Supporting Information

Synthesis of Pyrazolone Fused Benzodiazepines via Rh(III)-Catalyzed [4+3] Annulation of 1-Phenylpyrazolidinones with Propargyl Alcohols

Linghua Zhang, Yuanshuang Xu, Xiaopeng Zhang, Xinying Zhang*, and Xuesen Fan*

Henan Key Laboratory of Organic Functional Molecules and Drug Innovation, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China

E-mail: xinyingzhang@htu.cn; xuesen.fan@htu.cn

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I. General experimental information

Commercial reagents were used without further purification. 1-Phenylpyrazolidinones (1),[1,2] propargyl alcohols (2, 4, 6),[3,4] and [RhCp*Cl2]2[5] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The 1H NMR spectra were recorded at 400 MHz or 600 MHz. The 13C NMR spectra were recorded at 100 MHz or 150 MHz. The 19F NMR spectra were recorded at 376 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), br s (broad singlet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).
II. Experimental procedures and spectroscopic data

1. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3ee, 5a-5m and 7a-7q

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (1a, 48.7 mg, 0.3 mmol), toluene (2 mL), [RhCp*Cl2]2 (4.7 mg, 0.0075 mmol), Zn(OAc)2 (27.5 mg, 0.15 mmol), NaOAc (12.3 mg, 0.15 mmol) and 2-methyl-4-phenylbut-3-yn-2-ol (2a, 48.1 mg, 0.3 mmol). The resulting mixture was stirred at 100 °C (oil bath) for 4 h under air. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford 3a (80.5 mg, 88%). 3b-3ee, 5a-5m and 7a-7q were obtained in a similar manner.

5,5-Dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3a)

White solid (80.5 mg, 88%), mp 173.2-174.5 °C. \(^1\)H NMR (400 MHz, CDCl₃) δ 1.67 (s, 6H), 2.77 (t, \(J = 7.2\) Hz, 2H), 4.10 (t, \(J = 7.2\) Hz, 2H), 5.99 (s, 1H), 6.99-7.01 (m, 1H), 7.03-7.07 (m, 1H), 7.18-7.20 (m, 2H), 7.25-7.26 (m, 2H), 7.28-7.33 (m, 3H). \(^1\)C {\(^1\)H} NMR (100 MHz, CDCl₃) δ 26.9, 33.3, 49.0, 63.1, 116.3, 124.4, 127.4, 127.9, 128.1, 129.3, 132.1, 132.6, 136.5, 139.9, 144.4, 149.6, 173.6. HRMS calcd for C₂₀H₂₁N₂O: 305.1648 [M+H]+, found: 305.1647.

5,5,9-Trimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3b)

White solid (80.4 mg, 84%), mp 155.3-156.7 °C. \(^1\)H NMR (400 MHz, CDCl₃) δ 1.66 (s, 6H), 2.20 (s, 3H), 2.77 (t, \(J = 7.6\) Hz, 2H), 4.08 (t, \(J = 7.6\) Hz, 2H), 5.99 (s, 1H), 6.80 (s, 1H), 7.07 (d, \(J = 8.0\) Hz, 1H), 7.16 (d, \(J = 8.4\) Hz, 1H), 7.19-7.21 (m, 2H), 7.31-7.33 (m, 3H). \(^1\)C {\(^1\)H} NMR (100 MHz, CDCl₃) δ 20.8, 26.8, 33.3, 49.0, 62.7,

9-Methoxy-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3c)

Light yellow solid (70.2 mg, 70%), mp 170.1-172.0 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 1.65 (s, 6H), 2.77 (t, \(J = 7.2\) Hz, 2H), 3.65 (s, 3H), 4.06 (t, \(J = 7.2\) Hz, 2H), 6.02 (s, 1H), 6.54 (d, \(J = 2.4\) Hz, 1H), 6.81 (dd, \(J_1 = 9.2\) Hz, \(J_2 = 2.4\) Hz, 1H), 7.18-7.23 (m, 3H), 7.30-7.33 (m, 3H). \(^{13}\)C\{\(^1\)H\} NMR (150 MHz, CDCl\(_3\)) \(\delta\): 26.8, 33.4, 49.1, 55.4, 62.6, 113.1, 117.2, 117.3, 127.5, 128.2, 129.2, 134.0, 136.7, 140.1, 143.1, 143.9, 156.2, 172.9. HRMS calcd for C_{21}H_{23}N_{2}O_{2}: 335.1754 [M+H]^+, found: 335.1754.

9-Fluoro-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3d)

White solid (79.3 mg, 82%), mp 168.0-169.2 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 1.67 (s, 6H), 2.77 (t, \(J = 7.2\) Hz, 2H), 4.08 (t, \(J = 7.6\) Hz, 2H), 4.06 (t, \(J = 7.6\) Hz, 2H), 6.02 (s, 1H), 6.71 (dd, \(J_1 = 9.6\) Hz, \(J_2 = 2.8\) Hz, 1H), 6.95 (td, \(J_1 = 8.4\) Hz, \(J_2 = 2.8\) Hz, 1H), 7.18-7.23 (m, 3H), 7.32-7.35 (m, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\): 26.8, 33.2, 49.4, 63.1, 114.3 (d, \(J_{C,F} = 22.4\) Hz), 117.5 (d, \(J_{C,F} = 8.7\) Hz), 118.4 (d, \(J_{C,F} = 23.2\) Hz), 127.6, 128.3, 129.2, 134.6 (d, \(J_{C,F} = 7.3\) Hz), 135.6 (d, \(J_{C,F} = 2.1\) Hz), 141.0, 143.7, 145.8 (d, \(J_{C,F} = 2.9\) Hz), 159.4 (d, \(J_{C,F} = 242.0\) Hz), 173.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -118.14 – -118.08 (m). HRMS calcd for C_{20}H_{20}FN_{2}O: 323.1554 [M+H]^+, found: 323.1553.

9-Chloro-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3e)
White solid (74.1 mg, 73%), mp 179.0-180.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.67 (s, 6H), 2.75 (t, $J = 7.2$ Hz, 2H), 4.07 (t, $J = 7.2$ Hz, 2H), 6.00 (s, 1H), 6.97 (d, $J = 2.0$ Hz, 1H), 7.17-7.23 (m, 4H), 7.32-7.36 (m, 3H).

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 26.8, 33.1, 49.2, 63.3, 117.5, 127.6, 127.7, 128.4, 129.2, 129.8, 131.7, 134.3, 135.3, 141.2, 143.8, 148.2, 173.6. HRMS calcd for C$_{20}$H$_{20}$ClN$_2$O: 339.1259 [M+H]$^+$, found: 339.1242.

9-Bromo-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3f)

White solid (90.5 mg, 79%), mp 177.6-179.0 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.67 (s, 6H), 2.75 (t, $J = 7.2$ Hz, 2H), 4.07 (t, $J = 7.2$ Hz, 2H), 6.00 (s, 1H), 7.11-7.14 (m, 2H), 7.17-7.19 (m, 2H), 7.33-7.38 (m, 4H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 26.8, 33.1, 49.2, 63.3, 117.5, 117.9, 127.7, 128.4, 129.2, 130.5, 134.60, 134.63, 135.2, 141.3, 143.7, 148.7, 173.6. HRMS calcd for C$_{20}$H$_{20}$BrN$_2$O: 383.0754 [M+H]$^+$, found: 383.0751.

5,5-Dimethyl-7-phenyl-9-(trifluoromethyl)-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3g)

White solid (91.5 mg, 82%), mp 180.3-181.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.69 (s, 6H), 2.77 (t, $J = 7.2$ Hz, 2H), 4.13 (t, $J = 7.2$ Hz, 2H), 6.03 (s, 1H), 7.15-7.17 (m, 2H), 7.26 (s, 1H), 7.33-7.36 (m, 4H), 7.51 (d, $J = 8.4$ Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 26.9, 33.0, 49.3, 63.8, 116.4, 123.9 (q, $^1J_{C-F} = 270.1$ Hz), 124.5 (q, $^3J_{C-F} = 3.6$ Hz), 126.5 (q, $^2J_{C-F} = 32.5$ Hz), 127.8, 128.4, 129.17, 129.24 (q, $^3J_{C-F} = 3.6$ Hz), 132.9, 135.0, 141.6, 143.8, 152.5, 174.1. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.22 (s). HRMS calcd for C$_{21}$H$_{20}$F$_3$N$_2$O: 373.1522 [M+H]$^+$, found: 373.1523.
5,5-Dimethyl-3-oxo-7-phenyl-2,3-dihydro-1H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepine-9-carbonitrile (3h)

Light yellow solid (77.4 mg, 78%), mp 185.0-186.8 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.69 (s, 6H), 2.75 (t, $J$ = 7.2 Hz, 2H), 4.13 (t, $J$ = 7.2 Hz, 2H), 6.00 (s, 1H), 7.12-7.15 (m, 2H), 7.29 (d, $J$ = 1.2 Hz, 1H), 7.31-7.36 (m, 4H), 7.54 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.6 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 26.9, 32.9, 49.3, 64.2, 107.9, 116.8, 118.6, 127.9, 128.6, 129.2, 131.1, 133.3, 134.2, 136.2, 142.2, 143.7, 153.4, 174.4. HRMS calcd for C$_{21}$H$_{20}$N$_3$O: 330.1601 [M+H]$^+$, found: 330.1596.

11-Fluoro-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3i)

Light yellow solid (62.8 mg, 65%), mp 183.2-184.3 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.62 (s, 6H), 2.85 (t, $J$ = 7.2 Hz, 2H), 6.11 (s, 1H), 6.77-6.79 (m, 1H), 7.00-7.04 (m, 2H), 7.19-7.21 (m, 2H), 7.30-7.33 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 26.7, 35.0 (d, $^2$J$_{C-F}$ = 7.2 Hz), 51.6 (d, $^4$J$_{C-F}$ = 12.3 Hz), 62.4, 116.3 (d, $^2$J$_{C-F}$ = 24.5 Hz), 125.5 (d, $^3$J$_{C-F}$ = 9.3 Hz), 127.1 (d, $^3$J$_{C-F}$ = 2.9 Hz), 127.6, 128.2, 129.0, 136.1 (d, $^2$J$_{C-F}$ = 10.1 Hz), 137.0 (d, $^4$J$_{C-F}$ = 2.9 Hz), 137.2 (d, $^4$J$_{C-F}$ = 2.9 Hz), 140.4, 143.9, 153.9 (d, $^1$J$_{C-F}$ = 243.4 Hz), 174.0. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -119.91 (dd, $J_1$ = 10.9 Hz, $J_2$ = 5.6 Hz). HRMS calcd for C$_{20}$H$_{20}$FN$_2$O: 323.1554 [M+H]$^+$, found: 323.1551.

5,5,10-Trimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3j)

White solid (87.0 mg, 91%), mp 164.7-165.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.66 (s, 6H), 2.39 (s, 3H), 2.78 (t, $J$ = 7.6 Hz, 2H), 4.09 (t, $J$ = 7.6 Hz, 2H), 5.94 (s, 1H), 6.88 (s, 2H), 7.05 (s 1H), 7.18-7.20 (m, 2H), 7.29-7.33 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 21.7, 26.9, 33.3, 48.9, 63.0, 117.1, 125.3, 127.3, 128.1, 129.3, 129.9, 131.9, 136.5, 137.9, 139.1, 144.5, 149.4, 173.5. HRMS calcd for C$_{21}$H$_{23}$N$_2$O: 319.1805 [M+H]$^+$, found:
10-Methoxy-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3k)

Brown syrup (75.1 mg, 75%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.66 (s, 6H), 2.77 (t, $J = 7.2$ Hz, 2H), 3.82 (s, 3H), 4.06 (t, $J = 7.2$ Hz, 2H), 5.86 (s, 1H), 6.60 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 6.80 (d, $J = 2.4$ Hz, 1H), 6.92 (d, $J = 8.8$ Hz, 1H), 7.19-7.21 (m, 2H), 7.28-7.32 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 26.8, 33.4, 49.1, 55.4, 62.6, 113.1, 117.2, 127.5, 128.2, 129.2, 134.0, 136.7, 140.1, 143.1, 143.9, 156.2, 172.9. HRMS calcd for C$_{21}$H$_{23}$N$_2$O$_2$: 335.1754 [M+H]$^+$, found: 335.1754.

10-Bromo-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3l)

Light yellow solid (99.7 mg, 87%), mp 180.5-181.9 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.67 (s, 6H), 2.77 (t, $J = 7.6$ Hz, 2H), 4.07 (t, $J = 7.6$ Hz, 2H), 5.97 (s, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 7.16-7.19 (m, 3H), 7.31-7.33 (m, 3H), 7.38 (s, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 26.8, 33.1, 49.2, 63.3, 117.5, 127.6, 127.7, 128.4, 129.2, 129.8, 131.7, 134.3,135.3, 141.2, 143.8, 148.2, 173.6. HRMS calcd for C$_{20}$H$_{20}$BrN$_2$O: 383.0754 [M+H]$^+$, found: 383.0748.

10-Fluoro-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3m)

White solid (34.8 mg, 36%), mp 153.8-154.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.67 (s, 6H), 2.77 (t, $J = 7.6$ Hz, 2H), 4.06 (t, $J = 7.6$ Hz, 2H), 5.93 (s, 1H), 6.77 (td, $J_1 = 8.0$ Hz, $J_2= 2.4$ Hz, 1H), 6.95-6.98 (m, 2H), 7.16-7.18 (m, 2H), 7.30-7.33 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 26.9, 32.9, 49.2, 63.4, 104.1 (d, $^2$J$_{C,F} = 23.8$
Hz), 111.3 (d, $^2J_{C-F}$ = 20.9 Hz), 127.5, 128.2, 128.6 (d, $^4J_{C-F}$ = 2.9 Hz), 129.2, 133.6 (d, $^3J_{C-F}$ = 8.7 Hz), 135.5, 139.5, 144.3, 151.2 (d, $^3J_{C-F}$ = 6.5 Hz), 161.7 (d, $^1J_{C-F}$ = 247.0 Hz), 173.6. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -112.09 - -112.02 (m). HRMS calcd for C$_{20}$H$_{20}$FN$_2$O: 323.1554 [M+H]$^+$, found: 323.1555.

8-Fluoro-5,5-dimethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3m')

Light yellow solid (32.8 mg, 34%), mp 186.0-188.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.65 (s, 6H), 2.75 (brs, 2H), 4.07 (t, $J$ = 7.6 Hz, 2H), 6.22 (s, 1H), 6.84-6.89 (m, 1H), 7.11 (d, $J$ = 8.0 Hz, 1H), 7.14-7.17 (m, 2H), 7.27-7.33 (m, 4H). $^{13}$C {$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$ 26.8, 33.1, 49.0, 61.7, 112.4 (d, $^4J_{C-F}$ = 3.3 Hz), 113.1 (d, $^2J_{C-F}$ = 21.9 Hz), 120.8 (d, $^2J_{C-F}$ = 12.0 Hz), 126.7, 127.3, 128.2, 129.1 (d, $^3J_{C-F}$ = 9.9 Hz), 133.2, 141.8, 143.2 (d, $^4J_{C-F}$ = 2.3 Hz), 151.4 (d, $^3J_{C-F}$ = 5.4 Hz), 161.0 (d, $^1J_{C-F}$ = 250.5 Hz), 172.1. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -101.96 (dd, $J_1$ = 9.8 Hz, $J_2$ = 5.6 Hz). HRMS calcd for C$_{20}$H$_{20}$FN$_2$O: 323.1554 [M+H]$^+$, found: 323.1554.

2,2,5,5-Tetramethyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3n)

White solid (80.7 mg, 81%), mp 166.8-167.9 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.32 (s, 6H), 1.68 (s, 6H), 4.03 (s, 2H), 5.93 (s, 1H), 6.97-7.00 (m, 2H), 7.16-7.18 (m, 2H), 7.20-7.23 (m, 1H), 7.28-7.32 (m, 3H), 7.34 (d, $J$ = 7.8 Hz, 1H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 24.7, 26.8, 42.4, 59.8, 63.8, 117.2, 123.5, 127.0, 127.2, 128.1, 129.4, 131.9, 132.4, 136.4, 139.8, 145.0, 149.7, 180.4. HRMS calcd for C$_{22}$H$_{25}$N$_2$O: 333.1961 [M+H]$^+$, found: 333.1959.
5,5-Dimethyl-7-(p-tolyl)-1,2-dihydro-3\textit{H},5\textit{H}-benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepin-3-one (3o)

White solid (83 mg, 87%), mp 199.1-200.2 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.66 (s, 6H), 2.36 (s, 3H), 2.77 (t, $J = 7.2$ Hz, 2H), 4.09 (t, $J = 7.2$ Hz, 2H), 5.98 (s, 1H), 7.01-7.06 (m, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 7.8$ Hz, 2H), 7.24-7.25 (m, 2H). $^{13}$C{$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$ 21.2, 26.9, 33.3, 49.0, 63.0, 116.3, 124.4, 127.8, 128.8, 129.2, 132.1, 132.8, 136.4, 137.1, 139.4, 141.6, 149.5, 173.5. HRMS calcd for C$_{21}$H$_{23}$N$_2$O: 319.1805 [M+H]$^+$, found: 319.1807.

7-(4-Methoxyphenyl)-5,5-dimethyl-1,2-dihydro-3\textit{H},5\textit{H}-benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepin-3-one (3p)

White solid (83.9 mg, 84%), mp 184.5-185.2 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.66 (s, 6H), 2.77 (t, $J = 7.2$ Hz, 2H), 3.81 (s, 3H), 4.09 (t, $J = 7.2$ Hz, 2H), 5.98 (s, 1H), 6.83-6.85 (m, 2H), 7.03-7.07 (m, 2H), 7.10-7.13 (m, 2H), 7.25-7.26 (m, 2H). $^{13}$C{$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$ 26.9, 33.3, 49.0, 55.3, 62.8, 113.5, 116.3, 124.4, 127.8, 130.4, 132.1, 132.9, 136.1, 136.9, 139.0, 149.5, 159.1, 173.3. HRMS calcd for C$_{21}$H$_{23}$N$_2$O$_2$: 335.1754 [M+H]$^+$, found: 335.1760.

7-(4-Fluorophenyl)-5,5-dimethyl-1,2-dihydro-3\textit{H},5\textit{H}-benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepin-3-one (3q)

White solid (71.5 mg, 74%), mp 193.0-194.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.67(s, 6H), 2.77 (t, $J = 7.2$ Hz, 2H), 4.10 (t, $J = 7.2$ Hz, 2H), 5.97 (s, 1H), 6.97-7.02 (m, 3H), 7.04-7.08 (m, 1H), 7.14-7.17 (m, 2H), 7.25-7.27 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 26.9, 33.2, 49.0, 63.0, 115.0 (d, $^{2}$J$_{C,F} = 20.9$ Hz), 116.3, 124.5, 128.0, 130.8 (d, $^{3}$J$_{C,F} = 8.0$ Hz), 132.0, 132.4, 135.5, 139.9, 140.4 (d, $^{4}$J$_{C,F} = 2.8$ Hz), 149.6, 162.3 (d, $^{1}$J$_{C,F} = 244.8$ Hz), 173.5. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -115.13 – -115.06 (m). HRMS calcd for C$_{20}$H$_{20}$FN$_2$O:
323.1554 [M+H]$^+$, found: 323.1557.

7-(4-Chlorophenyl)-5,5-dimethyl-1,2-dihydro-3$H,5H$-benzo[c]pyrazolo[1,2-$a$][1,2]$d$iazepin-3-one (3r)

White solid (84.2 mg, 83%), mp 219.6-220.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.66 (s, 6H), 2.77 (t, $J = 7.2$ Hz, 2H), 4.10 (t, $J = 7.6$ Hz, 2H), 5.97 (s, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 7.05-7.09 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.27-7.29 (m, 4H). $^{13}$C{¹H} NMR (100 MHz, CDCl$_3$) δ 26.8, 33.2, 49.0, 63.1, 116.3, 124.5, 128.1, 128.3, 130.6, 131.9, 132.2, 133.3, 135.4, 140.2, 142.8, 149.6, 173.6. HRMS calcd for C$_{20}$H$_{20}$ClN$_2$O: 339.1259 [M+H]$^+$, found: 339.1258.

7-(4-Bromophenyl)-5,5-dimethyl-1,2-dihydro-3$H,5H$-benzo[c]pyrazolo[1,2-$a$][1,2]$d$iazepin-3-one (3s)

White solid (91.7 mg, 80%), mp 213.2-214.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.66 (s, 6H), 2.77 (t, $J = 7.6$ Hz, 2H), 4.10 (t, $J = 7.6$ Hz, 2H), 5.96 (s, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 7.04-7.08 (m, 3H), 7.26-7.30 (m, 2H), 7.44 (d, $J = 8.0$ Hz, 2H). $^{13}$C{¹H} NMR (100 MHz, CDCl$_3$) δ 26.8, 33.2, 49.0, 63.1, 116.3, 121.5, 124.5, 128.1, 130.9, 131.3, 131.9, 132.1, 135.4, 140.2, 143.3, 149.6, 173.6. HRMS calcd for C$_{20}$H$_{20}$BrN$_2$O: 383.0754 [M+H]$^+$, found: 383.0760.

5,5-Dimethyl-7-(4-(trifluoromethyl)phenyl)-1,2-dihydro-3$H,5H$-benzo[c]pyrazolo[1,2-$a$][1,2]$d$iazepin-3-one
e (3t)

White solid (90.4 mg, 81%), mp 126.4-127.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.68 (s, 6H), 2.78 (t, $J = 7.2$ Hz, 2H), 4.12 (t, $J = 7.2$ Hz, 2H), 5.99 (s, 1H), 6.93 (d, $J = 7.6$ Hz, 1H), 7.05-7.09 (m, 1H), 7.27-7.32 (m, 4H), 7.57 (d, $J = 8.0$ Hz, 2H). $^{13}$C$_I$($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 26.8, 33.2, 49.1, 63.3, 116.4, 124.2 (q, $^1$J$_{CF} = 270.8$ Hz), 124.6, 125.1 (q, $^3$J$_{CF} = 3.6$ Hz), 128.2, 129.5 (q, $^2$J$_{CF} = 31.8$ Hz), 129.6, 131.8, 131.9, 135.3, 141.1, 148.0, 149.7, 173.8. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.40 (s). HRMS calcd for C$_{21}$H$_{20}$F$_3$N$_2$O: 373.1522 [M+H]$^+$, found: 373.1527.

5,5-Dimethyl-7-(4-nitrophenyl)-1,2-dihydro-3$H$,5$H$-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3u)

Light yellow solid (68.1 mg, 65%), mp 168.6-170.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.70 (s, 6H), 2.79 (t, $J = 7.2$ Hz, 2H), 4.12 (t, $J = 7.6$ Hz, 2H), 6.03 (s, 1H), 6.89-6.91 (m, 1H), 7.07-7.11 (m, 1H), 7.29-7.32 (m, 2H), 7.34-7.31 (m, 2H), 8.16-8.19 (m, 2H). $^{13}$C$_I$($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 26.7, 33.2, 49.1, 63.4, 116.5, 123.5, 124.7, 128.5, 130.0, 131.4, 131.8, 134.7, 141.9, 147.1, 149.8, 151.0, 173.8. HRMS calcd for C$_{20}$H$_{20}$N$_3$O$_3$: 350.1499 [M+H]$^+$, found: 350.1497.

5,5-Dimethyl-7-($o$-tolyl)-1,2-dihydro-3$H$,5$H$-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3v)

White solid (85.9 mg, 90%), mp 132.8-134.1 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.69(s, 6H), 1.96 (s, 3H), 2.76 (brs, 2H), 4.11 (t, $J = 7.2$ Hz, 2H), 5.74 (s, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.94-6.98 (m, 1H), 7.13-7.16 (m, 2H), 7.17-7.24 (m, 4H). $^{13}$C$_I$($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 19.7, 26.9, 33.4, 49.2, 63.8, 115.9, 124.4, 125.7, 127.38, 127.40, 130.1, 130.2, 131.1, 132.3, 135.0, 136.5, 140.4, 144.0, 148.9, 174.6. HRMS calcd for C$_{21}$H$_{23}$N$_2$O:
7-(2-Bromophenyl)-5,5-dimethyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]-diazepin-3-one (3w)

White solid (99.7 mg, 87%), mp 177.4-179.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.71 (s, 6H), 2.77 (t, $J$ = 7.2 Hz, 2H), 4.13 (t, $J$ = 7.2 Hz, 2H), 5.75 (s, 1H), 6.77 (d, $J$ = 7.6 Hz, 1H), 6.98-7.02 (m, 1H), 7.16-7.31 (m, 5H), 7.59 (d, $J$ = 8.0 Hz, 1H). $^{13}$C {$^1$H} NMR (150 MHz, CDCl$_3$) δ 26.8, 33.2, 49.0, 63.2, 116.4, 124.6, 127.46, 127.50, 128.1, 129.3, 129.4, 131.9, 132.0, 134.0, 135.3, 140.6, 146.2, 149.6, 173.7. HRMS calcd for C$_{20}$H$_{20}$BrN$_2$O: 383.0754 [M+H]$^+$, found: 383.0757.

5,5-Dimethyl-7-((m-tolyl)-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]-diazepin-3-one (3x)

White solid (78.3 mg, 82%), mp 131.1-132.0 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.67 (s, 6H), 2.33 (s, 3H), 2.77 (t, $J$ = 7.6 Hz, 2H), 4.10 (t, $J$ = 7.2 Hz, 2H), 5.98 (s, 1H), 6.98-7.02 (m, 3H), 7.04-7.08 (m, 1H), 7.11 (d, $J$ = 7.6 Hz, 1H), 7.20 (t, $J$ = 7.2 Hz, 1H), 7.25-7.26 (m, 2H). $^{13}$C {$^1$H} NMR (150 MHz, CDCl$_3$) δ 21.4, 26.9, 33.3, 49.0, 63.0, 116.3, 124.4, 126.4, 127.8, 128.0, 128.1, 129.9, 132.2, 132.7, 136.5, 137.7, 139.7, 144.4, 149.5, 173.5. HRMS calcd for C$_{21}$H$_{23}$N$_2$O: 319.1805 [M+H]$^+$, found: 319.1807.

7-(3-Chlorophenyl)-5,5-dimethyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]-diazepin-3-one (3y)

Light yellow solid (74.1 mg, 73%), mp 143.0-144.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.69 (s, 6H), 2.77 (t, $J$ =
7.2 Hz, 2H), 4.10 (t, J = 7.2 Hz, 2H), 5.97 (s, 1H), 6.98 (d, J = 8.0 Hz, 1H), 7.06-7.10 (m, 2H), 7.20 (s, 1H), 7.22-7.28 (m, 4H). $^{13}$C$\{^1H\}$ NMR (150 MHz, CDCl₃) $\delta$ 26.8, 33.2, 49.0, 63.2, 116.4, 124.6, 127.46, 127.50, 128.1, 129.3, 129.4, 131.9, 132.0, 134.0, 135.3, 140.6, 146.2, 149.6, 173.7. HRMS calcd for C$_{20}$H$_{20}$ClN$_2$O: 339.1259 [M+H]$^+$, found: 339.1258.

5,5-Dimethyl-7-(thiophen-2-yl)-1,2-dihydro-3$H,5H$-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3z)

White solid (76.3 mg, 82%), mp 174.0-176.0 °C. $^1$H NMR (400 MHz, CDCl₃) $\delta$ 1.64 (s, 6H), 2.76 (t, J = 7.2 Hz, 2H), 4.07 (t, J = 7.2 Hz, 2H), 6.26 (s, 1H), 6.86 (d, J = 3.6 Hz, 1H), 6.97 (t, J = 4.0 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 5.2 Hz, 1H), 7.25-7.32 (m, 2H), 7.37 (d, J = 8.0 Hz, 1H). $^{13}$C$\{^1H\}$ NMR (150 MHz, CDCl₃) $\delta$ 26.7, 33.2, 48.8, 62.3, 116.6, 124.7, 124.9, 126.7, 127.0, 128.4, 130.3, 131.7, 132.2, 139.4, 146.7, 149.2, 172.8. HRMS calcd for C$_{18}$H$_{19}$N$_2$OS: 311.1213 [M+H]$^+$, found: 311.1218.

7-Cyclopropyl-5,5-dimethyl-1,2-dihydro-3$H,5H$-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3aa)

White solid (70.8 mg, 88%), mp 179.0-180.9 °C. $^1$H NMR (400 MHz, CDCl₃) $\delta$ 0.61 (q, J = 5.2 Hz, 2H), 0.82-0.87 (m, 2H), 1.54 (s, 6H), 1.58-1.62 (m, 1H), 2.73 (t, J = 7.2 Hz, 2H), 4.04 (t, J = 7.2 Hz, 2H), 5.66 (s, 1H), 7.18-7.26 (m, 3H), 7.90 (d, J = 7.6 Hz, 1H). $^{13}$C$\{^1H\}$ NMR (100 MHz, CDCl₃) $\delta$ 7.0, 19.2, 27.0, 33.3, 49.0, 62.7, 116.1, 124.6, 127.4, 128.9, 133.5, 134.3, 135.9, 148.4, 173.6. HRMS calcd for C$_{17}$H$_{21}$N$_2$O: 269.1648 [M+H]$^+$, found: 269.1649.
5-Ethyl-5-methyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3bb)

White solid (77.3 mg, 81%), mp 123.5-124.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 0.86 (t, $J = 7.2$ Hz, 3H), 1.60 (s, 3H), 1.63-1.72 (m, 1H), 2.53-2.62 (m, 1H), 2.68-2.75 (m, 1H), 2.83-2.91 (m, 1H), 4.03-4.10 (m, 1H), 4.14-4.21 (m, 1H), 5.92 (s, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 7.04-7.08 (m, 1H), 7.19-7.23 (m, 2H), 7.26-7.27 (m, 2H), 7.30-7.34 (m, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ 9.0, 26.3, 32.0, 33.3, 48.7, 66.7, 116.4, 124.5, 127.4, 127.8, 128.1, 129.2, 132.0, 133.0, 138.2, 144.4, 149.4, 172.8. HRMS calcd for C$_{21}$H$_{23}$N$_2$O: 319.1805 [M+H]$^+$, found: 319.1803.

5-(tert-Butyl)-5-methyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3cc)

White solid (69.6 mg, 67%), mp 176.2-171.1 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.16 (s, 9H), 1.74 (s, 3H), 2.49 (dd, $J_1 = 16.4$ Hz, $J_2 = 6.4$ Hz, 1H), 3.12-3.21 (m, 1H), 4.01 (td, $J_1 = 13.6$ Hz, $J_2 = 6.8$ Hz, 1H), 4.22 (dd, $J_1 = 12.8$ Hz, $J_2 = 6.8$ Hz, 1H), 6.19 (s, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.97-7.01 (m, 1H), 7.19-7.21 (m, 4H), 7.28-7.35 (m, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ 23.1, 27.8, 33.9, 42.7, 47.5, 72.1,115.8, 124.0, 127.1, 127.2, 128.1, 129.5, 131.8, 132.7, 135.9, 137.1, 145.6, 150.1, 174.9. HRMS calcd for C$_{23}$H$_{27}$N$_2$O: 347.2118 [M+H]$^+$, found: 347.2114.

5-Cyclohexyl-5-methyl-7-phenyl-1,2-dihydro-3H,5H-benzo[c]pyrazolo[1,2-a][1,2]diazepin-3-one (3dd)

White solid (79.3 mg, 71%), mp 191.5-193.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 0.92-1.01 (m, 1H), 1.07-1.32 (m, 4H), 1.50-1.53 (m, 1H), 1.61-1.64 (m, 5H), 1.79-1.82 (m, 1H),1.89-1.92 (m, 1H), 2.62-2.73 (m, 2H), 2.85-2.93 (m, 1H), 4.02-4.10 (m, 1H), 4.14-4.21 (m, 1H), 6.05 (s, 1H), 7.00 (d, $J = 7.6$Hz, 1H), 7.04-7.08 (m, 1H), 7.19-7.22 (m, 2H), 7.25-7.27 (m, 2H), 7.31-7.34 (m, 3H). $^{13}$C($^1$H) NMR (150 MHz, CDCl$_3$) δ 24.5, 26.3, 26.6,
26.8, 28.0, 28.7, 33.5, 45.4, 48.7, 69.6, 116.5, 124.6, 127.4, 127.7, 128.1, 129.2, 131.9, 133.3, 135.8, 138.0, 144.8, 149.2, 172.5. HRMS calcd for C_{25}H_{29}N_{2}O: 373.2274 [M+H]^+, found: 373.2275.

7-Butyl-5,5-diethyl-1,2-dihydro-3\textit{H},5\textit{H}-benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepin-3-one (3ee)

Yellow solid (77.7 mg, 83%), mp 95.2-96.4 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 0.78 (t, \( J = 7.6 \) Hz, 6H), 0.88 (t, \( J = 7.2 \) Hz, 3H), 1.26-1.33 (m, 2H), 1.35-1.43 (m, 2H), 1.50-1.59 (m, 2H), 2.30-2.39 (m, 2H), 2.52 (t, \( J = 6.8 \) Hz, 2H), 2.76 (t, \( J = 7.2 \) Hz, 2H), 4.05 (t, \( J = 7.2 \) Hz, 2H), 5.58 (s, 1H), 7.14-7.21 (m, 3H), 7.42 (d, \( J = 7.6 \) Hz, 1H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 8.8, 13.9, 22.3, 31.4, 31.7, 33.3, 38.5, 48.0, 69.5, 117.0, 124.9, 127.1, 128.0, 133.6, 134.2, 136.7, 148.6, 171.8. HRMS calcd for C\(_{20}\)H\(_{29}\)N\(_{2}\)O: 313.2274 [M+H]^+, found: 313.2271.

7-Phenyl-1,2-dihydro-3\textit{H}-spiro[benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepine-5,1'-cyclopentan]-3-one (5a)

White solid (67.4 mg, 68%), mp 156.0-157.8 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 1.70-1.77(m, 2H), 1.82-1.97 (m, 4H), 2.59-2.66 (m, 2H), 2.78 (t, \( J = 7.2 \) Hz, 2H), 4.07 (t, \( J = 7.2 \) Hz, 2H), 6.15 (s, 1H), 7.00-7.02 (m, 1H), 7.04-7.08 (m, 1H), 7.18-7.21 (m, 2H), 7.24-7.27 (m, 2H), 7.28-7.34 (m, 3H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 24.7, 33.5, 38.2, 48.5, 71.9, 116.8, 124.5, 127.4, 128.0, 128.2, 129.2, 131.9, 133.2, 137.1, 139.4, 144.1, 149.5, 172.3. HRMS calcd for C\(_{22}\)H\(_{23}\)N\(_{2}\)O: 331.1805 [M+H]^+, found: 331.1803.

9-Methyl-7-phenyl-1,2-dihydro-3\textit{H}-spiro[benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepine-5,1'-cyclopentan]-3-one (5b)

White solid (64.0 mg, 62%), mp 156.8-157.9 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 1.69-1.75 (m, 2H), 1.79-1.85 (m,
2H), 1.89-1.94 (m, 2H), 2.21 (s, 3H), 2.58-2.65 (m, 2H), 2.78 (t, J = 7.2 Hz, 2H), 4.04 (t, J = 7.2 Hz, 2H), 6.15 (s, 1H), 6.82 (d, J = 1.6 Hz, 1H), 7.06-7.09 (m, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.19-7.21 (m, 2H), 7.29-7.34 (m, 3H).

$^{13}$C$^\text{1H}$ NMR (100 MHz, CDCl$_3$) $\delta$ 20.8, 24.6, 33.6, 38.1, 48.4, 71.4, 116.8, 127.4, 128.1, 128.7, 129.1, 132.1, 133.3, 134.1, 137.5, 139.3, 144.0, 147.2, 171.9. HRMS calcd for C$_{23}$H$_{25}$N$_2$O: 345.1961 [M+H]$^+$, found: 345.1962.

9-Methyl-7-phenyl-1,2-dihydro-3$H$-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one (5c)

White solid (64.8 mg, 60%), mp 158.4-159.9 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.68-1.74 (m, 2H), 1.78-1.83 (m, 2H), 1.90-1.95 (m, 2H), 2.58-2.65 (m, 2H), 2.78 (t, J = 7.2 Hz, 2H), 3.65 (s, 3H), 4.02 (t, J = 7.2 Hz, 2H), 6.18 (s, 1H), 6.55 (d, J = 3.2 Hz, 1H), 6.81 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.8 Hz, 2H), 7.17-7.20 (m, 2H), 7.21-7.23 (m, 2H), 7.28-7.33 (m, 3H). $^{13}$C$^\text{1H}$ NMR (100 MHz, CDCl$_3$) $\delta$ 24.6, 33.6, 38.0, 48.4, 72.0, 113.4, 116.7, 177.9, 127.5, 128.2, 129.1, 134.8, 137.5, 139.6, 143.1, 143.5, 156.4, 171.7. HRMS calcd for C$_{23}$H$_{25}$N$_2$O: 361.1911 [M+H]$^+$, found: 361.1909.

9-Chloro-7-phenyl-1,2-dihydro-3$H$-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one (5d)

Brown syrup (71.0 mg, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.71-1.76 (m, 2H), 1.82-1.97 (m, 2H), 2.58-2.64 (m, 2H), 2.76 (t, J = 7.2 Hz, 2H), 4.03 (t, J = 7.2 Hz, 2H), 6.15 (s, 1H), 6.98 (d, J = 2.4 Hz, 1H), 7.16-7.24 (m, 4H), 7.30-7.36 (m, 3H). $^{13}$C$^\text{1H}$ NMR (100 MHz, CDCl$_3$) $\delta$ 24.8, 33.2, 38.3, 48.8, 72.2, 118.0, 127.67, 127.73, 128.4, 129.2, 129.9, 131.5, 134.8, 135.8, 140.7, 143.5, 148.2, 172.4. HRMS calcd for C$_{22}$H$_{22}$ClN$_2$O: 365.1415
9-Bromo-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one (5e)

White solid (77.1 mg, 63%), mp 186.2-187.1 °C. $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.70-1.76 (m, 2H), 1.82-1.95 (m, 4H), 2.58-2.65 (m, 2H), 2.76 (t, $J = 7.2$ Hz, 2H), 4.03 (t, $J = 7.2$ Hz, 2H), 6.15(s, 1H), 7.11-7.13 (m, 2H), 7.17-7.19 (m, 2H), 7.31-7.38 (m, 4H). $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) $\delta$ 24.8, 33.3, 38.3, 48.7, 72.2, 117.6, 118.3, 127.7, 128.4, 129.1, 130.7, 134.4, 135.2, 135.7, 140.8, 143.5, 148.7, 172.4. HRMS calcd for C$_{22}$H$_{22}$BrN$_2$O: 409.0910 [M+H]$^+$, found: 409.0906.

7-Phenyl-9-(trifluoromethyl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one (5f)

White solid (72.9 mg, 61%), mp 171.0-172.7 °C.$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.71-1.80 (m, 2H), 1.88-1.99 (m, 4H), 2.59-2.66 (m, 2H), 2.77 (t, $J = 7.2$ Hz, 2H), 4.10 (t, $J = 7.2$ Hz, 2H), 6.17(s, 1H), 7.15-7.19 (m, 2H), 7.26-7.27 (m, 1H), 7.31-7.37 (m, 4H), 7.51 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H). $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) $\delta$ 24.9, 33.2, 38.5, 49.0, 72.8, 116.7, 123.9 (q, $^1$J$_{C-F} = 270.1$ Hz), 124.6 (q, $^3$J$_{C-F} = 3.6$ Hz), 126.4 (q, $^2$J$_{C-F} = 32.5$ Hz), 127.8, 128.4, 129.1, 129.2 (q, $^3$J$_{C-F} = 4.4$ Hz), 133.2, 135.4, 141.0, 143.6, 152.5, 172.9. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.40 (s). HRMS calcd for C$_{22}$H$_{22}$F$_3$N$_2$O: 399.1679[M+H]$^+$, found: 399.1671.

10-Methyl-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one
White solid (74.3 mg, 72%), mp 146.3-147.8 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.70-1.75 (m, 2H), 1.80-1.96 (m, 4H), 2.39 (s, 3H), 2.58-2.65 (m, 2H), 2.78 (t, $J = 7.2$ Hz, 2H), 4.06 (t, $J = 7.2$ Hz, 2H), 6.11 (s, 1H), 6.86-6.91 (m, 2H), 7.04 (s, 1H), 7.18-7.20 (m, 2H), 7.26-7.33 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 20.8, 24.6, 33.6, 38.1, 48.4, 71.4, 116.8, 127.4, 128.1, 128.7, 129.1, 132.1, 133.3, 134.1, 137.5, 139.3, 144.0, 147.2, 171.9. HRMS calcd for C$_{23}$H$_{25}$N$_2$O: 345.1961 [M+H]$^+$, found: 345.1958.

10-Bromo-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one (5h)

White solid (85.7 mg, 70%), mp 131.3-133.0 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.71-1.77 (m, 2H), 1.83-1.97 (m, 4H), 2.58-2.65 (m, 2H), 2.78 (t, $J = 7.2$ Hz, 2H), 4.04 (t, $J = 7.2$ Hz, 2H), 6.12 (s, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 7.15-7.19 (m, 3H), 7.29-7.34 (m, 3H), 7.36 (d, $J = 2.0$ Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 24.8, 33.2, 38.3, 48.8, 72.4, 120.0, 121.2, 127.5, 127.6, 128.3, 129.2, 132.0, 133.3, 135.9, 140.0, 143.8, 150.8, 172.5. HRMS calcd for C$_{22}$H$_{22}$BrN$_2$O: 409.0910 [M+H]$^+$, found: 409.0904.

7-(p-Tolyl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one (5i)

White solid (77.4 mg, 75%), mp 124.2-126.1 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.68-1.75 (m, 2H), 1.80-1.94 (m, 4H), 2.36 (s, 3H), 2.58-2.65 (m, 2H), 2.78 (t, $J = 7.2$ Hz, 2H), 4.07 (t, $J = 7.2$ Hz, 2H), 6.13 (s, 1H), 7.02-7.13 (m, 6H), 7.23-7.27 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 21.2, 24.7, 33.5, 38.2, 48.5, 71.8, 116.8, 124.5, 128.0, 128.9, 129.0, 131.9, 133.4, 137.0, 137.1, 138.9, 141.2, 149.5, 172.2. HRMS calcd for C$_{23}$H$_{25}$N$_2$O:
7-(4-Methoxyphenyl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one (5j)

White solid (65.9 mg, 61%), mp 139.1-140.8 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.68-1.75 (m, 2H), 1.79-1.84 (m, 2H), 1.87-1.96 (m, 2H), 2.58-2.65 (m, 2H), 2.78 (t, $J = 7.2$ Hz, 2H), 3.82 (s, 3H), 4.07 (t, $J = 7.2$ Hz, 2H), 6.14 (s, 1H), 6.83-6.86 (m, 2H), 7.03-7.14 (m, 4H), 7.24-7.29 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 24.6, 33.5, 38.1, 48.4, 55.3, 71.5, 113.5, 116.9, 124.6, 128.0, 130.2, 131.8, 133.6, 136.5, 136.9, 138.4, 149.5, 159.1,172.0.

HRMS calcd for C$_{23}$H$_{25}$N$_2$O$_2$: 361.1911 [M+H]$^+$, found: 361.1911.

7-(4-Chlorophenyl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclopentan]-3-one (5k)

White solid (71.2 mg, 65%), mp 152.6-154.3 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.68-1.75 (m, 2H), 1.81-1.86 (m, 2H), 1.89-1.97 (m, 2H), 2.58-2.65 (m, 2H), 2.78 (t, $J = 7.2$ Hz, 2H), 4.07 (t, $J = 7.2$ Hz, 2H), 6.12 (s, 1H), 6.98 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.07 (td, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.11-7.14 (m, 2H), 7.24-7.29 (m, 4H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 24.8, 33.4, 38.2, 48.5, 72.0, 116.8, 124.6, 128.2, 128.4, 130.5, 131.8, 132.8, 133.3, 136.0, 139.7, 142.6, 149.6, 172.4. HRMS calcd for C$_{22}$H$_{22}$ClN$_2$O: 365.1415 [M+H]$^+$, found: 365.1416.
7-(4-(Trifluoromethyl)phenyl)-1,2-dihydro-3\textit{H}-spiro[benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepine-5,1'-cyclopentan]-3-one (5l)

White solid (75.3 mg, 63%), mp 143.9-145.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.71-1.78 (m, 2H), 1.84-1.99 (m, 4H), 2.60-2.67 (m, 2H), 2.79 (t, $J$ = 7.2 Hz, 2H), 4.08 (t, $J$ = 7.2 Hz, 2H), 6.13 (s, 1H), 6.93-6.95 (m, 1H), 7.05-7.09 (m, 1H), 7.25-7.32 (m, 4H), 7.57 (d, $J$ = 8.0 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 24.8, 33.4, 38.3, 48.7, 72.3, 116.8, 124.2 (q, $^1$J$_{C-F}$ = 270.1 Hz), 124.6, 125.2 (q, $^3$J$_{C-F}$ = 3.7 Hz), 128.3, 129.45 (q, $^2$J$_{C-F}$ = 31.8 Hz), 129.49, 131.8, 132.3, 135.7, 140.7, 147.8, 149.7, 172.7. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.22 (s).

HRMS calcd for C$_{23}$H$_{22}$F$_3$N$_2$O: 399.1679 [M+H]$^+$, found: 399.1674.

7-Cyclopropyl-1,2-dihydro-3\textit{H}-spiro[benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepine-5,1'-cyclopentan]-3-one (5m)

White solid (63.5 mg, 72%), mp 183.6-184.1 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 0.59-0.63 (m, 2H), 0.82-0.87 (m, 2H), 1.58-1.74 (m, 5H), 1.81-1.90 (m, 2H), 2.49-2.56 (m, 2H), 2.73 (t, $J$ = 7.2 Hz, 2H), 4.01 (t, $J$ = 7.2 Hz, 2H), 5.79 (d, $J$ = 0.8 Hz, 1H), 7.16-7.18 (m, 1H), 7.20-7.28 (m, 2H), 7.88 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 7.1, 19.0, 24.7, 33.5, 38.3, 48.6, 71.7, 116.5, 124.6, 127.5, 128.8, 134.0, 134.9, 135.3, 148.4, 172.4. HRMS calcd for C$_{19}$H$_{23}$N$_2$O: 295.1805[M+H]$^+$, found: 295.1804.

7-Phenyl-1,2-dihydro-3\textit{H}-spiro[benzo[c]pyrazolo[1,2-\textit{a}][1,2]diazepine-5,1'-cyclohexan]-3-one (7a)

White solid (89.8 mg, 87%), mp 162.7-164.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.31-1.40 (m, 1H), 1.56-1.74 (m, 2H), 2.55-2.62 (m, 2H), 2.71 (t, $J$ = 7.2 Hz, 2H), 3.95 (t, $J$ = 7.2 Hz, 2H), 5.81 (d, $J$ = 0.8 Hz, 1H), 7.00-7.04 (m, 2H), 7.17-7.19 (m, 1H), 7.20-7.28 (m, 2H), 7.83 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 8.0, 19.0, 24.7, 33.6, 38.3, 48.5, 71.7, 116.5, 124.6, 127.5, 128.8, 134.0, 134.9, 135.2, 148.3, 172.3. HRMS calcd for C$_{23}$H$_{23}$N$_2$O: 399.1679[M+H]$^+$, found: 399.1674.
(7a) 9-Methyl-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one

White solid (91.3 mg, 85%), mp 181.4-183.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 1.30-1.36 (m, 1H), 1.55-1.73 (m, 7H), 2.23 (s, 3H), 2.62-2.68 (m, 2H), 2.79 (t, J = 7.6 Hz, 2H), 4.01 (t, J = 7.6 Hz, 2H), 6.59 (s, 1H), 6.85 (d, J = 1.6 Hz, 1H), 7.09 (dd, J₁ = 8.0 Hz, J₂ = 1.6 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.21-7.24 (m, 2H), 7.30-7.35 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 20.8, 23.7, 24.8, 33.8, 33.9, 48.3, 64.0, 117.1, 127.6, 128.2, 129.0, 131.7, 134.0, 134.5, 135.3, 138.9, 144.0, 147.1, 170.8. HRMS calcd for C₂₄H₂₇N₂O: 359.2118 [M+H]^+, found: 359.2114.

(7b) 9-Methoxy-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one

Light yellow solid (86.4 mg, 77%), mp 176.2-177.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 1.30-1.37 (m, 1H), 1.54-1.74 (m, 7H), 2.65 (td, J₁ = 12.4 Hz, J₂ = 3.6 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 3.67 (s, 3H), 3.99 (t, J = 7.6 Hz, 2H), 6.58 (d, J = 2.8 Hz, 1H), 6.61 (s, 1H), 6.83 (dd, J₁ = 8.4 Hz, J₂ = 2.8 Hz, 1H), 7.20-7.28 (m, 3H), 7.29-7.34 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 23.7, 24.8, 33.8, 34.0, 48.4, 55.5, 63.9, 113.7, 116.2, 118.3, 127.7, 128.2, 129.0, 135.4, 135.6, 138.8, 143.0, 143.5, 156.6, 170.7. HRMS calcd for C₂₄H₂₇N₂O₂:
375.2067 [M+H]^+, found: 375.2055.

9-Fluoro-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one (7d)

White solid (79.3 mg, 73%), mp 175.3-176.1 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.30-1.39 (m, 1H), 1.54-1.75 (m, 7H), 2.63-2.69 (m, 2H), 2.80 (t, \(J = 7.2\) Hz, 2H), 4.01 (t, \(J = 7.2\) Hz, 2H), 6.65 (s, 1H), 6.75 (dd, \(J_1 = 9.6\) Hz, \(J_2 = 2.8\) Hz, 1H), 6.96-7.01 (m, 1H), 7.20-7.26 (m, 3H), 7.31-7.36 (m, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.6, 24.8, 33.8, 34.0, 48.7, 64.4, 114.9 (d, \(^2J_{C-F} = 22.4\) Hz), 117.7 (d, \(^2J_{C-F} = 22.4\) Hz), 118.6 (d, \(^3J_{C-F} = 8.7\) Hz), 127.8, 128.4, 129.0, 136.0 (d, \(^3J_{C-F} = 8.0\) Hz), 136.5, 137.8 (d, \(^4J_{C-F} = 2.1\) Hz), 143.3, 145.7 (d, \(^4J_{C-F} = 2.2\) Hz), 159.7 (d, \(^1J_{C-F} = 242.7\) Hz), 171.1. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -117.32 – -117.26 (m). HRMS calcd for C\(_{23}\)H\(_{24}\)FN\(_2\)O: 363.1867 [M+H]^+, found: 363.1861.

9-Bromo-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one (7e)

Light yellow solid (95.0 mg, 75%), mp 214.3-215.5 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.32-1.39 (m, 1H), 1.54-1.76 (m, 7H), 2.62-2.69 (m, 2H), 2.78 (t, \(J = 7.2\) Hz, 2H), 4.00 (t, \(J = 7.2\) Hz, 2H), 6.64 (s, 1H), 7.15-7.17 (m, 2H), 7.18-7.21 (m, 2H), 7.32-7.36 (m, 3H), 7.39 (dd, \(J_1 = 8.4\) Hz, \(J_2 = 2.4\) Hz, 1H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.6, 24.8, 33.6, 34.0, 48.6, 64.6, 118.0, 118.9, 127.9, 128.4, 129.0, 131.0, 134.0, 136.0, 136.8, 137.4, 143.4, 148.6, 171.2. HRMS calcd for C\(_{23}\)H\(_{24}\)BrN\(_2\)O: 423.1067 [M+H]^+, found: 423.1066.
7-Phenyl-9-(trifluoromethyl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one (7f)

White solid (103.9 mg, 84%), mp 202.3-203.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.32-1.42 (m, 1H), 1.56-1.75 (m, 7H), 2.64-2.72 (m, 2H), 2.79 (t, $J = 7.6$ Hz, 2H), 4.07 (t, $J = 7.6$ Hz, 2H), 6.70 (s, 1H), 7.16-7.20 (m, 2H), 7.30-7.38 (m, 5H), 7.54 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H). $^{13}$C $^1$H NMR (100 MHz, CDCl$_3$) $\delta$ 23.5, 24.8, 33.5, 34.2, 48.8, 65.1, 117.4, 123.9 (q, $^1J_{C-F} = 270.1$ Hz), 125.0 (q, $^3J_{C-F} = 3.6$ Hz), 126.9 (q, $^1J_{C-F} = 32.5$ Hz), 128.0, 128.5, 128.7 (q, $^3J_{C-F} = 3.6$ Hz), 129.0, 134.1, 137.2, 143.6, 152.3, 171.6. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.22 (s). HRMS calcd for C$_{24}$H$_{24}$F$_3$N$_2$O: 413.1835 [M+H$^+$], found: 413.1829.

10-Methoxy-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one (7g)

White solid (79.7 mg, 71%), mp 167.6-168.9 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.34-1.40 (m, 1H), 1.59-1.73 (m, 7H), 2.65 (td, $J_1 = 13.2$ Hz, $J_2 = 4.0$ Hz, 2H), 2.79 (t, $J = 7.6$ Hz, 2H), 3.84 (s, 3H), 4.01 (t, $J = 7.2$ Hz, 2H), 6.49 (s, 1H), 6.65 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, 1H), 6.81 (d, $J = 2.4$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 7.20-7.23 (m, 2H), 7.29-7.34 (m, 3H). $^{13}$C $^1$H NMR (100 MHz, CDCl$_3$) $\delta$ 23.6, 24.8, 33.6, 33.9, 48.5, 55.5, 64.4, 104.5, 109.1, 126.7, 127.5, 128.2, 129.0, 132.6, 133.7, 138.4, 144.2, 150.7, 159.4, 171.1. HRMS calcd for C$_{24}$H$_{27}$N$_2$O$_2$: 375.2067 [M+H$^+$], found: 375.2060.

10-Bromo-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one
White solid (103.8 mg, 82%), mp 157.8-159.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.33-1.39 (m, 1H), 1.54-1.75 (m, 7H), 2.66 (td, $J_1 = 13.6$ Hz, $J_2 = 4.8$ Hz, 2H), 2.79 (t, $J = 7.2$ Hz, 2H), 4.01 (t, $J = 7.2$ Hz, 2H), 6.62 (s, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 7.17-7.19 (m, 2H), 7.22 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H), 7.31-7.34 (m, 3H), 7.40 (d, $J = 1.6$ Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 23.6, 24.8, 33.5, 34.1, 48.6, 64.8, 120.6, 121.4, 127.8, 128.0, 128.3, 129.0, 132.8, 132.9, 136.1, 137.6, 143.7, 150.7, 171.3. HRMS calcd for C$_{23}$H$_{24}$BrN$_2$O: 423.1067 [M+H]$^+$, found: 423.1062.

**2-Methyl-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one (7i)**

White solid (79.5 mg, 74%), mp 141.3-143.0 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.24 (d, $J = 6.8$ Hz, 3H), 1.32-1.82 (m, 7H), 1.97 (d, $J = 12.8$ Hz, 1H), 2.51 (td, $J_1 = 13.2$ Hz, $J_2 = 4.8$ Hz, 1H), 2.82 (td, $J_1 = 13.2$ Hz, $J_2 = 4.4$ Hz, 1H), 3.14-3.23 (m, 1H), 3.50 (t, $J = 12.8$ Hz, 1H), 4.27-4.32 (m, 1H), 6.61 (s, 1H), 7.02-7.10 (m, 2H), 7.20-7.22 (m, 2H), 7.25-7.33 (m, 5H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 13.8, 23.4, 23.8, 24.9, 33.2, 34.7, 37.4, 56.3, 64.5, 117.4, 124.7, 127.5, 128.1, 128.2, 129.1, 131.6, 133.9, 135.5, 138.5, 144.2, 149.5, 173.8. HRMS calcd for C$_{24}$H$_{27}$N$_2$O: 359.2118 [M+H]$^+$, found: 359.2118.

**2,2-Dimethyl-7-phenyl-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one (7j)**

White solid (89.3 mg, 80%), mp 139.8-141.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.27 (s, 6H), 1.41-1.47 (m, 1H), 1.54-1.72 (m, 7H), 2.65-2.71 (m, 2H), 3.92 (s, 2H), 6.43 (s, 1H), 6.89-6.97 (m, 2H), 7.17-7.19 (m, 2H), 7.21-7.22
(m, 2H), 7.28-7.33 (m, 3H). \(^{13}\)C\(^{1}\){\(^{1}\)}H\ NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.1, 24.5, 25.2, 33.8, 42.8, 62.2, 63.3, 118.5, 122.7, 127.3, 127.9, 128.2, 129.0, 131.0, 132.4, 136.6, 139.6, 144.5, 150.5, 176.1. HRMS caled for C\(_{25}\)H\(_{29}\)N\(_2\)O: 373.2274 [M+H]^+, found: 373.2269.

**7-(4-Ethylphenyl)-1,2-dihydro-3\(\text{H}\)-spiro[benzo]\(_c\)[pyrazolo][1,2-\(a\)][1,2]diazepine-5,1'-cyclohexan]-3-one (7k)**

White solid (99.4 mg, 89%), mp 133.6-134.9 \(^{\circ}\)C. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.25 (t, \(J\) = 7.6 Hz, 3H), 1.32-1.37 (m, 1H), 1.58-1.72 (m, 7H), 2.62-2.69 (m, 4H), 2.80 (t, \(J\) = 7.2 Hz, 2H), 4.04 (t, \(J\) = 7.6 Hz, 2H), 6.60 (s, 1H), 7.06-7.16 (m, 6H), 7.27-7.29 (m, 2H). \(^{13}\)C\(^{1}\){\(^{1}\)}H\ NMR (100 MHz, CDCl\(_3\)) \(\delta\) 15.6, 23.6, 24.8, 28.6, 33.8, 33.9, 48.4, 64.3, 117.2, 124.8, 127.7, 128.2, 129.0, 131.6, 134.2, 134.9, 138.5, 141.4, 143.7, 149.4, 171.1. HRMS caled for C\(_{25}\)H\(_{29}\)N\(_2\)O: 373.2274 [M+H]^+, found: 373.2271.

**7-(4-Methoxyphenyl)-1,2-dihydro-3\(\text{H}\)-spiro[benzo]\(_c\)[pyrazolo][1,2-\(a\)][1,2]diazepine-5,1'-cyclohexan]-3-one (7l)**

Yellow syrup (86.6 mg, 77%). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.32-1.38 (m, 1H), 1.54-1.73 (m, 7H), 2.62-2.68 (m, 2H), 2.80 (t, \(J\) = 7.6 Hz, 2H), 3.81 (s, 3H), 4.03 (t, \(J\) = 7.6 Hz, 2H), 6.57 (s, 1H), 6.83-6.87 (m, 2H), 7.06-7.11 (m, 2H), 7.12-7.16 (m, 2H), 7.26-7.28 (m, 2H). \(^{13}\)C\(^{1}\){\(^{1}\)}H\ NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.7, 24.8, 33.8, 33.9, 48.3, 55.3, 64.2, 113.6, 117.2, 124.9, 128.3, 130.1, 131.5, 134.2, 134.3, 136.5, 138.3, 149.4, 159.3, 171.0. HRMS caled for C\(_{24}\)H\(_{27}\)N\(_2\)O\(_2\): 375.2067 [M+H]^+, found: 375.2059.
7-(4-(Trifluoromethyl)phenyl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one (7m)

Yellow solid (101.4 mg, 82%), mp 178.4-179.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.31-1.41 (m, 1H), 1.53-1.64 (m, 2H), 1.69-1.76 (m, 5H), 2.68 (td, $J_1 = 13.2$ Hz, $J_2 = 4.4$ Hz, 2H), 2.81 (t, $J = 7.2$ Hz, 2H), 4.05 (t, $J = 7.2$ Hz, 2H), 6.64 (s, 1H), 6.97-6.99 (m, 1H), 7.09-7.13 (m, 1H), 7.29-7.33 (m, 4H), 7.58 (d, $J = 8.0$ Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 23.6, 24.8, 33.7, 33.9, 48.5, 64.6, 117.3, 124.2 (q, $^1$J$_{C-F} = 270.2$ Hz), 125.0, 125.2 (q, $^3$J$_{C-F} = 3.6$ Hz), 128.6, 129.3, 129.6 (q, $^2$J$_{C-F} = 32.5$ Hz), 131.3, 133.2, 136.9, 137.4, 147.7, 149.5, 171.4. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.42 (s). HRMS calcd for C$_{24}$H$_{24}$F$_3$N$_2$O: 413.1835 [M+H]$^+$, found: 413.1833.

7-(m-Tolyl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one (7n)

Light yellow solid (92.4 mg, 86%), mp 163.0-164.7 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.33-1.38 (m, 1H), 1.55-1.74 (m, 7H), 2.33 (s, 3H), 2.62-2.70 (m, 2H), 2.80 (t, $J = 7.2$ Hz, 2H), 4.04 (t, $J = 7.6$ Hz, 2H), 6.59 (s, 1H), 6.99-7.05 (m, 3H), 7.08-7.12 (m, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 7.26-7.29 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 21.5, 23.6, 24.8, 33.8, 33.9, 48.4, 64.3, 117.2, 124.9, 126.2, 128.1, 128.2, 128.3, 129.7, 131.6, 134.1, 135.2, 137.8, 144.1, 149.4, 171.2. HRMS calcd for C$_{24}$H$_{27}$N$_2$O: 359.2118 [M+H]$^+$, found: 359.2114.

7-(3-Chlorophenyl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1'-cyclohexan]-3-one
7-(Thiophen-2-yl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1’-cyclohexan]-3-one (7p)

White solid (85.4 mg, 81%), mp 153.8-154.5 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.26-1.38 (m, 1H), 1.50-1.72 (m, 7H), 2.63 (td, \(J_1 = 12.4\) Hz, \(J_2 = 4.0\) Hz, 2H), 2.80 (t, \(J = 7.6\) Hz, 2H), 4.02 (t, \(J = 7.6\) Hz, 2H), 6.80 (dd, \(J_1 = 3.2\) Hz, \(J_2 = 0.8\) Hz, 1H), 6.97 (dd, \(J_1 = 5.2\) Hz, \(J_2 = 3.6\) Hz, 1H), 7.16-7.20 (m, 1H), 7.23 (dd, \(J_1 = 5.2\) Hz, \(J_2 = 1.2\) Hz, 1H), 7.27-7.29 (m, 1H), 7.31-7.35 (m, 1H), 7.41 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 1.6\) Hz, 1H). \(^{13}\)C{\(^1\)H} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.6, 24.7, 33.7, 33.8, 48.2, 64.0, 117.4, 125.0, 125.1, 126.6, 127.2, 128.8, 131.2, 132.1, 133.4, 134.8, 146.5, 149.1, 170.7. HRMS calcd for \(C_{21}H_{23}N_2OS\): 351.1526 [M+H]\(^+\), found: 351.1523.

7-(Pyridin-3-yl)-1,2-dihydro-3H-spiro[benzo[c]pyrazolo[1,2-a][1,2]diazepine-5,1’-cyclohexan]-3-one (7q)

White solid (86.9 mg, 84%), mp 138.2-139.1 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.34-1.41 (m, 1H), 1.54-1.65 (m, 2H), 1.73-1.76 (m, 5H), 2.68 (td, \(J_1 = 12.8\) Hz, \(J_2 = 4.0\) Hz, 2H), 2.81 (t, \(J = 7.6\) Hz, 2H), 4.06 (t, \(J = 7.6\) Hz, 2H), 6.65 (s, 1H), 7.00-7.01 (m, 1H), 7.10-7.14 (m, 1H), 7.23-7.28 (m, 1H), 7.31-7.33 (m, 2H), 7.47 (dt, \(J_1 = 8.0\) Hz, \(J_2 = 2.0\) Hz, 1H), 8.55-8.57 (m, 2H). \(^{13}\)C{\(^1\)H} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.6, 24.7, 33.7, 34.0, 48.6, 64.7, 117.3, 132.1, 133.4, 134.8, 146.5, 149.1, 170.7. HRMS calcd for \(C_{23}H_{24}ClN_2O\): 379.1572 [M+H]\(^+\), found: 379.1572.
123.1, 125.1, 128.7, 131.1, 133.0, 135.3, 136.3, 136.9, 139.7, 148.8, 149.5, 149.8, 171.5. HRMS calcd for 
C\textsubscript{22}H\textsubscript{24}N\textsubscript{3}O: 346.1914 [M+H]\textsuperscript{+}, found: 346.1908.

2. Structural elaborations of 3a

2.1. Synthesis of 8 from 3a

To a solution of 3a (60.8 mg, 0.2 mmol) in MeOH/DCM (2 mL, 10/3) was added Pd/C (10 wt%, 10 mg). The 
mixture was stirred at room temperature under H\textsubscript{2} (balloon, 1 atm) for 24 h. Upon completion, it was filtered 
through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel 
chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford 8 (58.2 mg, 95%).

![Chemical Structure of 8]

5,5-Dimethyl-7-phenyl-1,2,6,7-tetrahydro-3\textit{H},5\textit{H}-benzo[\textit{c}]pyrazolo[1,2-\textit{a}][1,2]diazepin-3-one (8)

White solid (58.2 mg, 95%), mp 101.1-102.4 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.53 (s, 3H), 1.65 (s, 3H), 1.78 
(dd, \(J_1 = 14.4\) Hz, \(J_2 = 4.4\) Hz, 1H), 2.42-2.49 (m, 1H), 2.83-2.95 (m, 2H), 3.78-3.86 (m, 1H), 4.12 (ddd, \(J_1 = 12.8\) Hz, 
\(J_2 = 7.2\) Hz, \(J_3 = 2.8\) Hz, 1H), 4.42 (ddd, \(J_1 = 12.4\) Hz, \(J_2 = 4.0\) Hz, 1H), 6.83 (d, \(J = 7.6\) Hz, 1H), 
6.89-6.92 (m, 1H), 7.07-7.11 (m, 2H), 7.14-7.21 (m, 3H), 7.27-7.30 (m, 2H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}) 
\(\delta\) 24.3, 27.2, 33.5, 46.9, 48.6, 48.7, 60.0, 116.4, 124.4, 126.3, 126.7, 128.3, 128.7, 132.6, 136.2, 147.7, 149.3, 
173.4. HRMS calcd for C\textsubscript{20}H\textsubscript{23}N\textsubscript{2}O: 307.1805 [M+H]\textsuperscript{+}, found: 307.1805.

2.2. Synthesis of 9 from 3a

To a solution of 3a (60.8 mg, 0.2mmol) in THF (5 mL) was added LiAlH\textsubscript{4} (0.4 mL, 1M) at 0 °C. It was then 
stirred at room temperature for 2 h. Upon completion, it was quenched with water, concentrated and extracted 
with EtOAc. The combined organic layers were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, and then concentrated under 
reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1)
as eluent to afford 9 (33.9 mg, 55%).

![Chemical structure](image)

3-(3,3-Dimethyl-5-phenyl-2,3-dihydro-1H-benzo[c][1,2]diazepin-1-yl)propan-1-ol (9)

Yellowish syrup (33.9 mg, 55%), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.35 (s, 6H), 1.95-2.01 (m, 2H), 3.61-3.64 (m, 4H), 3.80 (t, $J = 5.6$ Hz, 2H), 6.08 (s, 1H), 6.87 (td, $J_1 = 7.2$ Hz, $J_2 = 0.8$ Hz, 1H), 6.92 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 7.13-7.18 (m, 3H), 7.25-7.33 (m, 3H). $^{13}$C{$_1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 27.8, 30.2, 54.4, 61.5, 62.8, 115.4, 122.3, 126.8, 127.2, 128.0, 129.5, 130.5, 133.3, 136.2, 143.6, 146.0, 151.8. HRMS calcd for C$_{20}$H$_{25}$N$_2$O: 309.1961 [M+H]$^+$, found: 309.1962.

2.3. Gram-scale synthesis of 3a

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (1a, 814 mg, 5 mmol), toluene (20 mL), [RhCp*Cl$_2$]$_2$ (31 mg, 0.05 mmol), Zn(OAc)$_2$ (460 mg, 2.5 mmol), NaOAc (205 mg, 2.5 mmol) and 2-methyl-4-phenylbut-3-en-2-ol (2a, 801 mg, 5 mmol). The mixture was stirred at 100 °C (oil bath) for 10 h under air. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford 3a (1.16 g, 76%).
III. Mechanism studies

(1) H/D exchange experiments

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (1a, 32.4 mg, 0.2 mmol), toluene (2 mL), CD$_3$OD (0.08 mL, 2 mmol), [RhCp*Cl$_2$]$_2$ (3.1 mg, 0.005 mmol), Zn(OAc)$_2$ (18.3 mg, 0.1 mmol) and NaOAc (8.2 mg, 0.1 mmol). The mixture was stirred at 100 °C (oil bath) for 30 min under air. The resulting mixture was cooled to room temperature, concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to give 1a-$d_n$. Upon analyzing the $^1$H NMR spectrum of the product, the deuteration percentage was determined as 50%.

To a reaction tube equipped with a stir bar were charged with 1-phenylpyrazolidin-3-one (1a, 48.7 mg, 0.3 mmol), toluene (2 mL), CD$_3$OD (0.12 mL, 3 mmol), [RhCp*Cl$_2$]$_2$ (4.7 mg, 0.0075 mmol), Zn(OAc)$_2$ (27.5 mg, 0.15 mmol), NaOAc (12.3 mg, 0.15 mmol) and 1-(phenylethynyl)cyclopentan-1-ol (4a, 55.8 mg, 0.3 mmol). The mixture was stirred at 100 °C (oil bath) for 30 min under air. The resulting mixture was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified
by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to give 5a-d. Upon analyzing the ¹H NMR spectrum of the product, the deuteration percentage was determined as 20%.

(2) Competition experiment between 1c and 1g

To a reaction tube equipped with a stir bar were charged with 1-(4-methoxyphenyl)pyrazolidin-3-one (1c, 57.6 mg, 0.3 mmol), 1-(4-(trifluoromethyl)phenyl)pyrazolidin-3-one (1g, 69.0 mg, 0.3 mmol), 2-methyl-4-phenylbut-3-yn-2-ol (2a, 48.1 mg, 0.3 mmol), [Cp*RhCl₂]₂ (4.7 mg, 0.0075 mmol), Zn(OAc)₂ (27.5 mg, 0.15 mmol), NaOAc (12.3 mg, 0.15 mmol) and toluene (2 mL). The mixture was stirred at 100 °C (oil bath) for 4 h. The resulting mixture was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford 3c (12.0 mg, 12%) and 3g (81.4 mg, 73%).
IV. Copies of NMR spectra of 3a-3ee
The image contains a chemical structure labeled as 3g. The structure includes a fluorine atom (F) and a phenyl group (Ph). The diagram also shows a spectrum with a peak at -62.223 ppm.
3i

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6.00

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3i

F
Ph

F
Ph

3i
V. Copies of NMR spectra of 5a-5m
5c
V. Copies of NMR spectra of 7a-7q
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$7f$
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**Diagram:**

1. **Compound 7g**
   - Structure of compound 7g with specific chemical shifts indicated.

2. **Additional Compound:**
   - Similar structure to 7g with chemical shifts highlighted.

**Note:**
- The images show the proton nuclear magnetic resonance (1H NMR) spectra of the compounds 7g.
VII. Copies of NMR spectra of 8 and 9
VIII. X-ray crystal structure and data of 3a

Fig. S1 X-ray structure of 3a with 50% ellipsoid probability

**X-ray structure determination.** Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (3:1) solution of 3a. Crystal data collection and refinement parameters of 3a are summarized in Table S1. Intensity data were collected at 299 K on a SuperNova Dualdiffractometer using mirror-monochromated CuKα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.
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IX. X-ray crystal structure and data of 5a

Fig. S2 X-ray structure of 5a with 50% ellipsoid probability

**X-ray structure determination.** Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (1:3) solution of 5a. Crystal data collection and refinement parameters of 5a are summarized in Table S2. Intensity data were collected at 283 K on a SuperNova Dual diffractometer using mirror-monochromated MoKα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.
Table S2 Crystallographic data and structure refinement results of 5a

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{22}H_{22}N_{2}O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>330.41</td>
</tr>
<tr>
<td>Temp, K</td>
<td>283 (2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>(a), Å</td>
<td>7.6394(5)</td>
</tr>
<tr>
<td>(b), Å</td>
<td>22.9296(11)</td>
</tr>
<tr>
<td>(c), Å</td>
<td>10.4410(6)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>104.958(6)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>90</td>
</tr>
<tr>
<td>Volume, Å³</td>
<td>1766.96(18)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>(d_{calc}), g cm(^{-3})</td>
<td>1.242</td>
</tr>
<tr>
<td>(\lambda), Å</td>
<td>0.71073</td>
</tr>
<tr>
<td>(\mu), mm(^{-1})</td>
<td>0.077</td>
</tr>
<tr>
<td>No. of data collected</td>
<td>13029</td>
</tr>
<tr>
<td>No. of unique data</td>
<td>4177</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.0397</td>
</tr>
<tr>
<td>Goodness-of-fit on (R^2)</td>
<td>1.045</td>
</tr>
<tr>
<td>(R_1, wR_2) ((I &gt; 2\sigma(I)))</td>
<td>0.0581, 0.1318</td>
</tr>
<tr>
<td>(R_1, wR_2) (all data)</td>
<td>0.0815, 0.1467</td>
</tr>
</tbody>
</table>
X. References


