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Supporting Information

Nickel-Catalyzed Amination of Silyloxyarenes through C–O Bond Activation

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I. General Experimental Details

Unless otherwise noted, all reactions were conducted in flame-dried or oven-dried (120 °C) sealed tubes with magnetic stirring sealed in a nitrogen glovebox. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, Inc. Model # SPS-400-3 and PS-400-3). All liquid amines were distilled over calcium hydride before use and stored under nitrogen and solid amines were used without further purification, morpholine (Sigma-Aldrich), N-methylbutylamine (Sigma-Aldrich), dibutylamine (Sigma-Aldrich), 2-methylpiperdine (Sigma-Aldrich), 2,6-dimethylpiperdine, predominantly cis (Alfa Aesar), 1-methylpiperazine (Sigma-Aldrich), N-methylbenzylamine (Sigma-Aldrich), N-methylaniline (Sigma-Aldrich), 2,4,6-trimethylaniline (Oakwood Chemicals), 2,6-diisopropylaniline (Oakwood Chemicals), aniline (Sigma-Aldrich), octylamine (Sigma-Aldrich), sec-butylamine (Sigma-Aldrich), iso-butylamine (Sigma-Aldrich), cyclohexylamine (Sigma-Aldrich), 1-adamantylamine (Oakwood Chemicals), butylamine (Sigma-Aldrich), benzylamine (Sigma-Aldrich), pyrrolidine (Sigma-Aldrich), piperazine (Sigma-Aldrich), 2-(piperazin-1-yl)pyrimidine (Oakwood Chemicals). Anhydrous $Ni(acac)_2$ (Strem Chemicals), $Ni(COD)_2$ (Strem Chemicals), IPr^{Me}·HCl (made from known procedure[1]), $IMes^{Me}$·HCl (made from known procedure[1]), ICy·HCl (Sigma-Aldrich), IAd·HCl (Sigma-Aldrich), IPr^{Cl}·HCl (made from known procedure[2]), IPr·HCl (made from known procedure[3]), IMes·HCl (made from known procedure[3]), IPr*OMe·HCl (made from known procedure[4]), and NaO-*t*-Bu (Strem Chemicals) were stored and weighed in an inert atmosphere glovebox.

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 (250 µm silica gel) glass plates and compounds were visualized with UV light and *p*-anisaldehyde, potassium permanganate or ceric ammonium molybdate stains. Flash column chromatography was performed using Kieselgel 60 (230-400 mesh) silica gel. Eluent mixtures are reported as v:v percentages of the minor constituent in the major constituent. All compounds purified by column chromatography were sufficiently pure for use in further experiments unless otherwise indicated.

^{1}H NMR spectra were collected at 400 MHz on a Varian MR400, at 500 MHz on a Varian Inova 500 or Varian vnmrs 500, or at 700 MHz on a Varian vnmrs 700 instrument. The proton signal of the residual, nondeuterated solvent (δ 7.26 for $CHCl_3$ or 7.15 for C_6D_6) was used as the internal reference for ^{1}H NMR spectra. ^{13}C NMR spectra were completely heterodecoupled and measured at 125 MHz or 175 MHz. Chloroform-d (δ 77.00), dimethylsulfoxide-d_6 (δ 39.95), or benzene-d_6 (δ 128.0) was used as an internal reference. High resolution mass spectra were recorded on a VG 70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory. GCMS analysis was carried out on a HP 6980 Series GC system with HP-5MS column (30 m x 0.250 mm x 0.25 µm). GCFID analysis was carried out on a HP 6980N Series GC system with a HP-5 column (30 m x 0.32 mm x 0.25 µm).

II. General Procedures

General Procedure for the synthesis of silyloxyarenes (A):

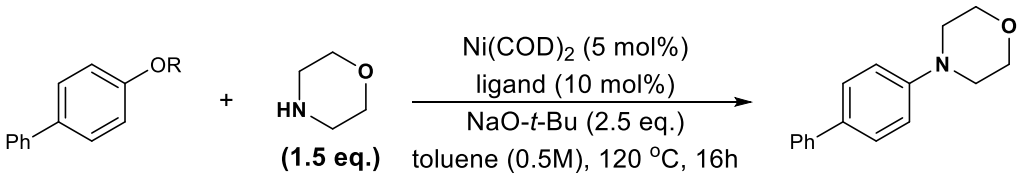
In a round bottom flask, aryl alcohol (1 equiv.) was dissolved in DMF or CH_2Cl_2 (5.0 mL). The solution was then charged with imidazole (2 equiv.) and *tert*-butyldimethylchlorosilane (1.5 equiv.) and stirred until the starting alcohol was fully consumed. The reaction was diluted with 25 mL Et_2O, washed with deionized H_2O (3 × 25 mL), dried over $MgSO_4$, filtered, concentrated under reduced pressure and purified by flash column chromatography on silica gel to afford the aryl silyl ether.

General Procedure for the $Ni(COD)_2$/IPr^{Me}·HCl promoted amination of silyloxyarenes using amines (B):

A reaction tube containing a stir bar was charged with aryl silyl ether (1 equiv.), $Ni(COD)_2$ (5 mol%), IPr^{Me}·HCl (10 mol%), NaO-*t*-Bu (2.5 equiv.), toluene (0.5 M) and amine (1.5 equiv.). The sealed reaction tube was brought outside the glovebox and placed in a heated block set to 120 °C and stirred for 16 hours, unless noted otherwise. The mixture was cooled to room temperature, quenched with dichloromethane (1 mL), and diluted with EtOAc (3 mL). The mixture was then run through a silica plug, concentrated under reduced pressure and purified by flash column chromatography on silica gel to afford the desired product.

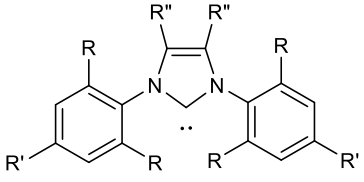
III. Supplementary Tables

Table S1. Summary of optimization of nickel-catalyzed amination of silyloxyarenes with morpholine.



entry	ligand	OR	yield[a]
1	PCy_3	$OSi(t\text{-}Bu)Me_2$	**trace**
2	ICy•HCl	$OSi(t\text{-}Bu)Me_2$	**NP**
3	IAd•HCl	$OSi(t\text{-}Bu)Me_2$	**NP**
4	IMes•HCl	$OSi(t\text{-}Bu)Me_2$	**NP**
5	$IMes^{Me}$•HCl	$OSi(t\text{-}Bu)Me_2$	**NP**
6	IPr^{Cl}•HCl	$OSi(t\text{-}Bu)Me_2$	**13%**
7	IPr•HCl	$OSi(t\text{-}Bu)Me_2$	**58%**
8	IPr^{Me}•HCl	$OSi(t\text{-}Bu)Me_2$	**93%**
9	IPr*OMe•HCl	$OSi(t\text{-}Bu)Me_2$	**trace**
10	IPr^{Me}•HCl	$OSi(t\text{-}Bu)Ph_2$	**84%**
11	IPr^{Me}•HCl	$OSi(i\text{-}Pr)_3$	**37%**
12	IPr^{Me}•HCl	$OSiEt_3$	**67%**
13	IPr^{Me}•HCl	OMe	**4%**
14	IPr^{Me}•HCl	OPh	**72%**
15	IPr^{Me}•HCl	OPiv	**54%**
16	IPr^{Me}•HCl	OTf	**78%**
17	IPr^{Me}•HCl	$OSi(t\text{-}Bu)Me_2$	**80%[b]**
18	IPr^{Me}•HCl	$OSi(t\text{-}Bu)Me_2$	**52%[c]**

(a) Yields were determined by isolation. NP = no product observed. (b) Reaction run in 1,4-dioxane. (c) Reaction run in THF.

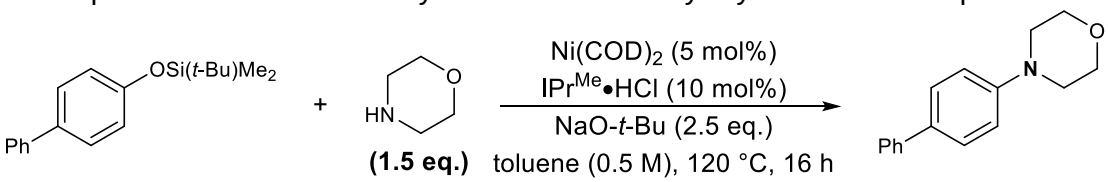


IMes	R = Me, R' = Me, R" = H
$IMes^{Me}$	R = Me, R' = Me, R" = Me
IPr^{Cl}	R = *i*-Pr, R' = H, R" = Cl
IPr	R = *i*-Pr, R' = H, R" = H
IPr^{Me}	R = *i*-Pr, R' = H, R" = Me
IPr*OMe	R = $CHPh_2$, R' = OMe, R = H

Discussion for optimization of silyloxyarene amination: Using model substrate, ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane, and morpholine, ligands previously utilized in the activation of aryl methyl ethers, such as PCy_3, ICy, or IAd were tested (Table S1, entries 1-3);

however, each resulted in no product. Additionally, small *N*-aryl NHC ligands such as IMes or $IMes^{Me}$ (Table S1, entries 4-5) also showed no evidence of product formation. However, when using bulky, aryl NHC ligands, such as IPr derivatives, there appeared to be a strong dependence on the electronic influence of the ligand. Placing electron-withdrawing substituents on the backbone, like IPr^{Cl} (Table S1, entry 6), resulted in low yields, whereas, electron-donating substituents, such as IPr^{Me} (Table S1, entries 8), resulted in high yields. Increasing size of the NHC ligand further to IPr*OMe, which has previously been demonstrated as a competent ligand in the C-O bond activation of silyloxyarenes, resulted in trace product formation (Table S1, entry 9). Exploring the use of other silyloxyarene derivatives showed a dependence on size and electronics of the silane protecting group, with TBS being optimal. High yields were still obtained with TBDPS (Table S1, entry 10), although lower yields were obtained with TIPS and TES (Table S1, entries 11-12). Other common aryl electrophiles resulted in inferior results with OMe only showing trace product and other phenol-derived electrophiles, including OPh, OPiv, and OTf (Table S1, entries 14-16), resulting in decreased yields. Additionally, aryl halides (Br, F) resulted in low yields, due to conversion of the aryl halide to biphenyl through reduction with the amine (see tables S2 and S3 below for more complete optimization). THF and dioxane are also suitable solvents but gave results inferior to toluene (Table 1, entries 17-18).

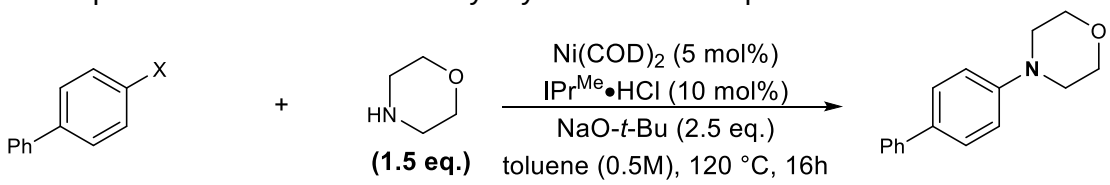
Table S2. Optimization of nickel-catalyzed amination of silyloxyarenes with morpholine.



entry	variations	yield[a]
1	-	**93%**
2	$Ni(acac)_2$	**88%**
3	5 mol% IPr^{Me}•HCl	**62%**
4	7.5 mol% IPr^{Me}•HCl	**80%**
5	$IPr^{*}OMe$•HCl for IPr^{Me}•HCl	**trace**
6	IPr•HCl	**58%**
7	IPr^{Cl}•HCl	**13%**
8	$IMes^{Me}$•HCl	**NP**
9	IMes•HCl	**NP**
10	ICy•HCl	**NP**
11	IAd•HCl	**NP**
12	PCy_3	**trace**
13	dcype (5 mol%)	**NP**
14	dppf (5 mol%)	**NP**
15	dtbbpy (5 mol%)	**NP**
16	1,10-phenanthroline (5 mol%)	**NP**
17	LiO-*t*-Bu for NaO-*t*-Bu	**64%**
18	KO-*t*-Bu for NaO-*t*-Bu	**NP**
19	NaOMe for NaO-*t*-Bu	**NP**
20	NaOPh for NaO-*t*-Bu	**NP**
21	NaOTMS for NaO-*t*-Bu	**NP**
22	0.25 M in toluene	**85%**
23	THF	**52%**
24	1,4-dioxanes	**80%**
25	6 h	**78%**
26	100 °C	**70%**
27	1 eq. base	**70%**
28	1 eq. amine	**77%**

(a) Yields were determined by isolation. NP = no product observed.

Table S3. Optimization of amination of silyloxyarenes with morpholine.



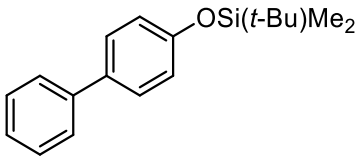
entry	X	yield[a]
1	OSi(*t*-Bu)Ph_2	**84%**
2	OSi(*i*-Pr)$_3$	**37%**
3	OSi(*t*-Bu)Me_2	**93%**
4	$OSiEt_3$	**67%**
5	OMe	**4%**
6	OPiv	**54%**
7	OTf	**78%**
8	OPh	**72%**
9	Br	**29%**
10	F	**39%**

(a) Yields were determined by isolation. NP = no product observed.

IV. Starting Material Synthesis

One Step Preparation:

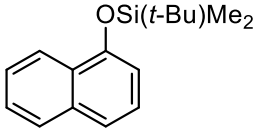
([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (1-TBS).



Following general procedure A, [1,1'-biphenyl]-4-ol (851 mg, 5 mmol), imidazole (681 mg, 10 mmol), *tert*-butyldimethylsilyl chloride (1.13 g, 7.5 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate = 99:1) to afford the desired product as a white solid (1.30 g, 4.57 mmol, 91% yield). The spectral data matches that previously reported in the literature.[5]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.46 (dt, *J* = 8.5, 1.9 Hz, 2 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.90 (dt, *J* = 8.5, 2.0 Hz, 2H), 1.00 (s, 9H), 0.23 (s, 6H).

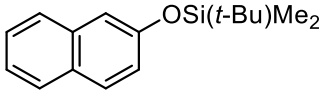
***tert*-butyldimethyl(naphthalen-1-yloxy)silane (2-SM).**



Following general procedure A, naphthalen-1-ol (1.44 g, 10 mmol), imidazole (1.36 g, 20 mmol), and *tert*-butyldimethylsilyl chloride (2.26 g, 15 mmol) gave a crude mixture which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product as a colorless oil (1.87 g, 7.24 mmol, 72% yield). The spectral data matches that previously reported in the literature.[6]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.20 (m, 1H), 7,80 (m, 1H), 7.46 (m, 3H), 7.33 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 1.11 (s, 9H), 0.30 (s, 6H).

***tert*-butyldimethyl(naphthalen-2-yloxy)silane (3-SM).**

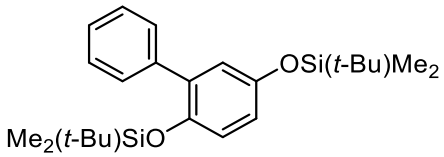


Following general procedure A, naphthalen-2-ol (720.5 mg, 5 mmol), imidazole (681 mg, 10 mmol), *tert*-butyldimethylsilyl chloride (1.13 g, 7.5 mmol) gave a crude residue which was

purified by flash chromatography (hexanes: ethyl acetate = 99:1) to afford the desired product as a colorless oil (1.23 g, 4.76 mmol, 95% yield. The spectral data matches that previously reported in the literature.[7]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.8, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.42 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.33 (dt, *J* = 6.8, 1.2, 1H), 7.19 (d, *J* = 2.2, 1H), 7.08 (dd, *J* = 8.8, 2.2 Hz, 1H), 1.04 (s, 9H), 0.26 (s, 6H).

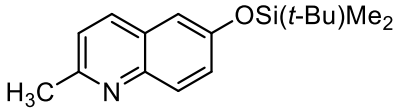
([1,1'-biphenyl]-2,5-diylbis(oxy))bis(*tert*-butyldimethylsilane) (6-SM).



Following general procedure A, [1,1':4',1''-terphenyl]-2'-ol (931 mg, 5 mmol), imidazole (1.36 g, 20 mmol), *tert*-butyldimethylsilyl chloride (2.26 g, 15 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product as a colorless oil (1.04 g, 2.89 mmol, 58% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 3.0 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.69 (dd, *J* = 8.5, 3.0 Hz, 1H), 0.99 (s, 9H), 0.81 (s, 9H), 0.19 (s, 6H), -0.12 (s, 9H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 149.8, 146.7, 139.1, 133.9, 129.8, 127.8, 126.37, 121.9, 120.9, 119.3, 25.7, 25.6, 18.2, 18.0, -4.5, -4.7.
IR (film, cm^{-1}): 2955, 2929, 2885, 2957, 1600, 1445, 1390.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{24}H_{38}O_2Si_2$, 415.2483; found, 415.2481.

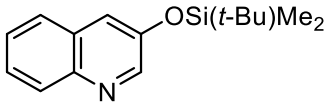
6-((*tert*-butyldimethylsilyl)oxy)-2-methylquinoline (7-SM).



Following general procedure A, 2-methylquinolin-6-ol (435 mg, 2.73 mmol), imidazole (340 mg, 5 mmol), *tert*-butyldimethylsilyl chloride (565 g, 3.75 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product as a white solid. (682 mg, 2.5 mmol, 91% yield). The spectral data matches that previously reported in the literature.[8]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.26 (m, 1H), 7.22 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.10 (m, 1H), 2.70 (s, 3H), 1.02 (s, 9H), 0.25 (s, 6H).

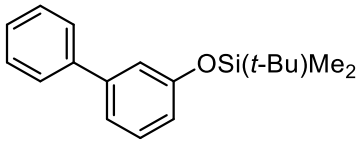
3-((*tert*-butyldimethylsilyl)oxy)quinoline (10-SM).



Following general procedure A, quinolin-3-ol (1.40 g, 9.64 mmol), imidazole (1.36 g, 20 mmol), *tert*-butyldimethylsilyl chloride (2.26 g, 15 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product as a colorless oil (1.89 g, 7.29 mmol, 76% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.60 (d, *J* = 3.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 3.0 Hz, 1H), 1.03 (s, 9H), 0.28 (s, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 149.2, 147.0, 143.9, 129.1, 129.0, 137.0, 126.9, 126.7, 121.4, 25.6, 18.2, -4.4.
IR (film, cm^{-1}): 2954, 2929, 2858, 1600, 1464, 1416.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{15}H_{21}NOSi$, 260.1465; found, 260.1468.

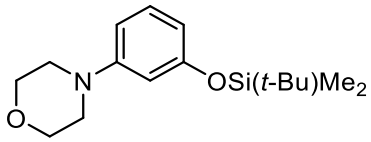
([1,1'-biphenyl]-3-yloxy)(*tert*-butyl)dimethylsilane (12-SM).



Following general procedure A, [1,1'-biphenyl]-3-ol (1.69 g, 9.93 mmol), imidazole (1.36 g, 20 mmol), *tert*-butyldimethylsilyl chloride (2.26 g, 15 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product as a colorless oil (1.67 g, 5.87 mmol, 59% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 1.03 (s, 9H), 0.25 (s, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 156.0, 142.7, 141.0, 129.6, 128.7, 127.3, 127.1, 120.2, 118.93, 118.90, 25.7, 18.2, -4.4.
IR (film, cm^{-1}): 3063, 2955, 2929, 2857, 1596, 1572, 1476, 1416.
HRMS (EI) *m/z*: $[M]^+$ predicted for $C_{18}H_{24}OSi$, 284.1596; found, 284.1594.

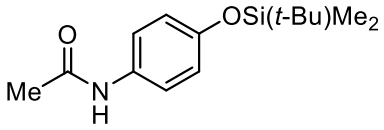
4-(3-((*tert*-butyldimethylsilyl)oxy)phenyl)morpholine (13-SM).



Following general procedure A, 3-morpholinophenol (445 mg, 2.5 mmol), imidazole (340 mg, 5 mmol), *tert*-butyldimethylsilyl chloride (565 g, 3.75 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product as a colorless oil (694 mg, 2.36 mmol, 95% yield). The spectral data matches that previously reported in the literature.[8]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.11 (t, *J* = 8.0 Hz, 1H), 6.53 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.39 (m,1H), 6.36 (d, *J* = 2.1 Hz, 1H), 3.85 (t, *J* = 4.9, 4H), 3.13 (t, *J* = 4.9 Hz, 4H), 0.98 (s, 9H), 0.20 (s, 6H).

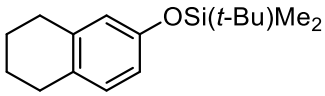
N-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)acetamide (14-SM).



Following general procedure A, N-(4-hydroxyphenyl)acetamide (755 mg, 5 mmol), imidazole (681 mg, 10 mmol), *tert*-butyldimethylsilyl chloride (1.13 g, 7.5 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 80:20) to afford the desired product as a white solid (1.18 g, 4.45 mmol, 89% yield). The spectral data matches that previously reported in the literature.[9]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.02 (bs, 1H), 6.80 (d, J = 8.8 Hz, 2H), 2.16 (s, 3H), 0.91 (s, 9H), 0.19 (s, 6H).

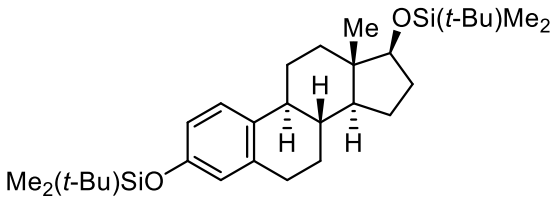
***tert*-butyldimethyl((5,6,7,8-tetrahydronaphthalen-2-yl)oxy)silane (15-SM).**



Following general procedure A, 5,6,7,8-tetrahydronaphthalen-2-ol (741 mg, 5 mmol), imidazole (681 mg, 10 mmol), *tert*-butyldimethylsilyl chloride (1.13 g, 7.5 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product as a colorless oil (1.26 g, 4.80 mmol, 96% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.90 (d, *J* = 8.5 Hz, 1H), 6.58 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 2.69 (m, 4H), 1.78 (m, 4H), 1.0 (s, 9H), 0.20 (s, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 153.1, 138.1, 129.7, 120.1, 117.3, 29.5, 28.6, 25.7, 23.4, 23.1, 18.2, -4.4.
IR (film, cm^{-1}): 2928, 2856, 1609, 1498, 1253.
HRMS (EI) *m/z*: $[M]^+$ predicted for $C_{16}H_{26}OSi$, 262.1753; found, 262.1757.

(((8R,9S,13S,14S,17S)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diyl)bis(oxy))bis(*tert*-butyldimethylsilane) (16-SM).

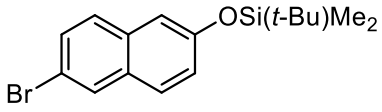


Following a modified general procedure A (doubling the amount of imidazole and *tert*-butyldimethylsilyl chloride), (8R,9S,13S,14S,17S)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol (272 mg, 1 mmol), imidazole (272 mg, 4 mmol), *tert*-butyldimethylsilyl chloride (578 mg, 3 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 98:2) to afford the desired product as a white solid (468 mg, 0.93 mmol, 93% yield). The spectral data matches that previously reported in the literature.[10]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.6 Hz, 1H), 6.62 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.56 (s, 1H), 3.65 (t, *J* = 8.3 Hz, 1H), 2.80 (m, 2H), 2.27 (dd, *J* = 13.7, 3.2 Hz, 1H), 2.18 (dt, *J* = 11.5, 3.7 Hz, 1H), 1.90 – 1.86 (m, 3H), 1.66 (dq, *J* = 12.0, 3.4 Hz, 1H), 1.54 – 1.27 (m, 7H), 0.99 (s, 9H), 0.91 (s, 9H), 0.76 (s, 3H), 0.20 (s, 6H), 0.04 (d, *J* = 6.3 Hz, 6H).

Synthesis of Silyloxyarenes involving Multiple Synthetic Manipulations:

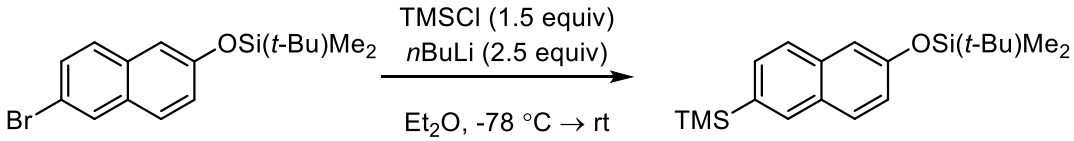
((6-bromonaphthalen-2-yl)oxy)(*tert*-butyl)dimethylsilane (4-INT).



Following general procedure A, 6-bromonaphthalen-2-ol (1.11 g, 5 mmol), imidazole (681 mg, 10 mmol), and *tert*-butyldimethylsilyl chloride (1.13 g, 7.5 mmol) gave a crude mixture which was purified by flash chromatography (hexanes: ethyl acetate 98:2) to afford the desired product as a white solid (1.25 g, 3.70 mmol, 74% yield). The spectral data matches that previously reported in the literature.[11]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.48 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.09 (dd, *J* = 9.0, 2.5 Hz, 1H), 1.01 (s, 9H), 0.24 (s, 6H).

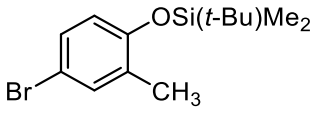
***tert*-butyldimethyl((6-(trimethylsilyl)naphthalen-2-yl)oxy)silane (4-SM).**



Following a previously published protocol[12], ((6-bromonaphthalen-2-yl)oxy)(*tert*-butyl)dimethylsilane (1.0 g, 3 mmol), trimethylsilyl chloride (570 µL, 4.5 mmol), and *n*-butyl lithium solution (2.5 M, 1.8 mL, 4.5 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product as a white solid (800 mg, 2.42 mmol, 81% yield). The spectral data matches that previously reported in the literature.[8]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.17 (s, 1H), 7.07 (dd, *J* = 8.5, 1.5 Hz, 1H), 1.02 (s, 9H), 0.33 (s, 9H), 0.24 (s, 6H).

(4-bromo-2-methylphenoxy)(*tert*-butyl)dimethylsilane (5-INT).

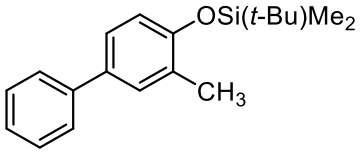


Following general procedure A, 4-bromo-2-methylphenol (1.81 g, 9.68 mmol), imidazole (1.36 g, 20 mmol), *tert*-butyldimethylsilyl chloride (2.26 g, 15 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product as

a colorless oil (2.54 g, 8.43 mmol, 87% yield). The spectral data matches that previously reported in the literature.[13]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 2.5 Hz, 1H), 7.15 (dd, *J* = 7.5, 2.5 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 2.17 (s, 3H), 1.00 (s, 9H), 0.20 (s, 6H).

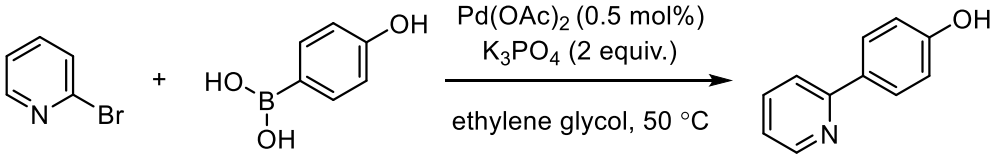
tert-butyldimethyl((3-methyl-[1,1'-biphenyl]-4-yl)oxy)silane (5-SM).



Following a previously published procedure,[14] (4-bromo-2-methylphenoxy)(*tert*-butyl)dimethylsilane (1.50 g, 4.98 mmol), phenyl boronic acid (915 mg, 7.5 mmol), potassium phosphate (6.37 g, 30 mmol), and $PdCl_2(PPh_3)_2$ (176 mg, 0.25 mmol) in a mixture of toluene (15 mL) and degassed water (15 mL) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product as a colorless oil (1.03 g, 3.45 mmol, 69% yield).

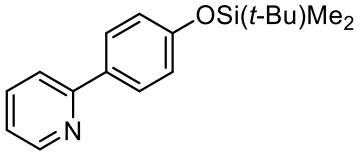
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.42-7.39 (m, 3H), 7.31-7.29 (m, 2H), 6.84 (dd, *J* = 7.5 Hz, 2.5 Hz, 1H), 2.29 (s, 3H), 1.05 (s, 9H), 0.27 (s, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 153.54, 141.09, 134.0, 129.7, 129.1, 128.6, 126.7, 126.5, 125.2, 118.7, 25.8, 18.3, 17.0, -4.2.
IR (film, cm^{-1}): 3029, 2956, 2927, 2857, 1610, 1510, 1486.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{19}H_{26}OSi$, 299.1826; found, 299.1827.

2-(4-((_tert_-butyldimethylsilyl)oxy)phenyl)pyridine (8-INT).



Following a previously published protocol[15], 2-bromopyridine (954 µL, 10 mmol), (4-hydroxyphenyl)boronic acid (2.07 g, 15 mmol), and palladium(II) acetate (11.2 mg, 0.05 mmol), and tripotassium phosphate (4.25 g, 20 mmol) gave a crude residue which was carried on to the next step of the synthesis without further purification.

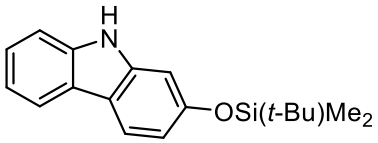
2-(4-((_tert_-butyldimethylsilyl)oxy)phenyl)pyridine (8-SM).



Following general procedure A, crude mixture of 2-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)pyridine, imidazole (1.36 g, 20 mmol), and *tert*-butyldimethylsilyl chloride (2.26 g, 15 mmol) gave a crude mixture which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product as a colorless oil (2.41 g, 8.44 mmol, 84% over two steps). The spectral data matches that previously reported in the literature.[8]

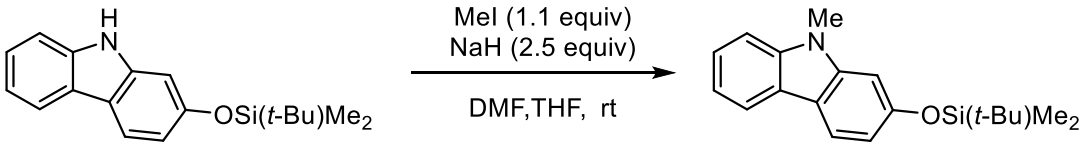
^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.65 (d, *J* = 5.0 Hz, 1H), 7.88 (m, 2H), 7.71 (dt, 8.0, 2.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.17 (dt, *J* = 6.0, 1.0 Hz, 1H), 6.93 (m, 2H), 1.00 (s, 9H), 0.23 (s, 6H).

2-((*tert*-butyldimethylsilyl)oxy)-9H-carbazole (9-INT).



Following general procedure A, 9H-carbazol-2-ol (940 mg, 5 mmol), imidazole (681 mg, 10 mmol), and *tert*-butyldimethylsilyl chloride (1.13 g, 7.5 mmol) gave a crude residue which was carried on to the next step of the synthesis without further purification.

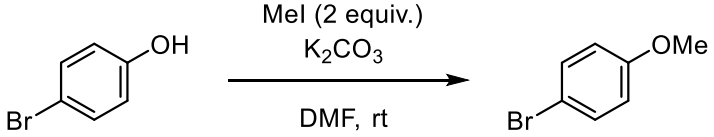
2-((*tert*-butyldimethylsilyl)oxy)-9-methyl-9H-carbazole (9-SM).



Following a previously published protocol[16], crude mixture of 2-((*tert*-butyldimethylsilyl)oxy)-9-methyl-9H-carbazole, methyl iodine (342 µg, 5.5 mmol), and sodium hydride (300 mg, 12.5 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 98:2) to afford the desired product as a white solid (544 mg, 1.75 mmol, 35% yield over two steps). The spectral data matches that previously reported in the literature.[8]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.40 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.78 (s, 3H), 1.04 (s, 9H), 0.26 (s, 6H).

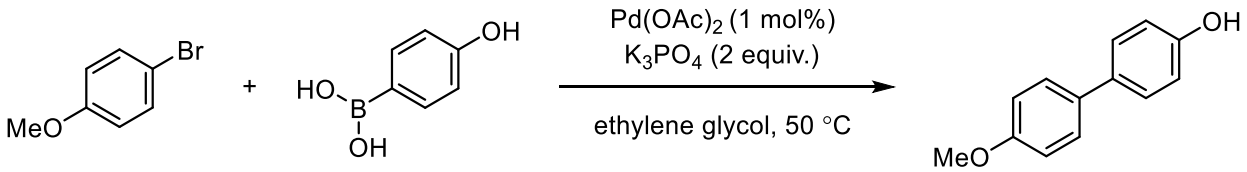
1-bromo-4-methoxybenzene (11-INT1).



Following a previously published protocol[17], 4-bromophenol (1.73 g, 10 mmol), methyl iodine (934 µL, 15 mmol), and potassium carbonate (2.76 g, 20 mmol) gave a crude residue which was purified by flash chromatography (100% hexanes) to afford the desired product as a clear oil (1.30 g, 6.95 mmol, 69%% yield). The spectral data matches that previously reported in the literature.[18]

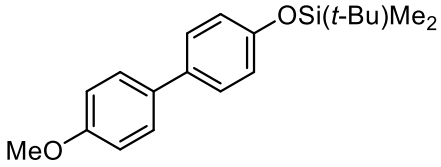
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47 (dt, *J* = 9.0, 2.0 Hz, 2H), 6.78 (dt, *J* = 9.0, 2.0 Hz, 2H), 3.78 (s, 3H).

4'-methoxy-[1,1'-biphenyl]-4-ol (11-INT2).



Following a previously published protocol[15], 1-bromo-4methoxybenzene (1.25 g, 7 mmol), (4-hydroxyphenyl)boronic acid (1.45 g, 10.5 mmol), and palladium(II) acetate (15.7 mg, 0.07 mmol), and tripotassium phosphate (2.97 g, 14 mmol) gave a crude residue which was carried on to the next step of the synthesis without further purification.

***tert*-butyl((4'-methoxy-[1,1'-biphenyl]-4-yl)oxy)dimethylsilane (11-SM).**

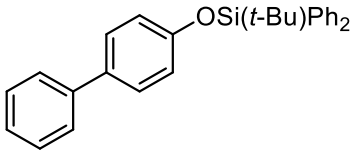


Following general procedure A, crude mixture of 4'-methoxy-[1,1'-biphenyl]-4-ol, imidazole (953 mg, 14 mmol), and *tert*-butyldimethylsilyl chloride (1.58 mg, 10.5 mmol) gave a crude mixture which was purified by recrystallization (EtOH) to afford the desired product as a white solid (1.06 g, 3.4 mmol, 49% yield over two steps). The spectral data matches that previously reported in the literature.[8]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 9.0, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H), 1.00 (s, 9H), 0.22 (s, 6H).

Other Protecting Groups

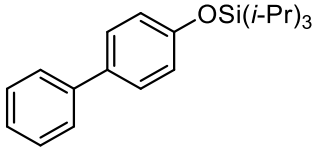
([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)diphenylsilane (1-TBDPS).



Following general procedure A, [1,1'-biphenyl]-4-ol (170 mg, 1 mmol), imidazole (136 mg, 2 mmol), *tert*-butyldiphenylsilyl chloride (0.39 mL, 1.5 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate = 99:1) to afford the desired product as a white solid (395 mg, 0.967 mmol, 97% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.5 Hz, 4H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.40 (m, 10H), 7.27 (m, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 1.15 (s, 9H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 155.2, 140.8, 135.5, 133.9, 132.9, 129.9, 128.6, 127.84, 127.78, 126.63, 126.55, 119.9, 26.5, 19.5.
IR (film, cm^{-1}): 2930, 2857, 1604, 1516, 1484, 1252.
HRMS (EI) *m/z*: $[M]^+$ predicted for $C_{28}H_{28}OSi$, 408.1909; found, 408.1915.

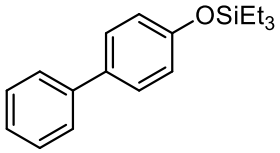
([1,1'-biphenyl]-4-yloxy)triisopropylsilane (1-TIPS).



Following general procedure A, [1,1'-biphenyl]-4-ol (440 mg, 2.588 mmol), imidazole (340 mg, 5 mmol), triisopropylsilyl chloride (0.80 mL, 3.75 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate = 99:1) to afford the desired product as a clear oil (722 mg, 2.211 mmol, 86% yield). The spectral data matches that previously reported in the literature.[8]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 6.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 1.29 (septet, *J* = 7.5 Hz, 3H), 1.13 (d, *J* = 7.5 Hz, 2H).

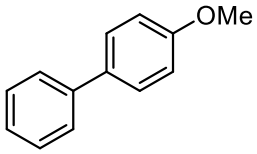
([1,1'-biphenyl]-4-yloxy)triethylsilane (1-TES).



Following general procedure A, [1,1'-biphenyl]-4-ol (3.57 g, 20.97 mmol), imidazole (2.86 g, 42 mmol), chlorotriethylsilane (4.03 mL, 24 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate = 99:1) to afford the desired product as a clear oil (5.01 g, 17.61 mmol, 84% yield). The spectral data matches that previously reported in the literature.[8]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.47 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.93 (m, 2H), 1.04 (t, *J* = 8.0 Hz, 9H), 0.78 (q, *J* = 7.0 Hz, 6H).

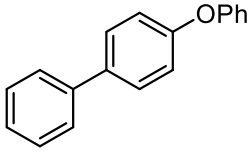
4-methoxy-1,1'-biphenyl (1-Me).



Following a previously published protocol[19], 4-phenylphenol (1.19 g, 7 mmol), iodomethane (0.87 mL, 14 mmol), potassium carbonate (4.93 g, 14 mmol) gave a crude residue that was purified by flash column chromatography (100% hexanes) to afford the desired product as a white solid (1.27 mg, 6.89 mmol, 99% yield). The spectral data matches that previously reported in the literature.[19]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54 (m, 4H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.98 (m, 2H), 3.86 (s, 3H).

4-phenoxy-1,1'-biphenyl (1-Ph).

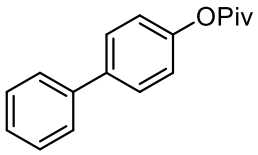


Following a previously published protocol[1], 4-phenylphenol (343 mg, 2 mmol), iodobenzene (336 µL, 3 mmol), iron (III) chloride (64.9 mg, 0.4 mmol), cesium carbonate (1.3 g, 4 mmol), 2,2,6,6-Tetramethyl-3,5-heptanedione (167 mg, 0.4 mmol) gave a crude residue that was purified by flash column chromatography (100% hexanes) to afford the desired product as a white solid (340 mg, 1.38 mmol, 69% yield). The spectral data matches that previously reported in the literature.[20]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (m, 4H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.35 (m, 3H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.07 (m, 4H).

[1,1'-biphenyl]-4-yl pivalate (1-Piv).

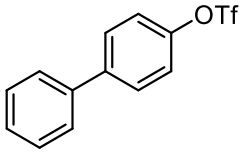
[1] Bistri, O.; Correa, A.; Bolm, C. *Angew. Chemie. Int. Ed.* **2008**, *47*, 586.



Following a previously published protocol[21], 4-phenylphenol (851 mg, 5 mmol), pivaloyl chloride (739 µL, 6 mmol), triethylamine (0.84 mL, 6 mmol), 4-(dimethylamino)-pyridine (61.1 mg, 0.6 mmol) gave a crude residue that was purified by flash column chromatography (100% hexanes) to afford the desired product as a white solid (1.108 g, 4.36 mmol, 85% yield). The spectral data matches that previously reported in the literature.[20]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.59 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.13 (m, 2H), 1.38 (s, 9H).

[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (1-Tf).

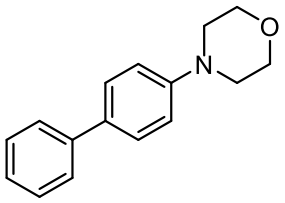


Following a previously published protocol[22], 4-phenylphenol (871 mg, 5.12 mmol), trifluoromethanesulfonic anhydride (841 µL, 5 mmol), 2,6-dimethylpyridine (1.75 mL, 15 mmol) gave a crude residue that was purified by flash column chromatography (100% hexanes) to afford the desired product as a white solid (1.34 g, 4.43 mmol, 84% yield). The spectral data matches that previously reported in the literature.[20]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.65 (m, 4H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.33 (m, 2H).

V. Amination of Silyloxyarenes

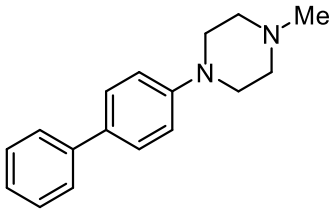
_N_-octyl-4-(pyridin-2-yl)aniline (1a).



Following a modified general procedure B (5 mol% catalyst loading), $Ni(COD)_2$ (4.1 mg, 0.015 mmol), IPr^{Me}·HCl (13.6 mg, 0.03 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (79.3 mg, 0.279 mmol), and morpholine (39 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 92.5:7.5) to afford the desired product (62.3 mg, 0.260 mmol, 93% yield). The spectral data matches that previously reported in the literature.[23]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.55 (m, 4H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.89 (t, *J* = 5.0 Hz, 4H), 3.22 (t, *J* = 5.0 Hz, 4H).

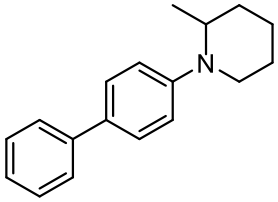
1-([1,1'-biphenyl]-4-yl)-4-methylpiperazine (1b).



Following general procedure B, $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (84.0 mg, 0.295 mmol), and 1-methylpiperazine (50 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate:triethylamine 72.5:25:2.5) to afford the desired product (64.6 mg, 0.256 mmol, 87% yield). The spectral data matches that previously reported in the literature.[24]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.0 Hz, 2H), 7.54 (dd, *J* = 8.0 Hz, 3.0 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 3.29 (t, *J* = 5.0 Hz, 4H), 2.61 (t, *J* = 5.0 Hz, 4H), 2.38 (s, 3H).

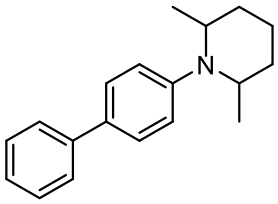
1-([1,1'-biphenyl]-4-yl)-2-methylpiperidine (1c).



Following general procedure B, $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (85.3 mg, 0.300 mmol), and 2-methylpiperidine (53 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (57.9 mg, 0.230 mmol, 77% yield). The spectral data matches that previously reported in the literature.[24]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.27 (m, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 4.02 (s, 1H), 3.32 (dt, *J* = 12.2, 4.0 Hz, 1H), 3.0 (t, *J* = 10.0 Hz, 1H), 1.88 (m, 1H), 1.77 (m, 1H), 1.62 (m, 4H), 1.05 (d, *J* = 6.5 Hz, 3H).

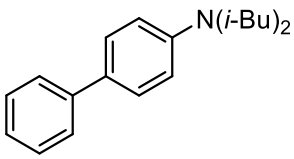
1-([1,1'-biphenyl]-4-yl)-2,6-dimethylpiperidine (1d).



Following general procedure B, $Ni(COD)_2$ (8.3 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (84.0 mg, 0.295 mmol), and 2,6-dimethylpiperdine (49 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (18.3 mg, 0.069 mmol, 23% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 3.10 (m, 2H), 1.77 (m, 3H), 1.53 (m, 3H), 0.87 (d, *J* = 6.5 Hz, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 150.0, 140.9, 136.3, 128.7, 128.3, 126.8, 126.7, 124.9, 55.9, 34.5, 22.6, 21.4.
IR (film, cm^{-1}): 2956, 2924, 2855, 2791, 1602, 1485.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{19}H_{23}N$, 266.1903; found, 266.1903.

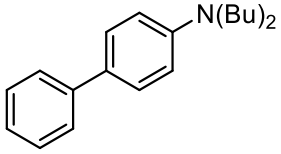
***N*,*N*-diisobutyl-[1,1'-biphenyl]-4-amine (1e).**



Following a modified general procedure B (15 mol% catalyst loading and 2.5 equiv. of amine), $Ni(COD)_2$ (12.4 mg, 0.045 mmol), IPr^{Me}·HCl (40.8 mg, 0.09 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (87.4 mg, 0.307 mmol), and diisobutylamine (131 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes) to afford the desired product (16.4 mg, 0.058 mmol, 19% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 2H), 3.19 (d, *J* = 7.0 Hz, 4H), 2.13 (septet, *J* = 7.0 Hz, 2H), 0.92 (d, *J* = 7.0 Hz, 12H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 147.6, 141.3, 128.8, 128.7, 128.6, 126.1, 125.7, 115.5, 60.4, 26.4, 20.4.
IR (film, cm^{-1}): 2948, 2929, 2863, 1609, 1518, 1486.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{20}H_{27}N$, 282.2216; found, 282.2219.

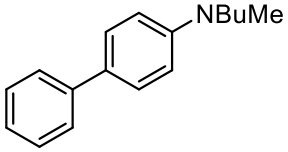
***N*,*N*-dibutyl-[1,1'-biphenyl]-4-amine (1f).**



Following a modified general procedure B (15 mol% catalyst loading and 2.5 equiv. of amine), $Ni(COD)_2$ (12.4 mg, 0.045 mmol), IPr^{Me}·HCl (40.8 mg, 0.09 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (85.9 mg, 0.302 mmol), and dibutylamine (126 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product (69.8 mg, 0.248 mmol, 82% yield). The spectral data matches that previously reported in the literature.[25]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.24 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 3.31 (t, *J* = 8.0 Hz, 4H), 1.61 (m, 4H), 1.38 (m, 4H), 0.98 (t, *J* = 7.5 Hz, 6H).

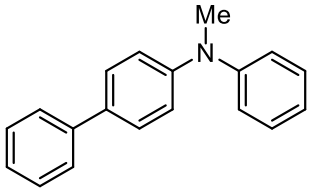
***N*-butyl-*N*-methyl-[1,1'-biphenyl]-4-amine (1g).**



Following general procedure B, $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (84.8 mg, 0.298 mmol), and *N*-methylbutylamine (53 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (63.8 mg, 0.267 mmol, 89% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 2H), 7.25 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 3.36 (t, *J* = 7.5 Hz, 2H), 2.98 (s, 3H), 1.60 (m, 2H), 1.38 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 148.7, 141.3, 128.6, 128.4, 127.7, 126.2, 125.8, 112.2, 52.5, 38.4, 28.9, 20.4, 14.0.
IR (film, cm^{-1}): 3033, 2952, 2870, 1608, 1527, 1491.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{17}H_{21}N$, 240.1747; found, 240.1748.

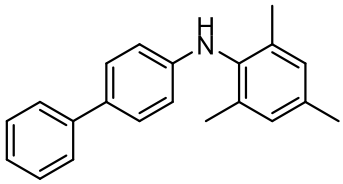
***N*-methyl-*N*-phenyl-[1,1'-biphenyl]-4-amine (1h).**



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (84.8 mg, 0.298 mmol), and *N*-methylaniline (81 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: toluene 90:10) to afford the desired product (33.2 mg, 0.128 mmol, 43% yield). The spectral data matches that previously reported in the literature.[26]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.31 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 7.01 (t, *J* = 7.0 Hz, 1H), 3.36 (s, 3H).

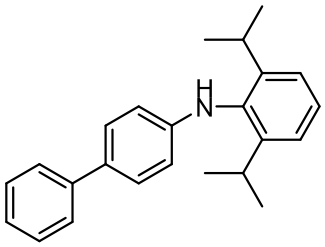
***N*-mesityl-[1,1'-biphenyl]-4-amine (1i).**



Following general procedure B, $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.6 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (84.1 mg, 0.296 mmol), and 2,4,6-trimethylaniline (63 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (68.0 mg, 0.237 mmol, 80% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.41 (m, 4H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.98 (s, 2H), 6.57 (d, *J* = 8.5 Hz, 2H), 2.34 (s, 3H), 2.22 (s, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.1, 141.2, 136.0, 135.5, 135.3, 130.8, 129.2, 128.6, 127.9, 126.3, 126.1, 113.5, 20.9, 18.3.
IR (film, cm^{-1}): 3390, 3022, 2916, 1613, 1519, 1484.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{21}H_{21}N$, 288.1747; found, 288.1753.

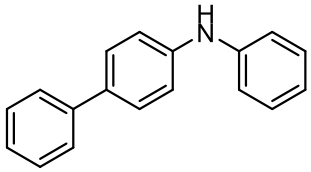
***N*-(2,6-diisopropylphenyl)-[1,1'-biphenyl]-4-amine (1j).**



Following a modified general procedure B (15 mol% catalyst loading and 2.5 equiv. of amine), $Ni(COD)_2$ (12.4 mg, 0.045 mmol), IPr^{Me}·HCl (40.8 mg, 0.09 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (84.7 mg, 0.298 mmol), and 2,6-diisopropylaniline (131 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (54.0 mg, 0.164 mmol, 55% yield).

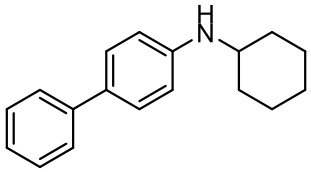
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.40 (m, 4H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 (m, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 1H), 3.25 (septet, *J* = 7.0 Hz, 2H), 1.18 (d, *J* = 7.0 Hz, 12H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 147.6, 141.1, 135.0, 130.5, 128.6, 127.8, 127.3, 126.2, 126.0, 123.9, 115.6, 113.2, 28.2, 23.9.
IR (film, cm^{-1}): 3398, 3031, 2961, 2867, 1612, 1521, 1486.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{24}H_{27}N$, 330.2216; found, 330.2217.

***N*-phenyl-[1,1'-biphenyl]-4-amine (1k).**



Following a modified general procedure B (15 mol% catalyst loading and 2.5 equiv. of amine), $Ni(COD)_2$ (12.4 mg, 0.045 mmol), IPr^{Me}·HCl (40.8 mg, 0.09 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (84.7 mg, 0.298 mmol), and aniline (68 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was analyzed by ^{1}H-NMR and GC-MS where the product was observed. The spectral data matches that previously reported in the literature.[27]

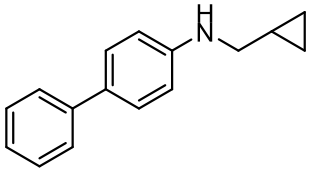
***N*-cyclohexyl-[1,1'-biphenyl]-4-amine (1l).**



Following general procedure B, $Ni(COD)_2$ (4.1 mg, 0.015 mmol), IPr^{Me}·HCl (13.6 mg, 0.03 mmol), NaO-*t*-Bu (36.0 mg, 0.375 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (41.2 mg, 0.145 mmol), and cyclohexylamine (26 µL, 0.225 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (31.8 mg, 0.127 mmol, 87% yield). The spectral data matches that previously reported in the literature.[28]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24 (m, 1H), 6.69 (m, 2H), 3.67 (bs, 1H), 3.30 (m, 1H), 2.09 (dd, *J* = 12.5 Hz, 3.0 Hz, 2H), 13.5 Hz, 4.0 Hz, 2H), 1.66 (m, 1H), 1.38 (m, 2H), 1.28-1.19 (m, 3H).

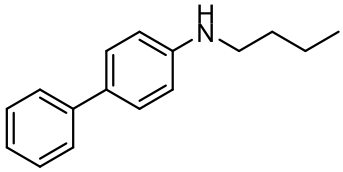
***N*-(cyclopropylmethyl)-[1,1'-biphenyl]-4-amine (1m).**



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.6 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (85.4 mg, 0.300 mmol), and cyclopropylmethylamine (65 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (47.4 mg, 0.212 mmol, 71% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.26 (m, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 3.88 (br, 1H), 3.01 (d, *J* = 7.0 Hz, 2H), 1.13 (m, 1H), 0.57 (d, *J* = 7.5 Hz, 2H), 0.27 (d, *J* = 5.0 Hz, 2H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 147.9, 141.3, 130.1, 128.6, 127.9, 126.3, 126.0, 113.0, 49.1, 10.9, 3.5.
IR (film, cm^{-1}): 2926, 2853, 1609, 1503, 1471.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{16}H_{17}N$, 224.1434; found, 224.1433.

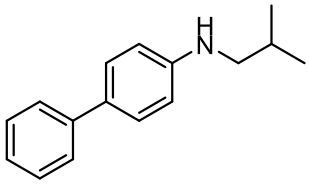
***N*-butyl-[1,1'-biphenyl]-4-amine (1n).**



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (87.3 mg, 0.307 mmol), and butylamine (74 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (48.0 mg, 0.213 mmol, 69% yield). The spectral data matches that previously reported in the literature.[29]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.0 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.25 (m, 1H), 6.70 (d, *J* = 8.5 Hz, 2H), 3.91 (bs, 1H), 3.16 (t, *J* = 7.0 Hz, 2H), 1.64 (pentet, *J* = 7.5 Hz, 2H), 1.45 (sextet, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).

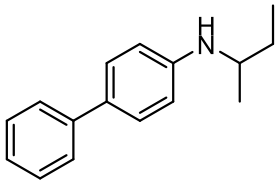
***N*-isobutyl-[1,1'-biphenyl]-4-amine (1o).**



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (83.9 mg, 0.295 mmol), and isobutylamine (75 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (50.0 mg, 0.222 mmol, 75% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 6.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.0 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 2H), 3.83 (bs, 1H), 3.00 (d, *J* = 7.0 Hz, 2H), 1.95 (septet, *J* = 7.0 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 148.0, 141.3, 129.8, 128.6, 127.9, 126.2, 125.9, 112.8, 51.8, 28.0, 20.5.
IR (film, cm^{-1}): 3393, 2951, 2927, 2854, 1610, 1492.
HRMS (EI) *m/z*: $[M]^+$ predicted for $C_{16}H_{19}N$, 225.1517; found, 225.1513.

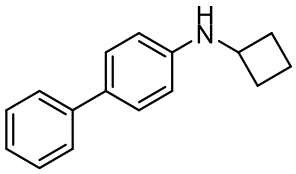
***N*-(*sec*-butyl)-[1,1'-biphenyl]-4-amine (1p).**



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (86.0 mg, 0.302 mmol), and sec-butylamine (76 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (45.4 mg, 0.201 mmol, 67% yield). The spectral data matches that previously reported in the literature.[30]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.44-7.37 (m, 4H), 7.25 (m, 11H), 6.65 (d, *J* = 7.0 Hz, 2H), 3.55 (bs, 1H), 3.44 (m, 1H), 1.61 (m, 1H), 1.50 (m, 1H), 1.21 (d, *J* = 5.5 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H).

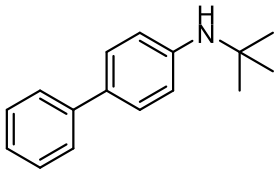
***N*-cyclobutyl-[1,1'-biphenyl]-4-amine (1q).**



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (87.5 mg, 0.308 mmol), and cyclobutylamine (64 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (37.7 mg, 0.169 mmol, 55% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 2H), 3.98 (m, 1H), 3.92 (bs, 1H), 2.47 (m, 2H), 1.88 (m, 4H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.6, 141.3, 130.2, 128.6, 127.9, 126.3, 126.0, 113.2, 48.9, 31.2, 15.3.
IR (film, cm^{-1}): 3380, 2954, 2928, 2853, 1607, 1518, 1472.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{16}H_{17}N$, 224.1434; found, 224.1438.

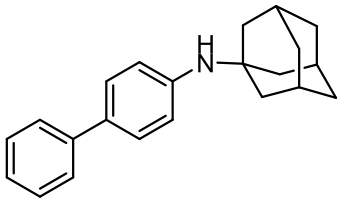
***N*-(*tert*-butyl)-[1,1'-biphenyl]-4-amine (1r).**



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (83.2 mg, 0.292 mmol), and *tert*-butylamine (79 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (10.2 mg, 0.045 mmol, 15% yield). The spectral data matches that previously reported in the literature.[31]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.43-7.37 (m, 4H), 7.26 (m, 1H), 6.82 (m, 2H), 3.62 (bs, 1H), 1.38 (s, 9H).

(3s,5s,7s)-*N*-([1,1'-biphenyl]-4-yl)adamantan-1-amine (1s).

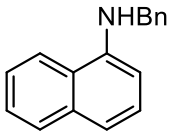


Following a modified general procedure B (15 mol% catalyst loading and 2.5 equiv. of amine), $Ni(COD)_2$ (12.4 mg, 0.045 mmol), IPr^{Me}·HCl (40.8 mg, 0.09 mmol), NaO-*t*-Bu (72.0 mg, 0.750

mmol), ([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (87.5 mg, 0.308 mmol), and 1-adamantylamine (113.4 mg, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (51.9 mg, 0.171 mmol, 56% yield). The spectral data matches that previously reported in the literature.[32]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.41-7.37 (m, 4H), 7.26 (m, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 3.45 (bs, 1H), 2.13 (m, 3H), 1.92 (m, 6H), 1.69 (m, 6H).

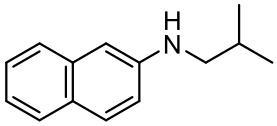
***N*-benzylnaphthalen-1-amine (2).**



Following a modified general procedure B (4.0 equiv. of base), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (115.6 mg, 1.20 mmol), *tert*-butyldimethyl(naphthalen-1-yloxy)silane (77.5 mg, 0.300 mmol), and benzylamine (50 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product (53.0 mg, 0.227 mmol, 76% yield). The spectral data matches that previously reported in the literature.[28]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.83 (t, *J* = 7.5 Hz, 2H), 7.46 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.34 (m, 2H), 7.27 (m, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 4.71 (b, 1H), 4.51 (s, 2H).

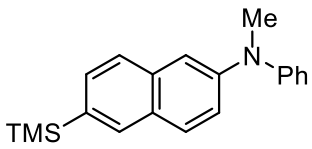
***N*-isobutylnaphthalen-2-amine (3).**



Following general procedure B, $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.75 mmol), *tert*-butyldimethyl(naphthalen-2-yloxy)silane (79.4 mg, 0.307 mmol), and isobutylamine (45 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (42.5 mg, 0.213 mmol, 69% yield). The spectral data matches that previously reported in the literature.[29]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.66 (8.0 Hz, 1H), 7.61 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.88 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 1H), 3.90 (bs, 1H), 3.05 (d, *J* = 7.0 Hz, 2H), 1.98 (septet, *J* = 6.5 Hz, 1H), 1.04 (d, *J* = 7.0 Hz, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.2, 135.3, 128.8, 127.6, 127.3, 126.2, 125.8, 121.7, 117.9, 104.1, 51.8, 28.0, 20.6.
IR (film, cm^{-1}): 3421, 3050, 2955, 2868, 1629, 1522.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{14}H_{17}N$, 200.1434; found, 200.1439.

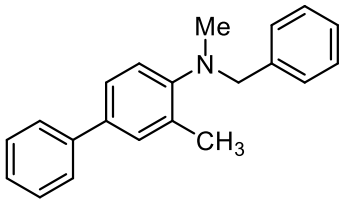
_N_-methyl-_N_-phenyl-6-(trimethylsilyl)naphthalen-2-amine (4).



Following general procedure B, $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), *tert*-butyldimethyl((6-(trimethylsilyl)naphthalen-2-yl)oxy)silane (99.8 mg, 0.302 mmol), and *N*-methylaniline (49 µL, 0.45 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99:1) to afford the desired product (56.4 mg, 0.184 mmol, 61% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.32 (m, 3H), 7.21 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 3.44 (s, 3H), 0.36 (s, 9H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 149.0, 146.9, 135.1, 134.9, 133.4, 130.3, 129.3, 128.7, 128.6, 125.8, 122.1, 121.64, 121.61, 114.0, 40.6, -1.0.
IR (film, cm^{-1}): 3038, 2952, 1625, 1589, 1488.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{20}H_{23}NSi$, 306.1673; found, 306.1669.

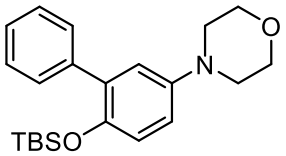
_N_-benzyl-_N_,3-dimethyl-[1,1'-biphenyl]-4-amine (5).



Following general procedure B, $Ni(COD)_2$ (4.1 mg, 0.015 mmol), IPr^{Me}·HCl (13.6 mg, 0.03 mmol), NaO-*t*-Bu (36.0 mg, 0.375 mmol), *tert*-butyldimethyl((3-methyl-[1,1'-biphenyl]-4-yl)oxy)silane (46.2 mg, 0.155 mmol), and *N*-benzylmethylamine (29 µL, 0.225 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (28.9 mg, 0.101 mmol, 65% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.46-7.16 (m, 10H), 7.15 (d, *J* = 8.0 Hz, 1H), 4.10 (s, 2H), 2.64 (s, 3H), 2.48 (s, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 151.8, 141.0, 139.0, 135.7, 132.9, 129.9, 128.6, 128.32, 128.30, 127.0, 126.8, 126.7, 125.1, 120.2, 60.7, 40.8, 18.7.
IR (film, cm^{-1}): 3060, 3028, 2948, 2791, 1603, 1485.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{21}H_{22}N$, 288.1747; found, 288.1748.

4-(6-((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)morpholine (6).



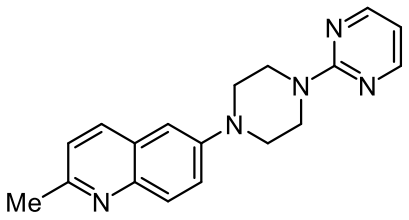
4-(6-((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)morpholine

Following a modified general procedure B (15 mol% catalyst loading, 2.5 equiv. of amine, 4.0 equiv. of base, at 130 °C), $Ni(COD)_2$ (6.2 mg, 0.0225 mmol), IPr^{Me}·HCl (20.4 mg, 0.045 mmol), NaO-*t*-Bu (57.7 mg, 0.6 mmol), ([1,1'-biphenyl]-2,5-diylbis(oxy))bis(*tert*-butyldimethylsilane) (63.2 mg, 0.152 mmol), and morpholine (33 µL, 0.375 mmol) at 130 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (27.0 mg, 0.073 mmol, 48% yield). The product was isolated as a mixture of the desired product and 4-([1,1'-biphenyl]-3-yl)morpholine. The spectral data for 4-([1,1'-biphenyl]-3-yl)morpholine matches that previously reported in the literature.[33]

Pure 4-(6-((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)morpholine (6) could be obtained by deprotecting the *tert*-butyldimethylsilyl group, separating 5-morpholino-[1,1'-biphenyl]-2-ol from 4-([1,1'-biphenyl]-3-yl)morpholine, and reprotecting 5-morpholino-[1,1'-biphenyl]-2-ol to obtain 4-(6-((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)morpholine (6): in a round bottom flask, the mixture of 4-(6-((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)morpholine and 4-([1,1'-biphenyl]-3-yl)morpholine was dissolved in THF (5 mL) and TBAF (6.5 equiv., 1.95 mmol, 1.95 mL of 1 M THF solution) was added and stirred for 1 hour at rt. The reaction mixture was quenched with deionized H_2O (5 mL) and extracted with ethyl acetate (3 x 20 mL) which gave a crude residue that was purified by flash column chromatography (hexanes ethyl acetate 80:20). In a round bottom flask, pure 5-morpholino-[1,1'-biphenyl]-2-ol was dissolved in CH_2Cl_2 (0.6 mL). The solution was then charged with imidazole (2 equiv., 40.8 mg, 0.6 mmol) and *tert*-butyldimethylchlorosilane (1.5 equiv., 67.8 mg, 0.45 mmol) and stirred for 30 minutes at rt. The reaction was quenched with deionized H_2O (10 mL), extracted with Et_2O (3 x 20 mL), dried over $MgSO_4$, filtered, concentrated under reduced pressure and purified by flash column chromatography on silica gel to afford the title compound.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 3.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.80 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.87 (t, *J* = 5.0 Hz, 4H), 3.11 (t, *J* = 5.0 Hz, 4H), 0.81 (s, 9H), -0.11 (s, 6H).
^{13}C-NMR (175 MHz, $CDCl_3$): δ 146.5, 145.9, 139.4, 133.8, 129.7, 127.8, 126.7, 120.9, 118.9, 116.2, 67.1, 50.5, 25.6, 18.0, -4.7.
IR (film, cm^{-1}): 3032, 2957, 2928, 2855, 1599, 1486.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{22}H_{31}NO_2S$, 370.2197; found, 370.2206.

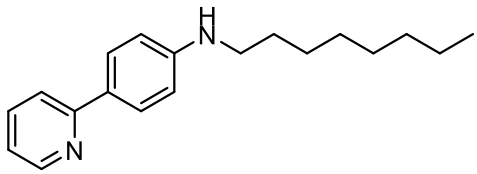
2-methyl-6-(4-(pyrimidin-2-yl)piperazin-1-yl)quinolone (7).



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), 6-((*tert*-butyldimethylsilyl)oxy)-2-methylquinoline (82.6 mg, 0.302 mmol), and 1-(2-pyrimidyl)piperazine (106 µL, 0.75 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate: triethylamine 85:12.5:2.5) to afford the desired product (65.8 mg, 0.215 mmol, 71% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.35 (d, *J* = 5 Hz, 2H), 7.92 (t, *J* = 9.0 Hz, 2H), 7.51 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 1.5 Hz, 1H), 6.53 (t, *J* = 4.5 Hz, 2H), 4.04 (t, *J* = 5.0 Hz, 4H), 3.36 (t, *J* = 5.0Hz, 4H), 2.70 (s, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 161.7, 157.7, 156.2, 148.8, 143.6, 135.0, 129.4, 127.4, 122.7, 122.2, 110.2, 110.0, 109.8, 49.5, 43.6, 25.0.
IR (film, cm^{-1}): 2362, 2322, 1584, 1546, 1498, 1448.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{18}H_{19}N_5$, 306.1713; found, 306.1708.

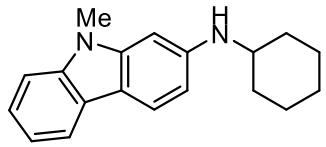
_N_-octyl-4-(pyridin-2-yl)aniline (8).



Following general procedure B, $Ni(COD)_2$ (8.2 mg, 0.03 mmol), IPr^{Me}·HCl (27.2 mg, 0.06 mmol), NaO-*t*-Bu (72.0 mg, 0.750 mmol), 2-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)pyridine (85.0 mg, 0.298 mmol), and *N*-octylamine (73 µL, 0.45 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 90:10) to afford the desired product (62.0 mg, 0.220 mmol, 74% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.61 (d, *J* = 5.0 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.64 (m, 2H), 7.09 (t, *J* = 5.5 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 2H), 3.83 (b, 1H), 3.16 (t, *J* = 7.0 Hz, 2H), 1.63 (pentet, *J* = 7.5 Hz, 2H), 1.40 (m, 2H), 1.31 (m, 8H), 0.90 (t, *J* = 8.0 Hz, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 157.6, 149.3, 149.3, 136.4, 128.0, 127.9, 120.5, 119.0, 112.5, 43.8, 29.5, 29.4, 29.2, 27.1, 22.6, 14.
IR (film, cm^{-1}): 3392, 2922, 2851, 2361, 1612, 1582, 1460.
HRMS (EI) *m/z*: $[M]^+$ predicted for $C_{19}H_{26}N_2$, 282.2096; found, 282.2093.

_N_-cyclohexyl-9-methyl-*9H*-carbazol-2-amine (9).

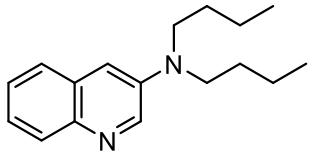


Following general procedure B, $Ni(COD)_2$ (4.1 mg, 0.015 mmol), IPr^{Me}·HCl (13.6 mg, 0.03 mmol), NaO-*t*-Bu (36.0 mg, 0.375 mmol), 2-((*tert*-butyldimethylsilyl)oxy)-9-methyl-9H-carbazole (46.9 mg, 0.151 mmol), and cyclohexylamine (26 µL, 0.225 mmol) at 120 °C for 16 h gave a

crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (30.4 mg, 0.109 mmol, 73% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.34-7.28 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.53 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 3.75 (s, 3H), 3.42 (m, 1H), 2.15 (dd, *J* = 13.5, 4.0 Hz, 2H), 1.81 (m, 2H), 1.70 (m, 1H), 1.45 (m, 2H), 1.25 (m, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.8, 143.1, 140.7, 123.64, 123.61, 123.3, 121.1, 118.6, 114.1, 107.8, 107.6, 91.2, 52.2, 33.6, 28.9, 26.0, 25.1.
IR (film, cm^{-1}): 3033, 2952, 2870, 1608, 1527, 1491.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{19}H_{22}N_2$, 279.1856; found, 279.1862.

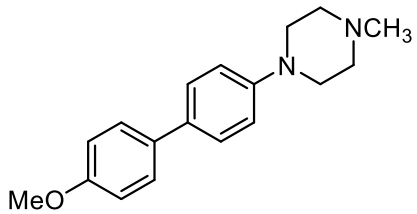
***N*,*N*-dibutylquinolin-3-amine (10).**



Following a modified general procedure B (2.5 equiv. of amine), $Ni(COD)_2$ (4.1 mg, 0.015 mmol), IPr^{Me}·HCl (13.6 mg, 0.03 mmol), NaO-*t*-Bu (36.0 mg, 0.375 mmol), 3-((*tert*-butyldimethylsilyl)oxy)quinoline (40.7 mg, 0.157 mmol), and dibutylamine (63 µL, 0.375 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (25.5 mg, 0.099 mmol, 63% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.63 (d, *J* = 3.0 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.38 (m, 2H), 7.04 (d, *J* = 3.0 Hz, 1H), 3.39 (t, *J* = 8.0 Hz, 4H), 1.63 (pentet, *J* = 8.0 Hz, 4H), 1.40 (sextet, *J* = 7.5 Hz, 4H), 0.98 (t, *J* = 7.5 Hz, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 141.7, 141.1, 140.8, 129.5, 128.8, 126.7, 125.8, 124.4, 111.4, 50.8, 29.3, 20.3, 14.0.
IR (film, cm^{-1}): 3062, 2956, 2929, 2871, 2208, 1697, 1594.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{17}H_{24}N_2$, 257.2012; found, 257.2014.

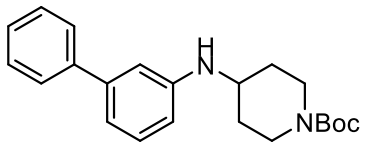
1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4-methylpiperazine (11).



Following a modified general procedure B (15 mol% catalyst loading, 4.0 equiv. of base), $Ni(COD)_2$ (12.4 mg, 0.045 mmol), IPr^{Me}·HCl (40.8 mg, 0.09 mmol), NaO-*t*-Bu (115.3 mg, 1.20 mmol), *tert*-butyl((4'-methoxy-[1,1'-biphenyl]-4-yl)oxy)dimethylsilane (95.4 mg, 0.303 mmol), and 1-methylpiperazine (50 µL, 0.45 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate: triethylamine 85:12.5:2.5) to afford the desired product (54.0 mg, 0.191 mmol, 63% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.48 (t, *J* = 8.0 Hz, 4H), 6.98 (m, 4H), 3.84 (m, 3H), 3.26 (t, *J* = 5.0 Hz, 4H), 2.60 (t, *J* = 5.0 Hz, 4H), 2.37 (s, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 158.5, 150.1, 133.5, 132.0, 127.5, 127.3, 116.1, 114.1, 55.3, 55.1, 49.0, 46.1.
IR (film, cm^{-1}): 2932, 2840, 2790, 1606, 1500, 1443.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{18}H_{22}N_2O$, 283.1805; found, 283.1802.

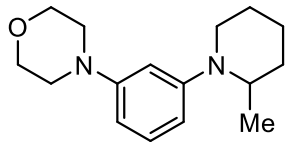
tert-butyl 4-([1,1'-biphenyl]-3-ylamino)piperidine-1-carboxylate (12).



Following general procedure B, $Ni(COD)_2$ (4.1 mg, 0.015 mmol), IPr^{Me}·HCl (13.6 mg, 0.03 mmol), NaO-*t*-Bu (36.0 mg, 0.375 mmol), ([1,1'-biphenyl]-3-yloxy)(*tert*-butyl)dimethylsilane (41.8 mg, 0.147 mmol), and *tert*-butyl 4-aminopiperidine-1-carboxylate (45.1 mg, 0.225 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (30.0 mg, 0.085 mmol, 60% yield).

^{1}H-NMR (700 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.80 (s, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 4.11 (m, 2H), 3.62 (s, 1H), 3.50 (pentet, *J* = 8.4 Hz, 1H), 2.94 (s, 2H), 2.07 (d, *J* = 13.3 Hz, 2H), 1.47 (s, 9H), 1.37 (m, 2H).
^{13}C-NMR (175 MHz, $CDCl_3$): δ 154.8, 147.1, 142.6, 141.7, 129.7, 128.6, 127.18, 127.16, 116.7, 112.2, 112.1, 79.6, 50.1, 32.4, 28.4.
IR (film, cm^{-1}): 3366, 2974, 2931, 2854, 1679, 1598, 1448.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{22}H_{28}N_2O_2$, 353.2224; found, 353.2230.

4-(3-(2-methylpiperidin-1-yl)phenyl)morpholine (13).

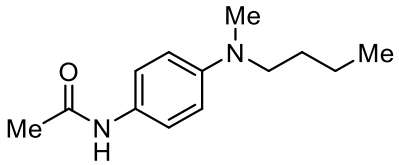


Following a modified general procedure B (15 mol% catalyst loading, 2.5 equiv. of amine, 4.0 equiv. of base, at 130 °C), $Ni(COD)_2$ (6.2 mg, 0.0225 mmol), IPr^{Me}·HCl (20.4 mg, 0.045 mmol), NaO-*t*-Bu (57.7 mg, 0.6 mmol), 4-(3-((*tert*-butyldimethylsilyl)oxy)phenyl)morpholine (45.6 mg, 0.155 mmol), and 2-methylpiperidine (44 µL, 0.375 mmol) at 130 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 90:10) to afford the desired product (25.0 mg, 0.096 mmol, 62% yield).

^{1}H-NMR (700 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.7 Hz, 1H), 6.52 (m, 2H), 6.43 (d, *J* = 8.4 Hz, 1H), 3.86 (m, 5H), 3.15 (m, 5H), 2.98 (dd, *J* = 10.5, 3.5 Hz, 1H), 1.86 (m, 1H), 1.74 (m, 1H), 1.64 (m, 2H), 1.57 (m, 2H), 0.99 (d, *J* = 7.0 Hz, 3H).

^{13}C-NMR (175 MHz, $CDCl_3$): δ 152.6, 152.3, 129.4, 110.3, 107.5, 106.2, 67.0, 51.8, 49.7, 45.6, 31.9, 26.2, 19.9, 14.1.
IR (film, cm^{-1}): 2928, 2850, 2816, 1595, 1576, 1498, 1448.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{16}H_{24}N_2O$, 261.1961; found, 261.1964.

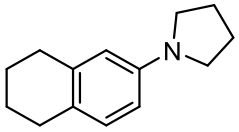
_N_-(4-(butyl(methyl)amino)phenyl)acetamide (14).



Following a modified general procedure B (15 mol% catalyst loading, 2.5 equiv. of amine, 4.0 equiv. of base, at 130 °C), $Ni(COD)_2$ (6.2 mg, 0.0225 mmol), IPr^{Me}·HCl (20.4 mg, 0.045 mmol), NaO-*t*-Bu (57.7 mg, 0.60 mmol), *N*-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)acetamide (42.4 mg, 0.160 mmol), and *N*-methylbutylamine (44 µL, 0.375 mmol) at 130 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 90:10) to afford the desired product (15.2 mg, 0.069 mmol, 43% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 9.0 Hz, 2H), 7.00 (br, 1H), 6.64 (d, *J* = 9.0 Hz, 2H), 3.27 (t, *J* = 7.5 Hz, 2H), 2.89 (s, 3H), 2.13 (s, 3H), 1.53 (pentet, *J* = 7.5 Hz, 2H), 1.32 (sextet, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.1, 146.8, 127.9, 126.9, 122.3, 112.4, 112.0, 52.8, 38.4, 28.7, 24.2, 20.3, 14.0
IR (film, cm^{-1}): 3284, 2955, 2870, 1653, 1598.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{13}H_{20}N_2O$, 220.1576; found, 220.1572.

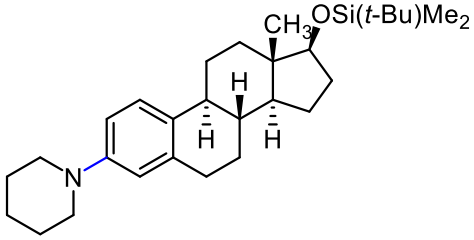
1-(5,6,7,8-tetrahydronaphthalen-2-yl)pyrrolidine (15).



Following a modified general procedure B (15 mol% catalyst loading, 2.5 equiv. of amine, 4.0 equiv. of base, at 130 °C), $Ni(COD)_2$ (12.4 mg, 0.045 mmol), IPr^{Me}·HCl (40.8 mg, 0.09 mmol), NaO-*t*-Bu (115.6 mg, 1.20 mmol), *tert*-butyldimethyl((5,6,7,8-tetrahydronaphthalen-2-yl)oxy)silane (79.7 mg, 0.300 mmol), and pyrrolidine (38 µL, 0.45 mmol) at 130 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 99.5:0.5) to afford the desired product (44.3 mg, 0.220 mmol, 72% yield). The spectral data matches that previously reported in the literature.[34]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.93 (d, *J* = 8.0 Hz, 1H), 6.40 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.28 (s, 1H), 3.25 (m, 4H), 2.71 (m, 4H), 1.98 (m, 4H), 1.77 (m, 4H).

1-((8*R*,9*S*,13*S*,14*S*,17*S*)-17-((*tert*-butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)piperidine (16).

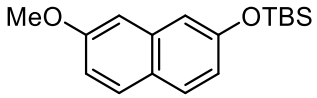


Following a modified general procedure B (15 mol% catalyst loading, 2.5 equiv. of amine, 4.0 equiv. of base, at 130 °C), $Ni(COD)_2$ (6.2 mg, 0.0225 mmol), IPr^{Me}·HCl (20.4 mg, 0.045 mmol), NaO-*t*-Bu (57.7 mg, 0.60 mmol), (((8R,9S,13S,14S,17S)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diyl)bis(oxy))bis(*tert*-butyldimethylsilane) (75.7 mg, 0.151 mmol), and piperidine (37 µL, 0.375 mmol) at 130 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 95:5) to afford the desired product (65.0 mg, 0.143 mmol, 95% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.5 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.67 (d, *J* = 3.0 Hz, 1H), 3.65 (t, *J* = 8.5 Hz, 1H), 3.10 (t, *J* = 5.5 Hz, 4H), 2.82 (m, 2H), 2.28 (dd, *J* = 13.5, 4.0 Hz, 1H), 2.16 (m, 1H), 1.94-1.85 (m, 3H), 1.73-1.62 (m, 5H), 1.58-1.12 (m, 10H), 0.91 (s, 9H), 0.75 (s, 3H), 0.04 (d, *J* = 6.0 Hz, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 150.2, 137.2, 131.7, 125.9, 117.0, 114.5, 81.8, 51.0, 49.7, 44.1, 43.6, 39.0, 37.2, 31.0, 30.0, 27.5, 26.3, 26.0, 25.9, 24.3, 23.3, 18.1, 11.4, -4.5, -4.8.
IR (film, cm^{-1}): 2926, 2854, 1608, 1503, 1450, 1127.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{29}H_{47}NOSi$, 454.3500; found, 454.3504.

VI. Orthogonal Couplings

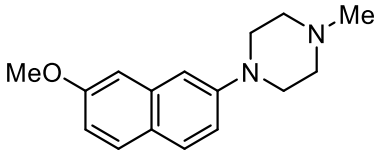
tert-butyl((7-methoxynaphthalen-2-yl)oxy)dimethylsilane (17).



Following general procedure A, 7-methoxynaphthalen-2-ol (890 mg, 5.1 mmol), imidazole (681 mg, 10 mmol), *tert*-butyldimethylsilyl chloride (1.13 g, 7.5 mmol) gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate = 99:1) to afford the desired product as a clear oil (1.43 g, 4.96 mmol, 97% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.65 (t, *J* = 8.5 Hz, 2H), 7.11 (m, 1H), 6.99 (m, 2H), 6.93 (dt, *J* = 9.0 Hz, 2.5 Hz, 1H), 3.91 (s, 3H), 1.03 (s, 9H), 0.25 (s, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 158.0, 154.1, 135.9, 129.1, 129.0, 124.7, 119.5, 116.5, 114.2, 104.8, 55.2, 25.7, 18.3, -4.3.
IR (film, cm^{-1}): 2954, 2928, 2857, 1631, 1511.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{17}H_{24}O_2Si$, 289.1618; found, 289.1620.

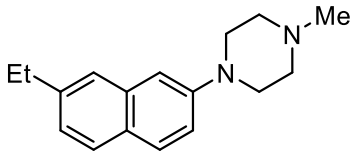
1-(7-methoxynaphthalen-2-yl)-4-methylpiperazine (18).



Following general procedure B, $Ni(COD)_2$ (4.1 mg, 0.015 mmol), IPr^{Me}·HCl (13.6 mg, 0.03 mmol), NaO-*t*-Bu (36.0 mg, 0.375 mmol), *tert*-butyl((7-methoxynaphthalen-2-yl)oxy)dimethylsilane (44.2 mg, 0.153 mmol), and 1-methylpiperazine (25 µL, 0.225 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate: triethylamine 75:24:1) to afford the desired product (32.2 mg, 0.125 mmol, 82% yield).

^{1}H-NMR (700 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 9.1 Hz, 1H), 7.05 (s, 1H), 7.02 (s, 1H), 6.95 (d, *J* = 9.1 Hz, 1H), 3.99 (s, 3H), 3.32 (t, *J* = 4.9 Hz, 4H), 2.63 (t, *J* = 4.9 Hz, 4H), 2.38 (s, 3H).
^{13}C-NMR (175 MHz, $CDCl_3$): δ 158.1, 149.6, 135.8, 128.9, 128.4, 123.8, 116.8, 115.8, 109.4, 105.1, 55.2, 55.1, 49.4, 46.2.
IR (film, cm^{-1}): 2932, 2839, 2798, 1629, 1515, 1462.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{16}H_{20}N_2O$, 257.1648; found, 257.1653.

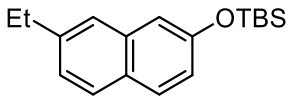
1-(7-ethylnaphthalen-2-yl)-4-methylpiperazine (20).



Following a previously published procedure,[35] $Ni(COD)_2$ (1.7 mg, 0.0062 mmol), 1,2-bis(dicylohexylphosphino)ethane (dcype) (2.6 mg, 0.0062 mmol), 1-(7-methoxynaphthalen-2-yl)-4-methylpiperazine (16.0 mg, 0.062 mmol), triethylaluminum (25 wt% in toluene, 34 µL), toluene (0.3 mL), and diisopropylether (0.3 mL) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate: triethylamine 72.5:25:2.5) to afford the desired product (15.0 mg, 0.059 mmol, 94% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 9.1 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 3.32 (t, *J* = 4.9 Hz, 4H), 2.77 (q, *J* = 7.7 Hz, 2H), 2.64 (t, *J* = 4.9 Hz, 4H), 2.39 (s, 3H), 1.31 (t, *J* = 7.7 Hz, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 149.2, 142.2, 134.8, 128.4, 127.3, 127.0, 124.6, 124.5, 118.6, 110.0, 55.1, 49.5, 46.2, 29.1, 15.5.
IR (film, cm^{-1}): 2963, 2928, 2839, 2787, 1629, 1514.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{17}H_{22}N_2$, 255.1856; found, 255.1856.

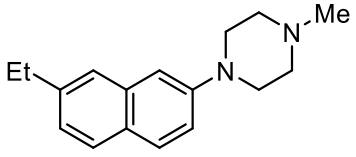
tert-butyl((7-ethylnaphthalen-2-yl)oxy)dimethylsilane (19).



Following a previously published procedure,[35] $Ni(COD)_2$ (4.1 mg, 0.015 mmol), 1,2-bis(dicylohexylphosphino)ethane (dcype) (6.3 mg, 0.015 mmol), *tert*-butyl((7-methoxynaphthalen-2-yl)oxy)dimethylsilane (43.2 mg, 0.150 mmol), triethylaluminum (25 wt% in toluene, 161 µL), toluene (0.3 mL), and diisopropylether (0.3 mL) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes) to afford the desired product (29.2 mg, 0.102 mmol, 68% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.69 (m, 2H), 7.49 (s, 1H), 7.21 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 7.02 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.79 (q, *J* = 8.0 Hz, 2H), 1.33 (t, *J* = 8.0 Hz, 3H), 1.03 (s, 9H), 0.25 (s, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 153.5, 142.1, 134.9, 129.0, 127.7, 127.5, 125.0, 124.4, 121.2, 114.6, 29.0, 25.7, 18.3, 15.5, -4.3.
IR (film, cm^{-1}): 2958, 2929, 2857, 1632, 1606, 1511, 1461.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{18}H_{26}OSi$, 287.1826; found, 287.1829.

1-(7-ethylnaphthalen-2-yl)-4-methylpiperazine (20).

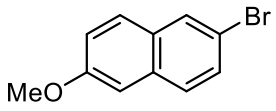


Following general procedure B, $Ni(COD)_2$ (3.0 mg, 0.011 mmol), IPr^{Me}·HCl (9.80 mg, 0.022 mmol), NaO-*t*-Bu (25.9 mg, 0.270 mmol), *tert*-butyl((7-ethylnaphthalen-2-yl)oxy)dimethylsilane (31.0 mg, 0.108 mmol), and 1-methylpiperazine (18 µL, 0.162 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate:triethylamine 72.5:25:2.5) to afford the desired product (26.8 mg, 0.105 mmol, 97% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 9.1 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 3.32 (t, *J* = 4.9 Hz, 4H), 2.77 (q, *J* = 7.7 Hz, 2H), 2.64 (t, *J* = 4.9 Hz, 4H), 2.39 (s, 3H), 1.31 (t, *J* = 7.7 Hz, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 149.2, 142.2, 134.8, 128.4, 127.3, 127.0, 124.6, 124.5, 118.6, 110.0, 55.1, 49.5, 46.2, 29.1, 15.5.
IR (film, cm^{-1}): 2963, 2928, 2839, 2787, 1629, 1514.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{17}H_{22}N_2$, 255.1856; found, 255.1856.

VII. Sequential Coupling

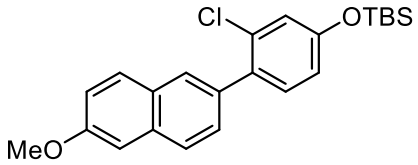
2-bromo-6-methoxynaphthalene (22).



Following a previously published procedure[17], 6-bromonaphthalen-2-ol (2.2 g, 9.86 mmol), K_2CO_3 (2.76 g, 10 mmol), methyl iodide (1.25 mL, 20 mmol), and DMF (10 mL) gave a crude residue which was purified by flash chromatography (hexanes) to afford the desired product as a white solid (2.065 g, 8.71 mmol, 88% yield).

^{1}H-NMR (700 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 9.0 Hz, 1H), 7.10 (s, 1H), 3.92 (s, 3H).
^{13}C-NMR (175 MHz, $CDCl_3$): δ 157.9, 133.0, 130.0, 129.64, 129.60, 128.5, 128.4, 119.8, 117.0, 105.7, 55.3.
IR (film, cm^{-1}): 3061, 2966, 2840, 1625, 1584, 1498.
HRMS (EI) *m/z*: $[M]^+$ predicted for $C_{11}H_9BrO$, 235.9837; found, 235.9836.

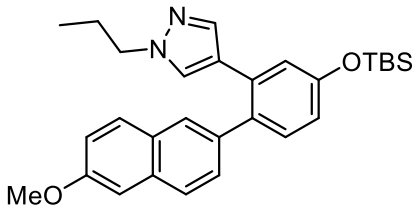
***tert*-butyl(3-chloro-4-(6-methoxynaphthalen-2-yl)phenoxy)dimethylsilane (24).**



Following a previously published procedure[8], 2-bromo-6-methoxynaphthalene (36.2 mg, 0.153 mmol), (4-((*tert*-butyldimethylsilyl)oxy)-2-chlorophenyl)boronic acid (64.5 mg, 0.225 mmol), K_3PO_4 (191 mg, 0.9 mmol), $PdCl_2(PPh_3)_2$ (5.3 mg, 0.0075 mmol), toluene (0.45 mL), and degassed H_2O (0.45 mL) at 90 °C for 16 hours gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate = 98:2) to afford the desired product (49.7 mg, 0.125 mmol, 82% yield).

^{1}H-NMR (700 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.77 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.18 (s, 2H), 7.00 (s, 1H), 6.83 (s, *J* = 8.3 Hz, 1H), 3.95 (s, 3H), 1.02 (s, 9H), 0.26 (s, 6H).
^{13}C-NMR (175 MHz, $CDCl_3$): δ 157.8, 155.4, 134.6, 133.64, 133.60, 132.8, 132.0, 129.6, 128.4, 128.1, 126.2, 121.4, 119.0, 118.8, 105.6, 55.3, 25.6, 18.2, -4.4.
IR (film, cm^{-1}): 2951, 2929, 2856, 1603, 1496, 1471.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{23}H_{27}ClO_2Si$, 399.1542; found, 399.1540.

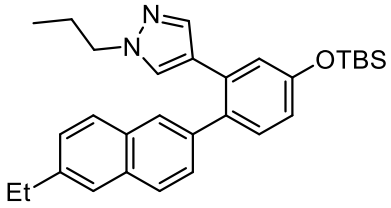
4-(5-((*tert*-butyldimethylsilyl)oxy)-2-(6-methoxynaphthalen-2-yl)phenyl)-1-propyl-1H-pyrazole (26).



Following a previously published procedure[36], *tert*-butyl(3-chloro-4-(6-methoxynaphthalen-2-yl)phenoxy)dimethylsilane (52.3 mg, 0.131 mmol), (1-propyl-1*H*-pyrazol-4-yl)boronic acid (23.1 mg, 0.15 mmol), K_3PO_4 (45.1 mg, 0.213 mmol), Pd_2dba_3 (11.4 mg, 0.0125 mmol), PCy_3 (3.5 mg, 0.0125 mmol), and dioxane (0.25 mL) at 80 °C for 16 hours gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 90:10) to afford the desired product (48.4 mg, 0.102 mmol, 78% yield).

^{1}H-NMR (700 MHz, $CDCl_3$): δ 7.69 (m, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 7.25 (m, 2H), 7.13 (m, 2H), 6.90 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.74 (s, 1H), 3.93 (s, 3H), 3.84 (t, *J* = 6.9 Hz, 2H), 1.67 (m, 2H), 1.04 (s, 9H), 0.72 (t, *J* = 7.4 Hz, 3H), 0.28 (s, 6H).
^{13}C-NMR (175 MHz, $CDCl_3$): δ 157.6, 155.1, 138.5, 133.30, 133.28, 132.5, 131.9, 129.4, 128.9, 128.5, 127.9, 126.1, 121.4, 120.3, 118.7, 118.1, 105.6, 55.3, 53.6, 25.7, 23.6, 18.2, 10.9, -4.3.
IR (film, cm^{-1}): 2956, 2929, 2857, 1605, 1496.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{29}H_{36}N_2O_2Si$, 473.2619; found, 473.2619.

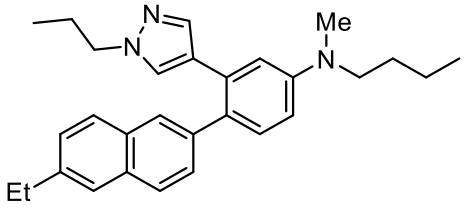
4-(5-((*tert*-butyldimethylsilyl)oxy)-2-(6-ethylnaphthalen-2-yl)phenyl)-1-propyl-1*H*-pyrazole (27).



Following a previously published procedure[35], 4-(5-((*tert*-butyldimethylsilyl)oxy)-2-(6-methoxynaphthalen-2-yl)phenyl)-1-propyl-1*H*-pyrazole (33.0 mg, 0.070 mmol), $Ni(COD)_2$ (1.9 mg, 0.007 mmol), 1,2-bis(dicylohexylphosphino)ethane (dcype) (3.0 mg, 0.007 mmol), triethylaluminum (25 wt% in toluene, 75 µL), toluene (0.14 mL), and diisopropylether (0.14 mL) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 90:10) to afford the desired product (31.0 mg, 0.066 mmol, 94% yield).

^{1}H-NMR (700 MHz, $CDCl_3$): δ 7.72 (t, *J* = 4.0 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.38 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.25 (m, 2H), 6.99 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.74 (s, 1H), 3.84 (t, *J* = 7.0 Hz, 2H), 2.82 (q, *J* = 7.6 Hz, 2H), 1.66 (sextet, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H), 1.04 (s, 9H), 0.72 (t, *J* = 7.7 Hz), 3H), 0.28 (s, 6H).
^{13}C-NMR (175 MHz, $CDCl_3$): δ 155.1, 141.7, 138.8, 138.5, 133.3, 132.5, 132.4, 132.0, 131.9, 128.5, 127.83, 127.77, 127.2, 126.7, 125.3, 121.4, 120.3, 118.1, 53.6, 29.0, 25.7, 23.6, 18.2, 15.5, 10.9, -4.3.
IR (film, cm^{-1}): 2959, 2929, 2857, 1602, 1495, 1472.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{30}H_{38}N_2OSi$, 471.2826; found, 471.2833.

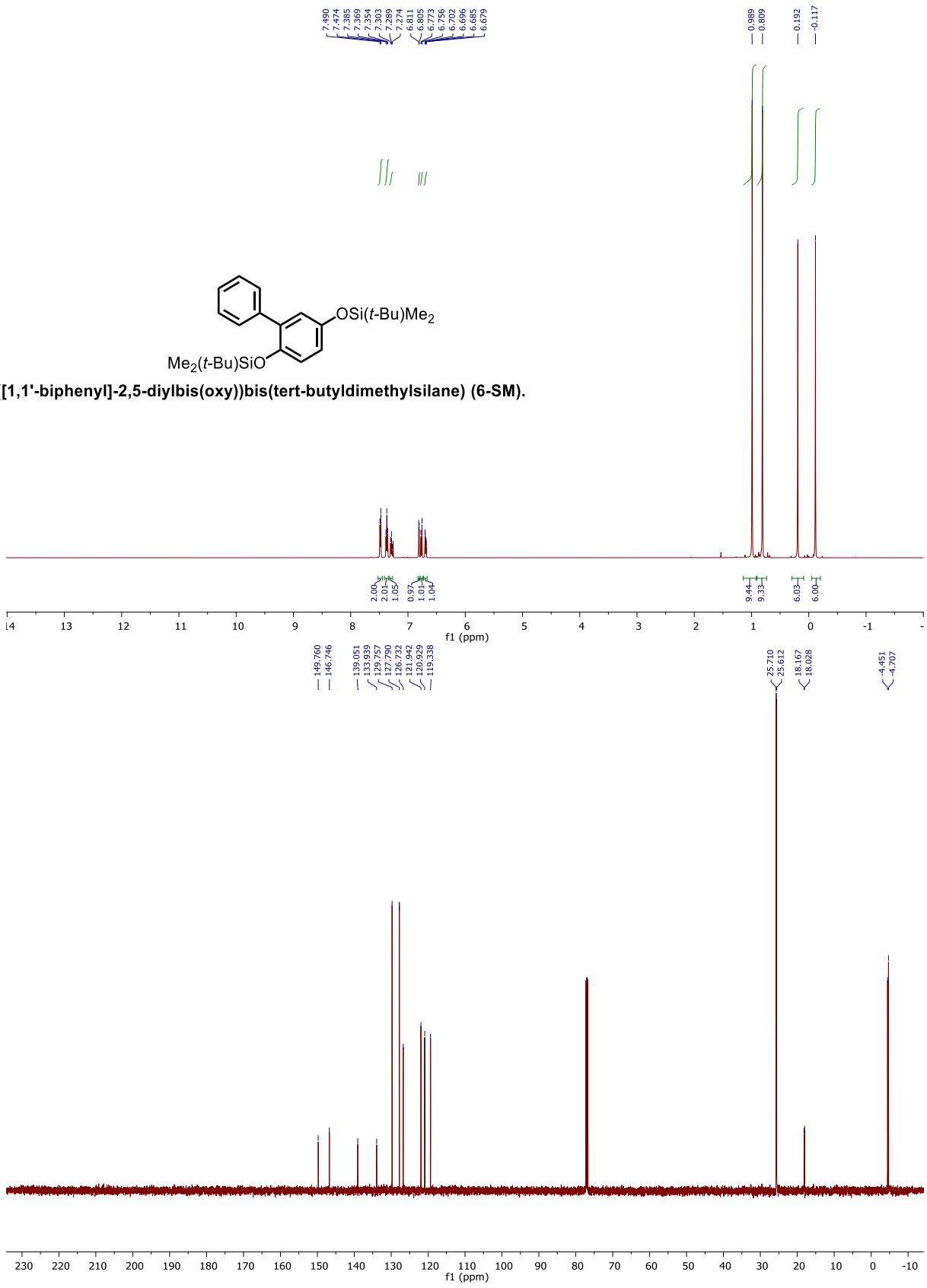
***N*-butyl-4-(6-ethylnaphthalen-2-yl)-*N*-methyl-3-(1-propyl-1*H*-pyrazol-4-yl)aniline (28).**



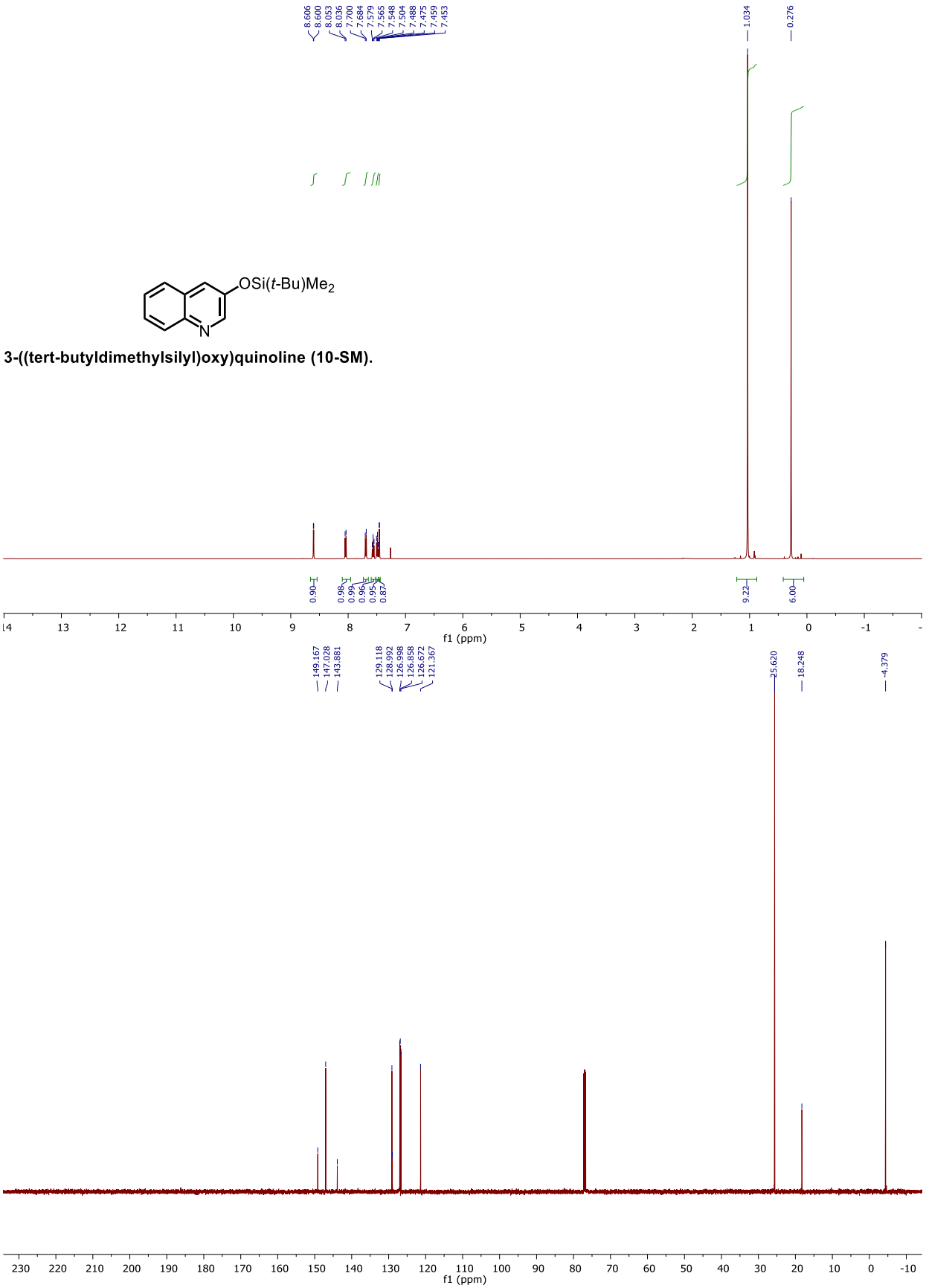
Following general procedure B, 4-(5-((*tert*-butyldimethylsilyl)oxy)-2-(6-ethylnaphthalen-2-yl)phenyl)-1-propyl-1*H*-pyrazole (42.8 mg, 0.091 mmol), $Ni(COD)_2$ (2.5 mg, 0.0091 mmol), IPr^{Me}·HCl (8.2 mg, 0.0182 mmol), NaO-*t*-Bu (21.9 mg, 0.228 mmol), and *N*-methylbutylamine (16.2 µL, 0.136 mmol) at 120 °C for 16 h gave a crude residue which was purified by flash chromatography (hexanes: ethyl acetate 90:10) to afford the desired product (29.0 mg, 0.068 mmol, 75% yield).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.71 (m, 2H), 7.59 (m, 2H), 7.46 (s, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 6.76 (s, 1H), 6.71 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.85 (t, *J* = 7.0 Hz, 2H), 3.39 (t, *J* = 7.0 Hz, 2H), 3.01 (s, 3H), 2.81 (q, *J* = 7.0 Hz, 2H), 1.65 (m, 4H), 1.41 (sextet, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H), 0.72 (t, *J* = 7.0 Hz, 3H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 148.8, 141.3, 139.2, 138.5, 132.2, 132.05, 131.99, 131.8 128.9, 128.8, 128.0, 127.8, 127.6, 127.0, 126.5, 125.3, 122.3, 112.5, 110.7, 55.6, 52.5, 38.4, 29.02, 29.01, 23.6, 20.4, 15.6, 14.0, 10.9.
IR (film, cm^{-1}): 2961, 2930, 2871, 1604, 1514, 1455.
HRMS (ESI+) *m/z*: $[M+H]^+$ predicted for $C_{29}H_{35}N_3$, 426.2904; found, 426.2912.

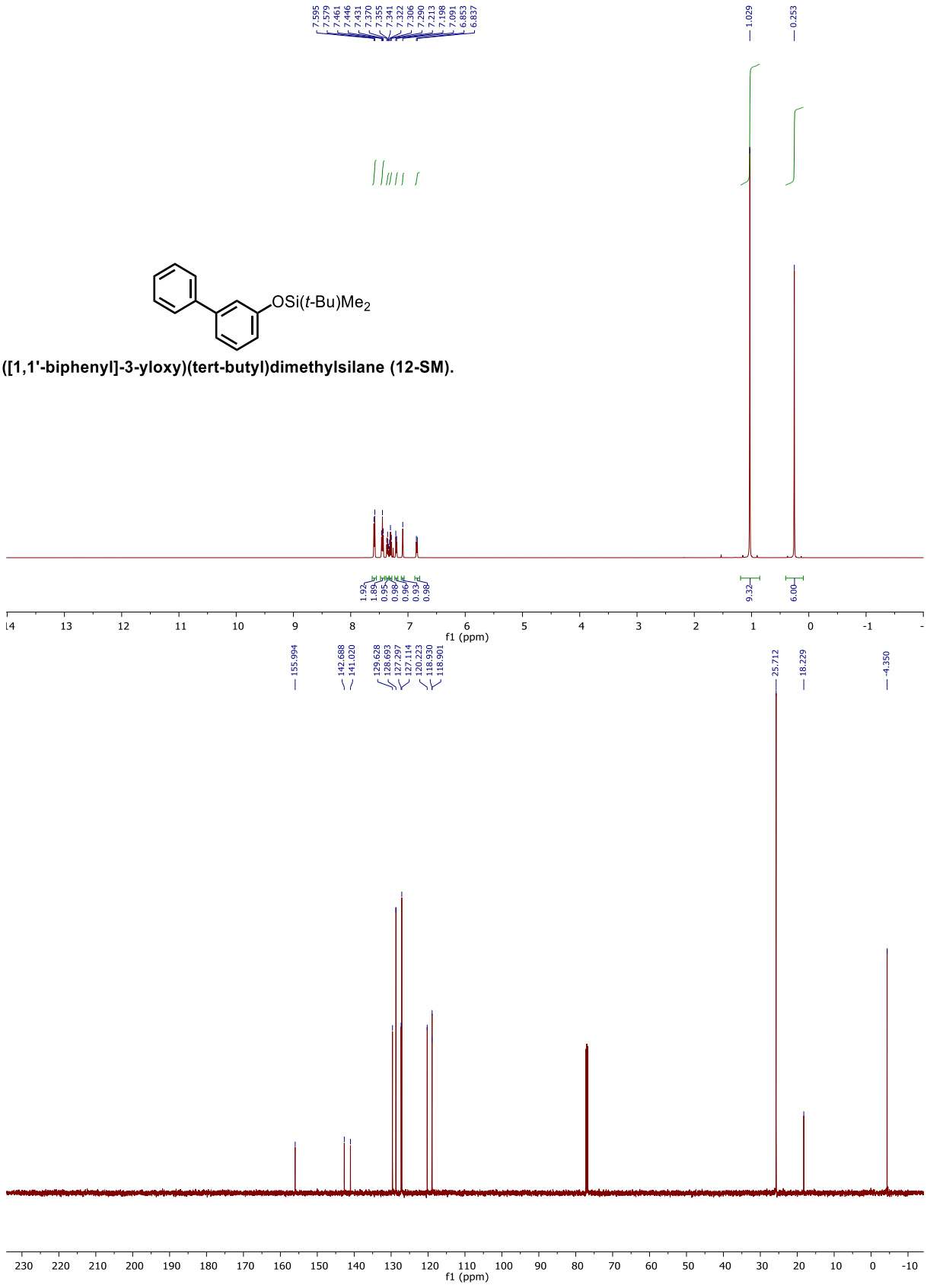
VIII. Spectra



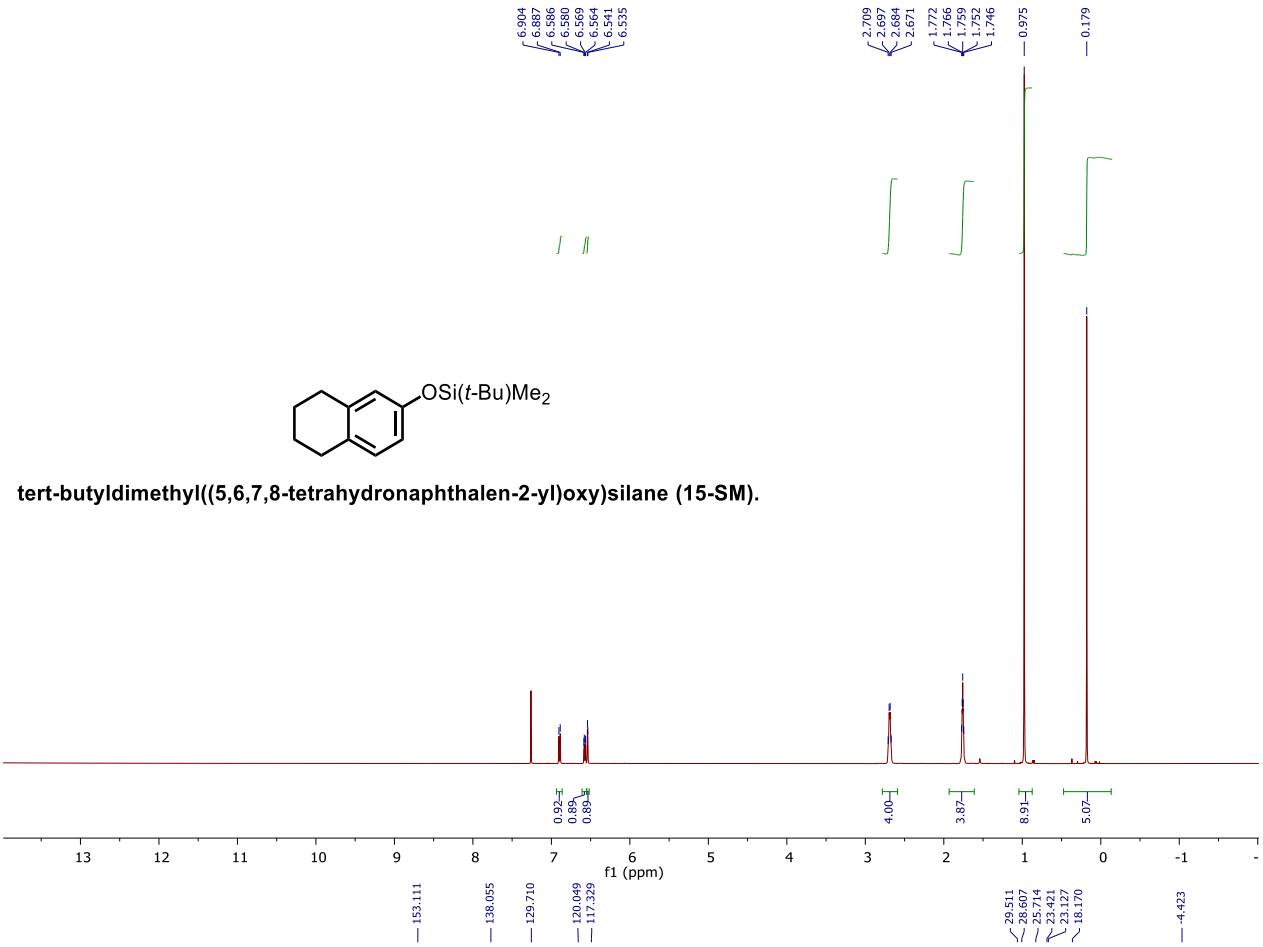
([1,1'-biphenyl]-2,5-diylbis(oxy))bis(tert-butyldimethylsilane) (6-SM).



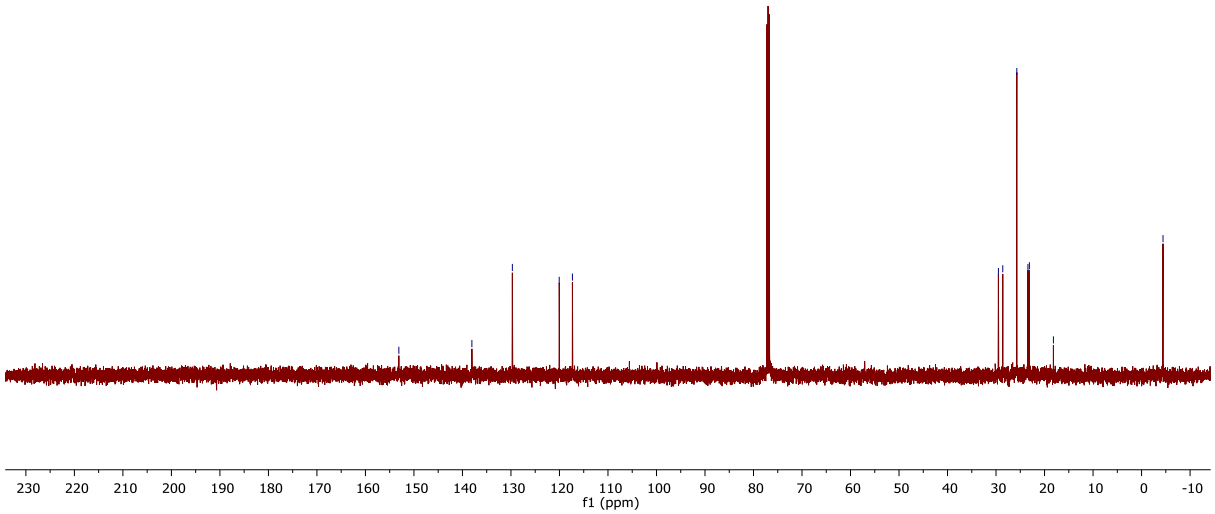
3-((tert-butyldimethylsilyl)oxy)quinoline (10-SM).

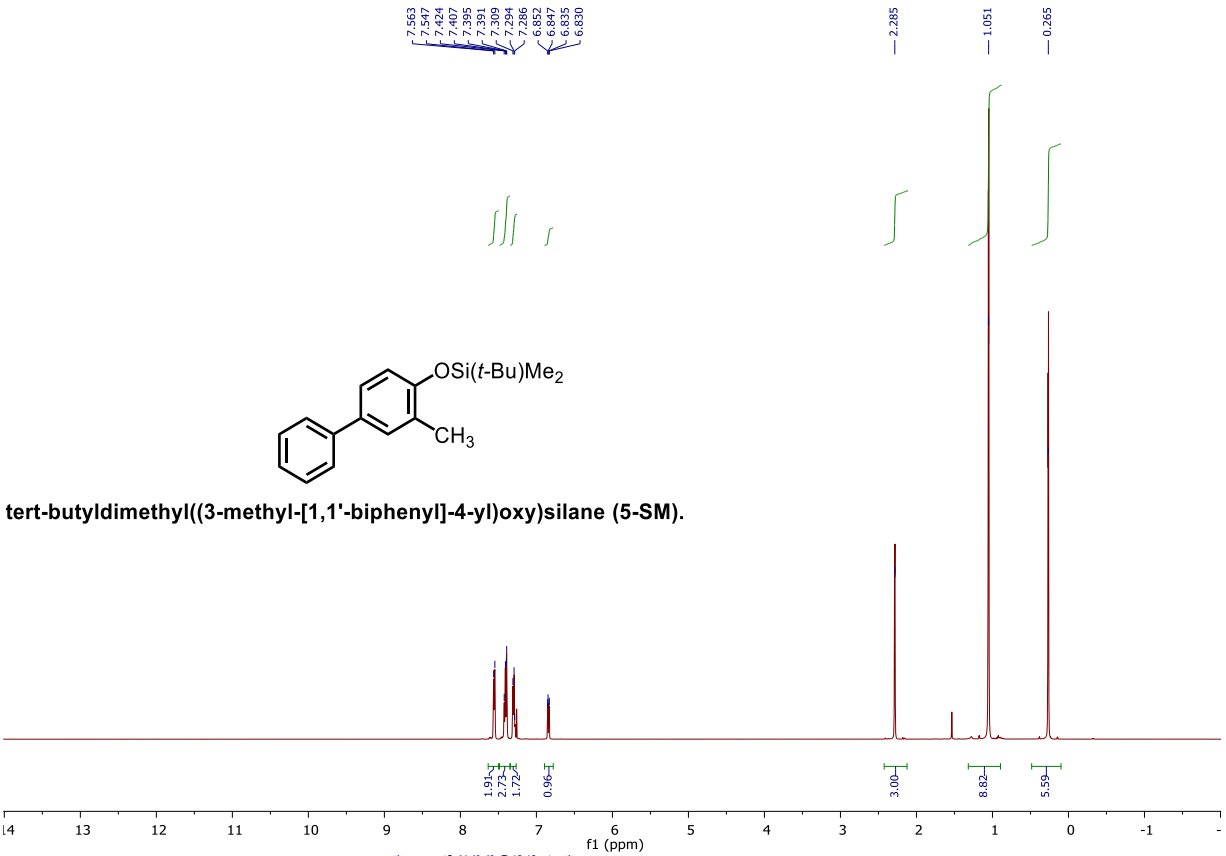


([1,1'-biphenyl]-3-yloxy)(tert-butyl)dimethylsilane (12-SM).

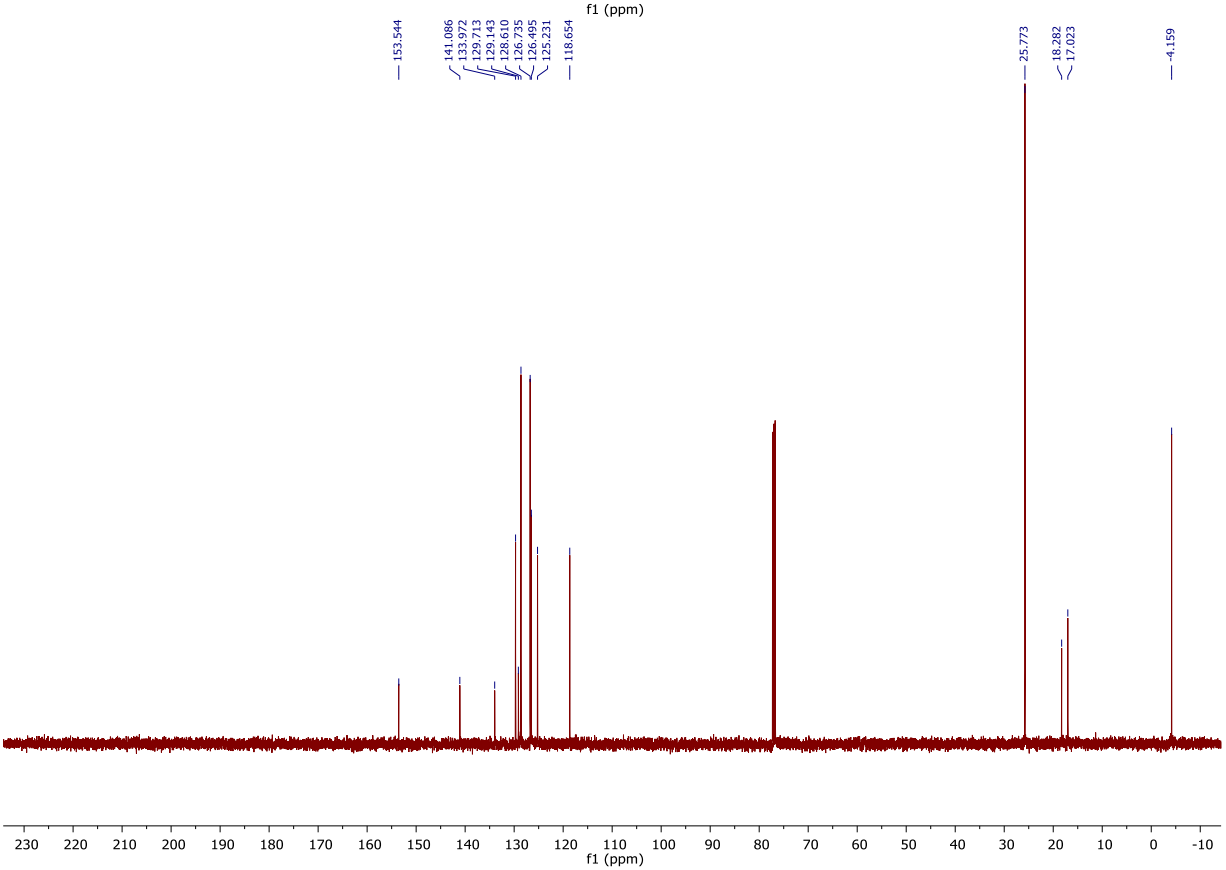


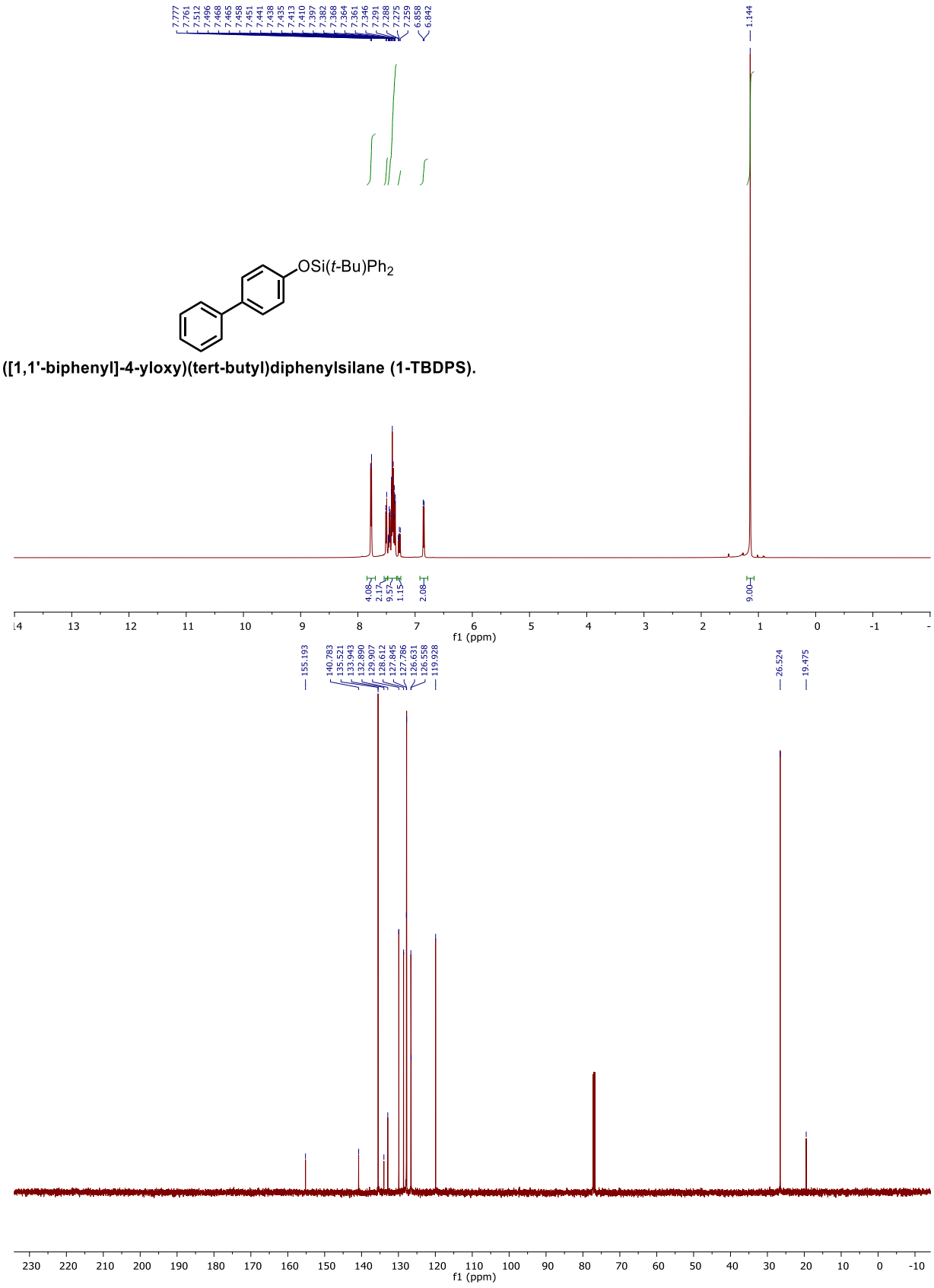
tert-butyldimethyl((5,6,7,8-tetrahydronaphthalen-2-yl)oxy)silane (15-SM).



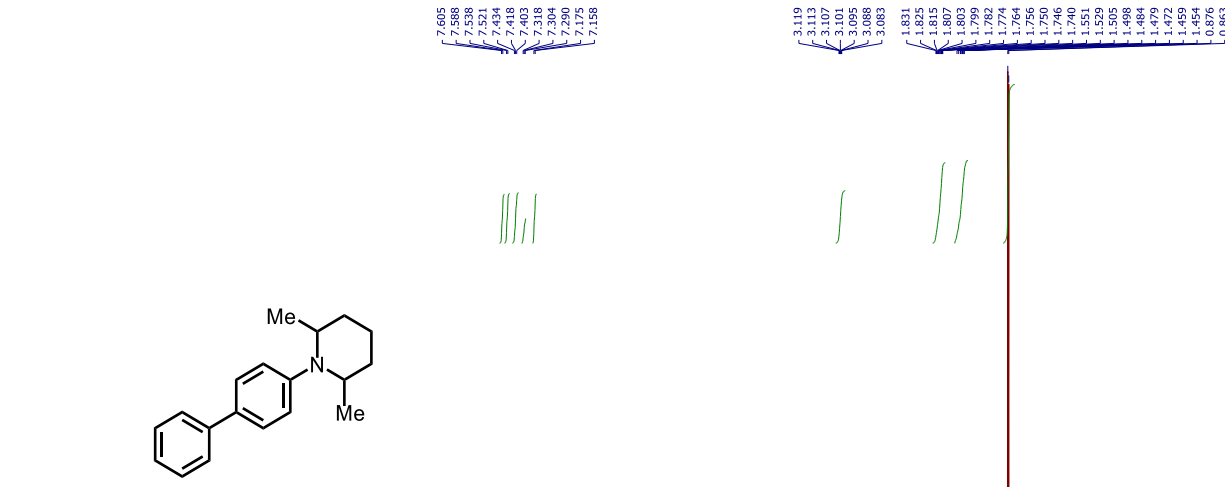


tert-butyldimethyl((3-methyl-[1,1'-biphenyl]-4-yl)oxy)silane (5-SM).

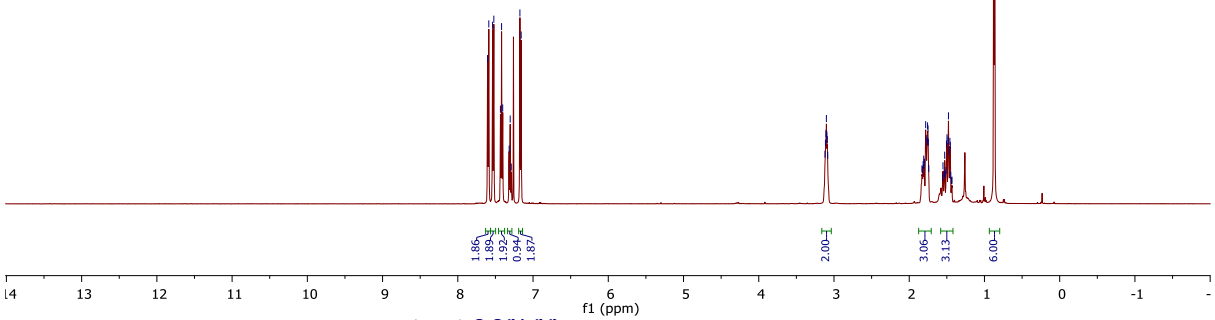


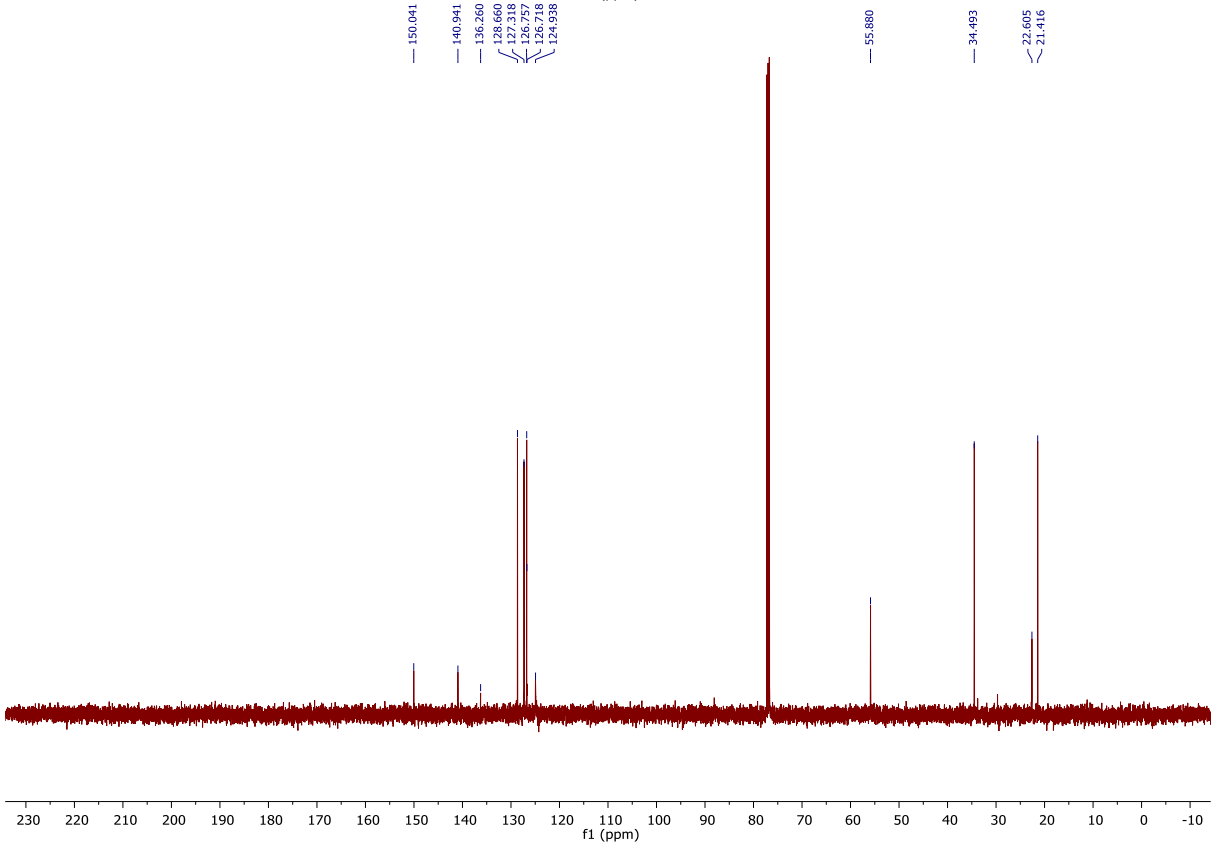


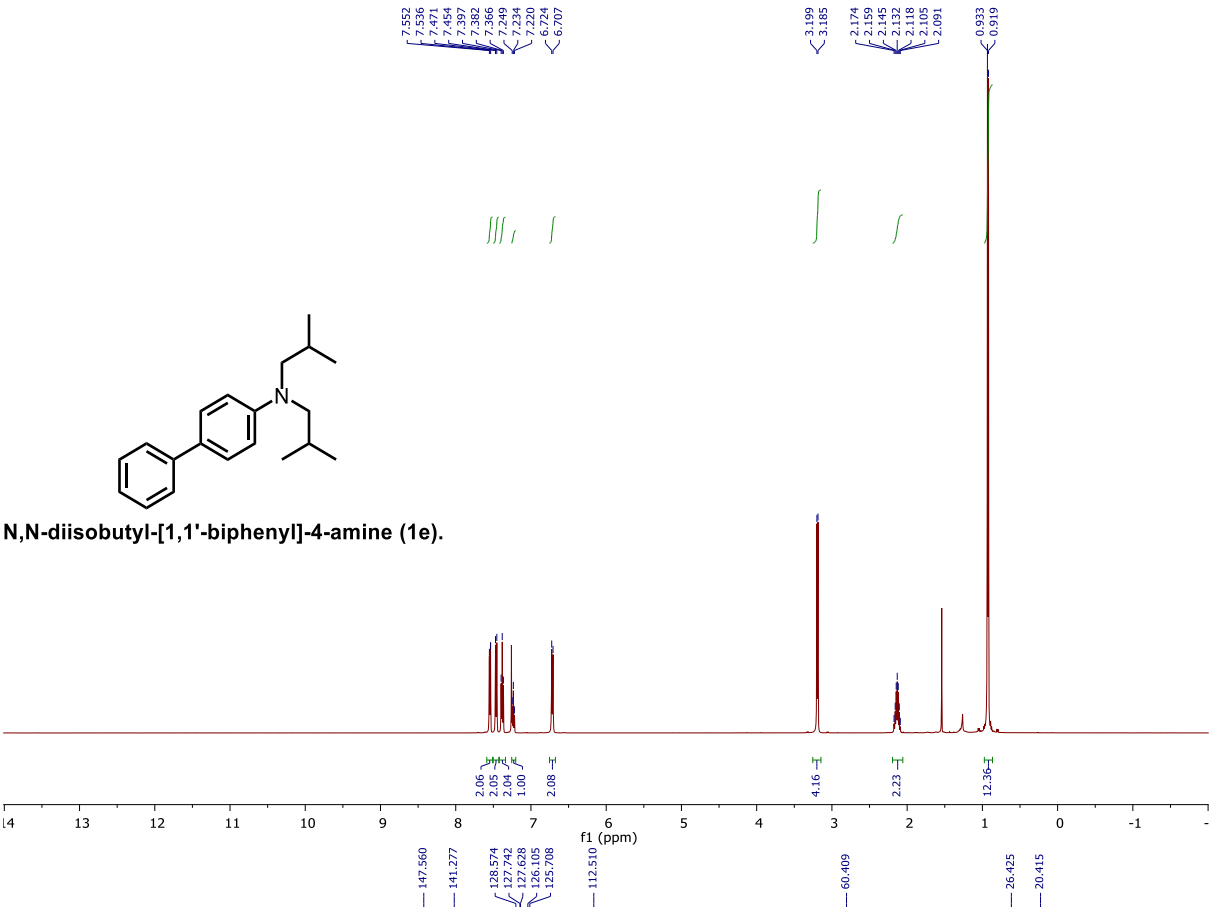
([1,1'-biphenyl]-4-yloxy)(tert-butyl)diphenylsilane (1-TBDPS).



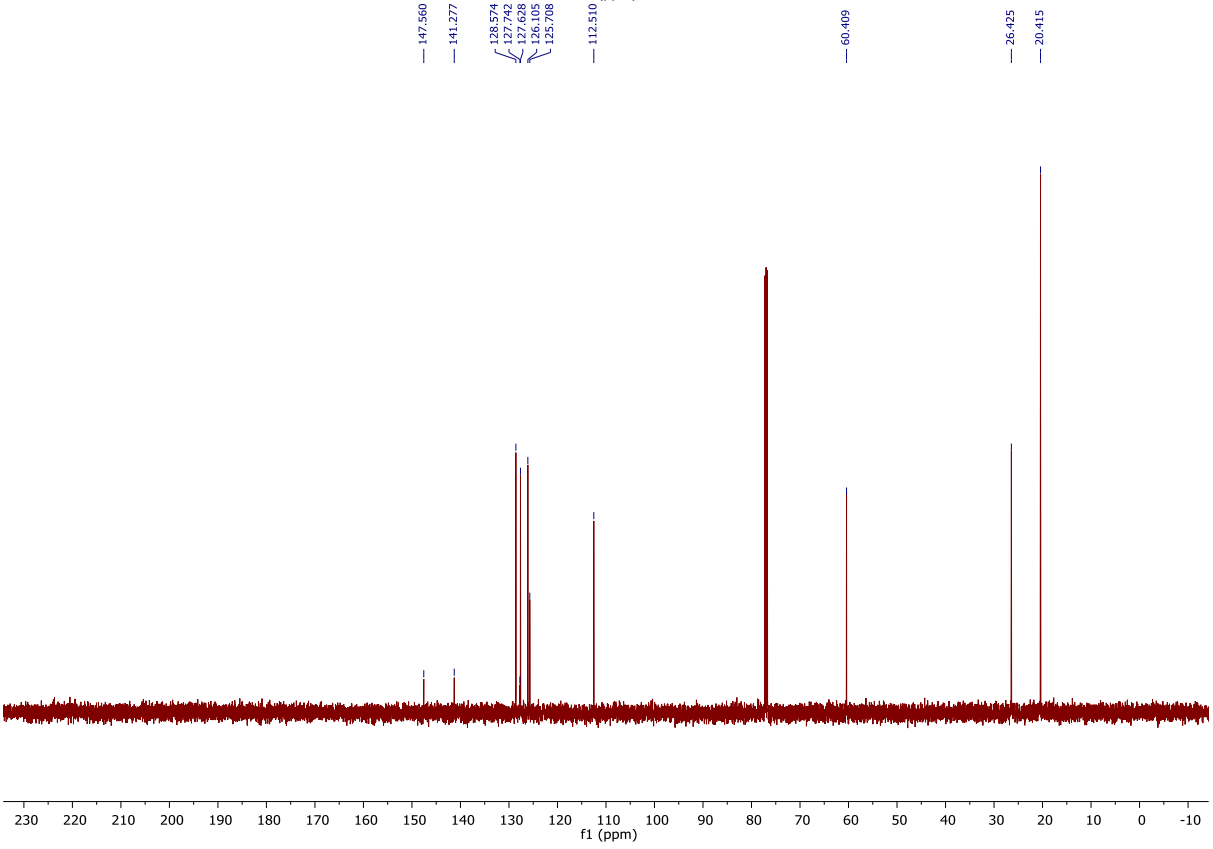
1-([1,1'-biphenyl]-4-yl)-2,6-dimethylpiperidine (1d).

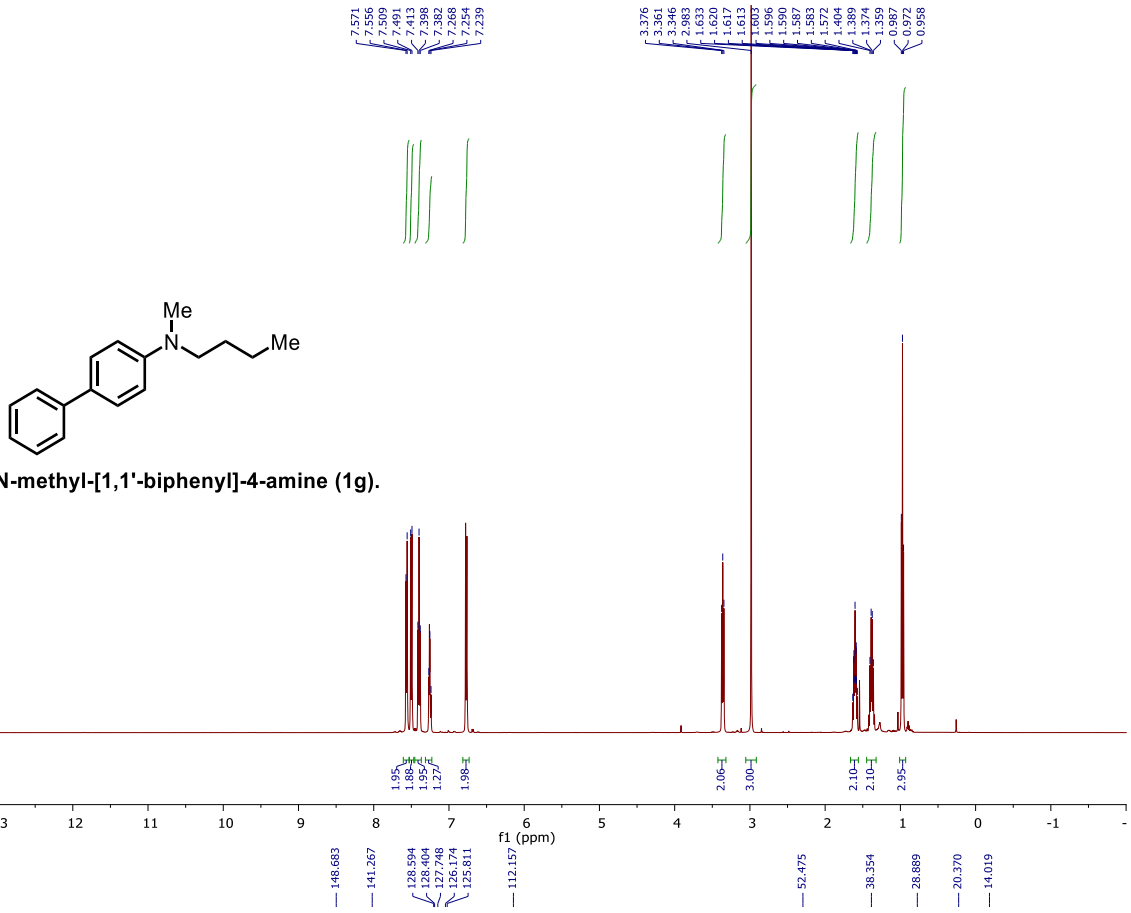




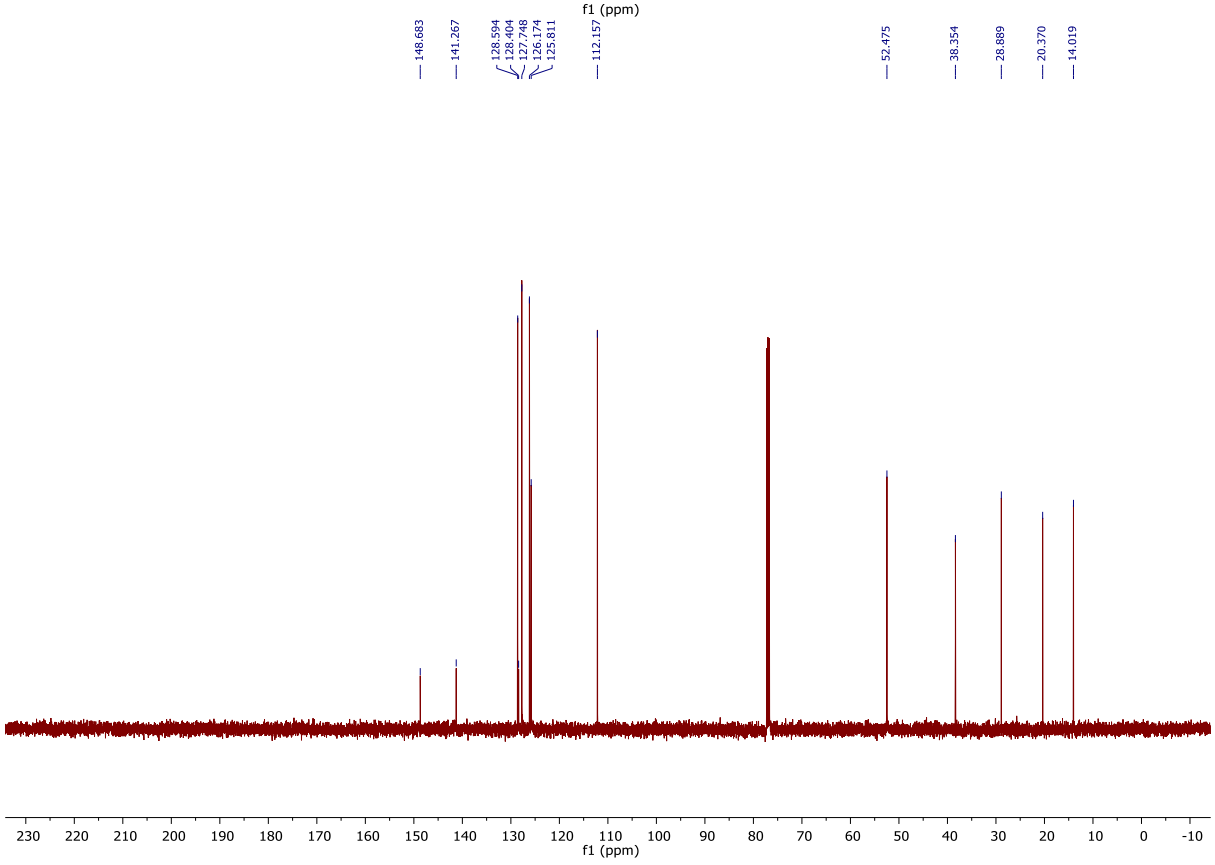


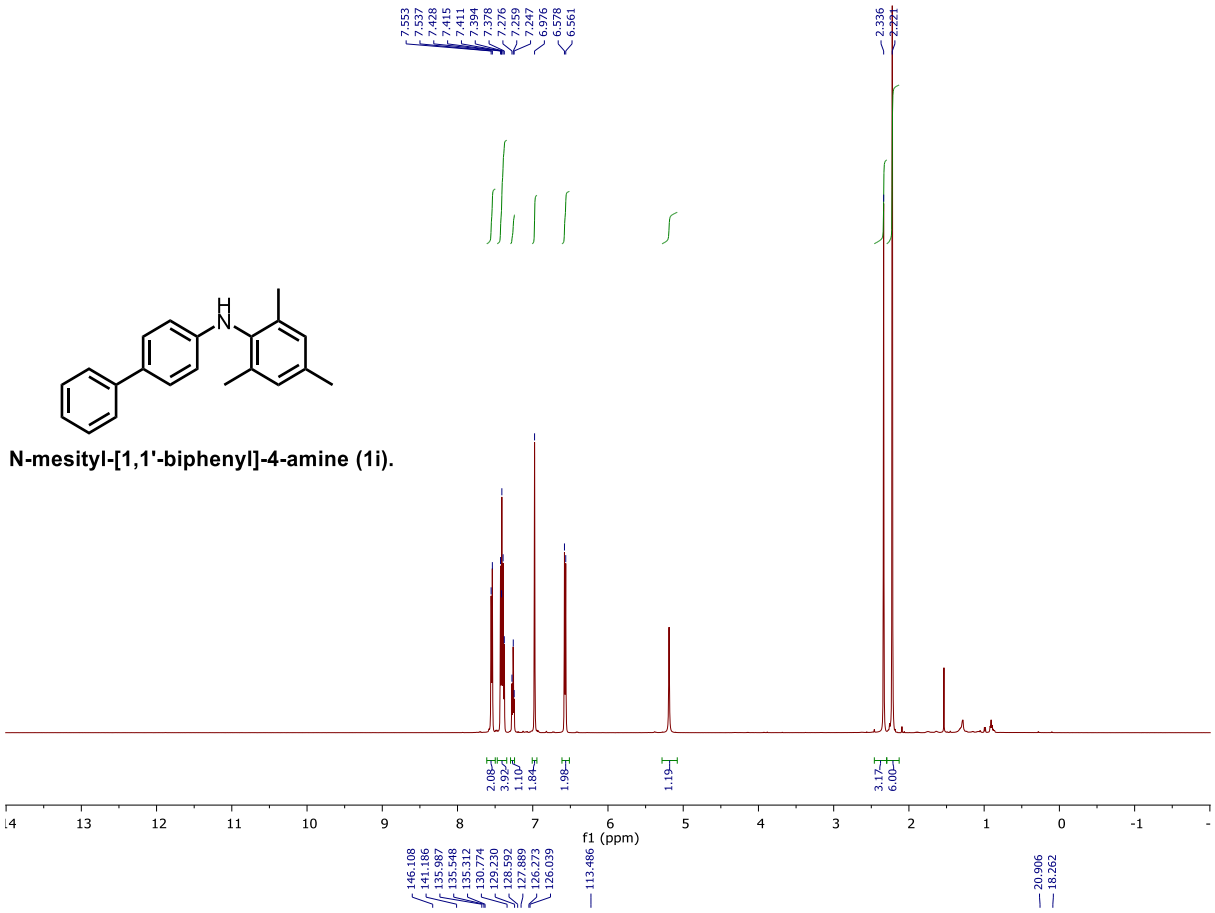
N,N-diisobutyl-[1,1'-biphenyl]-4-amine (1e).



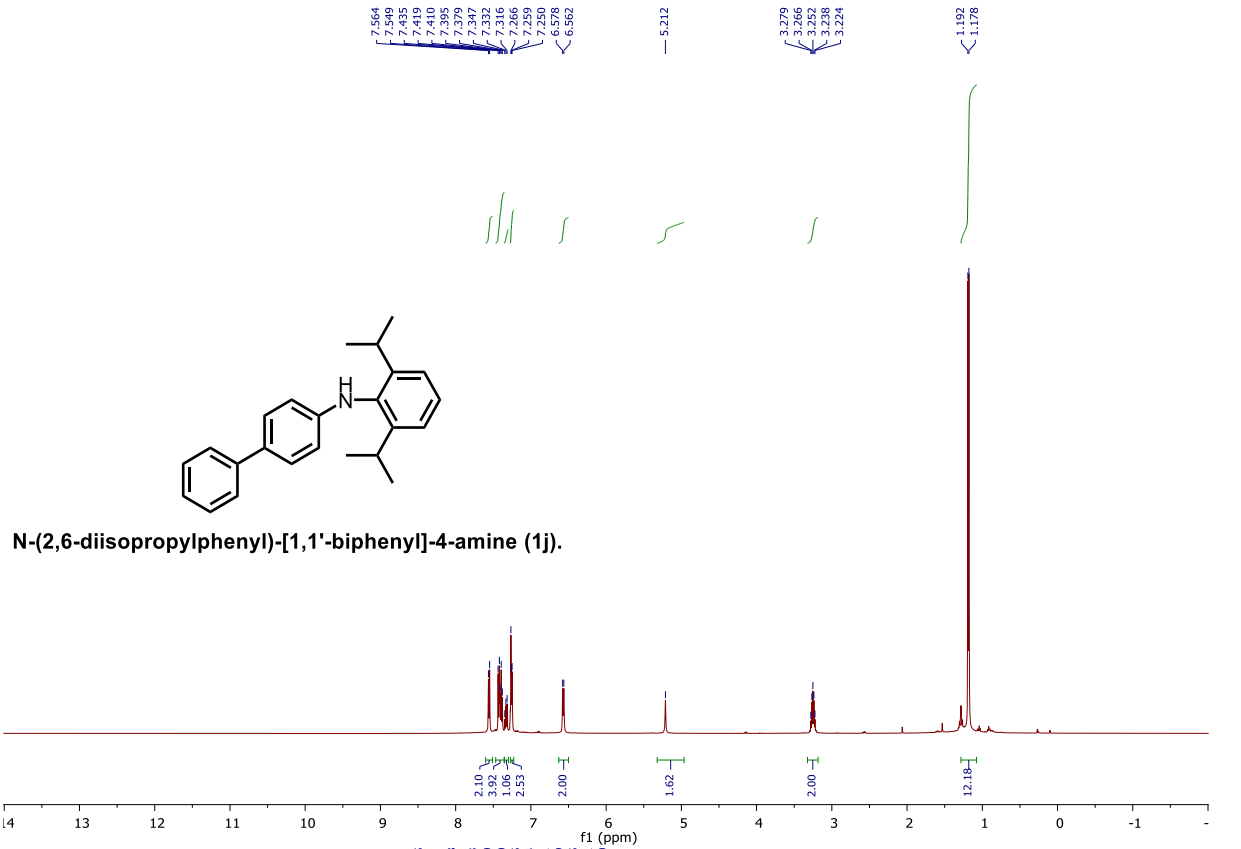


N-butyl-N-methyl-[1,1'-biphenyl]-4-amine (1g).

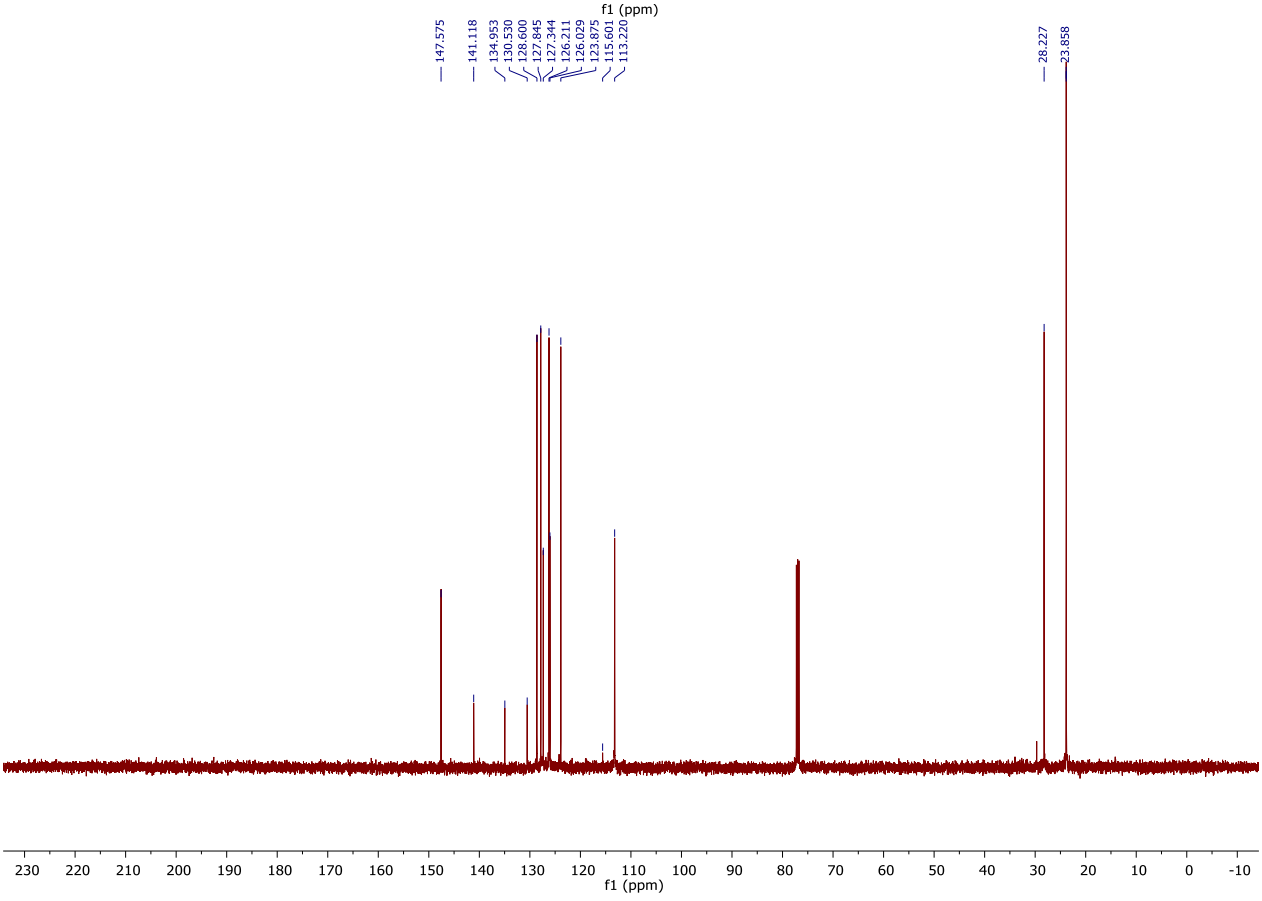


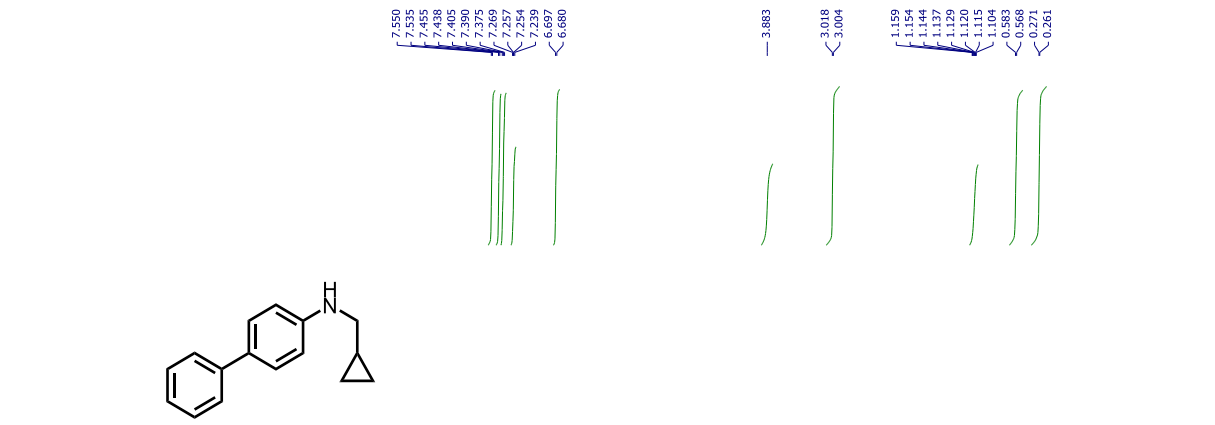


N-mesityl-[1,1'-biphenyl]-4-amine (1i).

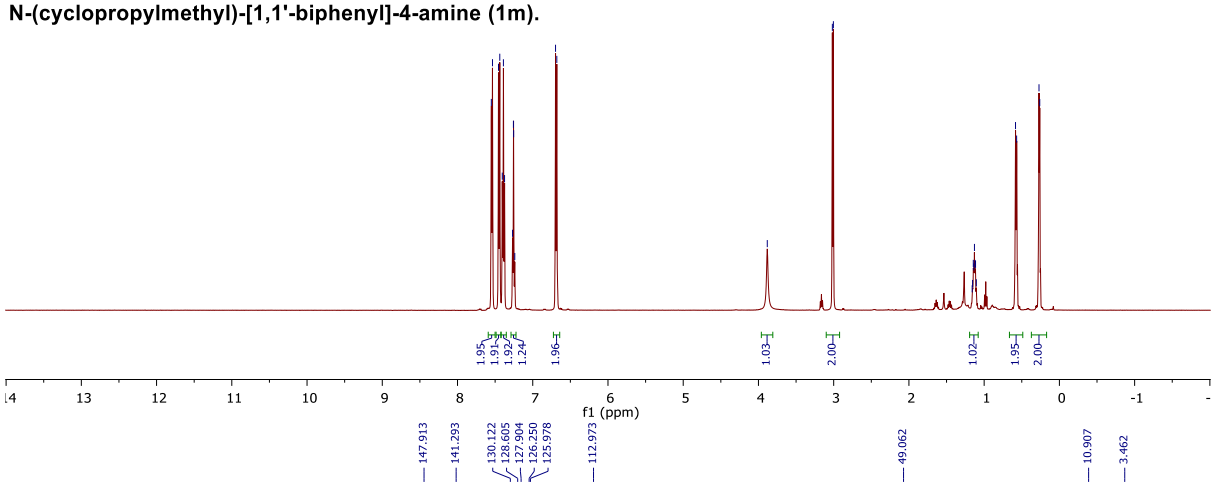


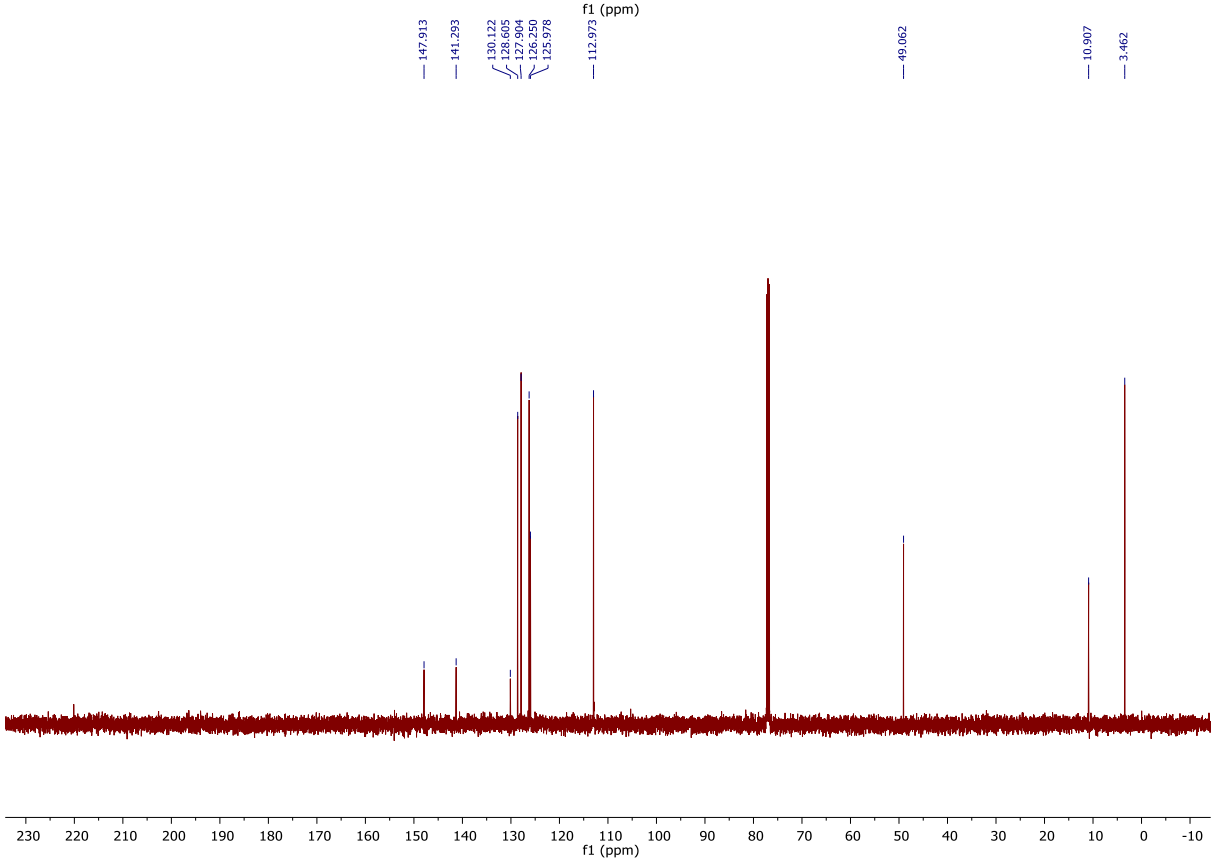
N-(2,6-diisopropylphenyl)-[1,1'-biphenyl]-4-amine (1j).

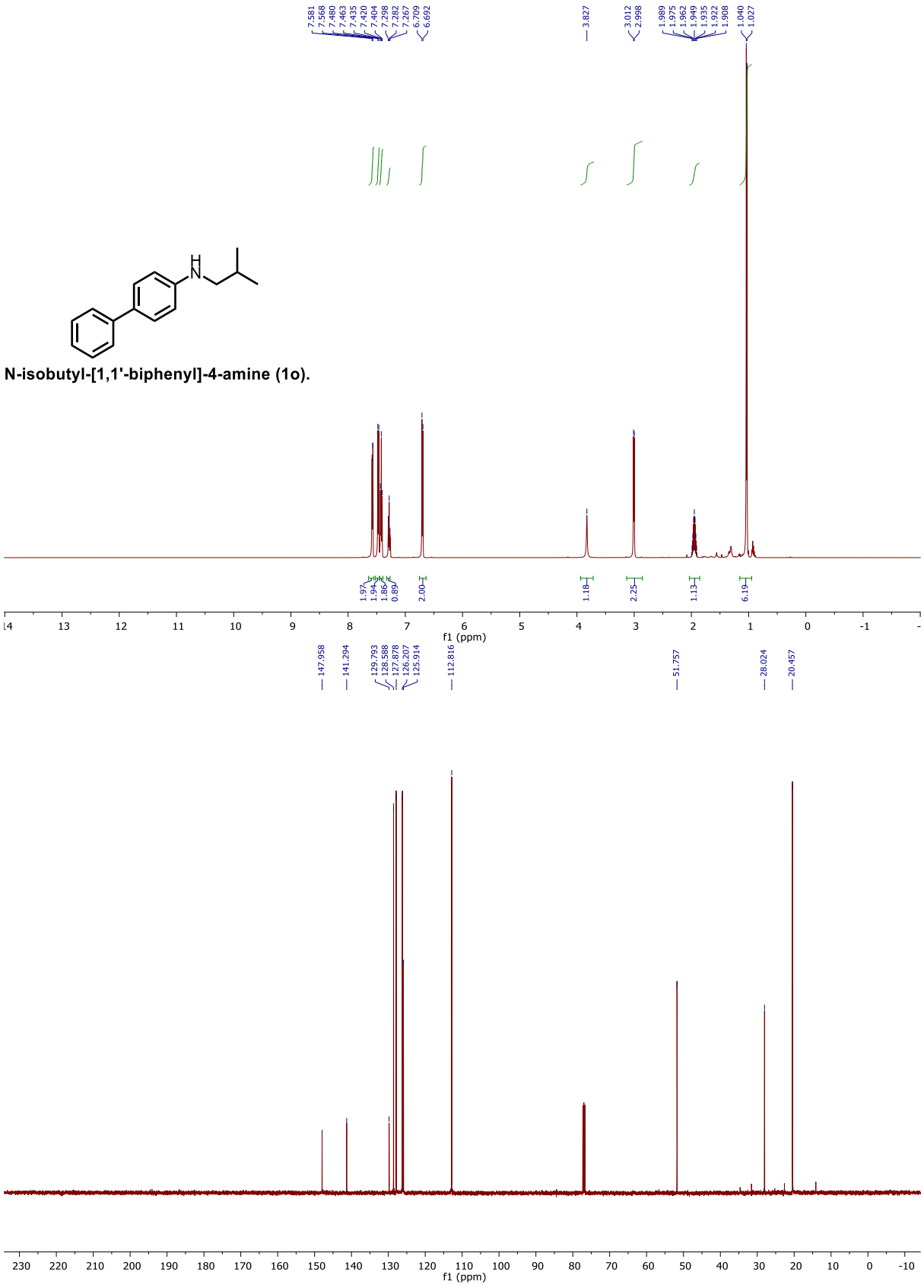




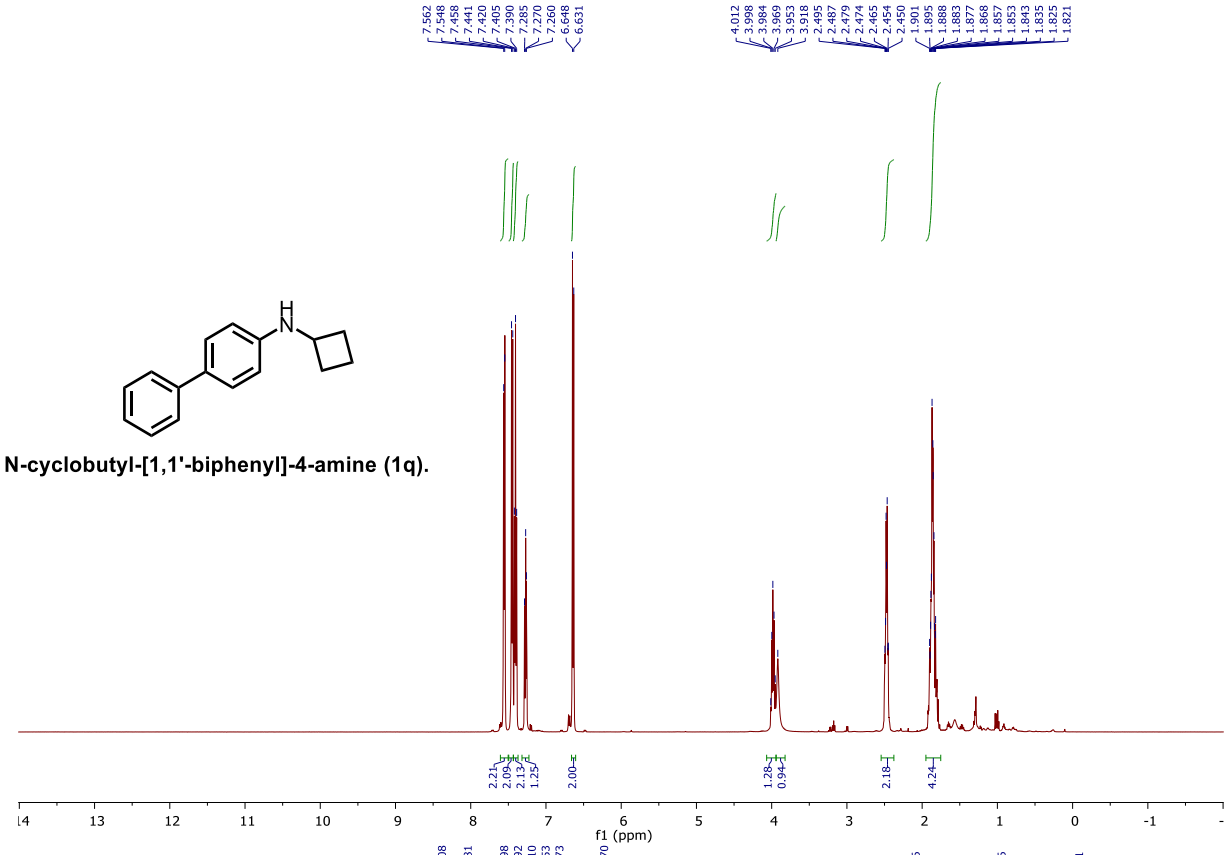
N-(cyclopropylmethyl)-[1,1'-biphenyl]-4-amine (1m).



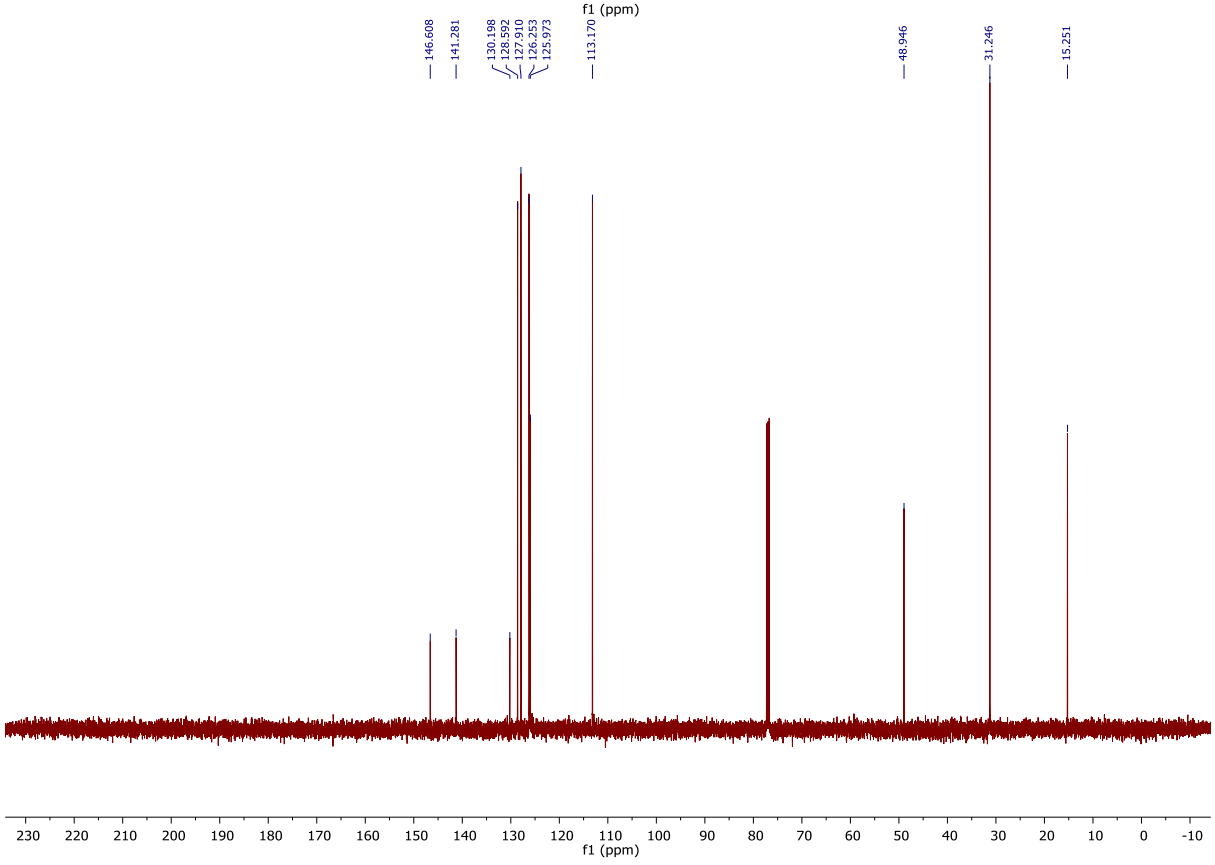


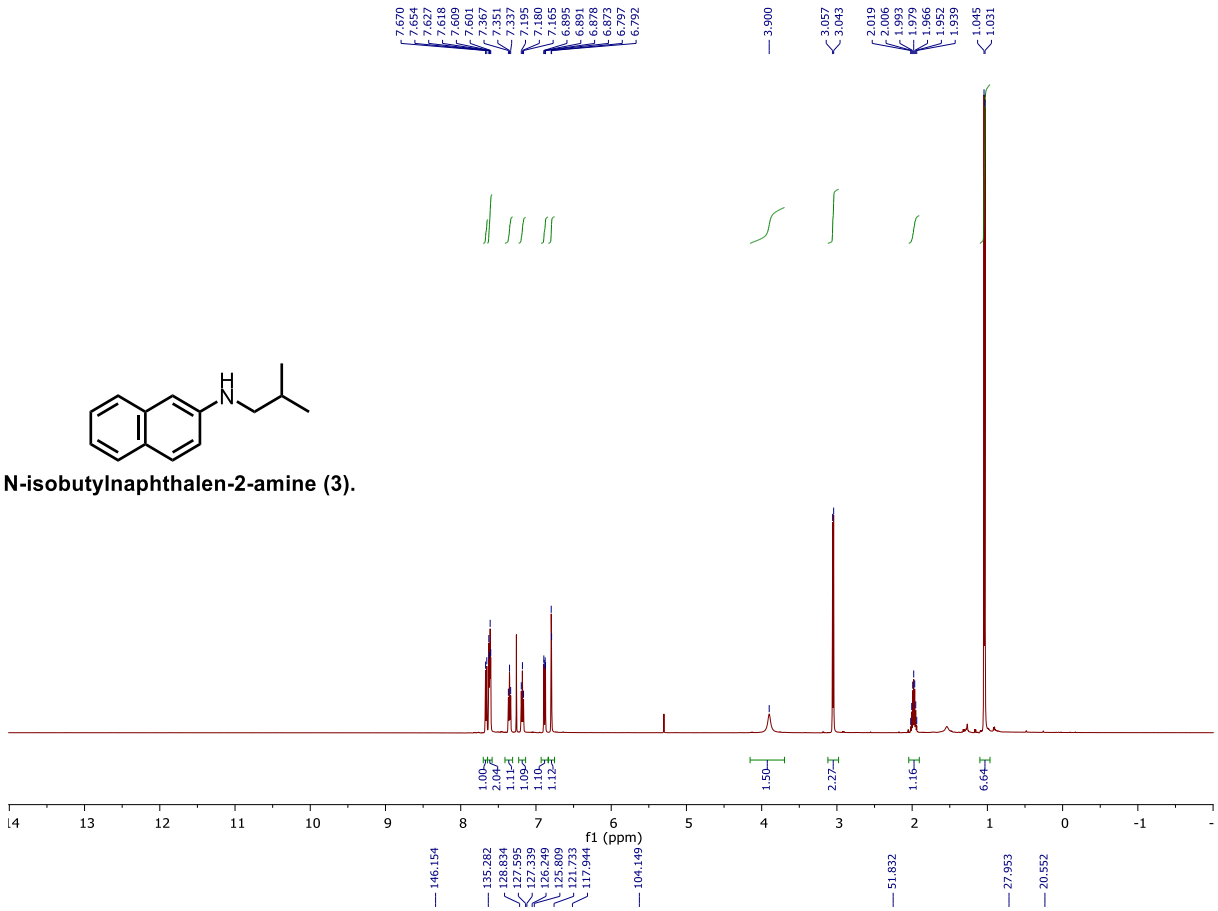


N-isobutyl-[1,1'-biphenyl]-4-amine (1o).

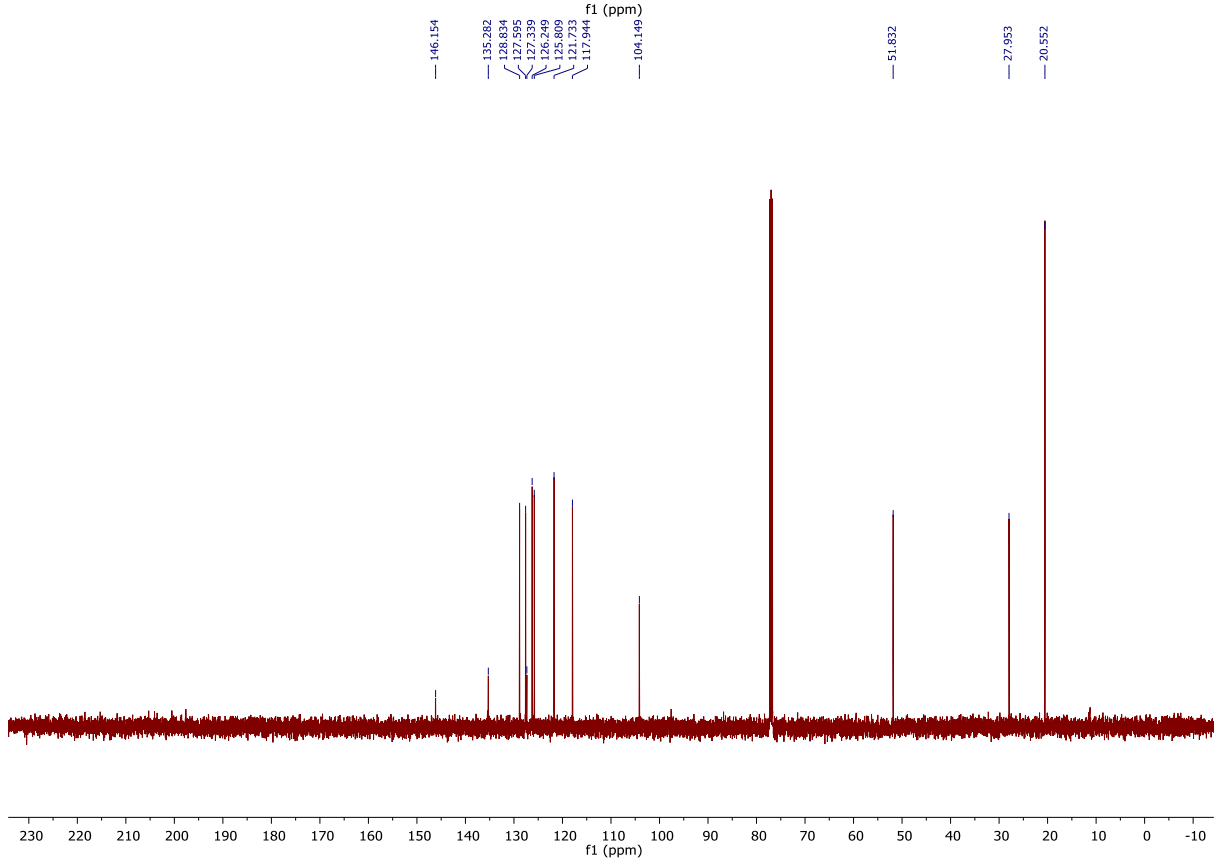


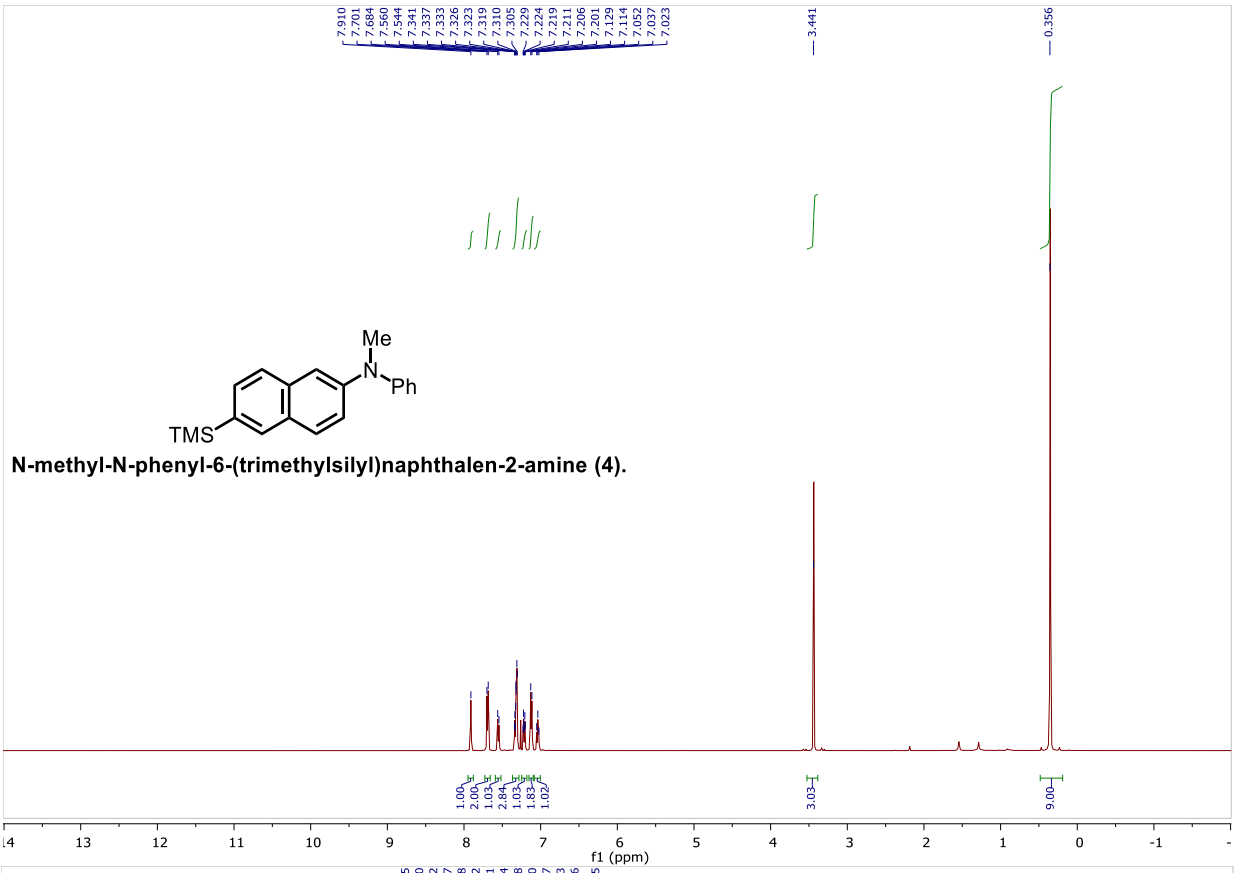
N-cyclobutyl-[1,1'-biphenyl]-4-amine (1q).



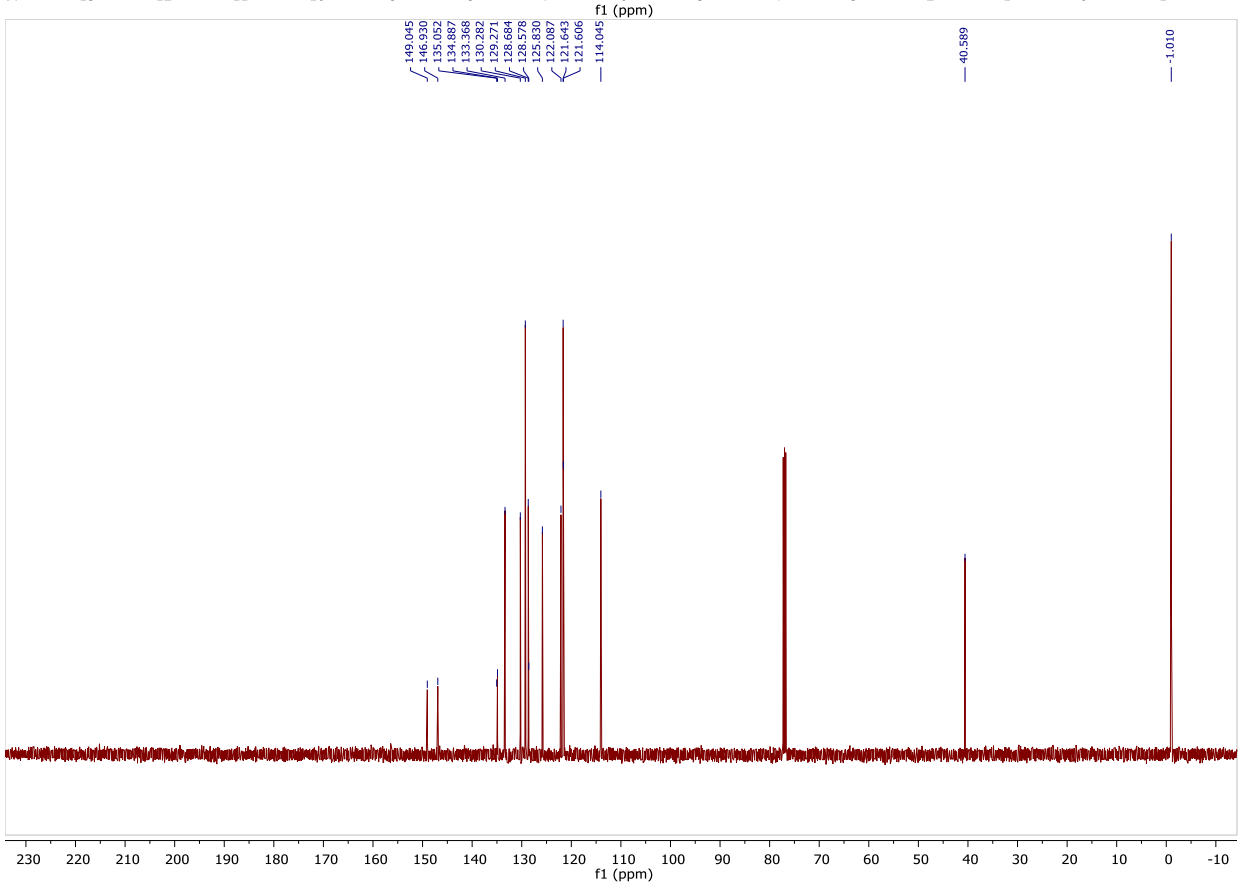


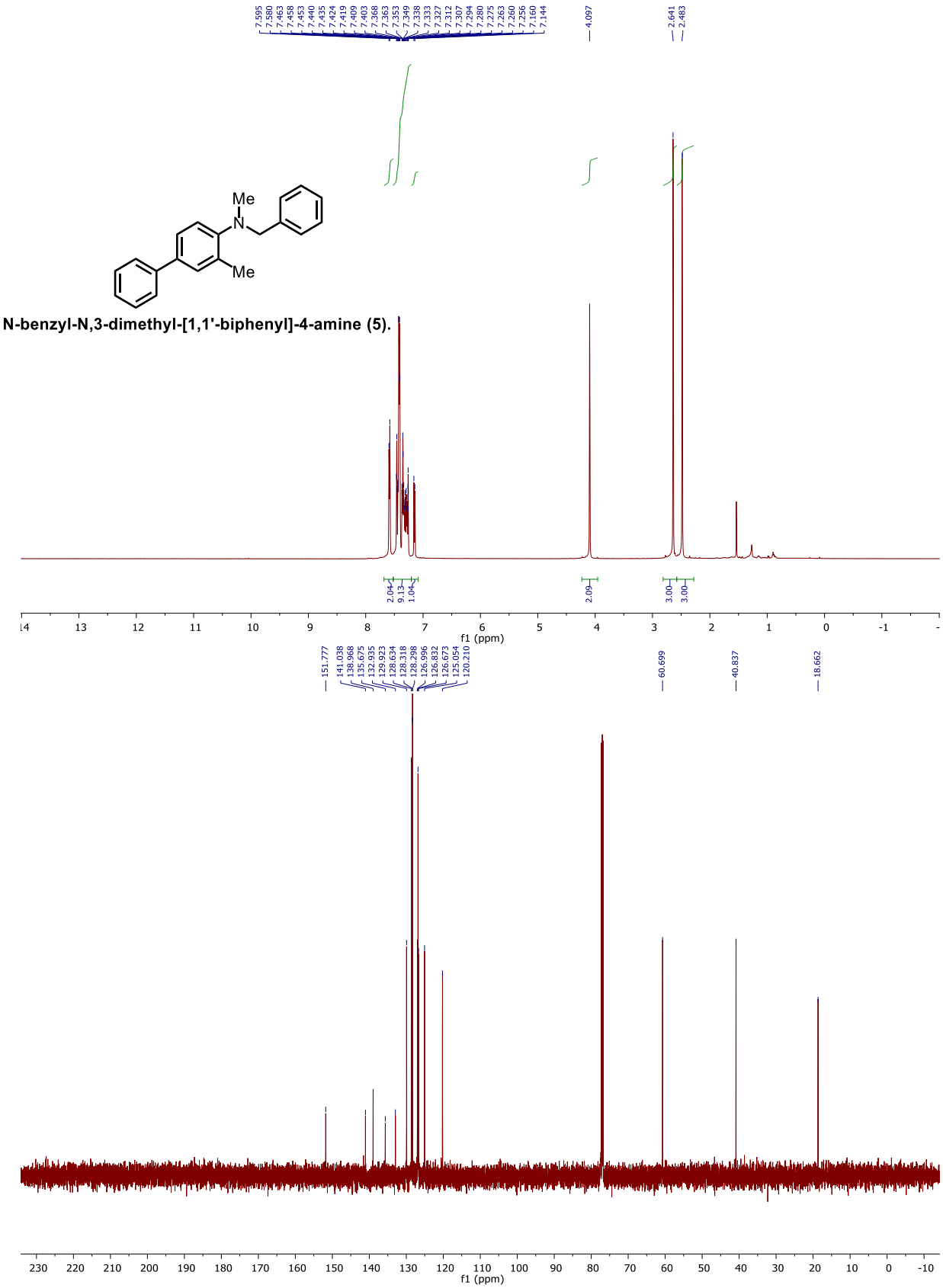
N-isobutylnaphthalen-2-amine (3).

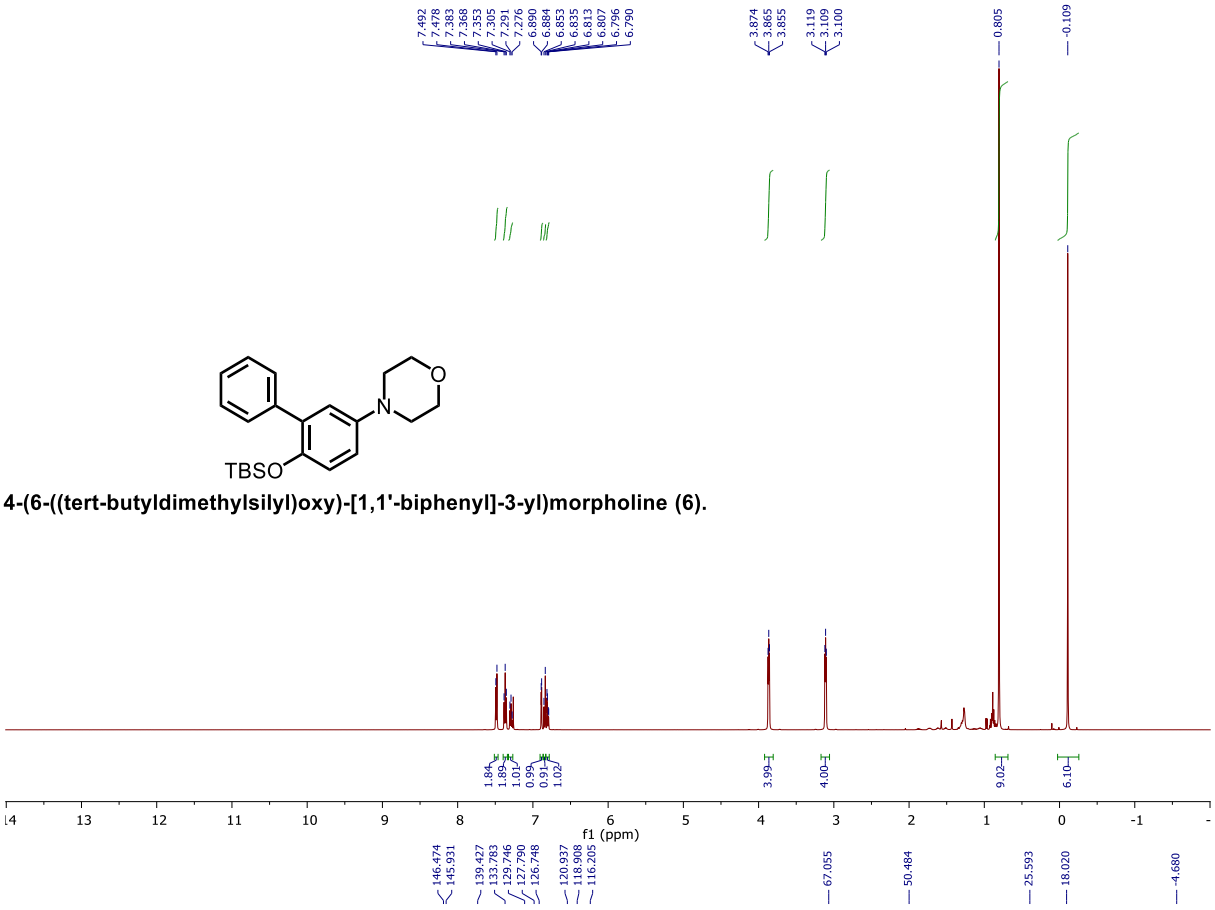




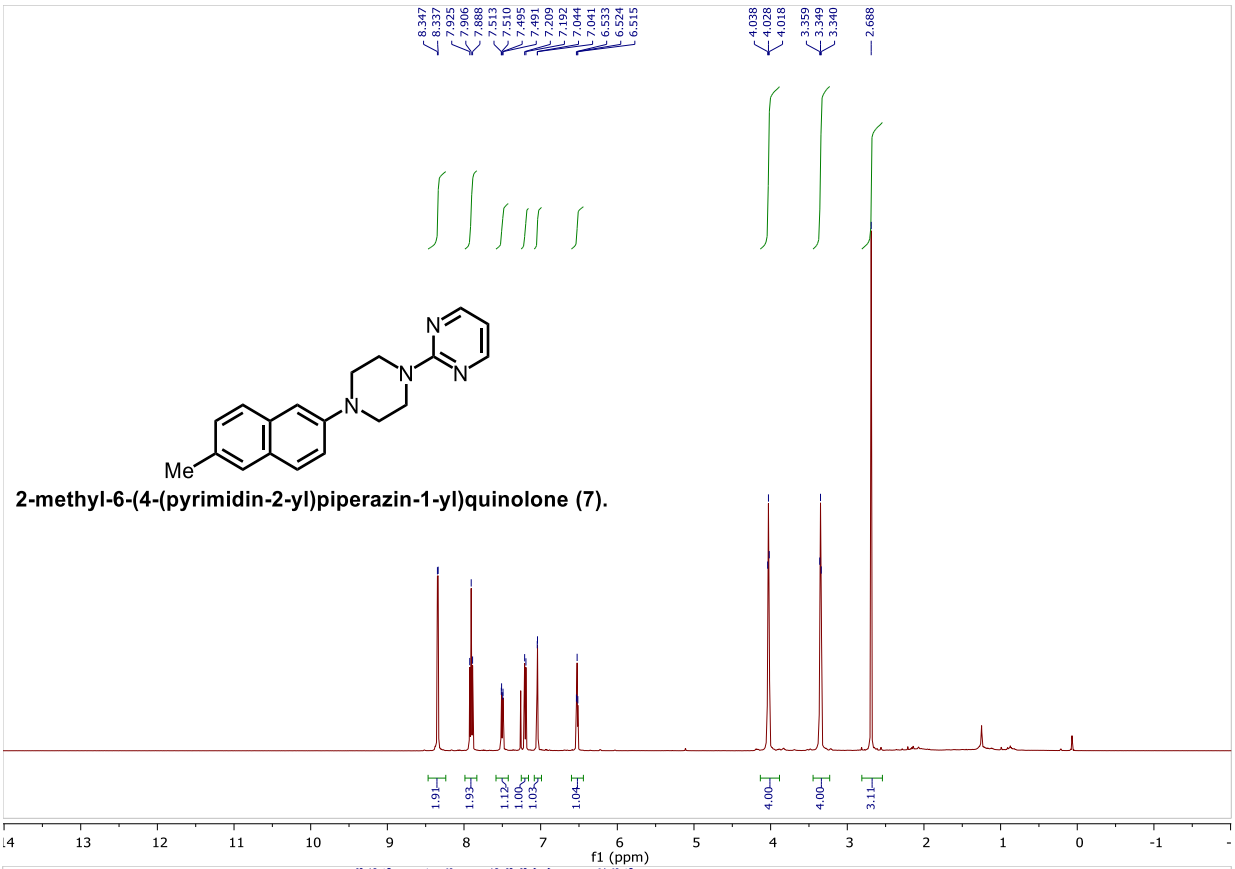
N-methyl-N-phenyl-6-(trimethylsilyl)naphthalen-2-amine (4).



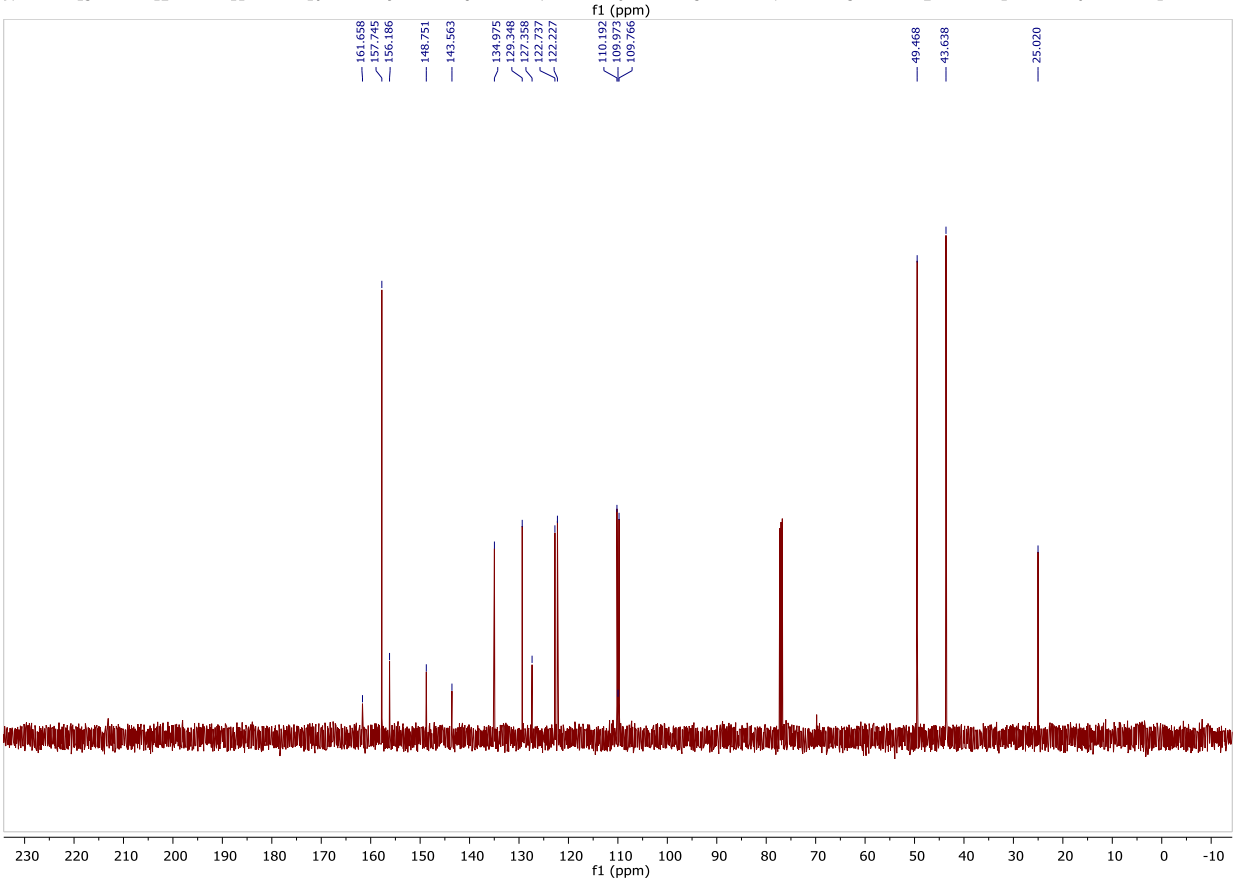

Me
N
Me
N-benzyl-N,3-dimethyl-[1,1'-biphenyl]-4-amine (5).
f1 (ppm)
f1 (ppm)

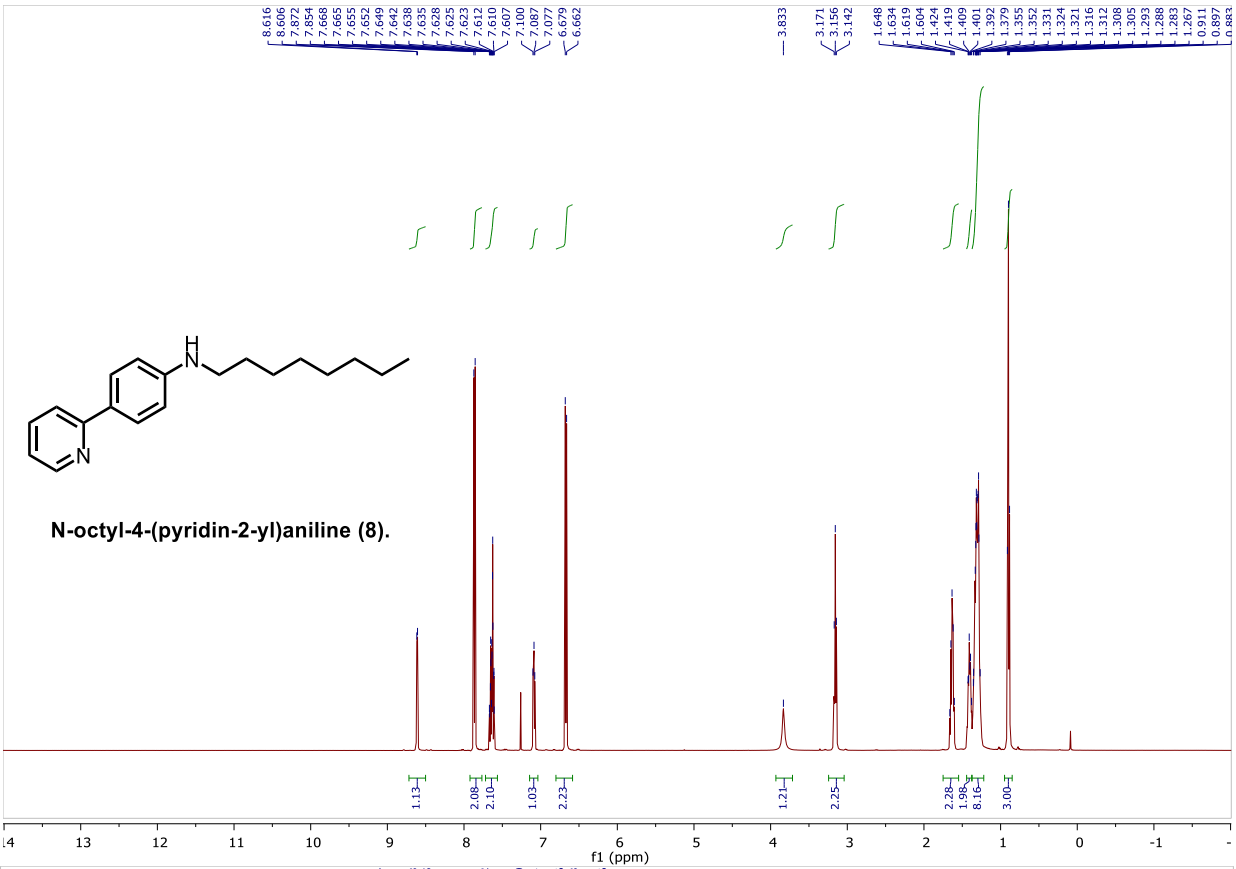


4-(6-((tert-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)morpholine (6).

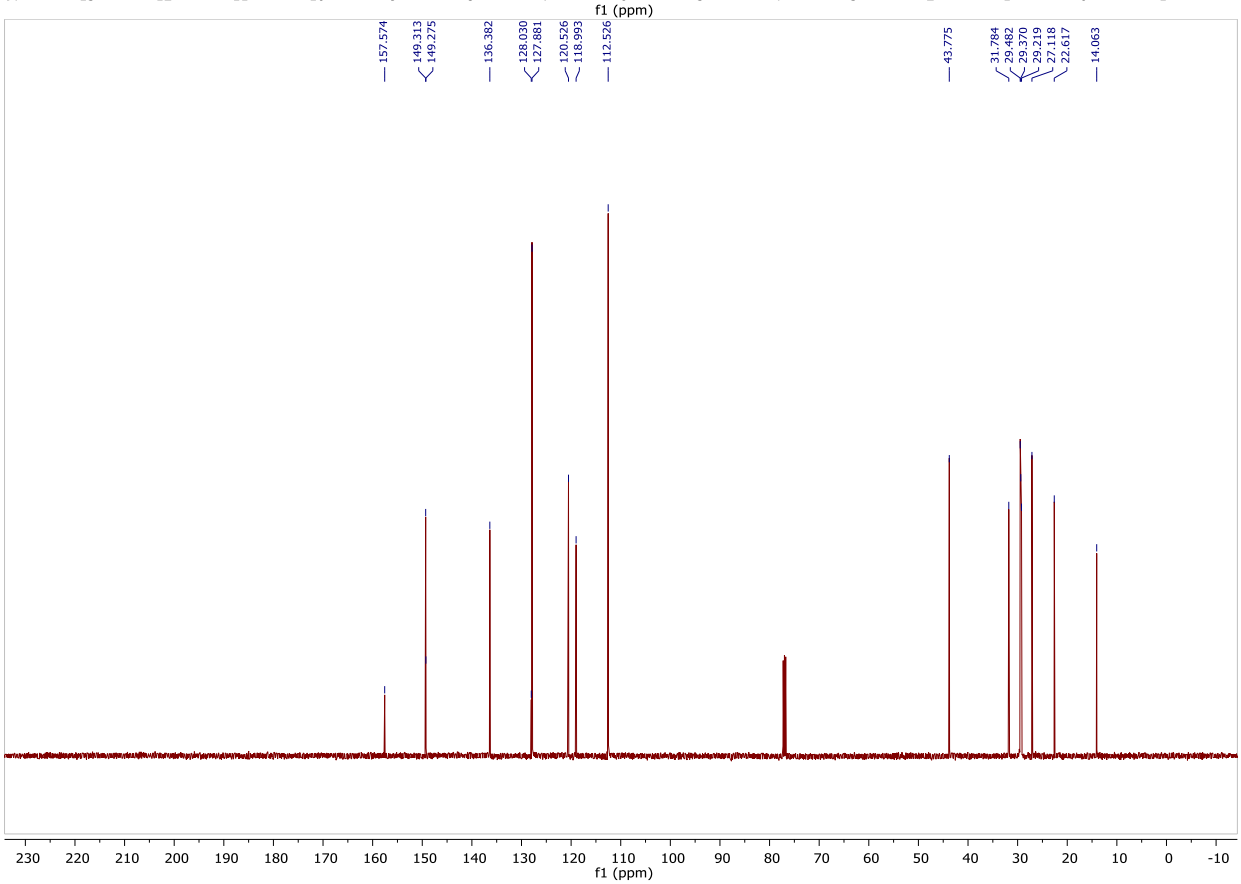


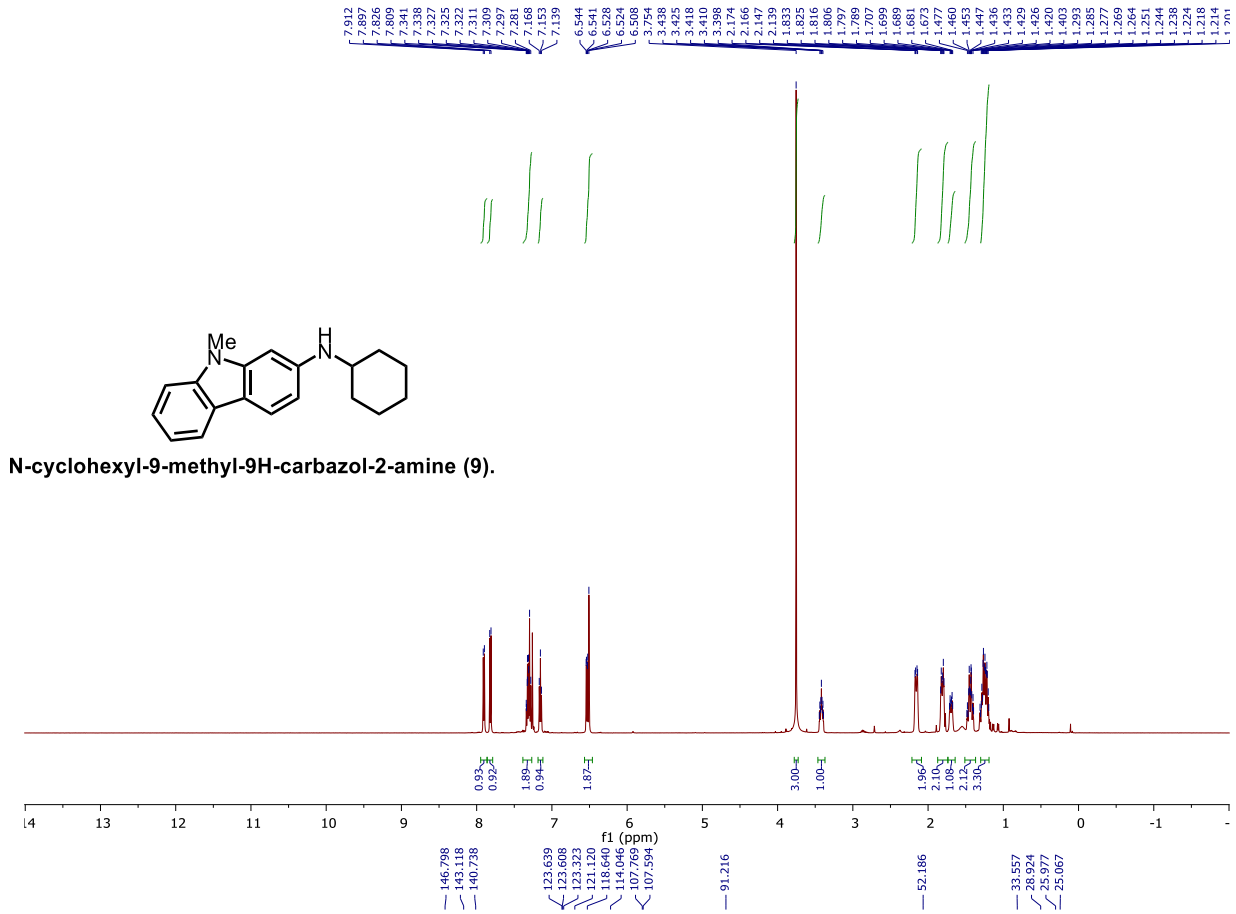
2-methyl-6-(4-(pyrimidin-2-yl)piperazin-1-yl)quinolone (7).



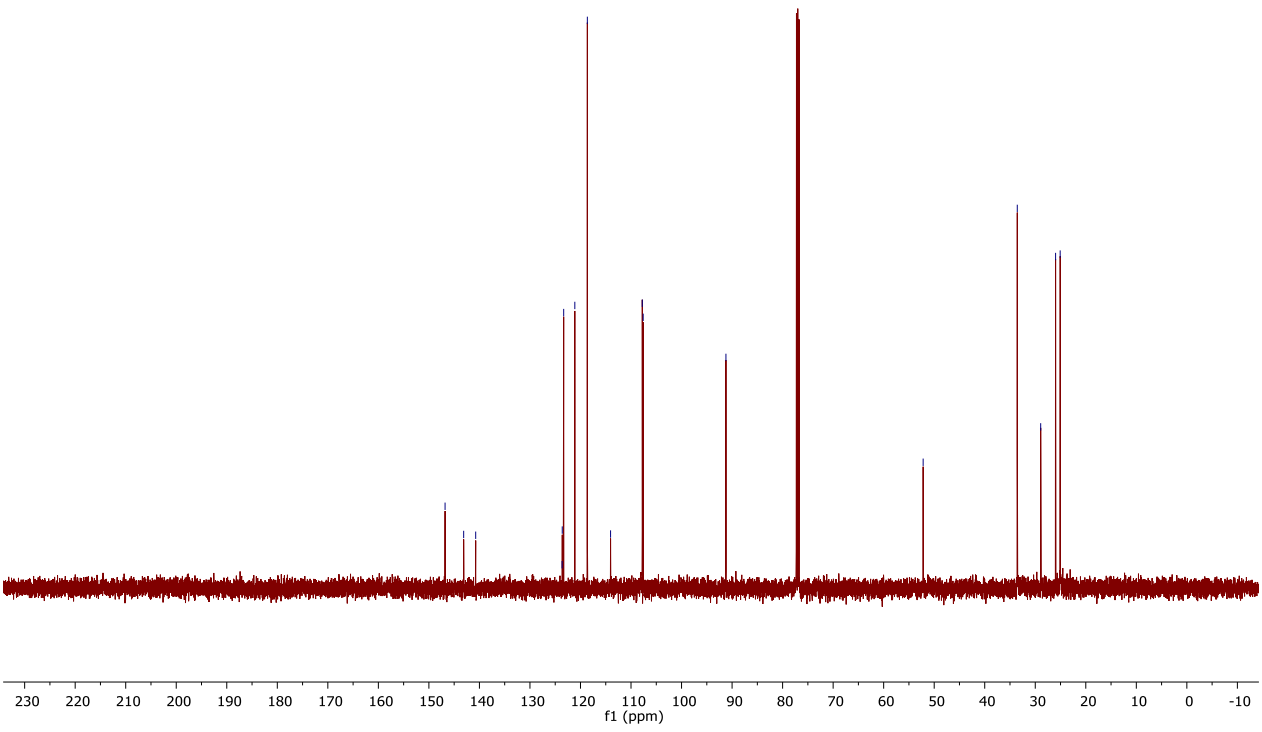


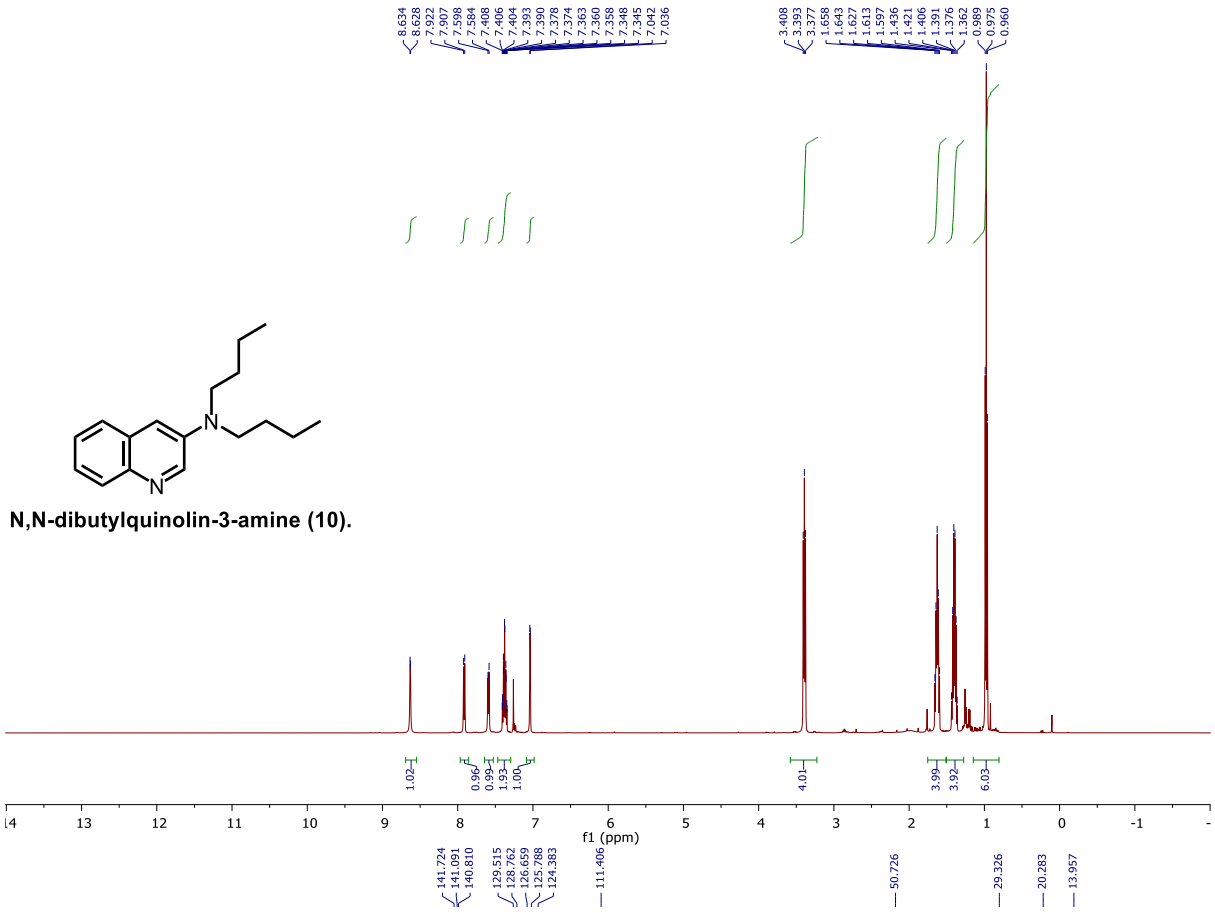
N-octyl-4-(pyridin-2-yl)aniline (8).



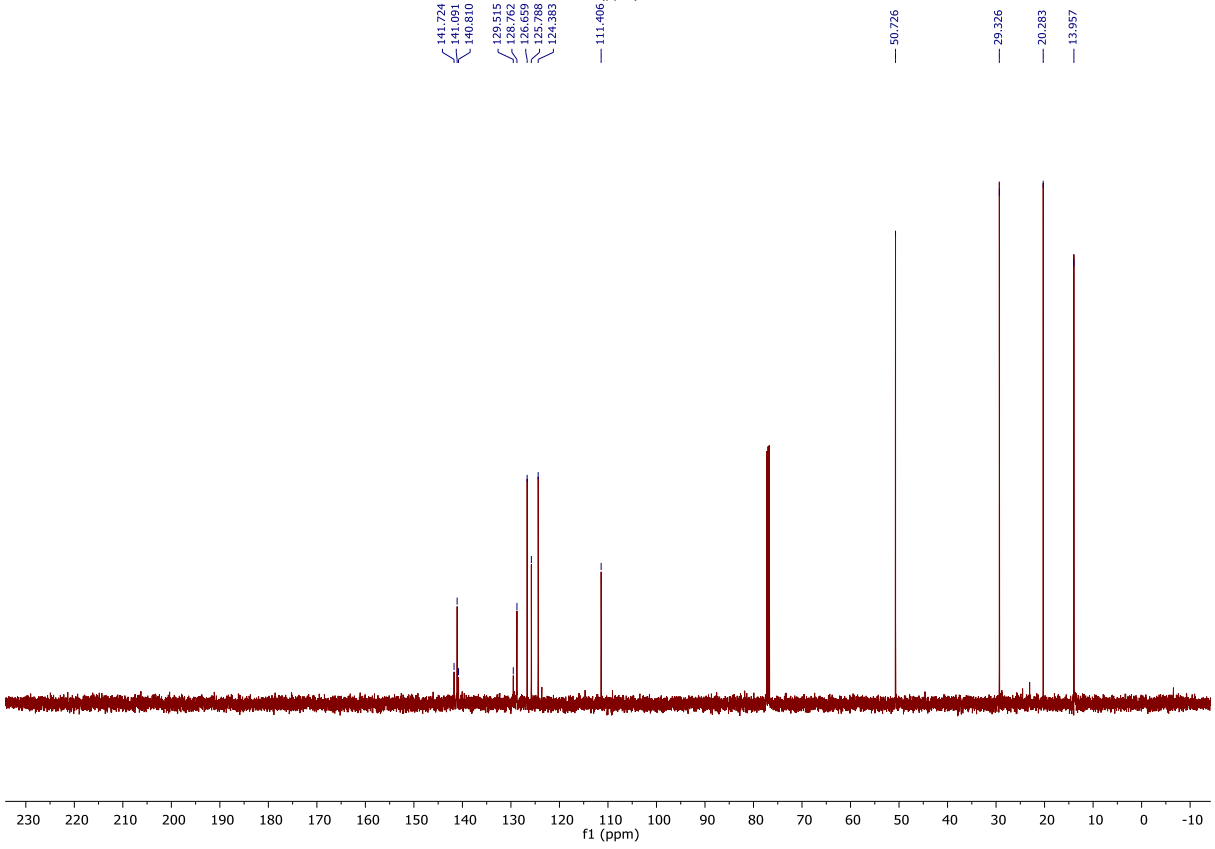


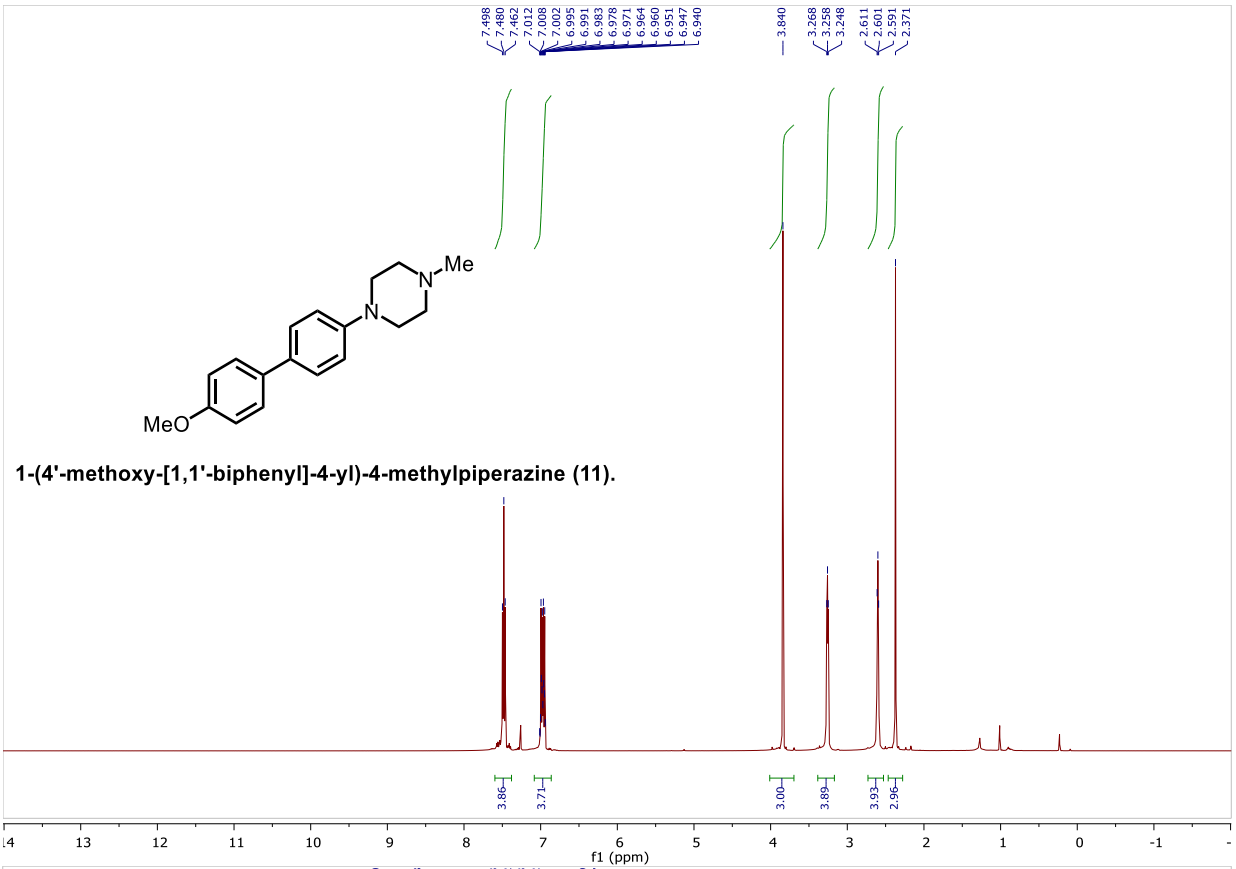
N-cyclohexyl-9-methyl-9H-carbazol-2-amine (9).



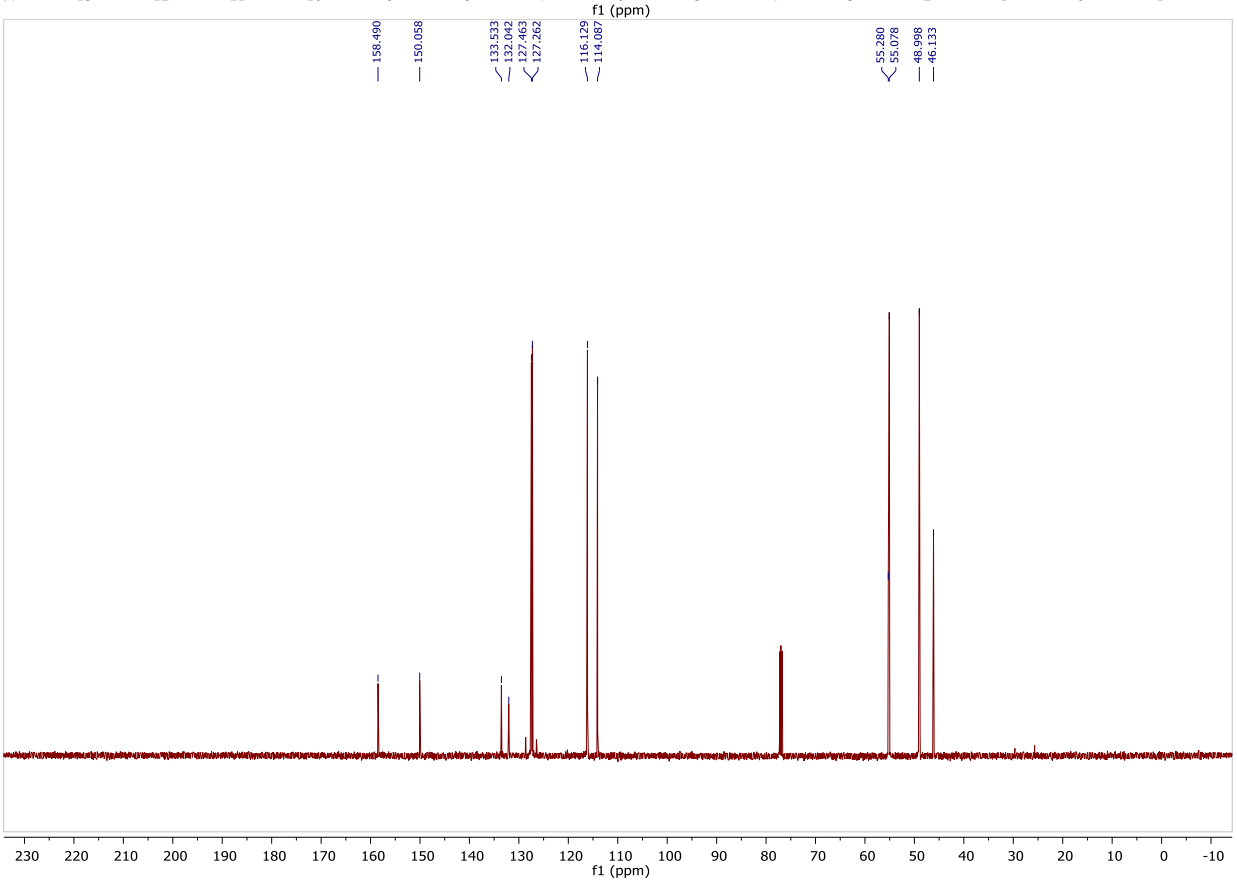


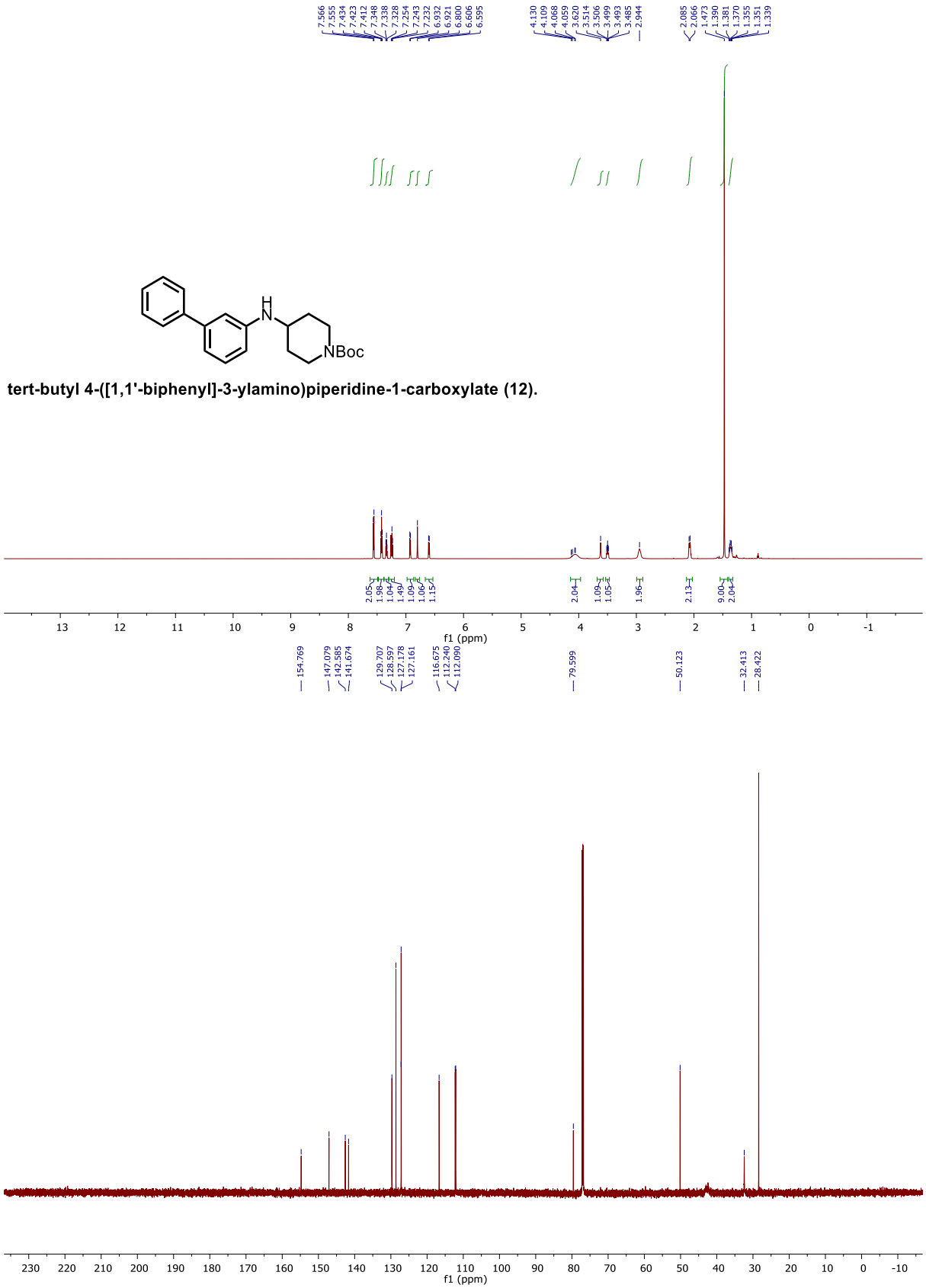
N,N-dibutylquinolin-3-amine (10).



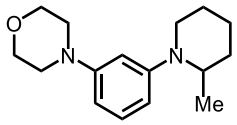


1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4-methylpiperazine (11).

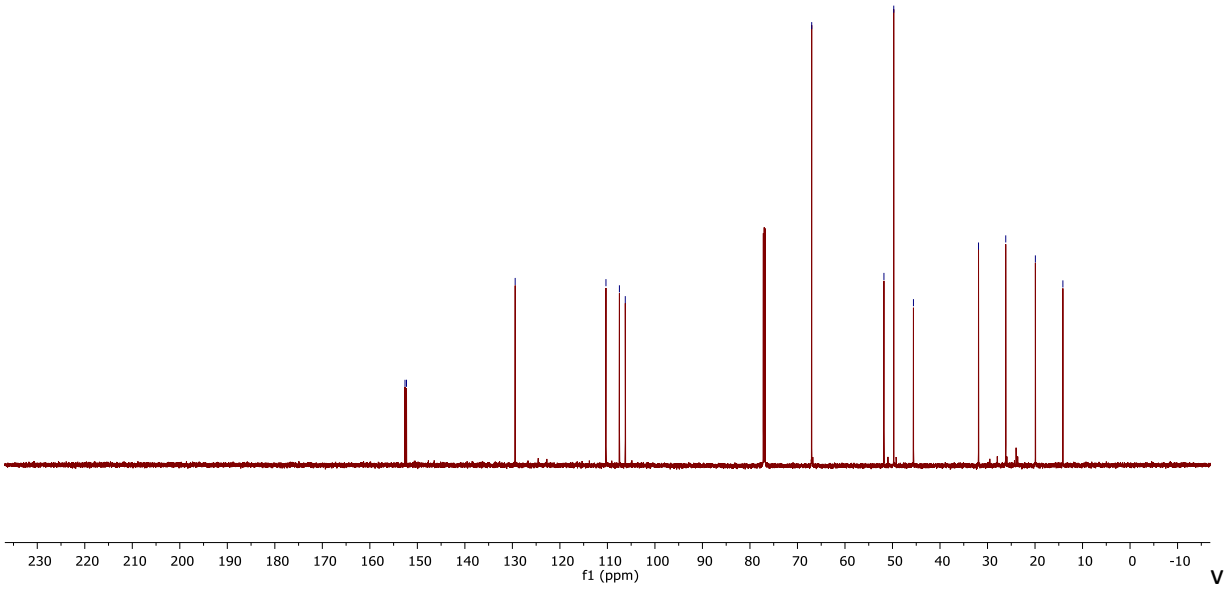


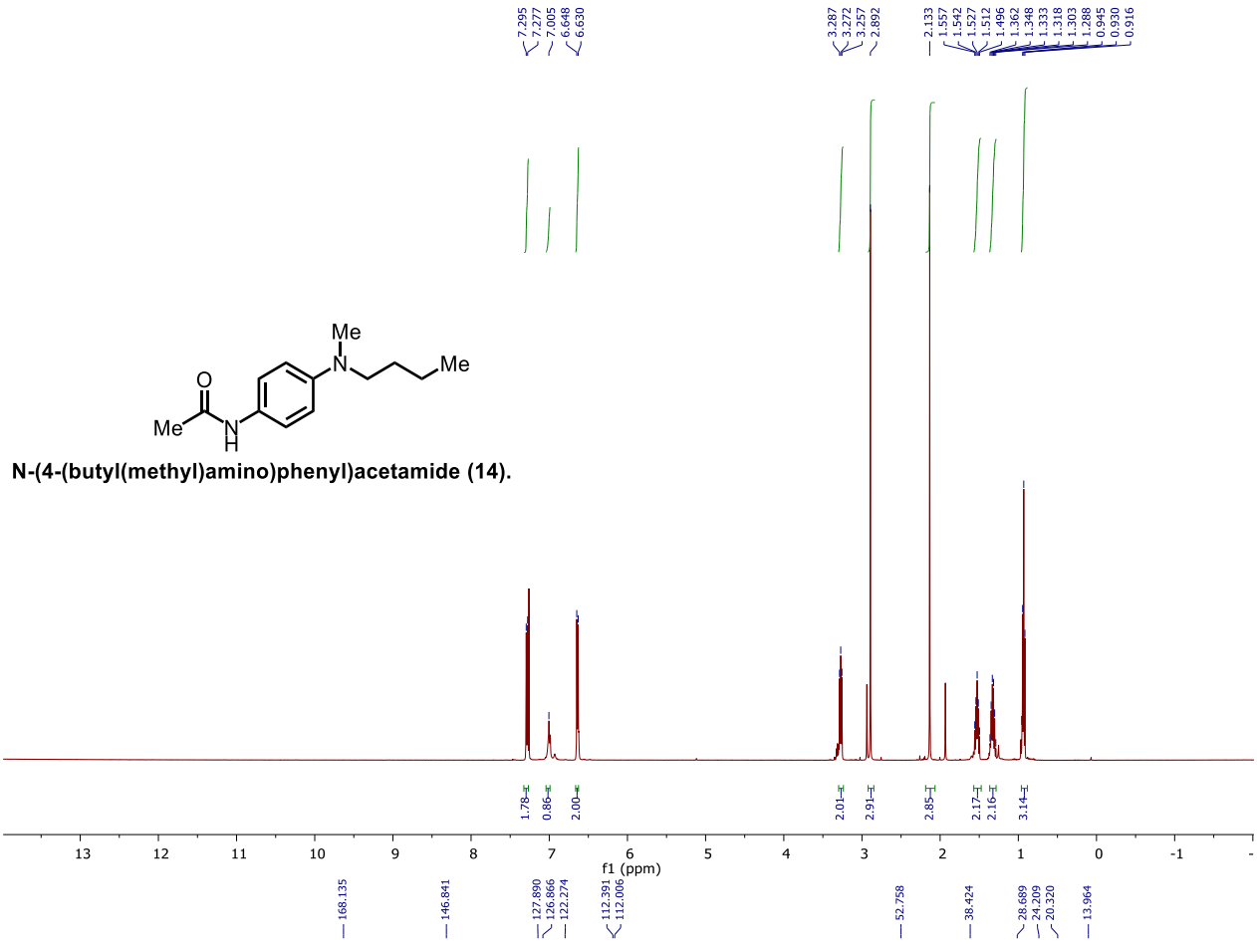


tert-butyl 4-([1,1'-biphenyl]-3-ylamino)piperidine-1-carboxylate (12).

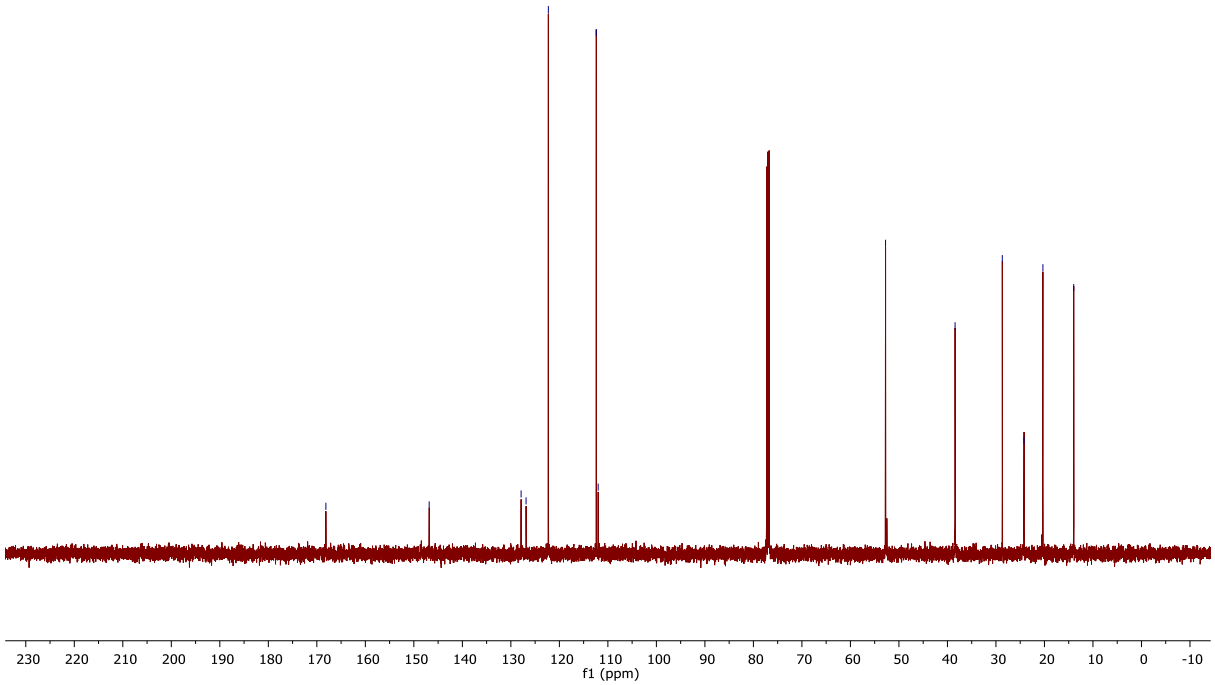


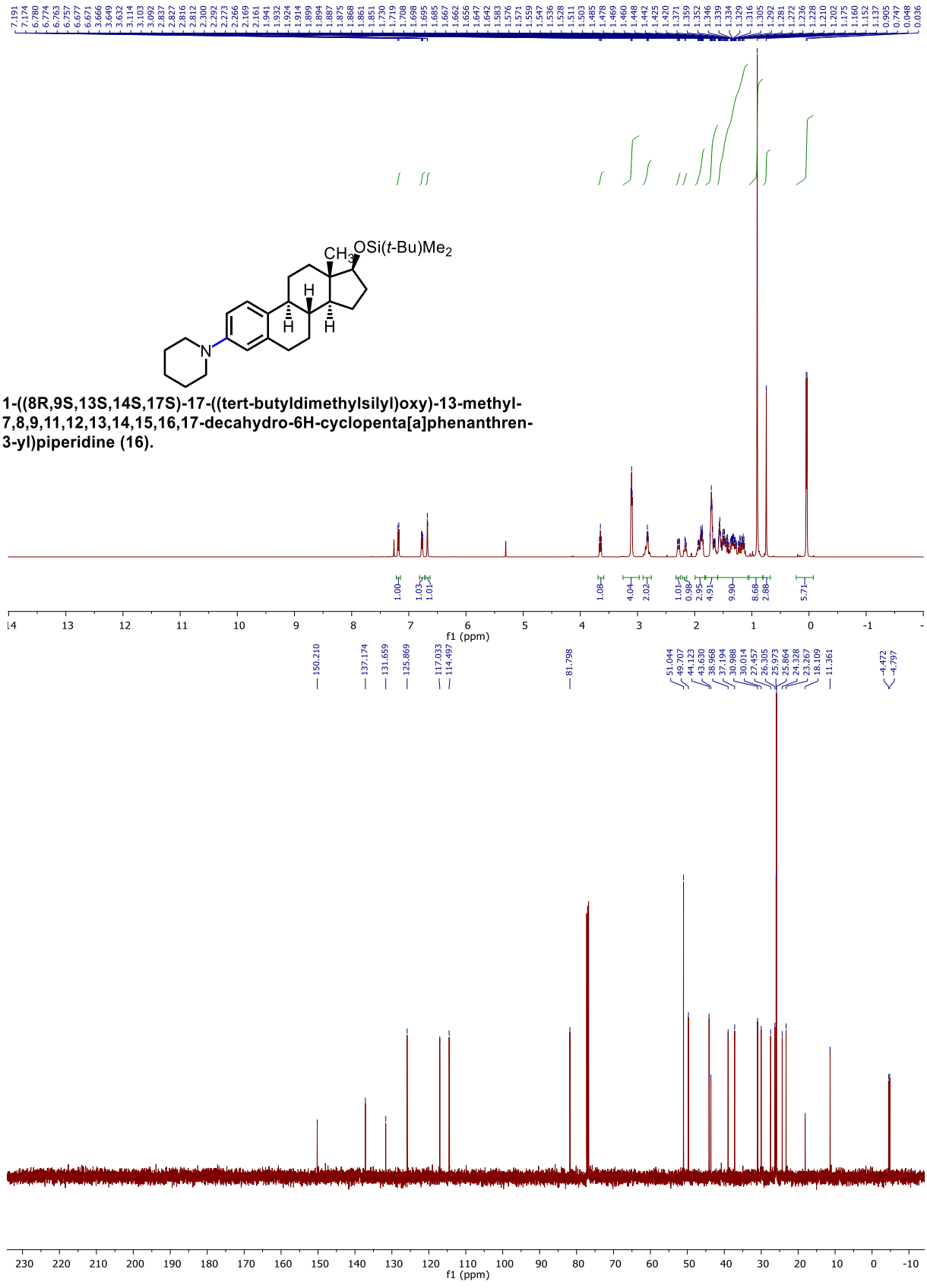
4-(3-(2-methylpiperidin-1-yl)phenyl)morpholine (13).



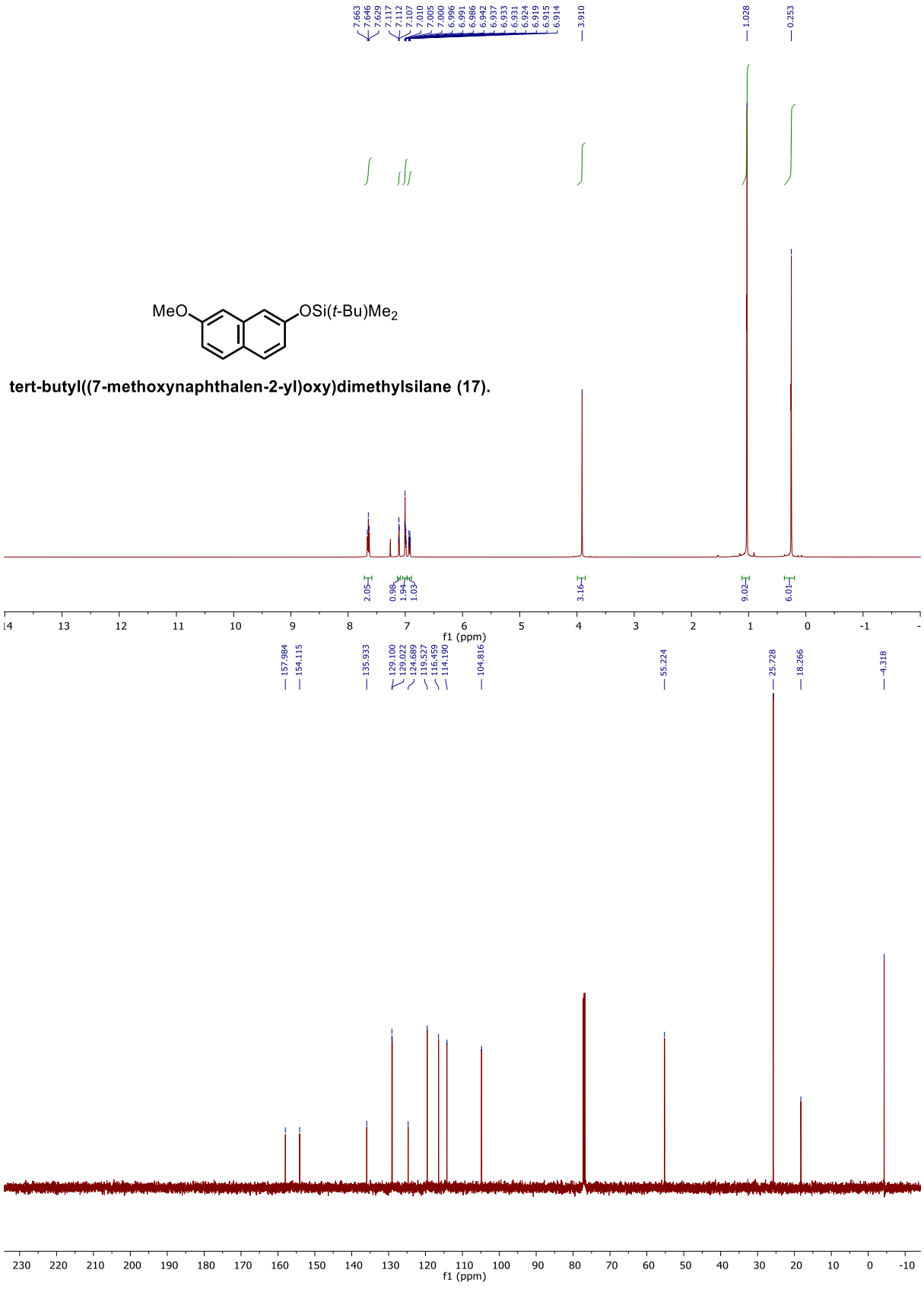


N-(4-(butyl(methyl)amino)phenyl)acetamide (14).

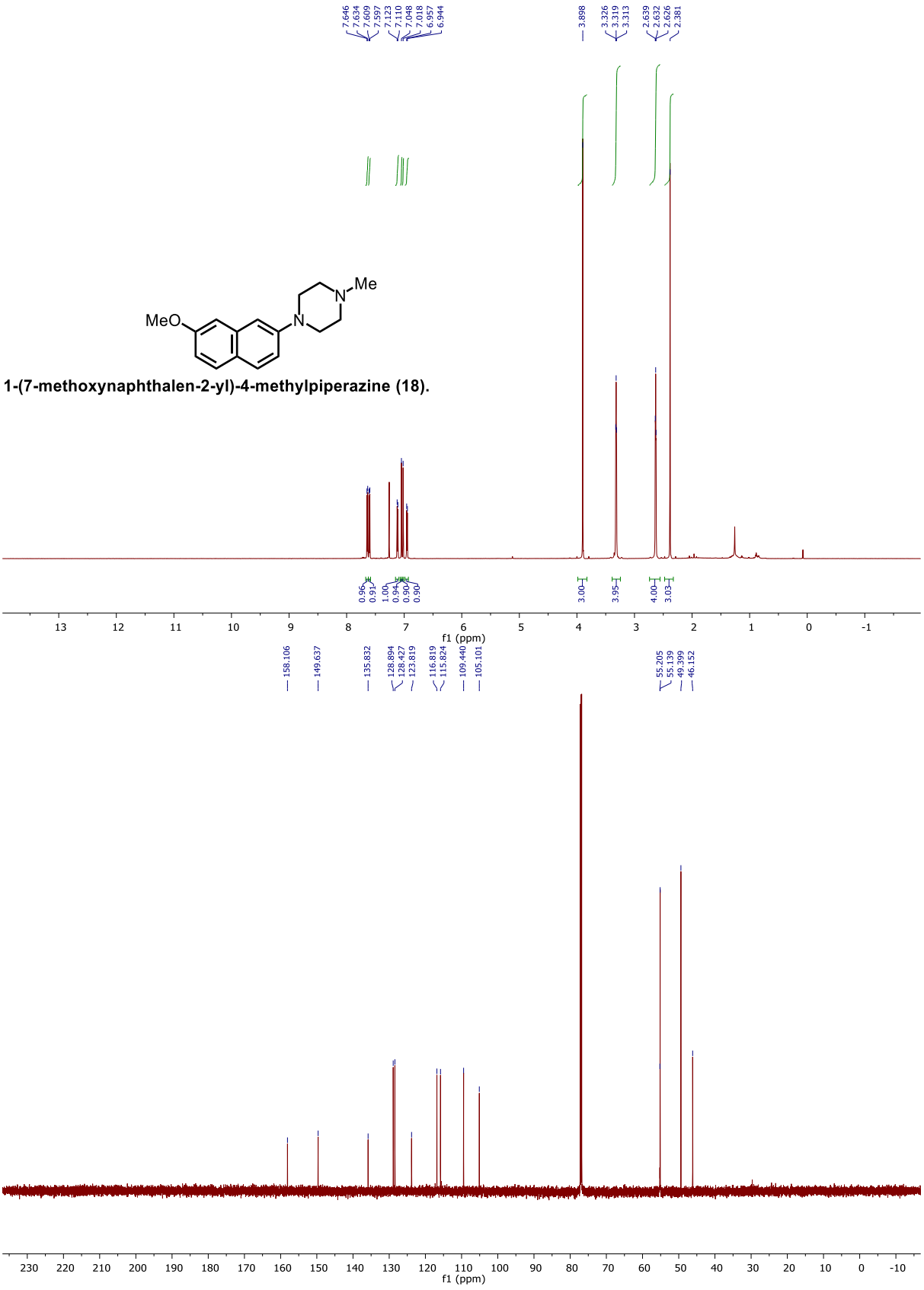




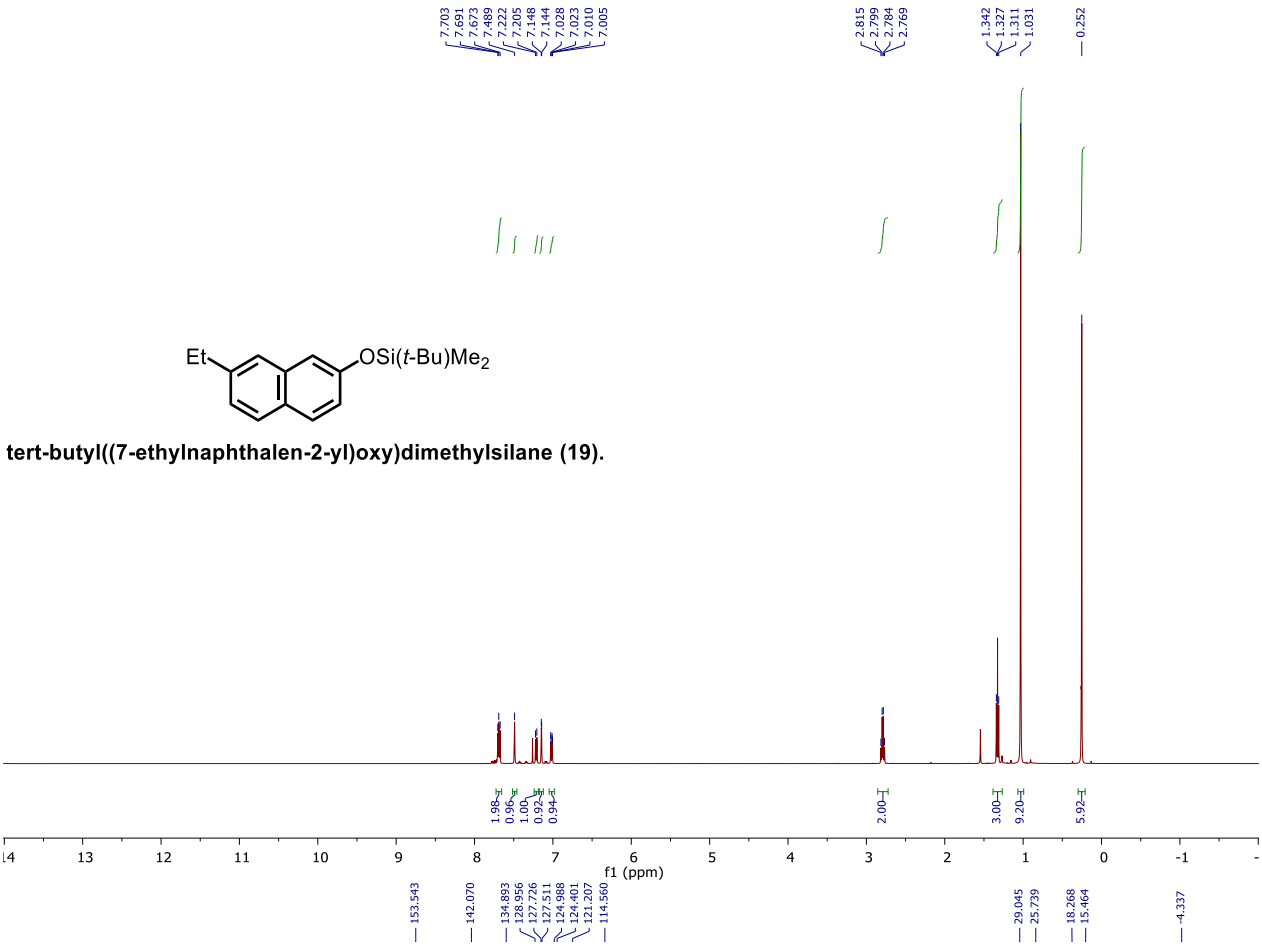
1-((8R,9S,13S,14S,17S)-17-((tert-butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)piperidine (16).



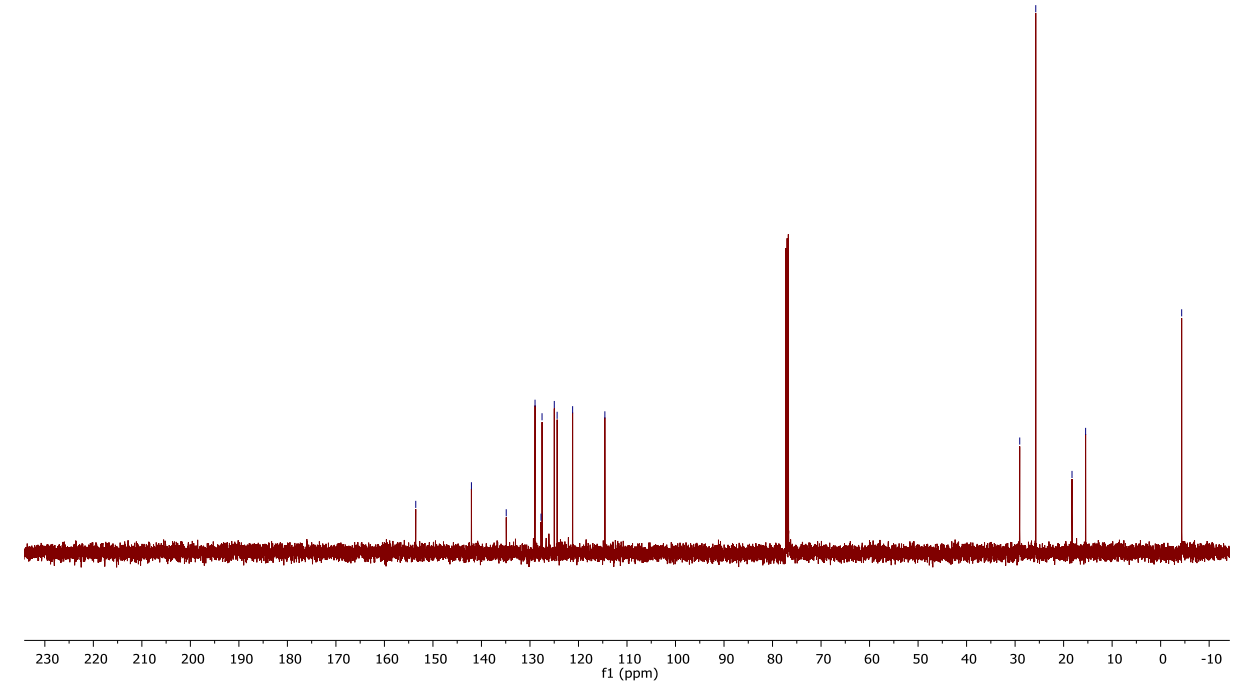
tert-butyl((7-methoxynaphthalen-2-yl)oxy)dimethylsilane (17).

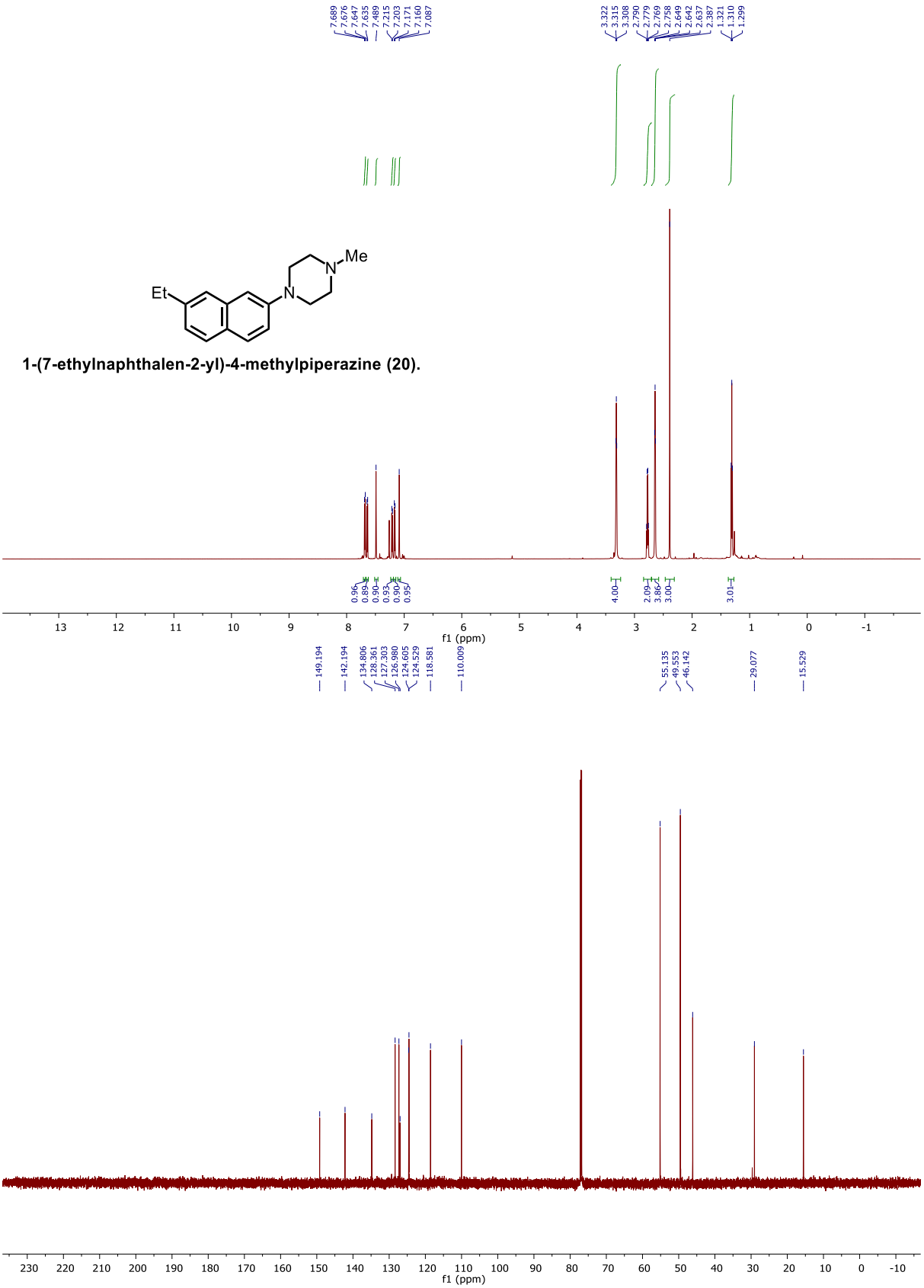


1-(7-methoxynaphthalen-2-yl)-4-methylpiperazine (18).

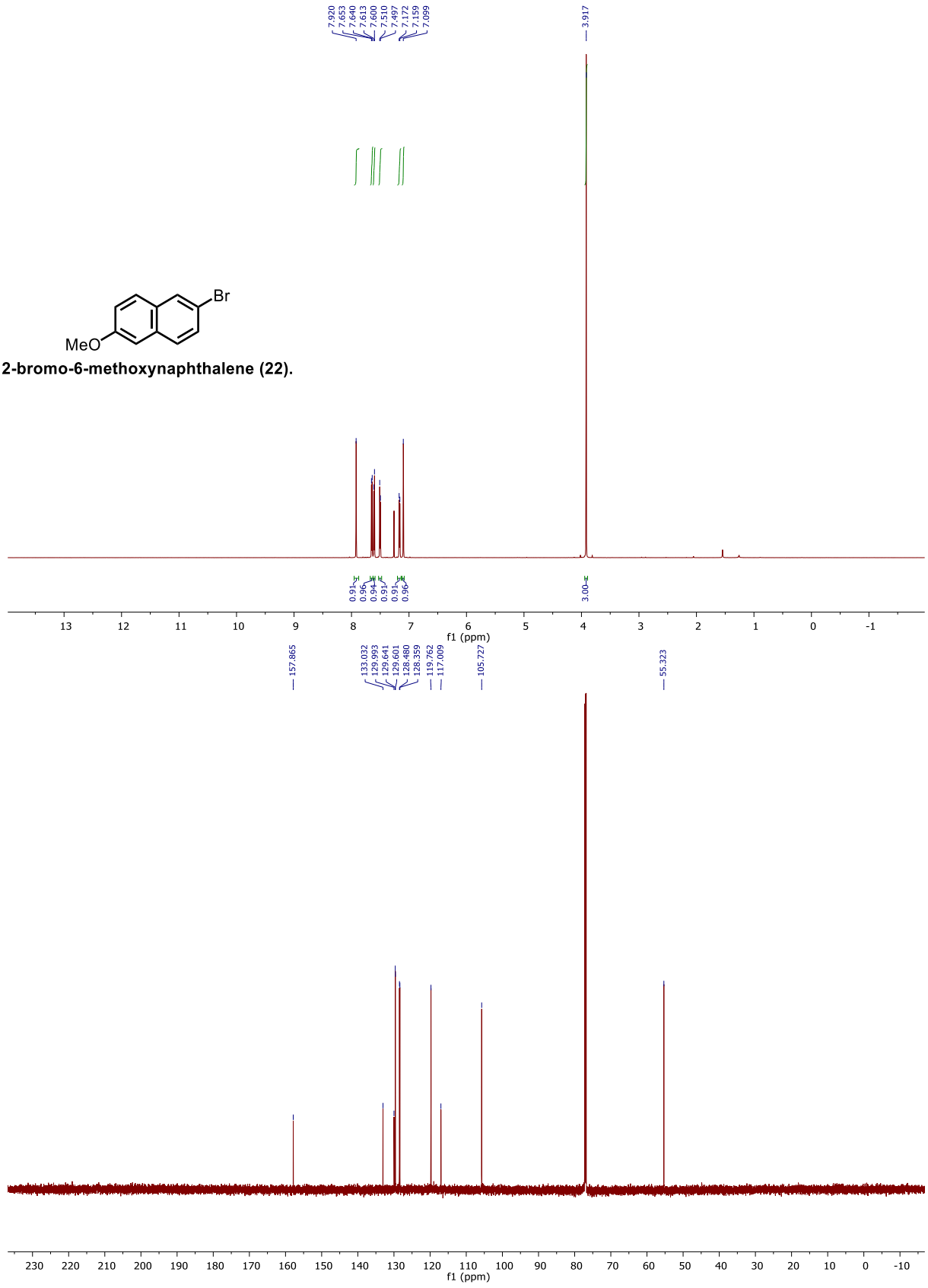


tert-butyl((7-ethylnaphthalen-2-yl)oxy)dimethylsilane (19).

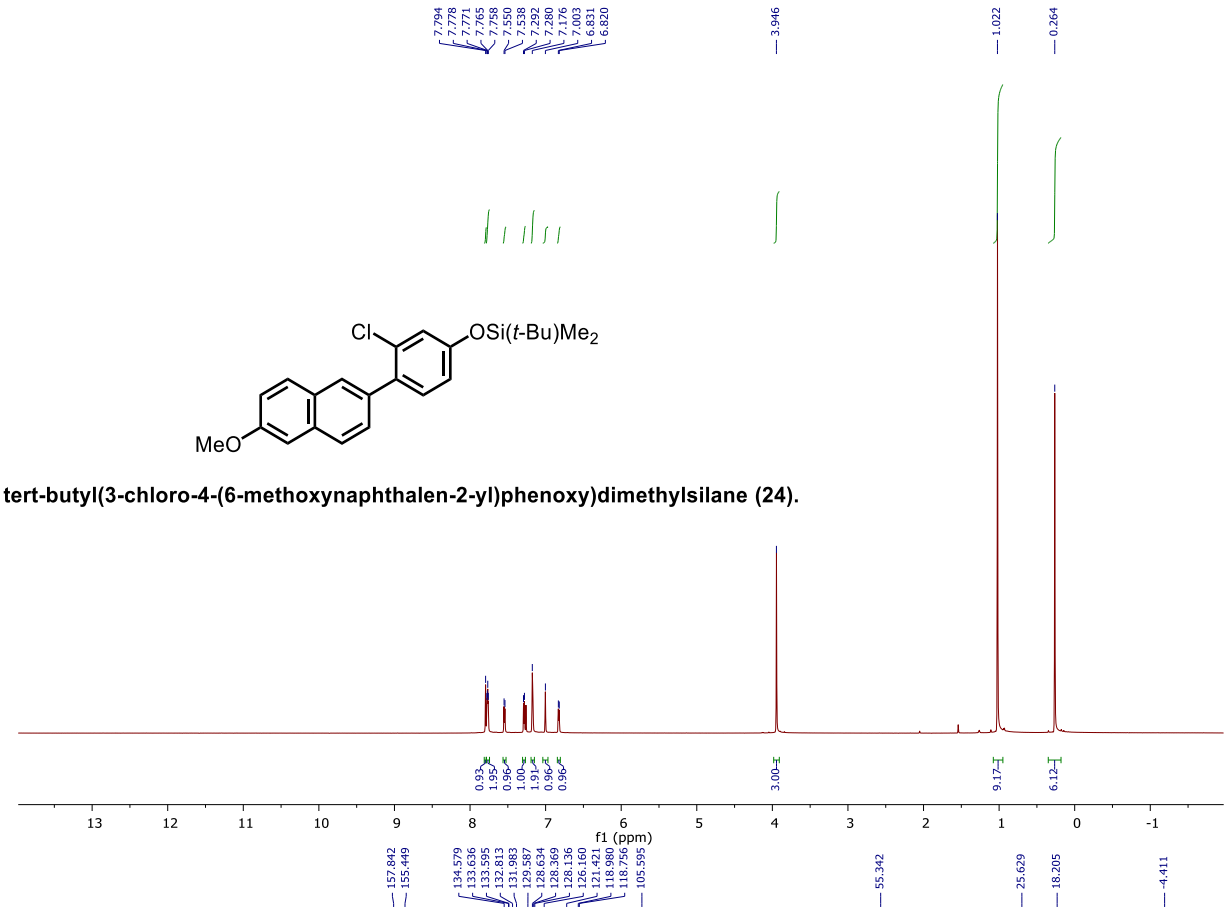




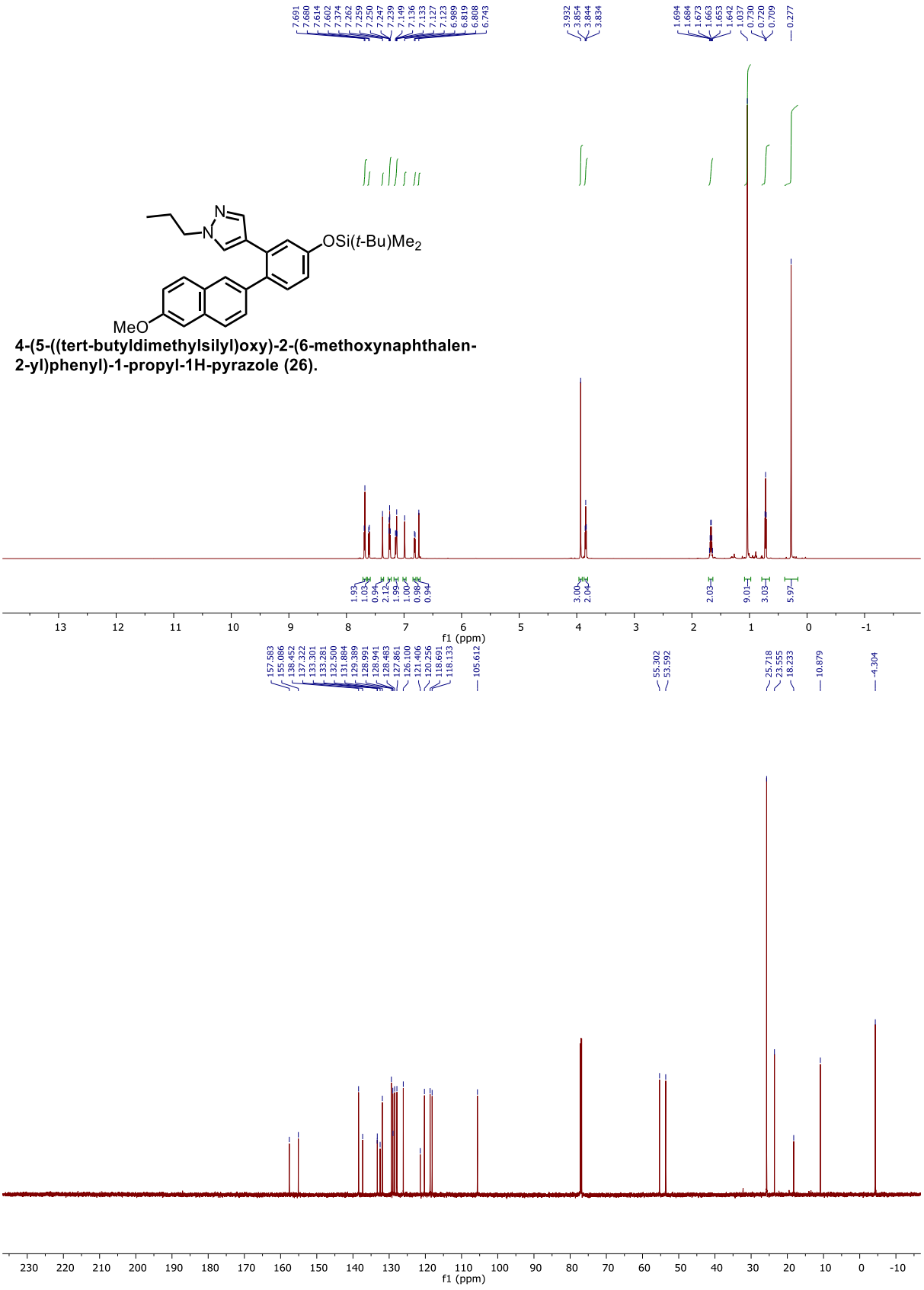
1-(7-ethylnaphthalen-2-yl)-4-methylpiperazine (20).



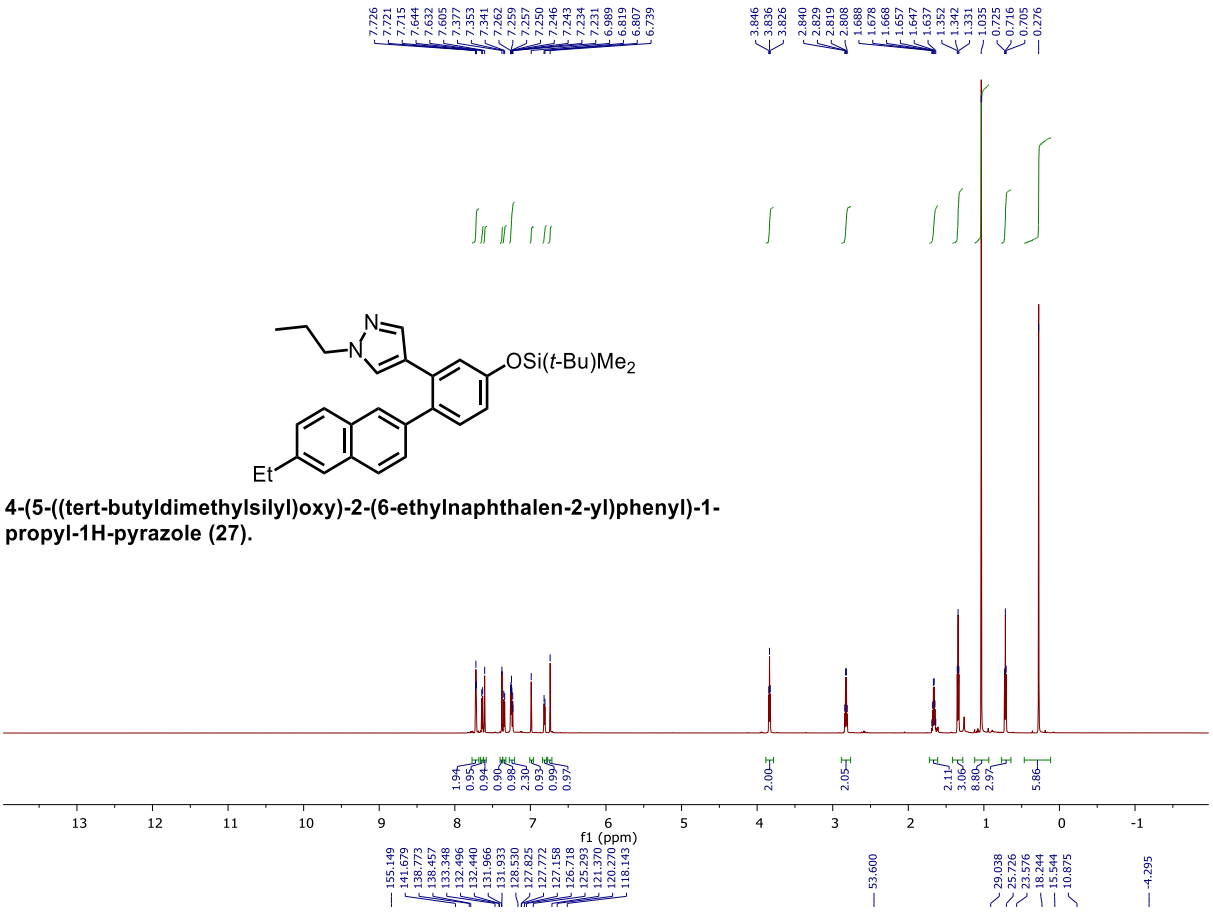
2-bromo-6-methoxynaphthalene (22).



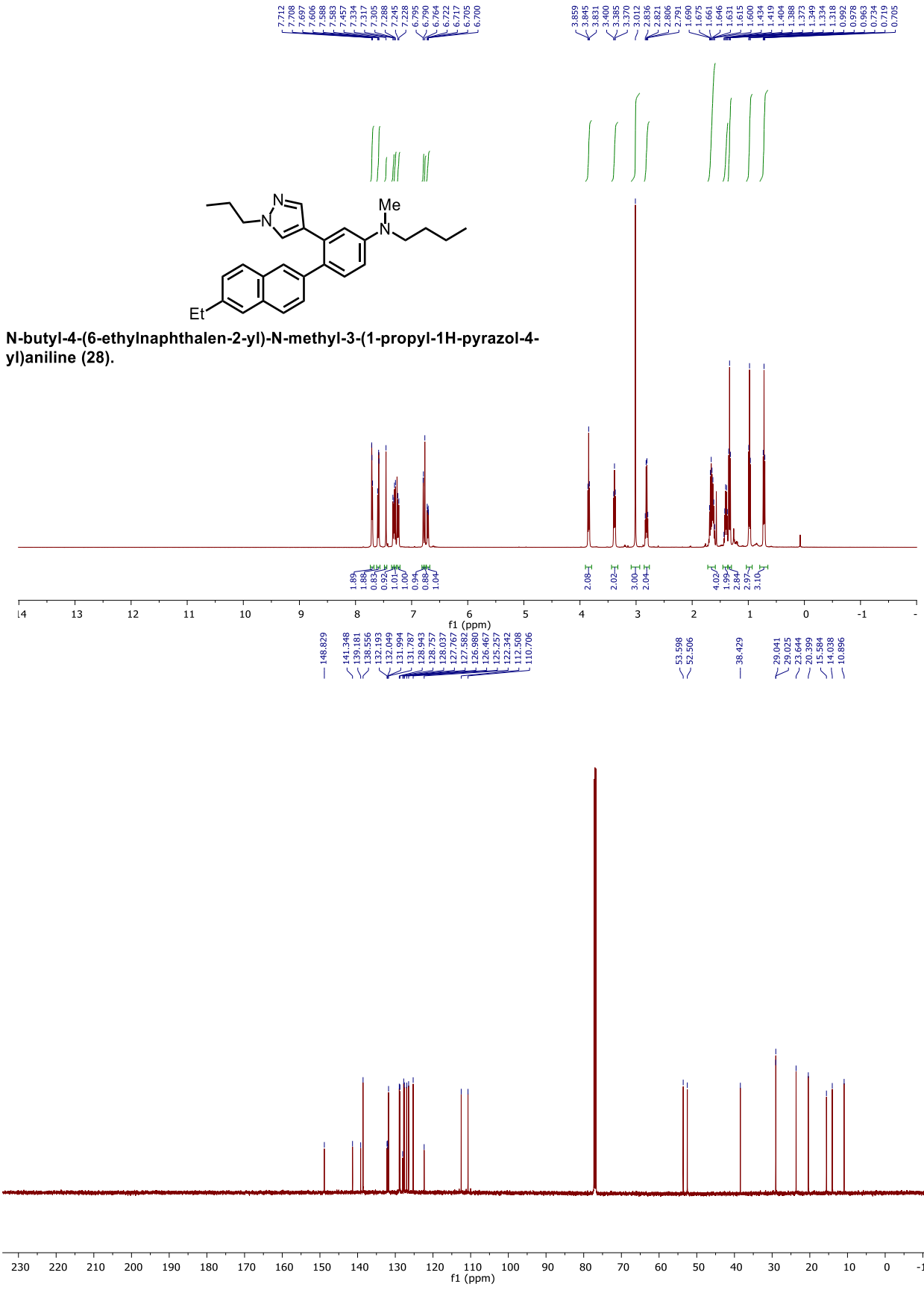
tert-butyl(3-chloro-4-(6-methoxynaphthalen-2-yl)phenoxy)dimethylsilane (24).



4-(5-((tert-butyldimethylsilyl)oxy)-2-(6-methoxynaphthalen-2-yl)phenyl)-1-propyl-1H-pyrazole (26).



4-(5-((tert-butyldimethylsilyl)oxy)-2-(6-ethylnaphthalen-2-yl)phenyl)-1-propyl-1H-pyrazole (27).



N-butyl-4-(6-ethylnaphthalen-2-yl)-N-methyl-3-(1-propyl-1H-pyrazol-4-yl)aniline (28).

IX. References:

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