Supporting Information for:

Intramolecular Hydrogen Bonding-Assisted Cyclocondensation of α-Diazo ketones with Various Amines: A Strategy for Catalytic Wolff 1,2,3-Triazole Synthesis

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Contents

Table of contents ------------------------------------------------------------------------------------------------------------------------------------------S1

I. General Information-------------------------------------------------------------------------------------------------------------------------------------S2

II. Synthesis and analytical data for α-diazo-β-oxoamides and 1,2,3-triazoles - S2-S19

III. Single-crystal X-ray diffraction data for compound 2a1 ----------------------------------------S19-S20

IV. 1H- and 13C-NMR Spectra Copies ----------------------------------------------------------------------------------------------------------------------S21-S74
I. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded at 25 °C at 300MHz or 400MHz or 500 MHz and 100MHz or 125 MHz, respectively, with TMS as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruker microTof by using ESI method.

II. Synthesis and analytical data for \(\alpha\)-diazo-\(\beta\)-oxoamides and 1,2,3-triazoles.

Synthesis of \(\alpha\)-diazo-1,3-dicarbonyl compounds (with \(1a\) as an example): To a solution of 3-oxo-N-phenylbutanamide (30 mmol) and triethylamine (60 mmol) in 50 mL of acetonitrile was added tosyl azide (33 mmol). The solution was stirred for 12 h at room temperature until the 3-oxo-N-phenylbutanamide disappeared (monitored by TLC). The reaction mixture was then treated with 250 mL brine, and extracted with dichloromethane (2 × 100 mL). The combined organic layer was washed with brine (3 × 100 mL), dried over MgSO\(_4\) and filtered. The filtrate was concentrated in vacuum, and purified by silica gel column chromatography to give \(1a\) as a yellowish solid.

2-diazo-3-oxo-N-phenylbutanamide

\((1a)\) Yellowish solid; mp 118-120 °C. \(^1\)H-NMR (CDCl\(_3\), 300 MHz) \(\delta\) 10.17 (s, 1H), 7.57-7.60 (m, 2H), 7.30 -7.36 (m, 2H), 7.09 -7.14 (m, 1H), 2.42 (s, 3H). \(^{13}\)C-NMR (CDCl\(_3\), 125Hz) \(\delta\) 189.8, 158.0, 137.8, 128.9, 124.3, 119.9, 78.3, 26.6. HRMS Calcd for C\(_{10}\)H\(_{10}\)N\(_3\)O\(_2\) ([M + H]\(^+\)) 204.0773; Found 204.0776.

2-diazo-3-oxo-N-\((\omega\)-tolyl)butanamide

\((1b)\) Yellow solid; mp 133-135 °C. \(^1\)H-NMR (CDCl\(_3\), 500 MHz) \(\delta\) 10.13 (s, 1H), 8.12 (d, \(J = 10.0\)Hz, 1H), 7.18-7.22 (m, 2H), 7.03-7.06 (m, 1H), 2.40 (s, 3H), 2.35 (s, 3H). \(^{13}\)C-NMR (CDCl\(_3\), 125Hz) \(\delta\) 190.0, 158.0, 136.3, 130.3, 127.7, 126.6, 124.4, 121.2, 78.5, 26.6, 17.9. HRMS Calcd for C\(_{11}\)H\(_{12}\)N\(_3\)O\(_2\) ([M + H]\(^+\)) 218.0930; Found
2-diazo-3-oxo-N-(p-tolyl)butanamide

(1c) Yellow solid; mp 137-139 °C. **^1H-NMR** (CDCl₃, 300 MHz) δ 10.08 (s, 1H), 7.45-7.48 (m, 2H), 7.09-7.16 (m, 2H), 2.41 (s, 3H), 2.32 (s, 3H). **^13C-NMR** (CDCl₃, 125Hz) δ 189.8, 157.8, 135.2, 133.9, 129.4, 119.9, 78.2, 26.6, 20.8. **HRMS** Calcd for C₁₁H₁₂N₃O₂ ([M + H]+) 218.0930; Found 218.0916.

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2-diazo-N-(2-methoxyphenyl)-3-oxobutanamide

(1d) Yellow solid; mp 138-140 °C. **^1H-NMR** (CDCl₃, 300 MHz) δ 10.61 (s, 1H), 8.34-8.37 (m, 1H), 7.03-7.09 (m, 1H), 6.89-6.98 (m, 2H), 3.94 (s, 3H), 2.41 (s, 3H). **^13C-NMR** (CDCl₃, 100Hz) δ 189.5, 157.8, 148.5, 127.9, 124.0, 120.8, 120.0, 110.1, 78.4, 55.8, 26.6. **HRMS** Calcd for C₁₁H₁₂N₃O₃ ([M + H]+) 234.0879; Found 234.0858.

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2-diazo-N-(4-methoxyphenyl)-3-oxobutanamide

(1e) Yellow solid; mp 111-113 °C. **^1H-NMR** (CDCl₃, 300 MHz) δ 10.03 (s, 1H), 7.47-7.50 (m, 2H), 6.85-6.88 (m, 2H), 3.79 (s, 3H), 2.41 (s, 3H). **^13C-NMR** (CDCl₃, 100Hz) δ 189.7, 157.6, 156.1, 130.9, 121.3, 113.8, 77.9, 55.2, 26.4. **HRMS** Calcd for C₁₁H₁₂N₃O₃ ([M + H]+) 234.0879; Found 234.0866.

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(1f) Yellow solid; mp 112-114 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 10.71 (s, 1H), 8.38-8.42 (m, 1H), 7.38-7.41 (m, 1H), 7.24-7.29 (m, 1H), 7.02-7.08 (m, 1H), 2.43 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 125Hz) δ 189.5, 158.4, 135.0, 129.1, 127.4, 124.6, 123.2, 121.5, 78.5, 26.5. HRMS Calcd for C$_{10}$H$_9$ClN$_3$O$_2$ ([M + H]$^+$) 238.0383; Found 238.0367.

$\text{N-(4-chlorophenyl)-2-diazo-3-oxobutanamide}$

(1g) Yellow solid; mp 134-136 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 10.20 (s, 1H), 7.52-7.55 (m, 2H), 7.27-7.30 (m, 2H), 2.41 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 125Hz) δ 189.8, 158.1, 136.4, 129.1, 128.9, 121.1, 78.2, 26.6. HRMS Calcd for C$_{10}$H$_9$ClN$_3$O$_2$ ([M + H]$^+$) 238.0383; Found 238.0362.

2-diazo-N-(2,4-dimethylphenyl)-3-oxobutanamide

(1h) Yellow solid; mp 129-131 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 10.04 (s, 1H), 7.90-7.97 (m, 1H), 7.00-7.02 (m, 2H), 2.41 (s, 3H), 2.30 (s, 3H), 2.29 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 190.0, 157.8, 134.0, 133.7, 130.9, 127.7, 127.0, 121.3, 78.3, 26.5, 20.7, 17.7. HRMS Calcd for C$_{12}$H$_{14}$N$_3$O$_2$ ([M + H]$^+$) 232.1086; Found 232.1040.

2-diazo-3-oxo-N-(4-(trifluoromethyl)phenyl)butanamide

(1i) Yellow solid; mp 137-139 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 10.41 (s, 1H), 7.72 (d, J = 9.0Hz, 2H), 7.58 (d, J = 9.0Hz, 2H), 2.44 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 189.9, 158.6, 140.8, 129.6, 126.2, 125.4, 122.7, 119.6, 78.4, 26.6. HRMS Calcd for C$_{11}$H$_8$F$_3$N$_3$O$_2$ ([M + H]$^+$) 272.0647; Found 272.0611.

S4
2-diazo-3-oxo-\(N\)-(pyridin-2-yl)butanamide

(1j) Yellowish solid; mp 155-158 °C. \(^1\text{H-NMR}\) (CDCl\(_3\), 400 MHz) \(\delta\) 10.61 (s, 1H), 8.31-8.32 (m, 1H), 8.14 (d, \(J = 8.4\)Hz, 1H), 7.66-7.70 (m, 1H), 7.02-7.05 (m, 1H), 2.41 (s, 3H). \(^{13}\text{C-NMR}\) (CDCl\(_3\), 100Hz) \(\delta\) 188.9, 158.6, 151.0, 148.0, 138.0, 119.8, 114.0, 78.0, 26.6. HRMS Calcd for C\(_9\)H\(_8\)N\(_4\)NaO\(_2\) ([M + Na]\(^+\)) 227.0545; Found 227.0690.

2-diazo-3-oxo-\(N\)-phenylhexanamide

(1k) Yellow solid; mp 68-70 °C. \(^1\text{H-NMR}\) (CDCl\(_3\), 400 MHz) \(\delta\) 10.26 (s, 1H), 7.56-7.61 (m, 2H), 7.29 -7.36 (m, 2H), 7.08 -7.14 (m, 1H), 2.60 (t, \(J = 7.6\)Hz, 2H), 1.72-1.79 (m, 2H), 1.02 (t, \(J = 7.6\)Hz, 3H). \(^{13}\text{C-NMR}\) (CDCl\(_3\), 100Hz) \(\delta\) 192.8, 158.3, 137.9, 128.9, 124.2, 119.8, 77.5, 40.8, 17.5, 13.4. HRMS Calcd for C\(_{12}\)H\(_{14}\)N\(_3\)O\(_2\) ([M + H]\(^+\)) 232.1086; Found 232.1097.

2-diazo-3-oxo-\(N\),3-diphenylpropanamide

(1l) Yellowish solid; mp 95-98 °C. \(^1\text{H-NMR}\) (CDCl\(_3\), 400 MHz) \(\delta\) 10.46 (s, 1H), 7.59-7.68 (m, 5H), 7.53 (t, \(J = 8.0\)Hz, 2H), 7.36 (t, \(J = 8.0\)Hz, 2H), 7.14 (t, \(J = 8.0\)Hz, 1H). \(^{13}\text{C-NMR}\) (CDCl\(_3\), 100Hz) \(\delta\) 187.9, 158.5, 137.8, 136.5, 132.7, 129.0, 127.0, 124.4, 120.0, 77.6. HRMS Calcd for C\(_{15}\)H\(_{12}\)N\(_3\)O\(_2\) ([M + H]\(^+\)) 266.0930; Found 266.0914.

2-diazo-5,5-dimethylcyclohexane-1,3-dione

(S2) Yellowish solid; mp 97-100 °C. \(^1\text{H-NMR}\) (CDCl\(_3\), 300 MHz) \(\delta\) 2.44 (s, 4H), 1.11
3-diazopiperidine-2,4-dione

(S3) White solid; mp 137-139 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 6.22 (s, 1H), 3.50 (t, $J = 6.0$ Hz, 2H), 2.65 (t, $J = 6.0$ Hz, 2H). $^{13}$C-NMR (CDCl$_3$, 100Hz) $\delta$ 188.0, 163.5, 75.4, 36.9, 36.2. HRMS Calcd for C$_5$H$_6$N$_3$O$_2$ ([M + H]$^+$) 140.0460; Found 140.0433.

2-diazo-N-methyl-3-oxo-N-phenylbutanamide

(S4) Yellow oil; $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 7.40-7.45 (m, 2H), 7.31-7.36 (m, 1H), 7.20 (d, $J = 6.0$ Hz, 2H), 3.38 (s, 3H), 2.50 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 125Hz) $\delta$ 191.6, 160.6, 142.7, 130.0, 127.7, 126.0, 74.2, 38.2, 28.2. HRMS Calcd for C$_{11}$H$_{11}$N$_3$O$_2$ ([M + H]$^+$) 217.0851; Found 217.0850.

Synthesis of 1,2,3-triazoles (with 2a1 as an example): To a solution of 1a (5 mmol) and aniline (5 mmol) in DMF (10 mL) was added 0.2 equiv of FeCl$_2$ (1 mmol). The mixture was warmed to 80 °C and stirred for 10 h. When 1a disappeared (monitored by TLC), the reaction mixture was then treated with 50 mL brine, and extracted with dichloromethane (2 × 50 mL). The combined organic layer was washed with brine (3 × 50 mL), dried over MgSO$_4$ and filtered. The filtrate was concentrated in vacuum, and then purified by silica gel column chromatography to give 2a1 as a white solid.
(2a1) White solid; mp 149-151 °C. $^1$H-NMR (CDCl$_3$, 400 MHz) δ 9.07 (s, 1H), 7.72 (d, $J = 8.0$Hz, 2H), 7.55-7.64 (m, 3H), 7.46-7.51 (m, 2H), 7.39 (t, $J = 8.0$Hz, 2H), 7.16 (t, $J = 7.6$Hz, 1H), 2.69 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 125Hz) δ 159.2, 138.5, 137.6, 137.3, 135.4, 130.0, 129.6, 129.0, 125.2, 124.3, 119.7, 9.8. HRMS Calcd for C$_{16}$H$_{15}$N$_4$O ([M + H]$^+$) 279.1246; Found 279.1240.

5-methyl-1-phenyl-N-(o-tolyl)-1H-1,2,3-triazole-4-carboxamide

(2a2) White solid; mp 104-106 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.03 (s, 1H), 8.12 (d, $J = 6.0$Hz, 1H), 7.55-7.65 (m, 3H), 7.46-7.52 (m, 2H), 7.21-7.32 (m, 2H), 7.08-7.13 (m, 1H), 2.69 (s, 3H), 2.43 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.0, 138.6, 137.1, 135.5, 130.4, 129.9, 129.5, 128.3, 126.6, 125.1, 124.6, 121.8, 17.6, 9.6. HRMS Calcd for C$_{17}$H$_{17}$N$_4$O ([M + H]$^+$) 293.1402; Found 293.1400.

5-methyl-1-phenyl-N-(p-tolyl)-1H-1,2,3-triazole-4-carboxamide

(2a3) White solid; mp 152-154 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.02 (s, 1H), 7.55-7.65 (m, 5H), 7.45-7.52 (m, 2H), 7.19 (d, $J = 8.1$Hz, 2H), 2.68 (s, 3H), 2.35 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.0, 138.6, 137.2, 135.4, 135.1, 133.8, 129.9, 129.6, 129.5, 125.2, 119.7, 20.8, 9.7. HRMS Calcd for C$_{17}$H$_{17}$N$_4$O ([M + H]$^+$) 293.1402; Found 293.1399.

N-(2-methoxyphenyl)-5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxamide

(2a4) Yellow solid; mp 184-185 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.70 (s, 1H), 8.49-8.54 (m, 1H), 7.55-7.63 (m, 3H), 7.46-7.52 (m, 2H), 6.92-7.13 (m, 3H), 3.96 (s, 3H), 2.69 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.1, 148.4, 138.9, 137.1, 135.5, 129.9, 129.6, 127.4, 125.2, 123.8, 120.8, 119.6, 110.0, 55.7, 9.7. HRMS Calcd for
N-(4-methoxyphenyl)-5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxamide

(2a5) White solid; mp 163-166 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 8.98 (s, 1H), 7.57-7.67 (m, 5H), 7.45-7.52 (m, 2H), 6.89-6.96 (m, 2H), 3.82 (s, 3H), 2.68 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.00, 156.4, 138.6, 137.1, 135.5, 130.8, 130.0, 129.6,125.2, 121.5, 114.2, 55.4, 9.7. HRMS Calcd for C$_{17}$H$_{17}$N$_4$O$_2$ ([M + H]$^+$) 309.1352; Found 309.1350.

N-(2-chlorophenyl)-5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxamide

(2a6) Yellow solid; mp 127-129 °C. $^1$H-NMR (CDCl$_3$, 400 MHz) δ 9.68 (s, 1H), 8.52-8.56 (m, 1H), 7.56-7.63(m, 3H), 7.41-7.51 (m, 3H), 7.30-7.34 (m, 1H), 7.06-7.11 (m, 1H), 2.69 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 125Hz) δ 159.2, 138.4, 137.5, 135.4, 134.5, 130.0, 129.6, 129.2, 127.5, 125.2, 124.6, 123.3, 121.2, 9.8. HRMS Calcd for C$_{16}$H$_{14}$ClN$_4$O ([M + H]$^+$) 313.0856; Found 313.0850.

N-(4-chlorophenyl)-5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxamide

(2a7) White solid; mp 175-177 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.07 (s, 1H), 7.66-7.69 (m, 2H), 7.56-7.63 (m, 3H), 7.45-7.51 (m, 2H), 7.32-7.36 (m, 2H), 2.68 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.2, 138.4, 137.5, 136.3, 135.4, 130.2, 129.7, 129.3, 129.1, 125.2, 121.0, 9.8. HRMS Calcd for C$_{16}$H$_{14}$ClN$_4$O ([M + H]$^+$) 313.0856; Found 313.0844.
$N$-(2,4-dimethylphenyl)-5-methyl-1-phenyl-1$H$-1,2,3-triazole-4-carboxamide

(2a8) White solid; mp 162-164 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 8.94 (s, 1H), 7.94 (d, $J = 9.0$ Hz, 1H), 7.56-7.64 (m, 3H), 7.45-7.51 (m, 2H), 7.04-7.08 (m, 2H), 2.68 (s, 3H), 2.38 (s, 3H), 2.32 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) $\delta$ 159.2, 138.8, 137.1, 135.6, 134.5, 132.9, 131.2, 130.0, 129.7, 128.8, 127.2, 125.2, 122.3, 20.8, 17.7, 9.8. HRMS Calcd for C$_{18}$H$_{19}$N$_4$O ([M + H]$^+$) 307.1559; Found 307.1542.

5-methyl-1-phenyl-$N$-(4-(trifluoromethyl)phenyl)-1$H$-1,2,3-triazole-4-carboxamide

(2a9) White solid; mp 212-214 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 9.23 (s, 1H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.58-7.68 (m, 5H), 7.48-7.52 (m, 2H), 2.70 (s, 3H). $^{13}$C-NMR (CDC$_3$, 100Hz) $\delta$ 159.4, 140.8, 138.2, 137.8, 135.3, 130.2, 129.7, 126.3, 126.3, 125.4, 125.2, 122.7, 119.3, 9.8. HRMS Calcd for C$_{17}$H$_{14}$F$_3$N$_4$O ([M + H]$^+$) 347.1120; Found 347.1117.

5-methyl-1-phenyl-$N$-(pyridin-2-yl)-1$H$-1,2,3-triazole-4-carboxamide

(2a10) White solid; mp 105-108 °C. $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 9.69 (s, 1H), 8.31-8.39 (m, 2H), 7.72-7.77 (m, 1H), 7.56-7.62 (m, 3H), 7.46-7.51 (m, 2H), 7.05-7.10 (m, 1H), 2.69 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) $\delta$ 159.5, 151.1, 148.1, 138.1, 137.6, 135.4, 130.0, 129.6, 125.1, 119.7, 113.8, 109.5, 9.8. HRMS Calcd for C$_{15}$H$_{14}$N$_5$O ([M + H]$^+$) 280.1198; Found 280.1199.

$N,1$-diphenyl-5-propyl-$1H$-1,2,3-triazole-4-carboxamide
(2a11) Yellow solid; mp 110-112 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.12 (s, 1H), 7.72 (d, $J = 6.0$ Hz, 2H), 7.59-7.61 (m, 3H), 7.44-7.47 (m, 2H), 7.39 (t, $J = 6.0$ Hz, 2H), 7.15 (t, $J = 7.5$ Hz, 1H), 3.00-3.10 (m, 2H), 1.56-1.66 (m, 2H), 0.88 (t, $J = 7.5$ Hz, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.0, 141.8, 138.2, 137.6, 135.7, 130.2, 129.6, 129.0, 125.7, 124.2, 119.8, 25.0, 22.2, 13.8. HRMS Calcd for C$_{18}$H$_{19}$N$_4$O ([M + H]$^+$) 307.1559; Found 307.1548.

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$N_1,5$-triphenyl-$1H$-1,2,3-triazole-4-carboxamide

(2a12) Yellow solid; mp 101-104 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.22 (s, 1H), 7.71 (d, $J = 6.0$ Hz, 2H), 7.27-7.46 (m, 12H), 7.14 (t, $J = 7.5$Hz, 1H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 158.0, 139.5, 138.7, 137.6, 135.9, 131.7, 130.5, 129.9, 129.3, 129.0, 128.3, 125.2, 124.3, 119.8. HRMS Calcd for C$_{21}$H$_{17}$N$_4$O ([M + H]$^+$) 341.1402; Found 341.1400.

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5-methyl-$N$-phenyl-1-(o-tolyl)-1$H$-1,2,3-triazole-4-carboxamide

(2b1) White solid; mp 143-145 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.10 (s, 1H), 7.70-7.75 (m, 2H), 7.36-7.55 (m, 5H), 7.23-7.27 (m, 1H), 7.12-7.19 (m, 1H), 2.50 (s, 3H), 2.07 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.2, 138.2, 138.0 137.6, 135.4, 134.2, 131.4, 130.7, 129.0, 127.1, 127.0, 124.2, 119.7, 17.1, 9.1. HRMS Calcd for C$_{17}$H$_{17}$N$_4$O ([M + H]$^+$) 293.1402; Found 293.1401.

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1-(2-methoxyphenyl)-5-methyl-$N$-phenyl-1$H$-1,2,3-triazole-4-carboxamide

(2b2) Yellow solid; mp 110-112 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.10 (s, 1H), 7.70-7.75 (m, 2H), 7.52-7.60 (m, 1H), 7.35-7.43 (m, 3H), 7.09-7.20 (m, 3H), 3.83 (s, 3H), 2.52 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.3, 153.8, 139.3, 137.7, 132.0,
5-methyl-N-phenyl-1-(p-tolyl)-1H-1,2,3-triazole-4-carboxamide

(2b3) Yellow solid; mp 210-213 °C. \(^1\text{H-NMR}\) (CDCl\(_3\), 300 MHz) \(\delta\) 9.08 (s, 1H), 7.68-7.76 (m, 2H), 7.33-7.42 (m, 6H), 7.13-7.19 (m, 1H), 2.66 (s, 3H), 2.48 (s, 3H). \(^1^3\text{C-NMR}\) (CDCl\(_3\), 100Hz) \(\delta\) 159.2, 140.4, 138.4, 137.7, 137.3, 133.0, 130.2, 129.0, 125.0, 124.2, 119.7, 21.2, 9.7. \text{HRMS} Calcd for C\(_{17}\)H\(_{17}\)N\(_4\)O\(_2\) ([M + H]\(^+\)) 309.1352; Found 309.1352.

1-(4-methoxyphenyl)-5-methyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide

(2b4) White solid; mp 214-216 °C. \(^1\text{H-NMR}\) (CDCl\(_3\), 300 MHz) \(\delta\) 9.08 (s, 1H), 7.69-7.75 (m, 2H), 7.35-7.42 (m, 4H), 7.12-7.19 (m, 1H), 7.05-7.11 (m, 2H), 3.90 (s, 3H), 2.65 (s, 3H). \(^1^3\text{C-NMR}\) (CDCl\(_3\), 100Hz) \(\delta\) 160.7, 159.3, 138.4, 137.7, 137.5, 129.0, 128.3, 126.6, 124.2, 119.8, 114.8, 55.6, 9.7. \text{HRMS} Calcd for C\(_{17}\)H\(_{17}\)N\(_4\)O\(_2\) ([M + H]\(^+\)) 309.1349; Found 309.1349.

1-(4-chlorophenyl)-5-methyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide

(2b5) White solid; mp 203-205 °C. \(^1\text{H-NMR}\) (CDCl\(_3\), 300 MHz) \(\delta\) 9.05 (s, 1H), 7.70-7.74 (m, 2H), 7.55-7.62 (m, 2H), 7.35-7.46 (m, 4H), 7.12-7.20 (m, 1H), 2.69 (s, 3H). \(^1^3\text{C-NMR}\) (CDCl\(_3\), 100Hz) \(\delta\) 159.0, 138.7, 137.5, 137.3, 136.2, 133.9, 129.9, 129.0, 126.4, 124.4, 119.8, 9.8. \text{HRMS} Calcd for C\(_{16}\)H\(_{14}\)ClN\(_4\)O ([M + H]\(^+\)) 313.0856; Found 313.0852.
5-methyl-N-phenyl-1-(pyridin-2-yl)-1H-1,2,3-triazole-4-carboxamide
(2b6) Yellow solid; mp 119-122 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.10 (s, 1H), 8.60-8.64 (m, 1H), 7.97-8.01 (m, 2H), 7.70-7.75 (m, 2H), 7.33-7.48 (m, 3H), 7.13-7.18 (m, 1H), 3.02 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.1, 150.0, 148.4, 139.0, 138.2, 137.5, 128.9, 128.8, 124.2, 124.0, 119.7, 118.0, 10.8. HRMS Calcd for C$_{15}$H$_{14}$N$_5$O ([M + H]$^+$) 280.1198; Found 280.1185.

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5-methyl-1-(naphthalen-1-yl)-N-phenyl-1H-1,2,3-triazole-4-carboxamide
(2b7) Yellow solid; mp 189-191 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.16 (s, 1H), 8.12 (d, $J = 8.4$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 7.5$ Hz, 2H), 7.51-7.70 (m, 4H), 7.41 (t, $J = 9.0$ Hz, 2H), 7.13-7.22 (m, 2H), 2.49 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.2, 139.4, 138.1, 137.7, 134.1, 131.5, 131.2, 129.3, 124.0, 128.4, 128.2, 127.3, 125.2, 125.0, 124.3, 121.8, 119.8, 9.2. HRMS Calcd for C$_{20}$H$_{17}$N$_4$O ([M + H]$^+$) 329.1402; Found 329.1390.

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1-benzyl-5-methyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide
(2b8) Yellow solid; mp 127-128 °C. $^1$H-NMR (CDCl$_3$, 500 MHz) δ 9.04 (s, 1H), 7.66-7.71 (m, 2H), 7.31-7.39 (m, 5H), 7.15-7.19 (m, 2H), 7.13 (t, $J = 7.5$Hz, 1H), 5.52 (s, 2H), 2.54 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 125Hz) δ 159.2, 138.7, 137.6, 136.8, 133.8, 129.0, 129.0, 128.5, 127.1, 124.2, 119.7, 51.8, 8.8. HRMS Calcd for C$_{17}$H$_{17}$N$_4$O ([M + H]$^+$) 293.1402; Found 293.1405.
5-methyl-N-phenyl-1-propyl-1H-1,2,3-triazole-4-carboxamide

(2b9) White solid; mp 116-118 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.02 (s, 1H), 7.65-7.72 (m, 2H), 7.33-7.41 (m, 2H), 7.11-7.17 (m, 1H), 4.27 (t, $J = 7.2$Hz, 2H), 2.67 (s, 3H), 1.90-1.98 (m, 2H), 1.00 (t, $J = 7.5$Hz, 3H). $^{13}$C-NMR (CDCl$_3$, 125Hz) δ 159.3, 138.2, 137.6, 136.2, 129.0, 124.1, 119.6, 49.4, 23.1, 11.0, 8.7. HRMS Calcd for C$_{13}$H$_{17}$N$_4$O ([M + H]$^+$) 245.1402; Found 245.1397.

5-methyl-1-octadecyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide

(2b10) White solid; mp 71-73 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 9.02 (s, 1H), 7.68 (d, $J = 7.8$Hz, 2H), 7.37 (t, $J = 7.5$Hz, 2H), 7.13 (t, $J = 7.5$Hz, 1H), 4.29 (t, $J = 7.5$Hz, 2H), 2.66 (s, 3H), 1.25-1.33 (m, 32H), 0.87 (t, $J = 6.0$Hz, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.4, 138.4, 138.3, 137.6, 129.0, 124.2, 119.7, 48.0, 31.9, 29.6, 29.5, 29.3, 29.0, 26.5, 22.6, 14.1, 8.7. HRMS Calcd for C$_{28}$H$_{46}$N$_4$O ([M + H]$^+$) 454.3672; Found 454.3670.

1-cyclopropyl-5-methyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide

(2b11) White solid; mp 102-105 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 8.98 (s, 1H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.36 (t, $J = 8.4$ Hz, 2H), 7.13 (t, $J = 7.2$ Hz, 1H), 3.42-3.54 (m, 1H), 2.74 (s, 3H), 1.21-1.40 (m, 4H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.2, 138.5, 138.3, 137.6, 128.8, 124.0, 119.6, 29.0, 8.8, 6.3. HRMS Calcd for C$_{13}$H$_{13}$N$_4$O ([M + H]$^+$) 243.1246; Found 243.1245.

1-cyclohexyl-5-methyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide
(2b12) White solid; mp 146-148 °C. \(^1^H\)-NMR (CDCl\(_3\), 300 MHz) δ 9.03 (s, 1H), 7.68 (d, \(J = 8.4\) Hz, 2H), 7.36 (t, \(J = 7.5\) Hz, 2H), 7.13 (t, \(J = 7.5\) Hz, 1H), 4.07-4.21 (m, 1H), 2.67 (s, 3H), 1.75-2.14 (m, 7H), 1.30-1.54 (m, 3H). \(^{13}\)C-NMR (CDCl\(_3\), 100Hz) δ 159.5, 138.0, 137.7, 135.5, 128.9, 124.0, 119.7, 58.1, 32.6, 25.4, 24.9, 8.6. HRMS Calcd for C\(_{16}\)H\(_{21}\)N\(_4\)O ([M + H]\(^+\)) 285.1715; Found 285.1710.

methyl 2-(5-methyl-4-(phenylcarbamoyl)-1\(H\)-1,2,3-triazol-1-yl)acetate

(2b13) White solid; mp 122-123 °C. \(^1^H\)-NMR (CDCl\(_3\), 400 MHz) δ 8.98 (s, 1H), 7.64-7.70 (m, 2H), 7.33-7.39 (m, 2H), 7.10-7.16 (m, 1H), 5.11 (s, 2H), 3.81 (s, 3H), 2.62 (s, 3H). \(^{13}\)C-NMR (CDCl\(_3\), 100Hz) δ 166.0, 159.0, 138.6, 137.8, 137.5, 129.0, 124.3, 119.8, 53.1, 48.6, 8.6. HRMS Calcd for C\(_{13}\)H\(_{15}\)N\(_4\)O\(_3\) ([M + H]\(^+\)) 275.1144; Found 275.1147.

tert-butyl (2-(5-methyl-4-(phenylcarbamoyl)-1\(H\)-1,2,3-triazol-1-yl)ethyl)carbamate

(2b14) White solid; mp 168-170 °C. \(^1^H\)-NMR (CDCl\(_3\), 500 MHz) δ 9.00 (s, 1H), 7.66-7.70 (m, 2H), 7.34-7.39 (m, 2H), 7.11-7.16 (m, 1H), 5.11 (s, 1H), 4.41-4.44 (m, 2H), 3.64-3.67 (m, 2H), 2.65 (s, 3H), 1.43 (s, 9H). \(^{13}\)C-NMR (CDCl\(_3\), 100Hz) δ 159.2, 155.8, 138.4, 137.6, 137.4, 129.0, 124.3, 119.8, 80.2, 47.2, 40.3, 28.3, 8.6. HRMS Calcd for C\(_{17}\)H\(_{24}\)N\(_5\)O\(_3\) ([M + H]\(^+\)) 346.1879; Found 346.1877.

1-(2-hydroxyethyl)-5-methyl-N-phenyl-1\(H\)-1,2,3-triazole-4-carboxamide

(2b15) White solid; mp 104-106 °C. \(^1^H\)-NMR (CDCl\(_3\), 300 MHz) δ 8.97 (s, 1H), 7.62-7.71 (m, 2H), 7.32-7.41 (m, 2H), 7.14 (t, \(J = 7.5\)Hz, 1H), 4.33-4.43 (m, 2H), 4.04-4.17 (m, 2H), 2.15-2.70 (m, 4H). \(^{13}\)C-NMR (CDCl\(_3\), 100Hz) δ 159.2, 137.9, 137.7, 137.3, 128.9, 124.3, 119.9, 60.7, 50.1, 8.7. HRMS Calcd for C\(_{12}\)H\(_{15}\)N\(_4\)O\(_2\) ([M + H]\(^+\)) 247.1195; Found 247.1187.
1-allyl-5-methyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide

(2b16) White solid; mp 85-87 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 9.01 (s, 1H), 7.69 (d, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.14 (t, $J = 7.5$ Hz, 1H), 5.89-6.07 (m, 1H), 5.35 (d, $J = 10.2$ Hz, 1H), 5.11 (d, $J = 17.1$ Hz, 1H), 4.94-5.00 (m, 2H), 2.64 (s, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) $\delta$ 159.2, 138.5, 137.6, 136.7, 130.4, 128.9, 124.1, 119.7, 119.0, 50.3, 8.6. HRMS Calcd for C$_{13}$H$_{15}$N$_4$O ([M + H]$^+$) 243.1246; Found 243.1246.

5-methyl-N-phenyl-1-(prop-2-yn-1-yl)-1H-1,2,3-triazole-4-carboxamide

(2b17) White solid; mp 93-95 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 8.99 (s, 1H), 7.68 (d, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.14 (t, $J = 7.5$ Hz, 1H), 5.15 (d, $J = 2.4$ Hz, 2H), 2.77 (s, 3H), 2.51 (t, $J = 2.4$ Hz, 1H). $^{13}$C-NMR (CDCl$_3$, 100Hz) $\delta$ 159.0, 138.8, 137.5, 137.0, 129.0, 124.3, 119.7, 75.3, 74.5, 37.9, 8.7. HRMS Calcd for C$_{13}$H$_{13}$N$_4$O ([M + H]$^+$) 241.1089; Found 241.1078.

(R)-5-methyl-N-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole-4-carboxamide

(2b18) White solid; mp 105-108 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 9.05 (s, 1H), 7.67 (d, $J = 9.0$ Hz, 2H), 7.31-7.39 (m, 5H), 7.09-7.22 (m, 3H), 5.58 (q, $J = 7.0$ Hz, 1H), 2.50 (s, 3H), 2.09 (d, $J = 6.0$ Hz, 3H). $^{13}$C-NMR (CDCl$_3$, 100Hz) $\delta$ 159.3, 139.7, 138.7, 137.6, 136.5, 129.0, 128.9, 128.3, 125.9, 124.1, 119.7, 58.8, 21.6, 8.7. HRMS Calcd for C$_{13}$H$_{13}$N$_4$O ([M + H]$^+$) 241.1089; Found 241.1078.
5-methyl-1-(methylamino)-N-phenyl-1H-1,2,3-triazole-4-carboxamide

(2b19) Yellowish solid; mp 123-125 °C. $^1H$-NMR (CDCl$_3$, 300 MHz) δ 8.97 (s, 1H), 7.68 (d, $J = 9.0$ Hz, 2H), 7.37 (t, $J = 9.0$ Hz, 2H), 7.14 (t, $J = 7.5$ Hz, 1H), 3.05 (s, 3H), 2.63 (s, 3H).

$^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.0, 137.5, 137.0, 136.0, 128.9, 124.1, 119.7, 39.9, 8.2. HRMS Calcd for C$_{11}$H$_{14}$N$_5$O ([M + H]$^+$) 232.1198; Found 232.1194.

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1-methoxy-5-methyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide

(2b20) Yellowish solid; mp 86-89 °C. $^1H$-NMR (CDCl$_3$, 400 MHz) δ 8.93 (s, 1H), 7.67 (d, $J = 8.0$Hz, 2H), 7.37 (t, $J = 8.0$Hz, 2H), 7.14 (t, $J = 7.5$ Hz, 1H), 4.31 (s, 3H), 2.64 (s, 3H).

$^{13}$C-NMR (CDCl$_3$, 100Hz) δ 158.5, 137.3, 136.5, 130.7, 128.9, 124.2, 119.6, 67.3, 7.5. HRMS Calcd for C$_{11}$H$_{13}$N$_4$O$_2$ ([M + H]$^+$) 233.1039; Found 233.1035.

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**Synthesis of NH-1,2,3-triazoles 2c1-2c5 (with 2c1 as an example):** To a solution of 1a (5 mmol) and ammonium acetate (7.5mmol) dissolved in 10 mL of DMF was added 0.2 equiv of FeCl$_2$. The mixture was warmed to 80 °C and stirred for 5 h. When 1a had disappeared (TLC). The reaction mixture was treated with 50 mL brine, and then extracted with dichloromethane (2 × 50 mL). The combined organic layer was washed with brine (3 × 50 mL), dried over MgSO$_4$ and filtered. The filtrate was concentrated in vacuum, and then purified by silica gel column chromatography to give 2c1 as a white solid.

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5-methyl-N-phenyl-1H-1,2,3-triazole-4-carboxamide

(2c1) White solid; mp 196-198 °C. $^1H$-NMR (DMSO, 500 MHz) δ 10.29 (s, 1H), 7.83 (d, $J = 10.0$ Hz, 2H), 7.32 (t, $J = 10.0$ Hz, 2H), 7.07 (t, $J = 7.5$Hz, 1H), 2.52 (s, 3H).

$^{13}$C-NMR (DMSO, 125Hz) δ 159.9, 138.7, 137.6, 128.6, 123.6, 120.3, 120.1, 9.3. HRMS Calcd for C$_{10}$H$_{11}$N$_4$O ([M + H]$^+$) 203.0933; Found 203.0929.
\(N\)-(4-methoxyphenyl)-5-methyl-1\(H\)-1,2,3-triazole-4-carboxamide

\((2c2)\) White solid; mp 180-182 °C. \(^1H\)-NMR (DMSO, 300 MHz) \(\delta\) 15.30 (s, 1H), 10.17 (s, 1H), 7.73 (d, \(J\) = 9.0Hz, 2H), 6.90 (d, \(J\) = 9.0Hz, 2H), 3.73 (s, 3H), 2.51 (s, 3H). \(^{13}C\)-NMR (DMSO, 100Hz) \(\delta\) 159.6, 155.6, 137.8, 131.9, 122.0, 113.7, 55.2, 9.3. HRMS Calcd for C_{11}H_{13}N_{4}O_{2} ([M + H]^+) 233.1039; Found 233.1040.

\(N\)-(2,4-dimethylphenyl)-5-methyl-1\(H\)-1,2,3-triazole-4-carboxamide

\((2c3)\) White solid; mp 184-187 °C. \(^1H\)-NMR (DMSO, 300 MHz) \(\delta\) 15.31 (s, 1H), 9.62 (s, 1H), 7.39 (d, \(J\) = 6.0 Hz, 1H), 7.06 (s, 1H), 7.00 (d, \(J\) = 6.0 Hz, 1H), 2.50 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H). \(^{13}C\)-NMR (DMSO, 100Hz) \(\delta\) 159.6, 134.4, 133.3, 131.7, 130.8, 129.3, 126.5, 125.6, 124.9, 20.5, 17.6, 9.1. HRMS Calcd for C_{12}H_{15}N_{4}O ([M + H]^+) 231.1246; Found 231.1246.

\(N\)-(4-chlorophenyl)-5-methyl-1\(H\)-1,2,3-triazole-4-carboxamide

\((2c4)\) White solid; mp 204-206 °C. \(^1H\)-NMR (DMSO, 400 MHz) \(\delta\) 15.32 (s, 1H), 10.41 (s, 1H), 7.86 (d, \(J\) = 8.8Hz, 2H), 7.33 (d, \(J\) = 8.8Hz, 2H), 2.50 (s, 3H). \(^{13}C\)-NMR (DMSO, 100Hz) \(\delta\) 159.9, 137.8, 137.5, 137.4, 128.4, 127.2, 121.8, 9.2. HRMS Calcd for C_{10}H_{10}ClN_{4}O ([M + H]^+) 237.0543; Found 237.0504.

\(N\)-phenyl-5-propyl-1\(H\)-1,2,3-triazole-4-carboxamide

S17
White solid; mp 106-109 °C. $^1$H-NMR (DMSO, 500 MHz) δ 10.30 (s, 1H), 7.84 (d, $J = 10.0$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.07 (t, $J = 7.5$ Hz, 1H), 2.96 (t, $J = 7.5$ Hz, 2H), 1.62-1.73 (m, 2H), 0.89 (t, $J = 7.5$ Hz, 3H). $^{13}$C-NMR (DMSO, 125Hz) δ 159.8, 138.8, 129.3, 128.6, 125.7, 123.6, 120.3, 25.3, 21.8, 13.6. HRMS Calcd for C$_{12}$H$_{15}$N$_4$O ([M + H]$^+$) 231.1246; Found 231.1292.

Synthesis of bis-triazoles 3a and 3b (with 3a as an example): To a solution of 1h (5 mmol) and 1,6-diaminohexane (2 mmol) dissolved in 10 mL of DMF was added 0.2 equiv of FeCl$_2$. The mixture was warmed to 80 °C and stirred for 10 h. When 1h had disappeared (TLC). The reaction mixture was treated with 50 mL brine, and then extracted with dichloromethane (2 × 50 mL). The combined organic layer was washed with brine (3 × 50 mL), dried over MgSO$_4$ and filtered. The filtrate was concentrated in vacuum, and then purified by silica gel column chromatography to give 3a as a pale pink solid.

1,1’-(hexane-1,6-diyl)bis(N-(2,4-dimethylphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxamide)

(3a) Pale pink; mp 175-178 °C. $^1$H-NMR (CDCl$_3$, 300 MHz) δ 8.86 (s, 2H), 7.90 (d, $J = 9.0$ Hz, 2H), 7.00-7.09 (m, 4H), 4.29 (t, $J = 6.0$ Hz, 4H), 2.65 (s, 6H), 2.34 (s, 6H), 2.31 (s, 6H), 1.84-1.99 (m, 4H), 1.35-1.48 (m, 4H). $^{13}$C-NMR (CDCl$_3$, 100Hz) δ 159.2, 138.5, 135.9, 134.2, 132.8, 131.0, 128.5, 127.0, 122.0, 47.4, 29.2, 26.8, 20.7, 17.5, 8.6. HRMS Calcd for C$_{30}$H$_{39}$N$_8$O$_2$ ([M + H]$^+$) 543.3196; Found 543.3176.
1,1′-(hexane-1,6-diyl)bis(N-phenyl-5-propyl-1H-1,2,3-triazole-4-carboxamide)

(3b) Yellow solid; mp 188-190 °C. \( ^1H-NMR \) (CDCl₃, 300 MHz) \( \delta \) 9.03 (s, 2H), 7.68 (d, \( J = 7.5 \) Hz, 4H), 7.36 (t, \( J = 7.8 \) Hz, 4H), 7.13 (t, \( J = 7.5 \) Hz, 2H), 4.28 (t, \( J = 7.2 \) Hz, 4H), 2.98-3.07 (m, 4H), 1.90-2.01 (m, 4H), 1.63-1.75 (m, 4H), 1.39-1.48 (m, 4H), 1.02 (t, \( J = 7.5 \) Hz, 6H). \( ^{13}C\text{-NMR} \) (CDCl₃, 100 Hz) \( \delta \) 159.1, 140.4, 138.1, 137.6, 129.0, 124.1, 119.7, 47.6, 29.7, 26.0, 24.7, 22.3, 13.8. \( \text{HRMS} \) Calcd for C\(_{30}\)H\(_{39}\)N\(_8\)O\(_2\) ([M + H]\(^+\)) 543.3196; Found 543.3185.

III. Single-crystal X-ray diffraction data for compound 2a1

Single-crystal X-ray diffraction data for compound 2a1 was collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-K\(\alpha\) (\( \lambda = 0.71073 \) Å) radiation with a \( \omega \) scan technique. The crystal structures were solved by direct method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined anisotropic, and hydrogen atoms of the ligands were refined as rigid groups. Basic information of crystal parameters and structure refinement are listed in Table 1-4.

1 (a) G. M. Sheldrick, SHELXS-97, Program for Solution of Crystal Structures, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
Table 1. Crystal data and structure refinement of 2a1.

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IV. $^1$H- and $^{13}$C-NMR Spectra Copies

[Graph showing NMR spectra with peaks labeled]

[Structural formula of compound 1a]

[Spectra details and chemical shifts indicated]
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S43