Efficient Gold(I) Acyclic Diaminecarbenes for the Synthesis of Propargylamines and Indolizines

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Experimental Section

Purification of reaction products was carried out by column chromatography using silical-gel (0.063-0.200 mm). Analytical thin layer chromatography was performed on 0.25 mm silical gel 60-F plates. ^{1}H and $^{13}C\{^{1}H\}$-APT NMR were recorded at room temperature on a BRUKER AVANCE 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) or on a BRUKER AVANCE II 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.5 MHz), with chemical shifts (ppm) reported relative to the solvent peaks of the deuterated solvent. $CDCl_3$, CD_2Cl_2, CD_3COCD_3 and CD_3OD were used as the deuterated solvents. Chemical shifts were reported in the δ scale relative to residual $CHCl_3$ (7.28 ppm), CH_2Cl_2 (5.32 ppm), CH_3COCH_3 (2.05 ppm) and MeOH (3.31) for ^{1}H-NMR and to the central line of $CDCl_3$ (77 ppm), CD_2Cl_2 (54 ppm), CD_3COCD_3 (29.84 ppm) and CD_3OD (49.0 ppm) for ^{13}C-APT-NMR. Mass spectra were recorded on a BRUKER ESQUIRE 3000 PLUS, with the electrospray (ESI) technique. The ATR-FTIR

spectra of solid samples were recorded on a PerkinElmer FT-IR spectrometer equipped with a universal ATR sampling accessory.

The isocyanide complexes [AuCl(CNR)] (R = cyclohexyl (**1a**), ^{t}Bu (**1b**)), previously synthesized,[1] were prepared by the reaction in dichloromethane of [AuCl(tht)] (tht= tetrahydrotiophene) and an equimolecular amount of the corresponding isocyanide CNR. All other reagents were commercially available. Solvents were used as received without purification or drying.

General procedure for the asymmetric Au-catalyzed three-component synthesis of propargylamine 7ab

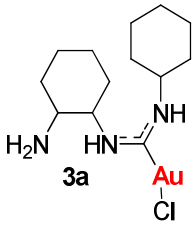
To a mixture of gold complex **3c** or **3d** (0.0025 mmol) and $AgNTf_2$ (2 mg, 0.005 mol), aldehyde **4a** (0.25 mmol), amine **6b** (0.275 mmol) and acetylene **5a** (0.30 mmol) were added under solvent-free conditions. The resulting reaction mixture was stirred at 60 °C for 5 h and monitored by thin-layer chromatography. After this reaction time, the product **7aa** was isolated by flash chromatography (SiO_2, using Hex:Et_2O 95:5). The ee value of **7ab** was 10% using **3c** and racemic mixture for **3d**. Determined by HPLC using a Daicel Chiralpak IA column (*n*-hexane/AcOEt = 95:5, flow rate 0.5 mL min^{-1}, λ = 254.0 nm).

General procedure of the synthesis of the complexes 3a and 3b. A mixture of [AuCl(CNR)] (R = Cy (0.0683 g, 0.2 mmol), R = ^{t}Bu (0.0613 g, 0.2 mmol) and 1,2-cyclohexanediamine (**2a**) (0.0228 g, 0.2 mmol) in dichloromethane (20 mL) was stirred at

[1] a) R. L. White-Morris, M. M. Olmstead, A. L. Balch. O. Elbjeirami, M. A. Omary, *Inorg. Chem.* **2003**, *42*, 6741-6748; b) J. A. McCleverty, M. M. Mota, *J. Chem. Soc. Dalton Trans.* **1973**, 2571-2574; c) A. S. K. Hashmi, Y. Yu, F. Rominger, *Organometallics* **2012**, *31*, 895-904.

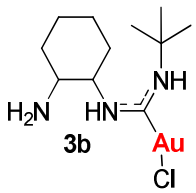
room temperature for 24 h. Complexes **3a** and **3b** precipitated as white solids and were filtered off.

Complex 3a. Yield: 0.0793 g (87%). Anal. Calcd. for $C_{13}H_{25}AuClN_3$ (455.78): C 34.26, H 5.53, N 9.22. Found: C 33.95, H 5.35, N 9.14. **^{1}H NMR** (CD_3OD, 400 MHz) δ 4.53-4.43 (m, CHcy), 4.36-4.22 (m, CHcy), 4.14-4.04 (m, CHcy), 3.94-3.86 (m, CHcy), 3.85-3.77 (m, CHcy), 3.56-3.46 (m, CHcy), 3.42-3.34 (m, CHcy), 2.28-1.17 (m, CH_2cy). **^{13}C-APT NMR** (CD_3OD, 101 MHz) δ 191.0 (s, $C_{carbene}$), 190.9 (s, $C_{carbene}$), 68.9 (s, CH), 68.7 (s, CH), 68.3 (s, CH), 68.1 (s, CH), 67.9 (s, CH), 67.7 (s, CH), 67.2 (s, CH), 67.0 (s, CH), 60.5 (s, CH), 60.3 (s, CH), 60.2 (s, CH), 59.2 (s, CH), 59.1 (s, CH), 58.7 (s, CH), 58.4 (s, CH), 58.3 (s, CH), 57.9 (s, CH), 53.1 (s, CH), 53.0 (s, CH), 35.9 (s, CH_2), 35.8 (s, CH_2), 35.7 (s, CH_2), 35.6 (s, CH_2), 35.5 (s, CH_2), 35.4 (s, CH_2), 35.3 (s, CH_2), 35.0 (s, CH_2), 34.9 (s, CH_2), 34.8 (s, CH_2), 34.6 (s, CH_2), 34.5 (s, CH_2), 33.2 (s, CH_2), 33.1 (s, CH_2), 33.0 (s, CH_2), 33.0 (s, CH_2), 32.9 (s, CH_2), 32.8 (s, CH_2), 32.5 (s, CH_2), 27.0 (s, CH_2), 26.9 (s, CH_2), 26.4 (s, CH_2), 26.2 (s, CH_2), 26.1 (s, CH_2), 25.9 (s, CH_2), 25.7 (s, CH_2), 25.0 (s, CH_2), 24.9 (s, CH_2), 24.8 (s, CH_2). HRMS (ESI-QTOF) m/z (%): $[M\text{-}Cl]^+$ (100 %) Calcd for $C_{13}H_{25}AuN_3$ 420.1709; Found 420.1759. **IR:** υ(NH): 3068, 2922, 2853; υ(Au-Cl): 310 cm^{-1}. $[\alpha]_D^{20}$ -1.12 (*c* 0.23, MeOH).



3a

Complex 3b. Yield: 0.0627 g (73%). Anal. Calcd for $C_{11}H_{23}AuClN_3$ (429.74): C 30.74, H 5.39, N 9.78. Found: C 30.48, H 5.31, N 9.79. **^{1}H NMR** (CD_3OD, 400 MHz) δ 4.47-4.37 (m, 1H, CHcy), 3.43-3.34 (m, 1H, CHcy), 2.24-2.15 (m, 1H, CH_2cy), 2.03-1.91 (m, 2H, CH_2cy), 1.90-181 (m, 1H, CH_2cy), 1.56 (s, 9H, CH_3), 1.64-1.27 (m, 4H, CH_2cy). **^{13}C-APT NMR** (CD_3OD, 101 MHz) δ 192.0 (s, 1C, $C_{carbene}$), 69.4 (s, 1C, CH), 58.3 (s, 1C, CH), 54.1 (s, 1C, CMe_3), 35.5 (s, 1C, CH_2), 33.2 (s,

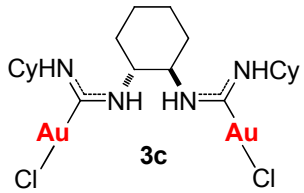


3b

1C, CH_2), 31.6 (s, 3C, CH_3), 26.9 (s, 1C, CH_2), 24.9 (s, 1C, CH_2). HRMS (ESI-QTOF) m/z (%): $[M+H]^+$ (1%) Calcd for $C_{11}H_{24}AuClN_3$ at m/z = 430.1319, Found 430.1327; $[M-Cl]^+$ (70%) Calcd for $C_{11}H_{23}AuN_3$ 394.1552, Found 394.1524. IR: υ(NH): 3107, 2957, 2885; υ(Au-Cl): 301 cm^{-1}.

General procedure of the synthesis of the complexes 3c and 3d. A mixture of [AuCl(CNR)] (R = Cy) (0.0683 g, 0.2 mmol) and (1*R*,2*R*)-1,2-cyclohexanediamine (**2b**) (0.0114 g, 0.1 mmol) or (1*R*,2*R*)-(-)-*N*-*p*-tosyl-1,2-cyclohexanediamine (**2c**) (0.0537 g, 0.2 mmol) in dichloromethane (20 mL), was stirred at room temperature for 4 days (**3c**) or 24 h (**3d**). The volume was reduced to 5 mL, and addition of *n*-hexane afforded **3c** or **3d** as white solids which were finally filtered.

Complex 3c. Yield: 0.0502 g (63%). Anal. Calcd for $C_{20}H_{36}Au_2Cl_2N_4$ (797.38): C 30.13, H 4.55, N 7.03. Found: C 30.54, H 4.80, N 6.94. **^{1}H NMR** (CD_3OD, 400 MHz) δ 4.53-4.42 (m, CHcy), 4.37-4.26 (m, CHcy), 4.19-4.06 (m, CHcy), 3.89-3.77 (m, CHcy), 3.56-3.45 (m, CHcy), 3.44-3.33 (m, CHcy), 2.25-1.13 (m, CH_2cy). **^{13}C-APT NMR** (CD_3OD, 101 MHz) δ 190.9 (s, $C_{carbene}$), 185.9 (s, $C_{carbene}$), 185.8 (s, $C_{carbene}$), 68.9 (s, CH), 68.7 (s, CH), 68.3 (s, CH), 68.1 (s, CH), 60.5 (s, CH), 58.3 (s, CH), 58.3 (s, CH), 57.8 (s, CH), 56.4 (s, CH), 56.4 (s, CH), 56.3 (s, CH), 53.1 (s, CH), 53.0 (s, CH), 35.8 (s, CH_2), 35.7 (s, CH_2), 35.6 (s, CH_2), 35.6 (s, CH_2), 35.0 (s, CH_2), 34.9 (s, CH_2), 34.8 (s, CH_2), 33.2 (s, CH_2), 33.1 (s, CH_2), 33.0 (s, CH_2), 32.9 (s, CH_2), 32.5 (s, CH_2), 27.0 (s, CH_2), 26.9 (s, CH_2), 26.4 (s, CH_2), 26.2 (s, CH_2), 26.0 (s, CH_2), 25.7 (s, CH_2), 25.0 (s, CH_2), 24.9 (s, CH_2), 23.8 (s, CH_2). HRMS (ESI-QTOF) m/z (%): $[M-Cl]^+$ (100 %) Calcd for $C_{20}H_{36}Au_2ClN_4$ 761.1954; Found 761.1910. IR: υ(NH): 3048, 2926, 2851; υ(Au-Cl): 322 cm^{-1}. $[\alpha]_D^{20}$ -26.07 (*c* 0.21, MeOH).



3c

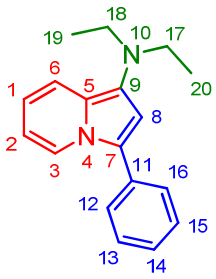
Complex 3d. Yield: 0.0829 g (68%). Anal. Calcd for $C_{20}H_{31}AuClN_3O_2S$ (609.97): C 39.38, H 5.12, N 6.90. Found: C 39.17, H 5.12, N 6.69. **^{1}H NMR** (CD_2Cl_2, 400 MHz) δ 7.89-7.83 (m, rotamer A, Ph), 7.77-7.70 (m, rotamer B, rotamer C, Ph), 7.38-7.28 (m, rotamer A, rotamer B, rotamer C, Ph), 4.00-3.79 (m, CHcy), 3.47-3.34 (m, CHcy), 3.29-3.00 (m, CHcy), 2.43 (s, rotamer B or C, CH_3), 2.42 (s, rotamer B or C, CH_3), 2.41 (s, rotamer A, CH_3), 2.30-1.02 (m, CH_2cy). **^{13}C-APT NMR** (CD_2Cl_2, 101 MHz) δ 144.4 (s, Ph), 144.3 (s, Ph), 139.0 (s, Ph), 138.8 (s, Ph), 138.5 (s, Ph), 130.4 (s, Ph), 130.3 (s, Ph), 127.5 (s, Ph), 127.3 (s, Ph), 127.1 (s, Ph), 64.1 (s, CH), 63.8 (s, CH), 59.4 (s, CH), 57.8 (s, CH), 57.4 (s, CH), 57.3 (s, CH), 54.9 (s, CH), 52.0 (s, CH), 35.3 (m, CH_2cy), 34.6 (m, CH_2cy), 34.5 (m, CH_2cy), 33.1 (m, CH_2cy), 32.5 (m, CH_2cy), 32.1 (m, CH_2cy), 31.8 (m, CH_2cy), 25.8 (m, CH_2cy), 25.7 (m, CH_2cy), 25.6 (m, CH_2cy), 25.4 (m, CH_2cy), 25.3 (m, CH_2cy), 25.1 (m, CH_2cy), 25.0 (m, CH_2cy), 24.8 (m, CH_2cy), 24.7 (m, CH_2cy), 24.5 (m, CH_2cy), 21.8 (s, 1C, CH_3). $[M\text{-}Cl]^+$ (3.46 %) Calcd for $C_{20}H_{31}AuN_3O_2S$ 574.1797; Found 574.1829. IR: (NH): 3084, 2926, 2855; (Au-Cl): 312 cm^{-1}.

***N*-butyl-*N*-(1-phenyl-3-p-tolylprop-2-ynyl)butan-1-amine (7abf)**

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63-7.56 (m, 2H, CH, $H_{3,5}$), 7.33 (d, $^1J_{H\text{-}H}$ = 8.1 Hz, 2H, CH, $H_{12,16}$), 7.26 (t, $^1J_{H\text{-}H}$ = 7.4 Hz, 2H, CH, $H_{2,6}$), 7.19-7.15 (m, 1H, CH, H_1), 7.05 (d, $^1J_{H\text{-}H}$ = 7.8 Hz, 2H, CH, $H_{13,14}$), 4.93 (s, 1H, CH, H_7), 2.41(t, $^1J_{H\text{-}H}$ = 7.2 Hz, 4H, CH_2, $H_{17,18}$), 2.29 (s, 3H, CH_3, H_{21}), 1.36-1.17 (m, 8H, CH_2, $H_{19,20,22,23}$), 0.77 (t, $^1J_{H\text{-}H}$ = 7.3 Hz, 6H, CH_3, $H_{24,25}$). **^{13}C-APT NMR** ($CDCl_3$, 100 MHz) δ 140.1 (s, 1C, C_q), 138.0 (s, 1C, C_q), 131.7 (s, 2C, C_{Ar}), 129.0 (s, 2C, C_{Ar}), 128.4 (s, 2C, C_{Ar}), 127.9 (s, 2C, C_{Ar}), 127.1 (s, 1C, C_{Ar}), 120.4 (s, 1C, C_q), 87.5 (s, 1C, C_8), 85.3 (s, 1C, C_{10}), 57.4 (s, 1C, C_7),

50.6 (s, 2C, $C_{17,18}$), 30.4 (s, 2C, $C_{19,20}$), 21.4 (s, 1C, C_{21}), 20.5 (s, 2C, $C_{22,23}$), 14.0 (s, 2C, $C_{24,25}$). HRMS (ESI-QTOF) m/z (%): $[M+H]^+$ Calcd for $C_{24}H_{32}N$ 334.2529; Found 334.2569.

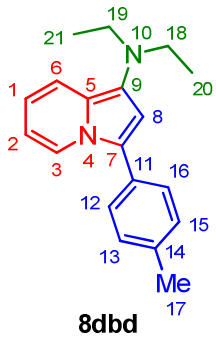
***N,N*-diethyl-3-phenylindolizin-1-amine (8dad)**



8dad

^{1}H NMR (CD_2Cl_2, 300 MHz) δ 8.24 (d, $^1J_{H\text{-}H}$ = 7.2 Hz, 1H, H_{Ar}), 7.60-7.57 (m, 2H, H_{Ar}), 7.50-7.45 (m, 3H, H_{Ar}), 7.34-7.29 (m, 1H, H_{Ar}), 6.78 (s, 1H, H_8), 6.59-6.54 (m, 1H, H_2), 6.44-6.39 (m, 1H, H_1), 3.09 (c, 4H, $H_{17,18}$), 1.04 (t, $^1J_{H\text{-}H}$ = 7.1 Hz, 6H, $H_{19,20}$). **^{13}C-APT NMR** (CD_2Cl_2, 75 MHz) δ 133.5 (s, 1C, C_q), 129.6 (s, 2C, $C_{13,15}$), 129.5 (s, 1C, C_q), 128.3 (s, 2C, $C_{12,16}$), 127.7 (s, 1C, C_q), 127.4 (s, 1C, C_{14}), 123.6 (s, 1C, C_q), 122.3 (s, 1C, C_3), 118.7 (s, 1C, C_6), 115.6 (s, 1C, C_2), 111.3 (s, 1C, C_1), 109.2 (s, 1C, C_8), 50.9 (s, 2C, $C_{17,18}$), 13.7 (s, 2C, $C_{19,20}$). HRMS (ESI-QTOF) m/z (%): $[M]^+$ Calcd for $C_{18}H_{20}N_2$ 264.1621; Found 264.1622.

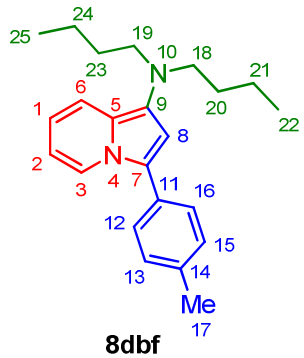
***N,N*-diethyl-3-*p*-tolylindolizin-1-amine (8dbd)**



8dbd

^{1}H NMR (CD_3COCD_3, 400 MHz) δ 8.24 (br s, $^1J_{H\text{-}H}$ = 7.2 Hz, 1H, H_{Ar}), 7.53-7.40 (m, 3H, H_{Ar}), 7.35-7.25 (m, 2H, H_{Ar}), 6.79 (s, 1H, H_8), 6.51-6.38 (m, 1H, H_1), 3.40-2.70 (m, 4H, $H_{18,19}$), 2.38 (s, 3H, H_{17}), 0.98 (t, $^1J_{H\text{-}H}$ = 7.1 Hz, 6H, $H_{20,21}$). **^{13}C-APT NMR** (CD_3COCD_3, 75 MHz) δ 137.2 (s, 1C, C_q), 130.4 (s, 2C, $C_{13,15}$), 129.7 (s, 1C, C_q), 128.4 (s, 2C, $C_{12,16}$), 127.5 (s, 1C, C_q), 123.8 (s, 1C, C_q), 122.5 (s, 1C, C_6), 118.7 (s, 1C, C_3), 115.6 (s, 1C, C_2), 111.6 (s, 1C, C_1), 108.9 (s, 1C, C_8), 51.0 (s, 2C, $C_{18,19}$), 21.2 (s, 1C, C_{17}), 13.7 (s, 2C, $C_{20,21}$). HRMS (ESI-QTOF) m/z (%): $[M]^+$ Calcd for $C_{19}H_{22}N_2$ 278.1778; Found 278.1769.

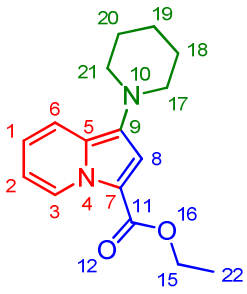
***N,N*-dibutyl-3-*p*-tolylindolizin-1-amine (8dbf)**



8dbf

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.18 (d, J = 7.2 Hz, 1H, H_3), 7.53-7.42 (m, 3H, $H_{6,12,16}$), 7.29 (d, J = 8.0 Hz, 2H, $H_{13,15}$), 6.75 (s, 1H, H_8), 6.53 (dd, J = 8.8 Hz, 6.4 Hz, 1H, H_2), 6.41-6.36 (m, 1H, H_1), 2.99 (t, J = 7.0 Hz, 4H, $H_{19,20}$), 2.41 (s, 3H_{17}), 1.50-1.30 (m, 8H, $H_{20,21,23,24}$), 0.90 (t, J = 7.1 Hz, 6H, $H_{22,25}$). **^{13}C-APT NMR** (CD_2Cl_2, 100 MHz): δ 133.2 (s, 1C, C_q),126.4 (s, 1C, C_q), 126.1 (s, 2C, $C_{13,15}$), 124.9 (s, 1C, C_q), 124.5 (s, 1C, C_q),124.1 (s, 2C, $C_{12,16}$), 119.5 (s, 1C, C_q), 118.2 (s, 1C, C_6), 114.5 (s, 1C, C_3), 111.1 (s, 1C, C_2), 107.0 (s, 1C, C_1), 104.7 (s, 1C, C_8), 53.3 (s, 2C, $C_{18,19}$), 26.9 (s, 2C, $C_{20,23}$), 17.5 (s, 1C, C_{17}), 17.0 (s, 2C, $C_{21,24}$),10.5 (s, 2C, $C_{22,25}$). HRMS (ESI-QTOF) m/z (%): $[M+H]^+$ Calcd for $C_{23}H_{31}N_2$ 335.2482; Found 335.2482.

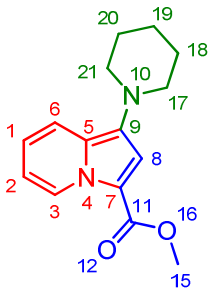
Ethyl 1-(piperidin-1-yl)indolizine-3-carboxylate (8dca)



8dca

^{1}H NMR ($CD_3C(O)CD_3$, 300 MHz) δ 8.19 (d, $^{1}J_{H\text{-}H}$ = 7.1 Hz, 1H, H_{Ar}), 7.33 (d, $^{1}J_{H\text{-}H}$ = 7.1 Hz, 1H, H_{Ar}), 6.74-6.56 (m, 3H, H_{Ar}), 4.31 (q, $^{1}J_{H\text{-}H}$ = 7.1 Hz, 2H, H_{15}), 3.45-3.36 (m, 1H, $H_{17,21}$), 3.27-3.15 (m, 1H, $H_{17,21}$), 2.88-2.70 (m, 2H, $H_{17,21}$), 1.85-1.51 (m, 6H, $H_{18,19,20}$), 1.37 (t, $^{1}J_{H\text{-}H}$ = 7.1 Hz, 6H, $H_{19,20}$). **^{13}C-APT NMR** ($CD_3C(O)CD_3$, 75 MHz) δ 165.2 (s, 1C, C_{11}), 136.4 (s, 1C, C_q), 128.2 (s, 1C, C_q), 122.7 (s, 1C, C_6), 120.5 (s, 1C, C_3), 118.8 (s, 1C, C_2), 113.4 (s, 1C, C_q), 112.1 (s, 1C, C_1), 100.3 (s, 1C, C_8), 60.4 (s, 1C, C_{15}), 51.2 (s, 2C, $C_{17,21}$), 27.8 (s, 2C, $C_{18,20}$), 24.9 (s, 1C, C_{19}), 14.9 (s, 1C, C_{22}). HRMS (ESI-QTOF) m/z (%): $[M+Na]^+$ Calcd for $C_{16}H_{20}N_2NaO_2$ 295.1417; Found 295.1424.

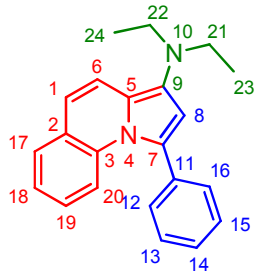
Methyl 1-(piperidin-1-yl)indolizine-3-carboxylate (8dda)



8dda

^{1}H NMR ($CD_3C(O)CD_3$, 300 MHz) δ 8.19 (d, $^{1}J_{H\text{-}H}$ = 7.1 Hz, 1H, H_{Ar}), 7.34 (d, $^{1}J_{H\text{-}H}$ = 7.1 Hz, 1H, H_{Ar}), 6.74-6.57 (m, 3H, H_{Ar}), 3.83 (s, 3H, H_{15}), 3.50-3.37 (m, 1H, $H_{17,21}$), 3.28-3.18 (m, 1H, $H_{17,21}$), 2.88-2.77 (m, 2H, $H_{17,21}$), 1.91-1.50 (m, 6H, $H_{18,19,20}$). **^{13}C-APT NMR** ($CD_3C(O)CD_3$, 75 MHz) δ 165.6 (s, 1C, C_{11}), 128.3 (s, 1C, C_q), 122.8 (s, 1C, C_6), 120.6 (s, 1C, C_3), 118.9 (s, 1C, C_2), 112.8 (s, 1C, C_q), 112.2 (s, 1C, C_1), 100.1 (s, 1C, C_8), 51.4 (s, 1C, C_{15}), 51.2 (s, 2C, $C_{17,21}$), 27.8 (s, 2C, $C_{18,20}$), 24.9 (s, 1C, C_{19}), 14.9 (s, 1C, C_{22}). HRMS (ESI-QTOF) m/z (%): $[M+Na]^+$ Calcd for $C_{15}H_{18}N_2NaO_2$ 281.1260; Found 281.1253.

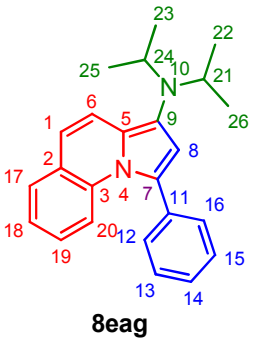
***N,N*-diethyl-1-phenylpyrrolo[1,2-*a*]quinolin-3-amine (8ead)**



8ead

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.64-7.37 (m, 8H, H_{Ar}), 7.25-7.17 (m, 1H, H_{Ar}), 7.13-7.05 (m, 1H, H_{Ar}), 6.93 (d, $^{1}J_{H\text{-}H}$ = 9.2 Hz,1H, H_{Ar}), 6.59 (s, 1H, H_8), 3.24-3.04 (m, 4H, $H_{20,21}$), 1.11 (t, $^{1}J_{H\text{-}H}$ = 7.1 Hz, 6H, $H_{23,24}$). **^{13}C-APT NMR** ($CDCl_3$, 75 MHz) δ: 135.6 (s, 1C C_q), 134.1 (s, 1C C_q), 129.1 (s, 2C C_{Ar}), 128.5 (s, 2C, C_{Ar}), 128.3 (s, 1C, C_{Ar}), 127.6 (s, 1C, C_q), 127.5 (s, 1C, C_{Ar}), 126.1 (s, 1C, C_{Ar}), 125.9 (s, 1C, C_q), 123.2 (s, 1C, C_{Ar}), 117.6 (s, 1C, C_{Ar}), 117.6 (s, 1C, C_{Ar}), 110.4 (s, 1C, C_{Ar}), 29.69 (s, 2C, $C_{21,22}$), 12.8 (s, 2C, $C_{23,24}$). HRMS (ESI-QTOF) m/z (%): $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$ 315.1856; Found 315.1846.

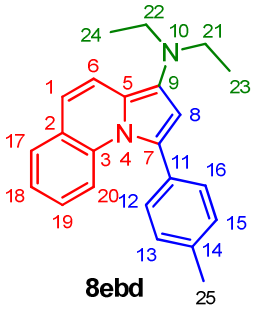
***N,N*-diisopropyl-1-phenylpyrrolo[1,2-a]quinolin-3-amine (8eag)**



8eag

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.60-7.41 (m, 8H, H_{Ar}), 7.20 (t, $^{1}J_{H\text{-}H}$ = 7.2 Hz, 1H, H_{Ar}), 7.10 (t, $^{1}J_{H\text{-}H}$ = 7.7 Hz, 1H, H_{Ar}), 6.92 (d, $^{1}J_{H\text{-}H}$ = 9.2 Hz, 1H, H_{Ar}), 6.59 (s, 1H, H_8), 3.59-3.41 (m, 2H, $H_{21,24}$),1.05 (d, $^{1}J_{H\text{-}H}$ = 6.4 Hz, 12H, $H_{22,23,25,26}$). **^{13}C-APT NMR** ($CDCl_3$, 100 MHz) δ: 135.9 (s, 1C, C_q), 134.1 (s, 1C, C_q), 132.1 (s, 1C, C_q), 129.2 (s, 2C, C_{Ar}), 128.4 (s, 2C, C_{Ar}), 128.2 (s, 1C, C_{Ar}), 127.5 (s, 1C, C_q), 127.2 (s, 1C, C_{Ar}), 125.9 (s, 1C, C_{Ar}), 123.9 (s, 1C, C_q), 122.9 (s, 1C, C_{Ar}), 118.4 (s, 1C, C_{Ar}), 117.5 (s, 2C, C_{Ar}), 117.0 (s, 1C, C_{Ar}), 50.5 (s, 2C, $C_{21,24}$), 21.5 (s, 4C, $C_{22,23,25,26}$). HRMS (ESI-QTOF) m/z (%): $[M+H]^+$ Calcd for $C_{24}H_{27}N_2$ 343.2169; Found 343.2185.

***N,N*-diethyl-1-p-tolylpyrrolo[1,2-a]quinolin-3-amine (8ebd)**



8ebd

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.56-7.49 (m, 3H, H_{Ar}), 7.41 (d, $^{1}J_{H\text{-}H}$ = 7.6 Hz, 1H, H_{Ar}), 7.26 (d, $^{1}J_{H\text{-}H}$ = 7.87 Hz, 2H, H_{Ar}), 7.19 (t, $^{1}J_{H\text{-}H}$ = 7.4 Hz, 2H, H_{Ar}), 7.08 (t, $^{1}J_{H\text{-}H}$ = 7.5 Hz, 1H, H_{Ar}), 6.89 (d, $^{1}J_{H\text{-}H}$ = 9.2 Hz, 1H, H_{Ar}), 6.55 (s, 1H, H_8), 3.17-3.05 (m, 4H, $H_{21,22}$), 2.46 (s, 3H, H_{25}), 1.08 (t, $^{1}J_{H\text{-}H}$ = 7.1 Hz, 6H, $H_{23,24}$). **^{13}C-APT NMR** ($CDCl_3$, 75 MHz) δ: 137.4 (s, 1C, C_q), 134.2 (s, 1C, C_q), 132.6 (s, 1C, C_q), 129.2 (s, 2C, C_{Ar}), 129.1 (s, 2C C_{Ar}), 128.2 (s, 1C, C_{Ar}), 127.4 (s, 1C, C_q), 126.1 (s, 1C, C_{Ar}), 125.9 (s, 1C, C_q), 123.2 (s, 1C, C_{Ar}), 117.6 (s, 2C, C_{Ar}), 110.2 (s, 1C, C_{Ar}), 51.0 (s, 2C, $C_{21,22}$), 21.3 (s, 1C, C_{25}), 12.8 (s, 2C, $C_{23,24}$). HRMS (ESI-QTOF) m/z (%): $[M+H]^+$ Calcd for $C_{23}H_{25}N_2$ 329.2012; Found 329.2002.

Figure S1. ^{1}H NMR gold (I) acyclic(amine)carbene 3a

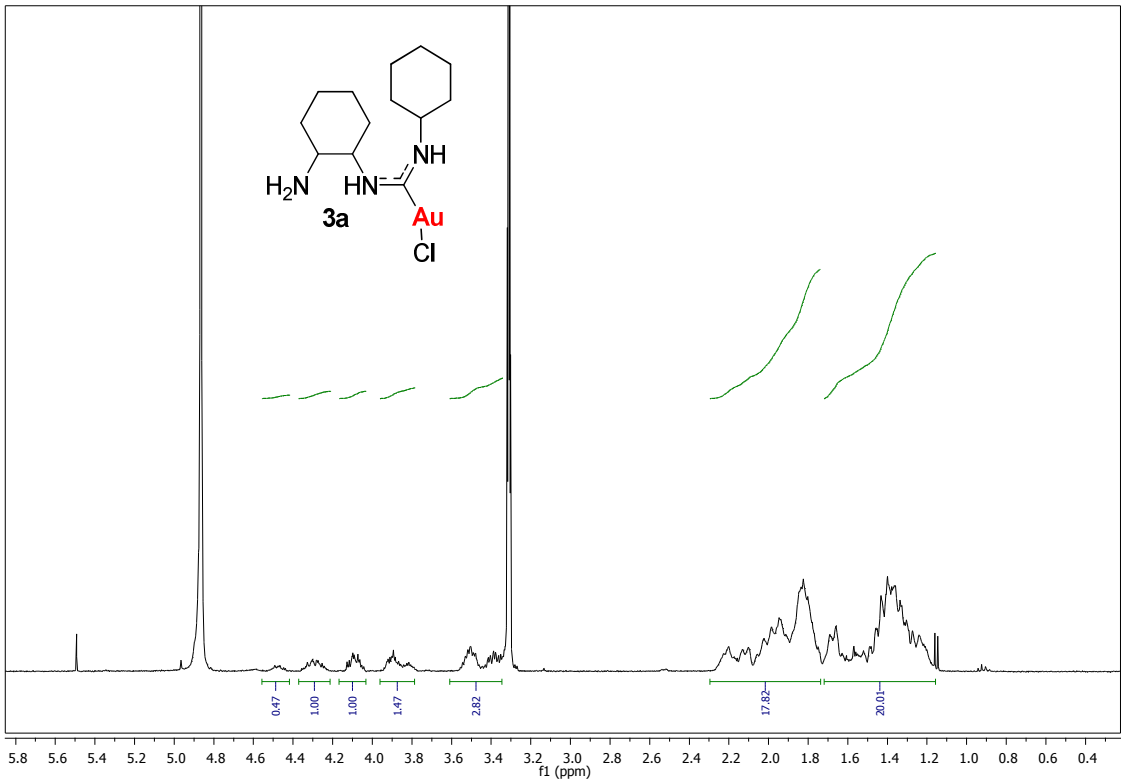


Figure S2. ^{13}C-APT NMR 3a

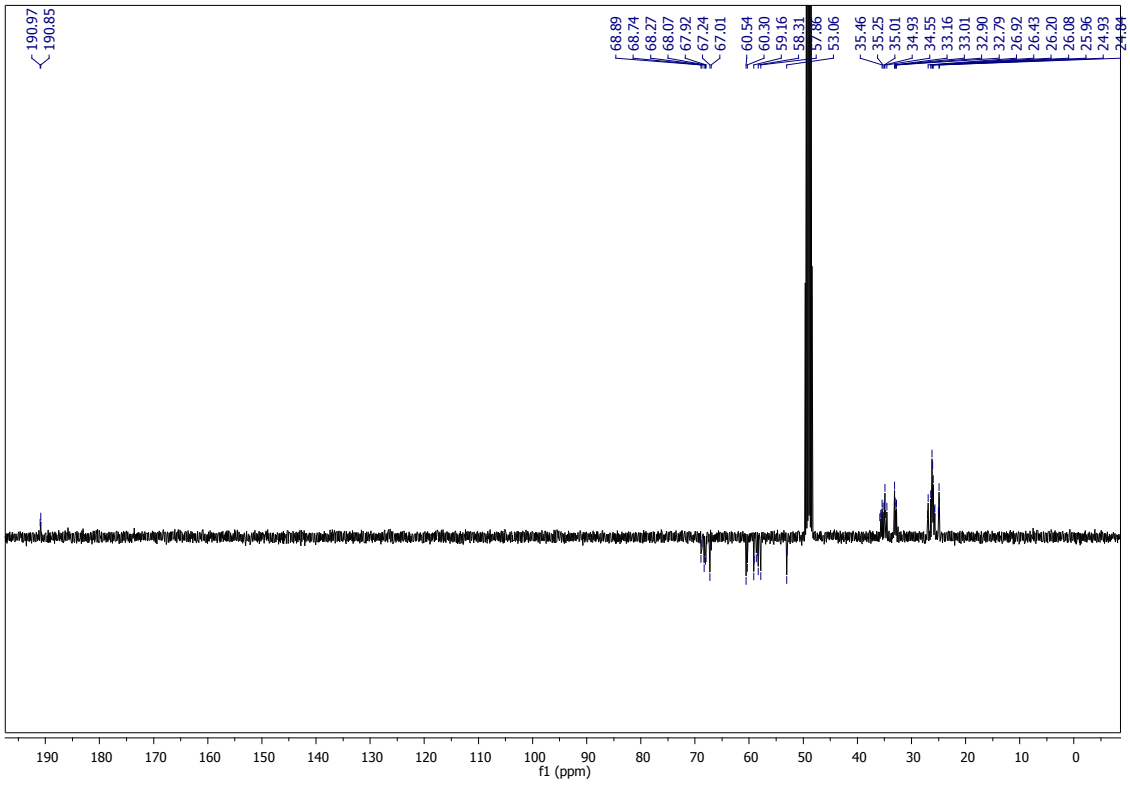


Figure S3. ^{1}H NMR gold (I) acyclic(amine)carbene 3b

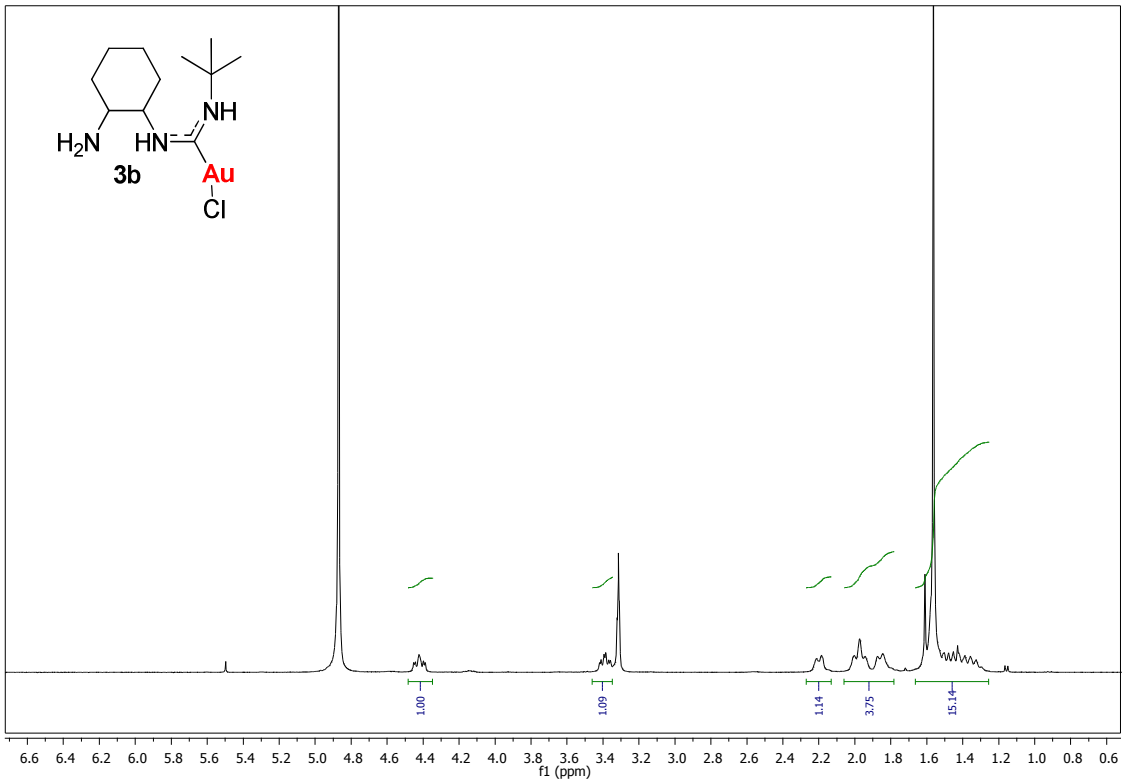


Figure S4. ^{13}C-APT NMR 3b

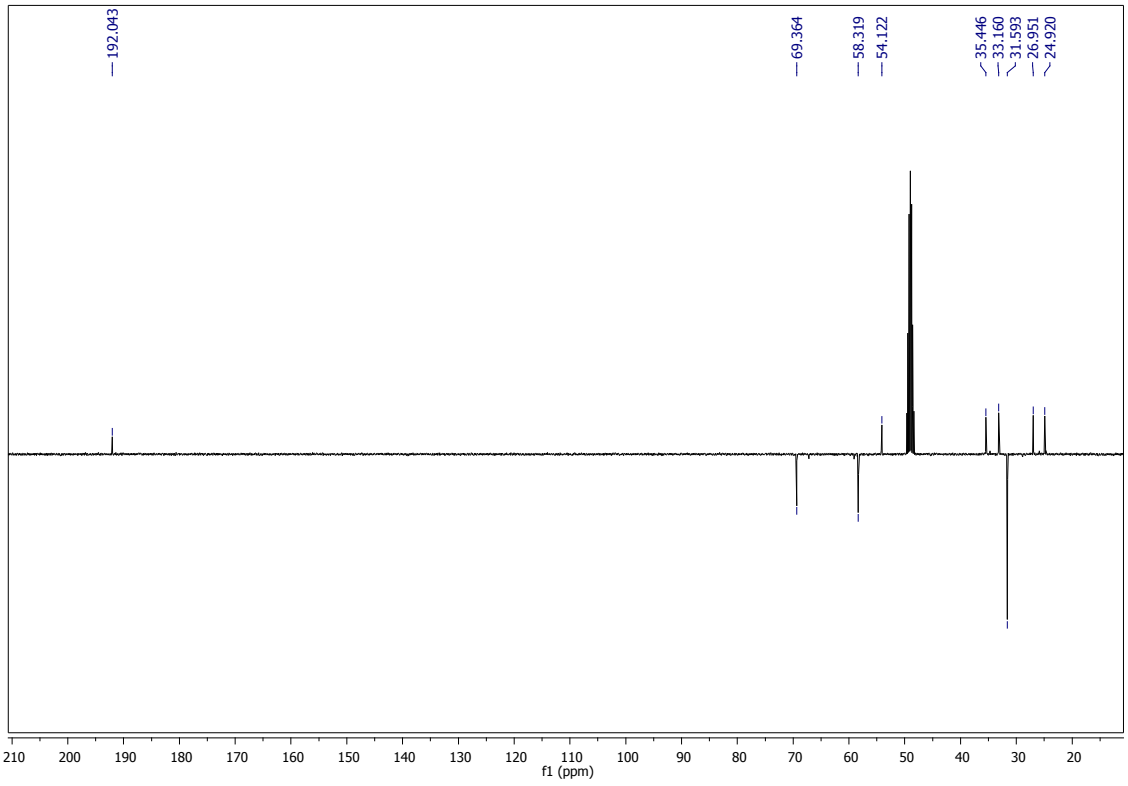


Figure S5. ^{1}H NMR gold (I) acyclic(amine)carbene 3c

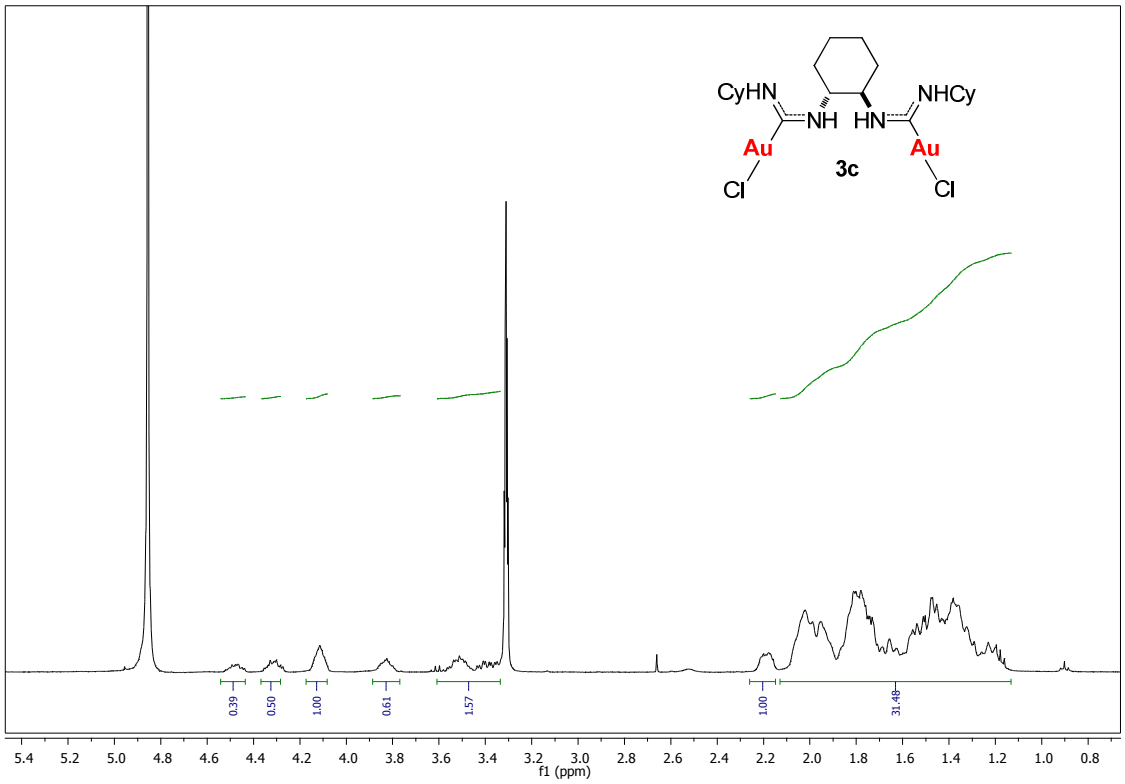


Figure S6. ^{13}C-APT NMR 3c

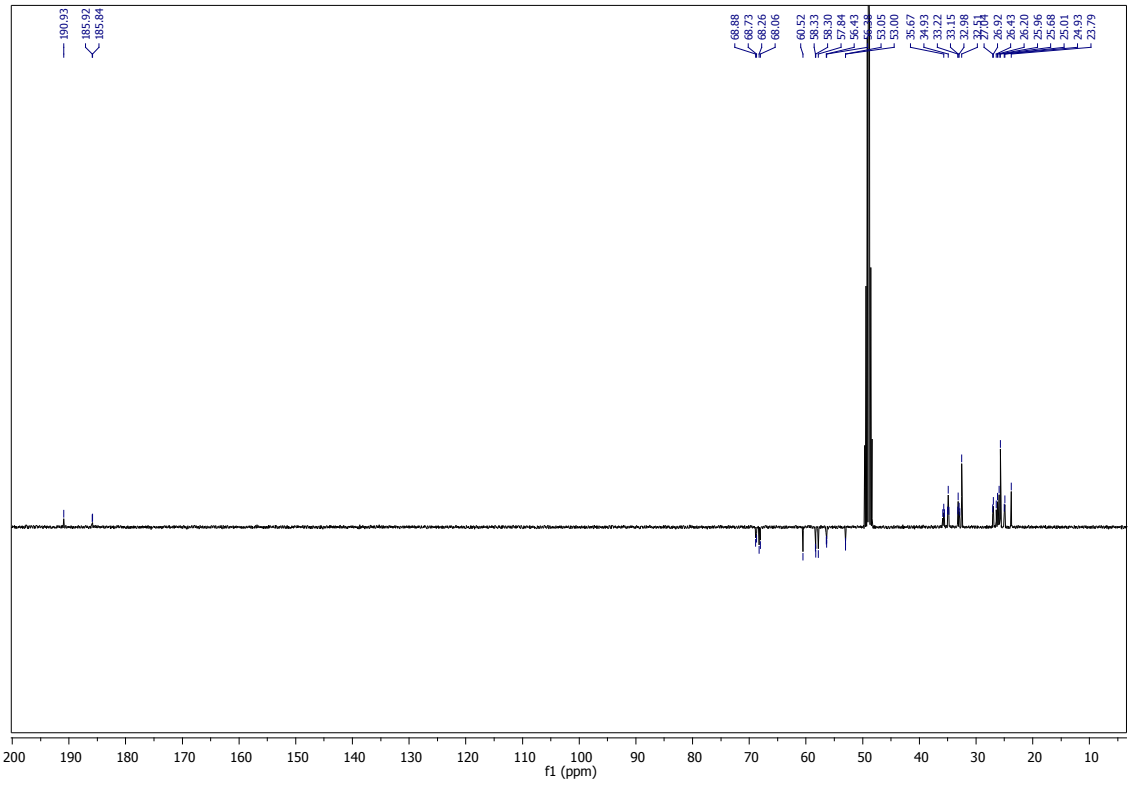


Figure S7. ^{1}H NMR gold (I) acyclic(amine)carbene 3d

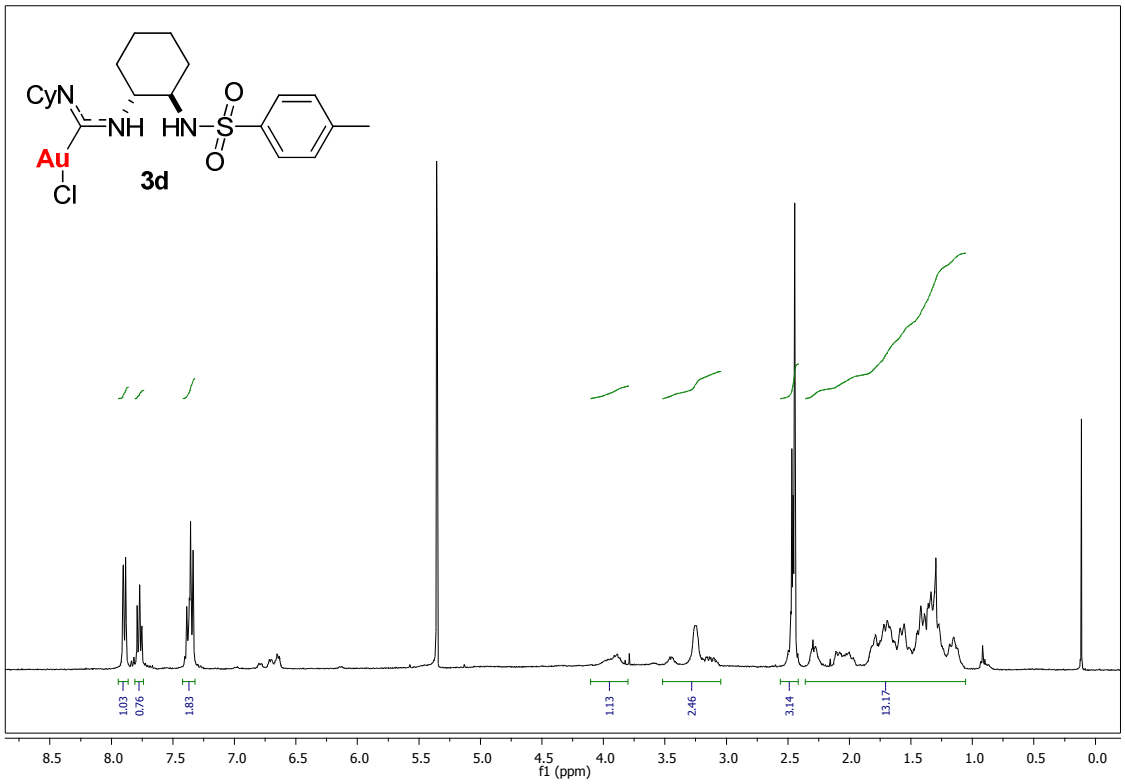


Figure S8. ^{13}C-APT NMR 3d

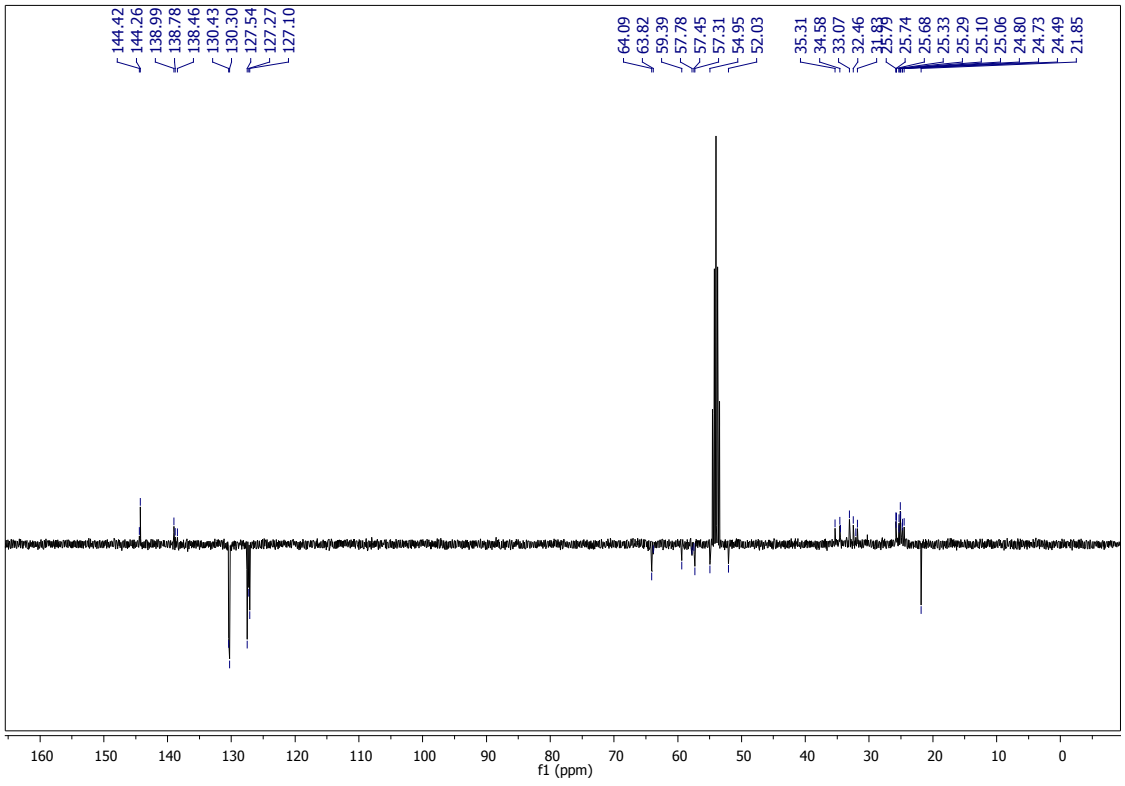


Figure S9. ^{1}H NMR *N*-butyl-*N*-(1-phenyl-3-p-tolylprop-2-ynyl)butan-1-amine (7abf)

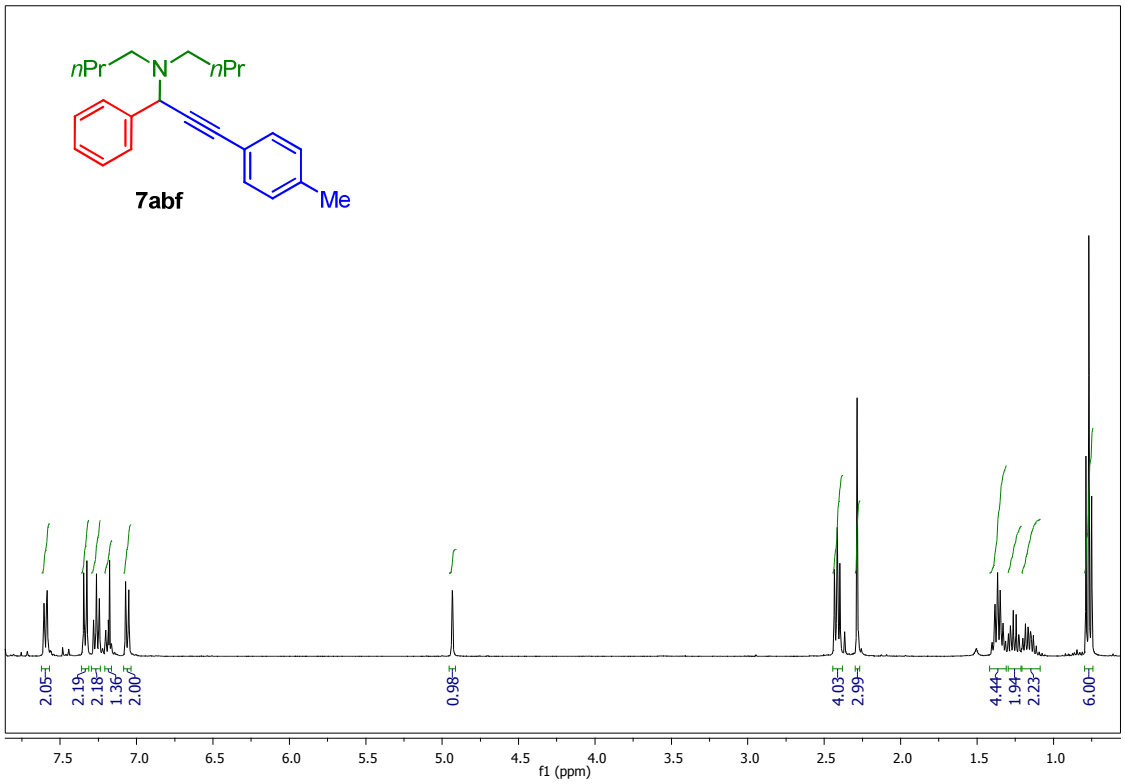


Figure S10. ^{13}C-APT NMR 7abf

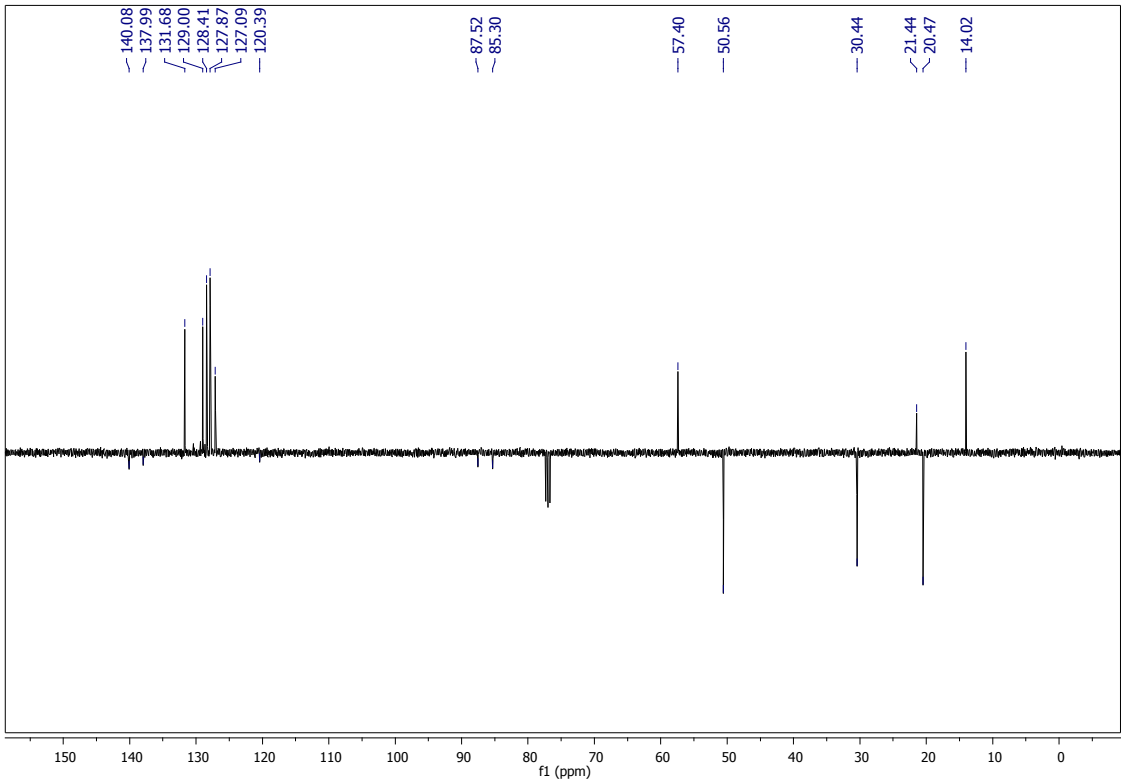


Figure S11. ^{1}H NMR *N,N*-diethyl-3-phenylindolizin-1-amine (8dad)

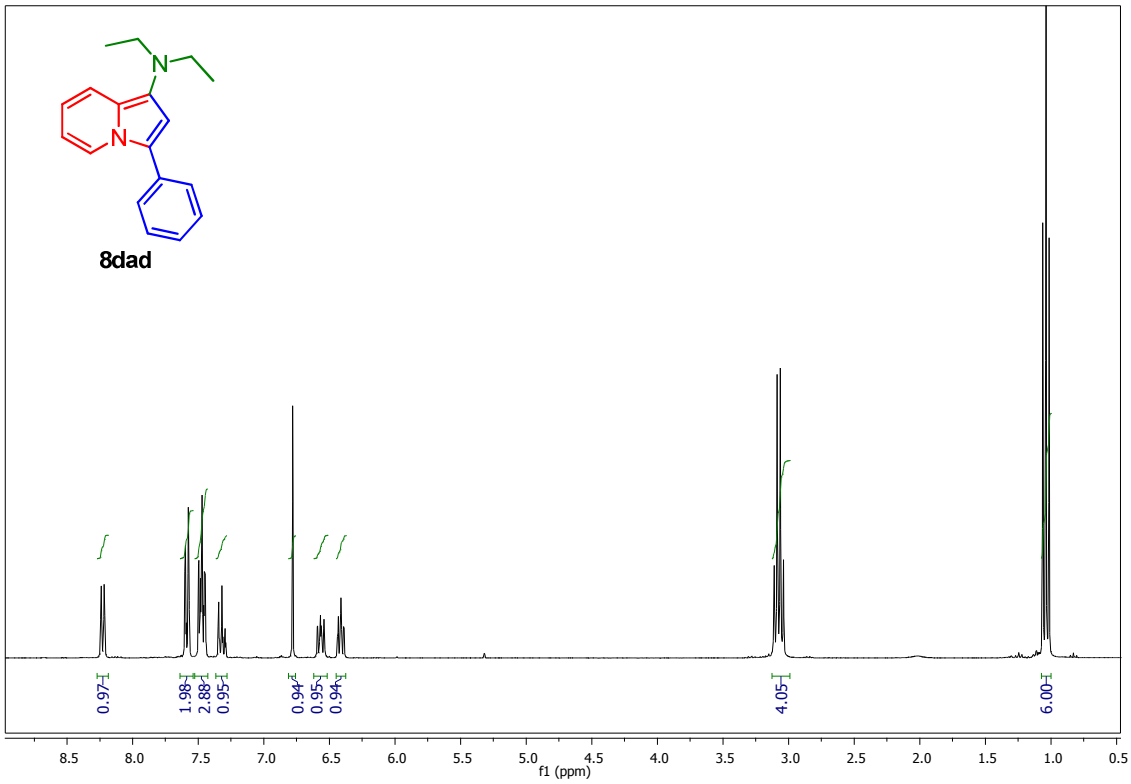


Figure S12. ^{13}C-APT NMR 8dad

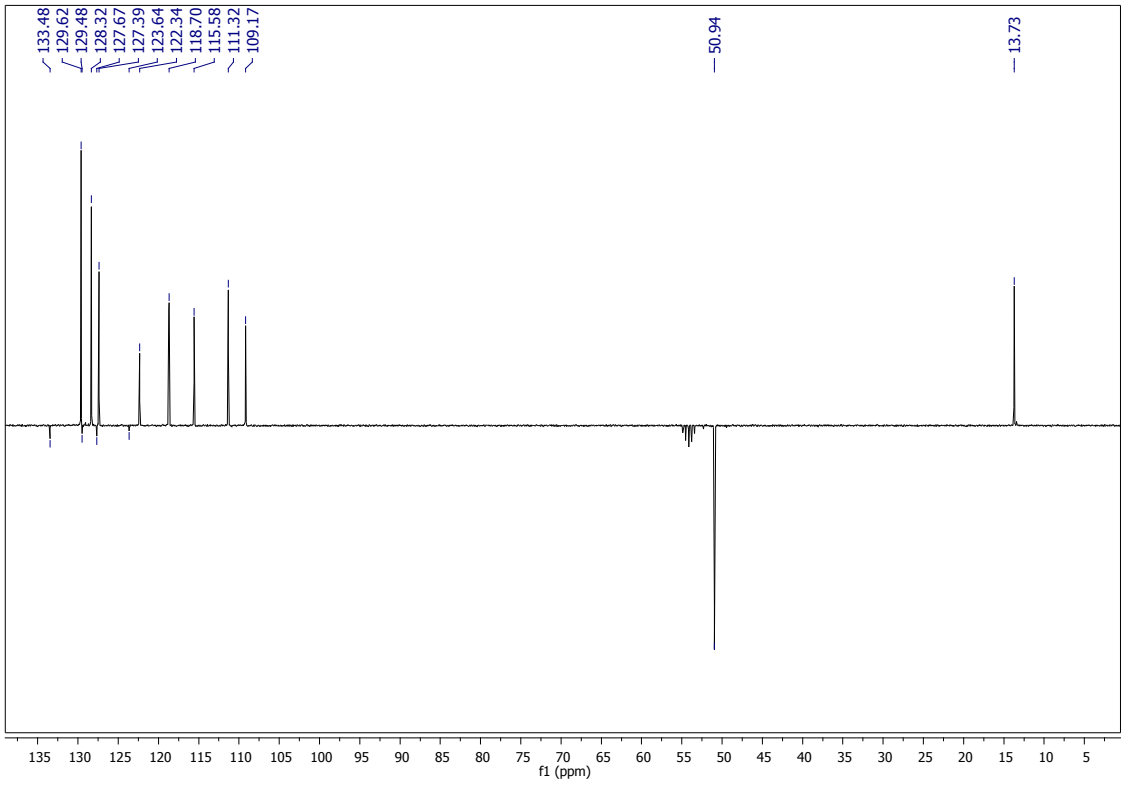


Figure S13. ^{1}H NMR *N,N*-diethyl-3-*p*-tolylindolizin-1-amine (8dbd)

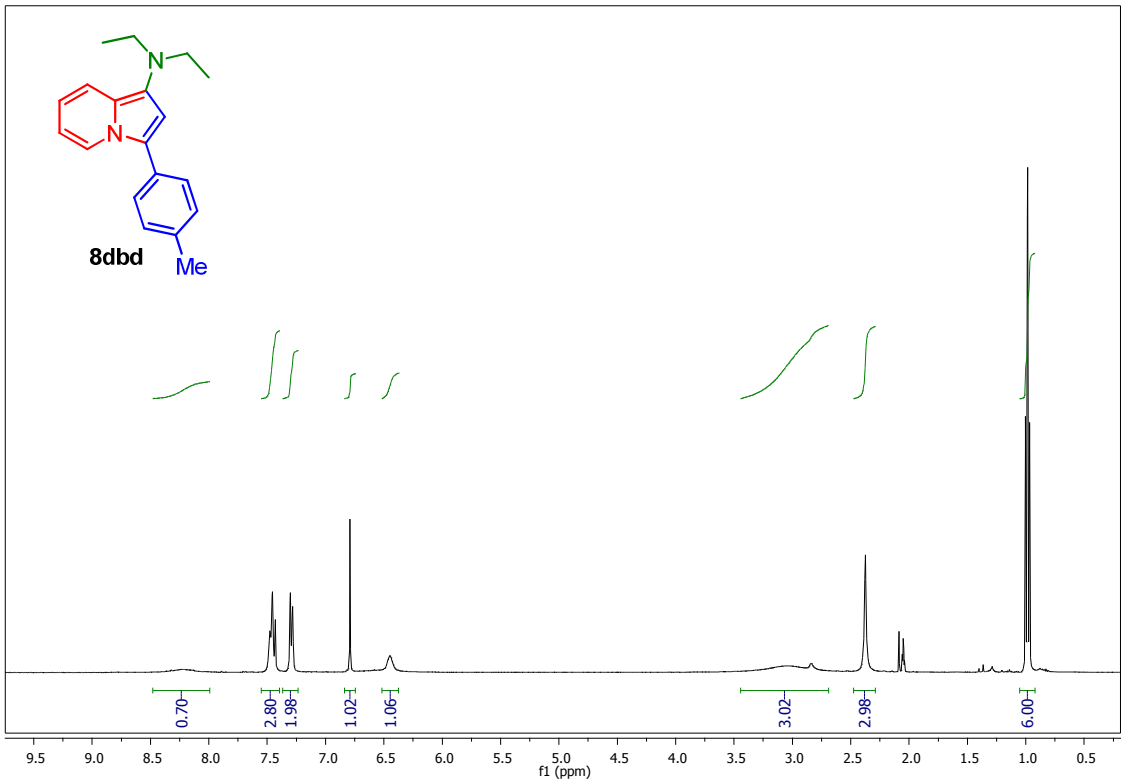


Figure S14. ^{13}C-APT NMR 8dbd

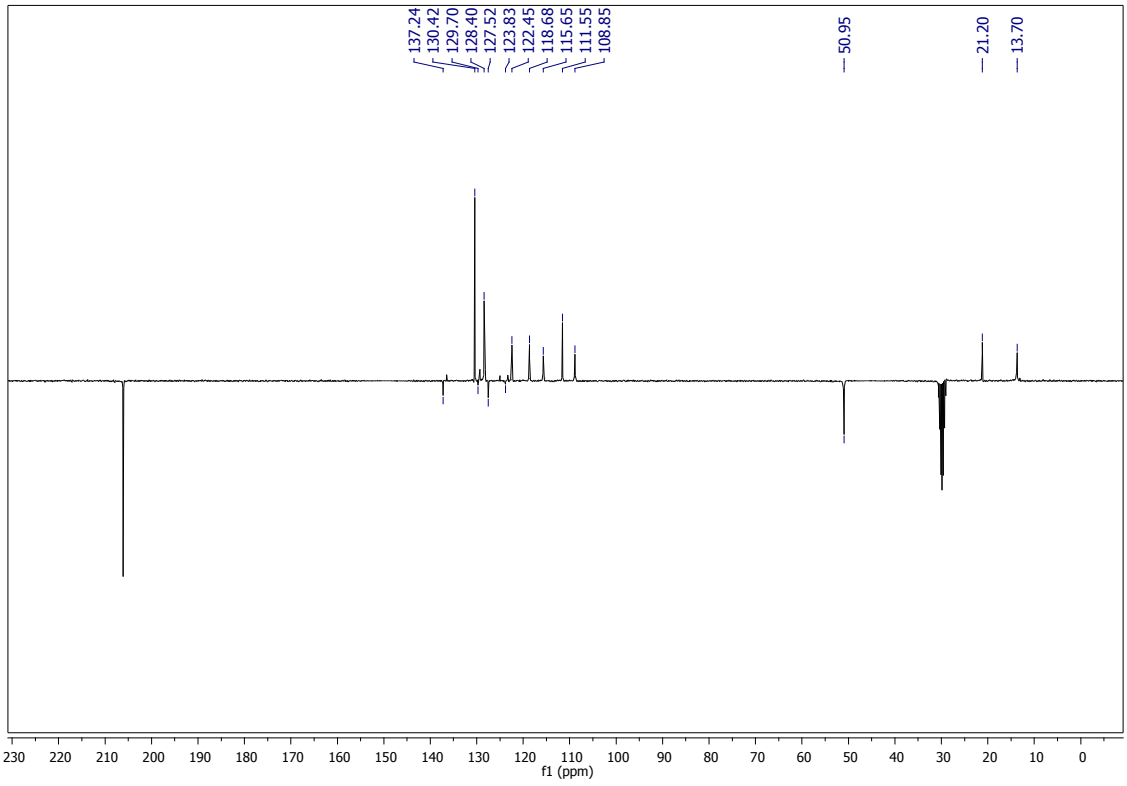


Figure S15. ^{1}H NMR *N,N*-dibutyl-3-*p*-tolylindolizin-1-amine (8dbf)

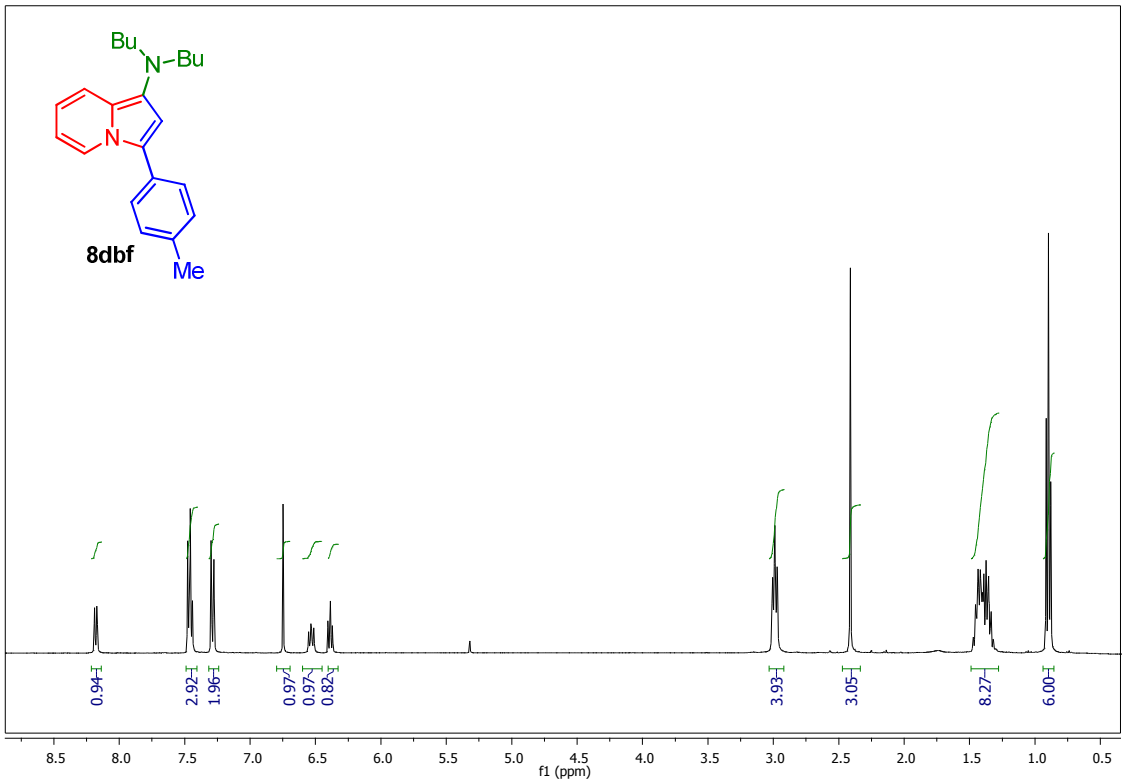


Figure S16. ^{13}C-APT NMR 8dbf

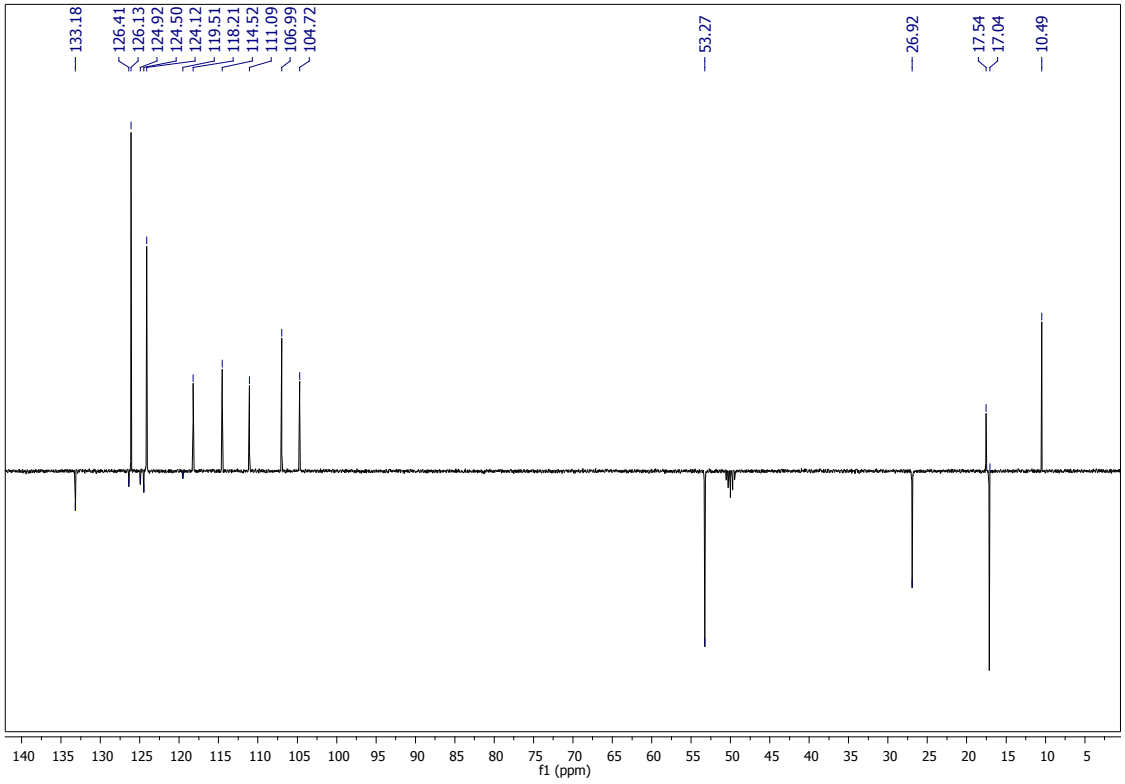


Figure S17. ^{1}H NMR Ethyl 1-(piperidin-1-yl)indolizine-3-carboxylate (8dca)

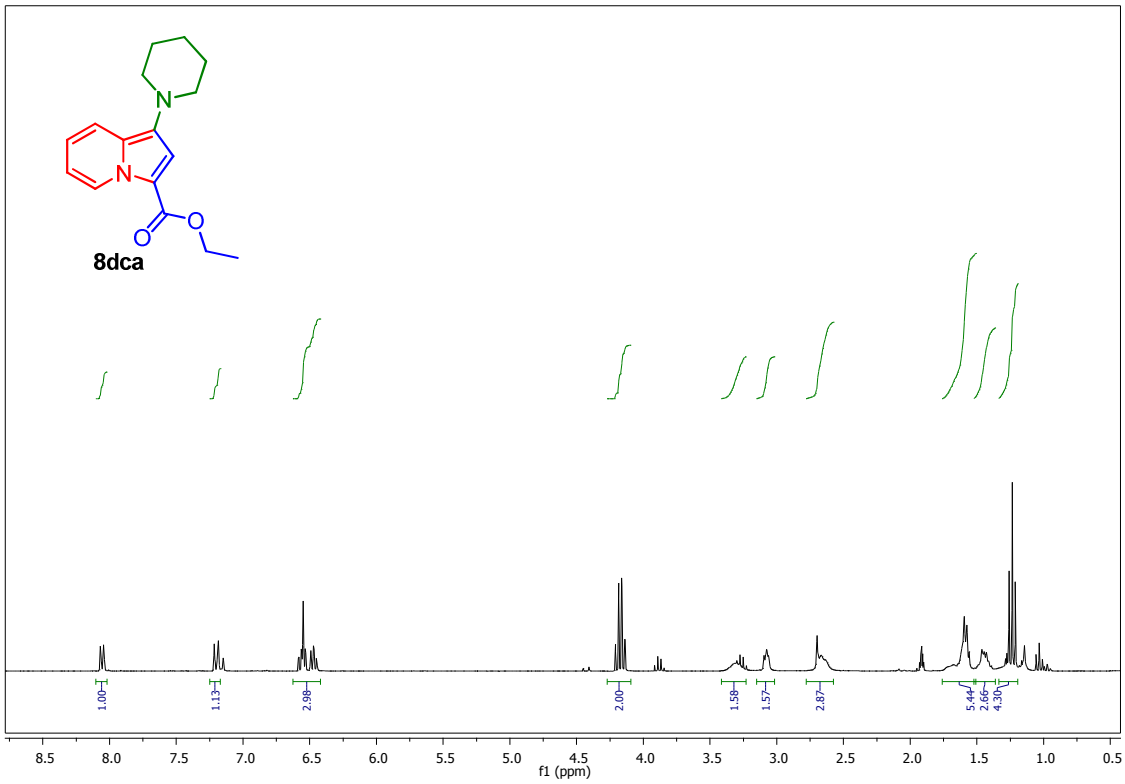


Figure S18. ^{13}C-APT NMR 8dca

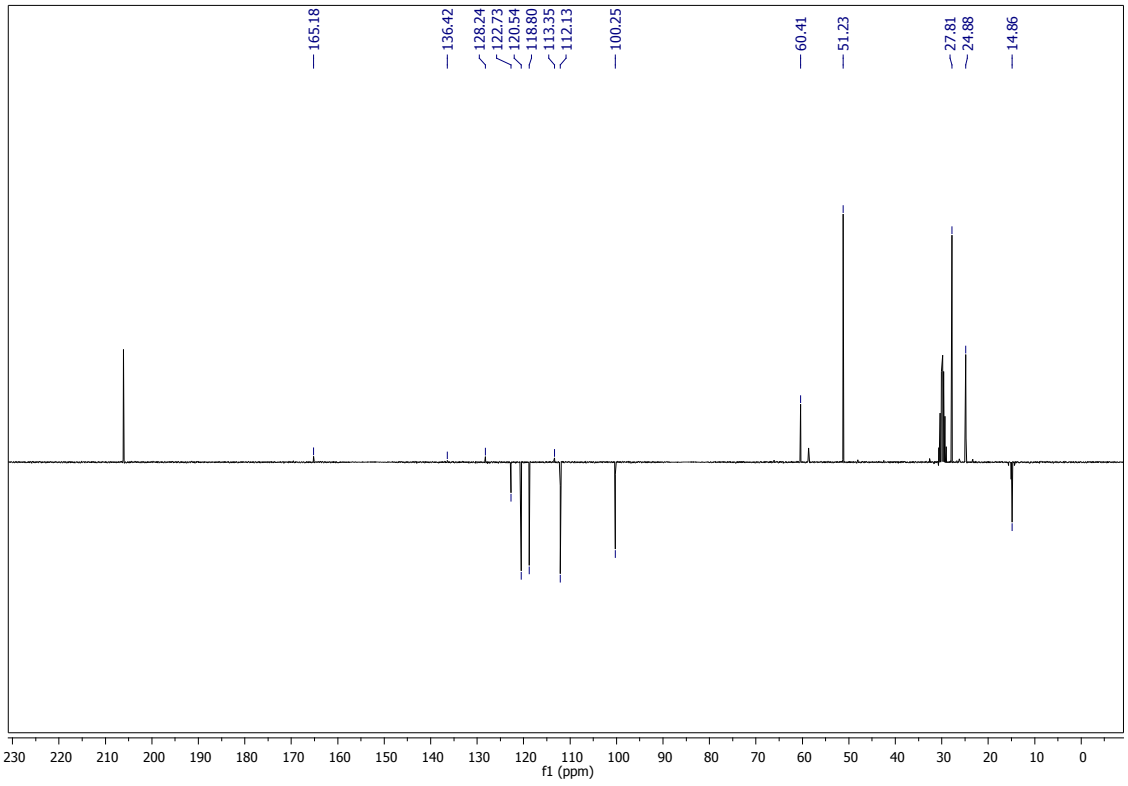


Figure S19. ^{1}H NMR Methyl 1-(piperidin-1-yl)indolizine-3-carboxylate (8dda)

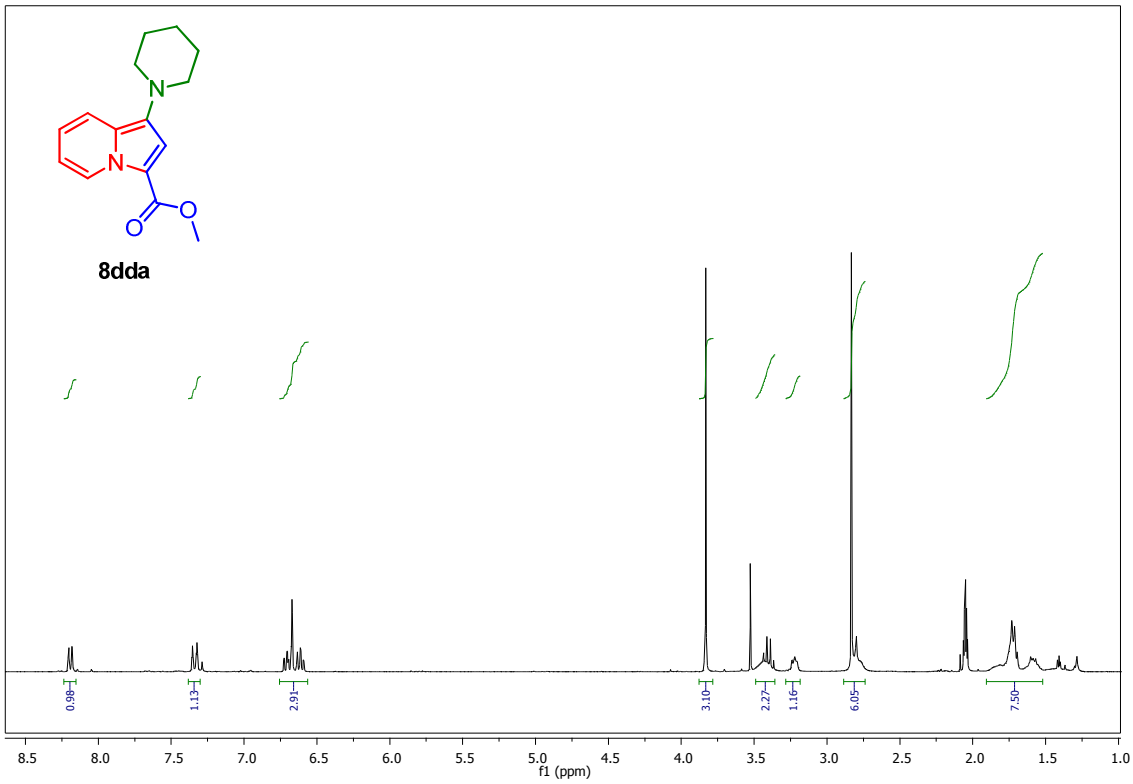


Figure S20. ^{13}C-APT NMR 8dda

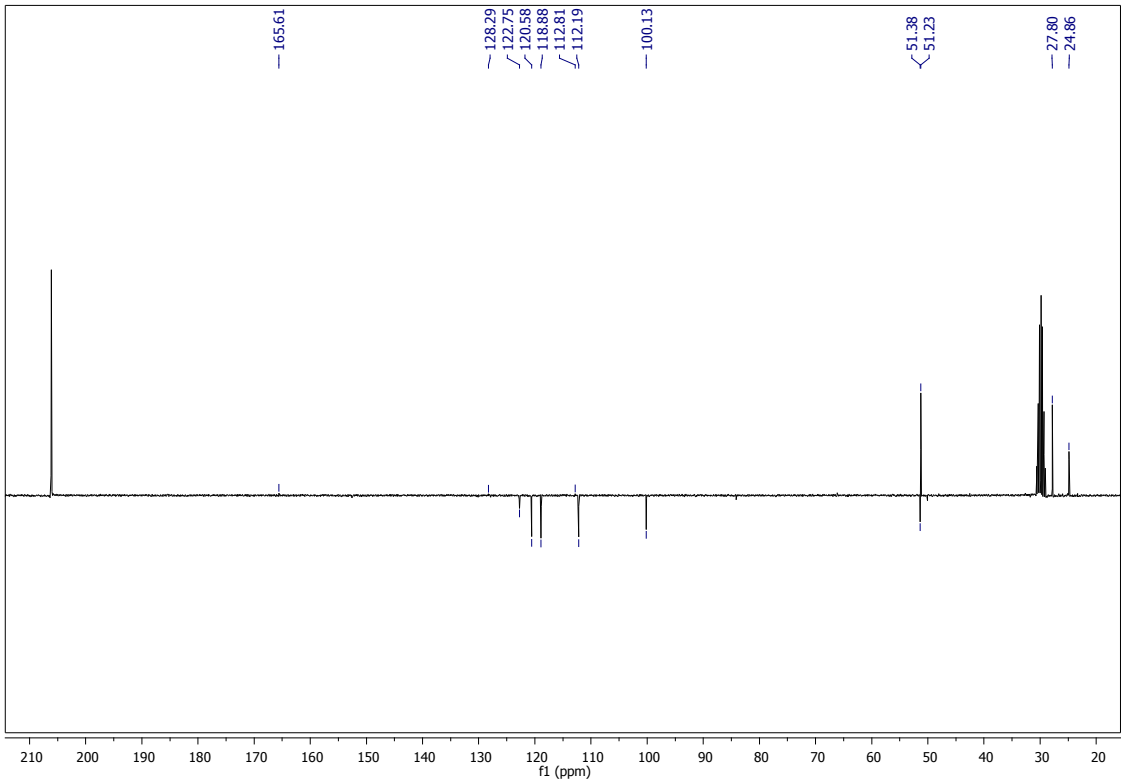


Figure S21. ^{1}H NMR *N,N*-diethyl-1-phenylpyrrolo[1,2-*a*]quinolin-3-amine (8ead)

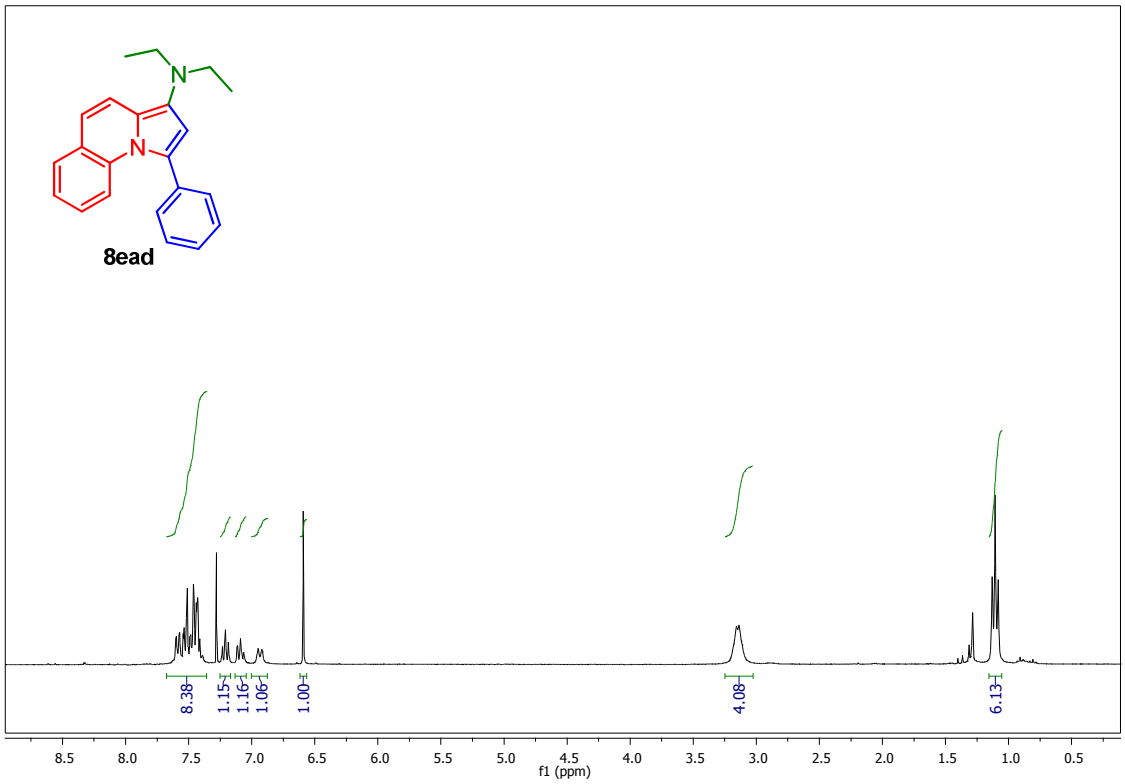


Figure S22. ^{13}C-APT NMR 8ead

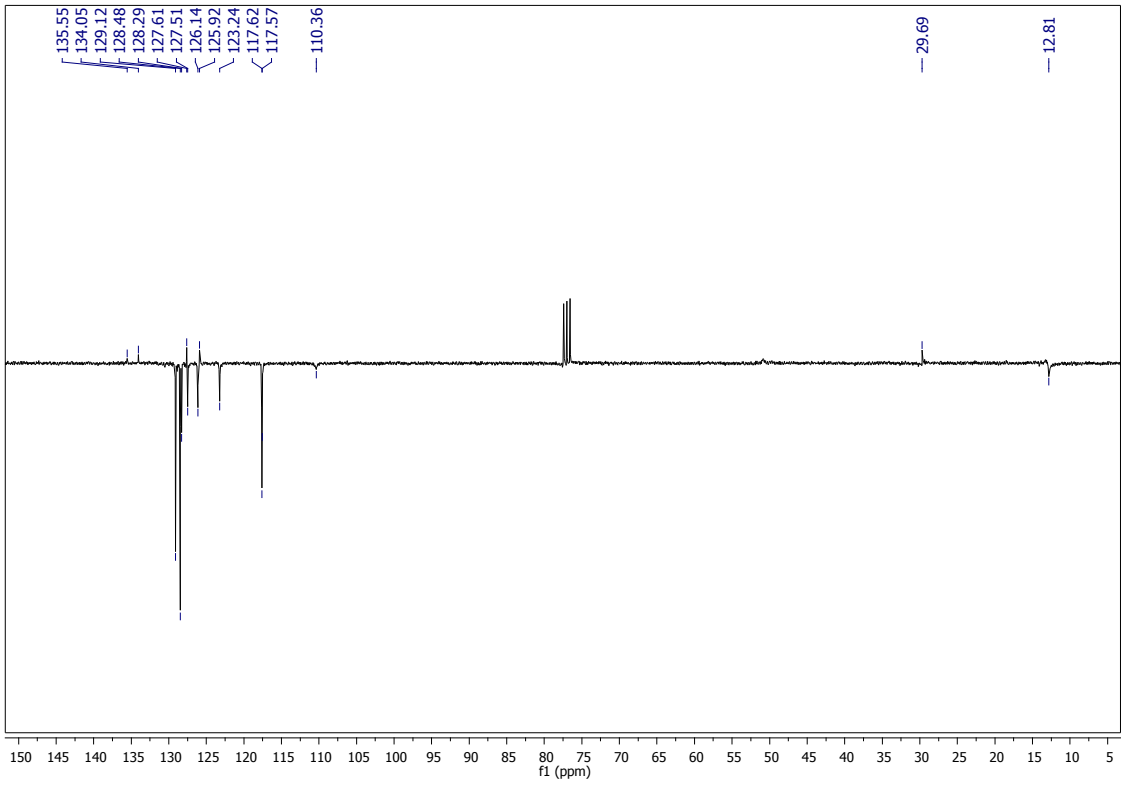


Figure S23. ^{1}H NMR *N,N*-diisopropyl-1-phenylpyrrolo[1,2-a]quinolin-3-amine (8eag)

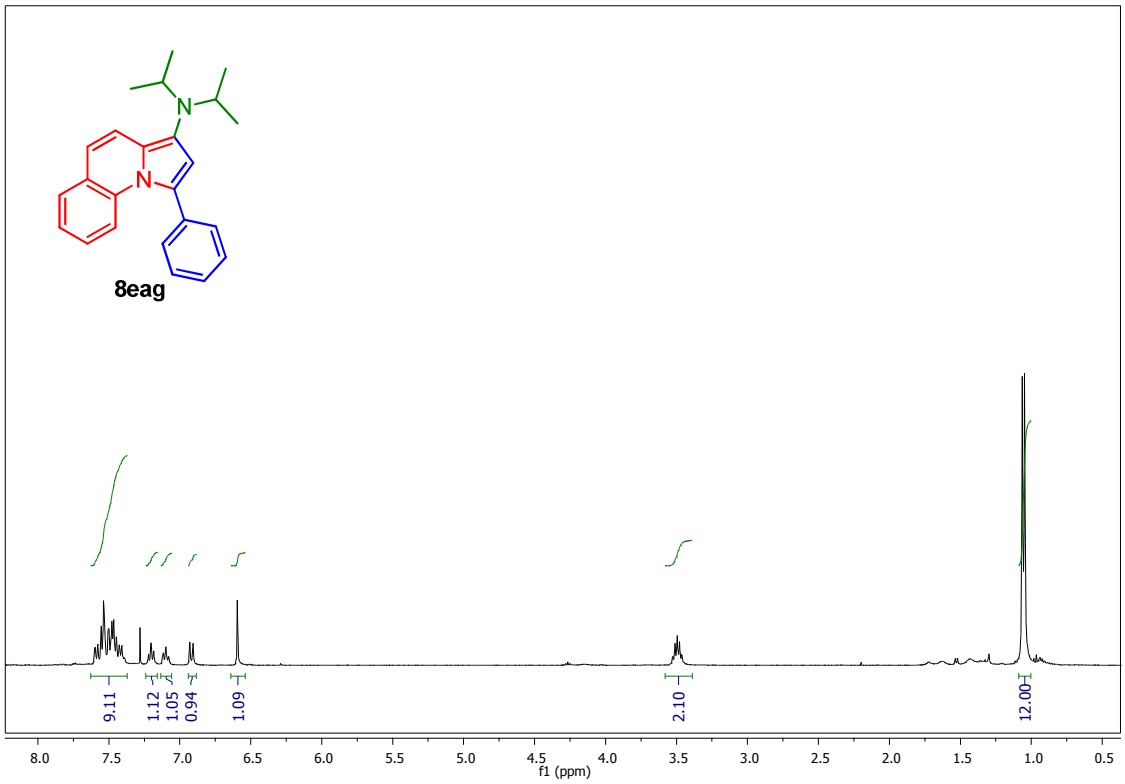


Figure S24. ^{13}C-APT NMR 8eag

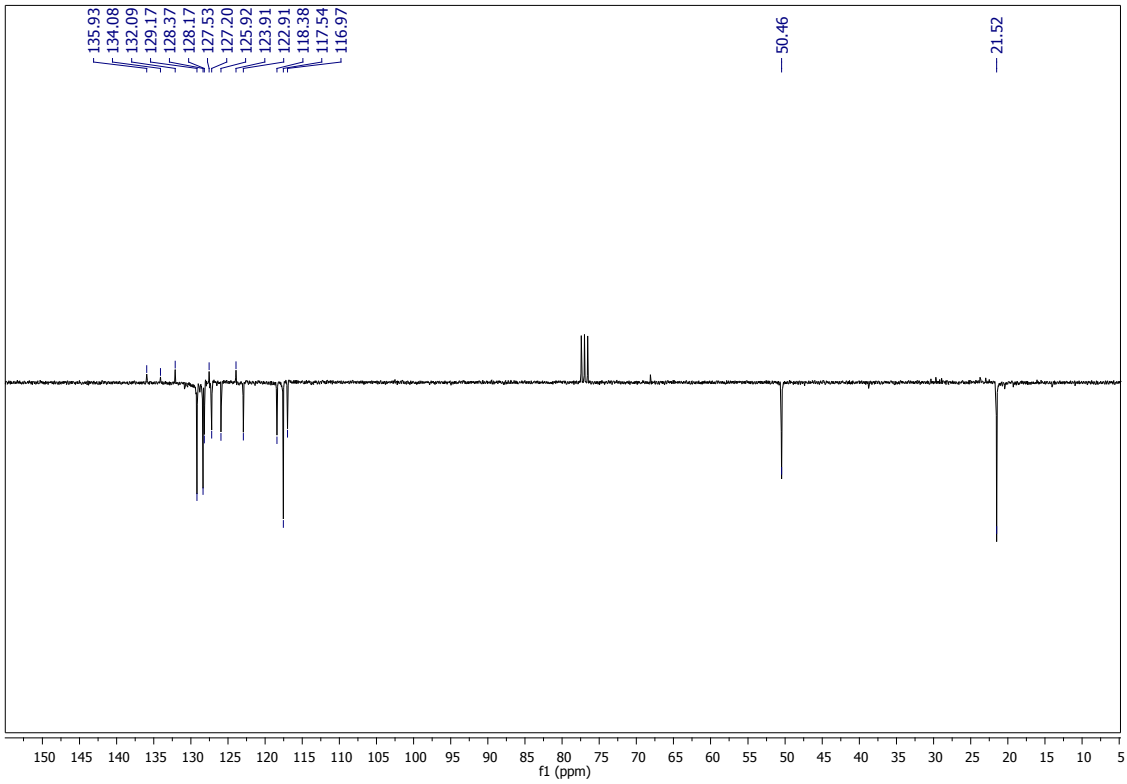


Figure S25. ^{1}H NMR *N,N*-diethyl-1-*p*-tolylpyrrolo[1,2-a]quinolin-3-amine (8ebd)

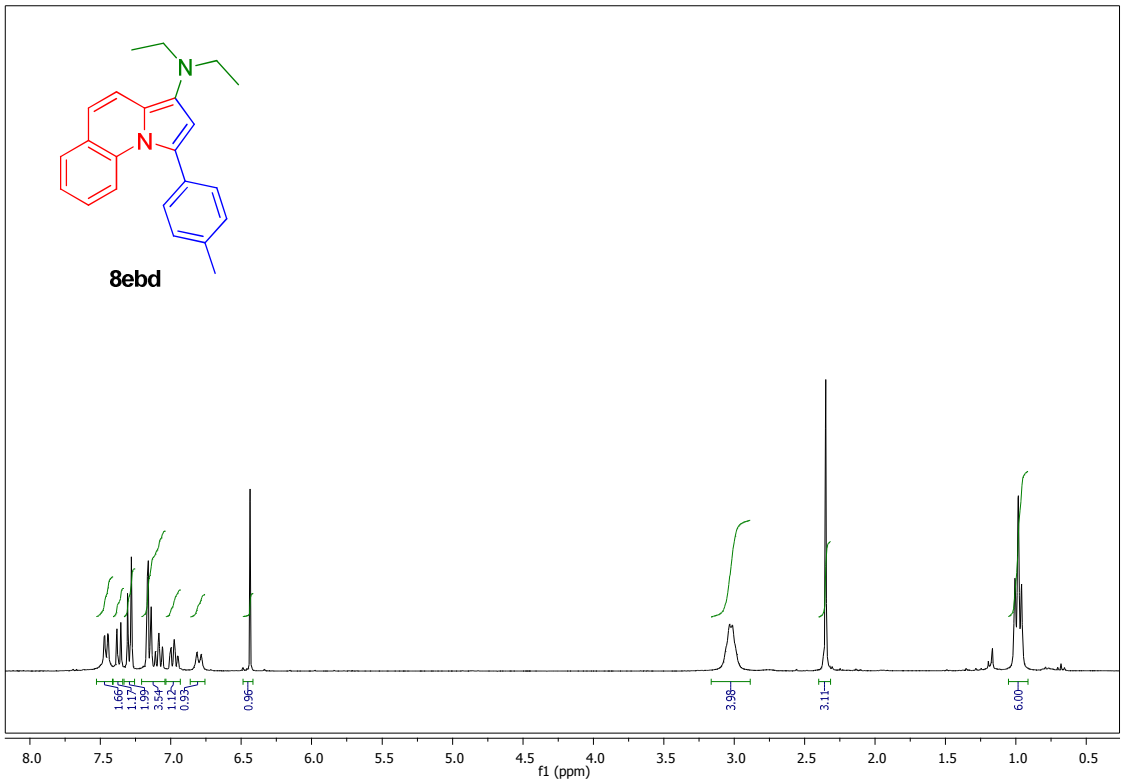


Figure S26. ^{13}C-APT NMR 8ebd