Supplementary Information

Cation Radical-Accelerated Nucleophilic Aromatic Substitution for Amination of Alkoxyarenes

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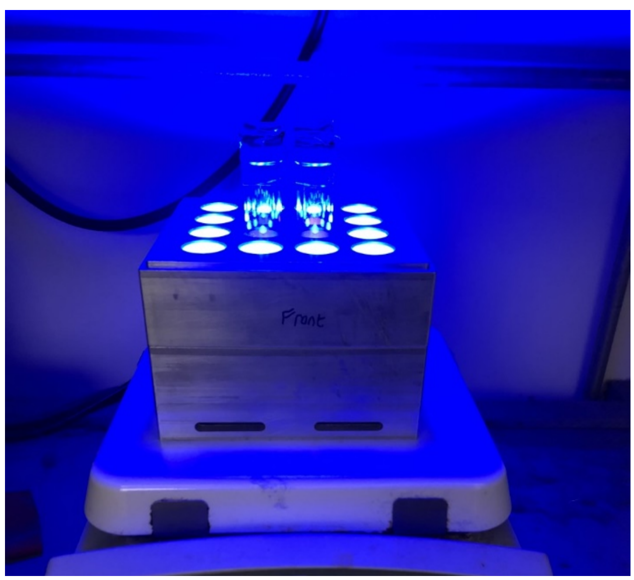
Note from the authors: Due to laboratory shutdowns as a result of COVID-19 the authors were unable to include high resolution mass spectrometry data. This data is now included in this amended Supporting Information.

Table of Contents:

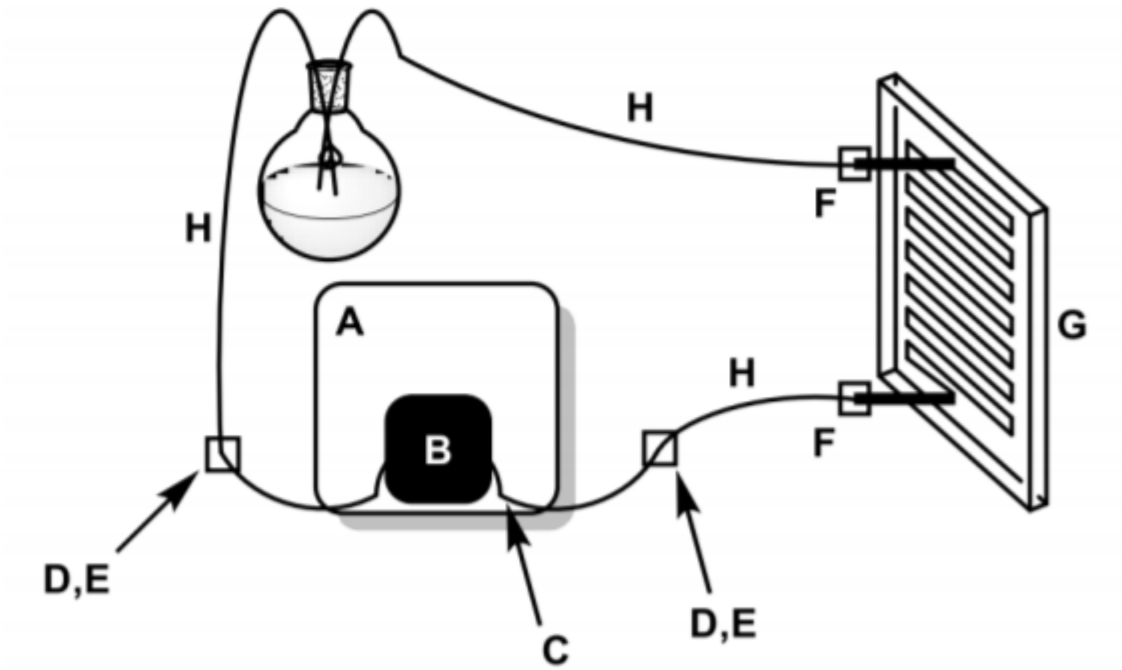
General Reagent Information: Commercially available reagents were purchased from Sigma-Aldrich, Fischer Scientific or TCI Corporation and were used without further purification. Anhydrous DCE and TFE were purchased through Sigma-Aldrich and used as is.

General Analytical Information: Proton and carbon (^{1}H and ^{13}C) magnetic resonance spectra were collected on a Bruker AVANCE III 600 CryoProbe (^{1}H NMR at 600 MHz and ^{13}C NMR at 151 MHz) spectrometer. Unless otherwise noted, spectra are referenced to CDCl3 (^{1}H NMR at 7.26 ppm and ^{13}C at 77.16 ppm) and reported as parts per million. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, ddddd = doublet of doublets of doublets of doublets of doublets, dt = doublet of triplets, ddt = doublet of doublets of triplets, td = triplet of doublets, tt = triplet of triplets, m = multiplet, q = quartet), coupling constants (Hz), and integration Attenuated total reflectance FTIR spectra were recorded on a Bruker Alpha FTIR Spectrometer with the Plantinum ATR attachment. Spectra were averaged over 24 scans with a spectral resolution of 4 cm-1. Data processing was performed using Bruker's OPUS spectroscopy software. High Resolution Mass Spectra (HRMS) were obtained via direct infusion using a Thermo LTQ FT mass spectrometer with positive mode electrospray ionization, via gas chromatography using an Exactive GC gas chromatographic system in positive mode chemical ionization, equipped with a Trace 1300 SSL injector and TriPlus RSH autosampler, or via liquid chromatography using Waters Acquity H-class liquid**.**

General Photoreactor Setup: The photoreactor used was a 16 well SynLED Parallel Reactor (Product # Z742680 at Millipore Sigma). Light reactions set up in 2-dram vials and illuminated from the bottom ~ 1 cm from the base of the vial. The reactor was placed onto a stir plate. The temperature of the SynLED was 33°C.

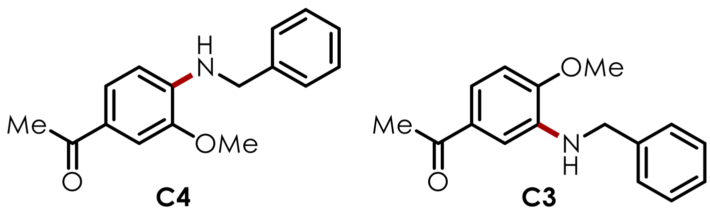


Flow Reactor Setup for 1.0 mmol scale reaction for preparation of compound 7:



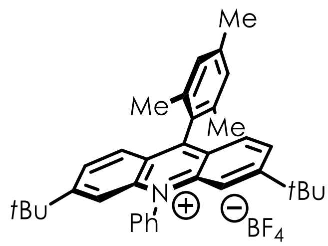
A. Masterflex L/S Variable-Speed Drive (Cole-Parmer # EW-07528-30)
B. Masterflex L/S Rigid PTFE-Tubing Pump Head (Cole-Parmer # EW-77390-00)
C. Masterflex PTFE-tubing 4mm O.D. (Cole-Parmer # EW-77390-50)
D. 4MM PTFE Male NPT Compression Adapter (Cole-Parmer # WU-31321-62)
E. 1/8” O.D. to 1/8” PTFE Female NPT Compression Adapter (Cole-Parmer # EW31320-50)
F. 1/4-28 flangeless fitting/ferrule for 1/8" O.D. tubing (Sigma-Aldrich SUPELCO # 58686)
G. Microreactor (Little Things Factory Gmbh # XXL-ST-02)
H. PTFE Tubing 1/16” I.D., 1/8” O.D. (Cole-Parmer # WU-06605-27)

To a Flame dried 20 mL vial with septum cap was added 3,6-Di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (28.7 mg, 0.050 mmol, 0.05 eq), 3,4-dimethoxyacetophenone (180 mg, 1.00 mmol, 1 eq), benzylamine (214 mg, 2.00 mmol, 218 μL, 2 eq), and 1,2-dicholoethatne (10 mL). The reaction vessel was sparged with nitrogen for 30 minutes with the vial placed in an ice bath to avoid loss of solvent to evaporation. The flow cell was then flushed with nitrogen sparged 1,2-dichloroethane to eliminate air bubbles. Then, the septum cap was pierced and the PTFE tubing (**H**) was inserted and the flow setup was turned on and allowed to pump continuously for 10 minutes to eliminate bubbles and fill the cell. At this point, 2, 455 nm flood lamps (Par38 Royal Blue Aquarium LED lamps Model #6851) were turned on pointing at both sides of the flow cell each 1 centimeter from the cell. It was allowed to run continuously for 24 hours. The flow cell was then flushed with dichloromethane (25 mL) and the reaction mixture was concentration using a rotary evaporator. The crude mixture was purified using column chromatography as a mixture of isomers, 60% EtOAc/Hexanes to afford **compound 7** (164.1 mg, 64% yield, 4:1 C4:C3) as a light orange solid.



7

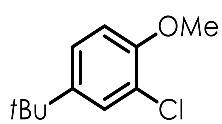
Catalyst and Substrate Synthesis:



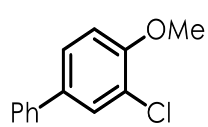
3,6-Di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate was prepared according to literature precedent. Spectral data matched that reported in the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.32 (s, 18H), 1.89 (s, 6H), 2.51 (s, 3H), 7.19 (d, J = 1.2 Hz, 2H), 7.44 (dd, J = 1.5, 0.7 Hz, 2H), 7.83 – 7.74 (m, 6H), 7.94 – 7.90 (m, 1H), 7.94 (s, 1H), 7.99 (td, J = 7.5, 6.7, 1.3 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 20.3, 21.33, 30.2, 36.7, 115.1, 124.0, 127.5, 128.0, 128.3, 128.9, 129.3, 131.6, 131.8, 136.2, 136.9, 140.2, 142.1, 162.2, 163.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -150.85, -154.50.

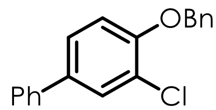
Preparation of Arene Substrates



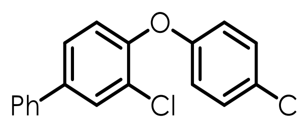
4-(tert-butyl)-2-chloro-1-methoxybenzene (1) was prepared according to a published procedure; spectra data were in agreement with literature values.[2]



3-chloro-4-methoxy-1,1'-biphenyl (3) 2-Chloro-4-phenylphenol (1.69 g, 8.26 mmol, 1.0 eq.) was added to a flame-dried round bottom flask charged with a magnetic stir bar, along with 1.71 g K_2CO_3 (12.4 mmol, 1.5 eq.). The solid reagents were then dissolved in 33 mL (0.33 M) dry acetone under N_2. Iodomethane (0.65 mL, 10.3 mmol, 1.25 eq.) was then added dropwise to the reaction mixture. The reaction was then refluxed overnight. At the end of the reaction, the mixture was cooled before 30 mL of H2O and 30 mL of EtOAc were added. The layers were separated and the aqueous layer was extracted twice with EtOAc (2 x 15 mL). The organic layers were then combined and subsequently washed with 2 M NaOH solution and brine before being dried over sodium sulfate and concentrated to provide a pale solid. The crude product was purified by flash chromatography (20% EtOAc:Hex) to afford a colorless solid (1.71 g, 95% yield). The spectra data were in agreement with literature values.[3]



4-(benzyloxy)-3-chloro-1,1'-biphenyl (4) To a flame dried round bottom flask was added 3-chloro-[1,1'-biphenyl]-4-ol(1.0 g, 4.9 mmol, 1 eq) and K_2CO_3 (2.0 g, 14.7 mmol, 3 eq). DMF (15 ml) was added to the reaction vessel and it was cooled to 0°C. Benzyl chloride (0.68 ml, 5.9 mmol, 1.2 eq) was then added dropwise and then the ice bath was removed and allowed to warm to room temperature for 1 hour. The reaction was then heated to 40°C in an oil bath and stirred for 4 hours. The reaction was allowed to cool and DI water was added. The organic layer was extracted with ethyl acetate (3 x 20 ml). The organic layer was then washed with water (3 x 15 ml), with aqueous Lithium Chloride (3 x 15 ml), and then with 2N HCl (2 x 15 ml). The organic layer was then dried of Na2SO4 and concentrated using rotary evaporator to give a white solid (1.4 g, 98% yield). No further purification was needed and the spectra data were in agreement with literature values.[4]

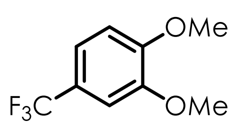


3-chloro-4-(4-chlorophenoxy)-1,1'-biphenyl (5)

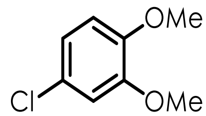
To a flame dried round bottom flask under N_2 was charged, 3-chloro-[1,1'-biphenyl]-4-ol (0.850 g, 1 Eq, 4.15 mmol), 1-chloro-4-iodobenzene (990 mg, 1 Eq, 4.15 mmol), copper(I) iodide (79.1 mg, 0.1 Eq, 415 µmol), tetrabutylammonium bromide (134 mg, 0.1 Eq, 415 µmol)and tripotassium phosphate (1.76 g, 2 Eq, 8.31 mmol) then DMF (2.5 mL)was added. The flask was fitted with a reflux condenser and the mixture heated to 150°C in an oi bath. After 20 h, the mixture was allowed to cool to room temperature and saturated NH_4Cl was added (10 mL). The mixture was extracted with Ethyl Acetate (15 mL x3) then the combined organics were washed with saturated NH_4Cl (10 mL x1), 2M NaOH (10 mL x2), water (10 mL x2), brine (10 mL x2) and dried of Na_2SO_4 and concentrated to give a brown liquid. The crude mixture was purified using column chromatography with a gradient of 0 to 2% ethyl acetate in hexane to give a colorless oil 3-chloro-4-(4-chlorophenoxy)-1,1'-biphenyl (387.7 mg, 1.230 mmol, 29.6 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 – 6.90 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.40 – 7.36 (m, 1H) , 7.52 – 7.43 (m, 3H), 7.59 – 7.54 (m, 2H) 7.70 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 119.0, 121.2, 126.3, 126.7, 127.0, 127.8, 128.4, 128.9, 129.0, 129.4, 129.8, 138.6, 139.1, 151.3, 155.7.

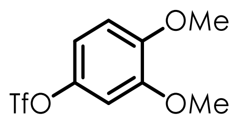
HRMS: m/z calculated for C18H12OCl2 [M+H]+: 315.03435; found 314.02624



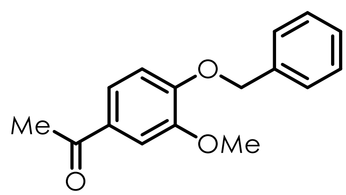
1,2-dimethoxy-4-(trifluoromethyl)benzene (10) was prepared according to a published procedure; spectra data were in agreement with literature values.[5]



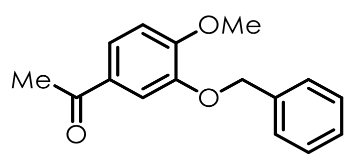
4-chloro-1,2-dimethoxybenzene (11) was prepared according to a published procedure; spectra data were in agreement with literature values.[6]



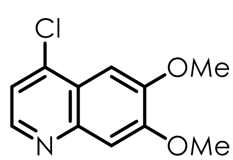
3,4-dimethoxyphenyl trifluoromethanesulfonate (12) was prepared according to a published procedure; spectra data were in agreement with literature values.[7]



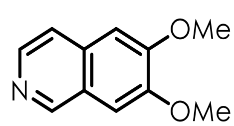
1-(4-(benzyloxy)-3-methoxyphenyl)ethan-1-one (15 & 16) was prepared according to a published procedure; spectra data were in agreement with literature values.[8]



1-(3-(benzyloxy)-4-methoxyphenyl)ethan-1-one (17 & 18) was prepared according to a published procedure; spectra data were in agreement with literature values.[9]



4-chloro-6,7-dimethoxyquinoline (23) was prepared according to a published procedure; spectra data were in agreement with literature values.[10]

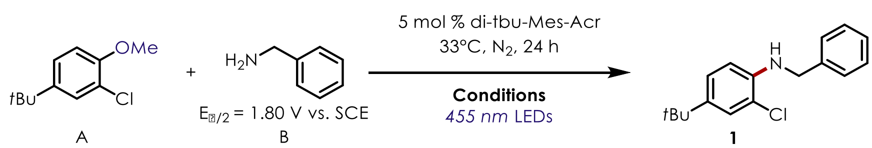


6,7-dimethoxyisoquinoline (24) was prepared according to a published procedure; spectra data were in agreement with literature values.[11]

Procedure for Product Synthesis:

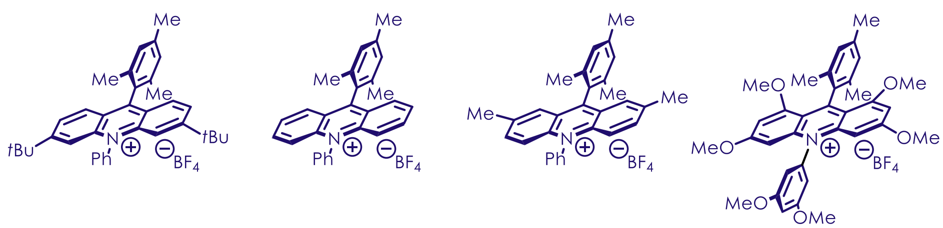
A 2-dram vial with stir bar was charged with 3,6-di-tert-butyl-9-mesityl-N-phenylacridinium (0.005 mmol, 0.05 eq.). The arene was then added (0.100 mmol, 1.0 eq.) followed by the addition of 1.0 mL of dry DCE. Then, the amine was added (0.200 mmol, 2.0 eq.). The reaction vessel was then sealed with a Teflon-lined screw cap, and sparged with N_2 for 10 minutes. After 10 minutes the sparging needles were removed and the caps were wrapped with Teflon tape to keep the anaerobic conditions within the vessel. The vials were stirred with irradiation from 455 nm blue LEDs irradiated from the bottom ~1cm from the vial (photoreactor setup: SynLED parallel reactor, product # Z742680 at Millipore Sigma) for 24 h. The reaction mixtures were then filtered through a silica plug using DCM and solvent was removed. The resultant crude residue was purified using flash chromatography on silica gel to afford the aniline product.

Optimization:

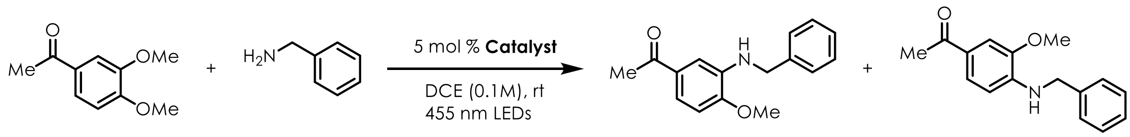


Entry	Solvent	Concentration [M]	Ratio A:B	NMR Yield % (Isolated)
1	1:1 DCE:TFE	0.1	1:1	23
2	2:1 DCE:TFE	0.1	1:1	28
3	1:2 DCE:TFE	0.1	1:1	17
4	TFE	0.1	1:1	13
5	MeCN	0.1	1:1	11
6	DCE	0.1	1:1	50
7	DCE	0.2	1:1	44
8	DCE	0.066	1:1	51
9	DCE	0.05	1:1	54
10	DCE	0.1	1.5:1	51
11	DCE	0.1	2:1	50

12	DCE	0.1	1:2	60 (52)
13	DCE	0.1	1:4	55

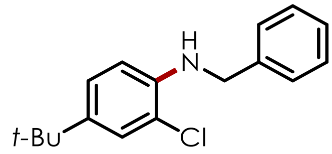


Catalyst A Catalyst B Catalyst C Catalyst D



Entry	**Catalyst**	**Combined Yield NMR (isolated)**
1	Catalyst A	82 (77)
2	Catalyst B	15
3	Catalyst C	50
4	Catalyst D	0

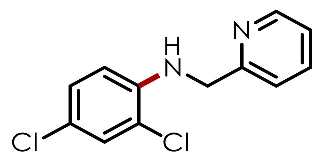
Characterization of Aniline Products:



1

Isolated by column chromatography with a gradient (0 to 5% EtOAc/Hex), as a light-yellow oil, 14.1 mg, 52%.

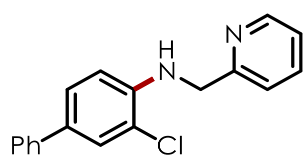
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27 (s, 9H), 4.39 (d, J = 3.5 Hz, 2H), 6.59 (d, J = 8.5 Hz, 1H), 7.12 (dd, J = 8.5, 2.2 Hz, 1H), 7.30 (d, J = 2.4 Hz, 2H), 7.44-7.37 (m, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 31.4, 34.0, 48.1, 111.3, 118.9, 123.3, 124.6, 126.3, 127.3, 127.3, 128.7, 139.1, 140.8, 141.6. **IR (thin film):** 1610, 1514, 1260, 806, 736, 696. **HRMS:** m/z calculated for C17H21NCl $[M+H]^+$: 274.13625; found 274.13611



2

Isolated by column chromatography (40% EtOAc/Hex) to give a tan solid, 5.6 mg, 23%.

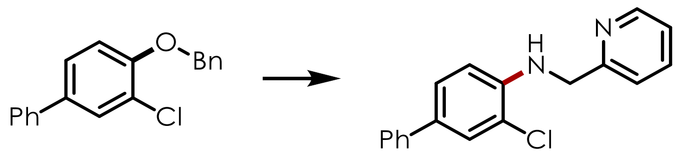
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.50 (d, J = 2.5 Hz, 2H) , 5.43 (s, 1H), 6.52 (d, J = 8.7 Hz, 1H) , 7.06 (dd, J = 8.7, 2.4 Hz, 1H), 7.21 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 7.28 (d, J = 2.4 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.66 (td, J = 7.6, 1.8 Hz, 1H), 8.68 – 8.49 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 49.0, 112.1, 119.7, 121.3, 121.5, 122.4, 127.8, 128.8, 136.8, 142.4, 149.4, 157.4. **IR (thin film):** 1592, 1505, 1322, 799, 754. **HRMS:** m/z calculated for C12H11N2Cl2 $[M+H]^+$: 253.02993; found 253.02982



3

Isolated by column chromatography (40% EtOAc/Hex) to give a tan solid, 14.2 mg, 48%.

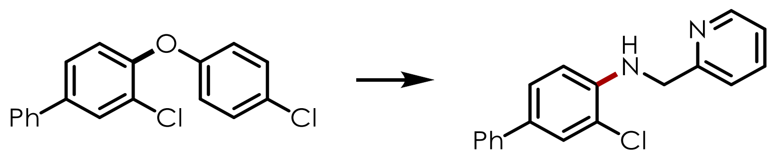
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.58 (d, J = 5.0 Hz, 2H), 5.47 (s, 1H), 6.68 (d, J = 8.4 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.30 – 7.26 (m, 1H), 7.37 – 7.34 (m, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.57 (d, J = 2.1 Hz, 1H), 7.67 (td, J = 7.7, 1.8 Hz, 1H), 8.63 (d, J = 4.6 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 49.0, 111.8, 119.8, 121.3, 122.3, 126.3, 126.4, 126.6, 127.7, 128.8, 130. 8, 136.8, 140.0, 142.9, 149.4, 157.9. **IR (thin film):** 1606, 1523, 1488, 1043, 756, 696. **HRMS:** m/z calculated for C18H16N2Cl1 $[M+H]^+$ 295.10020; found 295.10020.



4

Isolated by column chromatography using a gradient of (40-60% EtOAc/Hex) to give a tan solid, 7.5 mg, 25%.

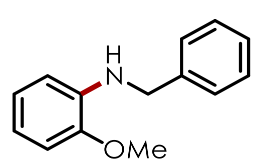
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.58 (d, J = 5.0 Hz, 2H), 5.47 (s, 1H), 6.68 (d, J = 8.4 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.30 – 7.26 (m, 1H), 7.37 – 7.34 (m, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.57 (d, J = 2.1 Hz, 1H), 7.67 (td, J = 7.7, 1.8 Hz, 1H), 8.63 (d, J = 4.6 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 49.0, 111.8, 119.8, 121.3, 122.3, 126.3, 126.4, 126.6, 127.7, 128.8, 130. 8, 136.8, 140.0, 142.9, 149.4, 157.9. **IR (thin film):** 1606, 1523, 1488, 1043, 756, 696. **HRMS:** m/z calculated for C18H16N2Cl1 $[M+H]^+$ 295.10020; found 295.10020.



5

Isolated by column chromatography using a gradient of (40-60% EtOAc/Hex) to give a tan solid, 7.8 mg, 26%.

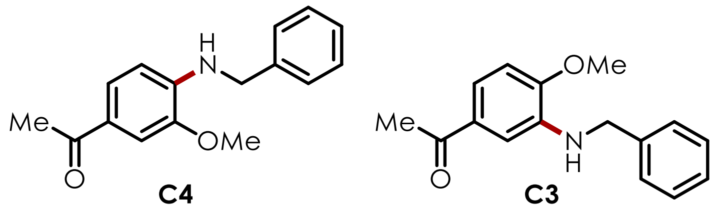
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.58 (d, J = 5.0 Hz, 2H), 5.47 (s, 1H), 6.68 (d, J = 8.4 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.30 – 7.26 (m, 1H), 7.37 – 7.34 (m, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.57 (d, J = 2.1 Hz, 1H), 7.67 (td, J = 7.7, 1.8 Hz, 1H), 8.63 (d, J = 4.6 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 49.0, 111.8, 119.8, 121.3, 122.3, 126.3, 126.4, 126.6, 127.7, 128.8, 130. 8, 136.8, 140.0, 142.9, 149.4, 157.9. **IR (thin film):** 1606, 1523, 1488, 1043, 756, 696. **HRMS:** m/z calculated for C18H16N2Cl1 $[M+H]^+$ 295.10020; found 295.10020.



6

Isolated by column chromatography (30% EtOAc/Hex), as a light-yellow oil, 6.1 mg, 28%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (s, 3H), 4.36 (s, 2H), 4.63 (s, 1H), 6.60 (dd, J = 7.8, 1.5 Hz, 1H), 6.68 (td, J = 7.7, 1.5 Hz, 1H), 6.79 (dd, J = 8.0, 1.3 Hz, 1H), 6.84 (td, J = 7.6, 1.4 Hz, 1H), 7.28 (d, J = 7.3 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.42 – 7.38 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 48.0, 55.4, 109.4, 110.0, 116.6, 121.3, 127.1, 127.5, 128.6, 138.1, 139.6, 146.8. **IR (thin film):** 2601, 1510, 1221, 1027, 734. **HRMS:** m/z calculated for C14H16N1O1 $[M+H]^+$ 214.12319; found 214.12327.



C4 **C3**

7

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a white crystalline solid 19.2 mg, 77%.

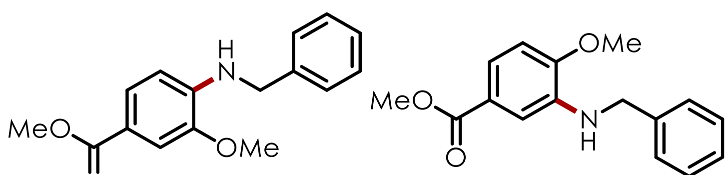
C4

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.51 (s, 3H), 3.91 (s, 3H), 4.44 (d, J = 5.7, 2H), 5.21 (bs, 1H), 6.50 (d, J = 8.2 Hz, 1H), 7.33-7.27 (m, 1H), 7.40-7.34 (m, 4H), 7.45 (d, J = 1.8 Hz, 1H), 7.50 (dd, J = 8.2, 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 47.3, 55.6, 107.6, 107.8, 124.9, 126.1, 127.4, 127.5, 127.8, 128.7, 128.8, 138.4, 142.6, 146.1, 196.6. **HRMS:** m/z calculated for C16H18N1O2 [M+H]$^+$ 256.13375; found 256.13392.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.51 (s, 3H), 4.39 (d, J = 4.3 Hz, 2H), 4.62 (bs, 1H), 6.78 (d, J = 8.3 Hz, 1H), 7.23 (d, J = 2.1 Hz, 1H), 7.29 (m, 2H), 7.40-7.33 (m, 5H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.4, 48.0, 55.7, 108.2, 108.7, 126.1, 127.5, 127.8, 128.7, 138.4, 142.6, 146.1, 197.7. **HRMS:** m/z calculated for C16H18N1O2 [M+H]$^+$ 256.13375; found 256.13392.

IR (thin film) 1661, 1593, 1531, 1276, 1026



C4 **C3**

8

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a white solid 19.2 mg, 71%.

C4

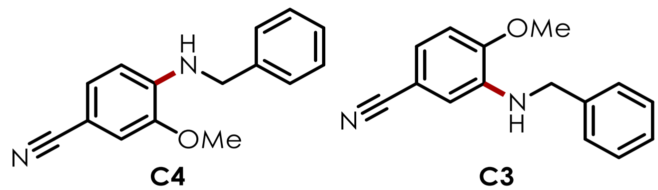
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.90 (s, 3H), 4.41 (d, J = 5.2 Hz, 2H), 5.05 (t, J = 7.0 Hz, 1H), 6.53 (d, J = 8.3 Hz, 1H), 7.29 (m, 1H), 7.35 (d, J = 4.4 Hz, 4H), 7.42 (d, J = 1.8 Hz, 1H), 7.59 (dd, J = 8.3, 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 47.4, 51.7, 55.6, 108.2, 109.8, 117.6, 124.6, 127.5, 127.8, 128.7, 128.8, 138.5, 142.2, 145.7, 167.5. **HRMS:** m/z calculated for C16H18N1O3 [M+H]$^+$ 272.12867; found 272.12842.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.89 (s, 3H), 4.38 (d, J = 5.3 Hz, 2H), 4.58 (bs, 1H), 6.78 (d, J = 8.4 Hz, 1H), 7.29 (m, 1H), 7.38-7.33 (m, 4H), 7.39 (s, 1H), 7.45 (dd, J = 8.3 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$)

δ 47.4, 51.7, 55.6, 108.2, 109.8, 117.6, 124.6, 127.5, 127.8, 128.7, 128.8, 138.5, 142.2, 145.7, 167.5. **HRMS:** m/z calculated for C16H18N1O3 $[M+H]^+$ 272.12867; found 272.12842.

IR (thin film): 1702, 1600, 1433, 1206, 764



9

Isolated by column chromatography as a mixture of isomers with a gradient (50-60% EtOAc/Hex), as a light green oil 16.2 mg, 62%.

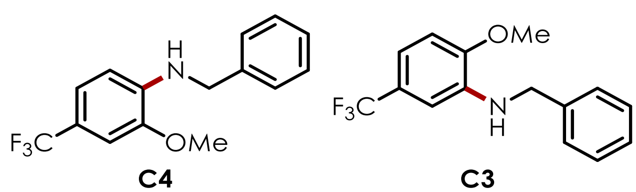
<u>**C4**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.87 (s, 3H), 4.40 (d, J = 5.6 Hz, 2H), 5.17 (bs, 1H), 6.50 (d, J = 8.2 Hz, 1H), 6.93 (s, 1H), 7.16 (dd, J = 8.2, 1.7 Hz, 1H), 7.46-7.27 (m, 5H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 47.2, 55.7, 97.8, 108.6, 111.6, 127.3, 127.3, 127.6, 128.8, 138.0, 141.9, 145.9. **HRMS:** m/z calculated for C15H16N2O $[M+H]^+$ 239.11844; found 239.11849.

<u>**C3**</u>

^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.87 (s, 3H), 4.34 (d, J = 5.5 Hz, 2H), 4.80 (bs, 1H), 6.72 (d, J = 1.9 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 7.01 (dd, J = 8.3, 1.9 Hz 1H), 7.46-7.27 (m, 5H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 47.2, 55.7, 97.8, 108.6, 111.6, 127.3, 111.6, 127.3, 127.6, 128.8, 138.0, 141.9, 145.9. **HRMS:** m/z calculated for C15H16N2O $[M+H]^+$ 239.11844; found 239.11849.

IR (thin film): 2924, 1598, 1495, 1267, 1033



10

Isolated by column chromatography as a mixture of isomers with a gradient (0-5% EtOAc/Hex), as a light green oil 13.7 mg, 49%.

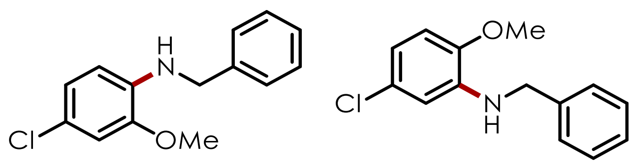
<u>**C4**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.9 (s, 3H), 4.40 (d, J = 5.4 Hz, 2H), 4.96 (t, J = 5.8 Hz, 1H), 6.55 (d, J = 8.2 Hz, 1H), 6.97-6.93 (m, 1H), 7.10 (dd, J = 8.2, 2.0 Hz 1H), 7.33-7.27 (m, 1H), 7.40- 7.34 (m, 5H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 47.5, 55.6, 108.5, 118.9, 127.4, 127.4, 127.5, 127.7, 128.8, 138.2, 138.7, 146.1. **HRMS:** m/z calculated for C15H15N1O1F3 $[M+H]^+$ 282.11057; found 282.11069.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.89 (s, 3H), 4.36 (d, J = 4.3 Hz, 2H), 4.71 (s, 1H), 6.79 (d, J = 6.3 Hz, 1H), 6.96 (dd, J = 2.1, 1.0 Hz, 1H), 7.10 (ddd, J = 8.2, 2.0, 1.0 Hz, 1H), 7.33-7.27 (m, 1H), 7.4- 7.34 (m, 5H). **^{13}C NMR** (151 MHz, $CDCl_3$) 31.4, 47.9, 55.6, 105.8, 108.5, 118.9, 127.4, 127.7, 138.2, 138.7, 140.7, 148.9. **HRMS:** m/z calculated for C15H15N1O1F3 $[M+H]^+$ 282.11057; found 282.11069.

IR (thin film) 1613, 1532, 1324, 1107, 1029



C4 **C3**

11

Isolated by column chromatography as a mixture of isomers with a gradient of (30-40% EtOAc/Hex) using fine silica gel, as a brown oil, 11.5 mg, 46%.

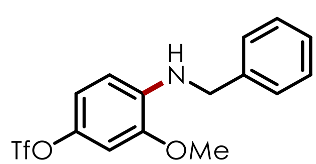
C4

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.84 (s, 3H), 4.33 (s, 2H), 4.59 (s, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 2.2 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.40 – 7.33 (m, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 55.7, 111.0, 115.2, 120.7, 122.8, 129.0, 129.8, 134.5, 134.8, 147.7, 192.5. **HRMS:** m/z calculated for C14H15N1O1Cl1 $[M+H]^+$ 248.08422; found 248.08441.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.83 (s, 3H), 4.31 (s, 2H), 4.66 (s, 1H), 6.54 (d, *J* = 2.3 Hz, 1H), 6.61 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.35 (d, *J* = 5.7 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 55.7, 111.0, 115.2, 120.7, 122.8, 129.0, 129.8, 134.5, 134.8, 147.7, 192.5. **HRMS:** m/z calculated for C14H15N1O1Cl1 $[M+H]^+$ 248.08422; found 248.08441.

IR (thin film): 2595, 1503, 1226, 1027, 877

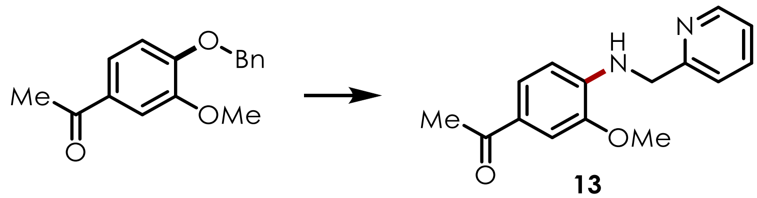


12

Isolated by column chromatography with a gradient of (0-15% EtOAc/Hex), as a green oil, 9.8 mg, 25%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 (s, 3H), 4.35 (s, 2H), 4.72 (s, 1H), 6.48 (d, J = 8.7 Hz, 1H), 6.66 (d, J = 2.7 Hz, 1H), 6.73 (dd, J = 8.7, 2.7 Hz, 1H), 7.29 (dq, J = 5.3, 3.9 Hz, 1H), 7.36 (d, J = 4.5 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 47.8, 55.8, 103.4, 108.7, 113.5, 127.5, 128.8, 138.0, 138.7, 140.1, 146.8. **HRMS:** m/z calculated for C15H15N1O4S1F3 $[M+H]^+$ 362.06739; found 362.06783.

IR (thin film): 1600, 1519, 1414, 1205, 1138, 936

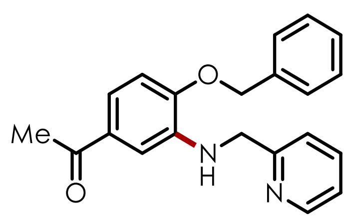


13

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a white solid, 11.8 mg, 46%.

^{1}H NMR (600 MHz, Chloroform-d) δ 8.67 – 8.54 (d, 1H), 7.65 (td, J = 7.6, 1.8 Hz, 1H), 7.49 (dd, J = 8.3, 1.8 Hz, 1H), 7.45 (d, J = 1.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.23 – 7.16 (m, 1H), 6.48 (d, J = 8.2 Hz, 1H), 5.82 (t, J = 5.8 Hz, 1H), 4.56 (d, J = 5.6 Hz, 2H), 3.94 (s, 3H), 2.51 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.5, 157.6, 149.4, 146.4, 142.4, 136.8, 126.3, 124.8, 122.3, 121.4, 107.9, 107.8, 55.7, 48.4, 25.9. **HRMS:** m/z calculated for C15H17N2O2 $[M+H]^+$ 257.12900; found 257.12902.

IR (thin film): 1657, 1592, 1532, 1278, 1032

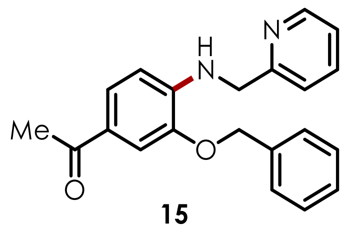


14

Isolated by column chromatography (40% EtOAc/Hex) to give a white solid, 4.4 mg, 14%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (dt, J = 4.0, 0.9 Hz, 1H), 7.67 (td, J = 7.7, 1.7 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.44 – 7.39 (m, 3H), 7.35 (t, J = 8.2 Hz, 2H), 7.32 (dd, J = 8.3, 2.1 Hz, 1H), 7.20 (d, J = 2.2 Hz, 2H), 6.86 (d, J = 8.3 Hz, 1H), 5.21 (s, 3H), 4.58 (s, 3H), 2.49 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.6, 158.1, 150.1, 138.0, 136.4, 131.0, 128.7, 128.2, 127.5, 122.3, 121.7, 119.2, 109.8, 109.1, 70.5, 26.4. **HRMS:** m/z calculated for C21H21N2O2 $[M+H]^+$ 333.16030; found 333.16043.

IR (thin film): 1659, 1595, 1532, 1354, 1275

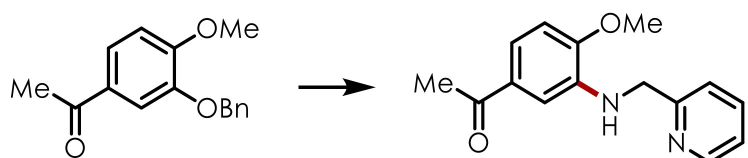


15

Isolated by column chromatography (40% EtOAc/Hex) to give a white solid, 15.7 mg, 46%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 – 8.55 (m, 1H), 7.64 (td, J = 7.7, 1.8 Hz, 1H), 7.56 (d, J = 1.9 Hz, 1H), 7.50 (ddd, J = 8.1, 4.7, 1.6 Hz, 3H), 7.42 (t, J = 7.4 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.22 – 7.18 (m, 1H), 6.49 (d, J = 8.3 Hz, 1H), 5.89 (d, J = 5.9 Hz, 1H), 5.18 (s, 2H), 4.58 (d, J = 4.2 Hz, 2H), 2.50 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.5, 157.8, 149.4, 145.5, 142.6, 136.9, 136.6, 128.7, 128.2, 127.8, 126.3, 125.1, 122.3, 121.2, 109.5, 108.1, 70.6, 48.4, 26.0. **HRMS:** m/z calculated for C21H21N2O2 $[M+H]^+$ 333.16030; found 333.16043.

IR (thin film): 1657, 1593, 1533, 1433, 1156

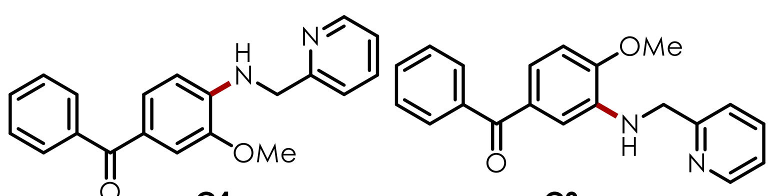


16

Isolated by column chromatography (40% EtOAc/Hex) to give a white solid, 1.3 mg, 5%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.51 (s, 3H), 3.94 (s, 3H), 4.53 (d, J = 4.9 Hz, 2H), 5.37 (s, 1H), 6.79 (d, J = 8.3 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.34 (s, 1H), 7.36 (dd, J = 8.3, 2.1 Hz, 1H), 7.65 (td, J = 7.6, 1.8 Hz, 1H), 8.61 (d, J = 4.8, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) 25.9, 48.4, 55.7, 107.8, 107.9, 121.4, 122.3, 124.8, 126.3, 136.8, 142.4, 146.4, 149.4, 157.6, 196.5. **HRMS:** m/z calculated for C15H17N2O2 $[M+H]^+$ 257.12900; found 257.12902.

IR (thin film): 1657, 1592, 1532, 1278, 1032



C4 **17** C3

Isolated by column chromatography as a mixture of isomers with fine silica gel using a gradient of (40-60% EtOAc/Hex) to give a bright green oil, 23.1 mg, 73%.

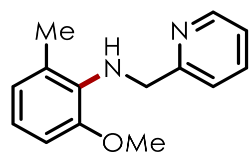
<u>**C4**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.97 (s, 3H), 4.58 (s, 2H), 5.88 (s, 1H), 6.47 (d, J = 8.3 Hz, 1H), 7.21 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.44 (dd, J = 8.2, 6.9 Hz, 2H), 7.48 (d, J = 1.8 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.67 (td, J = 7.7, 1.8 Hz, 1H), 7.73 – 7.69 (m, 2H), 8.61 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 48.3, 55.7, 107.5, 109.8, 121.4, 122.4, 125.7, 127.6, 128.0, 129.5, 131.1, 136.9, 139.3, 142.3, 146.5, 149.4, 157.5, 195.4. **HRMS:** m/z calculated for C20H19N2O2 $[M+H]^+$ 319.14465; found 319.14440.

<u>C3</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.92 (s, 3H), 4.53 (s, 2H), 6.65 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 7.17 (dd, *J* = 8.2, 2.0 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.45 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H), 7.75 – 7.69 (m, 1H), 8.81 (dt, *J* = 4.7, 1.3 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 48.7, 55.7, 108.1, 110.9, 125.7, 127.6, 129.8, 136.9, 131.1, 139.3, 142.3, 146.5, 149.4, 150.3, 157.9, 195.4. **HRMS:** m/z calculated for C20H19N2O2 $[M+H]^+$ 319.14465; found 319.14440.

IR (thin film) 1589, 1527, 1431, 1283, 1130, 717

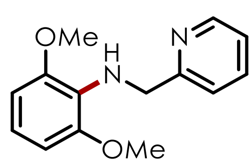


18

Isolated by column chromatography (40% EtOAc/Hex) to give a tan solid, 7.1 mg, 31%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.81 (s, 3H), 4.40 (s, 2H), 6.78 – 6.67 (m, 2H), 6.82 (t, J = 7.8 Hz, 1H), 7.16 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.61 (td, J = 7.6, 1.8 Hz, 1H), 8.58 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 18.5, 53.3, 55.8, 108.8, 121.1, 121.9, 123.5, 129.2, 136.4, 149.2, 151.3, 159.8. **HRMS:** m/z calculated for C14H17N2O1 $[M+H]^+$ 229.13409; found 229.13432.

IR (thin film): 1585, 1476, 1262, 1082, 769

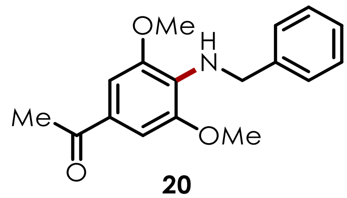


19

Isolated by column chromatography (50% EtOAc/Hex) to give a brown oil, 7.5 mg, 31%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.81 (s, 6H), 4.57 (s, 3H), 6.54 (d, J = 8.3 Hz, 3H), 6.80 (t, J = 8.3 Hz, 2H), 7.18 – 7.07 (m, 2H), 7.31 (d, J = 7.8 Hz, 1H), 7.60 (td, J = 7.6, 1.8 Hz, 2H), 8.61 – 8.51 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 52.4, 56.0, 104.8, 119.8, 121.7, 121.8, 127.1, 136.3, 149.0, 150.8, 160.5. **HRMS:** m/z calculated for C14H17N2O2 $[M+H]^+$ 245.12900; found 245.12910.

IR (thin film): 1595, 1479, 1253, 1110, 719

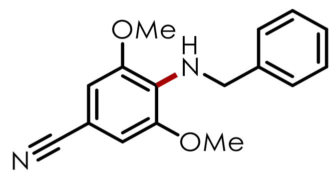


20

Isolated by column chromatography with fine silica gel with a gradient (40-50% EtOAc:Hex) to give a brown oil, 14.0 mg, 49% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.53 (s, 3H), 3.85 (s, 3H), 4.64 (s, 2H), 4.80 (bs, 1H), 7.18 (s, 2H), 7.25 – 7.21 (m, 1H), 7.30 (d, J = 5.7 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.2, 50.2, 56.2, 105.9, 127.0, 127.2, 127.5, 128.5, 132.9, 140.8, 148.3, 196.5. **HRMS:** m/z calculated for C17H18N1O3 $[M+H]^+$ 286.14432; found 286.13602.

IR (thin film): 1657, 1589, 1517, 1458, 1156, 605

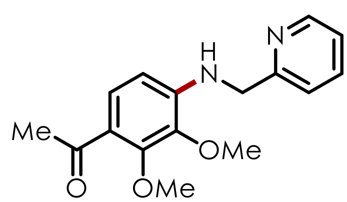


21

Isolated by column chromatography (40% EtOAc/Hex), as a white solid, 20.7 mg, 77%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.81 (s, 6H), 4.61 (s, 2H), 4.74 (s, 1H), 6.77 (s, 2H), 7.41 – 7.14 (m, 5H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 50.2, 56.3, 99.6, 109.1, 120.3, 127.1, 127.5 128.5, 132.4, 140.6, 148.6. **HRMS:** m/z calculated for C16H17N2O2 $[M+H]^+$ 269.12900; found 269.12910.

IR (thin film): 2213, 1587, 1509, 1453, 1127

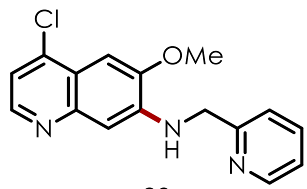


22

Isolated by column chromatography with a gradient of (40-60% EtOAc/Hex) to give a white solid, 7.9 mg, 28%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 – 8.52 (m, 1H), 7.62 (td, J = 7.7, 1.8 Hz, 1H), 7.30 – 7.23 (m, 3H), 6.64 (d, J = 8.7 Hz, 1H), 4.58 (s, 2H), 3.88 (s, 3H), 3.76 (s, 3H), 2.61 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.3, 159.4, 154.2, 150.3, 149.2, 136.5, 131.5, 126.4, 122.0, 122.0, 121.6, 106.3, 60.6, 56.1, 51.6, 30.5. **HRMS:** m/z calculated for C16H19N2O3 $[M+H]^+$ 287.13957; found 287.13990.

IR (thin film): 1669, 1589, 1462, 1410, 1289, 1101, 992

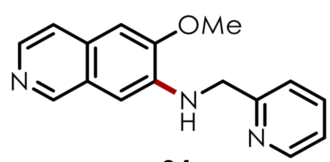


23

Isolated by column chromatography (20% (5% EtOAc:DCM)/EtOAc) to give a white solid, 9.2 mg, 31%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.06 (s, 3H), 4.63 (d, J = 5.2 Hz, 2H), 5.95 (t, J = 5.3 Hz, 1H), 6.97 (s, 1H), 7.25 – 7.21 (m, 1H), 7.27 (d, J = 5.1 Hz, 1H), 7.33 (s, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.68 (td, J = 7.7, 1.8 Hz, 1H), 8.41 (d, J = 4.8 Hz, 1H), 8.64 (dd, J = 5.0, 0.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 48.6, 56.0, 98.2, 106.3, 119.5, 121.8, 122.4, 123.4, 136.8, 139.1, 139.4, 144.7, 145.1, 149.4, 151.7, 157.2. **HRMS:** m/z calculated for C16H15N3O1Cl1 $[M+H]^{+}$ 300.09036; found 300.09075.

IR (thin film): 1593, 1523, 1477, 1255, 1152

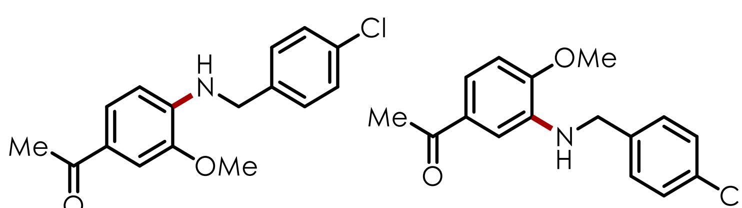


24

Isolated by column chromatography using fine silica gel (5% MeOh/EtOAc) as a dark yellow oil, 5.6 mg, 24% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.04 (s, 3H), 4.60 (d, *J* = 5.3 Hz, 2H), 5.77 (t, *J* = 5.4 Hz, 1H), 6.79 (s, 1H), 6.98 (s, 1H), 7.21 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 7.36 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.43 (d, *J* = 5.5 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 8.24 (d, *J* = 5.6 Hz, 1H), 8.64 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H),8.90 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 48.8, 55.8, 102.4, 102.8, 119.4, 121.6, 122.4, 126.0, 130.6, 136.8, 139.1, 140.0, 149.1, 149.5, 151.5, 157.6. **HRMS**: m/z calculated for C16H16N3O1 $[M+H]^{+}$ 266.12934; found 266.12926.

IR (thin film): 1593, 1523, 1480, 1257, 1152, 854



C4 **C3**

25

Isolated by column chromatography as a mixture of isomers with a gradient (50-60% EtOAc/Hex), as a white solid 20.1 mg, 69%.

<u>C4</u>

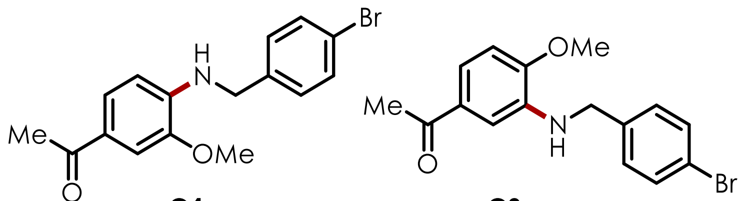
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.51 (s, 3H), 3.92 (s, 3H), 4.41 (d, J = 5.5 Hz, 2H), 5.21 (s, 1H), 6.44 (d, J = 8.2 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 1.8 Hz, 1H), 7.48 (dd, J = 8.2, 1.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 26.0, 46.6, 55.6, 107.7, 107.9, 124.8, 126.4, 128.6, 128.8, 128.9, 129.0, 133.2, 136.9, 142.3, 146.2, 196.6. **HRMS:** m/z calculated for C16H17N1O2Cl1 $[M+H]^+$ 290.09478; found 290.09486.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.51 (s, 3H), 3.92 (s, 3H) 4.37 (s, 2H), 4.63 (s, 1H), 6.79 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H), 7.28 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.36 (dd, J = 8.3, 2.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 46.6, 55.6, 107.7, 107.9, 124.8, 126.4, 128.6, 128.8, 128.9, 129.0, 133.2, 136.9, 142.3, 146.2, 196.6. **HRMS:** m/z calculated for C16H17N1O2Cl1 $[M+H]^+$ 290.09478; found 290.09486.

IR (thin film): 1659, 1593, 1282, 1217, 1032



C4 **C3**

26

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a white solid 23.5 mg, 70%.

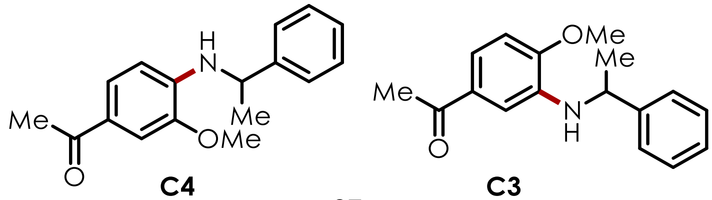
C4

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.51 (s, 3H), 3.92 (s, 3H), 4.40 (d, J = 5.8 Hz, 2H), 5.21 (s, 1H), 6.43 (d, J = 8.2 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 1.8 Hz, 1H), 7.47 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 46.7, 55.6, 107.7, 107.9, 121.2, 124.8, 126.4, 128.9, 131.9, 137.5, 142.2, 146.2, 196.6. **HRMS:** m/z calculated for C16H17N1O2Br1 $[M+H]^+$ 334.04427; found 334.04450.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.51 (s, 3H), 3.92 (s, 3H), 4.36 (d, J = 5.5 Hz, 2H), 4.64 (s, 1H), 6.79 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.36 (dd, J = 8.3, 2.1 Hz, 1H), 7.47 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 46.7, 55.6, 107.7, 107.9, 121.2, 124.8, 126.4, 128.9, 131.9, 137.5, 142.2, 146.2, 196.6. **HRMS:** m/z calculated for C16H17N1O2Br1 $[M+H]^+$ 334.04427; found 334.04450.

IR (thin film): 1663, 1592, 1523, 1276, 1147, 1010, 805



C4 **C3**

27

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a green oil, 16.5 mg, 61%.

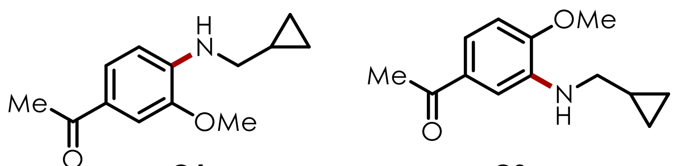
C4

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 1.59 (d, J = 6.8 Hz, 3H), 2.46 (s, 3H), 3.95 (s, 3H), 4.57 (p, J = 6.5 Hz, 1H), 5.17 (d, J = 5.7 Hz, 1H), 6.26 (d, J = 8.3 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.33 (d, J = 4.4 Hz, 4H), 7.36 (dd, J = 8.3, 1.9 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 24.9, 25.9, 52.9, 55.6, 107.7, 108.6, 124.8, 125.7, 127.2, 128.8, 141.7, 144.3, 146.0, 196.6. **HRMS:** m/z calculated for C17H20NO2 $[M+H]^+$ 270.14940; found 270.14946.

C3

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 1.57 (d, J = 6.8 Hz, 3H), 2.38 (s, 3H), 3.94 (s, 3H), 4.68 (s, 1H), 5.17 (d, J = 5.7 Hz, 1H), 6.76 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 2.1 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.28 (dd, J = 8.3, 2.1 Hz, 1H), 7.33 (d, J = 4.4 Hz, 4H), 7.38 (d, J = 1.6 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 24.7, 26.3, 53.1, 55.6, 55.7, 108.2, 110.1, 118.6, 125.9, 125.9, 127.1, 128.7, 130.7, 136.8, 144.8, 150.5, 197.6. **HRMS:** m/z calculated for C17H20NO2 $[M+H]^+$ 270.14940; found 270.14946.

IR (thin film): 1659, 1594, 1447, 1273, 1216, 1150, 1028, 701



C4 **C3**

28

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a green oil, 10.0 mg, 46%.

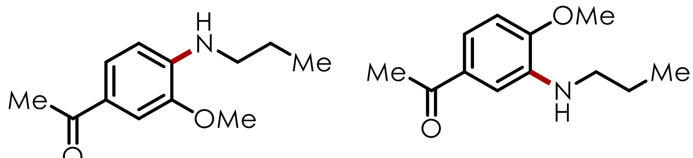
C4

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 0.28 (m, 2H) 0.66 – 0.49 (m, 2H), 1.14 (m, 1H), 2.52 (s, 3H), 3.04 (dd, J = 6.9, 4.6 Hz, 2H), 3.91 (s, 3H), 4.91 (s, 1H), 6.48 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H), 7.53 (dd, J = 8.3, 1.8 Hz, 1H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 3.6, 10.6, 25.9, 48.0, 55.6, 107.8, 125.0, 125.7, 143.0, 145.9, 196.5. **HRMS:** m/z calculated for C13H18N1O2 $[M+H]^+$ 220.13375; found 220.13392.

C3

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 0.32 – 0.14 (m, 2H), 0.72 – 0.49 (m, 2H), 1.26 (d, J = 6.2 Hz, 1H), 2.55 (s, 3H), 3.04 (dd, J = 6.9, 4.6 Hz, 2H), 3.92 (s, 3H), 3.92 (s, 3H), 4.38 (s, 1H), 6.76 (d, J = 8.1 Hz, 1H), 7.17 (d, J = 2.1 Hz, 1H), 7.33 (dd, J = 8.3, 2.1 Hz, 1H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 3.6, 10.6, 25.9, 48.0, 55.6, 107.1, 107.8, 119.0, 125.0, 125.7, 143.0, 145.9, 196.5. **HRMS:** m/z calculated for C13H18N1O2 $[M+H]^+$ 220.13375; found 220.13392.

IR (thin film): 1659, 1593, 1531, 1355, 1276, 1217, 1146, 1031



C4 **C3**

29

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a green oil, 13.4 mg, 65%.

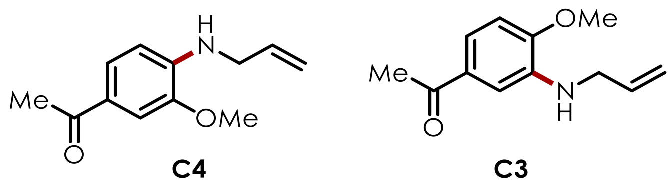
<u>**C4**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.02 (t, J = 7.4 Hz, 3H), 1.69 (m, 2H), 2.52 (s, 3H), 3.26 – 3.06 (m, 2H), 3.90 (s, 3H), 4.80 (s, 1H), 6.50 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 1.8 Hz, 1H), 7.54 (dd, J = 8.3, 1.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 11.7, 22.5, 25.9, 44.8, 55.6, 107.0, 107.8, 118.8, 125.1, 143.1, 145.9, 196.5. **HRMS:** m/z calculated for C12H18N1O2 $[M+H]^+$ 208.13375; found 208.13375.

<u>**C3**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.02 (t, J = 7.4 Hz, 3H), 1.69 (m, 2H), 2.55 (s, 3H), 3.19 – 3.13 (m, 2H), 3.91 (s, 3H), 4.23 (d, J = 18.0 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 2.1 Hz, 1H), 7.32 (dd, J = 8.3, 2.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 22.6, 26.4, 45.4, 55.6, 108.0, 108.3, 118.8, 125.5, 130.9, 138.3, 150.8, 197.8. **HRMS:** m/z calculated for C12H18N1O2 $[M+H]^+$ 208.13375; found 208.13375.

IR (thin film): 1658, 1592, 1531, 1353, 1030, 669



C4 **C3**

30

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a brown oil, 14.6 mg, 71%.

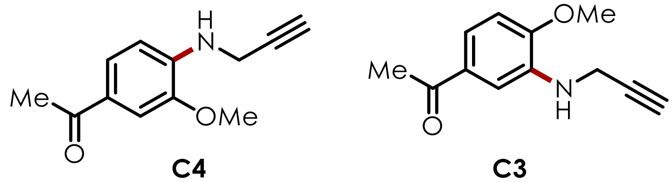
<u>**C4**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.89 – 3.85 (m, 2H), 3.91 (s, 3H), 4.96 (s, 1H), 5.20 (dd, J = 10.4, 1.5 Hz, 1H), 5.28 (dd, J = 17.2, 1.6 Hz, 1H), 5.94 (ddt, J = 17.2, 10.4, 5.2 Hz, 1H), 6.51 (d, J = 8.3 Hz, 1H), 7.43 (d, J = 1.9 Hz, 1H), 7.53 (dd, J = 8.3, 1.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 25.9, 45.5, 55.6, 196.6, 107.5, 107.9, 116.7, 124.9, 134.3, 142.6, 146.1. **HRMS:** m/z calculated for C12H16N1O2 $[M+H]^+$ 206.11810; found 206.11814.

<u>**C3**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.54 (s, 3H), 3.85 (s, 1H), 3.92 (s, 3H), 4.42 (s, 1H), 5.20 (dd, J = 10.4, 1.5 Hz, 1H), 5.29 (d, J = 1.6 Hz, 1H), 5.94 (ddt, J = 17.2, 10.4, 5.2 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 7.21 (d, J = 2.1 Hz, 1H), 7.34 (dd, J = 8.3, 2.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.4, 46.1, 55.7, 108.2, 108.8, 119.2, 126.0, 130.8, 134.9, 137.8, 150.9, 197.7. **HRMS:** m/z calculated for C12H16N1O2 $[M+H]^+$ 206.11810; found 206.11814.

IR (thin film): 1673, 1594, 1530, 1414, 1357, 1274, 1218, 1032



31

Isolated by column chromatography as a mixture of isomers (50% EtOAc/Hex), as a green oil, 12.2 mg, 50%.

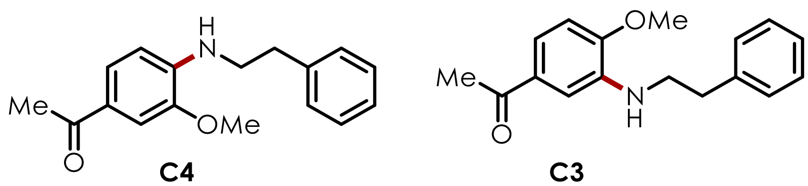
<u>**C4**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.25 (t, J = 2.4 Hz, 1H), 2.53 (s, 3H), 3.90 (s, 3H), 4.04 (dd, J = 6.1, 2.5 Hz, 2H), 5.01 (s, 1H), 6.64 (d, J = 8.2 Hz, 1H), 7.44 (d, J = 1.9 Hz, 1H), 7.57 (dd, J = 8.2, 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 32.7, 55.6, 71.7, 79.9, 108.1, 124.5, 127.1, 141.4, 146.5, 196.7. **HRMS:** m/z calculated for C12H14N1O2 $[M+H]^+$ 204.10245; found 204.10264.

<u>**C3**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.23 (t, J = 2.4 Hz, 1H), 2.56 (s, 3H), 3.91 (s, 3H), 4.04 (dd, J = 6.1, 2.5 Hz, 2H), 4.52 (s, 1H), 6.79 (d, J = 8.3 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.41 (dd, J = 8.3, 2.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.4, 33.1, 55.7, 71.5, 80.5, 108.4, 109.4, 120.3, 130.7, 136.7, 151.2, 197.5. **HRMS:** m/z calculated for C12H14N1O2 $[M+H]^+$ 204.10245; found 204.10264.

IR (thin film): 1657, 1593, 1529, 1421, 1355, 1276, 1217, 1150, 1030



32

Isolated by column chromatography as a mixture of isomers with a gradient of (30-40% EtOAc/Hex) using fine silica gel, as a green oil, 12.2 mg, 46%.

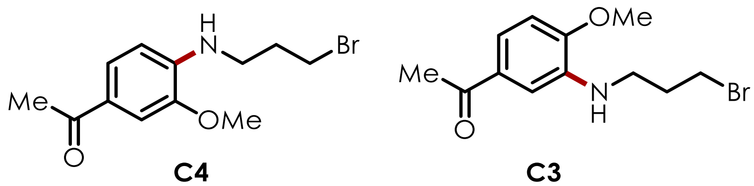
<u>**C4**</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.53 (s, 3H), 2.96 (t, J = 7.3 Hz, 3H), 3.47 (dd, J = 7.4, 5.3 Hz, 3H), 3.87 (s, 3H), 4.88 (t, J = 5.5 Hz, 1H), 6.56 (d, J = 8.3 Hz, 1H), 7.29 – 7.17 (m, 5H), 7.34 (t, J = 7.5 Hz, 3H), 7.42 (d, J = 1.9 Hz, 1H), 7.55 (dd, J = 8.2, 1.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 35.4, 44.4, 55.6, 107.2, 107.9, 125.0, 125.9, 126.6, 128.7, 128.8, 138.9, 142.6, 146.1, 196.5. **HRMS:** m/z calculated for C17H20NO2 $[M+H]^+$ 270.14940; found 270.14945.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.55 (s, 3H), 2.96 (t, J = 7.3 Hz, 2H), 3.47 (dd, J = 7.4, 5.3 Hz, 2H), 3.88 (s, 3H), 4.35 (s, 1H), 6.76 (d, J = 8.3 Hz, 1H), 7.29 – 7.19 (m, 5H), 7.34 (t, J = 7.5 Hz, 3H), 7.42 (d, J = 1.9 Hz, 1H), 7.55 (dd, J = 8.2, 1.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.4, 35.5, 44.8, 55.7, 108.2, 108.5, 119.2, 125.9, 126.4, 128.6, 128.8, 130.9, 137.9, 139.3, 150.9, 197.7. **HRMS:** m/z calculated for C17H20NO2 $[M+H]^+$ 270.14940; found 270.14945.

IR (thin film): 1660, 1594, 1532, 1451, 1354, 1278, 1146, 1032



C4 **C3**

33

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a brown oil, 7.7 mg, 27%.

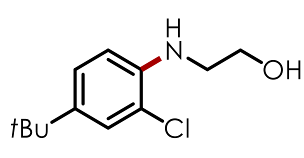
C4

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.20 (td, J = 6.5, 1.6 Hz, 2H), 2.52 (s, 3H), 3.43 (m, 2H), 3.51 (t, J = 6.3 Hz, 2H), 3.90 (s, 3H), 4.86 (s, 1H), 6.56 (d, J = 8.3 Hz, 1H), 7.42 (d, J = 1.9 Hz, 1H), 7.54 (dd, J = 8.3, 1.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 30.9, 31.8, 41.0, 55.6, 107.1, 107.9, 124.9, 126.0, 142.5, 146.1, 196.5. **HRMS:** m/z calculated for C12H17N1O2Br1 $[M+H]^+$ 286.04427; found 286.04471.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.26 – 2.13 (m, 2H), 2.55 (s, 3H), 3.47 – 3.39 (m, 2H), 3.51 (t, J = 6.3 Hz, 2H), 3.91 (s, 3H), 4.35 (s, 1H), 6.77 (d, J = 8.3 Hz, 1H), 7.23 (d, J = 2.1 Hz, 1H), 7.34 (dd, J = 8.3, 2.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.4, 31.1, 31.9, 41.5, 55.7, 108.2, 108.3, 119.2, 130.9, 137.7, 150.8, 197.7. **HRMS:** m/z calculated for C12H17N1O2Br1 $[M+H]^+$ 286.04427; found 286.04471.

IR (thin film): 1679, 1594, 1276, 1033

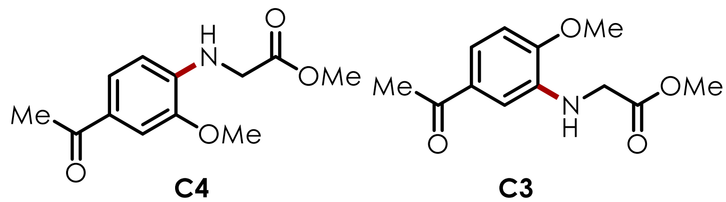


34

Isolated by column chromatography as a mixture of isomers (50% EtOAc/Hex), as a brown oil, 8.8 mg, 39%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27 (s, 9H), 1.75 (s, 1H), 3.36 (t, J = 5.2 Hz, 2H), 3.85 (t, J = 5.3 Hz, 2H), 4.46 (s, 1H), 6.67 (d, J = 8.5 Hz, 1H), 7.16 (dd, J = 8.5, 2.3 Hz, 1H), 7.29 (d, J = 2.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 31.4, 34.0, 46.0, 61.2, 111.3, 119.4, 124.6, 126.4, 141.2, 141.5. **HRMS:** m/z calculated for C12H19N1O1Cl1 $[M+H]^+$ 228.11552; found 228.11560.

IR (thin film): 2957, 1612, 1517, 1264, 1056



C4 **C3**

35

Isolated by column chromatography as a mixture of isomers (10% EtOAc/Hex), as a white solid, 4.3 mg, 18%.

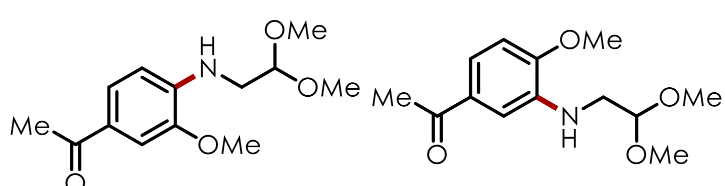
<u>C4</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.81 (s, 3H), 3.92 (s, 3H), 4.01 (d, J = 5.5 Hz, 2H), 5.34 (s, 1H), 6.41 (d, J = 8.2 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.53 (dd, J = 8.2, 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 26.0, 44.8, 52.5, 55.7, 107.5, 108.1, 112.5, 124.6, 141.5, 146.4, 170.7, 196.6. **HRMS:** m/z calculated for C12H16N1O4 $[M+H]^+$ 238.10793; found 238.10809.

<u>C3</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.81 (s, 3H), 3.92 (d, *J* = 9.4 Hz, 3H), 3.95 (d, *J* = 7.2 Hz, 1H), 4.01 (d, *J* = 5.5 Hz, 2H), 4.30 (s, 2H), 5.34 (s, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.53 (dd, *J* = 8.2, 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.1, 29.7, 44.8, 52.5, 55.6, 107.5, 108.1, 109.2, 112.5, 127.0, 127.9, 141.5, 146.4, 170.7, 196.6. **HRMS:** m/z calculated for C12H16N1O4 $[M+H]^+$ 238.10793; found 238.10809.

IR (thin film): 1744, 1659, 1595, 1535, 1425, 1360, 1282, 1217, 1156, 1030



C4 **36** **C3**

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a white solid 16.1 mg, 64%.

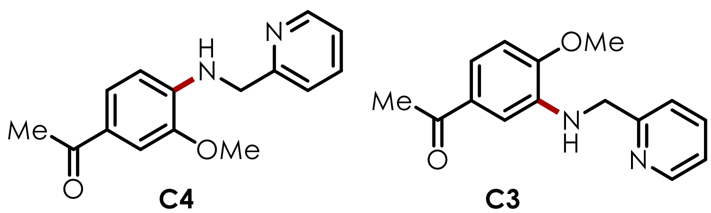
<u>C4</u>

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.34 (t, J = 5.6 Hz, 2H), 3.42 (s, 6H), 3.90 (s, 3H), 4.59 (t, J = 5.5 Hz, 1H), 4.96 (t, J = 5.8 Hz, 1H), 6.54 (d, J = 8.3 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H), 7.53 (dd, J = 8.2, 1.9 Hz, 1H). ^{13}**C NMR** (151 MHz, CDCl$_3$) δ 25.9, 44.5, 56.0, 55.6, 102.3, 107.3, 108.0, 124.8, 126.3, 142.5, 146.3, 196.5. **HRMS:** m/z calculated for C13H20N1O4 [M+H]$^{+}$ 254.13923; found 254.13923.

C3

^{1}**H NMR** (600 MHz, CDCl$_3$) δ 2.55 (s, 3H), 3.34 (t, J = 5.6 Hz, 2H), 3.91 (s, 3H), 4.45 (s, 1H), 4.61 (t, J = 5.5 Hz, 1H), 6.76 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 2.1 Hz, 1H), 7.35 (dd, J = 8.3, 2.1 Hz, 1H). ^{13}**C NMR** (151 MHz, CDCl$_3$) δ 25.9, 44.5, 54.0, 55.6, 102.3, 107.3, 108.0, 124.8, 126.3, 142.5, 146.3, 196.5. **HRMS:** m/z calculated for C13H20N1O4 [M+H]$^{+}$ 254.13923; found 254.13923.

IR (thin film): 1660, 1594, 1532, 1423, 1356, 1276, 1217, 1126, 1069



37

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a white solid, 16.3 mg, 64%.

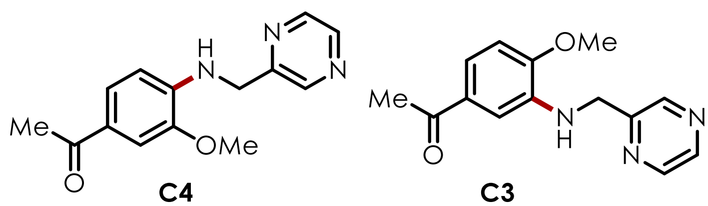
C4

^{1}**H NMR** (600 MHz, CDCl$_3$) δ 2.51 (s, 3H), 3.94 (s, 3H), 4.56 (d, J = 5.6 Hz, 2H), 5.82 (t, J = 5.8 Hz, 1H), 6.48 (d, J = 8.2 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 1.8 Hz, 1H), 7.49 (dd, J = 8.3, 1.8 Hz, 1H), 7.65 (td, J = 7.6, 1.8 Hz, 1H), 8.67 – 8.54 (d, 1H). ^{13}**C NMR** (151 MHz, CDCl$_3$) δ 25.9, 48.4, 55.7, 107.8, 107.9, 121.4, 122.3, 124.8, 126.3, 136.8, 142.4, 146.4, 149.4, 157.6, 196.5. **HRMS:** m/z calculated for C15H17N2O2 [M+H]$^{+}$ 257.12900; found 257.12902.

C3

^{1}**H NMR** (600 MHz, CDCl$_3$) δ 2.51 (s, 3H), 3.94 (s, 3H), 4.53 (d, J = 4.9 Hz, 2H), 5.37 (s, 1H), 6.79 (d, J = 8.3 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.34 (s, 1H), 7.36 (dd, J = 8.3, 2.1 Hz, 1H), 7.65 (td, J = 7.6, 1.8 Hz, 1H), 8.61 (d, J = 4.8, 1H). ^{13}**C NMR** (151 MHz, CDCl$_3$) δ 25.9, 48.4, 55.7, 107.8, 107.9, 121.4, 122.3, 124.8, 126.3, 136.8, 142.4, 146.4, 149.4, 157.6, 196.5. **HRMS:** m/z calculated for C15H17N2O2 [M+H]$^{+}$ 257.12900; found 257.12902.

IR (thin film): 1657, 1592, 1532, 1278, 1032



38

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a white solid, 14.9 mg, 58%.

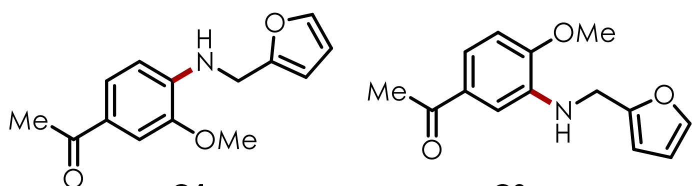
C4

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.95 (s, 3H), 4.62 (d, J = 5.7 Hz, 2H), 5.78 – 5.70 (m, 1H), 6.51 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 1.8 Hz, 1H), 7.51 (dd, J = 8.2, 1.8 Hz, 1H), 8.51 (d, J = 2.5 Hz, 1H), 8.58 (dd, J = 2.6, 1.5 Hz, 1H), 8.63 (d, J = 1.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 46.4, 55.7, 107.8, 108.0, 124.7, 126.9, 141.9, 143.6, 143.7, 144.1, 146.5, 153.3, 196.6. **HRMS:** m/z calculated for C14H16N3O2 $[M+H]^+$ 258.12425; found 258.12455.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.53 (s, 3H), 3.96 (s, 3H), 4.60 (d, J = 4.8 Hz, 2H), 5.27 (s, 1H), 6.81 (d, J = 8.3 Hz, 1H), 7.23 (d, J = 2.1 Hz, 1H), 7.39 (dd, J = 8.3, 2.1 Hz, 1H), 7.46 (d, J = 1.8 Hz, 1H), 7.51 (dd, J = 8.2, 1.8 Hz, 1H), 8.50 (d, J = 2.6 Hz, 1H), 8.58 (dd, J = 2.6, 1.5 Hz, 1H), 8.65 (d, J = 1.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.3, 46.7, 55.8, 108.3, 108.8, 120.0, 130.8, 137.3, 143.4, 143.9, 144.0, 151.2, 153.8, 197.5. **HRMS:** m/z calculated for C14H16N3O2 $[M+H]^+$ 258.12425; found 258.12455.

IR (thin film): 1657, 1593, 1528, 1448, 1355, 1277, 1217, 1152, 1019



C4 C3

39

Isolated by column chromatography as a mixture of isomers (60% EtOAc/Hex), as a yellow oil, 9.3 mg, 38%.

C4

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.90 (s, 3H), 4.41 (d, J = 5.8 Hz, 2H), 5.15 (s, 1H), 6.26 (dd, J = 3.2, 0.9 Hz, 1H), 6.33 (dd, J = 3.2, 1.9 Hz, 1H), 6.61 (d, J = 8.3 Hz, 1H), 7.38 (dd, J = 1.9, 0.9 Hz, 1H), 7.43 (d, J = 1.8 Hz, 1H), 7.53 (dd, J = 8.3, 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.0, 40.4, 55.6, 107.4, 107.6, 108.0, 110.4, 124.7, 126.5, 142.2, 142.2, 146.3, 151.7, 196.6. **HRMS:** m/z calculated for C14H16N1O3 $[M+H]^+$ 246.11302; found 246.11321.

C3

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.54 (s, 3H), 3.91 (s, 3H), 4.39 (s, 2H), 4.64 (s, 1H), 6.29 – 6.27 (m, 1H), 6.33 (dd, J = 3.2, 1.9 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 7.30 (d, J = 2.1 Hz, 1H), 7.58 (dd, J = 8.3, 2.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 26.3, 40.9, 56.0, 56.1, 107.4, 107.6, 108.0, 110.4, 126.5, 142.2, 146.3, 196.6. **HRMS:** m/z calculated for C14H16N1O3 $[M+H]^+$ 246.11302; found 246.11321.

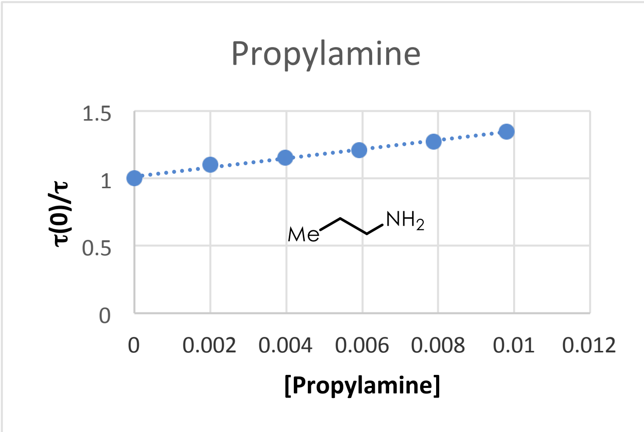
IR (thin film): 1661, 1595, 1532, 1450, 1356, 1200, 1150, 1032

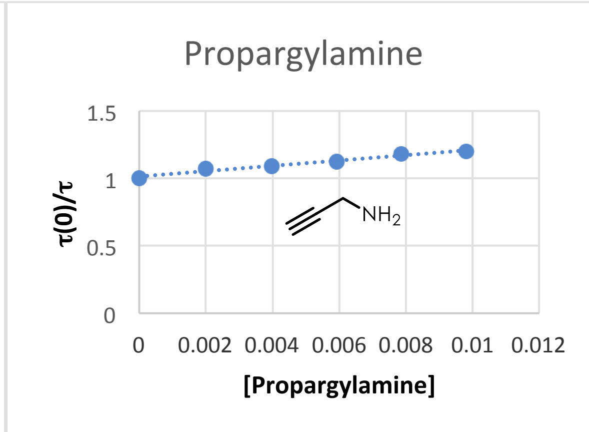
Stern-Volmer Studies:

Stern Volmer Analysis Emission lifetime measurements were taken at ambient temperature using a Edinburgh FLS920 spectrometer and fit to single exponential decay according to a modification of the method previously described by our laboratory.[12] Measurements were made by the time-correlated single photon counting (TCSPC) capability of the instrument with pulsed excitation light (444.2 nm, typical pulse width = 95 ps) generated by a Edinburgh EPL-445 ps pulsed laser diode operating at a repetition rate of 5 MHz. The maximum emission channel count rate was less than 5% of the laser channel count rate, and each data set collected greater than 10000 counts on the maximum channel. The lifetime of fluorescence was determined by reconvolution fit with the instrument response function using the Edinburgh FS900 software. In all cases, after reconvolution, fluorescence decay was satisfactorily fit with a monoexponential function of the form:

$$I_t = I_0 e^{-t/\tau}$$

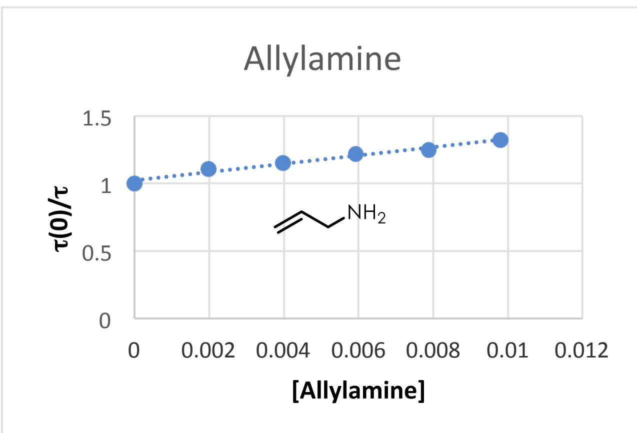
where I is the intensity (counts), and τ is the mean lifetime of fluorescence. Stern-Volmer analysis on the quenching of fluorescence lifetime was carried out in DCE with detection at 500 nm (15 nm bandwidth), where the concentration of acridinium was 1.6×10^{-5} M. The quenching constant was determined with quencher concentrations in the range of 0 M to 2.0×10^{-2} M. Bimolecular quenching constants, kq, were determined from the corresponding Stern-Volmer constant.[13] Quenching constants were determined for *t*-Bu_2-Mes-Acr^+ with a representative amine or arene. Comparison of UV-Vis absorption spectra taken before and after lifetime quenching studies verified that the acridinium was unchanged. UV-Vis spectra were taken on a Hewlett-Packard 8453 Chemstation spectrophotometer.

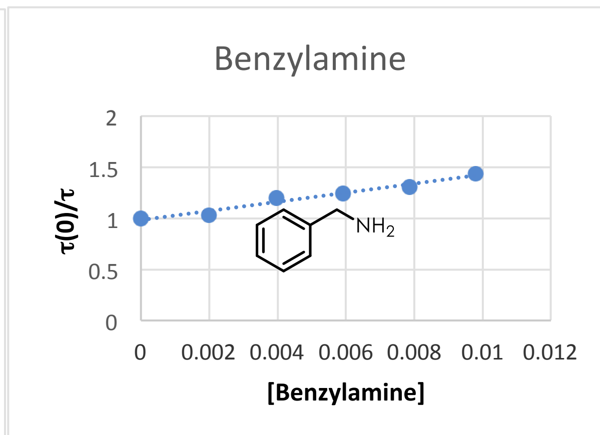




k_q = 2.41 X 10^9 $M^{-1}S^{-1}$

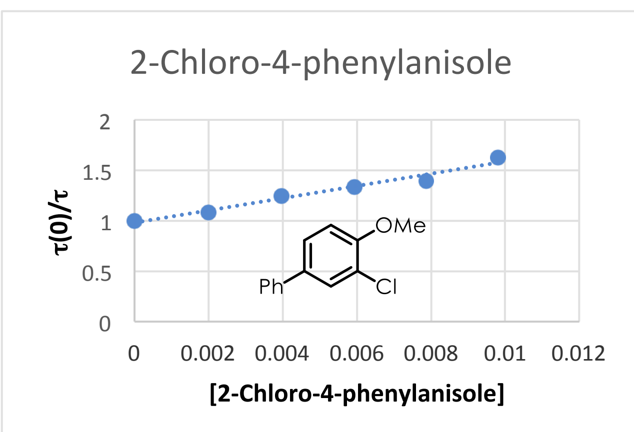
k_q = 1.41 X 10^9 $M^{-1}S^{-1}$

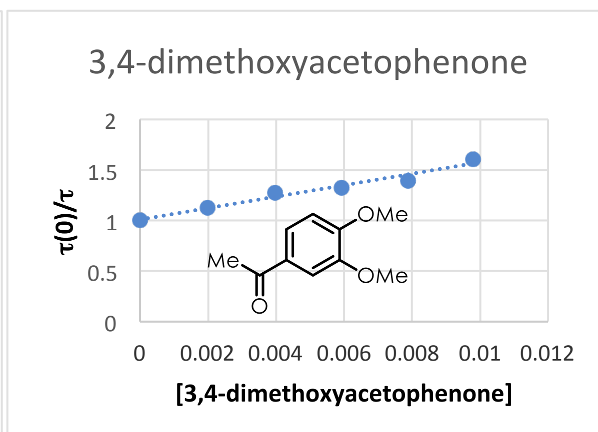




k_q = 2.41 X 10^9 $M^{-1}S^{-1}$

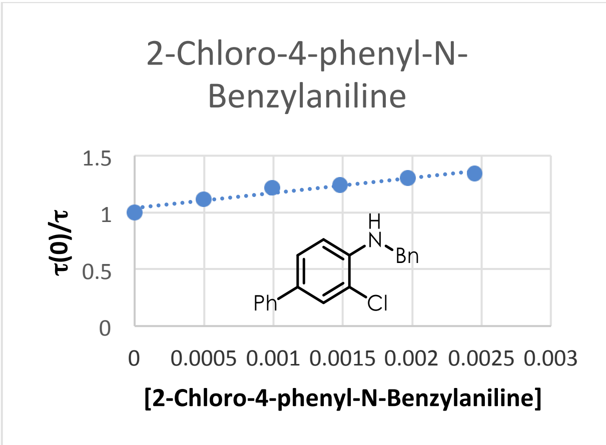
k_q = 3.25 X 10^9 $M^{-1}S^{-1}$

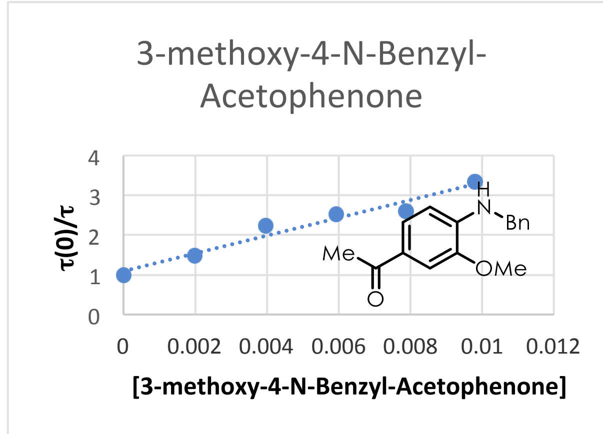




k_q = 4.42 X 10^9 $M^{-1}S^{-1}$

k_q = 4.13 X 10^9 $M^{-1}S^{-1}$



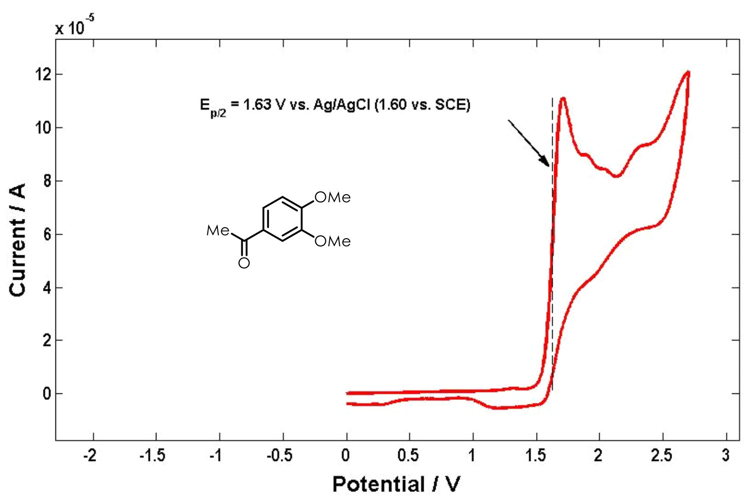


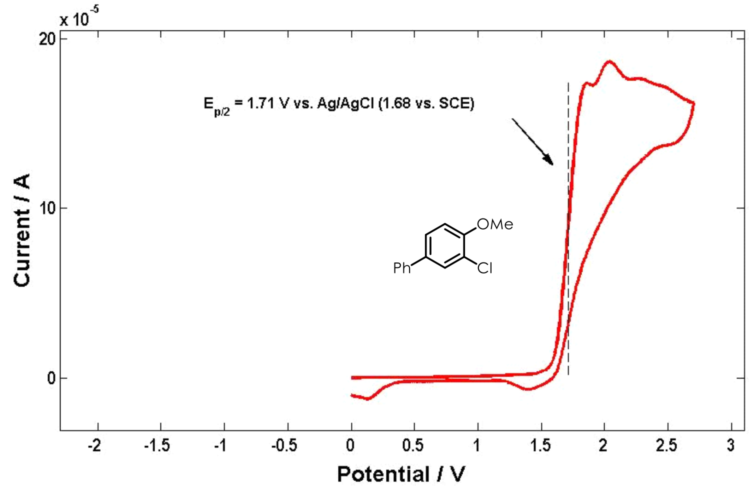
k_q = 9.64 X 10^{9} $M^{-1}S^{-1}$

k_q = 1.63 X 10^{10} $M^{-1}S^{-1}$

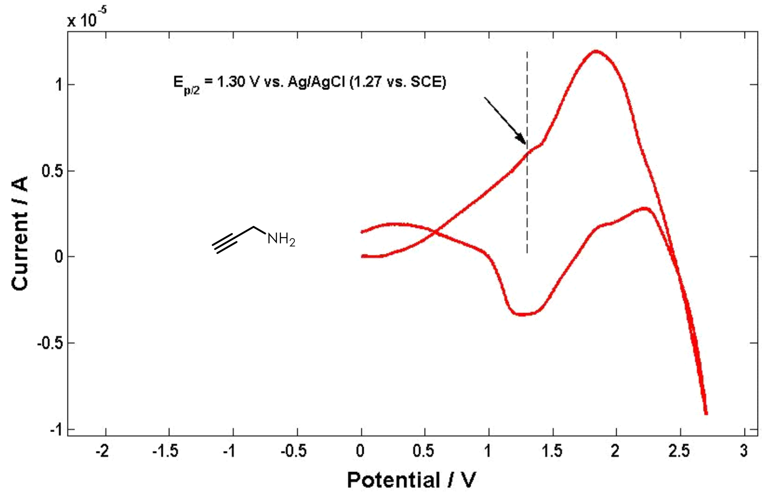
Ciclic Voltamatry Data:

Oxidation potential of benzylamine has been previously reported.[14] All other substrate redox potentials reported were determined using CV with the folowing method. Electrochemical potentials were obtained with a standard set of conditions to maintain internal consistency. Cyclic voltammograms were collected with a Pine WaveNow Potentiostat. Samples were prepared with 0.05 mmol of substrate in 5 mL of 0.1 M tetra-nbutylammonium hexafluorophosphate in dry, degassed acetonitrile. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, 3.5 M NaCl silver-silver chloride reference electrode, and a scan rate of 100 mV/s. Reductions were measured by scanning potentials in the negative direction and oxidations in the positive direction; the glassy carbon electrode was polished between each scan. Data was analyzed using MATLAB by subtracting a background current prior to identifying the maximum current (Cp) and determining the potential (Ep/2) at half this value (Cp/2). The obtained value was referenced to Ag|AgCl and converted to SCE by subtracting 0.03 V.

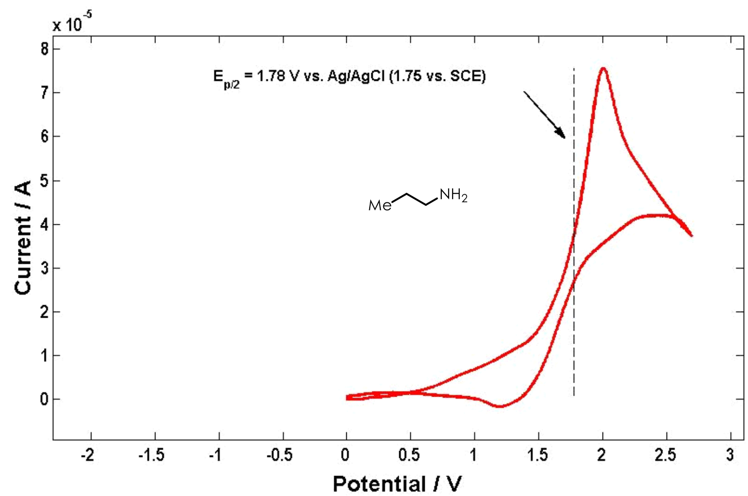




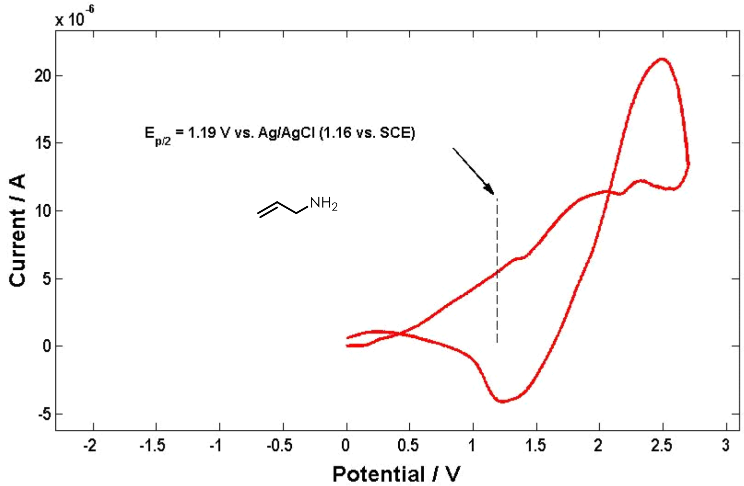
x 10^-5
$E_{p/2}$ = 1.71 V vs. Ag/AgCl (1.68 vs. SCE)
OMe
Ph
Cl
Current / A
Potential / V



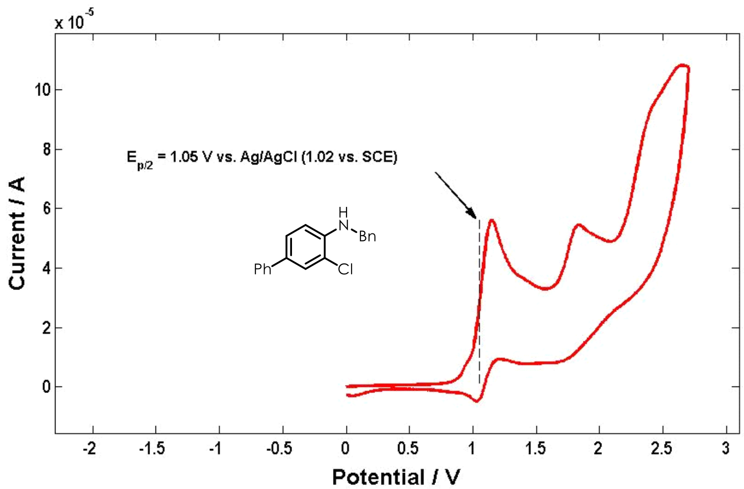
x 10^-5
$E_{p/2}$ = 1.30 V vs. Ag/AgCl (1.27 vs. SCE)
NH2
Current / A
Potential / V



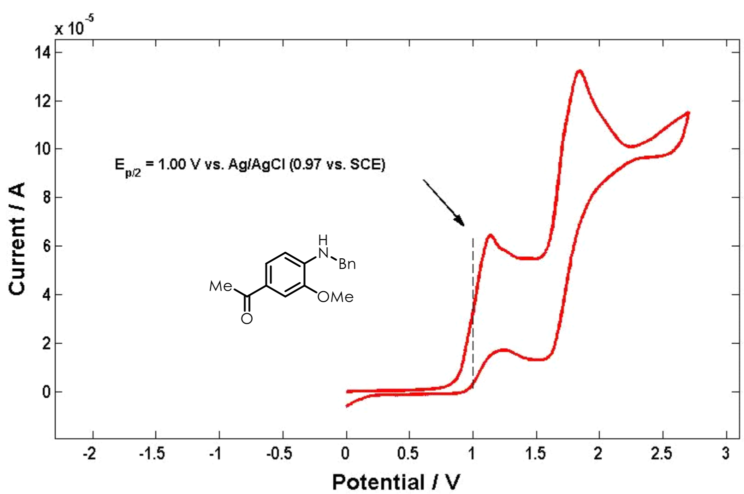
x 10^-5
$E_{p/2}$ = 1.78 V vs. Ag/AgCl (1.75 vs. SCE)
Me
NH2
Current / A
Potential / V



x 10^-6
$E_{p/2}$ = 1.19 V vs. Ag/AgCl (1.16 vs. SCE)
NH2
Current / A
Potential / V



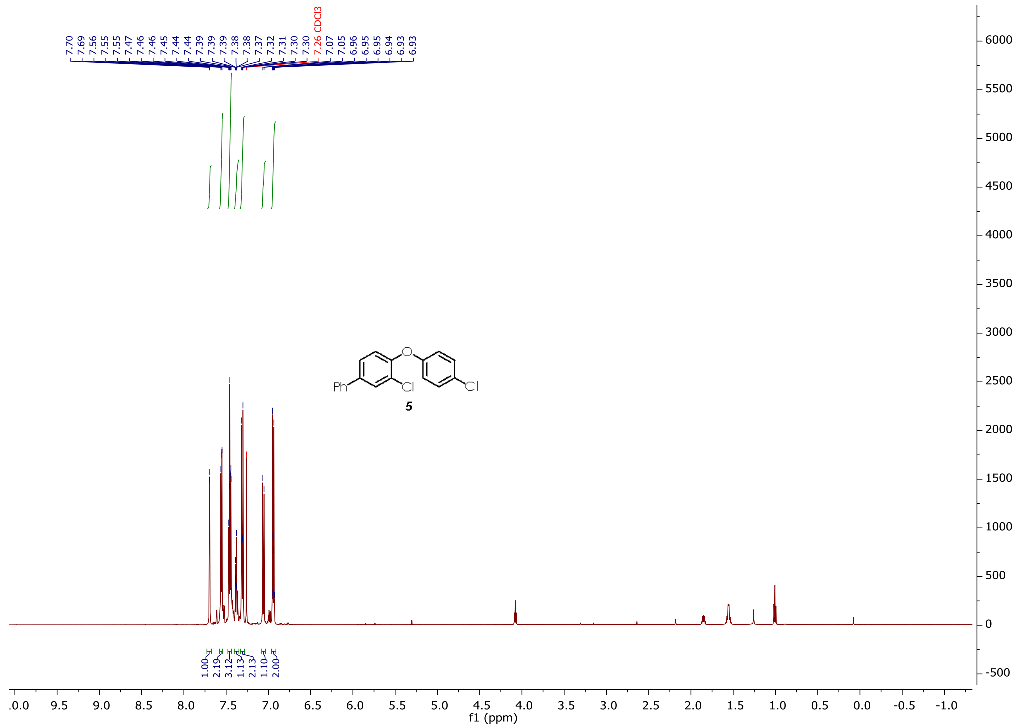
x 10^-5
$E_{p/2}$ = 1.05 V vs. Ag/AgCl (1.02 vs. SCE)
H
N
Bn
Ph
Cl
Current / A
Potential / V



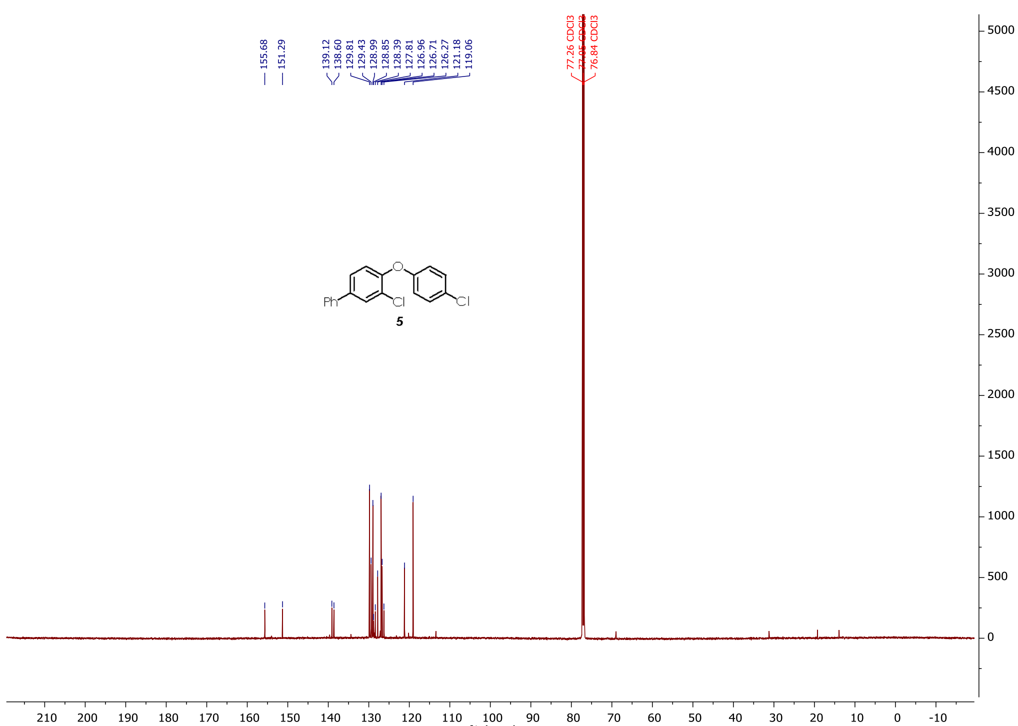
x 10^-5
$E_{p/2}$ = 1.00 V vs. Ag/AgCl (0.97 vs. SCE)
H
N
Bn
Me
O
OMe
Current / A
Potential / V

NMR Spectral Data:

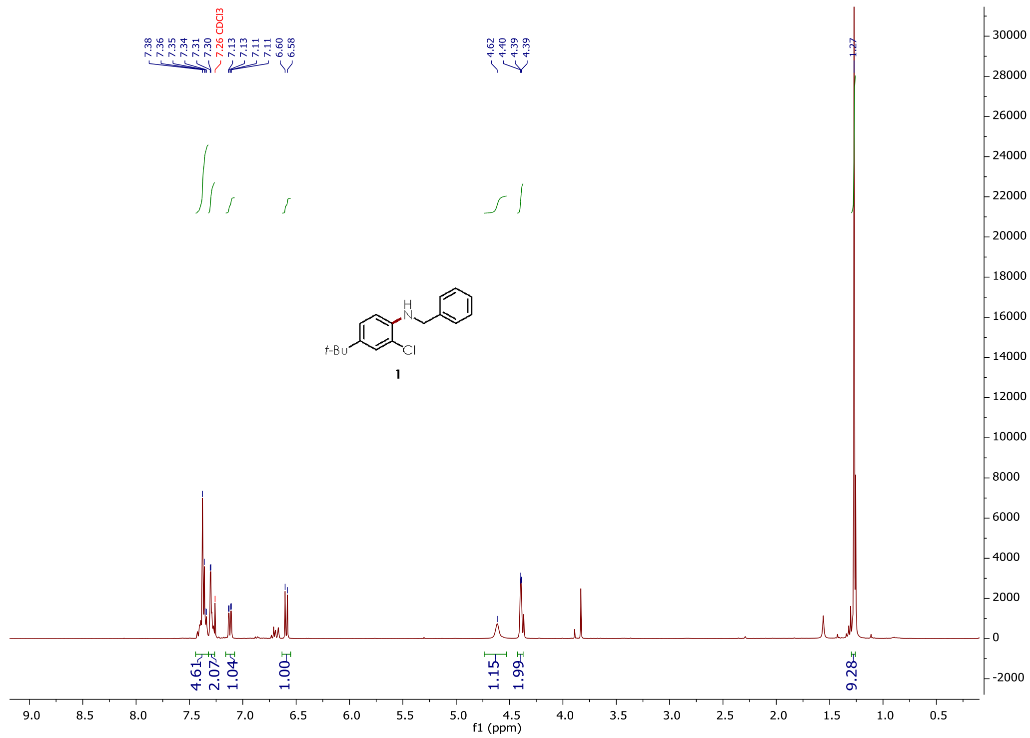
^{1}H NMR (600 MHz, $CDCl_3$) Compound **5** Starting Material



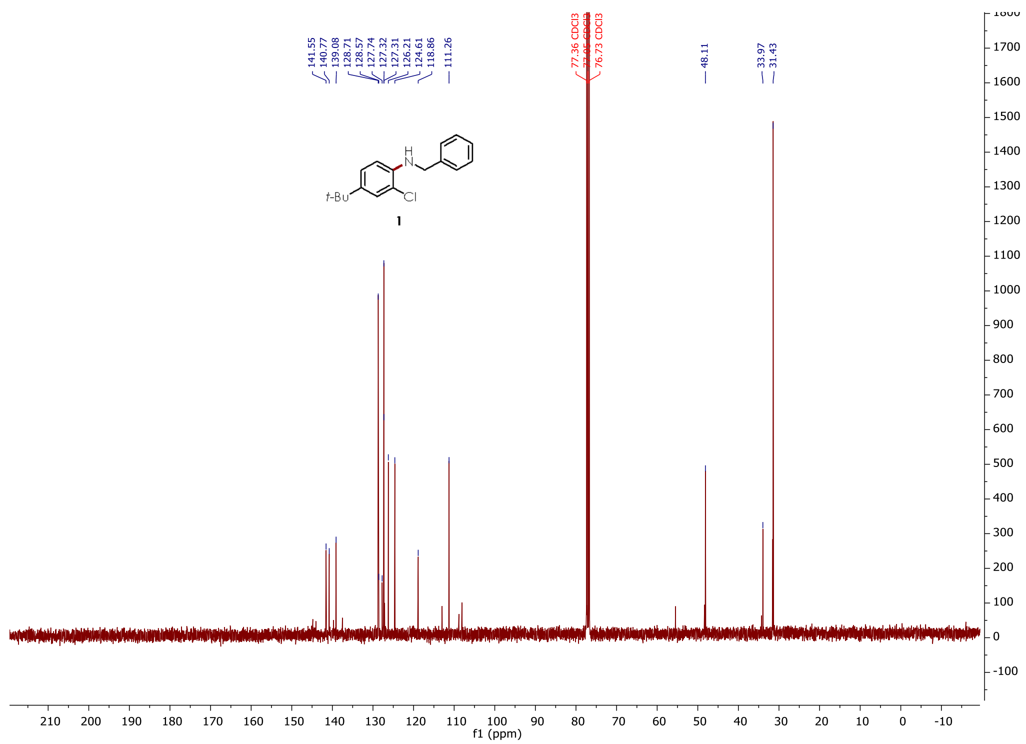
^{13}C NMR (151 MHz, $CDCl_3$) Compound **5** Starting Material



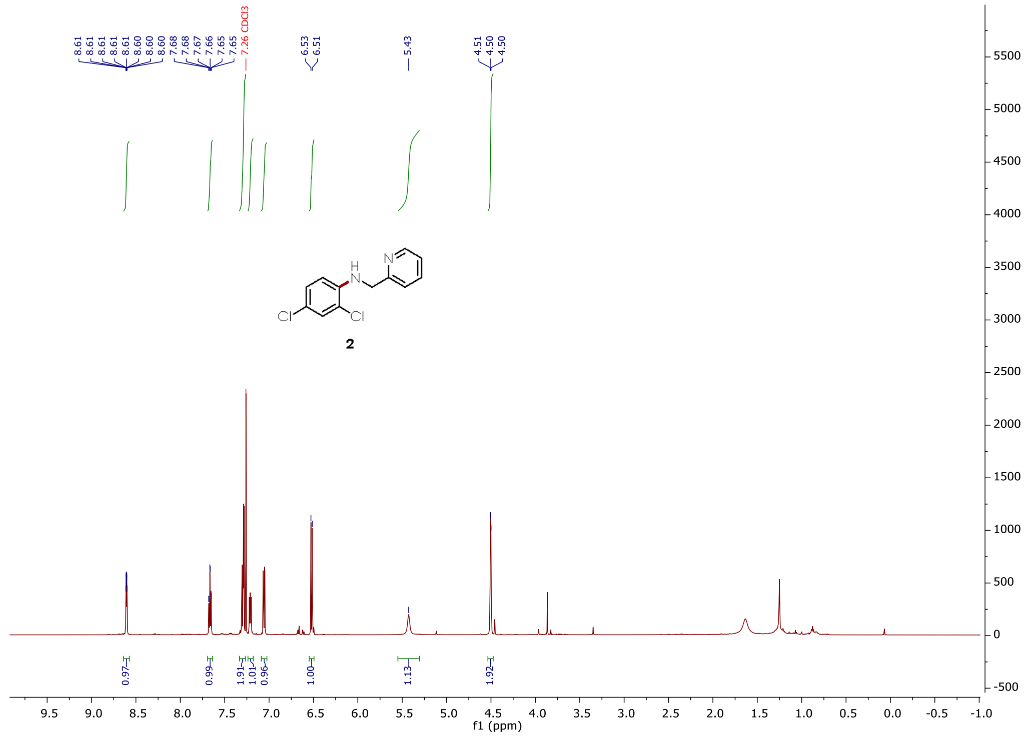
^{1}H NMR (600 MHz, $CDCl_3$) Compound **1**



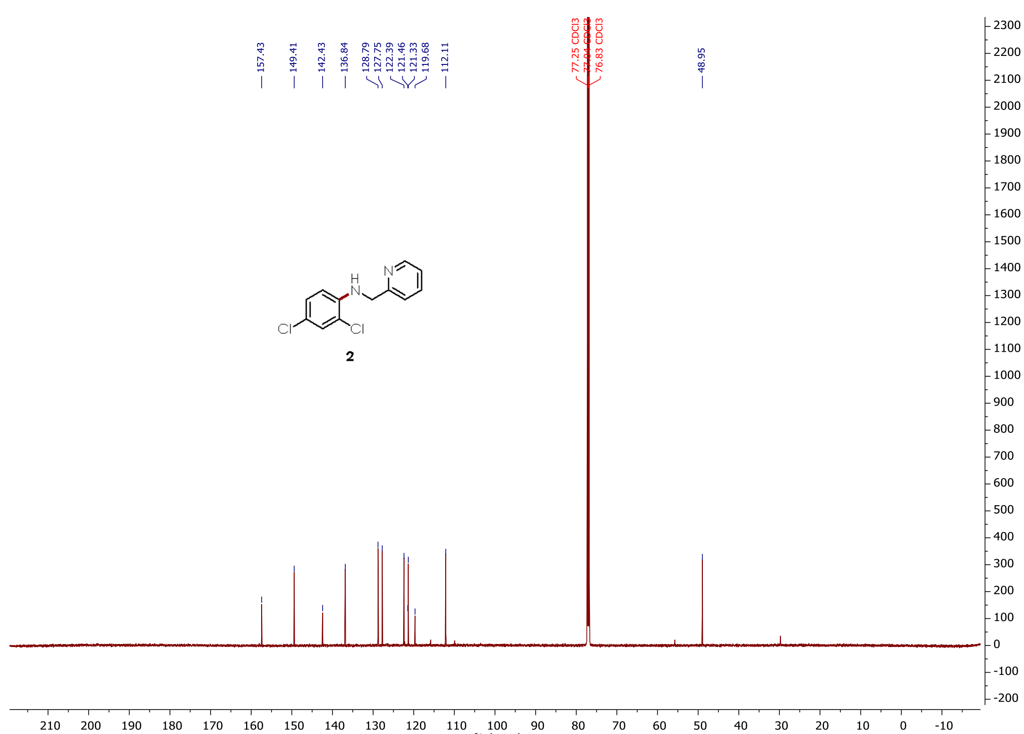
^{13}C NMR (151 MHz, $CDCl_3$) Compound **1**



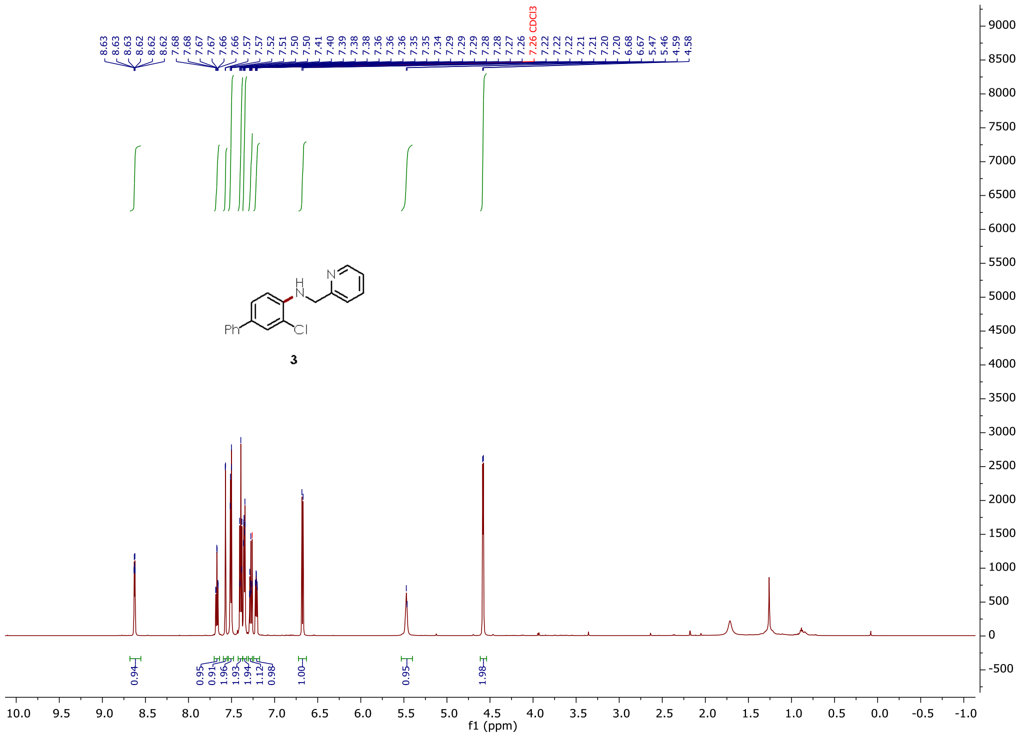
^{1}H NMR (600 MHz, $CDCl_3$) Compound **2**



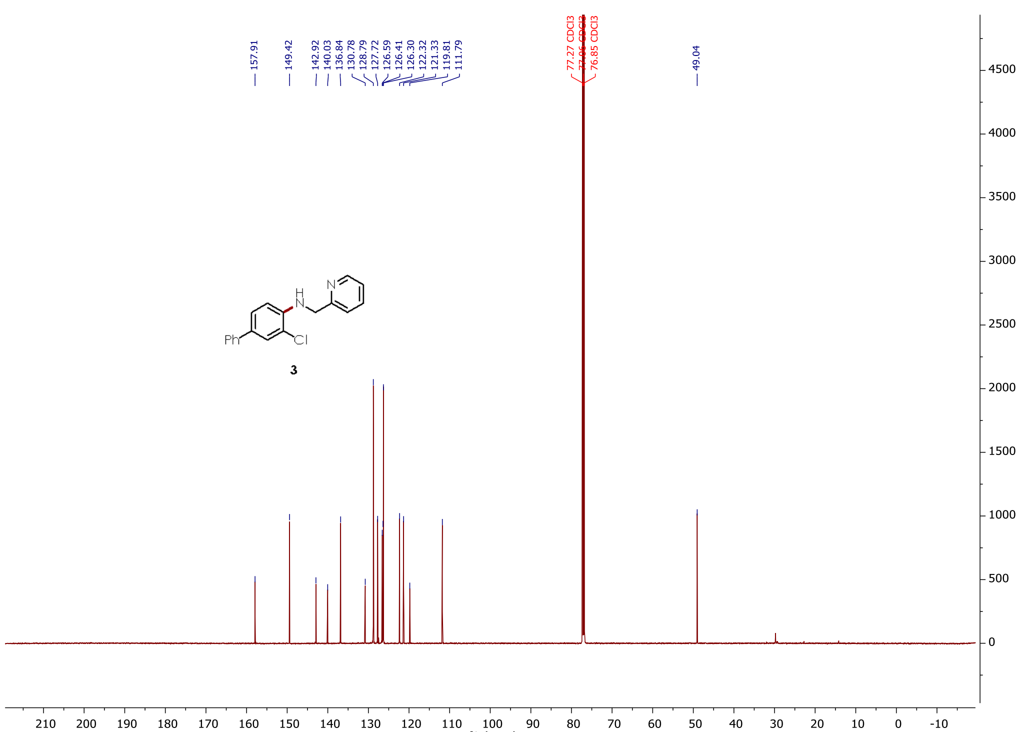
^{13}C NMR (151 MHz, $CDCl_3$) Compound **2**



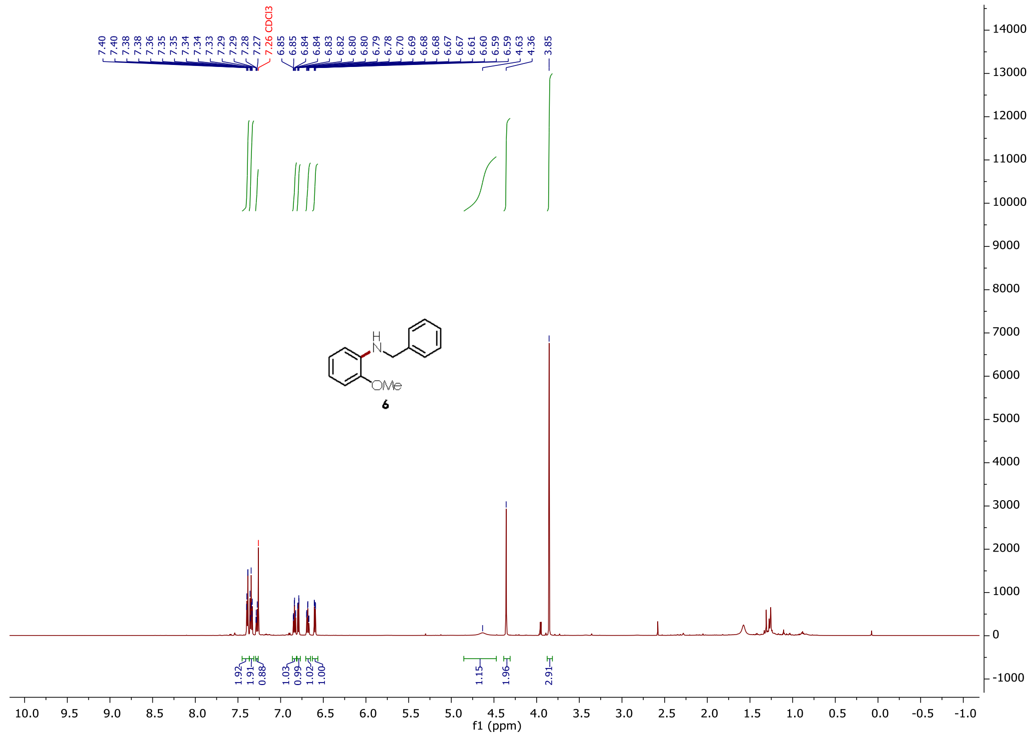
[1]H NMR (600 MHz, $CDCl_3$) Compound **3**



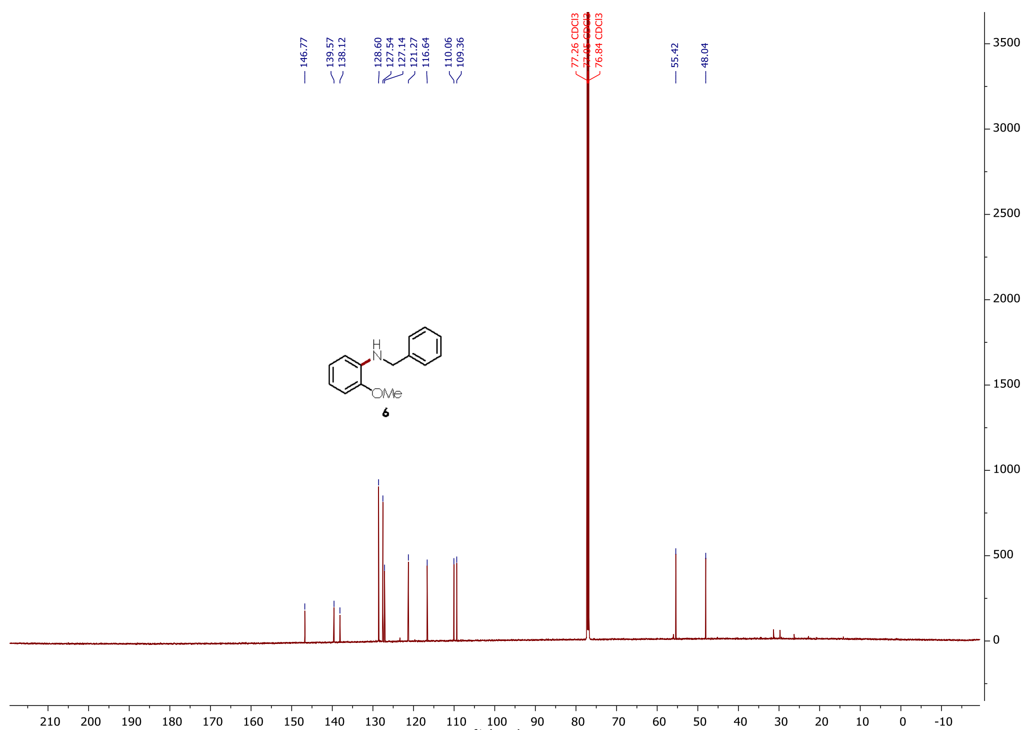
[13]C NMR (151 MHz, $CDCl_3$) Compound **3**



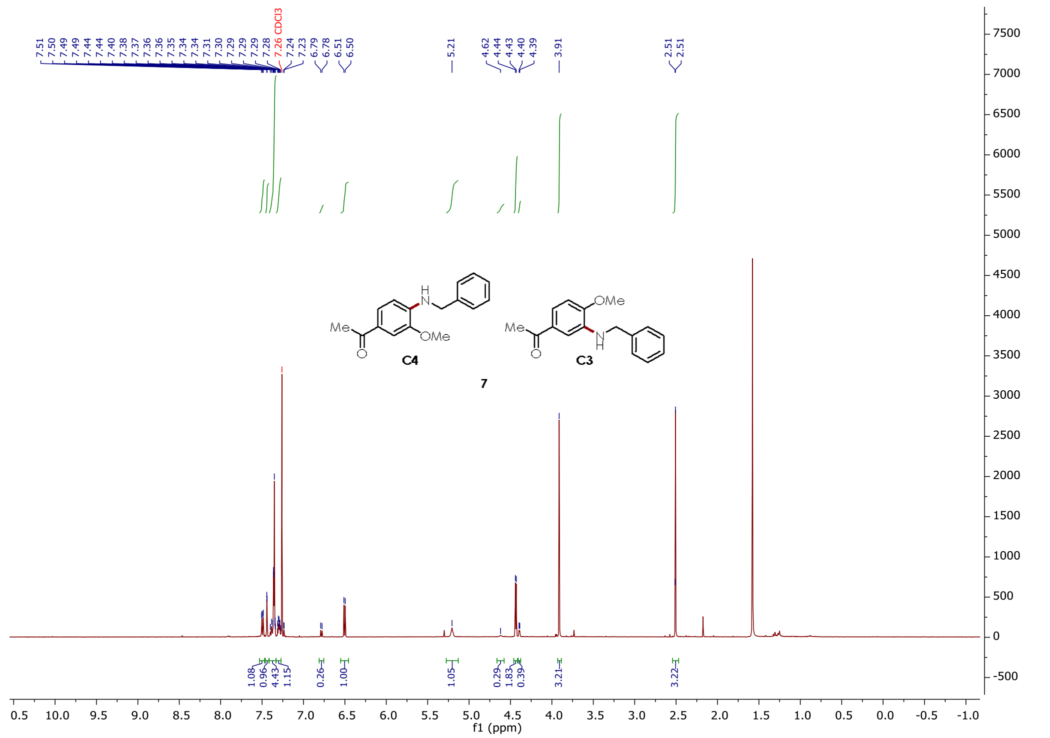
^{1}H NMR (600 MHz, $CDCl_3$) Compound **6**



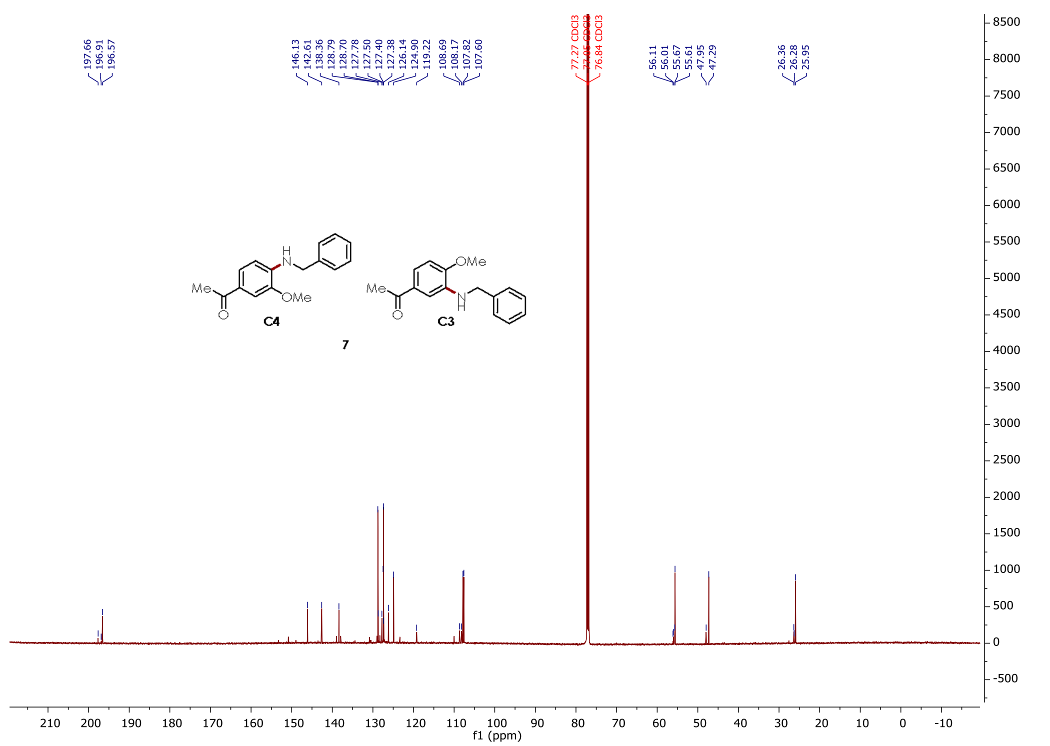
^{13}C NMR (151 MHz, $CDCl_3$) Compound **6**



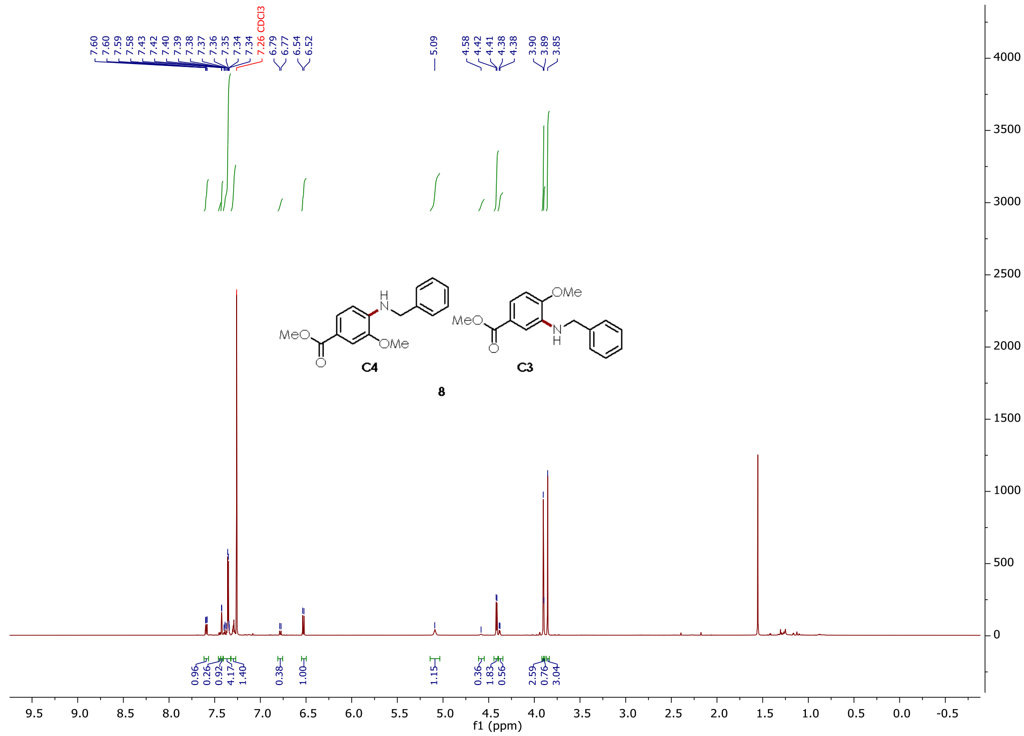
^{1}H NMR (600 MHz, $CDCl_3$) Compound **7**



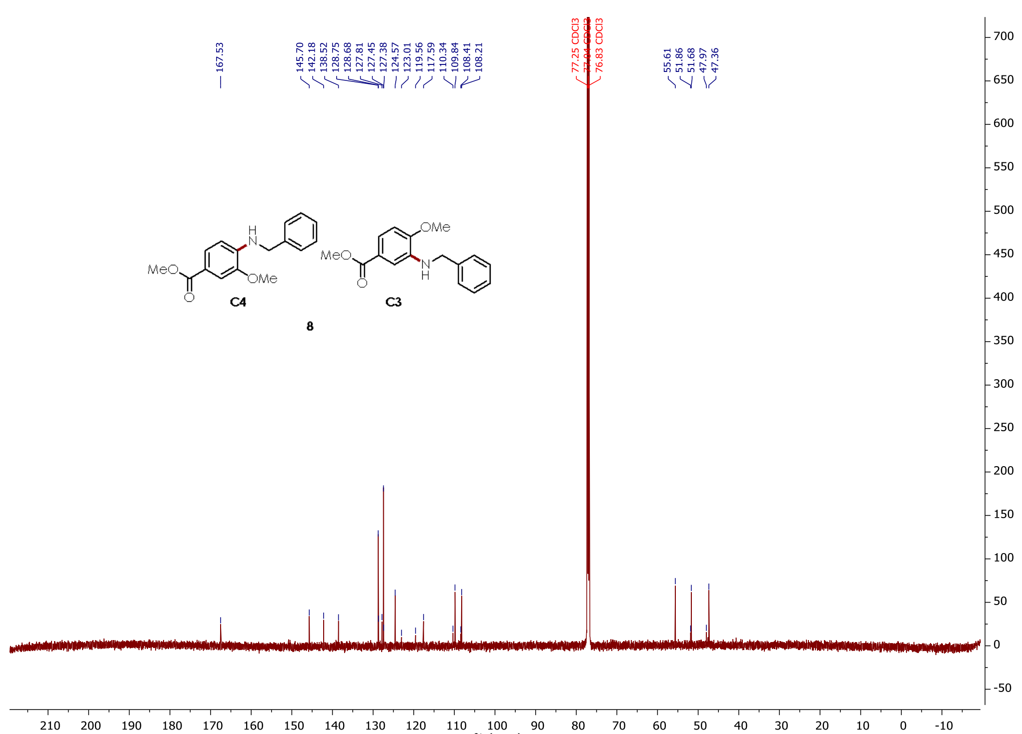
^{13}C NMR (151 MHz, $CDCl_3$) Compound **7**



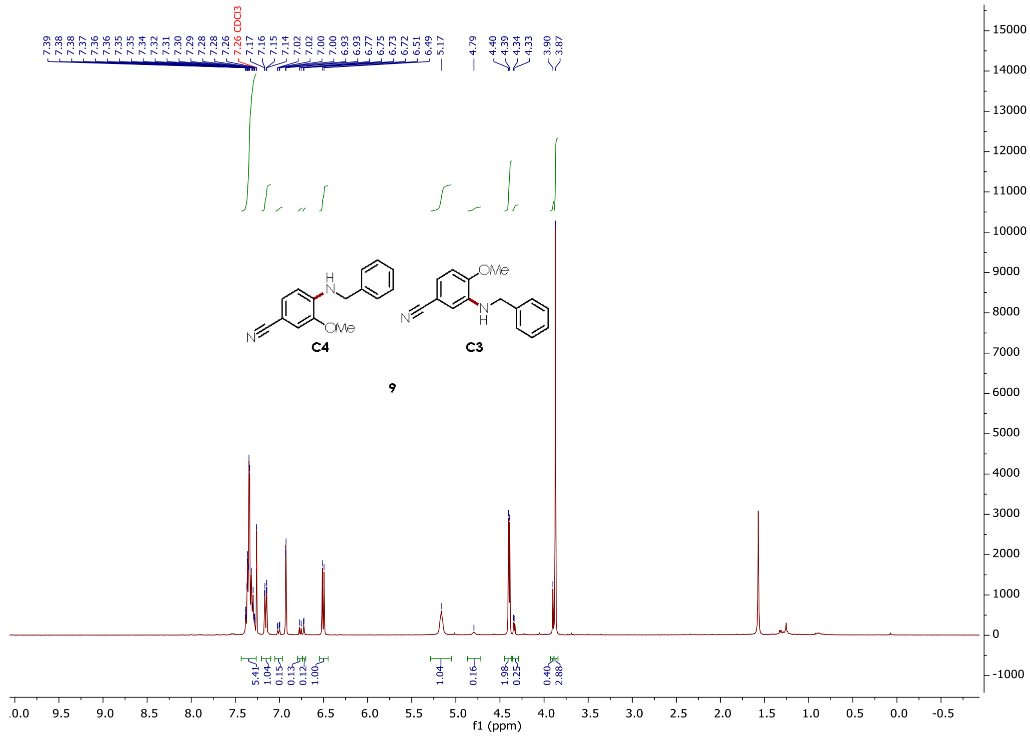
^{1}H NMR (600 MHz, $CDCl_3$) Compound **8**



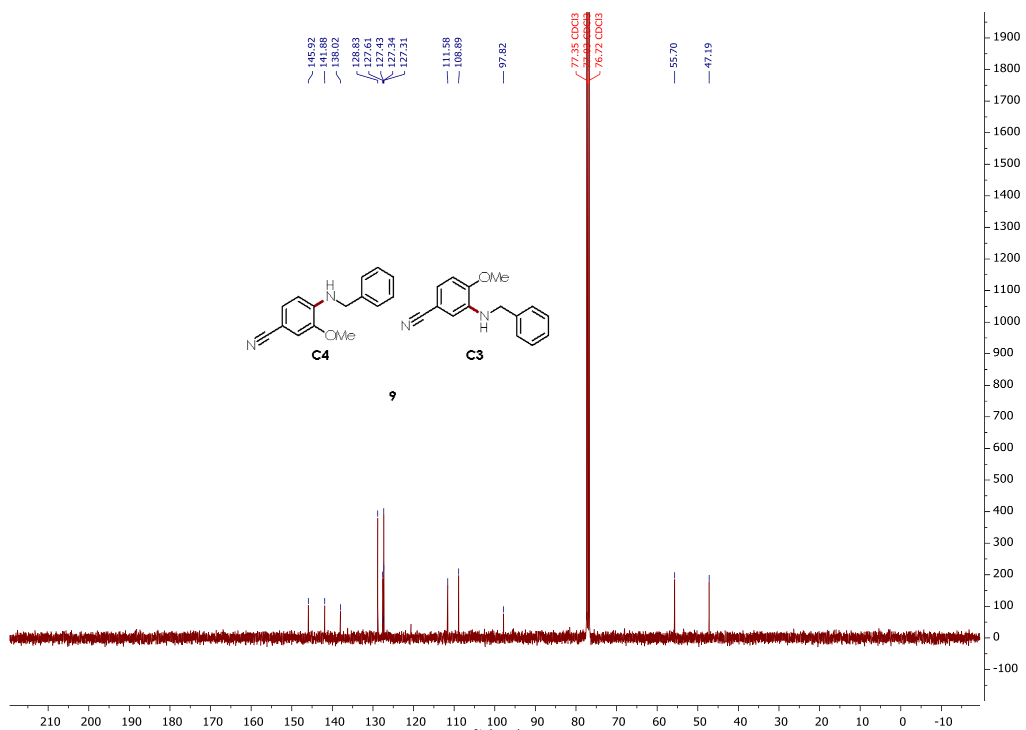
^{13}C NMR (151 MHz, $CDCl_3$) Compound **8**



^{1}H NMR (600 MHz, $CDCl_3$) Compound **9**



^{13}C NMR (151 MHz, $CDCl_3$) Compound **8**



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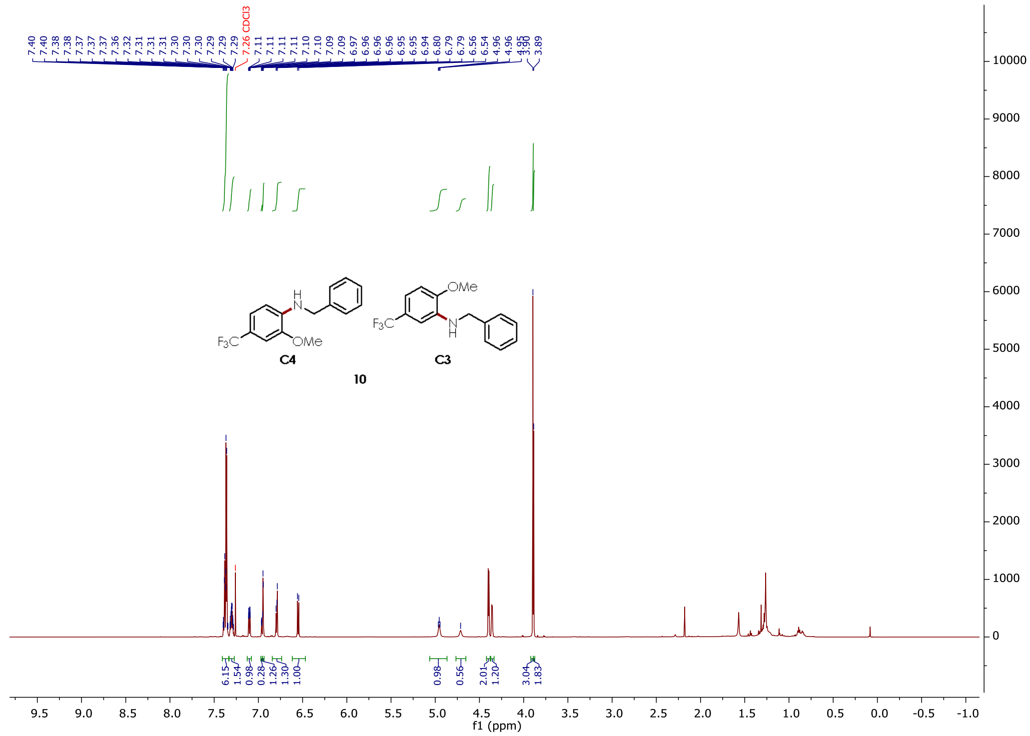
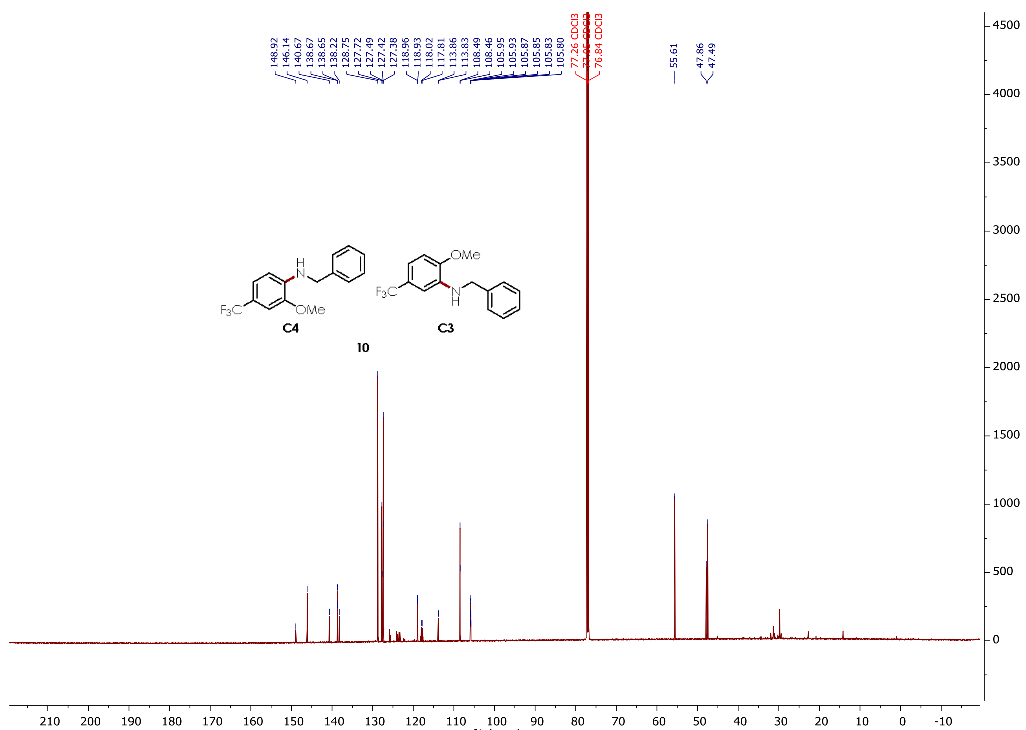
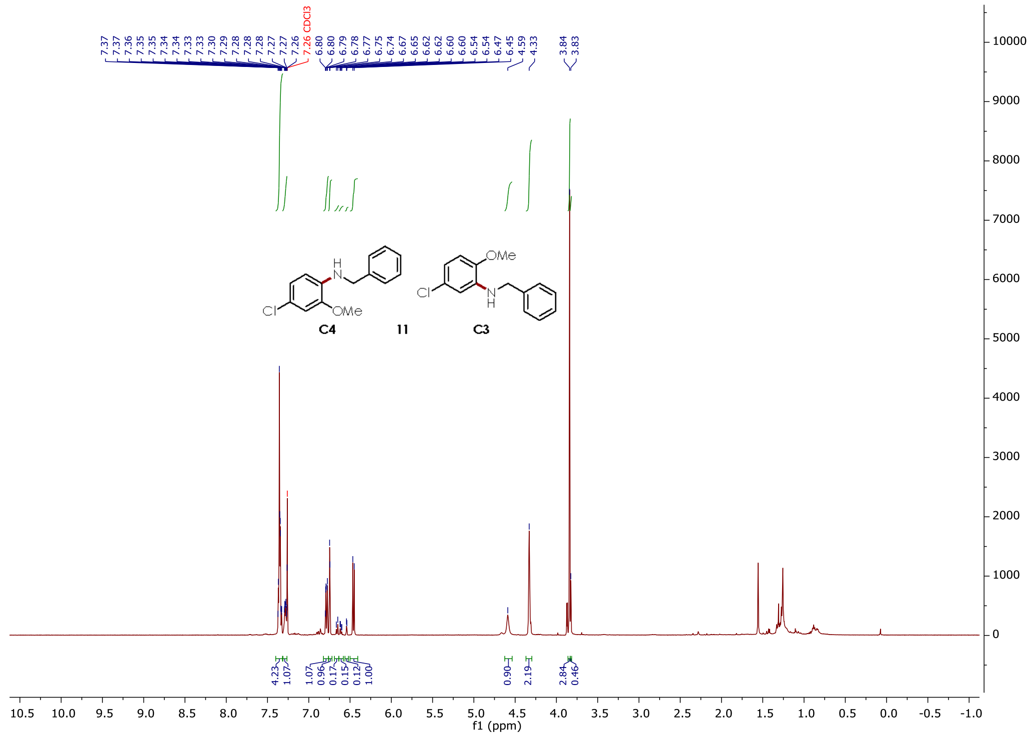


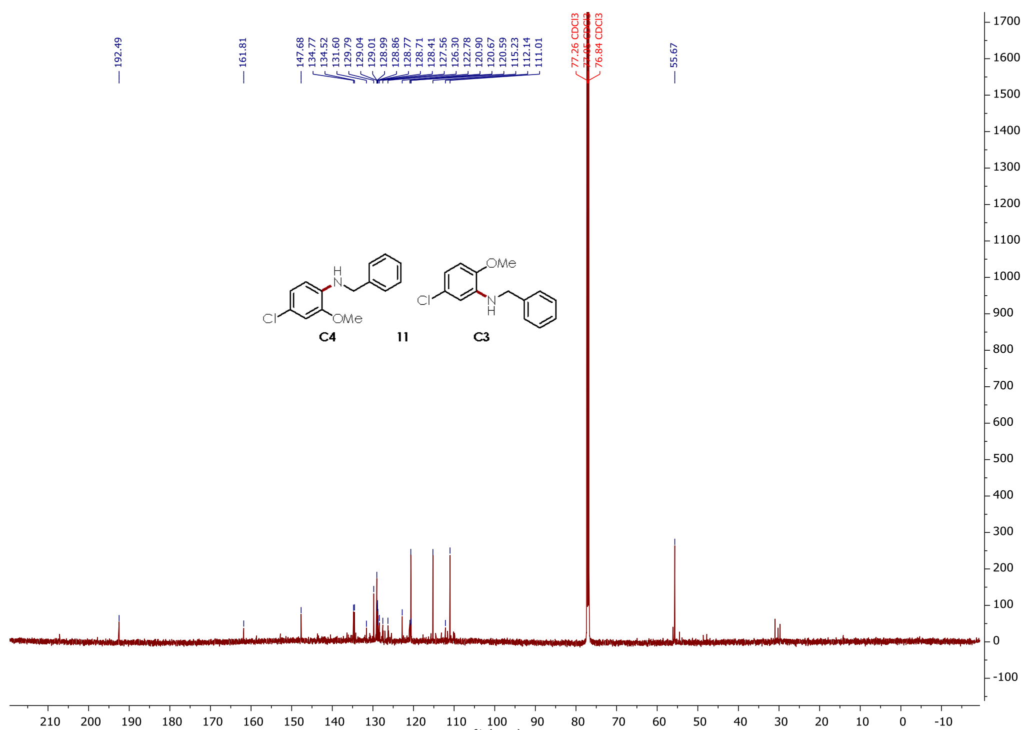
^{13}C NMR (151 MHz, $CDCl_3$) Compound **10**



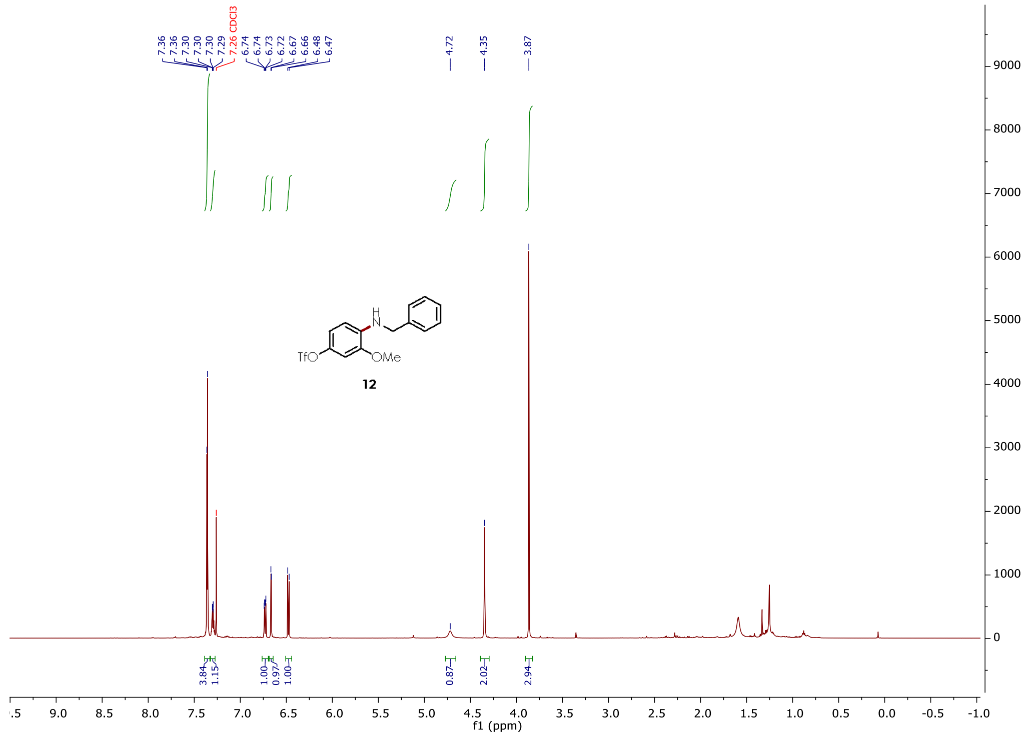
^{1}H NMR (600 MHz, $CDCl_3$) Compound **11**



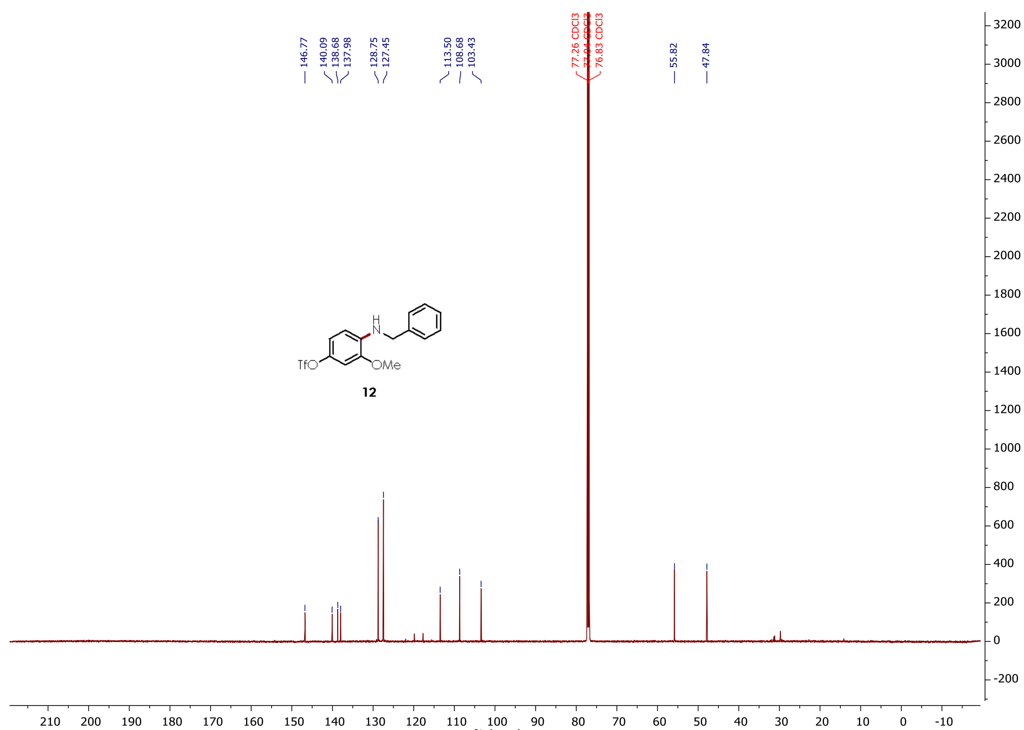
^{13}C NMR (151 MHz, $CDCl_3$) Compound **11**



^{1}H NMR (600 MHz, $CDCl_3$) Compound **12**



^{13}C NMR (151 MHz, $CDCl_3$) Compound **12**



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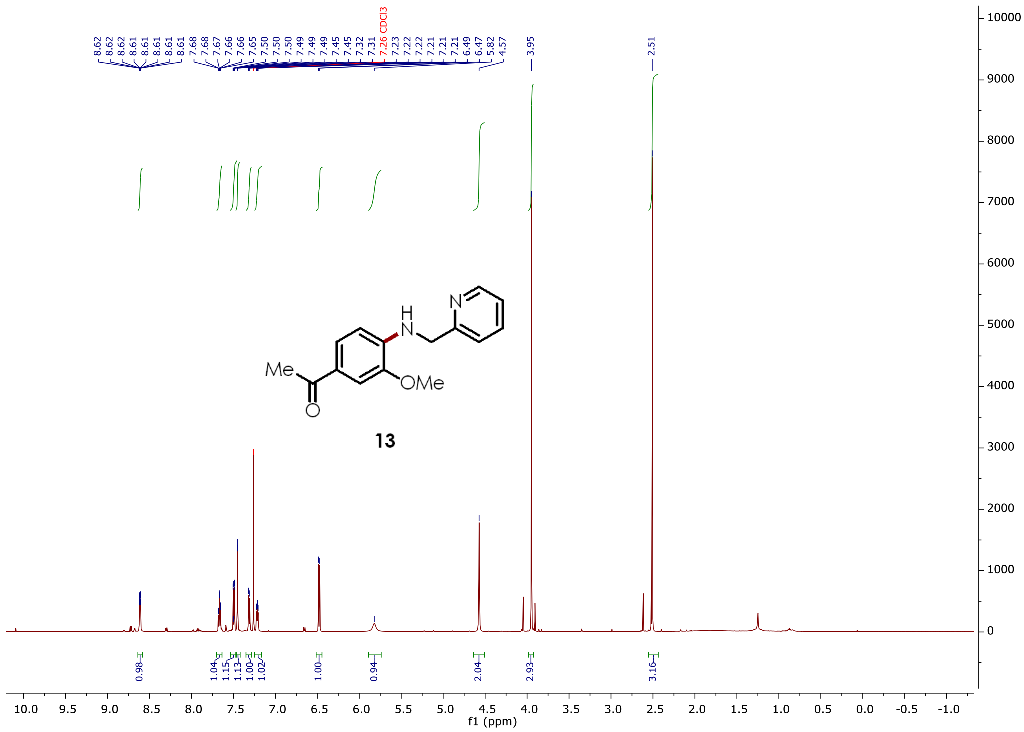
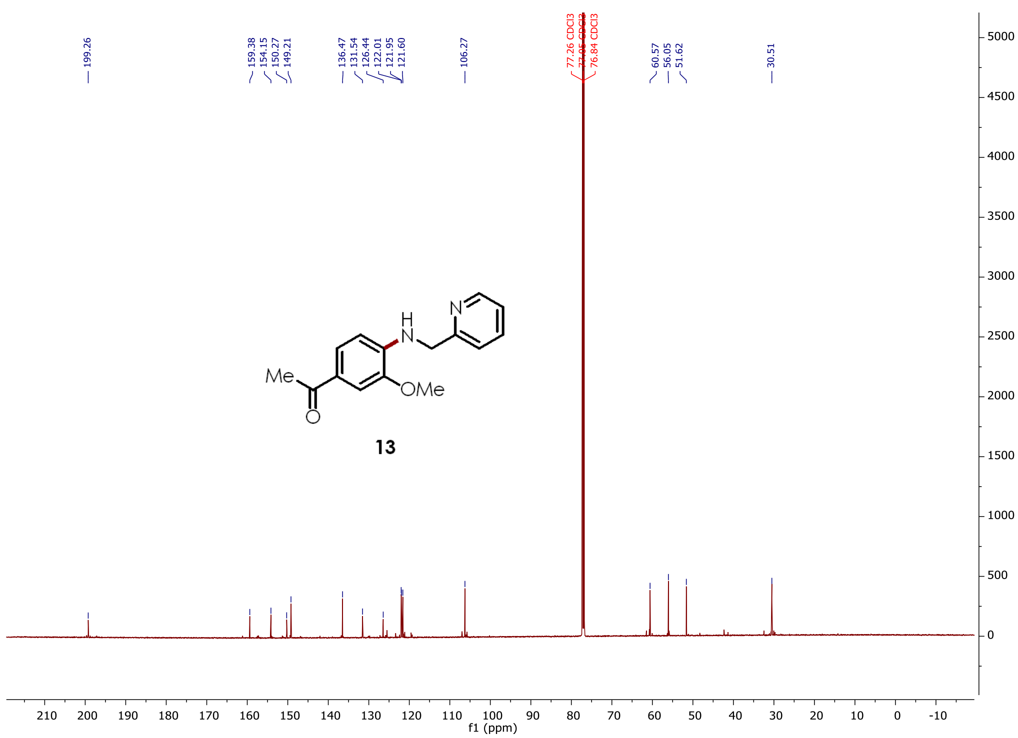
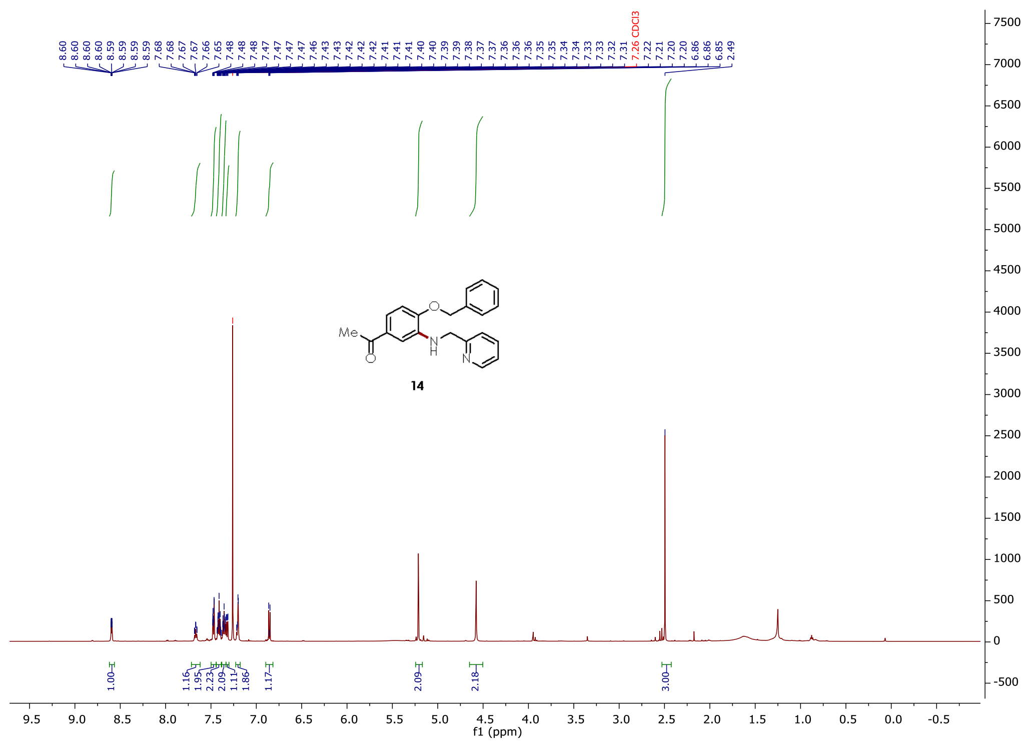


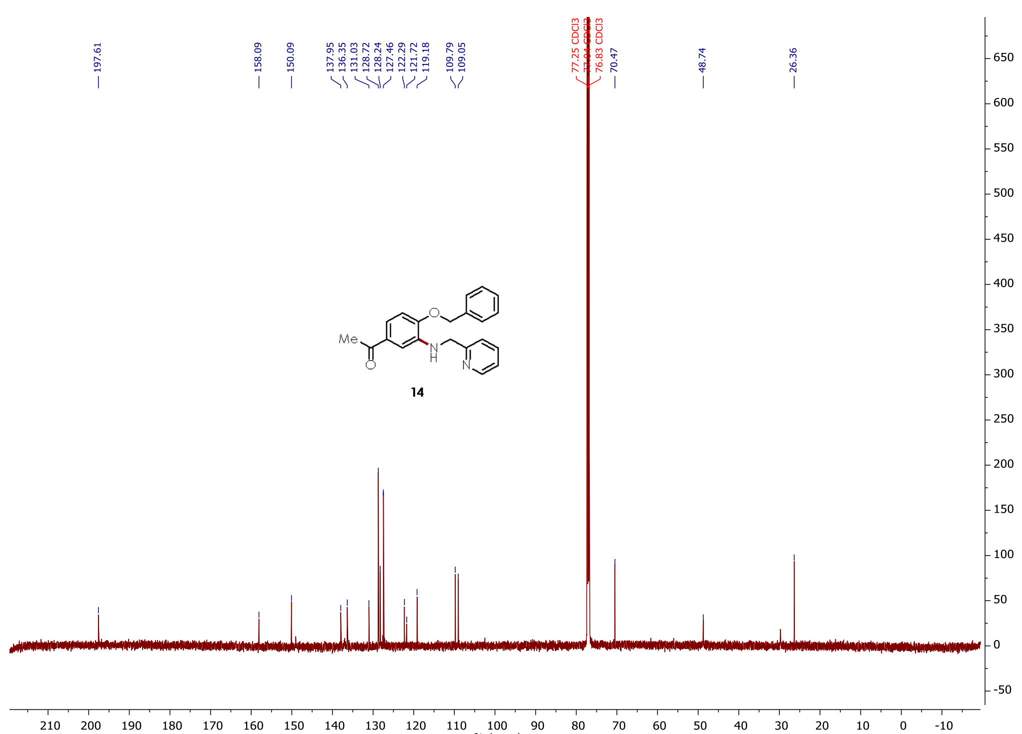
^{13}C NMR (151 MHz, $CDCl_3$) Compound **13**



^{1}H NMR (600 MHz, $CDCl_3$) Compound **14**



^{13}C NMR (151 MHz, $CDCl_3$) Compound **14**



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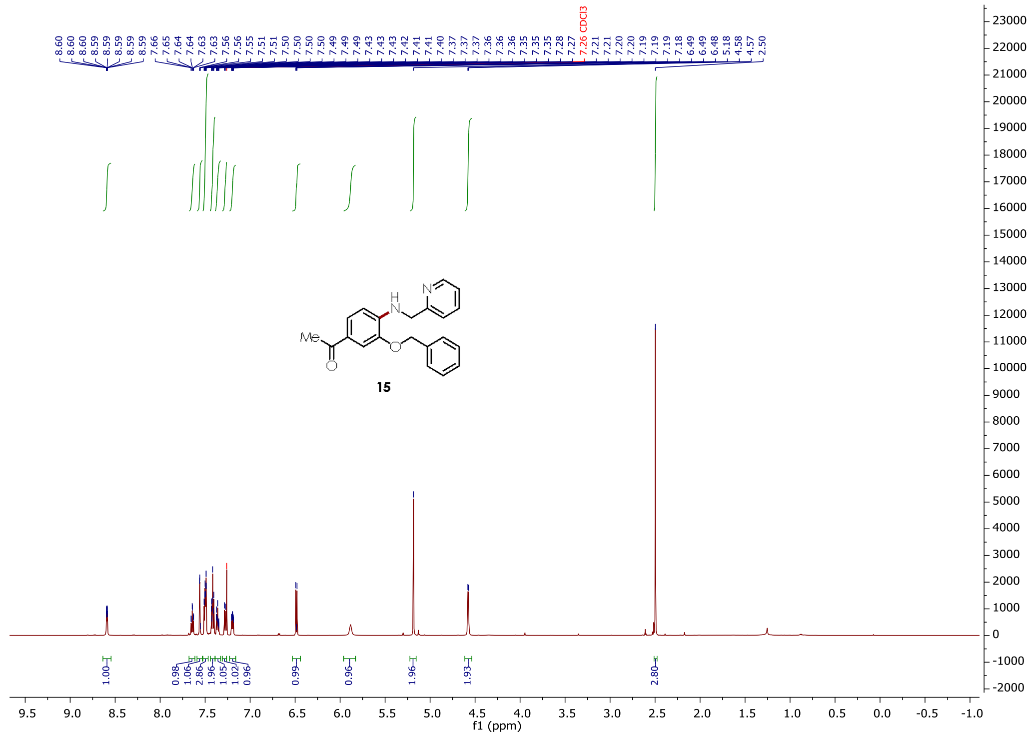
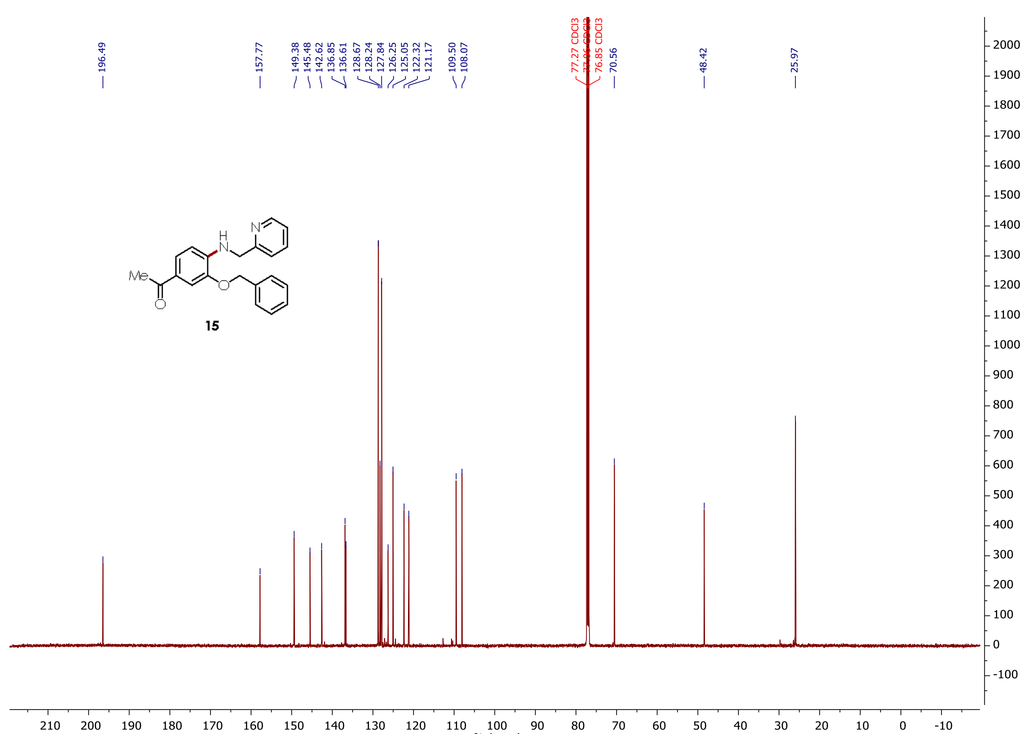


^{13}C NMR (151 MHz, $CDCl_3$) Compound **15**



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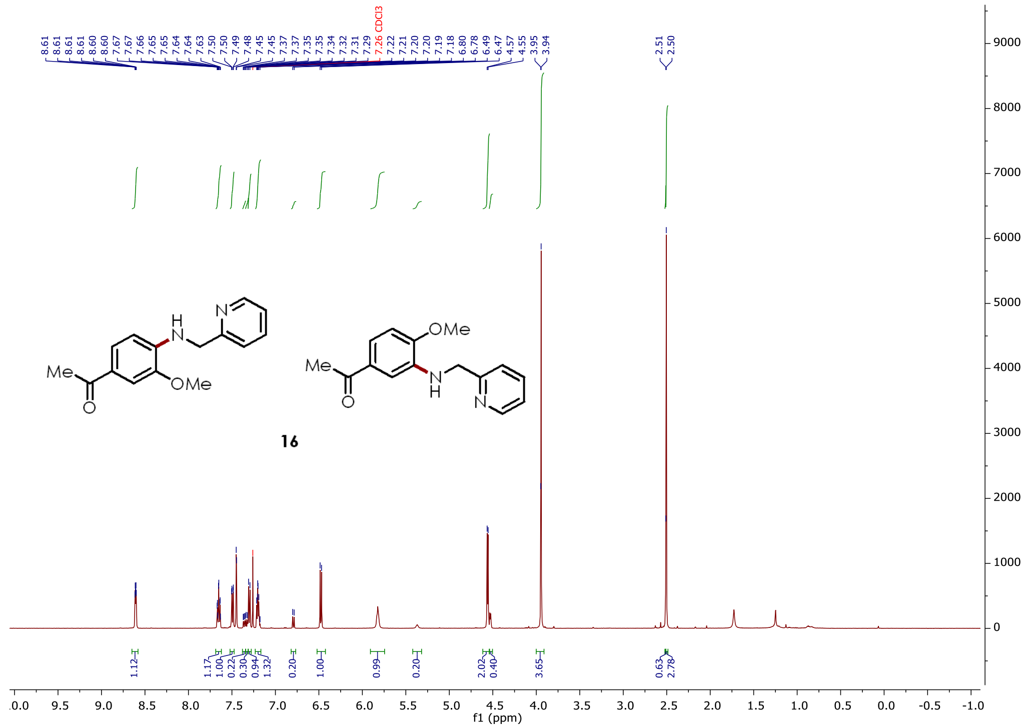
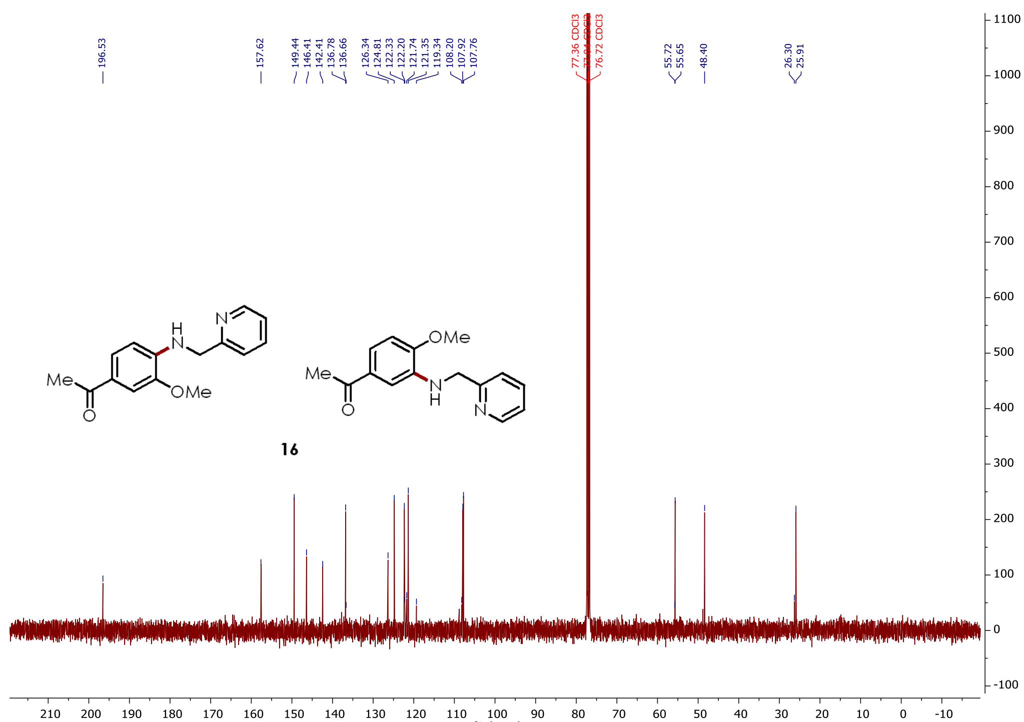


^{13}C NMR (151 MHz, $CDCl_3$) Compound **16**



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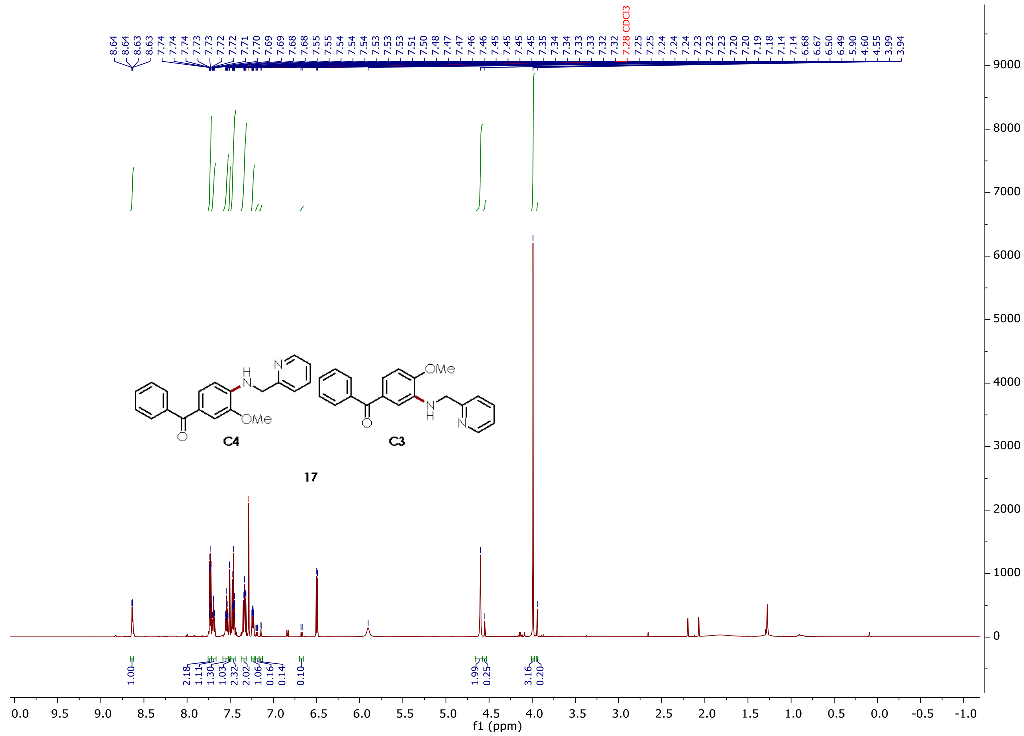

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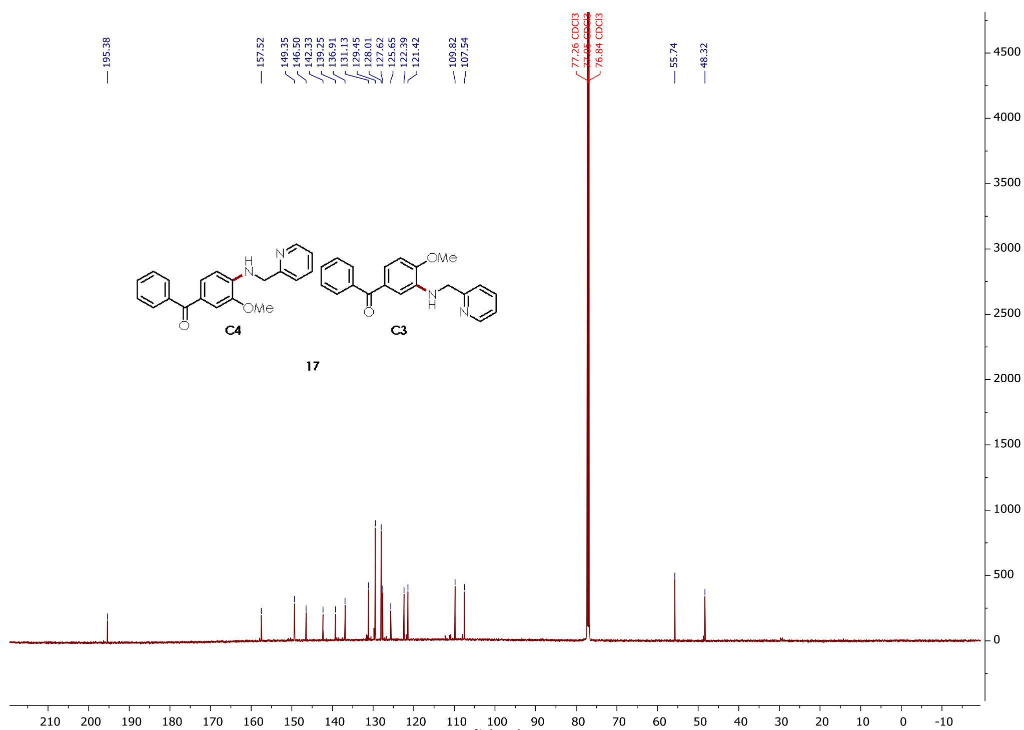
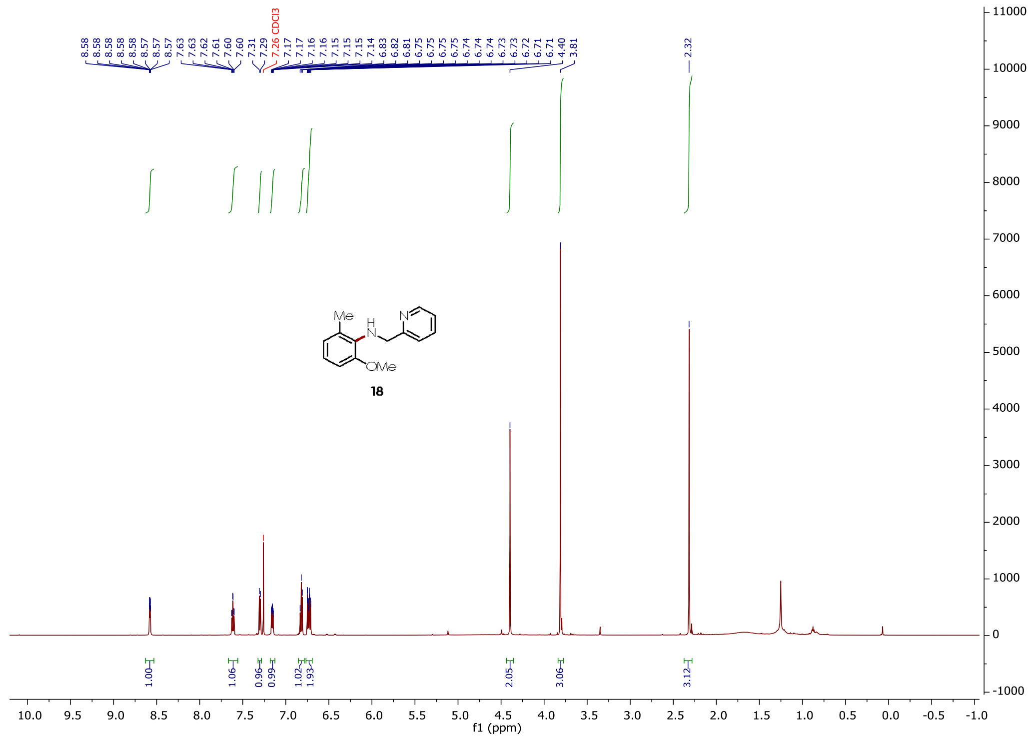
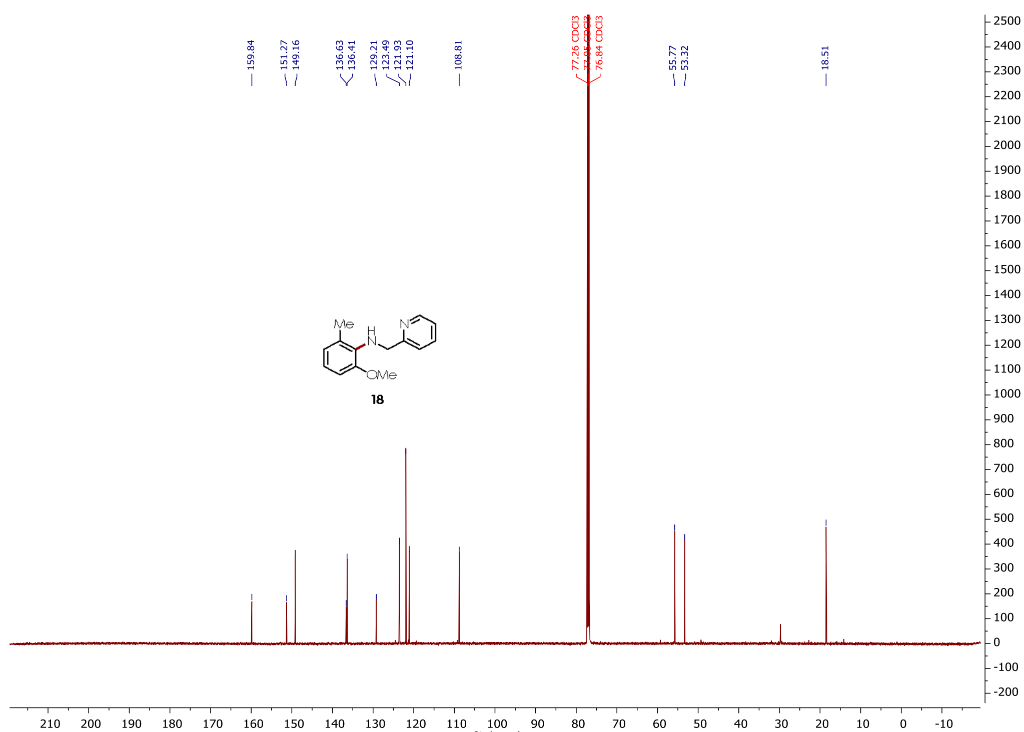


^{1}H NMR (600 MHz, $CDCl_3$) Compound **18**



^{13}C NMR (151 MHz, $CDCl_3$) Compound **18**



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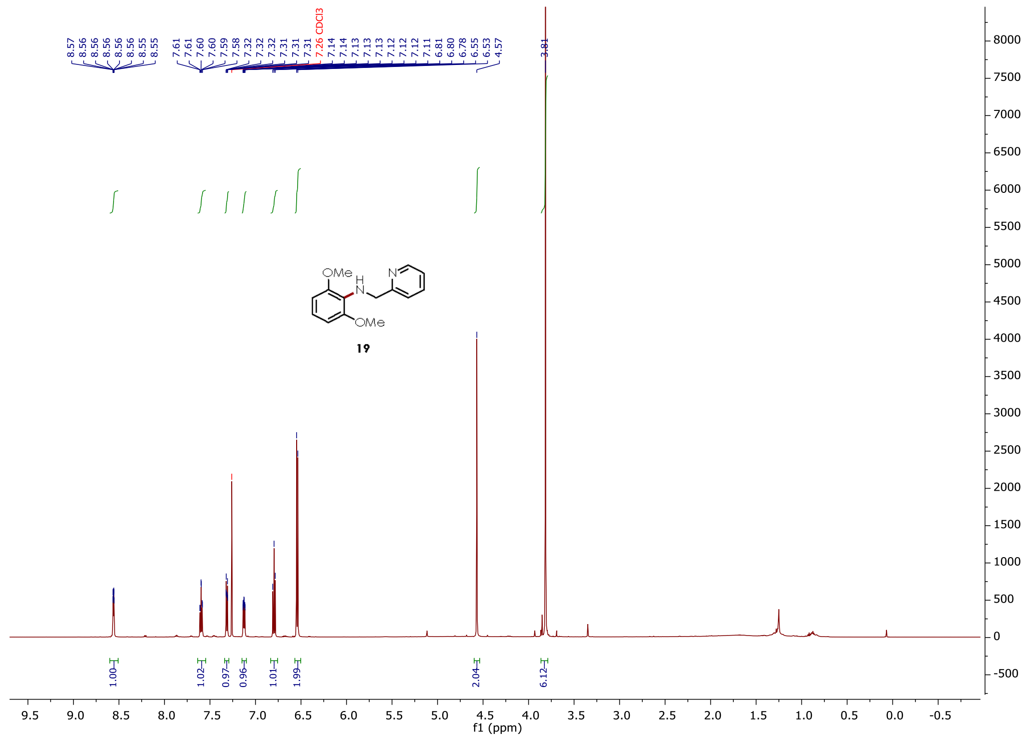

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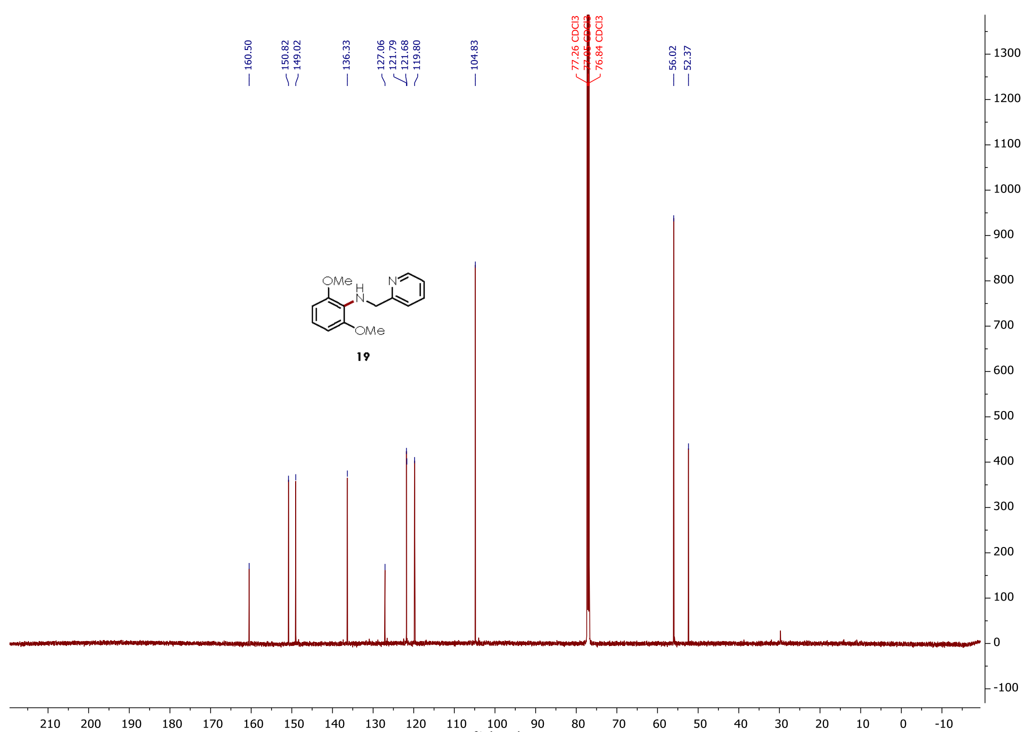

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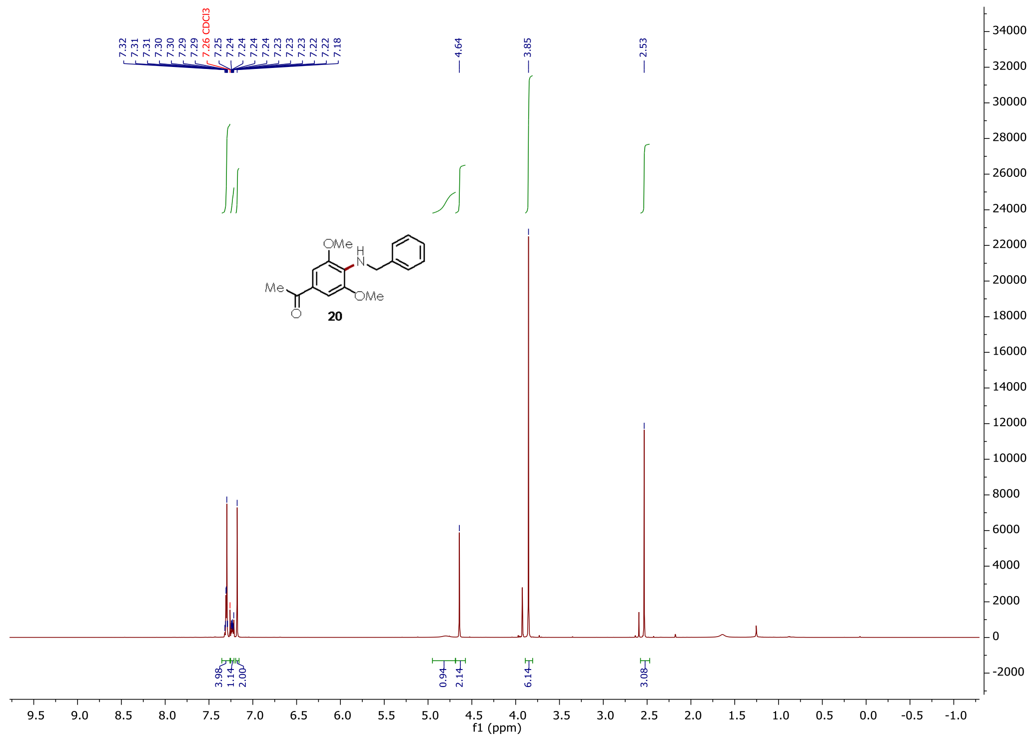
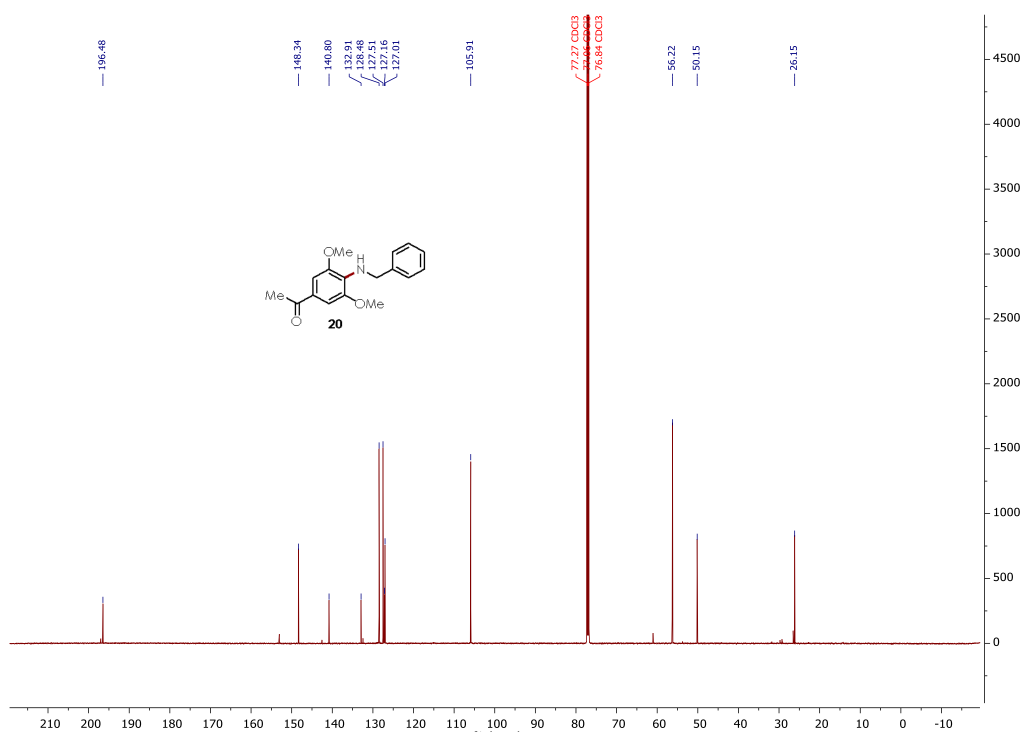


^{13}C NMR (151 MHz, $CDCl_3$) Compound **20**



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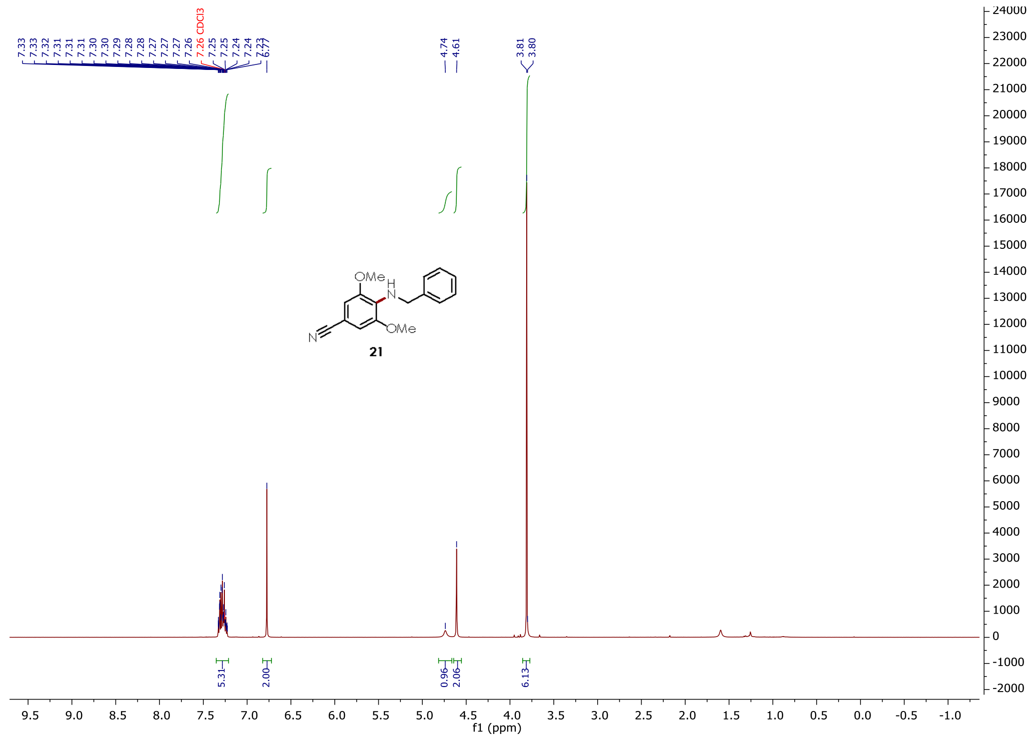

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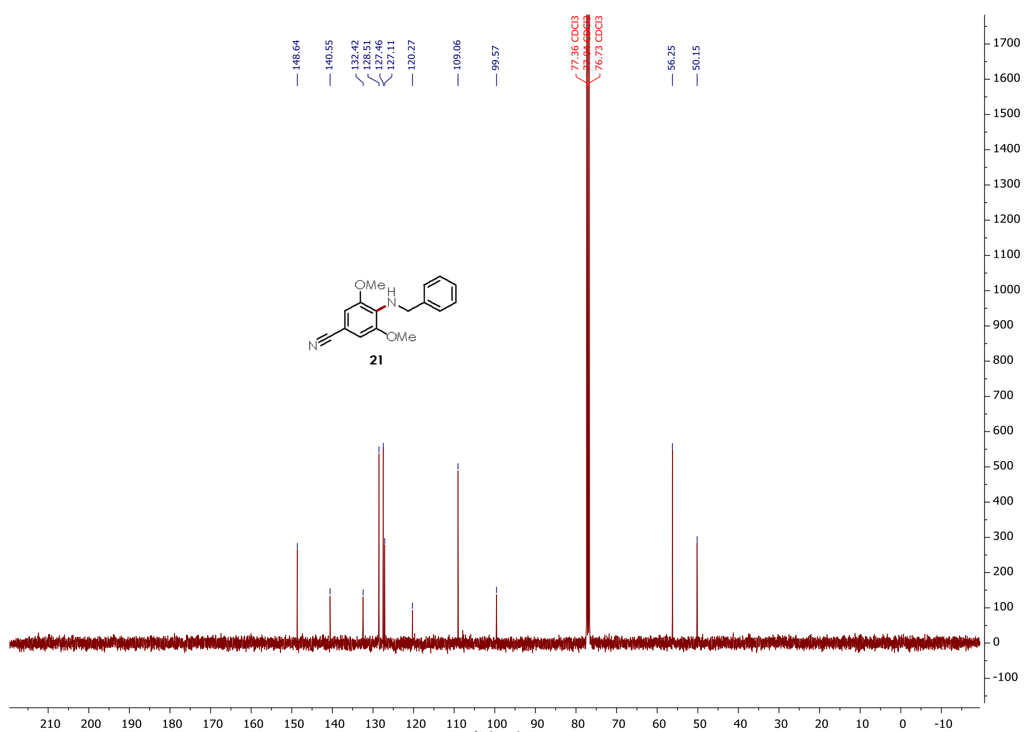

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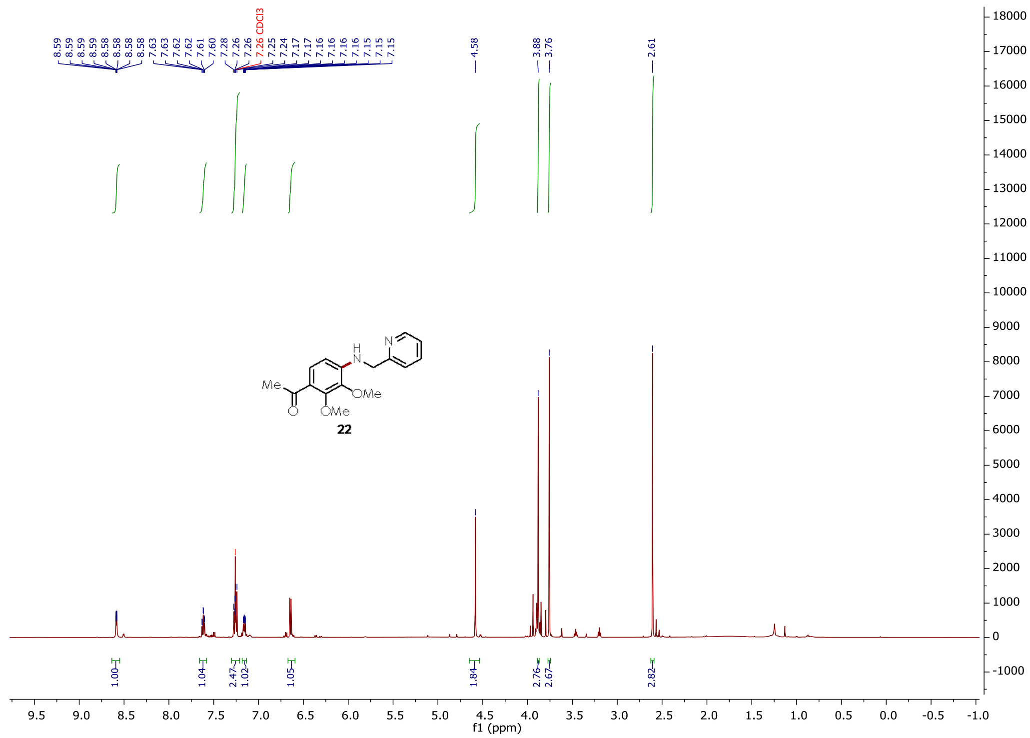

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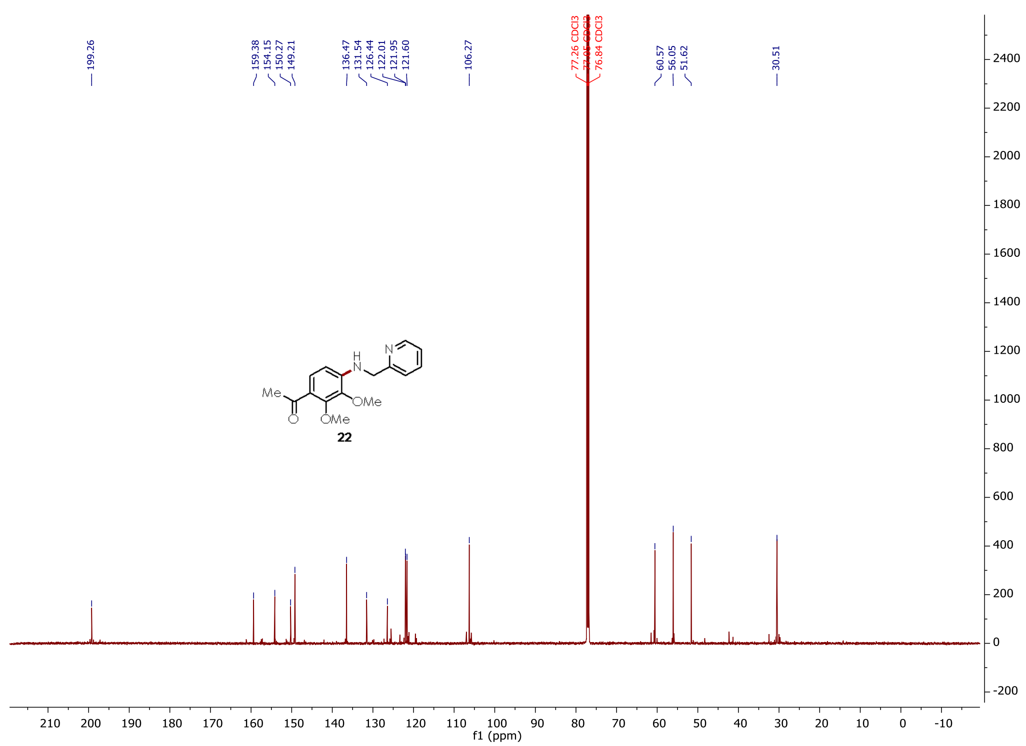

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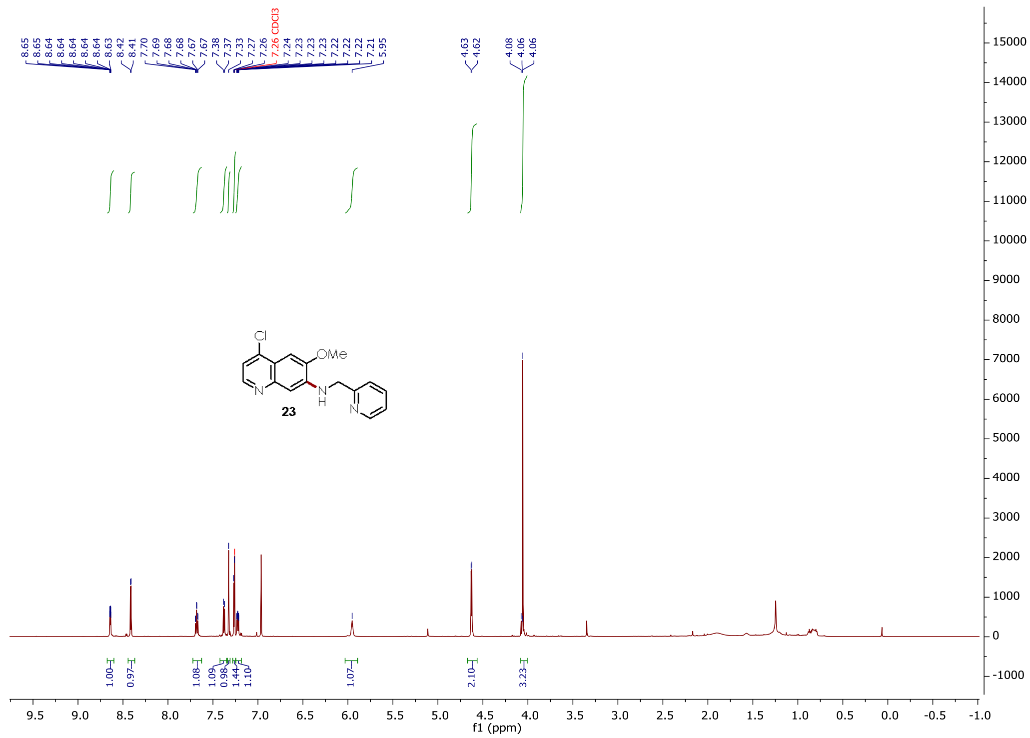
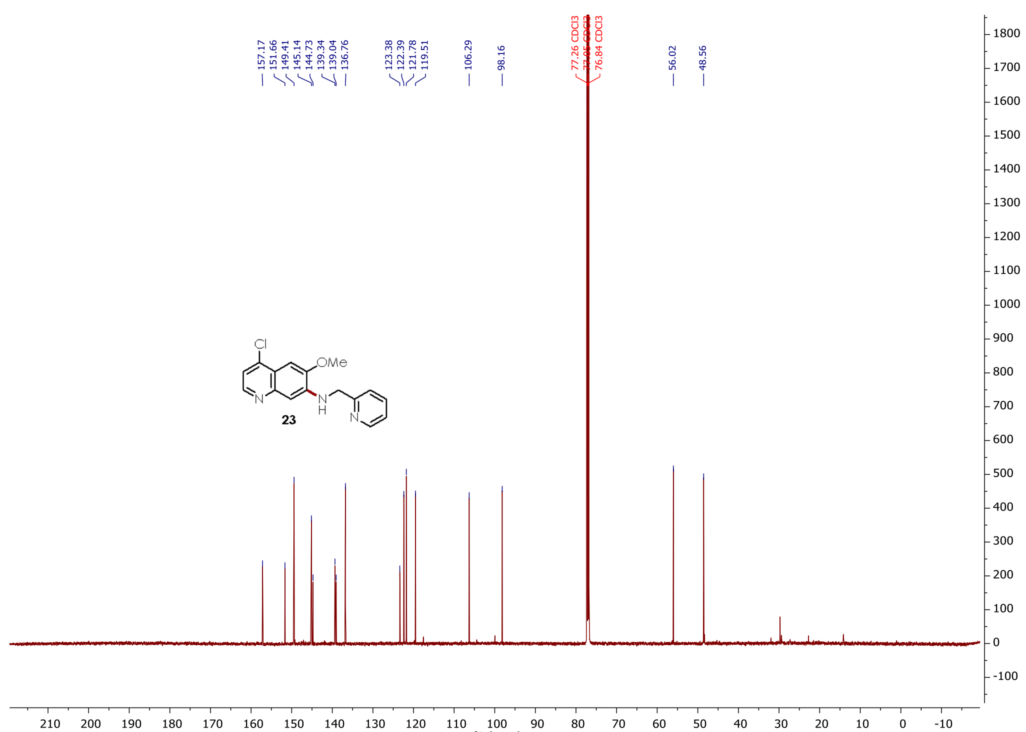
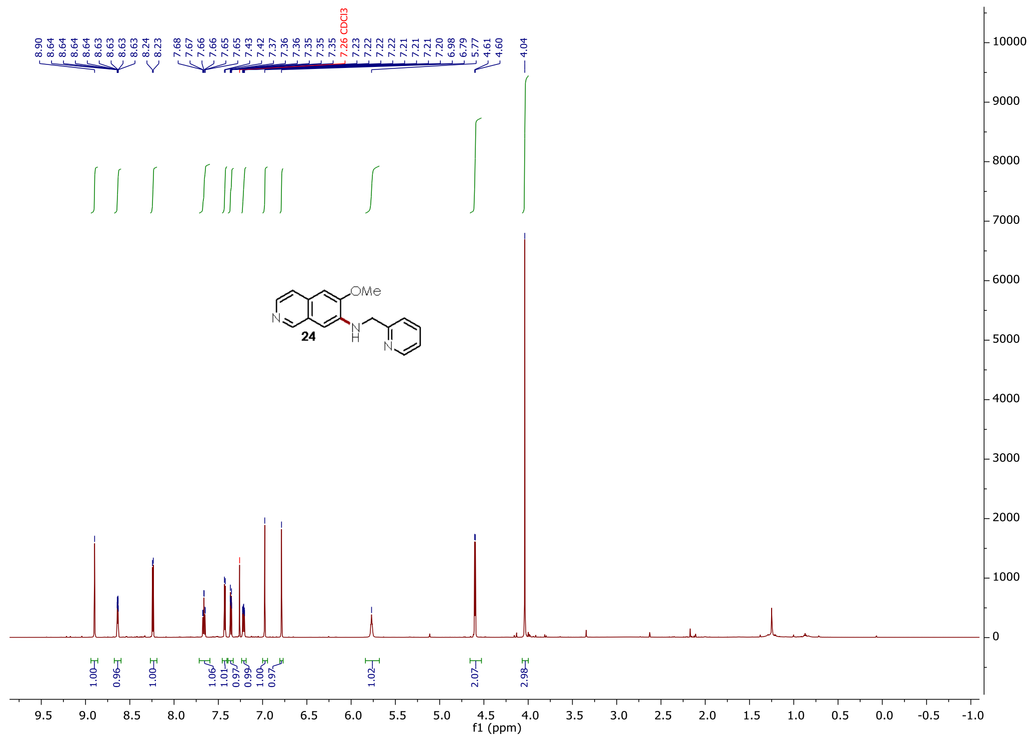


^{13}C NMR (151 MHz, $CDCl_3$) Compound **23**



^{1}H NMR (600 MHz, $CDCl_3$) Compound **24**



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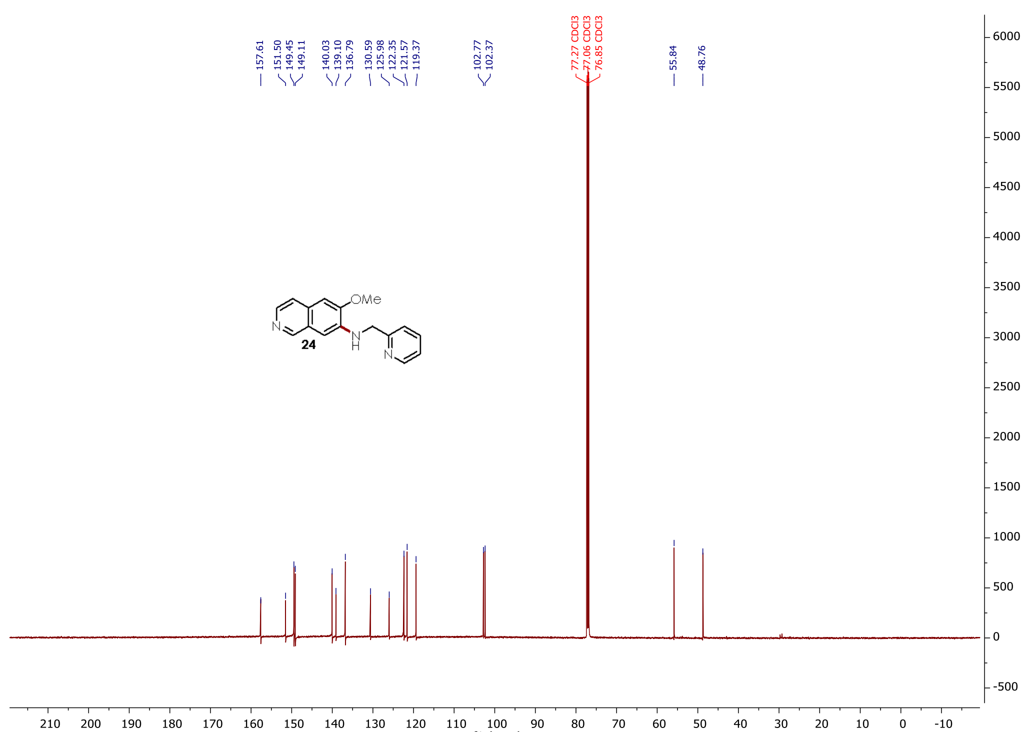
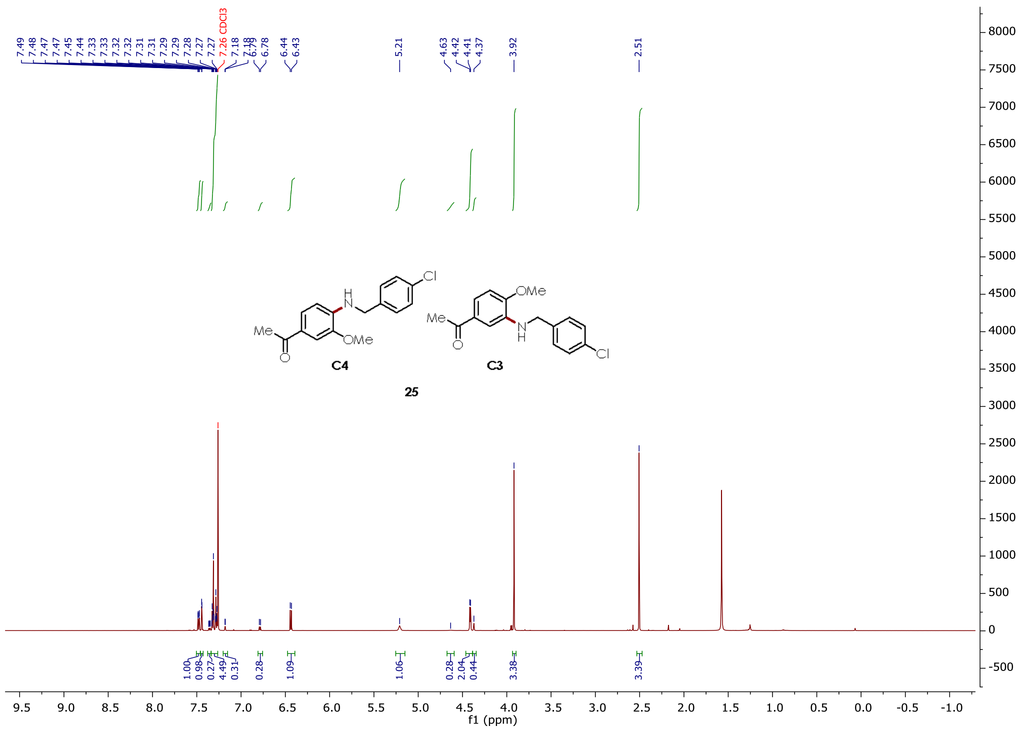


^{1}H NMR (600 MHz, $CDCl_3$) Compound **25**



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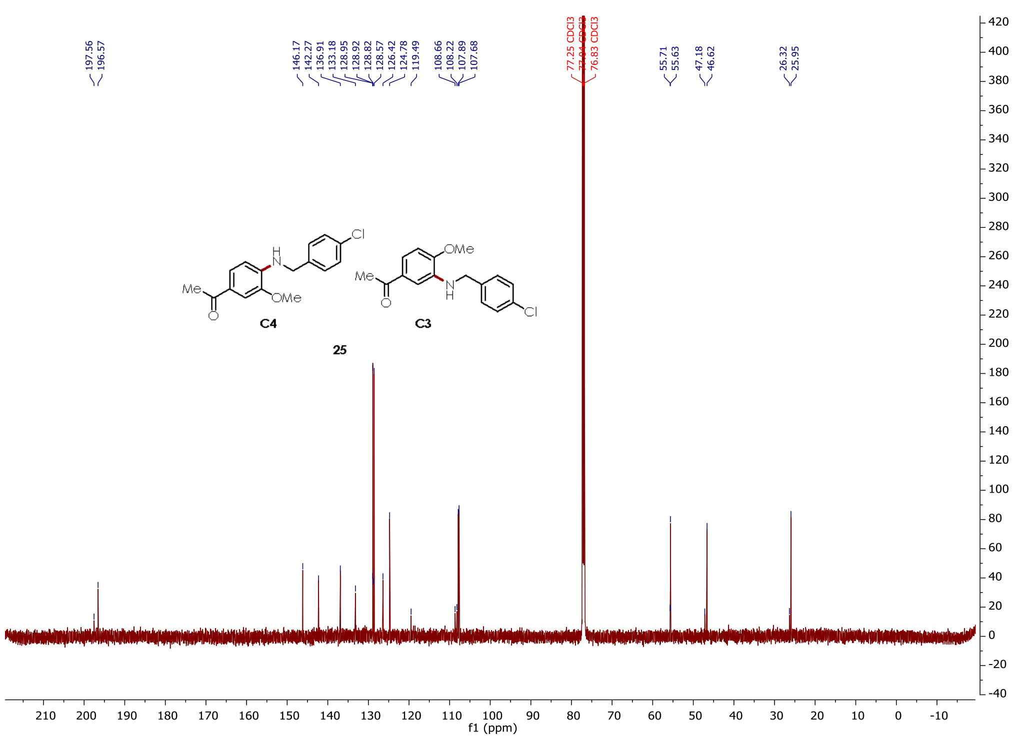
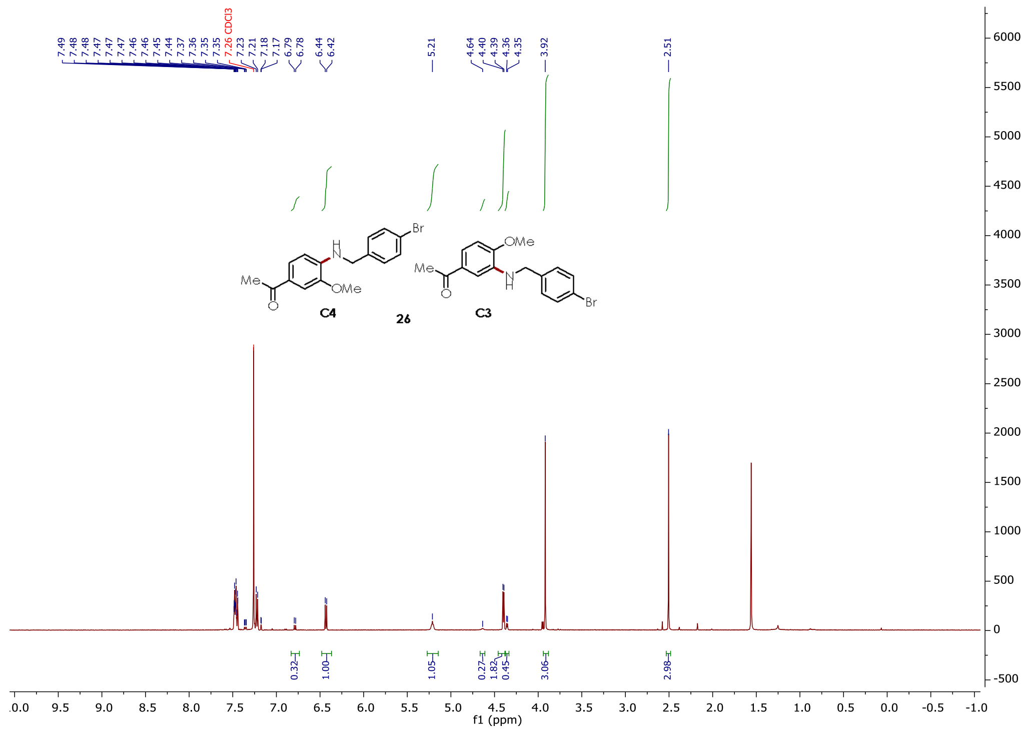
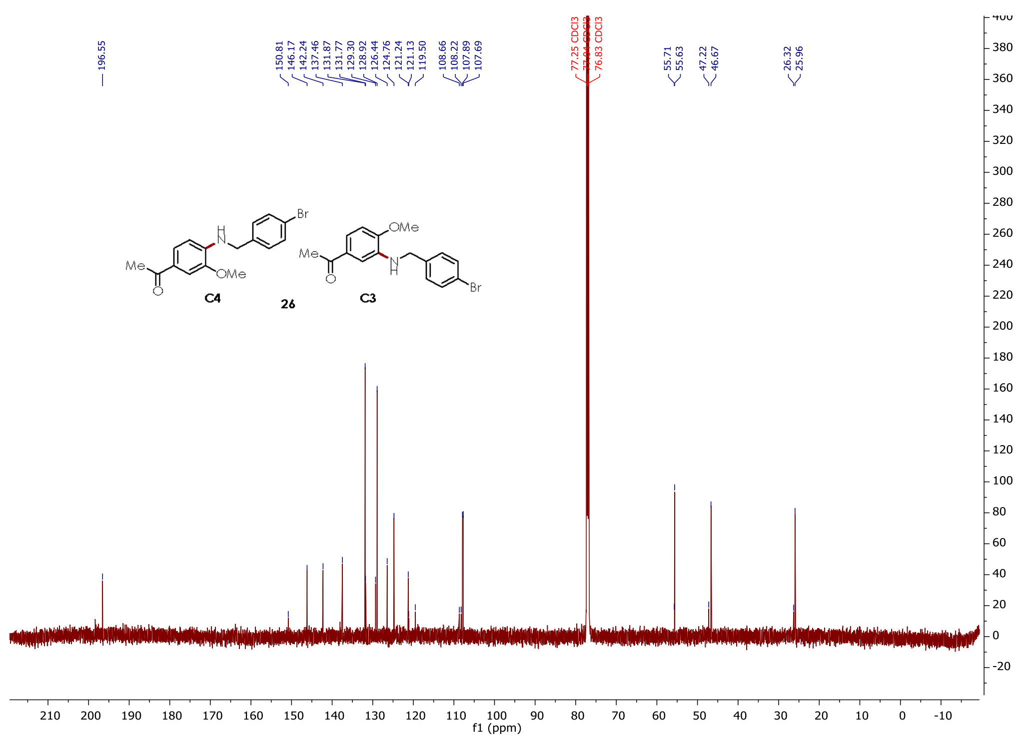


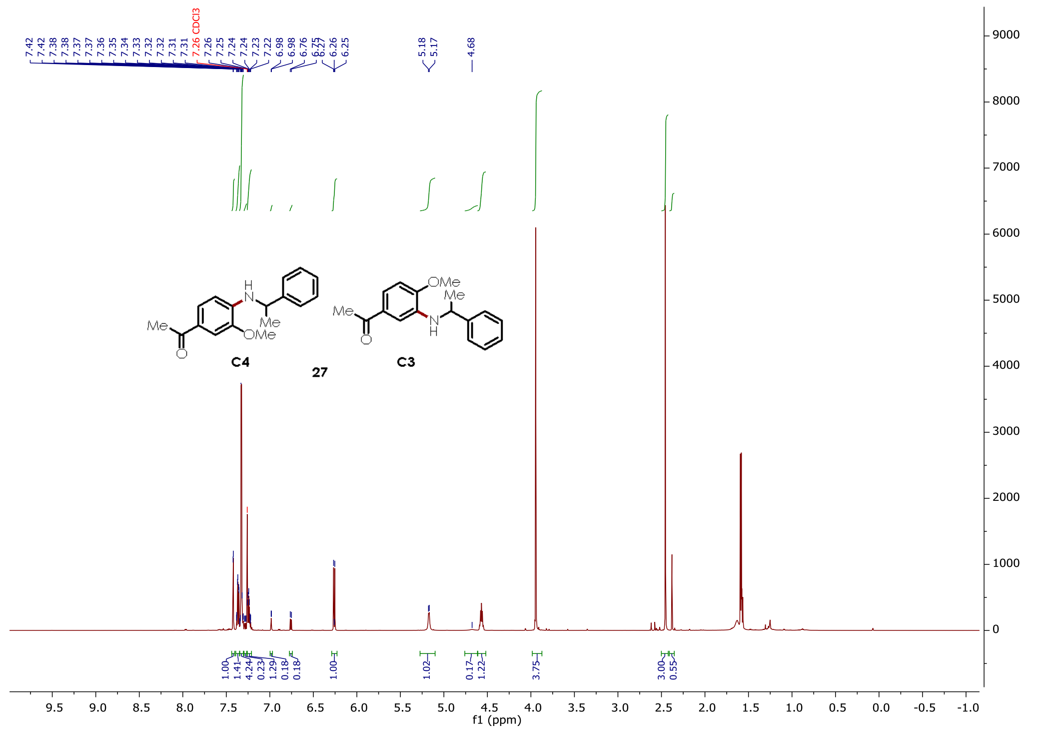
^{1}H NMR (600 MHz, $CDCl_3$) Compound **26**



^{13}C NMR (151 MHz, $CDCl_3$) Compound **26**



^{13}C NMR (151 MHz, $CDCl_3$) Compound **27**



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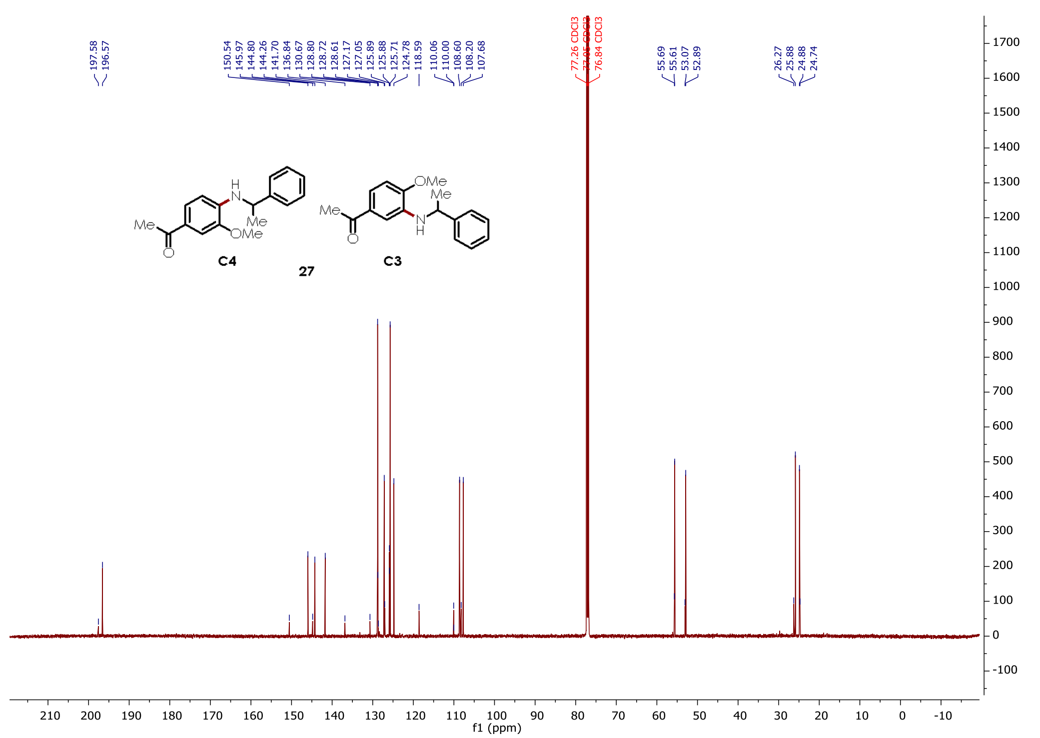

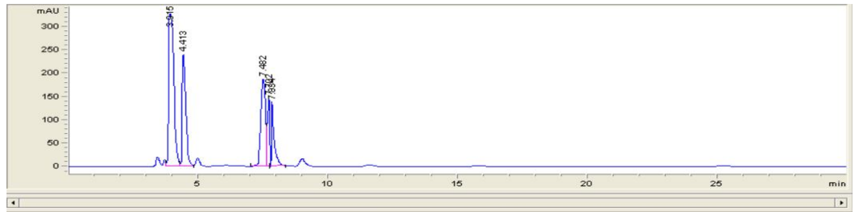

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Sample Info	
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Operator	NV
Method	IA_90A1_10B2_30.M
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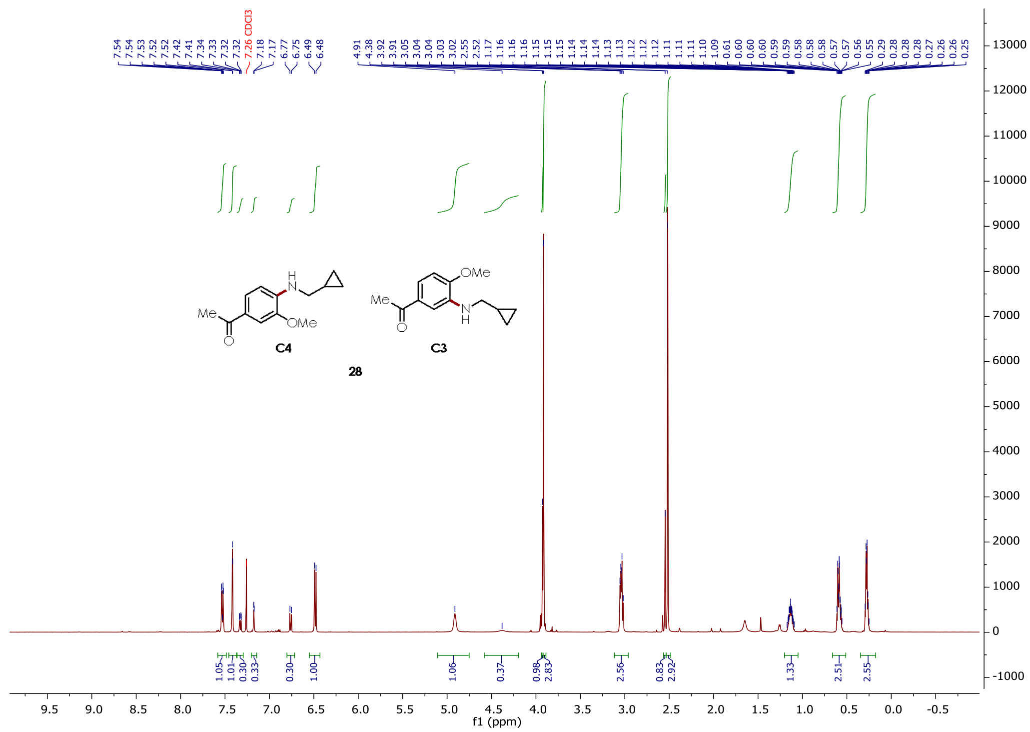
[1]H NMR (600 MHz, $CDCl_3$) Compound **28**



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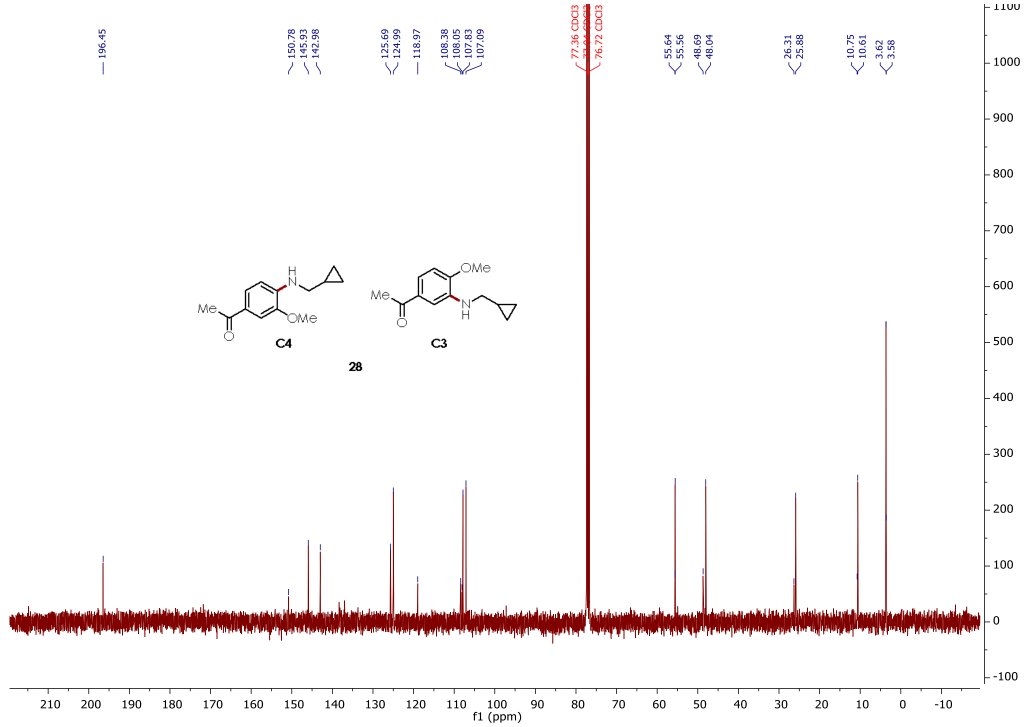

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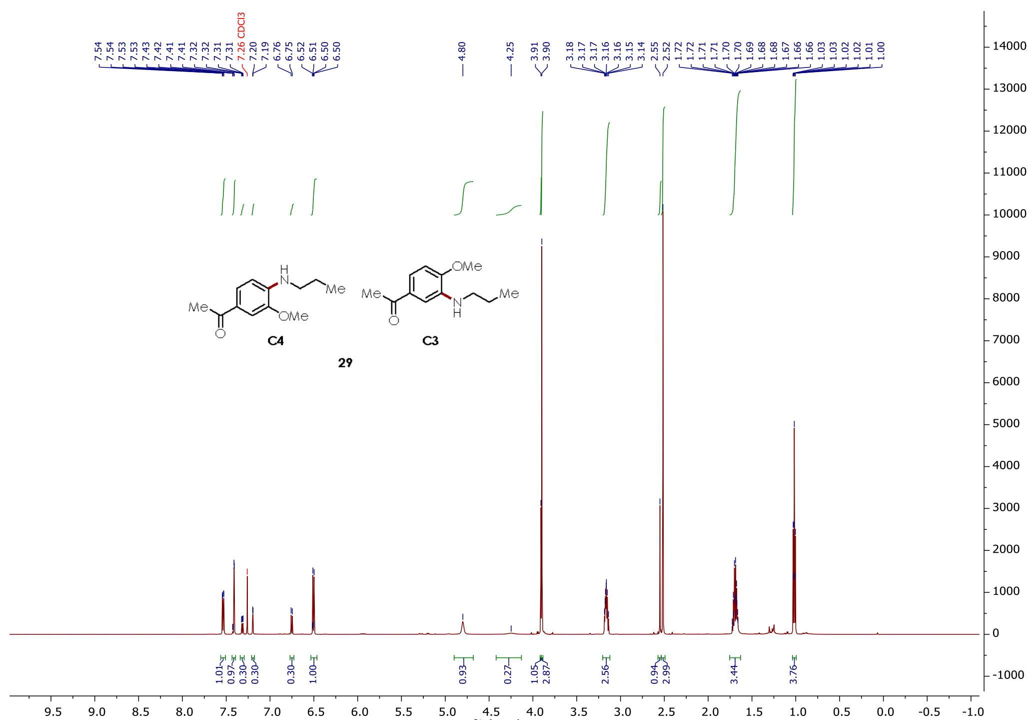

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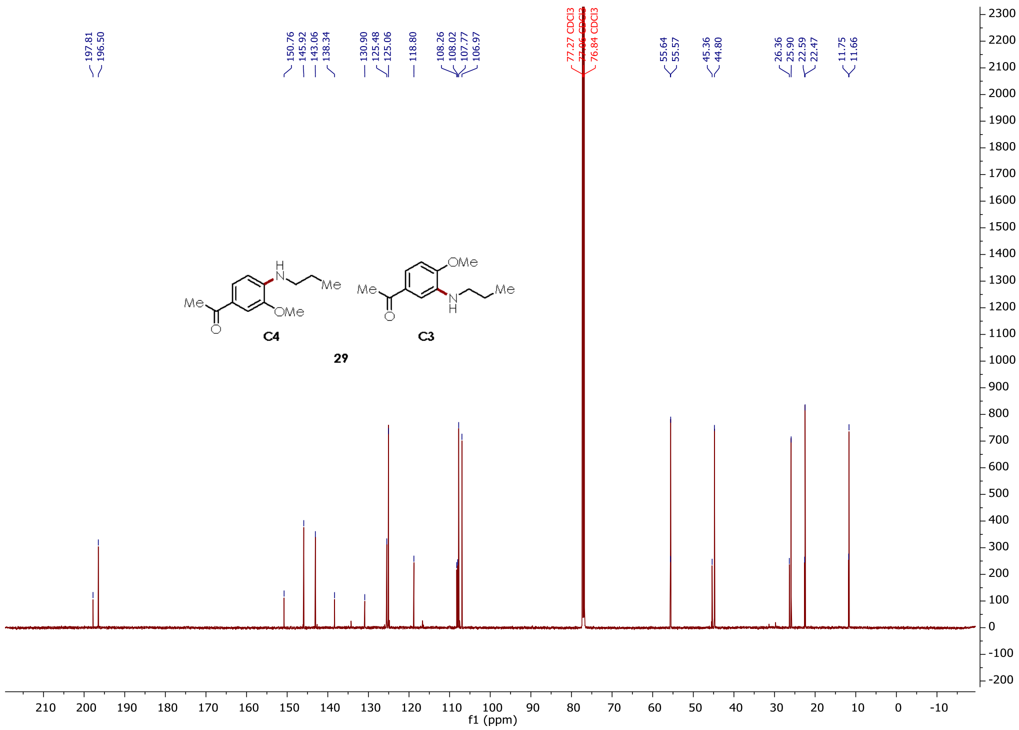

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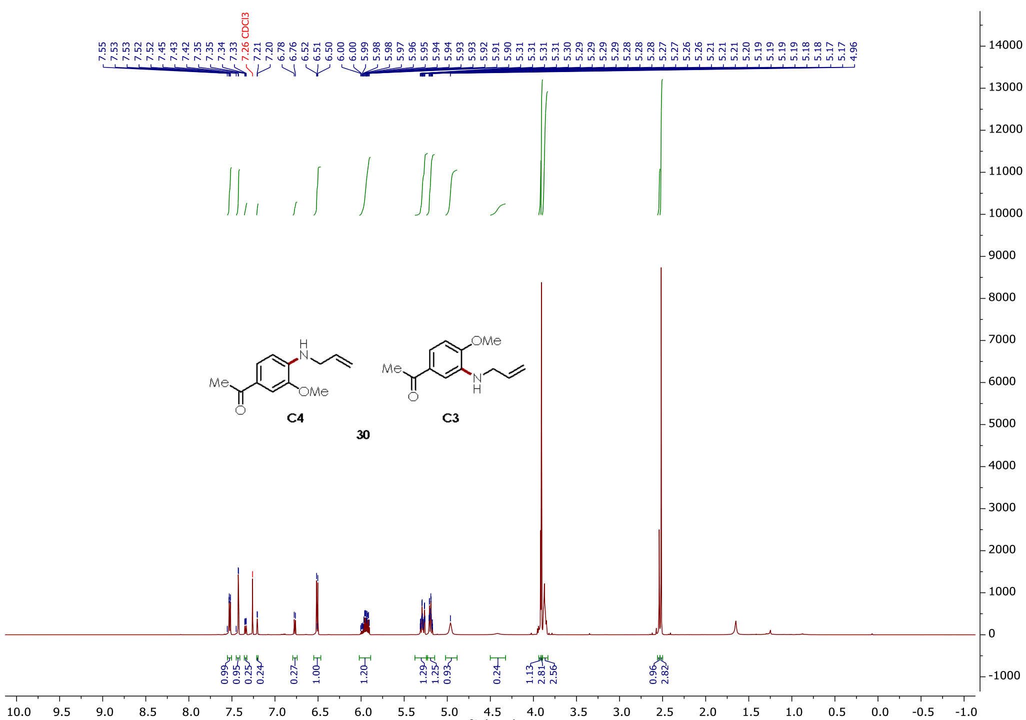

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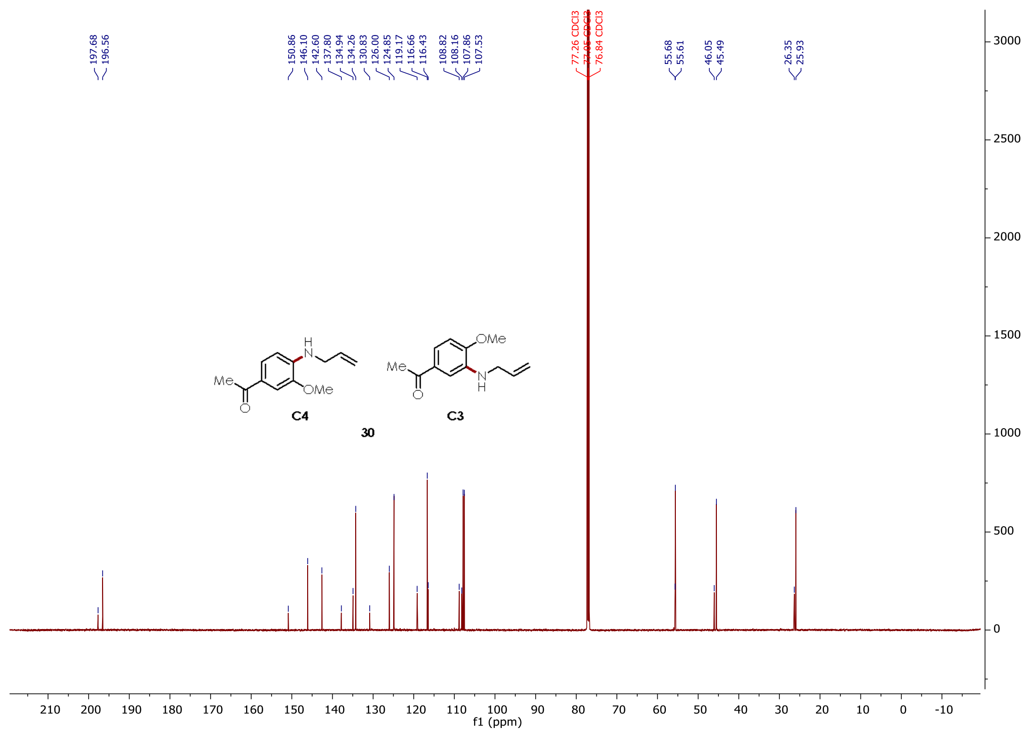

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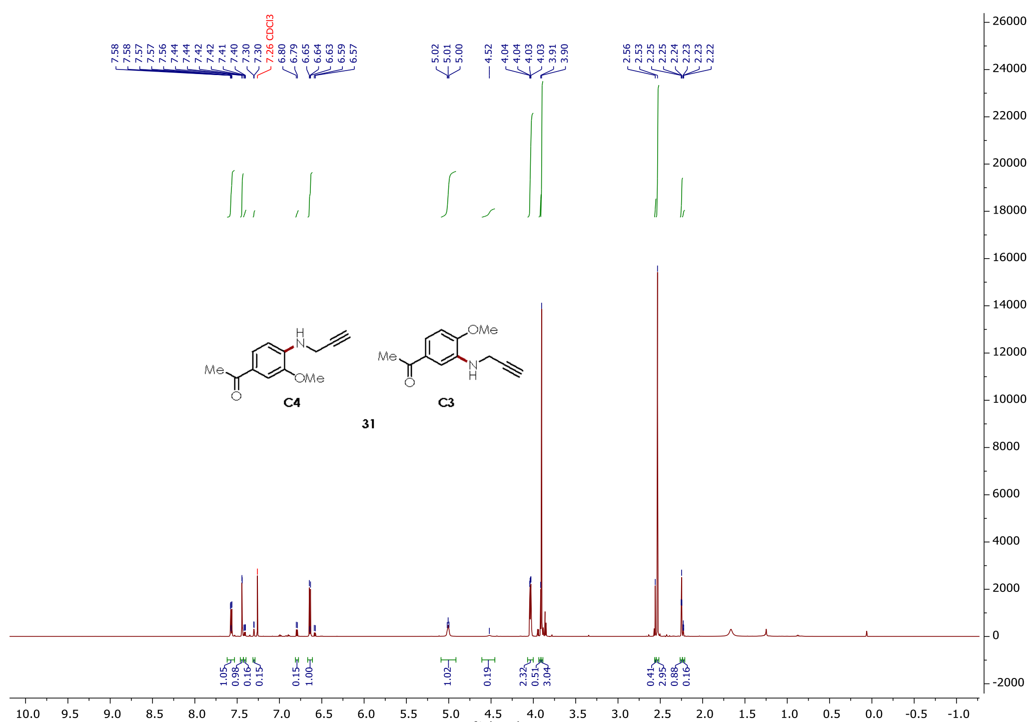

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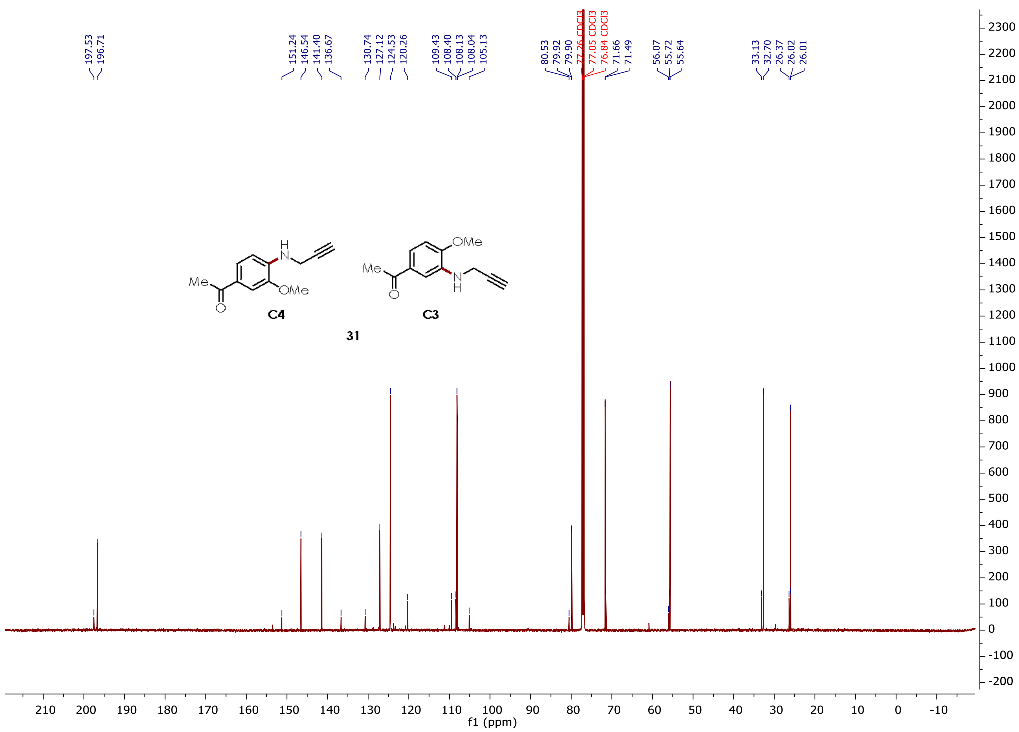
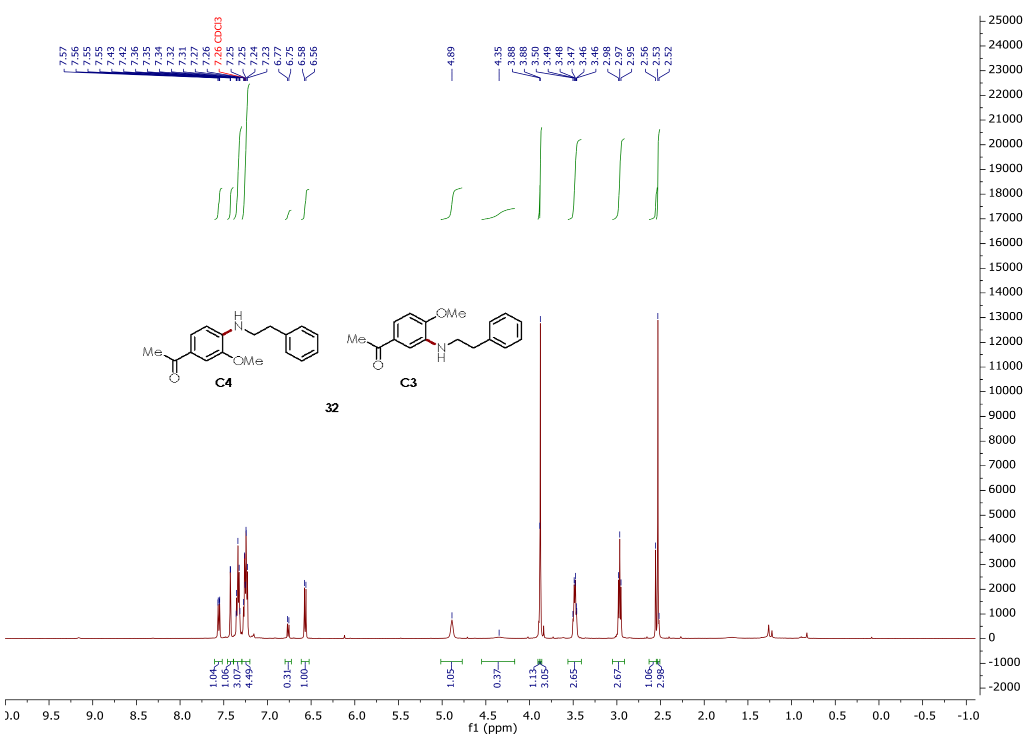


^{1}H NMR (600 MHz, $CDCl_3$) Compound **32**



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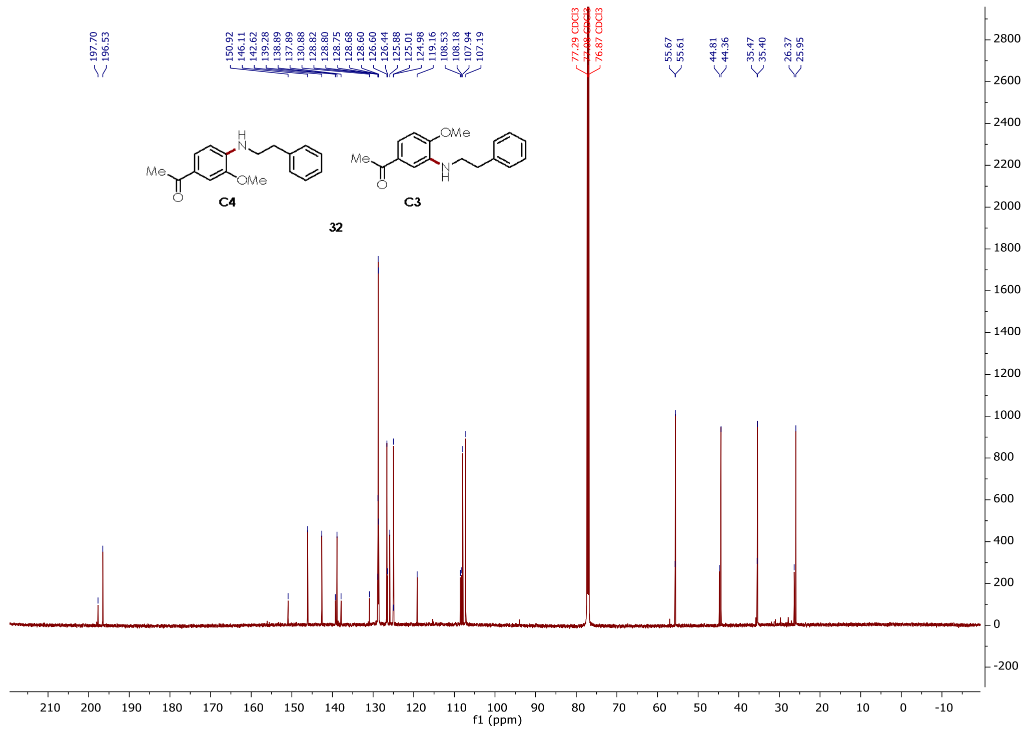

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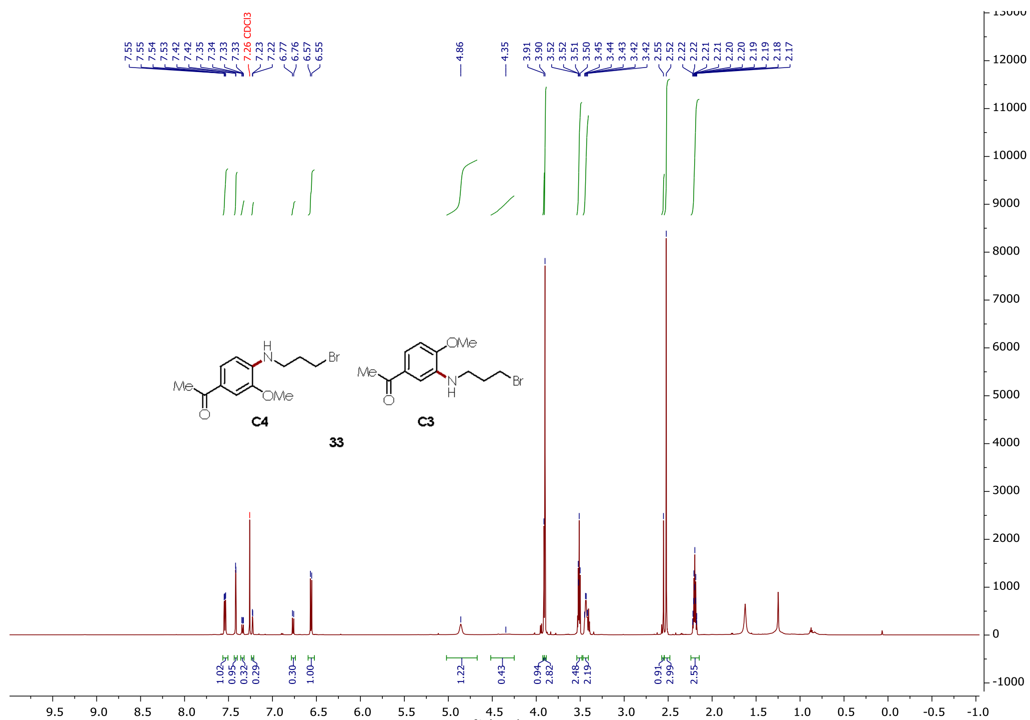

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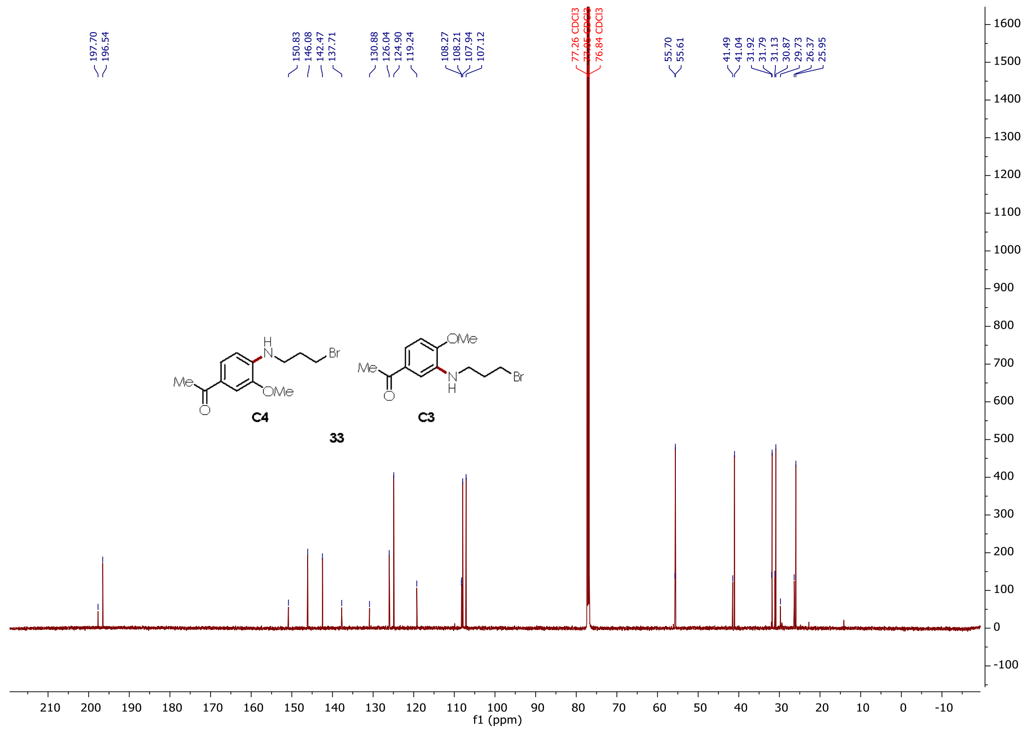

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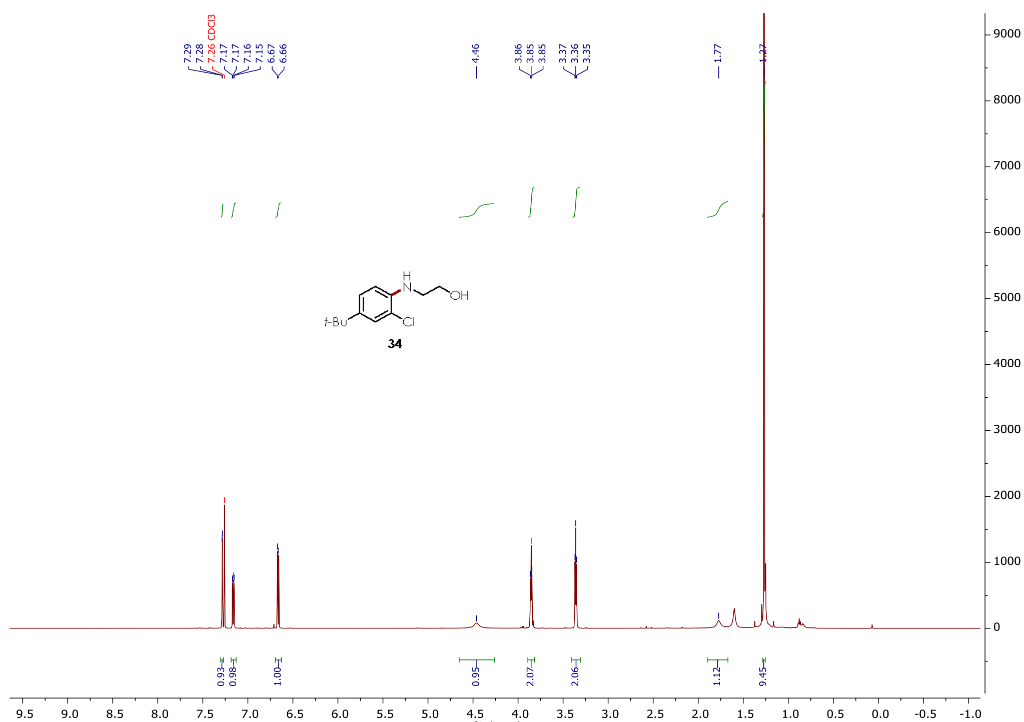

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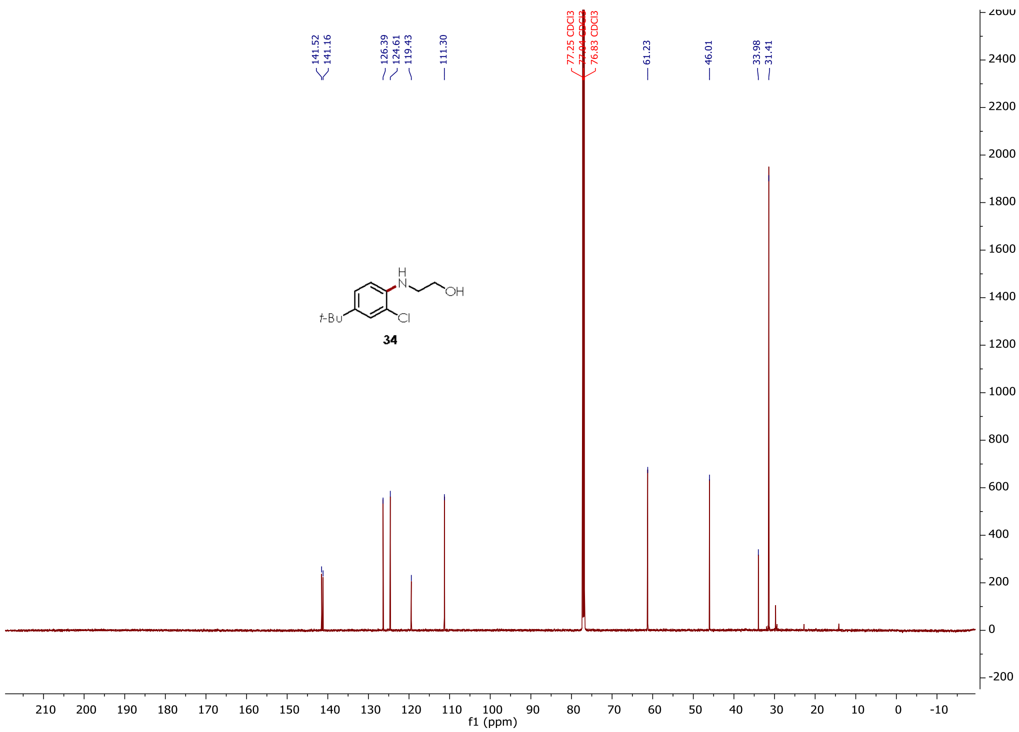
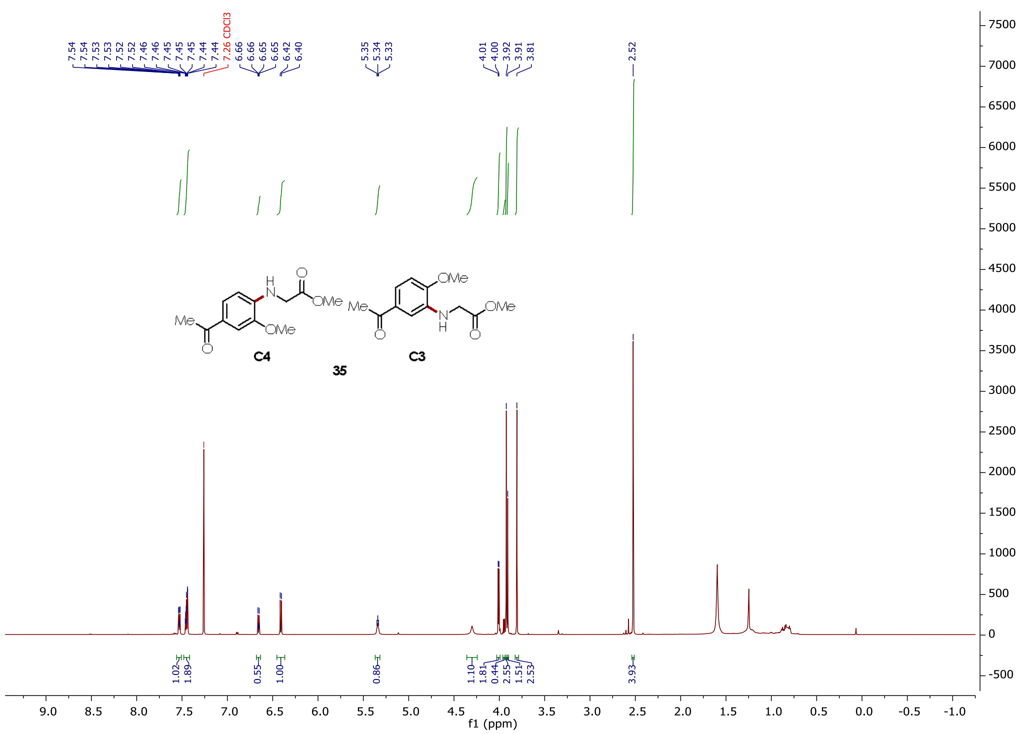


^{1}H NMR (600 MHz, $CDCl_3$) Compound **35**



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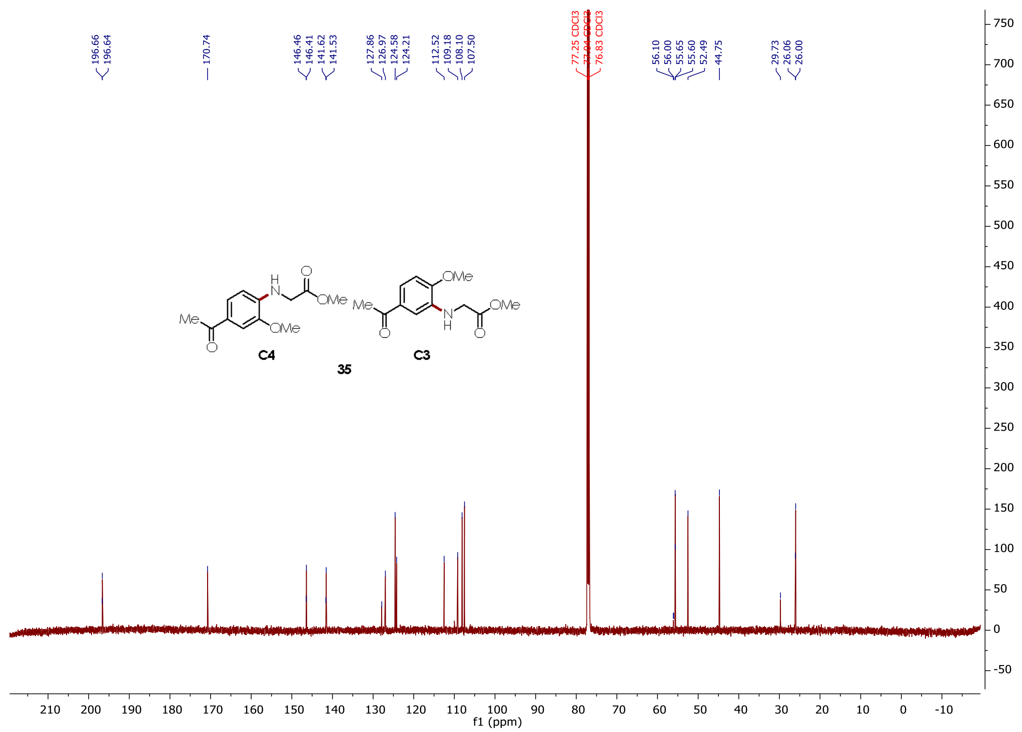

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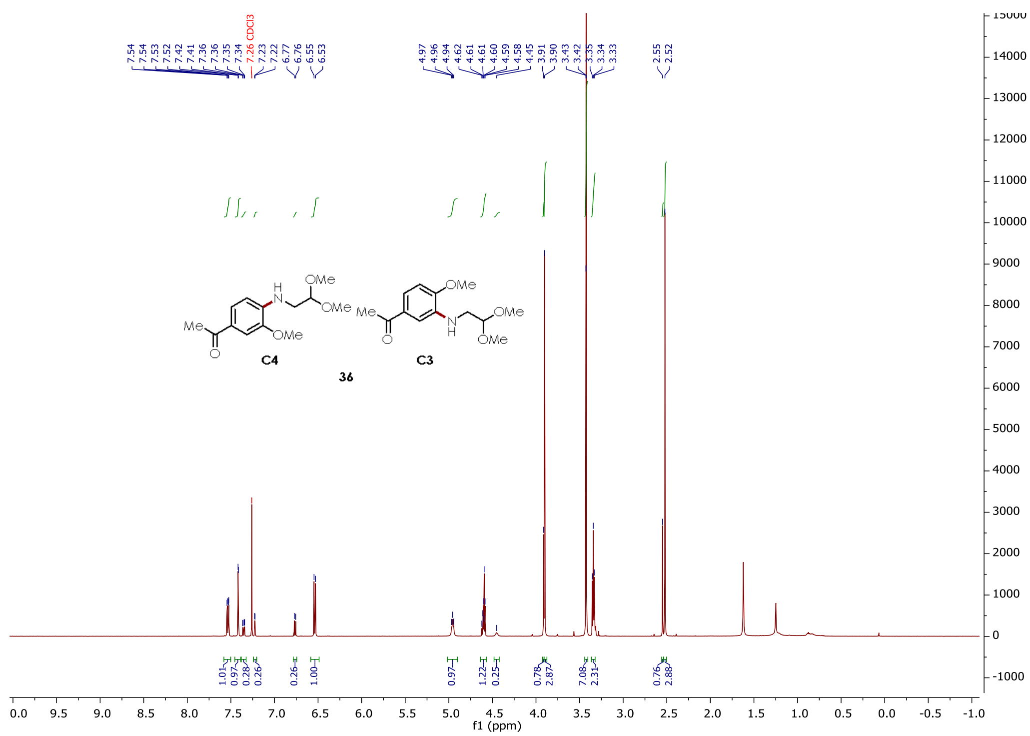

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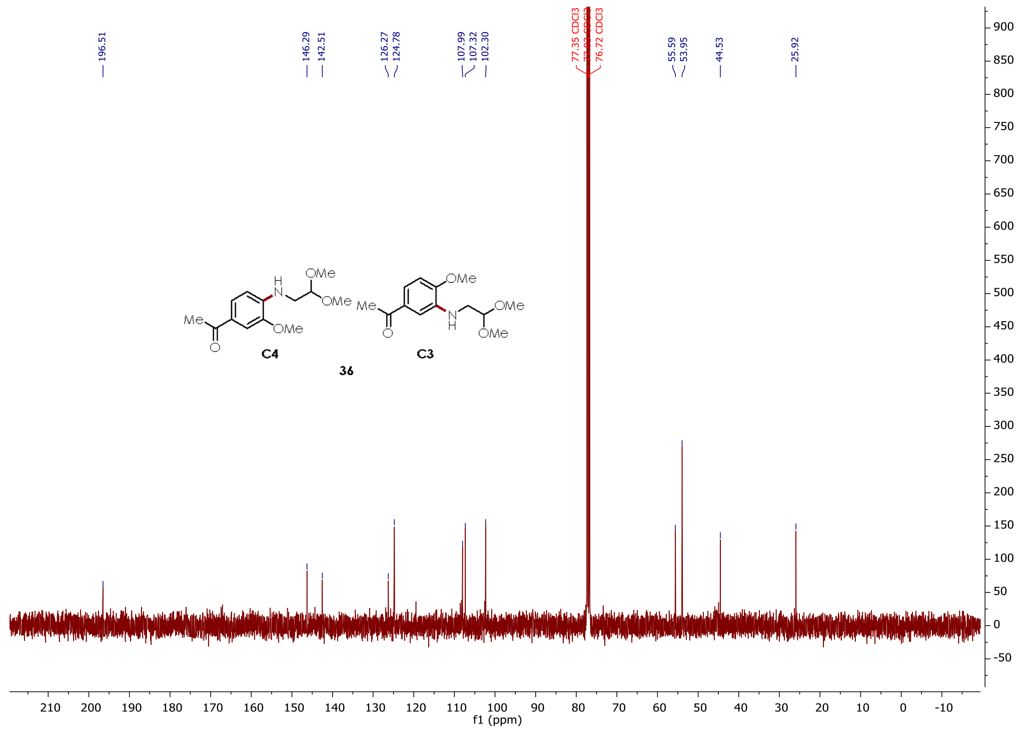

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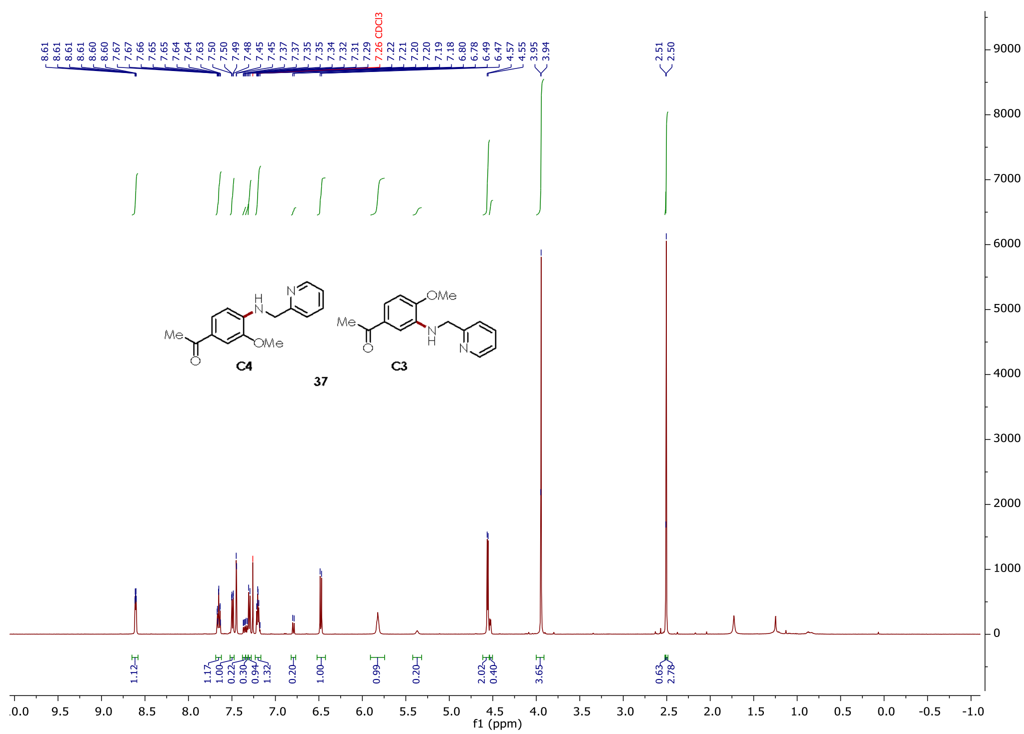

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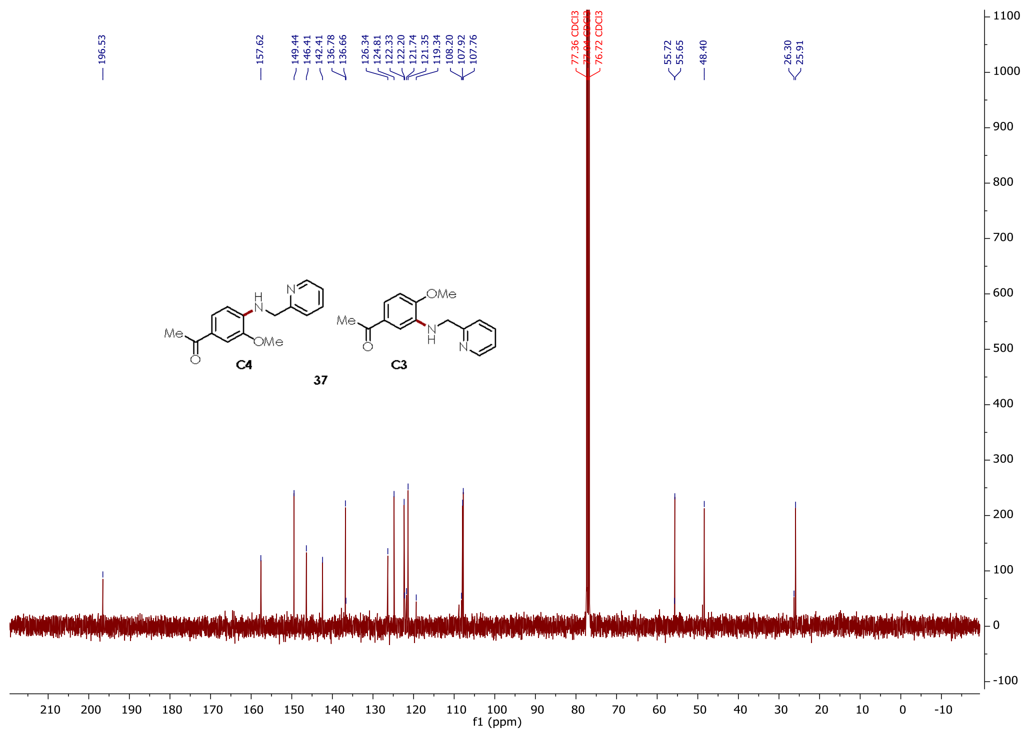
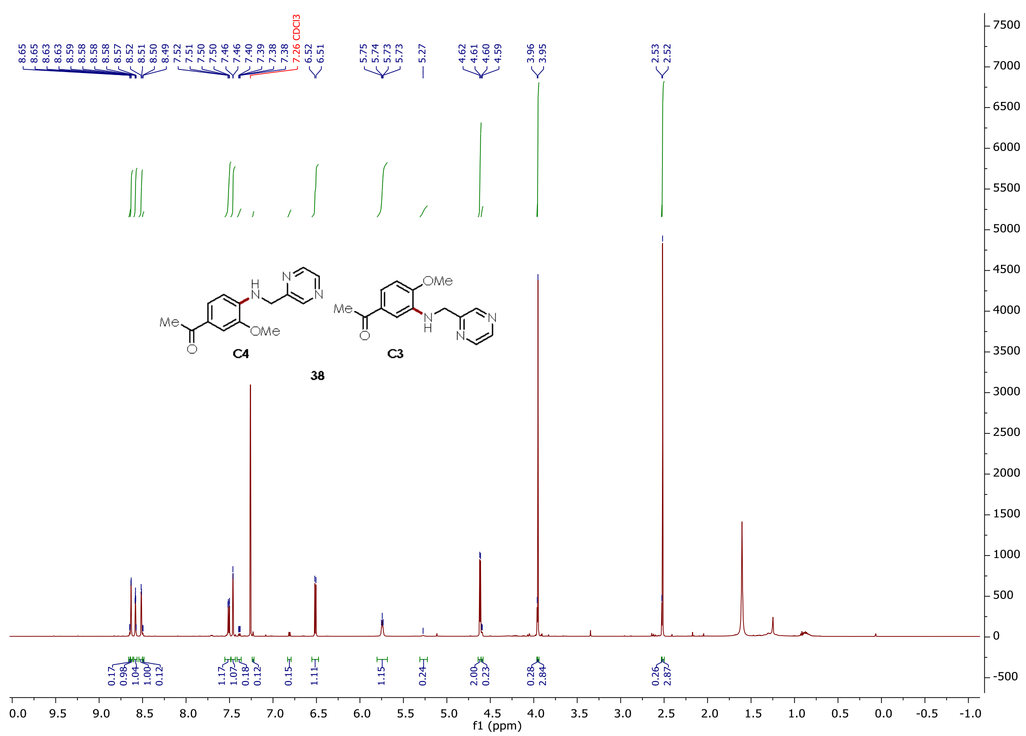
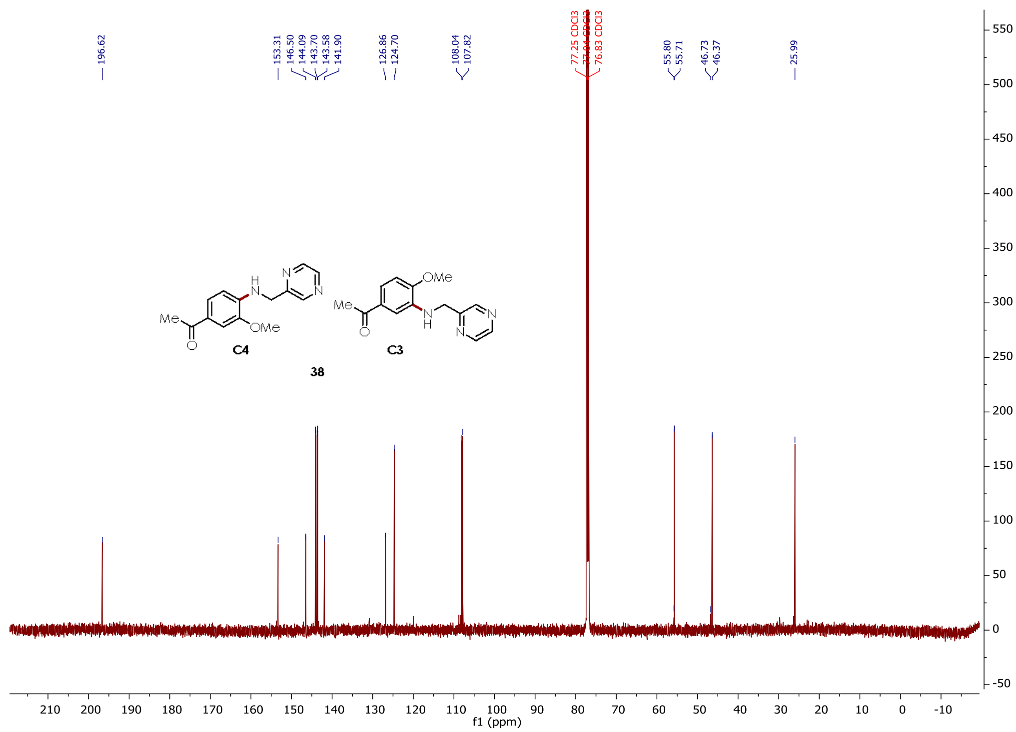


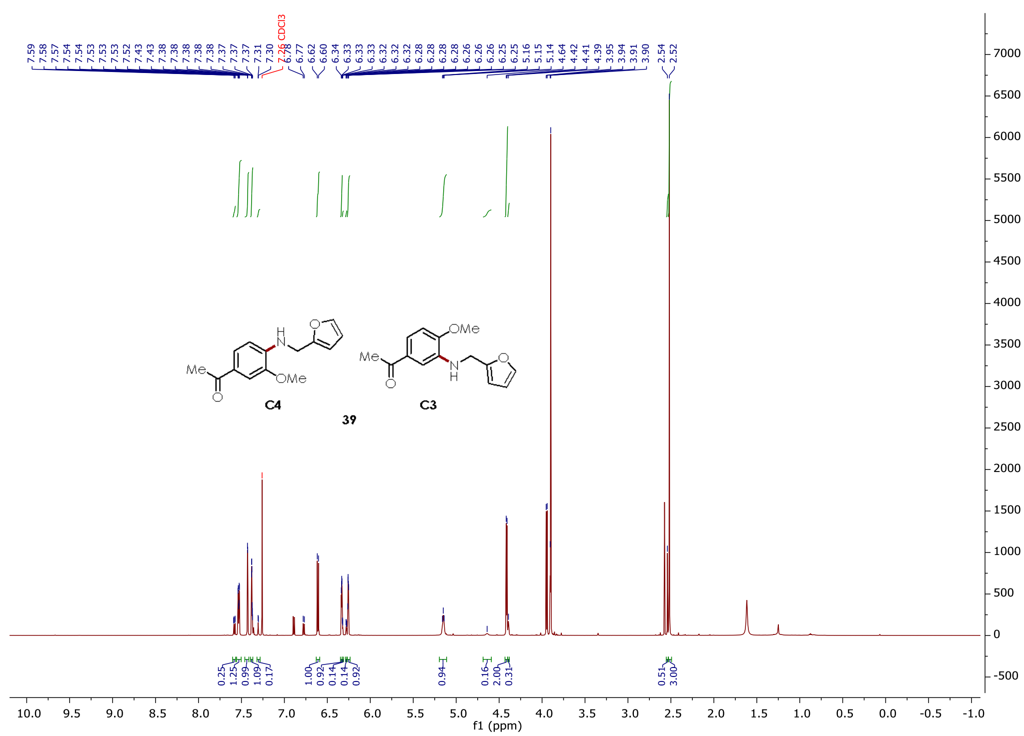
^{1}H NMR (600 MHz, $CDCl_3$) Compound **38**



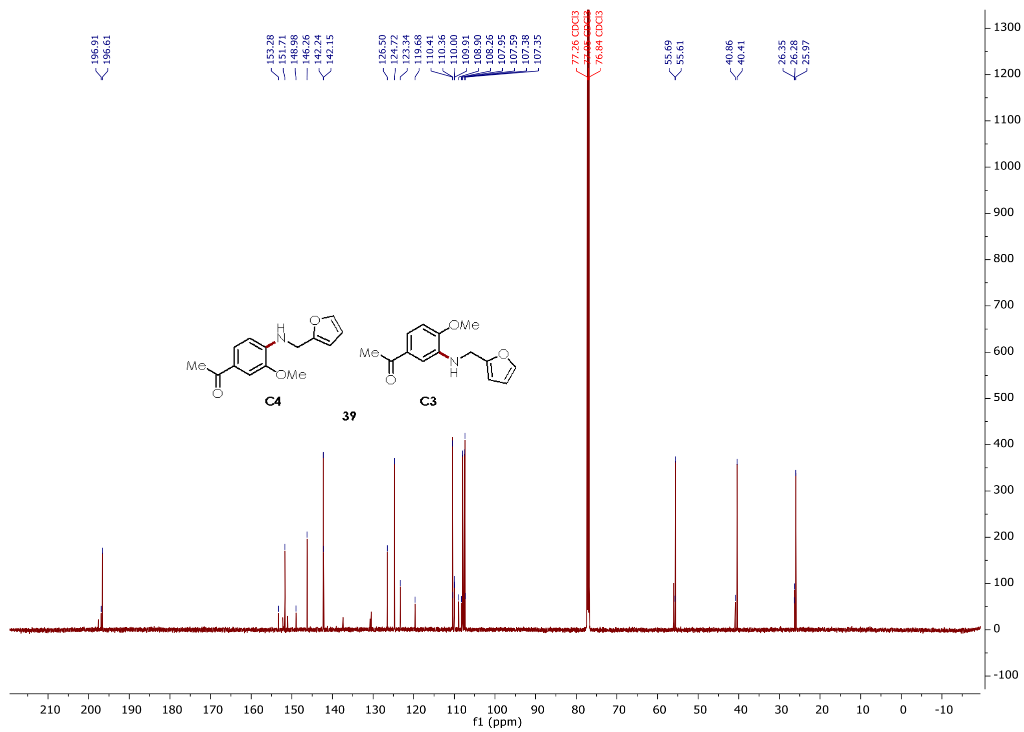
^{13}C NMR (151 MHz, $CDCl_3$) Compound **38**



^{1}H NMR (600 MHz, $CDCl_3$) Compound **39**



^{13}C NMR (151 MHz, $CDCl_3$) Compound **39**



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