Supporting Information-I

Organocatalytic Azomethine imine-Olefin Click Reaction: High-yielding Stereoselective Synthesis of Spiroindane-1,3-dione-pyrazolidinones

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. *N,N*-Cyclic azomethine imines **3a-i**[1] and 2-arylidene-1,3-indandiones **4** (**4a**, **4b**, **4f**, **4i** and **4j**)[2] were prepared according to the literature procedure.

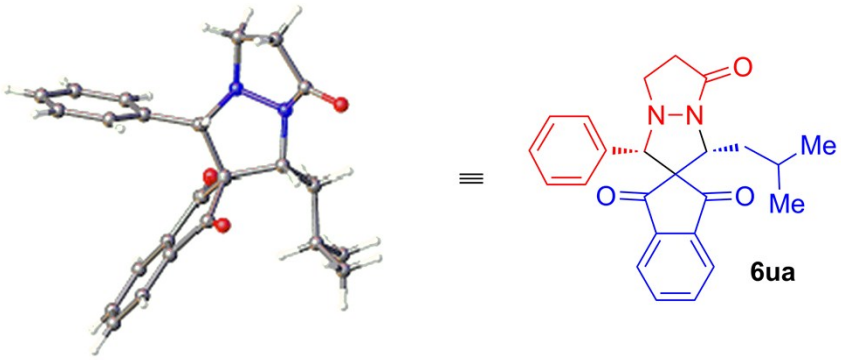


Fig S1. X-Ray crystal structure of (1'*S**,3'*R**)-3'-isobutyl-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (**6ua**).

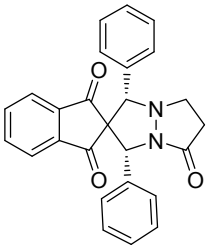
General Experimental Procedures

Procedure A: ***General procedure for L-proline catalyzed three-component synthesis of spiroindane-1,3-dione-pyrazolidinones*:** In an ordinary glass vial equipped with a magnetic stirring bar, to L-proline **5e** (5 mol%) in CH_3CN (0.5 mL), were added 1,3-indandione **1** (0.3 mmol) and aldehyde **2** (0.45 mmol, 1.5 equiv.) and the reaction mixture was stirred at ambient temperature for 15 to 20 minutes. When the reaction mixture solidified, more solvent (0.5 mL) was added. To the reaction mixture azomethine imine **3** (0.36 mmol, 1.2 equiv.) was added and stirred at 50 °C for 0.6-1.5 h. The reaction mixture was treated with saturated aqueous ammonium chloride solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, and concentrated. Pure products **6** were obtained by quick filtration (silica gel, mixture of hexane/ethyl acetate).

Procedure B: ***General procedure for the two-component synthesis of spiroindane-1,3-dione-pyrazolidinones*:** In an ordinary glass vial equipped with a magnetic stirring bar, to 2-arylideneindane-1,3-dione **4** (0.3 mmol) and azomethine imine **3** (0.36 mmol, 1.2 equiv.) were added in CH_3CN (1.0 mL) and stirred at 50 °C for 1.2-1.5 h. The reaction mixture was treated with saturated aqueous ammonium

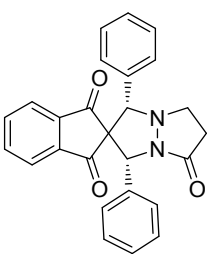
chloride solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, and concentrated. Pure products **6** were obtained by quick filtration (silica gel, mixture of hexane/ethyl acetate).

(1'*S,3'*R**)-1',3'-Diphenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*) trione (6aa):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 160-162 °C; *dr* = >99:1; IR (KBr): ν_{max} 3032, 2935, 1752, 1714, 1584, 1455, 1346, 1265, 1109, 920, 768, 698 and 617 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97 (1H, d, *J* = 8.0 Hz), 7.72 (1H, dt, *J* = 7.6, 0.4 Hz), 7.58 (1H, dt, *J* = 7.6, 0.4 Hz), 7.39 (1H, d, *J* = 7.6 Hz), 7.21-7.17 (2H, m), 7.16-7.13 (3H, m), 7.11-7.07 (5H, m), 5.81 (1H, s), 4.42 (1H, s), 3.89-3.79 (1H, m), 3.12-3.03 (2H, m), 2.93-2.85 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.2 (C, *C*=O), 194.5 (C, *C*=O), 172.4 (C, *C*=O), 143.2 (C), 141.3 (C), 136.2 (CH), 135.5 (CH), 135.2 (C), 131.7 (C), 128.8 (CH), 128.5 (2 x CH), 128.4 (2 x CH), 127.85 (CH), 127.82 (2 x CH), 125.8 (2 x CH), 123.23 (CH), 123.16 (CH), 77.4 (CH), 72.1 (C), 63.3 (CH), 48.1 (CH_2), 32.5 (CH_2); LCMS m/z 409.15 ($M + H^+$), calcd for $C_{26}H_{21}N_2O_3$ 409.1552; HRMS m/z 431.1373 ($M + Na^+$), calcd for $C_{26}H_{20}N_2O_3Na$ 431.1372; Anal. calcd for $C_{26}H_{20}N_2O_3$ (408.1474): C, 76.45; H, 4.94; N, 6.86. Found: C, 76.32; H, 4.98; N, 6.79%.



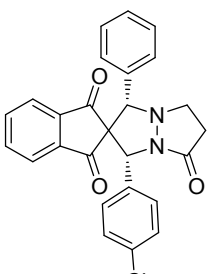
6aa

(1'*S,3'*R**)-3'-(4-Fluorophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2a] pyrazole]-1,3,5'(3'*H*)-trione (6ba):** Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 150-152 °C; *dr* = >99:1; IR (KBr): ν_{max} 2357, 2335, 1752, 1708, 1514, 1341, 1260, 1233, 1168, 763 and 703 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.95 (1H, d, *J* = 8.0 Hz), 7.70 (1H, t, *J* = 7.5 Hz), 7.58 (1H, t, *J* = 7.5 Hz), 7.39 (1H, d, *J* = 7.5 Hz), 7.18-7.16 (2H, m), 7.09-7.06 (5H, m), 6.82 (2H, t, *J* = 8.5 Hz), 5.75 (1H, s), 4.40 (1H, s), 3.83-3.78 (1H, m), 3.09-3.00 (2H, m), 2.91-2.84 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.0 (C, *C*=O), 194.5 (C, *C*=O), 172.7 (C, *C*=O), 162.2 (C, d, *J* = 245.0 Hz, *C*-F), 143.0 (C), 141.2 (C), 136.4 (CH), 135.7 (CH), 131.5 (C), 131.1 (C, d, *J* = 2.5 Hz), 128.9 (CH), 128.5 (2 x CH), 127.75 (3 x CH), 127.67 (CH), 123.2 (2 x CH, d, *J* = 12.5 Hz), 115.3 (2 x CH, d, *J* = 22.5 Hz), 77.3 (CH), 72.0 (C), 62.8 (CH), 48.0 (CH_2), 32.3 (CH_2); LCMS m/z 427.40 ($M + H^+$), calcd for $C_{26}H_{20}FN_2O_3$ 427.1458; HRMS m/z 449.1272 ($M + Na^+$), calcd for $C_{26}H_{19}FN_2O_3Na$ 449.1277; Anal. calcd for $C_{26}H_{19}FN_2O_3$ (426.1380): C, 73.23; H, 4.49; N, 6.57. Found: C, 73.15; H, 4.53; N, 6.49%.



6ba

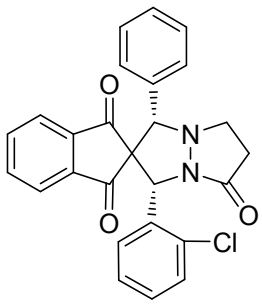
(1'*S,3'*R**)-3'-(4-Chlorophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2a] pyrazole]-1,3,5'(3'*H*)-trione (6ca):** Prepared by following the



6ca

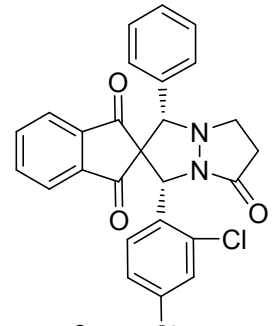
procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off-white solid. Mp 160-162 °C; *dr* = 8:1; IR (KBr): ν_{max} 2849, 2816, 1746, 1719, 1590, 1487, 1336, 1292, 1265, 1179, 1098, 1028, 768 and 703 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 7.96 (1H, d, *J* = 7.5 Hz), 7.73 (1H, t, *J* = 7.5 Hz), 7.61 (1H, t, *J* = 7.5 Hz), 7.42 (1H, d, *J* = 8.0 Hz), 7.18-7.17 (2H, m), 7.13 (2H, d, *J* = 8.0 Hz), 7.11-7.10 (3H, m), 7.06-7.01 (2H, m), 5.76 (1H, s), 4.40 (1H, s), 3.85-3.79 (1H, m), 3.10-3.02 (2H, m), 2.93-2.86 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 197.9 (C, *C*=O), 194.4 (C, *C*=O), 172.7 (C, *C*=O), 143.0 (C), 141.2 (C), 136.4 (CH), 135.7 (CH), 133.9 (C), 133.7 (C), 131.5 (C), 128.9 (CH), 128.6 (2 x CH), 128.5 (2 x CH), 127.8 (2 x CH), 127.4 (2 x CH), 123.3 (2 x CH), 77.4 (CH), 72.0 (C), 62.7 (CH), 48.0 (CH_2), 32.3 (CH_2); HRMS m/z 465.0982 ($M + Na^+$), calcd for $C_{26}H_{19}ClN_2O_3Na$ 465.0982.

(1'*S,3'*S**)-3'-(2-Chlorophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2a] pyrazole]-1,3,5'(3'*H*)-trione (6da):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 156-158 °C; *dr* = 7:1; IR (KBr): ν_{max} 2964, 2849, 1742, 1715, 1594, 1386, 1255, 1085, 888 and 756 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 7.96 (1H, d, *J* = 8.0 Hz), 7.79 (1H, dd, *J* = 8.0, 0.8 Hz), 7.71 (1H, dt, *J* = 7.6, 0.8 Hz), 7.57 (1H, dt, *J* = 7.6, 0.4 Hz), 7.34 (2H, d, *J* = 9.5 Hz), 7.16-7.12 (3H, m,), 7.10-7.05 (4H, m), 5.99 (1H, s), 4.36 (1H, s), 3.81 (1H, ddd, *J* = 11.6, 9.2, 8.0 Hz), 3.12 (1H, ddd, *J* = 11.6, 9.2, 6.8 Hz), 2.96-2.89 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 198.6 (C, *C*=O), 194.5 (C, *C*=O), 173.9 (C, *C*=O), 141.8 (C), 141.5 (C), 135.9 (CH), 135.5 (CH), 134.2 (C), 131.7 (C), 131.5 (C), 129.3 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.3 (2 x CH), 128.1 (2 x CH), 126.9 (CH), 123.04 (CH), 122.99 (CH), 78.1 (CH), 70.9 (C), 60.5 (CH), 45.9 (CH_2), 30.8 (CH_2); LCMS m/z 443.35 ($M + H^+$), calcd for $C_{26}H_{20}ClN_2O_3$ 443.1162; HRMS m/z 465.0986 ($M + Na^+$), calcd for $C_{26}H_{19}ClN_2O_3Na$ 465.0982; Anal. calcd for $C_{26}H_{19}ClN_2O_3$ (442.1084): C, 70.51; H, 4.32; N, 6.33. Found: C, 70.42; H, 4.28; N, 6.41%.



6da

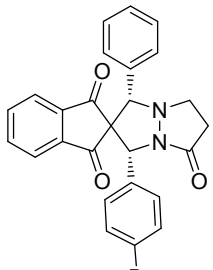
(1'*S,3'*S**)-3'-(2,4-Dichlorophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ea):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 174-176 °C; *dr* = >99:1; IR (KBr): ν_{max} 2919, 2849, 1746, 1708, 1649, 1590, 1471, 1341, 1255, 812, 763 and 709 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.95 (1H, d, *J* = 7.5 Hz), 7.73-7.70 (2H, m), 7.59 (1H, dt, *J* = 7.5,0.5 Hz), 7.36 (1H, d, *J* = 7.5 Hz), 7.32 (1H, dd, *J* = 8.5,



6ea

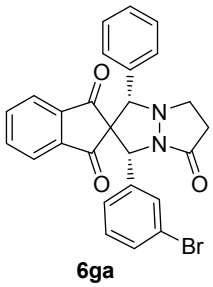
2.0 Hz), 7.12-7.10 (3H, m), 7.09-7.05 (3H, m), 5.92 (1H, s), 4.34 (1H, s), 3.83-3.77 (1H, m), 3.15-3.10 (1H, m), 2.98-2.84 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.3 (C, *C*=O), 194.5 (C, *C*=O), 174.3 (C, *C*=O), 141.8 (C), 141.4 (C), 136.0 (CH), 135.7 (CH), 134.2 (C), 133.1 (C), 132.1 (C), 131.5 (C), 130.5 (CH), 128.9 (CH), 128.7 (CH), 128.4 (2 x CH), 128.1 (2 x CH), 127.3 (CH), 123.11 (CH), 123.08 (CH), 78.1 (CH), 70.8 (C), 60.1 (CH), 45.8 (CH_2), 30.5 (CH_2); LCMS m/z 475.45 (M – H^+), calcd for $C_{26}H_{17}Cl_2N_2O_3$ 475.0616; HRMS m/z 499.0587 (M + Na^+), calcd for $C_{26}H_{18}Cl_2N_2O_3Na$ 499.0592; Anal. calcd for $C_{26}H_{18}Cl_2N_2O_3$ (476.0694): C, 65.42; H, 3.80; N, 5.87. Found: C, 65.34; H, 3.86; N, 5.81%.

(1'*S,3'*R**)-3'-(4-Bromophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6fa):** Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 152-154 °C; *dr* = 9:1; IR (KBr): ν_{max} 2926, 1742, 1704, 1589, 1485, 1408, 1342, 1255, 1129, 1074, 1014 and 761 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 7.96 (1H, d, *J* = 7.6 Hz), 7.73 (1H, dt, *J* = 7.6, 0.8 Hz), 7.61 (1H, dt, *J* = 7.6, 0.8 Hz), 7.43 (1H, d, *J* = 7.6 Hz), 7.29 (2H, d, *J* = 8.4 Hz), 7.19-7.16 (2H, m), 7.11-7.09 (3H, m), 6.99 (2H, d, *J* = 8.4 Hz), 5.74 (1H, s), 4.40 (1H, s), 3.85-3.78 (1H, m), 3.11-3.01 (2H, m), 2.93-2.85 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 197.9 (C, *C*=O), 194.4 (C, *C*=O), 172.7 (C, *C*=O), 143.0 (C), 141.2 (C), 136.4 (CH), 135.7 (CH), 134.4 (C), 131.5 (2 x CH), 131.4 (C), 128.9 (CH), 128.5 (2 x CH), 127.8 (2 x CH), 127.7 (2 x CH), 123.3 (2 x CH), 121.9 (C), 77.5 (CH), 71.9 (C), 62.7 (CH), 48.0 (CH_2), 32.3 (CH_2); HRMS m/z 487.0655 (M + H^+), calcd for $C_{26}H_{20}BrN_2O_3$ 487.0657.



6fa

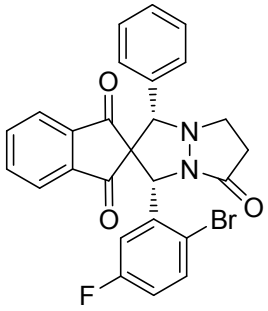
(1'*S,3'*R**)-3'-(3-Bromophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ga):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off-white solid. Mp 170-172 °C; *dr* = 7:1; IR (KBr): ν_{max} 2926, 1741, 1709, 1594, 1419, 1330, 1254, 1068, 1024 and 772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, for major isomer) δ 7.98 (1H, d, *J* = 7.5 Hz), 7.74 (1H, t, *J* = 7.5 Hz), 7.62 (1H, dt, *J* = 7.5, 0.5 Hz), 7.43(1H, d, *J* = 8.0 Hz), 7.31 (1H, br s), 7.28-7.27 (1H, m), 7.19-7.17 (2H, m), 7.11-7.09 (3H, m), 7.02 (1H, t, *J* = 7.5 Hz), 6.98 (1H, d, *J* = 7.5 Hz), 5.75 (1H, s), 4.39 (1H, s), 3.87-3.81 (1H, m), 3.12-3.02 (2H, m), 2.94-2.87 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 197.9 (C, *C*=O), 194.3 (C, *C*=O), 173.2 (C, *C*=O), 143.1 (C), 141.2 (C), 137.8 (C), 136.4 (CH), 135.7 (CH), 131.4 (C), 131.1 (CH), 129.9 (CH) , 129.1 (CH), 128.9 (CH), 128.5 (2 x CH), 127.8 (2 x CH), 124.5 (CH), 123.34 (CH), 123.26 (CH), 122.7 (C), 77.5 (CH), 72.0 (C), 62.6 (CH), 47.7 (CH_2), 32.0 (CH_2); LCMS m/z 487.30 (M + H^+), calcd for $C_{26}H_{20}BrN_2O_3$ 487.0657; HRMS m/z 509.0485 (M + Na^+), calcd for



6ga

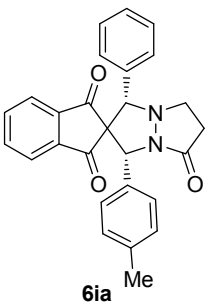
$C_{26}H_{19}BrN_2O_3Na$ 509.0477; Anal. calcd for $C_{26}H_{19}BrN_2O_3$ (486.0579): C, 64.08; H, 3.93; N, 5.75. Found: C, 64.15; H, 3.89; N, 5.82%.

(1'*S,3'*S**)-3'-(2-Bromo-5-fluorophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6ha):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 160-162 °C; *dr* = >99:1; IR (KBr): ν_{max} 2931, 1753, 1698, 1594, 1468, 1342, 1249, 1129, 1041 and 778 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97 (1H, d, *J* = 7.6 Hz), 7.73 (1H, dt, *J* = 7.6, 0.8 Hz), 7.61 (1H, dd, *J* = 7.6, 0.8 Hz), 7.58-7.55 (1H, m), 7.36 (1H, d, *J* = 7.6 Hz), 7.22 (1H, dd, *J* = 8.8, 5.2 Hz), 7.13-7.07 (5H, m), 6.84 (1H, dt, *J* = 8.0, 2.8 Hz), 5.90 (1H, s), 4.33 (1H, s), 3.86-3.78 (1H, m), 3.15 (1H, ddd, *J* = 12.0, 9.6, 5.2 Hz), 3.01-2.92 (1H, m), 2.85 (1H, ddd, *J* = 17.6, 9.6, 4.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.7 (C, *C*=O), 194.2 (C, *C*=O), 174.8 (C, *C*=O), 162.1 (C, d, *J* = 245.0 Hz, *C*-F), 142.0 (C), 141.5 (C), 138.7 (C, d, *J* = 8.0 Hz), 135.9 (CH), 135.6 (CH), 133.3 (CH, d, *J* = 8.0 Hz), 131.7 (C), 128.9 (CH), 128.3 (2 x CH), 128.2 (2 x CH), 123.1 (CH), 123.0 (CH), 117.5 (CH, d, *J* = 25.0 Hz), 116.8 (CH, d, *J* = 23.0 Hz), 115.8 (C, d, *J* = 3.0 Hz), 78.3 (CH), 70.6 (C), 62.2 (CH), 45.3 (CH_2), 30.0 (CH_2); LCMS m/z 504.45 (M^+), calcd for $C_{26}H_{18}BrFN_2O_3$ 504.0485; HRMS m/z 505.0569 (M + H^+), calcd for $C_{26}H_{19}BrFN_2O_3$ 505.0563; Anal. calcd for $C_{26}H_{18}BrFN_2O_3$ (504.0485): C, 61.80; H, 3.59; N, 5.54. Found: C, 61.92; H, 3.52; N, 5.48%.



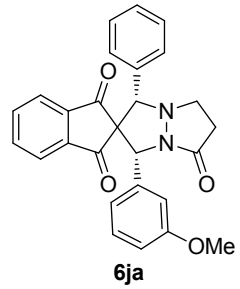
6ha

(1'*S,3'*R**)-1'-Phenyl-3'-(*p*-tolyl)-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6ia):** Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 154-156 °C; *dr* = >99:1; IR (KBr): ν_{max} 2962, 1752, 1714, 1590, 1514, 1455, 1341, 1292, 1260, 1184, 1093, 768 and 628 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (1H, d, *J* = 8.0 Hz), 7.71 (1H, dt, *J* = 7.6, 0.8 Hz), 7.58 (1H, dt, *J* = 7.6, 0.8 Hz), 7.41 (1H, d, *J* = 7.6 Hz), 7.21-7.19 (2H, m), 7.11-7.09 (3H, m), 6.98-6.93 (4H, m), 5.78 (1H, s), 4.41 (1H, s), 3.87-3.79 (1H, m), 3.13-3.02 (2H, m), 2.95-2.83 (1H, m), 2.20 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.3 (C, *C*=O), 194.6 (C, *C*=O), 171.9 (C, *C*=O), 143.2 (C), 141.3 (C), 137.5 (C), 136.2 (CH), 135.5 (CH), 132.0 (C), 131.7 (C), 129.1 (2 x CH), 128.8 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 125.7 (2 x CH), 123.2 (2 x CH), 77.4 (CH), 72.1 (C), 63.2 (CH), 48.4 (CH_2), 32.7 (CH_2), 21.1 (CH_3); HRMS m/z 423.1711 (M + H^+), calcd for $C_{27}H_{23}N_2O_3$ 423.1709.



6ia

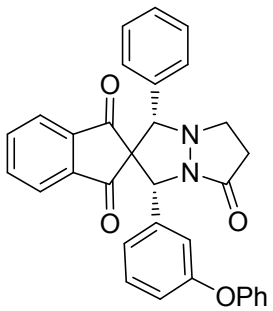
(1'*S,3'*R**)-3'-(3-Methoxyphenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]**



6ja

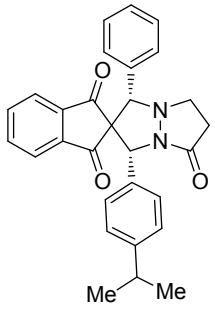
pyrazole]-1,3,5'(3'*H*)-trione (6ja): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as off-white solid. Mp 152-154 °C; *dr* = >99:1; IR (KBr): ν_{max} 2940, 1746, 1698, 1606, 1584, 1498, 1384, 1260, 1038, 768 and 644 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (1H, d, *J* = 7.6 Hz), 7.71 (1H, t, *J* = 7.6 Hz), 7.59 (1H, t, *J* = 7.6 Hz), 7.42 (1H, d, *J* = 7.6 Hz), 7.21-7.19 (2H, m), 7.11-7.07 (3H, m), 7.05 (1H, t, *J* = 8.0 Hz), 6.65 (2H, d, *J* = 8.4 Hz), 6.60 (1H, br s), 5.77 (1H, s), 4.41 (1H, s), 3.88-3.78 (1H, m), 3.61 (3H, s, OCH_3), 3.11-3.02 (2H, m), 2.94-2.82 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.2 (C, *C*=O), 194.4 (C, *C*=O), 172.6 (C, *C*=O), 159.6 (C), 143.2 (C), 141.2 (C), 136.8 (C), 136.3 (CH), 135.5 (CH), 131.6 (C), 129.5 (CH), 128.8 (CH), 128.5 (2 x CH), 127.8 (2 x CH), 123.22 (CH), 123.20 (CH), 118.1 (CH), 113.6 (CH), 111.4 (CH), 77.4 (CH), 72.0 (C), 63.3 (CH), 55.1 (CH_3, O*C*H_3), 48.1 (CH_2), 32.4 (CH_2); LCMS m/z 439.40 ($M + H^+$), calcd for $C_{27}H_{23}N_2O_4$ 439.1658; HRMS m/z 461.1477 ($M + Na^+$), calcd for $C_{27}H_{22}N_2O_4Na$ 461.1477; Anal. calcd for $C_{27}H_{22}N_2O_4$ (438.1580): C, 73.96; H, 5.06; N, 6.39. Found: C, 73.85; H, 5.10; N, 6.31%.

(1'*S,3'*R**)-3'-(3-Phenoxyphenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6ka):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off-white solid. Mp 138-140 °C; *dr* = 6:1; IR (KBr): ν_{max} 2957, 1741, 1708, 1584, 1487, 1249, 1217, 1109, 763 and 703 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 7.93 (1H, d, *J* = 7.6 Hz), 7.73 (1H, t, *J* = 7.6 Hz), 7.63 (1H, t, *J* = 7.6 Hz), 7.46 (1H, d, *J* = 7.6 Hz), 7.20-7.14 (5H, m), 7.11-7.10 (3H, m), 7.03 (1H, t, *J* = 7.6 Hz), 6.90 (1H, d, *J* = 7.6 Hz), 6.78-6.76 (3H, m), 6.69-6.65 (1H, m), 5.76 (1H, s), 4.39 (1H, s), 3.84-3.77 (1H, m), 3.10-2.98 (2H, m), 2.93-2.82 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 198.1 (C, *C*=O), 194.3 (C, *C*=O), 172.9 (C, *C*=O), 157.1 (C), 156.9 (C), 143.2 (C), 141.2 (C), 137.4 (C), 136.3 (CH), 135.5 (CH), 131.6 (C), 129.9 (CH), 129.6 (2 x CH), 128.8 (CH), 128.5 (2 x CH), 127.8 (2 x CH), 123.4 (CH), 123.1 (CH), 123.0 (CH), 120.8 (CH), 118.6 (2 x CH), 118.4 (CH), 116.4 (CH), 77.3 (CH), 71.9 (C), 63.0 (CH), 47.8 (CH_2), 32.2 (CH_2); LCMS m/z 501.30 ($M + H^+$), calcd for $C_{32}H_{25}N_2O_4$ 501.1814; HRMS m/z 523.1636 ($M + Na^+$), calcd for $C_{32}H_{24}N_2O_4Na$ 523.1634; Anal. calcd for $C_{32}H_{24}N_2O_4$ (500.1736): C, 76.78; H, 4.83; N, 5.60. Found: C, 76.65; H, 4.79; N, 5.68%.



6ka

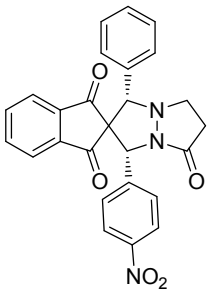
(1'*S,3'*R**)-3'-(4-Isopropylphenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]**



6la

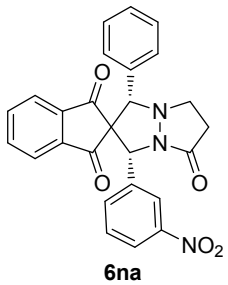
pyrazole]-1,3,5'(3'*H*)-trione (6la): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light yellow solid. Mp 120-122 °C; *dr* = >99:1; IR (KBr): ν_{max} 2953, 2909, 1742, 1709, 1589, 1457, 1266, 1194, 1090, 899 and 767 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.97 (1H, d, *J* = 8.0 Hz), 7.72 (1H, t, *J* = 7.6 Hz), 7.59 (1H, t, *J* = 7.6 Hz), 7.41 (1H, d, *J* = 7.6 Hz), 7.22-7.20 (2H, m), 7.11-7.10 (3H, m), 7.00 (4H, br s), 5.78 (1H, s), 4.42 (1H, s), 3.88-3.80 (1H, m), 3.14-3.02 (2H, m), 2.93-2.87 (1H, m), 2.77 (1H, heptate, *J* = 6.8 Hz, C*H*$(CH_3)_2$), 1.13 (6H, t, *J* = 6.4 Hz, CH(C*H*$_3)_2$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.3 (C, *C*=O), 194.6 (C, *C*=O), 171.9 (C, *C*=O), 148.3 (C), 143.2 (C), 141.3 (C), 136.2 (CH), 135.4 (CH), 132.2 (C), 131.7 (C), 128.8 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 126.5 (2 x CH), 125.7 (2 x CH), 123.20 (CH), 123.16 (CH), 77.3 (CH), 72.2 (C), 63.3 (CH), 48.5 (CH_2), 33.6 (CH, *C*H$(CH_3)_2$), 32.8 (CH_2), 23.8 (CH_3, CH(*C*H$_3)_2$), 23.7 (CH_3, CH(*C*H$_3)_2$); LCMS m/z 451.55 (M + H^+), calcd for $C_{29}H_{27}N_2O_3$ 451.2022; HRMS m/z 451.2027 (M + H^+), calcd for $C_{29}H_{27}N_2O_4$ 451.2022; Anal. calcd for $C_{29}H_{26}N_2O_3$ (450.1943): C, 77.31; H, 5.82; N, 6.22. Found: C, 77.23; H, 5.78; N, 6.31%.

(1'*S,3'*R**)-3'-(4-Nitrophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6ma):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Mp 132-134 °C; *dr* = 10:1; IR (KBr): ν_{max} 3054, 2989, 1752, 1714, 1676, 1525, 1487, 1357, 1260, 1238, 1114, 936, 860, and 774 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 8.06 (2H, d, *J* = 8.0 Hz), 8.00 (1H, d, *J* = 7.2 Hz), 7.77 (1H, t, *J* = 7.2 Hz), 7.64 (1H, t, *J* = 7.2 Hz), 7.41 (1H, d, *J* = 7.6 Hz), 7.33-7.29 (2H, m), 7.17-7.10 (5H, m), 5.87 (1H, s), 4.41 (1H, s), 3.90-3.83 (1H, m), 3.17-3.02 (2H, m), 2.99-2.89 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 197.5 (C, *C*=O), 194.4 (C, *C*=O), 173.7 (C, *C*=O), 147.5 (C), 143.1 (C), 142.8 (C), 141.1 (C), 136.7 (CH), 136.0 (CH), 131.0 (C), 129.1 (CH), 128.6 (2 x CH), 127.7 (2 x CH), 126.9 (2 x CH), 123.7 (2 x CH), 123.5 (CH), 123.3 (CH), 77.7 (CH), 72.1 (C), 62.3 (CH), 47.5 (CH_2), 31.8 (CH_2); HRMS m/z 454.1401 (M + H^+), calcd for $C_{26}H_{20}N_3O_5$ 454.1403.



6ma

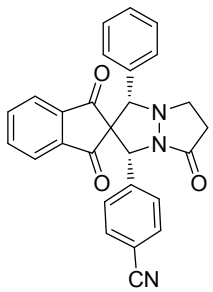
(1'*S,3'*R**)-3'-(3-Nitrophenyl)-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6na):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated yellow solid. Mp 164-166 °C; *dr* = 12:1; IR (KBr): ν_{max} 2926, 2855, 1748, 1704, 1594, 1534, 1348, 1255, 1178, 1019, 767 and 729 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 8.04-7.98 (3H, m), 7.74 (1H, dt, *J* = 7.5, 0.5 Hz), 7.60 (1H, dt, *J* = 7.5, 1.0 Hz), 7.46 (1H, d, *J* = 7.5 Hz), 7.39-7.35



6na

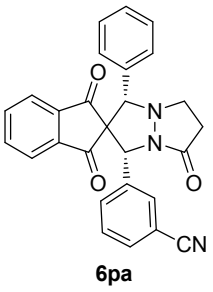
(2H, m), 7.16-7.14 (2H, m), 7.11-7.09 (3H, m), 5.84 (1H, s), 4.40 (1H, s), 3.86 (1H, ddd, *J* = 11.5, 9.5, 7.0 Hz), 3.15-3.09 (1H, m), 3.07-3.00 (1H, m), 2.95-2.88 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 197.6 (C, *C*=O), 194.4 (C, *C*=O), 173.9 (C, *C*=O), 148.2 (C), 142.9 (C), 141.1 (C), 138.0 (C), 136.6 (CH), 136.0 (CH), 132.2 (CH), 131.2 (C), 129.4 (CH), 129.1 (CH), 128.6 (2 x CH), 127.8 (2 x CH), 123.5 (CH), 123.2 (CH), 123.1 (CH), 121.3 (CH), 77.7 (CH), 71.9 (C), 62.2 (CH), 47.3 (CH_2), 31.7 (CH_2); LCMS m/z 452.35 (M − H^+), calcd for $C_{26}H_{18}N_3O_5$ 452.1246; HRMS m/z 454.1403 (M + H^+), calcd for $C_{26}H_{20}N_3O_5$ 454.1403; Anal. calcd for $C_{26}H_{19}N_3O_5$ (453.1325): C, 68.87; H, 4.22; N, 9.27. Found: C, 68.73; H, 4.26; N, 9.19%.

4-((1'*S,3'*R**)-1,3,5'-Trioxo-1'-phenyl-1,3,3',5',6',7'-hexahydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazol]-3'-yl)benzonitrile (6oa):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 124-126 °C; *dr* = >99:1; IR (KBr): ν_{max} 2926, 2838, 2230, 1742, 1709, 1687, 1589, 1490, 1336, 1265, 1156, 1063, 871 and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (1H, d, *J* = 7.6 Hz), 7.76 (1H, t, *J* = 7.6 Hz), 7.63 (1H, t, *J* = 7.6 Hz), 7.49 (2H, d, *J* = 8.4 Hz), 7.41 (1H, d, *J* = 8.0 Hz), 7.24 (2H, d, *J* = 8.0 Hz), 7.17-7.14 (2H, m), 7.12-7.09 (3H, m), 5.82 (1H, s), 4.39 (1H, s), 3.88-3.80 (1H, m), 3.15-3.00 (2H, m), 2.97-2.87 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 197.5 (C, *C*=O), 194.3 (C, *C*=O), 173.5 (C, *C*=O), 142.8 (C), 141.12 (C), 141.06 (C), 136.6 (CH), 135.9 (CH), 132.3 (2 x CH), 131.1 (C), 129.1 (CH), 128.6 (2 x CH), 127.7 (2 x CH), 126.7 (2 x CH), 123.4 (CH), 123.3 (CH), 118.5 (C, *C*≡N), 111.8 (C), 77.7 (CH), 72.0 (C), 62.5 (CH), 47.6 (CH_2), 31.9 (CH_2); LCMS m/z 434.20 (M + H^+), calcd for $C_{27}H_{20}N_3O_3$ 434.1505; HRMS m/z 434.1500 (M + H^+), calcd for $C_{27}H_{20}N_3O_3$ 434.1505; Anal. calcd for $C_{27}H_{19}N_3O_3$ (433.1426): C, 74.81; H, 4.42; N, 9.69. Found: C, 74.89; H, 4.38; N, 9.75%.



6oa

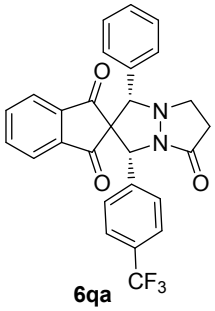
3-((1'*S,3'*R**)-1,3,5'-Trioxo-1'-phenyl-1,3,3',5',6',7'-hexahydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazol]-3'-yl)benzonitrile (6pa):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 180-182 °C; *dr* = 10:1; IR (KBr): ν_{max} 2964, 2860, 1698, 1594, 1293, 1260, 1118, 1074, 909 and 822 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, for major isomer) δ 7.99 (1H, d, *J* = 8.0 Hz), 7.76 (1H, dt, *J* = 7.5, 1.0 Hz), 7.63 (1H, dt, *J* = 7.5, 0.5 Hz), 7.49-7.46 (2H, m), 7.40 (1H, d, *J* = 7.5 Hz), 7.35-7.30 (2H, m), 7.16-7.15 (2H, m), 7.11-7.10 (3H, m), 5.79 (1H, s), 4.39 (1H, s), 3.85 (1H, ddd, *J* = 11.0, 9.5, 7.0 Hz), 3.12 (1H, ddd, *J* = 11.5, 9.5, 7.5 Hz), 3.08-3.01 (1H, m), 2.92 (1H, ddd, *J* = 16.5, 9.5, 7.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 197.6 (C, *C*=O), 194.3 (C, *C*=O), 173.7 (C, *C*=O), 142.9 (C), 141.1 (C), 137.4 (C), 136.6 (CH), 135.9 (CH), 131.6 (CH), 131.2 (C), 130.4 (CH), 129.8 (CH), 129.2 (CH), 129.1 (CH), 128.6



6pa

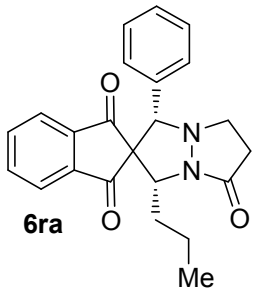
(2 x CH), 127.8 (2 x CH), 123.5 (CH), 123.2 (CH), 118.4 (C, *C*≡N), 112.7 (C), 77.7 (CH), 71.9 (C), 62.2 (CH), 47.4 (CH_2), 31.7 (CH_2); LCMS m/z 434.20 ($M + H^+$), calcd for $C_{27}H_{20}N_3O_3$ 434.1505; HRMS m/z 456.1329 ($M + Na^+$), calcd for $C_{27}H_{19}N_3O_3Na$ 456.1324; Anal. calcd for $C_{27}H_{19}N_3O_3$ (433.1426): C, 74.81; H, 4.42; N, 9.69. Found: C, 74.68; H, 4.48; N, 9.61%.

(1'*S,3'*R**)-1'-Phenyl-3'-(4-(trifluoromethyl)phenyl)-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6qa):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as off-white solid. Mp 132-134 °C; *dr* = 25:1; IR (KBr): ν_{max} 2924, 1757, 1714, 1622, 1595, 1492, 1455, 1325, 1260, 1125, 1017, 768 and 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 7.98 (1H, td, *J* = 7.5, 0.5 Hz), 7.74 (1H, dt, *J* = 7.5, 1.0 Hz), 7.62 (1H, dt, *J* = 7.5, 1.0 Hz), 7.45-7.41 (3H, m), 7.24 (2H, d, *J* = 8.5 Hz), 7.18-7.16 (2H, m), 7.12-7.09 (3H, m), 5.84 (1H, s), 4.41 (1H, s), 3.88-3.82 (1H, m), 3.13-3.04 (2H, m), 2.95-2.88 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 197.7 (C, *C*=O), 194.4 (C, *C*=O), 173.0 (C, *C*=O), 142.9 (C), 141.2 (C), 139.5 (C), 136.5 (CH), 135.8 (CH), 131.2 (C), 131.1 (C, q, *J* = 32.5 Hz), 129.0 (CH), 128.5 (2 x CH), 127.7 (2 x CH), 126.3 (2 x CH), 125.5 (2 x CH, q, *J* = 3.7 Hz), 123.9 (C, q, *J* = 270.0 Hz, *C*F_3), 123.35 (CH), 123.32 (CH), 77.6 (CH), 72.0 (C), 62.6 (CH), 47.9 (CH_2), 32.2 (CH_2); LCMS m/z 475.45 ($M - H^+$), calcd for $C_{27}H_{18}F_3N_2O_3$ 475.1270; HRMS m/z 477.1429 ($M + H^+$), calcd for $C_{27}H_{20}F_3N_2O_3$ 477.1426; Anal. calcd for $C_{27}H_{19}F_3N_2O_3$ (476.1348): C, 68.06; H, 4.02; N, 5.88. Found: C, 68.15; H, 4.08; N, 5.81%.



6qa

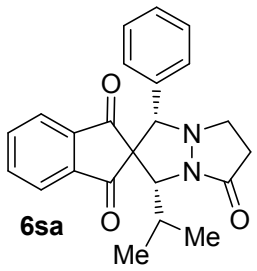
(1'*S,3'*R**)-1'-Phenyl-3'-propyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6ra):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Mp 136-138 °C; *dr* = >99:1; IR (KBr): ν_{max} 3065, 2957, 2924, 2881, 1741, 1708, 1595, 1498, 1460, 1336, 1255, 1179, 1071, 768, 736 and 693 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (1H, d, *J* = 7.6 Hz), 7.74 (1H, dt, *J* = 7.6, 1.6 Hz), 7.69-7.67 (1H, m), 7.65-7.63 (1H, m), 7.12-7.06 (5H m), 4.53 (1H, t, *J* = 7.6 Hz), 4.18 (1H, s), 3.66 (1H, ddd, *J* = 11.2, 9.2, 7.2 Hz), 2.96 (1H, ddd, *J* = 11.2, 10.0, 7.2 Hz), 2.89-2.74 (2H, m), 2.10-2.01 (1H, m), 1.51-1.43 (1H, m), 1.29-1.17 (1H, m), 1.03-0.90 (1H, m), 0.78 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.7 (C, *C*=O), 195.9 (C, *C*=O), 173.4 (C, *C*=O), 142.5 (C), 140.9 (C), 136.2 (CH), 135.7 (CH), 131.8 (C), 128.7 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 123.3 (CH), 123.1 (CH), 77.4 (CH), 69.9 (C), 60.6 (CH), 46.6 (CH_2), 33.2 (CH_2), 31.8 (CH_2), 20.3 (CH_2), 13.6 (CH_3); LCMS m/z 375.15 ($M + H^+$), calcd for $C_{23}H_{23}N_2O_3$ 375.1709; HRMS m/z 375.1708 ($M + H^+$), calcd for $C_{23}H_{23}N_2O_3$



6ra

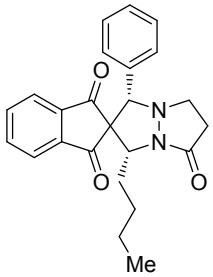
375.1709; Anal. calcd for $C_{23}H_{22}N_2O_3$ (374.1630): C, 73.78; H, 5.92; N, 7.48. Found: C, 73.89; H, 5.86; N, 7.41%.

(1'*S,3'*R**)-3'-Isopropyl-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6sa):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 180-182 °C; *dr* = >99:1; IR (KBr): ν_{max} 2959, 2871, 1742, 1704, 1594, 1457, 1337, 1238, 1183, 1068, 942, 866 and 763 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.90 (1H, d, *J* = 7.5 Hz), 7.72 (1H, dt, *J* = 7.5, 1.0 Hz), 7.64 (1H, dt, *J* = 7.5, 1.0 Hz), 7.59 (1H, d, *J* = 7.5 Hz), 7.06 (5H, br s), 4.20 (1H, d, *J* = 11.5 Hz), 4.12 (1H, s), 3.74-3.68 (1H, m), 3.05 (1H, ddd, *J* = 13.0, 10.0, 4.0 Hz), 2.86-2.79 (1H, m,), 2.69 (1H, ddd, *J* = 18.0, 10.0, 4.0 Hz), 2.39 (1H, ddd, *J* = 18.0, 13.0, 6.5 Hz), 1.11 (3H, d, *J* = 6.5 Hz, $CH(CH_3)_2$), 0.45 (3H, d, *J* = 6.5 Hz, $CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.0 (C, *C*=O), 196.4 (C, *C*=O), 178.2 (C, *C*=O), 142.4 (C), 140.3 (C), 136.1 (CH), 135.6 (CH), 131.7 (C), 128.8 (CH), 128.4 (2 x CH), 127.9 (2 x CH), 123.3 (CH), 122.9 (CH), 78.3 (CH), 69.7 (C), 68.2 (CH), 43.5 (CH_2), 29.6 (CH_2), 29.4 (CH, $CH(CH_3)_2$), 21.4 (CH_3, $CH(CH_3)_2$), 19.5 (CH_3, $CH(CH_3)_2$); LCMS m/z 375.30 (M + H^+), calcd for $C_{23}H_{23}N_2O_3$ 375.1709; HRMS m/z 375.1714 (M + H^+), calcd for $C_{23}H_{23}N_2O_3$ 375.1709; Anal. calcd for $C_{23}H_{22}N_2O_3$ (374.1630): C, 73.78; H, 5.92; N, 7.48. Found: C, 73.65; H, 5.87; N, 7.53%.



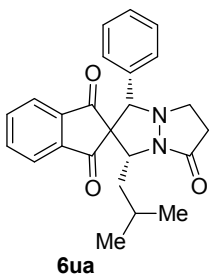
6sa

(1'*S,3'*R**)-3'-Butyl-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6ta):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 166-168 °C; *dr* = >99:1; IR (KBr): ν_{max} 2959, 2855, 1742, 1715, 1594, 1457, 1331, 1255, 1184, 1024, 937 and 767 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.93 (1H, td, *J* = 7.6, 0.8 Hz), 7.75 (1H, dt, *J* = 7.6, 1.6 Hz), 7.71-7.65 (2H, m), 7.14-7.09 (5H, m), 4.54 (1H, t, *J* = 7.6 Hz), 4.20 (1H, s), 3.69 (1H, ddd, *J* = 11.2, 9.6, 7.2 Hz,), 2.98 (1H, ddd, *J* = 11.6, 9.6, 7.2 Hz), 2.90-2.76 (2H, m), 2.14-2.04 (1H, m), 1.57-1.48 (1H, m), 1.26-1.17 (3H, m), 0.96-0.86 (1H, m), 0.74 (3H, t, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.8 (C, *C*=O), 196.0 (C, *C*=O), 173.4 (C, *C*=O), 142.6 (C), 140.9 (C), 136.2 (CH), 135.7 (CH), 131.9 (C), 128.7 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 123.3 (CH), 123.1 (CH), 77.5 (CH), 69.9 (C), 60.8 (CH), 46.7 (CH_2), 31.8 (CH_2), 30.8 (CH_2), 29.0 (CH_2), 22.2 (CH_2), 13.7 (CH_3); LCMS m/z 389.35 (M + H^+), calcd for $C_{24}H_{25}N_2O_3$ 389.1865; HRMS m/z 389.1868 (M + H^+), calcd for $C_{24}H_{25}N_2O_3$ 389.1865; Anal. calcd for $C_{24}H_{24}N_2O_3$ (388.1787): C, 74.21; H, 6.23; N, 7.21. Found: C, 74.32; H, 6.19; N, 7.28%.



6ta

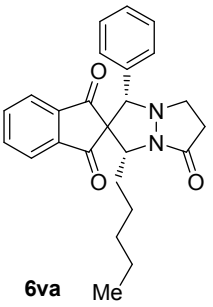
(1'*S,3'*R**)-3'-Isobutyl-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6ua):** Prepared by following the

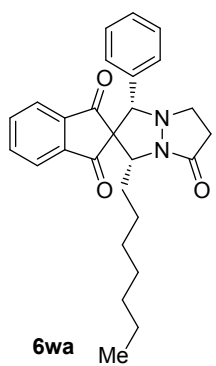


6ua

procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 132-134 °C; *dr* = >99:1; IR (KBr): ν_{max} 2957, 2930, 1741, 1709, 1590, 1455, 1363, 1250, 1098, 1017 and 763 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.93 (1H, d, *J* = 7.6 Hz), 7.76 (1H, dt, *J* = 7.2, 1.6 Hz), 7.71-7.65 (2H, m), 7.14-7.10 (5H, m), 4.64 (1H, dd, *J* = 8.8, 6.4 Hz), 4.20 (1H, s), 3.72-3.65 (1H, m,), 2.99 (1H, ddd, *J* = 12.0, 8.4, 7.6 Hz), 2.82 (2H, t, *J* = 8.4 Hz), 2.02 (1H, ddd, *J* = 13.6, 8.8, 6.4 Hz), 1.36 (1H, heptate, *J* = 6.4 Hz, C*H*$(CH_3)_2$), 1.28-1.21 (1H, m), 0.85 (3H, d, *J* = 2.8 Hz, CH(C*H*$_3)_2$), 0.83 (3H, d, *J* = 2.8 Hz, CH(C*H*$_3)_2$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.9 (C, *C*=O), 196.0 (C, *C*=O), 174.1 (C, *C*=O), 142.6 (C), 140.9 (C), 136.2 (CH), 135.7 (CH), 132.0 (C), 128.7 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 123.3 (CH), 123.1 (CH), 77.4 (CH), 70.0 (C), 59.1 (CH), 46.2 (CH_2), 40.2 (CH_2), 31.5 (CH_2, *C*H_2CH$(CH_3)_2$), 25.9 (CH, *C*H$(CH_3)_2$), 22.5 (CH_3, CH(*C*$H_3)_2$), 22.2 (CH_3, CH(*C*$H_3)_2$); LCMS m/z 387.20 (M – H^+), calcd for $C_{24}H_{23}N_2O_3$ 387.1709; HRMS m/z 389.1872 (M + H^+), calcd for $C_{24}H_{25}N_2O_3$ 389.1865; Anal. calcd for $C_{24}H_{24}N_2O_3$ (388.1787): C, 74.21; H, 6.23; N, 7.21. Found: C, 74.15; H, 6.29; N, 7.18%.

(1'*S,3'*R**)-3'-Pentyl-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6va):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 109-121 °C; *dr* = >99:1; IR (KBr): ν_{max} 2930, 2849, 1741, 1703, 1460, 1336, 1250, 1174, 1098, 936 and 769 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (1H, d, *J* = 7.6 Hz), 7.74 (1H, dt, *J* = 7.6, 1.6 Hz), 7.70-7.64 (2H, m), 7.12-7.08 (5H, m), 4.52 (1H, t, *J* = 7.6 Hz), 4.18 (1H, s), 3.67 (1H, ddd, *J* = 11.2, 9.2, 7.2 Hz,), 2.96 (1H, ddd, *J* = 11.2, 10.0, 7.2 Hz), 2.90-2.75 (2H, m), 2.11-2.02 (1H, m), 1.56-1.47 (1H, m), 1.20-1.06 (5H, m), 0.94-0.85 (1H, m), 0.70 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.8 (C, *C*=O), 196.0 (C, *C*=O), 173.3 (C, *C*=O), 142.5 (C), 140.9 (C), 136.2 (CH), 135.7 (CH), 131.8 (C), 128.7 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 123.3 (CH), 123.1 (CH), 77.5 (CH), 69.9 (C), 60.8 (CH), 46.7 (CH_2), 31.9 (CH_2), 31.2 (CH_2), 31.1 (CH_2), 26.5 (CH_2), 22.2 (CH_2), 13.7 (CH_3); LCMS m/z 403.25 (M + H^+), calcd for $C_{25}H_{27}N_2O_3$ 403.2022; HRMS m/z 425.1841 (M + Na^+), calcd for : $C_{25}H_{26}N_2O_3Na$ 425.1841; Anal. calcd for $C_{25}H_{26}N_2O_3$ (402.1943): C, 74.60; H, 6.51; N, 6.96. Found: C, 74.58; H, 6.57; N, 6.89%.

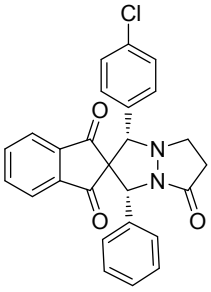




(1'*S,3'*R**)-3'-Heptyl-1'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'**

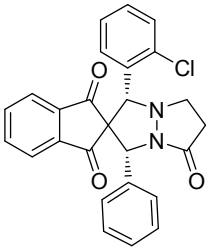
(3'*H*)-trione (6wa): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as brown semi solid. *dr* = >99:1; IR (Neat): ν_{max} 2926, 2849, 1742, 1709, 1594, 1452, 1386, 1266, 1183, 1014, 888, 767 and 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.92 (1H, d, *J* = 7.6 Hz), 7.74 (1H, dt, *J* = 6.8, 1.6 Hz), 7.70-7.64 (2H, m), 7.12-7.10 (5H, m), 4.53 (1H, t, *J* = 7.6 Hz), 4.19 (1H, s), 3.67 (1H, ddd, *J* = 11.2, 9.2, 7.2 Hz), 3.00-2.91 (1H, m), 2.89-2.75 (2H, m), 2.11-2.03 (1H, m), 1.57-1.48 (1H, m), 1.20-1.14 (5H, m), 1.10-1.07 (4H, m), 0.92-0.86 (1H, m), 0.78 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.8 (C, *C*=O), 195.9 (C, *C*=O), 173.2 (C, *C*=O), 142.6 (C), 140.9 (C), 136.2 (CH), 135.7 (CH), 131.8 (C), 128.7 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 123.3 (CH), 123.1 (CH), 77.5 (CH), 70.0 (C), 60.8 (CH), 46.8 (CH_2), 31.9 (CH_2), 31.5 (CH_2), 31.1 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 26.8 (CH_2), 22.4 (CH_2), 14.0 (CH_3); LCMS m/z 431.10 (M + H^+), calcd for $C_{27}H_{31}N_2O_3$ 431.2335; HRMS m/z 431.2334 (M + H^+), calcd for $C_{27}H_{31}N_2O_3$ 431.2335; Anal. calcd for $C_{27}H_{30}N_2O_3$ (430.2256): C, 75.32; H, 7.02; N, 6.51. Found: C, 75.23; H, 7.08; N, 6.61%.

(1'*S,3'*R**)-1'-(4-Chlorophenyl)-3'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ab):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light yellow solid. Mp 150-152 °C; *dr* = 20:1; IR (KBr): ν_{max} 2920, 2843, 1747, 1704, 1588, 1490, 1347, 1254, 1090, 882, 761 and 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 7.98 (1H, d, *J* = 7.6 Hz), 7.75 (1H, dt, *J* = 7.6, 0.8 Hz), 7.64 (1H, dt, *J* = 7.6, 0.8 Hz), 7.43 (1H, d, *J* = 8.0 Hz), 7.19-7.13 (5H m), 7.12-7.09 (2H, m), 7.06-7.04 (2H, m), 5.77 (1H, s), 4.40 (1H, s), 3.86-3.79 (1H, m), 3.11-3.01 (2H, m), 2.96-2.85 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 193.3 (C, *C*=O), 189.7 (C, *C*=O), 167.7 (C, *C*=O), 138.3 (C), 136.4 (C), 131.8 (CH), 131.0 (CH), 130.2 (C), 130.0 (C), 125.6 (C), 124.5 (2 x CH), 124.0 (2 x CH), 123.7 (2 x CH), 123.2 (CH), 121.1 (2 x CH), 118.59 (CH), 118.57 (CH), 71.6 (CH), 67.0 (C), 58.9 (CH), 43.3 (CH_2), 27.6 (CH_2); LCMS m/z 443.35 (M + H^+), calcd for $C_{26}H_{20}ClN_2O_3$ 443.1162; HRMS m/z 443.1163 (M + H^+), calcd for $C_{26}H_{20}ClN_2O_3$ 443.1162; Anal. calcd for $C_{26}H_{19}ClN_2O_3$ (442.1084): C, 70.51; H, 4.32; N, 6.33. Found: C, 70.42; H, 4.36; N, 6.27%.



6ab

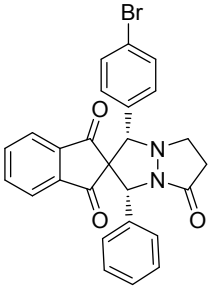
(1'*R,3'*R**)-1'-(2-Chlorophenyl)-3'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ac):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 142-144



6ac

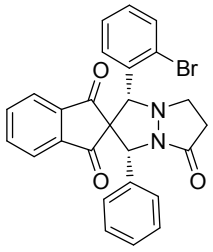
°C; *dr* = 3:1; IR (KBr): ν_{max} 2964, 2909, 1753, 1709, 1671, 1265, 1243, 1073, 882, 761, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 8.05 (1H, d, *J* = 7.6 Hz), 7.85 (1H, d, *J* = 7.6 Hz), 7.79 (1H, t, *J* = 7.6 Hz), 7.64 (1H, t, *J* = 7.6 Hz), 7.41 (1H, d, *J* = 7.6 Hz), 7.29-7.17 (4H, m), 7.15-7.08 (4H, m), 5.88 (1H, s), 4.84 (1H, s), 3.87-3.77 (1H, m), 3.14-3.07 (1H, m), 3.05-2.89 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 198.1 (C, *C*=O), 193.9 (C, *C*=O), 173.9 (C, *C*=O), 142.3 (C), 141.3 (C), 136.1 (CH), 135.8 (C), 135.7 (CH), 133.6 (C), 131.0 (CH), 130.8 (C), 129.6 (CH), 129.2 (CH), 128.4 (2 x CH), 127.9 (CH), 127.0 (CH), 126.1 (2 x CH), 123.7 (CH), 123.0 (CH), 72.0 (CH), 71.0 (C), 63.9 (CH), 46.9 (CH_2), 31.2 (CH_2); ^1H NMR ($CDCl_3$, 400 MHz, for minor isomer) δ 7.98 (1H, d, *J* = 7.6 Hz), 7.23 (1H, t, *J* = 7.6 Hz), 7.62-7.58 (1H, m), 7.41 (1H, d, *J* = 7.6 Hz), 7.29 (1H, br s), 7.26-7.17 (4H, m), 7.15-7.03 (4H, m), 5.83 (1H, s), 4.43 (1H, s), 3.87-3.77 (1H, m), 3.14-3.07 (1H, m), 3.05-2.89 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for minor isomer) δ 198.2 (C, *C*=O), 193.5 (C, *C*=O), 172.4 (C, *C*=O), 143.1 (C), 141.26 (C), 136.3 (CH), 135.7 (C), 135.6 (CH), 134.2 (C), 131.0 (CH), 130.8 (C), 129.5 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 127.8 (CH), 127.0 (CH), 125.7 (2 x CH), 123.3 (CH), 123.2 (CH), 72.1 (CH), 71.1 (C), 63.3 (CH), 48.2 (CH_2), 32.6 (CH_2); HRMS m/z 465.0981 ($M + Na^+$), calcd for $C_{26}H_{19}ClN_2O_3Na$ 465.0982.

(1'*S,3'*R**)-1'-(4-Bromophenyl)-3'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ad):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 162-164 °C; *dr* = >99:1; IR (KBr): ν_{max} 2962, 2854, 1742, 1709, 1643, 1589, 1463, 1353, 1227, 1079, 887 and 767 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.98 (1H, d, *J* = 7.5 Hz), 7.75 (1H, dt, *J* = 7.5, 0.5 Hz), 7.63 (1H, dt, *J* = 7.5, 1.0 Hz), 7.42 (1H, d, *J* = 7.5 Hz), 7.25 (2H, d, *J* = 8.5 Hz), 7.15-7.10 (5H, m), 7.06-7.04 (2H, m), 5.76 (1H, s), 4.39 (1H, s), 3.85-3.76 (1H, m), 3.08-3.01 (2H, m), 2.94-2.86 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.1 (C, *C*=O), 194.3 (C, *C*=O), 172.6 (C, *C*=O), 143.1 (C), 141.2 (C), 136.5 (CH), 135.7 (CH), 135.0 (C), 131.7 (2 x CH), 131.0 (C), 129.6 (2 x CH), 128.4 (2 x CH), 128.0 (CH), 125.9 (2 x CH), 123.34 (CH), 123.31 (CH), 122.9 (C), 76.3 (CH), 71.7 (C), 63.7 (CH), 47.9 (CH_2), 32.2 (CH_2); HRMS m/z 487.0655 ($M + H^+$), calcd for $C_{26}H_{20}BrN_2O_3$ 487.0657.



6ad

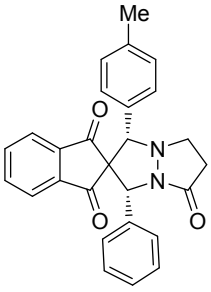
(1'*R,3'*R**)-1'-(2-Bromophenyl)-3'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ae):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light brown solid. Mp 138-140 °C; *dr* = 2:1; IR (KBr): ν_{max} 3024, 2969, 2909, 1742, 1709, 1583, 1534, 1473, 1271,



6ae

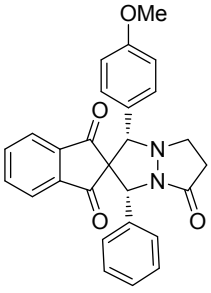
1178, 1024, 871, 761 and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 8.02 (1H, d, *J* = 7.6 Hz), 7.82 (1H, d, *J* = 7.6 Hz), 7.75 (1H, t, *J* = 7.6 Hz), 7.62 (1H, t, *J* = 7.6 Hz), 7.39 (1H, d, *J* = 8.0 Hz), 7.23-7.16 (4H, m), 7.12-7.05 (4H, m), 5.85 (1H, s), 4.82 (1H, s), 3.84-3.71 (1H, m), 3.11-3.01 (2H, m), 2.94-2.84 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 198.2 (C, *C*=O), 193.8 (C, *C*=O), 174.1 (C, *C*=O), 142.4 (C), 141.3 (C), 136.1 (CH), 135.9 (C), 135.7 (CH), 132.6 (CH), 132.4 (C), 131.7 (CH), 129.9 (CH), 128.4 (2 x CH), 127.9 (CH), 127.5 (CH), 126.1 (2 x CH), 124.0 (C), 123.8 (CH), 123.0 (CH), 74.0 (CH), 71.1 (C), 63.9 (CH), 46.8 (CH_2), 31.1 (CH_2); ^1H NMR ($CDCl_3$, 400 MHz, for minor isomer) δ 7.95 (1H, d, *J* = 7.6 Hz), 7.69 (1H, d, *J* = 7.6 Hz), 7.56 (1H, t, *J* = 7.6 Hz), 7.40-7.36 (1H, m), 7.27 (1H, br s), 7.23-7.14 (4H, m), 7.12-6.92 (4H, m), 5.79 (1H, s), 4.40 (1H, s), 3.84-3.81 (1H, m), 3.01-2.96 (2H, m), 2.94-2.84 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for minor isomer) δ 198.2 (C, *C*=O), 194.6 (C, *C*=O), 172.4 (C, *C*=O), 142.1 (C), 141.3 (C), 136.3 (CH), 135.9 (C), 135.5 (CH), 132.1 (CH), 132.0 (C), 131.6 (CH), 129.6 (CH), 128.5 (CH), 128.46 (CH), 127.8 (CH), 127.5 (CH), 125.7 (2 x CH), 123.3 (C), 123.2 (2 x CH), 74.02 (CH), 72.2 (C), 63.3 (CH), 48.2 (CH_2), 32.8 (CH_2); HRMS m/z 487.0656 ($M + H^+$), calcd for $C_{26}H_{20}BrN_2O_3$ 487.0657.

(1'*S,3'*R**)-3'-Phenyl-1'-(*p*-tolyl)-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'*H*)-trione (6af):** Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 144-146 °C; *dr* = 17:1; IR (KBr): ν_{max} 2947, 2931, 2854, 1742, 1709, 1682, 1583, 1484, 1353, 1260, 1178, 1095, 756, 613 and 586 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 7.97 (1H, d, *J* = 7.5 Hz), 7.72 (1H, t, *J* = 7.5 Hz), 7.60 (1H, t, *J* = 7.5 Hz), 7.42 (1H, d, *J* = 7.5 Hz), 7.17-7.12 (3H, m), 7.10-7.07 (4H, m), 6.91 (2H, d, *J* = 7.5 Hz), 5.80 (1H, s), 4.39 (1H, s), 3.85-3.79 (1H, m), 3.11-3.03 (2H, m), 2.94-2.81 (1H, m), 2.16 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 198.3 (C, *C*=O), 194.6 (C, *C*=O), 172.3 (C, *C*=O), 143.2 (C), 141.3 (C), 138.7 (C), 136.2 (CH), 135.4 (CH), 135.2 (C), 129.1 (2 x CH), 128.5 (C), 128.4 (2 x CH), 127.8 (CH), 127.7 (2 x CH), 125.8 (2 x CH), 123.2 (2 x CH), 77.3 (CH), 72.0 (C), 63.4 (CH), 48.1 (CH_2), 32.5 (CH_2), 21.0 (CH_3); LCMS m/z 423.45 ($M + H^+$), calcd for $C_{27}H_{23}N_2O_3$ 423.1709; HRMS m/z 445.1528 ($M + Na^+$), calcd for : $C_{27}H_{22}N_2O_3Na$ 445.1528; Anal. calcd for $C_{27}H_{22}N_2O_3$ (422.1630): C, 76.76; H, 5.25; N, 6.63. Found: C, 76.85; H, 5.21; N, 6.58%.



6af

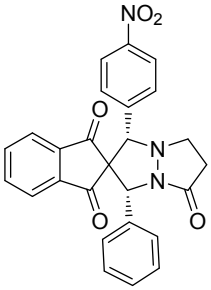
(1'*S,3'*R**)-1'-(4-Methoxyphenyl)-3'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ag):** Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 140-142 °C; *dr* = >99:1; IR (KBr): ν_{max} 2962, 2919, 1708, 1611, 1579, 1519, 1460, 1309, 1265, 1179,



6ag

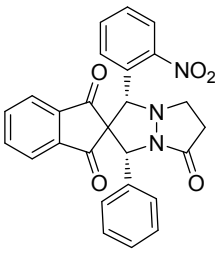
1033, 839, 774 and 703 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (1H, d, *J* = 7.6 Hz), 7.72 (1H, t, *J* = 7.6 Hz), 7.60 (1H, t, *J* = 7.2 Hz), 7.43 (1H, d, *J* = 7.6 Hz), 7.17-7.11 (5H, m), 7.08-7.06 (2H, m), 6.63 (2H, d, *J* = 8.8 Hz), 5.79 (1H, s), 4.36 (1H, s), 3.88-3.77 (1H, m), 3.66 (3H, s, OC*H*$_3$), 3.11-3.01 (2H, m), 2.95-2.84 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.3 (C, *C*=O), 194.8 (C, *C*=O), 172.4 (C, *C*=O), 159.8 (C), 143.2 (C), 141.3 (C), 136.3 (CH), 135.5 (CH), 135.2 (C), 129.1 (2 x CH), 128.4 (2 x CH), 127.8 (CH), 125.7 (2 x CH), 123.3 (C), 123.22 (CH), 123.21 (CH), 113.9 (2 x CH), 77.2 (CH), 72.0 (C), 63.2 (CH), 55.1 (CH_3, O*C*H_3), 48.1 (CH_2), 32.5 (CH_2); HRMS m/z 439.1653 ($M + H^+$), calcd for $C_{27}H_{23}N_2O_4$ 439.1658.

(1'*S,3'*R**)-1'-(4-Nitrophenyl)-3'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ah):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Mp 158-160 °C; *dr* = 4:1; IR (KBr): ν_{max} 2953, 2920, 1747, 1709, 1528, 1462, 1358, 1265, 767 and 706 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, for major isomer) δ 8.07-7.96 (3H, m), 7.79 (1H, t, *J* = 7.6 Hz), 7.66 (1H, t, *J* = 7.6 Hz), 7.46 (2H, d, *J* = 8.4 Hz), 7.41 (1H, d, *J* = 7.6 Hz), 7.19-7.15 (3H, m), 7.06-7.04 (2H, m), 5.76 (1H, s), 4.55 (1H, s), 3.93-3.81 (1H, m), 3.12-3.03 (2H, m), 2.98-2.89 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for major isomer) δ 197.8 (C, *C*=O), 194.0 (C, *C*=O), 172.7 (C, *C*=O), 148.0 (C), 143.0 (C), 141.0 (C), 139.6 (C), 136.8 (CH), 136.1 (CH), 134.7 (C), 128.9 (2 x CH), 128.5 (2 x CH), 128.2 (CH), 126.0 (2 x CH), 123.7 (2 x CH), 123.6 (CH), 123.4 (CH), 75.4 (CH), 71.7 (C), 64.1 (CH), 48.0 (CH_2), 32.0 (CH_2); ^1H NMR ($CDCl_3$, 400 MHz, for minor isomer) δ 8.07-7.96 (3H, m), 7.72 (1H, t, *J* = 7.6 Hz), 7.59 (1H, t, *J* = 7.6 Hz), 7.47-7.40 (3H, m), 7.19-7.15 (3H, m), 7.10-7.09 (2H, m), 5.82 (1H, s), 4.42 (1H, s), 3.93-3.81 (1H, m), 3.12-3.03 (2H, m), 2.98-2.89 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, for minor isomer) δ 196.3 (C, *C*=O), 191.5 (C, *C*=O), 172.4 (C, *C*=O), 148.1 (C), 143.1 (C), 141.3 (C), 140.3 (C), 137.3 (CH), 136.3 (CH), 135.2 (C), 128.8 (CH), 128.78 (CH), 128.5 (CH), 128.4 (CH), 127.8 (CH), 127.1 (CH), 125.8 (CH), 123.8 (CH), 123.77 (CH), 123.2 (CH), 123.19 (CH), 75.8 (CH), 71.5 (C), 63.0 (CH), 48.2 (CH_2), 32.5 (CH_2); HRMS m/z 454.1401 ($M + H^+$), calcd for $C_{26}H_{20}N_3O_5$ 454.1403.



6ah

(1'*S,3'*R**)-1'-(2-Nitrophenyl)-3'-phenyl-6',7'-dihydro-1'*H*-spiro[indene-2,2'-pyrazolo[1,2-a] pyrazole]-1,3,5'(3'*H*)-trione (6ai):** Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as light yellow solid. Mp 148-150 °C; *dr* = >99:1; IR (KBr): ν_{max} 2958, 2909, 2882, 1715, 1594, 1523, 1462, 1347, 1260, 1183, 767 and 723 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.40 (1H, d, *J* = 8.0 Hz), 8.12 (1H, d, *J* = 7.6 Hz), 7.84 (1H, t, *J* = 7.6 Hz), 7.76 (1H, d, *J* = 8.0 Hz), 7.73-7.65 (2H, m), 7.51 (1H, d, *J* = 7.6 Hz), 7.39 (1H, t, *J* = 7.6 Hz), 7.26-7.20 (3H,



6ai

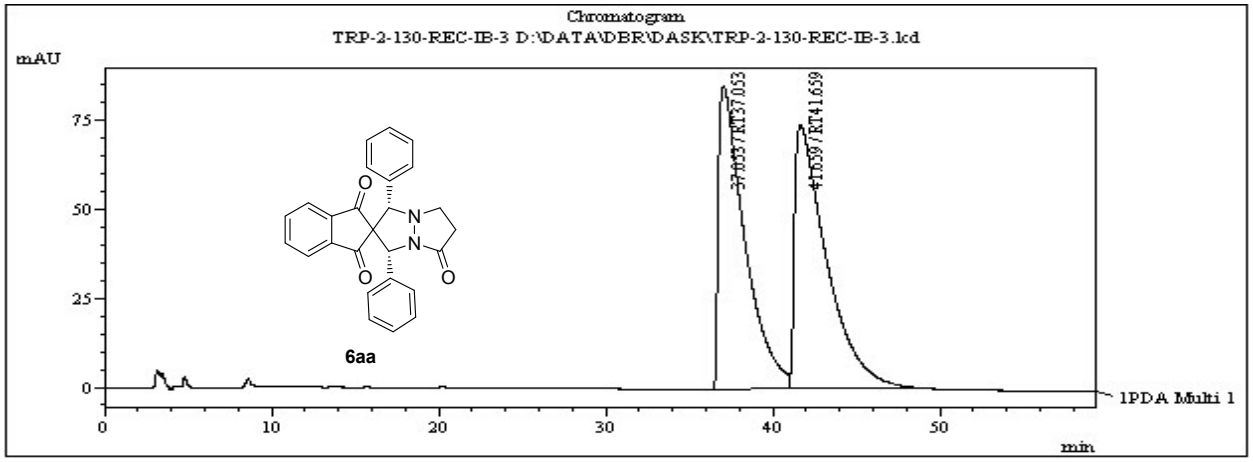
m), 7.14 (2H, d, *J* = 7.6 Hz), 5.64 (1H, s), 4.85 (1H, s), 3.86-3.79 (1H, m), 3.22-3.07 (2H, m), 2.80-2.73 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.9 (C, *C*=O), 193.4 (C, *C*=O), 175.7 (C, *C*=O), 148.3 (C), 142.1 (C), 140.5 (C), 136.0 (C), 135.96 (CH), 135.88 (CH), 133.5 (CH), 132.0 (CH), 131.4 (C), 129.1 (CH), 128.4 (2 x CH), 128.1 (CH), 126.8 (2 x CH), 124.6 (CH), 124.4 (CH), 123.2 (CH), 70.9 (C), 69.2 (CH), 65.0 (CH), 46.7 (CH_2), 30.1 (CH_2); HRMS m/z 454.1406 (M + H^+), calcd for $C_{26}H_{20}N_3O_5$ 454.1403.

References:

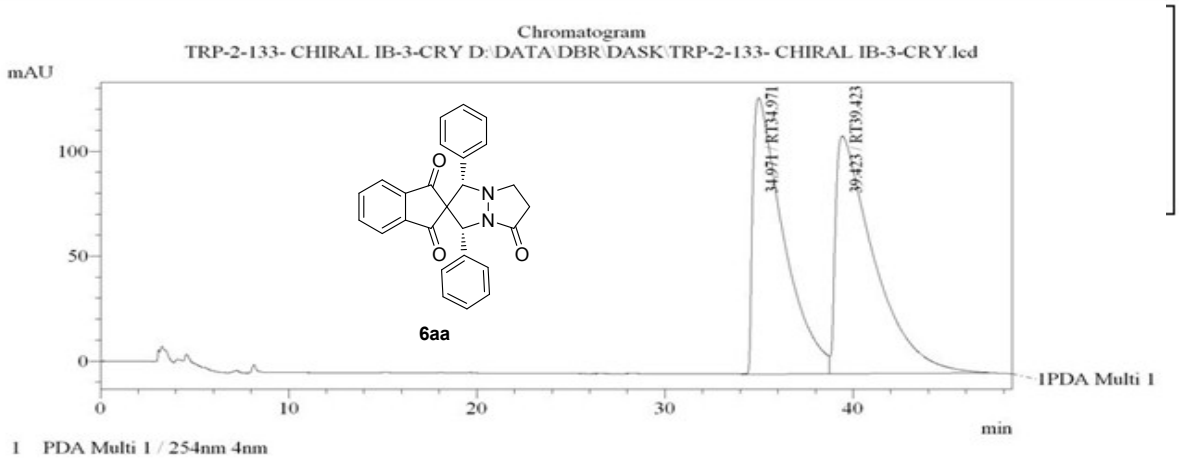
(1) Yin, C.; Lin, L.; Zhang, D.; Feng, J.; Liu, X.; Feng, X. *J. Org. Chem*. **2015**, *80*, 9691.

(2) Lee, C.-J.; Sheu, C.-N.; Tsai, C.-C.; Wu, Z.-Z.; W. Lin, *Chem. Commun*. **2014**, *50*, 5304.

RACEMIC 6aa:



Daicel Chiralpak IB-3, Hexane/ i-PrOH = 90:10, Flow Rate 1.0 mL/Min, 254 nm



CHIRAL 6aa (3.8% *ee*)

PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT34.971	34.971	14881012	131556	48.083	53.757
2	RT39.42	39.423	16067700	113167	51.917	46.243
Total			30948712	244723	100.000	100.000

Daicel Chiralpak IB-3, Hexane/ i-PrOH = 90:10, Flow Rate 1.0 mL/Min, 254 nm