Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Selective access to dihydrophenanthridines and phenanthridinones via cyclisation of aryl amines onto *N*-tethered arynes

Weitao Sun,† Maria Uttendorfer,† Fahima I. M. Idiris, A. Yannic R. Werling, Khushal Siddiq and Christopher R. Jones*

Department of Chemistry, Queen Mary University of London, Mile End Road, London, E1 4NS, UK.

Table of contents

1. General information **2**

2. Synthesis and characterization of *p*-methoxybenzyl aryne precursor tether **3**

3. Synthesis and characterization of *N*-methylaniline derivatives **5**

4. Synthesis and characterization of cyclisation precursors **7**

5. Synthesis and characterization of phenanthridine derivatives **16**

6. Cyclisation: substrate scope **24**

7. NMR spectra **26**

1. General information

General: All chemicals were used directly as obtained from commercial sources without prior purification. Dry tetrahydrofuran (THF) and dichloromethane were obtained from the MB SPS-80 solvent purification machine. Acetonitrile was distilled over CaH_2 and used as required. 1,2-Dimethoxyethane was distilled over Na/benzophenone and stored over molecular sieves. Reactions requiring anhydrous conditions were carried out in oven-dried apparatus under nitrogen. 3-(Chloromethyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7** was prepared according to the reported procedure.[1] *N*-Methylaniline, 4-methoxylaniline, 4-bromoaniline, 4-chloroaniline, 4-fluoroaniline, 2-mthylaniline, indoline, 1,2,3,4-tetrahydroquinoline, *N*-allylaniline, *N*-benzylaniline and *N*-tosylaniline were purchased from commercial suppliers and used without additional purification.

Chromatography: Flash column chromatography was carried out using 40-63 µm silica gel or Biotage Isolera One flash purification system using KP-Sil or KP-NH (amine modified) Snap cartridges. Thin-layer chromatography (TLC) was performed on aluminium backed plates pre-coated with Silica Gel 60 F_{254} and visualized using a UV lamp (254 nm) or Dragendorff reagent stain.

Nuclear Magnetic Resonance Spectroscopy: ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance UltraShield AV400 or AV(III)400 (400 MHz, 376 MHz and 101 MHz). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and referenced to the residual solvent peak at 7.26 ppm and solvent peak at 77.2 ppm. ^{19}F NMR spectra were recorded in C_6F_6 referenced to the solvent peak at -164.9 ppm. Chemical shifts are quoted in parts per million (ppm) to 2 dp for ^{1}H NMR spectra and 1 dp for the ^{13}C and ^{19}F NMR spectra. Coupling constants (*J*) were measured in Hertz (Hz) to 1 dp. Spectral data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, br = broad) and coupling constant (*J*).

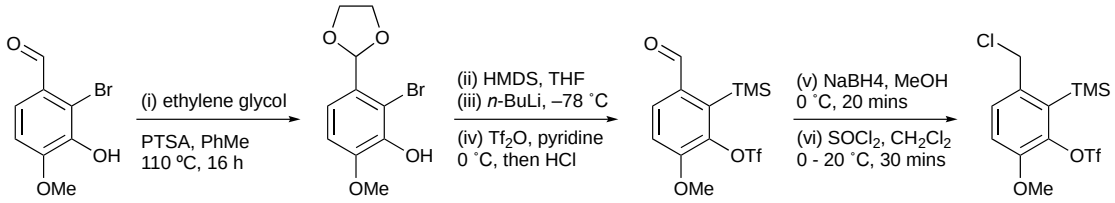
Infrared (IR) spectroscopy: IR spectra were recorded as solids or neat liquids on the PerkinElmer Spectrum 65 FT-IR spectrometer fitted with a Universal ATR sampling accessory and are reported in wavenumbers (cm^{-1}) to the nearest integer.

Mass Spectrometry: High resolution mass spectra were acquired by nanospray ionization (NSI), time-of-flight (TOF) or atmospheric pressure chemical ionization (APCI) at the EPSRC UK National Mass Spectrometry Facility at Swansea University. Low resolution mass spectra were recorded on the Agilent 1100 series LC-MS (comprising a 6310 ion trap) under electrospray ionization (ESI) or on the Agilent GC-MS (comprising a 6890 GC and 5973 MSD) under electron ionization (EI).

Melting points: All the melting points were determined in open glass capillaries and are uncorrected.

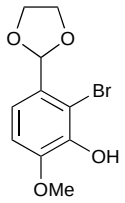
1 F. I. M. Idiris, C. E. Majesté, G. B. Craven and C. R. Jones, *Chem. Sci.* 2018, **9**, 2873.

2. Synthesis and characterization of *p*-methoxybenzyl aryne precursor tether



Scheme S1: Synthesis of chlorinated *p*-methoxybenzyl aryne precursor

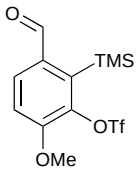
2-Bromo-3-(1,3-dioxolan-2-yl)-6-methoxyphenol, 16



Ethylene glycol (14.2 mL, 256 mmol) was added to a stirred solution of 2-bromo-3-hydroxy-4-methoxybenzaldehyde **15** (12.8 mL, 55.3 mmol) and pyridium *p*-toluenesulfonate (1.54 g, 6.10 mmol) in toluene (80 mL). The reaction flask was fitted with a Dean-Stark apparatus and refluxed for 16 hours. The solvent was removed *in vacuo* to afford the title compound as an off-white solid (15.2 g, 55.3 mmol, >99%) that was used in subsequent reactions without additional purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.15 (d, *J* 8.5, 1H), 6.82 (d, *J* 8.5, 1H), 6.00 (bs, 1H), 4.03-4.16 (m, 4H), 3.91 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 150.3, 145.9, 135.2, 123.0, 116.9, 110.5, 102.0, 64.8, 55.6; **IR (neat): ν_{max}/cm^{-1}** 3530, 2949, 2894, 1578, 1427, 1243; **HRMS** note, acetal proved unstable to range of ionisation techniques.

3-Formyl-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 17

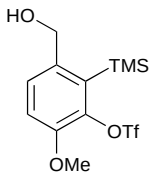


A solution of 2-bromo-3-(1,3-dioxolan-2-yl)-6-methoxyphenol (15.2 g, 55.3 mmol) and hexamethyldisilazane (7.17 g, 9.30 ml, 44.2 mmol) in THF (70 mL) was heated to reflux for 2 h. The mixture was concentrated *in vacuo*, the residue was then dissolved in THF (33 mL) and cooled to −78 °C. *n*-BuLi (1.6M in hexanes, 38.2 mL, 61.2 mmol) was added and the reaction mixture stirred for 30 mins. NH_4Cl (sat. aq., 50 mL) was added and the mixture extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with $NaHCO_3$ (sat. aq., 50 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was dissolved in CH_2Cl_2 (50 mL), cooled to 0 °C and then pyridine (13.1 g, 14.3 mL, 166 mmol) and trifluoromethanesulfonic anhydride (20.3 g, 14.3 mL, 12.1 mmol) were added. The cooling bath was removed and the reaction stirred for 3 h. Hydrochloric acid (4M, 25 mL) was added and the mixture stirred for 16 h. The mixture was extracted with CH_2Cl_2 (3 x 60 mL) and the combined organic layers washed with $NaHCO_3$ (sat. aq., 50 mL) and brine (25 mL). dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting residue was

purified by flash column chromatography (*n*-hexane:ethyl acetate, 4:1) to yield the title compound as a light yellow solid (11.5 g, 32.4 mmol, 59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.11 (s, 1H), 7.94 (d, *J* 8.5, 1H), 7.12 (d, *J* 5.2, 1H), 3.95 (s, 3H), 0.58 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 190.6, 155.1, 143.4, 139.1, 135.6, 133.0, 118.8 (q, *J* 321), 113.0, 56.2 (d, *J* 1.4), 2.3; **^{19}F NMR (376 MHz, $CDCl_3$):** δ_F –72.0 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2949, 2850, 2741, 1693, 1589, 1558, 1467, 1411, 1387, 1300, 1271, 1245, 1201, 1123, 1038, 976, 946, 870, 834, 775, 740, 729, 686, 666, 630, 609, 592, 575, 537, 523, 510, 504; **m.p.** 62 °C (CH_2Cl_2); **HRMS (APCI)** [M-H]+ calcd. for $C_{12}H_{16}F_3O_5SiS$ 357.0434, found 357.0433.

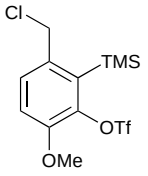
3-(Hydroxymethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 21



Sodium borohydride (637 mg, 16.8 mmol) was added to a solution of 3-formyl-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **xx** (5.00 g, 14.0 mmol) in methanol (40 mL) at 0 °C. The reaction mixture was stirred for 20 min, quenched with NH_4Cl (sat. aqueous, 100 mL) and extracted with ethyl acetate (3 x 70 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the title compound as a colourless solid (4.83 g, 13.5 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41 (d, *J* 8.4, 1H), 7.00 (d, *J* 8.4, 1H), 4.70 (s, 2H), 3.85 (s, 3H), 0.47 (s, 9H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.7, 143.0, 139.3, 133.9, 129.1, 118.7 (q, *J* 321), 113.3, 64.6, 55.5, 1.7; **^{19}F NMR (376 MHz, $CDCl_3$):** δ_F –72.1 (s, 3F); **m.p.** = 78 °C (MeOH); **IR (neat): ν_{max}/cm^{-1}** 3265, 3024, 2955, 2903, 1561, 1411, 1288, 1195; **HRMS (ESI)** [M+NH_4]+ calcd. for $C_{12}H_{17}F_3O_5SSiNH_4$ 376.0856 found, 376.0859.

3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 7b



3-(Hydroxymethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4.30 g, 12.0 mmol) was dissolved in dichloromethane (120 mL). Thionyl chloride (1.57 g, 959 µL, 13.2 mmol) was added slowly and the reaction mixture stirred at rt for 30 mins. The solvent was removed *in vacuo* to yield the title compound as an amorphous yellow solid (4.30 g, 11.4 mmol, 95%).

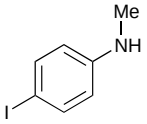
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, *J* 8.5, 1H), 7.02 (d, *J* 8.5, 1H), 4.67 (s, 2H), 3.86 (s, 3H), 0.52 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 150.1, 142.9, 135.7, 134.8, 131.7, 120.4, 115.4 (q, *J* 321), 55.5, 46.1, 17.5; **^{19}F NMR (376 MHz, $CDCl_3$):** δ_F –70.7 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2955, 2904, 1563, 1408, 1296, 1238, 1118, 1199 cm-1; **HRMS (ESI)** [M+NH_4]+ calcd. for $C_{12}H_{16}ClF_3O_4SSiNH_4$ 394.0517 found, 394.0516.

3. Synthesis and characterization of *N*-methylaniline derivatives

General procedure for the synthesis of N-methylanilines:

According to a modified literature procedure,[2] aniline (1.0 equiv.), paraformaldehyde (2.0 equiv.)) and sodium methoxide (5.0 equiv.) were dissolved in methanol (0.40 M) and the mixture was stirred for 16 h at room temperature. Sodium borohydride (1.0 equiv.) was then added and the mixture was heated under reflux for 1 h. The solvent was removed *in vacuo* and the residue then dissolved in ethyl acetate and basified by the addition of a saturated aqueous solution of $NaHCO_3$. The mixture was washed with brine (x 3), the combined organic phases then dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to afford the target compound.

4-Iodo-*N*-methylaniline, 22

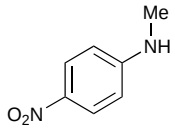


4-Iodoaniline (0.793 g, 3.62 mmol), paraformaldehyde (0.217 g, 7.17 mmol), sodium methoxide (0.978 g, 18.1 mmol) and sodium borohydride (0.138 g, 3.62 mmol) were subjected to the general procedure for the synthesis of *N*-methyl anilines to afford 4-iodo-*N*-methylaniline (0.818 g, 3.51 mmol, 97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (2H, d, *J* = 8.8, C3 & C5), 6.41 (2H, d, *J* = 8.8, C2 & C6), 4.50 (1H, br s, NH), 2.71 (3H, d, *J* = 5.2, NCH_3); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 151.1 (C1), 138.9 (C3 & C5), 115.8 (C2 & C6), 77.1 (C4), 30.7 (N***C***H_3).

This data was in accordance with the literature.[3]

4-Nitro-*N*-methylaniline, 23



4-Nitroaniline (0.500 g, 3.62 mmol), paraformaldehyde (0.217 g, 7.17 mmol), sodium methoxide (0.978 g, 18.1 mmol) and sodium borohydride (0.138 g, 3.62 mmol) were subjected to the general procedure for the synthesis of *N*-methyl anilines to afford 4-nitro-*N*-methylaniline (0.523 g, 3.44 mmol, 95%).

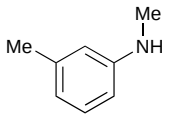
^{1}H NMR (400 MHz, $CDCl_3$): δ_H: 8.10 (2H, d, *J* = 9.2 Hz, C3 & C5), 6.54 (2H, d, *J* = 9.2 Hz, C2 & C6), 4.66 (1H, br s, NH), 2.94 (3H, s, NCH_3); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C: 154.3 (C1), 137.9 (C4), 126.4 (C3 & C5), 110.7 (C2 & C6), 30.1 (N***C***H_3).

---

2 J. Wu, Y. Zhou, Y. Zhou, C. Chiang and A. Lei, *Chem. Commun.*, 2017, **53**, 5542.
3 E. J. Linstad, A. L. Vavere, B. Hu, J. J. Pempinger, S. E. Snyder and S. G. DiMango, *Org. Biomol. Chem.*, 2017, **15**, 2246.

This data was in accordance with the literature.[4]

3-Methyl-*N*-methylaniline, 24

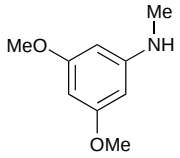


3-Methylaniline (0.387 g, 3.62 mmol), paraformaldehyde (0.217 g, 7.17 mmol), sodium methoxide (0.978 g, 18.1 mmol) and sodium borohydride (0.138 g, 3.62 mmol) were subjected to the general procedure for the synthesis of *N*-methyl anilines to afford 3-methyl-*N*-methylaniline (0.320 g, 2.64 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H: 7.09 (1H, t, *J* = 7.8 Hz, C5), 6.55 (1H, d, *J* = 7.6 Hz, C6), 6.45 (1H, s, C2), 6.44 (1H, d, *J* = 6.4 Hz, C4), 3.61 (1H, br s, NH), 2.83 (3H, s, NCH_3), 2.30 (3H, s, CH_3); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C: 149.4 (C1), 138.9 (C3), 129.0 (C5), 118.2 (C4), 113.1 (C2), 109.6 (C6), 30.8 (N***C***H_3), 21.6 (CH_3).

This data was in accordance with the literature.[5]

3,5-Dimethoxy-*N*-methylaniline, 25



3,5-Dimethoxyaniline (0.554 g, 3.62 mmol), paraformaldehyde (0.217 g, 7.17 mmol), sodium methoxide (0.978 g, 18.1 mmol) and sodium borohydride (0.138 g, 3.62 mmol) were subjected to the general procedure for the synthesis of *N*-methyl anilines to afford 3,5-dimethoxy-*N*-methylaniline (0.586 g, 3.51 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H: 5.89 (1H, t, *J* = 2.2 Hz, C4), 5.81 (2H, d, *J* = 2.2 Hz, C2 & C6), 3.76 (6H, s, 2 × OCH_3), 3.72 (1H, br s, NH), 2.81 (3H, s, NCH_3); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C: 161.7 (C3 & C5), 151.3 (C1), 91.3 (C2 & C6), 89.6 (C4), 55.1 (2 × OCH_3), 30.7 (NCH_3).

This data was in accordance with the literature.[6]

[4] D. Wang, D. Kuang, F. Zhang, C. Yang and X. Zhu, *Adv. Synth. Catal.*, 2015, **357**, 714.

[5] S. W. Youn and Y. H. Kim, *Org. Lett.*, 2016, **18**, 6140.

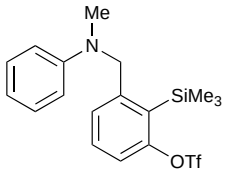
[6] B. P. Fors, D. A. Watson, M. R. Biscoe and S. L. Buchwald, *J. Am. Chem. Soc.*, 2008, **130**, 13552

4. Synthesis and characterization of cyclisation precursors

General procedure for the synthesis of N-tethered aryl amines:

N-Methylaniline (1.2 equiv.), potassium carbonate (3.0 equiv.) and potassium iodide (0.1 equiv.) were added to a solution of 3-(chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7a** (1.0 equiv.) or 3-(chloromethyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (1.0 equiv.) in acetonitrile [0.4 M]. The solution was stirred at room temperature and monitored by TLC. Upon completion, the solvent was removed *in vacuo* and the resulting residue purified by silica gel flash chromatography to afford the target compound.

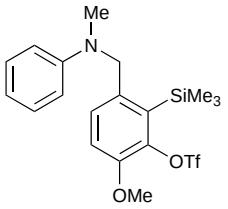
3-((Methyl(phenyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 12



3-(Chloromethyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate[1] **7a** (0.520 g, 1.50 mmol), *N*-methylaniline (0.193 g, 1.80 mmol), K_2CO_3 (0.621 g, 4.50 mmol) and KI (0.0250 g, 0.150 mmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **xx** (0.550 g, 1.32 mmol, 88%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 (1H, t, *J* = 7.9), 7.30-7.22 (4H, m), 6.76 (1H, t, *J* = 7.3), 6.71-6.66 (2H, m), 4.63 (2H, s), 3.02 (3H, s), 0.51 (9H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 155.4, 149.4, 148.0, 131.1, 129.8, 129.3, 125.5, 118.6 (q, *J* = 332), 118.6, 117.0, 112.1, 57.6, 38.5, 2.25; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –72.3 **IR (neat): ν_{max}/cm^{-1}** 2928, 1749, 1700, 1687, 1597, 1365, 1254, 1134, 1015, 926, 758; **HRMS (ESI)** [M+H]+ calcd. For $C_{18}H_{23}F_3NO_2SSi$ 418.110, found: 418.1120.

6-Methoxy-3-((methyl(phenyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18a

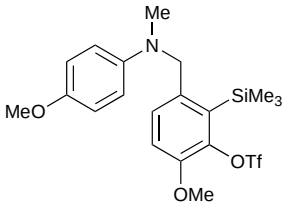


3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (0.500 g, 1.33 mmol), *N*-methylaniline (0.172 mL, 1.59 mmol), K_2CO_3 (0.550 g, 3.99 mmol) and KI (22.1 mg, 0.133 mmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18a** (0.499 g, 1.12 mmol, 84%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27-7.21 (m, 3H), 6.93 (d, *J* 8.5, 1H), 6.76 (t, *J* 7.1, 1H), 6.71 (d, *J* 8.4, 2H), 4.55 (s, 2H), 3.38 (s, 3H), 2.98 (s, 3H), 0.52 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.8, 149.4, 143.5, 137.5, 133.1, 129.4, 126.9, 119.1 (q, *J* 321), 117.1, 113.8, 112.4, 57.1, 55.7, 38.5,

2.3; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2943, 1600, 1507, 1410, 1289, 1204, 1122, 1047, 905, 834, 726, 649; **m.p.** = 65 °C (CH_2Cl_2); **HRMS (ESI)** [M+H]+ calcd. for $C_{19}H_{25}F_3NO_4SSi$ 448.1226, found: 448.1249.

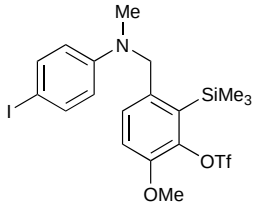
6-Methoxy-3-(((4-methoxyphenyl)(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18b



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (123 mg, 0.326 mmol), 4-methoxy-*N*-methylaniline (53.7 mg, 0.392 mmol), K_2CO_3 (135 mg, 0.979 mmol) and KI (5.4 mg, 32.6 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18b** (124 mg, 0.236 mmol, 72%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29 (d, *J* 8.5, 1H), 6.94 (d, *J* 8.5, 1H), 76.84 (d, *J* 9.1, 1H), 6.69 (d, *J* 9.1, 1H), 4.42 (s, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 2.86 (s, 3H), 0.48 (s, 9H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 152.2, 149.4, 144.9, 143.5, 138.0, 133.4, 127.5, 119.1 (q, *J* 322), 115.0, 114.5, 113.7 (m), 58.1, 55.9, 55.7, 39.3, 2.2; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.3 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2943, 1513, 1464, 1409, 1289, 1204, 1122, 1039, 905, 834, 726, 649; **HRMS (ESI)** [M+H]+ calcd. for $C_{20}H_{26}F_3NO_5SSi$ 478.1326, found: 478.1312.

3-(((4-Iodophenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18c

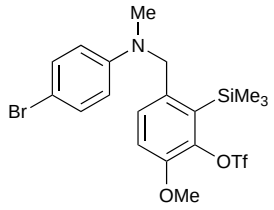


3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (120 mg, 0.318 mmol), 4-iodo-*N*-methylaniline (89.1 mg, 0.382 mmol), K_2CO_3 (132 mg, 0.955 mmol) and KI (5.3 mg, 31.8 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18c** (140 mg, 0.244 mmol, 77%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.46 (d, *J* 9.0, 2H), 7.10 (d, *J* 8.5, 1H), 6.92 (d, *J* 8.5, 1H), 6.45 (d, *J* 9.0, 2H), 4.51 (s, 2H), 3.82 (s, 3H), 2.95 (s, 3H), 0.49 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.6, 149.2, 143.5, 138.0, 136.7, 133.2, 126.6, 119.1 (q, *J* 321), 114.6, 113.8, 77.9, 56.8, 55.7, 38.6, 2.2; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F); **m.p.** = 140 °C (CH_2Cl_2); **IR (neat): ν_{max}/cm^{-1}**

3016, 2971, 1739, 1589, 1499, 1366, 1291, 1217, 1122, 927, 874; **HRMS (ESI)** [M+H]+ calcd. for $C_{19}H_{24}F_3INO_4SSi$ 574.0187, found: 574.0193.

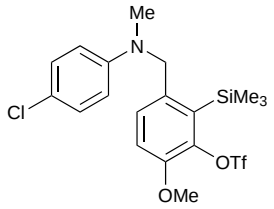
3-(((4-Bromophenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18d



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (220 mg, 0.584 mmol), 4-bromo-*N*-methylaniline (130 mg, 0.701 mmol), K_2CO_3 (242 mg, 1.75 mmol) and KI (9.6 mg, 58.4 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18d** (256 mg, 0.487 mmol, 83%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.30 (d, *J* 8.9, 2H), 7.13 (d, *J* 8.5, 1H), 6.92 (d, *J* 8.5, 1H), 6.55 (d, *J* 8.9, 2H), 4.51 (s, 2H), 3.82 (s, 3H), 2.95 (s, 3H), 0.50 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.6, 148.7, 143.5, 136.7, 133.2, 132.1, 126.7, 119.1 (q, *J* 321), 114.0, 113.8, 109.0, 57.0, 55.7, 38.7, 2.2; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F); **m.p.** = 134 °C (CH_2Cl_2); **IR (neat): ν_{max}/cm^{-1}** 2943, 2253, 1736, 1593, 1498, 1408, 1289, 1202, 1121, 1047, 906, 833, 728, 613; **HRMS (ESI)** [M+H]+ calcd. for $C_{19}H_{24}BrF_3NO_4SSi$ 526.0325, found: 526.037.

3-(((4-Chlorophenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18e

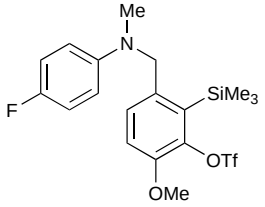


3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (200 mg, 0.531 mmol), 4-chloro-*N*-methylaniline (90.2 mg, 0.637 mmol), K_2CO_3 (220 mg, 1.59 mmol) and KI (8.8 mg, 53.1 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18e** (227 mg, 0.471 mmol, 89%) as an amorphous yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.16 (d, *J* 9.1, 2H), 7.14 (d, *J* 8.5, 1H), 6.93 (d, *J* 8.5, 1H), 6.59 (d, *J* 9.1, 2H), 4.51, (s, 2H), 3.82 (s, 3H), 2.95 (s, 3H), 0.50 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.6, 148.3, 143.5, 136.9, 133.2, 129.2, 126.8, 121.9, 119.0 (q, *J* 321), 113.8, 113.5, 57.1, 55.8, 38.8, 2.3; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.8 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 3457, 3016, 2970, 2841,

2134, 1739, 1598, 1502, 1436, 1366, 1291, 1217, 1122, 927, 875, 809; **HRMS (ESI)** [M+H]+ calcd. for $C_{19}H_{24}ClF_3NO_4SSi$ 482.083, found: 482.0832.

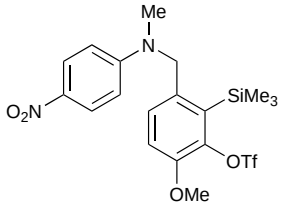
3-(((4-Fluorophenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18f



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (121 mg, 0.321 mmol), 4-fluoro-*N*-methylaniline (48.2 mg, 0.385 mmol), K_2CO_3 (133 mg, 0.962 mmol) and KI (5.3 mg, 32.1 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18f** (149 mg, 0.320 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.31 (d, *J* 8.5, 1H), 6.86 (dd, *J* 9.1 8.4, 2H), 6.86 (d, *J* 8.5, 1H), 6.70 (dd, *J* 9.1 4.2, 2H), 4.55 (s, 2), 3.88 (s, 3H), 2.98 (s, 3H), 0.57 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 155.8 (d, *J* 236), 149.5, 146.7, 143.5, 137.4, 133.3, 127.2, 119.1 (q, *J* 321), 115.7 (d, *J* 22.0), 113.8 (d, *J* 6.9), 113.8, 57.7, 55.6, 39.1, 2.1; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F) –128.6 (tt, J 8.3 4.3, 1F); **IR (neat): ν_{max}/cm^{-1}** 2944, 1511, 1408, 1289, 1198, 1120, 1045, 924, 832, 711, 606; **HRMS (ESI)** [M+H]+ calcd. for $C_{19}H_{24}F_4NO_4SSi$ 466.1126, found: 466.1125.

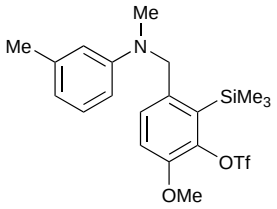
6-Methoxy-3-((methyl(4-nitrophenyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18g



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (149 mg, 0.395 mmol), 4-nitro-*N*-methylaniline (72.2 mg, 0.474 mmol), K_2CO_3 (164 mg, 1.19 mmol) and KI (6.6 mg, 39.5 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at 40 ˚C for 72 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18g** (69.2 mg, 0.140 mmol, 36%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.12 (d, *J* 9.4, 2H), 6.98 (d, *J* 8.6, 1H), 6.93 (d, *J* 8.6, 1H), 6.61 (d, *J* 9.4, 2H), 4.68 (s, 2H), 3.82 (s, 3H), 3.13 (s, 3H), 0.52 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 153.9, 149.9, 143.6, 137.9, 134.7, 133.4, 126.4, 126.0, 119.1 (q, *J* 321), 113.9, 110.7, 56.6, 55.8, 39.0, 2.2; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.1 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2950, 1597, 1492, 1408, 1311, 1199, 1109, 1046, 907, 828, 727, 615;

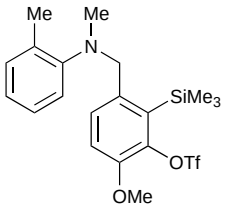
6-Methoxy-3-((methyl(m-tolyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18h



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (200 mg, 0.531 mmol), *N*,3-dimethylaniline (77.2 mg, 0.637 mmol), K_2CO_3 (220 mg, 1.59 mmol) and KI (8.8 mg, 53.1 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18h** (205 mg, 0.444 mmol, 84%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.28 (d, *J* 8.5, 1H), 5.17 (t, *J* 7.2, 1H), 6.97 (d, *J* 8.5, 1H), 6.62 (d, *J* 7.2, 1H), 6.58-6.55 (m, 2H), 4.57 (s, 2H), 3.86 (s, 3H), 3.01 (s, 3H), 2.35 (s, 3H), 0.56 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.9, 149.4, 143.4, 139.1, 137.7, 133.1, 129.3, 126.9, 119.1 (q, *J* 321), 118.0, 113.8, 113.2, 109.7, 57.2, 55.7, 38.6, 22.0, 2.2; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.3 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 3457, 3016, 2970, 1739, 1603, 1499, 1366, 1290, 1217, 1122, 1047, 935, 834, 768, 692, 614; **HRMS (ESI)** [M+H]+ calcd. for $C_{20}H_{27}F_3NO_4SSi$ 462.1377, found: 462.143.

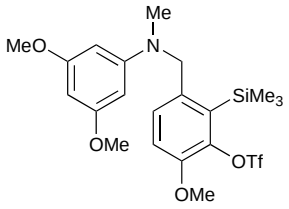
6-Methoxy-3-((methyl(o-tolyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18i



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (209 mg, 0.555 mmol), *N*,2-dimethylaniline (80.6 mg, 0.666 mmol), K_2CO_3 (230 mg, 1.66 mmol) and KI (9.2 mg, 55.5 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at 60 ˚C for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18i** (216 mg, 0.467 mmol, 84%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.84 (d, *J* 8.5, 1H), 7.28-7.22 (m, 2H), 7.17 (d, *J* 8.1, 1H), 7.08 (d, *J* 8.5, 1H), 7.05 (t, *J* 7.4, 1H), 4.17 (s, 2H), 3.90 (s, 3H), 2.59 (s, 3H), 2.41 (s, 3H), 0.53 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 152.6, 149.3, 143.1, 138.0, 134.0, 132.8, 131.4, 128.7, 126.8, 123.4, 120.0, 119.1 (q, *J* 321), 113.7, 60.3, 55.7, 41.1, 18.6, 2.4; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.3 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2950, 2844, 1562, 1493, 1410, 1287, 1199, 1122, 1049, 924, 835, 765, 613; **HRMS (ESI)** [M+H]+ calcd. for $C_{20}H_{27}F_3NO_4SSi$ 462.1377, found: 462.143.

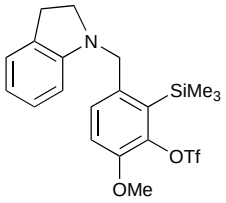
3-(((3,5-Dimethoxyphenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18j



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (206 mg, 0.547 mmol), 3,5-dimethoxy-*N*-methylaniline (110 mg, 0.656 mmol), K_2CO_3 (227 mg, 1.64 mmol) and KI (9.1 mg, 54.7 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at 60 ˚C for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18j** (227 mg, 0.447 mmol, 82%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.21 (d, *J* 8.5, 1H), 6.94 (d, *J* 8.5, 1H), 5.94 (s, 1H), 5.89 (s, 2H), 4.55 (s, 2H), 3.83 (s, 3H), 3.73 (s, 6H), 3.02 (s, 3H), 0.53 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 161.9, 151.4, 149.4, 143.3, 137.4, 132.9, 126.8, 119.1 (q, *J* 321), 113.9, 91.6, 89.4, 57.2, 55.7, 55.2, 39.1, 2.2; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.3 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2942, 2254, 1614, 1462, 1410, 1289, 1204, 1154, 904, 725, 649; **HRMS (ESI)** [M+H]+ calcd. for $C_{21}H_{29}F_3NO_6SSi$ 508.1431, found: 508.1467.

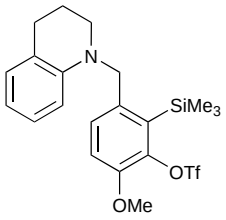
10-Methoxy-8-(trimethylsilyl)-4,5-dihydro-7H-pyrrolo[3,2,1-de]phenanthridin-9-yl trifluoromethanesulfonate, 18k



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (132 mg, 0.350 mmol), indoline (50.1 mg, 0.420 mmol), K_2CO_3 (145 mg, 1.05 mmol) and KI (5.8 mg, 35.0 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at 50 ˚C for 72 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18k** (51.2 mg, 0.111 mmol, 32%) as a colourless amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (d, *J* 8.4, 1H), 7.14 (d, *J* 7.2, 1H), 7.10 (t, *J* 7.7, 1H), 6.98 (d, *J* 8.4, 1H), 6.74 (t, *J* 7.4, 1H), 6.50 (d, *J* 7.8, 1H), 4.29 (s, 2H), 3.87 (s, 3H), 3.17 (t, *J* 8.1, 2H), 2.96 (d, *J* 8.1, 2H), 0.49 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 152.5, 149.7, 143.7, 137.2, 134.4, 130.6, 129.1, 127.5, 124.7, 119.1 (q, *J* 321), 118.5, 113.5, 107.6, 55.7, 54.7, 53.9, 28.6, 2.1; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2950, 2844, 1607, 1466, 1411, 1291, 1203, 1122, 1047, 935, 837, 747, 607; **HRMS (ESI)** [M+H]+ calcd. for $C_{20}H_{25}F_3NO_4SSi$ 460.122, found: 460.1272.

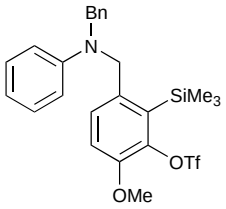
3-((3,4-Dihydroquinolin-1(2*H*)-yl)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18l



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (300 mg, 0.796 mmol), 1,2,3,4-tetrahydroquinoline (127 mg, 0.955 mmol), K_2CO_3 (330 mg, 2.39 mmol) and KI (13.4 mg, 79.6 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **18l** (191 mg, 0.447 mmol, 65%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29 (1H, d, *J* 8.6), 7.02-6.99 (2H, m), 6.93 (1H, d, *J* 8.6), 6.64-6.60 (1H, m), 6.38 (1H, br d, *J* 8.4), 4.51 (2H, s), 3.83 (3H, s), 3.34-3.31 (2H, m), 2.87-2.83 (2H, m), 2.07-2.01 (2H, m), 0.53 (9H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.0, 145.3, 143.1, 136.8, 132.6, 128.9, 127.2, 126.1, 122.2, 118.8 (q, *J* 321), 116.0, 113.5, 110.6, 55.6, 55.4, 49.6, 28.0, 22.2, 2.01; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 3017, 2930 & 2840, 1502 & 1409, 1287 & 1117, 1199; **HRMS (NSI)** [M+H]+ calcd. for $C_{21}H_{27}F_3NO_4SSi$ 474.1377, found 474.1363.

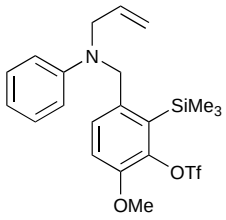
3-((Benzyl(phenyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18m



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (0.100 g, 0.265 mmol), *N*-benzylaniline (59.9 mg, 0.318 mmol), K_2CO_3 (110 mg, 0.796 mmol) and KI (4.4 mg, 26.5 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **18m** (115 mg, 0.220 mmol, 83%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27 (2H, t, *J* 8.5), 7.22-7.18 (2H, m), 7.17-7.10 (4H, m), 6.87 (1H, d, *J* 8.5), 6.68 (1H, t, *J* 7.3), 6.64 (2H, d, *J* 7.9), 4.58 (2H, s), 4.53 (2H, s), 3.76 (3H, s), 0.35 (9H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.5, 149.2, 143.6, 138.3, 136.8, 133.2, 129.5, 128.8, 127.9, 127.2, 126.8, 117.3 (q, *J* 321), 117.3, 113.8, 112.6, 55.0, 54.7, 54.1, 2.2; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2935, 1596, 1504, 1387, 1290, 1257, 1199, 1119, 1044, 929, 833, 733; **HRMS (NSI)** [M+H]+ calcd. for $C_{25}H_{29}F_3NO_4SSi$ 524.1533, found 524.1539.

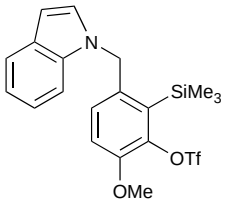
3-((Allyl(phenyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18n



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (0.100 g, 0.265 mmol), *N*-allylaniline (43.2 μL, 0.318 mmol), K_2CO_3 (110 mg, 0.796 mmol) and KI (4.4 mg, 26.5 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **18n** (89.6 mg, 0.189 mmol, 71%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.19-7.12 (3H, m), 6.86 (1H, d, *J* 8.5), 6.67 (1H, t, *J* 7.3), 6.62 (2H, d, *J* 8.0), 5.91-5.76 (1H, m), 5.18-5.10 (2H, m), 4.50 (2H, s), 3.89 (2H, d, *J* 4.8), 3.76 (3H, s), 0.45 (9H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 149.4, 149.0, 143.5, 137.2, 133.4, 133.0, 129.4, 129.3, 126.7, 118.2 (q, *J* 321), 117.0, 116.8, 113.8, 112.5, 55.7, 54.4, 52.8, 2.3; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2960, 1598, 1564, 1505, 1460, 1394, 1288, 1204, 1117, 924,794; **HRMS (NSI)** [M+H]+ calcd. for $C_{21}H_{27}F_3NO_4SSi$ 474.1377, found 474.1382.

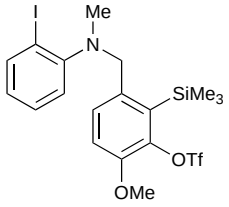
3-((1*H*-Indol-1-yl)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18o



NaH (10.7 mg, 0.318 mmol, 60% dispersion in mineral oil) was added portionwise to a solution of indole (62.2 mg, 0.531 mmol) in THF (10 mL) at 0 °C. After stirring for 3 h, 3-(chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (0.100 g, 0.265 mmol) was added dropwise and the resulting reaction mixture was allowed to warm to room temperature and then stirred overnight. After quenching with a saturated aqueous solution of NH_4Cl (10 mL) at 0 °C, the reaction mixture was extracted with diethyl ether (10 mL x 3). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **18o** (18.6 mg, 0.041 mmol, 15%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 (1H, s), 7.45 (1H, d, *J* 7.9), 7.36 (1H, d, *J* 7.7), 7.21 (1H, t, *J* 7.2), 7.16 – 7.07 (2H, m), 6.88 (1H, d, *J* 8.5), 6.67 (1H, s), 4.19 (2H, s), 3.82 (3H, s), 0.45 (9H, s). **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 148.8, 143.3, 139.7, 136.7, 134.3, 130.6, 127.3, 123.1, 122.4, 119.5 (q, *J* 321), 119.2, 116.8, 113.7, 111.3, 55.7, 31.9, 2.3; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.2 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2954, 2840, 1617, 1464, 1417, 1289, 1208, 1126, 1049, 938, 834, 741, 603; **HRMS (ESI)** [M+H]+ calcd. for $C_{20}H_{23}F_3NO_4SSi$ 458.5472, found 458.5476.

3-((Allyl(phenyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 18p



3-(Chloromethyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **7b** (0.135 g, 0.357 mmol), 2-iodo-*N*-methylaniline (99.8 mg, 0.428 mmol), K_2CO_3 (148 mg, 1.07 mmol) and KI (5.9 mg, 35.7 μmol) were subjected to the general procedure for the synthesis of *N*-tethered aryl amines. The solution was stirred at room temperature for 16 hours. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **18p** (153 mg, 0.267 mmol, 75%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.08 (1H, d, *J* 8.6), 7.91 (1H, d, *J* 7.8), 7.37 (1H, t, *J* 7.6), 7.17 (1H, d, *J* 7.8), 7.09 (1H, d, *J* 8.6), 6.85 (1H, t, *J* 7.5), 4.19 (2H, s), 3.87 (3H, s), 2.60 (3H, s), 0.51 (9H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 154.4, 149.4, 142.7, 140.4, 137.2, 133.7, 129.5, 129.4, 125.8, 122.4, 119.1 (q, J 321), 113.8, 98.3, 60.5, 55.7, 41.8, 2.4; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –71.5 (s, 3F); **IR (neat): ν_{max}/cm^{-1}** 2954, 2844, 1562, 1470, 1411, 1287, 1199, 1120, 1046, 923, 834, 727, 618; **HRMS (NSI)** [M+H]+ calcd. for $C_{19}H_{24}F_3INO_4SSi$ 574.0187, found: 574.0193.

5. Synthesis and characterization of phenanthridine derivatives

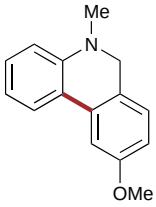
General procedure for the synthesis of dihydrophenanthridines:

Using Schlenk techniques under an argon atmosphere, *N*-tethered aryl amine aryne precursor **18** (1.0 equiv.), potassium fluoride (2.0 equiv.) and 18-crown-6 ether (2.0 equiv.) were dissolved in degassed DME [0.01 M] and the mixture was heated to 90 °C for 16 hours. The solvent was removed *in vacuo* and the resulting residue purified by silica gel flash chromatography, under a nitrogen atmosphere, to afford the target compound.

General procedure for the synthesis of phenanthridinones:

N-Tethered aryl amine aryne precursor **18** (1.0 equiv.), potassium fluoride (2.0 equiv.) and 18-crown-6 ether (2.0 equiv.) were dissolved in DME [0.01 M]. Air was bubbled through the reaction mixture, which was then heated to 90 °C for 16 hours under an atmosphere of air. The solvent was removed *in vacuo* and the resulting residue purified by silica gel flash chromatography to afford the target compound.

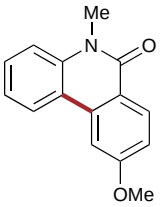
9-Methoxy-5-methyl-5,6-dihydrophenanthridine, 19a



6-Methoxy-3-((methyl(phenyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (72.5 mg, 0.162 mmol), potassium fluoride (18.8 mg, 0.324 mmol) and 18-crown-6 ether (86.5 mg, 0.324 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **19a** (30.0 mg, 0.133 mmol, 82%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.70 (dd, *J* 7.7 1.3, 1H), 7.27 (d, *J* 2.6, 1H), 7.26 (td, *J* 8.1 1.5, 1H), 7.07 (d, *J* 8.3, 1H), 6.89 (td, *J* 7.6 0.8, 1H), 6.81 (dd, *J* 8.3 2.5, 1H), 6.77 (d, *J* 8.1, 1H), 4.15 (s, 2H), 3.87 (s, 3H), 2.93 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 159.4, 147.4, 133.3, 129.4, 126.7, 125.9, 123.7, 123.4, 118.6, 112.9, 112.5, 107.9, 55.5, 54.6, 38.7; **IR (neat): ν_{max}/cm^{-1}** 2954, 2794, 1604, 1499, 1423, 1287, 1206, 1094, 1038, 906, 811, 726, 624; **HRMS (NSI)** [M+H]+ calcd. for $C_{15}H_{16}NO$ 226.2981, found: 226.2964.

9-Methoxy-5-methylphenanthridin-6(5H)-one, 20a

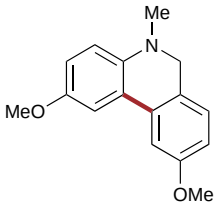


6-Methoxy-3-((methyl(phenyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (100 mg, 0.224 mmol), potassium fluoride (26.0 mg, 0.447 mmol) and 18-crown-6 ether (118

mg, 0.447 mmol) were subjected to the general procedure for the synthesis of phenanthridinones. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **20a** (42.2 mg, 0.177 mmol, 79%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.50 (1H, d, *J* 8.9), 8.23 (1H, d, *J* 8.0), 7.66 (1H, d, *J* 2.4), 7.59-7.55 (1H, m), 7.42 (1H, d, *J* 8.3), 7.34-7.31 (1H, m), 7.17 (1H, dd, *J* 8.9, 2.4), 4.01 (3H, s), 3.81 (3H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 162.6, 161.1, 138.1, 135.1, 130.8, 129.4, 122.9, 121.9, 119.1, 118.8, 115.5, 114.8, 104.1, 55.2, 29.4; **IR (neat): ν_{max}/cm^{-1}** 3009, 2970, 2948, 1739, 1606, 1501, 1443, 1217; **HRMS (NSI)** [M+H]+ calcd. for $C_{15}H_{14}NO_2$ 240.1019, found 240.1017.

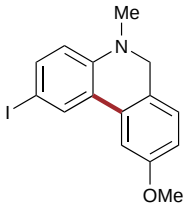
2,9-Dimethoxy-5-methyl-5,6-dihydrophenanthridine, 19b



6-Methoxy-3-(((4-methoxyphenyl)(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18b** (42.6 mg, 0.080 mmol), potassium fluoride (9.4 mg, 0.162 mmol) and 18-crown-6 ether (42.8 mg, 0.162 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **19b** (19.9 mg, 0.078 mmol, 98%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27 (d, *J* 2.9, 1H), 7.21 (d, *J* 2.5, 1H), 7.08 (d, *J* 8.3, 1H), 6.84 (dd, *J* 8.8 2.9, 1H), 6.80 (dd, *J* 8.3 2.5, 1H), 6.70 (d, *J* 8.8, 1H), 4.03 (s, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.87 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 160.4, 152.3, 136.7, 135.6, 128.8, 126.9, 122.1, 120.6, 119.9, 118.8, 106.1, 104.6, 57.3, 57.0, 56.0, 44.7; **IR (neat): ν_{max}/cm^{-1}** 3374, 2934, 2835, 2299, 2190, 1615, 1509, 1423, 1251, 1027, 924, 812, 726; **HRMS (ESI)** [M+H]+ calcd. for $C_{16}H_{18}NO_2$ 256.1332, found: 256.1365.

2-Iodo-9-methoxy-5-methyl-5,6-dihydrophenanthridine, 19c

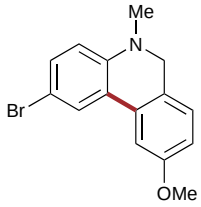


3-(((4-Iodophenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18c** (31.8 mg, 0.055 mmol), potassium fluoride (6.4 mg, 0.111 mmol) and 18-crown-6 ether (29.3 mg, 0.111 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **19c** (13.0 mg, 0.037 mmol, 67%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89 (d, *J* 2.1, 1H), 7.47 (dd, *J* 8.6 2.1, 1H), 7.15 (d, *J* 2.5, 1H), 7.04 (d, *J* 8.3, 1H), 6.81 (dd, *J* 8.3 2.5, 1H), 6.49 (d, *J* 8.6, 1H) 4.14 (s, 2H), 3.87 (s, 3H), 2.87 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.6, 146.9, 137.7, 132.1, 131.9, 126.9, 125.8, 125.6, 114.7, 113.8, 107.7, 80.3, 55.6, 54.4, 38.6; **IR (neat): ν_{max}/cm^{-1}** 2934, 2248, 1859, 1736, 1610, 1495, 1398, 1331, 1285, 1205, 1104, 1039, 905, 802, 728, 649; **HRMS (NSI)** [M+H]+ calcd. for $C_{15}H_{15}INO_2$ 352.1902, found: 352.0198

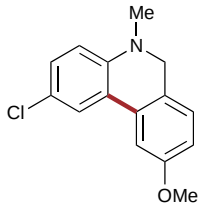
2-Bromo-9-methoxy-5-methyl-5,6-dihydrophenanthridine, 19d



3-(((4-Bromophenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18d** (55.0 mg, 0.104 mmol), potassium fluoride (12.1 mg, 0.209 mmol) and 18-crown-6 ether (55.2 mg, 0.209 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **19d** (16.5 mg, 0.054 mmol, 52%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.73 (d, *J* 2.3, 1H), 7.29 (dd, *J* 8.7 2.3, 1H), 7.16 (d, *J* 2.5, 1H), 7.05 (d, *J* 8.3, 1H), 6.82 (dd, *J* 8.3 2.5, 1H), 6.60 (d, *J* 8.7, 1H), 4.13 (s, 2H), 3.87 (s, 3H), 2.89 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 159.6, 146.3, 132.2, 132.1, 131.7, 126.9, 126.4, 125.7, 125.4, 114.3, 114.0, 107.7, 55.6, 54.4, 38.8 pm; **IR (neat): ν_{max}/cm^{-1}** 3375, 2925, 1732, 1610, 1494, 1399, 1254, 1107, 1038, 874, 805, 724, 608; **HRMS (ESI)** [M+H]+ calcd. for $C_{15}H_{15}BrNO$ 304.0332, found: 304.0341.

2-Chloro-9-methoxy-5-methyl-5,6-dihydrophenanthridine, 19e

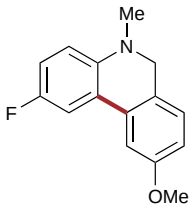


3-(((4-Chlorophenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18e** (52.0 mg, 0.108 mmol), potassium fluoride (12.5 mg, 0.216 mmol) and 18-crown-6 ether (57.0 mg, 0.216 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **19e** (13.4 mg, 0.052 mmol, 48%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.59 (d, *J* 2.4, 1H), 7.16 (d, *J* 2.5, 1H), 7.16 (dd, *J* 8.7 2.5, 1H), 7.05 (d, *J* 8.3, 1H), 6.81 (dd, *J* 8.3 2.5, 1H), 6.64 (d, *J* 8.7), 4.12 (s, 2H), 3.86 (s, 3H), 2.89 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 159.6, 146.0, 132.2, 128.8, 126.9, 125.9, 124.9, 123.7, 123.5, 113.9, 113.7, 107.8, 55.6, 54.5, 38.8; **IR (neat): ν_{max}/cm^{-1}** 3411, 2934, 2835, 1738, 1611, 1498, 1420,

1288, 1206, 1118, 1041, 869, 804, 620; **HRMS (ESI)** [M+H]+ calcd. for $C_{15}H_{15}ClNO$ 260.0837, found: 260.0857.

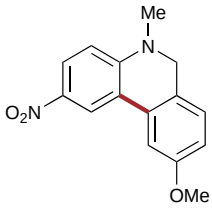
2-Fluoro-9-methoxy-5-methyl-5,6-dihydrophenanthridine, 19f



3-(((4-Fluorophenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18f** (40.1 mg, 0.086 mmol), potassium fluoride (10.0 mg, 0.172 mmol) and 18-crown-6 ether (45.5 mg, 0.172 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **19f** (14.6 mg, 0.060 mmol, 70%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37 (dd, *J* 9.7 2.9, 1H), 7.16 (d, *J* 2.5, 1H), 7.08 (d, *J* 8.3, 1H), 6.94 (ddd, *J* 8.9 8.3 2.9, 1H), 6.82 (dd, *J* 8.3 2.5, 1H), 6.66 (dd, *J* 8.9 4.7, 1H) , 4.08 (s, 2H), 3.86 (s, 3H), 2.89 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 159.6, 157.7, 143.9, 132.6, 126.9, 126.4, 125.0 (d, *J* 8.8), 115.4 (d, *J* 22.0), 113.8 (d, *J* 7.6), 113.7, 110.4 (d, *J* 23.4), 108.1, 55.6, 54.8, 39.2; **^{19}F NMR (377 MHz, $CDCl_3$):** δ_F –78.4 (s, 1F); **IR (neat): ν_{max}/cm^{-1}** 3387, 2954, 2791, 2175, 1611, 1509, 1424, 1275, 1230, 1119, 1039, 938, 864, 809, 688, 640; **HRMS (ESI)** [M+H]+ calcd. for $C_{15}H_{15}FNO$ 244.1132, found: 244.1155.

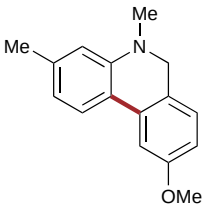
9-Methoxy-5-methyl-2-nitro-5,6-dihydrophenanthridine, 19g



6-Methoxy-3-((methyl(4-nitrophenyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18g** (70.8 mg, 0.144 mmol), potassium fluoride (16.7 mg, 0.287 mmol) and 18-crown-6 ether (76.0 mg, 0.287 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **19g** (13.3 mg, 0.049 mmol, 34%) as an amorphous orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.51 (d, *J* 2,5. 1H), 8.08 (dd, *J* 9.2 2.6, 1H), 7.26 (d, *J* 2.6, 1H), 7.03 (d, *J* 8.3, 1H), 6.86 (dd, *J* 8.4 2.6, 1H), 6.62 (d, *J* 9.2, 1H), 4.55 (s, 2H), 3.88 (s, 3H), 3.05 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 159.8, 151.6, 130.9, 127.0, 125.9, 125.1, 123.7, 121.4, 119.5, 115.0, 111.0, 107.4, 55.7, 54.1, 38.8; **IR (neat): ν_{max}/cm^{-1}** 3290, 2931, 1617, 1518, 1489, 1412, 1308, 1118, 1041, 906, 825, 726, 620;

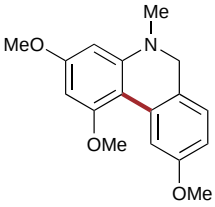
9-Methoxy-3,5-dimethyl-5,6-dihydrophenanthridine, 19h



6-Methoxy-3-((methyl(*m*-tolyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18h** (51.0 mg, 0.110 mmol), potassium fluoride (12.8 mg, 0.221 mmol) and 18-crown-6 ether (58.4 mg, 0.221 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **19h** (21.9 mg, 0.092 mmol, 83%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.30 (d, *J* 2.5, 1H), 7.17 (t, *J* 7.8, 1H), 7.15 (d, *J* 8.2, 1H), 6.82 (dd, *J* 8.2 2.5, 1H), 6.81 (d, *J* 8.0, 1H), 6.70 (d, *J* 8.1, 1H), 3.91 (s, 2H), 3.85 (s, 3H), 2.93 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 158.5, 149.6, 135.2, 133.5, 128.8, 128.3, 126.2, 124.1, 122.9, 113.5, 111.7, 110.6, 55.6, 55.3, 39.5, 23.3; **IR (neat): ν_{max}/cm^{-1}** 2992, 1709, 1611, 1499, 1360, 1286, 1120, 1042, 923, 834, 756, 614; **HRMS (ESI)** [M+H]+ calcd. for $C_{16}H_{18}NO$ 240.1383, found: 240.1478.

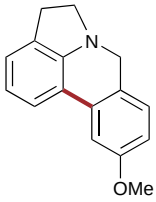
1,3,9-Trimethoxy-5-methyl-5,6-dihydrophenanthridine, 19j



3-(((3,5-Dimethoxyphenyl)(methyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18j** (67.8 mg, 0.134 mmol), potassium fluoride (15.5 mg, 0.267 mmol) and 18-crown-6 ether (70.6 mg, 0.267 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 9:1) afforded the title compound **19j** (20.8 mg, 0.073 mmol, 55%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.90 (d, J 2.6, 1H), 7.04 (d, J 8.2, 1H), 6.72 (dd, J 8.2 2.6, 1H), 6.12 (d, J 2.3, 1H), 6.02 (d, J 2.3, 1H), 3.98 (s, 2H), 3.91 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 2.92 (s, 3H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 160.9, 159.2, 158.8, 150.8, 132.0, 125.7, 125.6, 112.4, 111.1, 106.3, 91.5, 89.9, 55.5, 55.4, 55.3, 55.2, 39.4; **IR (neat): ν_{max}/cm^{-1}** 3380, 2937, 2835, 1602, 1464, 1211, 1155, 1073, 948, 864, 808, 706, 637; **HRMS (ESI)** [M+H]+ calcd. for $C_{17}H_{20}NO_3$ 286.1438, found: 286.1482.

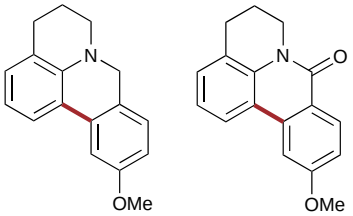
10-Methoxy-4,5-dihydro-7H-pyrrolo[3,2,1-de]phenanthridine, 19k



10-Methoxy-8-(trimethylsilyl)-4,5-dihydro-7H-pyrrolo[3,2,1-de]phenanthridin-9-yl trifluoromethanesulfonate **18k** (70.0 mg, 0.153 mmol), potassium fluoride (17.7 mg, 0.305 mmol) and 18-crown-6 ether (80.5 mg, 0.305 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **19k** (25.3 mg, 0.107 mmol, 70%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.77 (d, *J* 7.7, 1H), 7.22 (d, *J* 2.6, 1H), 7.06 (d, *J* 8.5, 1H), 7.04 (dd, *J* 7.5 0.8, 1H), 6.77 (t, *J* 7.5, 1H), 6.75 (dd, *J* 8.5 2.6, 1H), 4.11 (s, 2H), 3.86 (s, 3H), 3.34 (t, *J* 7.9, 2H), 3.03 (t, *J* 7.9, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 159.6, 136.1, 131.3, 128.1, 126.8, 124.4, 120.9, 120.7, 120.5, 120.3, 112.8, 107.8, 55.6, 55.5, 53.1, 29.2; **IR (neat): ν_{max}/cm^{-1}** 3377, 3055, 2929, 2833, 2751, 1605, 1474, 1337, 1221, 1033, 767, 607; **HRMS (ESI)** [M+H]+ calcd. for $C_{16}H_{16}NO$ 238.1226, found: 238.129.

11-Methoxy-5,6-dihydro-4*H*, 8*H*-pyrido[3,2,1-de]phenanthridine, 19l, & 11-methoxy-5,6-dihydro-4*H*,8*H*-pyrido[3,2,1-de]phenanthridin-8-one, 20l



3-((3,4-Dihydroquinolin-1(2H)-yl)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18l** (198 mg, 0.419 mmol), potassium fluoride (17.7 mg, 0.305 mmol) and 18-crown-6 ether (80.5 mg, 0.305 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. ^{1}H NMR spectroscopic analysis of the crude reaction mixture containing an internal standard showed 11-methoxy-5,6-dihydro-4*H*, 8*H*-pyrido[3,2,1-de]phenanthridine in 76% yield. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded a mixture of **19l** (36.8 mg, 0.147 mmol, 35%) and 11-methoxy-5,6-dihydro-4H,8H-pyrido[3,2,1-de]phenanthridin-8-one **20l** (45.6 mg, 0.172 mmol, 41%) as colourless oils.

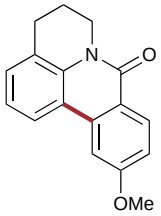
11-Methoxy-5,6-dihydro-4H,8H-pyrido[3,2,1- de]phenanthridine, 19l

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.50 (1H, d, *J* 7.5), 7.21-7.19 (1H, m), 7.05 (1H, d, *J* 8.3), 6.96-6.94 (1H, m), 6.79-6.72 (2H, m), 4.06 (2H, s), 3.85 (3H, s), 3.19-3.17 (2H, m), 2.83-2.80 (2H, m), 2.14-2.10 (2H, m); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 159.1, 143.4, 133.2, 129.4, 129.1, 126.4, 125.1, 123.4, 122.1, 117.9, 112.5, 107.8, 55.2, 53.5, 50.2, 27.3, 21.5; **IR (neat): ν_{max}/cm^{-1}** 3014, 2970, 2949, 1586, 1442, 1232; **LC-MS (ESI)** [M+H]+ 252.7, note: sample for HRMS oxidised *in situ*.

11-Methoxy-5,6-dihydro-4H,8H-pyrido[3,2,1- de]phenanthridin-8-one, 20l

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.47 (1H, d, *J* 8.9), 8.05 (1H, br d, *J* 7.3), 7.63-7.62 (1H, d, *J* 2.4), 7.30-7.28 (1H, m), 7.21-7.17 (1H, m), 7.14 (1H, dd, *J* 8.9 & 2.4), 4.31-4.28 (2H, m), 3.99 (3H, s), 3.01 (2H, t, *J* 6.2), 2.14 (2H, quint, *J* 6.2); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 162.7, 160.8, 135.4, 134.9, 130.6, 129.4, 125.5, 121.5, 121.1, 119.1, 118.8, 115.7, 104.3, 55.3, 42.4, 28.1, 20.6; **IR (neat): ν_{max}/cm^{-1}** 3014m, 2970, 2949, 1719, 1586, 1442, 1232; **HRMS (NSI)** [M+H]+ calcd. for $C_{17}H_{16}NO_2$ 266.1176, found 266.1176.

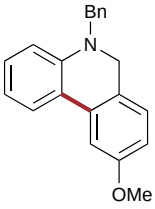
11-Methoxy-5,6-dihydro-4*H*,8*H*-pyrido[3,2,1-de]phenanthridin-8-one, 20l



3-((3,4-Dihydroquinolin-1(2H)-yl)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18l** (100 mg, 0.211 mmol), potassium fluoride (25.5 mg, 0.423 mmol) and 18-crown-6 ether (112 mg, 0.423 mmol) were subjected to the general procedure for the synthesis of phenanthridinones. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **20l** (44.3 mg, 0.167 mmol, 79%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.47 (1H, d, *J* 8.9), 8.05 (1H, br d, *J* 7.3), 7.63-7.62 (1H, d, *J* 2.4), 7.30-7.28 (1H, m), 7.21-7.17 (1H, m), 7.14 (1H, dd, *J* 8.9 & 2.4), 4.31-4.28 (2H, m), 3.99 (3H, s), 3.01 (2H, t, *J* 6.2), 2.14 (2H, quint, *J* 6.2); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 162.7, 160.8, 135.4, 134.9, 130.6, 129.4, 125.5, 121.5, 121.1, 119.1, 118.8, 115.7, 104.3, 55.3, 42.4, 28.1, 20.6; **IR (neat): ν_{max}/cm^{-1}** 3014m, 2970, 2949, 1719, 1586, 1442, 1232; **HRMS (NSI)** [M+H]+ calcd. for $C_{17}H_{16}NO_2$ 266.1176, found 266.1176.

5-Benzyl-9-methoxy-5,6-dihydrophenanthridine, 19m

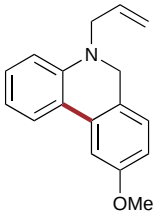


3-((Benyl(phenyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18m** (50.0 mg, 0.0955 mmol), potassium fluoride (16.6 mg, 0.286 mmol) and 18-crown-6 ether (70.5 mg, 0.286 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **19m** (24.4 mg, 0.0810 mmol, 85%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 (1H, d, *J* 7.8, 1.3), 7.31-7.25 (2H, m), 7.23 (1H, s), 7.16 (3H, td, *J* 10.0, 2.2), 7.10-7.03 (1H, m), 6.88 (1H, d, *J* 8.1), 6.75 (1H, td, *J* 7.3, 1.0), 6.66 (2H, td, *J* 7.9, 2.5), 4.40 (2H, s), 4.14 (2H, s), 3.37 (3H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C; 159.5, 146.6, 138.0, 133.4, 129.4, 128.8, 127.7, 127.2, 126.7, 125.8, 123.9, 123.2, 118.5, 113.2, 112.9, 108.0, 55.6, 54.8,

52.1; **IR (neat): ν_{max}/cm^{-1}** 2925, 1645, 1612, 1498, 1452, 1359, 1309, 1225,1177, 1036, 908, 732; **HRMS (ESI)** [M+H]+ calcd. for $C_{21}H_{20}NO$ 302.1539, found: 302.1545.

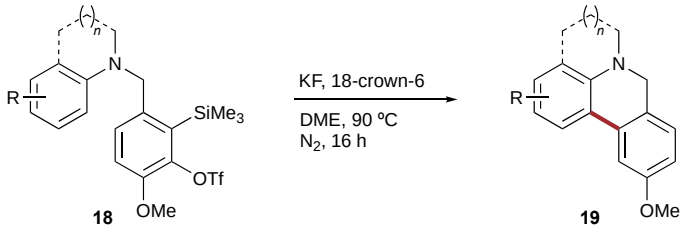
5-Allyl-9-methoxy-5,6-dihydrophenanthridine, 19n



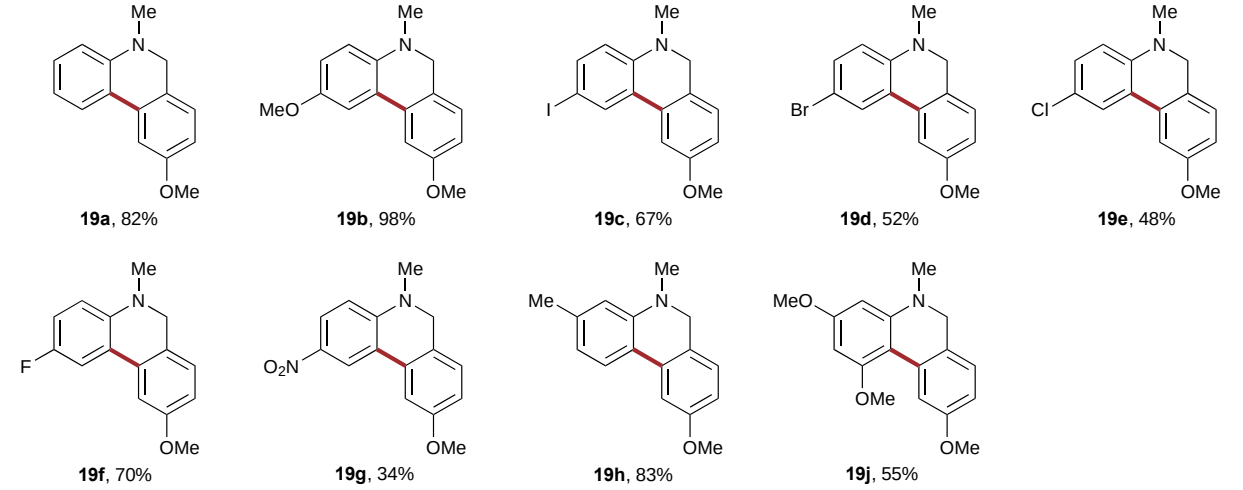
3-((Allyl(phenyl)amino)methyl)-6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18n** (109 mg, 0.230 mmol), potassium fluoride (40.1 mg, 0.691 mmol) and 18-crown-6 ether (0.170 g, 0.691 mmol) were subjected to the general procedure for the synthesis of dihydrophenanthridines. Silica gel flash column chromatography (1% Et_3N in *n*-hexane:ethyl acetate 4:1) afforded the title compound **19n** (39.9 mg, 0.159 mmol, 69%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.70 (1H, dd, *J* 7.7, 1.5), 7.25 (1H, d, *J* 2.5), 7.23-7.17 (1H, m), 7.07-7.02 (1H, m), 6.87-6.82 (1H, td, *J* 7.4, 1.1), 6.81-6.77 (2H, m), 5.97 (1H, ddt, *J* 16.1, 10.3, 5.8), 5.37-5.24 (2H, m), 4.20 (2H, s), 3.97-3.91 (2H, dt, *J* 5.7, 2.8), 3.86 (3H, s); **^{13}C NMR (101 MHz, $CDCl_3$):** δ_C 159.4, 146.3, 133.4, 129.3, 126.7, 125.9, 123.9, 123.3, 118.3, 118.1, 113.1, 113.0, 108.0, 55.6, 53.6, 51.7; **IR (neat): ν_{max}/cm^{-1}** 2925 , 1642, 1612, 1500, 1453, 1311, 1225, 1180, 1036, 909, 842, 749; **HRMS (ESI)** [M+H]+ calcd. for $C_{17}H_{18}NO$ 252.1383, found: 252.1388.

6. Cyclisation: substrate scope



meta- & *para*-substitution

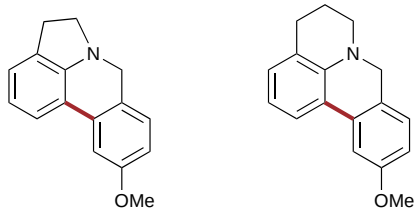


19a, 82% **19b**, 98% **19c**, 67% **19d**, 52% **19e**, 48%

19f, 70% **19g**, 34% **19h**, 83% **19j**, 55%

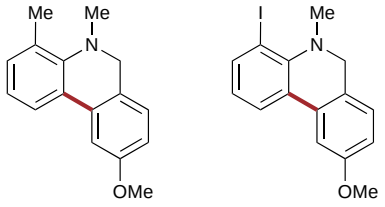
ortho-substitution

cyclic



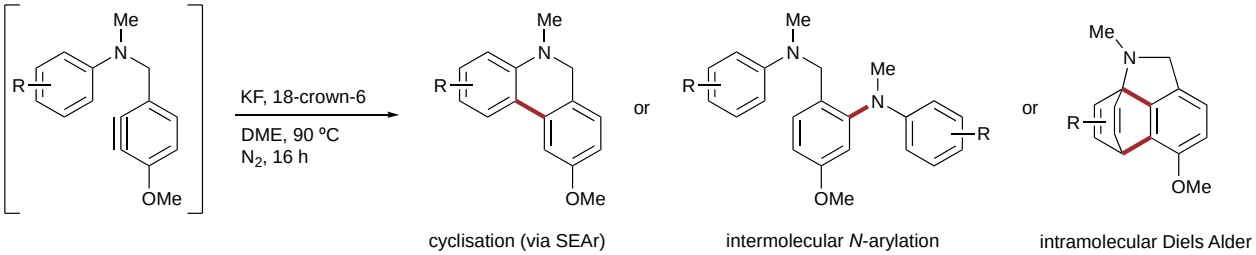
19k, 70% **19l**, 76%[a] **19o**, trace

acyclic



19i, trace **19p**, trace

Proposed: competing reaction modes



cyclisation (via SEAr) intermolecular *N*-arylation intramolecular Diels Alder

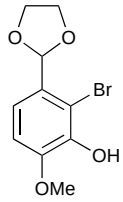
Table S1. Substrate scope and proposed competing modes of reactivity.

A range of *meta*- and *para*-substituted anilines **18** underwent the cyclisation to afford dihydrophenanthridines **19** in typically good to excellent yields. Both electron rich and electron poor substituents proved amenable to the transformation, with a drop in reactivity observed for the more electron deficient anilines, which is consistent with a proposed SEAr mechanism. The 3,5-dimethoxyaniline **18j** afforded the corresponding dihydrophenanthridine **19j** in a lower yield compared to the 4-methoxy aniline derivative **19b** (55% and 98% yields respectively). It is

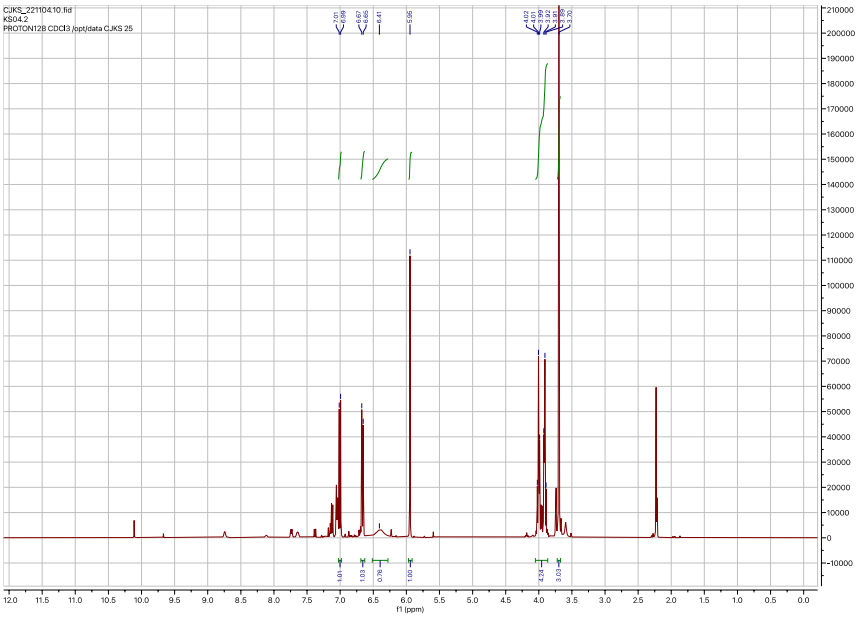
rationalised that the erosion in yield is due to increased steric hindrance experienced in **18j** (c.f. **18b**), despite the addition of a second electron donating group that would otherwise be expected to increase aniline nucleophilicity.

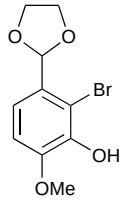
Steric hindrance plays a key role in substrates bearing *ortho*-substituents (2-methyl and 2-iodoaniline derivatives **18i** and **18p**), which do not undergo the SEAr. It is proposed that significant 1,5-strain occurs in the associated transition states required for cyclisation; instead favouring a mixture of an *N*-arylation by-product and an intramolecular dearomative aryne Diels-Alder cycloaddition. Interestingly, the more conformationally rigid indoline (**18k**) and tetrahydroquinoline (**18l**) precursors underwent efficient SEAr to furnish the corresponding tetracyclic products, **19k** and **19l**, respectively. Indole precursor **18o** did not undergo the desired cyclisation; with the C2/3 sites of the indole proposed to offer additional competing sites of reactivity.

7. NMR spectra

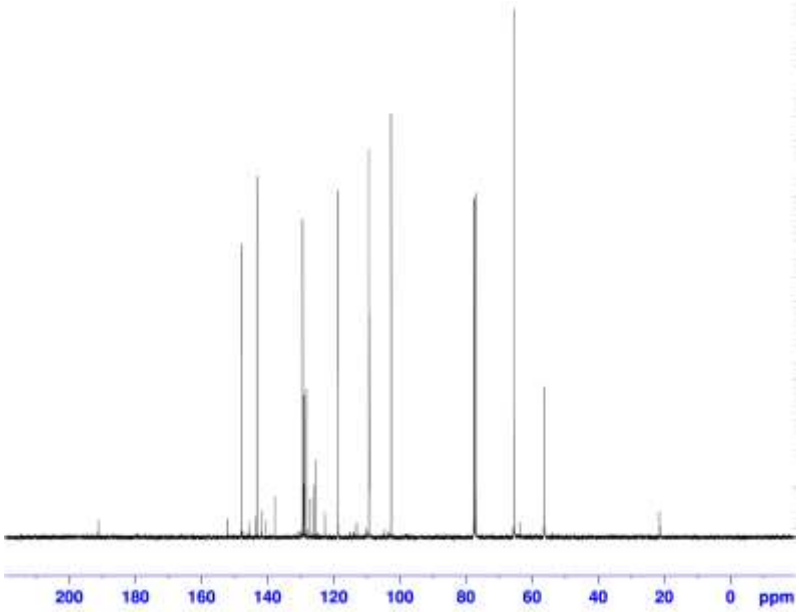


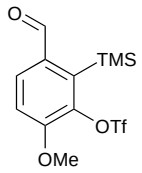
16 ^{1}H NMR (400 MHz, $CDCl_3$) note: acetal highly labile so some hydrolysis observed in NMR sample



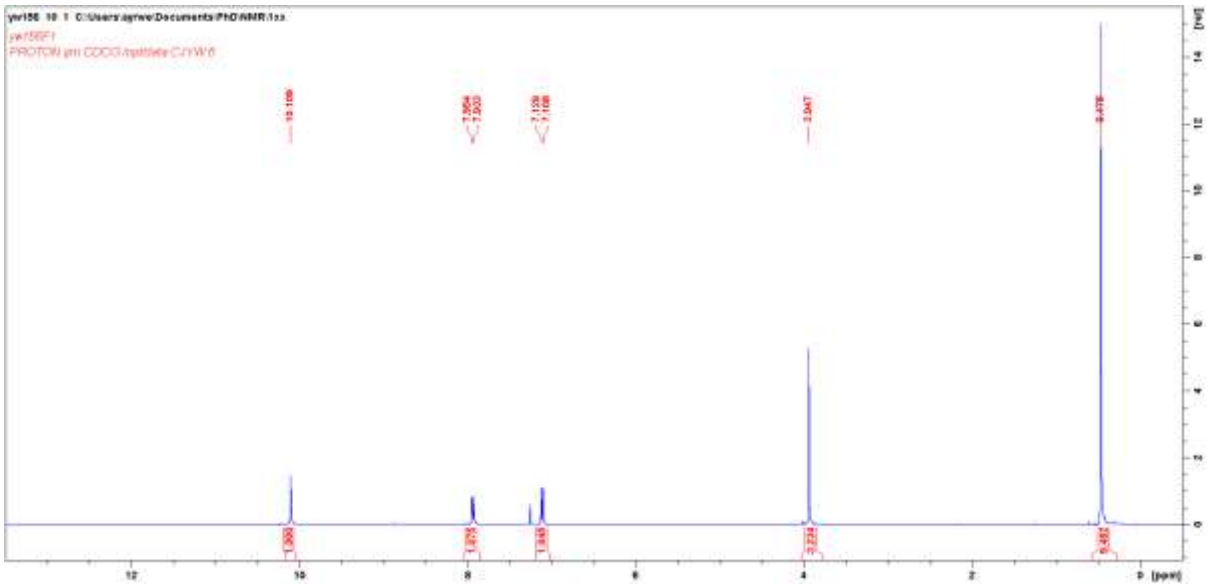


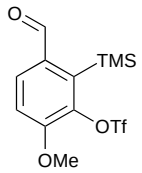
16 ^{13}C NMR (101 MHz, $CDCl_3$) note: acetal highly labile so some hydrolysis observed in NMR sample



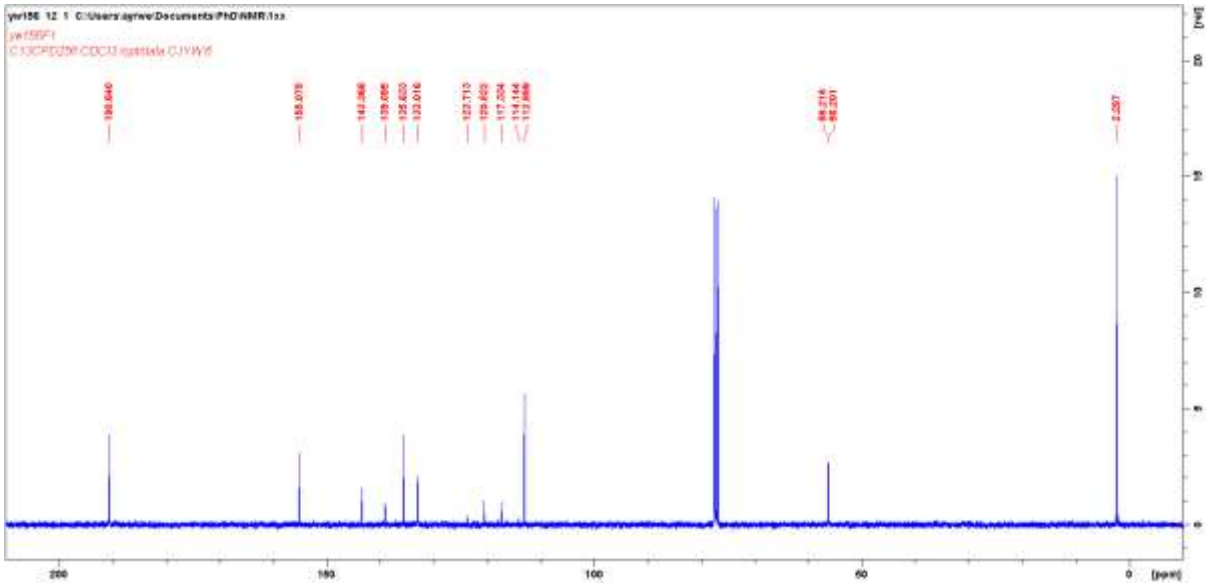


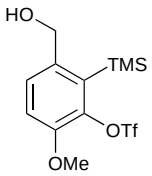
17 ^{1}H NMR (400 MHz, $CDCl_3$)



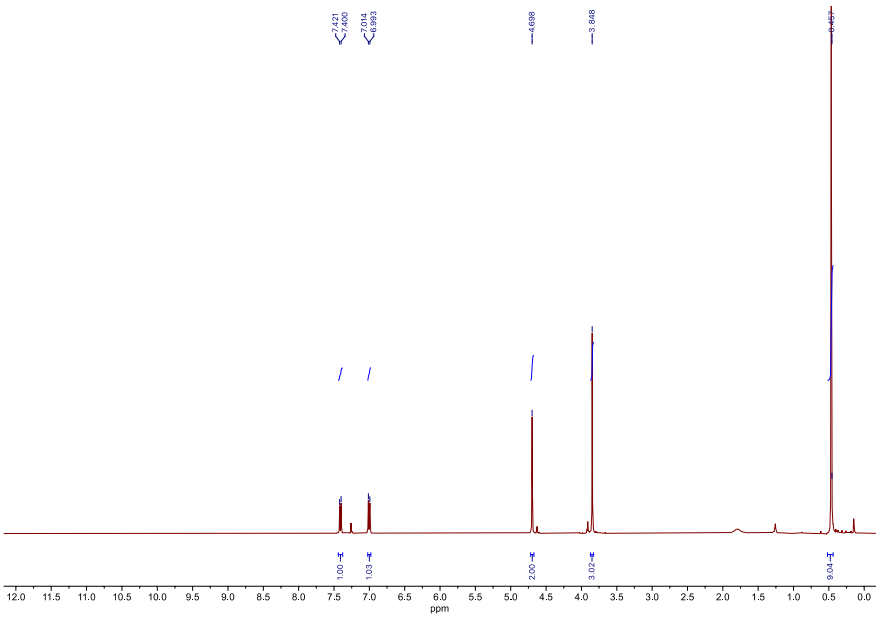


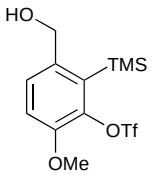
17 ^{13}C NMR (101 MHz, $CDCl_3$)



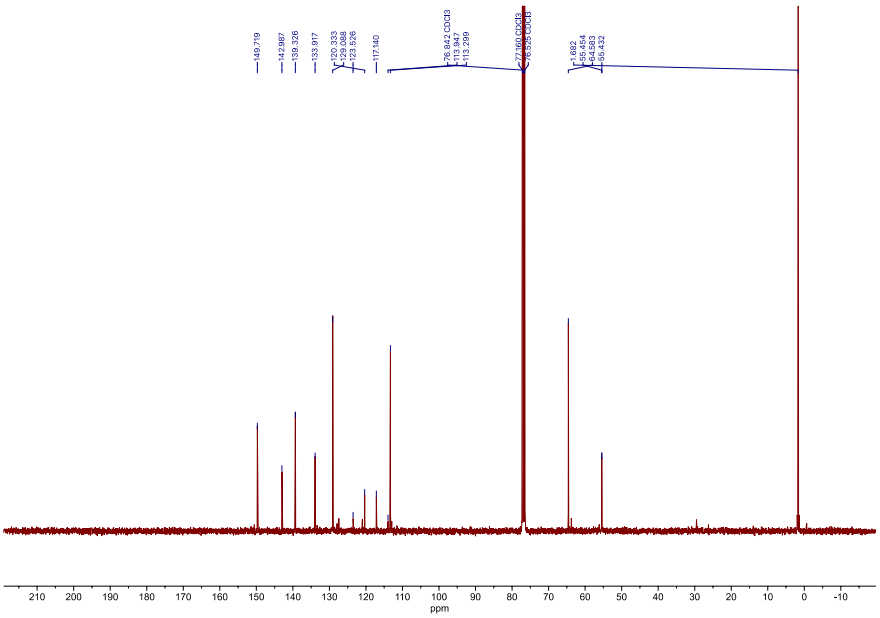


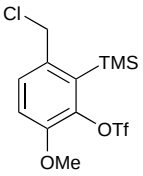
21 ^{1}H NMR (400 MHz, $CDCl_3$)



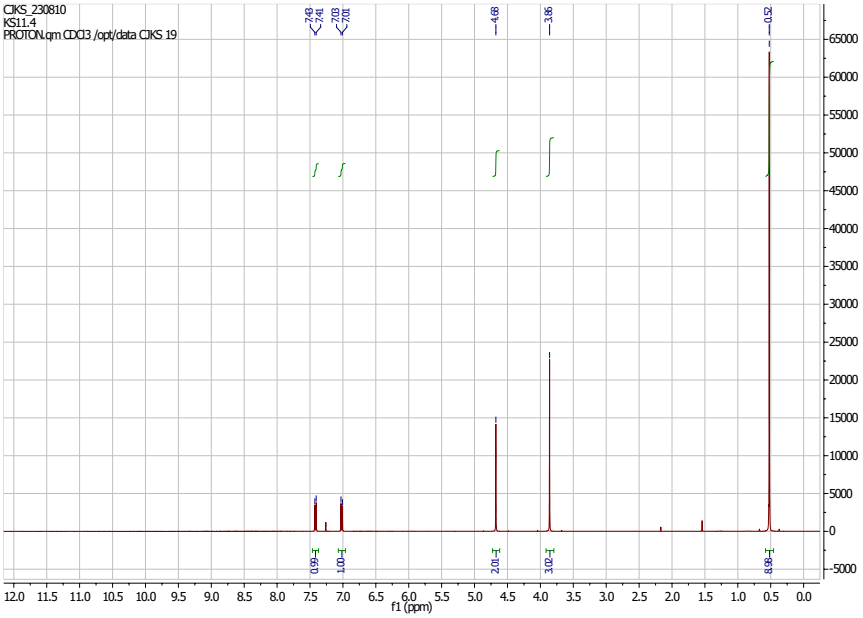


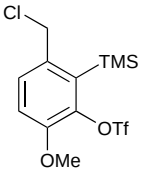
21 ^{13}C NMR (101 MHz, $CDCl_3$)



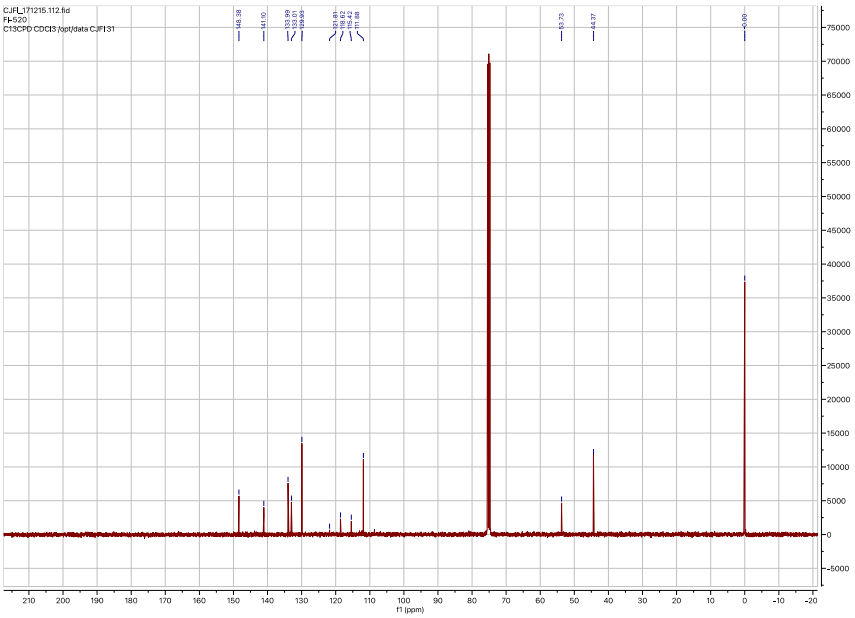


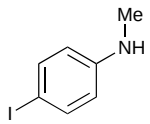
7b ^{1}H NMR (400 MHz, $CDCl_3$)



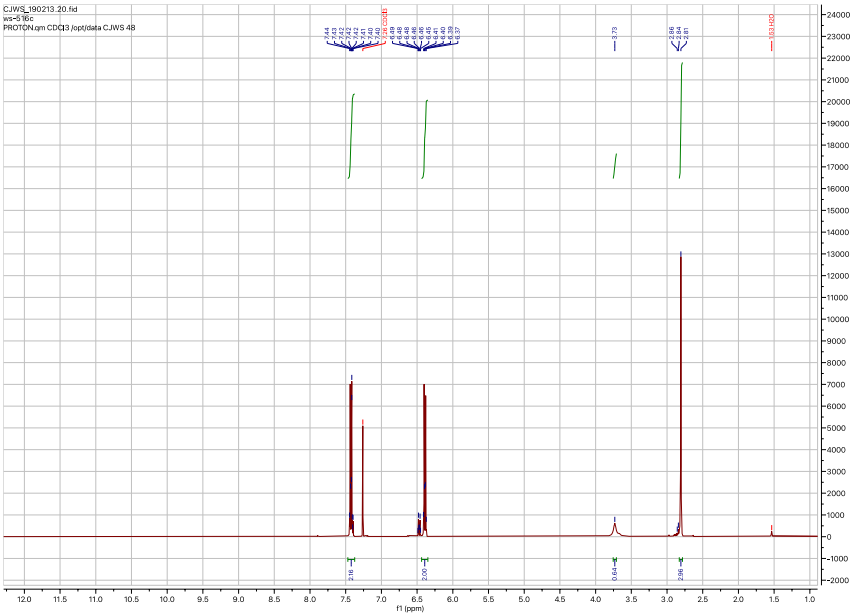


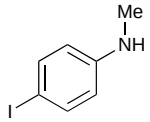
7b ^{13}C NMR (101 MHz, $CDCl_3$)



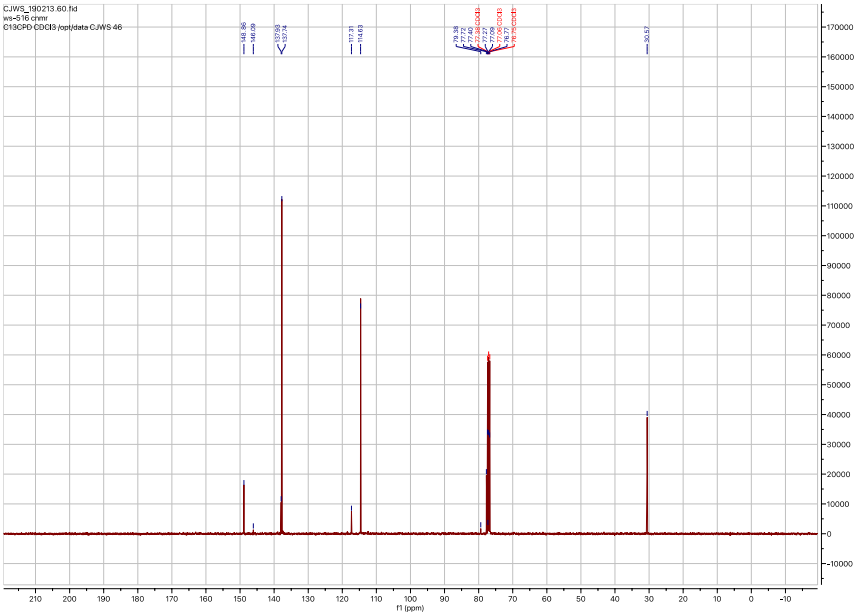


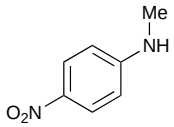
22 ^{1}H NMR (400 MHz, $CDCl_3$)



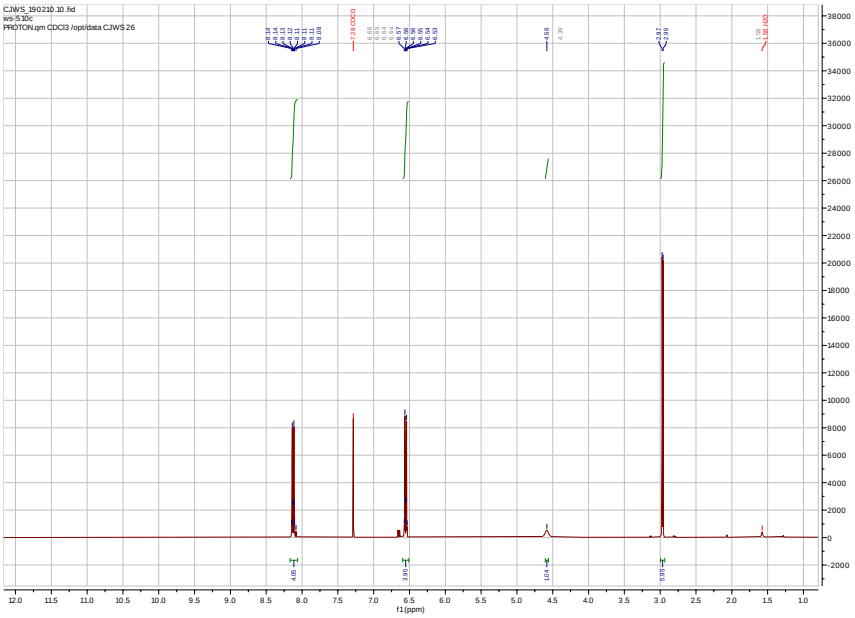


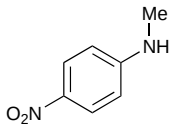
22 ^{13}C NMR (101 MHz, $CDCl_3$)



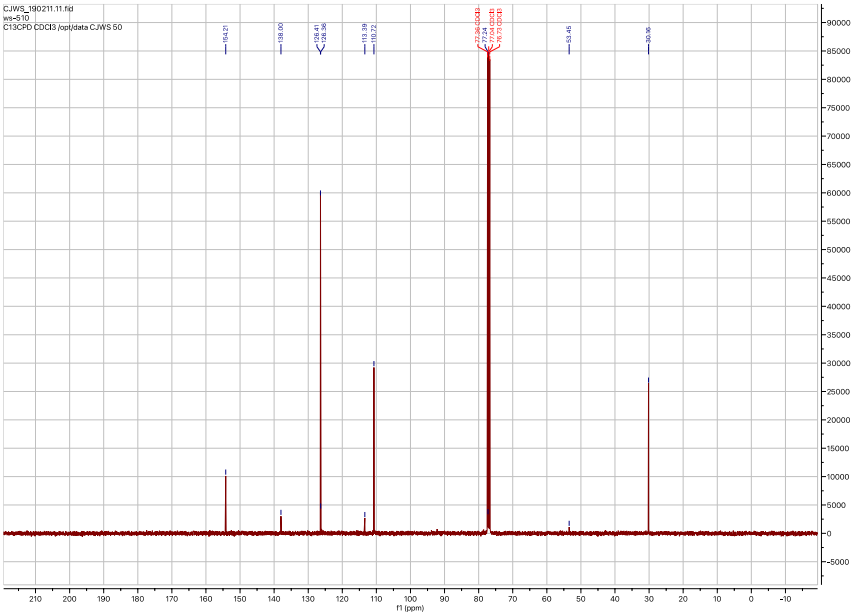


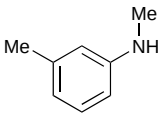
23 ^{1}H NMR (400 MHz, $CDCl_3$)



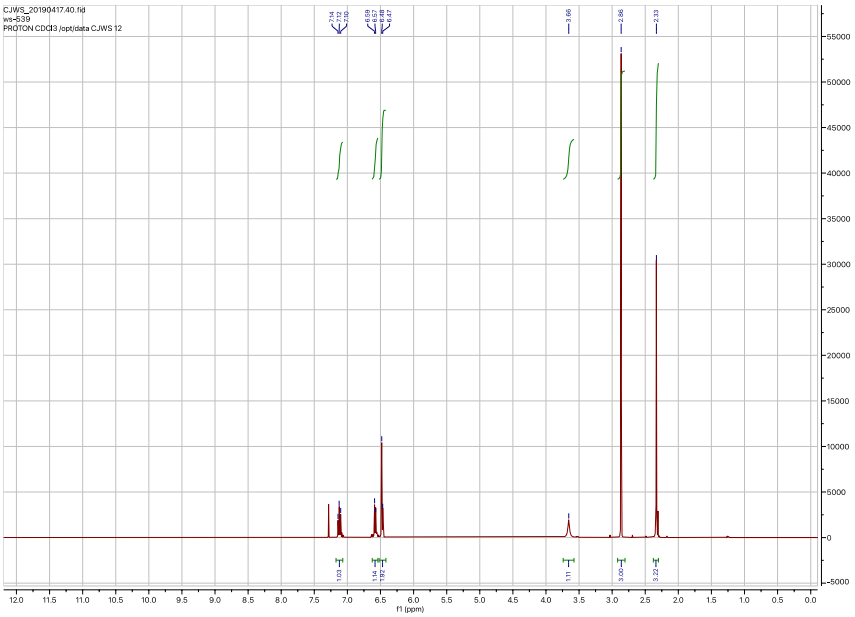


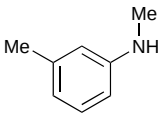
23 ^{13}C NMR (101 MHz, $CDCl_3$)



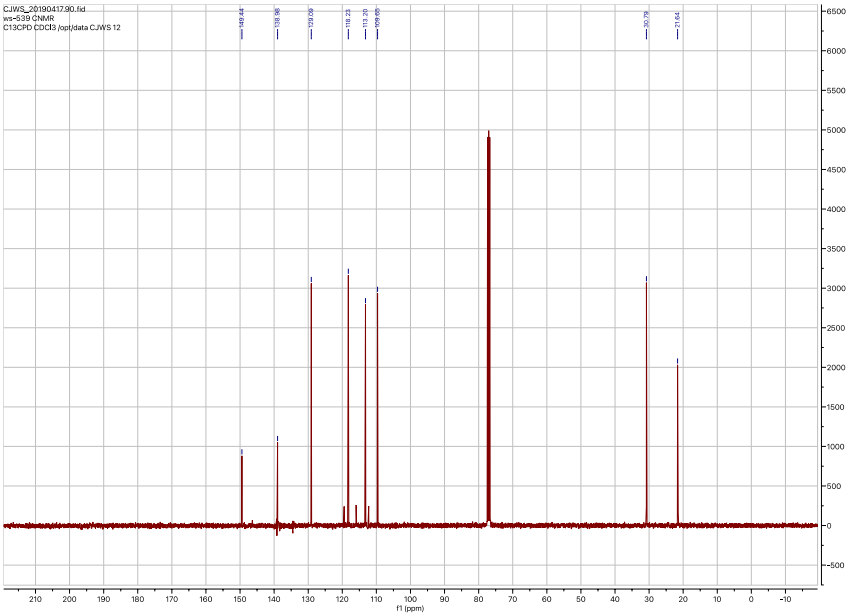


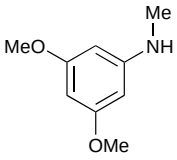
24 ^{1}H NMR (400 MHz, $CDCl_3$)



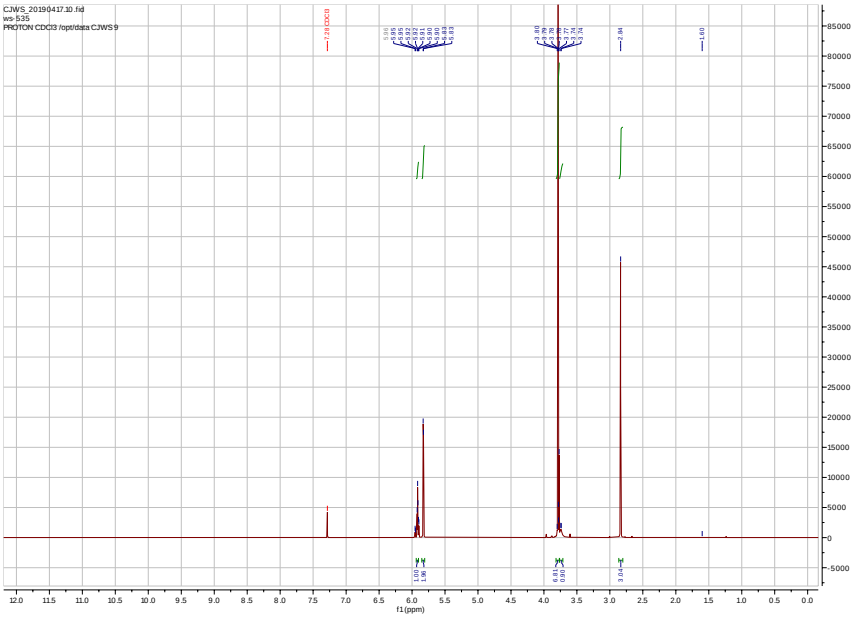


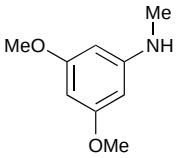
24 ^{13}C NMR (101 MHz, $CDCl_3$)



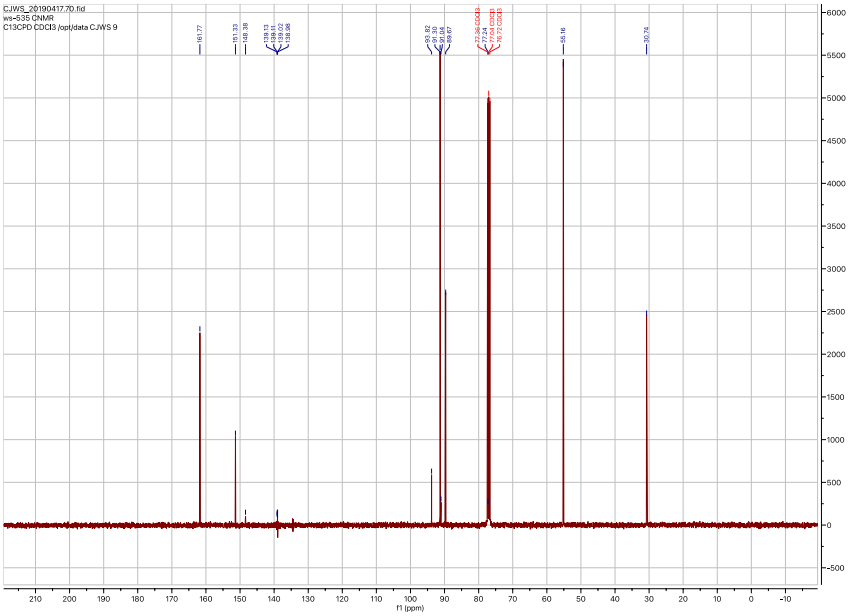


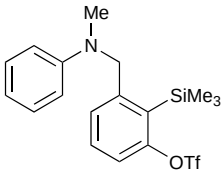
25 ^{1}H NMR (400 MHz, $CDCl_3$)



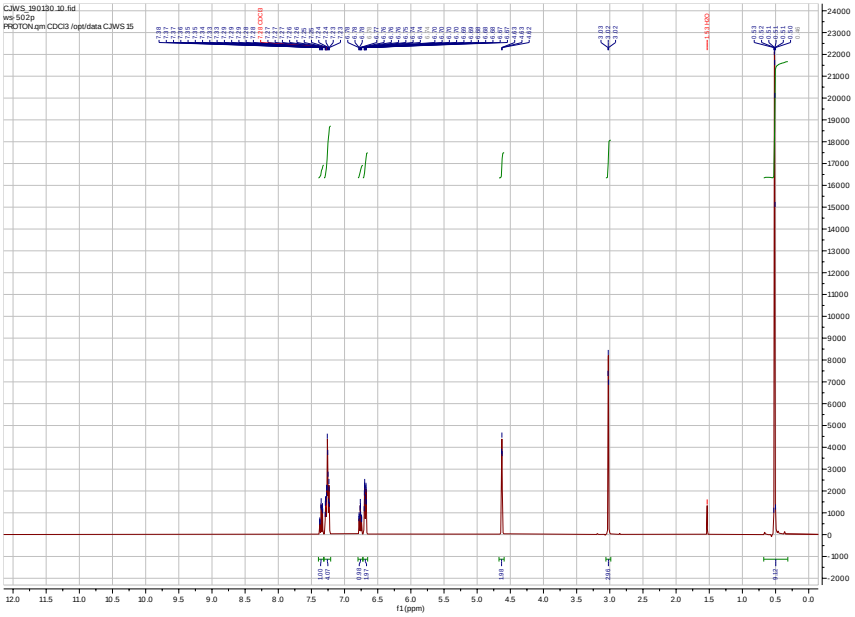


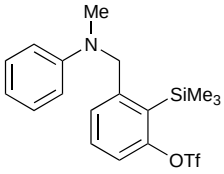
25 ^{13}C NMR (101 MHz, $CDCl_3$)



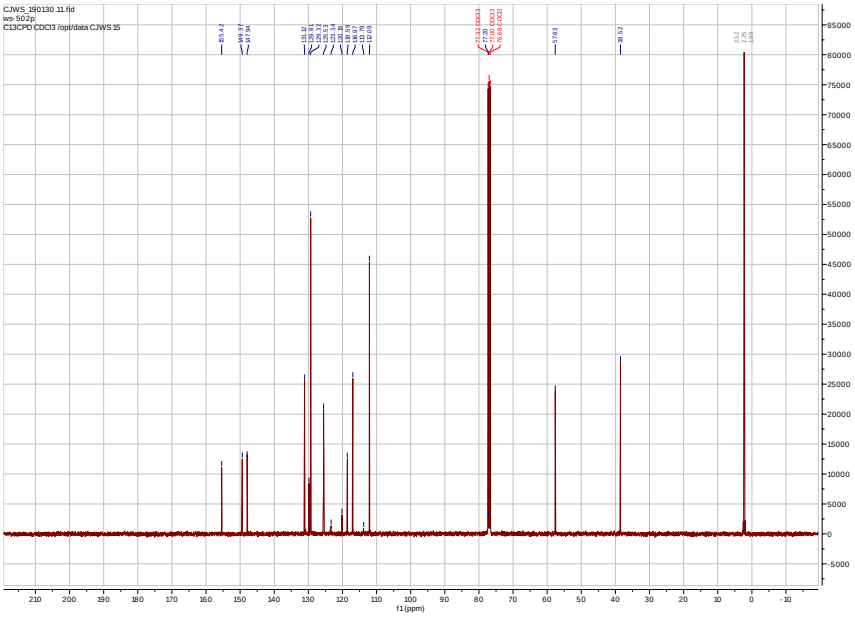


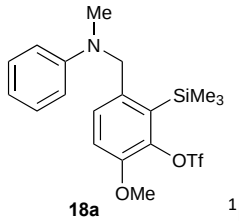
12 ^{1}H NMR (400 MHz, $CDCl_3$)





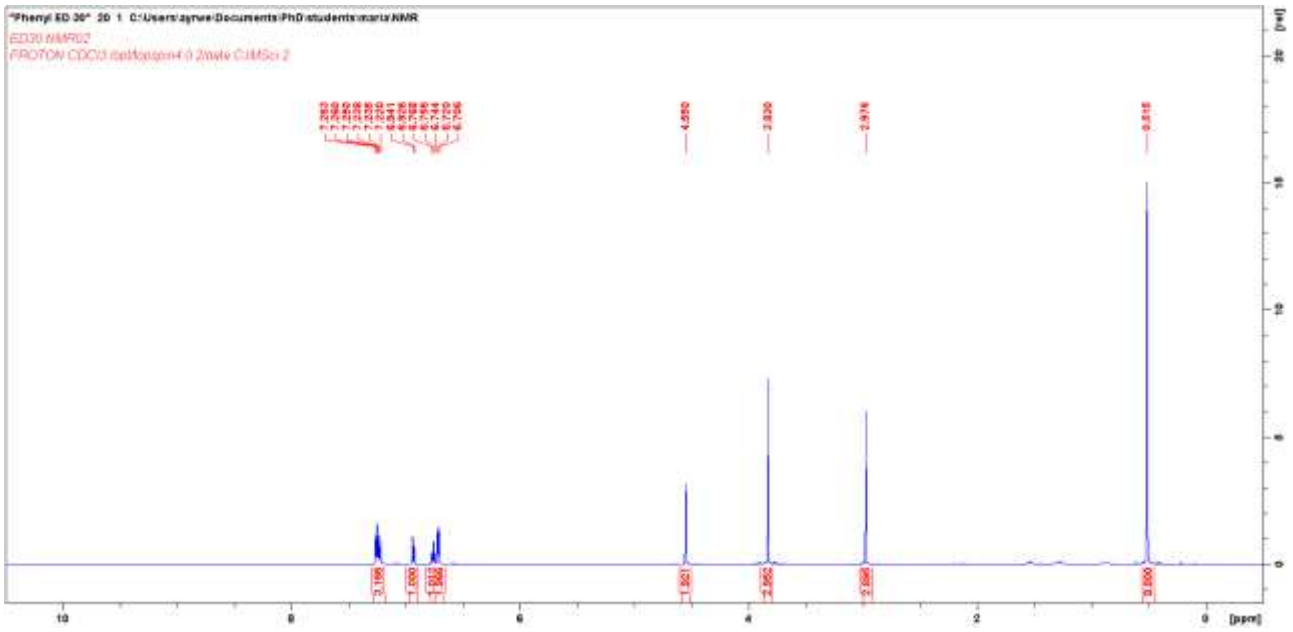
12 ^{13}C NMR (101 MHz, $CDCl_3$)

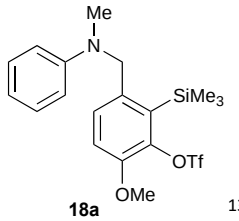




18a

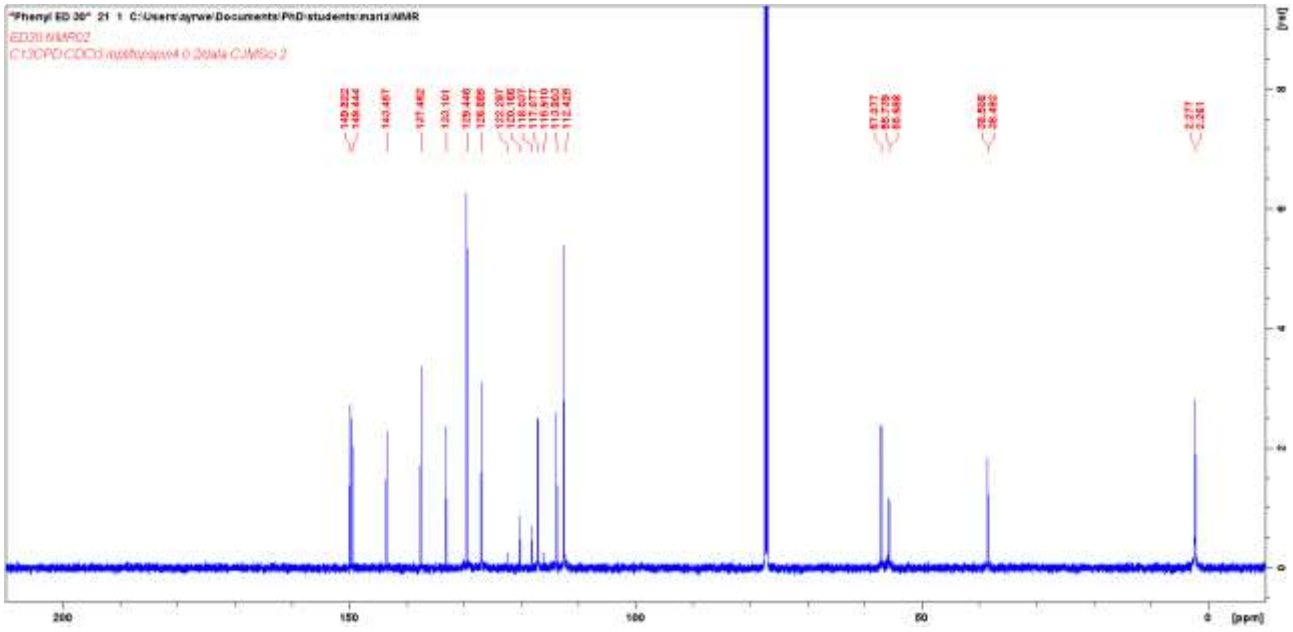
^{1}H NMR (400 MHz, $CDCl_3$)

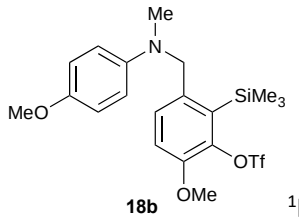




18a

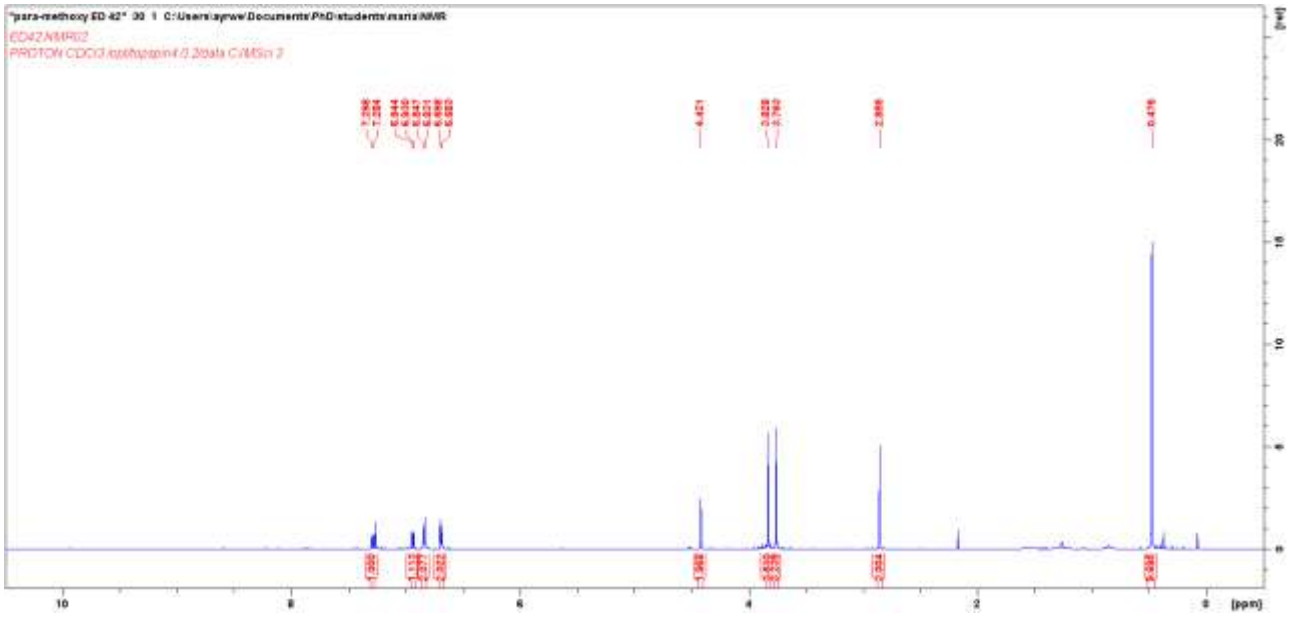
^{13}C NMR (101 MHz, $CDCl_3$)

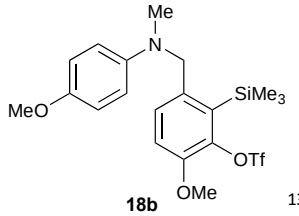




18b

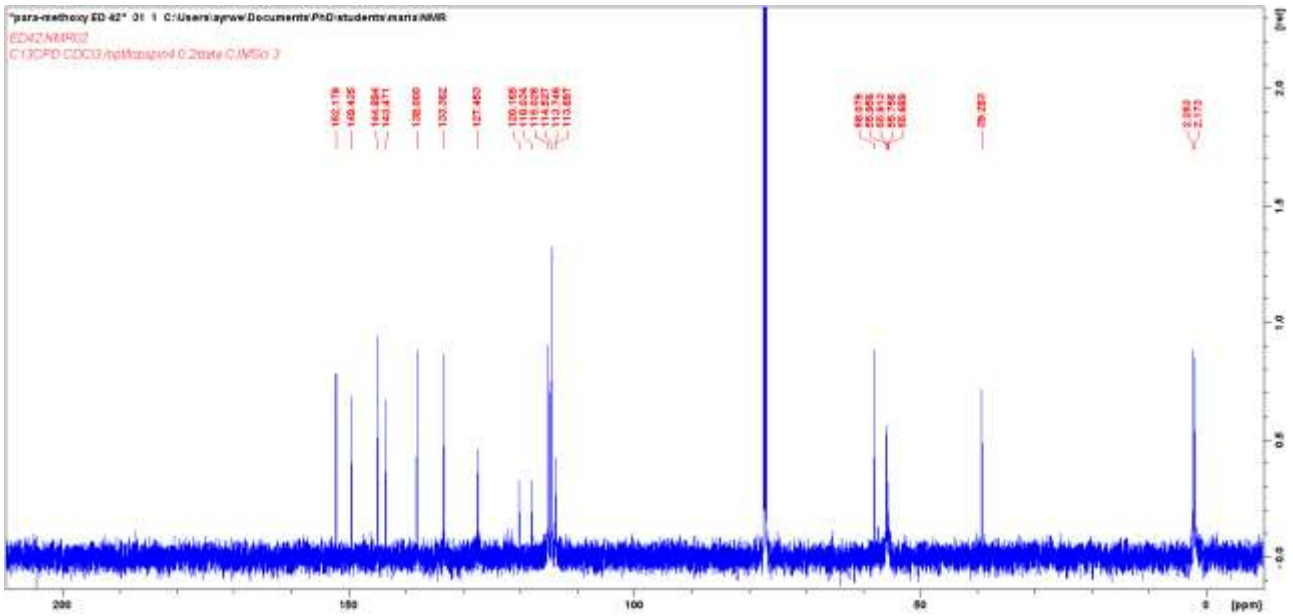
^{1}H NMR (400 MHz, $CDCl_3$)

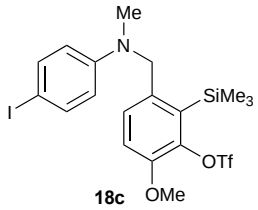




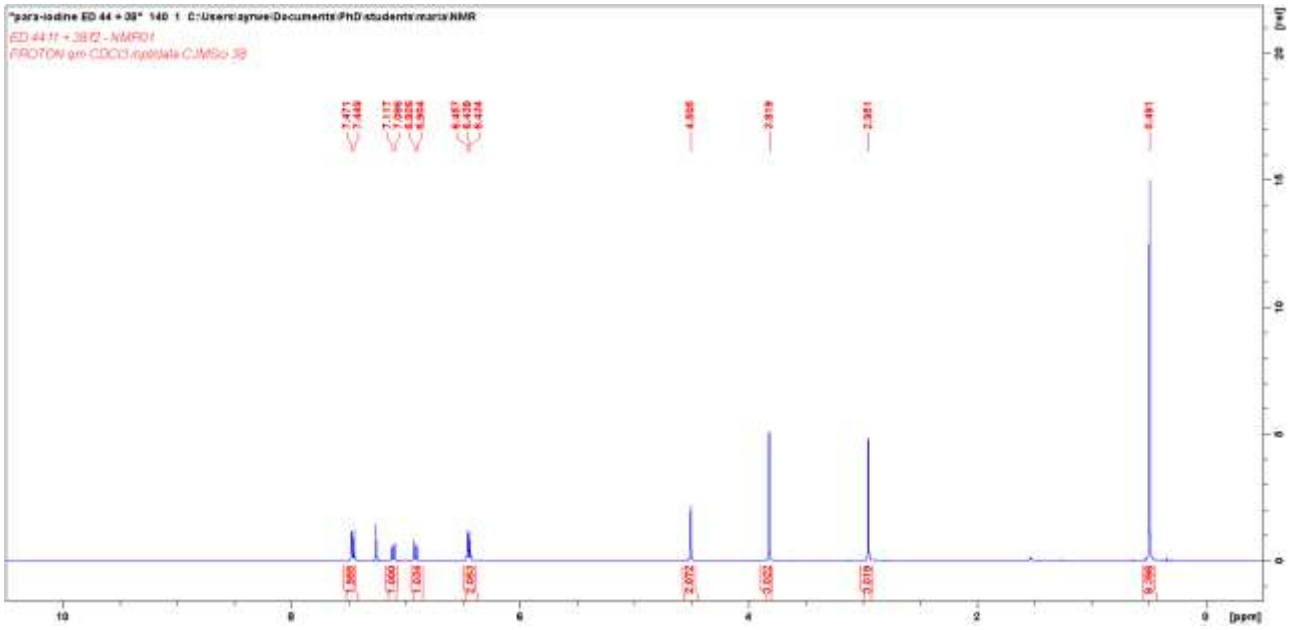
18b

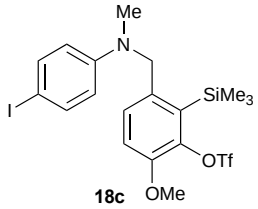
^{13}C NMR (101 MHz, $CDCl_3$)



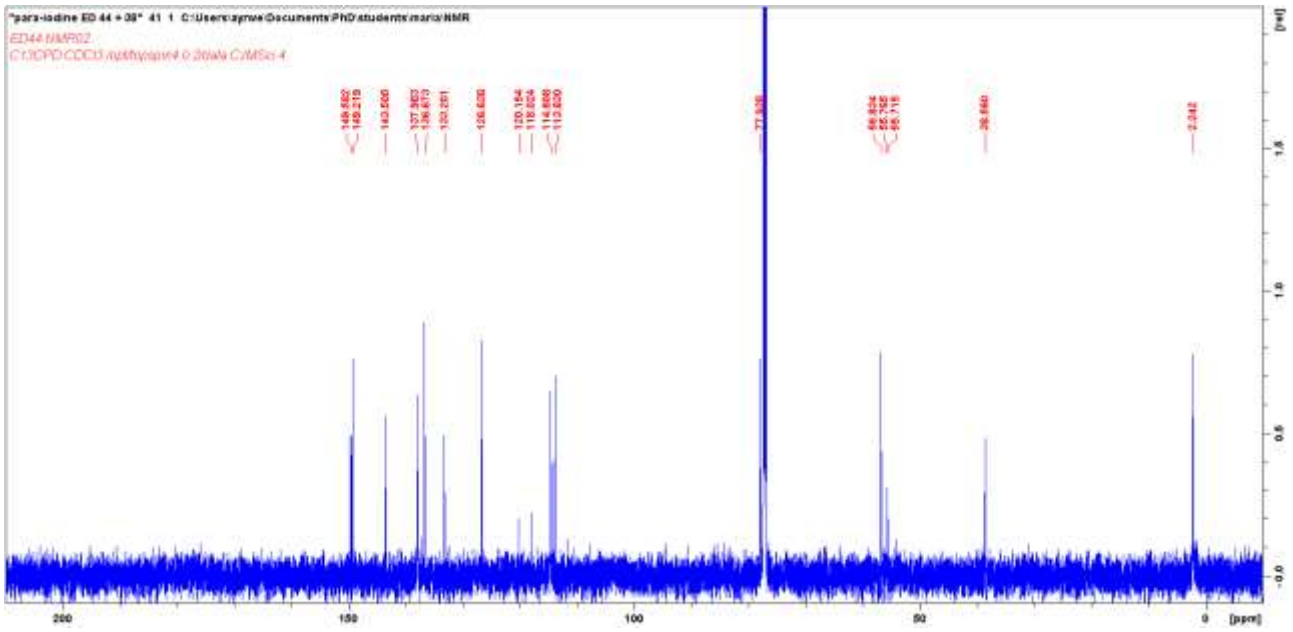


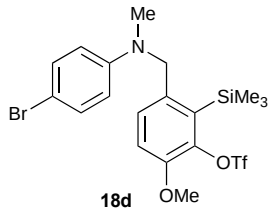
18c ^{1}H NMR (400 MHz, $CDCl_3$)



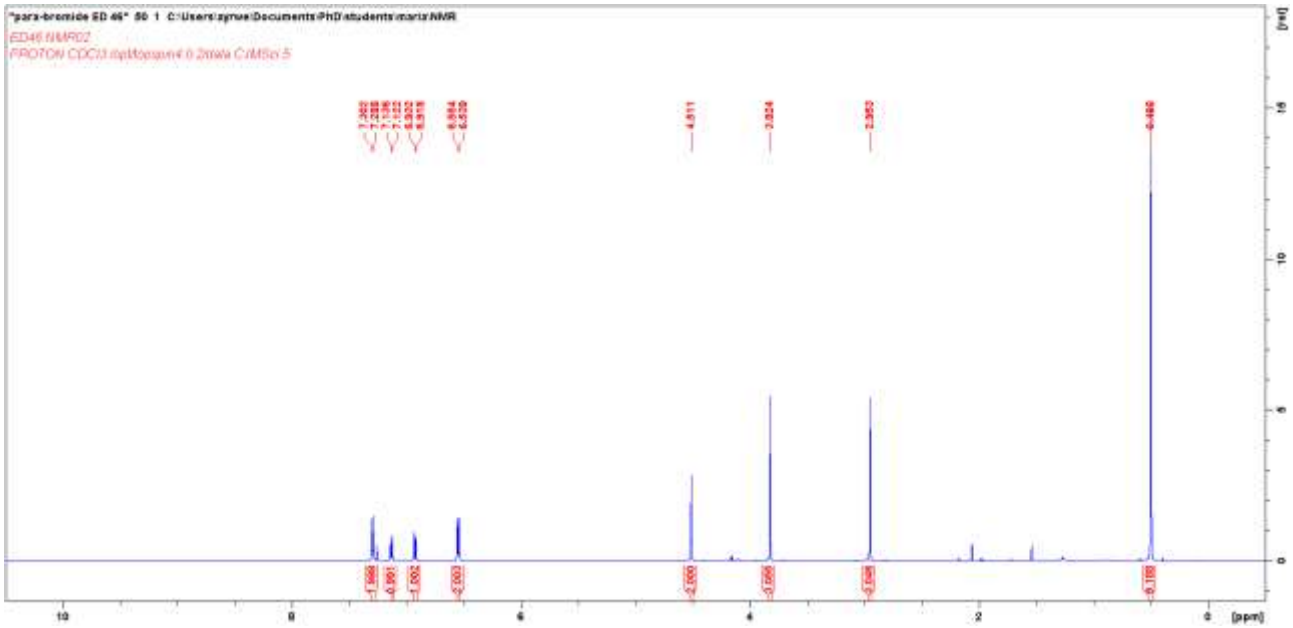


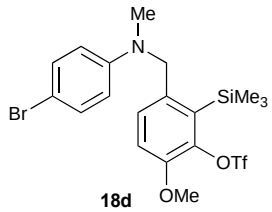
18c ^{13}C NMR (101 MHz, $CDCl_3$)



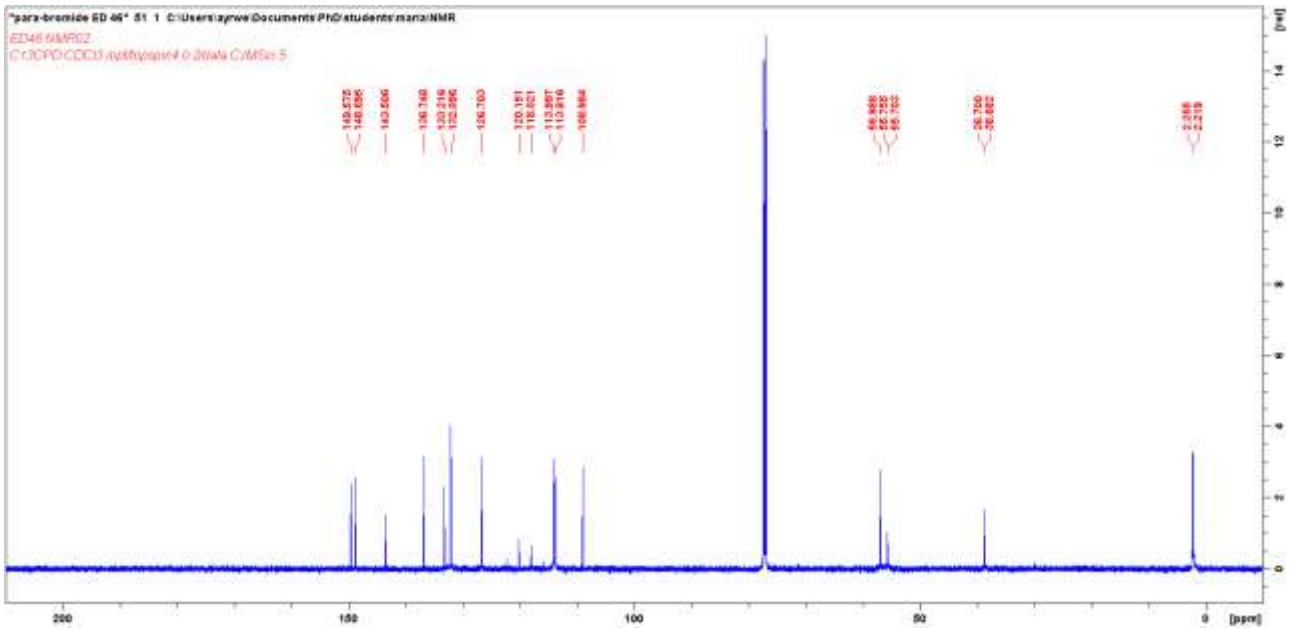


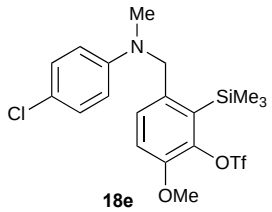
18d ^{1}H NMR (400 MHz, $CDCl_3$)



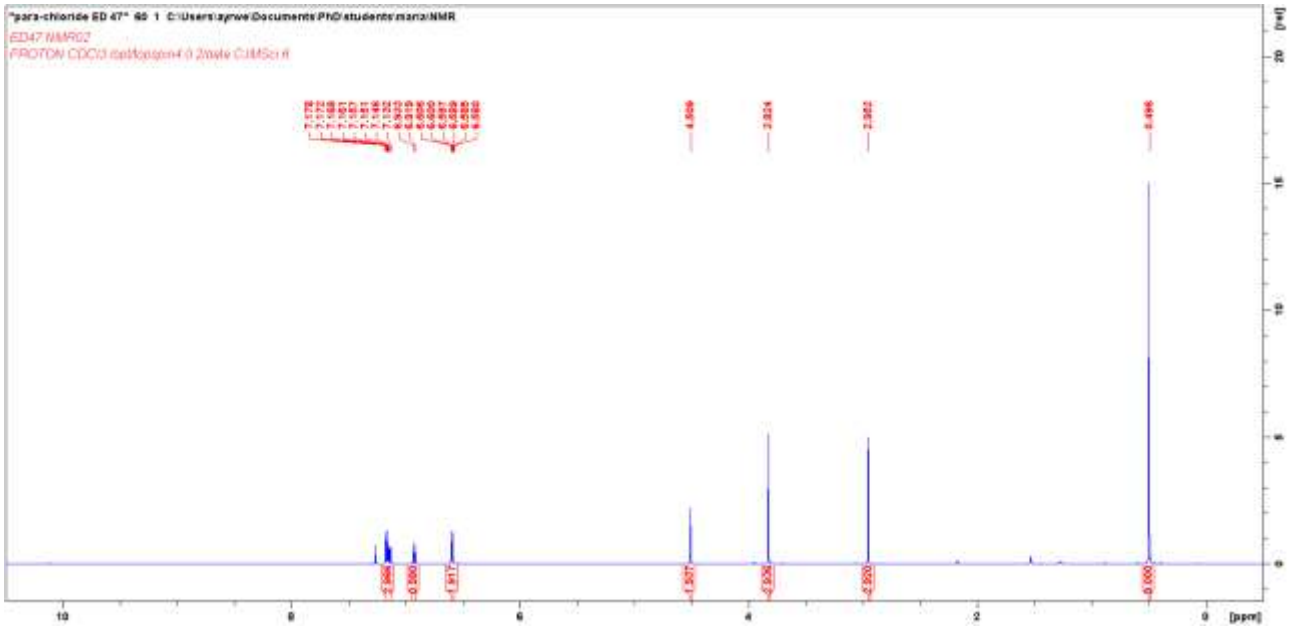


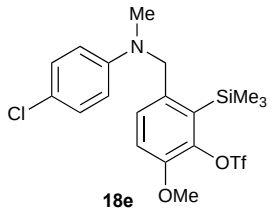
18d ^{13}C NMR (101 MHz, $CDCl_3$)



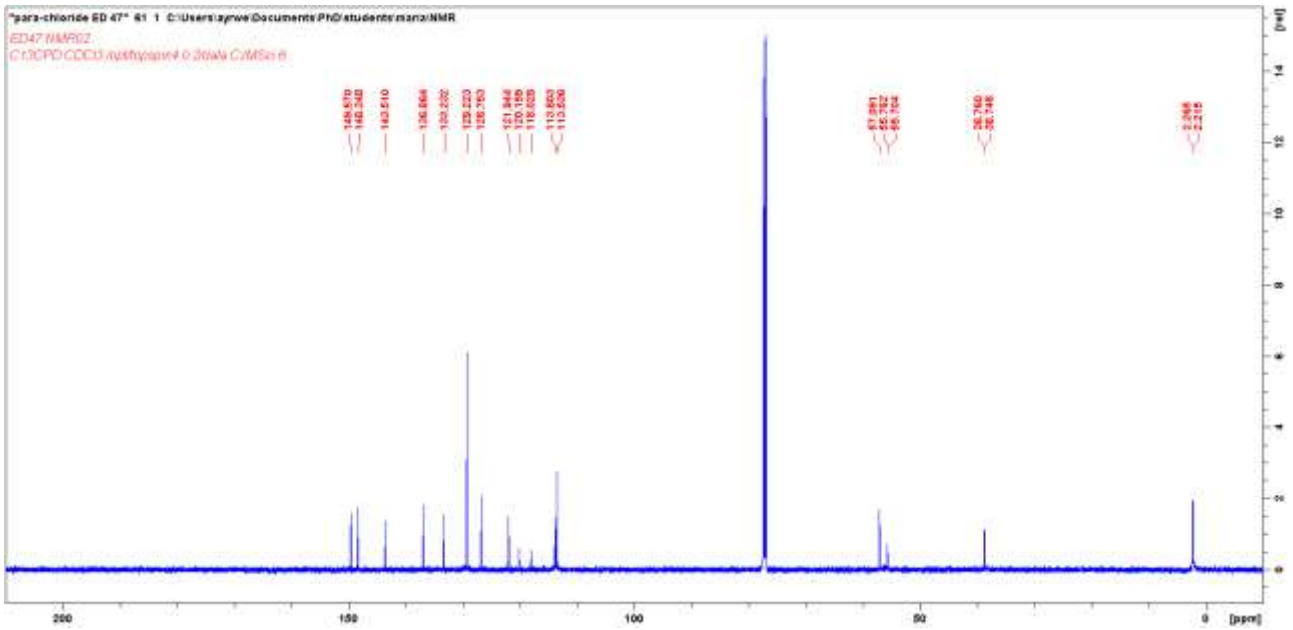


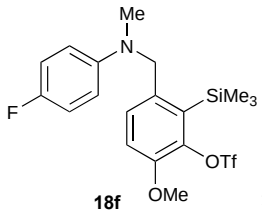
18e ^{1}H NMR (400 MHz, $CDCl_3$)





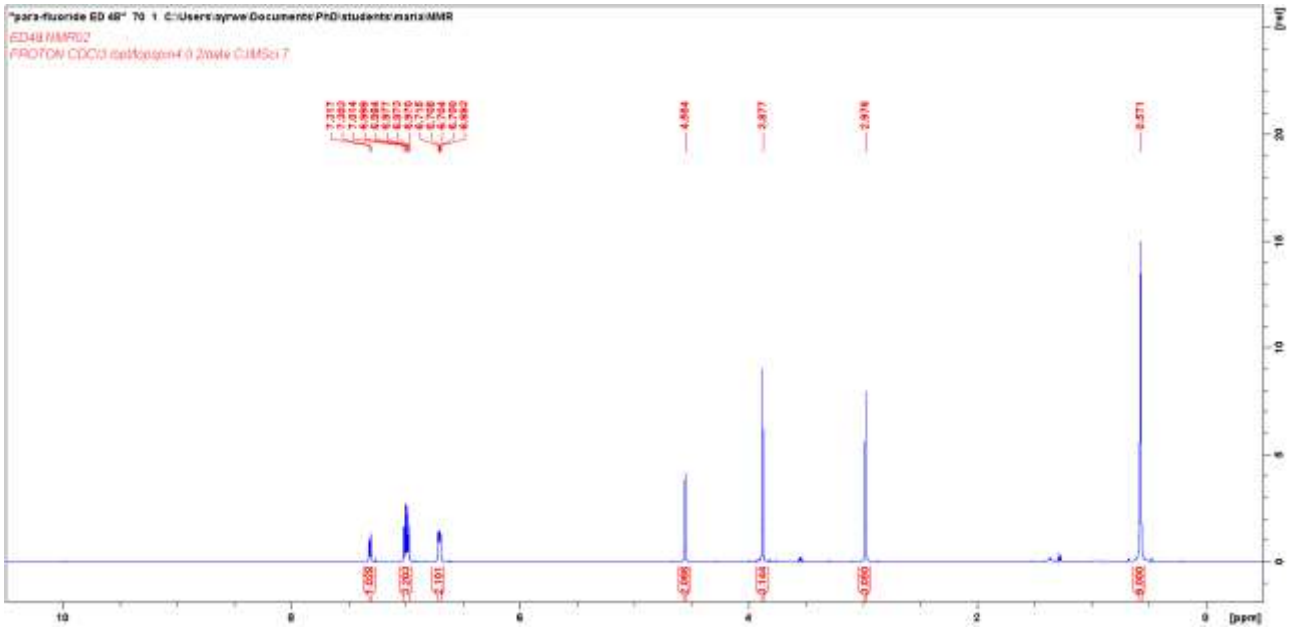
18e ^{13}C NMR (101 MHz, $CDCl_3$)

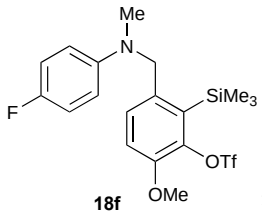




18f

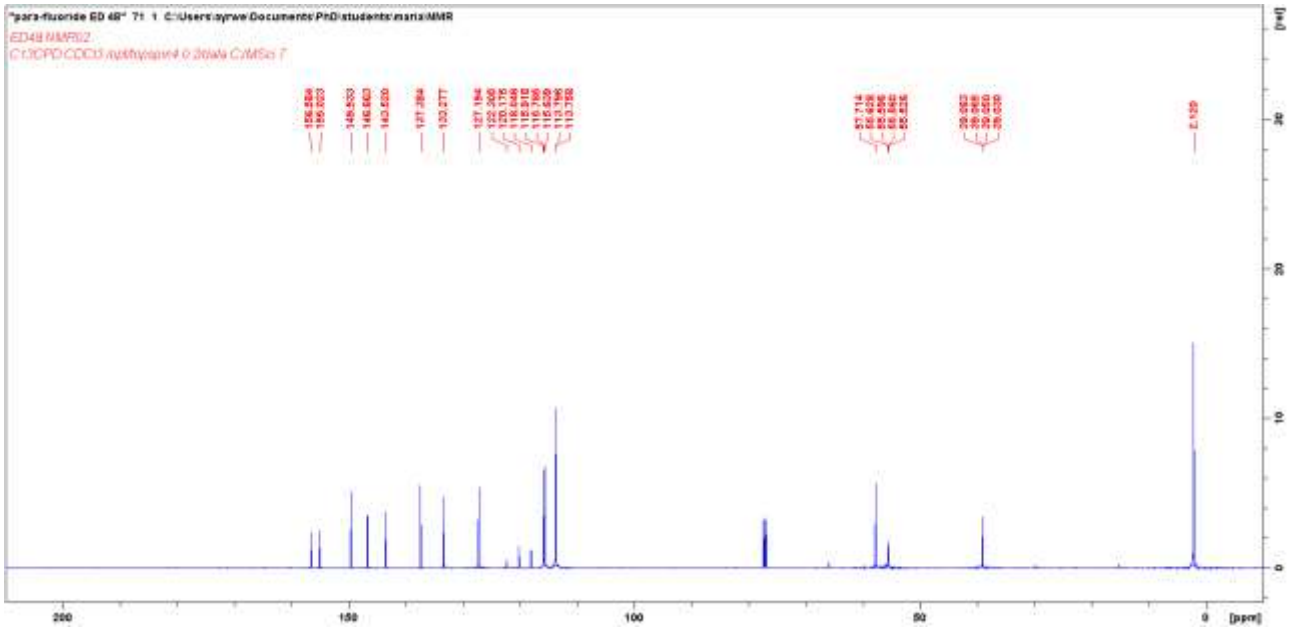
^{1}H NMR (400 MHz, $CDCl_3$)

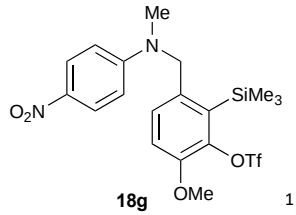




18f

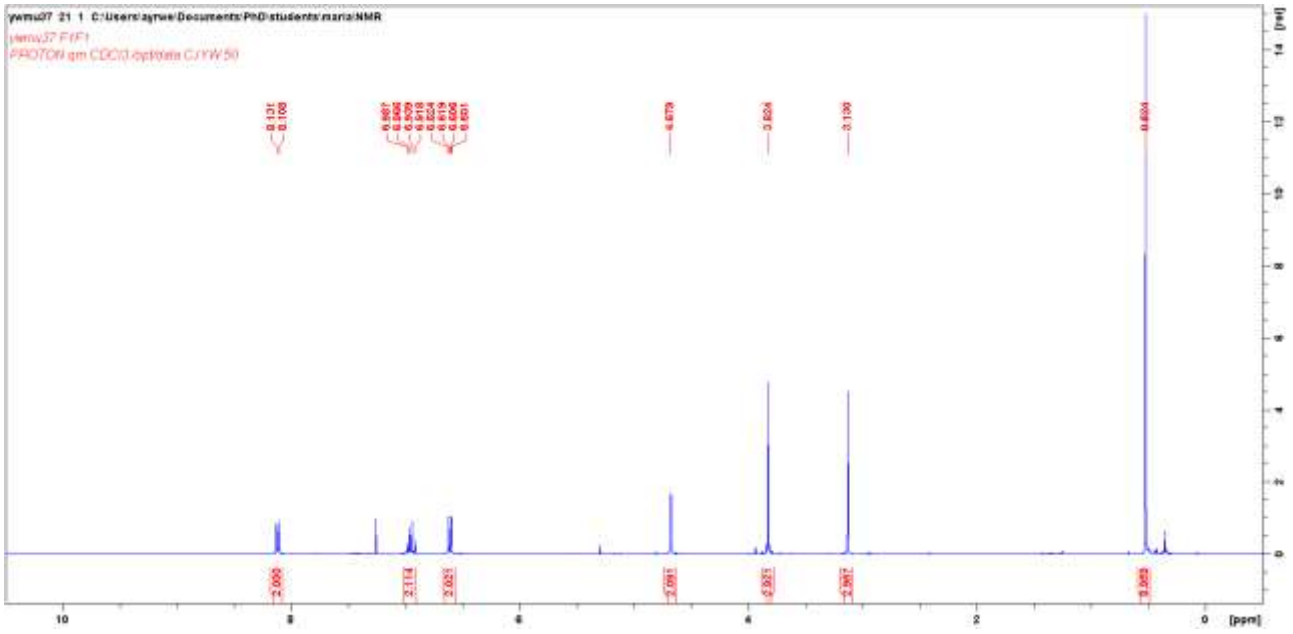
^{13}C NMR (101 MHz, $CDCl_3$)

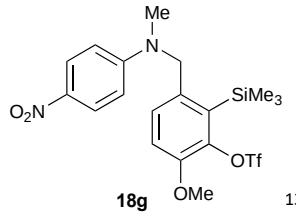




18g

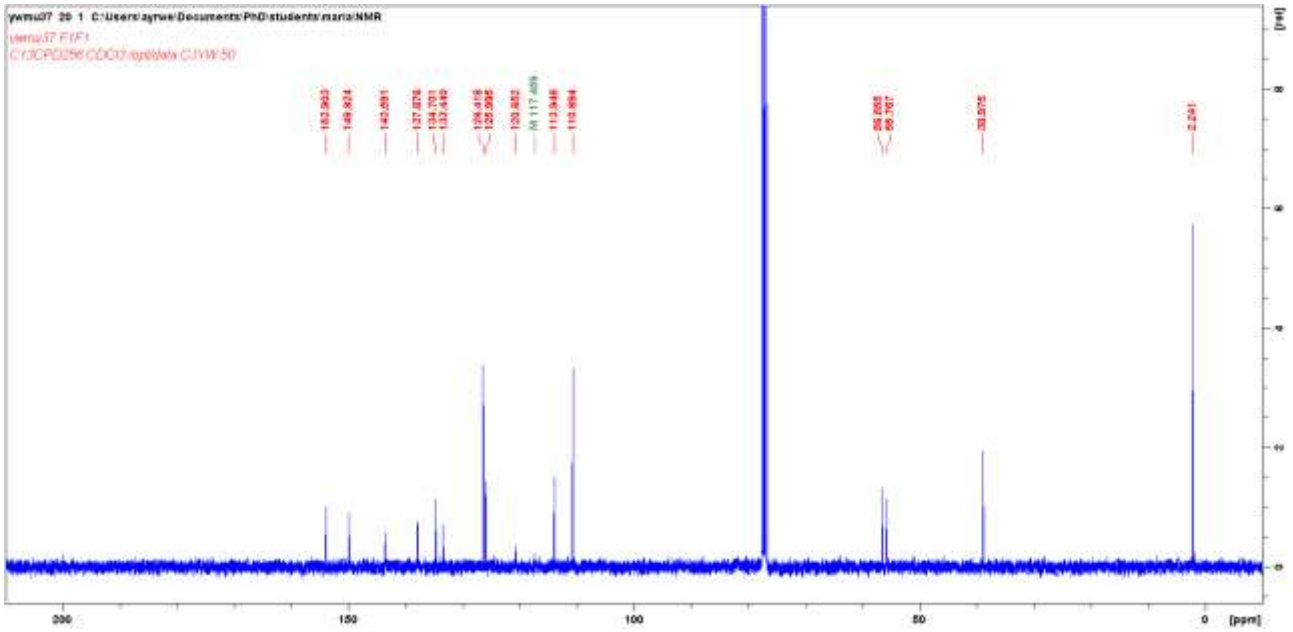
^{1}H NMR (400 MHz, $CDCl_3$)

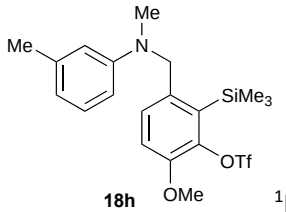




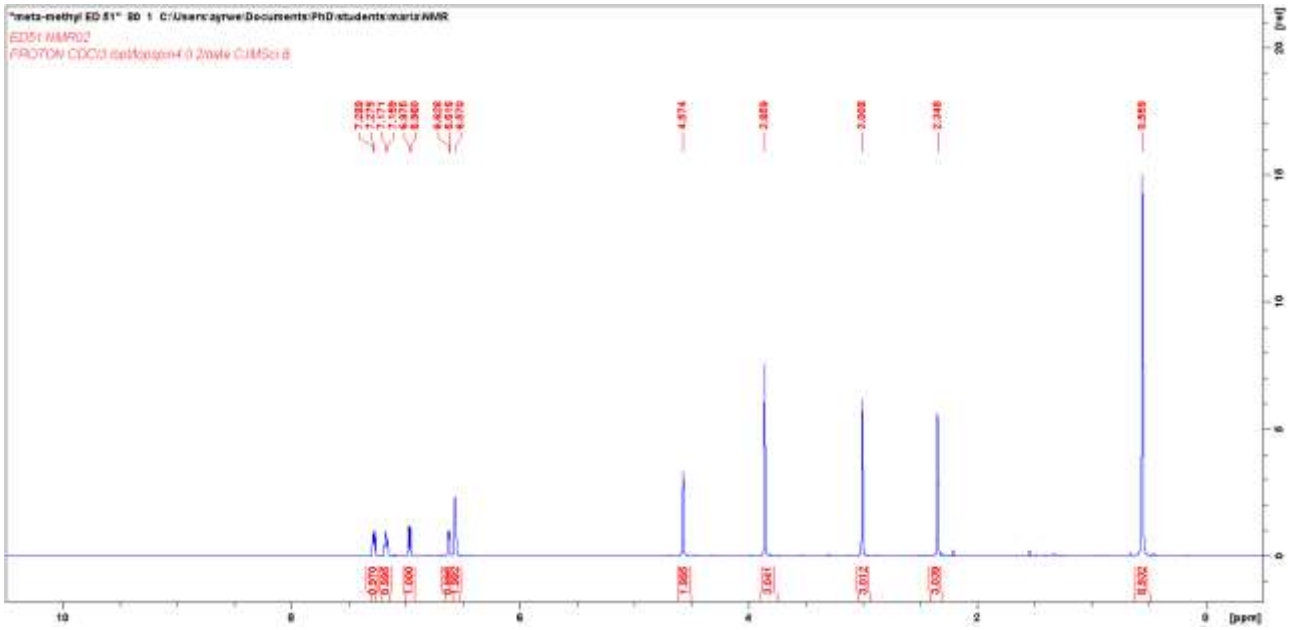
18g

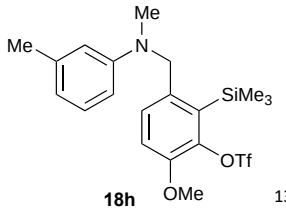
^{13}C NMR (101 MHz, $CDCl_3$)



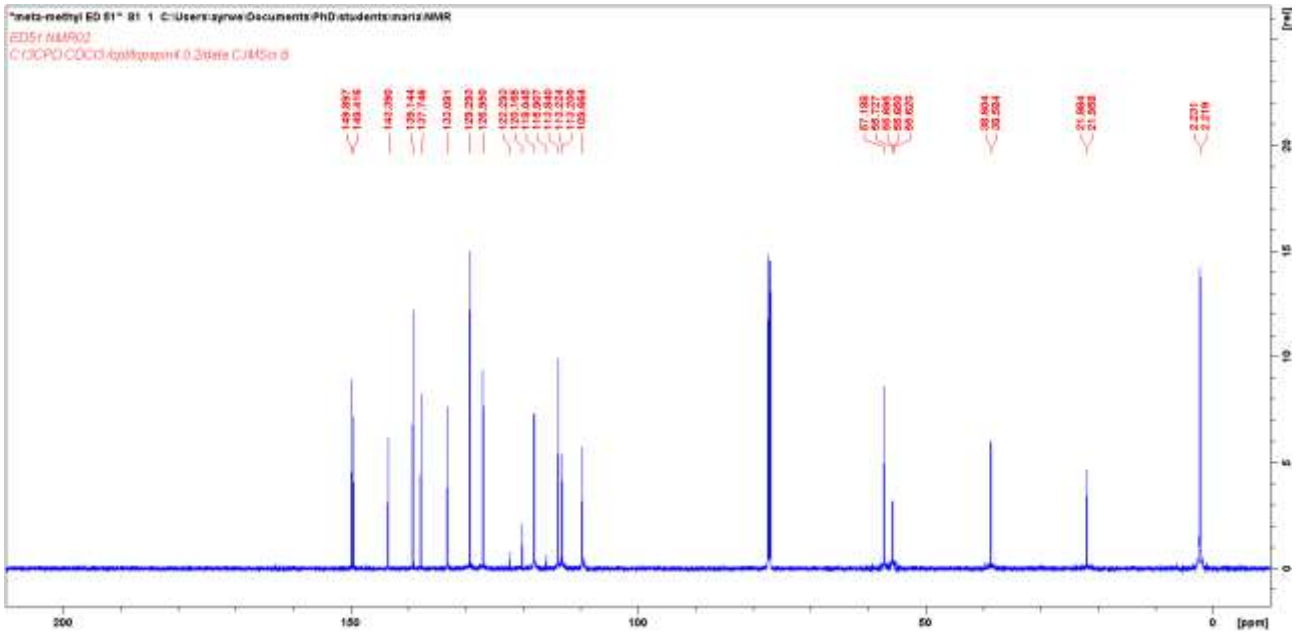


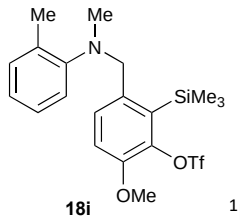
18h ^{1}H NMR (400 MHz, $CDCl_3$)





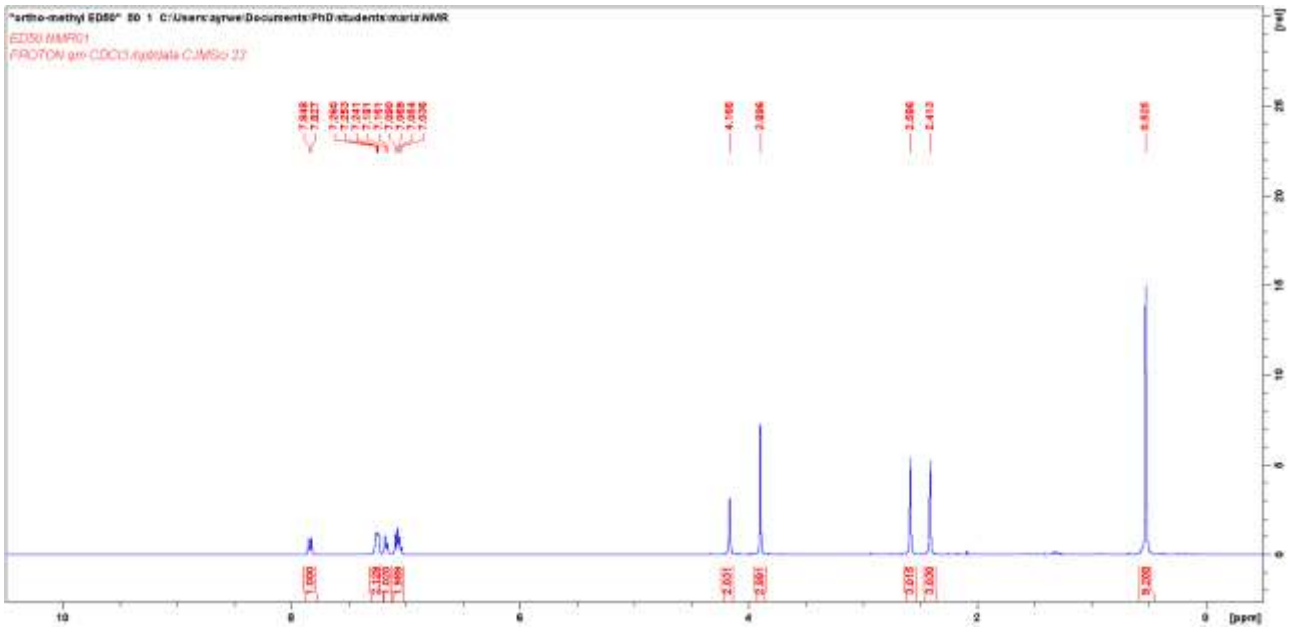
18h ^{13}C NMR (101 MHz, $CDCl_3$)

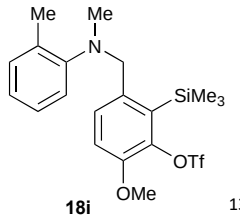




18i

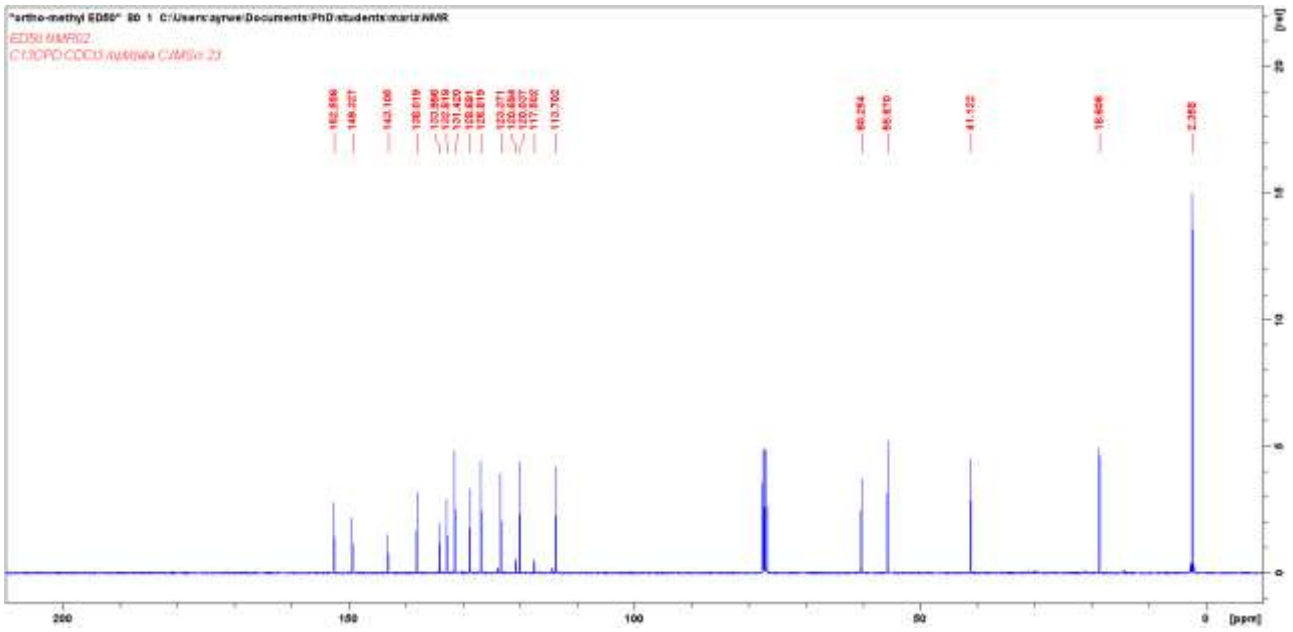
^{1}H NMR (400 MHz, $CDCl_3$)

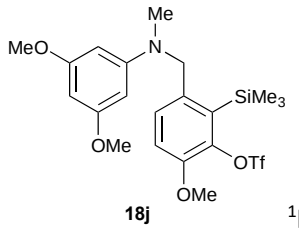




18i

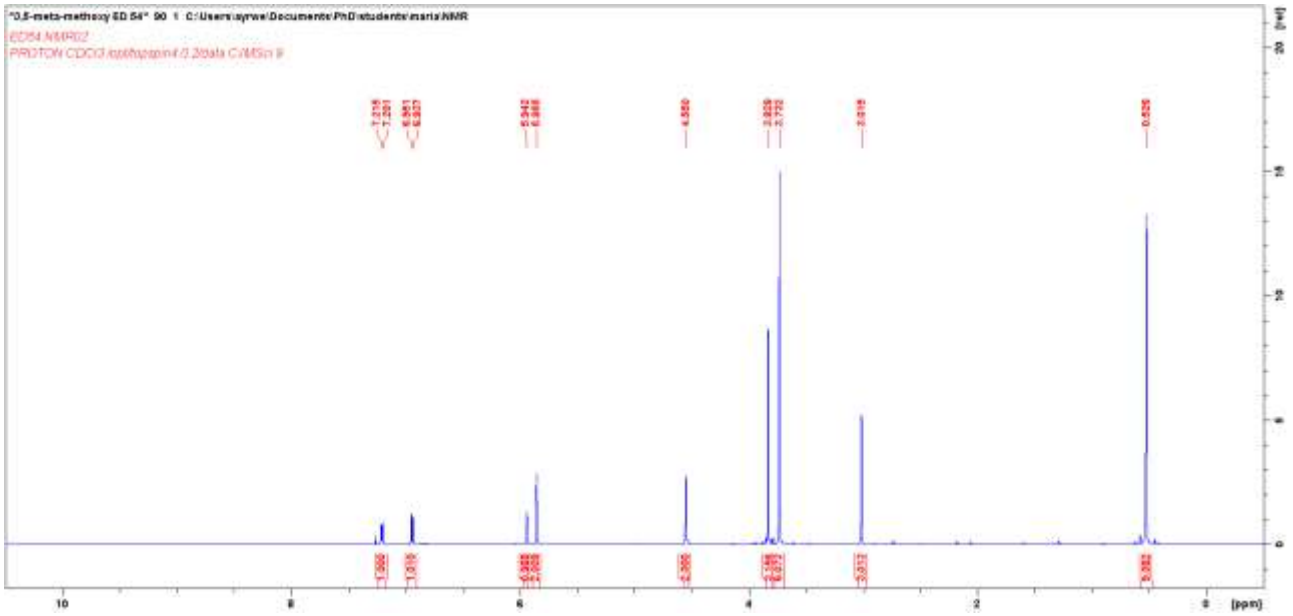
^{13}C NMR (101 MHz, $CDCl_3$)

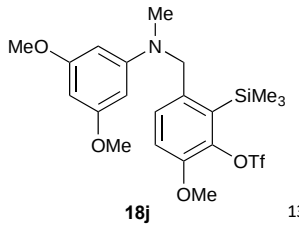




18j

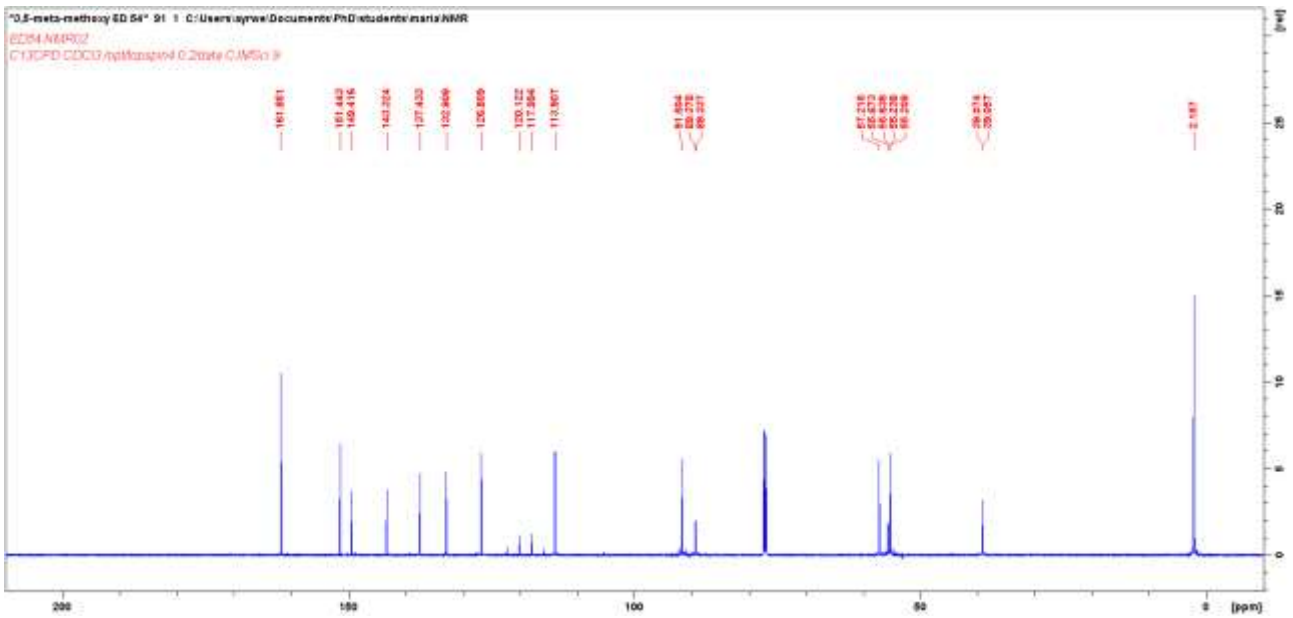
^{1}H NMR (400 MHz, $CDCl_3$)

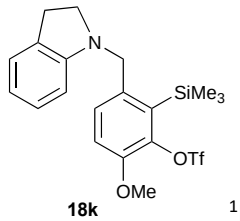




18j

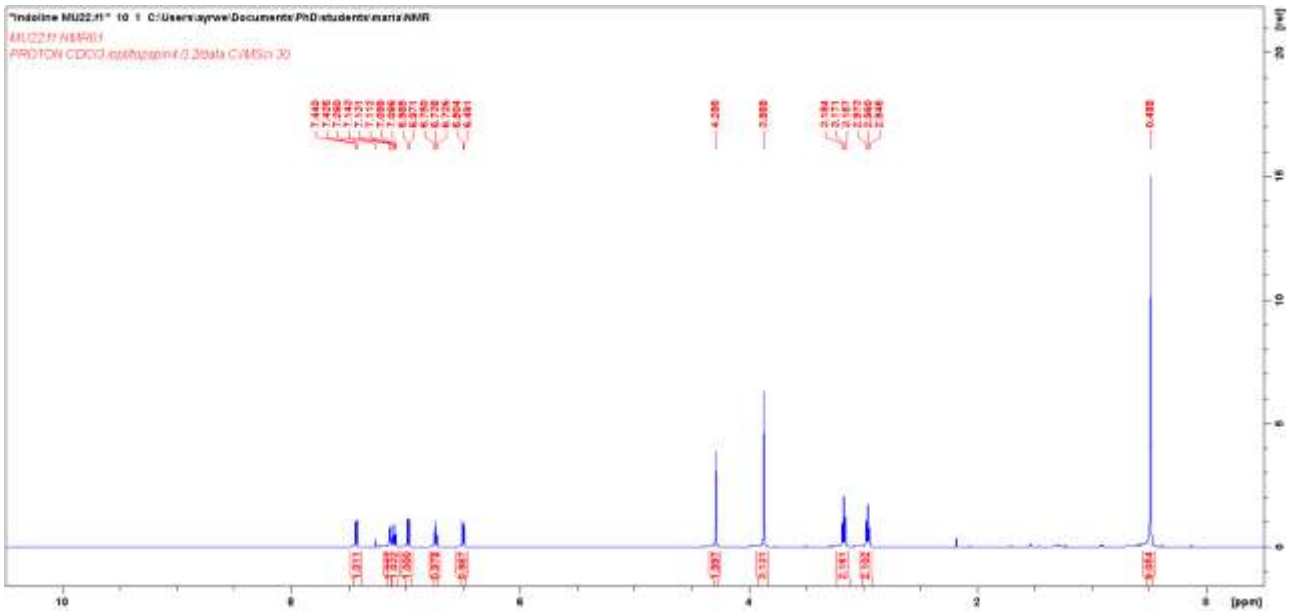
^{13}C NMR (101 MHz, $CDCl_3$)

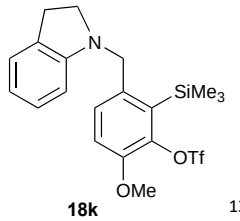




18k

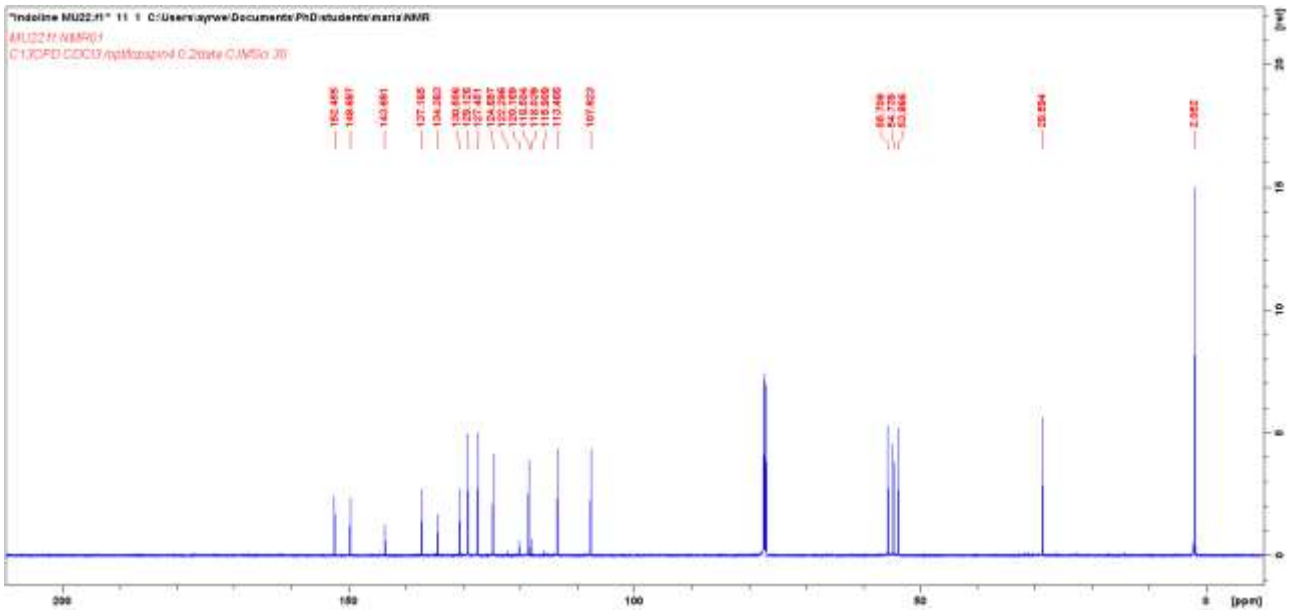
^{1}H NMR (400 MHz, $CDCl_3$)

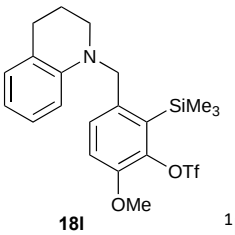




18k

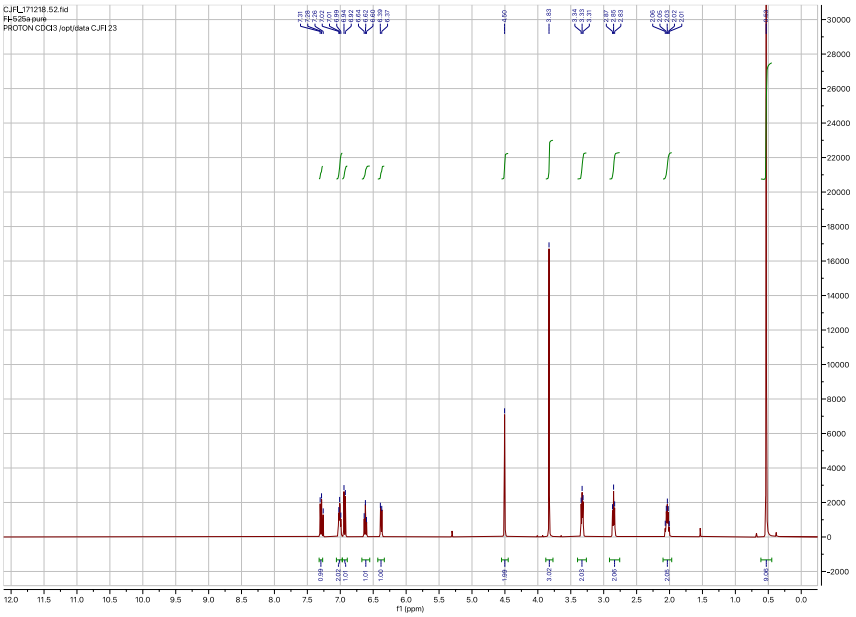
^{13}C NMR (101 MHz, $CDCl_3$)

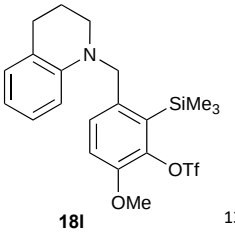




18l

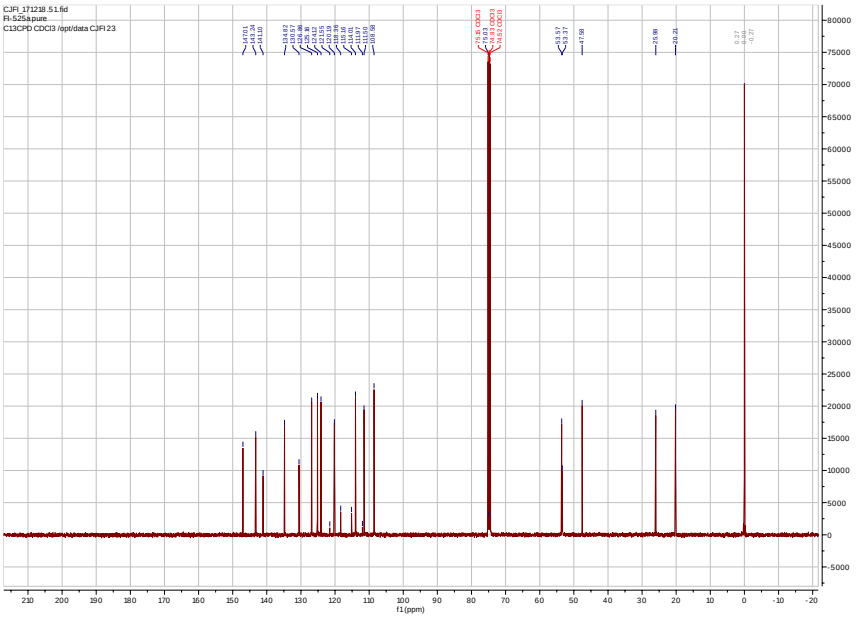
^{1}H NMR (400 MHz, $CDCl_3$)

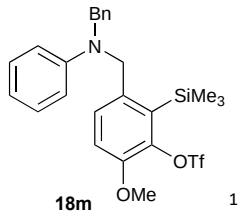




18l

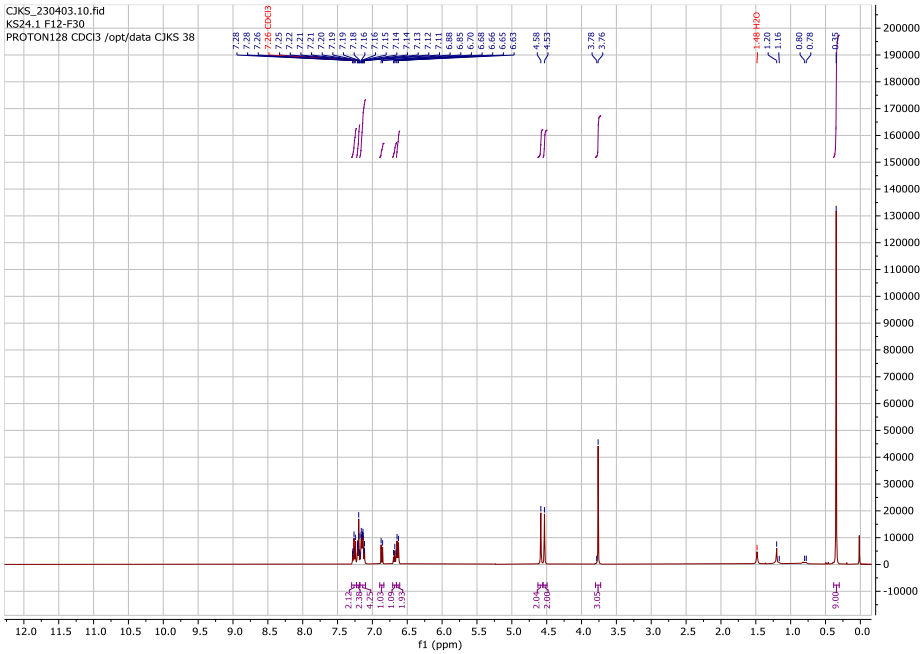
^{13}C NMR (101 MHz, $CDCl_3$)

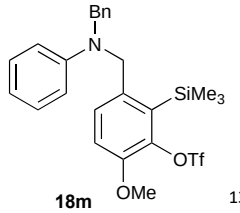




18m

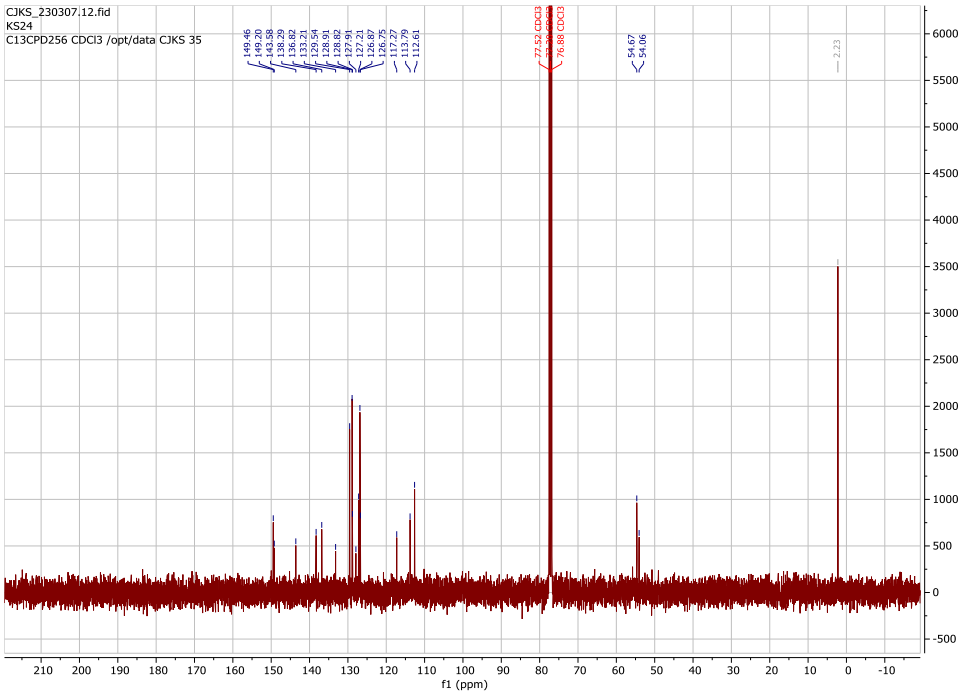
^{1}H NMR (400 MHz, $CDCl_3$)

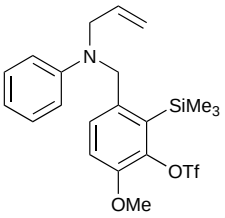




18m

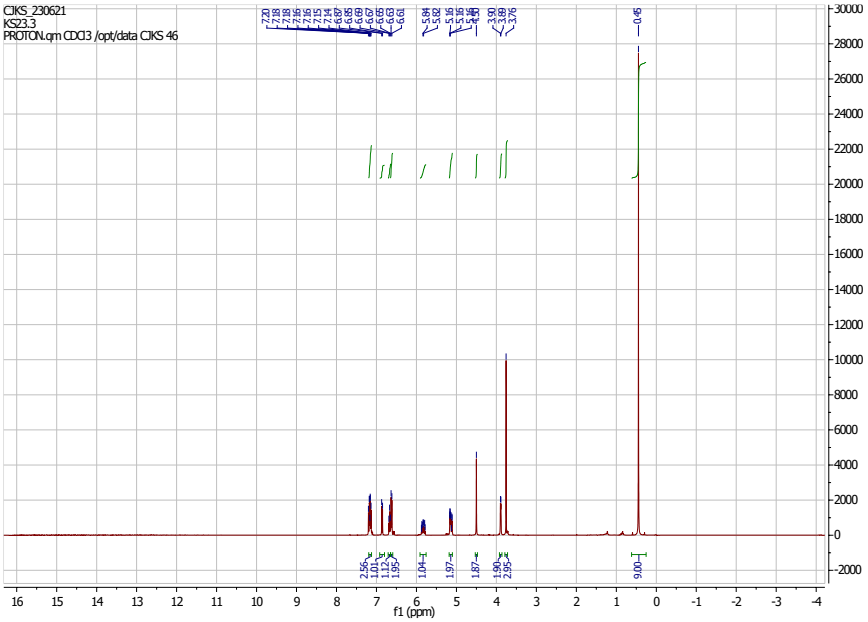
^{13}C NMR (101 MHz, $CDCl_3$)

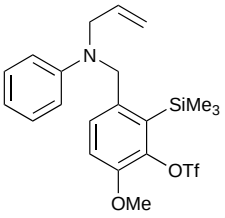




18n

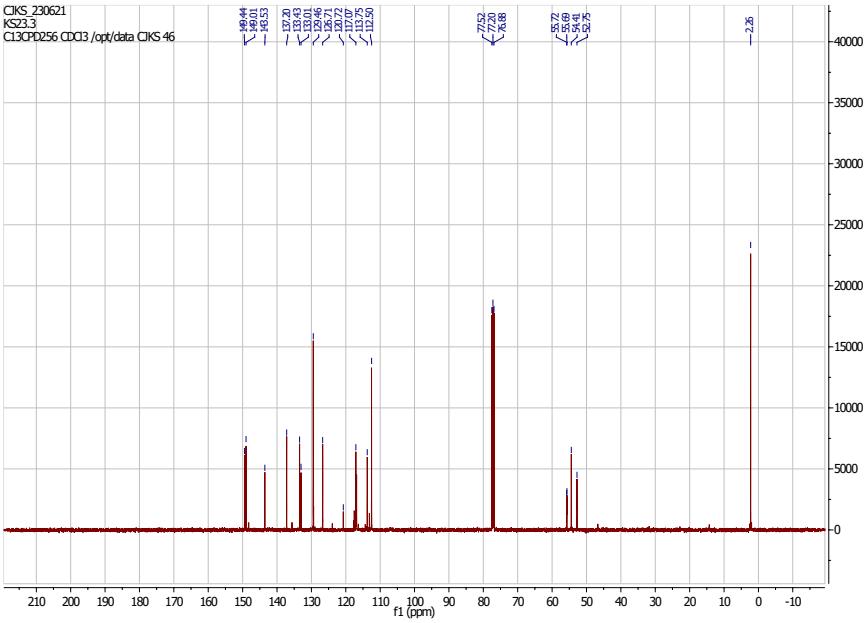
^{1}H NMR (400 MHz, $CDCl_3$)

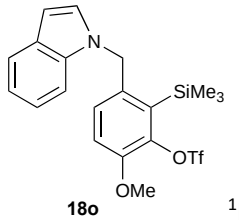




18n

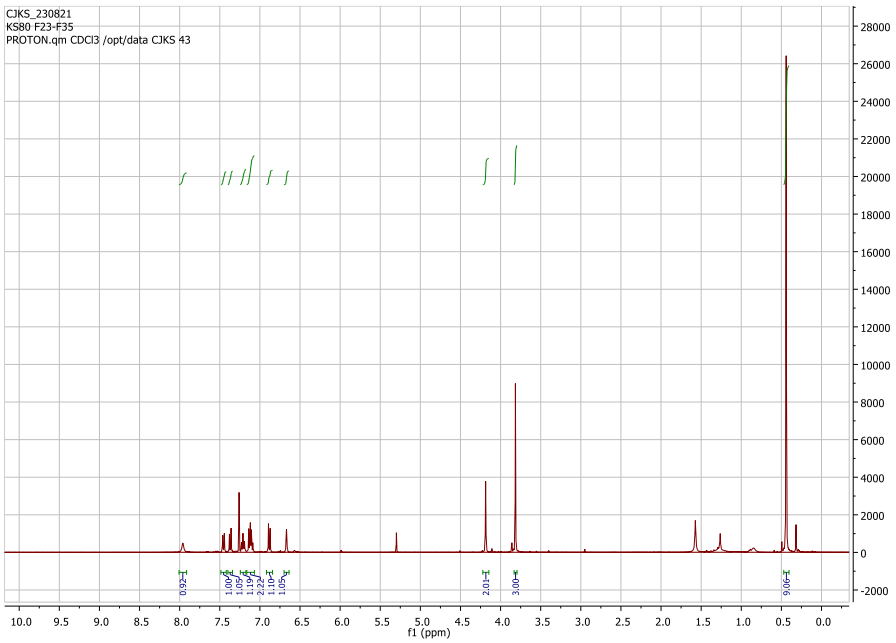
^{13}C NMR (101 MHz, $CDCl_3$)

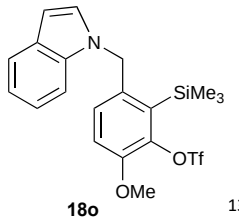




18o

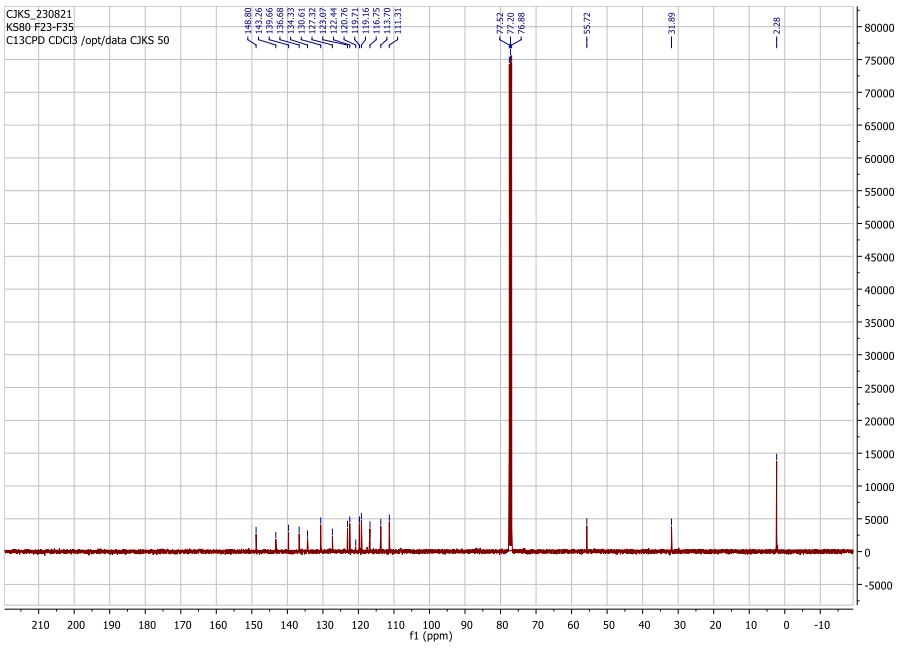
^{1}H NMR (400 MHz, $CDCl_3$)

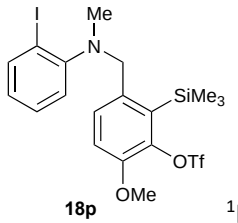




18o

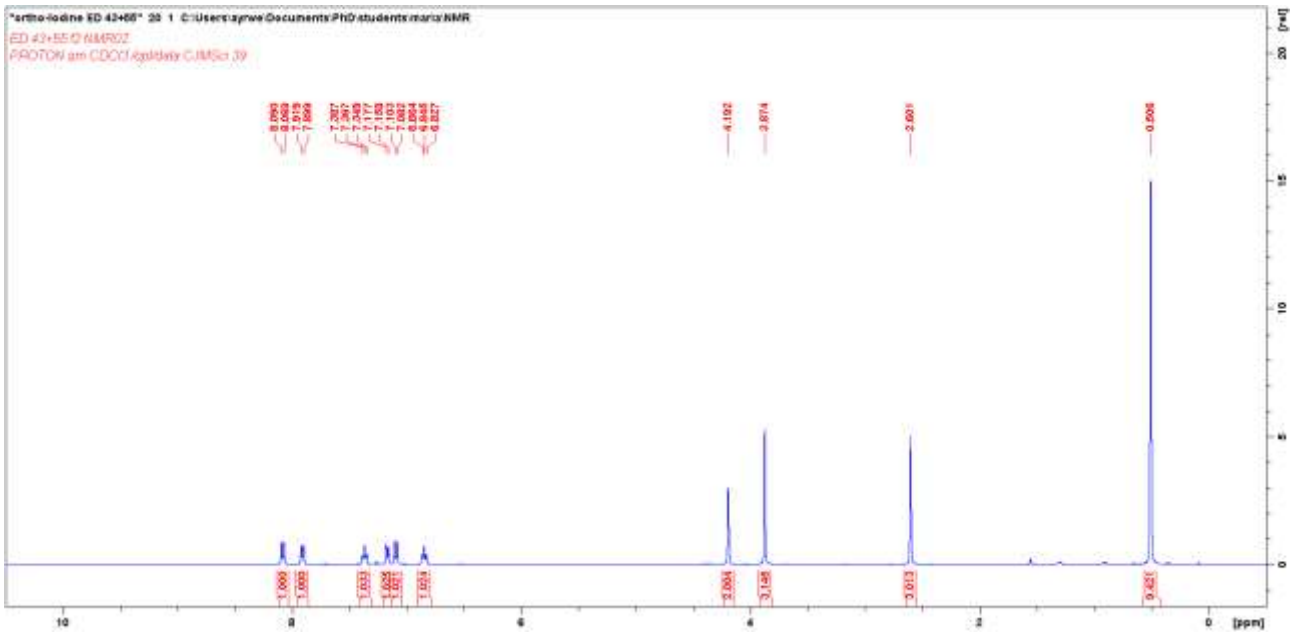
^{13}C NMR (101 MHz, $CDCl_3$)

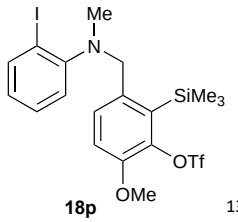




18p

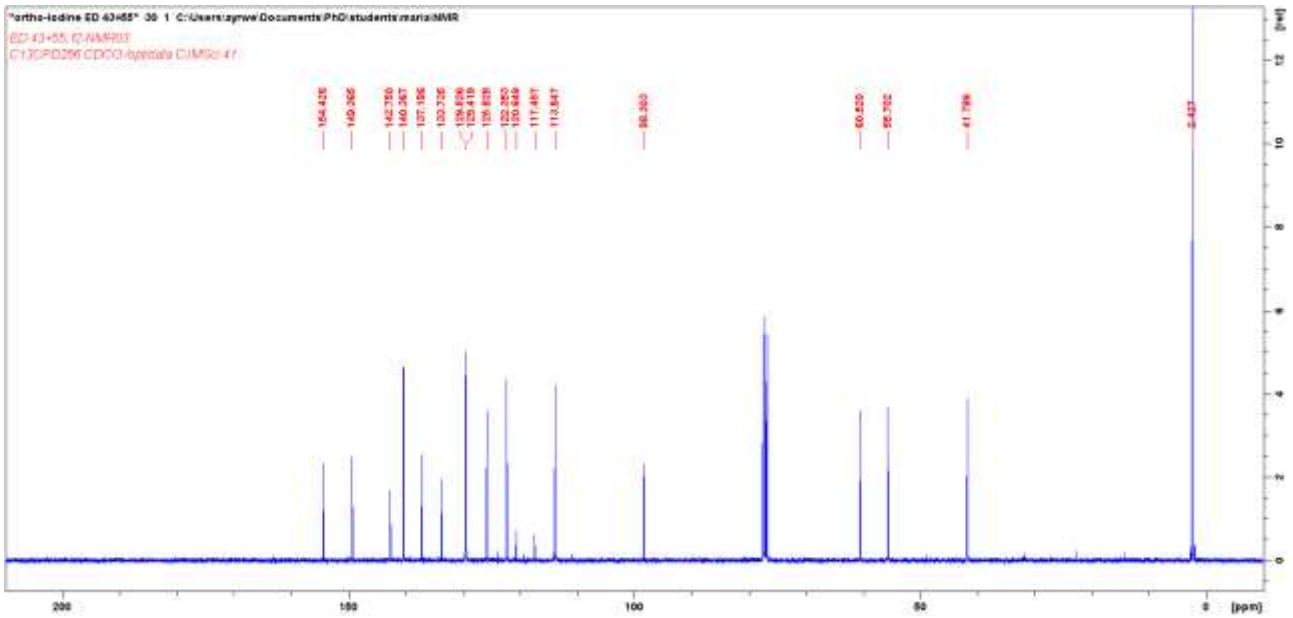
^{1}H NMR (400 MHz, $CDCl_3$)

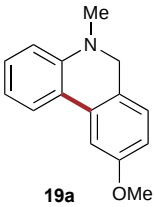




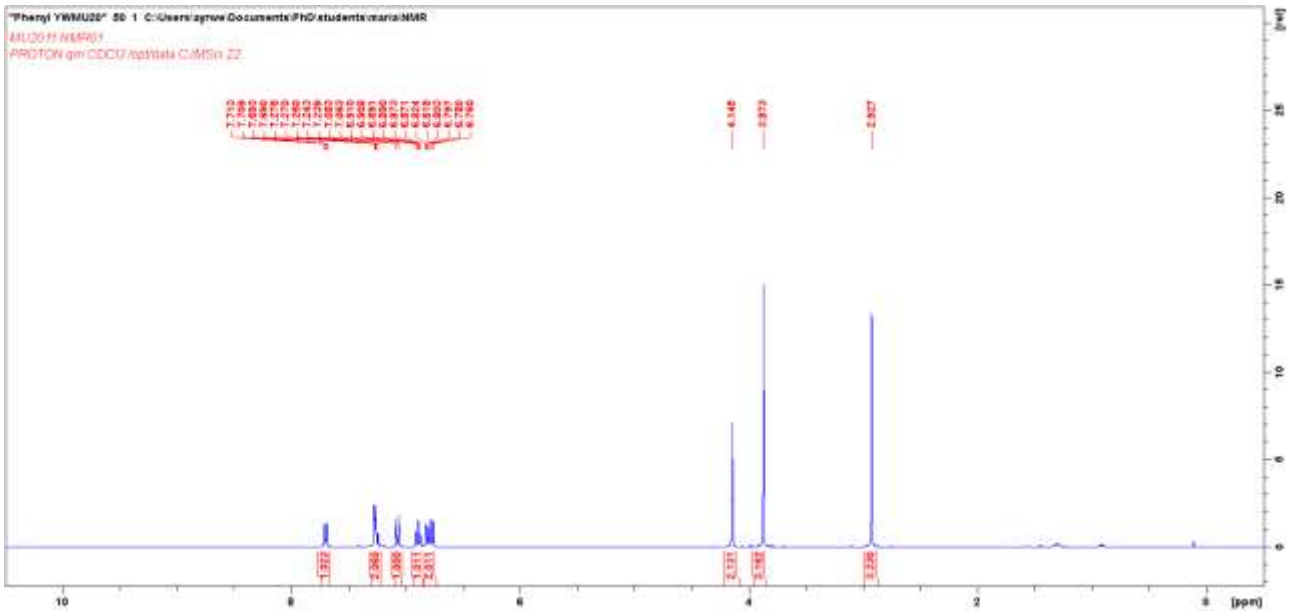
18p

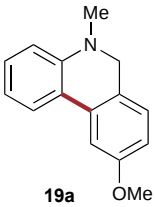
^{13}C NMR (101 MHz, $CDCl_3$)



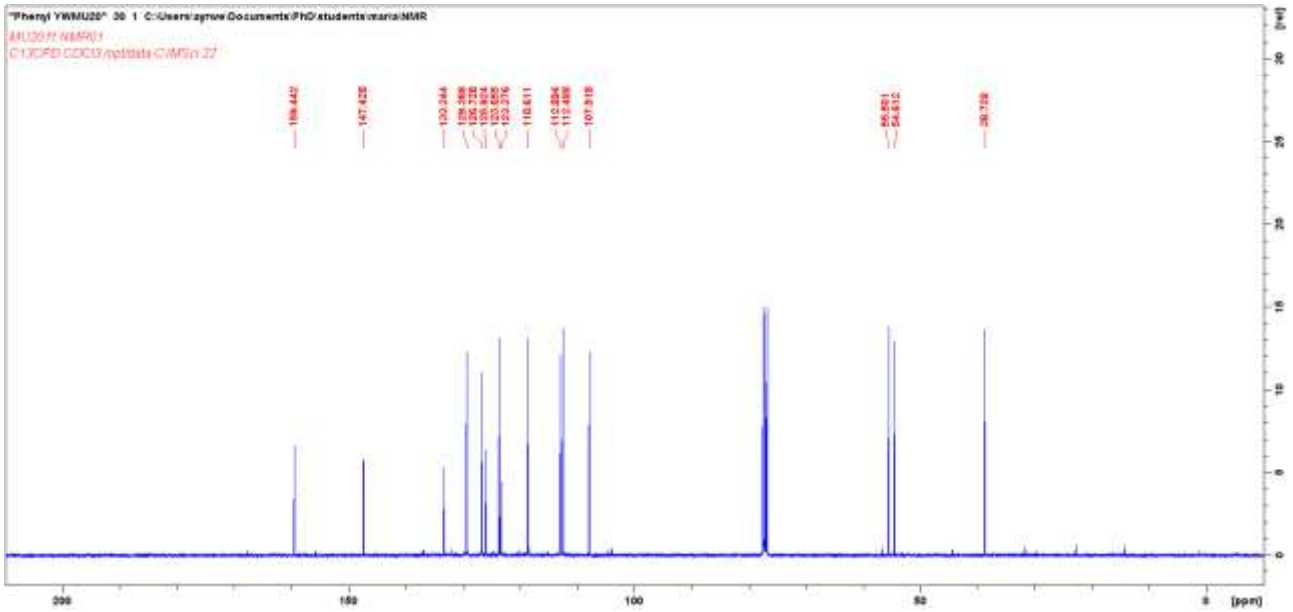


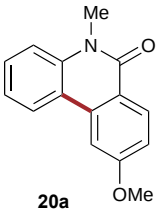
19a ^{1}H NMR (400 MHz, $CDCl_3$)



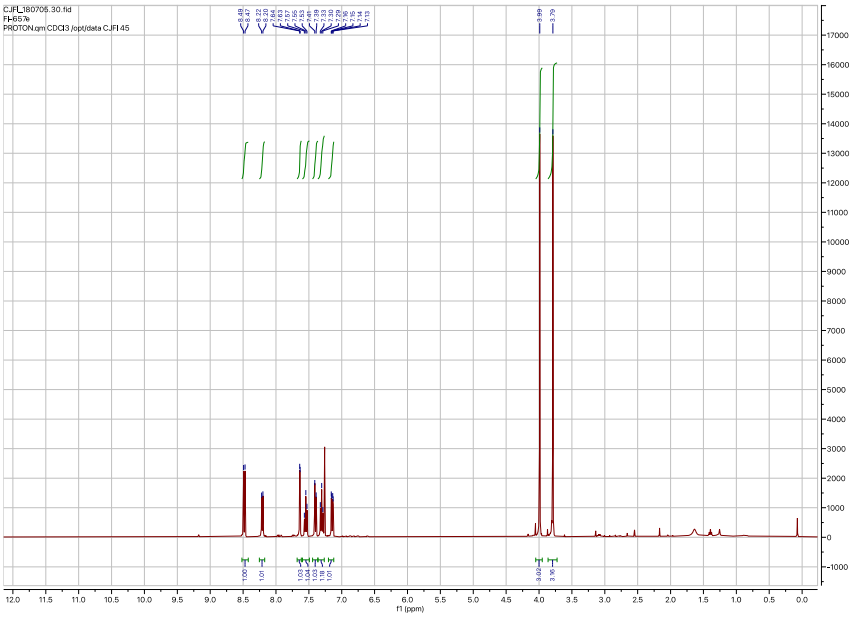


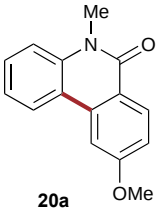
19a ^{13}C NMR (101 MHz, $CDCl_3$)



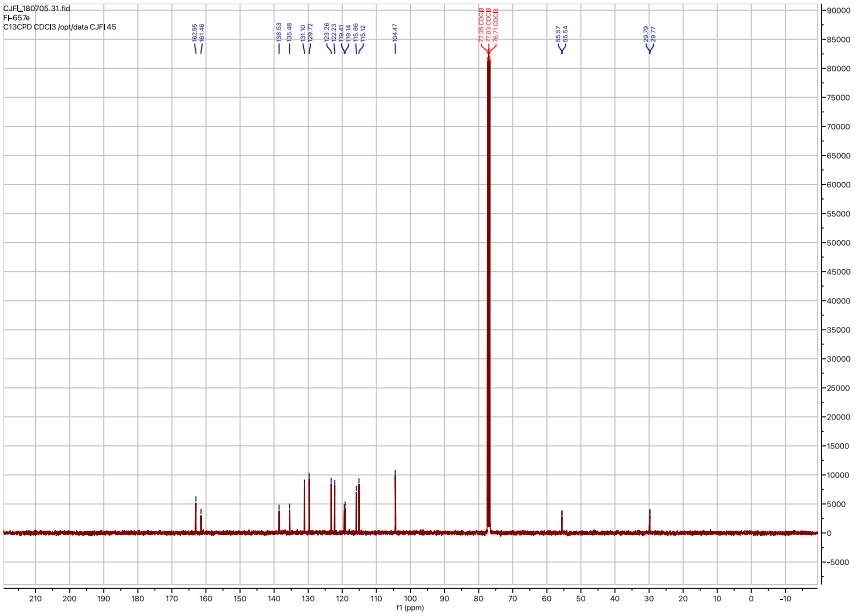


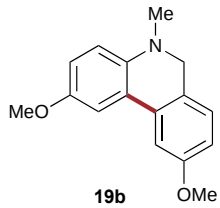
20a OMe ^{1}H NMR (400 MHz, $CDCl_3$)



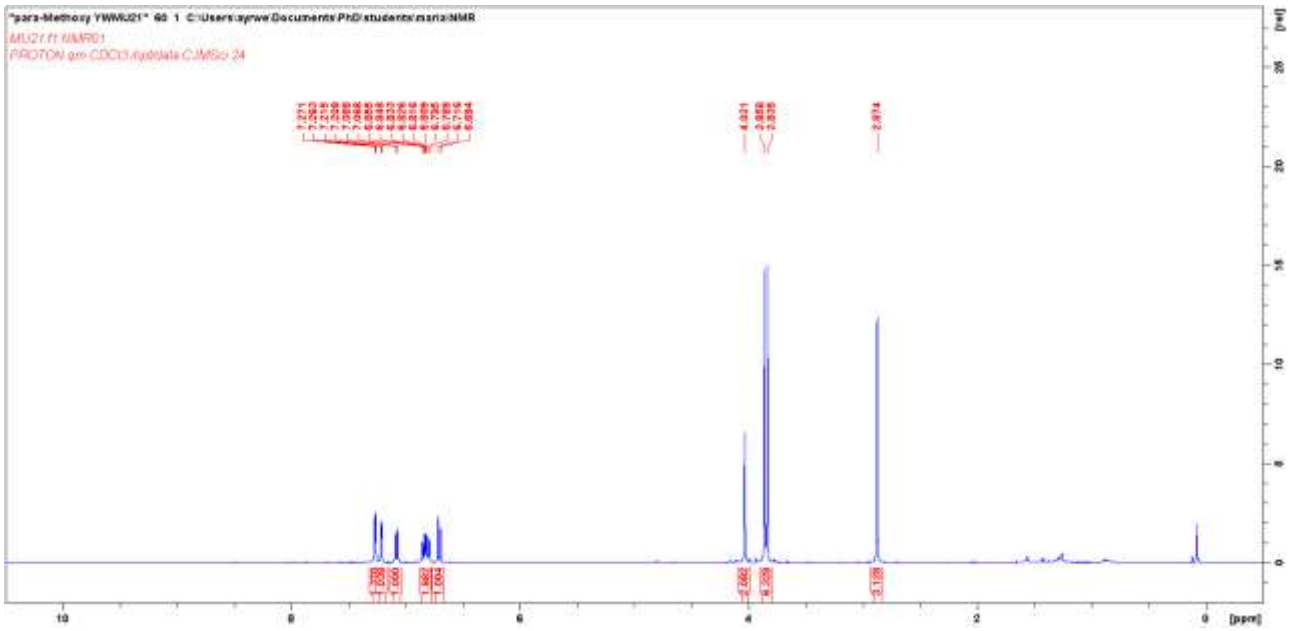


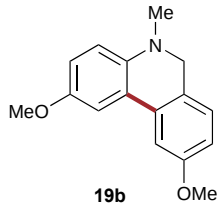
20a OMe ^{13}C NMR (101 MHz, $CDCl_3$)



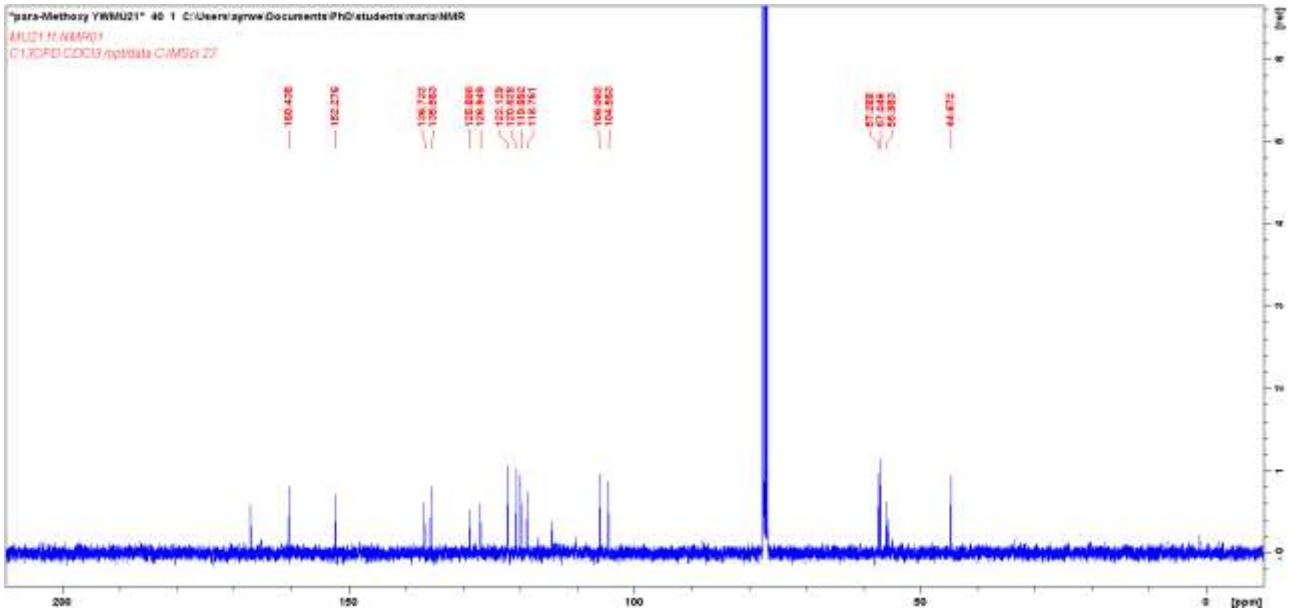


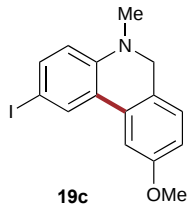
19b ^{1}H NMR (400 MHz, $CDCl_3$)



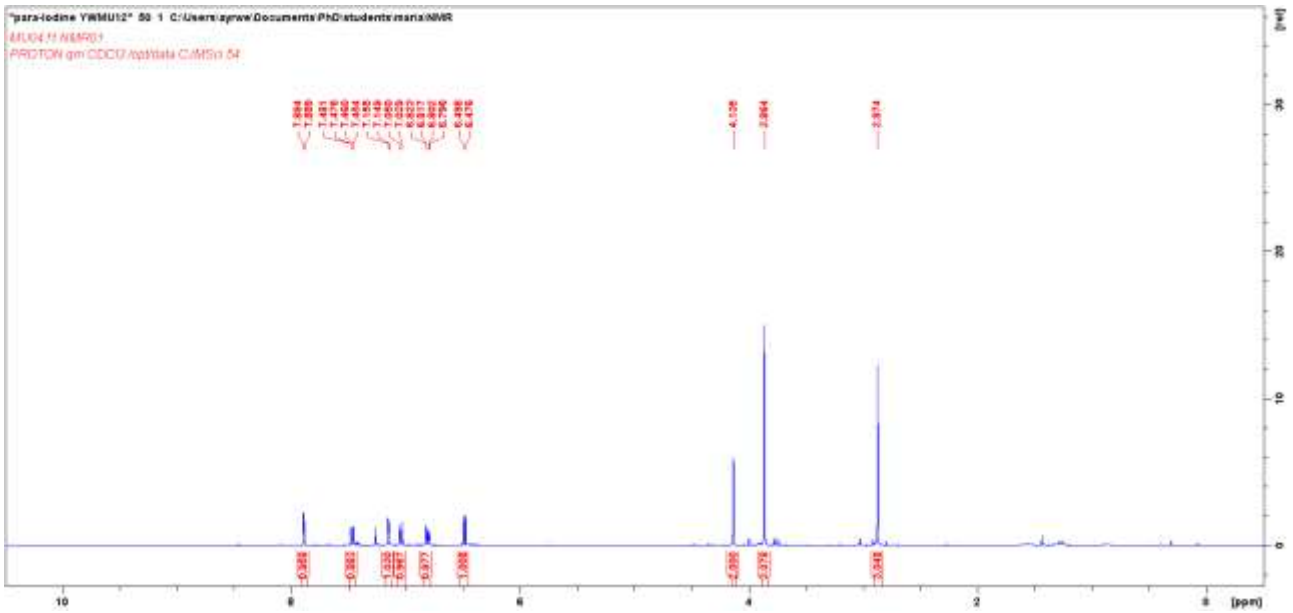


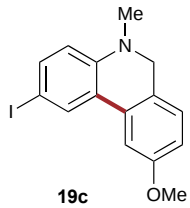
19b ^{13}C NMR (101 MHz, $CDCl_3$)



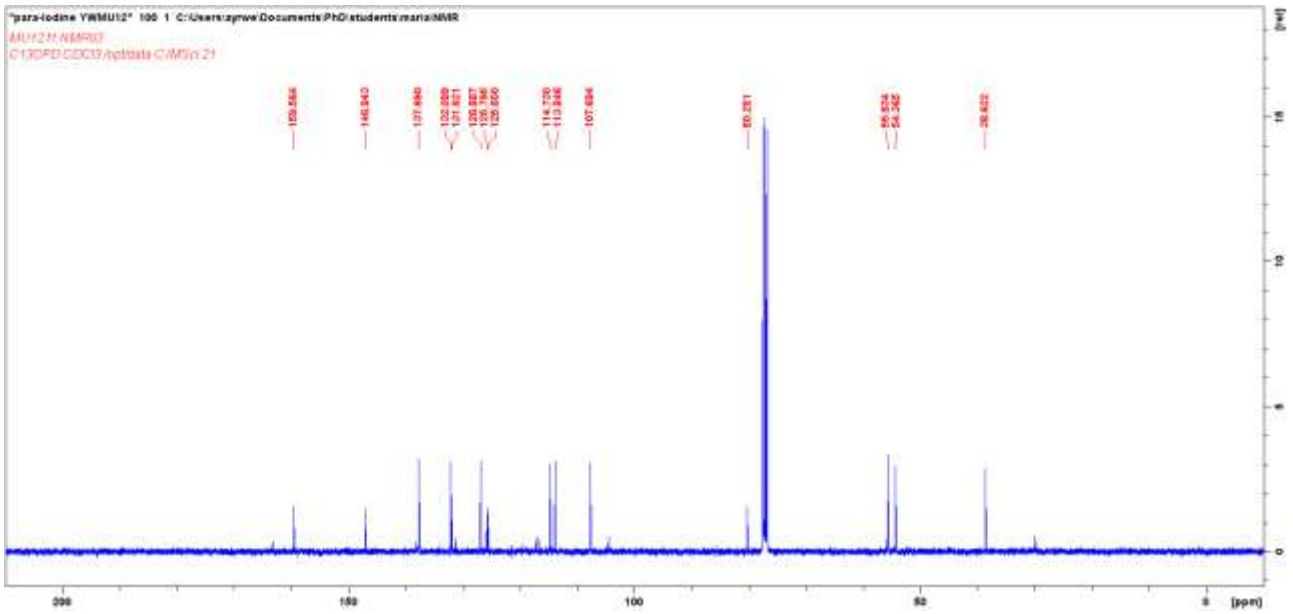


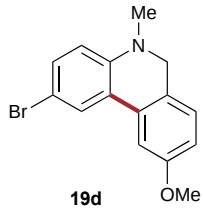
19c ^{1}H NMR (400 MHz, $CDCl_3$)



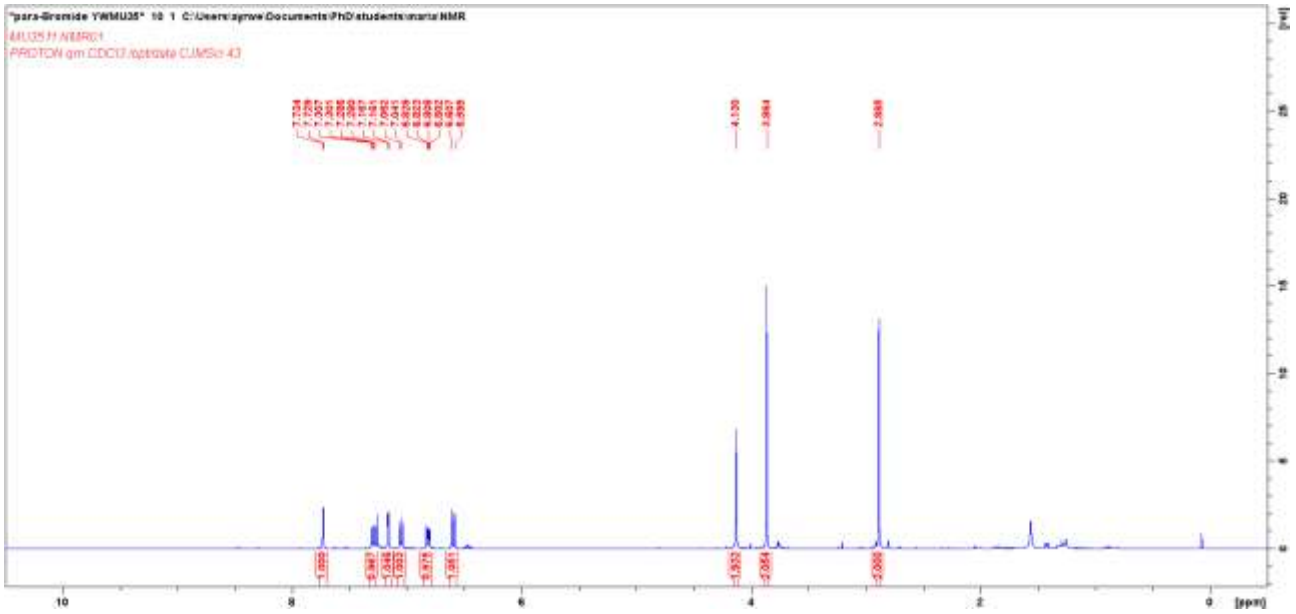


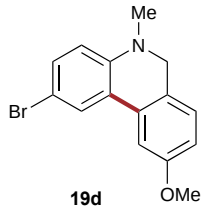
19c ^{13}C NMR (101 MHz, $CDCl_3$)



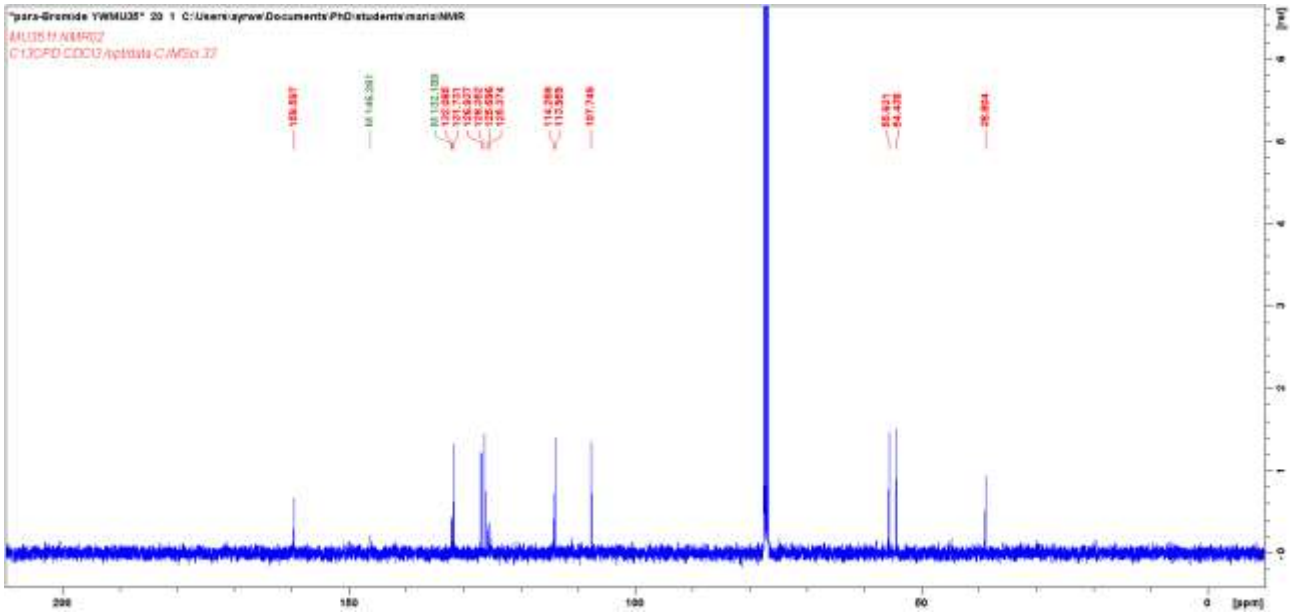


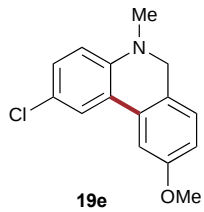
19d ^{1}H NMR (400 MHz, $CDCl_3$)



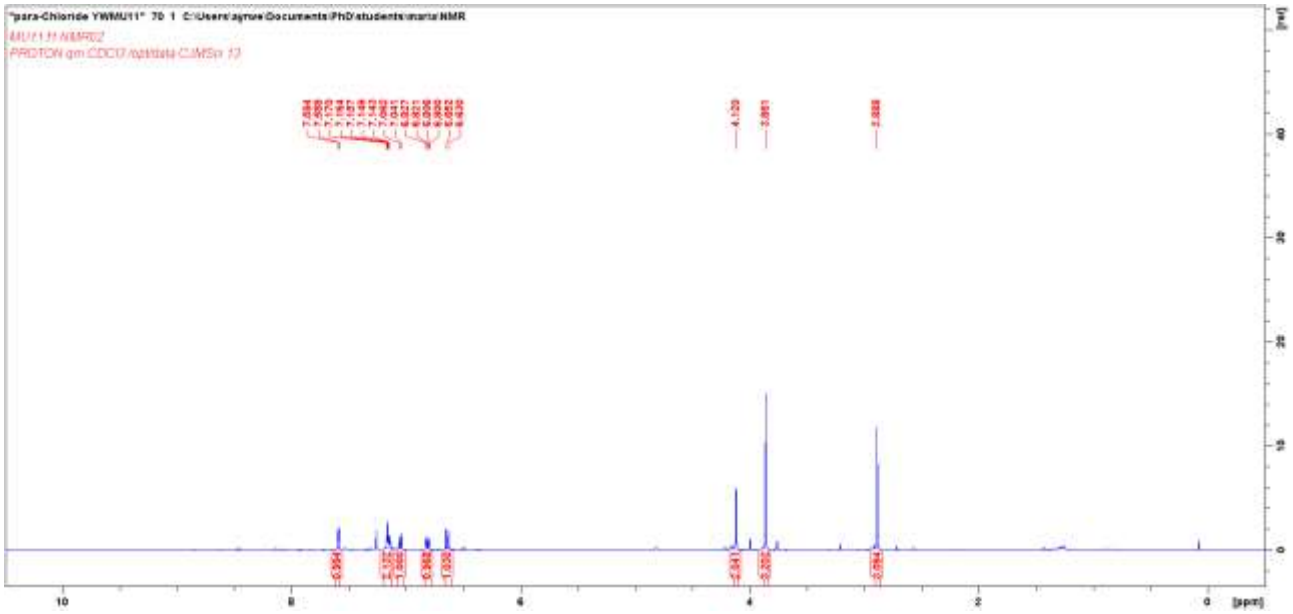


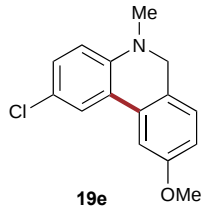
19d ^{13}C NMR (101 MHz, $CDCl_3$)



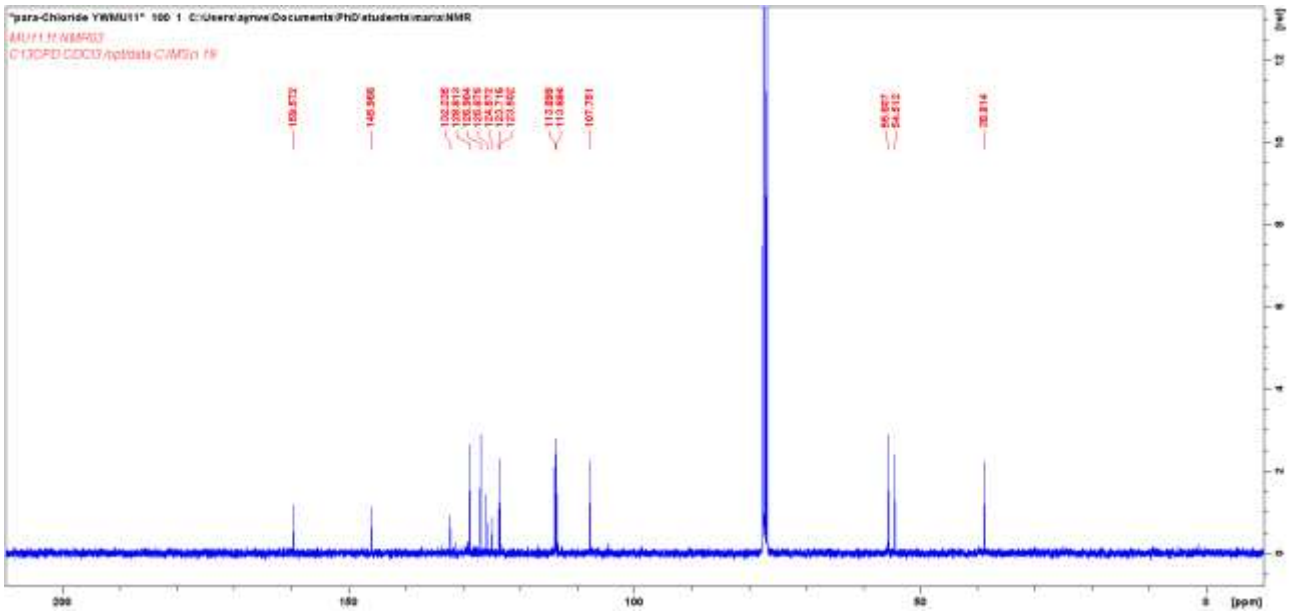


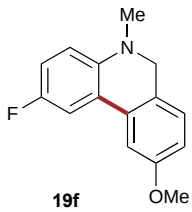
19e ^{1}H NMR (400 MHz, $CDCl_3$)



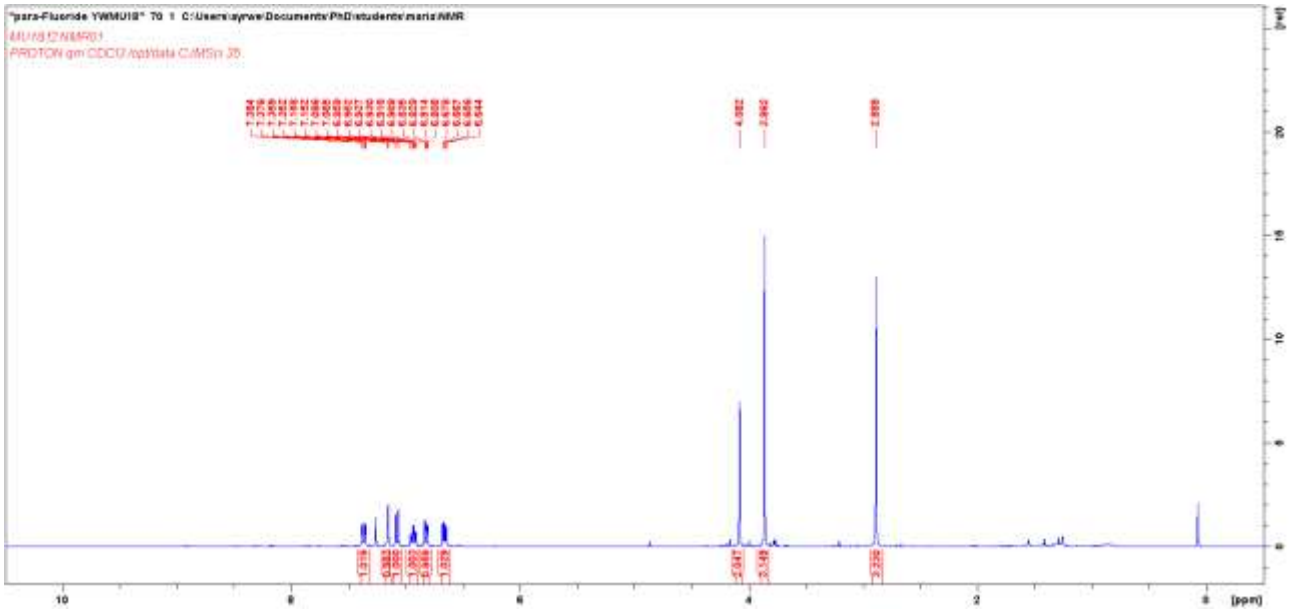


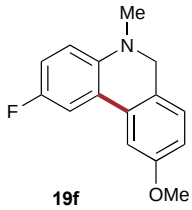
19e ^{13}C NMR (101 MHz, $CDCl_3$)



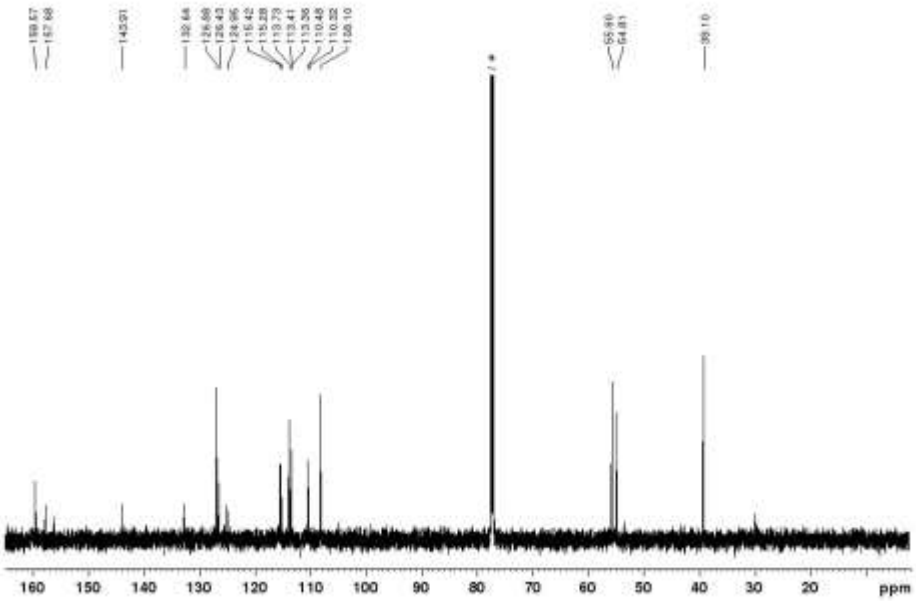


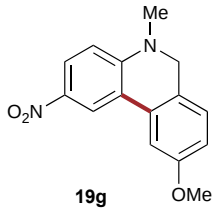
19f ^{1}H NMR (400 MHz, $CDCl_3$)



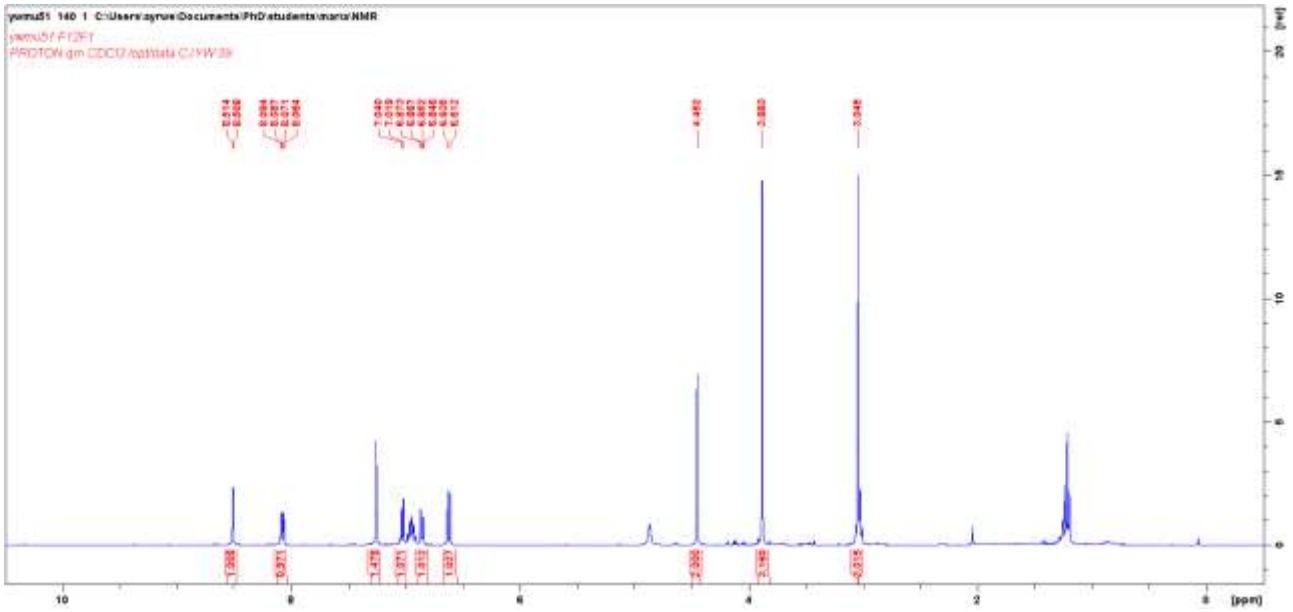


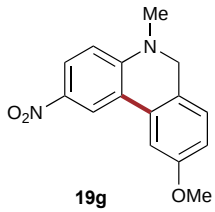
19f ^{13}C NMR (101 MHz, $CDCl_3$)



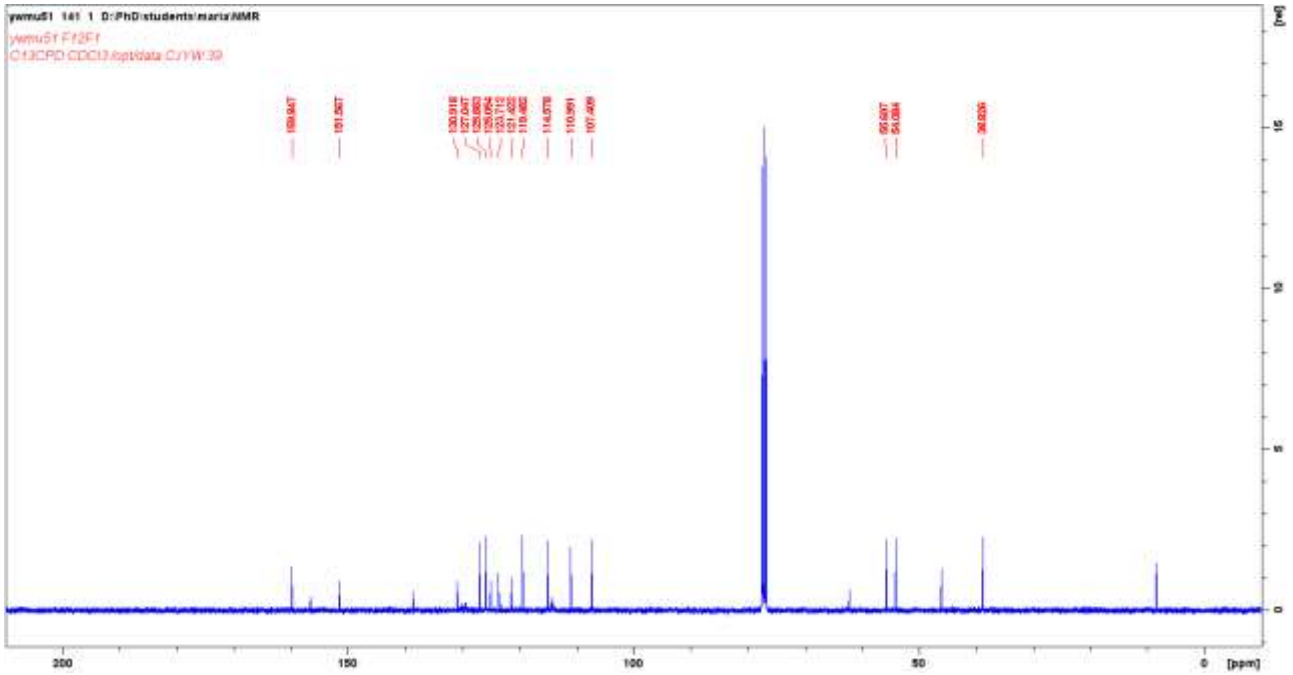


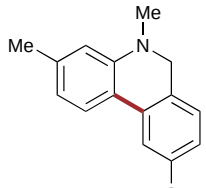
19g ^{1}H NMR (400 MHz, $CDCl_3$)



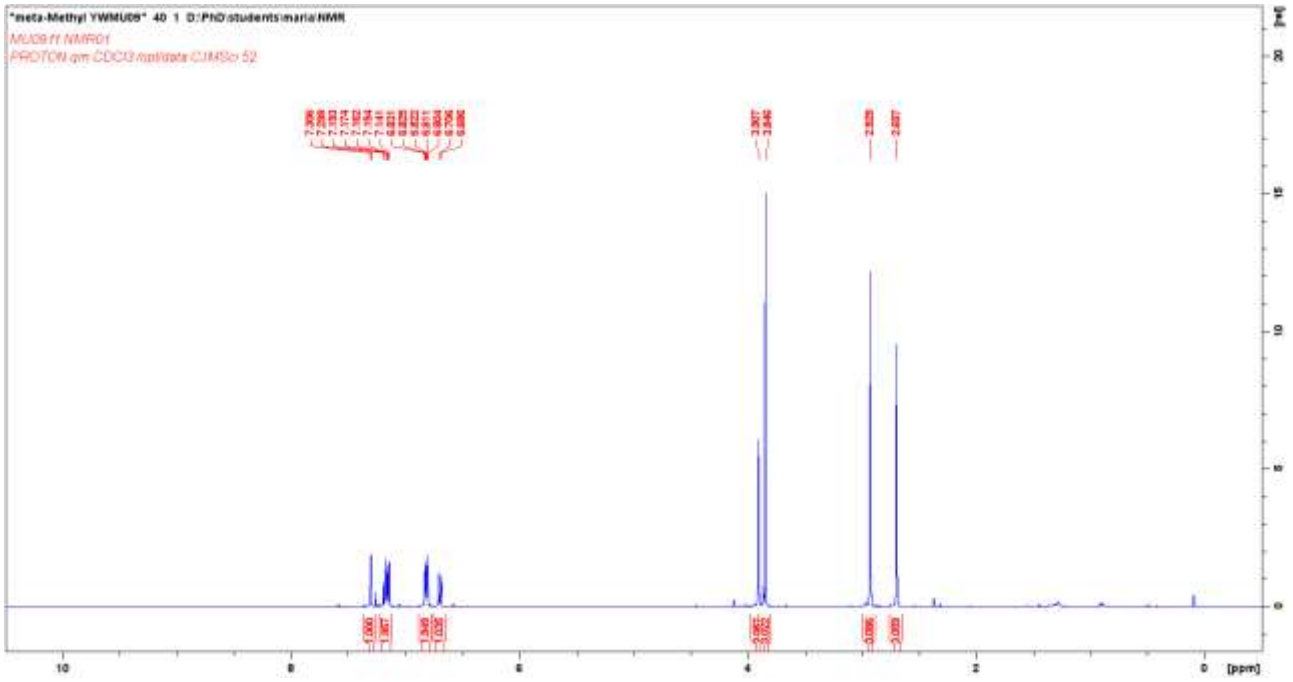


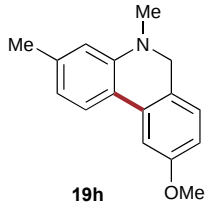
19g ^{13}C NMR (101 MHz, $CDCl_3$)



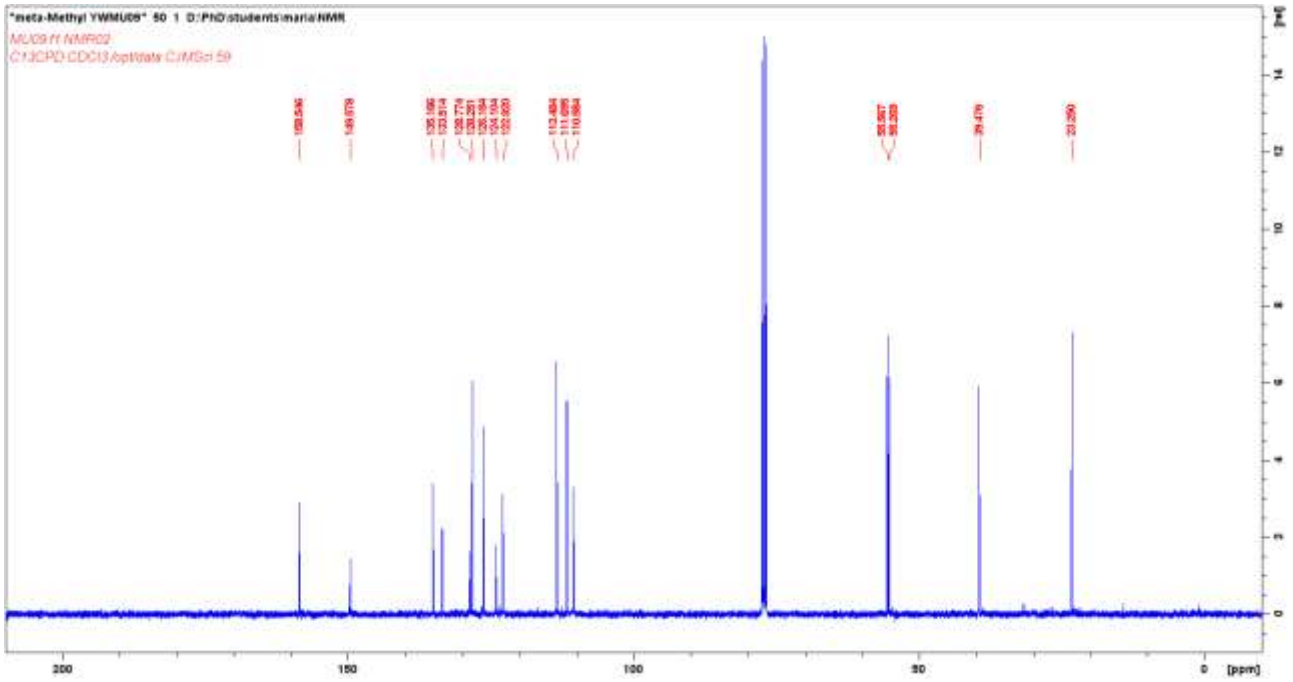


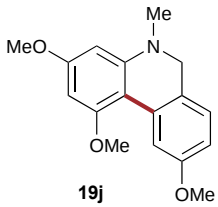
19h ^{1}H NMR (400 MHz, $CDCl_3$)



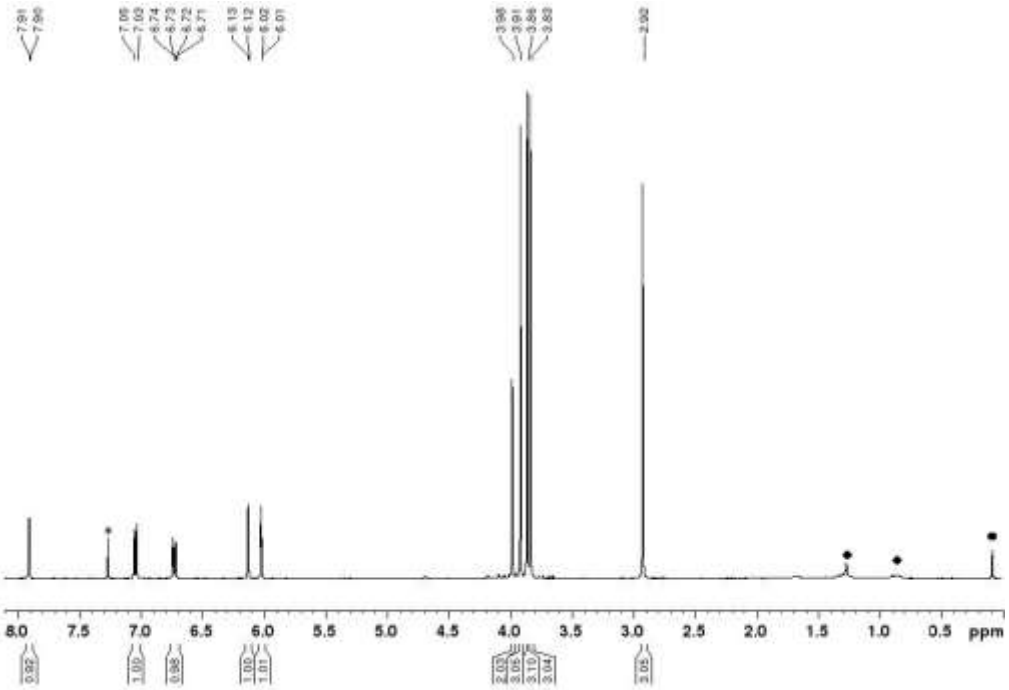


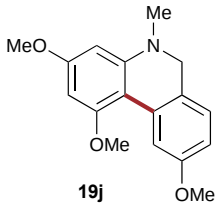
19h ^{13}C NMR (101 MHz, $CDCl_3$)



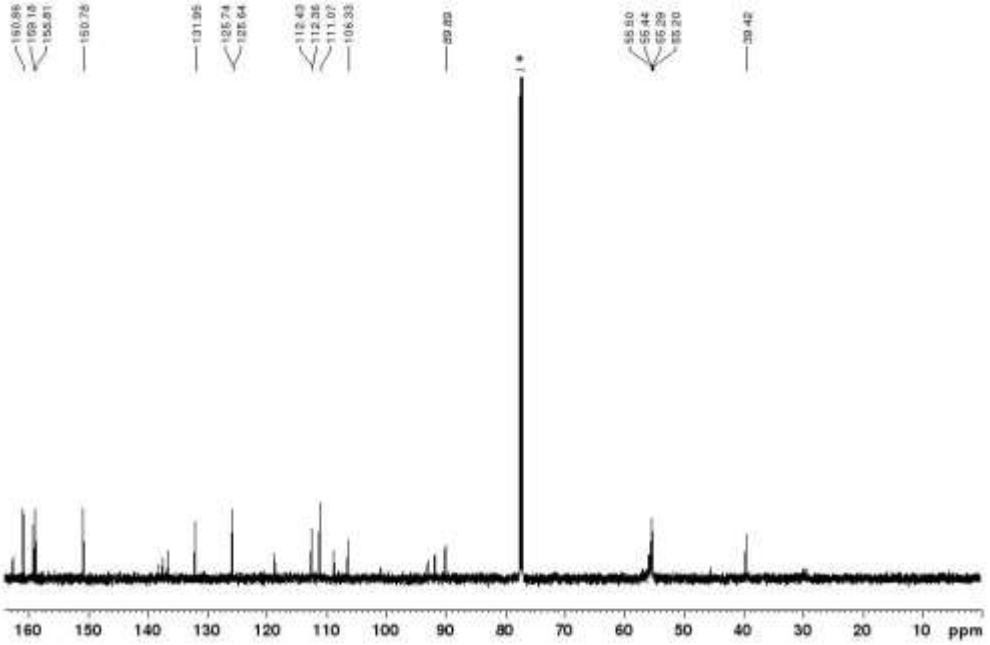


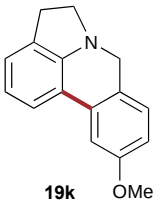
19j ^{1}H NMR (400 MHz, $CDCl_3$)



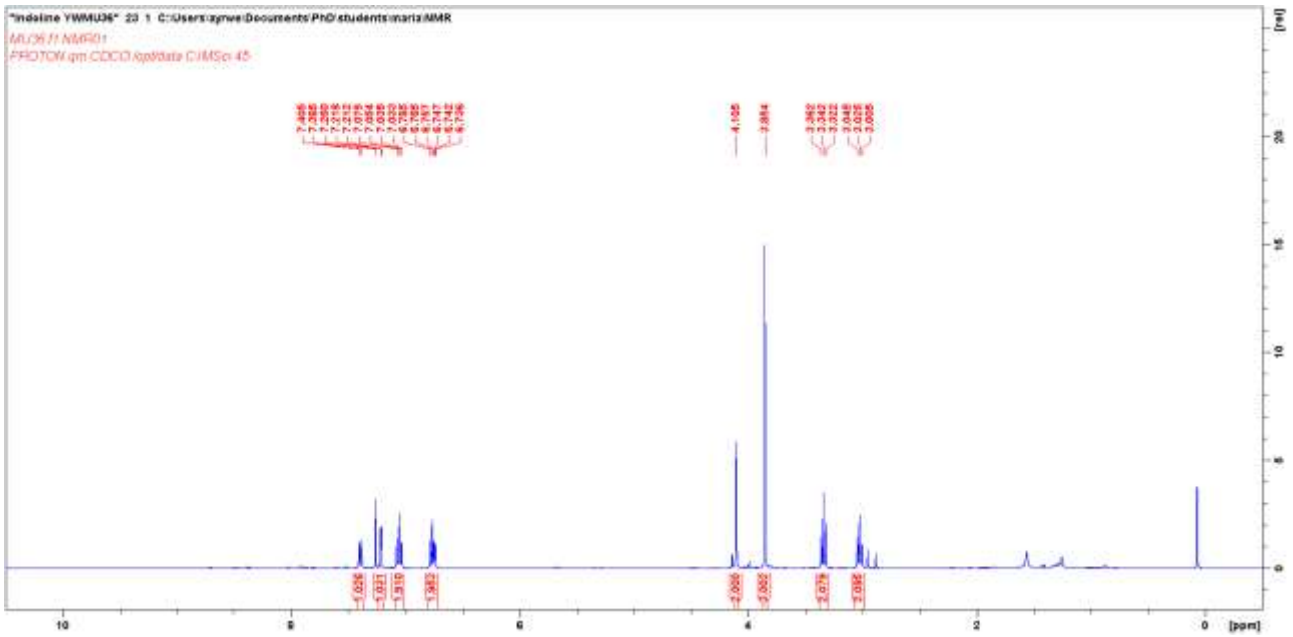


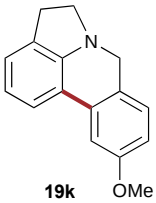
19j ^{13}C NMR (101 MHz, $CDCl_3$)



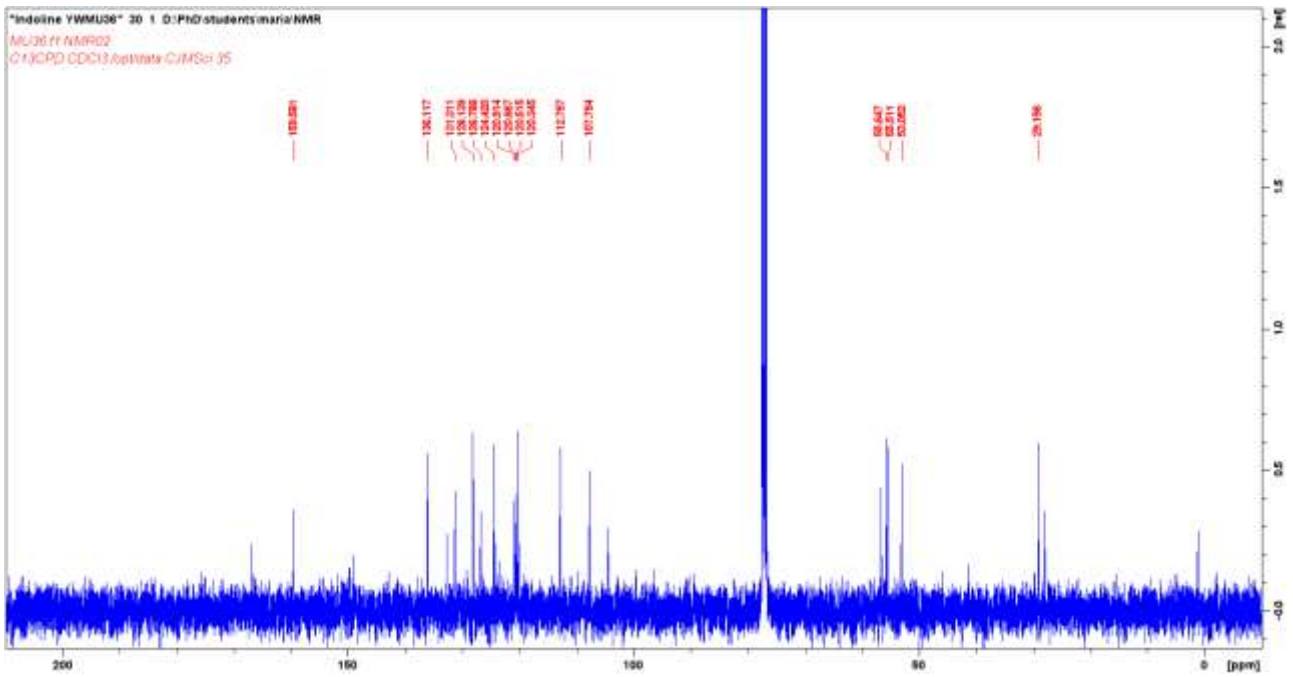


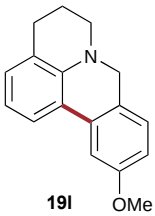
19k ^{1}H NMR (400 MHz, $CDCl_3$)



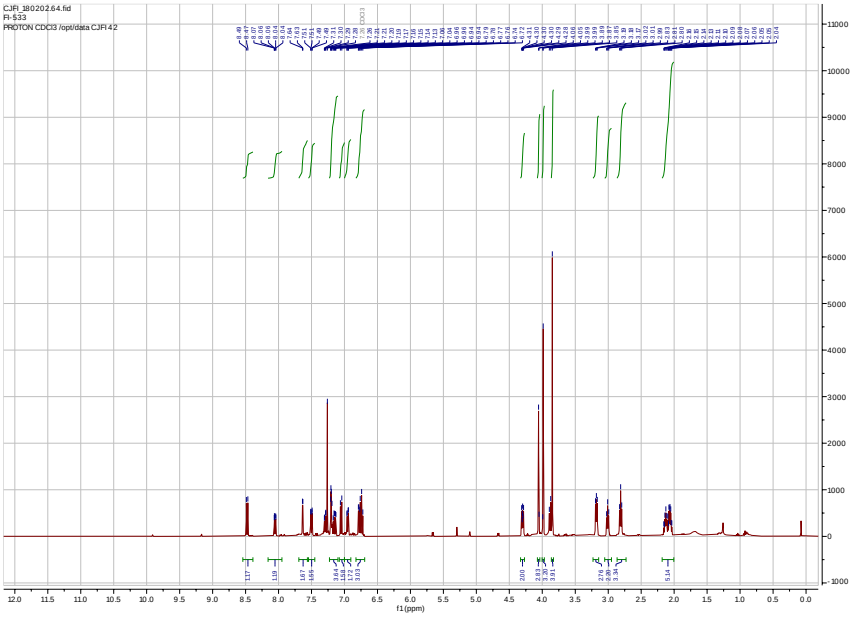


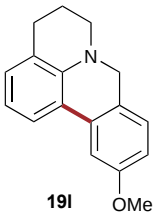
19k ^{13}C NMR (101 MHz, $CDCl_3$)



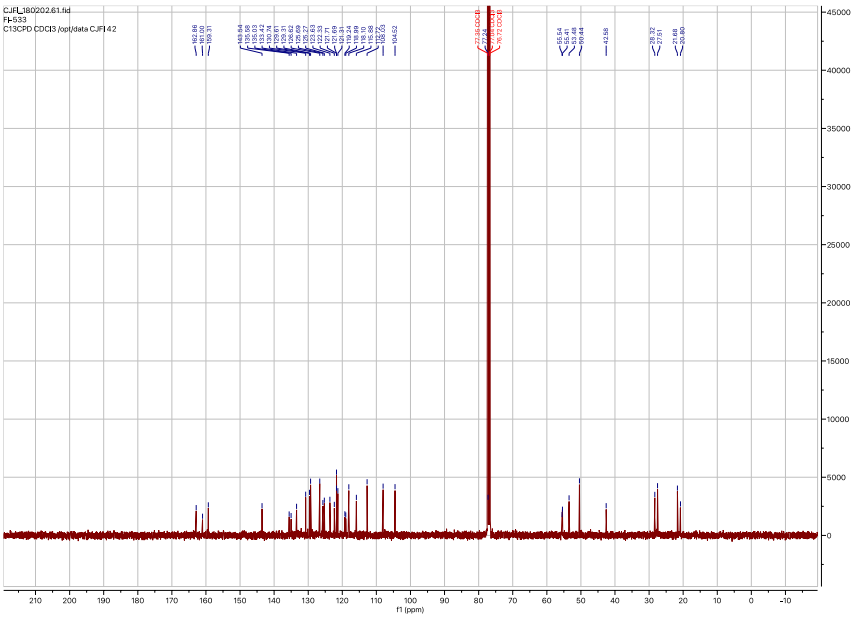


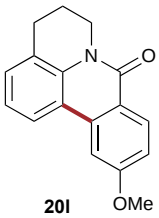
19l OMe ^{1}H NMR (400 MHz, $CDCl_3$) *note dihydrophenanthridine susceptible to aerobic oxidation during purification, isolated as ~1:1.2 mixture of dihydrophenanthridine:phenanthridinone*.



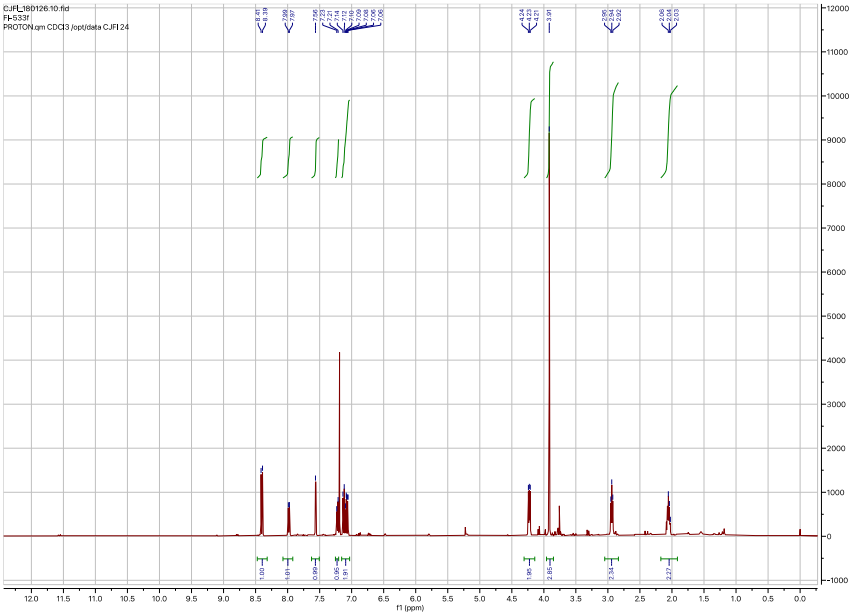


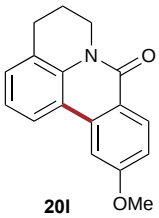
19l OMe ^{13}C NMR (101 MHz, $CDCl_3$) *note dihydrophenanthridine susceptible to aerobic oxidation during purification, isolated as ~1:1.2 mixture of dihydrophenanthridine:phenanthridinone*.



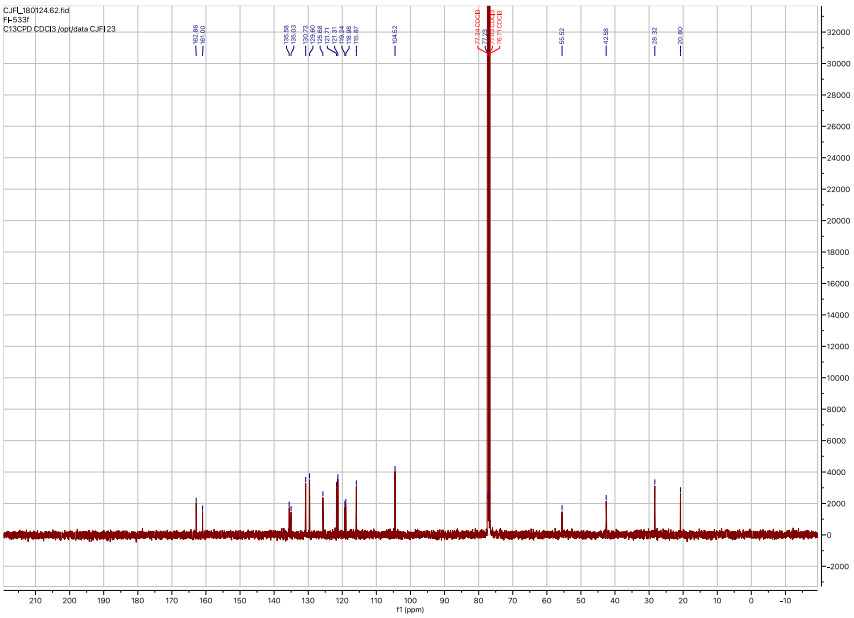


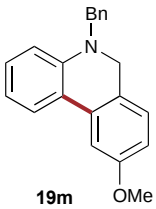
20l OMe ^{1}H NMR (400 MHz, $CDCl_3$)



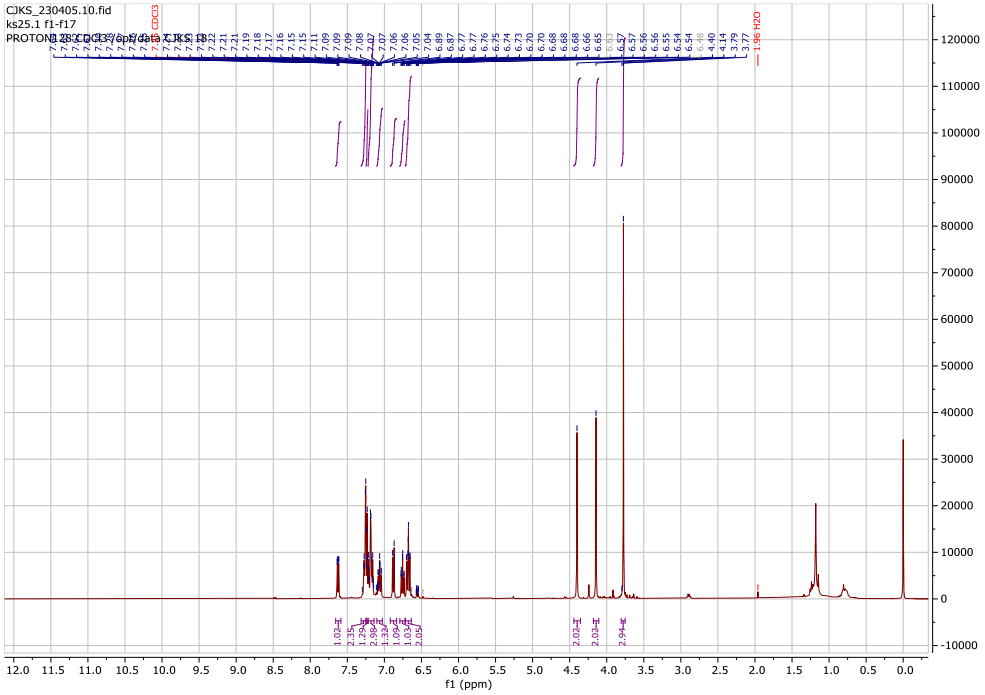


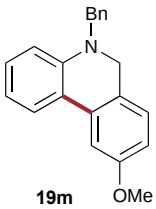
20l OMe ^{13}C NMR (101 MHz, $CDCl_3$)



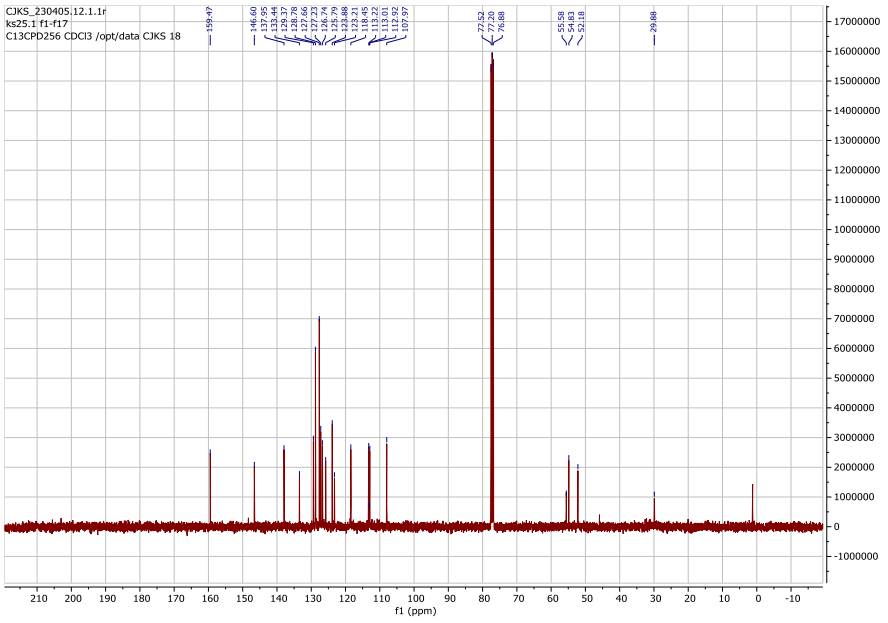


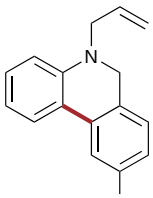
19m ^{1}H NMR (400 MHz, $CDCl_3$)



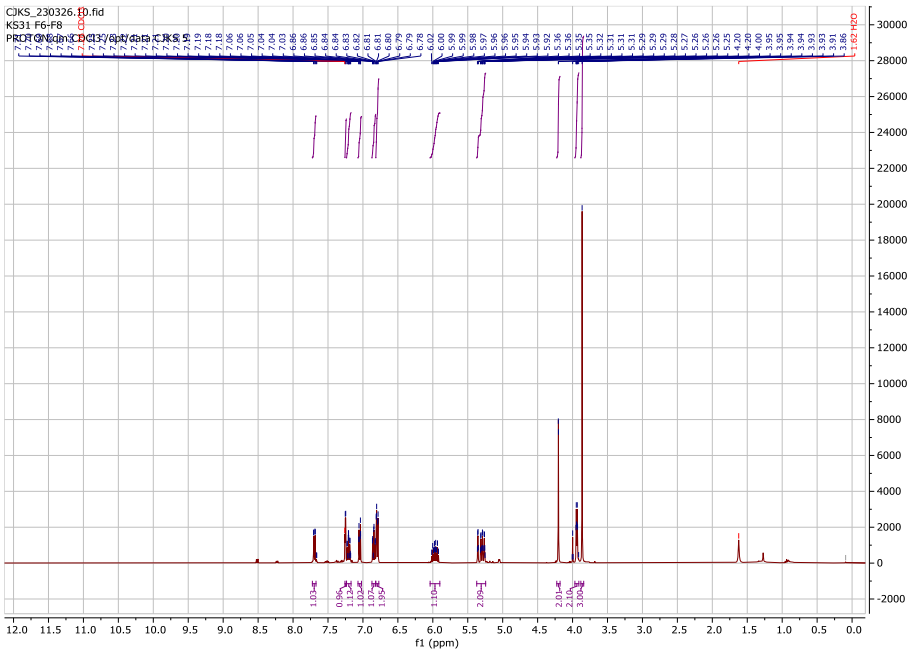


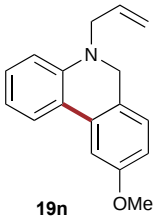
19m ^{13}C NMR (101 MHz, $CDCl_3$)





19n ^{1}H NMR (400 MHz, $CDCl_3$)





19n ^{13}C NMR (101 MHz, $CDCl_3$)