

**[4+2] Cycloaddition of *in situ* Generated
1,2-Diaza-1,3-dienes with Simple Olefins: Facile
Approaches to Tetrahydropyridazines**

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Supporting Information

Table of Contents

1. General Information and Materials.....	S1
2. Experimental Section.....	S1
4. Characterization.....	S3
5. References.....	S12
6. NMR Spectrum.....	S13

General Information: Commercial reagents were used as received, unless otherwise indicated. ^1H and ^{13}C , NMR spectra were measured on a NMR instrument (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard for ^1H NMR, and CDCl_3 served as the internal standard for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. HRMS was recorded on a commercial apparatus (ESI Source).

Materials: α -chloro- or α -bromo N-benzoyl hydrazones (**a1-a8**, **a10-a13**) and α -chloro N-benzenesulfonyl hydrazone (**a9**) were prepared according to literature procedures.¹ Simple olefins (**b1-b10**, **b12-b17**) were received from commercial sources without further purification, except for 2-vinylthiophene (**b11**), which was prepared according to the literature procedure.² Solvents were freshly dried according to *the purification handbook Purification of Laboratory Chemicals* before using.

Experimental Section

General Procedure I: [4+2] Cycloaddition of Hydrazones with Ethylene **b1**:

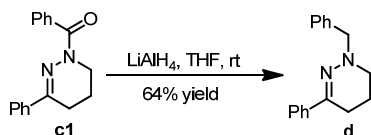
In a 300 ml stainless steel reactor with a magnetic stirring bar was charged with K_2CO_3 (2.0 equiv, 110.4 mg, 0.8 mmol), hydrazone **a1** (1.0 equiv, 109.0 mg, 0.4 mmol) and solvent CH_2Cl_2 (2 mL) under 16 atm ethylene **b1** atmosphere and the mixture was stirred at room temperature for 24 h. After carefully releasing the ethylene, the mixture was directly loaded on a silica column with EtOAc/PE as eluent to give **c1** (76.8 mg, 73%) as white solid.

General Procedure II: [4+2] Cycloaddition of Hydrazones with Other Olefins:

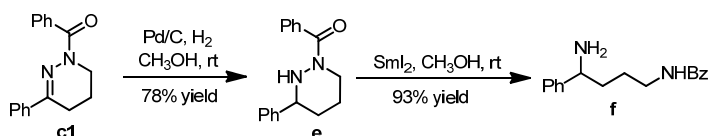
K_2CO_3 (2.0 equiv, 110.4 mg, 0.8 mmol) was added to a solution of hydrazone **a1** (1.0 equiv, 109.0 mg, 0.4 mmol) in dry dichloromethane (2.0 ml). To the stirring reaction mixture styrene **b4** (3.0 equiv, 125.0 mg, 1.2 mmol) was added and the mixture was stirring for 20 h at room temperature. Then the crude reaction mixture was directly

loaded on a silica column with EtOAc/PE as eluent to give **c14** (124.8 mg, 92%) as a white solid.

Transformation of Product **c1**

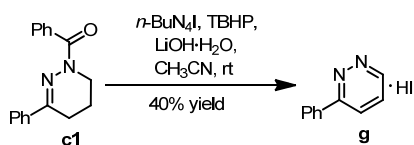


1-Benzyl-3-phenyl-1,4,5,6-tetrahydropyridazine **d**: To LiAlH_4 (4.0 equiv, 45.6 mg, 1.2 mmol) solution in THF (2 mL) was added N-benzoyl hydrazone **c1** (1.0 equiv, 79.2 mg, 0.3 mmol) at room temperature. After refluxing for 12 h, the reaction mixture was quenched by cold water, then extracted with EtOAc (2×20 mL). The combined organic layers were dried (Na_2SO_4), evaporated under reduced pressure and gave a colorless oil, which was purified by flash chromatography on silica gel to afford the desired product **d** (48.2 mg, 64%) as a colorless oil.



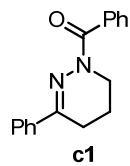
Phenyl(3-phenyltetrahydropyridazin-1(2H)-yl)methanone **e**: Degassed methanol (5.0 ml) was added to the mixture of Pd/C (10 wt %) and **c1** (1.0 equiv, 0.3 mmol, 79.2 mg). After stirring under 1 atm pressure of hydrogen overnight at room temperature, the reaction mixture was filtered, and then evaporated under reduced pressure. The crude product was purified by flash column chromatography to give hydrogenated product **e** (62.3 mg, 78%) as a colorless oil.

N-(4-amino-4-phenylbutyl)benzamide **f**: Samarium(II) iodide (0.1 M in THF, 5.0 equiv, 1.0 mmol, 10 ml) was added to the stirring solution of **e** (1.0 equiv, 0.2 mmol, 53.2 mg) in degassed dry methanol (2.0 ml) at 0°C . Then the resulting reaction mixture was stirred at room temperature for 24 h. Methanol was removed under vacuo. The crude product was purified by flash column chromatography to give the desired 1,4-diamine product **f** (49.7 mg, 93%) as a colorless oil.

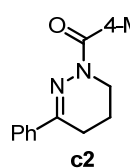


3-phenylpyridazine hydroiodide **g**: A mixture of **c1** (1.0 equiv, 52.8 mg, 0.2 mmol), TBHP (65 % in H_2O , 6.0 equiv, 1.2 mmol), TBAI (0.5 equiv, 36.9 mg, 0.1 mmol), $\text{LiOH}\cdot\text{H}_2\text{O}$ (1.0 equiv, 8.4 mg, 0.2 mmol) in acetonitrile (2 mL) was stirred at room temperature under air for 72 h. TBHP was added by three times every 24 hours (each for 2.0 equiv, 0.4 mmol). The reaction mixture was quenched with saturated sodium thiosulfate solution, then extracted with EtOAc, dried over anhydrous Na_2SO_4 , and evaporated. The residue was purified by flash column chromatography to give the pyridazine **g** (22.5 mg, 40%) as a white solid.

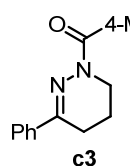
Characterization



White solid, Yield: 73%; M.P. = 83-85 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, J = 6.5 Hz, 2H), 7.58-7.57 (m, 2H), 7.48-7.40 (m, 3H), 7.31-7.31 (m, 3H), 4.00 (t, J = 5.6 Hz, 2H), 2.69 (t, J = 6.4 Hz, 2H), 2.14-2.08 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 146.9, 137.3, 135.3, 130.3, 130.1, 129.2, 128.5, 127.4, 125.4, 39.6, 22.8, 17.8 ppm; IR (KBr, cm^{-1}): 3057, 2935, 2869, 2362, 1650, 1405, 1347, 1270, 1144, 761, 692; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 287.1155, found 287.1152.

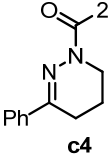


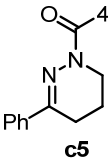
White solid, Yield: 72%; M.P. = 118-120 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, J = 8.9 Hz, 2H), 7.63 (dd, J = 3.0, 6.6 Hz, 2H), 7.33-7.32 (m, 3H), 6.93 (d, J = 8.9 Hz, 2H), 3.98 (t, J = 5.8 Hz, 2H), 3.87 (s, 3H), 2.69 (t, J = 6.5 Hz, 2H), 2.14-2.08 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.0, 161.4, 146.6, 137.5, 132.5, 129.2, 128.5, 127.3, 125.4, 112.7, 55.4, 39.7, 22.9, 17.9 ppm; IR (KBr, cm^{-1}): 3059, 2934, 2870, 2839, 1643, 1604, 1399, 1254, 1174, 759, 694; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 317.1261, found 317.1256.

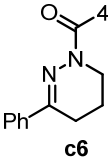


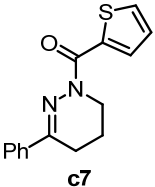
White solid, Yield: 78%; M.P. = 89-91 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, J = 8.1 Hz, 2H), 7.60 (dd, J = 3.0, 6.6 Hz, 2H), 7.32-7.31 (m, 3H), 7.23 (d, J = 7.6 Hz, 2H), 3.98 (t, J = 5.8 Hz, 2H), 2.68 (t, J = 6.5 Hz, 2H), 2.42 (s, 3H), 2.13-2.07 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.5, 146.7, 140.5, 137.4,

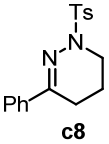
132.2, 130.4, 129.1, 128.5, 128.1, 125.4, 39.6, 22.9, 21.6, 17.9 ppm; IR (KBr, cm^{-1}): 3059, 2925, 2869, 1647, 1409, 1271, 1009, 829, 744, 693; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 301.1311, found 301.1310.

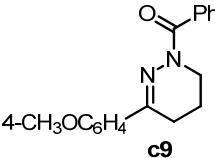
 **c4** White solid, Yield: 79%; M.P. = 79-81 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.22 (m, 9H), 4.02 (t, J = 5.8 Hz, 2H), 2.67 (t, J = 6.5 Hz, 2H), 2.11-2.05 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 169.1, 147.9, 137.1, 137.1, 131.2, 129.9, 129.3, 129.0, 128.5, 128.4, 126.5, 125.3, 39.2, 22.9, 17.5 ppm; IR (KBr, cm^{-1}): 3060, 2928, 2870, 1663, 1412, 1147, 1008, 746, 693; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{ON}_2\text{ClNa}^+$ ($\text{M}+\text{Na}$) $^+$ 321.0765, found 321.0762.

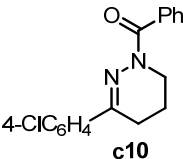
 **c5** White solid, Yield: 58%; M.P. = 126-128 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.73 (d, J = 8.5 Hz, 2H), 7.59-7.56 (m, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.34-7.33 (m, 3H), 3.99 (t, J = 5.8 Hz, 2H), 2.70 (t, J = 6.5 Hz, 2H), 2.15-2.09 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 169.5, 147.5, 137.2, 136.4, 133.7, 131.7, 129.5, 128.6, 127.7, 125.4, 39.7, 22.9, 17.8 ppm; IR (KBr, cm^{-1}): 3060, 2955, 2927, 2870, 1648, 1606, 1592, 1411, 1271, 1008, 838, 749, 692; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{ON}_2\text{ClNa}^+$ ($\text{M}+\text{Na}$) $^+$ 321.0765, found 321.0760.

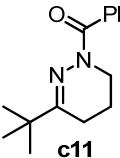
 **c6** White solid, Yield: 40%; M.P. = 134-136 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, J = 8.5 Hz, 2H), 7.59-7.55 (m, 4H), 7.35-7.33 (m, 3H), 3.99 (t, J = 5.8 Hz, 2H), 2.70 (t, J = 6.5 Hz, 2H), 2.15-2.09 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 169.5, 147.5, 137.1, 134.1, 131.9, 130.7, 129.5, 128.6, 125.4, 124.9, 39.7, 22.9, 17.8 ppm; IR (KBr, cm^{-1}): 3058, 2954, 2926, 2869, 1649, 1590, 1409, 1347, 1271, 1007, 745, 691; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{ON}_2\text{BrNa}^+$ ($\text{M}+\text{Na}$) $^+$ 365.0260, found 365.0253.

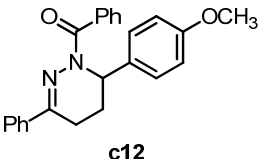
 **c7** Pale yellow solid, Yield: 51%; M.P. = 102-103 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.17-8.16 (m, 1H), 7.88 (d, J = 6.7 Hz, 2H), 7.60 (d, J = 5.0 Hz, 1H), 7.46-7.39 (m, 3H), 7.10 (d, J = 4.4 Hz, 1H), 4.00 (t, J = 5.8 Hz, 2H), 2.72 (t, J = 6.5 Hz, 2H), 2.10-2.04 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 162.1, 149.1, 137.4, 135.7, 134.3, 133.2, 129.5, 128.6, 126.6, 126.2, 39.6, 23.8, 17.8 ppm; IR (KBr, cm^{-1}): 3071, 2954, 2926, 2870, 1630, 1420, 1408, 1270, 1161, 1041, 731, 693; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{ON}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 293.0719, found 293.0716.


c8
 White solid, Yield: 48%; M.P. = 144-146 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.70-7.68 (m, 2H), 7.35-7.34 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.39 (t, *J* = 5.6 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 2.16-2.10 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 150.2, 144.1, 136.9, 133.0, 129.6, 129.5, 128.6, 128.4, 125.5, 42.9, 22.4, 21.7, 19.2 ppm; IR (KBr, cm⁻¹): 3063, 2925, 2854, 1597, 1494, 1447, 1356, 1171, 760, 668, 563, 552; HRMS (ESI) calcd for C₁₇H₁₈O₂N₂Na⁺ (M+Na)⁺ 337.0981, found 337.0976.

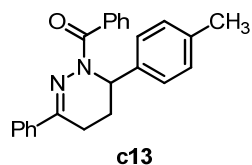

c9
 Colorless oil, Yield: 56%; ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.46-7.40 (m, 3H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.99 (t, *J* = 5.8 Hz, 2H), 3.80 (s, 3H), 2.67 (t, *J* = 6.5 Hz, 2H), 2.14-2.08 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 170.5, 160.6, 146.8, 135.5, 130.2, 130.1, 127.4, 126.8, 113.9, 55.4, 39.5, 22.8, 18.0 ppm; IR (KBr, cm⁻¹): 2935, 2837, 1647, 1609, 1511, 1402, 1254, 1176, 1034, 748, 711; HRMS (ESI) calcd for C₁₈H₁₈O₂N₂Na⁺ (M+Na)⁺ 317.1261, found 317.1256.


c10
 White solid, Yield: 93%; M.P. = 111-113 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.73-7.71 (m, 2H), 7.50-7.40 (m, 5H), 7.26 (d, *J* = 8.6 Hz, 2H), 3.99 (t, *J* = 5.8 Hz, 2H), 2.65 (d, *J* = 6.5 Hz, 2H), 2.15-2.08 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 170.7, 145.7, 135.8, 135.2, 135.2, 130.3, 130.0, 128.7, 127.5, 126.6, 39.5, 22.7, 17.7 ppm; IR (KBr, cm⁻¹): 3058, 2926, 1650, 1602, 1409, 1395, 1270, 1008, 829, 704, 650; HRMS (ESI) calcd for C₁₇H₁₅ON₂ClNa⁺ (M+Na)⁺ 321.0765, found 321.0761.

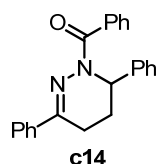

c11
 Colorless oil, Yield: 97%; ¹H NMR (400 MHz, CDCl₃): δ 7.69-7.67 (m, 2H), 7.37-7.32 (m, 3H), 3.86 (t, *J* = 6.0 Hz, 2H), 2.22 (t, *J* = 6.4 Hz, 2H), 1.94-1.87 (m, 2H), 1.01 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 170.2, 158.3, 135.6, 129.8, 129.7, 127.0, 39.5, 38.5, 27.7, 21.0, 17.9 ppm; IR (KBr, cm⁻¹): 3058, 2965, 2869, 1648, 1620, 1411, 1271, 1152, 961, 712, 694; HRMS (ESI) calcd for C₁₅H₂₀ON₂Na⁺ (M+Na)⁺ 267.1468, found 267.1464.


c12
 White solid, Yield: 99%; M.P. = 169-170 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.83-7.81 (m, 2H), 7.59-7.57 (m, 2H), 7.48-7.43 (m, 3H), 7.31-7.30 (m, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.85-6.83 (m, 2H), 6.03 (s, 1H), 3.76 (s, 3H), 2.69-2.65 (m, 1H), 2.36-2.18 (m, 3H), ppm; ¹³C NMR (100 MHz, CDCl₃): δ

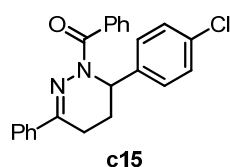
170.3, 158.9, 147.0, 137.3, 135.5, 132.0, 130.3, 130.1, 129.3, 128.5, 127.5, 126.7, 125.5, 114.3, 55.4, 51.3, 24.2, 18.8 ppm; IR (KBr, cm^{-1}): 3059, 2927, 2836, 1654, 1511, 1396, 1348, 1248, 1178, 1145, 693; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 393.1574, found 393.1568.



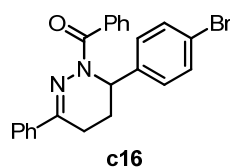
White solid, Yield: 99%; M.P. = 181-183 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.83-7.81 (m, 2H), 7.59-7.57 (m, 2H), 7.50-7.42 (m, 3H), 7.31-7.29 (m, 3H), 7.09 (dd, J = 8.1, 19.7 Hz, 4H), 6.04 (s, 1H), 2.69-2.63 (m, 1H), 2.39-2.17 (m, 6H), ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.3, 146.9, 137.3, 137.0, 136.9, 135.5, 130.3, 130.1, 129.6, 129.2, 128.5, 127.5, 125.5, 51.6, 24.1, 21.1, 18.8 ppm; IR (KBr, cm^{-1}): 3054, 2924, 2359, 1655, 1395, 1336, 1268, 1145, 757. 692; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 377.1624, found 377.1617.



White solid, Yield: 92%; M.P. = 147-149 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.83 (dd, J = 1.5, 7.8 Hz, 2H), 7.59-7.57 (m, 2H), 7.50-7.42 (m, 3H), 7.33-7.22 (m, 6H), 7.18 (d, J = 7.4 Hz, 2H), 6.09 (s, 1H), 2.70-2.65 (m, 1H), 2.42-2.15 (m, 3H), ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.3, 147.0, 140.0, 137.3, 135.4, 130.3, 130.1, 129.3, 128.9, 128.5, 127.5, 127.3, 125.6, 125.5, 51.8, 24.1, 18.8 ppm; IR (KBr, cm^{-1}): 2917, 2849, 2362, 1654, 1395, 1339, 1145, 956, 692; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{20}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 363.1468, found 363.1462.

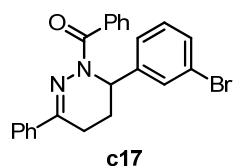


White solid, Yield: 86%; M.P. = 207-209 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, J = 6.6 Hz, 2H), 7.59-7.56 (m, 2H), 7.49-7.43 (m, 3H), 7.31-7.26 (m, 5H), 7.11 (d, J = 8.4 Hz, 2H), 6.03 (s, 1H), 2.71-2.66 (m, 1H), 2.37-2.12 (m, 3H), ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.3, 147.0, 138.6, 137.0, 135.1, 133.2, 130.5, 130.2, 129.4, 129.1, 128.6, 127.5, 127.0, 125.5, 51.3, 24.0, 18.7 ppm; IR (KBr, cm^{-1}): 3058, 2929, 1655, 1491, 1394, 1335, 1268, 1146, 1008, 693; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{ON}_2\text{ClNa}^+$ ($\text{M}+\text{Na}$) $^+$ 397.1078, found 397.1071.

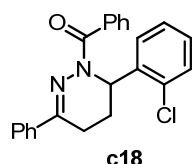


White solid, Yield: 79%; M.P. = 209-211 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, J = 6.6 Hz, 2H), 7.58-7.56 (m, 2H), 7.50-7.40 (m, 5H), 7.30-7.28 (m, 3H), 7.04 (d, J = 8.3 Hz, 2H), 6.00 (s, 1H), 2.69-2.64 (m, 1H), 2.33-2.10 (m, 3H), ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.2, 147.0, 139.1, 136.9, 135.0, 131.9, 130.5, 130.1, 129.4, 128.5, 127.5, 127.4, 125.4, 121.2, 51.3, 23.8, 18.6 ppm; IR (KBr, cm^{-1}): 3058,

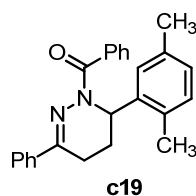
2926, 1655, 1393, 1333, 1268, 1145, 1007, 692; HRMS (ESI) calcd for $C_{23}H_{19}ON_2BrNa^+$ (M+Na)⁺ 441.0573, found 441.0567.



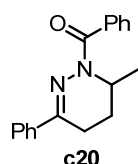
White solid, Yield: 79%; M.P. = 138-140 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, *J* = 6.6 Hz, 2H), 7.59-7.56 (m, 2H), 7.51-7.42 (m, 3H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.31-7.29 (m, 3H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.01 (s, 1H), 2.70-2.66 (m, 1H), 2.37-2.12 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 170.2, 147.1, 142.4, 137.0, 135.0, 130.5, 130.5, 130.4, 130.1, 129.4, 128.8, 128.5, 127.5, 125.5, 124.2, 123.1, 51.3, 23.8, 18.6 ppm; IR (KBr, cm⁻¹): 3058, 2926, 2854, 1655, 1394, 1335, 1269, 1146, 756, 692; HRMS (ESI) calcd for $C_{23}H_{19}ON_2BrNa^+$ (M+Na)⁺ 441.0573, found 441.0569.



White solid, Yield: 62%; M.P. = 159-161 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 6.8 Hz, 2H), 7.62-7.60 (m, 2H), 7.48-7.39 (m, 4H), 7.33-7.31 (m, 3H), 7.22-7.09 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.30 (s, 1H), 2.75-2.50 (m, 2H), 2.26-2.12 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 170.0, 146.6, 137.7, 137.1, 135.2, 132.0, 130.4, 130.4, 130.1, 129.4, 128.8, 128.6, 127.5, 127.1, 126.8, 125.5, 50.3, 21.3, 18.7 ppm; IR (KBr, cm⁻¹): 3059, 2926, 2359, 1656, 1394, 1336, 1267, 1147, 754, 693; HRMS (ESI) calcd for $C_{23}H_{19}ON_2ClNa^+$ (M+Na)⁺ 397.1078, found 397.1072.

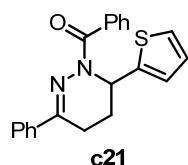


White solid, Yield: 92%; M.P. = 174-176 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.81-7.99 (m, 2H), 7.64-7.61 (m, 2H), 7.45-7.40 (m, 3H), 7.32-7.31 (m, 3H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 6.10 (s, 1H), 2.71-2.67 (m, 1H), 2.45 (s, 3H), 2.33-2.16 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 169.9, 146.3, 138.8, 137.3, 135.6, 135.5, 131.1, 131.1, 130.2, 130.1, 130.0, 129.2, 128.5, 128.1, 127.4, 125.5, 49.7, 21.8, 21.4, 18.7, 18.4 ppm; IR (KBr, cm⁻¹): 3058, 2924, 1655, 1396, 1338, 1271, 1148, 753, 692; HRMS (ESI) calcd for $C_{25}H_{24}ON_2Na^+$ (M+Na)⁺ 391.1781, found 391.1773.

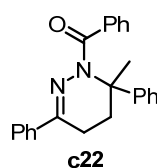


White solid, Yield: 62%; M.P. = 97-98 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 7.3 Hz, 2H), 7.60-7.58 (m, 2H), 7.46-7.40 (m, 3H), 7.32-7.30 (m, 3H), 5.05-5.03 (br, 1H), 2.78-2.62 (m, 2H), 2.07-2.04 (m, 2H), 1.32 (d, *J* = 6.7 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 170.2, 146.1, 137.4, 135.7, 130.2, 130.0, 129.2, 128.5, 127.4, 125.3, 43.6, 23.1, 18.8, 16.8 ppm; IR (KBr, cm⁻¹): 3058, 2928, 2851, 2359, 2340, 1651, 1606, 1398, 1340,

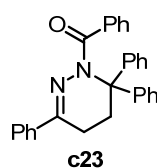
692; HRMS (ESI) calcd for $C_{18}H_{18}ON_2Na^+$ ($M+Na$) $^+$ 301.1311, found 301.1308.



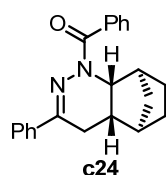
White solid, Yield: 91%; M.P. = 140-142 °C; 1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 7.4 Hz, 2H), 7.58-7.56 (m, 2H), 7.48-7.42 (m, 3H), 7.30-7.29 (m, 3H), 7.17 (d, J = 4.8 Hz, 1H), 6.91-6.88 (m, 2H), 6.32 (s, 1H), 2.77-2.72 (m, 1H), 2.54-2.46 (m, 2H), 2.32-2.24 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 146.9, 143.0, 137.0, 135.1, 130.4, 130.0, 129.3, 128.4, 127.5, 127.0, 125.4, 124.5, 124.4, 47.7, 24.2, 19.1 ppm; IR (KBr, cm^{-1}): 3058, 2933, 1655, 1608, 1395, 1351, 1328, 1146, 758, 692; HRMS (ESI) calcd for $C_{21}H_{18}ON_2SNa^+$ ($M+Na$) $^+$ 369.1032, found 369.1026.



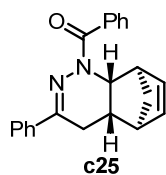
White solid, Yield: 87%; M.P. = 125-127 °C; 1H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 1.5, 8.0 Hz, 2H), 7.51-7.40 (m, 5H), 7.34-7.21 (m, 8H), 2.66-2.59 (m, 1H), 2.32-2.14 (m, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 145.0, 144.6, 137.3, 137.0, 130.3, 130.0, 129.0, 128.7, 128.5, 127.5, 126.8, 125.3, 124.7, 59.9, 36.1, 25.9, 20.3 ppm; IR (KBr, cm^{-1}): 3058, 2930, 1665, 1494, 1446, 1381, 1341, 1275, 1130, 1065, 694; HRMS (ESI) calcd for $C_{24}H_{22}ON_2Na^+$ ($M+Na$) $^+$ 377.1624, found 377.1618.



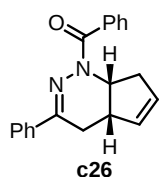
White solid, Yield: 50%; M.P. = 198-200 °C; 1H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (m, 2H), 7.47-7.33 (m, 12H), 7.29-7.23 (m, 6H), 2.76 (t, J = 6.3 Hz, 2H), 2.34 (t, J = 6.3 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 145.2, 141.3, 137.2, 136.5, 130.6, 130.3, 129.1, 128.5, 128.4, 127.5, 127.3, 125.3, 67.5, 35.4, 21.3 ppm; IR (KBr, cm^{-1}): 3057, 2925, 2361, 1671, 1379, 1339, 1272, 751, 694; HRMS (ESI) calcd for $C_{29}H_{24}ON_2Na^+$ ($M+Na$) $^+$ 439.1781, found 439.1774.



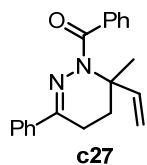
White solid, Yield: 94%; M.P. = 129-131 °C; 1H NMR (400 MHz, $CDCl_3$): δ 7.69-7.67 (m, 2H), 7.58-7.56 (m, 2H), 7.38-7.30 (m, 6H), 4.24 (d, J = 9.1 Hz, 1H), 2.74 (s, 1H), 2.61-2.57 (m, 2H), 2.46-2.45 (m, 1H), 2.12 (s, 1H), 1.55-1.44 (m, 4H), 1.32-1.31 (m, 1H), 1.05 (d, J = 10.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 151.7, 136.9, 136.1, 130.1, 129.9, 129.4, 128.5, 127.3, 125.5, 56.3, 45.1, 44.4, 40.1, 34.4, 29.1, 26.7, 25.1 ppm; IR (KBr, cm^{-1}): 2955, 2361, 1652, 1395, 1355, 691, 631; HRMS (ESI) calcd for $C_{22}H_{22}ON_2Na^+$ ($M+Na$) $^+$ 353.1624, found 353.1620.



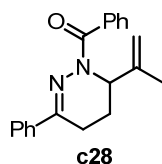
White solid, Yield: 80%; M.P. = 107-109 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.71-7.69 (m, 2H), 7.59-7.56 (m, 2H), 7.44-7.38 (m, 3H), 7.32-7.31 (m, 3H), 6.35-6.32 (m, 2H), 4.16 (dd, J = 1.1, 9.0 Hz, 1H), 3.35 (br, 1H), 2.92-2.86 (m, 1H), 2.74 (br, 1H), 2.60-2.55 (m, 1H), 2.43-2.39 (m, 1H), 1.57-1.44 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 150.2, 138.9, 137.0, 136.9, 136.2, 130.2, 129.9, 129.4, 128.5, 127.4, 125.5, 52.3, 50.6, 49.7, 43.9, 34.2, 26.5 ppm; IR (KBr, cm^{-1}): 3058, 2963, 1652, 1394, 1353, 1322, 1180, 720, 691; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{20}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 351.1468, found 351.1463.



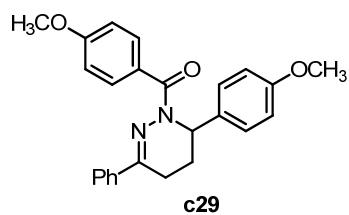
White solid, Yield: 96%; M.P. = 99-101 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, J = 6.8 Hz, 2H), 7.60-7.57 (m, 2H), 7.47-7.38 (m, 3H), 7.32-7.30 (m, 3H), 6.09-6.08 (m, 1H), 5.94-5.92 (m, 1H), 5.44-5.43 (m, 1H), 2.79-2.70 (m, 3H), 2.32-2.24 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 171.4, 149.4, 137.0, 135.8, 132.8, 131.5, 130.3, 130.0, 129.3, 128.5, 127.4, 125.6, 59.5, 39.0, 31.5, 25.8 ppm; IR (KBr, cm^{-1}): 2920, 2362, 1651, 1393, 1328, 1273, 1158, 1011, 692; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 325.1311, found 325.1308.



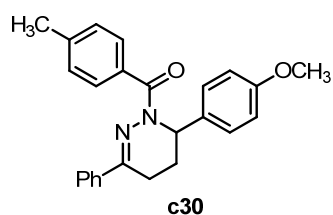
Colorless oil, Yield: 51%; ^1H NMR (400 MHz, CDCl_3): δ 7.73-7.71 (m, 2H), 7.49-7.37 (m, 5H), 7.27-7.24 (m, 3H), 6.03 (dd, J = 10.7, 17.3 Hz, 1H), 5.16 (d, J = 10.7 Hz, 1H), 5.08 (d, J = 17.3 Hz, 1H), 2.63-2.57 (m, 2H), 2.05-1.93 (m, 2H), 1.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 144.6, 141.4, 137.3, 137.1, 130.1, 129.8, 129.0, 128.4, 127.4, 125.3, 112.5, 58.0, 32.6, 23.8, 20.0 ppm; IR (KBr, cm^{-1}): 3059, 3025, 2968, 2933, 1666, 1382, 1341, 1275, 757, 693; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 327.1468, found 327.1463.



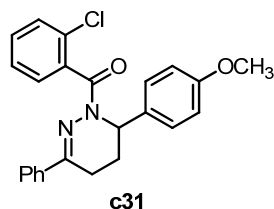
Colorless oil, Yield: 32%; ^1H NMR (400 MHz, CDCl_3): δ 7.78-7.76 (m, 2H), 7.59-7.56 (m, 2H), 7.47-7.40 (m, 3H), 7.31-7.29 (m, 3H), 5.31 (s, 1H), 4.93 (s, 1H), 4.66 (s, 1H), 2.74-2.68 (m, 1H), 2.47-2.28 (m, 2H), 2.02-1.94 (m, 1H), 1.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.2, 146.4, 140.8, 137.4, 135.6, 130.2, 130.0, 129.2, 128.5, 127.5, 125.4, 111.4, 53.1, 19.7, 19.6, 19.1 ppm; IR (KBr, cm^{-1}): 3058, 2937, 1649, 1397, 1349, 1147, 755, 693; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 327.1468, found 327.1463.



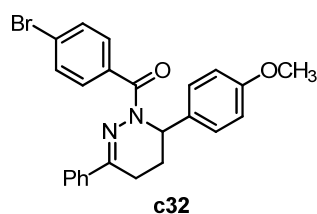
White solid, Yield: 99%; M.P. = 135-137 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.89 (d, J = 8.8 Hz, 2H), 7.65-7.63 (m, 2H), 7.34-7.32 (m, 3H), 7.08 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.02 (s, 1H), 3.89 (s, 3H), 3.75 (s, 3H), 2.70-2.66 (m, 1H), 2.36-2.21 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 169.5, 161.4, 158.8, 146.6, 137.4, 132.7, 132.2, 129.2, 128.5, 127.3, 126.7, 125.5, 114.3, 112.8, 55.5, 55.4, 51.4, 24.2, 18.9 ppm; IR (KBr, cm^{-1}): 2954, 2927, 2837, 1647, 1605, 1510, 1392, 1344, 1251, 1032, 759, 694; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{O}_3\text{N}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 423.1679, found 423.1673.



White solid, Yield: 99%; M.P. = 171-173 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, J = 8.1 Hz, 2H), 7.63-7.60 (m, 2H), 7.32-7.30 (m, 3H), 7.24 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.02 (s, 1H), 3.74 (s, 3H), 2.68-2.64 (m, 1H), 2.43 (s, 3H), 2.35-2.20 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 170.1, 158.8, 146.7, 140.6, 137.4, 132.3, 132.1, 130.5, 129.2, 128.5, 128.1, 126.7, 125.5, 114.3, 55.4, 51.3, 24.2, 21.7, 18.9 ppm; IR (KBr, cm^{-1}): 2925, 2359, 1650, 1511, 1392, 1346, 1248, 1179, 1145, 746, 693; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{ON}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 407.1730, found 407.1724.



White solid, Yield: 90%; M.P. = 147-149 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.23 (m, 9H), 7.15 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.02 (br, 1H), 3.76 (s, 3H), 2.69-2.63 (m, 1H), 2.32-2.20 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 169.0, 158.9, 147.9, 137.2, 137.1, 131.7, 131.1, 129.9, 129.3, 129.1, 128.5, 128.4, 126.8, 126.5, 125.4, 114.3, 55.4, 51.1, 24.0, 18.9 ppm; IR (KBr, cm^{-1}): 3060, 2955, 2928, 2836, 1666, 1512, 1402, 1249, 759, 693; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{O}_2\text{N}_2\text{ClNa}^+$ ($\text{M}+\text{Na}$) $^+$ 427.1184, found 427.1179.



White solid, Yield: 66%; M.P. = 145-146 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, J = 8.5 Hz, 2H), 7.59-7.57 (m, 4H), 7.35-7.33 (m, 3H), 7.07 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.00 (br, 1H), 3.76 (s, 3H), 2.71-2.67 (m, 1H), 2.35-2.22 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 169.1, 158.9, 147.6, 137.1, 134.2, 131.9, 131.8, 130.7, 129.5, 128.6, 126.6, 125.5, 124.9, 114.4, 55.4, 51.4, 24.1, 18.9 ppm; IR (KBr, cm^{-1}): 3060, 2955, 2928, 2835, 1651,

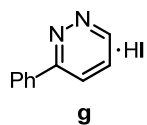
1512, 1403, 1348, 1248, 1178, 1146, 839, 757, 692; HRMS (ESI) calcd for $C_{24}H_{21}O_2N_2BrNa^+$ ($M+Na$)⁺ 471.0679, found 471.0672.

c33 Colorless oil, Yield: 75%; ¹H NMR (400 MHz, CDCl₃): δ 7.79-7.76 (m, 2H), 7.41-7.37 (m, 3H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.88 (s, 1H), 3.74 (s, 3H), 3.00-2.89 (m, 2H), 2.65-2.61 (m, 1H), 2.22-2.14 (m, 3H), 1.78-1.74 (m, 2H), 1.43-1.26 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 174.7, 158.7, 146.2, 137.6, 132.5, 129.2, 128.6, 126.6, 125.3, 114.2, 55.3, 50.3, 33.8, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 25.5, 24.0, 22.8, 18.8, 14.2 ppm; IR (KBr, cm⁻¹): 3061, 2925, 2853, 1676, 1610, 1512, 1397, 1249, 1037, 838, 757, 692; HRMS (ESI) calcd for $C_{29}H_{40}O_2N_2Na^+$ ($M+Na$)⁺ 471.2982, found 471.2973.

d Colorless oil, Yield: 64%; ¹H NMR (400 MHz, CDCl₃): δ 7.71-7.69 (m, 2H), 7.40-7.37 (m, 2H), 7.35-7.30 (m, 4H), 7.28-7.23 (m, 2H), 4.38 (s, 2H), 2.79 (t, *J* = 5.6 Hz, 2H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.06-2.00 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 141.9, 139.1, 138.0, 129.1, 128.4, 128.3, 127.5, 127.3, 124.4, 63.2, 45.9, 21.8, 20.1 ppm; IR (KBr, cm⁻¹): 3028, 2932, 2829, 1586, 1493, 1448, 1355, 1119, 1071, 931, 754, 694; HRMS (ESI) calcd for $C_{17}H_{19}N_2^+$ ($M+H$)⁺ 251.1543, found 251.1538.

e Colorless oil, Yield: 78%; ¹H NMR (400 MHz, CDCl₃): δ 7.42-7.25 (m, 11H), 3.91-3.89 (m, 2H), 3.43-3.37 (m, 1H), 1.95-1.60 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 141.4, 134.8, 134.8, 130.0, 128.6, 128.0, 127.3, 127.1, 62.2, 47.2, 32.8, 25.6 ppm; IR (KBr, cm⁻¹): 3263, 3058, 2924, 2853, 2361, 2341, 1618, 1577, 1400, 1273, 698; HRMS (ESI) calcd for $C_{17}H_{18}ON_2Na^+$ ($M+Na$)⁺ 289.1311, found 289.1307.

f Colorless oil, Yield: 93%; ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.49-7.45 (m, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34-7.28 (m, 4H), 7.24-7.22 (m, 1H), 6.63 (br, 1H), 3.93 (t, *J* = 6.8 Hz, 1H), 3.48-3.43 (m, 2H), 1.80-1.72 (m, 4H), 1.72-1.57 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 167.6, 146.2, 134.9, 131.4, 128.7, 128.6, 127.3, 127.0, 126.3, 56.1, 40.1, 37.0, 26.7 ppm; IR (KBr, cm⁻¹): 2954, 2925, 2854, 1458, 1260, 1095, 1026, 800; HRMS (ESI) calcd for $C_{17}H_{21}ON_2^+$ ($M+H$)⁺ 269.1648, found 269.1644.



White solid, Yield: 40%; M.P. = 264-266 °C; ^1H NMR (400 MHz, DMSO): δ 13.59 (br, 1H), 8.87 (s, 1H), 8.02-8.00 (m, 2H), 7.66-7.32 (m, 5H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 167.4, 150.2, 146.5, 134.7, 129.8, 129.2, 128.4, 91.9 ppm; IR (KBr, cm^{-1}): 3167, 3046, 2975, 2888, 1650, 1566, 1541, 1300, 1008, 790, 689; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_9\text{N}_2^+$ (M-I) $^+$ 157.0760, found 157.0758.

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