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DABCO-catalysed highly diastereoselective synthesis of 1,3-indandione containing fully saturated spirocyclopentanes involving 2-(2′-ketoalkyl)-1,3-indandiones and nitrostyrenes

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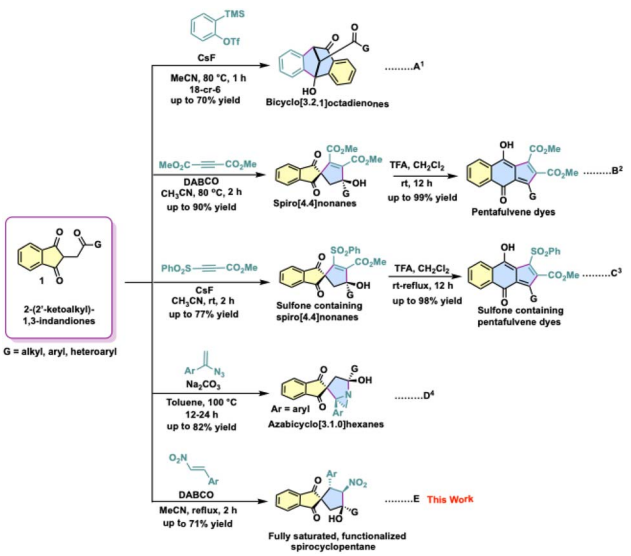
Highly functionalized 1,3-indandione containing spirocyclopentanes has been synthesized by reacting nitrostyrenes with 2-(2′-ketoalkyl)-1,3-indandiones using a catalytic amount of DABCO. The resultant products possess three consecutive chiral centres in addition to a spirocyclic centre and are obtained in a highly diastereoselective manner using a catalytic amount of the organic base, DABCO.

2-(2′-Ketoalkyl)-1,3-indandiones (**1**) were easily accessed from the commercially available 1,3-indandione, and this substrate has more electrophilic and nucleophilic sites compared to the parent compound 1,3-indanedione.[1–4] Accordingly, these compounds have been used for the synthesis of various carbo-, heterocycles in our laboratory (Scheme 1). In particular, the reaction of 2-(2′-ketoalkyl)-1,3-indandiones provided bicyclo [3.2.1]octadienones (Scheme 1A),[1] spiro[4.4]nonanes, pentafulvene dyes (Scheme 1B and C),[2,3] and azabicyclo[3.1.0]hexanes (Scheme 1D)[4] by reacting it with arynes, dimethylacetylenedicarboxylate (DMAD) or its derivatives and vinyl azides, respectively. As part of our ongoing research interest in exploring the reactivity of 2-(2′-ketoalkyl)-1,3-indandiones, we became interested in utilising the nitrostyrenes as an alternative reacting partner, because they serve as effective dipolarophiles, and have been extensively utilized in reactions with a 1,3-dipole to produce five-membered cyclic compounds that contain nitro groups.[5] Therefore, the reaction of nitrostyrenes with 2-(2′-ketoalkyl)-1,3-indandiones would provide fully saturated cyclopentanes embedded within the 1,3-indandione skeleton. However, there were similar systems that were synthesized by cycloaddition of vinyl cyclopropane derived from 1,3-indanedione with nitroalkenes in the presence of Pd^0 catalyst, in an asymmetric manner.[6] Therefore, we focused on developing transition metal-free conditions to access fully saturated spirocyclopentyl indane-1,3-dione compounds in our study. It is noteworthy to mention that 1,3-indandiones and their derivatives containing spirocyclopentane have garnered considerable interest due to their potential for creating architectural themes. 1,3-indandione structural motifs have been found in diverse fields, ranging from bioactive compounds[7–11] to functionalized materials.[12] For instance, fredericamycin A, which was isolated from a soil bacterium of *Streptomyces griseus* (FCRC-48), and found to be antibacterial, antifungal and cytotoxic.[13] Therefore, developing a novel method to construct 1,3-indandione containing spirocyclopentanes would be vital, specifically under transition metal-free conditions.



Scheme 1 Previous and current approaches by utilizing 2-(2′-ketoalkyl)-1,3-indandiones.

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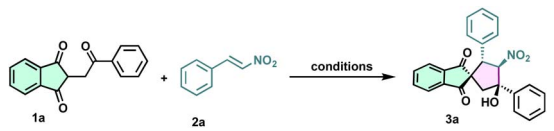
Accordingly, we started our investigation using 2-(2′-ketoalkyl)-1,3-indandiones **1a** and (*E*)-(2-nitrovinyl)benzene **2a** as a model substrate to check our initial hypothesis. Consequently, we have treated **1a** and **2a** with Et_3N as a base in MeCN

at room temperature. To our delight, we found the expected 1,3-indandione containing spirocyclopentane **3a** in 46% yield (Table 1, entry 1). Subsequently, the product **3a** was isolated and confirmed by the meticulous NMR experiments. However, the formation of a compound **3a** motivated us to screen the reaction conditions further to get better results. Accordingly, several bases were tested, and the results are described in Table 1. Potassium fluoride (KF) provided the required product, **3a**, in only 40% yield (Table 1, entry 2), while prolonged conditions up to 24 h by increasing the equivalents up to 3 decreased the yield to 29% (Table 1, entry 3). On the other hand, caesium fluoride failed to give the expected product (Table 1, entry 4). Next, the Carbonate bases such as K_2CO_3 and Cs_2CO_3 were also tested; surprisingly, they failed to give the desired product (Table 1, entries 5 & 6). Thereafter, we have tried the reaction with Na_2CO_3, but it resulted in only 50% yield of the product (Table 1, entry 7). These results forced us to switch back to the usage of organic bases for fruitful results. Consequently, a stoichiometric amount of DABCO was tested, which furnished the expected product in 40% yield (Table 1, entry 8), and further increasing the equivalents of base provided the required product **3a** in 55% yield (Table 1, entry 9). This persuaded us to employ a catalytic amount, allowing the reaction to proceed for longer hours by varying the temperature. To our astonishment, the required product **3a** was obtained in 50%, 61% & 70% yield (Table 1, entries 10, 11 & 12) in the presence of 20 mol%. The reaction did not benefit from reducing the catalyst loading to 10 mol%, which only produced a 53% yield (Table 1, entry 13). Next, DABCO was used in two different solvents, DMF and THF, at higher temperatures, which did not help us in providing better results in terms of yield (Table 1, entries 14 & 15). Furthermore, DBU and pyridine were also tested, which did not provide satisfactory results (Table 1, entries 16 & 17). Subsequently, DMAP was used at ambient and elevated temperatures, but the results were not satisfactory (Table 1, entries 18 & 19), even with the higher equivalents of base (Table 1, entry 20). Therefore, the optimised conditions for the synthesis of compound **3a** are 20 mol% DABCO, at 80 °C for 2 h in acetonitrile solvent (Table 1, entry 12). Afterwards, we explored the generality of the transformation with a series of 2-(2′-ketoalkyl)-1,3-indandiones and nitrostyrenes. The substituent on the aryl moiety of 2-(2′-ketoalkyl)-1,3-indandiones was summarised in Scheme 2.

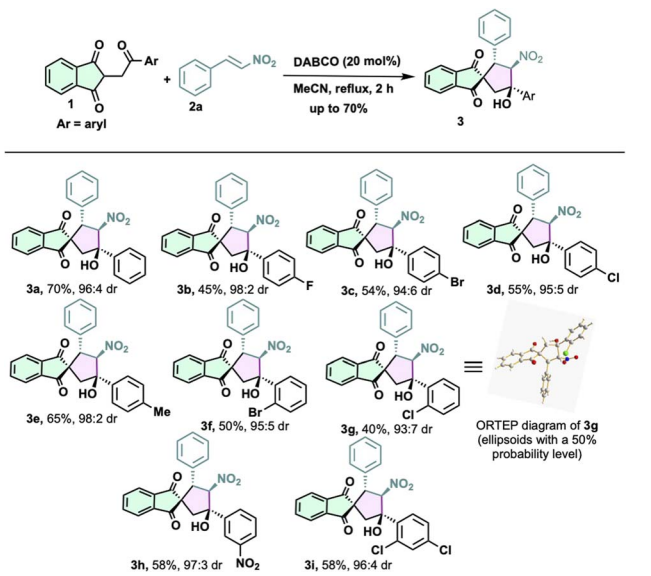
Accordingly, various halogen-containing compounds were tested for this method under standard reaction conditions and provided the required compounds **3b**, **3c** and **3d** in 45%, 54% and 55%, respectively. The lower yields might be due to the electron-withdrawing character of halogens. However, the methyl group at the para position exhibited smooth reactivity, yielding 65% of product **3e**. Next, the ortho substituent of the aryl group of 2-(2′-ketoalkyl)-1,3-indandiones was altered with the halogens to produce **3f** and **3g** in 50% and 40%, respectively. Compound **3g** was further characterised by its single-crystal X-ray diffraction analysis, confirming the relative configuration of substituents (CCDC 2456358). Further, an electron-withdrawing group at the meta position was well tolerated in the developed method and furnished 58% of the product **3h** in 58% yield. To our delight, dichlorinated 2-(2′-ketoalkyl)-1,3-

Table 1 Optimization of reaction conditions[a]



S. No.	Base (equiv.)	Time (h)	Temperature (°C)	Yield[b] (%)
1	Et_3N (1.1)	1	25	46
2	KF (1.5)	3	25	40
3	KF (3.0)	24	25	29
4	CsF (3)	1	25	ND
5	K_2CO_3 (1.5)	22	25	ND
6	Cs_2CO_3 (1.5)	22	25	ND
7	Na_2CO_3 (1.5)	5	25	50
8	DABCO (1.1)	3	25	40
9	DABCO (3)	3	25	55
10	DABCO (0.2)	8	25	50
11	DABCO (0.2)	6	60	61
12	**DABCO (0.2)**	**2**	**80**	**70**
13	DABCO (0.1)	2	80	53
14[c]	DABCO (0.2)	2	100	32
15[d]	DABCO (0.2)	2	65	28
16	DBU (1.1)	12	25	6
17	Pyridine (1.1)	12	25	ND
18	DMAP (1.1)	12	25	5
19	DMAP (1.1)	3	80	ND
20	DMAP (3)	3	Rt	Traces

[a] Reactions were performed on a 0.1 mmol scale of 2-(2′-ketoalkyl)-1,3-indandiones (**1a**) and 1.5 equiv. of nitrostyrenes (**2a**) in acetonitrile (0.1 M) solvent unless otherwise stated. [b] Isolated yields after silica gel column chromatography. ND: Not Detected. [c] DMF (0.1 M) was used as a solvent. [d] THF (0.1 M) was used as a solvent.

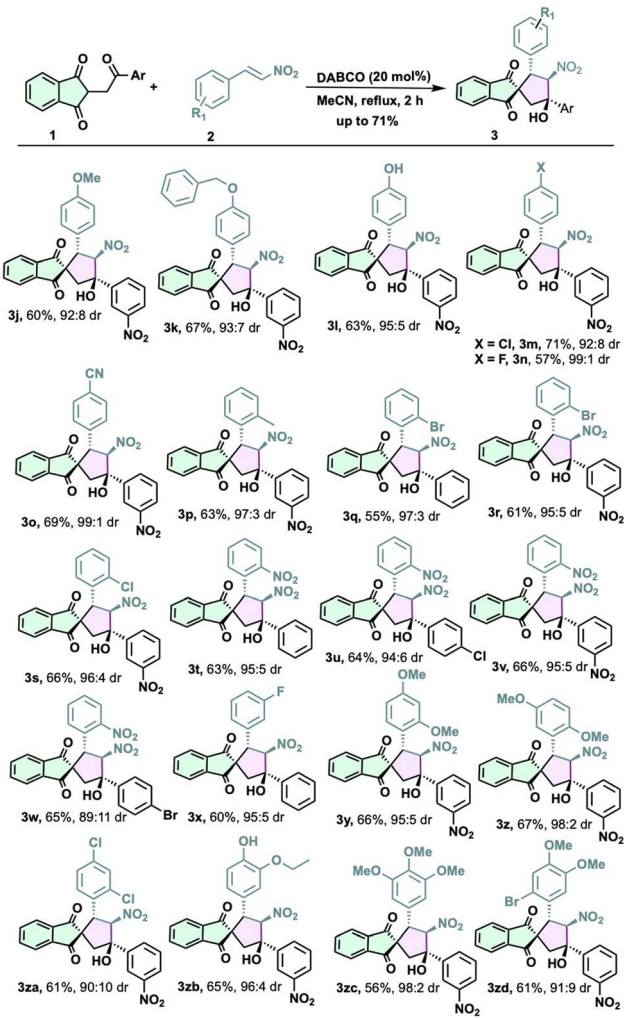


Scheme 2 Substrate scope of 2-(2′-ketoalkyl)-1,3-indandiones.

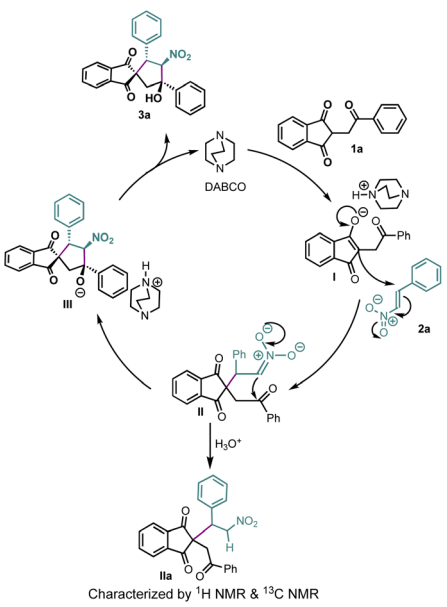
indandiones also yielded product **3i** in good yield of 58%. The diastereomeric ratio was determined by NMR analysis of the crude reaction mixture.

Next, we moved our attention towards the installation of the diverse substituents on nitrostyrenes (Scheme 3). Several groups at para-position were varied, furnishing respective products in moderate to good yields. Accordingly, the methoxy, benzyloxy, and hydroxyl groups were well tolerated in the developed method and provided the required products, **3j**, **3k**, and **3l**, in yields of 60%, 67%, and 63%, respectively. Next, fluoro- and chloro-containing nitrostyrenes were tested under standard conditions and provided the corresponding products, **3m** and **3n**, in 71% and 57% yield, respectively. Thereafter, a strong electron-withdrawing group, such as a cyano group, was endured, affording the product **3o** in 69% yield. Furthermore, the feasibility of the reaction was checked for ortho-substituted nitrostyrenes. Methyl-substituted nitrostyrene delivered corresponding spirocycle **3p** in 63% yield. Bromide or chloride substitution at the ortho position of the phenyl ring of the nitrostyrene gave **3q–3s** in moderate to good yields. Additionally, ortho-nitro nitrostyrene was further tested with a variety of 2-(2′-ketoalkyl)-1,3-indandiones, which yielded **3t–3w** in good yields. Interestingly, tri-nitro spirocyclopentane **3v** was synthesized in 66% yield. Meta-fluoro substituted nitrostyrene was also analysed in the developed method, and the corresponding spirocyclopentane **3x** was isolated with 60% yield. Notably, a variety of di- and tri-functionalized nitrostyrenes at various positions on the benzene moiety were well accommodated in this method. Moreover, the dimethoxy group located at two distinct positions was evaluated, yielding the respective spirocyclopentane compounds **3y** and **3z** in moderate yields. Dichloro-substituted spirocyclopentane **3za** was also synthesized in 61% yield. To our delight, nitrostyrene containing hydroxyl and ethoxy groups at the 1,2-position on the benzene moiety provided compound product, **3zb**, in 65% yield. Finally, trifunctionalized spirocyclopentanes **3zc** and **3zd** were also synthesised from corresponding nitrostyrenes under standard conditions (Scheme 3).

A plausible reaction mechanism for the formation of 1,3-indandione-containing spirocyclopentane is depicted in Scheme 4. The reaction pathway starts with the formation of enolate **I** from **1a** in the presence of DABCO, which undergoes Michael addition with nitrostyrene **2a**, leading to intermediates **II**. The intermediate **II** undergoes intramolecular annulation *via* Henry reaction. To our surprise, the intramolecular Henry reaction proceeds in a highly diastereoselective manner *via* Re-face attack of the carbonyl functionality provided the intermediate **III**, which upon protonation furnishes the 1,3-indandione containing spirocyclopentane **3a**. It was possible to isolate and thoroughly characterized **IIa**, the protonated form of **II**. The formation of side product **IIa** is inevitable in some cases, where the reaction is slow. This might be the reason for the lower yields for some substrates. However, our attempts were unsuccessful in converting **IIa** to the required product **3a** under



Scheme 3 Substrate scope of nitrostyrenes.



Scheme 4 Plausible reaction mechanism for the formation of 1,3-indandione containing spirocyclopentanes.

different conditions (see the SI for details). The syn relationship between the two phenyl groups was confirmed by single-crystal X-ray diffraction analysis of one of the examples, **3g** (CCDC 2456358).

Conclusions

In conclusion, we have divulged a facile method for the synthesis of highly functionalized 1,3-indandione containing spirocyclopentane under mild, organocatalytic conditions. The resultant products possess three consecutive chiral centres in addition to a spirocyclic centre. They are obtained in a highly diastereoselective manner using a catalytic amount of the organic base DABCO. The high degree of functional group tolerance was observed in both reacting partners.

General information

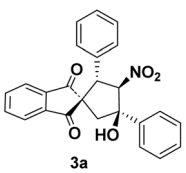
All reagents were used as supplied commercially without further purification unless otherwise stated. All the solvents are distilled before use and stored over molecular sieves. Air-sensitive reactions were carried out with the oven-dried glass apparatus with the flow of N_2 gas. All the column purifications were done with either silica gel 60–120 mesh or 230–400 mesh, in most cases eluent were a mixture of ethyl acetate and hexane unless mentioned. Analytical thin-layer chromatography (TLC) was performed on TLC Silica gel 60 F254 plates purchased from Merck, Germany. Visualisation was accomplished with UV light (254 nm) and exposure to either ethanolic phosphomolybdic acid (PMA), anisaldehyde or KMnO4 solution, CeSO4 + ammonium phosphomolybdate + 10% H_2SO_4, followed by heating. Melting points are uncorrected. 1H NMR spectra were acquired on a Bruker AVANCE NEO Ascend 400 (at 400 MHz), and chemical shifts are reported relative to the residual solvent peak (acetone-d6, $\delta = 2.05$ ppm, CDCl3, $\delta = 7.26$ ppm, methanol-d4, $\delta = 3.31$ ppm). 13C NMR spectra were acquired on Bruker AVANCE (at 100 MHz), and chemical shifts are reported in ppm relative to the residual solvent peak. Unless noted, NMR spectra were acquired in CDCl3, acetone-d6 and methanol-d4; individual peaks are reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet); coupling constants were in Hz. All IR spectra were obtained on Bruker Platinum ATR, and selected absorbance is reported in cm^{-1}. Melting points were determined with a digital melting point apparatus EI–India while keeping the sample on a melting point capillary and are uncorrected. High-resolution mass data were acquired using a Mass Spectrometer (HRMS) Xevo G2-XS QTOF Quadrupole Time of Flight Mass Spectrometer Waters, where MeOH or MeCN was used as a solvent. Chiral HPLC was performed using an Agilent 1260 Infinity II by using chiral phase columns and hexane, isopropanol are eluents. X-ray diffraction measurements were performed to determine the crystal structure of compounds at 273 K using APEX3 (Bruker, 2016; Bruker D8 Venture photon 100 CMOS detector) diffractometer having graphite-monochromatized (MoKα = 0.71073 Å).

General Procedure for the synthesis of spirocyclic compounds (3)

To a solution of compound **1** (0.2 mmol, 1 equiv.) and 1,4-diazabicyclo[2.2.2]octane (DABCO) in acetonitrile (1 mL), a solution of **2** (1.1 equiv.) in acetonitrile (1 mL) was added at room temperature. The reaction mixture was then refluxed for 2 h at 80 °C in an oil bath. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure. The resultant crude compound was diluted with CH_2Cl_2 (15 mL) and water (5 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with brine (2 × 10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resultant crude product was purified over silica gel column chromatography using ethyl acetate/hexane mixture as eluent afforded spirocyclic compounds **3**.

Characterization of spirocyclic compounds (3a–3zd)

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-3-nitro-2,4-diphenylspiro [cyclopentane-1,2′-indene]-1′,3′-dione (3a)



3a

The title compound **3a** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (70% yield; 96 : 4 dr). The spectral data are for the major diastereomer.

$R_f = 0.3$, eluent = 20% EtOAc/Hexane.

Melting point = 198–200 °C.

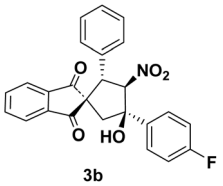
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J = 7.6$ Hz, 1H), 7.80 (dd, $J = 12.6$, 7.5 Hz, 3H), 7.72 (t, $J = 7.4$ Hz, 1H), 7.65 (d, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 7.3$ Hz, 1H), 7.11–7.03 (m, 5H), 6.14 (d, $J = 12.4$ Hz, 1H), 4.95 (d, $J = 12.4$ Hz, 1H), 2.85 (d, $J = 14.9$ Hz, 1H), 2.58 (d, $J = 15.0$ Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 201.8, 201.2, 142.2, 141.6, 139.7, 136.6, 136.2, 131.9, 128.7, 128.5, 128.4, 128.1, 125.3, 123.6, 123.4, 93.4, 81.5, 60.4, 54.4, 46.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3430, 3062, 3011, 2920, 2851, 1741, 1694, 1594, 1520, 1498, 1448.

HRMS (SI, m/z): calculated for $C_{25}H_{19}NO_5Na$ ($[M + Na]^+$): 436.1161; found: 436.1157.

(±) (2*S*,3*R*,4*R*)-4-(4-Fluorophenyl)-4-hydroxy-3-nitro-2-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3b)



3b

The title compound **3b** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (45% yield; 98 : 2 dr) The spectral data are for the major diastereomer.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 195–197 °C.

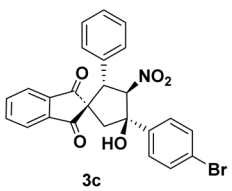
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.7 Hz, 1H), 7.85–7.76 (m, 3H), 7.73 (t, J = 7.3 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 8.3 Hz, 2H), 7.09 (s, 3H), 7.05 (s, 2H), 6.07 (d, J = 12.4 Hz, 1H), 4.90 (d, J = 12.4 Hz, 1H), 4.02 (s, 1H), 2.83 (d, J = 15.0 Hz, 1H), 2.56 (d, J = 15.0 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 201.8, 201.3, 163.9, 161.4, 142.2, 141.6, 136.5, 136.2, 136.3, 132.0, 128.7, 128.5, 128.1, 127.4, 127.3, 123.5 (d, J = 26.3 Hz), 115.6 (d, J = 21.6 Hz), 93.5, 81.2, 60.4, 54.3, 46.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3405, 3064, 3012, 2801, 1741, 1694, 1593, 1541, 1511, 1448, 1269.

HRMS (SI, m/z): calculated for $C_{25}H_{18}NO_5FNa$ ($[M + Na]^+$): 454.1067; found: 454.1063.

(±) (2*S*,3*R*,4*R*)-4-(4-Bromophenyl)-4-hydroxy-3-nitro-2-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3c)



3c

The title compound **3c** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (54% yield; 94 : 6 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 205–207 °C.

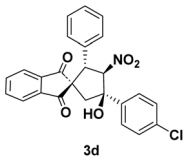
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.5 Hz, 1H), 7.80 (t, J = 7.3 Hz, 1H), 7.75–7.63 (m, 4H), 7.60 (d, J = 8.2 Hz, 2H), 7.09 (s, 3H), 7.04 (d, J = 2.7 Hz, 2H), 6.05 (d, J = 12.4 Hz, 1H), 4.89 (d, J = 12.4 Hz, 1H), 4.06 (s, 1H), 2.81 (d, J = 15.0 Hz, 1H), 2.55 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 201.8, 201.2, 142.2, 141.6, 139.7, 136.6, 136.3, 131.9, 128.7, 128.5, 128.1, 127.3, 123.7, 123.4, 122.6, 93.4, 81.2, 60.4, 54.3, 46.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3367, 3044, 2953, 2920, 2849, 1745, 1695, 1589, 1550, 1487, 1461, 698.

HRMS (SI, m/z): calculated for $C_{25}H_{18}NO_5NaBr$ ($[M + Na]^+$): 514.0266; found: 514.0266.

(±) (2*S*,3*R*,4*R*)-4-(4-chlorophenyl)-4-hydroxy-3-nitro-2-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3d)



3d

The title compound **3d** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (55% yield, 95 : 5 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 190–192 °C.

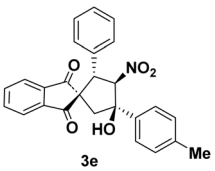
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.5 Hz, 1H), 7.82–7.71 (m, 4H), 7.65 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 7.6 Hz, 2H), 7.08 (s, 3H), 7.03 (s, 2H), 6.06 (d, J = 12.4 Hz, 1H), 4.90 (d, J = 12.4 Hz, 1H), 4.07 (s, 1H), 2.82 (d, J = 15.0 Hz, 1H), 2.56 (d, J = 15.0 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 201.8, 201.3, 142.2, 141.6, 139.1, 136.6, 136.2, 134.4, 131.8, 128.9, 128.7, 128.5, 128.1, 126.9, 123.7, 123.4, 93.4, 81.2, 60.4, 54.3, 46.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3282, 2979, 2947, 2881, 2855, 1750, 1695, 1591, 1552, 1491, 1474, 768.

HRMS (SI, m/z): calculated for $C_{25}H_{18}NO_5NaCl$ ($[M + Na]^+$): 470.0771; found: 470.0780.

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-3-nitro-2-phenyl-4-(*p*-tolyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3e)



3e

The title compound **3e** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (65% yield; 98 : 2 dr). The spectral data are for the major diastereomer.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 175–177 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.4 Hz, 1H), 7.79 (t, J = 7.1 Hz, 1H), 7.73–7.62 (m, 5H), 7.29 (s, 1H), 7.07 (d, J = 8.8 Hz,

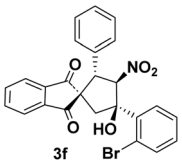
5H), 6.11 (d, J = 12.4 Hz, 1H), 4.93 (d, J = 12.3 Hz, 1H), 2.83 (d, J = 14.8 Hz, 1H), 2.55 (d, J = 14.9 Hz, 1H), 2.39 (s, 3H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 201.8, 201.5, 142.1, 141.7, 138.2, 137.5, 136.4, 136.1, 132.1, 129.4, 128.6, 128.3, 128.1, 125.2, 123.6, 123.3, 93.4, 81.5, 60.4, 54.4, 46.4, 21.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3436, 2914, 1743, 1707, 1554, 1538, 1495, 1455.

HRMS (SI, m/z): calculated for $C_{26}H_{21}NO_5Na$ ([M + Na]$^+$): 450.1317; found: 450.1311.

(±) (2*S*,3*R*,4*R*)-4-(2-Bromophenyl)-4-hydroxy-3-nitro-2-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3f)



3f

The title compound **3f** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (50% yield; 95 : 5 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 219–221 °C.

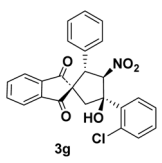
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 8.0, 1.4 Hz, 1H), 8.06 (d, J = 7.7 Hz, 1H), 7.83 (t, J = 7.4 Hz, 1H), 7.77–7.71 (m, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.45–7.43 (m, 1H), 7.24 (dd, J = 7.6, 1.4 Hz, 1H). 7.14–7.13 (m, 3H), 7.07 (dd, J = 6.5, 2.8 Hz, 2H), 6.97 (d, J = 11.3 Hz, 1H), 4.95 (s, 1H), 4.86 (d, J = 11.3 Hz, 1H), 3.78 (d, J = 15.1 Hz, 1H), 2.35 (d, J = 15.1 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 204.2, 199.0, 143.0, 140.8, 137.3, 136.8, 136.0, 135.2, 132.9, 130.1, 130.0, 128.8, 128.6, 128.3, 127.9, 123.9, 123.5, 120.2, 91.1, 82.1, 61.1, 53.9, 42.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3401, 3064, 3010, 2955, 2918, 1758, 1695, 1589, 1543, 1469, 1452, 692.

HRMS (SI, m/z): calculated for $C_{25}H_{19}BrNO_5$ ([M + H]$^+$): 492.0447; found: 492.0467.

(±) (2*S*,3*R*,4*R*)-4-(2-Chlorophenyl)-4-hydroxy-3-nitro-2-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3g)



3g

The title compound **3g** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (40% yield; 93 : 7 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 198–200 °C.

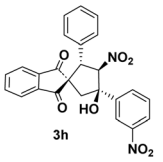
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.83 (t, J = 7.4 Hz, 1H), 7.75 (t, J = 7.4 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.37 (dt, J = 19.6, 7.2 Hz, 2H), 7.13 (d, J = 2.6 Hz, 3H), 7.06 (d, J = 3.1 Hz, 2H), 6.84 (d, J = 11.4 Hz, 1H), 4.87 (d, J = 13.8 Hz, 2H), 3.73 (d, J = 14.9 Hz, 1H), 2.30 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 204.2, 198.9, 143.0, 140.8, 136.8, 136.0, 135.8, 132.8, 131.6, 131.0, 129.9, 129.7, 128.8, 128.6, 128.3, 127.4, 123.9, 123.5, 91.1, 81.7, 61.1, 54.0, 42.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3530, 3066, 3035, 2954, 1741, 1695, 1592, 1544, 1495, 1467, 761.

HRMS (SI, m/z): calculated for $C_{25}H_{18}NO_5NaCl$ ([M + Na]$^+$): 470.0771; found: 470.0757.

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-3-nitro-4-(3-nitrophenyl)-2-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3h)



3h

The title compound **3h** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (58% yield; 97 : 3 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 198–200 °C.

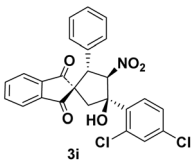
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (s, 1H), 8.32 (d, J = 7.8 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.89–7.76 (m, 3H), 7.68 (d, J = 7.5 Hz, 1H), 7.13 (s, 1H), 7.05 (d, J = 10.7 Hz, 5H), 6.24 (d, J = 12.2 Hz, 1H), 4.78 (d, J = 12.2 Hz, 1H), 2.80 (d, J = 15.5 Hz, 1H), 2.73 (d, J = 15.6 Hz, 1H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 203.1, 200.8, 148.3, 147.4, 142.3, 141.8, 136.9, 133.6, 133.1, 130.3, 128.9, 128.3, 127.9, 123.4, 123.0, 121.2, 93.6, 80.3, 60.7, 53.9, 47.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3320, 3062, 2976, 1741, 1687, 1588, 1553, 1526, 1441.

HRMS (SI, m/z): calculated for $C_{25}H_{18}N_2O_7Na$ ([M + Na]$^+$): 481.1012; found: 481.1025.

(±) (2*S*,3*R*,4*R*)-4-(2,4-Dichlorophenyl)-4-hydroxy-3-nitro-2-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3i)



3i

The title compound **3i** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was

obtained as a white solid (58% yield; 96 : 4 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 150–152 °C.

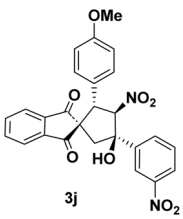
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.8, 4.7 Hz, 2H), 7.84 (t, J = 7.4 Hz, 1H), 7.76 (t, J = 7.4 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.53 (s, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 2.7 Hz, 3H), 7.03 (d, J = 3.6 Hz, 2H), 6.75 (d, J = 11.3 Hz, 1H), 5.01 (s, 1H), 4.83 (d, J = 11.3 Hz, 1H), 3.73 (d, J = 14.9 Hz, 1H), 2.23 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 204.4, 198.6, 143.0, 140.6, 137.0, 136.1, 135.1, 134.5, 132.7, 131.5, 131.2, 131.0, 128.8, 128.7, 128.4, 127.6, 124.0, 123.5, 91.2, 81.4, 61.1, 53.9, 41.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3372, 3118, 3088, 3040, 3040, 3012, 1745, 1693, 1591, 1550, 1471, 1417, 763.

HRMS (SI, m/z): calculated for $C_{25}H_{18}Cl_2NO_5$ ($[M + H]^+$): 482.0562; found: 482.0571.

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-2-(4-methoxyphenyl)-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3j)



The title compound **3j** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (60% yield; 92 : 8 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 218–220 °C.

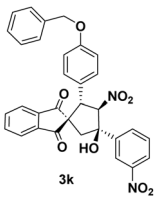
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 1H), 8.31 (d, J = 7.7 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.88 (t, J = 7.2 Hz, 1H), 7.85–7.80 (m, 2H), 7.73 (d, J = 7.4 Hz, 1H), 7.09 (s, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.4 Hz, 2H), 6.16 (d, J = 12.3 Hz, 1H), 4.73 (d, J = 12.3 Hz, 1H), 3.57 (s, 3H), 2.74 (q, J = 15.6 Hz, 2H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 203.3, 201.0, 159.1, 148.3, 147.4, 142.3, 141.8, 136.9, 133.1, 130.3, 129.2, 125.2, 123.4, 123.0, 121.2, 114.3, 94.0, 80.2, 60.7, 55.4, 53.3, 47.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3319, 3020, 2986, 2971, 2934, 1742, 1688, 1612, 1587, 1554, 1527.

HRMS (SI, m/z): calculated for $C_{26}H_{20}N_2O_8Na$ ($[M + Na]^+$): 511.1118; found: 511.1111.

(±) (2*S*,3*R*,4*R*)-2-(4-(Benzyloxy)phenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3k)



The title compound **3k** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (67% yield; 93 : 7 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 190–192 °C.

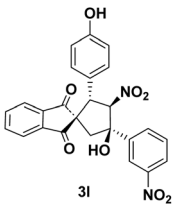
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 1H), 8.28 (dd, J = 25.6, 8.0 Hz, 2H), 7.95–7.80 (m, 4H), 7.72 (d, J = 7.4 Hz, 1H), 7.36–7.28 (m, 5H), 7.10 (s, 1H), 6.99 (d, J = 8.1 Hz, 2H), 6.71 (d, J = 8.0 Hz, 2H), 6.18 (d, J = 12.3 Hz, 1H), 4.91 (s, 2H), 4.73 (d, J = 12.3 Hz, 1H), 2.74 (q, J = 15.5 Hz, 2H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 203.3, 201.0, 158.2, 148.2, 147.4, 142.3, 141.8, 137.2, 136.9, 133.1, 130.3, 129.2, 128.8, 128.2, 128.1, 125.5, 123.4, 123.0, 121.2, 115.1, 93.9, 80.2, 69.5, 60.8, 53.3, 47.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3299, 3083, 3064, 3025, 2970, 2939, 1745, 1698, 1611, 1593, 1544, 1529.

HRMS (SI, m/z): calculated for $C_{32}H_{24}N_2O_8Na$ ($[M + Na]^+$): 587.1430; found: 587.1424.

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-2-(4-hydroxyphenyl)-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3l)



The title compound **3l** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (63% yield; 95 : 5 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 219–221 °C.

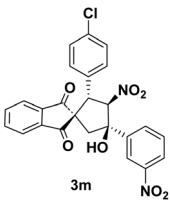
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 8.66 (t, J = 1.7 Hz, 1H), 8.32–8.23 (m, 2H), 7.94–7.80 (m, 4H), 7.73 (d, J = 7.4 Hz, 1H), 7.07 (s, 1H), 6.84 (d, J = 8.5 Hz, 2H), 6.43 (d, J = 8.5 Hz, 2H), 6.09 (d, J = 12.3 Hz, 1H), 4.68 (d, J = 12.3 Hz, 1H), 2.74 (q, J = 15.5 Hz, 2H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 203.5, 201.1, 157.2, 148.3, 147.5, 142.4, 141.9, 136.9, 136.8, 133.0, 130.3, 129.0, 123.4, 123.3, 123.0, 121.1, 115.7, 94.0, 80.1, 60.9, 53.5, 47.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3438, 3278, 3086, 3036, 2979, 2942, 1734, 1693, 1615, 1592, 1549, 1523.

HRMS (SI, m/z): calculated for $C_{25}H_{18}N_2O_8Na$ ($[M + Na]^+$): 497.0961; found: 497.0957.

(±) (2*S*,3*R*,4*R*)-2-(4-Chlorophenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3m)



The title compound **3m** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (71% yield; 92 : 8 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 246–248 °C.

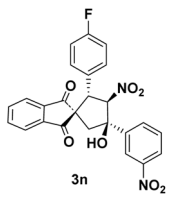
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 1H), 7.88 (t, J = 7.5 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.73–7.63 (m, 6H), 7.44 (d, J = 8.5 Hz, 2H), 7.39 (t, J = 7.7 Hz, 1H), 5.77 (d, J = 11.6 Hz, 1H), 5.41 (s, 1H), 5.36 (d, J = 11.6 Hz, 1H), 3.06 (d, J = 14.9 Hz, 1H), 2.41 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 201.8, 199.6, 147.2, 146.2, 141.2, 140.6, 136.0, 132.0, 131.9, 131.7, 129.2, 128.9, 127.8, 122.4, 121.9, 120.1, 92.3, 79.2, 59.5, 52.2, 46.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3445, 3091, 2979, 2907, 1741, 1691, 1588, 1543, 1524, 1494, 727.

HRMS (SI, m/z): calculated for $C_{25}H_{17}N_2O_7NaCl$ ([M + Na]$^+$): 515.0622; found: 515.0631.

(±) (2*S*,3*R*,4*R*)-2-(4-Fluorophenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3n)



The title compound **3n** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (57% yield; 99 : 1 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 195–197 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.70 (s, 1H), 8.26 (d, J = 8.3 Hz, 1H), 8.21 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.86 (t, J = 7.4 Hz, 1H), 7.80 (t, J = 7.3 Hz, 1H), 7.73–7.69 (m, 2H), 7.08 (dd, J = 8.1, 5.4 Hz, 2H), 6.84 (t, J = 8.5 Hz, 2H), 6.03 (d, J = 12.2 Hz, 1H), 4.86 (d, J = 12.2 Hz, 1H), 4.32 (s, 1H), 2.93 (d, J = 15.3 Hz, 1H), 2.60 (d, J = 15.3 Hz, 1H).

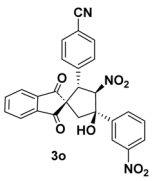
^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 203.01, 200.73, 161.89 (d, J = 244.7 Hz), 148.26, 147.36, 142.27, 141.73, 136.99, 133.13, 130.29, 130.13 (d, J = 8.2 Hz), 129.92 (d, J = 2.9 Hz), 123.38 (d, J = 1.6 Hz), 122.98, 121.21, 115.73 (d, J = 21.5 Hz), 93.58, 80.29, 60.76, 53.27, 47.42.

^{19}F NMR (377 MHz, CD_2Cl_2) δ −113.54.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3387, 3096, 3075, 2988, 2966, 1739, 1686, 1590, 1555, 1529, 1511, 729.

HRMS (SI, m/z): calculated for $C_{25}H_{17}FN_2O_7Na$ ([M + Na]$^+$): 499.0918; found: 499.0906.

(±) 4-((3*R*,4*R*,5*S*)-3-Hydroxy-4-nitro-3-(3-nitrophenyl)-1′,3′-dioxo-1′,3′-dihydrospiro[cyclopentane-1,2′-inden]-5-yl) benzonitrile (3o)



The title compound **3o** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (69% yield; 99 : 1 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 260–262 °C.

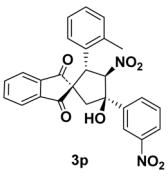
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (s, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.90 (t, J = 7.3 Hz, 1H), 7.85–7.81 (m, 2H), 7.70 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 (s, 1H), 6.44 (d, J = 12.1 Hz, 1H), 4.85 (d, J = 12.1 Hz, 1H), 2.81–2.72 (m, 2H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 202.4, 200.3, 148.2, 147.2, 142.2, 141.5, 139.7, 137.2, 137.2, 133.2, 132.7, 130.3, 129.3, 123.5, 123.4, 123.0, 121.2, 118.6, 111.1, 92.9, 80.4, 60.6, 53.7, 47.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3457, 3088, 2998, 2930, 2102, 1739, 1698, 1589, 1526, 1483, 1432.

HRMS (SI, m/z): calculated for $C_{25}H_{17}N_3O_9Na$ ([M + Na]$^+$): 506.0964; found: 506.0965.

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-3-nitro-4-(3-nitrophenyl)-2-(*o*-tolyl) spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3p)



The title compound **3p** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was

obtained as a white solid (63% yield; 97 : 3 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 195–197 °C.

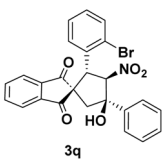
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.71 (s, 1H), 8.24 (dd, J = 14.4, 8.0 Hz, 2H), 8.03 (d, J = 7.6 Hz, 1H), 7.85 (t, J = 7.4 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.72 (t, J = 8.0 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 5.94 (d, J = 11.9 Hz, 1H), 5.17 (d, J = 11.9 Hz, 1H), 4.74 (s, 1H), 3.05 (d, J = 15.2 Hz, 1H), 2.56 (d, J = 15.2 Hz, 1H), 2.09 (s, 3H).

^{13}C{1H} NMR (100 MHz, CD_2Cl_2) δ 203.4, 199.8, 148.6, 142.9, 142.3, 140.9, 137.6, 137.1, 136.4, 131.8, 130.8, 130.3, 129.7, 128.2, 128.0, 126.2, 123.6, 123.4, 123.2, 121.0, 95.8, 81.2, 60.4, 49.4, 45.9, 19.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3367, 3118, 3088, 3068, 3027, 2983, 2910, 1746, 1691, 1591, 1551, 1524, 1438.

HRMS (SI, m/z): calculated for $C_{26}H_{20}N_2O_7Na$ ([M + Na]$^+$): 495.1169; found: 495.1169.

(±) (2*R*,3*R*,4*R*)-2-(2-Bromophenyl)-4-hydroxy-3-nitro-4-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3q)



3q

The title compound **3q** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (55% yield; 97 : 3 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 230–232 °C.

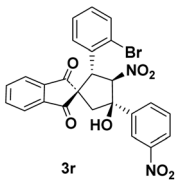
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 1H), 7.87–7.79 (m, 3H), 7.75 (t, J = 7.4 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.40 (dd, J = 17.2, 7.9 Hz, 2H), 7.29 (dd, J = 11.6, 6.7 Hz, 2H), 7.01 (t, J = 7.6 Hz, 1H), 5.89 (d, J = 11.9 Hz, 1H), 5.52 (d, J = 11.9 Hz, 1H), 4.80 (s, 1H), 3.03 (d, J = 14.9 Hz, 1H), 2.47 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 203.0, 199.7, 142.0, 141.8, 139.5, 136.6, 136.3, 133.3, 132.2, 129.8, 129.7, 128.7, 128.3, 127.7, 126.2, 125.4, 124.1, 123.2, 95.2, 81.8, 60.2, 52.1, 45.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3401, 3064, 3010, 2955, 2918, 2853, 1758, 1695, 1589, 1543, 1469, 1452, 692.

HRMS (SI, m/z): calculated for $C_{25}H_{18}NO_5NaBr$ ([M + Na]$^+$): 514.0266; found: 514.0231.

(±) (2*R*,3*R*,4*R*)-2-(2-Bromophenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3r)



3r

The title compound **3r** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (61% yield; 95 : 5 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 214–216 °C.

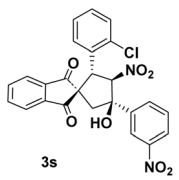
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 1H), 8.35 (d, J = 7.9 Hz, 1H), 8.25 (dd, J = 8.1, 2.1 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.87–7.81 (m, 2H), 7.76 (t, J = 7.4 Hz, 1H), 7.59 (d, J = 7.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.11 (s, 1H), 7.00–6.95 (m, 1H), 6.26 (d, J = 11.9 Hz, 1H), 5.37 (d, J = 11.9 Hz, 1H), 2.80 (s, 2H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 201.6, 199.0, 147.8, 146.6, 142.0, 141.2, 136.1, 136.1, 132.8, 132.8, 129.8, 129.6, 129.5, 127.6, 125.2, 123.0, 122.5, 122.4, 120.8, 94.0, 80.0, 60.4, 51.6, 45.7.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3457, 3116, 2998, 2930, 1738, 1698, 1590, 1548, 1528, 1477, 725.

HRMS (SI, m/z): calculated for $C_{25}H_{17}N_2O_7NaBr$ ([M + Na]$^+$): 559.0117; found: 559.0112.

(±) (2*R*,3*R*,4*R*)-2-(2-chlorophenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3s)



3s

The title compound **3s** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (66% yield; 96 : 4 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 242–244 °C.

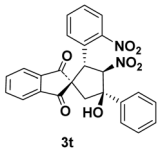
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 1H), 8.34 (d, J = 7.8 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.84 (dt, J = 11.9, 7.7 Hz, 1H), 7.76 (t, J = 7.4 Hz, 1H), 7.65–7.52 (m, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.13–7.01 (m, 2H), 6.28 (d, J = 12.0 Hz, 1H), 5.35 (d, J = 12.0 Hz, 1H), 2.79 (s, 1H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 202.2, 199.6, 148.3, 147.0, 142.4, 141.5, 136.7, 136.6, 134.4, 133.2, 131.7, 130.2, 129.8, 127.6, 123.4, 123.0, 122.9, 121.3, 94.1, 80.5, 60.7, 49.7, 46.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3457, 3088, 2998, 2930, 1739, 1698, 1590, 1549, 1528, 1483, 724.

HRMS (SI, m/z): calculated for $C_{25}H_{17}ClN_2O_7Na$ ([M + Na]$^+$): 515.0622; found: 515.0574.

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-3-nitro-2-(2-nitrophenyl)-4-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3t)



3t

The title compound **3t** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (63% yield; 95 : 5 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 214–216 °C.

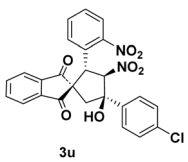
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.7 Hz, 1H), 7.88 (t, J = 7.4 Hz, 1H), 7.77 (t, J = 7.5 Hz, 3H), 7.68 (d, J = 15.4, 13.1, 7.9 Hz, 4H), 7.48 (t, J = 7.7 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 5.84 (d, J = 11.6 Hz, 1H), 5.38 (d, J = 11.6 Hz, 1H), 5.30 (s, 1H), 3.12 (d, J = 14.9 Hz, 1H), 2.44 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 203.6, 199.3, 150.2, 141.7, 141.4, 139.1, 136.7, 136.6, 133.0, 131.2, 129.4, 128.6, 128.4, 128.2, 125.5, 125.0, 124.4, 123.5, 96.6, 81.8, 59.9, 47.8, 46.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3469, 3083, 2955, 2917, 2851, 1736, 1690, 159, 1551, 1522, 1446.

HRMS (SI, m/z): calculated for $C_{25}H_{18}N_2O_7Na$ ([M + Na]$^+$): 481.1012; found: 481.1015.

(±) (2*S*,3*R*,4*R*)-4-(4-Chlorophenyl)-4-hydroxy-3-nitro-2-(2-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3u)



3u

The title compound **3u** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (64% yield; 94 : 6 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 210–212 °C.

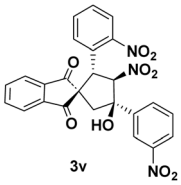
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 1H), 7.88 (t, J = 7.5 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.73–7.63 (m, 6H), 7.44 (d, J = 8.5 Hz, 2H), 7.39 (t, J = 7.7 Hz, 1H), 5.77 (d, J = 11.6 Hz, 1H), 5.41 (s, 1H), 5.36 (d, J = 11.6 Hz, 1H), 3.06 (d, J = 14.9 Hz, 1H), 2.41 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 203.6, 199.1, 150.2, 141.7, 141.4, 137.8, 136.8, 136.7, 134.3, 133.0, 131.1, 129.5, 128.8, 128.1, 127.0, 125.0, 124.5, 123.5, 96.4, 81.5, 59.8, 47.6, 46.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3476, 3114, 3082, 2922, 2854, 1736, 1697, 1594, 1550, 1519, 1437, 729.

HRMS (SI, m/z): calculated for $C_{25}H_{17}N_2O_7ClNa$ ([M + Na]$^+$): 515.0622; found: 515.0635.

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-3-nitro-2-(2-nitrophenyl)-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3v)



3v

The title compound **3v** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (66% yield; 95 : 5 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 215–217 °C.

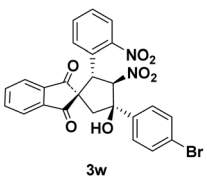
^{1}H NMR (700 MHz, DMSO-d_6) δ 8.67 (t, J = 2.0 Hz, 1H), 8.33 (d, J = 7.9 Hz, 1H), 8.26–8.24 (m, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.87–7.85 (m, 2H), 7.82 (t, J = 8.0 Hz, 1H), 7.78–7.76 (m, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.57–7.55 (m, 2H), 7.36–7.33 (m, 1H), 7.12 (s, 1H), 6.38 (d, J = 11.7 Hz, 1H), 5.25 (d, J = 11.7 Hz, 1H), 2.81 (d, J = 15.6 Hz, 1H), 2.76 (d, J = 15.7 Hz, 1H).

^{13}C{1H} NMR (177 MHz, DMSO-d_6) δ 201.5, 198.6, 150.1, 147.8, 146.3, 141.8, 141.0, 136.4, 136.2, 132.8, 132.6, 130.1, 129.7, 129.4, 127.0, 124.2, 123.2, 122.6, 122.6, 120.8, 93.9, 79.9, 60.5, 47.3, 45.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3368, 3116, 3094, 3068, 3046, 2983, 1743, 1690, 1593, 1551, 1522, 1439.

HRMS (SI, m/z): calculated for $C_{25}H_{17}N_3O_9Na$ ([M + Na]$^+$): 526.0863; found: 526.0870.

(±) (2*S*,3*R*,4*R*)-4-(4-Bromophenyl)-4-hydroxy-3-nitro-2-(2-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3w)



3w

The title compound **3w** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (65% yield; 89 : 11 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 25% EtOAc/Hexane.

Melting point = 208–210 °C.

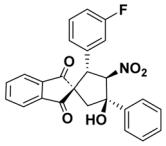
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 1H), 7.88 (t, J = 7.3 Hz, 1H), 7.80–7.76 (m, 1H), 7.68 (dd, J = 17.9, 7.8 Hz, 6H), 7.60 (d, J = 8.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 5.77 (d, J = 11.5 Hz, 1H), 5.35 (d, J = 11.5 Hz, 1H), 3.05 (d, J = 14.9 Hz, 1H), 2.41 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 203.6, 199.0, 150.2, 141.7, 141.4, 138.3, 136.8, 136.7, 133.0, 131.8, 131.1, 129.5, 128.1, 127.4, 125.0, 124.5, 123.5, 122.6, 96.4, 81.5, 59.8, 47.6, 46.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3480, 3111, 3079, 2953, 2923, 2853, 2849, 1737, 1696, 1591, 1551, 1520, 1488, 715.

HRMS (SI, *m*/*z*): calculated for $C_{25}H_{17}N_2O_7NaBr$ ($[M + Na]^+$): 559.0117; found: 559.0137.

(±) (2*S*,3*R*,4*R*)-2-(3-Fluorophenyl)-4-hydroxy-3-nitro-4-phenylspiro[cyclopentane-1,2′-indene]-1′,3′-dione (3x)



3x

The title compound **3x** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (60% yield; 95 : 5). The spectral data are for the major diastereomer.

R_f = 0.3, eluent = 20% EtOAc/Hexane.

Melting point = 245–247 °C.

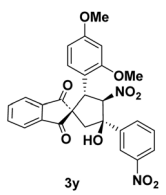
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.5 Hz, 1H), 7.83–7.71 (m, 5H), 7.49 (t, J = 7.5 Hz, 2H), 7.41–7.37 (m, 1H), 7.08 (dd, J = 14.8, 7.6 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 6.79 (d, J = 8.3 Hz, 2H), 6.10 (d, J = 12.4 Hz, 1H), 4.94 (d, J = 12.3 Hz, 1H), 2.83 (d, J = 15.0 Hz, 1H), 2.58 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 201.37, 201.30, 163.77, 161.30, 141.96, 141.66, 140.34, 136.59, 136.39, 134.74, 134.67, 130.36, 130.27, 128.79, 128.46, 125.28, 123.9 (d, J = 3.0 Hz), 123.75, 123.49, 115.41 (dd, J = 21.7, 14.4 Hz)., 93.29, 81.46, 60.06, 53.68, 46.74.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3337, 2899, 2885, 1702, 1650, 1552, 1449, 1427.

HRMS (SI, *m*/*z*): calculated for $C_{25}H_{18}NO_5NaF$ ($[M + Na]^+$): 454.1067; found: 454.1053.

(±) (2*S*,3*R*,4*R*)-2-(2,4-Dimethoxyphenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3y)



3y

The title compound **3y** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (66% yield; 95 : 5 dr). The spectral data are for the major diastereomer.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 207–209 °C.

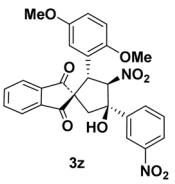
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.65 (s, 1H), 8.24 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.7 Hz, 1H), 7.89 (t, J = 7.4 Hz, 1H), 7.80 (t, J = 7.4 Hz, 1H), 7.69 (t, J = 8.5 Hz, 2H), 7.10 (d, J = 8.5 Hz, 1H), 6.45 (d, J = 8.3 Hz, 1H), 6.09 (s, 1H), 5.96 (d, J = 12.1 Hz, 1H), 5.22 (s, 1H), 5.04 (d, J = 12.1 Hz, 1H), 3.71 (s, 3H), 3.15 (s, 3H), 2.90 (d, J = 14.9 Hz, 1H), 2.43 (d, J = 14.9 Hz, 1H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 203.4, 199.3, 160.9, 157.3, 148.6, 142.4, 141.6, 141.4, 136.4, 136.0, 131.9, 129.6, 127.3, 123.2, 123.2, 121.0, 113.7, 104.3, 98.1, 93.3, 81.5, 59.5, 55.3, 54.0, 46.7, 45.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3432, 3075, 3001, 2932, 2837, 1745, 1696, 1614, 1586, 1547, 1529.

HRMS (SI, *m*/*z*): calculated for $C_{27}H_{22}N_2O_9Na$ ($[M + Na]^+$): 541.1223; found: 541.1220.

(±) (2*S*,3*R*,4*R*)-2-(2,5-Dimethoxyphenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3z)



3z

The title compound **3z** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (67% yield; 98 : 2 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 204–206 °C.

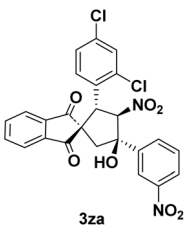
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.63 (s, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.24 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.88 (t, J = 7.4 Hz, 1H), 7.81 (t, J = 8.0 Hz, 1H), 7.75 (t, J = 7.4 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.84 (s, 1H), 6.59 (d, J = 8.9 Hz, 1H), 6.43 (d, J = 9.0 Hz, 1H), 6.22 (d, J = 12.2 Hz, 1H), 5.05 (d, J = 12.2 Hz, 1H), 3.62 (s, 3H), 3.29 (s, 3H), 2.75–2.67 (m, 2H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 202.5, 199.3, 153.3, 150.9, 148.2, 147.1, 142.8, 140.7, 136.4, 136.1, 133.2, 130.2, 123.2, 122.9, 122.8, 121.3, 114.7, 113.0, 110.9, 93.06, 80.7, 59.8, 56.0, 55.0, 47.3, 46.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3367, 3129, 3068, 3049, 3014, 2908, 2833, 1736, 1696, 1590, 1551, 1529, 1498, 1348.

HRMS (SI, *m*/*z*): calculated for $C_{27}H_{22}N_2O_9Na$ ($[M + Na]^+$): 541.1223; found: 541.1241.

(±) (2*R*,3*R*,4*R*)-2-(2,4-Dichlorophenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3za)



3za

The title compound **3za** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was

obtained as a white solid (61% yield; 90 : 10 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 210–213 °C.

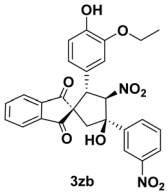
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (s, 1H), 8.32 (d, J = 7.9 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.89 (t, J = 7.4 Hz, 1H), 7.82 (dd, J = 13.6, 7.2 Hz, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 10.6 Hz, 2H), 7.13 (s, 1H), 6.34 (d, J = 11.9 Hz, 1H), 5.30 (d, J = 11.9 Hz, 1H), 2.78 (s, 2H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 202.0, 199.6, 148.3, 146.9, 142.3, 141.5, 136.9, 136.8, 135.4, 133.6, 133.2, 131.4, 131.1, 130.2, 129.2, 127.7, 123.5, 123.0, 121.3, 93.9, 80.6, 60.5, 49.3, 46.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3438, 3278, 3086, 3036, 2979, 2942, 1734, 1693, 1615, 1592, 1549, 1523.

HRMS (SI, m/z): calculated for $C_{25}H_{16}N_2O_7NaCl_2$ ([M + Na]$^+$): 549.0232; found: 549.0225.

(±) (2*S*,3*R*,4*R*)-2-(3-Ethoxy-4-hydroxyphenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3zb)



The title compound **3zb** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (65% yield; 96 : 4 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 35% EtOAc/Hexane.

Melting point = 231–233 °C.

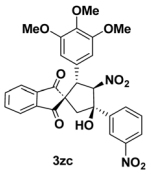
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.76 (s, 1H), 8.65 (s, 1H), 8.32 (d, J = 7.7 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.95–7.81 (m, 4H), 7.72 (d, J = 7.4 Hz, 1H), 7.04 (s, 1H), 6.50 (s, 1H), 6.44 (s, 2H), 6.11 (d, J = 12.6 Hz, 1H), 4.66 (d, J = 12.4 Hz, 1H), 3.86–3.82 (m, 1H), 3.76–3.73 (m, 1H), 2.73 (q, J = 16.2 Hz, 2H), 1.18 (t, J = 6.9 Hz, 3H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 203.5, 201.1, 148.2, 147.6, 146.9, 146.6, 142.4, 141.9, 136.9, 136.9, 133.1, 130.3, 124.0, 123.3, 123.2, 123.0, 121.2, 120.6, 115.9, 113.7, 93.8, 80.2, 64.3, 61.0, 54.0, 47.2, 15.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3460, 3017, 2983, 2906, 1744, 1697, 1595, 1545, 1529, 148, 737.

HRMS (SI, m/z): calculated for $C_{27}H_{22}N_2O_9Na$ ([M + Na]$^+$): 541.1223; found: 541.1220.

(±) (2*S*,3*R*,4*R*)-4-Hydroxy-3-nitro-4-(3-nitrophenyl)-2-(3,4,5-trimethoxyphenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3zc)



The title compound **3zc** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (56% yield; 98 : 2 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 226–228 °C.

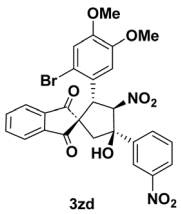
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (t, J = 1.9 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.25 (dd, J = 8.1, 1.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.87–7.74 (m, 3H), 7.57 (d, J = 7.6 Hz, 1H), 7.02 (s, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.58 (d, J = 8.8 Hz, 1H), 6.09 (d, J = 12.3 Hz, 1H), 5.01 (d, J = 12.3 Hz, 1H), 3.65 (s, 3H), 3.61 (s, 3H), 3.21 (s, 3H), 2.74 (s, 2H).

^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 207.6, 204.4, 158.0, 156.2, 153.0, 152.1, 147.7, 146.0, 141.1, 140.9, 137.9, 135.0, 128.1, 127.7, 127.5, 127.1, 125.9, 124.1, 112.5, 98.5, 85.2, 65.2, 65.2, 65.1, 60.9, 52.2, 51.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3457, 3234, 3009, 2969, 2936, 2836, 1747, 1700, 1638, 1596, 1551, 1500, 1306.

HRMS (SI, m/z): calculated for $C_{28}H_{24}N_2O_{10}Na$ ([M + Na]$^+$): 571.1329; found: 571.1318.

(±) (2*R*,3*R*,4*R*)-2-(6-Bromo-2,3-dimethoxyphenyl)-4-hydroxy-3-nitro-4-(3-nitrophenyl)spiro[cyclopentane-1,2′-indene]-1′,3′-dione (3zd)



The title compound **3zd** was prepared according to general procedure A on a 0.2 mmol scale. The desired product was obtained as a white solid (61% yield; 91 : 9 dr). The minor diastereomer was separated by silica gel column chromatography.

R_f = 0.3, eluent = 30% EtOAc/Hexane.

Melting point = 238–240 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (s, 1H), 8.37 (d, J = 7.7 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.83 (dt, J = 13.5, 7.2 Hz, 3H), 7.70 (d, J = 7.5 Hz, 1H), 7.02 (d, J =

13.8 Hz, 2H), 6.79 (s, 1H), 6.25 (d, J = 11.9 Hz, 1H), 5.29 (d, J = 11.9 Hz, 1H), 3.77 (s, 3H), 3.57 (s, 3H), 2.85–2.69 (m, 2H).

$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 207.8, 204.2, 153.7, 153.1, 153.0, 152.1, 147.1, 146.6, 141.4, 138.2, 135.0, 129.6, 128.1, 127.7, 127.6, 126.1, 120.8, 120.7, 118.1, 99.3, 85.2, 65.8, 61.4, 60.9, 57.0, 50.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3320, 3095, 3007, 2938, 283, 1731, 1690, 1591, 1542, 1511, 1464, 725.

HRMS (SI, m/z): calculated for $C_{27}H_{21}BrN_2O_9Na$ ($[M + Na]^+$): 619.0328; found: 619.0324.

Conflicts of interest

There are no conflicts to declare.

Data availability

CCDC 2456358 contains the supplementary crystallographic data for this paper.[14]

The data supporting this article have been included in the SI. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (**https://www.ccdc.cam.ac.uk/services/structures**) with CCDC reference number 2456358 for compound **3g**. See DOI: **https://doi.org/10.1039/d5ra04224k**.

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