Supporting Information

C=N Bonds Formation via Palladium-Catalyzed Carbene Insertion into N=N Bonds: Inhibiting the General 1,2-Migration Process of Ylide Intermediates

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Table of Contents

A. General Information...................................................................................................................1
B. General Procedure for the Carbene Insertion of N-tosylhydrazones with Azo Compounds ............................................................................................................................................................2
C. Analysis Data for the Products ..................................................................................................2
D. Procedure for the Gram-Scale Synthesis of 3a , 5a and 5g ...................................................18
E. Procedure for the Synthesis of Chiral Hydrozones.................................................................18
F. X-ray Crystallographic Data ....................................................................................................21
G. NMR Spectra of New Compounds ..........................................................................................23
A. General Information

Melting points were measured using a melting point instrument and are uncorrected. Chemical shifts were reported in ppm from the solvent resonance as the internal standard (CDCl$_3$ $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; D$_2$O $\delta_H = 4.79$ ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants were reported in Hertz (Hz). IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC–MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100–400 mesh silica gel plates (GF$_{254}$). X-ray structural analyses were conducted on an X-ray analysis instrument.

Materials. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone; 1,2-dichloroethane (DCE) was distilled from calcium hydride; acetonitrile (CH$_3$CN) was distilled from phosphorus pentoxide. Other commercially available reagents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF$_{254}$) using UV light as a visualizing agent. Flash column chromatography was carried out using silica gel (200–300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath temperatures.
B. General Procedure for the Carbene Insertion of N-Tosylhydrazones with Azo Compounds

\[
\begin{align*}
\text{NNHTs} & \quad \text{Pd(TFA)}_2 \quad \text{Cs}_2\text{CO}_3 \\
\text{R}_1\text{CONR}_2 & \quad \text{toluene, 90 °C} \\
\text{1 or 4} & \quad 12 \text{ h}, \text{N}_2 \\
\rightarrow & \quad \text{2} \quad \text{3 or 5}
\end{align*}
\]

A 25 mL Schlenk tube placed with a magnetic stirring bar, N-tosylhydrazones (0.2 mmol), Pd(TFA)_2 (10 mmol %), Cs_2CO_3 (0.2 mmol), toluene (2 mL), and azo compound 2 (0.1 mmol) was vigorously stirred at 90 °C for 12 h under N_2 in an oil bath. Then the resulting solution was cooled to room temperature, added water (10 mL), extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated \textit{in vacuo}. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product 3 or 5.

C. Analysis Data for the Products

\textbf{(E)-2-Benzylidene-\textit{N},\textit{N},\textit{N}',\textit{N}’-Tetramethylhydrazine-1,1-Dicarboxamide (3a)}

\[
\text{CONMe}_2
\quad \text{CONMe}_2
\quad \text{H}
\quad \text{H}
\quad \text{CONMe}_2
\quad \text{CONMe}_2
\]

23.8 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \( R_f = 0.40 \); \textit{H} NMR (400 MHz, CDCl_3) \( \delta \) 7.80 (s, 1H), 7.63–7.66 (m, 2H), 7.36–7.38 (m, 3H), 3.06 (s, 12H); \textit{C} NMR (100 MHz, CDCl_3) \( \delta \) 156.2, 145.7, 134.5, 129.9, 128.6, 127.1, 37.6; IR (KBr): 2930, 1688, 1487, 1380, 1261, 1160, 1061 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]+ Calcd. for C_{13}H_{18}N_4O_2+H, 263.1503; found, 263.1501.

\textbf{(E)-\textit{N},\textit{N},\textit{N}',\textit{N}’-Tetramethyl-2-(naphthalen-1-ylmethylene)hydrazine-1,1-Dicarboxamide (3b)}

\[
\text{CONMe}_2
\quad \text{CONMe}_2
\quad \text{H}
\quad \text{H}
\quad \text{CONMe}_2
\quad \text{CONMe}_2
\]

26.2 mg, 84% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \( R_f = 0.42 \); \textit{H} NMR (400 MHz, CDCl_3) \( \delta \) 7.63–7.66 (m, 2H), 7.86–7.89 (m, 3H), 7.46–7.57 (m, 3H), 3.09 (s,
12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.5, 146.1, 133.8, 131.0, 130.1, 128.7, 127.0, 126.8, 126.1, 125.3, 124.0, 37.7; IR (KBr): 2929, 1687, 1488, 1380, 1262, 1161, 1063 cm$^{-1}$; HRMS (ESI, m/z): [M+Na]$^+$ Calcd. for C$_{17}$H$_{20}$N$_4$O$_2$+Na, 335.1478; found, 335.1479.

((E)-2-(4-Fluorobenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3c))

24.6 mg, 88% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): $R_f$ = 0.41; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (s, 1H), 7.62–7.66 (m, 2H), 7.07 (t, $J$ = 8.8 Hz, 2H), 3.06 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.7 (d, $^1$J$_{F-C}$ = 248.7 Hz), 156.2, 145.0, 130.7 (d, $^4$J$_{F-C}$ = 3.2 Hz), 128.9 (d, $^3$J$_{F-C}$ = 8.4 Hz), 115.7 (d, $^2$J$_{F-C}$ = 21.8 Hz), 37.6; IR (KBr): 2929, 1688, 1495, 1377, 1230, 1156, 1061 cm$^{-1}$; HRMS (ESI, m/z): [M+H]$^+$ Calcd. for C$_{13}$H$_{17}$FN$_4$O$_2$+H, 281.1408; found, 281.1407.

((E)-2-(2-Chlorobenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3d))

25.2 mg, 85% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): $R_f$ = 0.41; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (s, 1H), 7.94–7.96 (m, 1H), 7.35–7.37 (m, 1H), 7.27–7.30 (m, 2H), 3.06 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.0, 142.2, 134.3, 132.0, 130.7, 129.8, 126.9, 126.8, 37.6; IR (KBr): 2931, 1686, 1498, 1381, 1262, 1158, 1054 cm$^{-1}$; HRMS (ESI, m/z): [M+Na]$^+$ Calcd. for C$_{13}$H$_{17}$ClN$_4$O$_2$+Na, 319.0932; found, 319.0935.

((E)-2-(4-Chlorobenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3e))

26.0 mg, 88% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): $R_f$ = 0.41; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (s, 1H), 7.58 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8.4 Hz, 2H), 3.06 (s,
(E)-2-(4-Bromobenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3f)

30.9 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \( R_f = 0.40 \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.77 (s, 1H), 7.44–7.58 (m, 4H), 3.06 (s, 12H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 156.0, 143.9, 136.6, 130.2, 129.5, 126.0, 122.9, 37.6; IR (KBr): 2929, 1688, 1483, 1381, 1261, 1158, 1060 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na\(^+\)] Calcd. for C\(_{13}\)H\(_{17}\)BrN\(_4\)O\(_2\)+Na, 363.0427; found, 363.0429.

(E)-2-(3-Bromobenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3g)

30.9 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \( R_f = 0.42 \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.82 (s, 1H), 7.75 (s, 1H), 7.52 (d, \( J = 8.0 \) Hz, 1H), 7.4 (d, \( J = 8.0 \) Hz, 1H), 7.25 (t, \( J = 8.0 \) Hz, 1H), 3.06 (s, 12H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 155.9, 143.9, 136.6, 130.2, 129.5, 126.0, 122.9, 37.6; IR (KBr): 2929, 1688, 1483, 1381, 1261, 1158, 1060 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na\(^+\)] Calcd. for C\(_{13}\)H\(_{17}\)BrN\(_4\)O\(_2\)+Na, 363.0427; found, 363.0429.

(E)-N,N,N',N'-Tetramethyl-2-(4-(Trifluoromethyl)benzylidene)hydrazine-1,1-Dicarboxamide (3h)

30.0 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \( R_f = 0.43 \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.83 (s, 1H), 7.78 (s, 1H), 7.52 (d, \( J = 8.0 \) Hz, 1H), 7.4 (d, \( J = 8.0 \) Hz, 1H), 7.25 (t, \( J = 8.0 \) Hz, 1H), 3.06 (s, 12H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 156.0, 143.9, 136.6, 130.2, 129.5, 126.0, 122.9, 37.6; IR (KBr): 2929, 1688, 1483, 1381, 1261, 1158, 1060 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na\(^+\)] Calcd. for C\(_{13}\)H\(_{17}\)F\(_3\)N\(_4\)O\(_2\)+Na, 363.0427; found, 363.0429.
NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (s, 1H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 3.08 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.5, 143.3, 138.2, 131.1 (q, $^{2}J_{F-C} = 33.4$ Hz), 127.3, 125.5 (q, $^{3}J_{F-C} = 3.8$ Hz), 121.3 (q, $^{1}J_{F-C} = 127.5$ Hz), 37.6; IR (KBr): 2933, 1691, 1495, 1324, 1261, 1162, 1064 cm$^{-1}$; HRMS (ESI, m/z): [M+H]$^+$ Calcd. for C$_{14}$H$_{17}$F$_{3}$N$_{4}$O$_{2}$+H, 331.1376; found, 331.1373.

($E$)-$N,N,N',N'$-Tetramethyl-2-(4-(Methylsulfonyl)benzylidene)hydrazine-1,1-Dicarboxamide (3i)

25.2 mg, 74% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): $R_f = 0.17$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.0$ Hz, 2H), 7.89 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 2H), 3.08 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.6, 142.9, 141.0, 139.8, 127.8, 127.6, 44.5, 37.6; IR (KBr): 2926, 2857, 1687, 1486, 1394, 1305, 1145, 1065 cm$^{-1}$; HRMS (ESI, m/z): [M+Na]$^+$ Calcd. for C$_{14}$H$_{20}$N$_{4}$O$_{4}$S+Na, 363.1097; found, 363.1098.

($E$)-$N,N,N',N'$-Tetramethyl-2-(4-Methylbenzylidene)hydrazine-1,1-Dicarboxamide (3j)

25.1 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): $R_f = 0.42$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (s, 1H), 7.53 (s, 2H), 7.18 (s, 2H), 3.05–3.05 (m, 12H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.3, 146.1, 140.2, 131.8, 129.4, 127.1, 37.6, 21.4; IR (KBr): 2927, 1688, 1488, 1374, 1261, 1159, 1059 cm$^{-1}$; HRMS (ESI, m/z): [M+H]$^+$ Calcd. for C$_{14}$H$_{20}$N$_{4}$O$_{2}$+H, 277.1659; found, 277.1656.

($E$)-$N,N,N',N'$-Tetramethyl-2-(2-Methylbenzylidene)hydrazine-1,1-Dicarboxamide (3k)
(E)-2-(4-(tert-Butyl)benzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3l)

28.6 mg, 90% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.41; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (s, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 3.06 (s, 12H), 1.33 (s, 9H); ^13C NMR (100 MHz, CDCl_3) δ 156.3, 153.3, 145.8, 131.8, 126.9, 125.6, 37.7, 34.8, 31.2; IR (KBr): 2955, 1686, 1486, 1374, 1262, 1159, 1060 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for C_{17}H_{26}N_{4}O_{2}+H, 319.2129; found, 319.2128.

(E)-2-(4-Methoxybenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3m)

26.6 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): R_f = 0.40; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.59 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H), 3.06 (s, 12H); ^13C NMR (100 MHz, CDCl_3) δ 161.1, 156.5, 146.2, 128.7, 127.3, 114.1, 55.3, 37.6; IR (KBr): 2925, 2854, 1682, 1606, 1497, 1377, 1252, 1161, 1029 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for C_{14}H_{20}N_{4}O_{3}+H, 293.1608; found, 293.1608.

(E)-2-(2,4-Dimethylbenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3n)
(E)-2-(4-Bromo-2-Methoxybenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3o)

30.2 mg, 83% yield; yellow solid, mp: 99−100 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): Rf = 0.41; 1H NMR (400 MHz, CDCl3) δ 8.09 (s, 1H), 7.98 (s, 1H), 7.41 (d, J = 8.8 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 3.81 (s, 3H), 3.05 (s, 12H); 13C NMR (100 MHz, CDCl3) δ 157.0, 156.2, 140.7, 133.5, 128.4, 124.9, 113.4, 112.9, 55.8, 37.6; IR (KBr): 2934, 1682, 1483, 1379, 1262, 1161, 1061 cm⁻¹; HRMS (ESI, m/z): [M+H]+ Calcd. for C14H19BrN4O3, 371.0713; found, 371.0711.

(E)-2-(2,6-Dimethylbenzylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (3p)

22.0 mg, 76% yield; yellow solid, mp: 110−111 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): Rf = 0.41; 1H NMR (400 MHz, CDCl3) δ 8.14 (s, 1H), 7.12−7.16 (m, 1H), 7.03−7.05 (m, 2H), 3.05 (s, 12H), 2.43 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 156.7, 148.4, 137.4, 131.7, 128.8, 128.4, 37.6, 21.0; IR (KBr): 2930, 1681, 1483, 1379, 1262, 1156, 1061 cm⁻¹; HRMS (ESI, m/z): [M+H]+ Calcd. for C15H22N4O2+H, 291.1816; found, 291.1817.
(E)-N,N',N'-Tetramethyl-2-(2,4,6-Trimethylbenzylidene)hydrazine-1,1-Dicarboxamide (3q)

22.5 mg, 74% yield; yellow solid, mp: 151−152 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): Rf = 0.43; 1H NMR (400 MHz, CDCl3) δ 8.13 (s, 1H), 6.88 (s, 2H), 3.05 (s, 12H), 2.41 (s, 6H), 2.29 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 156.8, 148.4, 138.8, 137.5, 129.4, 128.7, 37.6, 21.0; IR (KBr): 2928, 1679, 1486, 1378, 1262, 1156, 1059 cm−1; HRMS (ESI, m/z): [M+H]+ Calcd. for C_{16}H_{24}N_{4}O_{2}+H, 305.1972; found, 305.1974.

(E)-N'-Benzylidene-N-(Piperidine-1-Carbonylpiperidine-1-Carbohydrazide (3r)

30.4 mg, 89% yield; yellow solid, mp: 127−128 °C; TLC (petroleum ether/ethyl acetate, 1:1 v/v): Rf = 0.37; 1H NMR (400 MHz, CDCl3) δ 7.76 (s, 1H), 7.63−7.65 (s, 2H), 7.37−7.38 (s, 3H), 3.54 (s, 9H), 1.65 (s, 13H); 13C NMR (100 MHz, CDCl3) δ 155.1, 144.8, 134.6, 129.8, 128.7, 127.1, 46.6, 25.8, 24.4; IR (KBr): 2934, 2857, 1680, 1426, 1259, 1145, 1017 cm−1; HRMS (ESI, m/z): [M+H]+ Calcd. for C_{19}H_{26}N_{4}O_{2}+H, 343.2129; found, 343.2127.

(E)-N,N',N'-Tetramethyl-2-(1-Phenylethylidene)hydrazine-1,1-Dicarboxamide (5a)

24.8 mg, 90% yield; white solid, mp: 161−162 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): Rf = 0.23; 1H NMR (400 MHz, CDCl3) δ 7.81−7.83 (m, 2H), 7.37−7.39 (m, 3H), 3.01 (s, 12H), 2.16 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.6, 157.8, 137.6, 130.0, 128.3, 126.7, 37.3, 16.9; IR (KBr): 2929, 1677, 1488, 1378, 1265, 1177, 1067 cm−1; HRMS (ESI, m/z): [M+H]+ Calcd. for C_{14}H_{20}N_{4}O_{2}+H, 277.1659; found, 277.1658.

(E)-N,N',N'-Tetramethyl-2-(1-(p-tolyl)ethylidene)hydrazine-1,1-Dicarboxamide (5b)
26.1 mg, 90% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \( R_f = 0.23 \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.72 (d, \( J = 8.4 \) Hz, 2H), 7.18 (d, \( J = 8.0 \) Hz, 2H), 3.00 (s, 12H), 2.37 (s, 3H), 2.14 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 163.9, 157.9, 140.2, 134.8, 129.0, 126.7, 37.3, 21.3, 16.8; IR (KBr): 2929, 1677, 1489, 1377, 1265, 1178, 1066 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{15}\)H\(_{22}\)N\(_4\)O\(_2\)+H, 291.1816; found, 291.1815.

\((E)\)-\(N,N,N',N'\)-Tetramethyl-2-(1-(m-tolyl)ethylidene)hydrazine-1,1-Dicarboxamide (5c)

25.2 mg, 87% yield; white solid, mp: 104–105 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \( R_f \) = 0.23; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.64 (s, 1H), 7.58 (d, \( J = 7.6 \) Hz, 1H), 7.21–7.27 (m, 2H), 3.00 (s, 12H), 2.38 (s, 3H), 2.15 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.2, 157.8, 137.9, 137.6, 130.8, 128.2, 127.4, 123.9, 37.3, 21.4, 17.1; IR (KBr): 2929, 1676, 1488, 1377, 1264, 1173, 1063 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{15}\)H\(_{22}\)N\(_4\)O\(_2\)+H, 291.1816; found, 291.1818.

\((E)\)-2-(1-(4-Methoxyphenyl)ethylidene)-\(N,N,N',N'\)-Tetramethylhydrazine-1,1-Dicarboxamide (5d)

27.8 mg, 91% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \( R_f \) = 0.22; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.79 (d, \( J = 8.8 \) Hz, 2H), 6.89 (d, \( J = 8.8 \) Hz, 2H), 3.82 (s, 3H), 2.99 (s, 3H), 2.99 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 163.8, 161.2, 158.0, 130.0, 128.3, 113.6, 55.3, 37.3, 16.6; IR (KBr): 2932, 2853, 1682, 1497, 1378, 1258, 1176, 1029 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{15}\)H\(_{22}\)N\(_4\)O\(_3\)+H, 307.1765; found, 307.1766.

\((E)\)-2-(1-(3-Methoxyphenyl)ethylidene)-\(N,N,N',N'\)-Tetramethylhydrazine-1,1-Dicarboxamide
(5e)

\[
\text{MeO} \quad \begin{array}{c}
\text{N} \quad \text{CONMe}_2 \\
\text{Me} \quad \text{CONMe}_2
\end{array}
\]

26.3 mg, 86% yield; white solid, mp: 112−113 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f \) = 0.22; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.35−7.40 (m, 2H), 7.27−7.31 (m, 1H), 6.95 (dd, \(J = 0.8 \) Hz, \(J = 0.8 \) Hz, 1H), 3.83 (s, 3H), 3.00 (s, 12H), 2.15 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 163.7, 159.5, 157.8, 138.9, 129.2, 119.3, 115.8, 112.1, 55.4, 37.3, 17.1; IR (KBr): 2933, 1683, 1483, 1380, 1269, 1173, 1050 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{15}\)H\(_{22}\)N\(_4\)O\(_3\)+H, 307.1765; found, 307.1767.

\((E)-2\text{-}(1\text{-}(4\text{-Methoxyphenyl)ethylidene})\text{-N,\text{\text{\text{\text{}\text{\text{\text{}N,\text{\text{\text{}N,\text{\text{\text{}N',\text{\text{\text{}N'-Tetramethylhydrazine-1,1-Dicarboxamide}}}}}}}}}}}}\]

(5f)

\[
\text{MeS} \quad \begin{array}{c}
\text{N} \quad \text{CONMe}_2 \\
\text{Me} \quad \text{CONMe}_2
\end{array}
\]

25.8 mg, 80% yield; yellow solid, mp: 170−171 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f \) = 0.21; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.75 (d, \(J = 8.4 \) Hz, 2H), 7.22 (d, \(J = 8.4 \) Hz, 2H), 3.00 (s, 12H), 2.49 (s, 3H), 2.12 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 162.8, 157.8, 141.2, 134.1, 127.1, 125.6, 37.3, 16.6, 15.3; IR (KBr): 2927, 1681, 1488, 1378, 1264, 1177, 1067 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{15}\)H\(_{22}\)N\(_4\)O\(_2\)S+H, 323.1536; found, 323.1232.

\((E)-2\text{-}(1\text{-}(4\text{-Bromophenyl)ethylidene})\text{-N,\text{\text{\text{\text{}N,\text{\text{\text{}N,\text{\text{\text{}N',\text{\text{\text{}N'-Tetramethylhydrazine-1,1-Dicarboxamide}}}}}}}}}}\]

(5g)

\[
\text{Br} \quad \begin{array}{c}
\text{N} \quad \text{CONMe}_2 \\
\text{Me} \quad \text{CONMe}_2
\end{array}
\]

30.8 mg, 87% yield; white solid, mp: 173−174 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f \) = 0.23; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.67−7.70 (m, 2H), 7.48−7.50 (m, 2H), 2.99 (s, 12H), 2.11 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 162.0, 157.6, 136.5, 131.4, 128.3, 124.4, 37.3, 16.7; IR (KBr): 2927, 1681, 1488, 1378, 1264, 1177, 1067 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for
C_{14}H_{19}BrN_4O_2+H, 355.0764; found, 355.0767.

\((E)\)-2-(1-(3-Bromophenyl)ethyldene)-\(N,N,N',N'\)-Tetramethylhydrazine-1,1-Dicarboxamide (5h)

\[
\begin{align*}
\text{Br} & \quad \text{CONMe}_2 \\
\text{N} & \quad \text{CONMe}_2
\end{align*}
\]

32.4 mg, 91% yield; white solid, mp: 171–172 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.23\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.98\) (s, 1H), 7.72 (d, \(J = 7.6\) Hz, 1H), 7.52 (d, \(J = 8.0\) Hz, 1H), 7.26 (d, \(J = 8.4\) Hz, 1H), 3.01 (s, 12H), 2.12 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 161.6, 157.5, 139.6, 132.8, 129.7, 125.4, 122.6, 37.3, 16.9\); IR (KBr): 2931, 1680, 1487, 1377, 1264, 1173, 1065 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{14}H_{19}BrN_4O_2\)\(+\)H, 355.0764; found, 355.0765.

\((E)\)-2-(1-(4-Chlorophenyl)ethyldene)-\(N,N,N',N'\)-Tetramethylhydrazine-1,1-Dicarboxamide (5i)

\[
\begin{align*}
\text{Cl} & \quad \text{CONMe}_2 \\
\text{N} & \quad \text{CONMe}_2
\end{align*}
\]

27.9 mg, 90% yield; white solid, mp: 167–168 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.23\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.76\) (d, \(J = 8.4\) Hz, 2H), 7.34 (d, \(J = 8.4\) Hz, 2H), 3.00 (s, 12H), 2.13 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 162.0, 157.6, 136.0, 136.0, 128.5, 128.0, 37.3, 16.7\); IR (KBr): 2932, 1683, 1488, 1378, 1264, 1176, 1089 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{14}H_{19}ClN_4O_2\)\(+\)H, 311.1269; found, 311.1268.

\((E)\)-2-(1-(3-Chlorophenyl)ethyldene)-\(N,N,N',N'\)-Tetramethylhydrazine-1,1-Dicarboxamide (5j)

\[
\begin{align*}
\text{Cl} & \quad \text{CONMe}_2 \\
\text{N} & \quad \text{CONMe}_2
\end{align*}
\]

28.2 mg, 91% yield; white solid, mp: 156–157 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.23\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.98\) (s, 1H), 7.72 (d, \(J = 7.6\) Hz, 1H), 7.52 (d, \(J = 8.0\) Hz, 1H), 7.26 (d, \(J = 8.4\) Hz, 1H), 3.01 (s, 12H), 2.12 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 161.6, 157.5, 139.6, 132.8, 129.7, 125.4, 122.6, 37.3, 16.9\); IR (KBr): 2931, 1680, 1487, 1377, 1264, 1173, 1065 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{14}H_{19}ClN_4O_2\)\(+\)H, 311.1269; found, 311.1268.
= 0.23; 1H NMR (400 MHz, CDCl$_3$) δ 7.82–7.83 (m, 1H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 3.01 (s, 12H), 2.13 (s, 3H); 13C NMR (100 MHz, CDCl$_3$) δ 161.6, 157.5, 139.4, 134.4, 129.9, 129.5, 126.8, 124.9, 37.3, 16.9; IR (KBr): 2929, 1681, 1487, 1377, 1264, 1174, 1066 cm$^{-1}$; HRMS (ESI, m/z): [M+H]$^+$ Calcd. for C$_{14}$H$_{19}$ClN$_4$O$_2$+H, 311.1269; found, 311.1267.

(5k)

(5k) 25.6 mg, 87% yield; white solid; mp: 137–138 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): $R_f$ = 0.23; 1H NMR (400 MHz, CDCl$_3$) δ 7.80–7.84 (m, 2H), 7.05 (t, $J = 8.8$ Hz, 2H), 3.00 (s, 12H), 2.14 (s, 3H); 13C NMR (100 MHz, CDCl$_3$) δ 163.9 (d, $^1J_{F-C} = 248.3$ Hz), 162.3, 157.7, 133.7 (d, $^4J_{F-C} = 3.3$ Hz), 128.7 (d, $^3J_{F-C} = 8.4$ Hz), 115.2 (d, $^2J_{F-C} = 21.7$ Hz), 37.6, 16.8; IR (KBr): 2929, 1680, 1495, 1378, 1264, 1165, 1070 cm$^{-1}$; HRMS (ESI, m/z): [M+H]$^+$ Calcd. for C$_{14}$H$_{19}$FN$_4$O$_2$+H, 295.1565; found, 295.1562.

(5l)

(5l) 24.4 mg, 83% yield; yellow solid; mp: 139–140 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): $R_f$ = 0.24; 1H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.34 (q, $J = 7.2$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 3.00 (s, 12H), 2.13 (s, 3H); 13C NMR (100 MHz, CDCl$_3$) δ 162.7 (d, $^1J_{F-C} = 243.9$ Hz), 161.6 (d, $^7J_{F-C} = 2.3$ Hz), 157.6, 139.9 (d, $^3J_{F-C} = 7.5$ Hz), 129.8 (d, $^3J_{F-C} = 8.1$ Hz), 122.5 (d, $^4J_{F-C} = 2.8$ Hz), 116.7 (d, $^4J_{F-C} = 2.3$ Hz), 113.5 (d, $^2J_{F-C} = 22.9$ Hz), 37.3, 16.9; IR (KBr): 2931, 1680, 1487, 1378, 1264, 1170, 1068 cm$^{-1}$; HRMS (ESI, m/z): [M+H]$^+$ Calcd. for C$_{14}$H$_{19}$FN$_4$O$_2$+H, 295.1565; found, 295.1566.
(E)-2-(1-(4-Iodophenyl)ethylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide  
\[5m\]

32.6 mg, 81% yield; white solid, mp: 184–185 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.23\); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 7.71, 7.55, 3.00, 2.11\); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta 162.0, 157.6, 137.4, 128.4, 96.5, 37.3, 16.6\); IR (KBr): 2928, 1680, 1486, 1380, 1264, 1174, 1071 cm\(^{-1}\); HRMS (ESI, m/z): \([M+H]^+\) Calcd. for C\(_{14}\)H\(_{19}\)IN\(_4\)O\(_2\)+H, 403.0626; found, 403.0631.

(E)-2-(1-(4-Cyanophenyl)ethylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide  
\[5n\]

24.4 mg, 81% yield; white solid, mp: 193–194 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.23\); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 7.92, 7.66, 3.01, 2.15\); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta 160.4, 157.3, 141.7, 132.1, 127.2, 118.6, 113.2, 37.3, 18.6\); IR (KBr): 2928, 1681, 1489, 1379, 1264, 1174, 1073 cm\(^{-1}\); HRMS (ESI, m/z): \([M+H]^+\) Calcd. for C\(_{15}\)H\(_{19}\)N\(_5\)O\(_2\)+H, 302.1612; found, 302.1609.

Methyl (E)-4-(1-(2,2-Bis(dimethylcarbamoyl)hydrazono)ethyl)benzoate  
\[5o\]

30.1 mg, 90% yield; yellow solid, mp: 162–163 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.20\); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 8.04, 7.88, 3.93, 3.02, 2.17\); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta 166.6, 161.8, 157.5, 141.7, 131.1, \)
129.5, 126.6, 52.2, 37.3, 17.0; IR (KBr): 2933, 1683, 1490, 1379, 1277, 1180, 1110 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{16}\)H\(_{22}\)N\(_4\)O\(_4\)H, 335.1714; found, 335.1714.

\((E)\)-N,N,N',N'-Tetramethyl-2-(1-(4-(Trifluoromethyl)phenyl)ethylidene)hydrazine-1,1-Dicarboxamide (5p)

29.9 mg, 87% yield; yellow solid, mp: 176–177 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.24\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.93 (d, \(J = 8.0 \) Hz, 2H), 7.63 (d, \(J = 8.0 \) Hz, 2H), 3.01 (s, 12H), 2.17 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 161.3, 157.5, 141.0, 131.5 (q, \(2J_{F-C} = 31.4 \) Hz), 127.0, 125.2 (q, \(3J_{F-C} = 3.7 \) Hz), 124.0 (q, \(1J_{F-C} = 270.4 \) Hz), 37.3, 16.9; IR (KBr): 2937, 1681, 1485, 1390, 1265, 1166, 1116, 1068 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{15}\)H\(_{19}\)F\(_3\)N\(_4\)O\(_2\) + H, 345.1533; found, 345.1536.

\((E)\)-N,N,N',N'-Tetramethyl-2-(1-(4-(Methylsulfonyl)phenyl)ethylidene)hydrazine-1,1-Dicarboxamide (5q)

20.2 mg, 57% yield; white solid, mp: 197–198 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.15\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.93–8.01 (m, 4H), 3.05 (s, 3H), 3.02 (s, 12H), 2.18 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 160.5, 157.3, 142.7, 141.3, 127.6, 127.4, 44.5, 37.3, 17.0; IR (KBr): 2930, 1680, 1489, 1383, 1307, 1155, 1082 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{15}\)H\(_{22}\)N\(_4\)O\(_4\)S + H, 355.1435; found, 355.1434.

\((E)\)-N,N,N',N'-Tetramethyl-2-(1-(4-Nitrophenyl)ethylidene)hydrazine-1,1-Dicarboxamide (5r)

\((E)\)-N,N,N',N'-Tetramethyl-2-(1-(4-Nitrophenyl)ethylidene)hydrazine-1,1-Dicarboxamide (5r)
19.6 mg, 61% yield; yellow solid, mp: 197–198 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): 
Rf = 0.20; 1H NMR (400 MHz, CDCl3) δ 8.21 (d, J = 7.2 Hz, 2H), 7.99 (d, J = 7.2 Hz, 2H), 3.03 (s, 12H), 2.19 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 160.0, 157.3, 148.5, 143.5, 127.5, 123.5, 37.3, 17.0; IR (KBr): 2933, 1670, 1503, 1384, 1264, 1172, 1070 cm⁻¹; HRMS (ESI, m/z): [M+H]+ 
Calcd. for C14H19N5O4+H, 322.1510; found, 322.1511.

(E)-2-(1-(3,4-Dichlorophenyl)ethylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (5s)

31.3 mg, 91% yield; white solid, mp: 199–200 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): 
Rf = 0.23; 1H NMR (400 MHz, CDCl3) δ 7.93 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 3.00 (s, 12H), 2.11 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 160.5, 157.4, 137.5, 134.0, 132.6, 130.2, 128.6, 125.9, 37.3, 16.7; IR (KBr): 2927, 1678, 1452, 1377, 1261, 1177, 1067 cm⁻¹; HRMS (ESI, m/z): [M+Na]+ Calcd. for C14H18Cl2N4O2+Na, 367.0699; found, 367.0696.

(E)-N,N,N',N'-Tetramethyl-2-(1-(Naphthalen-2-yl)ethylidene)hydrazine-1,1-Dicarboxamide (5t)

29.3 mg, 90% yield; white solid, mp: 179–180 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): 
Rf = 0.23; 1H NMR (400 MHz, CDCl3) δ 8.16 (s, 1H), 8.07 (d, J = 8.8 Hz, 1H), 7.79–7.87 (m, 3H), 7.47–7.48 (m, 2H), 3.01 (s, 12H), 2.26 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.2, 157.8, 135.1, 134.1, 132.9, 128.7, 127.8, 127.6, 127.0, 126.3, 123.9, 37.4, 16.8; IR (KBr): 2930, 1681, 1488, 1377, 1264, 1175, 1067 cm⁻¹; HRMS (ESI, m/z): [M+H]+ Calcd. for C18H22N4O2+H,
327.1816; found, 327.1814.

\((E)-N,N,N',N'-\text{Tetramethyl-2-(1-\text{Thiophen-2-yl})\text{ethylidene}hydrazine-1,1-Dicarboxamide (5u)}}\)

\[
\begin{align*}
\text{CONMe}_2 & \quad \text{CONMe}_2 \\
\text{S} & \quad \text{Me}
\end{align*}
\]

14.9 mg, 53% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.17\); \(^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}\) \(\delta 7.34−7.36 \text{ (m, 2H)}, 7.03 \text{ (t, } J = 4.4 \text{ Hz, 1H)}, 3.00 \text{ (s, 12H)}, 1.61 \text{ (s, 3H)}; \)

\(^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}\) \(\delta 158.1, 157.5, 142.7, 128.7, 127.7, 127.1, 37.4, 16.7\); IR (KBr): 2925, 1681, 1488, 1373, 1264, 1172, 1062 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for \(C_{12}H_{18}N_4O_2S+H\), 283.1223; found, 283.1226.

\((E)-N,N,N',N'-\text{Tetramethyl-2-(1-\text{Phenylpropylidene}hydrazine-1,1-Dicarboxamide (5v)}}\)

\[
\begin{align*}
\text{CONMe}_2 & \quad \text{CONMe}_2 \\
\text{Et} & \quad \text{N}
\end{align*}
\]

22.1 mg, 76% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.23\); \(^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}\) \(\delta 7.71−7.74 \text{ (m, 2H)}, 7.38−7.40 \text{ (m, 3H)}, 3.00 \text{ (s, 12H)}, 2.60 \text{ (q, } J = 7.6 \text{ Hz, 2H)}, 1.05 \text{ (t, } J = 7.6 \text{ Hz, 3H}); \)

\(^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}\) \(\delta 169.7, 158.3, 136.3, 129.8, 128.3, 127.3, 37.3, 23.3, 10.1\); IR (KBr): 2930, 1678, 1488, 1378, 1265, 1183, 1060 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for \(C_{15}H_{22}N_4O_2S+H\), 291.1816; found, 291.1816.

\((E)-N,N,N',N'-\text{Tetramethyl-2-(1-\text{Phenylbutylidene}hydrazine-1,1-Dicarboxamide (5w)}}\)

\[
\begin{align*}
\text{CONMe}_2 & \quad \text{CONMe}_2 \\
\text{Pr} & \quad \text{N}
\end{align*}
\]

24.3 mg, 80% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:2 v/v): \(R_f = 0.31\); \(^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}\) \(\delta 7.69−7.71 \text{ (m, 2H)}, 7.34−7.39 \text{ (m, 3H)}, 3.01 \text{ (s, 12H)}, 2.54 \text{ (t, } J = 7.6 \text{ Hz, 2H)}, 1.45−1.52 \text{ (m, 2H)}, 0.90 \text{ (t, } J = 7.6 \text{ Hz, 3H}); \)

\(^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}\) \(\delta 168.6, 158.3, 136.8, 129.7, 128.33, 127.2, 37.3, 32.5, 19.1, 14.5\); IR (KBr): 2934, 1680, 1488, 1379, 1268, 1188,
(E)-2-(3,4-Dihydronaphthalen-1(2H)-ylidene)-N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide (5x)

22.3 mg, 74% yield; white solid, mp: 165–166 °C; TLC (petroleum ether/ethyl acetate, 1:2 v/v): $R_f = 0.23$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 (d, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 1H), 2.99 (s, 12H), 2.83 (t, $J = 6.0$ Hz, 2H), 2.25 (t, $J = 6.4$ Hz, 2H), 1.90 (quint, $J = 6.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.6, 157.9, 140.3, 131.9, 130.1, 128.6, 126.3, 125.9, 37.4, 29.6, 28.4, 22.3; IR (KBr): 2934, 1680, 1488, 1377, 1264, 1180, 1061 cm$^{-1}$; HRMS (ESI, m/z): [M+H]$^+$ Calcd. for C$_{16}$H$_{22}$N$_4$O$_2$+H, 303.1816; found, 303.1814.

(E)-N,N,N',N'-Tetramethyl-2-(6,7,8,9-Tetrahydro-5H-Benz[7]annulen-5-ylidene)hydrazine-1,1-Dicarboxamide (5y)

16.1 mg, 51% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:3 v/v): $R_f = 0.17$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.2$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 2.99 (s, 12H), 2.76 (t, $J = 6.4$ Hz, 2H), 2.45 (t, $J = 5.6$ Hz, 2H), 1.74–1.79 (m, 2H), 1.61 (quint, $J = 6.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.5, 157.9, 139.1, 137.6, 129.8, 128.6, 127.8, 126.5, 37.3, 30.2, 25.9, 21.3; IR (KBr): 2934, 2861, 1677, 1486, 1376, 1264, 1172, 1062 cm$^{-1}$; HRMS (ESI, m/z): [M+H]$^+$ Calcd. for C$_{17}$H$_{24}$N$_4$O$_2$+H, 317.1971; found, 317.1971.

(E)-N'(1-Phenylethyldiene)-N-(Piperidine-1-Carbonyl)piperidine-1-Carbohydrazide (5z)
31.7 mg, 89% yield; viscous liquid; TLC (petroleum ether/ethyl acetate, 1:1 v/v): Rf = 0.41; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.81−7.84 (m, 2H), 7.37−7.33 (m, 3H), 3.47 (brs, 9H), 2.18 (s, 3H), 1.61 (brs, 13H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.3, 156.9, 137.8, 129.8, 128.2, 126.7, 46.1, 25.8, 24.5, 16.8; IR (KBr): 2934, 2856, 1679, 1425, 1225, 1145, 1022 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{20}\)H\(_{28}\)N\(_4\)O\(_2\)H, 357.2285; found, 357.2283.

**D. Procedure for the Gram-Scale Synthesis of 3a, 5a and 5g**

![Chemical structure](image)

A 250 mL round bottom flask placed with a magnetic stirring bar, N-tosylhydrazones (10 mmol), Pd(TFA)$_2$ (10 mol %), Cs$_2$CO$_3$ (10 mmol), toluene (100 mL), and azo compound 2a (5 mmol) was vigorously stirred at 90 °C for 12 h under N$_2$ in an oil bath. Then the resulting solution was cooled to room temperature, added water (100 mL), extracted with EtOAc (3 × 100 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product 3a (87%, 1.14 g), 5a (85%, 1.17 g), and 5g (89%, 1.58 g).

**E. Procedure for the Synthesis of Chiral Hydrozones**

![Chemical structure](image)

A 50 mL round bottom flask placed with a magnetic stirring bar, aldehyde (S)-I\(^1\) (1.55 g, 5 mmol), TsNHNH$_2$ (2.23 g, 12 mmol), and MeOH (10 mL) was vigorously stirred at 65 °C for 1 h in an oil bath. Then the resulting solution was cooled to room temperature, concentrated in vacuo. Further
purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product (S)-6a.

3.17 g, 98% yield; yellow solid, mp > 180 °C (decomposed); [α]_D^20 = 4.9 (c 0.143, CH₂Cl₂); TLC (petroleum ether/ethyl acetate, 3:1 v/v): R_f = 0.40; 'H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.24–7.26 (m, 4H), 7.08–7.12 (m, 4H), 6.89 (d, J = 8.4 Hz, 2H), 2.38 (s, 6H); 'C NMR (100 MHz, CDCl₃) δ 145.0, 144.2, 135.2, 134.8, 134.1, 132.9, 130.8, 129.7, 129.1, 127.9, 127.2, 126.6, 122.5, 21.6; IR (KBr): 3034, 2949, 2871, 1678, 1600, 1443, 1358, 1319, 1163, 1071 cm⁻¹; HRMS (ESI, m/z): [M+Na]^+ Calcd. for C₃₆H₃₀N₄O₄S₂+Na, 669.1601; found, 669.1601.

A 25 mL Schlenk tube placed with a magnetic stirring bar, N-tosylhydrazone (S)-6a (0.3 mmol), Pd(TFA)₂ (10 mmol %), Cs₂CO₃ (0.6 mmol), toluene (6 mL), and azo compound 2 (0.9 mmol) was vigorously stirred at 90 °C for 12 h under N₂ in an oil bath. Then the resulting solution was cooled to room temperature, added water (10 mL), extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product 7.

2,2'-(((S)-[1,1'-Binaphthalene]-2,2'-diyl)bis(methanylylidene))bis(N,N,N',N'-Tetramethylhydrazine-1,1-Dicarboxamide) (7a)
125.0 mg, 67% yield; yellow solid, mp: 141−142 °C; [α]D20 = −7.3 (c 0.963, CH2Cl2); TLC (ethyl acetate): Rf = 0.30; 1H NMR (400 MHz, CDCl3) δ 8.21 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.27−7.31 (m, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.94 (s, 2H), 2.72 (s, 24H); 13C NMR (100 MHz, CDCl3) δ 155.1, 140.2, 134.9, 133.9, 133.2, 131.7, 128.9, 128.3, 127.3, 126.6, 122.1, 37.4; IR (KBr): 2931, 2861, 1693, 1483, 1452, 1374, 1262, 1155, 1057 cm−1; HRMS (ESI, m/z): [M+Na]+ Calcd. for C34H38N8O4+Na, 645.2908; found, 645.2913.

N′,N′′′-(((S)-[1,1′-Binaphthalene]-2,2′-diyl)bis(methanylylidene))bis(N-(Piperidine-1-Carbonyl)piperidine-1-Carbohydrazide) (7b)

150.0 mg, 64% yield; yellow solid, mp: 127−128 °C; [α]D20 = 34.4 (c 0.929, CH2Cl2); TLC (ethyl acetate): Rf = 0.30; 1H NMR (400 MHz, CDCl3) δ 8.22 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 7.25−7.29 (m, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.98 (s, 2H), 3.15−3.19 (m, 16H), 1.40−1.48 (m, 24H); 13C NMR (100 MHz, CDCl3) δ 154.0, 139.3, 134.8, 133.6, 133.2, 131.9, 128.9, 128.2, 127.3, 127.2, 126.7, 122.0, 46.4, 25.7, 24.3; IR (KBr): 2937, 2858, 1691, 1420, 1273, 1149, 1023 cm−1; HRMS (ESI, m/z): [M+H]+ Calcd. for C46H54N8O4+H, 783.4341; found, 783.4337.

N′,N′′′-(((S)-[1,1′-Binaphthalene]-2,2′-diyl)bis(methanylylidene))bis(N-(Morpholine-4-Carbonyl)morpholine-4-Carbohydrazide) (7c)
154.1 mg, 65% yield; yellow solid, mp: 147–148 °C; [α]D = 41.7 (c 0.885, CH2Cl2); TLC (ethyl acetate): Rf = 0.30; 1H NMR (400 MHz, CDCl3) δ 8.15 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.02 (s, 2H), 3.44–3.52 (m, 16H), 3.27–3.36 (m, 16H); 13C NMR (100 MHz, CDCl3) δ 153.8, 140.8, 135.1, 134.0, 133.1, 131.3, 129.2, 128.4, 127.7, 127.6, 126.6, 121.6, 66.4, 45.8; IR (KBr): 2965, 2858, 1694, 1452, 1420, 1269, 1222, 1114, 1006 cm⁻¹; HRMS (ESI, m/z): [M+Na]+ Calcd. for C42H46N8O8Na, 813.3331; found, 813.3339.

Reference:


F. X-ray Crystallographic Data

The X-ray crystallographic structure for 5g. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1486805.
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<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td></td>
<td>b = 12.446(3) Å, beta = 90 deg.</td>
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<tr>
<td></td>
<td>c = 25.390(5) Å, gamma = 90 deg.</td>
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<tr>
<td>Volume</td>
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<td>Z, Calculated density</td>
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<td>F(000)</td>
<td>728</td>
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<tr>
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<tr>
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<td>Limiting indices</td>
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<td>R indices (all data)</td>
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<tr>
<td>Largest diff. peak and hole</td>
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</table>
G. NMR Spectra of New Compounds

$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3a

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3a
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3b

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3b
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3c

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3c
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3d

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3d
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3e

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3e
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum for 3f

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3f
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3g

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3g
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3h

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3h
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3i

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3i
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3j

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3j
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3k

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3k
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3l

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3l
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3m

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3m
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3n

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3n
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3o

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3o
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum for 3p

$^{13}C$ NMR (150 MHz, CDCl$_3$) spectrum for 3p
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3q

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3q
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3r

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 3r
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5a

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5a
$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum for 5b

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5b
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5c

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5c
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum for 5d

$^{13}C$ NMR (100 MHz, CDCl$_3$) spectrum for 5d
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5e

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5e
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5f

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5f
\( ^1H \text{ NMR (400 MHz, CDCl}_3 \) spectrum for 5g

\[ \text{CONMe}_2 \]
\[ \text{N}^+ \text{CONMe}_2 \]
\[ \text{Me} \]
\[ \text{Br} \]

\( ^{13}C \text{ NMR (100 MHz, CDCl}_3 \) spectrum for 5g

\[ \text{CONMe}_2 \]
\[ \text{N}^+ \text{CONMe}_2 \]
\[ \text{Me} \]
\[ \text{Br} \]
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5h

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5h
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5i

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5i
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5j

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5j
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5k

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5k
\(^1\)H NMR (400 MHz, CDCl\(_3\)) spectrum for 5l

\[^{13}\]C NMR (100 MHz, CDCl\(_3\)) spectrum for 5l
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5m

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5m
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5n

![H NMR Spectrum](image)

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5n

![C NMR Spectrum](image)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5o

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5o
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5p

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5p
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5q

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5q
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5r

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5r
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5s

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5s
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5t

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5t
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5u

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5u
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5v

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5v
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5w

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5w
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5x

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5x
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5y

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5y
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5z

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 5z
$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum for 6a

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 6a
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 7a

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 7a
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 7b

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 7b
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 7c

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum for 7c