Supporting Information

Base-promoted 1,6-Conjugate Addition of Alkylazaarenes to *para*-Quinone Methides

Amritha Rayaroth, Rajat Kumar Singh, A. V. Kalyanakrishnan, Krishna Hari, Alagiri Kaliyamoorthy*

School of Chemistry, Indian Institute of Science Education and Research
Thiruvananthapuram, Kerala 695551, India
**Email*: alagiri@iisertvm.ac.in

Table of contents

General information

All reactions were conducted under nitrogen atmosphere using flame dried glassware. All solvents and reagents were obtained from commercial sources and distilled prior to use. Literature procedures were followed for the synthesis of *para*-Quinone Methides **1a-1g, 1i-1n, 1p-1r**.[1-6] Merck silica gel aluminium plates with F-254 indicator was used to perform analytical thin layer chromatography (TLC) and examined under UV light. Flash chromatography was performed on Merck silica gel 230-400 mesh using ethyl acetate (EtOAc) and pet ether as eluents. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on Brucker spectrometer (500 and 125 MHz respectively) using tetramethylsilane as the internal standard. Melting points were not corrected and determined by using a Stuart Melting Point SMP50 apparatus. FT-IR spectra were recorded using IR Prestige-21 SHIMADZU instrument using a KBr disc or pellet. HRMS was recorded using Thermo Scientific Q Exactive TM Bench top LC-HRMS instrument. The crystal structure was determined using Bruker Axs Kappa Apex II ScXRD instrument.

General Procedure for the Synthesis of Compounds 1h and 1o

In a Dean-Stark apparatus, a solution of 2,6-di-*tert*-butylphenol (1 equiv) and the corresponding aldehyde (1 equiv) in toluene (5 mL) was heated to reflux. Piperidine (2 equiv) was added dropwise, and then, the reaction mixture was continued to reflux for 12 h. After cooling just below the boiling point of the reaction mixture, acetic anhydride (2 equiv) was added, and stirring was continued for 30 min. Then, the reaction mixture was poured on ice-water and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was isolated by silica gel column chromatography using Pet ether/EtOAc (99:1) to obtain the desired the product.

General Procedure for the Synthesis of Compounds 3aa-3ka using $NaN(SiMe_3)_2$

To a flame-dried test tube equipped with a magnetic stirring bar, $NaN(SiMe_3)_2$ (2 equiv) and 1,4-dioxane (0.5 mL) was added at room temperature. To this solution, alkylazaarene (3 equiv) was added dropwise under nitrogen. After 5 minutes of stirring, *para*-quinone methide (30 mg, 1 equiv) dissolved in 1,4-dioxane (0.5 mL) was added and stirring was continued for 1 h. The progress of the reaction was monitored by TLC. Finally, the reaction mixture was quenched with water and extracted with ethyl acetate (3 x 20 mL). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography using Pet ether/EtOAc (10:1) to obtain the desired product.

General Procedure for the Synthesis of Compounds 3ea-3fa using $KN(SiMe_3)_2$

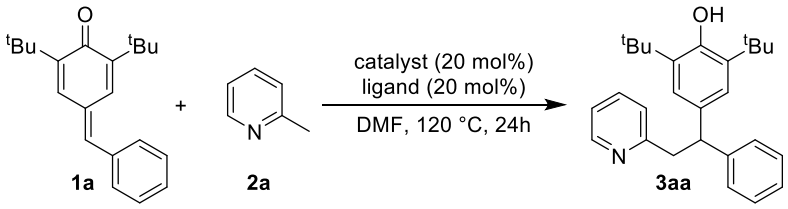
To a flame-dried test tube equipped with a magnetic stirring bar, alkylazaarene (3 equiv) and 1,4-dioxane (0.5 mL) was added at room temperature. To this solution, $KN(SiMe_3)_2$ (2 equiv) was added under nitrogen. After 5 minutes of stirring, *p*-QMs (30 mg, 1 equiv) dissolved in 1,4-dioxane (0.5 mL) was added and stirring was continued for 1 h. Progress of the reaction was monitored by TLC. Finally, the reaction mixture was quenched with water and extracted with ethyl acetate (3 x 20 mL). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography using silica gel to obtain the desired product.

Procedure for the Direct Synthesis of Compound 3aa[7]

In a Dean-Stark apparatus, a solution of 2,6-di-*tert*-butylphenol (58.3 mg, 1 equiv) and the benzaldehyde (30 mg, 1 equiv) in toluene (1 mL) was heated to reflux. Piperidine (55.9 µL, 2 equiv) was added dropwise. The reaction mixture was continued to reflux for 12 h. After cooling just below the boiling point, acetic anhydride (53.4 µL, 2 equiv) was added to the reaction mixture, and stirred for 1 h. Then, the reaction mixture was azeotropically concentrated with toluene and CH_2Cl_2 under reduced pressure. To the concentrated mixture, $NaN(SiMe_3)_2$ (103.7 mg, 2 equiv) and 1,4-dioxane (2.8 mL, 0.1 M) was added. To the stirring solution, 2-methylpyridine (0.08 mL, 3 equiv) was added drop wise and stirred for 1 h. The reaction mixture was quenched with water and extracted with EtOAc (3 x 20 mL). The crude product was isolated by flash column chromatography using petroleum ether and ethyl acetate and afforded the desired product as a white solid in 56% yield (60.9 mg).

Lewis acid Screening

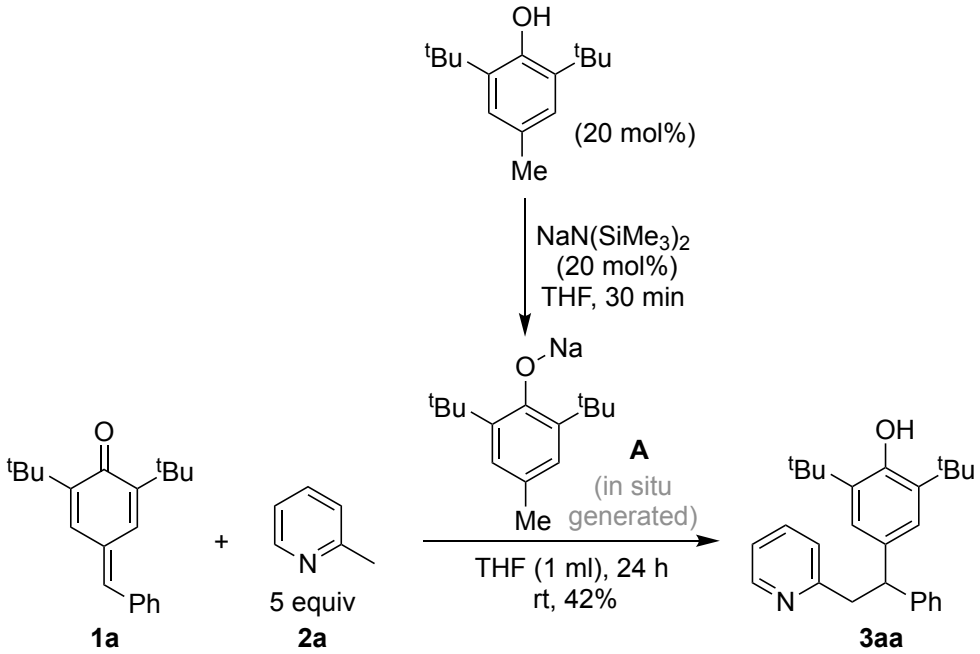
Experimental Procedure: To a flame-dried test tube equipped with a magnetic stirring bar, catalyst (20 mol%), ligand (20 mol%), and DMF (0.5 mL) was added at room temperature and stirred for 5 min. To this solution, 2-methylpyridine (50.3 µL, 5 equiv) was added under nitrogen. After 5 minutes of stirring, *p*-QM (30 mg, 1 equiv) dissolved in DMF (0.5 mL) was added and stirring was continued for 24 h at 120 °C. The reaction was monitored by TLC.



entry	catalyst	ligand	yield (%)
1	$Sc(OTf)_3$	-	n.r
2	$Yb(OTf)_3$	-	n.r
3	$La(OTf)_3$	-	n.r
4	$Mg(OTf)_2$	-	n.r
5	$Zn(OTf)_2$	-	n.r
6[a]	$Cu(OTf)_2$	1,10-phenanthroline	n.r
7[a]	$Pd(OAc)_2$	1,10-phenanthroline	n.r

[a]Toluene was used as the solvent. nr = no reaction.

Typical experimental procedure for the 1,6-conjugate addition reaction in the presence of a in situ generated sodium aryloxide base

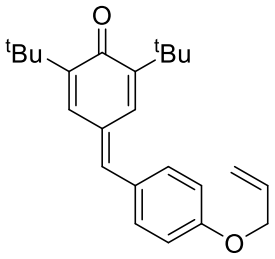


To a flame-dried test tube equipped with a magnetic stirring bar, $NaN(SiMe_3)_2$ (0.2 equiv), 2,6-di-*tert*-butyl-4-methylphenol (0.2 equiv) and THF (0.5 mL) was added at room temperature and stirred for 15 minutes. To this solution, 2-methylpyridine (5 equiv) was added dropwise under nitrogen. After 1 hour of stirring, *para*-quinone methide (30 mg, 1 equiv) dissolved in THF (0.5 mL) was added and stirring was continued for 24 h. Finally, the reaction mixture was

quenched with water and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography using petroleum ether/EtOAc (10:1) to obtain the desired product **3aa** (16.5 mg, 42%).

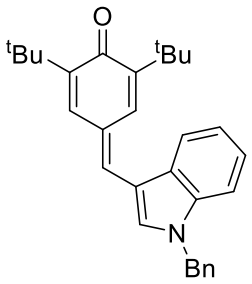
Characterization data

*4-(4-(allyloxy)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(1h)**.*



Orange gummy liquid (1.46 g, 75%, 900 mg of aldehyde was used). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J* = 2.3 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.13 (s, 1H), 7.00-6.99 (m, 3H), 6.11-6.04 (m, 1H), 5.45 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.33 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.61 (d, *J* = 5.3 Hz, 2H), 1.33 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (120 MHz, $CDCl_3$): δ (ppm) 186.5, 159.6, 149.0, 147.2, 142.6, 135.4, 132.7, 132.2, 130.6, 128.8, 127.8, 118.1, 115.2, 68.9, 35.4, 34.9, 29.6, 29.5. IR (FT IR, cm^{-1}): 3447, 2955, 1599, 1506, 1256, 1175, 1020, 823. HRMS (m/z): calculated for $C_{24}H_{30}O_2$ [M + H], 351.2318; found 351.2314.

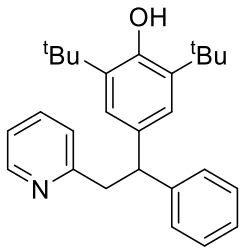
*4-((1-benzyl-1H-indol-3-yl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(1o)**.*



Orange solid (533 mg, 52%, 500 mg of 2,6-di-*tert*-butylphenol was used); mp, 130.5-133.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.46 (s, 1H), 7.41-7.24 (m, 9H), 7.11 (d, *J* = 2.4 Hz, 1H), 5.38 (s, 2H), 1.35 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (120 MHz, $CDCl_3$): δ (ppm) 186.4, 148.0, 146.1, 136.7, 135.6, 135.3, 134.5, 130.6, 129.2, 128.40, 128.38, 128.33, 128.1, 127.6, 123.5, 121.5, 119.3, 113.3, 110.3, 50.8, 35.4, 34.9,

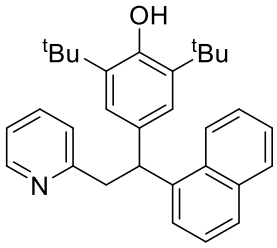
29.6, 29.58. IR (FT IR, cm^{-1}): 2951, 1601, 1545, 1510, 1352, 1175, 943, 745. HRMS (m/z): calculated for $C_{30}H_{33}NO$ [M + H], 424.2634; found 424.2634.

2,6-di-tert-butyl-4-(1-phenyl-2-(pyridin-2-yl)ethyl)phenol ***(3aa)***.



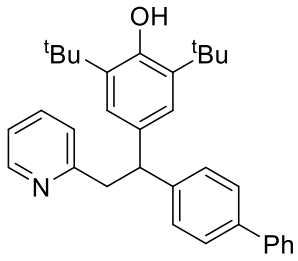
White solid (36 mg, 91%); mp, 160.4-167.1 °C. Recrystallised from $CHCl_3$/hexane. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.51 (d, *J* = 4.1 Hz, 1H), 7.40 (td, *J* = 7.6, 1.8 Hz, 1H), 7.25-7.21 (m, 4H), 7.14-7.11 (m, 1H), 7.03-7.00 (m, 1H), 6.98 (s, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.00 (s, 1H), 4.49 (t, *J* = 8.0 Hz, 1H), 3.52-3.41 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.4, 151.9, 149.1, 144.5, 135.8, 135.4, 134.9, 128.2, 128.1, 125.9, 124.5, 123.9, 120.9, 51.2, 45.2, 34.3, 30.3. IR (FT IR, cm^{-1}): 3312, 2957, 1595, 1435, 1097, 700, 469. HRMS (m/z): calculated for $C_{27}H_{33}NO$ [M + H], 388.2634; found: 388.2626.

2,6-di-tert-butyl-4-(1-(naphthalen-1-yl)-2-(pyridin-2-yl)ethyl)phenol ***(3ab)***.



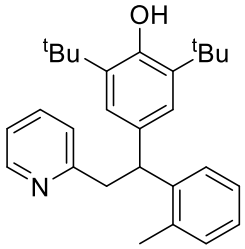
Brown solid (36.8 mg, 97%); mp, 159.6-163.6 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 4.7 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 7.81-7.79 (m, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 7.1 Hz, 1H), 7.46-7.35 (m, 4H), 7.01-6.99 (m, 1H), 6.97 (s, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.34 (t, *J* = 7.8 Hz, 1H), 4.95 (s, 1H), 3.66-3.62 (m, 1H), 3.55-3.50 (m, 1H), 1.31 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.5, 151.9, 149.2, 140.4, 135.8, 135.4, 134.4, 133.9, 132.0, 128.6, 126.8, 125.7, 125.3, 125.2, 124.7, 124.4, 124.2, 123.9, 120.9, 46.0, 45.4, 34.3, 30.3. IR (FT IR, cm^{-1}): 3377, 2953, 1595, 1433, 1190, 777. HRMS (m/z): calculated for $C_{31}H_{35}NO$ [M + H], 438.2791; found: 438.2783.

4-(1-([1,1'-biphenyl]-4-yl)-2-(pyridin-2-yl)ethyl)-2,6-di-tert-butylphenol ***(3ac)***.



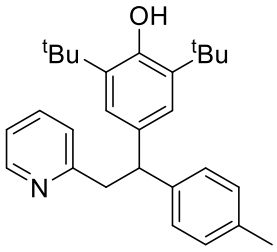
Brown gummy oil (34.5 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.57 (d, *J* = 4.7 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.48-7.44 (m, 3H), 7.42-7.38 (m, 2H), 7.34-7.29 (m, 3H), 7.08-7.05 (m, 1H), 7.02 (s, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.02 (s, 1H), 4.54 (t, *J* = 8 Hz, 1H), 3.59-3.46 (m, 2H), 1.37 (s, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.9, 152.1, 148.6, 143.5, 140.9, 138.7, 136.5, 135.6, 134.6, 128.7, 128.5,127.0, 126.9, 124.5, 124.2, 121.2, 50.9, 44.7, 34.4, 30.3. IR (FT IR, cm^{-1}): 3635, 2954, 1593, 1487, 1433, 1234, 763, 689. HRMS (m/z): calculated for $C_{33}H_{37}NO$ [M + H], 464.2947; found: 464.2944.

2,6-di-tert-butyl-4-(2-(pyridin-2-yl)-1-(o-tolyl)ethyl)phenol ***(3ad)***.



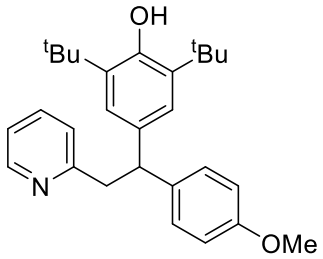
Yellow solid (37.2 mg, 95%); mp, 136.4-139.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 4.5 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.41-7.38 (m, 1H), 7.19-7.17 (m, 1H), 7.07-7.01 (m, 3H), 6.89 (s, 2H), 6.77 (d, *J* = 7.8 Hz, 1H)), 4.97 (s, 1H), 4.67 (t, *J* = 7.9Hz, 1H), 3.50-3.39 (m, 2H), 2.19 (s, 3H), 1.33 (s, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.5, 151.8, 149.0, 142.4, 136.4, 135.8, 135.3, 134.3, 130.3, 126.7, 125.82, 125.77, 124.7, 123.9, 120.9, 46.7, 45.2, 34.3, 30.3, 19.9. IR (FT IR, cm^{-1}): 3377, 2953, 1595, 1433, 1193, 1002, 754. HRMS (m/z): calculated for $C_{28}H_{35}NO$ [M + H], 402.2791; found: 402.2784.

2,6-di-tert-butyl-4-(2-(pyridin-2-yl)-1-(p-tolyl)ethyl)phenol ***(3ae)***.



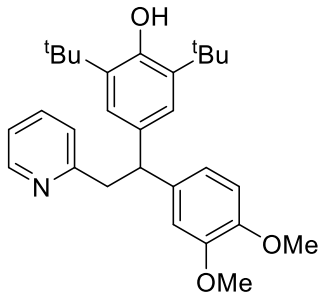
Yellow solid (35.9 mg, 92%); mp, 112.6-116.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.53 (d, *J* = 4.1 Hz, 1H), 7.45-7.42 (m, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.06-7.02 (m, 3H), 6.98 (s, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.99 (s, 1H), 4.45 (t, *J* = 8 Hz, 1H), 3.53-3.41 (m, 2H), 2.27 (s, 3H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.2, 151.9, 148.6, 141.3, 136.3, 135.45, 135.38, 134.9, 128.9, 127.9, 124.5, 124.1, 121.1, 50.8, 44.8, 34.3, 30.3, 21.0. IR (FT IR, cm^{-1}): 3435, 2957, 1595, 1435, 1197, 815, 617. HRMS (m/z): calculated for $C_{28}H_{35}NO$ [M + H], 402.2791; found 402.2787.

2,6-di-tert-butyl-4-(1-(4-methoxyphenyl)-2-(pyridin-2-yl)ethyl)phenol ***(3af).***



Yellowish brown solid (36.7 mg, 95%); mp, 120.5-123.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.53 (d, *J* = 4.2 Hz, 1H), 7.46-7.43 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07-7.05 (m, 1H), 6.97 (s, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.99 (s, 1H), 4.44 (t, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 3.50-3.40 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.5, 157.7, 151.9, 149.1, 136.6, 135.9, 135.4, 135.3, 128.9, 124.4, 123.9, 120.9, 113.6, 55.2, 50.4, 45.4, 34.3, 30.3. IR (FT IR, cm^{-1}): 3437, 2957, 1591, 1512, 1435, 1246, 1184, 1115, 1038, 770. HRMS (m/z): calculated for $C_{28}H_{35}NO_2$ [M + H], 418.2740; found: 418.2731.

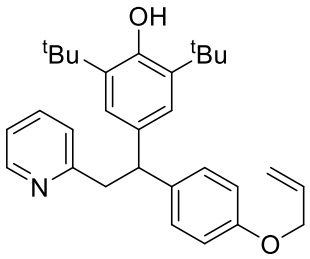
2,6-di-tert-butyl-4-(1-(3,4-dimethoxyphenyl)-2-(pyridin-2-yl)ethyl)phenol ***(3ag)****.*



Yellow gummy oil (26.5 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 4.0 Hz, 1H), 7.43-7.40 (m, 1H), 7.04-7.02 (m, 1H), 6.99 (s, 2H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.79-6.74 (m, 3H), 5.01 (s, 1H), 4.43 (t, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.46-3.38 (m, 2H), 1.37 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.4, 151.9, 149.1, 148.5, 147.1, 137.1,

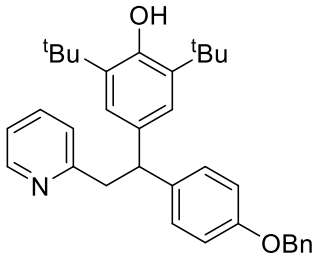
135.9, 135.5, 134.9, 124.4, 123.9, 120.9, 119.9, 111.8, 110.9, 55.80, 55.75, 50.8, 45.5, 34.4, 30.3. IR (FT IR, cm^{-1}): 3638, 2955, 1514, 1436, 1261, 1028, 768. HRMS (m/z): calculated for $C_{29}H_{37}NO_3$ [M + H], 448.2846; found: 448.2843.

4-(1-(4-(allyloxy)phenyl)-2-(pyridin-2-yl)ethyl)-2,6-di-tert-butylphenol ***(3ah)***.



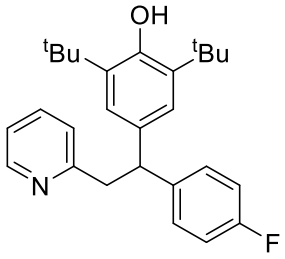
Brown solid (32.5 mg, 86%); mp, 107.7-109.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 4.2 Hz, 1H), 7.42-7.39 (m, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.04-7.01 (m, 1H), 6.96 (s, 2H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.07-5.99 (m, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.25(d, *J* = 10.3 Hz, 1H), 4.99 (s, 1H), 4.47 (d, *J* = 5.0 Hz, 2H), 4.43 (t, *J* = 8 Hz, 1H), 3.48-3.37 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.5, 156.8, 151.9, 149.1, 136.8, 135.8, 135.4, 135.2, 133.5, 129.0, 124.4, 123.9, 120.9, 117.5, 114.4, 68.8, 50.4, 45.4, 34.3, 30.3. IR (FT IR, cm^{-1}): 3638, 2954, 1589, 1510, 1433, 1228, 991, 826. HRMS (m/z): calculated for $C_{30}H_{37}NO_2$ [M + H], 444.2897; found: 444.2894.

4-(1-(4-(benzyloxy)phenyl)-2-(pyridin-2-yl)ethyl)-2,6-di-tert-butylphenol ***(3ai)***.



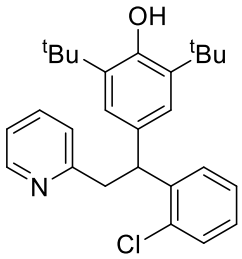
Yellowish brown solid (27.6 mg, 75%); mp, 122.6-125.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 4.0 Hz, 1H), 7.43-7.40 (m, 3H), 7.38-7.35 (m, 2H), 7.32-7.29 (m, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.04-7.02 (m, 1H), 6.96 (s, 2H), 6.85-6.82 (m, 3H), 5.00 (s, 3H), 4.44 (t, *J* = 8.0 Hz, 1H), 3.48-3.38 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.4, 157.0, 151.9, 148.9, 137.2, 136.9, 135.9, 135.4, 135.2, 129.0, 128.5, 127.9, 127.5, 124.4, 123.9, 120.9, 114.6, 69.9, 50.4, 45.2, 34.3, 30.3. IR (FT IR, cm^{-1}): 3638, 2955, 1510, 1435, 1246, 1042, 737. HRMS (m/z): calculated for $C_{34}H_{39}NO_2$ [M + H], 494.3053; found: 494.3051.

2,6-di-tert-butyl-4-(1-(4-fluorophenyl)-2-(pyridin-2-yl)ethyl)phenol ***(3aj)***.



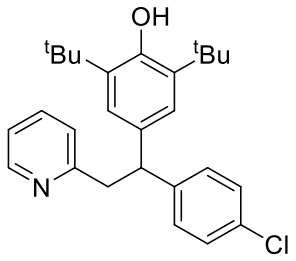
Yellow solid (34.3 mg, 88%); mp, 145.9-149.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.54 (d, *J* = 4.4 Hz, 1H), 7.46-7.43 (m, 1H), 7.20-7.18 (m, 2H), 7.07-7.05 (m,1H), 6.95 (s, 2H), 6.92-6.89 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.03 (s, 1H), 4.50 (t, *J* = 8.0 Hz, 1H), 3.49-3.40 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 162.2, 160.3, 159.9, 152.1, 148.8, 140.0 (d, *J* = 3 Hz), 136.3, 135.6, 134.6, 129.5 (d, *J* = 7.6), 124.4, 124.1, 121.2, 115.0, 114.9, 50.3, 44.9, 34.4, 30.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -117.49. IR (FT IR, cm^{-1}): 3442, 2957, 1595, 1508, 1435, 1228, 1097, 835. HRMS (m/z): calculated for $C_{27}H_{32}FNO$ [M + H], 406.2540; found: 406.2535.

2,6-di-tert-butyl-4-(1-(2-chlorophenyl)-2-(pyridin-2-yl)ethyl)phenol ***(3ak)***.



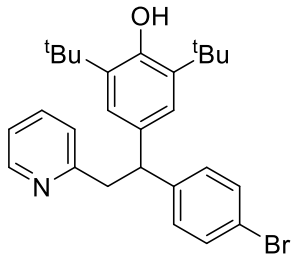
Off-white solid (37.2 mg, 97%); mp, 127.6-132.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.49 (d, *J* = 4.6 Hz, 1H), 7.45-7.42 (m, 2H), 7.27 (s, 1H), 7.22-7.19 (m, 1H), 7.08-7.01 (m, 4H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.05 (t, *J* = 8.1 Hz, 1H), 5.02 (s, 1H), 3.56-3.46 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.9, 152.1, 149.1, 141.9, 135.9, 135.4, 134.2, 133.4, 129.6, 128.7, 127.2, 126.7, 124.7, 123.4, 121.1, 46.4, 44.2, 34.3, 30.3. IR (FT IR, cm^{-1}): 2957, 1595, 1477, 1435, 1192, 754. HRMS (m/z): calculated for $C_{27}H_{32}ClNO$ [M + H], 422.2245; found: 422.2240.

2,6-di-tert-butyl-4-(1-(4-chlorophenyl)-2-(pyridin-2-yl)ethyl)phenol ***(3al)***.



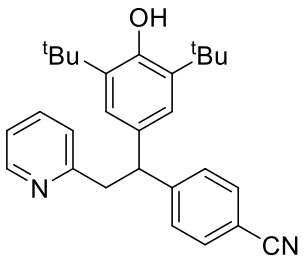
Off-white solid (35.1 mg, 91%); mp, 122.8-126.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 4.2 Hz, 1H), 7.45-7.42 (m, 1H), 7.19-7.15 (m, 4H), 7.06-7.03 (m, 1 H), 6.95 (s, 2 H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.03 (s, 1H), 4.48 (t, *J* = 8.0 Hz, 1H), 3.47-3.39 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.9, 152.1, 149.1, 142.9, 136.1, 135.6, 134.4, 131.6, 129.5, 128.3, 124.4, 123.9, 121.2, 50.5, 44.8, 34.4, 30.3. IR (FT IR, cm^{-1}): 3362, 2957, 1595, 1487, 1435, 1094, 1009, 625. HRMS (m/z): calculated for $C_{27}H_{32}ClNO$ [M + H], 422.2245; found: 422.2242.

4-(1-(4-bromophenyl)-2-(pyridin-2-yl)ethyl)-2,6-di-tert-butylphenol ***(3am)***.



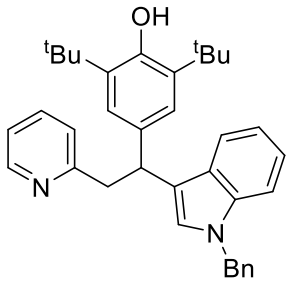
Yellow solid (28.6 mg, 76%); mp, 116.4-120.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.56 (d, *J* = 3.9 Hz, 1H), 7.49-7.47 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12-7.07 (m, 3 H), 6.95 (s, 2 H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.04 (s, 1H), 4.48 (t, *J* = 8.0 Hz, 1H), 3.51-3.41 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.5, 152.2, 148.5, 143.3, 136.8, 135.7, 134.0, 131.3, 129.9, 124.4, 124.2, 121.4, 119.8, 50.5, 44.3, 34.4, 30.3. IR (FT IR, cm^{-1}): 3298, 2957, 1595, 1485, 1435, 1115, 1007, 810, 758. HRMS (m/z): calculated for $C_{27}H_{32}BrNO$ [M + H], 466.1740; found: 466.1738.

4-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(pyridin-2-yl)ethyl)benzonitrile ***(3an)***.



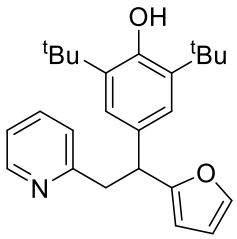
Yellow gummy oil (20.5 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.51 (d, *J* = 3.9 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.44 (td, *J* = 7.6, 1.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.07-7.04 (m, 1H), 6.93 (s, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 5.07 (s, 1H), 4.59 (t, *J* = 8.0 Hz, 1H), 3.46 (d, *J* = 8 Hz, 2H) 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.4, 152.4, 150.2, 149.2, 136.1, 135.9, 133.4, 132.1, 128.9, 124.4, 123.9, 121.3, 119.1, 109.8, 51.1, 44.4, 34.4, 30.3. IR (FT IR, cm^{-1}): 3427, 2951, 2361, 1595, 1433, 1132, 669. HRMS (m/z): calculated for $C_{28}H_{32}N_2O$ [M + H], 413.2587; found: 413.2588.

4-(1-(1-benzyl-1H-indol-3-yl)-2-(pyridin-2-yl)ethyl)-2,6-di-tert-butylphenol ***(3ao)***.



Brown solid (32.7 mg, 90%); mp, 129.2-135.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.51 (d, *J* = 4.1 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.37 (td, *J* = 7.7, 1.7 Hz, 1H), 7.25-7.22 (m, 3H), 7.18(d, *J* = 8.2 Hz, 1H), 7.11-7.08 (m, 1H), 7.05 (s, 2H), 7.03-7.00 (m, 3H), 6.99-6.96 (m, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.31-5.22 (m, 2H), 4.96 (s, 1H), 4.73 (t, *J* = 8.0 Hz, 1H), 3.65-3.60 (m, 1H), 3.44-3.39 (m, 1H), 1.33 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.7, 151.9, 148.8, 137.9, 136.8, 135.9, 135.3, 135.0, 128.7, 127.9, 127.4, 126.5, 125.9, 124.4, 123.9, 121.5, 120.9, 120.2, 118.8, 118.6, 109.4, 49.7, 45.5, 43.1, 34.3, 30.4. IR (FT IR, cm^{-1}): 3608, 3447, 2953, 1591, 1433, 1366, 1236, 1119, 742. HRMS (m/z): calculated for $C_{36}H_{40}N_2O$ [M + H], 517.3213; found 517.3209.

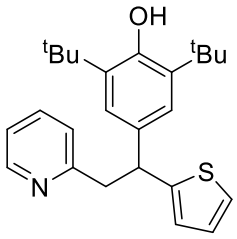
2,6-di-tert-butyl-4-(1-(furan-2-yl)-2-(pyridin-2-yl)ethyl)phenol ***(3ap)***.



Brown solid (32.1 mg, 81%); mp, 126.2-132.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.53 (d, *J* = 4.3 Hz, 1H), 7.44 (td, *J* = 7.6, 1.5 Hz, 1H), 7.31 (d, *J* = 1.1 Hz, 1H), 7.07-7.05 (m, 1H), 6.97 (s, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.23-6.22 (m, 1H), 6.03 (d, *J* = 3.1 Hz, 1H), 5.03 (s, 1H),

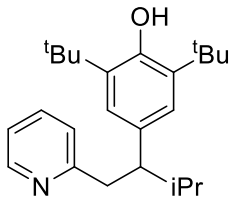
4.48 (t, J = 8.0 Hz, 1H), 3.54-3.50 (m, 1H), 3.28-3.23 (m, 1H), 1.37 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.8, 157.1, 152.3, 148.9, 141.2, 136.0, 135.6, 132.7, 124.4, 123.8, 121.2, 109.9, 105.9, 45.4, 44.3, 34.3, 30.3. IR (FT IR, cm^{-1}): 3423, 2957, 1435, 1115, 729. HRMS (m/z): calculated for $C_{25}H_{31}NO_2$ [M + H], 378.2427; found 378.2423.

2,6-di-tert-butyl-4-(2-(pyridin-2-yl)-1-(thiophen-2-yl)ethyl)phenol ***(3aq)***.



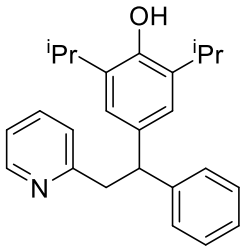
Brown solid (35.9 mg, 91%); mp, 141.8-144.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.54 (s, 1H), 7.42 (s, 1H), 7.09-7.04 (m, 4H), 6.85 (s, 2H), 6.77 (s, 1H), 5.03 (s, 1H), 4.73 (t, J = 7.8 Hz, 1H), 3.54-3.49 (m, 1H), 3.40-3.36 (m, 1H), 1.38 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.8, 152.3, 149.1, 148.8, 135.9, 135.5, 134.4, 126.3, 124.3, 124.2, 124.0, 123.3, 121.1, 46.97, 46.91, 34.3, 30.3. IR (FT IR, cm^{-1}): 3444, 2954, 2365, 1595, 1435, 692. HRMS (m/z): calculated for $C_{25}H_{31}NOS$ [M + H], 394.2199; found 394.2196.

2,6-di-tert-butyl-4-(3-methyl-1-(pyridin-2-yl)butan-2-yl)phenol ***(3ar)***.



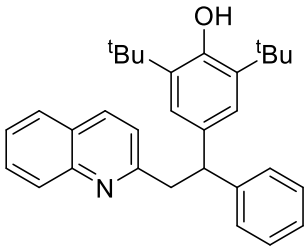
Brown gummy oil (18.6 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.48 (d, J = 3.7 Hz, 1H), 7.37-7.34 (m, 1H), 7.00-6.98 (m, 1H), 6.76 (s, 2H), 6.69 (d, J = 7.7 Hz, 1H), 4.92 (s, 1H), 3.29 (dd, J = 12.7, 5.5 Hz, 1H), 2.90-2.86 (m, 1H), 2.83-2.78 (m, 1H), 1.94-1.87 (m, 1H), 1.36 (s, 18H), 1.00 (d, J = 6.5 Hz, 3H), 0.81 (d, J = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 161.6, 151.6, 148.7, 135.7, 134.9, 133.4, 124.9, 123.9, 120.6, 52.9, 42.5, 34.2, 32.1, 30.4, 21.2, 20.1. IR (FT IR, cm^{-1}): 2960, 1595, 1433, 1223, 1007, 773. HRMS (m/z): calculated for $C_{24}H_{35}NO$ [M + H], 354.2791; found 354.2786.

2,6-diisopropyl-4-(1-phenyl-2-(pyridin-2-yl)ethyl)phenol ***(3as).***



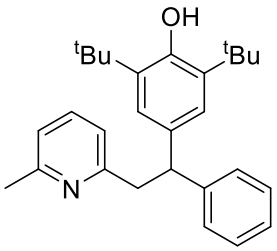
White solid (20.3 mg, 50%); mp, 149.8-154.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 4.0 Hz, 1H), 7.40 (td, *J* = 7.5, 1.5 Hz, 1H), 7.25-7.21 (m, 4H), 7.14-7.12 (m, 1H), 7.03-7.01 (m, 1H), 6.87 (s, 2H), 6.83 (d, *J* = 7.5 Hz, 1H) 4.75 (s, 1H), 4.51 (t, *J* = 8.0 Hz, 1H), 3.53-3.43 (m, 2H), 3.11-3.06 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 6H), 1.16 (d, *J* = 7.0 Hz, 6H), .^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.3, 149.1, 148.2, 144.6, 136.0, 135.9, 133.4, 128.2, 128.0, 125.9, 123.9, 123.1, 120.9, 50.9, 44.9, 27.2, 22.79, 22.74. IR (FT IR, cm^{-1}): 3317, 2972, 1692, 1466, 1129, 951, 816. HRMS (m/z): calculated for $C_{24}H_{35}NO$ [M + H], 360.2321; found 360.2312.

2,6-di-tert-butyl-4-(1-phenyl-2-(quinolin-2-yl)ethyl)phenol ***(3ba)***.



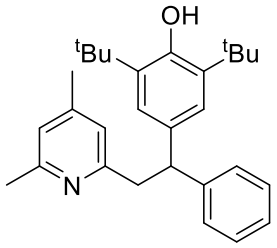
Off-white solid (43.7 mg, 98%); mp, 166.1-175.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.08-8.05 (m, 1H), 7.92-7.89 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.68-7.65 (m, 1H), 7.48-7.45 (m, 1H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.24-7.21 (m, 2H), 7.14-7.11 (m, 1H), 7.01 (s, 3H), 4.99 (s, 1H), 4.59 (t, *J* = 8.0 Hz, 1H), 3.75-3.63 (m, 2H), 1.33 (s, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 161.1, 152.0, 147.6, 144.5, 135.9, 135.5, 134.7, 129.4, 128.6, 128.3, 128.1, 127.4, 126.7, 126.0, 125.8, 124.6, 122.2, 51.3, 45.6, 34.3, 30.3. IR (FT IR, cm^{-1}): 2953, 2561, 1597, 1388, 1224, 1120, 819, 621. HRMS (m/z): calculated for $C_{31}H_{35}NO$ [M + H], 438.2791; found: 438.2787.

2,6-di-tert-butyl-4-(2-(6-methylpyridin-2-yl)-1-phenylethyl)phenol ***(3ca)***.



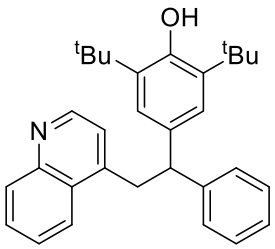
White solid (32.6 mg, 80%); mp, 121.9-127.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.31-7.21 (m, 5H), 7.14-7.11 (m, 1H), 6.96 (s, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 4.98 (s, 1H), 4.44 (t, *J* = 8 Hz, 1H), 3.50-3.38 (m, 2H), 2.51 (s, 3H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.7, 157.5, 151.9, 144.7, 135.9, 135.3, 135.0, 128.1, 125.9, 124.6, 120.6, 120.4, 51.1, 44.9, 34.3, 30.3, 24.4. IR (FT IR, cm^{-1}): 3366, 2957, 1595, 1456, 1113, 790, 702. HRMS (m/z): calculated for $C_{28}H_{35}NO$ [M + H], 402.2791; found: 402.2783.

2,6-di-tert-butyl-4-(2-(4,6-dimethylpyridin-2-yl)-1-phenylethyl)phenol ***(3da)***.



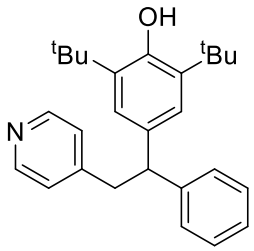
White solid (32.8 mg, 77%); mp, 144.5-148.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.27-7.21 (m, 4H), 7.14-7.11 (m, 1H), 6.93 (s, 2H), 6.70 (s, 1H), 6.44 (s, 1H), 4.97 (s, 1H), 4.42 (t, *J* = 8 Hz, 1H), 3.45-3.41 (m, 1H), 3.35-3.31 (m, 1H), 2.46 (s, 3H), 2.11 (s, 3H), 1.35 (s, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 159.5, 157.2, 151.8, 146.8, 144.8, 135.3, 135.1, 128.14, 128.11, 125.8, 124.6, 121.8, 121.4, 51.1, 44.8, 34.3, 30.3, 24.3, 20.7. IR (FT IR, cm^{-1}): 3312, 2949, 1612, 1439, 1223, 702. HRMS (m/z): calculated for $C_{29}H_{37}NO$ [M + H], 416.2947; found: 416.2939.

2,6-di-tert-butyl-4-(1-phenyl-2-(quinolin-4-yl)ethyl)phenol ***(3ea)***.



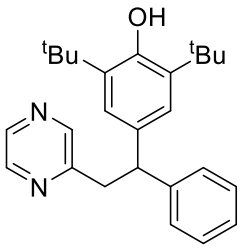
Off-white solid (22.5 mg, 50%); mp, 183.4-187.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.66 (d, *J* = 4.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.72-7.69 (m, 1H), 7.53-7.50 (m, 1H), 7.32-7.29 (m, 3H), 7.25-7.21 (m, 2H), 6.89 (s, 2H), 6.87 (d, *J* = 4.5 Hz, 1H), 5.06 (s, 1H), 4.34 (t, *J* = 7.6 Hz, 1H), 3.77 (d, *J* = 7.6 Hz, 2H), 1.35 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 152.3, 149.7, 148.2, 146.7, 144.2, 135.7, 134.3, 130.1, 128.9, 128.4, 127.9, 127.8, 126.4, 126.2, 124.4, 123.6, 122.1, 51.7, 38.9, 34.3, 30.2. IR (FT IR, cm^{-1}): 3339, 2943, 1591, 1431, 1228, 1114, 756. HRMS (m/z): calculated for $C_{31}H_{35}NO$ [M + H], 438.2791; found: 438.2787.

2,6-di-tert-butyl-4-(1-phenyl-2-(pyridin-4-yl)ethyl)phenol ***(3fa)***.



Off-white solid (83.7 mg, 64%, **1a** (100mg) used); mp, 169.3-172.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (d, *J* = 3.3 Hz, 2H), 7.27-7.24 (m, 2H), 7.20-7.16 (m, 3H), 6.93 (s, 2H), 6.91 (d, *J* = 4.3 Hz, 2H), 5.06 (s, 1 H), 4.11 (t, *J* = 7.8 Hz, 1H), 3.34-3.26 (m, 2H), 1.37 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 152.3, 150.5, 148.8, 143.9, 135.7, 134.1, 128.4, 127.9, 126.4, 124.8, 124.3, 52.3, 42.2, 34.4, 30.3. IR (FT IR, cm^{-1}): 3445, 2957, 1601, 1433, 1240, 1113, 700. HRMS (m/z): calculated for $C_{27}H_{33}NO$ [M + H], 388.2634; found: 388.2624.

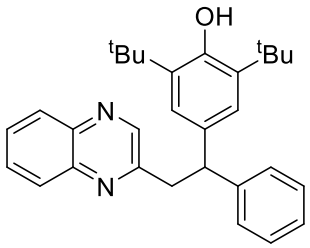
2,6-di-tert-butyl-4-(1-phenyl-2-(pyrazin-2-yl)ethyl)phenol ***(3ga)***.



Off-white solid (39.1 mg, 99%); mp, 128.6-131.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.47 (s, 1H), 8.30 (s, 1H), 8.11 (s, 1H), 7.25-7.24 (m, 4H), 7.16-7.14 (m, 1H), 6.98 (s, 2H), 5.04 (s, 1H), 4.47 (t, *J* = 8.0 Hz, 1H), 3.53-3.44 (m, 2H), 1.37 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 156.1, 152.2, 145.3, 143.9, 143.8, 141.9, 135.7, 134.1, 128.4, 127.9, 126.3,

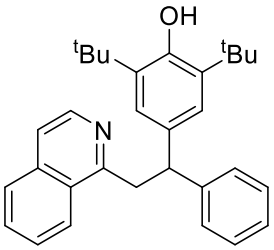
124.4, 50.9, 42.2, 34.3, 30.3. IR (FT IR, cm^{-1}): 3584, 2957, 1433, 1240, 1113, 698. HRMS (m/z): calculated for $C_{26}H_{32}N_2O$ [M + H], 389.2587; found: 389.2574.

2,6-di-tert-butyl-4-(1-phenyl-2-(quinoxalin-2-yl)ethyl)phenol ***(3ha)***.



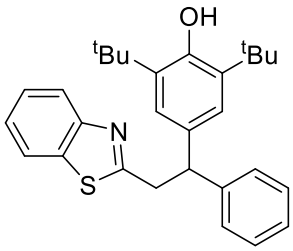
Brown solid (40.7 mg, 91%); mp, 149.7-156.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.34 (s, 1H), 8.04 (dd, *J* = 8.3, 0.9 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.75-7.66 (m, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.26-7.23 (m, 2H), 7.16-7.14 (m, 1H), 6.98 (s, 2H), 5.02 (s, 1H), 4.59 (t, *J* = 8.1 Hz, 1H), 3.75-3.65 (m, 2H), 1.32 (s, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 156.0, 152.3, 146.1, 143.9, 142.3, 141.0, 135.7, 134.0, 129.8, 129.1, 129.0, 128.8, 128.5, 127.9, 126.4, 124.5, 51.1, 43.0, 34.3, 30.3. IR (FT IR, cm^{-1}): 3487, 2963, 1433, 1238, 1117, 765, 698. HRMS (m/z): calculated for $C_{30}H_{34}N_2O$ [M + H], 439.2743; found: 439.2730.

2,6-di-tert-butyl-4-(2-(isoquinolin-1-yl)-1-phenylethyl)phenol ***(3ia)***.



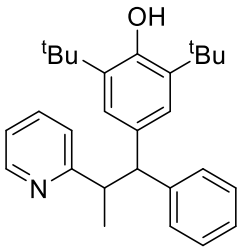
Off-white solid (41.3 mg, 93%); mp, 180.6-188.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.42 (d, *J* = 5.7 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.58-7.55 (m, 1H), 7.45 (d, *J* = 5.7 Hz, 1H), 7.41-7.38 (m, 1H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.26-7.22 (m, 2H), 7.16-7.13 (m, 1H), 6.83 (s, 2H), 4.90 (s, 1H), 4.70 (t, *J* = 7.8 Hz, 1H), 4.01-3.88 (m, 2H), 1.25 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.6, 151.9, 144.6, 141.8, 136.1, 135.3, 134.8, 129.5, 128.2, 128.1, 127.7, 127.1, 126.7, 125.9, 125.3, 124.6, 119.1, 51.2, 41.3, 34.2, 30.2. IR (FT IR, cm^{-1}): 3422, 2951, 1431, 1357, 1078, 704. HRMS (m/z): calculated for $C_{31}H_{35}NO$ [M + H], 438.2791; found: 438.2778.

4-(2-(benzo[d]thiazol-2-yl)-1-phenylethyl)-2,6-di-tert-butylphenol ***(3ja)***.



White solid (24.2 mg, 54%); mp, 167.9-169.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.43-7.40 (m, 1H), 7.34-7.32 (m, 2H), 7.30-7.26 (m, 3H), 7.19-7.16 (m, 1H), 7.06 (s, 2H), 5.05 (s, 1H), 4.56 (t, *J* = 8 Hz, 1H), 3.88-3.75 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 170.4, 152.9, 152.4, 143.5, 135.8, 135.3, 133.8, 128.5, 127.9, 126.5, 125.8, 124.6, 124.4, 122.5, 121.4, 51.2, 41.1, 34.4, 30.3. IR (FT IR, cm^{-1}): 3568, 2957, 1433, 1101, 802, 696. HRMS (m/z): calculated for $C_{29}H_{33}NOS$ [M + H], 444.2355; found 444.2353.

2,6-di-tert-butyl-4-(1-phenyl-2-(pyridin-2-yl)propyl)phenol ***(3ka)***.



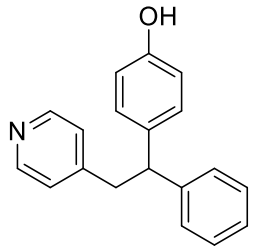
Brown gummy oil (31.6 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.51 (d, *J* = 4.7 Hz, 1H), 8.47 (d, *J* = 4.8 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.38 (td, *J* = 7.6, 1.6 Hz, 1H), 7.34-7.31 (m, 3H), 7.21-7.16 (m, 5H), 7.06-7.03 (m, 2H), 6.96-6.93 (m, 4H), 6.81 (s, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.01 (s, 1H), 4.81 (s, 1H), 4.18 (t, *J* = 11.4, 2H), 3.70-3.58 (m, 2H), 1.43 (s, 18H), 1.26-1.24 (m, 21H), 1.21 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 165.24, 165.18, 152.1, 151.4, 149.0, 148.9, 144.7, 144.2, 135.9, 135.64, 135.61, 134.9, 134.3, 134.2, 128.5, 128.1, 127.9, 126.0, 125.4, 124.8, 124.7, 123.5, 122.9, 120.9, 120.8, 58.1, 57.9, 47.4, 47.0, 34.4, 34.2, 30.4, 30.3, 20.7, 20.1. IR (FT IR, cm^{-1}): 3639, 3427, 2959, 1593, 1435, 1232, 700. HRMS (m/z): calculated for $C_{28}H_{35}NO$ [M + H], 402.2791; found: 402.2791.

Procedure for de *tert*-butylation of 2,6-di-*tert*-butyl-4-(1-phenyl-2-(pyridin-4-yl)ethyl)phenol (4a)[8]

A flame-dried round bottom flask equipped with a magnetic stirring bar, was charged with 2,6-di-*tert*-butyl-4-(1-phenyl-2-(pyridin-4-yl)ethyl)phenol (**3fa**) (150 mg, 1 equiv) in toluene (35

mL) at room temperature. Then a solution of $AlCl_3$ (311.2 mg, 6 equiv) in $MeNO_2$ (2 mL) was added in one portion. The mixture was immediately heated to 60 °C by using a preheated oil bath and maintained at the same temperature for 10 min. The mixture was subsequently cooled and poured into a separating funnel containing ice and Et_2O (1:1, 50 mL). The aqueous layer was extracted with Et_2O (3 x 50 mL). The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel and afforded the desired product as a white solid.

4-(1-phenyl-2-(pyridin-4-yl)ethyl)phenol ***(4a)***.[9]



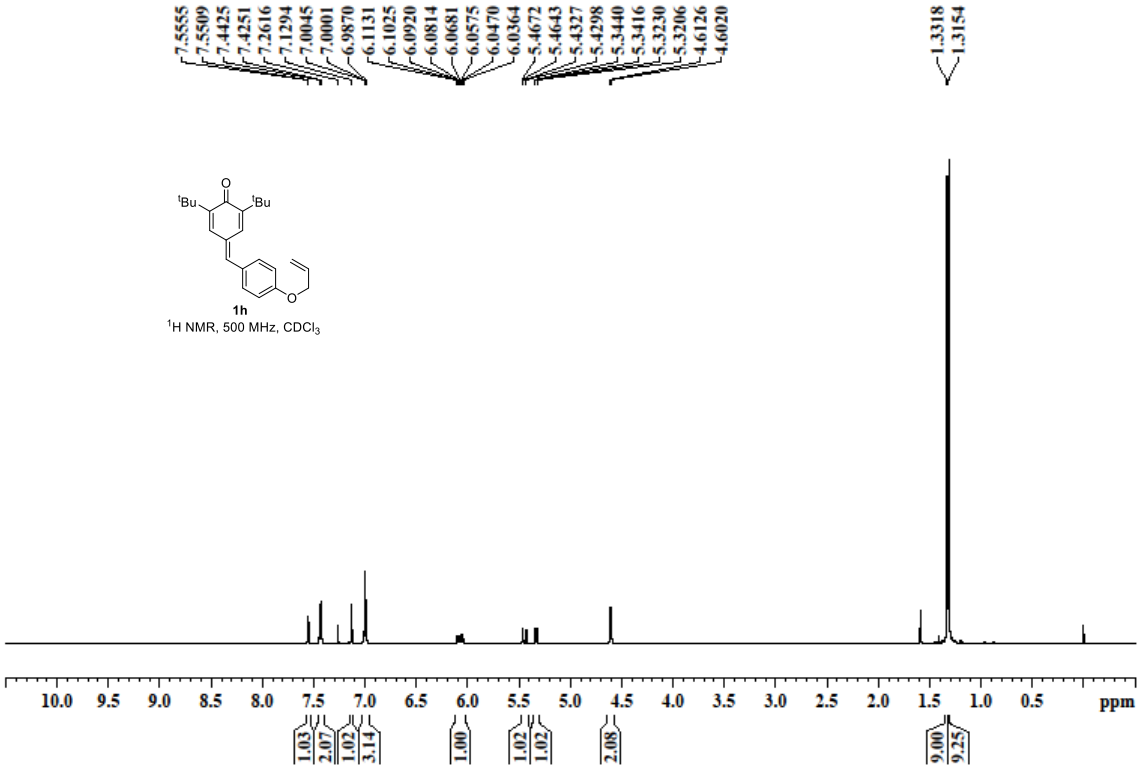
Off-white solid (93 mg, 87%); mp, 155.8-158.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.36 (d, J = 4.3 Hz, 2H), 7.28-7.25 (m, 3H), 7.20-7.17 (m, 3H), 6.97 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 4.7 Hz, 2H), 6.71 (d, J = 8.3 Hz, 2H), 4.14 (t, J = 7.9 Hz, 1H), 3.35-3.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.9, 150.1, 148.9, 144.0, 135.1, 129.0, 128.5, 127.7, 126.5, 124.8, 115.5, 51.4, 41.7. IR (FT IR, cm^{-1}): 3024, 2604, 1604, 1510, 1253, 833, 804, 559. HRMS (m/z): calculated for $C_{19}H_{17}NO$ [M + H], 276.1382; found 276.1380.

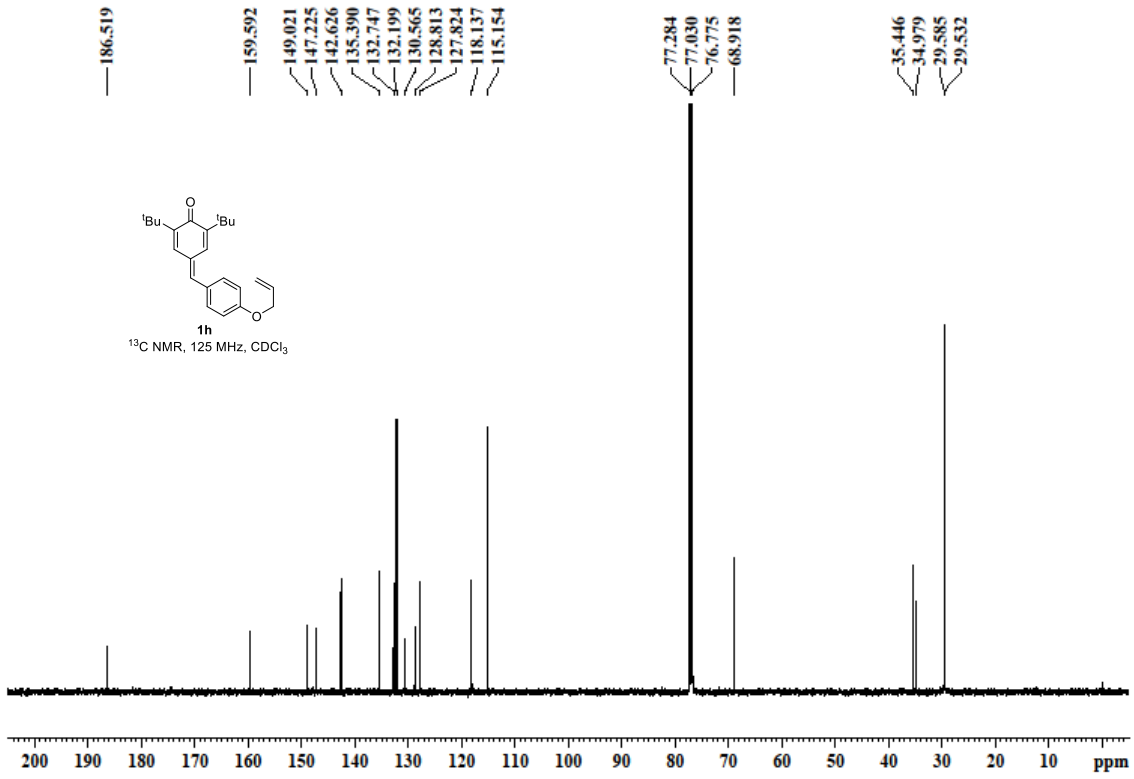
Crystal data and structure refinement for 3aa.

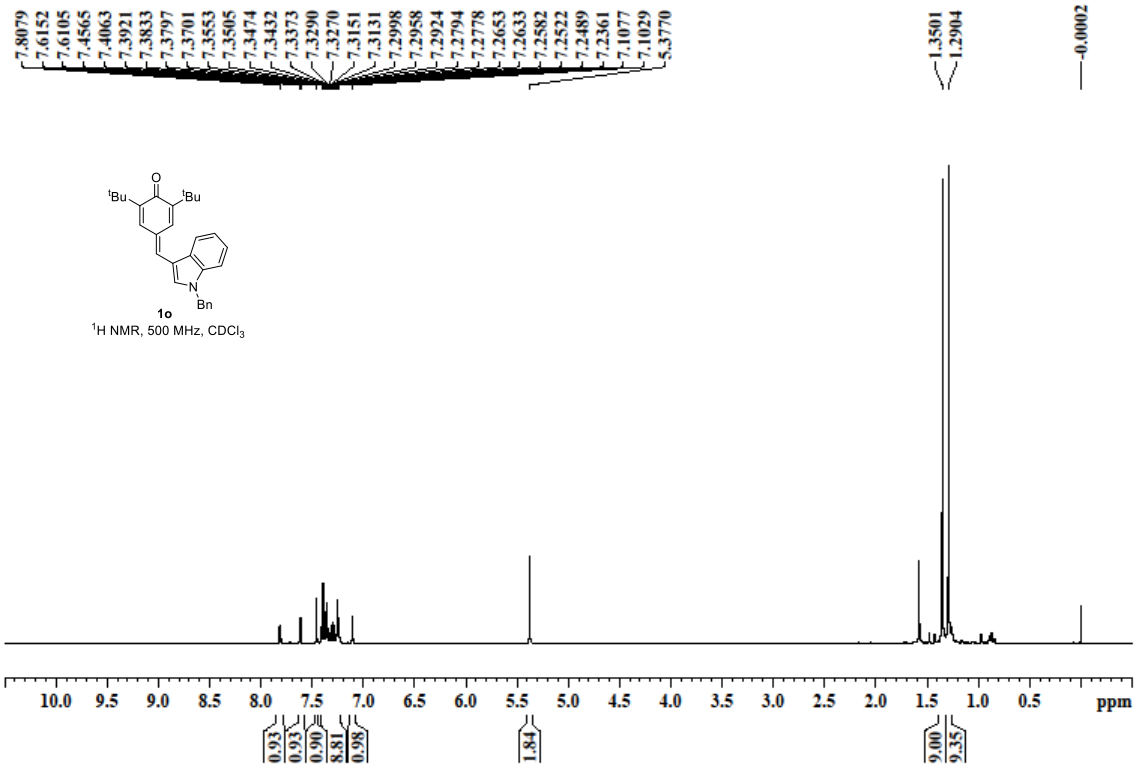
Identification code	Compound_3aa	
CCDC code	1979112	
Empirical formula	C27 H33 N O	
Formula weight	387.54	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.3170(9) Å	α= 90°.
	b = 18.704(2) Å	β= 93.967(4)°.
	c = 13.6865(14) Å	γ = 90°.
Volume	2379.4(4) $Å^3$	
Z	4	
Density (calculated)	1.082 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	840	
Crystal size	0.180 x 0.140 x 0.110 mm^3	
Theta range for data collection	2.178 to 24.998°.	
Index ranges	-10<=h<=11, -22<=k<=22, -16<=l<=16	
Reflections collected	32653	
Independent reflections	4184 [R(int) = 0.0426]	
Completeness to theta = 24.998°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.993 and 0.988	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4184 / 0 / 269	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1319	
R indices (all data)	R1 = 0.0955, wR2 = 0.1646	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.212 and -0.184 $e.Å^{-3}$	

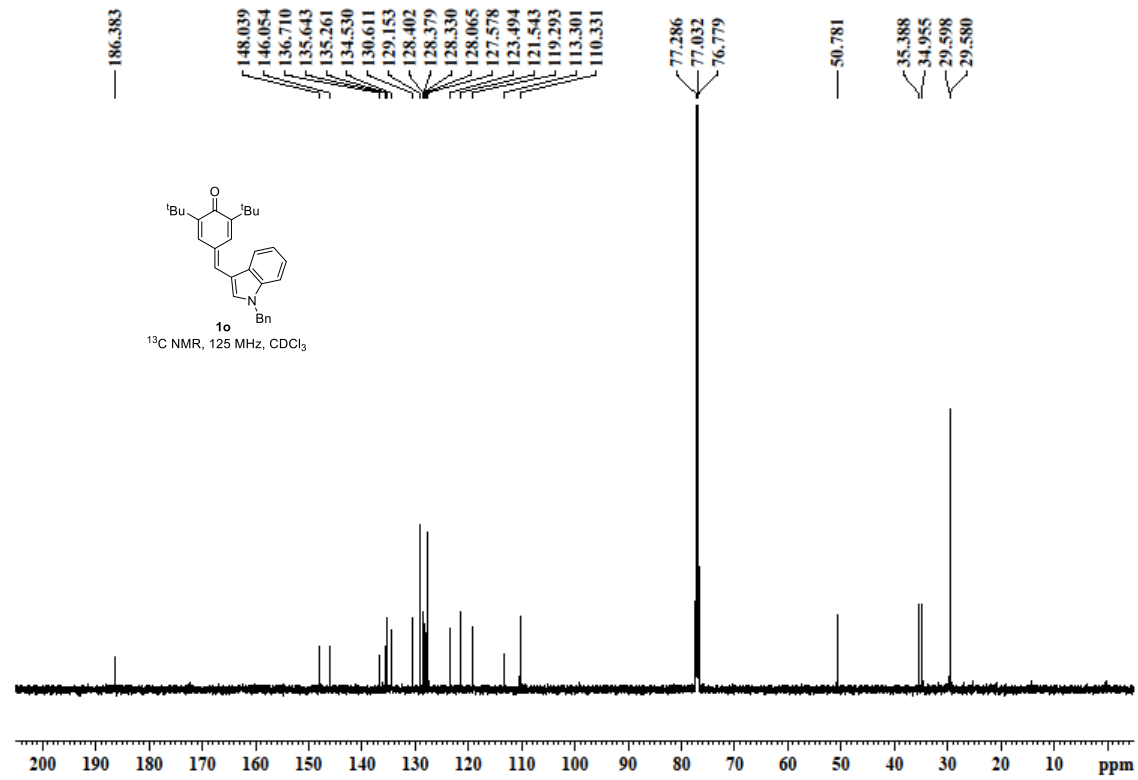
References

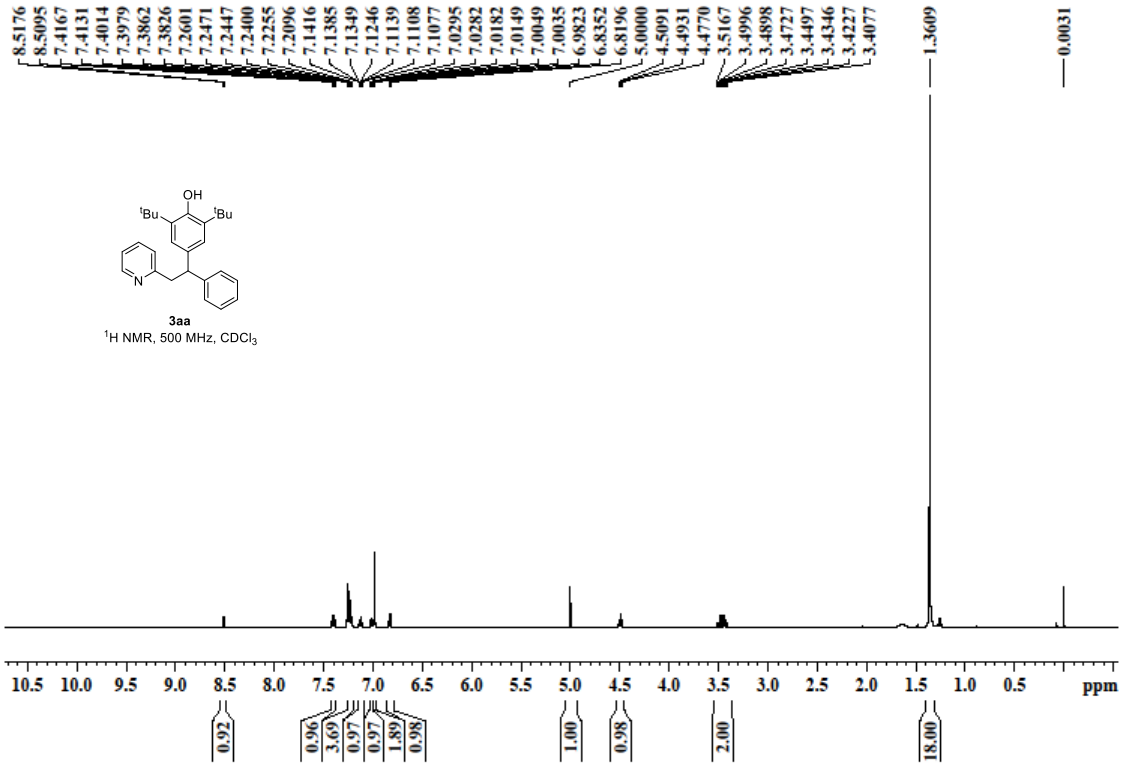
1. A. López, A. Parra, C. Jarava-Barrera and M. Tortosa, *Chem. Commun.,* 2015, **51**, 17684.
2. Y. Lou, P. Cao, T. Jia, Y. Zhang, M. Wang and J. Liao, *Angew. Chem. Int. Ed.,* 2015, **54**, 12134.
3. W.-D. Chu, L.-F. Zhang, X. Bao, X.-H. Zhao, C. Zeng, J.-Y. Du, G.-B. Zhang, F.-X. Wang, X.-Y. Ma and C.-A. Fan, *Angew. Chem. Int. Ed*., 2013, **52**, 9229.
4. K. G. Ghosh, P. Chandu, S. Mondal and D. Sureshkumar, *Tetrahedron,* 2019, **75**, 4471.
5. V. Reddy and R.V. Anand, *Org. Lett*., 2015, **17**, 3390.
6. S. Santra, A. Porey and J. Guin, *Asian J. Org. Chem*., 2018, **7**, 477.
7. L. Wang, Y.-X. Jia, J.-M. Zhang, C. Qian and X.-Z. Chen, *Monatsh Chem.* 2014, **145**, 1941.
8. J. R. Frost, C. B. Cheong and T. J. Donohoe, *Synthesis,* 2017, **49**, 910.
9. S. A. Haroutonian, A. W. Scribner and J. A. Katzenellenbogen, *Steroids,* 1995, **60**, 636.

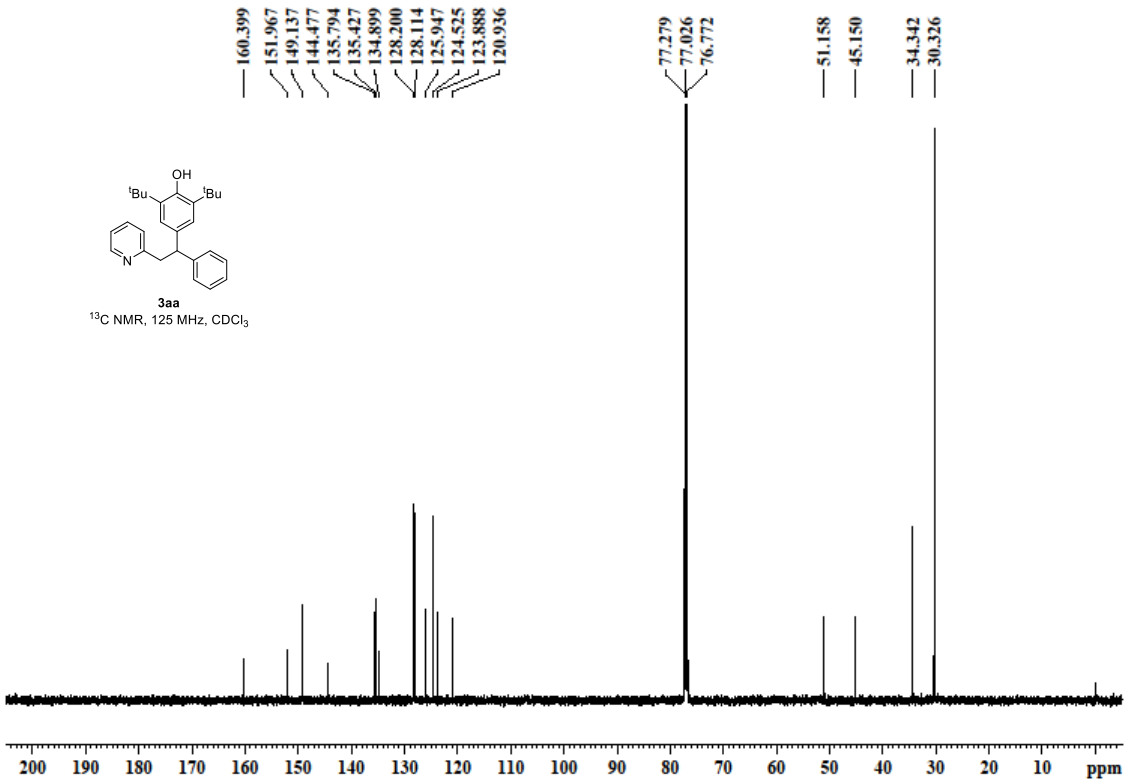

7.5555
7.5509
7.4425
7.4251
7.2616
7.1294
7.0045
7.0001
6.9870
6.1131
6.1025
6.0920
6.0814
6.0681
6.0575
6.0470
6.0364
5.4672
5.4643
5.4327
5.4298
5.3440
5.3416
5.3230
5.3206
4.6126
4.6020
1.3318
1.3154
tBu
tBu
O
O
1h
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03
2.07
1.02
3.14
1.00
1.02
1.02
2.08
9.00
9.25

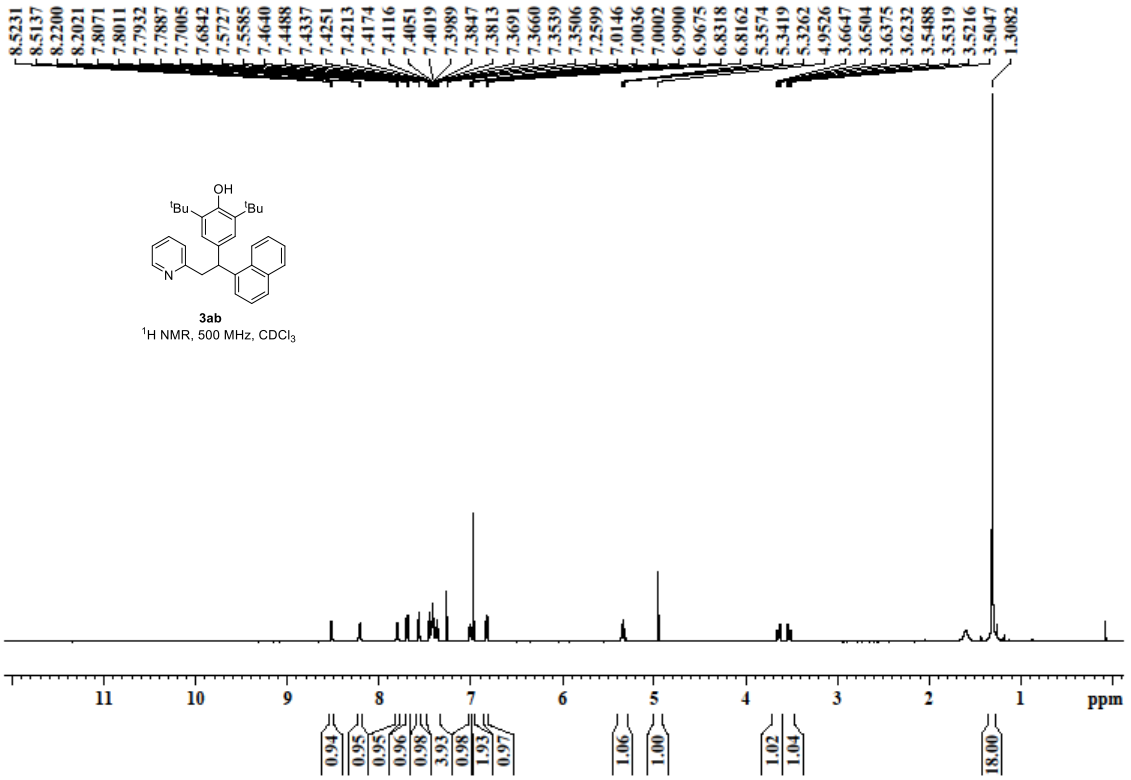

186.519
159.592
149.021
147.225
142.626
135.390
132.747
132.199
130.565
128.813
127.824
118.137
115.154
77.284
77.030
76.775
68.918
35.446
34.979
29.585
29.532
tBu
tBu
O
O
1h
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

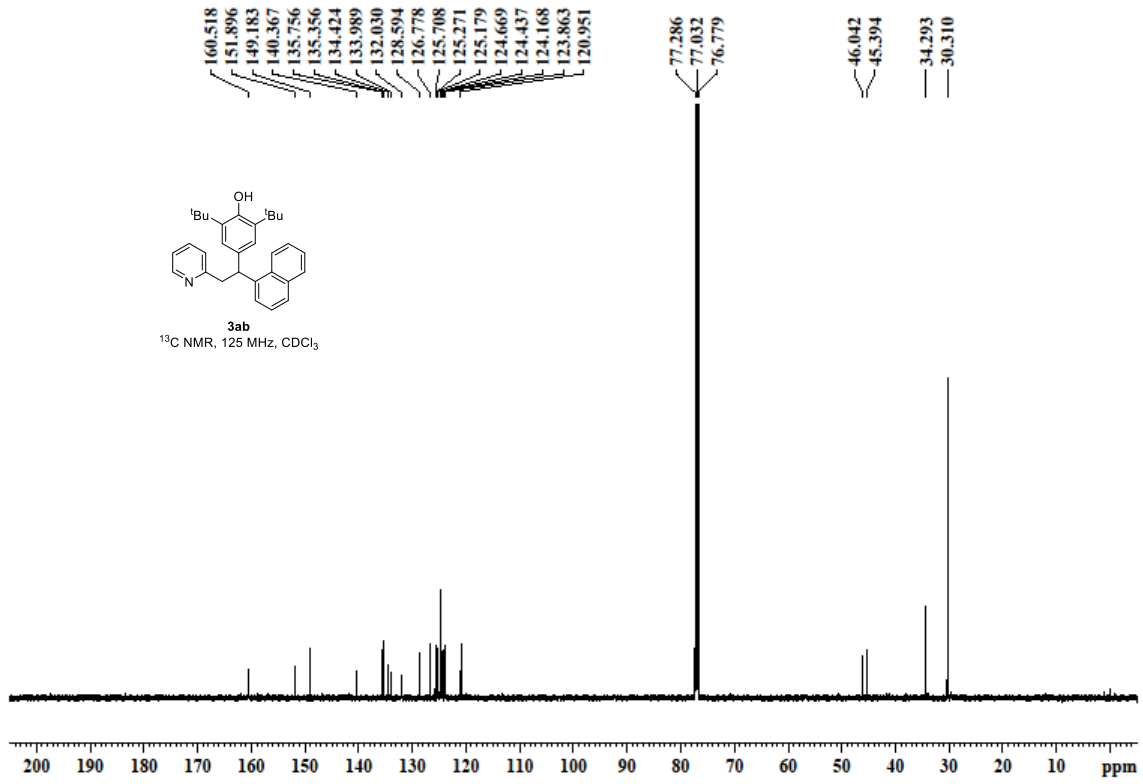

7.8079
7.6152
7.6105
7.4565
7.4063
7.3921
7.3833
7.3797
7.3701
7.3553
7.3505
7.3474
7.3432
7.3373
7.3290
7.3270
7.3151
7.3131
7.2998
7.2958
7.2924
7.2794
7.2778
7.2653
7.2633
7.2582
7.2522
7.2489
7.2361
7.1077
7.1029
5.3770
1.3501
1.2904
-0.0002
tBu
tBu
O
N
Bn
1o
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.93
0.93
0.90
8.81
0.98
1.84
9.00
9.35

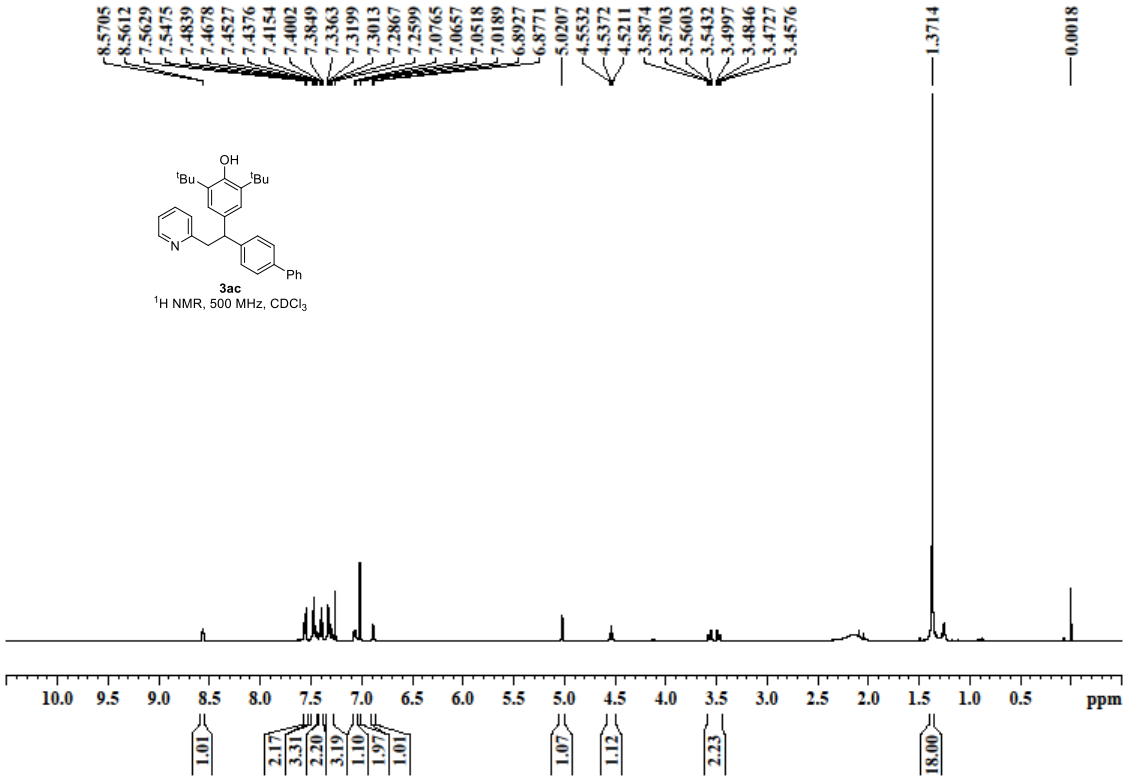

186.383
148.039
146.054
136.710
135.643
135.261
134.530
130.611
129.153
128.402
128.379
128.330
128.065
127.578
123.494
121.543
119.293
113.301
110.331
77.286
77.032
76.779
50.781
35.388
34.955
29.598
29.580
tBu
tBu
O
N
Bn
1o
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

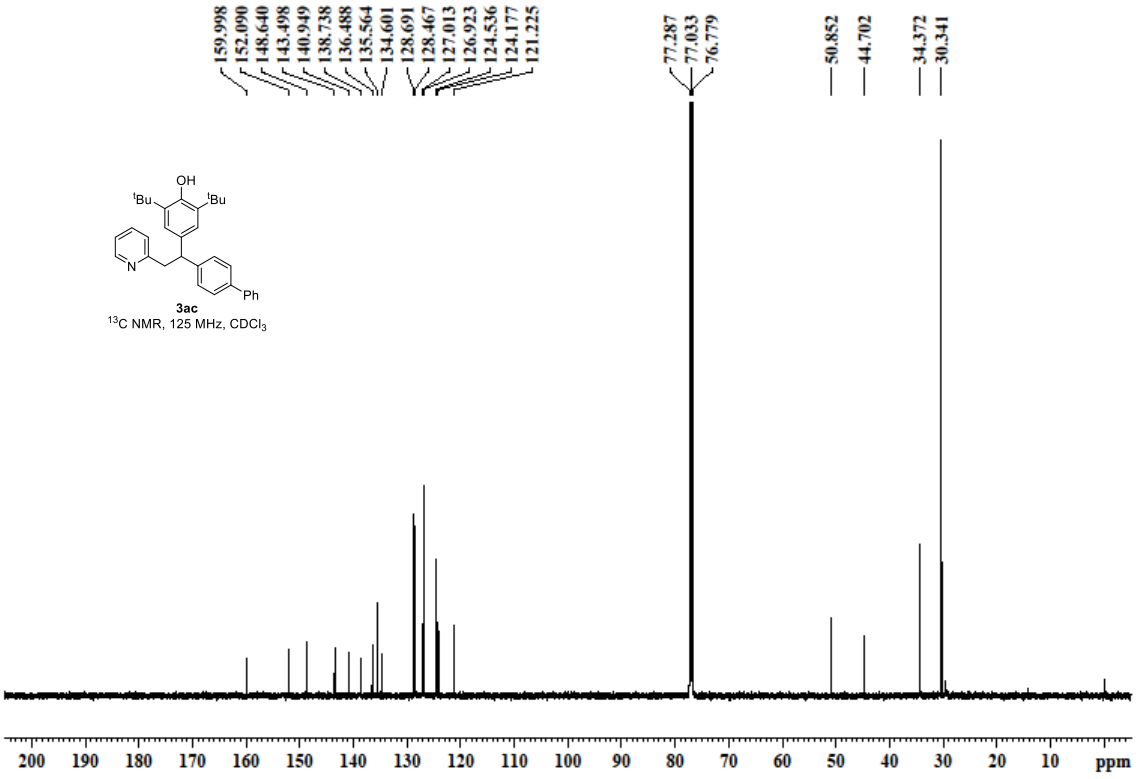

8.5176
8.5095
7.4167
7.4131
7.4014
7.3979
7.3862
7.3826
7.2601
7.2471
7.2447
7.2400
7.2255
7.2096
7.1416
7.1385
7.1349
7.1246
7.1139
7.1108
7.1077
7.0295
7.0282
7.0182
7.0149
7.0049
7.0035
6.9823
6.8352
6.8196
5.0000
4.5091
4.4931
4.4770
3.5167
3.4996
3.4898
3.4727
3.4497
3.4346
3.4227
3.4077
1.3609
0.0031
OH
tBu
tBu
N
3aa
1H NMR, 500 MHz, CDCl3
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.92
0.96
3.69
0.97
0.97
1.89
0.98
1.00
0.98
2.00
18.00

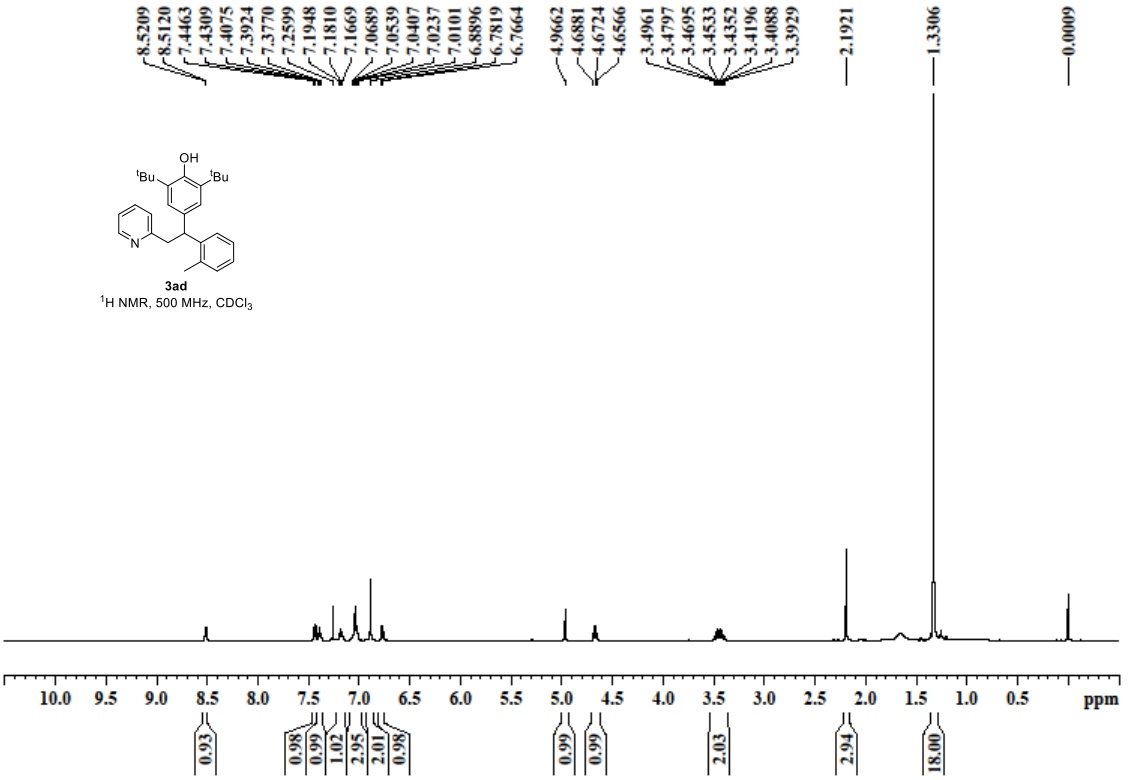

160.399
151.967
149.137
144.477
135.794
135.427
134.899
128.200
128.114
125.947
124.525
123.888
120.936
77.279
77.026
76.772
51.158
45.150
34.342
30.326
OH
tBu
tBu
N
3aa
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

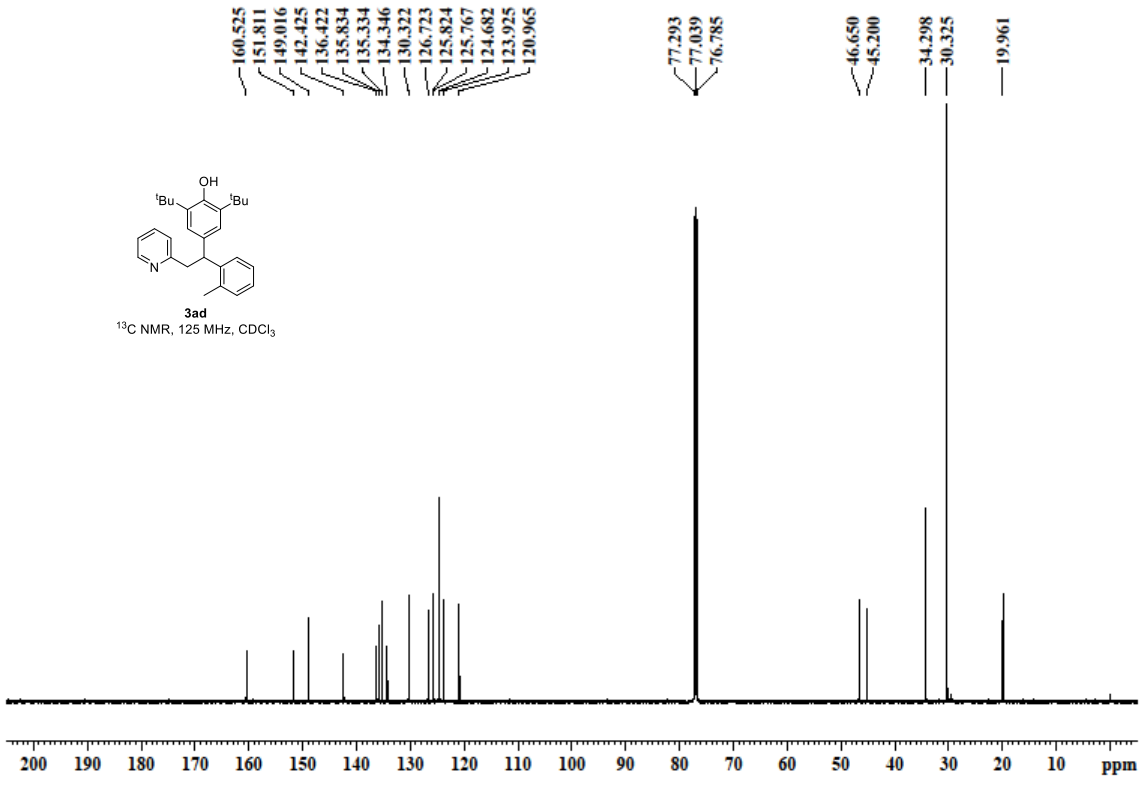

8.5231
8.5137
8.2200
8.2021
8.1071
7.8011
7.7932
7.7887
7.7005
7.6842
7.5727
7.5585
7.4640
7.4488
7.4337
7.4251
7.4213
7.4174
7.4116
7.4051
7.4019
7.3989
7.3847
7.3813
7.3691
7.3660
7.3539
7.3506
7.2599
7.0146
7.0036
7.0002
6.9900
6.9675
6.8318
6.8162
5.3574
5.3419
5.3262
4.9526
3.6647
3.6504
3.6375
3.6232
3.5488
3.5319
3.5216
3.5047
1.3082
OH
tBu
tBu
N
3ab
1H NMR, 500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
ppm
0.94
0.95
0.95
0.96
0.98
3.93
0.98
1.93
0.97
1.06
1.00
1.02
1.04
18.00

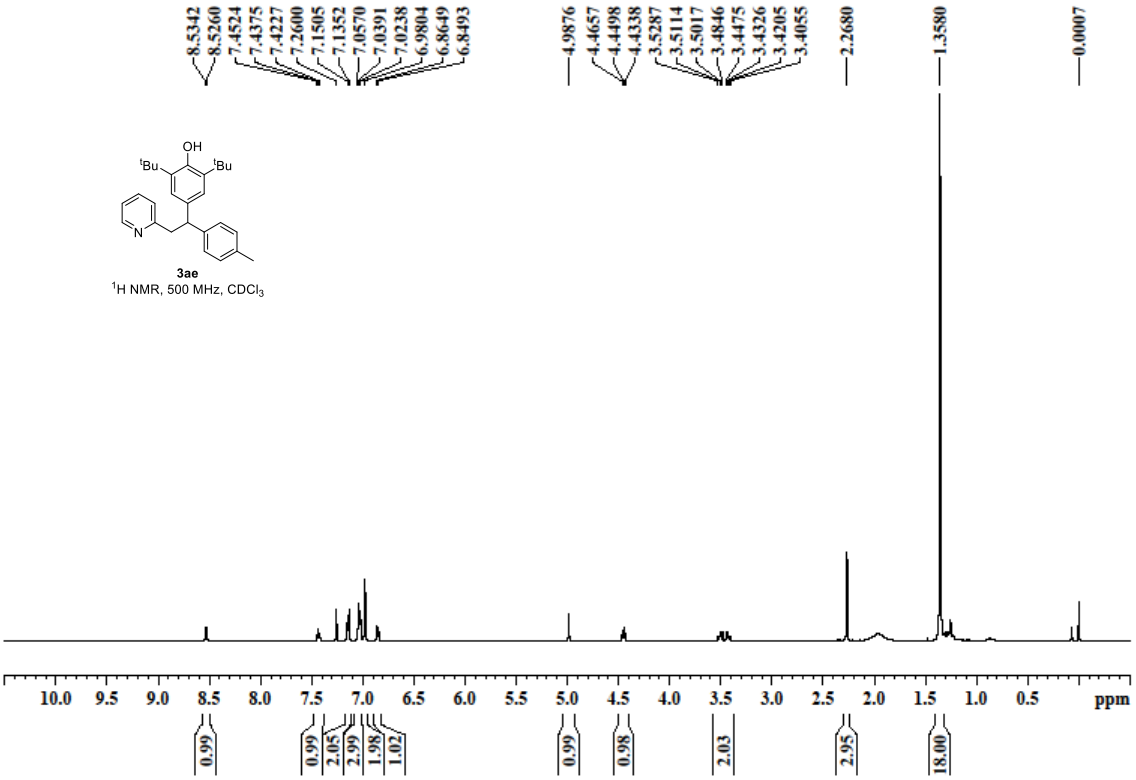

160.518
151.896
149.183
140.367
135.756
135.356
134.424
133.989
132.030
128.594
126.778
125.708
125.271
125.179
124.669
124.437
124.168
123.863
120.951
77.286
77.032
76.779
46.042
45.394
34.293
30.310
OH
tBu
tBu
N
3ab
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

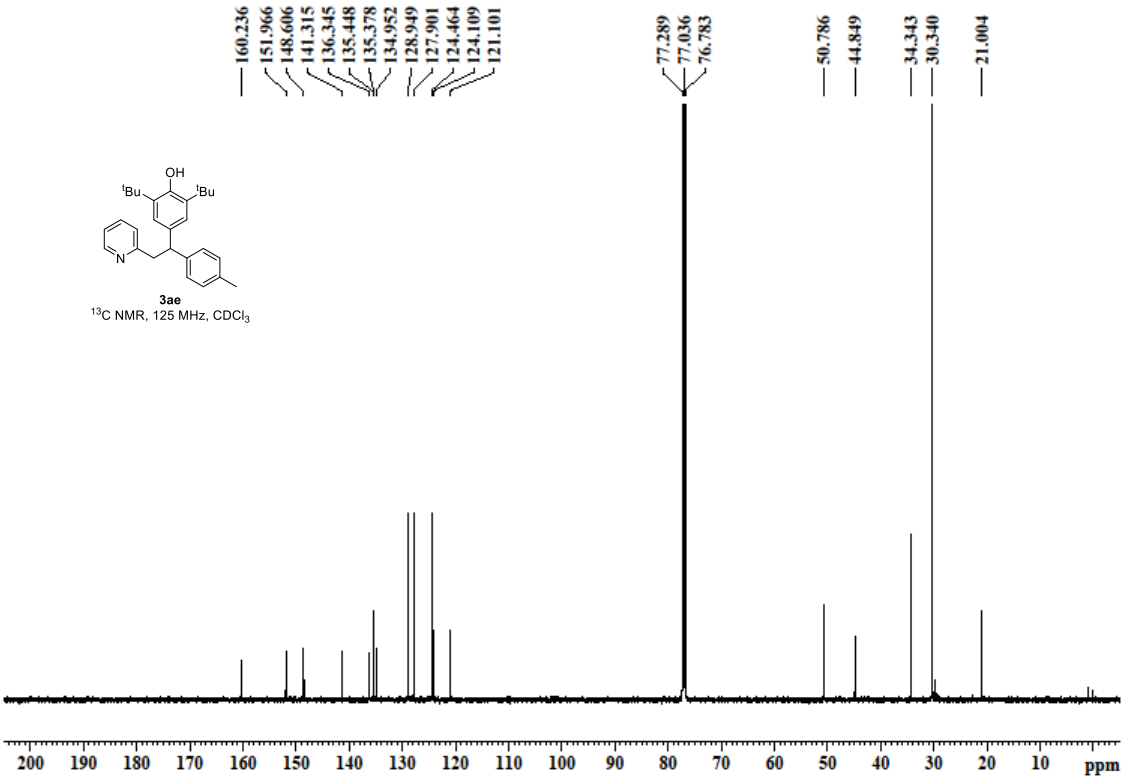

8.5705
8.5612
7.5629
7.5475
7.4839
7.4678
7.4527
7.4376
7.4154
7.4002
7.3849
7.3363
7.3199
7.3013
7.2867
7.2599
7.0765
7.0657
7.0518
7.0189
6.8927
6.8771
5.0207
4.5532
4.5372
4.5211
3.5874
3.5703
3.5603
3.5432
3.4997
3.4846
3.4727
3.4576
1.3714
0.0018
OH
tBu
tBu
N
Ph
3ac
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.01
2.17
3.31
2.20
3.19
1.10
1.97
1.01
1.07
1.12
2.23
18.00

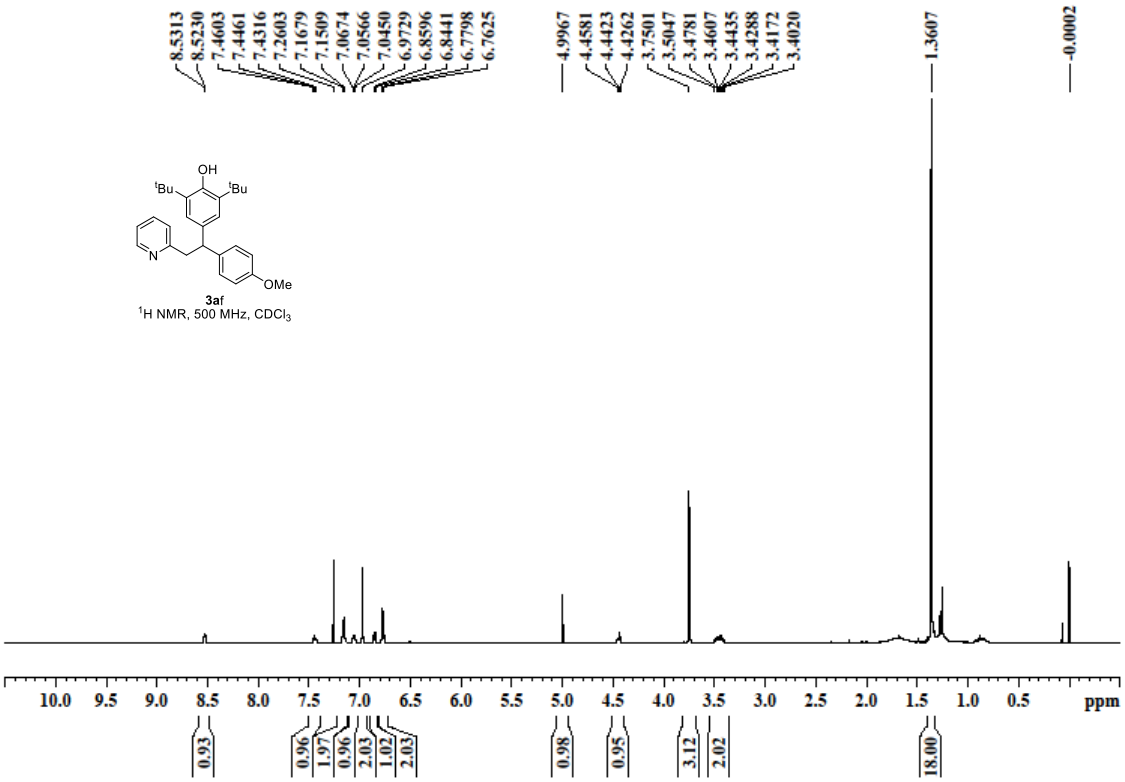

159.998
152.090
148.640
143.498
140.949
138.738
136.488
135.564
134.601
128.691
128.467
127.013
126.923
124.536
124.177
121.225
77.287
77.033
76.779
50.852
44.702
34.372
30.341
OH
tBu
tBu
N
Ph
3ac
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

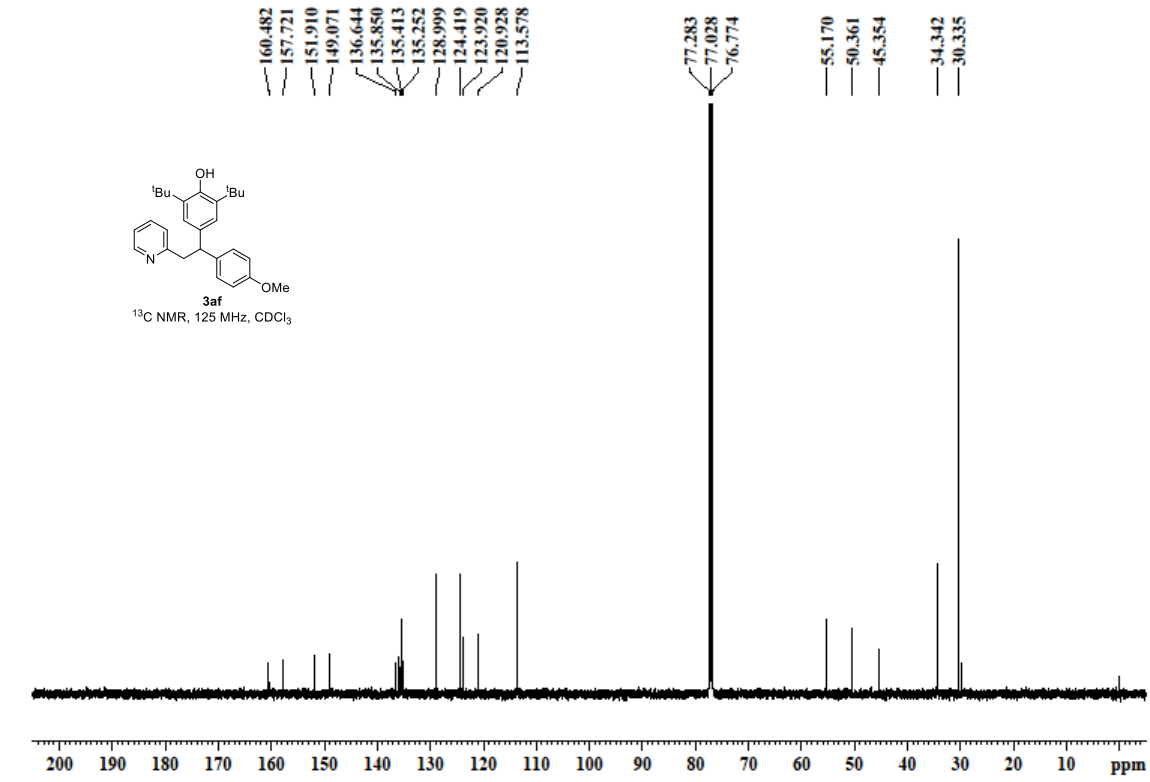

8.5209
8.5120
7.4463
7.4309
7.4075
7.3924
7.3770
7.2599
7.1948
7.1810
7.1669
7.0689
7.0539
7.0407
7.0237
7.0101
6.8896
6.7819
6.7664
4.9662
4.6881
4.6724
4.6566
3.4961
3.4797
3.4695
3.4533
3.4352
3.4196
3.4088
3.3929
2.1921
1.3306
0.0009
OH
tBu
tBu
N
3ad
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.93
0.98
0.99
1.02
2.95
2.01
0.98
0.99
0.99
2.03
2.94
18.00

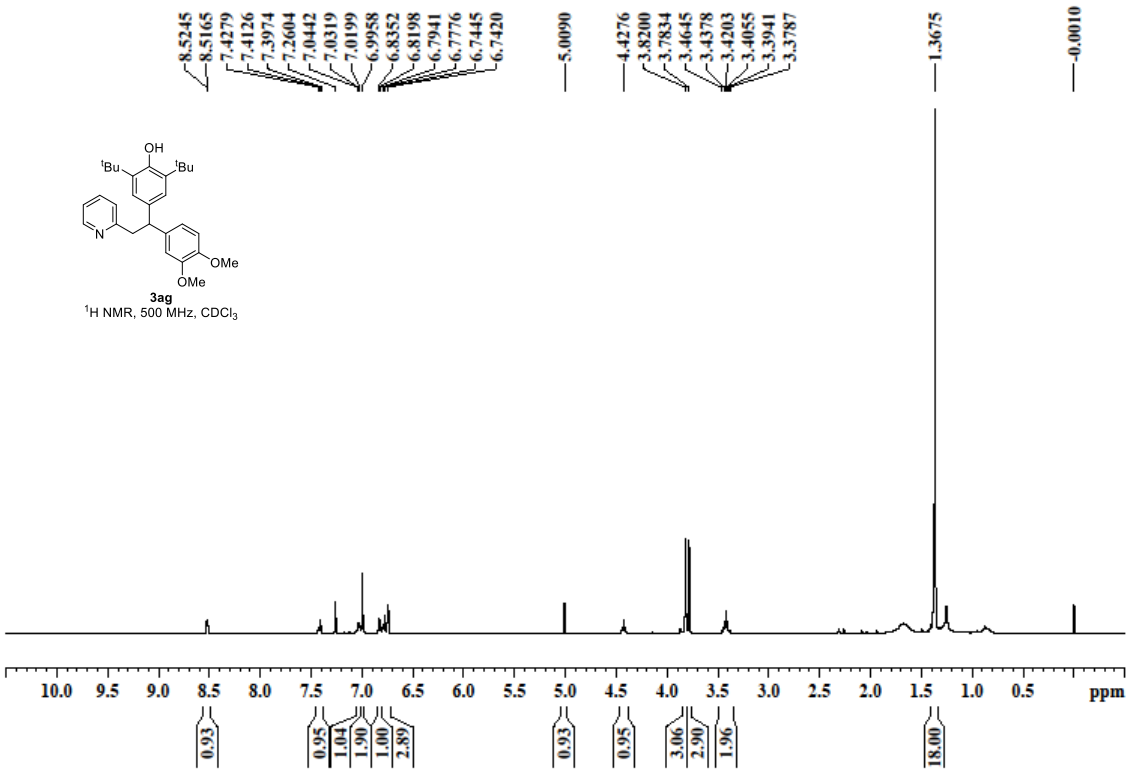

160.525
151.811
149.016
142.425
136.422
135.834
135.334
134.346
130.322
126.723
125.824
125.767
124.682
123.925
120.965
77.293
77.039
76.785
46.650
45.200
34.298
30.325
19.961
OH
tBu
tBu
N
3ad
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

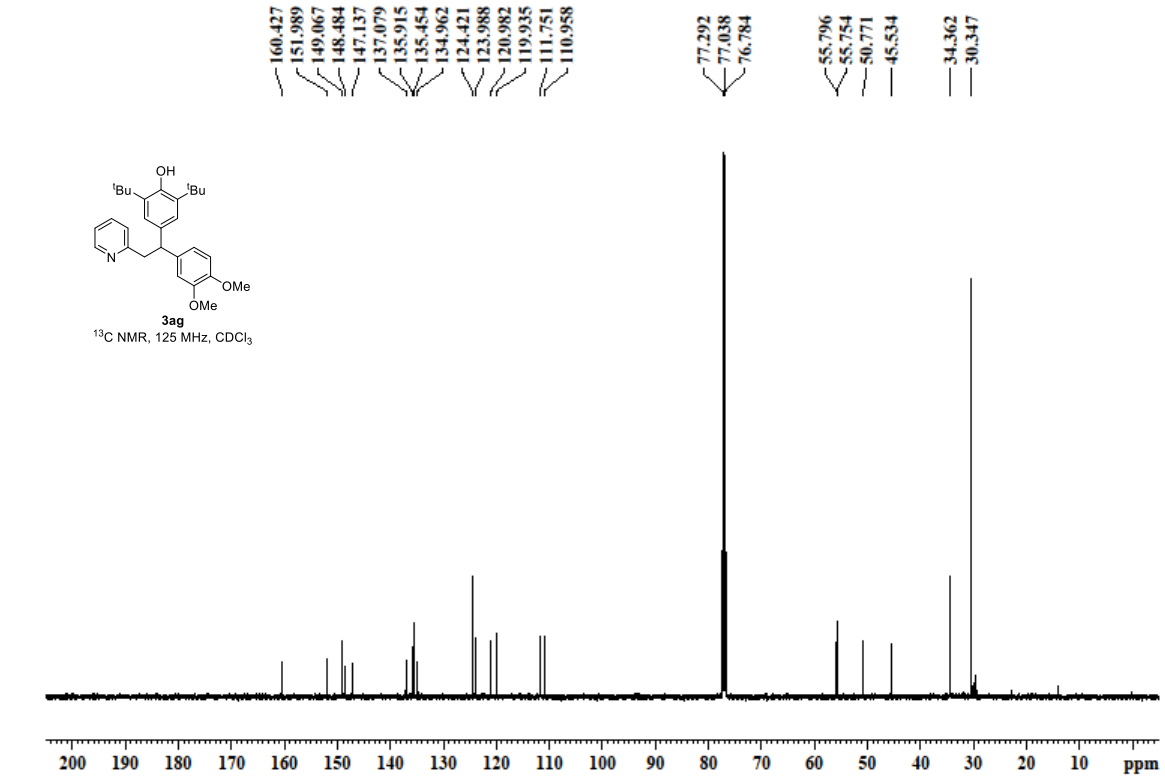

8.5342
8.5260
7.4524
7.4375
7.4227
7.2600
7.1505
7.1352
7.0570
7.0391
7.0238
6.9804
6.8649
6.8493
4.9876
4.4657
4.4498
4.4338
3.5287
3.5114
3.5017
3.4846
3.4475
3.4326
3.4205
3.4055
2.2680
1.3580
0.0007
OH
tBu
tBu
N
3ae
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
0.99
2.05
2.99
1.98
1.02
0.99
0.98
2.03
2.95
18.00

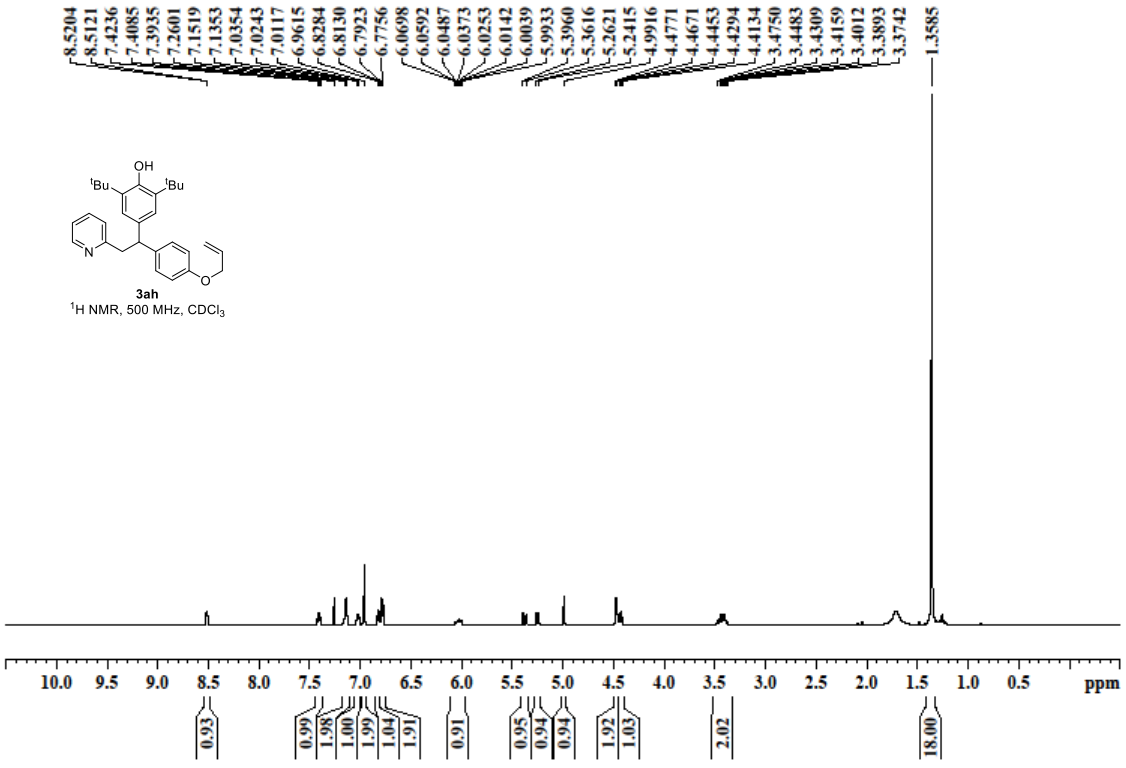

160.236
151.966
148.606
141.315
136.345
135.448
135.378
134.952
128.949
127.901
124.464
124.109
121.101
77.289
77.036
76.783
50.786
44.849
34.343
30.340
21.004
OH
tBu
tBu
N
3ae
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

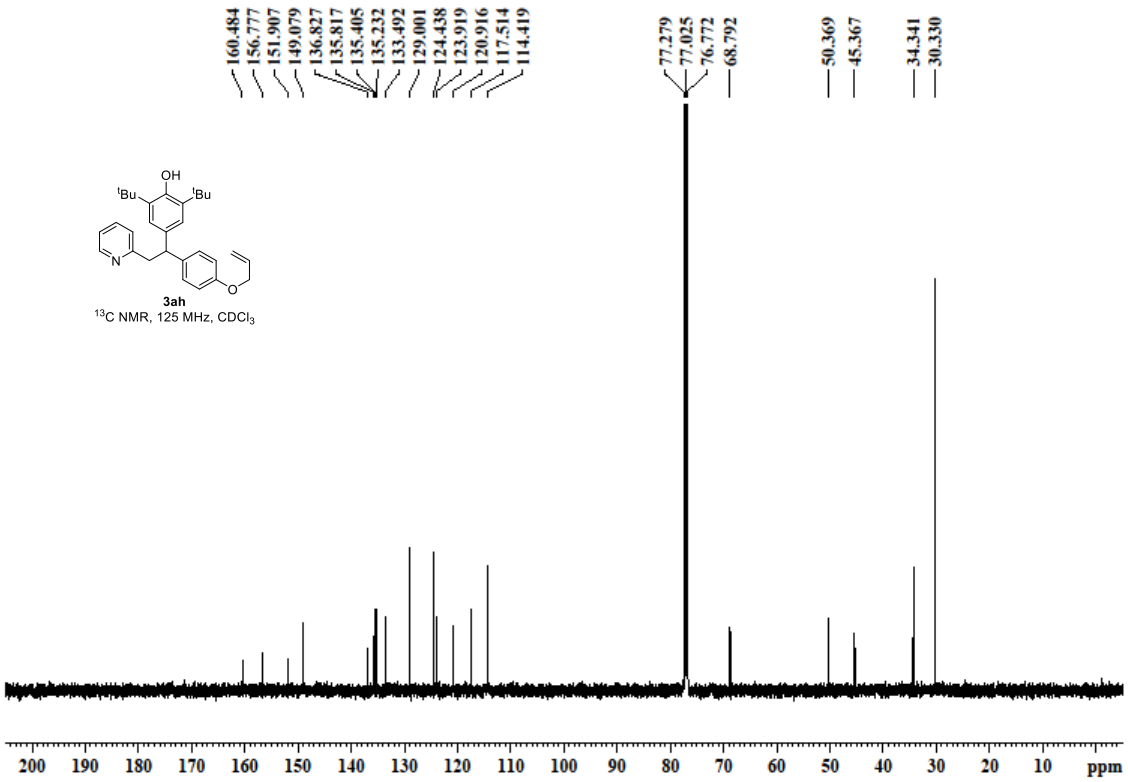

8.5313
8.5230
7.4603
7.4461
7.4316
7.2603
7.1679
7.1509
7.0674
7.0566
7.0450
6.9729
6.8596
6.8441
6.7798
6.7625
4.9967
4.4581
4.4423
4.4262
3.7501
3.5047
3.4781
3.4607
3.4435
3.4288
3.4172
3.4020
1.3607
-0.0002
OH
tBu
tBu
N
OMe
3af
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.93
0.96
1.97
0.96
2.03
1.02
2.03
0.98
0.95
3.12
2.02
18.00

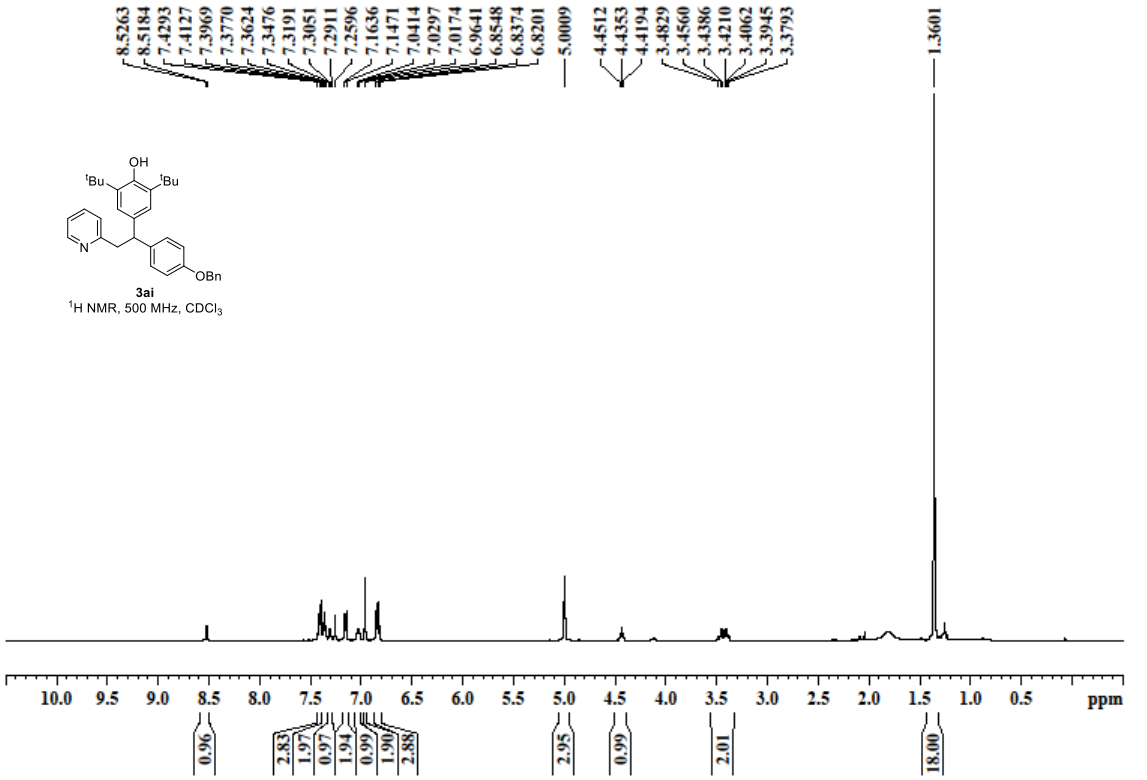

160.482
157.721
151.910
149.071
136.644
135.850
135.413
135.252
128.999
124.419
123.920
120.928
113.578
77.283
77.028
76.774
55.170
50.361
45.354
34.342
30.335
OH
tBu
tBu
N
OMe
3af
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

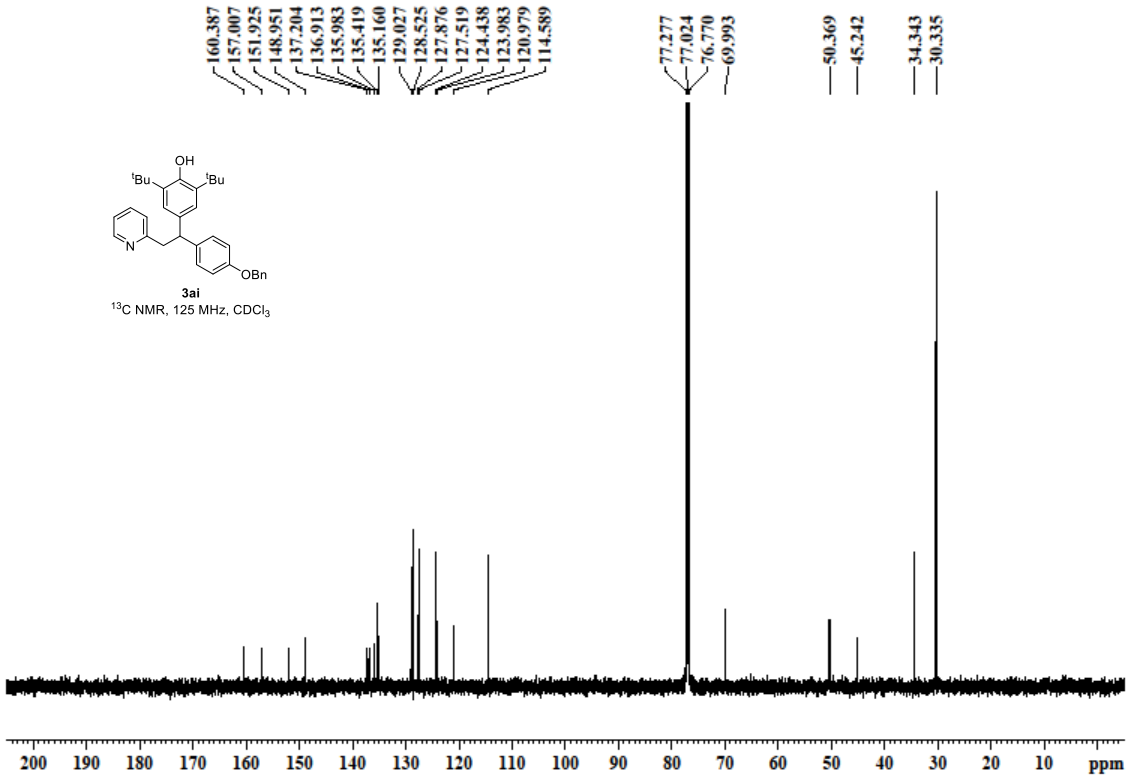

8.5245
8.5165
7.4279
7.4126
7.3974
7.2604
7.0442
7.0319
7.0199
6.9958
6.8352
6.8198
6.7941
6.7776
6.7445
6.7420
5.0090
4.4276
3.8200
3.7834
3.4645
3.4378
3.4203
3.4055
3.3941
3.3787
1.3675
-0.0010
OH
tBu
tBu
OMe
OMe
3ag
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.93
0.95
1.04
1.90
1.00
2.89
0.93
0.95
3.06
2.90
1.96
18.00

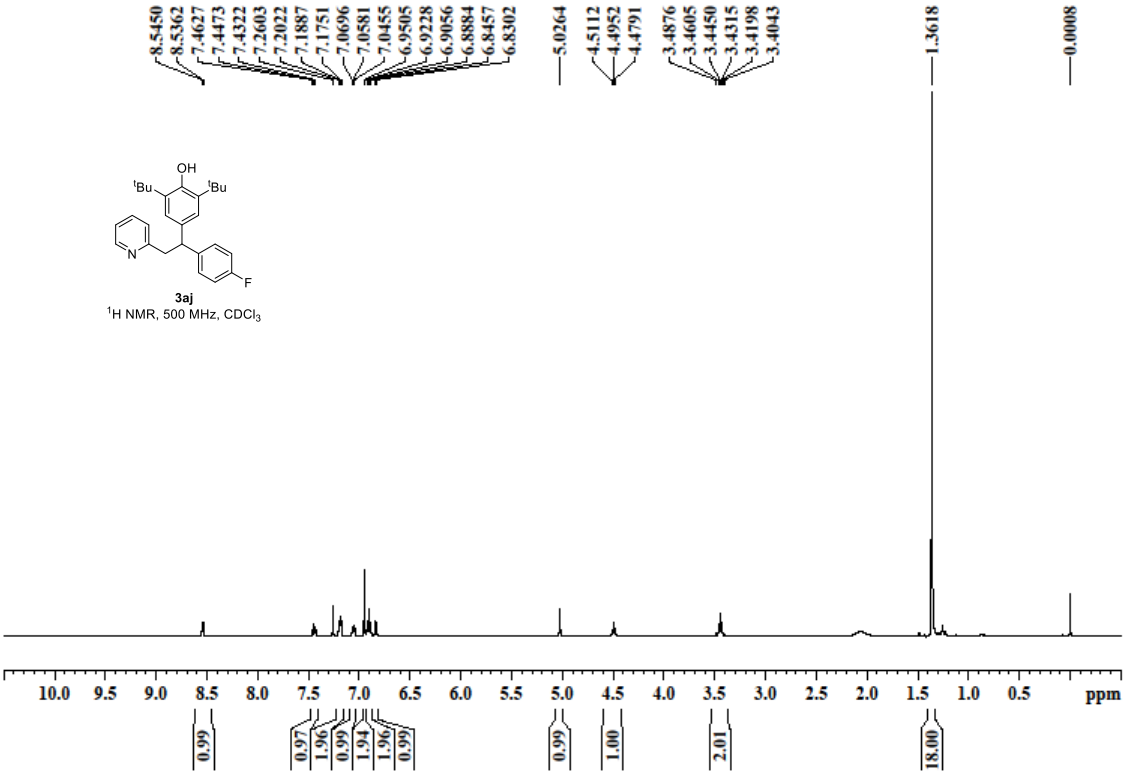

160.427
151.989
149.067
148.484
147.137
137.079
135.915
135.454
134.962
124.421
123.988
120.982
119.935
111.751
110.958
77.292
77.038
76.784
55.796
55.754
50.771
45.534
34.362
30.347
OH
tBu
tBu
OMe
OMe
3ag
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

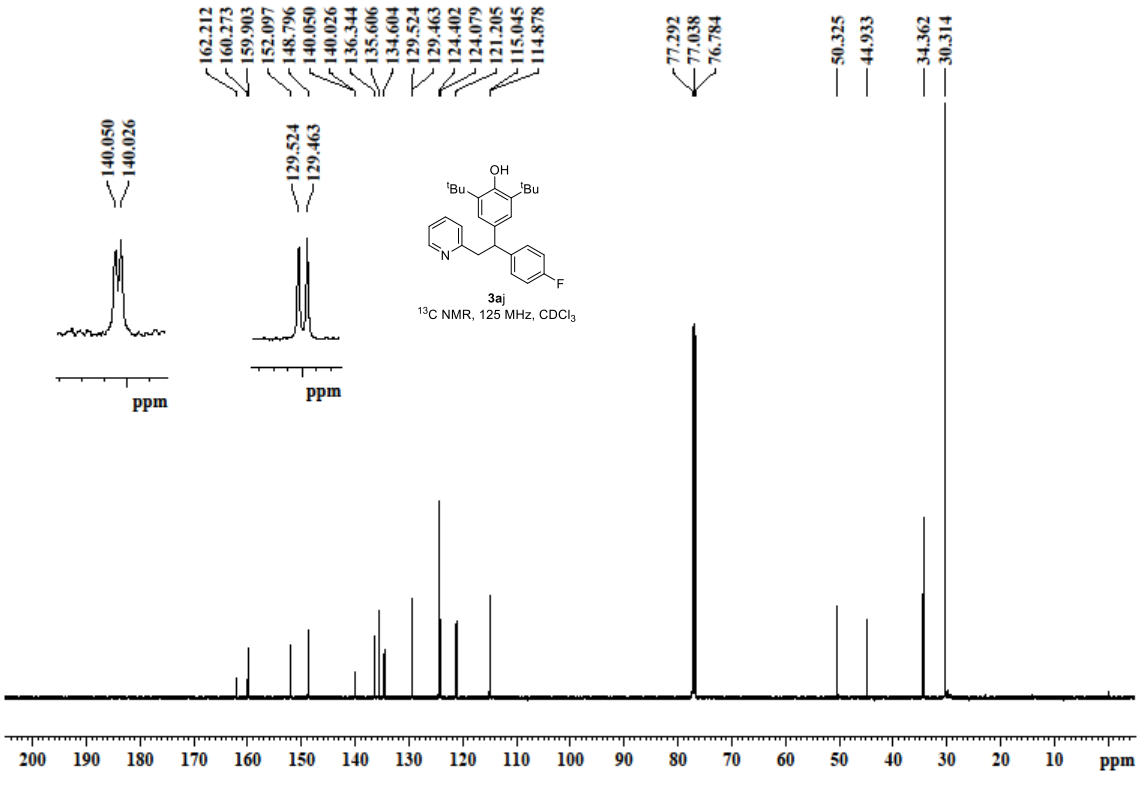

8.5204
8.5121
7.4236
7.4085
7.3935
7.2601
7.1519
7.1353
7.0354
7.0243
7.0117
6.9615
6.8284
6.8130
6.7923
6.7756
6.0698
6.0592
6.0487
6.0373
6.0253
6.0142
6.0039
5.9933
5.3960
5.3616
5.2621
5.2415
4.9916
4.4771
4.4671
4.4453
4.4294
4.4134
3.4750
3.4483
3.4309
3.4159
3.4012
3.3893
3.3742
1.3585
OH
tBu
tBu
N
O
3ah
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.93
0.99
1.98
1.00
1.99
1.04
1.91
0.91
0.95
0.94
0.94
1.92
1.03
2.02
18.00

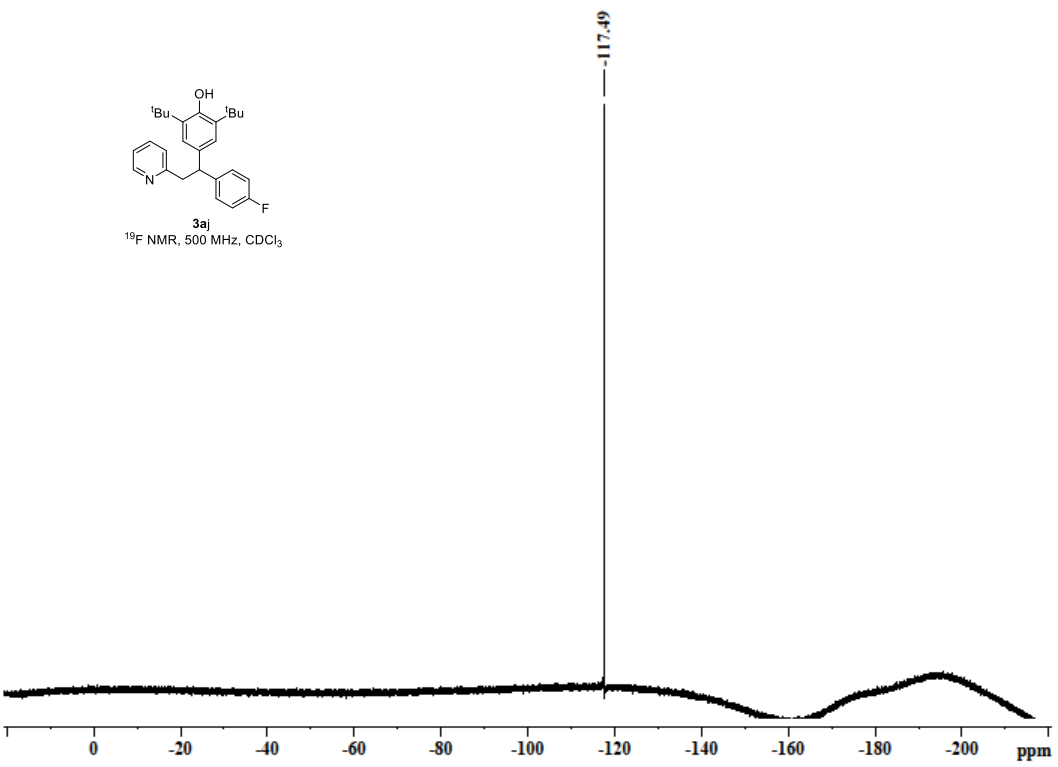

160.484
156.777
151.907
149.079
136.827
135.817
135.405
135.232
133.492
129.001
124.438
123.919
120.916
117.514
114.419
77.279
77.025
76.772
68.792
50.369
45.367
34.341
30.330
OH
tBu
tBu
N
O
3ah
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

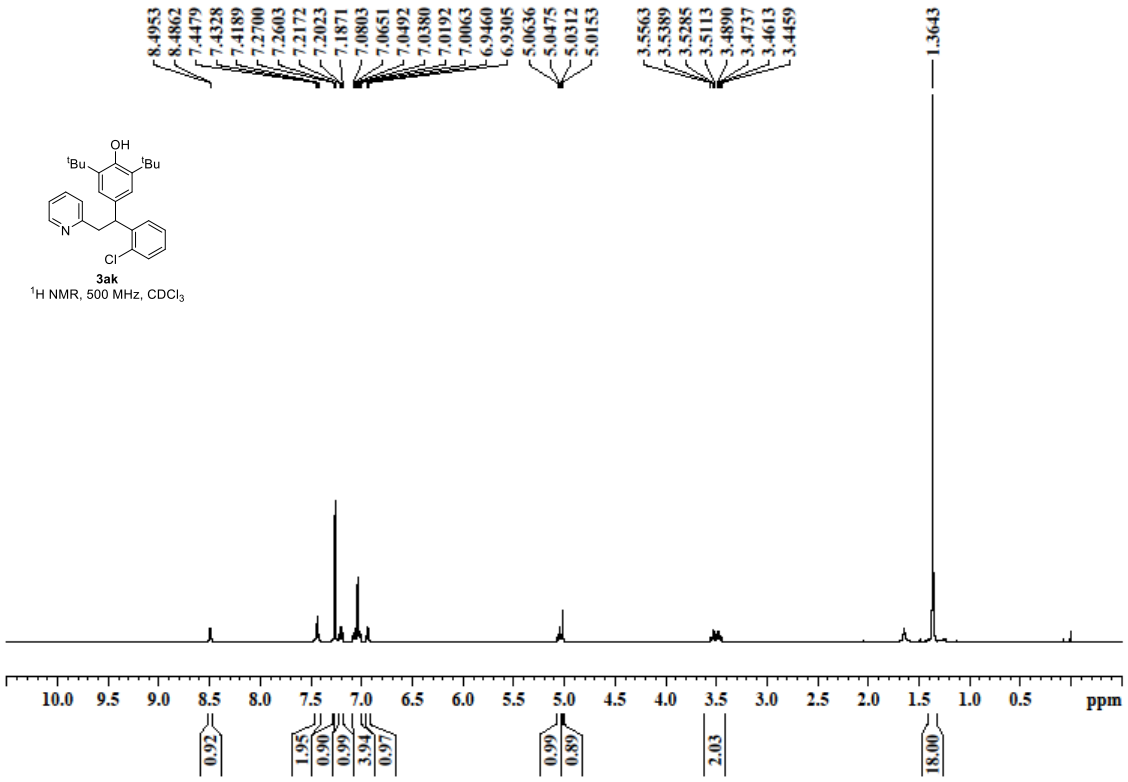

8.5263
8.5184
7.4293
7.4127
7.3969
7.3770
7.3624
7.3476
7.3191
7.3051
7.2911
7.2596
7.1636
7.1471
7.0414
7.0297
7.0174
6.9641
6.8548
6.8374
6.8201
5.0009
4.4512
4.4353
4.4194
3.4829
3.4560
3.4386
3.4210
3.4062
3.3945
3.3793
1.3601
OH
tBu
tBu
N
OBn
3ai
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.96
2.83
1.97
0.97
1.94
0.99
1.90
2.88
2.95
0.99
2.01
18.00

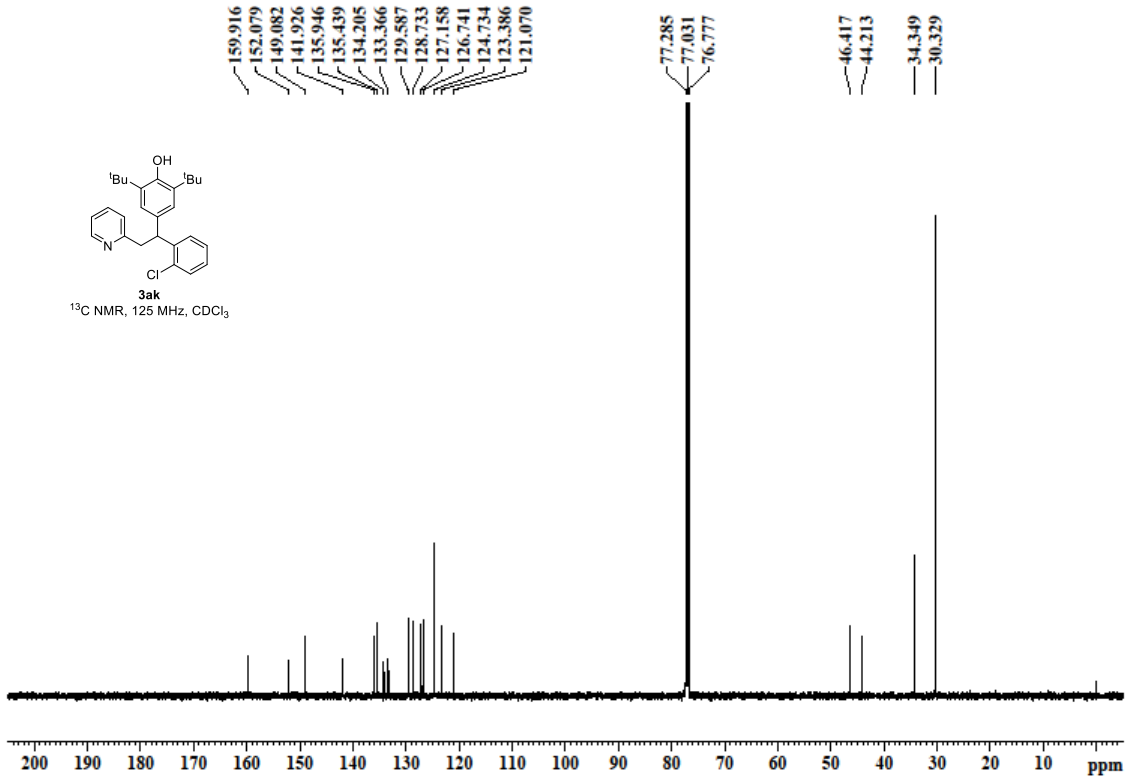

160.387
157.007
151.925
148.951
137.204
136.913
135.983
135.419
135.160
129.027
128.525
127.876
127.519
124.438
123.983
120.979
114.589
77.277
77.024
76.770
69.993
50.369
45.242
34.343
30.335
OH
tBu
tBu
N
OBn
3ai
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

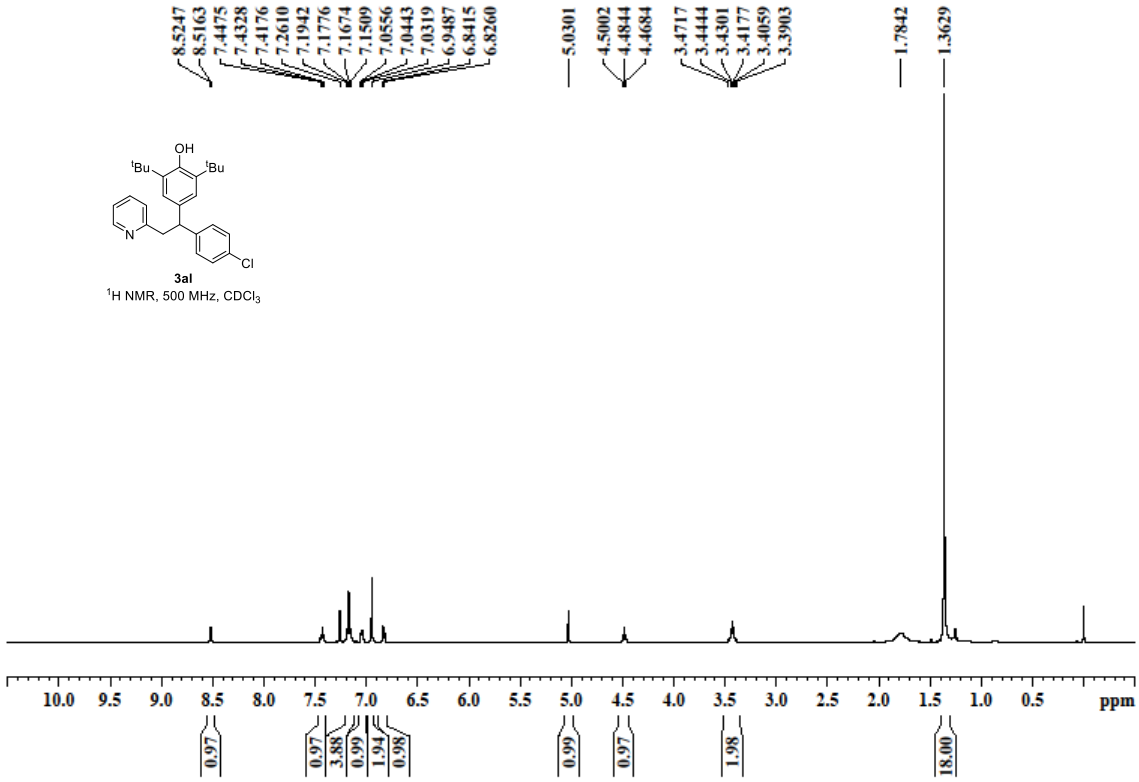

8.5450
8.5362
7.4627
7.4473
7.4322
7.2603
7.2022
7.1887
7.1751
7.0696
7.0581
7.0455
6.9505
6.9228
6.9056
6.8884
6.8457
6.8302
5.0264
4.5112
4.4952
4.4791
3.4876
3.4605
3.4450
3.4315
3.4198
3.4043
1.3618
0.0008
OH
tBu
tBu
N
F
3aj
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
0.97
1.96
0.99
1.94
1.96
0.99
0.99
1.00
2.01
18.00


162.212
160.273
159.903
152.097
148.796
140.050
140.026
136.344
135.606
134.604
129.524
129.463
124.402
124.079
121.205
115.045
114.878
77.292
77.038
76.784
50.325
44.933
34.362
30.314
140.050
140.026
129.524
129.463
ppm
ppm
OH
tBu
tBu
N
F
3aj
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OH
tBu
tBu
N
F
3aj
19F NMR, 500 MHz, CDCl3
-117.49
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

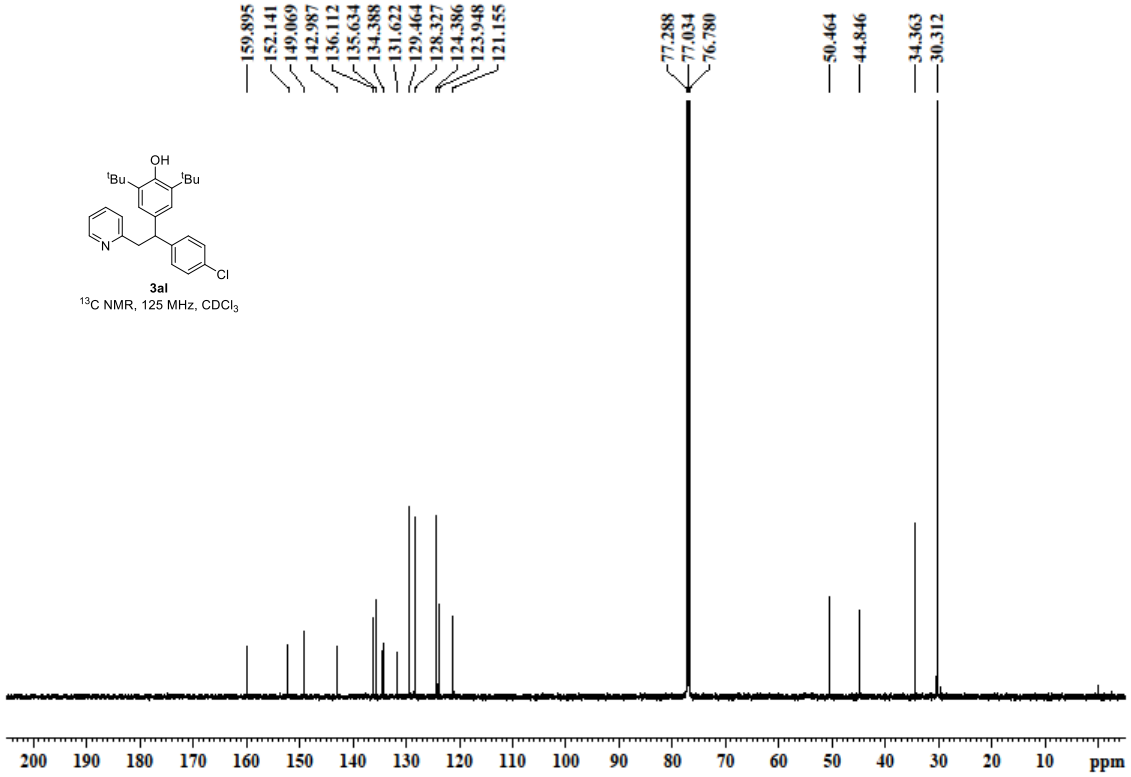

8.4953
8.4862
7.4479
7.4328
7.4189
7.2700
7.2603
7.2172
7.2023
7.1871
7.0803
7.0651
7.0492
7.0380
7.0192
7.0063
6.9460
6.9305
5.0636
5.0475
5.0312
5.0153
3.5563
3.5389
3.5285
3.5113
3.4890
3.4737
3.4613
3.4459
1.3643
OH
tBu
tBu
N
Cl
3ak
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.92
1.95
0.90
0.99
3.94
0.97
0.99
0.89
2.03
18.00


159.916
152.079
149.082
141.926
135.946
135.439
134.205
133.366
129.587
128.733
127.158
126.741
124.734
123.386
121.070
77.285
77.031
76.777
46.417
44.213
34.349
30.329
OH
tBu
tBu
N
Cl
3ak
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



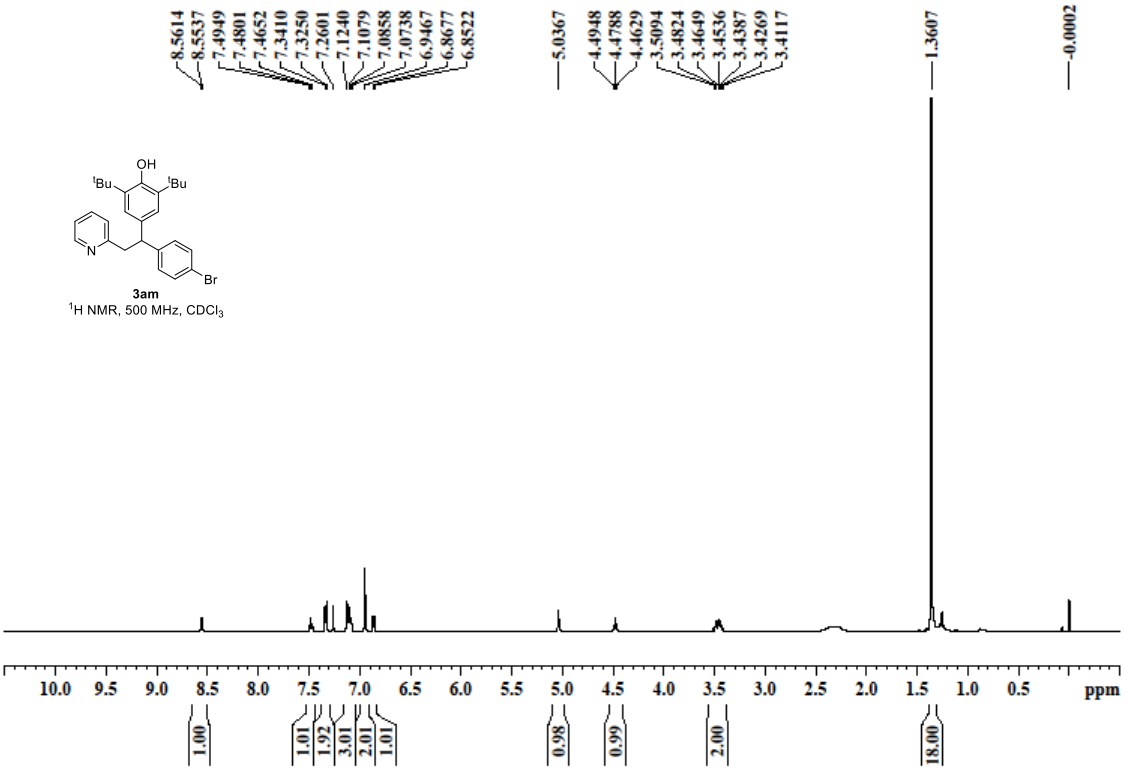
3al

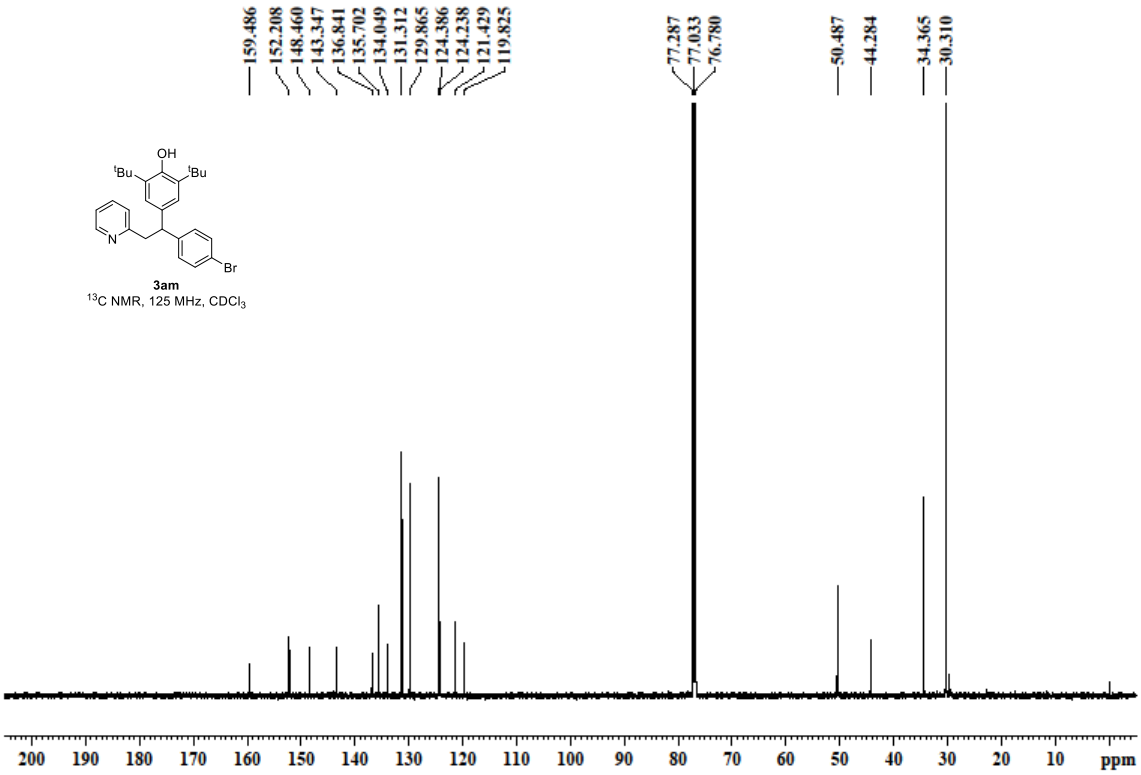
^{1}H NMR, 500 MHz, $CDCl_3$

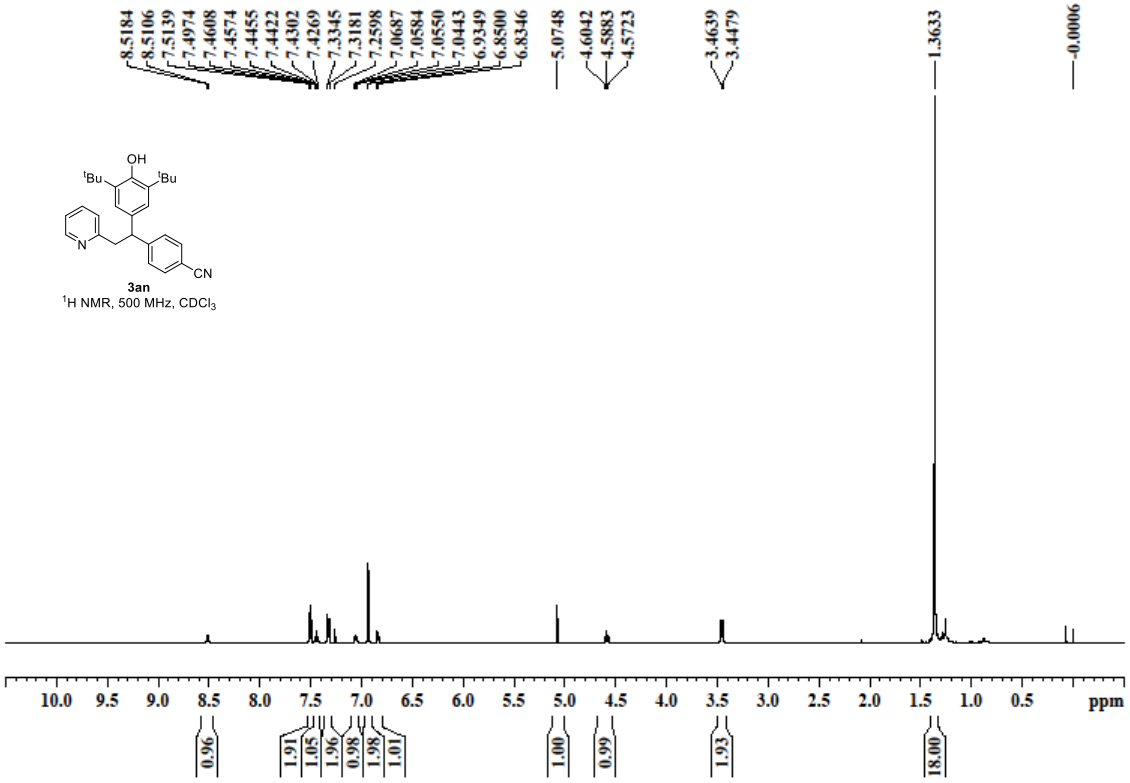


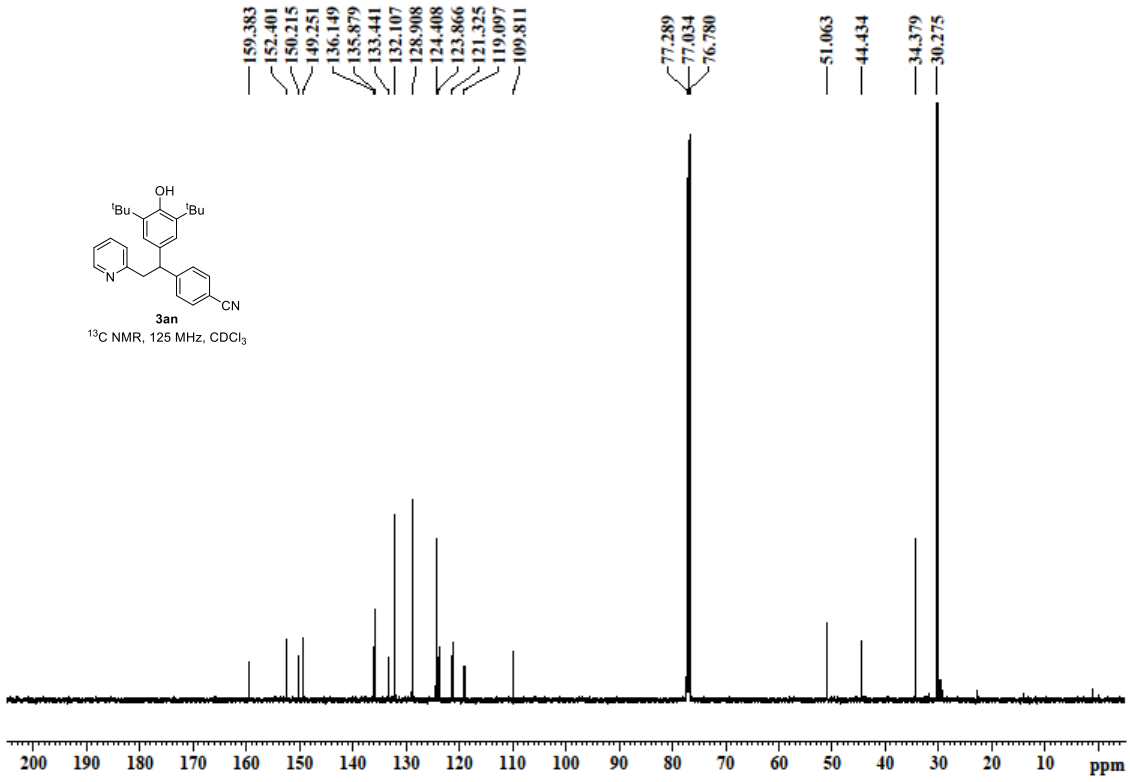
3al

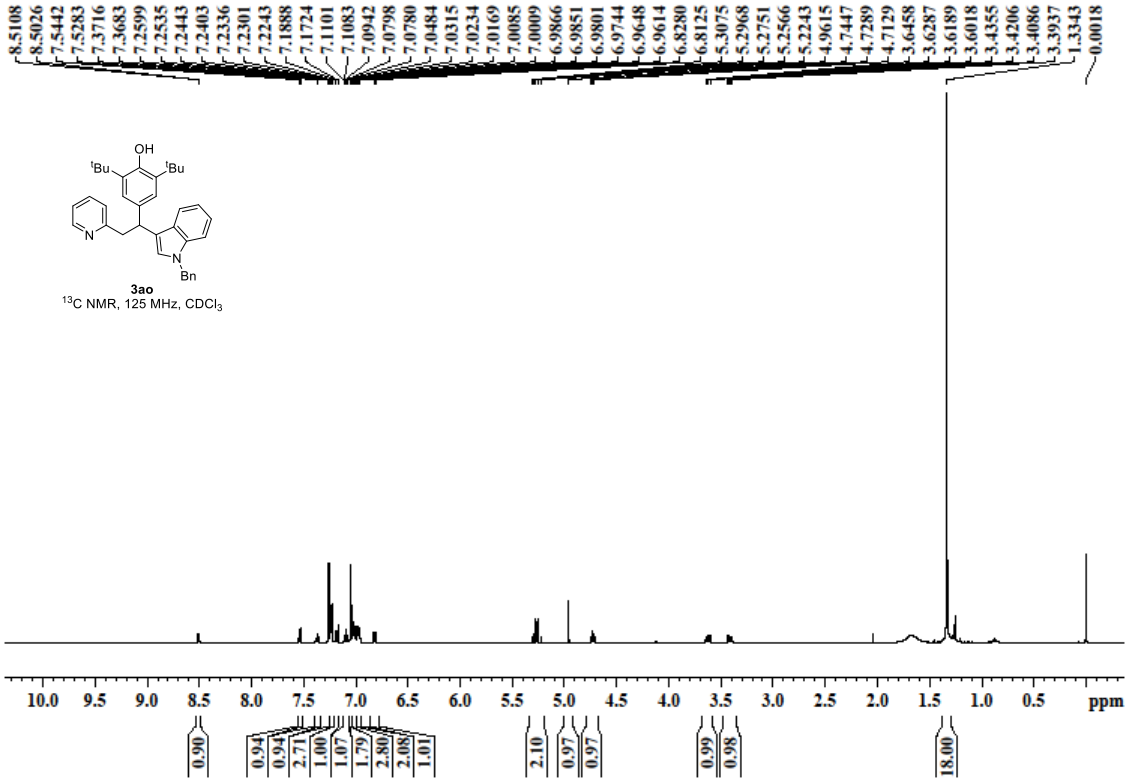
^{13}C NMR, 125 MHz, $CDCl_3$

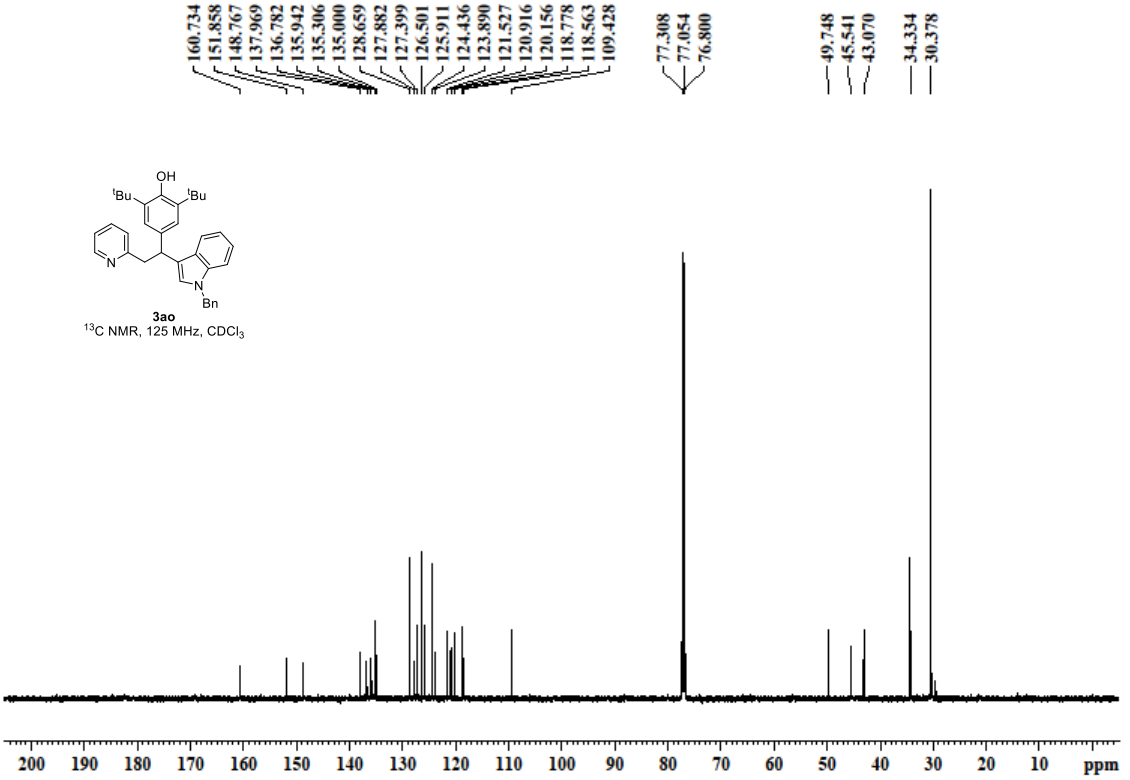

8.5614
8.5537
7.4949
7.4801
7.4652
7.3410
7.3250
7.2601
7.1240
7.1079
7.0858
7.0738
6.9467
6.8677
6.8522
5.0367
4.4948
4.4788
4.4629
3.5094
3.4824
3.4649
3.4536
3.4387
3.4269
3.4117
1.3607
-0.0002
OH
tBu
tBu
N
Br
3am
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.01
1.92
3.01
2.01
1.01
0.98
0.99
2.00
18.00

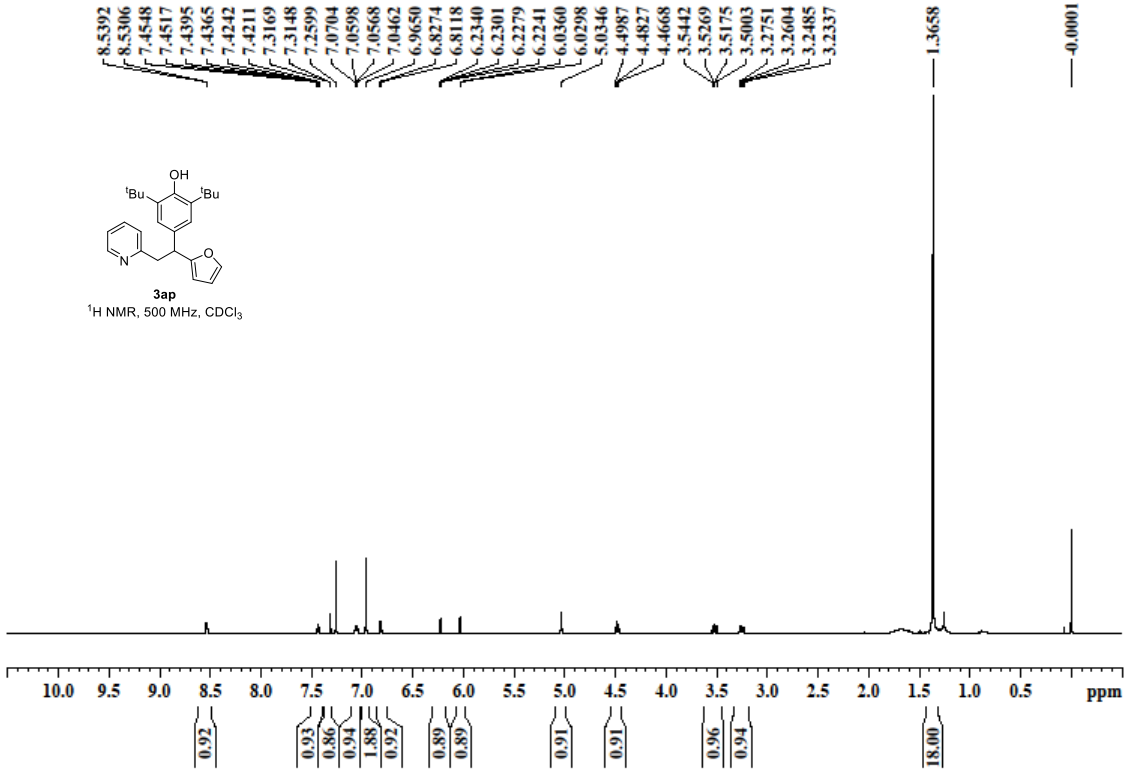

159.486
152.208
148.460
143.347
136.841
135.702
134.049
131.312
129.865
124.386
124.238
121.429
119.825
77.287
77.033
76.780
50.487
44.284
34.365
30.310
OH
tBu
tBu
N
Br
3am
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

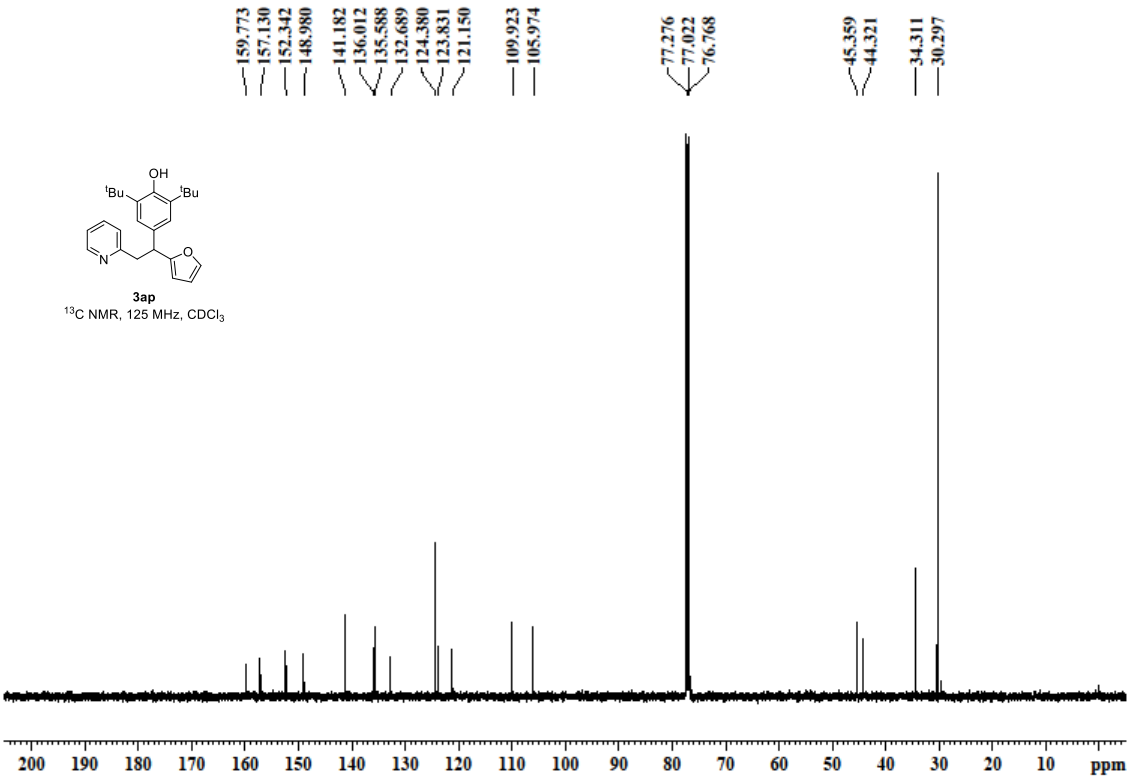

8.5184
8.5106
7.5139
7.4974
7.4608
7.4574
7.4455
7.4422
7.4302
7.4269
7.3345
7.3181
7.2598
7.0687
7.0584
7.0550
7.0443
6.9349
6.8500
6.8346
5.0748
4.6042
4.5883
4.5723
3.4639
3.4479
1.3633
-0.0006
OH
tBu
tBu
N
CN
3an
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.96
1.91
1.05
1.96
0.98
1.98
1.01
1.00
0.99
1.93
18.00

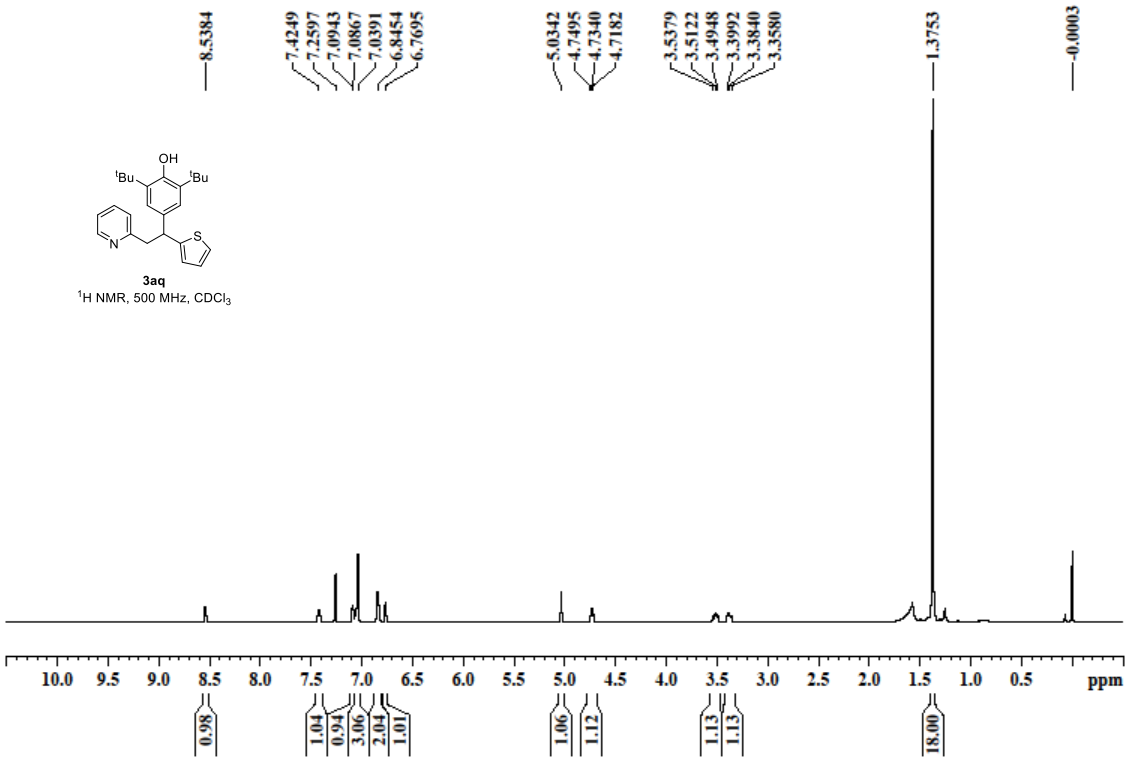

159.383
152.401
150.215
149.251
136.149
135.879
133.441
132.107
128.908
124.408
123.866
121.325
119.097
109.811
77.289
77.034
76.780
51.063
44.434
34.379
30.275
OH
tBu
tBu
N
CN
3an
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

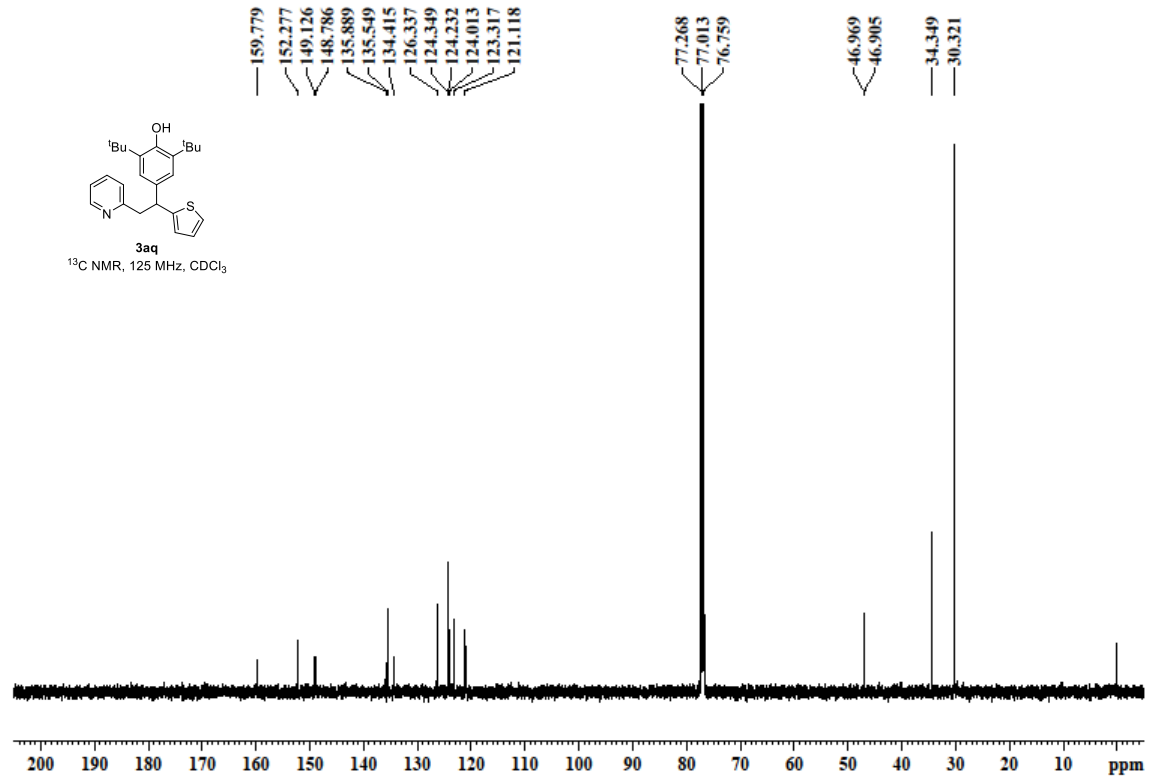

8.5108
8.5026
7.5442
7.5283
7.3716
7.3683
7.2599
7.2535
7.2443
7.2403
7.2336
7.2301
7.2243
7.1888
7.1724
7.1101
7.1083
7.0942
7.0798
7.0780
7.0484
7.0315
7.0234
7.0169
7.0085
7.0009
6.9866
6.9851
6.9801
6.9744
6.9648
6.9614
6.8280
6.8125
5.3075
5.2968
5.2751
5.2566
5.2243
4.9615
4.7447
4.7289
4.7129
3.6458
3.6287
3.6189
3.6018
3.4355
3.4206
3.4086
3.3937
1.3343
0.0018
OH
tBu
tBu
N
N
Bn
3ao
13C NMR, 125 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.90
0.94
0.94
2.71
1.00
1.07
1.79
2.80
2.08
1.01
2.10
0.97
0.97
0.99
0.98
18.00

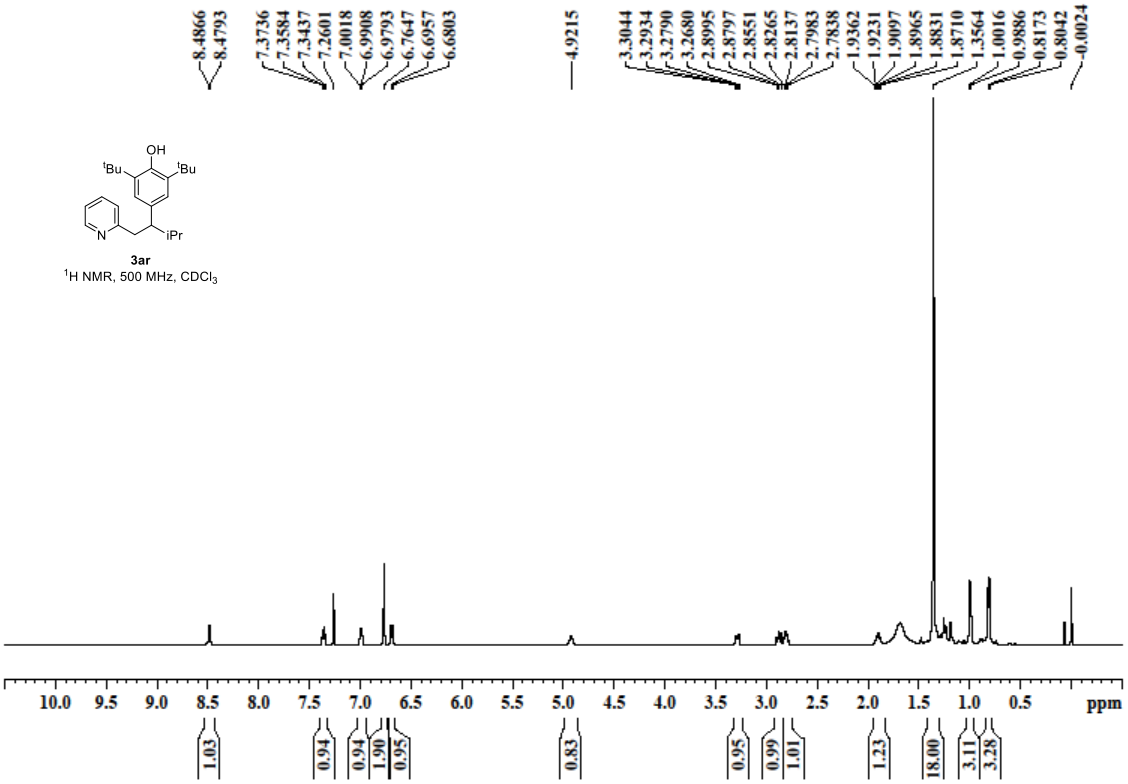

160.734
151.858
148.767
137.969
136.782
135.942
135.306
135.000
128.659
127.882
127.399
126.501
125.911
124.436
123.890
121.527
120.916
120.156
118.778
118.563
109.428
77.308
77.054
76.800
49.748
45.541
43.070
34.334
30.378
OH
tBu
tBu
N
N
Bn
3ao
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

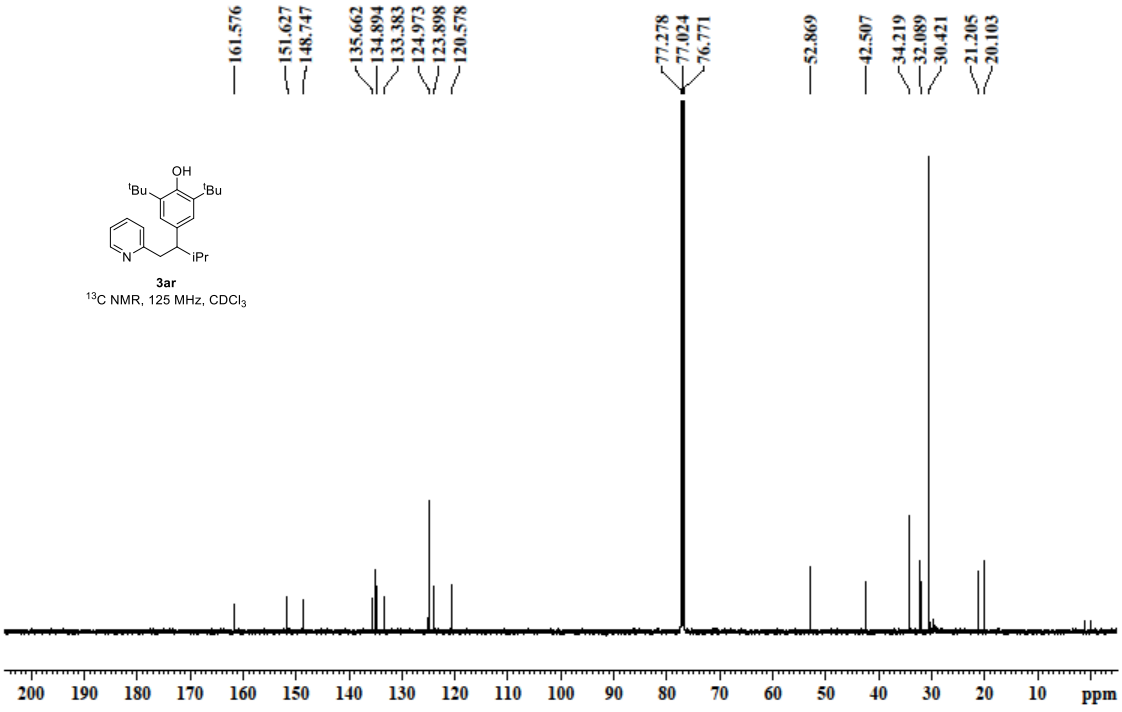

8.5392
8.5306
7.4548
7.4517
7.4395
7.4365
7.4242
7.4211
7.3169
7.3148
7.2599
7.0704
7.0598
7.0568
7.0462
6.9650
6.8274
6.8118
6.2340
6.2301
6.2279
6.2241
6.0360
6.0298
5.0346
4.4987
4.4827
4.4668
3.5442
3.5269
3.5175
3.5003
3.2751
3.2604
3.2485
3.2337
1.3658
-0.0001
OH
tBu
tBu
N
O
3ap
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.92
0.93
0.86
0.94
1.88
0.92
0.89
0.89
0.91
0.91
0.96
0.94
18.00

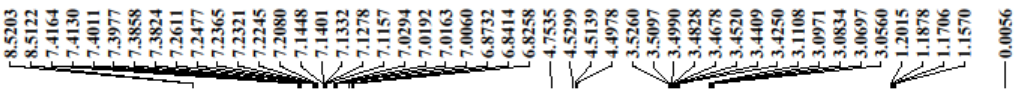

159.773
157.130
152.342
148.980
141.182
136.012
135.588
132.689
124.380
123.831
121.150
109.923
105.974
77.276
77.022
76.768
45.359
44.321
34.311
30.297
OH
tBu
tBu
N
O
3ap
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

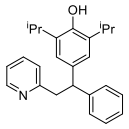

8.5384
7.4249
7.2597
7.0943
7.0867
7.0391
6.8454
6.7695
5.0342
4.7495
4.7340
4.7182
3.5379
3.5122
3.4948
3.3992
3.3840
3.3580
1.3753
-0.0003
OH
tBu
tBu
N
S
3aq
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98
1.04
0.94
3.06
2.04
1.01
1.06
1.12
1.13
1.13
18.00


159.779
152.277
149.126
148.786
135.889
135.549
134.415
126.337
124.349
124.232
124.013
123.317
121.118
77.268
77.013
76.759
46.969
46.905
34.349
30.321
OH
tBu
tBu
N
S
3aq
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.4866
8.4793
7.3736
7.3584
7.3437
7.2601
7.0018
6.9908
6.9793
6.7647
6.6957
6.6803
4.9215
3.3044
3.2934
3.2790
3.2680
2.8995
2.8797
2.8551
2.8265
2.8137
2.7983
2.7838
1.9362
1.9231
1.9097
1.8965
1.8831
1.8710
1.3564
1.0016
0.9886
0.8173
0.8042
-0.0024
OH
tBu
tBu
iPr
N
3ar
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03
0.94
0.94
1.90
0.95
0.83
0.95
0.99
1.01
1.23
18.00
3.11
3.28

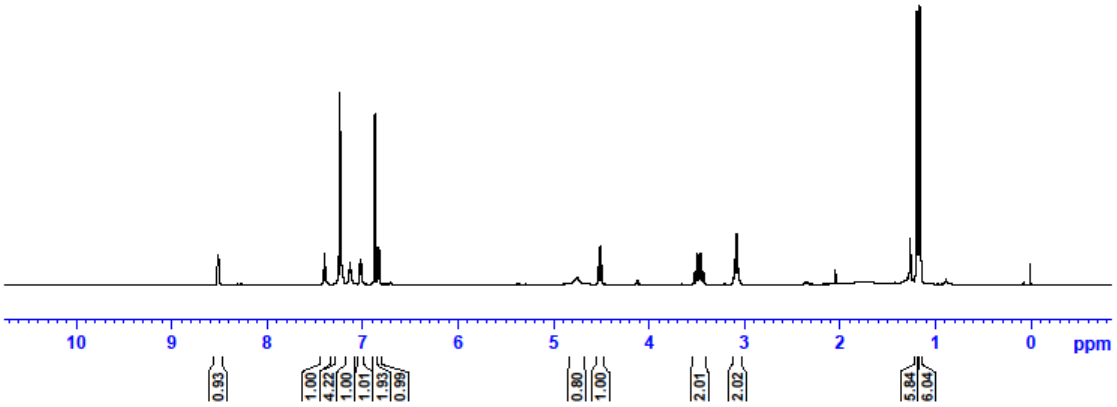

161.576
151.627
148.747
135.662
134.894
133.383
124.973
123.898
120.578
77.278
77.024
76.771
52.869
42.507
34.219
32.089
30.421
21.205
20.103
OH
tBu
tBu
iPr
N
3ar
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

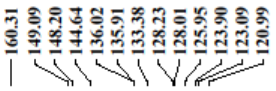


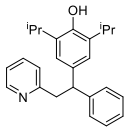


3as

^{1}H NMR, 500 MHz, $CDCl_3$

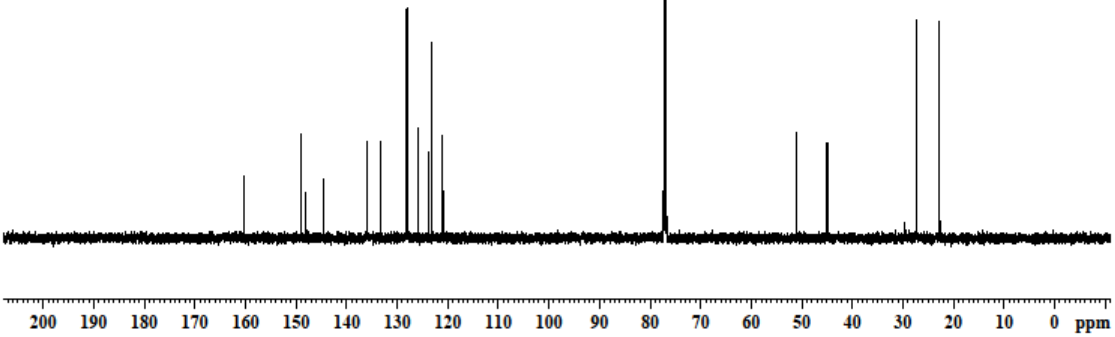


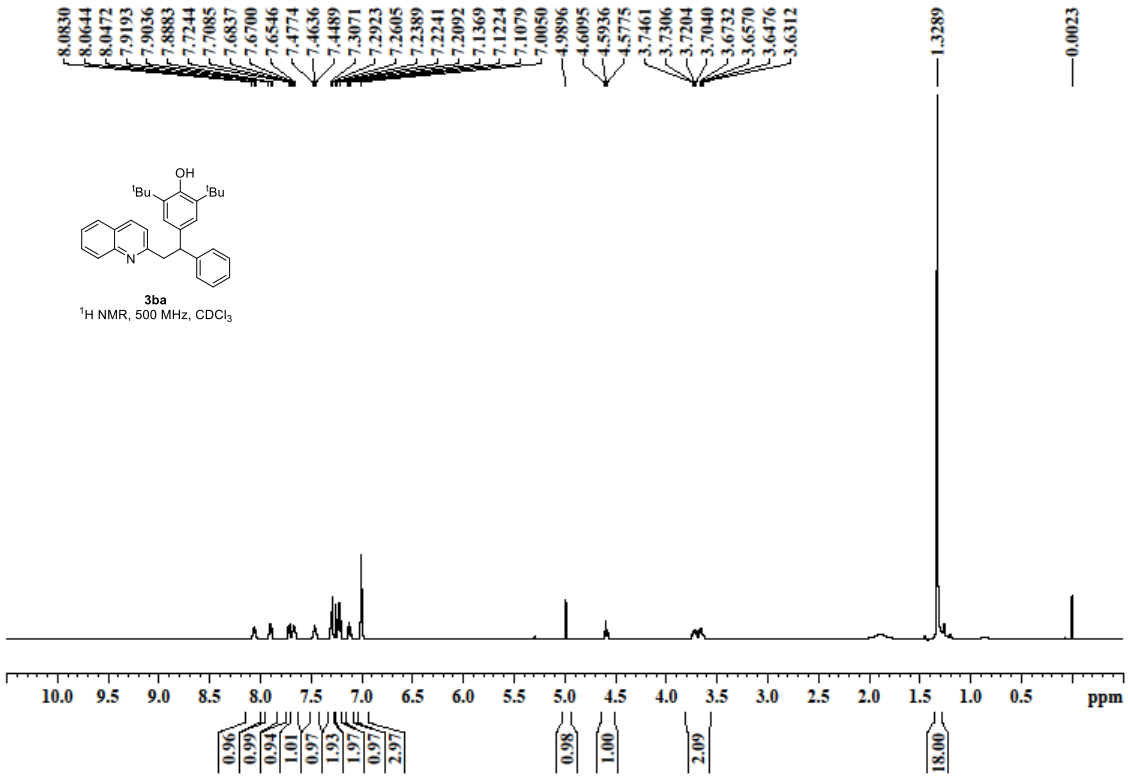


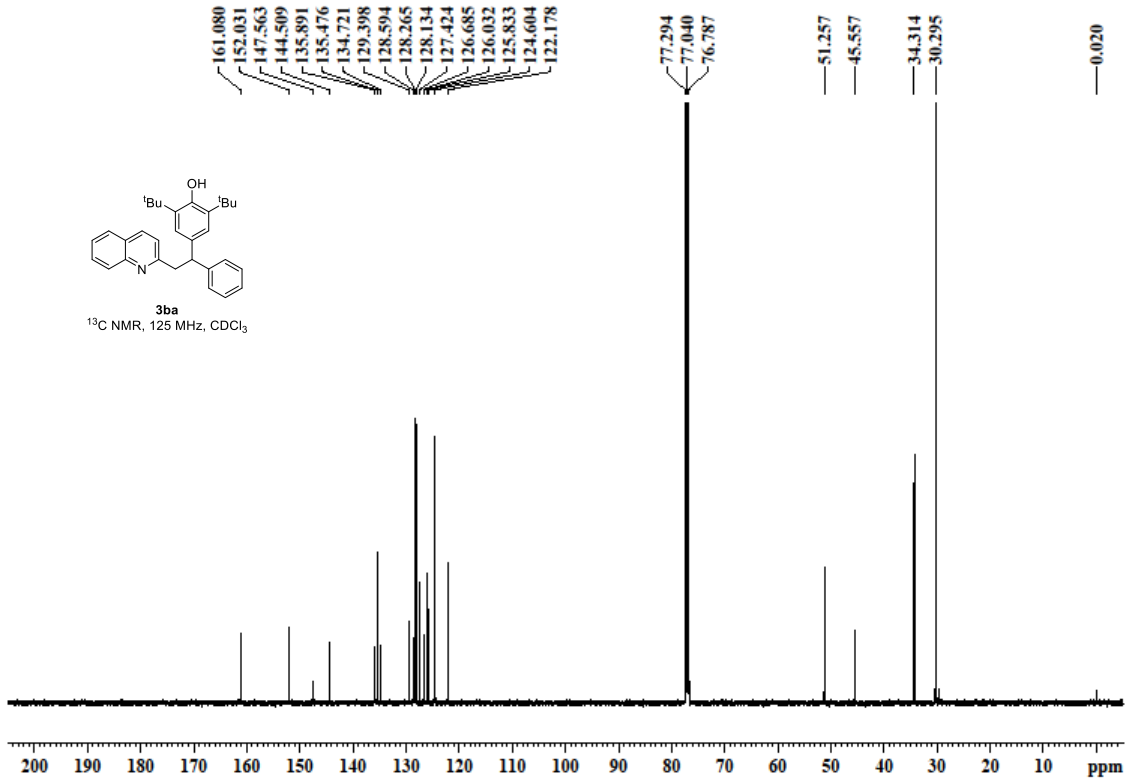


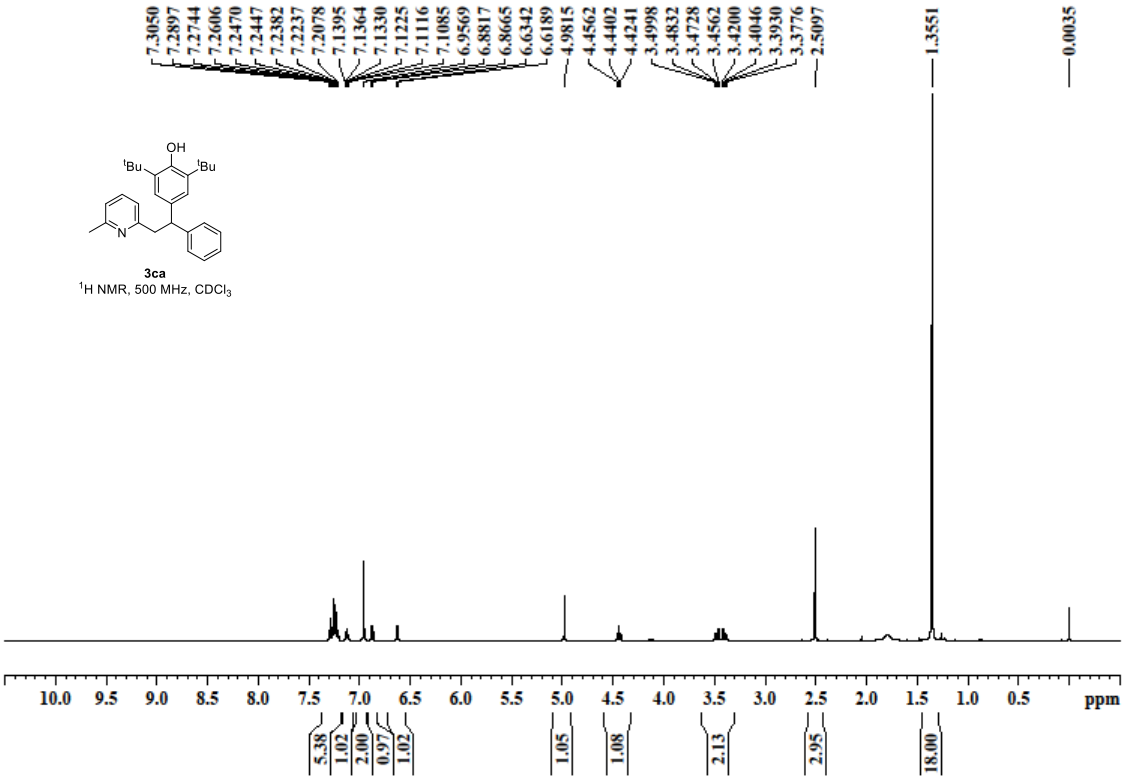
3as

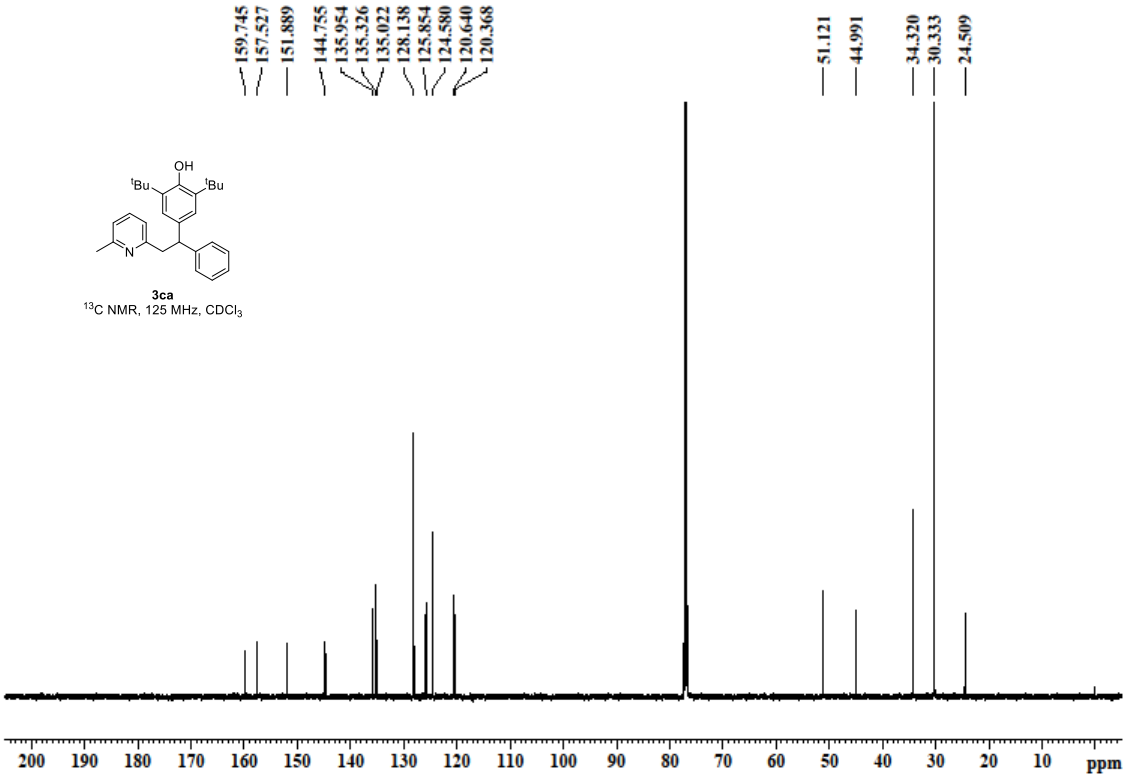
^{13}C NMR, 125 MHz, $CDCl_3$

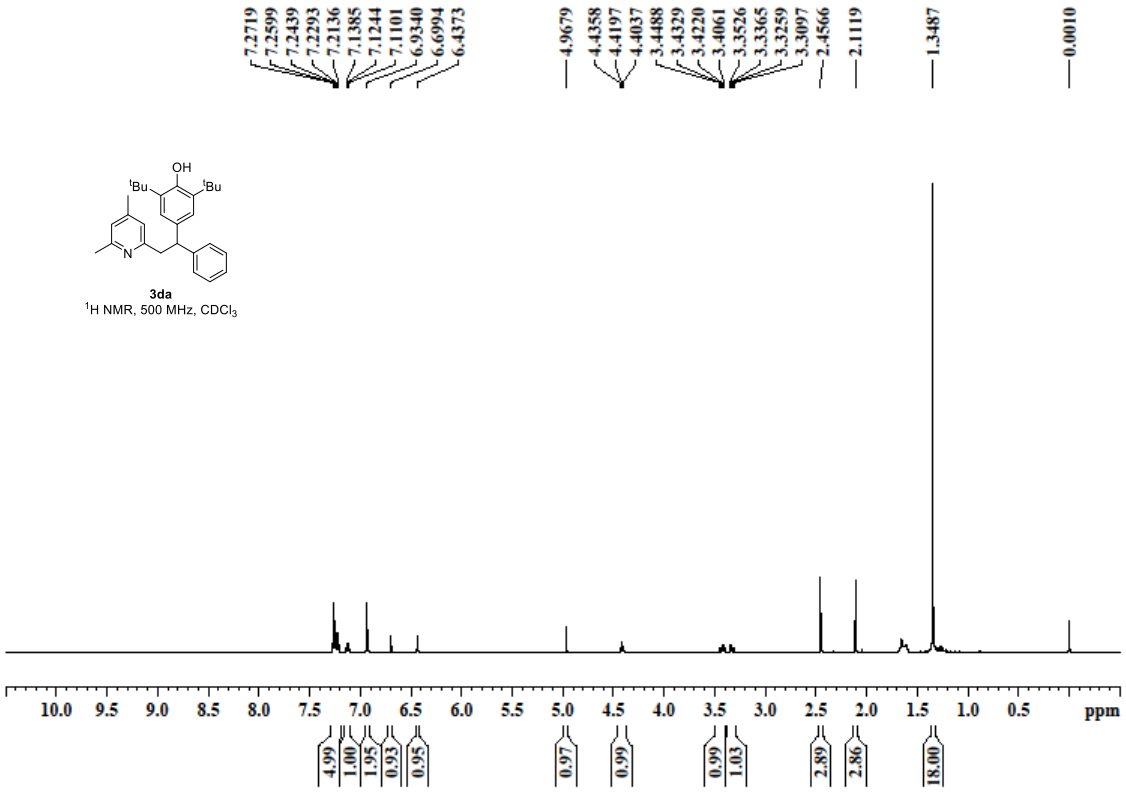


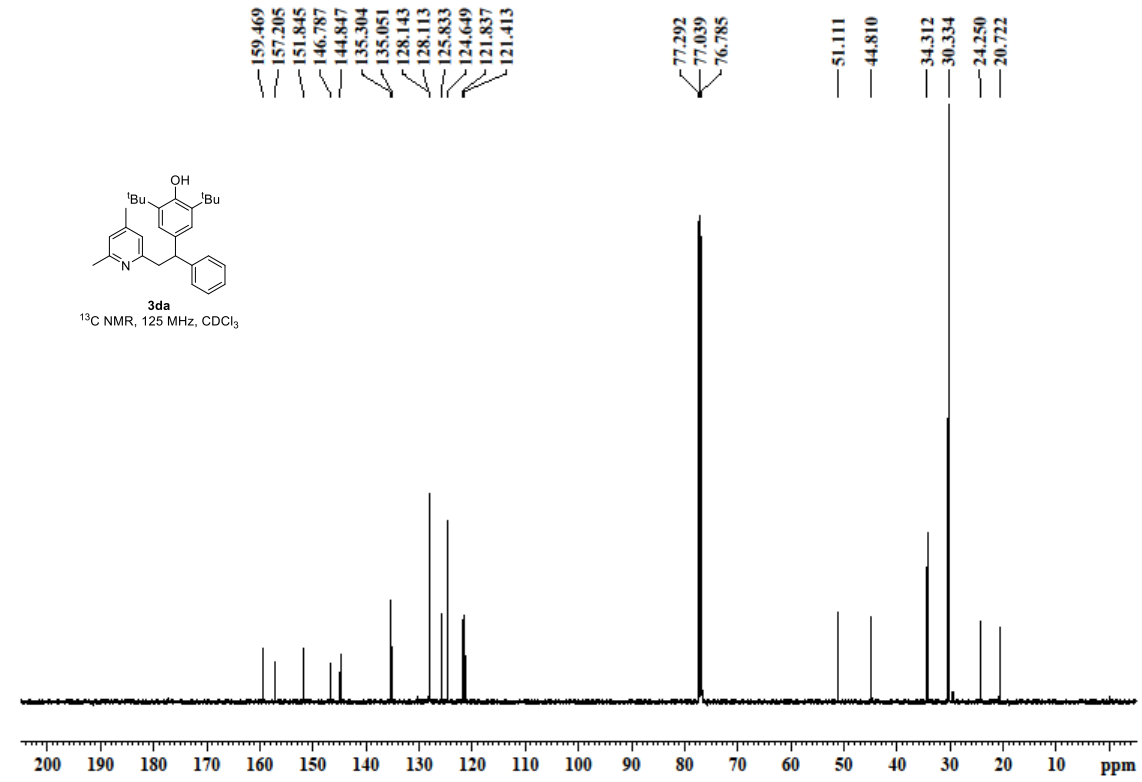

8.0830
8.0644
8.0472
7.9193
7.9036
7.8883
7.7244
7.7085
7.6837
7.6700
7.6546
7.4774
7.4636
7.4489
7.3071
7.2923
7.2605
7.2389
7.2241
7.2092
7.1369
7.1224
7.1079
7.0050
4.9896
4.6095
4.5936
4.5775
3.7461
3.7306
3.7204
3.7040
3.6732
3.6570
3.6476
3.6312
1.3289
0.0023
OH
tBu
tBu
N
3ba
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.96
0.99
0.94
1.01
0.97
1.93
1.97
0.97
2.97
0.98
1.00
2.09
18.00

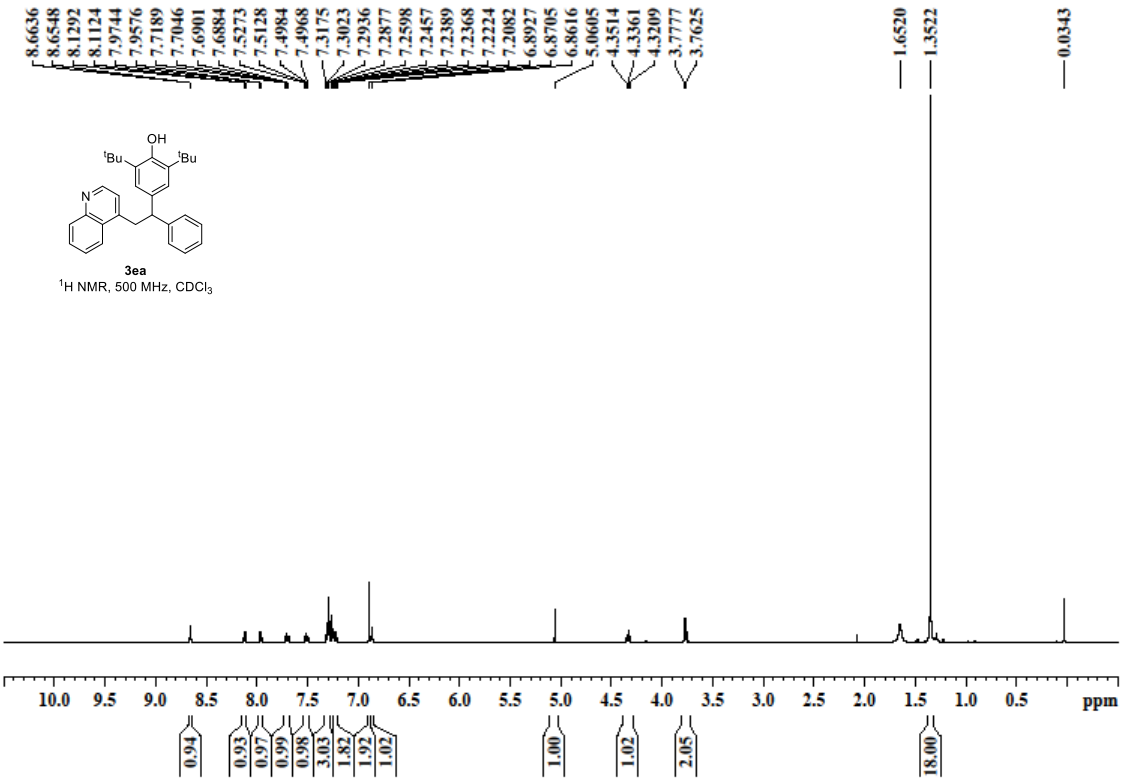

161.080
152.031
147.563
144.509
135.891
135.476
134.721
129.398
128.594
128.265
128.134
127.424
126.685
126.032
125.833
124.604
122.178
77.294
77.040
76.787
51.257
45.557
34.314
30.295
0.020
OH
tBu
tBu
N
3ba
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

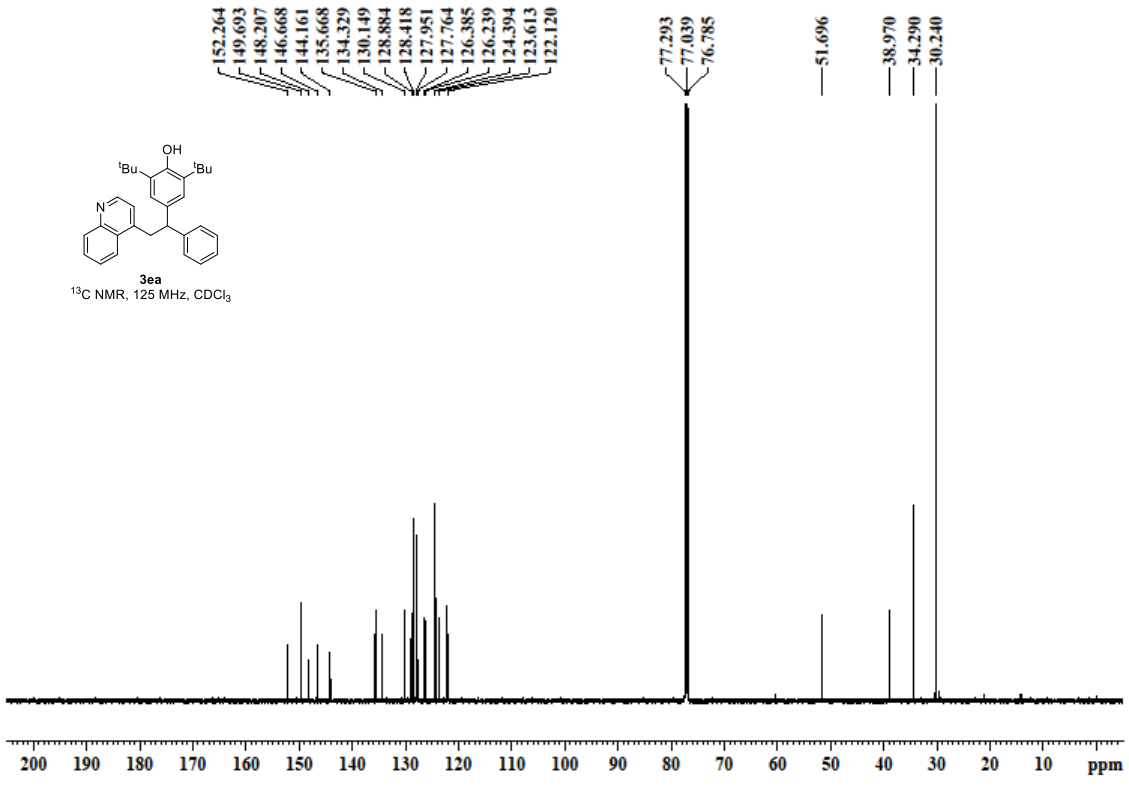

7.3050
7.2897
7.2744
7.2606
7.2470
7.2447
7.2382
7.2237
7.2078
7.1395
7.1364
7.1330
7.1225
7.1116
7.1085
6.9569
6.8817
6.8665
6.6342
6.6189
4.9815
4.4562
4.4402
4.4241
3.4998
3.4832
3.4728
3.4562
3.4200
3.4046
3.3930
3.3776
2.5097
1.3551
0.0035
OH
tBu
tBu
N
3ca
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.38
1.02
2.00
0.97
1.02
1.05
1.08
2.13
2.95
18.00

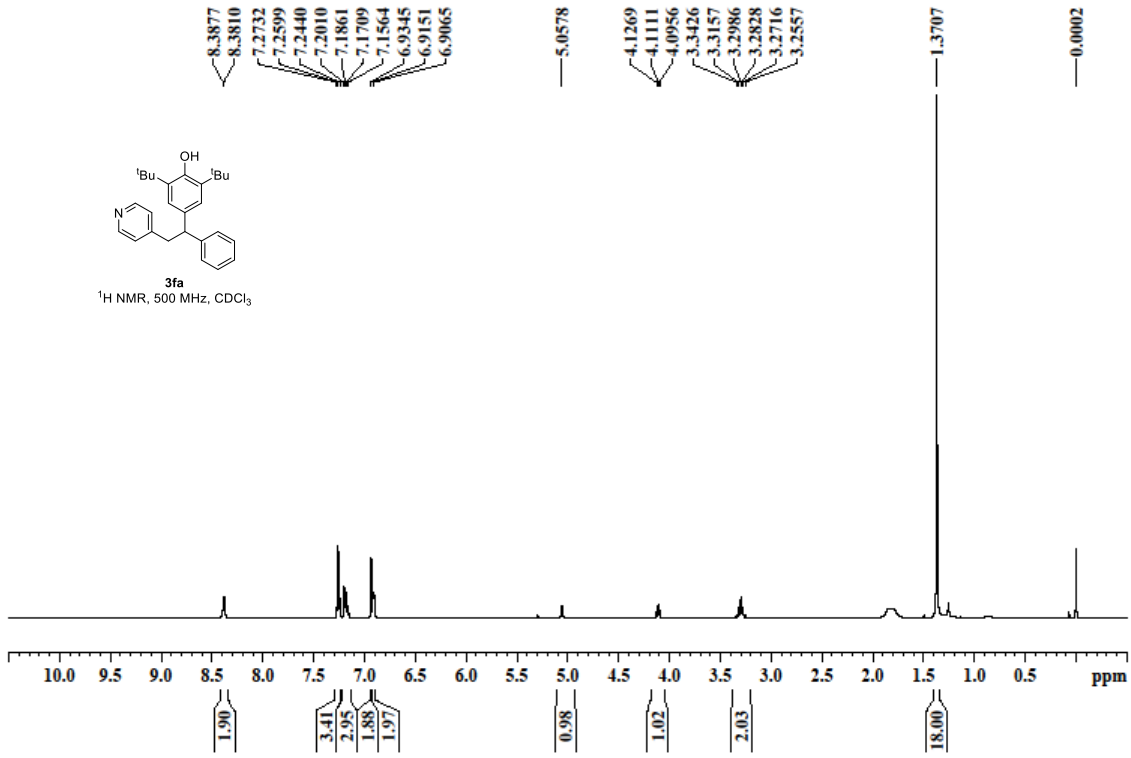

159.745
157.527
151.889
144.755
135.954
135.326
135.022
128.138
125.854
124.580
120.640
120.368
51.121
44.991
34.320
30.333
24.509
OH
tBu
tBu
N
3ca
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.2719
7.2599
7.2439
7.2293
7.2136
7.1385
7.1244
7.1101
6.9340
6.6994
6.4373
4.9679
4.4358
4.4197
4.4037
3.4488
3.4329
3.4220
3.4061
3.3526
3.3365
3.3259
3.3097
2.4566
2.1119
1.3487
0.0010
OH
tBu
tBu
N
3da
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.99
1.00
1.95
0.93
0.95
0.97
0.99
0.99
1.03
2.89
2.86
18.00

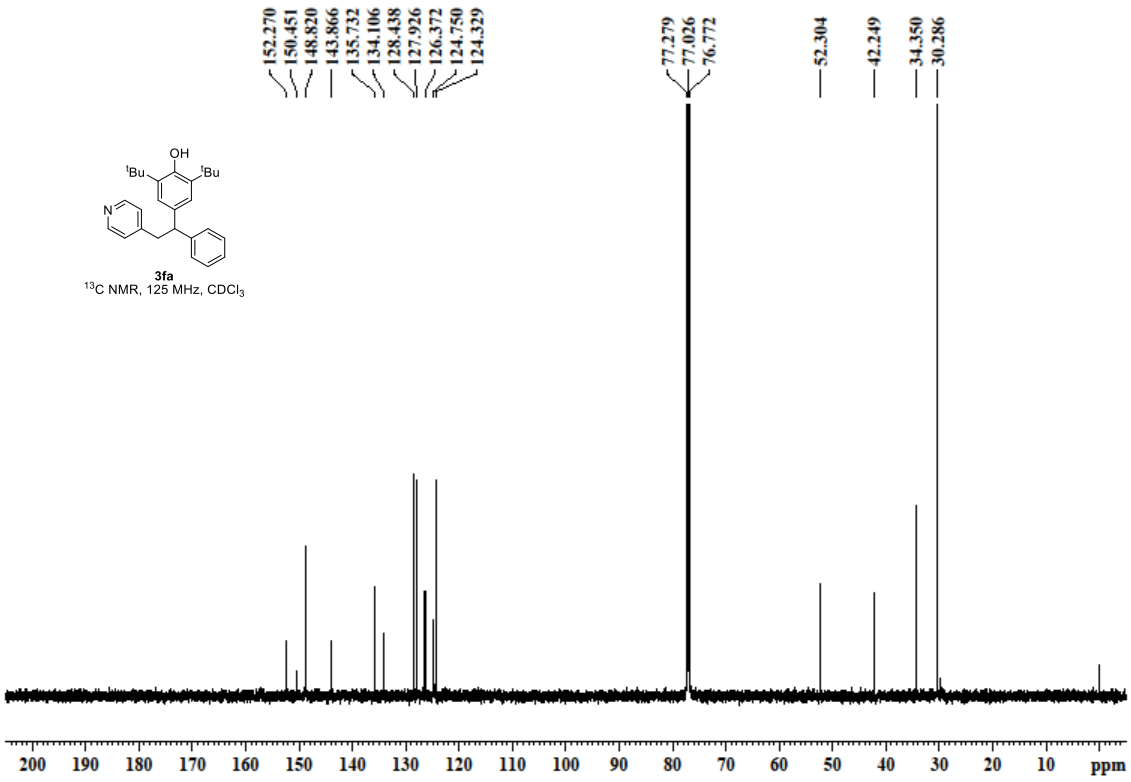

159.469
157.205
151.845
146.787
144.847
135.304
135.051
128.143
128.113
125.833
124.649
121.837
121.413
77.292
77.039
76.785
51.111
44.810
34.312
30.334
24.250
20.722
OH
tBu
tBu
N
3da
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.6636
8.6548
8.1292
8.1124
7.9744
7.9576
7.7189
7.7046
7.6901
7.6884
7.5273
7.5128
7.4984
7.4968
7.3175
7.3023
7.2936
7.2877
7.2598
7.2457
7.2389
7.2368
7.2224
7.2082
6.8927
6.8705
6.8616
5.0605
4.3514
4.3361
4.3209
3.7777
3.7625
1.6520
1.3522
0.0343
OH
tBu
tBu
N
3ea
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.94
0.93
0.97
0.99
0.98
3.03
1.82
1.92
1.02
1.00
1.02
2.05
18.00

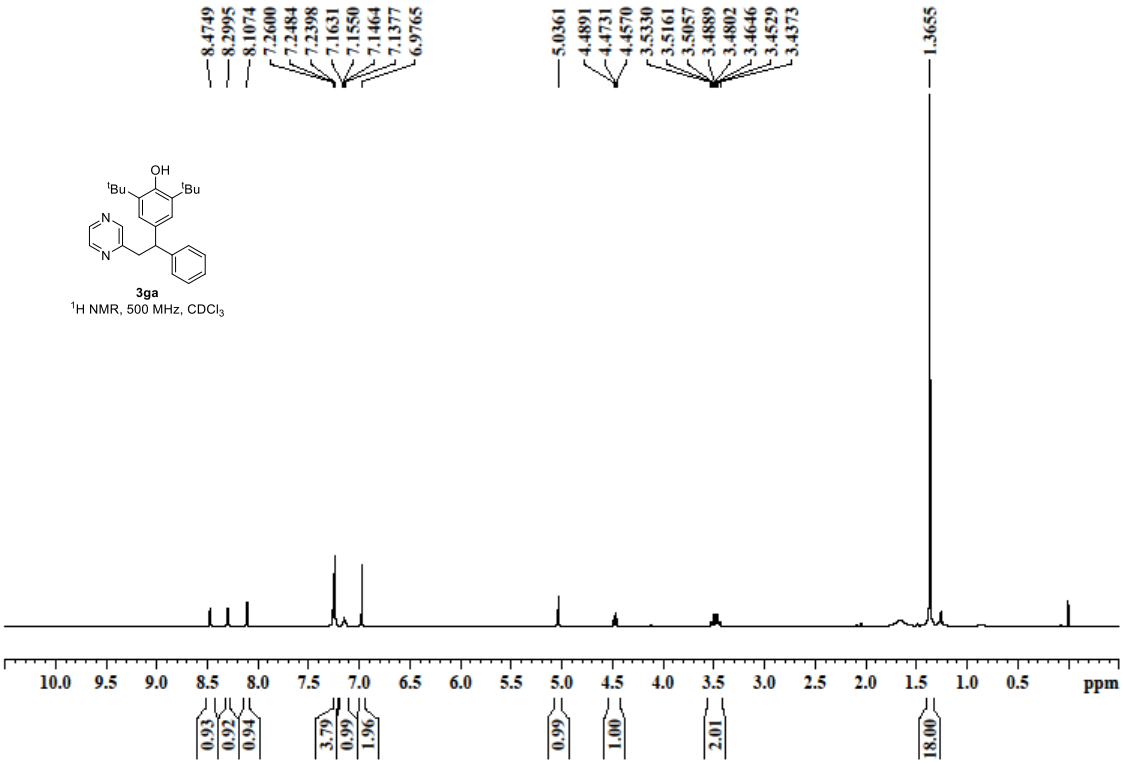

152.264
149.693
148.207
146.668
144.161
135.668
134.329
130.149
128.884
128.418
127.951
127.764
126.385
126.239
124.394
123.613
122.120
77.293
77.039
76.785
51.696
38.970
34.290
30.240
OH
tBu
tBu
N
3ea
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

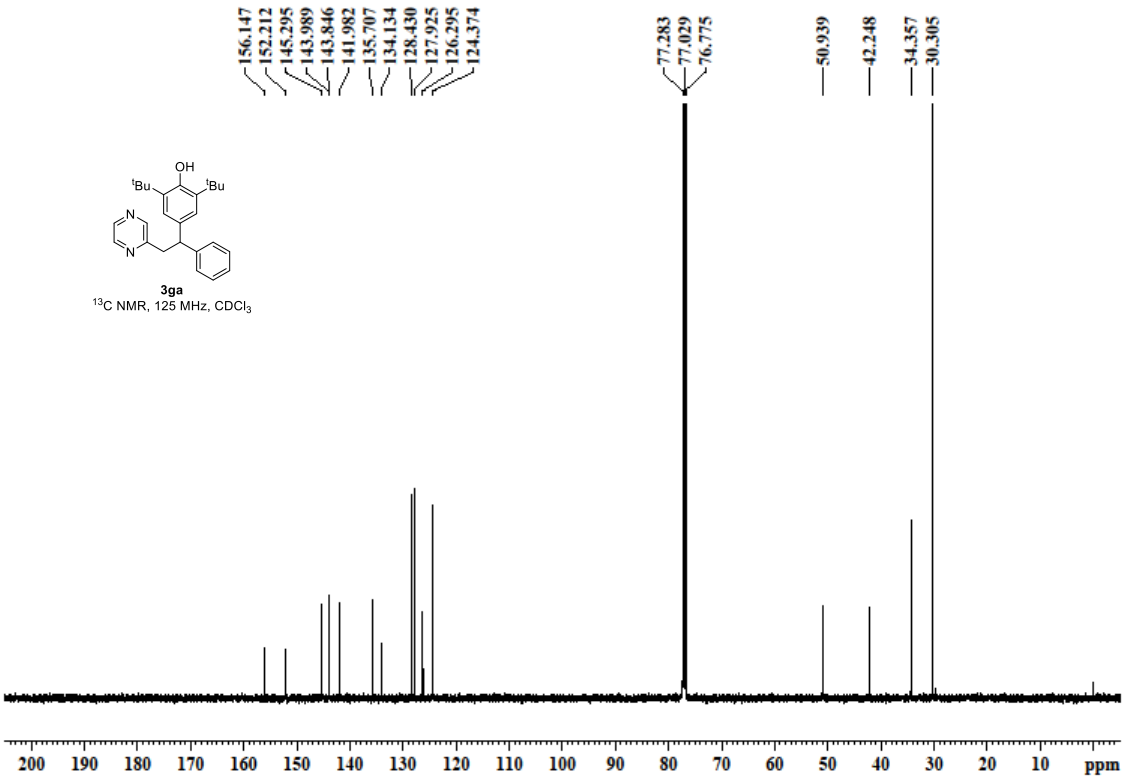


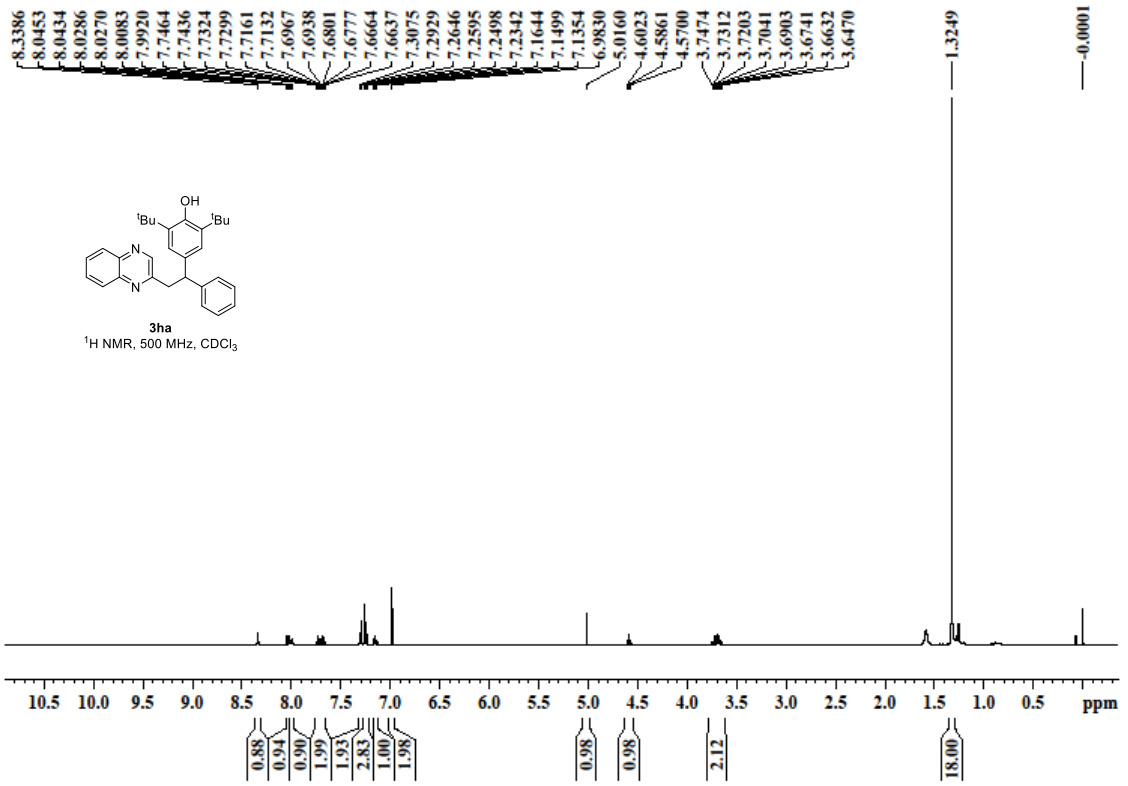
3fa
^{1}H NMR, 500 MHz, $CDCl_3$

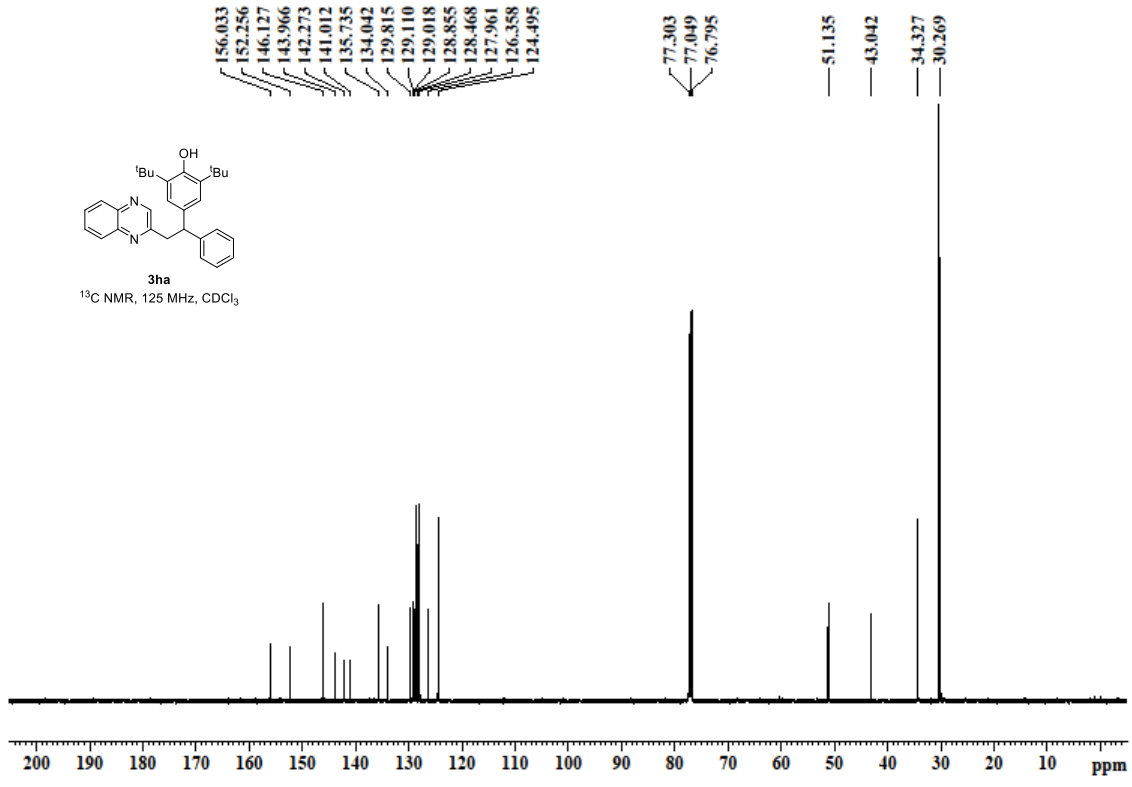


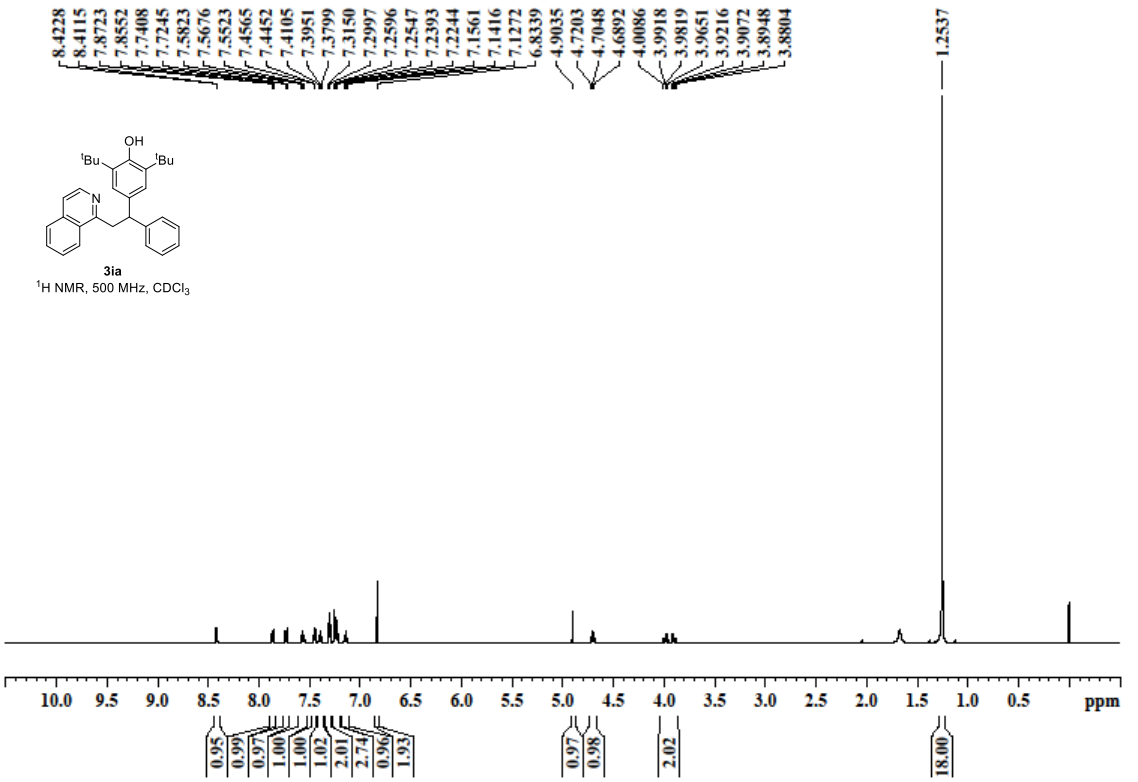
3fa
^{13}C NMR, 125 MHz, $CDCl_3$

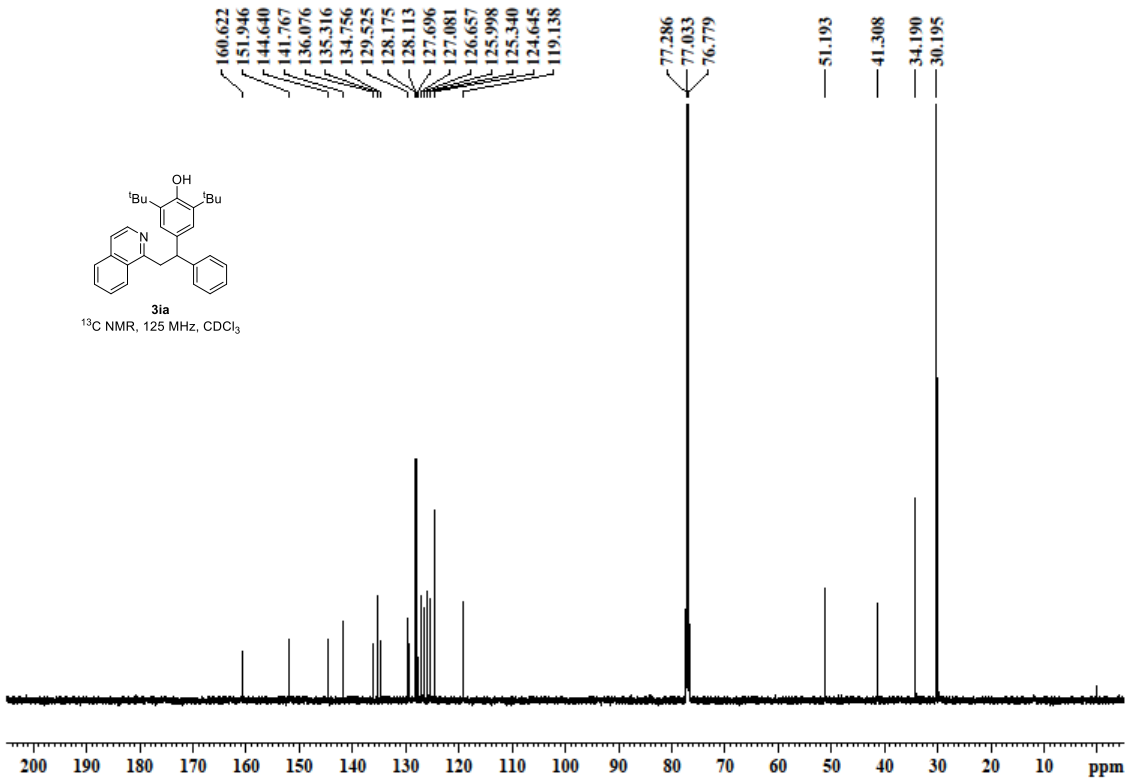

8.4749
8.2995
8.1074
7.2600
7.2484
7.2398
7.1631
7.1550
7.1464
7.1377
6.9765
5.0361
4.4891
4.4731
4.4570
3.5330
3.5161
3.5057
3.4889
3.4802
3.4646
3.4529
3.4373
1.3655
OH
tBu
tBu
N
N
3ga
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.93
0.92
0.94
3.79
0.99
1.96
0.99
1.00
2.01
18.00

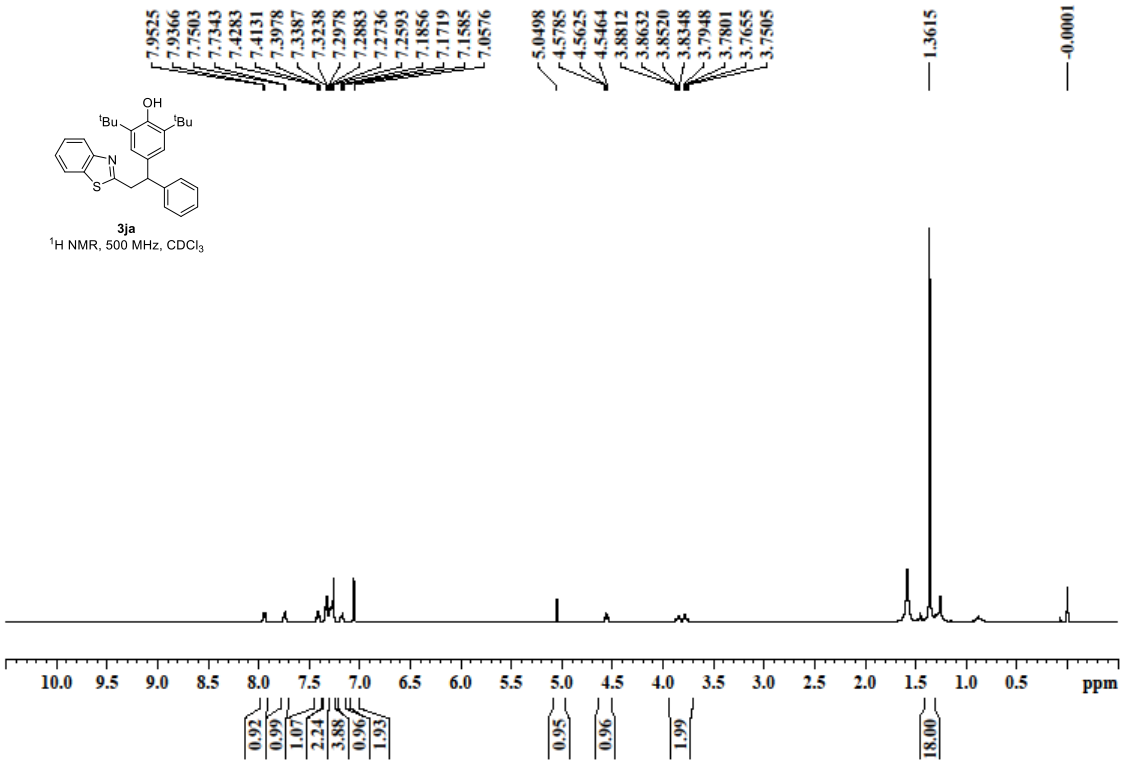

156.147
152.212
145.295
143.989
143.846
141.982
135.707
134.134
128.430
127.925
126.295
124.374
77.283
77.029
76.775
50.939
42.248
34.357
30.305
OH
tBu
tBu
N
N
3ga
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

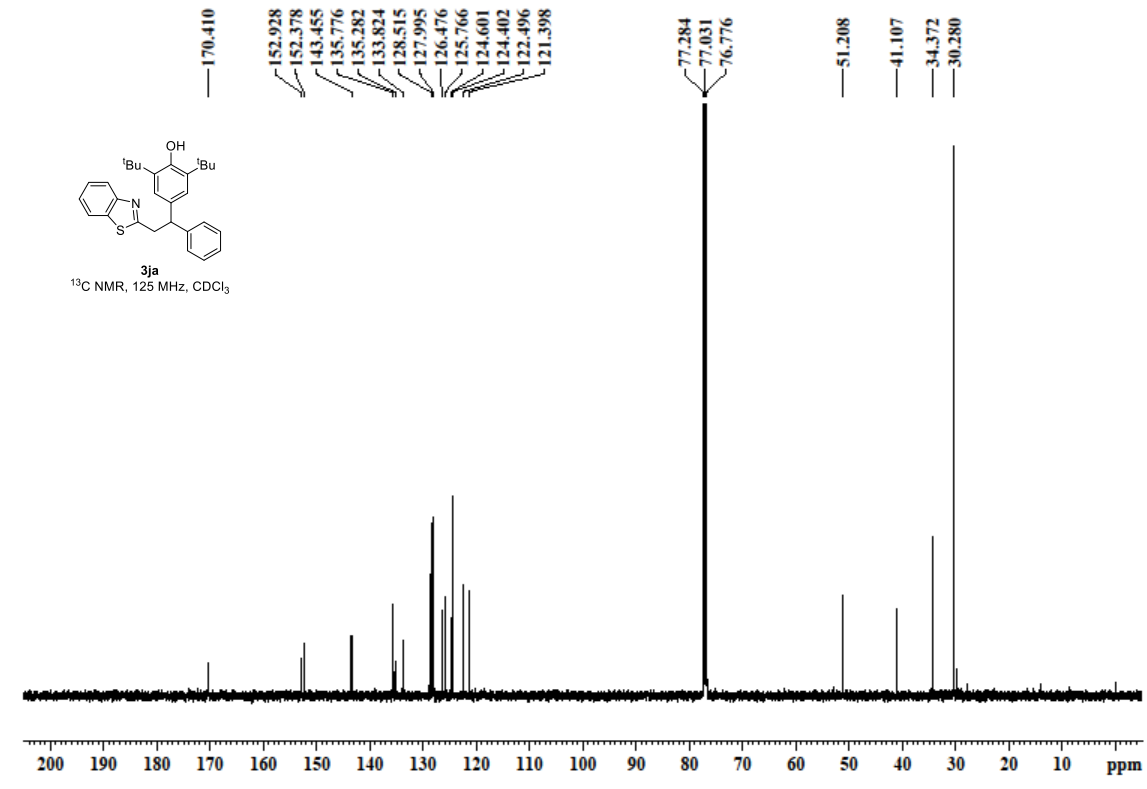

8.3386
8.0453
8.0434
8.0286
8.0270
8.0083
7.9920
7.7464
7.7436
7.7324
7.7299
7.7161
7.7132
7.6967
7.6938
7.6801
7.6777
7.6664
7.6637
7.3075
7.2929
7.2646
7.2595
7.2498
7.2342
7.1644
7.1499
7.1354
6.9830
5.0160
4.6023
4.5861
4.5700
3.7474
3.7312
3.7203
3.7041
3.6903
3.6741
3.6632
3.6470
1.3249
-0.0001
OH
tBu
tBu
N
N
3ha
1H NMR, 500 MHz, CDCl3
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.88
0.94
0.90
1.99
1.93
2.83
1.00
1.98
0.98
0.98
2.12
18.00

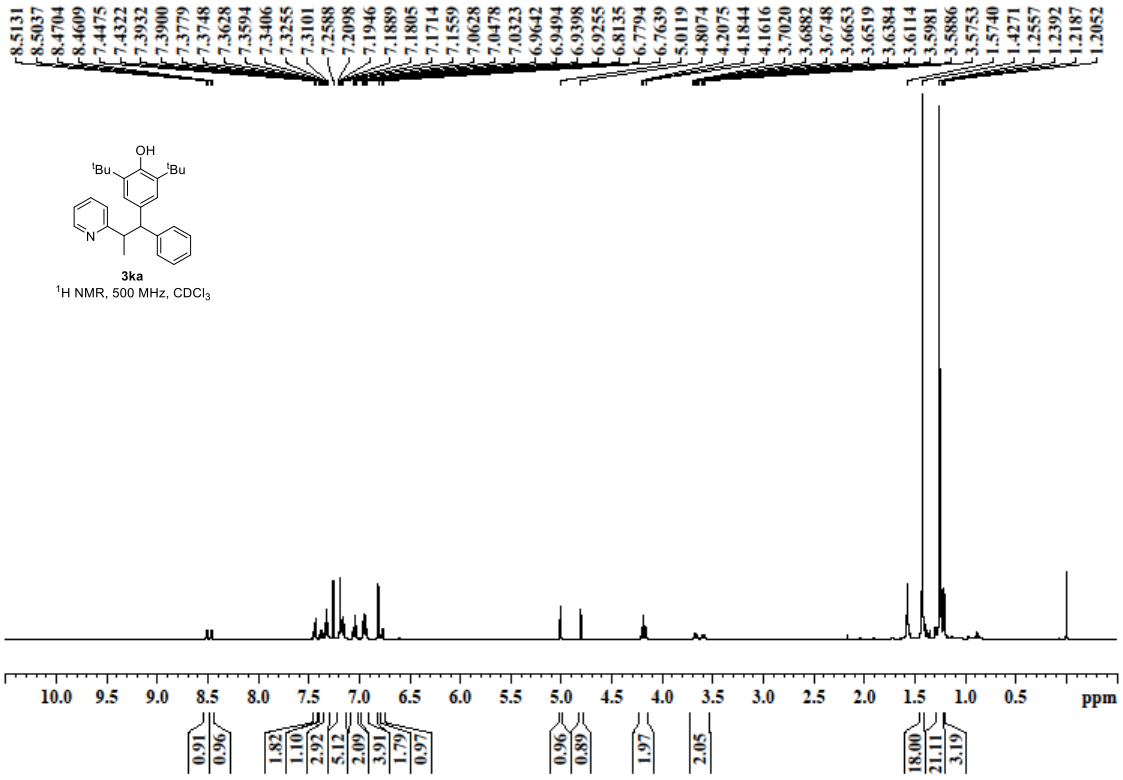

156.033
152.256
146.127
143.966
142.273
141.012
135.735
134.042
129.815
129.110
129.018
128.855
128.468
127.961
126.358
124.495
77.303
77.049
76.795
51.135
43.042
34.327
30.269
OH
tBu
tBu
N
N
3ha
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

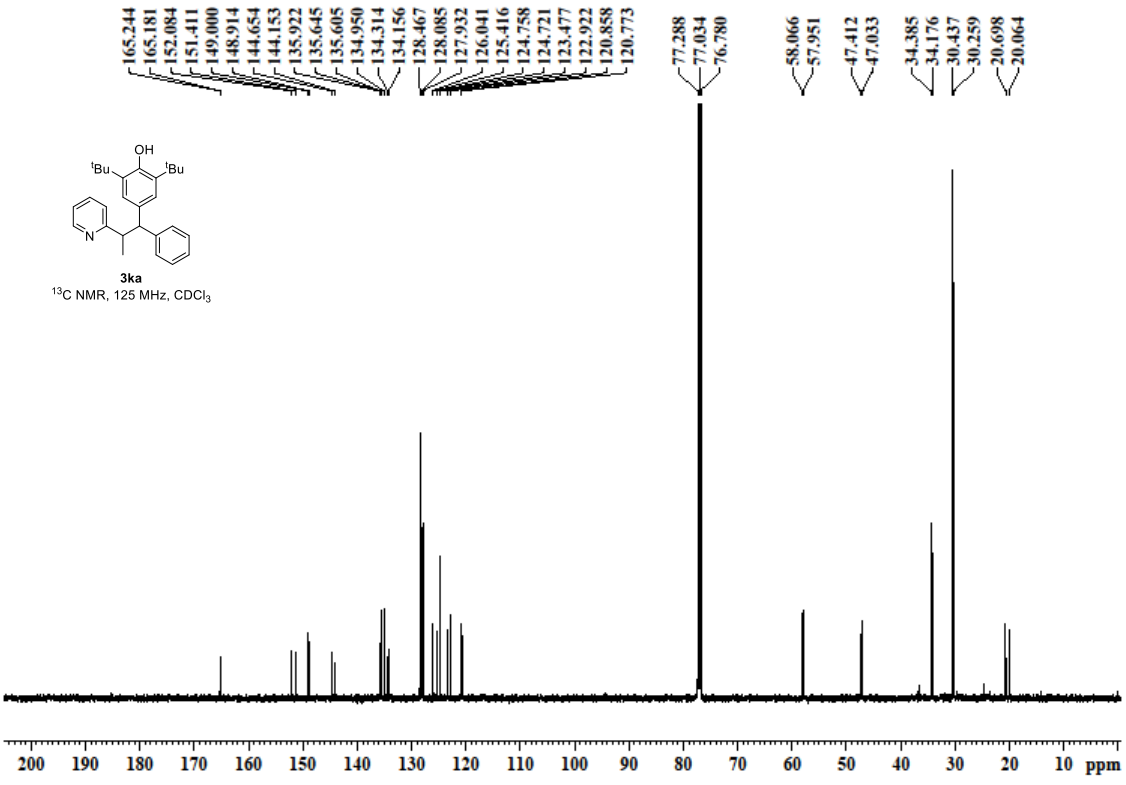

8.4228
8.4115
7.8723
7.8552
7.7408
7.7245
7.5823
7.5676
7.5523
7.4565
7.4452
7.4105
7.3951
7.3799
7.3150
7.2997
7.2596
7.2547
7.2393
7.2244
7.1561
7.1416
7.1272
6.8339
4.9035
4.7203
4.7048
4.6892
4.0086
3.9918
3.9819
3.9651
3.9216
3.9072
3.8948
3.8804
1.2537
OH
tBu
tBu
N
3ia
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.95
0.99
0.97
1.00
1.00
1.02
2.01
2.74
0.96
1.93
0.97
0.98
2.02
18.00

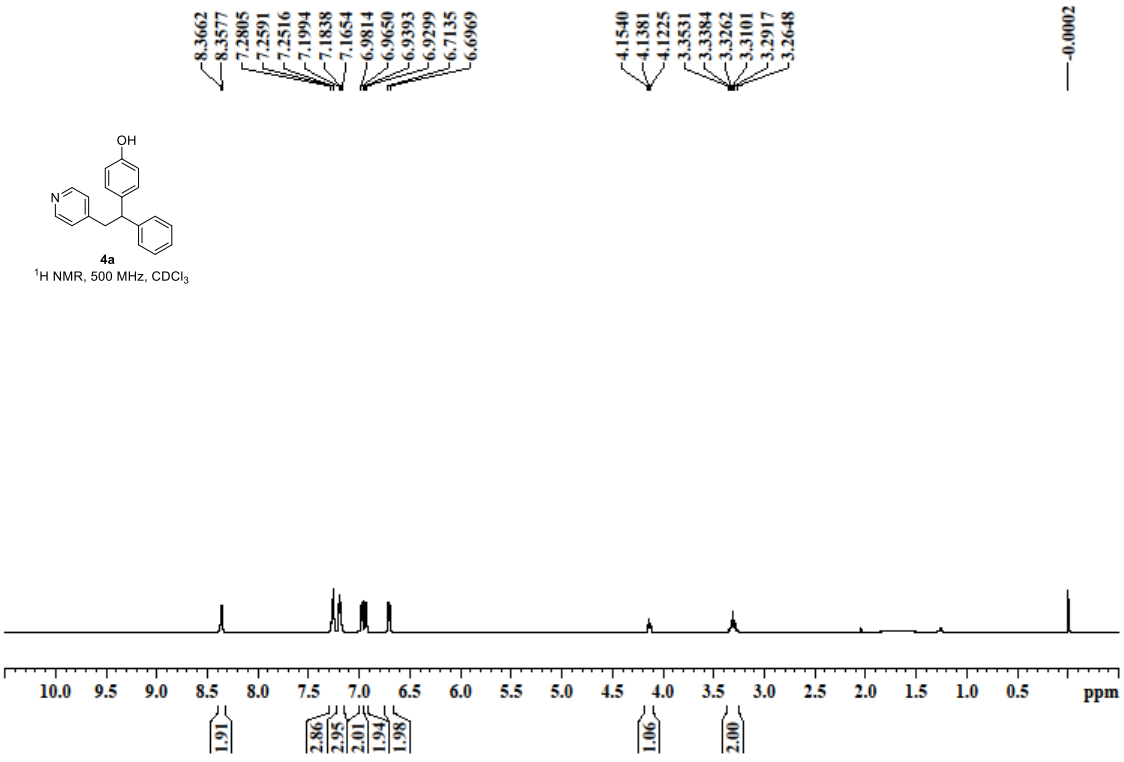

160.622
151.946
144.640
141.767
136.076
135.316
134.756
129.525
128.175
128.113
127.696
127.081
126.657
125.998
125.340
124.645
119.138
77.286
77.033
76.779
51.193
41.308
34.190
30.195
OH
tBu
tBu
N
3ia
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

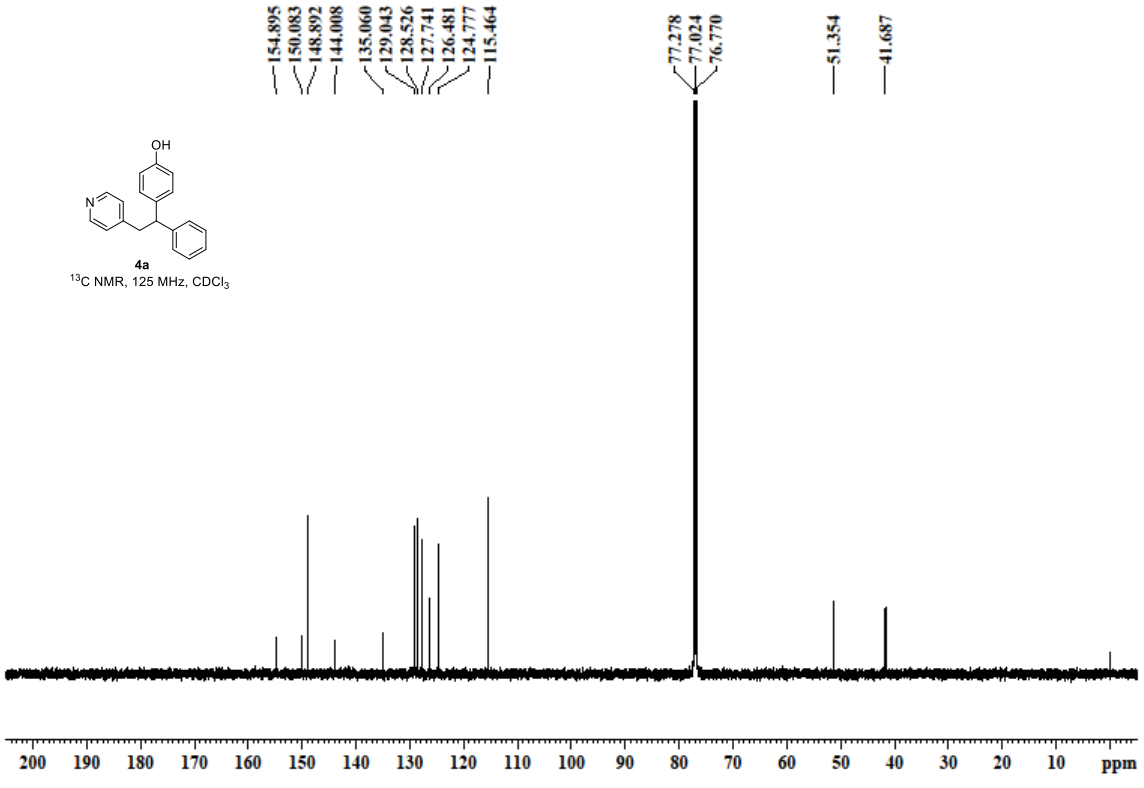

7.9525
7.9366
7.7503
7.7343
7.4283
7.4131
7.3978
7.3387
7.3238
7.2978
7.2883
7.2736
7.2593
7.1856
7.1719
7.1585
7.0576
5.0498
4.5785
4.5625
4.5464
3.8812
3.8632
3.8520
3.8348
3.7948
3.7801
3.7655
3.7505
1.3615
-0.0001
OH
tBu
tBu
N
S
3ja
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.92
0.99
1.07
2.24
3.88
0.96
1.93
0.95
0.96
1.99
18.00


170.410
152.928
152.378
143.455
135.776
135.282
133.824
128.515
127.995
126.476
125.766
124.601
124.402
122.496
121.398
77.284
77.031
76.776
51.208
41.107
34.372
30.280
OH
tBu
tBu
N
S
3ja
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.5131
8.5037
8.4704
8.4609
7.4475
7.4322
7.3932
7.3900
7.3779
7.3748
7.3628
7.3594
7.3406
7.3255
7.3101
7.2588
7.2098
7.1946
7.1889
7.1805
7.1714
7.1559
7.0628
7.0478
7.0323
6.9642
6.9494
6.9398
6.9255
6.8135
6.7794
6.7639
5.0119
4.8074
4.2075
4.1844
4.1616
3.7020
3.6882
3.6748
3.6653
3.6519
3.6384
3.6114
3.5981
3.5886
3.5753
1.5740
1.4271
1.2557
1.2392
1.2187
1.2052
OH
tBu
tBu
N
3ka
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.91 0.96 1.82 1.10 2.92 5.12 2.09 3.91 1.79 0.97 0.96 0.89 1.97 2.05 18.00 21.11 3.19


165.244
165.181
152.084
151.411
149.000
148.914
144.654
144.153
135.922
135.645
135.605
134.950
134.314
134.156
128.467
128.085
127.932
126.041
125.416
124.758
124.721
123.477
122.922
120.858
120.773
77.288
77.034
76.780
58.066
57.951
47.412
47.033
34.385
34.176
30.437
30.259
20.698
20.064
OH
tBu
tBu
N
3ka
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.3662
8.3577
7.2805
7.2591
7.2516
7.1994
7.1838
7.1654
6.9814
6.9650
6.9393
6.9299
6.7135
6.6969
4.1540
4.1381
4.1225
3.3531
3.3384
3.3262
3.3101
3.2917
3.2648
0.0002
OH
N
4a
1H NMR, 500 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.91
2.86
2.95
2.01
1.94
1.98
1.06
2.00


154.895
150.083
148.892
144.008
135.060
129.043
128.526
127.741
126.481
124.777
115.464
77.278
77.024
76.770
51.354
41.687
OH
N
4a
13C NMR, 125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm