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Supporting Information

Visible-Light Catalyzed Synthesis of 1,3-benzoxazines *via* Formal [4 + 2] Cycloaddition of Oximes with *o*-Hydroxybenzyl Alcohols

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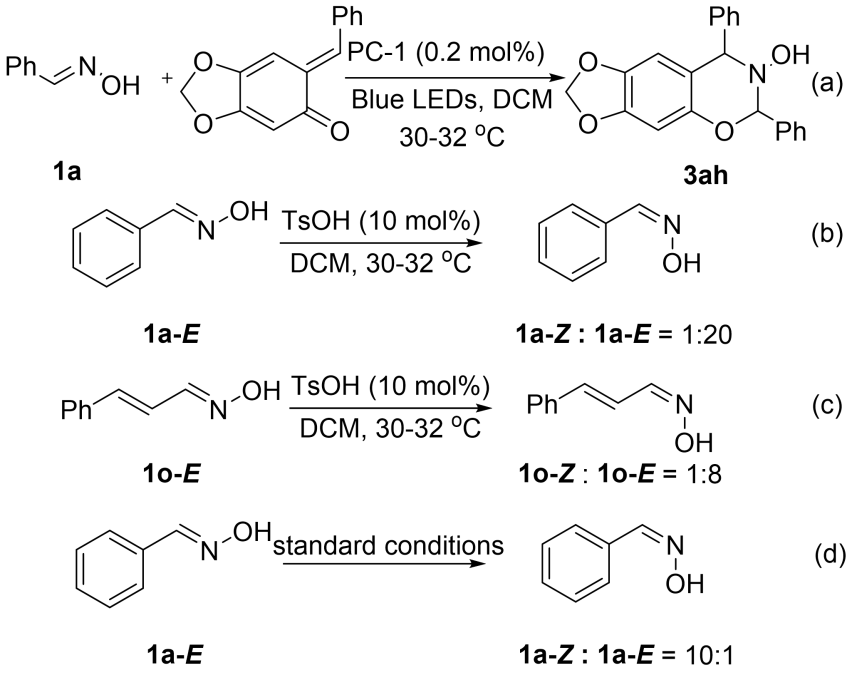
1. Genernal informations

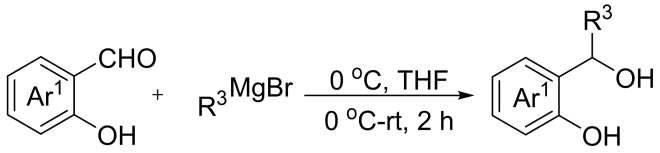
^{1}H NMR were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 100 MHz. Spectra were recorded in a $CDCl_3$, *J* values are given in hertz. IR spectra were recorded on Fourier Transform infrared spectrometer and listed in cm^{-1}. High-resolution mass spectral analyses (HRMS) were performed on a Q-TOF-MS spectrometer. Flash column chromatography was performed over silica gel (300-400 mesh). All commercially available reagents were used without further purification. Oximes were prepared according to the literature procedures.[1]

2. Scheme S1. Control experiments



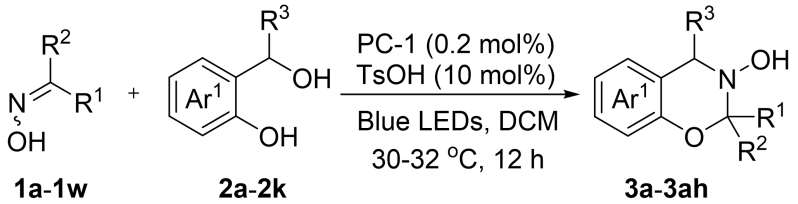
Scheme S1. Control experiments

3. General procedure for the *ortho*-hydroxy benzhydryl alcohols 2a-2k preparation from salicaldehyde derivatives with grignard reagents



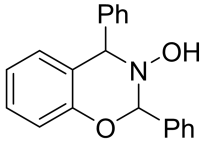
Under a nitrogen atmosphere, a solution of substituted salicylaldehyde (5.0 mmol) in tetrahydrofuran (10 mL) at 0°C was added dropwise to a solution of the grignard reagent (10.0 mmol, 1.0 M in THF, 10 mL), and the mixture was then removed from ice and stirred for 2 hours at rt. After complete conversion (monitored by TLC), the reaction mixture was quenched at 0°C with saturated NH_4Cl (10 mL), and extracted with EtOAc (3 x 25 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was chromatographed on silica gel eluting with petroleum ether/EtOAc (5:1, v/v) to give the products **2a**-**2k**.[2-3]

4. General procedure for the synthesis of 1,3-oxazines 3a-3ag

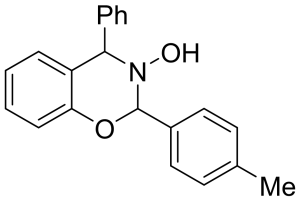


A mixture containing oxime **1** (0.2 mmol, 1.0 equiv), *o*-hydroxybenzyl alcohol **2** (0.22 mmol, 1.1 equiv) and PC-1 (0.2 mol%) were added under argon atmosphere to an over dried 10 mL reaction tube equipped with stir bar. Subsequently, dry toluene (1 mL) and , TsOH (10 mol%) were added under Ar atmosphere. The mixture was then irradiated by 12 W blue LEDs (purchased from Lingke Lighting Enterprise Store) and stirred at room temperature for 12 h. After the TLC analysis, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography to give the desired product to afford the **3a**-**3ah**.

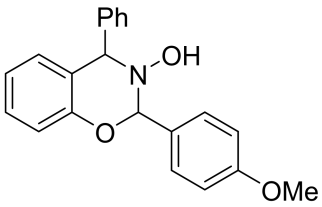
5. Characterization data of 1,3-oxazines 3a-3ag



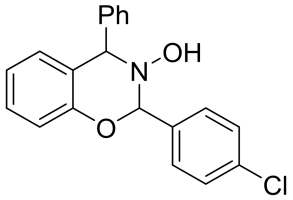
2,4-Diphenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3a).[4] According to the general procedure, 1,3-oxazine **3a** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (44.8 mg, 74% yield; eluent: PE/EtOAc = 10:1), mp 63-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (s, 1H), 7.64 (s, 1H), 7.56-7.53 (m, 2H), 7.42-7.30 (m, 8H), 7.25-7.21 (m, 1H), 6.99-6.96 (m, 2H), 6.85 (dt, J = 7.6, 1.2 Hz, 1H), 6.53 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 150.4, 138.6, 131.1, 130.5, 129.9, 129.8, 128.8, 128.4, 128.0, 127.4, 127.4, 126.3, 120.3, 117.6, 84.6 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{18}NO_2$: 304.1332; Found: 304.1331.



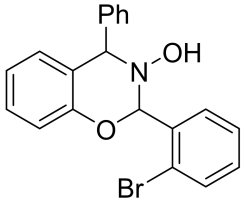
4-Phenyl-2-(*p*-tolyl)-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3b). According to the general procedure, 1,3-oxazine **3b** was obtained from 4-methylbenzaldehyde oxime (27 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (48.2 mg, 76% yield; eluent: PE/EtOAc = 10:1), mp 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 (s, 1H), 7.70 (s, 1H), 7.65-7.59 (m, 2H), 7.48-7.46 (m, 2H), 7.36-7.26 (m, 6H), 7.17-7.14 (m, 1H), 7.04-7.00 (m, 1H), 6.95-6.92 (m, 1H), 6.59 (s, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.0, 150.1, 137.9, 130.9, 130.2, 129.6, 129.4, 129.0, 128.5, 128.4, 127.7, 127.1, 126.1, 120.0, 117.1, 83.4, 20.9 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_2$: 318.1489; Found: 318.1487.



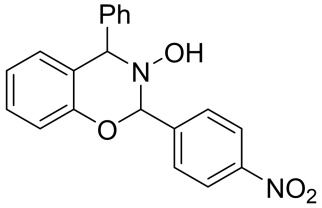
2-(4-Methoxyphenyl)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3c). According to the general procedure, 1,3-oxazine **3c** was obtained from 4-methoxybenzaldehyde oxime (30.5 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (54.0 mg, 81% yield; eluent: PE/EtOAc = 5:1), mp 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (s, 1H), 7.80 (s, 1H), 7.55-7.53 (m, 2H), 7.41-7.38 (m, 1H), 7.30-7.21 (m, 4H), 7.09-7.05 (m, 3H), 7.00-6.98 (m, 1H), 6.93-6.88 (m, 2H), 6.49 (s, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.0, 155.5, 150.4, 138.5, 131.3, 130.6, 129.7, 129.6, 128.1, 127.3, 126.4, 126.0, 120.2, 117.2, 113.0, 84.5, 55.3 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_3$: 334.1438; Found: 334.1436.



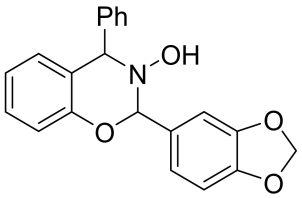
2-(4-Chlorophenyl)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3d). According to the general procedure, 1,3-oxazine **3d** was obtained from 4-chlorobenzaldehyde oxime (31.3 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (47.2 mg, 70% yield; eluent: PE/EtOAc = 10:1), mp 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (s, 1H), 7.43-7.37 (m, 2H), 7.31-7.23 (m, 8H), 7.17-7.13 (m, 1H), 6.93 (dt, J = 7.6, 2.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.81-6.77 (m, 1H), 6.46 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.1, 149.2, 138.5, 136.4, 129.9, 129.7, 129.1, 129.0, 128.5, 128.4, 128.2, 128.1, 127.4, 120.4, 117.4, 84.8 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{17}{}^{35}ClNO_2$: 338.0942; Found: 338.0941; $C_{20}H_{17}{}^{37}ClNO_2$: 340.0913; Found: 340.0916.



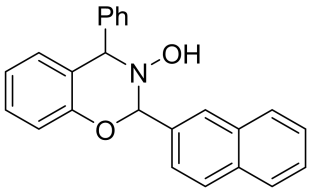
2-(2-Bromophenyl)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3e). According to the general procedure, 1,3-oxazine **3e** was obtained from 4-bromobenzaldehyde oxime (40.3 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as yellow solid (44.2 mg, 58% yield; eluent: PE/EtOAc = 10:1), mp 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56 (s, 1H), 7.69 (dd, J = 7.7, 1.9 Hz, 1H), 7.48 (dd, J = 7.9, 1.4 Hz, 1H), 7.36-7.26 (m, 5H), 7.23-7.13 (m, 4H), 6.95 (dd, J = 7.7, 1.7 Hz, 1H), 6.89 (dd, J = 8.1, 1.2 Hz, 1H), 6.80 (td, J = 7.5, 1.2 Hz, 1H), 6.48 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.1, 149.7, 138.5, 133.2, 131.6, 130.6, 129.9, 129.7, 128.5, 128.1, 127.7, 127.7, 127.5, 126.1, 124.1, 120.4, 117.4, 85.0 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{17}{}^{79}BrNO_2$: 382.0437; Found: 382.0435; $C_{20}H_{17}{}^{81}BrNO_2$: 384.0417; Found: 384.0422.



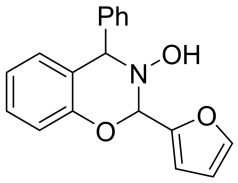
2-(4-Nitrophenyl)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3f). According to the general procedure, 1,3-oxazine **3f** was obtained from 4-nitrobenzaldehyde oxime (33.2 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (30.3 mg, 43% yield; eluent: PE/EtOAc = 4:1), mp 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 8.15-8.09 (m, 3H), 7.66-7.60 (m, 2H), 7.34-7.25 (m, 4H), 7.18-7.13 (m, 1H), 7.01 (dd, J = 7.6, 1.6 Hz, 1H), 6.86-6.80 (m, 2H), 6.65 (s, 1H), 6.53 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.5, 148.1, 138.4, 137.4, 129.9, 129.4, 128.5, 128.2, 127.9, 127.6, 127.5, 125.9, 124.0, 120.6, 117.1, 85.2 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{17}N_2O_4$: 349.1183; Found: 349.1181.



2-(Benzo[*d*][1,3]dioxol-5-yl)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3g). According to the general procedure, 1,3-oxazine **3g** was obtained from benzo[*d*][1,3]dioxole-5-carbaldehyde oxime (33.5 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (54.8 mg, 79% yield; eluent: PE/EtOAc = 4:1), mp 178-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (s, 1H), 7.85 (d, J = 5.0 Hz, 1H), 7.72-7.67 (m, 1H), 7.63-7.52 (m, 7H), 7.41-7.37 (m, 1H), 7.28-7.25 (m, 2H), 7.01 (td, J = 7.4, 2.0 Hz, 1H), 6.60 (s, 1H), 6.20 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.5, 153.8, 150.8, 149.4, 138.4, 135.2, 130.5, 129.6, 128.9, 128.5, 128.3, 128.0, 127.1, 120.9, 117.7, 105.5, 86.6 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{18}NO_4$: 348.1230; Found: 348.1232.

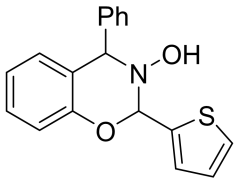


2-(Naphthalen-2-yl)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3h). According to the general procedure, 1,3-oxazine **3h** was obtained from 2-naphthaldehyde oxime (34.0 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (50.2 mg, 71% yield; eluent: PE/EtOAc = 10:1), mp 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 7.91-7.88 (m, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.68-7.64 (m, 2H), 7.56-7.53 (m, 2H), 7.47-7.41 (m, 3H), 7.26-7.11 (m, 5H), 7.02-6.99 (m, 1H), 6.83-6.79 (m, 1H), 6.62 (d, J = 7.6, 2.0 Hz, 1H), 6.46 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 150.7, 138.2, 136.3, 130.8, 129.8, 129.4, 128.9, 128.8, 128.4, 128.1, 128.0, 127.7, 127.5, 127.0, 126.1, 125.5, 122.5, 121.3, 120.6, 117.3, 84.2 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{20}NO_2$: 354.1489; Found: 354.1487.

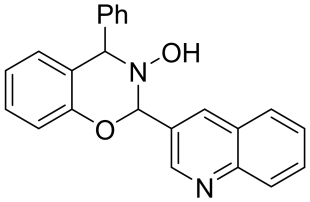


2-(Furan-2-yl)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3i). According to the general procedure, 1,3-oxazine **3i** was obtained furan-2-carbaldehyde oxime (22.2 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (38.7 mg, 66% yield; eluent: PE/EtOAc = 5:1), mp 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (s, 1H), 7.54-7.51 (m, 2H), 7.26-7.18 (m, 7H), 7.04-7.01 (m, 1H), 6.87-6.81 (m, 2H), 6.63 (d, J = 7.6, 2.0 Hz, 1H), 6.53 (s, 1H)

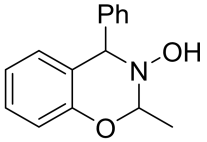
ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.5, 151.4, 144.9, 138.2, 131.3, 130.6, 129.8, 128.4, 127.9, 127.4, 127.1, 126.3, 125.5, 120.2, 117.6, 84.6 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{16}NO_3$: 294.1125; Found: 294.1126.



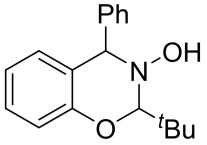
4-Phenyl-2-(thiophen-2-yl)-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3j). According to the general procedure, 1,3-oxazine **3j** was obtained from thiophene-2-carbaldehyde oxime (25.4 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (33.4 mg, 54% yield; eluent: PE/EtOAc = 10:1), mp 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (s, 1H), 7.79 (s, 1H), 7.71-7.65 (m, 2H), 7.42-7.32 (m, 6H), 7.13-7.11 (m, 1H), 7.01-6.96 (m, 2H), 6.85 (dd, J = 7.5, 2.0 Hz, 1H), 6.61 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 150.3, 138.2, 135.9, 130.5, 129.7, 128.8, 128.4, 127.9, 127.5, 127.3, 127.1, 126.6, 120.3, 117.5, 84.6 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{16}NO_2S$: 310.0896; Found: 310.0894.



4-Phenyl-2-(quinolin-3-yl)-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3k). According to the general procedure, 1,3-oxazine **3k** was obtained from quinoline-3-carbaldehyde oxime (34.7 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (37.6 mg, 39% yield; eluent: PE/EtOAc = 3:1), mp 217-219 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.74 (dd, J = 7.4, 1.4 Hz, 1H), 8.82 (s, 1H), 8.48 (s, 1H), 8.18-8.15 (m, 1H), 7.99-7.97 (m, 2H), 7.81-7.78 (m, 1H), 7.71-7.64 (m, 4H), 7.56-7.51 (m, 4H), 7.37-7.33 (m, 1H), 7.09 (td, J = 7.4, 2.0 Hz, 1H), 6.62 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 153.9, 152.8, 150.4, 138.7, 136.9, 131.8, 131.4, 130.9, 130.4, 130.1, 129.8, 129.6, 129.1, 128.6, 128.2, 127.8, 126.6, 120.8, 117.7, 84.9 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{19}N_2O_2$: 355.1441; Found: 355.1443.

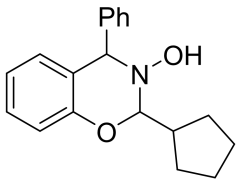


2-Methyl-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3l). According to the general procedure, 1,3-oxazine **3l** was obtained from acetaldehyde oxime (11.8 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as light yellow oil (36.2 mg, 75% yield; eluent: PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 7.45-7.39 (m, 4H), 7.31-7.26 (m, 2H), 7.04-6.99 (m, 1H), 6.92-6.89 (m, 2H), 6.80-6.75 (m, 1H), 6.45 (s, 1H), 1.92 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 154.4, 138.2, 129.4, 129.1, 128.5, 127.6, 127.2, 126.8, 119.8, 117.1, 84.6, 16.60 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{15}H_{16}NO_2$: 242.1176; Found: 242.1175.

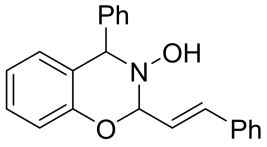


2-(*tert*-Butyl)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3m). According to the general procedure, 1,3-oxazine **3m** was obtained from pivalaldehyde oxime (20.2 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as

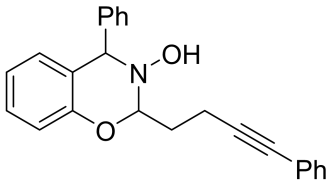
light yellow oil (39.6 mg, 70% yield; eluent: PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 7.37 (s, 1H), 7.29-7.19 (m, 5H), 7.16-7.11 (m, 1H), 6.90 (dd, J = 8.0, 1.2 Hz, 1H), 6.78-6.70 (m, 2H), 6.29 (s, 1H), 1.01 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.1, 155.8, 138.7, 129.9, 129.8, 128.3, 128.3, 127.7, 127.3, 120.1, 117.7, 83.3, 34.0, 27.3 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{22}NO_2$: 284.1645; Found: 284.1644.



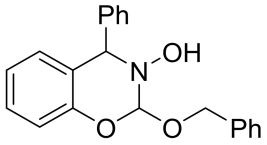
2-Cyclopentyl-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3n). According to the general procedure, 1,3-oxazine **3n** was obtained from cyclopentanecarbaldehyde oxime (22.6 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as light yellow oil (41.9 mg, 71% yield; eluent: PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.96 (s, 1H), 7.32-7.22 (m, 6H), 7.17-7.11 (m, 1H), 6.92-6.90 (m, 1H), 6.71-6.70 (m, 2H), 6.31 (s, 1H), 2.48-2.37 (m, 1H), 1.84 (s, 2H), 1.02-1.00 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.1, 156.3, 139.1, 130.0, 129.8, 128.2, 127.6, 127.5, 127.1, 119.9, 117.9, 82.5, 34.6, 19.6, 12.3 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{22}NO_2$: 296.1645; Found: 296.1643.



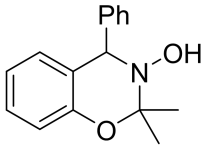
(*E*)-4-Phenyl-2-styryl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3o). According to the general procedure, 1,3-oxazine **3o** was obtained from (2*E*)-cinnamaldehyde oxime (29.4 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as light yellow oil (44.7 mg, 68% yield; eluent: PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 7.85-7.82 (m, 1H), 7.58-7.51 (m, 4H), 7.42-7.28 (m, 5H), 7.23-7.19 (m, 1H), 7.06-7.03 (m, 1H), 6.96-6.92 (m, 1H), 6.85 (dd, J = 15.0, 1.1 Hz, 1H), 6.77 (dd, J = 7.4, 2.0 Hz, 1H), 6.62 (dd, J = 6.2, 1.0 Hz, 1H), 6.45 (s, 1H), 5.53 (dd, J = 15.1, 6.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 150.3, 139.5, 131.5, 130.1, 129.7, 128.8, 128.0, 127.3, 127.1, 126.6, 126.2, 125.9, 124.1, 122.6, 120.6, 117.0, 83.4 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{20}NO_2$: 330.1489; Found: 330.1487.



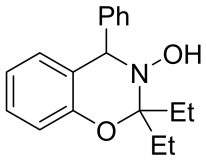
4-Phenyl-2-(4-phenylbut-3-yn-1-yl)-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3p). According to the general procedure, 1,3-oxazine **3p** was obtained from 5-phenylpent-4-ynal oxime (22.6 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as light yellow oil (49.7 mg, 70% yield; eluent: PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 7.66-7.64 (m, 1H), 7.57-7.53 (m, 2H), 7.47-7.42 (m, 1H), 7.36-7.27 (m, 4H), 7.18-7.11 (m, 3H), 6.98-6.95 (m, 1H), 6.88-6.83 (m, 2H), 6.69 (d, J = 7.6, 2.0 Hz, 1H), 6.51 (s, 1H), 2.68-2.53 (m, 2H), 2.19-2.04 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 150.3, 139.5, 132.0, 131.2, 129.6, 129.2, 128.8, 128.3, 127.6, 127.2, 126.8, 126.3, 125.4, 120.3, 88.1, 84.0, 81.6, 29.4, 23.1 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{22}NO_2$: 356.1645; Found: 356.1644.



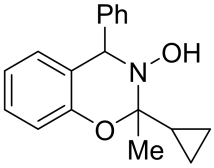
2-(Benzyloxy)-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3q). According to the general procedure, 1,3-oxazine **3q** was obtained from benzyl *N*-hydroxyformimidate (30.2 mg, 0.2 mmol) and2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as light yellow oil (43.3 mg, 65% yield; eluent: PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 1H), 7.56-7.52 (m, 2H), 7.47-7.43 (m, 1H), 7.37-7.25 (m, 5H), 7.13-7.04 (m, 5H), 6.97-6.92 (m, 1H), 6.87-6.83 (m, 1H), 6.78 (s, 1H), 4.71-4.63 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 155.2, 140.1, 130.1, 129.8, 129.2, 128.7, 128.5, 128.3, 128.2, 127.2, 125.2, 120.8, 118.7, 84.9, 66.9 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_3$: 334.1438; Found: 334.1436.



2,2-Dimethyl-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3r). According to the general procedure, 1,3-oxazine **3r** was obtained from propan-2-one oxime (14.1 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as light yellow oil (39.3 mg, 77% yield; eluent: PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.23 (m, 5H), 7.18-7.12 (m, 1H), 6.90 (dd, J = 8.0, 1.2 Hz, 1H), 6.78-6.70 (m, 2H), 6.30 (s, 1H), 1.90 (s, 3H), 1.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 156.1, 139.1, 130.0, 129.8, 128.3, 127.7, 127.3, 127.2, 120.0, 117.8, 83.1, 22.1, 16.0 ppm; HRMS (ESI) *m/z:* $[M+H]^+$ calcd. for $C_{16}H_{18}NO_2$: 256.1332; Found: 256.1333.

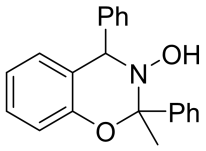


2,2-Diethyl-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3s). According to the general procedure, 1,3-oxazine **3s** was obtained from pentan-3-one oxime (20.3 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as light yellow oil (41.3 mg, 73% yield; eluent: PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.92 (s, 1H), 7.30-7.23 (m, 5H), 7.16-7.11 (m, 1H), 6.92-6.89 (m, 1H), 6.73-6.68 (m, 2H), 6.31 (s, 1H), 2.37-2.30 (m, 2H), 2.170 (q, J = 7.6 Hz, 2H), 1.04-0.99 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 156.3, 139.2, 130.0, 129.8, 128.2, 127.5, 127.1, 119.9, 117.8, 82.5, 27.2, 22.0, 10.5, 10.1 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{22}NO_2$: 284.1645; Found: 284.1643.

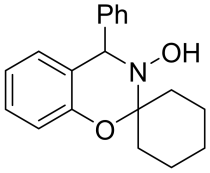


2-Cyclopropyl-2-methyl-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3t). According to the general procedure, 1,3-oxazine **3t** was obtained from 1-cyclopropylethan-1-one oxime (20.2 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as light yellow oil (38.8 mg, 69% yield; eluent: PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (s, 1H), 7.32-7.18 (m, 5H), 7.11-7.07 (m, 1H), 6.82-6.78 (m, 2H), 6.74-6.70 (m, 1H), 5.91 (s, 1H), 1.60 (s, 3H), 1.52-1.45 (m, 1H), 0.66-0.55 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.8, 155.3, 142.1, 129.1, 128.6, 128.2,

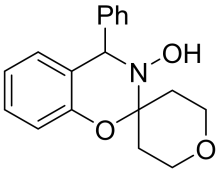
128.0, 127.0, 126.8, 119.8, 117.1, 76.5, 15.1, 10.5, 5.0, 4.5 ppm; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{18}H_{20}NO_2$: 282.1489; Found: 282.1488.



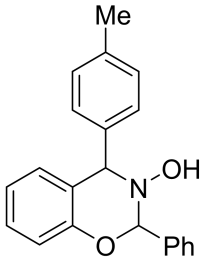
2-Methyl-2,4-diphenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3u). According to the general procedure, 1,3-oxazine **3u** was obtained from 1-phenylethan-1-one oxime (27.3 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (39.3 mg, 62% yield; eluent: PE/EtOAc = 8:1), mp 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (s, 1H), 7.56-7.48 (m, 2H), 7.36-7.24 (m, 8H), 7.16-7.12 (m, 1H), 6.92-6.89 (m, 1H), 6.85-6.81 (m, 1H), 6.76-6.71 (m, 1H), 6.50-6.49 (s, 1H), 2.28 (d, J = 2.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 155.9, 138.9, 135.5, 130.0, 129.9, 129.7, 128.6, 128.3, 127.7, 127.2, 126.2, 126.0, 120.1, 117.8, 83.7, 13.5 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_2$: 318.1489; Found: 318.1491.



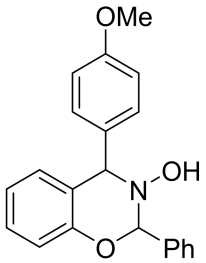
4-Phenylspiro[benzo[*e*][1,3]oxazine-2,1'-cyclohexan]-3(4*H*)-ol (3v). According to the general procedure, 1,3-oxazine **3v** was obtained from cyclohexanone oxime (22.6 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (44.1 mg, 0.22 mmol) as white solid (41.3 mg, 70% yield; eluent: PE/EtOAc = 5:1), mp 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (s, 1H), 7.58-7.42 (m, 5H), 7.25-7.22 (m, 1H), 7.06 (td, J = 7.2, 2.5 Hz, 1H), 6.87-6.80 (m, 2H), 6.47 (s, 1H), 2.18-2.11 (m, 1H), 2.06-2.01 (m, 1H), 1.86-1.77 (m, 3H), 1.66-1.58 (m, 2H), 1.52-1.45 (m, 1H), 1.32-1.23 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.5, 156.3, 140.2, 135.2, 130.5, 129.6, 129.2, 128.1, 127.8, 121.2, 117.9, 83.4, 35.4, 25.9, 23.1 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{22}NO_2$: 296.1645; Found: 296.1644.



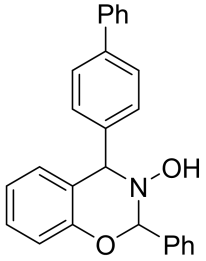
4-Phenyl-2',3',5',6'-tetrahydrospiro[benzo[*e*][1,3]oxazine-2,4'-pyran]-3(4*H*)-ol (3w). According to the general procedure, 1,3-oxazine **3w** was obtained tetrahydro-4*H*-pyran-4-one oxime (23.4 mg, 0.2 mmol) and 2-hydroxy benzylalcohol (38.1 mg, 0.22 mmol) as white solid (39.3 mg, 64% yield; eluent: PE/EtOAc = 4:1), mp 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (s, 1H), 7.73-7.61 (m, 5H), 7.36-7.34 (m, 1H), 7.18-7.14 (m, 1H), 6.95-6.91 (m, 2H), 6.65 (s, 1H), 4.33-4.26 (m, 1H), 3.99-3.92 (m, 1H), 3.69-3.60 (m, 1H), 3.49-3.42 (m, 1H), 2.65-2.51 (m, 2H), 2.32-2.25 (m, 1H), 1.87-1.80 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 157.6, 140.0, 136.3, 131.7, 131.2, 129.3, 128.4, 127.1, 120.1, 117.8, 86.8, 64.8, 35.8 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{20}NO_3$: 298.1438; Found: 298.1436.



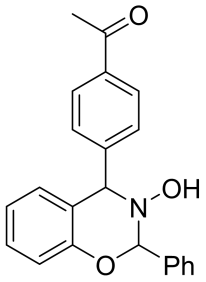
2-Phenyl-4-(*p*-tolyl)-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3x). According to the general procedure, 1,3-oxazine **3x** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-(hydroxy(*p*-tolyl)methyl)phenol (47.1 mg, 0.22 mmol) as white solid (45.7 mg, 72% yield; eluent: PE/EtOAc = 10:1), mp 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (s, 1H), 7.77-7.72 (m, 2H), 7.48-7.40 (m, 8H), 7.36-7.31 (m, 1H), 7.19-7.16 (m, 1H), 7.13-7.09 (m, 1H), 6.98 (dd, J = 7.5, 2.0 Hz, 1H), 6.73 (s, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 150.5, 138.5, 131.8, 129.8, 129.7, 129.3, 128.8, 128.4, 127.9, 127.4, 127.1, 126.3, 120.3, 117.4, 84.0, 20.5 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_2$: 318.1489; Found: 318.1487.



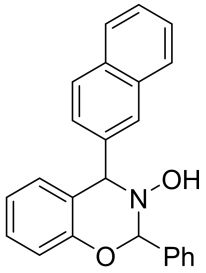
4-(4-Methoxyphenyl)-2-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3y). According to the general procedure, 1,3-oxazine **3y** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-(hydroxy(4-methoxyphenyl)methyl)phenol (50.9 mg, 0.22 mmol) as white solid (40.6 mg, 61% yield; eluent: PE/EtOAc = 10:1), mp 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (s, 1H), 7.76-7.73 (m, 2H), 7.60-7.52 (m, 7H), 7.44-7.40 (m, 1H), 7.39-7.27 (m, 1H), 7.19-7.16 (m, 2H), 7.05-7.01 (td, J = 7.4, 2.0 Hz, 1H), 6.72 (s, 1H), 4.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.6, 156.1, 151.1, 138.9, 137.2, 133.1, 131.5, 130.7, 130.3, 129.2, 128.5, 127.1, 126.5, 120.9, 117.8, 84.8, 64.6 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_3$: 334.1438; Found: 334.1436.



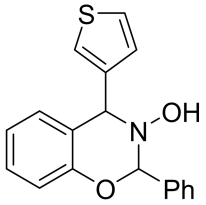
4-([1,1'-Biphenyl]-4-yl)-2-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3z). According to the general procedure, 1,3-oxazine **3z** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-([1,1'-biphenyl]-4-yl(hydroxy)methyl)phenol (61.2 mg, 0.22 mmol) as white solid (45.5 mg, 60% yield; eluent: PE/EtOAc = 10:1), mp 173-175 °C. ^{1}H NMR 8.43 (s, 1H), 7.84-7.81 (m, 2H), 7.77-7.71 (m, 4H), 7.66-7.53 (m, 8H), 7.50-7.45 (m, 1H), 7.25-7.12 (m, 3H), 6.91 (dd, J = 7.4, 2.0 Hz, 1H), 6.67 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 151.8, 139.1, 134.9, 131.5, 130.1, 129.8, 129.6, 129.4, 129.2, 129.0, 128.9, 128.7, 128.4, 128.2, 127.5, 126.5, 120.4, 117.5, 84.6 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{22}NO_2$: 380.1645; Found: 380.1642.



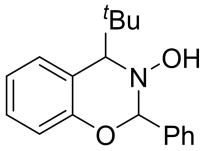
1-(4-(3-Hydroxy-2-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-4-yl)phenyl)ethan-1-one (3aa). According to the general procedure, 1,3-oxazine **3aa** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 1-(4-(hydroxy(2-hydroxyphenyl)methyl)phenyl)ethan-1-one (53.4 mg, 0.22 mmol) as white solid (48.4 mg, 70% yield; eluent: PE/EtOAc = 8:1), mp 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (s, 1H), 7.90-7.87 (m, 2H), 7.76-7.68 (m, 7H), 7.47-7.43 (m, 1H), 7.26-7.21 (m, 1H), 7.16-7.10 (m, 2H), 6.98 (dd, J = 7.4, 1.9 Hz, 1H), 6.72 (s, 1H), 2.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.6, 155.2, 151.1, 140.3, 137.8, 131.3, 131.1, 130.1, 129.9, 129.0, 128.5, 128.1, 127.5, 126.4, 120.6, 117.7, 84.8, 28.2 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{20}NO_3$: 346.1438; Found: 346.1435.



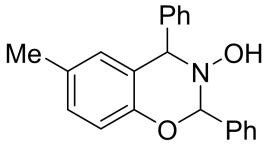
4-(Naphthalen-2-yl)-2-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3ab). According to the general procedure, 1,3-oxazine **3ab** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-(hydroxy(naphthalen-2-yl)methyl)phenol (55.2 mg, 0.22 mmol) as white solid (46.6 mg, 66% yield; eluent: PE/EtOAc = 10:1), mp 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (s, 1H), 8.13-8.09 (m, 2H), 8.05-8.03 (m, 1H), 7.91-7.87 (m, 1H), 7.82-7.76 (m, 3H), 7.70-7.63 (m, 2H), 7.60-7.53 (m, 4H), 7.42-7.38 (m, 1H), 7.13-7.06 (m, 2H), 6.90 (d, J = 7.6, 2.0 Hz, 1H), 6.59 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.0, 153.3, 138.0, 136.1, 132.8, 132.0, 131.3, 130.3, 129.7, 129.4, 129.3, 128.7, 128.4, 127.8, 127.5, 126.8, 126.0, 125.4, 125.2, 120.6, 117.7, 84.4 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{20}NO_2$: 354.1489; Found: 354.1486.



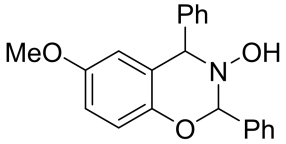
2-Phenyl-4-(thiophen-3-yl)-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3ac). According to the general procedure, 1,3-oxazine **3ac** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-(hydroxy(thiophen-3-yl)methyl)phenol (45.4 mg, 0.22 mmol) as white solid (35.2 mg, 57% yield; eluent: PE/EtOAc = 10:1), mp 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 7.78-7.74 (m, 2H), 7.62-7.53 (m, 3H), 7.42 (dd, J = 7.2, 5.5 Hz, 3H), 7.35-7.31 (m, 1H), 7.18-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.87 (dd, J = 7.5, 2.1 Hz, 1H), 6.62 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 149.8, 138.0, 133.9, 129.3, 129.1, 128.9, 128.6, 128.1, 127.8, 127.7, 127.4, 126.2, 120.7, 117.6, 84.6 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{16}NO_2S$: 310.0896; Found: 310.0894.



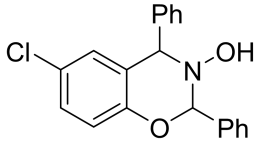
4-(*tert*-Butyl)-2-phenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3ad). According to the general procedure, 1,3-oxazine **3ad** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-(1-hydroxy-2,2-dimethylpropyl)phenol (40.1 mg, 0.22 mmol) as light yellow oil (38.5 mg, 68% yield; eluent: PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (s, 1H), 7.74-7.70 (m, 2H), 7.54-7.49 (m, 3H), 7.27-7.24 (m, 2H), 7.09 (dd, J = 7.5, 2.0 Hz, 1H), 6.99 (td, J = 7.5, 2.0 Hz, 1H), 6.57 (s, 1H), 4.93 (s, 1H), 1.13 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 155.4, 138.7, 129.5, 128.3, 127.9, 127.5, 127.2, 126.9, 120.8, 117.4, 84.0, 35.4, 26.8 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{22}NO_2$: 284.1645; Found: 284.1644.



6-Methyl-2,4-diphenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3ae). According to the general procedure, 1,3-oxazine **3ae** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-(hydroxy(phenyl)methyl)-4-methylphenol (47.1 mg, 0.22 mmol) as white solid (46.3 mg, 73% yield; eluent: PE/EtOAc = 10:1), mp 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (s, 1H), 7.91 (s, 1H), 7.68-7.64 (m, 2H), 7.52 (td, J = 7.5, 1.9 Hz, 1H), 7.45-7.37 (m, 5H), 7.33-7.30 (m, 1H), 7.16-7.10 (m, 1H), 7.06 (td, J = 7.4, 3.6 Hz, 2H), 6.96 (d, J = 7.5 Hz, 1H), 6.63 (s, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.7, 152.6, 139.3, 131.0, 130.1, 129.7, 129.4, 129.1, 128.9, 128.6, 128.2, 127.7, 126.5, 120.6, 117.6, 84.6, 23.1 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_2$: 318.1489; Found: 318.1486.

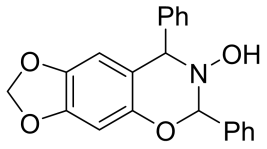


6-Methoxy-2,4-diphenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3af). According to the general procedure, 1,3-oxazine **3af** was obtained from benzaldehyde oxime (24.5 mg, 0.2 mmol) and 2-(hydroxy(phenyl)methyl)-4-methoxyphenol (50.6 mg, 0.22 mmol) as white solid (45.4 mg, 68% yield; eluent: PE/EtOAc = 8:1), mp 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (s, 1H), 7.76-7.70 (m, 2H), 7.63-7.39 (m, 8H), 7.34 (m, 1H), 7.08-7.01 (m, 2H), 6.94 (dd, J = 7.5, 2.0 Hz, 1H), 6.54 (s, 1H), 4.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.6, 154.8, 150.7, 138.4, 133.5, 130.9, 129.9, 128.9, 128.7, 127.8, 127.0, 126.1, 125.6, 120.9, 117.4, 84.6, 63.5 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_3$: 334.1438; Found: 334.1435.

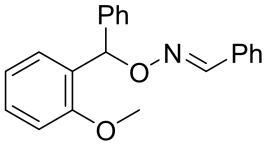


6-Chloro-2,4-diphenyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-ol (3ag). According to the general procedure, 1,3-oxazine **3ag** was obtained from benzaldehyde oxime (37.1 mg, 0.2 mmol) and 4-chloro-2-(hydroxy(phenyl)methyl)phenol (51.5 mg, 0.22 mmol) as white solid (39.3 mg, 55% yield; eluent: PE/EtOAc = 10:1), mp 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 (s, 1H), 7.72-7.69 (m, 2H), 7.57-7.49 (m, 8H), 7.41-7.37 (m, 1H), 7.08 (dd, J = 7.6, 2.0 Hz, 1H), 6.96 (d, J = 7.6 Hz, 2H), 6.54 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 149.0, 138.4, 136.4, 129.8, 129.6, 129.4,

129.3, 129.0, 128.7, 128.5, 128.2, 127.0, 120.3, 117.7, 84.6 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{17}{}^{35}ClNO_2$: 338.0942; Found: 338.0940; $C_{20}H_{17}{}^{35}ClNO_2$: 340.0913; Found: 340.0918.



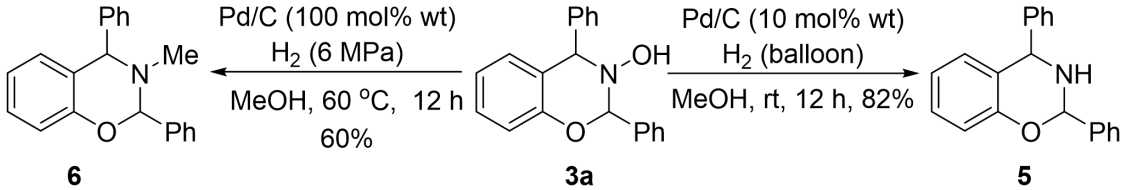
6,8-Diphenyl-6*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*e*][1,3]oxazin-7(8*H*)-ol (3ah). According to the general procedure, 1,3-oxazine **3ah** was obtained from benzaldehyde oxime (37.1 mg, 0.2 mmol) and 6-(hydroxy(phenyl)methyl)benzo[*d*][1,3]dioxol-5-ol (53.7 mg, 0.22 mmol) as white solid (43.0 mg, 62% yield; eluent: PE/EtOAc = 4:1), mp 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (s, 1H), 8.06 (s, 1H), 7.89-7.83 (m, 2H), 7.69-7.61 (m, 6H), 7.54 (td, J = 7.5, 2.1 Hz, 1H), 7.45 (td, J = 7.5, 2.1 Hz, 1H), 7.33 (td, J = 7.6, 2.0 Hz, 1H), 7.11-7.08 (m, 1H), 6.64 (s, 1H), 5.98 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 154.0, 152.8, 148.5, 140.0, 136.8, 133.7, 132.3, 130.6, 129.8, 128.8, 127.8, 127.0, 123.4, 117.3, 105.7, 85.3 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{18}NO_4$: 348.1230; Found: 348.1232.



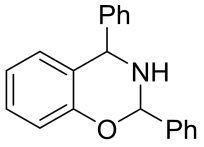
(*E*)-Benzaldehyde *O*-((2-methoxyphenyl)(phenyl)methyl) oxime (4). According to the general procedure, **4** was obtained from benzaldehyde oxime (37.1 mg, 0.2 mmol) and(2-methoxyphenyl)(phenyl)methanol (47 mg, 0.22 mmol) as white solid (48.8 mg, 77% yield; eluent: PE/EtOAc = 10:1), mp 142-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-8.30 (m, 2H), 7.89 (s, 1H), 7.50-7.44 (m, 3H), 7.36-7.31 (m, 4H), 7.27-7.24 (m, 2H), 7.21 (dd, J = 7.6, 1.7 Hz, 1H), 7.04 (dd, J = 8.2, 1.2 Hz, 1H), 6.91 (td, J = 7.4, 1.3 Hz, 1H), 6.22 (s, 1H), 3.93 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 137.6, 135.0, 131.9, 131.6, 131.4, 130.0, 129.3, 128.7, 128.7, 128.4, 126.8, 121.8, 119.6, 119.5, 84.6, 65.1 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO_2$: 318.1489; Found: 318.1487.

6. Synthetic transformations of 3a

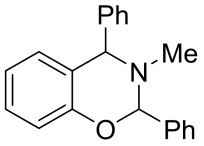
6.1 Hydrogenation of 3a catalyzed by Pd/C



To a solution of **3a** (151.7 mg, 0.5 mmol) in 5 mL methanol, 10% Pd/C (10% wt, 17.0 mg) was added and a hydrogen balloon was equipped to the reaction system and stirred for 12 h at room temperature. The pure compound **5** (124.2 mg, R_f = 0.25, PE:EA = 5:1) was obtained after filtration and general work-up treatment. Alternatively, increasing the hydrogen pressure to 6 MPa and 100% wt Pd/C (**3a**, 60.7 mg, 0.2 mmol, 2 mL MeOH; 67.6 mg Pd/C), *N*-methylation product **6** (36.4 mg, R_f = 0.4, PE:EA = 10:1) was obtained at 60 ˚C

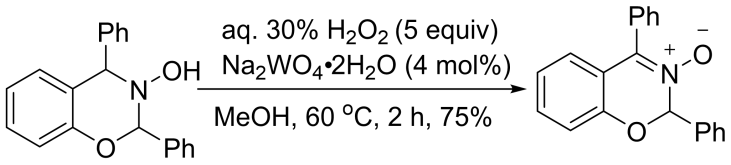


2,4-Diphenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine (5). According to the general procedure, 1,3-oxazine **5** was obtained from **3a** (151.7 mg, 0.5 mmol) as yellow oil (124.2 mg, 82% yield; eluent: PE/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (s, 1H), 7.81-7.77 (m, 2H), 7.60-7.39 (m, 8H), 7.24-7.21 (m, 2H), 7.11-7.08 (m, 1H), 6.91 (dd, J = 7.5, 2.1 Hz, 1H), 6.75 (s, 1H), 1.87 (br, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8, 150.7, 140.7, 131.4, 130.5, 130.0, 129.6, 129.3, 129.0, 128.8, 128.6, 128.0, 126.5, 120.8, 117.3, 85.7 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{18}NO$: 288.1383; Found: 288.1382.



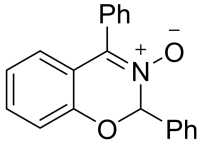
3-Methyl-2,4-diphenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine (6). According to the general procedure, *N*-methylation1,3-oxazine **6** was obtained from **3a** (60.7 mg, 0.2 mmol) as white solid (36.4 mg, 60% yield; eluent: PE/EtOAc = 10:1), mp 153-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.65 (s, 1H), 7.75-7.72 (m, 2H), 7.62-7.49 (m, 8H), 7.38 (td, J = 7.5, 2.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.10 (ddd, J = 7.5, 2.1, 1.0 Hz, 1H), 6.94 (dd, J = 7.5, 2.0 Hz, 1H), 6.57 (s, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.0, 150.5, 138.8, 132.3, 131.7, 131.2, 130.7, 130.4, 130.0, 129.6, 129.2, 128.8, 127.1, 121.0, 117.3, 84.6, 39.9 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{20}NO$: 302.1539; Found: 302.1537.

6.2 Oxidation of 3a by H_2O_2



3a **7**

In a 10 mL screw-cap vial, under nitrogen, **3a** (60.6 mg, 0.2 mmol) was dissolved in 2 mL of MeOH, followed by H_2O_2 (1 mmol, 30% in water) and $Na_2WO_4 \cdot 2H_2O$ (4 mol%), after 2 h at 60 °C, the reac-tion course was monitored via TLC. After the disappearance of the reagent, the solvent was removed under vacuum and the reaction mixture was purified directly via radial chromatography over silica gel.



2,4-Diphenyl-2*H*-benzo[*e*][1,3]oxazine 3-oxide (7). According to the general procedure, 1,3oxazine 3-oxide **7** was obtained from **3a** (60.6 mg, 0.2 mmol) as yellow oil (45.1 mg, 75% yield; eluent: EtOAc/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (dt, J = 7.4, 2.0 Hz, 1H), 8.13 (ddd, J = 6.9, 5.3, 3.7 Hz, 1H), 7.94-7.87 (m, 2H), 7.80-7.74 (m, 5H), 7.70-7.61 (m, 2H), 7.55 (dd, J = 7.5, 2.0 Hz, 1H), 7.36 (td, J = 7.5, 2.0 Hz, 1H), 7.11 (dd, J = 7.5, 2.1 Hz, 1H), 6.82 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.2, 153.6, 142.2, 138.8, 136.5, 133.7, 131.5, 129.5, 128.4, 127.8,

127.8, 126.5, 125.4, 122.3, 120.7, 118.7 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{16}NO_2$: 302.1176; Found: 302.1175.

7. References

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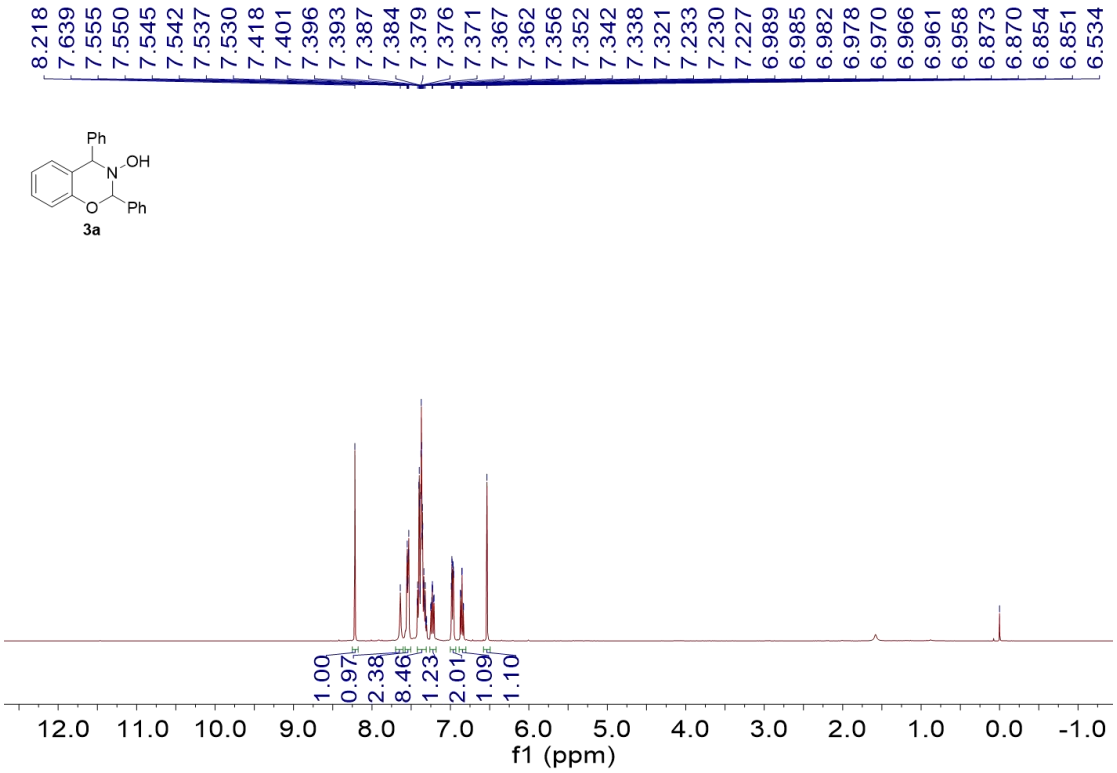
[3] C. R. Wong, G. Hummel, Y. Cai, S. E. Schaus, and J. S. Panek, [4 + 2]-Cycloaddition and 1,4-Addition of *ortho*-Quinone Methides by a Chiral Crotyl Silane, *Org. Lett.*, 2019, **21**, 32-35.

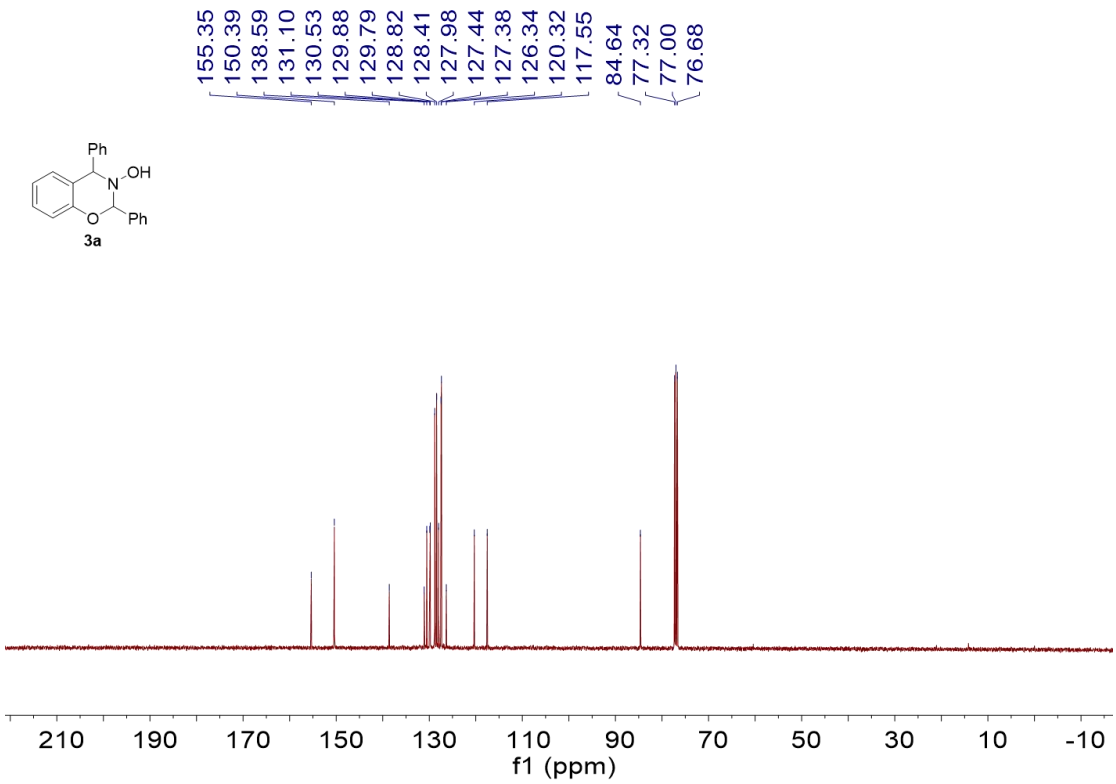
[4] C.-Y. Wang, J.-B. Han, L. Wang, and X.-Y. Tang, Lewis Acid Catalyzed [4 + 2] Cycloaddition of *N*-Tosylhydrazones with *ortho*-Quinone Methides, *J. Org. Chem.* 2019, **84**, 14258-14269.

8 Copies of NMR Spectra

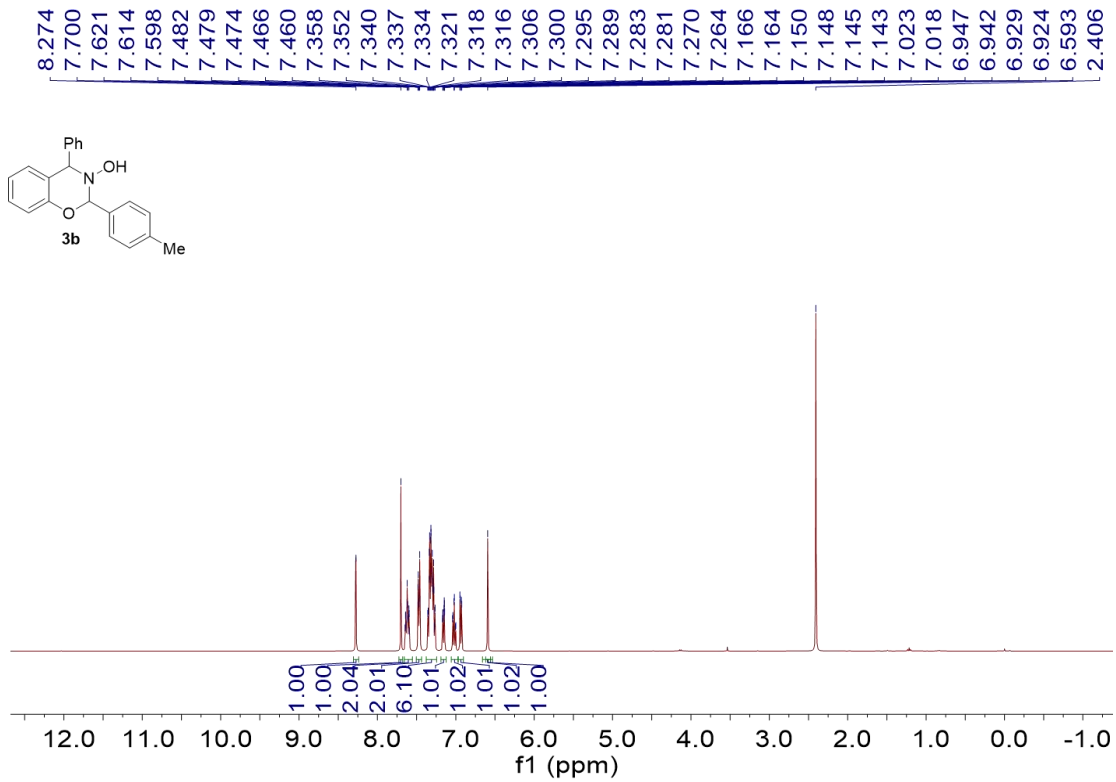
^{1}H NMR of **3a** (400 MHz, $CDCl_3$):



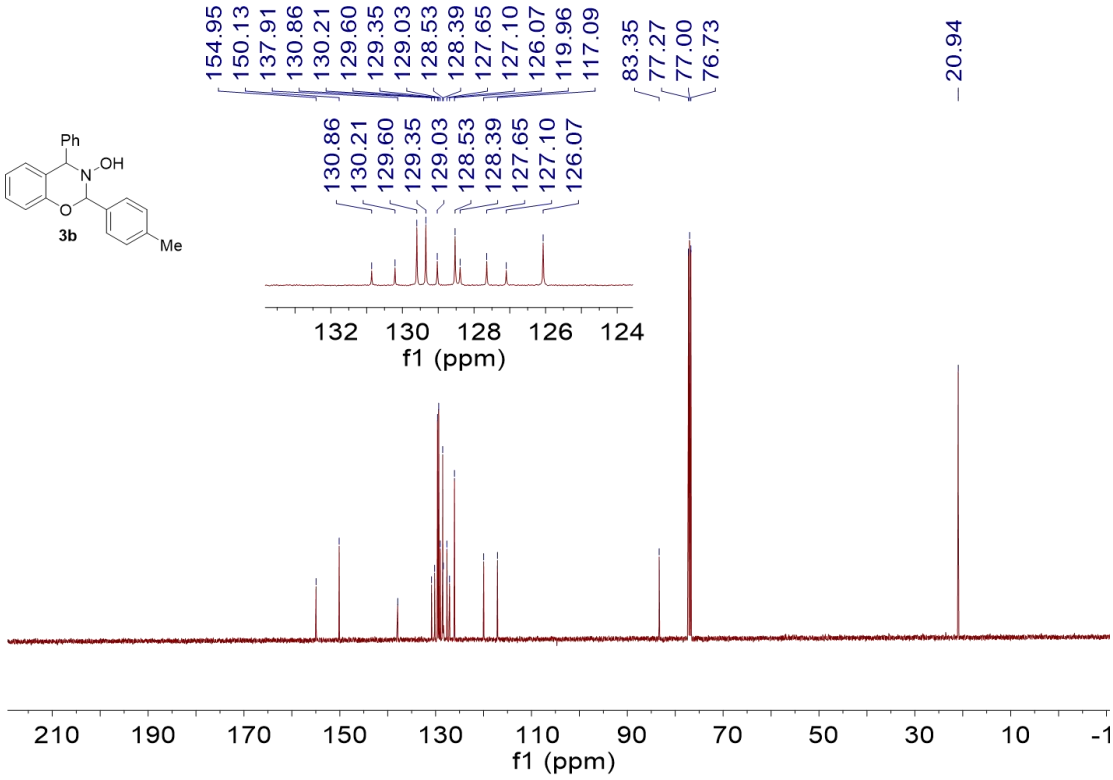
^{13}C NMR of **3a** (100 MHz, $CDCl_3$):



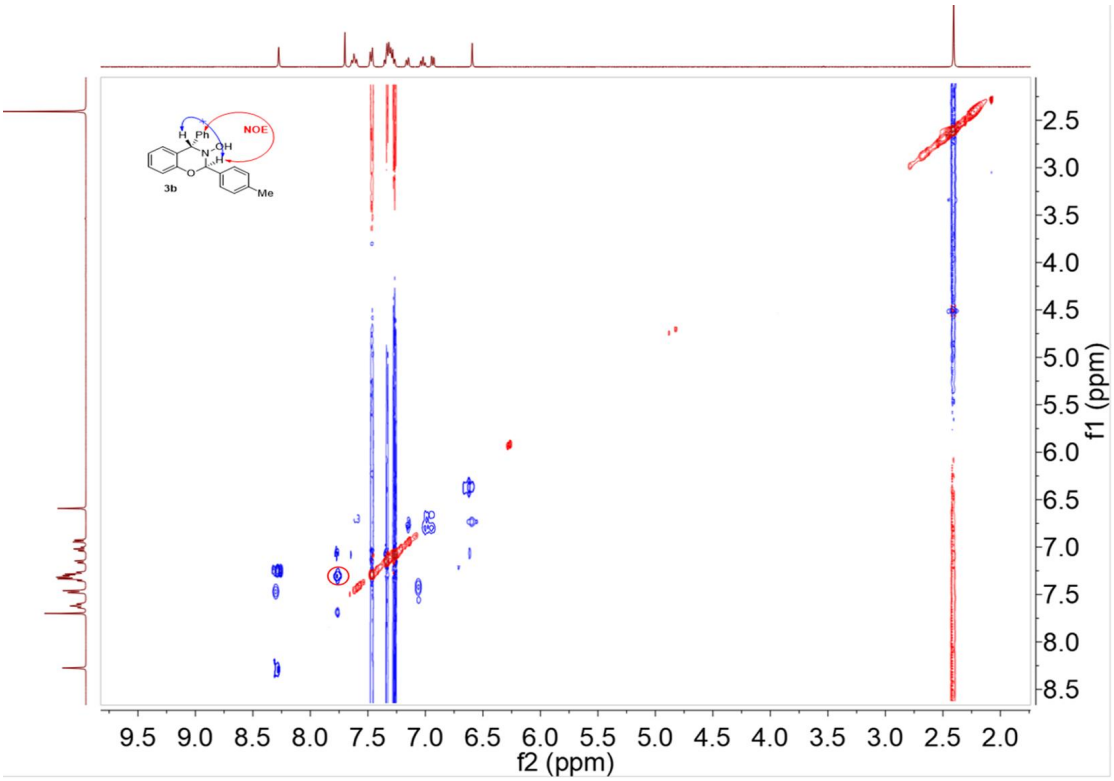
^{1}H NMR of **3b** (400 MHz, $CDCl_3$):



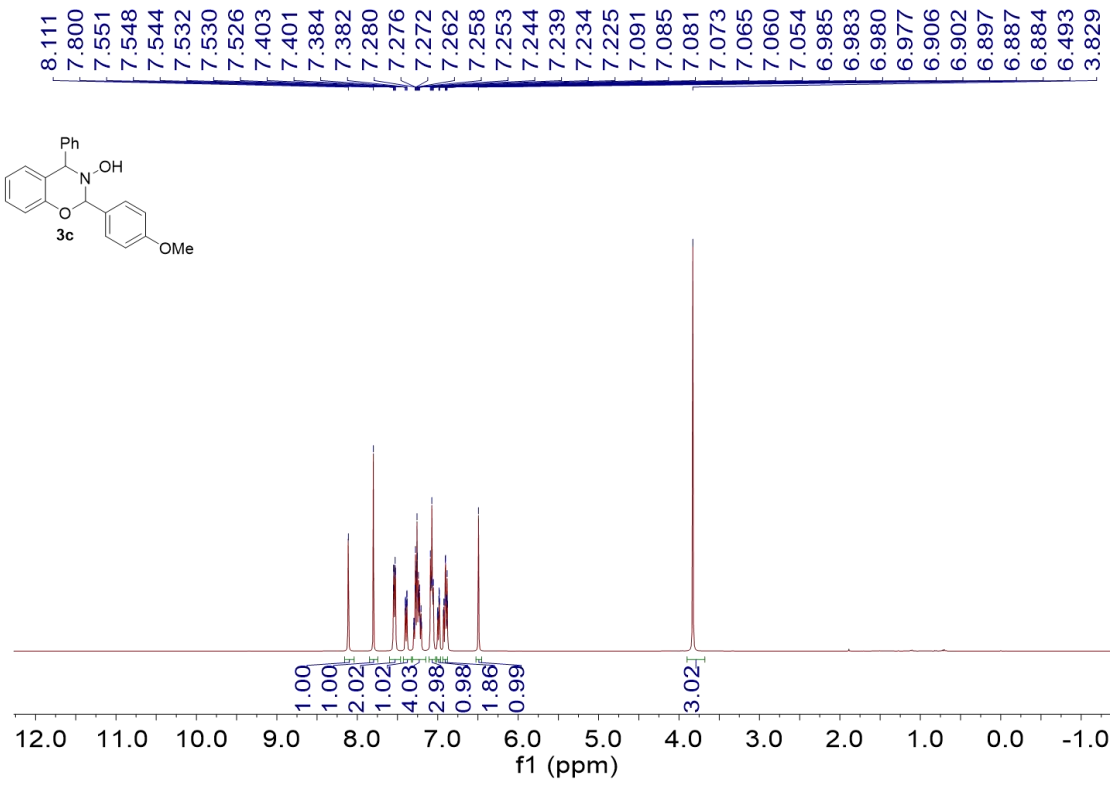
^{13}C NMR of **3b** (100 MHz, $CDCl_3$):



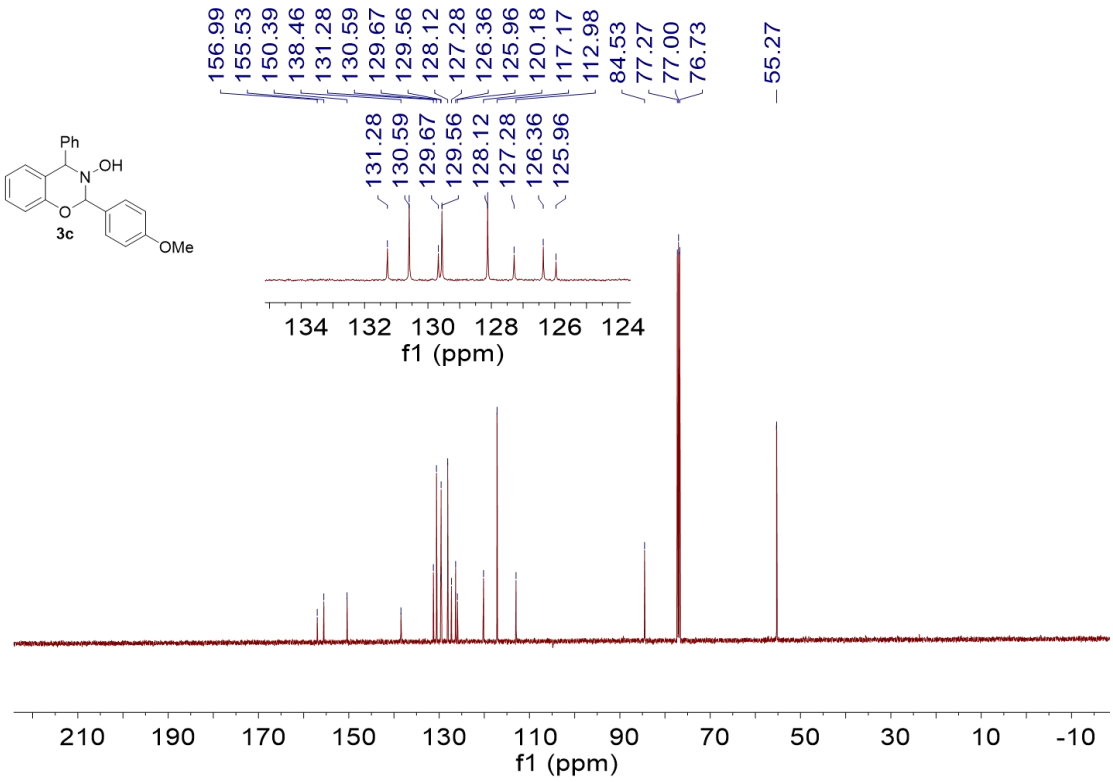
NOESY of **3b**



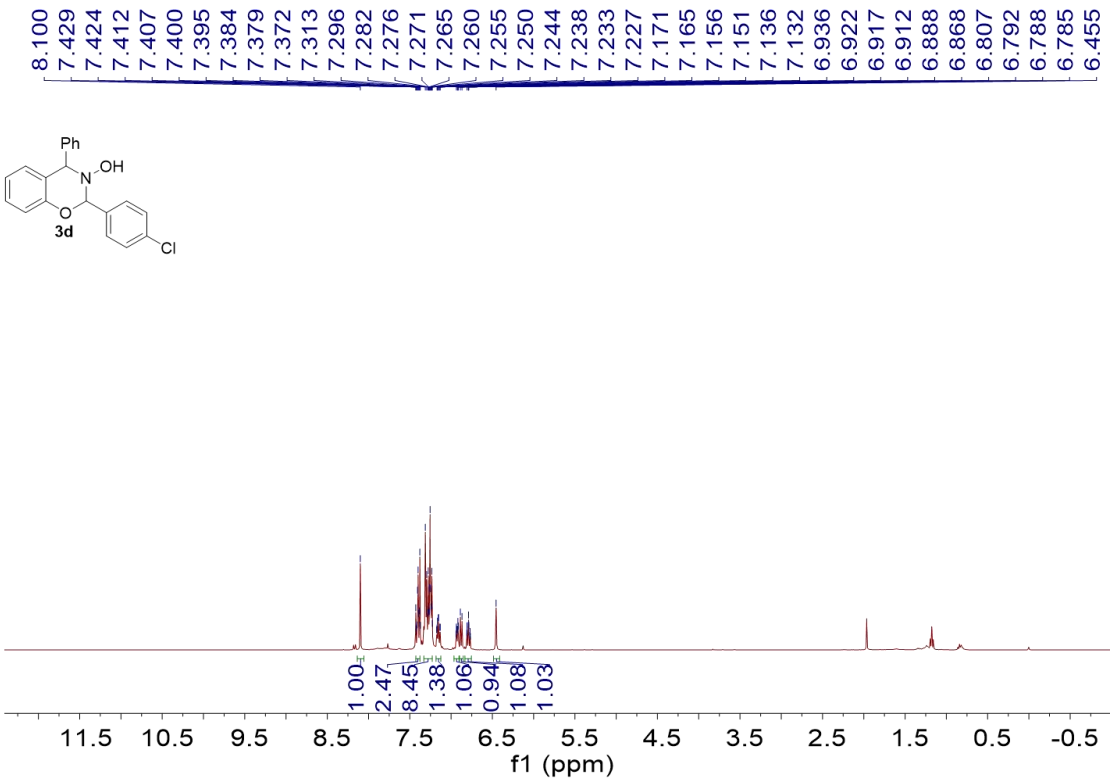
^{1}H NMR of **3c** (400 MHz, $CDCl_3$):



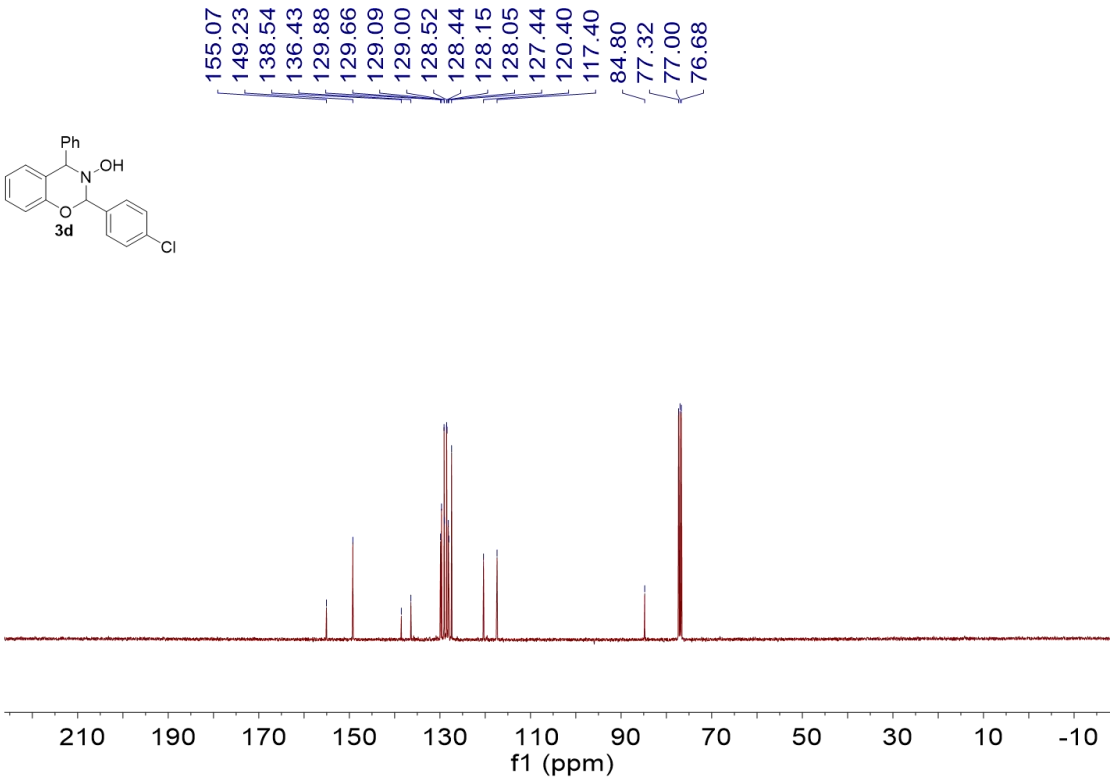
^{13}C NMR of **3c** (100 MHz, $CDCl_3$):



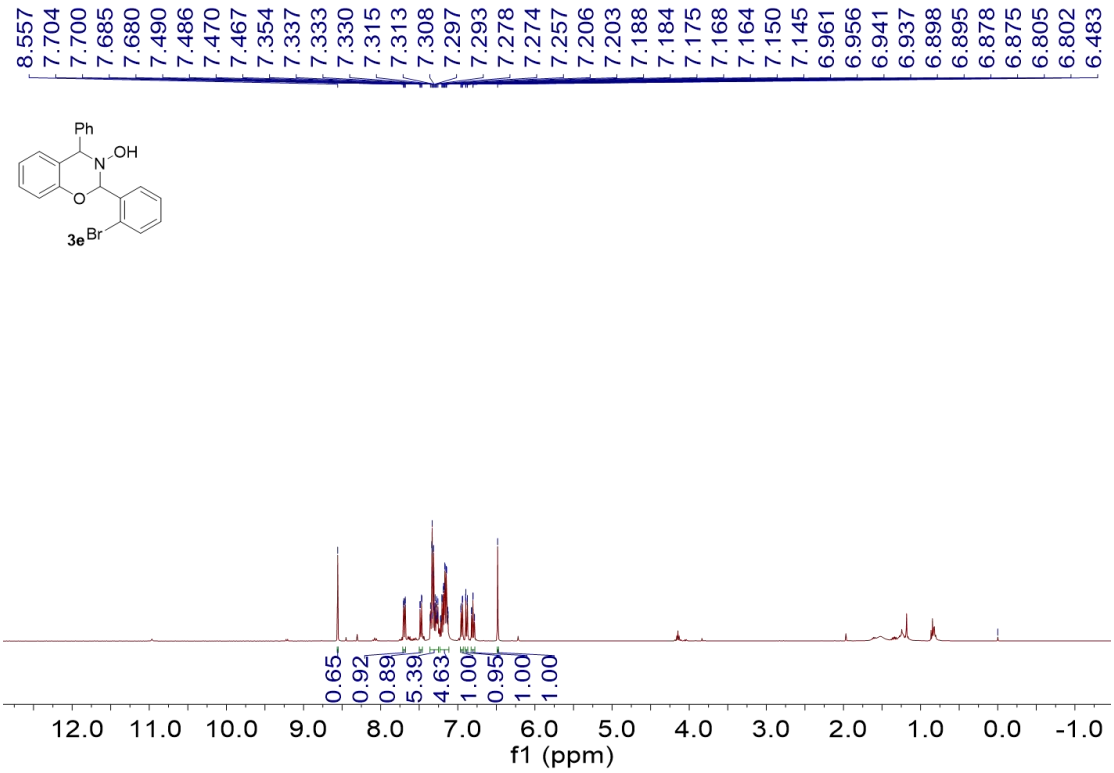
^{1}H NMR of **3d** (400 MHz, $CDCl_3$):



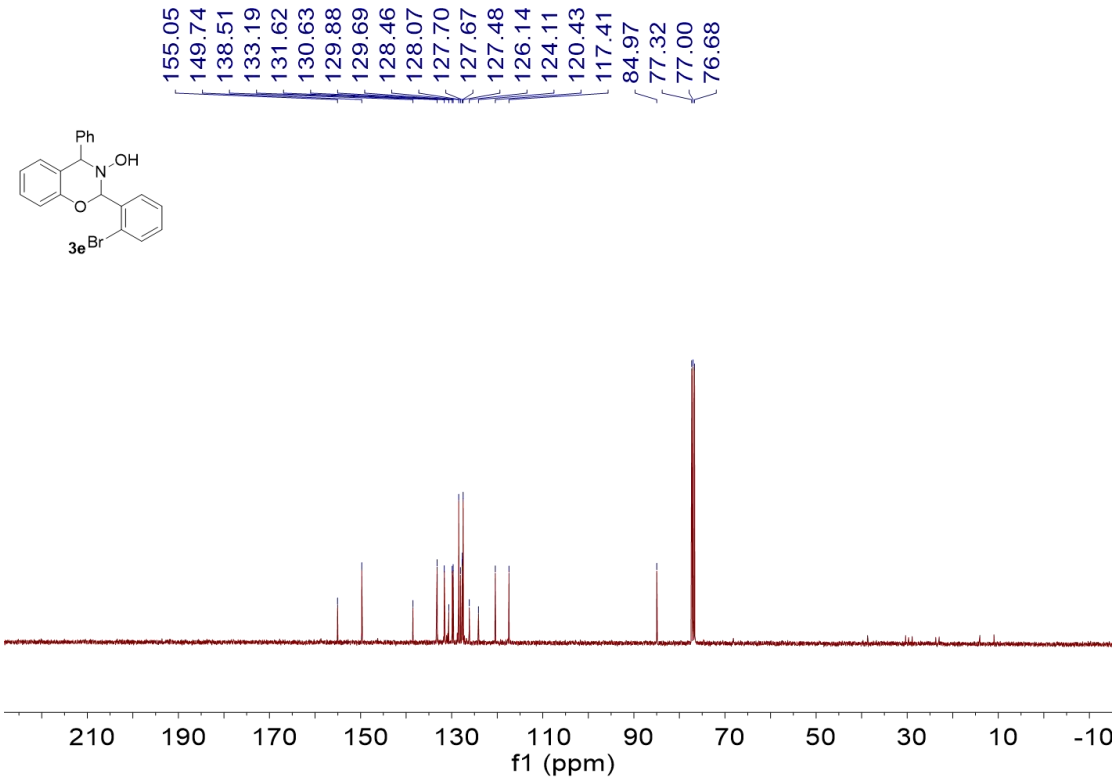
^{13}C NMR of **3d** (100 MHz, $CDCl_3$):



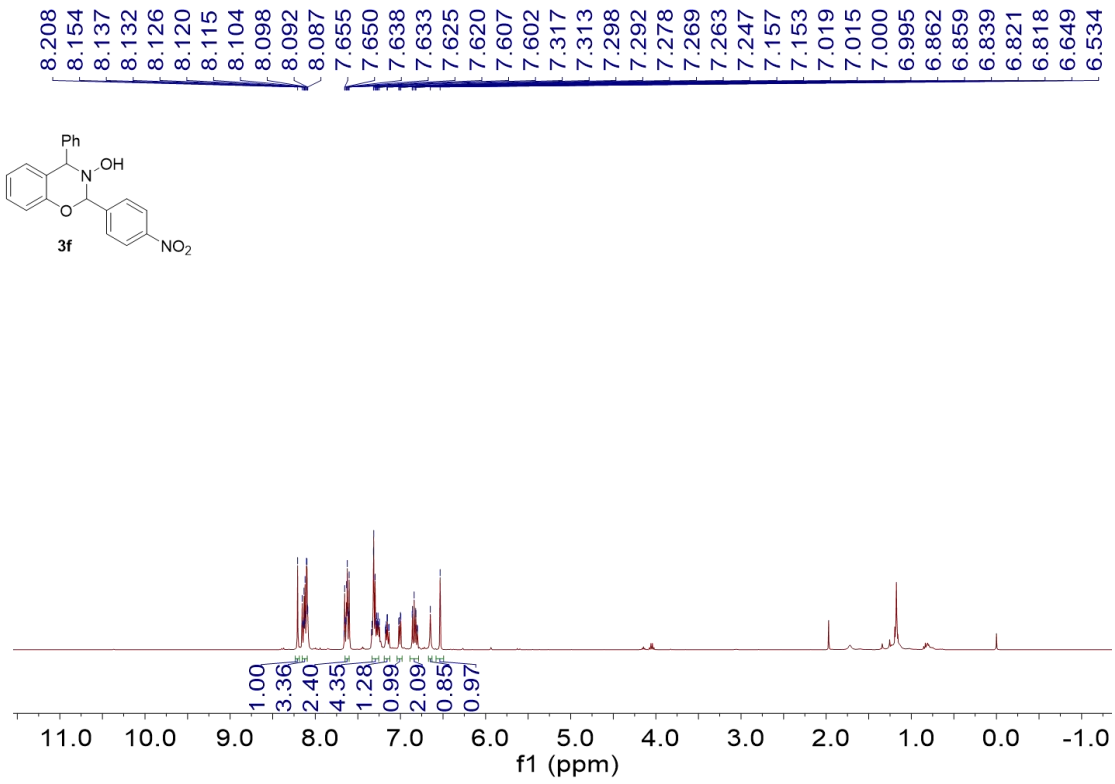
^{1}H NMR of **3e** (400 MHz, $CDCl_3$):



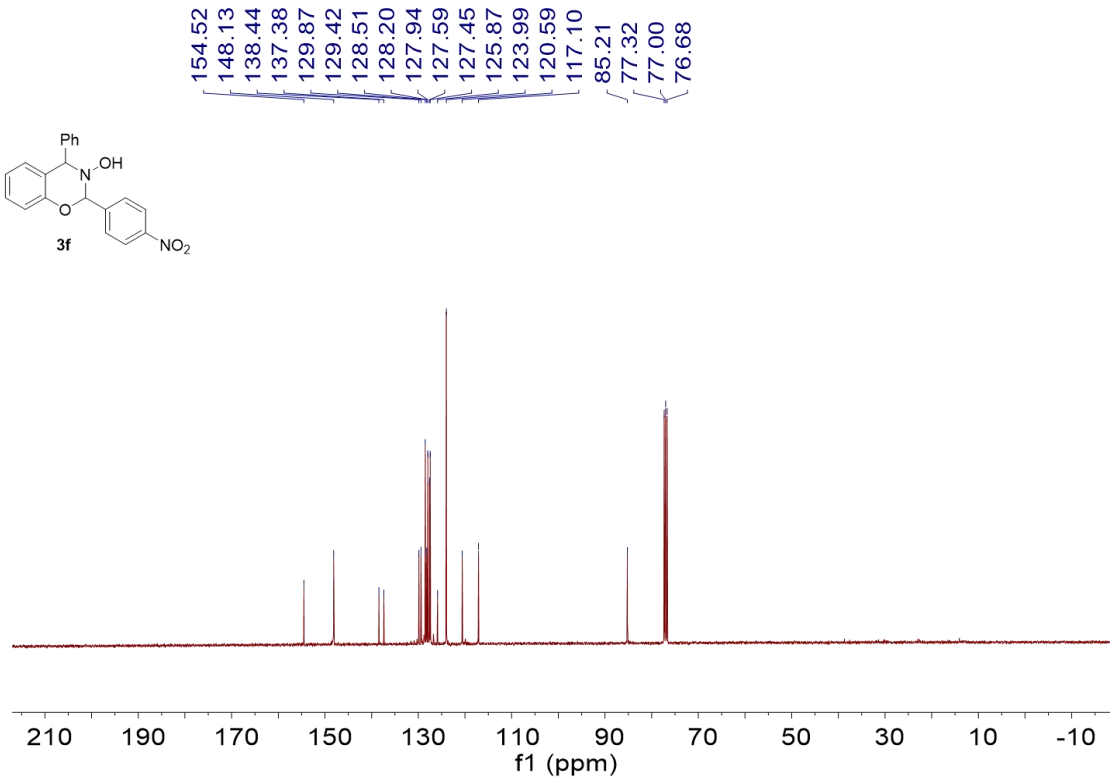
^{13}C NMR of **3e** (100 MHz, $CDCl_3$):



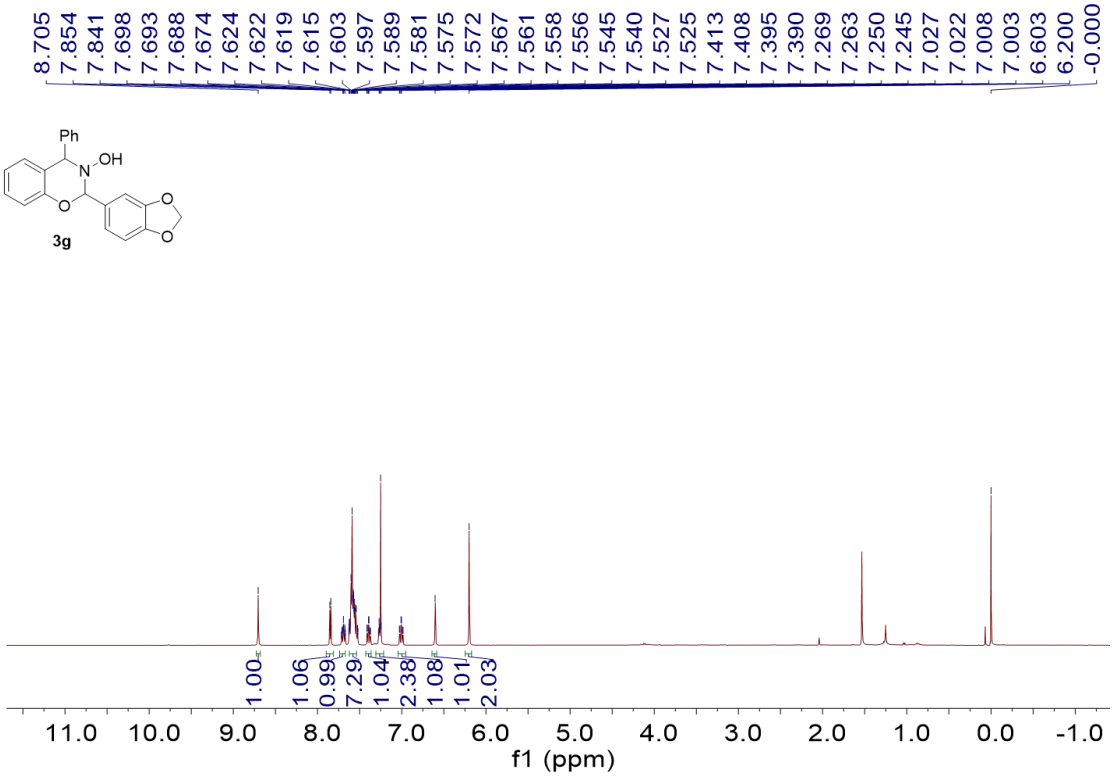
^{1}H NMR of **3f** (400 MHz, $CDCl_3$):



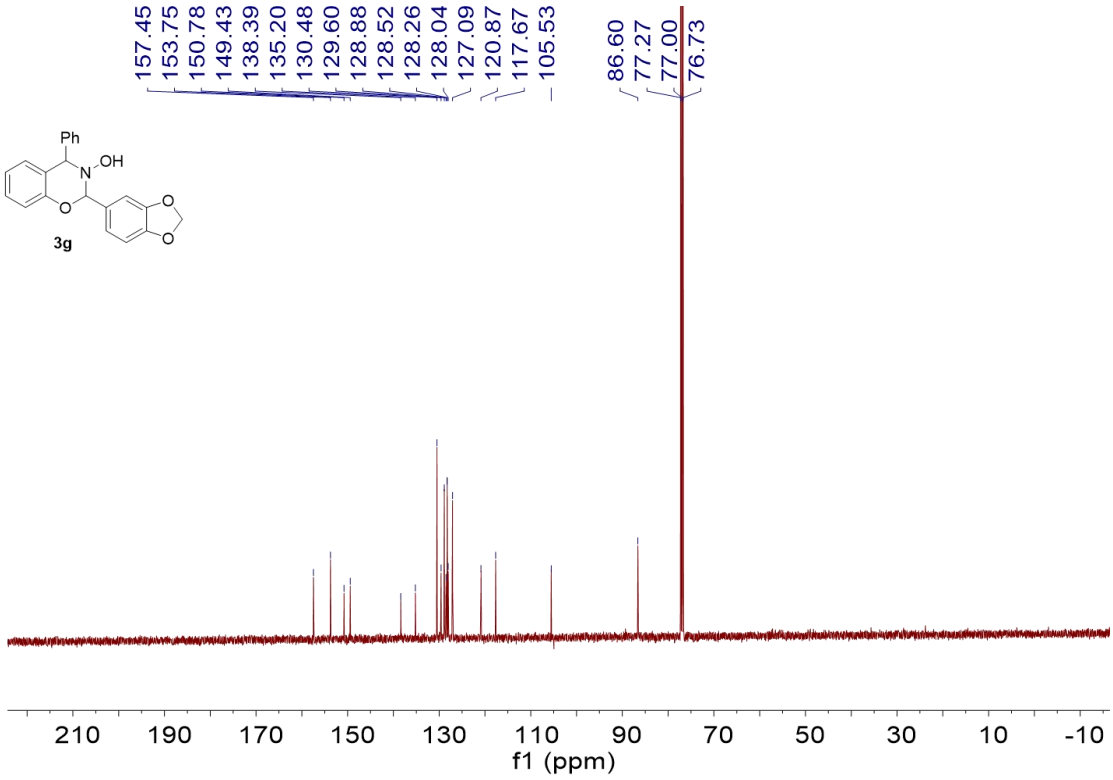
^{13}C NMR of **3f** (100 MHz, $CDCl_3$):



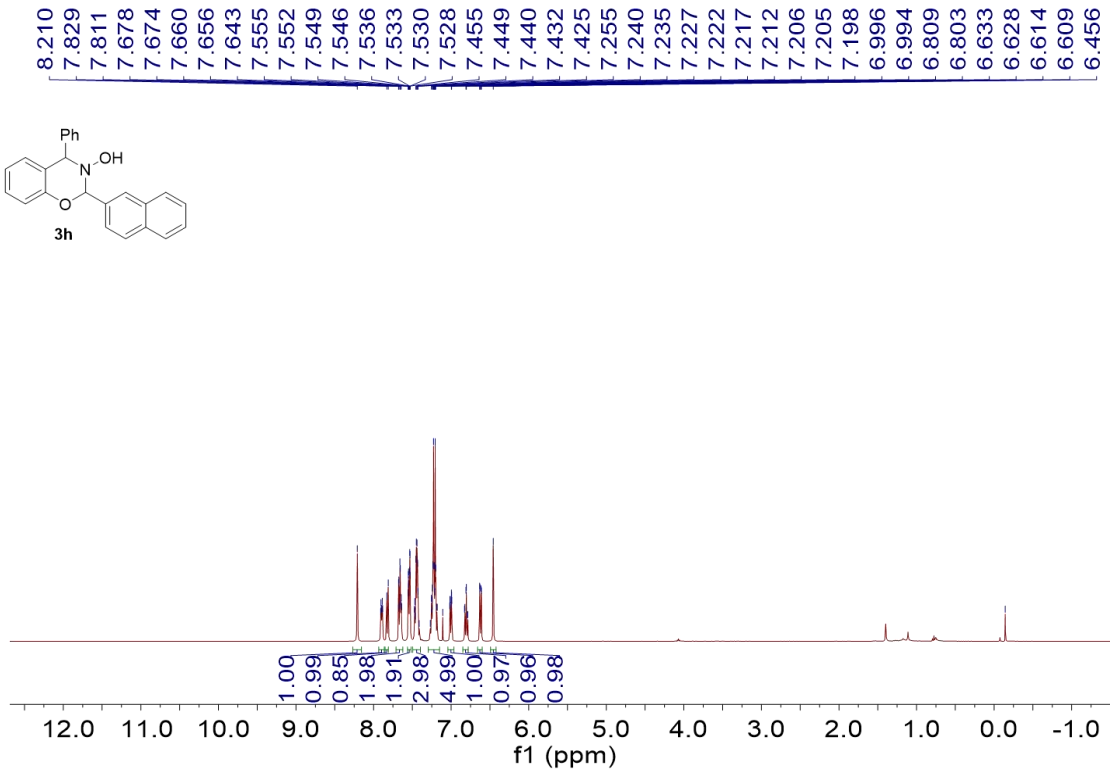
^{1}H NMR of **3g** (400 MHz, $CDCl_3$):



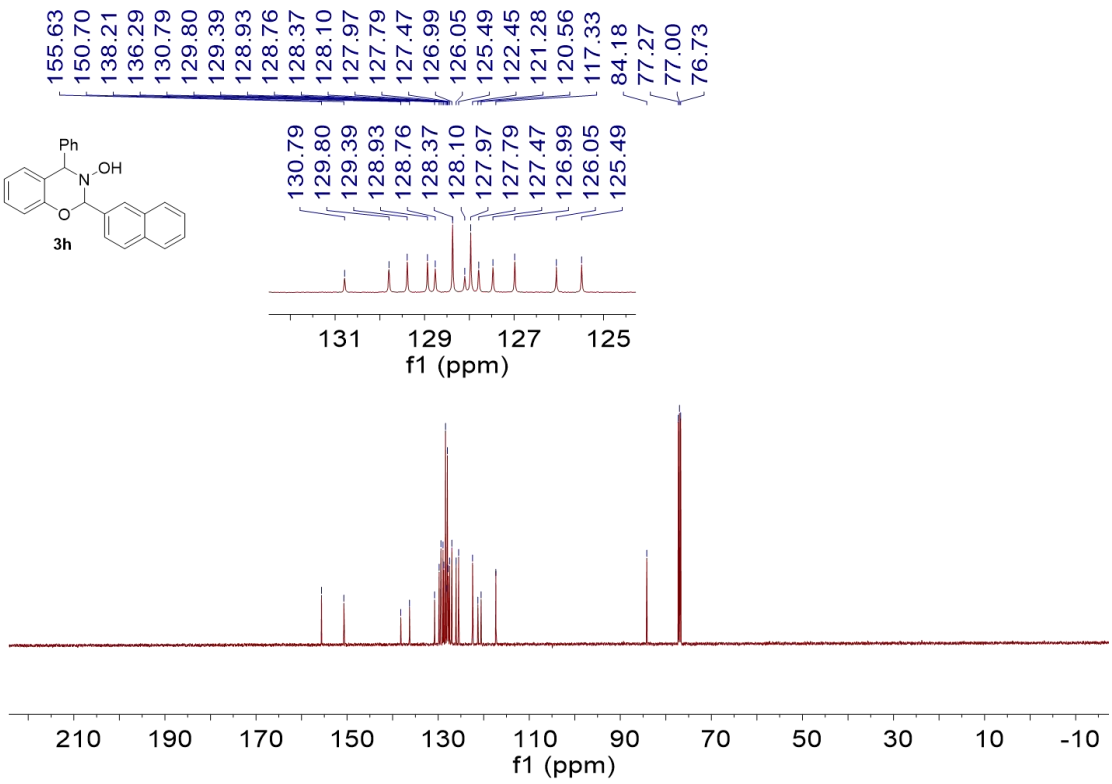
^{13}C NMR of **3g** (100 MHz, $CDCl_3$):



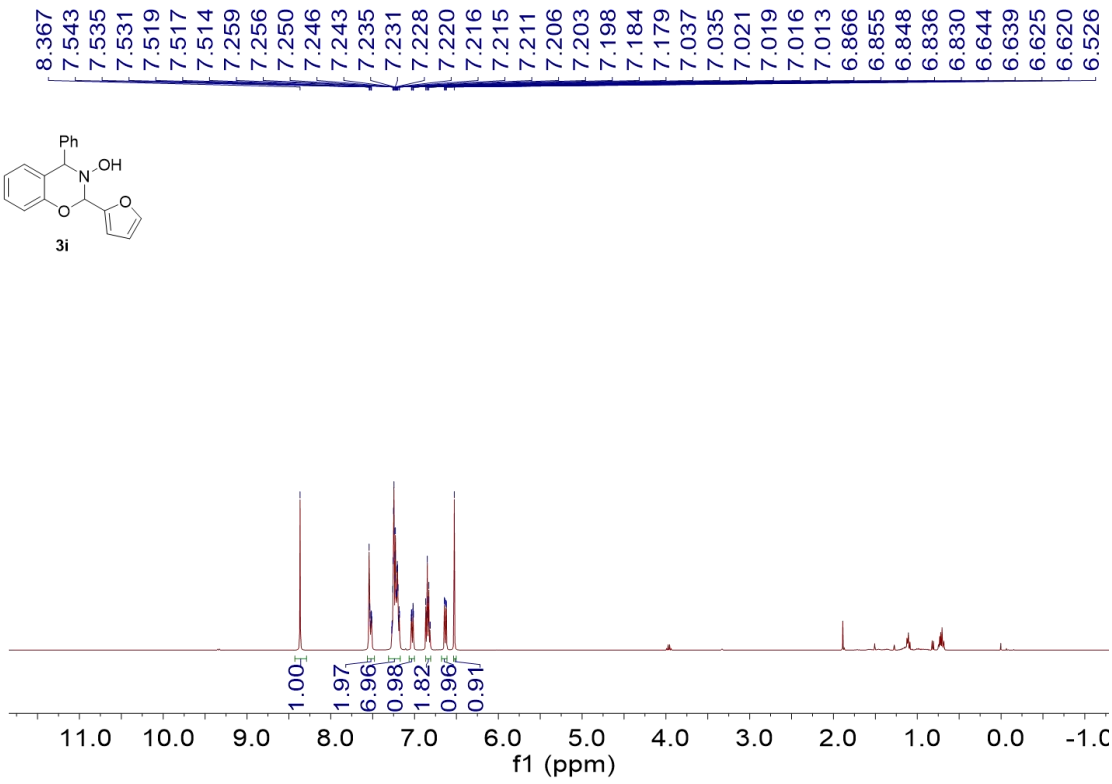
^{1}H NMR of **3h** (400 MHz, $CDCl_3$):



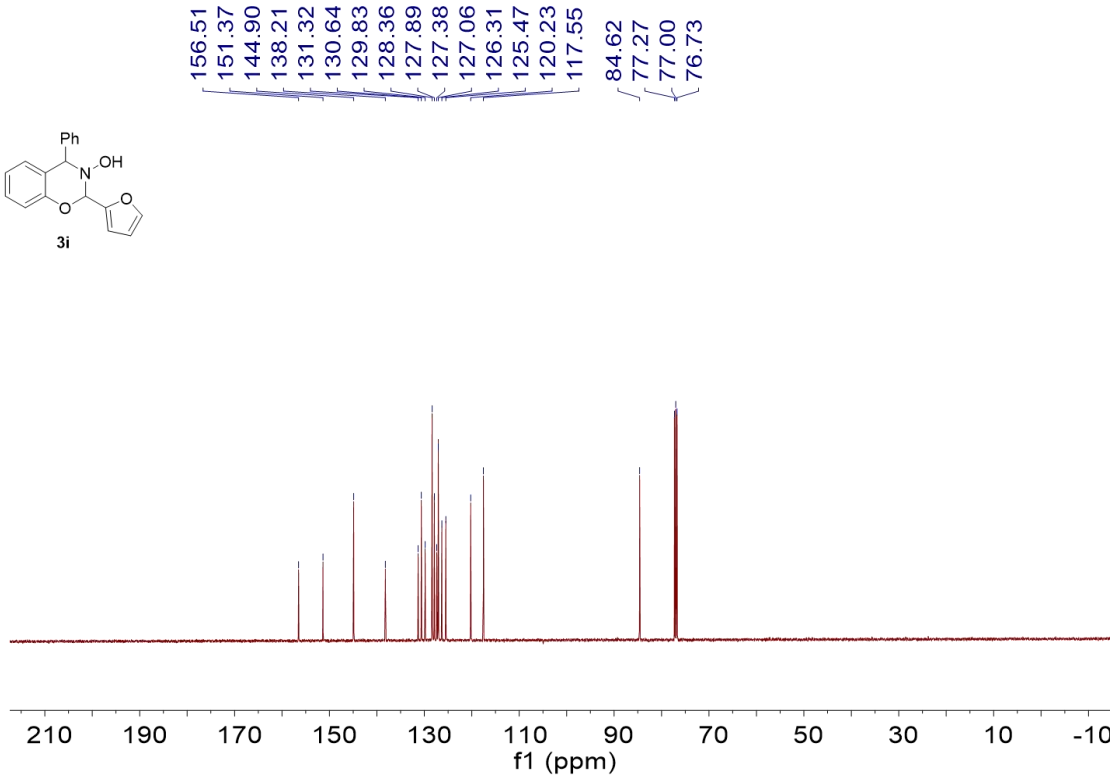
^{13}C NMR of **3h** (100 MHz, $CDCl_3$):



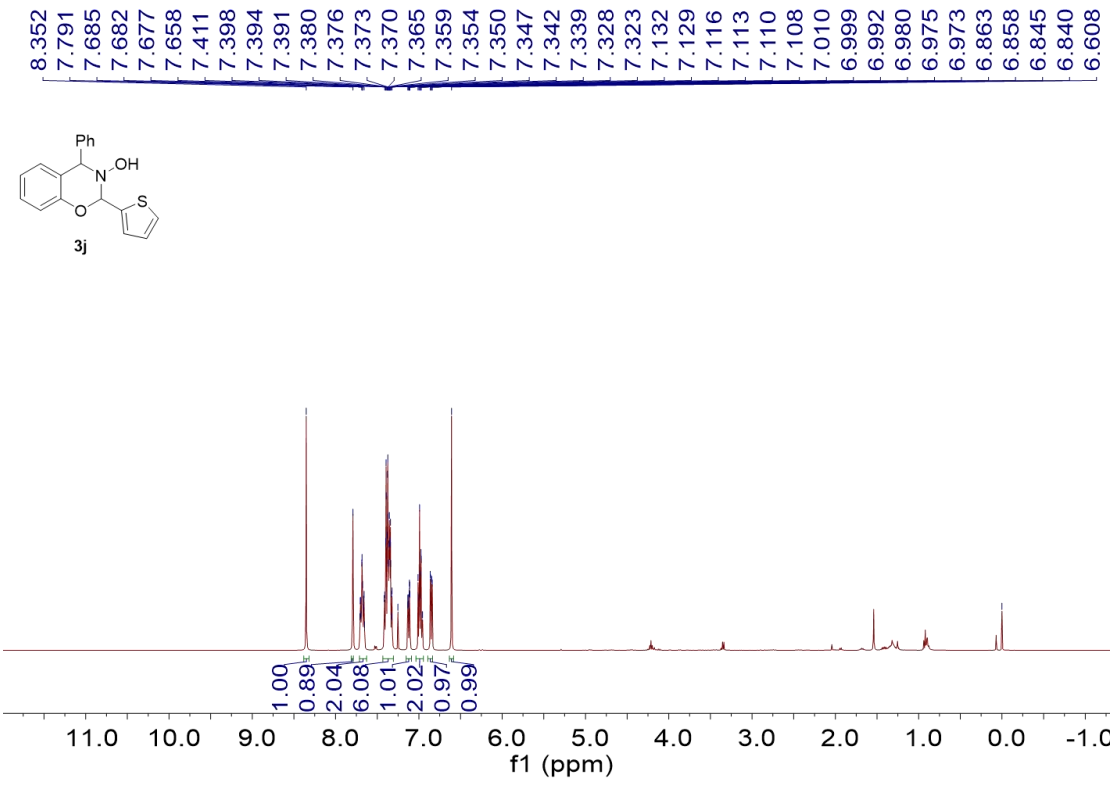
^{1}H NMR of **3i** (400 MHz, $CDCl_3$):



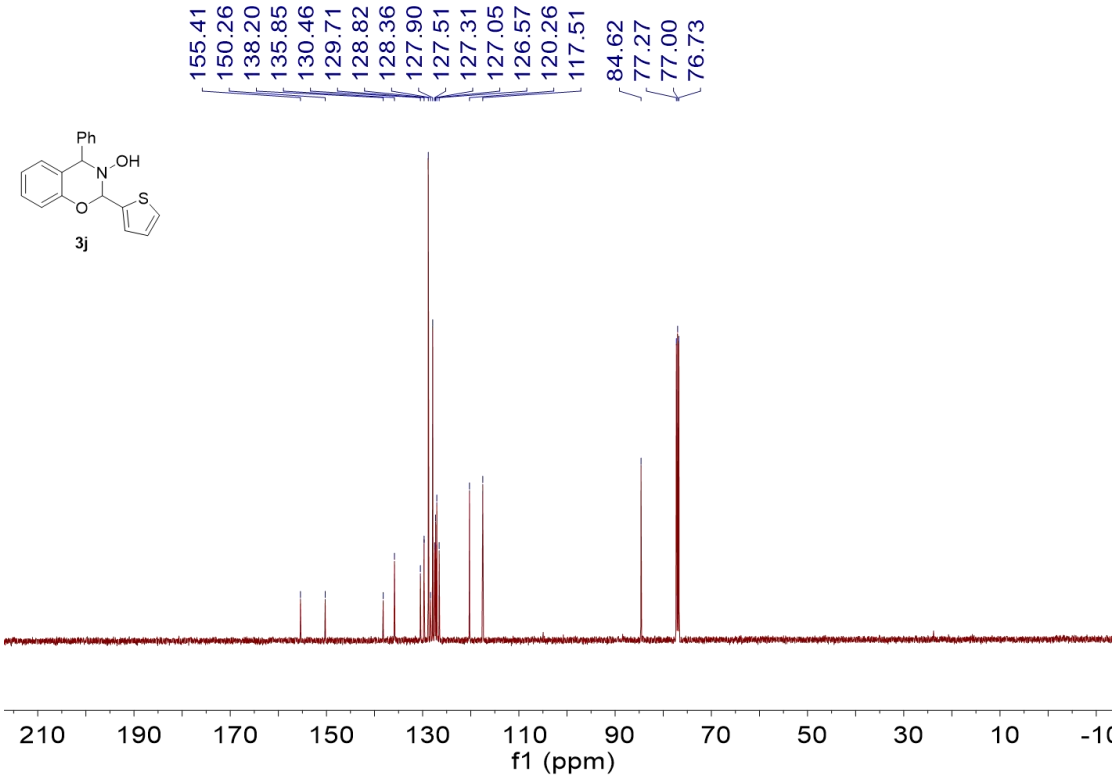
^{13}C NMR of **3i** (100 MHz, $CDCl_3$):



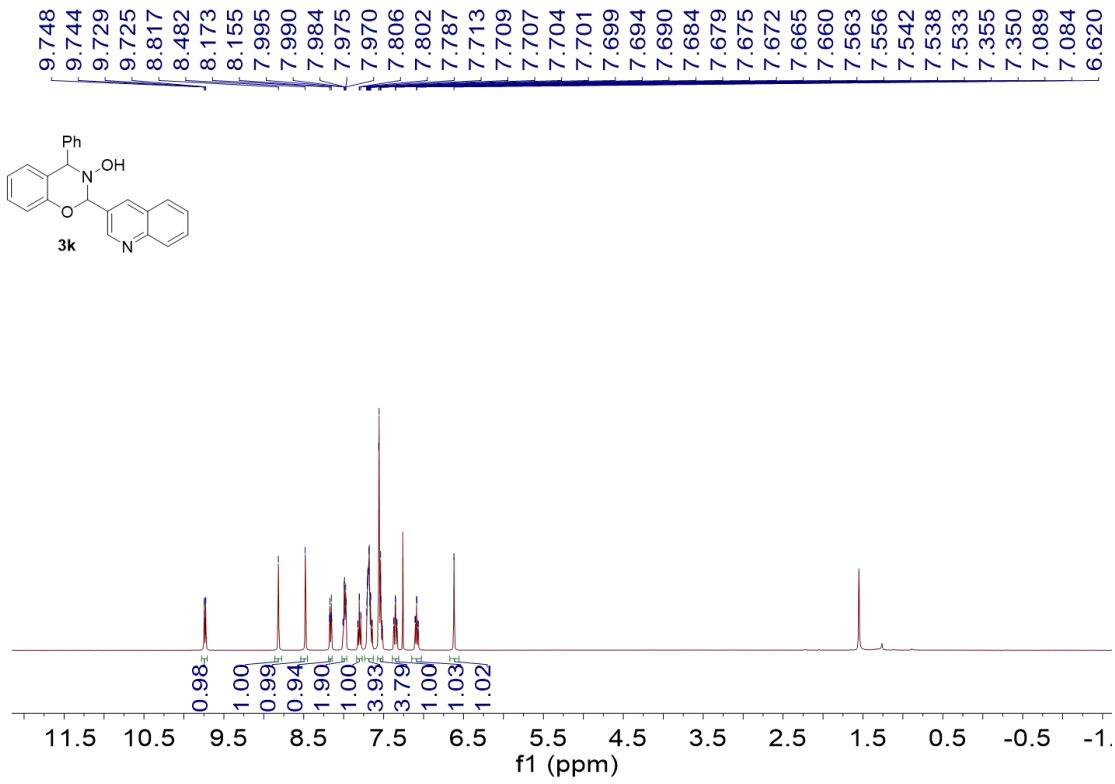
^{1}H NMR of **3j** (400 MHz, $CDCl_3$):



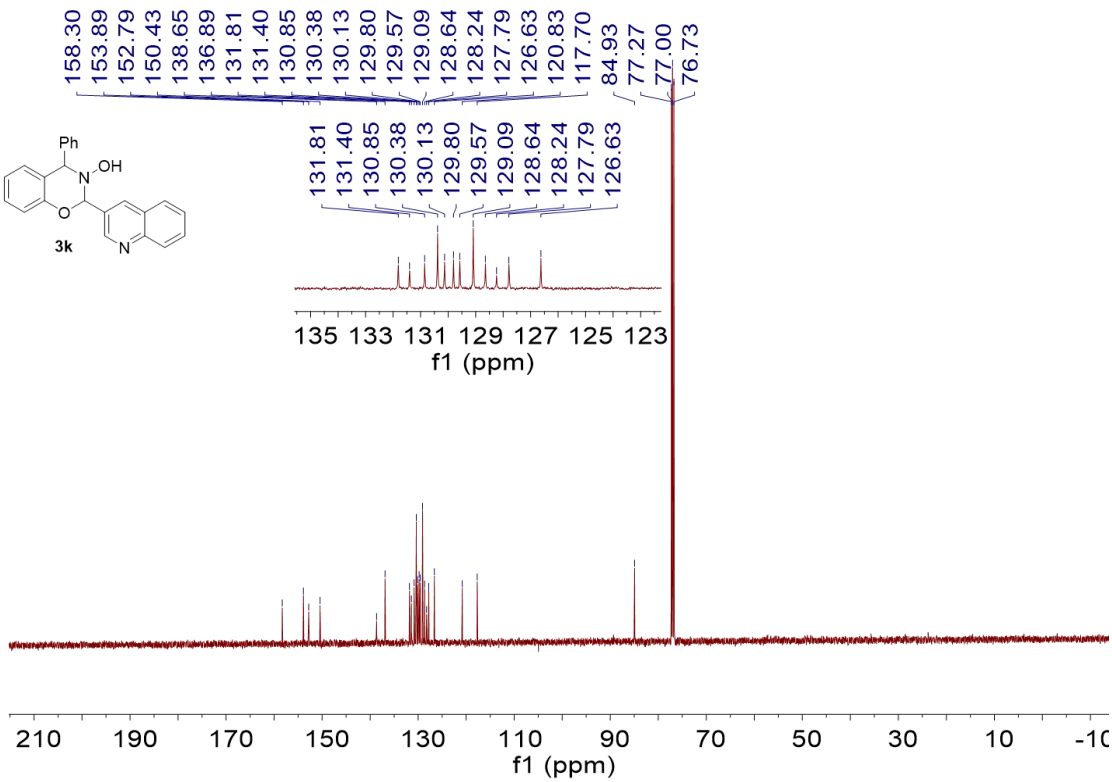
^{13}C NMR of **3j** (100 MHz, $CDCl_3$):



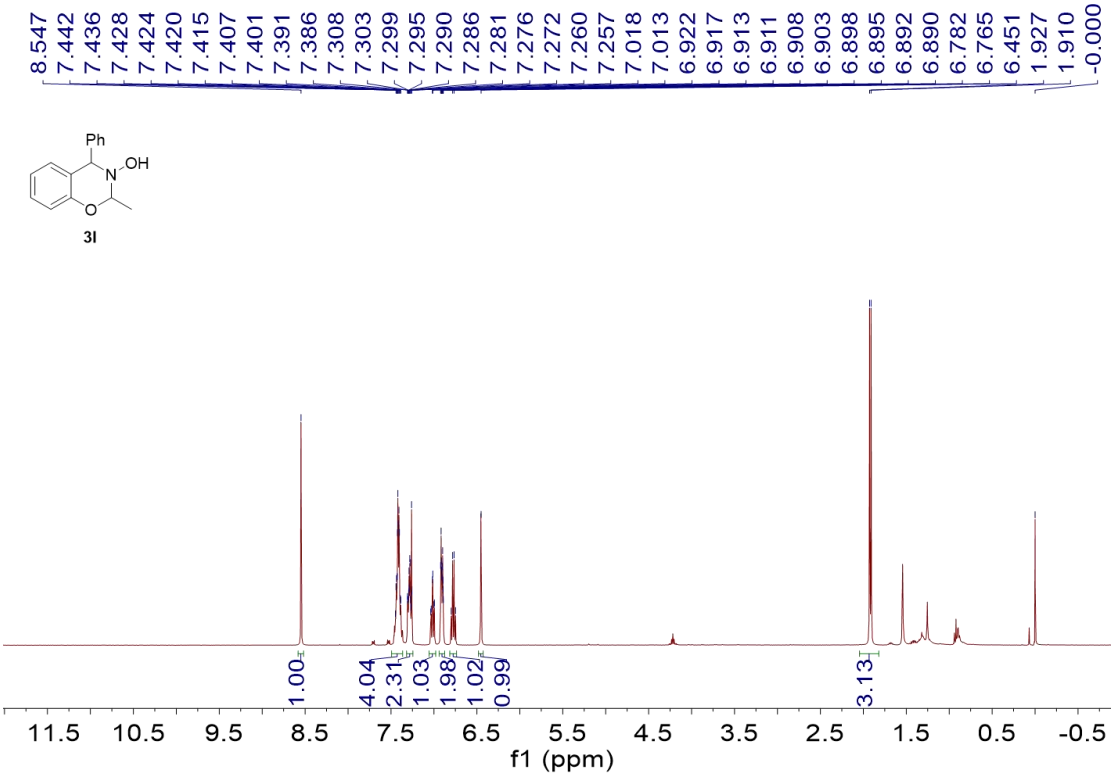
^{1}H NMR of **3k** (400 MHz, $CDCl_3$):



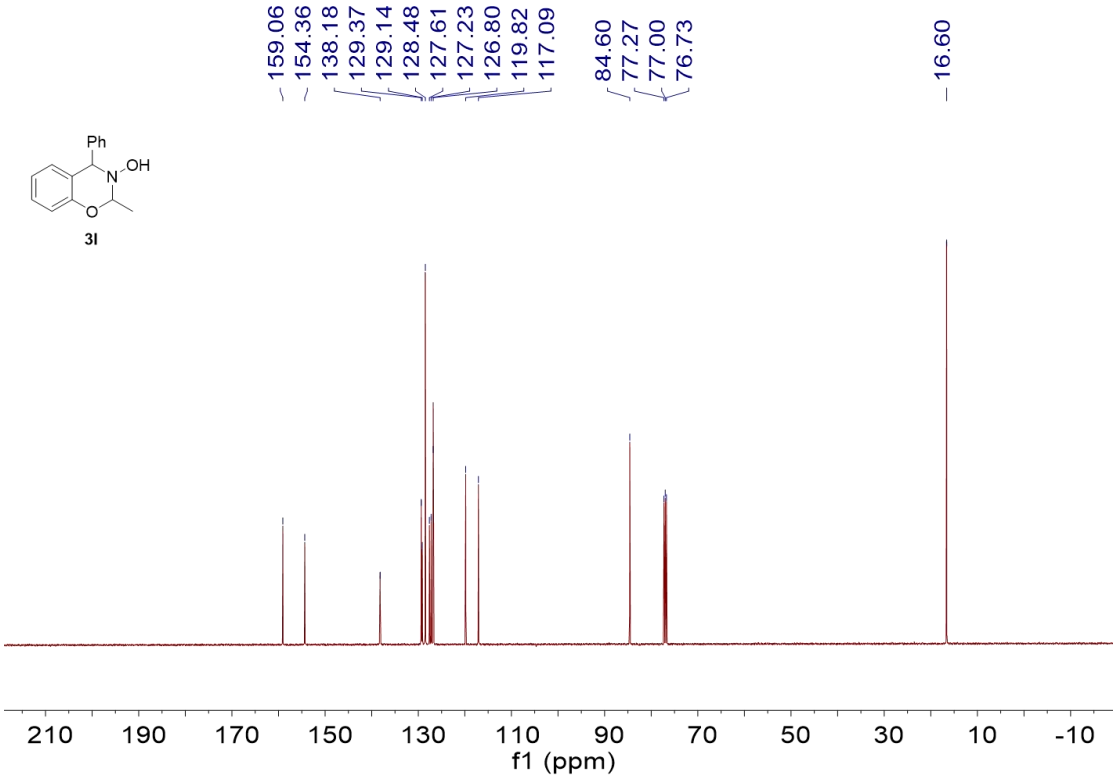
^{13}C NMR of **3k** (100 MHz, $CDCl_3$):



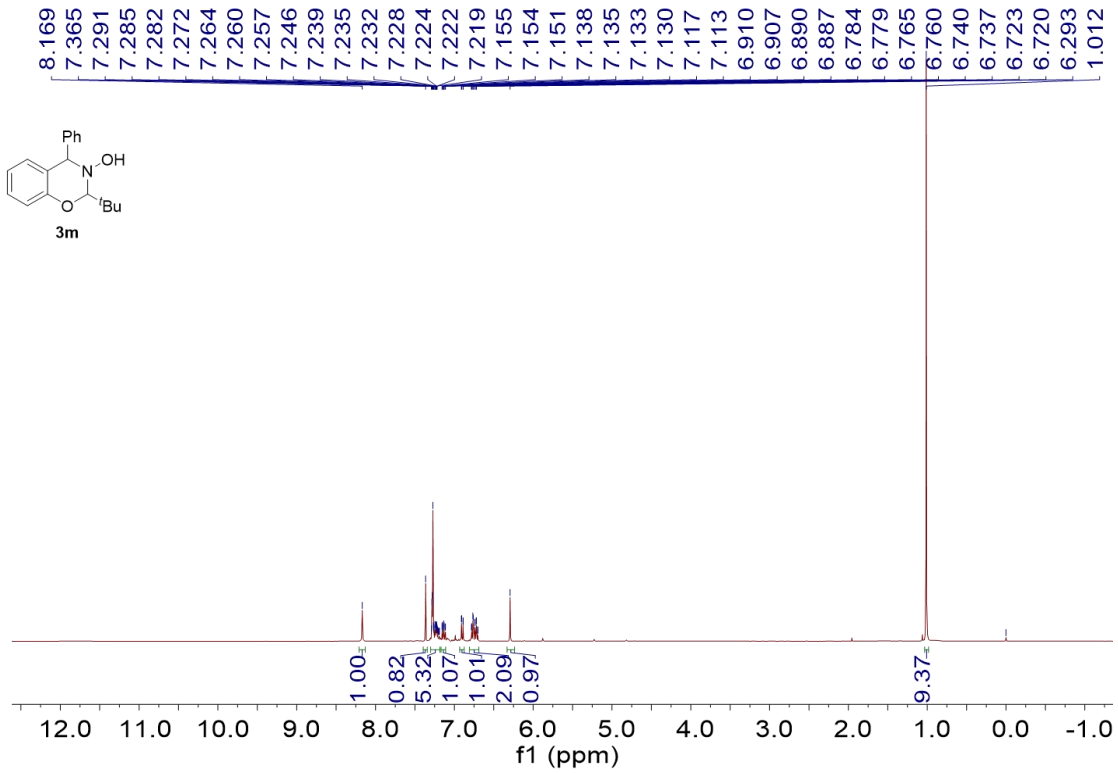
^{1}H NMR of **3l** (400 MHz, $CDCl_3$):



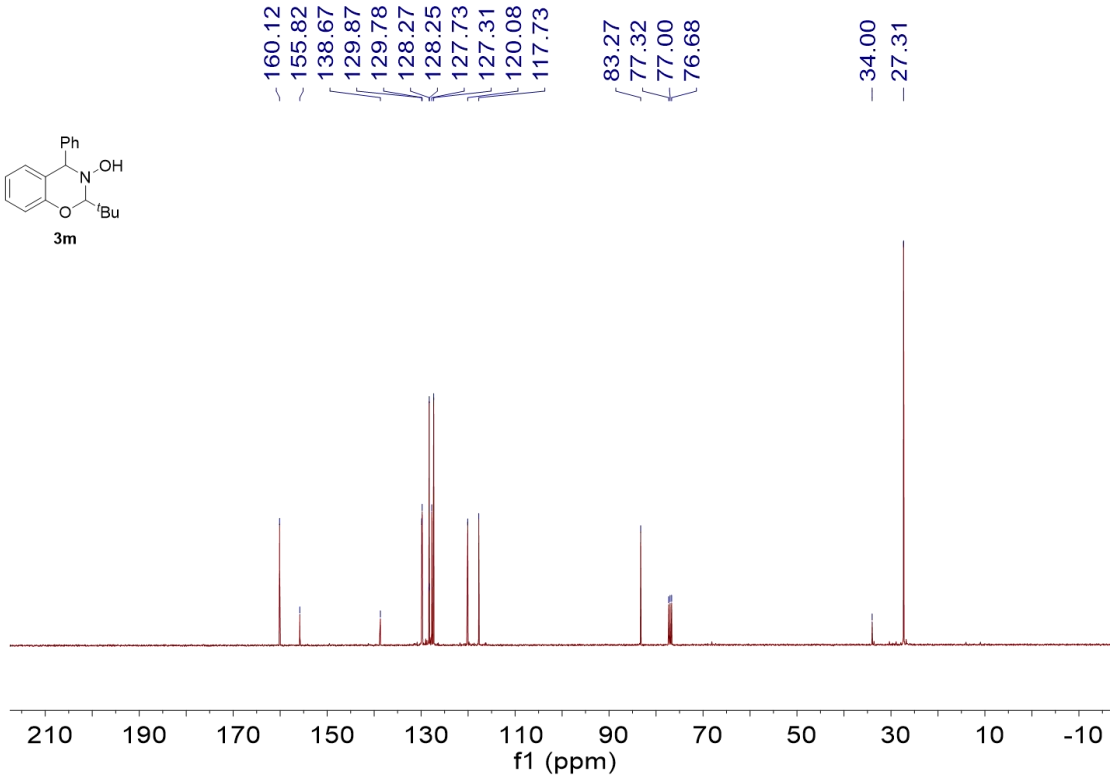
^{13}C NMR of **3l** (100 MHz, $CDCl_3$):



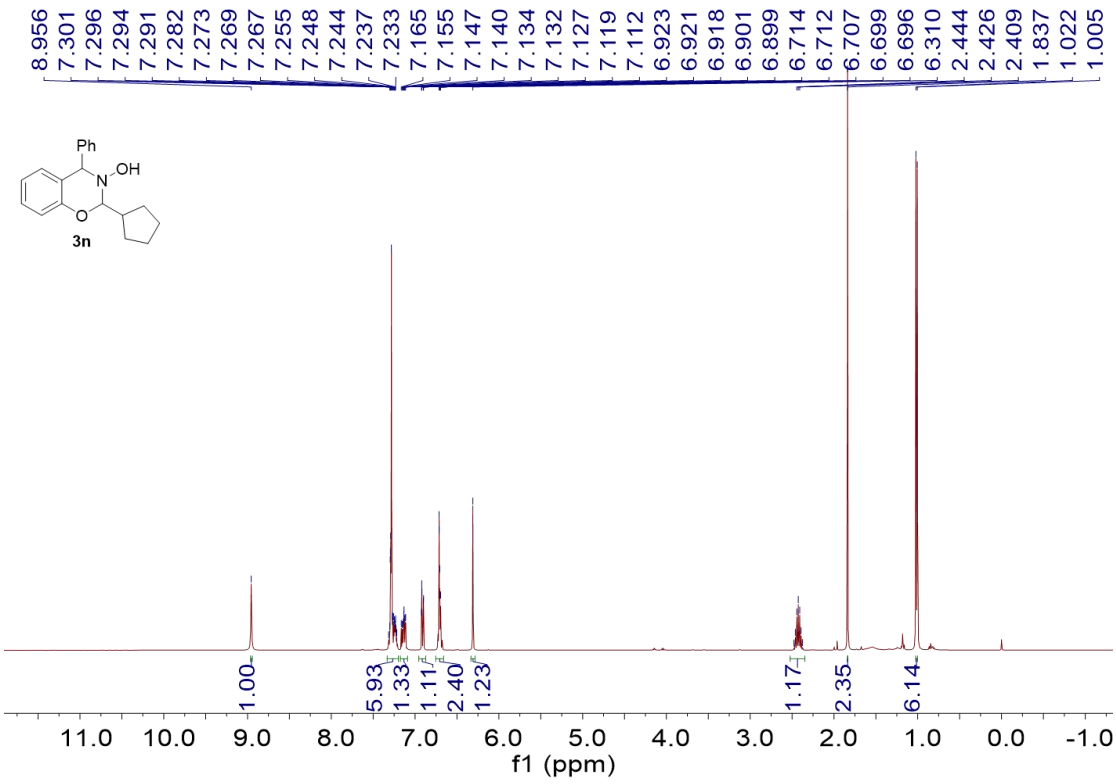
^{1}H NMR of **3m** (400 MHz, $CDCl_3$):



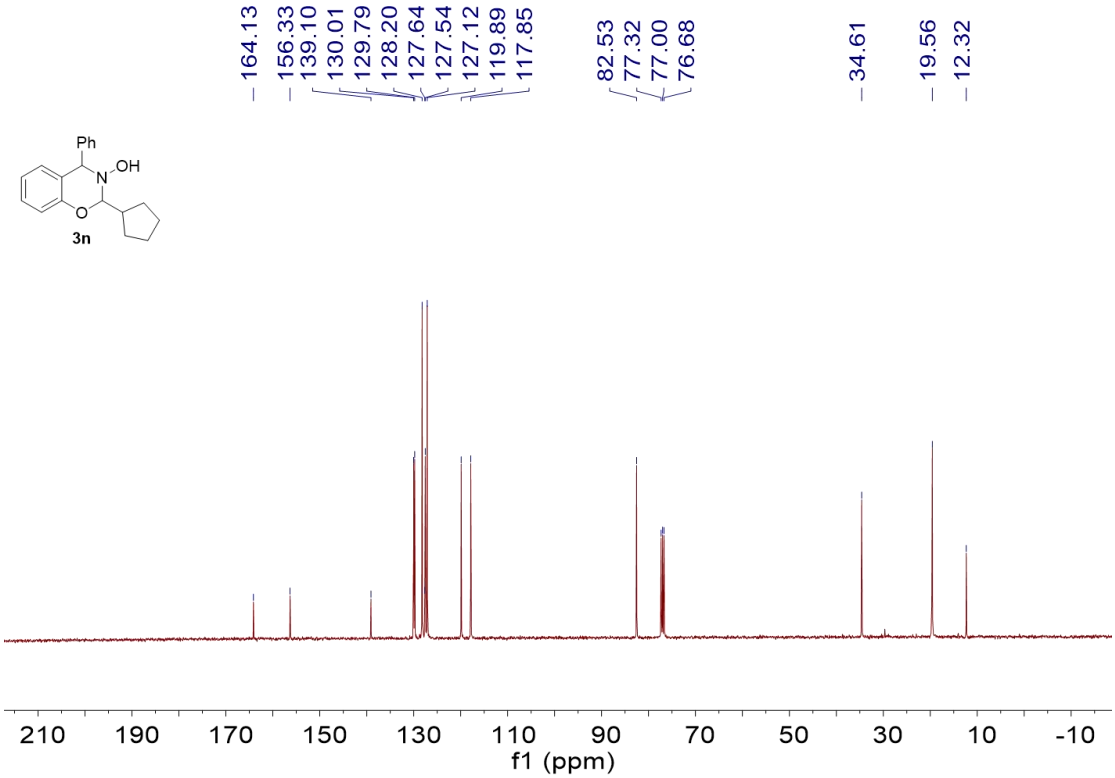
^{13}C NMR of **3m** (100 MHz, $CDCl_3$):



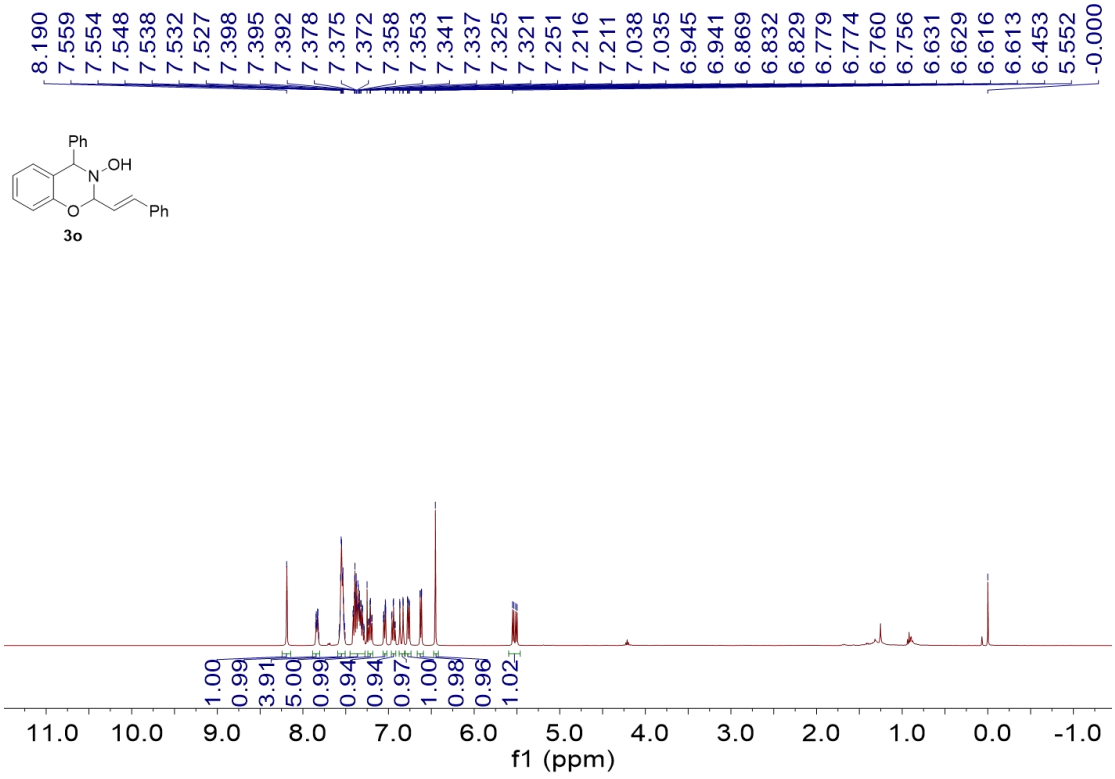
^{1}H NMR of **3n** (400 MHz, $CDCl_3$):



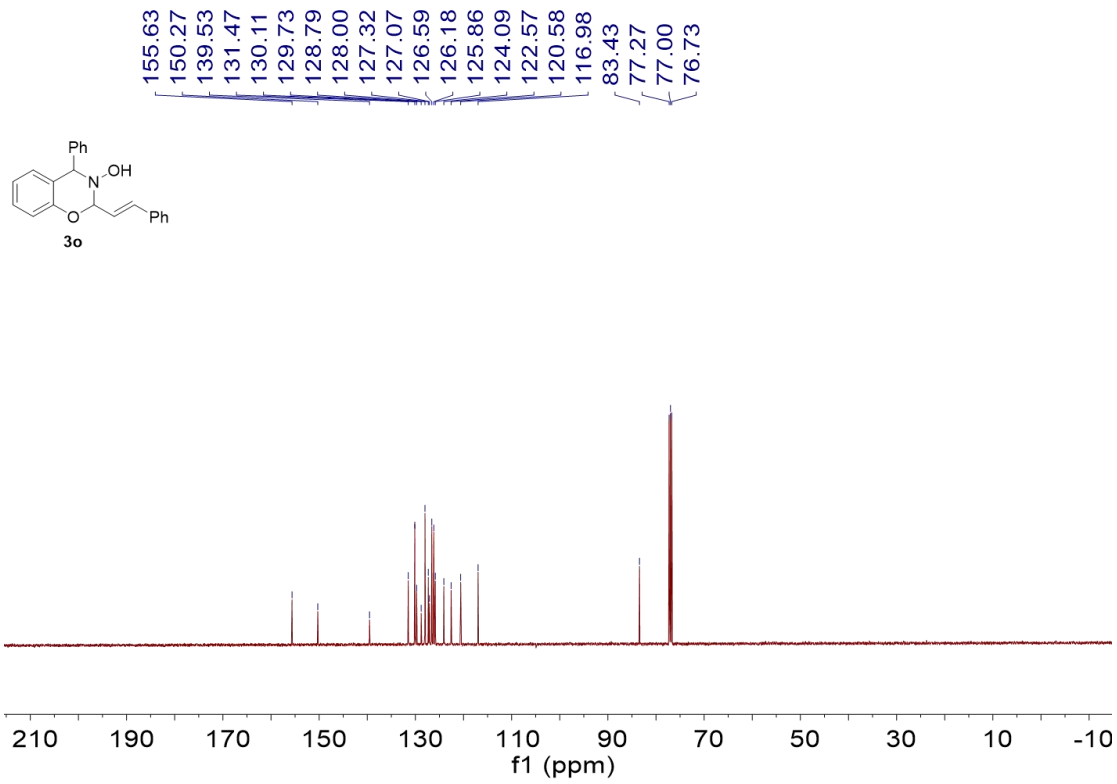
^{13}C NMR of **3n** (100 MHz, $CDCl_3$):



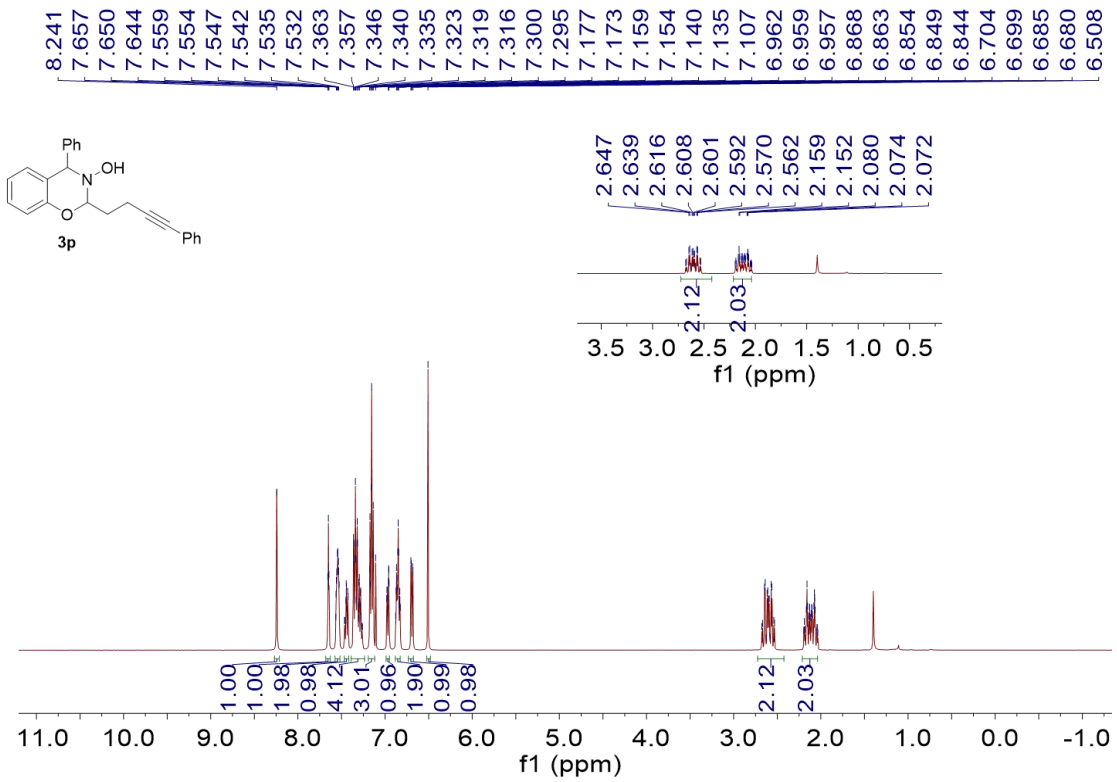
^{1}H NMR of **3o** (400 MHz, $CDCl_3$):



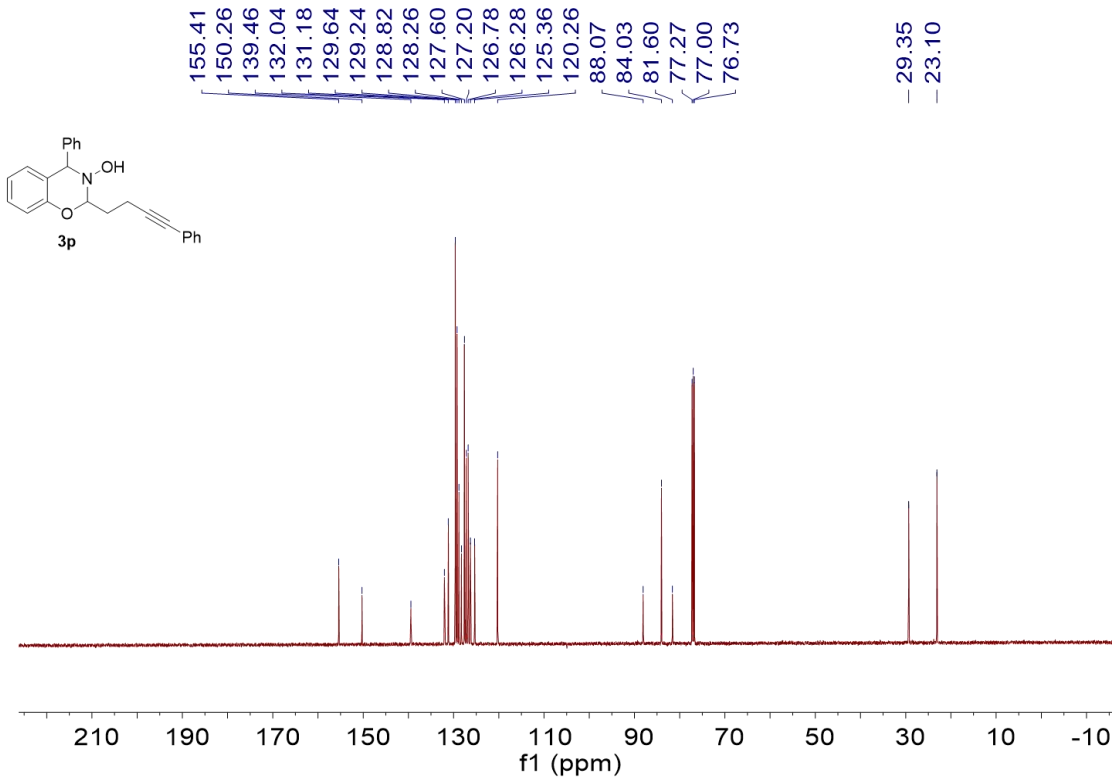
^{13}C NMR of **3o** (100 MHz, $CDCl_3$):



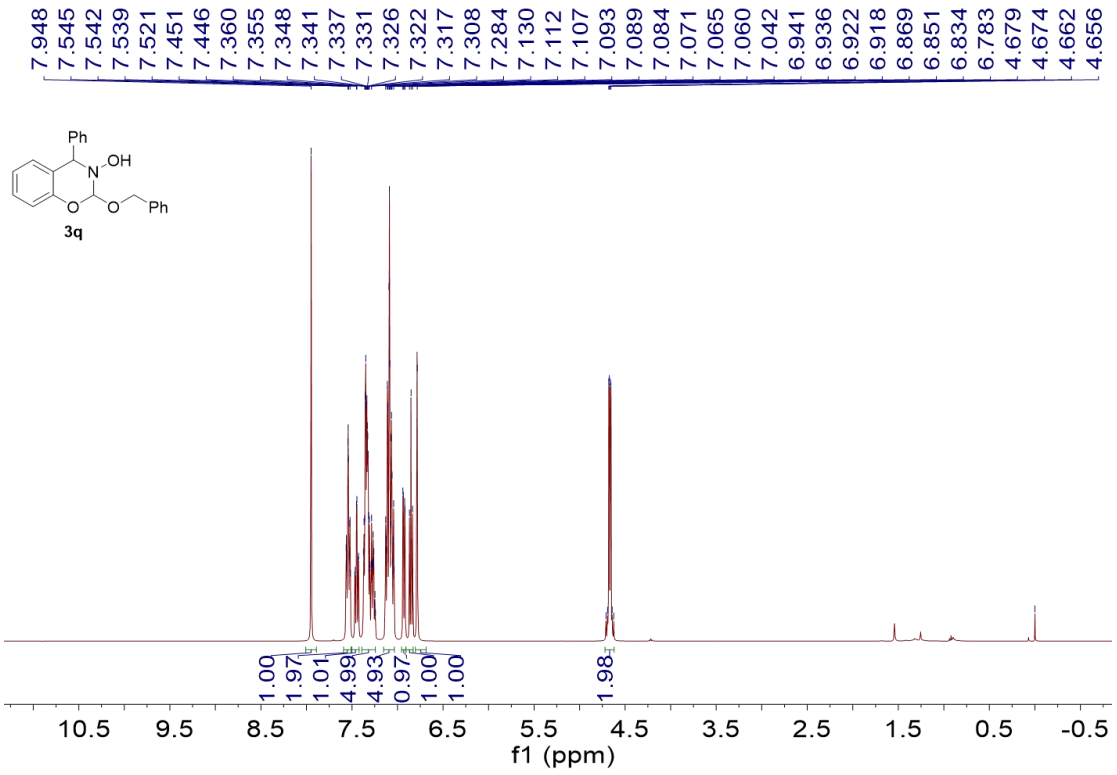
^{1}H NMR of **3p** (400 MHz, $CDCl_3$):



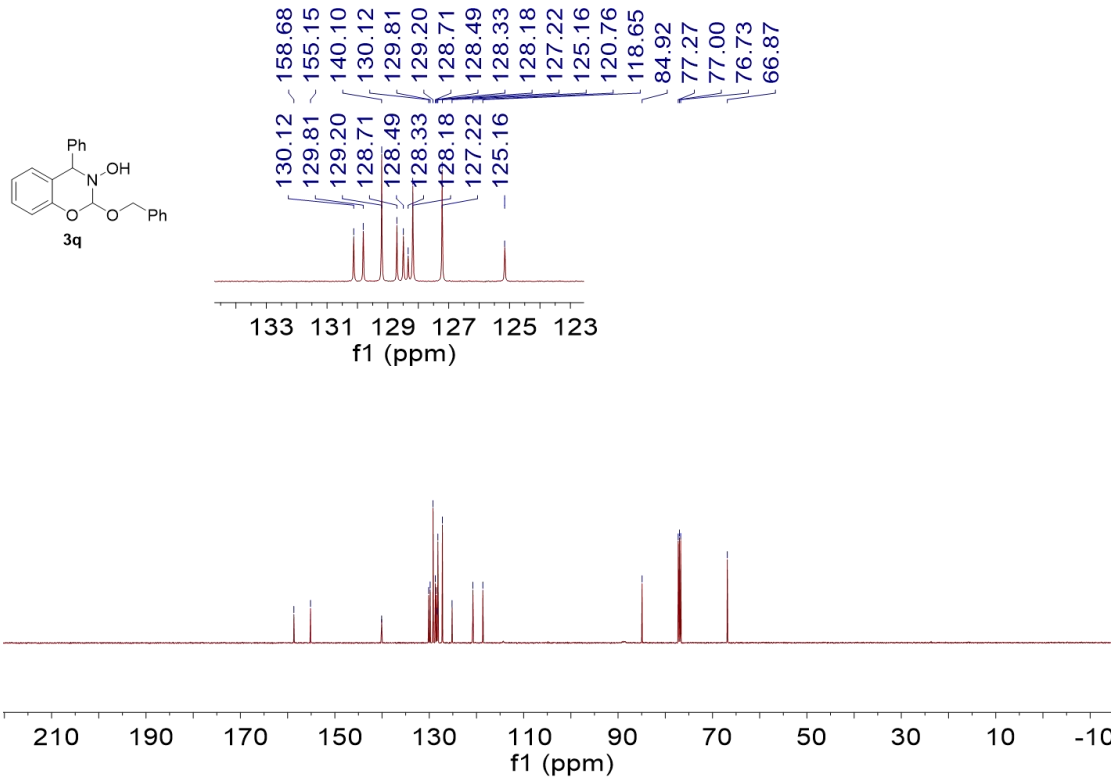
^{13}C NMR of **3p** (100 MHz, $CDCl_3$):



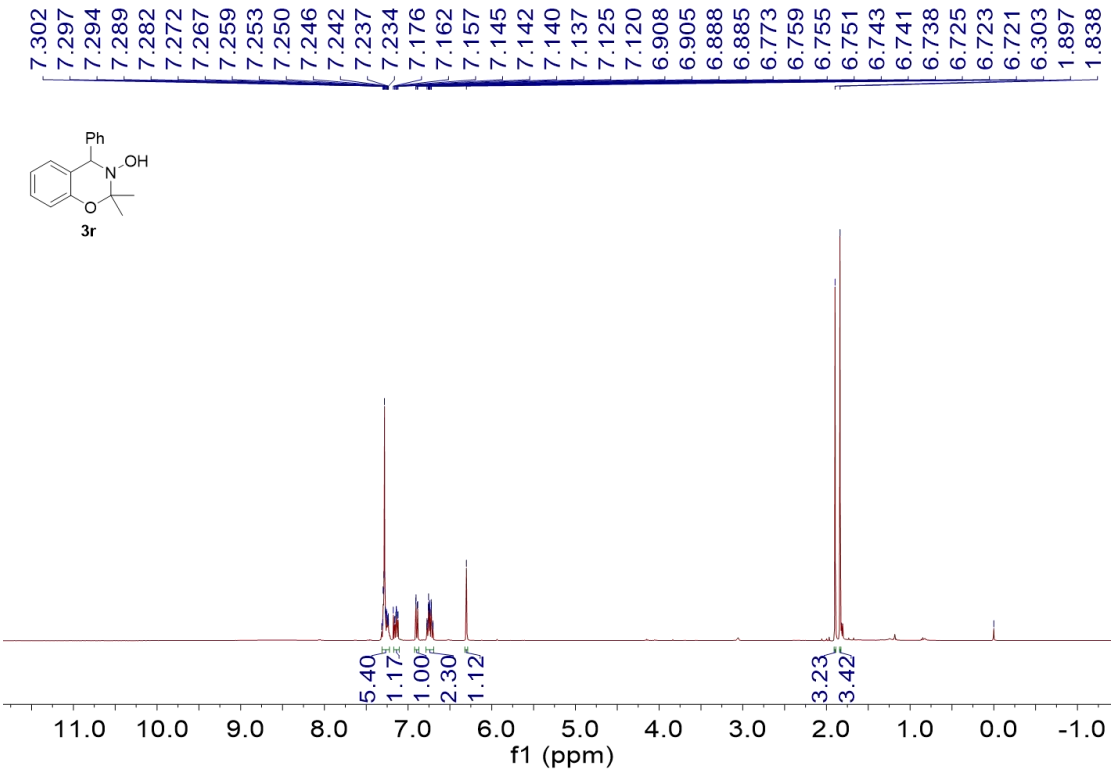
^{1}H NMR of **3q** (400 MHz, $CDCl_3$):



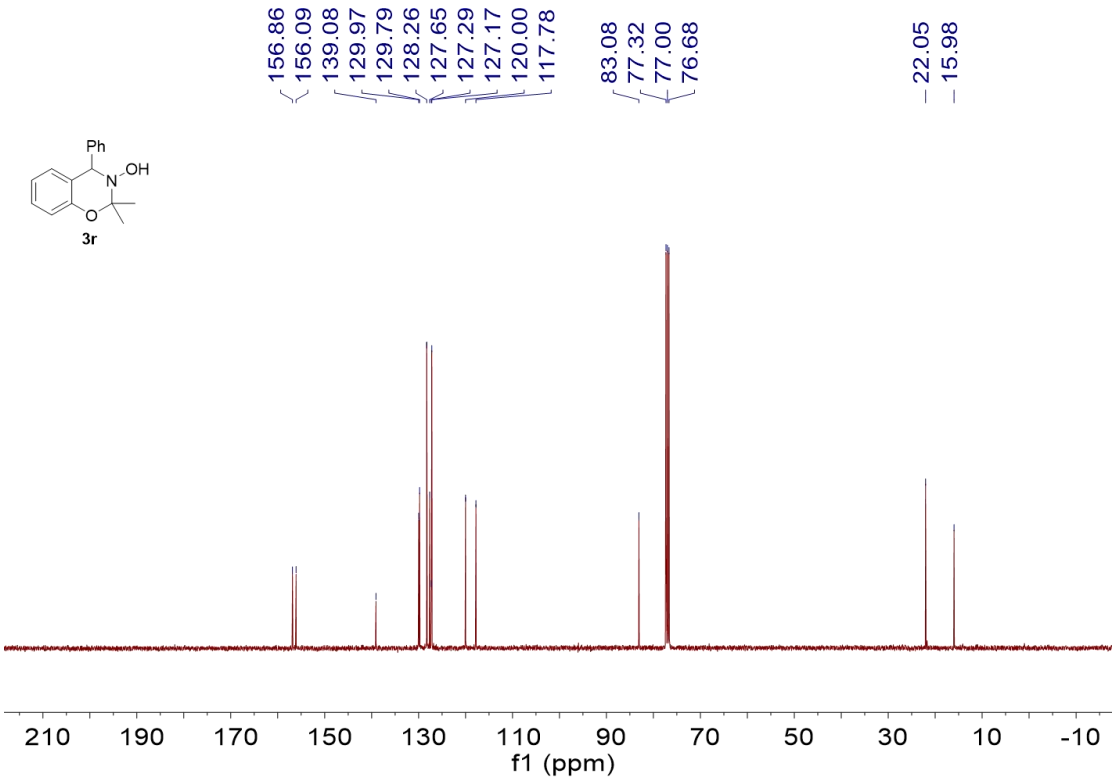
^{13}C NMR of **3q** (100 MHz, $CDCl_3$):



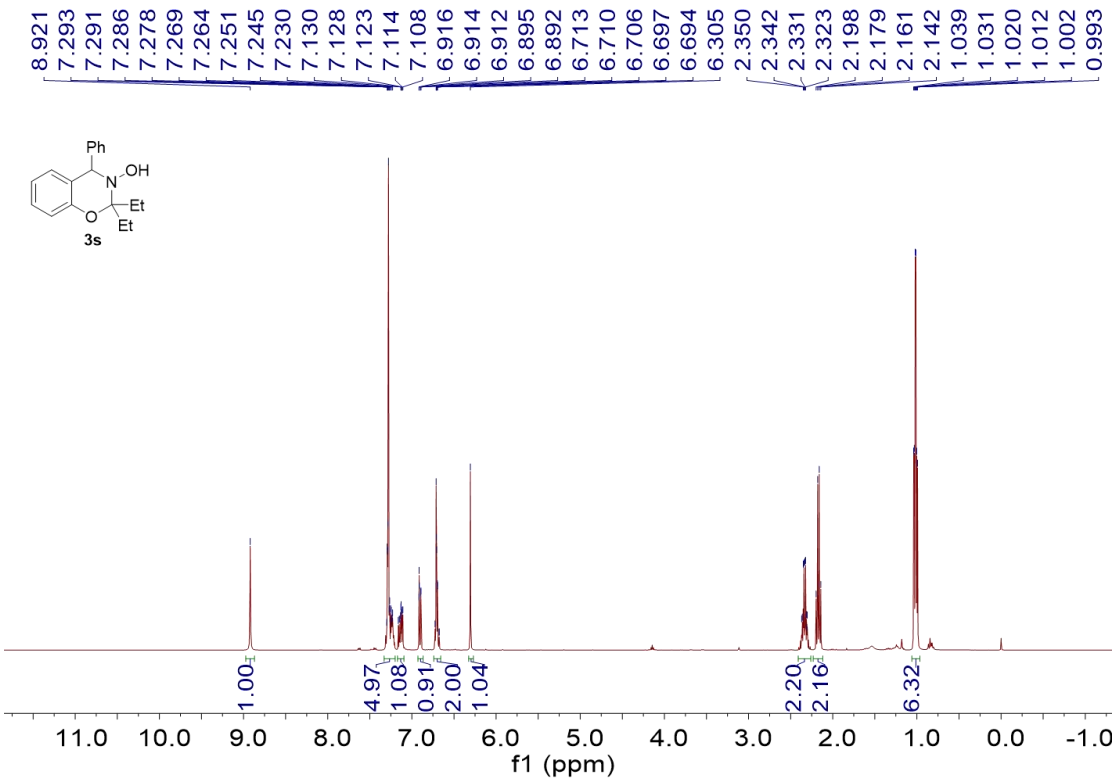
^{1}H NMR of **3r** (400 MHz, $CDCl_3$):



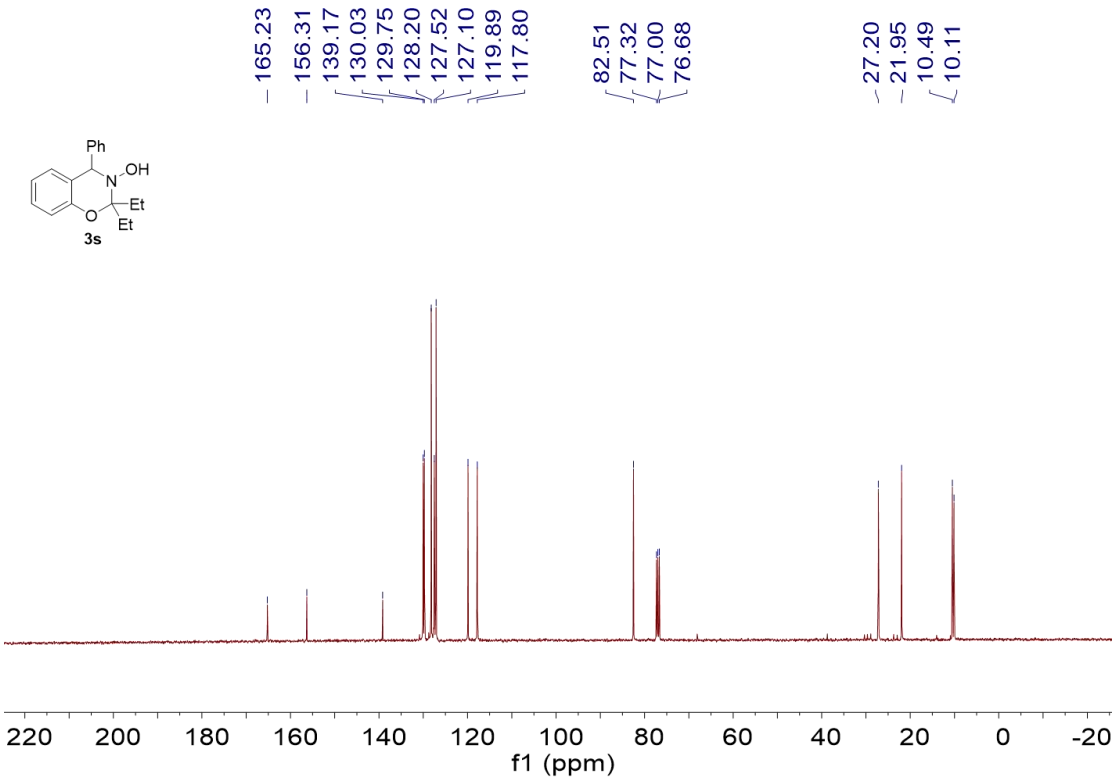
^{13}C NMR of **3r** (100 MHz, $CDCl_3$):



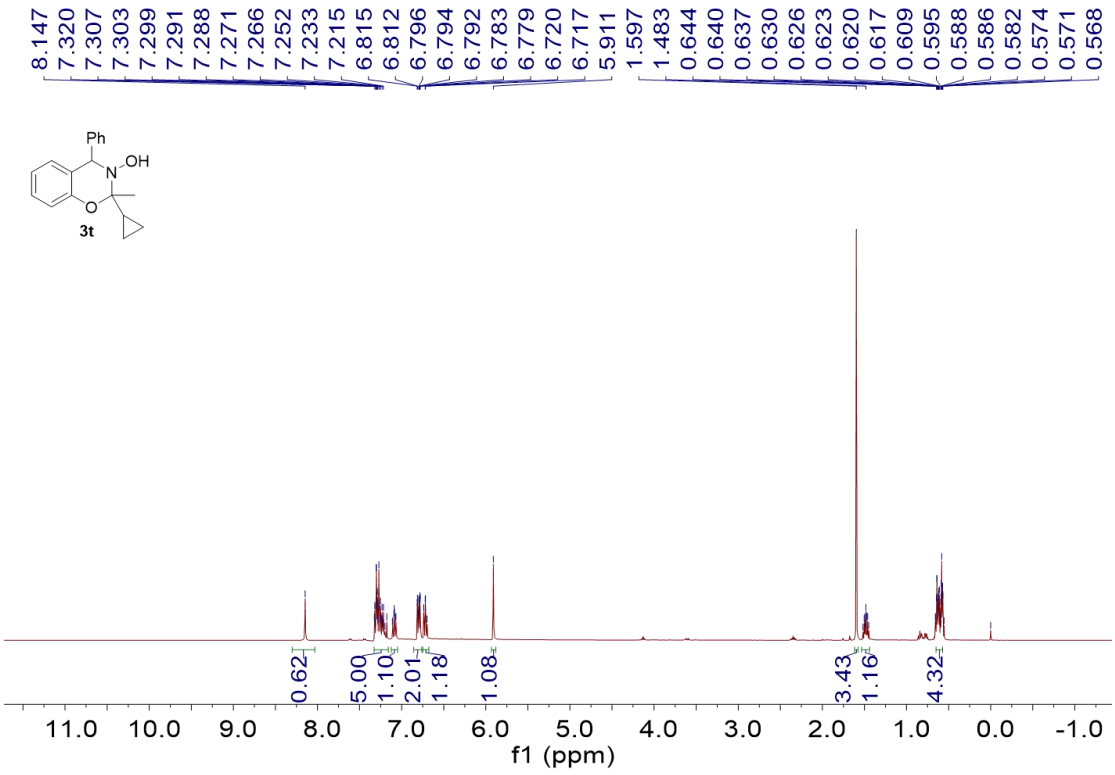
^{1}H NMR of **3s** (400 MHz, $CDCl_3$):



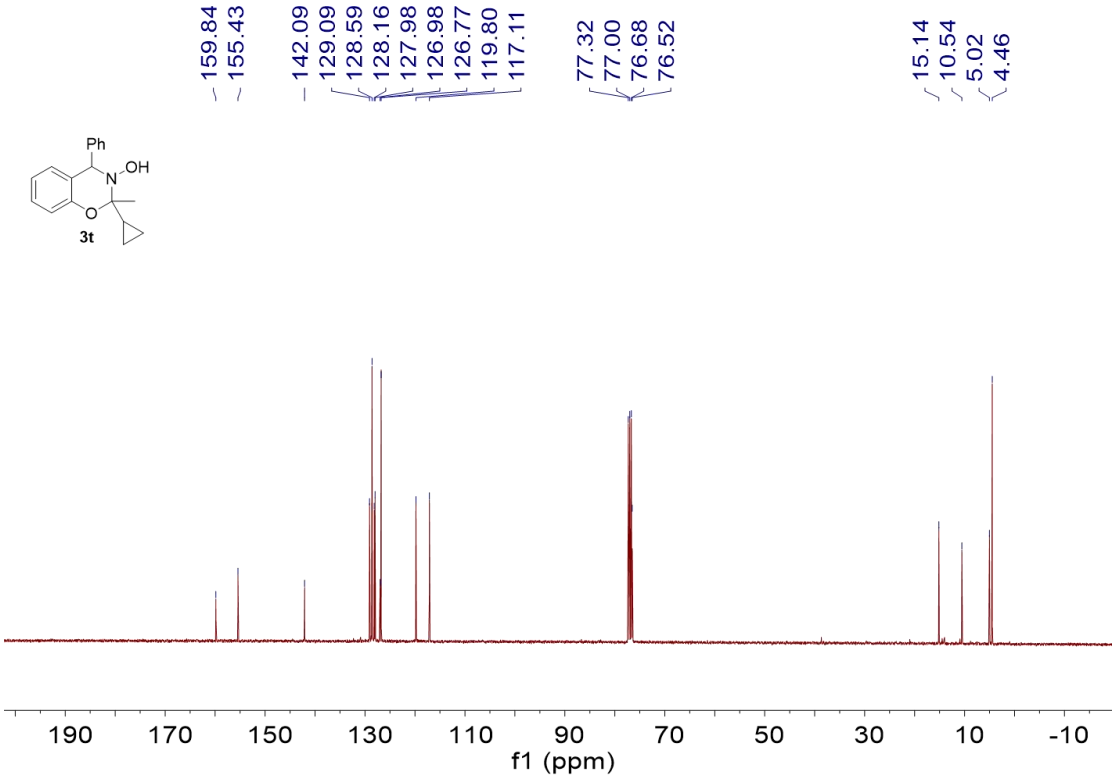
^{13}C NMR of **3s** (100 MHz, $CDCl_3$):



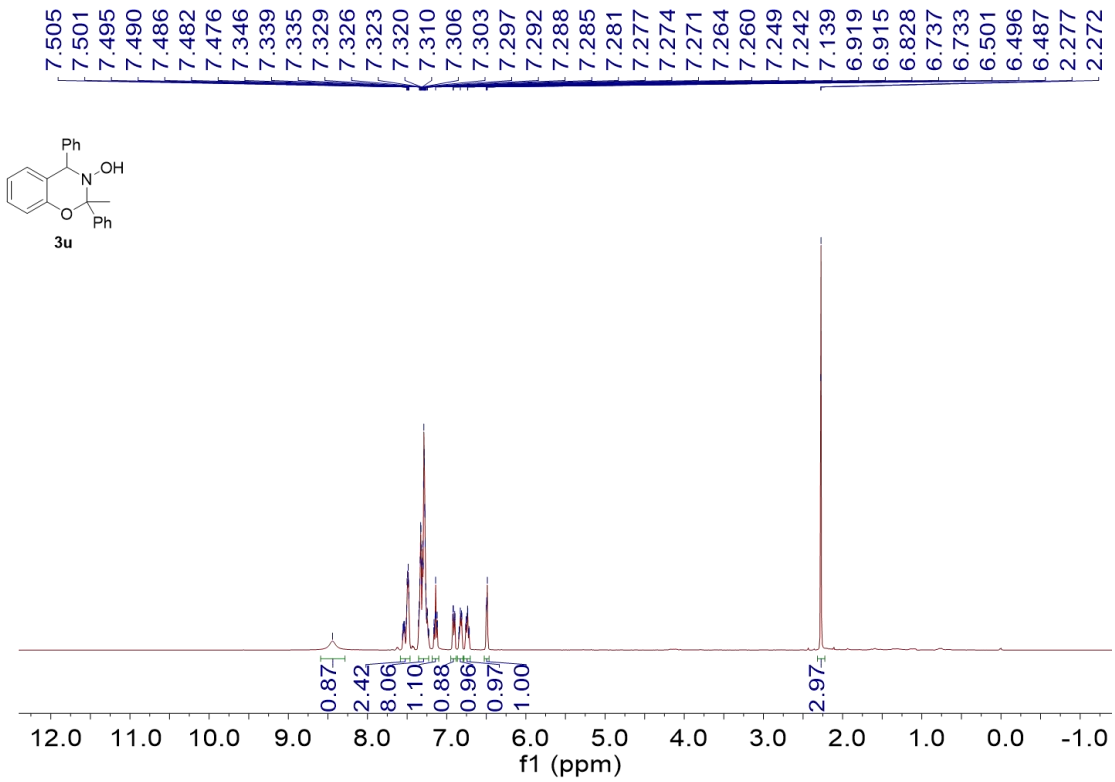
^{1}H NMR of **3t** (400 MHz, $CDCl_3$):



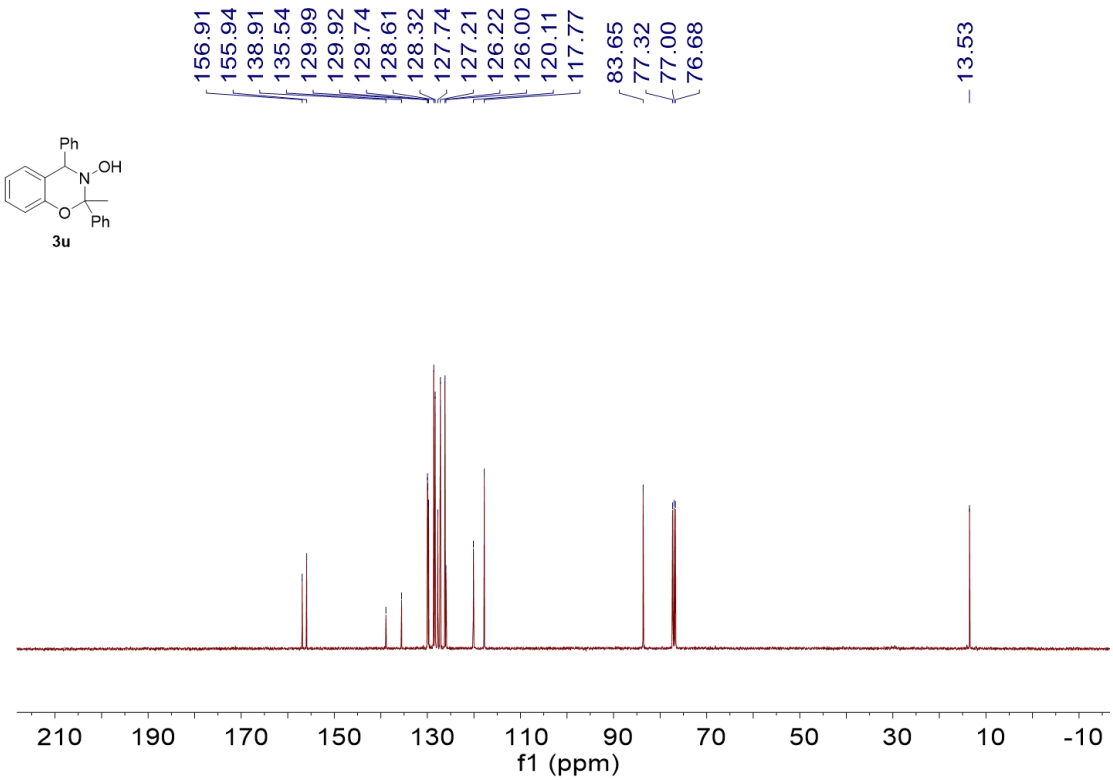
^{13}C NMR of **3t** (100 MHz, $CDCl_3$):



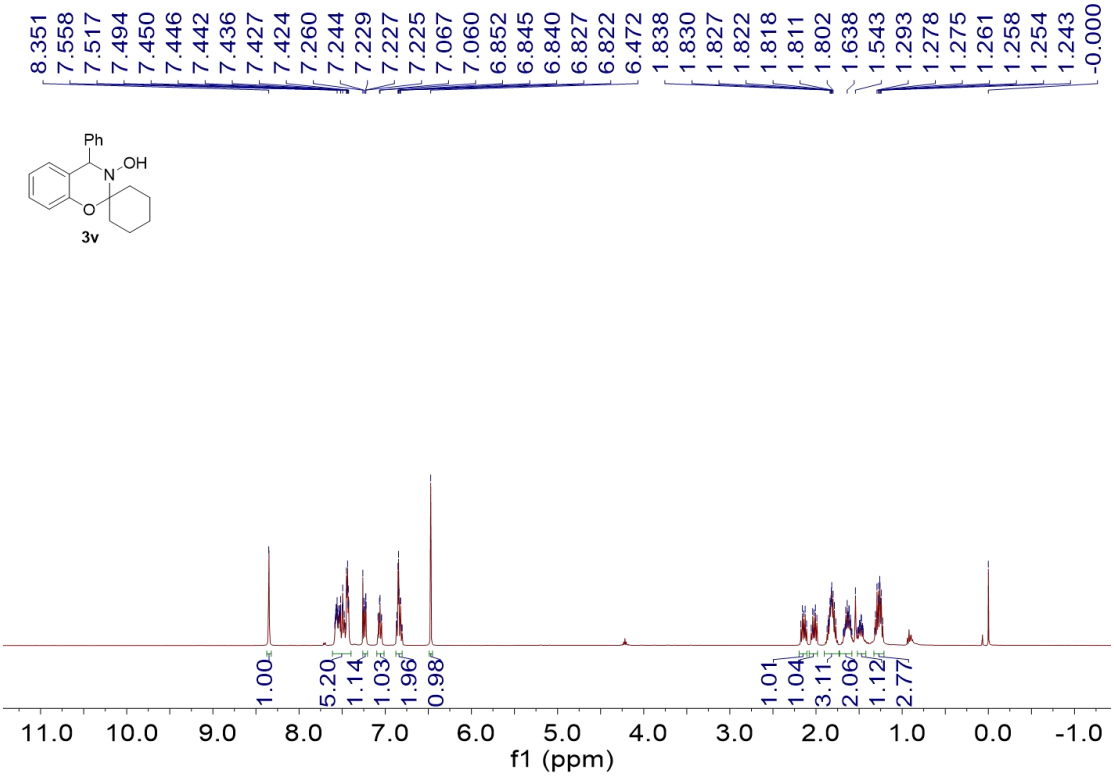
^{1}H NMR of **3u** (400 MHz, $CDCl_3$):



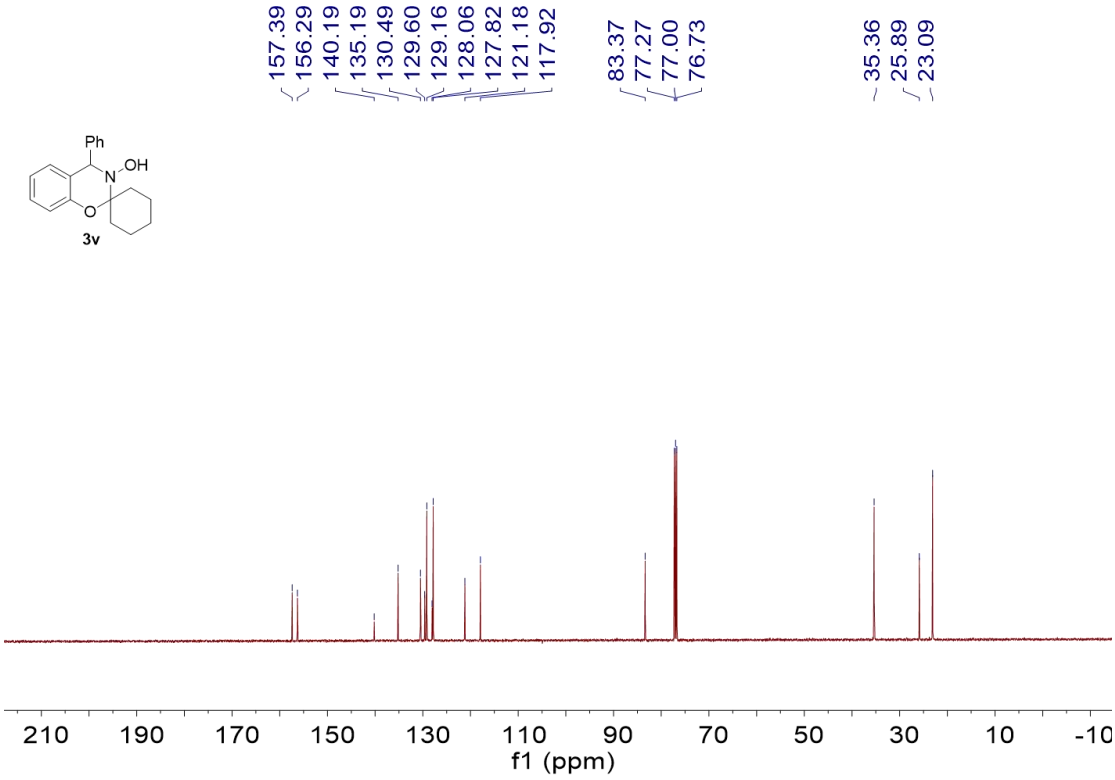
^{13}C NMR of **3u** (100 MHz, $CDCl_3$):



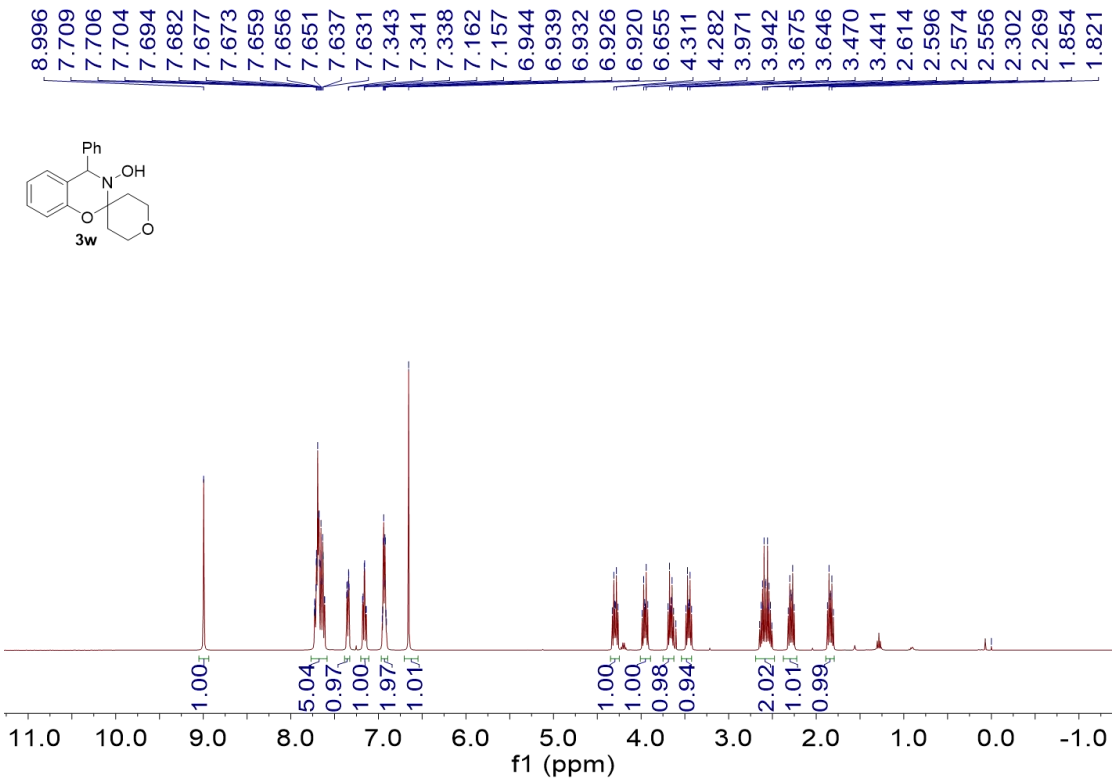
^{1}H NMR of **3v** (400 MHz, $CDCl_3$):



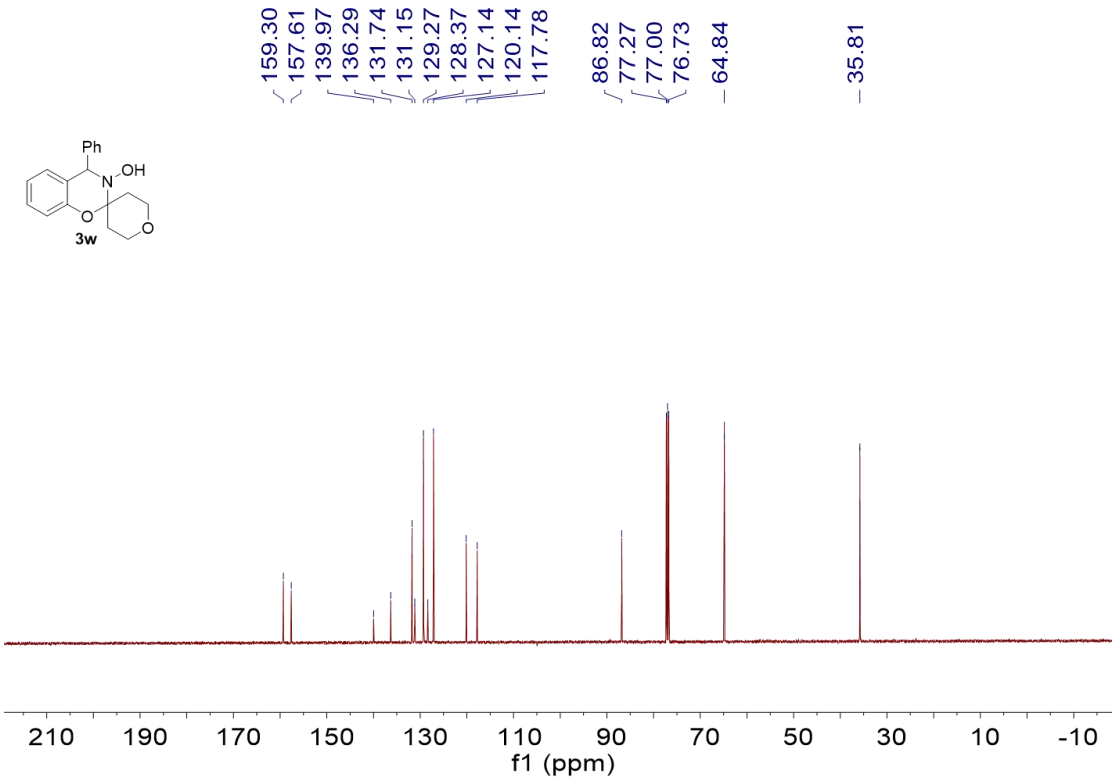
^{13}C NMR of **3v** (100 MHz, $CDCl_3$):



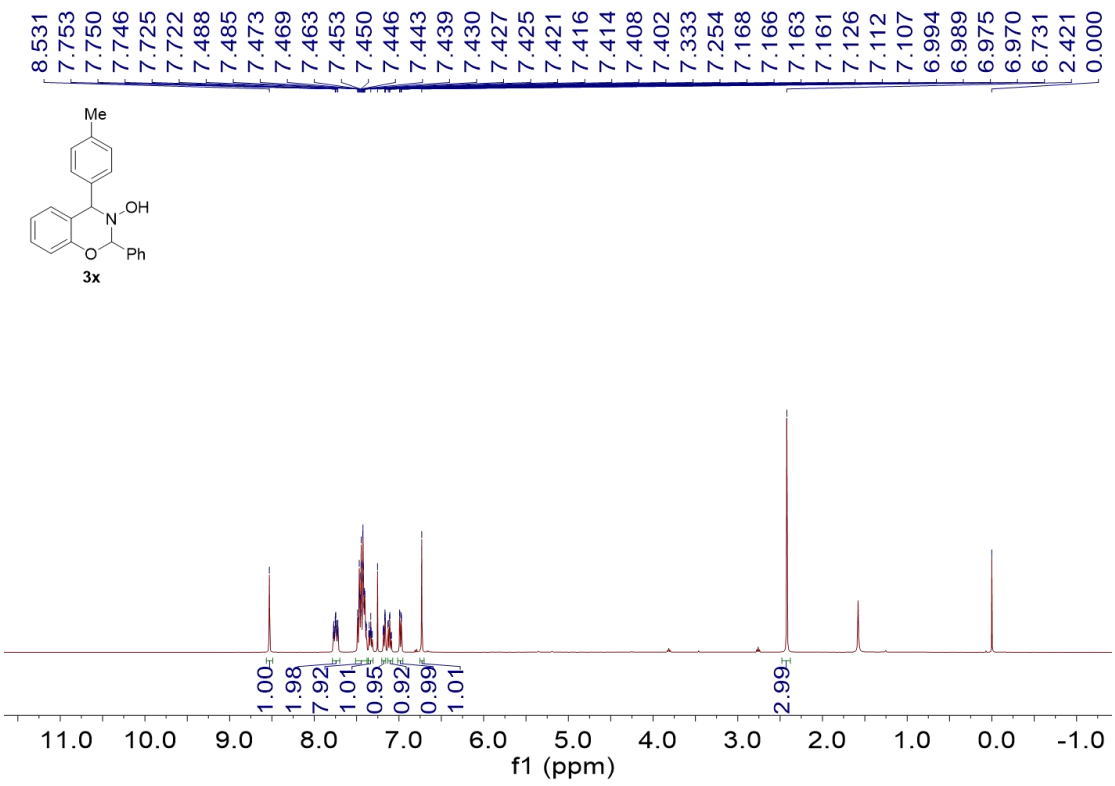
^{1}H NMR of **3w** (400 MHz, $CDCl_3$):



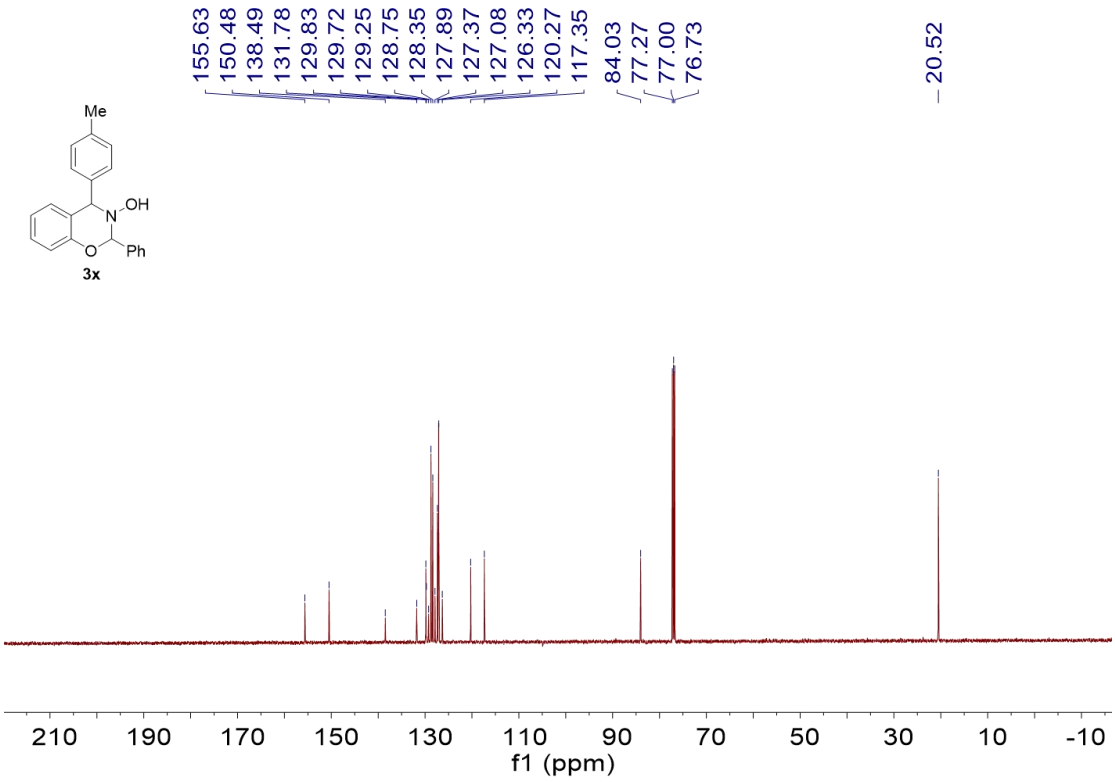
^{13}C NMR of **3w** (100 MHz, $CDCl_3$):



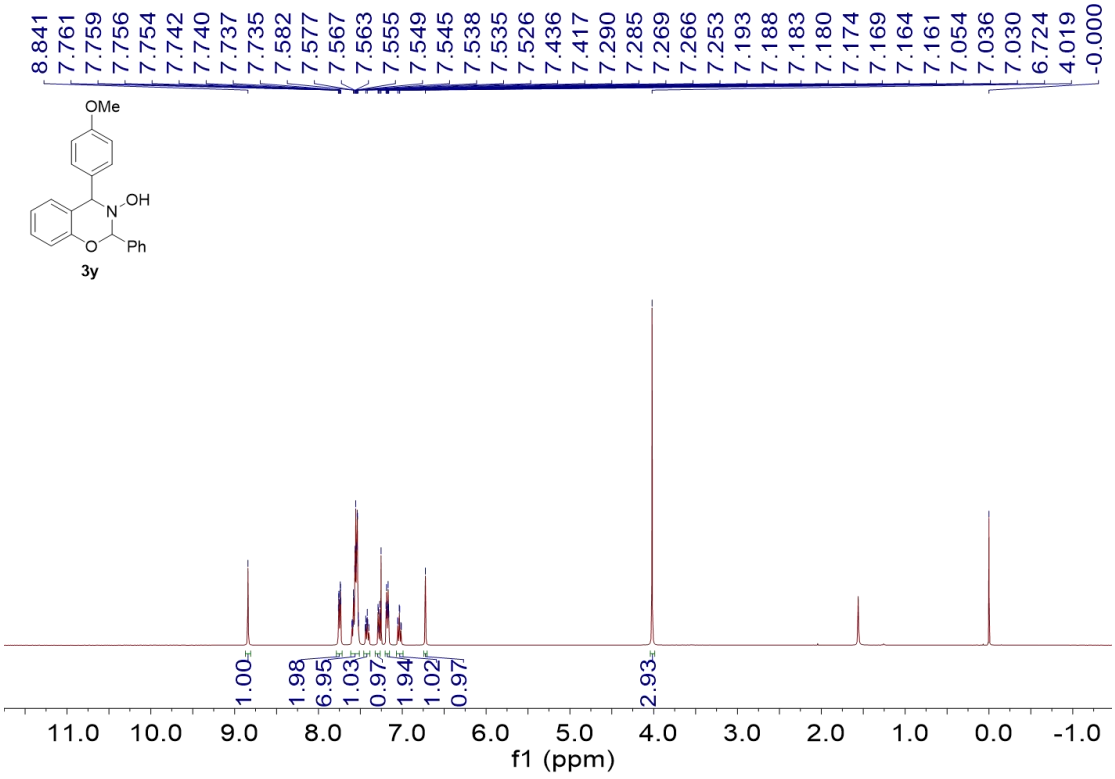
^{1}H NMR of **3x** (400 MHz, $CDCl_3$):



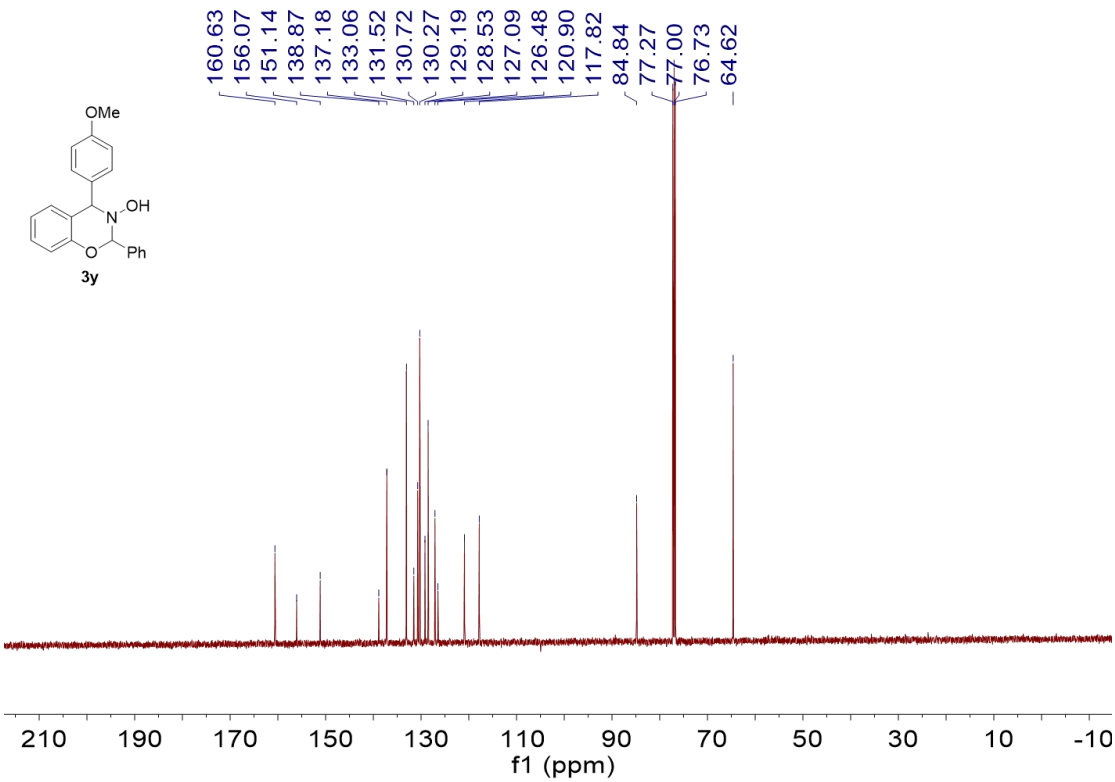
^{13}C NMR of **3x** (100 MHz, $CDCl_3$):



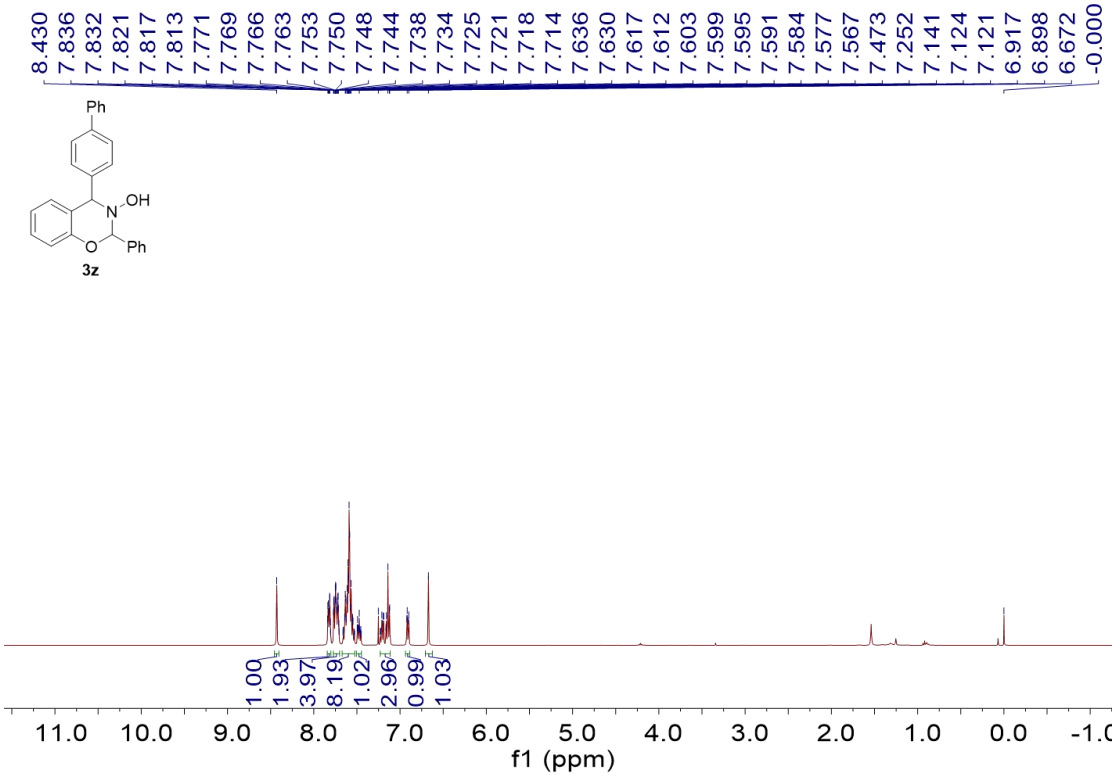
^{1}H NMR of **3y** (400 MHz, $CDCl_3$):



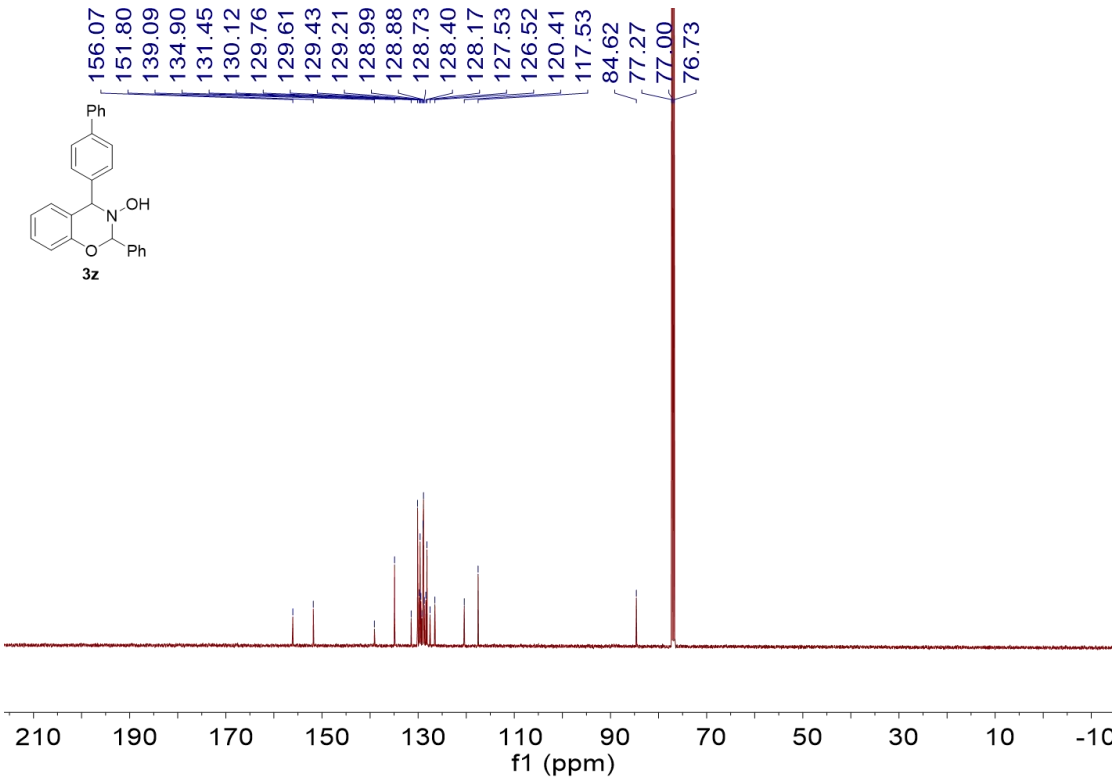
^{13}C NMR of **3y** (100 MHz, $CDCl_3$):



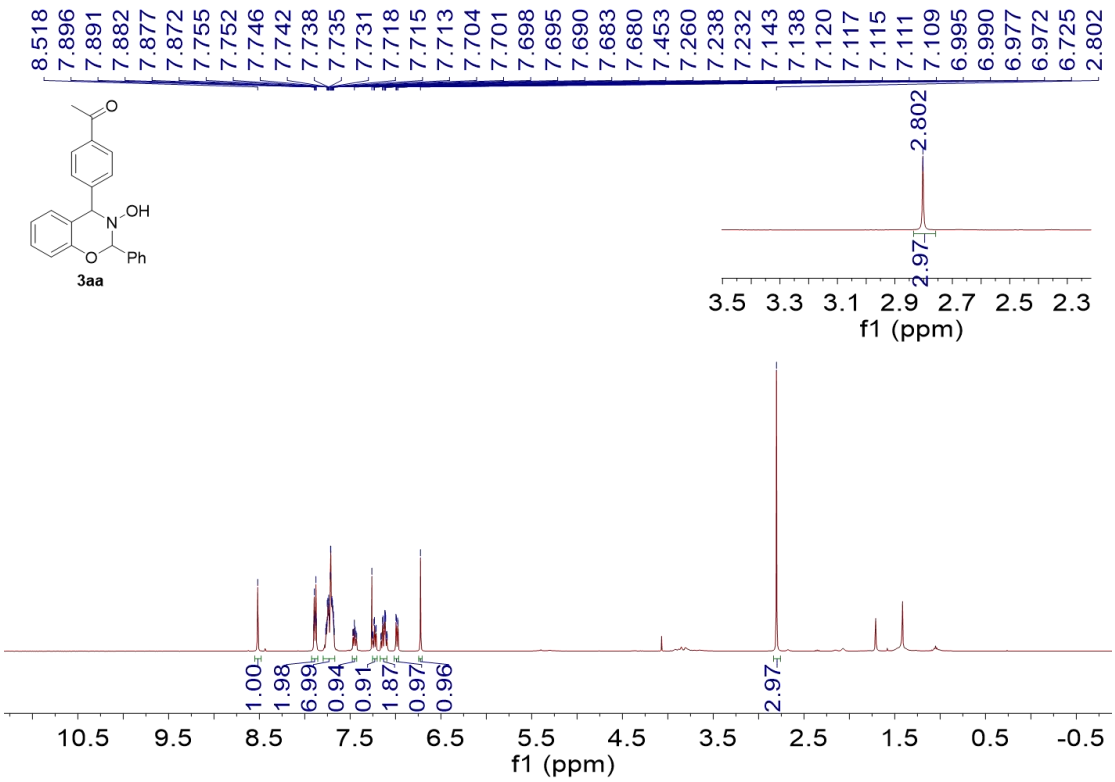
^{1}H NMR of **3z** (400 MHz, $CDCl_3$):



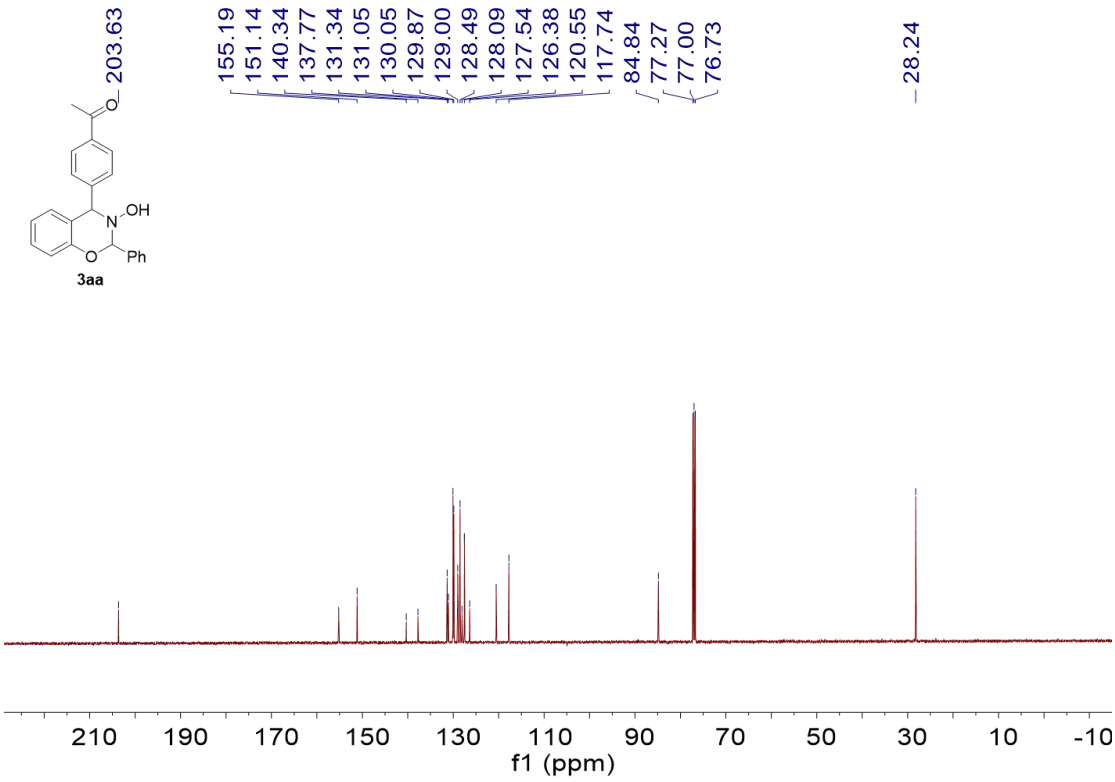
^{13}C NMR of **3z** (100 MHz, $CDCl_3$):



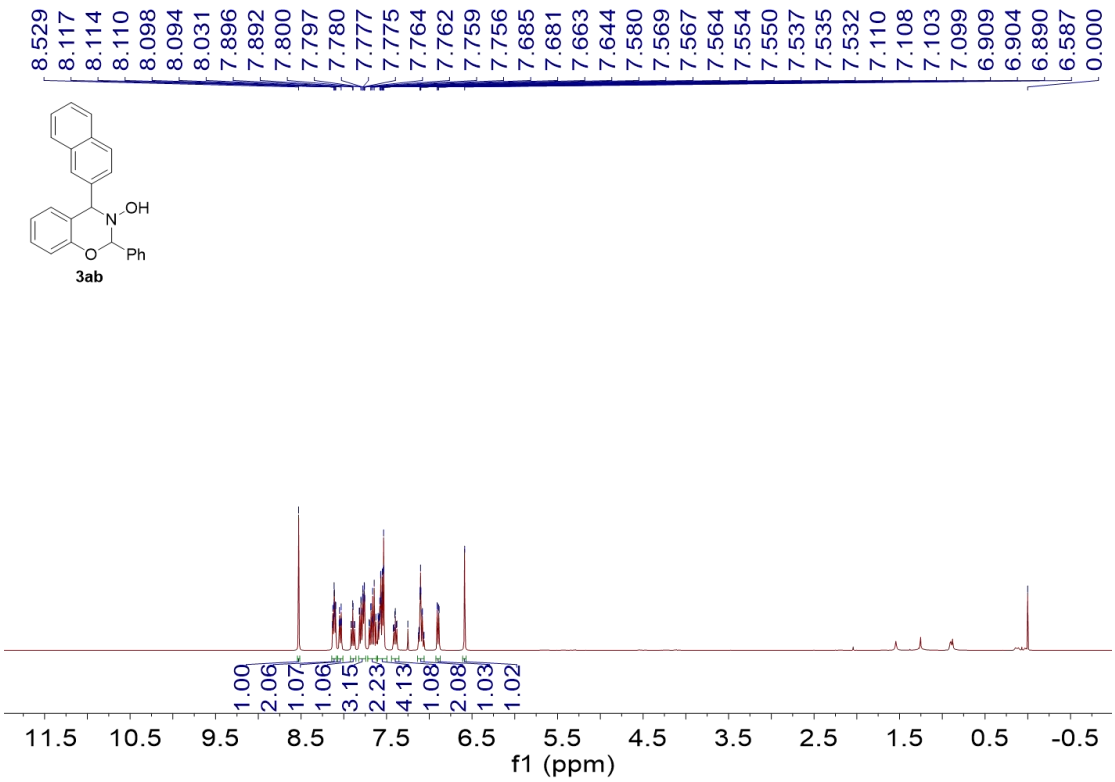
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$):



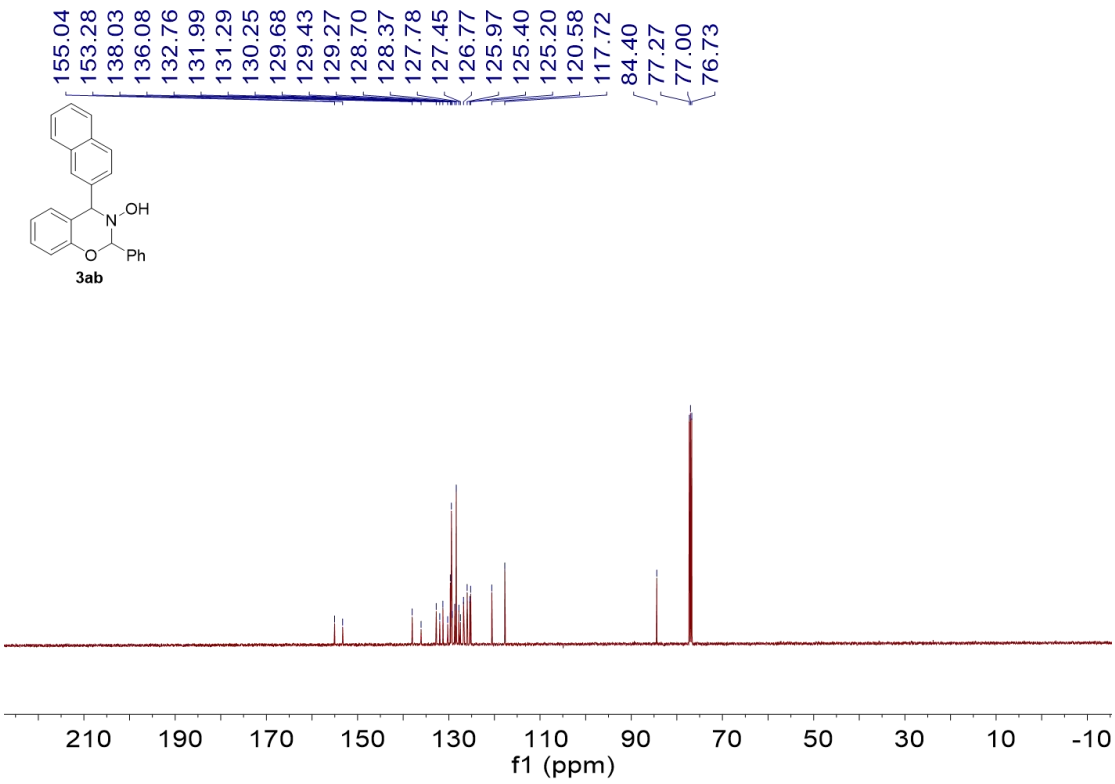
^{13}C NMR of **3aa** (100 MHz, $CDCl_3$):



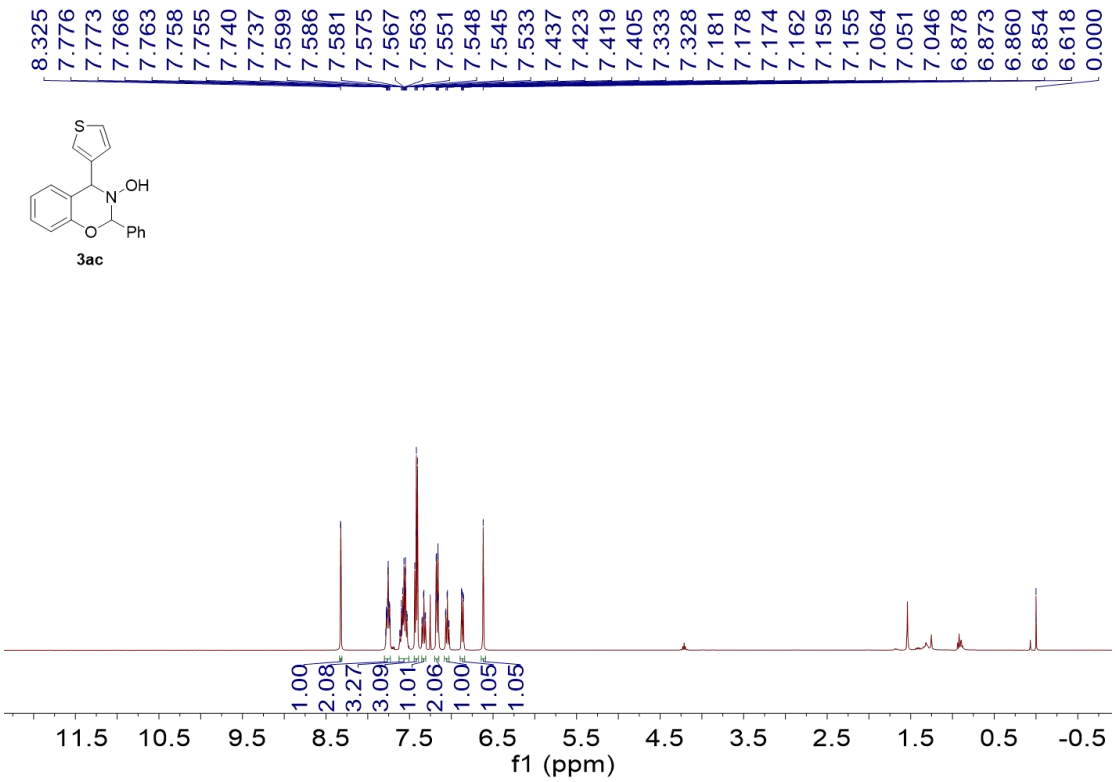
^{1}H NMR of **3ab** (400 MHz, $CDCl_3$):



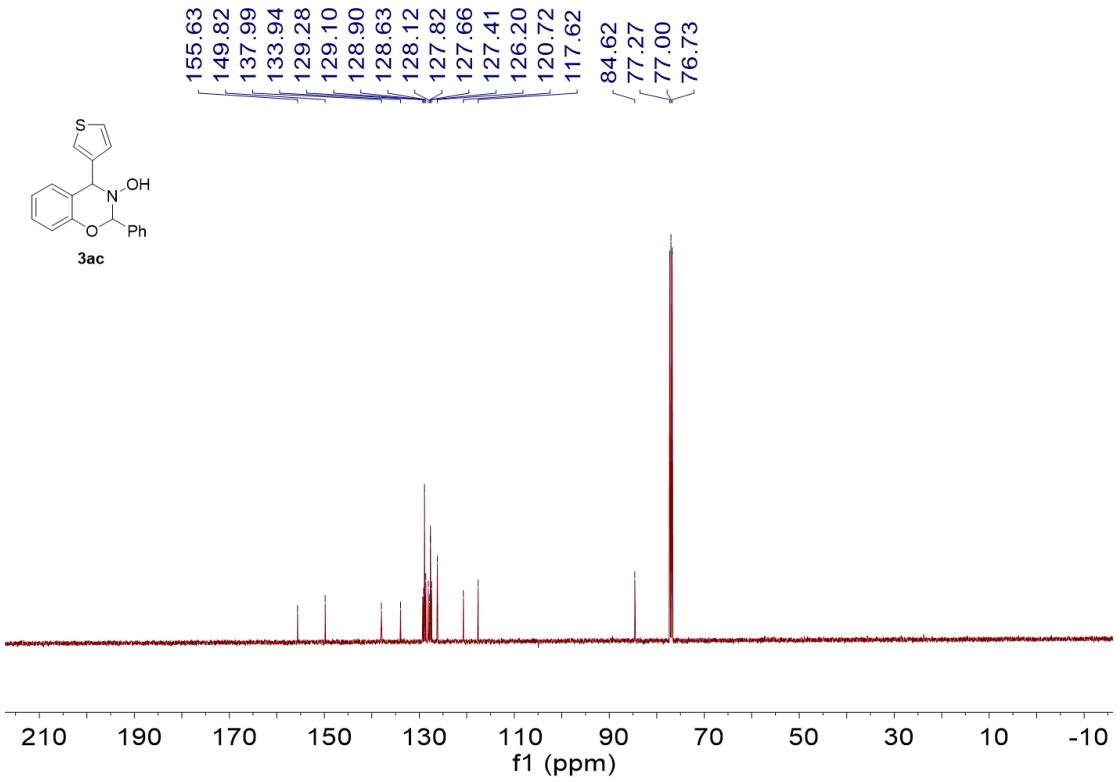
^{13}C NMR of **3ab** (100 MHz, $CDCl_3$):



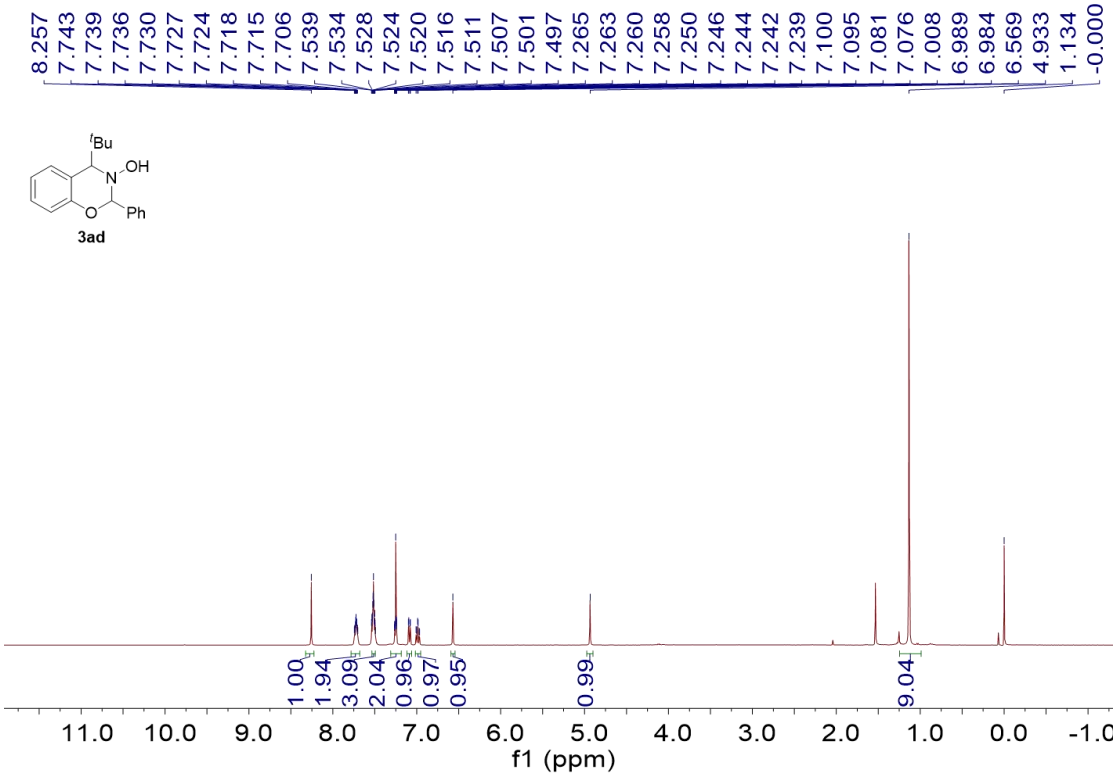
^{1}H NMR of **3ac** (400 MHz, $CDCl_3$):



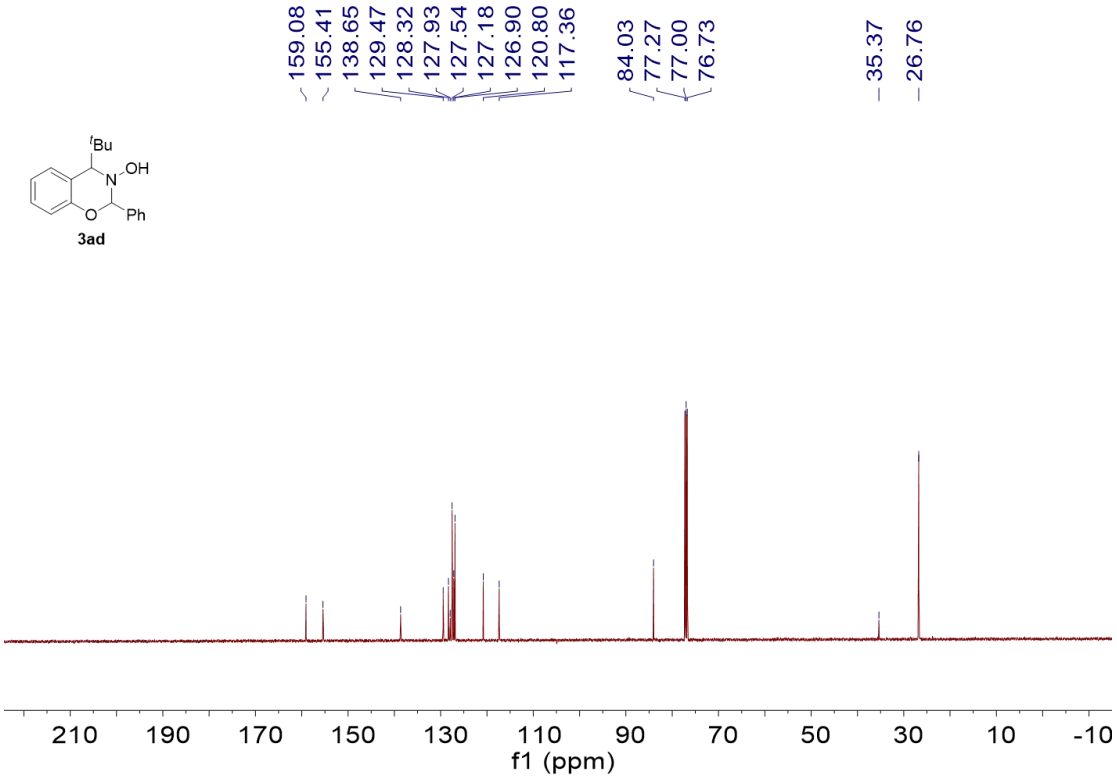
^{13}C NMR of **3ac** (100 MHz, $CDCl_3$):



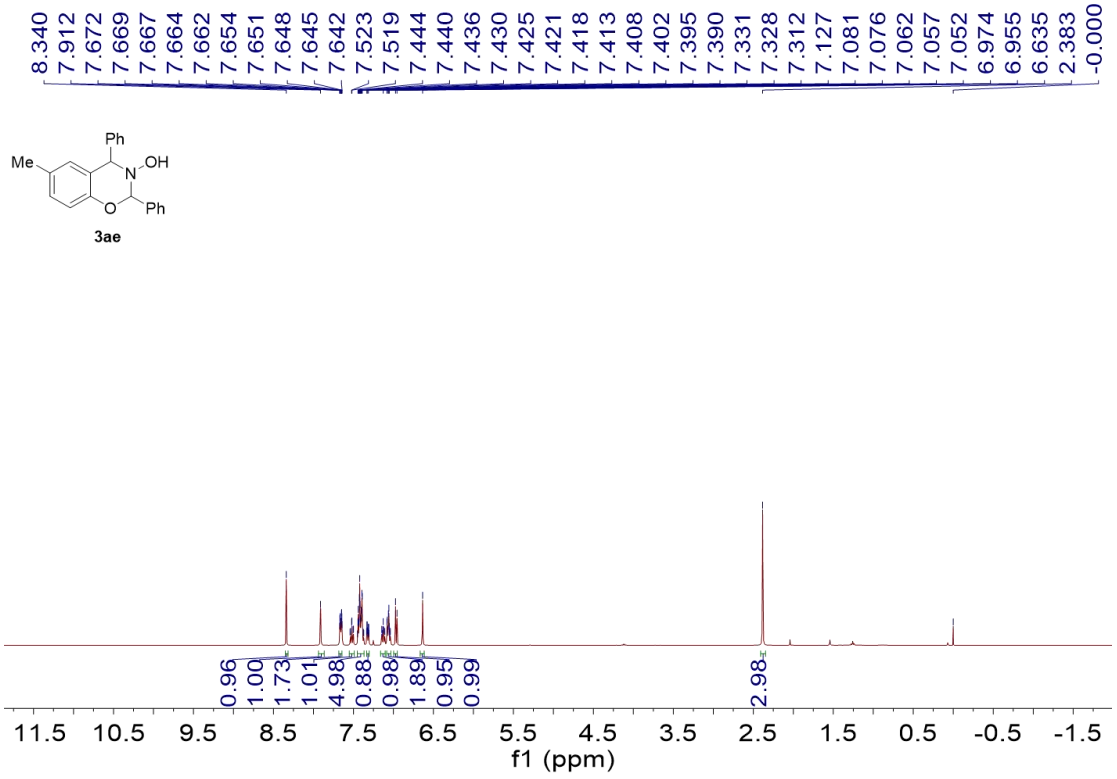
^{1}H NMR of **3ad** (400 MHz, $CDCl_3$):



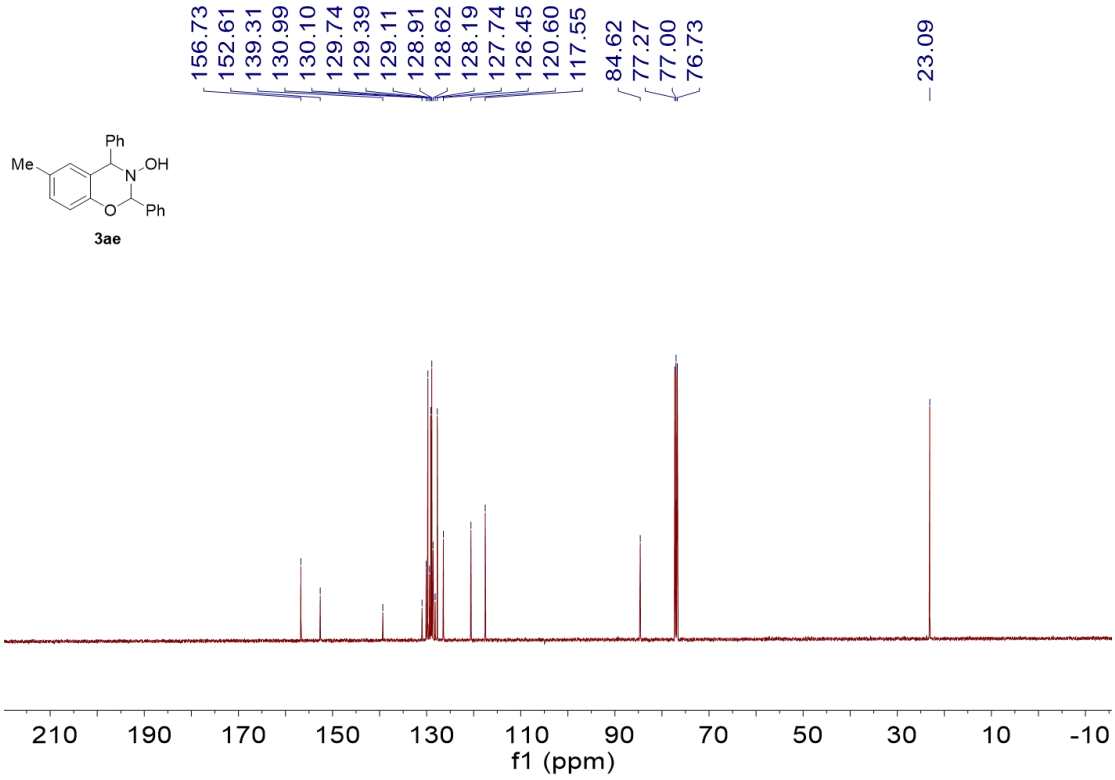
^{13}C NMR of **3ad** (100 MHz, $CDCl_3$):



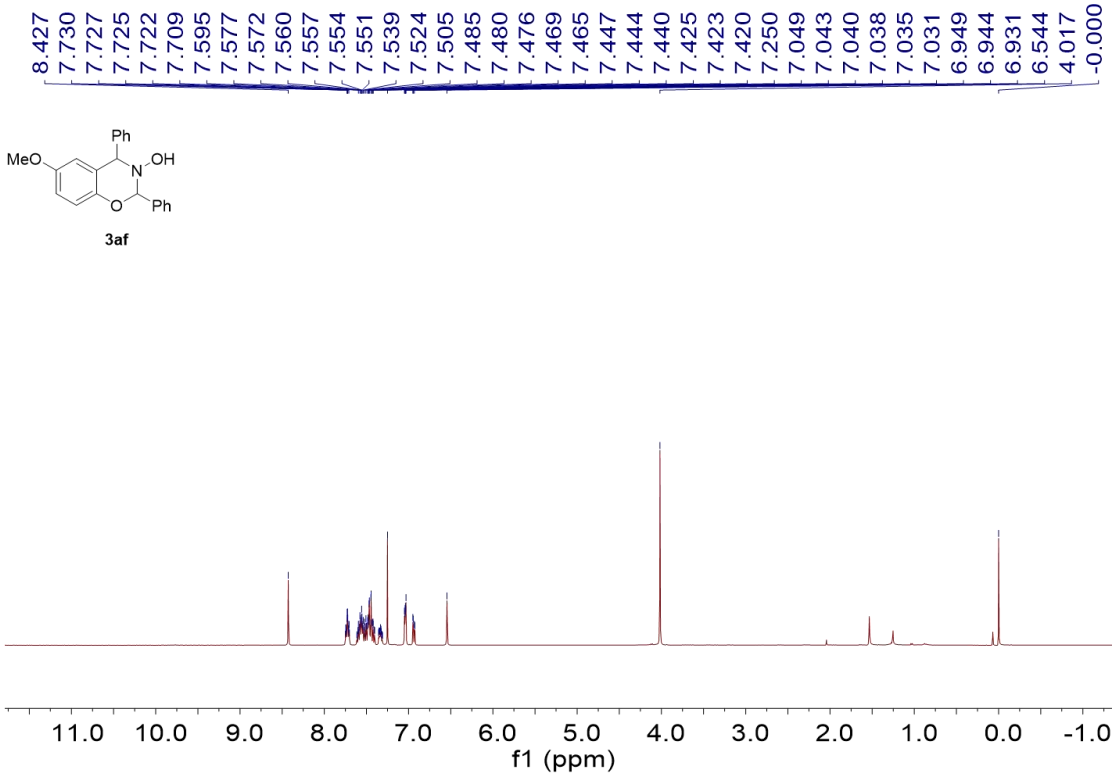
^{1}H NMR of **3ae** (400 MHz, $CDCl_3$):



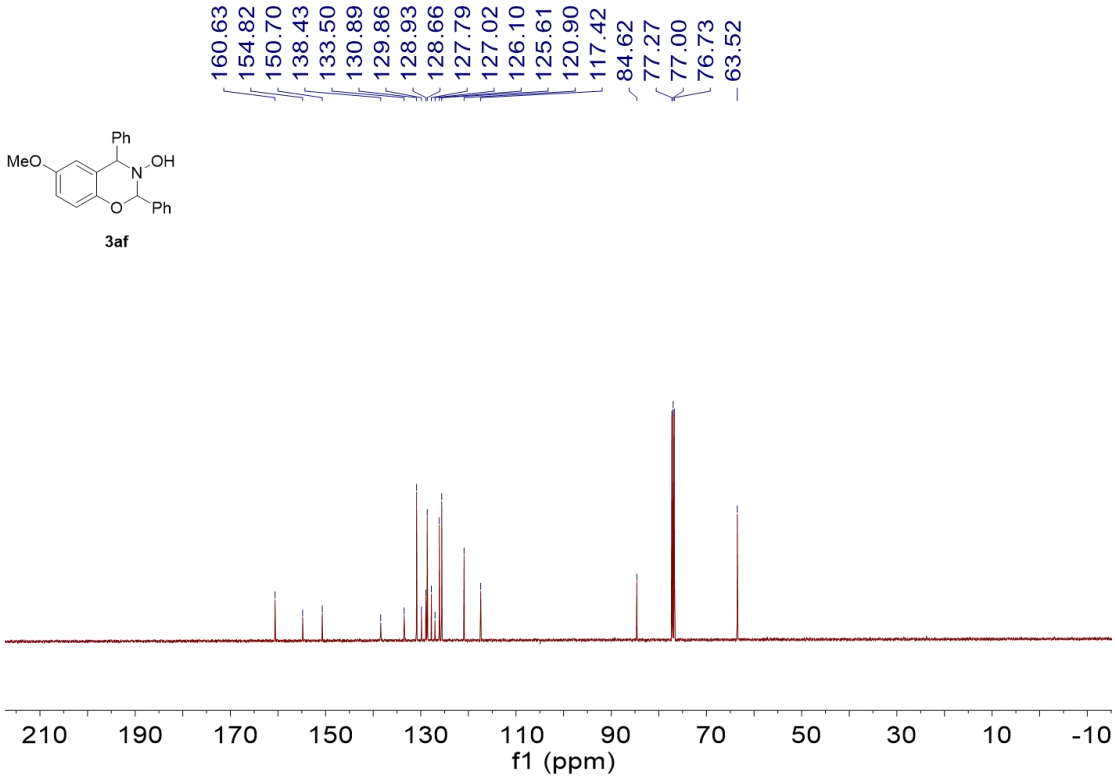
^{13}C NMR of **3ae** (100 MHz, $CDCl_3$):



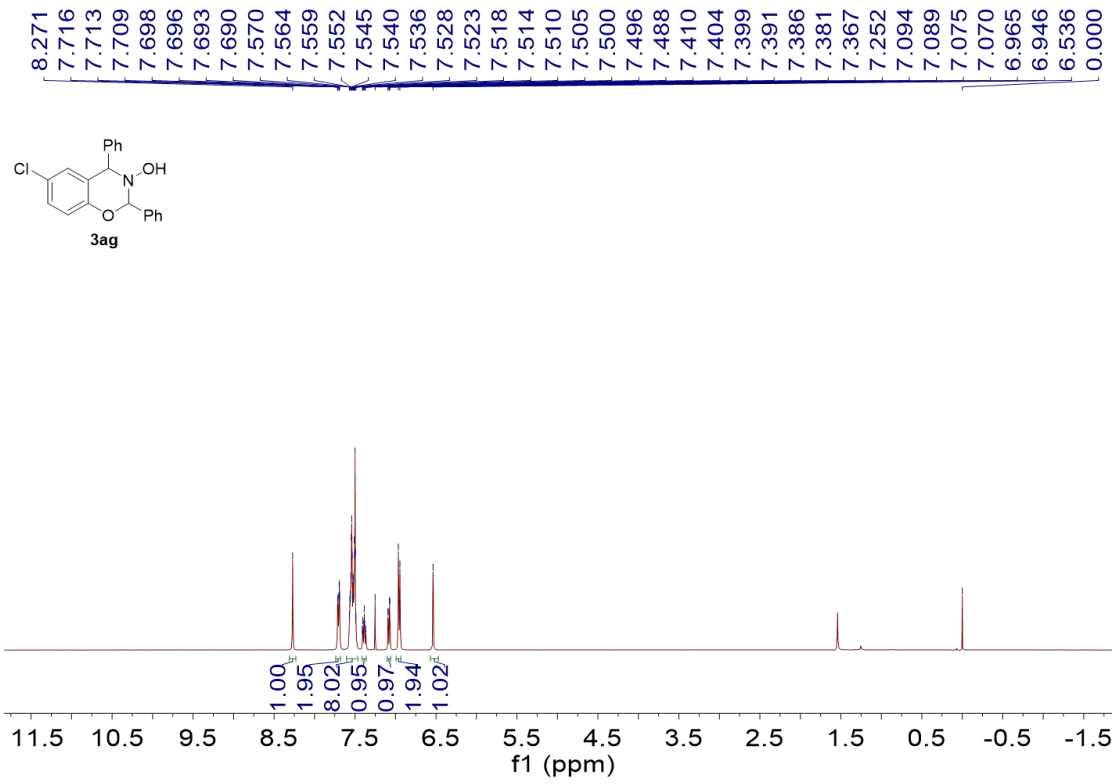
^{1}H NMR of **3af** (400 MHz, $CDCl_3$):



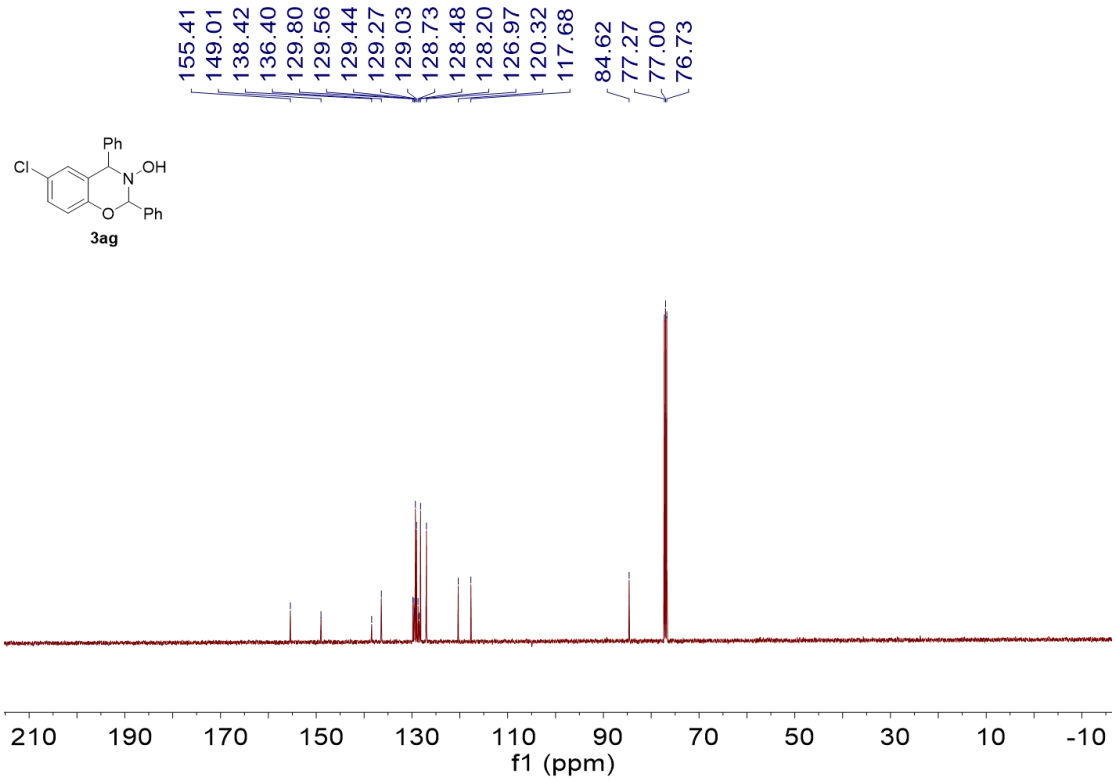
^{13}C NMR of **3af** (100 MHz, $CDCl_3$):



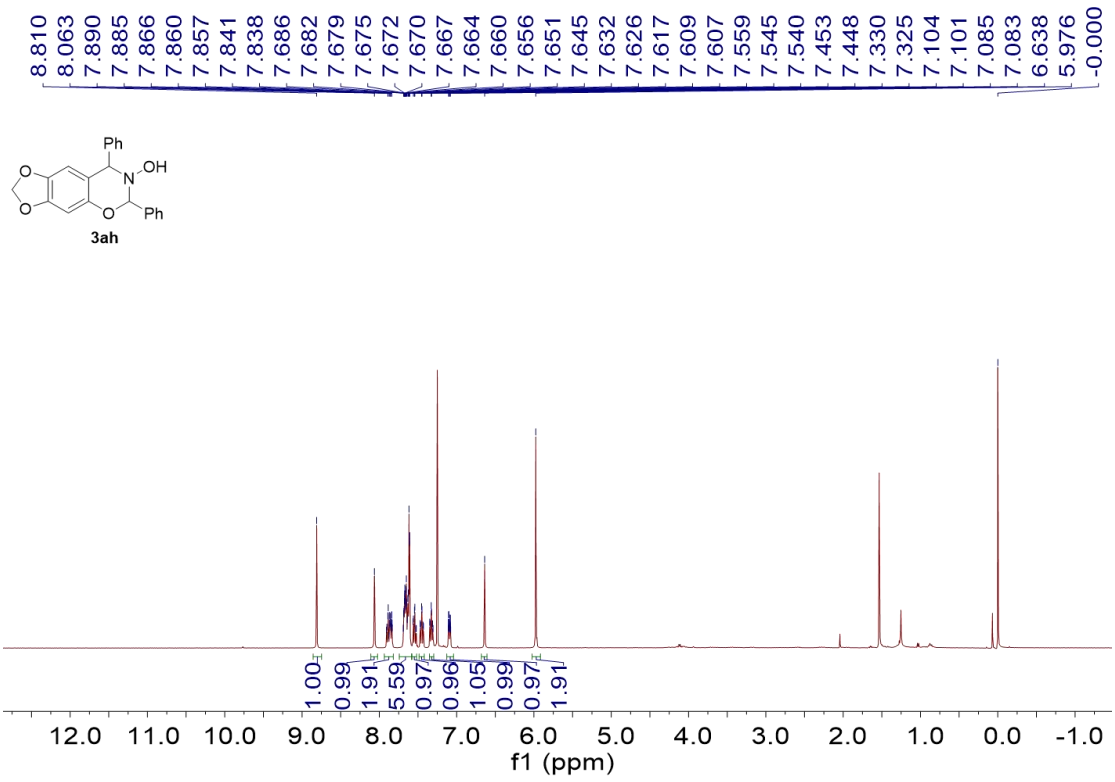
^{1}H NMR of **3ag** (400 MHz, $CDCl_3$):



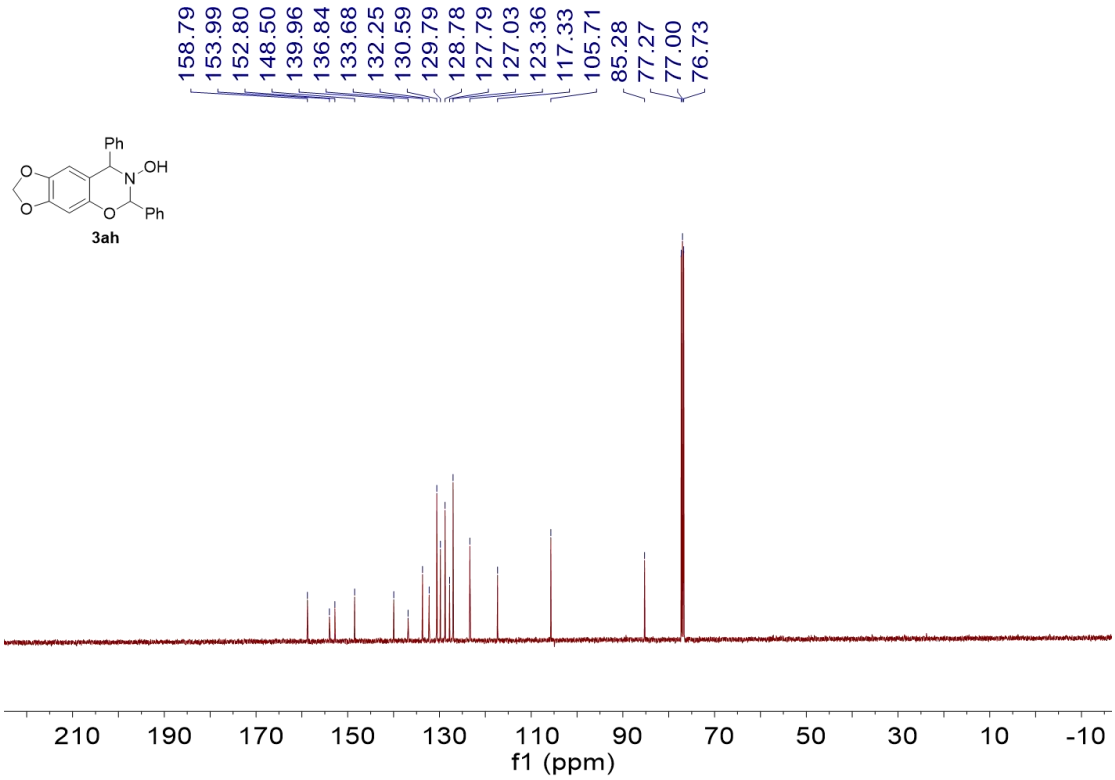
^{13}C NMR of **3ag** (**1**00 MHz, $CDCl_3$)**:**



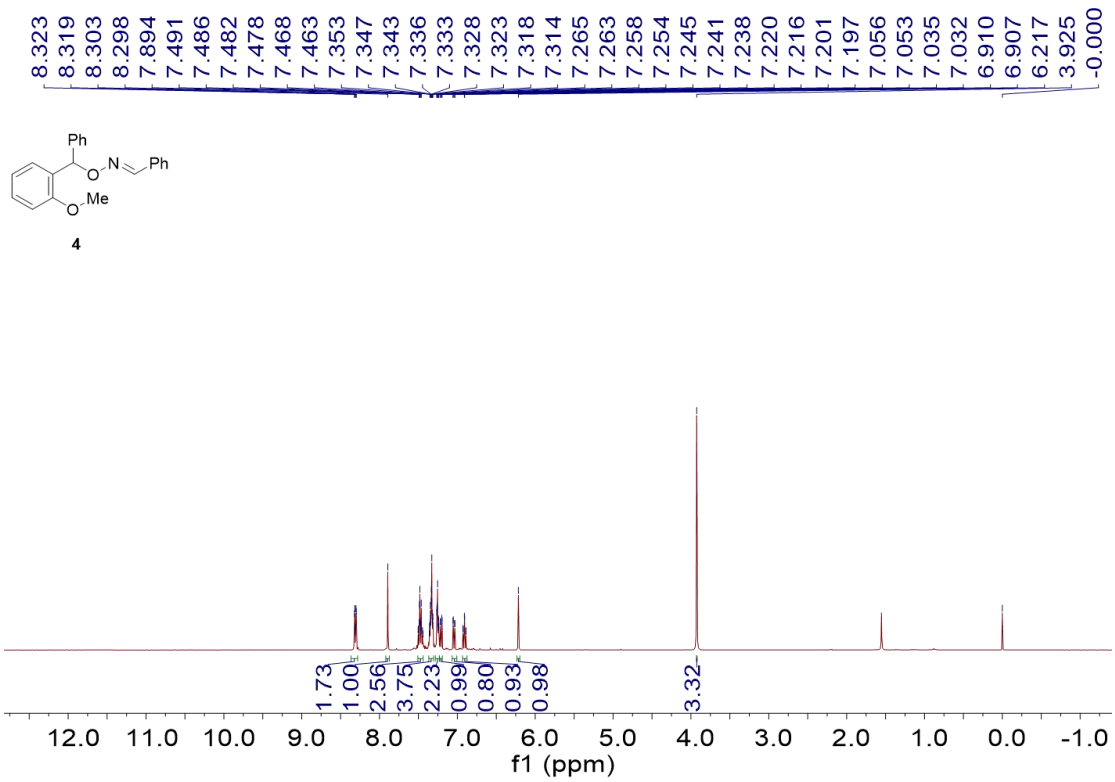
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$):



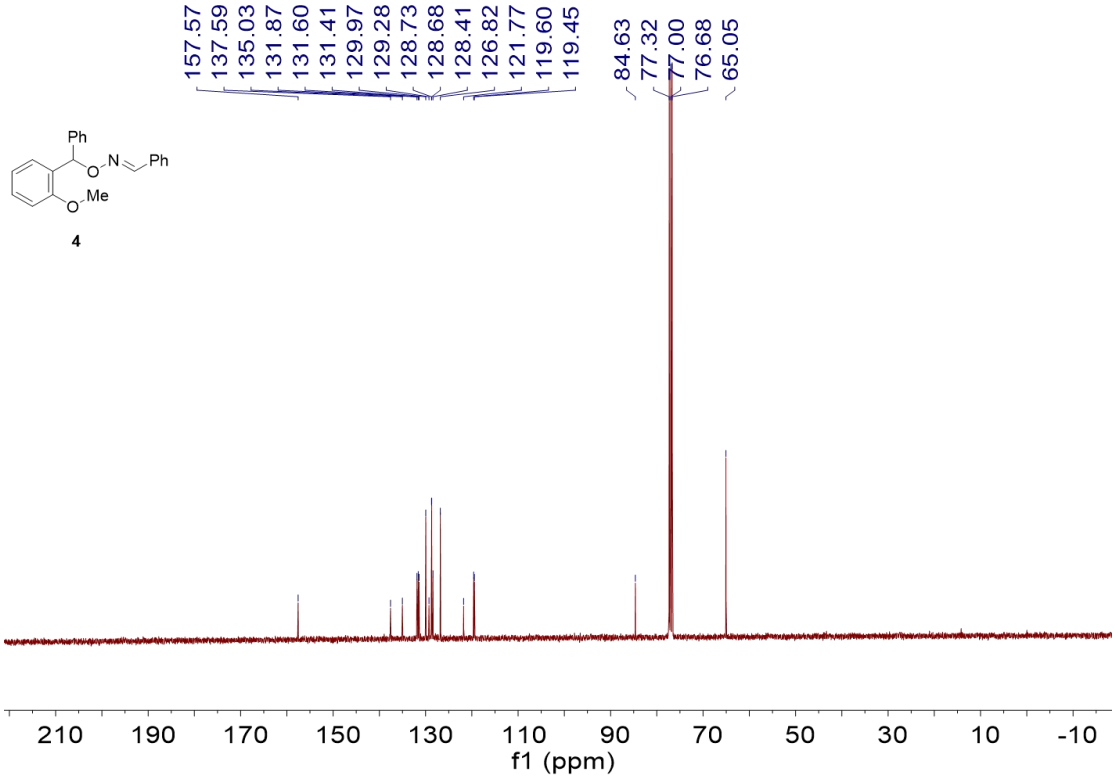
^{13}C NMR of **3ah** (**1**00 MHz, $CDCl_3$)**:**



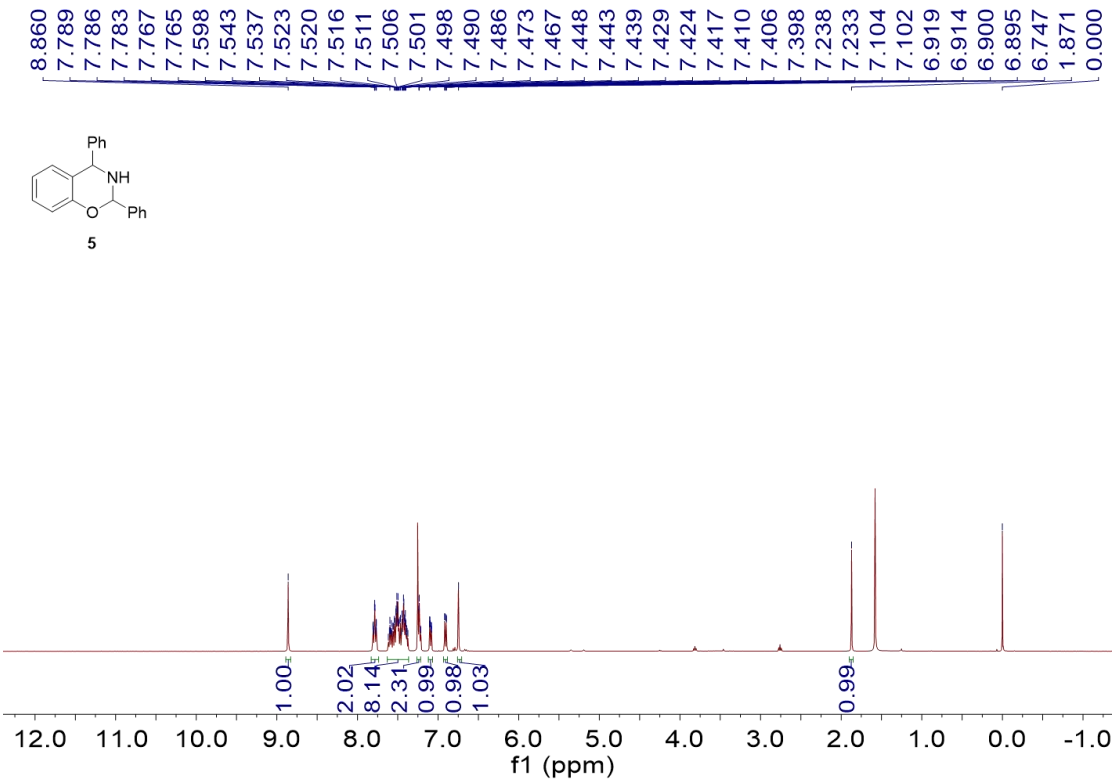
^{1}H NMR of **4** (400 MHz, $CDCl_3$):



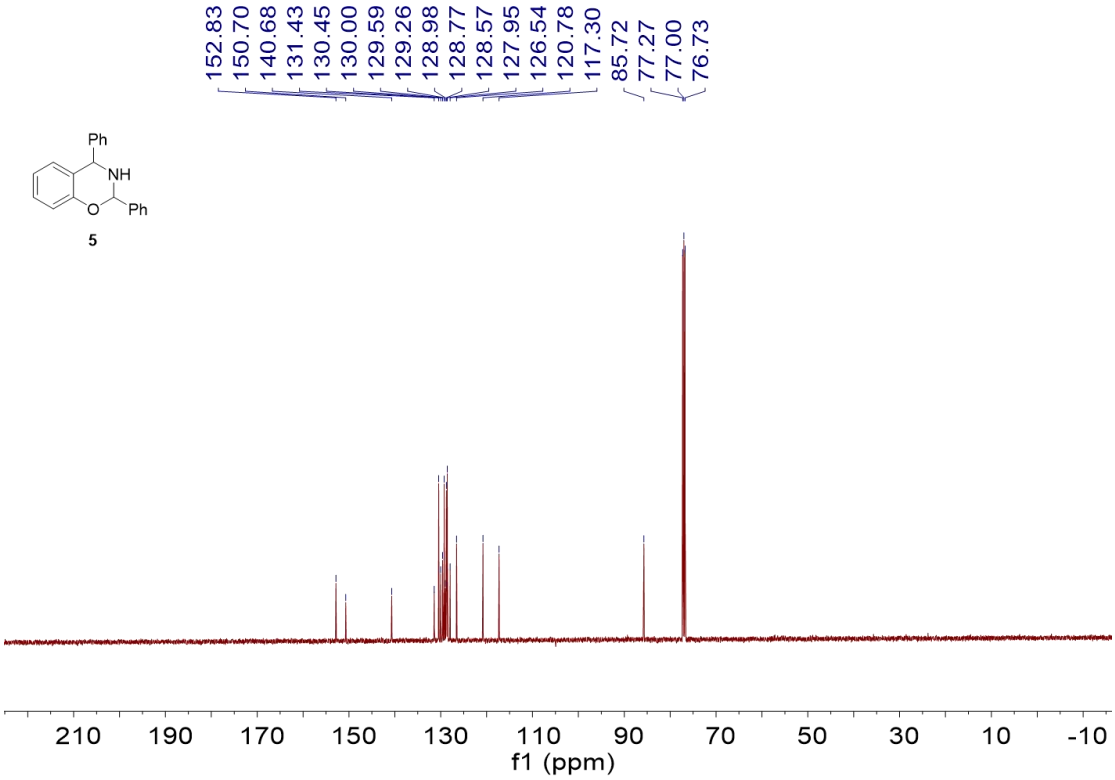
^{13}C NMR of **4** (**1**00 MHz, $CDCl_3$)**:**



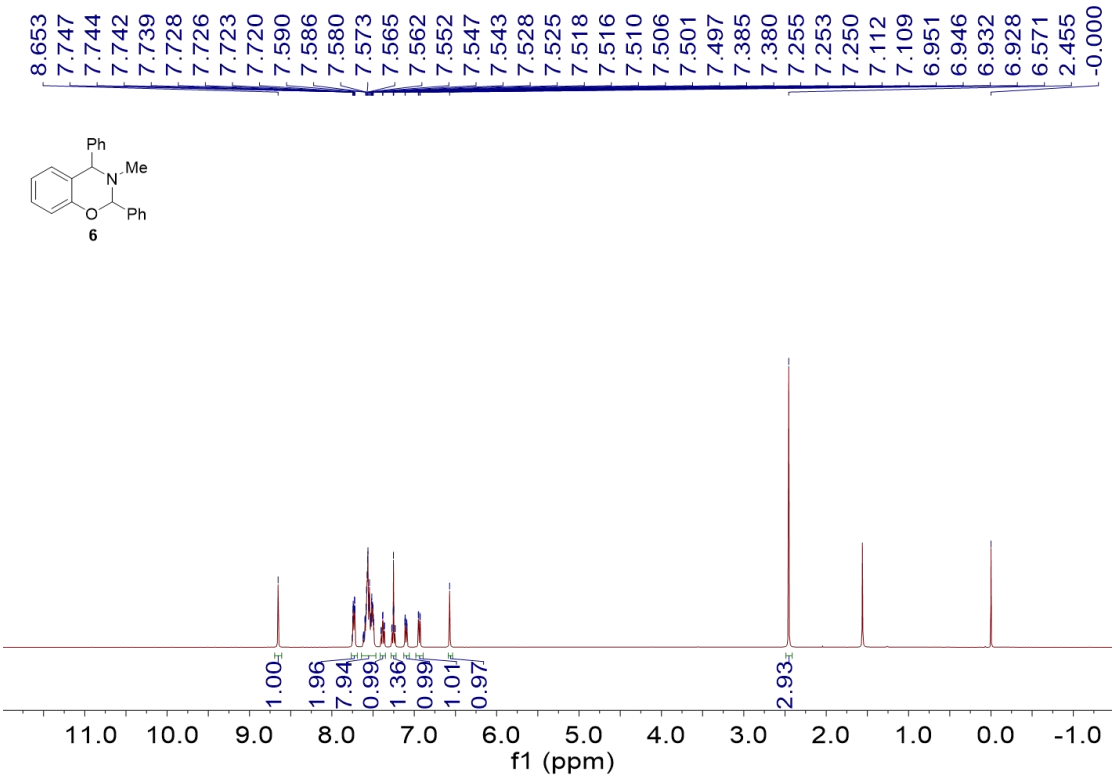
^{1}H NMR of **5** (400 MHz, $CDCl_3$):



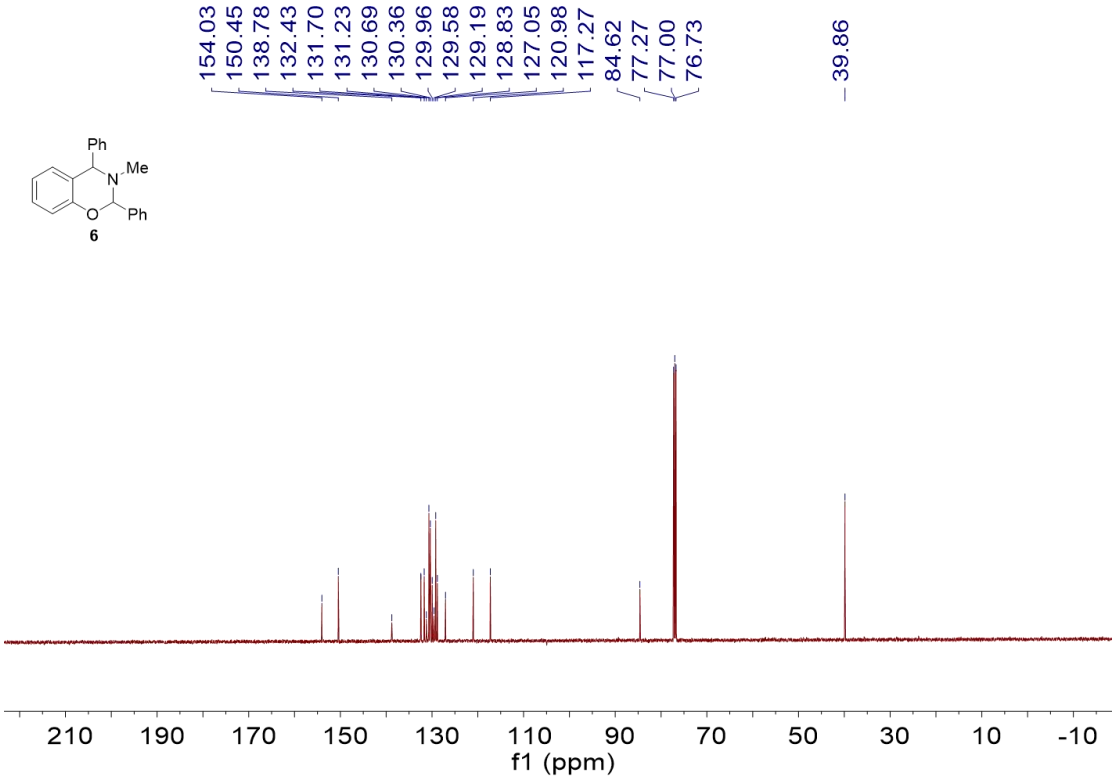
^{13}C NMR of **5** (**1**00 MHz, $CDCl_3$)**:**



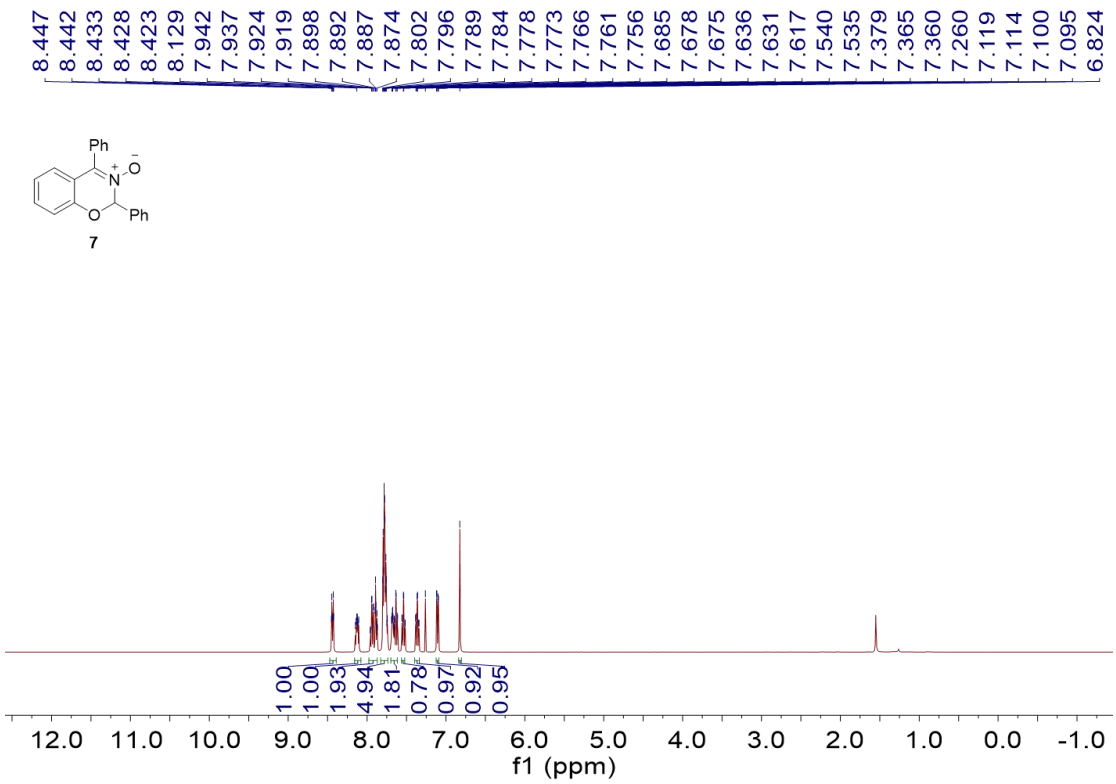
^{1}H NMR of **6** (400 MHz, $CDCl_3$):



^{13}C NMR of **6** (100 MHz, $CDCl_3$)**:**



^{1}H NMR of **7** (400 MHz, $CDCl_3$):



^{13}C NMR of **7** (**1**00 MHz, $CDCl_3$)**:**