Directing Group Assisted C–H Functionalization of 2-Arylbenzo[f]isoquinoline: A Robust Route to Decumbenine B Analogues with Photophysical Applications

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1. General information:

All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel. The air- and moisture-sensitive liquids and solutions were transferred via syringes or a PTFE cannula. Precoated silica gel 60 F254 TLC sheets (Merck) were used to monitor the reaction. The spots on TLC were visualized under UV 254 nm light. For purification in column chromatography 60-120 or 100-200 mesh silica gels (Sprectrochem Co.) were used. n-Hexane (Merck) or petroleum ether (boiling range 60-80 °C) and ethyl acetate eluent were used in column chromatographic separation.

Instrumentation

NMR spectroscopy

^{1}H and ^{13}C NMR spectra of all the synthesized compounds were recorded in 300 MHz, 400 MHz, and 700 MHz NMR spectrometers (Bruker Avance-300, Bruker Avance-400, and Bruker Avance-700) using $CDCl_3$ and DMSO-d_6 (99.9 atom% D) as a solvent with TMS as internal standard or without TMS. The proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethyl silane (TMS) and are referenced to TMS (δ 0.0), $CHCl_3$ (δ 7.26), and DMSO (δ = 2.50). The chemical shifts of the carbon atoms are reported in parts per million (ppm, δ scale) downfield from TMS and referenced to the carbon resonance of $CDCl_3$ (δ 77.16), DMSO-d_6 (δ 39.52) The data are presented as chemical shift, multiplicity (s = singlet, d = doublet, dd= doublet of doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplate and/or multiple resonances, and br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers.

HRMS

High-resolution mass spectra (HRMS) were recorded using fast atom bombardment (FAB) ionization with a Q-TOF mass spectrometer.

Materials

All chemical and solvent were purchased from Sigma-Aldrich Co., Tokyo Chemical Industry (India) Pvt. Ltd., Spectrochem Pvt. Ltd., Sisco Research Laboratory Pvt. Ltd., Thermo Fisher Scientific, BLD pharm, etc. $[Ru(p\text{-cymene})Cl_2]_2$ and $Pd(OAc)_2$ was purchased from bld pharm, $Cu(OAc)_2$ was purchased from Sigma-Aldrich .

2. General experimental procedure for C–H of activation reaction and characterization data of products:

General experimental procedure A: general experimental procedure of C–H activation of 2-arylbenzo(f)isoquinoline:

2-arylbenzo(f)isoquinoline (0.1 mmol), paraformaldehyde (0.3 mmol, 3 equiv.), $ZnBr_2$ (0.05 mmol, 0.5 equiv.) and AcOK (0.05 mmol, 0.5 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (10 mol%) and 2 mL of DCE, were taken in an oven-dried reaction vessel. The mixture was heated at 120 °C for 3h under nitrogen atmosphere. Reaction progress was monitored by TLC. Upon completion, the reaction mixture was cooled and CH_2Cl_2 was evaporated under reduced pressure, and H_2O was added. The aqueous phase was extracted with EtOH, the combined organic phases were extracted with brine, and dried with Na_2SO_4. Evaporation of the solvent. The crude product was purified by column chromatography on silica gel (100–200 mesh) using a hexane (or petroleum ether) and ethyl acetate mixture as the eluent to get the pure product.

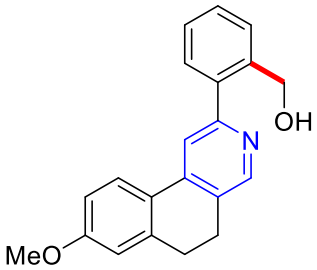
General experimental procedure B: general experimental procedure for bromination:

2-arylbenzo(f)isoquinoline (0.1 mmol), $Pd(OAc)_2$ (10 mol%), and NBS (0.1 mmol,1 equiv.) in 2 mL acetonitrile were taken in an oven-dried reaction vessel. The mixture was heated at 100 °C for 3h under a nitrogen atmosphere. Reaction progress was monitored by TLC. Upon completion, the reaction mixture was cooled, and H_2O was added. The aqueous phase was extracted with EtOH, the combined organic phases were extracted with brine, and dried with Na_2SO_4. Evaporation of the solvent. The crude product was purified by column chromatography on silica gel (100–200 mesh) using a hexane (or petroleum ether) and ethyl acetate mixture as the eluent to get the pure product.

General experimental procedure C: general experimental procedure for Selenylation:

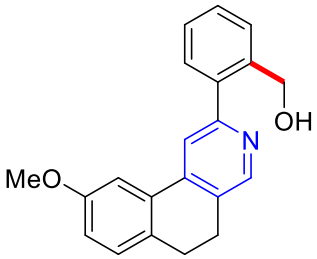
2-arylbenzo(f)isoquinoline (0.1 mmol), $Cu(OAc)_2$ (0.1 mmol,1 equiv.) and NBS (0.1 mmol,1 equiv.) in 1 mL DMSO were taken in an oven-dried reaction vessel. The mixture was heated at 150 °C for 6h under a nitrogen atmosphere. Reaction progress was monitored by TLC. Upon completion, the reaction mixture was cooled, and H_2O was added. The aqueous phase was extracted with EtOH, the combined organic phases were extracted with brine, and dried with Na_2SO_4. Evaporation of the solvent. The crude product was purified by column chromatography on silica gel (100–200 mesh) using a hexane (or petroleum ether) and ethyl acetate mixture as the eluent to get the pure product.

(2-(8-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3a):



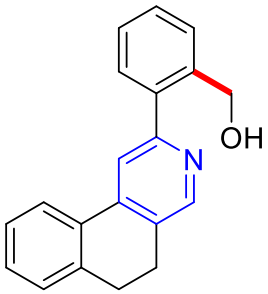
The reaction was carried out according to the general procedure A. 27 mg (85% yield), brown semi-liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ in ppm 8.44 (s, 1H), 7.82 – 7.78 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 – 7.48 (m, 1H), 7.44 – 7.39 (m, 2H), 6.90 (dd, J = 8.6, 2.7 Hz, 1H), 6.84 (d, J = 2.7 Hz, 1H), 4.50 (s, 2H), 3.87 (s, 3H), 2.93 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 155.2, 144.1, 140.4, 137.6, 137.4, 137.4, 128.2, 127.1, 126.9, 126.1, 125.2, 123.0, 121.6, 114.2, 111.0, 110.0, 61.9, 52.5, 25.93, 22.3. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{21}H_{20}NO_2$: 318.1489, Found 318.1487.

(2-(9-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3b):



The reaction was carried out according to the general procedure A. 26 mg, 81% yield), brown semi-liquid.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.86 (s, 1H), 7.64 – 7.61 (m, 1H), 7.52 – 7.49 (m, 1H), 7.46 – 7.42 (m, 2H), 7.38 (d, J = 2.6 Hz, 1H), 7.24 (d, J = 8.3 Hz, 1H), 6.93 (dd, J = 8.3, 2.6 Hz, 1H). 4.50 (s, 2H), 3.87 (s, 3H), 2.91 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 158.3, 147.4, 143.4, 140.4, 132.7, 131.2, 130.9, 130.6, 130.1, 129.7, 129.2, 128.3, 117.9, 115.3, 113.5, 110.1, 64.8, 55.6, 27.6, 25.5. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{21}H_{20}NO_2$: 318.1489, Found 318.1483.

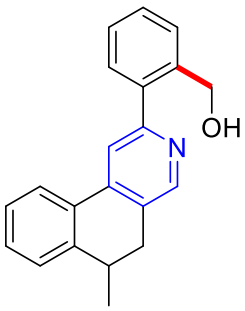
(2-(5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3c):



The reaction was carried out according to the general procedure A. 19 mg, 67% yield), brown semi-liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.91 – 7.81 (m, 2H), 7.64 – 7.60 (m, 1H), 7.52 – 7.30 (m, 6H), 4.50 (s, 2H), 3.00 - 2.93 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 147.4, 143.4, 140.5, 140.4, 138.5, 131.8, 131.3, 130.7, 130.1, 130.0, 129.2, 128.9, 128.3, 127.5, 124.5, 117.9, 64.9, 28.5, 25.2. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{20}H_{18}NO$: 288.1383, Found 288.1378.

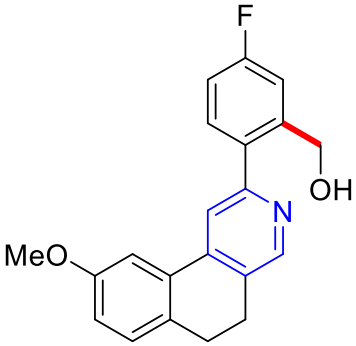
(2-(6-methyl-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3d):

The reaction was carried out according to the general procedure A. 24 mg (80% yield), brown semi-liquid.



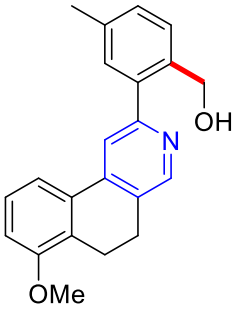
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.92 – 7.86 (m, 2H), 7.65 – 7.62 (m, 1H), 7.52 – 7.34 (m, 1H), 7.45 – 7.34 (m, 5H), 4.51 (s, 2H), 3.19 – 3.05 (m, 2H), 2.77 (dd, J = 15.0, 6.1 Hz, 1H), 1.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 147.9, 143.3, 143.0, 140.5, 140.4, 131.2, 130.9, 130.3, 130.1, 129.4, 129.2, 128.3, 127.4, 127.3, 124.7, 117.7, 64.9, 32.7, 32.6, 20.1. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{21}H_{20}NO$: 302.1539, Found 302.1543

(5-fluoro-2-(9-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3e):



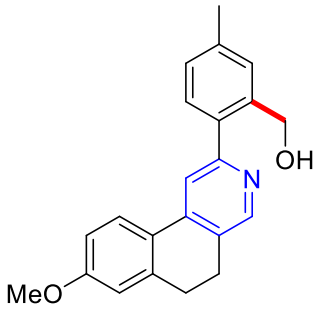
The reaction was carried out according to the general procedure A. 24 mg, (72% yield), brown semi-liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.80 (s, 1H), 7.59 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.37 (d, *J* = 2.6 Hz, 1H), 7.23 – 7.09 (m, 3H), 6.94 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.46 (s, 2H), 3.88 (s, 3H), 2.91 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.97 (d, *J* = 249.3 Hz), 159.1, 157.4, 147.5, 143.5, 142.89 (d, *J* = 6.8 Hz), 136.50 (d, *J* = 3.3 Hz), 132.6, 131.86 (d, *J* = 8.4 Hz), 130.84 (d, *J* = 27.9 Hz), 129.7, 118.1, 117.8, 117.7 115.4, 114.94 (d, *J* = 21.3 Hz), 110.2, 64.5, 55.7, 27.6, 25.6. HRMS (EI$^+$) m/z [M+H]$^+$ Calcd for $C_{21}H_{19}FNO_2$: 336.1394, Found 336.1393.

(2-(7-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)-4-methylphenyl)methanol (3f):



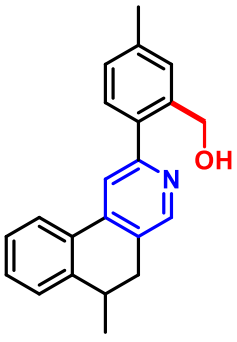
The reaction was carried out according to the general procedure A. 23 mg (71% yield), brown semi-liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.88 (s, 1H), 7.53 – 7.50 (m, 1H), 7.42 – 7.32 (m, 3H), 7.23 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.97 (dd, *J* = 8.2, 0.9 Hz, 1H), 4.46 (s, 2H), 3.90 (s, 3H), 3.00 – 2.95 (m, 2H), 2.92 – 2.87 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.31, 156.87, 147.28, 143.37, 140.43, 137.94, 137.63, 133.01, 131.20, 130.80, 130.66, 129.77, 127.64, 127.08, 118.18, 116.78, 111.72, 64.52, 55.80, 24.63, 21.37, 20.34. HRMS (EI$^+$) m/z [M+H]$^+$ Calcd for $C_{22}H_{22}NO_2$: 332.1645, Found 332.1649.

(2-(8-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)-5-methylphenyl)methanol (3g):



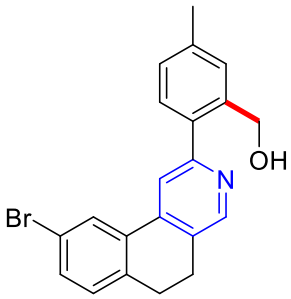
The reaction was carried out according to the general procedure A. 27 mg (80% yield), brown semi-liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.91 – 6.82 (m, 2H), 4.47 (s, 2H), 3.86 (s, 3H), 2.91 (s, 4H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 158.1, 147.0, 143.2, 140.3, 140.2, 139.0, 137.6, 131.9, 129.9, 129.5, 128.8, 126.0, 124.6, 116.9, 113.9, 113.0, 64.9, 55.4, 28.9, 25.2, 21.2. HRMS (EI$^+$) m/z [M+H]$^+$ Calcd for $C_{22}H_{22}NO_2$: 332.1645, Found 332.1639.

(5-methyl-2-(6-methyl-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3h):



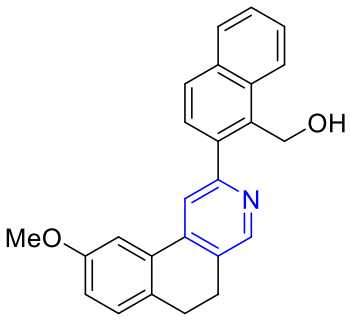
The reaction was carried out according to the general procedure A. (19 mg, 61% yield), yielding a brown semi-liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.91 – 7.84 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.43–7.22 (m, 5H), 4.48 (s, 2H), 3.17 – 3.02 (m, 2H), 2.75 (dd, *J* = 15.1, 6.2 Hz, 1H), 2.42 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 158.2, 147.8, 143.3, 143.0, 140.2, 139.2, 137.5, 132.0, 130.9, 130.3, 130.0, 129.1, 128.9, 127.4, 124.6, 117.4, 64.8, 60.5, 21.2, 20.0, 14.3. HRMS (EI$^+$) m/z [M+H]$^+$ Calcd for $C_{22}H_{22}NO$: 316.1696, Found 316.1700.

(2-(9-bromo-5,6-dihydrobenzo[f]isoquinolin-2-yl)-5-methylphenyl)methanol (3i)



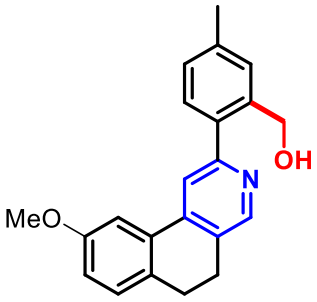
The reaction was carried out according to the general procedure A. 24 mg (65% yield), brown semi-liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.85 (s, 1H), 7.65 – 7.61 (m, 1H), 7.52 – 7.43 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 1H), 4.49 (s, 2H), 2.94 (s, 4H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 147.6, 142.2, 140.4, 140.1, 137.2, 133.9, 132.7, 131.3, 130.6, 130.5, 130.1, 129.4, 128.4, 127.5, 121.2, 117.9, 64.8, 29.8, 28.0, 25.0.

(2-(9-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)naphthalen-1-yl)methanol (3j):



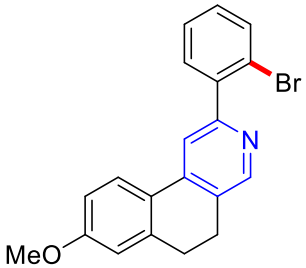
The reaction was carried out according to the general procedure A. 24 mg (65% yield), brown semi-liquid.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.08 (s, 1H), 8.00 – 7.87 (m, 4H), 7.58 – 7.51 (m, 2H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.23 (s, 1H), 6.94 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.67 (s, 2H), 3.88 (s, 3H), 2.92 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 158.4, 147.4, 143.5, 138.6, 137.9, 133.5, 132.9, 132.7, 131.0, 130.6, 130.1, 129.8, 129.7, 128.0, 127.8, 126.9, 126.6, 118.2, 115.2, 110.3, 65.1, 55.7, 27.6, 25.5.

(2-(9-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)-5-methylphenyl)methanol (3k):



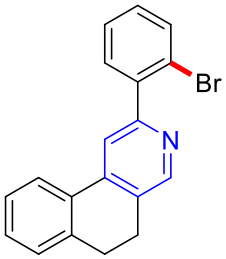
The reaction was carried out according to the general procedure A using 9-methoxy-2-(p-tolyl)-5,6-dihydrobenzo[f]isoquinoline (15 mg, 0.05 mmol). 16 mg (98% yield), brown liquid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.84 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 2.6 Hz, 1H), 7.32 (s, 1H), 7.24 (dd, *J* = 11.3, 7.4 Hz, 3H), 6.93 (dd, *J* = 8.4, 2.6 Hz, 1H), 4.47 (s, 2H), 3.88 (s, 3H), 2.91 (s, 4H), 2.43 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 159.1, 158.4, 147.4, 143.3, 140.3, 139.3, 137.6, 132.9, 132.0, 130.7, 130.67, 130.1, 129.7, 128.9, 117.7, 115.3, 110.1, 64.9, 55.7, 32.1, 27.7, 25.6. HRMS (EI^{+}) m/z $[M+H]^{+}$ Calcd for $C_{22}H_{22}NO_2$: 332.1643, Found 332.1638.

2-(2-bromophenyl)-8-methoxy-5,6-dihydrobenzo[f]isoquinoline (4a):



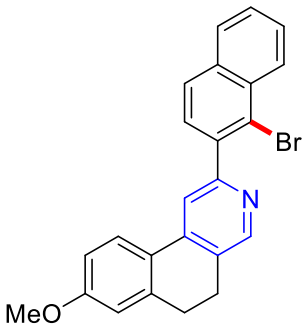
The reaction was carried out according to the general procedure B. 18 mg (51% yield) of yellowish-brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 11.4 Hz, 1H), 7.90 – 7.81 (m, 1H), 7.79 – 7.66 (m, 3H), 7.62 – 7.54 (m, 1H), 7.49 – 7.41 (m, 1H), 6.92 – 6.83 (m, 2H), 3.89 (s, 3H), 2.97 (d, *J* = 8.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.67, 148.57, 140.23, 133.42, 132.02, 131.56, 130.57, *129.69, 127.68, 126.11, 126.06, 124.26, 118.24, 117.94, 113.99,* 112.94, 108.98, 55.53, 29.02, 25.41. HRMS (EI^{+}) m/z $[M+H]^{+}$ Calcd for $C_{20}H_{17}BrNO$: 366.0488, Found 366.0484.

2-(2-bromophenyl)-5,6-dihydrobenzo[f]isoquinoline (4b):



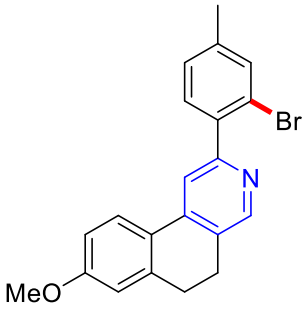
The reaction was carried out according to the general procedure B. 17 mg (52% yield) brown semi-liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.91 (s, 1H), 7.84 – 7.80 (m, 1H), 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.42 (td, *J* = 7.5, 1.2 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 7.27 (d, *J* = 1.6 Hz, 1H), 2.98-2.94 (m, 4H). ^{13}C NMR (101 MHz, CDCl3) δ 157.32, 148.80, 141.81, 141.55, 138.36, 133.45, 132.15, 131.57, 130.80, 129.76, 129.73, 128.73, 127.71, 127.46, 124.57, 122.11, 118.88, 28.58, 25.37. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{19}H_{15}BrN$: 336.0382, Found 336.0385.

2-(1-bromonaphthalen-2-yl)-8-methoxy-5,6-dihydrobenzo[f]isoquinoline (4c):



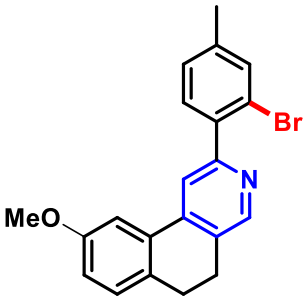
The reaction was carried out according to the general procedure B using 8-methoxy-2-(naphthalen-2-yl)-5,6-dihydrobenzo[f]isoquinoline (17 mg, 0.05 mmol), $Pd(OAc)_2$ (10 mol%), and NBS (0.05 mmol,1 equiv.). 11 mg (57% yield), brown semi-liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.08 (s, 1H), 8.01 – 7.87 (m, 4H), 7.58 – 7.50 (m, 2H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.23 (s, 1H), 6.94 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.67 (s, 2H), 3.88 (s, 3H), 2.92 (s, 4H).^{13}C NMR (75 MHz, $CDCl_3$) δ 156.76, 156.68, 149.08, 141.53, 139.46, 137.02, 135.35, 133.68, 129.56, 129.39, 128.83, 128.59, 127.81, 126.56, 126.44, 126.24, 125.15, 124.78, 114.39, 112.02, 110.32, 56.52, 28.96, 25.18. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{24}H_{19}BrNO$: 416.0645 and 418.0624, Found 416.0640 and 418.0628

2-(2-bromo-4-methylphenyl)-8-methoxy-5,6-dihydrobenzo[f]isoquinoline(4d):



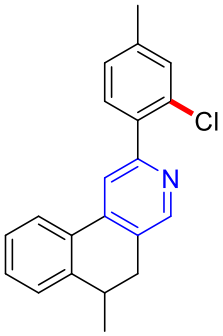
The reaction was carried out according to the general procedure B. 23 mg (60% yield), yellow semi liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.03 (s, 1H), 7.94 – 7.90 (m, 2H), 7.87 (s, 1H), 7.32 – 7.28 (m, 2H), 6.82 (s, 1H), 3.96 (s, 3H), 2.90 (s, 4H), 2.42 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.94, 156.61, 148.90, 141.34, 139.43, 138.88, 136.96, 129.61, 129.57, 129.34, 129.15, 126.85, 126.51, 113.81, 112.91, 112.00, 110.27, 56.51, 28.99, 25.15, 21.43. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{21}H_{19}BrNO$: 380.0645 and 382.0624, Found 380.0639 and 382.0619.

2-(2-bromo-4-methylphenyl)-9-methoxy-5,6-dihydrobenzo[f]isoquinoline (4e):



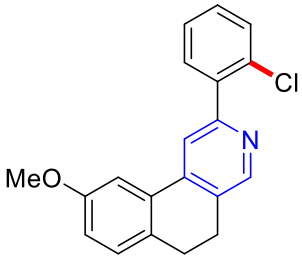
The reaction was carried out according to the general procedure A using 9-methoxy-2-(p-tolyl)-5,6-dihydrobenzo[f]isoquinoline (15 mg, 0.05 mmol). 12 mg (62% yield), brown semi-liquid.^{1}H NMR (700 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.55 (s, 1H), 7.48 (s, 2H), 7.31 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.91 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.85 (s, 3H), 2.93 (tt, *J* = 7.4, 3.8 Hz, 4H), 2.38 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 159.1, 157.6, 148.8, 141.3, 132.9, 132.6, 131.4, 130.55, 129.6, 123.7, 119.0, 119.0, 115.5, 113.5, 109.9, 55.7, 27.6, 25.7, 20.7. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{21}H_{19}BrNO$: 380.0645, Found 380.0641.

2-(2-chlorophenyl)-6-methyl-5,6-dihydrobenzo[f]isoquinoline (4f) :



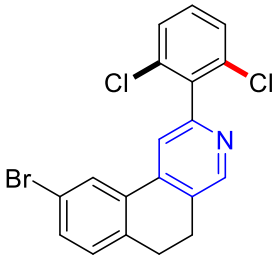
The reaction was carried out according to the general procedure B. 19 mg (62 % yield), brown semi-liquid. ^{1}H NMR (300 MHz, CDCl3) δ 8.56 (s, 1H), 7.96 (s, 1H), 7.84 – 7.81 (m, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.21-7.16 (m, 1H), 3.19 – 3.03 (m, 2H), 2.78 – 2.71 (m, 1H), 2.40 (s, 3H), 1.25(s,3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.80, 149.33, 143.15, 141.42, 139.89, 136.57, 134.77, 131.95, 131.42, 131.26, 130.69, 129.98, 129.28, 128.01, 127.27, 124.71, 118.80, 32.89, 32.69, 21.09, 20.08. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{21}H_{19}ClN$: 320.1201, Found 320.1204.

2-(2-chlorophenyl)-9-methoxy-5,6-dihydrobenzo[f]isoquinoline (4g):



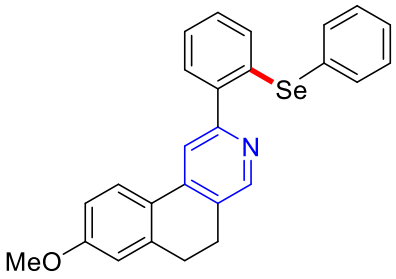
The reaction was carried out according to the general procedure B. (19 mg, 59% yield), brown semi-liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.92 (s, 1H), 7.65 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.92 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.86 (s, 3H), 2.92 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.07, 155.66, 148.69, 132.97, 132.39, 131.65, 131.11, 130.61, 130.29, 129.73, 129.62, 129.05, 127.21, 127.17, 119.03, 115.32, 110.03, 55.63, 27.66, 25.71. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{20}H_{17}ClNO$: 322.0993, Found 322.1998.

9-bromo-2-(2,6-dichlorophenyl)-5,6-dihydrobenzo[f]isoquinoline (4h):



The reaction was carried out according to the general procedure B. (18 mg, 45% yield), brown liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.93 (t, *J* = 3.7 Hz, 1H), 7.62 (s, 1H), 7.50 – 7.44 (m, 3H), 7.35 – 7.29 (m, 1H), 7.20 (s, 1H), 2.97 (d, *J* = 6.5 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.64, 149.21, 141.26, 137.12, 134.94, 133.92, 132.54, 131.19, 131.17, 130.36, 130.29, 130.06, 129.84, 128.33, 127.56, 121.07, 119.01, 27.95, 25.17. HRMS (EI^+) m/z $[M+H]^+$ Calcd for $C_{19}H_{13}BrCl_2N$: 403.9603 and 405.9582, Found 403.9598 and 405.9584.

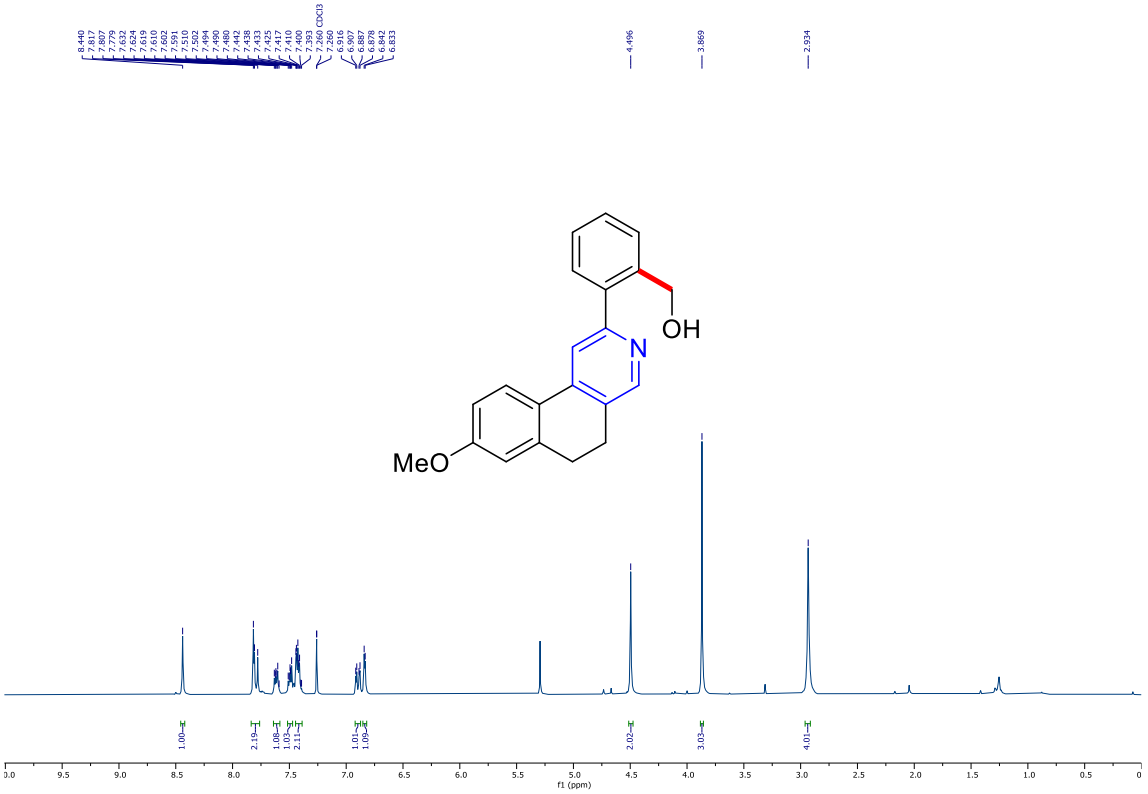
8-methoxy-2-(2-(phenylselanyl)phenyl)-5,6-dihydrobenzo[f]isoquinoline(5):

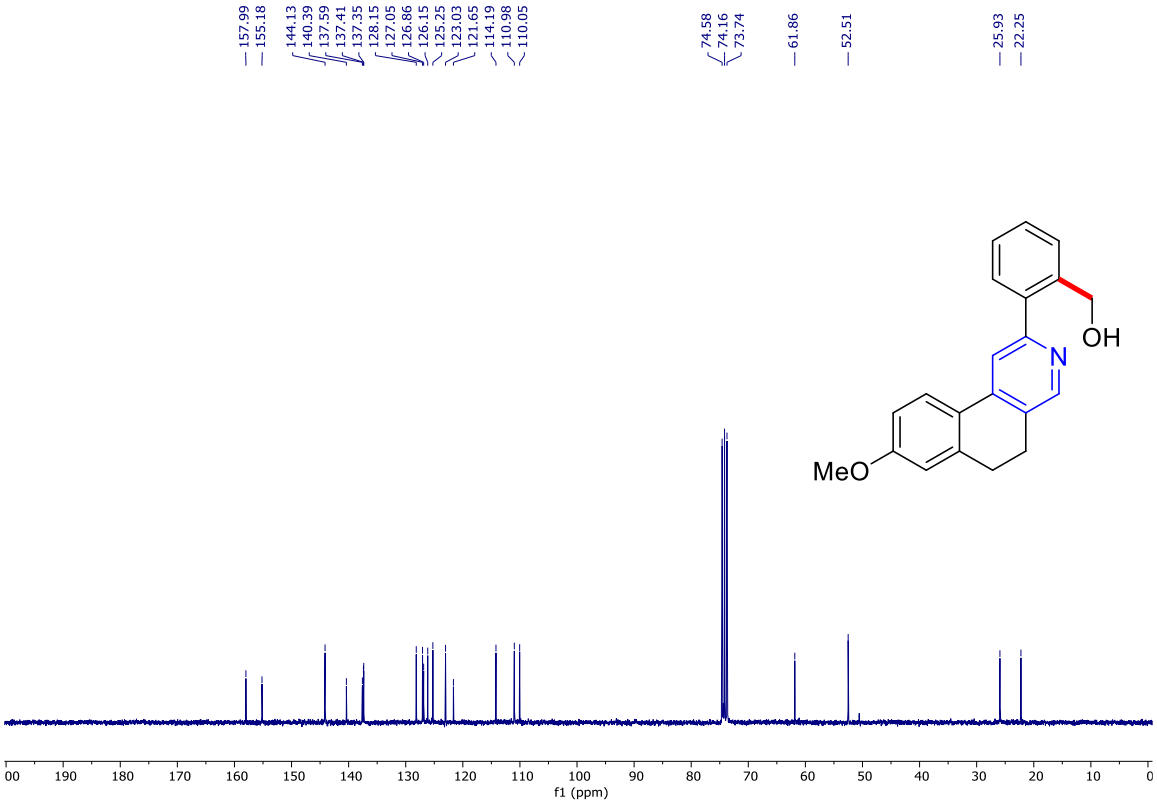


The reaction was carried out according to the general procedure C. brown semi-solid, 27 mg (61% yield). ^{1}H NMR (700 MHz, DMSO) δ 8.54 (s, 1H), 8.07 (s, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 6.9 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.21 (t, J = 7.7 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.95 – 6.95 (m, 2H), 3.82 (s, 3H), 2.89 (s, 4H). ^{13}C NMR (176 MHz, DMSO) δ 160.65, 156.81, 147.12, 142.15, 140.30, 139.76, 135.71, 133.97, 131.60, 130.87, 130.07, 130.02, 129.98, 129.86, 129.62, 129.06, 128.66, 126.70, 126.34, 124.35, 115.81, 113.87, 113.25, 55.51, 28.27, 24.69. HRMS (EI^{+}) m/z $[M+H]^{+}$ Calcd for $C_{26}H_{22}NOSe$: 444.0861, Found 444.0856.

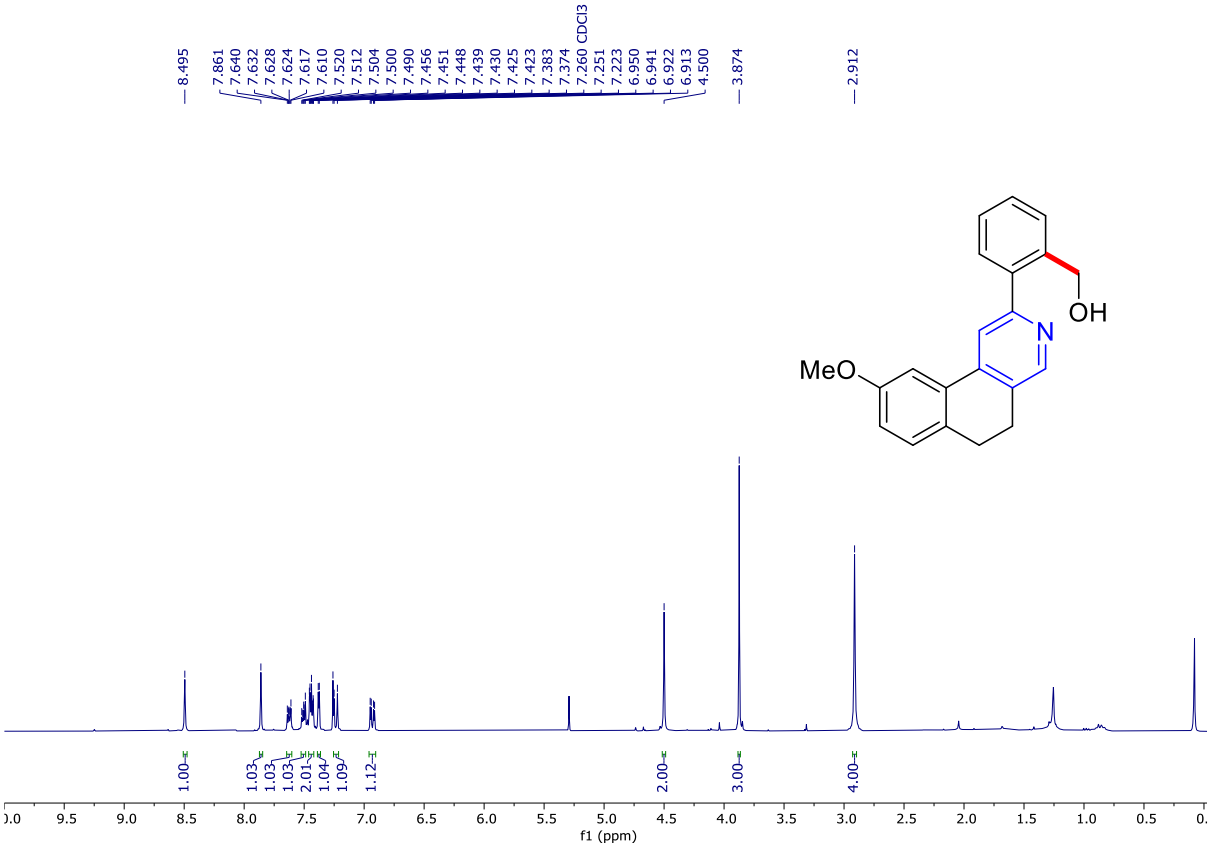
3. ^{1}H and ^{13}C NMR Spectra

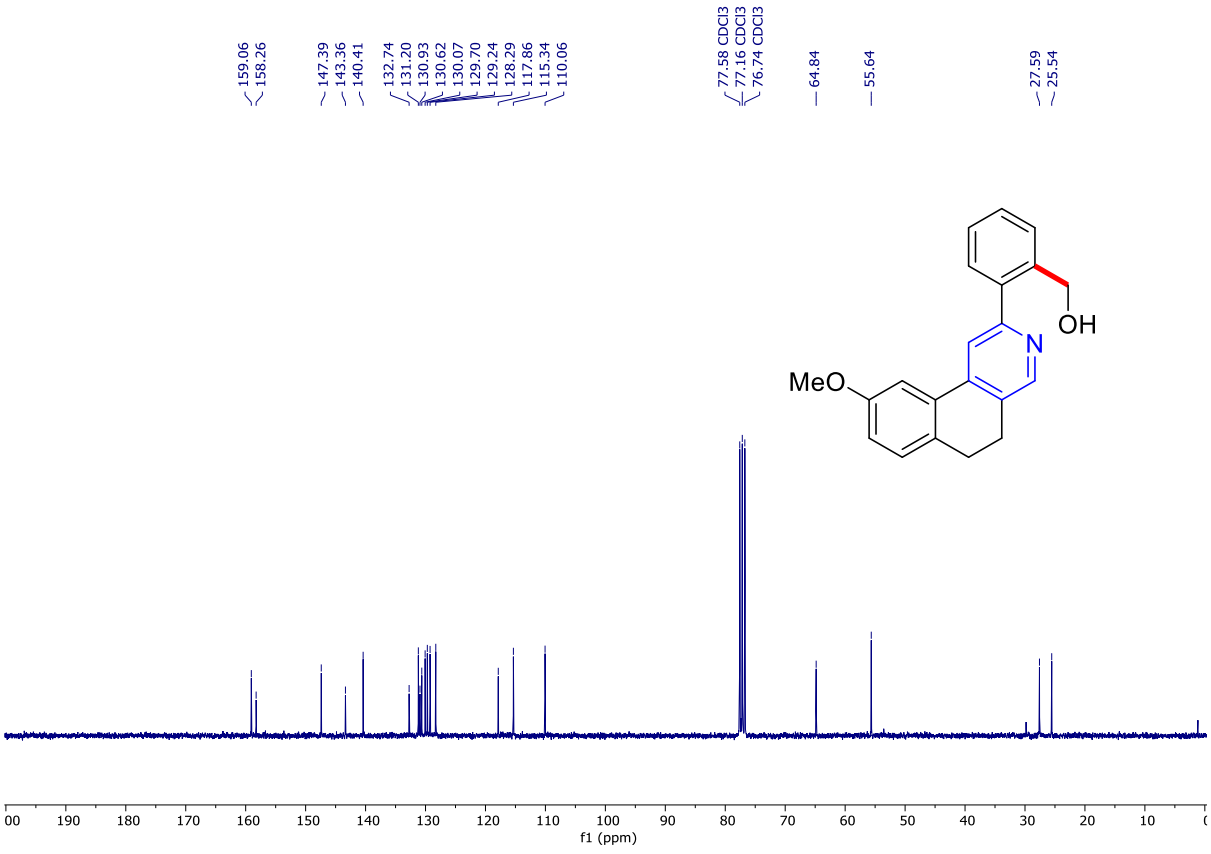
(2-(8-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3a):



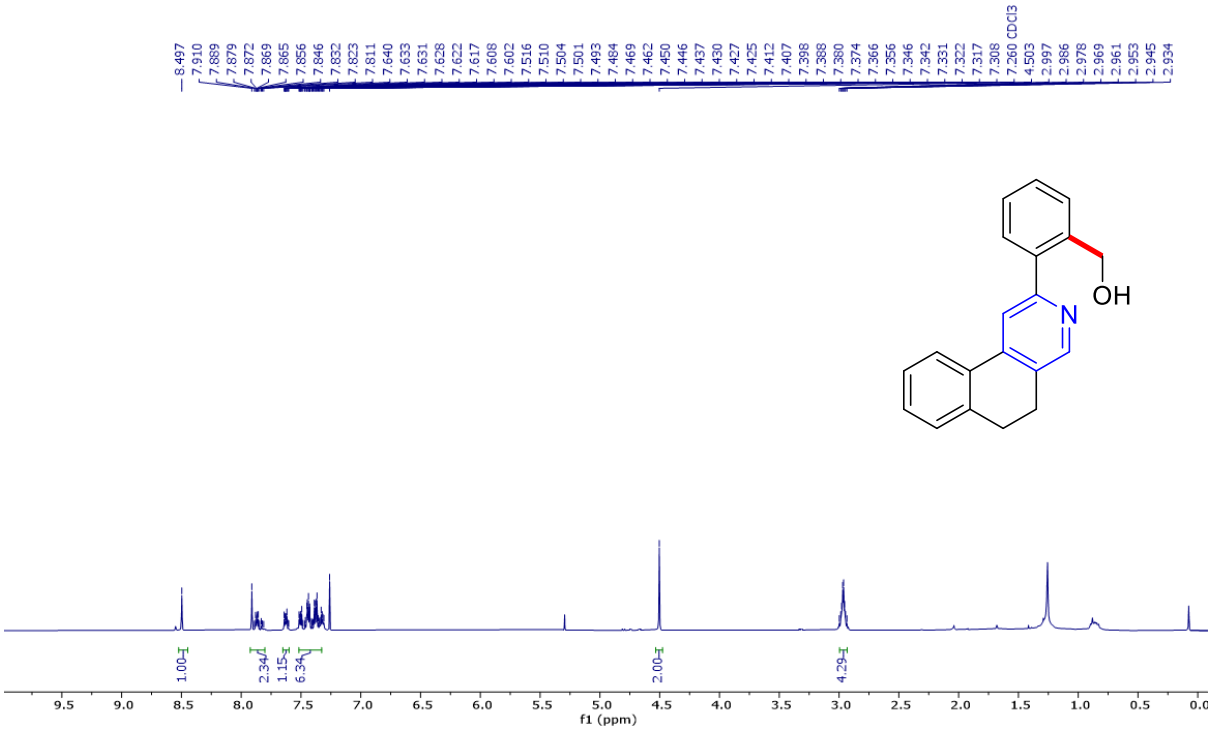


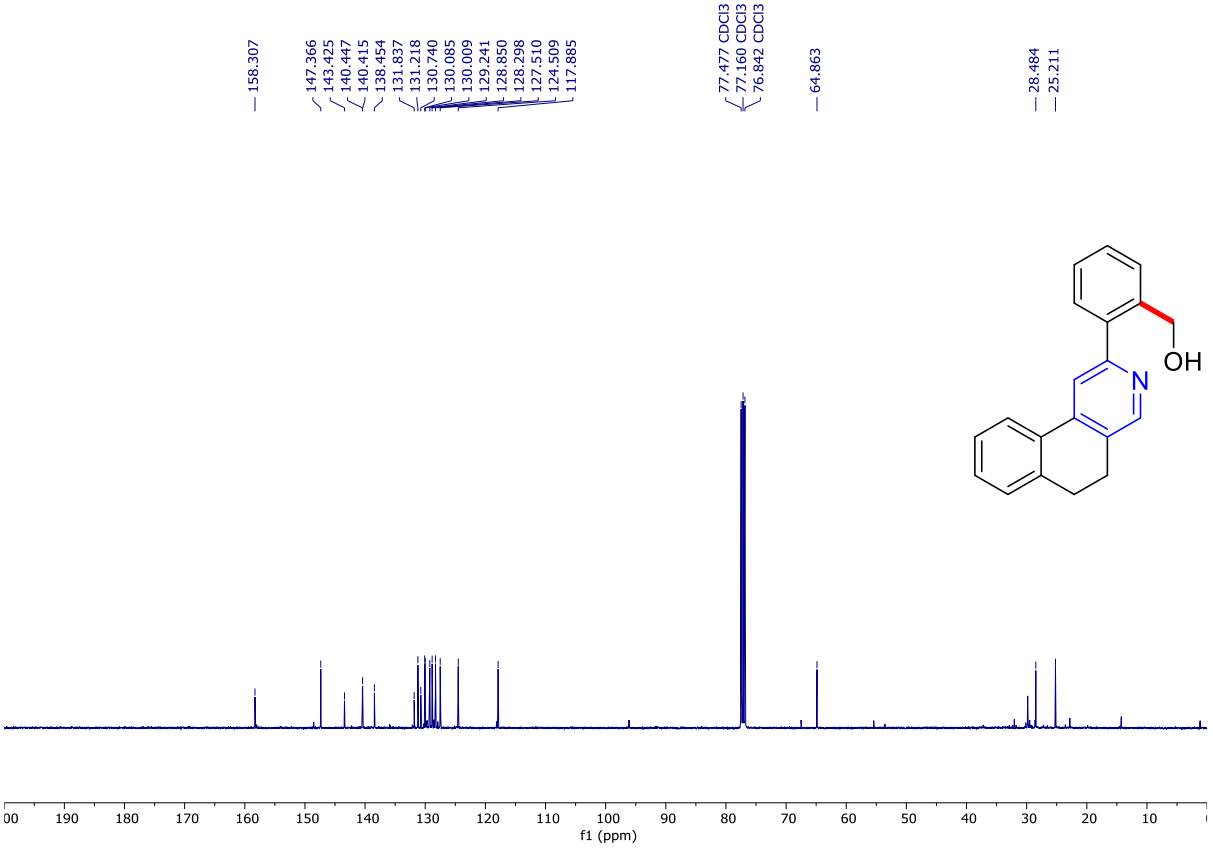
(2-(9-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3b):



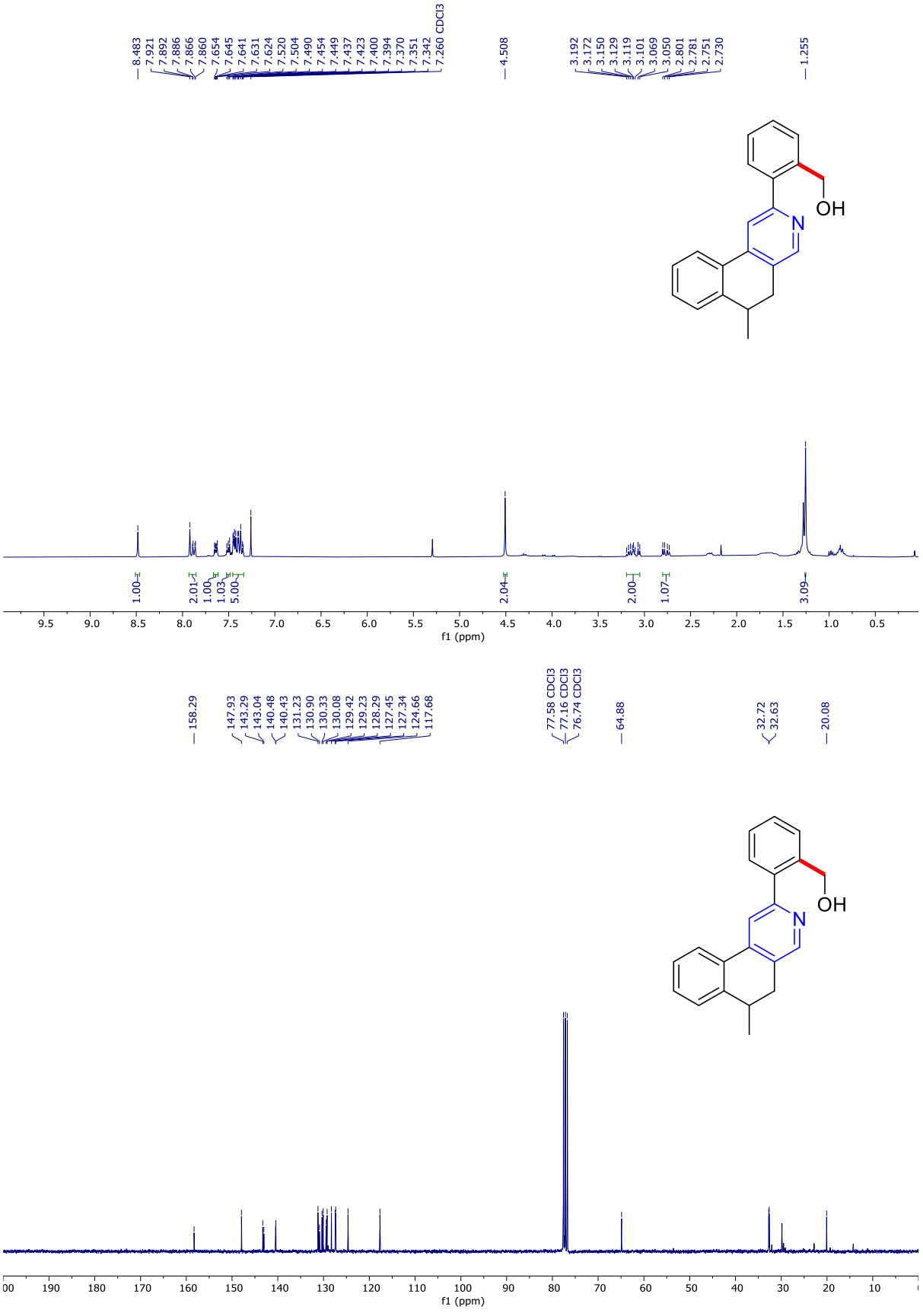


(2-(5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3c):

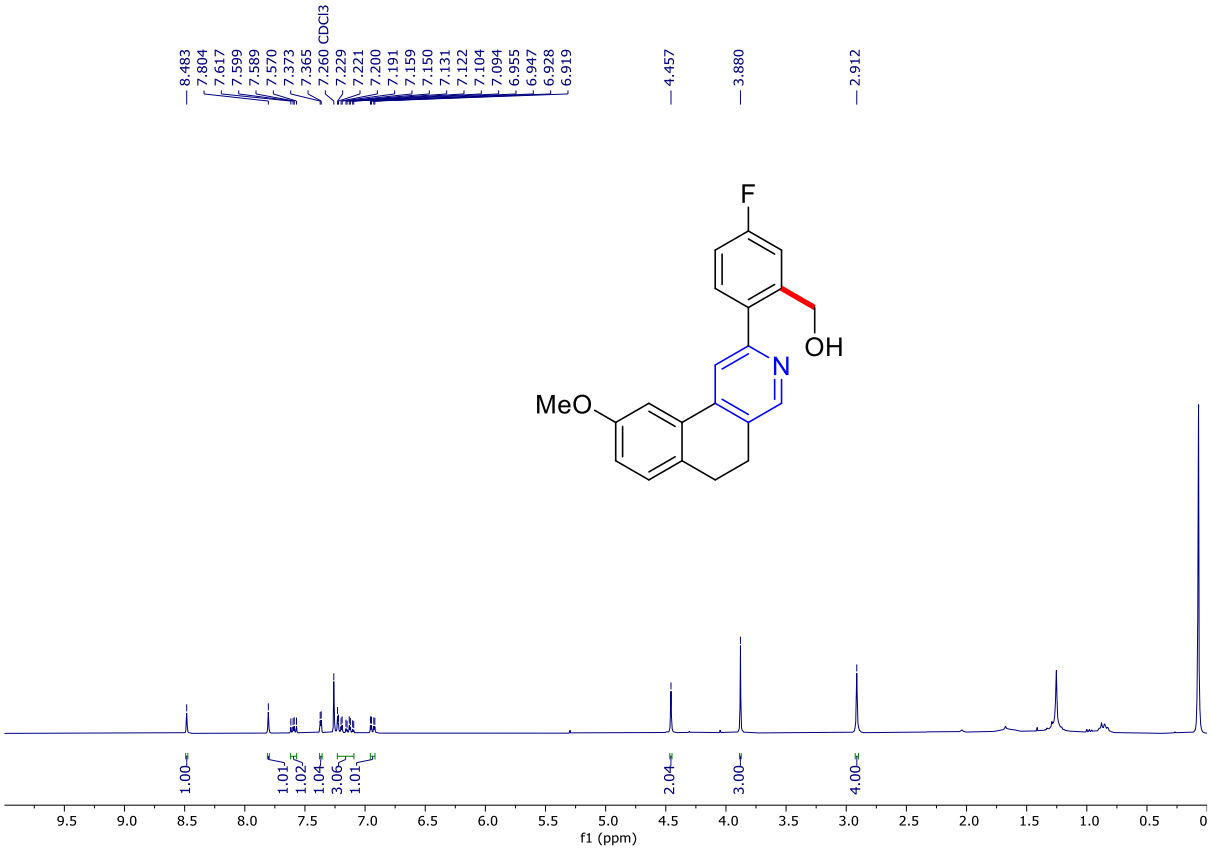


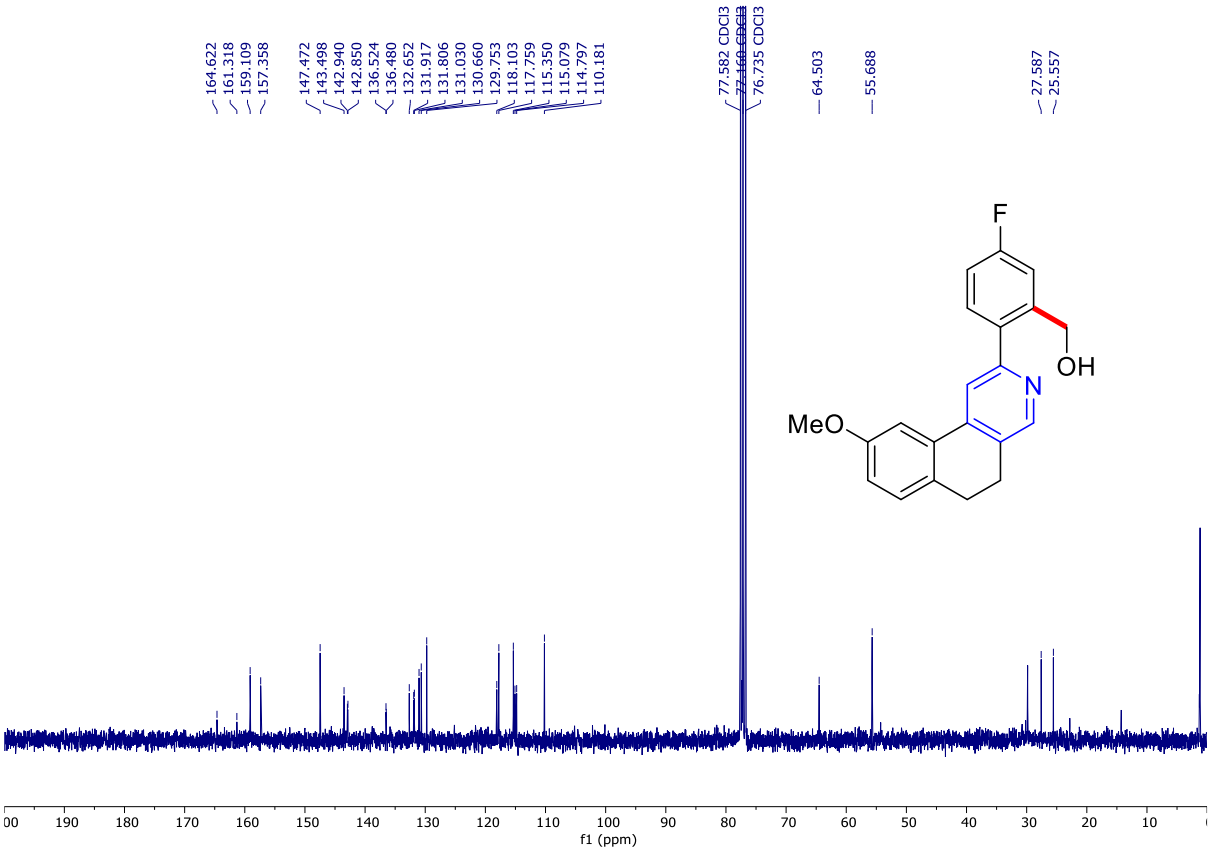


(2-(6-methyl-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3d):

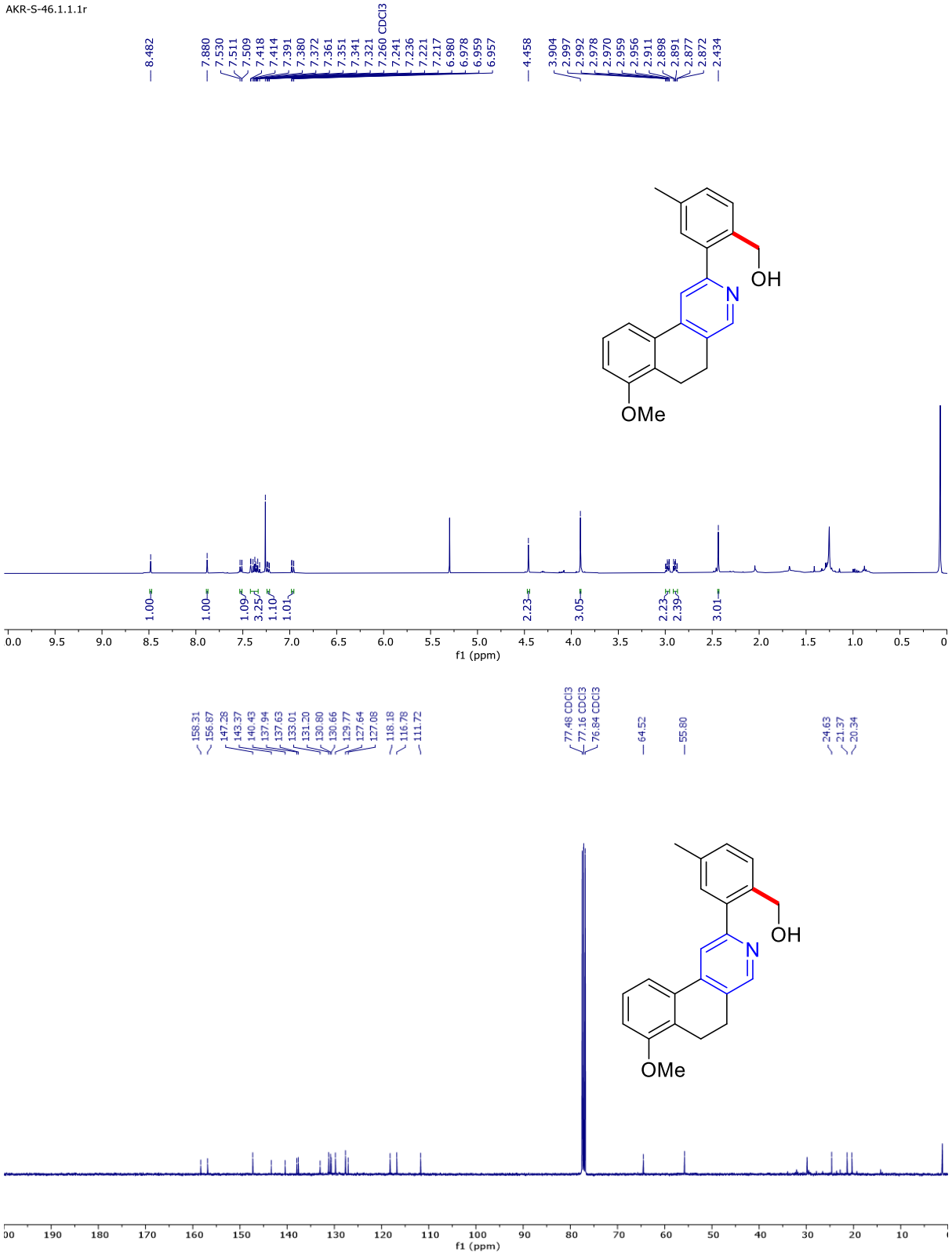


(5-fluoro-2-(9-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3e):

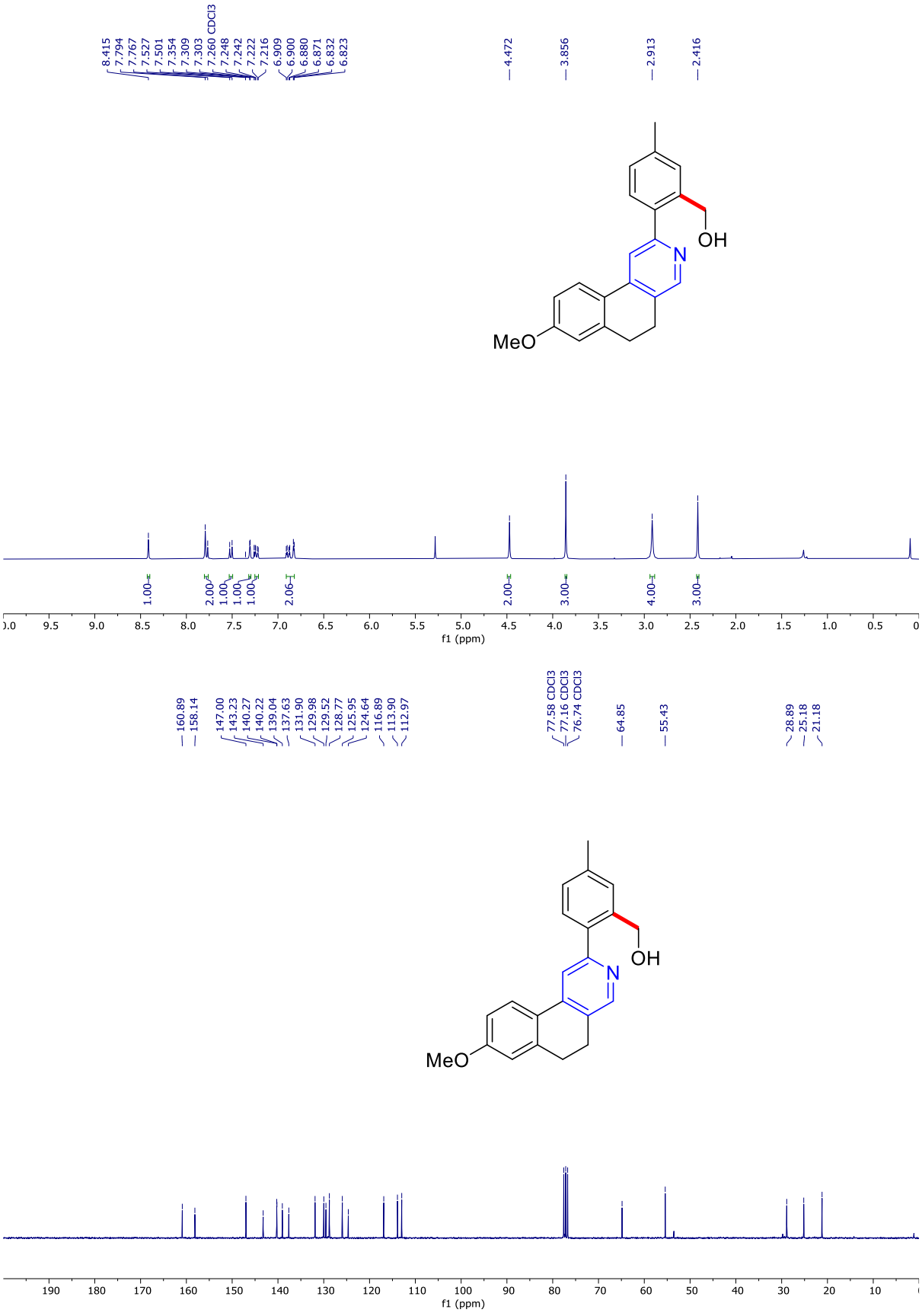




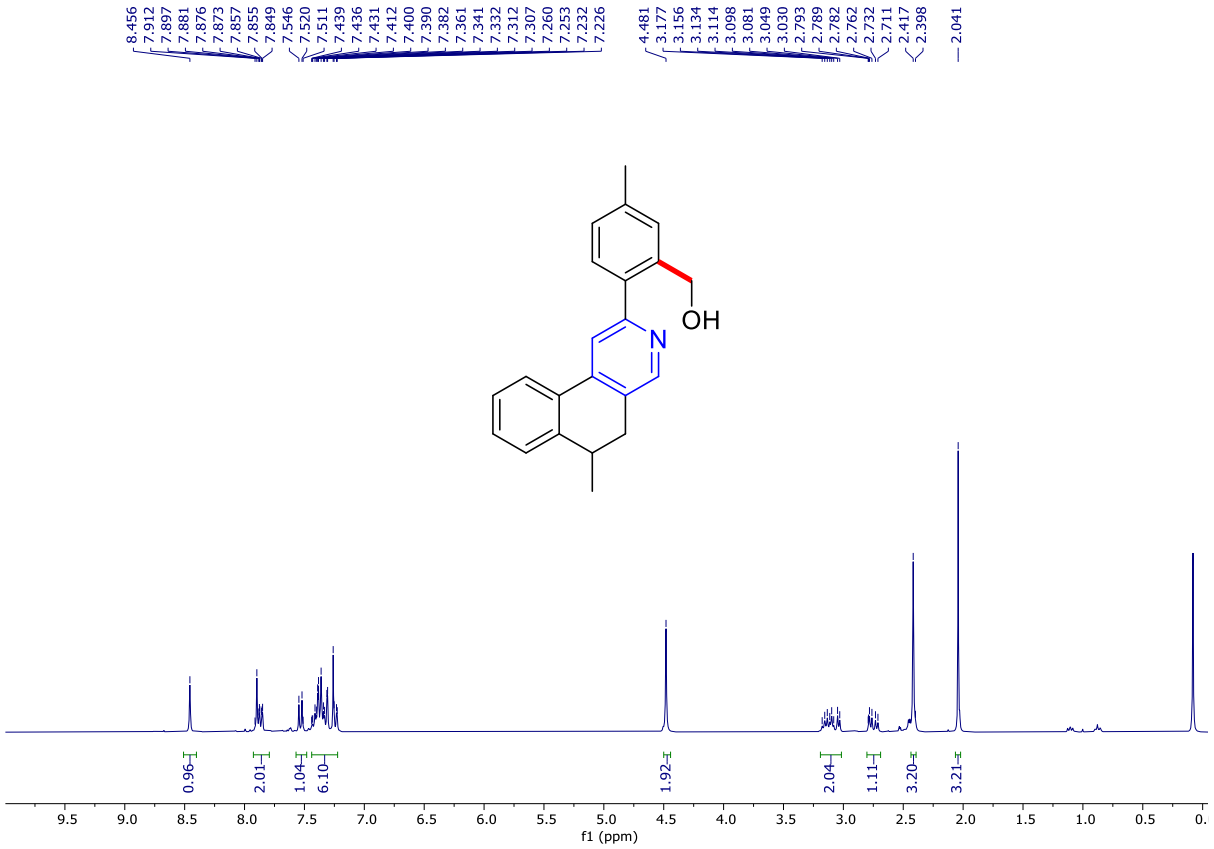
(2-(7-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)-4-methylphenyl)methanol (3f):

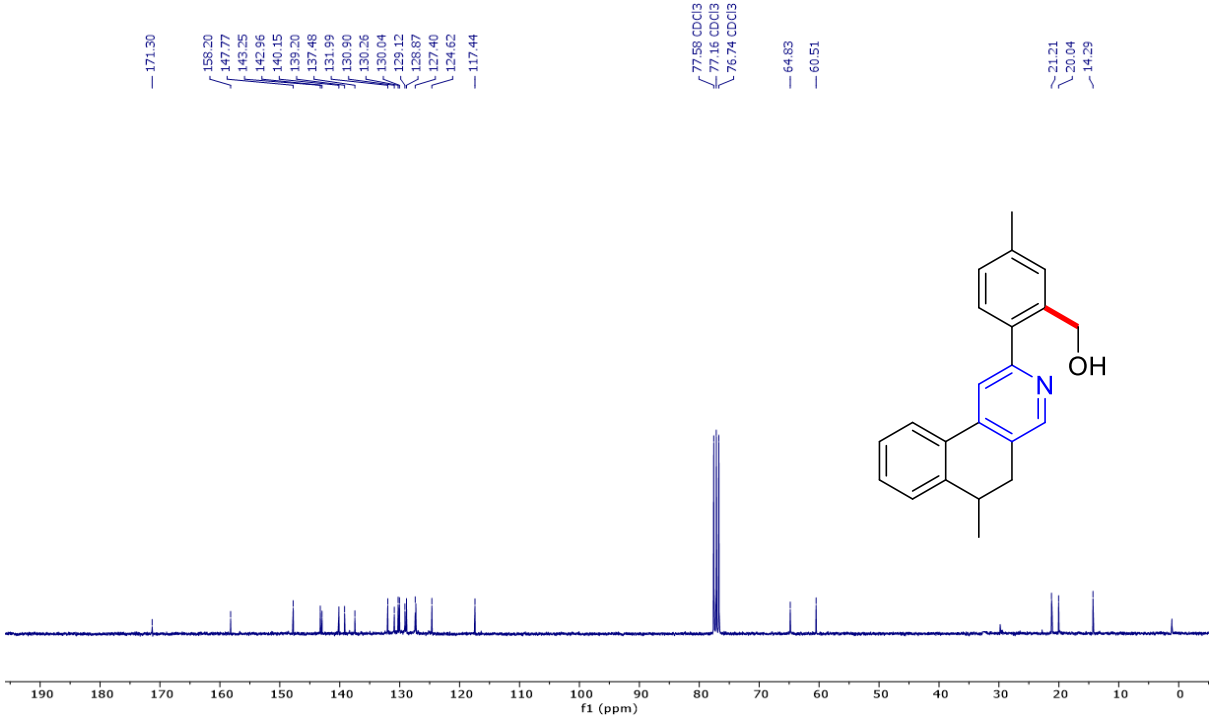


(2-(8-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)-5-methylphenyl)methanol (3g):

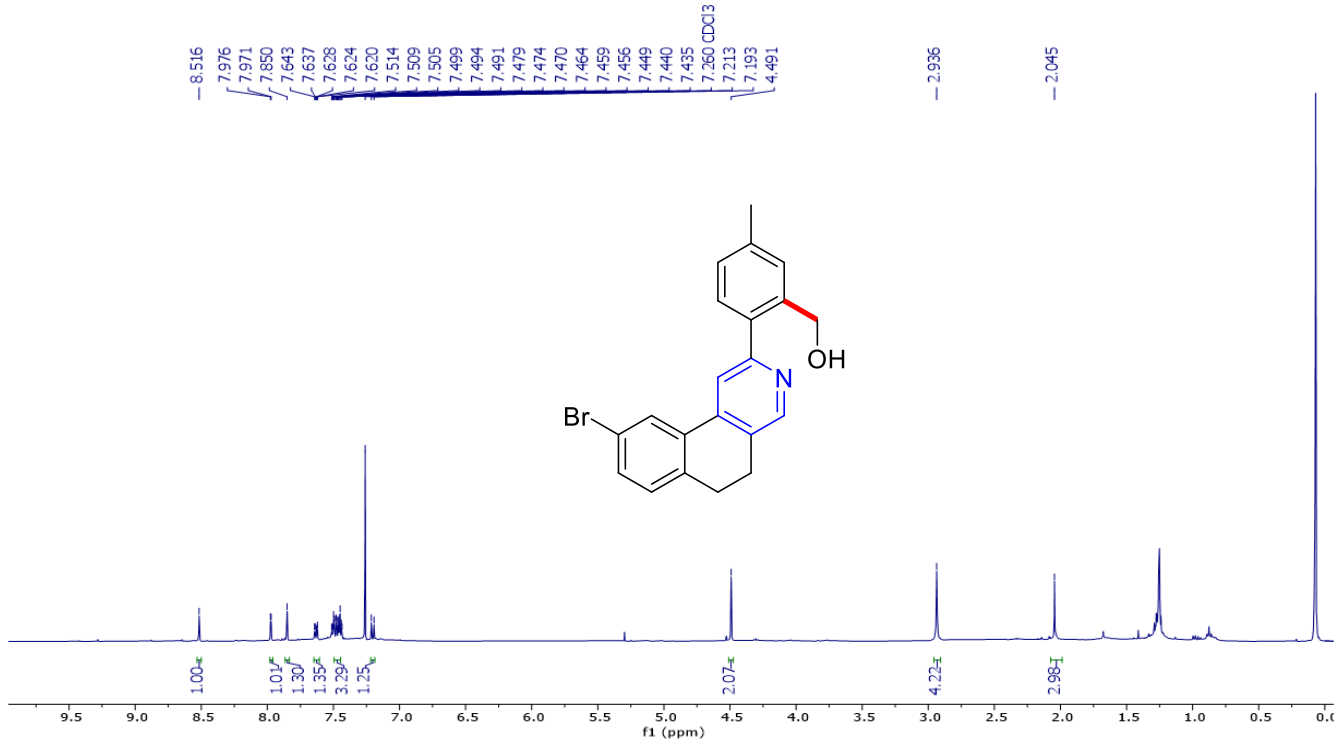


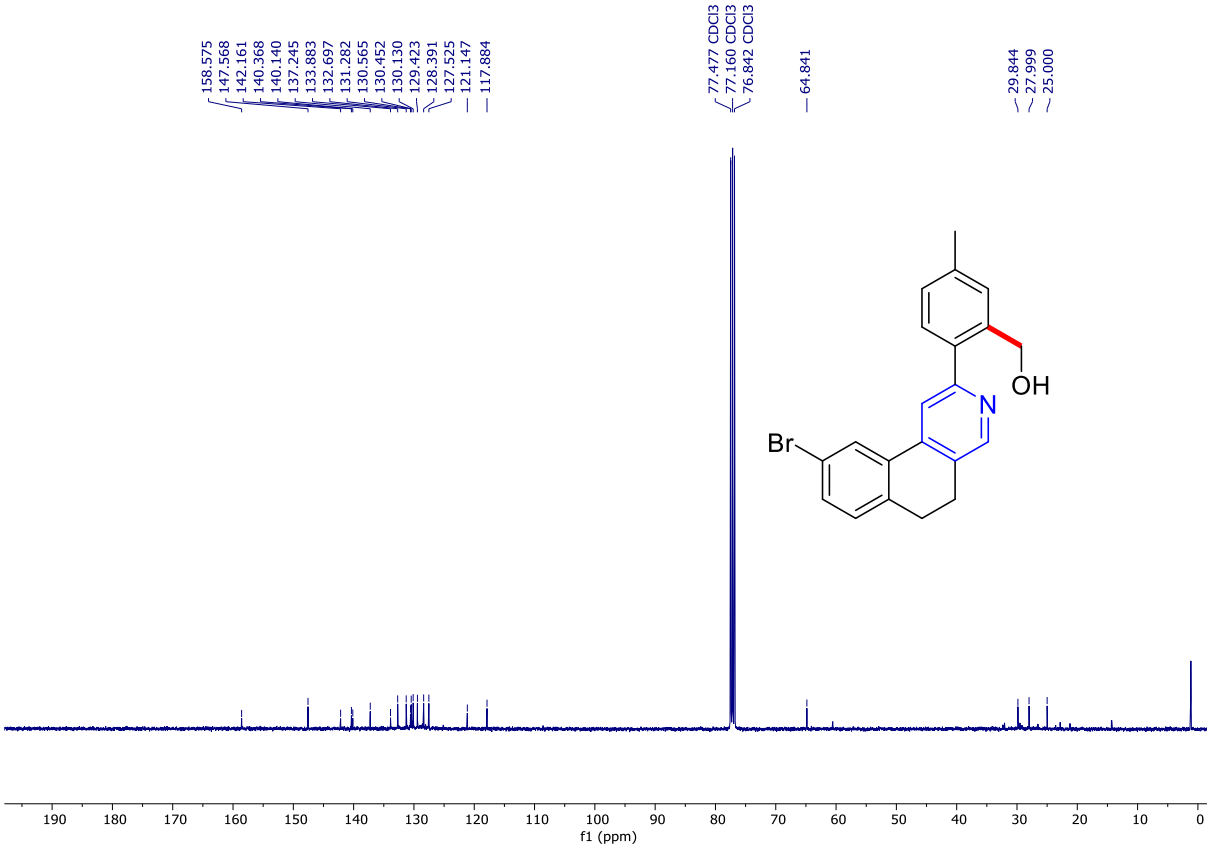
(5-methyl-2-(6-methyl-5,6-dihydrobenzo[f]isoquinolin-2-yl)phenyl)methanol (3h)



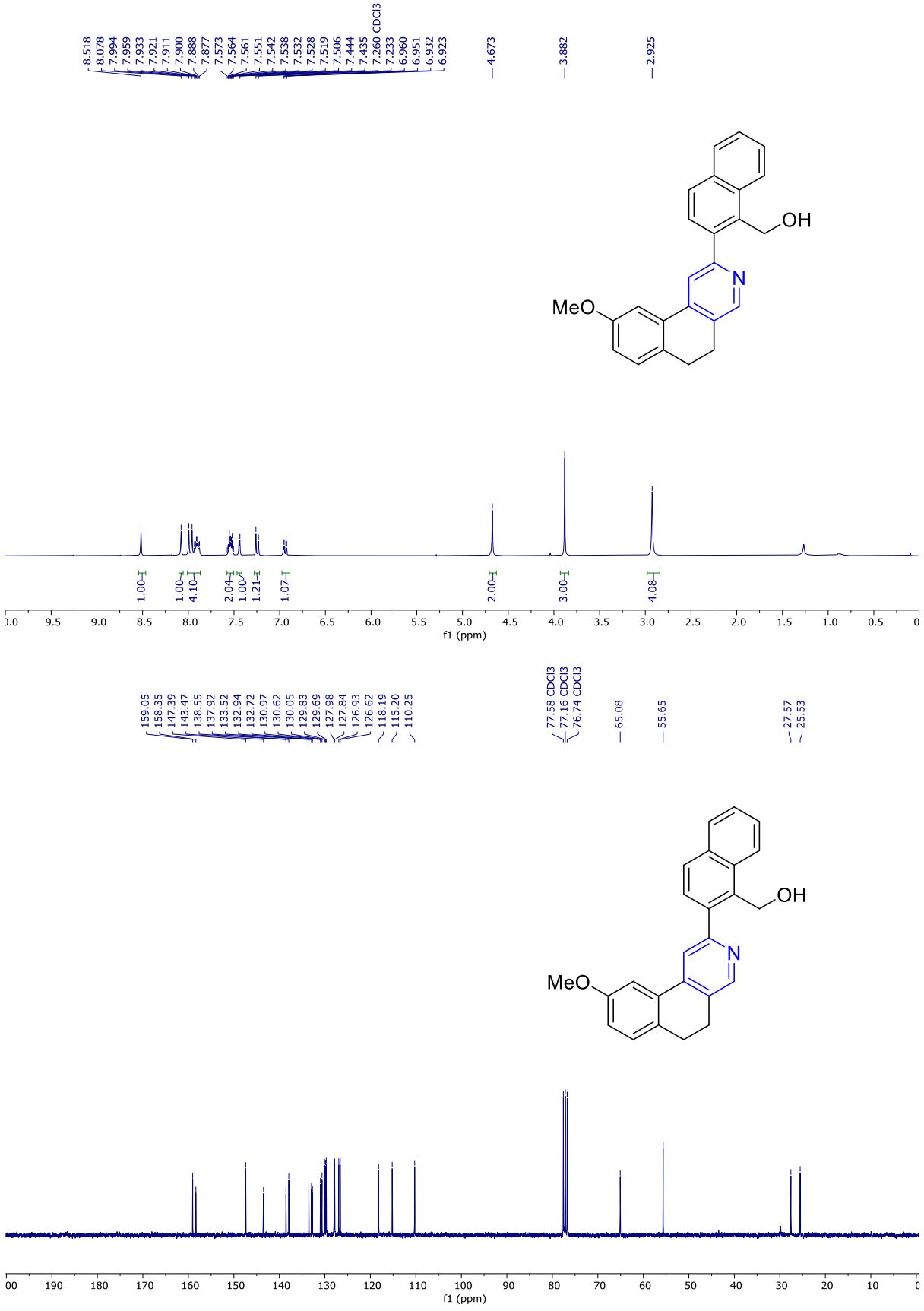


(2-(9-bromo-5,6-dihydrobenzo[f]isoquinolin-2-yl)-5-methylphenyl)methanol (3i)

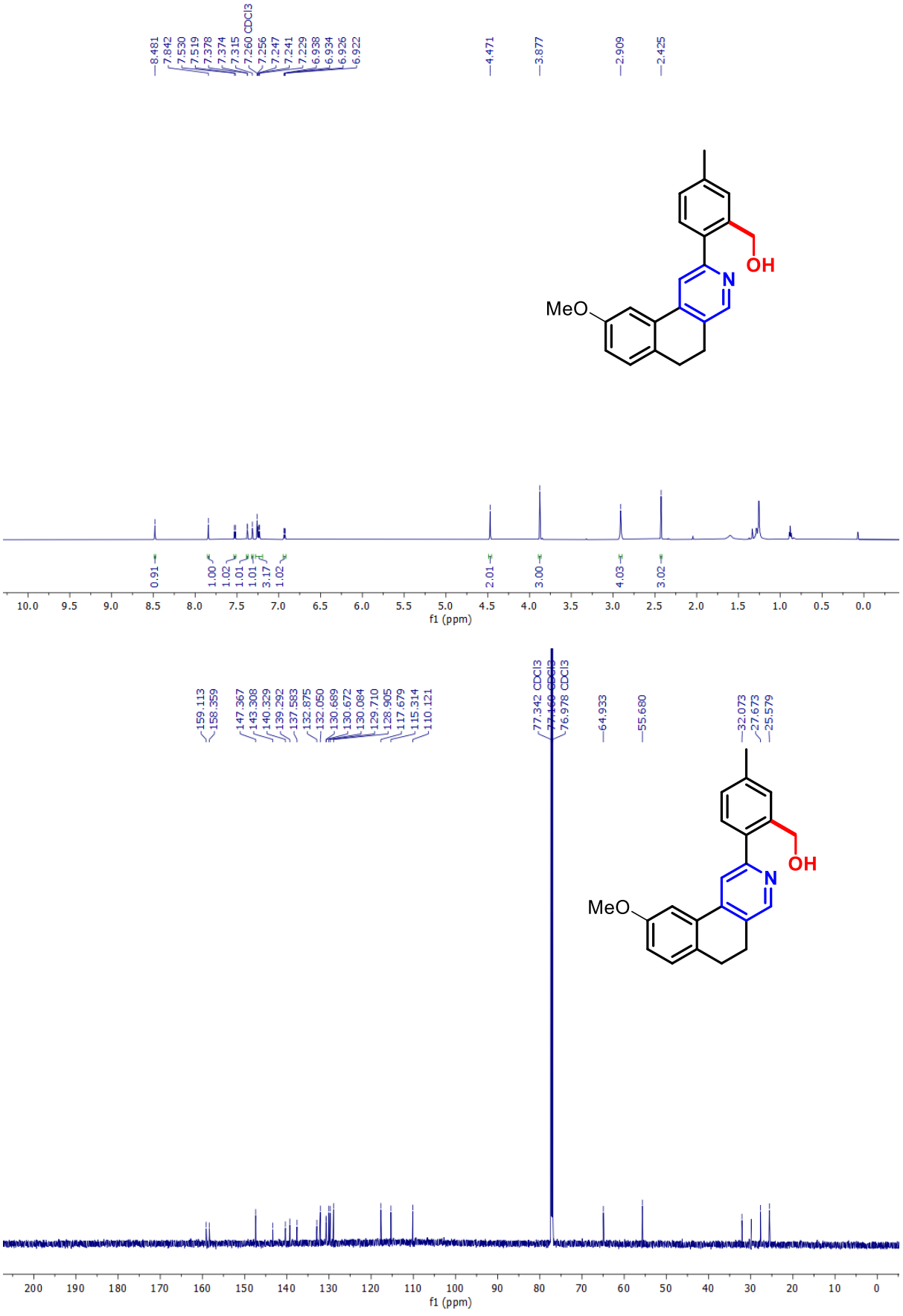




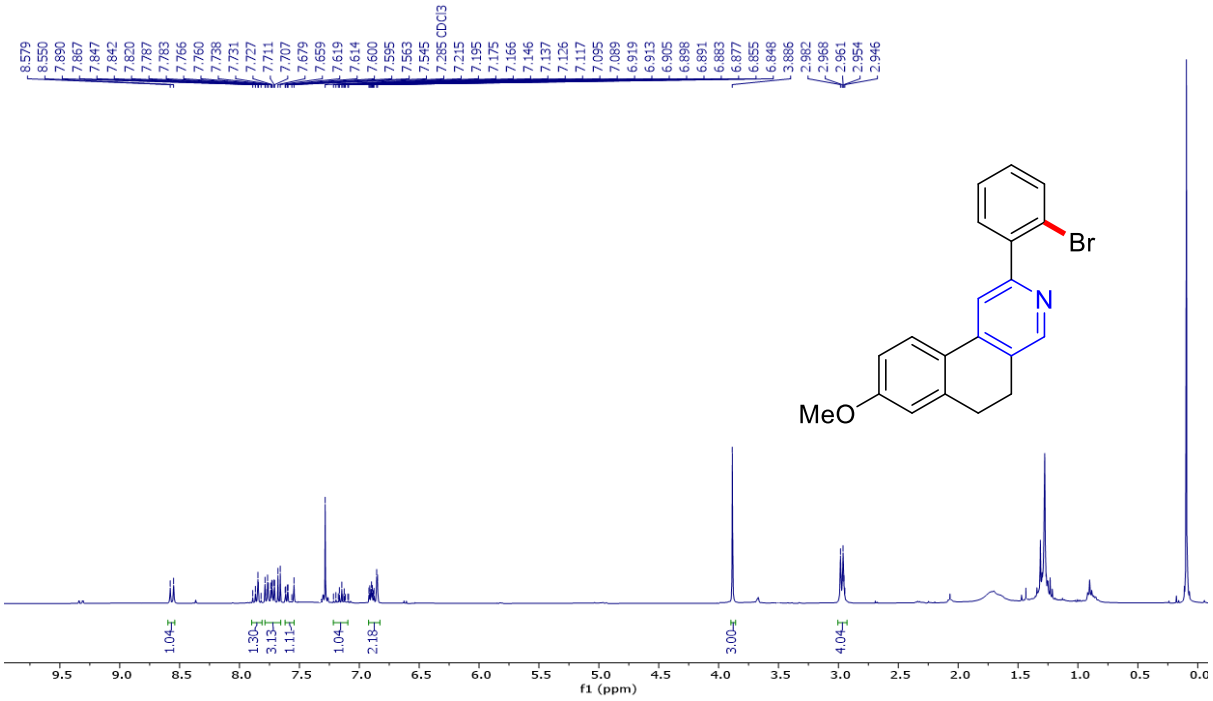
(2-(9-bromo-5,6-dihydrobenzo[f]isoquinolin-2-yl)-5-methylphenyl)methanol(3j):

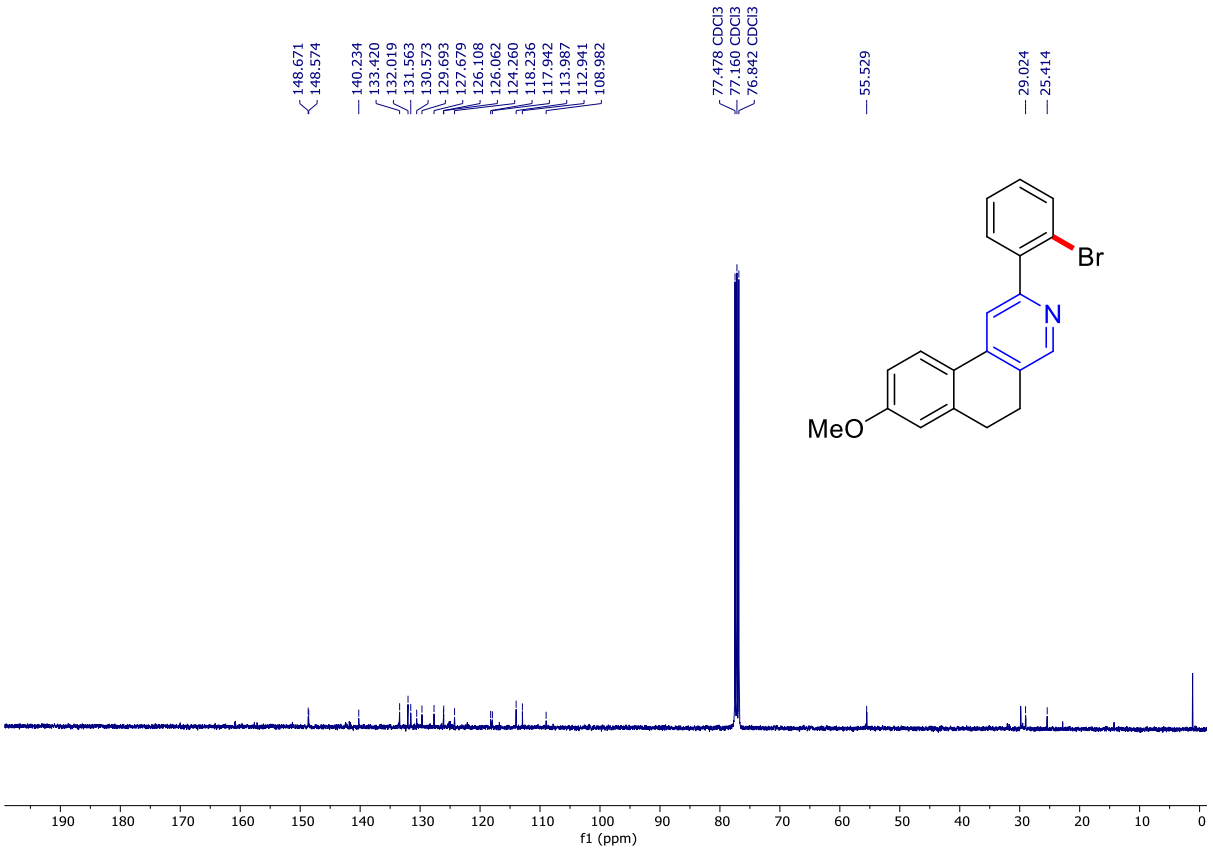


(2-(9-methoxy-5,6-dihydrobenzo[f]isoquinolin-2-yl)-5-methylphenyl)methanol (3k):

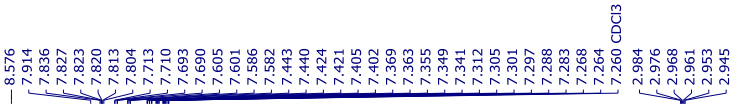


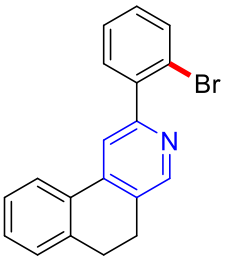
2-(2-bromophenyl)-8-methoxy-5,6-dihydrobenzo[f]isoquinoline (4a)

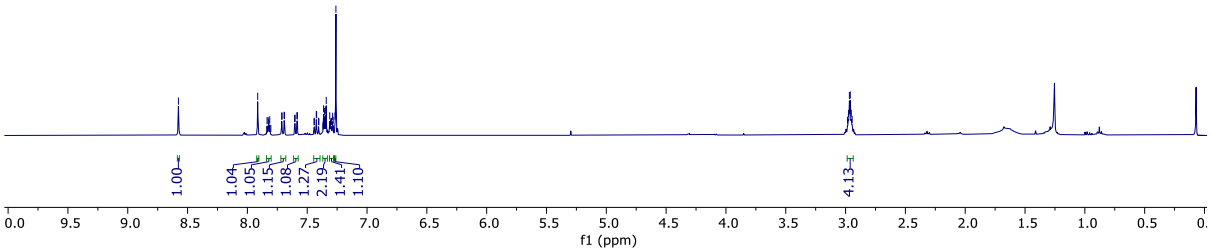


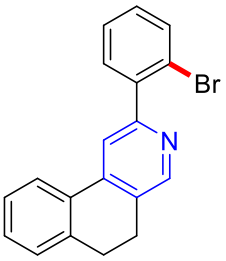


2-(2-bromophenyl)-5,6-dihydrobenzo[f]isoquinoline (4b):

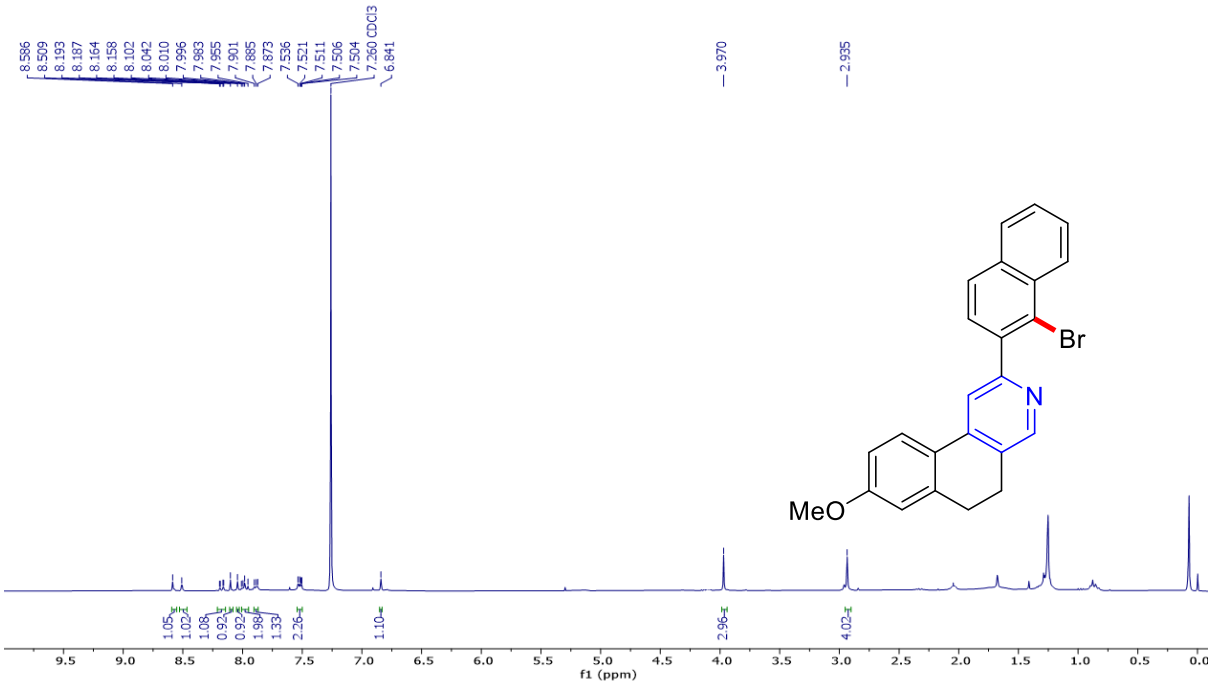


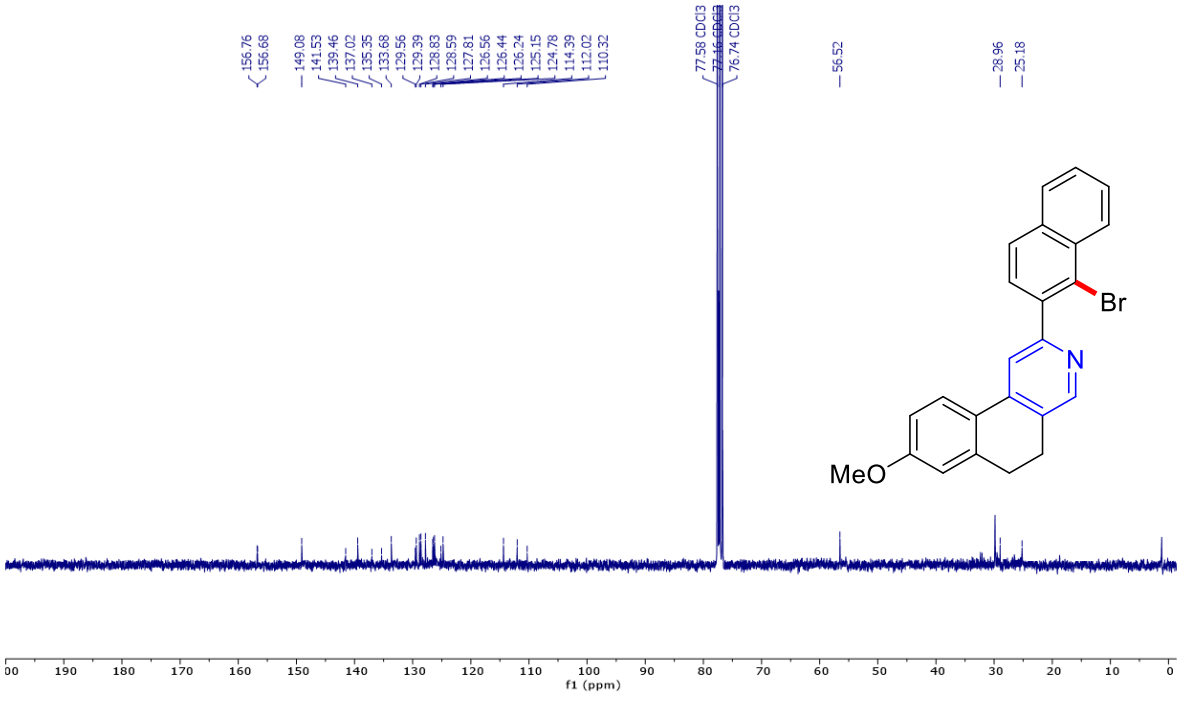




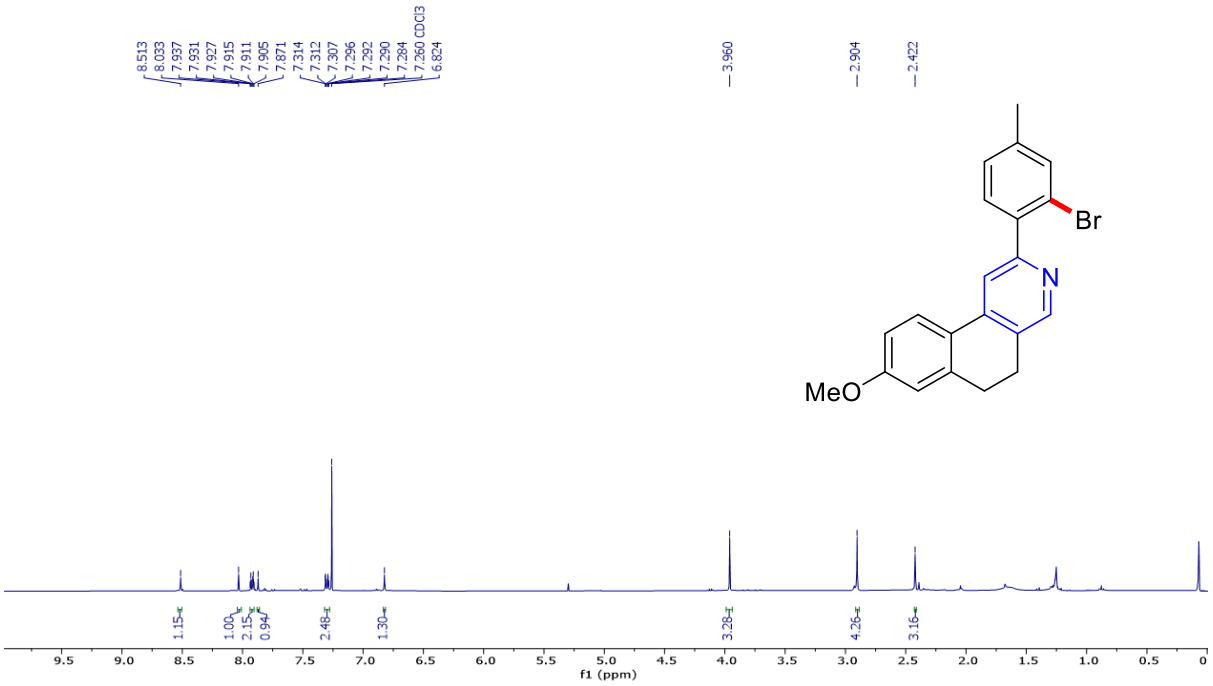


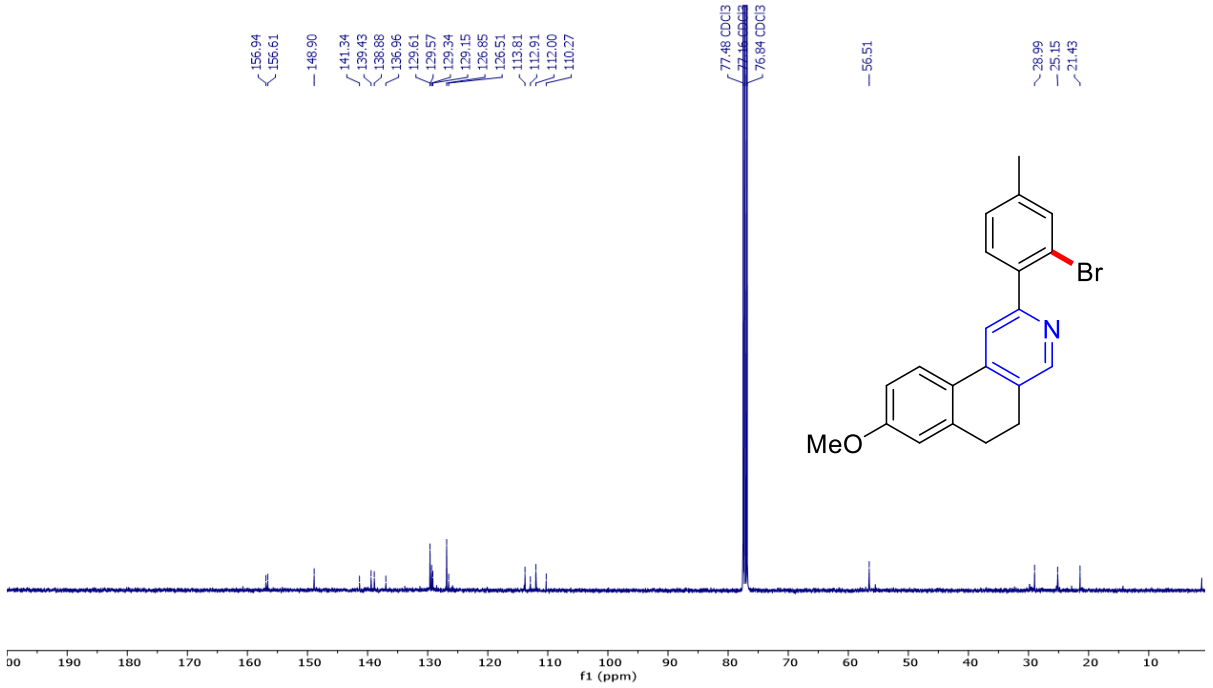
2-(1-bromonaphthalen-2-yl)-8-methoxy-5,6-dihydrobenzo[f]isoquinoline (4c):



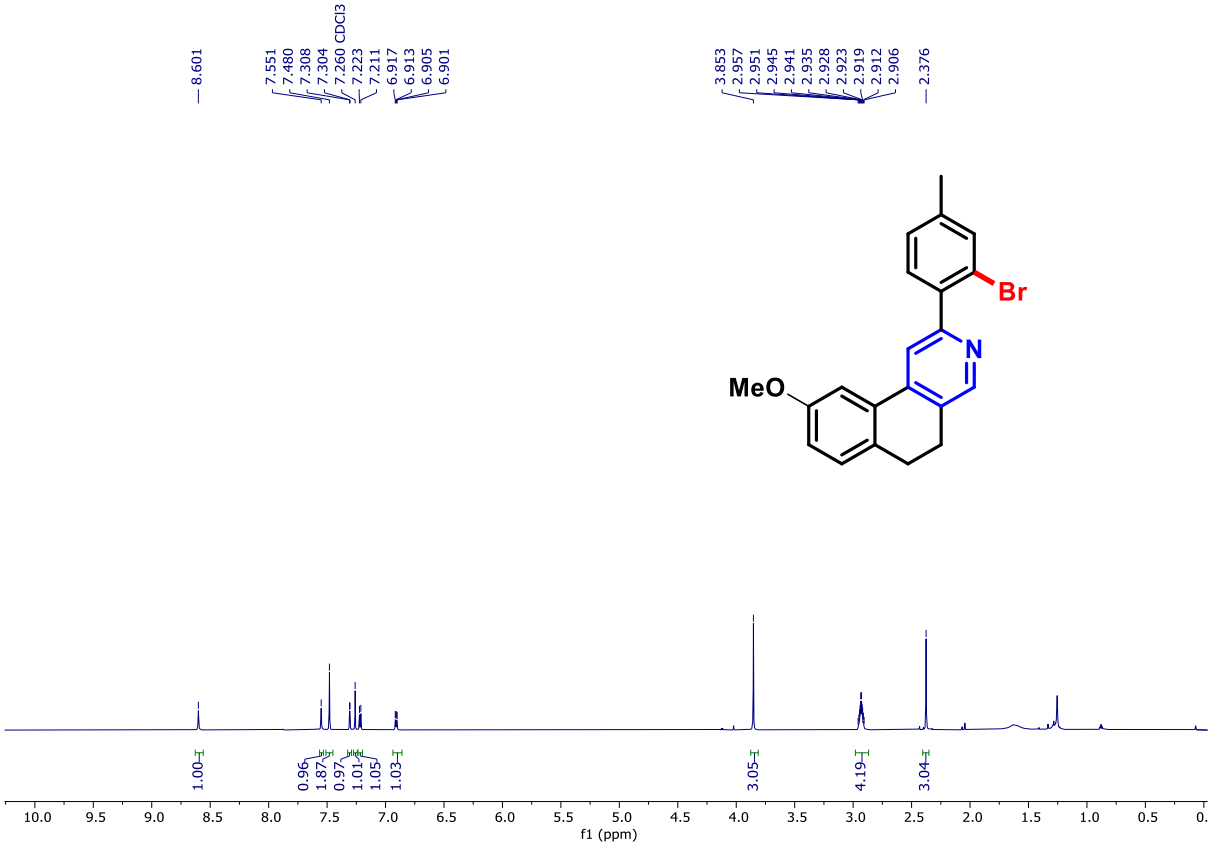


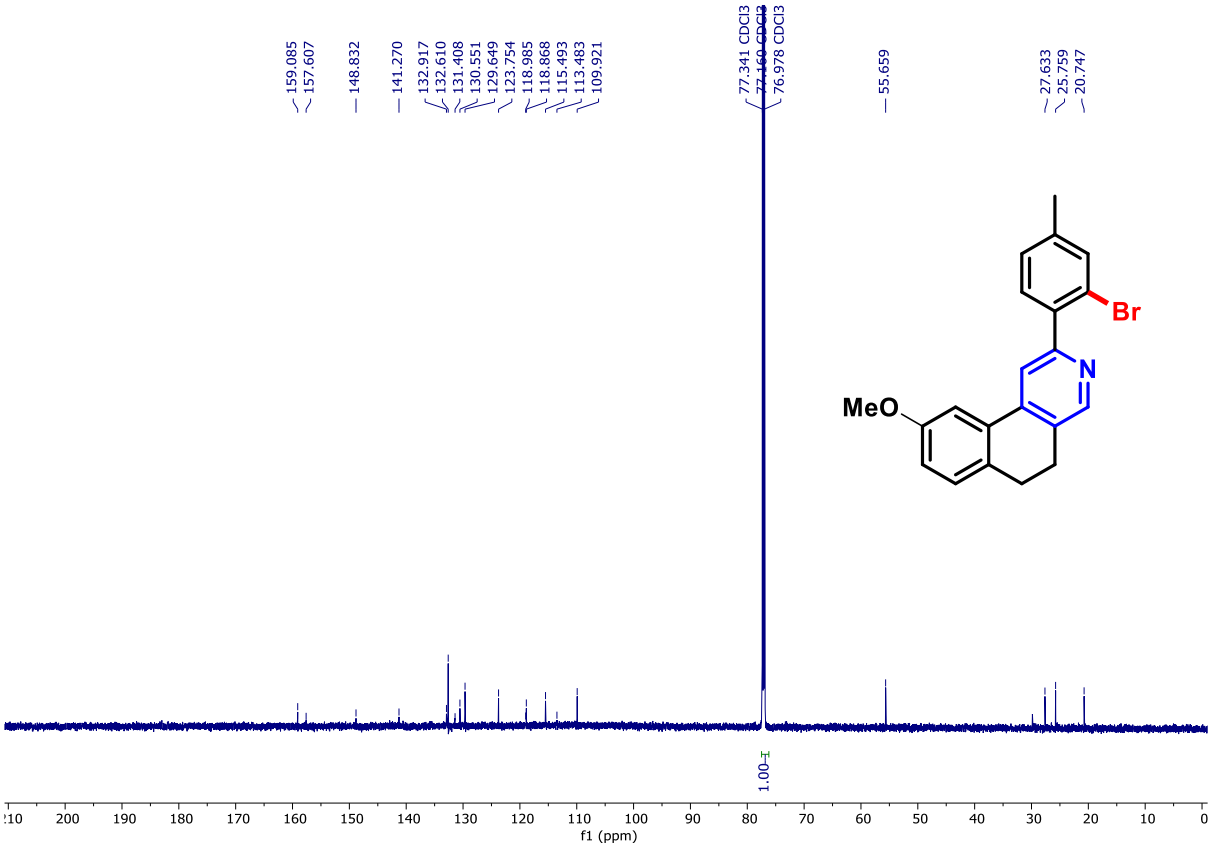
2-(2-bromo-4-methylphenyl)-8-methoxy-5,6-dihydrobenzo[f]isoquinoline (4d):



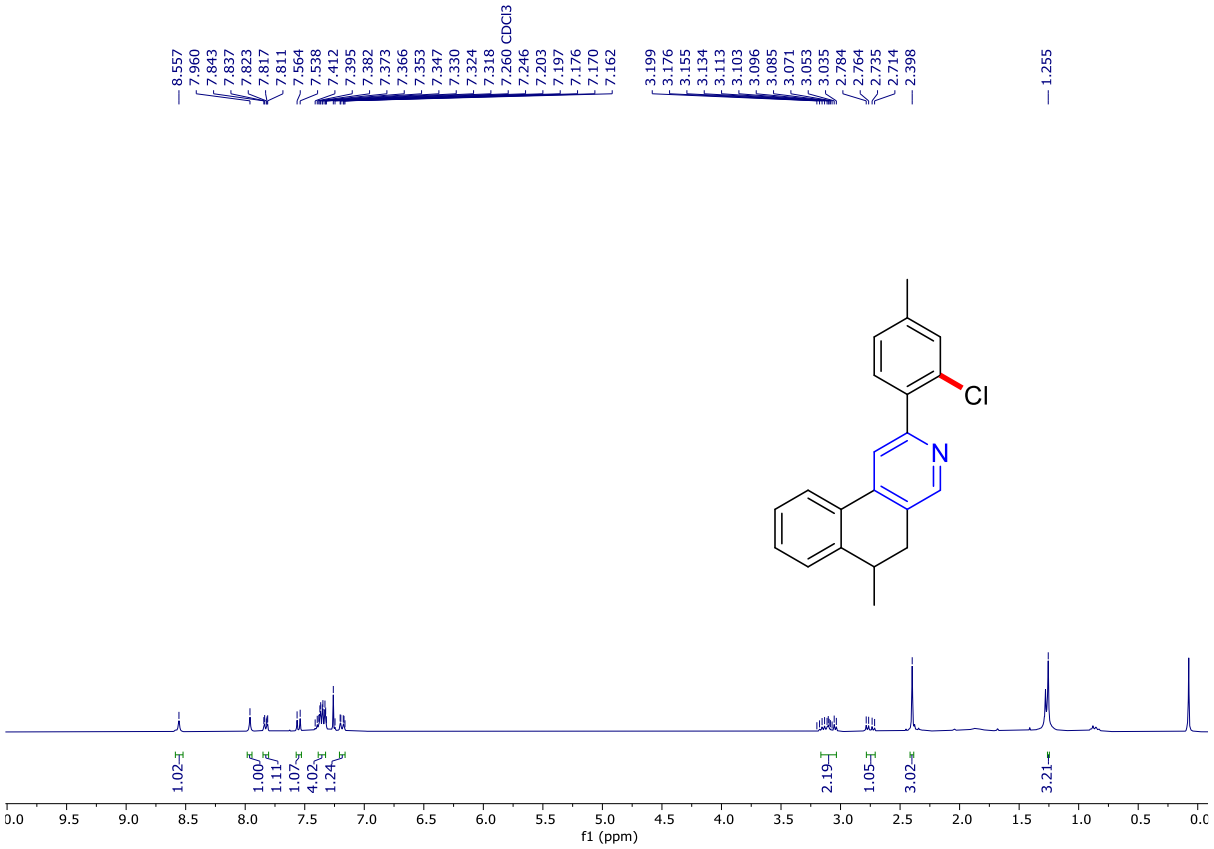


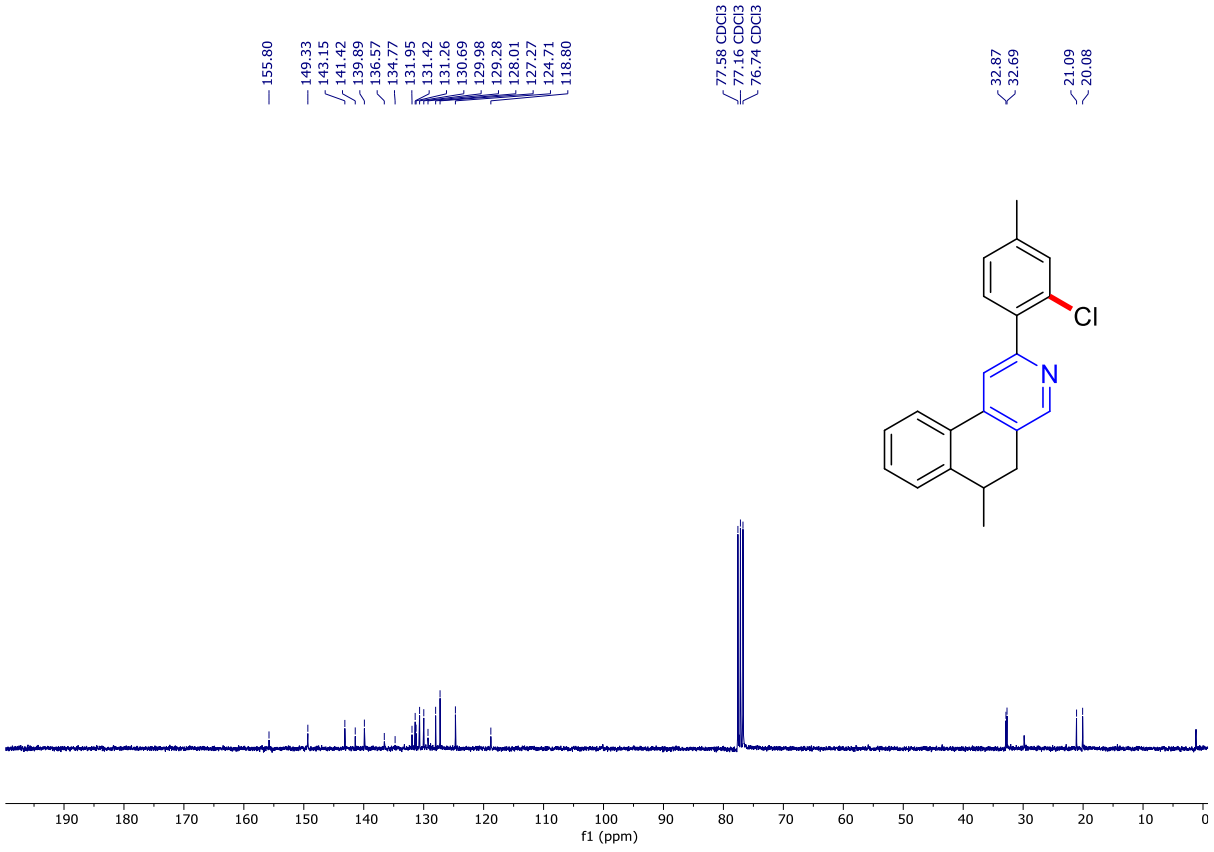
2-(2-bromo-4-methylphenyl)-9-methoxy-5,6-dihydrobenzo[f]isoquinoline (4e):



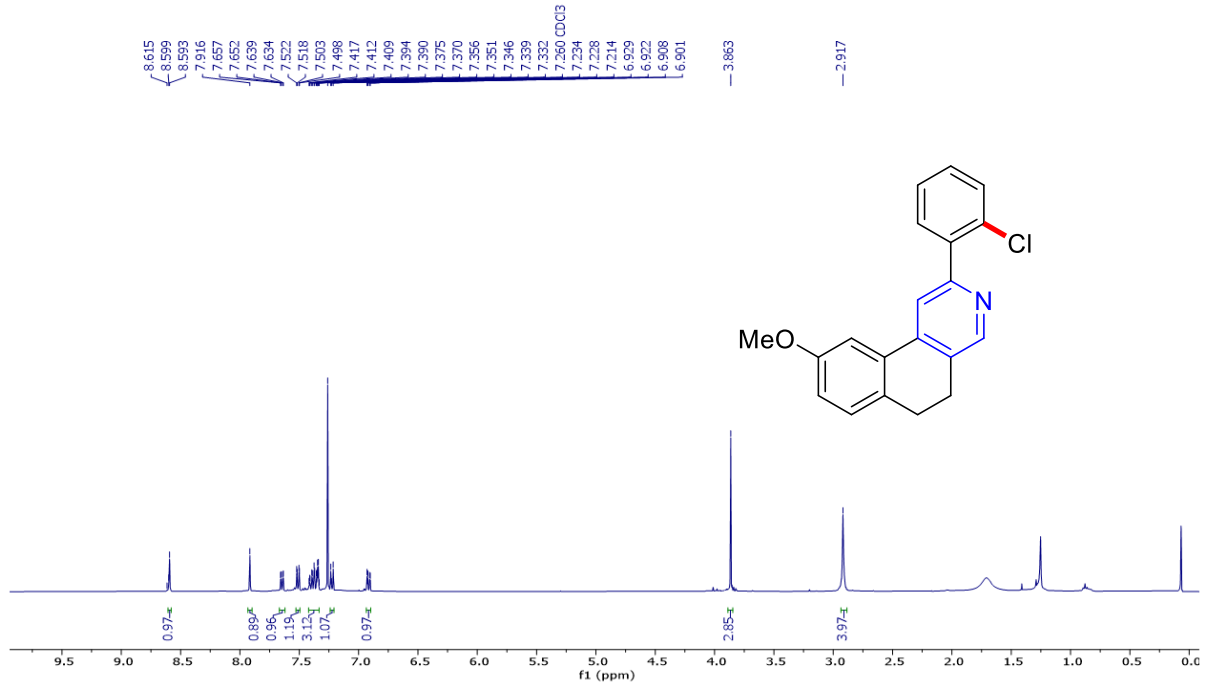


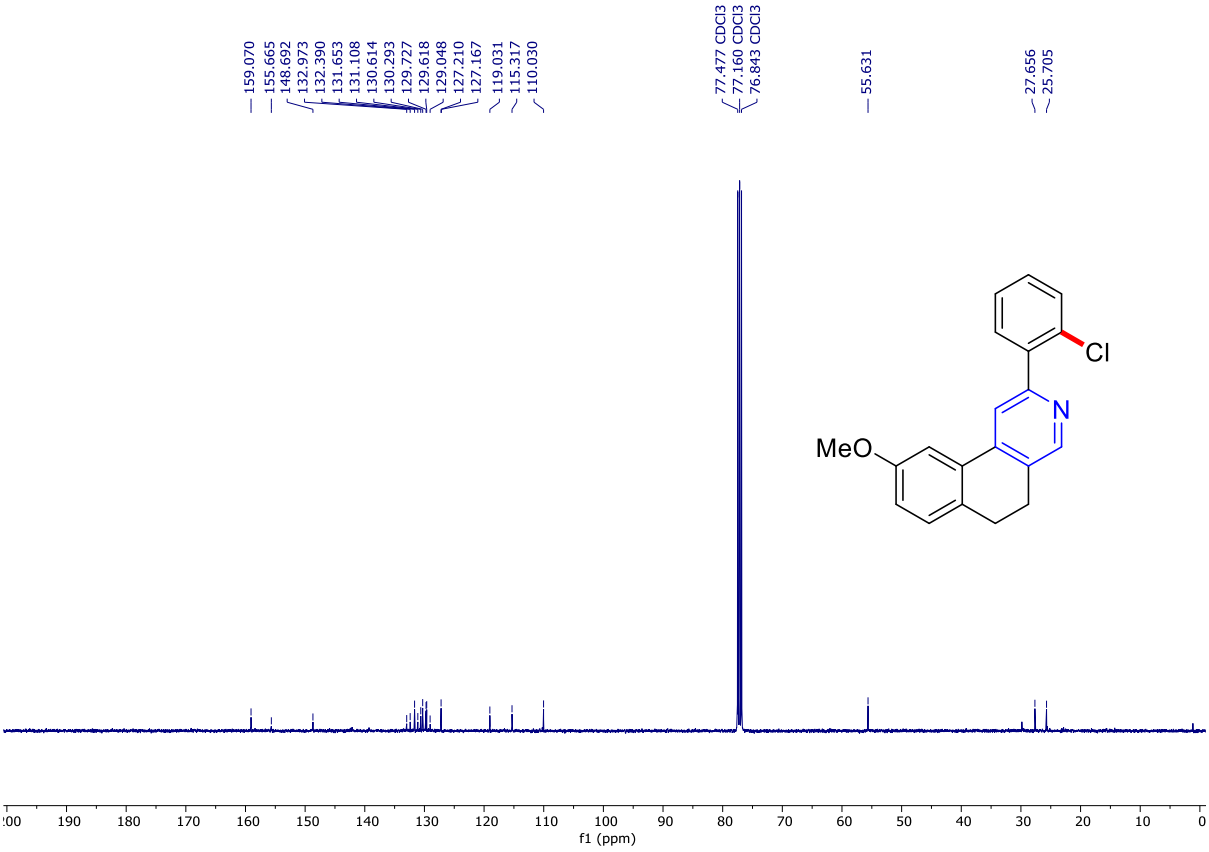
2-(2-chlorophenyl)-6-methyl-5,6-dihydrobenzo[f]isoquinoline (4f)



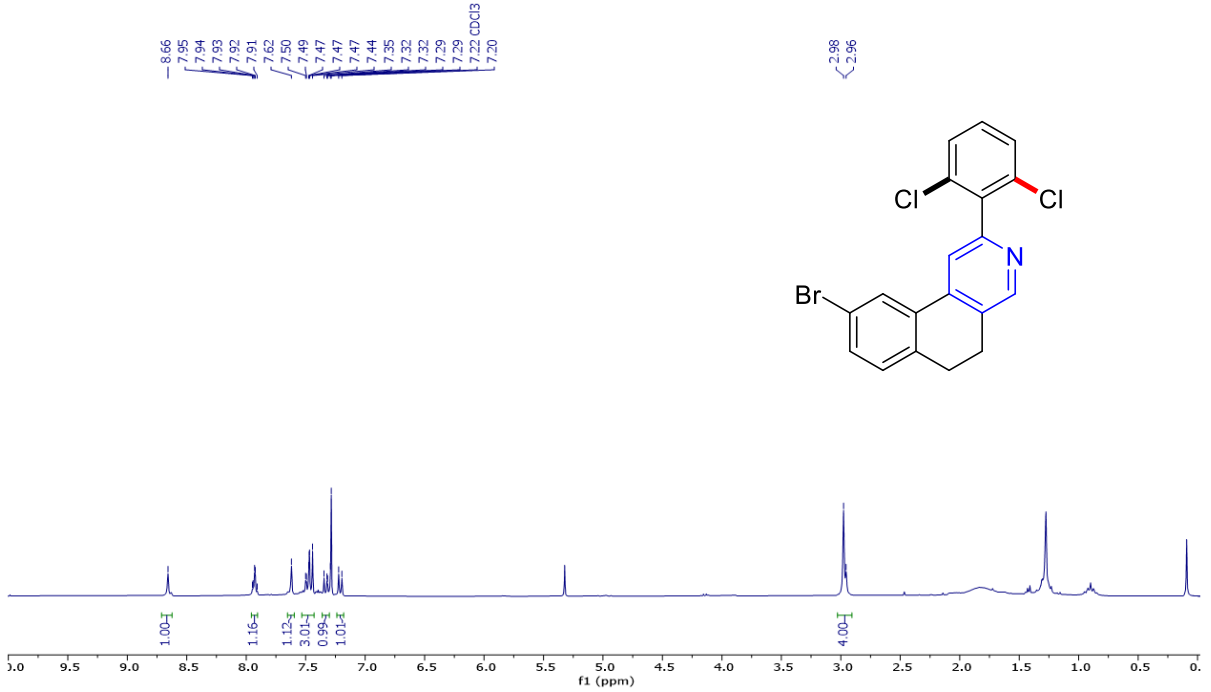


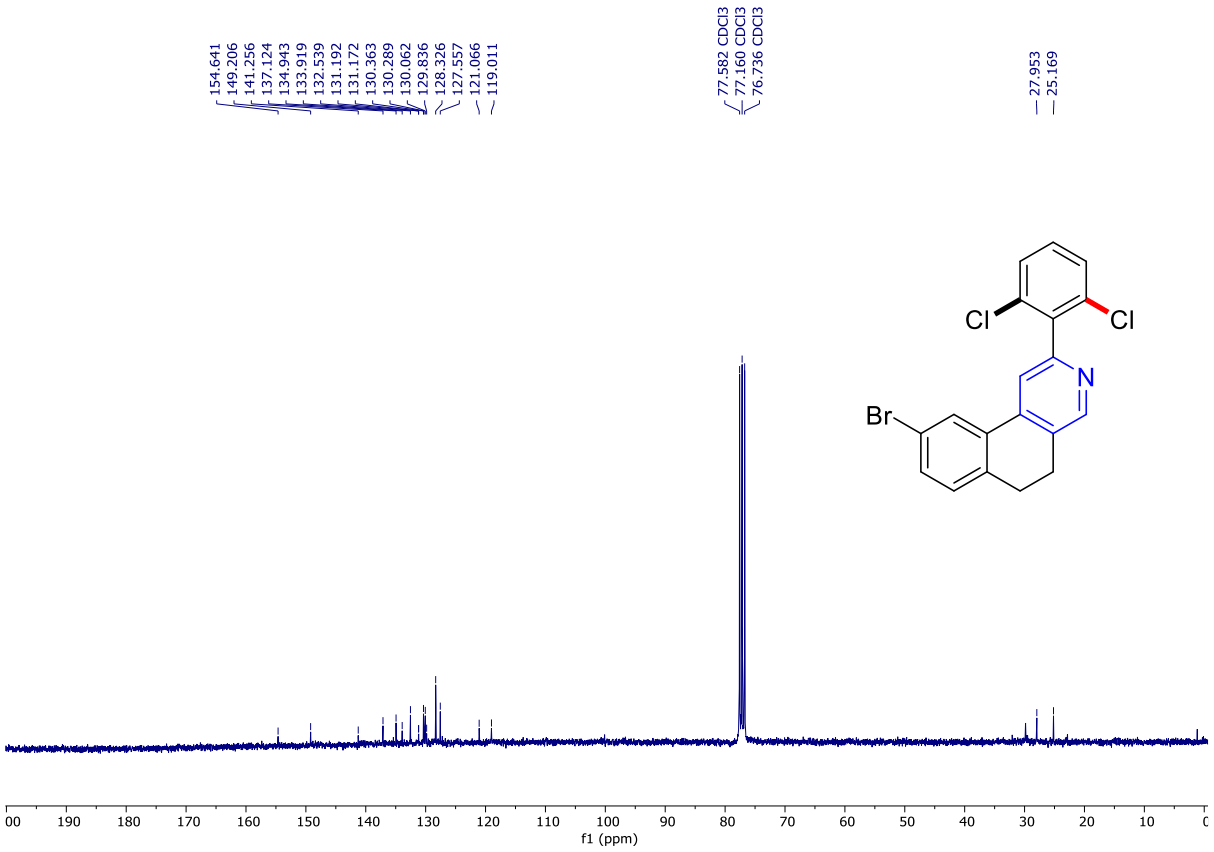
2-(2-chlorophenyl)-9-methoxy-5,6-dihydrobenzo[f]isoquinoline (4g):



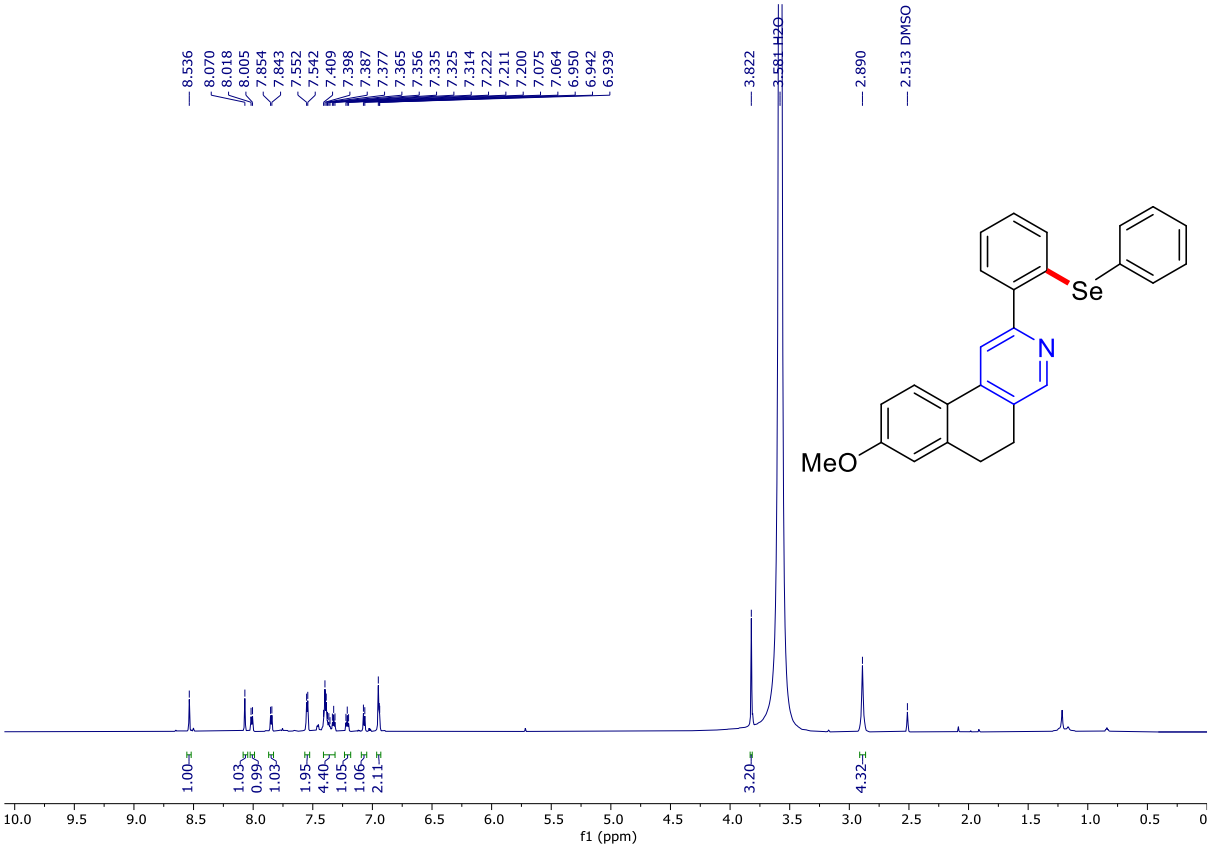


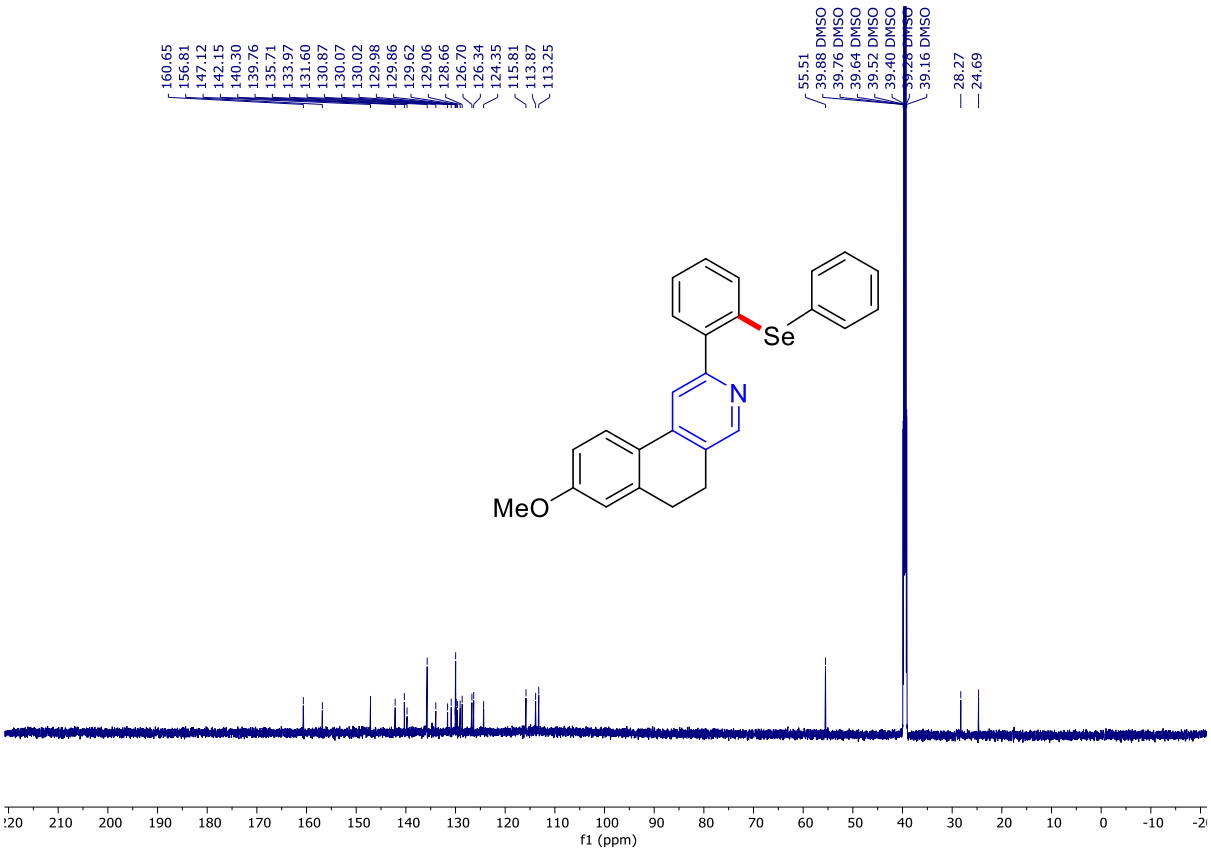
9-bromo-2-(2,6-dichlorophenyl)-5,6-dihydrobenzo[f]isoquinoline (4h):





8-methoxy-2-(2-(phenylselanyl)phenyl)-5,6-dihydrobenzo[f]isoquinoline(5):

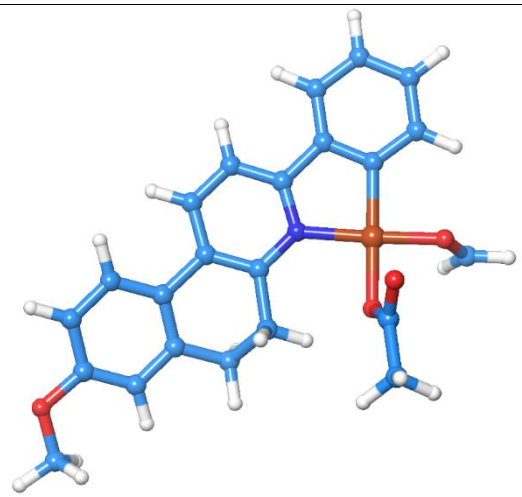




DFT calculations

Density functional theory (DFT) calculations were carried out using the Gaussian 09 software suite,[1] employing the mPW1PW91 exchange–correlation functional. For light atoms (H, C, O, Se, and N), the D95V basis set was applied, while transition metals (Cu, Pd, and Ru) were treated using the LANL2DZ basis set to account for relativistic effects.[2,3] All molecular systems were optimised in both the singlet ground state and the lowest-energy triplet excited state. Subsequent vibrational frequency analyses confirmed the nature of the stationary points, with all optimised geometries corresponding to true minima, as indicated by the absence of imaginary frequencies.

Coordinates

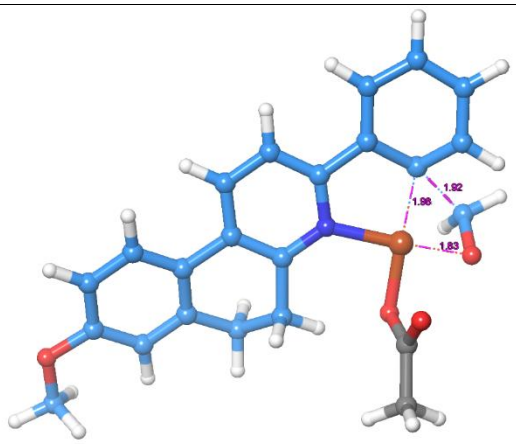


Sum of electronic and thermal Free Energies= -2869.808968

Symbolic Z-matrix:

Charge = 0 Multiplicity = 2

Cu	0.2948	0.30636	0.
O	-1.4532	0.09936	-0.501
C	-1.6982	-0.01664	-1.762
O	0.1818	2.06236	-0.504
C	-0.6232	2.76336	0.457
C	0.4158	-1.55564	0.533
C	-0.5932	-2.50964	0.444



Sum of electronic and thermal Free Energies= -2869.692289

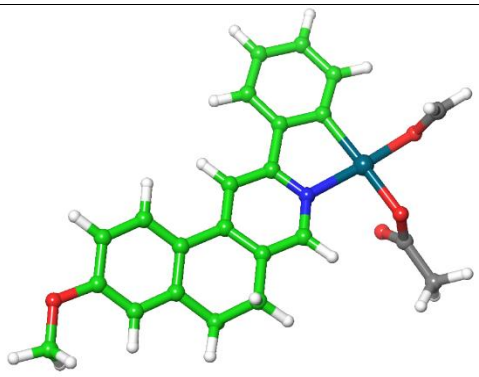
Symbolic Z-matrix:

Charge = 0 Multiplicity = 2

Cu	-0.03094	0.34653	0.
O	-1.77894	0.13953	-0.501
C	-1.20094	-0.86247	-1.065
O	-0.14394	2.10253	-0.504
C	-0.94894	2.80353	0.457
C	0.07906	-1.62047	0.152
C	-0.91894	-2.46947	0.444

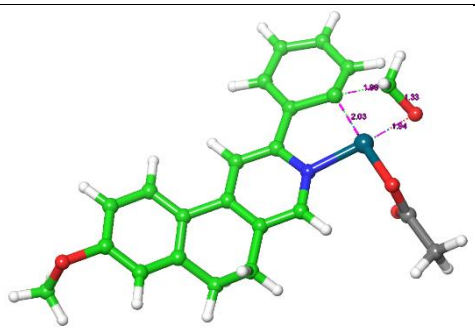
C	1.6408	-1.86564	1.06	1.31506	-1.82547	1.06
C	-0.3402	-3.80164	0.899	-0.66594	-3.76147	0.899
H	-1.5452	-2.25664	0.039	-1.87094	-2.21647	0.039
C	1.9068	-3.15364	1.517	1.58106	-3.11347	1.517
C	0.9068	-4.12264	1.434	0.58106	-4.08247	1.434
H	-1.1012	-4.54864	0.84	-1.42694	-4.50847	0.84
H	2.8558	-3.40364	1.923	2.53006	-3.36347	1.923
H	1.0948	-5.11664	1.782	0.76906	-5.07647	1.782
C	2.5808	-0.74064	1.058	2.25506	-0.70047	1.058
C	3.0428	1.47136	0.481	2.71706	1.51153	0.481
C	3.8588	-0.93864	1.554	3.53306	-0.89847	1.554
C	4.3528	1.30836	0.967	4.02706	1.34853	0.967
C	4.7568	0.10336	1.518	4.43106	0.14353	1.518
H	4.1498	-1.88164	1.95	3.82406	-1.84147	1.95
H	5.7448	-0.02964	1.887	5.41906	0.01053	1.887
N	2.1518	0.43436	0.547	1.82606	0.47453	0.547
C	2.7518	2.89236	-0.075	2.42606	2.93253	-0.075
H	1.9108	2.89536	-0.728	1.58506	2.93553	-0.728
H	2.5458	3.54836	0.781	2.22006	3.58853	0.781
C	3.9438	3.48236	-0.823	3.61806	3.52253	-0.823
H	3.7338	4.49636	-1.202	3.40806	4.53653	-1.202
H	4.1478	2.82136	-1.678	3.82206	2.86153	-1.678
C	5.1448	3.48836	0.032	4.81906	3.52853	0.032
C	5.3598	2.42336	0.895	5.03406	2.46353	0.895
C	6.0648	4.52836	-0.07	5.73906	4.56853	-0.07
C	6.5238	2.40136	1.661	6.19806	2.44153	1.661
C	7.2268	4.50936	0.704	6.90106	4.54953	0.704

C	7.4448	3.43936	1.567	C	7.11906	3.47953	1.567
H	6.7178	1.59436	2.327	H	6.39206	1.63453	2.327
O	8.2238	5.52936	0.657	O	7.89806	5.56953	0.657
H	8.3298	3.41236	2.16	H	8.00406	3.45253	2.16
H	5.8668	5.31636	-0.749	H	5.54106	5.35653	-0.749
C	7.9768	6.61736	-0.259	C	7.65106	6.65753	-0.259
H	8.8118	7.33136	-0.209	H	8.48606	7.37153	-0.209
H	7.0428	7.12836	0.015	H	6.71706	7.16853	0.015
H	7.8958	6.22536	-1.285	H	7.57006	6.26553	-1.285
C	-0.9992	4.23336	0.277	C	-1.32494	4.27353	0.277
O	-0.9752	2.14936	1.465	O	-1.30094	2.18953	1.465
H	-1.4262	4.65536	1.21	H	-1.75194	4.69553	1.21
H	-1.7492	4.30836	-0.532	H	-2.07494	4.34853	-0.532
H	-0.1172	4.80136	-0.057	H	-0.44294	4.84153	-0.057
H	-0.9072	0.00436	-2.468	H	-0.69194	-0.49547	-1.923
H	-2.7172	-0.14264	-2.105	H	-1.93894	-1.57647	-1.358



Sum of electronic and thermal Free Energies= -6154.856482

Symbolic Z-matrix:

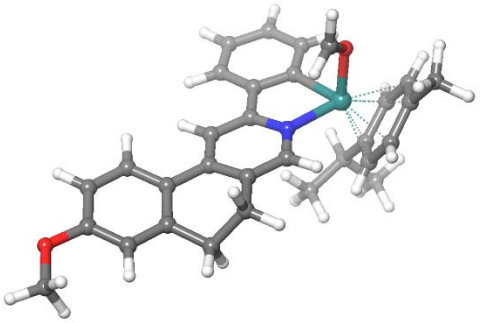


Sum of electronic and thermal Free Energies= -6154.700775

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1				Charge = 0 Multiplicity = 1			
Pd	-0.3651	0.37129	0.	Pd	0.08045	-0.24752	0.
O	-0.8501	1.96729	-0.991	O	-0.40455	1.34848	-0.991
O	1.4339	0.48329	-0.718	O	1.87945	-0.13552	-0.718
C	-2.1991	0.23229	0.891	C	-1.67955	-0.11852	0.997
C	-3.2861	1.08229	0.709	C	-2.84755	0.43348	0.615
C	-2.2741	-0.85971	1.744	C	-1.83455	-1.40652	1.839
C	-4.4651	0.82229	1.406	C	-4.03255	0.24848	1.35
H	-3.2231	1.91429	0.051	H	-2.78655	1.19048	-0.139
C	-3.4511	-1.11671	2.441	C	-2.99655	-1.58652	2.592
C	-4.5461	-0.27071	2.267	C	-4.10255	-0.75152	2.345
H	-5.3151	1.45929	1.281	H	-4.88255	0.86848	1.157
H	-3.5231	-1.94971	3.097	H	-3.04755	-2.34952	3.341
H	-5.4561	-0.46071	2.796	H	-5.00055	-0.87552	2.913
C	1.1769	-1.99071	1.086	C	1.63745	-2.69752	0.993
C	-1.0131	-1.70771	1.835	C	-0.56755	-2.29052	1.951
C	1.3219	-3.11971	1.888	C	1.78145	-3.81352	1.835
H	1.9919	-1.66271	0.492	H	2.40845	-2.43452	0.299
C	-0.9261	-2.82571	2.655	C	-0.43355	-3.37352	2.824
C	0.2619	-3.54871	2.681	C	0.74745	-4.13352	2.777
H	-1.7541	-3.12171	3.251	H	-1.21455	-3.61852	3.514
C	2.6369	-3.85471	1.948	C	3.05845	-4.70252	1.748
H	3.2609	-3.62271	1.071	H	3.46845	-4.65852	0.761
H	3.1599	-3.51671	2.855	H	3.80245	-4.38352	2.447
C	2.3969	-5.35771	2.107	C	2.58645	-6.11052	2.056
H	3.3399	-5.92771	2.195	H	3.36145	-6.84152	1.951
H	1.8619	-5.69171	1.206	H	1.79945	-6.32652	1.365

C	1.4949	-5.61771	3.286	C	2.04345 -6.13652 3.487
C	0.4379	-4.74971	3.543	C	0.97745 -5.30452 3.757
C	1.6989	-6.74171	4.081	C	2.57745 -6.94852 4.489
C	-0.4291	-5.02171	4.597	C	0.19645 -5.50252 4.898
C	0.8369	-7.00871	5.148	C	1.86845 -7.08652 5.695
H	2.5099	-7.38371	3.854	H	3.49945 -7.46952 4.336
C	-0.2251	-6.14271	5.393	C	0.64545 -6.40652 5.875
H	-1.2441	-4.37171	4.806	H	-0.71755 -4.96252 5.034
H	-0.8891	-6.33971	6.202	H	0.06545 -6.57252 6.758
N	0.0229	-1.31871	1.082	N	0.46845 -1.93752 1.082
C	-0.6031	3.12729	-0.482	C	-0.90155 1.54948 0.23
H	-0.1501	3.22529	0.473	H	-0.12355 1.89748 0.867
H	-0.8611	4.00729	-1.034	H	-1.65355 2.30448 0.173
C	1.4689	-0.22371	-1.943	C	1.92145 -0.82152 -1.957
O	0.4529	-0.85471	-2.246	O	0.91045 -1.44852 -2.282
C	2.7239	-0.28171	-2.827	C	3.18045 -0.85352 -2.838
C	2.0899	-9.01371	5.743	C	2.20845 -9.46652 6.434
H	3.0319	-8.45271	5.831	H	2.89645 -9.73852 5.661
H	2.0889	-9.83871	6.47	H	2.37345 -10.08252 7.293
H	1.9979	-9.42371	4.727	H	1.20645 -9.60452 6.084
O	0.9759	-8.13771	6.015	O	2.42045 -7.98952 6.814
H	2.5129	-0.79571	-3.783	H	2.96945 -1.32652 -3.815
H	3.5119	-0.81171	-2.278	H	3.96045 -1.41652 -2.309
H	3.1039	0.74229	-3.006	H	3.57045 0.17348 -2.971

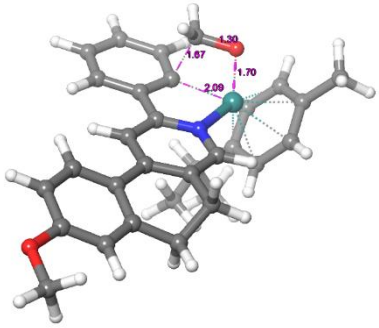


Sum of electronic and thermal Free Energies= -5820.309479

Symbolic Z-matrix:

Charge = 0 Multiplicity = 2

Ru	0.27847	-0.70545	0.
C	-0.59553	-0.06945	1.786
C	0.20847	-0.86345	-2.222
C	0.99047	-1.89945	-1.678
H	1.88147	-2.03745	-1.976
C	0.42347	-2.73345	-0.674
H	0.93847	-3.45145	-0.324
C	-0.86253	-2.52345	-0.192
C	-1.63453	-1.46845	-0.804
H	-2.52353	-1.31645	-0.508
C	-1.11453	-0.67545	-1.804
H	-1.65153	-0.00445	-2.209
C	0.76647	-0.01145	-3.309
H	0.68847	-0.56645	-4.255
H	0.19347	0.92355	-3.396
H	1.83347	0.17355	-3.121
C	-1.53853	-3.34545	0.883



Sum of electronic and thermal Free Energies= -5820.260976

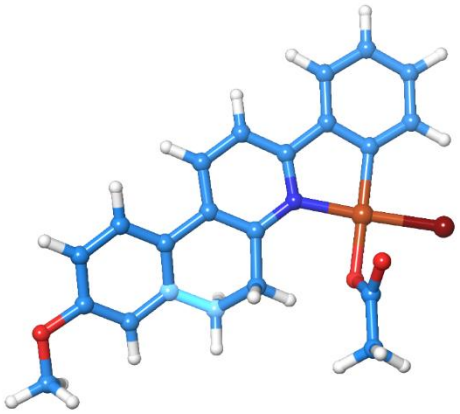
Symbolic Z-matrix:

Charge = 0 Multiplicity = 2

Ru	-1.307	2.589	7.576
C	-2.181	3.225	9.362
C	-1.377	2.431	5.354
C	-0.595	1.395	5.898
H	0.296	1.257	5.6
C	-1.162	0.561	6.902
H	-0.647	-0.157	7.252
C	-2.448	0.771	7.384
C	-3.22	1.826	6.772
H	-4.109	1.978	7.068
C	-2.7	2.619	5.772
H	-3.237	3.29	5.367
C	-0.819	3.283	4.267
H	-0.897	2.728	3.321
H	-1.392	4.218	4.18
H	0.248	3.468	4.455
C	-3.124	-0.051	8.459

H	-2.20853	-2.69345	1.463	H	-3.794	0.601	9.039
C	-2.37153	-4.45445	0.233	C	-3.957	-1.16	7.809
H	-2.87153	-5.03945	1.016	H	-4.457	-1.745	8.592
H	-3.12453	-4.00845	-0.431	H	-4.71	-0.714	7.145
H	-1.70953	-5.10945	-0.35	H	-3.295	-1.815	7.226
C	-0.50953	-4.02545	1.818	C	-2.095	-0.731	9.394
H	0.11747	-3.25945	2.294	H	-1.468	0.035	9.87
H	-1.04553	-4.59445	2.593	H	-2.631	-1.3	10.169
H	0.12347	-4.71345	1.239	H	-1.462	-1.419	8.815
C	-1.87653	0.46955	1.885	C	-3.462	3.764	9.461
H	-2.49053	0.58055	1.019	H	-4.076	3.875	8.595
C	-2.35653	0.86655	3.129	C	-3.942	4.161	10.705
H	-3.33453	1.27955	3.213	H	-4.92	4.574	10.789
C	-1.56053	0.72455	4.263	C	-3.146	4.019	11.839
H	-1.93453	1.03355	5.219	H	-3.52	4.328	12.795
C	-0.27953	0.18855	4.152	C	-1.865	3.483	11.728
H	0.32747	0.08655	5.015	H	-1.258	3.381	12.591
C	0.18847	-0.20345	2.899	C	-1.397	3.091	10.475
C	1.47847	-0.75645	2.62	C	-0.107	2.538	10.196
C	2.41047	-0.95845	3.635	C	0.825	2.336	11.211
H	2.17447	-0.70745	4.643	H	0.589	2.587	12.219
C	3.64947	-1.50145	3.317	C	2.064	1.793	10.893
C	3.92147	-1.80745	1.989	C	2.336	1.487	9.565
C	2.95347	-1.57845	1.012	C	1.368	1.716	8.588
H	3.17447	-1.81045	-0.001	H	1.589	1.484	7.575
N	1.75547	-1.06945	1.337	N	0.17	2.225	8.913
C	5.29447	-2.34645	1.621	C	3.709	0.948	9.197

H 5.28447 -2.82745 0.63	H 3.699 0.467 8.206
H 5.99347 -1.49545 1.598	H 4.408 1.799 9.174
C 5.79847 -3.29045 2.714	C 4.213 0.004 10.29
H 6.81247 -3.67445 2.502	H 5.227 -0.38 10.078
H 5.09947 -4.13645 2.756	H 3.514 -0.842 10.332
C 5.75347 -2.60245 4.053	C.168 0.692 11.629
C 4.69247 -1.75245 4.353	C.107 1.542 11.929
C 6.74747 -2.85645 4.993	C 5.162 0.438 12.569
H 7.53647 -3.51245 4.733	H 5.951 -0.218 12.309
C 6.68647 -2.25645 6.254	C 5.101 1.038 13.83
C 5.61947 -1.41445 6.552	C 4.034 1.88 14.128
H 5.56347 -0.95645 7.512	H 3.978 2.338 15.087
C 4.62447 -1.16345 5.613	C 3.039 2.131 13.189
H 3.82047 -0.51545 5.863	H 2.235 2.779 13.439
O 0.61547 1.10455 -0.515	O -1.37 4.285 7.433
C 1.80547 1.58655 -0.475	C -1.743 4.654 8.626
H 2.62347 0.98955 -0.176	H -0.947 5.134 9.149
H 1.97347 2.60055 -0.769	H -2.589 5.331 8.561
O 7.66547 -2.46345 7.277	O 6.08 0.831 14.853
C 8.76047 -3.34045 6.939	C 7.175 -0.046 14.515
H 9.43947 -3.42145 7.8	H 7.854 -0.127 15.376
H 9.31047 -2.93145 6.079	H 7.725 0.363 13.655
H 8.37047 -4.33845 6.688	H 6.786 -1.044 14.264

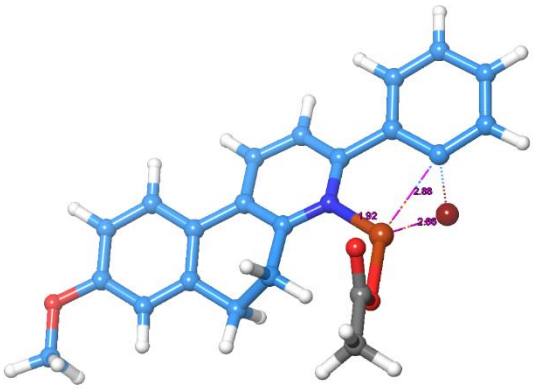


Sum of electronic and thermal Free Energies= -5317.853473

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Cu	0.24134	-0.29703	0.
Br	-1.96466	-0.55803	-0.632
O	0.12834	1.45897	-0.504
C	-0.63266	2.18297	0.474
C	0.38734	-2.16503	0.476
C	-0.58766	-3.15803	0.357
C	1.61334	-2.47003	1.011
C	-0.30466	-4.45303	0.782
H	-1.54066	-2.94103	-0.05
C	1.90834	-3.76103	1.44
C	0.94034	-4.75503	1.325
H	-1.04666	-5.21603	0.694
H	2.86034	-3.99503	1.849
H	1.15234	-5.75303	1.65
C	2.53234	-1.34403	1.046
C	2.98734	0.87197	0.504



Sum of electronic and thermal Free Energies= -5317.716572

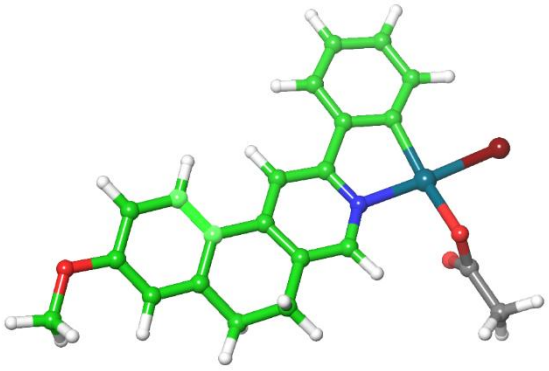
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Cu	-0.19183	-0.2104	0.
Br	0.00617	-2.6084	-1.552
O	-0.72883	1.5136	-0.577
C	-1.44983	2.2146	0.447
C	-0.27983	-3.0794	0.176
C	-1.10583	-4.2454	0.235
C	0.93617	-3.0854	0.936
C	-0.76483	-5.3364	1.019
H	-2.00083	-4.2874	-0.349
C	1.25017	-4.2114	1.705
C	0.41117	-5.3194	1.751
H	-1.39883	-6.1944	1.044
H	2.14517	-4.2344	2.269
H	0.67517	-6.1624	2.343
C	1.93517	-1.8814	0.91
C	2.53617	0.3436	0.511

C	3.80534	-1.54003	1.557	C	3.23217	-2.1454	1.351
C	4.29034	0.71597	1.012	C	3.84517	0.1146	0.932
C	4.69534	-0.49203	1.555	C	4.19417	-1.1504	1.368
H	4.09834	-2.48603	1.943	H	3.49817	-3.1194	1.675
H	5.67734	-0.62203	1.941	H	5.18317	-1.3624	1.702
N	2.09834	-0.16903	0.547	N	1.61017	-0.6294	0.507
C	2.70234	2.28997	-0.042	C	2.17817	1.7476	0.104
H	1.87734	2.28797	-0.72	H	1.27817	1.7536	-0.486
H	2.46034	2.93297	0.816	H	2.01217	2.3326	1.021
C	3.90334	2.90897	-0.748	C	3.32217	2.4076	-0.649
H	3.68534	3.92397	-1.117	H	3.08217	3.4416	-0.941
H	4.14734	2.26397	-1.608	H	3.49717	1.8096	-1.558
C	5.07534	2.92297	0.139	C	4.56917	2.3626	0.167
C	5.28434	1.84497	0.986	C	4.83917	1.2296	0.925
C	5.97634	3.98197	0.087	C	5.46017	3.4286	0.132
C	6.42534	1.82697	1.786	C	6.02617	1.1636	1.65
C	7.11434	3.96997	0.897	C	6.64517	3.3696	0.867
C	7.32834	2.88397	1.741	C	6.91817	2.2306	1.621
H	6.61334	1.00997	2.441	H	6.25517	0.3036	2.235
O	8.09034	5.01097	0.905	O	7.61117	4.4206	0.884
H	8.19534	2.86197	2.361	H	7.82317	2.1756	2.183
H	5.78334	4.78197	-0.58	H	5.21917	4.2706	-0.463
C	7.84234	6.11997	0.014	C	7.29917	5.5826	0.081
H	8.65934	6.85097	0.108	H	8.10917	6.3196	0.175
H	6.89034	6.60297	0.279	H	6.35617	6.0326	0.427
H	7.79634	5.75797	-1.024	H	7.20017	5.2846	-0.974
C	-1.00866	3.64797	0.28	C	-2.10683	3.5886	0.197

O	-0.95566	1.58397	1.501	O	-1.51683	1.6866	1.56
H	-1.42666	4.07897	1.21	H	-2.58583	3.9676	1.115
H	-1.76266	3.71497	-0.526	H	-2.84583	3.4866	-0.612
H	-0.12766	4.20797	-0.067	H	-1.34683	4.2956	-0.167

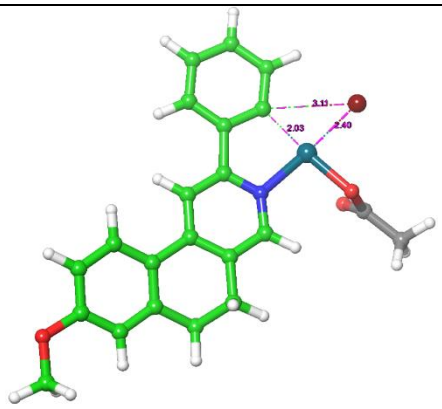


Sum of electronic and thermal Free Energies= -8602.861482

Symbolic Z-matrix:

Charge = 0 Multiplicity = 2

Pd	-0.51361	-0.19802	0.
Br	-1.11361	1.77598	-1.226
O	1.28539	-0.08602	-0.718
C	-2.27361	-0.06902	0.997
C	-3.29161	0.87198	0.886
C	-2.35761	-1.13302	1.896
C	-4.41561	0.73798	1.696
H	-3.22161	1.67698	0.2
C	-3.48461	-1.25902	2.703
C	-4.51061	-0.32002	2.599
H	-5.20761	1.44898	1.626



Sum of electronic and thermal Free Energies= -8602.843188

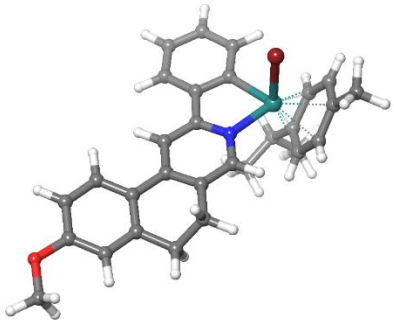
Symbolic Z-matrix:

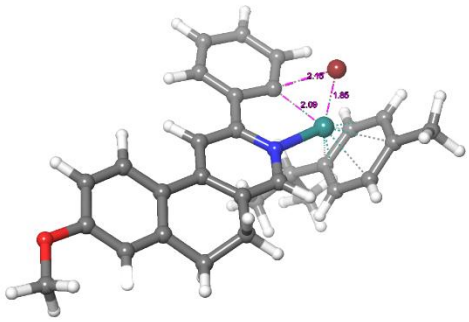
Charge = 0 Multiplicity = 2

Pd	-0.35269	-0.32178	-0.00462
Br	-1.29042	1.64403	-1.01258
O	1.44631	-0.20978	-0.72262
C	-2.11269	-0.19278	0.99238
C	-3.13069	0.74822	0.88138
C	-2.19669	-1.25678	1.89138
C	-4.25469	0.61422	1.69138
H	-3.06069	1.55322	0.19538
C	-3.32369	-1.38278	2.69838
C	-4.34969	-0.44378	2.59438
H	-5.04669	1.32522	1.62138

H	-3.56961	-2.06102	3.395	-3.40869	-2.18478	3.39038
H	-5.37861	-0.41002	3.215	-5.21769	-0.53378	3.21038
C	0.96639	-2.63902	1.009	1.12731	-2.76278	1.00438
C	-1.13361	-2.13302	1.925	-0.97269	-2.25678	1.92038
C	1.08039	-3.74602	1.845	1.24131	-3.86978	1.84038
H	1.74539	-2.38802	0.334	1.90631	-2.51178	0.32938
C	-1.06961	-3.22502	2.782	-0.90869	-3.34878	2.77738
C	0.05439	-4.04802	2.738	0.21531	-4.17178	2.73338
H	-1.86461	-3.42502	3.458	-1.70369	-3.54878	3.45338
C	2.32939	-4.59202	1.834	2.49031	-4.71578	1.82938
H	2.89539	-4.45102	0.9	3.05631	-4.57478	0.89538
H	2.95339	-4.26702	2.679	3.11431	-4.39078	2.67438
C	1.97639	-6.06002	2.079	2.13731	-6.18378	2.07438
H	2.87139	-6.70802	2.119	3.03231	-6.83178	2.11438
H	1.34139	-6.38002	1.241	1.50231	-6.50378	1.23638
C	1.15639	-6.19402	3.337	1.31731	-6.31778	3.33238
C	0.20139	-5.22702	3.637	0.36231	-5.35078	3.63238
C	1.33139	-7.30002	4.163	1.49231	-7.42378	4.15838
C	-0.59461	-5.38202	4.769	-0.43369	-5.50578	4.76438
C	0.54339	-7.44902	5.307	0.70431	-7.57278	5.30238
H	2.06439	-8.01802	3.902	2.22531	-8.14178	3.89738
C	-0.41861	-6.48502	5.597	-0.25769	-6.60878	5.59238
H	-1.33161	-4.65602	5.013	-1.17069	-4.77978	5.00838
H	-1.02661	-6.59202	6.464	-0.86569	-6.71578	6.45938
N	-0.12561	-1.88802	1.082	0.03531	-2.01178	1.07738
C	1.29539	-0.64602	-2.01	1.45631	-0.76978	-2.01462
O	0.26239	-1.20002	-2.394	0.42331	-1.32378	-2.39862

C	2.53739	-0.59902	-2.895	C	2.69831	-0.72278	-2.89962
C	1.66939	-9.53102	5.892	C	1.83031	-9.65478	5.88738
H	2.65939	-9.05002	5.879	H	2.82031	-9.17378	5.87438
H	1.66139	-10.32402	6.654	H	1.82231	-10.44778	6.64938
H	1.45939	-9.97102	4.906	H	1.62031	-10.09478	4.90138
O	0.65939	-8.55102	6.211	O	0.82031	-8.67478	6.20638
H	2.36339	-1.11402	-3.859	H	2.52431	-1.23778	-3.86362
H	3.38039	-1.05402	-2.354	H	3.54131	-1.17778	-2.35862
H	2.81739	0.45698	-3.071	H	2.97831	0.33322	-3.07562





Sum of electronic and thermal Free Energies= -8268.589906

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Ru	0.09282	0.61881	0.
C	-0.78118	1.25481	1.786
C	0.02282	0.46081	-2.222
C	0.80482	-0.57519	-1.678
H	1.69582	-0.71319	-1.976
C	0.23782	-1.40919	-0.674
H	0.75282	-2.12719	-0.324

Sum of electronic and thermal Free Energies= -8268.420985

Symbolic Z-matrix:

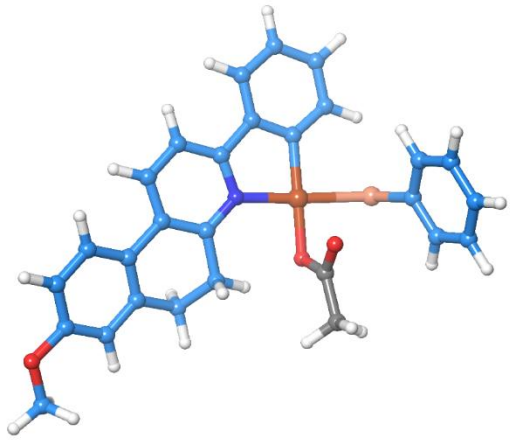
Charge = 0 Multiplicity = 1

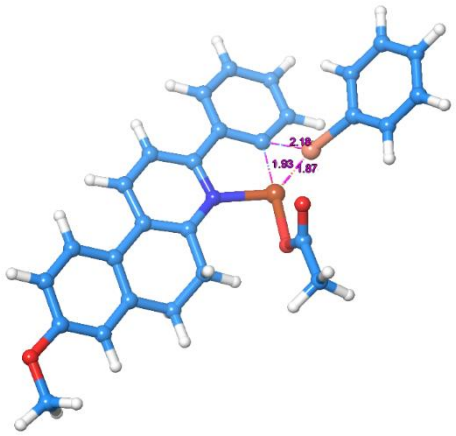
Ru	-0.3651	-0.70545	0.
C	-1.2391	-0.06945	1.786
C	-0.4351	-0.86345	-2.222
C	0.3469	-1.89945	-1.678
H	1.2379	-2.03745	-1.976
C	-0.2201	-2.73345	-0.674
H	0.2949	-3.45145	-0.324

C	-1.04818	-1.19919	-0.192	-1.5061	-2.52345	-0.192
C	-1.82018	-0.14419	-0.804	-2.2781	-1.46845	-0.804
H	-2.70918	0.00781	-0.508	-3.1671	-1.31645	-0.508
C	-1.30018	0.64881	-1.804	-1.7581	-0.67545	-1.804
H	-1.83718	1.31981	-2.209	-2.2951	-0.00445	-2.209
C	0.58082	1.31281	-3.309	0.1229	-0.01145	-3.309
H	0.50282	0.75781	-4.255	0.0449	-0.56645	-4.255
H	0.00782	2.24781	-3.396	-0.4501	0.92355	-3.396
H	1.64782	1.49781	-3.121	1.1899	0.17355	-3.121
C	-1.72418	-2.02119	0.883	-2.1821	-3.34545	0.883
H	-2.39418	-1.36919	1.463	-2.8521	-2.69345	1.463
C	-2.55718	-3.13019	0.233	-3.0151	-4.45445	0.233
H	-3.05718	-3.71519	1.016	-3.5151	-5.03945	1.016
H	-3.31018	-2.68419	-0.431	-3.7681	-4.00845	-0.431
H	-1.89518	-3.78519	-0.35	-2.3531	-5.10945	-0.35
C	-0.69518	-2.70119	1.818	-1.1531	-4.02545	1.818
H	-0.06818	-1.93519	2.294	-0.5261	-3.25945	2.294
H	-1.23118	-3.27019	2.593	-1.6891	-4.59445	2.593
H	-0.06218	-3.38919	1.239	-0.5201	-4.71345	1.239
C	-2.06218	1.79381	1.885	-2.5201	0.46955	1.885
H	-2.67618	1.90481	1.019	-3.1341	0.58055	1.019
C	-2.54218	2.19081	3.129	-3.0001	0.86655	3.129
H	-3.52018	2.60381	3.213	-3.9781	1.27955	3.213
C	-1.74618	2.04881	4.263	-2.2041	0.72455	4.263
H	-2.12018	2.35781	5.219	-2.5781	1.03355	5.219
C	-0.46518	1.51281	4.152	-0.9231	0.18855	4.152
H	0.14182	1.41081	5.015	-0.3161	0.08655	5.015

C	0.00282	1.12081	2.899	-0.4551	-0.20345	2.899
C	1.29282	0.56781	2.62	0.8349	-0.75645	2.62
C	2.22482	0.36581	3.635	1.7669	-0.95845	3.635
H	1.98882	0.61681	4.643	1.5309	-0.70745	4.643
C	3.46382	-0.17719	3.317	3.0059	-1.50145	3.317
C	3.73582	-0.48319	1.989	3.2779	-1.80745	1.989
C	2.76782	-0.25419	1.012	2.3099	-1.57845	1.012
H	2.98882	-0.48619	-0.001	2.5309	-1.81045	-0.001
N	1.56982	0.25481	1.337	1.1119	-1.06945	1.337
C	5.10882	-1.02219	1.621	4.6509	-2.34645	1.621
H	5.09882	-1.50319	0.63	4.6409	-2.82745	0.63
H	5.80782	-0.17119	1.598	5.3499	-1.49545	1.598
C	5.61282	-1.96619	2.714	5.1549	-3.29045	2.714
H	6.62682	-2.35019	2.502	6.1689	-3.67445	2.502
H	4.91382	-2.81219	2.756	4.4559	-4.13645	2.756
C	5.56782	-1.27819	4.053	5.1099	-2.60245	4.053
C	4.50682	-0.42819	4.353	4.0489	-1.75245	4.353
C	6.56182	-1.53219	4.993	6.1039	-2.85645	4.993
H	7.35082	-2.18819	4.733	6.8929	-3.51245	4.733
C	6.50082	-0.93219	6.254	6.0429	-2.25645	6.254
C	5.43382	-0.09019	6.552	4.9759	-1.41445	6.552
H	5.37782	0.36781	7.511	4.9199	-0.95645	7.511
C	4.43882	0.16081	5.613	3.9809	-1.16345	5.613
H	3.63482	0.80881	5.863	3.1769	-0.51545	5.863
O	7.47982	-1.13919	7.277	7.0219	-2.46345	7.277
C	8.57482	-2.01619	6.939	8.1169	-3.34045	6.939
H	9.25382	-2.09719	7.8	8.7959	-3.42145	7.8

H	9.12482	-1.60719	6.079	H	8.6669	-2.93145	6.079
H	8.18582	-3.01419	6.688	H	7.7279	-4.33845	6.688
Br	0.58905	2.87336	-0.57893	Br	-0.96259	1.00492	0.28286





Sum of electronic and thermal Free Energies= -5376.469513

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Cu	0.56312	-0.66832	0.
Se	-1.67188	-0.93332	-0.641
O	0.45012	1.08768	-0.504
C	-0.26488	1.83668	0.489
C	0.70912	-2.53632	0.476
C	-0.27188	-3.51932	0.352
C	1.93412	-2.84432	1.007
C	0.00412	-4.81732	0.773
H	-1.22488	-3.29232	-0.054
C	2.22412	-4.13932	1.432
C	1.25012	-5.12732	1.313
H	-0.74088	-5.57732	0.682

Sum of electronic and thermal Free Energies= -5376.434601

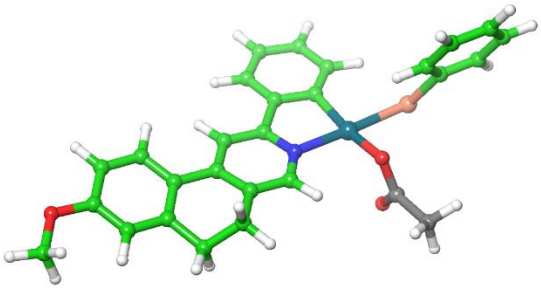
Symbolic Z-matrix:

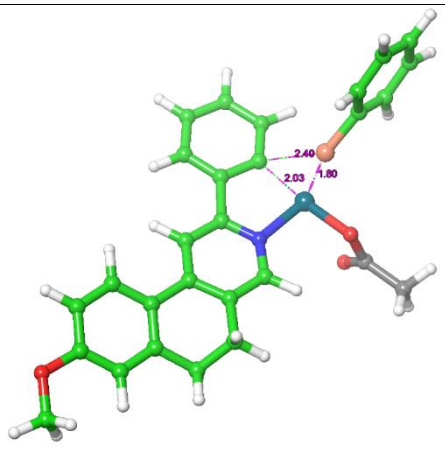
Charge = 0 Multiplicity = 1

Cu	0.81064	-0.07426	0.
Se	-0.64216	-0.75771	1.16506
O	0.69764	1.68174	-0.504
C	0.05264	2.51374	0.482
C	0.95664	-1.94226	0.476
C	0.09264	-3.04326	0.206
C	2.17464	-2.17226	1.141
C	0.42164	-4.30726	0.688
H	-0.82636	-2.89226	-0.308
C	2.49064	-3.44926	1.605
C	1.60664	-4.50626	1.393
H	-0.23836	-5.12926	0.517

H	3.17612	-4.37832	1.838	3.41564	-3.63426	2.093
H	1.45812	-6.12832	1.634	1.85164	-5.48626	1.748
C	2.85612	-1.71732	1.043	3.07764	-1.07726	1.146
C	3.30912	0.50068	0.51	3.55664	1.09474	0.51
C	4.12712	-1.91432	1.555	4.32964	-1.25026	1.714
C	4.61112	0.34368	1.021	4.84164	0.96674	1.071
C	5.01612	-0.86632	1.559	5.22564	-0.21126	1.685
H	4.42012	-2.86232	1.938	4.60364	-2.17126	2.165
H	5.99712	-0.99632	1.947	6.19364	-0.32326	2.114
N	2.42012	-0.54032	0.547	2.66764	0.05374	0.547
C	3.02612	1.91968	-0.03	3.28864	2.48874	-0.092
H	2.20412	1.91768	-0.712	2.48364	2.45574	-0.801
H	2.77712	2.55668	0.83	3.00964	3.15474	0.738
C	4.22612	2.54668	-0.725	4.50464	3.10374	-0.767
H	4.47612	1.90868	-1.587	4.78364	2.44274	-1.602
H	4.00612	3.56368	-1.088	4.28764	4.10774	-1.167
C	5.39412	2.55968	0.167	5.64764	3.15074	0.158
C	5.60212	1.47468	1.006	5.83364	2.09674	1.038
C	6.29112	3.62268	0.129	6.54664	4.21274	0.108
C	6.73912	1.45568	1.812	6.95064	2.10174	1.871
C	7.42412	3.60768	0.945	7.65864	4.22474	0.953
C	7.63812	2.51668	1.781	7.85164	3.15974	1.828
H	6.92712	0.63368	2.462	7.12264	1.30274	2.552
O	8.39412	4.65368	0.969	8.62864	5.26974	0.971
H	8.50112	2.49268	2.405	8.70064	3.15474	2.473
H	6.09712	4.42768	-0.532	6.37164	4.99674	-0.583
C	8.14612	5.77068	0.089	8.39764	6.36674	0.063

H	8.95912	6.50468	0.194	H	9.20964	7.10174	0.166
H	7.19012	6.24668	0.355	H	7.43864	6.84874	0.303
H	8.10612	5.41968	-0.953	H	8.37464	5.99274	-0.971
C	-0.61588	3.30768	0.286	C	-0.24836	3.98674	0.204
O	-0.57288	1.25968	1.534	O	-0.20836	2.02174	1.581
H	-1.05188	3.74568	1.204	H	-0.65536	4.48974	1.101
H	-1.34088	3.38968	-0.546	H	-0.97436	4.05274	-0.629
H	0.28412	3.85468	-0.031	H	0.66964	4.48274	-0.147
C	-2.90588	-0.43732	0.732	C	-2.15274	-0.71641	2.13783
C	-3.10188	-1.24432	1.849	C	-2.57053	-1.5028	3.20259
C	-3.99988	-0.85732	2.837	C	-3.83558	-1.2381	3.75291
C	-4.70488	0.33268	2.71	C	-4.65543	-0.21749	3.26287
C	-4.51788	1.13568	1.592	C	-4.22606	0.56185	2.20735
C	-3.61988	0.74968	0.604	C	-2.98626	0.30114	1.6667
H	-2.57388	-2.15132	1.953	H	-1.9672	-2.26176	3.59138
H	-4.14688	-1.47132	3.69	H	-4.18337	-1.81274	4.56164
H	-5.38588	0.62668	3.463	H	-5.60797	-0.0259	3.69205
H	-5.05788	2.04268	1.493	H	-4.83278	1.35659	1.81466
H	-3.47588	1.36468	-0.248	H	-2.65109	0.91105	0.85478





Sum of electronic and thermal Free Energies= -8661.478025	Sum of electronic and thermal Free Energies= -8661.213201
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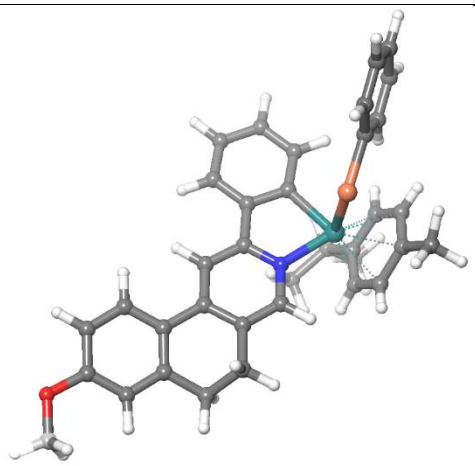
Pd 1.75124 -0.02475 0.	Pd 1.75124 -0.02475 0.
Se 1.14424 1.97425 -1.241	Se 1.14424 1.97425 -1.241
O 3.55024 0.08725 -0.718	O 3.55024 0.08725 -0.718
C -0.00876 0.10425 0.997	C -0.00876 0.10425 0.997
C -1.02676 1.04525 0.886	C -1.02676 1.04525 0.886
C -0.09276 -0.95975 1.896	C -0.09276 -0.95975 1.896
C -2.15076 0.91125 1.696	C -2.15076 0.91125 1.696
H -0.94676 1.87025 0.178	H -0.94676 1.87025 0.178
C -1.21976 -1.08575 2.703	C -1.21976 -1.08575 2.703
C -2.24576 -0.14675 2.599	C -2.24576 -0.14675 2.599
H -2.96076 1.63825 1.624	H -2.96076 1.63825 1.624
H -1.29976 -1.91075 3.411	H -1.29976 -1.91075 3.411
H -3.12976 -0.24175 3.229	H -3.12976 -0.24175 3.229
C 3.23124 -2.46575 1.009	C 3.23124 -2.46575 1.009
C 1.13124 -1.95975 1.925	C 1.13124 -1.95975 1.925
C 3.34524 -3.57275 1.845	C 3.34524 -3.57275 1.845
H 4.02624 -2.21875 0.305	H 4.02624 -2.21875 0.305
C 1.19524 -3.05175 2.782	C 1.19524 -3.05175 2.782
C 2.31924 -3.87475 2.738	C 2.31924 -3.87475 2.738
H 0.38124 -3.26075 3.476	H 0.38124 -3.26075 3.476
C 4.59424 -4.41875 1.834	C 4.59424 -4.41875 1.834
H 5.08524 -4.32375 0.865	H 5.08524 -4.32375 0.865
H 5.26824 -4.07475 2.619	

C	4.24124 -5.88675 2.079	H	5.26824 -4.07475 2.619
H	3.66624 -6.26475 1.234	C	4.24124 -5.88675 2.079
H	5.15824 -6.46575 2.184	H	3.66624 -6.26475 1.234
C	3.42124 -6.02075 3.337	H	5.15824 -6.46575 2.184
C	2.46624 -5.05375 3.637	C	3.42124 -6.02075 3.337
C	3.59624 -7.12675 4.163	C	2.46624 -5.05375 3.637
C	1.67024 -5.20875 4.769	C	3.59624 -7.12675 4.163
C	2.80824 -7.27575 5.307	C	1.67024 -5.20875 4.769
H	4.34824 -7.87675 3.918	C	2.80824 -7.27575 5.307
C	1.84624 -6.31175 5.597	H	4.34824 -7.87675 3.918
H	0.91024 -4.46475 5.006	C	1.84624 -6.31175 5.597
H	1.22224 -6.42375 6.484	H	0.91024 -4.46475 5.006
N	2.13924 -1.71475 1.082	H	1.22224 -6.42375 6.484
C	3.56024 -0.47275 -2.01	N	2.13924 -1.71475 1.082
O	2.52724 -1.02675 -2.394	C	3.56024 -0.47275 -2.01
C	4.80224 -0.42575 -2.895	O	2.52724 -1.02675 -2.394
C	3.93424 -9.35775 5.892	C	4.80224 -0.42575 -2.895
H	3.93024 -10.14475 6.646	C	3.93424 -9.35775 5.892
H	4.91324 -8.87775 5.874	H	3.93024 -10.14475 6.646
H	3.72524 -9.79075 4.914	H	4.91324 -8.87775 5.874
O	2.92424 -8.37775 6.211	H	3.72524 -9.79075 4.914
H	4.59024 -0.91475 -3.846	O	2.92424 -8.37775 6.211
H	5.62324 -0.94275 -2.397	H	4.59024 -0.91475 -3.846
H	5.08324 0.61125 -3.075	H	5.62324 -0.94275 -2.397
C	2.30424 3.40825 -0.782	H	5.08324 0.61125 -3.075
C	2.21124 4.61525 -1.467	C	2.30424 3.40825 -0.782
C	3.05724 5.66825 -1.14	C	2.21124 4.61525 -1.467

C	3.99624	5.51625	-0.126	C	3.05724	5.66825	-1.14
C	4.08924	4.31125	0.56	C	3.99624	5.51625	-0.126
C	3.24424	3.25725	0.232	C	4.08924	4.31125	0.56
H	1.49424	4.73225	-2.241	C	3.24424	3.25725	0.232
H	2.98624	6.58825	-1.664	H	1.49424	4.73225	-2.241
H	4.64224	6.32025	0.124	H	2.98624	6.58825	-1.664
H	4.80724	4.19725	1.336	H	4.64224	6.32025	0.124
H	3.31524	2.33925	0.755	H	4.80724	4.19725	1.336
				H	3.31524	2.33925	0.755

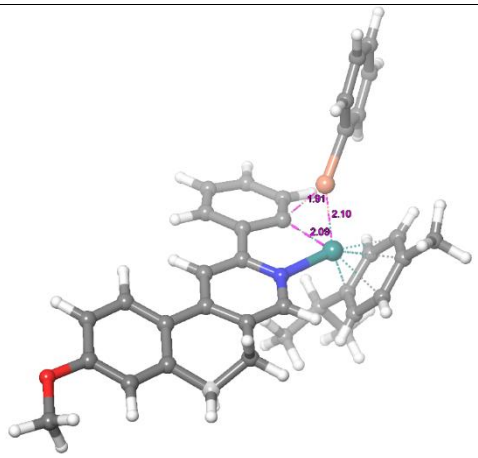


Sum of electronic and thermal Free Energies= -8327.027784

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Ru	1.05817	1.13861	0.
C	0.18417	1.77461	1.786
C	0.98817	0.98061	-2.222
C	1.77017	-0.05539	-1.678
H	2.66117	-0.19339	-1.976



Sum of electronic and thermal Free Energies= -8326.831862

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Ru	6.52847	-1.54703	0.
C	5.65447	-0.91103	1.786
C	6.45847	-1.70503	-2.222
C	7.24047	-2.74103	-1.678
H	8.13147	-2.87903	-1.976

C	1.20317	-0.88939	-0.674	6.67347	-3.57503	-0.674
H	1.71817	-1.60739	-0.324	7.18847	-4.29303	-0.324
C	-0.08283	-0.67939	-0.192	5.38747	-3.36503	-0.192
C	-0.85483	0.37561	-0.804	4.61547	-2.31003	-0.804
H	-1.74383	0.52761	-0.508	3.72647	-2.15803	-0.508
C	-0.33483	1.16861	-1.804	5.13547	-1.51703	-1.804
H	-0.87183	1.83961	-2.209	4.59847	-0.84603	-2.209
C	1.54617	1.83261	-3.309	7.01647	-0.85303	-3.309
H	1.46817	1.27761	-4.255	6.93847	-1.40803	-4.255
H	0.97317	2.76761	-3.396	6.44347	0.08197	-3.396
H	2.61317	2.01761	-3.121	8.08347	-0.66803	-3.121
C	-0.75883	-1.50139	0.883	4.71147	-4.18703	0.883
H	-1.42883	-0.84939	1.463	4.04147	-3.53503	1.463
C	-1.59183	-2.61039	0.233	3.87847	-5.29603	0.233
H	-2.09183	-3.19539	1.016	3.37847	-5.88103	1.016
H	-2.34483	-2.16439	-0.431	3.12547	-4.85003	-0.431
H	-0.92983	-3.26539	-0.35	4.54047	-5.95103	-0.35
C	0.27017	-2.18139	1.818	5.74047	-4.86703	1.818
H	0.89717	-1.41539	2.294	6.36747	-4.10103	2.294
H	-0.26583	-2.75039	2.593	5.20447	-5.43603	2.593
H	0.90317	-2.86939	1.239	6.37347	-5.55503	1.239
C	-1.11083	2.26461	1.946	4.27347	-0.69403	2.088
H	-1.75883	2.34761	1.118	3.54747	-0.71403	1.309
C	-1.56283	2.64761	3.206	3.88047	-0.35903	3.381
H	-2.55583	3.02761	3.326	2.85047	-0.14603	3.586
C	-0.72683	2.53761	4.313	4.81247	-0.30303	4.414
H	-1.08083	2.83361	5.281	4.49147	-0.05303	5.409

C	0.56117	2.03361	4.161	C	6.14447 -0.62703 4.17
H	1.19617	1.94061	5.007	H	6.82747 -0.66103 4.982
C	1.00017	1.65361	2.894	C	6.55547 -0.95703 2.88
C	2.30317	1.09861	2.613	C	7.82647 -1.50703 2.594
C	3.25517	0.91161	3.611	C	8.80047 -1.66803 3.577
H	3.04017	1.17361	4.62	H	8.61847 -1.35303 4.576
C	4.48617	0.36961	3.27	C	10.00647 -2.26203 3.237
C	4.72317	0.05861	1.937	C	10.19447 -2.65303 1.918
C	3.72917	0.27461	0.986	C	9.17847 -2.46003 0.986
H	3.92717	0.04361	-0.031	H	9.34447 -2.74903 -0.022
N	2.53517	0.77461	1.337	N	8.00547 -1.91103 1.337
C	6.08417	-0.46639	1.533	C	11.52647 -3.24103 1.507
H	6.04817	-0.94739	0.542	H	11.44947 -3.77103 0.545
H	6.77117	0.39261	1.487	H	12.23847 -2.40703 1.4
C	6.62817	-1.40539	2.613	C	12.06947 -4.14003 2.623
H	7.64017	-1.78039	2.374	H	13.06147 -4.56103 2.378
H	5.93917	-2.25939	2.675	H	11.35547 -4.96603 2.747
C	6.61317	-0.71739	3.955	C	12.11247 -3.38303 3.926
C	5.55517	0.12761	4.281	C	11.09247 -2.48503 4.232
C	7.63017	-0.96739	4.871	C	13.14247 -3.62203 4.83
H	8.41517	-1.62139	4.592	H	13.89747 -4.31703 4.568
C	7.59617	-0.36839	6.133	C	13.16247 -2.95703 6.059
C	6.53317	0.46961	6.457	C	12.13747 -2.06503 6.362
H	6.49717	0.92661	7.417	H	12.14247 -1.55703 7.298
C	5.51517	0.71661	5.541	C	11.10547 -1.83003 5.46
H	4.71317	1.36061	5.811	H	10.33347 -1.14503 5.714
Se	1.51017	3.43561	-0.642	Se	5.73547 0.36097 0.359

O	8.59817 -0.57239 7.133	O	14.18147 -3.14503 7.045
C	9.68717 -1.44839 6.772	C	15.22647 -4.08103 6.707
H	10.38617 -1.52739 7.617	H	15.94347 -4.14203 7.538
H	10.21617 -1.03939 5.899	H	15.74847 -3.74103 5.8
H	9.29317 -2.44639 6.53	H	14.78847 -5.07503 6.53
C	-0.15883 4.41761 -0.752	C	5.00347 2.10197 0.703
C	-1.46383 3.92161 -0.77	C	3.62347 2.27597 0.662
C	-2.55583 4.77861 -0.862	C	3.06347 3.52397 0.909
C	-2.36483 6.15161 -0.94	C	3.88347 4.60597 1.2
C	-1.07583 6.66061 -0.925	C	5.26247 4.43697 1.245
C	0.01017 5.79861 -0.833	C	5.82447 3.18897 0.998
H	-1.64383 2.90261 -0.713	H	2.99247 1.45197 0.439
H	-3.54083 4.38161 -0.873	H	2.00847 3.64897 0.874
H	-3.19983 6.80761 -1.011	H	3.45747 5.55897 1.388
H	-0.91883 7.70961 -0.985	H	5.88947 5.26397 1.466
H	0.99317 6.20261 -0.824	H	6.87647 3.07497 1.033

The limit of detection (LOD):

The limit of detection (LOD) was determined by incrementally adding very low equivalents of picric acid (PA) to the sample. The LOD was calculated using the standard equation.

$$\text{LOD} = 3 \times \frac{\sigma}{S}$$

Where, σ represents the standard deviation of the analytical response and S denotes the slope of the calibration curve. The LOD value was subsequently obtained using this relationship.

Using the graph and equation LOD value is calculated and the LOD value is 0.29 µM.

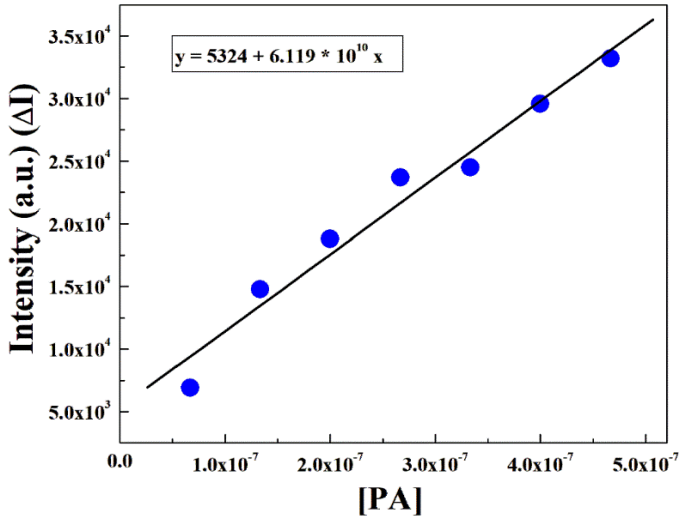


Figure S1: The limit of detection (LOD)

Absorption spectra toward picric acid sensing:

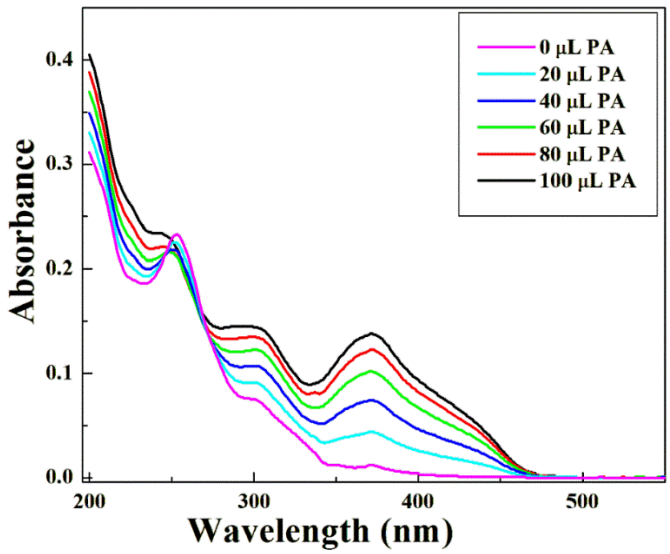


Figure S2: Absorption spectra toward picric acid sensing

The initial concentration of the sample was 8.33 µM. Upon incremental addition of picric acid, a new absorption band appeared at approximately 370 nm. The absorbance of this band (370nm) increased progressively with higher concentrations of picric acid. This emerging absorption feature can be attributed primarily to the formation of a picric acid–molecule complex.