Brønsted Acid or Lewis Acid Catalyzed [3 + 3] Cycloaddition of Azomethine Imines with N-Benzyl Azomethine Ylide: A Facile Access to Bicyclic N-Heterocycles

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**General Information:** All reactions were carried out under argon atmosphere in oven dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Organic solutions were concentrated under reduced pressure on a rotary evaporator or oil pump. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates (0.25 mm thickness, Qingdao Haiyang). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Perkin–Elmer Spectrum One FT-IR instrument. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ on Bruker ARX-400 as indicated. Chemical shifts ($\delta$ ppm) are relative to tetramethyrsilane (TMS) with the resonance of the undeuterated solvent or TMS as internal standard. $^1$H NMR data are reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $q$ = quartet, $m$ = multiplet), coupling constants (Hz) and integration. Data for $^{13}$C NMR spectra are presented in terms of chemical shift. Accurate mass measurements were performed using an Agilent instrument with the TOF-MS technique.

**Preparation of N-Benzyl Substituted Compound 1.** To a solution of chloromethyltrimethylsilane (13.4g, 0.11mol) in CH$_3$CN (100mL) was added benzylamine (23.45g, 0.22mol) and the reaction mixture was heated at reflux for 16h. The reaction mixture was cooled to room temperature, and the precipitate of benzylamine hydrochloride was removed by filtration. The filtrate was concentrated under vacuum and the residue was diluted with water (50mL). The reaction mixture was extracted with PE (50mL*2). The organic extracts were combined and washed with water (50mL*2) and brine (50mL) and dried over Na$_2$SO$_4$. The filtrate was concentrated under vacuum to give 18.8g crude product. 88.9% Yield. The above-mentioned crude product (18.8g, 0.098mol) was added to a mixture of 37% formaldehyde (9.49g 0.118mol) and methanol (3.78g, 0.118mol) at 0°C over a period of 60 min. The reaction mixture was further stirred at 0°C for 1.5h and at 10-15°C for 3h. To the reaction mixture was then added anhydrous K$_2$CO$_3$ (16.3g, 0.118mol), and this mixture stirred overnight. The oily layer was separated, added K$_2$CO$_3$ (1.63g, 0.012mol) and stirred for 15min and again decanted. The remaining residual material from the K$_2$CO$_3$ was recovered by washing all the solid K$_2$CO$_3$ with ether. Ether washings were mixed with the decanted oily product and concentrated on the rotary evaporator to give crude product of
N-Benzyl Substituted Compound 1 21g, 90.8% Yield.

General Procedure for the Synthesis of Azomethine Imines 3. The aldehyde (5 mmol) was added to a solution of pyrazolidin-3-one (5 mmol) in 1 mL of MeOH (0.50 mL). The resulting mixture was stirred for 1h-24h (depending on TLC monitor) at room temperature and then diluted with Et₂O (20 mL). The precipitate was collected by filtration, washed with Et₂O, and dried under vacuum to afford the corresponding azomethine imine as a solid in 40-90% yield.

General Procedure for the [3 + 3] Annulation Reaction of N-Benzyl Substituted Compound 1 and Azomethine Imines 3. To a solution of Azomethine Imines 3 (0.02 mmol) and N-Benzyl Azomethine Ylide 1 (0.03 mmol, 1.5 eq) at 0°C in DCM (2 mL) was added acid catalyst (0.002 mmol, 0.1 eq), the reaction mixture was stirred in refrigerated precision water baths at 10°C for 72h (depending on TLC monitor), N-Benzyl Azomethine Ylide 1 (0.05 mmol, 2.5 eq) was added during this period. After the completion of the reaction, the reaction mixture was cooled to 0°C, and was diluted with saturated sodium bicarbonate solution. The filtrate was concentrated under vacuum and purified by flash column (hexane / ethyl acetate = 1 / 9) to give the product 4.
2-benzyl-4-phenylhexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4a)

71% yield for TFA catalyzed reaction (70% yield for Zn(OTf)$_2$ catalyzed reaction), a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.36 – 7.27 (m, 10H), 4.91 (d, $J$ = 11.3 Hz, 1H), 3.78 – 3.68 (m, 4H), 3.36 – 3.25 (m, 1H), 2.96 – 2.89 (m, 1H), 2.84 – 2.75 (m, 1H), 2.69 – 2.60 (m, 2H), 2.50 – 2.39 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.35, 138.03, 137.03, 129.04, 128.75, 128.52, 128.33, 127.74, 127.52, 66.99, 61.58, 58.68, 57.61, 47.96, 30.09; IR (film) $\nu_{\text{max}}$ 3029, 2924, 2844, 1695, 1602, 1494, 1453, 1410, 1328, 1280, 1129, 1065, 1027, 979, 758, 100, 633, 569, 529, 498, 466 cm$^{-1}$; HRMS (MALDI) calcd for C$_{19}$H$_{22}$N$_3$O$^+$ [M+H]$^+$ 308.1757, found 308.1763.

2-benzyl-4-(o-tolyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4b)

69% yield for TFA catalyzed reaction (66% yield for Zn(OTf)$_2$ catalyzed reaction), a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.52 (d, $J$ = 7.5 Hz, 0H), 7.58 – 7.48 (m, 2H), 7.40 – 7.08 (m, 9H), 4.93 (dd, $J$ = 11.4, 1.9 Hz, 1H), 4.03 (dd, $J$ = 10.3, 2.7 Hz, 1H), 3.83 – 3.69 (m, 3H), 3.45 – 3.27 (m, 1H), 2.89 (dt, $J$ = 13.0, 2.3 Hz, 1H), 2.77 – 2.40 (m, 4H), 2.28 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.52, 137.11, 136.08, 135.47, 130.54, 129.00, 128.51, 127.59, 127.54, 126.96, 126.57, 62.07, 61.71, 57.41, 57.36, 47.95, 30.14, 19.41; IR (film) $\nu_{\text{max}}$ 3063, 3027, 2925, 2244, 1696, 1603, 1492, 1454, 1413, 1329, 1279, 1239, 1172, 1131, 1069, 1050, 1027, 1002, 311, 882, 848, 730, 699, 673, 645, 548, 480, 452 cm$^{-1}$; HRMS (MALDI) calcd for C$_{20}$H$_{24}$N$_3$O$^+$ [M+H]$^+$ 322.1914, found 322.1922.

2-benzyl-4-(m-tolyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4c)

s3
67% yield for TFA catalyzed reaction (65% yield for Zn(OTf)₂ catalyzed reaction), a white solid.¹H NMR (400 MHz, Chloroform-d) δ 7.52 (d, J = 7.6 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.30 – 7.11 (m, 5H), 4.93 (dd, J = 11.4, 1.9 Hz, 1H), 4.03 (dd, J = 10.4, 2.7 Hz, 1H), 3.86 – 3.72 (m, 3H), 3.42 – 3.31 (m, 1H), 2.93 – 2.85 (m, 1H), 2.75 – 2.42 (m, 4H), 2.28 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.52, 137.10, 136.07, 135.47, 130.53, 129.00, 128.51, 127.58, 127.53, 126.96, 126.56, 62.08, 61.71, 57.41, 57.35, 47.95, 30.14, 19.41; IR (film) νmax 3027, 2924, 1695, 1603, 1492, 1412, 1329, 1279, 1172, 1131, 1070, 1027, 912, 848, 755, 738, 699, 548, 452 cm⁻¹; HRMS (MALDI) calcd for C₂₀H₂₄N₃O⁺ [M+H]⁺ 322.1914, found 322.1928.

2-benzyl-4-(p-tolyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4d)

68% yield for TFA catalyzed reaction (67% yield for Zn(OTf)₂ catalyzed reaction), a white solid.¹H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.28 (m, 4H), 7.22 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.90 (d, J = 11.3 Hz, 1H), 3.79 – 3.61 (m, 4H), 3.37 – 3.24 (m, 1H), 2.95 – 2.86 (m, 1H), 2.84 – 2.73 (m, 1H), 2.68 – 2.58 (m, 2H), 2.51 – 2.40 (m, 1H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.35, 138.14, 137.04, 134.99, 129.42, 129.06, 128.50, 127.63, 127.50, 66.76, 61.57, 58.71, 57.63, 47.88, 30.10, 21.16; IR (film) νmax 3028, 2923, 2850, 1696, 1514, 1454, 1495, 1454, 1413, 1327, 1279, 1238, 1174, 1129, 1070, 1027, 984, 912, 817, 791, 735, 699, 545 cm⁻¹; HRMS (MALDI) calcd for C₂₀H₂₄N₃O⁺ [M+H]⁺ 322.1914, found 322.1923.

2-benzyl-4-(4-(tert-butyl)phenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4e)
64% yield for TFA catalyzed reaction (65% yield for Zn(OTf)₂ catalyzed reaction), a pale white solid. ¹H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.24 (m, 9H), 4.91 (d, J = 11.1 Hz, 1H), 3.77 – 3.64 (m, 4H), 3.35 – 3.27 (m, 1H), 2.94 – 2.88 (m, 1H), 2.85 – 2.76 (m, 1H), 2.69 – 2.59 (m, 2H), 2.49 – 2.38 (m, 1H), 1.30 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 170.41, 151.31, 137.09, 134.91, 129.04, 128.50, 127.49, 127.38, 125.60, 66.64, 61.61, 58.60, 57.62, 47.96, 34.58, 31.32, 30.10; IR (film) νmax 2960, 2925, 2867, 2853, 1697, 1454, 1409, 1362, 1278, 1268, 1131, 1119, 1108, 1026, 1017, 832, 736, 699, 570 cm⁻¹; HRMS (MALDI) calcd for C₂₃H₃₀N₃O⁺ [M+H]⁺ 364.2383, found 364.2391.

2-benzyl-4-(3,4-dimethylphenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4f)

65% yield for TFA catalyzed reaction (64% yield for Zn(OTf)₂ catalyzed reaction), a pale white solid. ¹H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.22 (m, 5H), 7.17 – 6.96 (m, 3H), 4.99 – 4.88 (m, 1H), 3.82 – 3.69 (m, 2H), 3.69 – 3.60 (m, 2H), 3.36 – 3.24 (m, 2H), 2.89 (dt, J = 12.6, 2.3 Hz, 1H), 2.86 – 2.74 (m, 1H), 2.73 – 2.57 (m, 2H), 2.52 – 2.39 (m, 1H), 2.24 (d, J = 3.5 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 170.55, 137.04, 136.90, 136.81, 135.31, 129.93, 129.12, 128.85, 128.50, 127.51, 125.17, 66.77, 61.59, 58.51, 57.57, 47.87, 30.04, 19.80, 19.50; IR (film) νmax 3029, 2923, 2852, 1690, 1502, 1497, 1454, 1416, 1357, 327, 1281, 1265, 1241, 1206, 1182, 1134, 1074, 1070, 1026, 911, 821, 800, 736, 719, 700 cm⁻¹; HRMS (MALDI) calcd for C₂₁H₂₆N₃O⁺ [M+H]⁺ 336.2070, found 336.2078.

2-benzyl-4-(2-methoxyphenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4g)

55% yield for TFA catalyzed reaction (57% yield for Zn(OTf)₂ catalyzed reaction), a pale white
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.46 (dd, $J = 7.7$, 1.7 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.27 – 7.21 (m, 2H), 6.96 (t, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 8.3$ Hz, 1H), 4.91 (d, $J = 11.7$ Hz, 1H), 4.39 (dd, $J = 10.3$, 2.3 Hz, 1H), 3.84 (d, $J = 11.6$ Hz, 1H), 3.78 (s, 3H), 3.76 (s, 2H), 3.42 – 3.33 (m, 1H), 3.00 – 2.93 (m, 1H), 2.85 – 2.76 (m, 1H), 2.73 – 2.55 (m, 2H), 2.49 – 2.37 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.39, 137.01, 135.50, 133.28, 129.08, 128.57, 128.54, 127.81, 127.73, 127.55, 127.12, 126.97, 126.85, 126.43, 126.27, 67.11, 61.60, 58.70, 57.66, 48.04, 30.11; IR (film) $\nu_{\text{max}}$ 2957, 2923, 2850, 1697, 1613, 1516, 1488, 1417, 1339, 1154, 1118, 1076, 861, 781, 746, 720, 679, 543 cm$^{-1}$; HRMS (MALDI) calcd for C$_{20}$H$_{24}$N$_3$O$_2$ $^+$ [M+H]$^+$ 338.1863, found 338.1870.

2-benzyl-4-(3-methoxyphenyl)hexahydro-8$^H$-pyrazolo[1,2-$a$][1,2,4]triazin-8-one (4h)

$\text{Ph}$

$\text{OMe}$

53% yield for TFA catalyzed reaction (55% yield for Zn(OTf)$_2$ catalyzed reaction), a pale white solid.$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.34 – 7.23 (m, 6H), 6.94 – 6.86 (m, 2H), 6.86 – 6.80 (m, 1H), 4.90 (d, $J = 11.2$ Hz, 1H), 3.81 (s, 3H), 3.77 – 3.64 (m, 4H), 3.38 – 3.29 (m, 1H), 2.96 – 2.88 (m, 1H), 2.85 – 2.75 (m, 1H), 2.71 – 2.58 (m, 2H), 2.52 – 2.38 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.38, 159.85, 139.66, 137.02, 129.76, 129.04, 128.52, 127.52, 120.05, 113.56, 113.26, 66.88, 61.52, 58.66, 57.59, 55.29, 47.93, 30.06; IR (film) $\nu_{\text{max}}$ 2957, 2923, 2850, 1697, 1613, 1516, 1488, 1417, 1339, 1154, 1118, 1076, 861, 781, 746, 720, 679, 543 cm$^{-1}$; HRMS (MALDI) calcd for C$_{20}$H$_{24}$N$_3$O$_2$ $^+$ [M+H]$^+$ 338.1863, found 338.1865.

2-benzyl-4-(4-methoxyphenyl)hexahydro-8$^H$-pyrazolo[1,2-$a$][1,2,4]triazin-8-one (4i)

$\text{Ph}$

$\text{MeO}$

60% yield for TFA catalyzed reaction (61% yield for Zn(OTf)$_2$ catalyzed reaction), a pale white solid.$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.26 – 7.18 (m, 7H), 6.83 – 6.77 (m, 2H), 4.84 (d, $J = 11.3$ Hz, 2H), 3.81 (s, 3H), 3.77 – 3.64 (m, 4H), 3.38 – 3.29 (m, 1H), 2.96 – 2.88 (m, 1H), 2.85 – 2.75 (m, 1H), 2.71 – 2.59 (m, 2H), 2.52 – 2.38 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.38, 159.85, 139.66, 137.02, 129.76, 129.04, 128.52, 127.52, 120.05, 113.56, 113.26, 66.88, 61.52, 58.66, 57.59, 55.29, 47.93, 30.06; IR (film) $\nu_{\text{max}}$ 2957, 2923, 2850, 1697, 1613, 1516, 1488, 1417, 1339, 1154, 1118, 1076, 861, 781, 746, 720, 679, 543 cm$^{-1}$; HRMS (MALDI) calcd for C$_{20}$H$_{24}$N$_3$O$_2$ $^+$ [M+H]$^+$ 338.1863, found 338.1865.
Hz, 1H), 3.73 (s, 3H), 3.69 – 3.57 (m, 4H), 3.26 – 3.18 (m, 1H), 2.86 – 2.80 (m, 1H), 2.76 – 2.68 (m, 1H), 2.62 – 2.52 (m, 2H), 2.44 – 2.34 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.32, 159.55, 137.05, 130.00, 129.05, 128.85, 128.50, 127.50, 114.10, 66.43, 61.59, 58.75, 57.66, 55.30, 47.82, 30.12;

IR (film) $\nu_{\max}$ 2954, 2925, 2851, 1693, 1611, 1513, 1495, 1413, 1327, 1302, 1278, 1248, 1174, 1129, 1110, 1070, 1030, 911, 834, 735, 699, 547 cm$^{-1}$; HRMS (MALDI) calcd for C$_{20}$H$_{24}$N$_3$O$_2^+$ [M+H]$^+$ 338.1863, found 338.1870.

2-benzyl-4-(2-chlorophenyl)hexahydro-8$H$-pyrazolo[1,2-a][1,2,4]triazin-8-one (4j)

74% yield for TFA catalyzed reaction (78% yield for Zn(OTf)$_2$ catalyzed reaction), a pale white solid.

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.58 (dd, $J$ = 7.7, 1.8 Hz, 1H), 7.36 – 7.19 (m, 8H), 4.92 (d, $J$ = 11.8 Hz, 1H), 4.41 (dd, $J$ = 10.4, 2.8 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.79 (s, 2H), 3.43 – 3.31 (m, 1H), 3.06 – 2.98 (m, 1H), 2.82 – 2.56 (m, 3H), 2.52 – 2.40 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.77, 137.18, 135.47, 133.38, 129.71, 129.11, 128.99, 128.70, 128.47, 127.51, 127.39, 61.33, 56.93, 56.60, 47.95, 29.92; IR (film) $\nu_{\max}$ 3063, 3029, 2924, 2851, 2245, 1693, 1495, 1475, 1442, 1412, 1329, 1280, 1204, 1124, 1070, 1037, 1002, 982, 911, 882, 846, 734, 701, 646, 548, 456 cm$^{-1}$; HRMS (MALDI) calcd for C$_{19}$H$_{21}$ClN$_3$O$^+$ [M+H]$^+$ 342.1368, found 342.1373.

2-benzyl-4-(3-chlorophenyl)hexahydro-8$H$-pyrazolo[1,2-a][1,2,4]triazin-8-one (4k)

72% yield for TFA catalyzed reaction (78% yield for Zn(OTf)$_2$ catalyzed reaction), a pale white solid.

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.34 – 7.27 (m, 9H), 4.91 (d, $J$ = 11.3 Hz, 1H), 3.79 – 3.67 (m, 4H), 3.36 – 3.23 (m, 1H), 2.95 – 2.90 (m, 1H), 2.83 – 2.75 (m, 1H), 2.69 – 2.60 (m, 2H), 2.49 – 2.39 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.77, 137.18, 135.47, 133.38, 129.71, 129.11, 128.99, 128.70, 128.47, 127.51, 127.39, 61.33, 56.93, 56.60, 47.95, 29.92; IR (film) $\nu_{\max}$ 3063, 3029, 2924, 2851, 2245, 1693, 1495, 1475, 1442, 1412, 1329, 1280, 1204, 1124, 1070, 1037, 1002, 982, 911, 882, 846, 734, 701, 646, 548, 456 cm$^{-1}$; HRMS (MALDI) calcd for C$_{19}$H$_{21}$ClN$_3$O$^+$ [M+H]$^+$ 342.1368, found 342.1373.
128.70, 128.47, 127.39, 127.34, 61.33, 61.31, 59.17, 58.60, 47.95, 29.92; IR (film) \(\nu_{\text{max}}\) 3029, 2925, 2850, 1693, 1597, 1573, 1495, 1431, 1413, 1357, 1326, 1281, 1238, 1204, 1175, 1130, 1096, 1078, 1027, 1001, 984, 911, 879, 782, 734, 697, 669, 646 cm\(^{-1}\); HRMS (MALDI) calcd for \(\text{C}_{19}\text{H}_{21}\text{ClN}_{3}\text{O}^+ [M+H]^+\) 342.1368, found 342.1377.

2-benzyl-4-(4-chlorophenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4l)

\[
\begin{align*}
\text{Cl} & \\
& \text{4l}
\end{align*}
\]

76% yield for TFA catalyzed reaction (80% yield for Zn(OTf)\(_2\) catalyzed reaction), a pale white solid.

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.37 – 7.27 (m, 9H), 4.91 (d, \(J = 11.3\) Hz, 1H), 3.78 – 3.60 (m, 4H), 3.36 – 3.24 (m, 1H), 2.93 – 2.86 (m, 1H), 2.80 – 2.71 (m, 1H), 2.67 – 2.54 (m, 2H), 2.50 – 2.40 (m, 1H); \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.27, 136.87, 136.52, 134.09, 129.03, 128.98, 128.95, 128.55, 127.58, 66.30, 61.53, 58.61, 57.57, 47.97, 30.00; IR (film) \(\nu_{\text{max}}\) 2954, 2925, 2850, 1693, 1492, 1454, 1409, 1280, 1200, 1175, 1130, 1089, 1069, 1027, 014, 830, 737, 719, 700, 531 cm\(^{-1}\); HRMS (MALDI) calcd for \(\text{C}_{19}\text{H}_{21}\text{ClN}_{3}\text{O}^+ [M+H]^+\) 342.1368, found 342.1372.

2-benzyl-4-(2-fluorophenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4m)

\[
\begin{align*}
\text{Ph} & \\
& \text{4m}
\end{align*}
\]

73% yield for TFA catalyzed reaction (82% yield for Zn(OTf)\(_2\) catalyzed reaction), a white solid.\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.51 (t, \(J = 8.1\) Hz, 1H), 7.34 – 7.23 (m, 6H), 7.19 – 7.12 (m, 1H), 7.07 – 7.00 (m, 1H), 4.97 – 4.87 (m, 1H), 4.22 (d, \(J = 10.4\) Hz, 1H), 3.86 – 3.72 (m, 3H), 3.41 – 3.29 (m, 1H), 3.00 – 2.93 (m, 1H), 2.85 – 2.78 (m, 1H), 2.76 – 2.63 (m, 2H), 2.51 – 2.40 (m, 1H); \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.58, 161.73, 159.27, 137.08, 129.49, 129.41, 129.10, 128.51, 127.52, 124.99, 124.87, 124.63, 124.60, 115.69, 115.47, 65.58, 61.42, 57.16, 56.96, 48.03, 29.92; IR (film) \(\nu_{\text{max}}\) 3063, 3029, 2925, 2852, 1696, 1616, 1586, 1491, 1455, 1412, 1347, 1329, 1280, 1229, 1182,
1131, 1098, 1027, 1002, 982, 912, 881, 853, 761, 734, 699, 673, 645, 547, 495 cm⁻¹; HRMS (MALDI) calcd for C₁₉H₂₁FN₃O⁺ [M+H]⁺ 326.1663, found 326.1670.

2-benzyl-4-(3-fluorophenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4n)

73% yield for TFA catalyzed reaction (79% yield for Zn(OTf)₂ catalyzed reaction), a white solid.¹H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.13 (m, 6H), 7.08 – 6.96 (m, 3H), 6.97 – 6.84 (m, 1H), 4.83 (dd, J = 11.3, 1.8 Hz, 1H), 3.69 – 3.57 (m, 4H), 3.32 – 3.19 (m, 1H), 2.90 – 2.78 (m, 1H), 2.77 – 2.64 (m, 1H), 2.65 – 2.50 (m, 2H), 2.45 – 2.30 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 170.30, 164.18, 161.73, 140.68, 136.92, 130.35, 130.27, 129.02, 128.55, 127.58, 123.42, 123.39, 115.38, 115.17, 114.66, 114.44, 66.38, 61.50, 58.65, 57.54, 48.01, 29.99; IR (film) ν max 3063, 3029, 2925, 2848, 1696, 1614, 1590, 1488, 1449, 1413, 1328, 1280, 1177, 1126, 1068, 1027, 975, 912, 787, 734, 697, 669, 646, 546, 489 cm⁻¹; HRMS (MALDI) calcd for C₁₉H₂₁FN₃O⁺ [M+H]⁺ 326.1663, found 326.1672.

2-benzyl-4-(4-fluorophenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4o)

75% yield for TFA catalyzed reaction (81% yield for Zn(OTf)₂ catalyzed reaction), a white solid.¹H NMR (400 MHz, Chloroform-d) δ 7.32 (dd, J = 8.2, 4.9 Hz, 7H), 7.07 – 6.99 (m, 2H), 4.91 (d, J = 11.3 Hz, 1H), 3.76 – 3.64 (m, 4H), 3.29 (ddd, J = 10.7, 9.3, 5.9 Hz, 1H), 2.93 – 2.86 (m, 1H), 2.81 – 2.72 (m, 1H), 2.68 – 2.55 (m, 2H), 2.50 – 2.39 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 170.26, 163.79, 161.33, 136.94, 133.80, 133.77, 129.36, 129.28, 128.02, 128.54, 127.56, 115.81, 115.60, 66.28, 61.57, 58.77, 57.62, 47.90, 30.05; IR (film) ν max 3030, 2925, 2851, 1695, 1605, 1510, 1454, 1414, 1327, 1279, 1223, 1174, 1157, 1130, 1097, 1069, 1027, 920, 88, 838, 793, 700, 669, 591, 545, 524
2-benzyl-4-(2,4,6-trifluorophenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4p)

81\% yield for TFA catalyzed reaction (85\% yield for Zn(OTf)₂ catalyzed reaction), a white solid.\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\): 7.63 (s, 1H), 7.60 – 7.51 (m, 2H), 7.50 – 7.44 (m, 1H), 7.34 (s, 2H), 7.33 (s, 2H), 7.30 – 7.27 (m, 1H), 4.92 (d, \(J = 11.5\) Hz, 1H), 3.81 – 3.67 (m, 4H), 3.37 – 3.28 (m, 1H), 2.98 – 2.90 (m, 1H), 2.81 – 2.71 (m, 1H), 2.71 – 2.58 (m, 2H), 2.53 – 2.41 (m, 1H); \(^{13}\)C NMR (101 MHz, CDCl₃) \(\delta\): 170.23, 139.17, 136.86, 131.38, 131.16, 131.06, 129.32, 129.00, 128.57, 127.61, 125.25, 125.21, 124.44, 124.40, 122.55, 66.55, 61.52, 58.69, 57.56, 48.08, 29.97; IR (film) \(\nu_{\max}\): 3031, 2925, 2851, 1696, 1586, 1490, 1455, 1412, 1347, 1328, 1280, 1229, 1129, 1097, 1027, 982, 912, 761, 734, 700, 673, 547 cm\(^{-1}\); HRMS (MALDI) calcd for C\(_{19}\)H\(_{21}\)FN\(_3\)O\(^+\) [M+H]\(^+\) 326.1663, found 326.1668.

2-benzyl-4-(4-nitrophenyl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4q)

70\% yield for TFA catalyzed reaction (69\% yield for Zn(OTf)₂ catalyzed reaction), a yellow solid.\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\): 8.26 – 8.17 (m, 2H), 7.60 – 7.48 (m, 2H), 7.36 – 7.27 (m, 5H), 4.92 (d, \(J = 11.5\) Hz, 1H), 3.85 (dd, \(J = 10.4, 2.9\) Hz, 1H), 3.81 – 3.66 (m, 3H), 3.39 – 3.30 (m, 1H), 2.96 – 2.87 (m, 1H), 2.79 – 2.56 (m, 3H), 2.54 – 2.42 (m, 1H); \(^{13}\)C NMR (101 MHz, CDCl₃) \(\delta\): 170.15, 147.88, 145.46, 136.71, 128.97, 128.58, 128.55, 127.67, 124.01, 66.19, 61.44, 58.45, 57.44, 48.18, 29.83; IR (film) \(\nu_{\max}\): 3054, 2954, 2852, 1692, 1599, 1520, 1454, 1412, 1347, 1328, 1280, 1229, 1128, 107, 1070, 855, 738, 751, 740, 698, 668 cm\(^{-1}\); HRMS (MALDI) calcd for C\(_{19}\)H\(_{19}\)F\(_3\)N\(_3\)O\(_3\)\(^+\) [M+H]\(^+\) 362.1475, found 362.1483.
2-benzyl-4-(naphthalen-1-yl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4r)

65% yield for TFA catalyzed reaction (69% yield for Zn(OTf)₂ catalyzed reaction), a white solid. H NMR (400 MHz, Chloroform-d) δ 8.03 – 7.92 (m, 1H), 7.90 – 7.83 (m, 1H), 7.83 – 7.69 (m, 2H), 7.54 – 7.44 (m, 3H), 7.42 – 7.26 (m, 5H), 4.99 (dd, J = 11.5, 1.9 Hz, 1H), 4.67 (dd, J = 10.3, 2.7 Hz, 1H), 3.95 – 3.72 (m, 3H), 3.54 – 3.33 (m, 1H), 3.21 – 3.07 (m, 1H), 2.85 – 2.61 (m, 3H), 2.54 – 2.41 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 170.60, 137.01, 133.79, 133.70, 130.98, 129.23, 129.04, 128.54, 128.23, 127.59, 126.55, 125.74, 125.68, 124.88, 121.80, 121.80, 61.56, 61.39, 58.38, 57.46, 48.08, 30.11; IR (film) νmax 3013, 2923, 2852, 1693, 1660, 1507, 1447, 1316, 1275, 1266, 1133, 1120, 1072, 1023, 871, 827, 749, 720, 668 cm⁻¹; HRMS (MALDI) calcd for C₂₃H₂₄N₃O⁺ [M+H]⁺ 358.1914, found 358.1915.

2-benzyl-4-(naphthalen-2-yl)hexahydro-8H-pyrazolo[1,2-a][1,2,4]triazin-8-one (4s)

69% yield for TFA catalyzed reaction (67% yield for Zn(OTf)₂ catalyzed reaction), a white solid. H NMR (400 MHz, Chloroform-d) δ 7.87 – 7.78 (m, 6H), 7.54 – 7.42 (m, 3H), 7.39 – 7.25 (m, 6H), 4.95 (dd, J = 11.3, 1.8 Hz, 1H), 3.92 – 3.68 (m, 5H), 3.40 – 3.27 (m, 1H), 2.99 (dd, J = 12.7, 2.9, 1.9 Hz, 1H), 2.90 – 2.61 (m, 3H), 2.54 – 2.41 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 170.39, 137.01, 135.50, 133.28, 129.08, 128.57, 128.54, 127.81, 127.73, 127.55, 127.12, 126.97, 126.85, 126.43, 126.27, 67.11, 61.60, 58.70, 57.66, 48.04, 30.11; IR (film) νmax 3057, 3029, 2924, 2849, 1693, 1661, 1508, 1495, 1454, 1414, 1352, 1325, 1283, 1265, 1179, 1133, 1121, 1070, 1027, 909, 883, 859, 820, 737, 700, 479 cm⁻¹; HRMS (MALDI) calcd for C₂₃H₂₄N₃O⁺ [M+H]⁺ 358.1914, found 358.1920.