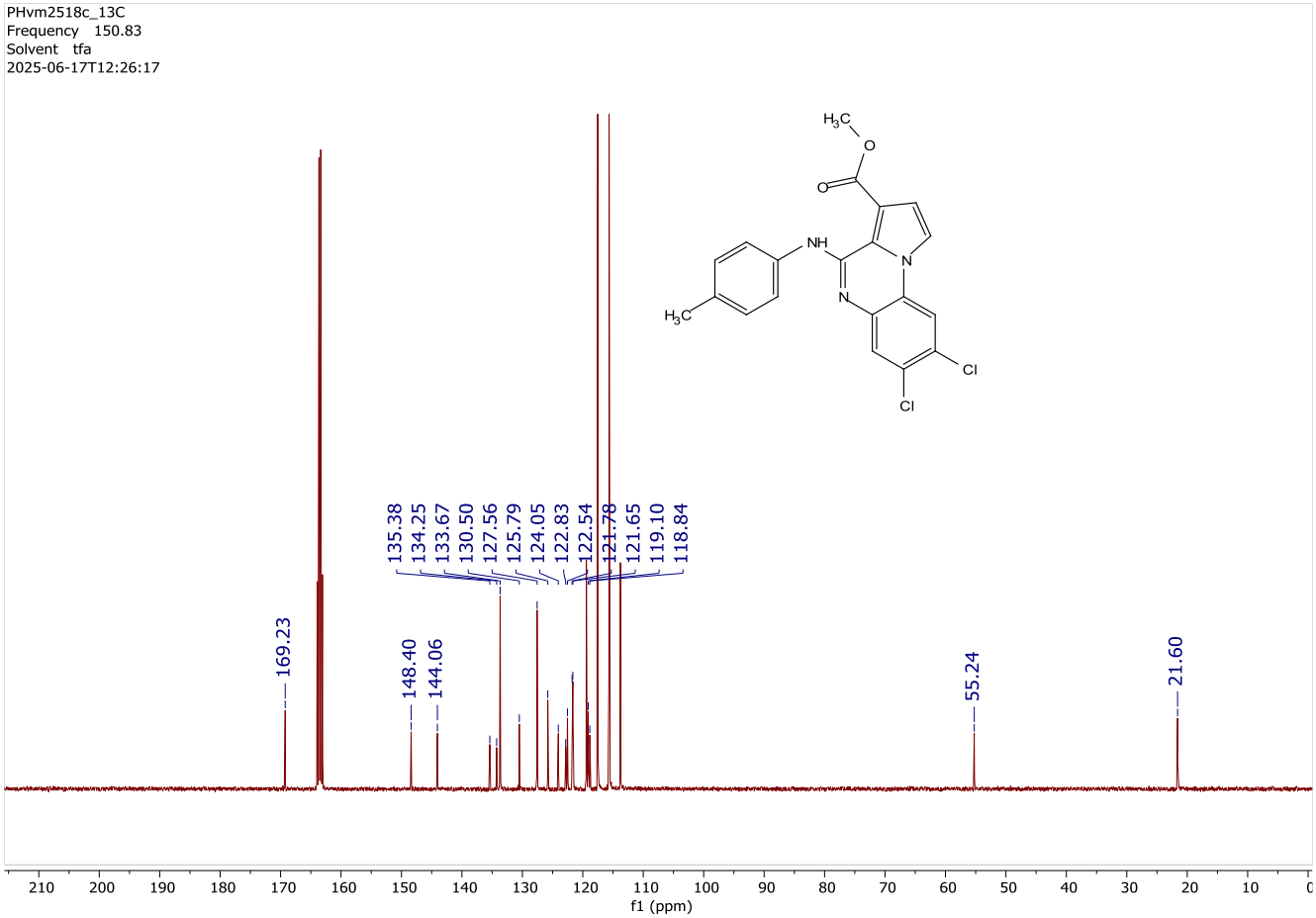
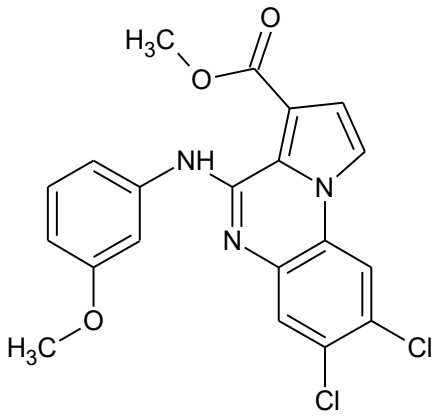


Figure S129. ^{13}C NMR spectrum of methyl 7,8-dichloro-4-(*p*-tolylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8m**) in TFA-d_1



Chemical characterization of methyl 7,8-dichloro-4-[(3-methoxyphenyl)amino]pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8n**). Beige solid (1.136 g, 91%). mp 204-205 °C.. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.81 (3H, s, OCH_3), 3.93 (3H, s, OCH_3), 6.65 (1H, s, CH aromatic), 7.20 (1H, s, CH pyrrole), 7.24-7.26 (2H, m, 2CH aromatic), 7.64 (1H, s, CH aromatic), 7.79 (1H, s, CH aromatic), 8.36 (1H, s, CH aromatic), 8.45 (1H, s, CH pyrrole), 11.92 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 52.81 (CH_3O), 55.48 (CH_3O), 106.53, 108.74, 111.06, 113.01, 114.64, 115.40, 117.05, 121.55, 123.30, 127.03, 128.00, 129.58, 130.42, 136.48, 141.07, 146.84 (C=N), 160.21 (CH_3O-C aromatic), 167.07 (C=O). ESI-MS: *m/z* 416.0 $[M+H]^+$. Anal. calcd for $C_{20}H_{15}Cl_2N_3O_3$ (416.26): C, 57.71; H, 3.63; N, 10.09. Found: C, 57.86; H, 3.65; N, 10.01.

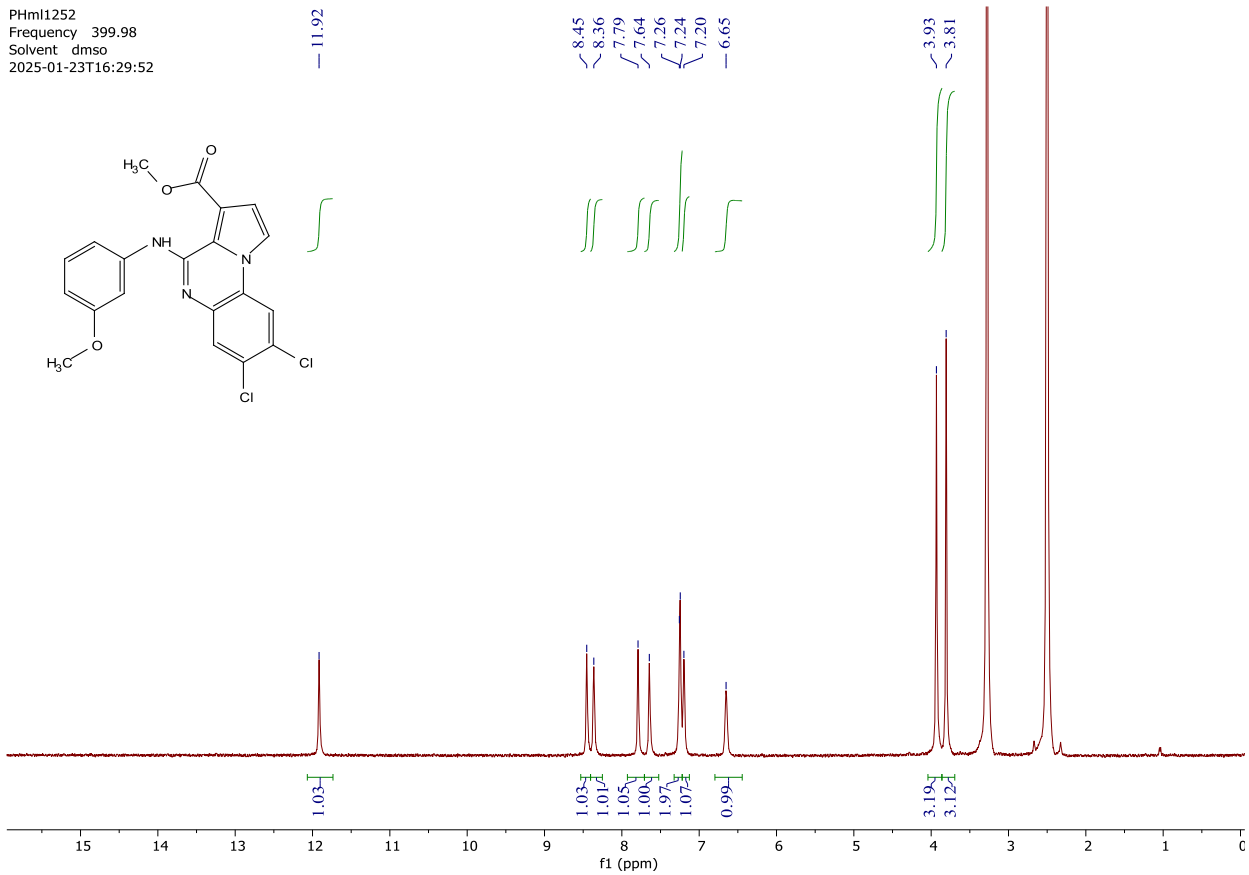


Figure S130. ^{1}H NMR spectrum of methyl 7,8-dichloro-4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8n**) in DMSO-d_6

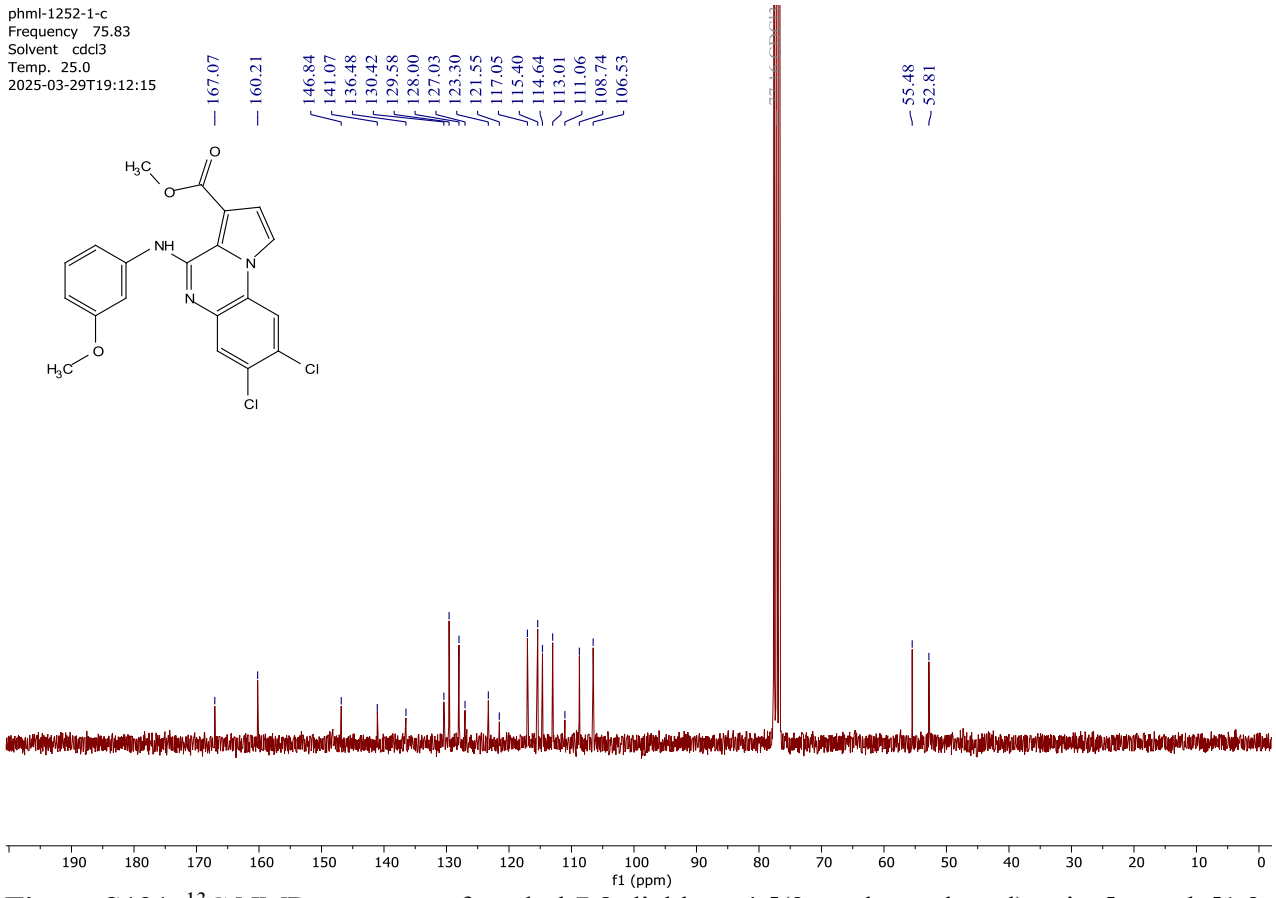
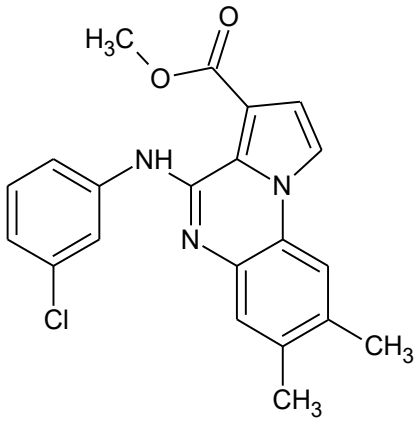


Figure S131. ^{13}C NMR spectrum of methyl 7,8-dichloro-4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8n**) in $CDCl_3$



Chemical characterization of methyl 4-((3-chlorophenyl)amino)-7,8-dimethylpyrrolo[1,2-a]quinoxaline-3-carboxylate (**8o**). Beige solid (1.014 g, 89%). mp 251-252 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 2.31 (3H, s, CH_3), 2.35 (3H, s, CH_3), 3.94 (3H, s, CH_3O), 7.06 (1H, d, $^{3}J_{HH}$ 8.0 Hz, CH aromatic), 7.21 (1H, s, CH pyrrole), 7.35-7.39 (2H, m, 2CH aromatic), 7.72 (1H, d, $^{3}J_{HH}$ 8.2 Hz, CH aromatic), 7.90 (1H, s, CH aromatic), 8.22-8.25 (2H, m, CH aromatic + CH pyrrole), 11.87 (1H, s, NH). ^{13}C NMR (TFA-d_1, 151 MHz): δ_C 20.10 (CH_3), 20.36 (CH_3), 55.12 (OCH_3), 118.57, 120.59, 121.41, 121.43, 121.93, 123.01, 124.06, 125.98, 128.18, 132.32, 133.97, 135.17, 139.08, 140.82, 141.60, 147.59 (C=N), 169.71 (COOCH$_3$). ESI-MS: m/z 380.2 $[M+H]^+$. Anal. calcd for $C_{21}H_{18}ClN_3O_2$ (379.84): C, 66.40; H, 4.78; N, 11.06. Found: C, 66.17; H, 4.74; N, 10.98.

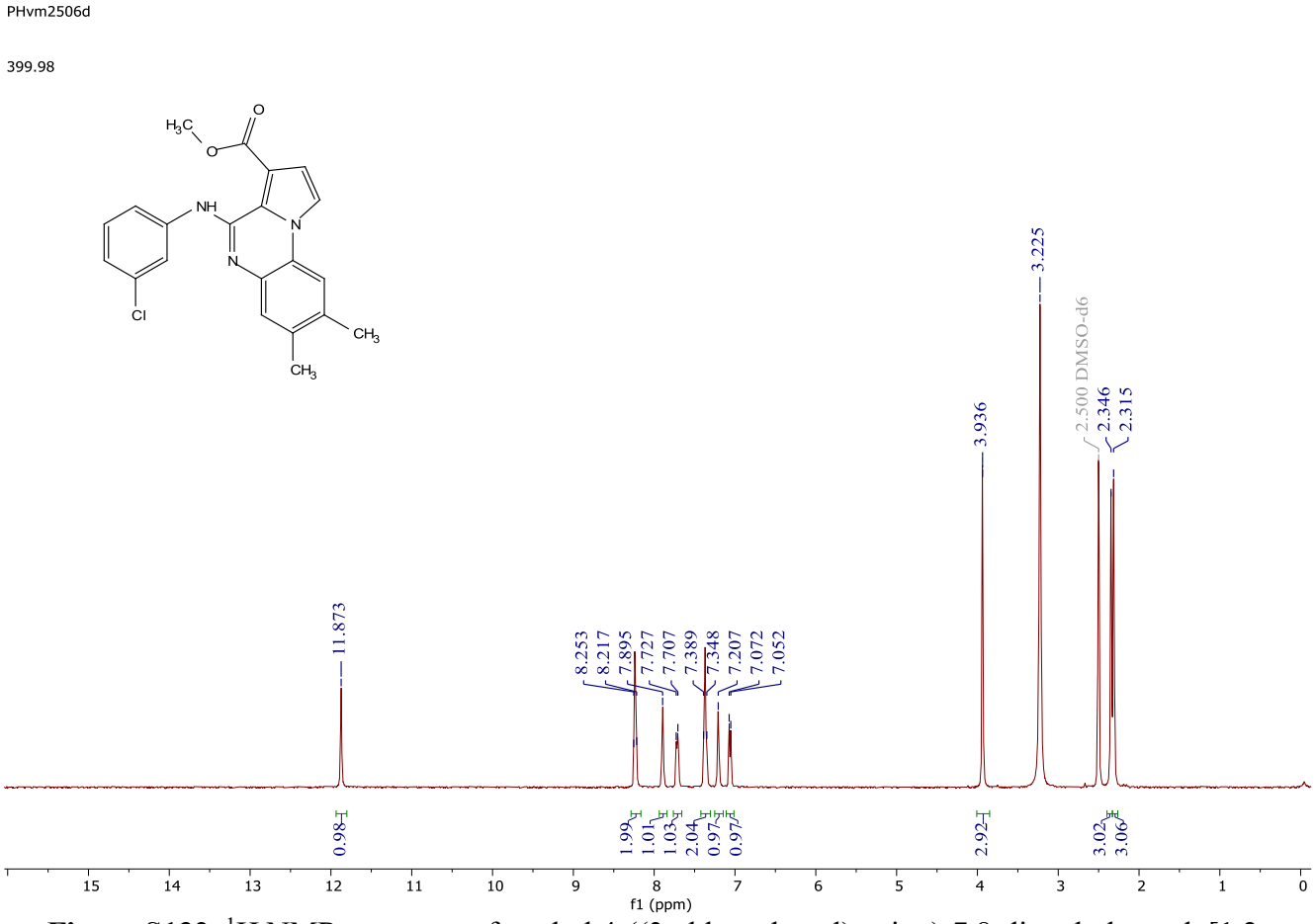


Figure S132. ^{1}H NMR spectrum of methyl 4-((3-chlorophenyl)amino)-7,8-dimethylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8o**) in DMSO-d_6

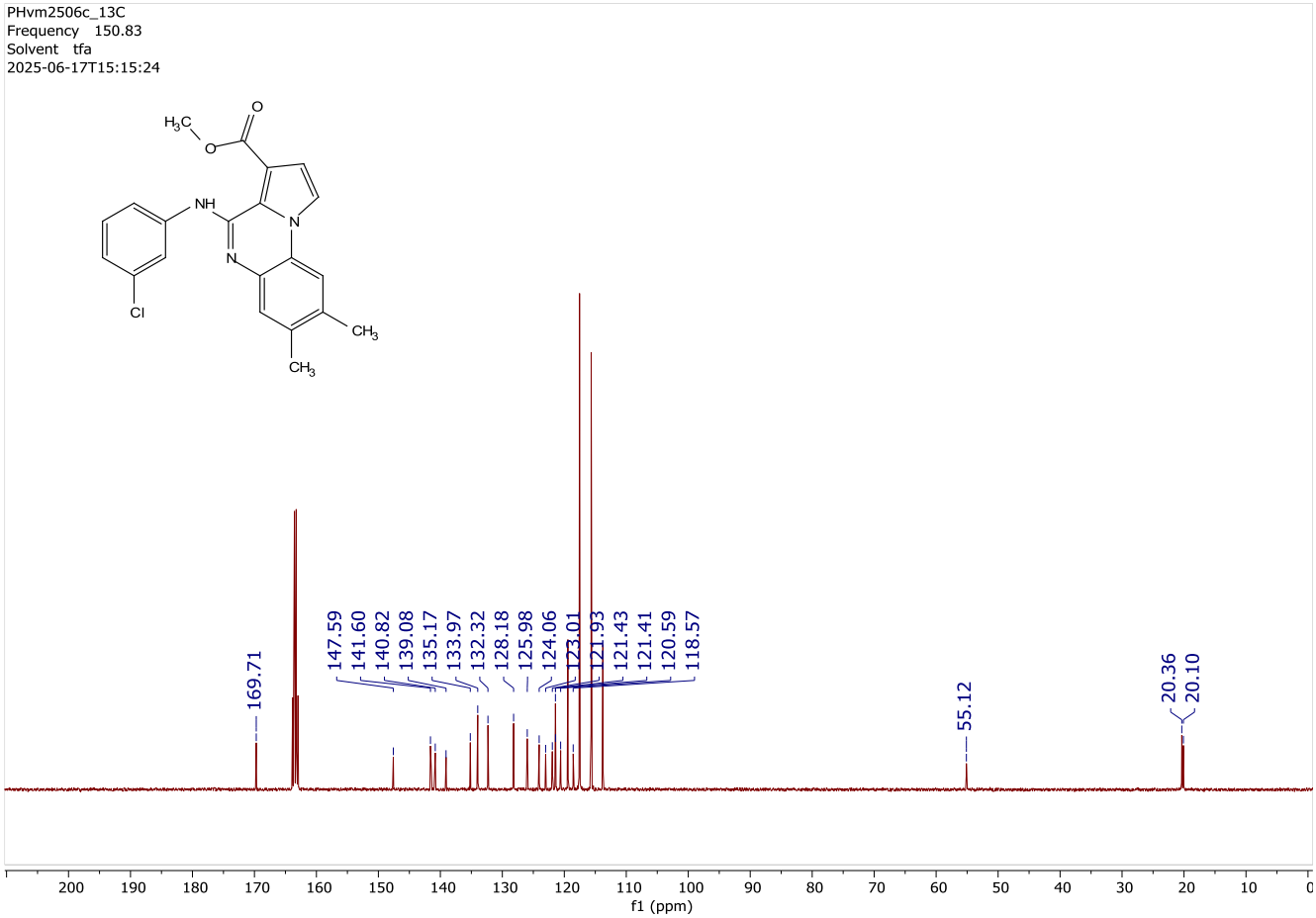
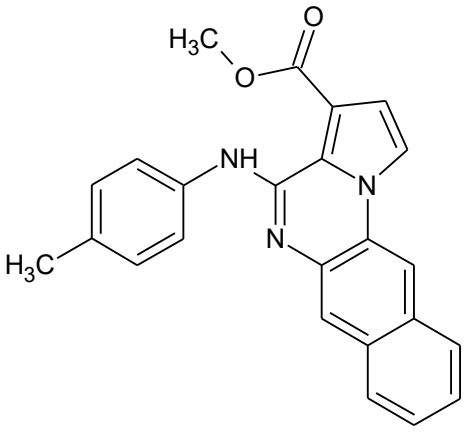


Figure S133. ^{13}C NMR spectrum of methyl 4-((3-chlorophenyl)amino)-7,8-dimethylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8o**) in TFA-d_1



Chemical characterization of methyl 4-(p-tolylamino)benzo[g]pyrrolo[1,2-a]quinoxaline-3-carboxylate (**8p**). Yellow solid (938 mg, 82%). mp 233-234 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 2.33 (3H, s, CH_3), 3.97 (3H, s, OCH_3), 7.24 (2H, d, $^3J_{HH}$ 8.0 Hz, 2CH aromatic), 7.31 (1H, s, CH pyrrole), 7.47-7.52 (2H, m, 2CH aromatic), 7.95-8.02 (4H, m, 4CH aromatic), 8.15 (1H, s, CH aromatic), 8.53 (1H, s, CH aromatic), 8.72 (1H, s, CH pyrrole), 11.90 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 21.13 (CH_3), 52.55 (OCH_3), 110.77, 111.17, 115.19, 116.11, 120.42, 121.99, 123.59, 124.21, 125.21, 125.64, 127.37, 127.48, 129.45, 130.03, 132.27, 132.45, 135.53, 137.81, 145.77 (C=N), 167.11 (C=O). ESI-MS: *m/z* 382.2 $[M+H]^+$. Anal. calcd for $C_{24}H_{19}N_3O_2$ (381.43): C, 75.57; H, 5.02; N, 11.02. Found: C, 75.36; H, 4.99; N, 11.10.

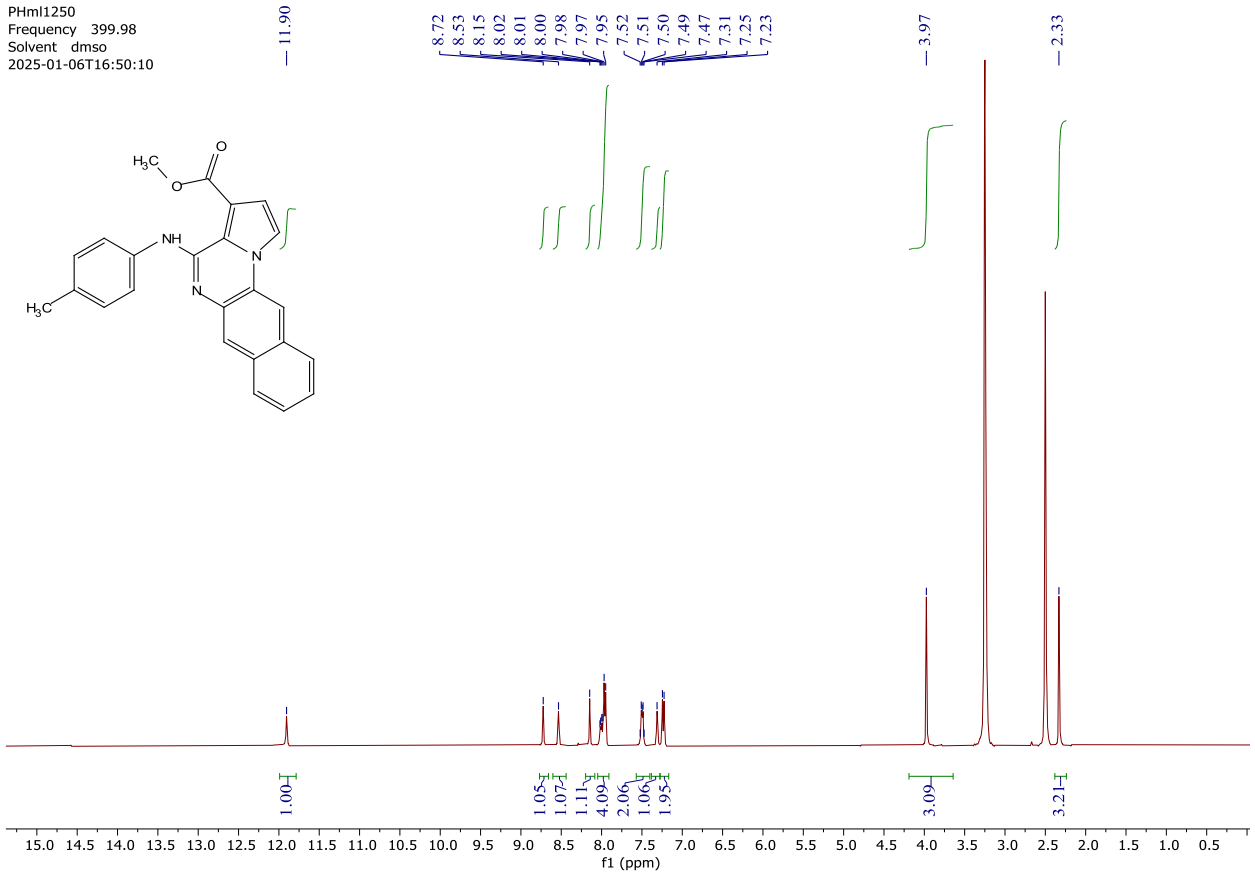


Figure S134. ^{1}H NMR spectrum of methyl 4-(*p*-tolylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8p**)in DMSO-d_6

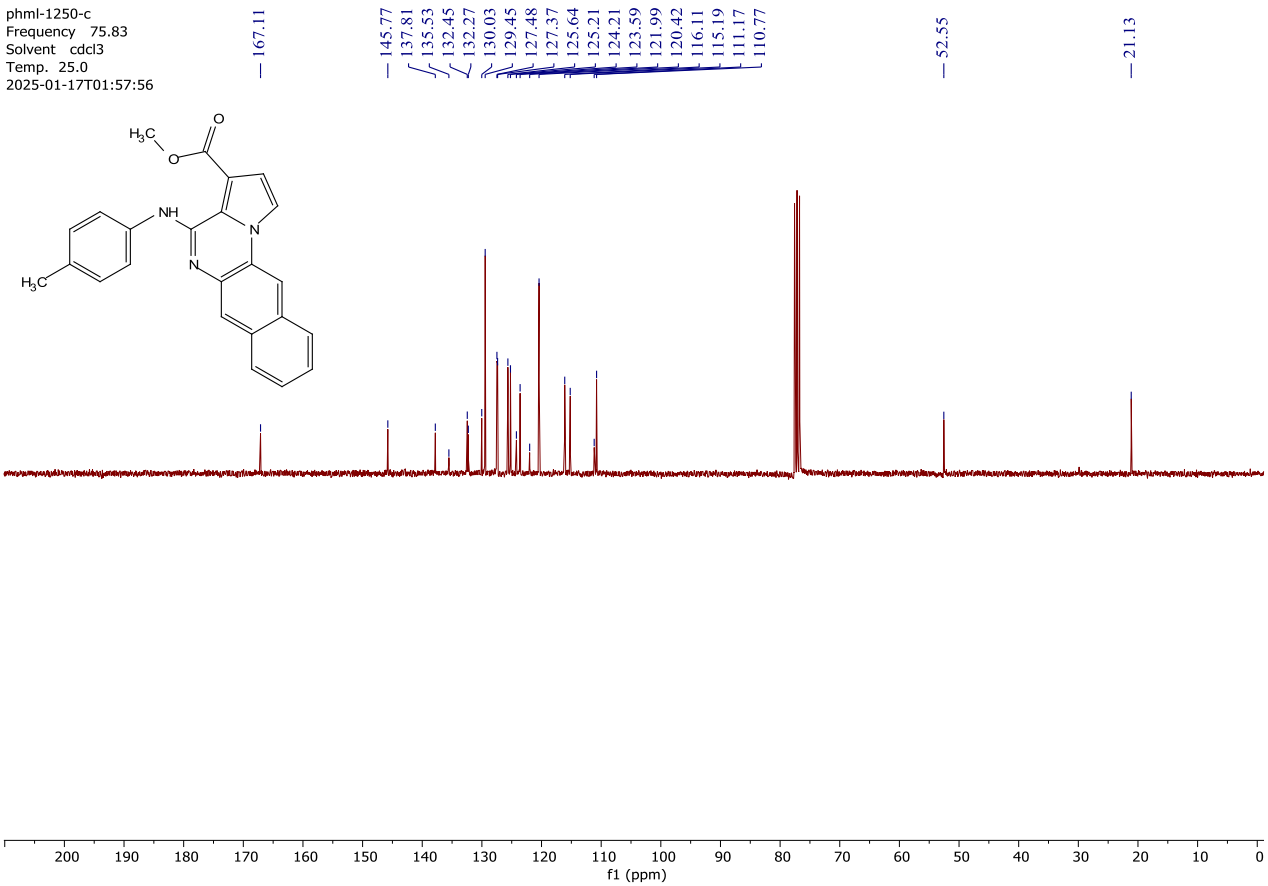
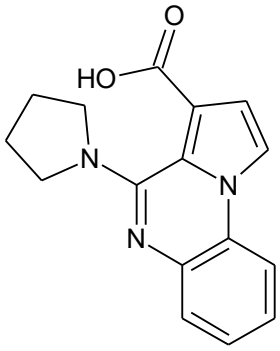


Figure S135. ^{13}C NMR spectrum of methyl 4-(*p*-tolylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8p**) in $CDCl_3$

Chemical characterization of 9a-p



Chemical characterization of 4-pyrrolidin-1-ylpyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9a**). White solid (222 mg, 79%). mp 234-235 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 1.95-2.03 (4H, m, 2CH_2 pyrrolidine), 3.84-3.92 (4H, m, 2CH_2 pyrrolidine), 7.23 (1H, s, CH pyrrole), 7.42-7.52 (2H, m, 2CH aromatic), 8.06-8.13 (1H, m, CH aromatic), 8.28 (1H, d, $^{3}J_{HH}$ 7.9 Hz, CH aromatic), 8.58 (1H, s, CH pyrrole) 12.21 (1H, broad s, OH). ^{13}C NMR (TFA-d_1, 126 MHz): δ_C 27.00 (2CH_2 pyrrolidine), 55.08 (2CH_2 pyrrolidine), 117.04, 118.21, 120.64, 120.81, 122.37, 123.13, 125.47, 127.72, 129.41, 130.78, 149.04 (C=N), 171.09 (C=O). ESI-MS: *m/z* 282.2 $[M+H]^+$. Anal. calcd for $C_{16}H_{15}N_3O_2$ (281.31): C, 68.31; H, 5.37; N, 14.94. Found: C, 68.52; H, 5.39; N, 14.88.

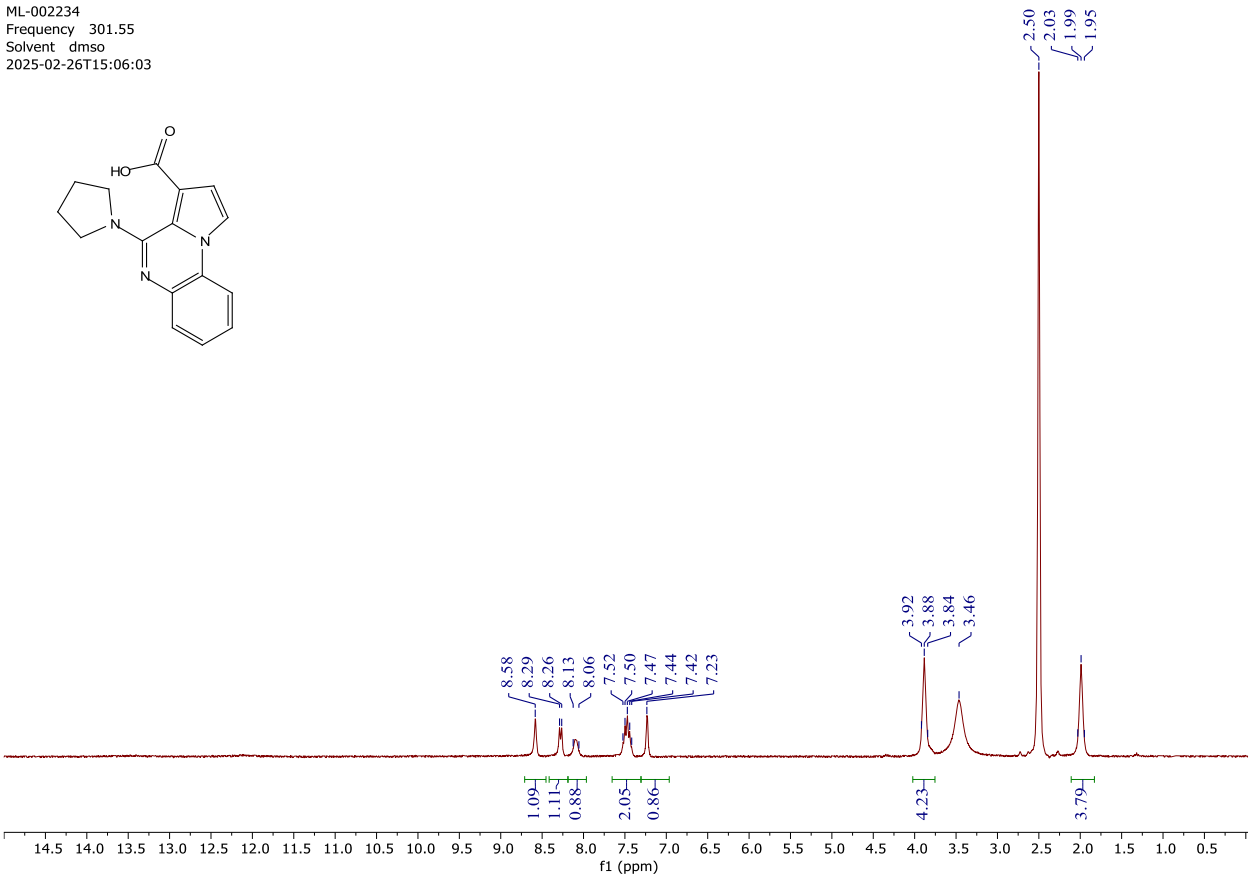


Figure S136. ^{1}H NMR spectrum of 4-pyrrolidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9a**) in DMSO-d_6

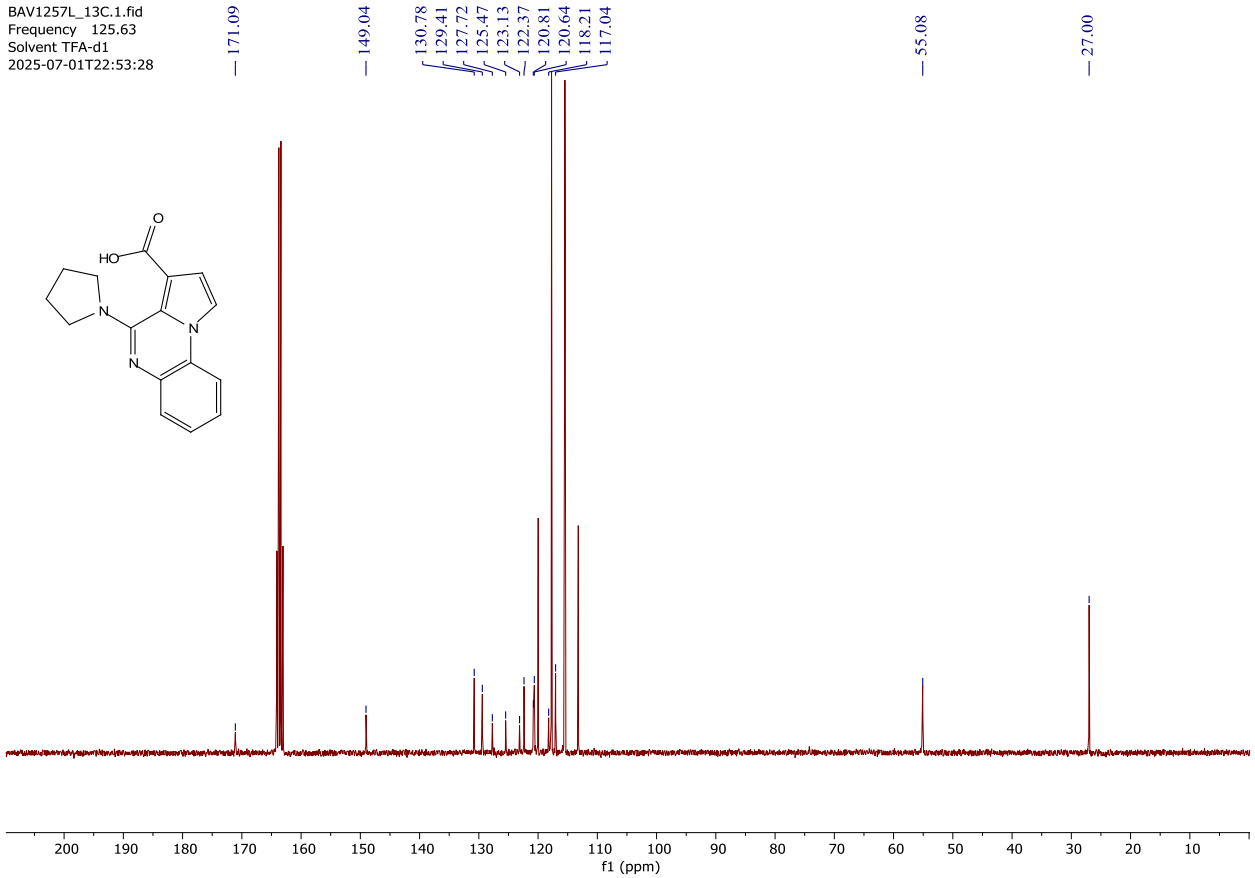
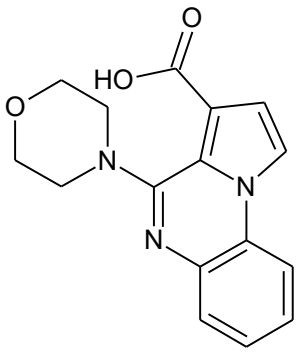


Figure S137. ^{13}C NMR spectrum of 4-pyrrolidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9a**) in TFA-d_1



Chemical characterization of 4-morpholin-4-ylpyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9b**). Beige solid (247 mg, 83%). mp 256-257 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.44-3.47 (4H, m, 2CH$_2$ morpholine), 3.79-3.81 (4H, m, 2CH$_2$ morpholine), 7.22 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 7.46-7.49 (2H, m, 2CH aromatic), 7.76-7.78 (1H, m, CH aromatic), 8.24-8.26 (1H, m, CH aromatic), 8.45 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole). ^{13}C NMR (DMSO-d_6, 126 MHz): δ_C 50.15 (2CH$_2$ morpholine), 65.48 (2CH$_2$ morpholine), 114.86, 116.52, 117.12, 117.80, 124.82, 125.85, 126.02, 126.34, 131.38, 133.33, 151.82 (C=N), 164.36 (C=O). ESI-MS: *m/z* 298.2 [M+H]$^+$. Anal. calcd for $C_{16}H_{15}N_3O_3$ (297.31): C, 64.64; H, 5.09; N, 14.13. Found: C, 64.81; H, 5.06; N, 14.04.

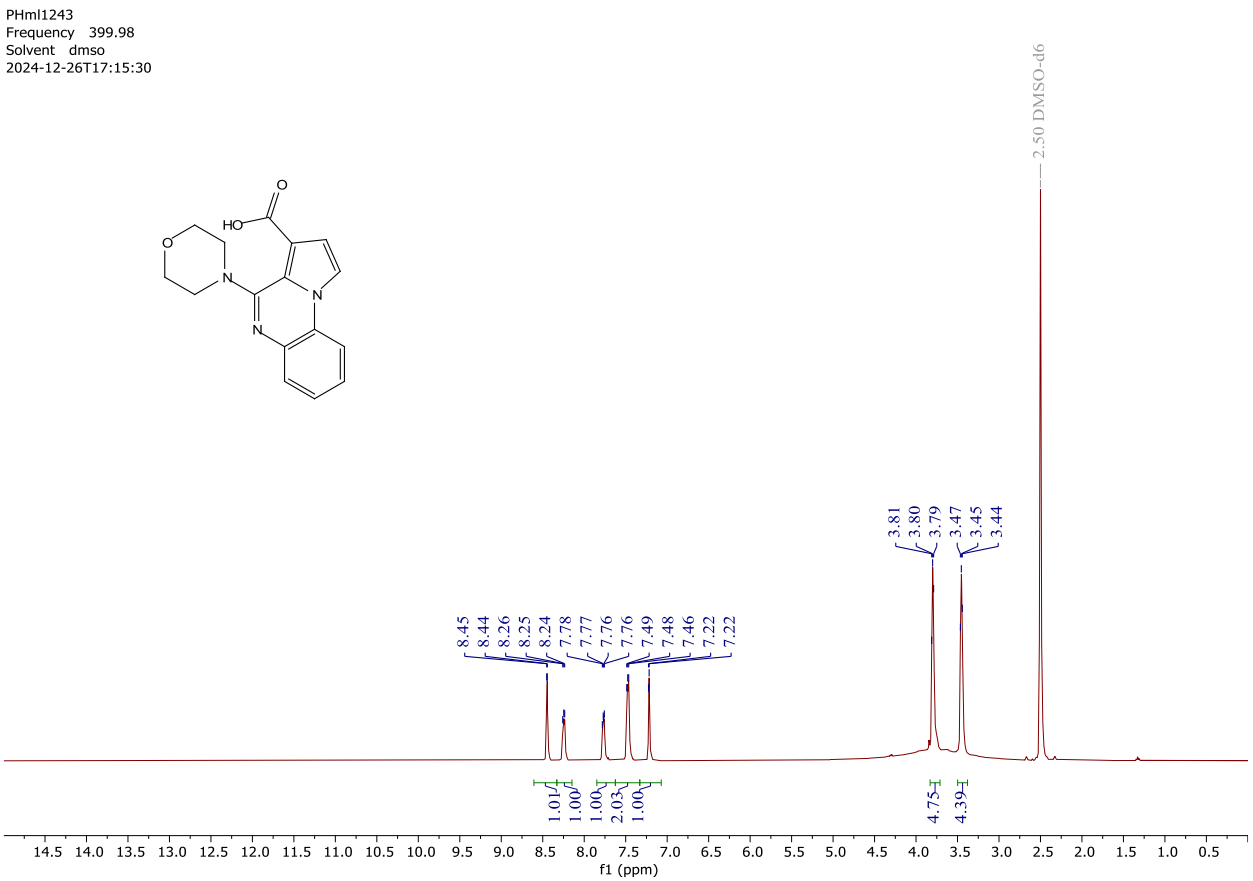


Figure S138. ^{1}H NMR spectrum of 4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9b)** in DMSO-d_6

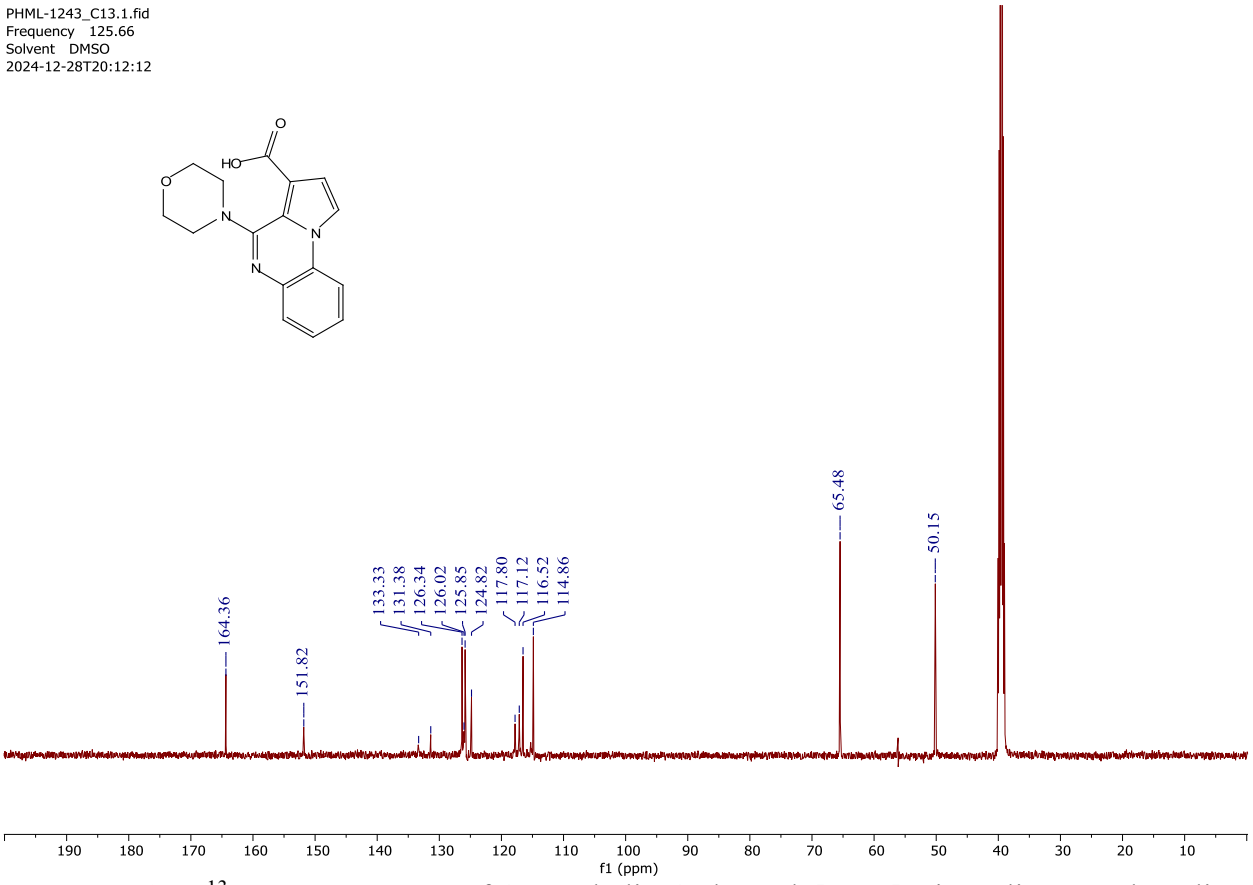
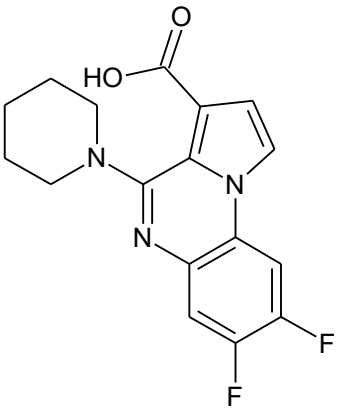


Figure S139. ^{13}C NMR spectrum of 4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9b)** in DMSO-d_6



Chemical characterization of 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9c**). Yellow solid (252 mg, 76%). mp 226-227 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.56-1.85 (2H, m, CH_2 piperidine), 1.91-1.99 (4H, m, $2CH_2$ piperidine), 3.27-3.34 (4H, m, $2CH_2$ piperidine), 7.60 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole), 7.71 (1H, dd, $^{3}J_{HF}$ 10.2, $^{3}J_{HH}$ 7.1 Hz, CH aromatic), 7.78 (1H, dd, $^{3}J_{HF}$ 10.4, $^{3}J_{HH}$ 8.0 Hz, CH aromatic), 7.84 (1H, d, $^{3}J_{HH}$ 3.0 Hz, CH pyrrole). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 23.25 (CH_2 piperidine), 24.36 ($2CH_2$ piperidine), 53.16 ($2CH_2$ piperidine), 103.10 (d, $^{2}J_{CF}$ 22.6 Hz, CH aromatic), 115.41, 116.15, 117.12 (d, $^{2}J_{CF}$ 18.2 Hz, CH aromatic), 119.79, 119.98, 123.20 (d, $^{3}J_{CF}$ 7.5 Hz, C aromatic), 131.84 (d, $^{3}J_{CF}$ 9.4 Hz, C aromatic), 148.94 (dd, $^{1}J_{CF}$ 249.9, $^{2}J_{CF}$ 14.0 Hz, CF aromatic), 150.47 (dd, $^{1}J_{CF}$ 254.0, $^{2}J_{CF}$ 14.8 Hz, CF aromatic), 154.61 (C=N), 164.08 (C=O). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -139.88 (ddd, $^{3}J_{FF}$ 23.0, $^{3}J_{HF}$ 11.4, $^{4}J_{HF}$ 7.9 Hz), -138.48 (ddd, $^{3}J_{FF}$ 23.3, $^{3}J_{HF}$ 12.0, $^{4}J_{HF}$ 7.8 Hz). ESI-MS: *m/z* 332.2 $[M+H]^+$. Anal. calcd for $C_{17}H_{15}F_2N_3O_2$ (331.32): C, 61.63; H, 4.56; N, 12.68. Found: C, 61.39; H, 4.59; N, 12.78.

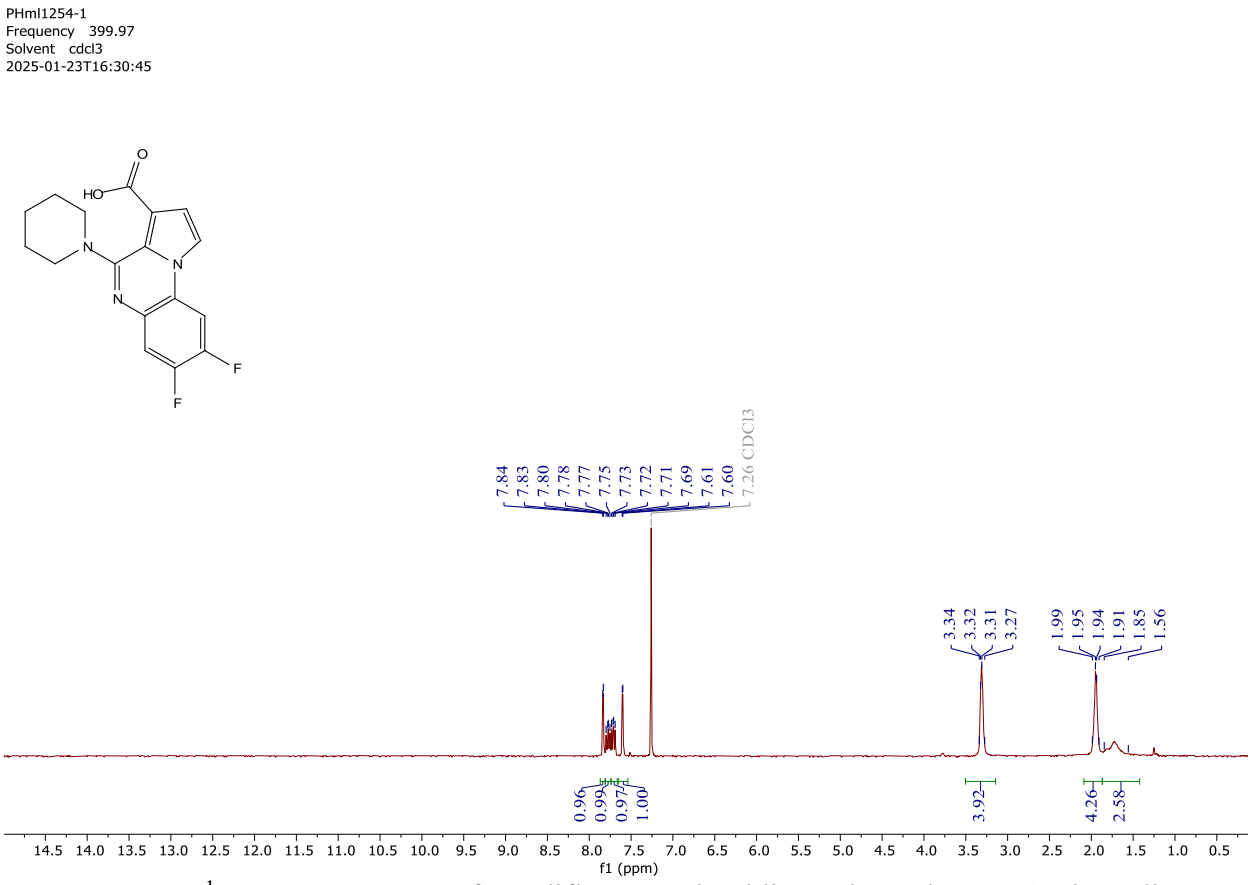


Figure S140. ^{1}H NMR spectrum of 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9c**) in $CDCl_3$

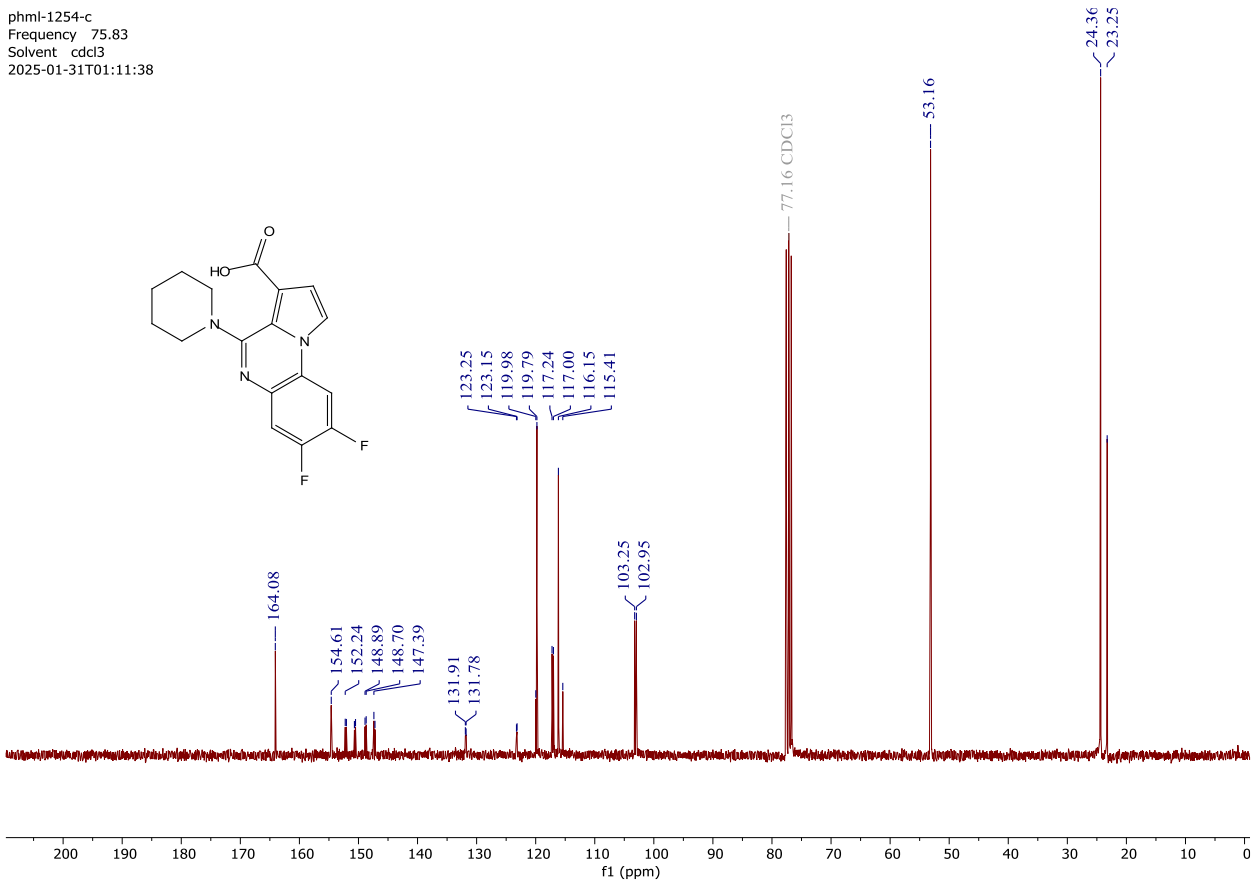


Figure S141. ^{13}C NMR spectrum of 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9c**) in $CDCl_3$

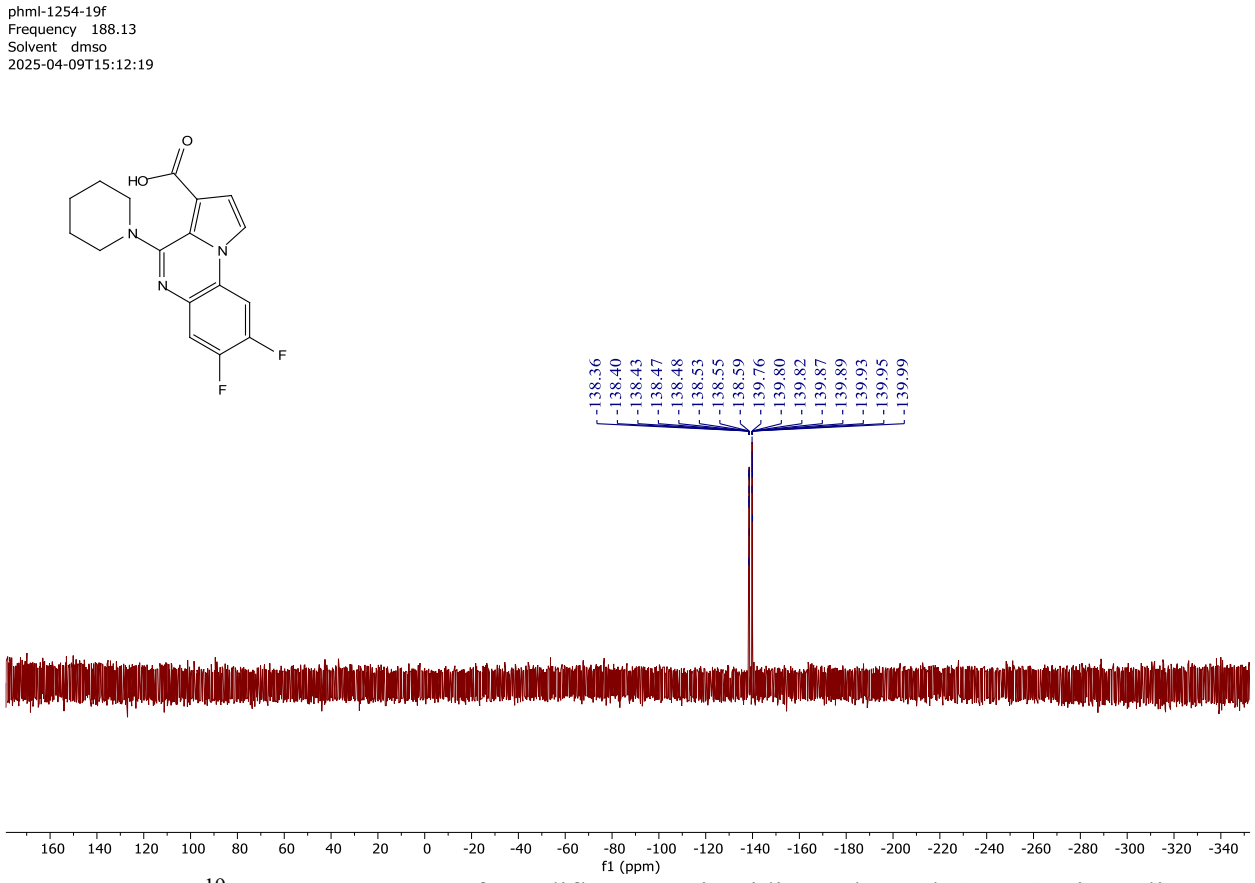
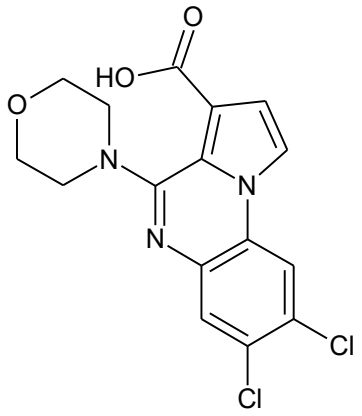


Figure S142. ^{19}F NMR spectrum of 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9c)** in DMSO-d_6



Chemical characterization of 7,8-dichloro-4-morpholin-4-ylpyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9d**). Colorless solid (344 mg, 94%). mp 260-261 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 3.42-3.49 (4H, m, CH_2 morpholine), 3.71-3.78 (4H, m, CH_2 morpholine), 7.17 (1H, s, CH pyrrole), 7.79 (1H, s, CH aromatic), 8.44 (1H, s, CH pyrrole), 8.56 (1H, s, CH aromatic), 12.75 (1H, s, OH). ^{13}C NMR (DMSO-*d*$_6$, 76 MHz): δ_C 49.49 ($2CH_2$ morpholine), 65.60 ($2CH_2$ morpholine), 114.86, 116.43, 116.63, 117.32, 117.67, 124.53, 126.44, 127.39, 128.14, 135.18, 153.18 (C=N), 164.71 (C=O). ESI-MS: *m/z* 366.2 $[M+H]^+$. Anal. calcd for $C_{16}H_{13}Cl_2N_3O_3$ (366.20): C, 52.48; H, 3.58; N, 11.47. Found: C, 52.65; H, 3.59; N, 11.34.

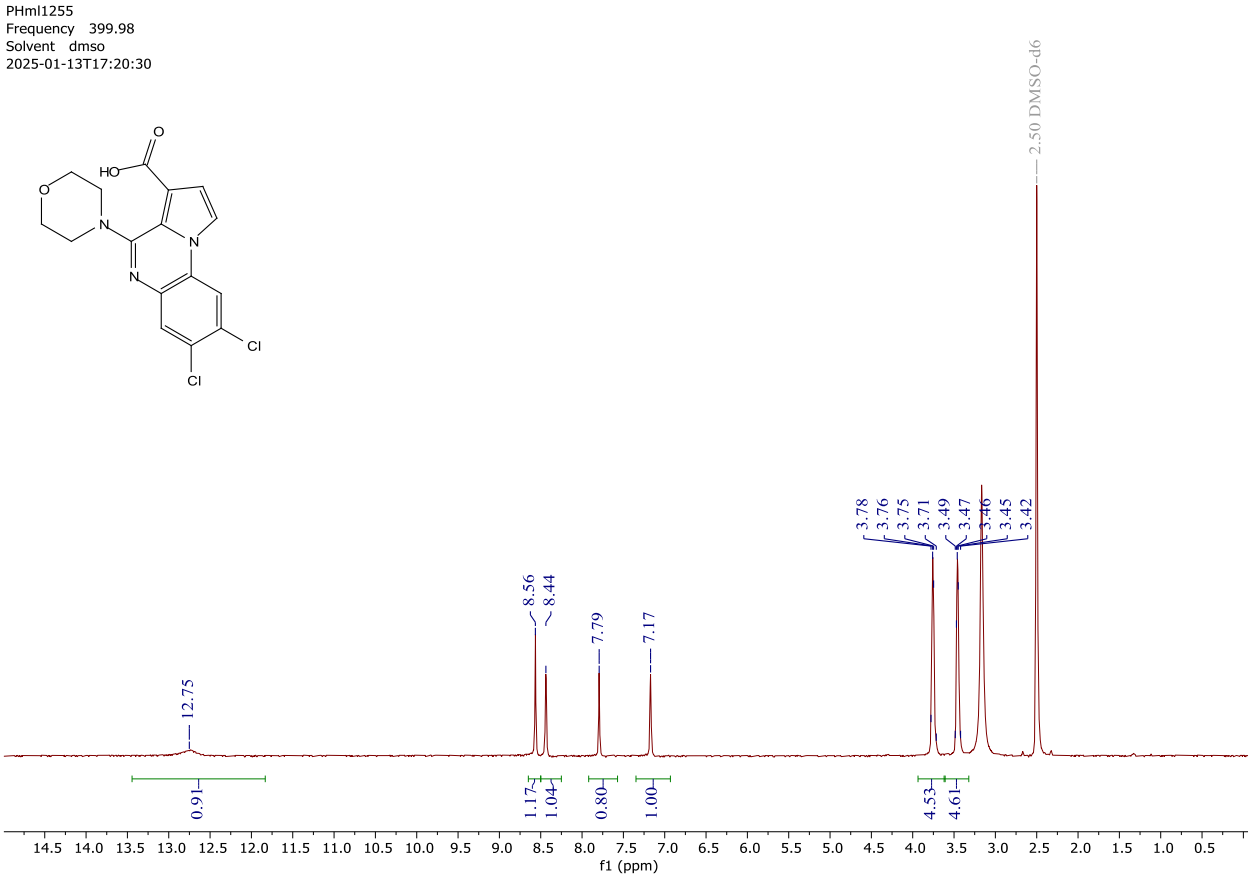


Figure S143. ^{1}H NMR spectrum of 7,8-dichloro-4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9d**) in DMSO-*d*$_6$

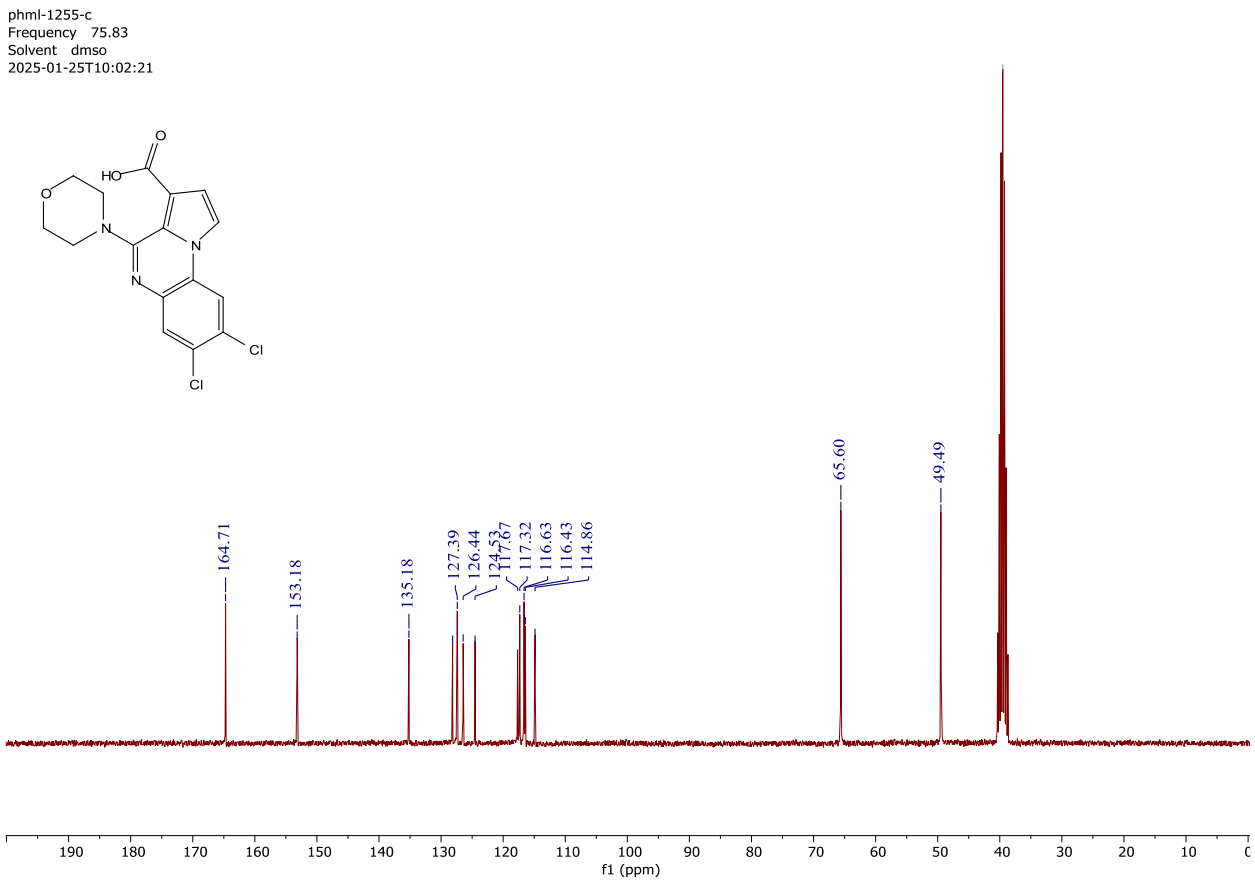
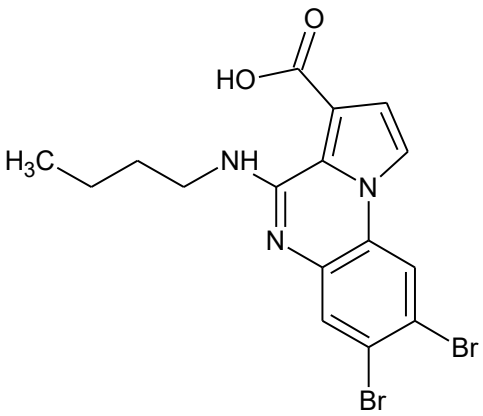


Figure S144. ^{13}C NMR spectrum of 7,8-dichloro-4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9d**) in DMSO-d_6



Chemical characterization of 7,8-dibromo-4-(butylamino)pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9e**). Colorless solid (349 mg, 85%). mp 265-266 °C. IR (solid, KBr, νmax, cm^{-1}): 3347, 2869, 1664, 1461, 1375, 1241, 893, 742. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 0.96 (3H, t, $^3J_{HH}$ 7.4 Hz, CH_3), 1.44-1.54 (2H, m, CH_2), 1.67-1.74 (2H, m, CH_2), 3.71-3.75 (2H, CH_2N), 7.27 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole), 8.35 (1H, s, CH aromatic), 8.51 (1H, d, $^3J_{HH}$ 3.2 Hz, CH pyrrole), 8.67 (1H, s, CH aromatic), 11.43 (1H, s, NH). ^{13}C NMR (DMSO-d_6, 76 MHz): δ_C 13.62 (CH_3), 19.51 (CH_2), 29.92 (CH_2), 42.62 (CH_2N), 116.91, 117.66, 118.42, 118.77, 119.29, 120.11, 121.47, 123.01, 124.41, 129.78, 146.78 (C=N), 167.65 (C=O). ESI-MS: *m/z* 442.0 $[M+H]^+$. Anal. calcd for $C_{16}H_{15}Br_2N_3O_2$ (441.12): C, 43.56; H, 3.43; N, 9.53. Found: C, 43.39; H, 3.47; N, 9.47.

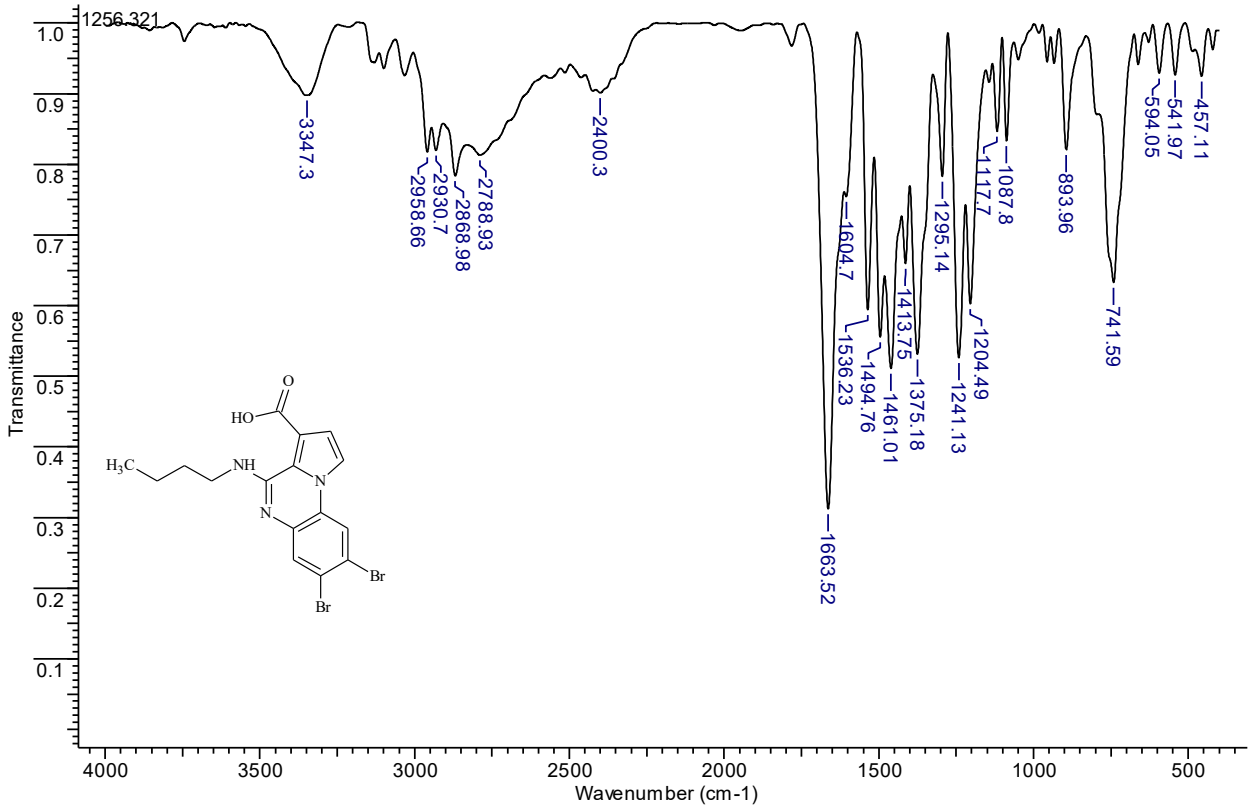


Figure S145. IR spectrum of 7,8-dibromo-4-(butylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9e**) in KBr pellet

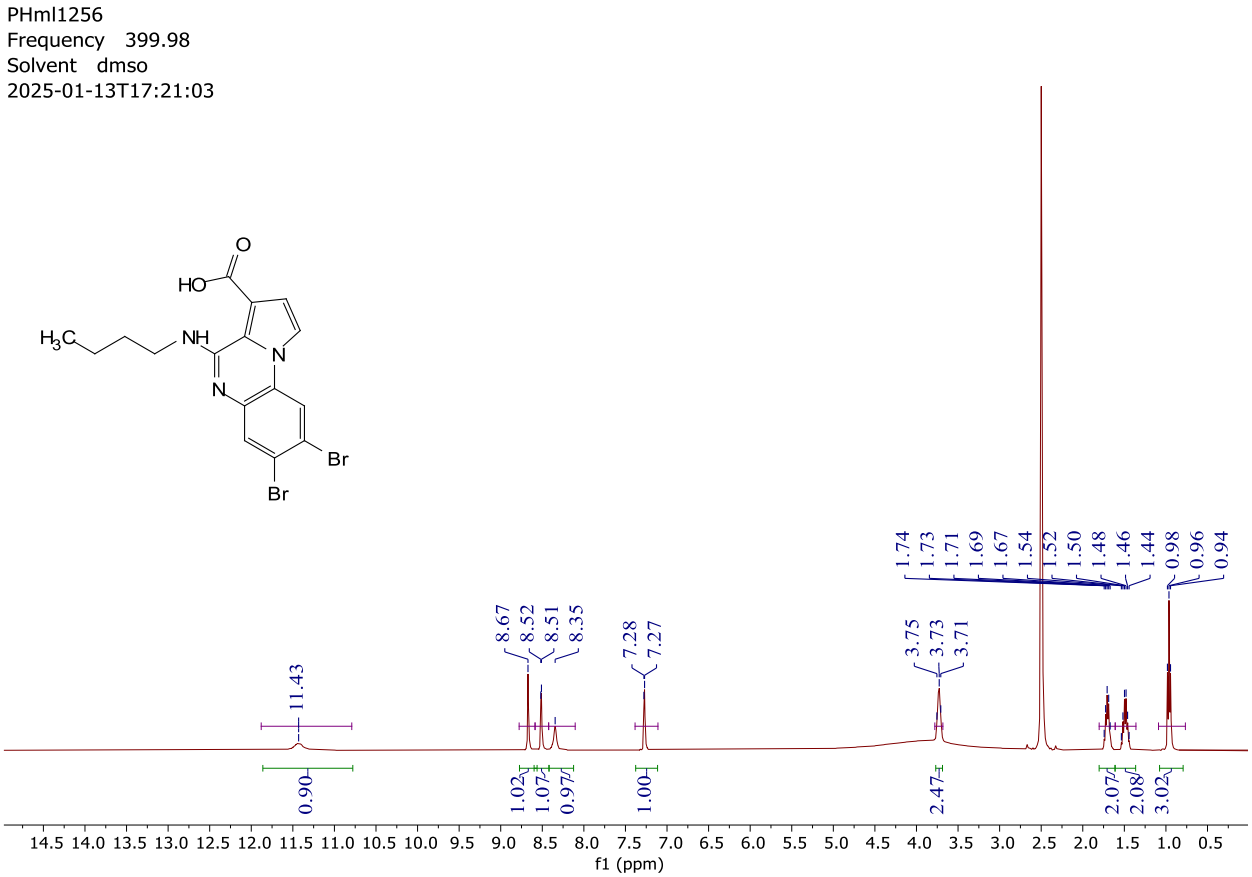


Figure S146. ^{1}H NMR spectrum of 7,8-dibromo-4-(butylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9e**) in DMSO-d_6

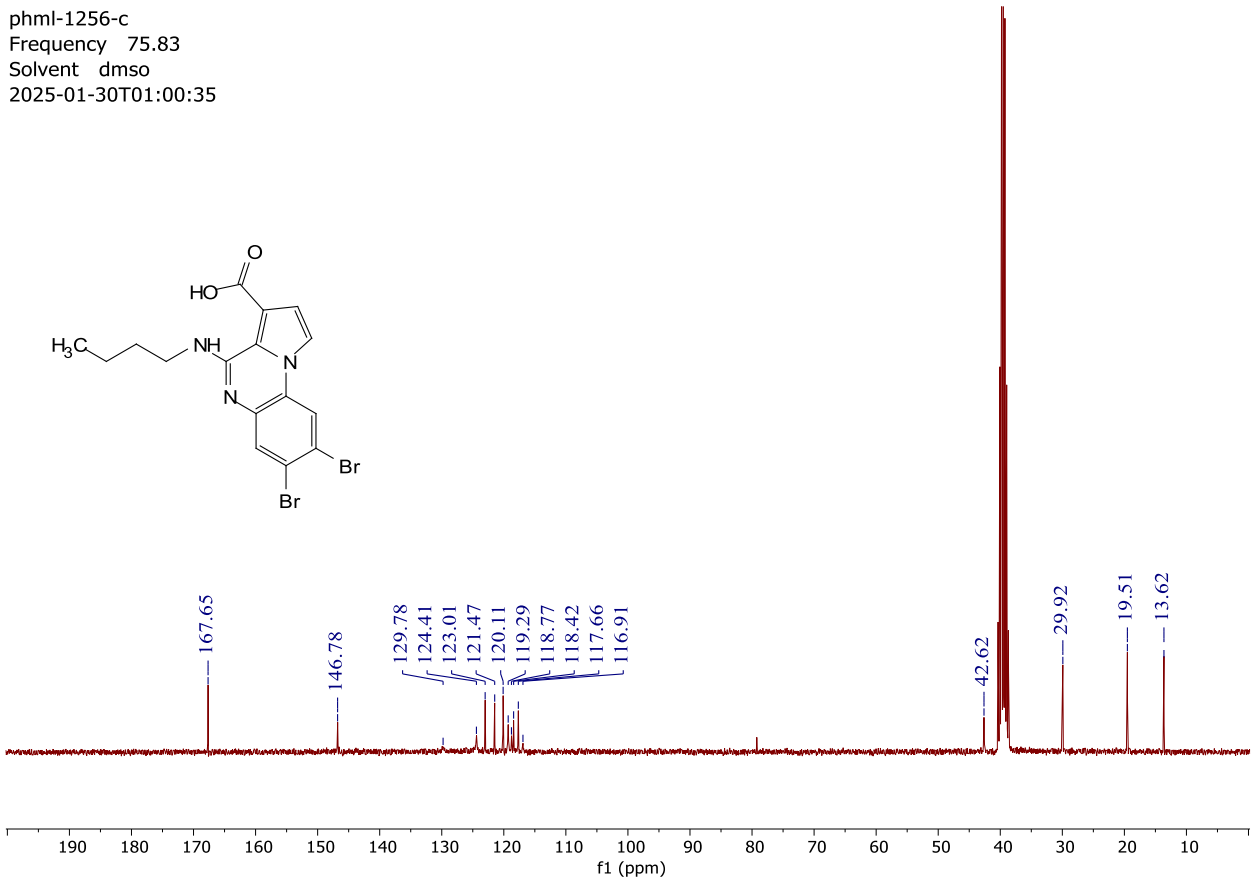
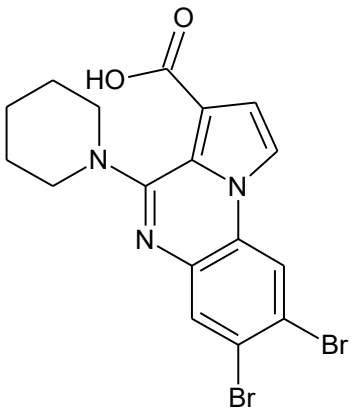


Figure S147. ^{13}C NMR spectrum of 7,8-dibromo-4-(butylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9e**) in DMSO-d_6



Chemical characterization of 7,8-dibromo-4-piperidin-1-ylpyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9f**). Yellow solid (390 mg, 86%). mp 237-238 °C. ^{1}H NMR (302 MHz, $CDCl_3$): δ_H 1.59-1.83 (2H, m, CH_2 piperidine), 1.89-1.99 (4H, m, $2CH_2$ piperidine), 3.24-3.33 (4H, m, $2CH_2$ piperidine), 7.59 (1H, s, CH pyrrole), 7.91 (1H, s, CH pyrrole), 8.18 (1H, s, CH aromatic), 8.22 (1H, s, CH aromatic). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 23.29 (CH_2 piperidine), 24.39 ($2CH_2$ piperidine), 53.22 ($2CH_2$ piperidine), 115.97, 116.31, 119.09, 120.01, 120.20, 122.19, 124.62, 126.41, 133.75, 135.17, 155.46 (C=N), 163.91 (C=O). ESI-MS: *m/z* 454.0 $[M+H]^+$. Anal. calcd for $C_{17}H_{15}Br_2N_3O_2$ (453.13): C, 45.06; H, 3.36; N, 9.27. Found: C, 45.21; H, 3.33; N, 9.19.

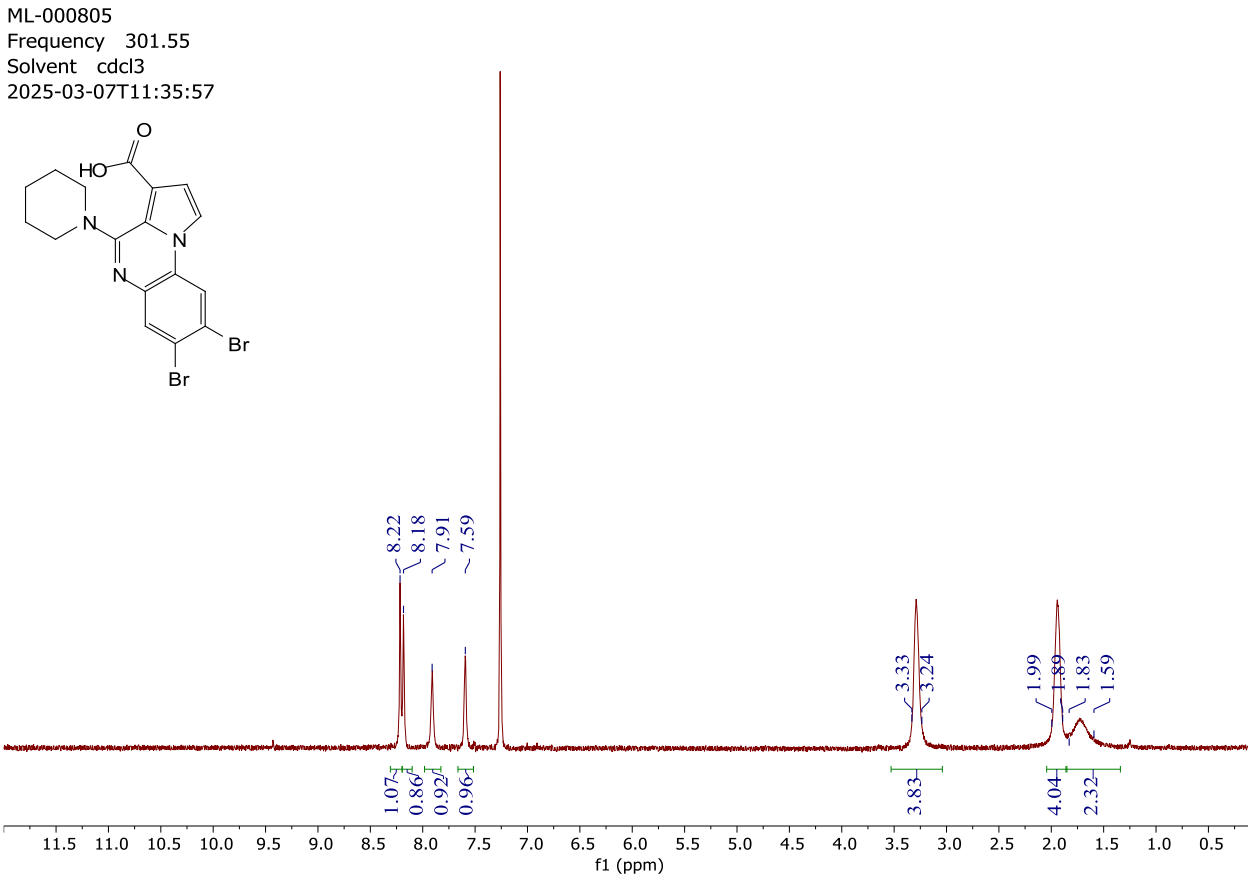


Figure S148. ^{1}H NMR spectrum of 7,8-dibromo-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9f**) in $CDCl_3$

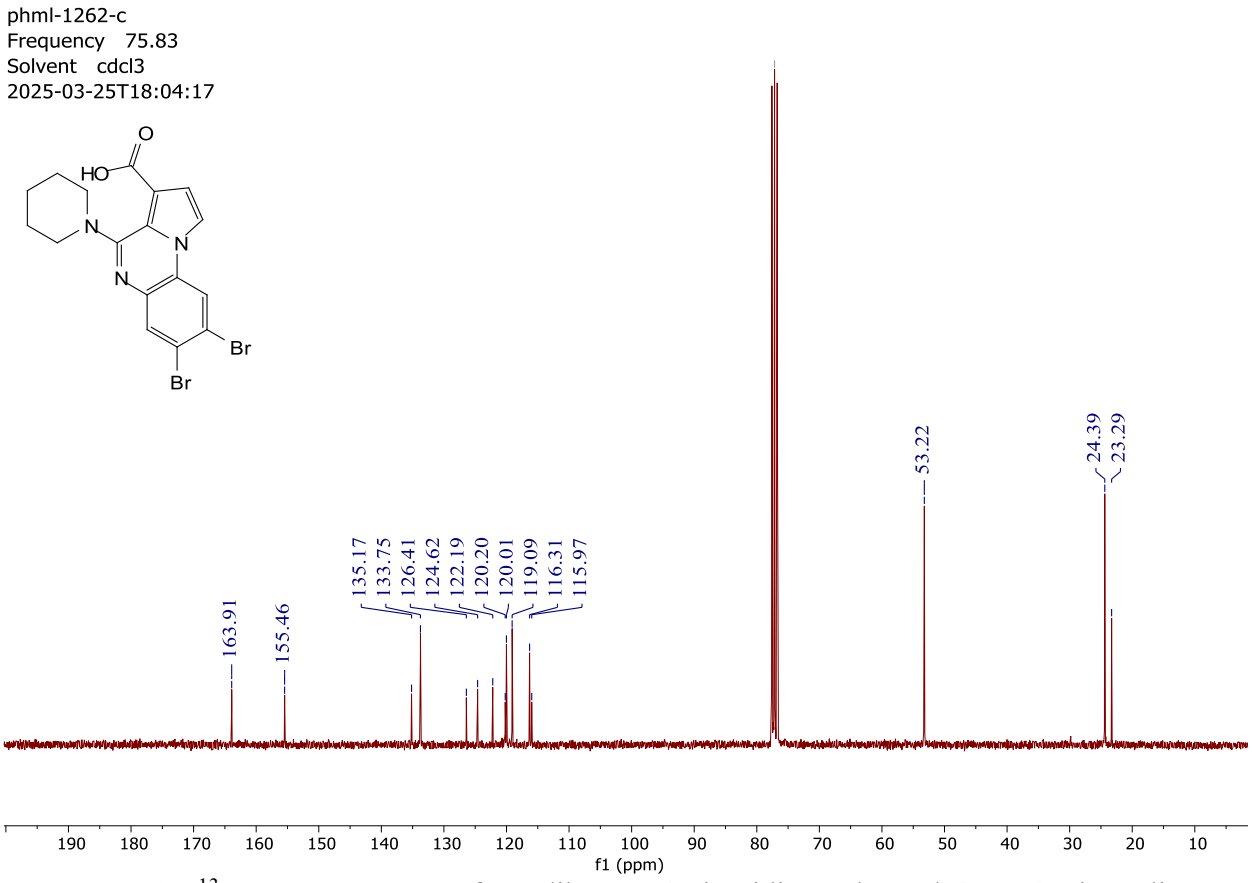
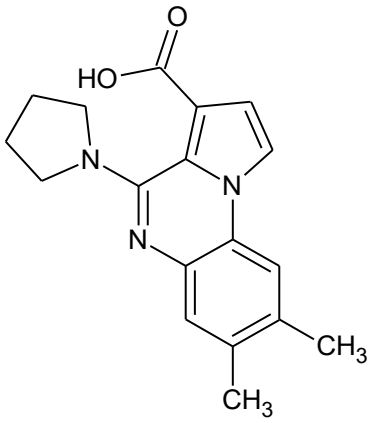


Figure S149. ^{13}C NMR spectrum of 7,8-dibromo-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9f**) in $CDCl_3$



Chemical characterization of 7,8-dimethyl-4-(pyrrolidin-1-yl)pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9g**). Beige solid (294 mg, 95%). mp 299-300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 1.93 – 1.99 (4H, m, 2CH_2), 2.30 (3H, s, CH_3), 2.34 (3H, s, CH_3), 3.80 – 3.87 (4H, m, 2CH_2), 7.14 (1H, d, J = 2.9 Hz, CH pyrrole), 7.81 (1H, s, CH aromatic), 8.00 (1H, s, CH aromatic), 8.39 (1H, d, J = 2.9 Hz, CH pyrrole). ^{13}C NMR (TFA-d_1, 76 MHz): δ_C 20.16 (CH_3), 20.35 (CH_3), 27.02 (2CH_2), 54.91 (N(CH_2)$_2$), 117.26, 118.22, 120.56, 120.94, 121.82, 122.31, 123.47, 125.62, 140.13, 141.45, 148.72(C=N), 171.43(C=O). ESI-MS: m/z 310.2 $[M+H]^+$. Anal. calcd for $C_{18}H_{19}N_3O_2$ (309.36): C, 69.88; H, 6.19; N, 13.58. Found: C, 70.06; H, 6.17; N, 13.40.

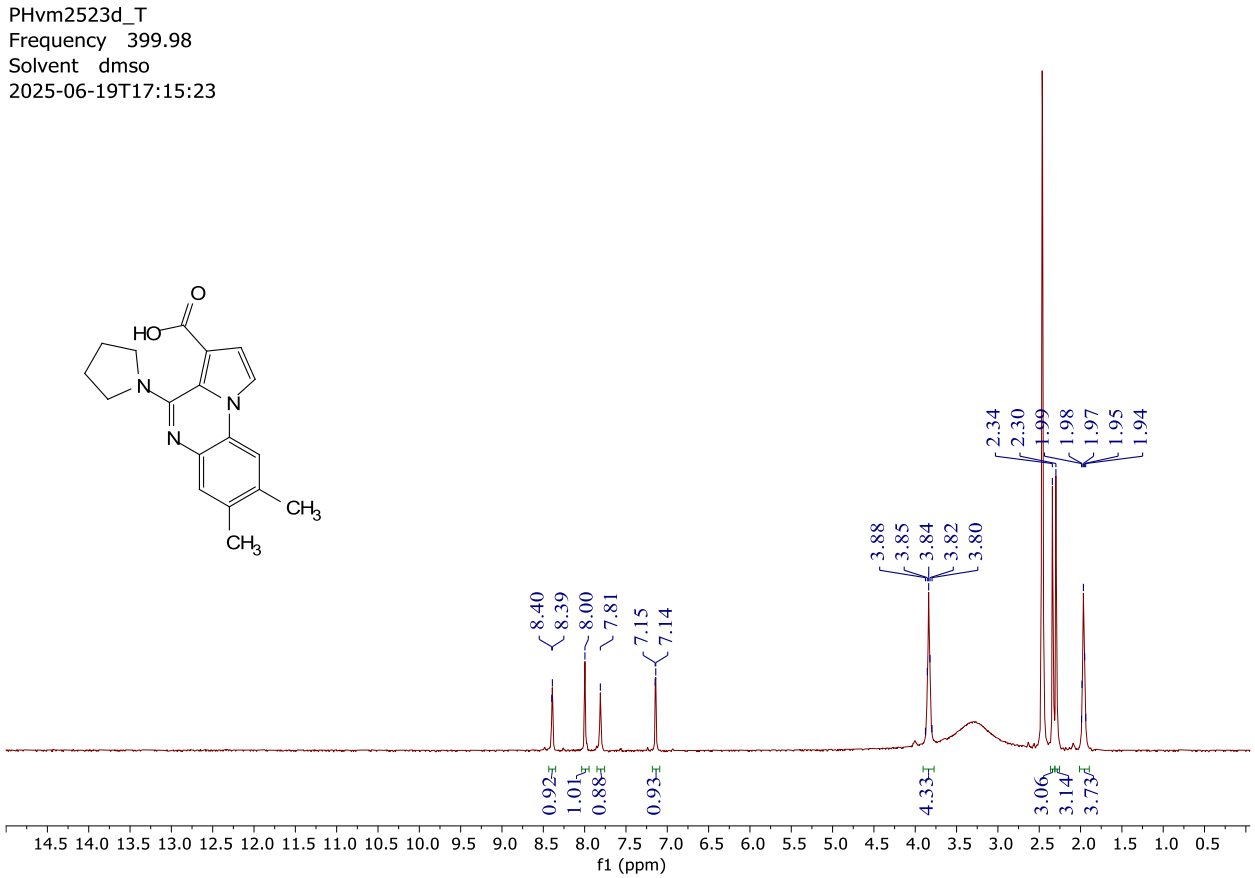


Figure S150. ^{1}H NMR spectrum of 7,8-dimethyl-4-(pyrrolidin-1-yl)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9g**) in DMSO-d_6

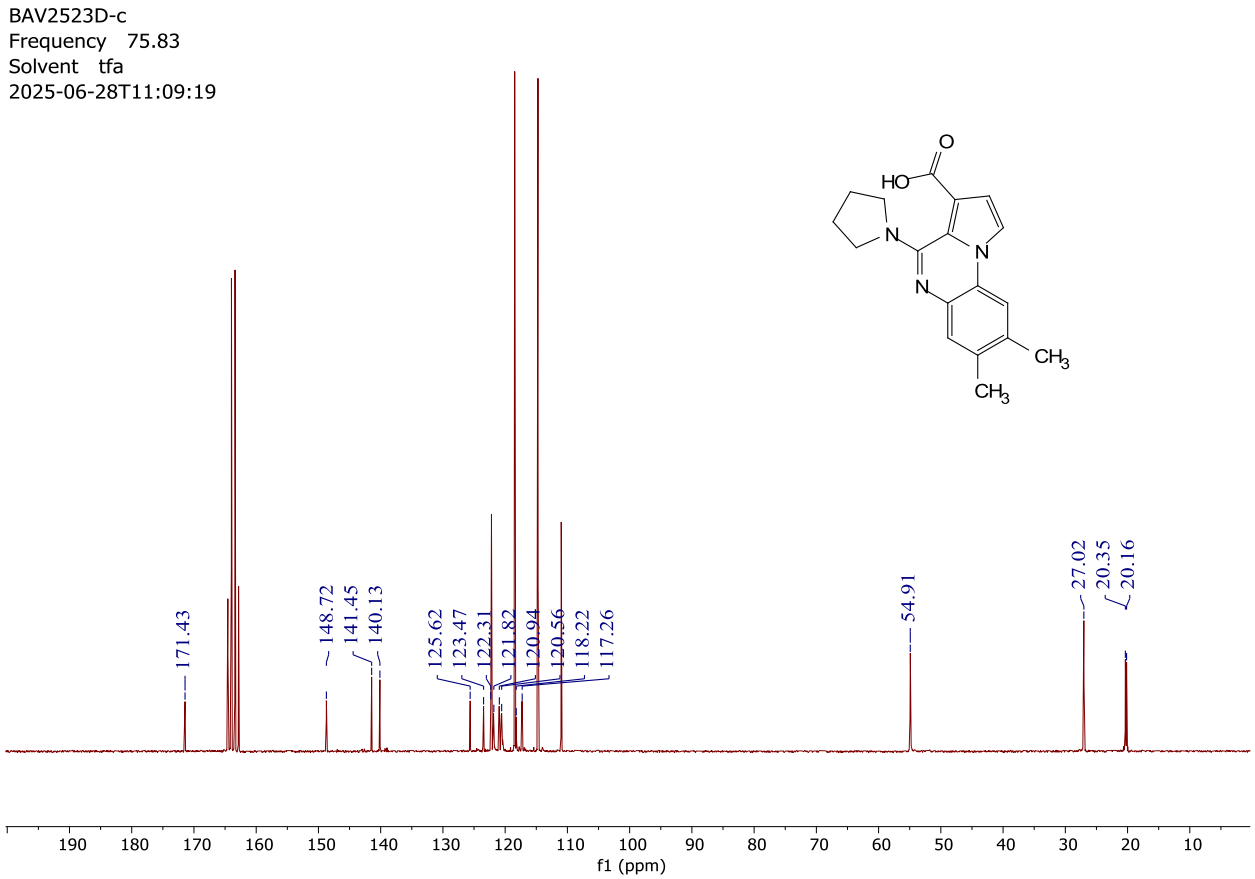
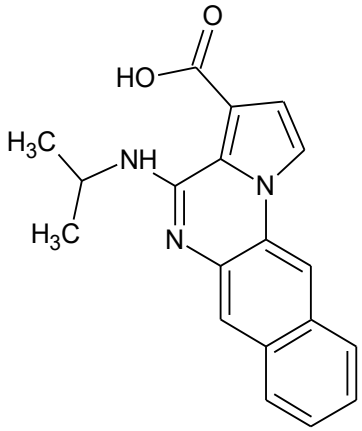


Figure S151. ^{13}C NMR spectrum of 7,8-dimethyl-4-(pyrrolidin-1-yl)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9g**) in TFA-d_1



Chemical characterization of 4-(isopropylamino)benzo[g]pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9h**). Beige solid (281 mg, 88%). mp > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 1.29 (6H, d, J = 6.5 Hz, 2CH$_3$), 4.33-4.42 (1H, m, CH-NH), 7.16 (1H, d, J = 3.1 Hz, CH pyrrole), 7.37-7.43 (2H, m, 2CH aromatic), 7.89 (2H, d, J = 7.6 Hz, 2CH aromatic), 7.95 (1H, s, CH aromatic), 8.40 (1H, d, J = 3.1 Hz, CH pyrrole), 8.63 (1H, s, CH aromatic), 10.01 (1H, s, NH). ^{13}C NMR (TFA-d_1, 126 MHz): δ_C 22.45((CH$_3$)$_2$CH), 47.79((CH$_3$)$_2$CH), 115.62, 117.83, 119.62, 120.47, 121.73, 122.23, 123.14, 124.98, 129.07, 129.56, 129.87, 130.30, 133.29, 134.22, 146.95 (C=N), 171.98 (C=O). ESI-MS: m/z 320.2 $[M+H]^+$. Anal. calcd for $C_{19}H_{17}N_3O_2$ (319.36): C, 71.46; H, 5.37; N, 13.16. Found: C, 71.29; H, 5.34; N, 12.98.

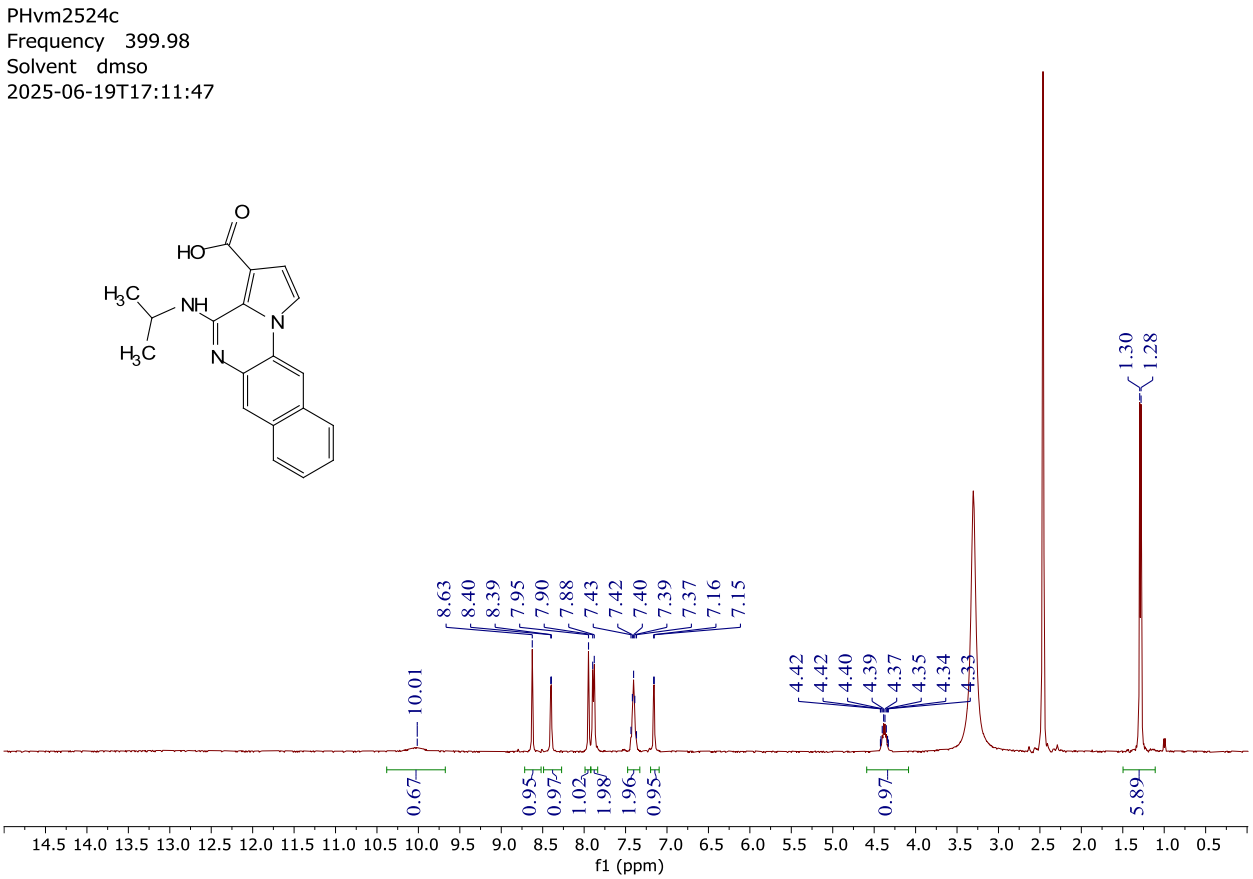


Figure S152. ^{1}H NMR spectrum of 4-(isopropylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9h**) in DMSO-d_6

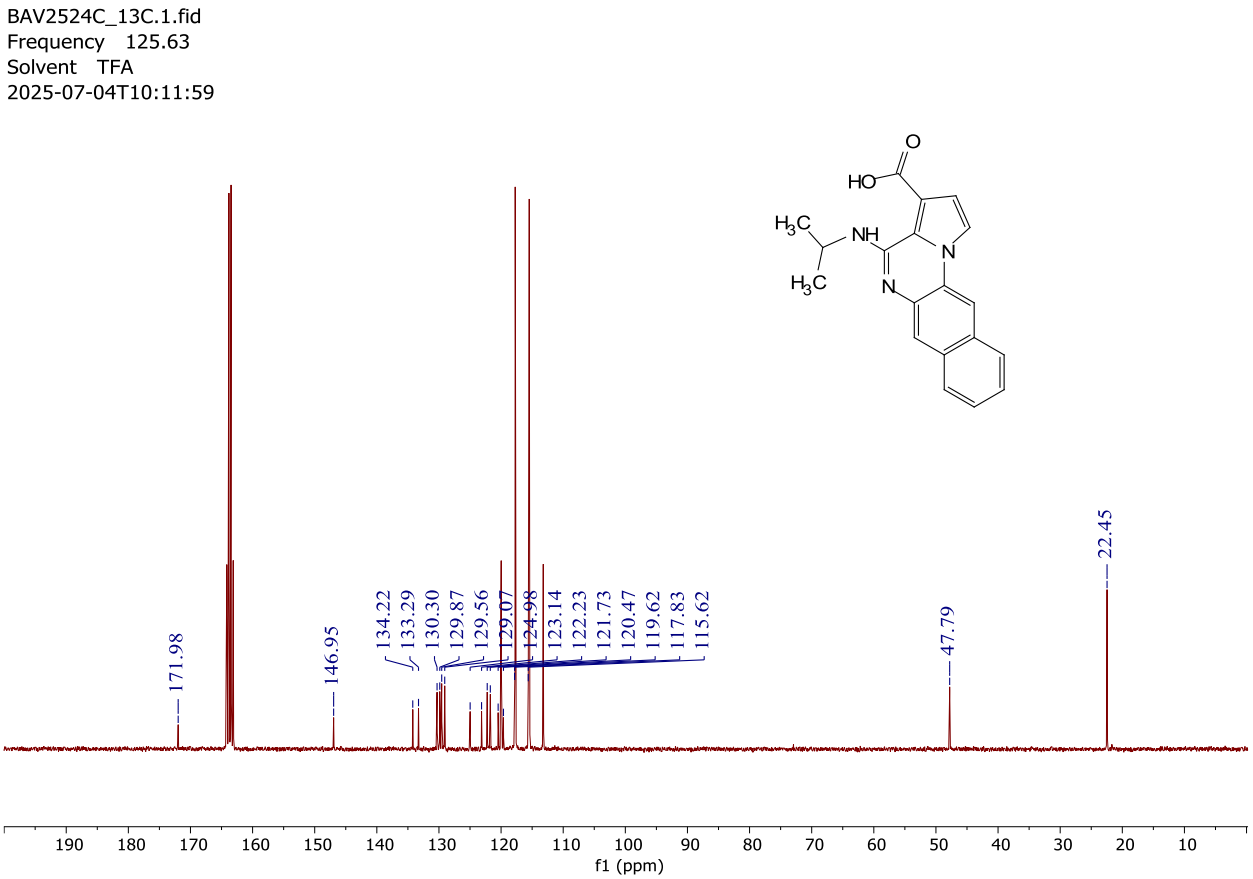
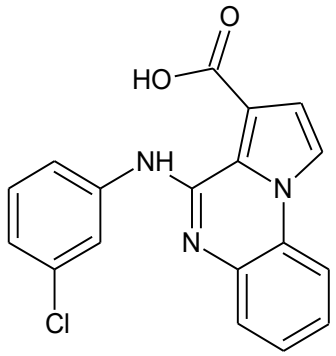


Figure S153. ^{13}C NMR spectrum of 4-(isopropylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9h**) in TFA-d_1



Chemical characterization of 4-((3-chlorophenyl)amino)pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9i**) [7]. Beige solid (243 mg, 72%). mp > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 7.10 (1H, d, $^{3}J_{HH}$ 8.0 Hz, CH aromatic), 7.31 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 7.41 (2H, t, $^{3}J_{HH}$ 8.2 Hz, CH aromatic), 7.48 (1H, t, $^{3}J_{HH}$ 7.5 Hz, CH aromatic), 7.69 (1H, d, $^{3}J_{HH}$ 7.7 Hz, CH aromatic), 7.73 (1H, d, $^{3}J_{HH}$ 8.0 Hz, CH aromatic), 8.26 (1H, d, $^{3}J_{HH}$ 8.2 Hz, CH aromatic), 8.37 (1H, s, CH aromatic), 8.46 (1H, d, *J* 3.1 Hz, CH pyrrole), 12.62 (1H, s, NH), 13.62 (1H, s, OH). ^{13}C NMR (DMSO-d_6, 101 MHz): δ_C 111.21, 115.48, 116.71, 117.23, 117.91, 118.99, 120.91, 122.13, 124.50, 125.06, 127.04, 127.18, 130.87, 133.71, 136.09, 142.20, 146.02 (C=N), 168.97 (C=O). ESI-MS: m/z 338.0 $[M+H]^+$. Anal. calcd for $C_{18}H_{12}ClN_3O_2$ (337.76): C, 64.01; H, 3.58; N, 12.44. Found: C, 63.92; H, 3.56; N, 12.56.

Literature

7. Guillon, J.; Le Borgne, M.; Rimbault, C.; at al. *European Journal of Medicinal Chemistry* **2013**, *65*, 205. https://doi.org/10.1016/j.ejmech.2013.04.051

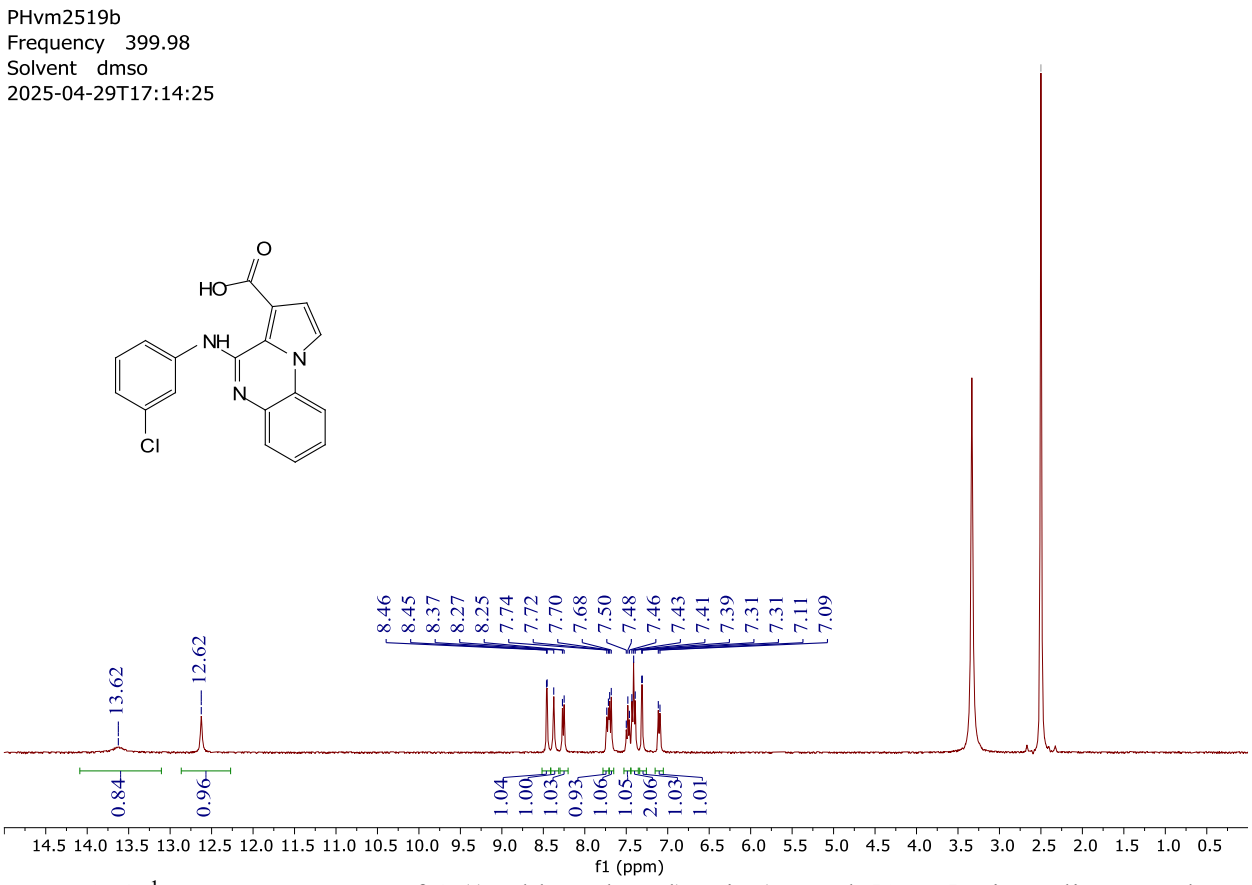


Figure S154. ^{1}H NMR spectrum of 4-((3-chlorophenyl)amino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9i**) in DMSO-d_6

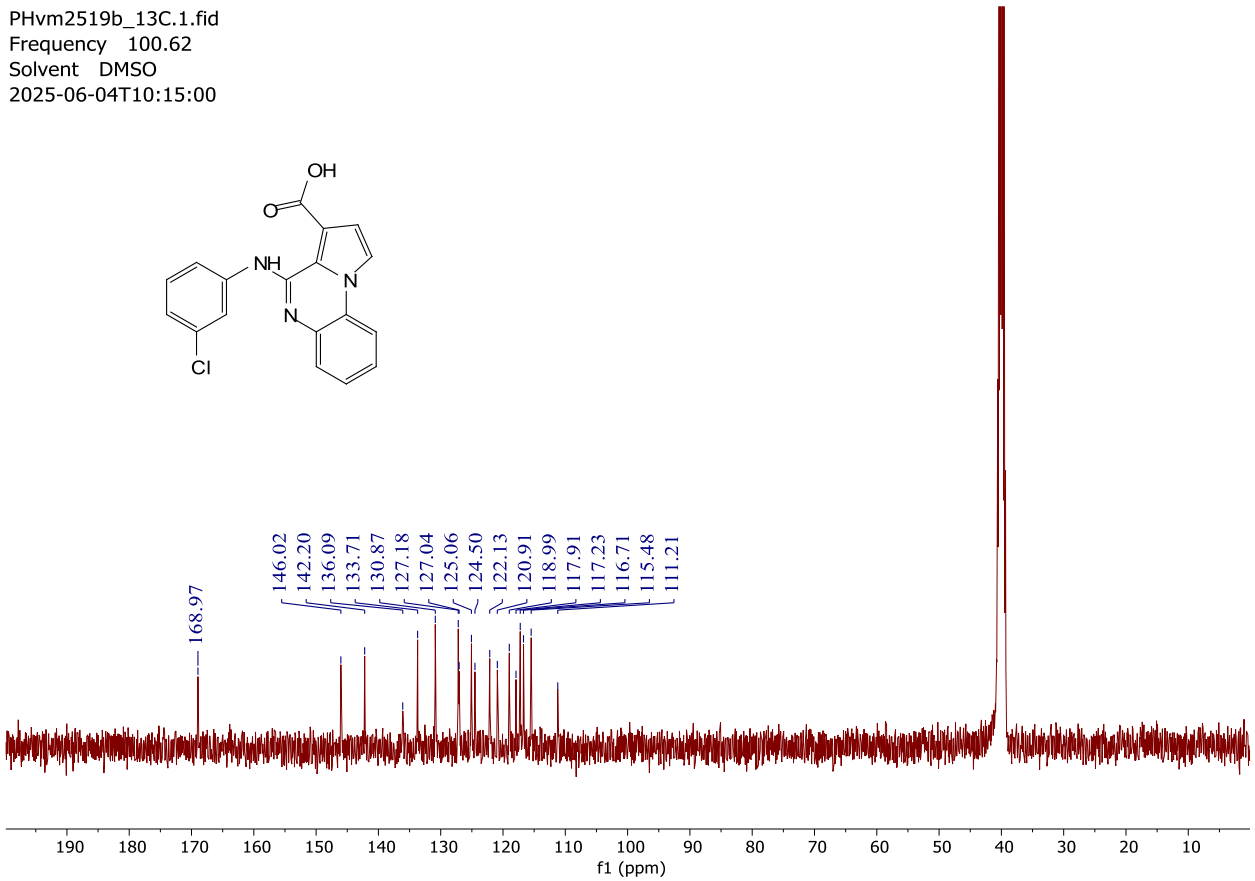
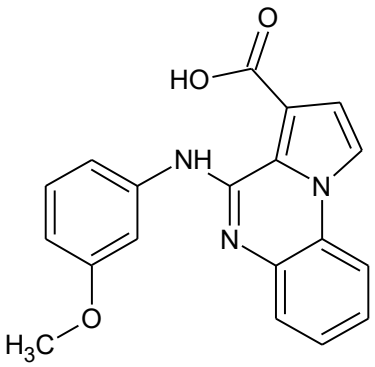


Figure S155. ^{13}C NMR spectrum of 4-((3-chlorophenyl)amino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9i**) in DMSO-d_6



Chemical characterization of 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9j**). Beige solid (280 mg, 84%). mp 290-291 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 3.82 (3H, s, OCH_3), 6.69-6.72 (1H, m, CH aromatic), 7.30-7.36 (3H, m, 3CH aromatic), 7.41 (1H, t, $^3J_{HH}$ 7.6 Hz, CH aromatic), 7.48 (1H, t, $^3J_{HH}$ 7.6 Hz, CH aromatic), 7.70 (1H, d, $^3J_{HH}$ 8.0 Hz, CH aromatic), 7.85 (1H, s), 8.26 (1H, d, $^3J_{HH}$ 8.1 Hz, CH aromatic), 8.48 (1H, d, $^3J_{HH}$ 3.2 Hz, CH pyrrole), 12.69 (1H, s, NH). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_C 55.10 (OCH_3), 106.81, 109.89, 113.26, 115.30, 117.31, 117.49, 119.87, 123.67, 124.12, 124.17, 124.94, 127.01, 130.05, 132.61, 139.44, 145.66 (N=C aromatic), 159.97 (O-C aromatic), 168.35 (C=O). ESI-MS: *m/z* 334.0 $[M+H]^+$. Anal. calcd for $C_{19}H_{15}N_3O_3$ (333.34): C, 68.46; H, 4.54; N, 12.61. Found: C, 68.25; H, 4.55; N, 12.53.

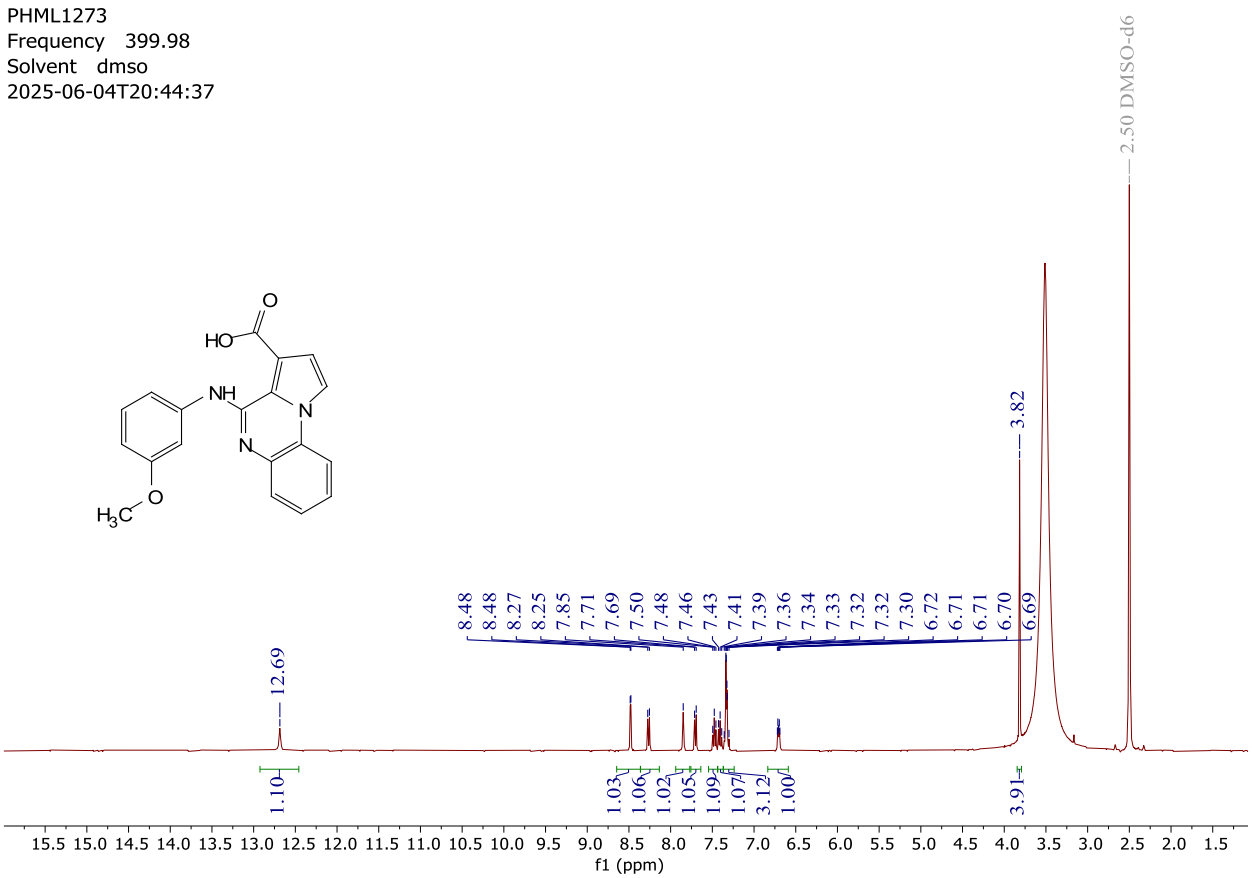


Figure S156. ^{1}H NMR spectrum of 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9j**) in DMSO-d_6

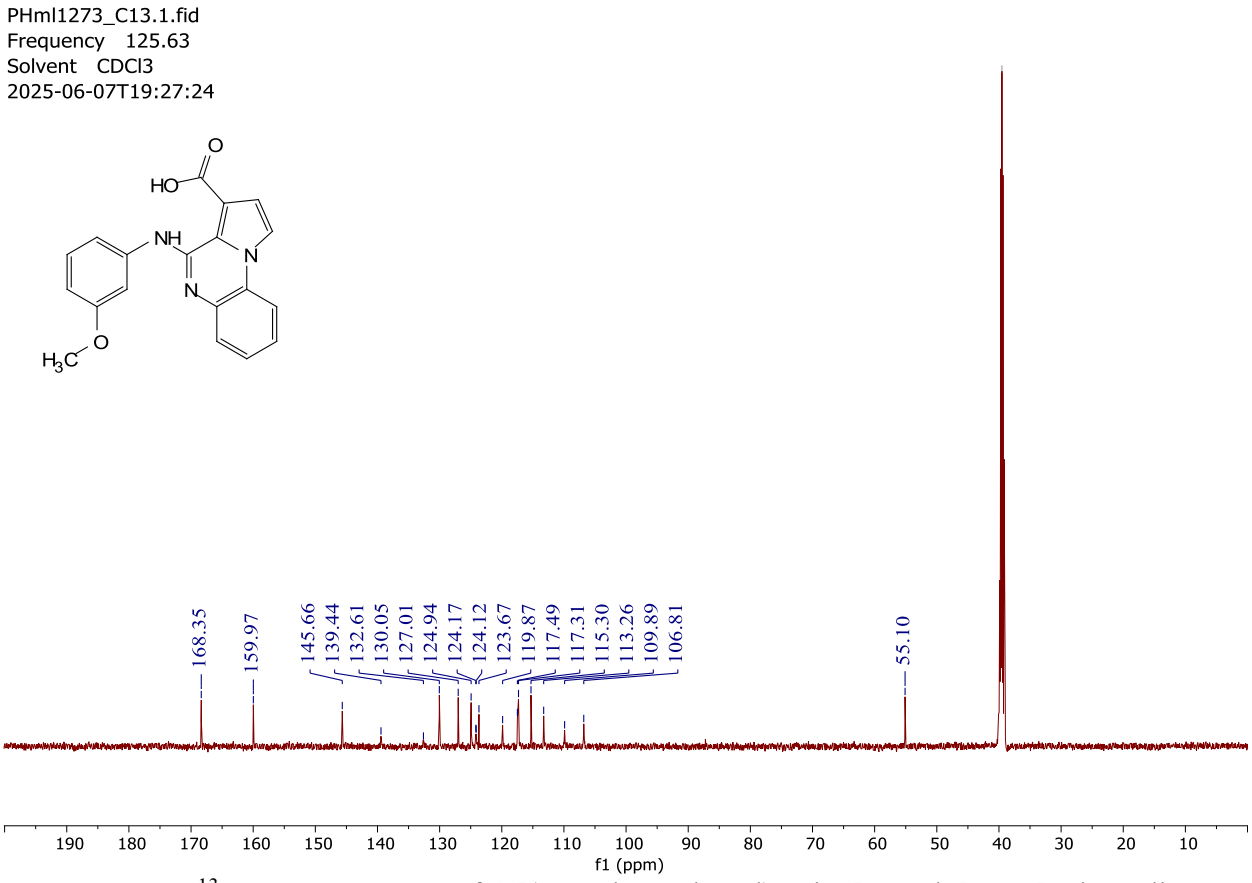
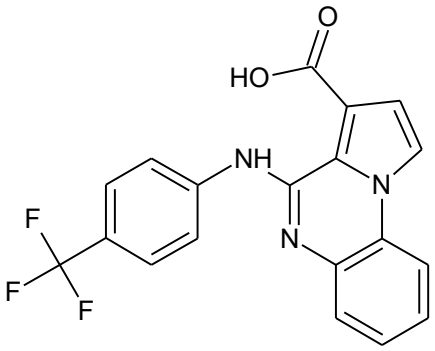


Figure S157. ^{13}C NMR spectrum of 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9j**) in $CDCl_3$



Chemical characterization of 4-{[4-(trifluoromethyl)phenyl]amino}pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9k**). White solid (327 mg, 88%). mp 261-262 °C. ^{1}H NMR (302 MHz, DMSO-d_6): δ_H 7.33 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 7.43 (1H, d, $^{3}J_{HH}$ 7.6 Hz, CH aromatic), 7.50 (1H, d, $^{3}J_{HH}$ 7.5 Hz, CH aromatic), 7.72-7.78 (3H, m, 3CH aromatic), 8.19-8.31 (3H, m, 3CH aromatic), 8.49 (1H, d, $^{3}J_{HH}$ 3.2 Hz, CH pyrrole), 12.81 (1H, s, NH), 13.66 (1H, s, OH). ^{13}C NMR (DMSO-d_6, 76 MHz): δ_C 110.81, 115.06, 116.35, 116.85, 118.78, 118.88, 120.42, 121.83 (q, $^{2}J_{CF}$ 31.8 Hz, C aromatic), 124.15, 124.61 (q, $^{1}J_{CF}$ 270.8 Hz, CF_3), 124.86, 126.12 (q, $^{3}J_{CF}$ 3.8 Hz, 2CH aromatic), 126.74, 135.54, 143.85, 145.51 (C=N), 168.52 (C=O). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -59.90. ESI-MS: *m/z* 372.0 $[M+H]^+$. Anal. calcd for $C_{19}H_{12}F_3N_3O_2$ (371.31): C, 61.46; H, 3.26; N, 11.32. Found: C, 61.22; H, 3.21; N, 11.43.

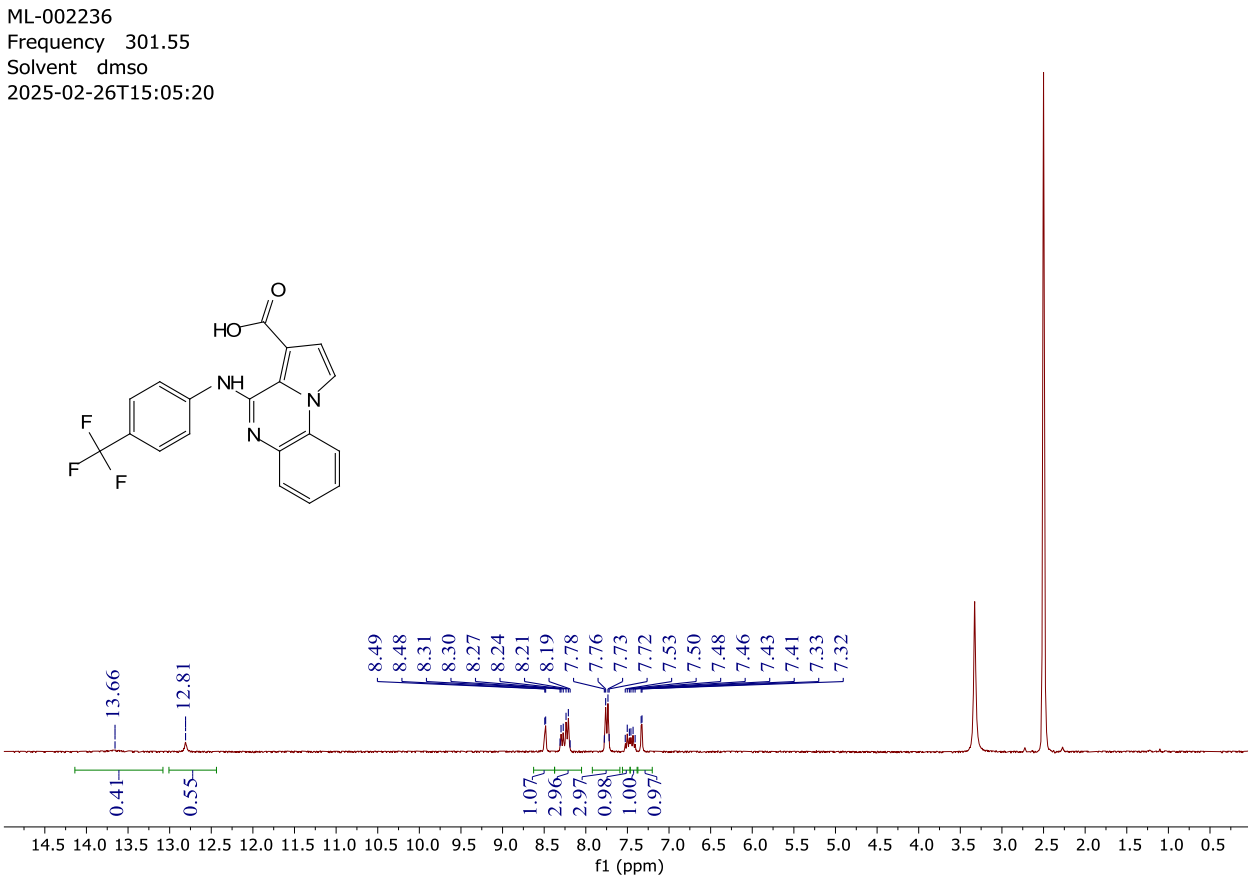


Figure S158. ^{1}H NMR spectrum of 4-{[4-(trifluoromethyl)phenyl]amino}pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9k**) in DMSO-d_6

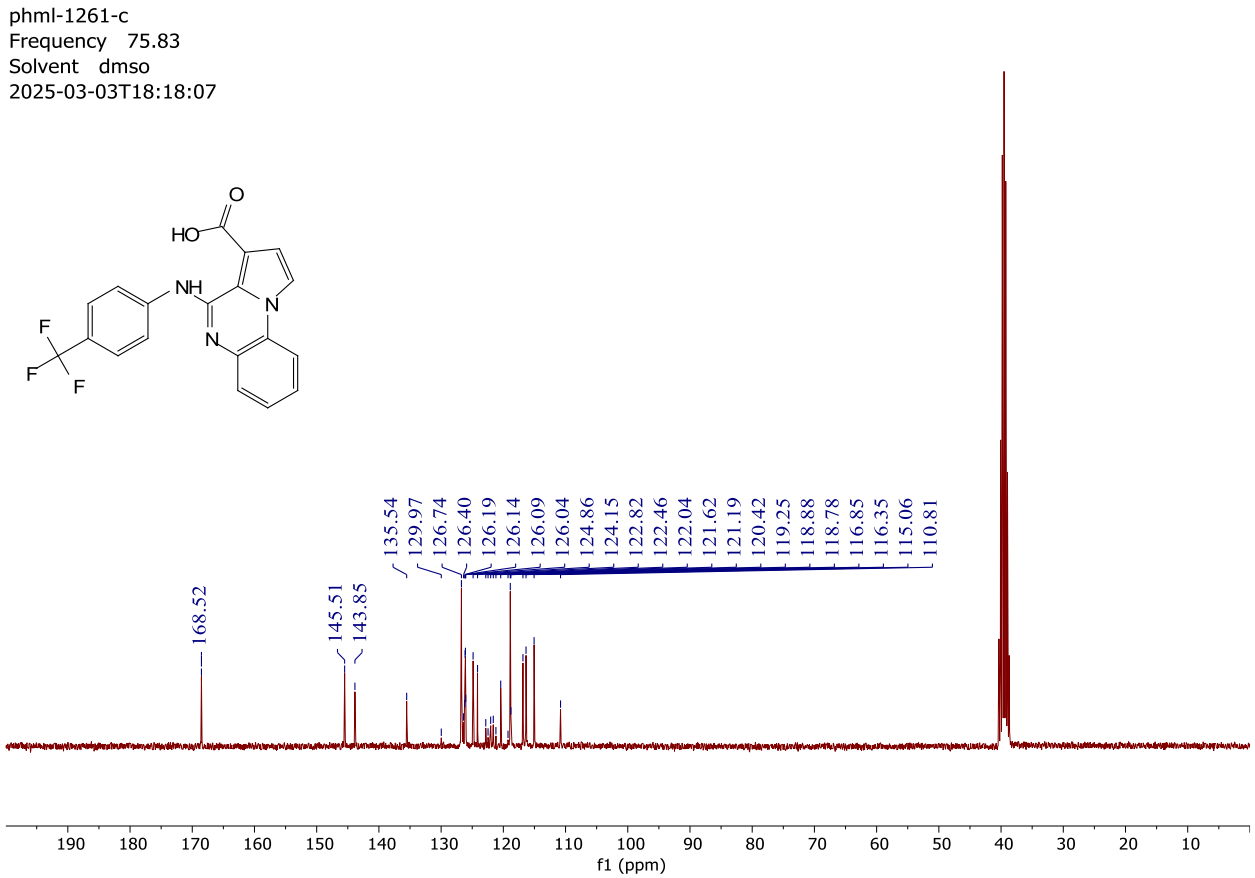


Figure S159. ^{13}C NMR spectrum of 4-{[4-(trifluoromethyl)phenyl]amino}pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9k**) in DMSO-d_6

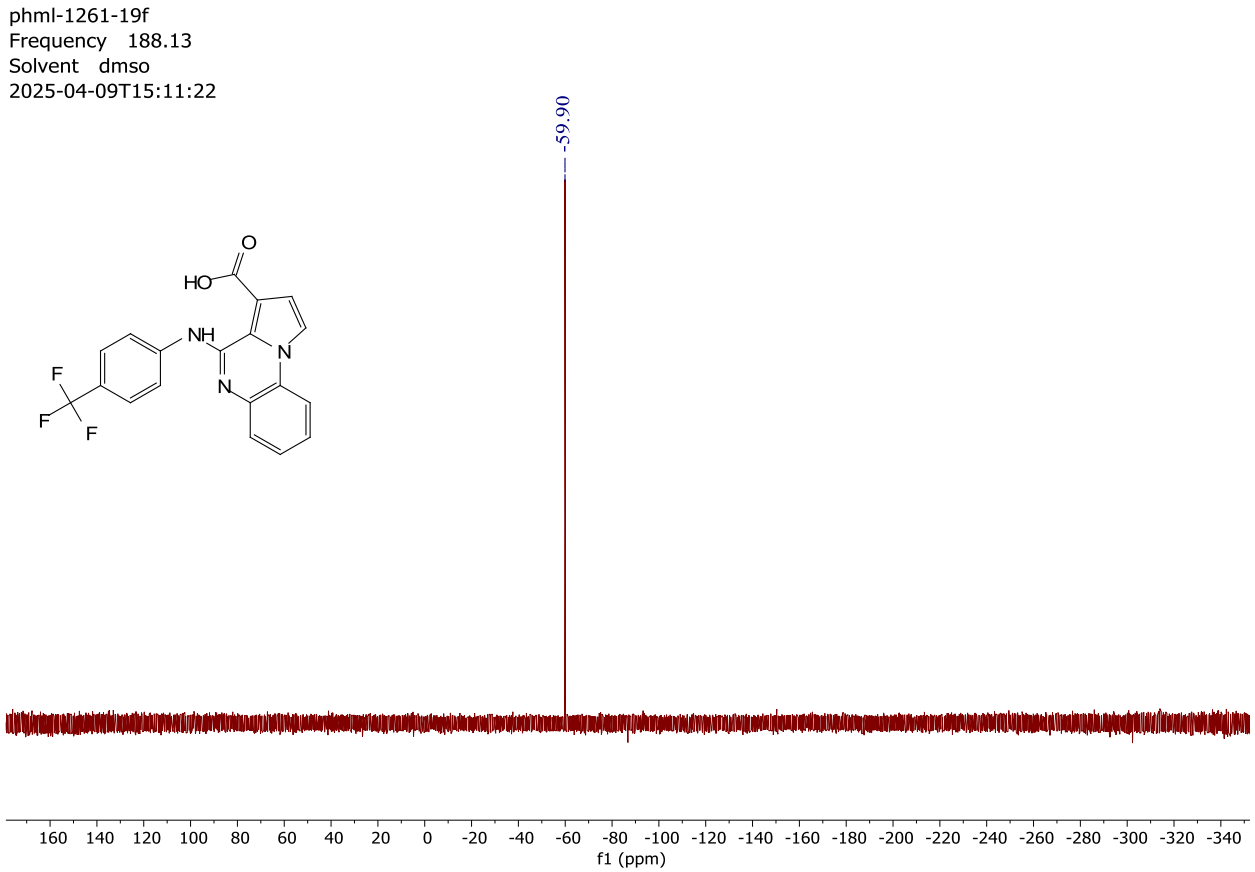
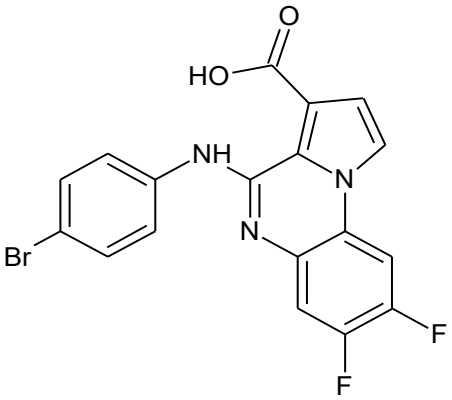


Figure S160. ^{19}F NMR spectrum of 4-{[4-(trifluoromethyl)phenyl]amino}pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9k**) in DMSO-d_6



Chemical characterization of 4-((4-bromophenyl)amino)-7,8-difluoropyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9l**). Light yellow solid (347 mg, 83%). mp > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 7.22 (1H, d, $^{3}J_{HH}$ 2.7 Hz, CH pyrrole), 7.46-758 (3H, m, 3CH aromatic), 7.86 (2H, d, $^{3}J_{HH}$ 8.5 Hz, 2CH aromatic), 8.27 (1H, d, $^{3}J_{HH}$ 2.8 Hz, CH pyrrole), 8.35 (1H, dd, $^{3}J_{HF}$ 11.7, $^{3}J_{HH}$ 7.9 Hz, CH aromatic), 12.48 (1H, s, NH) 13.60 (1H, s, OH). ^{13}C NMR (TFA-d_1, 151 MHz): δ_C 107.31 (d, $^{2}J_{CF}$ 24.0 Hz, CH aromatic), 109.86 (d, $^{2}J_{CF}$ 24.0 Hz, CH aromatic), 119.22, 121.30, 121.49 (d, $^{3}J_{CF}$ 8.0 Hz, C aromatic), 122.82, 122.99, 123.25 (d, $^{3}J_{CF}$ 8.7 Hz, C aromatic), 127.08, 129.61, 132.19, 136.56, 148.34 (C=N), 151.83 (dd, $^{1}J_{CF}$ 254.7, $^{2}J_{CF}$ 14.0 Hz, CF aromatic), 152.48 (dd, $^{1}J_{CF}$ 254.4, $^{2}J_{CF}$ 13.7 Hz, CF aromatic), 171.66 (C=O). ^{19}F NMR (DMSO-d_6, 188 MHz): δ_F -140.79 (ddd, $^{3}J_{FF}$ 23.7, $^{3}J_{HF}$ 11.5, $^{4}J_{HF}$ 8.5 Hz), -139.77 (ddd, $^{3}J_{FF}$ 23.9, $^{3}J_{HF}$ 11.5, $^{4}J_{HF}$ 8.3 Hz). ESI-MS: m/z 417.8, 419.8 $[M+H]^+$. Anal. calcd for $C_{18}H_{10}BrF_2N_3O_2$ (418.19): C, 51.70; H, 2.41; N, 10.05. Found: C, 51.83; H, 2.39; N, 9.98.

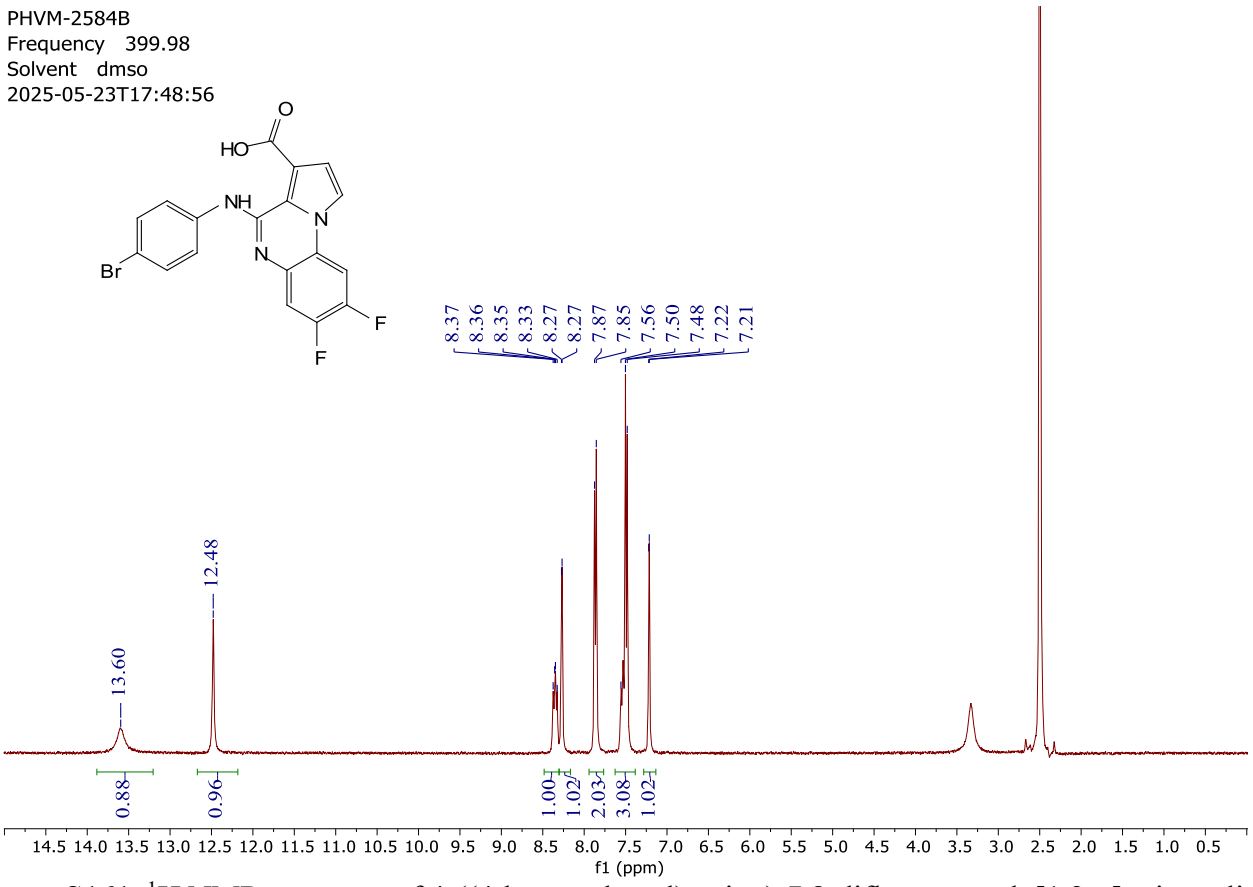


Figure S161. ^{1}H NMR spectrum of 4-((4-bromophenyl)amino)-7,8-difluoropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9l**) in DMSO-d_6

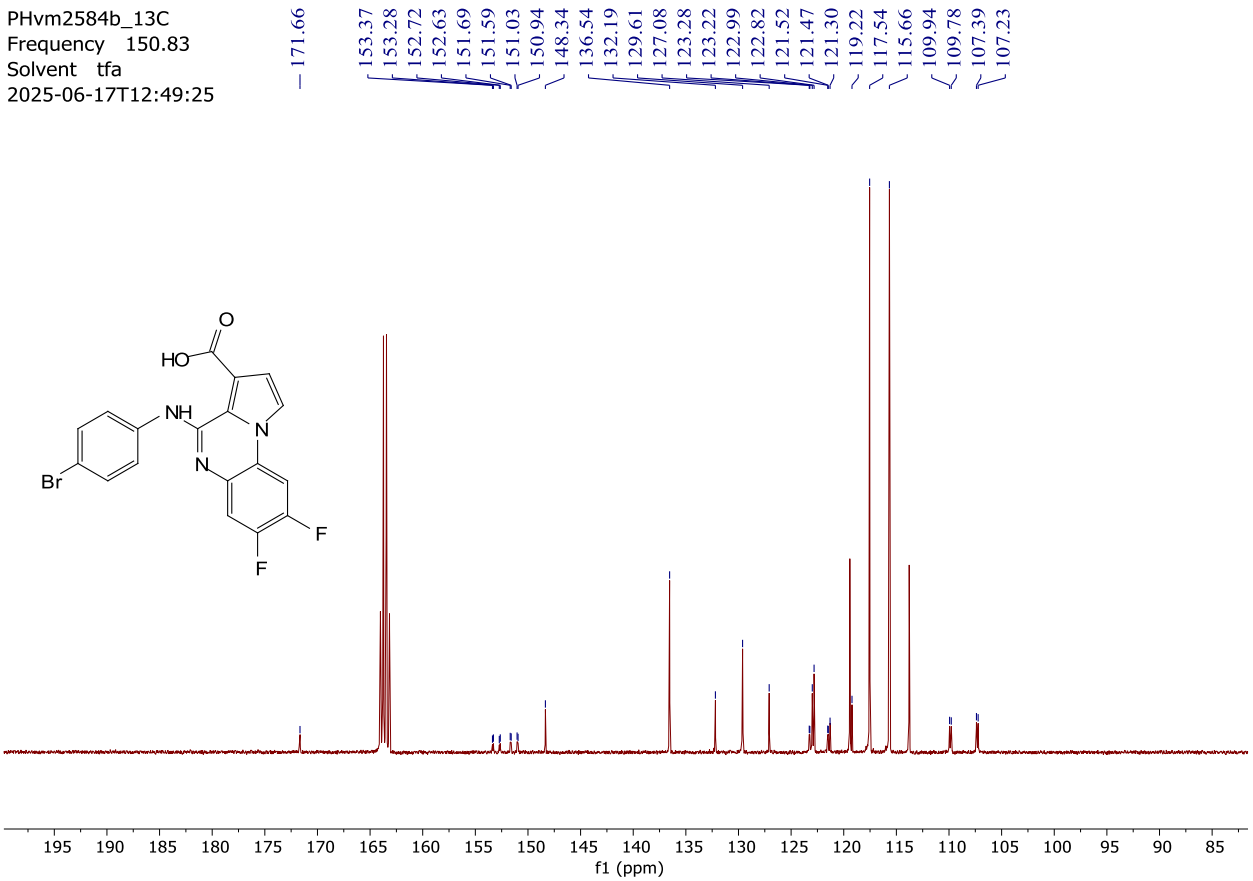


Figure S162. ^{13}C NMR spectrum of 4-((4-bromophenyl)amino)-7,8-difluoropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9l**) in TFA-d_1

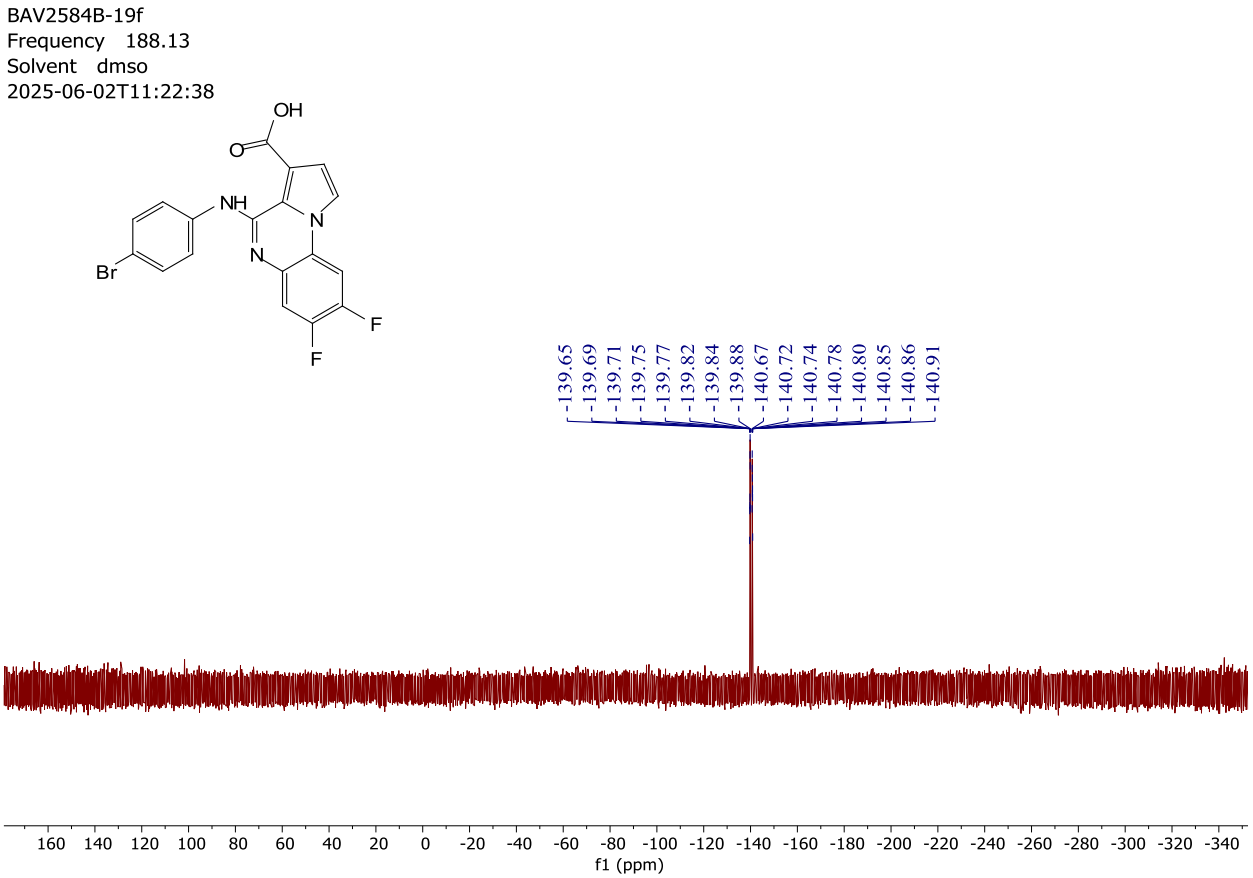
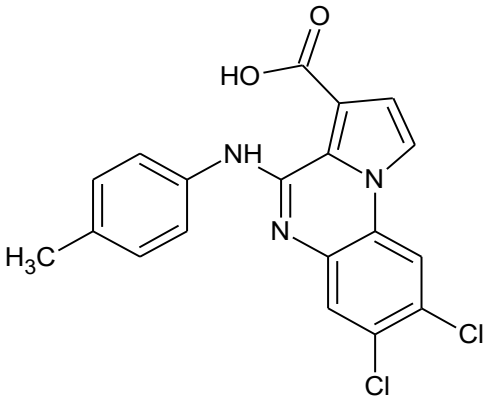


Figure S163. ^{19}F NMR spectrum of 4-((4-bromophenyl)amino)-7,8-difluoropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9l**) in DMSO-d_6



Chemical characterization of 7,8-dichloro-4-(p-tolylamino)pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9m**). Light yellow solid (274 mg, 71%). mp > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 2.30 (3H, s, CH_3), 7.17 (2H, d, $^{3}J_{HH}$ 8.2 Hz, 2CH aromatic), 7.24 (1H, d, $^{3}J_{HH}$ 3.2 Hz, CH pyrrole), 7.73 (1H, s, CH aromatic), 7.83 (2H, d, $^{3}J_{HH}$ 8.0 Hz, 2CH aromatic), 8.40 (1H, d, $^{3}J_{HH}$ 3.2 Hz, CH pyrrole), 8.50 (1H, s, CH aromatic), 12.42 (1H, s, NH), 13.61 (1H, s, OH). ^{13}C NMR (TFA-d_1, 151 MHz): δ_C 21.61 (CH_3), 115.66, 117.54, 119.24, 121.41, 121.87, 122.64, 122.77, 123.99, 125.85, 127.60, 130.25, 133.73, 134.49, 135.74, 144.27, 148.34 (C=N), 171.59 (C=O). ESI-MS: m/z 386.0 $[M+H]^+$. Anal. calcd for $C_{19}H_{13}Cl_2N_3O_2$ (386.23): C, 59.08; H, 3.39; N, 10.88. Found: C, 58.91; H, 3.41; N, 10.70.

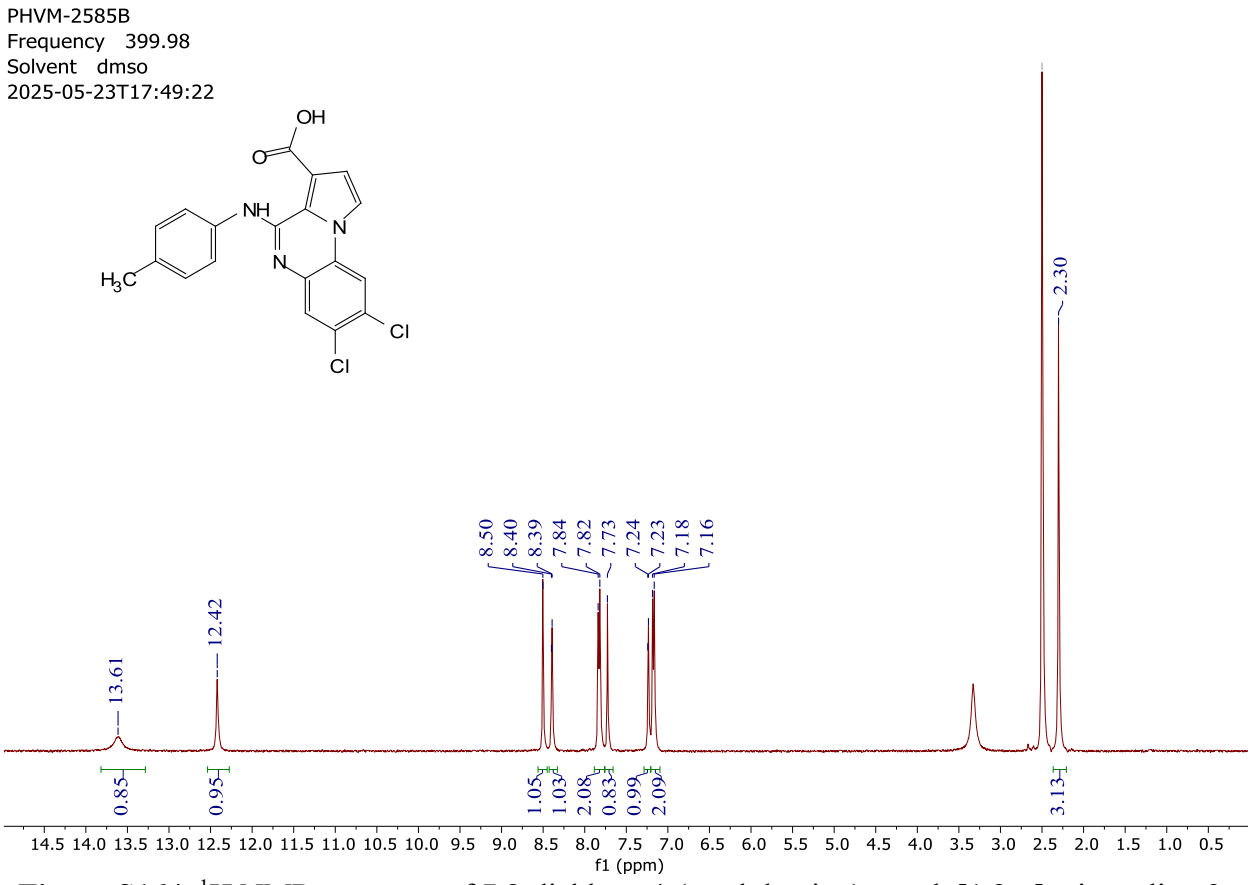


Figure S164. ^{1}H NMR spectrum of 7,8-dichloro-4-(*p*-tolylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9m**) in DMSO-d_6

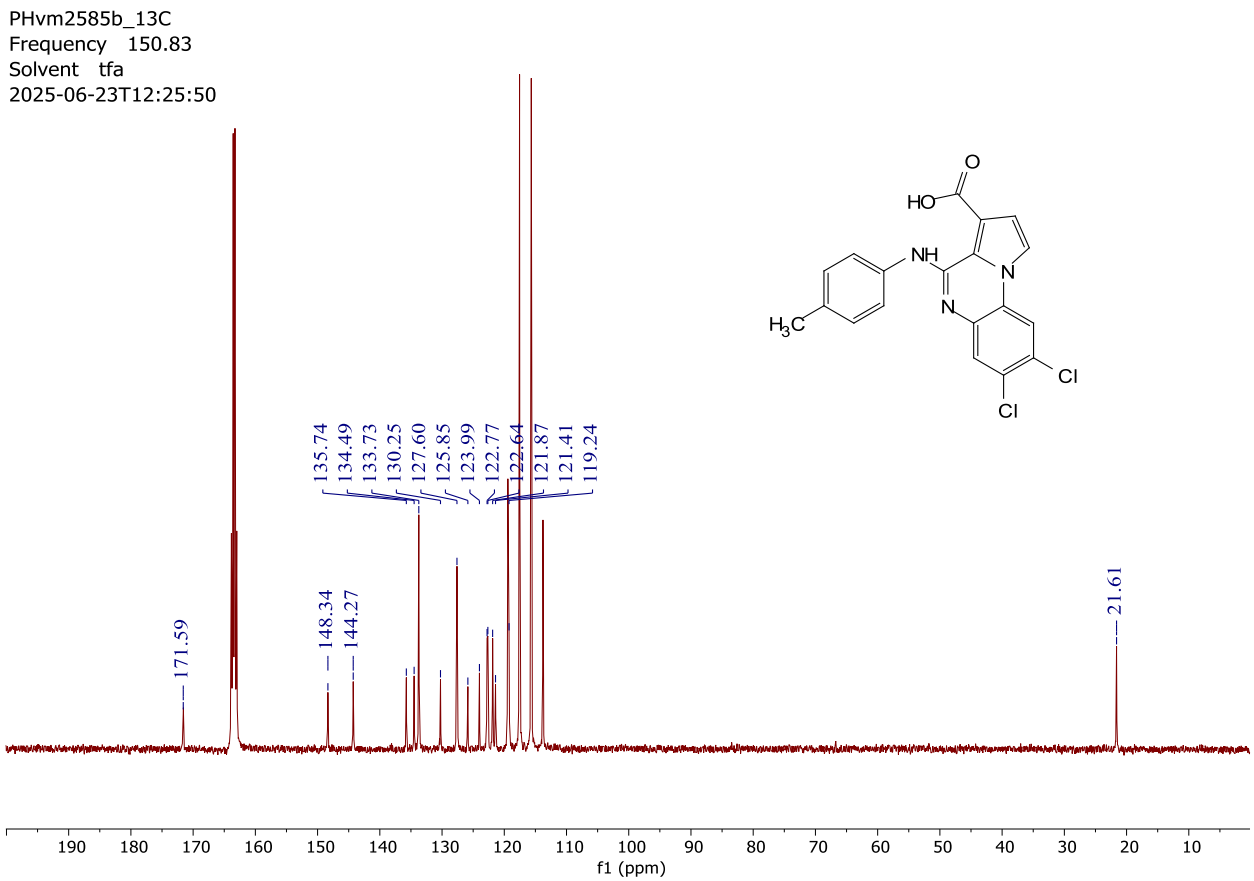
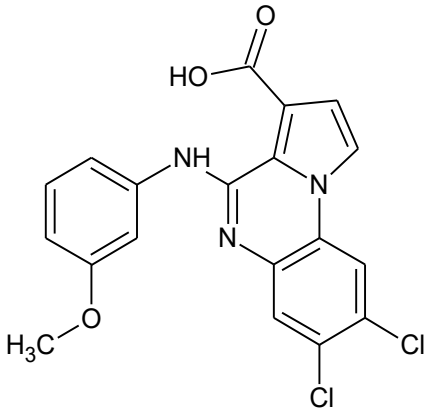


Figure S165. ^{13}C NMR spectrum of 7,8-dichloro-4-(*p*-tolylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9m**) in TFA-d_1



Chemical characterization of 7,8-dichloro-4-[(3-methoxyphenyl)amino]pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9n**). Light brown solid (370 mg, 92%). mp 280-281 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 3.80 (3H, s, OCH_3), 6.65 (1H, d, $^3J_{HH}$ 7.3 Hz, CH aromatic), 7.24-7.29 (2H, m, CH pyrrole + CH aromatic), 7.36 (1H, d, $^3J_{HH}$ 8.0 Hz, CH aromatic), 7.73 (1H, s, CH aromatic), 7.77 (1H, s, CH aromatic), 8.41 (1H, d, $^3J_{HH}$ 3.2 Hz, CH pyrrole), 8.53 (1H, s, CH aromatic), 12.52 (1H, s, NH), 13.70 (1H, s, OH). ^{13}C NMR (DMSO-d_6, 76 MHz): δ_C 54.93 (CH_3O), 105.06, 108.28, 111.51, 111.75, 116.69, 116.93, 120.31, 123.54, 125.56, 126.77, 128.59, 129.51, 136.03, 140.98, 146.41 (C=N), 159.61 (C-OCH_3), 168.29 (C=O). ESI-MS: *m/z* 402.0 $[M+H]^+$. Anal. calcd for $C_{19}H_{13}Cl_2N_3O_3$ (402.23): C, 56.73; H, 3.26; N, 10.45. Found: C, 56.57; H, 3.24; N, 10.55.

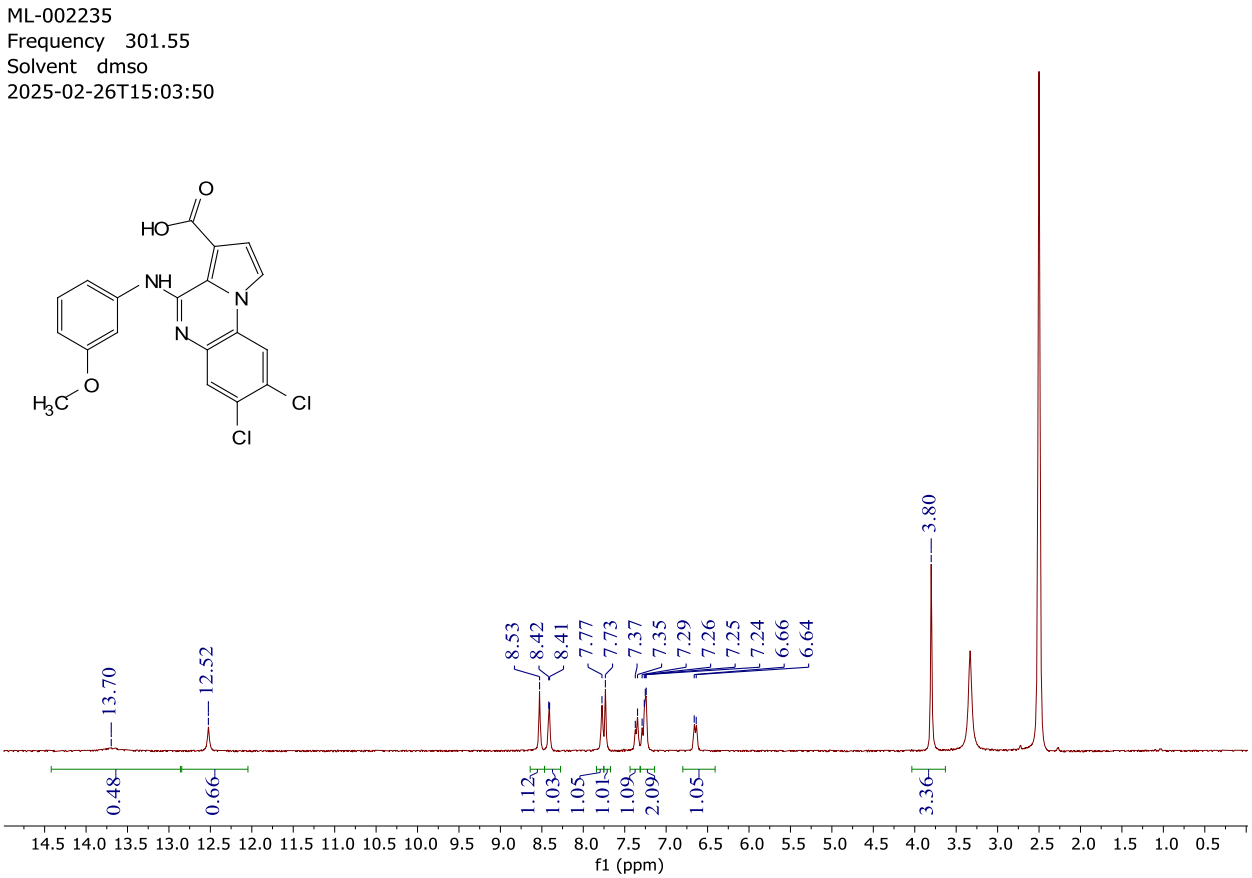


Figure S166. [1]H NMR spectrum of 7,8-dichloro-4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9n**) in DMSO-d_6

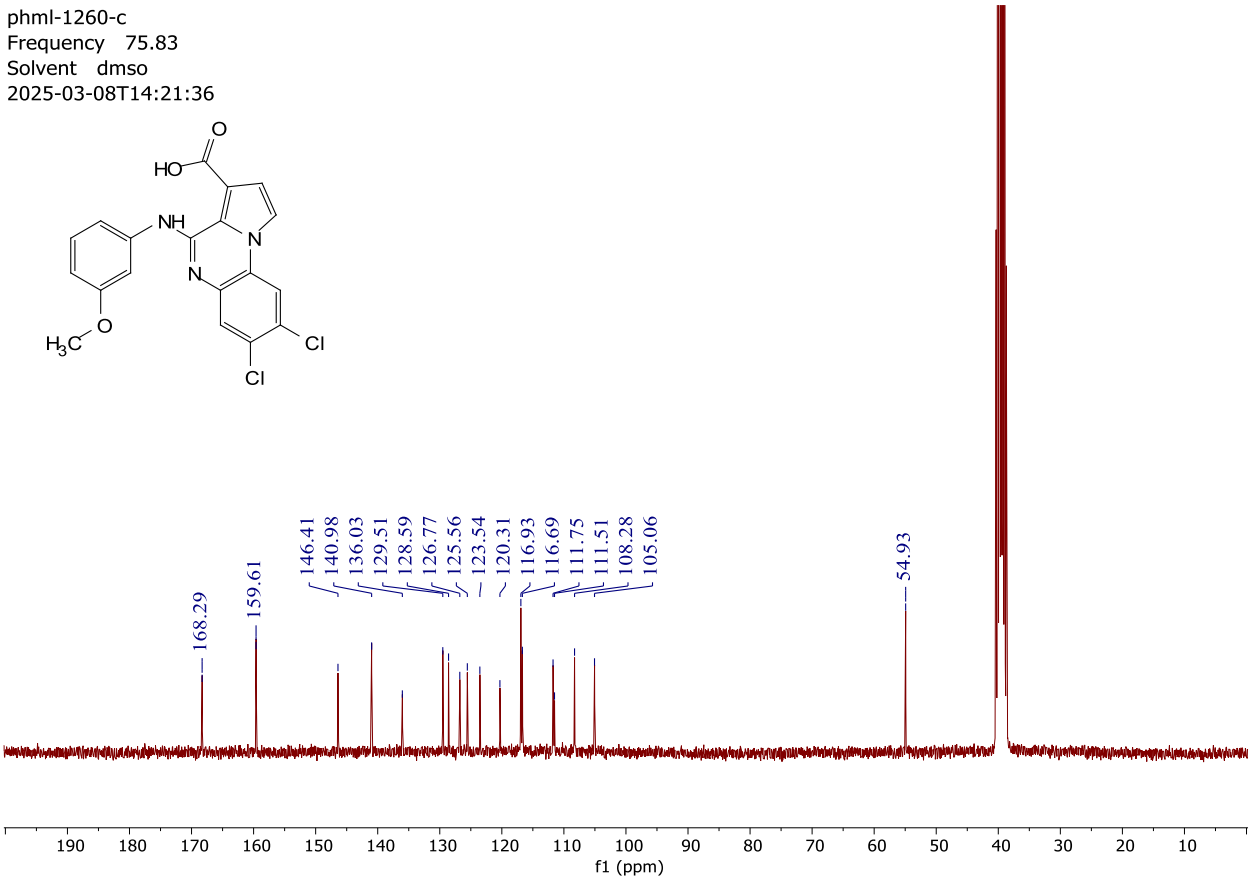
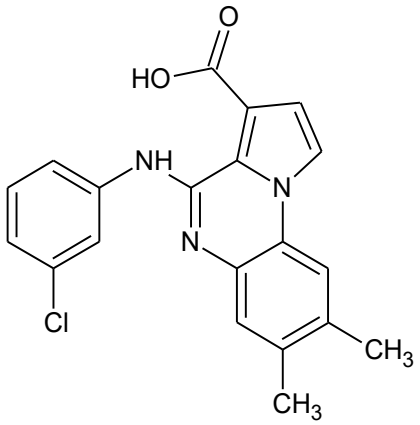


Figure S167. [13]C NMR spectrum of 7,8-dichloro-4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9n**) in DMSO-d_6



Chemical characterization of 4-((3-chlorophenyl)amino)-7,8-dimethylpyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9o**). Beige solid (274 mg, 75%). mp > 300 °C. ^{1}H NMR (302 MHz, DMSO-d_6): δ_H 2.33 (3H, s, CH_3), 2.36 (3H, s, CH_3), 7.08 (1H, d, $^{3}J_{HH}$ 7.9 Hz, CH aromatic), 7.26 (1H, d, $^{3}J_{HH}$ 3.1 Hz, CH pyrrole), 7.39 (1H, t, $^{3}J_{HH}$ 8.1 Hz, CH aromatic), 7.44 (1H, s, CH aromatic) 7.70 (1H, d, $^{3}J_{HH}$ 8.2 Hz, CH aromatic), 8.01 (1H, s, CH aromatic), 8.29-8.38 (2H, m, CH aromatic + CH pyrrole), 12.53 (1H, s, NH), 13.50 (1H, s, OH). ^{13}C NMR (TFA-d_1, 151 MHz): δ_C 20.15 (CH_3), 20.40 (CH_3), 117.65, 119.14, 119.90, 120.67, 122.18, 122.56, 123.01, 124.18, 126.14, 128.34, 132.63, 134.10, 134.86, 139.25, 141.19, 142.10, 147.57 (C=N), 172.21 (C=O). ESI-MS: m/z 366.0 $[M+H]^+$. Anal. calcd for $C_{20}H_{16}ClN_3O_2$ (365.81): C, 65.67; H, 4.41; N, 11.49. Found: C, 65.81; H, 4.39; N, 11.60.

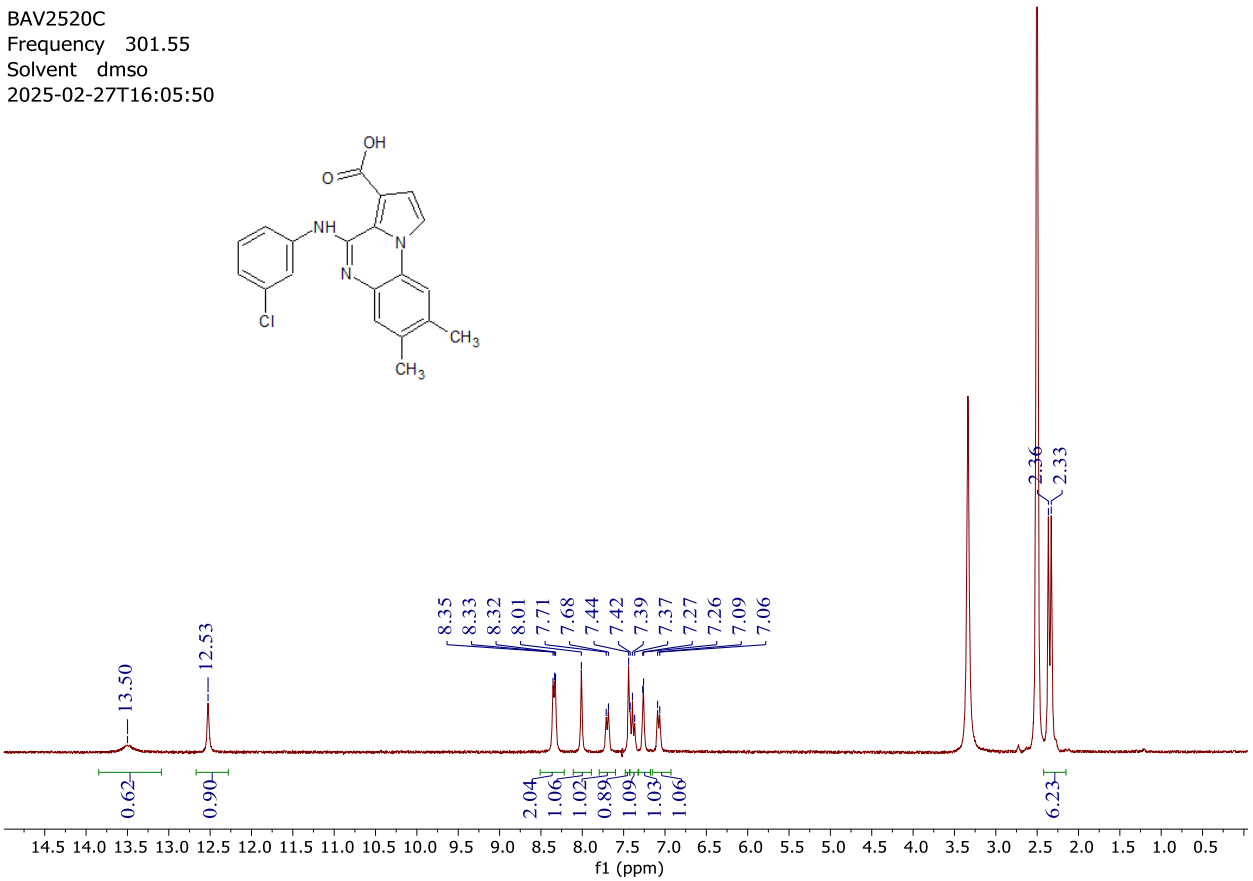


Figure S168. ^{1}H NMR spectrum of 4-((3-chlorophenyl)amino)-7,8-dimethylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9o**) in DMSO-d_6

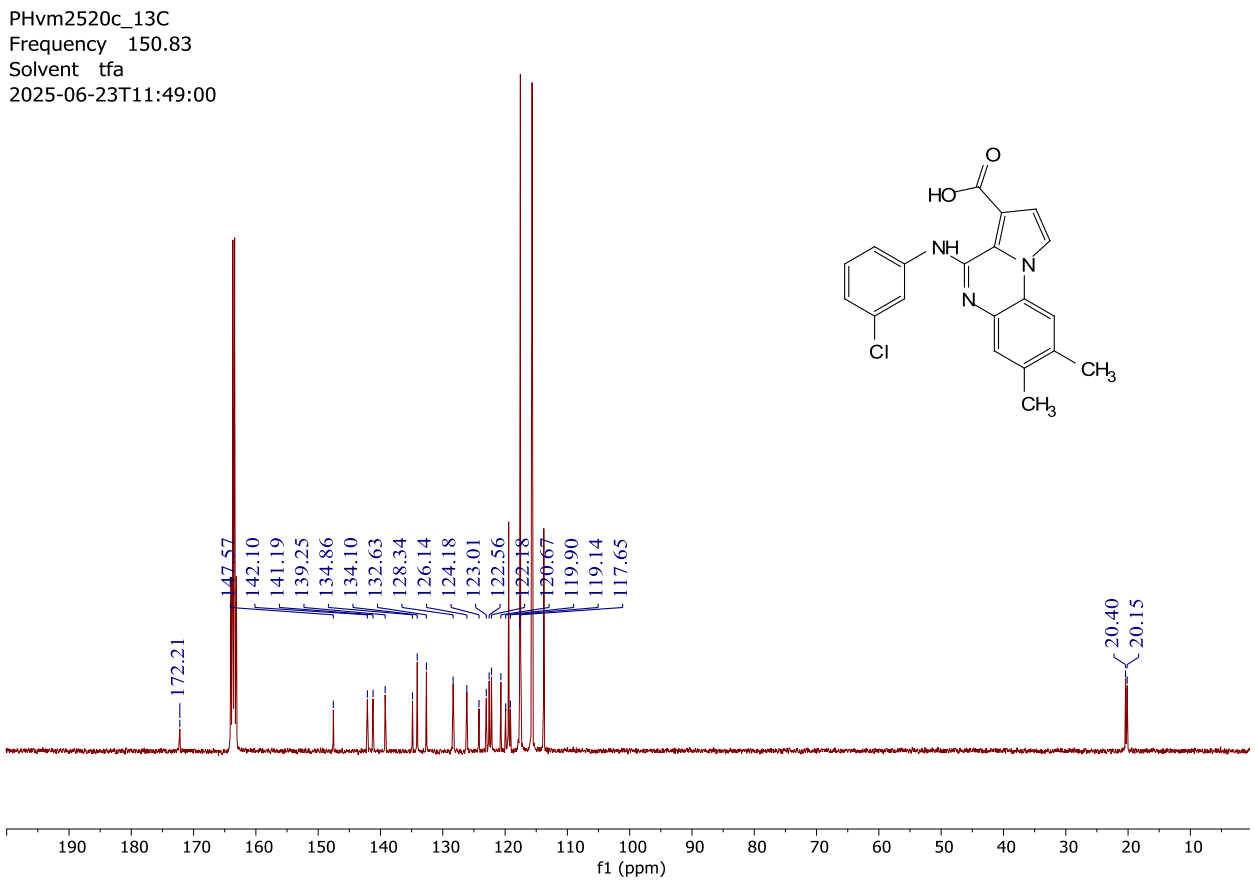
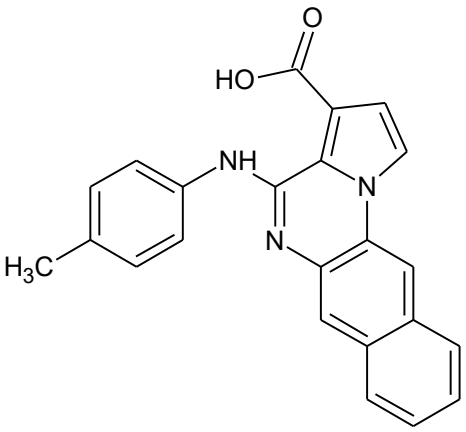


Figure S169. ^{13}C NMR spectrum of 4-((3-chlorophenyl)amino)-7,8-dimethylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9o**) in TFA-d_1



Chemical characterization of 4-(p-tolylamino)benzo[g]pyrrolo[1,2-a]quinoxaline-3-carboxylic acid (**9p**). Light brown solid (331 mg, 90%). mp 269-270 °C. IR (solid, KBr, νmax, cm^{-1}): 3422, 2754, 1655, 1512, 1466, 816, 746, 546. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 2.35 (3H, s, CH_3), 7.29 (2H, d, $^3J_{HH}$ 7.9 Hz, 2CH aromatic), 7.34 (1H, d, $^3J_{HH}$ 2.8 Hz, CH pyrrole), 7.50-7.52 (2H, m, 2CH aromatic), 7.81 (2H, d, $^3J_{HH}$ 7.8 Hz, 2CH aromatic), 7.96-7.98 (2H, m, 2CH aromatic), 8.16 (1H, s, CH aromatic), 8.59 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 8.78 (1H, s, CH aromatic), 12.87 (1H, s, NH). ^{13}C NMR (TFA-d_1, 76 MHz): δ_C 21.66 (CH_3), 115.73, 118.34, 119.25, 121.18, 123.07, 123.33, 124.51, 127.61, 129.20, 129.65, 130.09, 130.41, 130.51, 133.46, 133.86, 134.25, 144.24, 148.03(N=C) , 172.08 (C=O). ESI-MS: *m/z* 368.2 [M+H]$^+$. Anal. calcd for $C_{23}H_{17}N_3O_2$ (367.40): C, 75.19; H, 4.66; N, 11.44. Found: C, 75.38; H, 4.65; N, 11.33.

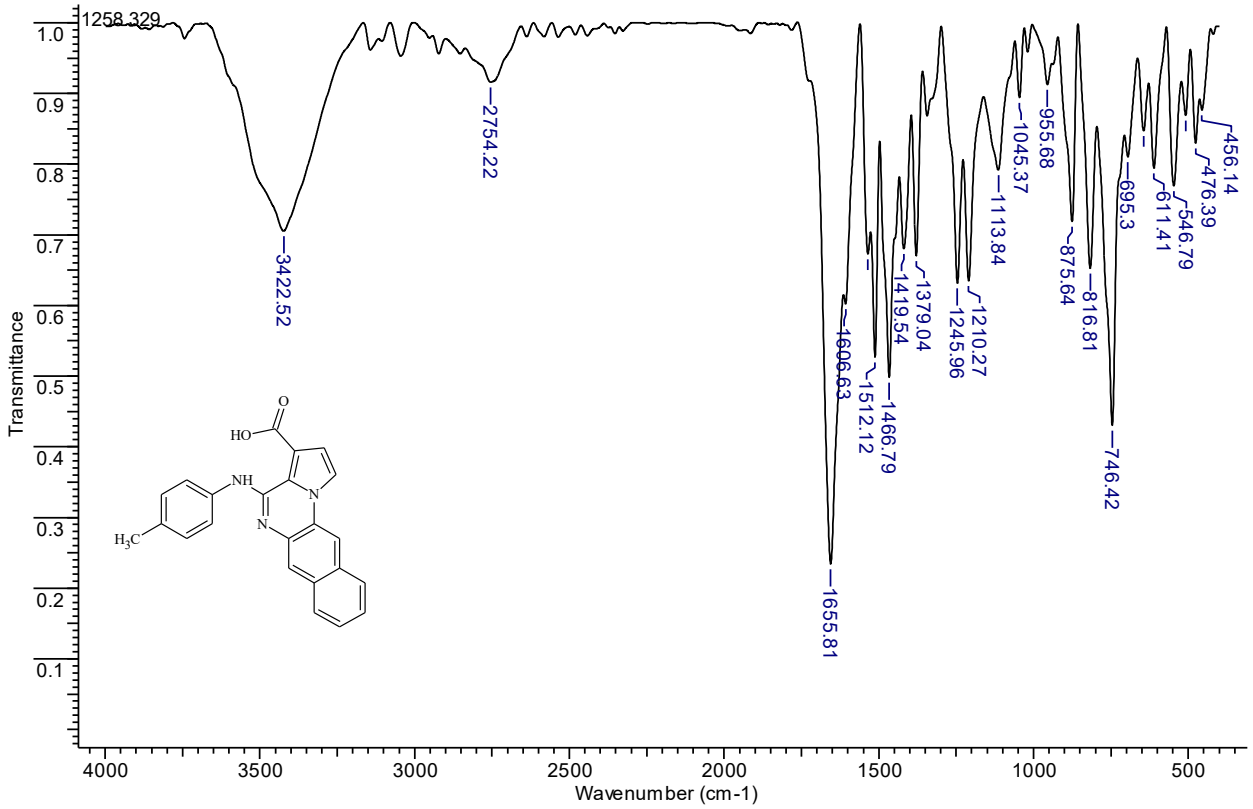


Figure S170. IR spectrum of 4-(*p*-tolylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9p**) in KBr pellet

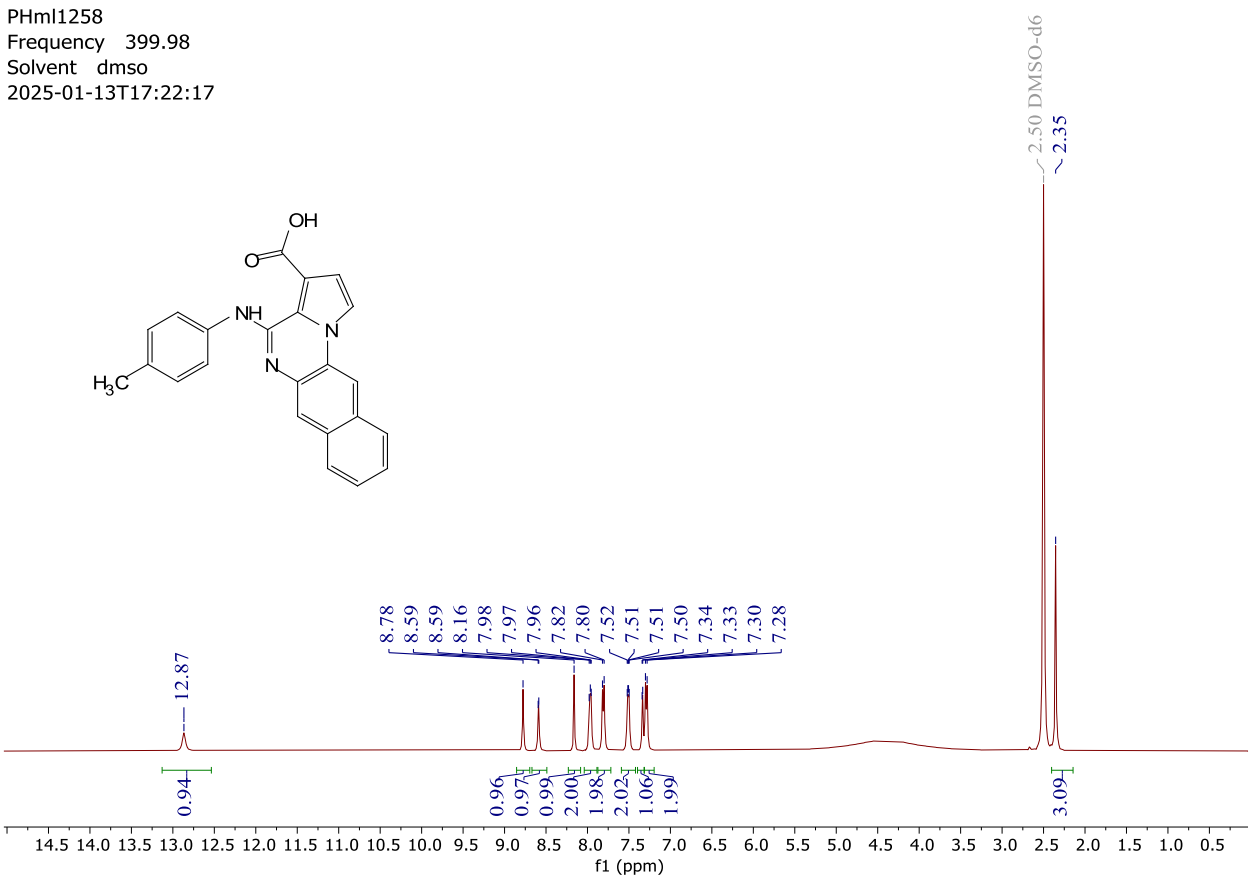


Figure S171. ^{1}H NMR spectrum of 4-(*p*-tolylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9p**) in DMSO-d_6

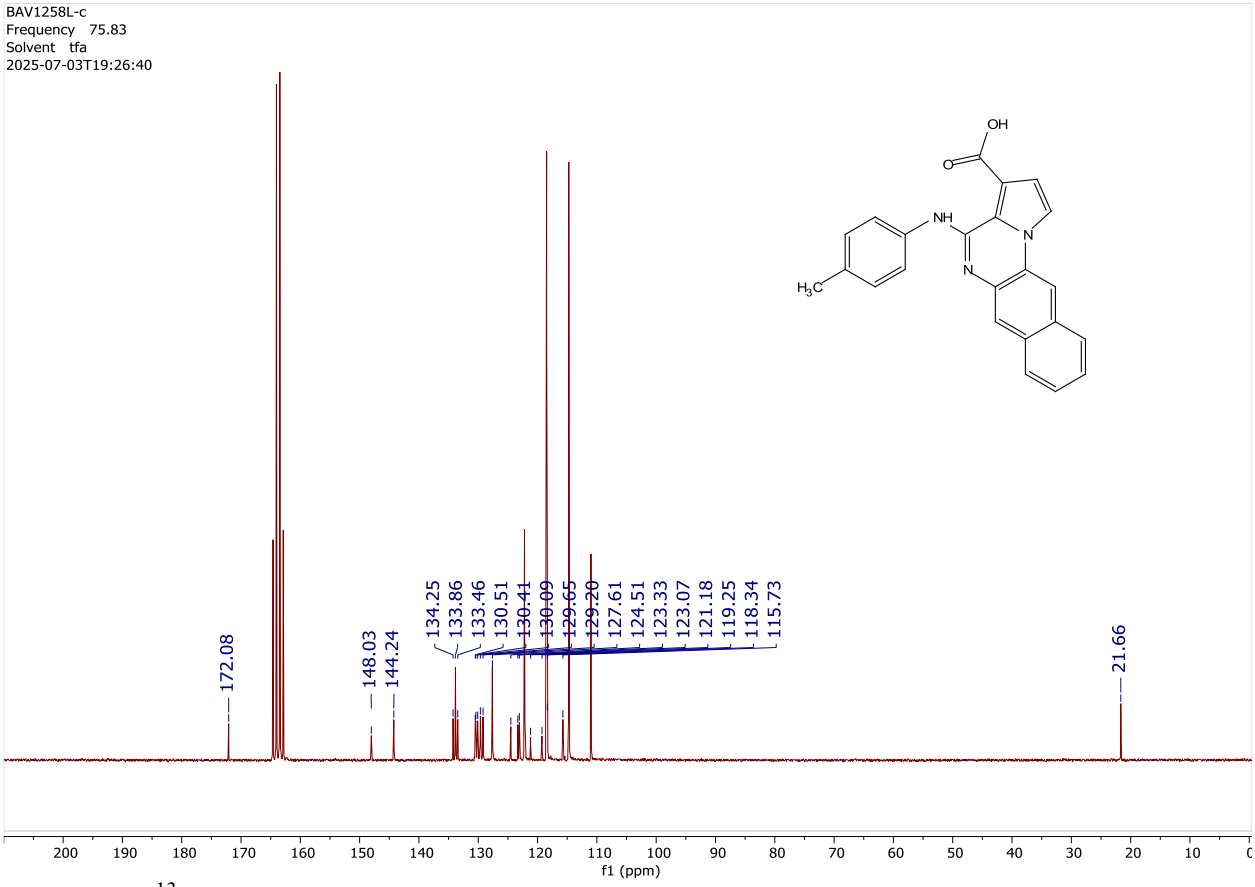


Figure S172. ^{13}C NMR spectrum of 4-(*p*-tolylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (**9p**) in TFA-d_1

