Supporting Information

Synthesis of Bicyclic Imidazoles via [2+3] Cycloaddition between Nitriles and Regioselectively Generated α-Imino Gold Carbene Intermediates

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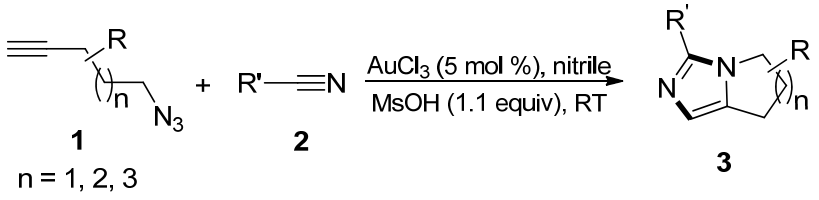
General. Diethyl ether (ACS grade), DMF (ACS grade) and Nitriles (ACS grade) were purchased from Fisher Scientific and used without further purification. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silicycle silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 500 MHz Unity plus spectrometer and a Varian 600 MHz spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization.

Preparation of Starting Materials

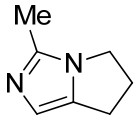
Azidoalkynes **1a-f, 1p, 1s** were easily synthesized according to the previously reported procedures.[1-5]

General procedure for the gold-catalyzed formation of the bicyclic imidazole 3.



To a vial containing a liquid nitrile (2.0 mL) were added sequentially was added an azidoalkyne (**1**, 0.10 mmol), MsOH (10.57mg, 0.11mmol) and $AuCl_3$ (0.005 mmol). The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. Upon the complete consumption of the alkyne, the mixture was basified with saturated aqueous Na_2CO_3 (1 ml) and extracted with DCM (4×3 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography (eluent: DCM /MeOH/NH_4OH = 100 / 5 / 1) to afford the desired bicyclic imidazole **3**.

3-Methyl-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3a):

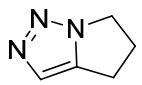


3a

The title compound **3a** was prepared in 89% yield by using 5-Azido-pent-1-yne (**1a**) as the substrate and acetonitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.53 (s, 1H), 3.83 – 3.80 (m, 2H), 2.81 (td, *J* = 7.3, 1.3 Hz, 2H), 2.65 – 2.55 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 136.4, 118.0, 43.3, 29.7, 22.2, 13.2; IR

(neat): 2961.3, 2921.6, 2869.5, 1648.3, 1569.4, 1499.7, 1422.6, 1376.4, 1305.4; MS (ES^+) Calculated for $[C_7H_{11}N_2]^+$: 123.09; Found: 123.09.

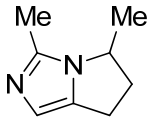
5,6-Dihydro-4H-pyrrolo[1,2-c][1,2,3]triazole (4a):



4a

This triazole side product was isolated from the reaction using BrettPhosAuNTf$_2$ as the catalyst. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 1H), 4.36 – 4.32 (m, 2H), 2.90-2.96 (tt, *J* = 7.3, 0.7 Hz, 2H), 2.84 – 2.76 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 126.7, 46.1, 28.2, 20.5; IR (neat): 2965.2, 2921.2, 1648.4, 1548.3, 1487.0, 1454.7, 1438.0, 1312.0; MS (ES^+) Calculated for $[C_5H_8N_3]^+$: 110.07; Found: 110.07.

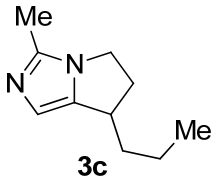
3,5-Dimethyl-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3b):



3b

The title compound **3b** was prepared in 77% yield by using 5-Azido-hex-1-yne **1b** as the substrate and acetonitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (s, 1H), 4.35 – 4.17 (m, 1H), 2.86 – 2.80 (m, 1H), 2.79 – 2.69 (m, 2H), 2.34 (s, 3H), 2.18 (dq, *J* = 12.0, 4.0 Hz, 1H), 1.38 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 136.1, 117.3, 51.9, 37.7, 20.7, 20.4, 13.3; IR (neat): 2972.9, 2932.0, 2871.8, 1642.9, 1571.0, 1495.7, 1418.0, 1382.3, 1346.2; MS (ES^+) Calculated for $[C_8H_{13}N_2]^+$: 137.11; Found: 137.11.

3-Methyl-7-propyl-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3c):

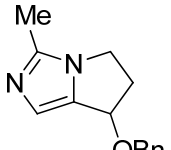


3c

The title compound **3c** was prepared in 71% yield by using 3-(2-azidoethyl)hex-1-yne **1c** as the substrate and acetonitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.54 (d, *J* = 1.2 Hz, 1H), 3.84 (ddd, *J* = 10.6, 8.4, 4.6 Hz, 1H), 3.75 (dt, *J* = 10.6, 7.6 Hz, 1H), 3.15 – 3.04 (m, 1H), 2.71 (dtd, *J* = 12.5, 7.8, 4.6 Hz, 1H), 2.29 (s, 3H), 2.20 (ddt, *J* = 12.8, 8.5, 7.1 Hz, 1H), 1.62 – 1.52 (m, 1H), 1.52 – 1.37 (m, 3H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 138.4, 117.7, 42.8, 36.8, 36.6, 35.7, 21.0, 14.0, 12.9; IR

(neat): 2959.4, 2931.6, 2873.0, 1641.7, 1500.0, 1423.0, 1380.2, 1302.1; MS (ES^+) Calculated for $[C_{10}H_{17}N_2]^+$: 165.14; Found: 165.11.

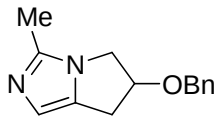
7-Benzyloxy-3-methyl-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3d):



3d

The title compound **3d** was prepared in 83% yield by using [1-(2-azidoethyl)prop-2-ynyloxymethyl]benzene **1d** as the substrate and acetonitrile as the solvent according to the general procedure. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.36 – 7.22 (m, 5H), 6.87 (s, 1H), 4.81 (dd, *J* = 6.2, 1.4 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.01 (ddd, *J* = 10.6, 8.7, 6.9 Hz, 1H), 3.82 (ddd, *J* = 10.7, 8.8, 2.1 Hz, 1H), 2.84 (dtd, *J* = 13.7, 8.8, 6.2 Hz, 1H), 2.67 (ddt, *J* = 13.8, 6.9, 1.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.0, 137.7, 135.8, 128.4, 128.0, 127.8, 120.9, 71.6, 70.2, 42.0, 38.1, 13.0; IR (neat): 2923.8, 2860.2, 1666.7, 1556.3, 1497.3, 1454.4, 1423.2, 1338.7; MS (ES^+) Calculated for $[C_{14}H_{17}N_2O]^+$: 229.13; Found: 229.11.

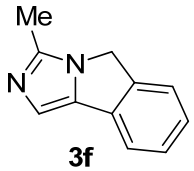
6-Benzyloxy-3-methyl-6,7-dihydro-5H-pyrrolo[1,2-c]imidazole (3e):



3e

The title compound **3e** was prepared in 90% yield by using (1-azidomethyl-but-3-ynyloxymethyl)benzene **1e** as the substrate and acetonitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 6.58 (s, 1H), 4.77 (tt, *J* = 6.5, 4.4 Hz, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.03 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.82 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.12 (ddd, *J* = 15.7, 6.7, 1.1 Hz, 1H), 2.91 (ddd, *J* = 15.7, 4.5, 1.2 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 137.3, 133.0, 128.5, 128.0, 127.7, 119.0, 82.4, 71.6, 49.3, 29.9, 13.1; IR (neat): 2922.9, 2869.0, 1717.5, 1600.2, 1498.7, 1454.5, 1421.9, 1379.0, 1350.1; MS (ES^+) Calculated for $[C_{14}H_{17}N_2O]^+$: 229.13; Found: 229.13.

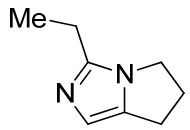
3-Methyl-5*H*-imidazo[5,1-*a*]isoindole (3f):



3f

The title compound **3f** was prepared in 60% yield by using 1-azidomethyl-2-ethynylbenzene **1f** as the substrate and acetonitrile according to the general procedure. The reaction was stopped in 20 h, and there was 14% **1f** remained unreacted. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 1H), 7.42 – 7.30 (m, 2H), 7.24 – 7.17 (m, 1H), 7.07 (s, 1H), 4.82 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 140.3, 137.9, 131.2, 128.2, 125.8, 123.6, 119.7, 117.4, 47.6, 13.2; IR (neat): 2924.0, 1616.2, 1502.1, 1471.2, 1454.8, 1408.9, 1381.2, 1316.0; MS (ES^+) Calculated for $[C_{11}H_{11}N_2]^+$: 171.09; Found: 171.08.

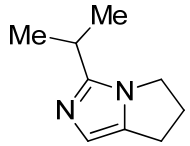
3-Ethyl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazole (3g):



3g

The title compound **3g** was prepared in 78% yield by using 5-azidopent-1-yne **1a** as the substrate and propiononitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (s, 1H), 3.87 – 3.81 (m, 2H), 2.84 – 2.79 (m, 2H), 2.69 – 2.58 (m, 4H), 1.30 (t, J = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 136.3, 117.6, 43.4, 29.6, 22.0, 20.9, 12.1; IR (neat): 2974.7, 2936.8, 1643.1, 1568.4, 1496.4, 1445.3, 1377.2, 1305.5; MS (ES^+) Calculated for $[C_8H_{13}N_2]^+$: 137.11; Found: 137.10.

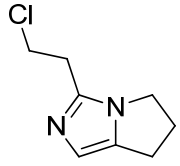
3-Isopropyl-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3h):



3h

The title compound **3h** was prepared in 61% by using 5-azidopent-1-yne **1a** as the substrate and isobutyronitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (s, 1H), 3.91 (t, J = 7.1 Hz, 2H), 2.99 (p, J = 7.0 Hz, 1H), 2.81 (td, J = 7.3, 1.3 Hz, 2H), 2.65 – 2.57 (m, 2H), 1.30 (d, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 136.5, 116.6, 44.0, 29.4, 27.4, 21.7, 21.0; IR (neat): 2969.8, 2929.1, 2871.6, 2144.1, 1673.9, 1494.4, 1441.8, 1378.7, 1365.0, 1321.7; MS (ES^+) Calculated for $[C_9H_{15}N_2]^+$: 151.12; Found: 151.11.

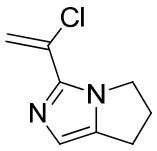
3-(2-Chloroethyl)-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3i):



3i

The title compound **3i** was prepared in 69% yield by using 5-azidopent-1-yne **1a** as the substrate, 3-chloropropionitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (s, 1H), 3.96 (t, *J* = 7.1 Hz, 2H), 3.90 (t, *J* = 6.9 Hz, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 2.86 (td, *J* = 7.3, 1.2 Hz, 2H), 2.64 (p, *J* = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3, 137.0, 117.0, 44.3, 42.8, 30.7, 29.2, 22.2; IR (neat): 2980.7, 2896.7, 2764.0, 1644.2, 1612.4, 1497.7, 1444.8, 1399.2, 1352.0, 1305.9; MS (ES^+) Calculated for $[C_8H_{12}ClN_2]^+$: 171.07; Found: 171.06.

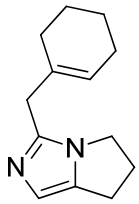
3-(1-Chlorovinyl)-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3j):



3j

The title compound **3j** was prepared in 60% yield by using 5-azidopent-1-yne **1a** as the substrate and 2-chloroacrylonitrile as the solvent according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.73 (s, 1H), 5.94 (d, *J* = 1.8 Hz, 1H), 5.50 (d, *J* = 1.8 Hz, 1H), 4.18 – 4.14 (m, 2H), 2.88 – 2.80 (m, 2H), 2.67-2.58 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 137.7, 129.1, 120.2, 113.9, 46.9, 29.4, 21.7; IR (neat): 2964.9, 2914.6, 1753.9, 1688.0, 1620.7, 1554.8, 1482.2, 1458.9, 1423.3, 1376.7, 1309.2; MS (ES^+) Calculated for $[C_8H_{10}ClN_2]^+$: 169.05; Found: 169.05.

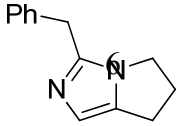
3-Cyclohex-1-enylmethyl-6,7-dihydro-5H-pyrrolo[1,2-c]imidazole (3k):



3k

The title compound **3k** was prepared in 50% yield by using 5-azidopent-1-yne **1a** as the substrate and cyclohex-1-enylacetonitrile as the solvent according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.56 (s, 1H), 5.44 (dt, *J* = 3.5, 1.9 Hz, 1H), 3.81 – 3.77 (m, 2H), 3.31 (d, *J* = 1.8 Hz, 2H), 2.82 – 2.77 (m, 2H), 2.61 – 2.55 (m, 2H), 1.99 (ddd, *J* = 6.0, 4.1, 2.0 Hz, 2H), 1.89 (q, *J* = 3.9, 3.4 Hz, 2H), 1.59 (tdd, *J* = 8.1, 4.9, 2.5 Hz, 2H), 1.54 (dtt, *J* = 9.1, 5.9, 2.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 136.7, 134.0, 123.5, 117.8, 43.7, 36.9, 29.6, 28.0, 25.2, 22.7, 22.2, 22.0; IR (neat): 2928.4, 2859.0, 2836.0, 2251.1, 2220.0, 1712.7, 1675.8, 1568.8, 1488.7, 1444.8, 1375.3; MS (ES^+) Calculated for $[C_{13}H_{19}N_2]^+$: 203.15; Found: 203.14.

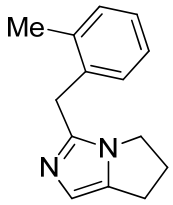
3-Benzyl-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3l)



3l

The title compound **3l** was prepared in 66% yield by using 5-azidopent-1-yne **1a** as the substrate and phenylacetonitrile as the solvent according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 5H), 6.63 (s, 1H), 4.07 (s, 2H), 3.60 (t, *J* = 7.1 Hz, 2H), 2.78 (td, *J* = 7.3, 1.1 Hz, 2H), 2.52 (p, *J* = 7.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 137.2, 137.0, 128.7, 128.6, 126.7, 117.5, 43.8, 34.3, 29.5, 22.0; IR (neat): 2960.1, 1678.3, 1602.9, 1495.0, 1456.8, 1443.3, 1382.6, 1305.1; MS (ES^+) Calculated for $[C_{13}H_{15}N_2]^+$: 199.12; Found: 199.13.

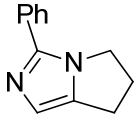
3-(2-Methyl-benzyl)-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3m):



3m

The title compound **3m** was prepared in 55% yield by using 5-azidopent-1-yne **1a** as the substrate and *o*-tolylacetonitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 3H), 7.09 – 7.05 (m, 1H), 6.62 (d, *J* = 1.2 Hz, 1H), 4.05 (s, 2H), 3.53 – 3.50 (m, 2H), 2.77 (td, *J* = 7.3, 1.2 Hz, 2H), 2.54 – 2.45 (m, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 137.0, 136.8, 135.4, 130.4, 129.3, 126.9, 126.0, 117.7, 43.9, 32.5, 29.5, 21.8, 19.6. IR (neat): 2958.7, 1604.3, 1566.6, 1489.1, 1443.0, 1381.2, 1305.1; MS (ES^+) Calculated for $[C_{14}H_{17}N_2]^+$: 213.14; Found: 213.14.

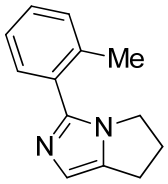
3-Phenyl-6,7-dihydro-5H-pyrrolo[1,2-c]imidazole (3n):



3n

The title compound **3n** was prepared in 80% yield by using 5-azidopent-1-yne **1a** as the substrate and benzonitrile as the solvent according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.73 (m, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.25 (m, 1H), 6.77 (s, 1H), 4.13 (t, *J* = 7.1 Hz, 2H), 2.87 – 2.81 (m, 2H), 2.64 – 2.58 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3, 138.9, 130.9, 128.5, 127.6, 125.6, 119.8, 46.1, 29.7, 21.6; IR (neat): 2961.4, 2961.4, 1676.5, 1604.3, 1562.3, 1512.7, 1481.4, 1460.6, 1446.1, 1412.2, 1370.7, 1310.4; MS (ES^+) Calculated for $[C_{12}H_{13}N_2]^+$: 185.11; Found: 185.12.

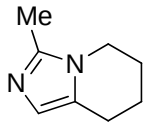
3-o-Tolyl-6,7-dihydro-5*H*-pyrrolo[1,2-*c*]imidazole (3o):



3o

The title compound **3o** was prepared in 75% yield by using 5-azidopent-1-yne **1a** as the substrate and 2-methyl-benzonitrile as the solvent according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.25-7.20 (m, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 2.92 (td, *J* = 7.3, 1.1 Hz, 2H), 2.63 (p, *J* = 7.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 137.6, 137.5, 130.9, 129.0, 128.6, 125.5, 118.8, 45.2, 29.7, 22.3, 20.4; IR (neat): 2961.7, 2926.0, 2866.0, 1755.2, 1671.6, 1562.9, 1507.8, 1482.3, 1467.3, 1412.8, 1369.5, 1305.6; MS (ES^+) Calculated for $[C_{13}H_{15}N_2]^+$: 199.12; Found: 199.11.

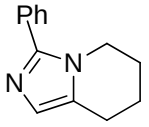
3-Methyl-5,6,7,8-tetrahydroimidazo[1,5-*a*]pyridine (3p):



3p

The title compound **3p** was prepared in 94% yield by using 6-azidohex-1-yne **1p** as the substrate and acetonitrile as the solvent according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.57 (s, 1H), 3.74 (t, *J* = 6.2 Hz, 2H), 2.70 (td, *J* = 6.4, 1.1 Hz, 2H), 2.27 (s, 3H), 1.94 – 1.87 (m, 2H), 1.76 – 1.70 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.6, 127.3, 122.4, 42.4, 23.2, 21.2, 20.3, 12.7; IR (neat): 2947.2, 2866.2, 1662.9, 1570.2, 1542.6, 1510.1, 1418.4, 1390.4, 1330.7; MS (ES^+) Calculated for $[C_8H_{13}N_2]^+$: 137.11; Found: 137.10.

3-Phenyl-5,6,7,8-tetrahydro-imidazo[1,5-a]pyridine (3q):

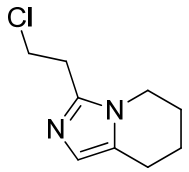


3q

The title compound **3q** was prepared in 84% yield by using 6-azidohex-1-yne **1p** as the substrate and benzonitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 2H), 7.43 (tt, *J* = 6.8, 0.9 Hz, 2H), 7.40 – 7.32 (m, 1H), 6.89 (s, 1H), 4.14 – 3.98 (m, 2H), 2.88 (td, *J* = 6.6, 1.2 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.90 – 1.82 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 131.0, 128.9, 128.3, 128.2, 128.0, 124.5, 44.8, 23.6, 21.2, 20.2; IR (neat):

2946.6, 2866.0, 1605.0, 1559.8, 1510.7, 1477.0, 1445.8, 1412.8, 1378.8, 1331.0; MS (ES^+) Calculated for $[C_{13}H_{14}N_2]^+$: 199.12; Found: 199.12.

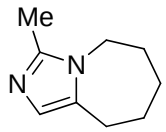
3-(2-Chloroethyl)-5,6,7,8-tetrahydroimidazo[1,5-*a*]pyridine (3r):



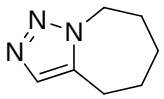
3r

The title compound **3r** was prepared in 75% yield by using 6-azidohex-1-yne **1p** as the substrate and 3-chloropropionitrile as the solvent according to the general procedure. ^{1}H NMR (500 MHz, Chloroform-d) δ 6.81 (s, 1H), 4.01-3.96 (m, 4H), 3.25 (t, *J* = 6.8 Hz, 2H), 2.80-2.77 (m, 2H), 2.06 – 1.95 (m, 2H), 1.88-1.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 128.5, 120.0, 43.2, 42.4, 29.2, 22.7, 20.9, 19.8; IR (neat): 2951.3, 2869.5, 1677.2, 1493.8, 1431.9, 1330.3 ; MS (ES^+) Calculated for $[C_9H_{14}ClN_2]^+$: 185.08; Found: 185.08.

3-Methyl-6,7,8,9-tetrahydro-5*H*-imidazo[1,5-*a*]azepine (3s) and 5,6,7,8-tetrahydro-4*H*-[1,2,3]triazolo[1,5-*a*]azepine (4s):



3s (20%)



4s (36%)

The title compound **3s** was prepared in 20% yield by using 7-azidohept-1-yne **1s** as the substrate and acetonitrile as the solvent according to the general procedure. The corresponding triazole product **4s** due to the intramolecular Huisgen reaction was formed in 36% yield. **3s**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (s, 1H), 3.89 – 3.83 (m, 2H), 2.67 – 2.62 (m, 2H), 2.33 (s, 3H), 1.79 (d, *J* = 5.3 Hz, 2H), 1.70 (t, *J* = 4.9 Hz, 2H), 1.63 (t, *J* = 5.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 133.9, 123.5, 45.9, 31.12, 29.2, 28.2, 25.6, 13.5; IR (neat): 2988.0, 2927.2, 2853.6, 2697.4, 2408.1, 2318.8, 2096.9, 1646.8, 1577.3, 1507.4, 1474.6, 1443.6, 1423.2, 1389.9, 1357.1, 1341.5; MS (ES^+) Calculated for $[C_9H_{15}N_2]^+$: 151.12; Found: 151.11. **4s**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 1H), 4.50 – 4.41 (m, 2H), 2.83 – 2.75 (m, 2H), 1.92 – 1.85 (m, 2H), 1.81 (qd, *J* = 5.7, 2.4 Hz, 2H), 1.68 (p, *J* = 5.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 132.7, 50.9, 30.5, 27.6, 26.6, 23.7; IR (neat): 2931.4, 2856.3, 2096.7, 1647.8, 1557.8, 1470.8, 1432.4, 1362.6, 1343.1; MS (ES^+) Calculated for $[C_7H_{11}N_3Na]^+$: 160.09; Found: 160.09.

Reference:

1. Saito, Y.; Matsumoto, K.; Bag, S. S.; Ogasawara, S.; Fujimoto, K.; Hanawa, K.; Saito, I. *Tetrahedron* **2008**, *64*, 3578-3588.
2. Zhao, S.-C. Shu, X.-Z. Ji, K.-G. Zhou, A.-X. He, T. Liu, X.-Y. and Liang Y.-M. *J. Org. Chem*. **2011**, *76*, 1941–1944.
3. Ko, H. M.; Lee, C. W.; Kwon, H. K.; Chung, H. S.; Choi, S. Y. Chung, Y. K. and Lee, E. *Angew. Chem. Int. Ed*. **2009**, *48*, 2364-2366.
4. Fischer, D.; Tomeba, H.; Pahadi, N. K.; Patil, N. T.; Yamamoto, Y. *Angew. Chem. Int. Ed*. **2007**, *46*, 4764-4766.
5. Karkat, H.; Weibel, J-M.; Pale, P. *Tetrahedron Lett.* **2007**, *48*, 1439-1442.

xiaoyj01-06-1HNMR
H1_CDCL3

Parameter	Value
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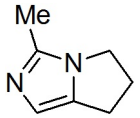
2 Title	xiaoyj01-06-1HNMR
3 Solvent	CDCl3

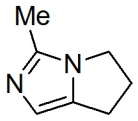


3a

xiaoyj01-06-1CNMR
Std carbon

138.84
136.36
117.96
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
43.28
29.68
22.23
13.18

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-06-1CNMR.fid/ fid
2 Title	xiaoyj01-06-1CNMR
3 Solvent	CDCl3



3a

f1 (ppm)

xiaoyj01-05-1
H1_CDCL3

Parameter	Value
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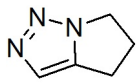
2 Title	xiaoyj01-05-1
3 Solvent	CDCl3

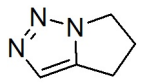


4a

xiaoyj01-05-1C
Std carbon

141.82
126.67
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
46.10
28.19
20.49

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-05-1C.fid/ fid
2 Title	xiaoyj01-05-1C
3 Solvent	CDCl3

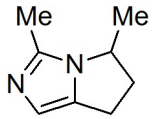


4a

f1 (ppm)

xiaoyj01-46-1bH

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-46-1bH.fid/ fid
2 Title	xiaoyj01-46-1bH
3 Solvent	CDCl3

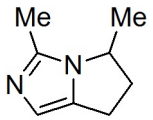


3b

xiaoyj01-46-1bC
Std carbon

138.46
136.05
117.32
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
51.94
37.70
20.74
20.41
13.29

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-46-1bC.fid/ fid
2 Title	xiaoyj01-46-1bC
3 Solvent	CDCl3

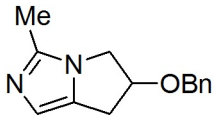


3b

f1 (ppm)

xiaoyj01-43-1H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-43-1H.fid/ fid
2 Title	xiaoyj01-43-1H
3 Solvent	CDCl3

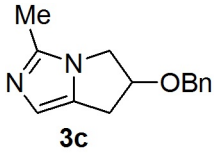


3c

xiaoyj01-43-1C
Std carbon

139.19
137.34
133.02
128.53
127.99
127.69
118.95
82.40
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
71.62
49.34
29.89
13.09

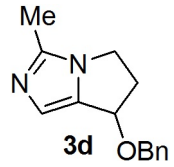
Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-43-1C.fid/ fid
2 Title	xiaoyj01-43-1C
3 Solvent	CDCl3



3c

xiaoyj01-43-5H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-43-5H.fid/ fid
2 Title	xiaoyj01-43-5H
3 Solvent	cdcl3

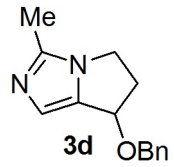


3d

xiaoyj01-43-5C
Std carbon

139.96
137.69
135.80
128.44
128.01
127.76
120.89
77.21 cdcl3
77.00 cdcl3
76.79 cdcl3
71.64
70.15
41.97
38.06
12.98

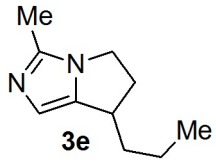
Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-43-5C.fid/ fid
2 Title	xiaoyj01-43-5C
3 Solvent	cdcl3



3d

xiaoyj01-52-2bH

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-52-2bH.fid/ fid
2 Title	xiaoyj01-52-2bH
3 Solvent	CDCl3

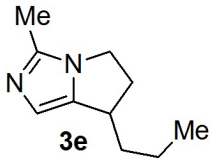


3e

xiaoyj01-52-2bC
Std carbon

140.26
138.41
117.74
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
42.77
36.82
36.57
35.73
20.95
13.96
12.90

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-52-2bC.fid/ fid
2 Title	xiaoyj01-52-2bC
3 Solvent	CDCl3

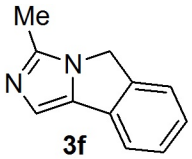


3e

f1 (ppm)

xiaoyj01-29-1b

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-29-1b.fid/ fid
2 Title	xiaoyj01-29-1b
3 Solvent	CDCl3

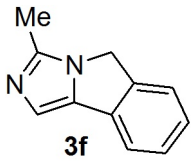


3f

xiaoyj01-29-1bC
Std carbon

140.91
140.34
137.90
131.16
128.20
125.76
123.56
119.69
117.42
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
47.62
13.20

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-29-1bC.fid/ fid
2 Title	xiaoyj01-29-1bC
3 Solvent	CDCl3



3f

f1 (ppm)

xiaoyj01-81-1H

Parameter	Value
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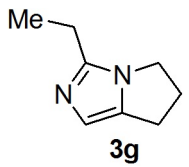
2 Title	xiaoyj01-81-1H
3 Solvent	CDCl3

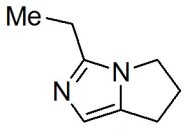


3g

xiaoyj01-81-1C
Std carbon

143.86
136.33
117.59
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
43.35
29.60
21.97
20.91
12.08

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-81-1C.fid/ fid
2 Title	xiaoyj01-81-1C
3 Solvent	CDCl3

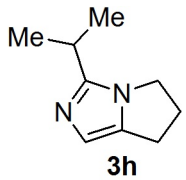


3g

f1 (ppm)

xiaoyj01-101-1H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-101-1H.fid/ fid
2 Title	xiaoyj01-101-1H
3 Solvent	CDCl3

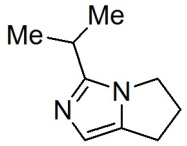


3h

xiaoyj01-101-1C
Std carbon

147.37
136.49
116.63
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
43.95
29.43
27.43
21.72
21.02

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-101-1C.fid/ fid
2 Title	xiaoyj01-101-1C
3 Solvent	CDCl3



3h

f1 (ppm)

xiaoyj01-99-3dH

Parameter	Value
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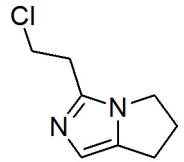
3 Solvent	CDCl3

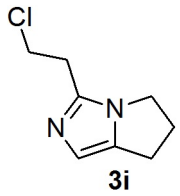


3i

xiaoyj01-99-6dC
Std carbon

139.28
136.98
117.02
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
44.30
42.77
30.68
29.23
22.24

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-99-6dC.fid/ fid
2 Title	xiaoyj01-99-6dC
3 Solvent	CDCl3

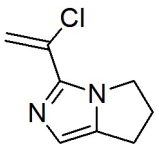


3i

f1 (ppm)

xyj101-5H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xyj101-5H.fid/ fid
2 Title	xyj101-5H
3 Solvent	cdcl3

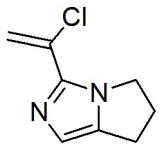


3j

xyj101-5C
Std carbon

139.78
137.70
129.11
120.18
113.85
77.21 cdcl3
77.00 cdcl3
76.79 cdcl3
46.93
29.40
21.66

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xyj101-5C.fid/ fid
2 Title	xyj101-5C
3 Solvent	cdcl3



3j

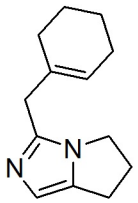
650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

xyj-101-7H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xyj-101-7H.fid/ fid
2 Title	xyj-101-7H
3 Solvent	cdcl3

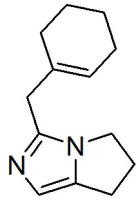


3k

xyj-101-7C
Std carbon

140.79
136.74
133.95
123.49
117.78
77.21 cdcl3
77.00 cdcl3
76.79 cdcl3
43.70
36.88
29.64
28.04
25.22
22.71
22.23
21.95

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xyj-101-7C.fid/ fid
2 Title	xyj-101-7C
3 Solvent	cdcl3

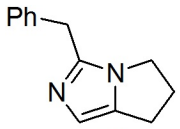


3k

f1 (ppm)

xiaoyj01-101-8H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-101-8H.fid/ fid
2 Title	xiaoyj01-101-8H
3 Solvent	cdcl3

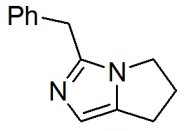


3l

xiaoyj01-101-8C
Std carbon

141.12
137.16
137.02
128.67
128.64
126.67
117.51
77.21 cdcl3
77.00 cdcl3
76.79 cdcl3
43.83
34.25
29.45
21.95

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-101-8C.fid/ fid
2 Title	xiaoyj01-101-8C
3 Solvent	cdcl3

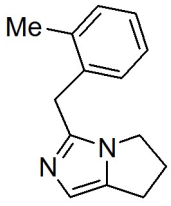


3l

f1 (ppm)

xiaoyj01-101-4H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-101-4H.fid/ fid
2 Title	xiaoyj01-101-4H
3 Solvent	CDCl3

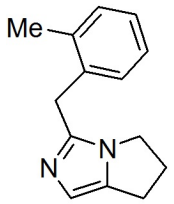


3m

xiaoyj01-101-4C
Std carbon

140.63
137.03
136.77
135.35
130.42
129.32
126.91
126.04
117.74
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
43.87
32.48
29.50
21.80
19.63

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-101-4C.fid/ fid
2 Title	xiaoyj01-101-4C
3 Solvent	CDCl3

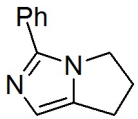


3m

f1 (ppm)

xyj-101-2H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xyj-101-2H.fid/ fid
2 Title	xyj-101-2H
3 Solvent	cdcl3

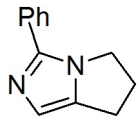


3n

xyj-101-2C
Std carbon

141.29
138.89
130.92
128.51
127.62
125.63
119.75
77.21 cdcl3
77.00 cdcl3
76.79 cdcl3
46.13
29.68
21.58

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xyj-101-2C.fid/ fid
2 Title	xyj-101-2C
3 Solvent	cdcl3

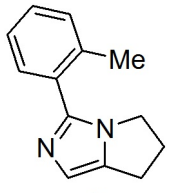


3n

f1 (ppm)

xyj-101-3H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xyj-101-3H.fid/ fid
2 Title	xyj-101-3H
3 Solvent	cdcl3

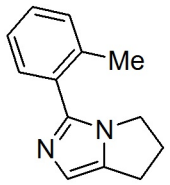


3o

xyj-101-3C
Std carbon

141.42
137.61
137.46
130.90
129.04
128.60
125.50
118.80
45.20
29.74
22.25
20.42

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xyj-101-3C.fid/ fid
2 Title	xyj-101-3C
3 Solvent	cdcl3

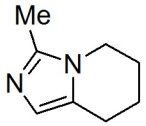


3o

f1 (ppm)

xiaoyj01-19-2-3

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-19-2-3.fid/ fid
2 Title	xiaoyj01-19-2-3
3 Solvent	cdcl3

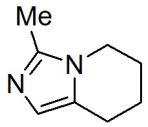


3p

xiaoyj01-19-2-3CNMR
Std carbon

142.64
127.34
122.43
77.21 cdcl3
77.00 cdcl3
76.79 cdcl3
42.41
23.17
21.20
20.33
12.72

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-19-2-3CNMR.fid/ fid
2 Title	xiaoyj01-19-2-3CNMR
3 Solvent	cdcl3

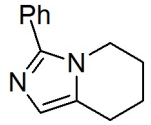


3p

f1 (ppm)

xiaoyj01-123-1H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-123-1H.fid/ fid
2 Title	xiaoyj01-123-1H
3 Solvent	CDCl3

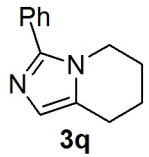


3q

xiaoyj01-123-1C
Std carbon

145.57
131.03
128.87
128.29
128.18
127.98
124.53
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
44.82
23.56
21.17
20.15

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-123-1C.fid/ fid
2 Title	xiaoyj01-123-1C
3 Solvent	CDCl3

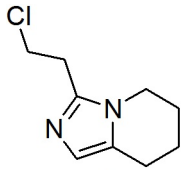


3q

f1 (ppm)

xiaoyj01-123-2H

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-123-2H.fid/ fid
2 Title	xiaoyj01-123-2H
3 Solvent	CDCl3

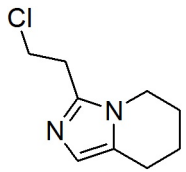


3r

xiaoyj01-123-2C
Std carbon

142.74
128.51
120.00
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
43.20
42.35
29.21
22.74
20.93
19.83

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-123-2C.fid/ fid
2 Title	xiaoyj01-123-2C
3 Solvent	CDCl3

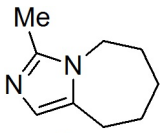


3r

f1 (ppm)

xiaoyj01-27-3aH

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-27-3aH.fid/ fid
2 Title	xiaoyj01-27-3aH
3 Solvent	CDCl3

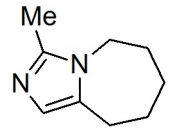


3s

xiaoyj01-27-3aC
Std carbon

143.60
133.90
123.51
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
45.88
31.12
29.17
28.20
25.64
13.53

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-27-3aC.fid/ fid
2 Title	xiaoyj01-27-3aC
3 Solvent	CDCl3

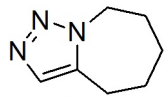


3s

f1 (ppm)

xiaoyj01-27-3bH

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-27-3bH.fid/ fid
2 Title	xiaoyj01-27-3bH
3 Solvent	CDCl3

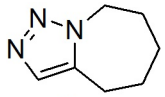


4s

xiaoyj01-27-3bC
Std carbon

138.25
132.67
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
50.88
30.52
27.63
26.60
23.66

Parameter	Value
1 Data File Name	C:/ Users/ zhanglab2/ Desktop/ NMR/ xyj/ xiaoyj01-27-3bC.fid/ fid
2 Title	xiaoyj01-27-3bC
3 Solvent	CDCl3



4s

f1 (ppm)