Supporting Information

Synthesis of Dinitrogen-Fused Spirocyclic Heterocycles via Organocatalytic 1,3-dipolar Cycloaddition of 2-Arylidene-1,3-indandiones and an Azomethine Imine

Jindian Duan, Jing Cheng, Yuyu Cheng, and Pengfei Li*[a]

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**Experimental section**

**General**

All reactions were carried out with dry, freshly distilled solvents in anhydrous conditions. All chemicals were used without further purification as commercially available unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300-400 mesh). NMR (400 MHz for $^1$H NMR, 100 MHz for $^{13}$C NMR) spectra were recorded in CDCl$_3$ with TMS as the internal standard. High resolution mass spectral (HRMS) analyses were measured using ESI techniques. UV detection was monitored at 254 nm. IR spectra were measured using IRPrestige-21.

A variety of 2-arylidene-1,3-indandiones 1 were synthesized via Knoevenagel reactions as reported in the literature,$^1$ and azomethine imine 2 was prepared using general procedures reported in the literature.$^2$

**General procedure for the synthesis of spiro indane-1,3-dione-pyrazolidinones**

To a stirred mixture of 2-arylidene-1,3-indandiones 1 (0.3 mmol) and azomethine imine 2 (0.36 mmol) in MeOH (2 mL) was added Et$_3$N (5 mol %) and then kept at room temperature for the time given, which was monitored by TLC. After removal of the solvent, the crude residue was purified by column chromatography (petroleum ether / ethyl acetate 3/1 v/v) on silica gel to give the corresponding products 3.
Compounds characterization

1',3'-Diphenyl-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3aa)

Prepared according to general procedure to afford 3aa (120 mg, 98% yield) as a white solid; m.p. 164-165 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.97 (d, $J = 7.6$ Hz, 1H), 7.72–7.68 (m, 1H), 7.58–7.55 (m, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.19–7.18 (m, 2H), 7.16–7.06 (m, 8H), 5.81 (s, 1H), 4.42 (s, 1H), 3.85–3.79 (m, 1H), 3.10–3.02 (m, 2H), 2.94–2.87 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 198.3, 194.6, 172.5, 143.1, 141.3, 136.4, 135.6, 135.2, 131.6, 128.8, 128.5, 128.6, 127.8, 127.7, 125.7, 123.3, 123.2, 77.4, 72.1, 63.3, 48.2, 32.5; HRMS (ESI): m/z calcd for C$_{26}$H$_{20}$N$_2$NaO$_3$ [M+Na]$^+$ 431.1372, Found 431.1366. IR ν max: 3448, 3059 cm$^{-1}$.  

3'-[(4-Fluorophenyl)-1'-phenyl-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3ba)

Prepared according to general procedure to afford 3ba (96 mg, 75% yield) as a white solid; m.p. 155-157 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.97 (d, $J = 7.6$ Hz, 1H), 7.74–7.70 (m, 1H), 7.62–7.58 (m, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.19–7.16 (m, 2H), 7.12–7.06 (m, 5H), 6.87–6.82 (m, 2H), 5.76 (s, 1H), 4.40 (s, 1H), 3.85–3.78 (m, 1H), 3.11–3.01 (m, 2H), 2.94–2.85 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 198.1, 194.6, 172.6, 163.4 ($J_{C,F} = 245.2$ Hz), 143.0, 141.2, 136.4, 135.7, 131.5, 130.9 ($J_{C,F} = 3.3$ Hz), 128.9, 128.5, 127.8, 127.7 ($J_{C,F} = 8.3$ Hz), 123.3, 123.2, 115.6 ($J_{C,F} = 22.2$ Hz), 72.0, 62.7, 48.2, 32.5; HRMS (ESI): m/z calcd for C$_{28}$H$_{21}$FNNaO$_3$ [M+Na]$^+$ 449.1277, Found 449.1272. IR ν max: 3210, 3059, 2926, 1657, 1603, 1508, 1233, 758, 694 cm$^{-1}$.  

3'-[(4-Chlorophenyl)-1'-phenyl-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3ca)

Prepared according to general procedure to afford 3ca (112 mg, 85% yield) as a white solid; m.p. 157-158 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.97 (d, $J = 7.6$ Hz, 1H), 7.74–7.70 (m, 1H), 7.62–7.58 (m, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.18–7.09 (m, 7H), 7.05–7.03 (m, 2H), 5.75 (s, 1H), 4.39 (s, 1H), 3.85–3.79 (m, 1H), 3.11–3.01 (m, 2H), 2.93–2.85 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 197.9, 194.5, 172.7, 143.0, 141.2, 136.5, 135.7, 133.8, 133.7, 131.4, 128.9, 128.7, 128.6, 127.8, 127.3, 123.3, 77.5, 71.9, 62.6, 48.1, 32.4; HRMS (ESI): m/z calcd for C$_{26}$H$_{19}$ClN$_2$NaO$_3$ [M+Na]$^+$ 465.0982, Found
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 (3da)

Prepared according to general procedure to afford 3da (122 mg, 84% yield) as a white solid; m.p. 150-151 ºC; 1H NMR (400 MHz, CDCl3) δ (ppm) 7.97 (d, J = 7.6 Hz, 1H), 7.74–7.70 (m, 1H), 7.62–7.59 (m, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.29–7.26 (m, 2H), 7.18–7.14 (m, 2H), 7.11–7.09 (m, 3H), 6.99–6.97 (m, 2H), 5.73 (s, 1H), 4.39 (s, 1H), 3.85–3.80 (m, 1H), 3.08–3.03 (m, 2H), 2.93–2.87 (m, 1H); 13C NMR (100 MHz, CDCl3) δ (ppm) 197.9, 194.5, 172.7, 142.9, 141.2, 136.5, 135.8, 134.4, 131.6, 131.4, 128.9, 128.6, 127.7, 127.6, 123.3, 121.9, 77.5, 71.9, 62.6, 48.1, 32.4; HRMS (ESI): m/z calcd for C26H19BrN2O3 [M+Na]+ 509.0477, Found 509.0471. IR ν max: 3210, 2931, 1667, 1589, 1485, 1396, 1273, 1069, 1011, 756, 694 cm⁻¹.

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 (3ea)

Prepared according to general procedure to afford 3ea (131 mg, 92% yield) as a white solid; m.p. 130-131 ºC; For major diastereomer (dr = 4:1): 1H NMR (400 MHz, CDCl3) δ (ppm) 8.01–7.96 (m, 1H), 7.80–7.71 (m, 1H), 7.68–7.59 (m, 1H), 7.44–7.33 (m, 4H), 7.25–7.08 (m, 6H), 5.83 (s, 1H), 4.41 (s, 1H), 3.87–3.80(m, 1H), 3.13–3.03 (m, 2H), 2.95–2.87 (m, 1H); 13C NMR (100 MHz, CDCl3) δ (ppm) 197.8, 194.4, 173.0, 142.9, 141.2, 139.5, 136.5, 135.8, 131.2, 129.0, 128.6, 128.3, 127.8, 127.8, 126.5, 126.3, 125.6(q, J = 3.7 Hz), 123.4, 123.3, 77.6, 72.0, 62.6, 47.9, 32.2; HRMS (ESI): m/z calcd for C27H24F3N2O3 [M+H]+ 477.1426, Found 477.1421. IR ν max: 3063, 2930, 1746, 1711, 1593, 1325, 1125, 768, 735, 700 cm⁻¹.

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 (3fa)

Prepared according to general procedure to afford 3fa (105 mg, 83% yield) as a white solid; m.p. 153-154 ºC; 1H NMR (400 MHz, CDCl3) δ (ppm) 7.96 (d, J = 7.6 Hz, 1H), 7.71–7.67 (m, 1H), 7.57–7.54 (m, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.21–7.18 (m, 2H), 7.11–7.08 (m, 3H), 6.97–6.92 (m, 4H), 5.78 (s, 1H), 4.41 (s, 1H), 3.83–3.78 (m, 1H), 3.09–3.01 (m, 2H), 2.90–2.85 (m, 1H), 2.17 (s, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 198.3, 194.8, 172.0, 143.1, 141.3, 137.5, 136.3, 135.6, 132.0, 131.6, 129.1, 128.8, 128.5, 127.8, 125.6, 123.2, 123.1, 77.4, 72.1, 63.1, 48.5, 32.8, 21.1; HRMS (ESI): m/z calcd for C27H23N2O3 [M+Na]+ 445.1528, Found 445.1523. IR ν max: 2922, 2853, 1715,
1701, 1653, 1258, 765 cm\(^{-1}\).

**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 (3ga)

Prepared according to general procedure to afford 3ga (95 mg, 65% yield) as a white solid; m.p. 171-172 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.98 (d, \(J = 7.6\) Hz, 1H), 7.75–7.71 (m, 1H), 7.63–7.59 (m, 1H), 7.42 (d, \(J = 7.6\) Hz, 1H), 7.31–7.25 (m, 2H), 7.18–7.16 (m, 2H), 7.10–7.09 (m, 3H), 7.02–6.95 (m, 2H), 5.74 (s, 1H), 4.39 (s, 1H), 3.86–3.79 (m, 1H), 3.11–2.99 (m, 2H), 2.93–2.85 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 197.9, 194.4, 173.3, 143.0, 141.2, 137.8, 136.5, 135.8, 131.4, 131.1, 129.9, 129.1, 128.9, 128.5, 127.8, 124.5, 123.4, 123.3, 122.8, 77.5, 71.9, 62.5, 47.7, 32.1; HRMS (ESI): m/z calcld for C\(_{26}\)H\(_{19}\)BrN\(_2\)NaO\(_3\) [M+Na]\(^+\) 509.0477, Found 509.0472. IR \(\nu\) max: 3061, 2926, 1744, 1709, 1593, 1260, 1236, 767, 733 cm\(^{-1}\).

**3'-**(3-Nitropheny1)-1'-phenyl-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3ha)

Prepared according to general procedure to afford 3ha (96 mg, 71% yield) as a white solid; m.p. 166-168 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.04–7.98 (m, 3H), 7.77–7.73 (m, 1H), 7.63–7.59 (m, 1H), 7.47–7.45 (m, 1H), 7.39–7.35 (m, 2H), 7.17–7.09 (m, 5H), 5.85 (s, 1H), 4.40 (s, 1H), 3.89–3.83 (m, 1H), 3.16–3.00 (m, 2H), 2.96–2.87 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 197.6, 194.5, 173.9, 148.2, 142.9, 141.1, 138.1, 136.7, 136.0, 132.2, 131.2, 129.5, 129.1, 128.6, 127.8, 123.6, 123.3, 123.1, 121.3, 77.7, 71.9, 62.2, 47.3, 31.7; HRMS (ESI): m/z calcld for C\(_{26}\)H\(_{19}\)BrN\(_2\)NaO\(_3\) [M+Na]\(^+\) 476.1222, Found 476.1217. IR \(\nu\) max: 2920, 2849, 1744, 1709, 1530, 1350, 1261, 1236, 766, 723, 700 cm\(^{-1}\).

**1'-Phenyl-3'-(m-tolyl)-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazol e]-1,3,5'(3'H)-trione (3ia)

Prepared according to general procedure to afford 3ia (117 mg, 93% yield) as a white solid; m.p. 142-143 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.96 (d, \(J = 8.0\) Hz, 1H), 7.72–7.68 (m, 1H), 7.59–7.55 (m, 1H), 7.41 (d, \(J = 8.0\) Hz, 1H), 7.20–7.18 (m, 2H), 7.09–7.08 (m, 3H), 6.97–6.92 (m, 4H), 5.77 (s, 1H), 4.41 (s, 1H), 3.83–3.78 (m, 1H), 3.10–3.00 (m, 2H), 2.91–2.85 (m, 1H), 2.19 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.3, 194.8, 171.9, 143.1, 141.3, 137.5, 136.3, 135.5, 132.0, 131.7, 129.2, 128.8, 128.5, 127.8, 125.6, 123.2, 77.4, 72.1, 63.2, 48.5, 32.8, 29.1; HRMS (ESI): m/z calcld for C\(_{25}\)H\(_{22}\)N\(_2\)NaO\(_3\) [M+Na]\(^+\) 445.1528, Found 445.1523. IR \(\nu\) max: 3059, 2922, 1744, 1709, 1591, 1260,
1182, 766, 733, 700 cm\(^{-1}\).

3'- (3-Methoxyphenyl)-1'-phenyl-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5' (3'H)-trione (3ja)

Prepared according to general procedure to afford 3ja (108 mg, 82% yield) as a white solid; m.p. 148-150 °C; For major diastereomer (\(dr = 7:1\)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.97-7.95 (m, 1H), 7.73–7.69 (m, 1H), 7.61–7.57 (m, 1H), 7.43 (d, \(J = 7.6\) Hz, 1H), 7.20–7.24 (m, 6H), 6.67–6.59 (m, 3H), 5.77 (s, 1H), 4.39 (s, 1H), 3.85–3.79 (m, 1H), 3.61 (s, 3H), 3.09–3.02 (m, 2H), 2.92–2.87 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.3, 194.5, 172.6, 159.6, 143.2, 141.2, 136.7, 136.3, 135.5, 131.6, 129.6, 128.9, 128.5, 127.8, 125.7, 123.3, 118.1, 113.7, 111.3, 77.4, 71.9, 63.3, 55.1, 48.2, 32.5; HRMS (ESI): m/z calcd for \(\text{C}_{27}\text{H}_{22}\text{N}_{2}\text{NaO}_4\) [M+Na]\(^+\) 461.1477, Found 461.1472. IR \(\nu\) max: 3059, 2932, 1744, 1709, 1589, 1260, 1042, 768, 731, 698 cm\(^{-1}\).

1'-Phenyl-3'-(thiophen-2-yl)-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5' (3'H)-trione (3ka)

Prepared according to general procedure to afford 3ka (87 mg, 70 % yield) as a white solid; m.p. 160-161 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.97 (d, \(J = 8.0\) Hz, 1H), 7.73–7.69 (m, 1H), 7.59–7.55 (m, 1H), 7.39 (d, \(J = 7.6\) Hz, 1H), 7.20–7.06 (m, 8H), 5.81 (s, 1H), 4.42 (s, 1H), 3.85–3.79 (m, 1H), 3.10–3.03 (m, 2H), 2.94–2.84 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.3, 194.7, 172.4, 143.1, 141.3, 136.3, 135.6, 135.1, 131.6, 129.6, 128.9, 128.5, 128.4, 127.9, 127.8, 125.7, 123.3, 123.2, 72.1, 63.3, 48.2, 32.6; HRMS (ESI): m/z calcd for \(\text{C}_{24}\text{H}_{19}\text{N}_{2}\text{O}_3\text{S}\) [M+H]\(^+\) 415.1116, Found 415.1111. IR \(\nu\) max: 2922, 2851, 1701, 1657, 1593, 1256, 764 cm\(^{-1}\).

References

Copies of $^1$H and $^{13}$C NMR spectra of 3aa-ka

1',3'-Diphenyl-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3aa)
3’-(4-Fluorophenyl)-1’-phenyl-6’,7’-dihydro-1’H-spiro[indene-2,2’-pyrazolo[1,2-a]pyrazole]-1,3,5’(3’H)-trione (3ba)
3’-(4-Chlorophenyl)-1’-phenyl-6’,7’-dihydro-1’H-spiro[indene-2,2’-pyrazolo[1,2-a]pyrazole]-1,3,5’(3’H)-trione (3ca)
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 (3da)
1'-Phenyl-3’-(4-(trifluoromethyl)phenyl)-6’,7’-dihydro-1'H-spiro[indene-2,2'-pyr azolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3ea)
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 (3fa)
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 (3ga)
3'-(3-Nitrophenyl)-1'-phenyl-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-α]pyrazole]-1,3,5'(3'H)-trione (3ha)
1'-Phenyl-3'-(m-tolyl)-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3ia)
3’-(3-Methoxyphenyl)-1’-phenyl-6’,7’-dihydro-1’H-spiro[indene-2,2’-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3ja)
1'-Phenyl-3'-(thiophen-2-yl)-6',7'-dihydro-1'H-spiro[indene-2,2'-pyrazolo[1,2-a]pyrazole]-1,3,5'(3'H)-trione (3ka)
Crystal structure and data for compound 3fa
Crystal data and structure refinement for 3fa

Identification code  shelx
Empirical formula  C_{27}H_{22}N_{2}O_{3}
Formula weight  422.46
Temperature  293(2) K
Wavelength  1.54187 Å
Crystal system  Triclinic
Space group  P -1
Unit cell dimensions
a = 9.34320(10) Å  a= 113.841(8)°.
b = 11.3125(2) Å  b= 108.881(8)°.
c = 12.1914(8) Å  g = 96.208(7)°.
Volume  1071.85(11) Å³
Z  2
Density (calculated)  1.309 Mg/m³
Absorption coefficient  0.690 mm⁻¹
F(000)  444
Crystal size  0.20 x 0.20 x 0.20 mm³
Theta range for data collection  7.267 to 89.479°.
Index ranges  -11<=h<=11, -13<=k<=13, -14<=l<=14
Reflections collected  12669
Independent reflections  3796 [R(int) = 0.0440]
Completeness to theta = 67.687°  96.6 %
Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  0.871 and 0.637
Refinement method  Full-matrix least-squares on F²
Data / restraints / parameters  3796 / 0 / 290
Goodness-of-fit on F²  1.141
Final R indices [I>2sigma(I)]  R1 = 0.0506, wR2 = 0.1244
R indices (all data)  R1 = 0.0558, wR2 = 0.1300
Extinction coefficient  n/a
Largest diff. peak and hole  0.238 and -0.297 e.Å⁻³