Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 177–179

Synthesis and transformations of mesoionic imidazol-3-ium-4-olate carbaldehydes

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Synthetic procedures and characterization of isolated compounds

General Information

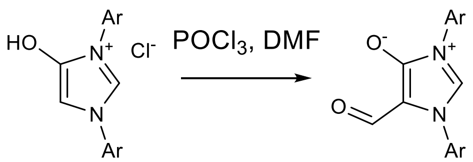
^{1}H and ^{13}C NMR spectra (300 and 75 MHz, respectively) were recorded on a Bruker Avance Neo 300 spectrometer. Chemical shifts (δ, ppm) are given relative to the residual signals of chloroform-*d* protons (7.26 ppm for ^{1}H NMR) or carbon signals in chloroform-*d* (77.16 ppm for ^{13}C NMR).

High-resolution mass spectra (HRMS) were recorded on a Bruker maXis Q-TOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. The measurements were performed in a positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: –500 V) with a scan range of *m/z* 50 – 1500. External calibration of the mass spectrometer was achieved using a low-concentration tuning mix solution (Agilent Technologies). Direct syringe injection was applied for the analysed solutions at a flow rate 3 μL min^{-1}. Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}). The dry temperature was established at 250 °C. All the spectra were recorded with 1 Hz frequency and processed using the Bruker Data Analysis 4.0 software package.

Melting points were determined in open capillary tubes using a Thiele apparatus and are uncorrected.

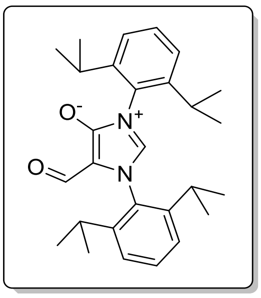
Materials. 1,3-Bis(2,6-diisopropylphenyl)-4-hydroxy-1*H*-imidazol-3-ium chloride **(1a)**,[S1] 4-hydroxy-1,3-dimesityl-1*H*-imidazol-3-ium chloride (**1b**),[S1] 1,3-bis(2,6-dimethylphenyl)-4-hydroxy-1*H*-imidazol-3-ium chloride **(1c)**[S2] were synthesized as described in the literature.

General procedure for the synthesis of compound 2a-c

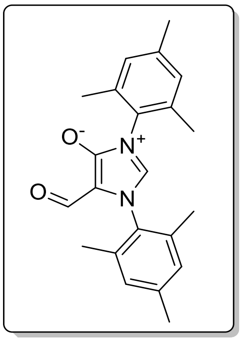


1a-c **2a-c**

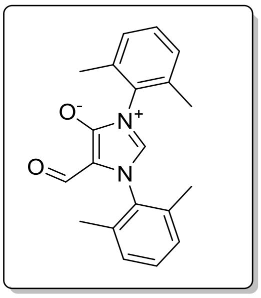
In a round-bottomed flask to 4 ml of dry DMF, 0.56 ml of $POCl_3$ was added dropwise at 0˚C. Then, to the resulting mixture, 4 mmol of the corresponding compound **1** was added in one portion. The resulting solution was heated to 60 ˚C and stirred at this temperature for 1.5 h. After this time, 10 mL of water was added, and resulting mixture was stirred at 100 ˚C for another 30 min. After completion of the reaction, the mixture was cooled to room temperature, and resulting precipitate was filtered off, washed with water, and dried at 100 ˚C under vacuum.



1,3-Bis(2,6-diisopropylphenyl)-5-formyl-1*H*-imidazol-3-ium-4-olate (2a) Yield 1.52 g (88%), white powder, mp = 265-266˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.08 – 1.27 (m, 24H), 2.56 – 2.78 (m, 4H), 7.28 – 7.44 (m, 4H), 7.44 – 7.59 (m, 2H), 9.11 (s, 1H), 9.26 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 22.9, 22.9, 23.9, 24.3, 28.5, 28.7, 107.8, 123.7, 124.0, 128.2, 130.2, 130.5, 132.0, 135.2, 144.8, 146.0, 171.7. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{28}H_{37}N_2O_2^+$ 433.2850, found *m/z* 433.2835.

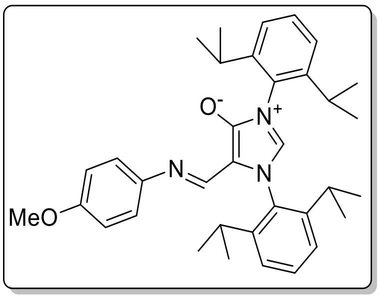


5-Formyl-1,3-dimesityl-1*H*-imidazol-3-ium-4-olate (2b). Yield 1.20 g (86%), white powder, mp >300 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.10 (s, 6H), 2.12 (s, 6H), 2.31 (s, 6H), 7.03 (s, 2H), 7.09 (s, 2H), 8.75 (s, 1H), 9.22 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 16.8, 17.4, 20.6, 34.3, 106.6, 128.6, 128.7, 128.9, 132.7, 134.2, 134.6, 135.4, 138.8, 139.1, 171.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{22}H_{25}N_2O_2^+$ 349.1911, found *m/z* 349.1900.

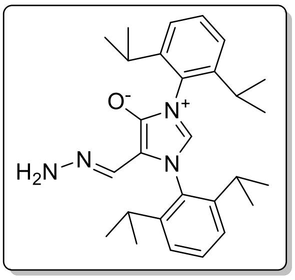


1,3-Bis(2,6-diimethylphenyl)-5-formyl-1*H*-imidazol-3-ium-4-olate (2c). Yield 1.52 g (88%), white powder, mp = 288-289 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.16 (s, 6H), 2.19 (s, 6H), 7.05 – 7.49 (m, 6H), 8.81 (s, 1H), 9.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 16.9, 17.5, 106.5, 128.1, 128.4, 129.4, 129.6, 131.3, 134.4, 134.6, 135.8, 171.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{20}H_{21}N_2O_2^+$ 321.1598, found *m/z* 321.1588.

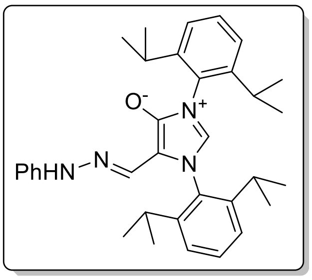
Post-functionalization of 2a



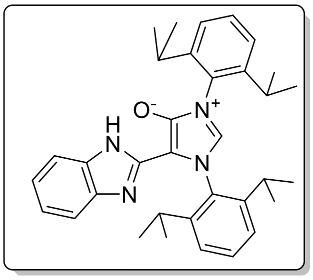
1,3-Bis(2,6-diisopropylphenyl)-5-((4-methoxyphenylimino)methyl)-1*H*-imidazol-3-ium-4-olate (3). A mixture of compound **2a** (0.5 mmol, 0.216 g) and *p*-anisidine (1 mmol, 0.123 g) in 2 mL of EtOH was stirred at 25 ˚C for 12 h. Then the solvent was evaporated *in vacuo* and residue was washed with hot hexane (3x10 mL) and dried at 100 ˚C under vacuum to give compound **3**. Yield 0.21 g (78%), yellow powder, mp = 255-256 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.07 – 1.29 (m, 24H), 2.61 – 2.84 (m, 3H), 3.67 (s, 3H), 6.64 – 6.82 (m, 3H), 7.29 – 7.43 (m, 4H), 7.44 – 7.58 (m, 2H), 8.05 (s, 1H), 8.88 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 22.8, 23.0, 24.1, 24.4, 28.5, 28.6, 55.1, 114.2, 114.5, 115.0, 120.9, 123.5, 123.8, 129.1, 130.2, 141.6, 143.3, 145.0, 146.1, 156.2, 156.8. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{35}H_{44}N_3O_2^+$ 538.3428, found *m/z* 538.3410.



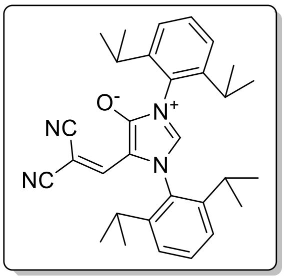
1,3-Bis(2,6-diisopropylphenyl)-5-(hydrazinylidenemethyl)-1*H*-imidazol-3-ium-4-olate (4a). A mixture of compound **2a** (0.5 mmol, 0.216 g) and hydrazine hydrate (40% aqueous solution) (1 mmol, 0.08 g) in 2 mL of EtOH was stirred at 25 ˚C for 12 h. Then the solvent was evaporated *in vacuo* and the residue was washed with hot hexane (3x10 mL) and dried at 100 ˚C under vacuum to give compound **4a**. Yield 0.138 g (62%), yellow powder, mp = 138-139˚C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): 1.11 – 1.26 (m, 24H), 2.52 – 2.84 (m, 4H), 5.89 (s, 1H), 7.23 – 7.40 (m, 4H), 7.41 – 7.63 (m, 4H), 8.80 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 22.9, 23.0, 24.0, 24.8, 28.3, 28.5, 103.4, 123.6, 123.7, 124.4, 127.2, 129.6, 129.8, 130.1, 131.0, 145.6, 146.0, 152.0. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{28}H_{39}N_4O^+$ 447.3118, found *m/z* 447.3120.



1,3-Bis(2,6-diisopropylphenyl)-5-((2-phenylhydrazinylidene)methyl)-1*H*-imidazol-3-ium-4-olate (4b).
A mixture of compound **2a** (0.5 mmol, 0.216 g) and phenylhydrazine (1 mmol, 0.108 g) in 2 mL of EtOH was stirred at 25 ˚C for 12 h. Then solvent was evaporated *in vacuo* and the residue was washed with hot hexane (3x10 mL) and dried at 100 ˚C under vacuum to give compound **4b**. Yield 0.17 g (65%), yellow powder, mp = 178-179 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.09 – 1.27 (m, 24H), 2.60 – 2.83 (m, 4H), 6.11 (d, *J* = 7.9 Hz, 2H), 6.46 (t, *J* = 7.3 Hz, 1H), 6.88 (t, *J* = 7.7 Hz, 2H), 7.32-7.40 (m, 4H), 7.50-7.58 (m, 2H), 7.66 (s, 1H), 8.61 (s, 1H), 9.38 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 22.7, 22.9, 24.0, 24.4, 28.4, 28.4, 40.4, 101.7, 110.9, 116.6, 123.6, 123.7, 126.3, 127.7, 128.4, 129.6, 129.7, 129.9, 133.3, 144.9, 146.1, 154.5. ESI-MS(TOF) *m/z*: [M+H]$^+$ Calcd. for $C_{34}H_{43}N_4O^+$ 523.3431, found *m/z* 523.3433.



5-(1*H*-Benzimidazol-2-yl)-1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-4-olate (5). A mixture of compound **2a** (0.5 mmol, 0.216 g), *o*-phenylenediamine (0.6 mmol, 0.065 g) and $Na_2S_2O_5$ (0.6 mmol, 0.114 g) in 3 mL of EtOH was stirred at 80 ˚C for 12 h. Then 5 ml of Et_2O was added to the mixture and resulting precipitate was filtered off, washed with Et_2O (2x5 mL) and dried at 100 ˚C under vacuum to give compound **5**. Yield 0.203 g (78%), white powder, mp = 278-279 ˚C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): 1.02 – 1.28 (m, 24H), 2.62 – 2.91 (m, 4H), 6.83 – 7.21 (m, 4H), 7.32 – 7.46 (m, 4H), 7.46 – 7.62 (m, 2H), 8.81 (s, 1H), 11.62 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 22.8, 23.0, 23.9, 24.3, 28.6, 97.8, 104.3, 120.4, 123.6, 123.8, 127.9, 129.2, 130.2, 132.7, 145.0, 145.3, 146.1, 154.8. ESI-MS(TOF) *m/z*: [M+H]$^+$ Calcd. for $C_{34}H_{41}N_4O^+$ 521.3275, found *m/z* 521.3270.



5-(2,2-Dicyanovinyl)-1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-4-olate (6). A mixture of compound **2a** (0.5 mmol, 0.216 g), malononitrile (1 mmol, 0.066 g) and 0.1 mL of Et_3N in 2 mL of EtOH was stirred at 80 ˚C for 12 h. Then the mixture was cooled to room temperature and 5 ml of Et_2O was added and the resulting precipitate was filtered off, washed with Et_2O (2x5 mL) and dried at 100 ˚C under vacuum to give compound **6**. Yield 0.19 g (79%), yellow powder, mp = 208-209 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.06 – 1.31 (m, 24H), 2.49 – 2.74 (m, 4H), 6.48 (s, 1H), 7.28 – 7.69 (m, 6H), 9.63 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 22.9, 23.0, 24.0, 24.7, 28.7, 28.8, 107.9, 118.4, 124.2, 125.1, 127.6, 131.0, 132.1, 137.1, 138.6, 145.9, 145.9, 154.4, 155.3. ESI-MS(TOF) *m/z*: [M+H]$^+$ Calcd. for $C_{31}H_{36}N_4O^+$ 480.2960, found *m/z* 480.2962.

S3. X-ray crystallographic data and refinement details.

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[S3] The structure was solved by direct methods using SHELXT [S4] and refined on F^2 using SHELXL-2018 [S5] in the OLEX2 program. [S6] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were found from the electron density-difference map but placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups.

Table S1. Crystal data and structure refinement for **2a**.

Identification code	**2a**
Empirical formula	$C_{28}H_{36}N_2O_2$
Formula weight	432.59
Temperature	99.9(5) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 16.96612(4) Å
b = 17.76330(5) Å	β= 91.2521(2)°.
c = 17.02899(5) Å	γ = 90°.
Volume	5130.87(2) Å^3
Z	8
Density (calculated)	1.120 g/cm^3
Absorption coefficient	0.545 mm^{-1}
F(000)	1872
Crystal size	0.22 x 0.21 x 0.08 mm^3
Theta range for data collection	3.596 to 79.803°.
Index ranges	-21<=h<=21, -22<=k<=22, -21<=l<=21
Reflections collected	131658
Independent reflections	11099 [R(int) = 0.0335]
Observed reflections	10661
Completeness to theta = 67.684°	100.0 %
Absorption correction	Analytical
Max. and min. transmission	0.963 and 0.900
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11099 / 0 / 594
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.1021
R indices (all data)	R1 = 0.0403, wR2 = 0.1030
Extinction coefficient	0.00034(4)
Largest diff. peak and hole	0.312 and -0.224 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9553(1)	2256(1)	7155(1)	24(1)
O(2)	7617(1)	3082(1)	8556(1)	37(1)
N(1)	7613(1)	2870(1)	6817(1)	16(1)
N(2)	8587(1)	2411(1)	6160(1)	16(1)
C(1)	7847(1)	2679(1)	6111(1)	16(1)
C(2)	8873(1)	2440(1)	6959(1)	17(1)
C(3)	8222(1)	2723(1)	7373(1)	18(1)
C(4)	8179(1)	2830(1)	8198(1)	24(1)
C(5)	6864(1)	3231(1)	6957(1)	17(1)
C(6)	6198(1)	2779(1)	7038(1)	19(1)
C(7)	5477(1)	3145(1)	7134(1)	24(1)
C(8)	5443(1)	3923(1)	7173(1)	25(1)
C(9)	6119(1)	4355(1)	7110(1)	24(1)
C(10)	6848(1)	4017(1)	6995(1)	20(1)
C(11)	6240(1)	1924(1)	7039(1)	22(1)
C(12)	5859(1)	1596(1)	6299(1)	43(1)
C(13)	5862(1)	1608(1)	7779(1)	40(1)
C(14)	7583(1)	4502(1)	6933(1)	24(1)
C(15)	7529(1)	5028(1)	6222(1)	39(1)
C(16)	7722(1)	4944(1)	7695(1)	37(1)
C(17)	9052(1)	2177(1)	5506(1)	19(1)
C(18)	9010(1)	1429(1)	5260(1)	24(1)
C(19)	9467(1)	1227(1)	4620(1)	32(1)
C(20)	9958(1)	1742(1)	4269(1)	35(1)
C(21)	9995(1)	2476(1)	4539(1)	32(1)
C(22)	9534(1)	2715(1)	5160(1)	24(1)
C(23)	8486(1)	858(1)	5656(1)	28(1)
C(24)	7739(1)	721(1)	5156(1)	52(1)
C(25)	8921(1)	123(1)	5831(1)	42(1)
C(26)	9521(1)	3533(1)	5413(1)	28(1)
C(27)	8973(1)	3980(1)	4860(1)	41(1)
C(28)	10338(1)	3887(1)	5459(1)	46(1)
O(3)	12143(1)	2444(1)	9490(1)	27(1)
O(4)	13656(1)	2472(1)	7464(1)	40(1)
N(3)	11920(1)	2747(1)	7468(1)	18(1)
N(4)	11186(1)	2657(1)	8498(1)	17(1)
C(29)	11189(1)	2760(1)	7717(1)	17(1)
C(30)	11982(1)	2558(1)	8789(1)	20(1)
C(31)	12441(1)	2615(1)	8109(1)	21(1)
C(32)	13268(1)	2488(1)	8062(1)	28(1)
C(33)	12113(1)	2883(1)	6656(1)	20(1)
C(34)	12058(1)	2278(1)	6135(1)	22(1)
C(35)	12189(1)	2430(1)	5344(1)	27(1)
C(36)	12390(1)	3147(1)	5101(1)	31(1)
C(37)	12462(1)	3729(1)	5638(1)	29(1)
C(38)	12319(1)	3614(1)	6434(1)	23(1)
C(39)	11897(1)	1482(1)	6412(1)	24(1)

C(40)	12576(1)	966(1)	6182(1)	38(1)
C(41)	11100(1)	1195(1)	6104(1)	38(1)
C(42)	12408(1)	4257(1)	7017(1)	26(1)
C(43)	13279(1)	4454(1)	7137(1)	50(1)
C(44)	11928(1)	4948(1)	6774(1)	44(1)
C(45)	10512(1)	2742(1)	8990(1)	18(1)
C(46)	10238(1)	2110(1)	9390(1)	21(1)
C(47)	9611(1)	2218(1)	9895(1)	26(1)
C(48)	9273(1)	2922(1)	9985(1)	28(1)
C(49)	9548(1)	3532(1)	9568(1)	26(1)
C(50)	10180(1)	3461(1)	9062(1)	21(1)
C(51)	10568(1)	1330(1)	9245(1)	24(1)
C(52)	10773(1)	916(1)	10009(1)	42(1)
C(53)	9979(1)	878(1)	8740(1)	36(1)
C(54)	10460(1)	4133(1)	8587(1)	26(1)
C(55)	10588(1)	4837(1)	9088(1)	36(1)
C(56)	9875(1)	4294(1)	7907(1)	36(1)

Table S3. Bond lengths [Å] and angles [°] for **2a**.

O(1)-C(2)	1.2378(11)
O(2)-C(4)	1.2257(13)
N(1)-C(1)	1.3194(12)
N(1)-C(3)	1.4097(11)
N(1)-C(5)	1.4487(11)
N(2)-C(1)	1.3433(11)
N(2)-C(2)	1.4352(11)
N(2)-C(17)	1.4389(11)
C(1)-H(1)	0.9500
C(2)-C(3)	1.4152(13)
C(3)-C(4)	1.4208(13)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3969(13)
C(5)-C(10)	1.3974(13)
C(6)-C(7)	1.3983(13)
C(6)-C(11)	1.5201(13)
C(7)-H(7)	0.9500
C(7)-C(8)	1.3849(15)
C(8)-H(8)	0.9500
C(8)-C(9)	1.3856(14)
C(9)-H(9)	0.9500
C(9)-C(10)	1.3928(13)
C(10)-C(14)	1.5209(13)
C(11)-H(11)	1.0000
C(11)-C(12)	1.5211(15)
C(11)-C(13)	1.5320(14)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14)	1.0000
C(14)-C(15)	1.5302(15)
C(14)-C(16)	1.5302(15)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.3950(14)
C(17)-C(22)	1.3980(14)
C(18)-C(19)	1.3981(14)
C(18)-C(23)	1.5165(15)
C(19)-H(19)	0.9500
C(19)-C(20)	1.3814(18)
C(20)-H(20)	0.9500
C(20)-C(21)	1.3822(19)
C(21)-H(21)	0.9500
C(21)-C(22)	1.3943(15)

C(22)-C(26)	1.5156(15)
C(23)-H(23)	1.0000
C(23)-C(24)	1.5297(17)
C(23)-C(25)	1.5263(16)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26)	1.0000
C(26)-C(27)	1.5322(16)
C(26)-C(28)	1.5231(16)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
O(3)-C(30)	1.2351(12)
O(4)-C(32)	1.2246(14)
N(3)-C(29)	1.3187(12)
N(3)-C(31)	1.4099(11)
N(3)-C(33)	1.4482(11)
N(4)-C(29)	1.3420(11)
N(4)-C(30)	1.4392(11)
N(4)-C(45)	1.4400(11)
C(29)-H(29)	0.9500
C(30)-C(31)	1.4134(13)
C(31)-C(32)	1.4244(13)
C(32)-H(32)	0.9500
C(33)-C(34)	1.3958(14)
C(33)-C(38)	1.3987(14)
C(34)-C(35)	1.3970(14)
C(34)-C(39)	1.5176(14)
C(35)-H(35)	0.9500
C(35)-C(36)	1.3844(17)
C(36)-H(36)	0.9500
C(36)-C(37)	1.3846(17)
C(37)-H(37)	0.9500
C(37)-C(38)	1.3979(14)
C(38)-C(42)	1.5201(15)
C(39)-H(39)	1.0000
C(39)-C(40)	1.5290(14)
C(39)-C(41)	1.5273(15)
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42)	1.0000
C(42)-C(43)	1.5283(15)

C(42)-C(44)	1.5238(16)
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800
C(45)-C(46)	1.3986(13)
C(45)-C(50)	1.4021(13)
C(46)-C(47)	1.3946(14)
C(46)-C(51)	1.5171(14)
C(47)-H(47)	0.9500
C(47)-C(48)	1.3858(16)
C(48)-H(48)	0.9500
C(48)-C(49)	1.3839(16)
C(49)-H(49)	0.9500
C(49)-C(50)	1.3949(14)
C(50)-C(54)	1.5235(14)
C(51)-H(51)	1.0000
C(51)-C(52)	1.5271(15)
C(51)-C(53)	1.5311(15)
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(54)-H(54)	1.0000
C(54)-C(55)	1.5278(15)
C(54)-C(56)	1.5345(16)
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800

C(1)-N(1)-C(3)	109.51(7)
C(1)-N(1)-C(5)	123.17(7)
C(3)-N(1)-C(5)	127.13(7)
C(1)-N(2)-C(2)	109.99(7)
C(1)-N(2)-C(17)	125.49(7)
C(2)-N(2)-C(17)	124.38(7)
N(1)-C(1)-N(2)	109.49(8)
N(1)-C(1)-H(1)	125.3
N(2)-C(1)-H(1)	125.3
O(1)-C(2)-N(2)	122.65(8)
O(1)-C(2)-C(3)	133.78(9)
C(3)-C(2)-N(2)	103.55(7)
N(1)-C(3)-C(2)	107.41(8)
N(1)-C(3)-C(4)	125.88(8)
C(2)-C(3)-C(4)	126.70(8)
O(2)-C(4)-C(3)	126.70(9)

O(2)-C(4)-H(4)	116.7
C(3)-C(4)-H(4)	116.7
C(6)-C(5)-N(1)	118.44(8)
C(6)-C(5)-C(10)	123.65(8)
C(10)-C(5)-N(1)	117.91(8)
C(5)-C(6)-C(7)	117.07(9)
C(5)-C(6)-C(11)	122.48(8)
C(7)-C(6)-C(11)	120.44(9)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-C(6)	120.50(9)
C(8)-C(7)-H(7)	119.8
C(7)-C(8)-H(8)	119.5
C(7)-C(8)-C(9)	120.92(9)
C(9)-C(8)-H(8)	119.5
C(8)-C(9)-H(9)	119.6
C(8)-C(9)-C(10)	120.74(9)
C(10)-C(9)-H(9)	119.6
C(5)-C(10)-C(14)	123.09(8)
C(9)-C(10)-C(5)	117.08(9)
C(9)-C(10)-C(14)	119.81(9)
C(6)-C(11)-H(11)	108.0
C(6)-C(11)-C(12)	111.23(8)
C(6)-C(11)-C(13)	110.25(8)
C(12)-C(11)-H(11)	108.0
C(12)-C(11)-C(13)	111.32(10)
C(13)-C(11)-H(11)	108.0
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14)	108.0
C(10)-C(14)-C(15)	111.45(8)
C(10)-C(14)-C(16)	110.09(9)
C(15)-C(14)-H(14)	108.0
C(16)-C(14)-H(14)	108.0
C(16)-C(14)-C(15)	111.28(10)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-N(2)	118.85(9)
C(18)-C(17)-C(22)	123.40(9)
C(22)-C(17)-N(2)	117.74(9)
C(17)-C(18)-C(19)	116.98(10)
C(17)-C(18)-C(23)	122.00(9)
C(19)-C(18)-C(23)	121.02(10)
C(18)-C(19)-H(19)	119.4
C(20)-C(19)-C(18)	121.12(11)
C(20)-C(19)-H(19)	119.4
C(19)-C(20)-H(20)	119.9
C(19)-C(20)-C(21)	120.25(10)
C(21)-C(20)-H(20)	119.9
C(20)-C(21)-H(21)	119.4
C(20)-C(21)-C(22)	121.18(11)
C(22)-C(21)-H(21)	119.4
C(17)-C(22)-C(26)	121.45(9)
C(21)-C(22)-C(17)	117.03(10)
C(21)-C(22)-C(26)	121.41(10)
C(18)-C(23)-H(23)	107.7
C(18)-C(23)-C(24)	110.28(10)
C(18)-C(23)-C(25)	111.89(9)
C(24)-C(23)-H(23)	107.7
C(25)-C(23)-H(23)	107.7
C(25)-C(23)-C(24)	111.33(10)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(22)-C(26)-H(26)	107.7
C(22)-C(26)-C(27)	109.55(9)
C(22)-C(26)-C(28)	112.99(10)
C(27)-C(26)-H(26)	107.7
C(28)-C(26)-H(26)	107.7
C(28)-C(26)-C(27)	110.87(10)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5

C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(29)-N(3)-C(31)	109.42(8)
C(29)-N(3)-C(33)	122.57(8)
C(31)-N(3)-C(33)	127.97(8)
C(29)-N(4)-C(30)	109.49(7)
C(29)-N(4)-C(45)	125.63(8)
C(30)-N(4)-C(45)	124.27(7)
N(3)-C(29)-N(4)	109.91(8)
N(3)-C(29)-H(29)	125.0
N(4)-C(29)-H(29)	125.0
O(3)-C(30)-N(4)	122.57(9)
O(3)-C(30)-C(31)	133.58(9)
C(31)-C(30)-N(4)	103.84(8)
N(3)-C(31)-C(30)	107.33(8)
N(3)-C(31)-C(32)	125.82(9)
C(30)-C(31)-C(32)	126.56(9)
O(4)-C(32)-C(31)	126.71(10)
O(4)-C(32)-H(32)	116.6
C(31)-C(32)-H(32)	116.6
C(34)-C(33)-N(3)	117.71(8)
C(34)-C(33)-C(38)	123.78(9)
C(38)-C(33)-N(3)	118.48(9)
C(33)-C(34)-C(35)	117.07(9)
C(33)-C(34)-C(39)	122.03(9)
C(35)-C(34)-C(39)	120.86(9)
C(34)-C(35)-H(35)	119.6
C(36)-C(35)-C(34)	120.75(10)
C(36)-C(35)-H(35)	119.6
C(35)-C(36)-H(36)	119.7
C(35)-C(36)-C(37)	120.63(9)
C(37)-C(36)-H(36)	119.7
C(36)-C(37)-H(37)	119.5
C(36)-C(37)-C(38)	121.03(10)
C(38)-C(37)-H(37)	119.5
C(33)-C(38)-C(42)	122.89(9)
C(37)-C(38)-C(33)	116.70(10)
C(37)-C(38)-C(42)	120.40(9)
C(34)-C(39)-H(39)	107.7
C(34)-C(39)-C(40)	109.73(9)
C(34)-C(39)-C(41)	111.58(9)
C(40)-C(39)-H(39)	107.7
C(41)-C(39)-H(39)	107.7
C(41)-C(39)-C(40)	112.32(10)
C(39)-C(40)-H(40A)	109.5
C(39)-C(40)-H(40B)	109.5
C(39)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(39)-C(41)-H(41A)	109.5

C(39)-C(41)-H(41B)	109.5
C(39)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(38)-C(42)-H(42)	107.6
C(38)-C(42)-C(43)	109.96(9)
C(38)-C(42)-C(44)	112.54(9)
C(43)-C(42)-H(42)	107.6
C(44)-C(42)-H(42)	107.6
C(44)-C(42)-C(43)	111.22(11)
C(42)-C(43)-H(43A)	109.5
C(42)-C(43)-H(43B)	109.5
C(42)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(42)-C(44)-H(44A)	109.5
C(42)-C(44)-H(44B)	109.5
C(42)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(46)-C(45)-N(4)	118.41(8)
C(46)-C(45)-C(50)	123.32(9)
C(50)-C(45)-N(4)	118.24(8)
C(45)-C(46)-C(51)	121.76(9)
C(47)-C(46)-C(45)	117.15(9)
C(47)-C(46)-C(51)	120.96(9)
C(46)-C(47)-H(47)	119.5
C(48)-C(47)-C(46)	121.04(10)
C(48)-C(47)-H(47)	119.5
C(47)-C(48)-H(48)	119.8
C(49)-C(48)-C(47)	120.31(9)
C(49)-C(48)-H(48)	119.8
C(48)-C(49)-H(49)	119.4
C(48)-C(49)-C(50)	121.21(10)
C(50)-C(49)-H(49)	119.4
C(45)-C(50)-C(54)	122.42(9)
C(49)-C(50)-C(45)	116.94(9)
C(49)-C(50)-C(54)	120.58(9)
C(46)-C(51)-H(51)	108.0
C(46)-C(51)-C(52)	112.27(9)
C(46)-C(51)-C(53)	109.38(9)
C(52)-C(51)-H(51)	108.0
C(52)-C(51)-C(53)	111.15(9)
C(53)-C(51)-H(51)	108.0
C(51)-C(52)-H(52A)	109.5
C(51)-C(52)-H(52B)	109.5
C(51)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5

C(51)-C(53)-H(53A)	109.5
C(51)-C(53)-H(53B)	109.5
C(51)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
C(50)-C(54)-H(54)	107.8
C(50)-C(54)-C(55)	112.76(9)
C(50)-C(54)-C(56)	110.09(9)
C(55)-C(54)-H(54)	107.8
C(55)-C(54)-C(56)	110.53(9)
C(56)-C(54)-H(54)	107.8
C(54)-C(55)-H(55A)	109.5
C(54)-C(55)-H(55B)	109.5
C(54)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(54)-C(56)-H(56A)	109.5
C(54)-C(56)-H(56B)	109.5
C(54)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56C)	109.5
H(56B)-C(56)-H(56C)	109.5

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	15(1)	34(1)	22(1)	-1(1)	-4(1)	4(1)
O(2)	32(1)	62(1)	17(1)	-1(1)	4(1)	12(1)
N(1)	13(1)	21(1)	14(1)	0(1)	-1(1)	1(1)
N(2)	14(1)	20(1)	14(1)	-1(1)	-1(1)	2(1)
C(1)	14(1)	19(1)	15(1)	0(1)	-1(1)	0(1)
C(2)	17(1)	20(1)	15(1)	1(1)	-2(1)	-1(1)
C(3)	15(1)	23(1)	15(1)	1(1)	-3(1)	0(1)
C(4)	23(1)	34(1)	16(1)	1(1)	-2(1)	2(1)
C(5)	14(1)	24(1)	14(1)	0(1)	0(1)	3(1)
C(6)	16(1)	26(1)	16(1)	1(1)	0(1)	1(1)
C(7)	15(1)	32(1)	24(1)	3(1)	2(1)	0(1)
C(8)	17(1)	33(1)	27(1)	2(1)	2(1)	7(1)
C(9)	22(1)	24(1)	26(1)	0(1)	0(1)	5(1)
C(10)	17(1)	24(1)	18(1)	0(1)	0(1)	1(1)
C(11)	18(1)	24(1)	22(1)	1(1)	0(1)	-1(1)
C(12)	59(1)	29(1)	41(1)	-3(1)	-23(1)	-4(1)
C(13)	42(1)	35(1)	44(1)	15(1)	19(1)	9(1)
C(14)	19(1)	22(1)	31(1)	0(1)	0(1)	-1(1)
C(15)	33(1)	40(1)	44(1)	13(1)	-1(1)	-9(1)
C(16)	31(1)	36(1)	43(1)	-10(1)	-3(1)	-6(1)
C(17)	15(1)	27(1)	15(1)	-1(1)	0(1)	4(1)
C(18)	20(1)	30(1)	22(1)	-5(1)	-2(1)	5(1)
C(19)	30(1)	41(1)	25(1)	-10(1)	0(1)	12(1)
C(20)	29(1)	58(1)	19(1)	-2(1)	6(1)	16(1)
C(21)	23(1)	50(1)	23(1)	10(1)	5(1)	6(1)
C(22)	18(1)	33(1)	20(1)	5(1)	0(1)	3(1)
C(23)	28(1)	24(1)	34(1)	-7(1)	1(1)	2(1)
C(24)	41(1)	38(1)	74(1)	7(1)	-20(1)	-12(1)
C(25)	47(1)	34(1)	44(1)	2(1)	7(1)	13(1)
C(26)	25(1)	31(1)	29(1)	7(1)	2(1)	-3(1)
C(27)	34(1)	34(1)	55(1)	12(1)	-7(1)	1(1)
C(28)	30(1)	46(1)	61(1)	9(1)	-8(1)	-10(1)
O(3)	24(1)	41(1)	16(1)	4(1)	-5(1)	-2(1)
O(4)	17(1)	70(1)	34(1)	6(1)	4(1)	3(1)
N(3)	14(1)	24(1)	15(1)	1(1)	-1(1)	0(1)
N(4)	15(1)	22(1)	15(1)	0(1)	-1(1)	-1(1)
C(29)	15(1)	20(1)	16(1)	0(1)	-1(1)	0(1)
C(30)	17(1)	24(1)	18(1)	1(1)	-4(1)	-2(1)
C(31)	16(1)	28(1)	18(1)	1(1)	-4(1)	-1(1)
C(32)	16(1)	42(1)	27(1)	5(1)	-4(1)	-1(1)
C(33)	13(1)	29(1)	16(1)	2(1)	0(1)	2(1)
C(34)	16(1)	31(1)	19(1)	0(1)	0(1)	4(1)
C(35)	24(1)	39(1)	19(1)	-2(1)	1(1)	8(1)
C(36)	27(1)	46(1)	18(1)	7(1)	6(1)	7(1)
C(37)	24(1)	36(1)	27(1)	9(1)	4(1)	1(1)
C(38)	16(1)	30(1)	23(1)	3(1)	0(1)	1(1)
C(39)	23(1)	27(1)	22(1)	-3(1)	-2(1)	3(1)

C(40)	35(1)	34(1)	44(1)	1(1)	5(1)	12(1)
C(41)	30(1)	34(1)	51(1)	1(1)	-12(1)	-3(1)
C(42)	23(1)	28(1)	28(1)	3(1)	-2(1)	-3(1)
C(43)	28(1)	55(1)	66(1)	-13(1)	-4(1)	-11(1)
C(44)	52(1)	35(1)	45(1)	-4(1)	-14(1)	10(1)
C(45)	15(1)	24(1)	14(1)	-2(1)	0(1)	-2(1)
C(46)	19(1)	26(1)	17(1)	-1(1)	-2(1)	-4(1)
C(47)	22(1)	36(1)	20(1)	1(1)	2(1)	-9(1)
C(48)	18(1)	44(1)	21(1)	-10(1)	3(1)	-4(1)
C(49)	19(1)	31(1)	27(1)	-10(1)	-1(1)	1(1)
C(50)	18(1)	24(1)	21(1)	-4(1)	-3(1)	-1(1)
C(51)	24(1)	23(1)	26(1)	3(1)	-1(1)	-3(1)
C(52)	54(1)	34(1)	35(1)	8(1)	-13(1)	1(1)
C(53)	39(1)	29(1)	41(1)	-7(1)	-12(1)	-1(1)
C(54)	24(1)	22(1)	33(1)	0(1)	3(1)	1(1)
C(55)	32(1)	26(1)	49(1)	-6(1)	4(1)	-3(1)
C(56)	38(1)	32(1)	38(1)	6(1)	-3(1)	5(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2a.**

	x	y	z	U(eq)
H(1)	7540	2724	5640	20
H(4)	8631	2692	8503	29
H(7)	5007	2859	7174	28
H(8)	4950	4164	7243	30
H(9)	6085	4888	7146	28
H(11)	6809	1776	7051	26
H(12A)	5927	1048	6298	65
H(12B)	6109	1811	5836	65
H(12C)	5295	1717	6284	65
H(13A)	5899	1058	7777	60
H(13B)	5306	1758	7788	60
H(13C)	6138	1808	8246	60
H(14)	8044	4160	6862	29
H(15A)	8019	5317	6187	58
H(15B)	7085	5374	6282	58
H(15C)	7450	4729	5743	58
H(16A)	8222	5218	7669	55
H(16B)	7742	4595	8140	55
H(16C)	7290	5303	7764	55
H(19)	9439	727	4422	39
H(20)	10271	1592	3841	42
H(21)	10340	2822	4298	38
H(23)	8322	1077	6168	34
H(24A)	7402	357	5422	77
H(24B)	7884	521	4643	77
H(24C)	7453	1196	5085	77
H(25A)	8570	-225	6100	62
H(25B)	9385	226	6167	62
H(25C)	9089	-105	5337	62
H(26)	9295	3554	5951	34
H(27A)	8929	4499	5050	62
H(27B)	8450	3746	4844	62
H(27C)	9189	3983	4331	62
H(28A)	10301	4394	5681	69
H(28B)	10553	3917	4930	69
H(28C)	10685	3578	5794	69
H(29)	10733	2832	7392	20
H(32)	13547	2407	8544	34
H(35)	12140	2036	4968	33
H(36)	12480	3240	4561	37
H(37)	12612	4216	5462	34
H(39)	11880	1491	6998	29
H(40A)	12486	459	6391	56
H(40B)	13073	1165	6401	56
H(40C)	12604	943	5609	56
H(41A)	11017	680	6290	58
H(41B)	11091	1201	5529	58

H(41C)	10680	1521	6297	58
H(42)	12206	4079	7532	32
H(43A)	13334	4851	7534	74
H(43B)	13493	4631	6640	74
H(43C)	13569	4005	7314	74
H(44A)	11982	5336	7181	66
H(44B)	11372	4808	6709	66
H(44C)	12123	5144	6277	66
H(47)	9413	1803	10181	31
H(48)	8849	2985	10335	33
H(49)	9303	4009	9626	31
H(51)	11063	1387	8943	29
H(52A)	11018	432	9888	62
H(52B)	10291	830	10303	62
H(52C)	11140	1222	10326	62
H(53A)	10202	382	8625	55
H(53B)	9871	1148	8247	55
H(53C)	9487	816	9024	55
H(54)	10977	3995	8355	32
H(55A)	10808	5239	8765	54
H(55B)	10956	4722	9524	54
H(55C)	10083	5002	9298	54
H(56A)	10074	4710	7589	54
H(56B)	9363	4432	8119	54
H(56C)	9816	3843	7580	54

Table S6. Torsion angles [°] for **2a**.

O(1)-C(2)-C(3)-N(1)	176.47(10)
O(1)-C(2)-C(3)-C(4)	-4.53(18)
N(1)-C(3)-C(4)-O(2)	-1.89(18)
N(1)-C(5)-C(6)-C(7)	-176.94(8)
N(1)-C(5)-C(6)-C(11)	4.26(13)
N(1)-C(5)-C(10)-C(9)	178.41(8)
N(1)-C(5)-C(10)-C(14)	-2.94(13)
N(2)-C(2)-C(3)-N(1)	-2.10(10)
N(2)-C(2)-C(3)-C(4)	176.90(9)
N(2)-C(17)-C(18)-C(19)	179.59(9)
N(2)-C(17)-C(18)-C(23)	0.57(14)
N(2)-C(17)-C(22)-C(21)	178.50(8)
N(2)-C(17)-C(22)-C(26)	-5.15(13)
C(1)-N(1)-C(3)-C(2)	1.47(10)
C(1)-N(1)-C(3)-C(4)	-177.54(9)
C(1)-N(1)-C(5)-C(6)	85.45(11)
C(1)-N(1)-C(5)-C(10)	-93.77(11)
C(1)-N(2)-C(2)-O(1)	-176.66(9)
C(1)-N(2)-C(2)-C(3)	2.11(10)
C(1)-N(2)-C(17)-C(18)	-89.88(11)
C(1)-N(2)-C(17)-C(22)	91.28(11)
C(2)-N(2)-C(1)-N(1)	-1.30(10)
C(2)-N(2)-C(17)-C(18)	94.84(11)
C(2)-N(2)-C(17)-C(22)	-84.00(11)
C(2)-C(3)-C(4)-O(2)	179.29(11)
C(3)-N(1)-C(1)-N(2)	-0.11(10)
C(3)-N(1)-C(5)-C(6)	-100.09(11)
C(3)-N(1)-C(5)-C(10)	80.69(11)
C(5)-N(1)-C(1)-N(2)	175.21(8)
C(5)-N(1)-C(3)-C(2)	-173.61(8)
C(5)-N(1)-C(3)-C(4)	7.38(15)
C(5)-C(6)-C(7)-C(8)	-2.09(14)
C(5)-C(6)-C(11)-C(12)	-110.47(11)
C(5)-C(6)-C(11)-C(13)	125.54(10)
C(5)-C(10)-C(14)-C(15)	118.72(11)
C(5)-C(10)-C(14)-C(16)	-117.29(10)
C(6)-C(5)-C(10)-C(9)	-0.77(14)
C(6)-C(5)-C(10)-C(14)	177.88(9)
C(6)-C(7)-C(8)-C(9)	0.58(15)
C(7)-C(6)-C(11)-C(12)	70.78(12)
C(7)-C(6)-C(11)-C(13)	-53.21(12)
C(7)-C(8)-C(9)-C(10)	0.97(15)
C(8)-C(9)-C(10)-C(5)	-0.87(14)
C(8)-C(9)-C(10)-C(14)	-179.57(9)
C(9)-C(10)-C(14)-C(15)	-62.67(13)
C(9)-C(10)-C(14)-C(16)	61.32(12)
C(10)-C(5)-C(6)-C(7)	2.23(14)
C(10)-C(5)-C(6)-C(11)	-176.56(9)
C(11)-C(6)-C(7)-C(8)	176.73(9)
C(17)-N(2)-C(1)-N(1)	-177.16(8)
C(17)-N(2)-C(2)-O(1)	-0.75(14)

C(17)-N(2)-C(2)-C(3)	178.03(8)
C(17)-C(18)-C(19)-C(20)	2.37(15)
C(17)-C(18)-C(23)-C(24)	102.38(12)
C(17)-C(18)-C(23)-C(25)	-133.13(11)
C(17)-C(22)-C(26)-C(27)	-96.20(12)
C(17)-C(22)-C(26)-C(28)	139.65(11)
C(18)-C(17)-C(22)-C(21)	-0.28(14)
C(18)-C(17)-C(22)-C(26)	176.06(9)
C(18)-C(19)-C(20)-C(21)	-1.19(17)
C(19)-C(18)-C(23)-C(24)	-76.60(13)
C(19)-C(18)-C(23)-C(25)	47.90(14)
C(19)-C(20)-C(21)-C(22)	-0.86(17)
C(20)-C(21)-C(22)-C(17)	1.56(15)
C(20)-C(21)-C(22)-C(26)	-174.79(10)
C(21)-C(22)-C(26)-C(27)	79.98(12)
C(21)-C(22)-C(26)-C(28)	-44.16(14)
C(22)-C(17)-C(18)-C(19)	-1.64(14)
C(22)-C(17)-C(18)-C(23)	179.35(9)
C(23)-C(18)-C(19)-C(20)	-178.61(10)
O(3)-C(30)-C(31)-N(3)	179.63(11)
O(3)-C(30)-C(31)-C(32)	5.52(19)
N(3)-C(31)-C(32)-O(4)	0.02(19)
N(3)-C(33)-C(34)-C(35)	175.38(8)
N(3)-C(33)-C(34)-C(39)	-7.13(13)
N(3)-C(33)-C(38)-C(37)	-176.89(8)
N(3)-C(33)-C(38)-C(42)	4.72(13)
N(4)-C(30)-C(31)-N(3)	0.45(10)
N(4)-C(30)-C(31)-C(32)	-173.65(10)
N(4)-C(45)-C(46)-C(47)	176.70(8)
N(4)-C(45)-C(46)-C(51)	-7.23(13)
N(4)-C(45)-C(50)-C(49)	-177.51(8)
N(4)-C(45)-C(50)-C(54)	5.40(13)
C(29)-N(3)-C(31)-C(30)	-0.92(11)
C(29)-N(3)-C(31)-C(32)	173.25(10)
C(29)-N(3)-C(33)-C(34)	-83.67(11)
C(29)-N(3)-C(33)-C(38)	94.33(11)
C(29)-N(4)-C(30)-O(3)	-179.15(9)
C(29)-N(4)-C(30)-C(31)	0.13(10)
C(29)-N(4)-C(45)-C(46)	116.93(10)
C(29)-N(4)-C(45)-C(50)	-64.96(12)
C(30)-N(4)-C(29)-N(3)	-0.72(10)
C(30)-N(4)-C(45)-C(46)	-72.94(11)
C(30)-N(4)-C(45)-C(50)	105.18(10)
C(30)-C(31)-C(32)-O(4)	173.08(12)
C(31)-N(3)-C(29)-N(4)	1.02(11)
C(31)-N(3)-C(33)-C(34)	99.13(11)
C(31)-N(3)-C(33)-C(38)	-82.86(12)
C(33)-N(3)-C(29)-N(4)	-176.64(8)
C(33)-N(3)-C(31)-C(30)	176.57(9)
C(33)-N(3)-C(31)-C(32)	-9.26(16)
C(33)-C(34)-C(35)-C(36)	2.10(14)
C(33)-C(34)-C(39)-C(40)	-120.45(10)
C(33)-C(34)-C(39)-C(41)	114.40(11)

C(33)-C(38)-C(42)-C(43)	107.42(12)
C(33)-C(38)-C(42)-C(44)	-127.99(11)
C(34)-C(33)-C(38)-C(37)	0.99(14)
C(34)-C(33)-C(38)-C(42)	-177.40(9)
C(34)-C(35)-C(36)-C(37)	-0.27(16)
C(35)-C(34)-C(39)-C(40)	56.95(12)
C(35)-C(34)-C(39)-C(41)	-68.21(12)
C(35)-C(36)-C(37)-C(38)	-1.34(16)
C(36)-C(37)-C(38)-C(33)	0.98(15)
C(36)-C(37)-C(38)-C(42)	179.42(9)
C(37)-C(38)-C(42)-C(43)	-70.92(13)
C(37)-C(38)-C(42)-C(44)	53.67(13)
C(38)-C(33)-C(34)-C(35)	-2.51(14)
C(38)-C(33)-C(34)-C(39)	174.98(9)
C(39)-C(34)-C(35)-C(36)	-175.42(9)
C(45)-N(4)-C(29)-N(3)	170.64(8)
C(45)-N(4)-C(30)-O(3)	9.34(14)
C(45)-N(4)-C(30)-C(31)	-171.37(8)
C(45)-C(46)-C(47)-C(48)	0.76(14)
C(45)-C(46)-C(51)-C(52)	132.30(10)
C(45)-C(46)-C(51)-C(53)	-103.83(11)
C(45)-C(50)-C(54)-C(55)	-133.36(10)
C(45)-C(50)-C(54)-C(56)	102.70(11)
C(46)-C(45)-C(50)-C(49)	0.50(14)
C(46)-C(45)-C(50)-C(54)	-176.59(9)
C(46)-C(47)-C(48)-C(49)	0.56(15)
C(47)-C(46)-C(51)-C(52)	-51.78(13)
C(47)-C(46)-C(51)-C(53)	72.09(12)
C(47)-C(48)-C(49)-C(50)	-1.43(15)
C(48)-C(49)-C(50)-C(45)	0.89(14)
C(48)-C(49)-C(50)-C(54)	178.03(9)
C(49)-C(50)-C(54)-C(55)	49.66(13)
C(49)-C(50)-C(54)-C(56)	-74.28(12)
C(50)-C(45)-C(46)-C(47)	-1.31(14)
C(50)-C(45)-C(46)-C(51)	174.76(9)
C(51)-C(46)-C(47)-C(48)	-175.34(9)

^{1}H and ^{13}C NMR spectra

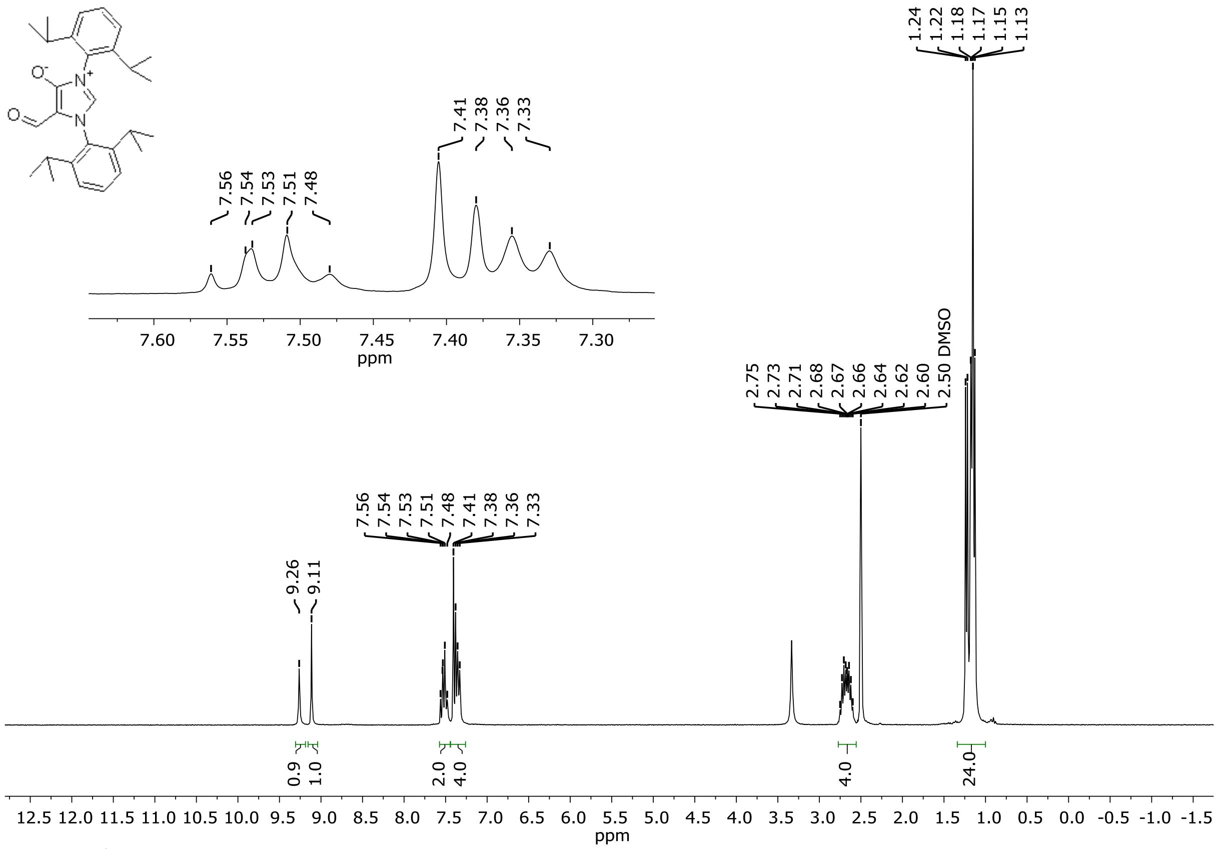


Figure S1. ^{1}H NMR spectrum of compound **2a** (300 MHz, DMSO-*d6*).

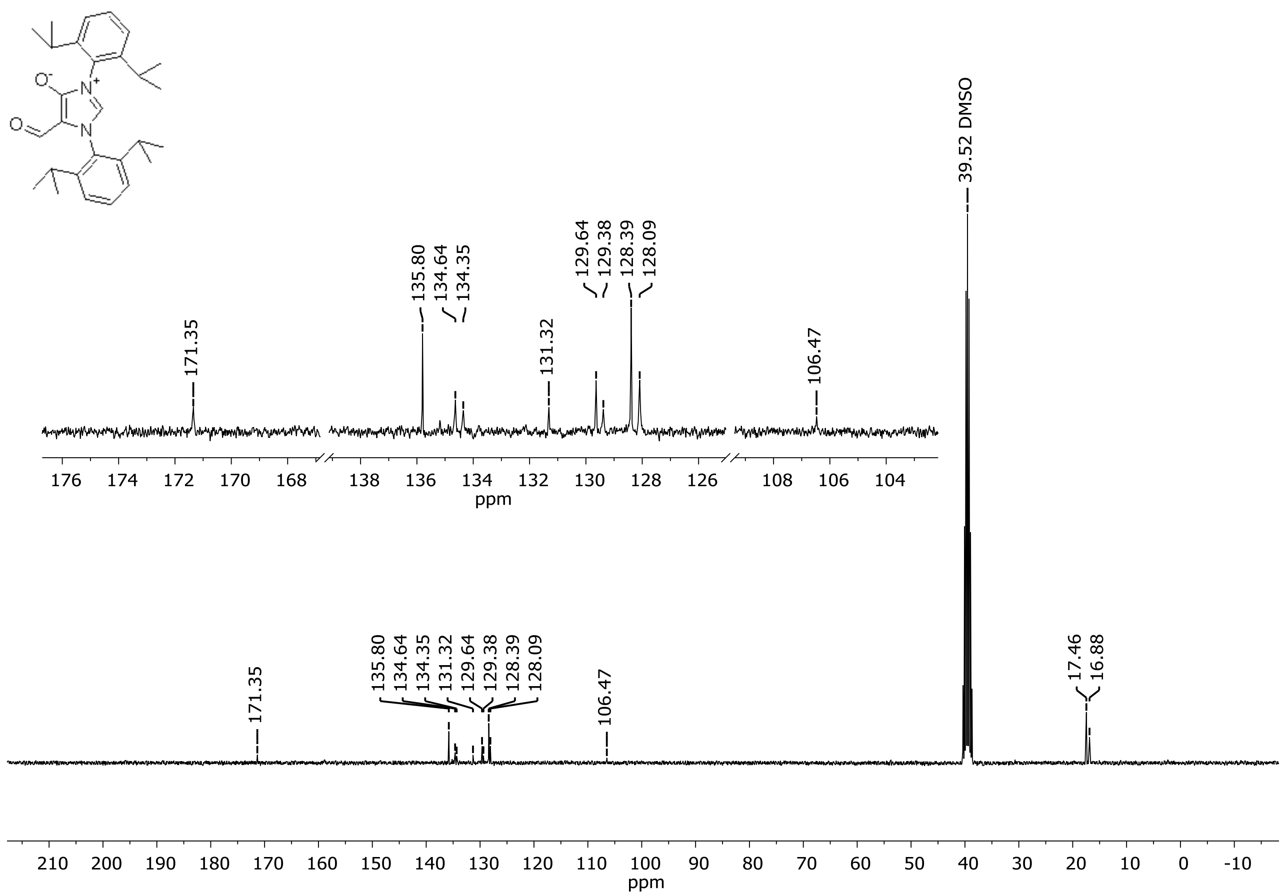


Figure S2. ^{13}C NMR spectrum of compound **2a** (75 MHz, DMSO-*d6*).

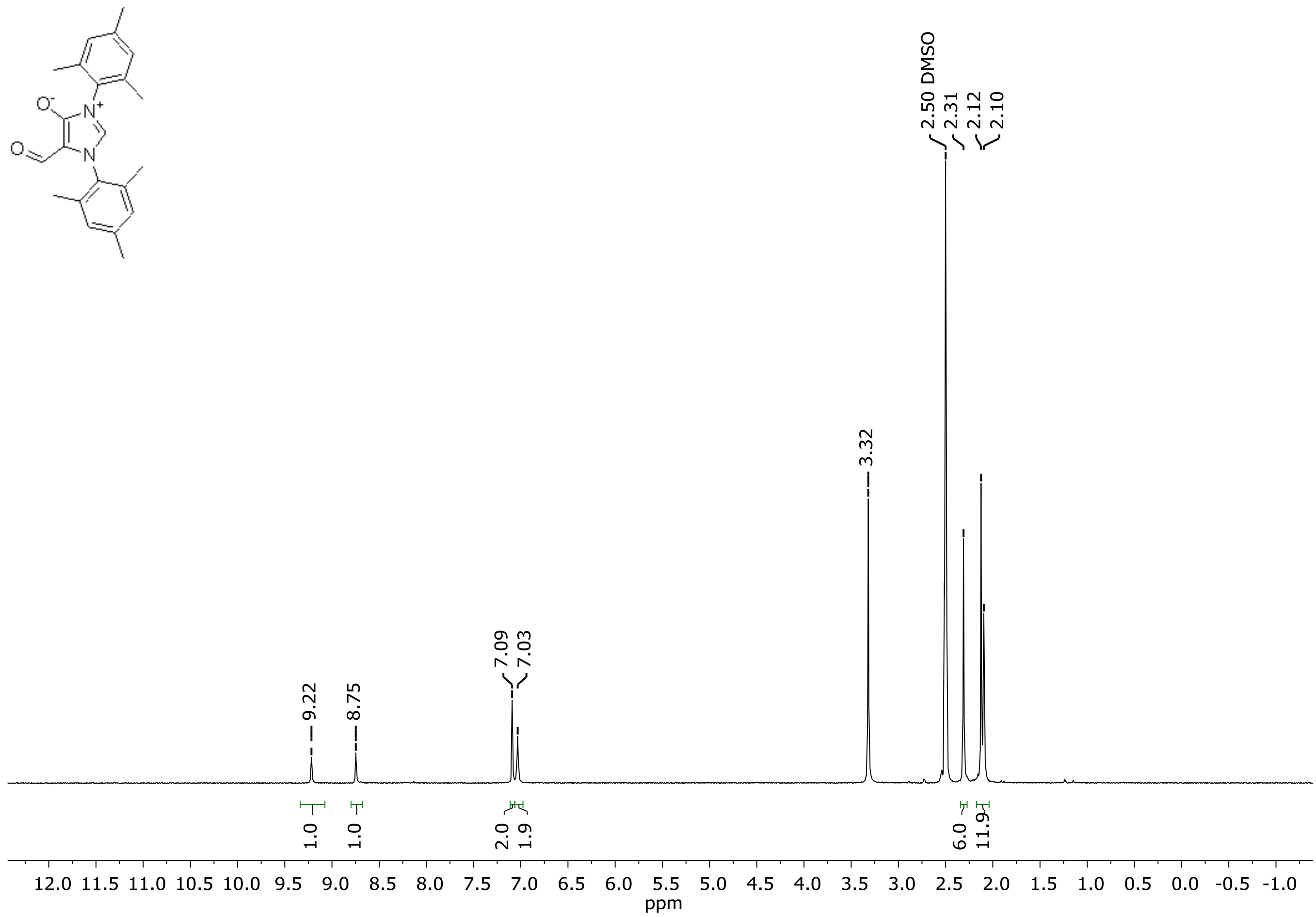


Figure S3. ^{1}H NMR spectrum of compound **2b** (300 MHz, DMSO-*d6*).

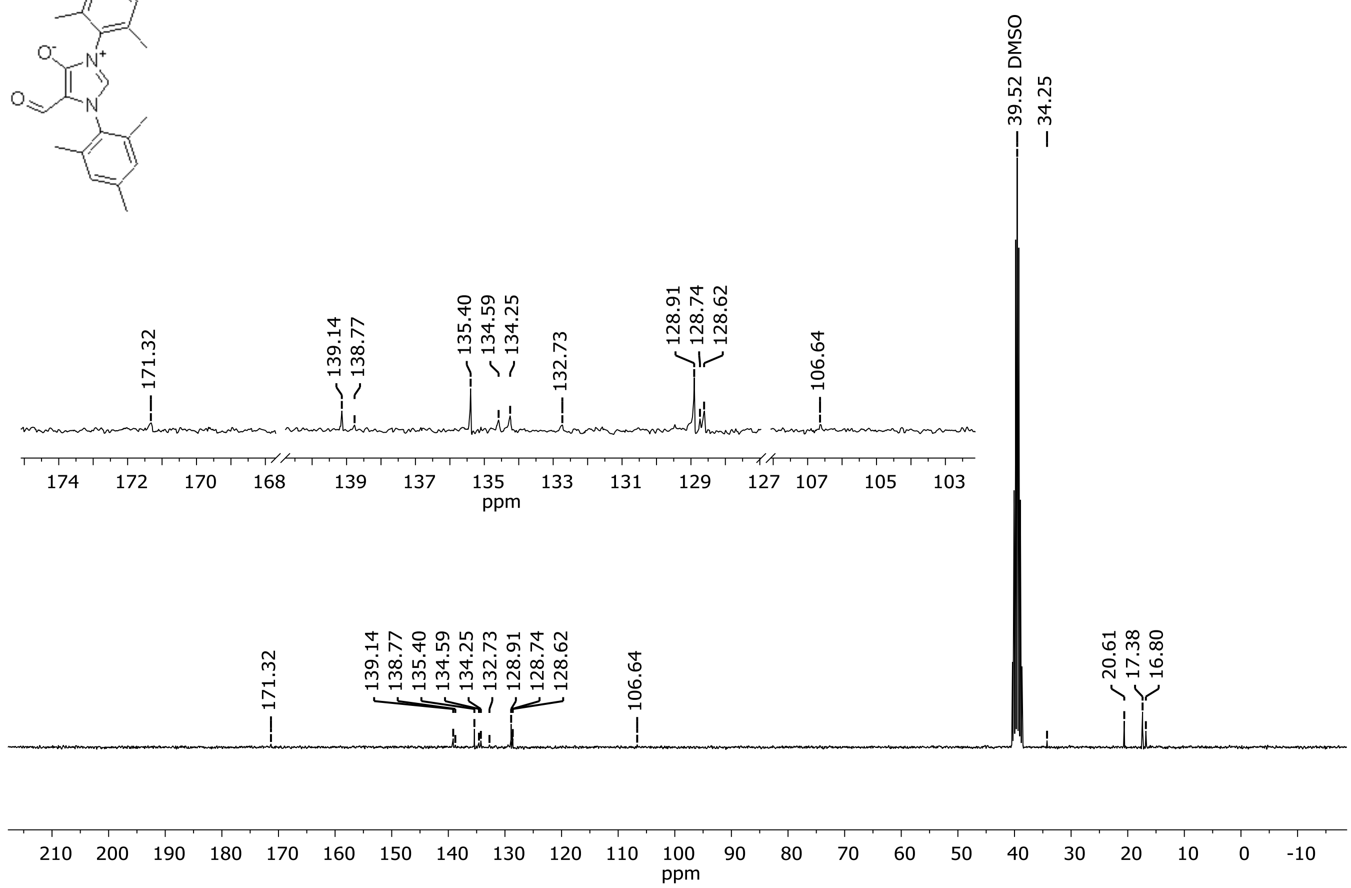


Figure S4. ^{13}C NMR spectrum of compound **2b** (75 MHz, DMSO-*d6*).

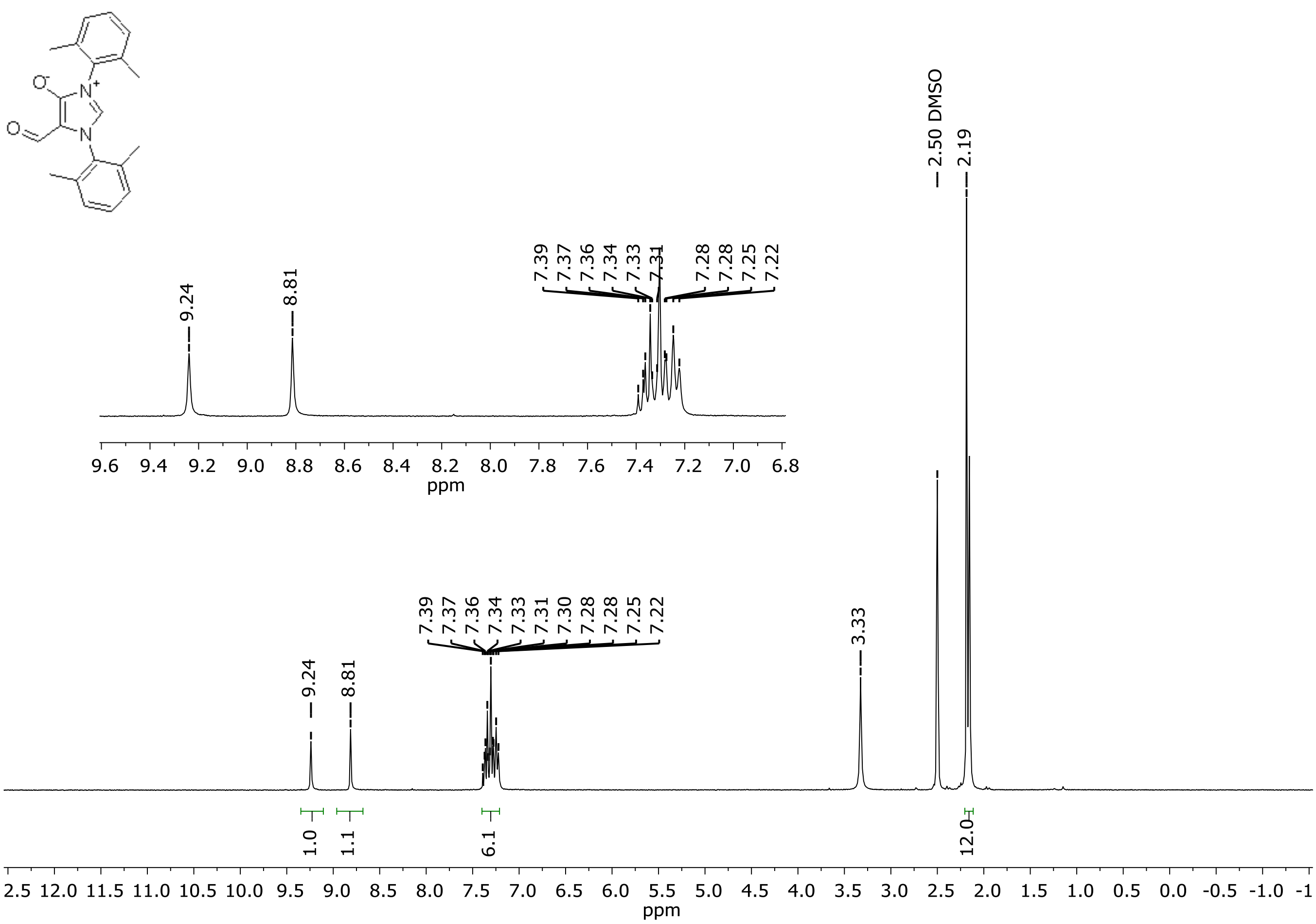


Figure S5. ^{1}H NMR spectrum of compound **2c** (300 MHz, DMSO-*d6*).

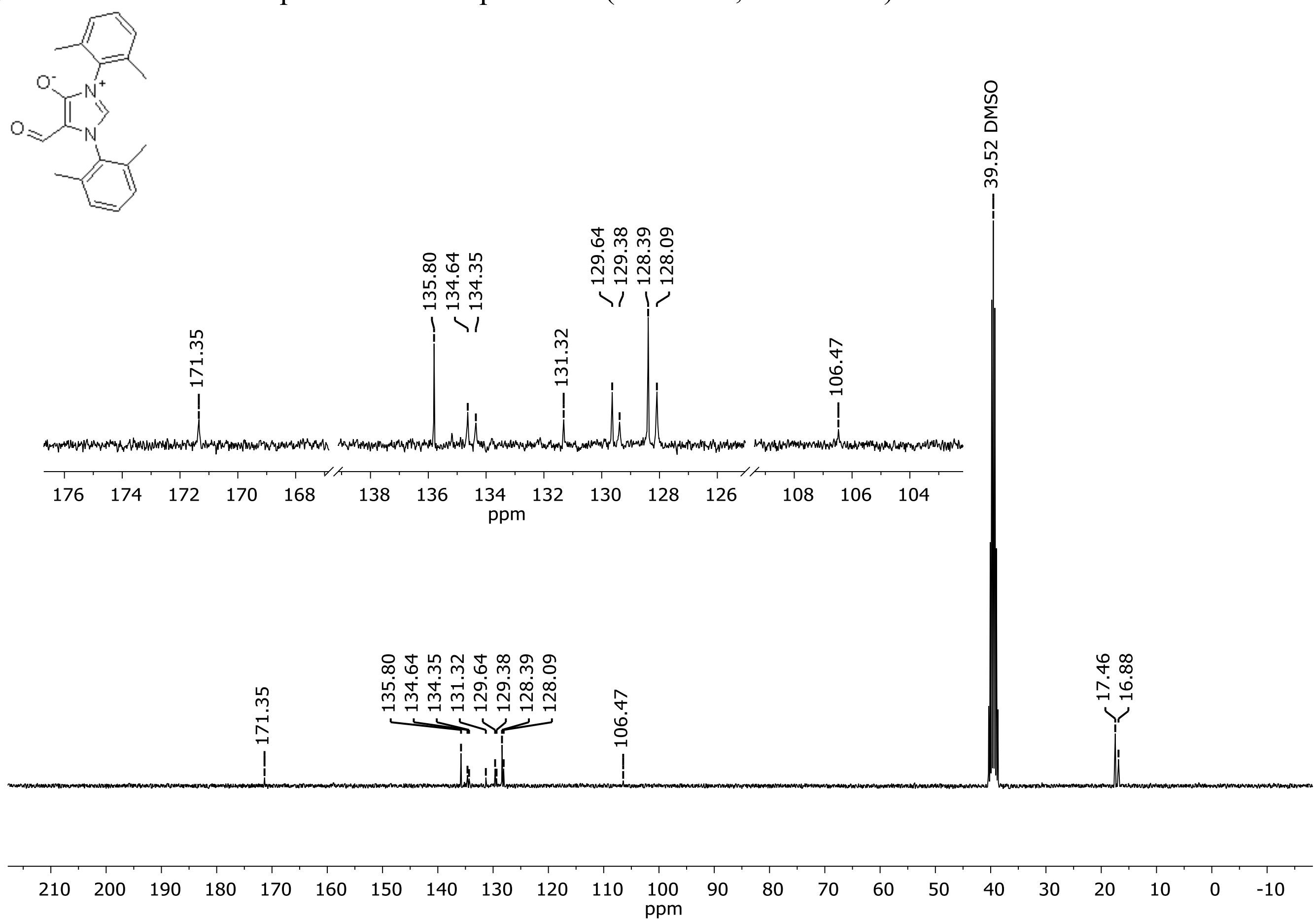


Figure S6. ^{13}C NMR spectrum of compound **2c** (75 MHz, DMSO-*d6*).

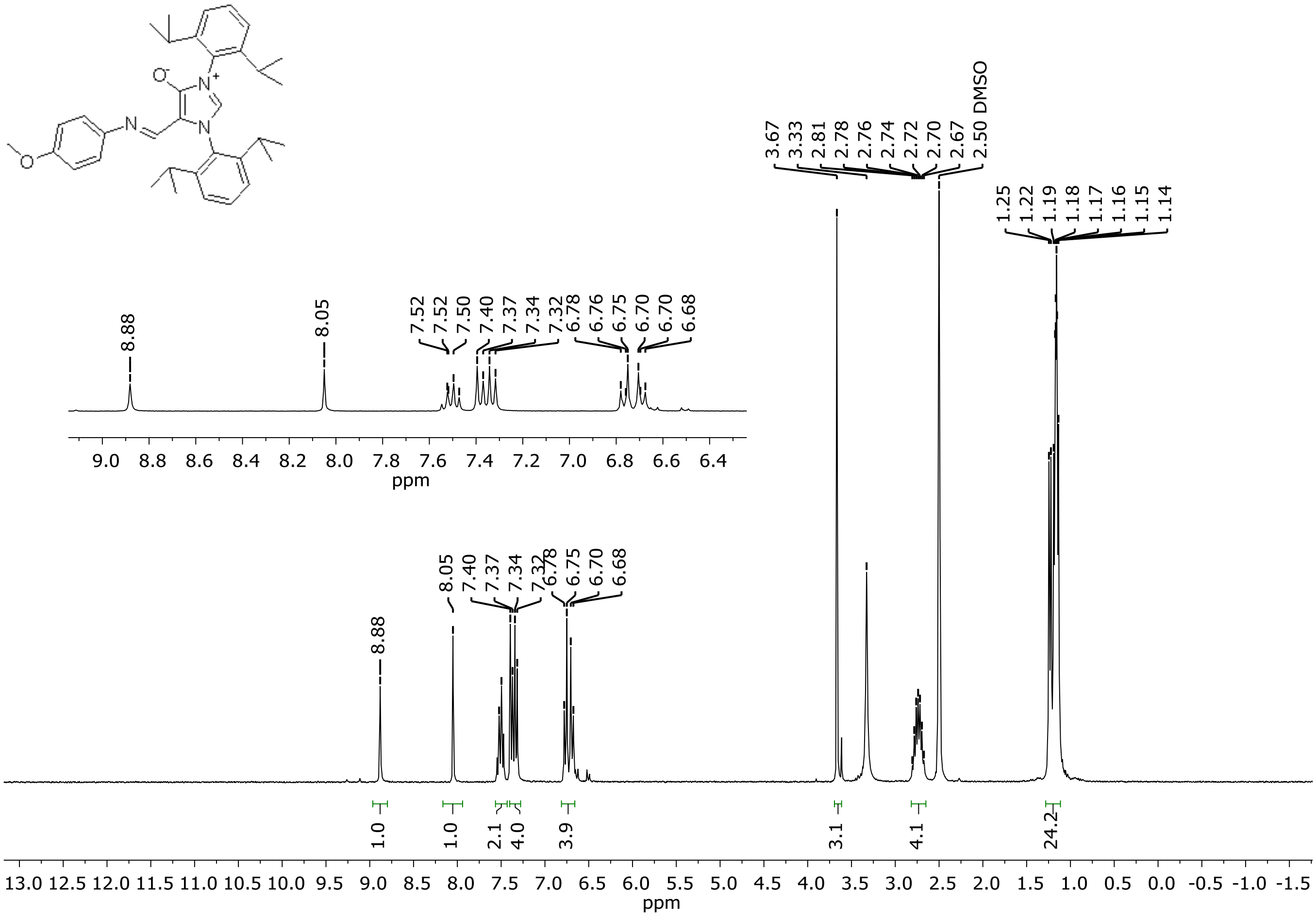


Figure S7. ^{1}H NMR spectrum of compound **3** (300 MHz, DMSO-*d6*).

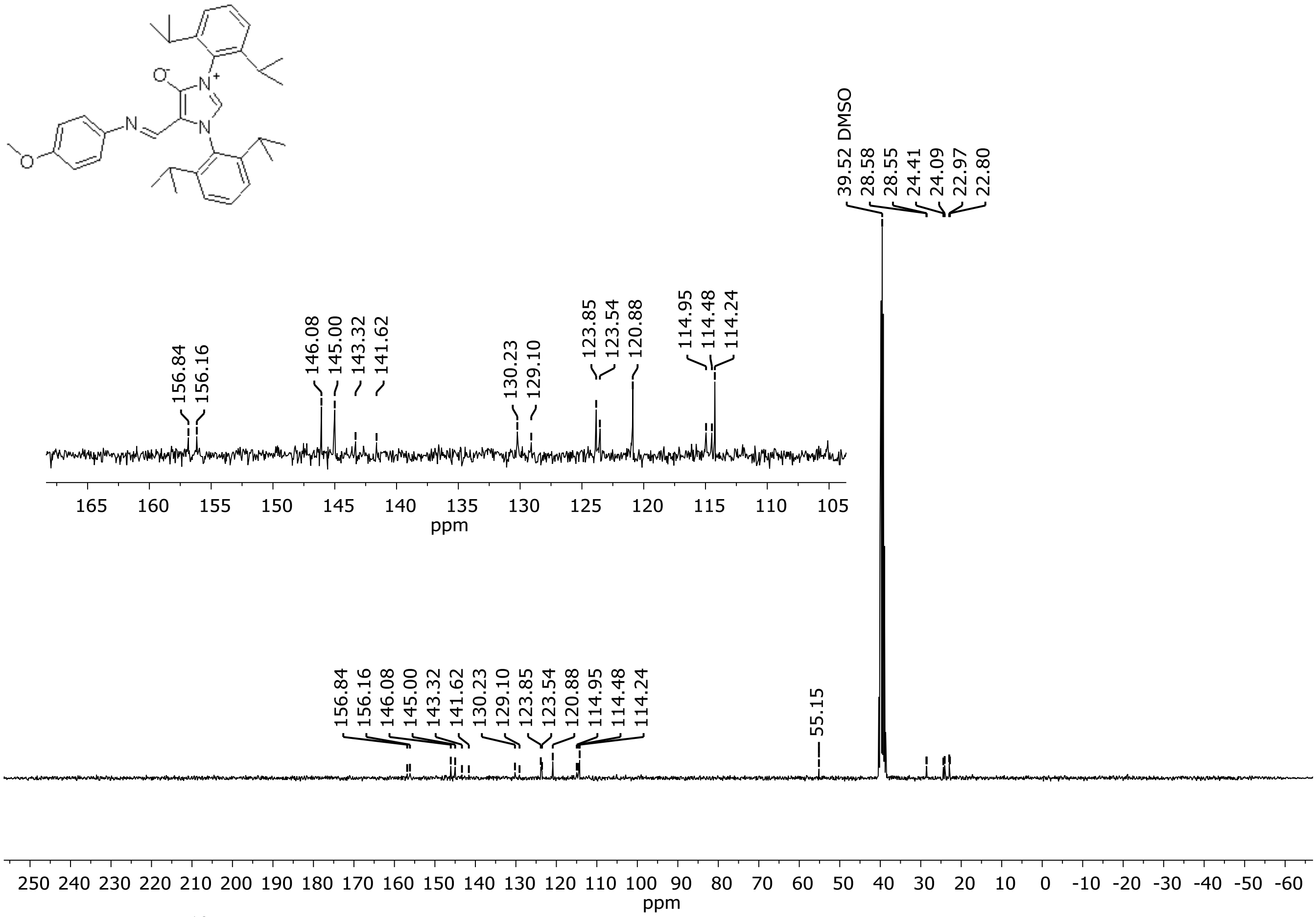


Figure S8. ^{13}C NMR spectrum of compound **3** (75 MHz, DMSO-*d6*).

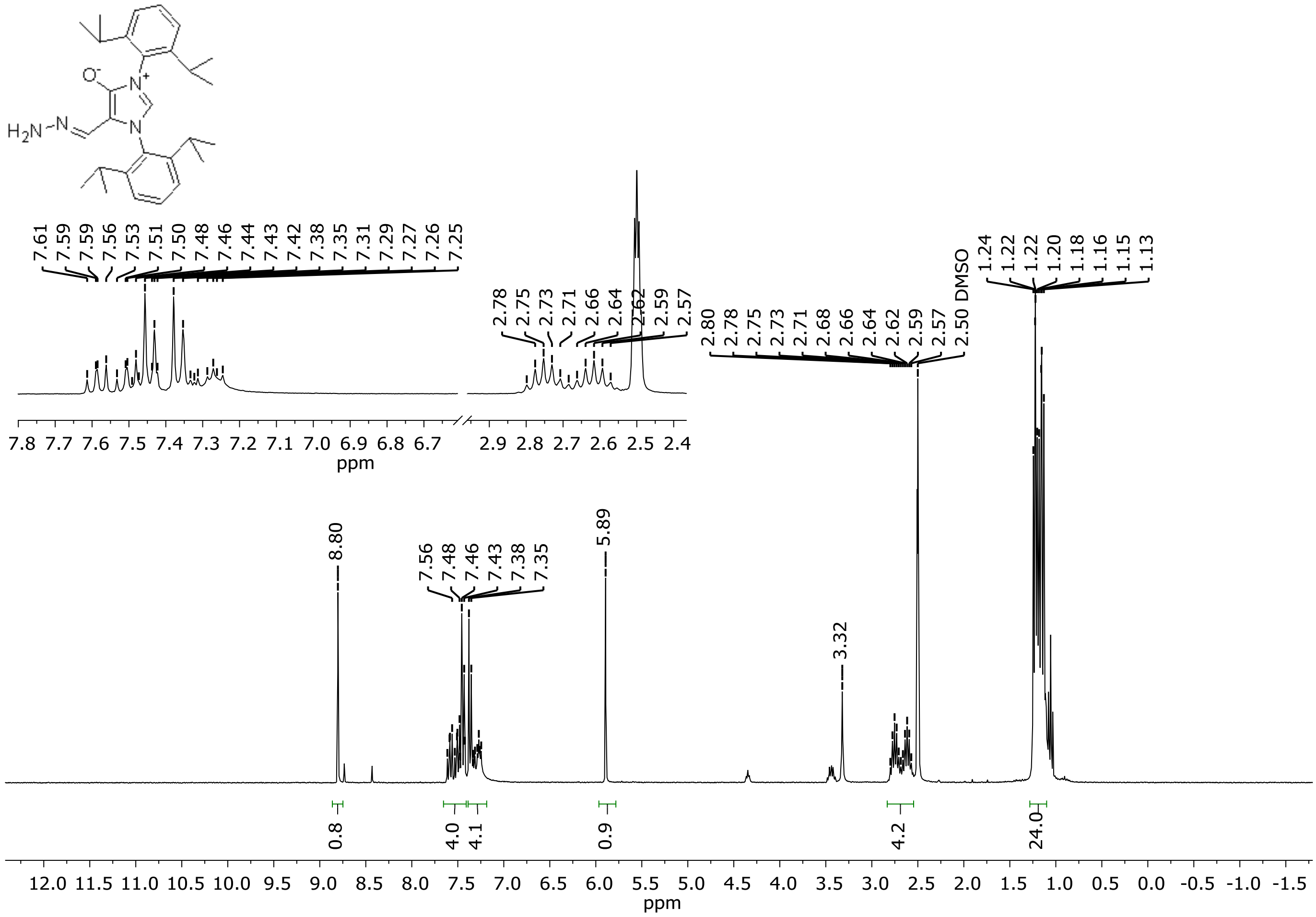


Figure S9. [1]H NMR spectrum of compound **4a** (300 MHz, DMSO-*d6*).

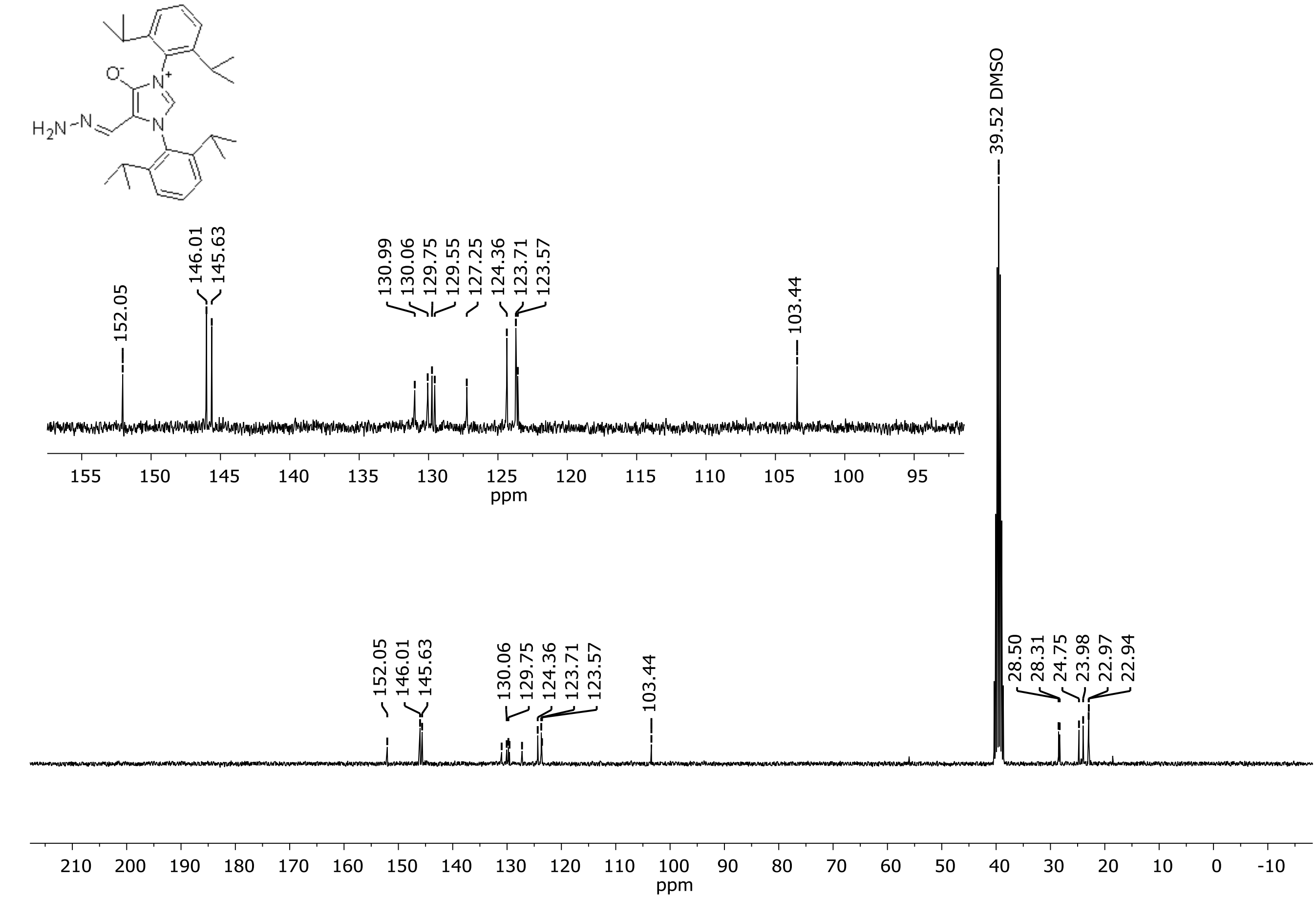


Figure S10. [13]C NMR spectrum of compound **4a** (75 MHz, DMSO-*d6*).

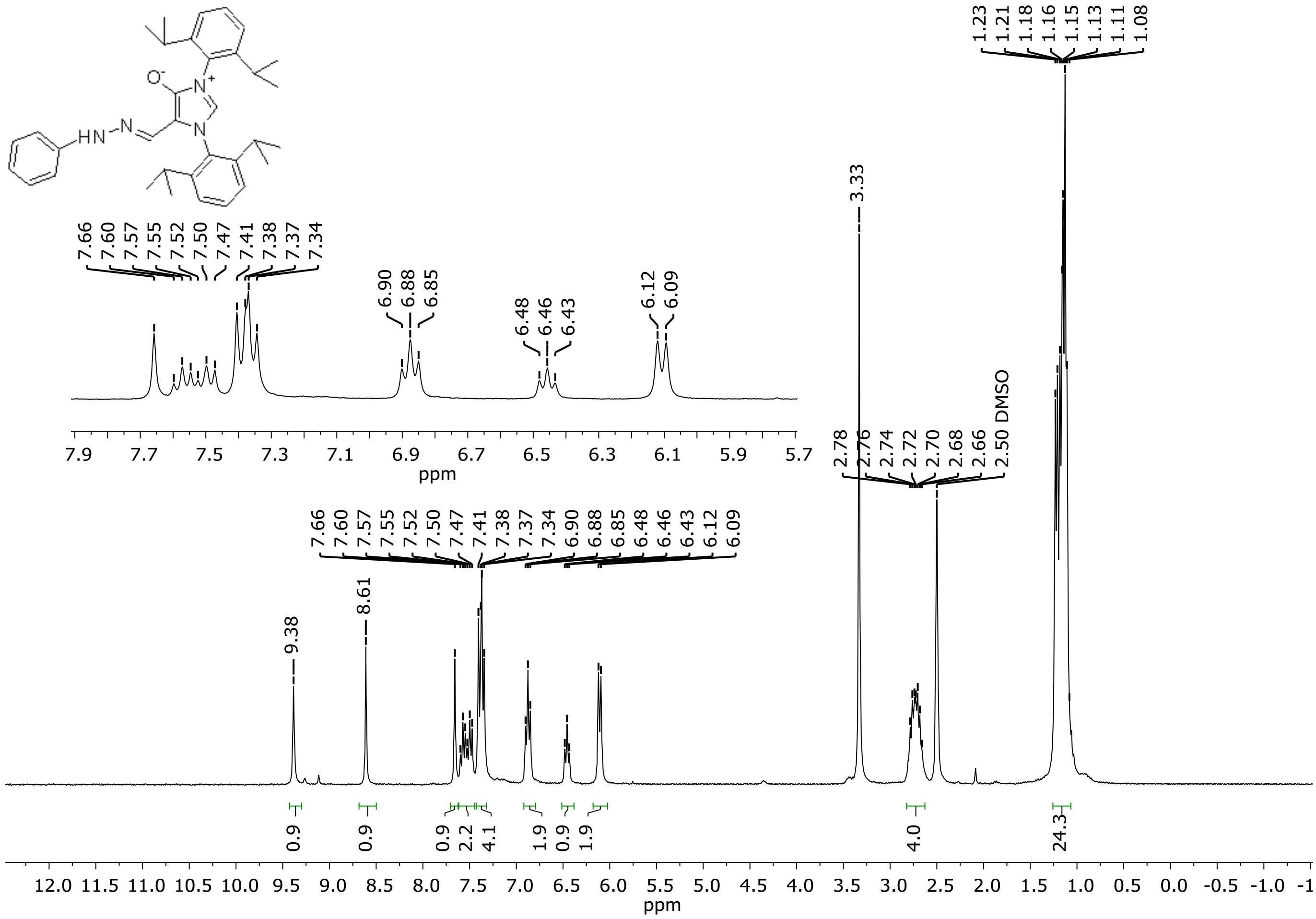


Figure S11. ^{1}H NMR spectrum of compound **4b** (300 MHz, DMSO-*d6*).

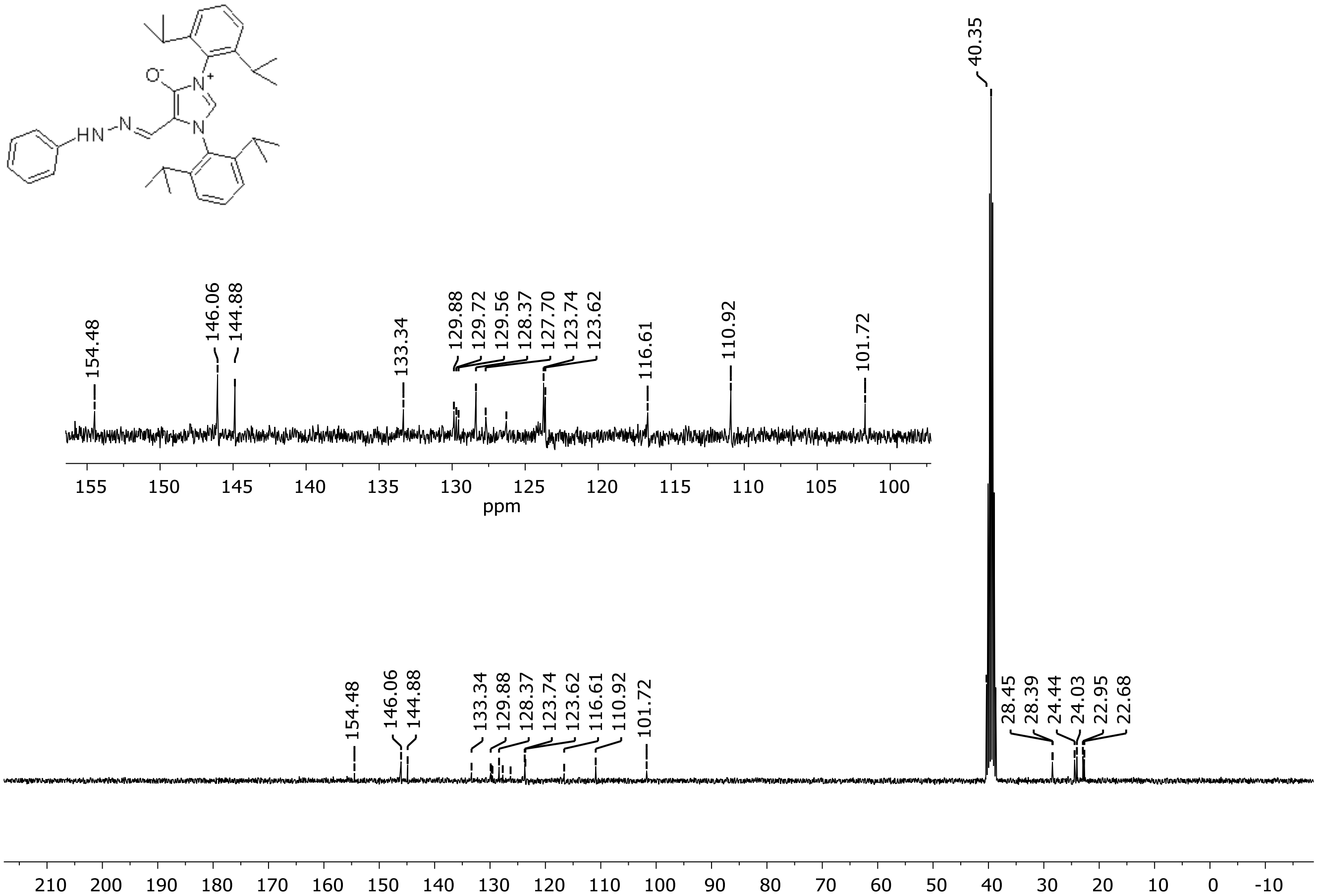


Figure S12. ^{13}C NMR spectrum of compound **4b**(75 MHz, DMSO-*d6*).

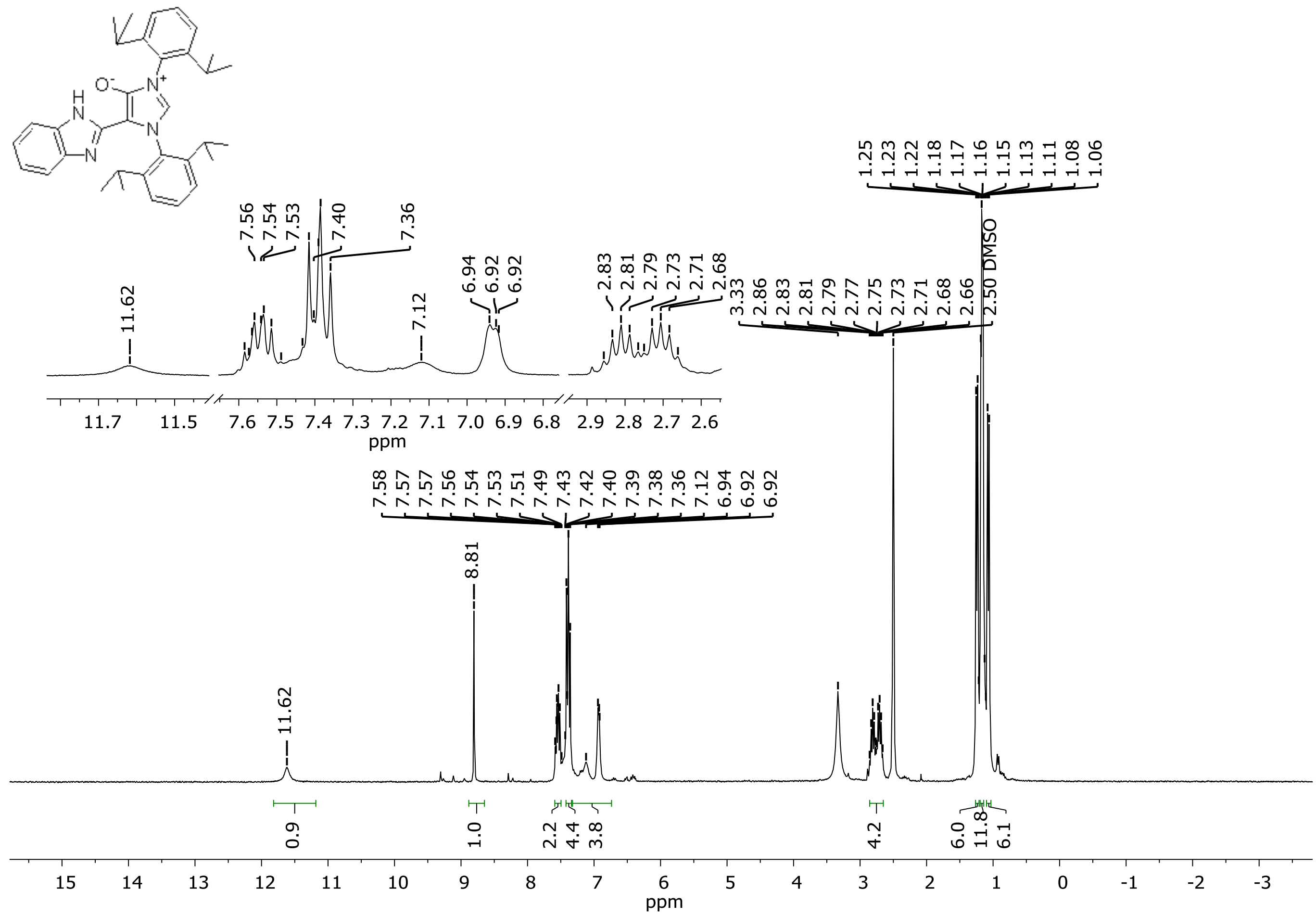


Figure S13. ^{1}H NMR spectrum of compound **5** (300 MHz, DMSO-*d6*).

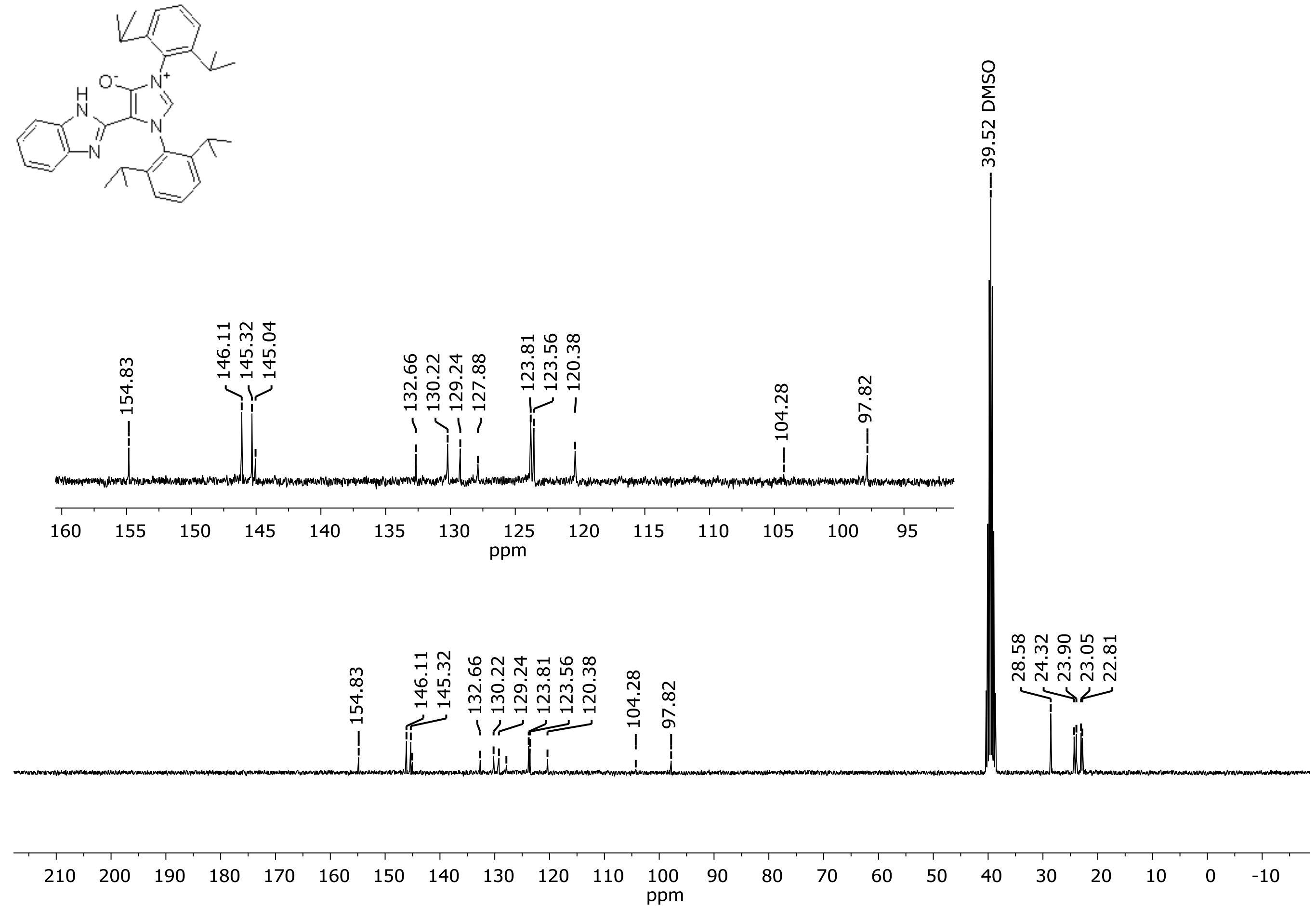


Figure S14. ^{13}C NMR spectrum of compound **5**(75 MHz, DMSO-*d6*).

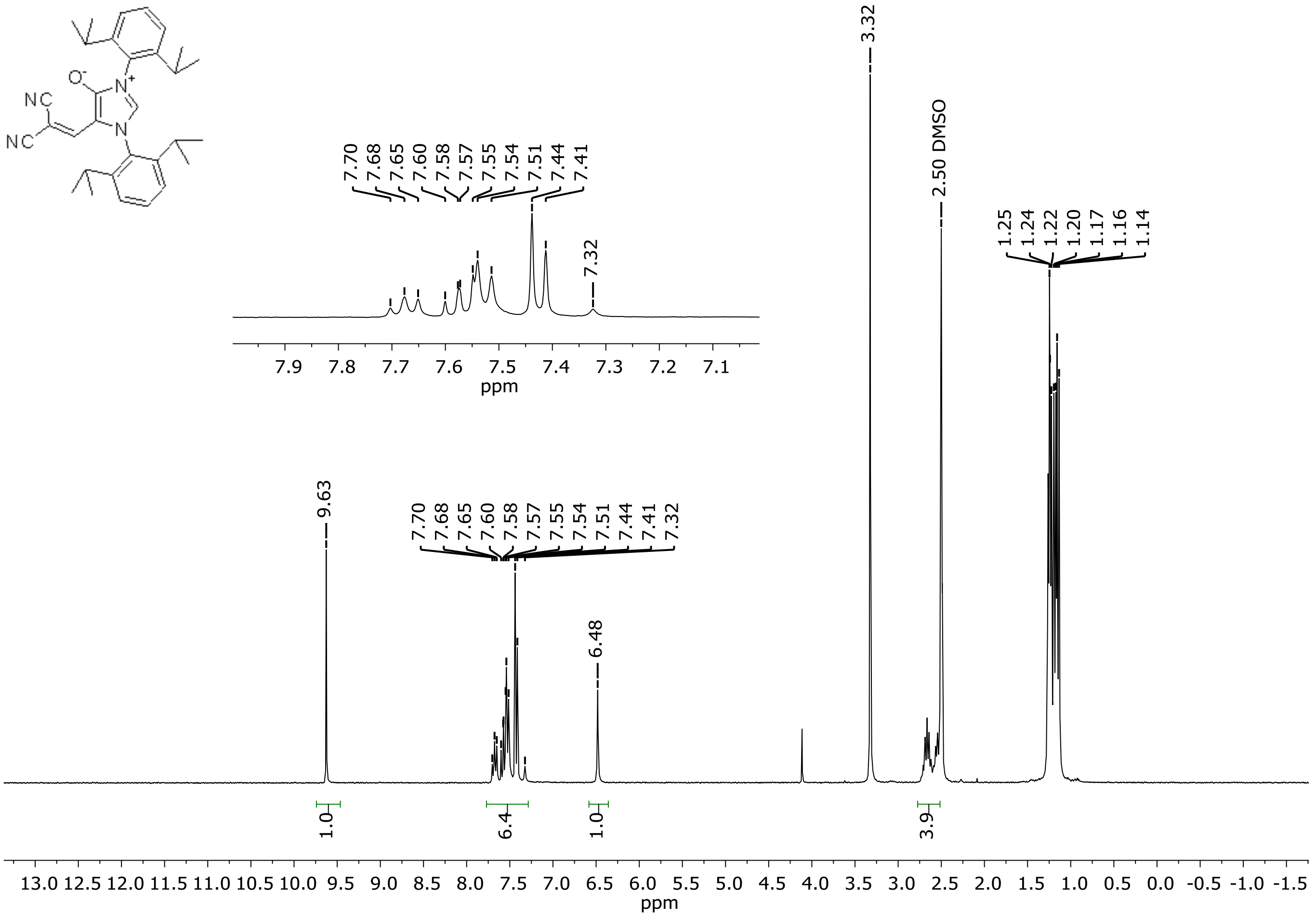


Figure S15. ^{1}H NMR spectrum of compound **6** (300 MHz, DMSO-*d6*).

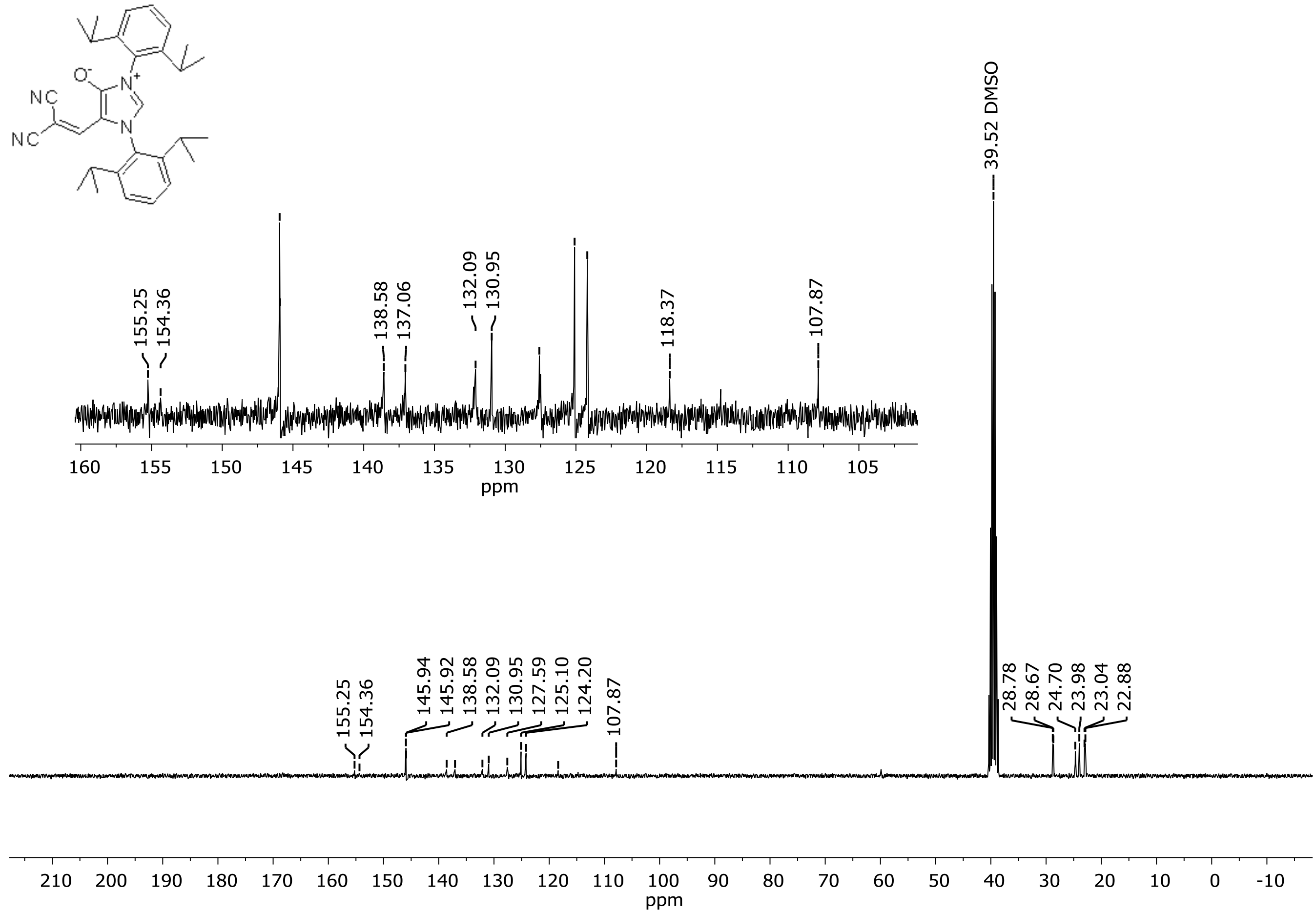


Figure S16. ^{13}C NMR spectrum of compound **6** (75 MHz, DMSO-*d6*).

Supplementary references

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