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Blue-light-promoted radical C–H azolation of cyclic nitrones enabled by Selectfluor®

ELECTRONIC SUPPORTING INFORMATION

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Abstract: An original approach to cause the C(sp^2)–H azolation of cyclic aldonitrones mediated by Selectfluor® has first been carried out. Exploiting a metal-free, visible-light-promoted cross-dehydrogenative C–N coupling reaction between model aldonitrones, 2*H*-imidazole 1-oxides, and NH-containing azoles, a series of novel azaheterocyclic derivatives have been obtained in yields up to 94%. The elaborated protocol has proved to be appropriate for gram-scale processes and displayed a potential for the utilization in the synthesis of novel structural analogues of lanabecestat. Besides, mechanistic studies have revealed that this coupling reaction is likely to proceed *via* a nitroxide-involving radical pathway, encompassing a chain of electron transfer events, such as hydrogen atom transfer (HAT) and single electron transfer (SET).

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1. General information

All the utilized reagents and solvents have been purchased from commercial suppliers (Sigma-Aldrich®, ABCR®, *etc.*) and used without further purification. All reactions mentioned in the study were carried out in aerobic conditions. The experiments exploiting blue light irradiation were fulfilled using an Aldrich® Micro Photochemical Reactor[1] equipped with a blue LED light ring (λ = 440 ± 5 nm). For these reactions, 4 mL Supelco® clear glass vials and Spinbar® magnetic stirring fleas were used. To prevent the scattering of blue light, which could have both decreased efficiency of the reactions and affected the laboratory staff, the reactor was exploited together with a self-made foil-surfaced protective shield (see Fig. S1). With this in mind, the operating temperature within the reaction setup was measured to be ~ 40–45 °C.

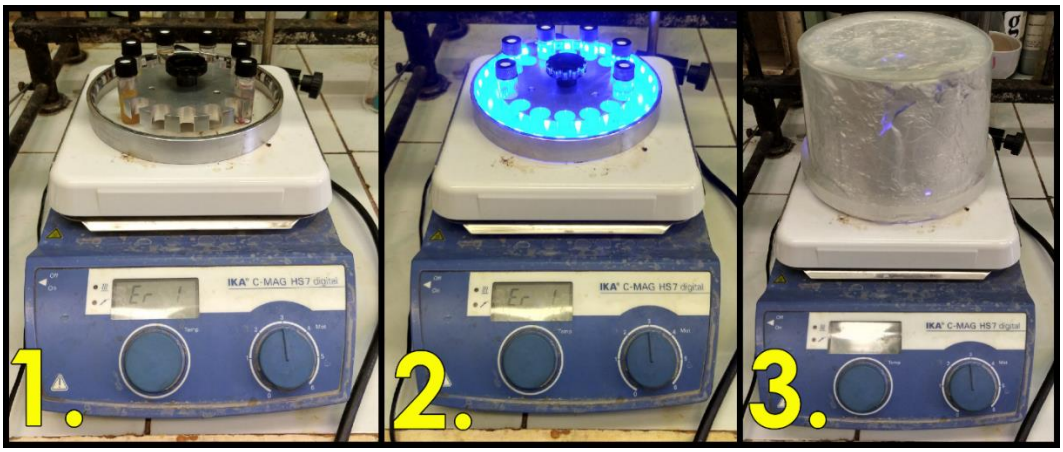


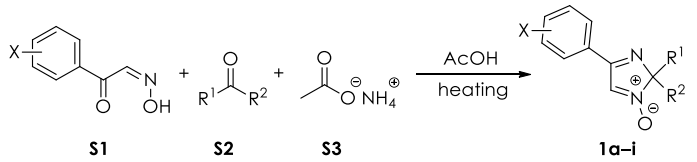
Fig. S1. Reaction setup.

NMR spectra were recorded either on a Bruker Avance II 400 spectrometer (at 400, 101, and 376 MHz frequencies for ^{1}H, ^{13}C, and ^{19}F NMR, respectively) or on a Bruker Avance NEO 600 apparatus (at 600 and 151 MHz frequencies for ^{1}H and ^{13}C NMR). Either DMSO-d_6 or $CDCl_3$ were used as deuterated solvents. ^{13}C NMR spectra were recorded in the mode of attached proton test (APT) or, where more applicable, in broadband (BB) mode with full proton decoupling. Quantitative characteristics of the spectra were estimated using MestReNova software; chemical shifts (δ) are presented in parts per million (ppm) relative to residual undeuterated solvent peaks (DMSO-d_6: 2.50 ppm for ^{1}H NMR, 39.52 ppm for ^{13}C NMR; $CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.36 ppm for ^{13}C NMR). Abbreviations used for the description of NMR spectra: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. *J* (Hz), denotes spin-spin coupling constants in general; J^F (Hz), designates the coupling with fluorine nuclei specifically.

LC-HRMS experiments were rendered using Agilent 1290 Infinity II chromatographic system coupled with Agilent 6545 Q-TOF LC/MS mass spectrometer (electrospray ionization). Mass spectra with electron ionization (70 eV) were recorded on a Shimadzu GCMS-QP2010 Ultra mass spectrometer. Infrared (IR) spectra – on a PerkinElmer Spectrum One B FT-IR spectrometer equipped with a diffuse reflectance accessory (DRA). UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer using 3.5 mL standard quartz cuvettes with 10 mm pathlength. EPR spectra were obtained using Bruker Elexsys E500 EPR spectrometer (modulation amplitude was set as 0.05 mT). Simulated EPR spectra were gained *via* EasySpin software,[2] hyperfine coupling constants being computed at B3LYP/IGLO-III[3] level of density functional theory (DFT) using ORCA v.4.2.1 software.[4] Other DFT calculations (*i.e.* optimization of molecular geometry and calculation of molecular orbital energies) were performed at B3LYP/def2-TZVP(CH_3CN) level of theory using Gaussian 09 software.[5] Elemental analysis was performed on a PerkinElmer PE 2400 Series II CHNS/O analyzer. X-ray analysis for compound **3aa** was executed on an Xcalibur 3 diffractometer (MoK\α radiation, graphite monochromator, 295(2) K, φ- and ω-scanning with a step of 1°). The reaction progress was monitored by thin-layer chromatography (0.25 mm silica gel plates, Merck 60F 254) visualized by UV irradiation (λ = 254 nm). Column chromatography was carried out on 220−440 mesh silica gel (60, 0.035−0.070 mm).

2. Synthesis of the starting materials

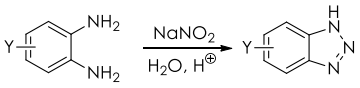
Nitrones **1a–i** are known compounds; they were prepared through the three-component condensation of 2-isonitrosoacetophenones **S1**, ketones **S2**, and ammonium acetate **S3** (Scheme S1) using previously described procedures.[6]



S1 **S2** **S3** **1a–i**

Scheme S1. General approach for the preparation of nitrones **1a–i**.

Functionalized benzotriazoles **2b–i** are also known compounds; they were synthesized from substituted *o*-phenylenediamines **S4** through their reaction with sodium nitrite in acidic media (Scheme S2). For these reactions, previously reported methodics were adopted as well.[7] Spectral characterisitics of all the synthesized starting materials correspond with their structures.



S4 **2b–i**

Scheme S2. General approach for the preparation of benzotriazoles **2b–i**.

All other azoles mentioned in the article (**2a**, **2j–2r**) were purchased from commercial suppliers.

3. General procedure for the optimization studies

Nitrone **1a**, 1*H*-benzotriazole **2a**, and Selectfluor® were weighed in accordance with experimental loadings indicated in Table S1 and subsequently dissolved using 4 mL of corresponding solvent within a clear glass vial equipped with a magnetic stir bar. The experiment in darkness (Table S1, entry 11) was carried out in a vial coated with aluminium foil. The experiment indicated in entry 16 was performed using *N*-fluorobenzenesulfonimide (205 mg, 0.65 mmol) instead of Selectfluor®. In all cases, the reaction mixtures were stirred for 4–6 hours (see Table S1) in air atmosphere. Upon completion of the planned reaction time, the reaction mixtures were quenched with water (4 mL) and extracted with dichloromethane (4 × 4 mL). The organic layers were dried over anhydrous Na_2SO_4. After that, 1,3,5-trimethoxybenzene (~ 0.1 mmol) was added to the separated organic extracts, and the resulting solutions were concentrated under reduced pressure. Then, aliquots from the residues were taken, dissolved in DMSO-d_6 and analyzed by ^{1}H NMR spectroscopy. The yields of **3aa** were calculated based on a comparison between the integrated intensities of the peak of **3aa** at 7.64–7.61 ppm (m, 1H) and the peak of the internal standard, 1,3,5-trimethoxybenzene, at 3.72 ppm (s, 9H).

Table S1. Conditions of the (re)optimization experiments.[a]

Entry	Loading of 1a	Loading of 2a	Loading of S.F.	Solvent	Stirring time, h	*t*, °C	Light mode	Yield of 3aa, %
1	114 mg (0.5 mmol)	89 mg (0.75 mmol)	230 mg (0.65 mmol)	MeCN	6	rt	amb.	45
2	114 mg (0.5 mmol)	89 mg (0.75 mmol)	354 mg (1.0 mmol)	MeCN	6	rt	amb.	43
3	114 mg (0.5 mmol)	89 mg (0.75 mmol)	230 mg (0.65 mmol)	MeCN	6	70	amb.	60
4	114 mg (0.5 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	MeCN	6	70	amb.	57
5	171 mg (0.75 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	MeCN	6	70	amb.	91
6	171 mg (0.75 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	MeCN	8	45	amb.	33
7	114 mg (0.5 mmol)	89 mg (0.75 mmol)	230 mg (0.65 mmol)	$MeNO_2$	5	70	amb.	95
8	171 mg (0.75 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	$MeNO_2$	4	rt	amb.	26
9	125 mg (0.55 mmol)	60 mg (0.5 mmol)	195 mg (0.55 mmol)	$MeNO_2$	4	70	amb.	85
10	171 mg (0.75 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	MeCN/H_2O (2:1)	6	70	amb.	67
11	114 mg (0.5 mmol)	89 mg (0.75 mmol)	230 mg (0.65 mmol)	MeCN	6	rt	dark.	47
12	114 mg (0.5 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	MeCN	6	rt	440 nm	64
13	171 mg (0.75 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	MeCN	6	rt	440 nm	96

14	114 mg (0.5 mmol)	89 mg (0.75 mmol)	230 mg (0.65 mmol)	MeCN	6	rt	440 nm	69
15	171 mg (0.75 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	MeCN/H_2O (2:1)	6	rt	440 nm	26
16	171 mg (0.75 mmol)	60 mg (0.5 mmol)	NFSI, 205 mg (0.65 mmol)	MeCN	6	rt	440 nm	trace
17	114 mg (0.5 mmol)	60 mg (0.5 mmol)	354 mg (1.0 mmol)	MeCN	6	rt	440 nm	68
18	171 mg (0.75 mmol)	60 mg (0.5 mmol)	230 mg (0.65 mmol)	acetone	6	rt	440 nm	16
19	171 mg (0.75 mmol)	60 mg (0.5 mmol)	–	MeCN	6	rt	440 nm	0

[a] Abbreviations used: S.F. = Selectfluor®; NFSI = *N*-fluorobenzenesulfonimide; amb. = ambient light; dark. = darkness.

4. Radical trapping experiments

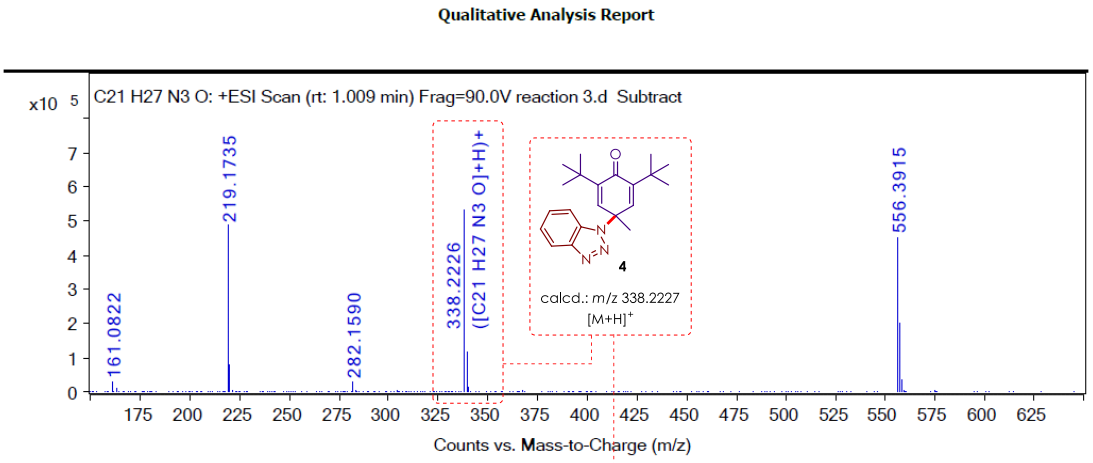
4.1. LC-HRMS control experiments

Nitrone **1b** (101 mg, 0.5 mmol), benzotriazole **2a** (89 mg, 0.75 mmol) and a radical trap [TEMPO (101 mg, 0.65 mmol) or BHT (143 mg, 0.65 mmol)] were dissolved in 4 mL of acetonitrile (analytical purity) within a clear glass vial equipped with a magnetic stir bar. Then, Selectfluor® (230 mg, 0.65 mmol) was added to the solution, and the resulting mixture was stirred for 6 hours at room temperature in ambient lighting. After that, the mixture was diluted with acetonitrile (HPLC grade) to the concentration acceptable for the chromatography, the resulting solution was centrifuged and injected into the chromatograph in a volume of 1 µL. Chromatographic separation was carried out on a Zorbax Eclipse Plus C18 RRHD 2.1 mm × 50 mm × 1.8 µm column equipped with a 5 mm guard column (isocratic mode; mobile phase – MeCN/0.1% aqueous formic acid, 7:3; flow rate = 0.4 mL/min; column oven temperature = 35 °C).

The mass spectrometer operated with an electrospray ionization source in the positive ionization mode. Nitrogen was used as a drying gas (*t* = 350 °C), supplied at 10 L/min rate. The superheated gas (*t* = 400 °C) was supplied at 12 L/min rate. The voltage across the fragmenter was selected to be 90 V. The mass spectra were recorded in 100–1700 Da range with a scanning speed of 1.5 spectra per second.

For the blank test in the absence of **1b** and **2a**, TEMPO (101 mg, 0.65 mmol) and Selectfluor® (230 mg, 0.65 mmol) were dissolved in 4 mL of MeCN (analytical purity) within a clear glass vial equipped with a magnetic stir bar. The following steps fully correspond with those described above in this section.

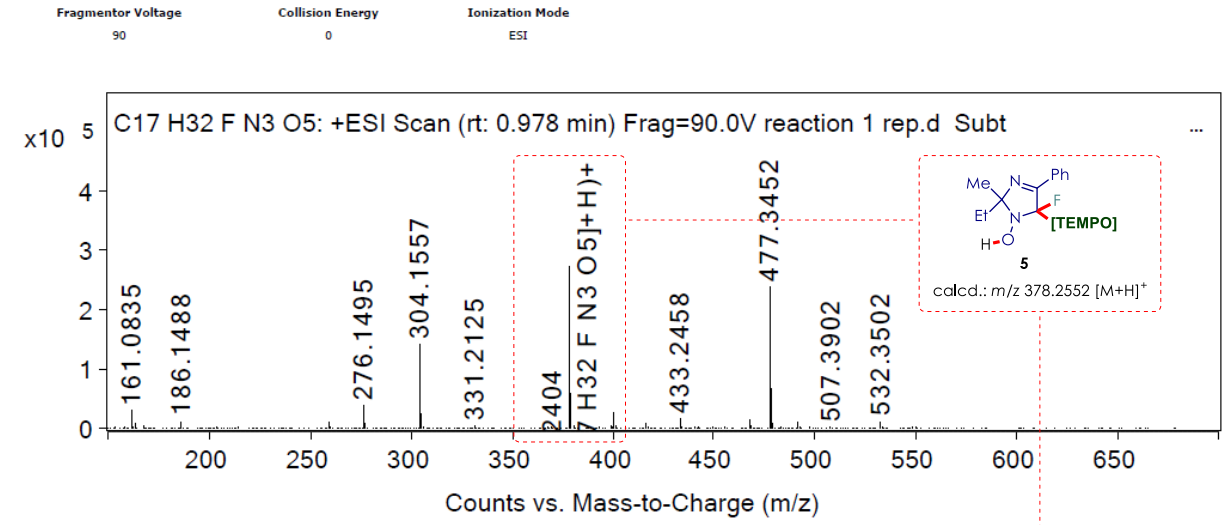
The fragments of the mass spectra depicted below (Fig. S2, S3) demonstrate the mass peaks, which have been suggested to refer to the radical adducts of the reactants with the traps.



Peak List

m/z	z	Abund	Formula	Ion
120.0543		111610.52		
161.0822		28587.35		
163.0794		8337.77		
163.1103		5783.5		
219.1735	1	488840.03		
220.1761	1	77965.71		
282.159		29036.61		
338.2226	1	531588	C21 H27 N3 O	(M+H)+
339.2249	1	117972.8	C21 H27 N3 O	(M+H)+
340.228	1	13900.39	C21 H27 N3 O	(M+H)+
556.3915	1	451335.78		
557.3929	1	203005.73		
558.3955	1	35335.46		

Fig. S2. Evidence for the formation of the radical adduct between benzotriazole **2a** and BHT.



Peak List

m/z	z	Abund	Formula	Ion
120.0556		4103.21		
121.0509		3835.13		
153.1384		3330.86		
158.0025		3612.91		
161.0835		31290.74		
163.0807		8882.65		
167.154		5393.05		
186.1488		12655.43		
259.191		10107.39		
276.1495	1	39828.6		
277.1519	1	7693.79		
304.1557	1	141228.41		
305.1584	1	24552.38		
331.2125		4726.93		
367.2898		2789.84		
369.2862		4166.99		
378.2404	1	272818.31	C17 H32 F N3 O5	(M+H)+
379.2431	1	58435.26	C17 H32 F N3 O5	(M+H)+
380.2439	1	7048.87	C17 H32 F N3 O5	(M+H)+
398.3376		6507.85		
400.222	1	28327.78		
401.2244	1	5990.05		
416.1952		9759.68		
433.2458	1	16751.09		
434.2495	1	4136.12		
440.1619		3013.52		
449.2907		3490.07		
467.2665	1	15208.12		
468.2708	1	5202.66		
477.3452	1	237728.89		
478.3481	1	65929.61		
479.3509	1	9110.01		
491.3604	1	10329.47		
492.3626	1	3519.33		
507.3902		2757.2		
532.3502	1	12540.66		
533.3534	1	3713.11		
746.549	1	13079.22		
747.5519	1	6318.41		
776.5647		2756.4		

Fig. S3. Evidence for the formation of the radical adduct between nitrone **1b** and TEMPO.

The fragment of the mass spectra depicted at Fig. S4 demonstrates the mass peak, which is likely to refer to the "reduced Selectfluor®" (**10**) cation. The similar peaks were detected at almost all obtained mass spectra of the reaction mixtures.

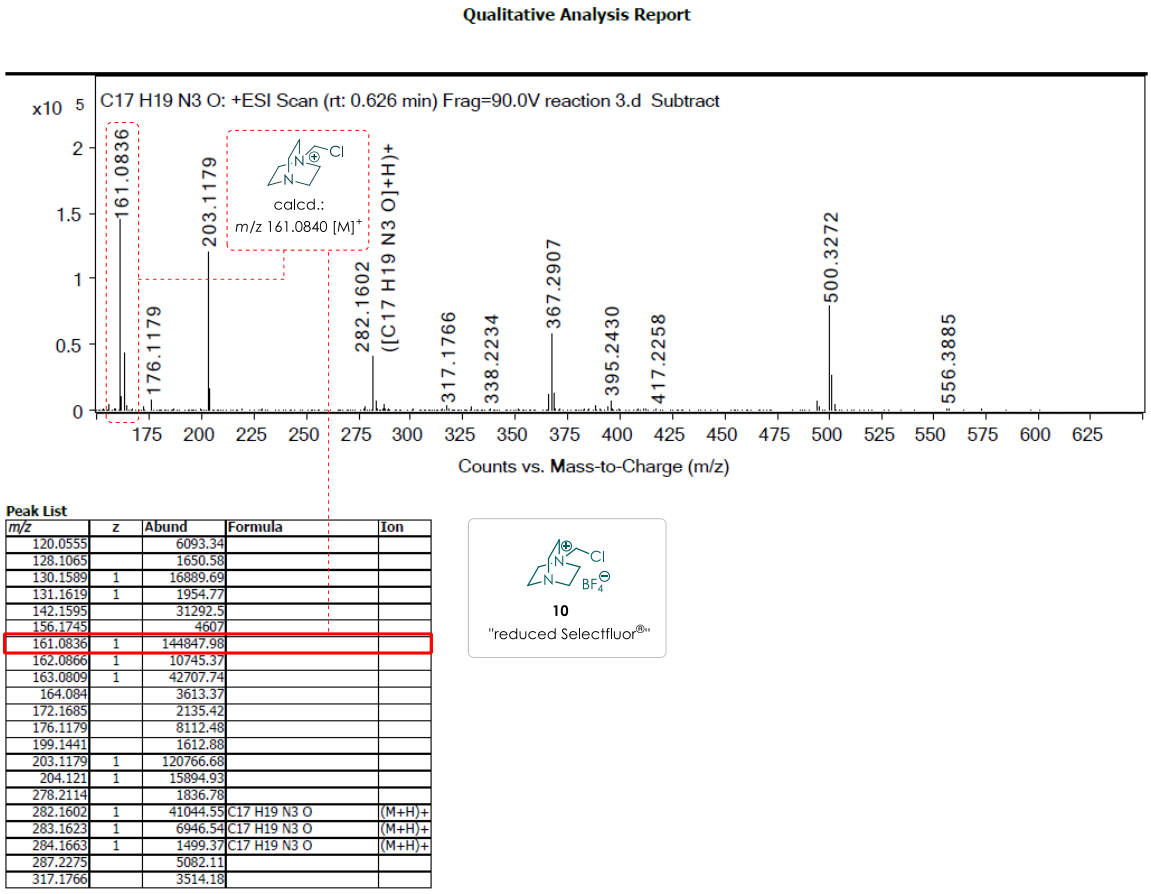


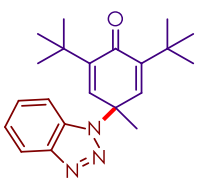
Fig. S4. Evidence for the formation of "reduced Selectfluor®" (**10**).

4.2. Procedure for the isolation of radical adduct 4

Nitrone **1b** (101 mg, 0.5 mmol), benzotriazole **2a** (89 mg, 0.75 mmol) and BHT (143 mg, 0.65 mmol) were dissolved in 4 mL of acetonitrile (analytical purity) within a clear glass vial equipped with a magnetic stir bar. Then, Selectfluor® (230 mg, 0.65 mmol) was added to the solution, and the resulting mixture was stirred for 6 hours at room temperature in ambient lighting. The reaction progress was controlled by TLC. Upon completion of the reaction, the resulting mixture was quenched with 4 mL of water and extracted with dichloromethane (4 × 4 mL). The organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was obtained by column chromatography on silica gel (eluent – hexane/ethyl acetate, 9.5:0.5). An analytically pure sample was achieved through cold recrystallization of the product from diethyl ether/heptane mixture (1:1).

Characterization data of the isolated radical adduct **4** are presented below. Please note that the yield of **4** has been calculated according to the loading of starting nitrone **1b**, since **1b** is supposed to take direct part in the radical trapping reaction.

4-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dienone (4)



4

Yield: 134 mg (80%), isolated as a yellow solid, mp = 80–85 °C. R_f = 0.63 (hexane/ethyl acetate, 3:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11–8.06 (m, 1H), 7.38–7.34 (m, 2H), 7.22–7.18 (m, 1H), 6.60 (s, 2H), 2.25 (s, 3H), 1.25 (s, 18H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz,

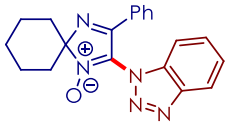
$CDCl_3$): δ 185.1, 148.0, 147.1, 140.3, 132.6, 127.5, 124.2, 120.4, 110.8, 60.9, 35.3, 29.5, 27.0 ppm. IR (DRA): ν 2957, 2932, 2867, 1726, 1666, 1646, 1448, 1363, 1279, 1164, 1122, 1076, 1033, 882, 781, 742, 711, 588 cm^{-1}. MS (EI): *m/z* (%) 337 (100), 338 (26) $[M]^+$. Anal. calcd for $C_{21}H_{27}N_3O$: C, 74.74; H, 8.06; N, 12.45. Found: C, 74.55; H, 7.98; N, 12.62.

5. General procedure for the synthesis of 3aa–3ia, 3ab–3aq, 6a

Nitrone **1** (0.75 mmol, 1.5 equiv.), azole **2** (0.5 mmol, 1.0 equiv.), and Selectfluor® (230 mg, 0.65 mmol, 1.3 equiv.) were successively dissolved in 4 mL of acetonitrile (analytical purity) within a clear glass vial equipped with a magnetic stir bar. The solution was stirred and irradiated by blue LEDs for 6–8 hours at the operating temperature of the reactor (40–45 °C) under air atmosphere. The reaction progress was controlled by TLC. Upon completion of the reaction, the resulting mixture was quenched with 4 mL of water and extracted with dichloromethane (4 × 4 mL). The organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The pure product was obtained by column chromatography on silica gel (eluent – hexane/ethyl acetate, 9:1, with subsequent gradual increase in polarity).

6. Characterization data of the products

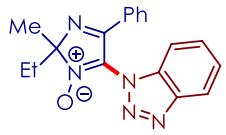
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3aa)



3aa

Yield: 145 mg (84%), isolated as a white solid, mp = 190–195 °C. R_f = 0.64 (hexane/ethyl acetate, 3:2). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.36–8.17 (m, 1H), 7.71–7.67 (m, 1H), 7.64–7.61 (m, 1H), 7.59–7.56 (m, 1H), 7.54–7.50 (m, 1H), 7.48–7.43 (m, 2H), 7.43–7.38 (m, 2H), 2.14–2.07 (m, 2H), 1.96–1.87 (m, 5H), 1.84–1.79 (m, 2H), 1.50–1.43 (m, 1H) ppm. ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 161.0, 144.7, 132.4, 131.7, 130.6, 130.3, 129.4, 128.8, 127.4, 125.5, 120.1, 111.8, 101.6, 34.6, 24.3, 22.6 ppm. IR (DRA): ν 2917, 2855, 1563, 1540, 1469, 1442, 1351, 1025, 962, 768, 750, 725, 704, 689 cm^{-1}. MS (EI): *m/z* (%) 345 (100), 346 (25) $[M]^+$. Anal. calcd for $C_{20}H_{19}N_5O$: C, 69.55; H, 5.54; N, 20.28. Found: C, 69.58; H, 5.75; N, 20.24.

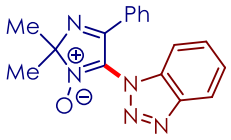
5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-ethyl-2-methyl-4-phenyl-2*H*-imidazole 1-oxide (3ba)



3ba

Yield: 135 mg (85%), isolated as a creamy-white solid, mp = 115–120 °C. R_f = 0.52 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.74–7.68 (m, 1H), 7.64–7.51 (m, 3H), 7.46–7.39 (m, 4H), 2.34–2.26 (m, 1H), 2.12–2.03 (m, 1H), 1.77 (s, 3H), 0.78 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.7, 144.7, 132.3, 131.8, 131.3, 129.9, 129.5, 128.9, 127.2, 125.5, 120.1, 111.6, 101.9, 30.3, 23.1, 6.8 ppm. IR (DRA): ν 2978, 1536, 1440, 1348, 1289, 1185, 1028, 952, 767, 743, 719, 692 cm^{-1}. MS (EI): *m/z* (%) 319 (100), 320 (23) $[M]^+$. Anal. calcd for $C_{18}H_{17}N_5O$: C, 67.70; H, 5.37; N, 21.93. Found: C, 67.44; H, 5.42; N, 21.55.

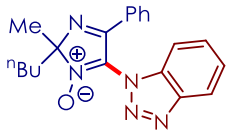
5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-phenyl-2*H*-imidazole 1-oxide (3ca)



3ca

Yield: 125 mg (82%), isolated as a white solid, mp = 142–147 °C. R_f = 0.46 (hexane/ethyl acetate, 3:2). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.20 (d, J = 8.5 Hz, 1H), 7.67–7.63 (m, 1H), 7.57–7.53 (m, 2H), 7.52–7.48 (m, 1H), 7.48–7.44 (m, 2H), 7.40–7.35 (m, 2H), 1.78 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.8, 144.7, 132.3, 131.7, 130.4, 130.1, 129.3, 128.8, 127.3, 125.4, 120.0, 111.9, 99.4, 24.1 ppm. IR (DRA): ν 2988, 1542, 1444, 1347, 1236, 1194, 1149, 1034, 951, 779, 762, 748, 722, 695, 673, 646 cm^{-1}. MS (EI): *m/z* (%) 305 (100), 306 (23) [M]$^+$. Anal. calcd for $C_{17}H_{15}N_5O$: C, 66.87; H, 4.95; N, 22.94. Found: C, 66.72; H, 4.84; N, 22.82.

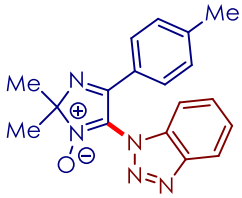
5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-butyl-2-methyl-4-phenyl-2*H*-imidazole 1-oxide (3da)



3da

Yield: 118 mg (68%), isolated as a creamy-white solid, mp = 93–98 °C. R_f = 0.56 (hexane/ethyl acetate, 3:2). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.21 (d, J = 8.4 Hz, 1H), 7.69–7.64 (m, 1H), 7.58–7.54 (m, 1H), 7.52–7.47 (m, 2H), 7.47–7.42 (m, 2H), 7.40–7.35 (m, 2H), 2.29–2.22 (m, 1H), 2.07–2.01 (m, 1H), 1.77 (s, 3H), 1.42–1.34 (m, 2H), 1.27–1.22 (m, 1H), 1.18–1.11 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.4, 144.7, 132.3, 131.8, 131.2, 129.9, 129.5, 128.9, 127.2, 125.5, 120.1, 111.6, 101.6, 36.6, 24.2, 23.5, 21.7, 13.7 ppm. IR (DRA): ν 2960, 2928, 2858, 1546, 1468, 1447, 1028, 962, 767, 751, 720, 693, 674, 637 cm^{-1}. MS (EI): *m/z* (%) 347 (100), 348 (26) [M]$^+$. Anal. calcd for $C_{20}H_{21}N_5O$: C, 69.14; H, 6.09; N, 20.16. Found: C, 69.08; H, 6.06; N, 20.52.

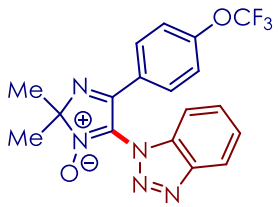
5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(*p*-tolyl)-2*H*-imidazole 1-oxide (3ea)



3ea

Yield: 140 mg (88%), isolated as a creamy-white solid, mp = 130–135 °C. R_f = 0.48 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.27 (d, J = 8.4 Hz, 1H), 7.72–7.64 (m, 2H), 7.61–7.55 (m, 1H), 7.34–7.28 (m, 2H), 7.23–7.18 (m, 2H), 2.30 (s, 3H), 1.75 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.5, 144.7, 141.8, 132.3, 130.3, 129.3, 127.3, 127.2, 125.4, 120.0, 111.8, 99.2, 24.2, 21.0 ppm. IR (DRA): ν 2927, 1542, 1440, 1343, 1235, 1180, 1026, 945, 822, 782, 766, 742, 651, 629 cm^{-1}. MS (EI): *m/z* (%) 319 (100), 320 (23) [M]$^+$. Anal. calcd for $C_{18}H_{17}N_5O$: C, 67.70; H, 5.37; N, 21.93. Found: C, 67.66; H, 5.31; N, 22.26.

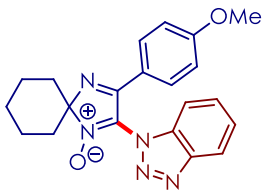
5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(4-(trifluoromethoxy)phenyl)-2*H*-imidazole 1-oxide (3fa)



3fa

Yield: 146 mg (75%), isolated as a creamy-white solid, mp = 82–87 °C. R_f = 0.50 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.26 (d, J = 8.4 Hz, 1H), 7.74–7.65 (m, 2H), 7.63–7.56 (m, 3H), 7.47–7.42 (m, 2H), 1.76 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 159.8, 150.5, 144.7, 132.2, 130.5, 129.8, 129.3, 129.2, 125.4, 121.1, 120.0, 118.6, 112.3, 99.4, 24.0 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –56.7 ppm. IR (DRA): ν 2933, 1539, 1467, 1205, 1158, 1024, 949, 855, 816, 740, 650, 560, 526 cm^{-1}. MS (EI): *m/z* (%) 389 (100), 390 (28) [M]$^+$. Anal. calcd for $C_{18}H_{14}F_3N_5O_2$: C, 55.53; H, 3.62; N, 17.99. Found: C, 55.50; H, 3.82; N, 17.83.

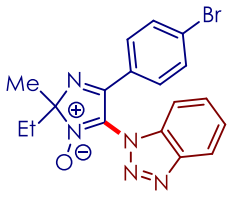
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-(4-methoxyphenyl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ga)



3ga

Reaction was carried out at 0.4 mmol scale. Yield: 125 mg (85%), isolated as a white solid, mp = 158–163 °C. R_f = 0.56 (hexane/ethyl acetate, 3:2). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.27 (d, J = 8.4 Hz, 1H), 7.70–7.67 (m, 1H), 7.62–7.56 (m, 2H), 7.41–7.36 (m, 2H), 6.97–6.94 (m, 2H), 3.75 (s, 3H), 2.12–2.06 (m, 2H), 1.94–1.87 (m, 5H), 1.81–1.77 (m, 2H), 1.49–1.42 (m, 1H) ppm. ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 161.9, 160.0, 144.7, 132.4, 130.4, 129.4, 129.0, 125.4, 122.6, 120.1, 114.3, 111.5, 101.2, 55.4, 34.7, 24.3, 22.5 ppm. IR (DRA): ν 2944, 2859, 1610, 1546, 1505, 1437, 1345, 1251, 1177, 1020, 960, 831, 781, 765, 745, 593 cm^{-1}. MS (EI): *m/z* (%) 375 (100), 376 (25) [M]$^+$. Anal. calcd for $C_{21}H_{21}N_5O_2$: C, 67.18; H, 5.64; N, 18.65. Found: C, 66.80; H, 5.51; N, 18.70.

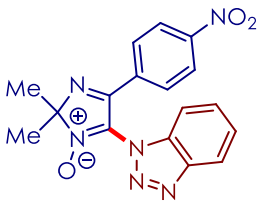
5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-4-(4-bromophenyl)-2-ethyl-2-methyl-2*H*-imidazole 1-oxide (3ha)



3ha

Yield: 131 mg (66%), isolated as a white solid, mp = 142–147 °C. R_f = 0.48 (hexane/ethyl acetate, 3:2). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.27 (d, J = 8.4 Hz, 1H), 7.73–7.70 (m, 1H), 7.67–7.64 (m, 2H), 7.62–7.57 (m, 2H), 7.41–7.38 (m, 2H), 2.32–2.26 (m, 1H), 2.09–2.03 (m, 1H), 1.76 (s, 3H), 0.77 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 161.1, 144.7, 132.3, 132.0, 131.3, 129.5, 129.4, 129.2, 125.6, 125.5, 120.2, 112.0, 102.0, 30.3, 23.0, 6.9 ppm. IR (DRA): ν 2933, 2875, 1588, 1550, 1433, 1397, 1339, 1285, 1176, 1003, 953, 827, 743, 658 cm^{-1}. MS (EI): *m/z* (%) 397 (100), 298 (23), 399 (95), 400 (21) [M]$^+$. Anal. calcd for $C_{18}H_{16}BrN_5O$: C, 54.28; H, 4.05; N, 17.59. Found: C, 54.65; H, 4.00; N, 17.72.

5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(4-nitrophenyl)-2*H*-imidazole 1-oxide (3ia)

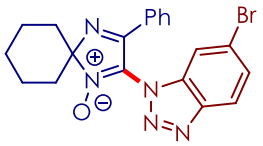


3ia

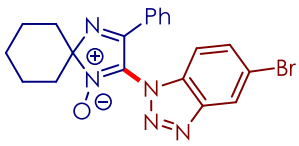
Yield: 112 mg (64%), isolated as a light beige solid, mp = 160–165 °C. R_f = 0.34 (hexane/ethyl acetate, 3:2). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.32–8.24 (m, 3H), 7.76–7.67 (m, 4H), 7.60–7.56 (m, 1H), 1.78 (s, 6H) ppm. ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 160.1, 149.1, 144.7, 136.0, 132.1, 130.7, 129.3, 129.2, 125.5, 123.9, 120.1, 112.8, 99.8, 23.9 ppm. IR (DRA): ν 2921, 2853, 1579, 1529, 1464, 1442, 1364, 1237, 1037, 948, 850, 808, 750, 711, 644, 556 cm^{-1}. MS (EI): *m/z* (%) 350 (100), 351 (26) [M]$^+$. Anal. calcd for $C_{17}H_{14}N_6O$: C, 58.28; H, 4.03; N, 23.99. Found: C, 58.37; H, 4.00; N, 24.02.

2-(6-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ab)

2-(5-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ab')



3ab

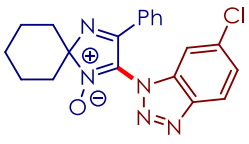


3ab'

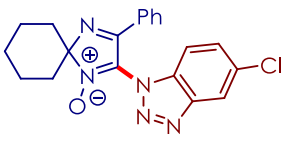
Isolated as an inseparable mixture of two isomers. Yield: 196 mg (92%, isomeric ratio 1.0:1.0), white solid, mp = 142–147 °C. R_f = 0.74 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.30 (s, 0.50H), 8.24 (d, *J* = 8.9 Hz, 0.50H), 7.71 (s, 0.50H), 7.68–7.65 (m, 0.50H), 7.62– 7.59 (m, 0.50H), 7.56–7.54 (m, 0.50H), 7.52–7.46 (m, 3H), 7.41–7.37 (m, 2H), 2.17–2.10 (m, 2H), 2.01–1.94 (m, 5H), 1.85–1.78 (m, 2H), 1.55–1.47 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.7, 145.9, 143.7, 133.3, 132.2, 131.6 (d, *J* = 3.8 Hz), 131.5, 130.5 (d, *J* = 5.6 Hz), 130.2 (d, *J* = 6.8 Hz), 128.7, 127.5, 122.9, 122.6, 121.8, 117.9, 115.0, 114.0, 101.7, 34.5 (d, *J* = 4.7 Hz), 24.3 (d, *J* = 2.6 Hz), 22.5 ppm. IR (DRA): ν 2931, 2858, 1566, 1539, 1444, 1347, 1287, 1020, 987, 959, 872, 800, 772, 721, 694, 656, 579 cm^{-1}. MS (EI): *m/z* (%) 423 (100), 424 (28), 425 (96), 426 (25) [M]$^+$. Anal. calcd for $C_{20}H_{18}BrN_5O$: C, 56.62; H, 4.28; N, 16.51. Found: C, 56.63; H, 4.27; N, 16.52.

2-(6-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ac)

2-(5-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ac')



3ac



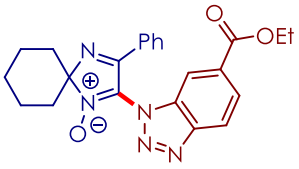
3ac'

Isolated as an inseparable mixture of two isomers. Yield: 179 mg (94%, isomeric ratio 1.0:1.0), creamy-white solid, mp = 157–162 °C. R_f = 0.76 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.45 (d, *J* = 1.0 Hz, 0.50H), 8.17 (d, *J* = 8.8 Hz, 0.50H), 7.87 (d, *J* = 1.1 Hz, 0.50H), 7.77 (dd, *J* = 8.8, 1.6 Hz, 0.50H), 7.67 (dd, *J* = 8.8, 1.6 Hz, 0.50H), 7.56–7.54 (m, 0.50H), 7.52–7.45 (m, 3H), 7.41–7.36 (m, 2H), 2.18–2.10 (m, 2H), 2.01–1.92 (m, 5H), 1.85–1.78 (m, 2H), 1.56–1.47 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.7 (d, *J* = 1.4 Hz), 145.4, 143.4, 134.3, 133.0, 131.6 (d, *J* = 2.4 Hz), 131.2, 130.4, 130.2 (d, *J* = 5.5 Hz), 130.0, 129.8, 128.7, 127.4, 126.2, 121.6, 119.4, 113.7, 112.0, 101.7, 34.5 (d, *J* = 3.7 Hz), 24.3, 22.5 ppm. IR (DRA): ν 2926,

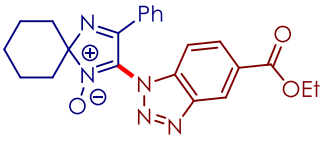
2857, 1564, 1539, 1476, 1445, 1348, 1288, 1022, 988, 959, 871, 807, 773, 691, 658, 628, 584 cm^{-1}. MS (EI): *m/z* (%) 379 (100), 380 (26), 381 (35), 382 (9) $[M]^+$. Anal. calcd for $C_{20}H_{18}ClN_5O$: C, 63.24; H, 4.78; N, 18.44. Found: C, 63.38; H, 4.90; N, 18.27.

2-(6-(ethoxycarbonyl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ad)

2-(5-(ethoxycarbonyl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ad')



3ad

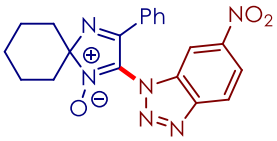


3ad'

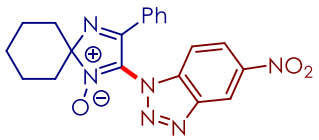
Isolated as an inseparable mixture of two isomers. Yield: 179 mg (86%, isomeric ratio 1.3:1.0), creamy-white solid, mp = 85–90 °C. R_f = 0.68 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.82 (s, 0.44H), 8.37 (d, *J* = 8.7 Hz, 0.56H), 8.30 (s, 0.56H), 8.22 (dd, *J* = 8.7, 1.2 Hz, 0.44H), 8.10 (dd, *J* = 8.7, 1.2 Hz, 0.56H), 7.75 (d, *J* = 8.7 Hz, 0.44H), 7.54–7.46 (m, 3H), 7.44–7.39 (m, 2H), 4.42–4.36 (m, 2H), 2.13–2.08 (m, 2H), 1.96–1.83 (m, 7H), 1.51–1.43 (m, 1H), 1.39–1.32 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 165.0 (d, *J* = 7.4 Hz), 160.8 (d, *J* = 13.7 Hz), 146.7, 144.5, 134.7, 132.1, 131.6 (d, *J* = 13.8 Hz), 130.8, 130.4–130.3 (m), 130.2, 129.3, 128.7 (d, *J* = 10.3 Hz), 127.5 (d, *J* = 13.4 Hz), 125.5, 122.1, 120.4, 114.6, 112.6, 101.7 (d, *J* = 8.6 Hz), 61.4 (d, *J* = 20.7 Hz), 34.5 (d, *J* = 9.8 Hz), 24.3, 22.5, 14.1 (d, *J* = 3.0 Hz) ppm. IR (DRA): ν 2936, 2858, 1715, 1542, 1445, 1304, 1288, 1015, 987, 959, 771, 744, 698, 658 cm^{-1}. MS (EI): *m/z* (%) 417 (100), 418 (28) $[M]^+$. Anal. calcd for $C_{23}H_{23}N_5O_3$: C, 66.17; H, 5.55; N, 16.78. Found: 66.16; H, 5.70; N, 16.54.

2-(6-nitro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ae)

2-(5-nitro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ae')



3ae

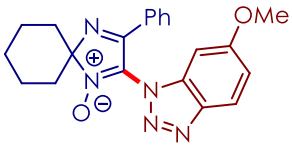


3ae'

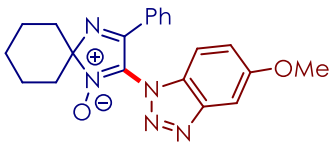
Isolated as an inseparable mixture of two isomers. Yield: 134 mg (69%, isomeric ratio 1.0:1.3), yellowish solid, mp = 140–145 °C. R_f = 0.77 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.24 (d, *J* = 1.6 Hz, 0.42H), 8.72 (d, *J* = 1.6 Hz, 0.58H), 8.54 (d, *J* = 9.1 Hz, 1H), 8.37 (dd, *J* = 9.1, 2.0 Hz, 0.58H), 7.88 (d, *J* = 9.1 Hz, 0.42H), 7.54–7.50 (m, 3H), 7.45–7.41 (m, 2H), 2.14–2.08 (m, 2H), 1.95–1.86 (m, 7H), 1.51–1.44 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.6 (d, *J* = 8.1 Hz), 147.3, 146.8, 145.3, 144.0, 135.1, 131.9, 131.6 (d, *J* = 9.7 Hz), 130.7, 130.4, 130.2, 130.1, 128.7 (d, *J* = 4.5 Hz), 127.6 (d, *J* = 3.5 Hz), 124.0, 121.5, 120.3, 117.3, 113.7, 109.9, 101.9, 34.5 (d, *J* = 7.7 Hz), 24.3 (d, *J* = 3.4 Hz), 22.5 ppm. IR (DRA): ν 2932, 2858, 1564, 1529, 1445, 1345, 1016, 988, 958, 904, 837, 794, 775, 733, 693, 657, 629, 520 cm^{-1}. MS (EI): *m/z* (%) 390 (100), 391 (24) $[M]^+$. Anal. calcd for $C_{20}H_{18}N_6O_3$: C, 61.53; H, 4.65; N, 21.53. Found: C, 61.90; H, 4.91; N, 21.18.

2-(6-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3af)

2-(5-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3af')



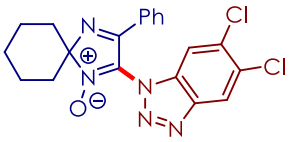
3af



3af'

Isolated as an inseparable mixture of two isomers. Yield: 39 mg (21%, isomeric ratio 1.0:1.7), light beige solid, mp = 200–205 °C. R_f = 0.5 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.11 (d, J = 9.1 Hz, 0.37H), 7.68 (d, J = 1.5 Hz, 0.63H), 7.54–7.50 (m, 1.63H), 7.47–7.40 (m, 4H), 7.32 (dd, J = 9.0, 2.0 Hz, 0.63H), 7.16 (dd, J = 9.1, 2.0 Hz, 0.37H), 7.02 (d, J = 1.6 Hz, 0.37H), 3.90 (s, 1.89H), 3.79 (s, 1.11H), 2.13–2.07 (m, 2H), 1.94–1.78 (m, 7H), 1.50–1.43 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.0, 160.9, 160.7, 157.6, 146.0, 139.8, 134.2, 131.6 (d, J = 3.7 Hz), 130.6, 130.4, 130.3 (d, J = 4.3 Hz), 128.8 (d, J = 6.2 Hz), 127.7, 127.3 (d, J = 9.5 Hz), 121.3, 120.8, 117.0, 112.5, 101.5 (d, J = 1.9 Hz), 99.5, 92.3, 56.0 (d, J = 15.0 Hz), 34.6, 24.3, 22.5 ppm. IR (DRA): ν 2922, 2854, 1541, 1439, 1346, 1296, 1232, 1149, 1022, 987, 958, 902, 838, 810, 772, 692, 660, 561 cm^{-1}. MS (EI): *m/z* (%) 375 (100), 376 (27) [M]$^+$. Anal. calcd for $C_{21}H_{21}N_5O_2$: C, 67.18; H, 5.64; N, 18.65. Found: C, 66.80; H, 5.94; N, 18.32.

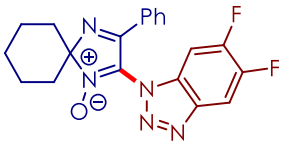
2-(5,6-dichloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ag)



3ag

Yield: 167 mg (81%), isolated as a light beige solid, mp = 135–140 °C. R_f = 0.72 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.72 (s, 1H), 8.10 (s, 1H), 7.55–7.52 (m, 1H), 7.49–7.48 (m, 2H), 7.44–7.40 (m, 2H), 2.12–2.06 (m, 2H), 1.93–1.83 (m, 7H), 1.47–1.45 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.5, 143.8, 132.6, 131.6, 131.5, 130.3, 130.1, 128.8, 128.6, 127.5, 121.5, 114.0, 101.8, 34.5, 24.3, 22.5 ppm. IR (DRA): ν 2924, 2858, 1565, 1544, 1479, 1445, 1424, 1348, 1283, 1199, 1026, 986, 876, 817, 773, 694, 657 cm^{-1}. MS (EI): *m/z* (%) 413 (100), 414 (29), 415 (72), 416 (18), 417 (13) [M]$^+$. Anal. calcd for $C_{20}H_{17}Cl_2N_5O$: C, 57.98; H, 4.14; N, 16.90. Found: C, 58.34; H, 4.27; N, 16.52.

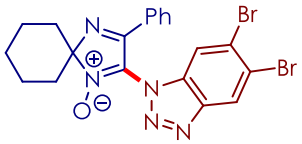
2-(5,6-difluoro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ah)



3ah

Yield: 166 mg (87%), isolated as a white solid, mp = 187–192 °C. R_f = 0.88 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.49 (dd, J = 9.4, 7.4 Hz, 1H), 7.85 (dd, J = 9.0, 7.1 Hz, 1H), 7.56–7.51 (m, 1H), 7.49–7.40 (m, 4H), 2.13–2.05 (m, 2H), 1.95–1.83 (m, 7H), 1.51–1.42 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.6, 152.6 (d, J^F = 16.7 Hz), 150.0 (dd, J^F = 16.4, 4.5 Hz), 147.6 (d, J^F = 16.2 Hz), 140.1 (d, J^F = 10.5 Hz), 131.7, 130.2, 130.1, 128.8, 127.4, 107.4 (d, J^F = 20.9 Hz), 101.8, 100.1 (d, J^F = 24.7 Hz), 34.5, 24.3, 22.5 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –130.96 (d, J^F = 20.8 Hz), –137.54 (d, J^F = 20.8 Hz) ppm. IR (DRA): ν 3040, 2944, 2858, 1565, 1540, 1474, 1243, 1132, 1042, 962, 860, 774, 701, 689, 635 cm^{-1}. MS (EI): *m/z* (%) 381 (100), 382 (25) [M]$^+$. Anal. calcd for $C_{20}H_{17}F_2N_5O$: C, 62.99; H, 4.49; N, 18.36. Found: C, 62.87; H, 4.54; N, 18.27.

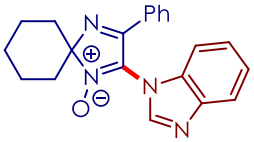
2-(5,6-dibromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ai)



3ai

Yield: 202 mg (80%), isolated as a light orange solid, mp = 150–155 °C. R_f = 0.84 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.82 (s, 1H), 8.23 (s, 1H), 7.54–7.41 (m, 5H), 2.12–2.05 (m, 2H), 1.94–1.83 (m, 7H), 1.50–1.42 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.6, 144.8, 132.2, 131.6, 130.4, 130.2, 128.8, 127.5, 125.2, 124.5, 120.6, 117.0, 101.8, 34.4, 24.3, 22.5 ppm. IR (DRA): ν 2925, 2855, 1566, 1544, 1474, 1445, 1419, 1347, 1284, 1193, 1021, 986, 942, 874, 841, 808, 774, 718, 696, 658, 631 cm^{-1}. MS (EI): *m/z* (%) 501 (49), 502 (18), 503 (100), 504 (27), 505 (49) [M]$^+$. Anal. calcd for $C_{20}H_{17}Br_2N_5O$: C, 47.74; H, 3.41; N, 13.92. Found: C, 48.10; H, 3.73; N, 13.55.

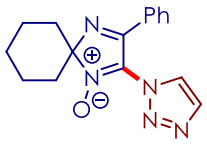
2-(1*H*-benzo[*d*]imidazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3aj)



3aj

Yield: 80 mg (47%), isolated as a beige solid, mp = 165–170 °C. R_f = 0.24 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.41 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.1 Hz, 1H), 7.45–7.38 (m, 4H), 7.33 (t, *J* = 7.1 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.21–7.17 (m, 1H), 2.13–2.05 (m, 2H), 1.95–1.86 (m, 5H), 1.78–1.72 (m, 2H), 1.50–1.42 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.5, 142.7, 132.1, 131.5, 130.5, 130.2, 128.8, 127.0, 124.0, 123.3, 120.1, 111.5, 100.5, 34.5, 24.3, 22.5 ppm. IR (DRA): ν 2932, 2858, 1563, 1536, 1492, 1443, 1297, 1260, 1159, 960, 935, 764, 747, 721, 701, 667, 631 cm^{-1}. MS (EI): *m/z* (%) 344 (100), 345 (26) [M]$^+$. Anal. calcd for $C_{21}H_{20}N_4O$: C, 73.23; H, 5.85; N, 16.27. Found: C, 72.88; H, 6.15; N, 16.00.

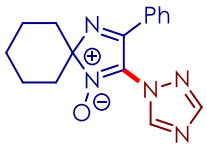
3-phenyl-2-(1*H*-1,2,3-triazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ak)



3ak

Yield: 115 mg (78%), isolated as a creamy-white solid, mp = 127–132 °C. R_f = 0.50 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.75–8.65 (m, 1H), 8.14–8.05 (m, 1H), 7.57–7.53 (m, 1H), 7.47–7.40 (m, 4H), 2.09–2.03 (m, 2H), 1.93–1.83 (m, 5H), 1.70–1.64 (m, 2H), 1.49–1.41 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.6, 133.9, 131.5, 131.1, 130.3, 128.6, 127.6, 127.4, 101.4, 34.4, 24.2, 22.5 ppm. IR (DRA): ν 3159, 2934, 2858, 1699, 1551, 1448, 1234, 1049, 999, 982, 963, 792, 774, 699, 660, 618 cm^{-1}. MS (EI): *m/z* (%) 295 (100), 296 (21) [M]$^+$. Anal. calcd for $C_{16}H_{17}N_5O$: C, 65.07; H, 5.80; N, 23.71. Found: C, 65.22; H, 5.74; N, 23.56.

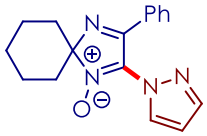
3-phenyl-2-(1*H*-1,2,4-triazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3al)



3al

Yield: 124 mg (84%), isolated as a creamy-white solid, mp = 187–192 °C. R_f = 0.27 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.16 (s, 1H), 8.39 (s, 1H), 7.58–7.50 (m, 3H), 7.48–7.42 (m, 2H), 2.09–2.02 (m, 2H), 1.92–1.83 (m, 5H), 1.65–1.60 (m, 2H), 1.48–1.40 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 160.8, 152.8, 147.0, 131.4, 131.2, 130.5, 128.5, 127.6, 101.0, 34.3, 24.2, 22.5 ppm. IR (DRA): ν 3151, 3107, 2952, 2864, 1545, 1439, 1258, 959, 906, 859, 774, 700, 658, 635 cm^{-1}. MS (EI): *m/z* (%) 295 (100), 296 (23) $[M]^+$. Anal. calcd for $C_{16}H_{17}N_5O$: C, 65.07; H, 5.80; N, 23.71. Found: C, 65.07; H, 6.01; N, 23.38.

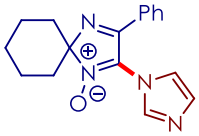
3-phenyl-2-(1*H*-pyrazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3am)



3am

Yield: 115 mg (78%), isolated as a white solid, mp = 155–160 °C. R_f = 0.53 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.33 (d, *J* = 2.4 Hz, 1H), 7.83 (d, *J* = 1.3 Hz, 1H), 7.55–7.50 (m, 1H), 7.46–7.40 (m, 4H), 6.66–6.60 (m, 1H), 2.10–2.02 (m, 2H), 1.92–1.82 (m, 5H), 1.62–1.56 (m, 2H), 1.48–1.38 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.5, 141.9, 133.2, 132.8, 131.2, 130.9, 128.3, 127.6, 107.8, 100.1, 34.4, 24.3, 22.5 ppm. IR (DRA): ν 2946, 1595, 1548, 1443, 1392, 1261, 776, 757, 700, 657, 604 cm^{-1}. MS (EI): *m/z* (%) 294 (100), 295 (23) $[M]^+$. Anal. calcd for $C_{17}H_{18}N_4O$: C, 69.37; H, 6.16; N, 19.03. Found: C, 69.39; H, 6.32; N, 19.13.

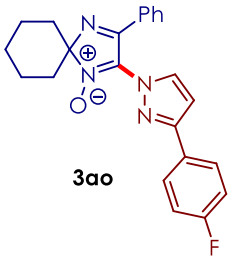
2-(1*H*-imidazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3an)



3an

A known compound.[8] Yield: 31 mg (21%), isolated as a creamy-white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.94 (s, 1H), 7.58–7.54 (m, 1H), 7.49–7.42 (m, 4H), 7.37 (s, 1H), 7.16 (s, 1H), 2.08–2.00 (m, 2H), 1.89–1.81 (m, 5H), 1.65–1.60 (m, 2H), 1.46–1.39 (m, 1H) ppm. ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 161.4, 137.5, 131.5, 131.1, 130.6, 129.2, 128.8, 127.3, 119.5, 100.2, 34.2, 24.4, 22.5 ppm. MS (EI): *m/z* (%) 294 (100), 295 (21) $[M]^+$.

2-(3-(4-fluorophenyl)-1*H*-pyrazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ao)

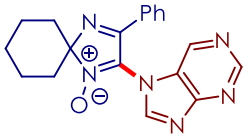


3ao

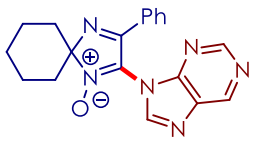
Yield: 70 mg (36%), isolated as a slightly yellowish solid, mp = 65–70 °C. R_f = 0.53 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47 (d, J = 2.4 Hz, 1H), 7.78 (dd, J = 8.3, 5.7 Hz, 2H), 7.59–7.51 (m, 3H), 7.47–7.42 (m, 2H), 7.24 (t, J = 8.8 Hz, 2H), 7.13 (d, J = 2.4 Hz, 1H), 2.13–2.04 (m, 2H), 1.93–1.82 (m, 5H), 1.66–1.59 (m, 2H), 1.48–1.38 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 163.5, 161.5, 161.1, 151.2, 134.3, 133.1, 131.1, 128.3 (d, J^F = 2.9 Hz), 128.2, 127.8 (d, J^F = 8.3 Hz), 115.70 (d, J^F = 21.6 Hz), 105.3, 100.1, 34.4, 24.3, 22.5 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –106.2–(–121.0) (m) ppm. IR (DRA): ν 3126, 2941, 2861, 1562, 1528, 1507, 1435, 1348, 1213, 963, 840, 774, 687, 660, 601 cm^{-1}. MS (EI): *m/z* (%) 388 (100), 389 (31) [M]$^+$. Anal. calcd for $C_{23}H_{21}FN_4O$: C, 71.12; H, 5.45; N, 14.42. Found: C, 70.80; H, 5.29; N, 14.02.

3-phenyl-2-(7*H*-purin-7-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ap)

3-phenyl-2-(9*H*-purin-9-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3ap')



3ap

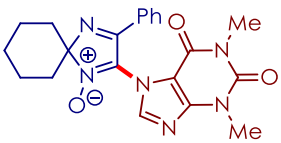


3ap'

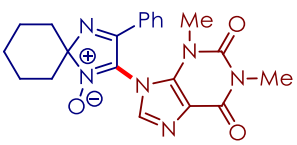
Isolated as an inseparable mixture of two isomers. Yield: 102 mg (59%, isomeric ratio 1.0:2.1), creamy-white solid, mp = 185–190 °C. R_f = 0.16 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.23 (s, 0.68H), 9.02 (s, 0.32H), 8.78 (d, J = 5.8 Hz, 1.37H), 8.69 (d, J = 17.1 Hz, 0.63H), 7.53–7.32 (m, 5H), 2.16–2.07 (m, 2H), 2.00–1.92 (m, 5H), 1.79–1.68 (m, 2H), 1.55–1.45 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.3, 160.8, 153.6, 153.4, 151.2, 149.1, 145.9, 143.0, 133.0, 131.6 (d, J = 3.6 Hz), 130.3 (d, J = 8.5 Hz), 130.0, 128.9, 128.5, 127.5, 126.9, 123.3, 101.0 (d, J = 12.0 Hz), 34.7, 34.2, 24.3 (d, J = 9.4 Hz), 22.5 ppm. IR (DRA): ν 2940, 2856, 1576, 1543, 1492, 1450, 1431, 1386, 1205, 963, 896, 792, 771, 721, 697, 655, 635, 601 cm^{-1}. MS (EI): *m/z* (%) 346 (100), 347 (26) [M]$^+$. Anal. calcd for $C_{19}H_{18}N_6O$: C, 65.88; H, 5.24; N, 24.26. Found: C, 65.51; H, 5.21; N, 23.97.

2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1*H*-purin-7(6*H*)-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3aq)

2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1*H*-purin-9(6*H*)-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (3aq')



3aq

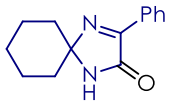


3aq'

Isolated as an inseparable mixture of two isomers. Yield: 56 mg (28%, isomeric ratio 1.0:2.7), light orange solid, mp = 55–60 °C. R_f = 0.12 (hexane/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.53 (s, 0.27H), 8.47 (s, 0.73H), 7.55–7.52 (m, 2H), 7.49–7.41 (m, 2H), 7.37–7.35 (m, 1H), 3.53–3.49 (m, 3H), 3.12 (s, 2.17H), 3.01 (s, 0.83H), 2.11–1.96 (m, 2H), 1.93–1.84 (m, 5H), 1.74–1.65 (m, 2H), 1.52–1.39 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.0, 159.9, 153.4, 153.3, 151.7, 151.0, 148.8, 148.6, 143.1, 131.6, 130.7, 130.5, 130.3, 129.5, 129.0, 128.5, 127.3, 126.9, 106.9, 106.3, 100.8, 100.6, 34.9, 33.6, 33.4, 29.8, 27.6 (d, J = 5.0 Hz), 24.3, 23.4, 22.4 (d, J = 4.2 Hz) ppm. IR (DRA): ν 2929, 2857, 1713, 1545, 1445, 1349, 1289, 1166, 1081,

1017, 958, 770, 743, 695 cm^{-1}. MS (EI): *m/z* 406 (100), 407 (27) $[M]^+$. Anal. calcd for $C_{21}H_{22}N_6O_3$: C, 62.06; H, 5.46; N, 20.68. Found: C, 62.04; H, 5.80; N, 20.29.

3-phenyl-1,4-diazaspiro[4.5]dec-3-en-2-one (6a)



6a

A known compound.[9] Yield: 107 mg (63%), isolated as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.21 (s, 1H), 8.32 (d, *J* = 7.1 Hz, 2H), 7.57–7.46 (m, 3H), 1.82–1.71 (m, 4H), 1.69–1.60 (m, 2H), 1.56–1.43 (m, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 164.2, 160.2, 131.3, 130.9, 128.4, 127.8, 81.8, 36.6, 24.6, 22.5 ppm. MS (EI): *m/z* (%) 228 (100), 229 (17) $[M]^+$.

7. Procedure for the gram-scale synthesis of 3aa

Nitrone **1a** (3.19 g, 14 mmol), benzotriazole **2a** (1.19 g, 10 mmol), and Selectfluor® (4.60 g, 13 mmol) were successively dissolved in 80 mL of acetonitrile (analytical purity) within a clear glass Erlenmeyer flask equipped with a magnetic stir bar. The solution was stirred and irradiated by blue LEDs for ~ 6 hours at the operating temperature of the reactor (40–45 °C) under air atmosphere. The reaction progress was controlled by TLC. Upon completion of the reaction, the resulting mixture was quenched with 80 mL of water and extracted with dichloromethane (4 × 80 mL). The organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The pure product (**3aa**) was obtained by column chromatography on silica gel (eluent – hexane/ethyl acetate, 9:1, with subsequent gradual increase in polarity). Yield: 2.81 g (82%), spectral characteristics of the product correspond with those described for the small-scale synthesis of **3aa** (*vide supra*).

8. Procedure for the deoxygenation of 3aa

Activation of Raney Ni catalyst

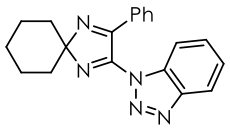
Few narrow spatulas of technical Raney Ni were suspended in the excess of aqueous NaOH at room temperature. In the course of this, vigorous hydrogen evolution occured. After the reaction slowed down, the suspension was heated until the gassing stopped. Next, the suspension was cooled back to room temperature, the solid residue was separated from the alkali solution *via* decanting, washed few times first with water to reach pH = 7, then with ethanol to get rid of water.

Caution: activated Raney nickel is highly pyrophoric!

Synthesis of **8**

3aa (86 mg, 0.25 mmol) was suspended in 5 mL of ethanol within a round-bottom flask; then, previously activated Raney Ni was carefully added to the suspension. The resulting mass was refluxed for 15 min; after that, hydrazine hydrate (26 μL, 0.5 mmol) dissolved in a small amount of ethanol was added dropwise to the reaction mixture. The mixture was refluxed for extra 1.5 h (progress monitoring by TLC), then cooled to room temperature and flash chromatographed on silica gel (eluent – ethyl acetate). The eluate was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The following column chromatography on silica gel (eluent – hexane/ethyl acetate, 9:1) afforded product **8** in 63% yield.

1-(3-phenyl-1,4-diazaspiro[4.5]deca-1,3-dien-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (8)



8

Yield: 52 mg (63%), isolated as a white solid, mp = 90–95 °C. R_f = 0.38 (hexane/ethyl acetate, 8:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.23 (t, J = 8.1 Hz, 2H), 7.80 (t, J = 7.7 Hz, 1H), 7.65–7.58 (m, 3H), 7.55–7.50 (m, 1H), 7.48–7.42 (m, 2H), 1.96–1.86 (m, 6H), 1.82–1.67 (m, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 159.8, 152.1, 145.0, 132.2, 132.2, 130.0, 129.8, 129.1, 127.8, 125.9, 119.7, 113.8, 101.6, 34.2, 25.0, 23.6 ppm. IR (DRA): ν 2932, 2852, 1555, 1487, 1449, 1414, 1284, 1026, 981, 770, 749, 694, 567 cm^{-1}. MS (EI): *m/z* (%) 329 (100), 330 (25) [M]$^+$. Anal. calcd for $C_{20}H_{19}N_5$: C, 72.93; H, 5.81; N, 21.26. Found: C, 72.60; H, 5.96; N, 21.44.

9. Procedure for the UV-vis spectroscopic investigation of the reaction mixtures

To examine the possibility of the visible-light-absorbing EDA complex formation during the reaction process, we prepared a series of six 0.1 M solutions of single starting materials (*i.e.* nitrone **1b**, benzotriazole **2a**, and Selectfluor®) and their binary mixtures in 4.0 mL of acetonitrile (HPLC grade). For the mixtures, the loadings were calculated so that the components would be in the same molar ratio as ones used for the synthesis of **3aa–ia** and **3ab–aq** (see Table S2).

Table S2. Loadings of the components for the UV-vis spectroscopic investigation.

Entry	Loadings of the components
1	**1b** (0.0808 g, 0.400 mmol)
2	**2a** (0.0476 g, 0.400 mmol)
3	Selectfluor® (0.1416 g, 0.400 mmol)
4	**1b** (0.0485 g, 0.240 mmol) + **2a** (0.0190 g, 0.160 mmol)
5	**2a** (0.0207 g, 0.174 mmol) + Selectfluor® (0.0800 g, 0.226 mmol)
6	**1b** (0.0433 g, 0.214 mmol) + Selectfluor® (0.0657 g, 0.186 mmol)

The prepared solutions were vigorously stirred for about 3 hours at room temperature and ambient lighting. After that, the aliquots from the resulting solutions were placed in a quartz cuvette and analyzed by UV-vis absorption spectroscopy (wavelength range – 600 to 200 nm). As a result, no significant bathochromic shifts for the solutions of the binary mixtures were observed, compared with the spectra of the single components solutions (see Fig. S5). This fact suggested that the visible-light-absorbing EDA complex is unlikely to form in case of the coupling reaction studied. The spectral evidence also corroborated with our visual observations: thus, for example, no intensification in solution colouring was noticed for the mixture of **1b** and Selectfluor® after 3 h stirring, compared with the single **1b** solution colouring; moreover, rather the opposite effect could be seen there (Fig. S6).

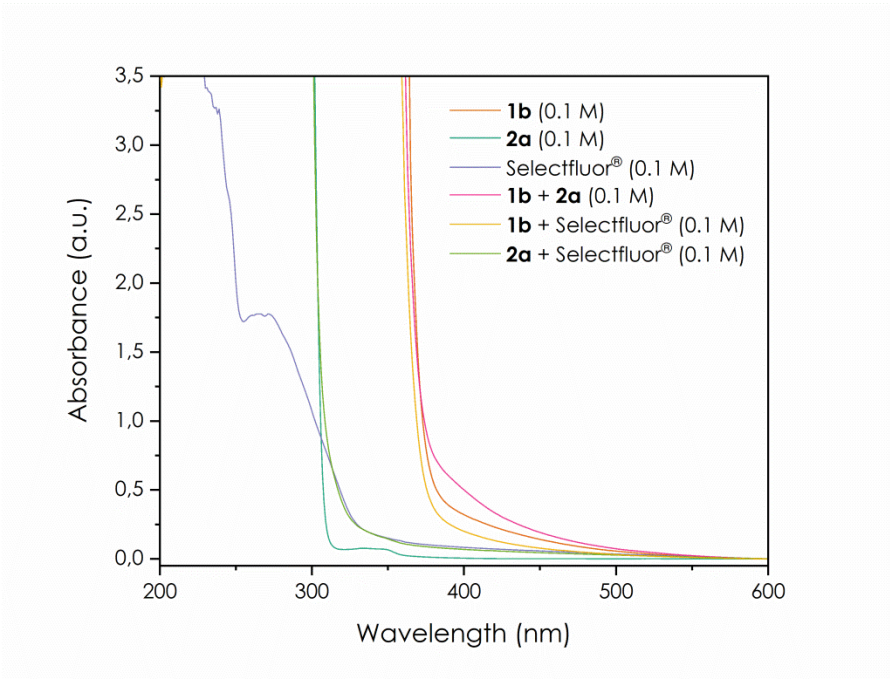


Fig. S5. UV-vis absorption spectra for the reaction components (solvent – MeCN).

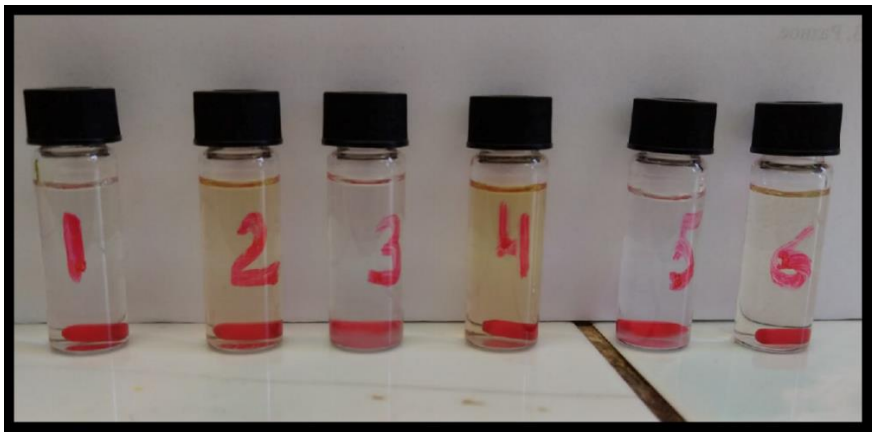


Fig. S6. Colouring of the investigated solutions after 3 h stirring (numeration of the vials corresponds with the entries of Table S2).

10. EPR spectroscopic investigation

10.1. Procedure for the primary EPR spectroscopic analysis of the reaction components

A series of six 0.1 M solutions of single starting materials (*i.e.* nitrone **1b**, benzotriazole **2a**, and Selectfluor®) and their binary mixtures in 500 µL of acetonitrile (HPLC grade) were prepared. For the mixtures, the loadings were calculated so that the components would be in the same molar ratio as ones used for the synthesis of **3aa–ia** and **3ab–aq** (see Table S3).

Table S3. Loadings of the components for the primary EPR spectroscopic investigation.

Entry	Loadings of the components
1	**1b** (0.0101 g, 50 µmol)
2	**2a** (0.0060 g, 50 µmol)
3	Selectfluor® (0.0177 g, 50 µmol)
4	**1b** (0.0061 g, 30 µmol) + **2a** (0.0024 g, 20 µmol)
5	**2a** (0.0026 g, 22 µmol) + Selectfluor® (0.0100 g, 28 µmol)
6	**1b** (0.0054 g, 27 µmol) + Selectfluor® (0.0082 g, 23 µmol)

The solutions were analyzed by direct-detection EPR spectroscopy. In the case of **1b** – Selectfluor® mixture (Table S3, entry 6), a distinct EPR signal was detected (as shown below). In the case of the single nitrone **1b** (entry 1), a signal corresponding to **1b** – OH spin adduct was detected right after dissolution of **1b** in acetonitrile (see Fig. S7). Its fadeout was observed within 30 min after the dissolution. When the **1b** solution was analyzed in >1 h after its preparation, no apparent signal was detected. As for the other analytes (entries 2–5), they were found to be EPR silent.

10.2. Procedure for the time-dependent EPR spectroscopic analysis of the 1b – Selectfluor® mixture in the absence / presence of blue light irradiation

Two 0.1 M acetonitrilic solutions of **1b** – Selectfluor® mixture were prepared in a similar manner as described in par. 10.1. For each analyte, the moment of complete dissolution of the reagents was followed by an EPR experiment, and the first measurement was taken as the time reference point (τ = 0 min). After that, one of the solutions was kept in darkness, while another one was exposed to blue light irradiation. Every 10 min, aliquots were taken from each solution and analyzed by EPR spectroscopy. In each case, the observation was carried out until the reaction reached its plateau (*i.e.* no significant change in signal intensities was detected for adjacent measurements (80 min for the blue-light-irradiated sample, 110 min for the sample kept in darkness). The consequent comparative analysis of the obtained intensity values allowed drawing conclusions about the influence of blue light on the reaction progress.

10.3. Relevant EPR spectra

9.3.1. EPR spectrum of **1b** – OH spin adduct

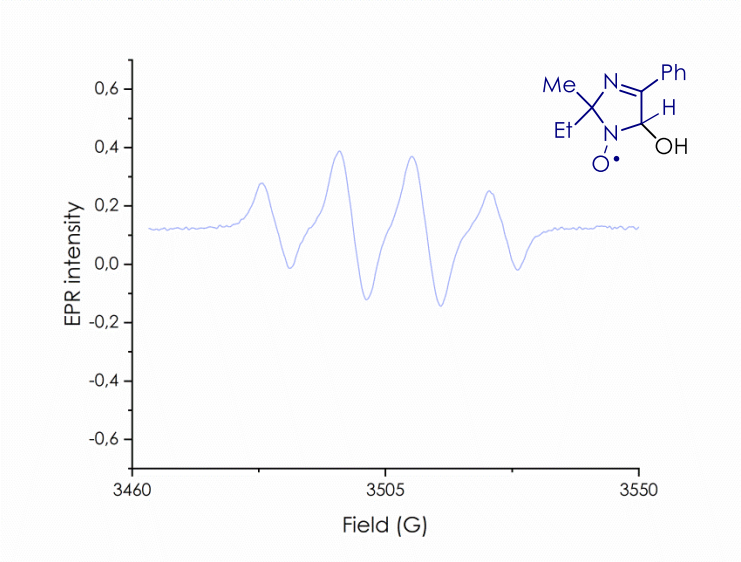


Fig. S7. EPR Spectrum of the **1b** – OH spin adduct

9.3.2. EPR spectra for the time-dependent experiments in the absence / presence of blue light irradiation

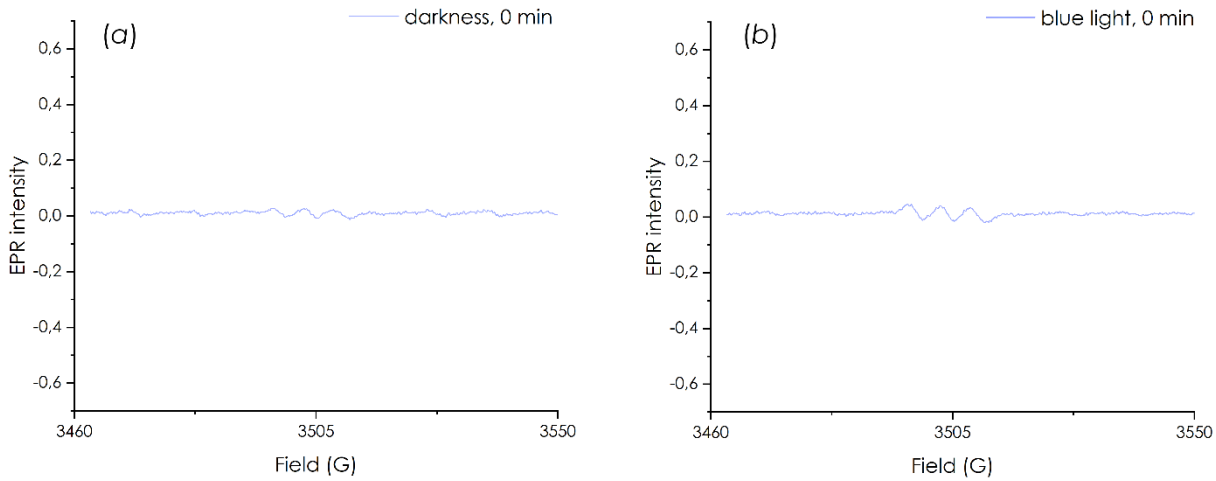


Fig. S8. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 0 min

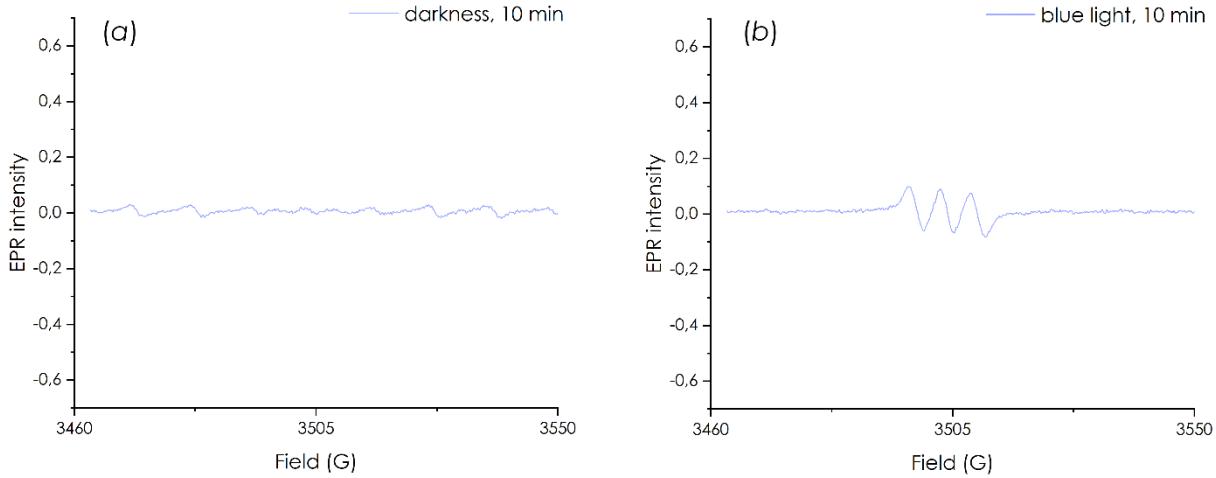


Fig. S9. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 10 min

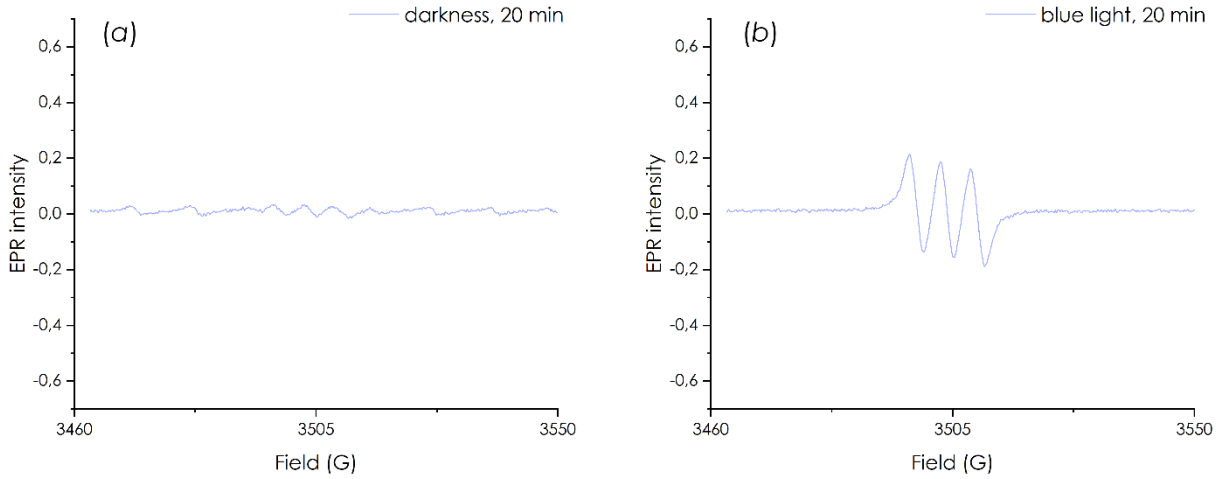


Fig. S10. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 20 min

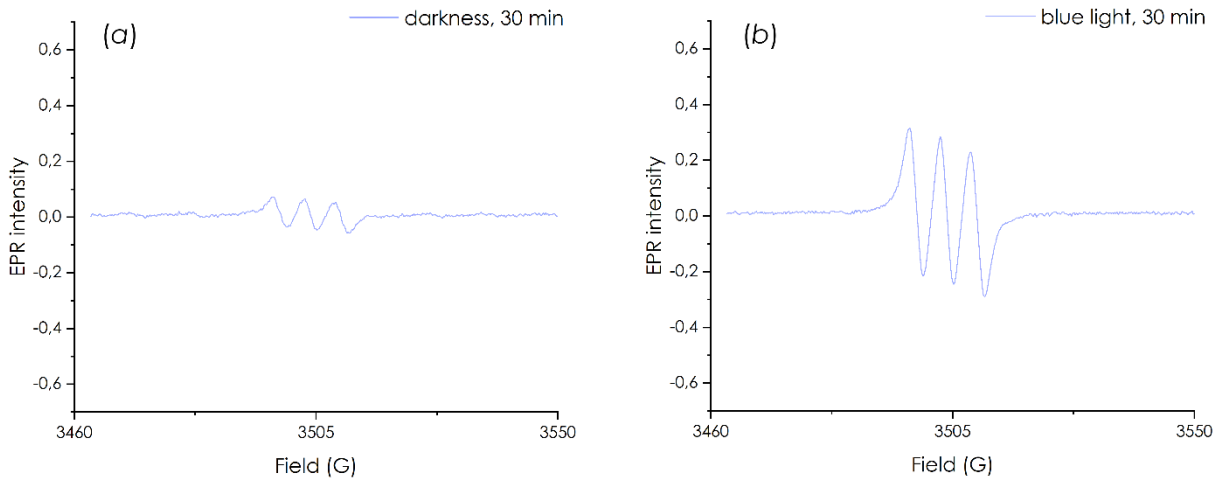


Fig. S11. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 30 min

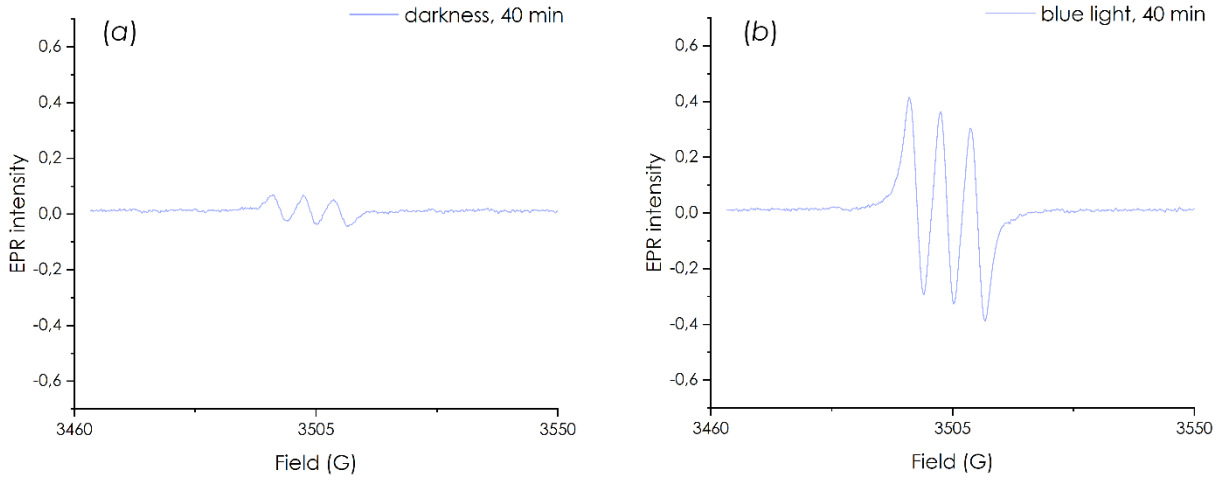


Fig. S12. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 40 min

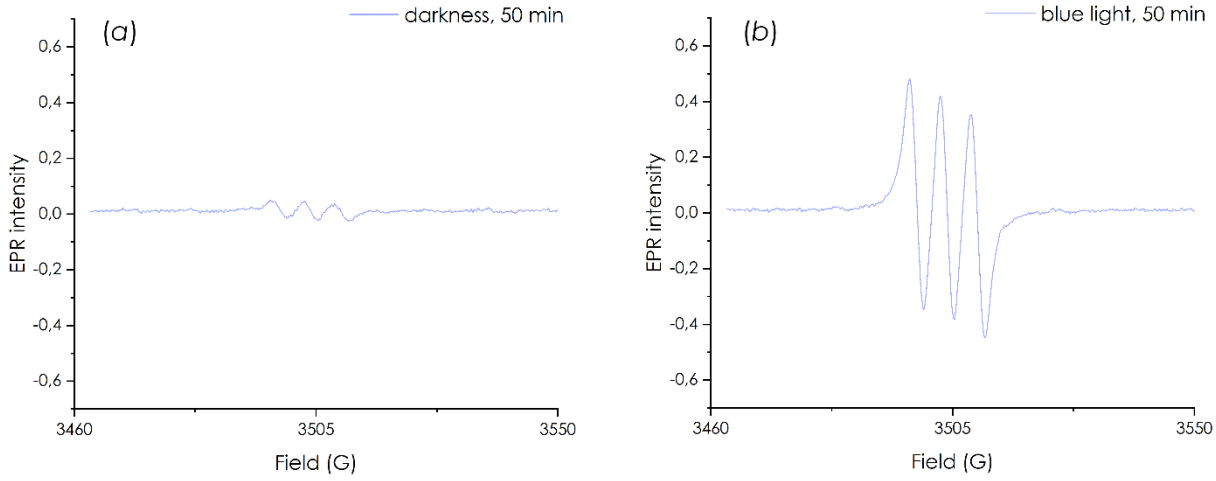


Fig. S13. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 50 min

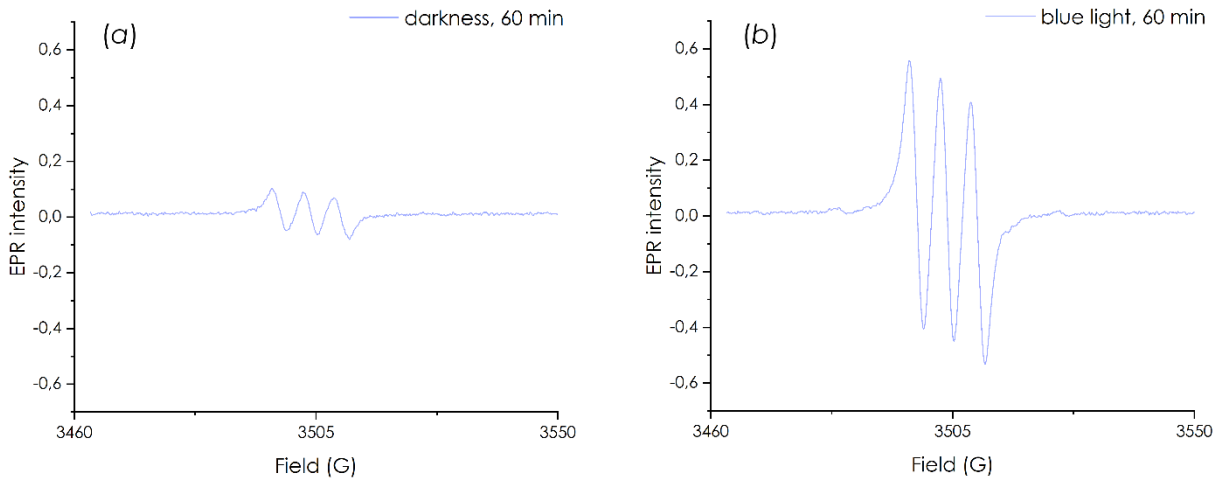


Fig. S14. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 60 min

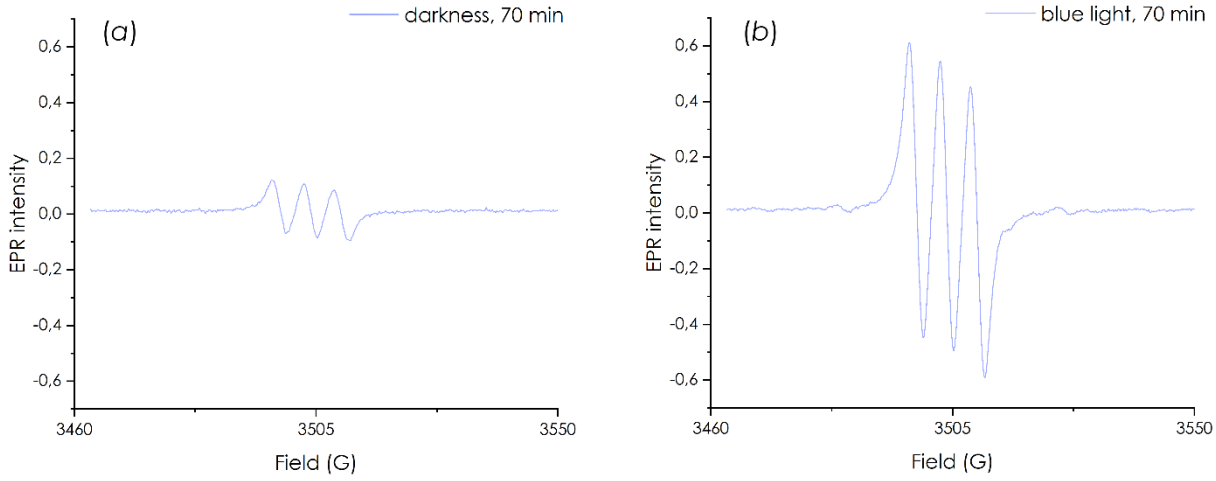


Fig. S15. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 70 min

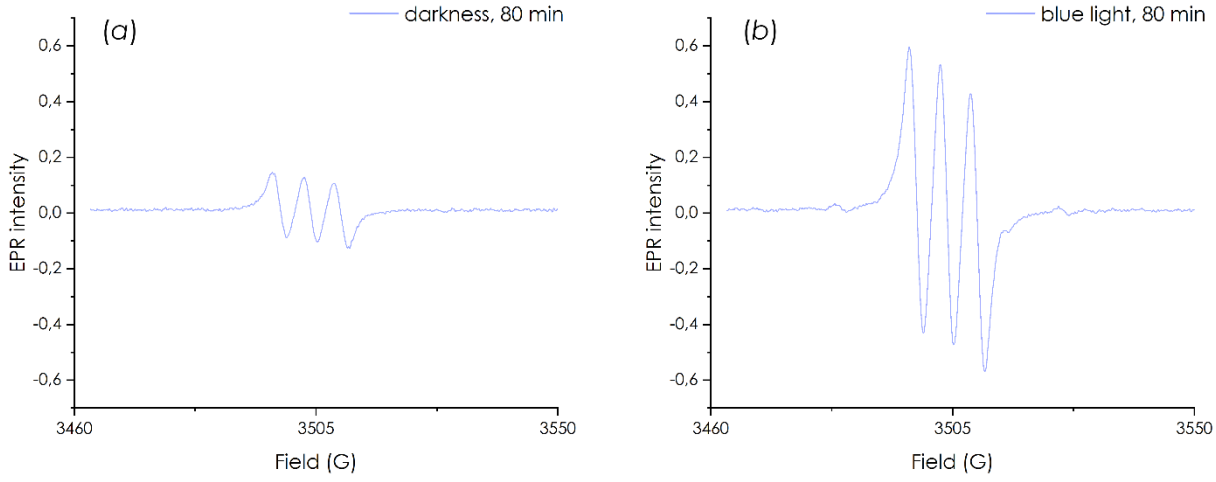


Fig. S16. EPR Spectra of the **1b** – Selectfluor® mixtures at τ = 80 min

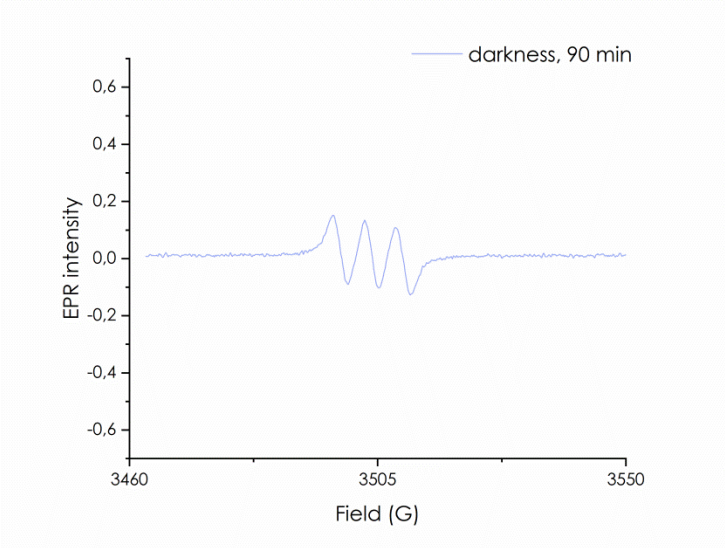


Fig. S17. EPR Spectra of the **1b** – Selectfluor® mixture kept in darkness at τ = 90 min

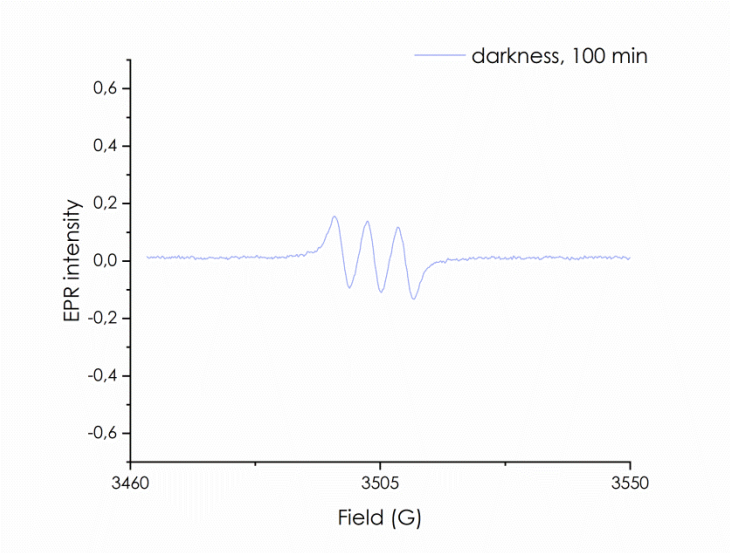


Fig. S18. EPR Spectra of the **1b** – Selectfluor® mixture kept in darkness at τ = 100 min

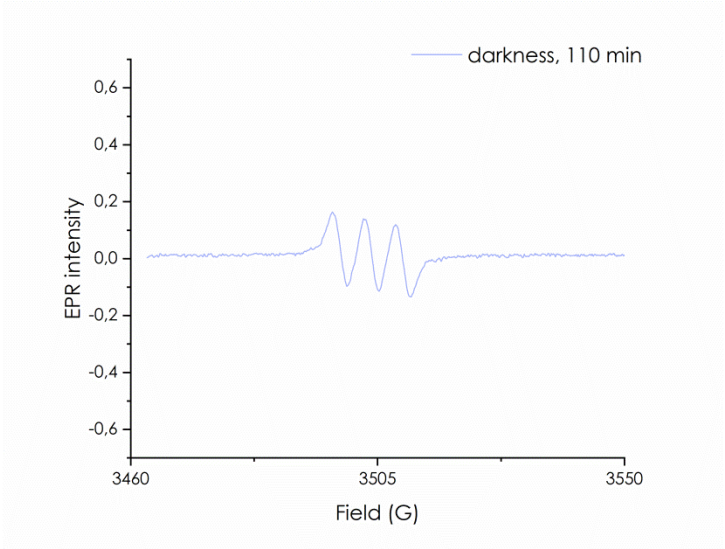


Fig. S19. EPR Spectra of the **1b** – Selectfluor® mixture kept in darkness at τ = 110 min

11. X-ray analysis data for the compound 3aa

The crystallographic data and basic refinement parameters for 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide **3aa** are shown in Table S4.

Table S4. X-ray analysis data and basic refinement parameters for **3aa**

Parameter	3aa
Molecular formula	$C_{20}H_{19}N_5O$
Molecular weight	345.40
T/K	295(2)
λ/Å	0.71073
Syngony	monoclinic
Space group	P2(1)/n
a/Å	6.7011(11)
b/Å	9.1071(11)
c/Å	28.951(3)
α/deg	90.00
β/deg	92.176(10)
γ/deg	90.00
V/Å^3	1765.5(4)
Z	4
d_{calc}/g·cm^{-3}	1.299
μ/mm^{-1}	0.084
F(000)	728
Crystal size/mm	0.41 × 0.18 × 0.03
2θ-Scan range/deg	3.595–21.729
Completeness based on $2\theta_{max}$	0.996
Completeness based on 2θ = 52°	0.996
hkl ranges	–8 < *h* < 8 –11 < *k* < 11 –36 < *l* < 36
Total number of reflections	12762
Number of independent reflections	3599
Number of reflections with *I* > 2σ(*I*)	1372
Number of refined parameters	252
Absorption correction	multi-scan
GOOF (based on F^2)	1.002
R factors (based on reflections with *I* > 2σ(*I*))	
R_1	0.0638
wR^2	0.1434
R factors (based on all reflections)	
R_1	0.1457
wR^2	0.1986
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, eÅ^{-3}	0.193 / –0.201

Crystallographic data (excluding structure factors) for the structure 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide **3aa** in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2008292. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

12. ESI references

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13. Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for compounds 3aa–ia, 3ab–aq, 4, 6a, 8

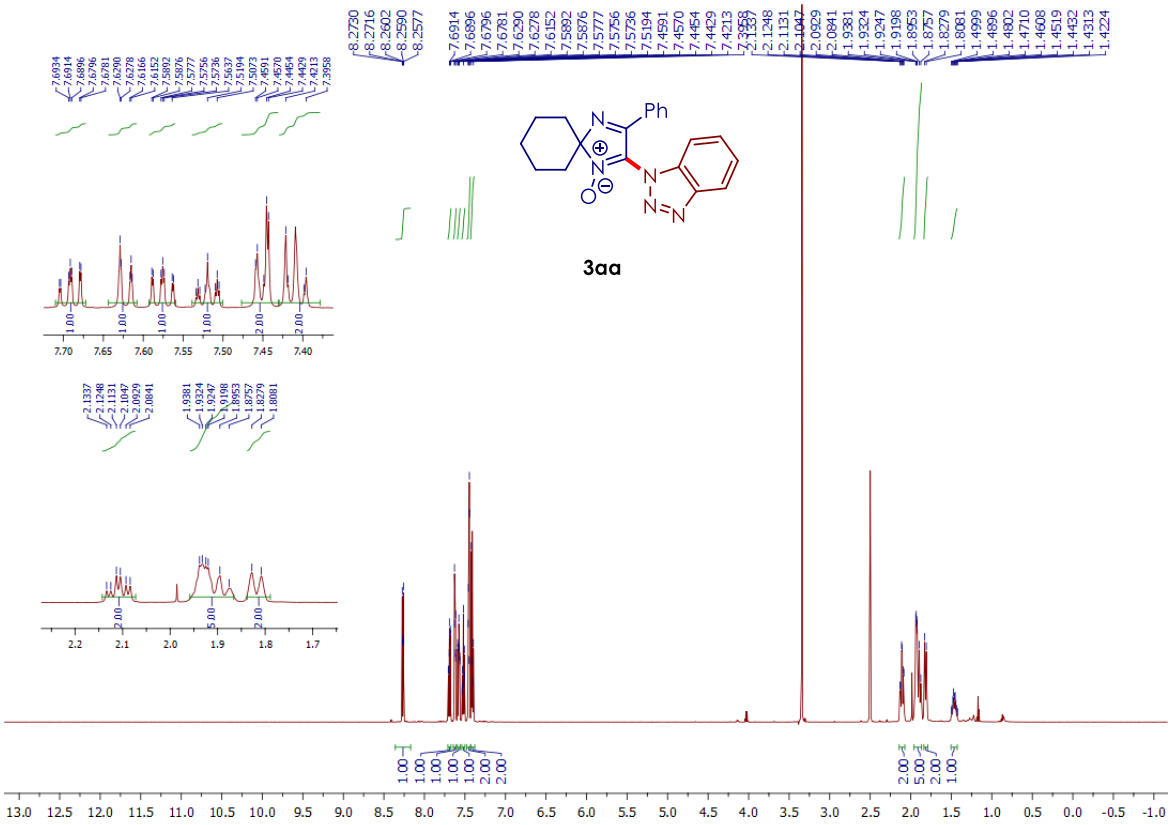

Fig. S20. ^{1}H NMR Spectrum (DMSO-d_6, 600 MHz) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3aa**).

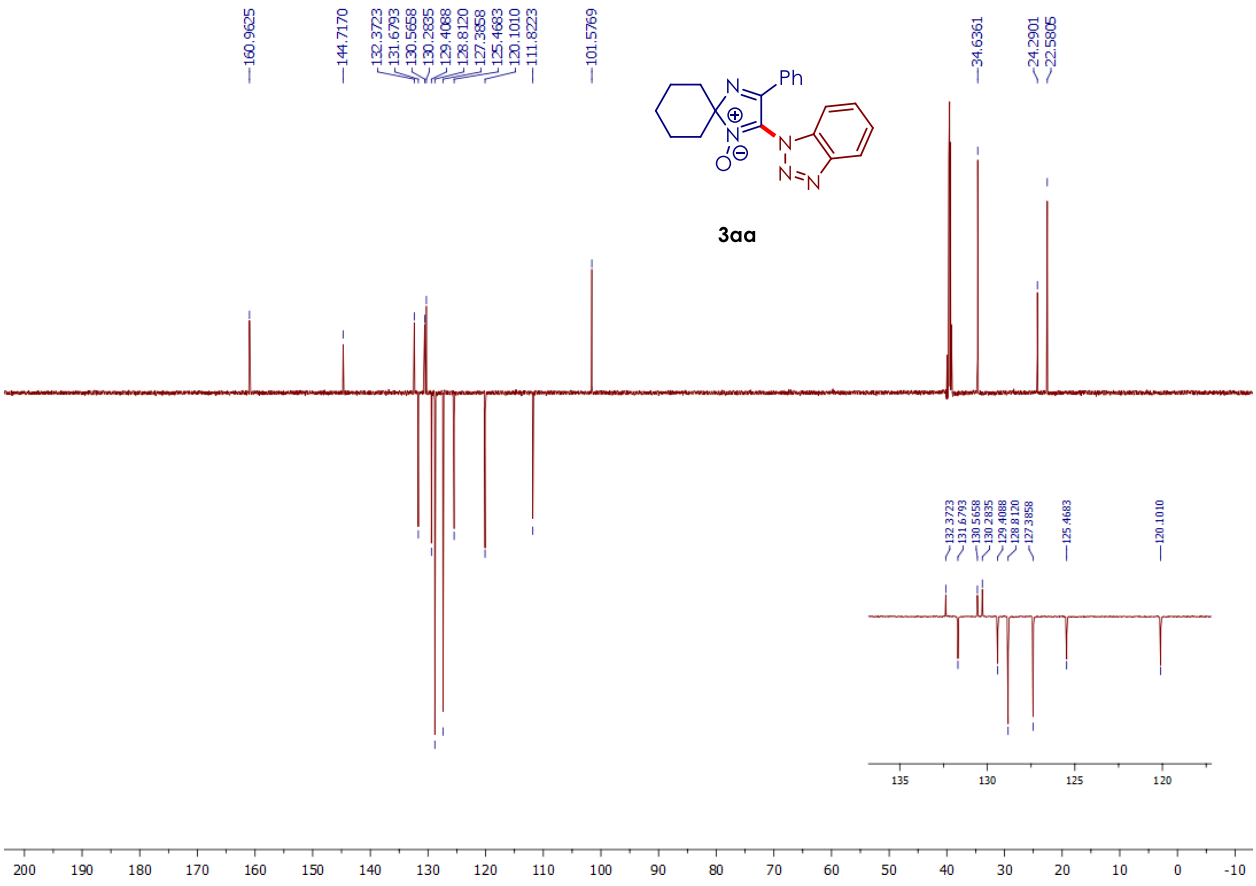

Fig. S21. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 151 MHz) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3aa**).

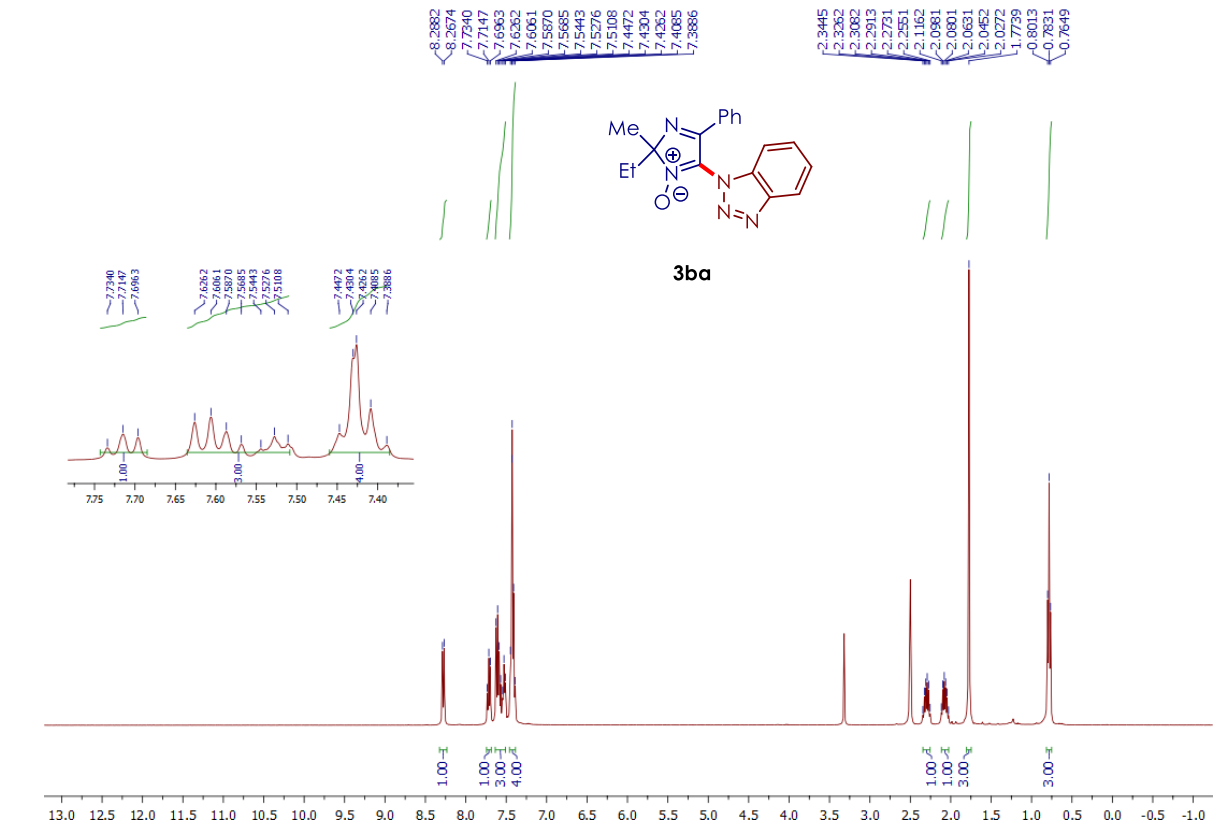

Fig. S22. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-ethyl-2-methyl-4-phenyl-2*H*-imidazole 1-oxide (**3ba**).

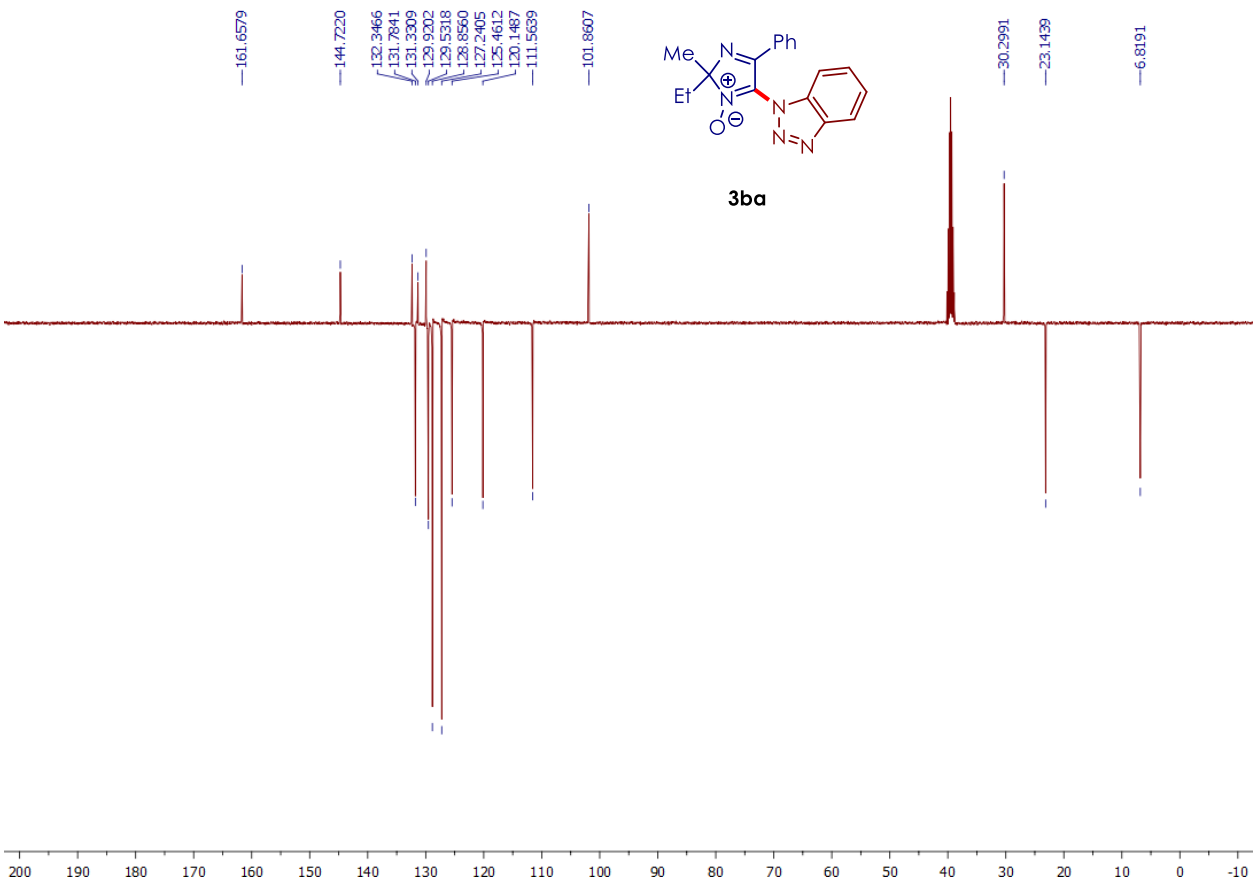

Fig. S23. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-ethyl-2-methyl-4-phenyl-2*H*-imidazole 1-oxide (**3ba**).

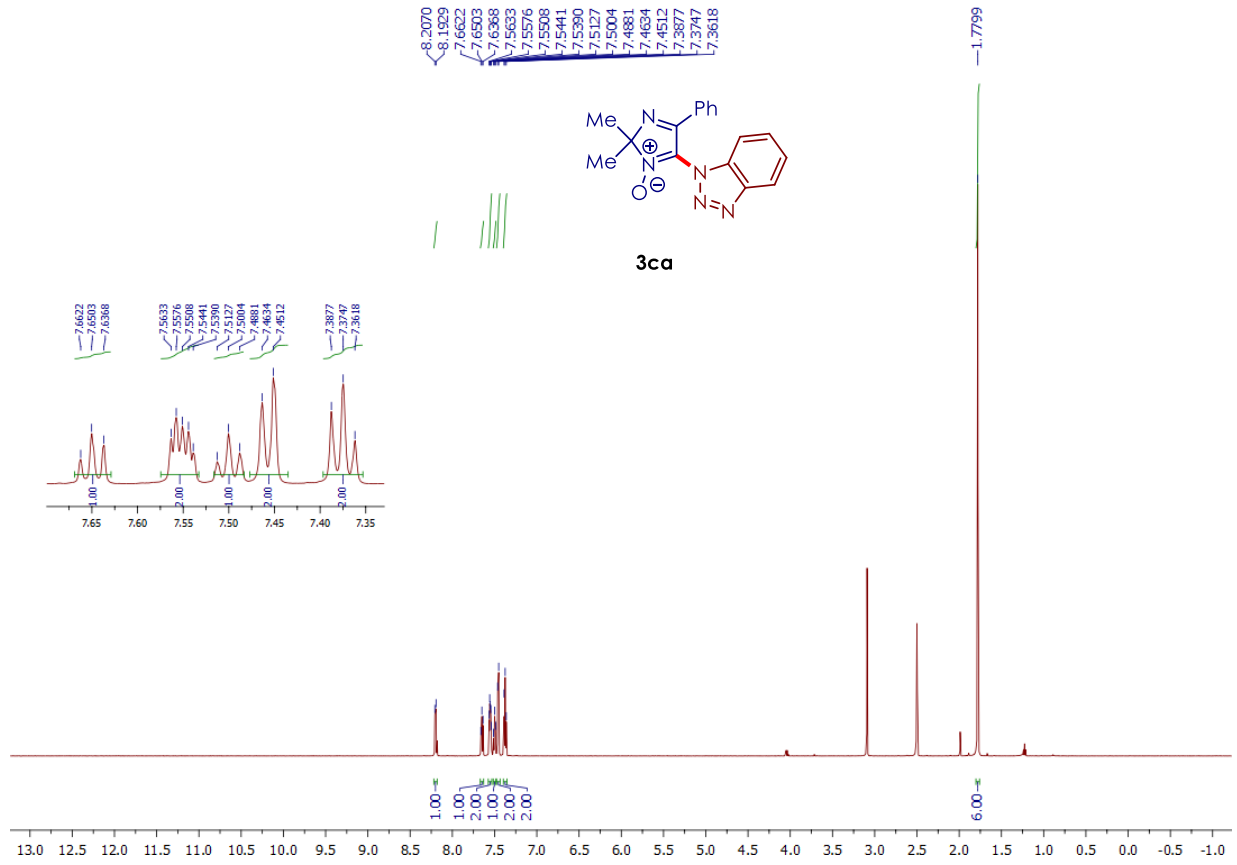

Fig. S24. ^{1}H NMR Spectrum (DMSO-d_6, 600 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-phenyl-2*H*-imidazole 1-oxide (**3ca**).

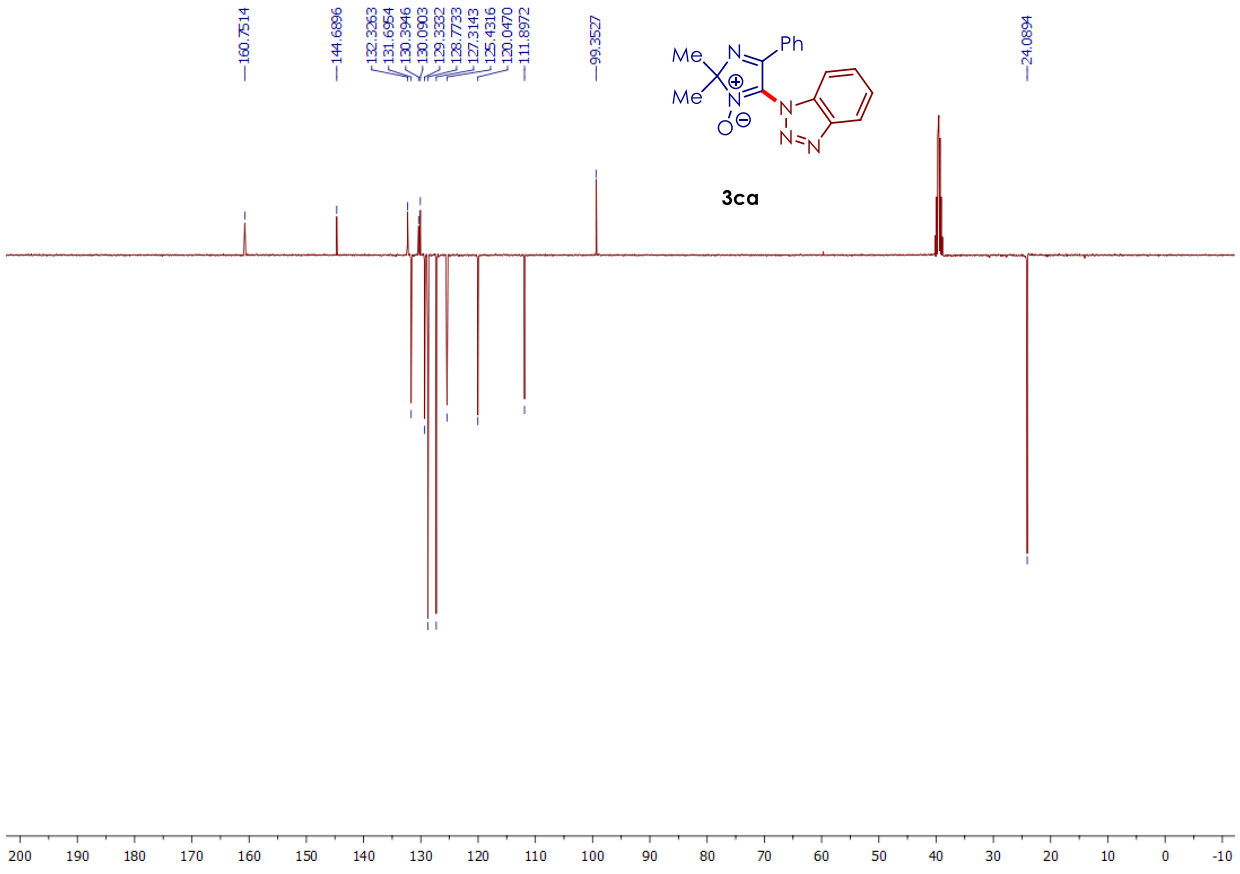

Fig. S25. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-phenyl-2*H*-imidazole 1-oxide (**3ca**).

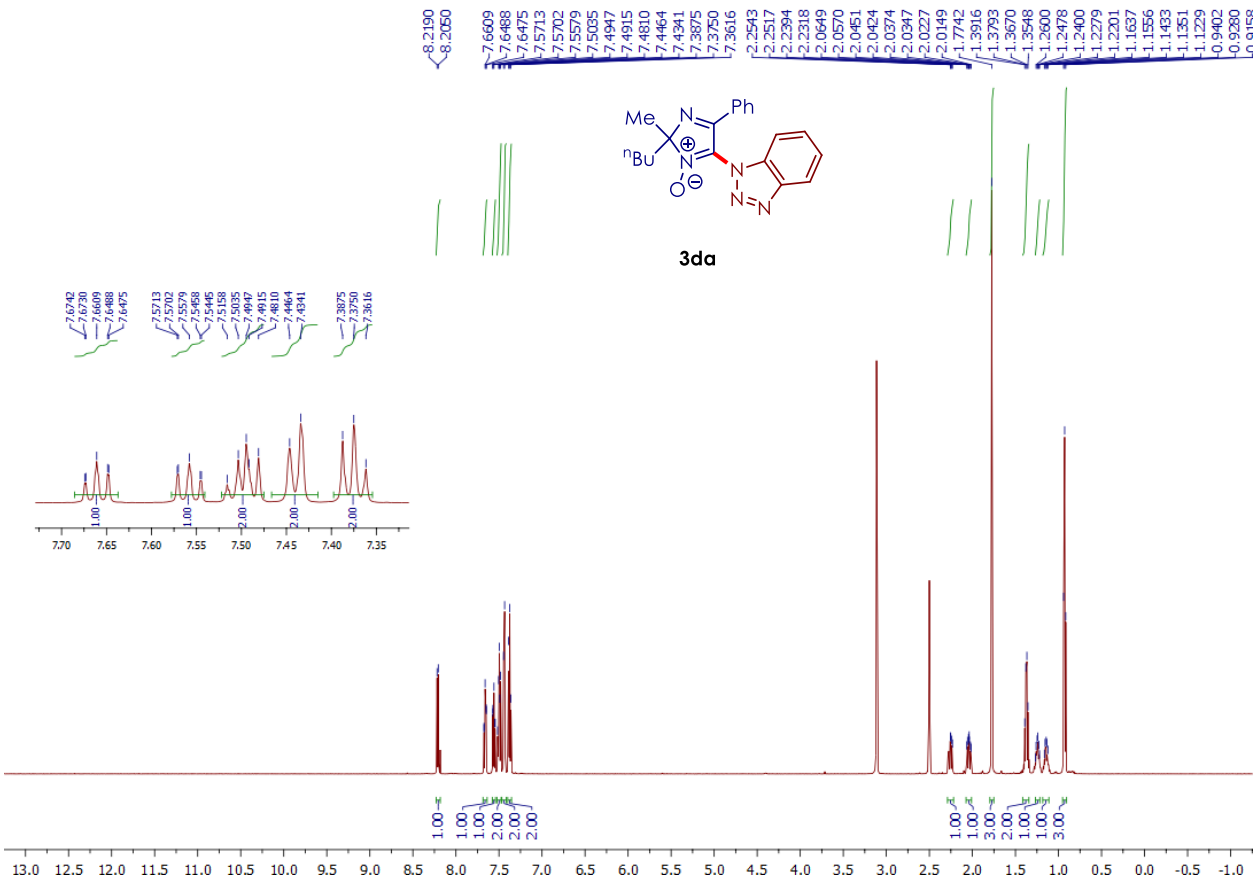

Fig. S26. ^{1}H NMR Spectrum (DMSO-d_6, 600 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-butyl-2-methyl-4-phenyl-2*H*-imidazole 1-oxide (**3da**).

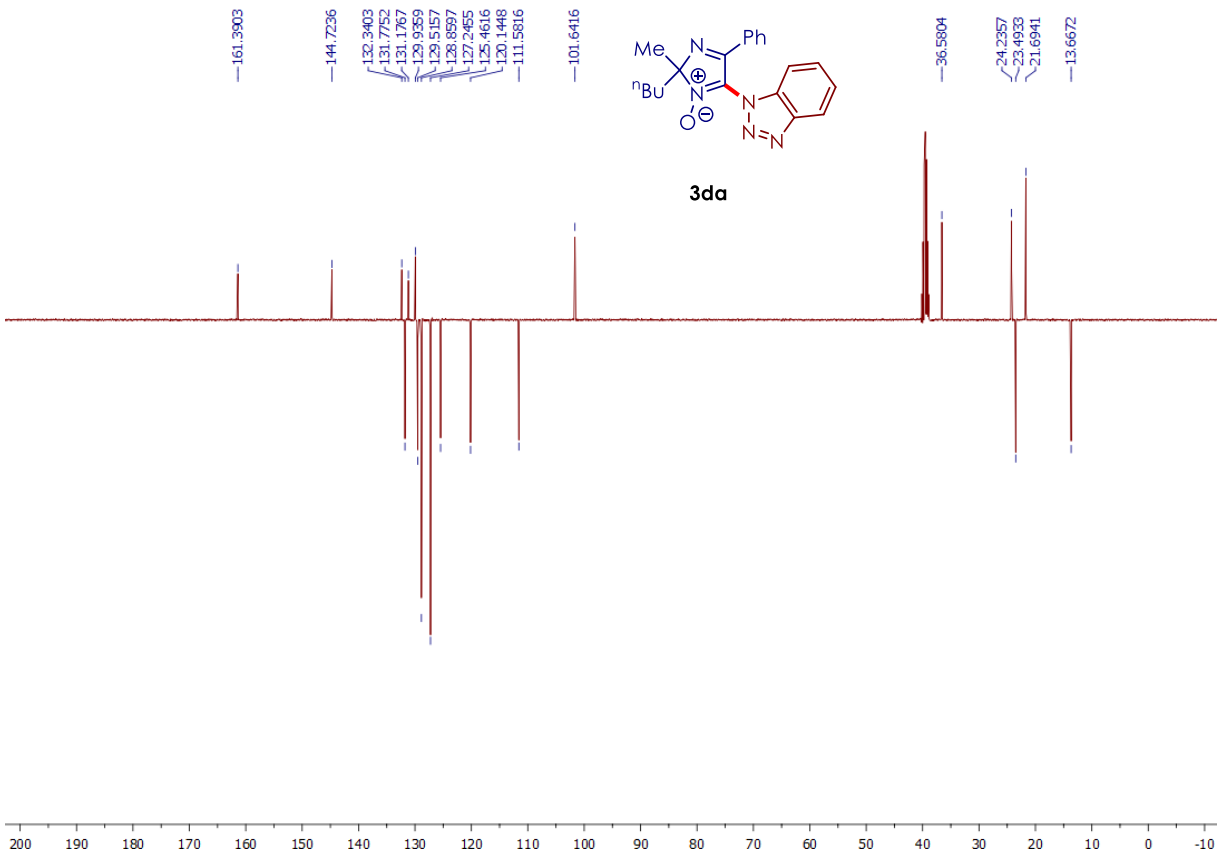

Fig. S27. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 151 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-butyl-2-methyl-4-phenyl-2*H*-imidazole 1-oxide (**3da**).

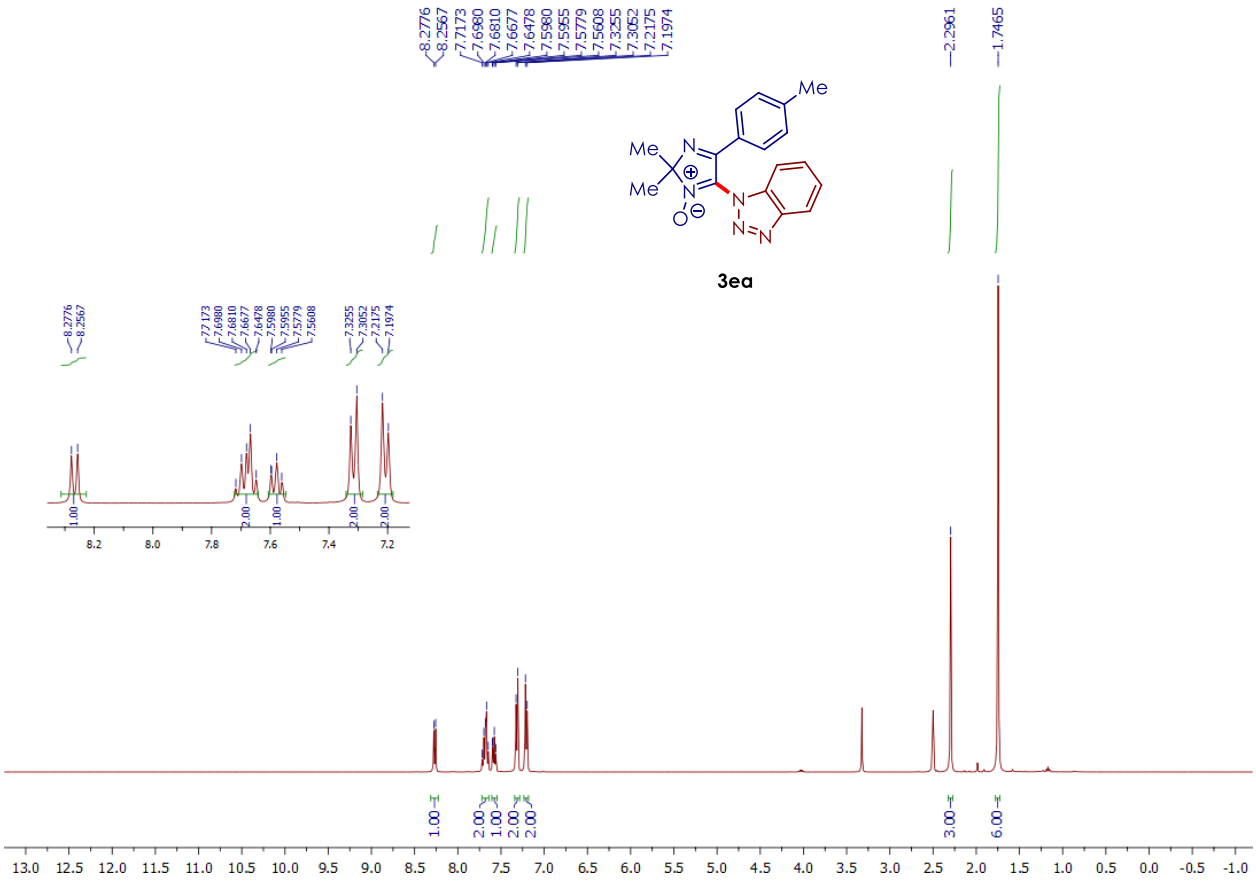

Fig. S28. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(*p*-tolyl)-2*H*-imidazole 1-oxide (**3ea**).

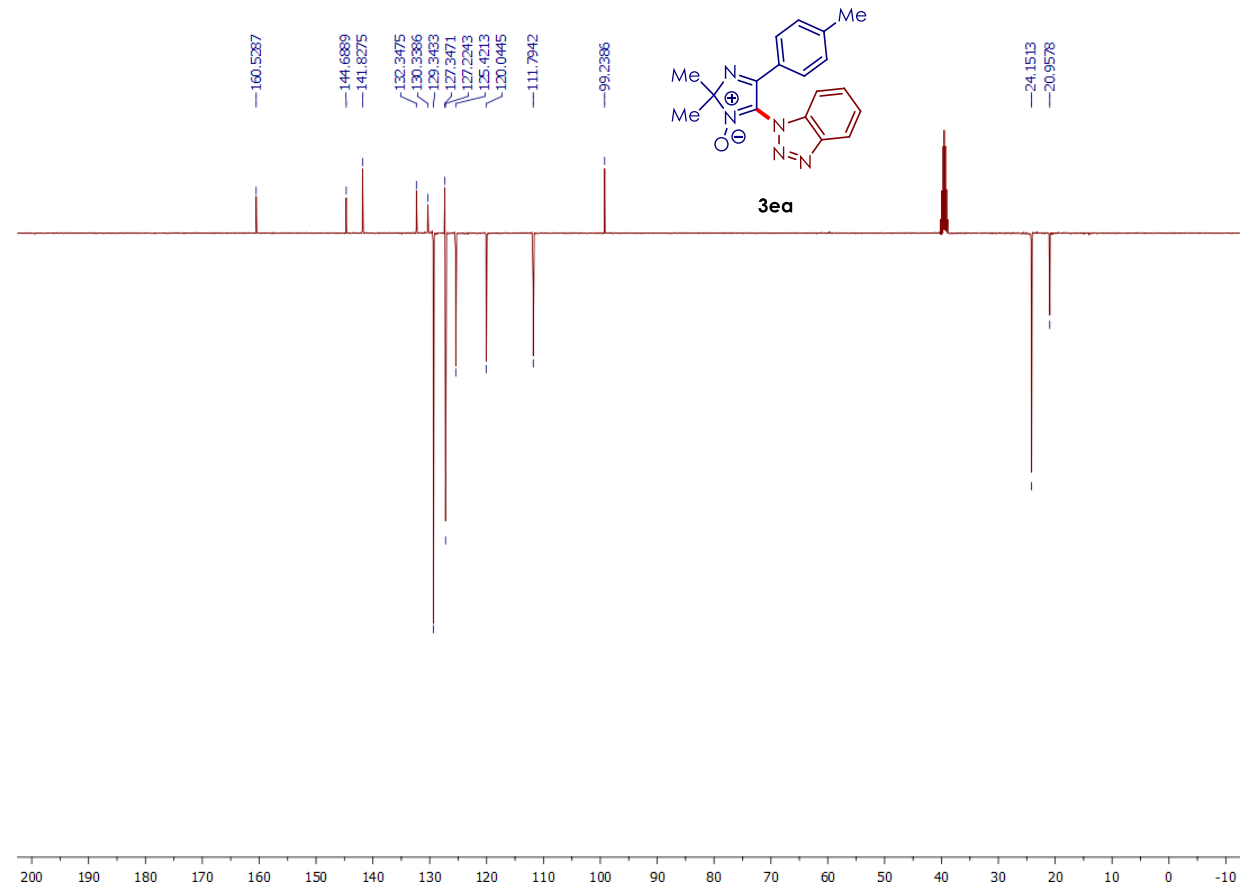

Fig. S29. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(*p*-tolyl)-2*H*-imidazole 1-oxide (**3ea**).

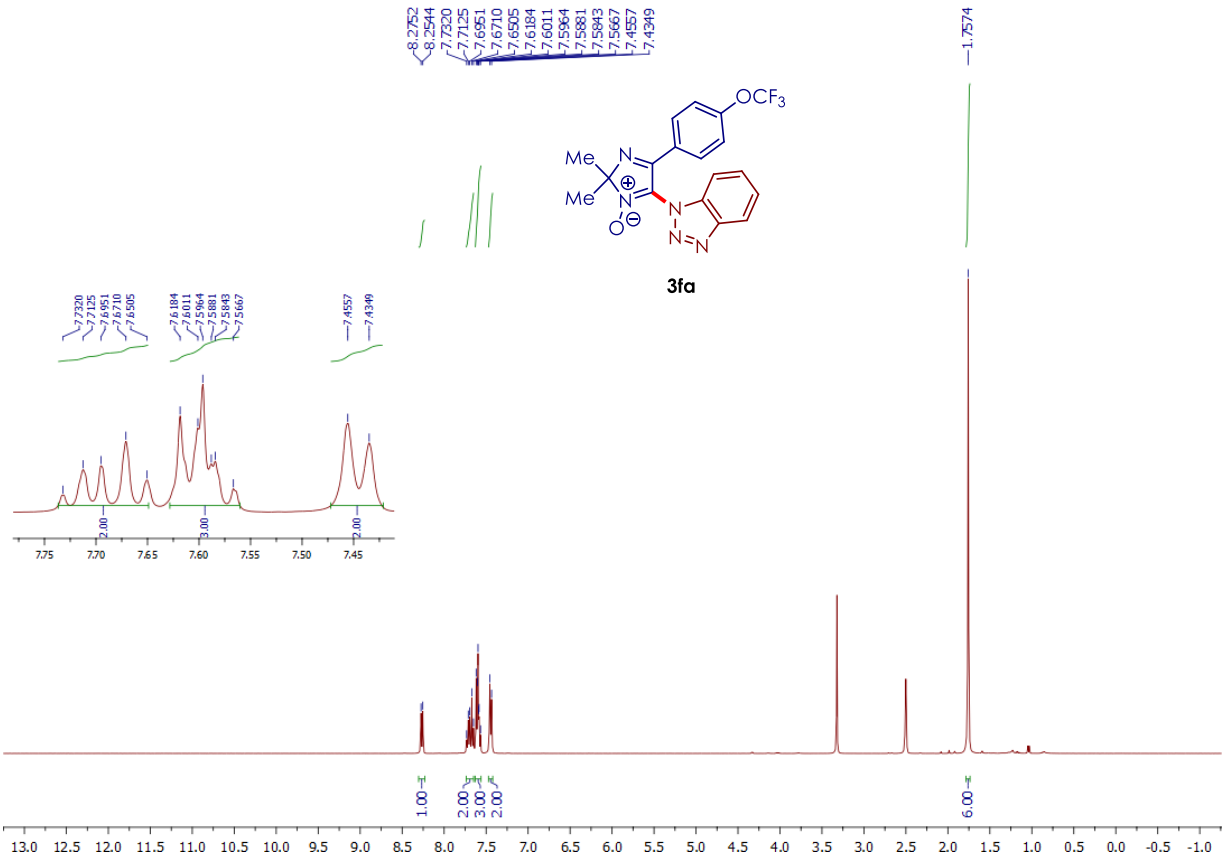

Fig. S30. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(4-(trifluoromethoxy)phenyl)-2*H*-imidazole 1-oxide (**3fa**).

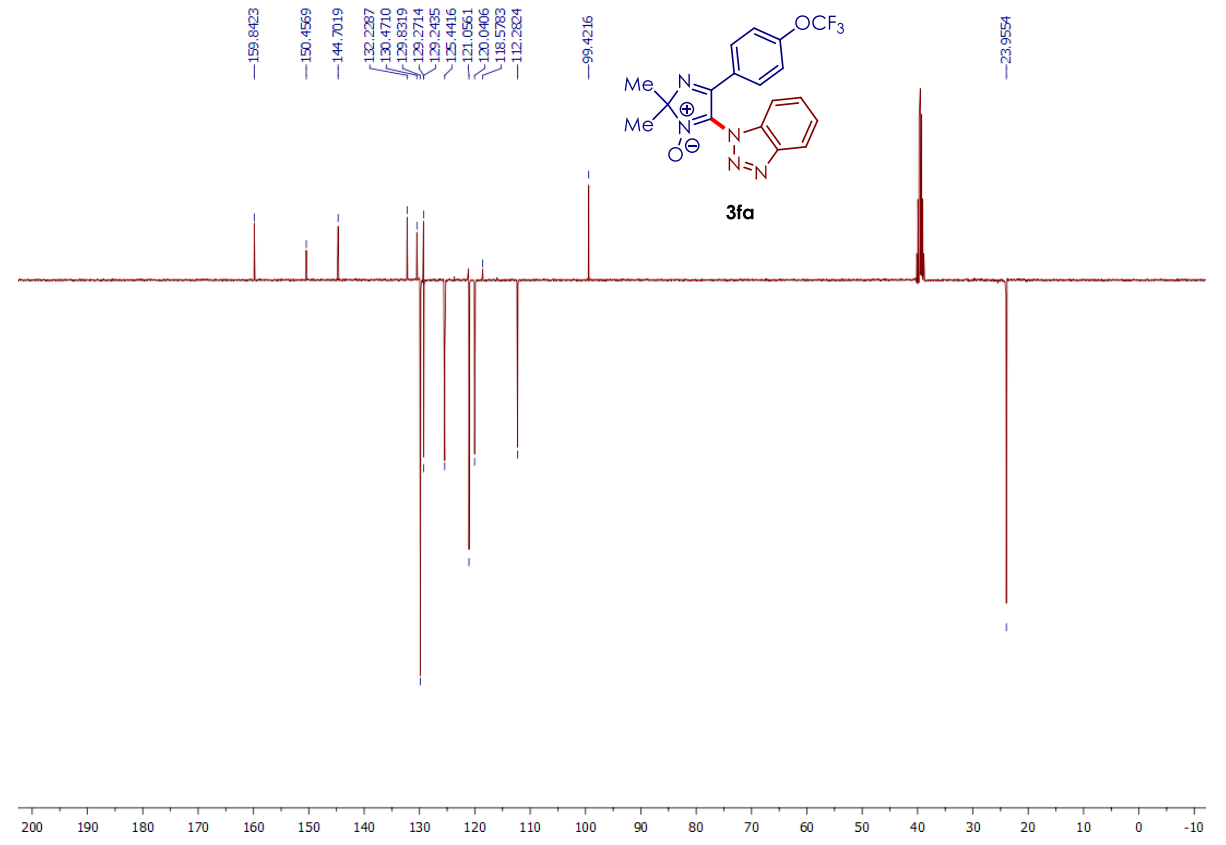

Fig. S31. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(4-(trifluoromethoxy)phenyl)-2*H*-imidazole 1-oxide (**3fa**).

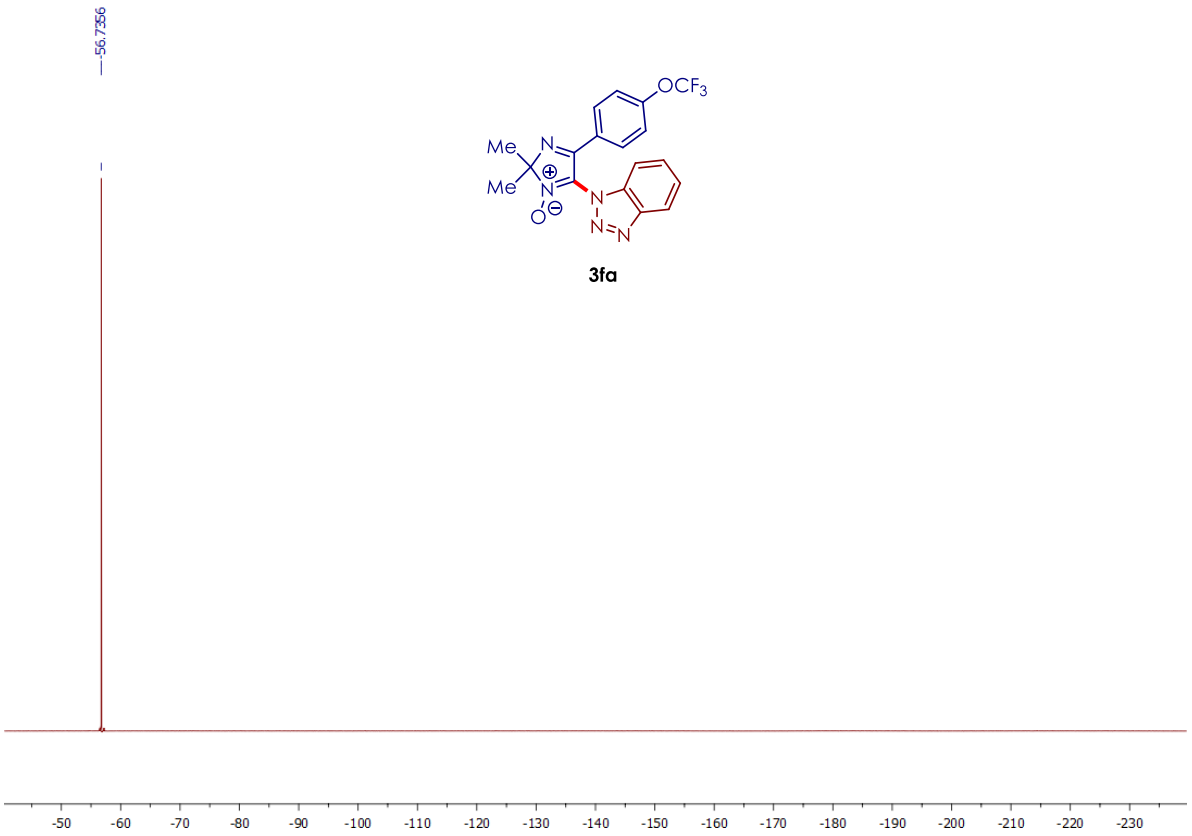

Fig. S32. ^{19}F NMR Spectrum (DMSO-d_6, 376 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(4-(trifluoromethoxy)phenyl)-2*H*-imidazole 1-oxide (**3fa**).

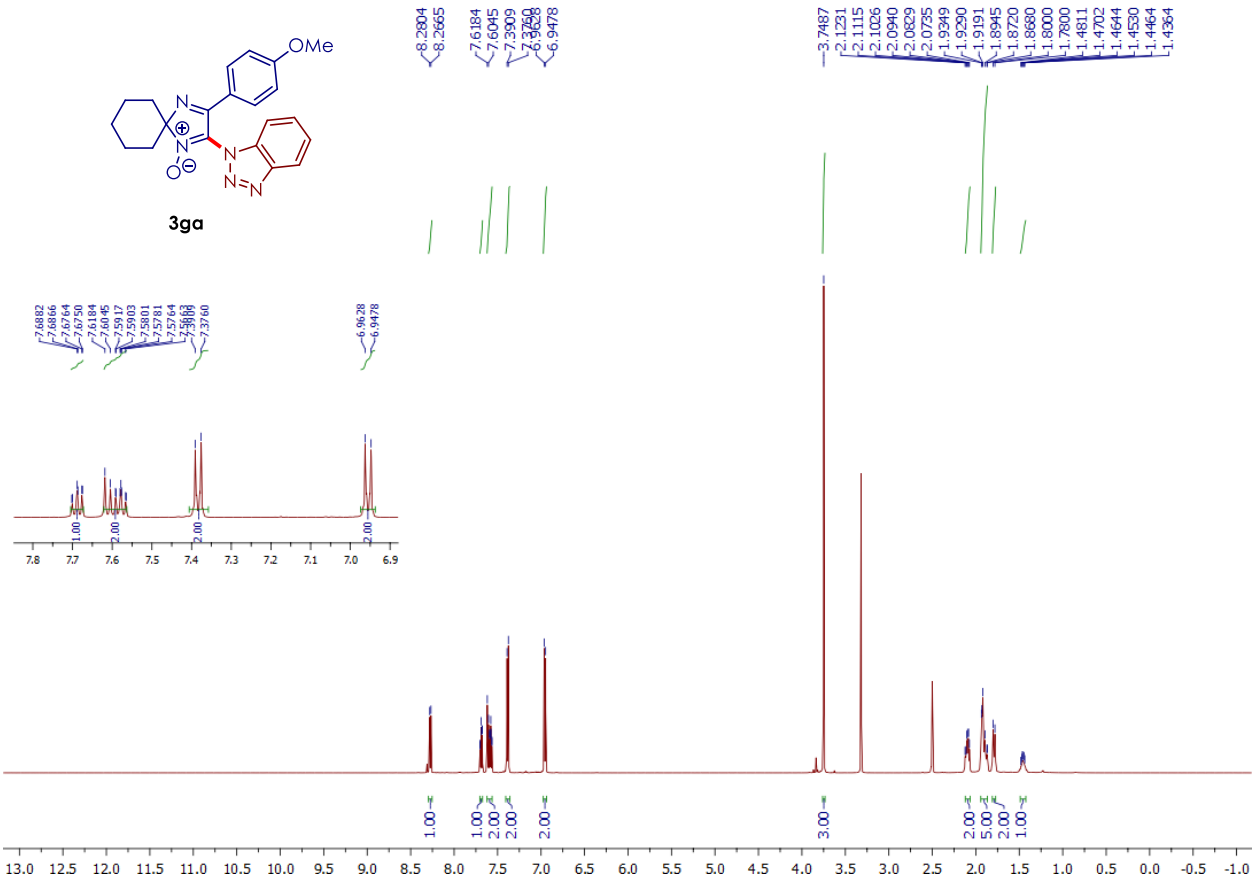

Fig. S33. ^{1}H NMR Spectrum (DMSO-d_6, 600 MHz) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-(4-methoxyphenyl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ga**).

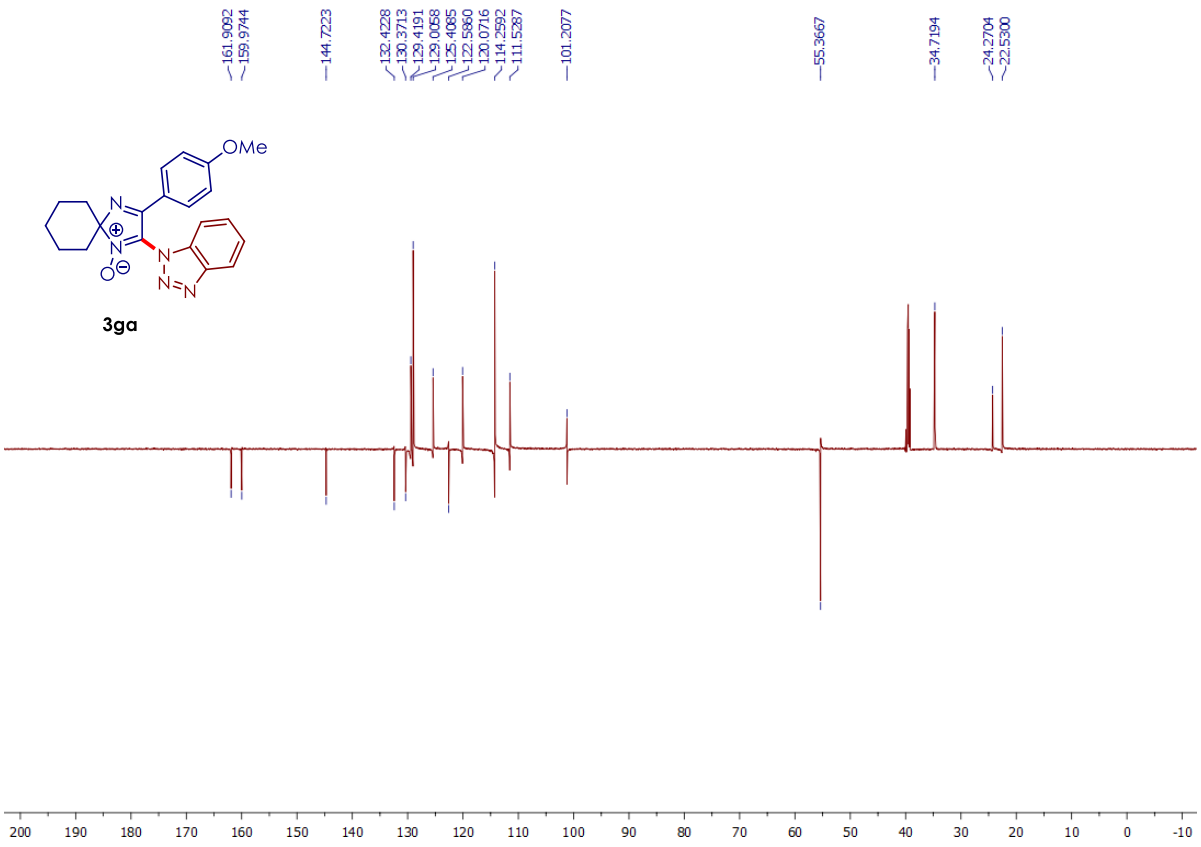

Fig. S34. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 151 MHz) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-(4-methoxyphenyl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ga**).

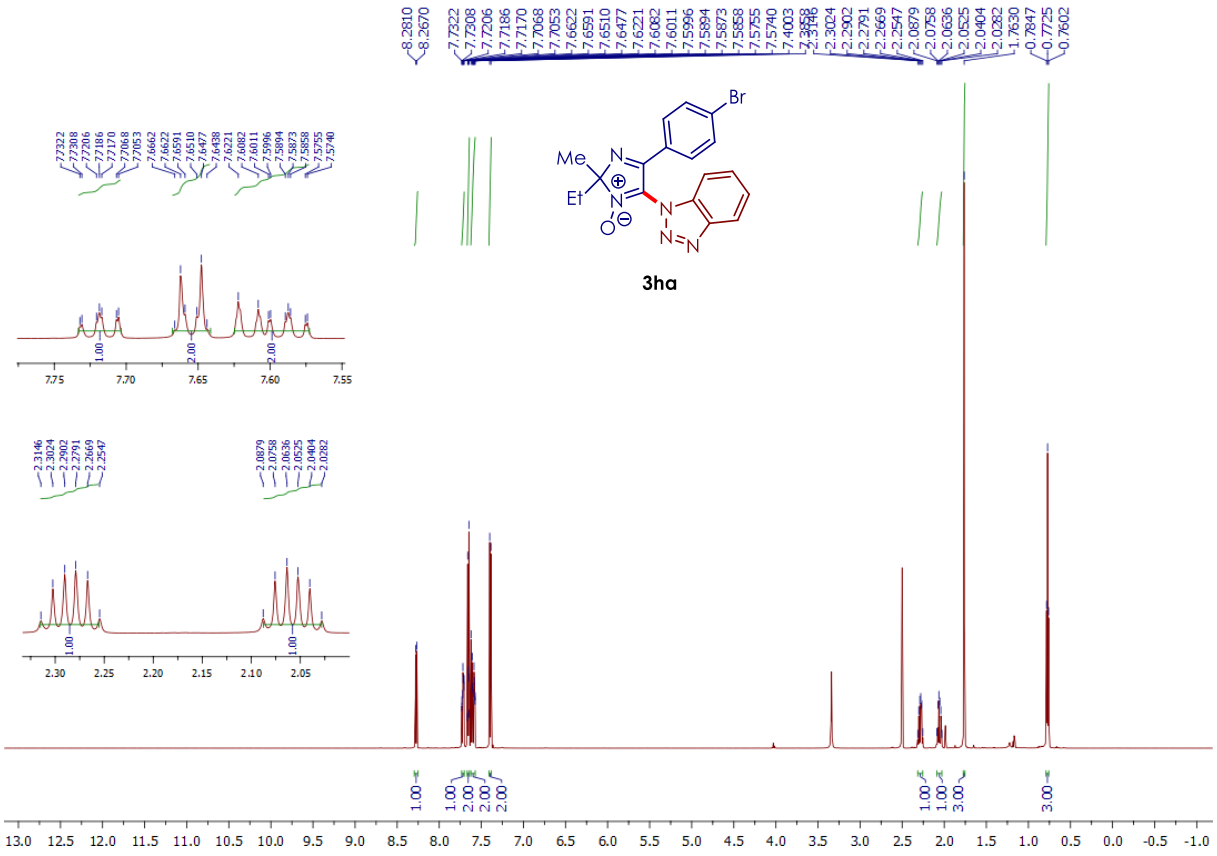

Fig. S35. ^{1}H NMR Spectrum (DMSO-d_6, 600 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-4-(4-bromophenyl)-2-ethyl-2-methyl-2*H*-imidazole 1-oxide (**3ha**).

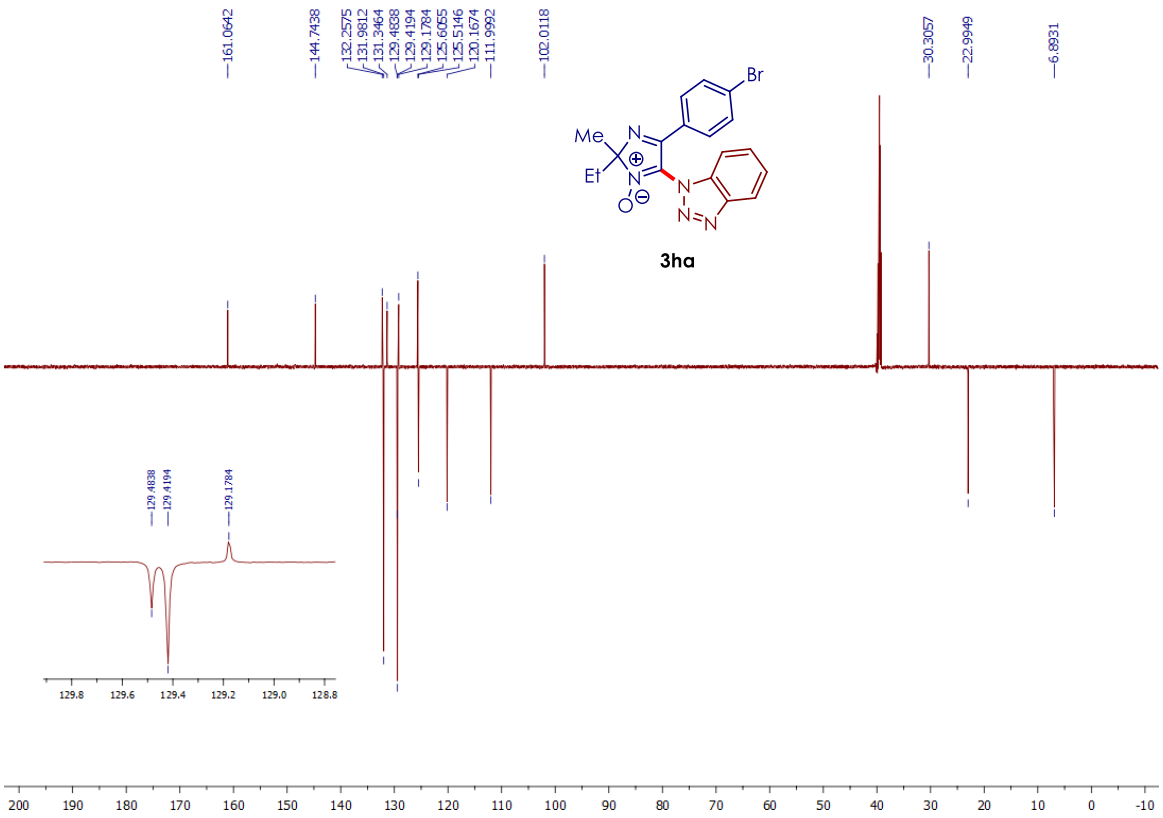

Fig. S36. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 151 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-4-(4-bromophenyl)-2-ethyl-2-methyl-2*H*-imidazole 1-oxide (**3ha**).

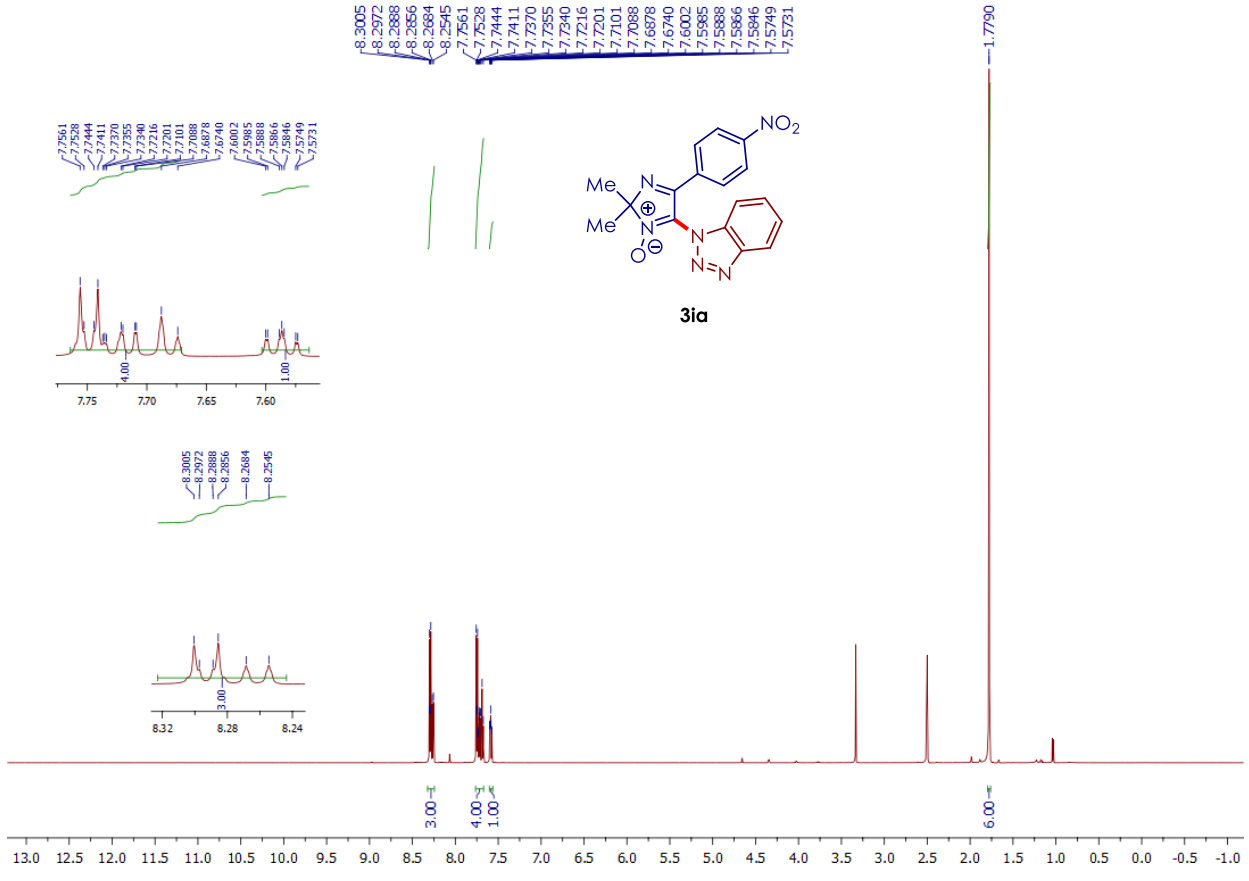

Fig. S37. ^{1}H NMR Spectrum (DMSO-d_6, 600 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(4-nitrophenyl)-2*H*-imidazole 1-oxide (**3ia**).

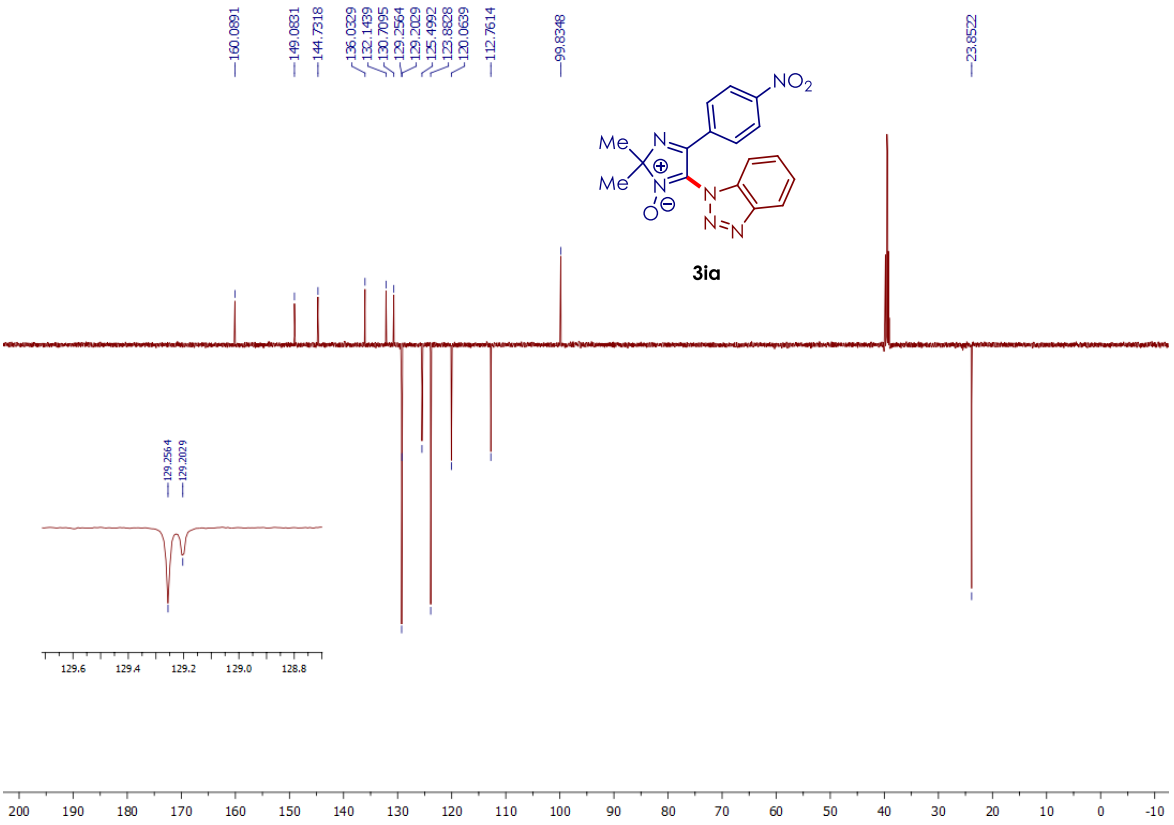

Fig. S38. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 151 MHz) of 5-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,2-dimethyl-4-(4-nitrophenyl)-2*H*-imidazole 1-oxide (**3ia**).

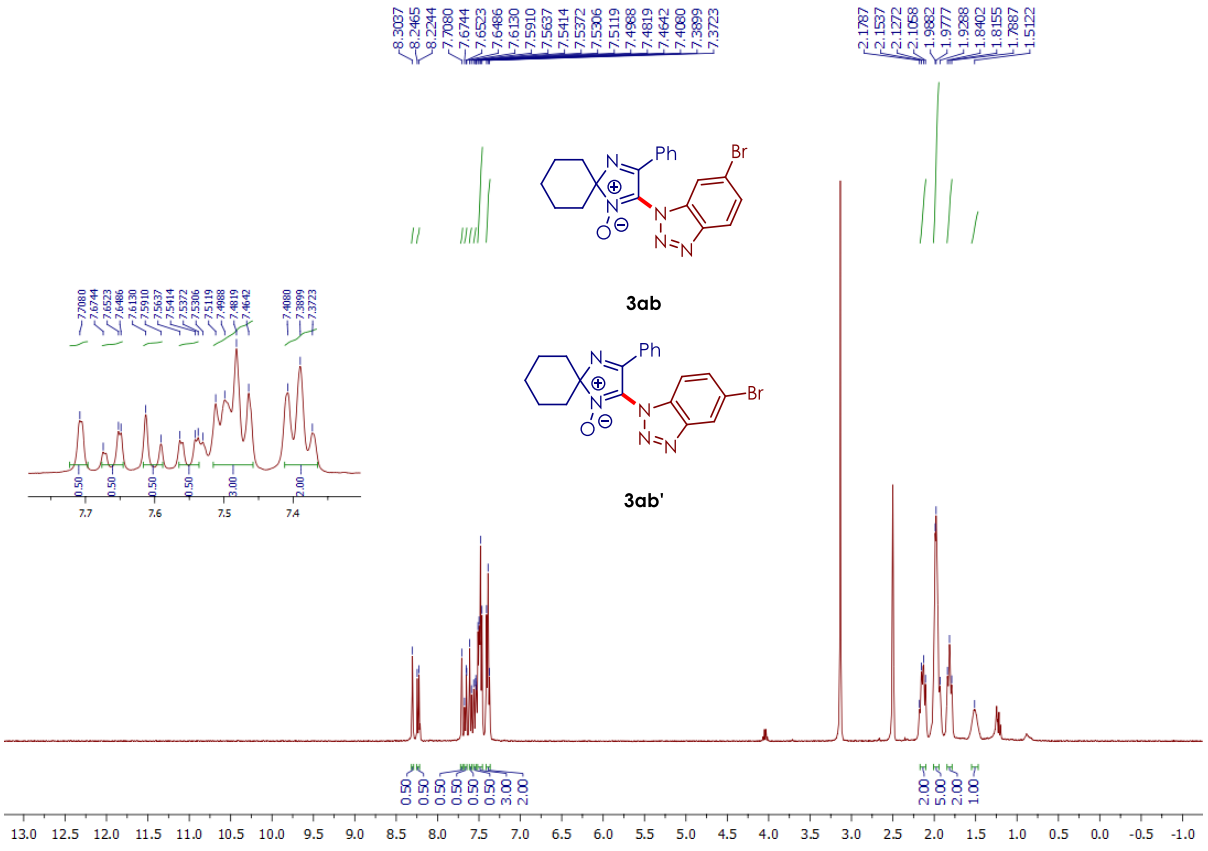

Fig. S39. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of regioisomeric mixture of 2-(6-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ab**) and 2-(5-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ab'**).

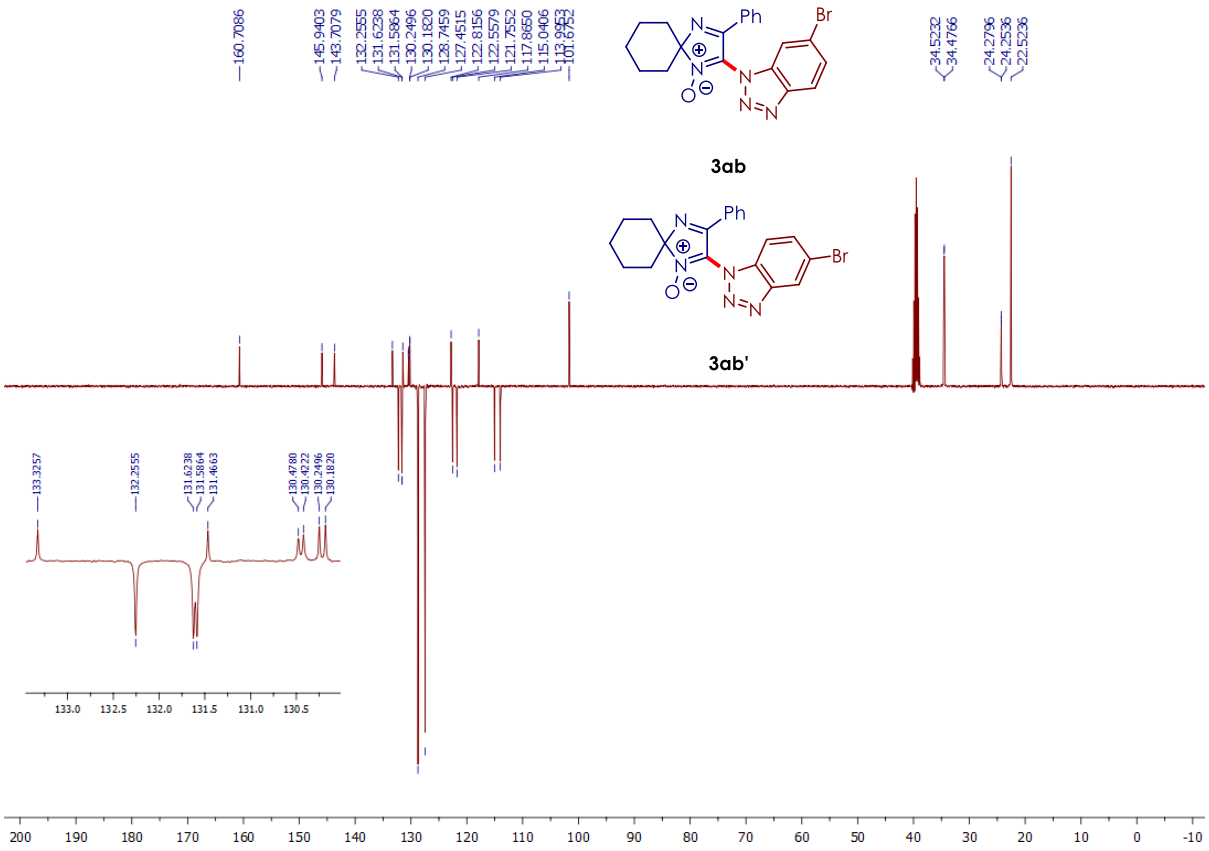

Fig. S40. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of regioisomeric mixture of 2-(6-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ab**) and 2-(5-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ab'**).

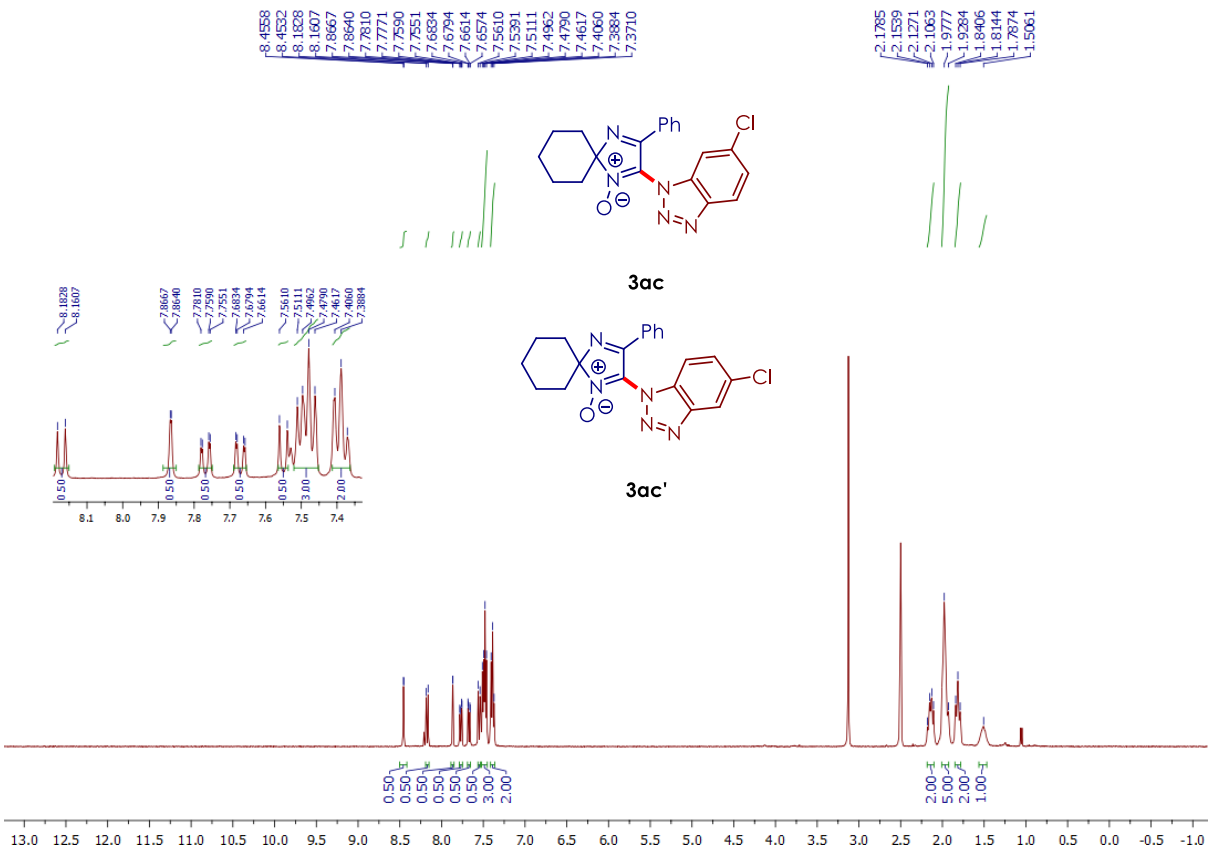

Fig. S41. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of regioisomeric mixture of 2-(6-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ac**) and 2-(5-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ac'**).

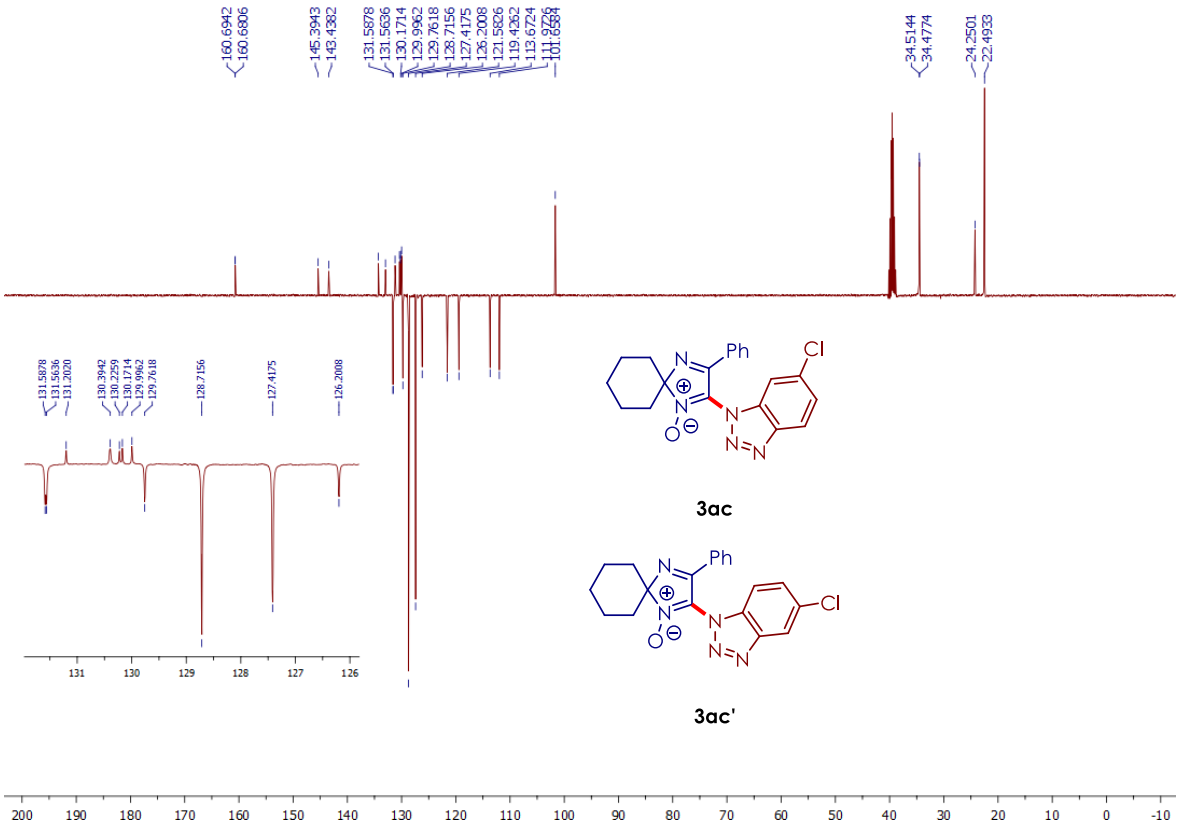

Fig. S42. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of regioisomeric mixture of 2-(6-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ac**) and 2-(5-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ac'**).

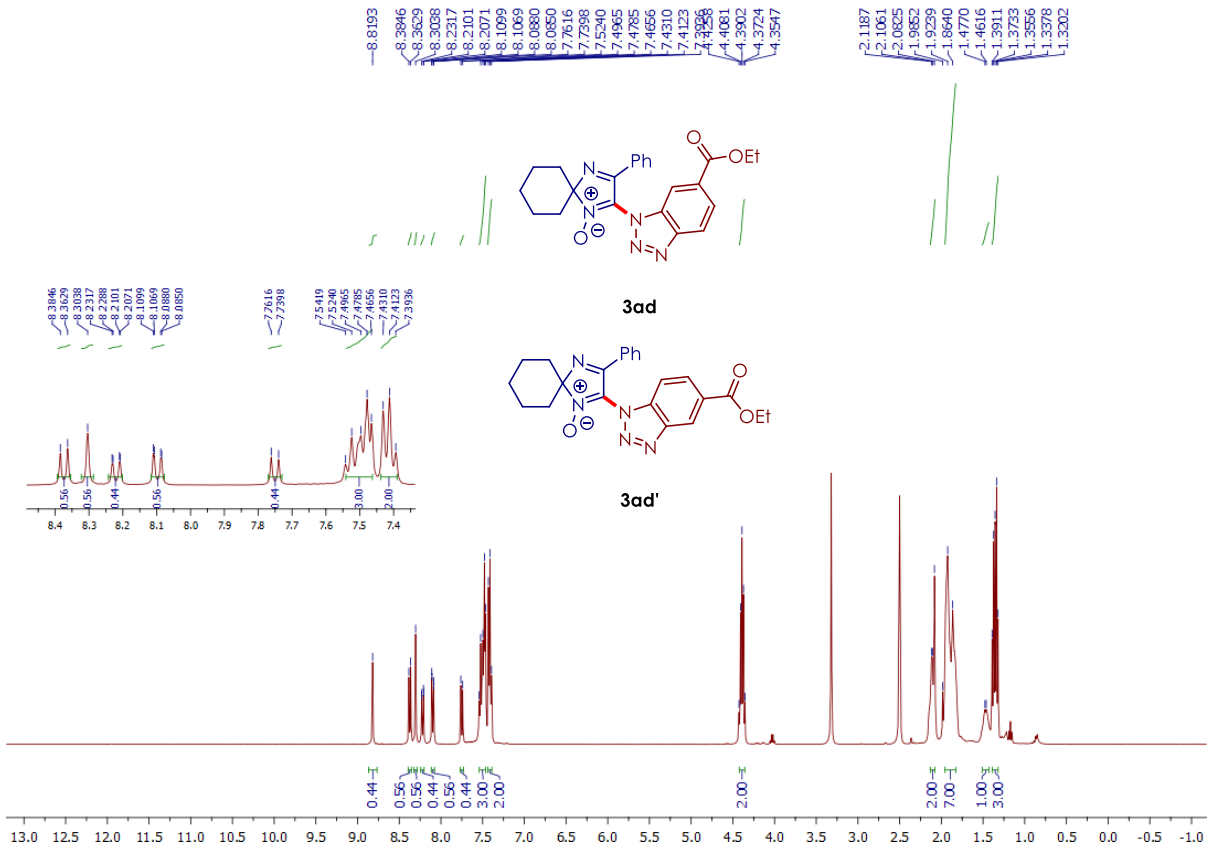

Fig. S43. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of regioisomeric mixture of 2-(6-(ethoxycarbonyl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ad**) and 2-(5-(ethoxycarbonyl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ad'**).

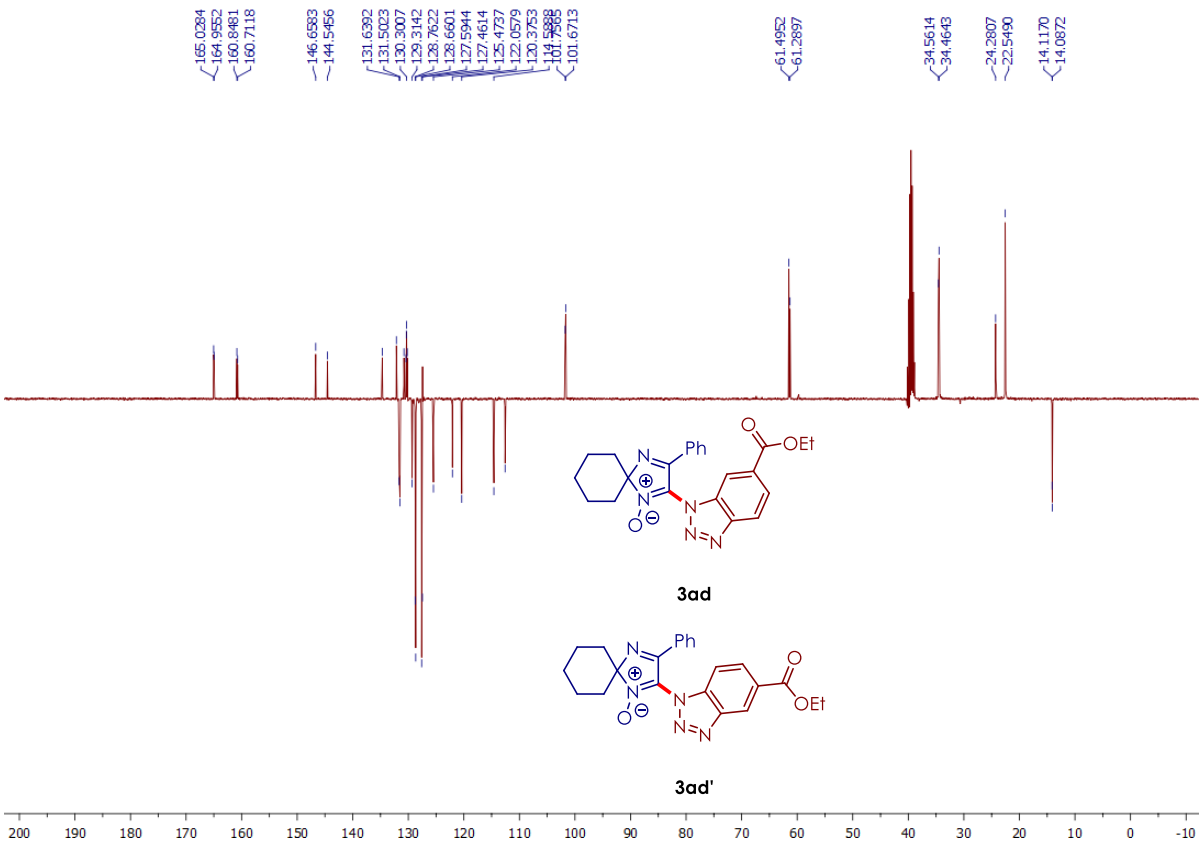

Fig. S44. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of regioisomeric mixture of 2-(6-(ethoxycarbonyl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ad**) and 2-(5-(ethoxycarbonyl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ad'**).

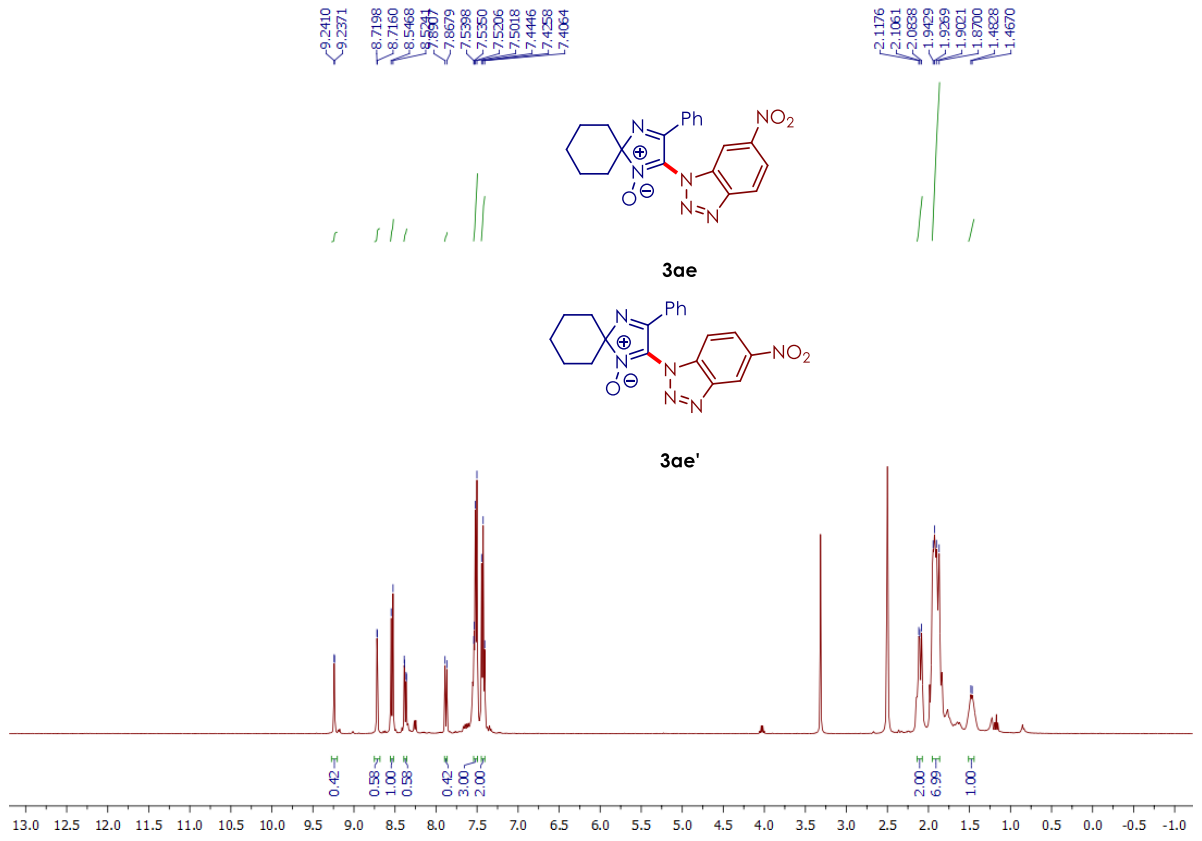

Fig. S45. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of regioisomeric mixture of 2-(6-nitro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ae**) and 2-(5-nitro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ae'**).

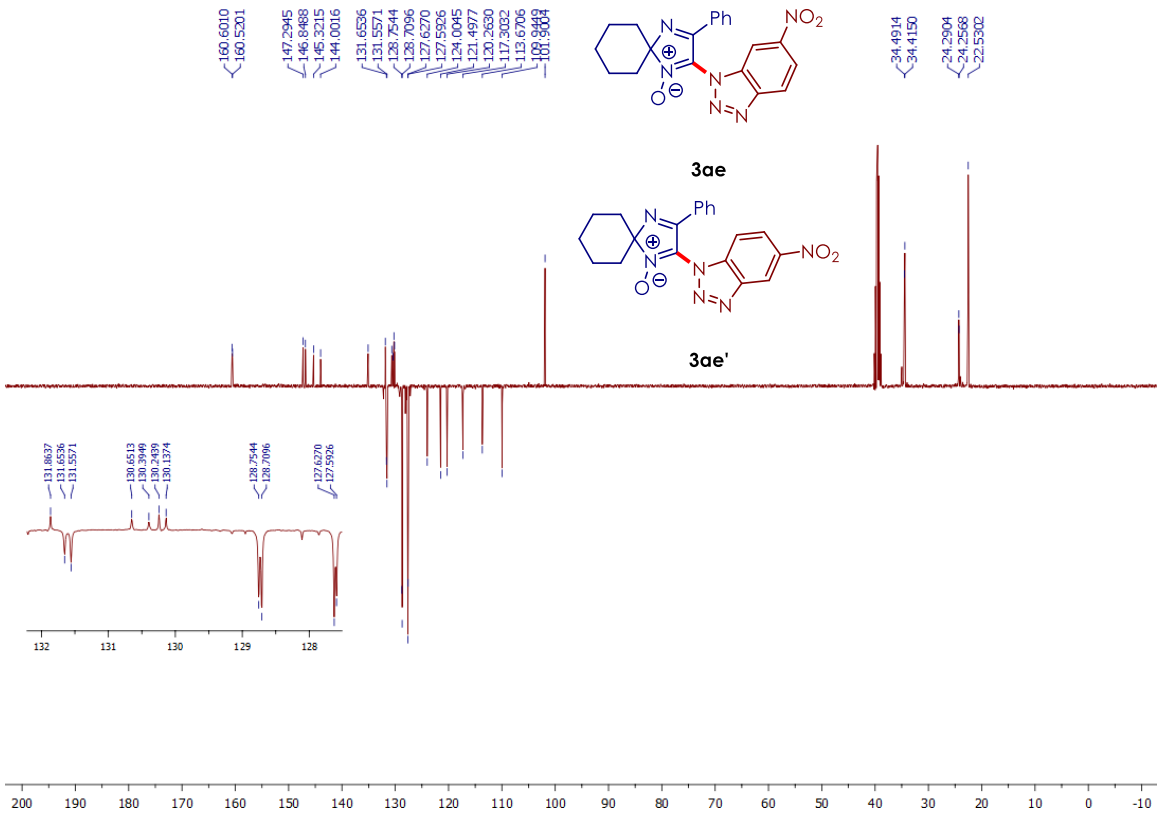

Fig. S46. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of regioisomeric mixture of 2-(6-nitro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ae**) and 2-(5-nitro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ae'**).

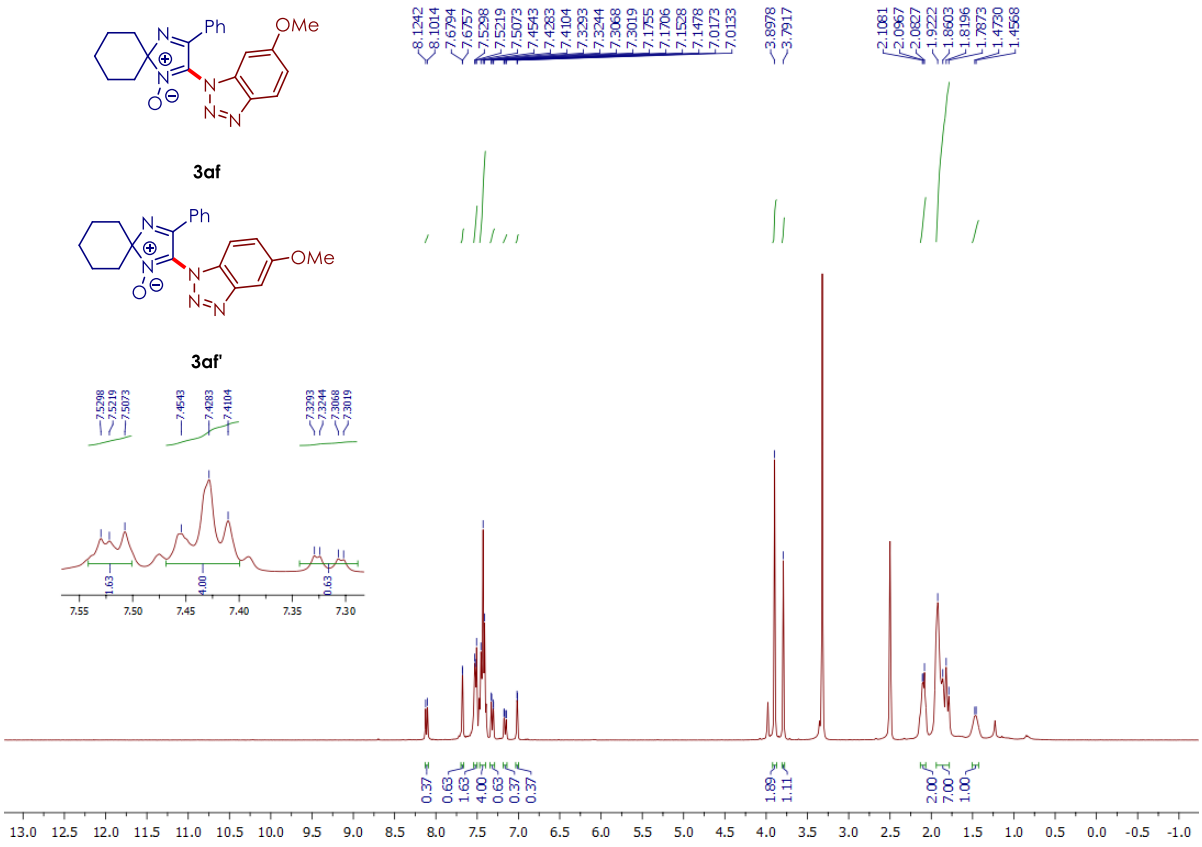

Fig. S47. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of regioisomeric mixture of 2-(6-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3af**) and 2-(5-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3af'**).

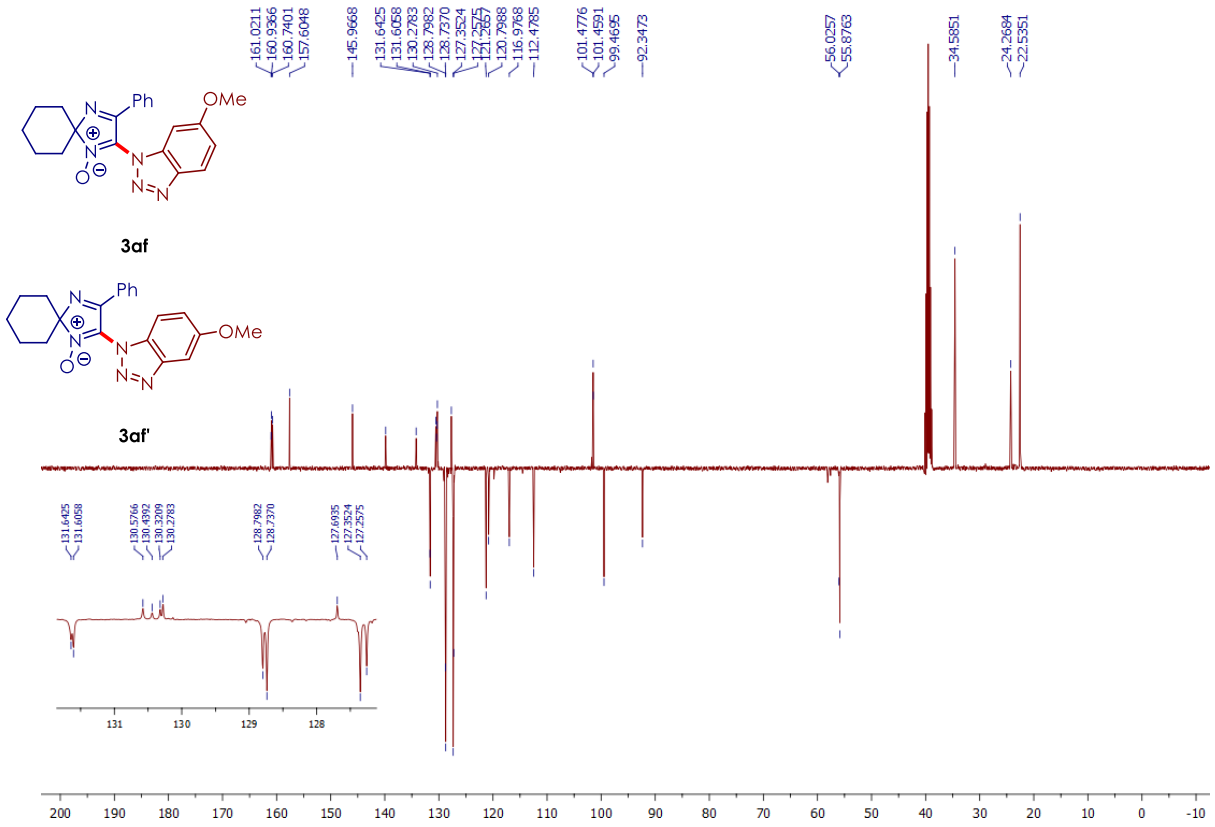

Fig. S48. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of regioisomeric mixture of 2-(6-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3af**) and 2-(5-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3af'**).

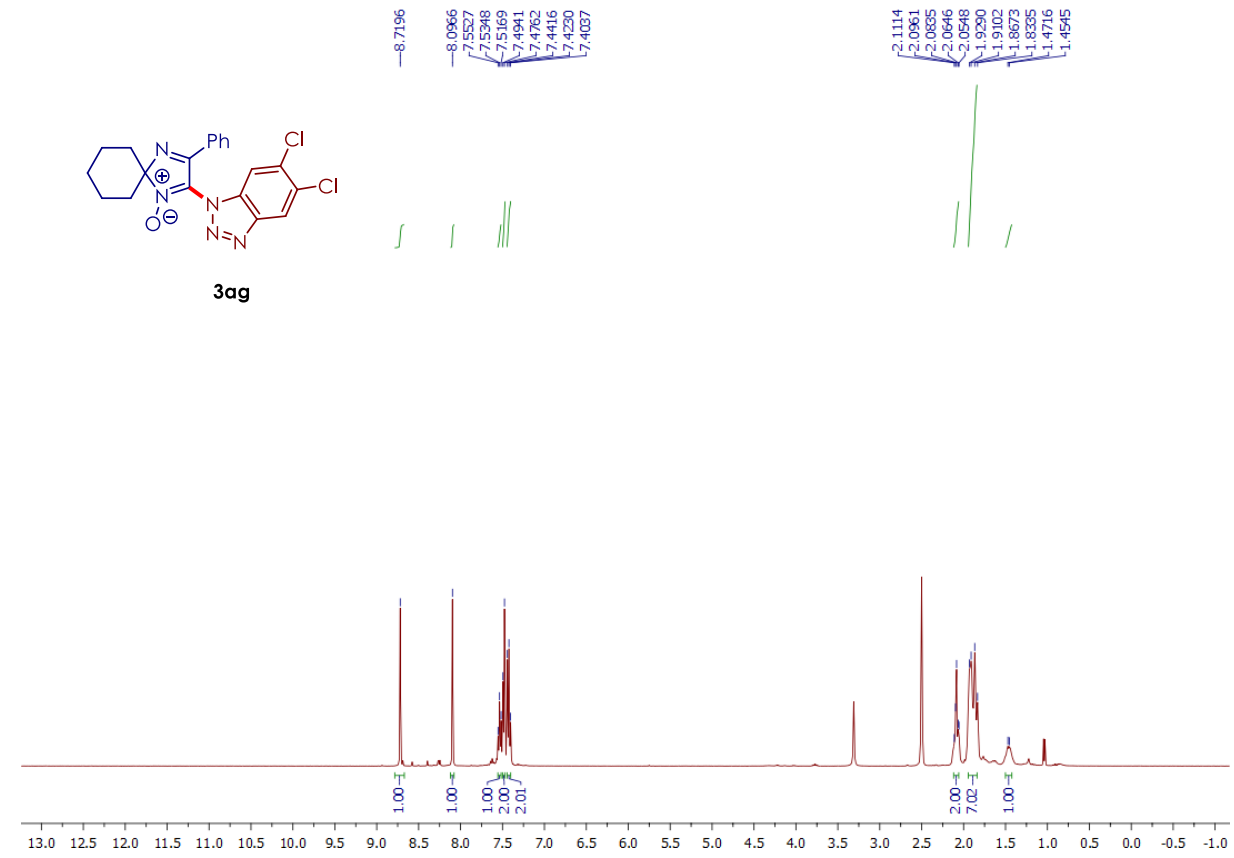

Fig. S49. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 2-(5,6-dichloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ag**).

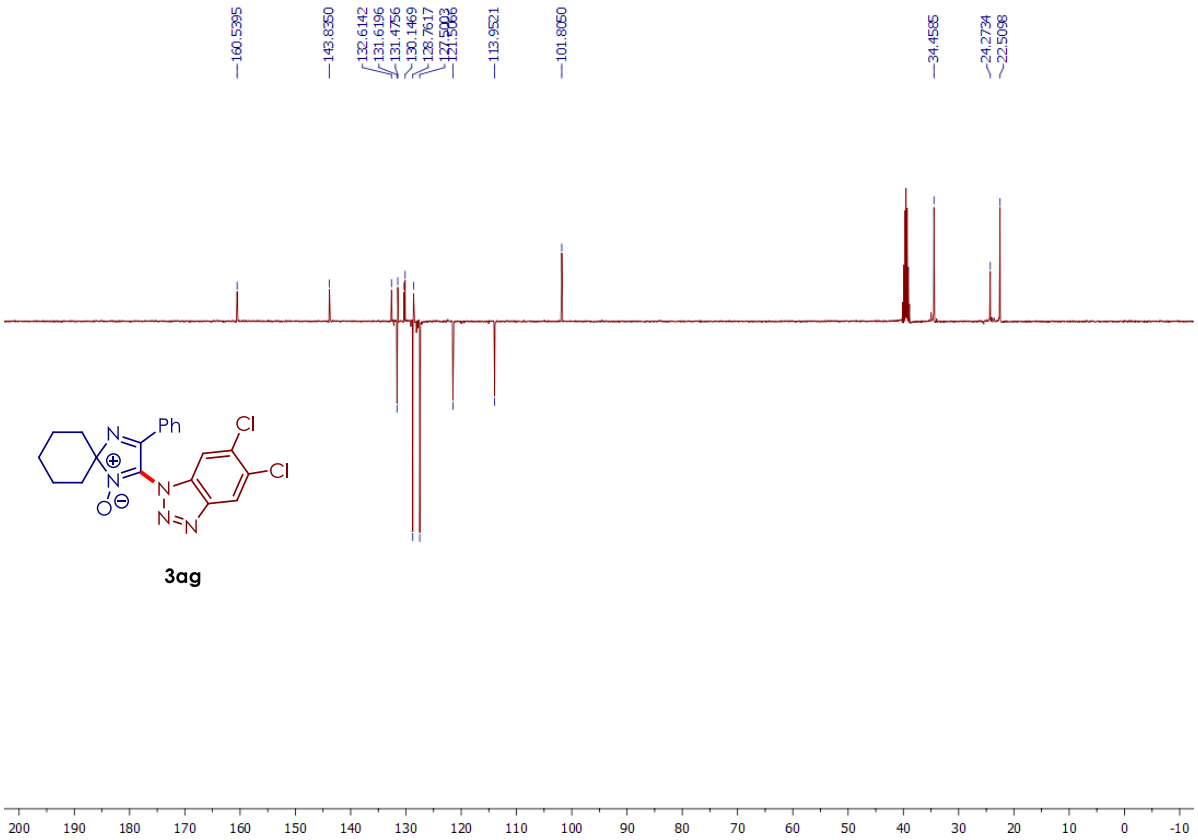

Fig. S50. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 2-(5,6-dichloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ag**).

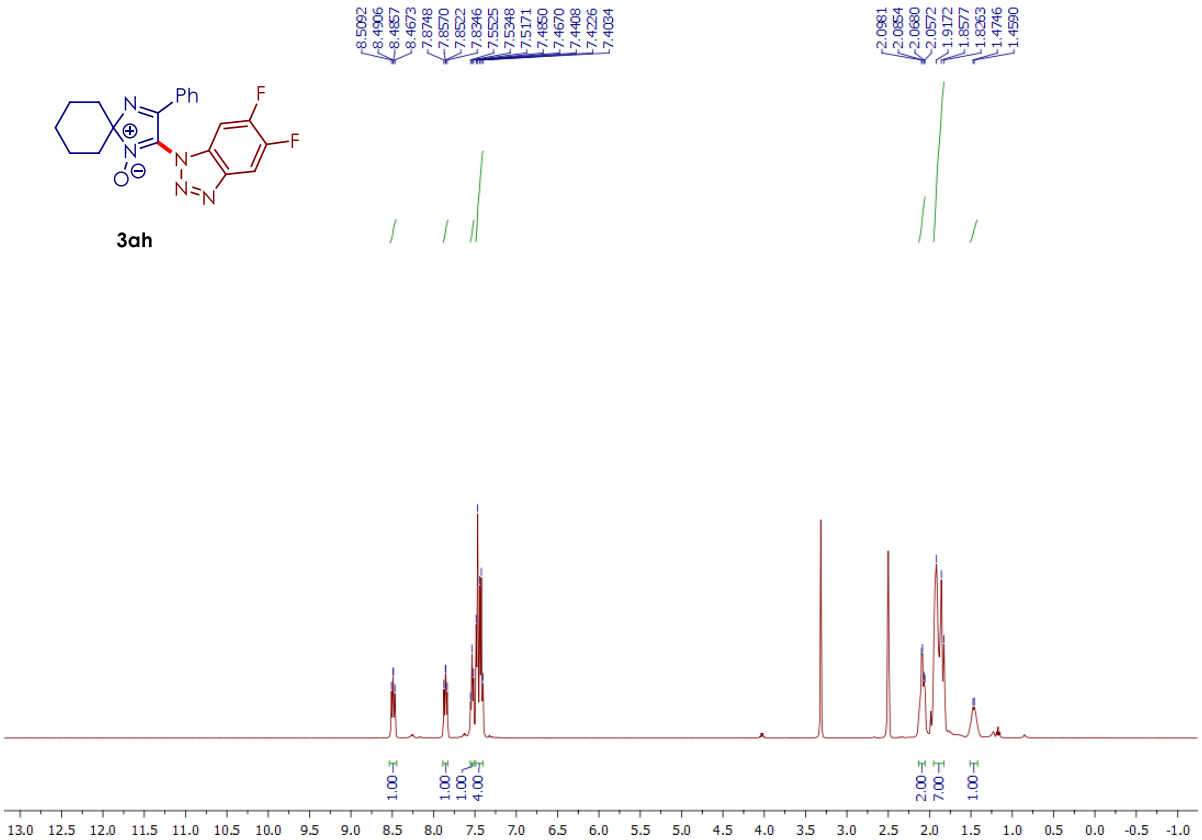

Fig. S51. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 2-(5,6-difluoro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ah**).

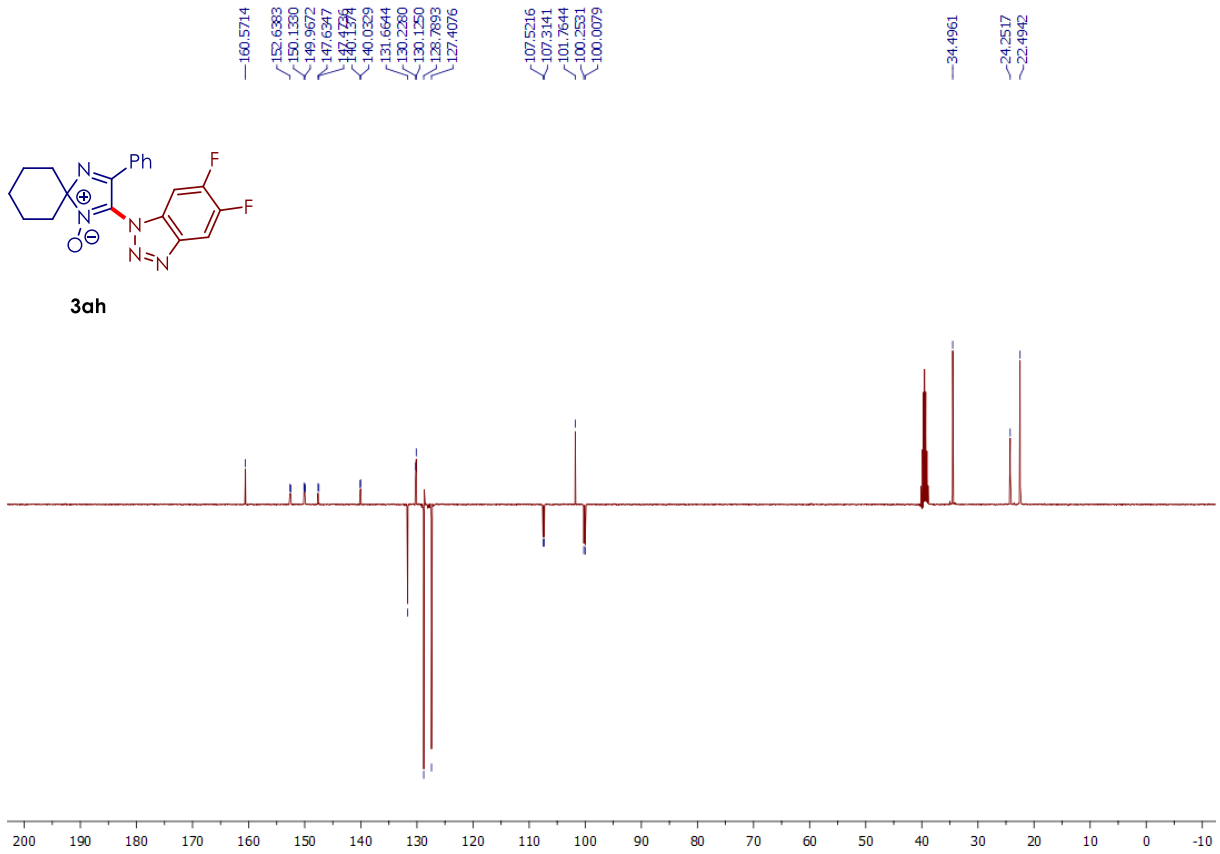

Fig. S52. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 2-(5,6-difluoro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ah**).

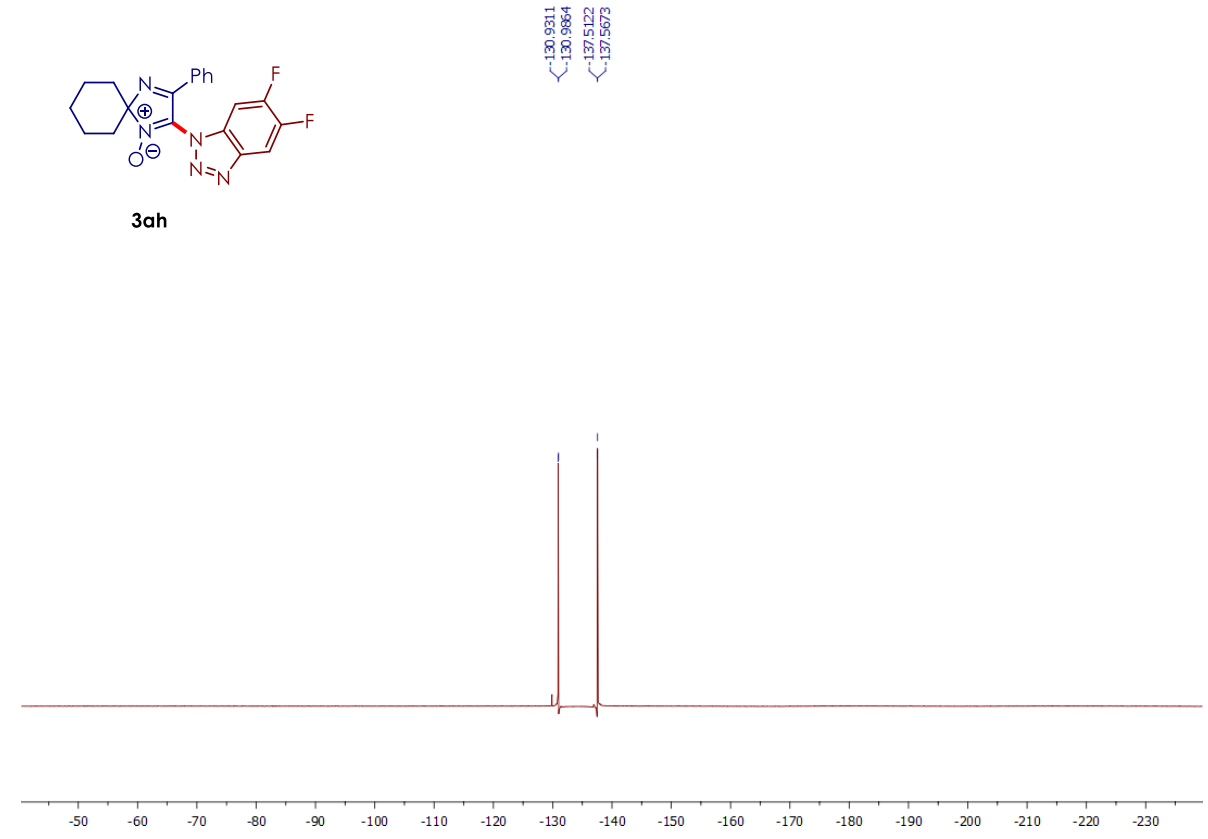

Fig. S53. ^{19}F NMR Spectrum (DMSO-d_6, 376 MHz) of 2-(5,6-difluoro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ah**).

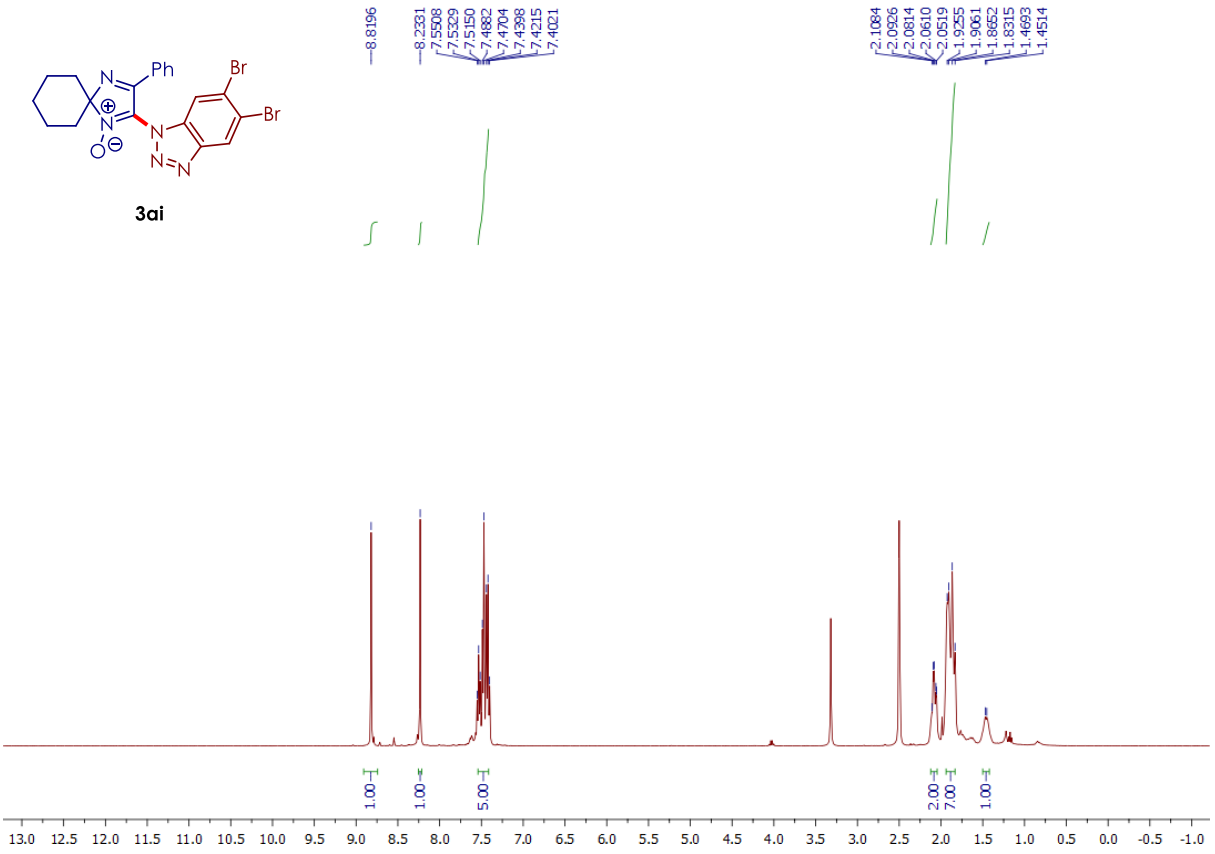

Fig. S54. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 2-(5,6-dibromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ai**).

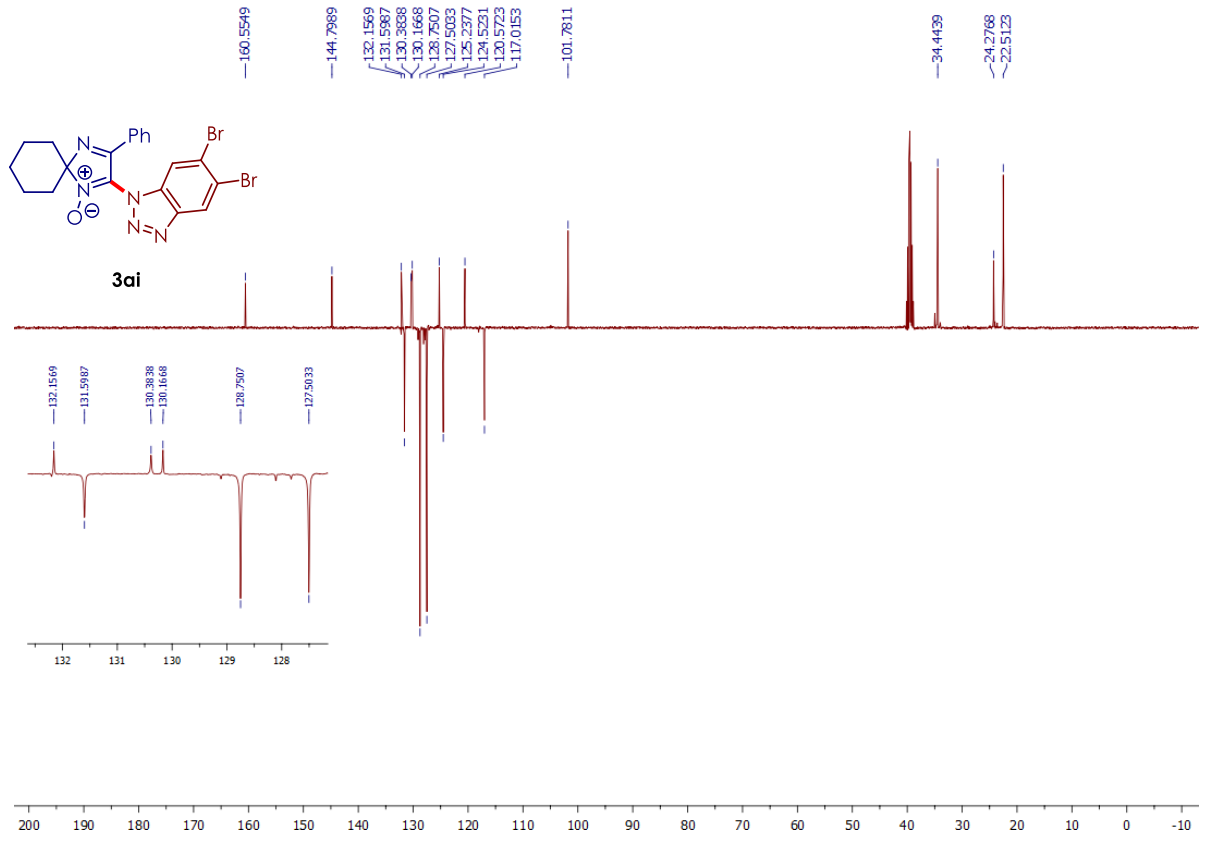

Fig. S55. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 2-(5,6-dibromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ai**).

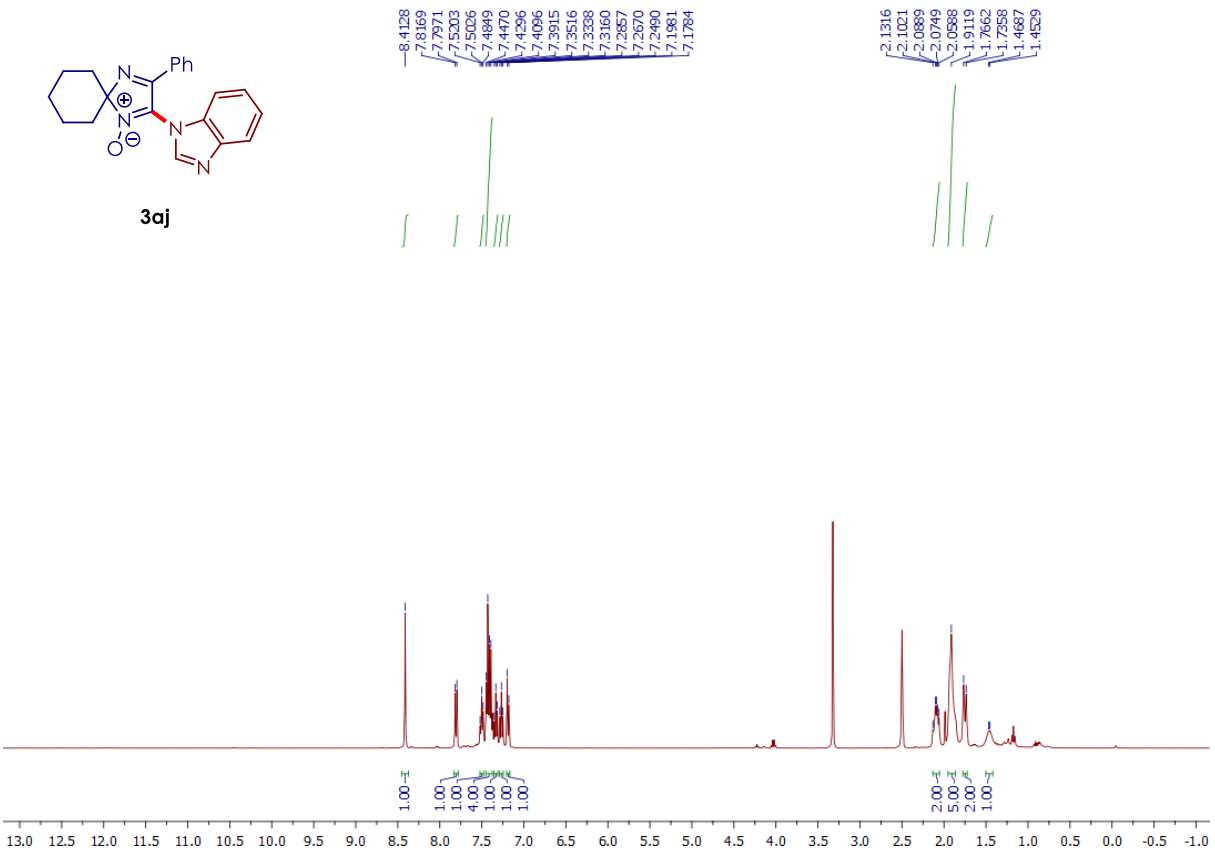

Fig. S56. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 2-(1*H*-benzo[*d*]imidazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3aj**).

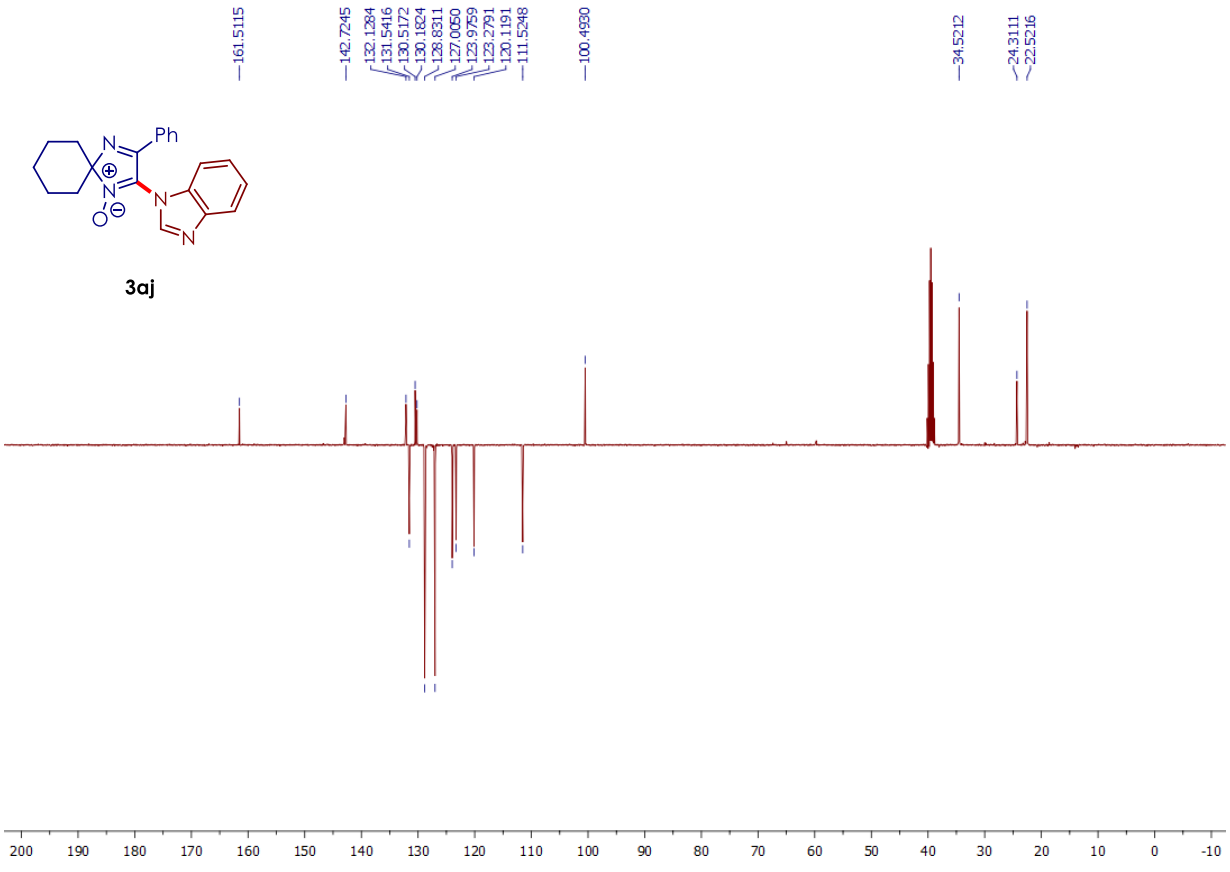

Fig. S57. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 2-(1*H*-benzo[*d*]imidazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3aj**).

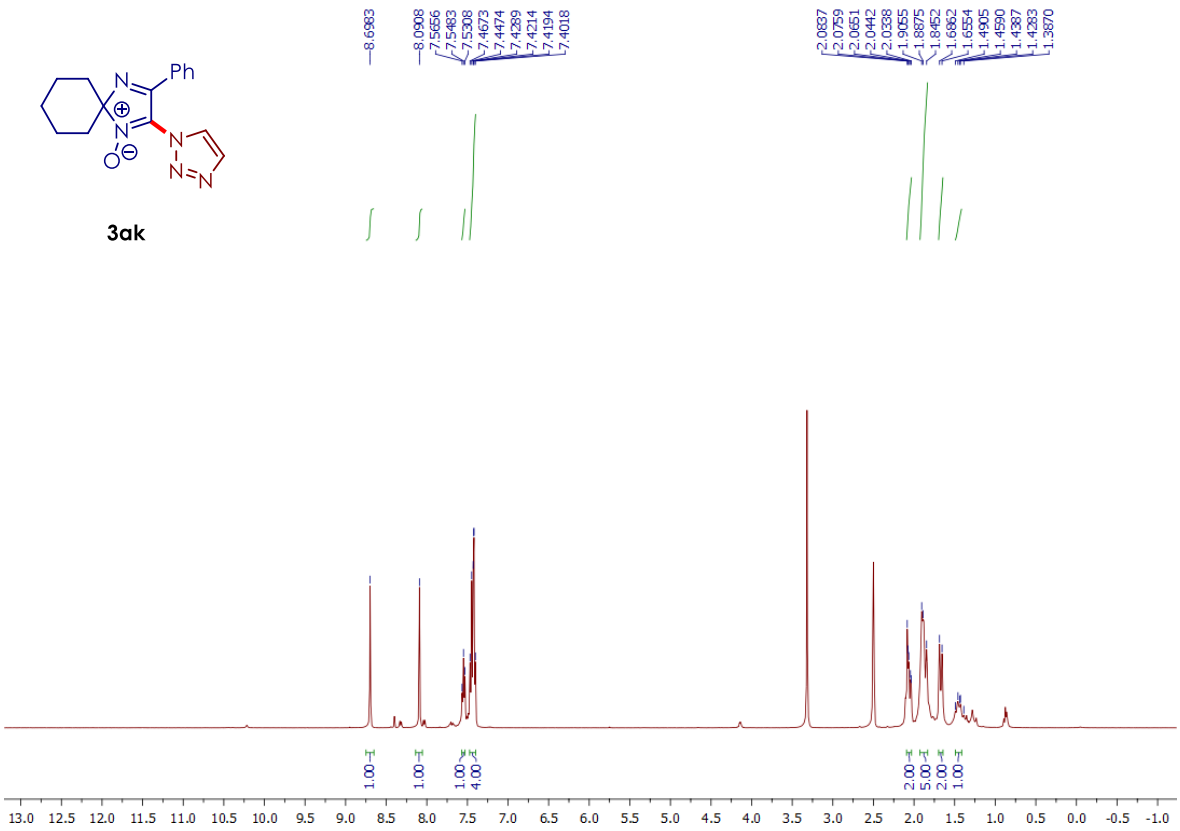

Fig. S58. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 3-phenyl-2-(1*H*-1,2,3-triazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ak**).

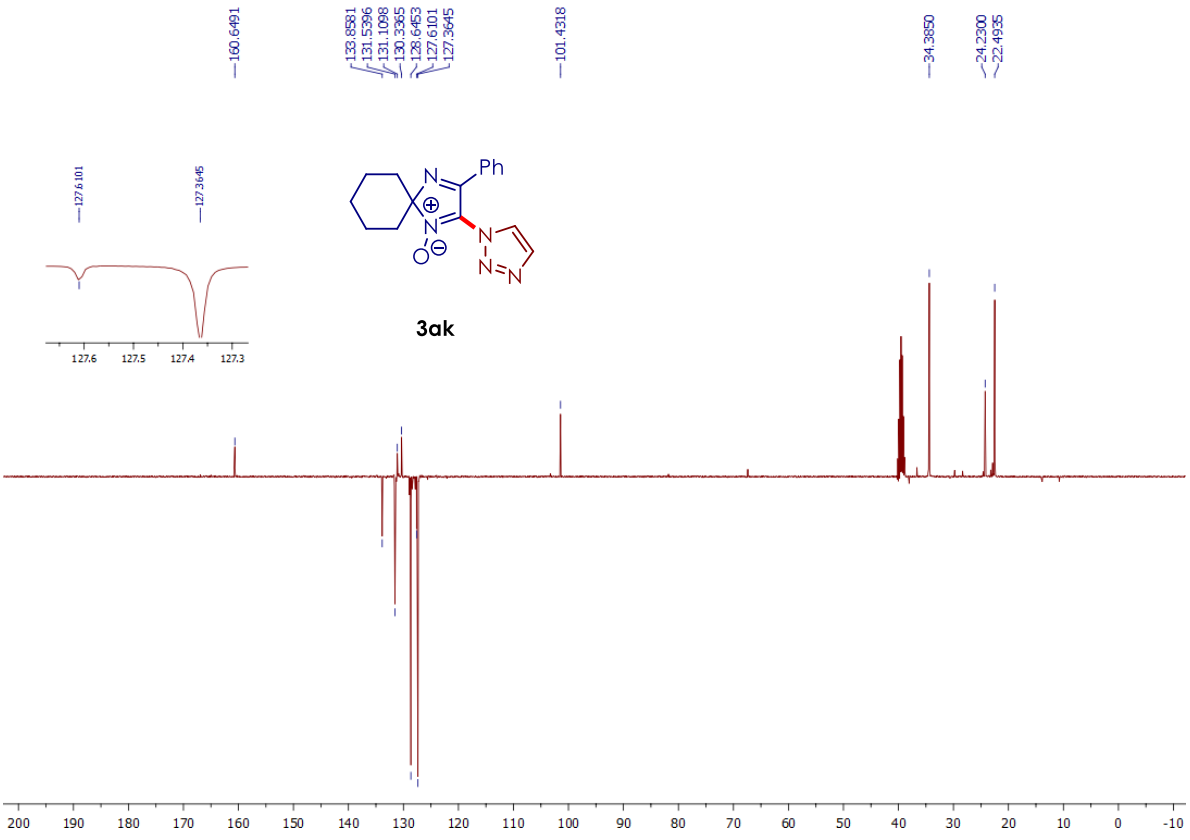

Fig. S59. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 3-phenyl-2-(1*H*-1,2,3-triazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ak**).

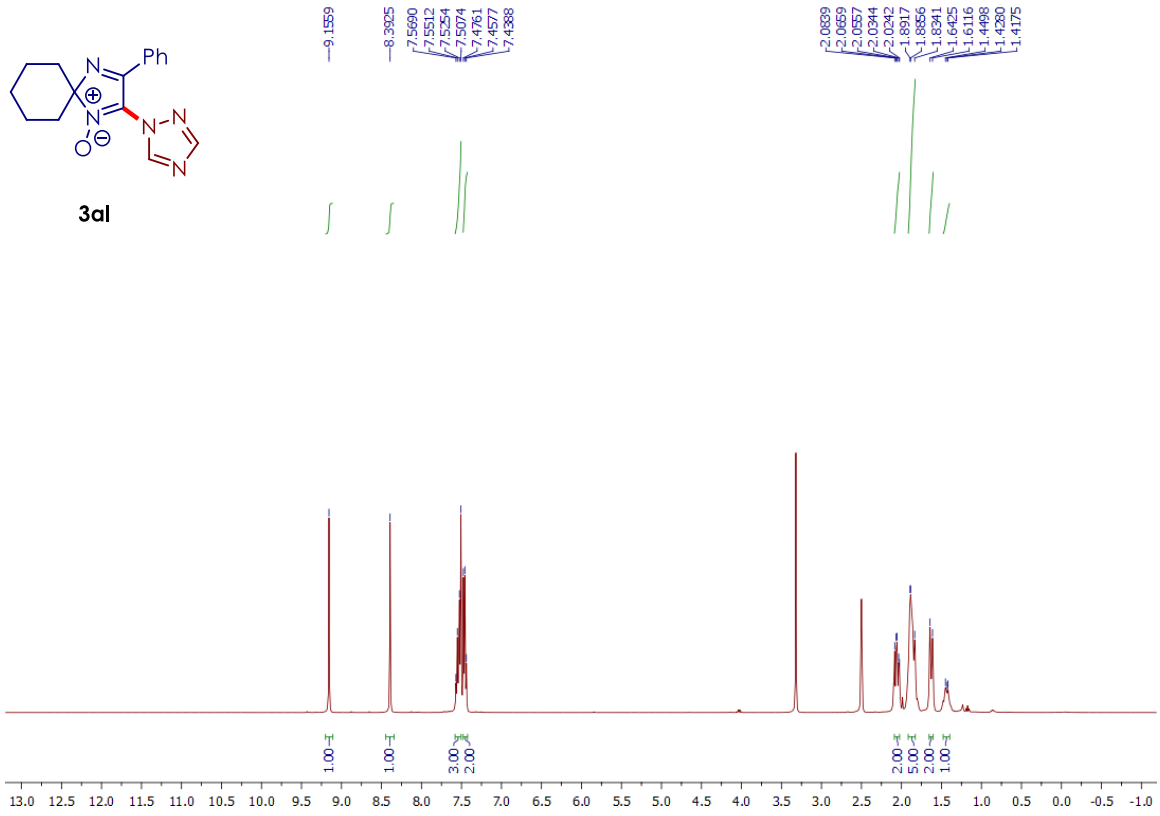

Fig. S60. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 3-phenyl-2-(1*H*-1,2,4-triazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3al**).

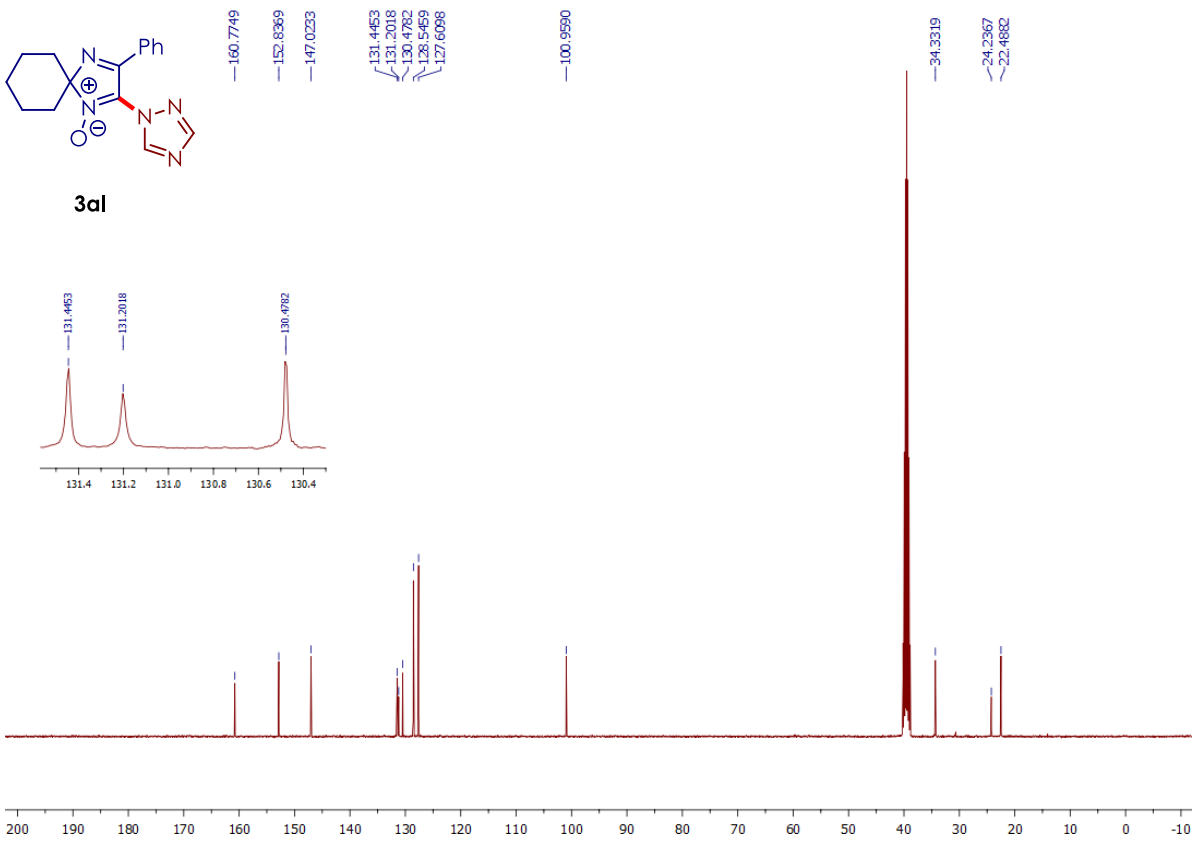

Fig. S61. ^{13}C{^{1}H} NMR Spectrum (BB, DMSO-d_6, 101 MHz) of 3-phenyl-2-(1*H*-1,2,4-triazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3al**).

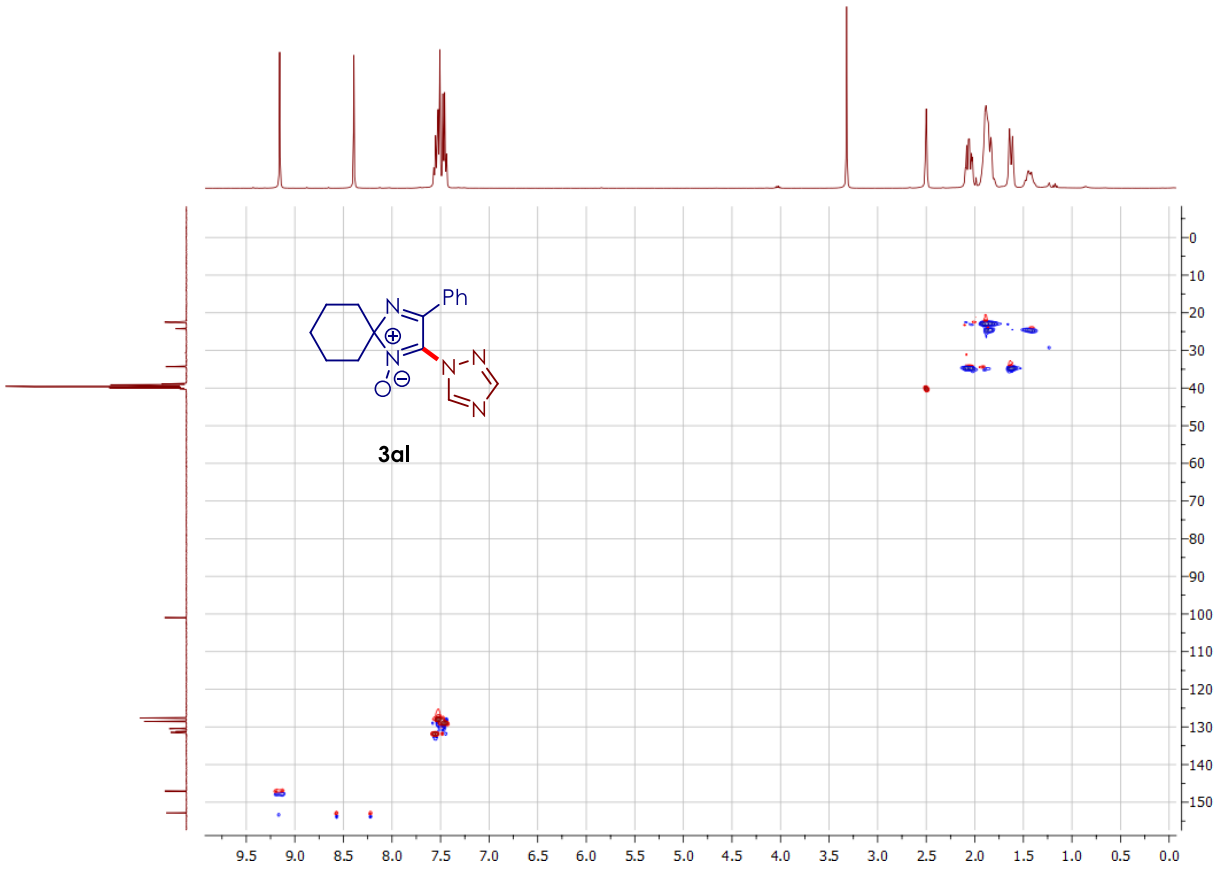

Fig. S62. $^{1}H-^{13}C$ HSQC 2D NMR Spectrum of 3-phenyl-2-(1*H*-1,2,4-triazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3al**).

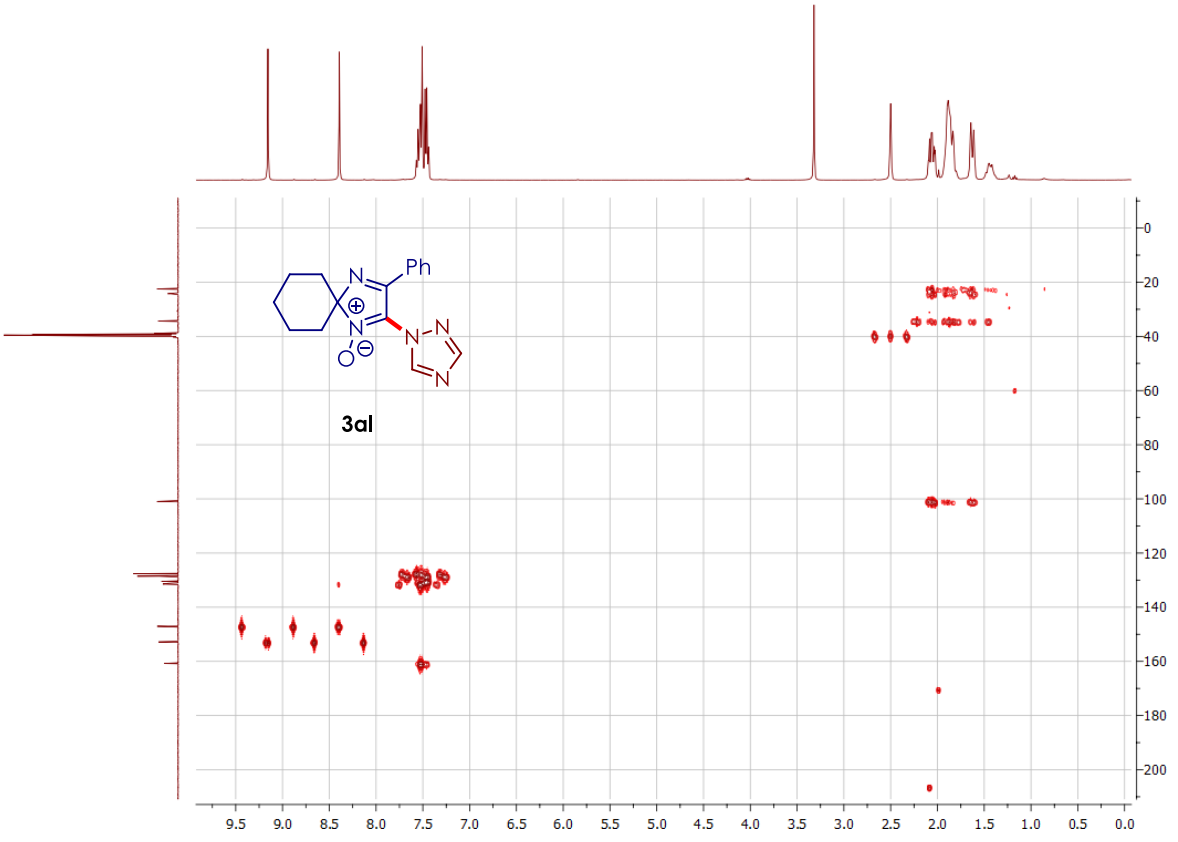

Fig. S63. $^{1}H-^{13}C$ HMBC 2D NMR Spectrum of 3-phenyl-2-(1*H*-1,2,4-triazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3al**).

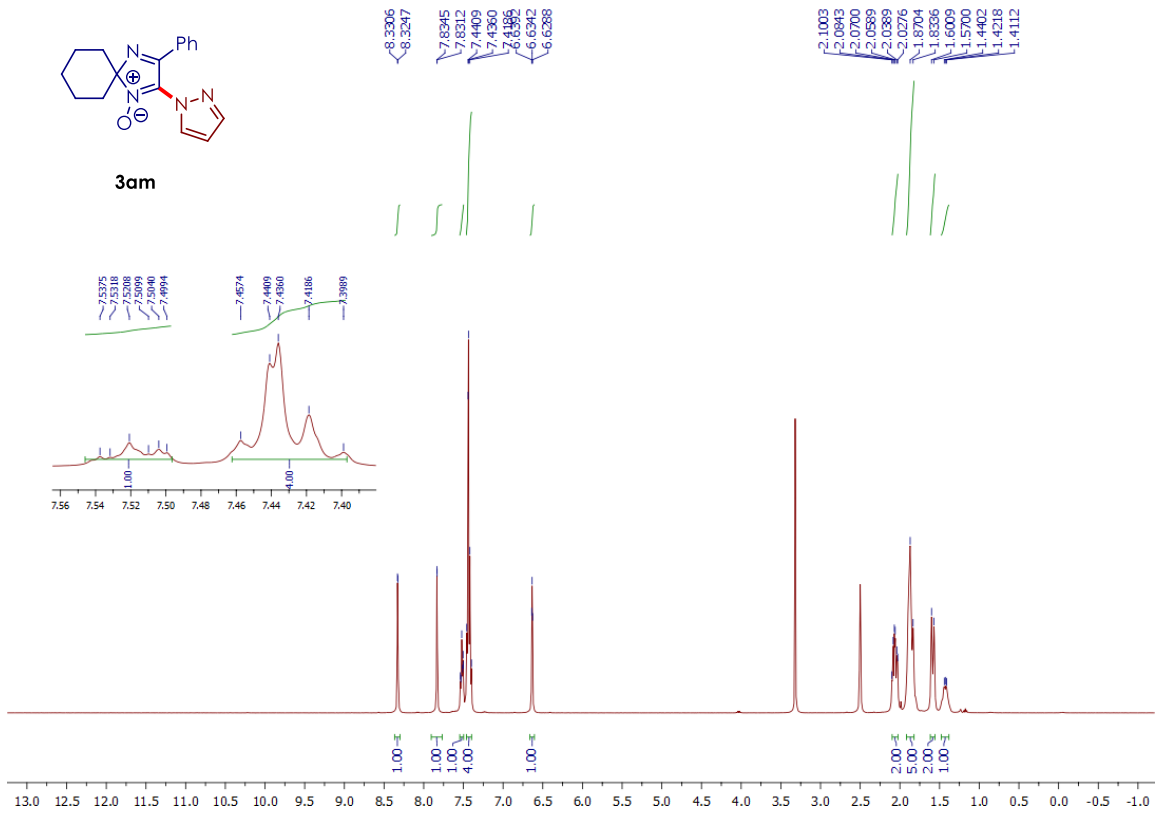

Fig. S64. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 3-phenyl-2-(1*H*-pyrazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3am**).

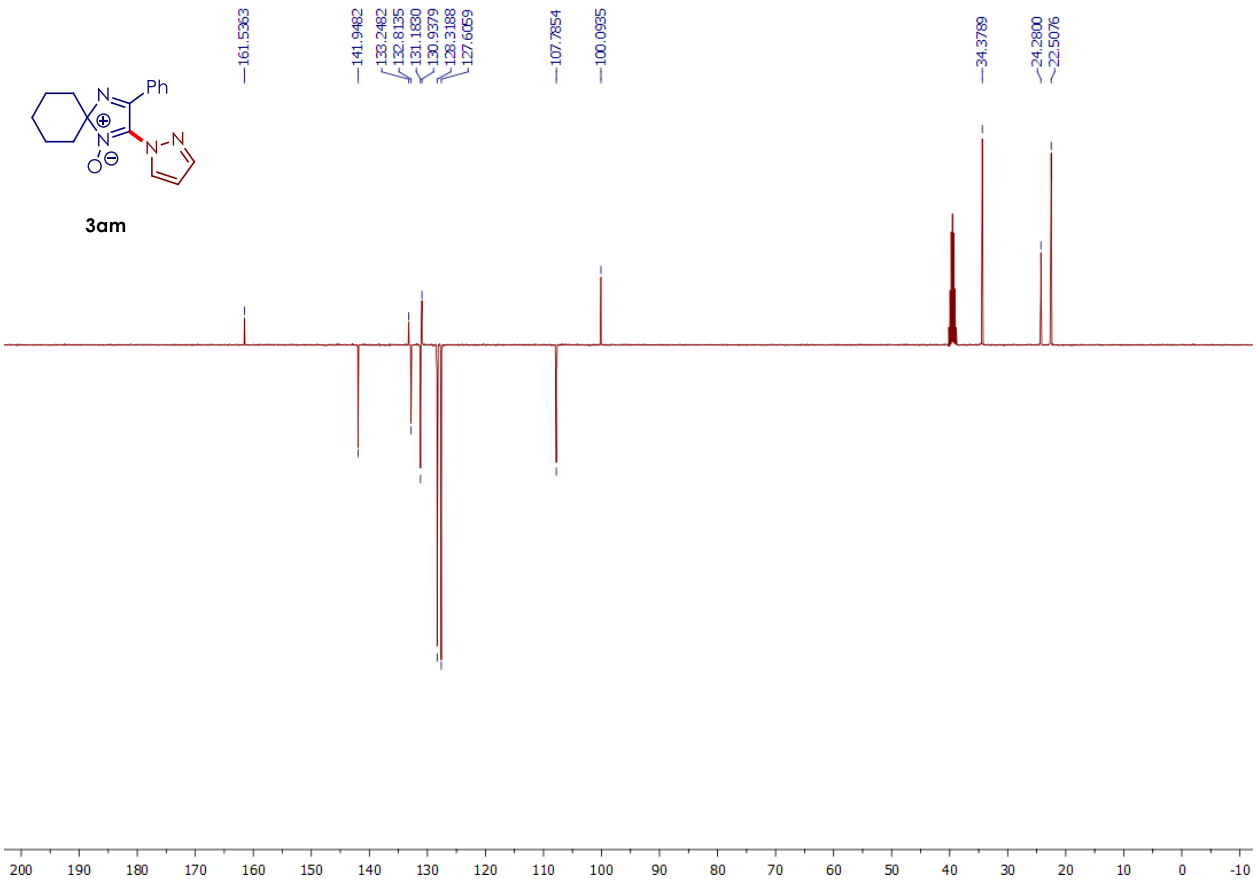

Fig. S65. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 3-phenyl-2-(1*H*-pyrazol-1-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3am**).

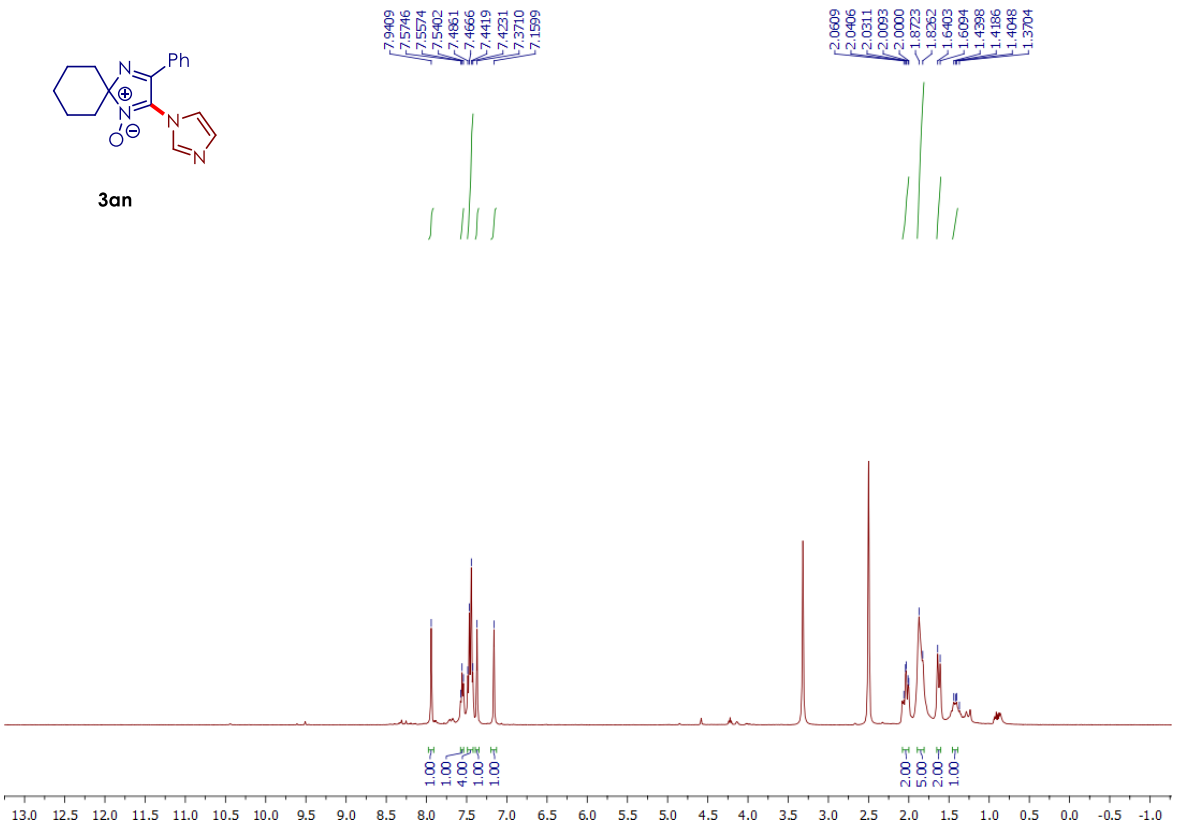

Fig. S66. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 2-(1*H*-imidazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3an**).

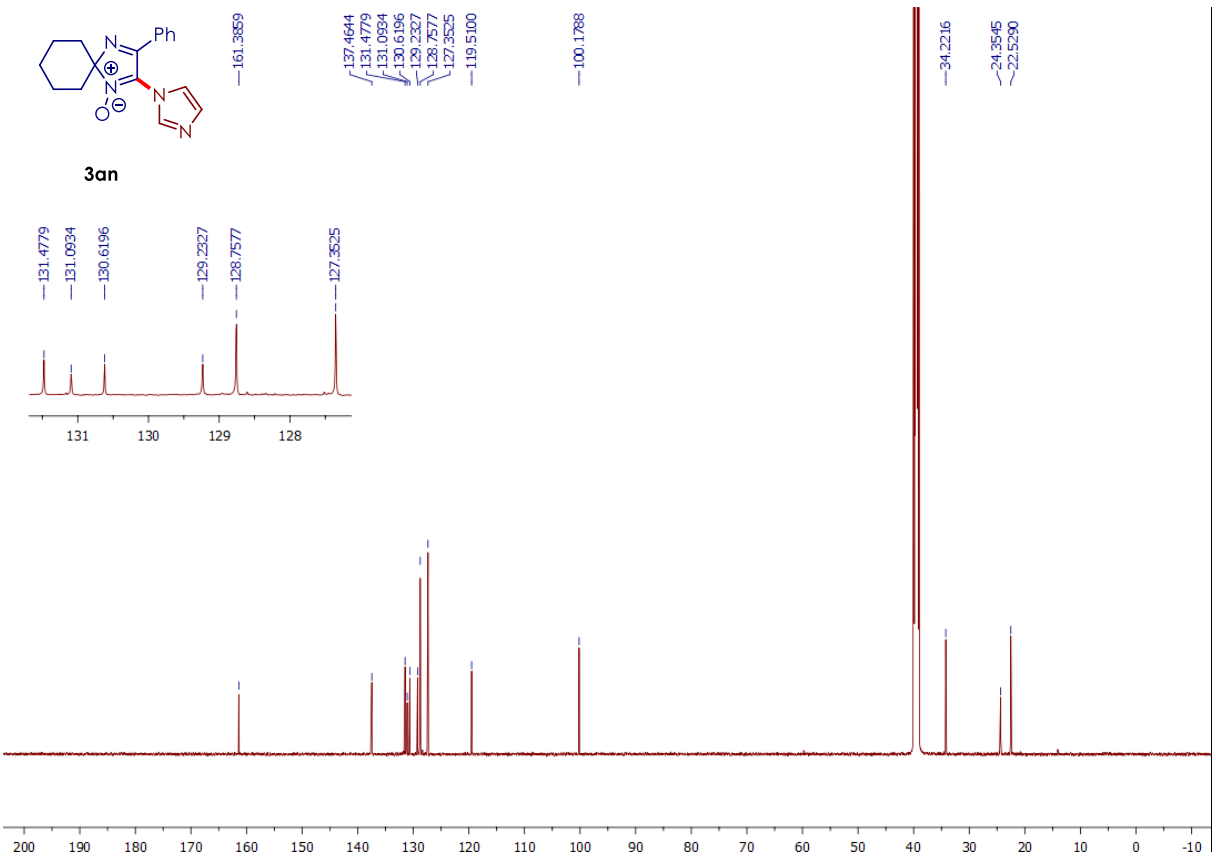

Fig. S67. ^{13}C{^{1}H} NMR Spectrum (BB, DMSO-d_6, 151 MHz) of 2-(1*H*-imidazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3an**).

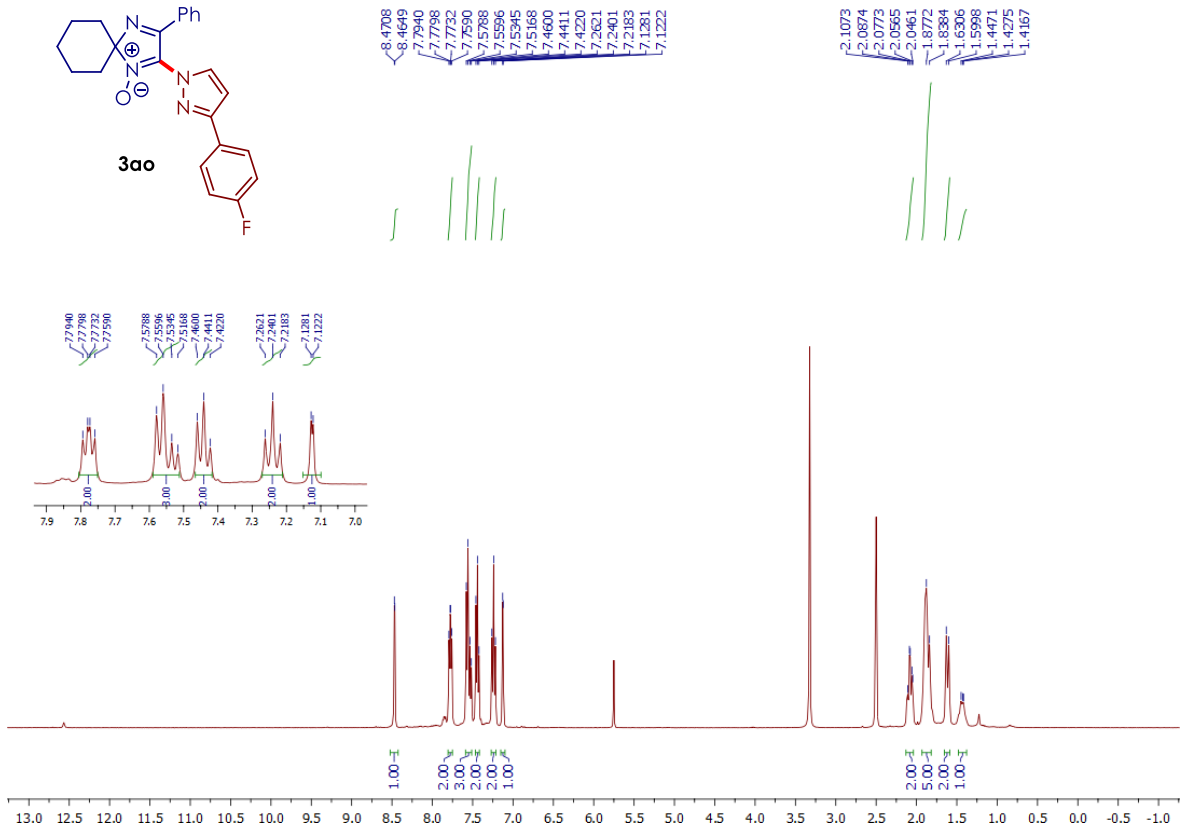

Fig. S68. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 2-(3-(4-fluorophenyl)-1*H*-pyrazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ao**).

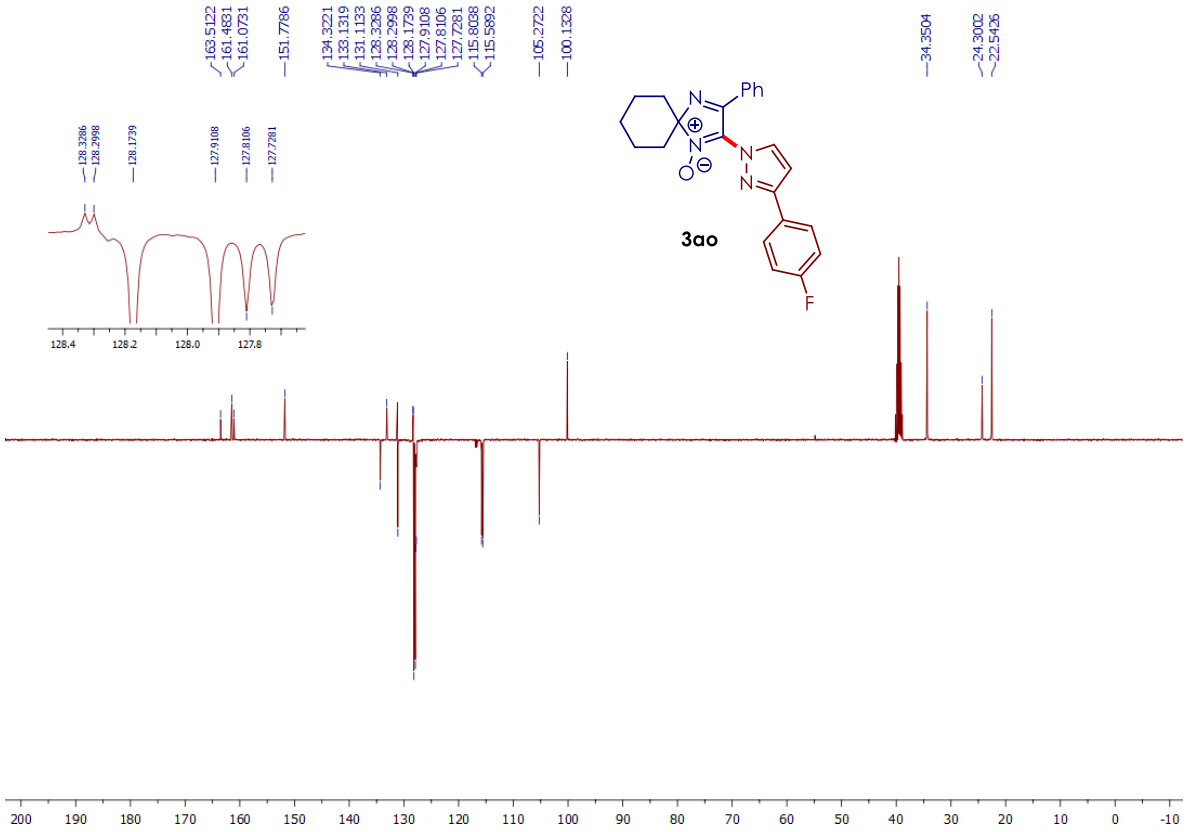

Fig. S69. ^{13}C{^{1}H} NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 2-(3-(4-fluorophenyl)-1*H*-pyrazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ao**).

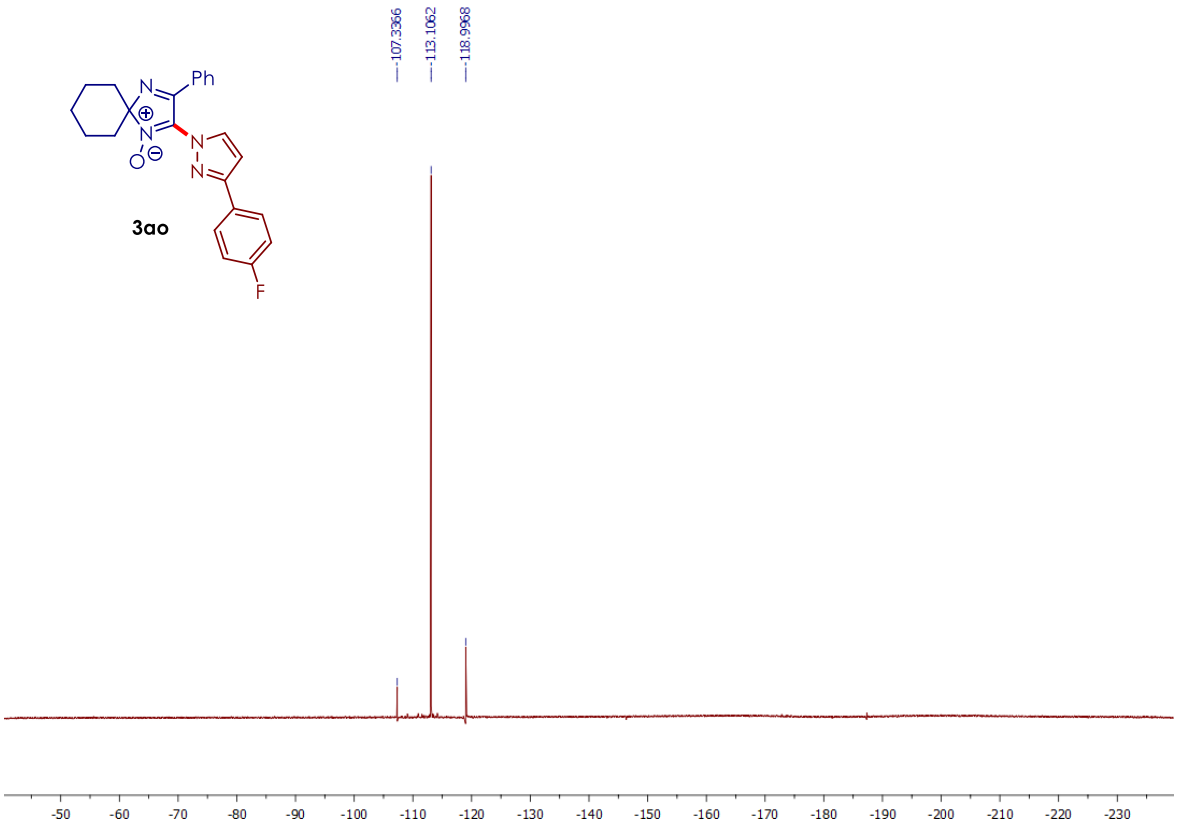

Fig. S70. ^{19}F NMR Spectrum (DMSO-d_6, 376 MHz) of 2-(3-(4-fluorophenyl)-1*H*-pyrazol-1-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ao**).

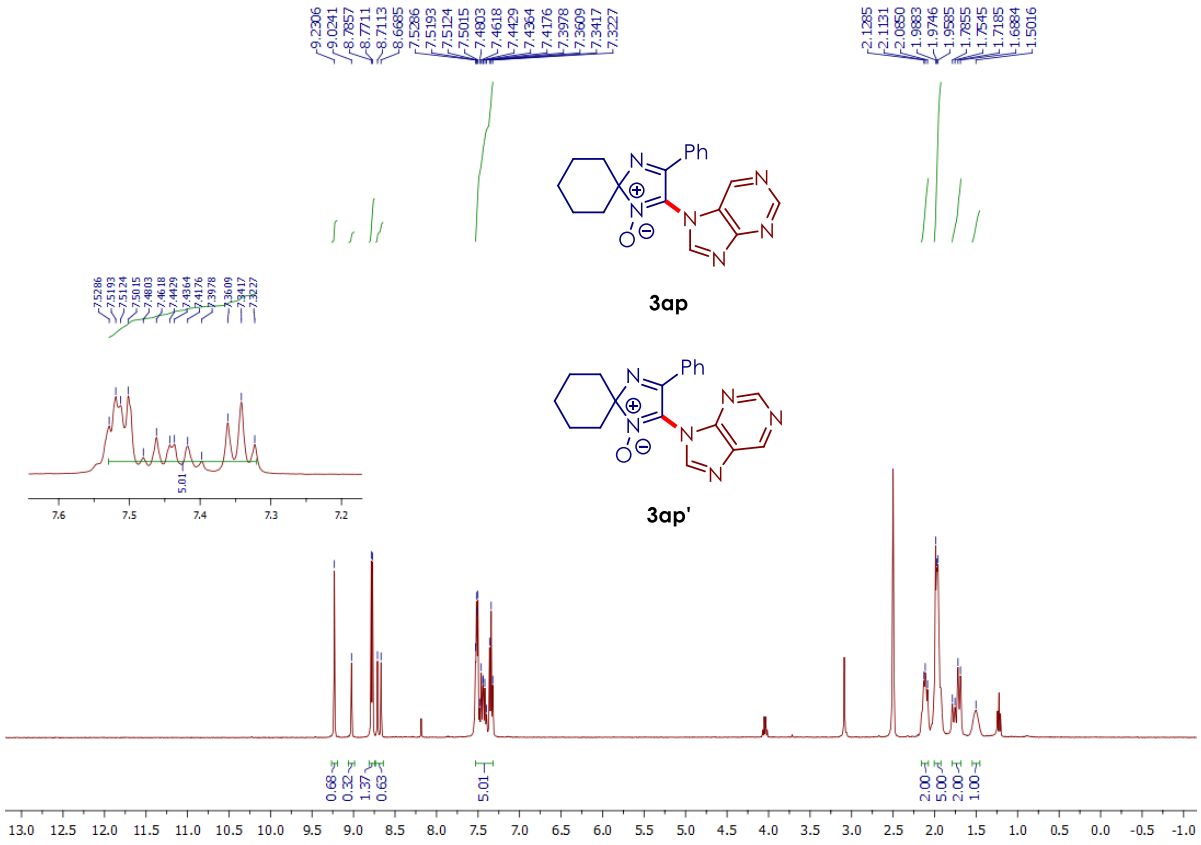

Fig. S71. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of regioisomeric mixture of 3-phenyl-2-(7*H*-purin-7-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ap**) and 3-phenyl-2-(9*H*-purin-9-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ap'**).

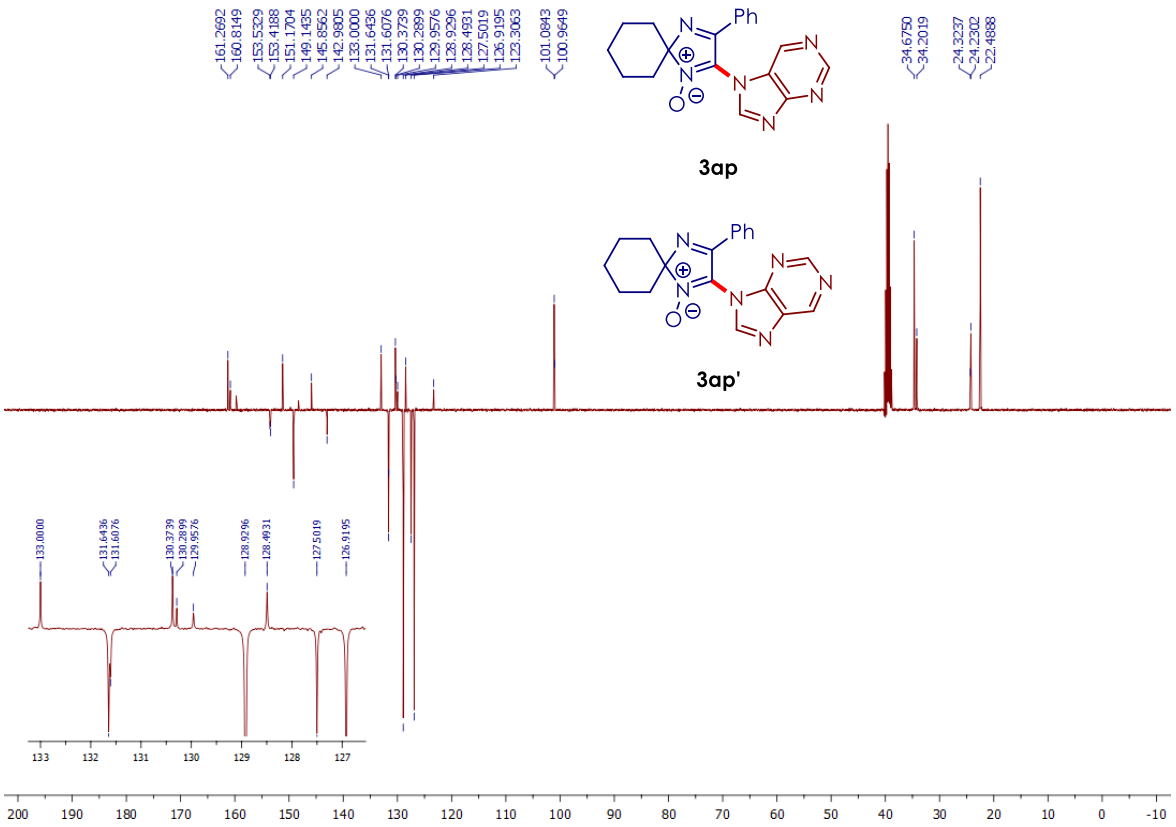

Fig. S72. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of regioisomeric mixture of 3-phenyl-2-(7*H*-purin-7-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ap**) and 3-phenyl-2-(9*H*-purin-9-yl)-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3ap'**).

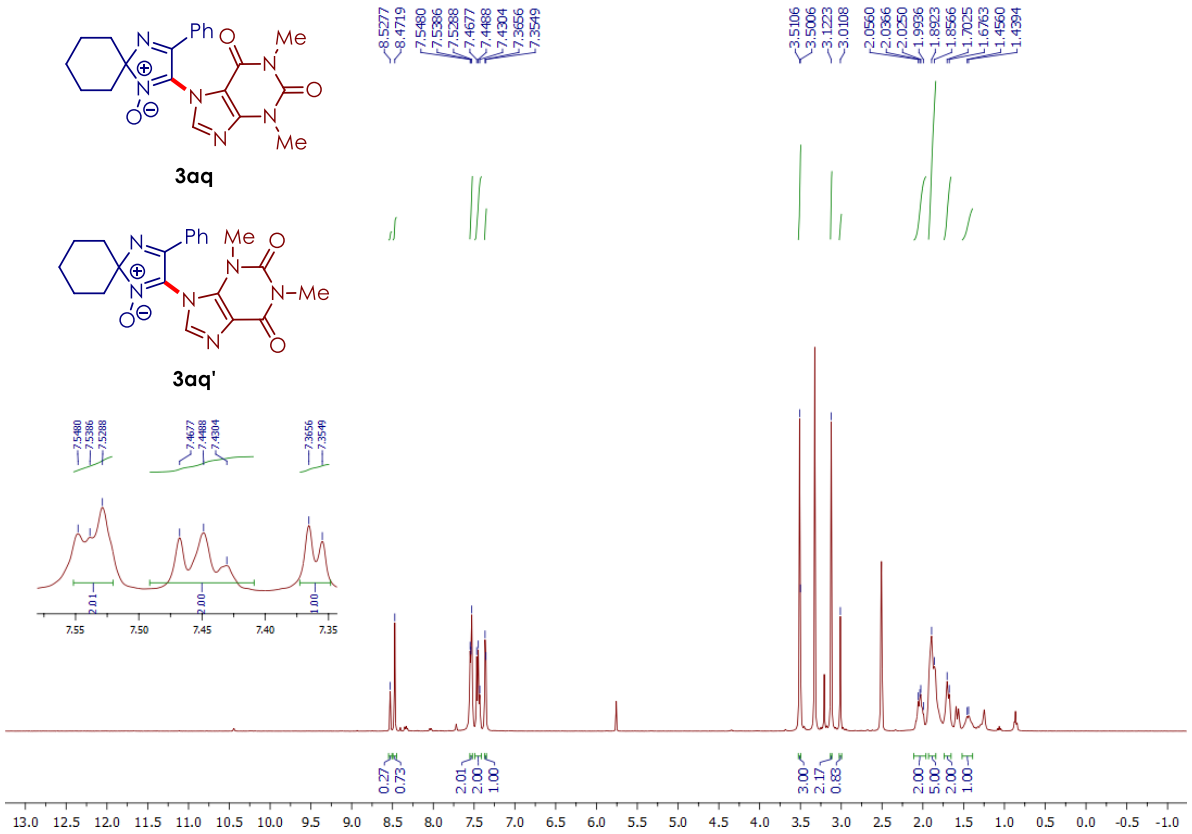

Fig. S73. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of regioisomeric mixture of 2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1*H*-purin-7(6*H*)-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3aq**) and 2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1*H*-purin-9(6*H*)-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3aq'**).

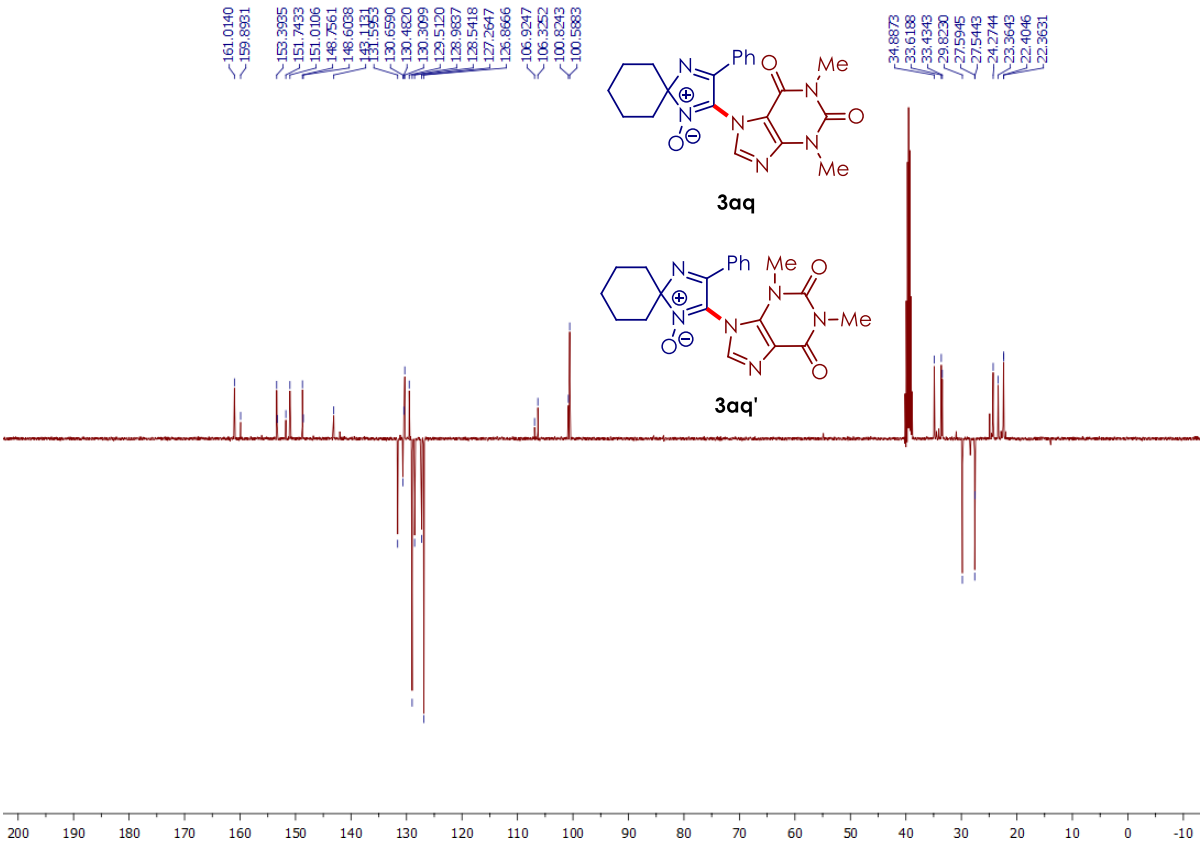

Fig. S74. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of regioisomeric mixture of 2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1*H*-purin-7(6*H*)-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3aq**) and 2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1*H*-purin-9(6*H*)-yl)-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**3aq'**).

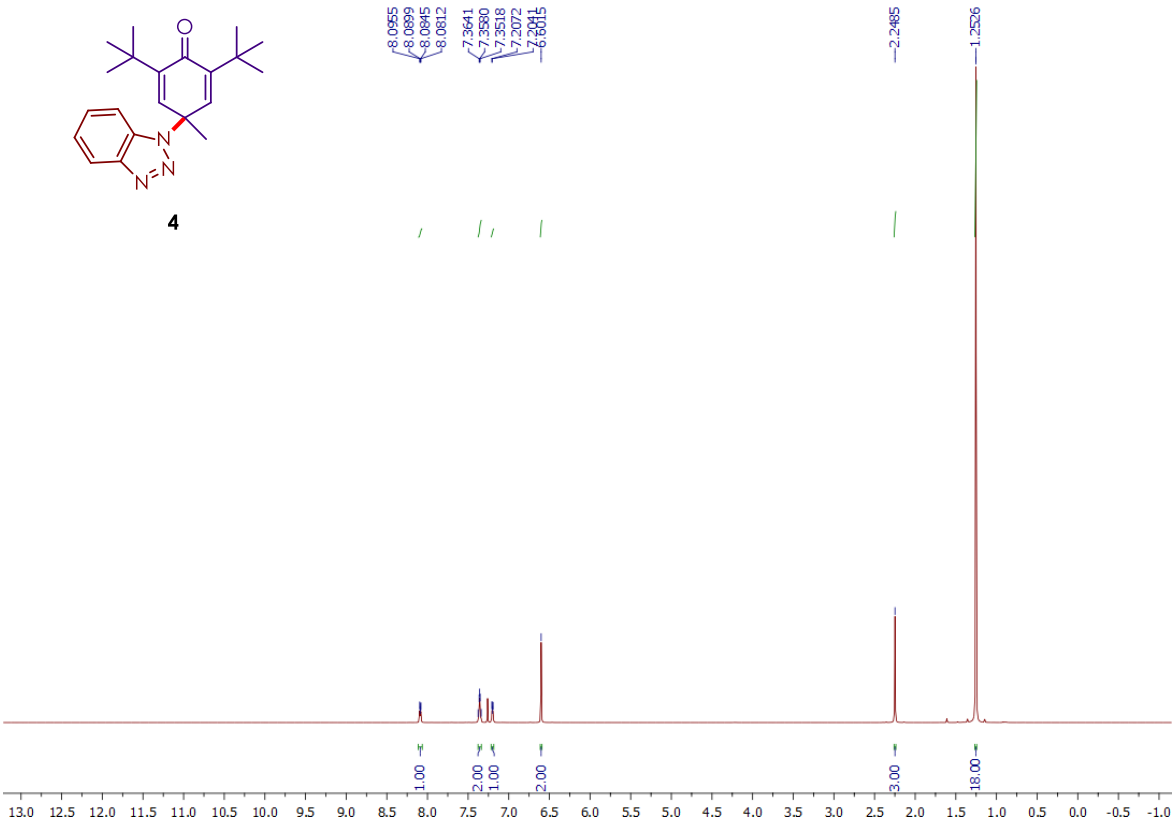

Fig. S75. ^{1}H NMR Spectrum ($CDCl_3$, 600 MHz) of 4-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dienone (**4**).

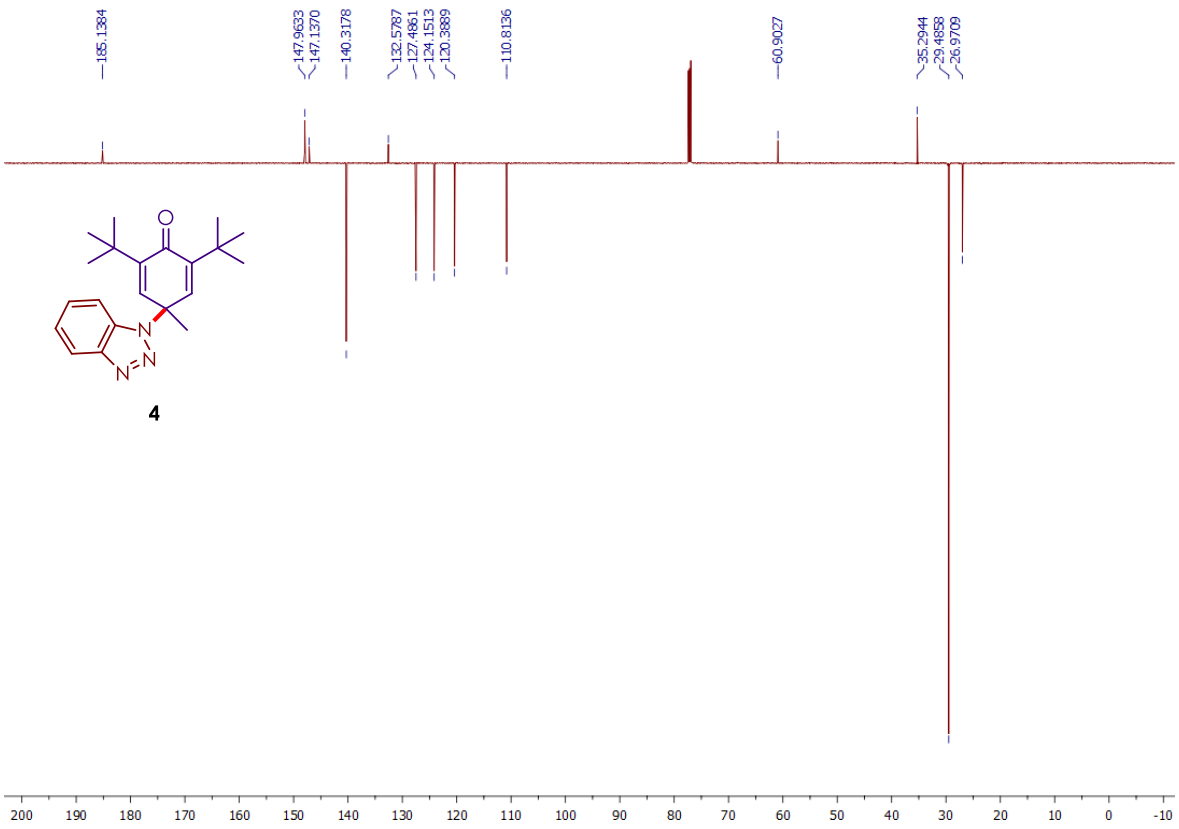

Fig. S76. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, $CDCl_3$, 151 MHz) of 4-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dienone (**4**).

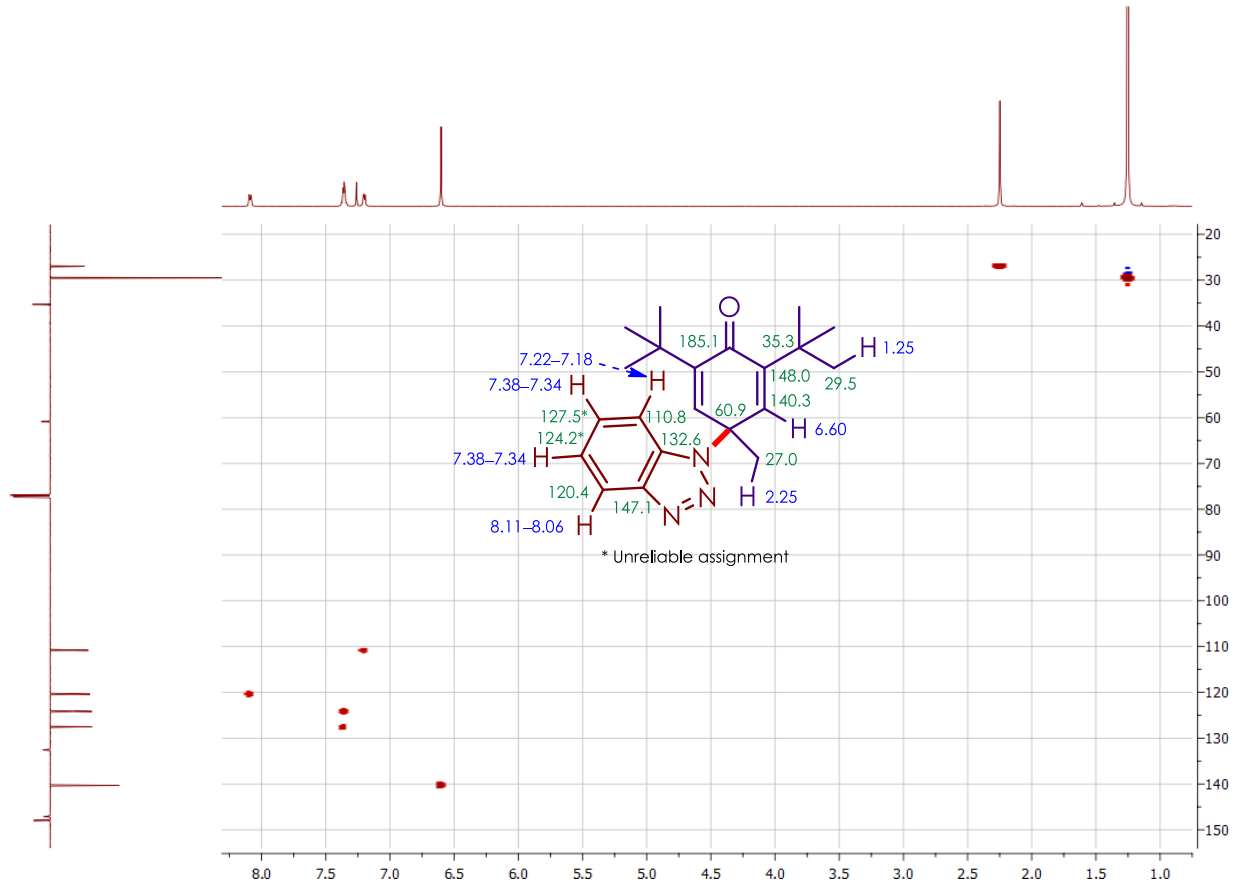

Fig. S77. $^{1}H - ^{13}C$ HSQC NMR Spectrum ($CDCl_3$) of 4-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dienone (**4**).

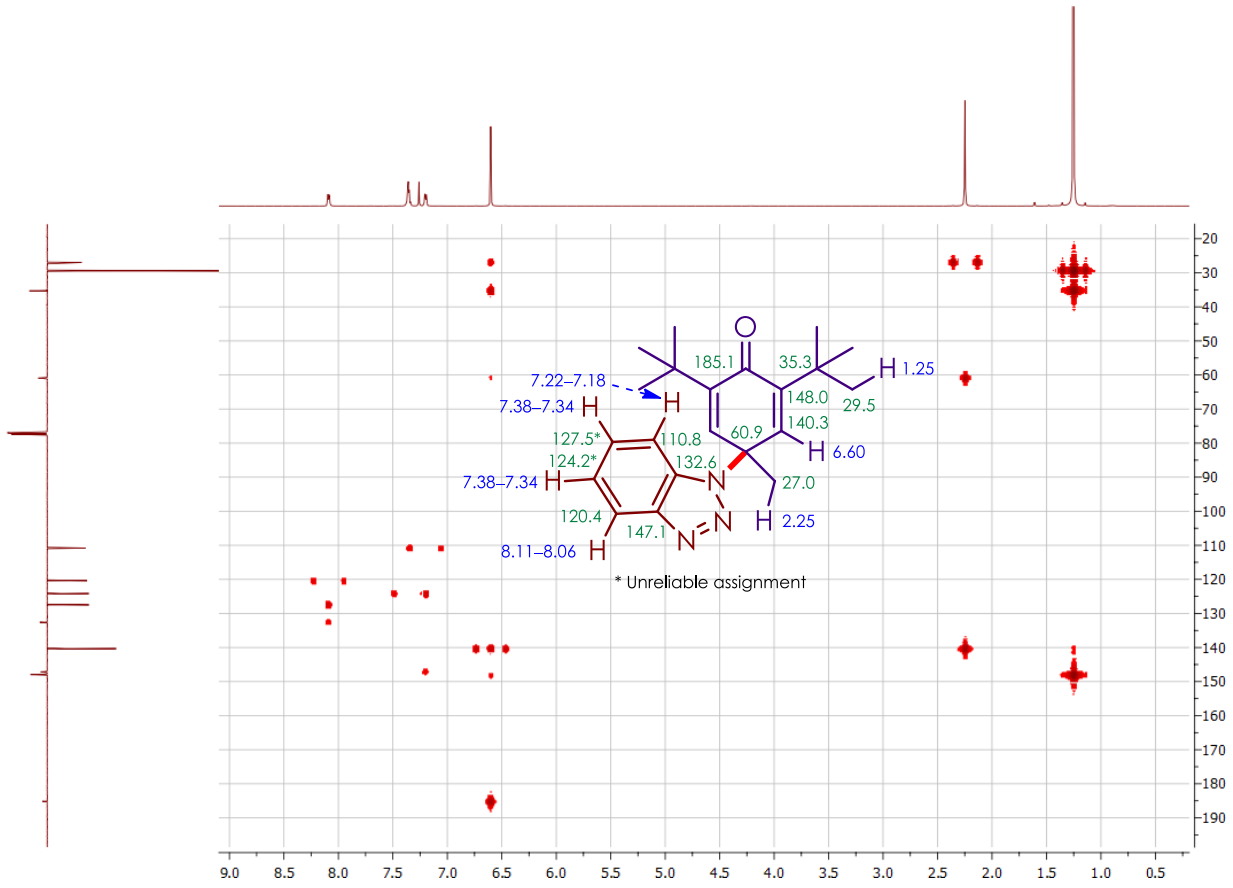

Fig. S78. $^{1}H - {}^{13}C$ HMBC NMR Spectrum ($CDCl_3$) of 4-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dienone (**4**).

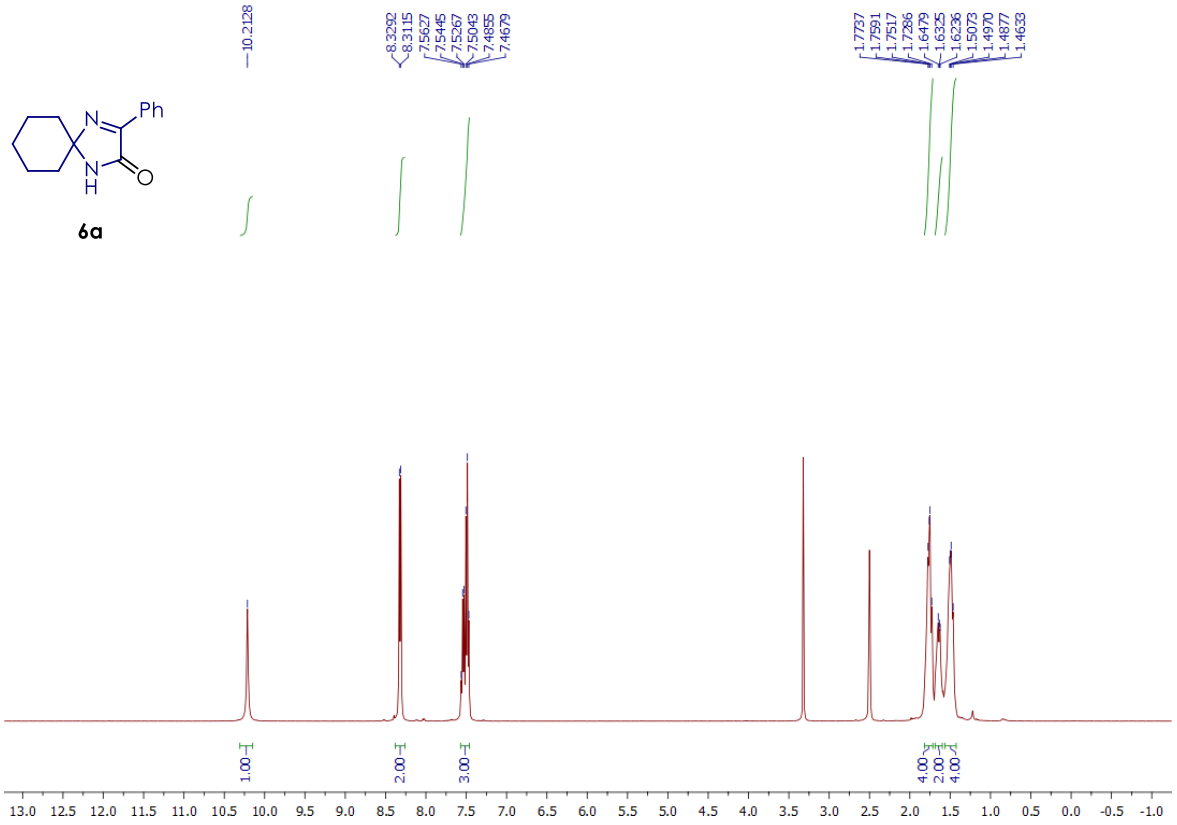

Fig. S79. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 3-phenyl-1,4-diazaspiro[4.5]dec-3-en-2-one (**6a**).

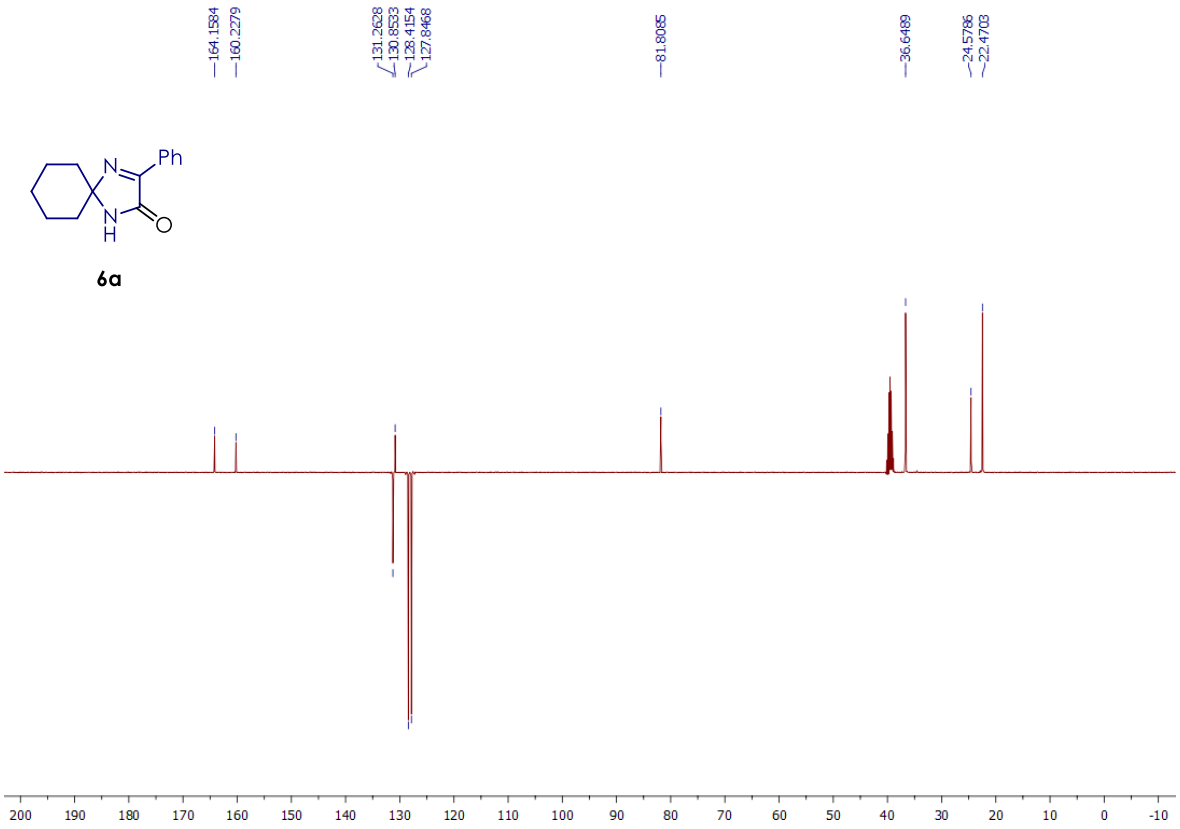

Fig. S80. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 3-phenyl-1,4-diazaspiro[4.5]dec-3-en-2-one (**6a**).

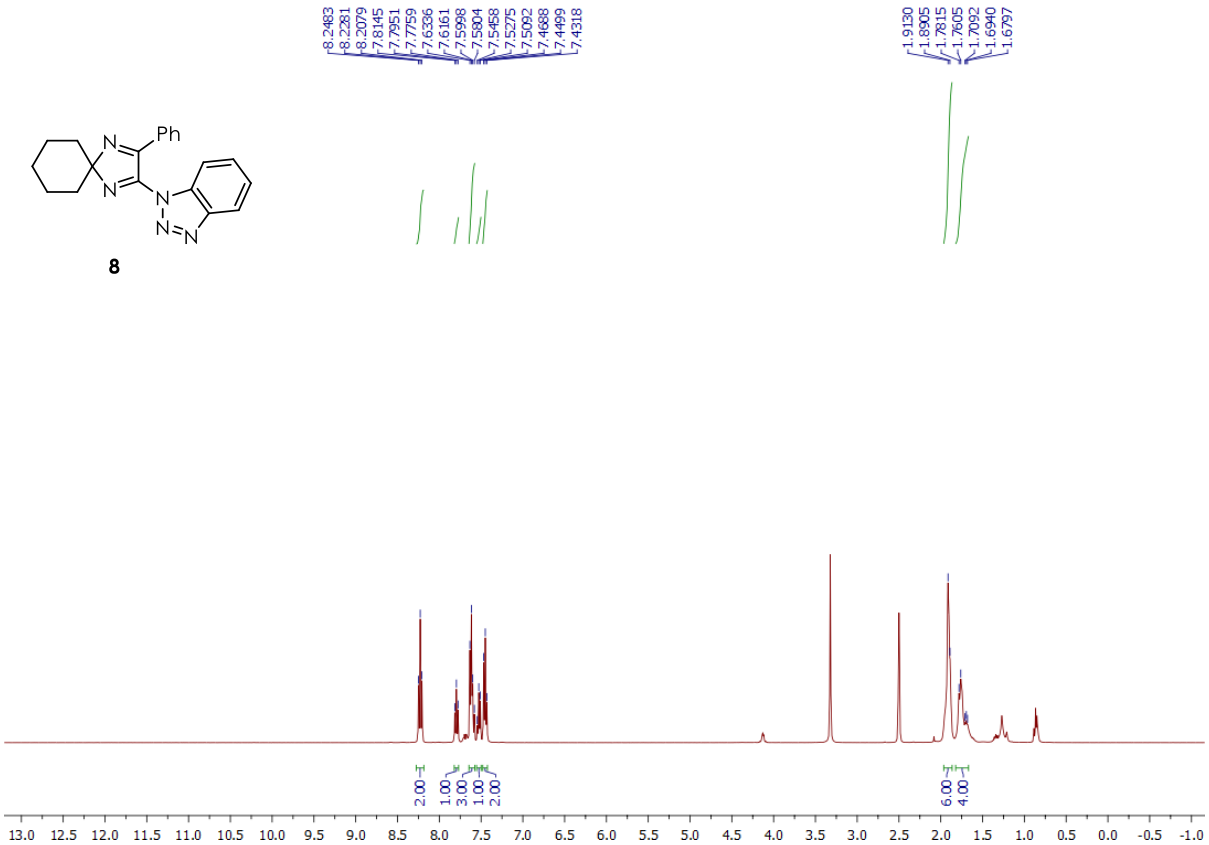

Fig. S81. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of 1-(3-phenyl-1,4-diazaspiro[4.5]deca-1,3-dien-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (**8**).

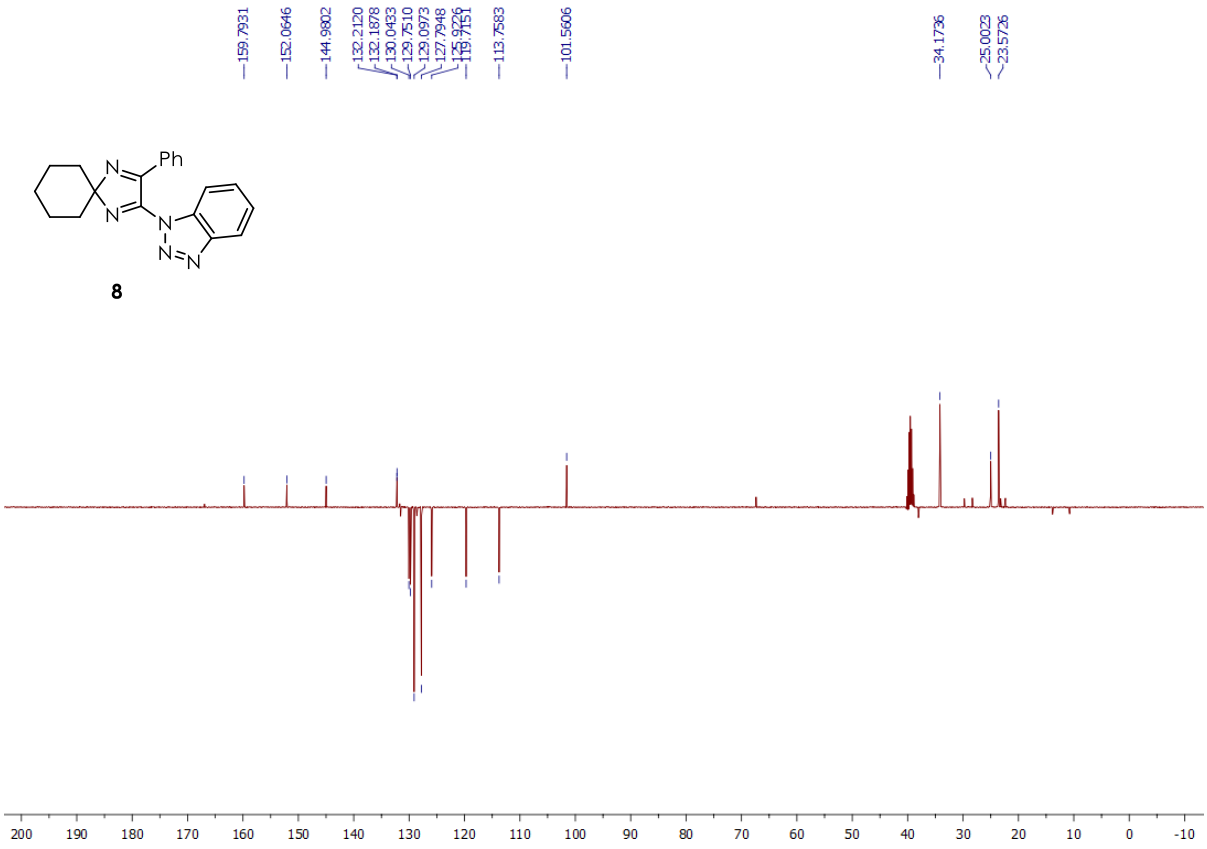

Fig. S82. $^{13}C\{^{1}H\}$ NMR Spectrum (APT, DMSO-d_6, 101 MHz) of 1-(3-phenyl-1,4-diazaspiro[4.5]deca-1,3-dien-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (**8**).